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Concise Synthesis of Well-Defined Linear and Branched Oligothiophenes with Nickel-Catalyzed Regiocontrolled Cross-Coupling of 3-Substituted Thiophenes by Catalytically Generated Magnesium Amide

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Abstract: The synthesis of linear and branched oligothiophenes of well-defined structures is performed with regioselective deprotonation of 3-substituted thiophenes and nickel-catalyzed cross-coupling of the thus formed metalated species with a bromothiophene. The reaction of 3-hexylthiophene with EtMgCl and 2,2,6,6-tetramethylpiperidine (TMP-H, 10 mol %) induces the metalation selectively at the 5-position by use of the catalytically generated hindered magnesium amide (TMPMgCl) and the subsequent reaction of a 2-halo-3-hexylthiophene (bromide or chloride) in the presence of a nickel catalyst affords a head-to-tail (HT)-type dimer. By repeating the same sequence, the linear oligothiophene up to a 4-mer is synthesized in good yield. The reaction of 3-hexylthiophene with 2,3-dibromothiophene also takes place to afford a branched oligothiophene 3-mer in quantitative yield. The obtained 3-mer is also metalated at the sterically less-hindered position in a regioselective manner furnishing a 7-mer in >99 % yield after a further coupling reaction with 2,3-dibromothiophene. These dendrimers react with several multifunctionalized organic electrophiles, leading to a variety of branched oligothiophenes.

Keywords: cross-coupling • dendrimers • NHC ligands • nickel catalysts • oligothiophenes

Introduction

Oligothiophenes and polythiophenes have recently attracted remarkable attention as materials showing conductive, semiconductive, nonlinear optical, and liquid–crystalline characteristics, among others. They are employed as thin-film organic transistors,[1] liquid–crystalline compounds,[2] and dye-sensitized organic photovoltaic cells.[3] Oligothiophenes composed of a thiophene unit bearing a substituent at the 3-position form three types of possible regioisomers, head-to-head (HH), tail-to-tail (TT), and head-to-tail (HT). Among these, the HT isomer generally shows a superior performance due to decreased steric congestion and thus extended π-conjugation.[1d,3b–d,4] Development of a concise preparative method of HT-type oligothiophenes is, therefore, an important issue in organic synthesis.[5,6]

Branched oligothiophene dendrimers have also been studied as represented by the pioneering work of Advincula and Bäuerle as potentially applicable light-harvesting,[7] self-assembly,[8] and optoelectronic materials.[9,10] These oligothiophene dendrimers have been synthesized by employing cross-coupling reactions of organoboron[11] and organotin[12] reagents and the synthesis requires a two-step sequence in each extension of the number of generations involving transition-metal-catalyzed coupling and further transformation of the thus coupled dendron into the corresponding organometallic reagent.[13] Accordingly, a rather multistep synthetic pathway has been repeated when oligothiophene dendrimers of higher order generations are designed. Development of a more concise preparative method for thiophene dendrimers is, therefore, intriguing.

On the other hand, we have been engaged in the coupling reaction at the C–H bond of heteroaromatic compounds with various organic electrophiles.[14,15] The method allows remarkable step efficiency by the direct activation of the C–H bond or in situ formation of metallic species by deprotonative metalation prior to the coupling compared with existing cross-coupling with the isolated organometallic compounds, such as boron, silicon, and tin reagents.

We have recently reported HT-type oligothiophene[16,17] and polythiophene[18] syntheses with nickel-catalyzed cross-coupling at the C–H bond of thiophene, in which a stoichiometric amount of magnesium amide TMPMgCl·LiCl (TMP-H = 2,2,6,6-tetramethylpiperidine), recognized as a Knochel–Hauser base,[19] served as an efficient deprotonating agent for in situ formation of the metalated species. A series of linear oligothiphenes can be synthesized by repeating the coupling reaction, in which a single one-pot reaction has extended a thiophene unit in a facile manner in contrast to multistep conventional cross-coupling pathways. Although

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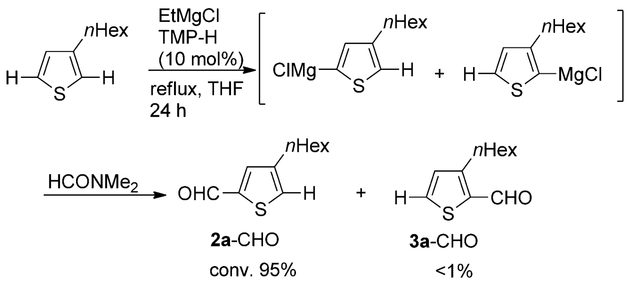
we have also shown that the combination of a Grignard reagent and catalytic secondary amine[20,21] is equally effective, for the metalation, as the use of a stoichiometric amount of the Knochel–Hauser base, the reaction conditions of such a catalytic metalation process have hardly been optimized and the scope and limitations are not yet clear. Herein, we describe further studies of such a catalytic system of deprotonation for the synthesis and the application to the concise stepwise synthesis of well-defined linear HT-type oligothiophenes.

Furthermore, we envisaged that such regioselective deprotonation of thiophene and the subsequent coupling reaction with 2,3-dibromothiophene in the presence of a nickel catalyst could afford a branched thiophene 3-mer and repeating of a similar reaction extends the generation leading to the oligothiophene dendron, which would be a much simpler and step-economic synthesis of oligothiophene dendrimers. We also disclose that a variety of well-defined branched oligothiophenes are synthesized by the stepwise regioselective metalation and the following cross-coupling reaction of multifunctionalized organic electrophiles.

