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ITERATIVE EXTENSION OF THIOPHENE RING LEADING TO HEAD-TO-TAIL-TYPE OLIGOTHIOPHENES *VIA* STEPWISE CH ARYLATION AND HALOGEN EXCHANGE SEQUENCE‡

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‡This paper is dedicated to Professor Albert Eschenmoser on the occasion of his 85th birthday.

Abstract – Iterative extension of the thiophene ring unit leads to oligothiophenes. The coupling reaction at the CH bond of thiophene with halo-thiophene occurs at the 5-position of 2-bromothiophene with 2-iodothiophene in the presence of a palladium catalyst and $AgNO_3$/KF as an activator to give the corresponding bithiophene, whose carbon-bromine bond remains. Halogen exchange converts the bromine atom to iodide, which also allows further reaction to form thiophene-thiophene bond. Oligothiophenes are obtained by repeating such sequense.

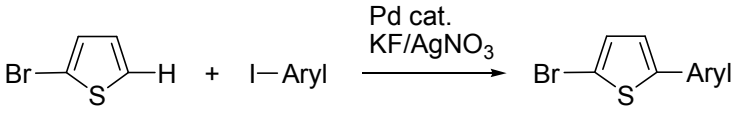
INTRODUCTION

As demand increases for oligothiophenes and polythiophenes as advanced electronic and photonic materials, such as organic TFT, liquid crystals, photovoltaic cells, etc.,[1,2] preparative methodologies of oligothiophenes have become a significant issue in organic synthesis.[3,4] We have recently shown that palladium-catalyzed homocoupling of bromothiophene derivatives, which occurs at the carbon-hydrogen

bond of thiophene adjacent to the sulfur atom and the carbon-bromine bond is completely intact, is a highly efficient synthetic pathway for well-defined oligothiophenes and indeed has prepared several oligomers bearing 2-8 thiophene units.[5] Although the method is effective for the head-to-head (HH) or tail-to-tail (TT) type oligomers, synthetic design of head-to-tail (HT) oligothiophene that generally shows a higher performance than other regioisomers has been difficult.

Accordingly, transition metal-catalyzed CH functionalization reactions are of great interest in organic synthesis since the reaction shows advantages in atom efficiency compared with related cross coupling with organometallic compounds.[6] The reaction of heteroaromatic compounds is particularly important because of their wide utilities in the synthesis of biologically active molecules and advanced organic materials.[7] We have recently shown that the catalytic carbon−carbon bond-forming reaction via CH functionalization has been achieved by the reaction of 2-bromothiophene with aryl halides as shown in Scheme 1, [8,9] in which carbon−bromine bond is also intact during the palladium-catalyzed reaction.

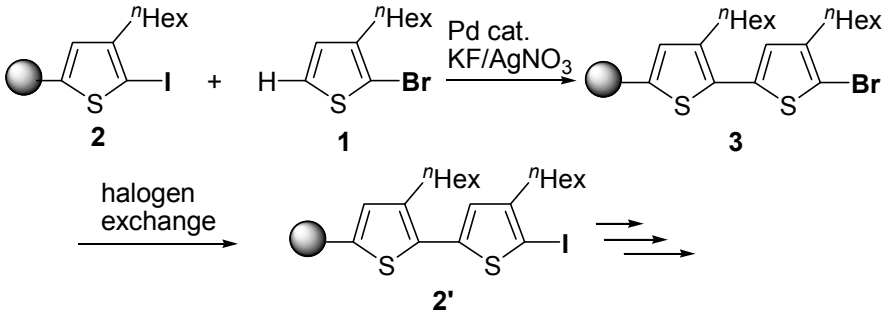
Thereby, a new synthetic strategy for HT oligothiophenes based on the CH coupling, which improves synthetic diversity efficiently, is intriguing.[10] In addition, recent progress of the HT-type oligothiophenes as materials for organic dye-sensitized[11,12] and thin-film[13] photovoltaic batteries as well as organic TFTs[1c] prompted us to develop a facile synthetic pathway for such materials. We herein describe stepwise synthesis of HT regioregular oligothiophenes via iterative palladium-catalyzed CH arylation and halogen exchange reactions leading to the oligomers bearing 2-4 thiophene units.[14]



Scheme 1

RESULTS AND DISCUSSION

Synthetic strategy of the HT-type oligothiophene based on the CH arylation of a 2-bromothiophene derivative at the CH bond is illustrated in Scheme 2. Since palladium-catalyzed CH arylation of heteroaromatic compounds we have shown selectively takes place with an aryl iodide, cross coupling of thiophene and thiophene forms HT bithiophene **3** bearing C–Br bond when the reaction of bromothiophene **1** and iodothiophene **2** is employed. Accordingly, halogen exchange of **3** into iodide **2'** and following coupling with **1** bring about additional extension of a thiophene unit and the iterative reactions would lead to HT oligothiophenes.

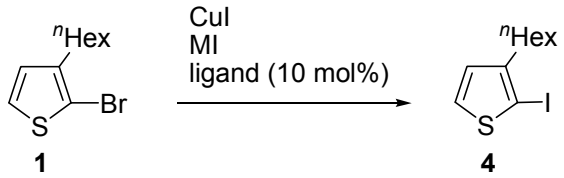


Scheme 2

We first studied the halogen exchange reaction of 2-bromo-3-hexylthiophene **1** leading to 3-hexyl-2-iodothiophene (**4**). Buchwald has shown that halogen exchange of aryl bromide takes place with sodium iodide in the presence of a catalytic amount of CuI, where sevral diamine ligands are effective to undergo the reaction, to afford the corresponding iodide.[15] Thus, we employed such reaction conditions toward the transformation of **1** into **4**. When the reaction of **1** was carried out with 2 equiv. of NaI in the presence of a catalytic amount of CuI with *N,N'*-dimethylethylenediamine under similar conditions shown in the literature, the reaction occurred to afford **4** in 78% yield. The reaction was also performed with several diamine derivatives. The results are summarized in Table 1.

Although the exchange reaction proceeded in moderate to good yields, we found that it is difficult to achieve quantitative conversion of the bromide into the corresponding iodide. Since separation of bromide **1** and iodide **4** by silica gel column chromatography is difficult, the result causes problems to perform further extension of the thiophene ring leading to oligothiophenes. Alternatively, it was found that complete conversion was successful when the transformation reaction was carried out with excess amounts of copper(I) iodide under heterogeneous conditons, which was employed by Yamashita to achieve transformation of an aromatic bromide into iodide.[16] After optimization of the conditions as shown in Table 1, almost complete conversion of **1** was achieved with 10 equiv. of CuI and 10 equiv. of LiI in DMSO at 150 ºC to isolate **4** in 97% yield.

Table 1. Halogen exchange reaction with copper(I) iodide



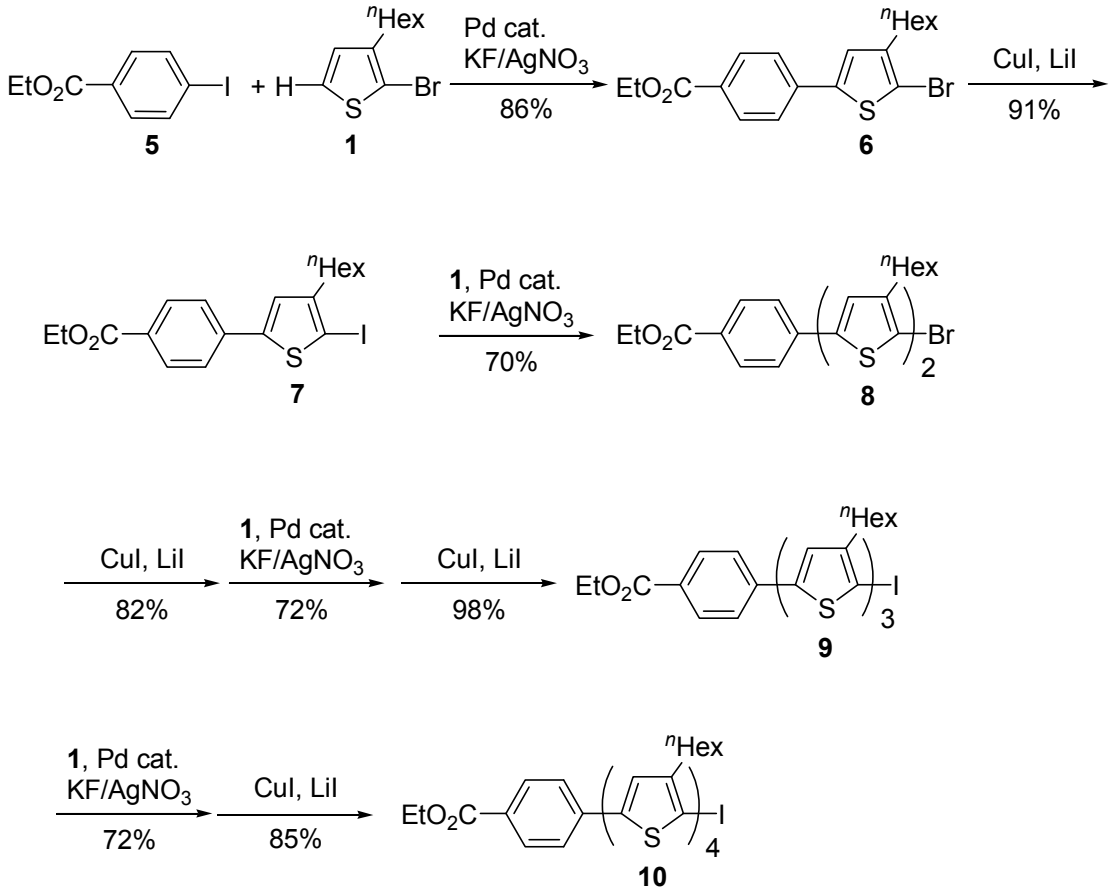
1 **4**

entry	CuI/ eq	MI (eq)	ligand	solvent (mL/mmol)	temp/ ºC	time/ h	yield/ %
1	0.05	NaI (2)	ethylene diamine	1,4-dioxane (2)	110	22	39
2	0.05	NaI (2)	*N,N*-dimethyl glycine	1,4-dioxane (4)	110	22	2
3	0.05	NaI (2)	1,2-diamino cyclohexane	1,4-dioxane (2)	110	22	9
4	0.05	NaI (2)	*N,N'*-Dimethyl ethylenediamine	1,4-dioxane (2)	110	22	78
5	5.0	-	-	DMSO (12)	150	2	81
6	1.0	LiI (4)	-	DMSO (12)	100	4	14
7	5.0	LiI (5)	-	DMSO (12)	100	4	9
8	5.0	LiI (5)	-	DMSO (12)	150	25	94
9	10.0	LiI (10)	-	DMSO (12)	150	25	97
10	2	LiI (8)	-	DMSO (12)	150	13	64

[a] The reaction was carried out with 2-bromo-3-hexylthiophene under a nitrogen atmosphere using a Schlenk tube. Progress of the reaction was monitored by GC analysis of the reaction mixture.

