ORGANOMETALLICS

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An Expedient Procedure for the Synthesis of Benzo[4,5]silolo[2,3-*b*]thiophenes and Related Systems

Susanne Bähr,[†] Hiroaki Ogasawara,[†,‡] Shigehiro Yamaguchi,*[,‡,§] and Martin Oestreich*[,†]

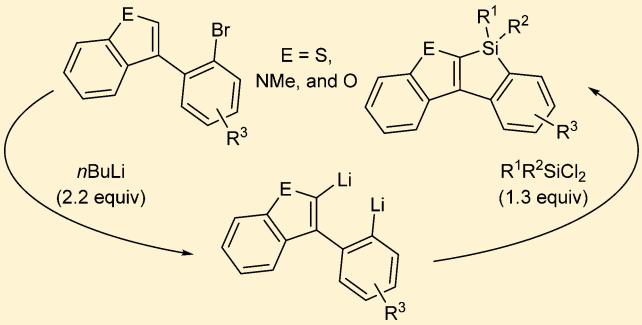
[†]Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 115, 10623 Berlin, Germany

[‡]Department of Chemistry, Graduate School of Science, Nagoya University, Furo, Chikusa, Nagoya 464-8602, Japan

[§]Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Furo, Chikusa, Nagoya 464-8602, Japan

S *Supporting Information*

ABSTRACT: The straightforward assembly of various thiophene-fused benzosiloles is accomplished by 2-fold metalation of benzo[*b*]thiophenes substituted at C3 with ortho-brominated aryl groups followed by electrophilic substitution with dichlorosilanes. The method relies on the innate acidity of the C(sp^2)−H bond at C2 of benzo[*b*]thiophenes and the halogen−metal exchange of the proximal C(sp^2)−Br bond. The related indole- and benzofuran-annulated systems are also accessible, but these siloles are chemically less stable. An example of a thiophene-fused benzogermole is included as well.



INTRODUCTION

Novel synthetic approaches[1] to benzannulated siloles, including those with annulated heterocycles, continue to attract attention due to their photophysical properties and potential application in polymer chemistry.[2] Especially thiophene as well as benzothiophene have been chosen as heterocycles fused to the silole core, resulting in polycyclic structures that are referred to as BST (benzo[4,5]silolo[3,2-*b*]thiophene) **1** or its regioisomer benzo[4,5]silolo[2,3-*b*]thiophene **2** (Figure 1).

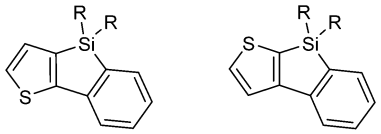
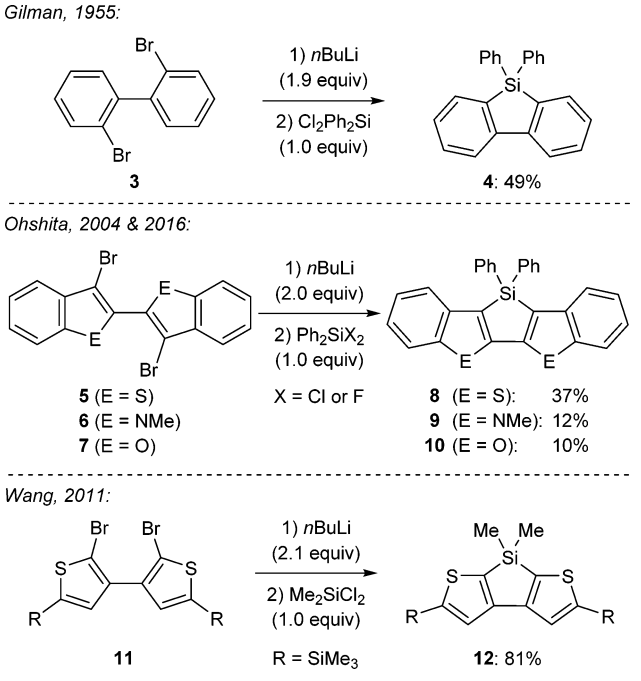


Figure 1. Regioisomeric benzosilolothiophenes **1** and **2** (R = alkyl, aryl).

The synthesis of motifs such as **1** and that of related siloles usually relies on stoichiometric reactions. These trace back to Gilman's dibenzosilole synthesis, where 2-fold bromine−lithium exchange is followed by the reaction with a dichlorosilane (**3** → **4**, Scheme 1, top).[3,4] Later, Ohshita and co-workers adopted this procedure for the assembly of systems such as **8** and **9** with benzothiophene and indole units, respectively (**5** → **8** and **6** → **9**, Scheme 1, middle).[5] A few years later, the benzofuran derivative **10** and the corresponding germole (not shown) were accessed the same way (**7** → **10**).[6] Yields were low though in all cases. Alternative stoichiometric syntheses of extended, ladder-type systems proceed through anionic cyclization[7] or successive 4-fold metalation/electrophilic substitution with dichlorosilanes.[8] Aside from these

Scheme 1. 2-Fold Halogen−Metal Exchange as an Entry into Stoichiometric Silole Synthesis



Received: August 12, 2017

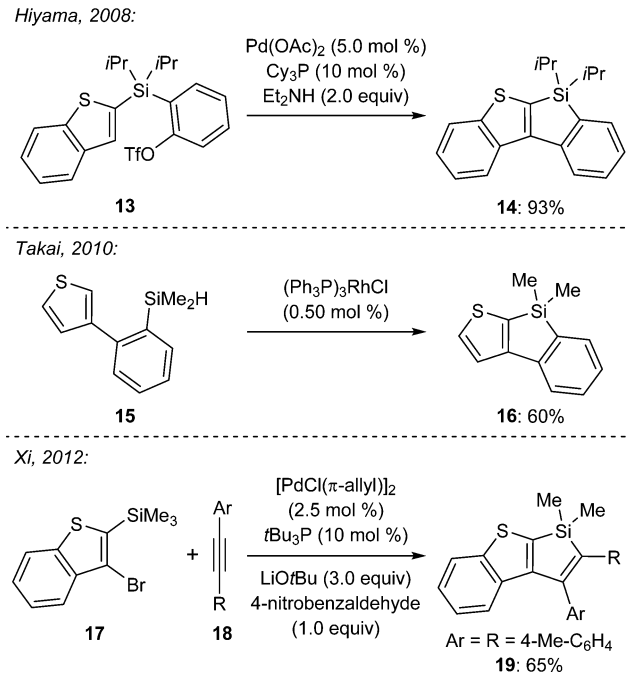
DOI: 10.1021/acs.organomet.7b00619
Organometallics XXXX, XXX, XXX−XXX

stoichiometric methods, a limited number of catalytic transformations lead to systems similar to **8**–**10**. These methods range from palladium-[9] and rhodium-catalyzed[10] processes to [2 + 2 + 2] cycloaddition[11] as well as Ru–S-catalyzed 2-fold electrophilic C–H silylation.[12] The 2-fold bromine–lithium exchange also works with regioisomeric thiophenes, as demonstrated by Wang's synthesis (**11** → **12**, Scheme 1, bottom).[13]