Results and Discussion

When 3-hexylthiophene (**1a**) was treated with ethyl magnesium chloride (EtMgCl) and TMP-H (10 mol %) for 24 h in THF under reflux, the reaction proceeded to give the metalothiophene at the C–H bond of the 5-position selectively, which was confirmed by treatment with DMF to afford the corresponding 2-formyl-4-hexylthiophene (**2a**-CHO), exclusively (Scheme 1).



Scheme 1. Regioselective deprotonation of 3-hexylthiophene with EtMgCl and TMP-H.

We examined the regioselectivity in the metalation of **1a** with ethylmagnesium chloride (EtMgCl) and a catalytic amount of several secondary amines to form the corresponding thienylmagnesium compounds. Table 1 summarizes the results. The progress of the reaction was confirmed by quenching the mixture with DMF to afford 2-formyl-4-hexylthiophene (**2a**-CHO) and 2-formyl-3-hexylthiophene (**3a**-CHO). The reaction with 10 mol % of TMP-H under reflux in THF for 24 h completely proceeded to afforded **2a**-CHO, exclusively, whereas shorter reaction periods (10 h) resulted in inferior conversion. Although the reaction with 10 mol % of TMP-H at room temperature for 24 h selectively afforded **2a**-CHO, the conversion fell to 28 %. The reaction with diisopropylamine ($i\mathrm{Pr_2NH}$) resulted in inferior regioselectivity and reactivity. The use of dicyclohexylamine ($\mathrm{Cy_2NH}$) was also found to induce slightly inferior regioselectivity although the reaction proceeded smoothly. We have recently shown that metalation of 2-chloro-3-hexylthiophene with EtMgCl and 10 mol % of $\mathrm{Cy_2NH}$ proceeded completely within 1 h;[18a] however, the reaction of 3-hexylthiophene, in which the C–H bond at the 5-position is less acidic, for 1 h underwent the metalation in insufficient conversion (26 %).

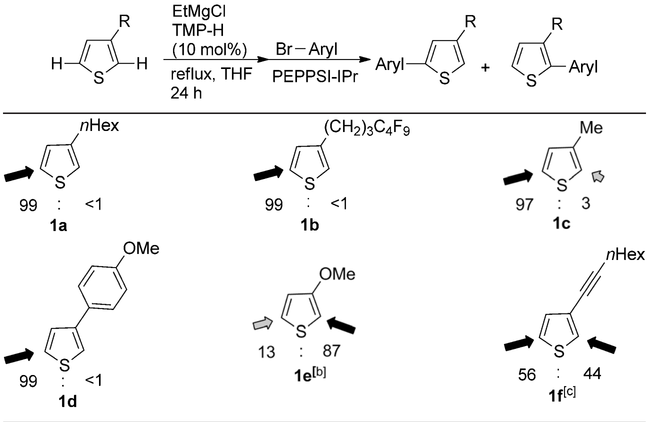
Table 1. Regioselectivity in the metalation of **1a** with several amines (10 mol %) and EtMgCl.[a]

Amine	T [°C]	t [h]	Conv. [%] (**2a**-CHO/**3a**-CHO)[b]
TMP-H	RT	24	28 (>99:1)
	reflux	10	56 (>99:1)
	reflux	24	95 (>99:1)
$i\mathrm{Pr_2NH}$	reflux	24	86 (93:7)
$\mathrm{Cy_2NH}$	reflux	24	80 (91:9)
	reflux	1	26 (96:4)

[a] The reaction was performed with **1a** (0.5 mmol), EtMgCl (0.6 mmol), and amine (0.05 mmol) in THF (0.6 mL). [b] Conversion and the ratio of **2a**-CHO/**3a**-CHO was estimated by ^{1}H NMR spectroscopic analysis.

The transition-metal-catalyzed cross-coupling reaction of 4-bromotoluene in the presence of a palladium catalyst (PEPPSI-IPr, [1,3-bis(2,6-diisopropylphenyl)immidazol-2-ylidene](3-chloropyridyl)palladium(II))[22] was carried out with the above optimized metalation conditions of **1a** at the 5-position by using EtMgCl and TMP-H (10 mol %) for 24 h to afford the 5-arylated product exclusively in 81 % yield. The arylation reactions with several 3-substituted thiophenes were then examined to study the selectivity for the C–H bond, as summarized in Table 2. The reaction of 3-fluoroal-

Table 2. Regiochemistry of the reaction with 3-substituted thiophenes.[a]

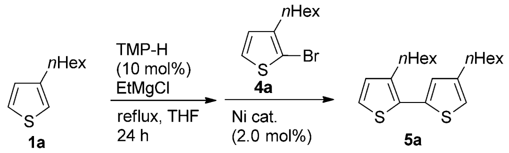


[a] Unless otherwise noted, the reaction was carried out with 3-substituted thiophene (0.50 mmol), 4-bromotoluene (0.75 mmol), EtMgCl (0.60 mmol), TMP-H (0.05 mmol), and PEPPSI-IPr (0.01 mmol) in THF (2.0 mL). The ratio of 2- and 5-arylated products was estimated by ^{1}H NMR spectroscopic analysis. [b] The ratio of 2- and 5-arylated products was determined by GC analysis. [c] The reaction was performed with 4-bromoanisole (0.75 mmol).

kylated thiophene **1b** and 3-arylated thiophene **1d** with 4-bromotoluene also occurred regioselectively at the 5-position. The reaction of 3-methylthiophene (**1c**) resulted in slightly inferior regioselectivity (97:3). By contrast, the reaction of 3-methoxythiophene (**1e**) resulted in predominantly the 2-arylated product, probably due to the directing effect of the methoxy group in the reaction with the magnesium amide. Less selective metalation was found to occur with an alkynyl-group-substituted thiophene **1f**.

