Advanced Synthesis & Catalysis

Accepted Article

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To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201700762

Link to VoR: http://dx.doi.org/10.1002/adsc.201700762

10.1002/adsc.201700762

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Direct C-H Arylation as Chemoselective Single-Step Access to π-Acceptor-π Type Building Blocks

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Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######

Abstract: Different from the traditional multi-step synthesis, a chemoselective direct C-H arylation is reported for the single-step synthesis of various useful π–acceptor–π (π–A–π) type building blocks for use in organic electronics. This well-optimized C-H heteroarylation exhibits good product yields, broad substrate scope, and high functional group compatibility. Application in the efficient synthesis of a new metal-free dye sensitizer for dye-sensitized solar cells (DSSCs) is also demonstrated.

Keywords: C-H Activation; Chemoselectivity; Dye-Sensitized Solar Cells; Organic Electronics

Introduction

Over the last decade, C-H bond activation/functionalization has advanced significantly in the field of synthetic organic chemistry.[1] Coupling of two reaction substrates without pre-functionalization steps makes this approach synthetically attractive and it gradually becomes the main stream in modern carbon-carbon or carbon-heteroatom bond formations. Among various types of C-H activations, facile construction of C_{sp2}–C_{sp2} bonds via direct C-H cleavage occupies a central place in not only synthetic methodology[2] but also in organic electronics[3] bacause the resulting (hetero)aryls usually exhibit prominent optoelectronic properties. For example, π-conjugated small molecules[4] or polymers[5] prepared by step-economical C-H arylations have been reported to show remarkable semiconducting and photovoltaic properties. More importantly, we found these organic electronic materials were stepwise synthesized starting mainly from a multi-function building block, π–acceptor–π (π–A–π), which could serve as core,[6] end,[7] π-spacer,[8] or monomers[9] respectively (Figure 1).

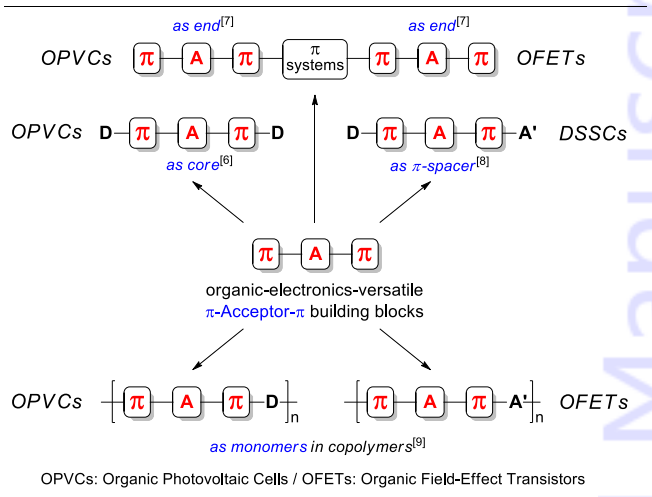
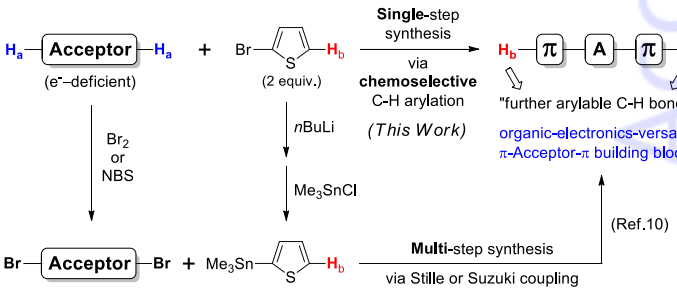


Figure 1. Versatile π-acceptor-π building blocks for the organic optoelectronic materials.

However, all these versatile π–A–π structures were synthesized by the multi-step Stille- or Suzuki coupling reactions that must include the bromination of electron-deficient heteroarenes under harsh conditions as well as the use/treatment of toxic organotin reagents (Scheme 1).[10] In contrast to the traditional synthetic route, we demonstrate herein a single-step synthesis of various useful π–A–π type building blocks via Pd-catalyzed C-H arylations in a chemoselective manner while keeping two further arylable C-H bonds at both ends (H_b, Scheme 1).



Scheme 1. π-acceptor-π building blocks accessed by multi-step Stille coupling or single-step chemoselective C-H arylation.

This report represents the substrate scope extension from our previous work,[11] which a variety of important thiophene–acceptor–thiophene molecular

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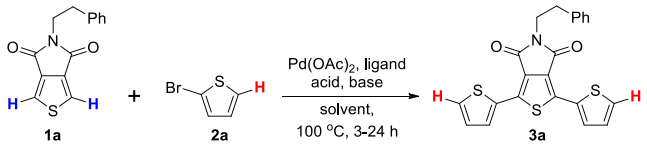
units can be straightforward prepared through one-step chemoselective direct heteroarylations.

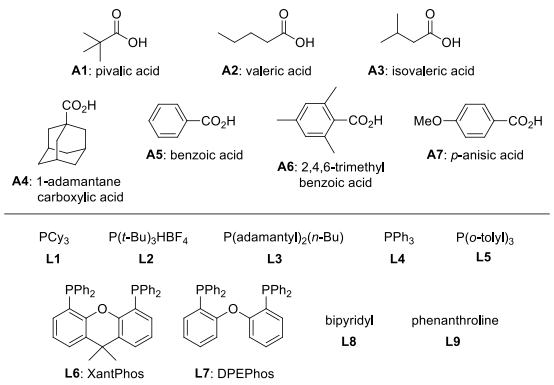
Results and Discussion

For organic electronic materials, thieno[3,4-*c*]pyrrole-4,6-dione (TPD, **1a** of Table 1) has been widely used as electron-deficient unit[12] and thiophene also regarded as one of the most important π-bridges, we therefore decided to connect **1a** with 2-bromothiophene (**2a**) via direct C-H bond cleavage to facilely construct thiophene–TPD–thiophene (**3a**) as a representative π–A–π building block. The optimization of reaction conditions was summarized in Table 1. Initially, the di-heteroarylation was performed with a commonly used acid additive (A1: PivOH), an inexpensive ligand (L1: PCy_3), and Cs_2CO_3 in toluene at 100 °C for 6 h. The target π–A–π molecule (**3a**) was isolated in 50% yield (entry 1). In addition to PivOH, we screened a variety of additives including aliphatic- and aromatic acids (A2~A7), giving the desired product in 23-70% yield (entries 2-7). Interestingly, we found that abundant and inexpensive acetic acid afforded **3a** in a promising yield (81%, entry 8). Other acid additives such as TFA, HCl, or H_2SO_4 gave unsatisfactory results (13-52%, entries 9-11). The C-H activation did not occur in the absense of organic carboxylate (entry 12). Subsequently, we tried to shorten (3 h) or lengthen (12, 24 h) the reaction time. However, this did not further improve the chemoselectivity or yield because most starting materials were recovered in the case of 3 h (entry 13) whereas a significant amount of complex mixtures were formed when the reaction time was extended to 12 or 24 h (entries 14, 15). Under present optimal conditions (AcOH, PCy_3, 6 h), we proceeded to examine different phosphine ligands (L2~L7). P(*t*Bu)$_3$•HBF_4 (L2) and tri-*o*-tolylphosphine (L5) were shown to give better yields of **3a** (84%, 83%; entries 16, 19). *N*,*N*-bidentate type ligands (L8, L9) were much less efficient and only a trace of **3a** was generated (entries 22, 23). Thus, we fixed on the use of relatively cheaper PCy_3 as optimal ligand for the following investigation of bases. It was found that K_2CO_3 and K_3PO_4 were almost as effective as Cs_2CO_3 (79%, 75%; entries 24, 26) while less basic Na_2CO_3 was inefficient in C-H activation reactions (trace, entry 25). Under base-free condition, the heteroarylation did not take place (entry 27). Finally, solvent effect was studied. Like toluene, nonpolar *p*-xylene gave good isolated yield of **3a** (78%, entry 28). In contrast, we found the reaction hardly proceeded in polar aprotic solvents such as DMAc, NMP, DMSO, and DMPU (entries 29-32).

