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Article

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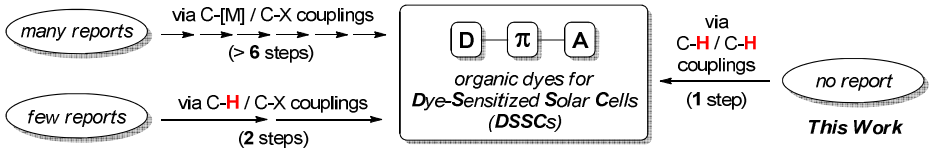
Cross-Dehydrogenative Coupling (CDC) as Key-Transformations to Various D-π-A Organic Dyes: C-H/C-H Synthetic Study directed toward Dye-Sensitized Solar Cells Applications

Yan-Syun Ciou,[†] Po-Han Lin,[†] Wei-Ming Li,[†] Kun-Mu Lee,[‡] and Ching-Yuan Liu*,[†]

[†]Department of Chemical and Materials Engineering, National Central University, Jhongli District 320, Taiwan (R.O.C) *E-mail: cyliu0312@ncu.edu.tw

[‡]Department of Chemical and Materials Engineering, Chang Gung University, Guishan District 333, Taiwan (R.O.C)



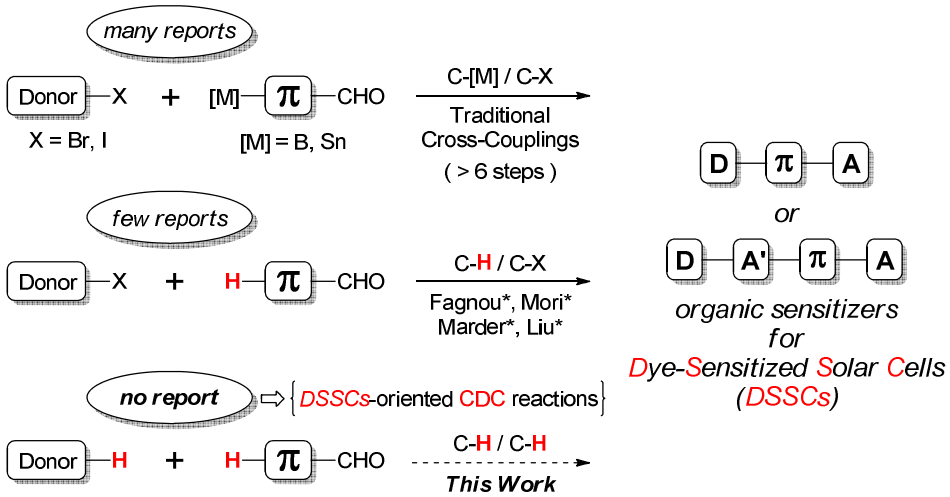
Abstract: A variety of push-pull type organic dyes are facilely synthesized through the most atom-economical C-H/C-H dehydrogenative coupling reactions. After comprehensive synthetic optimizations, a broad substrate scope is achieved and functional groups such as ester, ketone, nitrile, nitro, and triazene are well tolerated. The sensitive aldehyde group required for the conversion into anchoring groups for DSSCs applications is also compatible under present oxidant-containing reaction conditions. Based on this optimum C-H/C-H coupling approach, three new organic sensitizers are readily prepared and submitted to solar cell device fabrications, giving the power conversion efficiency (PCE) up to 4.85%. This work constitutes the first example that connects high atom-efficiency C-H/C-H green catalysis with dye-sensitized solar cell applications.

Introduction

Conversion of sunlight into electric power is one of the most promising green techniques for renewable energy.[1] Differing from the first-generation silicon-based photovoltaic cells, Grätzel and

co-workers designed efficient and inexpensive dye-sensitized solar cells (DSSCs) using a series of organometallic complexes as dye-sensitizers.[2-6] Among various dyes, metal-free organic sensitizers have been attracting considerable research interests since last decade because they had advantages of low cost, high extinction coefficient, and diverse molecular design.[7-11] Synthetically, accessing these D–π–A type dye molecules traditionally relied on Suzuki- or Stille-coupling reaction, which involves tedious pre-functionalization steps and requires the preparation of costly organoboron or toxic organotin species. With the aim of developing a step-saving and user-friendly synthetic approach for DSSCs, Fagnou,[12] Mori,[13] Marder,[14] and our group[15] reported alternative ways to access D–π–A organic dyes via direct C-H arylations (C-H/C-X). In order to further simplify the synthetic efficiency, we envisaged that D–π–A or D–A'–π–A configured dyes could be facilely constructed through the most step-economical C-H/C-H coupling method that might be facilitated coincidentally by the difference of proton acidity between two key components of an unsymmetrical dye molecule: Donor–**H** and Acceptor–**H**. Therefore, we demonstrate herein an in-depth synthetic study of cross-dehydrogenative couplings (CDC)[16] directed toward dye-sensitized solar cell applications (Scheme 1). To the best of our knowledge, no reports on the connection of C-H/C-H coupling methodologies with the metal-free dye sensitizers for DSSCs have appeared to date.

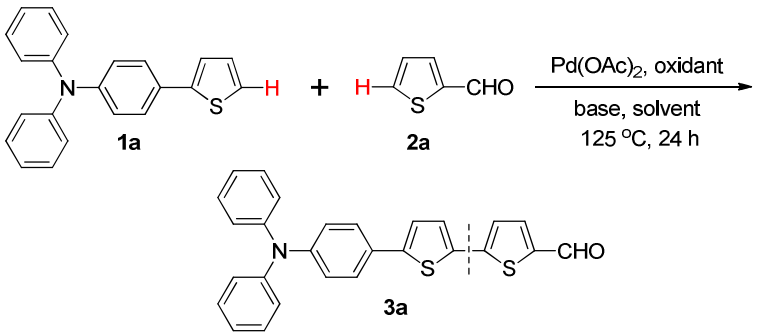
Scheme 1. The evolution of synthetic strategies for metal-free organic dye sensitizers: from C–[M]/C–X through C–/C–X to C–H/C–H.



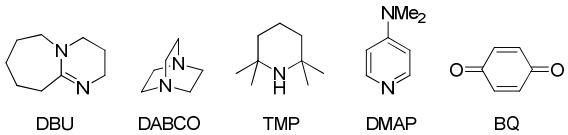
Results and Discussion

Since we aimed to obtain an unsymmetrical D–π–A type dye molecule **3a** through optimized cross-dehydrogenative couplings (CDC), triphenylamine-substituted thiophene **1a** and 2-thiophenecarboxaldehyde **2a** were directly coupled under various kinds of reaction conditions (results summarized in Table 1). Firstly, the C-H/C-H coupling reaction was conducted in nonpolar *o*-xylene using $Pd(OAc)_2$ as catalyst, $Cu(OAc)_2$ as oxidant, and K_2CO_3 as base. Desired product **3a** was isolated in only 8% yield (entry 1). Likewise, Cs_2CO_3 and K_3PO_4 gave poor yields of **3a** (7%, entries 2-3) and we found a significant amount of unreacted starting materials (**1a**, **2a**) along with some homocoupled adduct from **1a**. In the presence of strong base such as LiO*t*Bu or KO*t*Bu, product **3a** was not generated and both starting materials were recovered (entries 4-5). *N*-containing aliphatic bases were also less efficient for the CDC reactions (0~29%, entries 6-10), whereas the aromatic ones (prydine, DMAP) gave promising yields and we were pleased to isolate **3a** in 66%, 57% respectively (entries 11, 12). We then fixed on the use of pyridine as optimum base and proceeded to the screening of various oxidants. **3a** was obtained in 44% yield using $Cu(OAc)_2$ monohydrate as oxidant (entry 13), while other Cu(II)-based oxidants were shown to be ineffective (0~10%, entries 14-16). Subsequently, a series of Ag(I)-based oxidants were examined and desired molecule was produced in relatively higher yields (35~71%, entries 17-19) except for the case of AgOTf (no reaction, entry 20). Organic oxidants (BQ, DDQ, and $PhNO_2$) were much less efficient for CDC (no reaction or trace, entries 21-23). Under air, the CDC proceeded to yield **3a** in only 11% (entry 24). Finally, we decided to employ inexpensive $Cu(OAc)_2$ as optimum oxidant for solvent optimizations even though the costly Ag_2CO_3 gave a better result in entry 17. Interestingly, it was found that nonpolar xylene or toluene afforded **3a** in moderate yields (61~65%, entries 25-27), whereas the reaction performed in polar solvents including DMF, DMAc, DMSO, or NMP was inefficient (18~39%, entries 28-31).

Table 1. Facile synthesis of D–π–A type molecules via C–H/C–H coupling: optimization of reaction conditions.[a]



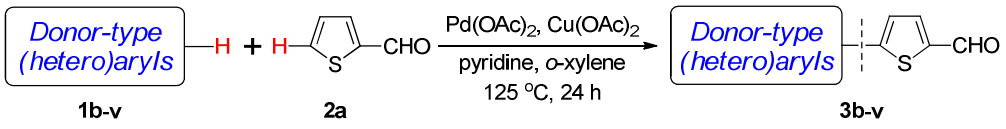
Entry	Oxidant	Base	Solvent	Yield[b]
1	$Cu(OAc)_2$	K_2CO_3	*o*-xylene	8
2	$Cu(OAc)_2$	Cs_2CO_3	*o*-xylene	7
3	$Cu(OAc)_2$	K_3PO_4	*o*-xylene	7
4	$Cu(OAc)_2$	LiO*t*Bu	*o*-xylene	0
5	$Cu(OAc)_2$	KO*t*Bu	*o*-xylene	0
6	$Cu(OAc)_2$	Et_3N	*o*-xylene	trace
7	$Cu(OAc)_2$	DBU	*o*-xylene	29
8	$Cu(OAc)_2$	DABCO	*o*-xylene	22
9	$Cu(OAc)_2$	piperidine	*o*-xylene	0
10	$Cu(OAc)_2$	TMP	*o*-xylene	16
11	$Cu(OAc)_2$	pyridine	*o*-xylene	66
12	$Cu(OAc)_2$	DMAP	*o*-xylene	57
13	$Cu(OAc)_2 \cdot H_2O$	pyridine	*o*-xylene	44
14	$Cu(OTf)_2$	pyridine	*o*-xylene	0
15	$CuCl_2$	pyridine	*o*-xylene	0
16	$Cu(acac)_2$	pyridine	*o*-xylene	10
17	Ag_2CO_3	pyridine	*o*-xylene	71
18	Ag_2O	pyridine	*o*-xylene	41
19	AgOAc	pyridine	*o*-xylene	35
20	AgOTf	pyridine	*o*-xylene	0
21	BQ	pyridine	*o*-xylene	trace
22	DDQ	pyridine	*o*-xylene	0
23	$PhNO_2$	pyridine	*o*-xylene	trace
24	air	pyridine	*o*-xylene	11
25	$Cu(OAc)_2$	pyridine	*m*-xylene	62
26	$Cu(OAc)_2$	pyridine	*p*-xylene	65
27	$Cu(OAc)_2$	pyridine	toluene	61
28	$Cu(OAc)_2$	pyridine	DMF	18
29	$Cu(OAc)_2$	pyridine	DMAc	32
30	$Cu(OAc)_2$	pyridine	DMSO	27
31	$Cu(OAc)_2$	pyridine	NMP	39



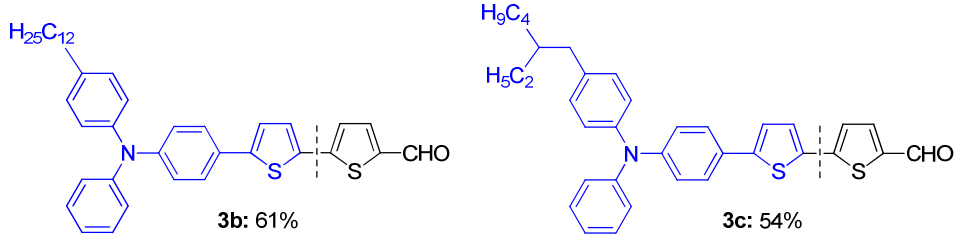
[a] Reaction conditions: **1a** (1.00 mmol), **2a** (1.50 mmol), $Pd(OAc)_2$ (0.05 mmol), oxidant (1.50 mmol), and base (1.50 mmol) in solvent (2 mL) at 125 °C for 24 h. [b] Isolated yields (%).

Next on, reaction scope with respect to the donor part of dye molecule was investigated using the optimum reaction conditions obtained in Table 1 (entries 11 and 17: either $Cu(OAc)_2$ or Ag_2CO_3 was employed as oxidant). Initially, as shown in Table 2, treatment of various triphenylamine (TPA)-substituted thiophene derivatives (**1b-1h**) with 2-thiophenecarboxaldehyde **2a** under optimum conditions led to the formation of desired D–π–A type products in moderate to good isolated yields (**3b-3h**, 52-70%). Functional groups including thioether, ester, aldehyde, and pyrrole-dione were compatible with current oxidant-containing reaction conditions. C-H/C-H coupling of **2a** with TPA-substituted *N*-methyl-pyrrole (**1i**) proceeded to yield **3i** in 51%. Further, we also examined a series of carbazole-based donors such as **1j-1l** or **1m-1r**, which gave the corresponding products (**3j-3l**) in 55-70% and (**3m-3r**) in 53-86% yields. Cyano- (**3g**) and ketone groups (**3r**) were well tolerated. When phenothiazine was used as donor, target dye molecules were obtained in moderate yields (**3s**, **3t**; 57%, 65%). Reaction of diphenylaminofluorene-substituted thiophene (**1u**) with **2a** produced **3u** in 61% yield. Interestingly, we found phenyltriazene[17]-substituted thiophene (**1v**) underwent dehydrogenative coupling smoothly and the desired product **3v** was isolated in 70% yield.