Synthesis of HT-type oligothiophene bearing an ester group was carried out with palladium-catalyzed CH arylation and copper-mediated halogen exchange protocols. Scheme 3 shows the synthetic pathway of the head-to-tail oligothiophene bearing four thiophene units and 4-(ethoxycarbonyl)phenyl group at the end group. The reaction of ethyl 4-iodobenzoate **5** with bromothiophene **1** in the presence of $PdCl_2(PPh_3)_2$ (5 mol%) and $AgNO_3$/KF proceeded smoothly to afford the bromothiophene bearing the aryl group **6** in an excellent yield. The obtained bromothiophene derivative **6** was subjected to the halogen exchange reaction, whose conditions were optimized in the model study, to afford iodothiophene **7** in 91% yield. The CH arylation reaction of **7** with **1** was performed in a similar manner to the reaction of **5** to afford the corresponding HT bithiophene **8**. Since CH arylation with aryl iodide bearing an electron-donating substituent has been shown to proceed with inferior yield to that with electron-deficient arenes, thienyl iodide that is recognized as an electron-enriched substrate would result in a lower yield.[9b] Indeed, the arylation reaction of **7** under similar conditions to that for **5** resulted in a low yield (26%). However, a slight modification of the conditions by a reduced amount of the solvent and repeating addition of

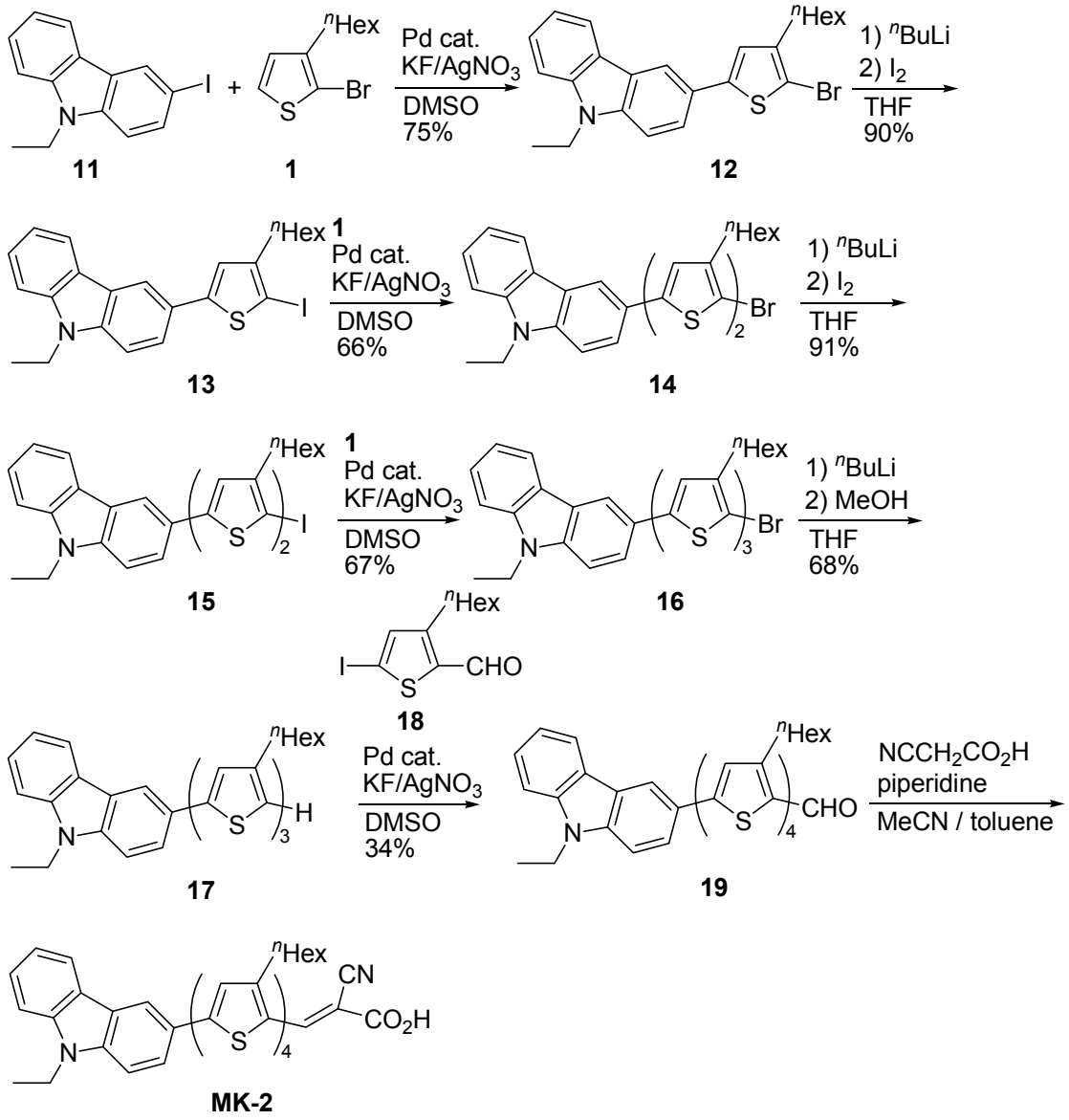
$AgNO_3$/KF improved the yield of **8** to 70%. By the iterative halogen-exchange reaction and palladium-catalyzed CH arylation in a similar manner, synthesis of HT-type oligothiophenes up to the tetramer **10** was successfully achieved.



Scheme 3

We then examined the synthesis of oligothiophene bearing a carbazole moiety. **MK-2** bearing carbazole as a donor and cyanoacrylic acid as an acceptor acts as a sensitizer for dye-sensitized solar cells (DSSCs), that we have previously reported.[11a] Introduction of the carbazole group was performed by the palladium-catalyzed CH arylation of 2-bromo-3-hexylthiophene **1** with *N*-ethyl-3-iodocarbazole **11** in the presence of silver(I) nitrate/KF to obtain the corresponding coupling product **12** in 75% yield. Although the halogen exchange reaction with excess amounts of copper salt was employed for the reaction of **12**, we only obtained the corresponding iodide **13** in only 21% yield, which would be due to the complexation of the copper reagent to the amino group of carbazole. However, transformation of the bromide into iodide was carried out with bromine–lithium exchange with *n*-butyllithium and following treatment of iodine at -78 ºC. The reaction proceeded smoothly to afford **13** in 90% yield. The CH coupling reaction of thus obtained **13** with bromothiophene **1** was carried out in the presence of the palladium catalyst and

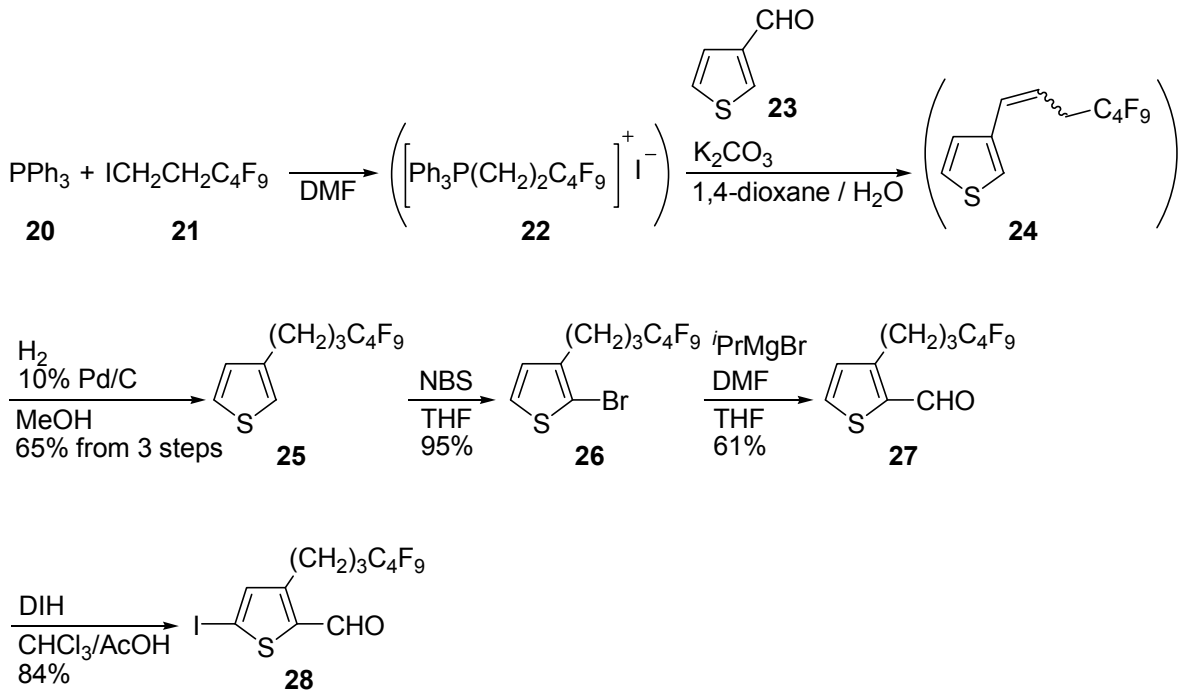
$AgNO_3$/KF to obtain bithiophene **14** (66% yield). Transformation into iodide **15** similarly proceeded (91%). As shown in Scheme 4, further extension of the thiophene unit was similarly successful to afford up to the corresponding trimer **16**, which was subjected to protonolysis and CH arylation with thienyl aldehyde **18** to give the tetramer **19**. The obtained **19** was identical with the corresponding precursor of the dye molecule **MK-2**. Transformation of **19** was shown to be performed by Knoevenagel reaction of the formyl group with cyanoacetic acid leading to **MK-2** as reported.[11b]



