JOC The Journal of Organic Chemistry

Article

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Access to Chiral Silicon Centers for Application to Circularly Polarized Luminescence Materials

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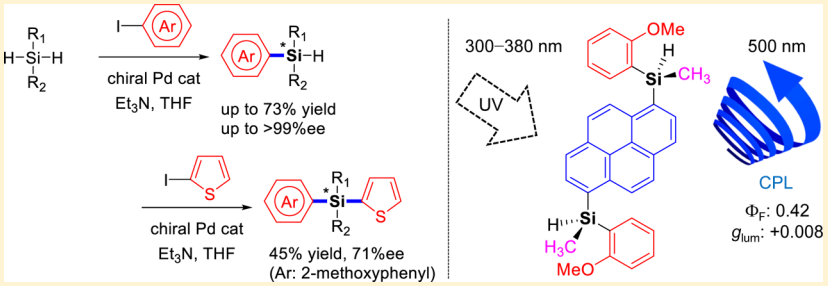
Supporting Information



ABSTRACT: Asymmetric arylation of secondary silanes catalyzed by a Pd-chiral phosphoramidite complex was developed for application to low-molecular-weight circularly polarized luminescence (CPL) materials. The asymmetric arylation provided a convenient, efficient synthetic method for a variety of chiral tertiary silanes (**2**–**21**), which were key intermediates for preparing the quaternary silicon center. A stepwise, one-pot procedure was used to transform the appropriate aryl iodide to the quaternary silane (**22**) with good yield and enantioselectivity. Among compounds synthesized in this work, four optically pure tertiary silanes (**18**–**21**) were selected to investigate the relationship between the structure and optical properties. Optically pure (*S*,*S*)-**21** displayed the highest CPL emission with a high fluorescence quantum yield (g_{lum}: +0.008, Φ_F: 0.42). This simple molecular design provides new strategies for developing small organic CPL dyes.

INTRODUCTION

There has been growing interest in the application of chiral compounds that display circularly polarized luminescence (CPL), which is the differential emission of right- and left-circularly polarized light from chiral fluorophores.[1] CPL has great potential for the development of photonic devices for advanced technologies, such as 3D displays, spintronic devices, and enantioselective chemo/biosensors.[2] Chiral lanthanide complexes[3] and aggregates with organic fluorophores[4] often exhibit CPL. Although simple (small, nonaggregated, non-polymeric) organic molecules that exhibit CPL are valuable owing to their high emission yields, good solubility, and appropriate size for applications, CPL emissions in element chiral center systems have not been extensively explored. Substitution of oligocyclic aromatic hydrocarbons with trimethylsilyl groups increased the fluorescence quantum yield of the chromophore through $\sigma-\pi$ conjugation.[5] Therefore, chromophores with silicon-stereogenic chiral centers may exhibit intense CPL emission properties, increasing the utility of these compounds.[6]

There has been longstanding interest in silicon-stereogenic organosilanes, and optically active tertiary silanes are key intermediates in the design of several complicated chiral organosilane compounds.[7] Among various synthetic strategies, transition-metal-catalyzed desymmetrization of prochiral secondary silanes without stoichiometric amounts of chiral reagents is a highly desirable strategy for forming chiral silicon centers. Typical approaches are as follows. Takaya et al. found that the $[RhCl(cod)]_2$-CyBINAP system served as an excellent catalyst for the stereoselective construction of silicon-stereogenic centers to give optically active 1-naphthylphenylalkoxysilanes in up to >99% ee.[8] Tomooka et al. studied the catalytic desymmetrization of secondary silanes based on Pt-catalyzed hydrosilylation with TADDOL-derived phosphonite ligands.[9] Enantioselective carbenoid insertion into secondary silanes achieved up to 99% ee using Ir/salen or Rh/chiral diene complexes.[10] However, the other types of Si–H bond functionalizations have been much less explored, and enantioselective synthesis of tertiary silanes remains a considerable challenge.

