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Ir-Catalyzed Synthesis of Substituted Tribenzosilepins by Dehydrogenative C-H/Si-H Coupling

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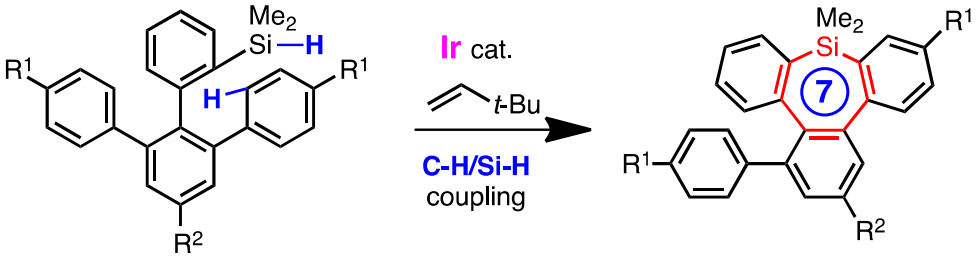


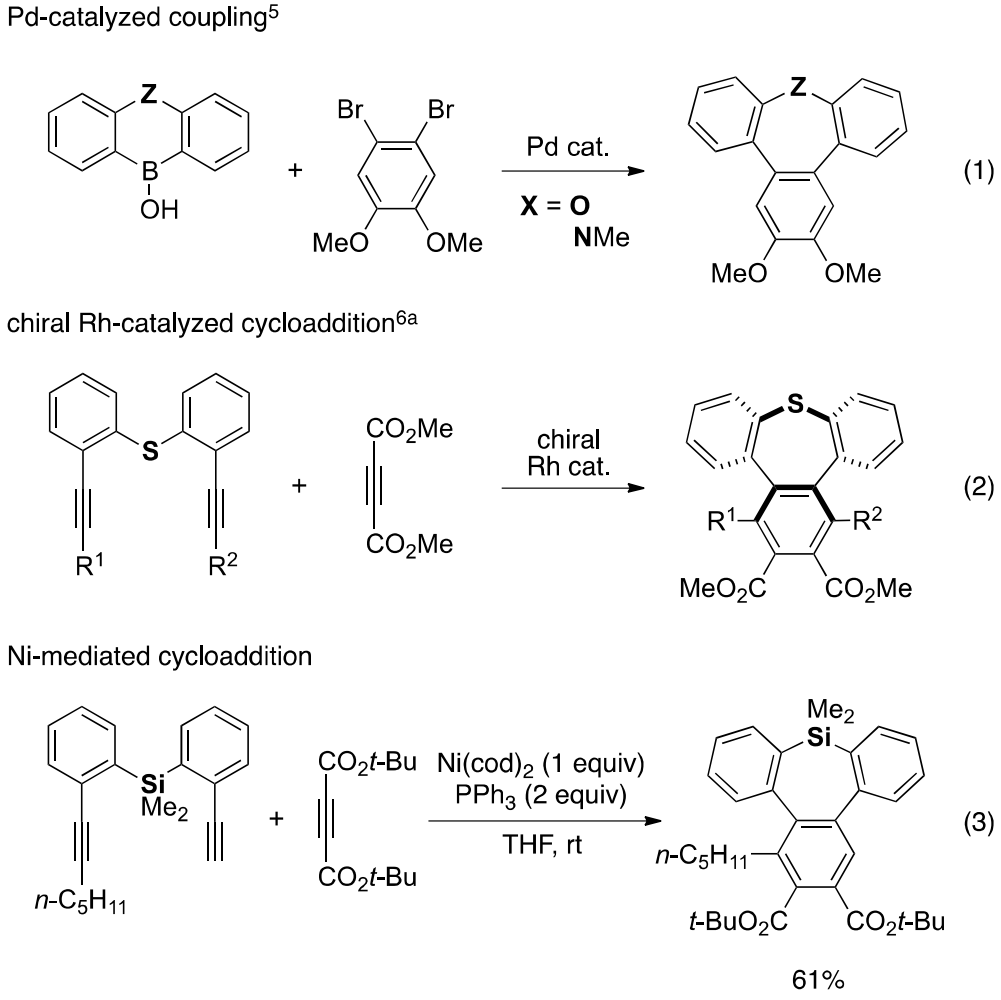
ABSTRACT. The Ir-catalyzed intramolecular reaction of 2',6'-diaryl-2-(hydrosilyl)biphenyls gave substituted tribenzosilepins by direct dehydrogenative C-H/Si-H coupling. This is the first example of catalytic construction of the tribenzosilepin skeleton. Enantiomerically pure tribenzosilepin was

prepared by optical resolution using chiral HPLC, and its inversion barrier was calculated by measurement of rate of racemization using the Eyring kinetic equation under heating conditions.

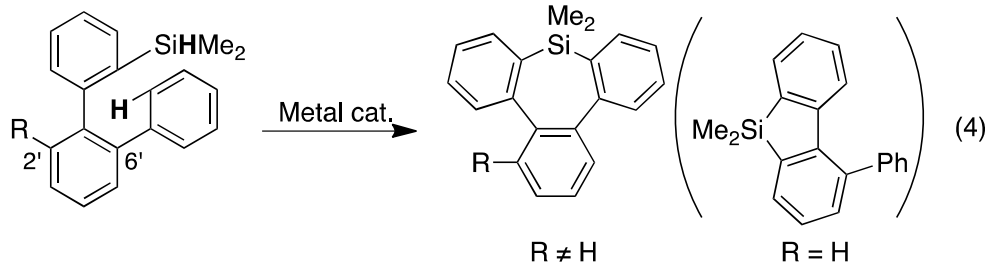
INTRODUCTION

Heteropin has a seven-membered 8π conjugated system including a heteroatom (Z) in the ring system. It is tub-shaped and non-aromatic.[1] Tribenzoheteropin is a three-benzene-fused heteropin, the saddle-shaped structure of which is generally more stable than that of heteropin.[2] Tribenzoheteropins, such as tribenzazepin (Z = NR), tribenzoxepin (Z = O), and tribenzosilepin (Z = SiR_2), are found in the substructures of functional materials.[3] Among various tribenzoheteropins, a method for the synthesis of tribenzosilepin remains undeveloped: the reaction of the dilithium salt of a teraryl compound with dimethylsilyl dichloride has been reported, but the yield is very low (3.5%).[4,5] While there are many reports on the synthesis of other tribenzoheteropins, strategy for the catalytic construction of the heteropin core have been quite limited: consecutive Suzuki-Miyaura coupling was reported for the synthesis of tribenzoxepins and a tribenzazepin (eq 1 in Scheme 1).[6] In contrast, we recently reported the catalytic and enantioselective [2+2+2] cycloaddition of sulfur-containing 1,8-diynes with an alkyne for the synthesis of chiral tribenzothiepins (eq 2 in Scheme 1).[7] In the course of this study, we examined the reaction of silicon-containing 1,8-diynes for the synthesis of tribenzosilepins and realized a Ni complex-mediated cycloaddition (eq 3 in Scheme 1), but we could not achieve a catalytic reaction.

