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Dissymetrisation of benzothiadiazole by direct C-H arylation: a way to symmetrical and unsymmetrical elongated π-conjugated molecules

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Abstract

5-(7-Bromo-2,1,3-benzothiadiazol-4-yl)-2-thiophenecarboxaldehyde is a small building block of great interest for its use in the elaboration of symmetrical or unsymmetrical donor-acceptor π-conjugated molecules, for optoelectronic applications. Herein, a convenient, one-pot, two-component synthesis of this intermediate is reported, based upon palladium-catalysed, phosphine and additive-free, direct C-H arylation process. The synthesis is studied in depth to obtain optimum yields and selectivity, according to an efficient and environmentally friendly strategy for sustainable synthesis.

Keywords

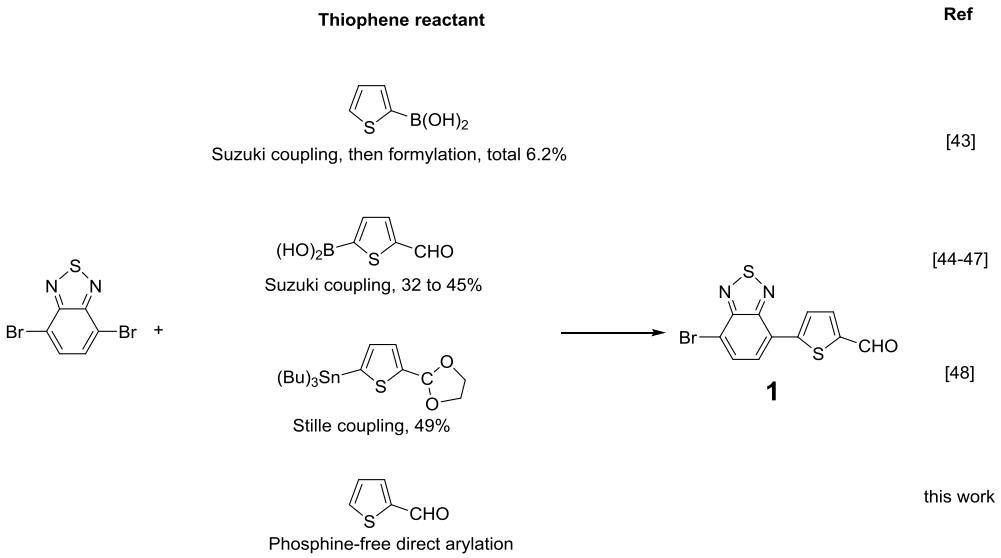
4,7-Dibromobenzo-2,1,3-thiadiazole; Direct C-H arylation; Phosphine-free Palladium catalyst; Mono-arylation; Thiophene

Introduction

Organic semiconductors for optoelectronics are often based on alternating electron donor and electron acceptor (D-A) moieties [1-7]. The classical synthetic approaches toward these D-A structural materials rely on traditional cross-coupling reactions, such as Suzuki coupling using arylene diboronic acids/esters [8,9] and Stille coupling using stannyl reagents [10]. Such transition metal-catalysed cross couplings are still considered as powerful tools for C-C bond formation. However, they involve the use of boron- or tin-aromatic derivatives that are potentially costly and toxic, respectively, with the probable production of stoichiometric amounts of environmentally risky by-products such as stannylated compounds. Therefore, transition-metal (Palladium, Rhodium, Ruthenium) catalysed coupling methods of non-preactivated aryl C-H bonds with aryl halides, belonging to the so-called direct arylation, have become a focus of interest [11-19]. These methods have emerged as sustainable synthetic protocols of π-conjugated materials using simplified reaction steps and reduced undesirable organometallic reagents [12,17-23]. In the field of photovoltaics, there have been fruitful successes in using thiophene-based molecules and polymers [27]. But so far, these materials are mostly obtained via Suzuki [28-30] or Stille [31-33] coupling. However, as demonstrated recently by M. Leclerc and co-workers [34], direct arylation assisted with phosphine ligands is a promising method to synthesize high molecular weight conjugated thiophene-based polymers with suitable yields in a faster and more environmentally friendly way. In the same time, H. Doucet and co-workers proposed the use of phosphine-free low loading Palladium catalyst at high temperature to yield highly selective 2- or 5-arylated heteroaromatics [35-39]. In a general manner, this last strategy offers great advantages: due to the reduced number of reactants, the workup is simplified and production cost is even reduced. Thus, it may be considered

