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Clean and Direct Synthesis of *α*,*α*′-Bithiophenes and Bipyrroles by Metal-Free Oxidative Coupling Using Recyclable Hypervalent Iodine(III) Reagents

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The facile and clean oxidative biaryl coupling reaction of thiophenes and pyrroles has been achieved using the recyclable hypervalent iodine(III) reagents having adamantane or methane structures. These iodine(III) reagents could be recovered from the reaction mixtures by a simple solid–liquid separation, *i.e.*, filtration.

Key words oxidative coupling; hypervalent iodine(III) reagent; recycling; heteroaromatic compound; biaryl

Biaryl compounds serve as key structures of bioactive natural products and chiral ligands for asymmetric reactions and as precursors of various organic materials due to their unique physical properties.[1—3] These beneficial features make them attractive as synthetic targets in modern organic chemistry.[4,5] A large number of the straightforward methods that involve the oxidative coupling processes of unfunctionalized aromatic compounds have been reported using oxidizing agents to produce these important biaryl compounds.[6] Over the past decade, we originally developed a new oxidative biaryl coupling method using the hypervalent iodine(III) reagents, such as phenyliodine bis(trifluoroacetate) (PIFA),[7] and have extended the method to work in alkylarenes,[8] and even in heteroaromatic compounds, *i.e.*, thiophenes[9] and pyrroles.[10] Our new biaryl coupling methods using the low toxic, safe and easy handling trivalent organoiodine oxidants have significant synthetic merits that avoid not only the pre-functionalization of aromatic compounds to the corresponding activated halide or metal forms, but also the use of toxic heavy-metal agent or metal catalyst.

The use of recyclable hypervalent iodine reagents, such as polymer-supported reagents, in the reactions should be a further promising and ecological approach for enhancing the practicability of the methods and for reducing the iodoarene wastes, as a result of the easy removal of the reagents from the reaction mixtures and their reuse.[11] During the course of this study, poly[bis(trifluoroacetoxy)iodo]styrene (PBTIS) has been already applied to the oxidative biaryl coupling reactions of phenyl ethers and alkylarenes.[12] However, we noted that the utilization of the polymer-supported reagent is not successful for the coupling reactions of heteroaromatic compounds, thiophenes and pyrroles, due to its low reactivity and insolubility in most organic solvent systems. Furthermore, PBTIS is sometimes degraded after repeated use.

We have succeeded in the practical oxidative coupling reactions of thiophenes and pyrroles using the non-polymer-supported recyclable iodine(III) reagents **1** (Fig. 1) that can directly provide useful classes of heteroaromatic biaryls.

Our recyclable hypervalent iodine(III) reagents **1**[13] and **3**[14] with an adamantane or methane core have several advantages over the conventional polymer-supported reagents in reactivity and recyclability; they typically show higher reactivities compared to the polymer-supported reagents and no degradation of their backbones after repeated use, which are derived from the well-defined tetrahedral structures. We thus initially attempted the biaryl coupling reaction of 3-hexylthiophene **5a** using the recyclable reagent **1a** based on the standard reaction conditions at −78 °C in CH_2Cl_2 in combination with the several Lewis acids, such as $BF_3 \cdot Et_2O$, TMSOTf, and TMSBr,[9,10] but unexpectedly, the product *α*,*α*′-bithiophene **6a** was only obtained in low yields and large amounts of the starting **5a** remained unchanged. We assumed that these results should be attributed to the low solubility of the reagent **1a** in CH_2Cl_2 at −78 °C, and therefore, decided to examine the reactions at room temperature. Although the reactions of **5a** using the reagent **1a** in ordinary solvents, such as CH_2Cl_2, CH_3CN and MeOH, were similarly not productive, the dimer **6a** was formed exclusively as a single regioisomer in 69% yield when the reaction was carried out in a highly polar, but low nucleophilic 1,1,1,3,3,3-hexafluoroisopropanol (HFIP, $(CF_3)_2CHOH$) solvent in the presence of TMSBr (Chart 1). One of the important roles of the HFIP