Scheme 1. Catalytic Construction of Heteropin Core and Cycloaddition for the Synthesis of Tribenzosilepin

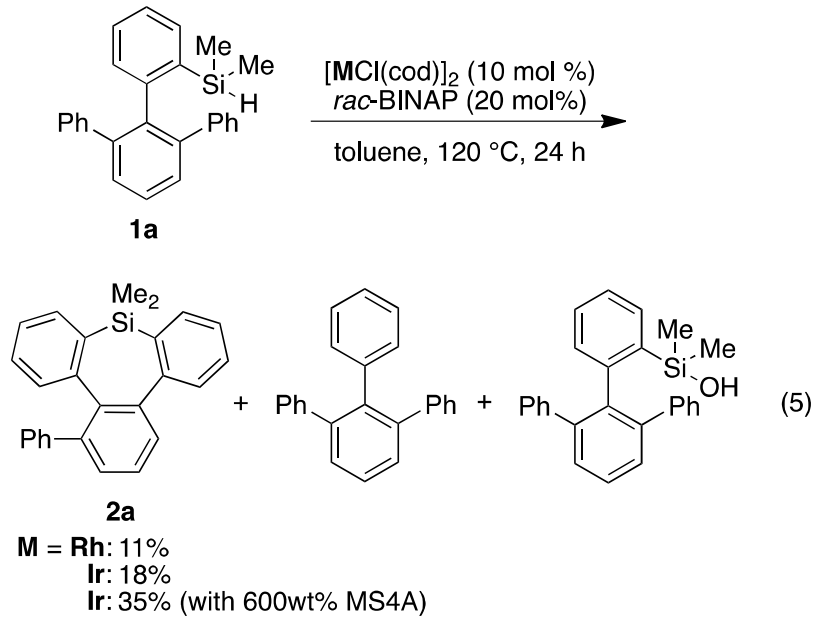


We here considered the use of dehydrogenative C-H/Si-H coupling for the construction of a silepin core. Kuninobu and Takai originally developed the Rh-catalyzed C-H/Si-H coupling of 2-biarylsilanes for the synthesis of dibenzosilole,[8] and Takai's group and another group reported the further use of this transformation,[9] including enantioselective variants.[10] To suppress the formation of five-membered silole, we designed a 2'-substituted-6'-aryl-2-biphenyl silane for the selective construction of a seven-membered ring (eq 4).



RESULTS AND DISCUSSION

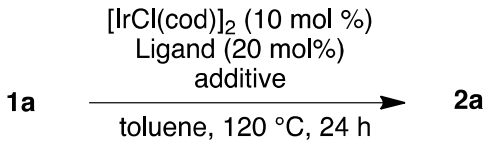
We chose 2',6'-diphenyl-2-(dimethylhydrosilyl)biphenyl (**1a**) as a model substrate and subjected it to dehydrogenative C-H/Si-H coupling using Rh or Ir catalyst having a *rac*-BINAP ligand in refluxing toluene (eq 5). The iridium catalyst gave desired tribenzosilepin **2a** in a better yield of 18% along with desilylated product and silanol, which is probably a hydrolyzed product resulting from the presence of water.[11] When the Ir-catalyzed reaction was conducted under dehydrated conditions in the presence of MS4A, a significant increase in the yield was observed.



To further increase the yield, we screened phosphine ligands for the Ir-catalyzed reaction (Table 1). While a mono-phosphine ligand was ineffective, a diphosphine ligand possessing a longer alkylene tether gave a better yield of **2a**, and DPPB achieved a moderate yield of 58% (entries 1-4). *ortho*-phenylene-tethered diphosphine resulted in the best yield of ca. 70% (entry 5). A comparable yield

was achieved in the absence of 4Å molecular sieves through the use of freshly distilled toluene as a solvent (entry 6). Since the addition of a bulky alkene as a hydrogen acceptor[8b] further increased the yield, we determined that this represented the optimal reaction conditions (entry 7). Moreover, recrystallization of **2a** gave a single crystal, which was submitted to X-ray analysis and its saddle-shaped structure was ascertained (Figure 1).

Table 1. Screening of Phosphine Ligand for Ir-Catalyzed C-H/Si-H Coupling of 1a



entry	ligand	additive	yield (%)
1	PPh_3[a]	4Å MS (600 wt%)	trace
2	DPPE	4Å MS (600 wt%)	6
3	DPPP	4Å MS (600 wt%)	11
4	DPPB	4Å MS (600 wt%)	58
5	DPPBen	4Å MS (600 wt%)	68
6[b]	DPPBen	none	68
7[b]	DPPBen	3,3-dimethylbut-1-ene (1 equiv)	77

[a] Triphenylphosphine (40 mol %) was used. [b] Freshly distilled toluene was used as a solvent.
Ligand: DPPE: 1,2-bis(diphenylphosphino)ethane; DPPP: 1,3-bis(diphenylphosphino)propane; DPPB: 1,4-bis(diphenylphosphino)butane; DPPBen: 1,2-bis(diphenylphosphino)benzene

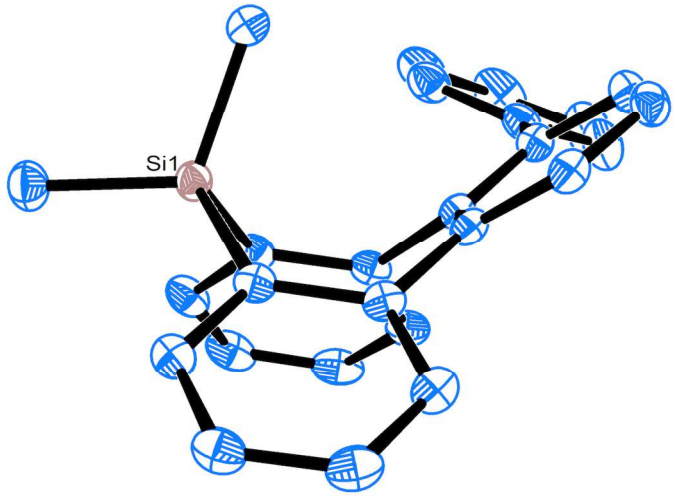
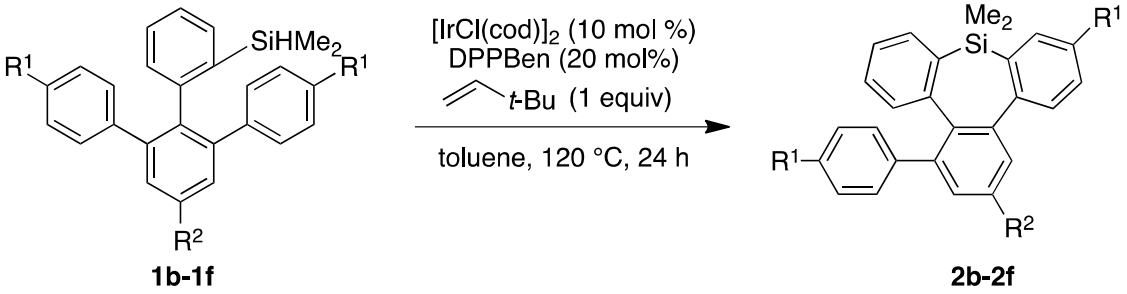


Figure 1. ORTEP Diagram of Compound 2a (thermal ellipsoids shown at 50% probability)

The substrate scope of the present Ir-catalyzed C-H/Si-H coupling was examined under the optimal conditions (Table 2). When both electron-donating and -withdrawing groups were installed at the *para*-position of the two aryl groups, the corresponding tribenzosilepins **2b**-**2d** were obtained in acceptable yields (entries 1-3). However, trifluoromethyl as a stronger electron-withdrawing group suppressed the reaction, **2e** was obtained in a moderate yield as a mixture with the desilylated product (entry 4). The methyl-substituted tetraarylsilane **1f** was transformed into tribenzosilepin **2f** in high yield (entry 5).