Table 1. Optimization of the chemoselective C-H heteroarylation using TPD (**1a**) and 2-bromothiophene (**2a**).[a]



entry	acid	ligand	base	solvent	time (h)	yield (%)[b]
1	A1	L1	Cs_2CO_3	toluene	6	50
2	A2	L1	Cs_2CO_3	toluene	6	62
3	A3	L1	Cs_2CO_3	toluene	6	64
4	A4	L1	Cs_2CO_3	toluene	6	53
5	A5	L1	Cs_2CO_3	toluene	6	66
6	A6	L1	Cs_2CO_3	toluene	6	23
7	A7	L1	Cs_2CO_3	toluene	6	70
8	AcOH	L1	Cs_2CO_3	toluene	6	81
9	TFA	L1	Cs_2CO_3	toluene	6	13
10	HCl	L1	Cs_2CO_3	toluene	6	52
11	H_2SO_4	L1	Cs_2CO_3	toluene	6	34
12	---	L1	Cs_2CO_3	toluene	6	0
13	AcOH	L1	Cs_2CO_3	toluene	3	11
14	AcOH	L1	Cs_2CO_3	toluene	12	40
15	AcOH	L1	Cs_2CO_3	toluene	24	47
16	AcOH	L2	Cs_2CO_3	toluene	6	84
17	AcOH	L3	Cs_2CO_3	toluene	6	37
18	AcOH	L4	Cs_2CO_3	toluene	6	46
19	AcOH	L5	Cs_2CO_3	toluene	6	83
20	AcOH	L6	Cs_2CO_3	toluene	6	62
21	AcOH	L7	Cs_2CO_3	toluene	6	45
22	AcOH	L8	Cs_2CO_3	toluene	6	trace
23	AcOH	L9	Cs_2CO_3	toluene	6	trace
24	AcOH	L1	K_2CO_3	toluene	6	79
25	AcOH	L1	Na_2CO_3	toluene	6	trace
26	AcOH	L1	K_3PO_4	toluene	6	75
27	AcOH	L1	---	toluene	6	0
28	AcOH	L1	Cs_2CO_3	*p*-xylene	6	78
29	AcOH	L1	Cs_2CO_3	DMAc	6	11
30	AcOH	L1	Cs_2CO_3	NMP	6	trace
31	AcOH	L1	Cs_2CO_3	DMSO	6	trace
32	AcOH	L1	Cs_2CO_3	DMPU	6	trace



[a] Unless specified, the reaction was conducted with TPD **1a** (1.00 mmol) and 2-bromothiophene **2a** (2.20 mmol) under N_2 in the presence of $Pd(OAc)_2$ (0.10 mmol), ligand (0.20 mmol), acid (0.30 mmol), and base (2.40 mmol) in solvent (3 mL) at 100 °C for 3-24 hrs. [b] Isolated yields.

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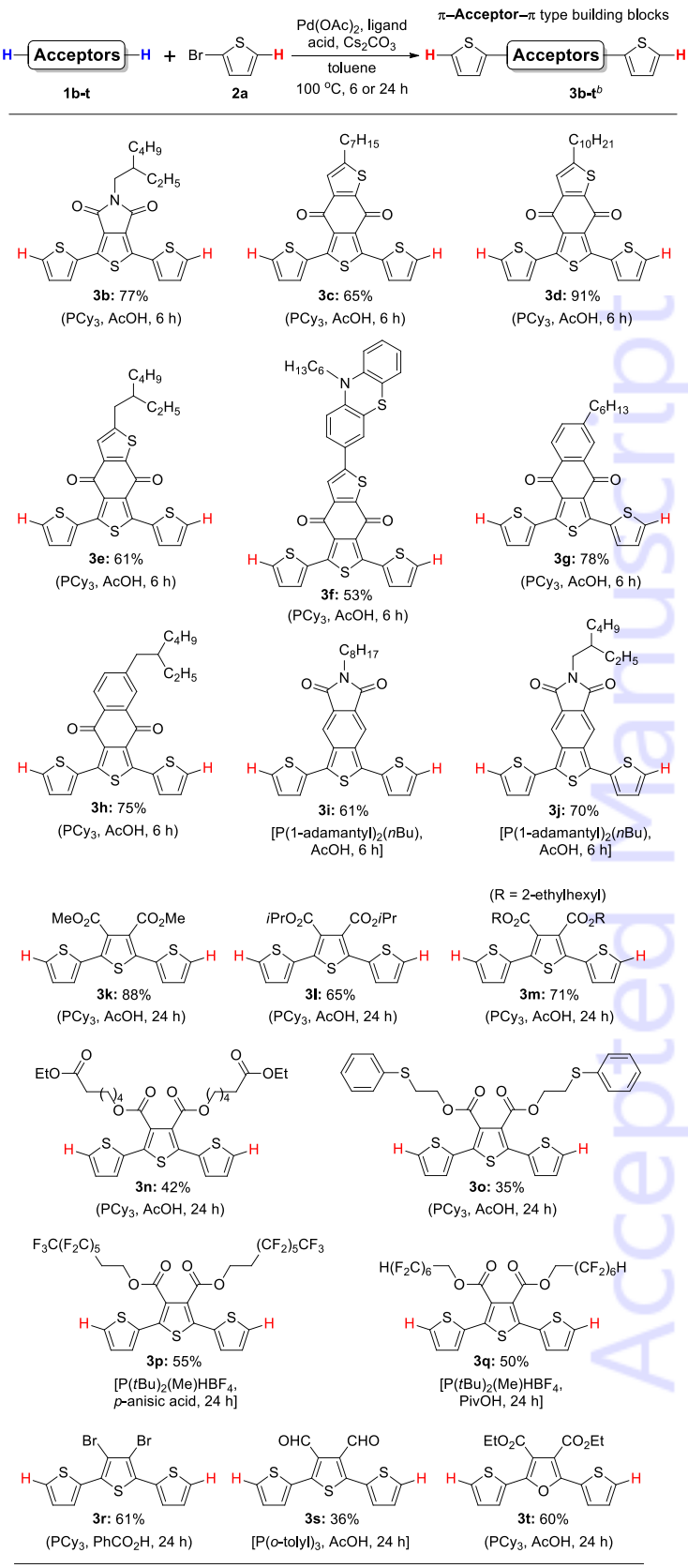
As shown in Table 2, in order to explore the reaction scope, we tested the chemoselective C-H di-heteroarylation with various acceptor type heteroaryls (**1b-t**), mainly under the optimum reaction conditions obtained in entry 8 of Table 1 (PCy_3, AcOH, Cs_2CO_3, toluene). In certain cases, the ligand or acid additive was further optimized to obtain the best isolated yield. First, reaction of 2-ethylhexyl substituted thieno[3,4-*c*]pyrrole-4,6-dione (TPD, **1b**) with **2a** afforded desired product **3b** in 77% yield. Benzo-dithiophene-diones (BDD, **1c-1e**), an important class of acceptor-type monomer for polymer semiconductors,[13] underwent C-H arylations smoothly to give π–A–π products in moderate to good yields (**3c**-**3e**, 61-91%). In addition to alkyl BDD, we found the phenothiazine-substituted BDD (**1f**) was also facilely arylated to generate **3f** in 53% yield. Traditionally, to access these compounds must rely on the use of Stille coupling reactions that needed the pre-functionalizations of both starintg materials. Likewise, direct C-H arylation of naphtho-thiophene-diones[14] (NaphTD, **1g-1h**) with **2a** was efficiently performed to provide compounds **3g**, **3h** in good yields (78%, 75%). Thieno-isoindole-diones (**1i-1j**), another popular acceptor-type monomers used in the synthesis of functional π-conjugated polymers,[15] were shown to undergo diarylations best with P(1-adamantyl)$_2$(*n*Bu), affording desired prodicts in 61-70% yields (**3i-3j**). In addition, we examined a series of 3,4-diester-substituted thiophenes (**1k-1o**) under optimum reaction time (24h). The target products (**3k-3o**) were isolated in 35-88% yields. C-H arylation of diester compounds with perfluoroalkyl chains (**1p-1q**) also proceeded successfully to yield **3p**, **3q** (55%, 50%) under modified reaction conditions. Interestingly, 3,4-dibromothiophene (**1r**) reacted with 2-bromothiophene regioselectively to produce a versatile synthetic intermediate **3r** in 61% yield. Two bromine atoms remaining on the middle thiophene may undergo further cross couplings to extend conjugation length. Finally, other acceptors including dialdehyde (**1s**) or diester furan (**1t**) were also tested, providing desired products **3s**-**3t**, respectively (36%, 60%).

The synthetic application of present methodology was realized by the use of **3b** as key building block in the facile preparation of D–π–A type organic sensitizer for dye-sensitized soalr cells (Scheme 2). One-pot sequential C-H arylations of **3b** with a triphenylamine (TPA)-based donor followed by a furan-containing acceptor led to the formation of desired aldehyde-terminated unsymmetrical oligoaryl **4**, which was further converted into cyanoacetic acid as required anchoring group by Knoevenagel condensation. To access compound **4** traditionally by Stille couplings would take at least ten synthetic steps.

Obtained sensitizer (**CYL-12**) was fabricated as dye-sensitized soalr cells (DSSCs, the detailed procedures for device fabrication and characterization were provided in Experimental Section).

Table 2. Reaction Scope: C-H heteroarylation of various acceptors (**1b-t**) with 2-bromothiophene (**2a**).[a]



[a] Unless specified, the C-H heteroarylation was conducted with acceptors **1b-1t** (1.00 mmol) and 2-bromothiophene **2a** (2.20 mmol) under N_2 in the presence of $Pd(OAc)_2$ (0.10 mmol), ligand (0.20 mmol), acid (0.30 mmol), and Cs_2CO_3 (2.40 mmol) in solvent (3 mL) at 100 °C for 6 or 24 hrs. [b] Isolated yields.