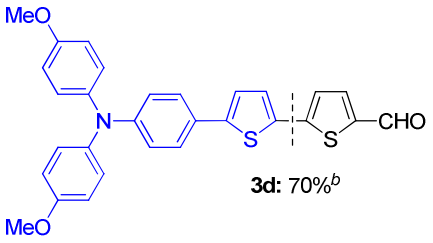
Table 2. Reaction scope with respect to the donor part:
C-H/C-H coupling of 2a with various donor-type (hetero)aryls 1b-v.[a]



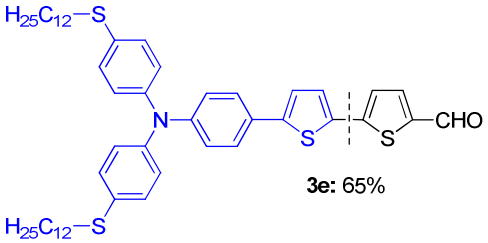
1b-v 2a 3b-v



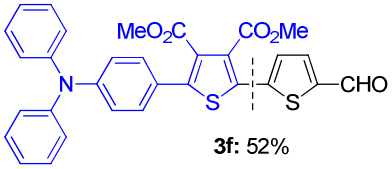
3b: 61% **3c:** 54%



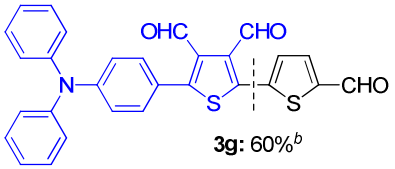
3d: 70%[b]



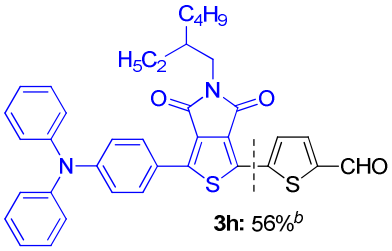
3e: 65%



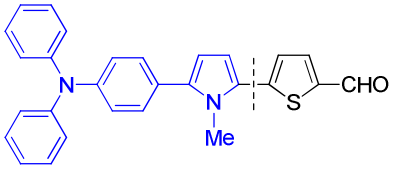
3f: 52%



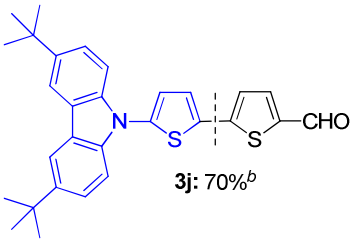
3g: 60%[b]



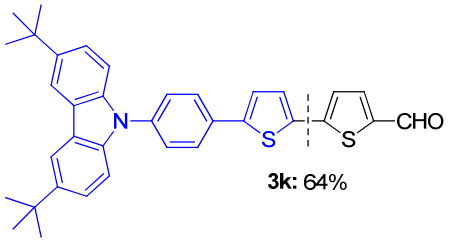
3h: 56%[b]



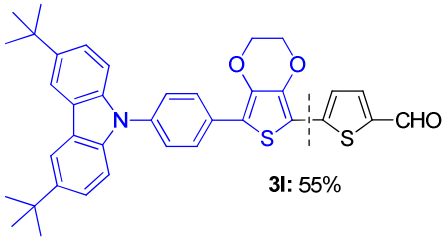
3i: 51%[b]



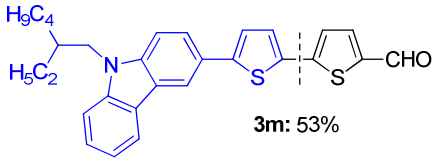
3j: 70%[b]



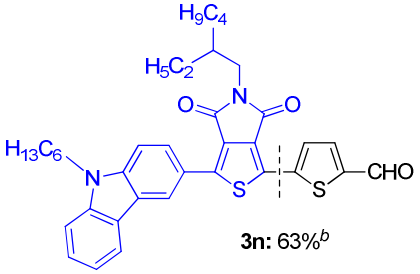
3k: 64%



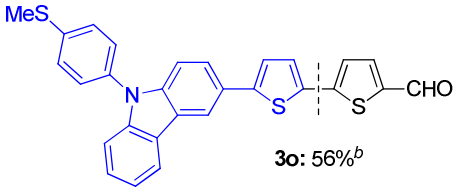
3l: 55%



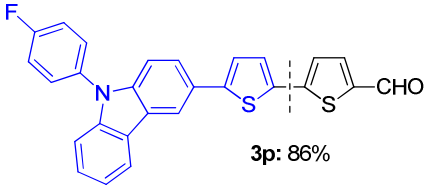
3m: 53%



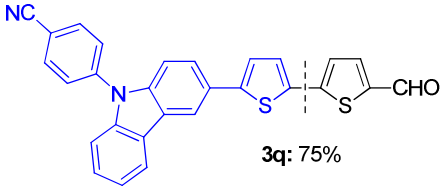
3n: 63%[b]



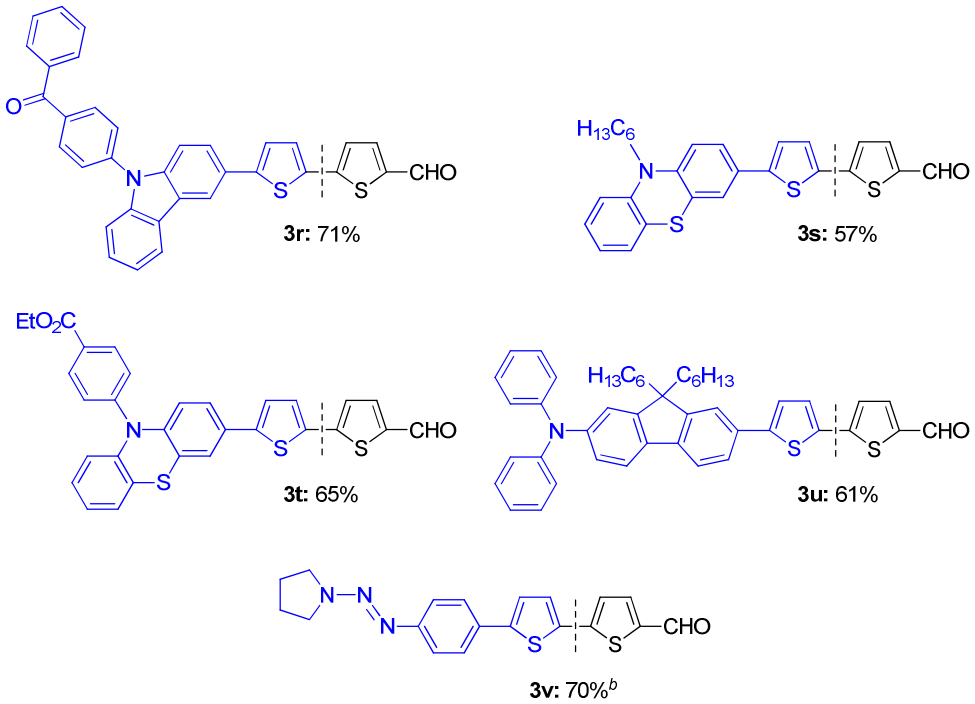
3o: 56%[b]



3p: 86%



3q: 75%

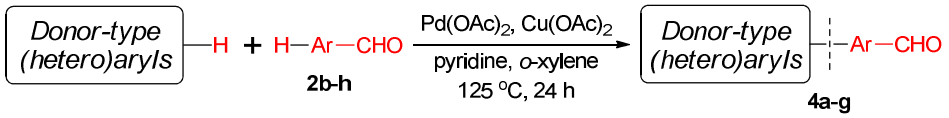


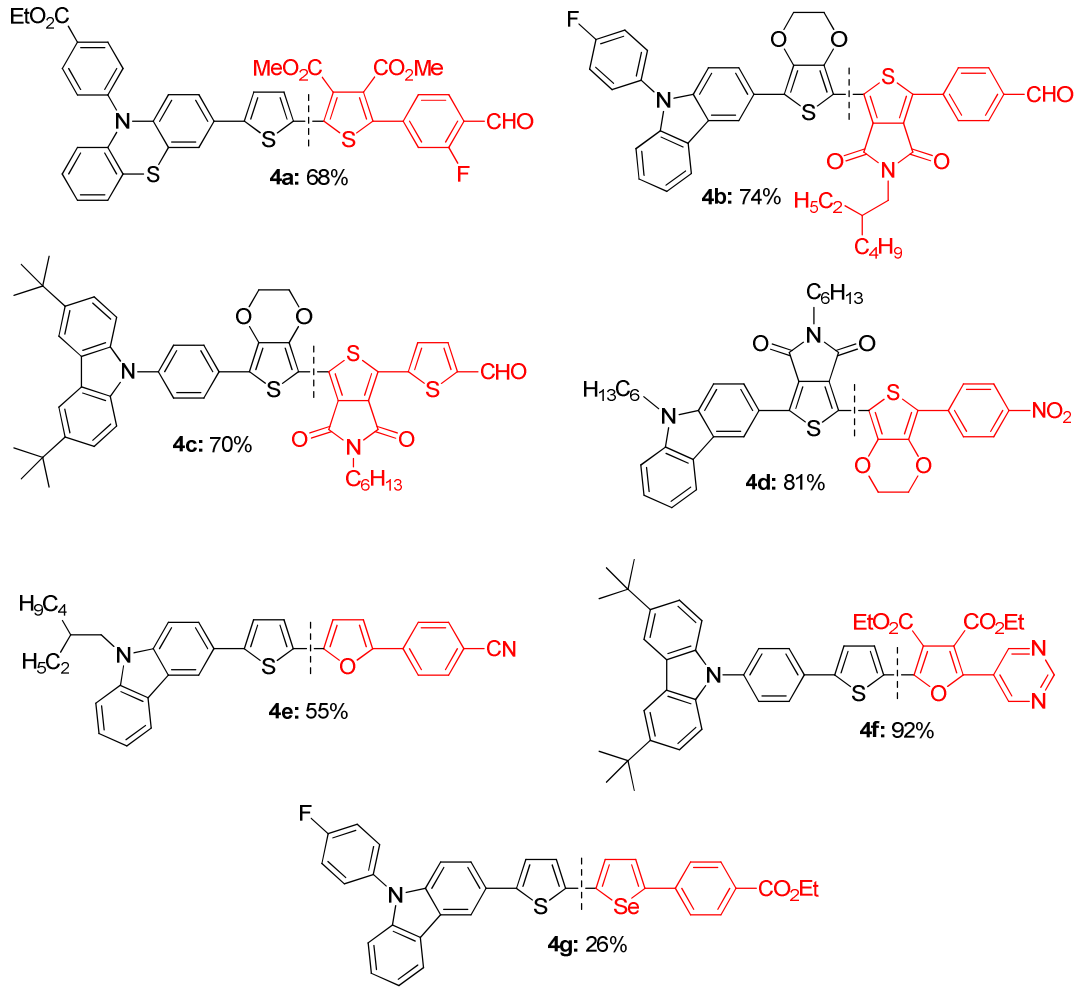
[a] Unless otherwise noted, the C-H/C-H coupling of **2a** (1.50 mmol) with donor-type (hetero)aryls **1b-v** (1.00 mmol) was conducted in the presence of $Pd(OAc)_2$ (5 mol%), $Cu(OAc)_2$ (1.50 mmol), and pyridine (1.50 mmol) in *o*-xylene (2 mL) at 125 °C for 24 h. [b] Reaction conducted at 100 °C for 12 h and the oxidant was replaced with Ag_2CO_3 (1.50 mmol).

In Table 3, reaction scope with respect to the acceptor part was also examined using various (hetero)aryl aldehydes (**2b-h**). Under optimum reaction conditions, we firstly tested electron-deficient thiophenes bearing diester group (**2b**) or a thieno[3,4-*c*]pyrrole-4,6-dione (TPD) moiety (**2c**, **2d**) as C-H coupling partners, affording the corresponding dye products in moderate isolated yields (**4a-4c**, 68-74%). In addition, when the substrate was changed to electron-rich ethylenedioxythiophene (EDOT), furan, or diester-substituted furan, the C-H/C-H coupling was shown to proceed smoothly and the terminal acceptor/anchoring groups (nitro, nitrile, pyrimidine) of desired D–π–A molecules were well tolerated (**4d-4f**, 55-92%). Finally, we found the dehydrogenative coupling between thiophene (donor part) and selenophene (acceptor part) was inefficient thus leading to a major recovery of both starting materials and a

poor yield of the desired cross-coupled product (**4g**, 26%).

Table 3. Reaction scope with respect to the acceptor part: C-H/C-H coupling of donor-type (hetero)aryls with various aldehydes 2b-h.[a]

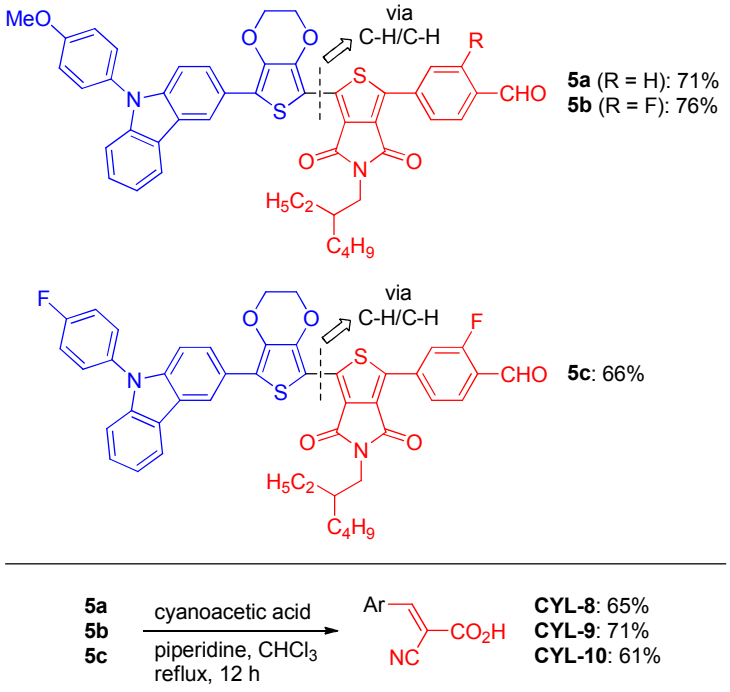




[a] Unless otherwise noted, the C-H/C-H coupling of donor-type (hetero)aryls (1.00 mmol) with aldehydes **2b-h** (1.50 mmol) was conducted in the presence of $Pd(OAc)_2$ (5 mol%), $Cu(OAc)_2$ (1.50 mmol), and pyridine (1.50 mmol) in *o*-xylene (2 mL) at 125 °C for 24 h.

In order to carry out photovoltaic applications in dye-sensitized solar cells (DSSCs), we synthesized three new organic sensitizers (**CYL-8~10**) based on the optimized C-H/C-H cross-coupling approach. As shown in Scheme 2, the cross-dehydrogenative coupling reactions were performed smoothly using different donor- (blue color) and acceptor-type molecules (red color), leading to the formation of the corresponding aldehydes as precursors of the dye sensitizers (**5a-5c**, 66-76%). Generation of the required anchoring groups by Knoevenagel condensations afforded target dye sensitizers **CYL-8~10** in 61-71% yields (see Experimental Section for the detailed reaction procedures).

Scheme 2. Facile synthesis of new organic sensitizers CYL-8~10 through direct C-H/C-H cross couplings.



