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# Synthesis and fluxional behavior of dinaphtho[2,1-*b*;1′,2′-*d*]-siloles and -germoles, involving the first example of optically active group 14 dinaphthoheterols

Shuji Yasuike,[a] Tomoyasu Iida,[a] Satoru Okajima,[a] Kentaro Yamaguchi,[b] Hiroko Seki[b] and Jyoji Kurita[a,*]

[a] *Faculty of Pharmaceutical Sciences, Hokuriku University, Kanagawa-machi, Kanazawa 920-1181, Japan*
[b] *Chemical Analysis Center, Chiba University, 1-33, Yayoicho, Inage-ku, Chiba 263-8322, Japan*

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**Abstract**—7-Substituted dinaphtho[2,1-*b*;1′,2′-*d*]-siloles **2** and -germoles **3**, involving the first isolated example of optically active group 14 dinaphthoheteroles, have been prepared from 2,2′-dibromo-1,1′-binaphthyl (DBBN) via 2,2′-dilithio-1,1′-binaphthyl intermediate. They are fluxional in the NMR time scale at elevated temperatures, and the energy barriers ($\Delta G^{\ddagger}$) for racemization arising from the flipping of the two naphthalene rings are estimated to be 76–77±2 kJ mol$^{-1}$ for siloles **2b**–**d** and 80±2 kJ mol$^{-1}$ for germole **3b**. The half-life ($t_{1/2}$) for racemization of the optically active silole (*R*)-**2b** prepared from optically active (*R*)-DBBN by the same procedure is determined to be 7.2 h in benzene at 19°C. © 2001 Elsevier Science Ltd. All rights reserved.

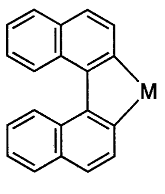
## 1. Introduction

During the last two decades, the chemistry of the 1,1′-binaphthyl group has become a popular subject in organic synthesis, largely due to its availability as a chiral auxiliary for a wide range of asymmetric reactions.[1–3] Accompanying these extensive studies, a variety of silicon-containing 1,1′-binaphthyl derivatives, such as 2,2′-bis(trimethylsilyl)-1,1′-binaphthyl,[4] dinaphtho[*b*,*d*]siloles,[4d,5,6] 3,4-disila-dibenzo[*c*,*g*]phenanthrens,[4d,6] and dinaphtho[*c*,*e*]-silepines[7] have been prepared mostly by the condensation of 2,2′-dilithio-1,1′-binaphthyl with the appropriate chlorosilane reagents. Additionally, optically active dinaphtho-[*c*,*e*]silepine derivatives were demonstrated to be useful for enantioselective reduction of enones and prochiral ketones.[7] Germanium-containing 2,2′-bis(trimethylgermyl)-1,1′-binaphthyl[4b] and tin-containing 2,2′-bis(trimethylstannyl)-1,1′-binaphthyl[4b,8] have also been prepared by a similar procedure. On the other hand, there have been many reports on group 15 (P,[9,10] As[10]) and group 16 (S,[11,12] Se,[12] Te[12]) dinaphthoheteroles, some of which allowed determination of the energy barrier to racemization resulting from the interconversion between the two enantiomeric conformations with switching of the two naphthalene rings (atropisomerism) by NMR analysis. We have very recently reported[13] the synthesis and fluxional behavior of dinaphtho[2,1-*b*;1′,2′-*d*]stibole **1c** involving the first isolated example of optically active dinaphthoheteroles. To the best of our knowledge, however, there have been no reports concerning the atropisomeric and optical behavior of group 14 dinaphthoheteroles, because the pertinent group 14 compounds for the study of their behavior have not been prepared, although several dinaphthosiloles were synthesized.[4d,5,6] In order to gain deeper insight into atropisomerism for dinaphthoheteroles, we anticipated that group 14 dinaphthoheteroles having different substituents on the heteroatoms (Si, Ge and Sn) would be useful to obtain such chiral information. We report here the synthesis and fluxional behavior of the title dinaphthoheteroles **2** and **3**, involving the first example of optically active group 14 dinaphthoheteroles (Fig. 1).

## 2. Results and discussion

### 2.1. Synthesis of dinaphtho-siloles 2 and -germoles 3

Syntheses of dinaphtho[2,1-*b*;1′,2′-*d*]-siloles **2** and -gelmoles **3** were achieved by the conventional method for the



**1a**: M = PPh
**1b**: M = AsPh
**1c**: M = Sb*p*-Tol
**2a**: M = $SiMe_2$
**2b**: M = SiHMe
**2c**: M = SiHEt
**2d**: M = SiHPh
**3a**: M = $GeMe_2$
**3b**: M = GeHMe
**4** : M = $SnMe_2$

**Figure 1.**

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*Keywords*: silicon heterocycles; germanium and compounds; fluxional behavior; atropisomerism; $C_2$-symmetry.