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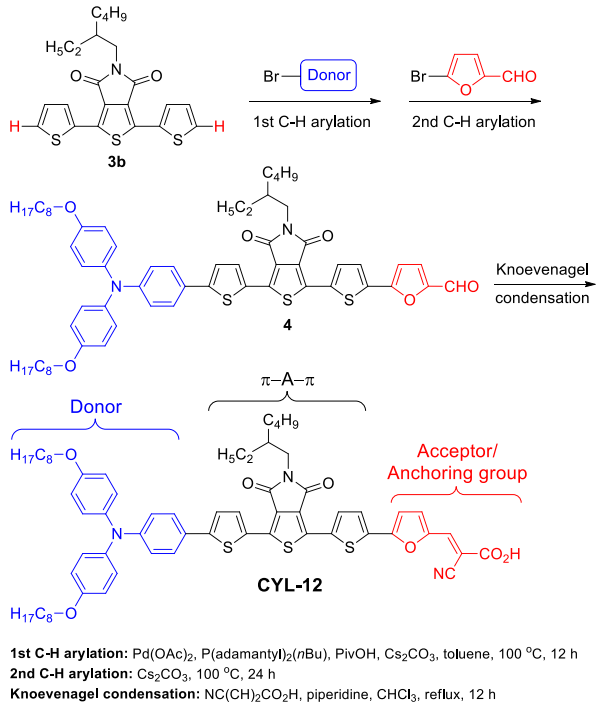


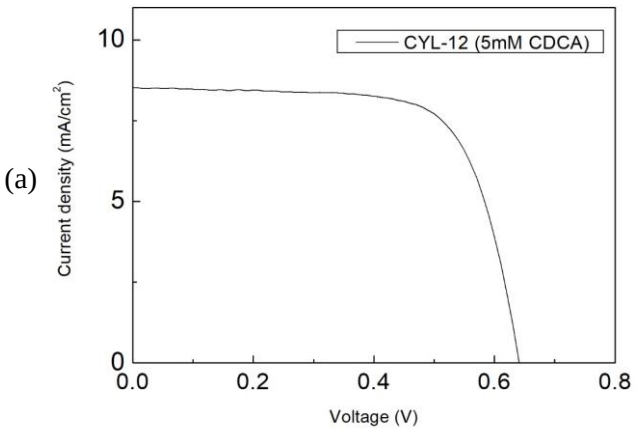
Scheme 2. Application of π-acceptor-π building block (**3b**) in the facile synthesis of new organic sensitizer **CYL-12**.

Table 3 and Figure 2 showed the photovoltaic parameters and characteristics of **CYL-12**. Compared to the commercially available *cis*-bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-di-nonyl-2'-bipyridyl)ruthenium(II) (**Z907**),[16] the open-circuit photovoltage (V_{oc}) and the fill factor (*FF*) of **CYL-12** were found to be slightly lower than those of the metal-containg dye (**Z907**). The short-circuit photocurrent density (J_{sc}) of **CYL-12**, however, was only 8.51 mA/cm^2, much smaller than that of **Z907** (J_{sc} = 14.75 mA/cm^2) thus leading to a relatively inferior power conversion efficiency (PCE) of 3.86%.

Table 3. Fabrication of DSSCs using **CYL-12** as dye sensitizer: photovoltaic parameters.[a]

DSSCs	V_{oc} [V]	J_{sc} [mA/cm^2]	*FF* [%]	*PCE* [%]
CYL-12	0.64	8.51	70.71	3.86
Z907[b]	0.69	14.75	69.50	7.07

[a] Chenodeoxycholic acid (CDCA) was added as co-adsorbent (5 mM for **CYL-12**). [b] cis-Bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-di-nonyl-2'-bipyridyl)ruthenium(II).



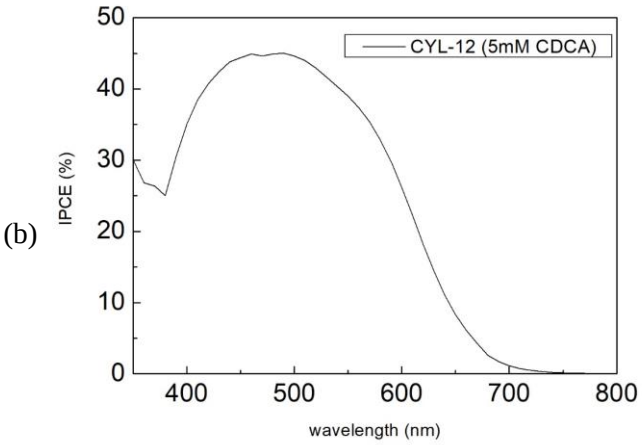


Figure 2. Photovoltaic characteristics of **CYL-12**: (a) photocurrent density vs. photovoltage; (b) incident photon-to-current conversion efficiency (IPCE)

Conclusion

In summary, this work demonstrated a single-step access to a variety of useful π–acceptor–π (π–A–π) type building blocks for use in organic π-functional materials. Under optimized reaction parameters, the direct C-H heteroarylation displayed promising isolated yields and tolerated important fuctional groups such as ester, ketone, aldehyde, sulfide, and bromide. In addition, good chemoselectivity[17] of this heteroarylation was also achieved thus remaining two further arylable C-H bonds on both ends of desired prodcuts, which enabled subsequent chemical transformations/π-extensions. To apply present methodology in the facile preparation of photovoltaic materials, a new organic dye sensitizer (**CYL-12**) was step-economically synthesized via sequential C-H arylations starting from one of the obtained π–A–π structures. Preparation of small-molecule photovoltaic organic materials by step-saving C-H (hetero)arylations is currently ongoing in our laboratory.

Experimental Section

General Information

Unless otherwise specified, all reactions were carried out with magnetic stirring and in flame-dried glassware under nitrogen if air or moisture sensitive. Reagents including $Pd(OAc)_2$, ligands, acids, and bases are commercially available. Anhydrous or reagent-grade solvents such as toluene, *p*-xylene, 1,4-dioxane, *N*,*N*-dimethylacetamide (DMA), *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), and *N*,*N*′-dimethylpropylene urea (DMPU) were purchased from Sigma-Aldrich, Acros, or Alfa Aesar 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, 40-75 μm) from Japan. The diameters of the columns and the amount of silica gel loaded were calculated according to

the recommendation of W. C. Still.[18] Melting points were measured on a Fargo MP-2D apparatus. NMR spectra were recorded on a Bruker Magnet System 300 or 500 MHz instrument. Chemical shifts were given relative to $CDCl_3$ (7.26 ppm for ^1H NMR, 77.0 ppm for ^{13}C NMR), CD_2Cl_2 (5.32 ppm for ^1H NMR, 54.0 ppm for ^{13}C NMR), DMSO-d_6 (2.50 ppm for ^1H NMR, 39.4 ppm for ^{13}C NMR), acetone-d_6 (2.04 ppm for ^1H NMR, 29.3 ppm for ^{13}C NMR). For the characterization of the observed signal multiplicities, the following abbreviations were applied: s (singlet), d (doublet), dd (doublet of doublets), dt (doublet of triplets), dm (doublet of multiplets), t (triplet), td (triplet of doublets), q (quartet), quint (quintet), m (multiplet), comp (complex), app (apparent), and 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 a 3-nitrobenzyl alcohol- or glycerine-matrix. Absorption spectra were measured on a Hitachi U-4100 UV-Vis spectrophotometer, and the HOMO-LUMO optical band gap (E_g^{opt}) was calculated according to the λ_{onset} obtained. The experiments of cyclic voltammetry were carried out with an Autolab electrochemical analyzer using a Pt working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode. The measurements were conducted in dry THF solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as a supporting electrolyte under a scan rate of 100 mVs^{-1}. The half-wave potential, $E_{1/2}$, was calculated by $(E_{pa}+E_{pc})/2$, where E_{pa} and E_{pc} are the potential energy of anodic and cathodic peaks, respectively. The HOMO energy level, E_{HOMO}, was calculated by $-(E_{1/2} + 0.197 + 4.500)$ eV (*vs.* Ag/AgCl and NHE); $E_{LUMO} = E_{HOMO} + E_g^{opt}$.

Procedures for the fabrication and performance characterization of dye-sensitized solar cells (DSSCs): The DSSCs were fabricated using **CYL-12** as sensitizers. The TiO_2 paste and TiO_2 film were prepared according to the methods described in the literature.[19] Photo-electrode (working electrode): TiO_2 screen printing was carried out on a piece of fluorine-doped tin oxide glass (FTO, sheet resistivity of 7 Ω/square). The TiO_2 film was composed of 16 μm thick mesoporous anatase-TiO_2 nanoparticles with a diameter of 20 nm and a 4 μm thick TiO_2 scattering layer with a diameter of 400 nm. After sintered at 350 ℃ for 15 mins and at 500 ℃ for 30 mins, the TiO_2 photo-electrode that has an active area of 0.160 cm^2 was immersed in the freshly prepared dye solution (anhydrous THF) at 40 ℃ for 24 hours. Counter electrode: another piece FTO glass coated with Pt was used as counter electrode. The electrolyte solution was prepared via mixing 0.6 M 1-butyl-3-methylimidazolium iodide ([bmim][I]), 0.1 M LiI, 0.05 M I_2, 0.1 M GuNCS, and 0.5 M 4-*t*-butylpyridine (TBP) in acetonitrile. To the dye solution containing 2.0 x 10^{-4} M of **CYL-12** in THF, chenodeoxycholic acid (CDCA, 1.0~10 mM in anhydrous THF) was added as co-adsorbent to see if the performance of DSSCs was improved (A CDCA-free dye solution was also prepared for the comparative experiment during the optimization of device performance of DSSCs). An IPCE spectrometer (EQE-R-3011, ENLI Technology Co. Ltd., Taiwan) calibrated with a single-crystal silicon reference cell for each measurement was used for the incident monochromatic photon-to-current conversion efficiency (IPCE) measurements. An AM 1.5G solar simulator (Yamashita Denso Corporation, YSS-50A) was used as the irradiation light source for the characteristic current density-voltage (J-V) measurements. The intensity of the simulated sunlight was calibrated to 100 mW/cm^2. The J-V characteristics of the cell under an illumination of AM 1.5G simulated sunlight were obtained by applying the external potential bias to the cell and measuring the photocurrent output with a Keithley model 2400 digital source meter (Keithley, USA).