Subsequently, the UV-Vis absorption and electrochemical characteristics of **CYL-8~10** were investigated and the obtained results were summarized in Table 4. Compared with **CYL-10**, in absorption spectra, **CYL-8** and **CYL-9** showed more red-shifted band and smaller optical band-gap, owing to their efficient intramolecular charge transfer (ICT) from anisole-substituted carbazole (donor) via thieno[3,4-*c*]pyrrole-4,6-dione to cyanoacetic acid (acceptor). For all sensitizers, their UV-Vis absorption on TiO_2 films exhibited blue shifts (compared to the solution state in THF), probably due

to the coordination/complexation of dye molecules to TiO_2. Among three sensitizers, we found that **CYL-9** had the highest molar extinction coefficient (ε = 31580 $M^{-1}cm^{-1}$), smallest optical band-gap (E_g^{opt} = 1.79 eV), and the lowest-lying HOMO/LUMO energy levels (E_{HOMO} = -5.92 eV/E_{LUMO} = -4.13 eV). We assumed that these results were resulted from the smooth ICT effect on **CYL-9** through appropriate donor-acceptor combination with an additional fluorine atom attached on the acceptor moiety.

Table 4. UV-Vis absorption and electrochemical properties of CYL-8~10.

Dyes	λ_{max} [nm][a]	ε [$M^{-1}cm^{-1}$][a]	λ_{max} on TiO_2 [nm][a]	E_g^{opt} [eV][b]	$E_{1/2}$ [V][c]	E_{HOMO}/E_{LUMO} [eV][d]
CYL-8	460	12642	439	1.89	1.13	-5.83/-3.93
CYL-9	462	31580	449	1.79	1.22	-5.92/-4.13
CYL-10	445	19499	423	1.92	1.16	-5.86/-3.94

[a] Measured in THF solutions (~10^{-5} M); ε: extinction coefficient. [b] The optical band gap, E_g^{opt}, was calculated by $1240/\lambda^{onset}$ (dyes on TiO_2 films). [c] 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 measurements are conducted in THF solutions (~10^{-4} M) containing $(n\text{-}C_4H_9)_4NPF_6$ as a supporting electrolyte under a scan rate of 100 mVs^{-1}. [d] The HOMO energy level, E_{HOMO}, was calculated by $-[(E_{1/2} + 0.197)_{vs.NHE} + 4.500]$ eV; $E_{LUMO} = E_{HOMO} + E_g^{opt}$.

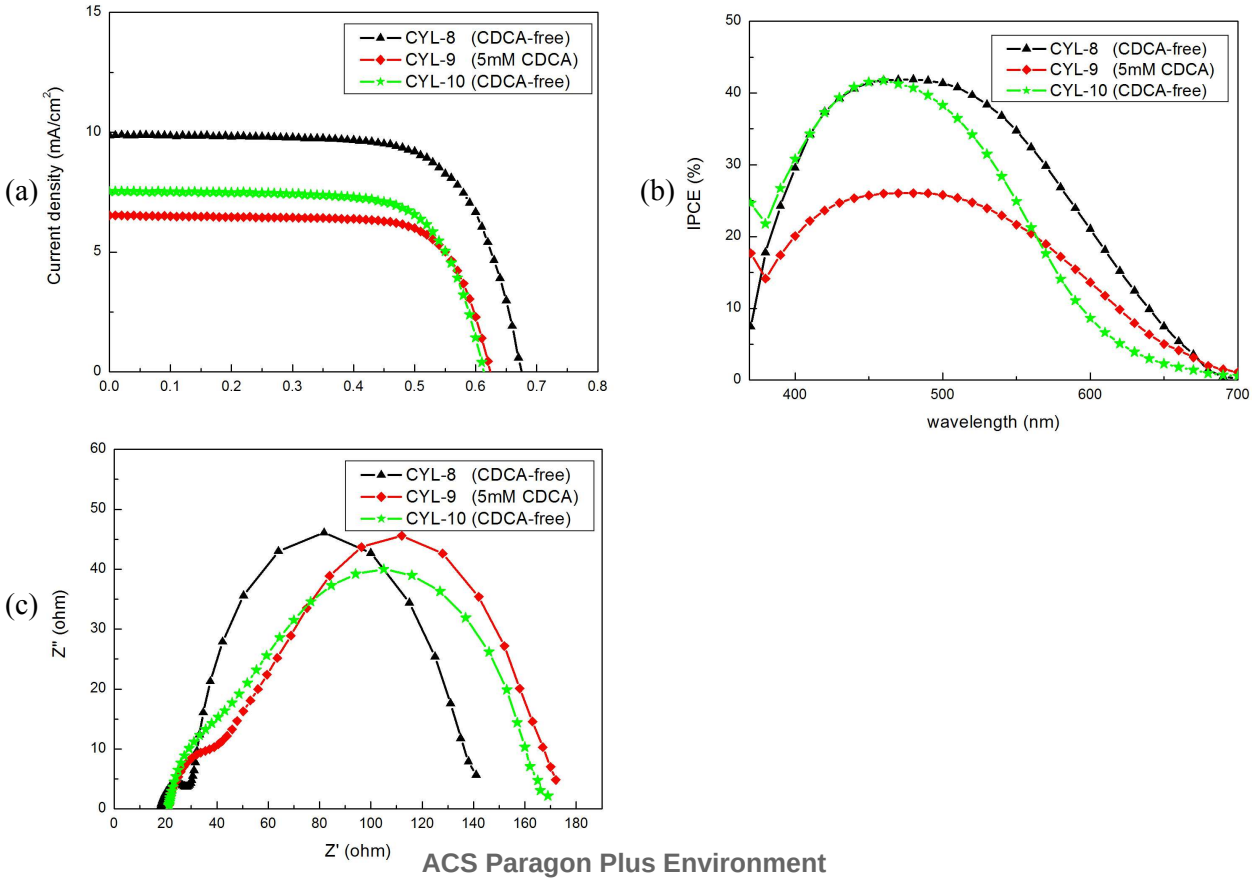
Dye-sensitized solar cells (DSSCs) were fabricated employing **CYL-8~10** as sensitizers and the photovoltaic parameters were collected in Table 5 and illustrated in Figure 1 (fabrication procedures and characterization of solar cells were detailed in Experimental Section). Although **CYL-9** appeared to generate efficient intramolecular charge transfer, as discussed in Table 4, it exhibited relatively lower short-circuit photocurrent density (J_{sc} = 6.52 mA/cm^2), thus leading to an inferior power conversion efficiency (PCE) of 3.00%. We speculated that this was owing to the resistant charge transport from the LUMO of **CYL-9** to TiO_2 (**CYL-9** LUMO = –4.13 eV, lower than the energy level of TiO_2 = –4.00 eV). In addition, we found **CYL-8** and **CYL-10** displayed similar incident photon-to-current conversion efficiency (IPCE, Figure 1b) in the absorption range of 400–500 nm. Between 500–700 nm, **CYL-8** showed stronger IPCE absorption, leading to a higher J_{sc}

Table 5. Photovoltaic performances of DSSCs fabricated using CYL-8, CYL-9, and CYL-10.[a, b]

DSSCs	V_{oc} [V]	J_{sc} [mA/cm^2]	*FF* [%]	*PCE* [%]
CYL-8	0.68	9.81	72.7	4.85
CYL-9	0.63	6.52	73.0	3.00
CYL-10	0.62	7.54	72.5	3.39
Z907[c]	0.69	14.75	69.5	7.07

[a] Irradiation light source: AM 1.5G solar simulator (100 mW/cm^2); Photo-electrode (working electrode): TiO_2 film was composed of 16 μm thick mesoporous anatase-TiO_2 nanoparticles with a diameter of 20 nm and has an active area of 0.160 cm^2; Electrolyte solution: a mixture of 0.6 M 1-butyl-3-methylimidazolium iodide ([bmim][I]), 0.1 M LiI, 0.05 M I_2, 0.1 M guanidinium thiocyanate (GuNCS) and 0.5 M 4-*t*-butylpyridine (TBP) in acetonitrile. [b] Chenodeoxycholic acid (CDCA) was added as co-adsorbent (5 mM for **CYL-9**; no CDCA was added for **CYL-8** & **CYL-10**). [c] cis-Bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-di-nonyl-2'-bipyridyl)ruthenium(II).

Figure 1. **Photovoltaic performances of CYL-8, CYL-9, and CYL-10: (a) photocurrent density vs. photovoltage; (b) Incident photon-to-current conversion efficiency (IPCE); (c) electrochemical impedance spectroscopy (EIS).**



of 9.81 mA/cm^2. It was noted that **CYL-8~10** possessed similar open-circuit voltage (V_{oc}) because they had been shown to exhibit similar charge transfer impedance under dark conditions (Nyquist plots, Figure 1c). Besides, addition of the chenodeoxycholic acid (CDCA) as co-adsorbent may influence the the amount of dyes adsorbed on TiO_2. In the case of **CYL-9**, the optimum PCE was observed when 5 mM of CDCA was added. Presumably the dye aggregation of **CYL-9** was reduced/broken by CDCA. On the contrary, in the cases of **CYL-8** and **CYL-10**, we found the best PCE could be only obtained under CDCA-free condition because CDCA may have adsorption competition with the dyes on TiO_2, thus lowing the dye adsorption amount. Finally, among three new sensitizers, **CYL-8** demonstrated a V_{oc} of 0.68 V, a J_{sc} of 9.81 mA/cm^2, and a fill factor (*FF*) of 72.7%, corresponding to the highest power conversion efficiency of 4.85 %.

Conclusion

We have demonstrated a highly atom-economical alternative route to various D–π–A type organic dyes via direct C-H/C-H cross-couplings. Under optimized synthetic conditions, a wide range of substrate scope was successfully explored along with excellent functional groups compatibility. For photovoltaic applications, we efficiently synthesized three new organic sensitizers (**CYL-8~10**) that were fabricated as dye-sensitized solar cells (DSSCs), showing the power conversion efficiency (PCE) up to 4.85%. Currently, development of atom/step-economical green catalysis reactions for organic photovoltaic materials is underway 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 $Pd(OAc)_2$, oxidants, and bases are commercially available. Anhydrous or reagent-grade solvents such as *o*-, *m*-, *p*-xylene, toluene, *N, N*-dimethylformamide (DMF), dimethyl sulfoxide

(DMSO), and *N*-methyl-2-pyrrolidone (NMP) 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, 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.[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-8**, **CYL-9**, or **CYL-10** 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 °C for 15 mins and at 500 °C 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 or $CHCl_3$) at 40 °C 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-8**, **CYL-9**, or **CYL-10** 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 the starting materials synthesis: C-H/C-Br coupling reactions

To a solution of $Pd(OAc)_2$ (0.05 mmol), ligand (0.10 mmol), PivOH (0.30 mmol), and K_2CO_3 (1.50 mmol) in DMF or toluene (3 mL) in a flame-dried Schlenk tube (20 mL) were added the corresponding (hetero)arene (2.00-5.00 mmol) and aryl bromide (1.00 mmol) under N_2. The reaction mixture was then heated at 110 °C 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 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 yielded the desired starting materials **1e-1w**.

4-(Dodecylthio)-*N*-(4-(dodecylthio)phenyl)-*N*-(4-(thiophen-2-yl)phenyl)aniline (1e) was prepared from 4-bromo-*N*,*N*-bis(4-(dodecylthio)phenyl)aniline[20] (725 mg, 1.00 mmol), thiophene (420 mg, 5.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), PPh_3 (26 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol), K_2CO_3 (207 mg, 1.50 mmol), and DMF (3 mL) according to the general procedure **A** and yielding after column chromatography (dichloromethane : hexanes = 20 : 80) the pure product **1e** (328 mg, 45 %). Colorless viscous liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.52 (d, J = 8.4 Hz, 2 H), 7.19-7.42 (comp, 6 H), 6.87-7.18 (comp, 7 H), 2.93 (t, J = 7.4 Hz, 4 H), 1.59-1.81 (comp, 4 H), 1.18-1.55 (comp, 36 H), 0.82-0.99 (comp, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 146.7, 145.5, 144.1, 130.8, 130.7, 129.0, 128.0, 126.8, 124.7, 124.2, 123.9, 122.4, 34.6, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 28.9, 22.8, 14.2; MS (FAB): 728 ($[M+H]^+$, 86 %), 527 (39 %), 55 (100 %); HRMS (FAB/Double Focusing) m/z: $[M+H]^+$ Calcd. for $C_{46}H_{65}NS_3$ 727.4279; found 727.4275.

2-(4-(Diphenylamino)phenyl)thiophene-3,4-dicarbaldehyde (1g) was prepared from 4-bromotriphenylamine (324 mg, 1.00 mmol), thiophene-3,4-dicarbaldehyde (280 mg, 2.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), PCy_3 (28 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol), K_2CO_3 (207 mg, 1.50 mmol), and toluene (3 mL) according to the general procedure **A** and

yielding after column chromatography (ethyl acetate : hexanes = 10 : 90) the pure product **1g** (211 mg, 55 %). Yellow solid; m.p.: 176.2.-176.6 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 10.49 (s, 1 H), 10.04 (s, 1 H), 8.09 (s, 1 H), 7.28-7.39 (comp, 5 H), 6.97-7.21 (comp, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 187.2, 187.0, 159.6, 149.8, 146.8, 141.2, 133.6, 131.4, 131.0, 129.7, 125.5, 124.3, 123.1, 121.5; MS (EI, 70 eV): 383 (M^+, 8 %), 167 (20 %), 77 (100 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{24}H_{17}NO_2S$ 383.0980; found 383.0974.

5-(2-Ethylhexyl)-1-(9-hexyl-9*H*-carbazol-3-yl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (1n) was prepared from 3-bromo-9-hexyl-9*H*-carbazole (330 mg, 1.00 mmol), 5-(2-ethylhexyl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (398 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), PCy_3 (28 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol), K_2CO_3 (207 mg, 1.50 mmol), and toluene (3 mL) according to the general procedure **A** and yielding after column chromatography (dichloromethane : hexanes = 50 : 50) the pure product **1n** (308 mg, 60 %). Red solid; m.p.: 84.5-85.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.80 (s, 1 H), 8.19 (app t, 2 H), 7.43-7.68 (comp, 2 H), 7.18-7.43 (comp, 3 H), 4.18 (t, J = 7.0 Hz, 2 H), 3.55 (d, J = 6.9 Hz, 2 H), 1.70-1.98 (comp, 3 H), 1.18-1.57 (comp, 14 H), 0.74-1.14 (comp, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 163.7, 163.0, 149.8, 141.3, 141.0, 137.9, 126.8, 126.3, 125.9, 123.1, 122.8, 121.8, 121.7, 120.8, 120.3, 119.6, 109.1, 108.9, 43.2, 42.4, 38.2, 31.6, 30.6, 28.9, 28.6, 26.9, 23.9, 23.1, 22.6, 14.2, 14.0, 10.5; MS (FAB): 514 (M^+, 100 %), 443 (48 %), 415 (32 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{32}H_{38}N_2O_2S$ 514.2654; found 514.2648.