[*] Corresponding author. Tel.: +81-76-229-1165; fax: +81-76-229-2781; e-mail: j-kurita@hokuriku-u.ac.jp

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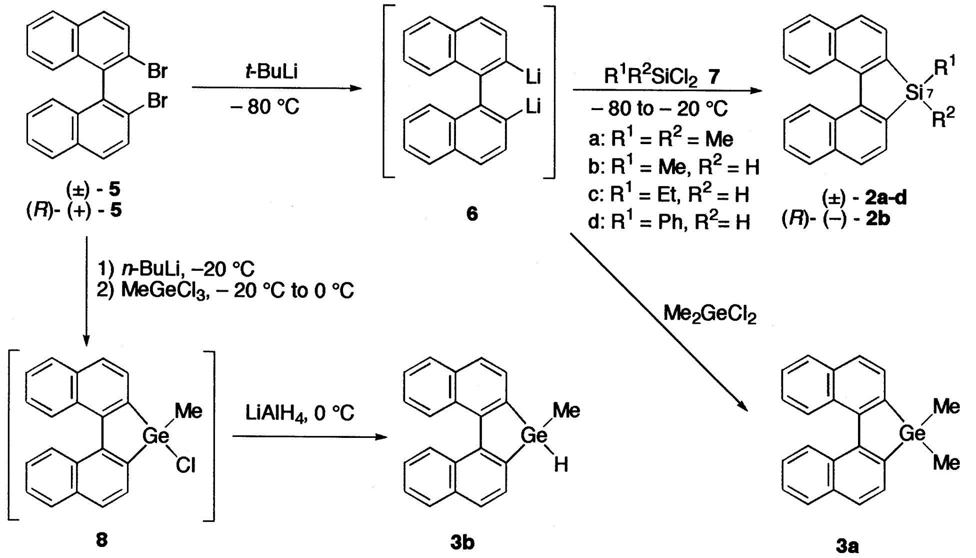

Scheme 1.

preparation of dinaphthoheteroles involving dilithiation of 2,2′-dibromo-1,1′-binaphthyl (DBBN) **5** followed by cyclization with halo-silane or -germane reagents, as shown in Scheme 1. Treatment of DBBN **5**, prepared from 2,2′-dihydroxy-1,1′-binaphthyl (BINOL) by the reaction with bromine and triphenylphosphane at high temperature (250–320°C),[14] with a large excess of *t*-BuLi (ca. 3 mol equiv.) under an argon atmosphere at low temperature (−80°C) afforded 2,2′-dilitho-1,1′-binaphthyl intermediate **6**,[4–6] which was reacted in situ with dichlorosilane reagents **7a–d** to give the expected dinaphtho[2,1-*b*;1′,2′-*d*]siloles **2a–d**.[5,6] The 7-methylsilole **2b** was isolated in 80% yield as crystals by recrystallization from hexane, whereas 7,7-dimethyl- **2a**,[4d,5,6] 7-ethyl- **2c**, and 7-phenyl-siloles **2d** were obtained as oils. When dichlorodimethylgermane was used instead of the silicon reagents **7** in the present reaction, dinaphthogermole **3a** was formed in 37% yield. However, all attempts to prepare dinaphthostannole **4** by the reaction of **6** with dichlorodimethylstannane or other tin reagents by a similar procedure failed. These results imply that appropriate bond length between carbon and heteroatom (Si, Ge, and Sn) and/or a preferable bond angle for carbon–heteroatom–carbon should be required for the formation of the heterole ring in the above reactions.[15]

These results prompted us to examine the preparation of germoles having different substituents on the germanium atom. For the preparation of the hydrogermole **3b**, condensation of the dilithium intermediate **6** with trichloromethylgermane and subsequent reduction of the resulted chlorogermole **8** with $LiAlH_4$ were performed due to the limited availability of dichloromethylgermane.[16] Additionally, in this reaction, a small excess of *n*-BuLi (1.1 mol equiv.) was employed instead of a large excess of *t*-BuLi as a lithium reagent to avoid undesirable reaction between resulted **8** and the excess lithium reagents. The DBBN **5** was subsequently treated with *n*-BuLi and trichloromethylgermane in anhydrous ether at −20 to 0°C to give the expected chlorogermole **8**. The chlorogermole **8** formed was characterizable by its $^1H$ NMR and mass spectra, but was susceptible to hydrolysis by moisture. Then the reaction mixture was applied to the next reduction step without isolation. When the reaction mixture was treated with excess $LiAlH_4$ in ether at 0°C, the desired hydrogermole **3b** was obtained in 44% yield (calculated from **5** used). We also tried alkylation and arylation of chlorogermole **8** with a variety of alkyl- and aryl-lithium or Grignard reagents, but all attempts failed.

