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Article

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Indium-Catalyzed Regioselective β-Alkylation of Pyrroles with Carbonyl Compounds and Hydrosilanes, and Its Application to Constructing a Quaternary Carbon Center with a β-Pyrrolyl Group

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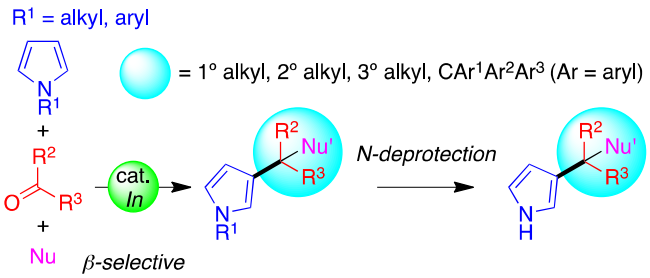
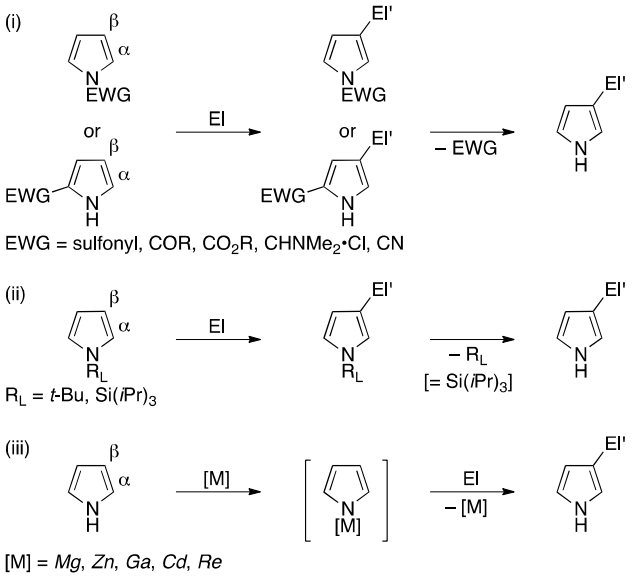
ABSTRACT: Treatment of *N*-substituted pyrroles with carbonyl compounds and nucleophiles under indium catalysis was found to be a promising method for preparing β-alkylpyrroles without contamination by α-alkylpyrroles. With this methodology, a variety of alkyl groups, which are primary, secondary and tertiary as well as cyclic and functionalized types, can be introduced in place onto the pyrrole ring. The simplicity performable as a catalytic one-step process is one of the important feature of this reaction. The substituent on the nitrogen atom of the product β-alkylpyrrole can be removed easily by literature procedures. Therefore, the indium-catalyzed β-alkylation plus the N-deprotection is a powerful system for all six variations, which are *N*-substituted and *N*-unsubstituted β-alkylpyrroles having primary, secondary and tertiary alkyl groups. Our method is applicable to synthesizing, albeit in two steps, β-pyrrolyl-group-connected unsymmetrical tetraarylmethanes that have not been able to be addressed thus far. Mechanistic studies showed the following three aspects: (1) dipyrrolylalkanes produced *in situ* from the pyrrole and carbonyl compound are key intermediates, (2) the selective β-alkylation is attributed to the selective elimination of an α-pyrrolyl group from the dipyrrolylalkane intermediates, and (3) the indium Lewis acid catalyst is indispensable for the progress of both the stages.



INTRODUCTION

A pyrrole ring is an important five-membered heteroaromatic motif containing one nitrogen atom. Alkyl-substituted pyrroles are of particular concern because the structure is found in not only many natural products and biologically active compounds[1] but also functional organic materials.[2] Because of sufficient aromaticity and π-excessive nature of the pyrrole ring, a straightforward approach to the alkyl-substituted pyrrole is likely to be direct installation of an alkyl unit onto the pyrrole ring by electrophilic aromatic substitution (S_EAr), and a large number of relevant studies have actually been reported.[3] The pyrrole ring has two electrically different carbon reaction sites, which are thus α-position of the C2 (C5) and β-position of the C3 (C4), and the S_EAr reaction on the pyrrole ring has been known to occur most predominantly at the α-position.[4] Accordingly, S_EAr-based regioselective β-alkylation of pyrroles is still a challenging research topic in the field of synthetic organic chemistry. In spite of such characteristics of pyrroles, three major strategies through the S_EAr mechanism have been utilized to change the α-orientation to β-orientation, albeit sometimes incompletely:[5] (i) use of pyrroles with an electron-withdrawing group (EWG) at the N1 or at the C2,[6,7] (ii) use of pyrroles with a bulky substituent (R_L) at the N1,[8,9] and (iii) use of pyrrolyl–metal complexes (Scheme 1).[10]

Scheme 1. Representative Strategies for β-Alkylation of Pyrroles

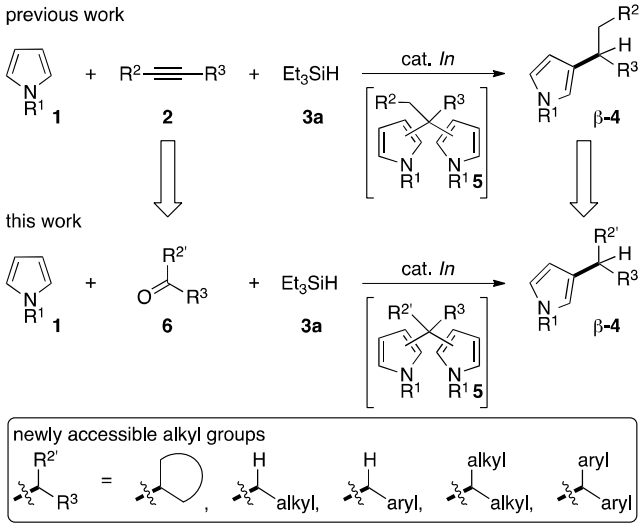


Other strategies not through the S_EAr route but including direct alkylation of the pyrrole ring have also emerged in the literature. For example, the η^2-pyrrole–osmium(II) complex, the pyrrole ring of which behaves as no longer an aromatic compound but as an enamine, has reportedly reacted with electrophiles at the β-position.[11] Moreover, the strategy of chelation-assisted C–H bond activation by transition metals such as Fe, Rh, and Pd has recently attracted attention (since 2014).[12] Although chemists have relied mainly on these S_EAr- and non-S_EAr-based strategies to obtain β-alkylpyrroles,[13] there has been no method capable of offering a series of β-alkylpyrroles with primary, secondary and tertiary as well as cyclic and functionalized alkyl groups, to the best of our knowledge.

Different from these precedents,[6–12] in 2009, we have developed a conceptually new strategy to synthesize β-alkylpyrroles, by simply mixing pyrroles **1**, alkynes **2** and Et_3SiH (**3a**) in the presence of an indium catalyst (Scheme 2).[14] This is the first case of the S_EAr-based pyrrole β-alkylation, performed in a catalytic single-step. As key intermediates, dipyrrolylalkanes **5** are found to be formed as a mixture of regioisomers concerning the pyrrole ring but lead to the single isomer of β-alkylpyrroles after reductive C–C(pyrrolyl) bond cleavage. The originality of the process will be attributed to such unique reaction

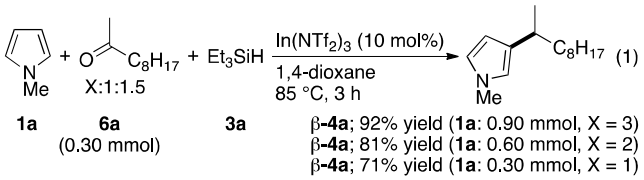
profile, and the feature of the process will be the exclusive formation of β-alkylpyrroles. However, when using alkynes **2**, cyclic and primary alkyl groups as well as a diarylmethyl unit ($CHAr_2$) are unable to be introduced intrinsically onto **1**. Regioselective introduction of a dialkylmethyl group with two identical alkyl moieties [$CH(alkyl)_2$] is also not an easy task. We therefore envisaged that, instead of alkynes **2**, the use of carbonyl compounds **6** having much higher skeletal and substitutional diversities would lead to overcoming the limitations of the alkyl groups. We disclose herein the details of the indium-catalyzed β-alkylation of pyrroles with carbonyl compounds and **3a**.[15,16,17] Carbon nucleophiles other than **3a** as a hydride nucleophile are available as well, and thus we also demonstrate here that the indium method is highly effective for creating a quaternary carbon center with a β-pyrrolyl group.[18]

Scheme 2. Indium-Catalyzed Reductive β-Alkylation of Pyrroles: Previous Work with Alkynes versus This Work with Carbonyl Compounds (*In* = an indium salt)



RESULTS AND DISCUSSION

Indium-Catalyzed Reductive β-Alkylation of Pyrroles with Carbonyl Compounds and Et_3SiH. Because of the high reliability of $In(NTf_2)_3$ (Tf = SO_2CF_3) as a catalyst for the alkyne-based reaction,[14] we first examined its catalytic performance in the reaction of 1-methylpyrrole (**1a**, 0.90 mmol) with 2-decanone (**6a**, 0.30 mmol) and Et_3SiH (**3a**, 0.45 mmol) (eq. 1, **1a**:**6a**:**3a** = 3:1:1.5). The reaction in 1,4-dioxane with 10 mol% of $In(NTf_2)_3$ at 85 °C for 3 h provided 3-(decan-2-yl)-1-methylpyrrole (**β-4a**) as a single regioisomer in 92% yield. The exclusive formation of **β-4a** without contamination by its α-isomer is remarkable. Reducing the quantity of **1a** to 0.60 mmol and then 0.30 mmol lowered the yield of **β-4a** gradually, indicating that 3 molar equivalents of **1a** is a favorable amount used to **6a**. However, the good yield can be maintained safely even with the reduced amount of **1a**. Considering these results, in the case that a pyrrole substrate is expensive and/or elaborate, its use less than 3 molar equivalents should be a possible and smart choice.

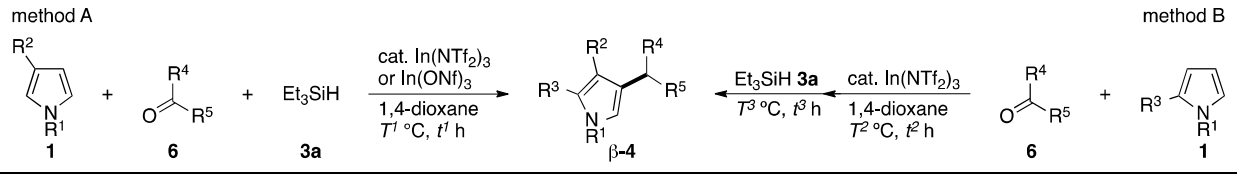


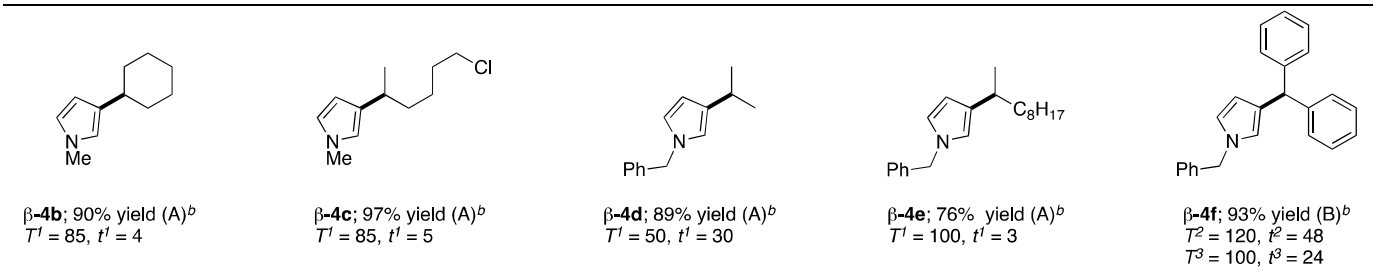
As already demonstrated, the same product (**β-4a**) can be prepared with 1-decyne instead of **6a**.[14] However, the use of carbonyl compound **6a** as the alkyl group source has the following advantages over using 1-decyne: (1) the reaction of **6a** is able to be performed with a smaller amount of $In(NTf_2)_3$ (10 mol%), compared to that (25 mol%) used for the reaction of 1-decyne, and (2) **6a** (e.g., 6,600 Japanese yen/25 g) is much cheaper than 1-decyne (e.g., 14,200 Japanese yen/25 g). Inspired by the above result, we next examined the substrate scope of this reaction, where methods A and B were adopted as experimental procedures. Method A is simply a simultaneous treatment of **1**, **6** and **3a** in the presence of an indium catalyst. Regarding method B, **3a** is added into a reaction vessel after consumption of **6**,

which means that dipyrrolylalkanes **5** are formed *in situ* as crucial intermediates.[19] Method B is particularly useful when **3a**-induced reduction of **6** and slight co-formation of an α-alkylpyrrole are observed in the use of method A. In order to avoid overlapping, new experimental results that have not appeared in the preceding communication[15] are collected in Table 1, and achievements that should be noted in Table 1 are as follows. To begin with, the benzyl group on the nitrogen atom of **β-4d**–**β-4f** underwent no N-debenzylation even under the heating Lewis acidic conditions.[20] The diphenylmethyl group, which is unavailable in the alkyne-based reaction, is derived from diphenylketone (**β-4f**). As pieces of pyrrole substrates, *N*-substituted pyrroles with sulfonylethyl ($RSO_2CH_2CH_2$; R = Me, Ph) and a series of ethoxycarbonylethyl ($EtO_2CCH_2CY_2$; Y = H, Me) units participated well in this protocol (**β-4h**–**β-4l**). These substituents are useful because they are removable from the nitrogen atom, when required, with easily available bases such as NaH and *t*-BuOK (see Scheme 4). While 1,2-dimethylpyrrole has the two unsymmetrical β-sites, the reductive alkylation with tetrahydro-4*H*-thiopyran-4-one proceeded regioselectively at the less hindered β-site of the C4 (**β-4n**). A particularly interesting observation is that even 1,3-dimethylpyrrole was alkylated selectively at the sterically congested β-site, despite that 1,3-dimethylpyrrole has the two more intrinsically nucleophilic α-sites (**β-4o**). This result triggered us to successively investigate whether the trend is compatible with β-alkylpyrroles synthesized by the present method. Thus, the 3-decylpyrrole, which has been prepared from decanal and 1-*tert*-butylpyrrole and **3a**, was again alkylated at the β-site in a regioselective manner (**β-4p**). Importantly, through column chromatography on silica gel, the starting 3-decylpyrrole remained unreacted was recovered with efficiency of 98% (see Table 1), which was calculated on the basis of the excess amount of the 3-decylpyrrole used to acetone, thus indicating that the starting β-alkylpyrrole of our own making are recoverable and will be reusable. Not only the secondary alkyl group, but linear and branched primary alkyl groups are also installable to the unoccupied β-position of the 3-decylpyrrole (**β-**

4q and **β-4r**). The iterative β-alkylation also proceeded regioselectively when the 3-(2-propyl)pyrrole with the bulkier pre-alkyl group was used (**β-4s** and **β-4t**). The β-alkylpyrrole substrates of other entries were always recovered with high efficiency over 90%.

Table 1. Indium-Catalyzed Reductive β-Alkylation of Pyrroles with Carbonyl Compounds and Et_3SiH[a]





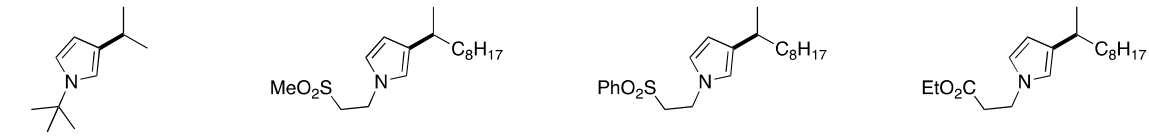
β-**4b**; 90% yield (A)[b]
T^1 = 85, t^1 = 4

β-**4c**; 97% yield (A)[b]
T^1 = 85, t^1 = 5

β-**4d**; 89% yield (A)[b]
T^1 = 50, t^1 = 30

β-**4e**; 76% yield (A)[b]
T^1 = 100, t^1 = 3

β-**4f**; 93% yield (B)[b]
T^2 = 120, t^2 = 48
T^3 = 100, t^3 = 24

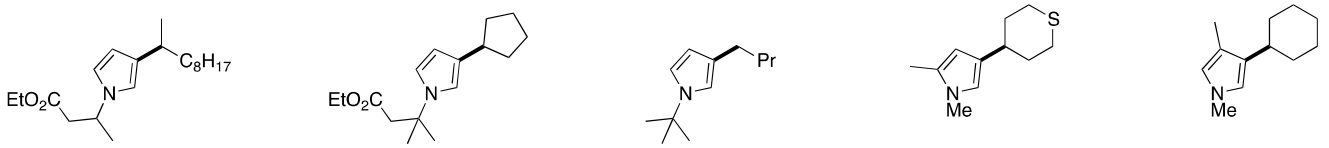


β-**4g**; 84% yield (A)[b]
T^1 = 50, t^1 = 18

β-**4h**; 86% yield (A)[b]
T^1 = 85, t^1 = 3

β-**4i**; 90% yield (A)[b]
T^1 = 85, t^1 = 3

β-**4j**; 97% yield (A)[b]
T^1 = 85, t^1 = 2



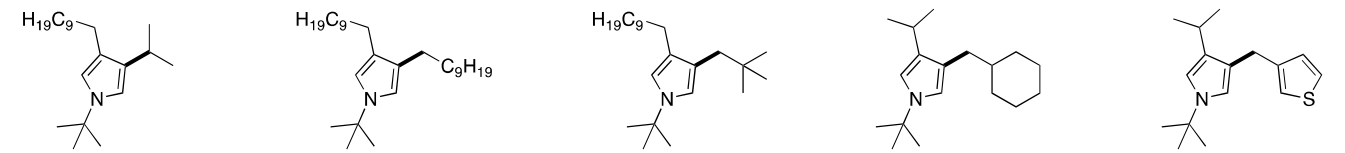
β-**4k**; 93% yield (A)[b]
T^1 = 85, t^1 = 2

β-**4l**; 80% yield (A)[b]
T^1 = 85, t^1 = 3

β-**4m**; 54% yield (A)[b]
T^1 = 85, t^1 = 7

β-**4n**; 60% yield (B)[b]
T^2 = 85 °C, t^2 = 3
T^3 = 85 °C, t^3 = 48

β-**4o**; 80% yield (A)[b]
T^1 = 85, t^1 = 5



β-**4p**; 93% yield (A)[b]
T^1 = 50, t^1 = 24 (98%)[c]

β-**4q**; 91% yield (A)[b]
T^1 = 85, t^1 = 3 (100%)[c]

β-**4r**; 93% yield (A)[b]
T^1 = 85, t^1 = 3 (90%)[c]

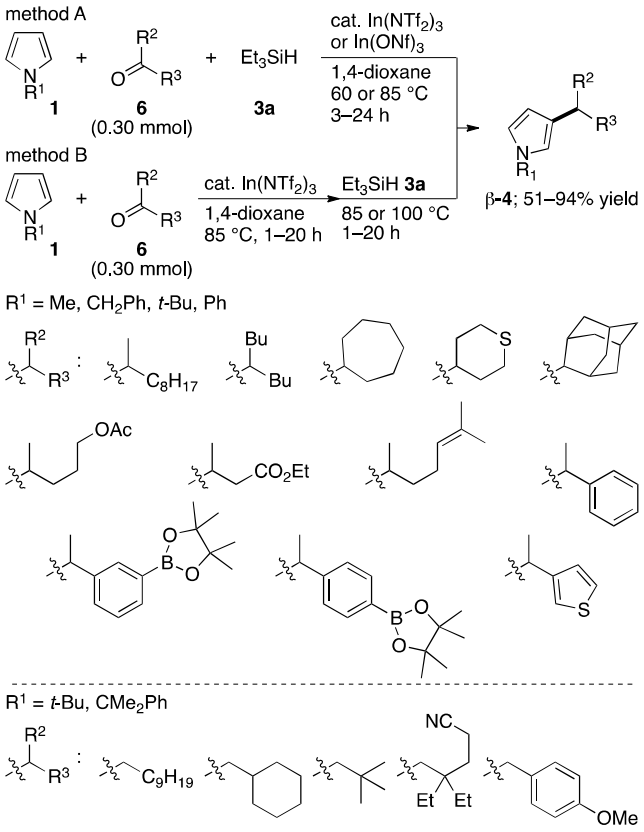
β-**4s**; 84% yield (A)[b]
T^1 = 85, t^1 = 5 (96%)[c]

β-**4t**; 73% yield (A)[b]
T^1 = 85, t^1 = 20 (92%)[c]

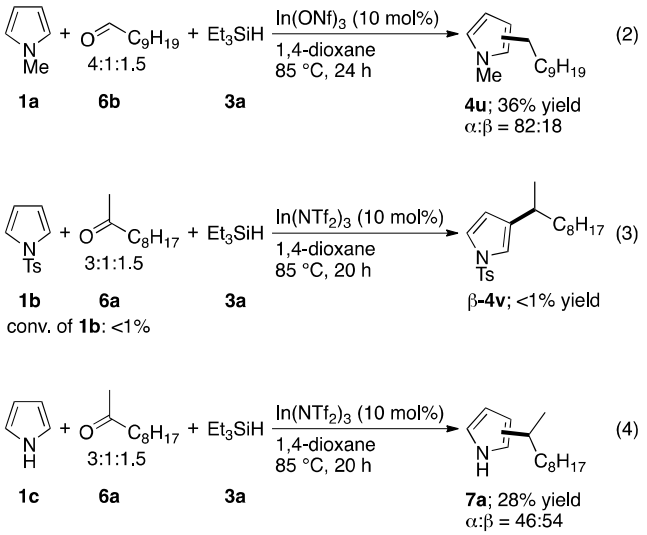
[a]Yields of **β-4** based on **6** are shown here. $In(NTf_2)_3$ was used as a catalyst for synthesizing **β-4b**–**β-4l** and **β-4n**–**β-4p**, and $In(ONf)_3$ (Nf = $SO_2C_4F_9$) was used a catalyst for the reaction to introduce a primary alkyl group (**β-4m** and **β-4q**–**β-4t**). See the Experimental Section for the details including the amount of **1** (0.1–0.3 mmol), **6**, **3a** and an indium catalyst used. [b]The method A or B used is shown in the parentheses. [c]Recovery efficiency of the pyrrole substrate (**1**) is shown in the parentheses.

