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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Pd-Catalyzed Direct C-H Arylation of Thieno[3,4-c]pyrrole-4,6-dione (TPD): A Step-Economical Synthetic Alternative to Access TPD-Centred Symmetrical Small Molecules

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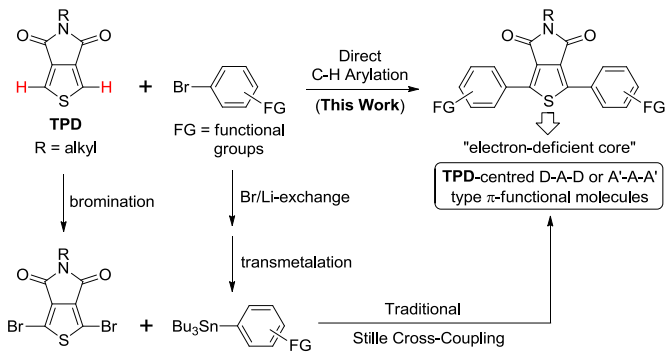
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

We demonstrate a step-economical and viable synthetic alternative to access a series of thieno[3,4-c]pyrrole-4,6-dione (TPD)-based π-conjugated molecules through Pd-catalyzed direct C-H arylations. A comprehensive synthetic study including the screening of various kinds of palladium catalysts, ligands, and bases is reported. Under the optimum reaction conditions, TPD and its common derivatives underwent efficient and mild direct C-H arylations with a variety of functionalized bromoarenes. Functional groups such as ester, nitrile, ketone, aldehyde, and halide were well-tolerated, which substantially extended the reaction scope. We wish the reported method would provide material scientists a relatively greener synthetic route to efficiently prepare the TPD-containing π-functional materials.

Introduction

In recent years, the transition-metal-catalyzed direct C-H (hetero)arylation is emerging as a viable and key synthetic alternative to traditional C(sp^2)-C(sp^2) forming reactions because it avoids the use of air-sensitive or toxic organometallic compounds such as Grignard reagents or organotin species.[1] More recently, further application of the direct C-H (hetero)arylations in the efficient synthesis of various functional π-conjugated oligomers and polymers has attracted particular research attention and numerous remarkable results have been disclosed by some research groups.[1c,2] In order to extend the substrate scope of the existing C-H arylation technology and, simultaneously, to bridge the research area of synthetic methodology with organic electronics, our attention has been drawn to the preparation of thieno[3,4-c]pyrrole-4,6-dione (TPD)- based functional small molecules[3] or polymers[4] and their potential applications as organic field-effect transistors (OFET)[5] and organic photovoltaic cells (OPVC).[6] TPD is an electron-deficient unit exhibiting superior planarity and solubility, which is beneficial to the charge transfer and device fabrication while incorporated into various conjugated systems.[7] Despite the employment of TPD as key conjugated backbone for optoelectronic applications has been widely investigated,[3-7] a step-economical and comprehensive synthetic study involving the screening of all required reaction parameters for the bidirectional facile conjugation extension from the electron-deficient TPD core-structure still remains, to the best of our knowledge, unexplored. Therefore, we report herein the Pd-catalyzed direct C-H arylation of TPD or its derivatives with a variety of functionalized bromoarenes can be achieved under pre-optimized reaction conditions. We anticipated that by examining carefully the reaction parameters and substrate scope would allow us to find an effective and broadly applicable catalytic system for the efficient synthesis TPD-centred D-A-D[3b] or A'-A-A'[9a,c,i] type (D: donor; A: acceptor) π-functional molecules (Scheme 1).

Scheme 1. Traditional and step-Economical synthetic routes to access thieno[3,4-c]pyrrole-4,6-dione (TPD)-based π-functional molecules.



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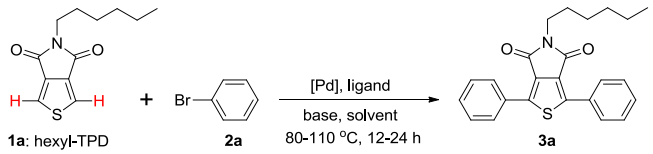
† Electronic Supplementary Information (ESI) available: NMR spectra (^{1}H and ^{13}C) for compounds **1**, **3**, **4**, **5**, **6** See DOI: 10.1039/b000000x//

Results and discussion

In order to obtain the optimum reaction conditions, the direct C-H arylation was first examined with 5-hexyl-4*H*-thieno[3,4-c]pyrrole-4,6-dione **1a** and bromobenzene **2a**. Initially, as shown in Table 1, we followed a general procedure often used in Pd-catalyzed C-H arylation of heteroarenes,[8] in which the two-fold phenylation of **1a** was conducted under a simple and phosphine-free reaction condition in polar aprotic solvent (palladium(II) acetate, potassium acetate, and tetrabutylammonium bromide in DMF, 100 °C, 12 h). However, the desired product **3a** was isolated in only 13% yield (entry 1, Table 1). In entry 2, an improved yield (40%) was obtained while KOAc was replaced with Cs_2CO_3 and a phosphine ligand (PPh_3) was added. Prolonging the reaction time to 24 h under identical reaction conditions described in entry 2 did not give a notable enhancement of yield (43%, entry 3). With these preliminary results in hand, we reasoned that switching the nature of solvent from polar to less polar might be crucial to the direct C-H arylation of TPD. Indeed, as the reaction was performed in nonpolar solvent (toluene), a considerably improved yield was observed (70%, entry 4). Therefore, we turned to use toluene as the primary solvent for the subsequent screening of other reaction parameters. Firstly, we endeavored to examine the direct C-H arylation using various kinds of palladium catalysts (entries 5-10). Both *cis*-$PdCl_2(PPh_3)_2$ and its *trans*-form were found to be much less effective and gave poor yields (trace to 10%, entries 5-6). Likewise, $PdCl_2$(dppf) was tested to afford the product in only 5% yield (entry 7). From entry 8 through 10, three kinds of commonly used Pd(0)-catalysts were also investigated under identical reaction conditions. However, none of them gave satisfactory results (0-20%). Accordingly, palladium(II) acetate was used as the optimum catalyst for subsequent optimization since it exhibits the highest activity.

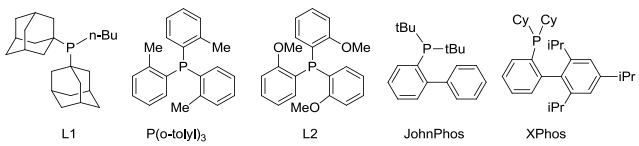
The direct C-H arylation of TPD was then examined with a variety of ligands (20 mol%) in the presence of $Pd(OAc)_2$ (10 mol%) and Cs_2CO_3 (2.4 equiv.) in toluene at 110 °C for 24 h (entries 11-22). Firstly, two monodentate trialkylphosphine ligands were successively employed to furnish the desired product in good yields (77-86%, entries 11-12). From entry 13 through 15, the arylation was performed, respectively, with three different kinds of constitutional isomers of tritolylphosphine, resulting in the formation of **3a** in moderate to excellent yields (71-96%). Further, the more electron-rich ligand (L2), however, did not provide a better yield (75%, entry 16), presumably due to the increased steric hindrance. The dialkylarylphosphine ligands, such as Johnphos and Xphos, were also tested to give the product in relatively poor to moderate yields (39 and 63%, entries 17, 18, respectively). In addition, we have carried out the C-H arylation using a number of bidentate ligands. In entries 19 and 20, the reaction underwent with dppb and dppf to afford **3a** in 85% and 34% yield, respectively, whereas the *N*, *N*-ligands such as bipyridyl and phenanthroline were shown to be ineffective in the direct arylations of TPD (0%, starting materials recovered, entries 21-22). Finally, under a phosphine-ligand-free condition, the C-H arylation hardly occurred and only trace amount of the desired product was isolated (entry 23). Subsequent screenings of base and solvent effects were carried out using the combination of

Table 1. Optimization of the Pd-catalyzed direct C-H arylation of hexyl-TPD with bromobenzene.[a]



