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Halodesilylation Route to 2,5-Difunctionalized 3,4-Dialkylsiloles and Their Derivatization to 2,2′-Bisilole

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A new synthetic route to 2,5-difunctionalized 3,4-dialkylsiloles has been developed based on the selective halodesilylation of 2,5-disilyl-1,1,3,4-tetraalkylsiloles. A series of 2,5-dihalosiloles having various alkyl groups on silicon and at the 3,4-positions were prepared. Some 2,5-dihalosiloles were further derivatized to unsymmetrical 2,5-difunctionalized siloles having boron or tin functionalities. A silole dimer, 2,2′-bisilole, was also prepared by the oxidative coupling using a copper complex starting from the 2,5-diiodosiloles. The crystal structure and UV−vis absorption spectral data of the 2,2′-bisilole have been compared to the 3,4-diphenyl analogue which we previously reported.

Introduction

Silole (silacyclopentadiene)[1]-based π-conjugated polymers and related compounds are receiving much attention because of their unique photophysical properties and their possible application to organic electroluminescent devices.[2−7] For the synthesis of these compounds, siloles having functionalities, such as $-$Br, $-$I, $-SnR_3$, and $-B(OH)_2$, at the 2,5-positions are crucial precursors, since the most straightforward route to the silole-based π-conjugated systems may be the transition metal-catalyzed or -mediated coupling reactions of the appropriate 2,5-difunctionalized siloles. However, the synthetic routes to the 2,5-difunctionalized siloles have been rather limited. Only two methodologies have been reported so far.[1] One is the preparation of 2,5-distannyl-3-borylsiloles from bis(stannylethynyl)silanes with trialkylboranes, but the 2,5-functionalities are restricted to only the stannyl groups.[8] The other, reported by us, is the synthesis of 2,5-difunctionalized 3,4-diphenylsiloles based on the intramolecular reductive cyclization of bis(phenylethynyl)silanes.[2b] This methodology allows us to introduce various functional groups at the 2,5-positions, but limits the 3,4-substituents to phenyl groups. Thus, the 2,5-difunctionalized siloles having alkyl groups at the 3,4-positions could not be accessed by the existing methods, despite their great potentials as new precursors. We now report a new synthetic route to the 2,5-difunctionalized 3,4-di*alkyl*siloles and their derivatization to some unsymmetrical 2,5-difunctionalized siloles and silole dimers, 2,2′-bisiloles, whose structures and properties will also be described.

Results and Discussion

Halodesilylation of 2,5-Disilyl-3,4-diphenylsiloles. Our strategy to obtain the 2,5-difunctionalized siloles is based on the halodesilylation[9] of 2,5-disilylsiloles. For this reaction, there are two possible reaction centers, the 2,5-silyl groups and the ring silicon atom. The difficulty in achieving this reaction is the much higher reactivity of the ring silicon toward halodesilylation reagents.[1a] To prevent the reaction on the ring silicon atom, the introduction of bulky groups may be required. We initially examined the effect of the 1,1-substituents on the halodesilylation. A series of 2,5-bis(trimethylsilyl)-3,4-diphenylsiloles **1** having various 1,1-dialkyl groups, readily obtainable by our method mentioned above,[2b] were treated with pyridinium bromide perbromide, PyHBr$_3$, in THF as shown in Scheme 1. Although the reaction of the methyl and ethyl derivatives indeed resulted in the formation of unidentified complex mixtures most probably due to ring-opening reactions, the *i*-Pr group was found to be bulky enough to produce the

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[1] Recent reviews for siloles: (a) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215. (b) Colomer, E.; Corriu, R, J. P.; Lheureux, M. *Chem. Rev.* **1990**, *90*, 265. (c) Dubac, J.; Guerin, C.; Meunier, P. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Ed.; John Wiley & Sons: New York, Vol. 2, in press.

[2] (a) Tamao, K.; Yamaguchi, S.; Shiozaki, M.; Nakagawa, Y.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 5867. (b) Tamao, K.; Yamaguchi, S.; Shiro, M. *J. Am. Chem. Soc.* **1994**, *116*, 11715. (c) Tamao, K.; Yamaguchi, S.; Ito, Y.; Matsuzaki, Y.; Yamabe, T.; Fukushima, M.; Mori, S. *Macromolecules* **1995**, *28*, 8668. (d) Tamao, K.; Ohno, S.; Yamaguchi, S. *Chem. Commun.* **1996**, 1873. (e) Yamaguchi, S.; Tamao, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2327. (f) Tamao, K.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Yamaguchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 11974. (g) Tamao, K.; Yamaguchi, S. *Pure Appl. Chem.* **1996**, *68*, 139. (h) Yamaguchi, S.; Iimura, K.; Tamao, K. *Chem. Lett.* **1998**, 89.

[3] (a) Shinar, J.; Ijadi-Maghsoodi, S.; Ni, Q.-X.; Pang, Y.; Barton, T. J. *Synth. Met.* **1989**, *28*, C593. (b) Barton, T. J.; Ijadi-Maghsoodi, S.; Pang, Y. *Macromolecules* **1991**, *24*, 1257. (c) Chen, W.; Ijadi-Maghsoodi, S.; Barton, T. J. *Polym. Prepr.* **1997**, *38*, 189.

[4] Grigoras, S.; Lie, G. C.; Barton, T. J.; Ijadi-Maghsoodi, S.; Pang, Y.; Shinar, J.; Vardeny, Z. V.; Wong, K. S.; Han, S. G. *Synth. Met.* **1992**, *49−50*, 293.

[5] (a) Frapper, G.; Kertész, M. *Organometallics* **1992**, *11*, 3178. (b) Frapper, G.; Kertész, M. *Synth. Met.* **1993**, *55−57*, 4255. (c) Kürti, J.; Surján, P. R.; Kertész, M.; Frapper, G. *Synth. Met.* **1993**, *55−57*, 4338.