Table 2. Substrate Scope of Ir-Catalyzed C-H/Si-H Coupling

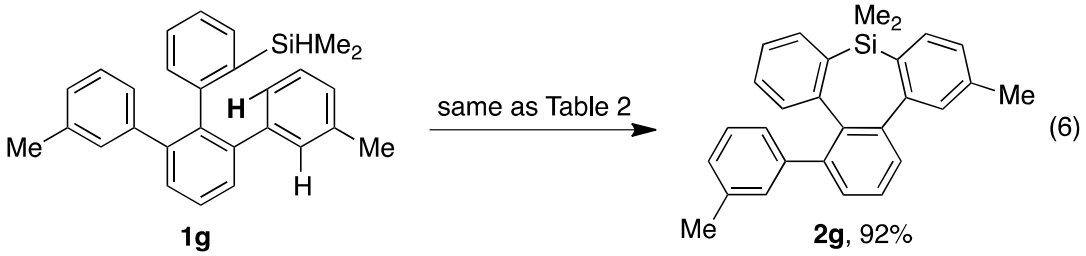


1b-1f **2b-2f**

entry		R^1	R^2	yield (%)
1	**1b**	MeO	H	**2b**, 67
2	**1c**	Me	H	**2c**, 84
3	**1d**	Cl	H	**2d**, 67
4	**1e**	CF_3	H	**2e**, 45[a]
5	**1f**	H	Me	**2f**, 90

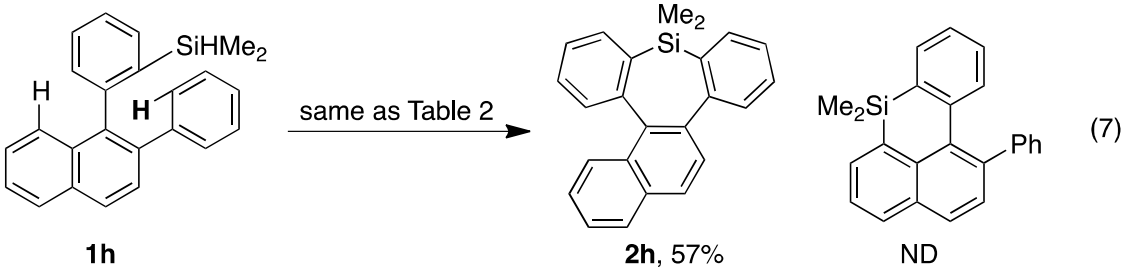
[a] NMR yield.

In the reaction of *meta*-substituted substrate **1g**, while there are two C-H bonds that may be cleaved, the less hindered C-H bond was selectively cleaved, and tribenzosilepin **2g** was obtained as a sole product in the best yield of 92% among all entries (eq 6).



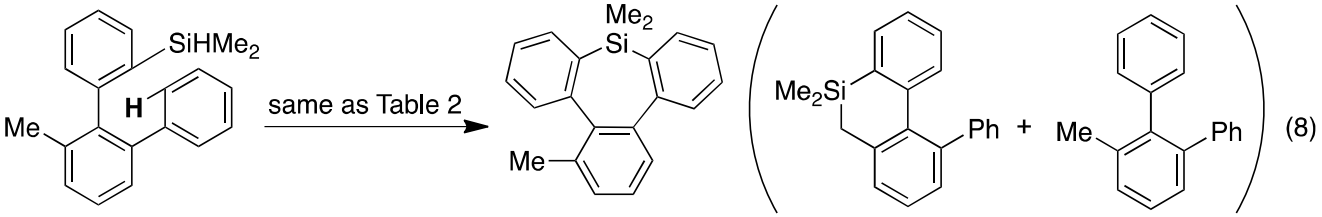
1g **2g**, 92%

Naphthalene-containing substrate **1h** was also used in this reaction, and selective formation of a seven-membered ring was achieved, while the formation of a six-membered ring by C-H bond activation of the peri position of the naphthalene ring was not be observed at all (eq 7).[12]



1h **2h**, 57% ND

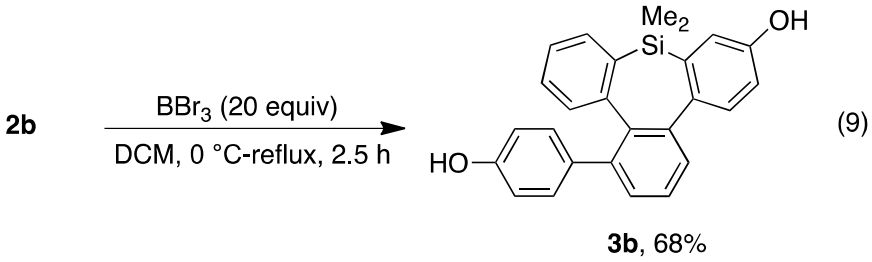
In the reaction of methyl- and phenyl-substituted biphenylsilane **1i**, sp^3 C-H bond cleavage at the benzylic position also proceeded[13] in addition to sp^2 C-H bond cleavage, and the yield of tribenzosilepin **2i** was low (eq 8).



1i **2i**, 24% ca. 30% (2.5/1 by NMR)

All of substituted tribenzoheteropins potentially have chirality, but their stability strongly depends on the heteroatom and the substituent(s).[6a] We examined the optical resolution of tribenzosilepin **2b** by

chiral HPLC, but could not completely resolve the racemic mixture because of its low polarity. However, when we transformed it to polar diol **3b** by using an excess amount of BBr_3 (eq 9),[14] we achieved complete separation by chiral HPLC. We measured the circular dichroism (CD) spectra of the two isolated fractions (faster and slower): they displayed perfect mirror symmetry, which indicated that they are enantiomers (Figure 2). The simulated CD spectrum of (*S*,*R*)-**3b** was in good agreement with the experimental results, and revealed that it corresponded to the slower peak.