9-(4-(Methylthio)phenyl)-3-(thiophen-2-yl)-9*H*-carbazole (1o) was prepared from 3-bromo-9-(4-(methylthio)phenyl)-9*H*-carbazole (368 mg, 1.00 mmol), thiophene (420 mg, 5.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), P(adamantyl)$_2$(*n*-Bu) (36 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol), K_2CO_3 (207 mg, 1.50 mmol), and DMF (3 mL) according to the general procedure **A** and yielding after column chromatography (ethyl acetate : hexanes = 5 : 95) the pure product **1o** (186 mg, 50 %). Transparent viscous liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.46 (app s, 1

H), 8.25 (d, J = 7.2 Hz, 1 H), 7.72 (d, J = 8.7 Hz, 1 H), 7.28-7.52 (comp, 10 H), 7.10-7.22 (m, 1 H), 2.60 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 145.6, 141.4, 140.4, 138.2, 134.4, 128.2, 127.7, 127.5, 126.9, 126.5, 124.7, 124.0, 123.9, 123.4, 122.4, 120.7, 120.4, 117.9, 110.2, 110.0, 15.9; MS (EI, 70 eV): 371 (M^+, 2 %), 177 (6 %), 133 (16 %), 63 (100 %); HRMS (EI/Double Focusing) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}NS_2$ 371.0802; found 371.0810.

9-(4-Fluorophenyl)-3-(thiophen-2-yl)-9*H*-carbazole (1p) was prepared from 3-bromo-9-(4-fluorophenyl)-9*H*-carbazole (340 mg, 1.00 mmol), thiophene (420 mg, 5.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), PPh_3 (26 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol), K_2CO_3 (207 mg, 1.50 mmol), and DMF (3 mL) according to the general procedure **A** and yielding after column chromatography (hexanes) the pure product **1p** (154 mg, 45 %). Pale green liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.52 (app s, 1 H), 8.31 (d, J = 7.8 Hz, 1 H), 7.78 (d, J = 8.4 Hz, 1 H), 7.10-7.70 (comp, 11 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 161.8 (d, $^1J_{C\text{-}F}$ = 245.9 Hz), 145.6, 141.6, 140.6, 133.5 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 129.0 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 128.3, 127.1, 126.6, 124.8, 124.1, 124.0, 123.4, 122.5, 120.8, 120.5, 118.0, 117.0 (d, $^2J_{C\text{-}F}$ = 22.6 Hz), 110.0, 109.9; MS (EI, 70 eV): 343 (M^+, 100 %), 156 (18 %), 141 (20 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{22}H_{14}FNS$ 343.0831; found 343.0827.

4-(3-(Thiophen-2-yl)-9*H*-carbazol-9-yl)benzonitrile (1q) was prepared from 4-(3-bromo-9*H*-carbazol-9-yl)benzonitrile (347 mg, 1.00 mmol), thiophene (420 mg, 5.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), PPh_3 (26 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol), K_2CO_3 (207 mg, 1.50 mmol), and DMF (3 mL) according to the general procedure **A** and yielding after column chromatography (ethyl acetate : hexanes = 5 : 95) the pure product **1q** (179 mg, 51 %). White solid; m.p.: 193.9-194.8 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.34 (d, J = 1.5 Hz, 1 H), 8.17 (d, J = 7.5 Hz, 1 H), 7.87-7.98 (comp, 2 H), 7.58-7.78 (comp, 3 H), 7.26-7.55 (comp, 6 H), 7.15 (dd, J = 5.1, 3.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 145.0, 141.7, 140.3, 139.2, 134.0, 128.2, 127.8, 126.9, 126.8, 124.8, 124.5, 124.3, 123.9, 122.6, 121.3, 120.8, 118.5, 117.9,

110.5, 110.0, 109.8; MS (EI, 70 eV): 350 (M^+, 41 %), 248 (17 %), 102 (100 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{23}H_{14}N_2S$ 350.0878; found 350.0884.

Phenyl(4-(3-(thiophen-2-yl)-9*H*-carbazol-9-yl)phenyl)methanone (1r) was prepared from (4-(3-bromo-9*H*-carbazol-9-yl)phenyl)(phenyl)methanone (426 mg, 1.00 mmol), thiophene (420 mg, 5.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), PPh_3 (26 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol), K_2CO_3 (207 mg, 1.50 mmol), and DMF (3 mL) according to the general procedure **A** and yielding after column chromatography (ethyl acetate : hexanes = 5 : 95) the pure product **1r** (258 mg, 60 %). Pale green solid; m.p.: 180.0-181.2 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.35-8.48 (m, 1 H), 8.20 (d, J = 7.2 Hz, 1 H), 8.10 (d, J = 8.4 Hz, 2 H), 8.04-8.87 (comp, 2 H), 7.66-7.78 (comp, 4 H), 7.46-7.65 (comp, 5 H), 7.27-7.44 (comp, 3 H), 7.10-7.22 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 195.6, 145.3, 141.4, 140.7, 139.7, 137.4, 136.0, 132.8, 132.0, 130.2, 128.6, 128.2, 127.5, 126.7, 126.1, 124.8, 124.1, 123.8, 122.5, 120.9, 120.7, 117.9, 110.2, 110.1; MS (EI, 70 eV): 430 ($[M+1]^+$, 100 %), 348 (32 %), 84 (75 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{29}H_{19}NOS$ 429.1187; found: 429.1181.

Ethyl 4-(3-(thiophen-2-yl)-10*H*-phenothiazin-10-yl)benzoate (1t) was prepared from ethyl 4-(3-bromo-10*H*-phenothiazin-10-yl)benzoate (426 mg, 1.00 mmol), thiophene (420 mg, 5.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), PCy_3 (28 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol), K_2CO_3 (207 mg, 1.50 mmol), and DMF (3 mL) according to the general procedure **A** and yielding after column chromatography (ethyl acetate : hexanes = 2 : 98) the pure product **1t** (176 mg, 41 %). Transparent viscous liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.20 (d, J = 7.5 Hz, 2 H), 7.47 (s, 1 H), 7.35 (d, J = 7.5 Hz, 2 H), 6.92-7.32 (comp, 7 H), 6.38-6.90 (comp, 2 H), 4.46 (q, J = 7.0 Hz, 2 H), 1.47 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 165.9, 146.7, 143.0, 142.6, 142.0, 131.9, 130.6, 128.2, 127.8, 127.6, 127.2, 126.3, 125.2, 124.8, 124.7, 124.6, 124.3, 123.0, 120.3, 120.2, 61.1, 14.6; MS (EI, 70 eV): 429 (M^+, 12 %), 239 (15 %), 84 (96 %), 57 (100 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{25}H_{19}NO_2S_2$ 429.0857; found 429.0861.

(*E*)-1-((4-(Thiophen-2-yl)phenyl)diazenyl)pyrrolidine (1v) was prepared from (*E*)-1-((4-bromophenyl)diazenyl)pyrrolidine[21] (254 mg, 1.00 mmol), thiophene (420 mg, 5.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), PPh_3 (26 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol), K_2CO_3 (207 mg, 1.50 mmol), and DMF (3 mL) according to the general procedure **A** and yielding after column chromatography (ethyl acetate : hexanes = 5 : 95) the pure product **1v** (162 mg, 63 %). Transparent viscous liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.69 (d, J = 8.7 Hz, 2 H), 7.56 (d, J = 8.7 Hz, 2 H), 7.36 (dd, J = 3.6, 0.9 Hz, 1 H), 7.30 (dd, J = 5.1, 0.9 Hz, 1 H), 7.12 (dd, J = 5.1, 3.6 Hz, 1 H), 3.84 (app s, 4 H), 2.01 (t, J = 6.6 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 150.9, 144.7, 131.2, 128.2, 126.5, 124.3, 122.5, 120.9, 23.9; MS (EI, 70 eV): 257 (M^+, 17 %), 159 (48 %), 84 (100 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{14}H_{15}N_3S$ 257.0987; found 257.0981.

3-(2,3-Dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-9-(4-fluorophenyl)-9*H*-carbazole (1w) was prepared from 9-(4-fluorophenyl)-9*H*-carbazole (261 mg, 1.00 mmol), EDOT (710 mg, 5.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), PPh_3 (26 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol), K_2CO_3 (207 mg, 1.50 mmol), and DMF (3 mL) according to the general procedure **A** and yielding after column chromatography (ethyl acetate : hexanes = 2 : 98) the pure product **1w** (173 mg, 43 %). Light green viscous liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.72 (app s, 1 H), 8.36 (d, J = 8.0 Hz, 1 H), 7.95 (d, J = 8.5 Hz, 1 H), 7.51-7.66 (comp, 3 H), 7.42-7.51 (comp, 3 H), 7.33-7.41 (comp, 2 H), 6.45 (s, 1 H), 4.35-4.41 (comp, 2 H), 4.27-4.33 (comp, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 161.7 (d, $^1J_{C\text{-}F}$ = 246.3 Hz), 142.6, 141.5, 140.0, 137.5, 133.7, 129.0 (d, $^3J_{C\text{-}F}$ = 7.5 Hz), 126.5, 125.8, 125.1, 123.8, 123.6, 120.8, 120.4, 118.6, 118.3, 117.0 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 109.9, 96.8, 64.9, 64.6; MS (EI, 70 eV): 401 (M^+, 55 %), 304 (40 %), 191 (38 %), 84 (100 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{24}H_{16}FNO_2S$ 401.0886; found 401.0885.

General procedure B for Table 1: Optimization of the C-H/C-H coupling reaction between *N*,

N-diphenyl-4-(thiophen-2-yl)aniline (1a) and thiophene-2-carbaldehyde (2a)

To a solution of $Pd(OAc)_2$ (0.05 mmol), oxidant (1.50 mmol), and base (1.50 mmol) in solvent (2 mL) in a flame-dried Schlenk tube were added *N*, *N*-diphenyl-4-(thiophen-2-yl)aniline (**1a**) (1.00 mmol) and thiophene-2-carbaldehyde (**2a**) (1.50 mmol) under N_2. The reaction mixture was then heated at 130 °C 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 × 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'-(4-(Diphenylamino)phenyl)-[2,2'-bithiophene]-5-carbaldehyde[22] **(3a)** was prepared from **1a**[23a] (327 mg, 1.00 mmol), **2a** (168 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **B** and yielding after column chromatography (dichloromethane : hexanes = 40 : 60) the pure product **3a** (289 mg, 66 %). Orange solid; m.p.: 150.0-150.4 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.86 (s, 1 H), 7.67 (d, J = 3.9 Hz, 1 H), 7.43-7.55 (comp, 2 H), 7.27-7.40 (comp, 5 H), 7.25 (d, J = 3.9 Hz, 1 H), 7.00-7.23 (comp, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.4, 148.1, 147.4, 147.3, 146.3, 141.3, 137.5, 134.1, 129.5, 127.3, 127.1, 126.7, 124.9, 123.8, 123.5, 123.2, 123.1.

General procedure C for Table 2 & Table 3: Substrate scope of the heteroarenes

To a solution of $Pd(OAc)_2$ (0.05 mmol), $Cu(OAc)_2$ or Ag_2CO_3 (1.50 mmol), and pyridine (1.50 mmol) in *o*-xylene (2 mL) in a flame-dried Schlenk tube were added the heteroarene (**1b-w**) (1.00 mmol) and the aldehyde-containing heteroarene (**2a-h**) (1.50 mmol) under N_2. The reaction mixture was then heated at 100~130 °C under N_2 for 12~24 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-v** and **4a-g**.

5'-(4-((4-Dodecylphenyl)(phenyl)amino)phenyl)-[2,2'-bithiophene]-5-carbaldehyde (3b) was prepared from **1b**[23a] (496 mg, 1.00 mmol), **2a** (168 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (dichloromethane : hexanes = 60 : 40) the pure product **3b** (369 mg, 61 %). Golden yellow solid; m.p.: 104.3-104.9 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.85 (s, 1 H), 7.65 (d, J = 3.9 Hz, 1 H), 7.44 (d, J = 8.7 Hz, 2 H), 7.24-7.35 (comp, 3 H), 7.22 (d, J = 3.9 Hz, 1 H), 6.98-7.19 (comp, 10 H), 2.60 (t, J = 7.8 Hz, 2 H), 1.57-1.72 (comp, 2 H), 1.21-1.48 (comp, 18 H), 0.91 (t, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.3, 148.3, 147.5, 147.4, 146.4, 144.7, 141.2, 138.7, 137.5, 133.9, 129.5, 129.4, 127.3, 126.64, 126.57, 125.3, 124.5, 123.7, 123.2, 123.1, 122.6, 35.5, 32.0, 31.6, 29.8 (two peaks), 29.7 (two peaks), 29.6, 29.52, 29.48, 22.8, 14.3; MS (EI, 70 eV): 606 ($[M+H]^+$, 3 %), 472 (100 %), 457 (73 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{39}H_{43}NOS_2$ 605.2786; found 605.2776.

5'-(4-((4-(2-Ethylhexyl)phenyl)(phenyl)amino)phenyl)-[2,2'-bithiophene]-5-carbaldehyde (3c) was prepared from **1c**[23a] (440 mg, 1.00 mmol), **2a** (168 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (dichloromethane : hexanes = 60 : 40) the pure product **3c** (296 mg, 54 %). Orange solid; m.p.: 88.3-89.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.87 (s, 1 H), 7.67 (d, J = 3.9 Hz, 1 H), 7.43-7.56 (comp, 2 H), 7.26-7.36 (comp, 3 H), 7.24 (d, J = 4.2 Hz, 1 H), 7.00-7.22 (comp, 10 H), 2.54 (d, J = 6.9 Hz, 2 H), 1.52-1.65 (m, 1 H), 1.23-1.44 (comp, 8 H), 0.93 (app t, J = 7.2 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.4, 148.3, 147.5, 147.4, 146.4, 144.7, 141.2, 137.6, 137.5, 133.9, 130.2, 129.4, 127.3, 126.63, 126.57, 125.1, 124.5, 123.7, 123.2, 123.1, 122.6, 41.1, 39.6, 32.4, 28.9, 25.6, 23.1, 14.2, 10.9; MS (EI, 70 eV): 550 ($[M+H]^+$, 75 %), 451 (51 %), 84 (100

%); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{35}H_{35}NOS_2$ 549.2160; found 549.2166.