Scheme 4

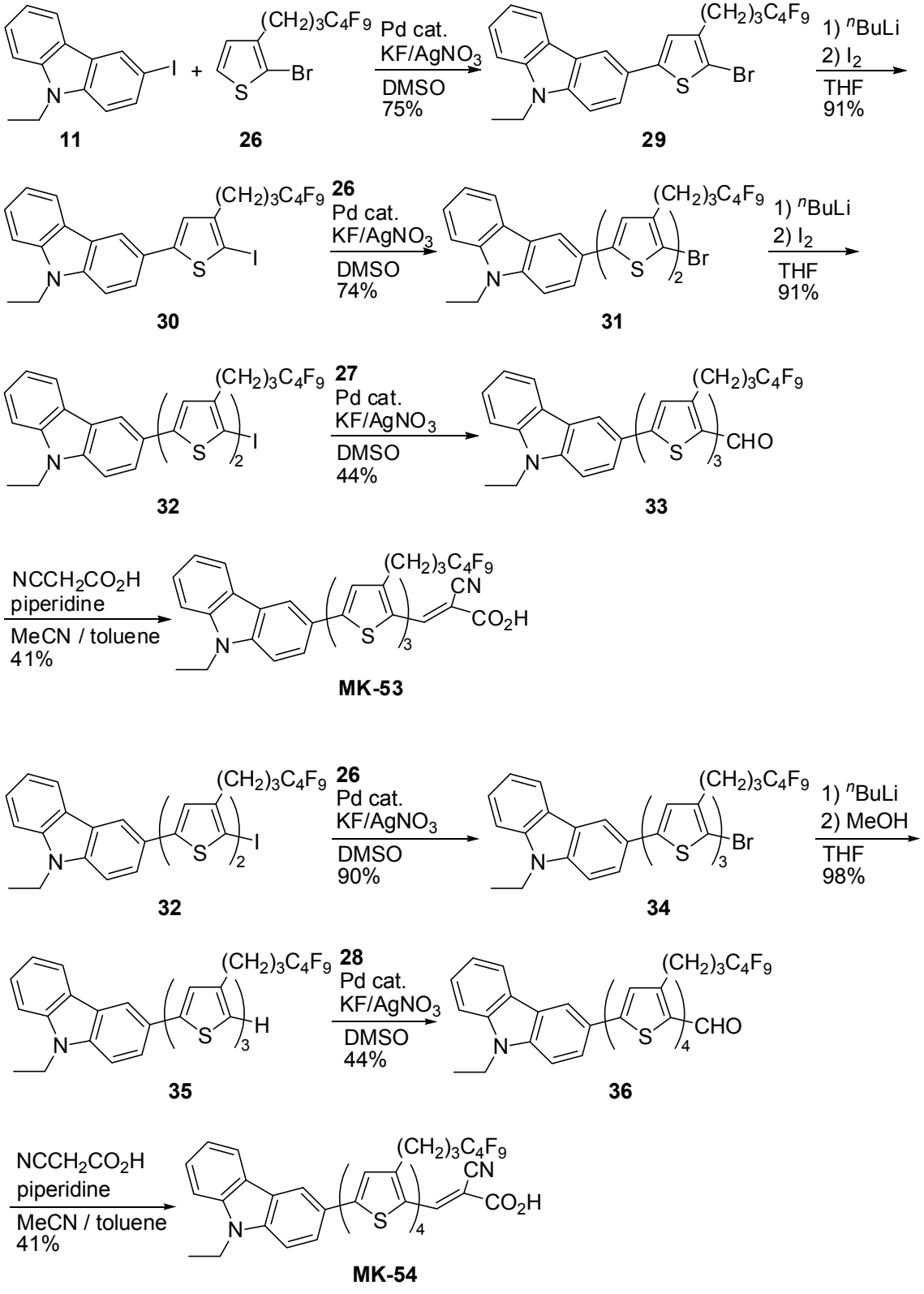
Effect of the substituent at the 3-position of the thiophene ring plays key role in the design of HT-type oligothiophene to achieve high performance as materials, namely, to improve the planarity between the thiophene rings for the extension of π-conjugation, solubility of oligothiophene in organic solvents by

suppressing intermolecular interaction of oligothiophene molecules. It is thereby intriguing that modification of the structure of the substituent of thiophene. We envisaged that introduction of poly-fluorinated alkyl group into the thiophene ring show remarkable characteristics and designed $–(CH_2)_3–(CF_2)_3–CF_3$ group, which may improve intermolecular repulsion by the effect of the fluorine atom.[17] Nevertheless, electron-negative effect of fluorine would not influence the electronic characteristics to oligothiophene by the introduction of alkyl spacer group, $–(CH_2)_3–$, at the thiophene ring. Synthesis of such thiophene derivative **25** was carried out with Wittig reaction of the phosphonium salt **22** with 3-formylthiophene (**23**) and following catalytic hydrogenation of the carbon–carbon double bond with Pd/C.[18] Further transformation reactions of **25** into **26-28** were performed as shown in Scheme 5.



Scheme 5

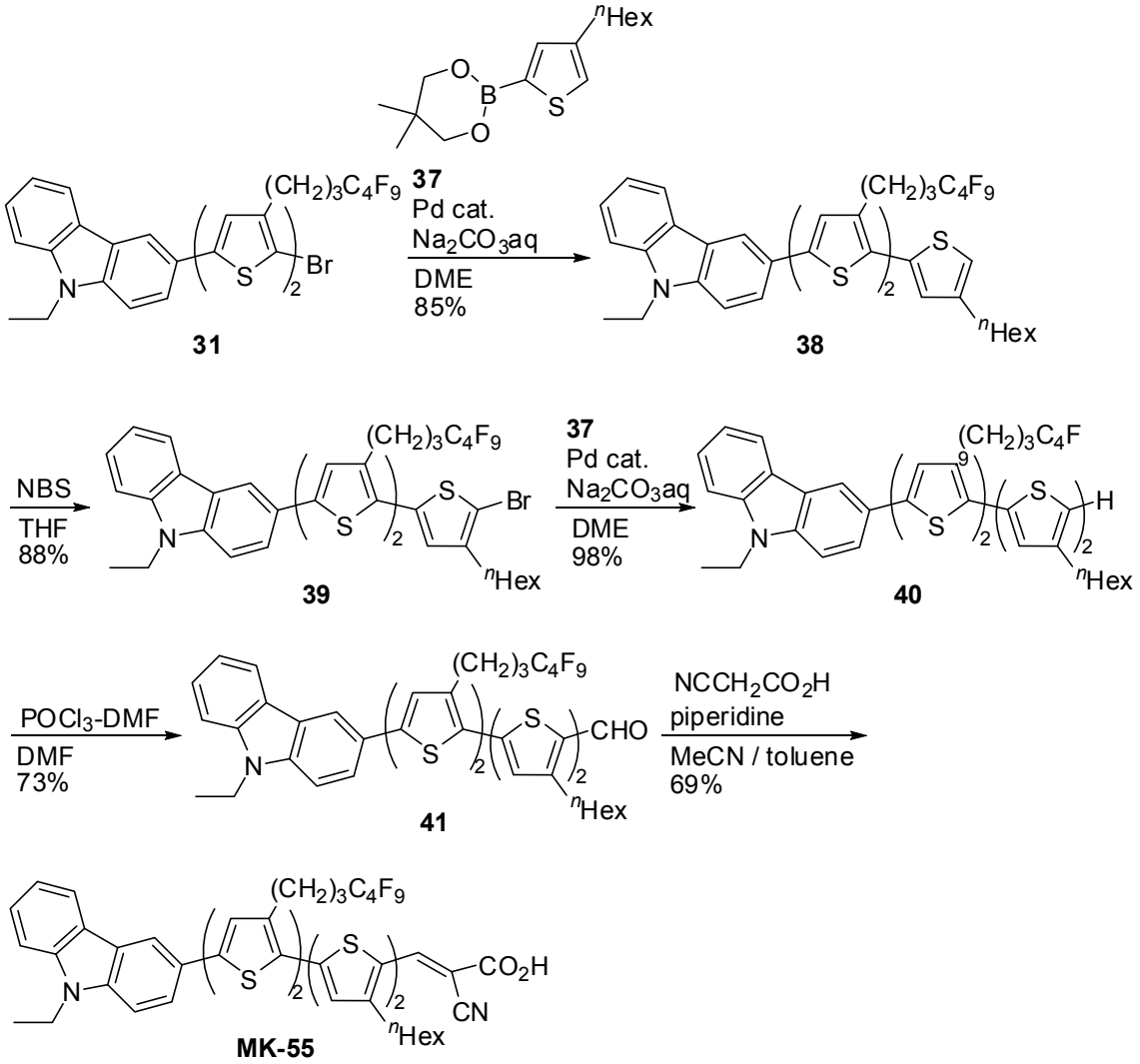
Oligothiophene synthesis with thus obtained 3-substituted thiophene **MK-53, MK-54** was carried out as outlined in Schme 6. The CH arylation reaction of bromothiophene derivatives bearing a fluoroalkyl substituent and the following halogen exchange with $^{n}BuLi/I_2$ occured similarly to the case of the hexylthiophene derivatives. The reaction of **32** and **35** with 2-formylthiophene **27** and the following reaction with cyanoacetic acid also proceeded similarly leading to **MK-53**, **MK-54**, respectively.



Scheme 6

It was also possible to synthesize HT oligothiophene bearing partly fluoroalkylated and partly alkylated moieties as shown in Scheme 7. Synthesis of bithiophenebromide **31** was performed in a similar manner

shown in Scheme 6. The obtained bithiophenebromide **31** was subjected to Suzuki-Miyaura coupling[19] of a 2-boronic acid ester of 4-hexylthiophene **37** in the presence of a palladium catalyst to afford terthiophene **38**, which contains two fluoroalkylated and one alkylated thiophene rings, in 85% yield. Bromination of **38** with NBS and further coupling of the boron reagent **37** afforded the corresponding tetramer composed of two fluoroalkylated and two alkylated thiophenes **40** in a quantitative yield. Introduction of the formyl group with Vilsmeier reaction and the following Knoevenagel reaction with cyanoacetic acid afforded **MK-55** in 73% and 69% yields, respectively.[11b]



Scheme 7

Studies on the properties of the obtained oligothiophenes **MK-53**, **MK-54** and **MK-55** were carried out. Table 2 summarizes the results. Measurements of UV-vis absorption and photoluminescent spectra indicated that there was little difference of the wavelengths from the structure of the substituent at the 3-position. This is due to the introduction of alkylene spacer connected to the thiophene ring to avoid the

influence of the electronegative effect of the perfuluoroalkyl group into oligothiophene. The energy conversion efficiency of oligothiophenes (η) was also preliminary measured. Although the η value of **MK-53** and **MK-54** was lower than that of **MK-2**, it was found to slightly improve the value of **MK-55** (6.5%). Further investigation of photovoltaic performances of solar cells with **MK-53**, **MK-54**, and **MK-55** is to be described in due course.