In order to understand the whole aspect, in particular, the scope of carbonyl compounds **6** with respect to the indium-catalyzed reductive β-alkylation of pyrroles, the results that have been disclosed in the preceding communication are summarized in Scheme 3. Including the results of Table 1 for which no particular explanation was provided, important features of this method are described as follows. (1) Regioselective introduction of a dialkylmethyl group with two identical alkyl moieties, e.g., the 5-nonyl group ($CHBu_2$) is possible. (2) The cyclic frameworks can be handled with ease. (3) Primary alkyl groups can be installed through the treatment of aldehydes. (4) A variety of functional groups, which are chloro, sulfonyl, ester, sulfide, alkenyl, boryl, cyano, and alkoxy functionalities, are well-tolerated under the reaction conditions. (5) In all cases, the β-regioselectivity is controlled perfectly. In particular, (1), (2) and (3) cannot be achieved through the alkyne-based reaction.[14]

Scheme 3. Summary of Other Substrate Scope on Indium-Catalyzed Reductive β-Alkylation of Pyrroles with Carbonyl Compounds and Et_3SiH

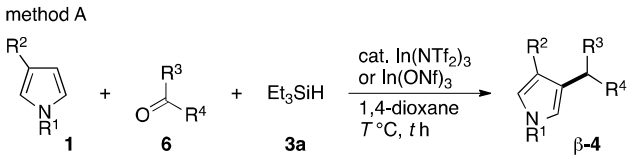


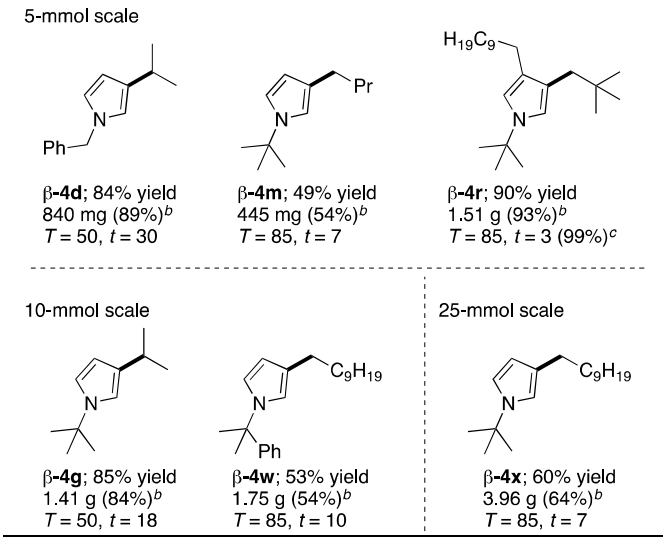
As shown in Table 1 and Scheme 3, the bulkiness such as the *tert*-butyl and 2-phenyl-2-propyl (cumyl) groups is required on the nitrogen atom of **1** to attain complete β-selectivity and also high conversion of **5** in the reaction of an aldehyde for introducing a primary alkyl group. In fact, when the pyrrole substrate has the sterically less hindered *N*-methyl group, the α-alkylpyrrole was formed predominately in a low yield (eq. 2). Different from the series of electron-rich pyrroles that successfully participated in this reaction, no desired β-alkylation occurred in the use of an electron-deficient pyrrole such as 1-Ts–pyrrole (**1b**; Ts = *p*-toluenesulfonyl), thus being recovered quantitatively (eq. 3). Simple pyrrole **1c** without a substituent on the nitrogen atom was also subjected to the standard reaction conditions, but was found not to show good performance in view of both of the β-selectivity and the yield (eq. 4).



In order to evaluate the practical utility of this system, we attempted the preparation of the β-alkylpyrrole in a larger scale than the 0.1–0.3-mmol scale reactions shown in Table 1 and Scheme 3. The results are collected in Table 2. For example, the reductive β-alkylation of 1-*tert*-butylpyrrole with decanal (**6b**) and **3a** was performed on a 25-mmol scale, thereby giving 3.96 g of **β-4x** in 60% yield, which is comparable to the yield of 64% when performed on the 0.3-mmol small scale. The other cases of different scales also proceeded comparably to each of the corresponding small scale reactions, thus indicating that the present method can respond to a range of scalability as a synthetic organic reaction.

Table 2. Preparative Scale Synthesis of β-Alkylpyrroles[a]



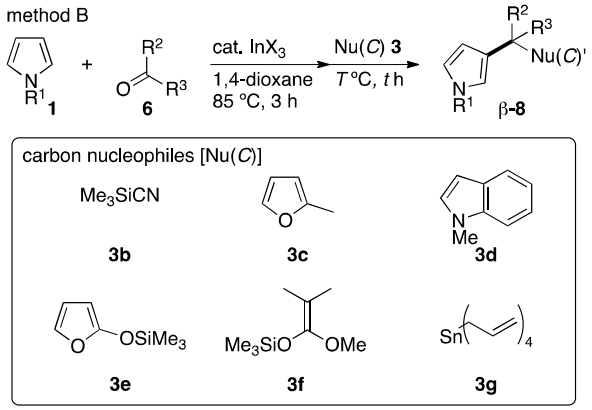


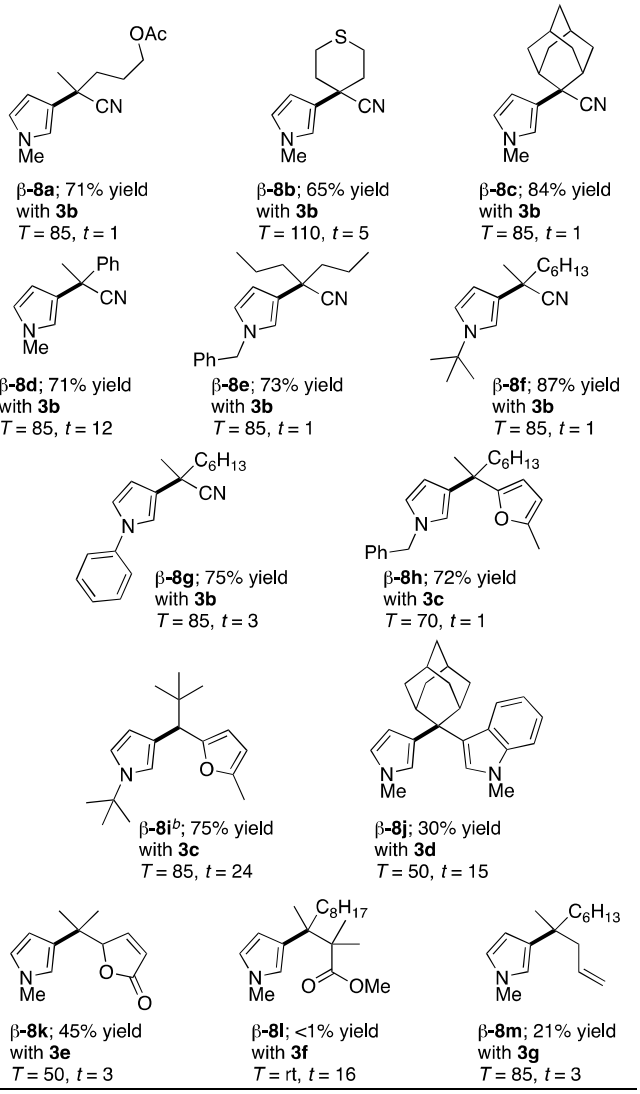
[a]Yields of **β-4** based on **6** are shown here. Further details on the reaction conditions for each reaction are given in the Experimental Section. [b]The yield of the 0.1- or 0.3-mmol scale reaction is shown in the parentheses. [c]Recovery efficiency of the pyrrole substrate (**1**) is shown in the parentheses.

Indium-Catalyzed β-Alkylation of Pyrroles with Carbonyl Compounds and Carbon Nucleophiles. As shown in the preceding section, the combination of ketones **6** as electrophiles and Et_3SiH (**3a**) as a hydride nucleophile is incorporated as a secondary alkyl group onto the pyrrole ring. We therefore considered that the combination of ketones and carbon nucleophiles [Nu(*C*)] would be available for the introduction of a tertiary alkyl group.[21] The results of the reactions performed on the basis of this consideration are shown in Table 3, which includes only the experimental results that have not been disclosed previously.[15] With method B at 85 °C in the presence of a catalytic amount of $In(OTf)_3$, the reaction of 1-methylpyrrole (**1a**) and 5-acetyloxy-2-pentanone with Me_3SiCN (**3b**) as a cyanide carbon nucleophile proceeded as expected, thus providing **β-8a** with the 5-acetyloxy-2-cyano-2-pentyl framework on the β-carbon in 71% yield. Here again, the corresponding α-isomer was not formed at all. The 5-acetyloxy-2-pentyl moiety can be easily replaced with other alkyl chains by the choice of carbonyl compounds **6** (**β-8b**–**β-8k** and **β-8m**), and other pyrroles also serve as one piece for

the alteration of the target structure (**β-8e**–**β-8i**). Importantly, carbon nucleophiles can be extended to not only heteroarenes such as 2-methylfuran (**3c**) and 1-methylindole (**3d**), but also 2-(trimethylsilyloxy)furan (**3e**) and tetraallyltin (**3g**), whereas some of the reactions resulted in low yields. It should be noted that, by the use of **3c** and **3d**, two different heteroaryl rings can be introduced onto the carbonyl carbon by the single-step method without complicated operation (**β-8h**–**β-8j**). Besides the carbon nucleophiles shown here, 2,3-dimethylthiophene and 4-vinylanisole have been found to be available, as previously demonstrated.[15] Contrary to the successful entries, silyl enolate **3f** did not work as a carbon nucleophile (**β-8l**).

Table 3. Indium-Catalyzed β-Alkylation of Pyrroles with Carbonyl Compounds and Carbon Nucleophiles[a]



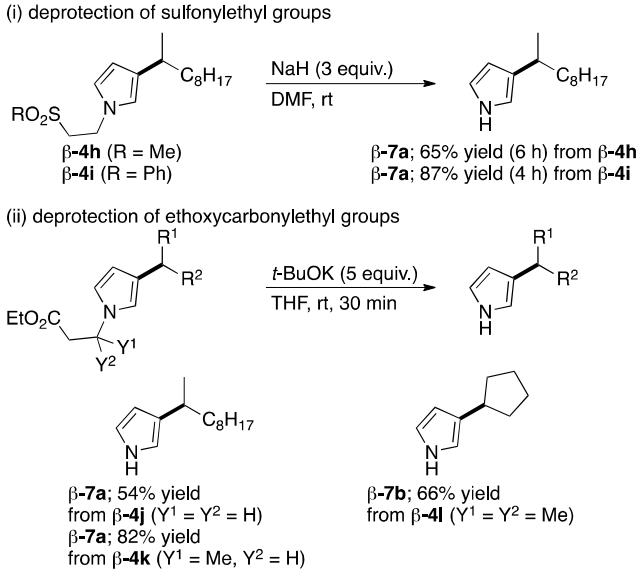


[a]Yields of **β-8** based on **6** are shown here. $In(OTf)_3$ was used as a catalyst for synthesizing **β-8a**–**β-8c**, **β-8j**, **β-8k** and **β-8m**. $In(NTf_2)_3$ was used a catalyst for synthesizing **β-8d**–**β-8h** and **β-8l**. $In(ONf)_3$ was used as a catalyst for synthesizing **β-8i**. Further details on the reaction conditions for each reaction are given in the Experimental Section. [b]The process before adding **3c** was performed for 1 h.

N-Deprotection: Synthesis of *N*-Unsubstituted β-Alkylpyrroles. Removal of the functional group on the nitrogen atom of β-alkylpyrroles prepared by our approach enables the access to *N*-unsubstituted β-alkylpyrroles (Scheme 4). For instance, the sulfonylethyl groups ($RSO_2CH_2CH_2$) of **β-4h** and **β-4i** are

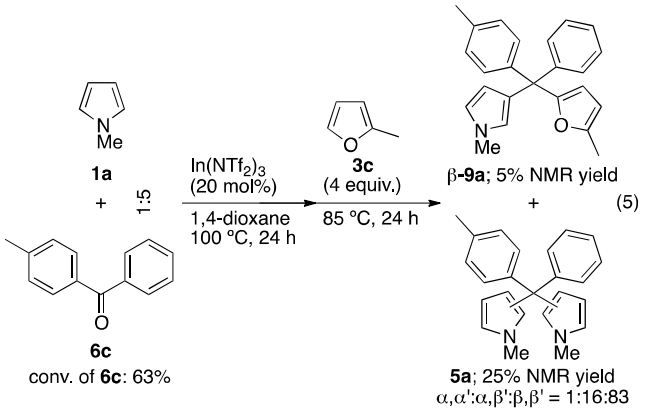
able to be removed with NaH in DMF at room temperature, thereby giving *N*-deprotected **β-7a** in good to high yields (Scheme 4, (i)).[22] Similarly, the deprotection reaction of a series of ethoxycarbonylethyl groups ($EtO_2CCH_2CY_2$) proceeded smoothly with *t*-BuOK in THF to afford **β-7a** and **β-7b** in good yields (Scheme 4, (ii)).[23] In addition to these substituents, we have previously demonstrated that the benzyl and cumyl groups of, for instance, **β-4e** and **β-4w** can be also deprotected by treating with the system consisting of $TiCl_3$/Li/I_2 in THF.[14,15,24] At present, the direct synthesis of the *N*-unsubstituted β-alkylpyrrole with a high yield and a high β-selectivity seems to be difficult for our strategy. However, utilizing the sequence of the indium-catalyzed β-alkylation of *N*-substituted pyrroles followed by the deprotection reactions enables preparation of all six types including *N*-substituted and *N*-unsubstituted β-alkylpyrroles having primary, secondary and tertiary alkyl units.

Scheme 4. N-Deprotection of *N*-Substituted β-Alkylpyrroles



Synthesis of Methanes with Four Different Aryl Groups Including a β-Pyrrolyl Group. A tetraarylmethane structure has played a significant role for the development of molecular chemistry, and

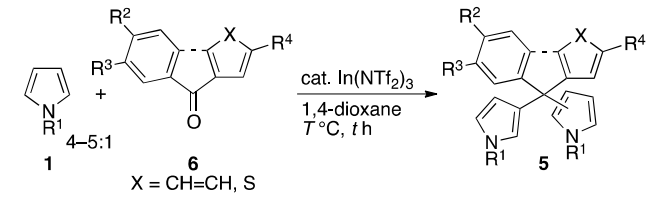
is thus widely found in functional organic molecules associated with not only material chemistry[25] but also medical chemistry.[26] But in this context, there are only a handful of reports for the synthesis of methanes having four different aryl groups,[27] which itself have formative beauty genuinely and, in addition, would be expected to impart unique properties that are not observed in simple tetraarylmethanes. At present, a synthetic strategy of methanes with four different aryl groups, one of which is a β-pyrrolyl group, has no precedent, to the best of our knowledge.[28] We expected that the utilization of our strategy by mixing the *N*-substituted pyrrole, an unsymmetrical diaryl ketone and a heteroarene would be just suited for the synthesis of such unique molecules like no others. With such a prospect, a mixture of 1-methylpyrrole (**1a**) and 4-methylbenzophenone (**6c**) was treated with a catalytic amount of $In(NTf_2)_3$, followed by the addition of 2-methylfuran (**3c**) as a carbon nucleophile (eq. 5). As a result, desired tetraarylmethane **β-9a** consisting of all different (hetero)aryl parts was obtained as a single isomer, albeit disappointingly in a low NMR yield, and phenyl(*p*-tolyl)dipyrrolylmethane **5a**, which is an intermediate for **β-9a**, was also produced in 25% NMR yield as a regioisomeric mixture. The low yield may be attributed in part to oligomerization of **β-9a** and/or **5a**, based on analysis of ^{1}H NMR spectra.

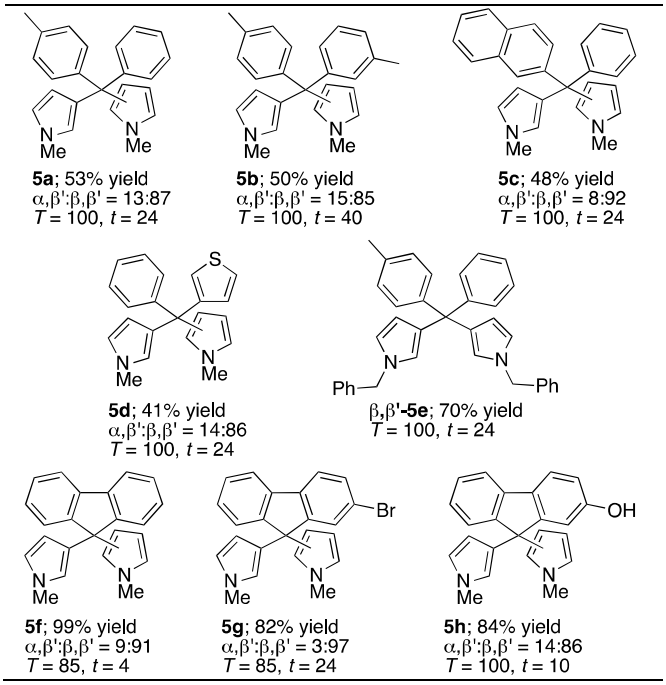


On the basis of this result, we successively investigated the potentiality of the two-step approach: the first stage is the synthesis of intermediary diaryldipyrrolylmethane **5**, and replacing the one pyrrolyl

group of **5** with the other heteroaryl ring is the next step to yield **β-9**.[18] In order to realize the two-step approach, the catalytic activity of some indium salts by the reaction of **1a** with **6c** was first tested in case to confirm the generation efficiency of **5a**, and $In(NTf_2)_3$ was found to exhibit the better performance, thus giving **5a** as a mixture of α,β'- and β,β'-isomers (13:87) in 53% yield (Table 4).[29] With the aid of catalyst $In(NTf_2)_3$, we successively explored the scope of the diaryldipyrrolylmethane synthesis. In addition to the phenyl and *p*-tolyl groups, a diaryl ketone with a *m*-tolyl, naphthyl or 3-thienyl group reacted with 1-methylpyrrole (**1a**) to give the corresponding product in a moderate yield, respectively (**5b–5d**). In the use of the pyrrole substrate bearing the benzyl group on the nitrogen atom, only **β,β'-5e** was obtained without producing other regioisomers, the reason of which will be due mainly to steric constraints in the α,α'- and α,β'-isomers based on the larger benzyl group, as previously demonstrated.[30] Fluorenone derivatives including the symmetrical simple type were found to be quite promising, thereby giving **5f**–**5h** in high yields.

Table 4. Indium-Catalyzed Synthesis of Diaryldipyrrolylmethanes[a]



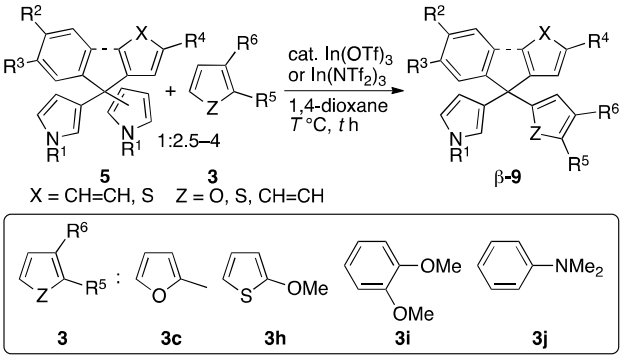


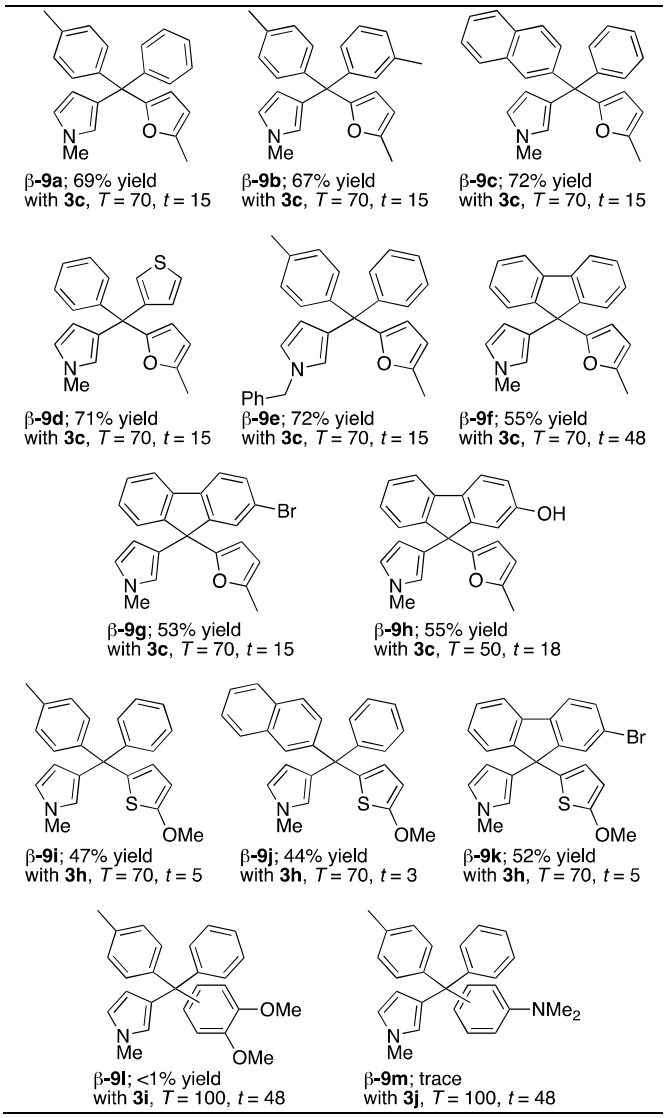
[a]Yields of **5** based on **6** are shown here. Further details on the reaction conditions for each reaction are given in the Experimental Section.