environmentally and economically attractive as well as efficient. In this spirit, we recently performed the synthesis of benzothiadiazole- (Bz) based symmetrical molecules by using dibromobenzothiadiazole (diBrBz) and 2-thiophenecarboxaldehyde (ThCHO) as starting materials (Figure 1 top), through phosphine and additive-free direct C-H arylation [40].

In the present study, we investigated the disymmetrisation of the Bz unit by the synthesis of the monoadduct 5-(7-bromo-2,1,3-benzothiadiazol-4-yl)-2-thiophenecarboxaldehyde (molecule **1**, Scheme 1). Note that the synthesis of the difluorobenzothiadiazole (DFBT) analogue in 74% yield using a palladium redox catalytic cycle has been recently reported, where $Pd(TFA)_2$ and Ag_2O were used as the catalyst and the oxidant, respectively [41]. These reactions conditions lead satisfactorily via dual C–H functionalization to the thienylation of DFBT with various thiophene derivatives. However, they were not applicable to non-fluorinated benzothiadiazole and we never succeeded in obtaining molecule **1** in that way. As molecule **1** is not yet commercially available but constitutes a unique building block for creating symmetrical or unsymmetrical π-conjugated D-A molecules [42-48], the suggestion for an effective and simple synthesis protocol should be of interest to many chemists. So far, there are a few reports about the synthesis of **1** in good yields (i.e. more than 40%), and the related synthetic protocols are based on Suzuki [43-47] or Stille [48] couplings (see Scheme 1).



Scheme 1: use of diBrBz in synthetic pathways leading to molecule **1** with related yields

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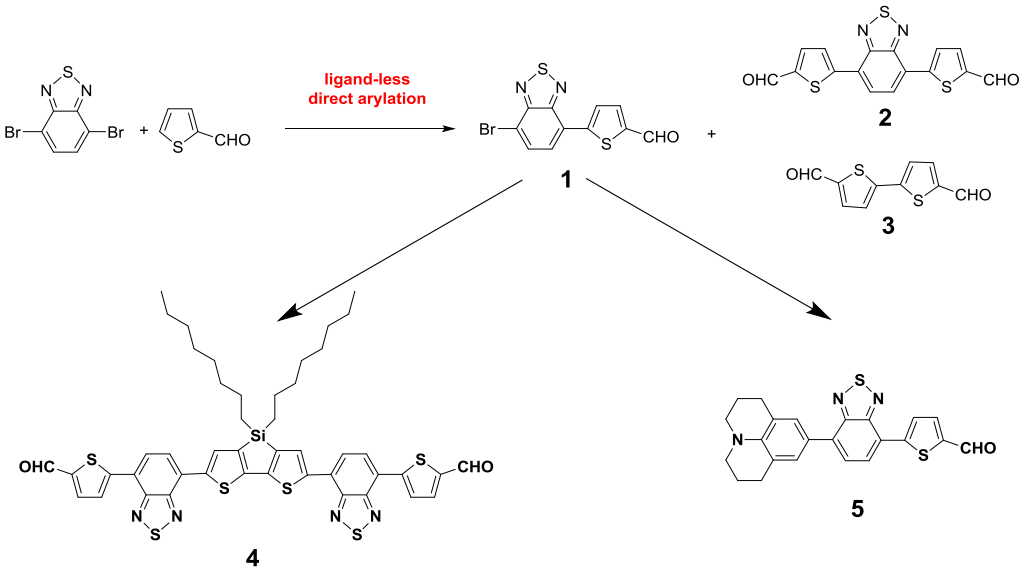
X. Yang *et al.* recently proposed its synthesis in two steps, first a Suzuki coupling providing the intermediate 4-bromo-7(-thiophen-2-yl)benzo[1,2,5]thiadiazole (54% intermediate yield), which was then formylated through a classical way to afford **1**. Note that this pathway offers a low overall yield of 6.24% [43]. At almost the same time, Y. Geng and co-workers proposed the synthesis of **1** from diBrBz and 5-carboxythiophene-2-boronic acid as reagents through Suzuki coupling using microwaves. They obtained the desired molecule in 40% yield [44]. More recently, K. Seo *et al.* employed Stille coupling with diBrBz and (5-(1,3-dioxolan-2-yl)thiophen-2-yl)tributylstannane in tetrahydrofuran (THF) for getting **1** in 49% yield [48]. These examples involve the purchase or preparation of intermediate organometallic reactants. Thus considering the simplest possible starting materials, namely diBrBz and ThCHO, the overall yield in molecule **1** is still low, if one takes into account the preparation of the building blocks. To our knowledge, the direct C-H activation approach has never been described for the synthesis of molecule **1**, maybe because of the difficulty of dissymetrisation, and the eventual occurring of side reactions like homocoupling [49]. This work is thus expected to benefit the synthesis of **1** simply based on diBrBz and ThCHO via direct C-H activation (see Scheme 2) for the purpose of constructing extended π-conjugated D-A molecules such as **4** or **5**, as shown in Scheme 2.