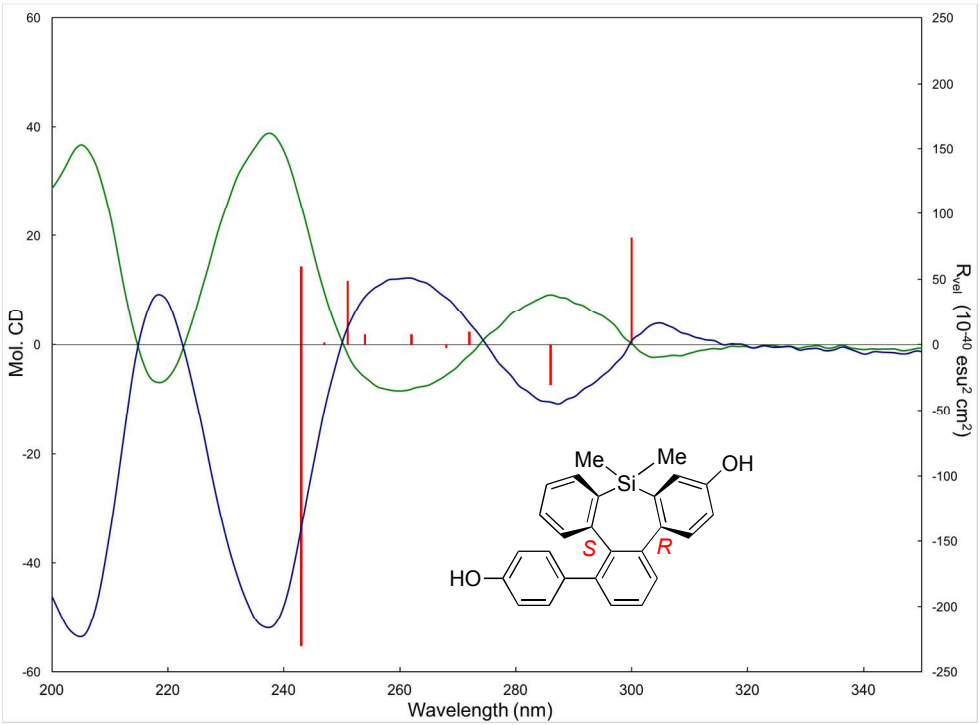


Figure 2. (a) CD spectra of both enantiomers of **3b** (faster: green curve, slower: blue curve). CD spectra of **3b** in CH_3CN solution (green:1.27×10^{-3} M, blue:1.01×10^{-3} M). Maximum values were 205, 219, 238, 260, 286, 304 nm. (b) TD-DFT calculations of (*S*,*R*)-isomer (red bar). Simulated CD spectrum was calculated by time-dependent DFT method at the CAM-B3LYP level of theory with 6-31G(d,p) basis set using Gaussian 09 program.

Tribenzosilepin **3b** was stable at 60 °C for 1 h, but racemization was observed at 90 °C. The rate constant of racemization for **3b** at 90 °C (363 K) was determined to be 1.03×10^{-5} s^{-1}, and the barrier to saddle inversion ($\Delta G^{\ddagger}$) was calculated to be 29.7 kcal per mole, according to the Eyring equation (Figure 3),[15] which means that the half-life of **3b** at 20 °C (293 K) is 24 years,[16] and that it hardly racemizes at room temperature.

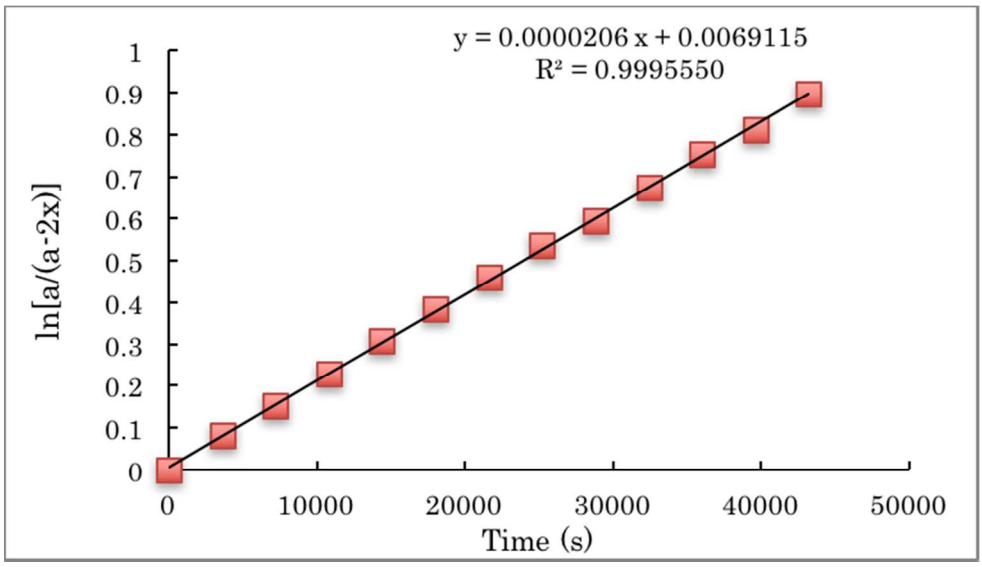


Figure 3. Rate of racemization. Plot of ln[a/(a-2x)] versus t (s), a is the concentration of an enantiomer of **3b** (a = 1.00) and x is the concentration of newly generated opposite enantiomer at time t. A linear curve fitting equation

CONCLUSIONS

In summary, we achieved the first catalytic construction of a tribenzosilepin skeleton by Ir-catalyzed C-H/Si-H coupling. The intramolecular reaction of 2',6'-diaryl-2-(dimethylhydrosilyl)biphenyls gave substituted tribenzosilepin derivatives along with the formation of a seven-membered ring. An enantiomerically pure tribenzosilepin was prepared by optical resolution, and the inversion barrier of the chiral saddle-shaped molecule was elucidated.

EXPERIMENTAL SECTION

General: ^{1}H-NMR spectra were recorded on JEOL AL-500 (500 MHz) spectrometers. The chemical shifts were reported in parts per million (δ) relative to internal TMS (0 ppm) for $CDCl_3$. The coupling constants, J, are reported in Hertz (Hz). ^{13}C NMR spectra were obtained by JEOL AL-500 (125 MHz) spectrometer and referenced to the internal solvent signal (central peak is 77.0 ppm) in $CDCl_3$). ^{19}F NMR spectra were obtained by JEOL AL-500 (470 MHz) spectrometer and trifluoroacetic acid was used as an external standard. $CDCl_3$ was used as a NMR solvent. High-resolution mass spectra (HRMS) were measured on a TOFMS using JMS-T100CS with ESI (Electro Spray Ionization) method and DART (Direct Analysis in Real Time) method.[16] Preparative thin-layer chromatography (PTLC) was performed with silica gel-precoated glass plates (Wakogel B-5F) prepared in our laboratory. Flash column chromatography was performed over silica gel 200-300. All reagents were weighed and handled in air and backfilled with argon at room temperature. Unless otherwise noted, all reactions were conducted under an argon atmosphere. Toluene was distilled from CaH_2 under an argon atmosphere and was used immediately as a solvent. All reagents were purchased from Wako, Kanto, Aldrich, TCI, and Strem and used without further purification.

Synthetic scheme for the preparation of substrates 1

An experimental procedure for the synthesis of 2,6-diphenyliodobenzene: A solution of phenylmagnesium bromide was prepared from Mg (390 mg, 16 mmol) in dry THF (15 ml) and bromobenzene (1.7 ml, 16 mmol). To this solution, a solution of 1,3-dibromo-2-iodobenzene (1.45 g, 4.0 mmol) in dry THF (12 ml) was added dropwise, and the resulting mixture was stirred at room temperature for 3 hours. After cooling to 0 °C, a solution of I_2 (3.25 g, 12.8 mmol) in dry THF (12 ml) was added dropwise to the above mixture. The solution was stirred overnight at 0 °C. After the quenched with a saturated aqueous $Na_2S_2O_3$, the mixture was extracted with Et_2O. the organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure.[18] The crude products were purified by column chromatography on silica gel (hexane only) to give 2,6-diphenyliodobenzene (981 mg, 2.75 mmol, 69%), whose physical properties were accorded with those in the literature.[19] In the

case of substituted 2,6-diphenyliodobenzenes, the crude products were passed through a short plug of silica gel and subject them to next reaction without further purification.