General procedure A for Table 1: Optimization of the regioselective C-H arylation using 5-phenethyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (TPD, 1a) and 2-bromothiophene (2a)
To a solution of $Pd(OAc)_2$ (0.10 mmol), ligand (0.20 mmol), acid (0.30 mmol), and base (2.40 mmol) in solvent (3 mL) in a flame-dried Schlenk tube were added TPD (**1a**) (1.00 mmol) and 2-bromothiophene (**2a**) (2.20 mmol) under N_2. The reaction mixture was then heated at 100 °C under N_2 for 3~24 h. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The mixture was extracted with ethyl acetate (2 × 20 mL), and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by flash chromatography yielded the desired product **3a**.

5-Phenethyl-1,3-di(thiophen-2-yl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (3a) was prepared from **1a** (257 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), tricyclohexylphosphine (56 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **A** and yielding after column chromatography (dichloromethane : hexanes = 50 : 50) the pure product **3a** (354 mg, 84 %). Yellow powder; m.p.: 175.1-178.0 °C. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.99 (dd, J = 3.8, 0.8 Hz, 2 H), 7.43 (dd, J = 5.0, 0.8 Hz, 2 H), 7.19-7.36 (comp, 5 H), 7.12 (dd, J = 5.0, 3.8 Hz, 2 H), 3.83-3.94 (comp, 2 H), 2.94-3.04 (comp, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.3, 138.2, 136.7, 132.4, 129.9, 128.9, 128.7, 128.6, 128.5, 128.3, 126.6, 39.9, 34.7; MS (EI, 70 eV): 421 (M^+, 47 %), 384 (100 %), 330 (91 %); HRMS (EI): calcd. for $C_{22}H_{15}NO_2S_3$: 421.0265, found: 421.0258.
Synthesis and characterization of (**1a**): starting material **1a** was prepared according to the procedures reported in *RSC Adv.* **2014**, *4*, 35868-35878. Pale yellow solid; m.p.: 154.3-155.2 °C. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.80 (s, 2 H), 7.19-7.35 (comp, 5 H), 3.82-3.92 (comp, 2 H), 2.92-3.02 (comp, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.4, 138.0, 136.5, 128.9, 128.6, 126.7, 125.7, 39.7, 39.5; MS (EI, 70 eV): 257 (M^+, 17 %), 166 (100 %), 139 (78 %), 91 (79 %); HRMS (EI): calcd. for $C_{14}H_{11}NO_2S$: 257.0510, found: 257.0507.

General procedure B for Table 2: Exploration of the substrate scope
To a solution of $Pd(OAc)_2$ (0.10 mmol), ligand (0.20 mmol), acid (0.30 mmol), and Cs_2CO_3 (2.40 mmol) in toluene (3 mL) in a flame-dried Schlenk tube were added the corresponding substrates (**1b-t**) (1.00 mmol) and 2-bromothiophene (**2a**) (2.20 mmol) under N_2. The reaction mixture was then heated at 100 °C under N_2 for 6~24 h. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The mixture was extracted with ethyl acetate (2 × 20 mL), and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by flash chromatography yielded the desired products **3b-t**.

5-(2-Ethylhexyl)-1,3-di(thiophen-2-yl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione[20] **(3b)** was prepared from 5-(2-ethylhexyl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (**1b**) (265 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), tricyclohexylphosphine (56 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** and yielding after column chromatography (ethyl acetate : hexanes = 5 : 95) the pure product **3b** (330 mg, 77 %). Yellow powder; m.p.: 126.0-126.3 °C. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.01 (dd, J = 3.8, 1.2 Hz, 2 H), 7.42 (dd, J = 5.1, 1.2 Hz, 2 H), 7.11 (dd, J = 5.1, 3.8 Hz, 2 H), 3.55 (d, J = 7.2 Hz, 2 H), 1.77-1.93 (m, 1 H), 1.20-1.46 (comp, 8 H), 0.82-1.05 (comp, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.8, 136.4, 132.5, 129.9, 128.6, 128.4 (two peaks), 42.5, 38.3, 30.6, 28.6, 23.9, 23.1, 14.1, 10.5.

2-Heptyl-5,7-di(thiophen-2-yl)benzo[1,2-*b*:4,5-*c'*]dithiophene-4,8-dione (3c) was prepared from 2-heptylbenzo[1,2-*b*:4,5-

c']dithiophene-4,8-dione (**1c**) (318 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), tricyclohexylphosphine (56 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** and yielding after column chromatography (dichloromethane : hexanes = 50 : 50) the pure product **3c** (313 mg, 65 %). Dark red solid; m.p.: 117.9-118.6 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.71-7.82 (comp, 2 H), 7.47 (app d, 2 H), 7.24 (s, 1 H), 7.06 (app t, 2 H), 2.81 (t, J = 7.5 Hz, 2 H), 1.59-1.79 (comp, 2 H), 1.20-1.42 (comp, 8 H), 0.89 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 175.8, 174.2, 156.6, 145.2, 144.3, 143.9, 143.6, 132.8, 132.7, 131.3, 131.2, 130.1, 129.97, 129.96, 129.8, 127.33, 127.28, 123.4, 37.7, 31.0, 30.8, 28.97, 28.96, 22.6, 14.1; MS (EI, 70 eV): 482 (M^+, 100 %), 368 (54%), 71 (51%); HRMS (EI): calcd. for $C_{25}H_{22}O_2S_4$: 482.0503, found: 482.0500.

Synthesis and characterization of (**1c**): (i) To a solution of 3,4-thiophenedicarboxylic acid (516 mg, 3.00 mmol) in anhydrous CH_2Cl_2 (4.5 mL), oxalyl chloride (1.5 mL) was added. Few drops of *N*,*N*-dimetheylformamide was added to the mixture till it produced bubbles. The reaction mixture was then stirred at room temperature for 12 h before the solvent was distilled off under ambient pressure. The crude product (di-acid chloride) was used directly for the next step without further purification; (ii) To a solution of the di-acid chloride and aluminium chloride (1596 mg, 12.0 mmol) in anhydrous CH_2Cl_2 (3 mL), 2-heptylthiophene (601 mg, 3.30 mmol) diluted in anhydrous CH_2Cl_2 (3 mL) was added dropwise at 0 ˚C for a period of 0.5 h. The reaction mixture was then stirred at room temperature for 12 h before it was quenched with 1M $HCl_{(aq)}$. The mixture was extracted with dichloromethane (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 (dichloromethane : hexanes = 60 : 40) yielded the desired staring material **1c**. Pale yellow solid; m.p.: 169.9-171.4 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.19 (app s, 2 H), 7.33 (s, 1 H), 2.87 (t, J = 7.6 Hz, 2 H), 1.62-1.85 (comp, 2 H), 1.14-1.48 (comp, 8 H), 0.77-0.98 (app s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 175.6, 174.0, 157.0, 145.1, 144.7, 137.9, 137.7, 132.3, 131.9, 123.8, 31.7, 31.1, 30.8, 28.9 (two peaks), 22.6, 14.0; MS (EI, 70 eV): 318 (M^+, 20 %), 234 (100 %), 205 (40 %), 177 (22 %); HRMS (EI): calcd. for $C_{17}H_{18}O_2S_2$: 318.0748, found: 318.0745.

2-Decyl-5,7-di(thiophen-2-yl)benzo[1,2-*b*:4,5-*c'*]dithiophene-4,8-dione (3d) was prepared from 2-decylbenzo[1,2-*b*:4,5-*c'*]dithiophene-4,8-dione (**1d**) (360 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), tricyclohexylphosphine (56 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** and yielding after column chromatography (dichloromethane : hexanes = 60 : 40) the pure product **3d** (478 mg, 91 %). Red liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.70-7.84 (comp, 2 H), 7.47 (app d, 2 H), 7.25 (s, 1 H), 7.03-7.12 (comp, 2 H), 2.81 (t, J = 7.5 Hz, 2 H), 1.61-1.77 (comp, 2 H), 1.45-1.66 (comp, 14 H), 0.81-0.96 (comp, 3 H) ; ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 175.9, 174.3, 156.6, 145.2, 144.4, 143.9, 143.6, 132.8, 132.7, 131.3, 131.2, 130.2, 130.0 (two peaks), 129.8, 127.3, 127.3, 123.5, 31.9, 31.0, 30.8, 29.6, 29.5, 29.34, 29.30, 29.0, 22.7, 14.2; MS (EI, 70 eV): 525 [$(M+1)^+$, 1 %], 436 (21 %), 421 (24 %), 71 (100 %), 57 (95 %); HRMS (EI): calcd. for $C_{28}H_{28}O_2S_4$: 524.0972, found: 524.0965.