1a: hexyl-TPD **2a** **3a**

Entry	[Pd]	Ligand	Base	Solvent	Yield(%)[g]
1[b,c]	$Pd(OAc)_2$	—	KOAc	DMF	13
2[c]	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	DMF	40
3	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	DMF	43
4	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	toluene	70
5	$PdCl_2(PPh_3)_2$	PPh_3	Cs_2CO_3	toluene	10
6[d]	$PdCl_2(PPh_3)_2$	PPh_3	Cs_2CO_3	toluene	trace
7	$PdCl_2$(dppf)	PPh_3	Cs_2CO_3	toluene	5
8	$Pd_2(dba)_3$	PPh_3	Cs_2CO_3	toluene	20
9	Pd/C	PPh_3	Cs_2CO_3	toluene	0
10	$Pd(PPh_3)_4$	—	Cs_2CO_3	toluene	15
11	$Pd(OAc)_2$	PCy_3	Cs_2CO_3	toluene	81
12	$Pd(OAc)_2$	L1	Cs_2CO_3	toluene	86
13	$Pd(OAc)_2$	P(*p*-tolyl)$_3$	Cs_2CO_3	toluene	90
14	**$Pd(OAc)_2$**	**P(*m*-tolyl)$_3$**	**Cs_2CO_3**	**toluene**	**96**
15	$Pd(OAc)_2$	P(*o*-tolyl)$_3$	Cs_2CO_3	toluene	71
16	$Pd(OAc)_2$	L2	Cs_2CO_3	toluene	75
17	$Pd(OAc)_2$	JohnPhos	Cs_2CO_3	toluene	39
18	$Pd(OAc)_2$	XPhos	Cs_2CO_3	toluene	63
19	$Pd(OAc)_2$	dppb	Cs_2CO_3	toluene	85
20	$Pd(OAc)_2$	dppf	Cs_2CO_3	toluene	34
21	$Pd(OAc)_2$	bipyridyl	Cs_2CO_3	toluene	0
22	$Pd(OAc)_2$	phenanthroline	Cs_2CO_3	toluene	0
23	$Pd(OAc)_2$	—	Cs_2CO_3	toluene	trace
24	$Pd(OAc)_2$	P(*m*-tolyl)$_3$	K_2CO_3	toluene	90
25	$Pd(OAc)_2$	P(*m*-tolyl)$_3$	K_3PO_4	toluene	88
26	$Pd(OAc)_2$	P(*m*-tolyl)$_3$	Na_2CO_3	toluene	31
27	$Pd(OAc)_2$	P(*m*-tolyl)$_3$	—	toluene	trace
28	$Pd(OAc)_2$	P(*m*-tolyl)$_3$	Cs_2CO_3	*o*-xylene	93
29[e]	$Pd(OAc)_2$	P(*m*-tolyl)$_3$	Cs_2CO_3	dioxane	91
30	$Pd(OAc)_2$	P(*m*-tolyl)$_3$	Cs_2CO_3	NMP	17
31	$Pd(OAc)_2$	P(*m*-tolyl)$_3$	Cs_2CO_3	DMSO	12
32[f]	$Pd(OAc)_2$	P(*m*-tolyl)$_3$	Cs_2CO_3	CH_3CN	29



L1 P(*o*-tolyl)$_3$ L2 JohnPhos XPhos

[a] Unless specified, the C-H arylation was conducted with TPD **1a** (1 equiv.) and bromobenzene **2a** (2.5 equiv.) in the presence of [Pd]-catalyst (10 mol%), ligand (20 mol%), base (2.4 equiv.) in 3 mL solvent at 110 °C for 24 h. [b] In additon to KOAc, tetrabutylammonium bromide (TBAB, 1.0 equiv.) was added. [c] The reaction time was 12 h. [d] *trans*-$PdCl_2(PPh_3)_2$ was used. [e] The reaction temperature was 100 °C. [f] The reaction temperature was 80 °C. [g] Isolated yields.

$Pd(OAc)_2$ and P(*m*-tolyl)$_3$ since entry 14 had shown the optimum result. As expected, K_2CO_3 provided a comparable yield (90%, entry 24). Importantly, another inorganic base, tripotassium phosphate (K_3PO_4), which has excellent solubility in nonpolar solvent also afforded the product with a good yield (88%, entry 25), whereas the less basic Na_2CO_3 gave a diminished yield

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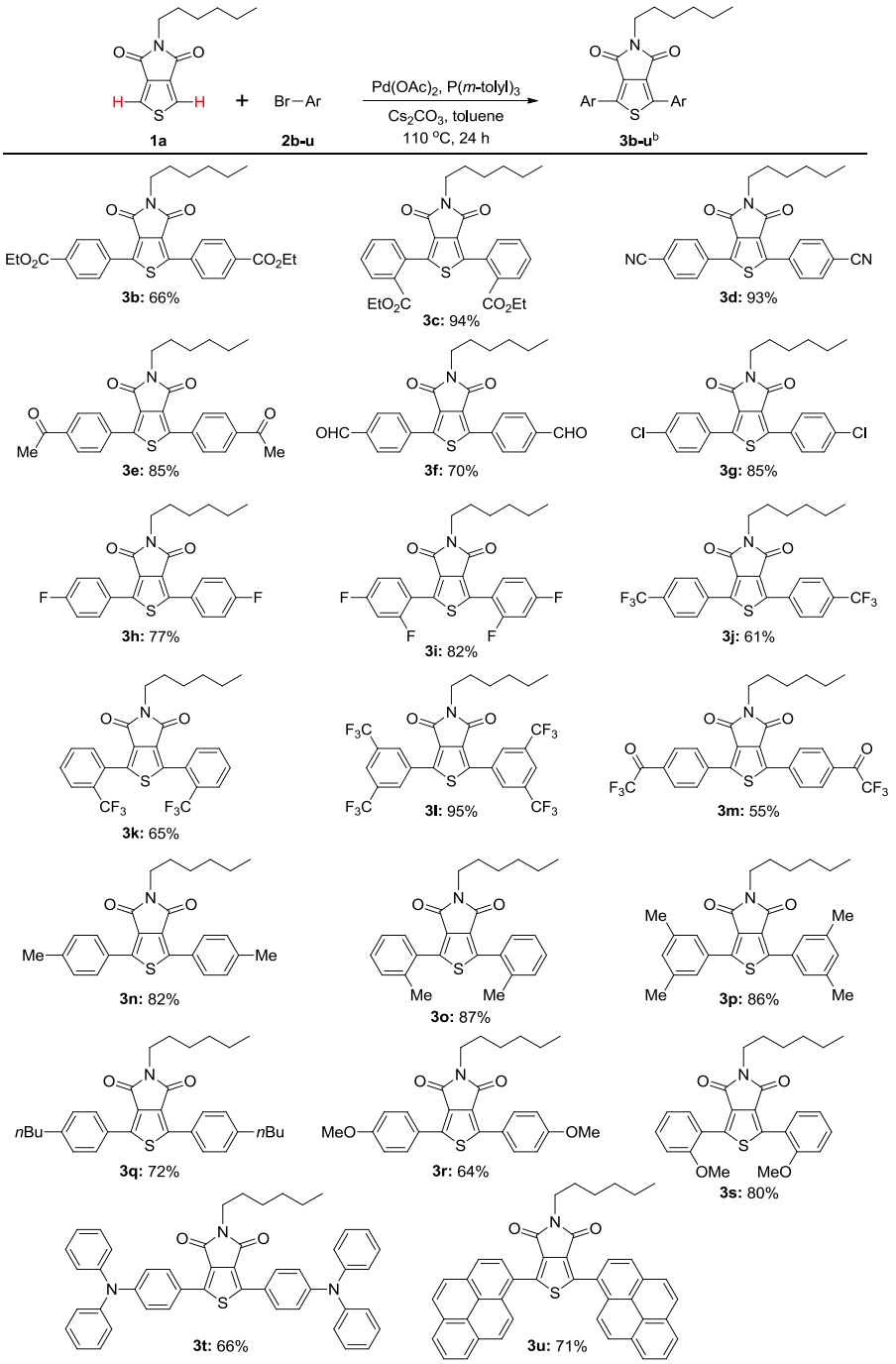
(31%, entry 26). In the absence of base, **3a** was formed in trace amount (entry 27). Therefore, we selected Cs_2CO_3 for the final solvent optimization. Firstly, another frequently used nonpolar solvent (*o*-xylene) was tested and we were pleased to find that the product was isolated in excellent yield (93%, entry 28). Besides, it is worth noting that, 1, 4-dioxane, a low-polarity ethereal solvent, was demonstrated to promote the direct C-H arylation of TPD (91%, entry 29). On the contrary, the reaction was also performed with a series of polar aprotic solvents, respectively. It appears, however, that the direct arylation of TPD was impeded in polar solvents, and **3a** was then obtained all in poor yields (12-29%, entries 30-32). Thus, we concluded that the polarity of solvent would have a significant influence on the reaction conversion while utilizing TPD as the C-H activation substrate. Accordingly, the nonpolar toluene or *o*-xylene would be selected as the best solvent for the subsequent investigation of substrate scope.