Scheme 2: Formation of molecule **1** via direct arylation and subsequent possible symmetrical (**4**) and unsymmetrical (**5**) π-conjugated D-A molecules. The di-adduct **2** and homocoupling derivative **3** are probable by-products of direct arylation.

Results and Discussion

Suzuki coupling

As a reference, and inspired by the work of Y. Geng and co-workers [44], the Suzuki coupling reaction was first tested in modified conditions (see ESI): we used diBrBz and 5-formyl-2-thiopheneboronic acid pinacol ester as reagents and $Pd(PPh_3)_4/K_2CO_3$ as the catalyst/base system. This reaction is established to occur by oxidative addition, transmetallation and reductive elimination. The oxidative addition on the bromo-compound is often the rate-determining step [50-52], so the main difficulty here is linked to the likely high reactivity of ThCHO with regard to that of diBrBz. We were unable to get the desired product with acceptable yields under microwave irradiation, but better results were obtained in classical conditions at 80°C, and in adding drop-wisely ThCHO to the reactive medium. At best a 30% yield was reached, which can be considered as a minimum value for an acceptable alternative protocol.

Direct arylation

As a preliminary screening, we tested direct arylation with and without phosphine ligand, using diBrBz and ThCHO as the reactants (Table 1). Phosphine-assisted direct arylation was adapted from conditions defined by Marder *et al.* [53], using $Pd(OAc)_2$ and $P^tBu_2Me.HBF_4$ as the catalytic system in toluene, with pivalic acid (PivOH) as the additive and K_2CO_3 as the base. We tested various diBrBz/ThCHO ratios, the amount of catalyst, phosphine and pivalic acid, and the time of reaction (see Supporting Information). At best, the desired product was isolated in 20% yield for a use of 5% catalyst. The main by-product is the symmetrical di-adduct **2** (See

Scheme 1). It is worth to note that this di-adduct may be synthesized in quantitative yield by using a diBrBz/ThCHO ratio of 0.45 (see SI). For comparison, a phopsphine-free process was tested, following a procedure similar to that suggested by Doucet *et al.* who used a reduced amount of base in order to decrease the amount of wastes [54]. We engaged the two reactants with 1 mol% of Pd catalyst and 1 base equivalent in dimethylacetamide (DMAc) as the solvent. We obtained similar yields than with phosphine-assisted arylation (Table1).

Table 1: Reaction of diBrBz with ThCHO following two direct arylation procedures.

entry	diBrBz/ ThCHO	$Pd(OAc)_2$ (%)	ligand (mol %)	PivOH (mol %)	base (eq)	solvent	temp (°C)	time (h)	yield (%)*
1	1.4	5	10%	30%	3[a]	toluene	110°C	24	24 (20)
2	1	1	0	0	1[b]	DMAc	115°C	24	17 (14)

[a] base = K_2CO_3; [b] base = KOAc; * NMR and isolated (in parentheses) yields

We decided to explore further the phosphine-free procedure because it offers several potential advantages making it particularly attractive [54,55]: i) it is efficient for electron-deficient aryl bromide such as diBrBz, ii) it needs neither phosphine ligand nor additive, iii) it uses a little amount of catalyst. Moreover, we highlighted that this reaction is rather clean: mostly the target molecule **1**, the di-adduct **2**, and molecule **3** arising from the 5,5'-homocoupling of ThCHO, were present in significant amounts in the crude, along with the eventual presence of non-reacted starting reactants diBrBz and ThCHO (see NMR spectra in SI). This renders easy the analysis of the course of the reaction and makes it possible to evaluate the reaction yield by a simple NMR analysis.