5'-(4-(Bis(4-methoxyphenyl)amino)phenyl)-[2,2'-bithiophene]-5-carbaldehyde (3d) was prepared from 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(thiophen-2-yl)phenyl)aniline[24] (**1d**) (387 mg, 1.00 mmol), **2a** (336 mg, 3.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), Ag_2CO_3 (413 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** (100 ^oC, 12 h for this example) and yielding after column chromatography (using the eluent with a gradient polarity: from dichloromethane : hexanes = 40 : 60 to dichloromethane : hexanes = 80 : 20) the pure product **3d** (348 mg, 70 %). Red solid; m.p.: 205.3-205.8 ^oC. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.83 (s, 1 H), 7.64 (d, J = 4.2 Hz, 1 H), 7.39 (d, J = 8.7 Hz, 2 H), 7.29 (d, J = 3.9 Hz, 1 H), 7.21 (d, J = 4.2 Hz, 1 H), 7.02-7.15 (comp, 5 H), 6.79-6.95 (comp, 6 H), 3.81 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.4, 156.3, 149.0, 147.6, 146.7, 141.1, 140.3, 137.6, 133.5, 127.3, 127.0, 126.5, 125.1, 123.6, 122.7, 120.0, 114.8, 55.5; MS (EI, 70 eV): 498 ($[M+H]^+$, 52 %), 395 (38 %), 133 (42 %), 71 (100 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{29}H_{23}NO_3S_2$ 497.1119; found 497.1115.

5'-(4-(Bis(4-(dodecylthio)phenyl)amino)phenyl)-[2,2'-bithiophene]-5-carbaldehyde (3e) was prepared from 4-(dodecylthio)-*N*-(4-(dodecylthio)phenyl)-*N*-(4-(thiophen-2-yl)phenyl)aniline (**1e**) (727 mg, 1.00 mmol), **2a** (168 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (dichloromethane : hexanes = 60 : 40) the pure product **3e** (544 mg, 65 %). Orange solid; m.p.: 83.8-85.0 ^oC. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.87 (s, 1 H), 7.69 (d, J = 4.2 Hz, 1 H), 7.48 (d, J = 8.7 Hz, 2 H), 7.33 (d, J = 3.9 Hz, 1 H), 7.10-7.30 (comp, 6 H), 6.79-7.10 (comp, 6 H), 2.91 (t, J = 7.4 Hz, 4 H), 1.56-1.75 (comp, 4 H), 1.10-1.49 (comp, 36 H), 0.90 (t, J = 6.5 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.4, 147.5, 147.4, 146.1, 145.1, 141.3, 137.5, 134.2, 131.2, 130.7, 127.4, 127.3, 126.7, 125.0, 123.8, 123.3, 34.4, 32.0, 29.7, 29.68, 29.64, 29.57, 29.4, 29.3, 29.2, 28.9, 22.7, 14.2; MS (FAB): 838

([M+H]$^+$, 26 %), 538 (7 %), 73 (100 %); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{51}H_{67}NOS_4$ 837.4105; found 837.4096.

Dimethyl 5-(4-(diphenylamino)phenyl)-5'-formyl-[2,2'-bithiophene]-3,4-dicarboxylate (3f) was prepared from dimethyl 2-(4-(diphenylamino)phenyl)thiophene-3,4-dicarboxylate[23a] (**1f**) (443 mg, 1.00 mmol), **2a** (168 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (using the eluent with a gradient polarity: from dichloromethane : hexanes = 20 : 80 to dichloromethane : hexanes = 40 : 60) the pure product **3f** (288 mg, 52 %). Orange solid; m.p.: 164.5-165.4 ^oC. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.91 (s, 1 H), 7.72 (d, J = 3.9 Hz, 1 H), 7.42 (d, J = 3.9 Hz, 1 H), 7.26-7.39 (comp, 6 H), 7.00-7.22 (comp, 8 H), 3.90 (s, 3 H), 3.82 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.7, 164.2 (two peaks), 149.1, 148.2, 147.0, 144.3, 142.5, 136.3, 135.1, 131.3, 129.8, 129.5, 129.0, 128.8, 125.4 (two peaks), 124.0, 121.5, 52.8, 52.5; MS (EI, 70 eV): 553 (M^+, 1 %), 472 (100 %), 457 (75 %), 189 (47 %), 57 (54 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{31}H_{23}NO_5S_2$ 553.1018; found 553.1014.

5-(4-(Diphenylamino)phenyl)-[2,2'-bithiophene]-3,4,5'-tricarbaldehyde (3g) was prepared from 2-(4-(diphenylamino)phenyl)thiophene-3,4-dicarbaldehyde (**1g**) (383 mg, 1.00 mmol), **2a** (168 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), Ag_2CO_3 (413 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** (100 ^oC, 12 h for this example) and yielding after column chromatography (ethyl acetate : dichloromethane : hexanes = 1 : 80 : 19) the pure product **3g** (296 mg, 60 %). Red liquid. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 10.39 (s, 1 H), 10.04 (s, 1H), 9.92 (s, 1 H), 7.75 (d, J = 3.9 Hz, 1 H), 7.67 (d, J = 3.9 Hz, 1 H), 7.20-7.40 (comp, 6 H), 6.85-7.20 (comp, 8 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 187.4, 186.7, 182.9, 157.2, 150.2, 146.6, 145.2, 141.3, 139.6, 136.15, 136.10, 135.6, 131.0 (two peaks), 129.7, 125.7, 124.5, 121.8, 121.2; MS (EI, 70 eV): 493 (M^+, 5 %), 191 (14 %), 84 (100

%); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{29}H_{19}NO_3S_2$ 493.0806; found 493.0813.

5-(3-(4-(Diphenylamino)phenyl)-5-(2-ethylhexyl)-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)thiophene-2-carbaldehyde[15] **(3h)** was prepared from 1-(4-(diphenylamino)phenyl)-5-(2-ethylhexyl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione[15] (**1h**) (508 mg, 1.00 mmol), **2a** (336 mg, 3.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), Ag_2CO_3 (413 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** (100 ^oC, 12 h for this example) and yielding after column chromatography (using the eluent with a gradient polarity: from dichloromethane : hexanes = 40 : 60 to dichloromethane : hexanes = 60 : 40) the pure product **3h** (363 mg, 56 %). Red solid; m.p.: 153.4-154.5 ^oC. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.89 (s, 1 H), 8.17 (d, J = 4.2 Hz, 1 H), 7.96 (d, J = 8.9 Hz, 2 H), 7.71 (d, J = 4.2 Hz, 1 H), 7.27-7.47 (comp, 4 H), 7.08-7.25 (comp, 6 H), 7.03 (d, J = 8.9 Hz, 2 H), 3.54 (d, J = 7.2 Hz, 2 H), 1.74-1.98 (m, 1 H), 1.26-1.47 (comp, 8 H), 0.81-1.04 (comp, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.5, 163.0, 162.7, 150.1, 146.8, 146.5, 144.1, 141.4, 136.7, 133.3, 132.2, 129.9, 129.6, 129.3, 128.1, 125.8, 124.5, 122.6, 120.7, 42.6, 38.3, 30.6, 28.6, 23.9, 23.0, 14.1, 10.5.

5-(5-(4-(Diphenylamino)phenyl)-1-methyl-1*H*-pyrrol-2-yl)thiophene-2-carbaldehyde[25] **(3i)** was prepared from 4-(1-methyl-1*H*-pyrrol-2-yl)-*N*,*N*-diphenylaniline[23a] (**1i**) (324 mg, 1.00 mmol), **2a** (336 mg, 3.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), Ag_2CO_3 (413 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** (100 ^oC, 12 h for this example) and yielding after column chromatography (using the eluent with a gradient polarity: from dichloromethane : hexanes = 40 : 60 to dichloromethane : hexanes = 80 : 20) the pure product **3i** (221 mg, 51 %). Dark liquid. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.85 (s, 1 H), 7.72 (d, J = 3.9 Hz, 1 H), 7.26-7.42 (comp, 6 H), 7.01-7.21 (comp, 9 H), 6.63 (d, J = 3.9 Hz, 1 H), 6.28 (d, J = 3.9 Hz, 1 H), 3.79 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.5, 147.4, 145.8, 140.7, 139.7, 137.5, 129.7, 129.4, 128.2, 125.9, 124.8, 124.1, 123.4, 122.9, 112.2, 109.5, 34.6.

5'-(3,6-Di-*tert*-butyl-9*H*-carbazol-9-yl)-[2,2'-bithiophene]-5-carbaldehyde (3j) was prepared from 3,6-di-*tert*-butyl-9-(thiophen-2-yl)-9*H*-carbazole[26] (**1j**) (362 mg, 1.00 mmol), **2a** (336 mg, 3.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), Ag_2CO_3 (413 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** (100 °C, 12 h for this example) and yielding after column chromatography (dichloromethane : hexanes = 60 : 40) the pure product **3j** (351 mg, 70 %). Golden yellow solid; m.p.: 194.0-194.9 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.88 (s, 1 H), 8.11-8.20 (comp, 2 H), 7.67 (d, J = 3.9 Hz, 1 H), 7.46-7.60 (comp, 4 H), 7.41 (d, J = 3.9 Hz, 1 H), 7.25 (d, J = 3.9 Hz, 1 H), 7.15 (d, J = 3.9 Hz, 1 H), 1.50 (s, 18 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.5, 146.8, 144.2, 141.9, 140.9, 139.8, 137.4, 133.2, 125.1, 124.7, 124.2 (two peaks), 123.9, 116.4, 109.7, 34.8, 32.0; MS (EI, 70 eV): 472 ($[M+H]^+$, 3 %), 280 (36 %), 234 (66 %), 167 (42 %), 149 (100 %); HRMS (EI/Double Focusing) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{29}NOS_2$ 471.1691; found 471.1678.

5'-(4-(3,6-Di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)-[2,2'-bithiophene]-5-carbaldehyde[27] **(3k)** was prepared from 3,6-di-*tert*-butyl-9-(4-(thiophen-2-yl)phenyl)-9*H*-carbazole[23a] (**1k**) (437 mg, 1.00 mmol), **2a** (168 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (dichloromethane : hexanes = 60 : 40) the pure product **3k** (350 mg, 64 %). Golden yellow solid; m.p.: 235.0-235.6 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.88 (s, 1 H), 8.25 (d, J = 1.5 Hz, 2 H), 7.81 (d, J = 8.4 Hz, 2 H), 7.60-7.69 (comp, 3 H), 7.51-7.57 (comp, 2 H), 7.46 (d, J = 8.4 Hz, 2 H), 7.34 (dd, J = 10.5, 3.9 Hz, 2 H), 7.27 (d, J = 3.9 Hz, 1 H), 1.56 (s, 18 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.5, 146.9, 145.2, 143.3, 141.7, 139.0, 138.1, 137.5, 135.4, 131.9, 127.3, 127.1, 127.0, 124.6, 124.2, 123.8, 123.7, 116.4, 109.3, 34.8, 32.1.

5-(7-(4-(3,6-Di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)

thiophene-2-carbaldehyde (3l) was prepared from 3,6-di-*tert*-butyl-9-(4-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)phenyl)-9*H*-carbazole[23a] (**1l**) (496 mg, 1.00 mmol), **2a** (168 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (using the eluent with a gradient polarity: from dichloromethane : hexanes = 40 : 60 to dichloromethane : hexanes = 80 : 20) the pure product **3l** (333mg, 55 %). Golden yellow solid; m.p.: 232.9-233.5 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.87 (s, 1 H), 8.19 (d, J = 1.5 Hz, 2 H), 7.96 (d, J = 8.7 Hz, 2 H), 7.55-7.70 (comp, 3 H), 7.38-7.54 (comp, 4 H), 7.30 (d, J = 4.2 Hz, 1 H), 4.33-4.50 (comp, 4 H), 1.51 (s, 18 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.6, 144.6, 143.1, 140.9, 140.7, 139.0, 138.6, 137.1, 137.0, 130.7, 127.5, 126.8, 123.7, 123.5, 123.1, 117.4, 116.4, 109.5, 109.3, 65.1, 64.8, 34.8, 32.1; MS (EI, 70 eV): 606 ($[M+H]^+$, 2 %), 554 (100 %), 526 (6 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{37}H_{35}NO_3S_2$ 605.2058; found 605.2053.

5'-(9-(2-Ethylhexyl)-9*H*-carbazol-3-yl)-[2,2'-bithiophene]-5-carbaldehyde (3m) was prepared from 9-(2-ethylhexyl)-3-(thiophen-2-yl)-9*H*-carbazole[23a] (**1m**) (362 mg, 1.00 mmol), **2a** (168 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (using the eluent with a gradient polarity: from dichloromethane : hexanes = 20 : 80 to dichloromethane : hexanes = 40 : 60) the pure product **3m** (250 mg, 53 %). Orange solid; m.p.: 110.5-110.9 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.83 (s, 1 H), 8.27 (d, J = 1.8 Hz, 1 H), 8.13 (d, J = 7.5 Hz, 1 H), 7.67 (dd, J = 8.7, 1.8 Hz, 1 H), 7.61 (d, J = 3.9 Hz, 1 H), 7.44-7.55 (m, 1 H), 7.23-7.44 (comp, 5 H), 7.20 (d, J = 3.9 Hz, 1 H), 4.11 (d, J = 6.0 Hz, 2 H), 1.97-2.16 (m, 1 H), 1.19-1.51 (comp, 8 H), 0.79-1.00 (comp, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.4, 147.9, 147.7, 141.4, 140.94, 140.85, 137.6, 133.6, 127.3, 126.2, 124.5, 123.8, 123.5, 123.3, 122.9, 122.7, 120.5, 119.3, 117.6, 109.41, 109.37, 47.4, 39.4, 31.0, 28.9, 24.5, 23.1, 14.1, 11.0; MS (EI, 70 eV): 472 ($[M+H]^+$, 2 %), 84 (100 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for

$C_{29}H_{29}NOS_2$ 471.1691; found 471.1685.