[6] (a) Yamaguchi, Y.; Shioya, J. *Mol. Eng.* **1993**, *2*, 339. (b) Yamaguchi, Y. *Mol. Eng.* **1994**, *3*, 311. (c) Yamaguchi, Y.; Yamabe, T. *Int. J. Quantum Chem.* **1996**, *57*, 73.

[7] (a) Hong, S. Y.; Marynick, D. S. *Macromolecules* **1995**, *28*, 4991. (b) Hong, S. Y.; Kwon, S. J.; Kim, S. C. *J. Chem. Phys.* **1995**, *103*, 1871. (c) Hong, S. Y. *Bull. Korean Chem. Soc.* **1995**, *16*, 845. (d) Hong, S. Y.; Kwon, S. J.; Kim, S. C.; Marynick, D. S. *Synth. Met.* **1995**, *69*, 701. (e) Hong, S. Y.; Kwon, S. J.; Kim, S. C. *J. Chem. Phys.* **1996**, *104*, 1140.

[8] (a) Wrackmeyer, B. *J. Chem. Soc., Chem. Commun.* **1986**, 397. (b) Wrackmeyer, B. *J. Organomet. Chem.* **1986**, *310*, 151. (c) Köster, R.; Seidel, G.; Suβ, J.; Wrackmeyer, B. *Chem. Ber.* **1993**, *126*, 1107. (d) Wrackmeyer, B.; Kehr, G.; Suβ, J. *Chem. Ber.* **1993**, *126*, 2221.

[9] Colvin, E. W. *Silicon in Organic Synthesis*; Robert E. Krieger Publishing Co.: Malabar, FL, 1981; Chapter 7.

10.1021/om980619y CCC: $15.00

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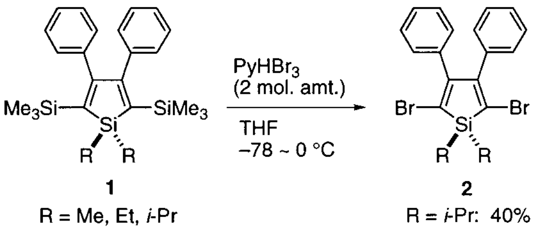
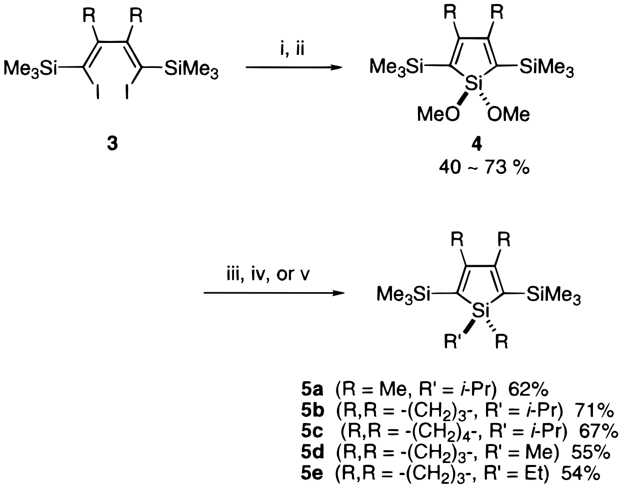
Scheme 1



Scheme 2

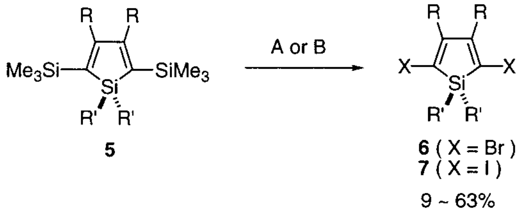


Reagents and conditions: i, *n*-BuLi (2 mol. amount), Et_2O, −78 °C, 1 h; ii, $Si(OMe)_4$ (1 mol. amount), Et_2O, −78 °C ~ 0 °C; iii, *i*-PrMgBr (4 mol. amount), CuCN (0.2 mol. amount), THF, reflux, 12 h; iv, EtMgBr (4 mol. amount), CuCN (1 mol. amount), THF, reflux, 10 h; v, MeLi (2.5 mol. amount), THF, −78 °C ~ 0 °C, 30 min.

desired product, 2,5-dibromosilole **2**, in 40% yield. On the basis of these results, we next examined the synthesis of the 2,5-dihalo-3,4-dialkylsiloles.

Synthesis of 2,5-Disilyl-3,4-dialkylsiloles. As starting materials, a series of 1,1-dialkyl-2,5-bis(trimethylsilyl)-3,4-dialkylsiloles **5** were prepared in two steps from the corresponding 1,4-diiodobutadienes according to our new procedures,[10] as shown in Scheme 2.[11] Thus, 1,4-diiodobutadiene **3** was lithiated with *n*-BuLi followed by the treatment with $Si(OMe)_4$ to give 1,1-dimethoxysiloles **4**, which were further treated with ethyl or isopropyl Grignard reagents in the presence of CuCN[12] to afford the disilylsiloles **5**, except for **5d**, which was prepared by the reaction of the dimethoxysilole with MeLi without the CuCN catalyst. While the facile isomerization of 3,4-dimethyl-2,5-dihydrosiloles to the corresponding transoid isomers (i.e., 3-methyl-4-methylene-2-silolenes) under basic conditions has been well-known in the literature,[1a] no such transoid products were obtained in our reactions of 3,4-dialkyl-2,5-disilylsiloles **4** and **5**.

Scheme 3



Reagents and conditions: A, $PyHBr_3$ (2 mol. amount), THF, −78 °C ~ rt., 6h; B, ICl (2 mol. amount), $AgBF_4$ (2 mol. amount), MeOH, 0 °C, or MeOH/THF = 2/1, −78 °C, 30 min.