## 2.2. Fluxional behavior of dinaphtho-siloles 2 and -germoles 3

The structure of dinaphthoheteroles **2** and **3** was elucidated mainly by their IR, MS (HR-MS) and $^1H$ NMR analyses. Absorptions of 2123–2133 $cm^{-1}$ for **2b–d** and 2046 $cm^{-1}$ for **3b** in their IR spectra showed the presence of Si–H and Ge–H bonds in their molecules, respectively. In the $^1H$ NMR spectrum of dimethyl compounds **2a** and **3a**, two methyl groups on the heteroatoms (Si and Ge) and all of the corresponding aromatic protons on the two naphthalene rings are equivalent, while in that of hydrosilole derivatives **2b–d** (in benzene-$d_6$; 400 MHz), some of the corresponding signals on the two naphthalene rings are non-equivalent and appear as two sets of signals as we anticipated; e.g. $\delta$ 7.30 and 7.31 (each *t*), and $\delta$ 8.09 and 8.13 (each *d*) for **2b**. The lowest pair of doublet signals at $\delta$ 8.09 and 8.13 was assigned to H(4) and H(10) due to the presence of NOE enhancement between the signals for H(5) and H(9) which appeared at $\delta$ 7.65–7.9 as multiplet. Furthermore, the $^1H$ NMR spectrum of **2b** exhibits temperature-dependent spectra, and the selected variable temperature $^1H$ NMR spectra of the aromatic region in toluene-$d_8$ are given in Fig. 2. At 27°C, the signals for H(4) and H(10) showed two sets of doublets centered at $\delta$ 7.99 and 8.02. At 75°C these signals coalesced, and at higher temperature (80°C) they changed to a doublet at $\delta$ 8.10. This spectral alteration should be attributable to the rapid interconversion between the atropisomeric conformations of the dinaphthyl backbone. Consequently, the free energy of activation ($\Delta G^{\ddagger}$) for racemization of **2b** arising from the flipping of the two naphthalene rings was calculated to be 77±2 kJ $mol^{-1}$ by the coalescence temperature method with these data. A

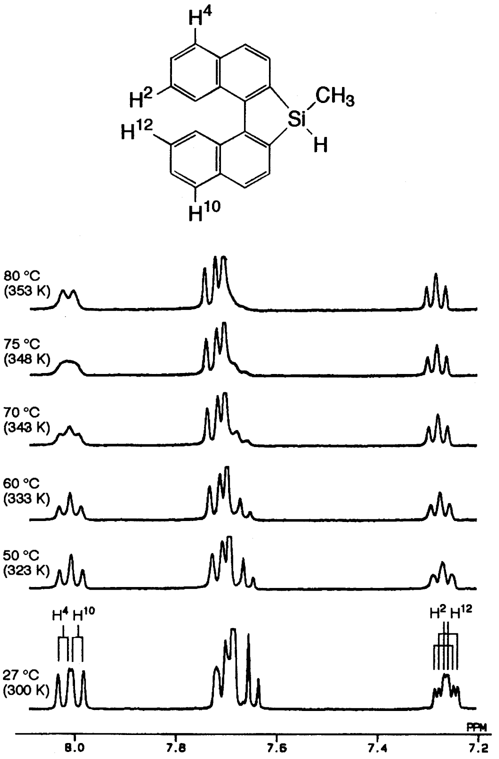

**Figure 2.** Variable temperature $^{1}H$ NMR data of the aromatic region for (±)-**2b** in toluene-$d_8$.

slightly lower value was obtained when the analysis was made by use of the signals for H(2) and H(12) instead of the signals for H(4) and H(10). A similar magnetic feature of the naphthyl protons on **2c**, **2d** and **3b** was also observed, and their $\Delta G^{\ddagger}$ values were estimated to be 77, 76 and 80±2 kJ mol$^{-1}$ in toluene-$d_8$, respectively (Table 2). These $\Delta G^{\ddagger}$ values are lower than those reported for the corresponding stibole derivative **1c** (85 kJ mol$^{-1}$),[13] but higher than those for phosphorus **1a** (56 kJ mol$^{-1}$),[9,10] arsenic **1b** (59 kJ mol$^{-1}$),[10] and sulfur (1: M=S$^{+}$–Me BF$_4^{-}$; 47–48 kJ mol$^{-1}$)[17] analogs.

**Table 2.** $^{1}H$ NMR data (toluene-$d_8$) and free energies of activation ($\Delta G_c^{\ddagger}$) obtained by the coalescence method for the exchange of $H^4$ and $H^{10}$ in **2b–d** and **3b**

| Compound (M) | $\Delta\delta$[a] ($H^4$–$H^{10}$ in Hz) | $T_c$[b] (K) | $\Delta G_c^{\ddagger}$[c] (kJ mol$^{-1}$) |
|---|---|---|---|
| **2b** (SiHMe) | 9.9 | 348 | 77 ± 2 |
| | 3.3 | 323 | 74 ± 2[d] |
| **2c** (SiHEt) | 13.7 | 353 | 77 ± 2 |
| **2d** (SiHPh) | 18.5 | 353 | 76 ± 2 |
| **3b** (GeHMe) | 7.9 | 358 | 80 ± 2 |

[a] ±0.37 Hz.

[b] ±5°C.

[c] The free energies of activation ($\Delta G_c^{\ddagger}$) were calculated using the equations: $k_r = \pi(\nu_{H(4)} - \nu_{H(10)})/\sqrt{2}$, $\Delta G_c^{\ddagger} = 19.1T_c[10.32 + \log(T_c/k_r)]10^{-3}$ kJ mol$^{-1}$.

[d] For the exchange of $H^2$ and $H^{12}$.

### 2.3. X-Ray crystal structure of 2b

Two alternative views of the molecular structure of 7-methyldinaphtho[2,1-*b*;1′,2′-*d*]silole **2b** are shown in Fig. 3. The important geometrical parameters are shown in Table 3.