5-(5-(2-Ethylhexyl)-3-(9-hexyl-9*H*-carbazol-3-yl)-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)thiophene-2-carbaldehyde (3n) was prepared from 5-(2-ethylhexyl)-1-(9-hexyl-9*H*-carbazol-3-yl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (**1n**) (514 mg, 1.00 mmol), **2a** (336 mg, 3.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), Ag_2CO_3 (413 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** (100 ^oC, 12 h for this example) and yielding after column chromatography (dichloromethane : hexanes = 60 : 40) the pure product **3n** (393 mg, 63 %). Red solid; m.p.: 195.8-197.3 ^oC. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.79 (s, 1 H), 8.74 (s, 1 H), 8.06-8.28 (comp, 2 H), 8.00 (d, J = 3.3 Hz, 1 H), 7.53 (d, J = 3.3 Hz, 1 H), 7.41-7.50 (m, 1 H), 7.17-7.38 (comp, 3 H), 4.18 (t, J = 6.9 Hz, 2 H), 3.49 (d, J = 7.2 Hz, 2 H), 1.72 (app s, 3 H), 1.34 (app s, 14 H), 0.64-1.13 (comp, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.5, 162.9, 162.6, 148.2, 143.7, 141.39, 141.35, 140.9, 136.5, 132.8, 132.1, 129.6, 127.7, 126.4, 125.9, 123.1, 122.7, 121.0, 120.9, 120.5, 119.8, 109.1, 108.8, 43.2, 42.5, 38.3, 31.5, 30.6, 28.9, 28.6, 26.9, 23.9, 23.1, 22.6, 14.2, 14.1, 10.5; MS (FAB): 626 ($[M+2]^+$, 100 %), 553 (29 %), 495 (19 %); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{37}H_{40}N_2O_3S_2$ 624.2480; found 624.2479.

5'-(9-(4-(Methylthio)phenyl)-9*H*-carbazol-3-yl)-[2,2'-bithiophene]-5-carbaldehyde (3o) was prepared from 9-(4-(methylthio)phenyl)-3-(thiophen-2-yl)-9*H*-carbazole (**1o**) (371 mg, 1.00 mmol), **2a** (336 mg, 3.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), Ag_2CO_3 (413 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** (100 ^oC, 12 h for this example) and yielding after column chromatography (dichloromethane : hexanes = 50 : 50) the pure product **3o** (269 mg, 56 %). Orange solid; m.p.: 180.9-182.3 ^oC. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.84 (s, 1 H), 8.32 (d, J = 1.2 Hz, 1 H), 8.18 (d, J = 7.8 Hz, 1 H), 7.59-7.68 (comp, 2 H), 7.02-7.52 (comp, 11 H), 2.60 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.4, 147.55, 147.52, 141.4, 141.1, 140.8, 138.4, 137.5, 134.1, 133.9, 127.7, 127.4, 127.3,

126.6, 125.7, 124.2, 123.9, 123.6, 123.2, 123.1, 120.5, 120.4, 117.7, 110.2, 110.0, 15.9; MS (EI, 70 eV): 481 (M^+, 1 %), 334 (8 %), 135 (42 %), 57 (100 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{28}H_{19}NOS_3$ 481.0629; found 481.0629.

5'-(9-(4-Fluorophenyl)-9*H*-carbazol-3-yl)-[2,2'-bithiophene]-5-carbaldehyde (3p) was prepared from 9-(4-fluorophenyl)-3-(thiophen-2-yl)-9*H*-carbazole (**1p**) (343 mg, 1.00 mmol), **2a** (168 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (dichloromethane : hexanes = 50 : 50) the pure product **3p** (390 mg, 86 %). Yellow solid; m.p.: 177.0-178.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.83 (s, 1 H), 8.33 (d, J = 1.5 Hz, 1 H), 8.07-8.29 (m, 1 H), 7.26-7.83 (comp, 12 H), 7.23 (d, J = 3.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.5, 147.5, 147.4, 141.6, 141.1, 140.9, 137.6, 134.0, 133.2 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 128.9 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 127.3, 126.7, 125.8, 124.3, 123.9, 123.7, 123.3, 123.1, 120.6, 120.5, 117.0 (d, $^2J_{C\text{-}F}$ = 22.7 Hz), 110.0, 109.9; MS (EI, 70 eV): 453 (M^+, 9 %), 411 (18 %), 167 (41 %), 149 (58 %), 84 (100 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{27}H_{16}FNOS_2$ 453.0657; found 453.0650.

4-(3-(5'-Formyl-[2,2'-bithiophen]-5-yl)-9*H*-carbazol-9-yl)benzonitrile (3q) was prepared from 4-(3-(thiophen-2-yl)-9*H*-carbazol-9-yl)benzonitrile (**1q**) (350 mg, 1.00 mmol), **2a** (168 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (dichloromethane : hexanes = 80 : 20) the pure product **3q** (345 mg, 75 %). Golden yellow solid; m.p.: 219.2-220.1 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.88 (s, 1 H), 8.35 (d, J = 1.5 Hz, 1 H), 8.20 (d, J = 7.5 Hz, 1 H), 7.95 (d, J = 8.4 Hz, 2 H), 7.75 (d, J = 8.4 Hz, 2 H), 7.65-7.73 (comp, 2 H), 7.29-7.54 (comp, 7 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.5, 147.4, 146.9, 141.6, 141.3, 140.5, 139.7, 137.5, 134.4, 134.1, 127.3, 127.1, 127.0, 126.8, 124.63, 124.58, 123.8, 123.7, 123.6, 121.5, 120.8, 117.9, 110.9, 110.1, 109.8; MS (EI, 70 eV): 460 (M^+, 7

%), 441 (23 %), 84 (100 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{28}H_{16}N_2OS_2$ 460.0704; found 460.0711.

5'-(9-(4-Benzoylphenyl)-9*H*-carbazol-3-yl)-[2,2'-bithiophene]-5-carbaldehyde (3r) was prepared from phenyl(4-(3-(thiophen-2-yl)-9*H*-carbazol-9-yl)phenyl)methanone (**1r**) (429 mg, 1.00 mmol), **2a** (168 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (dichloromethane : hexanes = 80 : 20) the pure product **3r** (383 mg, 71 %). Red solid; m.p.: 189.5-190.0 ^oC. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.83 (s, 1 H), 8.30 (d, J = 1.5 Hz, 1 H), 8.18 (d, J = 7.5 Hz, 1 H), 8.08 (d, J = 8.4 Hz, 2 H), 7.93 (d, J = 7.2 Hz, 2 H), 7.42-7.77 (comp, 10 H), 7.37 (app t, 1 H), 7.32 (d, J = 3.9 Hz, 1 H), 7.27 (d, J = 3.9 Hz, 1 H), 7.23 (d, J = 3.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 195.5, 182.4, 147.4, 147.1, 141.2, 141.1, 140.8, 140.0, 137.6, 137.3, 136.2, 134.1, 132.8, 132.0, 130.1, 128.5, 127.3, 126.8, 126.3, 126.1, 124.4, 123.7, 123.6, 123.4, 121.1, 120.7, 117.7, 110.3, 110.1; MS (FAB): 539 (M^+, 3 %), 501 (5 %), 307 (50 %), 89 (100 %); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{34}H_{21}NO_2S_2$ 539.1014; found 539.1020.

5'-(10-Hexyl-10*H*-phenothiazin-3-yl)-[2,2'-bithiophene]-5-carbaldehyde (3s) was prepared from 10-hexyl-3-(thiophen-2-yl)-10*H*-phenothiazine[28] (**1s**) (365 mg, 1.00 mmol), **2a** (168 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (using the eluent with a gradient polarity: from dichloromethane : hexanes = 40 : 60 to dichloromethane : hexanes = 60 : 40) the pure product **3s** (271 mg, 57 %). Red viscous liquid. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.85 (s, 1 H), 7.65 (d, J = 3.9 Hz, 1 H), 7.32-7.44 (comp, 2 H), 7.29 (d, J = 3.6 Hz, 1 H), 7.02-7.14 (comp, 3 H), 7.13 (d, J = 3.9 Hz, 1 H), 6.77-7.02 (comp, 3 H), 3.85 (t, J = 7.2 Hz, 2 H), 1.70-2.02 (comp, 2 H), 1.26-1.53 (comp, 6 H), 0.90 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.5, 147.3, 145.4, 145.2, 144.6, 141.2, 137.6,

134.2, 127.8, 127.50, 127.46, 127.2, 125.4, 124.8, 124.4, 123.9, 123.8, 123.2, 122.7, 115.5, 47.6, 31.5, 26.8, 26.7, 22.7, 14.1; MS (EI, 70 eV): 476 ($[M+1]^+$, 6 %), 317 (64 %), 57 (100 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{27}H_{25}NOS_3$ 475.1098; found 475.1107.

Ethyl 4-(3-(5'-formyl-[2,2'-bithiophen]-5-yl)-10*H*-phenothiazin-10-yl)benzoate (3t) was prepared from ethyl 4-(3-(thiophen-2-yl)-10*H*-phenothiazin-10-yl)benzoate (**1t**) (429 mg, 1.00 mmol), **2a** (168 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (dichloromethane : hexanes = 60 : 40) the pure product **3t** (350 mg, 65 %). Orange solid; m.p.: 172.0-172.5 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.80 (s, 1 H), 8.20 (d, J = 8.7 Hz, 2 H), 7.60 (d, J = 3.9 Hz, 1 H), 6.91-7.39 (comp, 10 H), 6.34-6.56 (comp, 2 H), 4.43 (q, J = 7.1 Hz, 2 H), 1.44 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.4, 165.9, 147.0, 145.9, 144.6, 142.8, 142.5, 141.4, 137.4, 134.6, 132.0, 129.0, 128.6, 127.4, 127.2, 127.1, 126.7, 124.7, 124.4, 124.2, 124.0, 123.9, 123.7, 123.2, 118.9, 61.2, 14.4; MS (FAB): 539 (M^+, 12 %), 469 (16 %), 77 (45 %), 57 (100 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{30}H_{21}NO_3S_3$ 539.0684; found 539.0685.

5'-(7-(Diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl)-[2,2'-bithiophene]-5-carbaldehyde (3u) was prepared from 9,9-dihexyl-*N*,*N*-diphenyl-7-(thiophen-2-yl)-9*H*-fluoren-2-amine[23a] (**1u**) (584 mg, 1.00 mmol), **2a** (168 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (dichloromethane : hexanes = 50 : 50) the pure product **3u** (423 mg, 61 %). Orange solid; m.p.: 137.7-139.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.90 (s, 1 H), 7.69 (d, J = 3.9 Hz, 1 H), 7.54-7.67 (comp, 4 H), 7.27-7.51 (comp, 7 H), 7.15-7.27 (comp, 5 H), 7.00-7.15 (comp, 3 H), 1.82-2.18 (comp, 4 H), 1.06-1.39 (comp, 12 H), 0.64-1.01 (comp, 10 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.4, 152.5, 151.7, 148.0, 147.6, 147.4, 147.2, 141.5, 141.4, 137.6, 135.4, 134.5, 131.4, 129.3, 127.3, 124.9, 124.0, 123.9, 123.8,

123.5, 122.8, 120.7, 119.9, 119.7, 119.1, 55.3, 40.3, 31.6, 29.7, 23.9, 22.6, 14.2; MS (FAB): 694 ($[M+1]^+$, 100 %), 537 (25 %), 136 (55 %); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{46}H_{47}NOS_2$ 693.3099; found 693.3102.

(*E*)-5'-(4-(Pyrrolidin-1-yldiazenyl)phenyl)-[2,2'-bithiophene]-5-carbaldehyde (3v) was prepared from (*E*)-1-((4-(thiophen-2-yl)phenyl)diazenyl)pyrrolidine (**1v**) (257 mg, 1.00 mmol), **2a** (336 mg, 3.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), Ag_2CO_3 (413 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** (100 ^oC, 12 h for this example) and yielding after column chromatography (ethyl acetate : dichloromethane : hexanes = 1 : 50 : 49) the pure product **3v** (257 mg, 70 %). Orange solid; m.p.: 200.9-202.3 ^oC. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.84 (s, 1 H), 7.65 (d, J = 3.9 Hz, 1 H), 7.56 (d, J = 8.5 Hz, 2 H), 7.44 (d, J = 8.5 Hz, 2 H), 7.31 (d, J = 3.9 Hz, 1 H), 7.14-7.25 (comp, 2 H), 3.80 (app s, 4 H), 1.90-2.11 (comp, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.5, 151.5, 147.5, 146.6, 141.2, 137.6, 134.3, 130.1, 127.3, 126.3, 123.8, 123.5, 120.9, 23.8 (two peaks); MS (EI, 70 eV): 368 ($[M+H]^+$, 11 %), 367 (M^+, 45 %), 269 (100 %), 240 (21 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{19}H_{17}N_3OS_2$ 367.0813; found 367.0815.

Dimethyl 5'-(10-(4-(ethoxycarbonyl)phenyl)-10*H*-phenothiazin-3-yl)-5-(3-fluoro-4-formyl-phenyl)-[2,2'-bithiophene]-3,4-dicarboxylate (4a) was prepared from ethyl 4-(3-(thiophen-2-yl)-10*H*-phenothiazin-10-yl)benzoate (**1t**) (429 mg, 1.00 mmol), dimethyl 2-(3-fluoro-4-formylphenyl)thiophene-3,4-dicarboxylate (**2b**) (483 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (ethyl acetate : dichloromethane : hexanes = 1 : 50 : 49) the pure product **4a** (509 mg, 68 %). Red solid; m.p.: 196.0-196.5 ^oC. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 10.34 (s, 1 H), 8.10-8.28 (comp, 2 H), 7.93-8.81 (comp, 1 H), 7.27-7.43 (comp, 6 H), 7.08-7.23 (comp, 3 H), 6.85-7.04 (comp, 2 H), 6.39-6.61 (comp, 2 H), 4.41 (q, J = 7.2 Hz, 2 H), 3.88 (s, 3 H), 3.79 (s, 3 H), 1.41 (t, J = 7.2

Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 186.3 (d, $^{3}J_{C\text{-}F}$ = 6.0 Hz), 165.9, 164.1 (d, $^{1}J_{C\text{-}F}$ = 258.0 Hz), 164.0, 163.8, 145.94, 145.91, 142.9, 142.5, 141.6 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 140.0, 139.9 (d, $^{2}J_{C\text{-}F}$ = 9.0 Hz), 132.0, 131.2, 130.9, 129.9, 129.3, 129.1, 128.9 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 128.6, 127.4, 127.2, 126.6, 125.3 (d, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.8, 124.6, 124.4, 124.0, 123.9 (d, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 123.28, 123.26, 119.0, 118.9, 116.9 (d, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 61.2, 52.7, 52.6, 14.4; MS (FAB): 749 (M^+, 2 %), 663 (12 %), 647 (11 %), 57 (100 %); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{40}H_{28}FNO_7S_3$ 749.1012; found 749.1008.

Synthesis and characterization of **2b**: compound **2b** was prepared according to the reported procedures in literature.[23a] Yellow solid; m.p.: 114.1-115.5 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 10.25 (s, 1 H), 8.04 (s, 1 H), 7.80 (app t, 1 H), 7.20-7.36 (comp, 2 H), 3.81 (s, 3 H), 3.80 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 186.2 (d, $^{3}J_{C\text{-}F}$ = 6.0 Hz), 165.7, 164.3 (d, $^{1}J_{C\text{-}F}$ = 258.0 Hz), 161.7, 140.8 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 139.9 (d, $^{2}J_{C\text{-}F}$ = 9.8 Hz), 133.5, 132.9, 132.2, 129.3 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 124.4 (d, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 123.8 (d, $^{3}J_{C\text{-}F}$ = 9.0 Hz), 116.0 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 53.0, 52.3; MS (EI, 70 eV): 322 (M^+, 70 %), 290 (100 %), 131 (20 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{15}H_{11}FO_5S$ 322.0311; found 322.0310.