Halodesilylation of 2,5-Disilyl-3,4-dialkylsiloles. We examined two reaction conditions, i.e., $PyHBr_3$ in THF and $ICl/AgBF_4$ in MeOH for the bromo- and iododesilylations, respectively, as shown in Scheme 3. The conditions for the iododesilylation were originally reported by Jacob et al.[13] These results are summarized in Table 1. The bromodesilylation of 1,1-diisopropyl-3,4-dimethylsilole **5a** gave the desired dibromosilole **6a** in moderate isolated yield (entry 1). However, when the bicyclic substrate **5b** was employed, an unexpected product **6b′** was obtained in 10% yield as well as the dibromosilole **6b** in 9% yield (entry 2). The mechanism of the formation of **6b′** remains open at this stage. In contrast to this, the iododesilylation cleanly proceeded not only in the case of **5a** but also for the bicyclic siloles **5b** and **5c**, and column chromatography purification using pentane as an eluent afforded the 2,5-diiodo-3,4-dialkylsiloles **7a**−**c** in 47−63% isolated yields (entries 3−5). Surprisingly, the present iododesilylation also successfully gave the 1,1-dimethyl- and 1,1-diethyl-2,5-diiodosiloles, **7d** and **7e**, respectively, when the reaction was conducted in a MeOH/THF = 2/1 mixed solvent at low temperature (entries 6 and 7). This is in sharp contrast to the case of the 3,4-di*phenyl* analogues **1** (R = Me or Et), the reaction of which under the same conditions only afforded unidentified complex mixtures, suggesting the significant dependence of the silole reactivity on the 3,4-substituents. The 2,5-dihalosiloles prepared herein are stable enough for handling in air without special care, but must be kept in a freezer. They may decompose within several days at ambient temperature even in a capped flask.

Crystal Structure of 2,5-Diiodosilole 7a. An X-ray crystal structural analysis of 2,5-diiodosilole **7a** was carried out using a single crystal obtained from ethanol. Its ORTEP drawing is shown in Figure 1 together with selected bond lengths and angles. The carbon−iodine bond lengths, I1−C1 and I2−C4, are normal C(sp^2)−iodine bonds. All the bond lengths and angles of the silole ring are also in the normal range except for the angle C1−Si1−C4, which is the smallest among the hitherto reported silole derivative structures. Electronegative groups at the 2,5-positions tend to sharpen the angle.[2h]

Derivatization from 2,5-Diiodo-3,4-dialkylsiloles. The diiodides **7** were further transformed into unsymmetrical 2,5-difunctionalized siloles, as shown in Scheme 4. Thus, selective monolithiation of **7** with a 1 molar

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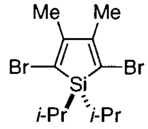
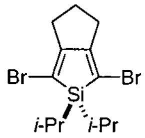
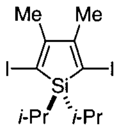
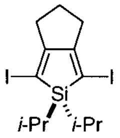
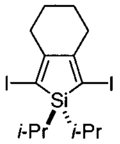
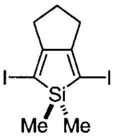
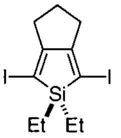
[10] (a) Yamaguchi, S.; Jin, R.-Z.; Tamao, K.; Sato, F. Submitted for publication. (b) Yamaguchi, S.; Jin, R.-Z.; Tamao, K. *J. Organomet. Chem.* **1998**, *559*, 73.

[11] Other metallole synthesis starting from 1,4-dilithiobutadienes: (a) Ashe, A. J., III; Kampf, J. W.; Al-Taweel, S. M. *J. Am. Chem. Soc.* **1992**, *114*, 372. (b) Ashe, A. J., III; Kampf, J. W.; Al-Taweel, S. M. *Organometallics* **1992**, *11*, 1491. (c) Ashe, A. J., III; Kampf, J. W.; Pilotek, S.; Rousseau, R. *Organometallics* **1994**, *13*, 4067. (d) Bankwitz, U.; Sohn, H.; Powell, D. R.; West, R. *J. Organomet. Chem.* **1995**, *499*, C7. (e) Freeman, W. P.; Tilley, T. D.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 10457. (f) Xi, C.; Huo, S.; Afifi, T. H.; Hara, R.; Takahashi, T. *Tetrahedron Lett.* **1997**, *38*, 4099.

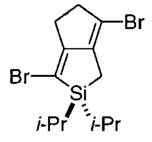
[12] Lennon, P. J.; Mack, D. P.; Thompson, Q. E. *Organometallics* **1989**, *8*, 1121.

[13] (a) Wilson, S. R.; Jacob, L. A. *J. Org. Chem.* **1986**, *51*, 4833. (b) Jacob, L. A.; Chen, B.-L.; Stec, D. *Synthesis* **1993**, 611.

Table 1. Halodesilylation of 2,5-Disilyl-3,4-dialkylsiloles 5

entry	compound	condition[a]	product	yield (%)[b]
1	**5a**	A	 **6a**	26
2	**5b**	A	 **6b**	9[c]
3	**5a**	B	 **7a**	63
4	**5b**	B[d]	 **7b**	47
5	**5c**	B	 **7c**	59
6	**5d**	B[d,e]	 **7d**	30
7	**5e**	B[d,e]	 **7e**	56

[a] A) PyHBr$_3$ (2 mol. amount), THF, −78 °C ~ rt., 6h. B) ICl (2 mol. amount), AgBF$_4$ (2 mol. amount), MeOH, 0 °C, 30 min. [b] Isolated yields. [c] **6b'** was obtained as a by-product. [d] At −78 °C. [e] MeOH/THF = 2/1 mixed solvent was used instead of MeOH only.