A remarkable expansion of the acyclic moieties of the silylene bridged binaphthyl groups reflects the presence of significant repulsion in the binaphthyl groups; the distance between H(C1)–H(C13) is estimated to be 2.48(4) Å. It is also apparent that the two naphthalene groups are non-planar but somewhat bent; the torsion angles C(1)–C(13d)–C(4a)–C(5) and C(9)–C(9a)–C(13a)–C(13) are 171.3 and 170.0°, respectively. Around the five-membered silole moiety of **2b**, the bond lengths and bond angles of the silole ring are essentially the same as that of the 7,7-diphenyldinaphthosilole.[5] The geometry of the silicon atom is significantly deformed from the tetrahedral shape; the bond angles of C(6a)–Si(7)–C(14) and C(7a)–Si(7)–C(14) are expanded to 111.6 and 119.3°, respectively, while that of C(6a)–Si(7)–C(7a) in the five-membered ring is extremely narrowed to 91.6° which is significantly small compared to the idealized value of sp$^3$-hybridized silicon of 109.5°. This deformation suggests that some strain should be present in the silole ring. Although the silole ring is almost planar (standard deviation 0.08 Å), its inner (C(6a)–C(13c)–C(13b)–C(7a), 23.4°) and outer (C(13a)–C(13b)–C(13c)–C(13d), 39.4°) dihedral angles are relatively large compared to those for the corresponding thiophen (X=S, 10.8 and 25.9°),[17] phosphole (**1a**: 13.6 and 24.2°),[9b,c] arsole (**1b**: 15.3 and 26.4°),[10] and stibole (**1c**: 21.1 and 37.6°)[13] analoges. The larger value of the outer dihedral angle than that of the inner one for **2b** shows the presence of high steric repulsion between the

**Table 1.** Dinaphthoheteroles **2** and **3**

| Compound (M) | Reagent | Yield (%)[a] | IR (M–H) $\nu_{max}$ (cm$^{-1}$) | Formula | HR-MS (*m/z*: M$^{+}$) | |
|---|---|---|---|---|---|---|
| | | | | | Found | Required |
| **2a**[b] (SiMe$_2$) | Me$_2$SiCl$_2$ | 74 | – | $C_{22}H_{18}Si$ | 310.1181 | 310.1178 |
| **2b** (SiHMe) | MeHSiCl$_2$ | 80[c] | 2127 (KBr) | $C_{21}H_{16}Si$ | 296.1025 | 296.1021 |
| **2c** (SiHEt) | EtHSiCl$_2$ | 45 | 2123 (film) | $C_{22}H_{18}Si$ | 310.1180 | 310.1178 |
| **2d** (SiHPh) | PhHSiCl$_2$ | 25 | 2133 (film) | $C_{26}H_{18}Si$ | 358.1179 | 358.1178 |
| **3a** (GeMe$_2$) | Me$_2$GeCl$_2$ | 37 | – | $C_{22}H_{18}Ge$ | 356.0613 | 356.0625 |
| **3b** (GeHMe) | (1) MeGeCl$_3$, (2) LiAlH$_4$[d] | 41[e] | 2046 (film) | $C_{21}H_{16}Ge$ | 342.0458 | 342.0468 |

[a] Isolated yields.

[b] Lit.[5]

[c] Colorless prisms, mp 110–113°C.

[d] The chlorogermole **8** initially formed was reduced by treatment with LiAlH$_4$ without isolation. (See Section 4).

[e] The yield of **3b** was calculated from **5** used.

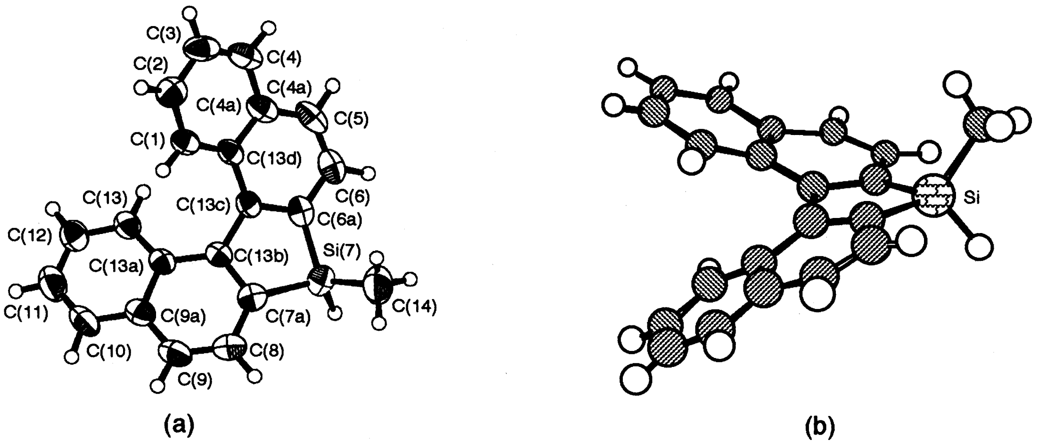

**Figure 3.** The X-ray crystal structures of 7-methyldinaphtho[2,1-*b*;1′,2′-*d*]silole **2b**: (a) ORTEP drawing, (b) side view.

two naphthalene rings fixed with the silole moiety. It is noteworthy that the inner and outer dihedral angles for **2b** are the largest among all of the dinaphthoheterols reported.

### 2.4. Synthesis of optically active (*R*)-7-methyldinaphtho[2,1-*b*;1′,2′-*d*]-silole 2b

It has been believed that, to isolate an isomer at ambient temperature, more than 95 kJ mol$^{-1}$ at 300 K of free energy of activation ($\Delta G^{\ddagger}$) was required between the isomers.[10] We undertook the preparation of optically active **2** from optically active DBBN (**5**), because, very recently, we successfully isolated optically active dinaphthostibole **1c**, of which the $\Delta G^{\ddagger}$ value has been calculated to be 85 kJ mol$^{-1}$ at 393 K by the coalescence method noted above.[13] (*R*)-(−)-**2b**.