We first tested various temperatures for a 24 h reaction as shown in Table 2. Note that when the temperature of the reaction mixture reached 130°C, only molecule **2** was formed. As stated by de Vries [56], $Pd(OAc)_2$ catalysed reactions (Heck or Suzuki couplings) proceed through the formation of soluble palladium(0) colloids or nanoparticles formed at elevated temperature.

The conversion rate of diBrBz indicates that for the present case, the optimum reaction temperature for allowing the catalytic system to effectively take place is of around 105°C. At higher temperature, the selectivity dramatically decreases in such a way that we obtained the exclusive formation of **2** at 130°C. In rising the reaction temperature, we faced a compromise between selectivity (in favour to **1** at low temperature) and conversion rate (which decreases when significant amount of **2** is formed), thus a quantitative yield for molecule **1** cannot be awaited. The optimal conditions correspond to an operating temperature of 105°C giving a selectivity of 2.5 for a conversion rate of 33.4% (Table 2, entry 3).

Table 2: Effect of temperature on phosphine-free direct arylation of ThCHO with diBrBz in DMAc. Fixed parameters: 1 to 1 eq. of engaged ThCHO and diBrBz; catalyst = 1% $Pd(OAc)_2$, base = 2 eq. KOAc, and time of reaction = 24h.

entry	temp (°C)	molar ratios in the crude[a]			selectivity[b]	conv. rate [c] (%)	yield in **1** (%)[d]
		2	diBrBz	**3**			
1	60	0.1	15	-	10	6.8	6
2	95	0.1	5.85	0.09	10	15.9	14.5
3	105	0.4	2.8	-	2.5	33.4	24
4	115	0.8	5.5	0.05	1.25	24.6	13.7

[a] relative to **1** and according to ^{1}H NMR analysis; [b] **1**:**2** molar ratio according to NMR analysis; [c] % of reacted diBrBz; [d] isolated yield.

One way to improve the yield was to adapt the optimal conditions by involving a default of ThCHO. By means of 0.5 equivalent of ThCHO for 1 equivalent of diBrBz, a better yield of 35% in **1** (related to the involved ThCHO) was reached. This is however not fully satisfactory because a significant amount of diBrBz (up to 85%) remained non-reacted.

Another way was to raise the amount of catalyst up to 5% (entry 2, Table 3). This proved however to be unfruitful since the selectivity dramatically decreased despite very similar obtained yields. Finally, we found that increasing the time of reaction was the simplest way for improving the yield. A duration of up to 3 days played a decisive role in achieving an optimum 45% yield for a selectivity of 2.7, *i.e.* the best results we have ever reached. It is also noted that,

by doubling the amount of starting materials (without changing the co-reagent ratios), the yield is unchanged. The relevant details are summarized in the following table:

Table 3: Optimization of $Pd(OAc)_2$-catalysed direct arylation of ThCHO with diBrBz in DMAc at 105°C.

entry	% Pd	time (h)	molar ratios in the crude[a]			Selectivity[b]	conv. Rate [c] (%)	yield in **1** (%)[d]
			2	diBrBz	**3**			
1	1	24	0.4	2. 8	-	2.5	33.4	24
2	5	24	1	2.3	0.25	1.0	46.4	23
3	1	72	0.37	0.85	0.06	2.7	62	45

[a] relative to **1** and according to ^{1}H NMR analysis; [b] Selectivity = **1**/**2** molar ratio according to NMR analysis; [c] % of reacted diBrBz; [d] isolated yield.