For benzosilolothiophene **2** there is no stoichiometric protocol available. However, a few catalytic examples do exist (Scheme 2). The aforementioned intramolecular palladium-catalyzed cross-coupling of regioisomeric precursors worked equally well (e.g., **13** → **14**, Scheme 2, top); the benzothiophene could also be replaced by thiophene and benzofuran rings (not shown).[9a] A rhodium-catalyzed dehydrogenative coupling employing Wilkinson's catalyst was later reported (**15** → **16**, Scheme 2, middle).[14] The same transformation was later accomplished with a platinum catalyst which led to **16** from **15** with an improved yield of 94% (not shown).[15] A similar scaffold was obtained by a palladium-catalyzed annulation starting from a prefunctionalized benzothiophene and internal acetylenes (e.g., **17**/**18** → **19**, Scheme 2, bottom).[16] Also, siloloindoles were synthesized with the same catalyst system starting from C3-arylated indole precursors (not shown).[17]

The above catalytic methods mostly require multistep substrate syntheses, often involving metalated reagents in at least one step. We thought that we could directly exploit the innate acidity of the C(sp^2)–H bond at C2 of sulfur-, nitrogen-, and oxygen-containing five-membered heterocycles. Moreover, we intended to combine this with a halogen–metal exchange in the ortho position of the aryl ring attached to C3 of that heterocycle. This would result in a 2-fold metalation, and addition of a silicon electrophile would deliver the desired silole.

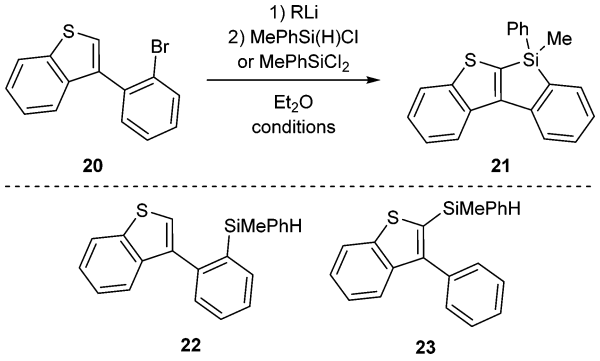
Scheme 2. Reported Catalytic Syntheses of Silolo[2,3-*b*]thiophenes



RESULTS AND DISCUSSION

We chose readily available **20** as the model compound (Table 1).[18] We indeed observed silole **21** in low yield when **20** was subsequently treated with stoichiometric amounts of *n*BuLi and MePhSi(H)Cl (entry 1); most of the starting material **20** had remained unconsumed after hydrolysis. The use of *t*BuLi was no improvement, and hydrosilanes **22** and **23** were observed (entry 2), but increasing the reaction temperature to room temperature for both steps led to good isolated yield (entry 3). We finally obtained **21** in 85% isolated yield by using $MePhSiCl_2$ instead of MePhSi(H)Cl as the electrophile (entry 4). This also facilitated the purification, as the formation of **22** and **23** is avoided. The molecular structure of **21** was secured by X-ray diffraction analysis (Figure 2, top left).

Table 1. Optimization of the Silole Formation[a]



entry	RLi (equiv), T (°C), t (h)	electrophile (equiv), T (°C), t (h)	yield of **21** (%)
1	*n*BuLi (2.2), −78 → −20, 4	MePhSi(H)Cl (1.3), −78 → room temp, 19	18[b]
2[c]	*t*BuLi (3.0), −78 → −25, 1.5	MePhSi(H)Cl (1.3), −78 → room temp, 19	*d*
3	*n*BuLi (2.2), room temp, 4	MePhSi(H)Cl (1.3), room temp, 4	72
4	*n*BuLi (2.2), room temp, 4	$MePhSiCl_2$ (1.3), room temp, 4	85

[a]All reactions were performed according to GP2 (see the Experimental Section). [b]Incomplete conversion of **20**. [c]THF was used as solvent. [d]Dehalogenated starting material and hydrosilanes **22** and **23** were obtained as major components, as determined by GLC/GC MS analysis.

DOI: 10.1021/acs.organomet.7b00619
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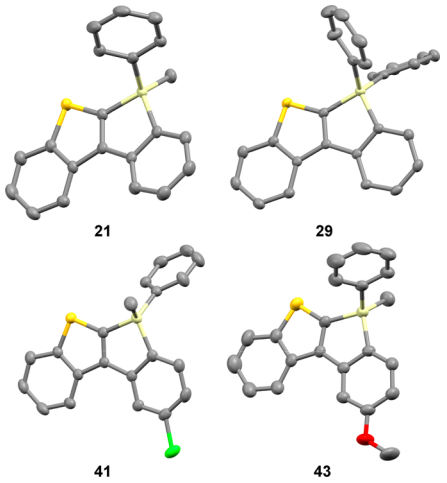
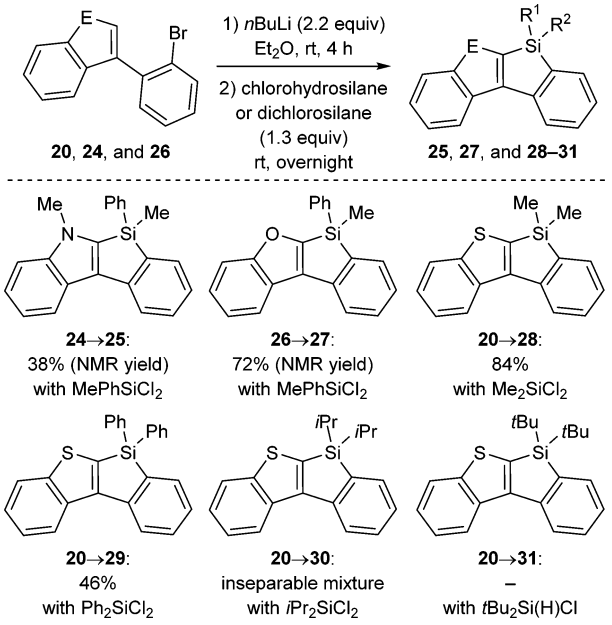


Figure 2. Molecular structures of siloles **21**, **29**, **41**, and **43**.

