Solvent-free Pd-catalyzed Heteroaryl-Aryl Coupling via C–H Bond Activation for the Synthesis of Extended Heteroaromatic Conjugated Molecules.

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ABSTRACT: Direct arylation of thienopyrrolodione, diketopyrrolopyrroles, benzodithiophene derivatives and fluorinated heteroarenes with functionalized aryl iodides via C–H bond activation is demonstrated in solvent-free and non-anhydrous conditions. The reaction is performed without exclusion of air and tolerates a variety of functional groups on both the coupling partners, enabling a convenient synthesis of extended heteroaromatic conjugated molecules.

INTRODUCTION

Palladium-catalyzed direct arylation via C-H bond activation[1] is a convenient and step-economical route to organic complex molecules, since it can be performed without need of preliminary preparation of air and moisture sensitive, expensive and toxic organometallic reagents. The major drawback in the wide application of direct arylation reaction is still represented by the use of highly polar and toxic solvents such as *N*,*N*-dimethylformamide, *N*-methyl-2-pyrrolidone and *N*,*N*-dimethylacetamide. Recently, direct arylation protocols based on the use of more environmentally friendly solvents have been reported, including dialkyl carbonates,[2] poly(ethylene glycol)s,[2b] water[2b,3] and ionic liquids.[4] In our recent work, we have also described the use of the choline chloride/urea mixture as a green and inexpensive deep eutectic solvent for thiophene-aryl direct coupling reactions.[5] The development of fully solvent-free experimental conditions would represent a major improvement, leading to much more convenient protocols for direct arylation. In fact, solvent-free conditions not only avoid the hazards and toxicity associated with some solvents, but can also reduce energy costs due to shorter reaction times and simplification of work-up operations. A very limited number of examples of direct arylation reactions in solvent-free conditions has been reported thus far, mainly limited to the synthesis of specific classes of small molecules[6] and often requiring anhydrous and inert reaction conditions.[6a-c] Bedford first reported the solvent-free direct ortho mono-arylation of aryl carbamates with diaryliodonium salts, using $Pd(OAc)_2$ as the catalyst.[6d] Then, Doucet investigated the first solvent-free and Pd catalyzed direct 5-arylation of heteroarenes (thiazoles, thiophenes, furans, and pyrroles) only with electron-poor aryl bromides.[6b] A metal-free direct arylation of unbiased arenes with diaryliodonium triflates in the absence of solvents and additives was reported by Rodríguez.[6c] Finally, Punji et al. developed a solvent-free method for C-H bond arylation of (2-pyridinyl)arenes and indoles, which is selective for mono-arylation and tolerates sensitive and structurally diverse functionalities. However, this protocol requires anhydrous conditions, inert atmosphere and the use of a non-commercial Ni-catalyst.[6a] In the frame of our studies on organometallic methods[7] and particularly on direct arylation of heterocyclic structures for the synthesis of molecular and polymeric organic semiconductors,[5,8] we report herein a general palladium-catalyzed direct arylation protocol that is performed in (i) solvent-free, (ii) non-anhydrous conditions and (iii) without exclusion of air, enabling the synthesis of heteroaryl-based conjugated molecules far more complex than those accessible in similar conditions so far according to the literature. In particular, we describe for the first time the double aromatic C–H activation reactions in solvent-free conditions of diverse thiophene-based conjugated cores and fluorinated arenes, which are useful building blocks in the synthesis of materials for organic electronics.

RESULTS AND DISCUSSION

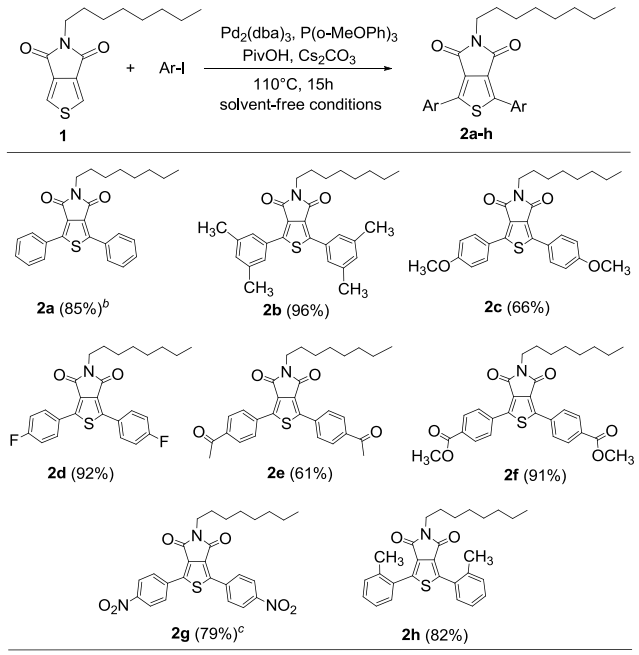
Direct arylation of thienopyrrolodione

We started our study from direct arylation reaction of the 5-octylthieno[3,4-*c*]pyrrole-4,6-dione **1** with a variety of aryl iodides in solvent-free conditions. **1** was initially selected since it is frequently used as electron-withdrawing building block of low-band-gap copolymers for organic electronics.[9] We had previously reported the synthesis of these molecules *via* direct arylation reactions of **1** in a deep eutectic solvent made of choline chloride and urea.[5] In the

present study, we carried out the solvent-free direct arylation reaction of **1** with various substrates in non-anhydrous conditions and without exclusion of air, using $Pd_2(dba)_3$ as the catalyst in the presence of Cs_2CO_3, P(o-MeOPh)$_3$, and pivalic acid (PivOH) as the base, the ligand, and the additive, respectively (Table 1). The thiophene-aryl coupling reactions occur in good to excellent yields using aryl iodides functionalized with both electron-donating functionalities, such as methyl, also in ortho position, and methoxy groups (**2b**: 96%, **2h**: 82% and **2c**: 66%, respectively) and electron-withdrawing groups (**2d**-**2g**: 61-92%). With the exception of 1-iodo-4-nitrobenzene, all aryl iodides coupled with **1** are liquid at the reaction temperature of 110°C, so the reactants result easily miscible. When 1-iodo-4-nitrobenzene was used, the temperature was increased up to the melting point of the aryl halide in the reaction medium (140°C). We also reacted TPD **1** with bromobenzene and chlorobenzene instead of iodobenzene. Compound **2a** was obtained in slightly lower yield with bromobenzene compared to iodobenzene (71% *vs* 85%), while it was not obtained when chlorobenzene was used as the coupling partner.

The solvent-free approach reported here for the synthesis of compounds **2a-h** compares favorably with our previously reported direct arylations of **1** with aryl iodides in choline chloride and urea.[5] In fact, although comparable yields are obtained, solvent-free conditions allow to reduce the reaction times (15h *vs* 48h), the TPD **1** : aryl iodide ratio (1:3 *vs* 1:5) and the catalyst amount (2 mol% *vs* 5 mol%).

Table 1. Synthesis of TPD-based compounds **2a-h.**[a]

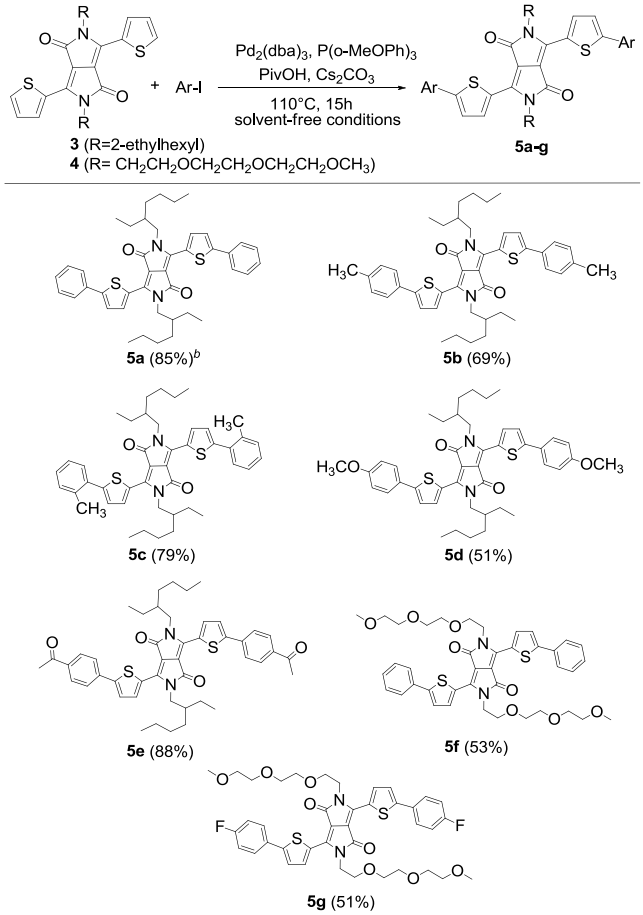


[a]Unless specified, the C-H arylation was carried out as it follows: TPD **1** (1 equiv), aryl iodide (3 equiv), $Pd_2(dba)_3$ (2 mol%), P(o-MeOPh)$_3$ (4 mol%), PivOH (30 mol%), Cs_2CO_3 (2 equiv) in solvent-free and non-anhydrous conditions and without exclusion of air at 110 °C for 15h. Yields refer to isolated products. [b]The use of bromobenzene in the same experimental conditions led to **2a** in 71% yield; the formation of **2a** was not observed with chlorobenzene. [c]Reaction carried out at 140°C.