The optimum reaction condition acquired in entry 14 was used to further explore the substrate scope of this methodology by treating hexyl-substituted TPD **1a** with various functionalized aryl bromides **2b-u** (Table 2). Firstly, reaction of **1a** with ethyl 4-bromobenzoate **2b** under [$Pd(OAc)_2$, $P(m\text{-tolyl})_3$, and Cs_2CO_3 in toluene at 110 °C for 24h] led to the formation of para-diester **3b** in 66% yield. Interestingly, when 2-bromobenzoate **2c** was used, ortho-diester **3c** was obtained in excellent yield (94%), presumably owing to the formation of coordinatively stabilized oxidative-addition intermediate [Ar-Pd(II)-Br] resulting from the chelation of *ortho*-ester group to Pd(II). Subsequently, we found that the sensitive but synthetically useful functionalities such as nitrile, ketone, and aldehyde were well tolerated under present reaction conditions, which step-economically elongated the conjugation length of TPD and simultaneously installed these readily transformable functional groups at both

Table 2. Substrate scope: Pd-catalysed direct C-H arylation of hexyl-substituted TPD **1a** with various aryl bromides **2b-u**.[a]



[a] Unless specified, the C-H arylation was conducted with TPD **1a** (1 mmol) and the corresponding aryl bromides **2b-u** (2.5 mmol) in the presence of $Pd(OAc)_2$ (10 mol%), $P(m\text{-tolyl})_3$ (20 mol%), and Cs_2CO_3 (2.4 mmol) in toluene (3 mL) at 110 °C for 24 h. [b] Isolated yield.

ends, affording desired **3d**-**3f** in good to excellent yields (70-93%). A chemoselective direct C-H arylation was achieved by the reaction of TPD with 1-bromo-4-chlorobenzene

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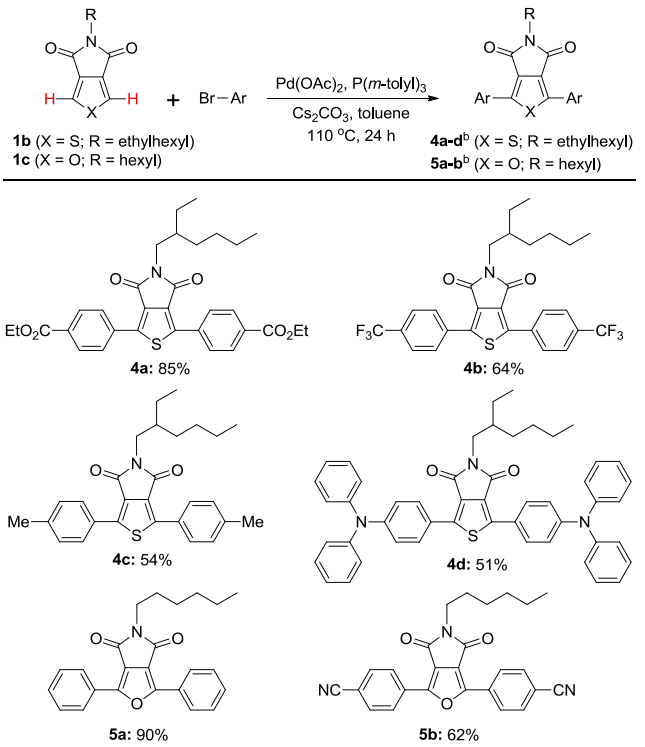
2g, giving the dichloro species **3g** in 85% yield. Next on, we examined a series of fluorine-containing coupling partners **2h-2m**. The resulting TPD-based (poly)fluorinated oligomers **3h-3m** were readily isolated in 55-95% yields. Because of the alkyl chain of TPD, these compounds generally exhibit good solubility in acetone, chloroform, and THF, which is important for further device fabrications. These fluorine-containing or -terminated products **3h-3m** could be important for the application of organic field-effect transistors.[9]

In addition to the electron-withdrawing bromoarenes, we've also tested a number of electron-donating/-rich ones **2n-u**. We found that the isolated yields obtained by treating TPD with the corresponding 2- or 4-bromotoluene did not differ greatly (82% for **3n**; 87% for **3o**). Other alkylated products **3p** and **3q** exhibiting superior solubility in most organic solvents were synthesized in moderate yields (86% and 72%). Similar to the ester group, the stabilization effect was observed again while the *ortho*-methoxy group was involved, furnishing **3s** in 80% yield (64% for the *para*-isomer **3r**). Of particular importance, triphenyamine (TPA), a good hole-transporting moiety,[10] could be step-economically installed at both ends of TPD, thus leading to the formation of a donor-acceptor-donor (D-A-D) type molecule **3t** in 66% yield. In addition, the pyrene-capped TPD **3u** was also efficiently prepared through present methodology (71%).

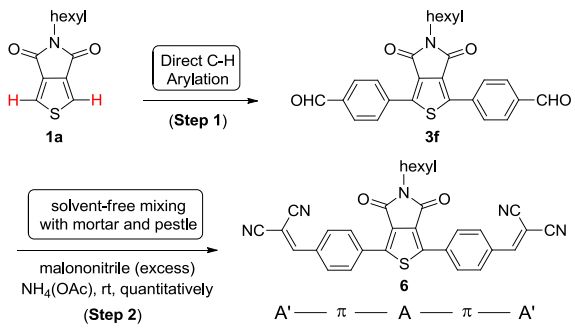
The scope of the direct C-H arylation with respect to TPD's derivatives was then investigated in Table 3. Reaction of ethylhexyl-substituted TPD (**1b**) with bromoarenes carrying electron-withdrawing groups such as ester or trifluoromethyl group gave moderate to good yields (**4a**, **4b**). However, while the electron-donating methyl or triphenyamino group, relatively lower isolated yields were obtained (**4c** and **4d**) because in both cases the separation of desired **4c** or **4d** from the mono-arylated byproduct was difficult. On the other hand, the congener of TPD, furo[3,4-c]pyrrole-4,6-dione (FPD) (**1c**) was found to successfully undergo the C-H arylation under our optimized conditions and offered a good yield (**5a**) in the reaction with bromobenzene. The other example using FPD demonstrated that the versatile cyano group was also tolerated and the resulting di-nitrile product (**5b**) was isolated in 62% yield.

Table 3. Substrate scope: Pd-catalysed direct C-H arylation using TPD's derivative (**1b**) and its furan congener (**1c**).[a]



[a] Reaction conditions: **1b-c** (1 mmol), aryl bromides (2.5 mmol), $Pd(OAc)_2$ (10 mol%), P(*m*-tolyl)$_3$ (20 mol%), and Cs_2CO_3 (2.4 mmol), toluene (3 mL), 110 °C, 24 h. [b] Isolated yield.

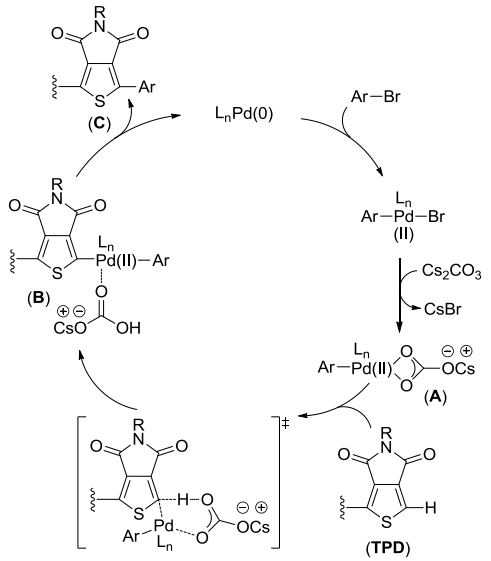
Scheme 2. A two-step facile synthesis of the dicyano-terminated A'-π-A-π-A' type oligomer.



In order to shed light on the importance of high functional-group compatibility of our method and demonstrate this strategy could become a step-economical and viable synthetic alternative for the preparation of TPD-incorporated functional small molecules, we describe a two-step facile synthesis, in which the readily available di-aldehyde species (**3f**) of Table 2 was further end-capped with the strongly electron-withdrawing dicyanovinyl groups by an operationally simple and solvent-free mixing procedure under air,[11] which resulted in the formation of the A'-π-A-π-A'[12](A or A': acceptors) type oligomer (**6**) in quantitative yield (Scheme 2).

A plausible reaction mechanism was proposed in Scheme 3. After the oxidative addition, coordination of the bicarbonate ion to palladium center generated the intermediate **A**. Subsequently, the proton abstraction of TPD would take place possibly via a concerted metalation-deprotonation (CMD) mechanism to afford intermediate **B**, which would then undergo the reductive

Scheme 3. Plausible reaction mechanism.



elimination to give the desired arylated product **C** and regenerate Pd(0) species.