Synthesis and characterization of (**1d**): compound **1d** was prepared under the same reaction conditions as described for **1c**. Red solid; m.p.: 197.6-198.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.22 (app s, 2 H), 7.36 (s, 1 H), 2.88 (t, J = 6.5 Hz, 2 H), 1.81-1.86 (comp, 2 H), 1.15-1.45 (comp, 14 H), 0.87 (app s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 175.5, 173.9, 157.0, 145.1, 144.7, 137.9, 137.7, 132.4, 131.9, 123.8, 31.9, 31.1, 30.8, 29.6, 29.5, 29.30, 29.25, 29.0, 22.7, 14.1; MS (EI, 70 eV): 360 (M^+, 100 %), 234 (69 %), 149 (57 %); HRMS (EI): calcd. for $C_{20}H_{24}O_2S_2$: 360.1218, found: 360.1219.

2-(2-Ethylhexyl)-5,7-di(thiophen-2-yl)benzo[1,2-*b*:4,5-*c'*]dithiophene-4,8-dione (3e) was prepared from 2-(2-ethylhexyl)benzo[1,2-*b*:4,5-*c'*]dithiophene-4,8-dione (**1e**) (332 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), tricyclohexylphosphine (56 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** and yielding after column chromatography (dichloromethane : hexanes = 60 : 40) the pure product **3e** (303 mg, 61 %). Red liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.71-7.86 (comp, 2 H), 7.47 (app dd, 2 H), 7.25 (s, 1 H), 7.00-7.14 (comp, 2 H), 2.77 (d, J = 6.6 Hz, 2 H), 1.55-1.71 (m, 1 H), 1.20-1.42 (comp, 8 H), 0.89 (app dd, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 175.9, 174.3, 155.4, 145.5, 144.3, 143.9, 143.6, 132.8, 132.7, 131.3, 131.2, 130.2, 130.0, 129.9 (two peaks), 127.4, 127.3 124.5, 41.4, 34.8, 32.4, 28.8, 25.5, 23.0, 14.1, 10.8 ; MS (EI, 70 eV): 497 ($[M+1]^+$, 5 %), 149 (47 %), 97 (68 %), 71 (93 %), 57 (100 %); HRMS (EI): calcd. for $C_{26}H_{24}O_2S_4$: 496.0659, found: 496.0667.

Synthesis and characterization of (**1e**): compound **1e** was prepared under the same reaction conditions as described for **1c**. Pale brown solid; m.p.: 104.1-104.7 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.15 (app s, 2 H), 7.26 (s, 1 H), 2.77 (d, J = 6.6 Hz, 2 H), 1.49-1.73 (m, 1 H), 1.10-1.42 (comp, 8 H), 0.86 (app t, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 175.4, 173.7, 155.7, 145.2, 144.5, 137.8, 137.6, 132.3, 131.9, 124.7, 41.4, 34.7, 32.3, 28.8, 25.5, 22.9, 14.1, 10.8; MS (EI, 70 eV): 333 ($[M+1]^+$, 24 %), 234 (100 %), 207 (77 %); HRMS (EI): calcd. for $C_{18}H_{20}O_2S_2$: 332.0905, found: 332.0908.

2-(10-Hexyl-10*H*-phenothiazin-3-yl)-5,7-di(thiophen-2-yl)benzo[1,2-b:4,5-*c'*]dithiophene-4,8-dione (3f) was prepared from 2-(10-hexyl-10*H*-phenothiazin-3-yl)benzo[1,2-b:4,5-*c'*]dithiophene-4,8-dione (**1f**) (501 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), tricyclohexylphosphine (56 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** and yielding after column chromatography (dichloromethane : hexanes = 40 : 60) the pure product **3f** (352 mg, 53 %). Red solid; m.p.: 154.1-154.5 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.71-7.81 (comp, 2 H), 7.52-7.57 (m, 1 H), 7.44.-7.51 (comp, 2 H), 7.27-7.36 (m, 1 H), 7.19-7.26 (m, 1 H), 7.12-7.18 (m, 1 H), 7.04-7.11 (comp, 3 H), 6.93 (app t, 1 H), 6.81 (app d, 1 H), 6.67-6.74 (m, 1 H), 3.76 (app s, 2 H), 1.71-1.83 (comp, 2 H), 1.24-1.48 (comp, 6 H), 0.91 (t, J = 6.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 175.6, 174.0, 152.5, 146.3, 145.0, 144.6, 144.1, 143.5, 132.8, 132.7, 131.31, 131.28, 130.03, 129.85, 127.4, 127.34, 127.31, 126.7, 125.5, 125.4, 125.3, 124.6, 123.6, 122.9, 120.3, 115.4, 115.2, 47.7, 31.4, 26.7, 26.6, 22.6, 14.0; MS (FAB): 665 (M^+, 5 %), 95 (100 %); HRMS (FAB): calcd. for $C_{36}H_{27}NO_2S_5$: 665.0645, found: 665.0639.

Synthesis and characterization of (**1f**): compound **1f** was prepared under similar reaction conditions described for **1c**. Orange solid; m.p.: 206.1-206.8 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.21 (d, J = 3.0 Hz, 1 H), 8.19 (d, J = 3.0 Hz, 1 H), 7.68 (s, 1 H), 7.37-7.48 (comp, 2 H), 7.09-7.20 (comp, 2 H), 6.89-6.99 (m, 1 H), 6.79-6.89 (comp, 2 H), 3.84 (t, J = 7.2 Hz, 2 H), 1.73-1.89 (comp, 2 H), 1.25-1.53 (comp, 6 H), 0.88 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 175.5, 173.8, 153.0, 146.6, 145.4, 144.4, 144.1, 137.73, 137.70, 132.6, 131.9, 127.5, 126.6, 125.6, 125.5, 124.9, 123.6, 123.0, 120.7, 115.6, 115.4, 47.7, 31.5, 26.8, 26.6, 22.6, 14.0; MS (EI, 70 eV): 501 (M^+, 3 %), 111 (35 %), 83 (50 %), 71 (65 %), 57 (100 %); HRMS (EI): calcd. for $C_{28}H_{23}NO_2S_3$: 501.0891, found: 501.0894.

6-Hexyl-1,3-di(thiophen-2-yl)naphtho[2,3-*c*]thiophene-4,9-dione (3g) was prepared from 6-hexylnaphtho[2,3-*c*]thiophene-

4,9-dione (**1g**) (298 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), tricyclohexylphosphine (56 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** and yielding after column chromatography (dichloromethane : hexanes = 30 : 70) the pure product **3g** (360 mg, 78 %). Red liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.15 (d, J = 8.0 Hz, 1 H), 8.06 (d, J = 1.6 Hz, 1 H), 7.80 (app d, J = 3.8 Hz, 2 H), 7.45-7.55 (comp, 3 H), 7.09-7.12 (comp, 2 H), 2.72 (t, J = 7.7 Hz, 2 H), 1.62-1.71 (comp, 2 H), 1.23-1.41 (comp, 6 H), 0.86-0.90 (comp, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 179.9, 179.5, 149.7, 143.8, 143.6, 134.6, 134.0, 132.9, 132.6, 131.0, 130.9, 129.9, 129.8, 129.7, 127.4, 127.3, 126.8, 36.1, 31.6, 30.7, 28.8, 22.5, 14.0; MS (FAB): 462 (M^+, 3 %), 249 (40 %), 228 (90 %), 77 (60 %), 51 (100 %); HRMS (FAB): calcd. for $C_{26}H_{22}O_2S_3$: 462.0782, found: 462.0777.

Synthesis and characterization of (**1g**): compound **1g** was prepared under the same reaction conditions as described for **1c**. White solid; m.p.: 77.4-78.3 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.33 (d, J = 3.1 Hz, 1 H), 8.31 (d, J = 3.1 Hz, 1 H), 8.19 (d, J = 8.0 Hz, 1 H), 8.08 (d, J = 1.7 Hz, 1 H), 7.56 (dd, J = 8.0, 1.7 Hz, 1 H), 2.75 (t, J = 7.7 Hz, 2 H), 1.58-1.79 (comp, 2 H), 1.21-1.49 (comp, 6 H), 0.81-0.97 (comp, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 179.5, 179.1, 150.2, 137.4, 134.8, 134.3, 132.7, 132.6, 132.4, 127.9, 127.3, 36.1, 28.9, 22.5, 14.0; MS (EI, 70 eV): 299 ([M+1]$^+$, 4 %), 109 (66 %), 95 (46 %), 81 (72 %), 69 (100 %); HRMS (EI): calcd. for $C_{18}H_{18}O_2S$: 298.1028, found: 298.1029.