Direct arylation of diketopyrrolopyrrole derivatives

To investigate the versatility of our protocol we also used diketopyrrolopyrroles (DPP) and benzodithiophene (BDT)-based cores discussed below as the substrates. These molecules were also selected to study the reaction regioselectivity since they have two C–H activated bonds in the free 2 and 3 positions. DPPs are technologically important molecules that, besides their use as high-performance organic industrial pigments, have emerged as extremely attractive building blocks for the construction of a wide variety of conjugated materials with applications ranging from organic electronics[10] to sensing and bioimaging.[11] Two DPP derivatives endowed with substituents of different polarity on the N-atom of the lactam groups, namely 2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione **3** and 2,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethyl}-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione **4**, were coupled with different aryl iodides under solvent-free conditions (Table 2).

Table 2. Synthesis of DPP-based compounds **5a-g.**[a]



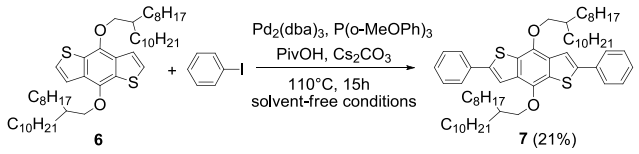
[a]Unless specified, the C-H arylation was carried out as it follows: DPP **3** or **4** (1 equiv), aryl iodide (4 equiv), $Pd_2(dba)_3$ (5 mol%), P(o-MeOPh)$_3$ (10 mol%), PivOH (30 mol%), Cs_2CO_3 (2 equiv) in solvent-free and non-anhydrous conditions and without exclusion of air at 110 °C for 15h. Yields refer to isolated products. [b]The use of bromobenzene in the same experimental conditions led to **5a** in 50% yield.

The direct arylation reactions of **3** occurred with both electron-rich and electron-poor aryl iodides affording compounds **5a-e** in fair to excellent yields, also in the presence of an ortho substituent (51-88%). The reaction of **3** with bromobenzene produced the expected compound **5a** in a markedly lower yield than that obtained using iodobenzene as a coupling partner (50% *vs* 85%). Noteworthy, compared to the protocols reported in the literature, which require the use of *N,N*-dimethylacetamide as the solvent, our procedure allows a more sustainable synthesis of **5c**, recently reported as active material in efficient luminescent solar concentrators.[12] Similarly, the direct arylation of **4** afforded compounds **5f-g** functionalized with polar triethylene glycol (TEG) chains that induce a strong self-assembling effect[7b,8a] and increase the solubility of DPP derivatives in environmentally friendly polar solvents.[7b] The coupling reaction was expected to occur regioselectively in the 2 position of the DPP thiophene moieties, even when the 3 position of thiophene is not functionalized. In fact, sulfur is known to promote an effective C-H activation at the 2(5) positions of heteroaromatic rings. Conversely, the 3(4) positions are less reactive and their activation to the direct coupling with aryl halides can be promoted when electron-withdrawing groups are bound to the 2(5) positions.[13] For the direct arylation reactions carried out with **3** and **4** reagents, the selective α C-H bond activation was confirmed by ^{1}H-NMR spectra, clearly showing the presence of equivalent thiophene rings substituted at the 2 and 5 positions as deduced from the presence of doublets with typical $^{3,4}J$ coupling constants.[14]

Direct arylation of benzodithiophene derivatives

We also investigated solvent-free direct arylation reactions of BDT-based derivatives, which are prominent building blocks for the synthesis of molecular and polymeric electron donor materials for organic photovoltaics (OPV).[8b,15] Starting from the BDT **6**, the expected product **7** was isolated in low yield (21%) under our experimental conditions (Scheme 1). This result could be likely due to a reduced activation of the benzodithiophene core that exhibits electron donor properties.

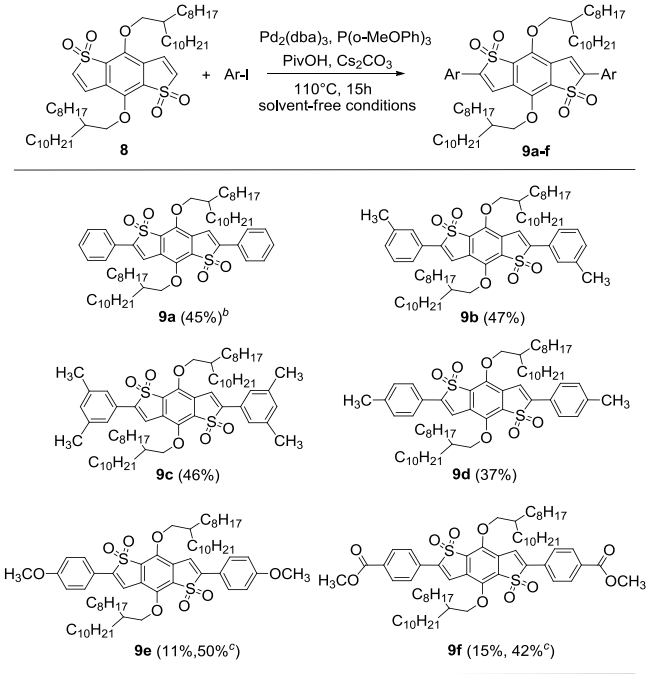
Scheme 1. Synthesis of BDT-based compound **7**.[a]



[a]The C-H arylation was carried out as it follows: BDT **6** (1 equiv), iodobenzene (4 equiv), $Pd_2(dba)_3$ (5 mol%), P(*o*-MeOPh)$_3$ (10 mol%), PivOH (30 mol%), Cs_2CO_3 (2 equiv) at 110 °C for 15h, in solvent-free and non-anhydrous conditions and without exclusion of air. Yield refers to the isolated product.

To verify this hypothesis and further explore the suitability of our procedure, the electron-rich compound **6** was oxidized to the benzodithiophene-S,S-tetraoxide **8**.[16] Despite being an electron-poor heterocyclic compound with promise for development of electron acceptor materials, **8** has been rarely used as building block for the synthesis of organic semiconductors.[17] To the best of our knowledge, only one example of regioselective direct arylation of benzodithiophene-S,S-tetraoxide has been reported so far,[18] based on the use of inexpensive Cu catalyst, but requiring anhydrous and inert conditions, toxic organic solvent (*N,N*-dimethylformamide) and large excess of aryl iodides (10 equiv). Conversely, our reaction protocol does not require the use of toxic solvents, it tolerates non-anhydrous conditions and requires a significantly lower amount of aryl iodide (4 equiv), thus being a promising alternative to the literature protocol.

Table 3. Synthesis of BDT-based compounds **9a-f**.[a]



[a]Unless specified, the C-H arylation was carried out using BDT **8** (1 equiv), aryl iodide (4 equiv), $Pd_2(dba)_3$ (5 mol%), P(*o*-MeOPh)$_3$ (10 mol%), PivOH (30 mol%), Cs_2CO_3 (2 equiv) in solvent-free and non-anhydrous conditions and without exclusion of air at 110 °C for 15h. Yields refer to isolated products. [b]The use of bromobenzene in the same experimental conditions led to **9a** in traces. [c]Reaction carried out as it follows: BDT **8** (1 equiv), aryl iodide (4 equiv), $Pd(OPiv)_2$ (5 mol%), P(*o*-MeOPh)$_3$ (10 mol%), Ag_2CO_3 (1 equiv) in solvent-free and non-anhydrous conditions and without exclusion of air at 110 °C for 2h.