4-(5-(2-Ethylhexyl)-3-(7-(9-(4-fluorophenyl)-9*H*-carbazol-3-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)benzaldehyde (4b) was prepared from 3-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-9-(4-fluorophenyl)-9*H*-carbazole (**1w**) (401 mg, 1.00 mmol), 4-(5-(2-ethylhexyl)-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)benzaldehyde (**2c**) (554 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (using the eluent with a gradient polarity: from dichloromethane : hexanes = 40 : 60 to dichloromethane : hexanes = 80 : 20) the pure product **4b** (569 mg, 74 %). Dark red solid; m.p.: 154.3-155.5 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.71 (s, 1 H), 8.24 (s, 1 H), 8.01 (d, J = 7.5 Hz, 1 H), 7.92 (d, J = 8.1 Hz, 2 H), 7.61 (d, J = 8.8 Hz, 1 H), 7.53 (d, J =

8.1 Hz, 2 H), 7.12-7.47 (comp, 7 H), 7.03 (d, J = 8.6 Hz, 1 H), 4.34 (app s, 2 H), 4.25 (app s, 2 H), 3.40 (d, J = 7.2 Hz, 2 H), 1.75-1.95 (m, 1 H), 1.22-1.43 (comp, 8 H), 0.79-1.11 (comp, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 191.0, 162.9, 162.7, 159.8, 142.5, 141.1, 139.9, 139.8, 136.1, 136.0, 135.6, 133.13, 133.09, 130.0, 129.5, 128.6 (d, $^3J_{C\text{-}F}$ = 7.5 Hz), 127.6, 126.7, 126.2, 124.7, 124.2, 123.3, 123.14, 123.11, 120.6, 120.3, 118.2, 116.8 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 109.6, 109.2, 106.0, 65.1, 64.0, 42.4, 38.3, 30.6, 28.6, 23.8, 23.1, 14.1, 10.5; MS (FAB): 768 (M^+, 2 %), 249 (23 %), 228 (50 %), 51 (100 %); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{45}H_{37}FN_2O_5S_2$ 768.2128; found 768.2131.

Synthesis and characterization of **2c**: compound **2c** was prepared according to the reported procedures in literature.[23a] Yellow solid; m.p.: 143.3-143.9 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 10.00 (s, 1 H), 8.24 (d, J = 8.4 Hz, 2 H), 7.91 (d, J = 8.4 Hz, 2 H), 7.79 (s, 1 H), 3.51 (d, J = 7.2 Hz, 2 H), 1.71-1.85 (m, 1 H), 1.16-1.42 (comp, 8 H), 0.73-0.97 (comp, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 191.2, 163.1, 162.4, 145.2, 138.2, 136.7, 135.9, 130.8, 130.2, 128.3, 124.5, 42.5, 38.2, 30.5, 28.5, 23.8, 23.0, 14.1, 10.4; MS (EI, 70 eV): 369 (M^+, 16 %), 257 (31 %), 159 (100 %), 115 (78 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{21}H_{23}NO_3S$ 369.1399; found 369.1400.

5-(3-(7-(4-(3,6-Di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-5-hexyl-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)thiophene-2-carbaldehyde (4c) was prepared from 3,6-di-*tert*-butyl-9-(4-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)phenyl)-9*H*-carbazole[23a] (**1l**) (495 mg, 1.00 mmol), 5-(5-hexyl-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)thiophene-2-carbaldehyde (**2d**) (520 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (dichloromethane) the pure product **4c** (589 mg, 70 %). Red solid; m.p.: 335.7-336.5 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.87 (s, 1 H), 8.13-8.31 (comp, 3 H),

8.01 (d, *J* = 8.6 Hz, 2 H), 7.69 (d, *J* = 3.9 Hz, 1 H), 7.58 (d, *J* = 8.6 Hz, 2 H), 7.47 (dd, *J* = 8.7, 1.8 Hz, 2 H), 7.40 (d, *J* = 8.7 Hz, 2 H), 4.52-4.66 (comp, 2 H), 4.41-4.51 (comp, 2 H), 3.65 (t, *J* = 7.2 Hz, 2 H), 1.65-1.80 (comp, 2 H), 1.48 (s, 18 H), 1.29-1.41 (comp, 6 H), 0.90 (t, *J* = 6.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): *δ* 182.5, 162.5, 162.4, 143.9, 143.1, 142.7, 141.4, 138.9, 137.6, 137.5, 136.8, 135.7, 133.5, 130.4, 130.3, 129.8, 127.8, 127.4, 126.6, 123.7, 123.5, 121.4, 116.3, 109.2, 107.4, 65.5, 64.4, 38.7, 34.7, 32.0, 31.4, 28.5, 26.7, 22.5, 14.0; MS (FAB): 841 ($[M+H]^+$, 2 %), 228 (30 %), 136 (70 %), 51 (100 %); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{49}H_{48}N_2O_5S_3$ 840.2725; found 840.2729.

Synthesis and characterization of **2d**: compound **2d** was prepared according to the reported procedures in literature.[23a] Yellow solid; m.p.: 153.9-154.4 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): *δ* 9.93 (s, 1 H), 8.15 (d, *J* = 3.9 Hz, 1 H), 7.75 (d, *J* = 3.9 Hz, 1 H), 7.73 (s, 1 H), 3.64 (t, *J* = 7.4 Hz, 2 H), 1.60-1.72 (comp, 2 H), 1.24-1.38 (comp, 6 H), 0.87 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): *δ* 182.6, 162.5, 161.9, 144.7, 141.0, 137.9, 136.5, 130.8, 130.1, 124.2, 38.7, 31.3, 28.4, 26.5, 22.5, 14.0; MS (EI, 70 eV): 347 (M^+, 3 %), 222 (78 %), 221 (54 %), 166 (43 %), 57 (100 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{17}H_{17}NO_3S_2$ 347.0650; found 347.0655.

5-Hexyl-1-(9-hexyl-9*H*-carbazol-3-yl)-3-(7-(4-nitrophenyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (4d) was prepared from 5-hexyl-1-(9-hexyl-9*H*-carbazol-3-yl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (486 mg, 1.00 mmol), 5-(4-nitrophenyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (**2e**) (395 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (dichloromethane : hexanes = 60 : 40) the pure product **4d** (628 mg, 81 %). Red solid; m.p.: 222.1-223.1 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): *δ* 8.75 (d, *J* = 1.8 Hz, 1 H), 8.18 (dd, *J* = 8.7, 2.0 Hz, 1 H), 8.14 (d, *J* = 7.8 Hz, 1 H), 7.90-8.07 (comp, 2 H), 7.59-7.84 (comp, 2 H), 7.39-7.57 (m, 1 H), 7.16-7.38 (comp, 3 H), 4.42 (t, *J* = 2.6 Hz, 2 H), 4.34 (t, *J* = 2.6 Hz, 2 H),

4.13 (t, J = 7.2 Hz, 2 H), 3.61 (t, J = 7.5 Hz, 2 H), 1.62-1.98 (comp, 4 H), 1.19-1.48 (comp, 12 H), 0.75-1.05 (comp, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 163.1, 162.6, 146.8, 145.63, 145.56, 141.1, 140.9, 139.3, 138.6, 132.0, 129.05, 128.98, 126.2, 125.9, 125.8, 123.6, 123.0, 122.9, 121.7, 120.7, 120.2, 119.5, 117.0, 110.6, 109.0, 108.5, 64.9, 64.4, 43.2, 38.5, 31.5, 29.6, 28.8, 28.6, 26.9, 26.7, 22.6, 22.5, 14.0, 13.9; MS (FAB): 747 (M^+, 2 %), 663 (24 %), 647 (22 %), 57 (100 %); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{42}H_{41}N_3O_6S_2$ 747.2437; found 747.2433.

Synthesis and characterization of **2e**: compound **2e** was prepared according to the reported procedures in literature.[23b] Yellow solid; m.p.: 192.8-193.1 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.12-8.25 (comp, 2 H), 7.79-7.88 (comp, 2 H), 6.46 (s, 1 H), 4.33-4.40 (comp, 2 H), 4.24-4.31 (comp, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 145.4, 142.5, 140.6, 139.8, 125.7, 124.1, 115.2, 101.0, 65.0, 64.3.

4-(5-(5-(9-(2-Ethylhexyl)-9*H*-carbazol-3-yl)thiophen-2-yl)furan-2-yl)benzonitrile (4e) was prepared from 9-(2-ethylhexyl)-3-(thiophen-2-yl)-9*H*-carbazole[23a] (**1m**) (362 mg, 1.00 mmol), 4-(furan-2-yl)benzonitrile (**2f**) (254 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (dichloromethane : hexanes = 40 : 60) the pure product **4e** (290 mg, 55 %). Dark liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.27-8.38 (m, 1 H), 8.14 (d, J = 7.8 Hz, 1 H), 7.15-7.93 (comp, 11 H), 6.83 (d, J = 3.6 Hz, 1 H), 6.60 (d, J = 3.6 Hz, 1 H), 4.05-4.22 (comp, 2 H), 1.98-2.17 (m, 1 H), 1.28-1.43 (comp, 8 H), 0.86-1.02 (comp, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 150.8, 150.5, 145.7, 141.4, 140.7, 134.2, 132.5, 130.6, 126.1, 124.9, 124.5, 123.8, 123.6, 123.3, 122.7, 122.5, 120.5, 119.2, 119.1, 117.5, 110.6, 109.8, 109.4, 109.3, 107.2, 47.5, 39.4, 31.0, 28.8, 24.4, 23.1, 14.1, 10.9; MS (EI, 70 eV): 528 (M^+, 24 %), 429 (15 %), 307 (26 %), 149 (100 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{35}H_{32}N_2OS$ 528.2235; found 528.2243.

Synthesis and characterization of **2f**: compound **2f** was prepared according to the reported procedures in literature.[23c] Dark liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.38-7.71 (comp, 5

H), 6.73 (d, J = 3.6 Hz, 1 H), 6.37-6.53 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 151.8, 143.7, 134.5, 132.5, 123.8, 119.0, 112.3, 110.1, 108.3.

Diethyl 2-(5-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)thiophen-2-yl)-5-(pyrimidin-5-yl)furan-3,4-dicarboxylate (4f) was prepared from 3,6-di-*tert*-butyl-9-(4-(thiophen-2-yl)phenyl)-9*H*-carbazole[23a] (**1k**) (437 mg, 1.00 mmol), diethyl 2-(pyrimidin-5-yl)furan-3,4-dicarboxylate (**2g**) (435 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (using the eluent with a gradient polarity: ethyl acetate : hexanes = from 10 : 90 to 20 : 80) the pure product **4f** (667 mg, 92 %). Yellow solid; m.p.: 210.0-211.5 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.28 (s, 1 H), 9.26 (s, 2 H), 8.21 (s, 2 H), 7.97 (d, J = 3.9 Hz, 1 H), 7.88 (d, J = 8.4 Hz, 2 H), 7.64 (d, J = 8.4 Hz, 2 H), 7.38-7.57 (comp, 5 H), 4.38-4.56 (comp, 4 H), 1.39-1.62 (comp, 24 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.9, 162.5, 158.4, 154.6, 151.6, 147.0, 146.0, 143.2, 138.9, 138.3, 131.8, 130.4, 128.9, 127.3, 127.0, 124.1, 123.8, 123.6, 118.8, 116.4, 113.8, 109.3, 62.1, 61.7, 34.8, 32.0, 14.2, 14.1; MS (FAB): 725 (M^+, 20 %), 663 (15 %), 57 (100 %); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{44}H_{43}N_3O_5S$ 725.2923; found 725.2924.

Synthesis and characterization of **2g**: compound **2g** was prepared according to the reported procedures in literature.[23a] Yellow solid; m.p.: 64.5-65.0 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.11 (s, 1 H), 9.01 (s, 2 H), 7.99 (s, 1 H), 4.14-4.40 (comp, 4 H), 1.21-1.37 (comp, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.8, 161.1, 158.4, 154.3, 148.7, 147.5, 123.6, 120.6, 116.6, 62.0, 61.1, 14.1, 13.8; MS (EI, 70 eV): 290 (M^+, 73 %), 245 (33 %), 217 (100 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{14}H_{14}N_2O_5$ 290.0903; found 290.0902.

Ethyl 4-(5-(5-(9-(4-fluorophenyl)-9*H*-carbazol-3-yl)thiophen-2-yl)selenophen-2-yl)benzoate (4g) was prepared from 9-(4-fluorophenyl)-3-(thiophen-2-yl)-9*H*-carbazole (**1p**) (343 mg, 1.00 mmol), ethyl 4-(selenophen-2-yl)benzoate (**2h**) (419 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05

mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (dichloromethane : hexanes = 50 : 50) the pure product **4g** (161 mg, 26 %). Yellow solid; m.p.: 243.5-244.2 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.38 (app s, 1 H), 8.21 (d, J = 7.2 Hz, 1 H), 8.06 (d, J = 7.4 Hz, 2 H), 7.13-7.75 (comp, 15 H), 4.42 (app d, 2 H), 1.44 (t, J = 6.6 Hz, 3 H); an analytically valid ^{13}C NMR spectrum of this compound was not obtained owing to its poor solubility in commonly used d-solvents; MS (FAB): 621 (M^+, 3 %), 469 (18 %), 107 (100 %); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{35}H_{24}FNO_2SSe$ 621.0677; found 621.0680.

Synthesis and characterization of **2h**: compound **2h** was prepared according to the reported procedures in literature.[23a] White solid; m.p.: 57.6-58.7 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.97-8.29 (comp, 3 H), 7.55-7.78 (comp, 3 H), 7.30-7.46 (m, 1 H), 4.41 (q, J = 7.1 Hz, 2 H), 1.43 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 166.2, 149.4, 140.5, 131.6, 130.8, 130.3, 129.2, 126.7, 126.0, 61.0, 14.4; MS (EI, 70 eV): 280 (M^+, 76 %), 234 (100 %), 221 (83 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{13}H_{12}O_2Se$ 280.0003; found 280.0002.