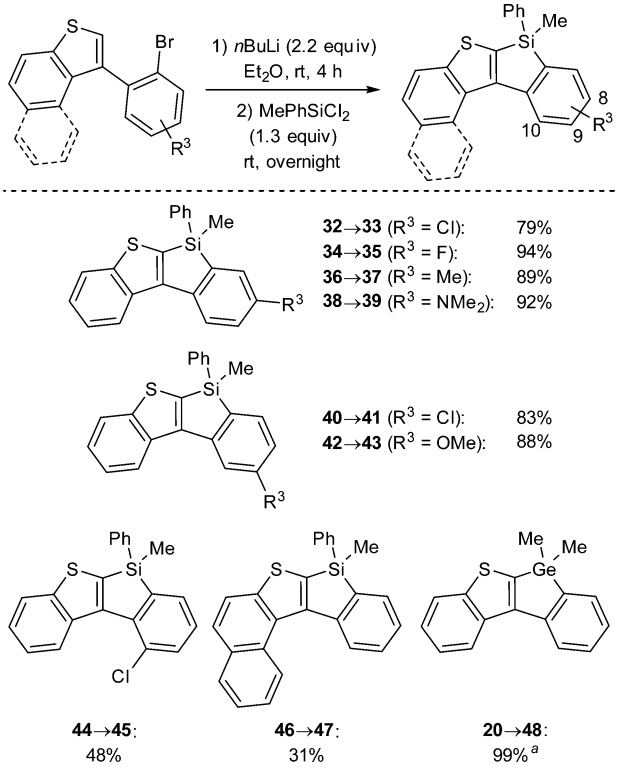
Scheme 3. Scope I: Variation of the Silicon Electrophile and Testing of Different Heterocycles



With a high-yielding protocol in hand, we verified its generality by testing substrates containing indole and benzofuran units (**24** → **25** and **26** → **27**, Scheme 3). Both **25** and **27** were indeed formed, but these siloles turned out to be highly sensitive toward silica gel chromatography. Returning to benzothiophenes, we were more successful when reacting the doubly metalated intermediate derived from **20** with differently substituted dichlorosilanes. The use of Me_2SiCl_2 resulted in good yield (**20** → **28**), whereas Ph_2SiCl_2 led to lower yield (**20** → **29** and molecular structure of **29**, Figure 2, top right). Sterically hindered iPr_2SiCl_2 reacted to give the corresponding silole but was obtained along with an unknown byproduct (**20** → **30**). Two *tert*-butyl groups at the silicon atom were sterically too demanding, and the formation of **31** was not observed with $tBu_2Si(H)Cl$.

With $MePhSiCl_2$ as the optimal silicon electrophile, we found that several functionalized precursors were suitable for this transformation (Scheme 4). Electron-withdrawing (**32** → **33** and **34** → **35**) as well as electron-donating groups (**36** → **37** and **38** → **39**) in the C8 position were tolerated and the siloles were isolated in high yields. Substrates with a chloro (**40** → **41**) and a methoxy substituent (**42** → **43**) para to the newly formed C(sp^2)–Si bond participated well. For siloles **41** and **43**, the molecular structures were confirmed by X-ray diffraction analysis (Figure 2, bottom). Furthermore, chlorination at C10 was accepted (**44** → **45**), and a naphthosilolothiophene derivative was also successfully synthesized (**46** → **47**), even though isolated yields were lower. By the addition of Me_2GeCl_2 to doubly metalated **20** instead of $MePhSiCl_2$, the corresponding germole was formed quantitatively (**20** → **48**).[19]

Scheme 4. Scope II: Preparation of Functionalized Silolothiophenes and a Related Germole



[a] Me_2GeCl_2 was used instead of $MePhSiCl_2$ under otherwise identical reaction conditions.

Among the benzo[4,5]silolo[2,3-*b*]thiophene derivatives thus obtained, the UV–vis absorption and fluorescence spectra of compounds **21**, **29**, **39**, **41**, and **43** were measured in CH_2Cl_2. Their spectra are shown in Figures 3 and 4, and their

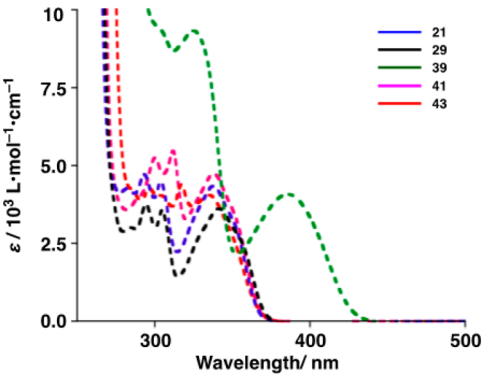


Figure 3. UV–vis absorption spectra of siloles **21**, **29**, **39**, **41**, and **43**.

DOI: 10.1021/acs.organomet.7b00619
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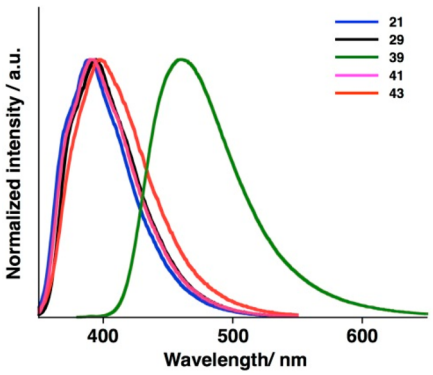

Figure 4. Fluorescence spectra of siloles **21**, **29**, **39**, **41**, and **43**.

data are summarized in Table 2. In the absorption spectra, all the derivatives have their longest absorption maxima and

Table 2. Photophysical Data for Benzosilolothiophenes in CH_2Cl_2

	absorption		fluorescence	
compd	λ_{max} (nm)[a]	log ε	λ_{max} (nm)[b]	Φ_F[c]
21	338	3.64	388	0.08
29	336	3.56	398	0.09
39	386	3.61	460	0.63
41	338	3.68	390	0.08
43	342	3.61	394	0.09

[a]The longest absorption maximum wavelength. [b]Excited at the absorption maximum wavelength. [c]Absolute fluorescence quantum yield determined by a calibrated integrating sphere system.

emission maxima around 340 and 390 nm, respectively, except for **39** with an electron-donating amino group. It showed a longer absorption maximum at 386 nm and an intense blue emission with a maximum at 460 nm as well as a fluorescence quantum yield of $\Phi_F = 0.63$, which is much higher than those of the other compounds ($\Phi_F < 0.1$).

CONCLUSION

In summary, we have developed a short synthesis of benzosilolothiophenes using easily accessible brominated precursors. Application to nitrogen- and oxygen-containing heterocycles as well as germoles was shown to be possible in principle. Although stoichiometric in the metalating reagent, the utility of this method lies in the simplicity of the procedure, allowing for the construction of heteroaryl-fused siloles in one synthetic operation.

