(CDCl$_3$) δ 3.9 (t), 7.6 (q), 14.0 (q), 22.7 (t), 27.8 (t), 28.6 (t), 31.6 (t), 34.0 (t), 130.1 (d), 163.7 (s); IR (neat) 2960, 1535, 1465, 1345, 1240, 1020, 860, 730 cm^{-1}. Anal. Calcd for $C_{14}H_{29}NO_2Si$: C, 61.94; H, 10.77; N, 5.16. Found: C, 61.77; 11.04; N, 5.09.

2e: ^1H NMR (CDCl$_3$) δ 0.57–1.46 (m, 30 H, aliphatic H), 2.62 (t, J = 7.2 Hz, 2 H), 5.86 (s, 1 H, olefinic H); ^{13}C NMR (CDCl$_3$) δ 3.9 (t), 7.6 (q), 14.1 (q), 22.8 (t), 27.8 (t), 28.9 (t), 29.3 (t), 29.3 (t), 31.9 (t), 34.0 (t), 130.0 (d), 163.7 (s); IR (neat) 2950, 1530, 1465, 1340, 1235, 1025, 860, 730 cm^{-1}. Anal. Calcd for $C_{16}H_{33}NO_2Si$: C, 64.16; H, 11.10; N, 4.68. Found: C, 64.41; H, 11.13; N, 4.67.

Diels–Alder Reaction of 2a. The reactions were performed under the conditions indicated in Table II by using an excess of diene without solvent except for the case of cyclopentadiene. Spectral and analytical data of the adducts are described below.

4:[5] ^1H NMR (CDCl$_3$) δ 0.07 (s, 9 H, SiMe), 1.12–1.86 (m, 3 H, H-5 and 7), 2.84 (br m, 1 H, H-4), 3.52 (br m, 1H, H-1), 4.83 (dd, J = 3.9, 5.0 Hz, 1 H, H-6), 5.78 (dd, J = 3.0, 5.6 Hz, H-3 or 2), 6.48 (dd, J = 3.0, 5.6 Hz, H-2 or 3); ^{13}C NMR (CDCl$_3$) δ −2.2 (q), 32.0 (d), 44.3 (d), 47.3 (t), 48.8 (d), 87.8 (d), 129.5 (d), 142.2 (d); IR (neat) 3080, 2960, 1640, 1545, 1370, 1250, 875, 833, 715 cm^{-1}. Anal. Calcd for $C_{10}H_{17}NO_2Si$: C, 56.83; H, 8.11; N, 6.63. Found: C, 56.92; H, 8.13; N, 6.51.

5:[5] ^1H NMR (CDCl$_3$) δ 0.07 (s, 9 H, SiMe), 1.11–1.69 (m, 5 H, H-5, 7, and 8), 2.67 (br m, 1 H, H-4), 3.28 (br m, 1 H, H-1), 4.47 (dd, J = 2.8, 5.6 Hz, 1 H, H-6), 5.93 (t, J = 7.6 Hz, 1 H, H-3 or 2), 6.52 (t, J = 7.6 Hz, 1 H, H-2); ^{13}C NMR (CDCl$_3$) δ −2.0 (q), 21.9 (t), 22.8 (t), 30.5 (d), 30.9 (d), 36.1 (d), 87.6 (d), 127.4 (d), 139.2 (d); IR (neat) 3050, 2950, 1610, 1545, 1365, 1250, 855, 835, 750, 685 cm^{-1}. Anal. Calcd for $C_{11}H_{19}NO_2Si$: C, 58.63; H, 8.50; N, 6.22. Found: C, 58.34; H, 8.33; N, 6.48.

6a and **6b**: ^1H NMR (CDCl$_3$) δ 0.03 (s, 9 H, SiMe), 1.67 (br s, 3 H, Me), 1.74–2.94 (m, 5 H, allylic H and CHSi–), 4.42–4.74 (m, 1 H, CHNO$_2$), 5.19–5.49 (m, 1H, olefinic H); ^{13}C NMR (CDCl$_3$) δ −3.1 (q, SiMe), 23.0 (q, Me), 23.1 (q, Me), 24.1 (d), 25.1 (d), 25.6 (d), 28.8 (t), 29.7 (t), 33.8 (t), 84.0 (d), 84.6 (d), 116.8 (d, C-2, major), 120.7 (d, C-2, minor), 129.8 (s, C-1, minor), 133.9 (s, C-1, major); IR (neat) 2960, 1630, 1545, 1370, 1250, 840 cm^{-1}. Anal. Calcd for $C_{10}H_{19}NO_2Si$: C, 56.30; H, 8.98; N, 6.57. Found: C, 56.50; H, 8.69; N, 6.72.