Table 2. Spectroscopic and photovoltaic battery properties of oligothiophenes.

Compound	λ_{max} (nm) [a]	ε ($M^{-1}\cdot cm^{-1}$)	Em (nm) [b]	η [c]
MK-2	480	38800	-	6.3
MK-53	474	31800	604	5.5
MK-54	462	32500	607	4.4
MK-55	467	39400	601	6.5

a) Absorption maxima of UV-vis spectra (nm): Measured as a 2.22 x 10^{-4} M (**MK-2**), 1.64 x 10^{-4} M (**MK-53**), 1.30 x 10^{-4} M (**MK-54**) and 2.52 x 10^{-4} M (**MK-55**) 20% THF-toluene solution. b) Emission maxima of photoluminescent spectra: Measured as 1.34 x 10^{-5} M (**MK-53**), 9.20 x 10^{-6} M (**MK-54**) and 2.28 x 10^{-5} M (**MK-55**) 20% THF-toluene solution. c) Overall energy conversion efficiency: Fabrication and measurement as a solar cell were performed as described in ref 11e.

CONCLUSION

In conclusion, several oligothiophens are synthesized in a stepwise manner involving palladium-catalyzed CH arylation and halogen exchange sequence. Extension of the thiophene ring was successfully performed with characteristics of the iodide specific CH coupling by the effect of $AgNO_3$/KF as an additive system to remain the carbon–bromine bond on the thiophene ring being intact and efficient halogen exchange reaction. With this methodology synthesis of oligothiophenes bearing each different substituent would be successfully performed allowing the synthesis of well-defined oligothiophenes of complex structure in a facile manner.

EXPERIMENTAL

General: ^{1}H NMR (400 MHz, 500 MHz) and ^{13}C NMR (100 MHz, 125 MHz) spectra were measured on a Bruker Avance 400 or 500 spectrometer. The chemical shifts were expressed in ppm with $CHCl_3$ (7.26 ppm for ^{1}H) or $^{13}CDCl_3$ (77.0 ppm for ^{13}C) as internal standards. IR spectra were recorded on PERKIN ELMER FT-IR Spectrometer SPECTRUM 1000, JASCO FT/IR-660 plus Fourier Transform Infrared Spectrometer, or Bruker Alpha with an ATR attachment (Ge). High-resolution mass spectra (EI, FAB, or ESI) were measured by JEOL JMS-700 MStation at the Graduate School of Material Science, Nara

Institute of Science and Technology. For thin layer chromatography (TLC) analyses throughout this work, Merck precorted TLC plates (silica gel 60 F254) were used. UV-vis spectra were measured with SHIMADZU UV-3101PC. Photoluminescent spectra were measured with HITACHI F-7000. 1,3-Diiodo-5,5-dimethylhydantoin (DIH) was kindly donated by Nippoh Chemicals Co. Ltd. THF, DMSO, 1,4-dioxane, diethyl ether, acetonitrile, toluene, and DMF (anhydrous grade) were purchased from Wako Pure Chemicals Co. Ltd, or Kanto Chemicals Co. Ltd. and stored under nitrogen atmosphere. Fabrication of solar cells and measurements of the photovoltaic performances were carried out in similar manners to those shown in our previous works.[11e]

2-Bromo-5-(4-ethoxycarbonylphenyl)-3-hexylthiophene (6): To a 25 mL schlenk tube equipped with a magnetic stirring bar were added $PdCl_2(PPh_3)_2$ (8.8 mg, 0.01 mmol), 2-bromo-3-hexylthiophene **1** (0.07 mL, 0.3 mmol), ethyl 4-iodobenzoate (**5**, 69 mg, 0.25 mmol), potassium fluoride (18.2 mg, 0.31 mmol), and anhydrous DMSO (3 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 100 °C for 5 h. Silver nitrate (10.6 mg, 0.31 mmol) was then added in five portions with 1 h interval. After cooling to room temperature, the mixture was passed through a Celite pad, which was washed repeatedly with $CHCl_3$. The filtrate was washed with water twice (50mL x 2) and brine. Then the organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel using hexane:AcOEt (20:1) as an eluent to afford 85 mg of **15** as a yellow solid (86% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (3H, t, *J* = 7.2 Hz), 1.33 (6H, m), 1.40 (3H, t, *J* = 7.1 Hz), 1.61 (2H, t, *J* = 7.5 Hz), 2.57 (2H, t, J = 7.5 Hz), 4.38 (2H, q, J = 7.3 Hz), 7.10 (1H, s), 7.55 (2H, d, J = 8.5 Hz), 8.02 (2H, d, J = 8.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 14.5, 22.7, 29.1, 29.8, 31.8, 61.2, 110.1, 125.1, 125.4, 129.5, 130.4, 138.1, 142.5, 143.7, 166.3; IR (neat) 1108, 1185, 1276, 1442, 1606, 1715, 2856, 2925 cm^{-1}; HRMS (EI+) Calcd for $C_{19}H_{23}BrO_2S$: 394.0602 ; found: m/z 394.0602.

2-Iodo-5-(4-ethoxycarbonylphenyl)-3-hexylthiophene (7): To a 100 mL of schlenk tube equipped with a magnetic stirring bar were added **6** (0.874 g, 2.21 mmol) and 25 mL of anhydrous DMSO under a nitrogen atmosphere. To the solution were added copper(I) iodide (4.2 g, 22.1 mmol) and lithium iodide (2.96 g, 22.1 mmol) and the mixture was stirred at 150 °C for 25 h. After cooling to room temperature, the mixture was poured into water. The mixture was passed through a Celite pad and the cake was washed with $CHCl_3$ repeatedly. The filtrate was washed with aqueous $Na_2S_2O_3$ and water (100mL x 3). The organic layer was dried over anhydrous sodium sulfate. Removal of the dried solvent left a crude solid, which was purified by chromatography on silica gel using hexane:AcOEt (20:1) as an eluent to afford 0.941 g of **7** as an orange solid (96% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (3H, t, *J* = 6.7 Hz),

1.25-1.45 (9H, m), 1.61 (2H, t, *J* = 7.5 Hz), 2.55 (2H, t, *J* = 7.6 Hz), 4.38 (2H, q, *J* = 7.3 Hz), 7.05 (1H, s), 7.56 (2H, d, *J* = 8.2 Hz), 8.03 (2H, d, *J* = 8.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 14.5, 22.7, 29.1, 30.1, 31.8, 32.6, 61.2, 75.5, 125.1, 125.2, 129.6, 130.4, 138.1, 147.6, 148.8, 166.3; IR (neat) 1108, 1185, 1277, 1607, 1711, 2931 cm^{-1}; HRMS (EI+) Calcd for $C_{19}H_{23}IO_2S$: 442.0463; found: m/z 442.0459.

Ethyl 4-(5'-bromo-3,4'-dihexyl-2,2'-bithiophen-5-yl)benzoate (8): The reaction carried out in a similar manner to the synthesis of **6** (70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (6H, t, d, *J* = 6.9, 2.5 Hz), 1.28-1.42 (15H, m), 1.57-1.69 (4H, m), 2.57 (2H, t, *J* = 7.6 Hz), 2.72 (2H, t, *J* = 7.9 Hz), 4.39 (2H, q, *J* = 7.3 Hz), 6.85 (1H, s), 7.23 (1H, s), 7.62 (2H, d, *J* = 8.2 Hz), 8.03 (2H, d, *J* = 8.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) 14.2, 14.5, 22.8, 29.1, 29.4, 29.6, 29.7, 29.8, 30.7, 31.8, 31.8, 61.1, 109.1, 125.2, 127.0, 127.5, 129.3, 130.4, 131.3, 135.4, 138.2, 140.8, 141.2, 142.7, 166.4; IR (neat) 1281, 1368, 1605, 1706, 2852, 2920, 2951 cm^{-1}; HRMS (EI+) Calcd for $C_{29}H_{37}BrO_2S_2$: 560.1418; found: m/z 560.1408.

Ethyl 4-(3,4',4''-trihexyl-5''-iodo[2,2',5',2'']terthiophen-5-yl)benzoate (9): The reaction was carried out by sequential halogen exchange of **7**, CH arylation with **1**, and further halogen exchange.(overall yield: 58%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87-0.93 (9H, m), 1.24-1.44 (21H, m), 1.57-1.72 (6H, m), 2.55 (2H, t, *J* = 7.7 Hz), 2.72 (2H, t, *J* = 7.9 Hz), 2.79 (2H, t, *J* = 7.9 Hz), 4.39 (2H, q, *J* = 7.1 Hz), 6.79 (1H, s), 6.98 (1H, s), 7.26 (1H, s), 7.64 (2H, d, *J* = 8.5 Hz), 8.04 (2H, d, *J* = 8.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) 14.2, 14.4, 22.7, 22.7, 22.7, 29.0, 29.3, 29.3, 29.4, 29.7, 30.0, 30.6, 30.6, 31.7, 31.7, 32.4, 41.1, 61.1, 70.7, 74.2, 125.1, 126.5, 127.6, 128.7, 128.8, 129.1, 130.3, 130.4, 131.7, 134.0, 138.2, 140.3, 140.4, 140.4, 140.9, 147.7, 166.3; IR (neat) 1112, 1268, 1604, 1707, 2855, 2925, 2952; HRMS (EI+) Calcd for $C_{39}H_{51}IO_2S_3$: 774.2096; found: m/z 774.2089.

Ethyl 4-(3,4',4'',4'''-tetrahexyl-5'''-iodo[2,2',5',2'',5'',2''']quaterthiophen-5-yl)benzoate (10): The reaction was carried out by CH arylation of **1** and further halogen exchange.(overall yield: 58%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91-0.98 (12H, m), 1.30-1.50 (27H, m), 1.60-1.77 (8H, m), 2.57 (2H, t, *J* = 7.6 Hz), 2.74 (2H, t, *J* = 7.9 Hz), 2.76-2.84 (4H, m), 4.41 (2H, q, *J* = 7.1 Hz), 6.82 (1H, s), 6.98 (1H, s), 7.02 (1H, s), 7.26 (1H, s), 7.64 (2H, d, *J* = 8.2 Hz), 8.06 (2H, d, *J* = 8.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ14.22, 14.24, 14.5, 22.75, 22.78, 29.1, 29.2, 29.35, 29.40, 29.42, 29.6, 29.7, 29.8, 30.1, 30.5, 30.59, 30.62, 30.65, 30.67, 31.79, 31.82, 32.5, 61.0, 74.1, 108.8, 125.0, 126.4, 126.7, 127.2, 127.6, 128.5, 128.6, 128.9, 129.1, 130.2, 130.28, 130.31, 130.7, 131.9, 133.9, 134.1, 135.5, 135.6, 138.2, 138.3, 140.0, 140.2, 140.25, 140.27, 140.6, 140.8, 142.6, 147.7, 166.3; IR (neat) 1112, 1188, 1267, 1467, 1604, 1717, 2855, 2924 cm^{-1}; HRMS (FAB+) Calcd for $C_{49}H_{65}IO_2S_4$: 940.2912; found: m/z 940.2920.