EXPERIMENTAL SECTION

General Remarks. All reactions were performed in flame-dried glassware using conventional Schlenk techniques under a static pressure nitrogen. Liquids and solutions were transferred with syringes. Benzene was purified and dried using a MBraun solvent system. Technical grade solvents (cyclohexane, *tert*-butyl methyl ether, EtOH) were distilled prior to use. Et_2O and THF were dried and purified following standard procedures. 1-Methyl-3-(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)indole,[20] 3-bromo-4-iodo-*N*,*N*-dimethylaniline,[21] 4-bromo-3-iodoanisole,[22] and 1-(2-bromophenyl)-naphtha[2,1-*b*]thiophene (**46**)[18] were synthesized according to reported procedures. All other commercially available reagents were used as received. Analytical thin-layer chromatography (TLC) was performed on silica gel SIL G-25 glass plates from Macherey-Nagel. Flash column chromatography was performed on silica gel 60 (40−63 μm, 230−400 mesh, ASTM) by Merck using the indicated solvents. ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were recorded in $CDCl_3$ or C_6D_6 on Bruker AV 400 and Bruker AV 500 instruments. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ 7.26 ppm for ^1H NMR and $CDCl_3$: δ 77.16 ppm for ^{13}C NMR, C_6D_5H: δ 7.16 ppm for ^1H NMR and C_6D_6: δ 128.06 ppm for ^{13}C NMR). ^{19}F and ^{29}Si NMR spectra were calibrated according to the IUPAC recommendation using a unified chemical shift scale based on the proton resonance of trimethylsilane as a primary reference. Data are reported as follows: chemical shift, multiplicity (s_{br} = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, m_c = centrosymmetric multiplet), coupling constant (Hz), and integration. Infrared (IR) spectra were recorded on an Agilent Technologies Cary 630 FT-IR spectrometer equipped with an ATR unit, and the signals are reported in wavenumbers (cm^{-1}). Melting points (mp) were determined using a Leica Galen III melting point apparatus (Wagner & Munz) and are not corrected. High-resolution mass spectrometry (HRMS) was performed by the Analytical Facility of the Institut für Chemie, Technische Universität Berlin. Data for the single-crystal structure determination were collected with an Agilent SuperNova diffractometer equipped with a CCD area Atlas detector and a mirror monochromator by utilizing Cu Kα radiation (λ = 1.5418 Å). Software packages used: CrysAlis PRO for data collection, cell refinement, and data reduction,[23] SHELXS-97 for structure solution,[24] SHELXL-97 for structure refinement,[25] and Mercury 3.1.1[26] for graphics. UV−vis absorption and fluorescence spectra were measured with a Shimadzu UV-1800 spectrometer and a HORIBA FluoroMax-4 spectrometer, respectively, in spectral grade CH_2Cl_2. Absolute fluorescence quantum yields were determined with a Hamamatsu photonics PMA-11 calibrated integrating sphere system.

General Procedure for Suzuki−Miyaura Cross-Coupling Reactions (GP1). In a Schlenk flask, the boronic acid or boronic acid ester (1.0−1.1 equiv), the corresponding 2-bromoiodobenzene (1.0−1.1 equiv), $(Ph_3P)_4Pd$ (1.0−10 mol %), and K_2CO_3 (1.5−1.7 equiv) were suspended in a degassed mixture of benzene, EtOH, and H_2O. The reaction mixture was heated to the indicated temperature for 1−4 days. The reaction was quenched by the addition of H_2O. The phases were separated, the aqueous phase was extracted with *tert*-butyl methyl ether (3 ×), and the combined organic phases were dried over $MgSO_4$. The crude product was purified by flash column chromatography on silica gel using cyclohexane or cyclohexane/*tert*-butyl methyl ether as eluent.

General Procedure for the Optimization of the Silole Synthesis (GP2). In a flame-dried 10 mL Schlenk flask equipped with a magnetic stir bar, the precursor (73 mg, 0.25 mmol, 1.0 equiv) was dissolved in Et_2O (1 mL). The organolithium reagent (2.2−3.0 equiv) was added at the indicated temperature, and the reaction mixture was stirred for 1.5−4 h. Chlorohydrosilane or dichlorosilane (1.3 equiv) was added at the indicated temperature, and the resulting suspension was stirred for 3−20 h. The reaction was quenched by the addition of H_2O (5 mL). The phases were separated, the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 5 mL), and the combined organic phases were dried over $MgSO_4$. The crude product was purified by flash column chromatography on silica gel using cyclohexane or cyclohexane/*tert*-butyl methyl ether as eluent.

General Procedure for the Synthesis of Siloles and the Germole (GP3). In a flame-dried 10 mL Schlenk flask equipped with a magnetic stir bar the corresponding ortho-brominated heteroarylphenyl derivative (0.25−0.33 mmol) was dissolved in Et_2O (1 mL). *n*BuLi (2.6 M in hexanes, 2.2 equiv) was added at room temperature, and the reaction mixture was stirred for 4 h. Dichlorosilane or dichlorogermane (1.3 equiv) was added, and the resulting suspension was stirred at room temperature for 18 h. The reaction was quenched by the addition of H_2O (5 mL). The phases were separated, the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 5 mL), and the combined organic phases were dried over $MgSO_4$. The crude product was purified by flash column chromatography on silica gel or filtration.

DOI: 10.1021/acs.organomet.7b00619
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6-Methyl-6-phenyl-6*H*-benzo[*b*]benzo[4,5]silolo[3,2-*d*]-thiophene (21). This compound was prepared according to GP3 from **20** (73 mg, 0.25 mmol, 1.0 equiv), *n*BuLi (2.6 M in hexanes, 0.21 mL, 0.55 mmol, 2.2 equiv), and dichloro(methyl)phenylsilane (53 μL, 0.33 mmol, 1.3 equiv). The crude product was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford **21** (70 mg, 85%) as a colorless oil that slowly solidified. Single crystals of **21** suitable for X-ray diffraction were obtained by slow vaporization of a CH_2Cl_2/cyclohexane (approximately 1/1) solution (see the Supporting Information for further details). Mp: 118 °C (cyclohexane). R_f = 0.56 (cyclohexane). IR (ATR): $\tilde{\nu}$/cm^{-1} 3035 (w), 2920 (w), 2889 (w), 2110 (w), 1579 (w), 1547 (w), 1427 (w), 1347 (w), 1249 (w), 1111 (m), 1083 (m), 804 (m), 771 (s), 726 (s), 700 (s). HRMS (APCI) for $C_{21}H_{17}SSi^+$ [M + H]$^+$: calculated 329.0815, found 329.0810. ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 0.83 (s, 3H), 7.26 (m$_c$, 1H), 7.33−7.37 (m, 2H), 7.38−7.42 (m, 2H), 7.50 (m$_c$, 2H), 7.60−7.63 (m, 3H), 7.95 (dm, ^3J = 8.1 Hz, 1H), 8.16 (d, ^3J = 7.8 Hz, 1H), 8.47 (d, ^3J = 8.1 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ/ppm −4.8 (s), 121.6 (s), 123.1 (s), 123.6 (s), 124.6 (s), 124.7 (s), 126.4 (s), 128.3 (s, 2C), 130.4 (s), 130.6 (s), 133.3 (s), 133.5 (s), 134.7 (s, 2C), 135.9 (s), 138.9 (s), 140.4 (s), 146.1 (s), 149.0 (s), 150.5 (s). ^{29}Si{^{1}H} DEPT NMR (99 MHz, $CDCl_3$, optimized for J = 7 Hz): δ/ppm −8.8. The crystallographic data are available online in the CCDC database under number CCDC 1567746.

5,6-Dimethyl-6-phenyl-5,6-dihydrobenzo[4,5]silolo[2,3-*b*]-indole (25). This compound was prepared according to GP3 from **24** (73 mg, 0.25 mmol, 1.0 equiv), *n*BuLi (2.6 M in hexanes, 0.21 mL, 0.55 mmol, 2.2 equiv), and dichloro(methyl)phenylsilane (53 μL, 0.33 mmol, 1.3 equiv). Toluene (7.2 mg) was added as internal standard to the crude product, and the yield of **25** was determined to be 38% by integration of baseline-separated signals in the ^{1}H NMR spectrum. Attempts to purify **25** by flash column chromatography on silica gel or aluminum oxide failed. HRMS (APCI) for $C_{22}H_{20}NSi^+$ [M + H]$^+$: calculated 326.1360, found 326.1360. Selected NMR spectroscopic data are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 0.84 (s, 3H), 3.77 (s, 3H), 7.79 (m$_c$, 1H), 8.02 (m$_c$, 1H). ^{1}H,^{29}Si HMQC NMR (500/99 MHz, $CDCl_3$, optimized for J = 7 Hz): δ/ppm 0.84/(−16.2).