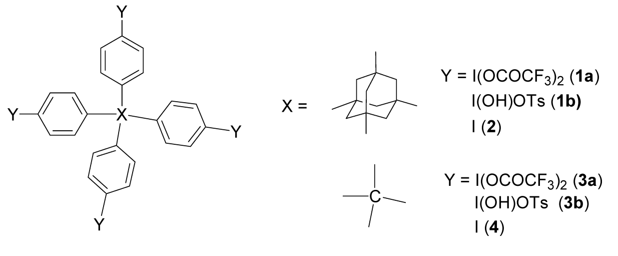
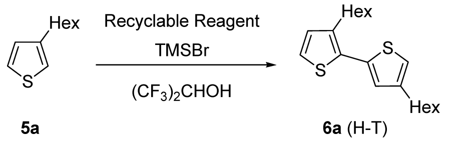


Fig. 1. Recyclable Hypervalent Iodine(III) Reagents Having Tetrahedral Cores



(1)

Recyclable Reagent; **1a**: 69%
1b: 75%
3b: 70%

The molar ratio of thiophene **5a**, **1a**, **b** or **3b**, TMSBr is 1 : 0.5×1/4 : 1. The percentages indicate the isolated yields of **6a** after purification.

Chart 1

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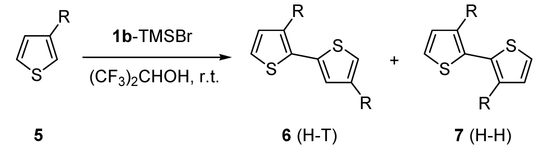
solvent selected in the reactions is considered to be the enhancement of the reactivity of the reagent **1a** to generate reactive aromatic cation intermediates of thiophene **5a**.[15,16] The use of trifluoroethanol (TFE) instead of HFIP or other Lewis acids such as $BF_3 \cdot Et_2O$ and TMSOTf in HFIP resulted in no production of the desired coupling product, because formation of the diaryliodonium salts occurred.[17] We also evaluated the reactivities of the related reagents **1b** and **3b** in the coupling reaction. The reagent **1b** could work more effectively, giving the product **6a** in higher yield than the reagent **1a** and an alternative reagent having a methane core **3b**. In contrast, the polymer-supported reagent, PBTIS, was still ineffective under the given conditions due to its low solubility in the HFIP solvent.

The oxidants **1a, b** or **3b** could be easily separated from the reaction mixtures as the corresponding reduced forms, *i.e.*, the tetraiodide **2** (from **1a** and **1b**) or **4** (from **3b**), by a simple solid–liquid separation. The procedure to recover the tetraiodides was started with the removal of the solvent under reduced pressure by a rotary evaporator. MeOH was then added to the resulting oily residues to precipitate the tetraiodide **2** or **4**. As the tetraiodides are hardly soluble in MeOH, they were simultaneously precipitated as a white powder by adding MeOH and were collected by filtration to recover the tetraiodide **2** or **4**. A series of recycle processes was finally completed by reoxidation of the recovered tetraiodide **2** or **4** to the initial reagents **1a, b** or **3b** using *m*-chloroperbenzoic acid (*m*CPBA). In this way, the reagents could be reproduced with almost the same purity and have been repeatedly used without any loss of activities.[11] Indeed, the reuse of the reagent **1b** in the same reaction gave a comparable result (3 h, 70% yield of coupling product **6a**), and the tetraiodide **2** was also recovered in over 95% yield.