As shown in Table 3, our method, based on the use of $Pd_2(dba)_3$ as the catalyst in the presence of Cs_2CO_3, P(*o*-MeOPh)$_3$ and pivalic acid, led to the direct arylation of **8** with iodobenzene and its methyl or dimethyl derivatives, affording the expected products **9a-d** in fair yields (37-47%). Lower yields were observed by coupling **8** with functionalized iodobenzenes bearing either electron rich

(methoxy) or electron poor (ester) groups. In this case, the yields of the expected products **9e,f** were improved by slightly changing the experimental conditions. Here $Pd(PivO)_2$ was used as the catalyst, $P(o\text{-}MeOPh)_3$ as the additional ligand and Ag_2CO_3 as the base, respectively. We examined Ag_2CO_3 because this base was previously supposed to abstract halide anions from transition-metal complexes, thus making them more electrophilic and facilitating the catalytic cycle.[19] The overall moderate yields recorded in the reactions carried out on **8** are likely due to the observed partial decomposition of the starting material in the reaction media. To determine the regiochemistry of the cross-coupling reaction, 2D NOESY spectra of **9a** were acquired. When the arylation occurs at the α-position of thiophene dioxide rings, the β-hydrogen atoms are in close proximity to the methylene moieties of the alkoxy chains on the benzene ring (Figure 1). Hence, the through-space dipolar coupling between the thienyl proton and the methylene protons are expected to produce a cross-correlation peak in the 2D NOESY spectrum. In the case of β-functionalization, no Overhauser effect between OCH_2 and the thienyl proton can be observed. The 2D NOESY spectrum of **9a** clearly shows a cross-peak between the methylene protons at 4.43 ppm and the thienyl proton at 7.44 ppm, this proving the α substitutions at the benzodithiophene-S,S-tetraoxide unit (Figure 1).

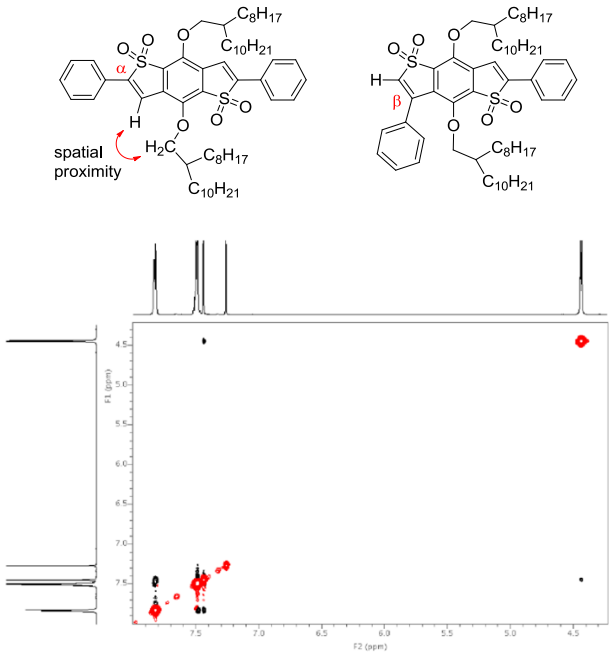
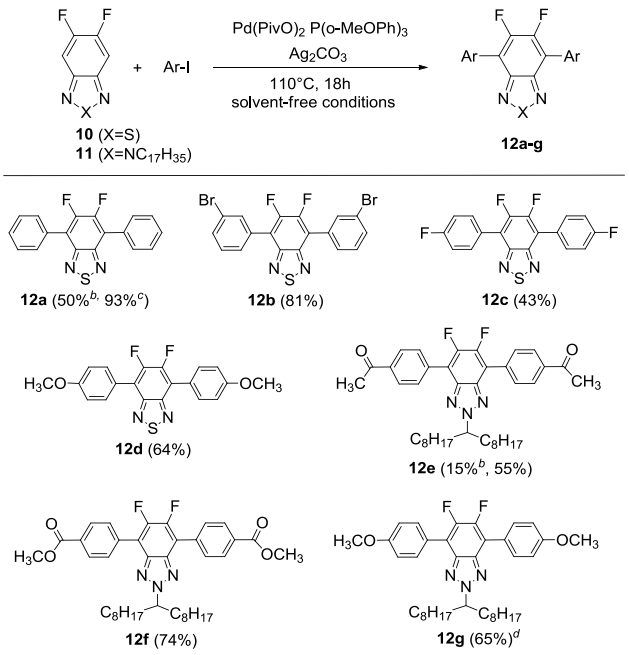


Figure 1. (top) Chemical structures of **9a** regioisomers resulting from the direct phenylation of **8** at the α and β positions. (bottom) Expansion of 500 MHz 2D NOESY spectrum of **9a**, acquired in $CDCl_3$, showing the cross region of OCH_2/thienyl protons of the benzodithiophene-S,S-tetraoxide moiety.

Direct arylation of fluorinated arenes

Finally, we extended the scope of the C-H arylation to fluorinated arenes, such as the 5,6-difluorobenzo[*c*][1,2,5]thiadiazole (DFBT) **10** and the 5,6-difluoro-2-heptadecyl-2*H*-benzo[*d*][1,2,3]triazole ($DFBT_Z$) **11**. Fluorine substitution of aromatic units and/or double bonds in conjugated compounds is known to confer intriguing charge transport properties, to modulate optical behavior and to increase the stability of the resulting organic semiconductors.[20] In particular, fluorinated benzothiadiazoles have recently gained great attention for the optimization of polymer photovoltaic properties.[21] Protocols based on direct arylation[19a, 22] have been developed as alternative to traditional cross-coupling reactions since synthesizing appropriate intermediates for inclusion of fluorinated BT moieties (especially DFBT) into conjugated structures can require several steps and/or harsh conditions, and 4,7-diiodo-DFBT is reportedly unstable.[22a,23] The literature protocols of direct arylation on DFBT require the use of toxic organic solvents, anhydrous conditions and inert atmosphere, that can be avoided by our protocol. We carried out the direct arylation reaction of both the fluorinated benzothiadiazole **10** and the benzotriazole **11** with a variety of substituted iodobenzenes, using reaction conditions based either on $Pd(PivO)_2$ and Ag_2CO_3 or on $Pd_2(dba)_3$ and Cs_2CO_3 as the catalyst and the base, respectively. The expected products **12a-f** were obtained in higher yields in the former experimental conditions (Table 4).

Table 4. Synthesis of compounds **12a-g**.[a]



[a]Unless specified, the C-H arylation was carried out as it follows: compound **10** (1 equiv), aryl iodide (4 equiv), $Pd(OPiv)_2$ (5 mol%), $P(o\text{-}MeOPh)_3$ (10 mol%), Ag_2CO_3 (1 equiv) or **11** (1 equiv), aryl iodide (4 equiv), $Pd(OPiv)_2$ (10 mol%), $P(o\text{-}MeOPh)_3$ (20 mol%), Ag_2CO_3 (1 equiv) in solvent-free and non-anhydrous conditions and without exclusion of air at 110 °C for 18h. Yields refer to isolated products. [b]Reaction carried out using compound **10** or **11** (1 equiv), aryl iodide (4 equiv), $Pd_2(dba)_3$ (5 mol%), $P(o\text{-}MeOPh)_3$ (10 mol%), PivOH (30 mol%), Cs_2CO_3 (2 equiv) in solvent-free and non-anhydrous conditions and without exclusion of air at 110 °C for 18h. [c]The

use of bromobenzene in the same experimental conditions led to **12d** in 13% yield. [d]The use of 1-bromo-4-methoxybenzene in the same experimental conditions led to **12g** in 8% yield.

Versatile functional groups such as an ester, a methyl ketone and a methoxy group were compatible with the reaction system. Since aryl bromides were found to be not effective coupling partners for **10** and **11**, also bromine, in addition to the less reactive fluorine, can be tolerated as a substituent on the aryl iodides as shown for **12b**. Remarkably, the successful formation of **12b,** potential versatile building block *via* transformation of the bromine atoms, provides good opportunities for further synthetic steps towards more complex molecules or polymerization. Direct arylation reactions of **10** and **11** with ortho substituted aryl iodides (2-iodotoluene and 1-iodo-2-methoxybenzene) led to the expected coupling products only in traces, suggesting a strong sensitivity to steric effects for direct arylation reactions on these substrates.

CONCLUSION

In conclusion, we have investigated a Pd-catalyzed direct coupling reaction *via* C–H bond activation in solvent-free conditions, which represents a general and an environmentally attractive procedure for the preparation of a variety of extended heteroaryl-based conjugated molecules, avoiding the hazards and toxicity associated to the use of solvents. Moreover, the reaction is performed in non-anhydrous conditions and without exclusion of air. It also tolerates a number of functional groups on both coupling partners. We have investigated the protocol using TPD-, DPP-, BDT-, DFBT-, and $DFBT_Z$-based cores as the C–H activated substrates, in consideration of the importance of these aromatic moieties in the synthesis of push-pull molecular and polymeric semiconductors, which are interesting systems in organic electronics and polymer solar cells. Studies aimed at the extension of such synthetic procedure to more complex materials such as conjugated polymers for organic electronics, are currently underway in our laboratories.