Synthesis and characterization of compounds 5a-c and CYL-8~10 (Scheme 2):

4-(5-(2-Ethylhexyl)-3-(7-(9-(4-methoxyphenyl)-9*H*-carbazol-3-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)benzaldehyde (5a) was prepared from 3-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-9-(4-methoxyphenyl)-9*H*-carbazole (**1x**) (413 mg, 1.00 mmol), 4-(5-(2-ethylhexyl)-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)benzaldehyde (**2c**) (554 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (ethyl acetate : dichloromethane : hexanes = 5 : 30 : 65) the pure product **5a** (554 mg, 71 %). Dark red solid; m.p.: 132.0-133.5 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.81 (s, 1 H), 8.35 (s, 1 H), 7.96-8.24 (comp, 3 H), 7.58- 7.85 (comp, 3 H), 7.18-7.50 (comp, 5 H), 7.13 (d, J = 8.6 Hz, 1 H), 7.06 (d, J = 8.7 Hz, 2 H), 4.37 (app s, 2 H), 4.28 (app s, 2 H), 3.89 (s, 3

H), 3.44 (d, J = 7.2 Hz, 2 H), 1.74-2.01 (m, 1 H), 1.20-1.61 (comp, 8 H), 0.78-1.12 (comp, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 191.1, 163.0, 162.8, 158.8, 142.7, 141.5, 140.4, 139.9, 136.3, 136.2, 136.1, 135.8, 130.2, 129.8, 129.7, 128.2, 127.8, 126.8, 126.1, 124.7, 123.9, 123.5, 123.2, 123.0, 120.6, 120.0, 118.3, 115.0, 109.9, 109.5, 106.0, 65.2, 64.0, 55.6, 42.5, 38.3, 30.6, 28.6, 23.9, 23.1, 14.1, 10.5; MS (FAB): 780 (M^+, 15 %), 307 (16 %), 77 (100 %); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{46}H_{40}N_2O_6S_2$ 780.2328; found 780.2336.

Synthesis and characterization of **1x** (the donor part in blue color): compound **1x** was prepared according to the general procedure **A**. White solid; m.p.: 185.2-186.3 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.51-8.78 (m, 1 H), 8.30 (d, J = 7.2 Hz, 1 H), 7.83-7.98 (m, 1 H), 7.34-7.63 (comp, 6 H), 7.16 (d, J = 8.7 Hz, 2 H), 6.39 (s, 1 H), 4.33-4.45 (comp, 2 H), 4.15-4.33 (comp, 2 H), 3.93 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 159.0, 142.5, 141.9, 140.3, 137.3, 130.2, 128.5, 126.2, 125.3, 124.9, 123.5, 123.3, 120.6, 119.9, 118.7, 118.2, 115.2, 109.9, 96.5, 64.9, 64.6, 55.6; MS (FAB): 413 (M^+, 11 %), 316 (7 %), 228 (35 %), 51 (100 %); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{25}H_{19}NO_3S$ 413.1086; found 413.1095.

4-(5-(2-Ethylhexyl)-3-(7-(9-(4-methoxyphenyl)-9*H*-carbazol-3-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)-2-fluorobenzaldehyde (5b) was prepared from 3-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-9-(4-methoxyphenyl)-9*H*-carbazole (**1x**) (413 mg, 1.00 mmol), 4-(5-(2-ethylhexyl)-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)-2-fluorobenzaldehyde (**2i**) (580 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (using the eluent with a gradient polarity: from dichloromethane : hexanes = 60 : 40 to dichloromethane : hexanes = 80 : 20) the pure product **5b** (606 mg, 76 %). Dark red solid; m.p.: 161.3-162.9 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.88 (s, 1 H), 8.06 (app s, 1 H), 7.85 (d, J = 7.5 Hz, 1 H), 7.68 (d, J = 12.0 Hz, 1 H), 7.04-7.59 (comp, 9 H), 7.01 (d,

J = 8.5 Hz, 1 H), 6.94 (d, J = 8.6 Hz, 1 H), 4.29 (app s, 2 H), 4.20 (app s, 2 H), 3.87 (s, 3 H), 3.35 (d, J = 6.3 Hz, 2 H), 1.79 (app s, 1 H), 1.27-1.42 (comp, 8 H), 0.85-0.98 (comp, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 186.0 (d, $^3J_{C\text{-}F}$ = 4.5 Hz), 164.3 (d, $^1J_{C\text{-}F}$ = 256.5 Hz), 163.0, 162.8, 158.9, 143.0, 141.6, 140.6, 138.4 (d, $^3J_{C\text{-}F}$ = 6.0 Hz), 136.7, 136.2, 131.0, 129.9, 128.6, 128.2, 126.9, 126.2, 124.7, 124.1, 123.7, 123.5 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 123.3, 123.2, 123.0, 120.5, 120.0, 118.4, 115.3, 115.1, 109.9, 109.6, 105.9, 65.4, 64.2, 55.6, 42.6, 38.2, 30.6, 28.6, 23.9, 23.1, 14.1, 10.5; MS (FAB): 798 (M^+, 13 %), 664 (34 %), 647 (36 %), 57 (100 %); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{46}H_{39}FN_2O_6S_2$ 798.2234; found 798.2229.

Synthesis and characterization of **2i**: compound **2i** was prepared according to the reported procedures in literature.[23a] Yellow solid; m.p.: 105.7-106.2 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 10.31 (s, 1 H), 8.13 (d, J = 10.8 Hz, 1 H), 7.87 (app d, 2 H), 7.82 (s, 1 H), 3.51 (d, J = 7.3 Hz, 2 H), 1.71-1.89 (m, 1 H), 1.14-1.43 (comp, 8 H), 0.61-1.05 (comp, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 186.1 (d, $^3J_{C\text{-}F}$ = 6.0 Hz), 164.5 (d, $^1J_{C\text{-}F}$ = 257.3 Hz), 162.9, 162.2, 143.7 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 138.3, 138.0 (d, $^2J_{C\text{-}F}$ = 9.8 Hz), 131.6, 129.3 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 125.0, 124.4 (d, $^3J_{C\text{-}F}$ = 9.0 Hz), 123.7 (d, $^3J_{C\text{-}F}$ = 3.0 Hz), 115.8 (d, $^2J_{C\text{-}F}$ = 24.0 Hz), 42.6, 38.2, 30.5, 28.5, 23.8, 23.0, 14.0, 10.4; MS (EI, 70 eV): 388 ($[M+1]^+$, 15 %), 387 (M^+, 62 %), 288 (72 %), 270 (100 %); HRMS (EI/Double Focusing) m/z: M^+ Calcd. for $C_{21}H_{22}FNO_3S$ 387.1304; found 387.1302.

4-(5-(2-Ethylhexyl)-3-(7-(9-(4-fluorophenyl)-9*H*-carbazol-3-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)-2-fluorobenzaldehyde (5c) was prepared from 3-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-9-(4-fluorophenyl)-9*H*-carbazole (**1w**) (401 mg, 1.00 mmol), 4-(5-(2-ethylhexyl)-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)-2-fluorobenzaldehyde (**2i**) (580 mg, 1.50 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol), $Cu(OAc)_2$ (273 mg, 1.50 mmol), pyridine (119 mg, 1.50 mmol), and *o*-xylene (2 mL) according to the general procedure **C** and yielding after column chromatography (using the eluent with a gradient polarity: from dichloromethane : hexanes = 40 : 60 to dichloromethane : hexanes = 80 : 20) the pure product **5c** (519 mg, 66 %).

Dark red solid; m.p.: 213.2-215.4 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.94 (s, 1 H), 8.19 (app s, 1 H), 7.96 (d, J = 7.5 Hz, 1 H), 7.81 (d, J = 11.9 Hz, 1 H), 7.12-7.74 (comp, 10 H), 7.03 (d, J = 8.7 Hz, 1 H), 4.39-4.60 (app s, 2 H), 4.19-4.39 (app s, 2 H), 3.44 (d, J = 6.9 Hz, 2 H), 1.80-1.99 (m, 1 H), 1.26-1.50 (comp, 8 H), 0.82-1.12 (comp, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 185.8 (d, $^3J_{C\text{-}F}$ = 6.0 Hz), 162.8, 162.6, 162.3, 161.6 (d, $^1J_{C\text{-}F}$ = 246.0 Hz), 142.7, 141.1, 139.9, 138.2, 136.4, 136.1, 133.09, 133.05, 130.8, 128.6 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 128.2 (d, $^4J_{C\text{-}F}$ = 1.5 Hz), 126.7 (d, $^4J_{C\text{-}F}$ = 1.5 Hz), 126.3, 124.5, 124.0, 123.6, 123.3, 123.2 (d, $^3J_{C\text{-}F}$ = 9.0 Hz), 123.0, 122.7, 120.4 (d, $^2J_{C\text{-}F}$ = 16.5 Hz), 118.12, 118.09, 116.8 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 114.8 (d, $^2J_{C\text{-}F}$ = 23.3 Hz), 109.6, 109.3, 65.2, 64.0, 42.5, 38.3, 30.6, 28.6, 23.8, 23.1, 14.1, 10.5; MS (FAB): 786 (M^+, 29 %), 304 (100 %), 228 (49 %), 95 (70 %); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{45}H_{36}F_2N_2O_5S_2$ 786.2034; found 786.2040.

General procedure D for sensitizers CYL-8, **CYL-9**, **CYL-10 (Knoevenagel condensations):** To a cosolvent of toluene (5 mL) and glacial acetic acid (5 mL) were added the synthesized aldehyde (**5a**, **5b**, or **5c**) (0.50 mmol), cyanoacetic acid (6.0 mmol), and ammonium acetate (2.50 mmol) at room temperature. The reaction mixture was then heated at 110 °C under N_2 for 6 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 flash chromatography yielded the desired products **CYL-8**, **CYL-9** and **CYL-10**.

(*E*)-2-Cyano-3-(4-(5-(2-ethylhexyl)-3-(7-(9-(4-methoxyphenyl)-9*H*-carbazol-3-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)phenyl)acrylic acid (CYL-8) was prepared from **5a** (390 mg, 0.50 mmol), cyanoacetic acid (510 mg, 6.0 mmol), ammonium acetate (193 mg, 2.50 mmol), and toluene (5 mL)/glacial acetic acid (5 mL) according to the general procedure **D** and yielding after column chromatography (using the eluent with a gradient polarity: from 100 % dichloromethane to dichloromethane : methanol = 90 : 10)

the pure product **CYL-8** (275 mg, 65 %). Dark red solid; m.p.: 299.1-300.0 ^{o}C. ^{1}H NMR ($CDCl_3$ and few drops of CD_3OD, 300 MHz, ppm): δ 7.36-8.38 (comp, 6 H), 6.04-7.26 (comp, 10 H), 4.39 (app s, 2 H), 4.33 (app s, 2 H), 3.80 (s, 3 H), 3.49 (app s, 2 H), 1.82 (app s, 1 H), 1.27 (app s, 8 H), 0.80-0.91 (comp, 6 H); an analytically valid ^{13}C NMR spectrum of **CYL-8** was not obtained owing to its poor solubility in commonly used organic solvents; MS (FAB): 847 ($[M]^+$, 4 %), 228 (16 %), 107 (75 %), 77 (100%); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{49}H_{41}N_3O_7S_2$ 847.2386; found 847.2391.

(*E*)-2-Cyano-3-(4-(5-(2-ethylhexyl)-3-(7-(9-(4-methoxyphenyl)-9*H*-carbazol-3-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)-2-fluorophenyl)acrylic acid (CYL-9) was prepared from **5b** (399 mg, 0.50 mmol), cyanoacetic acid (510 mg, 6.0 mmol), ammonium acetate (193 mg, 2.50 mmol), and toluene (5 mL)/glacial acetic acid (5 mL) according to the general procedure **D** and yielding after column chromatography (using the eluent with a gradient polarity: from 100 % dichloromethane to dichloromethane : methanol = 90 : 10) the pure product **CYL-9** (307 mg, 71 %). Dark red solid; m.p.: 213.5-214.8 ^{o}C. ^{1}H NMR ($CDCl_3$ and few drops of CD_3OD, 300 MHz, ppm): δ 8.04-8.42 (comp, 3 H), 7.94 (d, J = 6.6 Hz, 2 H), 7.56 (d, J = 8.9 Hz, 1 H), 7.36 (d, J = 6.2 Hz, 1 H), 6.44-7.26 (comp, 8 H), 4.41 (app s, 2 H), 4.36 (app s, 2 H), 3.79 (s, 3 H), 3.41-3.58 (comp, 2 H), 1.75-1.90 (m, 1 H), 1.19-1.34 (comp, 8 H), 0.79-0.94 (comp, 6 H); an analytically valid ^{13}C NMR spectrum of **CYL-9** was not obtained owing to its poor solubility in commonly used organic solvents; MS (FAB): 865 (M^+, 4 %), 316 (20 %), 73 (100 %); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{49}H_{40}FN_3O_7S_2$ 865.2292; found 865.2289.

(*E*)-2-Cyano-3-(4-(5-(2-ethylhexyl)-3-(7-(9-(4-fluorophenyl)-9*H*-carbazol-3-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-4,6-dioxo-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrol-1-yl)-2-fluorophenyl)acrylic acid (CYL-10) was prepared from **5c** (393 mg, 0.50 mmol), cyanoacetic acid (510 mg, 6.0 mmol), ammonium acetate (193 mg, 2.50 mmol), and toluene (5 mL)/glacial acetic acid (5

mL) according to the general procedure **D** and yielding after column chromatography (using the eluent with a gradient polarity: from 100 % dichloromethane to dichloromethane : methanol = 90 : 10) the pure product **CYL-10** (260 mg, 61 %). Dark red solid; m.p.: 102.4.1-103.7 ^{o}C. ^{1}H NMR ($CDCl_3$ and few drops of CD_3OD, 300 MHz, ppm): δ 8.29-8.63 (m, 1 H), 7.90-8.25 (comp, 2 H), 7.60-7.88 (m, 1 H), 6.16-7.60 (comp, 11 H), 4.06-4.70 (comp, 4 H), 2.89-3.05 (comp, 2 H), 1.74 (app s, 1 H), 1.18-1.37 (comp, 8 H), 0.77-0.96 (comp, 6 H); an analytically valid ^{13}C NMR spectrum of **CYL-10** was not obtained owing to its poor solubility in commonly used organic solvents; MS (FAB): 854 ($[M+H]^+$, 2 %), 228 (50 %), 95 (60 %), 51 (100 %); HRMS (FAB/Double Focusing) m/z: M^+ Calcd. for $C_{48}H_{37}F_2N_3O_6S_2$ 853.2092; found 853.2086.

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Supporting information: Copies of the ^{1}H and ^{13}C NMR spectra of all synthesized compounds, UV-Vis absorption spectra and cyclic voltammograms of new organic sensitizers (**CYL-8**~**10**) are provided in the supporting information file. This material is available free of charge via the internet at http://pubs.acs.org.

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