CH functionalization of 2-bromo-3-hexylthiophene (1) with *N*-ethyl-3-iodo-carbazole (11) leading to

12: To a 25 mL schlenk tube equipped with a magnetic stirring bar were added $PdCl_2(PPh_3)_2$ (88.8 mg, 0.13 mmol), 2-bromo-3-hexylthiophene **1** (0.65 mL, 3.04 mmol), *N*-ethyl-3-iodo-carbazole (**5**) (814 mg, 2.53 mmol), potassium fluoride (368 mg, 6.33 mmol), and anhydrous DMSO (10 mL) under a nitrogen atmosphere. The reaction was stirred at 100 °C for 5 h. Silver nitrate (215 mg, 1.27 mmol) was then added in five portions with an hour interval. After cooling to room temperature, the mixture was passed through a Celite pad, which was washed repeatedly with $CHCl_3$. The filtrate was washed with water twice (50mL x 2) and brine. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel using hexane:AcOEt (50:1) as an eluent to afford 839 mg of **12** as a yellow solid (75% yield).

9-Ethyl-3-(5-iodo-3-*n*-hexylthiophene2-yl)-9-*H*-carbazole (13): To a 25 mL schlenk tube equipped with a magnetic stirring bar were added **6** (570 mg, 1.3 mmol) and anhydrous THF (10 mL). Then, a hexane solution of *n*-BuLi (1.57 M, 1 mL) was added dropwise at -78 ºC under a nitrogen atmosphere. After stirring for 30 min, iodine (660 mg, 2.6 mmol) was added to the resulting solution and stirring was continued for further 30 min at room temperature. The mixture was poured into 5 mL of water and the organic phase was separated. Aqueous was extracted with diethyl ether (30 mL x 2). The combined organic layer was dried over anhydrous sodium sulfate and concentrated to leave a crude oil. Purification by column chromatography on silica gel using hexane:AcOEt (50:1) as an eluent afforded 570 mg of **7** as a colorless solid (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (3H, t, J = 6.8 Hz), 1.30-1.43, (6H, m), 1.45 (3H, t, J = 7.4 Hz), 1.62-1.67 (2H, m), 2.59 (2H, br t, J = 7.7 Hz), 4.37 (2H, q, J = 7.2 Hz), 7.01 (1H, s), 7.26 (1H, dd, J = 14.9, 0.8 Hz), 7.38 (1H, br d, J = 8.2 Hz), 7.42 (1H, br d, J = 8.2 Hz), 7.50 (1H, ddd, J = 8.2, 7.1, 0.9 Hz), 7.64 (1H, dd, J = 8.6, 1.7 Hz), 8.13 (1H, br d, J = 8.2 Hz), 8.24 (1H, d, J = 1.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 14.3, 22.8, 29.1, 30.2, 31.8, 32.7, 37.8, 71.7, 108.8, 108.9, 117.7, 119.3, 120.7, 122.9, 123.0, 123.5, 124.0, 125.4, 126.2, 139.8, 140.6, 148.4, 150.3; IR (neat) 1151, 1236, 1330, 1344, 1444, 1470, 1490, 1598, 2852, 2924, 2949, 3043 cm^{-1}; HRMS (EI+) Calcd for $C_{24}H_{26}INS$: 487.0831; found: m/z 487.0824.

CH arylation of 1 with 13 leading to 14: The reaction was performed in a similar manner to the synthesis of **5** (66% yield).[11b]

9-Ethyl-3-(5'-iodo-3',4-di-*n*-hexyl[2,2']bithiophen-5-yl)-9-*H*-carbazole (15): The reaction was performed in a similar manner to the synthesis of **13** (91% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85-0.94 (6H, m), 1.23-1.43 (12H, m), 1.45 (3H, t, J = 7.1 Hz), 1.60-1.74 (4H, m), 2.56 (2H, br t, J = 7.8 Hz), 2.75 (2H, br t, J = 7.9 Hz), 4.38 (2H, q, J = 7.2 Hz), 6.82 (1H, s), 7.17 (1H, s), 7.25-7.27 (1H, m), 7.40 (1H, br d, J = 8.6 Hz), 7.42 (1H, br d, J = 8.4 Hz), 7.49 (1H, ddd, J = 8.4, 7.0, 0.9 Hz), 7.70 (1H, dd,

J = 8.6, 1.5 Hz), 8.14 (1H, br d, *J* = 7.6 Hz), 8.29 (1H, d, *J* = 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 14.3, 22.7, 22.8, 29.1, 29.4, 29.7, 30.1, 30.8, 31.8, 31.9, 32.5, 37.7, 73.5, 108.7, 108.8, 117.6, 119.2, 120.7, 123.0, 123.5, 124.0, 124.9, 125.3, 126.0, 126.1, 128.5, 139.7, 140.5, 141.0, 141.4, 143.8, 147.6; IR (neat) 1152, 1235, 1344, 1454, 1491, 1597, 2852, 2923, 2950, 3044 cm^{-1}; HRMS (EI+) Calcd for $C_{34}H_{40}INS_2$: 653.1647; found: m/z 653.1649.

Debromination of 16 leading to 17: To a 25 mL schlenk tube equipped with a magnetic stirring bar were added **16** (67.7 mg, 0.088 mmol) and anhydrous Et_2O (2 mL). Then, a hexane solution of ^{n}BuLi (1.57 M, 1 mL) was added dropwise at -78 ºC under a nitrogen atmosphere. After stirring for 30 min, MeOH (1 mL) was added to the resulting solution and stirring was continued for further 30 min. The mixture was poured into 5 mL of water and the organic phase was separated. Aqueous was extracted with diethyl ether (30 mL x 2). The combined organic layer was dried over anhydrous sodium sulfate and concentrated to leave a crude oil. Purification by column chromatography on silica gel using hexane:AcOEt (50:1) as an eluent afforded 41.1 mg of **17** as a colorless solid (68% yield).

3-Hexyl-5-iodo-2-thiophenecarbaldehyde (18): To a 25 mL of schlenk tube were added 3-hexyl-2-thiophenecarboaldehyde[20] (98.2 mg, 0.5 mmol), acetic acid (1.5 mL), and $CHCl_3$ (5 mL). To the solution was added NIS (135 mg, 0.6 mmol) and stirring was continued at 0 ºC for 18 h. The mixture was poured into 10 mL of water and the organic phase was separated. Aqueous was extracted with hexane (20 mL x 2). The combined organic layer was dried over anhydrous sodium sulfate and concentrated to leave a crude oil. Purification by column chromatography on silica gel using hexane:AcOEt (5:1) as an eluent afforded 147 mg of **11** as a pale yellow solid (65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.8 Hz), 1.27-1.37 (6H, m), 1.64 (2H, t, *J* = 7.7 Hz), 2.90 (2H, t, *J* = 7.7 Hz), 7.18 (1H, s), 9.87 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 22.6, 28.2, 29.0, 31.4, 31.6, 87.3, 140.7, 143.8, 153.9, 180.6; IR (ATR) 838, 990, 1217, 1250, 1369, 1391, 1417, 1463, 1528, 1656, 2856, 2926, 2953 cm^{-1}; Calcd for $C_{11}H_{15}IOS$: 321.9888; found: m/z 321.9890.

3-(4,4,5,5,6,6,7,7,7-Nonafluoroheptyl)thiophene (25): Ph_3P (8.73 g, 33 mmol, $ICH_2CH_2C_4F_9$ (11.19 g, 30 mmol) was dissolved in 16 mL of DMF and the mixture was stirred vigorously for 24 h at 105 °C. DMF was removed under reduced pressure. The waxy solid was triturated with diethyl ether, collected by filtration, washed with diethyl ether, and dried under reduced pressure to give 17.9 g of **21** as a white solid, which was used for the following reaction without further purification. Crude **21**, 3-formylthiophene (**22**: 2.47 mL, 28.14 mmol), and K_2CO_3 (5.06 g, 36.58 mmol), was dissolved in 1,4-dioxane (150 mL) and H_2O (6 mL). The resulting mixture was stirred at 95 °C for 20 h. The solvents were removed under reduced pressure, and CH_2Cl_2 (50 mL) and H_2O (50 mL) were added to the orange

residue. The aqueous layer was extracted with CH_2Cl_2 (50 mL) and the organic layers were combined and dried over anhydrous sodium sulfate. Removal of the solvent by rotary evaporator under reduced pressure left an oily solid, which was purified by short-path silica gel chromatography with hexanes to give 7.45 g **23** as a yellow oil. To a Schlenk flask with a magnetic stirring bar were added with **23**, 10% Pd/C (0.676 g, 0.63 mmol), and MeOH (80 mL). The resulting mixture was stirred under H_2 atmosphere for 24 h at room temperature. After the reaction was complete, the mixture was filtered through Celite pad. The filtrate was concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel using hexane as an eluent to give 6.63 g of **24** as a colorless oil (overall yield: 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.89-2.00 (2H, m), 2.02-2.15 (2H, m), 2.74 (2H, t, *J* = 8.3 Hz), 6.94 (1H, dd, *J* = 5.0, 1.2 Hz), 6.96-6.99 (1H, m), 7.29 (1H, dd, *J* = 5.0, 3.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) (partial) δ 21.3, 29.6, 30.2, 30.4, 30.6, 120.8, 126.0, 127.9, 141.1; IR (ATR) 718, 768, 880, 1010, 1132, 1220 cm^{-1}; HRMS (EI+) Calcd for $C_{11}H_9F_9S$: 344.0281; found: m/z 344.0277.