An experimental procedure for the synthesis of 2-bromo-6'-phenyl-1,1':2',1"-terphenyl: To a solution of 2,6-diphenyliodobenzene (425 mg, 1.2 mmol) in dry toluene (18 ml) at -20 °C was added *n*-BuLi (1.6 ml, 1.55 M in hexane) dropwise over 5 min under an atmosphere of argon. After stirring for 5 min, 1,2-dibromobenzene (0.22 ml, 1.8 mmol) was added dropwise over 5 min, and the resulting mixture was allowed to warm to room temperature, and stirred for 2 h. After the reaction was quenched with MeOH (9 ml) at -78 °C, the mixture was allowed to warm to room temperature for 1 h. After the solvent was evaporated, the residue was purified by column chromatography on silica gel (hexane/DCM = 20/1) and recrystallization with hexane to afford 2-bromo-6'-phenyl-1,1':2',1"-terphenyl (288 mg, 0.75 mmol, 63%).[20] Mp 180-182 °C; ^{1}H NMR δ 7.55-7.51 (m, 1H), 7.44-7.42 (m, 2H),7.26-7.25 (m, 3H), 7.15-7.14 (m, 8H), 7.00-6.99 (m, 2H), 6.91-6.87(m, 1H); ^{13}C NMR δ 142.0, 141.3, 140.7, 138.0, 133.4, 132.0, 129.6, 129.3, 128.2, 128.0, 127.4, 126.4, 126.2, 125.1; HRMS(DART, positive) calcd for $C_{24}H_{21}{}^{79}BrN$ $[M + NH_4]^+$: 402.0852; found: 402.0844. In the case of substituted 2-bromo-6'-phenyl-1,1':2',1"-terphenyls, the crude products were isolated by column chromatography on silica gel and subject them to next reaction without further purification.

An experimental procedure for the synthesis of Dimethyl(6'-phenyl-[1,1':2',1"-terphenyl]-2-yl)silane (1a): A solution of 2-bromo-6'-phenyl-1,1':2',1"-terphenyl (78 mg, 0.2 mmol) in THF (1 ml) was cooled to -78 °C, and *n*-BuLi (0.4 ml, 1.55 M in hexane) was added dropwise under an atmosphere of argon. After 15 min, chlorodimethylsilane (88 μl, 0.8 mmol) was added dropwise at -78 °C and the mixture was allowed to warm to room temperature slowly. After 12 h, the reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with DCM. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was isolated by column chromatography on silica gel (hexane only) and thin-layer chromatography (hexane/DCM = 20/1) to give dimethyl(6'-phenyl-[1,1':2',1"-terphenyl]-2-yl)silane (**1a**) (45.5mg, 0.12 mmol, 62%).[10b] Mp 67-70 °C;

^{1}H NMR δ 7.51-7.48 (m, 1H), 7.42-7.41 (m, 2H), 7.20-7.18 (m, 1H), 7.14-7.04 (m, 12H), 6.98-7.97 (m, 1H), 3.89-3.3.86 (m, 1H), -0.18 (d, J = 3.7 Hz, 6H); ^{13}C NMR δ 145.3, 141.8, 141.7, 140.1, 137.8, 133.8, 132.2, 130.2, 129.3, 127.7, 127.5, 127.4, 126.1, 125.8, -3.4; HRMS(ESI, positive) calcd for $C_{26}H_{24}NaSi$ $[M + Na]^+$: 387.1539; found: 387.1540.

Typical experimental procedure for intramolecular silylation of 1: $[Ir(cod)_2Cl]_2$ (3.4 mg, 0.005 mmol), DPPBen (4.5 mg, 0.01 mmol), silane (18.2 mg, 0.05 mmol) and 3,3-dimethyl-1-butene (6.5 µl, 0.05 mmol) were dissolved in distilled toluene (1 ml). The resulting mixture was stirred at 120 °C. After stirring for 24 h, the solution was filtered through a short plug of silica gel with ethyl acetate and the filtrate was evaporated under reduced pressure. The crude products were purified by thin-layer chromatography (hexane/dichloromethane = 20/1) to give compound **2**.

Dimethyl(6'-phenyl-[1,1':2',1"-terphenyl]-2-yl)silane (1a). Isolated by thin-layer chromatography (hexane/dichloromethane = 20/1, Rf = 0.3). The title compound was obtained as a white solid (41.5 mg, 0.12 mmol, 62%). Mp 67-70 °C; ^{1}H NMR δ 7.51-7.48 (m, 1H), 7.42-7.41 (m, 2H), 7.20-7.18 (m, 1H), 7.14-7.04 (m, 12H), 6.98-6.97 (m, 1H), 3.89-3.86 (m, 1H), -0.18 (d, J = 3.7 Hz, 6H); ^{13}C NMR δ 145.3, 141.8, 141.7, 140.1, 137.8, 133.8, 132.2, 130.2, 129.3, 127.7, 127.5, 127.4, 126.1, 125.8, -3.4; HRMS(ESI, positive) calcd for $C_{26}H_{24}NaSi$ $[M+Na]^+$: 387.1539; found: 387.1540.

Dimethyl(4"-methoxy-6'-(4-methoxyphenyl)-[1,1':2',1"-terphenyl]-2-yl) silane (1b). Isolated by silica gel column chromatography (hexane/ethyl acetate = 8/1) + thin-layer chromatography (hexane/dichloromethane = 20/1, 4 times, Rf = 0.6). The title compound was obtained as a white solid (93.2 mg, 20% in three steps). Mp 108-110 °C; ^{1}H NMR δ 7.46-7.42 (m, 1H), 7.36-7.35 (m, 2H), 7.23-7.22 (m, 1H), 7.08-7.06 (m, 2H), 6.99-6.96 (m, 5H), 6.66 (d, J = 8.9 Hz, 4H), 3.89-3.84 (m, 1H), 3.72 (s, 6H), -0.16 (d, J = 3.8 Hz, 6H); ^{13}C NMR δ 158.0, 145.8, 141.4, 140.0, 137.8, 134.3, 133.9, 132.2, 131.2, 128.9, 127.8, 127.4, 125.7, 112.9, 55.1, -3.4; HRMS(ESI, positive) calcd for $C_{28}H_{28}NaO_2Si$ $[M+Na]^+$: 447.1751; found: 447.1753.

Dimethyl(4"-methyl-6'-(*p*-tolyl)-[1,1':2',1"-terphenyl]-2-yl)silane (1c). Isolated by thin-layer chromatography (hexane/dichloromethane = 20/1, 4 times, Rf = 0.5). The title compound was obtained

as a colorless solid (238.5 mg, 38%, in three steps). Mp 112-113 °C; ^{1}H NMR δ 7.47-7.44 (m, 1H), 7.38-7.36 (m, 2H), 7.22-7.20 (m, 1H), 7.08-7.06 (m, 2H), 6.99-6.91 (m, 9H), 3.88-3.85 (m, 1H), 2.24 (s, 6H), -0.18 (d, J = 3.8 Hz, 6H); ^{13}C NMR δ 145.7,141.8, 140.0, 138.8, 137.8, 135.6, 133.8, 132.2, 130.1, 129.1, 128.1, 127.7, 127.4, 125.6, 21.0, -3.4; HRMS(ESI, positive) calcd for $C_{28}H_{28}NaSi$ $[M+Na]^{+}$: 415.1852; found: 415.1852.