EXPERIMENTAL SECTION

General remarks: Reagents and solvents were purchased at the highest commercial quality and used without further purification. 5-Octylthieno[3,4-*c*]pyrrole-4,6-dione **1** was purchased from TCI Europe. 2,5-Bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione **3** was prepared according to the literature.[24] 2,5-Bis{2-[2-(2-methoxyethoxy)ethoxy]ethyl}-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione **4**, 4,8-bis((2-octyldodecyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene **6**, 5,6-difluorobenzo[*c*][1,2,5]thiadiazole **10** and 5,6-difluoro-2-heptadecyl-2*H*-benzo[*d*][1,2,3]triazole **11** were purchased from SunaTech Inc. 4,8-Bis((2-octyldodecyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene 1,1,5,5-tetraoxide **8** was prepared from **6** according to the literature.[16] Preparative column chromatography was carried out using Macherey-Nagel silica gel (60, particle size 0.063-0.2 mm). Macherey-Nagel aluminum sheets with silica gel 60 F254 were used for TLC analyses. All new compounds were characterized by ^{1}H-NMR, ^{13}C-NMR and LC-MS analysis. ^{1}H-NMR and ^{13}C-NMR spectra were on an Agilent 500 spectrometer at 500 and at 126 MHz, respectively, by using the residual proton peak of $CDCl_3$ at δ = 7.26 ppm as internal standard for ^{1}H spectra and the signals of $CDCl_3$ at δ = 77.16 ppm as internal standard for ^{13}C spectra. GC/mass-spectrometry analyses were performed on a Shimadzu GCMS-QP5000 gas chromatograph-mass spectrometer equipped with a Supelco SLB™-5ms capillary column (30 m × 0.25 mm id). High-resolution mass spectra were acquired with a Shimadzu high-performance liquid chromatography ion trap time of flight (LC-IT-TOF) mass spectrometer *via* direct infusion of the samples. Melting points were determined on a Stuart Scientific Melting point apparatus SMP3.

General procedure for the synthesis of compounds 2a-g: A schlenk tube (ø = 1.8÷2.5 cm) with a screw cap and equipped with a magnetic stirrer was charged with 5-octylthieno[3,4-*c*]pyrrole-4,6-dione **1** (1 equiv), aryl halide (3 equiv), Cs_2CO_3 (2 equiv), pivalic acid (30 mol%), $Pd_2(dba)_3$ (2 mol %), P(*o*-MeOPh)$_3$ (4 mol%). The resulting heterogeneous reaction mixture was reacted at 110 °C (sand bath) under magnetic stirring. After 15 h, the mixture was cooled to room temperature, diluted with CH_2Cl_2, filtered to remove insoluble inorganic materials, and concentrated under reduced pressure. The crude product was purified by column chromatography.

5-octyl-1,3-diphenyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (2a).[5] Compound **2a** was synthesized from **1** (100 mg, 0.38 mmol) and iodobenzene (233 mg, 1.14 mmol) in accordance with the general procedure. Purification by column chromatography (hexane:ethyl acetate = 9:1) afforded 135 mg of compound **2a** as a pale yellow solid (85% yield). Both melting point value and spectroscopic data are in perfect agreement with those previously reported in literature.[5]

1,3-bis(3,5-dimethylphenyl)-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (2b).[5] Compound **2b** was synthesized from **1** (160 mg, 0.60 mmol) and 1-iodo-3,5-dimethylbenzene (418 mg, 1.80 mmol) in accordance with the general procedure. Purification by column chromatography (hexane:ethyl acetate = 9:1) afforded 274 mg of compound **2b** (96% yield) as a pale yellow solid. Both melting point value and spectroscopic data are in perfect agreement with those previously reported in literature.[5]

1,3-bis(4-methoxyphenyl)-5-octyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (2c).[5] Compound **2c** was synthesized from **1** (100 mg, 0.38 mmol) and 1-iodo-4-methoxybenzene (267 mg, 1.14 mmol) in accordance with the general procedure. Purification by column chromatography (CH_2Cl_2:hexane = 6:4) afforded compound **2c** (120 mg, 66% yield) as a pale yellow solid. Both melting point value and spectroscopic data are in perfect agreement with those previously reported in literature.[5]

5-octyl-1,3-bis(4-fluorophenyl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (2d).[5] Compound **2d** was synthesized

from **1** (160 mg, 0.60 mmol) and 1-fluoro-4-iodobenzene (400 mg, 1.80 mmol) in accordance with the general procedure. Purification by column chromatography (hexane:ethyl acetate = 9:1) afforded compound **2d** (250 mg, 92% yield) as a yellow solid. Both melting point value and spectroscopic data are in perfect agreement with those previously reported in literature.[5]

1,3-bis(4-acetylphenyl)-5-octyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (2e).[5] Compound **2e** was synthesized from **1** (100 mg, 0.38 mmol) and 1-(4-iodophenyl)ethanone (280 mg, 1.14 mmol) in accordance with the general procedure. Purification by column chromatography (hexane:ethyl acetate = 7:3) afforded compound **2e** (116 mg, 61% yield) as a yellow solid. Both melting point value and spectroscopic data are in perfect agreement with those previously reported in literature.[5]

dimethyl 4,4'-(5-octyl-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrole-1,3-diyl)dibenzoate (2f).[5] Compound **2f** was synthesized from **1** (160 mg, 0.60 mmol) and methyl 4-iodobenzoate (472 mg,1.80 mmol) in accordance with the general procedure. Purification by column chromatography (from hexane:ethyl acetate = 8:2 to hexane:ethyl acetate:CH_2Cl_2=3:2:1) afforded compound **2f** (291 mg, 91% yield) as a yellow solid. Both melting point value and spectroscopic data are in perfect agreement with those previously reported in literature.[5]

1,3-bis(4-nitrophenyl)-5-octyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (2g).[5] Compound **2g** was synthesized from **1** (160 mg, 0.60 mmol) and 1-iodo-4-nitrobenzene (448 mg, 1.80 mmol), in accordance with the general procedure with the exception of the reaction temperature which was increased to 140 °C. Purification by column chromatography (from hexane:ethyl acetate = 8:2 to hexane:ethyl acetate = 7:3) afforded compound **2g** (241 mg, 79% yield) as a yellow solid. Both melting point value and spectroscopic data are in perfect agreement with those previously reported in literature.[5]

5-octyl-1,3-di-*o*-tolyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (2h).[5] Compound **2h** was synthesized from **1** (160 mg, 0.60 mmol) and 2-iodotoluene (392 mg, 1.80 mmol) in accordance with the general procedure. Purification by column chromatography (hexane:ethyl acetate = 9:1) afforded 220 mg of compound **2h** (82% yield) as a pale yellow viscous liquid. Spectroscopic data are in perfect agreement with those previously reported in literature.[5]

General procedure for the synthesis of compounds 5a-f: A schlenk tube (ø = 1.8÷2.5 cm) with a screw cap and equipped with a magnetic stirrer was charged with 2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**3**) or 2,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethyl}-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**4**) (1 equiv), aryl iodide (4 equiv), Cs_2CO_3 (2 equiv), pivalic acid (30 mol%), $Pd_2(dba)_3$ (5 mol %), P(o-MeOPh)$_3$ (10 mol%). The resulting heterogeneous reaction mixture was reacted at 110 °C (sand bath) under magnetic stirring. After 15 h, the mixture was cooled to room temperature, diluted with CH_2Cl_2, filtered to remove insoluble inorganic materials, and concentrated under reduced pressure. The crude product was purified by column chromatography.

2,5-bis(2-ethylhexyl)-3,6-bis(5-phenylthiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (5a).[25] Compound **5a** was synthesized from **3** (100 mg, 0.191 mmol) and iodobenzene (155 mg, 0.76 mmol) in accordance with the general procedure. Purification by column chromatography (CH_2Cl_2:hexane = 6:4) afforded 110 mg of compound **5a** (85% yield) as a dark solid, m.p. = 192-194 °C (after washing with hexane). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.97 (br d, J = 3.5 Hz, 2H), 7.68 (d, J = 7.5 Hz, 4H), 7.47 (d, J = 4.0 Hz, 2H), 7.43 (t, J = 7.5 Hz, 4H), 7.36 (t, J = 7.5 Hz 2H), 4.14-4.02 (m, 4H), 2.00-1.89 (m, 2H), 1.47-1.22 (m, 16H), 0.92 (t, J = 7.2 Hz, 6H), 0.87 (t, J = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 161.9, 149.8, 140.0, 136.9, 133.3, 129.3, 129.0, 129.0, 126.3, 124.6, 108.4, 46.1, 39.4, 30.5, 28.7, 23.9, 23.3, 14.2, 10.7. HRMS (LC-IT-TOF, elution with 0.1% (v/v) formic acid in methanol) m/z: $[M+Na]^+$ Calcd. for $C_{42}H_{48}N_2O_2S_2Na$ 699.3049; Found 699.3017.