With regioselective metalation at the 5-position of 3-substituted thiophene, we focused on the application to the formation of a HT-type thiophene–thiophene bond. The reaction of **1a** with 2-bromo-3-hexylthiophene (**4a**) was examined with several transition-metal catalysts. As shown in Table 3, the reaction with a nickel catalyst bearing a bidentate diphosphine, [NiCl$_2$(dppp)] (dppp = 1,3-bis(diphenylphosphino)propane), at 60 °C for 24 h proceeded to afford the HT-type dimer **5a** in an excellent yield (90 %). The reaction of [NiCl$_2$(dppe)] (dppe = 1,2-bis(diphenylphosphino)-ethane) also resulted in a good yield. The use of a combination of [Ni(cod)$_2$] and an N-heterocyclic carbene (NHC) ligand,[23] *N,N'*-bis[2,6-diisopropylphenyl)-4,5-dihydroimidazol]-2-ylidene (SIPr), which showed excellent performance in the reaction of **1a** with **4a** by using a Knochel–Hauser base, resulted in 77 % yield. Higher catalytic activity was achieved with nickel catalyst [NiCl$_2$(IPr)(PPh$_3$)][24] bearing PPh$_3$ and the NHC ligand *N,N'*-bis[(2,6-diisopropylphenyl)-imidazol]-2-ylidene (IPr) to afford **5a** in a quantitative yield at 60 °C for 24 h. The reaction with [NiCl$_2$(IPr)(PPh$_3$)] afforded **5a** in 89 % yield within 2 h.

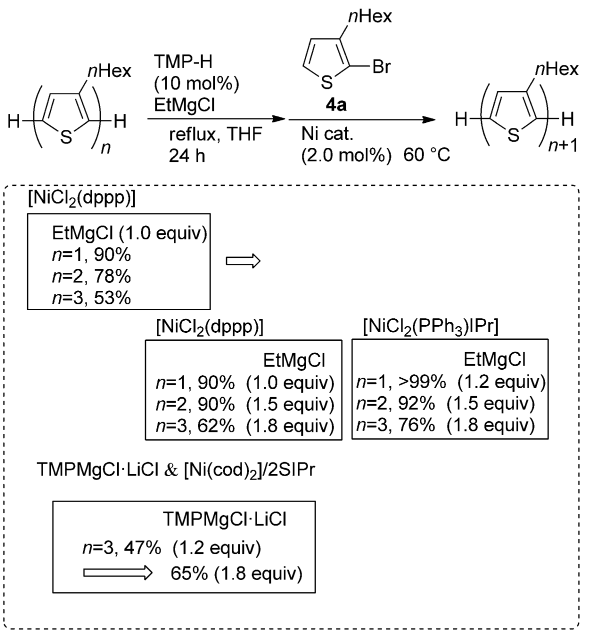
Table 3. The reaction of **1a** with 2-bromo-3-hexylthiophene (**4a**) with transition-metal catalyst.[a]



Catalyst	EtMgCl [equiv]	**4a** [equiv]	*T* [°C]	*t* [h]	Yield [%][c]
[NiCl$_2$(dppp)]	1.0	1.0	60	24	90
[NiCl$_2$(dppe)]	1.0[b]	1.0	60	24	77
[Ni(cod)$_2$]/2 SIPr	1.0	1.0	60	20	77
[NiCl$_2$(IPr)(PPh$_3$)]	1.2	1.2	60	2	89
[NiCl$_2$(IPr)(PPh$_3$)]	1.2[b]	1.2	60	20	> 99

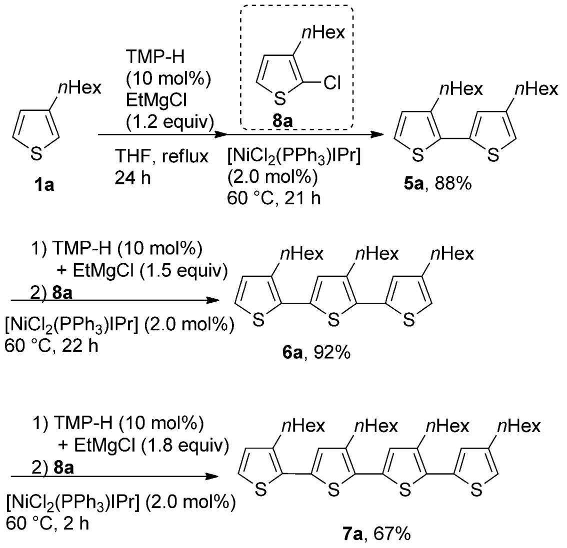
[a] Unless otherwise noted, the reaction was performed with **1a** (0.50 mmol) in THF (2.0 mL). [b] The reaction was carried out with **1a** (1.0 mmol) in THF (3.0 mL). [c] Yield of the isolated product.