6-Methyl-6-phenyl-6*H*-benzo[4,5]silolo[2,3-*b*]benzofuran (27). This compound was prepared according to GP3 from **26** (74 mg, 0.27 mmol, 1.0 equiv), *n*BuLi (2.6 M in hexanes, 0.23 mL, 0.59 mmol, 2.2 equiv), and dichloro(methyl)phenylsilane (60 μL, 0.37 mmol, 1.3 equiv). Toluene (11.9 mg) was added as internal standard to the crude product, and the yield of **27** was determined to be 72% by integration of baseline-separated signals in the ^{1}H NMR spectrum. Attempts to purify **27** by flash column chromatography on silica gel or aluminum oxide failed. HRMS (EI) for $C_{21}H_{16}OSi^+$ [M]$^+$: calculated 312.0965, found 312.0956. Selected NMR spectroscopic data are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 0.83 (s, 3H), 7.62 (m$_c$, 2H), 7.76 (ddd, ^3J = 7.5 Hz, ^4J = 0.8 Hz, ^4J = 0.8 Hz, 1H), 7.95−7.97 (m$_c$, 1H). ^{1}H,^{29}Si HMQC NMR (500/99 MHz, $CDCl_3$, optimized for J = 7 Hz): δ/ppm 0.83/(−18.5).

6,6-Dimethyl-6*H*-benzo[*b*]benzo[4,5]silolo[3,2-*d*]thiophene (28). This compound was prepared according to GP3 from **20** (73 mg, 0.25 mmol, 1.0 equiv), *n*BuLi (2.6 M in hexanes, 0.21 mL, 0.55 mmol, 2.2 equiv), and dichlorodimethylsilane (40 μL, 0.33 mmol, 1.3 equiv). The crude product was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford **28** (56 mg, 84%) as a colorless viscous oil. R_f = 0.54 (cyclohexane). IR (ATR): $\tilde{\nu}$/cm^{-1} 3049 (w), 2952 (w), 2849 (w), 1587 (m), 1458 (m), 1345 (m), 1246 (m), 1080 (m), 1044 (w), 918 (w), 839 (m), 774 (s), 747 (m), 723 (m), 723 (s), 671 (m). HRMS (APCI) for $C_{16}H_{15}SSi^+$ [M + H]$^+$ calculated 267.0658, found 267.0659. ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 0.52 (s, 6H), 7.26 (m$_c$, 1H), 7.38 (ddd, ^3J = 8.1 Hz, ^3J = 7.0 Hz, ^4J = 1.1 Hz, 1H), 7.46−7.50 (m, 2H), 7.61 (m$_c$, 1H), 7.95 (m$_c$, 1H), 8.12 (d, ^3J = 7.8 Hz, 1H), 8.44 (d, ^3J = 8.2 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ/ppm −2.9 (s, 2C), 121.4 (s), 123.0 (s), 123.6 (s), 124.4 (s), 124.7 (s), 126.1 (s), 130.3 (s), 132.8 (s), 135.9 (s), 140.4 (s), 141.7 (s), 145.7 (s), 148.7 (s), 149.5 (s). ^{29}Si{^{1}H} DEPT NMR (99 MHz, $CDCl_3$, optimized for J = 7 Hz): δ/ppm −2.2.

6,6-Diphenyl-6*H*-benzo[*b*]benzo[4,5]silolo[3,2-*d*]thiophene (29). This compound was prepared according to GP3 from **20** (73 mg, 0.25 mmol, 1.0 equiv), *n*BuLi (2.6 M in hexanes, 0.21 mL, 0.55 mmol, 2.2 equiv), and dichlorodiphenylsilane (60 μL, 0.33 mmol, 1.3 equiv). The crude product was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford **29** (45 mg, 46%) as a white solid. Single crystals of **29** suitable for X-ray diffraction were obtained by slow vaporization of a CH_2Cl_2/cyclohexane (approximately 1/1) solution (see the Supporting Information for further details). Mp: 163 °C (cyclohexane). R_f = 0.41 (cyclohexane). IR (ATR): $\tilde{\nu}$/cm^{-1} 3043 (w), 2920 (w), 2850 (w), 2112 (w), 1583 (w), 1458 (w), 1424 (m), 1348 (w), 1257 (w), 1156 (w), 1106 (m), 1025 (w), 774 (s), 733 (m), 707 (s). HRMS (APCI) for $C_{26}H_{19}SSi^+$ [M + H]$^+$: calculated 391.0971, found 391.0970. ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.29 (m$_c$, 1H), 7.36−7.46 (m, 7H), 7.50 (m$_c$, 1H), 7.52 (m$_c$, 1H), 7.69−7.72 (m, 4H), 7.76 (m$_c$, 1H), 7.96 (d, ^3J = 8.1 Hz, 1H), 8.18 (d, ^3J = 7.7 Hz, 1H), 8.48 (d, ^3J = 8.3 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ/ppm 121.9 (s), 123.2 (s), 123.7 (s), 124.7 (s), 124.8 (s), 126.6 (s), 128.4 (s, 4C), 130.6 (s, 2C), 130.8 (s), 131.5 (s, 2C), 134.2 (s), 135.7 (s, 4C), 135.9 (s), 137.4 (s), 139.0 (s), 146.4 (s), 149.3 (s), 151.0 (s). ^{29}Si{^{1}H} DEPT NMR (99 MHz, $CDCl_3$, optimized for J = 7 Hz): δ/ppm −14.8. The crystallographic data are available online in the CCDC database under number CCDC 1567747.