2-Bromo-3-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)thiophene (**26**): To a 500 mL of Schlenk tube equipped with a magnetic stirring bar were added **3c** (6.63 g, 19.3 mmol) and 100 mL of THF. The resulting colorless solution was cooled in an ice bath and NBS (3.56 g, 20 mmol) was added in five portions with 1 h interval. Stirring was continued at 0 °C for 5 h and the mixture was poured into water. Aqueous layer was extracted with hexane, the combined organic layer was dried over anhydrous sodium sulfate, and then concentrated under vacuum. An oily residue was purified by chromatography on silica gel using hexanes and following distillation under reduced pressure to afford 7.71g of **26** as a colorless oil (95% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87-2.00 (2H, m), 2.02-2.16 (2H, m), 2.69 (2H, t, *J* = 7.7 Hz), 6.81 (1H, d, *J* = 5.5 Hz), 7.24 (1H, d, *J* = 5.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) (partial) δ 20.6, 28.7, 29.6, 30.2, 30.3, 30.5, 110.0, 126.1, 127.9, 140.0, 142.2, 145.5; IR (ATR) 720, 878, 1008, 1132, 1218 cm^{-1}; HRMS (EI+) Calcd for $C_{11}H_8BrF_9S$: 421.9386; found: m/z 421.9388.

3-(4,4,5,5,6,6,7,7,7-Nonafluoroheptyl)-2-thiophenecarbaldehyde (**27**): To a 50 mL schlenk tube equipped with a magnetic stirring bar were added **26** (2.12 g, 5.0 mmol) and anhydrous THF (15 mL). A THF solution of ^{i}PrMgBr (0.78 M, 8.3 mL) was then added dropwise at -40 ºC under a nitrogen atmosphere. After stirring for 30 min, DMF (5 mL) was added to the resulting solution and stirring was continued for further 30 min. The mixture was poured into 5 mL of water and the organic phase was separated. Aqueous was extracted with diethyl ether (50 mL x 2). The combined organic layer was dried over anhydrous sodium sulfate and concentrated to leave a crude oil. Purification by column chromatography on silica gel using hexane:AcOEt (5:1) as an eluent afforded 1.13 g of **27** as a colorless oil (61% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.96-2.06 (2H, m), 2.07-2.21 (2H, m), 3.10 (2H, t, *J* = 7.8

Hz), 7.05 (1H, d, *J* = 5.0 Hz), 7.71 (1H, d, *J* = 5.0 Hz), 10.02 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) (partial) δ 14.1, 14.2, 21.0, 21.8, 22.7, 27.8, 30.1, 30.3, 30.5, 31.7, 60.5, 130.6, 135.0, 138.2, 149.8, 182.0; IR (ATR) 880, 1008, 1132, 1221, 1424, 1663 cm^{-1}; HRMS (EI+) Calcd for $C_{12}H_9F_9OS$: 372.0230; found: m/z 372.0230.

5-Iodo-3-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-2-thiophenecarbaldehyde (**28**): To a 25 mL of schlenk tube were added **27** (395 mg, 1.1 mmol), 0.5 mL of acetic acid, and 0.5 mL of $CHCl_3$. To the solution was added DIH (222 mg, 0.58 mmol) and stirring was continued at room temperature for 24 h. The mixture was poured into 5 mL of water and the organic phase was separated. Aqueous was extracted with diethyl ether (30 mL x 2). The combined organic layer was dried over anhydrous sodium sulfate and concentrated to leave a crude oil. Purification by column chromatography on silica gel using hexane:AcOEt (5:1) as an eluent afforded 443 mg of **28** as a pale yellow solid (84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.94-2.03 (2H, m), 2.07-2.22 (2H, m), 3.04 (2H, t, *J* = 7.9 Hz), 7.21 (1H, s), 9.86 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) (partial) δ 21.9, 27.4, 30.1, 30.3, 30.5, 87.6, 140.3, 144.1, 150.9, 180.1; IR (ATR) 880, 1132, 1220, 1419, 1658 cm^{-1}; HRMS (EI+) Calcd for $C_{12}H_8F_9IOS$: 497.9197; found: m/z 497.9197.

9-Ethyl-3-(5-bromo-4-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)thiophene-2-yl)-9-*H*-carbazole (29): The reaction was performed in a similar manner to the synthesis of **12** (75% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45 (3H, t, *J* = 7.6 Hz), 1.95-2.05 (2H, m), 2.11-2.23 (2H, m), 2.72 (2H, t, *J* = 7.6 Hz), 4.38 (2H, q, *J* = 7.3 Hz), 7.03 (1H, s), 7.24-7.28 (1H, m), 7.40 (1H, br d, *J* = 8.5 Hz), 7.43 (1H, br d, *J* = 8.1 Hz), 7.50 (1H, ddd, *J* = 8.1, 7.3, 0.7 Hz), 7.62 (1H, dd, *J* = 8.5, 1.7 Hz), 8.13 (1H, br d, *J* = 7.8 Hz), 8.22 (1H, d, *J* = 1.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) (partial) δ 13.9, 20.6, 29.1, 30.3, 30.5, 30.6, 37.8, 107.5, 108.9, 109.0, 117.7, 119.4, 120.7, 122.4, 122.9, 123.6, 123.9, 124.9, 126.3, 139.8, 140.6, 140.9, 146.1; IR (ATR) 880, 1007, 1132, 1231 cm^{-1}; HRMS (EI+) Calcd for $C_{25}H_{19}BrF_9NS$: 615.0278; found: m/z 615.0278.

9-Ethyl-3-(5-iode-4-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)thiophene2-yl)-9-*H*-carbazole (30): The reaction was performed in a similar manner to the synthesis of **13** (91% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45 (3H, t, *J* = 7.6 Hz), 1.95-2.05 (2H, m), 2.11-2.23 (2H, m), 2.72 (2H, t, *J* = 7.6 Hz), 4.38 (2H, q, *J* = 7.3 Hz), 7.03 (1H, s), 7.24-7.28 (1H, m), 7.40 (1H, br d, *J* = 8.5 Hz), 7.43 (1H, br d, *J* = 8.1 Hz), 7.50 (1H, ddd, *J* = 8.1, 7.3, 0.7 Hz), 7.62 (1H, dd, *J* = 8.5, 1.7 Hz), 8.13 (1H, br d, *J* = 7.8 Hz), 8.22 (1H, d, *J* = 1.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) (partial) δ 13.9, 20.9, 30.3, 30.5, 30.6, 31.9, 37.8, 72.4, 108.9, 108.9, 117.8, 119.4, 120.7, 122.4, 122.9, 123.5, 124.0, 125.1, 126.3, 139.9, 140.6, 146.1, 151.2; IR (ATR) 802, 847, 884, 1009, 1088, 1128, 1205, 1230, 1273, 1340, 1436, 1470, 1490 cm^{-1}; HRMS (FAB+) Calcd for $C_{25}H_{19}F_9INS$: 663.0139; found: m/z 663.0137.

9-Ethyl-3-(5'-bromo-3,4'-di-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-[2,2']bithiophen-5-yl)-9-*H*-carbazole (31): The reaction was performed in a similar manner to the synthesis of **12** (74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (3H, t, *J* = 7.0 Hz), 1.93-2.07 (4H, m), 2.09-2.22 (4H, m), 2.71 (2H, t, *J* = 7.5 Hz), 2.86 (2H, t, *J* = 7.9 Hz), 4.39 (2H, q, *J* = 7.3 Hz), 6.85 (1H, s), 7.18 (1H, s),7.24-7.28 (1H, m), 7.42 (1H, br d, *J* = 8.3 Hz), 7.43 (1H, br d, *J* = 8.3 Hz), 7.50 (1H, ddd, *J* = 8.3, 7.1, 1.2 Hz), 7.70 (1H, dd, *J* = 8.3, 1.8 Hz), 8.14 (1H, br d, *J* = 7.8 Hz), 8.29 (1H, d, *J* = 1.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) (partial) δ 13.9, 20.5 , 21.4, 28.8, 28.9, 30.2, 30.4, 30.6, 37.8, 108.9, 109.0, 109.5, 117.8, 119.4, 120.7, 123.0, 123.6, 124.0, 124.2, 124.9, 126.3, 126.3, 128.7, 136.4, 139.0, 139.9, 140.6, 140.6, 145.1; IR (ATR) 847, 875, 1009, 1132, 1215, 1271, 1348, 1454 cm^{-1}; HRMS (FAB+) Calcd for $C_{36}H_{26}BrF_{18}NS_2$: 957.0403; found: m/z 957.0403.

9-Ethyl-3-(5'-iode-3,4'-di-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-[2,2']bithiophen-5-yl)-9-*H*-carbazole (32): The reaction was performed in a similar manner to the synthesis of **13** (91% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (3H, t, *J* = 7.3 Hz), 1.92-2.07 (4H, m), 2.10-2.24 (4H, m), 2.69 (2H, t, *J* = 7.9 Hz), 2.87 (2H, t, *J* = 7.9 Hz), 4.39 (2H, q, *J* = 7.2 Hz), 6.81 (1H, s), 7.18 (1H, s), 7.24-7.29 (1H, m), 7.42 (1H, br d, *J* = 8.1 Hz), 7.43 (1H, br d, *J* = 8.3 Hz), 7.50 (1H, ddd, *J* = 8.3, 7.1, 1.2 Hz), 7.70 (1H, dd, *J* = 8.1, 1.3 Hz), 8.14 (1H, br d, *J* = 7.8 Hz), 8.29 (1H, br s); ^{13}C NMR (125 MHz, $CDCl_3$) (partial) δ 14.0, 20.8, 21.3, 28.8, 30.4, 30.5, 30.6, 30.6, 30.8, 31.7, 31.7, 37.8, 74.7, 108.9, 109.0, 117.8, 119.4, 120.7, 123.0, 123.6, 124.0, 124.2, 124.9, 126.1, 126.3, 128.8, 139.0, 139.9, 140.6, 141.5, 145.1, 145.7; IR (ATR) 877, 1006, 1130, 1218, 1341, 1453 cm^{-1}; HRMS (FAB+) Calcd for $C_{36}H_{26}F_{18}INS_2$: 1005.0264; found: m/z 1005.0258.