Received: March 20, 2017
Published: May 12, 2017

DOI: 10.1021/acs.joc.7b00583
J. Org. Chem. 2017, 82, 6108–6117

Scheme 1. Previous Work

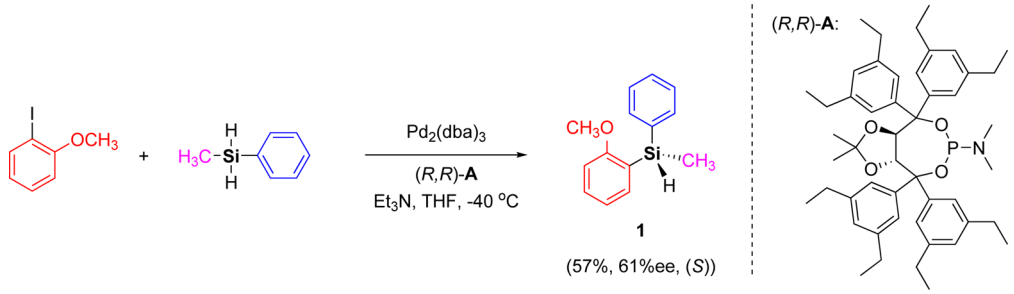
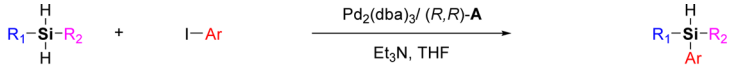
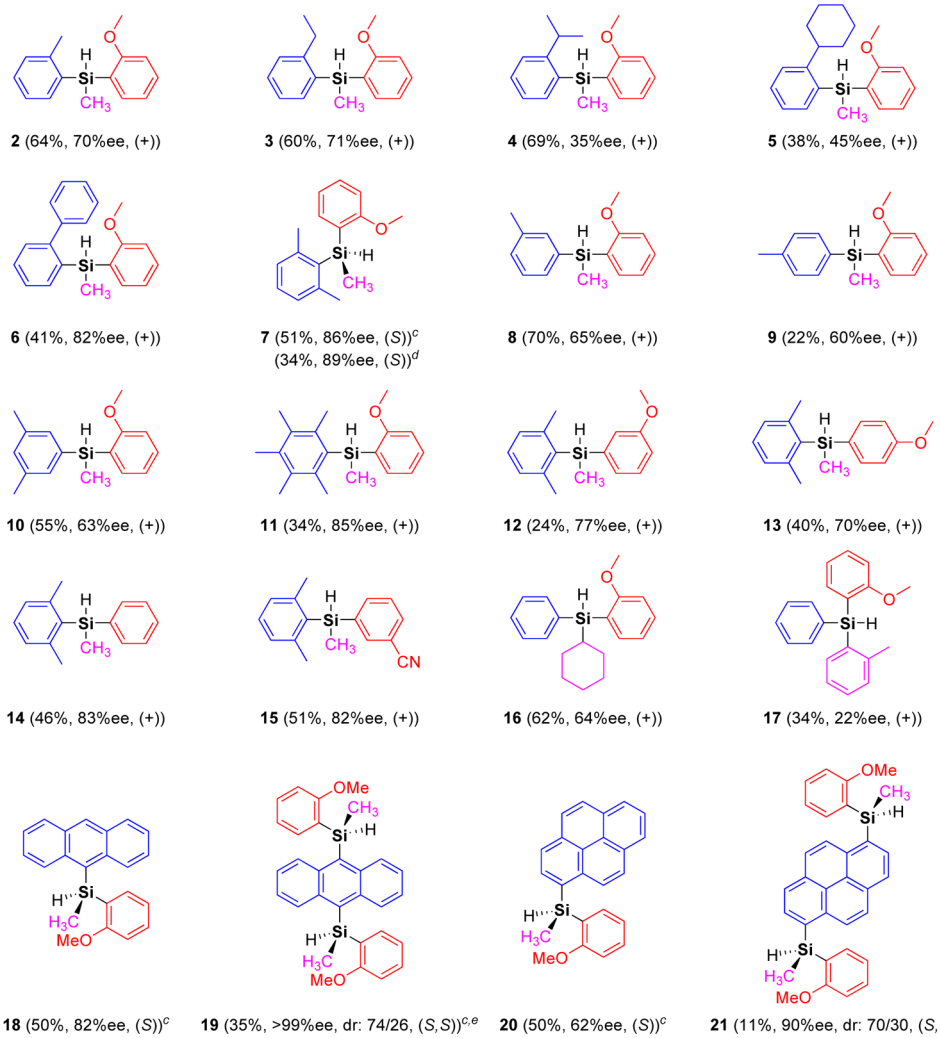


Table 1. Pd-Catalyzed Asymmetric Arylation of Secondary Silanes[a,b]





[a]Reaction conditions: aryl iodide (1.0 mmol), secondary silane (1.5 mmol), $Pd_2(dba)_3$ (0.025 mmol), (*R*,*R*)-**A** (0.075 mmol), triethylamine (3.0 mmol), THF (2.0 mL), −40 °C, 3 d. [b]Enantiomeric excess was determined by HPLC analysis with a chiral column. [c]Absolute configurations were determined by X-ray analysis. [d]Result when reaction was carried out at −60 °C. [e]*dl*/*meso* ratio (dr) was determined by ^{1}H NMR. [f]*dl*/*meso* ratio (dr) was determined by ^{13}C NMR.

In our previous paper, we reported that $Pd(P(t\text{-}Bu)_3)_2$ was a good catalyst in the stepwise cross-coupling reaction of primary, secondary, and tertiary silanes with aryl iodides.[11] The reactions proceeded smoothly in the presence of a catalyst and base to give the products in good to high yields with wide structural diversity. The approach was suitable for arylating secondary silanes to afford enantiomerically enriched tertiary silanes.[12] In the present work, we report highly emissive CPL-active

DOI: 10.1021/acs.joc.7b00583
J. Org. Chem. 2017, 82, 6108−6117

organosilanes that have chiral silicon centers to expand the structural diversity of simple organic molecules that show CPL through a thorough examination of asymmetric arylation.

RESULTS AND DISCUSSION

Substrate Scope of Secondary Silanes in the Enantioselective Arylation. We reported that TADDOL-based phosphoramidite ligands showed good enantioselectivity for Pd-catalyzed arylation of secondary silanes to give silicon-stereogenic tertiary silanes.[12a] For example, methylphenylsilane reacted with 2-iodoanisole in the presence of (*R*,*R*)-**A** and $Pd_2(dba)_3$ to give (*S*)-phenyl(2-methoxyphenyl)methylsilane (**1**) in 57% yield and 61% ee (Scheme 1).