The synthesis of HT-type oligomers of 3-hexylthiophene by using a combination of EtMgCl and TMP-H (10 mol %) was carried out as summarized in Scheme 2. The obtained HT-bithiophene (**5a**) was subjected to further reaction with **4a** in the presence of [NiCl$_2$(dppp)] to afford the HT-type terthiophene **6a** in 78 % yield. The obtained **6a** reacted with **4a** to give HT-type tetramer **7a** in a similar manner, furnishing the quaterthiophene in 53 % yield. It was observed that the yield decreased as the number of thiophene units increased. When the deprotonation was performed with a stoichiometric amount of EtMgCl along with TMP-H (10 mol %) in the reaction of **5a**, it was found that only 83 % of the dimer underwent the deprotonation, which was confirmed to lead to the corresponding aldehyde by treatment with DMF. Increasing the amount of EtMgCl to 1.5 equivalents resulted in the formation of a dianion, which suggested deprotonation also at the more hindered 2-position to afford mono- and diformylated products in 69 and 31 % yields, respectively. However, it was found that no coupling reaction at the hindered position took place in the reaction of **5a** with **4a**, providing **6a** in 90 % yield with [NiCl$_2$-(dppp)] (2.0 mol %) or 92 % yield with [NiCl$_2$(IPr)(PPh$_3$)] (2.0 mol %) as the sole product. The yield of the reaction of **6a** with 1.8 equivalents of EtMgCl improved to 76 % with [NiCl(IPr)(PPh$_3$)] (2.0 mol %). A similar trend was also observed in the reaction with a stoichiometric amount of TMPMgCl•LiCl to afford a 65 % yield of **7a**, whereas the yield was much lower (47 %) from the deprotonation with 1.2 equivalents of the corresponding base.[16]



Scheme 2. HT-type oligothiophene synthesis with regioselective cross-coupling.

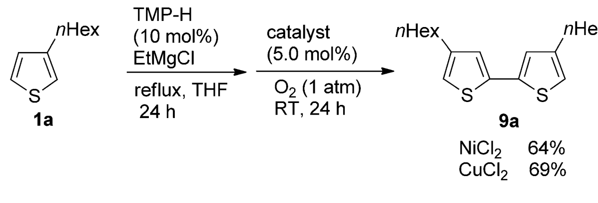
We envisaged a further improvement of the atom efficiency of the HT-type oligothiophene synthesis with 2-chloro-3-hexylthiophene (**8a**) instead of bromide **4a**. However, the reaction of **1a** with 2-chloro-3-hexylthiophene (**8a**) in the presence of [NiCl$_2$(dppp)] as the catalyst at 60 °C for 20 h only afforded **5a** in 19 % yield. Nevertheless, as shown in Scheme 3, the reaction with **8a** was found to take place successfully with [NiCl$_2$(IPr)(PPh$_3$)] (2.0 mol %) the catalyst to give **5a** in excellent yield. It is worth noting that the effect of the NHCs is markedly different from the one in the reac-



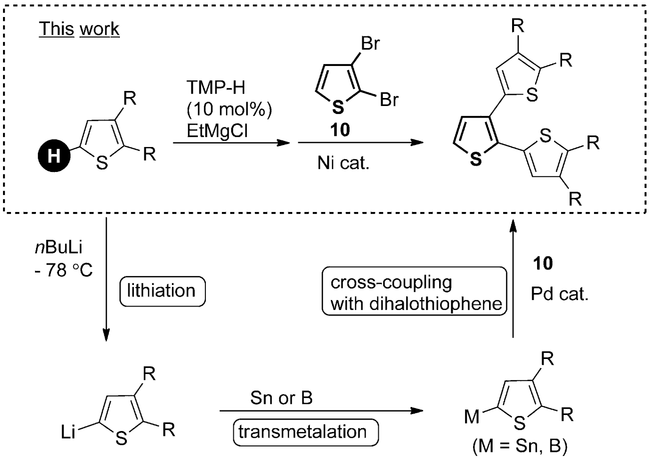
Scheme 3. HT-type oligothiophene synthesis with 2-chloro-3-hexylthiophene (**8a**).

tion with bromothiophene, which has reacted smoothly with bidentate phosphines as a ligand. The HT-trimer (**6a**) and tetramer (**7a**) were also obtained in good to excellent yields in a similar manner.

Oxidative homocoupling through the regioselective deprotonation of **1a** was also examined.[25] The reaction of **1a** with a transition-metal salt under an oxygen atmosphere proceeded to afford tail-to-tail (TT)-type bithiophene (**9a**). The reaction with 5.0 mol% of nickel chloride at room temperature for 24 h took place to give **9a** exclusively in 64% yield. The use of copper chloride resulted in 69% yield (Scheme 4). It is remarkable that the TT-type bithiophene is synthesized in a single step, whereas conventional synthesis has been performed with two or more steps involving a much less atom- and step-economic bromination/debrominative homocoupling sequence.



Scheme 4. Synthesis of TT-type bithiophene by oxidative homocoupling of **1a**.