With the reagent **1b** (0.5×1/4 eq, 50 mol% of iodine(III) atom relative to the substrates **5**), the reactions of the thiophenes **5** smoothly proceeded under the homogeneous conditions in the HFIP solvent in the presence of TMSBr (Table 1). This facile and clean method could mainly give the head to tail (H-T) linked dimers **6** from various 3-substituted thiophenes **5** under mild conditions. Typically, the high reactivity of **1b** allowed no requirement for excess amounts of the reagent in the reactions. In each case, the recovery of the reagent **1b** was over 95% by the above mentioned recycling procedure, and thus the crude products **6** could be obtained from the MeOH filtrates and purified by short column chromatography on silica gel. Similar to the substrate **5a**, the 3-substituted thiophenes **5b**—**d** having the shorter or longer alkyl substituents gave the desired products **6b**—**d** in comparable yields with a high degree of regioselectivities (entries 2—4). The bulkier substituents did not affect the yield of the products **6e** and **6f** (entries 5, 6). In our metal-free method, the bromo group in the substrate **5g** was tolerable during the reaction (entry 7). The thiophene **5h** having the alkoxy group was subjected to the reaction to give the corresponding coupling dimer **6h** in an excellent yield without any reoptimization of the reaction conditions (entry 8). The synthesis of electron-rich alkoxy substituted bithiophenes is known to be especially challenging in other oxidation strategies due to their low oxidation potentials for facilitating additional *in situ* undesired oligomerizations of the formed dimers.[18]

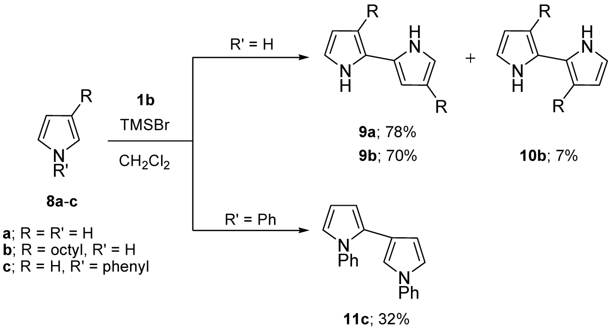
Table 1. Oxidative Biaryl Coupling Reaction of 3-Substituted Thiophenes Using **1b** (Eq. 2)



(2)

Entry[a]	Substrate 5 R		Product	Total yield (%)[b]
1	Hex	(**5a**)	**6a** : **7a**=>99 : 1	75
2	Me	(**5b**)	**6b** : **7b**=93 : 7	64
3	Butyl	(**5c**)	**6c** : **7c**=98 : 2	62
4	Octyl	(**5d**)	**6d** : **7d**=>99 : 1	54
5	*i*-Butyl	(**5e**)	**6e** : **7e**=98 : 2	71
6	*c*-Hex	(**5f**)	**6f** : **7f**=>99 : 1	54
7	$(CH_2)_6Br$	(**5g**)	**6g** : **7g**=>99 : 1	50
8	OMe	(**5h**)	**6h** : **7h**=>99 : 1	67

a) The molar ratio of thiophenes **5**, **1b**, TMSBr is 1 : 0.5×1/4 : 1. In each case, 10—20% of the starting materials **5** were recovered. *b*) Isolated yield after purification.



The molar ratio of pyrroles **8**, **1b**, TMSBr is 1 : 0.5×1/4 : 1. The percentages indicate the isolated yields of **9**—**11** after purification.

Chart 2

We next tried to extend the coupling method to more reactive N–*H* pyrroles, but the acid-sensitive N–*H* pyrrole **8a** gave a number of insoluble identified byproducts in acidic HFIP. Therefore, we screened other non-acidic solvents, and CH_2Cl_2 gave a better result for N–*H* pyrrole **8a** (Chart 2). The reaction of 3-alkylpyrrole **8b** was, unfortunately, not as selective as thiophenes **5**, but the two regioisomers **9b** and **10b** could be separated by column chromatography techniques.[19] The N-substituted pyrrole **8c**, on the other hand, reacted at the both α- and β-positions to give the α,β'-bipyrrole **11c**[20] rather than the α,α'-bipyrrole albeit in low yield.