6b'

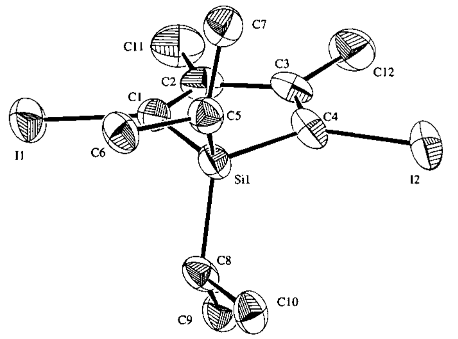
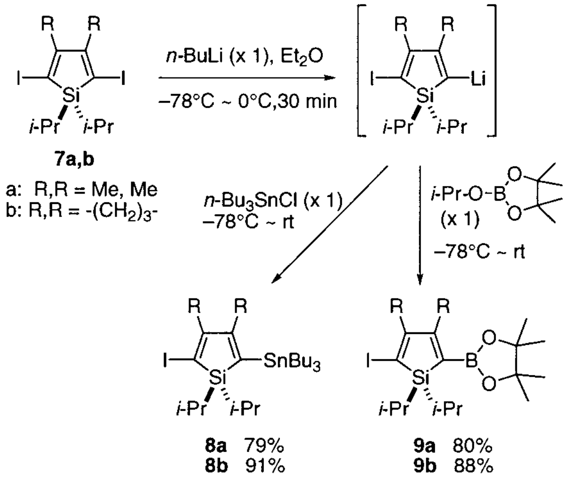
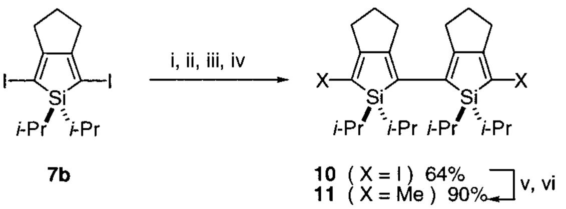


Figure 1. ORTEP drawing of **7a** (50% probability for thermal ellipsoids). Selected bond lengths [Å] and angles [deg]: I1−C1 2.103(7), I2−C2 2.085(8), Si1−C1 1.874(7), Si1−C5 1.874(7), C1−C2 1.32(1), C2−C3 1.52(1), C1−Si1−C4 89.3(4), I1−C1−Si1 123.9(4), Si1−C1−C2 111.0(5), C5−Si1−C8 112.8(3), C1−C2−C3 115.4(6).

Scheme 4



Scheme 5



Reagents and conditions: i, *n*-BuLi (1 mol. amount), Et$_2$O, −78 °C ~ 0 °C; ii, CuCN (0.5 mol. amount), THF; iii, TMEDA (1.5 mol. amount); iv, *p*-dinitrobenzene (5 mol. amount); v, *n*-BuLi (2 mol. amount), Et$_2$O, −78 °C ~ 0 °C; vi, (MeO)$_2$SO$_2$ (2 mol. amount).

amount of *n*-BuLi in ether at 0 °C afforded 2-iodo-5-lithiosilole intermediates, which were trapped with electrophiles, such as *n*-Bu$_3$SnCl or an alkoxyborane, to give 2-iodo-5-stannylsiloles **8** and 2-iodo-5-borylsiloles **9**, respectively. On the other hand, 2,5-dibromosilole **6a** underwent an incomplete halogen−lithium exchange reaction even using a large excess of *n*-BuLi, indicating its lower reactivity than the diiodide. This is also in contrast to the ready monolithiation from 2,5-dibromo-3,4-diphenylsilole **2**,[2b] again suggesting a significant dependence of the silole reactivity on the 3,4-substituents.

Silole Dimer, 2,2′-Bisilole. Diiodide **7b** was also converted into 5,5′-diiodo-2,2′-bisiloles **10** in one pot by the oxidative coupling via the so-called "higher order cyanocuprate",[14] as shown in Scheme 5. Thus, the 2-iodo-5-lithiosilole, prepared from **7b** with *n*-BuLi, was treated with a 0.5 molar amount of CuCN followed by

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[14] Lipshutz, B. H.; Siegmann, K.; Garcia, E.; Kayser, F. *J. Am. Chem. Soc.* **1993**, *115*, 9276.

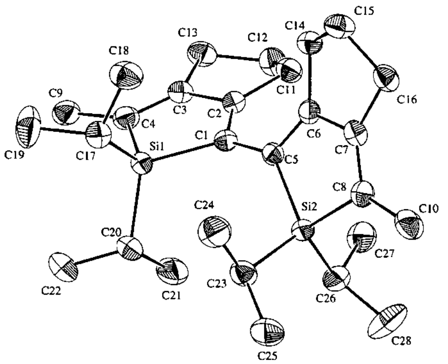


Figure 2. ORTEP drawing of **11** (50% probability for thermal ellipsoids). Selected bond lengths [Å] and angles [deg]: Si1−C1 1.893(3), Si1−C4 1.886(3), Si1−C17 1.904(3), C1−C2 1.375(3), C2−C3 1.478(3), C1−C5 1.462(4), C1−Si1−C4 94.3(1), Si1−C1−C2 104.2(2), C1−C2−C3 117.7(2), C17−Si1−C20 112.2(1), C5−Si2−C8 94.3(1), Si1−C1−C5−Si2 57.1(3).

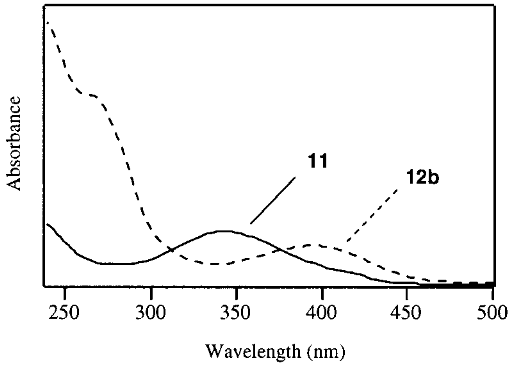
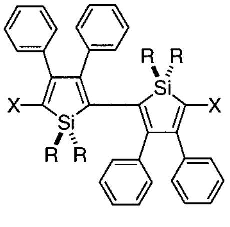


Figure 3. UV−vis absorption spectra of the 2,2′-bisiloles **11** and **12b**.

the oxidation with *p*-dinitrobenzene to produce **10** as yellow crystals in 64% yield. This procedure is essentially the same as that for **12a** from 3,4-diphenyl-2,5-dibromosilole **2**.[2b]



12a (R = Et, X = Br)
12b (R = *i*-Pr, X = H)

The bisilole **10** was further transformed into 5,5′-dimethyl-2,2′-bisilole **11** (Scheme 3). The molecular structure of **11** determined by an X-ray structure analysis is shown in Figure 2. Compound **11** has a highly twisted syn conformation with respect to the two silole rings. The dihedral angle between the two silole mean planes is 52.2°. This is in sharp contrast to the anti conformation with a dihedral angle of 62.3° in the phenyl counterpart **12b**, which we have previously reported.[2b] The bisilole **11** also shows a significantly different UV−vis absorption spectrum from that of **12b**, as shown in Figure 3. The absorption maximum of **11** (λ_{max} 343 nm, log ϵ 3.88) is about 50 nm shorter than that of **12b** (λ_{max} 396 nm, log ϵ 3.75), demonstrating the effect exerted by the 3,4-substituents on the electronic structures.