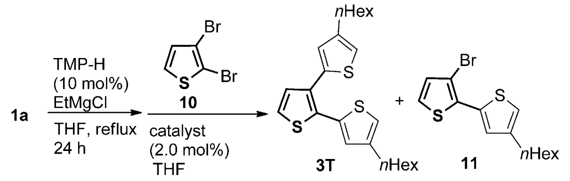


Scheme 5. Synthetic strategy of thiophene dendrimers.

Our interest then turned to the synthesis of dendritic oligothiophenes with the regioselective cross-coupling reaction of 3-substituted thiophenes. We envisaged that the regioselective deprotonation of thiophene and the subsequent reaction with 2,3-dibromothiophene (**10**) in the presence of a nickel catalyst would afford a thiophene dendron 3-mer and repeating the similar reaction would extend the generation of the thiophene dendron. A step-economic synthesis of oligothiophene dendrimers compared with conventional protocols involving the formation of thienyl boron or tin reagents, followed by cross-coupling is depicted in Scheme 5.[13]

The reaction of 3-hexylthiophene (**1a**) with 2,3-dibromothiophene (**10**) was first carried out in a similar manner to the reaction of linear oligothiophenes. As shown in Table 4, the reaction of **1a** with EtMgCl and TMP-H (10 mol%) under reflux in THF for 24 h induced the metalation at the 5-position selectively. The following addition of 2,3-dibromothiophene (**10**) in the presence of [NiCl$_2$(IPr)(PPh$_3$)] (2.0 mol%) at room temperature for 24 h afforded thiophene dendron 3-mer (**3T**) in a quantitative yield (Table 4, entry 1). It is also remarkable that the reaction was found to be rather fast and proceeded in 78% yield within 10 min,

Table 4. The reaction of **1a** with **10** in the presence of nickel catalyst.[a]



Entry	**1a**/**10**	Catalyst	T [°C]	t	Yield [%]	
					3T	**11**
1[b]	2.5:1	[NiCl$_2$(IPr)(PPh$_3$)]	RT	24 h	>99[c]	0
2	2.5:1	[NiCl$_2$(IPr)(PPh$_3$)]	RT	10 min	78[c]	0
3	1:1	[NiCl$_2$(PPh$_3$)]	RT	10 min	41[c]	0
4	1:1	PEPPSI-IPr	60	23 h	17[c]	32
5	1:1	[NiCl$_2$(dppe)]	60	24 h	33[d]	0
6	1:1	[NiCl$_2$(dppp)]	60	24 h	6[d]	14
7	1:1	[NiCl$_2$(dppf)]	60	24 h	<1[d]	21
8	1:1	[Pd(PtBu$_3$)$_2$]	60	24 h	<1[d]	26

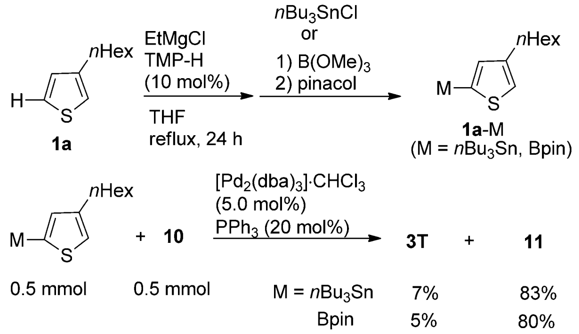
[a] Unless otherwise noted, the reaction was carried out with **1a** (0.50 mmol), TMP-H (0.05 mmol), EtMgCl (0.50 mmol), and nickel catalyst (0.01 mmol) in THF (2.0 mL). [b] The reaction was performed with **1a** (3.0 mmol). [c] Yield of the isolated product. [d] The yield of **3T** and **11** was estimated by ^{1}H NMR spectroscopic analysis.

whereas monocoupling product **11** was not observed at all in spite of the fact that the carbon–bromine bond at the 3-position is much less reactive than that at the 2-position (Table 4, entry 2).