2,5-bis(2-ethylhexyl)-3,6-bis(5-(*p*-tolyl)thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (5b).[25b] Compound **5b** was synthesized from **3** (100 mg, 0.191 mmol) and 4-iodotoluene (161 mg, 0.76 mmol) in accordance with the general procedure. Purification by column chromatography (CH_2Cl_2:hexane = 2:1), afforded compound **5b** (93 mg, 69% yield) as a dark solid, m.p. = 224-227 °C (after crystallization from CH_2Cl_2/CH_3OH). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.95 (d, J = 4.1 Hz, 2H), 7.57 (d, J = 7.9 Hz, 4H), 7.43 (d, J = 4.1 Hz, 2H), 7.23 (d, J = 7.9 Hz, 4H), 4.14-4.02 (m, 4H), 2.40 (s, 6H), 1.99-1.91 (m, 2H), 1.46-1.22 (m, 16H), 0.91 (J = 7.4 Hz, 6H), 0.87 (J = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 161.8, 150.0, 140.0, 139.2, 137.0, 130.5, 130.0, 128.5, 126.2, 124.2, 108.2, 46.1, 39.4, 30.5, 28.7, 23.8, 23.8, 21.5, 14.2, 10.7. HRMS (LC-IT-TOF, elution with 0.1% (v/v) formic acid in methanol) m/z: $[M+H]^+$ Calcd. for $C_{44}H_{53}N_2O_2S_2$ 705.3543; Found 705.3550.

2,5-bis(2-ethylhexyl)-3,6-bis(5-(*o*-tolyl)thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (5c). Compound **5c** was synthesized from **3** (100 mg, 0.191 mmol) and 2-iodotoluene (166 mg, 0.76 mmol) in accordance with the general procedure. Purification by column chromatography (CH_2Cl_2:hexane = 1:1), afforded compound **5c** (107 mg, 79% yield) as a dark solid, m.p. = 108-110°C (after washing with hexane). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.98 (d, J = 4.0 Hz, 2H), 7.47 (d, J = 7.2 Hz, 2H), 7.33-7.30 (m, 4H), 7.30-7.27 (m, 2H), 7.26 (d, J = 4.0 Hz, 2H), 4.13-4.01 (m, 4H), 2.50 (s, 6H), 1.99-1.91 (m, 2H), 1.45-1.23 (m, 16H), 0.90 (J = 7.4 Hz, 6H), 0.86 (J = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 162.0, 149.1, 140.3, 136.3, 136.1, 133.0, 131.3, 130.4, 129.6, 128.9, 128.2, 126.4, 108.1, 46.2, 39.4, 30.4, 28.7, 23.7, 23.3, 21.4, 14.2, 10.7. HRMS (LC-IT-TOF, elution with 0.1% (v/v) formic acid in methanol) m/z: $[M+H]^+$ Calcd. For $C_{44}H_{53}N_2O_2S_2$ 705.3543; Found 705.3537.

2,5-bis(2-ethylhexyl)-3,6-bis(5-(4-methoxyphenyl)thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (5d).[12] Compound **5d** was synthesized from **3** (100 mg, 0.191 mmol) and 1-iodo-4-methoxybenzene (179 mg, 0.76 mmol)

in accordance with the general procedure. Purification by column chromatography (hexane:ethyl acetate = 4:1), afforded compound **5d** (72 mg, 51% yield) as a dark solid, m.p. = 216-218 °C (after washing with hexane) (lit. 214-216 °C).[12a] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.94 (d, J = 4.1 Hz, 2H), 7.62 (d, J = 8.7 Hz, 4H), 7.36 (d, J = 4.1 Hz, 2H), 6.96 (d, J = 8.7 Hz, 4H), 4.14-4.02 (m, 4H), 3.86 (s, 6H), 1.99-1.91 (m, 2H), 1.46-1.22 (m, 16H), 0.91 (J = 7.4 Hz, 6H), 0.87 (J = 6.7 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 161.9, 160.5, 149.8, 139.9, 137.0, 128.1, 127.7, 126.3, 123.6, 114.9, 108.2, 55.6, 46.2, 39.4, 30.6, 28.8, 23.9, 23.3, 14.2, 10.8. HRMS (LC-IT-TOF, elution with 0.1% (v/v) formic acid in methanol) m/z: $[M+H]^+$ Calcd. for $C_{44}H_{53}N_2O_4S_2$ 737.3441; Found 737.3432.

3,6-bis(5-(4-acetylphenyl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (5e). Compound **5e** was synthesized from **3** (100 mg, 0.191 mmol) and 1-(4-iodophenyl)ethanone (188 mg, 0.76 mmol) in accordance with the general procedure. Purification by column chromatography (from pure CH_2Cl_2 to CH_2Cl_2: ethyl acetate = 9:1), afforded compound **5e** (128 mg, 88% yield) as a dark solid, m.p. = 209-211 °C (after washing with hexane). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.96 (d, J = 4.1 Hz, 2H), 7.99 (d, J = 8.0 Hz, 4H), 7.23 (d, J = 8.0 Hz, 4H), 7.53 (d, J = 4.1 Hz, 2H), 4.12-4.00 (m, 4H), 2.62 (s, 6H), 1.96-1.86 (m, 2H), 1.45-1.25 (m, 16H), 0.91 (t, J = 7.2 Hz, 6H), 0.87 (t, J = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 197.2, 161.7, 147.9, 139.8, 137.4, 137.0, 136.8, 130.3, 129.4, 126.0, 125.9, 108.8, 46.1, 39.4, 30.5, 28.7, 26.8, 23.8, 23.2, 14.2, 10.7. HRMS (LC-IT-TOF, elution with 0.1% (v/v) formic acid in methanol) m/z: [M$^-$] Calcd. for $C_{46}H_{52}N_2O_4S_2$ 760.3374; Found 760.3354.

2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-3,6-bis(5-phenylthiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (5f). Compound **5f** was synthesized from **4** (150 mg, 0.253 mmol) and iodobenzene (207 mg, 1.01 mmol) in accordance with the general procedure. Purification by column chromatography (CH_2Cl_2:ethyl acetate = 1:1), afforded compound **5f** (101 mg, 53% yield) as a dark solid, m.p. = 172-174 °C (after washing with hexane). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.82 (d, J= 4.0 Hz, 2H), 7.70 (d, J =7.5 Hz, 4H), 7.46 (d, J =4.1 Hz, 2H), 7.43 (t, J = 7.5 Hz, 4H), 7.36 (t, J = 7.3 Hz, 2H), 4.34 (t, J = 6.3 Hz, 4H), 3.83 (t, J = 6.3 Hz, 4H), 3.69-3.66 (m, 4H), 3.63-3.59 (m, 4H), 3.58-3.55 (m, 4H), 3.47-3.43 (m, 4H), 3.31 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 161.6, 150.1, 140.0, 136.4, 133.3, 129.3, 129.0, 128.9, 126.4, 124.6, 108.2, 72.0, 70.9, 70.7, 69.2, 59.1, 42.1. HRMS (LC-IT-TOF, elution with 0.1% (v/v) formic acid in methanol) m/z: $[M+H]^+$ Calcd. for $C_{40}H_{45}N_2O_8S_2$ 745.2612 ; Found 745.2579.

3,6-bis(5-(4-fluorophenyl)thiophen-2-yl)-2,5-bis(2-(2-(2-ethoxyethoxy)ethoxy)ethyl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (5g). Compound **5g** was synthesized from **4** (150 mg, 0.253 mmol) and 1-fluoro-4-iodobenzene (225 mg, 1.01 mmol) in accordance with the general procedure. Purification by column chromatography (CH_2Cl_2: acetone = 4:1), afforded compound **5g** (100 mg, 51% yield) as a dark solid, m.p. = 208-211 °C (after crystallization with CH_2Cl_2/hexane). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.78 (d, J = 4.2 Hz, 2H), 7.65 (app dd, J = 8.6, 5.2 Hz, 4H), 7.35 (d, J = 4.2 Hz, 2H), 7.11 (app t, J = 8.6 Hz, 4H), 4.31 (t, J = 6.2 Hz, 4H), 3.82 (t, J = 6.2 Hz, 4H), 3.68-3.65 (m, 4H), 3.62-3.58 (m, 4H), 3.75-3.54 (m, 4H), 3.47-3.43 (m, 4H), 3.31 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 163.2 (d, J = 250.7 Hz), 161.6, 148.9, 139.9, 136.3, 129.6 (d, J = 3.8 Hz), 128.9, 128.2 (d, J = 7.6 Hz), 124.6, 116.3 (d, J = 21.4 Hz), 108.2, 72.0, 70.9, 70.7, 70.7, 69.2, 59.1, 42.2. HRMS (LC-IT-TOF, elution with 0.1% (v/v) formic acid in methanol) m/z: $[M+Na]^+$ Calcd. for $C_{40}H_{42}F_2N_2O_8S_2Na$ 803.2243; Found 803.2214.