With some diaryldipyrrolylmethanes **5** in hand, we moved to the next stage, and again first examined the effect of indium catalysts in the reaction of **5a** with 2-methylfuran (**3c**), where **5a** was used as a mixture of the α,β'- and β,β'-isomers (13:87) without separation (Table 5). Even though the starting substrate includes the α,β'-isomer, desired **β-9a** with the *p*-tolyl, phenyl, 1-methyl-3-pyrrolyl and 5-methyl-2-furanyl groups at the same carbon atom was produced in a yield of 69% without contamination by its α-isomer, by using catalyst $In(OTf)_3$.[29] Table 5 shows the scope of the tetraarylmethane synthesis. A series of diaryldipyrrolylmethanes **5b**–**5h**, which were used as a mixture of the α,β'- and β,β'-isomers as in the case of **5a**, also reacted with **3c** to produce the corresponding tetraarylmethanes in moderate to good yields (**β-9b**–**β-9h**). Among them, **β-9d** seems to have the most unique structure consisting of essentially four different rings, which are the phenyl, thienyl, pyrrolyl and furanyl groups. Besides 2-methylfuran (**3c**), 2-methoxythiophene (**3h**) is available, where $In(NTf_2)_3$ showed a better catalytic

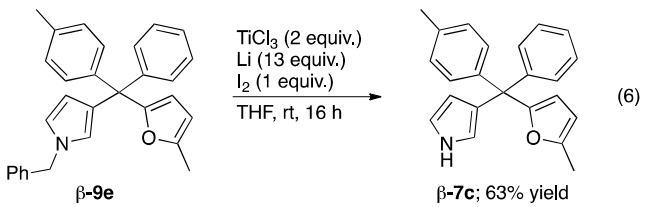
performance (**β-9i**–**β-9k**). Different from the successful heteroaryl nucleophiles, aromatic ones such as 1,2-dimethoxybenzene (**3i**) and *N*,*N*-dimethylaniline (**3j**) unfortunately did not participate in this reaction.[31] As eq. 6 shows, the benzyl group on the nitrogen atom of **β-9e** can be also removed by the $TiCl_3/Li/I_2$ reagent system.

Table 5. Indium-Catalyzed Synthesis of Methanes with Four Different Aryl Groups Including a β-Pyrrolyl Group[a]





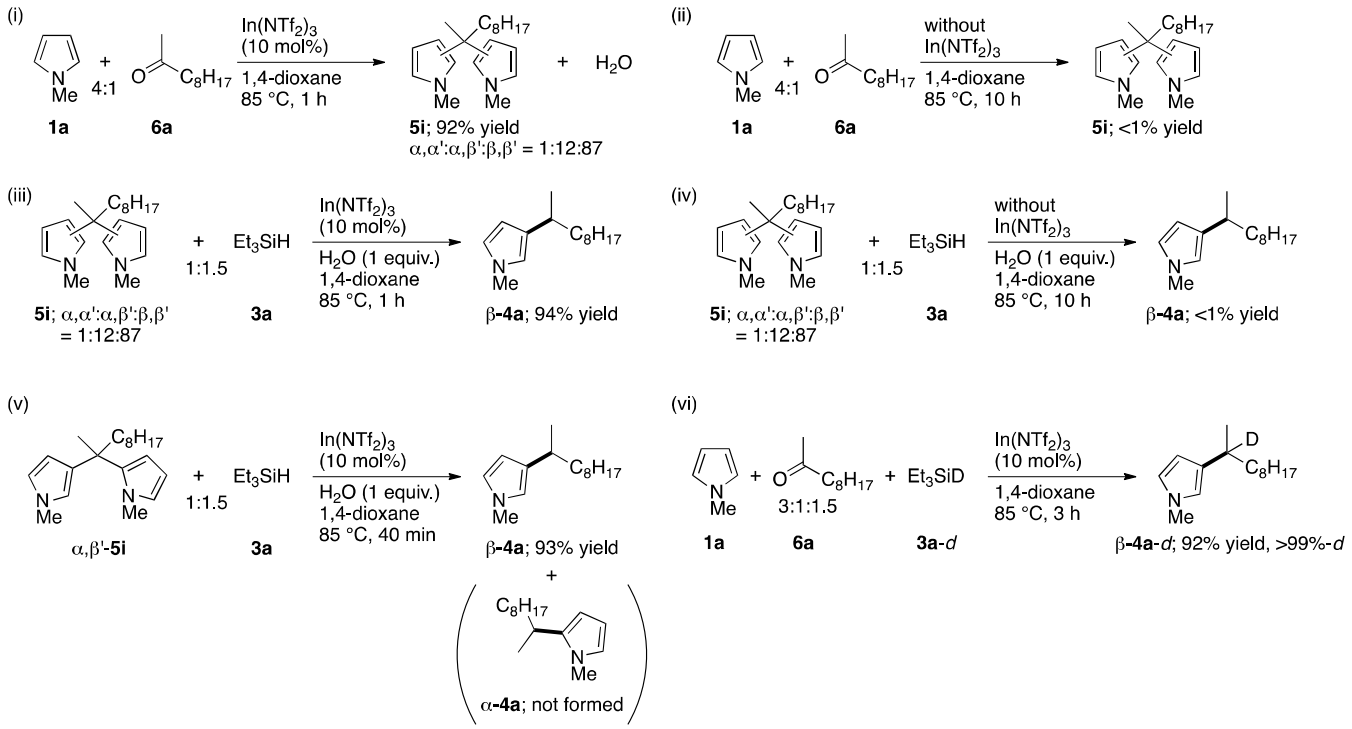
[a]Reagents: **5** (0.20 mmol), **3** (0.50–0.80 mmol), $In(OTf)_3$ (20–40 μmol) for preparing **β-9a**–**β-9h**, **β-9l** and **β-9m** or $In(NTf_2)_3$ (40 μmol) for preparing **β-9i**–**β-9k**, and 1,4-dioxane (1.0 mL). See the Experimental Section for further details.



(6)

A Reaction Mechanism. Some experimental observations are available for the mechanistic study of this transformation (Scheme 5). At first, the indium-catalyzed reaction of 1-methylpyrrole (**1a**) with 2-decanone (**6a**) was conducted but in the absence of Et_3SiH (**3a**), and was confirmed to indeed give an isomeric mixture of dipyrrolyldecanes **5i** in 92% yield (Scheme 5, (i)). Subsequently, in the presence of H_2O as the by-product in the preceding reaction (Scheme 5, (i)), the treatment of the isomeric mixture of **5i** with **3a** and $In(NTf_2)_3$ (10 mol%) resulted in the exclusive of and in the high-yield formation of **β-4a** (Scheme 5, (iii)). Neither of the reactions proceeded at all without the indium catalyst (Scheme 5, (ii) and (iv)). These results indicate that dipyrrolylalkanes **5** are intermediates for the reductive β-alkylation, and the indium catalyst is essential for both the stages. Importantly, using single isomer **α,β'-5i**, which has the possibility to lead to another isomer α-**4a** when the β-pyrrolyl group is eliminated, again provided β-**4a** exclusively, thus suggesting that the α-pyrrolyl group compared to the β-pyrrolyl group has a superior leaving ability (Scheme 5, (v)). With **3a**-*d* instead of **3a** in the three-component reaction, the deuterium atom of **3a**-*d* was incorporated regioselectively at the carbon atom within the alkyl chain (Scheme 5, (vi)).

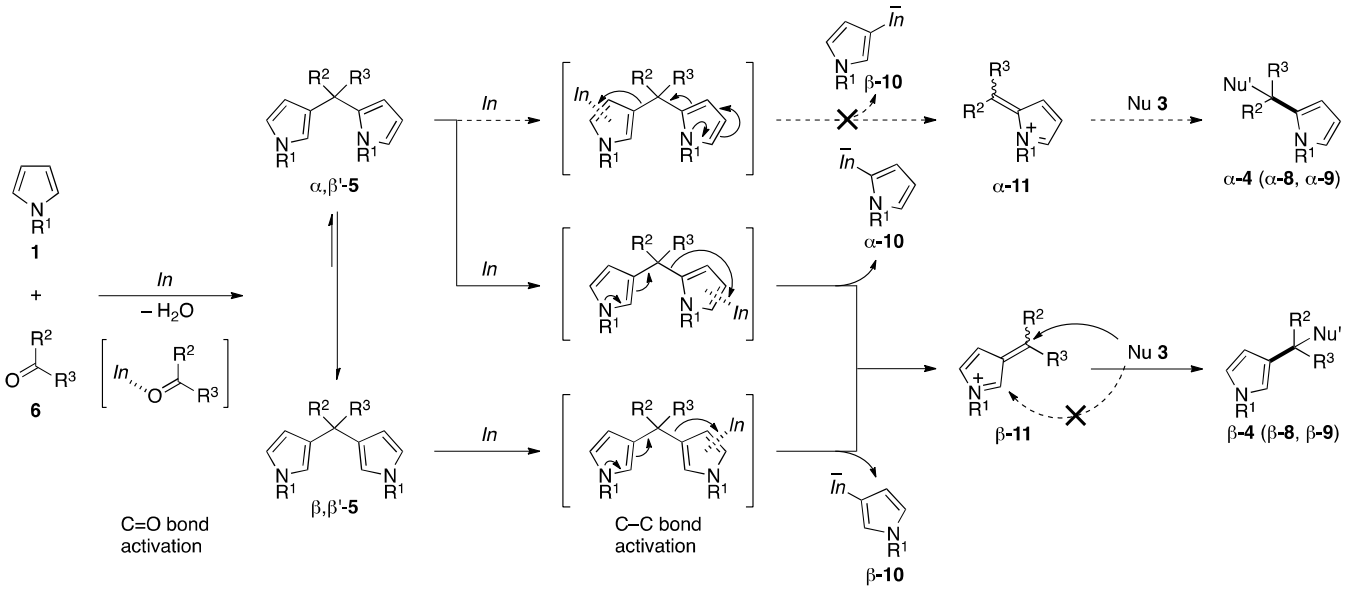
Scheme 5. Mechanistic Studies



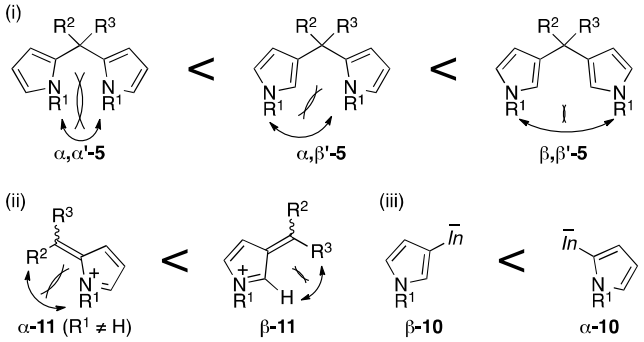
On the basis of these experimental results, and, in addition, of the previous ones reported by us and others, plausible reaction mechanisms are depicted in Scheme 6, where **α,α'-5** is omitted, due actually to the non-formation of **α-4** derived inevitably from **α,α'-5**. At first, the indium(III) Lewis acid (*In*), which will work as an activator of the C=O bond of **6**, assembles **1** and **6** into dipyrrolylalkanes **5**, the formation of which is the well-known process most frequently promoted by a (Lewis) acid.[32] The predominant generation of **β,β'-5** over the other two isomers results from the highest thermodynamic stability, probably because of the least steric repulsion between the two R^1 groups (Scheme 7, (i)), as previously observed.[30] Next, the α-pyrrolyl group of **α,β'-5** would coordinate to *In*,[33] and then eliminate as anionic α-pyrrolylindium **α-10** to give cationic species **β-11** through the C–C(α-pyrrolyl) bond cleavage. Although there may be a possibility to afford another cationic species **α-11** from same intermediate **α,β'-5**, the selective formation of **β-11** thus leading to **β-4** is likely to be due, at least in

part, to two synergistic effects. One is the higher stability of **β-11** itself compared to the corresponding **α-11** that has the higher 1,3-allylic-type strain between R^1 (≠ H) and R^2 (Scheme 7, (ii)).[34] The other is the higher leaving group character of the α-pyrrolyl group than the β-pyrrolyl group (see Scheme 5, (v)), and this experimental fact should thus be attributed to the higher stability of α-pyrrolylindium **α-10** than β-pyrrolylindium **β-10** (Scheme 7, (iii)) because, in general, an α-pyrrolylmetal, which means an α-pyrrolyanion, is relatively more stable.[35] Finally, **β-11** reacts with hydride or carbon nucleophile **3** at the carbon atom sandwiched between R^2 and R^3, not at the iminium-like carbon, thereby arriving at the exclusive formation of **β-4**. The process from **β,β'-5** to **β-4** is also considered to proceed in a similar way.

Scheme 6. Plausible Reaction Mechanisms



Scheme 7. Stability Profiles of Key Intermediates



CONCLUSIONS

We have demonstrated in detail that a broad range of β-alkylpyrroles can be easily constructed by mixing *N*-substituted pyrroles, carbonyl compounds and nucleophiles under indium catalysis.[36] Using the carbonyl compound as the source of the alkyl group has several distinct advantages over the corresponding alkyne-based variant: (1) the reaction with the carbonyl compound can be performed with a more reduced amount of an indium catalyst, (2) the carbonyl compound is more reasonable in price in many cases, and (3) the most marked superiority is that alkyl groups with structural diversity including not only primary, secondary and tertiary alkyl units but also cyclic and functionalized types can be introduced onto the pyrrole ring. The perfect regioselectivities achieved in all the cases will enhance the reliability of this process. Since the *N*-deprotection of the product is readily performable, preparing a series of *N*-unsubstituted β-alkylpyrroles is also feasible. Importantly, this protocol is well applicable to the synthesis of unique tetraarylmethanes with four different aryl moieties, one of which is a β-pyrrolyl group. Mechanistic investigations revealed that the formation of the dipyrrolylalkane intermediate is the first stage, and the elimination of the one pyrrolyl group from the dipyrrolylalkane is the second stage for providing the β-alkylpyrrole. The indium catalyst is necessary for both the processes. The selective

generation of the β-alkylpyrrole was proved to be attributed to the selective elimination of the α-pyrrolyl group from the intermediate dipyrrolylalkane.

EXPERIMENTAL SECTION

General Remarks. All manipulations were conducted with a standard Schlenk technique under an argon atmosphere. Nuclear magnetic resonance (NMR) spectra (^{1}H, 400 and 500 MHz; ^{13}C{^{1}H}, 100 and 125 MHz) were taken using tetramethylsilane as an internal standard. ^{2}H NMR spectral data were recorded at 61 MHz and chemical shifts are reported relative to $CDCl_3$ (7.26 ppm) as an internal standard. Analytical gas chromatography (GC) was performed with a capillary column coated with 5% phenyl polysilphenylene-siloxane (30 m x 0.25 mm x 0.25 μm) or with 5% diphenyl- and 95% dimethylpolysiloxane (30 m x 0.25 mm x 0.25 μm) using nitrogen as carrier gas. Gas chromatography-mass spectrometry (GC-MS) analyses were performed with a capillary column coated with 5% phenyl polysilphenylene-siloxane (30 m x 0.25 mm x 0.25 μm) or with 5% diphenyl- and 95% dimethylpolysiloxane (30 m x 0.25 mm x 0.25 μm) by electron ionization at 70 eV using helium as carrier gas. High resolution mass spectra (HRMS) were obtained by GC-FI-TOF or FD-TOF. Preparative recycling high-performance liquid chromatography (HPLC) was performed with a standard normal phase column packed with pore size 120 Å silica gel using a mixture of hexane–ethyl acetate (EtOAc) as eluent. Preparative recycling gel permeation chromatography (GPC) was performed with a highly cross-linked polystyrene/divinylbenzene packed column using chloroform as eluent. Melting points were determined on a micro hot stage apparatus and are uncorrected. 1,4-Dioxane was distilled under argon from sodium just prior to use. Tetrahydrofuran (THF) was distilled under argon from sodium benzophenone ketyl just prior to use. The following compounds, 5-acetyloxy-2-pentanone,[37] 1-[2-(phenylsulfonyl)ethyl]-1*H*-pyrrole, [38] 1-*tert*-butyl-1*H*-pyrrole,[36] 3-benzoylthiophene, [39] 2-(1-

methylpyrrol-2-yl)-2-(1-methylpyrrol-3-yl)decane (**α,β'-5i**)[14] were prepared according to the respective literature methods. $In(ONf)_3$[40] and $In(NTf_2)_3$[41] were prepared by the respective literature procedures. Unless otherwise noted, other substrates and reagents were commercially available and used as received without further purification.

Synthesis of 1-[2-(Methylsulfonyl)ethyl]-1*H*-pyrrole. Based on the literature procedure,[38] 1-[2-(methylsulfonyl)ethyl]-1*H*-pyrrole was synthesized with the following reagents and conditions: 1*H*-pyrrole (**1c**) (67.1 mg, 1.00 mmol), methyl vinyl sulfone (106 mg, 1.00 mmol), KOH (56.1 mg, 1.00 mmol), MeCN (5.0 mL), room temperature, 6 h, and was isolated by column chromatography on silica gel (hexane/EtOAc = 3:1) in 87% yield (151 mg) as a white solid; mp 88–89 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (t, *J* = 0.7 Hz, 3 H), 3.40 (tq, *J* = 6.2, 0.8 Hz, 2 H), 4.38–4.47 (m, 2 H), 6.19 (t, *J* = 2.2 Hz, 2 H), 6.74 (t, *J* = 2.1 Hz, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 41.1, 43.6, 55.9, 109.7, 120.6. HRMS (FI) Calcd for $C_7H_{11}NO_2S$: M, 173.0510. Found: *m*/*z* 173.0491.

Synthesis of Ethyl 1*H*-pyrrole-1-propionate. Based on the literature procedure,[42] ethyl 1*H*-pyrrole-1-propionate was synthesized with the following reagents and conditions: ethyl 3-aminopropanoate hydrochloride (5.04 g, 32.8 mmol), 2,5-dimethoxytetrahydrofuran (4.33 g, 32.8 mmol), NaOAc (2.96 g, 36.1 mmol), acetic acid (13.7 mL), 80 ºC, 3 h, and was isolated by short-path distillation under reduced pressure (81 ºC/3.0 hPa) in 27% yield (1.51 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.1 Hz, 3 H), 2.76 (t, *J* = 7.0 Hz, 2 H), 4.15 (q, *J* = 7.2 Hz, 2 H), 4.21 (t, *J* = 7.0 Hz, 2 H), 6.13 (t, *J* = 2.2 Hz, 2 H), 6.66 (t, *J* = 2.2 Hz, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.1, 36.6, 44.9, 60.9, 108.4, 120.5, 171.1. HRMS (FI) Calcd for $C_9H_{13}NO_2$: M, 167.0946. Found: *m*/*z* 167.0926.

Synthesis of Ethyl β-methyl-1*H*-pyrrole-1-propionate. Based on the literature procedure,[43] ethyl β-methyl-1*H*-pyrrole-1-propionate was synthesized with the following reagents and conditions: ethyl 3-aminobutyrate (5.25 g, 40.0 mmol), 2,5-dimethoxytetrahydrofuran (5.29 g, 40.0 mmol), acetic acid (10.0

mL), 80 ºC, 8 h, and was isolated by short-path distillation under reduced pressure (78 ºC/2.5 hPa) in 69% yield (5.03 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 7.1 Hz, 3 H), 1.52 (d, *J* = 6.9 Hz, 3 H), 2.62–2.83 (m, 2 H), 4.05–4.15 (m, 2 H), 4.59 (sext, *J* = 7.0 Hz, 1 H), 6.13 (t, *J* = 2.2 Hz, 2 H), 6.71 (t, *J* = 2.2 Hz, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.1, 21.7, 43.3, 51.9, 60.7, 108.0, 118.5, 170.7. HRMS (FD) Calcd for $C_{10}H_{15}NO_2$: M, 181.1103. Found: *m*/*z* 181.1111.

Synthesis of Ethyl β,β-dimethyl-1*H*-pyrrole-1-propionate. Based on the literature procedure,[42] ethyl β,β-dimethyl-1*H*-pyrrole-1-propionate was synthesized with the following reagents and conditions: ethyl 3-amino-3-methylbutyrate hydrochloride (1.21 g, 6.64 mmol), 2,5-dimethoxytetrahydrofuran (878 mg, 6.64 mmol), NaOAc (599 mg, 7.30 mmol), acetic acid (5.3 mL), 80 ºC, 2 h, and was isolated by Kugelrohr bulb-to-bulb distillation under reduced pressure (80 ºC/90 Pa) in 71% yield (923 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17 (t, *J* = 7.2 Hz, 3 H), 1.69 (s, 6 H), 2.72 (s, 2 H), 4.04 (q, *J* = 7.2 Hz, 2 H), 6.15 (t, *J* = 2.2 Hz, 2 H), 6.83 (t, *J* = 2.2 Hz, 2 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 14.0, 28.4, 48.4, 55.8, 60.5, 107.9, 117.7, 170.1. HRMS (FI) Calcd for $C_{11}H_{17}NO_2$: M, 195.1259. Found: *m*/*z* 195.1245.

Synthesis of 1,2-Dimethyl-1*H*-pyrrole. Based on the literature procedure,[44] 1,2-dimethyl-1*H*-pyrrole was synthesized with the following reagents and conditions: 2-formyl-1-methyl-1*H*-pyrrole (3.44 g, 31.5 mmol), hydrazine monohydrate (6.47 g, 129 mmol), KOH (6.01 g, 107 mmol), ethylene glycol (45.0 ml), 180 ºC, 1.5 h, and was isolated by Kugelrohr bulb-to-bulb distillation under reduced pressure (90 ºC/11 kPa) in 57% yield (1.73 g) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.21 (d, *J* = 0.6 Hz, 3 H), 3.52 (s, 3 H), 5.85–5.89 (m, 1 H), 6.03 (t, *J* = 3.2 Hz, 1 H), 6.54 (dd, *J* = 2.1, 1.6 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 11.9, 33.5, 106.35, 106.45, 120.9, 128.8. HRMS (FI) Calcd for C_6H_9N: M, 95.0735. Found: *m*/*z* 95.0748.