In summary, we have established the first facile and clean method for the oxidative biaryl coupling reaction of heteroaromatic compounds using recyclable hypervalent iodine reagents. The present protocol is quite simple, and cleanly gave the useful H-T dimers **6** and **9**, the oligomers or polymers of which have recently gained considerable attention as unique electroactive organic materials having excellent degree of co-planarity of the heteroaromatic rings.[21,22]

Experimental

General The ^1H- and ^{13}C-NMR spectra were recorded by a JEOL JMN-300 spectrometer operating at 300 MHz in $CDCl_3$ at 25 °C with tetramethylsilane as the internal standard. The data are reported as follows: chemical shift in ppm (δ), integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, br=broad singlet, m=multiplet), and coupling constant (Hz). The infrared spectra (IR) were obtained using a Hitachi 270-50 spectrometer; absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). The mass spectra were obtained using a Shimadzu GCMS-QP 5000 instrument with ionization voltages of 70 eV. The high resolution mass spectra and elemental analysis were performed by the Elemental Analysis Section of Osaka University. The column chromatography and TLC were carried out on Merck Silica gel 60 (230—400 mesh) and Merck Silica gel F_{254} plates (0.25 mm), respectively. The spots and bands were detected by UV irradiation (254, 365 nm).

All commercially available reagents and solvents were used as received without further purification.

Preparation of 1b To a stirred solution of 1,3,5,7-tetrakis(4-iodophenyl)adamantane **2** (1.42 g, 1.5 mmol) in CH_2Cl_2 (150 ml)–AcOH (150 ml) was added *m*-chloroperbenzoic acid (*m*CPBA) (*ca.* 69% purity, 3.12 g, 18 mmol) at room temperature. The mixture was stirred for 12 h under the same reaction conditions until the cloudy solution became clear. The resultant mixture was filtered, and CH_2Cl_2 was removed using a rotary evaporator. Hexane was added to the residue to precipitate 1,3,5,7-tetrakis[4-(diacetoxyiodo)phenyl]adamantane. After filtration, the crude product was obtained in nearly quantitative yield.

1,3,5,7-Tetrakis[4-(diacetoxyiodo)phenyl]adamantane (1.01 g, 0.71 mmol) was dissolved in CH_3CN (15 ml), then *p*-toluenesulfonic acid monohydrate (1.64 g, 5.6 mmol) was added to the solution at room temperature. The mixture was stirred for an additional 3 h. The resulting precipitate was filtered and washed several times with CH_3CN and hexane, then dried *in vacuo* to give **1b** (1.05 g, 94%) as a slightly yellow solid.

1,3,5,7-Tetrakis[4-{hydroxy(tosyloxy)iodo}phenyl]adamantane (**1b**)[13]: Slightly yellow crystals. mp (decomp.) 183—190 °C. ^{1}H-NMR ($CDCl_3$/CF_3CO_2H=10/1) δ: 2.26 (12H, s), 2.38 (12H, s), 7.26 (8H, d, J=8.1 Hz), 7.65 (8H, d, J=8.4 Hz), 7.70 (8H, d, J=8.9 Hz), 8.25 (8H, d, J=8.9 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$/CF_3CO_2H=10/1) δ: 21.4, 39.9, 45.8, 121.1, 126.3, 129.0, 129.8, 135.1, 135.9, 144.5, 154.2. *Anal.* Calcd for $C_{62}H_{60}I_4O_{16}S_4 \cdot 4H_2O$: C, 42.09; H, 3.87; I, 28.69, S, 7.25. Found: C, 42.03; H, 3.64; I, 28.32, S, 7.25.

Typical Procedure for Direct Oxidative Biaryl Coupling Reaction Using 1b To a stirred solution of 3-hexylthiophene **5a** (101 mg, 0.6 mmol) in $(CF_3)_2CHOH$ (6 ml) was added **1b** (127.8 mg, 0.3×1/4 mmol) and then TMSBr (0.08 ml, 0.6 mmol) at room temperature when the color of the solution immediately changed to brown. After stirring for 3 h, CH_2Cl_2, saturated $NaHCO_3$ aq. and solid $Na_2S_2O_3 \cdot 5H_2O$ were successively added to the reaction mixture with stirring. The organic layer was then separated and evaporated to dryness. MeOH (10 ml) was added to the reaction mixture, and it was filtered to give the tetraiodide **2** (confirmed by ^{1}H-NMR analysis and TLC), which was washed several times with small portions of MeOH for purification. The filtrate was evaporated and subjected to column chromatography (SiO_2, hexane) to give 3,4′-dihexyl-2,2′-bithiophene **6a** (75 mg, 75%) as a slightly yellow oil. The regiochemistry of the product **6a** was determined by comparing it to the authentic sample.