Synthesis of 4,8-bis((2-octyldodecyl)oxy)-2,6-diphenylbenzo[1,2-*b*:4,5-*b*′]dithiophene (7): A schlenk tube (ø = 1.8÷2.5 cm) with a screw cap was charged with 4,8-bis((2-octyldodecyl)oxy)benzo[1,2-*b*:4,5-*b*′]dithiophene **6** (200 mg, 0.26 mmol), iodobenzene (208 mg, 1.02 mmol), Cs_2CO_3 (166 mg, 0.51 mmol), pivalic acid (8 mg, 0.08 mmol), $Pd_2(dba)_3$ (12 mg, 0.01 mmol), P(o-MeOPh)$_3$ (8 mg, 0.03 mmol). %). The resulting heterogeneous reaction mixture was reacted at 110 °C (sand bath) under magnetic stirring. After 15 h, the mixture was cooled to room temperature, diluted with CH_2Cl_2, filtered to remove insoluble inorganic materials, and concentrated under reduced pressure. Purification by column chromatography (hexane:CH_2Cl_2= 9.5:0.5), afforded compound **7** (51 mg, 21% yield) as a pale yellow solid, m.p. = 109-110°C (after washing with hexane). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.75 (d, J = 7.7 Hz, 4H), 7.67 (br s, 2H), 7.44 (app t, J = 7.6 Hz, 4H), 7.36 (t, J = 7.3 Hz, 2H), 4.22 (br s, 4H), 1.94-1.86 (m, 2H), 1.72-1.63 (m, 4H), 1.55-1.20 (m, 60H), 0.87 (t, J = 6.5 Hz, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 144.5, 143.6, 134.5, 132.8, 129.6, 129.1, 128.5, 126.6, 116.0, 76.5, 39.4, 32.1, 32.1, 31.5, 30.4, 30.0, 29.9, 29.9, 29.9, 29.6, 29.5, 27.2, 22.0, 14.3. HRMS (LC-IT-TOF, elution with 0.01% (v/v) trifluoroacetic acid in acetonitrile) m/z: [M$^+$] Calcd. for $C_{62}H_{94}O_2S_2$ 934.6690; Found 934.6667.

Synthesis of 4,8-bis((2-octyldodecyl)oxy)benzo[1,2-*b*:4,5-*b*′]dithiophene 1,1,5,5-tetraoxide (8): *m*-Chloroperbenzoic acid (15.3 mmol) was added at room temperature over a 30 min period in 10 min increments to a solution of 4,8-bis((2-octyldodecyl)oxy)benzo[1,2-*b*:4,5-*b*′]dithiophene **6** (2.00g, 2.6 mmol) in CH_2Cl_2 (70 mL). The reaction vessel was covered in foil to prevent light exposure and stirred for 20h. The reaction mixture was washed with a saturated aqueous solution of $NaHCO_3$, dried with Na_2SO_4, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel (hexane:CH_2Cl_2, 1:1). A yellow low-melting solid was isolated (1.707 g, 78%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.38 (d, J = 6.9 Hz, 2H), 6.69 (d, J = 6.9 Hz, 2H), 4.35 (d, J = 5.3Hz, 4H), 1.89-1.80 (m, 2H), 1.52-1.22 (m, 64H), 0.88 (t, J = 6.8 Hz, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 145.2, 131.2, 130.8, 128.3, 127.2, 79.3, 39.0, 32.1, 32.0, 31.2, 30.1, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 26.9, 22.8, 22.8, 14.3. HRMS (LC-IT-TOF, elution with 0.1% (v/v) formic acid in methanol) m/z: [M+Cl]$^-$ Calcd. for $C_{50}H_{86}O_6S_2Cl$ 881.5560; Found 881.5551.

General procedure for the synthesis of compounds 9a-d: A round-bottomed flask (10 mL) with a screw cap and equipped with a magnetic stirrer was charged with 4,8-bis((2-octyldodecyl)oxy)benzo[1,2-*b*:4,5-*b*′]dithiophene

1,1,5,5-tetraoxide **8** (1 equiv), aryl iodide (4 equiv), Cs_2CO_3 (2 equiv), pivalic acid (30 mol%), $Pd_2(dba)_3$ (5 mol %), P(o-MeOPh)$_3$ (10 mol%).%). The resulting heterogeneous reaction mixture was reacted at 110 °C (sand bath) under magnetic stirring. After 15 h, the mixture was cooled to room temperature, diluted with CH_2Cl_2, percoled on silica gel to remove insoluble inorganic materials, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel and/or washing with hexane.

4,8-bis((2-octyldodecyl)oxy)-2,6-diphenylbenzo[1,2-*b*:4,5-*b'*]dithiophene 1,1,5,5-tetraoxide (9a). Compound **9a** was synthesized from **8** (200 mg, 0.24 mmol) and iodobenzene (194 mg, 0.95 mmol) in accordance with the general procedure. After washing with hexane, pure **9a** was isolated as a yellow solid (107 mg, 45%), m.p. = 130-132 °C (after crystallization from CH_2Cl_2/CH_3CH_2OH). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.84-7.81 (m, 4H), 7.52-7.47 (m, 6H), 7.44 (s, 2H), 4.43 (d, J = 5.4 Hz, 4H), 1.97-1.88 (m, 2H), 1.62-1.20 (m, 64H), 0.87 (t, J = 6.9 Hz, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 142.3, 142.8, 131.6, 130.9, 129.5, 127.6, 127.0, 126.9, 118.5, 79.6, 39.1, 32.1, 32.1, 31.3, 30.2, 29.9, 29.8, 29.8, 29.8, 29.5, 27.0, 22.8, 14.3. HRMS (LC-IT-TOF, elution with 0.01% (v/v) trifluoroacetic acid in acetonitrile) m/z: [M+Na]$^+$ Calcd. for $C_{62}H_{94}O_6S_2Na$ 1021.6384; Found 1021.6356.

4,8-bis((2-octyldodecyl)oxy)-2,6-di-*m*-tolylbenzo[1,2-*b*:4,5-*b'*]dithiophene 1,1,5,5-tetraoxide (9b). Compound **9b** was synthesized from **8** (150 mg, 0.18 mmol) and 1-iodo-3-methylbenzene (155 mg, 0.72 mmol) in accordance with the general procedure. After washing with hexane, pure **9b** was isolated as a yellow solid (85 mg, 47%), m.p. = 154-156 °C (after crystallization from CH_2Cl_2/CH_3CH_2OH). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.65-7.60 (m, 4H), 7.42 (s, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 7.6 Hz, 2H), 4.43 (d, J = 5.3 Hz, 4H), 2.43 (s, 6H), 1.97-1.89 (m, 2H), 1.62-1.22 (m, 64H), 0.87 (t, J = 6.7 Hz, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 145.2, 142.9, 139.3, 131.8, 131.7, 129.3, 127.6, 127.3, 126.9, 124.1, 118.3, 79.6, 39.1, 32.0, 32.0, 31.3, 30.2, 29.9, 29.8, 29.8, 29.8, 29.5, 27.0, 22.8, 21.6, 14.3. HRMS (LC-IT-TOF, elution with 0.01% (v/v) trifluoroacetic acid in acetonitrile) m/z: [M+Na]$^+$ Calcd. for $C_{64}H_{98}O_6S_2Na$ 1049.6697; Found 1049.6728.

2,6-bis(3,5-dimethylphenyl)-4,8-bis((2-octyldodecyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene 1,1,5,5-tetraoxide (9c). Compound **9c** was synthesized from **8** (150 mg, 0.18 mmol) and 1-iodo-3,5-dimethylbenzene (167 mg, 0.72 mmol) in accordance with the general procedure. The crude product was purified by column chromatography on silica gel (hexane:CH_2Cl_2, 7:3). After washing with hexane, pure **9c** was isolated as an orange solid (92 mg, 46%), m.p. = 214-215 °C (after crystallization from CH_2Cl_2/CH_3CH_2OH). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.43 (br s, 4H), 7.39 (s, 2H), 7.12 (br s, 2H), 4.43 (d, J = 5.4 Hz, 4H), 2.39 (s, 12H), 1.98-1.89 (m, 2H), 1.64-1.20 (m, 64H), 0.89-0.85 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 145.2, 143.0, 139.1, 132.8, 131.7, 127.6, 126.8, 124.5, 118.2, 79.6, 39.1, 32.1, 32.0, 31.3, 30.2, 29.9, 29.8, 20.8, 29.8, 29.5, 27.0, 22.8, 21.5, 14.3. HRMS (LC-IT-TOF, elution with 0.01% (v/v) trifluoroacetic acid in acetonitrile) m/z: [M+Na]$^+$ Calcd. for $C_{66}H_{102}O_6S_2Na$ 1077.7010; Found 1077.6982.