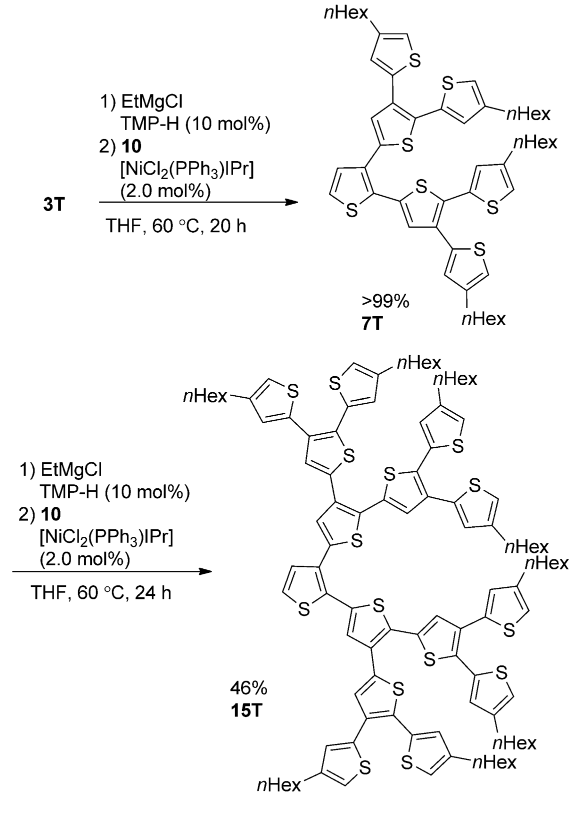
We next performed the reaction of an equimolar amount of 3-hexylthiophene (**1a**) with 2,3-dibromothiophene (**10**) in the presence of [$NiCl_2$(IPr)(PPh_3)] (Table 4, entry 3). Even when the reaction was carried out with a 1:1 ratio of **1a** and **10** and 2.0 mol % of the catalyst, complete consumption of **1a** was confirmed at room temperature after 10 min to afford **3T** in 41 % yield with recovery of 2,3-dibromothiophene (54 %) and the monocoupling product **11** was not observed at all. A similar effect was observed with a palladium catalyst PEPPSI-IPr in the reaction of several multihalogenated organic electrophiles with a variety of organometallic reagents;[26,27] however, the reaction of thiophene catalyzed by [$NiCl_2$(IPr)(PPh_3)] indicated the improved performance to undergo the multiple coupling reaction. Indeed, the reaction of **1a** and **10** with PEPPSI-IPr (2.0 mol %) as the catalyst at 60 °C for 23 h resulted in a mixture of **3T** and **11** in 17 and 32 % yields, respectively (Table 4, entry 4). We also carried out the reaction with other nickel and palladium catalysts (Table 4, entries 5–8). The reaction with [$NiCl_2$(dppe)] at 60 °C for 24 h gave **3T** in 33 % yield, and the monocoupling product **11** was not observed at all. The reaction with a nickel catalyst with a bidentate diphosphine ligand, [$NiCl_2$(dppp)], at 60 °C for 24 h occurred to give a mixture of **3T** and **11** (6 and 14 % yield, respectively). The reaction with [$NiCl_2$(dppf)] (dppf = 1,1′-bis(diphenylphosphino)ferrocene) proceeded to afford **11** in a poor yield. Although the reaction with a palladium catalyst with a bulky phosphine ligand, [Pd(P*t*Bu$_3$)$_2$], proceeded, the yield was found to be much inferior.

The observed multiple coupling seems to be the specific case in the reaction of a thienyl magnesium reagent with a nickel NHC catalyst, whereas such a drastic effect has not been found in the preceding synthesis of thiophene dendrimers with thienyl boron and tin reagents. Indeed, the related reaction of 4-hexyl-2-tributylstannylthiophene (**1a**-*n*Bu$_3$Sn) with **10** preferentially afforded the monocoupling product **11** in 83 % yield and **3T** in a poor yield (7 %) when the reaction was carried out employing an equimolar amount of the organometallic reagent and dibromothiophene **10** (Scheme 6). A similar trend was also observed in the reaction of thienylboronate pinacol ester (**1a**-Bpin) to afford an 80 % yield of **11** along with a 5 % yield of **3T**. Accordingly, it has been necessary to accomplish complete conversion with the Suzuki–Miyaura or Migita–Kosugi–Stille protocols,[28] thus, longer reaction periods and use of excess of the organometallic reagent have been conducted in the conventional reactions. In addition, separation of the once-formed monocoupled byproduct and the desired dendrimer must be performed. By contrast, the reaction of **1a** with the nickel catalyst does not require such troublesome separation of the undesired byproducts.

We next performed further extension of thiophene dendrimer up to a 15-mer in a similar manner (Scheme 7). The obtained **3T** was also metalated selectively at the sterically less-hindered position by TMP-H/EtMgCl and the reaction with **10** at 60 °C for 20 h led to the thiophene dendron 7-mer (**7T**) in a quantitative yield. Treatment of **7T** with TMP-H (10 mol %) and EtMgCl and the reaction with **10** at 60 °C for 24 h led to the 15-mer **15T** in 46 % yield.

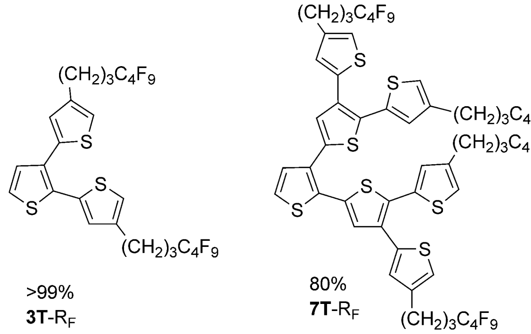


Scheme 6. Reaction of **10** with a thienyl boronic acid ester and thienylstannannes. dba = dibenzylideneacetone.



Scheme 7. Thiophene dendrimer synthesis up to the 15-mer.

The synthesis of the thiophene dendrimer bearing the fluoroalkyl group,[29,15b] –$(CH_2)_3C_4F_9$, was also achieved successfully in a similar manner, as shown in Scheme 8. The deprotonation reaction of 3-fluoroalkylated thiophene **1b** with EtMgCl/TMP-H (10 mol %) also took place at the 5-position selectively and the subsequent reaction with **10** in the presence of [$NiCl_2$(IPr)(PPh_3)] (2.0 mol %) at 60 °C for 27 h af-