The desired optically active **2b** could be readily prepared from optically active DBBN (*R*)-(+)-**5**[4a] ($[\alpha]_D^{23}=+32.6°$, >99% ee) according to the same procedure noted above as a mixture of (−)-**2b** and (+)-**2b** in 48% yield ($[\alpha]_D^{22}=-12.2$, *c* 1.22, benzene). Recrystallization of the product from pentane gave racemic (±)-**2b** as crystals, and more optically active (−)-**2b** having the specific rotation ($[\alpha]_D^{22}=-16.8°$ (*c* 3.45, benzene)) could be obtained from the mother liquid as an oil.[18] The optical rotation of (−)-**2b** isolated here decreased gradually at room temperature and the half-life ($t_{1/2}$) for racemization of (−)-**2b** was determined to be 7.2 h at 19°C in benzene. This result indicates that (−)-**2b** is slightly more optically stable than the corresponding antimony analogue (**1c**; $t_{1/2}$ 5.2 h at 20°C, benzene) at ambient temperature.

**Table 3.** Selected bond lengths, bond angles and torsion angles of **2b**

| | |
|---|---|
| Bond lengths (Å) | |
| $Si^{7}-C^{6a}$ | 1.865(3) |
| $Si^{7}-C^{7a}$ | 1.859(3) |
| $Si^{7}-C^{14}$ | 1.844(4) |
| $H^{1}-H^{13}$ | 2.48(4) |
| $C^{6a}-C^{13c}$ | 1.393(4) |
| $C^{7a}-C^{13b}$ | 1.386(4) |
| $C^{13b}-C^{13c}$ | 1.499(4) |
| Bond angles (°) | |
| $C^{6a}-Si^{7}-C^{7a}$ | 91.6(4) |
| $C^{6a}-Si^{7}-C^{14}$ | 111.6(2) |
| $C^{7a}-Si^{7}-C^{14}$ | 119.3(2) |
| $Si^{7}-C^{6a}-C^{13c}$ | 108.2(2) |
| $Si^{7}-C^{7a}-C^{13b}$ | 108.5(2) |
| $C^{6a}-C^{13c}-C^{13b}$ | 113.8(2) |
| $C^{7a}-C^{13b}-C^{13c}$ | 113.8(2) |
| Torsion angles (°) | |
| $C^{6a}-C^{13c}-C^{13b}-C^{7a}$ | 23.4(3) |
| $Si^{7}-C^{6a}-C^{13c}-C^{13b}$ | 16.4(3) |
| $C^{1}-C^{13d}-C^{4a}-C^{5}$ | 171.3(3) |
| $C^{13a}-C^{13b}-C^{13c}-C^{13d}$ | 39.4(4) |
| $Si^{7}-C^{7a}-C^{13b}-C^{13c}$ | 17.6(3) |
| $C^{9}-C^{9a}-C^{13a}-C^{13}$ | 170.0(3) |

## 3. Conclusion

To gain deeper insight into atropisomerism for dinaphthoheteroles, we have studied the synthesis of group 14 dinaphthoheteroles having different substituents on the hetero atom, and demonstrated that the condensation of 2,2′-dilithio-1,1′-binaphthyl, generated in situ from 2,2′-dibromo-1,1′-binaphthyl, with chlorosilane and chlorogermane reagents gave 7-substituted dinaphtho[2,1-*b*;1′,2′-*d*]-siloles **2** and -gelmoles **3**, respectively. The dinaphthoheterols obtained here are fluxional in the NMR time scale at elevated temperature as we expected, and the energy barrier for racemization of siloles **2b–d** and germole **3b** was estimated to be 76–77±2 and 80±2 kJ mol$^{-1}$, respectively. The half-life ($t_{1/2}$) for racemization of the optically active 7-methylsilole (*R*)-**2b** synthesized from optically active (*R*)-DBBN was also determined to be 7.2 h in benzene at 19°C.

## 4. Experimental

### 4.1. General

Melting points were determined on a Yanagimoto micro melting point hot-stage apparatus and are uncorrected. IR spectra were recorded with a Hitachi 270-30 spectrometer. Mass spectra (MS) and high-resolution mass spectra (HR-MS) were measured on a JEOL JMP-DX300 instrument (70 eV, 300 μA). NMR spectra were recorded on JEOL JNM-GSX-400 (400 MHz), JNM-ECP500 (500 MHz) or JNM-LA600 (600 MHz) spectrometers in the solvents noted in the experimental. Chemical shifts were given in δ values (ppm) referenced to the signals indicated in the experimental, and spectral assignments were confirmed by spin-decoupling and NOE experiments. UV absorption spectra were recorded on a Shimadzu UV-3000 spectrophotometer. Optical rotations were measured on a JASCO DIP-370 digital polarimeter in benzene. All chromatographic isolations were accomplished with either Kieselgel 60 (Merck) or Silica Gel 60N (Kanto Chemical). Ether was distilled from its $LiAlH_4$ suspension and dried over sodium wire. All of the silicon and germanium reagents were purchased from Gelest-Azmax, Japan, and used without further purification. All reactions were carried out under an argon atmosphere.