Conclusions

In summary, we have demonstrated a step-economical synthetic strategy through direct C-H arylations for the facile preparation of a variety of thieno[3,4-c]pyrrole-4,6-dione (TPD)-based symmetrical oligoarenes. A broad range of important functional groups such as ester, nitrile, ketone, aldehyde, and halide are compatible with the optimum reaction conditions, in which a comprehensive screening of all required reaction parameters was carried out. Interestingly, it was found that the direct C-H arylation of TPD would be best performed in nonpolar solvents such as toluene, xylene, or dioxane. In addition, the direct C-H arylation also proceeded smoothly with TPD's derivative and its furan congener (FPD), which further extended the reaction scope. Therefore, we wish present synthetic approach would become a more efficient and viable synthetic alternative to traditional cross-couplings, thereby providing a relatively greener route to access TPD-containing π-functional small molecules. Further application in organic electronics of the obtained products is currently underway in our laboratory.

Experimental

General information

Unless otherwise indicated, all reactions were carried out with magnetic stirring and, if air or moisture sensitive, in flame-dried glassware under nitrogen. 5-(Alkyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (TPD) (**1a-b**) and its congener (FPD) (**1c**) were synthesized according to the literatures.[13,14] Reagents including various bromoarenes (**2a-u**), palladium catalysts, ligands, and additives (bases) are commercially available. Anhydrous solvents such as *N*, *N*-dimethylformamide (DMF), toluene, *o*-xylene, dioxane, *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO) and acetonitrile were purchased from Sigma-Aldrich and used directly without further purifications. Syringes used to transfer reagents and solvents were purged with nitrogen prior to use. Reactions were monitored by thin layer chromatography (TLC, aluminum plates coated with silica gel, Merck 60, F-254). The spots were visualized by UV light. Flash column chromatography was performed using silica gel 60 (spherical, 63-210 μm) from Merck. The diameters of the columns and the amount of silica gel loaded were calculated according to the recommendation of W. C. Still.[15] Melting points were measured on a Fargo MP-2D apparatus. NMR spectra were recorded on a Bruker Magnet System 300 MHz/54mm instrument. Chemical shifts were given relative to $CDCl_3$ (7.26 ppm for ^{1}H NMR, 77.0 ppm for ^{13}C NMR), DMSO-d_6 (2.50 ppm for ^{1}H NMR, 39.4 ppm for ^{13}C NMR), CD_2Cl_2 (5.32 ppm for ^{1}H NMR, 54.0 ppm for ^{13}C NMR). For the characterization of the observed signal multiplicities, the following abbreviations were applied: s (singlet), d (doublet), dd (double doublet), dt (double triplet), t (triplet), td (triple doublet), q (quartet), quint (quintet), m (multiplet), as well as br (broad). Mass spectra were recorded on a JEOL JMS-700 for electron impact ionization (EI) and high resolution mass spectra (HRMS) on a JEOL JMS-700 spectrometers. Fast atom bombardment (FAB) samples were recorded in either a 3-nitrobenzyl alcohol matrix.

General procedure for the synthesis of TPD (1a-b):

(i) Synthesis of 1*H*,3*H*-thieno[3,4-c]furan-1,3-dione: In a 500 mL double-necked round-bottom flask equipped with a reflux condenser, 3,4-thiophenedicarboxylic acid (1.0 equiv.) was dissolved in acetic anhydride and the solution was stirred at 140 ℃ for overnight. The reaction mixture was then cooled to room temperature and the solvent was removed under reduced pressure to yield a dark brown solid, and the crude product was used directly for the next step without further purification.

(ii) Synthesis of 5-(alkyl)-4*H*-thieno[3,4-c]pyrrole-4,6(5*H*)-dione: The crude product obtained from the previous step was dissolved in toluene and the corresponding amine (1.5 equiv.) was then added to the stirring solution. The reaction mixture was heated at reflux (~140 ℃) for 24 h before it was cooled to room temperature. The solvent was evaporated under reduced pressure. The resulting solid was dissolved in thionyl chloride. The mixture was then heated at reflux for 3 hours before it was cooled to room temperature. The solvent was distilled off under ambient pressure by simple distillation. Purification by flash chromatography gave the desired products **1a-b**.

5-Hexyl-4*H*-thieno[3,4-c]pyrrole-4,6(5*H*)-dione[13] **(1a).** The title compound was prepared from 3,4-thiophenedicarboxylic acid (5.40 g, 31.4 mmol), acetic anhydride (60 mL), 1-hexylamine (4.80 g, 47.2 mmol), toluene (100 mL), and thionyl chloride (200 mL) according to the general procedure for the synthesis of TPD and yielding after column chromatography (ethyl acetate : hexane = 1 : 9) the pure product **1a** (5.90 g, 79 %). A pale orange solid; m.p.: 120.3-122.3 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.79 (s, 2 H), 3.59 (t, J = 6.00 Hz, 2 H), 1.55-1.68 (m, 2 H), 1.22-1.37 (m, 6 H), 0.86 (t, J = 6.00, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.6, 136.6, 125.4, 38.4, 31.3, 28.4, 26.5, 22.5, 14.0.

5-(2-Ethylhexyl)-4*H*-thieno[3,4-c]pyrrole-4,6(5*H*)-dione[13] **(1b).** The title compound was prepared from 3,4-thiophenedicarboxylic acid (5.40 g, 31.4 mmol), acetic anhydride (60 mL), 2- ethylhexylamine (6.10 g, 47.2 mmol), toluene (100 mL), and thionyl chloride (200 mL) according to the general procedure for the synthesis of TPD and yielding after column chromatography (ethyl acetate : hexane = 1 : 9) the pure product **1b** (6.20

g, 75 %). A pale brown solid; m.p.: 72.4-74.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.80 (s, 2 H), 3.51 (d, J = 7.3 Hz, 2 H), 1.72-1.87 (m, 1 H), 1.19-1.40 (m, 8 H), 0.83-0.93 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.9, 136.6, 125.4, 42.3, 38.1, 30.4, 28.4, 23.8, 23.0, 14.0, 10.4.

General procedure for the synthesis of FPD[14] (1c)

(i) **Synthesis of furan-3,4-dicarboxylic acid**

Dimethyl-3,4-furandicarboxylate (2.75 g, 14.9 mmol) and ethanol (88 mL) were placed in a round-bottomed flask mounted over a magnetic stirrer and maintained at 50~60˚C. Subsequently, KOH (3.35 g, 59.6 mmol) was added and the reaction mixture was stirred for 2 h before it was quenched by water. The unreacted dimethyl-3,4-furandicarboxylate was removed by ether extraction and the desired carboxylic acid was obtained by the following method: The aqueous phase was acidified (pH = 2) with 6 N HCl and then extracted with ether. The combined ether extracts were dried with Na_2SO_4 and concentrated in *vacuo*. The pure product was obtained after drying under vacuum (1.82 g, 86 %).

(ii) **Synthesis of furan-3,4-dicarbonyl dichloride**

Oxalyl chloride (32.5 mL) was added slowly to the furan-3,4-dicarboxylic acid (2.00 g, 12.8 mmol). The mixture was then heated at reflux for 2 h before it was cooled to room temperature. The volatiles were removed under reduced pressure, and the obtained crude product was used directly in the next step without further purification.

(iii) **Synthesis of 5-hexyl-4H-furo[3,4-c]pyrrole-4,6(5H)-dione**

A mixture of 1-hexylamine (1.35 g, 13.3 mmol), furan-3,4-dicarbonyl dichloride (2.00 g, 12.8 mmol) and DMAP (470 mg, 3.85 mmol) was heated at 140 ˚C for 2 h before the mixture was cooled to room temperature. The mixture was extracted with ethyl acetate (2 × 30 mL), and the combined organic layers were washed with sodium carbonate (100 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by column chromatography (dichloromethane : hexane = 2 : 1) yielded the desired product **1c**.

5-Hexyl-4H-furo[3,4-c]pyrrole-4,6(5H)-dione (1c). The title compound was prepared from dimethyl-3,4-furandicarboxylate (2.75 g, 14.9 mmol), ethanol (90 mL), KOH (3.35 g , 59.6 mmol), oxalyl chloride (32.5 mL), 1-hexylamine (1.35 g, 13.3 mmol), and DMAP (470 mg, 3.85 mmol) according to the general procedure for the synthesis of FPD and yielding after column chromatography (dichloromethane : hexane = 2 : 1) the pure product **1c** (1.19 g, 36 %). A white solid; m.p.: 116.2-116.6 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.74 (s, 2 H), 3.57 (t, J = 7.5 Hz, 2 H), 1.54-1.67(m, 2 H), 1.21-1.35 (m, 6 H), 0.86 (t, J = 7.1, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 161.6, 138.5, 122.4, 38.5, 31.2, 28.2, 26.4, 22.4, 13.9; MS (EI, 70 ev): 221 (M^+, 6 %), 150 (82 %), 123 (93 %), 66 (100 %); HRMS (EI): calcd. for $C_{12}H_{15}NO_3$: 221.1052, found: 221.1054.

General procedure for Table 1.