7: ^1H NMR (CDCl$_3$) δ 0.02 (s, 9 H, SiMe), 1.61 (s, 6 H, Me), 1.70–2.86 (m, 5 H, allylic H and CHSi), 4.57 (m, 1 H, CHNO$_2$), ^{13}C NMR (CDCl$_3$) δ −3.1 (q, SiMe), 18.5 (q, 2 × Me), 26.1 (d, C-4), 30.5 (t, C-3), 35.5 (t, C-6), 84.9 (d, C-5), 121.7 (s, C-2), 125.6 (s, C-1); IR (neat) 2960, 1630, 1545, 1370, 1255, 840, 695 cm^{-1}. Anal. Calcd for $C_{11}H_{21}NO_2Si$: C, 58.11; H, 9.31; N, 6.16. Found: C, 57.87; H, 9.52; N, 6.28.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research No. 443007 from the Ministry of Education, Science and Culture.

Registry No. **1a**, 754-05-2; **1b**, 42067-72-1; **1c**, 57365-47-6; **1d**, 31930-43-5; **1e**, 90584-19-3; **2a**, 91201-28-4; **2b**, 91190-96-4; **2c**, 91190-97-5; **2d**, 91190-98-6; **2e**, 91190-99-7; **3a**, 91191-00-3; **3b**, 91191-01-4; **3c**, 91191-02-5; **3d**, 91191-03-6; **3e**, 91191-04-7; 4, 91237-30-8; **5**, 91237-31-9; **6a**, 91190-93-1; **6b**, 91190-94-2; 7, 91190-95-3; cyclopentadiene, 542-92-7; cyclohexadiene, 29797-09-9; isoprene, 78-79-5; 2,3–dimethyl-1,3-butadiene, 513-81-5.

Reactions of Phenylytterbium Iodide with Organic Halides in the Presence of Transition-Metal Catalysts

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Although numerous compounds with lanthanoid metals (Ln) have been prepared and characterized,[1] their applications to organic synthesis are still rare. Luche et al. reported that trichlorolanthanoid catalyzed selective 1,2-reduction of α,β-unsaturated ketones with sodium borohydride and alcohols.[2] Kagan et al. described unique SmI$_2$-mediated reactions such as reduction, alkylation, and coupling,[3] and Imamoto et al. utilized cerium compounds to organic synthesis.[4]

Table I. Copper-Catalyzed Coupling of PhYbI with *n*-BuI[a]

	product and yield, %	
catalyst (mol %)	*n*-BuPh[b]	PhPh[c]
none	trace	3
CuI (0.05)	21 (190)	13
CuBr (0.05)	38 (380)	6[d]
CuCl (0.06)	31 (240)	3
CuCl$_2$ (0.04)	8 (100)	1
Cu(OAc)$_2$ (0.05)	11 (120)	4

[a] PhYbI was prepared from Yb (0.5 mmol) and PhI (0.75 mmol) in THF (3 mL) at −30 °C, and the coupling reactions were carried out at room temperature with stirring overnight by using *n*-BuI (0.75 mmol) and copper catalysts. [b] GC yields based on Yb and numbers in parentheses are yields based on the copper catalyst. [c] GC yields based on PhI. [d] A 0.7% yield (based on Yb) of *n*-octane was also formed.

The first divalent organolanthanoid σ complexes of type RLnI were prepared from lanthanoid metals and organic iodides (RI) in tetrahydrofuran (THF) by Evans et al.[5] We reported some reactions of organolanthanoids, RLnI, with ketones, aldehyde, esters, nitriles, and acid chlorides[6] and showed that the reaction with esters gives ketones as main products rather than tertiary alcohols[6a] and that the addition reaction to α,β-unsaturated carbonyl compounds proceeds regioselectively at the 1,2-positions.[6c] It has also been found that the type of the reaction caused by RLnI differs depending upon Ln: addition reaction being caused by Eu and Yb, Tishchenko condensation by Pr, Nd, and Dy, and coupling by Sm.[7] As part of our interest in utilizing organolanthanoid complexes for organic synthesis, we have investigated the reactions of PhYbI with organic halides (RX). We describe the coupling reactions of PhYbI with RX in the presence of transition-metal catalysts.