6-(2-Ethylhexyl)-1,3-di(thiophen-2-yl)naphtho[2,3-*c*]thiophene-4,9-dione (3h) was prepared from 6-(2-ethylhexyl)naphtho[2,3-*c*]thiophene-4,9-dione (**1h**) (326 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), tricyclohexylphosphine (56 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** and yielding after column chromatography (ethyl acetate: hexanes = 20 : 80) the pure product **3h** (367 mg, 75 %). Red liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.14 (d, J = 7.9 Hz, 1 H), 8.03 (s, 1 H), 7.75-7.84 (comp, 2 H), 7.43-7.53 (comp, 3 H), 7.05-7.13 (comp, 2 H), 2.64 (d, J = 7.2 Hz, 2 H), 1.57-1.76 (m, 1 H), 1.16-1.36 (comp, 8 H), 0.87 (app t, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 179.6, 179.2, 149.5, 137.5, 135.4, 134.63, 134.55, 132.7, 132.6, 132.4, 129.4, 129.1, 128.1, 127.6, 41.0, 40.4, 32.3, 28.8, 25.5, 23.0, 14.1, 10.8; MS (FAB): 491 ([M+1]$^+$, 6 %), 228 (31 %), 107 (62 %), 77 (100 %); HRMS (FAB): calcd. for $C_{28}H_{26}O_2S_3$: 490.1095, found: 490.1089.

Synthesis and characterization of (**1h**): compound **1h** was prepared under the same reaction conditions as described for **1c**. Pale yellow solid; m.p.: 59.0-60.8 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.23-7.31 (comp, 2 H), 7.12-7.22 (comp, 3 H), 2.53 (d, J = 5.4 Hz, 2 H), 1.47-1.65 (m, 1 H), 1.14-1.45 (comp, 8 H), 0.88 (app, t, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 179.6, 179.2, 149.5, 137.5, 135.0, 134.7, 132.7, 132.6, 132.4, 128.1, 127.8, 41.0, 40.4, 32.3, 28.8, 25.5, 23.0, 14.1, 10.8; MS (FAB): 327 ([M+1]$^+$, 54 %), 229 (29 %), 217 (32 %), 67 (100 %); HRMS (FAB): calcd. for $C_{20}H_{22}O_2S$: 326.1341, found: 326.1342.

6-Octyl-1,3-di(thiophen-2-yl)-5*H*-thieno[3,4-*f*]isoindole-5,7(6*H*)-dione (3i) was prepared from 6-octyl-5*H*-thieno[3,4-*f*]isoindole-5,7(6*H*)-dione[21] (**1i**) (315 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), P(1-adamantyl)$_2$(*n*Bu) (72 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** and yielding after column chromatography (ethyl acetate : hexanes = 10 : 90) the pure product **3i** (292 mg, 61 %). Orange/red solid; m.p.: 143.1-144.3 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.35 (s, 2 H), 7.47 (dd, J = 5.1, 1.2 Hz, 2 H), 7.18 (dd, J = 3.6, 1.2 Hz, 2 H), 7.18 (dd, J = 5.1, 3.6 Hz, 2 H), 3.70 (t, J = 7.2 Hz, 2 H), 1.60-1.78 (comp, 2 H), 1.16-1.44 (comp, 10 H), 0.87 (t, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 167.6, 135.3, 133.7, 132.5, 128.3, 127.3, 127.2, 126.8, 119.1, 38.5, 31.8, 29.2, 28.5, 26.9, 22.6, 14.1; MS (EI, 70 eV): 479 (M^+, 18 %), 414 (21 %), 305 (14 %), 84 (69 %), 57 (100 %); HRMS (EI): calcd. for $C_{26}H_{25}NO_2S_3$: 479.1047, found: 479.1049.

6-(2-Ethylhexyl)-1,3-di(thiophen-2-yl)-5*H*-thieno[3,4-*f*]isoindole-5,7(6*H*)-dione (3j) was prepared from 6-(2-ethylhexyl)-5*H*-thieno[3,4-*f*]isoindole-5,7(6*H*)-dione[21] (**1j**) (315 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), P(1-adamantyl)$_2$(*n*Bu) (72 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** and yielding after column chromatography (ethyl acetate : hexanes = 8 : 92) the pure product **3j** (335 mg, 70 %). Orange/red solid; m.p.: 152.2-154.4 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.33 (s, 2 H), 7.45 (dd, J = 5.1, 1.2 Hz, 2 H), 7.35 (dd, J = 3.6, 1.2 Hz, 2 H), 7.16 (dd, J = 5.1, 3.6 Hz, 2 H), 3.60 (d, J = 7.2 Hz, 2 H), 1.79-1.97 (m, 1 H), 1.22-1.46 (comp, 8 H), 0.80-1.12 (comp, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 167.8, 135.3, 133.7, 132.4, 128.3, 127.3, 127.2, 126.7, 119.1, 42.3, 38.2, 30.6, 28.5, 23.9, 23.0, 14.1, 10.5; MS (EI, 70 eV): 479 (M^+, 29 %), 380 (11 %), 263 (100 %), 234 (96 %), 218 (48 %); HRMS (EI): calcd. for $C_{26}H_{25}NO_2S_3$: 479.1047, found: 479.1044.

Dimethyl [2,2':5',2''-terthiophene]-3',4'-dicarboxylate (3k) was prepared from dimethyl thiophene-3,4-dicarboxylate[22] (**1k**) (200 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), tricyclohexylphosphine (56 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** (reaction time: 24 h) and yielding after column chromatography (ethyl acetate : hexanes = 30 : 70) the pure product **3k** (320 mg, 88 %). Yellow liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.40 (dd, J = 5.2, 1.2 Hz, 2 H), 7.34 (dd, J = 3.6, 1.2 Hz, 2 H), 7.07 (dd, J = 5.2, 3.6 Hz, 2 H), 3.84 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 164.1, 138.2, 132.5, 129.4, 128.7, 128.0, 127.7, 52.5; MS (FAB): 364 ([M+1]$^+$, 4 %), 249 (25 %), 280 (50 %), 51 (100 %); HRMS (FAB): calcd. for $C_{16}H_{12}O_4S_3$: 363.9898, found: 363.9901.

Diisopropyl [2,2':5',2''-terthiophene]-3',4'-dicarboxylate (3l) was prepared from diisopropyl thiophene-3,4-dicarboxylate (**1l**) (256 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), tricyclohexylphosphine (56 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** (reaction time: 24 h) and yielding after column chromatography (ethyl acetate : hexanes = 30 : 70) the pure product **3l** (273 mg, 65 %). Yellow liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.39 (dd, J = 5.1, 1.2 Hz, 2 H), 7.29 (dd, J = 3.6, 1.2 Hz, 2 H), 7.05 (dd, J = 5.1, 3.6 Hz, 2 H), 5.16 (septet, J = 6.3 Hz, 2 H), 1.25 (d, J = 6.3 Hz, 12 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 163.3, 137.6, 132.6, 130.8, 128.7, 127.7, 127.4, 69.5, 21.6; MS (EI, 70 eV): 420 (M^+, 18 %), 336 (28 %), 127 (100 %), 111 (61 %); HRMS (EI): calcd. for $C_{20}H_{20}O_4S_3$: 420.0524, found: 420.0515.

Synthesis and characterization of (**1l**): compound **1l** was prepared under the same reaction conditions as reported in literature.[5] Pale yellow liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.79 (s, 2 H), 5.19 (septet, J = 6.3 Hz, 2 H), 1.34 (d, J = 6.3 Hz, 12 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.7, 134.2, 131.1, 68.9, 21.8; MS (EI, 70 eV): 256 (M^+, 1 %), 155 (100 %), 128 (25 %), 59 (25 %); HRMS (EI): calcd. for $C_{12}H_{16}O_4S$: 256.0769, found: 256.0774.

Bis(2-ethylhexyl) [2,2':5',2''-terthiophene]-3',4'-dicarboxylate (3m) was prepared from bis(2-ethylhexyl) thiophene-3,4-dicarboxylate (**1m**) (397 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), tricyclohexylphosphine

(56 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** (reaction time: 24 h) and yielding after column chromatography (dichloromethane : hexanes = 30 : 70) the pure product **3m** (398 mg, 71 %). Brown liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.35 (dd, J = 5.1, 1.2 Hz, 2 H), 7.28 (dd, J = 3.6, 1.2 Hz, 2 H), 7.02 (dd, J = 5.1, 3.6 Hz, 2 H), 4.10-4.24 (comp, 4 H), 1.51-1.64 (comp, 2 H), 1.18-1.40 (comp, 16 H), 0.79-0.97 (comp, 12 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 164.0, 137.7, 132.6, 130.5, 128.5, 127.7, 127.6, 68.2, 38.6, 30.1, 28.9, 23.5, 23.0, 14.1, 10.9; MS (EI, 70 eV): 561 ([M+1]$^+$, 73 %), 319 (19 %), 71 (61 %), 57 (100 %); HRMS (EI): calcd. for $C_{30}H_{40}O_4S_3$: 560.2089, found: 560.2087.