To a solution of $Pd(OAc)_2$ (10 mol%), P(m-tolyl)$_3$ (20 mol%), and Cs_2CO_3 (2.40 mmol) in toluene (3 mL) in a flame-dried Schlenk tube (20 mL) were added TPD (1.00 mmol) and the corresponding bromobenzene (2.50 mmol) under N_2. The reaction mixture was then heated at 110 ℃ under N_2 for 24 h. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The mixture was extracted with ethyl acetate (2 × 30 mL), and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by flash chromatography (ethyl acetate/hexane) yielded the desired products **3a**.

Representative example of Table 1:

5-Hexyl-1,3-diphenyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3a). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and bromobenzene (**2a**) (393 mg, 2.50 mmol) according to the general procedure for Table 1 and yielding after column chromatography (ethyl acetate : hexane = 3 : 97) the pure product **3a** (374 mg, 96 %). A white solid; m.p.: 97.9-98.2 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.13 (dd, J = 7.8, 1.5 Hz, 4 H), 7.35-7.55 (m, 6 H), 3.67 (t, J = 7.5 Hz, 2 H), 1.60-1.75 (m, 2 H), 1.21-1.43 (m, 6 H), 0.88 (t, J = 6.82 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 163.0, 145.0, 130.5, 130.4, 130.1, 128.9, 128.1, 38.6, 31.4, 28.4, 26.6, 22.5, 14.0; MS (FAB): 390 ([M+1]$^+$, 100 %), 318 (46 %), 228 (51 %); HRMS (FAB): calcd. for $C_{24}H_{23}NO_2S$: 389.1449, found: 389.1453.

General procedure for Table 2.

To a solution of $Pd(OAc)_2$ (10 mol%), P(m-tolyl)$_3$ (20 mol%), and Cs_2CO_3 (2.40 mmol) in toluene (3 mL) in a flame-dried Schlenk tube (20 mL) were added TPD **1a** (1.00 mmol) and the corresponding aryl bromides (2.50 mmol) under N_2. The reaction mixture was then heated at 110 ℃ under N_2 for 24 h. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The mixture was extracted with ethyl acetate (2 × 30 mL), and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by flash chromatography (ethyl acetate/hexane) yielded the desired products **3b-u**.

Diethyl 4,4'-(5-hexyl-4,6-dioxo-5,6-dihydro-4H-thieno[3,4-c]pyrrole-1,3-diyl) dibenzoate (3b). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and ethyl 4-bromobenzoate (**2b**) (573 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 10 : 90) the pure product **3b** (352 mg, 66 %). A yellow solid; m.p.: 167.9-168.4 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.20 (d, J = 8.6 Hz, 4 H), 8.12 (d, J = 8.6 Hz, 4 H), 4.40 (q, J = 7.1 Hz, 4 H), 3.67 (t, J = 7.3 Hz, 2 H), 1.59-1.75 (m, 2 H), 1.24-1.47 (m, 12 H), 0.88 (t, J = 6.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 165.4, 162.1, 143.5, 133.8, 131.7, 131.3, 129.8, 127.6, 61.1, 38.6, 31.2, 28.2, 26.5, 22.4, 14.1, 13.9; MS (FAB): 534 ([M+1]$^+$, 46 %), 488 (31 %), 141 (55 %), 106 (64 %), 51 (100 %); HRMS (FAB): calcd. for $C_{30}H_{31}NO_6S$: 533.1872, found: 533.1876.

Diethyl 2,2'-(5-hexyl-4,6-dioxo-5,6-dihydro-4H-thieno[3,4-c]pyrrole-1,3-diyl) dibenzoate (3c). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and ethyl 2-bromobenzoate (**2c**) (573 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 15 : 85) the pure product **3c** (502 mg, 94 %). Viscous liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.03 (d, J = 7.1 Hz, 2 H), 7.46-7.62 (m, 6 H), 4.26 (q, J = 7.2 Hz, 4 H), 3.51 (t, J = 7.2 Hz, 2 H), 1.48-1.66 (m, 2 H), 1.19-1.36 (m, 12 H), 0.84 (t, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm):*d* 166.4, 162.6, 142.8, 131.6, 131.5, 131.23, 131.15, 130.8, 130.0, 129.5, 61.1, 38.0, 31.2, 28.2, 26.3, 22.3, 13.8; MS (EI, 70 ev): 533 (M^+, 35 %), 85 (38 %), 71 (55 %),

57 (100 %); HRMS (EI): calcd. for $C_{30}H_{31}NO_6S$: 533.1872, found: 533.1871.

4,4'-(5-Hexyl-4,6-dioxo-5,6-dihydro-4H-thieno[3,4-c]pyrrole-1,3-diyl)dibenzonitrile (3d). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and 4-bromobenzonitrile (**2d**) (455 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 20 : 80) the pure product **3d** (409 mg, 93 %). A yellow solid; m.p.: 193.5-194.2 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.27 (d, J = 8.5 Hz, 4 H), 7.77 (d, J = 8.5 Hz, 4 H), 3.68 (t, J = 7.3 Hz, 2 H), 1.55-1.75 (m, 2 H), 1.25-1.45 (m, 6 H), 0.88 (t, J = 6.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.3, 143.1, 134.0, 132.7, 128.5, 127.9, 118.1, 113.6, 38.9, 31.3, 28.3, 26.5, 22.4, 13.9; MS (EI, 70 ev): 439 (M^+, 83 %), 370 (31 %), 204 (100 %); HRMS (EI): calcd. for $C_{26}H_{21}N_3O_2S$:439.1354, found: 439.1347.

1,3-Bis(4-acetylphenyl)-5-hexyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3e). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and 4-bromoacetophenone (**2e**) (498 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 20 : 80) the pure product **3e** (403 mg, 85 %). A yellow solid; m.p.: 173.1-175.0 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.25 (d, J = 8.4 Hz, 4 H), 8.06 (d, J = 8.4 Hz, 4 H), 3.69 (t, J = 7.2 Hz, 2 H), 2.64 (s, 6 H), 1.62-1.79 (m, 2 H), 1.24-1.47 (m, 6 H), 0.88 (t, J = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 196.5, 162.0, 143.3, 137.5, 133.8, 131.9, 128.6, 127.8, 38.6, 31.2, 28.1, 26.40, 26.35, 22.3, 13.8 ; MS (EI, 70 ev): 473 (M^+, 90 %), 251 (100 %), 238 (47 %), 223 (96 %), 147 (43 %); HRMS (EI): calcd. for $C_{28}H_{27}NO_4S$: 473.1661, found: 473.1659.

4,4'-(5-Hexyl-4,6-dioxo-5,6-dihydro-4H-thieno[3,4-c]pyrrole-1,3-diyl)dibenzaldehyde (3f). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and 4-bromobenzaldehyde (**2f**) (463 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 20 : 80) the pure product **3f** (312 mg, 70 %). A yellow solid; m.p.: 163.6-164.4 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 10.03 (s, 2 H), 8.29 (d, J = 7.9 Hz, 4 H), 7.95 (d, J = 7.9 Hz, 4 H), 3.66 (t, J = 6.9Hz, 2H), 1.57-1.81 (m, 2 H), 1.18-1.49 (m, 6 H), 0.87 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 191.1, 162.4, 143.8, 137.0, 135.5, 132.6, 130.2, 128.6, 38.9, 31.4, 28.4, 26.6, 22.5, 14.0; MS (EI, 70 ev): 445 (M^+, 60 %), 374 (46 %), 149 (50 %), 71(42%), 58(100%); HRMS (EI): calcd. for $C_{26}H_{23}NO_4S$: 445.1348, found: 445.1340.

1,3-Bis(4-chlorophenyl)-5-hexyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3g). The title compound was prepared from 1a (237 mg, 1.00 mmol) and 1-bromo-4-chlorobenzene (2g) (479 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate: hexane = 5 : 95) the pure product 3g (390 mg, 85 %). A pale yellow solid; m.p.: 147.2-147.6 oC. 1H NMR (CDCl3, 300MHz, ppm): δ 8.08 (d, J = 8.3 Hz, 4 H), 7.44 (d, J = 8.3 Hz, 4 H), 3.66 (t, J = 7.3 Hz, 2 H), 1.61-1.74 (m, 2 H), 1.26-1.42 (m, 6 H), 0.88 (t, J = 6.2 Hz, 3 H); ^{13}C NMR (CDCl3, 75 MHz, ppm): δ 162.7, 143.5, 136.3, 130.7, 129.3, 129.2, 128.8, 38.7, 31.4, 28.4, 26.6, 22.5, 14.0; MS (EI, 70 ev): 457 (M+, 35 %), 417 (18 %), 386 (24 %), 373 (13 %), 57 (100 %); HRMS (EI): calcd. for $C_{24}H_{21}C_{l2}NO_2S$: 457.0670, found: 457.0673.