Results and Discussion

Coupling Reactions of PhYbI with Butyl Halides. PhYbI, prepared in situ from Yb metal and iodobenzene (PhI) in THF at −30 °C, was allowed to react with *n*-butyl iodide (*n*-BuI) in the presence of cuprous bromide (CuBr) to give the cross-coupled product *n*-butylbenzene (*n*-BuPh)

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(2) (a) Luche, J. L.; Gemal, A. L. *J. Am. Chem. Soc.* **1979**, *101*, 5848; (b) **1981**, *103*, 5454.

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0022-3263/84/1949-3237$01.50/0

Table II. Coupling of PhYbI with Allyl Halides by CuBr Catalyst[a]

	product and yield, %	
allyl halide	allylbenzene[b]	PhPh[c]
allyl iodide	30	trace
allyl iodide[d]	32	2
allyl bromide	33	trace
allyl bromide[d]	29	2
allyl chloride	15	trace

[a] Reactions were conducted by using CuBr (10 mol%), allyl halide (1.0 mmol), and PhYbI prepared in situ from Yb (0.5 mmol) and PhI (0.6 mmol) in THF (3 mL), at room temperature with stirring overnight. [b] GC yields based on Yb. [c] GC yields based on PhI. [d] No catalyst used.

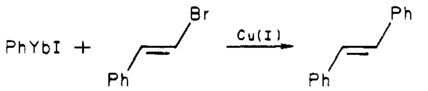
in 38% yield based on Yb together with biphenyl (PhPh) and a trace amount of n-octane (eq 1). Absence of the

$$\text{PhI} + \text{Yb} \xrightarrow{\text{THF}} \text{PhYbI} \xrightarrow[\text{CuBr}]{n\text{-BuI}} n\text{-BuPh} + \text{PhPh} \quad (1)$$

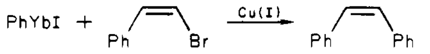
catalyst resulted in almost no formation of n-BuPh. Table I summarizes results of coupling reaction by copper catalysts. From Table I, it can be seen that CuBr is the most effective for cross-coupling (380% yield based on CuBr). Then we carried out the reactions of PhYbI with n-BuBr, n-BuCl, *sec*-BuI, *t*-BuI, and *t*-BuCl in the presence of CuBr. The reactions with n-BuBr and n-BuCl gave n-BuPh in 21% and 3% yields, respectively, together with biphenyl in 3% yield. However, the reactions with *sec*-BuI, *t*-BuI, and *t*-BuCl gave the corresponding BuPh in only trace amounts.

Judging from the yield, the qualitative trends in the reactivities of butyl halides follows the order: I > Br > Cl, and primary > secondary ≥ tertiary, which are essentially the same as that obtained in the copper-catalyzed cross-coupling reaction of the Grignard reagents with alkyl halides.[8]

Reactions with *cis*- and *trans*-Styryl Bromides. Stereochemistry of the Coupling Reaction. In order to test the stereochemistry of this reaction, the cross-coupling reactions of *cis*- and *trans*-styryl bromides were performed by using CuBr as a catalyst. From reaction of PhYbI with *cis*-styryl bromide, *cis*- and *trans*-stilbenes were obtained in 22% and 1% yields, respectively with the unreacted starting bromide (eq 2 and 3). Similarly, from reaction with *trans*-styryl bromide, *trans*- and *cis*-stilbenes were obtained in 15% and 7% yields, respectively with the starting bromide.[9] These results seem to indicate that cross-coupling proceeds with predominant retention of configuration at a vinylic center.