As initially proposed, we used molecule **1** for elaborating symmetrical and unsymmetrical π-conjugated molecules. The two elongated molecules, **4** and **5** were obtained through Suzuki coupling in good yields, of around 60%. Their synthesis *via* direct arylation is not straightforward, and is currently under investigations. These new molecules are end-capped by aldehyde functions that will be later engaged in Knoevenagel condensations for the generation of new materials for organic photovoltaics, opening the way to new families of donor-acceptor π-conjugated molecules based on the benzothiadiazole-thiophene fragment.

Conclusion

In summary, we have demonstrated that phosphine-free direct arylation is a convenient tool for obtaining the mono-adduct **1**, despite its pronounced ability to undergo a second arylation leading to the symmetrical molecule **2**. By using 1 mol% of $Pd(Ac)_2$ at a moderate reaction temperature of 105°C in DMAc under argon atmosphere, the direct 5-arylation *via* C-H bond activation of thiophene derivative proceeds in satisfactory yields, up to 45%. When the amount of catalyst is increased up to 5 mol%, no improvement in the yield was observed, and the selectivity of the reaction is decreased. This low catalyst loading procedure is easy to carry out,

as well as the purification process and may be applied to a variety of coupling reactions when mono-adduct is preferred.

Experimental Section

General: Solvents: All reactions and manipulations were carried out under Ar, with degassed solvents, by the use of standard inert atmosphere and Schlenk techniques. All the synthetic procedures were repeated at least five times, the reported results were averaged. Anhydrous toluene, potassium carbonate and potassium acetate were purchased from Aldrich. $Pd(OAc)_2$ (99+%) was purchased from Strem Chemicals. Pivalic acid was purchased from Acros. 2-Thiophenecarboxaldehyde (ThCHO), and $PtBu_2Me.HBF4$ were purchased from Alfa Aesar. N,N-Dimethylacetamide, 99.5%, Extra Dry over Molecular Sieve, AcroSeal® was purchased from Acros Organics. 4,7-Dibromo-2,1,3-benzothiadiazole (diBrBz) and 5-formyl-2-thiopheneboronic acid pinacol ester were bought from Interchim. 9-(Tributylstannyl)-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinoline was synthesized in a similar way as the preparation of N,N-diphenyl-4-(tributylstannyl)aniline [57]. 4,4'-Dioctyl-5,5'-bis(tributyltin)-dithieno[3,2-b:2',3'-d]silole was synthesized according to literature procedure [58].

^{1}H and ^{13}C NMR spectra were acquired in $CDCl_3$ and DMSO-*d6* using Bruker Avance 300 and Avance 400 spectrometers and the signals were referenced using the corresponding solvent peaks. The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet).

Chromatographic separations were performed using standard column chromatography methods using silica gel purchased from Sigma-Aldrich (60 Å, 63-200 μm).

Suzuki coupling for the synthesis of molecule 1:

Method a, microwave: diBrBz (706 mg, 2.4 mmol), 5-formyl-2-thiopheneboronic acid pinacol ester (381 mg, 1.6 mmol), and Pd(PPh3)4/K2CO3 (92 mg/11 mg, 5% mol) were mixed in dry

toluene (4 ml) and dry methanol (1 ml) under argon atmosphere. The solution was irradiated using microwaves (T= 100°C, 2 cycles of 30 minutes at 25 W). The red mixture was filtered and washed with toluene and dichloromethane. The combined organic phases were evaporated and purified by column chromatography first using dichloromethane and pentane (1:1) and then using petroleum ether and ethyl acetate (4:1) as eluent, giving rise to 13 mg of pure orange mono-arylated product (3%).