### 4.2. General procedure for the synthesis of 7-substituted-dinaphtho[2,1-*b*;1′,2′-*d*]siloles 2a–d

To a stirred solution of *t*-BuLi (1.56 M solution in pentane, 7.4 mL, 11.5 mmol) in anhydrous ether (20 mL) was added a solution of (±)-**5** (824 mg, 2.0 mmol) in anhydrous ether (20 mL) dropwise over 15 min at −80°C. After the solution was stirred for an additional 1 h at the same temperature, a solution of chlorosilane reagents ($Me_2SiCl_2$, $MeHSiCl_2$, $EtHSiCl_2$, or $PhHSiCl_2$: 5 mmol) in anhydrous ether (20 mL) was added dropwise over 10 min to the mixture with stirring at −80°C. The mixture was allowed to warm slowly to −20°C, then the stirring was continued for an additional 1 h. Benzene (100 mL) and water (50 mL) were added to the reaction mixture with stirring. The resulting organic layer was separated and the aqueous layer was extracted with benzene (50 mL). The combined organic layer was washed with brine, dried with anhydrous $Na_2SO_4$, filtered, and evaporated in vacuo. The residue was subjected to column chromatography on silica gel with a mixture of hexane–benzene (20:1–10:1) to give the dinaphthosiloles **2a**–**d**. The dinaphthosiloles **2a**–**d** thus obtained are listed together with the reagents used, yields, IR, and HR-MS analytical data in Table 1.

**4.2.1. 7,7-Dimethyldinaphtho[2,1-*b*;1′,2′-*d*]siloles 2a.** Colorless oil (lit.,[5] mp 36–38°C); $^1$H NMR ($CDCl_3$, 400 MHz, *J* in Hz, standard, $CH_2Cl_2$ δ 5.30) δ 0.48 (6H, s, $SiMe_2$), 7.38 (2H, m, 3- and 11-H), 7.51 (2H, m, 2- and 12-H), 7.82 (d, *J*=7.7 Hz) and 7.90 (d, *J*=7.7 Hz) (each 2H, 5-, 6-, 8- and 11-H), 7.94 (2H, d, *J*=7.7 Hz, 1- and 13-H), 8.00 (2H, d, *J*=8.8 Hz, 4- and 10-H); MS (EI) *m/z* 310 ($M^+$, 100%), 295 (31), 252 (19).

**4.2.2. 7-Methyldinaphtho[2,1-*b*;1′,2′-*d*]-silole 2b.** Pale yellow prisms, mp 110–113°C (hexane); $^1$H NMR (benzene-$d_6$, 400 MHz, *J* in Hz, standard, benzene δ 7.20) δ 0.36 (3H, d, *J*=3.7 Hz, Si–Me), 5.13 (1H, q, *J*=3.7 Hz, Si–H), 7.15 (2H, m, 3- and 11-H), 7.30 (t, *J*=7.0 Hz) and 7.31 (t, *J*=7.3 Hz) (each 1H, 2- and 12-H), 7.70 (1H, d, *J*=8.1 Hz, Naph–H), 7.74–7.89 (5H, m, Naph–H), 8.09 (d, *J*=8.4 Hz) and 8.13 (d, *J*=8.7 Hz) (each 1H, 4- and 10-H); $^{13}$C NMR ($CDCl_3$, 100 MHz, standard, $CDCl_3$ δ 77.00) δ −6.08(q), 124.42(d), 124.45(d), 126.01(d), 127.78(d), 127.81(d), 127.88(d), 128.14(d), 128.29(d), 128.35(d), 128.96(d), 129.06(d), 129.78(s), 129.86(s), 135.79(s), 135.86(s), 136.59(s), 136.72(s), 148.12(s), 148.18(s); $^{29}$Si NMR (benzene-$d_6$, 119.3 MHz, standard, TMS δ 0.00) δ −15.84; UV ($C_6H_{12}$) $\lambda_{max}$ nm (log ε) 228(4.41), 247(4.37), 260(4.27), 271(4.21), 286sh(3.61), 328sh(3.70), 344(3.90), 362(3.89); MS (EI) *m/z* 296 ($M^+$, 100%), 281 (39), 252 (45). Anal. Calcd for $C_{21}H_{16}Si$: C, 85.09; H, 5.44. Found: C, 85.33; H, 5.72.

**4.2.3. 7-Ethyldinaphtho[2,1-*b*; 1′,2′-*d*]silole 2c.** Colorless oil; $^1$H NMR (benzene-$d_6$, 400 MHz, *J* in Hz, standard, benzene δ 7.20) δ 0.91 (2H, dq, *J*=3.0 and 6.2 Hz, Si–$CH_2$), 0.99 (3H, t, *J*=6.2 Hz, $CH_3$), 5.11 (1H, t, *J*=3.0 Hz, Si–H), 7.15 (2H, m, 3- and 11-H), 7.30 (t, *J*=7.0 Hz) and 7.31 (t, *J*=7.0 Hz) (each 1H, 2- and 12-H), 7.67–7.74 (6H, m, Naph–H), 8.09 (d, *J*=8.8 Hz) and 8.13 (d, *J*=8.8 Hz) (each 1H, 4- and 10-H); MS (EI); $^{13}$C NMR ($CDCl_3$, 100 MHz, standard, $CDCl_3$ δ 77.00) δ 3.47(t), 7.86(q), 124.36(d), 125.98(d), 127.76(d), 127.89(d), 127.94(d), 128.23(d), 128.30(d), 129.22(d), 129.27(d), 129.73(s), 129.82(s), 135.69(s), 135.78(s), 135.83(s), 148.46(s), 148.55(s); $^{29}$Si NMR ($CDCl_3$, 119.3 MHz, standard, TMS δ 0.00) δ −11.86; *m/z* 310 ($M^+$, 51%), 281 (23), 252 (100).