4,8-bis((2-octyldodecyl)oxy)-2,6-di-*p*-tolylbenzo[1,2-*b*:4,5-*b'*]dithiophene 1,1,5,5-tetraoxide (9d). Compound **9d** was synthesized from **8** (150 mg, 0.18 mmol) and 1-iodo-4-methylbenzene (154 mg, 0.72 mmol) in accordance with the general procedure. After washing with hexane, pure **9d** was isolated as a yellow-orange solid (68 mg, 37%), m.p. = 151-153 °C (after crystallization from CH_2Cl_2/CH_3CH_2OH). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.72 (d, J = 8.1 Hz, 4H), 7.37 (s, 2H), 7.29 (d, J = 8.1 Hz, 4H), 4.42 (d, J = 5.3 Hz, 4H), 2.42 (s, 6H), 1.97-1.88 (m, 2H), 1.62-1.22 (m, 64H), 0.88 (t, J = 6.9 Hz, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 145.2, 142.7, 141.4, 131.6, 130.2, 127.6, 126.7, 124.2, 117.4, 79.5, 39.1, 32.1, 32.1, 31.3, 30.2, 29.9, 29.8, 29.8, 29.8, 29.5, 27.0, 22.8, 21.7, 14.3. HRMS (LC-IT-TOF, elution with 0.01% (v/v) trifluoroacetic acid in acetonitrile) m/z: [M+Na]$^+$ Calcd. for $C_{64}H_{98}O_6S_2Na$ 1049.6697; Found 1049.6663.

General procedure for the synthesis of compounds 9e-f: A round-bottomed flask (10 mL) with a screw cap and equipped with a magnetic stirrer was charged with 4,8-bis((2-octyldodecyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene 1,1,5,5-tetraoxide **8** (1 equiv), aryl iodide (4 equiv), $Pd(OPiv)_2$ (5 mol%), P(o-MeOPh)$_3$ (10 mol%) and Ag_2CO_3 (1 equiv). %). The resulting heterogeneous reaction mixture was reacted at 110 °C (sand bath) under magnetic stirring. After 2 h, the mixture was cooled to room temperature, diluted with CH_2Cl_2, percoled on silica gel to remove insoluble inorganic materials, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel and/or washing with hexane.

2,6-bis(4-methoxyphenyl)-4,8-bis((2-octyldodecyl)oxy)benzo[1,2-b:4,5-b']dithiophene 1,1,5,5-tetraoxide (9e). Compound **9e** was synthesized from **8** (150 mg, 0.18 mmol) and 1-iodo-3-methoxybenzene (166 mg, 0.71 mmol) in accordance with the general procedure. After washing with hexane, pure **9e** was isolated as an orange solid (101 mg, 50%), m.p. = 120-122 °C (after crystallization from CH_2Cl_2/CH_3CH_2OH). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.77 (d, J = 8.7 Hz, 4H), 7.28 (s, 2H), 7.00 (d, J = 8.7 Hz, 4H), 4.40 (d, J = 5.3 Hz, 4H), 3.87 (s, 6H), 1.96-1.88 (m, 2H), 1.62-1.20 (m, 64H), 0.87 (t, J = 6.7 Hz, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 161.7, 145.1, 142.4, 131.5, 128.5, 127.6, 119.6, 116.0, 115.0, 79.5, 55.6, 39.1, 32.1, 31.3, 30.2, 29.9, 29.8, 29.8, 29.8, 29.5, 27.0, 22.8, 14.3. HRMS (LC-IT-TOF, elution with 0.01% (v/v) trifluoroacetic acid in acetonitrile) m/z: [M+Na]$^+$ Calcd. for $C_{64}H_{98}O_8S_2Na$ 1081.6595; Found 1081.6585.

dimethyl 4,4'-(4,8-bis((2-octyldodecyl)oxy)-1,1,5,5-tetraoxidobenzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)dibenzoate (9f). Compound **9f** was synthesized from **8** (150 mg, 0.18 mmol) and methyl 4-iodobenzoate (186 mg, 0.71 mmol) in accordance with the general procedure. The crude product was purified by column chromatography on silica gel (from hexane: ethyl acetate 9:1 to CH_2Cl_2). After washing with hexane, pure **9f** was isolated as a yellow solid (83 mg, 42%), m.p. =174-175 °C (after crystallization from

CH_2Cl_2/CH_3CH_2OH). ^1H NMR ($CDCl_3$, 500 MHz) δ: 8.12 (d, J = 8.2 Hz, 4H), 7.86 (d, J = 8.2 Hz, 4H), 7.54 (s, 2H), 4.45 (d, J = 5.4 Hz, 4H), 3.95 (s, 6H), 1.97-1.89 (m, 2H), 1.61-1.21 (m, 64H), 0.89-0.85 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ: 166.1, 145.4, 141.7, 131.9, 131.5, 130.9, 130.5, 127.6, 126.7, 120.4, 79.6, 52.6, 39.1, 32.1, 31.3, 30.2, 29.9, 29.8, 29.8, 29.5, 29.5, 27.0, 22.8, 14.3. HRMS (LC-IT-TOF, elution with 0.01% (v/v) trifluoroacetic acid in acetonitrile) m/z: $[M+Na]^+$ Calcd. for $C_{66}H_{98}O_{10}S_2Na$ 1137.6494; Found 1137.6485.

General procedure for the synthesis of compounds 12a-d. A round-bottomed flask (10 mL) with a screw cap and equipped with a magnetic stirrer was charged with **10** (1 equiv), aryl iodide (4 equiv), $Pd(OPiv)_2$ (5 mol%), P(*o*-MeOPh)$_3$ (10 mol%) and Ag_2CO_3 (1 equiv). The resulting heterogeneous reaction mixture was reacted at 110 °C (sand bath) under magnetic stirring. After 18 h, the mixture was cooled to room temperature and the crude product was purified by column chromatography on silica gel.

5,6-difluoro-4,7-diphenylbenzo[*c*][1,2,5]thiadiazole (12a). Compound **12a** was synthesized from **10** (100 mg, 0.58 mmol) and iodobenzene (474 mg, 2.32 mmol) in accordance with the general procedure. The crude product was purified by column chromatography on silica gel (hexane: ethyl acetate 9.8:0.2) and by washing with ethyl acetate affording **12a** (175 mg, 93%) as a white solid, m.p. = 203-204 °C (after washing with ethyl acetate). ^1H NMR ($CDCl_3$, 500 MHz) δ: 7.83 (d, J = 7.5 Hz, 4H), 7.59 (t, J = 7.5 Hz, 4H), 7.52 (t, J = 7.5 Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ: 150.6 (d, J = 3.8 Hz), 150.4 (dd, J = 258.7, 20.4 Hz), 130.6, 130.4, 129.3, 128.7, 118.9 (dd, J = 10.6, 4.7 Hz). HRMS (LC-IT-TOF, elution with 0.01% (v/v) trifluoroacetic acid in acetonitrile) m/z: $[M+H]^+$ calcd. for $C_{18}H_{11}F_2N_2S$ 325.0606; Found 325.0608.

4,7-bis(3-bromophenyl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (12b). Compound **12b** was synthesized from **10** (100 mg, 0.58 mmol) and 1-bromo-3-iodobenzene (658 mg, 2.32 mmol) in accordance with the general procedure. The crude product was purified by column chromatography on silica gel (from hexane: ethyl acetate 9.5:0.5 to CH_2Cl_2) and by washing with ethyl acetate affording **12b** (225 mg, 81%) as a beige solid, m.p. = 225-226 °C (after washing with ethyl acetate). ^1H NMR ($CDCl_3$, 500 MHz) δ: 7.99 (br s, 2H), 7.77 (d, J = 7.9 Hz, 2H), 7.67-7.64 (m, 2H), 7.46 (t, J = 7.9 Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ: 150.5 (dd, J = 260.1, 20.4 Hz), 150.2 (t, J = 3.7 Hz), 133.5, 132.5, 132.1, 130.2, 129.3, 122.7, 118.0 (dd, J = 10.4, 4.6 Hz). HRMS (LC-IT-TOF, elution with 0.01% (v/v) trifluoroacetic acid in acetonitrile) m/z: $[M-H]^-$ Calcd. for $C_{18}H_7Br_2F_2N_2S$ 478.8670; Found 478.8695.