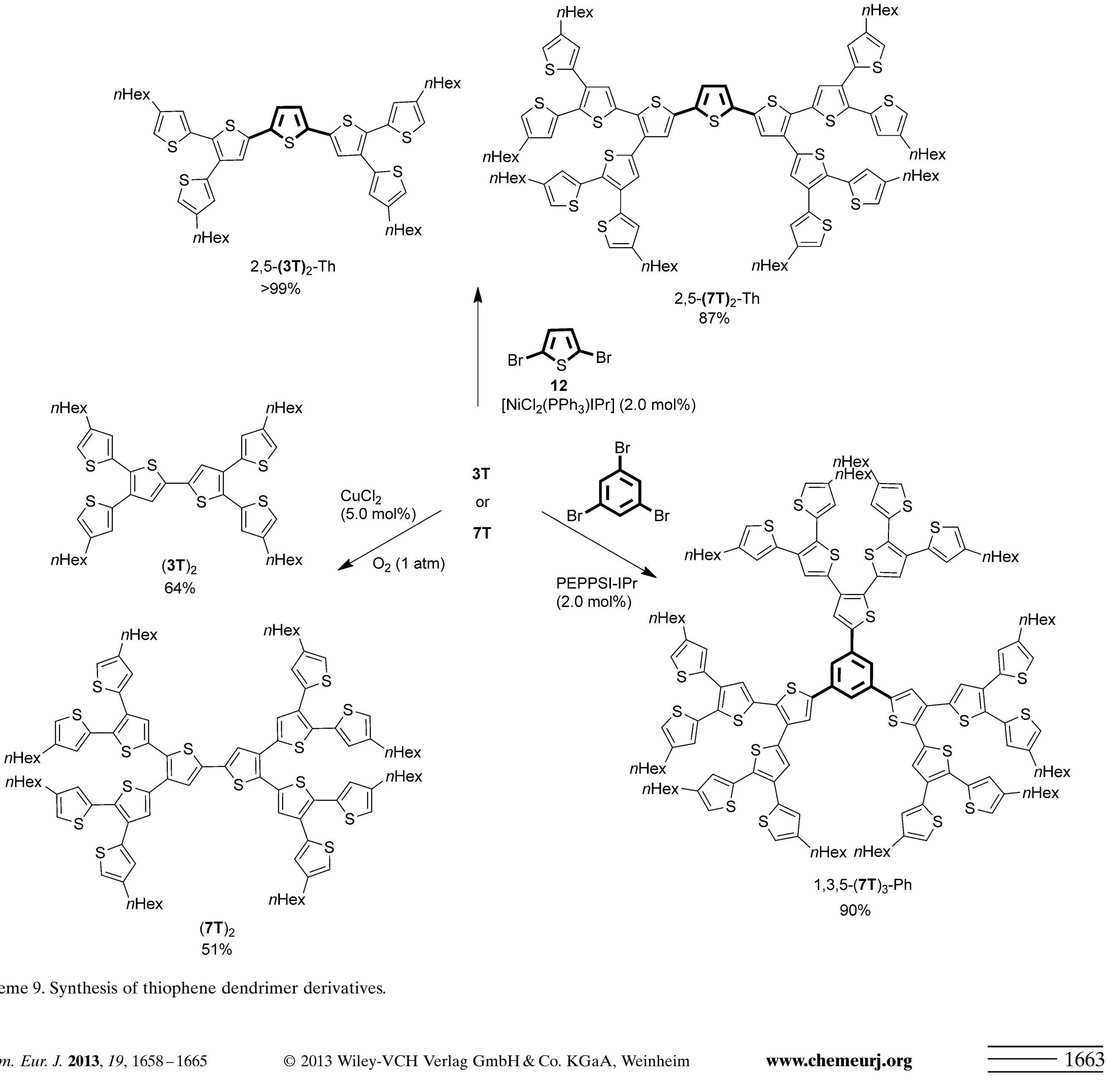


Scheme 8. Synthesis of 3-fluoroalkylated thiophene dendrimers.

forded **3T**-R$_F$ in a quantitative yield. In addition, **7T**-R$_F$ was also obtained by the cross-coupling reaction of **3T**-R$_F$ with **10** in 80 % yield.

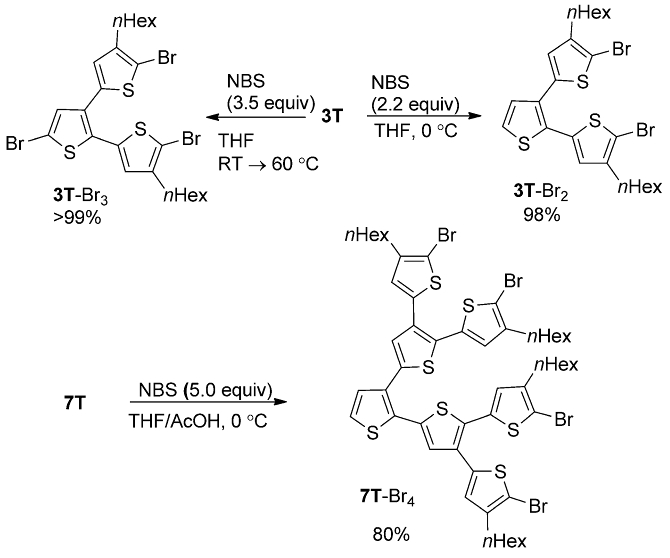
Our further concern is the regioselective coupling of thiophene dendrimers with several bromothiophenes and aryl halides. These results are summarized in Scheme 9. The reaction of **3T** with 2,5-dibromothiophene (**12**) at 60 °C for 23 h smoothly took place to give 2,5-(**3T**)$_2$-Th in >99 % yield. The reaction of **7T** with **12** also occurred to afford 2,5-(**7T**)$_2$-Th in 87 % yield. A benzene-ring-centered thiophene dendrimer was obtained by the reaction of **7T** with 1,3,5-tribromobenzene in the presence of palladium catalyst PEPPSI-IPr to give 1,3,5-(**7T**)$_3$-Ph in 90 % yield. The reaction of **3T** in the presence of $CuCl_2$ (5.0 mol %) under an oxygen atmosphere at 60 °C for 26 h proceeded to afford homocoupling product (**3T**)$_2$ in 64 % yield. The homocoupling reaction of **7T** also afforded (**7T**)$_2$ in 51 % yield.