In our previous paper, we only examined monoarylation of methylphenylsilane and 1-naphthylmethylsilane as the model substrates. In the present work, we focused on the enantioselective arylation of various arylalkylsilanes with aryl iodides to develop effective CPL materials. The results are summarized in Table 1. Initially, a series of arylmethylsilanes bearing different substituent groups on the phenyl ring were investigated. The asymmetric arylation of arylmethylsilanes bearing methyl or ethyl groups in the *ortho* position of the phenyl ring afforded the corresponding tertiary silanes in better enantioselectivities (**2**: 70% ee and **3**: 71% ee). Nevertheless, bulkier substituents, such as isopropyl and cyclohexyl groups, at the *ortho* position showed lower optical yields of the products (**4**: 35% ee and **5**: 45% ee). The substrate with the 2-phenyl group provided the desired product with higher enantioselectivity (**6**: 82% ee). The substrates containing 2,6-dimethyl substituents on the phenyl ring gave the highest enantioselectivity (**7**: 86% ee). The stereoselectivity was improved to 89% ee at −60 °C with a longer reaction time. Substituents in the *ortho* position of the aromatic ring of secondary silanes gave better enantioselectivities than those in the *meta* or *para* positions (**8**: 65% ee, **9**: 60% ee, and **10**: 63% ee). Arylation of (2,3,4,5,6-pentamethylphenyl)methylsilane also gave excellent catalytic results (**11**: 85% ee). The optical yields of the products also depended on the position of the substituents on the aryl iodides. Substituents in the *meta* or *para* positions on the aromatic ring resulted in decreased enantioselectivities (**12**: 77% ee and **13**: 70% ee). Iodobenzene gave an optically active tertiary silane in excellent ee (**14**: 83% ee). Additionally, a cyano group on the aromatic ring was tolerated under the enantioselective conditions to afford the tertiary silane in excellent ee (**15**: 82% ee). In contrast with the arylation of methylphenylsilane, (cyclohexyl)phenylsilane exhibited good enantioselectivity (**16**: 64% ee). Phenyl(2-methylphenyl)silane provided the product with a low ee (**17**: 22% ee). To exhibit effective fluorescence, the compound must contain a sufficiently extended set of conjugated double bonds to absorb long-wave UV light. The asymmetric synthesis of tertiary silanes **18**−**21**, which have anthracene and pyrene skeletons, was performed to prepare fluorescent organosilane dyes. Sterically congested *ortho*-substituted aryl iodides reacted in moderate-to-good chemical yields and good to excellent optical yields in the presence of a catalyst. Disubstituted tertiary silanes **19** and **21** were obtained as *dl*/*meso* mixtures with ratios of 74:26 and 70:30, respectively, according to NMR analysis. In all cases, aryl iodides were reduced in a side reaction to give the corresponding hydrocarbons, which were consistently confirmed as major byproducts by GC−MS.

The absolute configurations of **7**, **19**, and **21** (>99% ee, after recrystallization) were unambiguously determined to be (*S*), (*S*,*S*), and (*S*,*S*), respectively, by single-crystal X-ray diffraction (Figure 1 and Figures S1−S3).[13] Although the unit cell of **21** contains two independent molecules in the crystal, both structures show (*S*,*S*) configuration. Therefore, the absolute configurations of **18** and **20** were assigned as (*S*) by analogy to **19** and **21**.

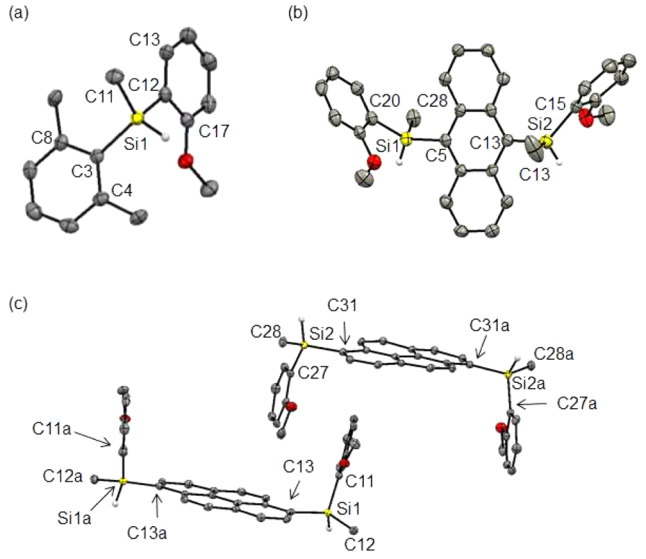
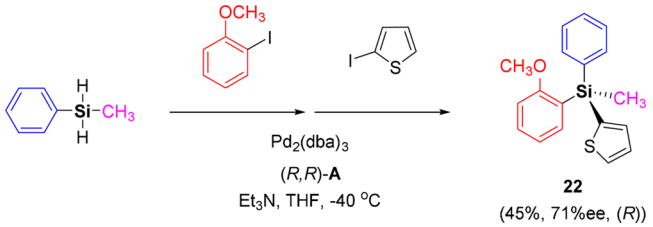


Figure 1. X-ray crystallographic structures of (a) (*S*)-**7**, (b) (*S*,*S*)-**19**, and (c) (*S*,*S*)-**21** using 50% probability ellipsoids. Hydrogen atoms except for Si−H have been removed for clarity.

Construction of Chiral Quaternary Silanes. For the synthetic utility of the current arylation reaction to be explored further, the subsequent transformation to quaternary silicon compounds was examined as an application of this method (Scheme 2).[14] The stepwise arylation of methylphenylsilane with 2-iodoanisole and 2-iodothiophene proceeded smoothly to give doubly arylated product **22** in 45% yield and 71% ee. The absolute configuration of **22** was elucidated by X-ray crystallography as the (*R*) form (Figure S4), indicating that the stereochemistry was retained in the reaction.[15] The chirality was mainly determined in the first arylation process.

Scheme 2. Construction of a Silicon-Stereogenic Quaternary Silane from Secondary One



Application to Intense CPL Materials. The optical properties of enantiopure **18**−**21** were investigated to examine the chirality in the excited state, and the data are summarized in Table 2 and Figures S5−S12. The vibronic patterns for the absorption spectra of the compounds were similar to those of anthracene or pyrene, and the peak position was slightly red-shifted compared with anthracene or pyrene. In addition, the disubstituted derivatives (**19** and **21**) displayed red-shifted absorption and emission compared with the monosubstituted