5''-(9-Ethyl-9*H*-carbazol-3-yl)-3',3'',4-tri-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-[2,2',5',2'']terthiophene-5-carbaldehyde (33): To a 25 mL of Schlenk tube equipped with a magnetic stirring bar were added $PdCl_2(PPh_3)_2$ (5.3 mg, 0.0075 mmol), **27** (112 mg, 0.30 mmol), **32** (152 mg, 0.15 mmol), potassium fluoride (22 mg, 0.375 mmol), and anhydrous DMSO (1 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 100 °C for 5 h. Silver nitrate (64 mg, 0.375 mmol) was then added in five portions with 1 hour interval. After cooling to room temperature, the mixture was passed through a Celite pad and the cake was washed repeatedly with $CHCl_3$. The filtrate was washed with water twice (50mL x 2) and brine. The combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel using hexane:AcOEt (5:1) as an eluent to afford 83 mg of **33** as a orange solid (44% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (3H, t, *J* = 7.2 Hz), 2.00-2.29 (12H, m), 2.95 (4H, m), 3.08 (2H, t, *J* = 7.7 Hz), 4.39 (2H, q, *J* = 7.2 Hz), 7.03 (1H, s), 7.07 (1H, s), 7.21 (1H, s), 7.24-7.31 (1H, m), 7.39-7.46 (2H, m),

7.51 (1H, ddd, *J* = 8.2, 7.2, 1.0 Hz), 7.72 (1H, dd, *J* = 8.5, 1.6 Hz), 8.15 (1H, d, *J* = 7.8 Hz), 8.31 (1H, d, *J* = 1.6 Hz) 10.00 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) (partial) δ 14.0, 21.0, 21.3, 21.9, 27.9, 29.0, 29.1, 30.3, 30.4, 30.6, 37.9, 108.9, 109.0, 117.9, 119.4, 120.7, 123.0, 123.7, 124.0, 124.6, 124.8, 126.4, 128.3, 128.5, 129.9, 137.0, 137.1, 139.4, 140.0, 140.4, 140.6, 144.9, 145.5, 150.4, 181.3; IR (ATR) 1132, 1221, 1435, 1639 cm^{-1}; HRMS (FAB+) Calcd for $C_{48}H_{34}F_{27}NOS_3$: 1249.1371; found: m/z 1249.1377.

2-Cyano-3-[5''-(9-Ethyl-9*H*-carbazol-3-yl)-3',3'',4-tri-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-[2,2',5',2'']terthiophen-5-yl]acrylic acid (MK-53): A mixture of aldehyde **33** (81 mg, 0.065 mmol) and cyanoacetic acid (28 mg, 0.32 mmol) in MeCN (2 mL), toluene (2 mL), and piperidine (0.5 mL) was refluxed for 24 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2, and the organic layer was washed with aqueous HCl (1 M), H_2O and brine. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography ($CHCl_3$/EtOH, gradient: 100/0 to 10/1) to obtain **MK-53** (35 mg, 41%) as dark-red solid. ^{1}H NMR (400 MHz, THF-d_8) δ 1.46 (3H, t, *J* = 7,2 Hz), 1.95-2.13 (6H, m), 2.27-2.46 (6H, m), 2.98-3.08 (6H, m), 4.45 (2H, q, *J* = 7.2 Hz), 7.20 (1H, m), 7.21 (1H, s), 7.32 (1H, s), 7.41 (1H, s), 7.44 (1H, m), 7.50 (1H, br d, *J* = 8.2 Hz), 7.54 (1H, br d, *J* = 8.6 Hz), 7.74 (1H, dd, *J* = 8.6, 1.7 Hz), 8.14 (1H, d, *J* = 7.8 Hz), 8.40 (1H, d, *J* = 1.7 Hz), 8.43 (1H, s).

9-Ethyl-3-(5''-bromo-3,4',4''-tri-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-[2,2',5',2'']terthiophen-5-yl)-9-*H*-carbazole (34): The reaction was performed in a similar manner to the synthesis of **12** (40% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (3H, t, *J* = 7.1 Hz), 1.92-2.24 (12H, m), 2.71 (2H, t, *J* = 7.6 Hz), 2.84 (2H, t, *J* = 8.0 Hz), 2.93 (2H, t, *J* = 7.7 Hz), 4.40 (2H, q, *J* = 7.1 Hz), 6.83 (1H, s), 6.98 (1H, s), 7.19 (1H, s), 7.24-7.29 (1H, m), 7.40-7.45 (2H, m), 7.50 (1H, ddd, *J* = 8.3, 7.1, 1.0 Hz), 7.71 (1H, dd, *J* = 8.5, 1.5 Hz), 8.15 (1H, br d, *J* = 7.8 Hz), 8.31 (1H, d, *J* = 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) (partial) δ 13.9, 20.5, 21.3, 28.5, 28.9, 29.0, 30.2, 30.4, 30.5, 30.7, 30.7, 37.8, 108.9, 109.0, 110.2, 117.8, 119.4, 120.7, 123.0, 123.6, 124.0, 124.5, 124.9, 126.3, 126.8, 127.8, 129.0, 130.3, 135.5, 135.6, 138.4, 138.8, 139.9, 140.6, 140.7, 144.9; IR (ATR) 877, 1007, 1132, 1220, 1347, 1453 cm^{-1}; HRMS (FAB+) Calcd for $C_{47}H_{34}BrF_{27}NS_3$ $[M+H]^+$: 1300.0606; found: m/z 1300.0547.

9-Ethyl-3-(3,4',4''-tri-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-[2,2',5',2'']terthiophen-5-yl)-9-*H*-carbazole (35): The reaction was performed in a similar manner to the synthesis of **17** (98% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (3H, t, *J* = 7.0 Hz), 1.97-2.29 (12H, m), 2.76 (2H, t, *J* = 7.2 Hz), 2.90 (2H, t, *J* = 7.8 Hz), 2.95 (2H, t, *J* = 7.7 Hz), 4.38 (2H, q, *J* = 7.1 Hz), 6.98-7.06 (3H, m), 7.21 (1H, s), 7.25-7.32 (1H, m), 7.39-7.47 (2H, m), 7.49-7.56 (1H, m), 7.73 (1H, dd, *J* = 8.4, 1.2 Hz), 8.17 (1H, br d, *J*

= 7.6 Hz), 8.33 (1H, br d, *J* = 1.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) (partial) δ 13.8, 21.1, 21.1, 21.3, 21.3, 21.4, 21.4, 28.6, 29.0, 29.7, 30.4, 30.5, 30.6, 30.6, 30.7, 37.7, 76.9, 77.2, 77.4, 108.9, 109.0, 117.7, 119.4, 120.7, 121.4, 123.0, 123.7, 123.9, 124.4, 125.1, 126.3, 127.2, 127.9, 129.3, 131.5, 134.9, 135.8, 137.9, 138.7, 139.9, 140.7, 141.8, 144.6; IR (ATR) 880, 1010, 1132, 1220 cm^{-1}; HRMS (ESI+) Calcd for $C_{47}H_{34}F_{27}NS_3$: 1221.1422; found: m/z 1221.1422.

5'''-(9-Ethyl-9*H*-carbazol-3-yl)-3',3'',3''',4-tetra-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-[2,2',5',2'',5'', 2''']quaterthiophene-5-carbaldehyde (36): To a 25 mL schlenk tube equipped with a magnetic stirring bar were added $PdCl_2(PPh_3)_2$ (4.4 mg, 0.0062 mmol), **28** (174 mg, 0.14 mmol), **35** (151 mg, 0.12 mmol), potassium fluoride (18 mg, 0.31 mmol), and anhydrous DMSO (2 mL) under a nitrogen atmosphere. The mixture was stirred at 100 °C for 5 h. Silver nitrate (53 mg, 0.31 mmol) was then added in five portions with 1 h interval. After cooling to room temperature, the mixture was passed through a Celite pad, which was washed repeatedly with $CHCl_3$. The filtrate was washed with water twice (50mL x 2) and brine. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel using hexane:AcOEt (5:1) as an eluent to afford 86 mg of **36a** as a reddish solid (44% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (3H, t, *J* = 7.3 Hz), 1.99-2.28 (16H, m), 2.89-2.99 (6H, m), 3.10 (2H, t, *J* = 7.4 Hz), 4.40 (2H, q, *J* = 7.2 Hz), 7.02 (1H, s), 7.02 (1H, s), 7.08 (1H, s), 7.21 (1H, s), 7.24-7.30 (1H, m), 7.43 (1H, br d, *J* = 8.5 Hz), 7.44 (1H, br d, *J* = 8.2 Hz), 7.50 (1H, ddd, *J* = 8.2, 7.1, 1.1 Hz), 7.72 (1H, dd, *J* = 8.5, 1.8 Hz), 8.15 (1H, br d, *J* = 7.7 Hz), 8.31 (1H, br d, *J* = 1.8 Hz), 10.01 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) (partial) δ 14.0, 21.1, 21.3, 21.4, 21.9, 27.9, 28.8, 28.9, 29.0, 30.4, 30.6, 30.7, 37.9, 108.9, 109.0, 117.8, 119.4, 120.7, 123.0, 123.6, 124.0, 124.6, 124.9, 126.3, 128.1, 128.5, 128.7, 128.9, 130.1, 130.5, 135.8, 136.2, 137.2, 138.8, 139.0, 139.9, 140.4, 140.7, 144.6, 145.0, 150.4, 181.3; IR (ATR) 876, 1007, 1132, 1220, 1657 cm^{-1}; HRMS (FAB+) Calcd for $C_{59}H_{41}F_{36}NOS_4$: 1591.1496; found: m/z 1591.1510.

2-Cyano-3-[5'''-(9-Ethyl-9*H*-carbazol-3-yl)-3',3'',3''',4-tetra-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-[2, 2',5',2'',5'',2''']quaterthiophenyl-5-yl]acrylic acid (MK-54): The reaction was performed in a similar manner to the synthesis of **MK-53** (41% yield). ^{1}H NMR spectrum was measured to be very broad due to the heavy dye-aggregation, therefore we could not analyze the coupling constant of each chemical shift. ^{1}H NMR (400 MHz, THF-d_8) δ 1.41 (3H), 1.96-2.12 (8H, m), 2.30-2.45 (8H, m), 2.96-3.08 (8H, m), 4.43 (2H), 7.16-7.21 (3H, m), 7.30 (1H), 7.39-7.45 (2H, m), 7.46-7.56 (2H, m), 7.73 (1H), 8.13 (1H), 8.40 (1H), 8.43 (1H).