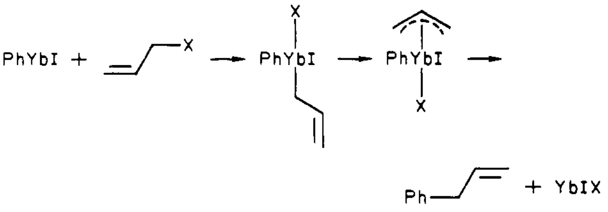


(2)



(3)

Reactions with Allyl Halides. Similarly, the reactions of PhYbI with allyl halides afforded allylbenzene, the cross-coupling product. Table II lists the results. As can be seen from Table II, the cross-coupling also occurs even in the absence of the copper catalyst which is in marked contrast with the Grignard reagent. This is partly due to the higher reactivity of allyl halides than usual organic halides such as butyl. One possibility is that since the ionic radius of a Yb^{2+} ion is large enough to coordinate larger number of ligands compared to a Mg^{2+} ion,[10,11] allyl halides might undergo oxidative addition to Yb(II) to give a four-coordinate π-allyl intermediate which would give allylbenzene by reductive elimination (eq 4). The other is that Yb^{2+} abstracts the halide anion X^- from allyl halides to form an allyl cation followed by nucleophilic attack of Ph^- of PhYbI. We favor the latter because a Yb(IV) species in eq 4 is very unstable.



(4)

Table III. Coupling of PhYbI with *n*-BuLi by Transition-Metal Catalysts[a]

	product and yield, %		
catalyst	n-BuPh^B	n-octane[c]	PhPh[d]
$FeCl_3$	13	1	14
$CoCl_2$	10		15
$PdCl_2$			14
$Pd(PPh_3)_4$	trace		48
$NiCl_2$	4	trace	25
AgI[e]	2	25	2

[a] Reactions were performed by adding metal catalysts (10 mol % to Yb) to a mixture of n-BuI (0.75 mmol) and PhYbI, prepared from Yb (0.5 mmol) and PhI (0.75 mmol) in THF (3 mL), at room temperature with stirring overnight. [b] GC yields based on Yb. [c] GC yields based on n-BuI. [d] GC yields based on PhI. [e] PhYbI was added to AgI and then n-BuI was added.

Reactions with Benzyl Bromide. The reaction of PhYbI with benzyl bromide afforded bibenzyl and biphenyl, the homo-coupled products in 53% and 10% yields, respectively (eq 5), and no cross-coupled product was formed.

$$\text{PhYbI} + \text{PhCH}_2\text{Br} \xrightarrow{\text{CuBr}} \text{PhCH}_2\text{CH}_2\text{Ph} + \text{PhPh} \quad (5)$$

Reactions with Other Transition-Metal Catalysts. Similar coupling reactions of PhYbI with n-BuI were performed by using transition-metal catalysts such as Fe, Co, Pd, Ag, and Ni salts. The results are shown in Table III.

An interesting point is that $FeCl_3$, $CoCl_2$, $NiCl_2$, and Pd salts give inferior yields of cross-coupled products than the copper catalysts and that, instead, the homo-coupled product becomes a main product.

Conclusions. We have attempted to show that PhYbI reacts with organic halides to give cross-coupled products. Since PhYbI can be prepared at far lower temperature (even at −30 °C) than PhMgX, the former may provide a convenient synthetic tool.

Experimental Section

General Methods. Gas chromatographic analyses were performed on a Shimadzu Model GC-3BF instrument using an OV-17 column (1.5 m). Ytterbium was ca. 40-mesh powder from Research Chemicals. *cis*-Styryl bromide was prepared from cinnamic acid by bromination followed by debromocarboxylation.[12] The starting *trans*-styryl bromide was purchased and contained 10% of cis isomer. Other materials were commercial grade. THF was freshly

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[8] Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.

[9] The starting *trans*-styryl bromide contained 10% of its cis isomer which would give *cis*-stilbene.

[10] The ionic radii of Yb^{2+} and Mg^{2+} are 0.93 and 0.65 Å, respectively.[11]

[11] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, 1962.

[12] Grovenstein, E., Jr.; Lee, D. E. *J. Am. Chem. Soc.* **1953**, *53*, 2639.

distilled under nitrogen from benzophenone ketyl before use.