Synthesis and characterization of (**1m**): compound **1m** was prepared under the same reaction conditions as reported in literature.[22] Yellow liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.81 (s, 2 H), 4.11-4.29 (comp, 4 H), 1.57-1.77 (comp, 2 H), 1.19-1.52 (comp, 16 H), 0.91 (app t, 12 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 163.2, 133.8, 131.5, 67.8, 38.8, 30.4, 28.9, 23.8, 23.0, 14.1, 11.0; MS (EI, 70 eV): 396 (M$^+$, 1 %), 173 (68 %), 155 (80 %), 57 (100 %); HRMS (EI): calcd. for $C_{22}H_{36}O_4S$: 396.2334, found: 396.2336.

Bis(6-ethoxy-6-oxohexyl) [2,2':5',2''-terthiophene]-3',4'-dicarboxylate (3n) was prepared from bis(6-ethoxy-6-oxohexyl) thiophene-3,4-dicarboxylate (**1n**) (456 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), tricyclohexylphosphine (56 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** (reaction time: 24 h) and yielding after column chromatography (ethyl acetate : hexanes = 30 : 70) the pure product **3n** (260 mg, 42 %). Yellow liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.38 (dd, J = 5.1, 1.1 Hz, 2 H), 7.28 (dd, J = 3.7, 1.1 Hz, 2 H), 7.04 (dd, J = 5.1, 3.7 Hz, 2 H), 4.20 (t, J = 6.6 Hz, 4 H), 4.10 (q, J = 7.1 Hz, 4 H), 2.24 (t, J = 7.5 Hz, 4 H), 1.51-1.68 (comp, 8 H), 1.18-1.36 (comp, 10 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 173.4, 163.6, 137.8, 132.4, 130.0, 128.6, 127.7, 127.4, 65.4, 60.1, 34.0, 28.0, 25.3, 24.5, 14.2; MS (EI, 70 eV): 621 ([M+1]$^+$, 21 %), 430 (91 %), 143 (57 %), 69 (100 %); HRMS (EI): calcd. for $C_{30}H_{36}O_8S_3$: 620.1572, found: 620.1572.

Synthesis and characterization of (**1n**): (i) To a solution of 3, 4-thiophenedicarboxylic acid (516 mg, 3.00 mmol) in anhydrous CH_2Cl_2 (4.5 mL), oxalyl chloride (1.5 mL) was added. Few drops of *N*, *N*-dimetheylformamide were added to the mixture till it produced bubbles. The reaction mixture was then stirred at room temperature for 12 h before the solvent was distilled off under ambient pressure. The crude product (di-acid chloride) was used directly for the next step without further purification; (ii) To a solution of the corresponding R-OH (1200 mg, 7.5 mmol) in anhydrous CH_2Cl_2 (4 mL), pyridine (711 mg, 9.0 mmol) was added dropwise at ice-bath temperature. The reaction mixture was then stirred at room temperature for 6 h before it was quenched with water. The mixture was extracted with dichloromethane (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 : hexanes = 30 : 70) yielded the desired staring material **1n**. Yellow liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.82 (s, 2 H), 4.25 (t, J = 6.6 Hz, 4 H), 4.10 (q, J = 7.2 Hz, 4 H), 2.30 (t, J = 7.5 Hz, 4 H), 1.60-1.82 (comp, 8 H), 1.37-1.50 (comp, 4 H), 1.22 (t, J = 7.2 Hz, 6 H) ; ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 173.5, 163.1, 133.5, 131.6, 65.2, 60.3, 34.2, 28.3, 25.5, 24.6, 14.2; MS (EI, 70 eV): 457([M+1]$^+$, 2 %), 183 (50 %), 155 (100 %), 142 (65 %); HRMS (EI): calcd. for $C_{22}H_{32}O_8S$: 456.1818, found: 456.1814.

Bis(2-(phenylthio)ethyl) [2,2':5',2''-terthiophene]-3',4'-dicarboxylate (3o) was prepared from bis(2-(phenylthio)ethyl) thiophene-3,4-dicarboxylate (**1o**) (445 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), tricyclohexylphosphine (56 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** (reaction time: 24 h) and yielding after column chromatography (dichloromethane : hexanes = 40 : 60)z the pure product **3o** (155 mg, 35 %). Brown liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.39-7.43 (comp, 2 H), 7.25-7.39 (comp, 10 H), 7.19-7.24 (comp, 2 H), 7.05-7.10 (comp, 2 H), 4.38 (t, J = 7.2 Hz, 4 H), 3.13 (t, J = 7.2 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 163.3, 138.5, 134.9, 132.3, 129.8, 129.4, 129.2, 128.9, 128.0, 127.7, 126.7, 63.9, 31.8; MS (EI, 70 eV): 608 (M$^+$, 66 %), 524 (74 %), 336 (86 %), 137 (80 %), 109 (100 %); HRMS (EI): calcd. for $C_{30}H_{24}O_4S_5$: 608.0278, found: 608.0277.

Synthesis and characterization of (**1o**): compound **1o** was synthesized according to the procedures described for **1n**. Yellow liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.78 (s, 2 H), 7.20-7.51 (comp, 10 H), 4.46 (t, J = 6.9 Hz, 4 H), 2.26 (t, J = 6.9 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.5, 135.1, 132.9, 132.4, 129.9, 129.2, 126.7, 63.8, 32.3; MS (EI, 70 eV): 444 (M$^+$, 9 %), 136 (100 %), 109 (26 %) ; HRMS (EI): calcd. for $C_{22}H_{20}O_4S_3$: 444.0524, found: 444.0527.

Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) [2,2':5',2''-terthiophene]-3',4'-dicarboxylate (3p) was prepared from bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) thiophene-3,4-dicarboxylate (**1p**) (864 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), P(tBu)$_2$(Me) • HBF_4 (50 mg, 0.20 mmol), *p*-anisic acid (46 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** (reaction time: 24 h) and yielding after column chromatography (ethyl acetate : dichloromethane : hexanes = 5 : 15 : 80) the pure product **3p** (565 mg, 55 %). Yellow solid; m.p.: 102.6-103.3 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.43 (dd, J = 5.1, 1.2 Hz, 2 H), 7.27-7.30 (comp, 2 H), 7.00-7.14 (comp, 2 H), 4.51 (t, J = 6.6 Hz, 4 H), 2.45 (tt, J = 18.3, 6.3 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 163.1, 139.0, 132.0, 129.1, 129.0, 128.1, 127.6, 117.4 (q, $^1J_{C\text{-}F}$ = 255 Hz), 108.6 (t, $^2J_{C\text{-}F}$ = 33.3 Hz), 57.3, 30.2 (t, $^2J_{C\text{-}F}$ = 21.8 Hz); MS (FAB): 1027 (M$^+$, 18 %), 746 (6 %), 654 (15 %), 69 (100 %); HRMS (FAB): calcd. for $C_{30}H_{14}F_{26}O_4S_3$: 1027.9639, found: 1027.9637.

Synthesis and characterization of (**1p**): compound **1p** was prepared under the same reaction conditions as reported in literature.[23] Transparent liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.87 (s, 2 H), 4.56 (t, J = 6.5 Hz, 4 H), 2.55 (tt, J = 18.3, 6.3 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 162.1, 132.62, 132.58, 117.5 (q, $^1J_{C\text{-}F}$ = 152.6 Hz), 112.9 (t, $^2J_{C\text{-}F}$ = 19.9 Hz), 108.3 (t, $^3J_{C\text{-}F}$ = 3.0 Hz), 57.0, 30.3 (t, $^2J_{C\text{-}F}$ = 13.1 Hz); MS (FAB): 864 ([M+1]$^+$, 16 %), 501 (80 %), 155 (100 %), 69 (61 %); HRMS (FAB): calcd. for $C_{22}H_{10}F_{26}O_4S$: 863.9885, found: 863.9889.

Bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)[2,2':5',2''-terthiophene]-3',4'-dicarboxylate (3q) was prepared from bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl) thiophene-3,4-dicarboxylate (**1q**) (799 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), P(tBu)$_2$(Me) • HBF_4 (50 mg, 0.20 mmol), PivOH (31 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** (reaction time: 24 h) and yielding after column chromatography (ethyl acetate : dichloromethane : hexanes = 5 : 15 : 80) the pure product **3q** (482 mg, 50 %). Yellow solid; m.p.: 79.9-80.6 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.45 (dd, J = 5.1, 1.2 Hz, 2 H), 7.35 (dd, J = 3.6, 1.2 Hz, 2 H), 7.09 (dd, J = 5.1, 3.6 Hz, 2 H), 6.03 (tt, J = 51.9, 5.1 Hz, 2 H), 4.68 (t, J = 14.0 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 161.8, 140.4, 131.3, 129.4, 128.5, 127.8, 127.5, 112.9 (t, $^2J_{C\text{-}F}$ = 31.3 Hz), 60.6 (t, $^2J_{C\text{-}F}$ = 25 Hz); MS (FAB): 963 (M$^+$, 100 %), 632 (85 %), 127 (52 %), 111 (40 %), 51 (70 %); HRMS (FAB): calcd. for $C_{28}H_{12}F_{24}O_4S_3$:

963.9514, found: 963.9509.
Synthesis and characterization of (**1q**): compound **1q** was prepared under the same reaction conditions as reported in literature.[23] Transparent liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.02 (s, 2 H), 6.04 (tt, J = 51.9, 5.1 Hz, 2 H), 4.77 (t, J = 13.5 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 160.4, 134.2, 131.2, 104.2 (t, $^2J_{C-F}$ = 53.1 Hz), 60.1 (t, $^2J_{C-F}$ = 45 Hz) ; MS (FAB): 799 (M^+, 5 %), 469 (100 %), 157 (12 %), 110 (16 %); HRMS (FAB): calcd. for $C_{20}H_8F_{24}O_4S$: 799.9760, found: 799.9761.