Synthesis of 1,3-Dimethyl-1*H*-pyrrole. Based on the literature procedure,[45] 1,3-dimethyl-1*H*-pyrrole was synthesized with the following reagents and conditions: 3-methyl-1*H*-pyrrole (852 mg, 10.5 mmol), iodomethane (1.79 g, 12.6 mmol), KOH (2.36 g, 42.0 mmol), dimethyl sulfoxide (DMSO) (26.0 mL), room temperature, 30 min, and was isolated by short-path distillation under reduced pressure (75 ºC/23 kPa) in 30% yield (302 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.09 (s, 3 H), 3.59 (s, 3 H), 5.95 (t, *J* = 2.1 Hz, 1 H), 6.36–6.40 (m, 1 H), 6.49 (t, *J* = 2.4 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 11.8, 35.9, 109.2, 118.9, 119.7, 121.4. HRMS (FI) Calcd for C_6H_9N: M, 95.0735. Found: *m*/*z* 95.0715.

Synthesis of 1-(2-Phenylpropan-2-yl)-1*H*-pyrrole. Based on the literature procedure,[43] 1-(2-phenylpropan-2-yl)-1*H*-pyrrole was synthesized with the following reagents and conditions: cumylamine (4.06 g, 30.0 mmol), 2,5-dimethoxyhydrofuran (3.96 g, 30.0 mmol), acetic acid (13.5 mL), 80 ºC, 7 h, and was isolated by short-path distillation under reduced pressure (80 ºC/1.3 hPa) in 80% yield (4.45 g). This compound has already appeared in the literature, and its spectral and analytical data are in good agreement with those reported in reference 15. Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.89 (s, 6 H), 6.20 (t, *J* = 2.0 Hz, 2 H), 6.79 (t, *J* = 2.3 Hz, 2 H), 6.98 (dt, *J* = 7.5, 2.3 Hz, 2 H), 7.22 (tt, *J* = 7.2, 1.6 Hz, 1 H), 7.28 (td, *J* = 6.6, 1.7 Hz, 2 H).

Indium-Catalyzed Reductive β-Alkylation of Pyrroles with Carbonyl Compounds and Et_3SiH; A General Procedure of Method A for eq. 1–4, and Table 1, 2. The experimental procedure performed on a 0.3-mmol scale based on carbonyl compound **6** is shown here as a representative. $In(NTf_2)_3$ (28.7 mg, 30.0 μmol) or $In(ONf)_3$ [(15.2 mg, 15.0 μmol) or (30.4 mg, 30.0 μmol)] was placed in a 20 mL Schlenk tube, which was heated at 150 ºC in vacuo for 2 h. The tube was cooled down to room temperature and filled with argon. 1,4-Dioxane (0.50 mL) was added to the tube, and the mixture was then stirred at room temperature for 10 min. To this were added carbonyl compound **6** (0.300 mmol),

pyrrole derivative **1** (0.300, 0.600, 0.840, 0.900 or 1.20 mmol) and Et_3SiH (**3a**) [(52.3 mg, 0.450 mmol)], and the resulting mixture was stirred at T^1 °C. After stirring for t^1 h, a saturated $NaHCO_3$ aqueous solution (0.3 mL) was added, and the aqueous phase was extracted with EtOAc (5 mL x 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by purification gave the corresponding product (**4** or **7a**). In our preceding communication, the synthesis of **β-4a**, **β-4w** and **β-4x** has been already achieved, and their spectral and analytical data are thus provided in reference 15. Unless otherwise noted, new products **4** synthesized here were fully characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and HRMS.

Indium-Catalyzed Reductive β-Alkylation of Pyrroles with Carbonyl Compounds and Et_3SiH; A General Procedure of Method B for Table 1. $In(NTf_2)_3$ [(57.3 mg, 60.0 μmol) or (86.0 mg, 90.0 μmol)] was placed in a 20 mL Schlenk tube, which was heated at 150 ºC in vacuo for 2 h. The tube was cooled down to room temperature and filled with argon. 1,4-Dioxane (0.50 mL) was added to the tube, and the mixture was then stirred at room temperature for 10 min. To this were added carbonyl compound **6** (0.300 mmol), pyrrole derivative **1** (0.900, 1.20 or 1.50 mmol), and the resulting mixture was stirred at T^2 °C for t^2 h. Et_3SiH (**3a**) [(52.3 mg, 0.450 mmol) or (105 mg, 0.900 mmol)] was then added to this solution, and the resulting mixture was stirred further at T^3 ºC. After stirring for t^3 h, the work-up process was carried out similarly as above. Unless otherwise noted, new products **β-4** synthesized here were fully characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and HRMS.

3-Cyclohexyl-1-methyl-1*H*-pyrrole (β-4b). The title compound was synthesized with the following reagents based on method A: 1-methylpyrrole (**1a**) (73.0 mg, 0.900 mmol), cyclohexanone (29.4 mg, 0.300 mmol), Et_3SiH (**3a**) (52.3 mg, 0.450 mmol), $In(NTf_2)_3$ (28.7 mg, 30.0 μmol) and 1,4-dioxane (0.50 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 40:1) in 90%

yield (44.1 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16–1.41 (m, 5 H), 1.69 (dtt, *J* = 14.0, 4.7, 3.2 Hz, 1 H), 1.74–1.81 (m, 2 H), 1.90–1.98 (m, 2 H), 2.42 (tt, *J* = 11.2, 3.6 Hz, 1 H), 3.60 (s, 3 H), 6.01 (t, *J* = 2.3 Hz, 1 H), 6.38 (t, *J* = 1.9 Hz, 1 H), 6.50 (t, *J* = 2.3 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 26.4, 26.7, 34.8, 36.0, 36.3, 106.5, 117.6, 121.2, 131.3. HRMS (FI) Calcd for $C_{11}H_{17}N$: M, 163.1361. Found: *m*/*z* 163.1359.

3-(6-Chlorohexan-2-yl)-1-methyl-1*H*-pyrrole (β-4c). The title compound was synthesized with the following reagents based on method A: **1a** (73.0 mg, 0.900 mmol), 6-chlorohexan-2-one (40.4 mg, 0.300 mmol), **3a** (52.3 mg, 0.450 mmol), $In(NTf_2)_3$ (28.7 mg, 30.0 μmol) and 1,4-dioxane (0.50 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 20:1) in 97% yield (58.6 mg). Compound **β-4c** has already appeared in reference 14, and its spectral and analytical data are in good agreement with those reported in the literature. Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19 (d, *J* = 6.9 Hz, 3 H), 1.37–1.59 (m, 4 H), 1.76 (quint, *J* = 7.1 Hz, 2 H), 2.62 (sext, *J* = 6.8 Hz, 1 H), 3.52 (t, *J* = 6.9 Hz, 2 H), 3.60 (s, 3 H), 5.98 (t, *J* = 2.2 Hz, 1 H), 6.37 (t, *J* = 1.9 Hz, 1 H), 6.51 (t, *J* = 2.5 Hz, 1 H).

1-Benzyl-3-isopropyl-1*H*-pyrrole (β-4d). The title compound was synthesized with the following reagents based on method A: for the 0.3-mmol scale reaction: 1-benzylpyrrole (141 mg, 0.900 mmol), acetone (17.4 mg, 0.300 mmol), **3a** (52.3 mg, 0.450 mmol), $In(NTf_2)_3$ (28.7 mg, 30.0 μmol) and 1,4-dioxane (0.50 mL), and was isolated by column chromatography on silica gel twice (first: hexane/EtOAc = 40:1; second: hexane/$CHCl_3$ = 5:1) in 89% yield (53.3 mg) as a colorless oil; for the 5-mmol scale reaction: 1-benzylpyrrole (2.36 g, 15.0 mmol), acetone (290 mg, 5.00 mmol), **3a** (872 mg, 7.50 mmol), $In(NTf_2)_3$ (478 mg, 0.500 mmol) and 1,4-dioxane (8.3 mL), and was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 5:1) in 84% yield (840 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (d, *J* = 6.9 Hz, 6 H), 2.81 (sept, *J* = 6.9 Hz, 1 H), 5.00 (s, 2 H), 6.07 (t, *J* = 2.3

Hz, 1 H), 6.46 (t, *J* = 1.8 Hz, 1 H), 6.59 (t, *J* = 2.3 Hz, 1 H), 7.12 (d, *J* = 7.4 Hz, 2 H), 7.23–7.29 (m, 1 H), 7.29–7.35 (m, 2 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 24.1, 26.5, 53.3, 106.9, 117.0, 120.8, 127.1, 127.5, 128.7, 132.3, 138.4. HRMS (FD) Calcd for $C_{14}H_{17}N$: M, 199.1361. Found: *m*/*z* 199.1360.

1-Benzyl-3-(decan-2-yl)-1*H*-pyrrrole (β-4e). The title compound was synthesized with the following reagents based on method A: 1-benzylpyrrole (141 mg, 0.900 mmol), 2-decanone (**6a**) (46.9 mg, 0.300 mmol), **3a** (52.3 mg, 0.450 mmol), $In(NTf_2)_3$ (28.7 mg, 30.0 μmol) and 1,4-dioxane (0.50 mL), and was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 5:1) in 76% yield (68.0 mg). Compound **β-4e** has already appeared in reference 14, and its spectral and analytical data are in good agreement with those reported in the literature. Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 3 H), 1.17 (d, *J* = 6.9 Hz, 3 H), 1.20–1.34 (m, 12 H), 1.38–1.47 (m, 1 H), 1.48–1.58 (m, 1 H), 2.61 (sext, *J* = 6.9 Hz, 1 H), 5.00 (s, 2 H), 6.03 (dd, *J* = 2.5, 2.0 Hz, 1 H), 6.44 (t, *J* = 1.8 Hz, 1 H), 6.59 (t, *J* = 2.5 Hz, 1 H), 7.07–7.11 (m, 2 H), 7.24–7.28 (m, 1 H), 7.31 (tt, *J* = 7.2, 1.6 Hz, 2 H).

1-Benzyl-3-(diphenylmethyl)-1*H*-pyrrole (β-4f). The title compound was synthesized with the following reagents based on method B: 1-benzylpyrrole (236 mg, 1.50 mmol), benzophenone (54.7 mg, 0.300 mmol), **3a** (52.3 mg, 0.450 mmol), $In(NTf_2)_3$ (86.0 mg, 90.0 μmol) and 1,4-dioxane (0.50 mL), and was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 3:1) in 93% yield (91.1 mg) as a white solid; mp 96–97 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.97 (s, 2 H), 5.35 (s, 1 H), 5.95 (dd, *J* = 2.4, 1.9 Hz, 1 H), 6.22–6.27 (m, 1 H), 6.61 (t, *J* = 2.6 Hz, 1 H), 7.06–7.12 (m, 2 H), 7.17 (tt, *J* = 7.0, 1.8 Hz, 2 H), 7.13–7.20 (m, 9 H), 7.31 (tt, *J* = 7.3, 1.7 Hz, 2 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 50.1, 53.3, 109.4, 120.6, 121.3, 125.9, 126.9, 127.2, 127.5, 128.1, 128.7, 128.9, 138.3, 145.3. HRMS (FI) Calcd for $C_{24}H_{21}N$: M, 323.1674. Found: *m*/*z* 323.1666.

1-*tert*-Butyl-3-isopropyl-1*H*-pyrrole (β-4g). The title compound was synthesized with the following reagents based on method A: for the 0.3-mmol scale reaction: 1-*tert*-butylpyrrole (111 mg, 0.900 mmol), acetone (17.4 mg, 0.300 mmol), **3a** (52.3 mg, 0.450 mmol), $In(NTf_2)_3$ (28.7 mg, 30.0 μmol) and 1,4-dioxane (0.50 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 50:1) in 84% yield (41.9 mg) as a colorless oil; for the 10-mmol scale reaction: 1-*tert*-butylpyrrole (3.70 g, 30.0 mmol), acetone (581 mg, 10.0 mmol), **3a** (1.74 g, 15.0 mmol), $In(NTf_2)_3$ (955 mg, 1.00 mmol) and 1,4-dioxane (16.7 mL), and was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 10:1) in 85% yield (1.41 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (d, *J* = 6.9 Hz, 6 H), 1.51 (s, 9 H), 2.82 (sept, *J* = 6.8 Hz, 1 H), 6.03 (t, *J* = 2.3 Hz, 1 H), 6.57–6.62 (m, 1 H), 6.74 (t, *J* = 2.5 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 24.0, 26.5, 30.7, 54.4, 105.7, 113.5, 117.0, 131.0. HRMS (FI) Calcd for $C_{11}H_{19}N$: M, 165.1517. Found: *m*/*z* 165.1502.

3-(Decan-2-yl)-1-[2-(methylsulfonyl)ethyl]-1*H*-pyrrole (β-4h). The title compound was synthesized with the following reagents based on method A: 1-[2-(methylsulfonyl)ethyl]-1*H*-pyrrole (156 mg, 0.900 mmol), **6a** (46.9 mg, 0.300 mmol), **3a** (52.3 mg, 0.450 mmol), $In(NTf_2)_3$ (28.7 mg, 30.0 μmol) and 1,4-dioxane (0.50 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 2:1) in 86% yield (81.3 mg) as a white solid; mp 78–79 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.9 Hz, 3 H), 1.14 (d, *J* = 6.9 Hz, 3 H), 1.17–1.35 (m, 12 H), 1.36–1.54 (m, 2 H), 2.38 (t, *J* = 0.7, 3 H), 2.58 (sext, *J* = 6.9 Hz, 1 H), 3.37 (tq, *J* = 6.1, 0.8 Hz, 2 H), 4.32–4.39 (m, 2 H), 6.03 (dd, *J* = 2.5, 1.8 Hz, 1 H), 6.49 (t, *J* = 1.9 Hz, 1 H), 6.64 (t, *J* = 2.5 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.1, 22.3, 22.7, 27.6, 29.4, 29.7, 29.8, 31.8, 31.9, 38.5, 40.9, 43.7, 55.9, 108.3, 116.7, 120.4, 132.5. HRMS (FD) Calcd for $C_{17}H_{31}NO_2S$: M, 313.2075. Found: *m*/*z* 313.2064.

3-(Decan-2-yl)-1-[2-(phenylsulfonyl)ethyl]-1*H*-pyrrole (β-4i). The title compound was synthesized with the following reagents based on method A: 1-[2-(phenylsulfonyl)ethyl]-1*H*-pyrrole (212 mg, 0.900

mmol), **6a** (46.9 mg, 0.300 mmol), **3a** (52.3 mg, 0.450 mmol), $In(NTf_2)_3$ (28.7 mg, 30.0 μmol) and 1,4-dioxane (0.50 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 4:1) in 90% yield (102 mg) as a white solid; mp 33–34 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.9 Hz, 3 H), 1.11 (d, *J* = 6.9 Hz, 3 H), 1.15–1.52 (m, 14 H), 2.52 (sext, *J* = 6.9 Hz, 1 H), 3.47–3.55 (m, 2 H), 4.21–4.29 (m, 2 H), 5.93 (dd, *J* = 2.8, 1.8 Hz, 1 H), 6.28 (t, *J* = 1.9 Hz, 1 H), 6.44 (t, *J* = 2.5 Hz, 1 H), 7.46–7.60 (tt, *J* = 7.8, 1.6 Hz, 2 H), 7.66 (tt, *J* = 7.4, 1.5 Hz, 1 H), 7.84–7.90 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.1, 21.9, 22.7, 27.6, 29.4, 29.6, 29.8, 31.8, 31.9, 38.5, 42.8, 57.2, 107.9, 116.5, 120.1, 127.8, 129.4, 132.0, 134.0, 139.0. HRMS (FD) Calcd for $C_{22}H_{33}NO_2S$: M, 375.2232. Found: *m*/*z* 375.2228.

Ethyl 3-(decan-2-yl)-1*H*-pyrrole-1-propionate (β-4j). The title compound was synthesized with the following reagents based on method A: ethyl 1*H*-pyrrole-1-propionate (150 mg, 0.900 mmol), **6a** (46.9 mg, 0.300 mmol), **3a** (52.3 mg, 0.450 mmol), $In(NTf_2)_3$ (28.7 mg, 30.0 μmol) 1,4-dioxane (0.50 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 8:1) in 97% yield (89.7 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.9 Hz, 3 H), 1.16 (d, *J* = 6.8 Hz, 3 H), 1.18–1.33 (m, 15 H), 1.35–1.45 (m, 1 H), 1.46–1.53 (m, 1 H), 2.58 (sext, *J* = 6.8 Hz, 1 H), 2.74 (t, *J* = 7.1 Hz, 2 H), 4.13 (t, *J* = 7.6 Hz, 2 H), 4.14 (q, *J* = 7.2 Hz, 2 H), 5.97 (dd, *J* = 2.5, 1.8 Hz, 1 H), 6.40 (t, *J* = 1.8 Hz, 1 H), 6.55 (t, *J* = 2.4 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 14.13, 14.15, 22.0, 22.7, 27.6, 29.4, 29.7, 29.9, 31.8, 31.9, 36.7, 38.7, 44.9, 60.8, 107.0, 116.8, 120.1, 131.1, 171.2. HRMS (FD) Calcd for $C_{19}H_{33}NO_2$: M, 307.2511. Found: *m*/*z* 307.2509.

Ethyl 3-(decan-2-yl)-β-methyl-1*H*-pyrrole-1-propionate (β-4k). The title compound was synthesized with the following reagents based on method A: ethyl β-methyl-1*H*-pyrrole-1-propionate (163 mg, 0.900 mmol), **6a** (46.9 mg, 0.300 mmol), **3a** (52.3 mg, 0.450 mmol), $In(NTf_2)_3$ (28.7 mg, 30.0 μmol) and 1,4-dioxane (0.50 mL), and was isolated by column chromatography on silica gel

(hexane/EtOAc = 8:1) in 93% yield (90.2 mg) as a colorless oil. This compound has two chiral centers, and thus was produced as a mixture of diastereomers in an approximately 1:1 ratio. ^{1}H NMR as a mixture of diastereomers (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 3 H), 1.16 (d, *J* = 6.9 Hz, 3 H), 1.19–1.33 (m, 15 H), 1.36–1.44 (m, 1 H), 1.46–1.53 (m, 1 H), 1.49 (d, *J* = 6.9 Hz, 3 H), 2.58 (sext, *J* = 7.0 Hz, 1 H), 2.61–2.80 (m, 2 H), 4.10 (q, *J* = 7.1 Hz, 2 H), 4.50 (sext, *J* = 7.0 Hz, 1 H), 5.97 (t, *J* = 2.2 Hz, 1 H), 6.45 (t, *J* = 1.9 Hz, 1 H), 6.60 (t, *J* = 2.6 Hz, 1 H); ^{13}C{^{1}H} NMR as a mixture of diastereomers (125 MHz, $CDCl_3$) δ 14.1, 21.6, 21.91, 21.93, 22.7, 27.6, 29.4, 29.7, 29.9, 31.90, 31.94, 38.7, 43.4, 51.8, 60.7, 106.52, 106.55, 114.75, 114.80, 117.88, 117.94, 130.65, 130.66, 170.9. HRMS (FD) Calcd for $C_{20}H_{35}NO_2$: M, 321.2668. Found: *m*/*z* 321.2662.

Ethyl 3-cyclopentyl-β,β-dimethyl-1*H*-pyrrole-1-propionate (β-4l). The title compound was synthesized with the following reagents based on method A: ethyl β,β-dimethyl-1*H*-pyrrole-1-propionate (176 mg, 0.900 mmol), cyclopentanone (25.2 mg, 0.300 mmol), **3a** (52.3 mg, 0.450 mmol), $In(NTf_2)_3$ (28.7 mg, 30.0 μmol) and 1,4-dioxane (0.50 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 30:1) in 80% yield (63.2 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (t, *J* = 7.1 Hz, 3 H), 1.42–1.53 (m, 2 H), 1.55–1.64 (m, 2 H), 1.66 (s, 6 H), 1.68–1.79 (m, 2 H), 1.91–2.03 (m, 2 H), 2.68 (s, 2 H), 2.87 (tt, *J* = 9.5, 7.4 Hz, 1 H), 4.03 (q, *J* = 7.1 Hz, 2 H), 6.01 (dd, *J* = 2.7, 1.9 Hz, 1 H), 6.56–6.61 (m, 1 H), 6.72 (t, *J* = 2.6 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.0, 25.1, 28.2, 34.5, 38.4, 48.6, 55.6, 60.4, 106.7, 114.1, 117.3, 128.7, 170.3. HRMS (FD) Calcd for $C_{16}H_{25}NO_2$: M, 263.1885. Found: *m*/*z* 263.1906.

1-*tert*-Butyl-3-butyl-1*H*-pyrrole (β-4m). The title compound was synthesized with the following reagents based on method A: for the 0.3-mmol scale reaction: 1-*tert*-butylpyrrole (148 mg, 1.20 mmol), butanal (21.6 mg, 0.300 mmol), **3a** (52.3 mg, 0.450 mmol), $In(ONf)_3$ (30.4 mg, 30.0 μmol) and 1,4-dioxane (0.50 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 50:1) in

54% yield (29.2 mg) as a colorless oil; for the 5-mmol scale reaction: 1-*tert*-butylpyrrole (2.66 g, 20.0 mmol), butanal (361 mg, 5.00 mmol), **3a** (872 mg, 7.50 mmol), $In(ONf)_3$ (506 mg, 0.500 mmol) and 1,4-dioxane (8.3 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 50:1) in 49% yield (445 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.3 Hz, 3 H), 1.37 (sext, *J* = 7.4 Hz, 2 H), 1.50 (s, 9 H), 1.51–1.60 (m, 2 H), 2.46 (t, *J* = 7.8 Hz, 2 H), 5.99 (t, *J* = 2.3 Hz, 1 H), 6.57–6.62 (m, 1 H), 6.73 (t, *J* = 2.5 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.0, 22.7, 27.0, 30.7, 33.4, 54.3, 107.3, 114.9, 117.1, 124.0. HRMS (FI) Calcd for $C_{12}H_{21}N$: M, 179.1674. Found: *m*/*z* 179.1666.