9-Ethyl-3-(4''-*n*-hexyl-3,4'-di-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-[2,2',5',2'']terthiophen-5-yl)-9-*H*-carbazole (38): The mixture of **31** (236 mg, 0.25 mmol), 4-hexylthiophene-2-boronic acid ester **37** (103

mg, 0.37 mmol), tetrakis(triphenylphosphine)palladium (14 mg, 0.012 mmol) and 1.5 mL of 2 M aqueous solution of Na_2CO_3 in dimethoxyethane (5 mL) was refluxed for 24 h. After cooling to room temperature, H_2O was added and the reaction mixture was extracted with AcOEt three times. The combined organic layer was washed with H_2O and brine and dried over anhydrous $MgSO_4$. The dried solvent was concentrated under reduced pressure to leave a crude product, which was purified by column chromatography on silica gel (hexane/EtOAc = 50/1) and successive HPLC on silica gel (hexane/EtOAc = 50/1) to obtain bithiophene **2** (220 mg, 85%) as a slightly yellow oil. The product was employed for the following reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (3H, t, *J* = 7.0 Hz), 1.30-1.40 (6H, m), 1.46 (3H, t, *J* = 7.2 Hz), 1.61-1.70 (2H, m), 1.98-2.09 (4H, m), 2.10-2.23 (4H, m), 2.63 (2H, t, *J* = 7.7 Hz), 2.89 (2H, t, *J* = 7.7 Hz), 2.94 (2H, t, *J* = 7.7 Hz), 4.39 (2H, q, *J* = 7.2 Hz), 6.94-6.95 (1H, m), 6.97-6.98 (2H, m), 7.19 (1H, s), 7.27 (1H, ddd, *J* = 7.8, 7.0, 1.0 Hz), 7.42 (1H, br d, *J* = 8.5 Hz), 7.43 (1H, br d, *J* = 8.2 Hz), 7.50 (1H, ddd, *J* = 8.2, 7.0, 1.2 Hz), 7.72 (1H, dd, *J* = 8.5, 1.8 Hz), 8.14 (1H, br d, *J* = 7.8 Hz), 8.29 (1H, d, *J* = 1.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) (partial) δ 13.7, 14.0, 21.1, 21.2, 22.6, 28.4, 28.8, 29.0, 30.37, 30.46, 30.51, 31.7, 37.6, 108.7, 108.8, 117.5, 119.2, 120.4, 120.6, 122.8, 123.4, 123.8, 124.2, 124.9, 126.1, 127.65, 127.70, 129.2, 131.8, 134.4, 134.7, 137.4, 138.3, 139.7, 140.4, 143.9, 144.3.

9-Ethyl-3-(5''-bromo-4"-*n*-hexyl-3,4'-di-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-[2,2',5',2'']terthiophen-5-yl)-9-*H*-carbazole (39): To a solution of **38** (210 mg, 0.20 mmol) in THF (5 mL) was added *N*-bromosuccinimide (36 mg, 0.20 mmol). The reaction mixture was stirred at room temperature for 30 min and quenched with 10% aqueous solution of Na_2CO_3 and extracted with EtOAc three times. The combined organic layer was washed with H_2O and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 50/1) and successive HPLC on silica gel (hexane/EtOAc = 50/1) to obtain bromide **39** (200 mg, 88%) as a slightly yellow oil. The product was employed for the following reaction. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (3H, t, *J* = 7.0 Hz), 1.30-1.40 (6H, m), 1.46 (3H, t, *J* = 7.2 Hz), 1.58-1.66 (2H, m), 1.96-2.10 (4H, m), 2.14-2.27 (4H, m), 2.58 (2H, t, *J* = 7.7 Hz), 2.85 (2H, t, *J* = 7.7 Hz), 2.93 (2H, t, *J* = 7.7 Hz), 4.39 (2H, q, *J* = 7.2 Hz), 6.83 (1H, s), 6.97 (1H, s), 7.19 (1H, s), 7.27 (1H, ddd, *J* = 7.8, 7.0, 1.0 Hz), 7.42 (1H, br d, *J* = 8.5 Hz), 7.43 (1H, br d, *J* = 8.2 Hz), 7.50 (1H, ddd, *J* = 8.2, 7.0, 1.2 Hz), 7.72 (1H, dd, *J* = 8.5, 1.7 Hz), 8.14 (1H, br d, *J* = 7.8 Hz), 8.30 (1H, d, *J* = 1.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) (partial) δ 13.8, 14.0, 21.1, 21.2, 22.6, 28.4, 28.8, 28.9, 29.56, 29.63, 30.2, 30.3, 30.4, 30.5, 30.6, 30.7, 31.6, 37.6, 108.7, 108.8, 109.1, 117.5, 119.2, 120.6, 122.8, 123.4, 123.8, 124.2, 124.8, 126.1, 127.2, 127.6, 129.0, 130.6, 134.6, 135.0, 138.0, 138.5, 139.7, 140.5, 142.8, 144.6.

5’’’-(9-Ethyl-9*H*-carbazol-3-yl)-3’,4-di-*n*-hexyl-3”,3’’’-di-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-[2,2’, 5’,2’’,5’’,2’’’]quaterthiophene (40): The reaction was performed in a similar manner to the synthesis of **38** (98% yield) and employed for the following reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.925 (3H, t, *J* = 7.0 Hz), 0.931 (3H, t, *J* = 7.0 Hz), 1.31-1.44 (12H, m), 1.47 (3H, t, *J* = 7.2 Hz), 1.64-1.74 (4H, m), 2.01-2.13 (4H, m), 2.14-2.30 (4H, m), 2.65 (2H, t, *J* = 7.7 Hz), 2.79 (2H, t, *J* = 7.8 Hz), 2.94 (2H, t, *J* = 7.9 Hz), 2.96 (2H, t, *J* = 7.9 Hz), 4.39 (2H, q, *J* = 7.2 Hz), 6.94-6.95 (1H, m), 7.00 (1H, m) 7.01 (1H, s), 7.02 (1H, d, *J* = 1.4 Hz), 7.21 (1H, s), 7.29 (1H, ddd, *J* = 7.8, 7.1, 1.0 Hz), 7.42 (1H, br d, *J* = 8.5 Hz), 7.43 (1H, br d, *J* = 8.2 Hz), 7.52 (1H, ddd, *J* = 8.2, 7.1, 1.2 Hz), 7.73 (1H, dd, *J* = 8.5, 1.8 Hz), 8.17 (1H, br d, *J* = 7.8 Hz), 8.33 (1H, d, *J* = 1.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) (partial) δ 13.7, 13.98, 14.02, 21.09, 21.12, 21.2, 22.6, 28.5, 28.8, 29.0, 29.27, 29.31, 30.26, 30.30, 30.40, 30.49, 30.52, 30.6, 30.70, 30.74, 31.6, 31.7, 37.6, 108.7, 108.8, 115.7, 116.0, 116.4, 117.5, 118.0, 118.27, 118.35, 118.6, 118.9, 119.2, 120.2, 120.6, 122.8, 123.4, 123.8, 124.2, 124.9, 126.1, 127.3, 127.7, 128.9, 129.2, 131.3, 131.6, 132.7, 134.4, 135.3, 137.5, 138.4, 139.7, 139.8, 140.4, 143.8, 144.4.

5’’’-(9-Ethyl-9*H*-carbazol-3-yl)-3’,4-di-*n*-hexyl-3”,3’’’-di-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-[2,2’, 5’,2’’,5’’,2’’’]quaterthiophene-5-carbaldehyde (41): To a solution of quoterthiophene **40** (190 mg, 0.16 mmol) in dry DMF (2 mL) at 0 °C was added 0.17 mL of a 2.68 M solution in DMF of Vilsmeier reagent. The mixture was stirred at 70 °C for 7 h and cooled to room temperature. The mixture was quenched with 10% aqueous solution of NaOAc (30 mL). Two layers were separated and the aqueous layer was extracted with EtOAc three times. The combined organic layer was washed with H_2O and brine, dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 20/1) and successive HPLC on silica gel (hexane/EtOAc = 7/1) to obtain aldehyde **41a** (142 mg, 73%) as a reddish solid, which was used for further reaction. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (3+3H, t, *J* = 7.0 Hz), 1.33-1.46 (12H, m), 1.46 (3H, t, *J* = 7.2 Hz), 1.66-1.76 (4H, m), 2.01-2.12 (4H, m), 2.15-2.29 (4H, m), 2.84 (2H, t, *J* = 7.7 Hz), 2.91-2.98 (6H, m), 4.39 (2H, q, *J* = 7.2 Hz), 7.01 (1+1H, s), 7.06 (1H, s), 7.20 (1H, s), 7.27 (1H, ddd, *J* = 7.8, 7.0, 1.0 Hz), 7.42 (1H, br d, *J* = 8.5 Hz), 7.43 (1H, br d, *J* = 8.2 Hz), 7.51 (1H, ddd, *J* = 8.2, 7.0, 1.2 Hz), 7.71 (1H, dd, *J* = 8.5, 1.8 Hz), 8.15 (1H, br d, *J* = 7.8 Hz), 8.31 (1H, d, *J* = 1.8 Hz), 10.03 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) (partial) δ 13.7, 13.9, 21.0, 21.1, 22.5, 22.6, 28.4, 28.8, 29.0, 29.2, 29.8, 30.17, 30.25, 30.4, 30.5, 30.6, 30.7, 31.4, 31.5, 31.6, 37.6, 108.7, 108.8, 116.0, 117.5, 118.8, 119.2, 120.5, 120.6, 122.8, 123.4, 123.7, 124.2, 124.7, 126.1, 127.7, 128.2, 128.9, 129.2, 129.9, 130.5, 134.9, 135.2, 136.4, 138.2, 138.6, 139.7, 140.4, 142.5, 144.6, 144.7, 153.3, 181.5.

2-Cyano-3-[5’’’-(9-Ethyl-9*H*-carbazol-3-yl)-3’,4-di-*n*-hexyl-3”,3’’’-di-(4,4,5,5,6,6,7,7,7-nonafluoro-

heptyl)-[2,2',5',2'',5'',2''']quaterthiophenyl-5-yl]acrylic acid (MK-55): The reaction was performed in a similar manner to the synthesis of **MK-53** (69% yield). ^{1}H NMR spectrum was measured to be very broad as well as **MK-54**, therefore we could not analyze the coupling constant of each chemical shift. ^{1}H NMR (400 MHz, THF-d_8) δ 0.91 (6H, m), 1.31-1.44 (15H, m), 1.46-1.52 (2H, m), 1.64-1.70 (2H, m), 2.02-2.12 (4H, m), 2.26-2.41 (4H, m), 4.44 (2H), 7.14-7.24 (4H, m), 7.39 (1H), 7.43 (1H), 7.48-7.54 (2H, m), 7.73 (1H), 8.14 (1H), 8.39 (1H), 8.42 (1H).

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