1,3-Bis(4-fluorophenyl)-5-hexyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3h). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and 1-bromo-4-fluorobenzene (**2h**) (438 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 2 : 98) the pure product **3h** (328 mg, 77 %). A white solid; m.p.: 122.8-123.1 ºC. ^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 8.07-8.17 (m, 4 H), 7.09-7.20 (m, 4 H), 3.65 (t, J = 7.4 Hz, 2 H), 1.60-1.73 (m, 2 H), 1.26-1.40 (m, 6 H), 0.88 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 163.6 (d, $^1J_{C,F}$ = 251 Hz), 162.7, 143.4, 130.1 (d, $^3J_{C,F}$ = 9 Hz), 126.69, 126.65, 116.0 (d, $^2J_{C,F}$ = 22 Hz), 38.6, 31.4, 28.4, 26.6, 22.5, 14.0; MS (EI, 70 ev): 425 (M^+, 100 %), 368 (8 %), 354 (85 %); HRMS (EI): calcd. for $C_{24}H_{21}F_2NO_2S$: 425.1261, found: 425.1255.

1,3-Bis(2,4-difluorophenyl)-5-hexyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3i). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and 1-bromo-2,4-difluorobenzene (**2i**) (483 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 4 : 96) the pure product **3i** (378 mg, 82 %). A white solid; m.p.: 118.4-119.7 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.35-8.55 (m, 2 H), 6.90-7.18 (m, 4 H), 3.65 (t, J = 7.5 Hz, 2 H), 1.59-1.82 (m, 2 H), 1.21-1.49 (m, 6 H), 0.87 (t, J = 6.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 163.7 (dd, $^1J_{C,F}$ = 253 Hz, $^3J_{C,F}$ = 12 Hz), 162.6, 159.6 (dd, $^1J_{C,F}$ = 257 Hz, $^3J_{C,F}$ = 16 Hz), 137.6 (dd, $^3J_{C,F}$ = 7 Hz, $^3J_{C,F}$ = 5 Hz), 132.7 (dd, $^3J_{C,F}$ = 10 Hz, $^5J_{C,F}$ = 3 Hz), 131.4, 114.7 (dd, $^2J_{C,F}$ = 13 Hz, $^4J_{C,F}$ = 4 Hz), 112.0 (dd, $^2J_{C,F}$ = 21 Hz, $^4J_{C,F}$ = 3 Hz), 104.5 (t, $^2J_{C,F}$ = 26 Hz), 38.6, 31.3, 28.3, 26.5, 22.4, 13.9; MS (EI, 70 ev): 461 (M^+, 79 %), 390 (100 %), 338 (58 %); HRMS (FAB): calcd. for $C_{24}H_{19}F_4NO_2S$: 461.1073, found: 461.1067.

5-Hexyl-1,3-bis(4-(trifluoromethyl)phenyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3j). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and 4-bromobenzotrifluoride (**2j**) (563 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 2 : 98) the pure product **3j** (321 mg, 61 %). A pale yellow solid; m.p.: 101.0-102.3 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.23 (d, J = 8.3 Hz, 4 H), 7.71 (d, J = 8.3 Hz, 4 H), 3.64 (t, J = 7.5 Hz, 2 H), 1.58-1.75 (m, 2 H), 1.22-1.43 (m, 6 H), 0.88 (t, J = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.1, 143.0, 133.1, 132.0, 131.7 (q, $^2J_{C,F}$ = 33 Hz), 128.0, 125.8, 123.6 (q, $^1J_{C,F}$ = 271 Hz), 38.6, 31.2, 28.2, 26.5, 22.4, 13.8; MS (EI, 70 ev): 525 (M^+, 76 %), 454 (100 %), 372 (49 %); HRMS (EI): calcd. for $C_{26}H_{21}F_6NO_2S$: 525.1197, found: 525.1191.

5-Hexyl-1,3-bis(2-(trifluoromethyl)phenyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3k). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and 2-bromobenzotrifluoride (**2k**) (563 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 15 : 85) the pure product **3k** (342 mg, 65 %). Viscous liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.83 (d, J = 7.2 Hz, 2 H), 7.54-7.73 (m, 6 H), 3.55 (t, J = 7.3 Hz, 2 H), 1.55-1.69 (m, 2 H), 1.19-1.40 (m, 6 H), 0.86 (t, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.0, 140.7, 132.9, 132.8, 131.6, 130.0, 129.7 (q, $^2J_{C,F}$ = 31 Hz), 128.0, 126.6 (q, $^3J_{C,F}$ = 5 Hz), 123.5 (q , $^1J_{C,F}$ = 272 Hz), 38.4, 31.2, 28.2, 26.4, 22.4, 13.9; MS (EI, 70 ev): 525 (M^+, 56

%), 454 (100 %), 407 (35 %), 379 (36%); HRMS (EI): calcd. for $C_{26}H_{21}F_6NO_2S$: 525.1197, found: 525.1191.

1,3-Bis(3,5-bis(trifluoromethyl)phenyl)-5-hexyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3l). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and 1-bromo-3,5-bis(trifluoromethyl)benzene (**2l**) (733 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 3 : 97) the pure product **3l** (628 mg, 95 %). A white solid; m.p.: 170.0-170.8 ^oC. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.69 (s, 4 H), 7.98 (s, 2 H), 3.73 (t, J = 7.5 Hz, 2 H), 1.62-1.78 (m, 2 H), 1.23-1.44 (m, 6 H), 0.89 (t, J = 6.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.2, 141.6, 133.1, 132.8, (q, $^2J_{C,F}$ = 34 Hz), 131.9, 128.1, 123.8, 122.9, (q, $^1J_{C,F}$ = 272 Hz), 39.2, 31.4, 28.4, 26.6, 22.5, 13.9; MS (EI, 70 ev): 661 (M^+, 56 %), 590 (100%), 257 (25%); HRMS (EI): calcd. for $C_{28}H_{19}F_{12}NO_2S$: 661.0945, found: 661.0942.

5-Hexyl-1,3-bis(4-(2,2,2-trifluoroacetyl)phenyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3m). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and 4'-bromo-2,2,2-trifluoroacetophenone (**2m**) (557 mg, 2.20 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 30 : 70) the pure product **3m** (320 mg, 55 %). A yellow solid; m.p.: 153.0-154.9 ^oC. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.36 (d, J = 8.3 Hz, 4 H), 8.20 (d, J = 8.3 Hz, 4 H), 3.72 (t, J = 7.2 Hz, 2 H), 1.64-1.78 (m, 2 H), 1.27-1.43 (m, 6 H), 0.89 (t, J = 6.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 179.5 (q , $^2J_{C,F}$ = 36 Hz), 162.2, 143.3, 136.3, 133.2, 130.7, 130.6, 128.5, 116.5 (q , $^1J_{C,F}$ = 289 Hz), 39.0, 31.3, 28.3, 26.5, 22.5, 14.0; MS (FAB): 582 ($[M+1]^+$, 1 %), 461 (2 %), 401 (2 %), 141 (85 %), 106 (100 %); HRMS (FAB): calcd. for $C_{28}H_{21}F_6NO_4S$: 581.1095, found: 581.1089.

5-Hexyl-1,3-di-*p*-tolyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3n). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and 4-bromotoluene (**2q**) (428 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 2 : 98) the pure product **3q** (342 mg, 82 %). A white solid; m.p.: 147.8-149.5 ^oC. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.02 (d, J = 8.2 Hz, 4 H), 7.27 (d, J = 8.2 Hz, 4H), 3.65 (t, J = 7.5 Hz, 2 H), 2.40 (s, 6H), 1.61-1.76(m, 2H), 1.22-1.42 (m, 6 H), 0.88 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.9, 144.6, 140.3, 129.7, 129.4, 127.8, 38.4, 31.4, 28.4, 26.6, 22.5, 21.4, 14.0; MS (FAB): 418 ($[M+1]^+$, 100 %), 346 (63 %), 316 (46 %), 139 (42 %), 106 (56 %); HRMS (FAB): calcd. for $C_{26}H_{27}NO_2S$: 417.1762, found: 417.1770.

5-Hexyl-1,3-di-o-tolyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3o). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and 2-bromotoluene (**2o**) (428 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 5 : 95) the pure product **3o** (363 mg, 87 %). Viscous liquid; ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.57 (d, J = 7.4 Hz, 2 H), 7.25-7.44 (m, 6 H), 3.64 (t, J = 7.3 Hz, 2 H), 2.53 (s, 6 H), 1.60-1.77 (m, 2 H), 1.25-1.45 (m, 6 H), 0.91 (t, J = 6.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.5, 144.2, 137.0, 131.3, 130.71, 130.65, 129.7, 129.3, 125.7, 38.2, 31.2, 28.2, 26.4, 22.3, 20.3, 13.8; MS (EI, 70 ev): 417 (M^+, 66 %), 346 (51 %), 81 (30 %), 58 (100 %); HRMS (EI): calcd. for $C_{26}H_{27}NO_2S$: 417.1762, found:417.1754.