DOI: 10.1021/acs.joc.7b00583
J. Org. Chem. 2017, 82, 6108−6117

Table 2. Optical Properties of Optically Pure 18−21 in CH_2Cl_2

compound	λ_{abs} (nm)[a]	ε (dm^3 $mol^{-1}cm^{-1}$)[b]	λ_{ex} (nm)	λ_{em} (nm)	Φ_F[c]	τ(ns)	g_{abs}	g_{lum}
(*S*)-**18**	367, 387	9,700	367	395, 416	0.55	7.5	-1.2×10^{-4} (386 nm)	$+8.5 \times 10^{-4}$[d] (427 nm)
(*S,S*)-**19**	381, 402	11,900	402	417, 436	0.97	9.1	-2.2×10^{-4} (401 nm)	-1.4×10^{-3}[d] (416 nm)
(*S*)-**20**	279, 331, 348	41,300	348	376, 394[e]	0.13[e]	23.4[e]	$+2.3 \times 10^{-4}$ (347 nm)	e,f
				393, 478[g]	0.13[g]	44.5[g]		-1.6×10^{-3} (490 nm)[g]
(*S,S*)-**21**	283, 341, 358	46,200	358	382, 402[e]	0.45[e]	30.4[e]	$+1.3 \times 10^{-4}$ (356 nm)	e,f
				402, 500[g]	0.42[g]	73.2[g]		$+8.0 \times 10^{-3}$ (500 nm)[g]

[a]Underlined values are wavelengths that show the highest peak intensity. [b]Values at underlined λ_{abs}. [c]Absolute fluorescence quantum yield measured with an integrating sphere. [d]Concentration: 1.0×10^{-2} M. [e]Concentration: 1.0×10^{-5} M. [f]CPL intensity was smaller than detection limit of the apparatus ($g_{lum} < 1 \times 10^{-4}$). [g]Concentration: 4.0×10^{-3} M.

derivatives (**18** and **20**), indicating an extended conjugation in the monosubstituted derivatives. The extinction coefficients were similar to those of anthracene or pyrene. Compounds (*S*)-**18**, (*S,S*)-**19**, (*S*)-**20**, and (*S,S*)-**21** exhibited sufficient quantum yields (Φ_F: up to 0.97, efficient radiative relaxation) for use as chiroptical materials. The fluorescence lifetimes were different for anthracene ((*S*)-**18** and (*S,S*)-**19**) and pyrene ((*S*)-**20** and (*S,S*)-**21**) chromophores. A dilute solution of (*S*)-**20** and (*S,S*)-**21** in CH_2Cl_2 (0.01 mM) showed fluorescence bands from 380 to 480 nm, which were attributed to the $\pi-\pi^*$ transitions of the monomer pyrene chromophore (Figures S10 and S12). The higher concentration (4.0 mM) resulted in a red-shifted, broad emission from a pyrene excimer (Figure 2(a and b)). The asymmetric factor, g_{abs}, at the $\pi-\pi^*$ transition showed values of $\sim 10^{-4}$ for all compounds.

The size and type of substituents on the silicon atoms substantially affected the CPL properties. The CPL strength

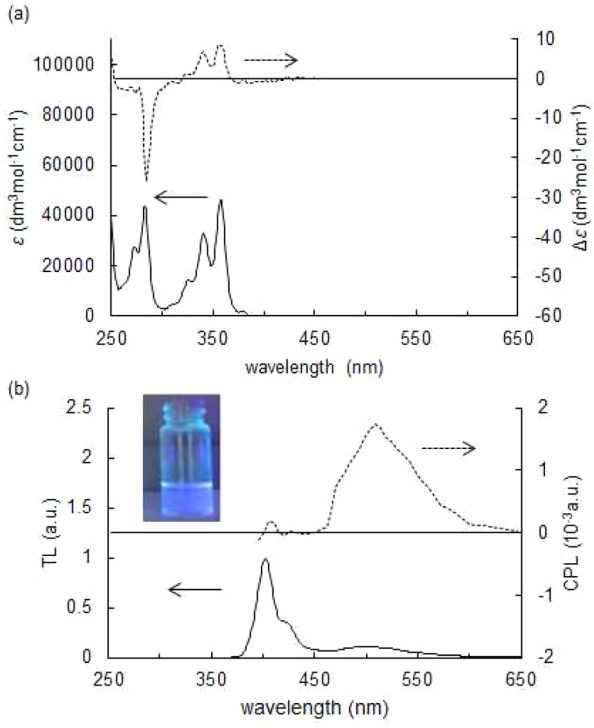


Figure 2. (a) UV−vis absorption (solid line) and CD spectra (dotted line) of (*S,S*)-**21** in CH_2Cl_2. (b) TL (solid line) and CPL (dotted line) of (*S,S*)-**21** in CH_2Cl_2 (4.0 mM) upon excitation at 300−380 nm. (inset) Photograph of (*S,S*)-**21** in CH_2Cl_2 (4.0 mM) under irradiation at 365 nm. TL: $I_L + I_R$. CPL: $I_L - I_R$. I_L and I_R: emission intensity of left and right-circularly polarized light, respectively.

increased as the acene unit lengthened (anthracene < pyrene) and as the number of chiral silicon stereogenic groups increased (monosubstituted < disubstituted). Figures 2 and Figures S7 and S8 show the UV−vis, circular dichroism (CD), total luminescence (TL), and CPL spectra for the CH_2Cl_2 solution of (*S,S*)-**21**. The CD spectrum showed positive Cotton effects at 356 nm (g_{abs}: $+1.3 \times 10^{-4}$). Compound (*S,S*)-**21** exhibited intense left-CPL. The CPL signal was observed in the excimer-emissive region of the spectrum for the pyrene core. Although no CPL was observed at lower concentrations, the g_{lum} value was +0.008 at 500 nm at higher concentrations, resulting from the two stacked pyrenes.[16,17] It is rare that small organic compounds with an element chiral center exhibit a large g_{lum} value near the order of 10^{-2}. The absolute values of g_{lum} for single molecules are generally smaller than 1×10^{-4}. Recently, small molecules that exhibit CPL in dilute solution have been extensively studied; helically and axially chiral compounds can exhibit CPL with large g_{lum} values on the order of 10^{-2}.[18,19] This is an example of low-molecular-weight organic fluorophores having asymmetric silicon that show both high fluorescence efficiency and high CPL properties. These CPL-active small molecules with a stereogenic center have great potential for sophisticated optical devices compared with that of conventional CD-active materials.