(4"-Chloro-6'-(4-chlorophenyl)-[1,1':2',1"-terphenyl]-2-yl)dimethylsilane (1d). Isolated by thin-layer chromatography (hexane/dichloromethane = 20/1, twice, Rf = 0.5) + GPC (chloroform). The title compound was obtained as a colorless solid (69.2 mg, 8% in three steps). Mp 141-142 °C; ^{1}H NMR δ 7.50-7.46 (m, 1H), 7.38-7.37 (m, 2H), 7.24-7.22 (m, 1H), 7.11-7.07 (m, 6H), 6.99 (d, J = 8.6 Hz, 4H), 6.95-6.93 (m, 1H), 3.85-3.82 (m, 1H), -0.15 (d, J = 3.8 Hz, 6H); ^{13}C NMR δ 144.8, 140.8, 140.0, 140.0, 137.6, 134.2, 132.4, 132.0, 131.4, 129.4, 128.1, 127.7, 127.6, 126.2, -3.4; HRMS(DART, positive) calcd for $C_{26}H_{26}{}^{35}Cl_2NSi$ $[M+NH_4]^{+}$: 450.1206; found: 450.1203.

Dimethyl(4"-(trifluoromethyl)-6'-(4-(trifluoromethyl)phenyl)-[1,1':2',1"-terphenyl]-2-yl)silane (1e). Isolated by thin-layer chromatography (hexane, twice, Rf = 0.5) + GPC (chloroform). The title compound was obtained as colorless solid (92.2 mg, 4% in three steps). Mp 126-129 °C; ^{1}H NMR δ 7.56-7.53 (m, 1H), 7.45-7.43 (m, 2H), 7.39 (d, J = 8.1 Hz, 4H), 7.24-7.22 (m, 1H), 7.18 (d, J = 8.0 Hz, 4H), 7.13-7.07 (m, 2H), 6.95-6.93 (m, 1H), 3.87-3.84 (m, 1H), -0.16 (d, J = 3.8 Hz, 6H); ^{13}C NMR δ 145.1 (q, J = 1.5 Hz), 144.3, 140.7, 140.1, 137.7, 134.3, 132.0, 130.4, 129.9, 128.5 (q, J = 32.2 Hz), 128.2, 127.9, 126.5, 124.4 (q, J = 3.9 Hz), 124.2 (q, J = 272.1 Hz), -3.5; ^{19}F NMR δ -63.5; HRMS(DART, positive) calcd for $C_{28}H_{26}F_6NSi$ $[M+NH_4]^{+}$: 518.1733; found: 518.1732.

Dimethyl(4'-methyl-6'-phenyl-[1,1':2',1"-terphenyl]-2-yl)silane (1f). Isolated by thin-layer chromatography (hexane/dichloromethane = 20/1, 4 times, Rf = 0.7). The title compound was obtained as a white solid (81.1 mg, 6% in three steps). Mp 83-85 °C; ^{1}H NMR δ 7.24 (d, J = 0.6 Hz, 2H), 7.19-7.17 (m, 1H), 7.13-7.03 (m, 12H), 6.96-6.95 (m, 1H), 3.91-3.88 (m, 1H), 2.48 (s, 3H), -0.18 (d, J = 3.7 Hz, 6H); ^{13}C NMR δ 145.4, 141.9, 141.7, 138.0, 137.3, 136.9, 133.7, 132.4, 130.2, 130.0, 127.7,

127.3, 126.0, 125.6, 21.2, -3.3; HRMS(ESI, positive) calcd for $C_{27}H_{26}NaSi$ $[M+Na]^+$: 401.1696; found: 401.1697.

Dimethyl(3"-methyl-6'-(*m*-tolyl)-[1,1':2',1"-terphenyl]-2-yl)silane (1g). Isolated by thin-layer chromatography (hexane/dichloromethane = 20/1, Rf = 0.5). The title compound was obtained as colorless oil (255.0 mg, 24% in three steps).; ^{1}H NMR δ 7.48-7.45 (m, 1H), 7.40-7.38 (m, 2H), 7.19-7.17 (m, 1H), 7.05-7.03 (m, 2H), 7.01-6.96 (m, 3H), 6.91-6.90 (m, 4H), 6.86 (d, J = 7.6 Hz, 2H), 3.88-3.85 (m, 1H), 2.2 (s, 6H), -0.17 (d, J = 3.7 Hz, 6H); ^{13}C NMR δ 145.5, 141.9, 141.6, 140.2, 137.9, 136.8, 133.6, 132.1, 131.1, 129.0, 127.5, 127.3, 127.3, 127.2, 126.8, 125.7, 21.2, -3.4; HRMS(ESI, positive) calcd for $C_{28}H_{28}NaSi$ $[M+Na]^+$: 415.1852; found: 415.1852.

Dimethyl(2-(2-phenylnaphthalen-1-yl)phenyl)silane (1h). Prepared from 1-iodo-2-phenylnaphthalene, whose physical properties were reported in the literature.[21] Isolated by thin-layer chromatography (hexane/ethyl acetate = 20/1, twice, Rf = 0.5). The title compound was obtained as a white solid (89.7 mg, 20% in two steps). Mp 100-103 °C; ^{1}H NMR δ 7.94 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 8.5 Hz, 1H), 7.51-7.44 (m, 2H), 7.39-7.29 (m, 4H), 7.25-7.23 (m, 1H, overlapped with $CHCl_3$), 7.21-7.10 (m, 5H), 3.73-3.69 (m, 1H), -0.16 (d, J = 3.8 Hz, 3H), -0.31 (d, J = 3.8 Hz, 3H); ^{13}C NMR δ 145.0, 141.7, 138.3, 138.1, 137.9, 134.5, 133.4, 132.4, 131.6, 130.3, 128.4, 128.2, 127.7, 127.7, 127.4, 127.3, 126.4, 126.2, 126.0, 125.6, -3.1, -3.7; HRMS(ESI, positive) calcd for $C_{24}H_{22}NaSi$ $[M+Na]^+$: 361.1383; found: 361.1383.

Dimethyl(6'-methyl-[1,1':2',1"-terphenyl]-2-yl)silane (1i). Prepared from 2-bromo-6'-methyl-1,1':2',1"-terphenyl, whose physical properties were reported in the literature.[22] Isolated by thin-layer chromatography (hexane/ethyl acetate = 20/1, Rf = 0.5). The title compound was obtained as colorless oil (165 mg, 0.55 mmol, 70%). ^{1}H NMR δ 7.40-7.38 (m, 1H), 7.35-7.28 (m, 2H), 7.25-7.19 (m, 3H), 7.17-7.15 (m, 1H), 7.11-7.06 (m, 5H), 3.87-3.84 (m, 1H) , 2.04 (s, 3H), -0.07 (d, J = 3.8 Hz, 3H), -0.09 (d, J = 3.8 Hz, 3H); ^{13}C NMR δ 146.4, 141.7, 141.2, 141.2, 136.7, 136.5, 134.5, 130.6, 130.1, 128.8, 128.4, 127.6, 127.4, 127.2, 126.0, 126.0, 21.3, -3.2, -3.8; HRMS(ESI, positive) calcd for $C_{21}H_{22}NaSi$ $[M+Na]^+$: 325.1383; found: 325.1383.