General Procedure for Coupling of PhYbI with Organic Halides. In a 50-mL centrifuge tube, Yb powder and a magnetic stirring bar were placed under air, and the tube was sealed with a serum cap. After the tube was dried by heating under nitrogen, THF was added by a syringe. Then iodobenzene was added slowly to the tube at −30 °C during 5–10 min. After a short induction period (ca. 10 min), ytterbium started to react with the iodide, and the mixture was further stirred for ca. 2 h at −30 °C. To the resulting red brown THF solution of PhYbI was added the organic halide by syringe at −30 °C. Then the serum cap was removed and the catalysts (10 mol % to Yb) was added all at once to the tube. After the tube was sealed again with a serum cap, the mixture was allowed to warm to room temperature slowly with stirring overnight. The resulting mixture was quenched with 2 N HCl and the products were extracted with ether (5 times). The ethereal layer was treated with saturated NaCl aqueous solution and dried over anhydrous sodium sulfate. After evaporation of the solvent, the products were analyzed by GLC. Considerable amounts of the starting halides were also detected. Identities with the products were performed by NMR and retention time comparison with authentic samples. The results are summarized in Tables I–III.

Coupling Reactions of PhYbI with *cis*- and *trans*-Styryl Bromides. To the THF solution of PhYbI, prepared from Yb (0.5 mmol), PhI (0.75 mmol), and THF (30 mL) as described above, cis-styryl bromide (0.75 mmol) was added by a syringe and then CuBr (0.05 mmol) was added to the mixture at −30 °C. The mixture was allowed to warm slowly to room temperature and stirred overnight. Treatment of the resulting mixture as above gave cis- and trans-stilbenes in 22 and 1% yields, respectively with recovery of the starting cis bromide. Similarly, the reaction with trans-styryl bromide was also carried out to give trans- and cis-stilbenes in 15 and 7% yields, respectively with the unreacted starting bromide.

Acknowledgment. This work was supported by a Grant-in-Aid (No. 58550547) for Scientific Research from the Ministry of Education of Japan for which we are grateful.

Registry No. PhYbI, 26138-28-3; CuI, 7681-65-4; CuBr, 7787-70-4; CuCl, 7758-89-6; $CuCl_2$, 7447-39-4; $Cu(OAc)_2$, 142-71-2; $FeCl_3$, 7705-08-0; $CoCl_2$, 7646-79-9; $PdCl_2$, 7647-10-1; $Pd(PPh_3)_4$, 14221-01-3; $NiCl_2$, 7718-54-9; AgI, 7783-96-2; *n*-BuPh, 104-51-8; PhPh, 92-52-4; *n*-BuI, 542-69-8; PhI, 591-50-4; *n*-BuBr, 109-65-9; $PhCH_2Br$, 28807-97-8; $PhCH_2CH_2Ph$, 103-29-7; *n*-BuCl, 109-69-3; Yb, 7440-64-4; allyl iodide, 556-56-9; allyl bromide, 106-95-6; allyl chloride, 107-05-1; allylbenzene, 300-57-2; *cis*-styryl bromide, 588-73-8; *cis*-stilbene, 645-49-8; *trans*-styryl bromide, 588-72-7; *trans*-stilbene, 103-30-0; *n*-octane, 111-65-9.

A Synthesis of 3-Substituted Pyrroles through the Halogen–Metal Exchange Reaction of 3-Bromo-1-(triisopropylsilyl)pyrrole

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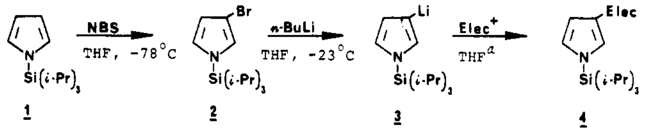
In our efforts to develop new, practical entries to several unique classes of indole-containing natural products, we needed to develop a method for achieving selective functionalization of the *β*-position of pyrrole. While interaction of pyrrole with an electrophilic agent generally leads to introduction of a new group into its *α*-position,[1] it has been demonstrated recently that protection of the pyrrole ring nitrogen with a phenylsulfonyl group[2] or the bulky triisopropylsilyl group[3] can lead to substitution at the *β*-position. Thus, while NBS reacts with the *N*-*tert*-butyldiphenylsilyl derivative of pyrrole to give a mixture of bromopyrroles,[4] the *N*-triisopropylsilyl derivative **1** gives predominantly the corresponding 3-bromo derivative **2**.[3]