Theoretical Calculations. DFT and TD-DFT calculations were carried out to elucidate the electronic structures of **18**−**21**. The HOMOs and LUMOs were situated on the anthracene or pyrene π rings with a partial overlap of orbitals at the silicon atom. However, there was no contribution from the 2-methoxyphenyl π-orbital in either the HOMO or LUMO (Figure S13). According to the TD-DFT calculations, the HOMO → LUMO transition was predominant in the lowest-energy transitions (S_1 state). The longest wavelength peaks in the absorption spectra were assigned to the $\pi-\pi^*$ S_1 excitation in the anthracene or pyrene cores. The absorption maxima observed for these compounds closely resembled the calculated results (Tables S13−S16). The absorption spectra of **18**−**21** were slightly red-shifted relative to anthracene or pyrene and were affected by the nature of the organosilicon substituent on the aromatic ring. The bathochromic shift in the absorption of the disubstituted derivatives (**19** and **21**) in comparison to the monosubstituted derivatives (**18** and **20**) is easily explained by comparing the HOMO and LUMO of the respective molecules.

Reaction Mechanism. On the basis of the absolute configuration of the products, a possible transition state is proposed in Figure 3 to elucidate the origin of the asymmetric induction. To simplify the reaction intermediate, we considered (*R,R*)-**B** as a chiral source, methylphenylsilane as a secondary silane, and 2-iodoanisole as an aryl iodide. In the transition state, the chiral ligand and secondary silane coordinate to

DOI: 10.1021/acs.joc.7b00583
J. Org. Chem. 2017, 82, 6108−6117

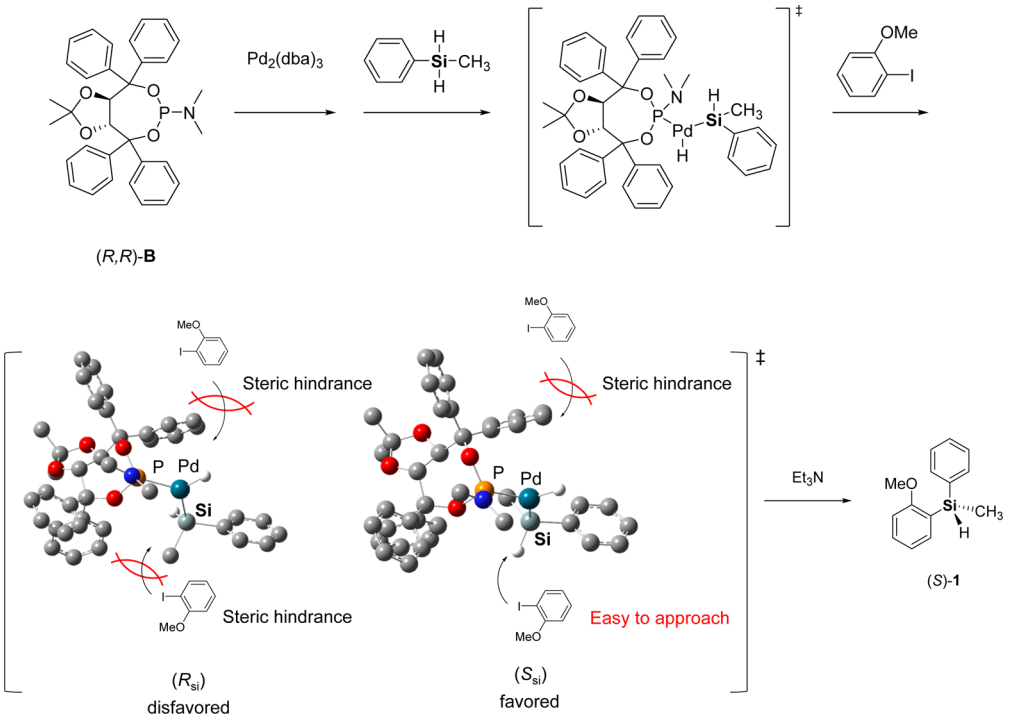


Figure 3. Proposed reaction scheme and transition state for the stereoselective arylation of methylphenylsilane with 2-iodoanisole. Hydrogen atoms except for Si−H and Pd−H have been removed for clarity.

Pd(II) in a trigonal planar geometry after the oxidative addition of methylphenylsilane to Pd(0). We used the intermediate model in which the Si−Ph moiety is farthest from (*R*,*R*)-**B**. Subsequently, 2-iodoanisole undergoes σ-bond metathesis to avoid steric congestion. The enantioselectivity of the silicon center is presumably determined at this step. The (*R*) silicon-stereogenic intermediate is shielded by the aryl moiety of the chiral ligand and by the Si−CH_3 group. In contrast, the (*S*) silicon-stereogenic intermediate is located in the relatively open space of the Si−H position. The selective approach of 2-iodoanisole to the favored intermediate leads to the desired product with an (*S*) configuration via the assistance of the base, which is consistent with the observed absolute configuration of the product. The ethyl groups at the 3,5-position of (*R*,*R*)-**A** may contribute to the improvement of the enantioselectivity owing to the steric repulsion between the 3,5-diethylphenyl groups and 2-iodoanisole.

CONCLUSIONS

The present symmetric reaction may be useful for the preparation of various chiral tertiary silanes and could be extended to constructing chiral quaternary organosilanes through stepwise arylation from secondary silanes. The utility of this method was illustrated by the synthesis of effective CPL materials. Among the compounds synthesized in this work, optically pure (*S*,*S*)-**21** showed remarkable g_{lum} values for a simple organic molecule with a high emission efficiency (g_{lum}: +0.008, Φ_F: 0.42), which is the first example of silicon-sterogenic compounds with effective CPL properties. A possible transition state was proposed based on the stereochemistry of the product. Our method is useful for the synthesis of chiroptical organosilane compounds.