8-Chloro-6-methyl-6-phenyl-6*H*-benzo[*b*]benzo[4,5]silolo-[3,2-*d*]thiophene (33). This compound was prepared according to GP3 from **32** (81 mg, 0.25 mmol, 1.0 equiv), *n*BuLi (2.6 M in hexanes, 0.21 mL, 0.55 mmol, 2.2 equiv), and dichloro(methyl)phenylsilane (53 μL, 0.33 mmol, 1.3 equiv). The crude product was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford **33** (69 mg, 79%) as a white solid. Mp: 49 °C ($CDCl_3$). R_f = 0.33 (cyclohexane). IR (ATR): $\tilde{\nu}$/cm^{-1} 3084 (w), 2920 (m), 2847 (m), 1580 (w), 1558 (w), 1445 (m), 1426 (m), 1375 (w), 1346 (m), 1249 (m), 1155 (w), 1111 (m), 1080 (m), 918 (w), 885 (w), 812 (s), 786 (m), 742 (s), 692 (s). HRMS (EI) for $C_{21}H_{15}ClSSi^+$ [M]$^+$: calculated 362.0347, found 362.0345. ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 0.85 (s, 3H), 7.36−7.39 (m, 2H), 7.40−7.44 (m, 2H), 7.46 (dd, ^3J = 8.2 Hz, ^4J = 2.2 Hz, 1H), 7.51 (ddd, ^3J = 8.2 Hz, ^3J = 7.1 Hz, ^4J = 1.1 Hz, 1H), 7.56 (d, ^4J = 2.2 Hz, 1H), 7.59−7.61 (m, 2H), 7.96 (d, ^3J = 8.0 Hz, 1H), 8.06 (d, ^3J = 8.2 Hz, 1H), 8.41 (d, ^3J = 8.1 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ/ppm −5.0 (s), 122.4 (s), 122.9 (s), 123.7 (s), 124.8 (s), 124.9 (s), 128.5 (s, 2C), 130.3 (s), 130.7 (s), 132.4 (s), 132.5 (s), 133.3 (s), 134.6 (s, 2C), 135.6 (s), 138.7 (s), 143.2 (s), 144.2 (s), 149.0 (s), 149.6 (s). ^{29}Si{^{1}H} DEPT NMR (99 MHz, $CDCl_3$, optimized for J = 7 Hz): δ/ppm −8.3.

8-Fluoro-6-methyl-6-phenyl-6*H*-benzo[*b*]benzo[4,5]silolo-[3,2-*d*]thiophene (35). This compound was prepared according to GP3 from **34** (77 mg, 0.25 mmol, 1.0 equiv), *n*BuLi (2.6 M in hexanes, 0.21 mL, 0.55 mmol, 2.2 equiv), and dichloro(methyl)phenylsilane (53 μL, 0.33 mmol, 1.3 equiv). The crude product was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford **35** (85 mg, 94%) as a colorless oil. R_f = 0.31 (cyclohexane). IR (ATR): $\tilde{\nu}$/cm^{-1} 3084 (w), 2959 (w), 2920 (m), 2107 (w), 1591 (m), 1476 (m), 1458 (m), 1426 (m), 1381 (m), 1340 (m), 1251 (m), 1201 (m), 1161 (w), 1134 (m), 1110 (m), 1080 (s), 1057 (m), 968 (m), 853 (s), 791 (s), 725 (s), 693 (s). HRMS (APCI) for $C_{21}H_{16}FSSi^+$ [M + H]$^+$: calculated 347.0721, found 347.0718. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 0.82 (s, 3H), 6.95 (m$_c$, 1H), 7.33−7.44 (m, 4H), 7.49−7.60 (m, 4H), 7.81−7.84 (m, 1H), 7.95 (dm$_c$, ^3J = 8.2 Hz, 1H), 8.39 (d, ^3J = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ/ppm −4.9 (s), 109.7 (d, $^2J_{C,F}$ = 22.9 Hz), 112.7 (d, $^2J_{C,F}$ = 20.8 Hz), 122.8 (s), 123.7 (s), 124.8 (s), 125.0 (s), 128.4 (s, 2C), 130.5 (s), 132.9 (s), 134.6 (d, $^3J_{C,F}$ = 7.9 Hz), 134.6 (s, 2C), 135.4 (d, $^4J_{C,F}$ = 3.5 Hz), 135.6 (s), 140.8 (s), 148.3 (d, $^3J_{C,F}$ = 8.4 Hz), 148.9 (s), 149.0 (d, $^4J_{C,F}$ = 2.9 Hz), 165.2 (d, $^1J_{C,F}$ = 246 Hz). ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$): δ/ppm −110.2. ^{29}Si{^{1}H} DEPT NMR (99 MHz, $CDCl_3$, optimized for J = 7 Hz): δ/ppm −9.1.

6,8-Dimethyl-6-phenyl-6*H*-benzo[*b*]benzo[4,5]silolo[3,2-*d*]-thiophene (37). This compound was prepared according to GP3 from **36** (76 mg, 0.25 mmol, 1.0 equiv), *n*BuLi (2.6 M in hexanes, 0.21

DOI: 10.1021/acs.organomet.7b00619
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mL, 0.55 mmol, 2.2 equiv), and dichloro(methyl)phenylsilane (53 μL, 0.33 mmol, 1.3 equiv). The crude product was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford **37** (76 mg, 89%) as a colorless oil that slowly solidified. Mp: 44 °C (cyclohexane). R_f = 0.38 (cyclohexane). IR (ATR): $\tilde{\nu}$/cm^{-1} 3084 (w), 2997 (w), 2920 (m), 2847 (m), 1458 (m), 1427 (m), 1405 (m), 1348 (m), 1248 (m), 1155 (w), 1111 (m), 1081 (m), 862 (m), 791 (s), 774 (m), 725 (s), 694 (s). HRMS (APCI) for $C_{22}H_{19}SSi^+$ [M + H]$^+$: calculated 343.0971, found 343.0968. ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 0.84 (s, 3H), 2.40 (s, 3H), 7.32 (m_c, 1H), 7.36−7.45 (m, 4H), 7.46 (s_{br}, 1H), 7.51 (ddd, ^3J = 8.1 Hz, ^3J = 7.1 Hz, ^4J = 1.1 Hz, 1H), 7.64 (m_c, 2H), 7.96 (d, ^3J = 8.1 Hz, 1H), 8.06 (d, ^3J = 7.9 Hz, 1H), 8.48 (d, ^3J = 8.2 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ/ppm −4.8 (s), 21.3 (s), 121.3 (s), 123.1 (s), 123.6 (s), 124.5 (s), 124.6 (s), 128.3 (s, 2C), 130.3 (s), 131.0 (s), 133.5 (s), 134.4 (s), 134.7 (s, 2C), 135.9 (s), 135.9 (s), 137.8 (s), 140.6 (s), 143.4 (s), 149.0 (s), 150.6 (s). ^{29}Si{^{1}H} DEPT NMR (99 MHz, $CDCl_3$, optimized for J = 7 Hz): δ/ppm −8.8.