9,9-Dimethyl-1-phenyl-9*H*-tribenzo[*b*,*d*,*f*]silepin (2a). Isolated by thin-layer chromatography (hexane/dichloromethane = 20/1, 7 times, Rf = 0.5). The title compound was obtained as a white solid (14.5 mg, 83%). Mp 183-185 °C; ^{1}H NMR δ 7.50-7.40 (m, 6H), 7.37 (ddd, J = 7.5, 7.5, 1.4 Hz, 1H), 7.27-7.23 (m, 1H, overlapped with $CHCl_3$), 7.15-7.10 (m, 3H), 7.04-7.00 (m, 3H), 6.80 (ddd, J = 7.6, 7.6, 1.4 Hz, 1H), 6.69 (d, J = 7.7 Hz, 1H), 0.78 (s, 3H), -0.01 (s, 3H); ^{13}C NMR δ 146.4, 143.2, 143.0, 142.7, 142.6, 142.2, 141.9, 139.3, 132.6, 131.2, 130.7, 130.3, 129.9, 129.8, 129.8, 129.3, 127.8, 127.6, 127.2, 126.1, 125.9, 125.6, -4.3, -5.5; HRMS(ESI, positive) calcd for $C_{26}H_{22}NaSi$ $[M+Na]^+$: 385.1383; found: 385.1384. The crystal data of compound **2a**: $C_{26}H_{22}Si$, M = 362.55, orthorhombic, space group Pbca (#61), a = 15.2591(3) Å, b = 6.82403(12) Å, c = 37.8298(7) Å, V = 3939.17(12) Å^3, Z = 8, μ(Cu-Kα) = 10.811 cm^{-1}; number of reflections measured: total 41798 and unique 3610, R1 = 0.0372, wR2 = 0.1035. CCDC 1824338. The CIF file is available in Supporting Information.

7-Methoxy-1-(4-methoxyphenyl)-9,9-dimethyl-9*H*-tribenzo[*b*,*d*,*f*]silepin (2b). Isolated by thin-layer chromatography (hexane/dichloromethane = 40/1, 4 times, Rf = 0.5). The title compound was obtained as a white solid (13.8 mg, 67%). Mp 138-141 °C; ^{1}H NMR δ 7.44-7.35 (m, 5H), 7.02 (ddd, J = 7.4, 7.4, 1.3 Hz, 1H), 6.99 (d, J = 2.3 Hz, 1H), 6.91-6.87 (m, 3H), 6.83 (ddd, J = 7.6, 7.6, 1.4 Hz, 1H), 6.70 (d, J = 7.7 Hz, 1H), 6.67 (d, J = 8.9 Hz, 2H), 3.79 (s, 3H), 3.74 (s, 3H), 0.76 (s, 3H), -0.02 (s, 3H); ^{13}C NMR δ 157.9, 157.8, 143.7, 143.7, 142.3, 142.2, 141.5, 139.3, 139.1, 135.6, 132.6, 131.1, 130.8, 130.7, 130.3, 129.5, 128.0, 127.2, 125.6, 116.6, 113.9, 113.1, 55.1, 55.1, -4.4, -5.5; HRMS(ESI, positive) calcd for $C_{28}H_{26}NaO_2Si$ $[M+Na]^+$: 445.1594; found: 445.1594.

1-(*p*-Tolyl)-7,9,9-Trimethyl-9*H*-tribenzo[*b*,*d*,*f*]silepin (2c). Isolated by thin-layer chromatography (hexane/dichloromethane = 20/1, twice, Rf = 0.5). The title compound was obtained as a white solid (16.2 mg, 84%). Mp 164-166 °C; ^{1}H NMR δ 7.45-7.34 (m, 5H), 7.24 (s, 1H), 7.17 (dd, J = 7.9, 1.2 Hz, 1H), 7.02 (ddd, J = 7.4, 7.4, 1.1 Hz, 1H), 6.95-6.87 (m, 4H), 6.81 (ddd, J = 7.5, 7.5, 1.4 Hz, 1H), 6.70 (d, J = 7.7 Hz, 1H), 2.33 (s, 3H), 2.26 (s, 3H), 0.76 (s, 3H), -0.03 (s, 3H); ^{13}C NMR δ 143.7, 143.5, 142.7, 142.6, 142.0, 141.8, 140.2, 139.3, 135.5, 135.4, 132.6, 131.5, 130.9, 130.2, 130.0, 129.8, 129.8, 129.7,

128.3, 127.8, 127.2, 125.5, 21.1, 21.1, -4.3, -5.5; HRMS(ESI, positive) calcd for $C_{28}H_{27}Si$ $[M+H]^+$: 391.1877; found: 391.1877.

7-Chloro-1-(4-chlorophenyl)-9,9-dimethyl-9*H*-tribenzo[*b*,*d*,*f*]silepin (2d). Isolated by thin-layer chromatography (hexane/dichloromethane = 20/1, twice and hexane, Rf =0.7). The title compound was obtained as white solid (14.6 mg, 67%). Mp 180-182 °C; ^{1}H NMR δ 7.48-7.45 (m, 1H), 7.42-7.36 (m, 5H), 7.32-7.30 (m, 1H), 7.11-7.05 (m, 3H), 6.90-6.85 (m, 3H), 6.66 (d, J = 7.8 Hz, 1H), 0.78 (s, 3H), -0.04 (s, 3H); ^{13}C NMR δ 144.5, 144.4, 142.8, 141.9, 141.6, 141.3, 140.9, 139.2, 133.0, 132.5, 132.1, 131.3, 131.2, 131.0, 130.6, 130.5, 130.0, 129.2, 128.4, 127.9, 127.5, 126.1, -4.5, -5.6; HRMS(DART, positive) calcd for $C_{26}H_{24}{}^{35}Cl_2NSi$ $[M+NH_4]^+$: 448.1050; found: 448.1035.

9,9-Dimethyl-7-(trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)-9*H*-tribenzo[*b*,*d*,*f*]silepin (2e). Isolated by thin-layer chromatography (hexane only, 4 times, Rf = 0.5). The title compound was obtained as a white solid (45%, NMR yield). Mp 148-150 °C; ^{1}H NMR δ 7.66 (s, 1H), 7.63-7.61 (m, 1H), 7.56-7.51 (m, 2H), 7.46-7.42 (m, 3H, contained desilylated starting material), 7.40 (d, J = 8.4 Hz, 2H), 7.10-7.06 (m, 3H), 6.84 (ddd, J = 7.7, 7.7, 1.3 Hz, 1H), 6.64 (d, J = 7.7 Hz, 1H), 0.83 (s, 3H), -0.00 (s, 3H); ^{13}C NMR δ 149.5 (q, J = 1.5 Hz), 146.4 (q, J = 1.5 Hz), 143.3, 142.4, 141.9, 141.5, 140.9, 139.3, 132.6, 131.6, 131.4, 130.8, 130.4, 130.1 (q, J = 1.8 Hz), 130.0, 130.0, 128.5, 128.3 (q, J = 31.9 Hz), 128.3 (q, J = 32.5 Hz), 127.7, 127.6 (q, J = 3.6 Hz), 126.4, 126.1 (q, J = 3.6 Hz), 124.6 (q, J = 3.9 Hz), 124.5 (q, J = 272.4 Hz), 124.2 (q, J = 271.8 Hz), -4.5, -5.6; ^{19}F NMR δ -63.4, -63.3; HRMS(DART, positive) calcd for $C_{28}H_{24}F_6NSi$ $[M+NH_4]^+$: 516.1577; found: 516.1569.