EXPERIMENTAL SECTION

General Information. All oxygen- and moisture-sensitive reactions were carried out under an argon atmosphere with oven-dried glassware. Solvents were supplied by a solvent purification system through columns of activated alumina and supported copper catalyst. Water was purified with a water purification system (AUTOPURE WD500). Melting points were measured using a Yanaco MP-500D apparatus and are reported uncorrected. NMR spectra were measured with a Bruker US-500 spectrometer using $CDCl_3$ as the solvent at ambient temperature. Chemical shifts are reported in ppm with TMS (0.00 ppm) as the reference for ^{1}H NMR spectra and $CDCl_3$ (77.0 ppm) as the reference for ^{13}C NMR spectra. ^{13}C NMR spectra were recorded with complete proton decoupling. GC−MS spectra were recorded with a SHIMADZU GC-MS-QP2010 spectrometer with positive EI at 70 eV. Elemental analysis was performed with Yanaco Technical Science carbon/hydrogen/nitrogen simultaneous quantitative equipment CHN coder MT-6. HPLC was performed by JASCO LC-2000 Plus equipped with a variable wavelength detector and a refractive index detector using the corresponding commercial chiral stationary column (DAICEL). FAB mass spectra were measured with a JEOL MStation JMS-700 spectrometer. High-resolution mass spectrometry (HRMS) data were obtained by FAB with a magnetic sector double focusing-geometry mass analyzer. UV−vis absorption spectra were measured with a JASCO V-570 spectrometer. Fluorescence spectra and absolute quantum yields were measured with a Hitachi F-4500 spectrometer, a JASCO F-8600 spectrometer, and a Hamamatsu C9920-02 spectrometer. Fluorescence lifetimes were measured with a Hamamatsu Quantaurus-Tau C11367 spectrometer. CD spectra were recorded with a JACSO J-1500 spectrometer. Optical rotations of **2**−**17** and **22** were measured in solution after the purification with silica gel with a JASCO P-1030 polarimeter and calibrated with pure solvent as a blank. The optical resolutions of **18**−**21** were measured in solution as optically pure compounds. The CPL spectra were recorded using a lab-made CPL measurement system, the details of which have been reported previously.[20]

Methyl(2,6-dimethylphenyl)silane,[21] methyl(3-methylphenyl)-silane,[22] methyl(4-methylphenyl)silane,[22] phenylcyclohexylsilane,[23]

DOI: 10.1021/acs.joc.7b00583
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and phenyl(2-methylphenyl)silane[24] were prepared according to methods described previously and purified by distillation. All spectral data for these compounds are consistent with the literature data.

X-ray Analysis. X-ray diffraction data for **7**, **19**, and **22** were collected at 113 K (**7** and **22**) or 123 K (**19**) with an AFC10 diffractometer coupled to a Rigaku Saturn CCD system equipped with a rotating-anode X-ray generator producing graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). X-ray diffraction data for **21** were collected at 93 K on a Rigaku Saturn 724 (Varimax dual) diffractometer with multilayer mirror monochromated Mo Kα radiation (λ = 0.7107 Å). Lorentz polarization and empirical absorption corrections were performed with the program Crystal Clear 1.3.6. The structures were solved by direct methods using SIR-92[25] and were refined by the full-matrix least-squares techniques against F^2 implementing SHELXL-97.[26] Details of the data collections are presented in Tables S1–S8.

Theoretical Calculations. DFT and TD-DFT calculations were executed using Gaussian09.[27] The ground-state geometries of **18**–**21** were optimized by the DFT method with the B3LYP functional and 6-31G (d) basis sets. Cartesian coordinates of all the optimized geometries are listed in the Supporting Information. Frequency calculations were performed to investigate the total energy and to ensure that the optimized geometries were minima on the potential energy surface in which no imaginary frequencies were observed in any of the compounds.

Representative Experimental Procedure for Preparing Secondary Silanes. To a solution of methyldichlorosilane (4.1 mL, 40 mmol) in THF (90 mL) was added 2-MeC_6H_4MgBr (2 M, 20 mL, diethyl ether solution) at −78 °C. The mixture was stirred for 2 h, and the temperature was allowed to increase to room temperature. After overnight stirring, to the mixture was added $LiAlH_4$ (1.651 g, 40.8 mmol) at 0 °C and stirred for an additional night. To the reaction mixture was sequentially carefully added 1.6 mL of water, 1.6 mL of 4 M aqueous NaOH, and 4.8 mL of water. The resulting slurry was filtered through Celite. The filtrate was extracted with ether three times. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Distillation of the crude product (50–58 °C/7.5 mmHg) afforded methyl(2-methylphenyl)silane as a colorless oil (1.93 g, 35%).

Methyl(2-methylphenyl)silane. Colorless oil (1.93 g, 35%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, 1H, J = 7.6 Hz), 7.30 (t, 1H, J = 7.6 Hz), 7.18–7.22 (m, 2H), 4.36 (q, 2H, J = 4.2 Hz), 2.44 (s, 3H), 0.41 (t, 3H, J = 4.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): 144.0 (C_q), 135.7 (C_q), 132.7 (CH), 130.0 (CH), 129.3 (CH), 125.2 (CH), 22.3 (CH_3), −7.8 (CH_3). EI–MS m/z: 136 ($M^{+\bullet}$). HRMS (FAB) m/z: $[M - H]^+$ calcd for $C_8H_{11}Si$ 135.0630; found 135.0634.

Methyl(2-ethylphenyl)silane. Colorless oil (11.20 g, 56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (dd, 1H, J = 7.3 Hz, 1.3 Hz), 7.35 (td, 1H, J = 7.6 Hz, 1.6 Hz), 7.22 (d, 1H, J = 7.4 Hz), 7.18 (td, 1H, J = 7.4 Hz, 1.1 Hz), 4.39 (q, 2H, J = 4.2 Hz), 2.75 (q, 2H, J = 7.6 Hz), 1.25 (t, 3H, J = 7.6 Hz), 0.42 (t, 3H, J = 4.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.4 (C_q), 135.9 (CH), 132.0 (C_q), 130.2 (CH), 127.7 (CH), 125.2 (CH), 29.3 (CH_2), 16.0 (CH_3), −7.2 (CH_3). EI–MS m/z: 150 ($M^{+\bullet}$). Anal. Calcd (%) for $C_9H_{14}Si$: C, 71.92; H, 9.39. Found: C, 71.78; H, 9.57.