3',4'-Dibromo-2,2':5',2''-terthiophene[24] **(3r)** was prepared from 3,4-dibromothiophene (**1r**) (242 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), tricyclohexylphosphine (56 mg, 0.20 mmol), benzoic acid (37 mg, 0.30 mmol), K_2CO_3 (331 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** (reaction time: 24 h) and yielding after column chromatography (hexanes) the pure product **3r** (248 mg, 61 %). Yellow solid; m.p.: 101.5-102.6 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.44-7.55 (comp, 2 H), 7.34-7.43 (comp, 2 H), 7.05-7.19 (comp, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 134.0, 131.0, 112.4, 77.3, 77.1, 76.8.

[2,2':5',2''-Terthiophene]-3',4'-dicarbaldehyde (3s) was prepared from thiophene-3,4-dicarbaldehyde (**1s**) (140 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), P(*o*-tolyl)$_3$ (61 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** (reaction time: 24 h) and yielding after column chromatography (ethyl acetate : dichloromethane : hexanes = 10 : 15 : 75) the pure product **3s** (104 mg, 36 %). Yellow solid; m.p.: 107.6-108.1 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 10.27 (s, 2 H), 7.40-7.80 (comp, 4 H), 7.06-7.23 (comp, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 186.7, 144.9, 135.3, 131.3, 130.7, 129.6, 128.2; MS (EI, 70 eV): 303 (M^+, 3 %), 220 (13 %), 154 (100 %), 89 (49 %), 77 (49 %); HRMS (EI): calcd. for $C_{14}H_8O_2S_3$: 303.9686, found: 303.9693.

Diethyl 2,5-di(thiophen-2-yl)furan-3,4-dicarboxylate (3t) was prepared from diethyl furan-3,4-dicarboxylate (**1t**) (212 mg, 1.00 mmol), **2a** (359 mg, 2.20 mmol), $Pd(OAc)_2$ (24 mg, 0.10 mmol), tricyclohexylphosphine (56 mg, 0.20 mmol), acetic acid (18 mg, 0.30 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and toluene (3 mL) according to the general procedure **B** (reaction time: 24 h) and yielding after column chromatography (ethyl acetate : hexanes = 10 : 90) the pure product **3t** (226 mg, 60 %). Green liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.79 (dd, J = 3.9, 1.0 Hz, 2 H), 7.44 (dd, J = 5.1, 1.0 Hz, 2 H), 7.11 (dd, J = 5.1, 3.9 Hz, 2 H), 4.37 (q, J = 7.2 Hz, 4 H), 1.37 (t, J = 7.2 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 163.2, 148.8, 130.2, 128.3, 128.2, 127.7, 113.8, 61.5, 14.2; MS (EI, 70 eV): 376 (M^+, 7 %), 203 (11 %), 111 (100 %), 83 (12 %); HRMS (EI): calcd. for $C_{18}H_{16}O_5S_2$: 376.0439, found: 376.0446.

Synthesis and characterization of compounds 4a and **CYL-12 (Scheme 2):**
5-(5-(3-(5-(4-(Bis(4-(octyloxy)phenyl)amino)phenyl)thiophen-2-yl)-5-(2-ethylhexyl)-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)thiophen-2-yl)furan-2-carbaldehyde (4a): To a solution of $Pd(OAc)_2$ (12 mg, 5 mol%), P(1-adamantyl)$_2$(*n*Bu) (36 mg, 10 mol%), PivOH (31 mg, 30 mol%), and Cs_2CO_3 (391 mg, 1.20 mmol) in toluene (3.0 mL) in a flame-dried Schlenk tube were added **3b** (559 mg, 1.30 mmol) and 4-bromo-*N*,*N*-bis(4-(octyloxy)phenyl)aniline (580 mg, 1.00 mmol) under N_2. The reaction mixture was then heated at 100 °C under N_2 for 12 hours. After the oil bath had been removed, 5-bromofuran-2-carbaldehyde (350 mg, 2.00 mmol) and another portion of Cs_2CO_3 (391 mg, 1.20 mmol) were added to the solution without the isolation of intermediates and byproducts. The reaction mixture was then heated again to 100 °C under N_2 and kept at the same temperature for 24 hours. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The mixture was extracted with dichloromethane (2 × 30 mL), and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by column chromatography (hexane : ethyl acetate = 85 : 15) afforded the pure product **4a** (286 mg, 28 %). Dark red solid; m.p.: 36.1-38.1 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.63 (s, 1 H), 7.97 (dd, J = 21.0, 4.0 Hz, 2 H), 7.47 (d, J = 4.0 Hz, 1 H), 7.41 (d, J = 8.7 Hz, 2 H), 7.29 (d, J = 3.8 Hz, 1 H), 7.16 (d, J = 4.0 Hz, 1 H), 7.07 (d, J = 8.9 Hz, 4 H), 6.78-6.96 (comp, 6 H), 6.75 (d, J = 3.7 Hz, 1 H), 3.94 (t, J = 6.5 Hz, 4 H), 3.56 (d, J = 7.2 Hz, 2 H), 1.72-1.89 (comp, 5 H), 1.23-1.50 (comp, 28 H), 0.80-1.04 (comp, 12 H).; ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.9, 162.8, 155.9, 154.9, 154.3, 153.6, 151.9, 149.3, 148.9, 140.2, 140.0, 137.7, 134.3, 134.1, 133.6, 131.8, 130.4, 129.7, 127.0, 126.7, 124.6, 122.8, 119.6, 115.4, 108.9, 68.3, 38.3, 31.9, 31.8, 30.6, 30.1, 29.7, 29.4, 29.3, 28.6, 26.1, 23.9, 23.1, 22.7, 14.1, 10.5; MS (FAB): 1022 (M^+, 21 %), 909 (8 %), 51 (100 %); HRMS (FAB): calcd. for $C_{61}H_{70}N_2O_6S_3$: 1022.4396, found: 1022.4398.

Knoevenagel condensations:
(*E*)-3-(5-(5-(3-(5-(4-(Bis(4-(octyloxy)phenyl)amino)phenyl)thiophen-2-yl)-5-(2-ethylhexyl)-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)thiophen-2-yl)furan-2-yl)-2-cyanoacrylic acid (CYL-12): To a solution of the aldehyde (**4a**) (255 mg, 0.25 mmol) in chloroform (5 mL) were added cyanoacetic acid (10.0 mmol) and piperidine (0.5 mL) at room temperature. The reaction mixture was then heated at reflux under N_2 for 12 h. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The mixture was extracted with dichloromethane (2 × 20 mL), and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by column chromatography (using the eluent with a gradient polarity: from dichloromethane : methanol = 95 : 5 to dichloromethane : methanol = 85 : 15) gave the pure product **CYL-12** (232 mg, 85 %). Dark red solid; m.p.: 139.1-141.8 ˚C. ^{1}H NMR ($CDCl_3$ and few drops of CD_3OD, 300 MHz, ppm): δ 7.63-7.96 (comp, 3 H), 7.26-7.46 (comp, 4 H), 7.06-7.18 (comp, 2 H), 6.90-7.04 (comp, 4 H), 6.69-6.87 (comp, 5 H), 6.59-6.67 (m, 1 H), 3.85 (t, J = 6.4 Hz, 4 H), 3.28 (dt, J = 3.2, 1.6 Hz, 2 H), 1.61-1.82 (comp, 5 H), 1.14-1.41 (comp, 28 H), 0.67-0.95 (comp, 12 H); MS (FAB): 1090 ($[M+1]^+$, 5 %), 654 (3 %), 77 (100 %); HRMS (FAB): calcd. for $C_{64}H_{71}N_3O_7S_3$: 1089.4454, found: 1089.4456.

Acknowledgements

Financial support provided by the Ministry of Science and Technology (MOST), Taiwan (MOST 105-2113-M-008-005) and the National Central University (NCU) are gratefully acknowledged. Mr. Kuan-Ming Lu and Mr. Wei-Ming Li contributed equally to this work.

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[17] The proton acidity of acceptors (**1a-t**, proton in blue colour, H_a) is different from that of 2-bromothiophene (proton in red colour, H_b) thus leading to different reactivity and selectivity in present C-H heteroarylations. The proton acidity difference was expected to be the main reason why good chemoselectivity was observed. Moreover, we speculate that side reactions such as self-oligomerization of **2a** (2-bromothiophene) and further C-H reaction of desired product **3a** with **2a** might take place. Nevertheless, by controlling the reaction time (reaction time screening shown in entries 13-15 of Table 1), these side reactions can be suppressed/minimized in most cases (Table 1 & Table 2), rendering the desired C-H di-heteroarylations proceed with moderate to good isolated yields.

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10.1002/adsc.201700762

FULL PAPER

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