3,4′-Dihexyl-2,2′-bithiophene (**6a**)[23]: Slightly yellow oil; ^{1}H-NMR ($CDCl_3$) δ: 0.84—0.92 (6H, m), 1.20—1.35 (12H, m), 1.52—1.70 (4H, m), 2.63 (2H, t, J=8.4 Hz), 2.74 (2H, t, J=8.4 Hz), 6.89—6.92 (2H, m), 7.03 (1H, s), 7.12 (1H, d, J=5.5 Hz) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 14.1, 22.6, 29.0, 29.1, 29.2, 29.7, 30.4, 30.5, 30.7, 31.6, 31.7, 119.9, 123.4, 127.3, 129.9, 130.9, 135.8, 139.3, 143.5 ppm. HR-FAB-MS: *m/z* 334.1784 $[M]^+$ (Calcd for $C_{20}H_{30}S_2$: 334.1789).

3,4′-Dimethyl-2,2′-bithiophene (**6b**): Slightly yellow oil; ^{1}H-NMR ($CDCl_3$) δ: 2.28 (3H, s), 2.38 (3H, s), 6.86—6.87 (2H, m), 6.94 (1H, s), 7.11 (1H, d, J=5.1 Hz) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 15.3, 15.7, 120.4, 123.0, 127.8, 131.3, 133.7, 136.3, 138.0, 141.3 ppm.

3,4′-Dibutyl-2,2′-bithiophene (**6c**): Slightly yellow oil; ^{1}H-NMR ($CDCl_3$) δ: 0.83—0.96 (6H, m), 1.29—1.42 (4H, m), 1.58—1.67 (4H, m), 2.61 (2H, t, J=7.5 Hz), 2.75 (2H, t, J=7.5 Hz), 6.87—6.96 (3H, m), 7.13 (1H, d, J=5.1 Hz) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 13.9, 22.4, 22.6, 28.9, 30.2 (×2), 32.6, 32.9, 119.9, 123.4, 127.3, 129.9, 130.9, 134.1, 139.3, 143.5 ppm. IR (KBr) cm^{-1}: 3051 w, 2930 s, 2858 s, 1732 w, 1456 m, 1377 m, 1263 s, 1088 w, 831 m, 748 s, 652 m. *Anal.* Calcd for $C_{16}H_{22}S_2$: C, 69.01; H, 7.96; S, 23.03. Found: C, 69.01; H, 7.93; S, 22.74.

3,4′-Dioctyl-2,2′-bithiophene (**6d**): Slightly yellow oil; ^{1}H-NMR ($CDCl_3$) δ: 0.86—0.88 (6H, m), 1.20—1.30 (20H, m), 1.56—1.63 (4H, m), 2.52 (2H, t, J=7.5 Hz), 2.74 (2H, t, J=7.5 Hz), 6.80—6.86 (3H, m), 7.05 (1H, d, J=5.1 Hz) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 14.1, 15.3, 22.7, 29.1, 29.3, 29.4 (×3), 29.6, 30.4, 30.5, 30.7, 31.9, 119.9, 123.4, 127.3, 129.9, 131.0, 135.8, 139.4, 143.5 ppm. IR (KBr) cm^{-1}: 2923 s, 2853 s, 1464 m, 1377 w, 1200 w, 1086 w, 831 m, 721 m, 652 w. *Anal.* Calcd for $C_{24}H_{38}S_2$: C, 73.78; H, 9.80; S, 16.41. Found: C, 73.83; H, 9.82; S, 16.13.