1,2-Dimethyl-4-(tetrahydro-2*H*-thiopyran-4-yl)-1*H*-pyrrole (β-4n). The title compound was synthesized with the following reagents based on method B: 1,2-dimethylpyrrole (85.6 mg, 0.900 mmol), tetrahydro-4*H*-thiopyran-4-one (34.9 mg, 0.300 mmol), **3a** (105 mg, 0.900 mmol), $In(NTf_2)_3$ (57.3 mg, 60.0 μmol) and 1,4-dioxane (0.50 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 20:1) in 60% yield (35.6 mg). Compound **β-4n** has already appeared in reference 36, and its spectral and analytical data are in good agreement with those reported in the literature. Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.71 (dtd, *J* = 13.2, 12.2, 3.4 Hz, 2 H), 2.16–2.22 (m, 2 H), 2.18 (d, *J* = 0.9 Hz, 3 H), 2.42 (tt, *J* = 11.7, 3.2 Hz, 1 H), 2.62–2.69 (m, 2 H), 2.78 (ddd, *J* = 12.0, 7.3, 5.9 Hz, 2 H), 3.46 (s, 3 H), 5.72–5.78 (m, 1 H), 6.31 (d, *J* = 2.1 Hz, 1 H).

3-Cyclohexyl-1,4-dimethyl-1*H*-pyrrole (β-4o). The title compound was synthesized with the following reagents based on method A: 1,3-dimethylpyrrole (85.6 mg, 0.900 mmol), cyclohexanone (29.4 mg, 0.300 mmol), **3a** (52.3 mg, 0.450 mmol), $In(NTf_2)_3$ (28.7 mg, 30.0 μmol) and 1,4-dioxane (0.50 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc/Et_3N = 100:1:3) in 80% yield (42.6 mg) as a colorless oil. ^{1}H NMR (400 MHz, acetone-d_6) δ 1.15–1.30 (m, 3 H), 1.36 (qt, *J*

= 12.7, 3.1 Hz, 2 H), 1.65–1.80 (m, 3 H), 1.81–1.89 (m, 2 H), 1.95 (s, 3 H), 2.34 (tt, *J* = 11.7, 3.4 Hz, 1 H), 3.50 (s, 3 H), 6.27 (s, 2 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, acetone-d_6) δ 10.5, 27.2, 27.7, 35.3, 35.7, 36.3, 116.6, 118.0, 120.4, 129.7. HRMS (FI) Calcd for $C_{12}H_{19}N$: M, 177.1517. Found: *m*/*z* 177.1542.

1-*tert*-Butyl-3-(decan-1-yl)-4-(propan-2-yl)-1*H*-pyrrole (β-4p). The title compound was synthesized with the following reagents based on method A (0.1-mmol scale reaction): 1-*tert*-butyl-3-(decan-1-yl)-1*H*-pyrrole (**β-4x**) (79.0 mg, 0.300 mmol), acetone (5.81 mg, 0.100 mmol), **3a** (17.4 mg, 0.150 mmol), $In(NTf_2)_3$ (9.55 mg, 10.0 μmol) and 1,4-dioxane (0.17 mL), and was isolated by column chromatography on silica gel (hexane) in 93% yield (28.6 mg) as a colorless oil. Through the purification process, 51.9 mg of pyrrole substrate **β-4x** was recovered at an efficiency of 98% [= 51.9 mg/52.7 mg (0.200 mmol)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.7 Hz, 3 H), 1.19 (d, *J* = 6.9 Hz, 6 H), 1.22–1.42 (m, 14 H), 1.48 (s, 9 H), 1.53–1.64 (m, 2 H), 2.42 (t, *J* = 8.0 Hz, 2 H), 2.82 (sept, *J* = 6.9 Hz, 1 H), 6.51 (d, *J* = 2.9 Hz, 1 H), 6.52 (d, *J* = 3.0 Hz, 1 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 24.1, 25.3, 25.7, 29.4, 29.62, 29.67, 29.69, 30.0, 30.4, 30.7, 31.9, 54.2, 112.8, 114.6, 121.5, 128.9. HRMS (FD) Calcd for $C_{21}H_{39}N$: M, 305.3083. Found: *m*/*z* 305.3089.

1-*tert*-Butyl-3,4-di(decan-1-yl)-1*H*-pyrrole (β-4q). The title compound was synthesized with the following reagents based on method A (0.1-mmol scale reaction): **β-4x** (79.0 mg, 0.300 mmol), decanal (**6b**) (15.6 mg, 0.100 mmol), **3a** (17.4 mg, 0.150 mmol), $In(ONf)_3$ (5.06 mg, 5.00 μmol) and 1,4-dioxane (0.17 mL), and was isolated by column chromatography on silica gel (hexane) in 91% yield (36.9 mg) as a colorless oil. Through the purification process, 53.1 mg of pyrrole substrate **β-4x** was recovered at an efficiency of 100% [= 53.1 mg/52.7 mg (0.200 mmol)] ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 6 H), 1.20–1.40 (m, 28 H), 1.48 (s, 9 H), 1.54 (quint, *J* = 7.6 Hz, 4 H), 2.37 (t, *J* = 8.0 Hz, 4 H), 6.52 (s, 2 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 14.1, 22.7, 25.6, 29.4, 29.6, 29.7, 29.9, 30.5, 30.8, 32.0,

54.1, 114.6, 122.2 (One carbon signal is missing due to overlapping). HRMS (FD) Calcd for $C_{28}H_{53}N$: M, 403.4178. Found: *m*/*z* 403.4204.

1-*tert*-Butyl-3-(decane-1-yl)-4-(2,2-dimethylpropan-1-yl)-1*H*-pyrrole (β-4r). The title compound was synthesized with the following reagents based on method A: for the 0.1-mmol scale reaction: **β-4x** (73.7 mg, 0.280 mmol), trimethylacetaldehyde (8.61 mg, 0.100 mmol), **3a** (17.4 mg, 0.150 mmol), $In(ONf)_3$ (10.1 mg, 10.0 μmol) and 1,4-dioxane (0.17 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 30/1) in 93% yield (31.2 mg) as a colorless oil. Through the purification process, 42.9 mg of pyrrole substrate **β-4x** was recovered at an efficiency of 90% [= 42.9 mg/47.4 mg (0.180 mmol)]; for the 5-mmol scale reaction: **β-4x** (3.69 g, 14.0 mmol), trimethylacetaldehyde (431 mg, 5.00 mmol), **3a** (872 mg, 7.50 mmol), $In(ONf)_3$ (506 mg, 0.500 mmol) and 1,4-dioxane (10.0 mL), and was isolated by column chromatography on silica gel twice (first: hexane/EtOAc = 30/1; second: hexane/$CHCl_3$ = 10:1) in 90% yield (1.51 g) as a colorless oil. Through the purification process, 2.36 g of pyrrole substrate **β-4x** was recovered at an efficiency of 99% [= 2.36 g/2.37 g (9.00 mmol)]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 3 H), 0.89 (s, 9 H), 1.21–1.40 (m, 14 H), 1.48 (s, 9 H), 1.51–1.59 (m, 2 H), 2.27 (s, 2 H), 2.36 (t, *J* = 8.0 Hz, 2 H), 6.49 (d, *J* = 2.3 Hz, 1 H), 6.51 (d, *J* = 2.3 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 14.1, 22.7, 25.8, 29.4, 29.5, 29.64, 29.67, 29.69, 30.0, 30.4, 30.7, 31.89, 31.94, 39.1, 54.0, 113.7, 116.6, 118.8, 123.3. HRMS (FD) Calcd for $C_{23}H_{43}N$: M, 333.3396. Found: *m*/*z* 333.3412.

1-*tert*-Butyl-3-cyclohexylmethyl-4-(propan-2-yl)-1*H*-pyrrole (β-4s). The title compound was synthesized with the following reagents based on method A (0.2-mmol scale reaction): 1-*tert*-butyl-3-(propan-2-yl)-1*H*-pyrrole (**β-4g**) (132 mg, 0.800 mmol), cyclohexanecarboxaldehyde (22.4 mg, 0.200 mmol), **3a** (34.9 mg, 0.300 mmol), $In(ONf)_3$ (20.2 mg, 20.0 μmol) and 1,4-dioxane (0.35 mL), and was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 20/1) in 84% yield (44.1 mg) as a

colorless oil. Through the purification process, 95.3 mg of pyrrole substrate **β-4g** was recovered at an efficiency of 96% [= 95.3 mg/99.2 mg (0.600 mmol)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (qd, *J* = 11.9, 3.0 Hz, 2 H), 1.12–1.27 (m, 3 H), 1.18 (d, *J* = 6.9 Hz, 6 H), 1.36–1.45 (m, 1 H), 1.48 (s, 9 H), 1.60–1.73 (m, 3 H), 1.75–1.82 (m, 2 H), 2.29 (d, *J* = 6.9 Hz, 2 H), 2.80 (sept, *J* = 6.8 Hz, 1 H), 6.47 (d, *J* = 2.8 Hz, 1 H), 6.50 (d, *J* = 2.8 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 24.4, 25.2, 26.5, 26.8, 30.7, 33.6, 33.7, 38.9, 54.1, 112.6, 115.5, 119.5, 129.3. HRMS (FI) Calcd for $C_{18}H_{31}N$: M, 261.2457. Found: *m*/*z* 261.2460.

1-*tert*-Butyl-3-(propan-2-yl)-4-(3-thienylmethyl)-1*H*-pyrrole (β-4t). The title compound was synthesized with the following reagents based on method A (0.2-mmol scale reaction): **β-4g** (132 mg, 0.800 mmol), 3-thiophenecarboxaldehyde (22.4 mg, 0.200 mmol), **3a** (34.9 mg, 0.300 mmol), $In(ONf)_3$ (20.2 mg, 20.0 μmol) and 1,4-dioxane (0.35 mL), and was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 20/1) in 73% yield (38.3 mg) as a white solid; mp 78–79 ºC. Through the purification process, 91.6 mg of pyrrole substrate **β-4g** was recovered at an efficiency of 92% [= 91.6 mg/99.2 mg (0.600 mmol)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (d, *J* = 6.9 Hz, 6 H), 1.46 (s, 9 H), 2.78 (septd, *J* = 6.8, 0.6 Hz, 1 H), 3.80 (t, *J* = 1.0 Hz, 2 H), 6.42 (dt, *J* = 2.6, 0.7 Hz, 1 H), 6.54 (dd, *J* = 2.6, 0.7 Hz, 1 H), 6.90–6.94 (m, 1 H), 6.97 (dd, *J* = 4.9, 1.3 Hz, 1 H), 7.22 (dd, *J* = 4.9, 3.0 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 24.0, 25.3, 26.7, 30.7, 54.3, 113.1, 115.9, 119.5, 120.6, 124.8, 128.8, 129.0, 142.9. HRMS (FI) Calcd for $C_{16}H_{23}NS$: M, 261.1551. Found: *m*/*z* 261.1557.

2-Decyl-1-methyl-1*H*-pyrrole (α-4u). The title compound was synthesized with the following reagents based on method A (1.2-mmol scale reaction): **1a** (389 mg, 4.80 mmol), **6b** (188 mg, 1.20 mmol), **3a** (209 mg, 1.80 mmol), $In(ONf)_3$ (121 mg, 0.121 mmol) and 1,4-dioxane (2.0 mL). Column chromatography on silica gel (hexane/EtOAc = 50:1) of the resulting crude reaction mixture provided a mixture of **α-4u** and **β-4u** (82:18) in 36% yield (97.4 mg), which was then separated by recycling GPC

to give pure **α-4u** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 3 H), 1.19–1.44 (m, 14 H), 1.62 (quint, *J* = 7.6 Hz, 2 H), 2.51 (t, *J* = 7.6 Hz, 2 H), 3.52 (s, 3 H), 5.84–5.90 (m, 1 H), 6.04 (t, *J* = 3.0 Hz, 1 H), 6.53 (t, *J* = 2.3 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 14.1, 22.7, 26.3, 28.9, 29.3, 29.50, 29.55, 29.62, 29.63, 31.9, 33.5, 105.3, 106.4, 120.9, 133.8. HRMS (FI) Calcd for $C_{15}H_{27}N$: M, 221.2143. Found: *m*/*z* 221.2143.

3-Decyl-1-methyl-1*H*-pyrrole (β-4u). The title compound was synthesized and purified in the same way as the above, and was obtained as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 3 H), 1.22–1.36 (m, 14 H), 1.49–1.55 (m, 2 H), 2.43 (t, *J* = 7.7 Hz, 2 H), 3.59 (s, 3 H), 5.97 (t, *J* = 2.2 Hz, 1 H), 6.37 (t, *J* = 2.0 Hz, 1 H), 6.50 (t, *J* = 2.3 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 14.1, 22.7, 27.1, 29.4, 29.6, 29.67, 29.72, 31.4, 31.9, 36.0, 108.2, 119.0, 121.3, 125.0 (One carbon signal is missing due to overlapping). HRMS (FI) Calcd for $C_{15}H_{27}N$: M, 221.2143. Found: *m*/*z* 221.2136.

A Mixture of 2-(Decan-2-yl)-1*H*-pyrrole (α-7a) and 3-(Decan-2-yl)-1*H*-pyrrole (β-7a). The mixture was synthesized with the following reagents based on method A: pyrrole (**1c**) (60.4 mg, 0.900 mmol), **6a** (46.9 mg, 0.300 mmol), **3a** (52.3 mg, 0.450 mmol), $In(NTf_2)_3$ (28.7 mg, 30.0 μmol) and 1,4-dioxane (0.50 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 30:1) in 28% yield (17.9 mg, **α-7a**:**β-7a** = 46:54). The two isomers, **α-7a** and **β-7a**, have already appeared in reference 14, and their spectral and analytical data are in good agreement with those reported in the literature.

3-(Decan-1-yl)-1-(2-phenylpropan-2-yl)-1*H*-pyrrole (β-4w). The title compound was synthesized with the following reagents based on method A (10-mmol scale reaction): 1-(2-phenylpropan-2-yl)-1*H*-pyrrole (7.41 g, 40.0 mmol), **6b** (1.56 g, 10.0 mmol), **3a** (1.74 g, 15.0 mmol), $In(ONf)_3$ (1.01 g, 1.00 mmol) and 1,4-dioxane (16.7 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 70:1) in 53% yield (1.75 g). The corresponding 0.3-mmol scale reaction has been

already reported in our previous communication, and its spectral and analytical data are collected in reference 15. Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 3 H), 1.21–1.37 (m, 14 H), 1.56 (quint, *J* = 7.3 Hz, 2 H), 1.86 (s, 6 H), 2.45 (t, *J* = 7.7 Hz, 2 H), 6.03 (t, *J* = 2.3 Hz, 1 H), 6.53 (t, *J* = 2.0 Hz, 1 H), 6.70 (t, *J* = 2.6 Hz, 1 H), 6.95–6.99 (m, 2 H), 7.21 (tt, *J* = 7.5, 1.6 Hz, 1 H), 7.24–7.29 (m, 2 H).

1-*tert*-Butyl-3-decyl-1*H*-pyrrole (β-4x). The title compound was synthesized with the following reagents based on method A (25-mmol scale reaction): 1-*tert*-butylpyrrole (12.3 g, 100 mmol), **6b** (3.91 g, 25.0 mmol), **3a** (4.36 g, 37.5 mmol), $In(ONf)_3$ (2.53 g, 2.50 mmol) and 1,4-dioxane (42.0 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 30:1) in 60% yield (3.96 g). The corresponding 0.3-mmol scale reaction has been already reported in our previous communication, and its spectral and analytical data are collected in reference 15. Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.9 Hz, 3 H), 1.20–1.39 (m, 14 H), 1.44–1.61 (m, 2 H), 1.50 (s, 9 H), 2.44 (t, *J* = 7.8 Hz, 2 H), 5.99 (t, *J* = 2.3 Hz, 1 H), 6.59 (t, *J* = 2.1 Hz, 1 H), 6.73 (t, *J* = 2.5 Hz, 1 H).

Indium-Catalyzed β-Alkylation of Pyrroles with Carbonyl Compounds and Carbon Nucleophiles; A General Procedure for Table 3. The experimental procedure performed on a 0.3-mmol scale based on carbonyl compound **6** is shown here as a representative. $In(NTf_2)_3$ [(43.0 mg, 45.0 μmol) or (57.3 mg, 60.0 μmol)], $In(OTf)_3$ [(25.3 mg, 45.0 μmol), (33.7 mg, 60.0 μmol) or (42.2 mg, 90.0 μmol)] or $In(ONf)_3$ (60.7 mg, 60.0 μmol) was placed in a 20 mL Schlenk tube, which was heated at 150 ºC in vacuo for 2 h. The tube was cooled down to room temperature and filled with argon. 1,4-Dioxane (0.30, 0.84 or 2.4 mL) was added to the tube, and the mixture was then stirred at room temperature for 10 min. To this were added carbonyl compound **6** (0.300 mmol), pyrrole derivative **1** (1.20 mmol), and the resulting mixture was stirred at 85 °C for 1 or 3 h. Carbon nucleophile **3** (0.0900,

0.450, 0.750, 0.900 or 1.50 mmol) was then added to this solution, and the resulting mixture was stirred further at *T* ºC. After stirring for *t* h, the work-up process was carried out in the same way as in the reaction with **3a** as a nucleophile. Unless otherwise noted, new products **β-8** synthesized here were fully characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, and HRMS.

5-Acetyloxy-2-methyl-2-(1-methyl-1*H*-pyrrol-3-yl)pentanenitrile (β-8a). The title compound was synthesized with the following reagents (0.25-mmol scale reaction): 1-methylpyrrole (**1a**) (81.1 mg, 1.00 mmol**)**, 5-acetyloxy-2-pentanone (36.0 mg, 0.250 mmol), Me_3SiCN (**3b**) (37.2 mg, 0.375 mmol), $In(OTf)_3$ (21.1 mg, 37.5 μmol) and 1,4-dioxane (0.25 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 3:1) in 71% yield (42.0 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.64 (s, 3 H), 1.65–1.94 (m, 4 H), 2.04 (s, 3 H), 3.63 (s, 3 H), 4.05 (t, *J* = 6.3 Hz, 2 H), 6.02 (dd, *J* = 2.9, 1.7 Hz, 1 H), 6.56 (t, *J* = 2.9 Hz, 1 H), 6.62 (t, *J* = 1.8 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 20.9, 25.0, 27.8, 36.1, 36.3, 38.6, 63.9, 105.3, 118.9, 122.6, 124.08, 124.12, 171.1. HRMS (FI) Calcd for $C_{13}H_{18}N_2O_2$: M, 234.1368. Found: *m*/*z* 234.1369.

Tetrahydro-4-(1-methyl-1*H*-pyrrol-3-yl)-2*H*-thiopyran-4-carbonitrile (β-8b). The title compound was synthesized with the following reagents (0.25-mmol scale reaction): **1a** (81.1 mg, 1.00 mmol), tetrahydro-4*H*-thiopyran-4-one (29.0 mg, 0.250 mmol), **3b** (37.2 mg, 0.375 mmol), $In(OTf)_3$ (28.1 mg, 50.0 μmol) and 1,4-dioxane (0.25 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 5:1) in 65% yield (33.5 mg) as a white solid; mp 73–74 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.04 (ddd, *J* = 13.9, 12.7, 3.3 Hz, 2 H), 2.38–2.44 (m, 2 H), 2.59–2.70 (m, 2 H), 3.13 (ddd, *J* = 14.6, 12.3, 2.3 Hz, 2 H), 3.64 (s, 3 H), 6.10 (t, *J* = 2.6 Hz, 1 H), 6.57 (t, *J* = 2.6 Hz, 1 H), 6.63 (t, *J* = 2.0 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 25.7, 36.3, 38.0, 38.6, 105.5, 118.2, 122.3, 122.5, 125.3. HRMS (FI) Calcd for $C_{11}H_{14}N_2S$: M, 206.0878. Found: *m*/*z* 206.0873.

2-(1-Methyl-1*H*-pyrrol-3-yl)adamantane-2-carbonitrile (β-8c). The title compound was synthesized with the following reagents (0.25-mmol scale reaction): **1a** (81.1 mg, 1.00 mmol), 2-adamantanone (37.6 mg, 0.250 mmol), **3b** (37.2 mg, 0.375 mmol), $In(OTf)_3$ (21.1 mg, 37.5 μmol) and 1,4-dioxane (0.25 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 7:1) in 84% yield (50.6 mg). Compound **β-8c** has already appeared in reference 36, and its spectral and analytical data are in good agreement with those reported in the literature. Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.61 (ddd, *J* = 13.0, 3.8, 2.6 Hz, 2 H), 1.69–1.79 (m, 3 H), 1.92 (ddd, *J* = 13.4, 3.6, 2.7 Hz, 2 H), 1.97–2.06 (m, 3 H), 2.41 (dd, *J* = 13.1, 2.1 Hz, 2 H), 2.46 (t, *J* = 2.7 Hz, 2 H), 3.64 (s, 3 H), 6.10 (dd, *J* = 2.8, 2.0 Hz, 1 H), 6.55 (t, *J* = 2.0 Hz, 1 H), 6.57 (t, *J* = 2.5 Hz, 1 H).

2-(1-Methyl-1*H*-pyrrol-3-yl)-2-phenylpropanenitrile (β-8d). The title compound was synthesized with the following reagents: **1a** (97.3mg, 1.20 mmol), acetophenone (36.0 mg, 0.300 mmol), **3b** (44.6 mg, 0.450 mmol), $In(NTf_2)_3$ (57.3 mg, 60.0 μmol) and 1,4-dioxane (0.30 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 10:1) in 71% yield (44.8 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.00 (s, 3 H), 3.62 (s, 3 H), 6.04 (dd, *J* = 2.9, 1.7 Hz, 1 H), 6.52 (t, *J* = 2.0 Hz, 1 H), 6.56 (t, *J* = 2.6 Hz, 1 H), 7.28 (tt, *J* = 7.5, 1.5 Hz, 1 H), 7.35 (tt, *J* = 7.5, 1.8 Hz, 2 H), 7.44–7.49 (m, 2 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 29.0, 36.3, 40.9, 107.1, 119.7, 122.6, 124.0, 125.1, 126.1, 127.5, 128.6, 142.3. HRMS (FI) Calcd for $C_{14}H_{14}N_2$: M, 210.1157. Found: *m*/*z* 210.1153.