1-Phenyl-3,9,9-trimethyl-9*H*-tribenzo[*b*,*d*,*f*]silepin (2f). Isolated by thin-layer chromatography (hexane/dichloromethane = 20/1, 4 times, Rf = 0.6). The title compound was obtained as colorless oil (16.9 mg, 90%). ^{1}H NMR δ 7.46-7.44 (m, 2H), 7.40-7.34 (m, 2H), 7.24-7.22 (m, 3H), 7.12-7.08 (m, 3H), 7.01-6.98 (m, 3H), 6.80-6.77 (m, 1H), 6.67 (d, J = 7.8 Hz, 1H), 2.47 (s, 3H), 0.76 (s, 3H), 0.01 (s, 3H); ^{13}C NMR δ 146.6, 143.3, 143.2, 142.7, 142.6, 142.1, 141.8, 136.7, 136.6, 132.7, 131.8, 130.8, 130.7, 130.3, 129.8, 129.8, 129.2, 127.8, 127.5, 126.1, 125.8, 125.5, 21.1, -4.2, -5.5; HRMS(ESI, positive) calcd for $C_{27}H_{24}NaSi$ $[M + Na]^+$: 399.1539; found: 399.1540.

1-(*m*-Tolyl)-6,9,9-trimethyl-9H-tribenzo[*b*,*d*,*f*]silepin (2g). Isolated by thin-layer chromatography (hexane/dichloromethane = 20/1, 3 times, Rf = 0.5). The title compound was obtained as white solid (18.3 mg, 92%). Mp 131-133 °C; ^{1}H NMR δ 7.46-7.38 (m, 4H), 7.34 (d, J = 7.4 Hz, 1H), 7.28 (s, 1H), 7.06 (d, J = 7.4 Hz, 1H), 7.02-6.96 (m, 2H), 6.91 (d, J = 7.6 Hz, 1H), 6.85 (s, 1H), 6.80 (ddd, J = 7.4, 7.4, 1.4 Hz, 1H), 6.73 (d, J = 7.2 Hz, 1H), 6.68 (d, J = 7.8 Hz, 1H), 2.33 (s, 3H), 2.21 (s, 3H), 0.75 (s, 3H), -0.03 (s, 3H); ^{13}C NMR δ 146.6, 143.4, 143.0, 142.9, 142.8, 141.9, 139.4, 139.0, 138.8, 137.1, 132.5, 131.0, 130.9, 130.8, 130.7, 130.2, 129.8, 127.7, 127.3, 127.1, 127.0, 126.9, 126.6, 125.6, 21.4, 21.4, -4.1, -5.5; HRMS(ESI, positive) calcd for $C_{28}H_{27}Si$ $[M+H]^+$: 391.1877; found: 391.1877.

9,9-Dimethyl-9*H*-dibenzo[b,f]naphtho[1,2-*d*]silepine (2h). Isolated by thin-layer chromatography (hexane/dichloromethane = 20/1, 5 times, Rf = 0.5). The title compound was obtained as a white solid (9.5 mg, 57%). Mp 56-60 °C; ^{1}H NMR δ 7.89 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 8.5 Hz, 1H), 7.58-7.55 (m, 3H), 7.50-7.45 (m, 2H), 7.42-7.37 (m, 2H), 7.35-7.7.29 (m, 3H), 7.28-7.24 (m, 1H, overlapped with $CHCl_3$), 0.73 (s, 3H), -0.41 (s, 3H); ^{13}C NMR δ 146.5, 1443.5, 142.9, 142.0, 138.3, 137.4, 133.1, 132.8, 132.3, 131.2, 130.9, 129.8, 129.7, 129.2, 127.8, 127.8, 127.7, 127.6, 126.5, 126.1, 126.1, 125.7, -4.6, -5.5; HRMS(ESI, positive) calcd for $C_{24}H_{21}Si$ $[M+H]^+$: 337.1407; found: 337.1407.

1,9,9-Trimethyl-9*H*-tribenzo[*b*,*d*,*f*]silepin (2i). Isolated by thin-layer chromatography (hexane/dichloromethane = 20/1, twice, Rf = 0.5). The title compound was obtained as pale yellow oil (4.0 mg, 24%). ^{1}H NMR δ 7.48-7.47 (m, 1H), 7.43 (d, J = 7.4 Hz, 1H), 7.40 (dd, J = 7.3, 1.2 Hz, 1H), 7.34 (dd, J = 7.5, 1.4 Hz, 1H), 7.30-7.25 (m, 3H, overlapped with $CHCl_3$), 7.23-7.18 (m, 4H), 2.17 (s, 3H), 0.70 (s, 3H), -0.29 (s, 3H); ^{13}C NMR δ 146.7, 143.4, 142.3, 142.2, 141.6, 140.1, 136.9, 130.9, 130.9, 130.7, 129.5, 129.4, 129.2, 129.2, 128.0, 126.9, 126.0, 125.8, 22.3, -4.5, -5.5; HRMS(ESI, positive) calcd for $C_{21}H_{21}Si$ $[M+H]^+$: 301.1407; found: 301.1408.

9,9-Dimethyl-1-(4-hydroxyphenyl)-9*H*-tribenzo[*b*,*d*,*f*]silepin-7-ol (3b). Isolated by thin-layer chromatography (hexane/ethyl acetate = 1/1, Rf = 0.5). The title compound was obtained as a white solid (7.7 mg, 68%). Mp 200-203 °C; ^{1}H NMR δ 7.44-7.39 (m, 2H), 7.37-7.32 (m, 3H), 7.03 (ddd, J = 7.4, 7.4, 1.1 Hz, 1H), 6.91 (d, J =2.1 Hz, 1H), 6.86-6.83 (m, 3H), 6.81 (dd, J = 8.3, 2.8 Hz, 1H), 6.70 (d,

J = 7.4 Hz, 1H), 6.60-6.59 (m, 2H), 4.74 (br s, 2H), 0.74 (s, 3H), -0.03 (s, 3H); ^{13}C NMR δ 153.9, 153.7, 144.0, 143.6, 142.2, 141.4, 139.3, 139.2, 1358, 132.6, 131.4, 131.4, 131.1, 130.7, 130.3, 129.5, 128.0, 127.2, 125.6, 117.5, 116.0, 114.6, -4.4, -5.5; HRMS(ESI, positive) calcd for $C_{26}H_{22}NaO_2Si$ $[M+Na]^+$: 417.1281; found: 417.1280. Enantiomers of **3b** were resolved using a Daicel Chiralpak AD-H (10 x 250 mm, 254 nm UV detector, rt, eluent: 10% 2-propanol in hexane, flow rate: 2.0 ml/min, retention time: 28.3 min and 36.4 min).

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Supporting Information Available

NMR spectra of products This material is available free of charge via the internet at http://pubs.acs.org.

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