Conclusion

A new synthetic route to 2,5-dihalo-3,4-dialkylsiloles has been developed based on the halodesilylation of 2,5-disilylsiloles. The derivatization from the dihalosiloles to some difunctionalized siloles has also been described. By using the combination of the present procedure and the former general synthesis of 3,4-diphenylsilole derivatives,[2b] we are now in a position to prepare a variety of 2,5-difunctionalized siloles. In other words, we can now select the substitution modes on the silole rings depending on the application. As exemplified by the synthesis of the bisilole, the 2,5-functionalized 3,4-dialkylsiloles prepared herein would work as key precursors for new silole-containing π-conjugated systems, including poly(2,5-silole)s, which are interesting target molecules but still unknown.[4−7] Further studies along this line are now in progress in our laboratory.

Experimental Section

General Procedures. Melting point (mp) determinations were performed using a Yanaco MP-S3 instrument. ^{1}H and ^{13}C NMR spectra were measured with a JEOL EX-270 (270 MHz for ^{1}H, 67.8 MHz for ^{13}C, and 53.5 MHz for ^{29}Si) spectrometer in C_6D_6 and $CDCl_3$. Chemical shifts are reported in δ ppm with reference relative to the residual protio-solvent (i.e., $CHCl_3$, C_6H_6) peak. UV−visible absorption spectra were measured with a Shimadzu UV-3100PC spectrometer in spectral grade chloroform. Thin-layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using Kieselgel 60 (70−230 mesh; Merck). High-performance liquid chromatography (HPLC) was done using a 20 mm × 250 mm Wakosil 5Sil column (Wako). Recycle preparative gel permeation chromatography (GPC) was performed using polystyrene gel columns (JAIGEL 1H and 2H, Japan Analytical Industry) with 1,2-dichloroethane as an eluent.

Materials. Tetrahydrofuran and diethyl ether were freshly distilled before use from sodium/benzophenone and lithium aluminum hydride, respectively. Copper cyanide, *p*-dinitrobenzene, iodine monochloride, silver tetrafluoroborate, and pyridinium bromide perbromide ($PyHBr_3$) were purchased from commercial sources and used without further purification. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared by the reaction of B(O*i*-Pr)$_3$ with pinacol.[15] All reactions were carried out under nitrogen.

A Series of 1,1-dialkyl-3,4-dialkyl-2,5-bis(trimethylsilyl)siloles 5 were prepared essentially in the same manner for the synthesis of **5a**, which we previously reported,[10b] from the corresponding 1,4-diiodobutadienes **4** via 1,1-dimethoxysiloles **3**. The spectral and analytical data for **5** are as follows.

1,1-Diisopropyl-3,4-trimethylene-2,5-bis(trimethylsilyl)-silole (5b). Colorless solid: mp 30−32 °C. ^{1}H NMR ($CDCl_3$): δ 0.11 (s, 18H), 0.95 (d, $J = 7.3$ Hz, 12H), 1.19 (sep, $J = 7.3$ Hz, 2H), 1.93 (quin, $J = 7.4$ Hz, 2H), 2.43 (t, $J = 7.4$ Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 0.56, 12.22, 18.46, 26.40, 31.29, 129.76, 175.60. ^{29}Si NMR ($CDCl_3$): δ −9.82, 48.24. Anal. Calcd for $C_{19}H_{38}Si_3$: C, 65.06; H, 10.92. Found: C, 64.88; H, 11.11.

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(15) Andersen, M. W.; Hildebrandt, B.; Köster, G.; Hoffmann, R. W. *Chem. Ber.* **1989**, *122*, 1777.

1,1-Diisopropyl-3,4-tetramethylene-2,5-bis(trimethylsilyl)silole (5c). Colorless solid: mp 54−56 °C. ^{1}H NMR ($CDCl_3$): δ 0.13 (s, 18H), 0.94 (d, J = 7.3 Hz, 12H), 1.22 (sep, J = 7.3 Hz, 2H), 1.55−1.69 (m, 4H), 2.51−2.66 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 1.10, 11.74, 18.78, 23.13, 32.56, 134.93, 168.80. ^{29}Si NMR ($CDCl_3$): δ −11.35, 30.71. Anal. Calcd for $C_{20}H_{40}Si_3$: C, 65.85; H, 11.05. Found: C, 65.48; H, 11.16.

1,1-Dimethyl-3,4-trimethylene-2,5-bis(trimethylsilyl)silole (5d). Colorless solid: mp 43−45 °C. ^{1}H NMR ($CDCl_3$): δ 0.09 (s, 18H), 0.20 (s, 6H), 1.95 (quin, J = 7.3 Hz, 2H), 2.42 (t, J = 7.3 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ −2.37, 0.20, 26.13, 30.86, 133.78, 173.06. Anal. Calcd for $C_{15}H_{30}Si_3$: C, 61.14; H, 10.26. Found: C, 60.87; H, 10.16.