1,3-Bis(3,5-dimethylphenyl)-5-hexyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3p). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and 1-bromo-3,5-dimethylbenzene (**2p**) (463 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 3 : 97) the pure product **3p** (383 mg, 86 %). A pale yellow solid; m.p.: 129.9-131.4 ^oC. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.75(s, 4 H), 7.07 (s, 2H), 3.66 (t, J = 6.0 Hz, 2 H), 2.4 (s, 12 H), 1.60-1.75(m, 2H), 1.23-1.44 (m, 6 H) , 0.88 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.9, 145.2, 138.5, 131.8, 130.4, 130.0, 125.8, 38.6, 31.5, 28.5, 26.6, 22.5, 21.3, 14.0; MS (FAB): 446 ($[M+1]^+$, 100 %), 374 (41 %), 344 (33 %), 130 (27 %); HRMS (FAB): calcd. for $C_{28}H_{31}NO_2S$: 445.2075, found: 445.2074.

1,3-Bis(4-butylphenyl)-5-hexyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3q). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and 1-bromo-4-butylbenzene (**2q**) (533 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 6 : 94) the pure product **3q** (361 mg, 72 %). A yellow solid; m.p.: 64.3-65.2 ^oC. ^1H NMR (CD_2Cl_2, 300 MHz, ppm): δ 8.02 (d, J = 8.2 Hz, 4 H), 7.26 (d, J = 8.2 Hz, 4 H), 3.61 (t, J = 7.2 Hz, 2 H), 2.66 (t, J = 7.5 Hz, 4 H), 1.58-1.77 (m, 6 H), 1.27-1.51 (m, 10 H), 0.86-1.08 (m, 9 H); ^{13}C NMR (CD_2Cl_2, 75 MHz, ppm): δ 163.4, 146.1, 145.0, 130.6, 129.4, 128.7, 128.5, 39.0, 36.1, 34.0, 32.1, 29.0, 27.2, 23.2, 23.0, 14.4, 14.3; MS (EI, 70 ev): 501 (M^+, 19 %), 101 (36 %), 87 (100 %); HRMS (EI): calcd. for $C_{32}H_{39}NO_2S$: 501.2702, found:501.2703.

5-Hexyl-1,3-bis(4-methoxyphenyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3r). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and 4-bromoanisole (**2r**) (468 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 6 : 94) the pure product **3r** (288 mg, 64 %). A pale yellow solid; m.p.: 135.5-136.0 ^oC. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.09 (d, J = 8.9 Hz, 4 H), 6.97 (d, J = 8.9 Hz, 4H), 3.86 (s, 6H), 3.64 (t, J = 7.4 Hz, 2 H), 1.60-1.72(m, 2H), 1.20-1.45 (m, 6 H), 0.88 (t, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 163.1, 160.9, 144.2, 129.6, 128.8, 123.5, 114.2, 55.4, 38.5, 31.4, 28.4, 26.6, 22.5, 14.0; MS (EI, 70 ev): 449 (M^+, 100 %), 418 (3 %), 378 (26 %); HRMS (EI): calcd. for $C_{26}H_{27}NO_4S$: 449.1661, found: 449.1665.

5-Hexyl-1,3-bis(2-methoxyphenyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3s). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and 2-bromoanisole (**2s**) (468 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 15 : 85) the pure product **3s** (360 mg, 80 %). Viscous liquid. ^1H NMR ($CDCl_3$, 300MHz, ppm): δ 8.32 (dd, J = 7.8, 1.6 Hz, 2 H), 7.32-7.44 (m, 2 H), 7.10 (t, J = 8.0 Hz, 2 H), 7.00 (d, J = 8.0 Hz, 2 H), 3.91 (s, 6H), 3.65(t, J = 7.2 Hz, 6 H), 1.60-1.75 (m, 2 H),1.24-1.41 (m, 6 H), 0.89 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 163.1, 156.0, 141.2, 131.3, 130.8, 130.2, 120.6, 119.7, 111.1, 55.4, 38.1, 31.3, 28.3, 26.5, 22.4, 13.9; MS (EI, 70 ev): 449 (M^+, 100 %), 417 (6 %), 378 (35 %)); HRMS (EI): calcd. for $C_{26}H_{27}NO_4S$: 449.1661, found: 449.1663.

1,3-Bis(4-(diphenylamino)phenyl)-5-hexyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3t). The title compound was prepared from **1a** (237 mg,

1.00 mmol) and 4-bromotriphenylamine (**2t**) (811 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (ethyl acetate : hexane = 4 : 96) the pure product **3t** (478 mg, 66 %). A yellow solid; m.p.: 148.6-149.9 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.97-8.05 (m, , 4 H), 7.27-7.38 (m, 8 H), 7.00-7.23 (m, 16 H), 3.64 (t, J = 7.2 Hz, 2 H), 1.60-1.74 (m, 2 H), 1.21-1.45 (m, 6 H), 0.89 (t, J = 6.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 163.2, 149.4, 146.9, 144.2, 129.5, 129.1, 128.8, 125.4, 124.0, 123.8, 121.5, 38.5, 31.5, 28.5, 26.7, 22.5, 14.1; MS (FAB): 723 (M^+, 100 %), 141 (60 %), 106 (90 %); HRMS (FAB): calcd. for $C_{48}H_{41}N_3O_2S$: 723.2919, found: 723.2928.

1-(1,2-Dihydropyren-1-yl)-3-(8,10-dihydropyren-1-yl)-5-hexyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3u). The title compound was prepared from **1a** (237 mg, 1.00 mmol) and 1-bromopyrene (**2u**) (703 mg, 2.50 mmol) according to the general procedure for Table 2 and yielding after column chromatography (dichloromethane : hexane = 30 : 70) the pure product **3u** (453 mg, 71 %). A yellow solid; m.p.:235.0-236.5 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.55 (d, J = 9.2 Hz, 2 H), 7.96-8.49 (m, 16 H), 3.66 (t, J = 7.5 Hz, 2 H), 1.60-1.82 (m, 2 H), 1.15-1.50 (m, 6 H), 0.85 (t, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.7, 144.6, 132.6, 132.5, 131.2, 130.8, 129.2, 128.8, 128.7, 128.6, 127.2, 126.3, 126.0, 125.8, 124.9, 124.6, 124.49, 124.46, 124.2, 38.5, 31.3, 28.4, 26.6, 22.5, 14.0; MS (FAB): 637 (M^+, 3 %), 537 (2 %), 141 (95 %), 106 (100 %); HRMS (FAB): calcd. for $C_{44}H_{31}NO_2S$: 637.2075, found: 637.2079.

General procedure for Table 3.

To a solution of $Pd(OAc)_2$ (10 mol%), P(*m*-tolyl)$_3$ (20 mol%), and Cs_2CO_3 (2.40 mmol) in toluene (3 mL) in a flame-dried Schlenk tube (20 mL) were added TPD **1b** or FPD **1c** (1.00 mmol) and the corresponding aryl bromides (2.50 mmol) under N_2. The reaction mixture was then heated at 110 ℃ under N_2 for 24 h. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The mixture was extracted with ethyl acetate (2 × 30 mL), and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by flash chromatography (ethyl acetate/hexane) yielded the desired products **4a-d, 5a-b**.

Diethyl 4,4'-(5-(2-ethylhexyl)-4,6-dioxo-5,6-dihydro-4H-thieno[3,4-c]pyrrole-1,3-diyl) dibenzoate (4a). The title compound was prepared from **1b** (265 mg, 1.00 mmol) and ethyl 4-bromobenzoate (**2b**) (573 mg, 2.50 mmol) according to the general procedure for Table 3 and yielding after column chromatography (ethyl acetate : hexane = 10 : 90) the pure product **4a** (477 mg, 85 %). A pale yellow solid; m.p.:140.6-142.6 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.17 (d, J = 8.4 Hz, 4 H), 8.09 (d, J = 8.4 Hz, 4 H), 4.38 (q, J = 7.1 Hz, 4 H), 3.54 (d, J = 7.2 Hz, 2 H), 1.75-1.89 (m, 1 H), 1.18-1.49 (m, 14 H), 0.82-0.98 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 165.5, 162.6, 143.6, 134.0, 131.7, 131.4, 129.9, 127.8, 61.1, 42.5, 38.2, 30.5, 28.4, 23.8, 22.9, 14.2, 14.0, 10.3; MS (EI, 70 ev): 561 (M^+, 69 %), 462 (63 %), 449 (45 %), 390 (34 %), 57 (100%); HRMS (EI): calcd. for $C_{32}H_{35}NO_6S$: 561.2185, found: 561.2181.