Further transformations of the obtained dendrimers **3T** and **7T** are plausible when the synthesis is performed with a regioselective deprotonative coupling reaction with 3-hex-



Scheme 9. Synthesis of thiophene dendrimer derivatives.

ylthiophene (**1a**), in contrast to the fact that conventional thiophene dendrimers bearing hexyl groups adjacent to the sulfur atom would limit the related transformations. As shown in Scheme 10, the reaction of **3T** with NBS (2.2 equiv) at 0 °C proceeded at the C−H bond adjacent to the hexyl group selectively to afford dibrominated product **3T**-Br_2 in an excellent yield (98 %), whereas the similar reaction with 3.5 equivalents of NBS at 60 °C led to the tribrominated product **3T**-Br_3 in a quantitative yield. These results suggest that further transformation of the thus prepared bromides would be possible. The similar reaction of **7T** with 5.0 equivalents of NBS in THF and acetic acid at 0 °C afforded the tetrabrominated **7T**-Br_4 in 80 % yield.



Scheme 10. Regioselective bromination of thiophene dendrimers with *N*-bromosuccinimide (NBS).

Conclusion

We have shown that regioselective deprotonation of 3-substituted thiophenes with a combination of a catalytic amount of TMP-H and EtMgCl as a selective metalating agent allows them to undergo the reaction with bromothiophenes and chlorothiophenes to form the thiophene–thiophene bond. Linear oligothiophenes were synthesized efficiently by repeating the reaction. It was also found that several oligothiophene dendrimers could be synthesized by the sequential regioselective metalation of thiophene and the cross-coupling with 2,3-dibromothiophene, the reaction of which would also be remarkable due to an unexpected rate acceleration in the coupling at the second carbon–bromine bond of dibromothiophene. With these methods, a wide variety of well-defined linear and branched oligothiophene derivatives can be synthesized in an extremely facile manner compared with conventional oligothiophene syntheses.

Experimental Section

General procedure for the reaction of 3-hexylthiophene (1a) with EtMgCl/TMP-H (10 mol %) and 2-bromo-3-hexylthiophene (4a): A solution of EtMgCl in THF (1.21 mL, 1.2 mmol) and TMP-H (0.017 mL, 0.1 mmol) were added to a Schlenk tube (20 mL) equipped with a magnetic stirring bar. 3-Hexylthiophene (**1a**, 0.180 mL, 1.0 mmol) was added to the solution and stirring was continued under reflux for 24 h. Then, THF (1.8 mL), 2-bromo-3-hexylthiophene (**4a**, 0.239 mL, 1.2 mmol), and [$NiCl_2$(IPr)(PPh_3)] (15.6 mg, 0.02 mmol) were added successively. The mixture was allowed to stir at 60 °C for 20 h. After cooling to room temperature, the mixture was quenched with a saturated aqueous solution of ammonium chloride (1.0 mL). The solution was poured into a mixture of diethyl ether/water and two phases were separated. The aqueous layer was extracted twice with diethyl ether and the combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by column chromatography on silica gel by using hexanes as the eluent to afford 5-(3-hexylthiophen-2-yl)-3-hexylthiophene (**5a**, light-yellow oil, 335.2 mg, > 99 %).

General procedure for the reaction of 3-hexylthiophene (1a) and 2,3-dibromothiophene (10) with EtMgCl/TMP-H (10 mol %): EtMgCl (0.99 M, 7.5 mL, 7.5 mmol) in THF and TMP-H (0.01 mL, 0.75 mmol) were added to a Schlenk tube (50 mL) equipped with a magnetic stirring bar. 3-Hexylthiophene (**1a**, 0.048 mL, 7.5 mmol) was added to the solution and stirring was continued under reflux for 24 h. The reaction mixture was cooled to 0 °C (**CAUTION!** Exotherm by the reaction causes boiling of the solvent) and then THF (1.5 mL), 2,3-dibromothiophene (**10**, 0.074 mL, 3.0 mmol), and [$NiCl_2$(IPr)(PPh_3)] (7.8 mg, 0.01 mmol) were added successively. The mixture was allowed to stir at room temperature for 24 h. The mixture was quenched with a saturated aqueous solution of ammonium chloride (1.0 mL). The solution was poured into a mixture of diethyl ether/water and the two phases were separated. The aqueous layer was extracted with twice diethyl ether and the combined organic layers were dried over anhydrous sodium sulfate. Concentration of the solvent under reduced pressure left a crude oil, which was purified by column chromatography on silica gel by using hexanes as an eluent to afford **3T** (1.25 g, yellow oil, > 99 %).

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