3,4′-Bis(2-methylpropyl)-2,2′-bithiophene (**6e**)[24]: Slightly yellow oil; ^{1}H-NMR ($CDCl_3$) δ: 0.90—0.94 (12H, m), 1.83—1.96 (2H, m), 2.46 (2H, d, J=7.2 Hz), 2.61 (2H, d, J=7.2 Hz), 6.85 (1H, d, J=1.2 Hz), 6.89 (1H, d, J=5.1 Hz), 6.90 (1H, d, J=1.2 Hz), 7.13 (1H, d, J=5.1 Hz) ppm. HR-FAB-MS *m/z*: 278.1152 $[M]^+$ (Calcd for $C_{16}H_{22}S_2$: 278.1163).

3,4′-Dicyclohexyl-2,2′-bithiophene (**6f**): Slightly yellow oil; ^{1}H-NMR ($CDCl_3$) δ: 1.26—1.56 (12H, m), 1.72—1.87 (6H, m), 1.99—2.02 (2H, m), 2.57—2.59 (1H, m), 2.96—3.01 (1H, m), 6.91 (1H, s), 6.97—7.03 (2H, m), 7.15 (1H, d, J=5.4 Hz) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 26.1 (×2), 26.6, 26.7, 34.1, 34.4, 38.2, 39.6, 118.5, 123.8, 126.4, 127.3, 130.1, 135.5, 144.8, 149.3 ppm. IR (KBr) cm^{-1}: 2923 s, 2851 s, 1728 w, 1448 s, 1263 m, 1124 w, 943 w, 833 m, 731 m, 708 w, 650 m. HR-FAB-MS *m/z*: 330.1470 $[M]^+$ (Calcd for $C_{20}H_{26}S_2$: 330.1476).

3,4′-Bis(6-bromohexyl)-2,2′-bithiophene (**6g**): Slightly yellow oil; ^{1}H-NMR ($CDCl_3$) δ: 1.30—1.51 (8H, m), 1.59—1.71 (4H, m), 1.80—1.92 (4H, m), 2.61 (2H, t, J=7.5 Hz), 2.75 (2H, t, J=7.5 Hz), 3.40 (4H, q, J=7.5 Hz), 6.89—6.92 (3H, m), 7.20 (1H, d, J=5.1 Hz) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 27.9, 28.4, 28.5, 28.9, 30.1, 30.2, 30.3, 30.4, 32.7, 33.9 (×2), 120.0, 123.6, 127.3, 129.8, 131.0, 135.8, 139.0, 143.2 ppm. HR-FAB-MS *m/z*: 489.9988 $[M]^+$ (Calcd for $C_{20}H_{28}Br_2S_2$: 489.9999).

3,4′-Dimethoxy-2,2′-bithiophene (**6h**)[25]: Slightly yellow oil; ^{1}H-NMR ($CDCl_3$) δ: 3.81 (3H, s), 3.94 (3H, s), 6.12 (1H, d, J=1.2 Hz), 6.85 (1H, d, J=5.4 Hz), 6.89 (1H, d, J=1.2 Hz), 7.06 (1H, d, J=5.4 Hz) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 57.2, 58.8, 95.0, 114.7, 115.1, 116.8, 121.7, 133.9, 153.7, 157.9 ppm.

Bipyrrole compounds **9**—**11** were obtained by a procedure similar to that described for the thiophenes **5**. CH_2Cl_2 was used as solvent instead of HFIP.

2,2′-Bipyrrole (**9a**)[26]: White solid; mp: 187—189 °C; Rf=0.32 (hexane/EtOAc=4/1); ^{1}H-NMR ($CDCl_3$) δ: 6.05—6.19 (4H, m), 6.70—6.72 (2H, m), 8.23 (2H, bs) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 103.5, 109.4, 117.6, 125.9 ppm. IR (KBr) cm^{-1}: 3366 m, 3123 w, 3103 w, 1574 w, 1518 w, 1454 w, 1425 w, 1404 w, 1261 w, 1097 m, 1032 m, 912 s, 891 w, 775 m, 743 s, 658 w. *Anal.* Calcd for $C_8H_8N_2$: C, 72.70; H, 6.10; S, 21.20. Found: C, 72.41; H, 6.22; S, 20.92.