5,6-difluoro-4,7-bis(4-fluorophenyl)benzo[*c*][1,2,5]thiadiazole (12c).[22b,26] Compound **12c** was synthesized from **10** (100 mg, 0.58 mmol) and 1-fluoro-4-iodobenzene (516 mg, 2.32 mmol) in accordance with the general procedure. The crude product was purified by column chromatography on silica gel (from hexane: ethyl acetate 9.5:0.5 to CH_2Cl_2) and by washing with ethyl acetate affording **12c** (90 mg, 43%) as a pale yellow solid, m.p. = 261-263 °C (after washing with ethyl acetate) (lit. 233-240 °C).[26] ^1H NMR ($CDCl_3$, 500 MHz) δ: 7.83 (dd, J = 8.7, 5.4 Hz, 4H), 7.28 (d, J = 8.7 Hz, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ: 163.3 (d, J = 249.9 Hz), 150.5 (t, J = 3.7 Hz), 150.4 (dd, J = 258.8, 20.4 Hz), 132.6 (d, J = 8.4 Hz), 126.2 (d, J = 3.6 Hz), 118.0 (dd, J = 10.4, 4.7 Hz), 115.9 (d, J = 21.8 Hz). MS (70 eV): *m*/*z* (%) 360 (M^+, 100), 341 (15), 327 (32).

5,6-difluoro-4,7-bis(4-methoxyphenyl)benzo[*c*][1,2,5]thiadiazole (12d).[22b,26] Compound **12d** was synthesized from **10** (100 mg, 0.58 mmol) and 1-iodo-4-methoxybenzene (544 mg, 2.32 mmol) in accordance with the general procedure. The crude product was purified by column chromatography on silica gel (hexane: ethyl acetate from 9:1 to 7:3) affording **12d** (142 mg, 64%) as a yellow solid, m.p. = 208-210 °C (after washing with ethyl acetate) (lit. 214-215 °C).[26] ^1H NMR ($CDCl_3$, 500 MHz) δ: 7.80 (d, J = 8.8 Hz, 4H), 7.10 (d, J = 8.8 Hz, 4H), 3.91 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ: 106.3, 150.8 (t, J = 3.9 Hz), 150.3 (dd, J = 257.2, 20.4 Hz), 132.0, 122.7, 118.1 (dd, J = 10.4, 4.8 Hz), 114.2, 55.5. HRMS (LC-IT-TOF, elution with 0.01% (v/v) trifluoroacetic acid in acetonitrile) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{15}F_2N_2O_2S$ 385.0817; Found 385.0800.

General procedure for the synthesis of compounds 12e-g: A round-bottomed flask (10 mL) with a screw cap and equipped with a magnetic stirrer was charged with **11** (1 equiv), aryl iodide (4 equiv), $Pd(OPiv)_2$ (10 mol%), P(*o*-MeOPh)$_3$ (20 mol%) and Ag_2CO_3 (1 equiv). %). The resulting heterogeneous reaction mixture was reacted at 110 °C (sand bath) under magnetic stirring. After 18 h, the mixture was cooled to room temperature and the crude product was purified by column chromatography on silica gel.

1,1'-((5,6-difluoro-2-(heptadecan-9-yl)-2*H*-benzo[*d*][1,2,3]triazole-4,7-diyl)bis(4,1-phenylene))diethanone (12e). Compound **12e** was synthesized from **11** (100 mg, 0.25 mmol) and 1-(4-iodophenyl)ethanone (250 mg, 1.02 mmol) in accordance with the general procedure. The crude product was purified by column chromatography on silica gel (from hexane: ethyl acetate 9.5:0.5) affording **12e** (88 mg, 55%) as a white solid, m.p. = 84-85 °C (after crystallization from hexane). ^1H NMR ($CDCl_3$, 500 MHz) δ: 8.14 (d, J = 8.3 Hz, 4H), 8.07 (d, J = 8.3 Hz, 4H), 4.85-4.78 (m, 1H), 2.68 (s, 6H), 2.19-2.09 (m, 2H), 1.95-1.86 (m, 2H), 1.33-1.16 (m, 22H), 1.06-0.97 (m, 2H), 0.84 (t, J = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ: 197.6, 147.9 (dd, J = 252.9, 19.4 Hz), 138.6 (t, J = 4.0 Hz),136.8, 135.5, 130.5, 128.4, 116.4 (dd, J = 10.3, 3.6 Hz), 68.8, 35.4, 31.8, 29.3, 29.1, 29.1, 26.7, 26.0, 22.6, 14.0. HRMS (LC-IT-TOF, elution with methanol) m/z: $[M+Na]^+$ Calcd. for $C_{39}H_{49}F_2N_3O_2Na$ 652.3674; Found 652.3670.

dimethyl 4,4'-(5,6-difluoro-2-(heptadecan-9-yl)-2*H*-benzo[*d*][1,2,3]triazole-4,7-diyl)dibenzoate (12f). Compound **12f** was synthesized from **11** (100 mg, 0.25 mmol) and methyl 4-iodobenzoate (266 mg, 1.02 mmol) in accordance with the general procedure. The crude product was purified by column chromatography on silica gel (from hexane: ethyl acetate 9.5:0.5) affording **12f** (124 mg, 74%) as a white solid, m.p. = 92-93 °C (after crystallization from hexane). ^1H NMR ($CDCl_3$, 500 MHz) δ: 8.22 (d, J = 8.6 Hz, 4H), 8.04

(d, J = 8.6 Hz, 4H), 4.85-4.77 (m, 1H), 3.97 (s, 6H), 2.18-2.08 (m, 2H), 1.95-1.86 (m, 2H), 1.34-1.16 (m, 22H), 1.07-0.97 (m, 2H), 0.84 (t, J = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ: 166.9, 148.0 (dd, J = 253.1, 19.8 Hz), 138.8 (t, J = 3.6 Hz), 135.6, 130.5, 130.2, 129.8, 116.6 (dd, J = 10.5, 3.4 Hz), 68.9, 52.4, 35.6, 31.9, 29.5, 29.3, 29.2, 26.1, 22.8, 14.2. HRMS (LC-IT-TOF, elution with methanol) m/z: $[M+Na]^+$ Calcd. for $C_{39}H_{49}F_2N_3O_4Na$ 684.3583; Found 684.3568.

5,6-difluoro-2-(heptadecan-9-yl)-4,7-bis(4-methoxyphenyl)-2*H*-benzo[*d*][1,2,3]triazole (12g). Compound **12g** was synthesized from **11** (100 mg, 0.25 mmol) and 1-iodo-4-methoxybenzene (238 mg, 1.02 mmol) in accordance with the general procedure. The crude product was purified by column chromatography on silica gel (from hexane: ethyl acetate 9.5:0.5) affording **12g** (100 mg, 65%) as a white solid, m.p. = 69-70 °C (after crystallization from hexane). ^1H NMR ($CDCl_3$, 500 MHz) δ: 7.93 (d, J = 8.6 Hz, 4H), 7.08 (d, J = 8.6 Hz, 4H), 4.84-4.76 (m, 1H), 3.90 (s, 6H), 2.19-2.10 (m, 2H), 1.95-1.85 (m, 2H), 1.32-1.17 (m, 22H), 1.07-0.98 (m, 2H), 0.85 (t, J = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ: 159.8, 147.6 (dd, J = 249.3, 19.5 Hz), 139.1 (t, J = 4.2 Hz), 131.7, 123.7, 115.8 (dd, J = 10.1, 3.6 Hz), 114.1, 68.6, 55.5, 35.6, 31.9, 29.5, 29.3, 29.3, 26.2, 22.8, 14.2. HRMS (LC-IT-TOF, elution with methanol) m/z: $[M+Na]^+$ Calcd. for $C_{37}H_{49}F_2N_3O_2Na$ 628.3685; Found 628.3686.

ASSOCIATED CONTENT

Supporting Information. Copy of ^1H NMR spectra of known compounds. Copy of ^1H and ^{13}C NMR spectra of new compounds. "This material is available free of charge via the Internet at http://pubs.acs.org."

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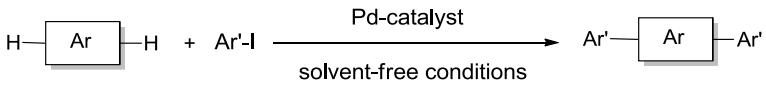

Ar = TPD, DPP, BDT, DFBT, DFBTz