Method b, drop-wise method: All solvents and basic solutions were previously degassed by bubbling through argon for 20 min. diBrBz (500 mg, 1.7 mmol) was placed in an oven dried three-necked flask under an inert atmosphere. Toluene (30 mL), K_2CO_3 (2.0 M, 2 mL), H_2O (6 mL) and Aliquat 336 (4–5 drops) were sequentially added under argon and the mixture was vigorously stirred for 10 min at room temperature. $Pd(PPh_3)_4$ (3 mol%) was then added and the reaction was maintained under strong stirring until it reached 80°C. Then, 5-formyl-2-thiopheneboronic acid pinacol ester (365 mg, 1.55 mmol) previously dissolved in 10 mL toluene and degassed for 15 min, was added drop-wisely for 3 hours. The mixture was allowed to react at 80°C until TLC reveal that 5-formyl-2-thiopheneboronic acid pinacol ester disappeared, *i.e.* after 14 h. After cooling down to room temperature, the mixture was extracted twice with dichloromethane. The organic extracts were gathered, dried over $MgSO_4$, filtered, combined and concentrated under vacuum. The residue was purified by column chromatography on silica (eluent = petroleum ether: ethyl acetate, from 4:1 to 0:1) to give 150 mg of molecule **1** as a yellow-orange powder (30% yield). TLC (pentane:dichloromethane 1:1): Rf = 0.63. IR (Neat): ν_{max} = 3098, 3084, 2882, 2788, 2722, 2156, 1660, 1652, 1512, 1440, 1386 cm^{-1}. HRMS (TOF-ESI) (m/z): calcd. for $(M+H)^+$ $C_{11}H_6N_2OS_2Br$: 324.9105, found: 324.9102. Element. Anal. Found: C, 40.56; H, 1.45; N, 8.80 %; molecular formula $C_{11}H_5N_2OS_2Br$ requires C, 40.59; H, 1.54; N, 8.61 %. NMR analyses on molecule **1**: ^{1}H NMR (400 MHz, Chloroform-*d*, 25°C): δ = 10.01 (s, 1H, CHO), 8.21 (d, ^3J = 4 Hz, 1H, H thiophene), 7.95 (d, ^3J = 7.7 Hz, 1H, H benzothiadiazole), 7.88 (d, ^3J = 4 Hz, 1H, H thiophene), 7.87 (d, J = ^3J = 7.7

Hz, 1H, H benzothiadiazole) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*, 25°C) δ = 182.97, 147.54, 143.97, 136.65, 134.03, 132.12, 131.33, 128.53, 127.37, 125.75, 115.11 ppm. ^{1}H NMR (400 MHz, DMSO-d_6, 25°C) δ = 10.01 (s, 1H, CHO), 8.28 (d, ^{3}J = 4 Hz, 1H, H thiophene), 8.22 (d, ^{3}J = 7.7 Hz, 1H, H benzothiadiazole), 8.15 (d, ^{3}J = 7.7 Hz, 1H, H benzothiadiazole), 8.14 (d, ^{3}J = 4 Hz, 1H, H thiophene) ppm. ^{13}C NMR (101 MHz, DMSO-d_6, 25°C) δ = 185.08, 144.55, 138.43, 135.29, 132.98, 131.03, 129.00, 128.45, 125.23, 119.96, 114.59 ppm.

Direct C-H arylation methods:

1) Phosphine ligand-assisted reaction

Synthesis of molecule 1: In an oven-dried three-necked flask containing a stirring bar, equipped with a thermometer, a condenser and septum cap, palladium acetate ($Pd(OAc)_2$), $P^tBu_2Me.HBF_4$, PivOH, diBrBz (500 mg, 1.7 mmol), K_2CO_3 (705 mg, 3 eq), and ThCHO (r eq, where "r" stands for the diBrBz/ThCHO molar ratio) were sequentially added under Ar flow. Dry toluene (7.5 mL) was added under argon atmosphere. The reaction mixture was refluxed for a given reaction time (See Table S1). The resulting mixture was cooled down to room temperature and filtered through a layer of Celite® using dichloromethane (DCM). The filtrate was concentrated under reduced pressure, and the residue was dried under vacuum. The reaction yield was estimated using ^{1}HNMR results in DMSO-*d6* (see Table 4). For the best estimated yield (the case of entry 6), the desired product was isolated by column chromatography (silica gel, ethyl acetate/pentane = 30:70) affording 80 mg of 1 (20 % yield of isolated product).

Table 4: Optimization of ligand-assisted direct arylation of ThCHO with diBrBz.