**4.2.4. 7-Phenyldinaphtho[2,1-*b*;1′,2′-*d*]siloles 2d.** Colorless oil; $^1$H NMR (benzene-$d_6$, 400 MHz; *J* in Hz, standard, benzene δ 7.20) δ 5.69 (1H, s, Si–H), 7.09 (2H, t, *J*=6.6 Hz, Ph–H), 7.17 (1H, t, *J*=6.6 Hz, Ph–H), 7.19 (2H, m, 3- and 11-H), 7.30 (t, *J*=7.0 Hz) and 7.31 (t, *J*=7.0 Hz) (each 1H, 2-H and 12-H), 7.56 (2H, d, *J*=6.6 Hz, Ph–H), 7.67–7.76 (6H, m, Naph–H), 8.12 (d, *J*=8.4 Hz) and 8.17 (d, *J*=8.4 Hz) (each 1H, 4- and 10-H); MS (EI); $^{13}$C NMR ($CDCl_3$, 100 MHz, standard, $CDCl_3$ δ 77.00) δ 124.49(d), 126.23(d), 127.86(d), 128.00(d), 128.07(d), 128.29(d), 128.38(d), 129.35(d), 129.72(d), 130.48(d), 135.47(d), 129.91(s), 131.38(s), 134.89(s), 135.56(s), 135.98(s), 136.11(s), 148.75(s), 149.13(s); $^{29}$Si NMR ($CDCl_3$, 119.3 MHz, standard, TMS δ 0.00) δ −18.02; *m/z* 358 ($M^+$, 100%), 279 (24), 252 (36).

**4.2.5. Synthesis of 7,7-dimethyldinaphtho[2,1-*b*;1′,2′-*d*]-germole 3a.** To a stirred solution of 2,2′-dilithio-1,1′-binaphthyl, prepared from (±)-**5** (417 mg, 1.01 mmol) and *t*-BuLi (1.60 M solution in pentane, 3.8 mL, 6.1 mmol) in anhydrous ether (20 mL) as described for the preparation of **2**, was added a solution of dichlorodimethylgermane (427 mg, 2.46 mmol) in ether (10 mL) at −80°C. After the solution was stirred for 1 h at the same temperature, the mixture was allowed to warm slowly to −20°C, then the stirring was continued for an additional 1 h. The reaction mixture was diluted with benzene (50 mL) and the reaction was quenched by addition of water (30 mL). The resulting organic layer was separated and the aqueous layer was extracted with benzene (30 mL). The combined organic layer was washed with brine, dried with anhydrous $Na_2SO_4$, filtered, and evaporated in vacuo. The residue was subjected to column chromatography on silica gel with a mixture of hexane–$CH_2Cl_2$ (10:1) to give **3a** (137 mg, 37%) as a colorless oil, $^1$H NMR ($CDCl_3$, 500 MHz, *J* in Hz, standard, $CH_2Cl_2$ δ 5.30) δ 0.64 (6H, s, $SiMe_2$), 7.35 (2H, t, *J*=7.3 Hz, 3- and 11-H), 7.49 (2H, t, *J*=7.3 Hz, 2- and 12-H), 7.82 (d, *J*=7.8 Hz) and 7.90 (d, *J*=7.8 Hz) (each 2H, 5-, 6-, 8- and 9-H), 7.93 (2H, d, *J*=7.3 Hz, 1- and 13-H), 7.95 (2H, d, *J*=7.3 Hz, 4- and 10-H); $^{13}$C NMR ($CDCl_3$, 100 MHz, standard, $CDCl_3$ δ 77.00) δ −2.57(q), 124.25(d), 125.23(d), 127.88(d), 127.92(d), 128.23(d), 128.92(d), 130.21(s), 135.22(s), 142.45(s), 145.26(s); MS (EI) *m*/*z* 356 ($M^+$, 81%), 341 (63), 252 (100).