2-(1-Benzyl-1*H*-pyrrol-3-yl)-2-propylpentanenitrile (β-8e). The title compound was synthesized with the following reagents (3-mmol scale reaction): 1-benzylpyrrole (1.89 g, 12.0 mmol), 4-heptanone (343 mg, 3.00 mmol), **3b** (446 mg, 4.50 mmol), $In(NTf_2)_3$ (573 mg, 0.600 mmol) and 1,4-dioxane (3.0 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 20:1) in 73% yield (618 mg) as a reddish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.4 Hz, 6 H), 1.23–1.39 (m, 2 H),

1.41–1.54 (m, 2 H), 1.65–174 (m, 2 H), 1.79–1.88 (m, 2 H), 5.02 (s, 2 H), 6.00 (t, J = 2.3 Hz, 1 H), 6.63 (t, J = 2.6 Hz, 1 H), 6.69 (t, J = 1.7 Hz, 1 H), 7.08 (d, J = 6.9 Hz, 2 H), 7.27–7.38 (m, 3 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 14.0, 18.6, 42.0, 43.0, 53.4, 105.6, 119.2, 122.0, 123.4, 123.7, 126.8, 127.7, 128.7, 137.9. HRMS (FI) Calcd for $C_{19}H_{24}N_2$: M, 280.1939. Found: *m*/*z* 280.1937.

2-(1-*tert*-Butyl-1*H*-pyrrol-3-yl)-2-methyloctanenitrile (β-8f). The title compound was synthesized with the following reagents: 1-*tert*-butylpyrrole (148 mg, 1.20 mmol), 2-octanone (38.5 mg, 0.300 mmol), **3b** (44.6 mg, 0.450 mmol), $In(NTf_2)_3$ (43.0 mg, 45.0 μmol) and 1,4-dioxane (0.30 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 10:1) in 87% yield (68.7 mg) as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, J = 6.9 Hz, 3 H), 1.21–1.50 (m, 8 H), 1.51 (s, 9 H), 1.62 (s, 3 H), 1.73–1.82 (m, 2 H), 6.02 (dd, J = 2.9, 1.7 Hz, 1 H), 6.77 (t, J = 2.6 Hz, 1 H), 6.80 (t, J = 2.3 Hz, 1 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 25.4, 27.6, 29.1, 30.7, 31.6, 36.5, 42.2, 54.9, 104.5, 114.7, 118.2, 124.1, 124.8. HRMS (FI) Calcd for $C_{17}H_{28}N_2$: M, 260.2252. Found: *m*/*z* 260.2252.

2-Methyl-2-(1-phenyl-1*H*-pyrrol-3-yl)octanenitrile (β-8g). The title compound was synthesized with the following reagents: 1-phenylpyrrole (172 mg, 1.20 mmol), 2-octanone (38.5 mg, 0.300 mmol), **3b** (44.6 mg, 0.450 mmol), $In(NTf_2)_3$ (57.3 mg, 60.0 μmol) and 1,4-dioxane (0.30 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 10:1) in 75% yield (63.3 mg) as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, J = 6.9 Hz, 3 H), 1.23–1.57 (m, 8 H), 1.68 (s, 3 H), 1.79–1.89 (m, 2 H), 6.25 (dd, J = 2.9, 1.7 Hz, 1 H), 7.05 (t, J = 2.9 Hz, 1 H), 7.09 (t, J = 2.0 Hz, 1 H), 7.24–7.29 (m, 1 H), 7.38 (dt, J = 7.5, 1.4 Hz, 2 H), 7.43 (tt, J = 8.0, 1.8 Hz, 2 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 25.5, 27.5, 29.1, 31.6, 36.5, 41.9, 107.7, 116.3, 120.0, 120.3, 124.3, 125.9, 127.0, 129.6, 140.3. HRMS (FI) Calcd for $C_{19}H_{24}N_2$: M, 280.1939. Found: *m*/*z* 280.1940.

2-(1-Benzyl-1*H*-pyrrol-3-yl)-2-(5-methylfuran-2-yl)octane (β-8h). The title compound was synthesized with the following reagents: 1-benzylpyrrole (189 mg, 1.20 mmol), 2-octanone (38.5 mg, 0.300 mmol), 2-methylfuran (**3c**) (61.6 mg, 0.750 mmol), $In(NTf_2)_3$ (43.0 mg, 45.0 μmol) and 1,4-dioxane (2.4 mL), and was isolated by recycling GPC after column chromatography on silica gel (hexane/EtOAc = 10:1) in 72% yield (76.0 mg). Compound **β-8h** has already appeared in reference 18, and its spectral and analytical data are in good agreement with those reported in the literature. Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, *J* = 6.8 Hz, 3 H), 1.07–1.35 (m, 8 H), 1.51 (s, 3 H), 1.76–1.87 (m, 1 H), 1.89–2.01 (m, 1 H), 2.24 (d, *J* = 0.9 Hz, 3 H), 5.00 (s, 2 H), 5.81 (dq, *J* = 3.0, 1.0 Hz, 1 H), 5.85 (d, *J* = 3.0 Hz, 1 H), 6.06 (dd, *J* = 2.7, 1.8 Hz, 1 H), 6.45 (t, *J* = 2.0 Hz, 1 H), 6.56 (t, *J* = 2.5 Hz, 1 H), 7.04–7.10 (m, 2 H), 7.22–7.34 (m, 3 H).

1-(1-*tert*-Butyl-1*H*-pyrrol-3-yl)-2,2-dimethyl-1-(5-methylfuran-2-yl)propane (β-8i). The title compound was synthesized with the following reagents: 1-*tert*-butylpyrrole (148 mg, 1.20 mmol), pivalaldehyde (25.8 mg, 0.300 mmol), **3c** (61.6 mg, 0.750 mmol), $In(ONf)_3$ (60.7 mg, 60.0 μmol) and 1,4-dioxane (2.4 mL), and was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 6:1) in 75% yield (62.1 mg) as a white solid; mp 46–47 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (s, 9 H), 1.49 (s, 9 H), 2.26 (d, *J* = 1.2 Hz, 3 H), 3.58 (s, 1 H), 5.82 (dq, *J* = 3.0, 1.0 Hz, 1 H), 5.94 (d, *J* = 3.0 Hz, 1 H), 6.13 (t, *J* = 2.4 Hz, 1 H), 6.66–6.70 (m, 2 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 13.7, 28.4, 30.7, 34.7, 49.6, 54.2, 105.5, 106.7, 109.0, 116.1, 116.9, 121.7, 149.4, 156.3. HRMS (FI) Calcd for $C_{18}H_{27}NO$: M, 273.2093. Found: *m*/*z* 273.2119.

2-(1-Methyl-1*H*-indol-3-yl)-2-(1-methyl-1*H*-pyrrol-3-yl)adamantane (β-8j). The title compound was synthesized with the following reagents: **1a** (97.3 mg, 1.20 mmol), 2-adamantanone (45.1 mg, 0.300 mmol), 1-methylindole (**3d**) (197 mg, 1.50 mmol), $In(OTf)_3$ (33.7 mg, 60.0 μmol) and 1,4-dioxane (0.30 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 20/1) in 30% yield

(31.2 mg) as a viscous colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.64–1.84 (m, 8 H), 2.25 (d, *J* = 11.7 Hz, 2 H), 2.35 (ddd, *J* = 12.8, 4.9, 3.2 Hz, 2 H), 3.04 (s, 2 H), 3.48 (s, 3 H), 3.67 (s, 3 H), 6.05 (dd, *J* = 2.7, 1.9 Hz, 1 H), 6.34 (t, *J* = 2.5 Hz, 1 H), 6.47 (t, *J* = 2.0 Hz, 1 H), 6.87 (s, 1 H), 7.00 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1 H), 7.10 (ddd, *J* = 8.8, 6.5, 1.0 Hz, 1 H), 7.17 (dt, *J* = 8.1, 0.9 Hz, 1 H), 7.86 (dt, *J* = 8.0, 0.9 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 14.2, 27.8, 27.9, 32.7, 33.8, 33.9, 34.2, 36.1, 38.7, 45.1, 106.0, 109.1, 117.9, 118.1, 120.36, 120.38, 121.4, 124.2, 126.0, 126.1, 133.4, 137.1. HRMS (FD) Calcd for $C_{24}H_{28}N_2$: M, 344.2252. Found: *m*/*z* 344.2245.

5-[1-Methyl-1-(1-methyl-1*H*-pyrrol-3-yl)ethyl]-2(5*H*)-furanone (β-8k). The title compound was synthesized with the following reagents: **1a** (97.3 mg, 1.20 mmol), acetone (17.4 mg, 0.300 mmol), 2-(trimethylsilyloxy)furan (**3e**) (117 mg, 0.750 mmol), $In(OTf)_3$ (25.3 mg, 45.0 μmol) and 1,4-dioxane (2.4 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 3/1) in 45% yield (28.0 mg) as a white solid; mp 73–74 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18 (s, 3 H), 1.41 (s, 3 H), 3.62 (s, 3 H), 4.94 (dd, *J* = 2.0, 1.4 Hz, 1 H), 6.02 (dd, *J* = 2.7, 1.9 Hz, 1 H), 6.05 (dd, *J* = 5.7, 2.0 Hz, 1 H), 6.44 (t, *J* = 2.2 Hz, 1 H), 6.54 (t, *J* = 2.4 Hz, 1 H), 7.28 (dd, *J* = 5.9, 1.6 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 22.4, 26.8, 36.2, 37.7, 91.0, 106.5, 118.7, 121.8, 122.2, 128.2, 155.4, 173.7. HRMS (FD) Calcd for $C_{12}H_{15}NO_2$: M, 205.1103. Found: *m*/*z* 205.1099.

4-Methyl-4-(1-methyl-1*H*-pyrrol-3-yl)dec-1-ene (β-8m). The title compound was synthesized with the following reagents (0.25 mmol-scale reaction): **1a** (81.1 mg, 1.00 mmol), 2-octanone (32.1 mg, 0.250 mmol), tetraallyltin (**3g**) (21.2 mg, 75.0 μmol), $In(OTf)_3$ (35.1 mg, 62.5 μmol) and 1,4-dioxane (0.70 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 20:1) in 21% yield (12.7 mg). Compound **β-8m** has already appeared in reference 18, and its spectral and analytical data are in good agreement with those reported in the literature. Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.2 Hz, 3 H), 1.14 (s, 3 H), 1.15–1.30 (m, 8

H), 1.39–1.53 (m, 2 H), 2.19–2.33 (m, 2 H), 3.60 (s, 3 H), 4.93–5.02 (m, 2 H), 5.72 (ddt, *J* = 17.2, 9.8, 7.9 Hz, 1 H), 5.97 (t, *J* = 2.3 Hz, 1 H), 6.32 (t, *J* = 2.0 Hz, 1 H), 6.51 (t, *J* = 2.6 Hz, 1 H).

N-Deprotection of *N*-Substituted β-Alkylpyrroles; A Procedure for Scheme 4, (i).[22] A flame-dried 20 mL Schlenk tube was filled with argon, and then charged with anhydrous *N*,*N*-dimethylformamide (DMF) (0.70 mL), **β-4h** (31.3 mg, 0.100 mmol) or **β-4i** (37.6 mg, 0.100 mmol), and a 55% dispersion of sodium hydride (13.1 mg, 0.300 mmol) in paraffin oil. The resulting mixture was stirred at room temperature for 6 h (for the case of **β-4h**) or 4 h (for the case of **β-4i**) followed by dilution with Et_2O (5 mL). The organic phase was washed with water (5 mL x 4) and brine (5 mL), and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 15:1 for the case of **β-4h** or hexane/EtOAc/Et_3N = 100:6:1 for the case of **β-4i**) gave 3-(decan-2-yl)-1*H*-pyrrole (**β-7a**) in 65% yield (13.6 mg) for the case of **β-4h** or in 87% yield (18.1 mg) for the case of **β-4i**. Compound **β-7a** has already appeared in reference 14, and its spectral and analytical data are in good agreement with those reported in the literature. Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.9 Hz, 3 H), 1.20 (d, *J* = 6.9 Hz, 3 H), 1.21–1.34 (m, 12 H), 1.39–1.61 (m, 2 H), 2.65 (sext, *J* = 6.9 Hz, 1 H), 6.11 (dt, *J* = 2.7, 1.5 Hz, 1 H), 6.56 (q, *J* = 1.7 Hz, 1 H), 6.73 (q, *J* = 2.4 Hz, 1 H), 7.97 (bs, 1 H).

N-Deprotection of *N*-Substituted β-Alkylpyrroles; A Procedure for Scheme 4, (ii).[23b] The experimental procedure for the synthesis of **β-7a** is shown here as a representative. *t*-BuOK (29.2 mg, 0.260 mmol) was placed in a 20 mL Schlenk tube, which was heated at 80 ºC in vacuo for 30 min. The tube was cooled down to room temperature and filled with argon. To this were added THF (1.00 mL), and **β-4j** (16.0 mg, 0.0520 mmol) or **β-4k** (16.7 mg, 0.0520 mmol), and the resulting mixture was stirred at room temperature for 30 min. A saturated NH_4Cl aqueous solution (1 mL) was added to the mixture, and the aqueous phase was extracted with EtOAc (5 mL x 3). The combined organic layer was washed

with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc/Et_3N = 100:6:3) gave 3-(decan-2-yl)-1*H*-pyrrole (**β-7a**) in 54% yield (5.90 mg) for the case of **β-4j** or in 82% yield (8.90 mg) for the case of **β-4k**. As described in the above section, the spectral and analytical data of **β-7a** are shown in reference 14.

3-Cyclopentyl-1*H*-pyrrole (β-7b). The title compound was synthesized with the following reagents (0.1-mmol scale reaction): **β-4l** (26.3 mg, 0.100 mmol), *t*-BuOK (56.1 mg, 0.500 mmol) and THF (1.9 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc/Et_3N = 100:6:3) in 66% yield (9.00 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46–1.55 (m, 2 H), 1.58–1.80 (m, 4 H), 1.94–2.07 (m, 2 H), 2.93 (tt, *J* = 9.2, 7.4 Hz, 1 H), 6.13 (td, *J* = 2.7, 1.6 Hz, 1 H) 6.57–6.62 (m, 1 H), 6.73 (td, *J* = 2.6, 2.1 Hz, 1 H), 7.98 (bs, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 25.1, 34.5, 38.2, 107.5, 113.9, 117.7, 129.0. HRMS (FI) Calcd for $C_9H_{13}N$: M, 135.1048. Found: *m*/*z* 135.1024.

Indium-Catalyzed Synthesis of Diaryldipyrrolylmethanes; A General Procedure for Table 4. The experimental procedure performed on a 0.4-mmol scale based on diaryl ketone **6** is shown here as a representative. $In(NTf_2)_3$ [(38.2 mg, 40.0 μmol) or (76.4 mg, 80.0 μmol)] was placed in a 20 mL Schlenk tube, which was heated at 150 ºC in vacuo for 2 h. The tube was cooled down to room temperature and filled with argon. 1,4-Dioxane (0.40 mL) was added to the tube, and the mixture was then stirred at room temperature for 10 min. To this were added diaryl ketone **6** (0.400 mmol), pyrrole derivative **1** (1.60 or 2.00 mmol), and the resulting mixture was stirred at *T* °C. After stirring for *t* h, a saturated $NaHCO_3$ aqueous solution (0.3 mL) was added, and the aqueous phase was extracted with EtOAc (5 mL x 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by purification gave the

corresponding products (**5**). Unless otherwise noted, products **5** synthesized here were fully characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, and HRMS.

(4-Methylphenyl)(1-methyl-1*H*-pyrrol-2-yl)(1-methyl-1*H*-pyrrol-3-yl)phenylmethane (α,β'-5a). The title compound was synthesized with the following reagents: 1-methylpyrrole (**1a**) (162 mg, 2.00 mmol), 4-methylbenzophenone (**6c**) (78.5 mg, 0.400 mmol), $In(NTf_2)_3$ (76.4 mg, 80.0 μmol) and 1,4-dioxane (0.40 mL). Column chromatography on silica gel (hexane/$CHCl_3$ = 3:1) of the resulting crude reaction mixture provided a mixture of **α,β'-5a** and **β,β'-5a** (13:87) in 53% yield (72.7 mg). In the course of the purification, some fractions including pure **α,β'-5a** were collected. Accordingly, **α,β'-5a** as a viscous colorless oil could be characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, and HRMS. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3 H), 2.95 (s, 3 H), 3.58 (s, 3 H), 5.59 (dd, *J* = 3.7, 2.3 Hz, 1 H), 5.80 (t, *J* = 2.3 Hz, 1 H), 6.01 (dd, *J* = 3.7, 2.7 Hz, 1 H), 6.22 (t, *J* = 2.1 Hz, 1 H), 6.54 (t, *J* = 2.5 Hz, 1 H), 6.59 (t, *J* = 2.3 Hz, 1 H), 7.02–7.10 (m, 4 H), 7.15–7.25 (m, 5 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 20.9, 36.2, 36.4, 54.3, 105.4, 111.0, 111.1, 121.3, 121.8, 123.2, 125.8, 127.3, 128.1, 129.7, 129.8, 135.3, 139.2, 144.1, 147.3 (one carbon signal is missing due to overlapping). HRMS (FD) Calcd for $C_{24}H_{24}N_2$: M, 340.1939. Found: *m*/*z* 340.1929.

(4-Methylphenyl)bis(1-methyl-1*H*-pyrrol-3-yl)phenylmethane (β,β'-5a). The title compound was synthesized and purified in the same way as the above, and was obtained as a white solid; mp 108–109 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3 H), 3.55 (s, 6 H), 5.96 (dd, *J* = 2.8, 1.8 Hz, 2 H), 6.16 (t, *J* = 2.1 Hz, 2 H), 6.53 (t, *J* = 2.5 Hz, 2 H), 7.02 (d, *J* = 8.0 Hz, 2 H), 7.13 (dt, *J* = 8.2, 1.8 Hz, 2 H), 7.15–7.27 (m, 5 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 20.9, 36.1, 53.7, 111.0, 120.9, 122.1, 125.4, 127.0, 127.7, 129.7, 129.8, 132.2, 134.8, 146.4, 149.5. HRMS (FD) Calcd for $C_{24}H_{24}N_2$: M, 340.1939. Found: *m*/*z* 340.1969.

(4-Methylphenyl)bis(1-methyl-1*H*-pyrrol-2-yl)phenylmethane (α,α'-5a). The title compound was formed as a minor isomer in the reaction performed with the intention of synthesizing **5a** (**α,α'-5a**:**α,β'-5a**:**β,β'-5a** = 1:15:84). However, in the case of 0.4-mmol scale reaction of **6c**, pure **α,α'-5a** could not be obtained in an amount that is required for measuring NMR spectra. Accordingly, a larger-scale reaction using $In(OTf)_3$ instead of $In(NTf_2)_3$ was carried out with the following reagents and conditions: **1a** (487 mg, 6.00 mmol), **6c** (235 mg, 1.20 mmol), $In(OTf)_3$ (135 mg, 0.240 mmol), 1,4-dioxane (1.20 mL), 100 ºC, 2.5 h, and was isolated by recycling GPC after column chromatography on silica gel (hexane/$CHCl_3$ = 3:1) in 2% yield (11.9 mg) as a viscous colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3 H), 2.88 (s, 6 H), 5.84 (s, 2 H), 6.03 (dd, *J* = 3.6, 2.8 Hz, 2 H), 6.61 (t, *J* = 2.3 Hz, 2 H), 6.97 (d, *J* = 8.0 Hz, 2 H), 7.06 (d, *J* = 8.2 Hz, 2 H), 7.09 (d, *J* = 7.1 Hz, 2 H), 7.19 (tt, *J* = 6.9, 2.0 Hz, 1 H), 7.22–7.28 (m, 2 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 21.0, 35.7, 55.2, 105.8, 111.8, 123.9, 126.3, 127.6, 128.3, 129.7, 129.8, 135.9 (three carbon signals are missing due to overlapping). HRMS (FD) Calcd for $C_{24}H_{24}N_2$: M, 340.1939. Found: *m*/*z* 340.1947.

(3-Methylphenyl)(4-methylphenyl)(1-methyl-1*H*-pyrrol-2-yl)(1-methyl-1*H*-pyrrol-3-yl)methane (α,β'-5b). The title compound was synthesized with the following reagents (10-mmol scale reaction): **1a** (4.06 g, 50.0 mmol), 3,4'-dimethylbenzophenone (2.10 g, 10.0 mmol), $In(NTf_2)_3$ (1.91 g, 2.00 mmol) and 1,4-dioxane (10.0 mL). Column chromatography on silica gel (hexane/$CHCl_3$ = 3:2) of the resulting crude reaction mixture provided a mixture of **α,β'-5b** and **β,β'-5b** (15:85) in 50% yield (1.78 g). In the course of the purification, some fractions including pure **α,β'-5b** were collected. Accordingly, **α,β'-5b** as a viscous colorless oil could be characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, and HRMS. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.27 (s, 3 H), 2.32 (s, 3 H), 2.95 (s, 3 H), 3.58 (s, 3 H), 5.58 (dd, *J* = 3.5, 1.7 Hz, 1 H), 5.79 (t, *J* = 2.3 Hz, 1 H), 6.01 (t, *J* = 3.2 Hz, 1 H), 6.21 (t, *J* = 2.0 Hz, 1 H), 6.53 (t, *J* = 2.6 Hz, 1 H), 6.58 (t, *J* = 2.3 Hz, 1 H), 6.96–7.01 (m, 2 H), 7.02–7.09 (m, 5 H), 7.12 (t, *J* = 7.7 Hz, 1 H);

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 21.0, 21.7, 36.2, 36.4, 54.3, 105.4, 110.9, 111.2, 121.2, 121.8, 123.2, 126.6, 127.0, 127.2, 128.0, 129.66, 129.69, 130.3, 135.2, 136.7, 139.3, 144.3, 147.1. HRMS (FD) Calcd for $C_{25}H_{26}N_2$: M, 354.2096. Found: *m*/*z* 354.2118.