Entry	r	$Pd(OAc)_2$ (mole %)*	Ligand (eq)*	PivOH (eq)*	Time (h)	^{1}H NMR Yield (%)	**1/2****
1	1	10	0.2	1	4	16	3
2	1	10	0.2	1	4	10	5
3	2	10	0.2	1	6	11	10
4	1	10	0.2	0.3	24	12	1.6

5	1.1	5	0.1	0.3	24	13	2.5
6	1.4	5	0.1	0.3	24	24	0.4
7	1.4	1	0.1	0.3	18	22	1

* % and equivalents are relative to the molar amount of diBrBz; ** evaluated (molecule **1**/molecule **2**) ratio according to ^{1}H NMR analysis of the crude in DMSO-d_6.

Synthesis of molecule 2: In an oven-dried three-necked flask containing a stirring bar, equipped with a thermometer, a condenser and septum cap, palladium acetate ($Pd(OAc)_2$, 7.6 mg, 3.4 10^{-5} mol), $P^tBu_2Me.HBF_4$ (16.9 mg, 6.8 10^{-5} mol), pivalic acid (PivOH, 35 mg, 0.34 mmol), diBrBz (100 mg, 0.34 mmol, 1 eq), potassium carbonate (K_2CO_3, 140 mg, 1.02 mmol), and ThCHO (70 μL, 0.75 mmol) were sequentially added under a flow of Ar. Dry toluene (7.5 mL) was added under argon atmosphere. The reaction mixture was refluxed for 5.5 h, then cooled down to room temperature and filtered. The resulting solid was washed with water, ethyl acetate, and then petroleum ether, affording molecule **2** as a red-orange powder which was dried under vacuum (116 mg, 98% yield). NMR analyses on molecule **2**: ^{1}H NMR (400 MHz, Chloroform-*d*, 25°C): δ = 10.02 (s, 2H, CHO), 8.29 (d, *J* = 4 Hz, 2H, H thiophene), 8.09 (s, 2H, H benzothiadiazole) 7.90 (d, *J* = 4 Hz, 2H, H thiophene) ppm. (the molecule was too poorly soluble to allow ^{13}C NMR analysis)

^{1}H NMR (400 MHz, DMSO-d_6, 25°C) δ = 10.03 (s, 1H, CHO), 8.43 (s, 2H, H benzothiadiazole), 8.38 (d, *J* = 4 Hz, 2H, H thiophene), 8.17 (d, *J* = 4 Hz, 2H, H thiophene) ppm. (the molecule was too poorly soluble to allow ^{13}C NMR analysis).

2) Phosphine-free reaction

Synthesis of molecule 1, using the procedure for reactions mentioned in Table 2: In an oven-dried Schlenk containing a stirring bar and septum cap, diBrBz (500 mg, 1.7 mmol, 1 eq), KOAc (330 mg, 3.4 mmol, 1.5 eq), $Pd(OAc)_2$ (4 mg, 1.8 10^{-5} mol, 1 mol %), were sequentially added under a flow of Ar. Dry and degassed dimethylacetamide (7.5 mL) was added under argon atmosphere, then ThCHO, (320 μL, 3.4 mmol, 1 eq) was added under stirring. The

mixture was stirred for 24 h at a given temperature, between 60 and 130°C (see Table 2 of main paper). After cooling down to 50°C, the solvent was evaporated and the crude dried under reduced pressure. The reaction yield was estimated from the ^{1}HNMR analysis of the crude product, which was then purified by column chromatography (silica gel, EtOAc/pentane = 30:70) for recovering the non-reacted diBrBz and isolating the pure molecule 1.

Synthesis of molecule 1, using the procedure for reactions mentioned in Table 3: The same procedure as above was applied, but by starting from 1 g of diBrBz and, i) by using an amount of $Pd(OAc)_2$ of 40 mg, i.e. 5 mol % (instead of 1 mol %), and ii) with increasing the reaction time to 72 h (instead of 24 h). Surprisingly, it appeared that operating either in Schlenk or in three-necked flask had an impact on the results. Working in Schenk flask led to similar yields of **1**, but with a better selectivity than in a three-necked flask.

3) Synthesis of the extended π-conjugated D-A molecules.