1,1-Diethyl-3,4-trimethylene-2,5-bis(trimethylsilyl)silole (5e). Colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.10 (s, 18H), 0.66−0.91 (m, 10H), 1.95 (quin, J = 7.3 Hz, 2H), 2.43 (t, J = 7.3 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 0.04, 5.79, 7.55, 26.31, 31.00, 130.60, 174.91. Anal. Calcd for $C_{17}H_{34}Si_3$: C, 63.27; H, 10.62. Found: C, 63.56; H, 10.87.

A Typical Procedure of the Bromodesilylation of 2,5-Disilylsiloles. 1,1-Diisopropyl-3,4-dimethyl-2,5-dibromosilole (6a). To a THF (30 mL) solution of **5a** (1.69 g, 5.0 mmol) was added a THF (15 mL) solution of $PyHBr_3$ (3.36 g, 10.5 mmol) at −78 °C. The mixture was stirred at the same temperature for 30 min and then allowed to warm to room temperature over 6 h. After addition of water and extraction with ether, the combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was passed through a short silica gel column chromatography using hexane as an eluent. The resulting mixture was recrystallized from pentane at −25 °C to afford **6a** (0.46 g, 1.3 mmol) in 26% yield as pale yellow crystals: mp 46−48 °C. ^{1}H NMR ($CDCl_3$): δ 1.09 (d, J = 7.3 Hz, 12H), 1.31 (sep, J = 7.3 Hz, 2H), 2.02 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 9.62, 17.22, 17.63, 117.72, 153.30. Anal. Calcd for $C_{12}H_{20}Br_2Si$: C, 40.93; H, 5.72. Found: C, 41.05; H, 5.61.

1,1-Diisopropyl-3,4-trimethylene-2,5-dibromosilole (6b). This compound was obtained in essentially the same manner as described for **6a**. Purification using preparative GPC with 1,2-dichloroethane as an eluent gave **6b** in 9% yield and the unexpected product **6b′** in 10% yield. **6b**: ^{1}H NMR ($CDCl_3$): δ 1.11 (d, J = 7.0 Hz, 12H), 1.31 (sep, J = 7.0 Hz, 2H), 1.98 (quin, J = 7.2 Hz, 2H), 2.45 (t, J = 7.2 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 10.26, 17.29, 25.14, 31.04, 109.49, 162.46. Anal. Calcd for $C_{13}H_{20}Br_2Si$: C, 42.87; H, 5.54. Found: C, 42.77; H, 5.56. HRMS (EI) Calcd: 363.9681. Found: 363.9692. **6b′**: ^{1}H NMR ($CDCl_3$): δ 1.02 (d, J = 4.9 Hz, 6H), 1.05 (d, J = 4.9 Hz, 6H), 1.10−1.26 (m, 2H), 1.33 (t, J = 2.6 Hz, 2H), 2.52−2.63 (m, 2H), 2.83−2.94 (m, 2H). ^{13}C NMR (270 MHz, $CDCl_3$): δ 5.07, 11.38, 17.50, 17.75, 27.93, 39.91, 111.88, 123.88, 147.22, 167.56. The structure was also confirmed by NOE measurement of ^{1}H NMR. Thus, the irradiation at the peak of δ 1.33 ($SiCH_2$) induced 1.3% of NOE for two peaks of $SiCH(CH_3)_2$ at δ 1.02 and 1.05. Moreover, the NOE-enhanced coupled ^{13}C NMR (400 MHz, $CDCl_3$) spectrum showed one triplet at δ 5.29 ($^1J_{CH}$ = 122.0 Hz) and two triple-triplets at δ 28.06 ($^1J_{CH}$ = 132.3 Hz and $^2J_{CH}$ = 2.5 Hz) and δ 40.00 ($^1J_{CH}$ = 133.9 Hz and $^2J_{CH}$ = 2.5 Hz), which are consistent with the existence of one isolated methylene and two vicinal methylene groups. HRMS (EI) Calcd for $C_{13}H_{20}Br_2Si$: 363.9681. Found: 363.9667. Satisfactory elemental analysis could not be obtained due to unstability.

A Typical Procedure of the Iododesilylation of 2,5-Disilylsiloles. 1,1-Diisopropyl-3,4-dimethyl-2,5-diiodosilole (7a). To a mixture of **5a** (6.19 g, 18.3 mmol) and $AgBF_4$ (7.82 g, 40.2 mmol) in 40 mL of MeOH was added iodine monochloride (2.05 mL, 40.2 mmol) at 0 °C. The mixture was stirred at the same temperature for 30 min. After filtration through a Celite layer, water was added to the filtrate. The mixture was extracted with ether. The combined extract was washed with a saturated aqueous solution of $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was subjected to silica gel column chromatography using pentane as an eluent (R_f = 0.81) to afford **7a** (5.20 g, 11.7 mmol) in 63% yield as a colorless solid: mp 49−51 °C. ^{1}H NMR ($CDCl_3$): δ 1.09 (d, J = 7.3 Hz, 12H), 1.35 (sep, J = 7.3 Hz, 2H), 2.13 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 9.63, 17.16, 23.15, 92.76, 158.58. ^{29}Si NMR ($CDCl_3$): δ 5.61. Anal. Calcd for $C_{12}H_{20}I_2Si$: C, 32.30; H, 4.52. Found: C, 32.34; H, 4.62.

1,1-Diisopropyl-3,4-trimethylene-2,5-diiodosilole (7b). This compound was obtained in 59% yield as light red oil. ^{1}H NMR ($CDCl_3$): δ 1.10 (d, J = 6.8 Hz, 12H), 1.35 (sep, J = 6.8 Hz, 2H), 2.00 (quin, J = 7.4 Hz, 2H), 2.44 (t, J = 7.4 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 10.28, 17.34, 24.01, 34.90, 81.01, 169.22. ^{29}Si NMR ($CDCl_3$): δ 19.09. Anal. Calcd for $C_{13}H_{20}I_2Si$: C, 34.08; H, 4.40. Found: C, 34.03; H, 4.42.