3,4′-Dioctyl-2,2′-bipyrrole (**9b**): Slightly brown oil; ^{1}H-NMR ($CDCl_3$) δ: 0.86—0.89 (6H, m), 1.23—1.28 (20H, m), 1.55—1.60 (4H, m), 2.48 (2H, t, J=7.8 Hz), 2.56 (2H, t, J=7.8 Hz), 6.02—6.04 (1H, m), 6.12 (1H, t, J=2.7 Hz), 6.54–6.57 (1H, m), 6.68 (1H, t, J=2.7 Hz), 7.88 (1H, bs), 7.93 (1H, bs) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 14.1, 22.7, 26.5, 27.0, 29.3, 29.5, 29.6, 29.7, 29.9, 31.1, 31.2, 31.9 (×2), 106.0, 109.8, 114.6, 116.6, 120.4, 121.7, 125.4, 125.6 ppm. IR (KBr) cm^{-1}: 3053 m, 2986 m, 2928 s, 2359 m, 2340 m, 2307 m, 1421 m, 1261 w, 1155 s, 895 m, 748 w, 704 w. HR-FAB-MS *m/z*: 356.3191 $[M]^+$ (Calcd for $C_{24}H_{40}N_2$: 356.3197).

3,3′-Dioctyl-2,2′-bipyrrole (**10b**): Slightly yellow oil; ^{1}H-NMR ($CDCl_3$) δ: 0.84—0.89 (6H, m), 1.23—1.27 (20H, m), 1.43—1.56 (4H, m), 2.42 (4H, t, J=7.8 Hz), 6.16 (2H, t, J=2.7 Hz), 6.77 (2H, t, J=2.7 Hz), 7.90 (2H, bs) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 13.9, 22.5, 26.1, 29.1, 29.3, 29.4, 31.2, 31.7, 108.9, 116.9, 120.5, 122.8 ppm. IR (KBr) cm^{-1}: 3942 s, 3053 m, 2986 m, 2959 m, 2928 m, 2855 m, 2685 s, 2359 s, 2305 m, 1421 m, 1377 s, 1261 w, 1157 s, 895 m, 748 w, 706 w. HR-FAB-MS *m/z*: 356.3191 $[M]^+$ (Calcd for $C_{24}H_{40}N_2$: 356.3186).

1,1′-Diphenyl-2,3′-bipyrrole (**11c**): Slightly yellow oil; ^{1}H-NMR ($CDCl_3$) δ: 6.07 (1H, dd, J=3.3, 1.7 Hz), 6.31—6.40 (2H, m), 6.63—6.66 (1H, m), 6.83—6.86 (1H, m), 6.90—6.94 (1H, m), 7.16—7.28 (4H, m), 7.31—7.40 (6H, m) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 107.9, 108.7, 110.5, 116.2, 118.4, 118.8, 119.8, 122.8, 125.3, 126.5, 126.9, 128.7, 129.0, 129.4, 140.2, 140.7 ppm. IR (KBr) cm^{-1}: 3058 w, 1599 w, 1504 m, 1462 w, 1352 w, 1319 w, 1184 w, 1074 w, 1036 w, 912 s, 743 s, 694 w, 650 w. HR-FAB-MS *m/z*: 285.1394 $[M+H]^+$ (Calcd for $C_{20}H_{17}N_2$: 285.1392).

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References and Notes

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19) The coupling reaction of other 3-substituted pyrroles **8** proceeded in good yields, but the selectivity of H-T and H-H dimers is not so high as that of thiophenes **5** under the present conditions. Further optimization for control of the regioselectivity in the bipyrrole synthesis will be described in due course.

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