Synthesis of molecule 4: A solution of 4,4'-dioctyl-5,5'-bis(tributyltin)-dithieno[3,2-b:2',3'-d]silole (0.613 g, 0.61 mmol) and molecule **1** (0.4 g, 1.23 mmol) in dry toluene (20 ml) was bubbled with argon for 25 min, then $Pd(PPh_3)_4$ (35 mg, 3 10^{-5} mol) was added to the mixture. After stirring under reflux for 17 h, the reaction mixture was allowed to cool down to 50°C, then the toluene was evaporated under vacuum. The crude product was dispersed in 10 ml AcOEt under sonication, then filtered. The solid was washed with 20 ml of AcOEt, and dried under vacuum, leading to 400 mg of pure molecule **4** as a black solid (52%). IR (Neat): ν_{max} = 3318, 2952, 2917, 2848, 1659, 1532, 1519, 1436, 1339 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*, 25°C) δ = 10.00 (s, 2H CHO) , 8.26 (s, 2H, thiophene), 8.25 (d, *J* = 4 Hz, 2H, thiophene), 8.02 (d, *J* = 8 Hz, 2H, benzothiadiazole), 7.94 (d, *J* = 8 Hz, 2H, benzothiadiazole), 7.88 (d, *J* = 4 Hz, 2H, thiophene), 1.52-1.49 (m, 4H, Si-*CH*$_2$-), 1.41-1.36 (m, 4H, Si-CH_2-*CH*$_2$-), 1.32-1.22 (m, 16H, alkyles), 1.11-1.07 (m, 4H, -*CH*$_2$-CH_3), 0.87-0.82 (m, 6H, -CH_2-*CH*$_3$) ppm ; MS (CI-NH3) : found: 907.00 [MH+] calculated for $C_{46}H_{47}N_4O_2S_6Si$: 907.17. Element. Anal. Found:

C, 60.01; H, 4.79; N, 6.27%; molecular formula $C_{23}H_{19}N_3OS_2$ + 0.45 H_2O requires C, 60.35; H, 5.16; N, 6.12 %.

Synthesis of molecule 5: A mixture of 9-(tributylstannyl)-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinoline (0.470 g, 1.01 mmol), **1** (0.300 g, 0.923 mmol), $Pd(PPh_3)_4$ (30 mg, 2.3 10^{-5} mol) in 10 mL of dry toluene was heated at reflux overnight under Ar atmosphere. The solvent was removed and the residue was extract with dichloromethane. The organic phase was washed with water, dried over magnesium sulphate, and the solvent was evaporated. The target compound was purified by two successive recrystallizations in ethyl acetate to give pure molecule **3** as a deep purple solid (230mg, 60%). IR (Neat): ν_{max} = 2952, 2938, 2938, 2830, 2793, 2156, 1662, 1602, 1537, 1506, 1461, 1440 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*, 25°C) δ = 9.99 (1H, s, CHO), 8.22 (1H, d, *J* = 4.1 Hz, thiophene), 8.02 (1H, d, *J* = 7.6 Hz, benzothiadiazole), 7.86 (1H, d, *J* = 4.1 Hz, thiophene), 7.68 (1H, d, *J* = 7.6 Hz, benzothiadiazole), 7.54 (2H, s, 8,10-H julolidine), 3.27 (4H, t, *J* = 5.6 Hz, 1,7-H julolidine), 2.90 (4H, t, *J* = 6.5 Hz, 3,5-H julolidine), 2.05 (4H, m, 2,6-H julolidine) ppm.^{13}C NMR (101 MHz, Chloroform-*d*, 25°C) δ = 182.95, 153.97, 152.81, 149.60, 143.68, 142.73, 136.90, 135.74, 128.00, 127.89, 127.24, 125.20, 123.48, 122.65, 121.34, 49.98, 27.92, 21.90 ppm. HRMS (TOF-ESI) (m/z): calcd. for $(M+H)^+$ $C_{23}H_{20}N_3OS_2$: 418.1048, found: 418.1040. Element. Anal. Found: C, 64.45; H, 3.93; N, 9.75%; molecular formula $C_{23}H_{19}N_3OS_2$ + 0.2 CH_2Cl_2 requires C, 64.13; H, 4.50; N, 9.67 %.

Supporting Information

^1H and ^{13}C NMR spectra are included in the Supporting Information.

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