***N,N*,6-Trimethyl-6-phenyl-6*H*-benzo[*b*]benzo[4,5]silolo[3,2-*d*]thiophen-8-amine (39).** This compound was prepared according to GP3 from **38** (83 mg, 0.25 mmol, 1.0 equiv), *n*BuLi (2.6 M in hexanes, 0.21 mL, 0.55 mmol, 2.2 equiv), and dichloro(methyl)-phenylsilane (53 μL, 0.33 mmol, 1.3 equiv). The crude product was purified by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether (50/1) as eluent to afford **39** (85 mg, 92%) as a yellow oil. R_f = 0.30 (cyclohexane/*tert*-butyl methyl ether = 50/1). IR (ATR): $\tilde{\nu}$/cm^{-1} 3089 (w), 3879 (w), 2806 (w), 1598 (m), 1525 (m), 1491 (m), 1423 (m), 1361 (m), 1256 (w), 1222 (m), 1172 (w), 1062 (m), 1024 (m), 953 (m), 830 (m), 807 (m), 787 (s), 758 (s), 733 (s), 667 (m). HRMS (APCI) for $C_{23}H_{21}NSSi^+$ [M]$^+$: calculated 371.1158, found 371.1157. ^{1}H NMR (500 MHz, C_6D_6): δ/ppm 0.70 (s, 3H), 2.51 (s, 6H), 6.68 (dd, ^3J = 8.6 Hz, ^4J = 2.7 Hz, 1H), 7.05 (d, ^4J = 2.7 Hz, 1H), 7.08−7.14 (m, 4H), 7.29 (m_c, 1H), 7.63 (m_c, 2H), 7.68 (d, ^3J = 8.1 Hz, 1H), 8.09 (d, ^3J = 8.4 Hz, 1H), 8.45 (d, ^3J = 8.2 Hz, 1H) ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ/ppm −4.8 (s), 40.3 (s, 2C), 113.6 (s), 118.5 (s), 122.6 (s), 123.5 (s), 123.8 (s), 124.5 (s), 124.6 (s), 128.5 (s, 2C), 130.3 (s), 134.3 (s), 134.7 (s), 135.0 (s, 2C), 135.5 (s), 136.4 (s), 142.3 (s), 149.6 (s), 149.7 (s), 151.9 (s). ^{29}Si{^{1}H} DEPT NMR (99 MHz, C_6D_6, optimized for J = 7 Hz): δ/ppm −8.5.

9-Chloro-6-methyl-6-phenyl-6*H*-benzo[*b*]benzo[4,5]silolo-[3,2-*d*]thiophene (41). This compound was prepared according to GP3 from **40** (81 mg, 0.25 mmol, 1.0 equiv), *n*BuLi (2.6 M in hexanes, 0.21 mL, 0.55 mmol, 2.2 equiv), and dichloro(methyl)phenylsilane (53 μL, 0.33 mmol, 1.3 equiv). The crude product was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford **41** (75 mg, 83%) as a white solid. Single crystals of **41** suitable for X-ray diffraction were obtained by slow vaporization of a $CDCl_3$ solution (see the Supporting Information for further details). Mp: 45 °C ($CDCl_3$). R_f = 0.57 (cyclohexane). IR (ATR): $\tilde{\nu}$/cm^{-1} 3048 (w), 2960 (w), 2921 (w), 2847 (w), 1575 (m), 1458 (m), 1426 (m), 1374 (w), 1249 (m), 1170 (w), 1100 (m), 1082 (m), 1010 (m), 939 (w), 859 (w), 811 (s), 789 (m), 724 (s), 693 (s). HRMS (APCI) for $C_{21}H_{16}ClSSi^+$ [M + H]$^+$: calculated 363.0425, found 363.0422. ^{1}H NMR (500 MHz, C_6D_6): δ/ppm 0.53 (s, 3H), 7.05−7.11 (m, 5H), 7.12−7.16 (m, 2H), 7.47 (m_c, 2H), 7.57 (d, ^3J = 8.0 Hz, 1H), 8.12 (d, ^3J = 8.2 Hz, 1H), 8.17 (s_{br}, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ/ppm −5.0 (s), 122.0 (s), 122.9 (s), 123.7 (s), 124.8 (s), 125.0 (s), 126.1 (s), 128.4 (s, 2C), 130.6 (s), 132.6 (s), 134.2 (s), 134.6 (s, 2C), 135.5 (s), 137.0 (s), 138.5 (s), 140.4 (s), 147.7 (s), 148.9 (s), 149.1 (s). ^{29}Si{^{1}H} DEPT NMR (99 MHz, C_6D_6, optimized for J = 7 Hz): δ/ppm −8.9. The crystallographic data are available online in the CCDC database under number CCDC 1567748.

9-Methoxy-6-methyl-6-phenyl-6*H*-benzo[*b*]benzo[4,5]silolo-[3,2-*d*]thiophene (43). This compound was prepared according to GP3 from **42** (80 mg, 0.25 mmol, 1.0 equiv), *n*BuLi (2.6 M in hexanes, 0.21 mL, 0.55 mmol, 2.2 equiv), and dichloro(methyl)phenylsilane (53 μL, 0.33 mmol, 1.3 equiv). The crude product was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford **43** (79 mg, 88%) as a white solid. Single crystals of **43** suitable for X-ray diffraction were obtained by slow vaporization of a cyclohexane/CH_2Cl_2 (approximately 10/1) solution (see the Supporting Information for further details). Mp: 112 °C (cyclohexane). R_f = 0.24 (cyclohexane). IR (ATR): $\tilde{\nu}$/cm^{-1} 3052 (w), 2924 (m), 2093 (w), 1594 (m), 1562 (m), 1476 (m), 1460 (m), 1426 (m), 1382 (m), 1338 (m), 1298 (m), 1258 (m), 1215 (m), 1143 (m), 1110 (m), 1062 (s), 931 (w), 840 (m), 789 (s), 773 (m), 725 (s), 697 (s). HRMS (APCI) for $C_{22}H_{18}OSSi^+$ [M]$^+$: calculated 358.0842, found 358.0843. ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 0.81 (s, 3H), 3.93 (s, 3H), 6.79 (dd, ^3J = 7.9 Hz, ^4J = 2.2 Hz, 1H), 7.32−7.41 (m, 4H), 7.49 (ddd, ^3J = 8.1 Hz, ^3J = 7.1 Hz, ^4J = 1.1 Hz, 1H), 7.53 (d, ^3J = 7.8 Hz, 1H), 7.59 (m_c, 2H), 7.73−7.74 (m, 1H), 7.94 (d, ^3J = 8.1 Hz, 1H), 8.44 (d, ^3J = 8.1 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ/ppm −4.6 (s), 55.5 (s), 109.8 (s), 110.1 (s), 123.0 (s), 123.6 (s), 124.5 (s), 124.8 (s), 128.3 (s, 2C), 130.3 (s), 130.9 (s), 133.7 (s), 134.4 (s), 134.6 (s, 2C), 135.8 (s), 140.5 (s), 147.8 (s), 148.9 (s), 149.7 (s), 162.1 (s). ^{29}Si{^{1}H} DEPT NMR (99 MHz, $CDCl_3$, optimized for J = 7 Hz): δ/ppm −9.4. The crystallographic data are available online in the CCDC database under number CCDC 1567749.