1,1-Diisopropyl-3,4-tetramethylene-2,5-diiodosilole (7c). This compound was obtained in 47% yield as light red oil. ^{1}H NMR ($CDCl_3$): δ 1.08 (d, J = 7.3 Hz, 12H), 1.35 (sep, J = 7.3 Hz, 2H), 1.52−1.71 (m, 4H), 2.21−2.41 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 9.72, 17.24, 23.92, 34.61, 92.35, 160.20. ^{29}Si NMR ($CDCl_3$): δ 4.43. Anal. Calcd for $C_{14}H_{22}I_2Si$: C, 35.61; H, 4.70. Found: C, 36.00; H, 4.82.

1,1-Dimethyl-3,4-trimethylene-2,5-diiodosilole (7d) was prepared in 30% yield by essentially the same manner as described for **7a** using MeOH/THF = 2/1 mixed solvent as a solvent. Light red oil. ^{1}H NMR ($CDCl_3$): δ 0.20 (s, 6H), 2.01 (quin, J = 7.3 Hz, 2H), 2.42 (t, J = 7.3 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ −6.13, 23.94, 34.58, 85.50, 167.76. Anal. Calcd for $C_9H_{12}I_2Si$: C, 26.88; H, 3.01. Found: C, 26.43; H, 2.87.

1,1-Diethyl-3,4-trimethylene-2,5-diiodosilole (7e) was also prepared in 56% yield by essentially the same manner described for **7a** using MeOH/THF = 2/1 mixed solvent as a solvent. Light red oil. ^{1}H NMR ($CDCl_3$): δ 0.69−1.06 (m, 10H), 2.01 (quin, J = 7.3 Hz, 2H), 2.43 (t, J = 7.3 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 1.93, 6.58, 24.03, 34.70, 82.82, 168.77. Anal. Calcd for $C_{11}H_{16}I_2Si$: C, 30.72; H, 3.75. Found: C, 30.91; H, 3.68.

1,1-Diisopropyl-3,4-dimethyl-2-iodo-5-(tributylstannyl)silole (8a). To a solution of **7a** (223 mg, 0.50 mmol) in 4 mL of ether was added a hexane solution of n-BuLi (0.36 mL, 1.59 M, 0.55 mmol) at −78 °C. The resulting solution was warmed to 0 °C and stirred for 30 min. After the solution was cooled to −78 °C, tributylstannyl chloride (0.15 mL, 0.55 mmol) was added. The mixture was gradually warmed to room temperature over 10 h. The mixture was hydrolyzed with water and extracted with hexane. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and condensed. The residue was subjected to silica gel column chromatography using hexane as an eluent (R_f = 0.82) to afford **8a** (0.24 g, 0.39 mmol) in 79% yield as light yellow oil. ^{1}H NMR ($CDCl_3$): δ 0.74−1.62 (m, 41H), 2.07 (s, 3H), 2.19 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 10.64, 13.64, 17.79, 17.94, 22.37, 25.27, 27.42, 29.27, 97.68, 136.68, 159.19, 165.12. Anal. Calcd for $C_{24}H_{47}ISiSn$: C, 47.31; H, 7.77. Found: C, 47.24; H, 7.89.

1,1-Diisopropyl-3,4-trimethylene-2-iodo-5-tributylstannylsilole (8b). This compound was obtained in 91% yield as light yellow oil. ^{1}H NMR ($CDCl_3$): δ 0.72−1.66 (m, 41H), 1.86−2.05 (m, 2H), 2.32 (t, J = 7.3 Hz, 2H), 2.53 (t, J = 7.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 10.14, 11.12, 13.66, 17.83, 17.97, 25.00, 27.42, 29.27, 33.23, 35.31, 85.70, 128.34, 168.84, 175.16. Anal. Calcd for $C_{25}H_{47}ISiSn$: C, 48.33; H, 7.62. Found: C, 48.39; H, 7.78.

1,1-Diisopropyl-3,4-dimethyl-2-iodo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silole (9a). To a solution of **5a** (223 mg, 0.50 mmol) in 4 mL of ether was added a hexane solution of n-BuLi (0.36 mL, 1.59 M, 0.55 mmol) at −78 °C. The resulting solution was warmed to 0 °C and stirred for 30 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (102 mg, 0.55 mmol) was added to the mixture at −78 °C. The mixture was gradually warmed to room temperature over 10 h. The mixture was hydrolyzed with water and extracted with hexane. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and condensed. The residue was subjected to preparative GPC using 1,2-dichloroethane as an eluent to afford **9a** (180 mg, 0.40 mmol) in 80% yield as a light yellow solid, mp 64−65 °C. ^{1}H NMR ($CDCl_3$): δ 0.92−1.10 (m, 12H), 1.24 (s, 12H), 1.25 (sep, J = 7.6 Hz, 2H), 2.05 (s, 3H), 2.31 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 10.32, 17.76, 21.39, 21.71, 24.85, 82.44, 100.86, 159.77, 169.24. Anal. Calcd for $C_{18}H_{32}BIO_2Si$: C, 48.45; H, 7.23. Found: C, 48.68; H, 7.40.

1,1-Diisopropyl-3,4-trimethylene-2-iodo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silole (9b). This compound was obtained in 88% yield as a light yellow solid, mp 63−65 °C. ^{1}H NMR ($CDCl_3$): δ 0.97−1.11 (m, 12H), 1.22 (s, 12H), 1.27 (sep, J = 7.4 Hz, 2H), 1.95 (quin, J = 7.3 Hz, 2H), 2.28 (t, J = 7.3 Hz, 2H), 2.74 (t, J = 7.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 10.93, 17.92, 24.84, 25.12, 32.92, 33.69, 82.37, 90.06, 169.81, 179.17. ^{29}Si NMR ($CDCl_3$): δ 31.69. Anal. Calcd for $C_{19}H_{32}BIO_2Si$: C, 49.80; H, 7.04. Found: C, 49.65; H, 7.14.