(3-Methylphenyl)(4-methylphenyl)bis(1-methyl-1*H*-pyrrol-3-yl)methane (β,β'-5b). The title compound was synthesized and purified in the same way as the above, and was obtained as a white solid; mp 122–123 ºC. ^1H NMR (500 MHz, $CDCl_3$) δ 2.26 (s, 3 H), 2.31 (s, 3 H), 3.54 (s, 6 H), 5.96 (t, *J* = 2.3 Hz, 2 H), 6.15 (t, *J* = 2.3 Hz, 2 H), 6.53 (t, *J* = 2.6 Hz, 2 H), 6.98 (d, *J* = 6.9 Hz, 1 H), 7.00–7.05 (m, 3 H), 7.08–7.14 (m, 4 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 20.9, 21.7, 36.1, 53.7, 111.0, 120.9, 122.1, 126.2, 126.8, 127.1, 127.7, 129.7, 130.4, 132.2, 134.7, 136.3, 146.5, 149.4. HRMS (FD) Calcd for $C_{25}H_{26}N_2$: M, 354.2096. Found: *m*/*z* 354.2125.

(1-Methyl-1*H*-pyrrol-2-yl)(1-methyl-1*H*-pyrrol-3-yl)(2-naphthyl)phenylmethane (α,β'-5c). The title compound was synthesized with the following reagents: **1a** (162 mg, 2.00 mmol), 2-benzoylnaphthalene (92.9 mg, 0.400 mmol), $In(NTf_2)_3$ (76.4 mg, 80.0 μmol) and 1,4-dioxane (0.40 mL). Column chromatography on silica gel (hexane/$CHCl_3$ = 3:2) of the resulting crude reaction mixture provided a mixture of **α,β'-5c** and **β,β'-5c** (8:92) in 48% yield (73.4 mg). In the course of the purification, some fractions including pure **α,β'-5c** were collected. Accordingly, **α,β'-5c** as a viscous colorless oil could be characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and HRMS. ^1H NMR (500 MHz, $CDCl_3$) δ 2.98 (s, 3 H), 3.59 (s, 3 H), 5.66 (dd, *J* = 3.5, 2.3 Hz, 1 H), 5.83 (dd, *J* = 2.9, 1.7 Hz, 1 H), 6.05 (t, *J* = 3.2 Hz, 1 H), 6.26 (t, *J* = 2.3 Hz, 1 H), 6.56 (t, *J* = 2.6 Hz, 1 H), 6.62 (t, *J* = 2.6 Hz, 1 H), 7.17–7.31 (m, 5 H), 7.33 (dd, *J* = 8.6, 1.8 Hz, 1 H), 7.40–7.46 (m, 2 H), 7.64 (d, *J* = 1.8 Hz, 1 H), 7.69 (d, *J* = 8.6 Hz, 1 H), 7.72 (dd, *J* = 6.9, 2.3 Hz, 1 H), 7.79 (dd, *J* = 6.6, 2.6 Hz, 1 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 36.2, 36.5, 54.8, 105.6, 111.18, 111.22, 121.4, 121.9, 123.5, 125.62, 125.65, 126.0,

126.5, 127.0, 127.3, 127.5, 128.4, 129.2, 129.6, 129.9, 131.9, 133.0, 138.7, 144.7, 146.7. HRMS (FD) Calcd for $C_{27}H_{24}N_2$: M, 376.1939. Found: *m*/*z* 376.1961.

Bis(1-methyl-1*H*-pyrrol-3-yl)(2-naphthyl)phenylmethane (β,β'-5c). The title compound was synthesized and purified in the same way as the above, and was obtained as a white solid; mp 183–184 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (s, 6 H), 6.00 (dd, *J* = 2.7, 1.8 Hz, 2 H), 6.20 (t, *J* = 2.1 Hz, 2 H), 6.56 (t, *J* = 2.5 Hz, 2 H), 7.12–7.23 (m, 3 H), 7.27–7.33 (m, 2 H), 7.37–7.44 (m, 3 H), 7.63–7.72 (m, 3 H), 7.78 (dd, *J* = 6.2, 2.5 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 36.1, 54.2, 111.0, 121.1, 122.2, 125.3, 125.4, 125.6, 126.0, 127.1, 127.2, 127.3, 128.4, 129.7, 129.9, 131.8, 132.9, 147.0, 149.1 (One carbon signal is missing due to overlapping). HRMS (FD) Calcd for $C_{27}H_{24}N_2$: M, 376.1939. Found: *m*/*z* 376.1963.

(1-Methyl-1*H*-pyrrol-2-yl)(1-methyl-1*H*-pyrrol-3-yl)phenyl(thien-3-yl)methane (α,β'-5d). The title compound was synthesized with the following reagents (4-mmol scale reaction): **1a** (1.62 g, 20.0 mmol), 3-benzoylthiophene (753 mg, 4.00 mmol), $In(NTf_2)_3$ (764 mg, 0.800 mmol) and 1,4-dioxane (4.0 mL). Column chromatography on silica gel (hexane/$CHCl_3$ = 3:2) of the resulting crude reaction mixture provided a mixture of **α,β'-5d** and **β,β'-5d** (14:86) in 41% yield (547 mg). In the course of the purification, some fractions including pure **α,β'-5d** were collected. Accordingly, **α,β'-5d** as a white solid; mp 136–137 ºC could be characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, and HRMS. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.99 (s, 3 H), 3.58 (s, 3 H), 5.61 (dd, *J* = 3.7, 2.0 Hz, 1 H), 5.85 (dd, *J* = 2.9, 1.7 Hz, 1 H), 6.02 (dd, *J* = 3.7, 2.6 Hz, 1 H), 6.21 (t, *J* = 2.0 Hz, 1 H), 6.54 (t, *J* = 2.6 Hz, 1 H), 6.58 (t, *J* = 2.3 Hz, 1 H), 6.84 (dd, *J* = 4.9, 1.4 Hz, 1 H), 6.88 (dd, *J* = 2.9, 1.2 Hz, 1 H), 7.17–7.29 (m, 6 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 36.20, 36.21, 51.7, 105.5, 110.2, 110.4, 121.25, 121.33, 122.5, 123.3, 124.0, 126.1, 127.5, 129.1, 129.6, 130.4, 138.8, 146.7, 148.7. HRMS (FD) Calcd for $C_{21}H_{20}N_2S$: M, 332.1347. Found: *m*/*z* 332.1370.

Bis(1-methyl-1*H*-pyrrol-3-yl)phenyl(thien-3-yl)methane (β,β'-5d). The title compound was synthesized and purified in the same way as the above, and was obtained as a white solid; mp 145–146 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.55 (s, 6 H), 5.99 (dd, *J* = 2.8, 1.8 Hz, 2 H), 6.17 (t, *J* = 2.1 Hz, 2 H), 6.54 (t, *J* = 2.5 Hz, 2 H), 6.87 (dd, *J* = 3.0, 1.1 Hz, 1 H), 6.98 (dd, *J* = 5.0, 1.4 Hz, 1 H), 7.13–7.24 (m, 6 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 36.1, 51.1, 110.2, 121.1, 121.5, 122.5, 123.6, 125.6, 127.1, 129.2, 130.3, 131.9, 149.2, 150.8. HRMS (FD) Calcd for $C_{21}H_{20}N_2S$: M, 332.1347. Found: *m*/*z* 332.1371.

Bis(1-benzyl-1*H*-pyrrol-3-yl)(4-methylphenyl)phenylmethane (β,β'-5e). The title compound was synthesized with the following reagents: 1-benzylpyrrole (314 mg, 2.00 mmol), **6c** (78.5 mg 0.400 mmol), $In(NTf_2)_3$ (76.4 mg, 80.0 μmol) and 1,4-dioxane (0.40 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 10:1) in 70% yield (139 mg) as a white solid; mp 121–122 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.31 (s, 3 H), 4.95 (s, 4 H), 6.02 (dd, *J* = 2.6, 2.0 Hz, 2 H), 6.31 (t, *J* = 2.3 Hz, 2 H), 6.58 (t, *J* = 2.3 Hz, 2 H), 6.97–7.09 (m, 6 H), 7.11–7.39 (m, 13 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 20.9, 53.2, 53.8, 111.5, 120.4, 121.9, 125.4, 126.6, 127.0, 127.4, 127.8, 128.6, 129.7, 129.9, 132.3, 134.9, 138.7, 146.3, 149.4. HRMS (FD) Calcd for $C_{36}H_{32}N_2$: M, 492.2565. Found: *m*/*z* 492.2590.

9-(1-Methyl-1*H*-pyrrol-2-yl)-9-(1-methyl-1*H*-pyrrol-3-yl)-9*H*-fluorene (α,β'-5f). The title compound was synthesized with the following reagents: **1a** (130 mg, 1.60 mmol), 9-fluorenone (72.1 mg, 0.400 mmol), $In(NTf_2)_3$ (38.2 mg, 40.0 μmol) and 1,4-dioxane (0.40 mL). Column chromatography on silica gel (hexane/$CHCl_3$ = 1:1) of the resulting crude reaction mixture provided a mixture of **α,β'-5f** and **β,β'-5f** (9:91) in 99% yield (129 mg). In the course of the purification, some fractions including pure **α,β'-5f** were collected. Accordingly, **α,β'-5f** as a viscous colorless oil could be characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, and HRMS. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3 H), 3.46 (s, 3 H),

6.02 (dd, *J* = 3.6, 2.8 Hz, 1 H), 6.07 (t, *J* = 2.1 Hz, 1 H), 6.25 (dd, *J* = 3.7, 1.8 Hz, 1 H), 6.37 (dd, *J* = 2.8, 1.8 Hz, 1 H), 6.39 (t, *J* = 2.3 Hz, 1 H), 6.50 (t, *J* = 2.5 Hz, 1 H), 7.24–7.30 (m, 2 H), 7.35 (td, *J* = 7.3, 1.4 Hz, 2 H), 7.44 (dd, *J* = 7.3, 1.4 Hz, 2 H), 7.74 (dd, *J* = 7.3, 1.4 Hz, 2 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 34.0, 36.1, 55.5, 105.4, 109.6, 111.5, 120.1, 120.2, 121.6, 123.6, 125.4, 126.4, 127.3, 127.5, 134.8, 139.6, 150.9. HRMS (FD) Calcd for $C_{23}H_{20}N_2$: M, 324.1626. Found: *m*/*z* 324.1645.

9,9-Bis(1-methyl-1*H*-pyrrol-3-yl)-9*H*-fluorene (β,β'-5f). The title compound was synthesized and purified in the same way as the above, and was obtained as a white solid; mp 220–221 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (s, 6 H), 6.04 (dd, *J* = 2.7, 1.8 Hz, 2 H), 6.26 (t, *J* = 2.1 Hz, 2 H), 6.46 (t, *J* = 2.5 Hz, 2 H), 7.22–7.27 (m, 2 H), 7.30 (dt, *J* = 7.3, 1.4 Hz, 2 H), 7.52 (dd, *J* = 6.6, 1.1 Hz, 2 H), 7.71 (dd, *J* = 6.9, 1.4 Hz, 2 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 36.1, 54.7, 108.5, 119.7, 119.9, 121.5, 125.4, 126.7, 127.2, 128.8, 139.3, 153.5. HRMS (FD) Calcd for $C_{23}H_{20}N_2$: M, 324.1626. Found: *m*/*z* 324.1653.

2-Bromo-9-(1-methyl-1*H*-pyrrol-2-yl)-9-(1-methyl-1*H*-pyrrol-3-yl)-9*H*-fluorene (α,β'-5g). The title compound was synthesized with the following reagents: **1a** (130 mg, 1.60 mmol), 2-bromo-9-fluorenone (104 mg, 0.400 mmol), $In(NTf_2)_3$ (38.2 mg, 40.0 μmol) and 1,4-dioxane (0.40 mL). Column chromatography on silica gel (hexane/$CHCl_3$ = 1:1) of the resulting crude reaction mixture provided a mixture of **α,β'-5g** and **β,β'-5g** (3:97) in 82% yield (134 mg). In the course of the purification, some fractions including pure **α,β'-5g** were collected. Accordingly, **α,β'-5g** as a viscous colorless oil could be characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, and HRMS. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (s, 3 H), 3.48 (s, 3 H), 6.02 (dd, *J* = 3.7, 2.8 Hz, 1 H), 6.06 (t, *J* = 2.1 Hz, 1 H), 6.23 (dd, *J* = 3.6, 1.8 Hz, 1 H), 6.33 (dd, *J* = 2.7, 1.8 Hz, 1 H), 6.42 (t, *J* = 2.5 Hz, 1 H), 6.51 (t, *J* = 2.5 Hz, 1 H), 7.30 (td, *J* = 7.3, 1.4 Hz, 1 H), 7.35 (td, *J* = 7.3, 1.4 Hz, 1 H), 7.41 (dd, *J* = 7.1, 1.1 Hz, 1 H), 7.47 (dd, *J* = 8.0, 2.1 Hz, 1 H), 7.57 (d, *J* = 1.8 Hz, 1 H), 7.59 (d, *J* = 8.2 Hz, 1 H), 7.71 (dd, *J* = 7.8, 0.9 Hz, 1 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 34.1, 36.1, 55.5, 105.5, 109.5, 111.8, 120.1, 120.3, 121.3, 121.6, 121.9, 124.0,

125.4, 125.8, 127.5, 127.9, 128.5, 130.5, 133.8, 138.5, 138.6, 150.7, 153.0. HRMS (FD) Calcd for $C_{23}H_{19}BrN_2$: M, 402.0732. Found: *m*/*z* 402.0752.

2-Bromo-9,9-bis(1-methyl-1*H*-pyrrol-3-yl)-9*H*-fluorene (β,β'-5g). The title compound was synthesized and purified in the same way as the above, and was obtained as a yellow solid; mp 174–175 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.51 (s, 6 H), 6.00 (t, *J* = 2.0 Hz, 2 H), 6.25 (t, *J* = 2.0 Hz, 2 H), 6.47 (t, *J* = 2.6 Hz, 2 H), 7.25–7.33 (m, 2 H), 7.41 (dd, *J* = 8.0, 1.7 Hz, 1 H), 7.49 (dd, *J* = 6.6, 1.4 Hz, 1 H), 7.56 (d, *J* = 8.1 Hz, 1 H), 7.63 (d, *J* = 1.7 Hz, 1 H), 7.67 (d, *J* = 6.9 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 36.1, 54.8, 108.4, 119.8, 119.9, 120.9, 121.1, 121.7, 125.5, 126.9, 127.7, 128.0, 128.7, 129.9, 138.2, 138.3, 153.3, 155.6. HRMS (FD) Calcd for $C_{23}H_{19}BrN_2$: M, 402.0732. Found: *m*/*z* 402.0749.

2-Hydroxy-9-(1-methyl-1*H*-pyrrol-2-yl)-9-(1-methyl-1*H*-pyrrol-3-yl)-9*H*-fluorene (α,β'-5h). The title compound was synthesized with the following reagents (0.25-mmol scale reaction): **1a** (81.1 mg, 1.00 mmol), 2-hydroxy-9-fluorenone (49.1 mg, 0.250 mmol), $In(NTf_2)_3$ (23.9 mg, 25.0 μmol) and 1,4-dioxane (0.25 mL). Column chromatography on silica gel (hexane/EtOAc = 2:1) of the resulting crude reaction mixture provided a mixture of **α,β'-5h** and **β,β'-5h** (14:86) in 84% yield (72.1 mg). In the course of the purification, some fractions including pure **α,β'-5h** were collected. Accordingly, **α,β'-5h** as a viscous colorless oil could be characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, and HRMS. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (s, 3 H), 3.47 (s, 3 H), 4.77 (bs, 1 H), 6.02 (t, *J* = 3.2 Hz, 1 H), 6.09 (t, *J* = 1.9 Hz, 1 H), 6.24 (dd, *J* = 3.6, 1.8 Hz, 1 H), 6.35 (t, *J* = 2.1 Hz, 1 H), 6.40 (t, *J* = 2.3 Hz, 1 H), 6.50 (t, *J* = 2.5 Hz, 1 H), 6.83 (dd, *J* = 8.1, 2.2 Hz, 1 H), 6.88 (d, *J* = 2.3 Hz, 1 H), 7.20 (t, *J* = 7.3 Hz, 1 H), 7.31 (t, *J* = 7.3 Hz, 1 H), 7.39 (d, *J* = 7.6 Hz, 1 H), 7.60 (d, *J* = 8.2 Hz, 1 H), 7.63 (d, *J* = 7.6 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 34.0, 36.1, 55.3, 105.4, 109.5, 111.5, 112.5, 114.6, 119.4, 120.1, 121.3, 121.7, 123.7, 125.2, 126.35, 126.40, 127.3, 132.7, 134.7, 139.4, 150.4, 153.0, 155.5. HRMS (FD) Calcd for $C_{23}H_{20}N_2O$: M, 340.1576. Found: *m*/*z* 340.1558.

2-Hydroxy-9,9-bis(1-methyl-1*H*-pyrrol-3-yl)-9*H*-fluorene (β,β'-5h). The title compound was synthesized and purified in the same way as the above, and was obtained as a yellow solid; mp 230–231 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.50 (s, 6 H), 4.67 (bs, 1 H), 6.03 (dd, *J* = 2.5, 1.8 Hz, 2 H), 6.27 (t, *J* = 1.9 Hz, 2 H), 6.47 (t, *J* = 2.4 Hz, 2 H), 6.77 (dd, *J* = 8.1, 2.4 Hz, 1 H), 6.96 (d, *J* = 2.5 Hz, 1 H), 7.18 (td, *J* = 7.3, 1.1 Hz, 1 H), 7.26 (td, *J* = 7.4, 1.1 Hz, 1 H), 7.47 (d, *J* = 7.6 Hz, 1 H), 7.56 (d, *J* = 8.0 Hz, 1 H), 7.60 (d, *J* = 7.6 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 36.1, 54.6, 108.4, 112.6, 114.1, 118.9, 120.0, 120.7, 121.5, 125.3, 126.2, 126.7, 128.7, 132.4, 139.1, 153.1, 155.1, 155.6. HRMS (FD) Calcd for $C_{23}H_{20}N_2O$: M, 340.1576. Found: *m*/*z* 340.1601.

Indium-Catalyzed Synthesis of Tetraarylmethanes; A General Procedure for Table 5. $In(OTf)_3$ [(11.2 mg, 20.0 μmol) or (22.5 mg, 40.0 μmol)] or $In(NTf_2)_3$ (38.2 mg, 40.0 μmol) was placed in a 20 mL Schlenk tube, which was heated at 150 ºC in vacuo for 2 h. The tube was cooled down to room temperature and filled with argon. 1,4-Dioxane (1.00 mL) was added to the tube, and the mixture was then stirred at room temperature for 10 min. To this were added diaryldipyrrolylmethane **5** (0.200 mmol), 2-methylfuran (**3c**) [(41.1 mg, 0.500 mmol) or (65.7 mg, 0.800 mmol)] or 2-methoxythiophene (**3h**) (91.3 mg, 0.800 mmol), and the resulting mixture was stirred at *T* °C. After stirring for *t* h, a saturated $NaHCO_3$ aqueous solution (0.3 mL) was added, and the aqueous phase was extracted with EtOAc (5 mL x 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by purification gave the corresponding product (**β-9**). Unless otherwise noted, products **β-9** synthesized here were fully characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, and HRMS.

(5-Methylfuran-2-yl)(4-methylphenyl)(1-methyl-1*H*-pyrrol-3-yl)phenylmethane (β-9a). The title compound was synthesized with the following reagents: a 13:87 mixture of **α,β'-5a** and **β,β'-5a** (68.1 mg, 0.200 mmol), 2-methylfuran (**3c**) (41.1 mg, 0.500 mmol), $In(OTf)_3$ (22.5 mg, 40.0 μmol) and 1,4-

dioxane (1.00 mL), and was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 2:1) in 69% yield (47.2 mg) as a white solid; mp 148–149 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (d, *J* = 0.4 Hz, 3 H), 2.33 (s, 3 H), 3.56 (s, 3 H), 5.80 (d, *J* = 3.2 Hz, 1 H), 5.84–5.88 (m, 1 H), 6.01 (dd, *J* = 2.8, 1.8 Hz, 1 H), 6.17 (t, *J* = 2.1 Hz, 1 H), 6.55 (t, *J* = 2.5 Hz, 1 H), 7.00 (dt, *J* = 8.2, 2.1 Hz, 2 H), 7.05 (d, *J* = 8.2 Hz, 2 H), 7.13 (dt, *J* = 6.4, 1.8 Hz, 2 H), 7.18–7.25 (m, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 13.9, 21.0, 36.2, 55.1, 105.5, 110.4, 110.8, 121.0, 122.2, 126.1, 127.3, 128.1, 129.1, 129.5, 129.6, 135.6, 143.8, 146.9, 151.3, 158.3. HRMS (FD) Calcd for $C_{24}H_{23}NO$: M, 341.1780. Found: *m*/*z* 341.1770.

(5-Methylfuran-2-yl)(3-methylphenyl)(4-methylphenyl)(1-methyl-1*H*-pyrrol-3-yl)methane (β-9b). The title compound was synthesized with the following reagents: a 15:85 mixture of **α,β'-5b** and **β,β'-5b** (70.9 mg, 0.200 mmol), **3c** (41.1 mg, 0.500 mmol), $In(OTf)_3$ (22.5 mg, 40.0 μmol) and 1,4-dioxane (1.00 mL), and was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 2:1) in 67% yield (47.9 mg) as a white solid; mp 133–134 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.27 (s, 3 H), 2.28 (s, 3 H), 2.33 (s, 3 H), 3.56 (s, 3 H), 5.80 (d, *J* = 3.5 Hz, 1 H), 5.84–5.87 (m, 1 H), 6.01 (dd, *J* = 2.9, 1.7 Hz, 1 H), 6.16 (t, *J* = 2.0 Hz, 1 H), 6.55 (t, *J* = 2.6 Hz, 1 H), 6.90 (d, *J* = 8.0 Hz, 1 H), 6.96 (dd, *J* = 2.3, 1.7 Hz, 1 H), 6.98–7.07 (m, 5 H), 7.13 (t, *J* = 7.7 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 13.9, 21.0, 21.7, 36.2, 55.1, 105.5, 110.4, 110.8, 121.0, 122.2, 126.8, 126.9, 127.1, 128.0, 129.2, 129.5, 130.2, 135.6, 136.7, 143.9, 146.7, 151.2, 158.4. HRMS (FD) Calcd for $C_{25}H_{25}NO$: M, 355.1936. Found: *m*/*z* 355.1959.