10-Chloro-6-methyl-6-phenyl-6*H*-benzo[*b*]benzo[4,5]silolo-[3,2-*d*]thiophene (45). This compound was prepared according to GP3 from **44** (81 mg, 0.25 mmol, 1.0 equiv), *n*BuLi (2.6 M in hexanes, 0.21 mL, 0.55 mmol, 2.2 equiv), and dichloro(methyl)phenylsilane (53 μL, 0.33 mmol, 1.3 equiv). The crude product was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford **45** (44 mg, 48%) as a colorless oil. R_f = 0.45 (cyclohexane). IR (ATR): $\tilde{\nu}$/cm^{-1} 3049 (w), 2921 (w), 2847 (w), 1573 (w), 1544 (w), 1453 (m), 1427 (m), 1402 (w), 1376 (w), 1328 (w), 1249 (m), 1086 (m), 1023 (w), 917 (w), 791 (m), 762 (s), 723 (s), 694 (s). HRMS (APCI) for $C_{21}H_{16}ClSSi^+$ [M + H]$^+$: calculated 363.0425, found 363.0426. ^{1}H NMR (500 MHz, C_6D_6): δ/ppm 0.48 (s, 3H), 6.74 (dd, ^3J = 7.4 Hz, ^3J = 7.4 Hz, 1H), 7.02−7.12 (m, 5H), 7.26−7.31 (m, 2H), 7.40 (m_c, 2H), 7.58 (d, ^3J = 8.1 Hz, 1H), 9.12 (d, ^3J = 8.5 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ/ppm −5.2 (s), 123.3 (s), 123.9 (s), 124.8 (s), 127.6 (s), 128.0 (s), 128.3 (s, 2C), 128.6 (s), 130.7 (s), 131.6 (s), 132.8 (s), 133.7 (s), 134.8 (s, 2C), 136.1 (s), 142.1 (s), 144.5 (s), 145.1 (s), 149.8 (s), 151.6 (s). ^{29}Si{^{1}H} DEPT NMR (99 MHz, C_6D_6, optimized for J = 7 Hz): δ/ppm −8.0.

8-Methyl-8-phenyl-8*H*-benzo[4,5]silolo[3,2-*b*]naphtho[1,2-*d*]thiophene (47). This compound was prepared according to GP3 from **46** (85 mg, 0.25 mmol, 1.0 equiv), *n*BuLi (2.6 M in hexanes, 0.21 mL, 0.55 mmol, 2.2 equiv), and dichloro(methyl)phenylsilane (53 μL, 0.33 mmol, 1.3 equiv). The crude product was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford **47** (29 mg, 31%) as a colorless oil that slowly solidified. Mp: 42−44 °C ($CDCl_3$). R_f = 0.43 (cyclohexane). IR (ATR): $\tilde{\nu}$/cm^{-1} 3046 (w), 2997 (w), 2955 (w), 2850 (w), 2083 (w), 1582 (m), 1543 (w), 1505 (w), 1427 (m), 1385 (w), 1299 (m), 1247 (m), 1151 (w), 1111 (m), 1091 (m), 1051 (m), 914 (w), 795 (m), 760 (m), 726 (s), 693 (s). HRMS (APCI) for $C_{25}H_{19}SSi^+$ [M + H]$^+$: calculated 379.0971, found 379.0970. ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 0.86 (s, 3H), 7.26 (m_c, 1H), 7.36 (m_c, 2H), 7.42 (tt, ^3J = 7.4 Hz, ^4J = 1.6 Hz, 1H), 7.47 (ddd, ^3J = 7.6 Hz, ^3J = 7.6 Hz, ^4J = 1.3 Hz, 1H), 7.55−7.60 (m, 2H), 7.63−7.66 (m, 3H), 7.76 (d, ^3J = 8.4 Hz, 1H), 7.86 (d, ^3J = 8.5 Hz, 1H), 7.97−7.99 (m, 1H), 8.33 (d, ^3J = 7.8 Hz, 1H), 8.97 (m_c, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ/ppm −4.6 (s), 121.4 (s), 123.9 (s), 124.9 (s), 125.5 (s), 126.3 (s), 126.3 (s), 126.4 (s), 128.4 (s, 2C), 128.7 (s), 129.7 (s), 130.0 (s), 130.4 (s), 132.1 (s), 132.4 (s), 133.6 (s), 133.7 (s), 134.7 (s, 2C), 139.6 (s), 140.8 (s), 147.0 (s), 147.8 (s), 153.2 (s). ^{29}Si{^{1}H} DEPT NMR (99 MHz, $CDCl_3$, optimized for J = 7 Hz): δ/ppm −9.6.

6,6-Dimethyl-6*H*-benzo[*b*]benzo[4,5]germolo[3,2-*d*]-thiophene (48). This compound was prepared according to GP3 from **20** (73 mg, 0.25 mmol, 1.0 equiv), *n*BuLi (2.6 M in hexanes, 0.21 mL, 0.55 mmol, 2.2 equiv), and dichlorodimethylgermane (37 μL, 0.33 mmol, 1.3 equiv). The crude product was purified by filtration over Celite covered with a small plug of silica gel and using cyclohexane as eluent to afford **48** (80 mg, >99%) as a clear liquid. R_f = 0.38 (cyclohexane). IR (ATR): $\tilde{\nu}$/cm^{-1} 3050 (w), 2903 (w), 2105 (w), 1580 (m), 1457 (m), 1395 (w), 1341 (m), 1236 (w), 1155 (w), 1072 (m), 1029 (m), 935 (w), 915 (w), 837 (m), 801 (m), 767 (s), 724 (s).

DOI: 10.1021/acs.organomet.7b00619
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HRMS (EI) for $C_{16}H_{14}GeS^+$ $[M]^+$: calculated 312.0023, found 312.0026. ^1H NMR (500 MHz, $CDCl_3$): δ/ppm 0.70 (s, 6H), 7.27 (ddd, ^3J = 7.3 Hz, ^3J = 7.3 Hz, ^4J = 0.9 Hz, 1H), 7.36 (ddd, ^3J = 8.1 Hz, ^3J = 7.0 Hz, ^4J = 1.1 Hz, 1H), 7.45−7.49 (m, 2H), 7.60 (dd, ^3J = 7.0 Hz, ^4J = 1.2 Hz, 1H), 7.94 (d, ^3J = 8.0 Hz, 1H), 8.19 (d, ^3J = 7.8 Hz, 1H), 8.46 (d, ^3J = 8.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ/ppm −2.1 (s, 2C), 122.0 (s), 122.7 (s), 123.4 (s), 123.9 (s), 124.6 (s), 126.1 (s), 129.6 (s), 132.8 (s), 136.1 (s), 142.8 (s), 144.1 (s), 144.7 (s), 146.8 (s), 148.3 (s). The analytical data are in accordance with those reported.[19]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications Web site. (PDF) Crystallographic data (CIF) The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00619.

Experimental details and characterization data, NMR spectra for all compounds, and crystallographic data of siloles **21**, **29**, **41**, and **43** (PDF)

Accession Codes

CCDC 1567746−1567749 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for S.Y.: yamaguchi@chem.nagoya-u.ac.jp.
*E-mail for M.O.: martin.oestreich@tu-berlin.de.

ORCID

Susanne Bähr: 0000-0001-5113-7646
Hiroaki Ogasawara: 0000-0001-8462-562X
Shigehiro Yamaguchi: 0000-0003-0072-8969
Martin Oestreich: 0000-0002-1487-9218

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

S.B. thanks the Studienstiftung des deutschen Volkes for a predoctoral fellowship (2015−2018). Support through the JSPS Core-to-Core Program (Advanced Research Networks) is gratefully acknowledged. M.O. is indebted to the Einstein Foundation (Berlin) for an endowed professorship. We thank Dr. Elisabeth Irran (TU Berlin) for the X-ray analyses.

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DOI: 10.1021/acs.organomet.7b00619
Organometallics XXXX, XXX, XXX−XXX