5-(2-Ethylhexyl)-1,3-bis(4-(trifluoromethyl)phenyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (4b). The title compound was prepared from **1b** (265 mg, 1.00 mmol) and 4-bromobenzotrifluoride (**2j**) (563 mg, 2.50 mmol) according to the general procedure for Table 3 and yielding after column chromatography (ethyl acetate : hexane = 1 : 99) the pure product **4b** (354 mg, 64 %). A pale yellow solid; m.p.: 101.5-102.6 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.25 (d, J = 8.4 Hz, 4 H), 7.74 (d, J = 8.4 Hz, 4 H), 3.57 (d, J = 7.2 Hz, 2 H), 1.75-1.93 (m, 1 H), 1.20-1.44 (m, 8 H), 0.83-0.98 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.7, 143.3, 133.4, 132.0, 131.9 (q, $^2J_{C,F}$ = 32 Hz), 128.3, 126.0 (q, $^3J_{C,F}$ = 4 Hz), 123.7 (q, $^1J_{C,F}$ = 271 Hz), 42.7, 38.3, 30.6, 28.6, 23.9, 23.0, 14.0, 10.4; MS (FAB): 554 ([M+1]$^+$, 67 %), 534 (28 %), 454 (100 %), 424 (38 %); HRMS (FAB): calcd. for $C_{28}H_{25}F_6NO_2S$: 553.1510, found: 553.1512.

5-(2-Ethylhexyl)-1,3-di-p-tolyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (4c). The title compound was prepared from **1b** (265 mg, 1.00 mmol) and 4-bromotoluene (**2n**) (428 mg, 2.50 mmol) according to the general procedure for Table 3 and yielding after column chromatography (ethyl acetate : hexane = 5 : 95) the pure product **4c** (241 mg, 54 %). A white solid; m.p.: 121.1-122.4 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz, ppm): δ 8.01 (d, J = 7.8 Hz, 4 H), 7.26 (d, J = 7.8 Hz, 4 H), 3.50 (d, J = 7.0 Hz, 2 H), 2.39 (s, 6 H), 1.73-1.87 (m, 1 H), 1.22-1.46 (m, 8 H), 0.84-1.00 (m, 6 H); ^{13}C NMR (CD_2Cl_2, 75 MHz, ppm): δ 163.6, 144.9, 141.0, 130.4, 130.0, 128.5, 42.7, 38.9, 31.2, 29.2, 24.5, 23.6, 21.8, 14.5, 10.9 ; MS (EI, 70 ev): 445 (M^+, 63 %), 346 (72 %), 333 (941 %), 84 (100 %); HRMS (EI): calcd. for $C_{28}H_{31}NO_2S$: 445.2075, found: 445.2080.

1,3-Bis(4-(diphenylamino)phenyl)-5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (4d). The title compound was prepared from **1b** (237 mg, 1.00 mmol) and 4-bromotriphenylamine (**2t**) (811 mg, 2.50 mmol) according to the general procedure for Table 3 and yielding after column chromatography (ethyl acetate : hexane = 5 : 95) the pure product **4d** (383 mg, 51 %). An orange solid; m.p.: 176.7-178.7 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.95-8.05 (m, 4 H), 7.27-7.40 (m, 8 H), 7.00-7.23 (m, 16 H), 3.54 (d, J = 7.2 Hz, 2 H), 1.75-1.91 (m, 1 H), 1.25-1.40 (m, 8 H), 0.82-0.98(m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 163.4, 149.3,146.8, 144.1, 129.4, 129.0, 128.6, 125.4, 124.0, 123.7, 121.4, 42.4, 38.2, 30.6, 28.6, 23.9, 23.0, 14.1, 10.5; MS (FAB): 751 (M^+, 100 %); HRMS (FAB): calcd. for $C_{50}H_{45}N_3O_2S$: 751.3232, found: 751.3227.

5-Hexyl-1,3-diphenyl-4H-furo[3,4-c]pyrrole-4,6(5H)-dione (5a). The title compound was prepared from **1c** (221 mg, 1.00 mmol) and bromobenzene (**2a**) (393 mg, 2.50 mmol) according to the general procedure for Table 3 and yielding after column chromatography (ethyl acetate : hexane = 5 : 95) the pure product **5a** (336 mg, 90 %). A white solid; m.p.: 114.9-115.1 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.11 (dd, J = 7.9, 1.5 Hz, 4 H), 7.32-7.47 (m, 6 H), 3.58 (t, J = 6.0 Hz, 2 H), 1.60-1.72 (m, 2 H), 1.23-1.45 (m, 6 H), 0.90 (t, J = 6.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 161.9, 149.0, 130.1, 128.6, 127.1,127.7, 117.2, 38.5, 31.2, 28.2, 26.4, 22.4, 13.9; MS (FAB): 374 ([M+1]$^+$, 100 %), 302 (40 %), 272 (45 %), 63 (82 %); HRMS (FAB): calcd. for $C_{24}H_{23}NO_3$: 373.1678, found: 373.1680.

4,4'-(5-Hexyl-4,6-dioxo-5,6-dihydro-4H-furo[3,4-c]pyrrole-1,3-diyl)dibenzonitrile (5b). The title compound was prepared from **1c** (221 mg, 1.00 mmol) and 4-bromobenzonitrile (**2d**) (455 mg, 2.50 mmol) according to the general procedure for Table 3 and yielding after column chromatography (ethyl acetate : hexane = 20 : 80) the pure product **5b** (263 mg, 62 %). A green solid; m.p.: 248.0-249.3 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.38 (d, J = 8.4 Hz, 4 H), 7.81 (d, J = 8.4 Hz, 4 H), 3.71 (t, J = 7.2 Hz, 2 H), 1.62-1.78 (m, 2 H), 1.21-1.49 (m, 6 H), 0.88 (t, J

= 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75MHz, ppm): δ 161.7, 148.2, 132.9, 130.7, 126.6, 120.6, 118.1, 114.0, 39.2, 31.3, 28.3, 26.5, 22.4, 14.0; MS (EI, 70 ev): 423 (M^+, 100 %), 412 (53 %), 352 (70 %), 130 (83 %), 84 (78 %); HRMS (EI): calcd. for $C_{26}H_{21}N_3O_3$: 423.1583, found: 423.1577.

Procedure for 2,2'-(((5-Hexyl-4,6-dioxo-5,6-dihydro-4H-thieno[3,4-c]pyrrole-1,3-diyl)bis(4,1-phenylene))bis(methanylylidene)) dimalononitrile (6). The starting material **3f** (446 mg, 1.00 mmol) and a large excess of both ammonium acetate and malononitrile were mixed in a mortar under air. The reaction mixture was then ground at room temperature and the reaction progress was monitored by TLC analysis. While the compound **3f** had disappeared, dichloromethane (20 mL) was added and the organic layer was washed with water (30 mL). Then the organic layer was dried (Na_2SO_4) and concentrated in *vacuo* to afford the crude product. Purification by recrystallization (ethanol) yielded the desired product **6** quantitatively. An orange solid; m.p.: 231.1-232.4 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.36 (d, J = 8.5 Hz, 4 H), 8.03 (d, J = 8.5 Hz, 4 H), 7.80 (s, 2 H), 3.71 (t, J = 7.5 Hz, 2 H), 1.60-1.81 (m, 2 H), 1.22-1.45 (m, 6 H), 0.89 (t, J = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.3, 158.1, 143.3, 135.4, 133.2, 132.1, 131.3, 129.0, 113.4, 112.4, 84.0, 39.0, 31.3, 28.3, 26.6, 22.5, 14.0; MS (EI, 70 ev): 542 ($[M+1]^+$, 100 %), 493 (99 %), 470 (83 %), 423 (91 %), 422 (77 %); HRMS (EI): calcd. for $C_{32}H_{23}N_5O_2S$: 541.1572, found: 541.1567.

Acknowledgements

Financial support provided by the Ministry of Science and Technology (MOST), Taiwan (NSC 101-2113-M-008-007-MY2) and the National Central University are gratefully acknowledged.

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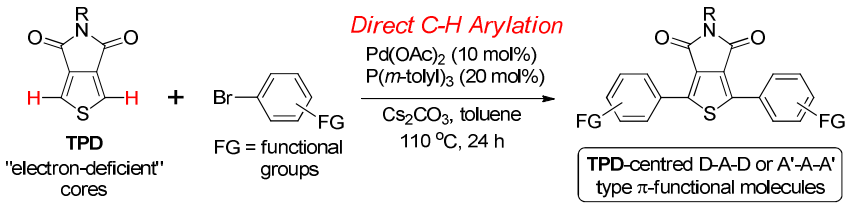

A viable synthetic alternative for the facile construction of various thieno[3,4-c]pyrrole-4,6-dione (TPD)-based π-functional small molecules through direct C-H arylations has been demonstrated.