**4.2.6. Synthesis of 7-methyldinaphtho[2,1-*b*;1′,2′-*d*]germole 3b via chlorogermole 8.** To a stirred solution of (±)-**5** (416 mg, 1.01 mmol) in anhydrous ether (30 mL) was added a hexane solution of *n*-BuLi (1.0 mL, 1.50 M, 1.50 mmol) at −20°C. After the reaction mixture was stirred for 1 h at the same temperature, a solution of trichloromethylgermane (424 mg, 2.19 mmol) in ether (10 mL) was added dropwise. After the addition was complete, the reaction mixture was warmed to 0°C and stirred for an additional 1 h. The chlorogermole **8** formed was susceptible to hydrolysis by moisture, then the reaction mixture was applied to the next reduction step without isolation. The above reaction mixture containing chlorogermole **8** was added to a suspension of $LiAlH_4$ (95%, 115 mg, 2.87 mmol) in ether (5 mL) from syringe over 10 min at 0°C, and the mixture was stirred for an additional 1 h. The mixture was diluted with ether (50 mL) and the reaction was quenched by careful addition of water (50 mL). After the reaction mixture was filtered, the filtrate was separated and the aqueous layer was extracted with ether (50 mL). The combined organic layer was washed with brine, dried with anhydrous $Na_2SO_4$, filtered, and evaporated in vacuo. The residue was subjected to column chromatography on silica gel with a mixture of hexane–$CH_2Cl_2$ (10:1) to give the dinaphthogermole **3b** (142 mg, 41%) as a colorless oil, $^1H$ NMR (benzene-$d_6$, 40 MHz, *J* in Hz, standard, benzene $\delta$ 7.20) $\delta$ 0.49 (3H, d, $J$=3.3, Ge–Me), 5.40 (1H, q, $J$=3.3 Hz, Ge–H), 7.14 (2H, m, 3- and 11-H), 7.29 (t, $J$=7.0 Hz) and 7.31 (t, $J$=7.0 Hz) (each 1H, 2- and 12-H), 7.68–7.82 (6H, m, Naph–H), 8.09 (d, $J$=9.2 Hz) and 8.11 (d, $J$=9.2 Hz) (each 1H, 4- and 10-H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, standard, $CDCl_3$ $\delta$ 77.00) $\delta$ −5.07(q), 124.35(d), 125.62(d), 127.82(d), 128.20(d), 128.26(d), 129.31(d), 129.37(d), 129.88(s), 129.95(s), 135.24(s), 135.28(s), 139.18(s), 139.44(s), 145.83(s), 145.90(s); MS (EI) *m*/*z* 342 ($M^+$, 28%), 327 (26), 252 (100).

**4.2.7. 7-Chloro-7-methyldinaphtho[2,1-*b*;1′,2′-*d*]germole 8.** $^1H$ NMR (benzene-$d_6$, 400 MHz; *J* in Hz, standard, benzene $\delta$ 7.20) $\delta$ 1.84 (3H, s, Ge–Me), 8.09 (2H, m, 3- and 11-H), 8.26 (2H, m, 2- and 12-H), 8.64–8.73 (6H, m, Naph–H), 8.85 (d, $J$=8.4 Hz) and 8.97 (d, $J$=8.8 Hz) (each 1H, 4- and 10-H); MS (EI) *m*/*z* 376 ($M^+$, 20%), 325 (13), 252 (100).

**4.2.8. Synthesis of optically active (*R*)-(−)-7-methyldinaphtho[2,1-*b*;1′,2′-*d*]siloles 2b.** All operations in this procedure were performed below rt. The reaction was carried out essentially the same as in the reaction with the silicon reagent described earlier, except for the use of optically active (*R*)-(+)-DBBN **5** instead of the racemic (±)-**5**. The reaction mixture obtained from the reaction of (*R*)-(+)-**5** ($[\alpha]_D^{23}=+32.6°$, 712 mg, 1.15 mol) with *t*-BuLi (1.56 M, 6.5 mL, 10.1 mmol) and dichloromethylsilane (430 mg, 3.74 mmol) was separated by column chromatography on silica gel with a mixture of pentane–$CH_2Cl_2$ (10:1) to give a mixture of (−)-**2b** and (+)-**2b** ($[\alpha]_D^{19}=-12.2°$, 248 mg, 48 % yield). Recrystallization of the mixture (236 mg) from pentane (ca. 1.0 mL) gave racemic (±)-**2b** (110 mg) as crystals and a more optically active product (121 mg, $[\alpha]_D^{19}=-18.8°$(*c* 3.5 benzene)) as an oil.[18]

**4.3. Racemization experiment of optically active 2b.** The decrease of the $[\alpha]_D$ value of a solution of optically active **2b** ($[\alpha]_D^{19}=-12.2°$, *c* 1.2 benzene) was monitored every 30 min for 20 h by digital polarimeter. The first order rate constant for racemization of **2b** is $k^{19°C}=2.66\times10^{-5}\ s^{-1}$ (benzene).

**4.4. Crystal structure determination of 2b.** Crystal data. $C_{21}H_{16}Si$, $M$=296.44, monoclinic, $a$=8.9300(10), $b$=11.4831(13), $c$=15.437(2) Å, $\beta$=92.565(2), $V$=1581.4(3) $Å^3$, $T$=296 K, space group $P2_1/c$ (# 14), $Z$=4, $D_{calc}=1.245\ g\ cm^{-3}$. Crystal dimensions $0.55\times0.40\times0.35\ mm^3$, $\mu$(Mo K$\alpha$)=$1.42\ cm^{-1}$. Data collection and processing: Brucker Smart 1000 CCD diffractometer with graphite monochromated Mo K$\alpha$ ($\lambda$=0.71069 Å) radiation, 3877 reflections measured, giving 1584 with $I>1.00\sigma(I)$. Absorption correction was not applied. The structure was solved by direct methods using SIR92[19] and was refined by full-matrix least-squares techniques using DIRDIF94.[20] The non-hydrogen atoms were refined anisotropically. The final residuals for reflections with $I>1.00\sigma(I)$ were $R$=0.042, $Rw$=0.038. Full details of the crystallographic results have been deposited with the Cambridge Crystallographic Data Center (no. CCDC 174116).

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