5,5′-Diiodo-1,1,1′,1′-tetraisopropyl-2,2′-bi(3,4-trimethylenesilole) (10). To a solution of **7c** (459 mg, 1 mmol) in ether (6 mL) was added a hexane solution of *n*-BuLi (0.71 mL, 1.55 M, 1.1 mmol) at −78 °C. The resulting mixture was warmed to 0 °C and stirred for 30 min. After removal of the volatiles in vacuo at 0 °C for 1 h, CuCN (45 mg, 0.5 mmol) was added to the mixture as a solid under argon stream. After addition of dry THF (6 mL) at −78 °C, the reaction mixture was stirred for 5 min at the same temperature and then stirred at −40 to −30 °C for 1 h. The resulting orange-yellow solution was cooled again to −78 °C. To the mixture was added TMEDA (0.23 mL, 1.5 mmol), and then the mixture was stirred for 20 min at the same temperature. To the resulting orange solution was added a THF (12 mL) solution of *p*-dinitrobenzene (840 mg, 5 mmol). After stirring at −78 °C for 2 h, a 1/1 mixture (4 mL) of a saturated aqueous solution of $NaHSO_3$ and MeOH was added to the mixture. The bright yellow suspension was warmed to room temperature, diluted with water, and extracted with ether. The combined extract was washed with brine, dried over $MgSO_4$, and concentrated. After addition of hexane, the insoluble materials were filtered out. The filtrate was condensed, and the residue was subjected to silica gel column chromatography (hexane as an eluent, R_f = 0.56) to afford a yellow solid **10** (209 mg, 0.32 mmol) in 64% yield, mp 100 °C (dec). ^{1}H NMR ($CDCl_3$): δ 1.00 (d, J = 6.8 Hz, 12H), 1.15 (d, J = 6.8 Hz, 12H), 1.26 (sep, J = 6.8 Hz, 4H), 1.90 (quin, J = 7.3 Hz, 4H), 2.23−2.40 (m, 8H). ^{13}C NMR (C_6D_6): δ 11.96, 18.05, 18.35, 25.43, 32.17, 34.20, 79.56, 134.16, 156.64, 169.92. ^{29}Si NMR (C_6D_6): δ 22.67. Anal. Calcd for $C_{26}H_{40}I_2Si_2$: C, 47.13; H, 6.08. Found: C, 47.41; H, 6.21.

5,5′-Dimethyl-1,1,1′,1′-tetraisopropyl-2,2′-bi(3,4-trimethylenesilole) (11). To a solution of **10** (200 mg, 0.30 mmol) in 6 mL of ether was added a hexane solution of *n*-BuLi (0.42 mL, 1.59 M, 0.66 mmol) at −78 °C. The resulting solution was warmed to 0 °C and stirred for 30 min. Dimethyl sulfate (63 μL, 0.66 mmol) was added to the mixture at −78 °C. The mixture was gradually warmed to room temperature and stirred for 10 h. The mixture was hydrolyzed with water and extracted with hexane. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and condensed. The residue was recrystallized from pentane to afford **11** (118 mg, 0.27 mmol) in 90% yield as yellow crystals, mp 86−87 °C. ^{1}H NMR (C_6D_6): δ 1.15−1.52 (m, 28H), 1.81 (quin, J = 7.0 Hz, 4H), 1.99 (s, 6H), 2.20−2.40 (m, 8H). ^{13}C NMR (C_6D_6): δ 12.48, 16.74, 18.75, 18.84, 26.87, 27.55, 31.20, 124.19, 130.05, 156.86, 159.27. ^{29}Si NMR (C_6D_6): δ 25.50. Anal. Calcd for $C_{28}H_{46}Si_2$: C, 76.63; H, 10.57. Found: C, 76.83; H, 10.70.

Table 2. Crystal and Intensity Collection Data for 7a and 11

	7a	**11**
formula	$C_{12}H_{20}SiI_2$	$C_{28}H_{46}Si_2$
mol wt	446.18	438.84
cryst dimens, mm	0.30 × 0.10 × 0.10	0.40 × 0.30 × 0.30
cryst syst	triclinic	monoclinic
lattice type	primitive	primitive
cell const		
a, Å	8.278(2)	7.7046(3)
b, Å	13.155(3)	21.0225(4)
c, Å	7.860(1)	16.7455(6)
α, deg	103.86(1)	
β, deg	99.306(9)	90.0894(8)
γ, deg	72.884(9)	
V, Å^3	790.3000	2712.2600
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
Z	2	4
D_{calcd}, g cm^{-3}	1.875	1.075
F_{000}	424.00	968.00
μ(Mo Kα), cm^{-1}	40.31	1.43
radiation	Mo Kα (λ = 0.71070 Å)	
temp, °C	−100	−100
$2\theta_{max}$, deg	55.3	55.2
no. of unique rflns	2420 ($I > 4\sigma(I)$)	4058 ($I > 5\sigma(I)$)
no. of variables	137	272
R^a	0.073	0.068
R$_w$^{b}	0.108	0.111
goodness of fit	1.25	1.22

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

X-ray Crystal Structural Analysis of 7a and 11. Single crystals of **7a** and **11** suitable for X-ray crystal analysis were obtained by recrystallization from ethanol and pentane. Intensity data were collected at −100 °C on a Rigaku RAXIS-IV imaging plate area detector with graphite-monochromated Mo Kα radiation to a maximum 2θ value of 55°. A total of 24 oscillation images (6.0°), each being exposed for 40 min, and a total of 25 oscillation images (5.0°), each being exposed for 30.0 min, were collected for **7a** and **11**, respectively. The data were corrected for Lorentz and polarization effects and secondary extinction. The crystal structure was solved by direct methods in *SIR92*,[16] and a full-matrix least-squares refinement was carried out for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions but not refined. All the calculations were performed using the teXsan crystallographic package from the Molecular Stracture Corp. The crystal data and analytical conditions are listed in Table 2.

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Supporting Information Available: Crystal data and intensity data, atomic coordinates, anisotropic displacement parameters, and bond distances and angles for **7a** and **11** (9 pages). Ordering information is given on any current masthead page.

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(16) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.