We have now shown that 3-bromo-1-(triisopropylsilyl)pyrrole will undergo rapid halogen–metal[5] exchange with *n*-butyllithium in THF to generate the corresponding 3-lithiopyrrole **3**.[6] This anion can be trapped in turn by various electrophiles to provide the corresponding 3-substituted pyrroles **4**. The yields obtained were high in the majority of cases studied (Table I). We believe that the present methodology should find considerable use in the synthesis of compounds of pharmaceutical interest.[7]

Experimental Section

Low-resolution mass spectra were determined on an LKB-9000 instrument. High-resolution mass spectra were determined on a Varian MAT CH-5DF instrument by peak matching. ^1H NMR spectra were recorded at 60 MHz (Varian EM-360) or at 300 MHz (Brüker WH-300). Chemical shifts (δ) are reported downfield from internal Me_4Si. Infrared spectra were obtained on a Perkin-Elmer 247 or 137 spectrophotometer.

3-Bromo-1-(triisopropylsilyl)pyrrole (2). To a solution of **1** (963 mg, 4.32 mmol) in 40 mL of dry THF cooled to −78 °C was added dropwise a solution of *N*-bromosuccinimide (771 mg, 4.33 mmol) in 20 mL of THF. After addition was completed the cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. The reaction mixture was concentrated under reduced pressure, carbon tetrachloride was added to precipitate the succinimide, and this mixture was filtered. The filter cake was washed with additional carbon tetrachloride, the filtrates were concentrated, and the resulting oil was chromatographed on silica gel to furnish 1.18 g (90%) of **2** as a colorless oil: IR (neat) 2900, 2800, 1470, 1200, 1190, 1075, 910, 880, 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.73 (dd, 1 H, J = 2.3, 1.4 Hz), 6.67 (dd, 1 H, J = 2.8, 2.4 Hz), 6.29 (dd, 1 H, J = 2.8, 1.4 Hz), 1.43 (heptet, 3 H, J = 7.4 Hz), 1.09 (d, 18 H, J = 7.4 Hz); exact mass calcd for $C_{13}H_{24}{}^{79}BrNSi$ 301.0861, found 301.0862.

3-Allyl-1-(triisopropylsilyl)pyrrole. To a solution of **2** (247 mg, 0.82 mmol) in 10 mL of dry THF cooled to −23 °C (dry ice/CCl_4 bath) was added dropwise 1.1 mL of 1.5 M *n*-butyllithium in hexanes. The reaction mixture was kept at −23 °C for 2 h, and then a solution of allyl bromide (3–4 equiv) in 10 mL of THF was

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[2] Kakushima, M.; Hamel, P.; Frenette, R.; Rokach, J. *J. Org. Chem.* **1983**, *48*, 3214. Rokach, J.; Hamel, P.; Kakushima, M.; Smith, G. M. *Tetrahedron Lett.* **1981**, *22*, 4901. Xu, R. X.; Anderson, H. J.; Gogan, N. J.; Loader, C. E.; McDonald, R. *Ibid.* **1981**, *22*, 4899.

[3] Muchowski, J. M.; Solas, D. R. *Tetrahedron Lett.* **1983**, *24*, 3455.

[4] A mixture results if the bromination reaction is performed at −78 °C. Bromination at −90 °C, on the other hand, does appear to afford primarily the 3-substituted product, but this bromide rapidly darkens and decomposes upon silica gel chromatography.

[5] Parham, W. E.; Bradsher, C. K. *Acc. Chem. Res.* **1982**, *15*, 300.

[6] Interestingly, an attempted halogen–metal exchange reaction on *N*-benzyl-3-bromopyrrole failed using *n*-butyllithium. The reaction was, however, successful with lithium metal, and the resulting *β*-lithiopyrrole was trapped with carbon dioxide: Anderson, H. J.; Griffiths, S. J. *Can. J. Chem.* **1967**, *45*, 2227. The treatment of *N*-(trimethylsilyl)pyrrole with *tert*-butyllithium followed by carbon dioxide, HCl, and diazomethane affords the 3-carbomethoxy derivative as the major product along with the 1- and 2-mono esters and the 2,5-diester: Chadwick, D. J.; Hodgson, S. T. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1833.

[7] An oxazoline group located at the 2-position of *N*-methylpyrrole has been shown to direct metalation predominantly to the 3-position: Chadwick, D. J.; McKnight, M. V.; Ngochindo, R. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1343.

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