Methyl(2-isopropylphenyl)silane. Colorless oil (11.39 g, 56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (dd, 1H, J = 7.3 Hz, 1.0 Hz), 7.39 (td, 1H, J = 7.6 Hz, 1.5 Hz), 7.30 (d, 1H, J = 7.6 Hz), 7.17 (td, 1H, J = 7.3 Hz, 1.2 Hz), 4.41 (q, 2H, J = 4.2 Hz), 3.10 (sept, 1H, J = 6.8 Hz), 1.27 (d, 6H, J = 7.0 Hz), 0.42 (t, 3H, J = 4.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.2 (C_q), 136.0 (CH), 131.6 (C_q), 130.4 (CH), 125.4 (CH), 124.6 (CH), 34.2 (CH), 24.2 (CH_3), −6.9 (CH_3). EI–MS m/z: 164 ($M^{+\bullet}$). Anal. Calcd (%) for $C_{10}H_{16}Si$: C, 73.09; H, 9.81. Found: C, 72.92; H, 9.94.

Methyl(2-cyclohexylphenyl)silane. Colorless oil (3.76 g, 45%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (dd, 1H, J = 7.3 Hz, 1.0 Hz), 7.37 (td, 1H, J = 7.6 Hz, 1.5 Hz), 7.27 (d, 1H, J = 7.6 Hz), 7.17 (td, 1H, J = 7.3 Hz, 1.2 Hz), 4.40 (q, 2H, J = 4.2 Hz), 2.67 (tt, 1H, J = 11.0 Hz, 2.1 Hz), 1.85–1.24 (m, 10H), 0.41 (t, 3H, J = 4.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.2 (C_q), 136.0 (CH), 131.9 (C_q), 130.2 (CH), 125.4 (CH), 125.3 (CH), 45.1 (CH), 34.6 (CH_2), 26.9 (CH_2), 26.1 (CH_2), −6.8 (CH_3). EI–MS m/z: 204 ($M^{+\bullet}$). HRMS (FAB) m/z: $[M]^{+\bullet}$ calcd for $C_{13}H_{20}Si$ 204.1329; found 204.1339.

Methyl(2-phenylphenyl)silane. Colorless oil (21.43 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (dd, 1H, J = 7.3 Hz, 0.6 Hz), 7.45 (td, 1H, J = 7.6 Hz, 1.3 Hz), 7.42–7.33 (m, 7H), 4.23 (q, 2H, J = 4.2 Hz), 0.04 (t, 3H, J = 4.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.5 (C_q), 143.4 (C_q), 136.4 (CH), 132.5 (C_q), 129.7 (CH), 129.1 (CH), 128.9 (CH), 128.1 (CH), 127.2 (CH), 126.4 (CH), −7.4 (CH_3). EI–MS m/z: 198 ($M^{+\bullet}$). Anal. Calcd (%) for $C_{13}H_{14}Si$: C, 78.72; H, 7.12. Found: C, 78.88; H, 7.09.

Methyl(3,5-dimethylphenyl)silane. Colorless oil (4.77 g, 54%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (s, 2H), 7.02 (s, 1H), 4.29 (q, 2H, J = 4.2 Hz), 2.30 (d, 6H, J = 0.7 Hz), 0.39 (t, 3H, J = 4.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.3 (C_q), 133.1 (C_q), 132.6 (CH), 131.3 (CH), 21.2 (CH_3), −7.6 (CH_3). EI–MS m/z: 150 ($M^{+\bullet}$). Anal. Calcd (%) for $C_9H_{14}Si$: C, 71.92; H, 9.39. Found: C, 71.90; H, 9.33.

Methyl(2,3,4,5,6-pentamethylphenyl)silane. Colorless solid (9.23 g, 82%). Mp: 49.2–50.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.50 (q, 2H, J = 4.2 Hz), 2.43 (s, 6H), 2.25 (s, 3H), 2.21 (s, 6H), 0.37 (t, 3H, J = 4.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.6 (C_q), 137.0 (C_q), 132.5 (CH), 129.8 (C_q), 21.3 (CH_3), 16.9 (CH_3), 16.5 (CH_3), −6.7 (CH_3). EI–MS m/z: 192 ($M^{+\bullet}$). HRMS (FAB) m/z: $[M]^{+\bullet}$ calcd for $C_{12}H_{20}Si$ 192.1329; found 192.1311.

(9-Anthracenyl)(methyl)silane. Pale yellow solid (5.73 g, 86%). Mp: 46.1–46.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.52 (d, 2H, J = 5.0 Hz), 8.03 (d, 2H, J = 8.3 Hz), 7.55–7.51 (m, 2H), 7.49–7.46 (m, 2H), 5.12 (q, 2H, J = 4.2 Hz), 0.57 (t, 3H, J = 4.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.0 (C_q), 131.1 (C_q), 130.2 (CH), 129.4 (CH), 128.0 (CH), 125.8 (CH), 124.8 (CH), −6.5 (CH_3). EI–MS m/z: 222 ($M^{+\bullet}$). HRMS (FAB) m/z: $[M]^{+\bullet}$ calcd for $C_{15}H_{14}Si$ 222.0859; found 222.0880.