(5-Methylfuran-2-yl)(1-methyl-1*H*-pyrrol-3-yl)(2-naphthyl)phenylmethane (β-9c). The title compound was synthesized with the following reagents: a 8:92 mixture of **α,β'-5c** and **β,β'-5c** (75.3 mg, 0.200 mmol), **3c** (41.1 mg, 0.500 mmol), $In(OTf)_3$ (22.5 mg, 40.0 μmol) and 1,4-dioxane (1.00 mL), and was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 2:1) in 72% yield (54.9 mg) as a white solid, mp 120–121 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (d, *J* = 0.9 Hz, 3 H), 3.57 (s, 3 H), 5.85

(d, *J* = 3.2 Hz, 1 H), 5.87–5.90 (m, 1 H), 6.04 (dd, *J* = 2.8, 1.8 Hz, 1 H), 6.20 (t, *J* = 1.8 Hz, 1 H), 6.58 (t, *J* = 2.5 Hz, 1 H), 7.15–7.20 (m, 2 H), 7.21–7.30 (m, 3 H), 7.36–7.48 (m, 4 H), 7.65–7.73 (m, 2 H), 7.80 (dd, *J* = 7.3, 1.4 Hz, 1 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 13.9, 36.2, 55.6, 105.6, 110.6, 110.9, 121.2, 122.3, 125.5, 125.6, 126.3, 126.5, 127.3, 127.4, 127.7, 128.4, 128.8, 128.9, 129.7, 132.1, 132.9, 144.3, 146.5, 151.4, 158.0. HRMS (FD) Calcd for $C_{27}H_{23}NO$: M, 377.1780. Found: *m*/*z* 377.1802.

(5-Methylfuran-2-yl)(1-methyl-1*H*-pyrrol-3-yl)phenyl(thien-3-yl)methane (β-9d). The title compound was synthesized with the following reagents: a 14:86 mixture of **α,β'-5d** and **β,β'-5d** (66.5 mg, 0.200 mmol), **3c** (41.1 mg, 0.500 mmol), $In(OTf)_3$ (22.5 mg, 40.0 μmol) and 1,4-dioxane (1.00 mL), and was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 3:1) in 71% yield (47.5 mg) as a white solid; mp 139–140 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (d, *J* = 0.9 Hz, 3 H), 3.56 (s, 3 H), 5.83 (d, *J* = 3.2 Hz, 1 H), 5.85–5.89 (m, 1 H), 6.02 (dd, *J* = 2.8, 1.8 Hz, 1 H), 6.11 (t, *J* = 2.1 Hz, 1 H), 6.55 (t, *J* = 2.3 Hz, 1 H), 6.81 (dd, *J* = 3.2, 1.4 Hz, 1 H), 7.04 (dd, *J* = 5.0, 0.9 Hz, 1 H), 7.07 (dt, *J* = 6.4, 1.8 Hz, 2 H), 7.18–7.28 (m, 4 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 13.9, 36.2, 52.5, 105.5, 109.8, 110.2, 121.2, 121.7, 123.3, 123.9, 126.3, 127.5, 128.8, 128.9, 130.0, 146.8, 147.7, 151.3, 157.7. HRMS (FD) Calcd for $C_{21}H_{19}NOS$: M, 333.1187. Found: *m*/*z* 333.1212.

(1-Benzyl-1*H*-pyrrol-3-yl)(5-methylfuran-2-yl)(4-methylphenyl)phenylmethane (β-9e). The title compound was synthesized with the following reagents: **β,β'-5e** (98.5 mg, 0.200 mmol), **3c** (41.1 mg, 0.500 mmol), $In(OTf)_3$ (22.5 mg, 40.0 μmol) and 1,4-dioxane (1.00 mL), and was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 3:1) in 72% yield (60.6 mg) as a white solid; mp 136–137 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.27 (d, *J* = 0.6 Hz, 3 H), 2.32 (s, 3 H), 4.98 (s, 2 H), 5.80 (d, *J* = 2.9 Hz, 1 H), 5.85–5.88 (m, 1 H), 6.08 (dd, *J* = 2.9, 1.7 Hz, 1 H), 6.31 (t, *J* = 2.0 Hz, 1 H), 6.60 (t, *J* = 2.6 Hz, 1 H), 7.01 (dt, *J* = 8.6, 2.1 Hz, 2 H), 7.03–7.09 (m, 4 H), 7.13 (dt, *J* = 6.9, 1.7 Hz, 2 H), 7.18–7.28 (m, 4 H), 7.29–7.33 (m, 2 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 13.9, 21.0, 53.2, 55.2, 105.5,

110.4, 111.3, 120.5, 122.0, 126.1, 126.7, 127.3, 127.4, 128.1, 128.6, 129.2, 129.4, 129.6, 135.7, 138.4, 143.7, 146.7, 151.3, 158.3. HRMS (FD) Calcd for $C_{30}H_{27}NO$: M, 417.2093. Found: *m*/*z* 417.2117.

9-(5-Methylfuran-2-yl)-9-(1-methyl-1*H*-pyrrol-3-yl)-9*H*-fluorene (β-9f). The title compound was synthesized with the following reagents: a 9:91 mixture of **α,β'-5f** and **β,β'-5f** (64.8 mg, 0.200 mmol), **3c** (41.1 mg, 0.500 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol) and 1,4-dioxane (1.00 mL), and was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 2:1) in 55% yield (36.0 mg) as a white solid; mp 118–119 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.24 (s, 3 H), 3.50 (s, 3 H), 5.75–5.79 (m, 1 H), 5.83 (d, *J* = 3.5 Hz, 1 H), 6.01 (dd, *J* = 2.6, 2.0 Hz, 1 H), 6.23 (t, *J* = 2.0 Hz, 1 H), 6.47 (t, *J* = 2.3 Hz, 1 H), 7.29 (td, *J* = 7.5, 1.2 Hz, 2 H), 7.35 (td, *J* = 7.5, 1.2 Hz, 2 H), 7.66 (d, *J* = 7.5 Hz, 2 H), 7.73 (d, *J* = 7.5 Hz, 2 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 13.9, 36.1, 55.4, 105.5, 106.9, 107.9, 119.6, 119.9, 121.7, 125.8, 126.3, 127.3, 127.4, 139.6, 149.8, 151.8, 155.1. HRMS (FD) Calcd for $C_{23}H_{19}NO$: M, 325.1467. Found: *m*/*z* 325.1473.

2-Bromo-9-(5-methylfuran-2-yl)-9-(1-methyl-1*H*-pyrrol-3-yl)-9*H*-fluorene (β-9g). The title compound was synthesized with the following reagents: a 3:97 mixture of **α,β'-5g** and **β,β'-5g** (80.7 mg, 0.200 mmol), **3c** (65.7 mg, 0.800 mmol), $In(OTf)_3$ (22.5 mg, 40.0 μmol) and 1,4-dioxane (1.00 mL), and was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 2:1) in 53% yield (43.1 mg) as a yellow solid; mp 124–125 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25 (d, *J* = 0.6 Hz, 3 H), 3.52 (s, 3 H), 5.77–5.80 (m, 1 H), 5.85 (d, *J* = 3.4 Hz, 1 H), 5.97 (t, *J* = 2.0 Hz, 1 H), 6.23 (t, *J* = 2.0 Hz, 1 H), 6.48 (t, *J* = 2.6 Hz, 1 H), 7.32 (td, *J* = 7.3, 1.3 Hz, 1 H), 7.36 (td, *J* = 7.5, 1.2 Hz, 1 H), 7.46 (dd, *J* = 8.0, 1.7 Hz, 1 H), 7.58 (d, *J* = 8.6 Hz, 1 H), 7.62 (dd, *J* = 6.9, 1.2 Hz, 1 H), 7.69 (dd, *J* = 6.9, 1.1 Hz, 1 H), 7.77 (d, *J* = 1.7 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 13.9, 36.2, 55.5, 105.6, 107.3, 107.9, 119.6, 120.0, 121.0, 121.3, 121.9, 125.5, 125.9, 127.6, 127.7, 129.0, 130.6, 138.6, 149.5, 151.8, 152.1, 154.3.

(One carbon signal is missing due to overlapping). HRMS (FD) Calcd for $C_{23}H_{18}BrNO$: M, 403.0572. Found: *m*/*z* 403.0586.

2-Hydroxy-9-(5-methylfuran-2-yl)-9-(1-methyl-1*H*-pyrrol-3-yl)-9*H*-fluorene (β-9h). The title compound was synthesized with the following reagents: a 14:86 mixture of **α,β'-5h** and **β,β'-5h** (68.1 mg, 0.200 mmol), **3c** (41.1 mg, 0.500 mmol), $In(OTf)_3$ (22.5 mg, 40.0 μmol) and 1,4-dioxane (1.00 mL), and was isolated by column chromatography on silica gel (hexane/EtOAc = 3:1) in 55% yield (37.7 mg) as a yellow solid; mp 148–149 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25 (d, *J* = 0.6 Hz, 3 H), 3.51 (s, 3 H), 4.72 (bs, 1 H), 5.76–5.79 (m, 1 H), 5.85 (d, *J* = 3.4 Hz, 1 H), 6.00 (dd, *J* = 2.9, 1.8 Hz, 1 H), 6.24 (t, *J* = 2.0 Hz, 1 H), 6.48 (t, *J* = 2.6 Hz, 1 H), 6.83 (dd, *J* = 8.0, 2.3 Hz, 1 H), 7.12 (d, *J* = 2.3 Hz, 1 H), 7.23 (td, *J* = 7.5, 1.2 Hz, 1 H), 7.32 (td, *J* = 7.4, 1.1 Hz, 1 H), 7.57–7.61 (m, 2 H), 7.63 (d, *J* = 7.5 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 13.9, 36.1, 55.4, 105.6, 107.1, 108.0, 113.1, 114.8, 119.1, 119.6, 120.9, 121.8, 125.7, 126.3, 126.4, 127.4, 132.7, 139.5, 149.4, 151.89, 151.92, 155.0, 155.2. HRMS (FD) Calcd for $C_{23}H_{19}NO_2$: M, 341.1416. Found: *m*/*z* 341.1423.

(5-Methoxythien-2-yl)(4-methylphenyl)(1-methyl-1*H*-pyrrol-3-yl)phenylmethane (β-9i). The title compound was synthesized with the following reagents: a 13:87 mixture of **α,β'-5a** and **β,β'-5a** (68.1 mg, 0.200 mmol), 2-methoxythiophene (**3h**) (91.3 mg, 0.800 mmol), $In(NTf_2)_3$ (38.2 mg, 40.0 μmol) and 1,4-dioxane (1.00 mL), and was isolated by recycling HPLC (hexane/EtOAc = 10:1) after column chromatography on silica gel (hexane/toluene = 1:1) in 47% yield (35.2 mg) as a viscous colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3 H), 3.56 (s, 3 H), 3.82 (s, 3 H), 5.99 (d, *J* = 3.7 Hz, 1 H), 6.02 (dd, *J* = 2.8, 1.8 Hz, 1 H), 6.16 (t, *J* = 2.3 Hz, 1 H), 6.33 (d, *J* = 4.1 Hz, 1 H), 6.57 (t, *J* = 2.5 Hz, 1 H), 7.05 (dt, *J* = 8.2, 2.3 Hz, 2 H), 7.11 (dt, *J* = 8.3, 1.9 Hz, 2 H), 7.18–7.25 (m, 5 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 21.0, 36.2, 56.5, 60.0, 102.3, 111.2, 121.3, 122.6, 124.9, 126.2, 127.2, 128.0, 129.7,

129.8, 130.8, 135.7, 139.7, 144.9, 148.0, 165.3. HRMS (FD) Calcd for $C_{24}H_{23}NOS$: M, 373.1500. Found: *m*/*z* 373.1502.

(5-Methoxythien-2-yl)(1-methyl-1*H*-pyrrol-3-yl)(2-naphthyl)phenylmethane (β-9j). The title compound was synthesized with the following reagents: a 8:92 mixture of **α,β'-5c** and **β,β'-5c** (75.3 mg, 0.200 mmol), **3h** (91.3 mg, 0.800 mmol), $In(NTf_2)_3$ (38.2 mg, 40.0 μmol) and 1,4-dioxane (1.00 mL), and was isolated by column chromatography on silica gel (hexane/benzene = 1:1) in 44% yield (36.5 mg) as a white solid; mp 155–156 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (s, 3 H), 3.82 (s, 3 H), 6.01 (d, *J* = 3.6 Hz, 1 H), 6.06 (dd, *J* = 2.5, 2.1 Hz, 1 H), 6.20 (t, *J* = 2.1 Hz, 1 H), 6.37 (d, *J* = 4.1 Hz, 1 H), 6.59 (t, *J* = 2.5 Hz, 1 H), 7.20–7.32 (m, 5 H), 7.38–7.47 (m, 3 H), 7.62 (d, *J* = 1.4 Hz, 1 H), 7.71 (dd, *J* = 7.8, 2.8 Hz, 2 H), 7.80 (dd, *J* = 7.1, 2.1 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 36.2, 56.9, 60.0, 102.3, 111.2, 121.4, 122.6, 125.2, 125.6, 125.7, 126.29, 126.31, 127.26, 127.34, 127.6, 128.5, 129.3, 129.9, 130.6, 132.1, 132.9, 139.2, 145.5, 147.6, 165.5. HRMS (FD) Calcd for $C_{27}H_{23}NOS$: M, 409.1500. Found: *m*/*z* 409.1524.

2-Bromo-9-(5-methoxythien-2-yl)-9-(1-methyl-1*H*-pyrrol-3-yl)-9*H*-fluorene (β-9k). The title compound was synthesized with the following reagents: a 3:97 mixture of **α,β'-5g** and **β,β'-5g** (80.7 mg, 0.200 mmol), **3h** (91.3 mg, 0.800 mmol), $In(NTf_2)_3$ (38.2 mg, 40.0 μmol) and 1,4-dioxane (1.00 mL), and was isolated by column chromatography on silica gel (hexane/benzene = 1:1) in 52% yield (46.0 mg) as a white solid; mp 132–133 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.52 (s, 3 H), 3.78 (s, 3 H), 5.91 (d, *J* = 4.1 Hz, 1 H), 6.13 (dd, *J* = 2.8, 1.8 Hz, 1 H), 6.26 (dd, *J* = 2.3, 1.8 Hz, 1 H), 6.36 (d, *J* = 4.1 Hz, 1 H), 6.51 (t, *J* = 2.5 Hz, 1 H), 7.27–7.37 (m, 2 H), 7.46 (dd, *J* = 8.2, 1.8 Hz, 1 H), 7.54 (dt, *J* = 7.8, 1.2 Hz, 1 H), 7.57 (d, *J* = 7.8 Hz, 1 H), 7.66–7.70 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 36.2, 57.1, 60.0, 102.6, 108.7, 120.0, 120.3, 121.1, 121.4, 122.1, 122.5, 125.6, 126.4, 127.6, 127.8, 128.9,

130.6, 135.5, 138.1, 138.3, 151.6, 153.8, 165.1. HRMS (FD) Calcd for $C_{23}H_{18}BrNOS$: M, 435.0292. Found: *m*/*z* 435.0288.

N-Deprotection of β-9e; A Procedure for eq. 6.[14,15,24] Under an argon atmosphere, a mixture of $TiCl_3$ (92.5 mg, 0.600 mmol) and Li (27.1 mg, 3.90 mmol) in THF (6.0 mL) was placed in a 20 mL Schlenk tube, which was stirred at 65 ºC for 3 h. Iodine (76.1 mg, 0.300 mmol) was then added in one portion at room temperature and the mixture was stirred for 5 min. To this was added a THF (0.30 mL) solution of **β-9e** (125 mg, 0.300 mmol), and the mixture was stirred at room temperature for 16 h. The resulting mixture was diluted with hexane (10 mL) and filtered through a pad of Celite, which was then rinsed out with a mixture of hexane–EtOAc (4:1, 20 mL). The filtrate was washed with brine (2 mL) and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 5:1) gave (5-methylfuran-2-yl)(4-methylphenyl)phenyl(1*H*-pyrrol-3-yl)methane (**β-7c**) in 63% yield (62.2 mg) as a viscous colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.27 (d, *J* = 0.6 Hz, 3 H), 2.32 (s, 3 H), 5.81 (d, *J* = 2.9 Hz, 1 H), 5.84–5.88 (m, 1 H), 6.15 (td, *J* = 2.7, 1.4 Hz, 1 H), 6.36 (td, *J* = 2.3, 1.7 Hz, 1 H), 6.76 (td, *J* = 2.3, 1.7 Hz, 1 H), 7.00 (dt, *J* = 8.6, 2.0 Hz, 2 H), 7.05 (d, *J* = 8.6 Hz, 2 H), 7.13 (dt, *J* = 6.9, 1.7 Hz, 2 H), 7.18–7.25 (m, 3 H), 8.01 (bs, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 13.9, 21.0, 55.1, 105.5, 110.5, 111.0, 117.2, 118.3, 126.2, 127.3, 128.1, 129.2, 129.5, 129.6, 135.7, 143.7, 146.8, 151.3, 158.2. HRMS (FD) Calcd for $C_{23}H_{21}NO$: M, 327.1623. Found: *m*/*z* 327.1643.

Indium-Catalyzed Synthesis of Dipyrrolyldecanes 5i; A Procedure for Scheme 5, (i). $In(NTf_2)_3$ (287 mg, 0.300 mmol) was placed in a 200 mL Schlenk tube, which was heated at 150 °C in vacuo for 2 h. The tube was cooled down to room temperature and filled with argon. 1,4-Dioxane (5.0 mL) was added to the tube, and the mixture was then stirred at room temperature for 10 min. To this were added 2-decanone (**6a**) (469 mg, 3.00 mmol) and 1-methylpyrrole (**1a**) (973 mg, 12.0 mmol), and the resulting

mixture was stirred at 85 °C for 1 h. A saturated $NaHCO_3$ aqueous solution (3 mL) was added, and the aqueous phase was extracted with EtOAc (50 mL x 3). The combined organic phase was washed with brine (10 mL) and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 30:1) gave dipyrrolyldecanes **5i** (833 mg, 92% yield) as a mixture of three isomers that are **α,α'-5i**, **α,β'-5i** and **β,β'-5i**. The ratio of **α,α'-5i**:**α,β'-5i**:**β,β'-5i** was determined to be 1:12:87 by GC analysis. The three isomers, **α,α'-5i**, **α,β'-5i** and **β,β'-5i** have already appeared in references 14 and 36, and their spectral and analytical data are in good agreement with those reported in the literatures. The reaction of (ii) in Scheme 5 was performed in a similar way, but without catalyst $In(NTf_2)_3$.

Indium-Catalyzed Synthesis of 3-(Decan-2-yl)-1-methyl-1*H*-pyrrole (β-4a) from Dipyrrolyldecanes 5i; A Procedure for Scheme 5, (iii). $In(NTf_2)_3$ (28.7 mg, 30.0 μmol) was placed in a 20 mL Schlenk tube, which was heated at 150 °C in vacuo for 2 h. The tube was cooled down to room temperature and filled with argon. 1,4-Dioxane (0.50 mL) was added to the tube, and the mixture was then stirred at room temperature for 10 min. To this were added a 1:12:87 mixture of dipyrrolyldecanes **5i** (90.1 mg, 0.300 mmol), Et_3SiH (**3a**) (52.3 mg, 0.450 mmol) and H_2O (5.40 mg, 0.300 mmol), and the resulting mixture was stirred at 85 °C for 1 h. A saturated $NaHCO_3$ aqueous solution (0.3 mL) was added and the aqueous phase was extracted with EtOAc (5 mL x 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 60:1) gave **β-4a** in 94% yield (62.9 mg). The full data on ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and HRMS analysis of **β-4a** have been already collected in our preceding communication.[15] The reaction of (iv) in Scheme 5 was performed in a similar way, but without catalyst $In(NTf_2)_3$. The reaction of (v) in Scheme 5 was also carried out in a similar way, but with **α,β'-5i** instead of the isomeric mixture of **5i**.

Indium-Catalyzed Reductive β-Alkylation of 1-Methylpyrrole with 2-Decanone and Et_3SiD; A Procedure for Scheme 5, (vi). $In(NTf_2)_3$ (14.3 mg, 15.0 μmol) was placed in a 20 mL Schlenk tube, which was heated at 150 ºC in vacuo for 2 h. The tube was cooled down to room temperature and filled with argon. 1,4-Dioxane (0.25 mL) was added to the tube, and the mixture was then stirred at room temperature for 10 min. To this were added 2-decanone (**6a**) (23.4 mg, 0.150 mmol), 1-methylpyrrole (**1a**) (36.5 mg, 0.450 mmol) and Et_3SiD (**3a**-*d*) (26.4 mg, 0.225 mmol), and the resulting mixture was stirred at 85 ºC for 3 h. A saturated $NaHCO_3$ aqueous solution (0.3 mL) was added, and the aqueous phase was extracted with EtOAc (5 mL x 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 60:1) gave 3-(decan-2-yl-*2*-*d*)-1-methyl-1*H*-pyrrole (**β-4a**-*d*) in 92% yield (30.7 mg) with a deuterium content of >99% determined by ^{1}H NMR, as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.9 Hz, 3 H), 1.16 (s, 3 H), 1.20–1.34 (m, 12 H), 1.38–1.46 (m, 1 H), 1.47–1.58 (m, 1 H), 3.60 (s, 3 H), 5.98 (dd, *J* = 2.4, 1.9 Hz, 1 H), 6.37 (t, *J* = 2.0 Hz, 1 H), 6.50 (t, *J* = 2.5 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 14.1, 22.1, 22.7, 27.6, 29.4, 29.7, 29.9, 31.4 (t, *J* = 19.1 Hz), 31.9, 36.0, 38.7, 106.7, 118.0, 121.2, 131.0; ^{2}H NMR (61 MHz, $CHCl_3$) δ 2.61 (bs). HRMS (FI) Calcd for $C_{15}H_{26}DN$: M, 222.2206. Found: *m*/*z* 222.2209.

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Notes

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DEDICATION

Dedicated to Professor Tamejiro Hiyama on the occasion of his 70th birthday.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Table S1 and Table S2 for the effect of indium catalysts to synthesize **5a** and **β-9a**, respectively, and ^{1}H, ^{2}H and ^{13}C NMR spectra (PDF)

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