9,10-Bis(methylsilyl)anthracene. Yellow solid (1.52 g, 39%). Mp: 69.9–71.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (dd, 4H, J = 6.8 Hz, 3.3 Hz), 7.54 (dd, 4H, J = 6.9 Hz, 3.2 Hz), 5.13 (q, 4H, J = 4.2 Hz), 0.59 (t, 6H, J = 4.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.3 (C_q), 133.7 (C_q), 129.2 (CH), 125.2 (CH), −6.5 (CH_3). EI–MS m/z: 266 ($M^{+\bullet}$). HRMS (FAB) m/z: $[M]^{+\bullet}$ calcd for $C_{16}H_{18}Si_2$ 266.0942; found 266.0928.

(1-Pyrenyl)(methyl)silane. Colorless oil (0.92 g, 30%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (d, 1H, J = 9.2 Hz), 8.25 (d, 1H, J = 7.6 Hz), 8.22 (d, 1H, J = 7.6 Hz), 8.20 (d, 1H, J = 7.6 Hz), 8.16 (d, 1H, J = 7.3 Hz), 8.15 (d, 1H, J = 9.1 Hz), 8.10 (d, 1H, J = 8.8 Hz), 8.06 (d, 1H, J = 8.8 Hz), 8.02 (t, 1H, J = 7.6 Hz), 4.87 (q, 2H, J = 4.4 Hz), 0.64 (t, 3H, J = 4.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.0 (CH), 133.6 (C_q), 132.7 (C_q), 131.2 (C_q), 130.8 (C_q), 129.1 (C_q), 128.1 (CH), 127.7 (CH), 127.4 (CH), 127.0 (CH), 125.9 (CH), 125.4 (CH), 125.3 (CH), 124.7 (C_q), 124.4 (C_q), 124.2 (CH), −6.9 (CH_3). EI–MS m/z: 246 ($M^{+\bullet}$). HRMS (FAB) m/z: $[M]^{+\bullet}$ calcd for $C_{17}H_{14}Si$ 246.0859; found 246.0848.

1,6-Bis(methylsilyl)pyrene. Colorless solid (1.86 g, 43%). Mp: 153.9–156.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.35 (d, 2H, J = 9.1 Hz), 8.27 (d, 2H, J = 7.6 Hz), 8.20 (d, 2H, J = 7.6 Hz), 8.14 (d, 2H, J = 8.8 Hz), 4.88 (q, 4H, J = 4.2 Hz), 0.65 (t, 6H, J = 4.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.1 (C_q), 133.6 (CH), 132.2 (C_q), 129.5 (C_q), 127.8 (CH), 124.6 (CH), 124.4 (C_q), −6.9 (CH_3). EI–MS m/z: 290 ($M^{+\bullet}$). HRMS (FAB) m/z: $[M]^{+\bullet}$ calcd for $C_{18}H_{18}Si_2$ 290.0942; found 290.0920.

Representative Experimental Procedure for the Preparation of Optically Active Tertiary Silanes 2–21 Using Palladium-Catalyzed Asymmetric Arylation of Secondary Silanes. Under an argon atmosphere, a solution of $Pd_2(dba)_3$ (23 mg, 0.025 mmol) and phosphoramidite ligand **A** (0.075 mmol) in THF (2 mL) was stirred for 2 h at room temperature. The reaction mixture was cooled to −40 °C and stirred for 10 min. To the reaction mixture were added triethylamine (3.0 mmol), 2-iodoanisole (1.0 mmol) and methyl(2,6-dimethylphenyl)silane (1.5 mmol) at the same temperature. The reaction progress was monitored by GC–MS. After stirring for 4 d, the reaction mixture was quenched with water, extracted with dichloromethane three times, and dried over sodium sulfate. The solvent was

DOI: 10.1021/acs.joc.7b00583
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evaporated under reduced pressure, and the residue was purified by preparative TLC (silica gel, eluent: hexane) to afford (2-methoxyphenyl) (methyl)(2,6-dimethylphenyl)silane (**7**) as a colorless oil (131 mg, 51%). The ee was determined to be 86% by HPLC analysis with a chiral stationary phase.

*(+)-(2-Methoxyphenyl)(methyl)(2-methylphenyl)silane (**2**).* Colorless oil (155 mg, 64%). HPLC (OD-H, hexane, flow rate 1.0 mL/min, λ = 220 nm), t_r (minor, −) = 8.9 min, t_r (minor, +) = 10.1 min, 70% ee. $[\alpha]_D^{18}$ +9.9 (*c* 0.81, hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, 1H, *J* = 7.3 Hz), 7.39−7.35 (m, 1H), 7.31−7.28 (m, 2H), 7.16 (t, 2H, *J* = 7.4 Hz), 6.92 (t, 1H, *J* = 7.0 Hz), 6.84 (d, 1H, *J* = 8.4 Hz), 5.03 (q, 1H, *J* = 3.9 Hz), 3.76 (s, 3H), 2.39 (s, 3H), 0.62 (d, 3H, *J* = 3.9 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.4 (C_q), 144.0 (C_q), 136.5 (C_q), 135.7 (CH), 134.4 (CH), 131.4 (CH), 129.9 (CH), 129.4 (CH), 124.9 (CH), 123.5 (CH), 120.6 (CH), 109.7 (C_q), 55.2 (CH_3), 22.5 (CH_3), −5.0 (CH_3). EI−MS *m*/*z*: 242 ($M^{+\bullet}$). HRMS (FAB) *m*/*z*: $[M]^{+\bullet}$ calcd for $C_{15}H_{18}OSi$ 242.1121; found 242.1119.

*(+)-(2-Methoxyphenyl)(methyl)(2-ethylphenyl)silane (**3**).* Colorless oil (154 mg, 60%). HPLC (OJ-H, hexane, flow rate 0.2 mL/min, λ = 220 nm), t_r (minor, −) = 38.9 min, t_r (major, +) = 42.2 min, 71% ee. $[\alpha]_D^{19}$ +5.0 (*c* 0.41, hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (dd, 1H, *J* = 7.3 Hz, 1.3 Hz), 7.38−7.32 (m, 2H), 7.29 (dd, 1H, *J* = 7.1 Hz, 1.7 Hz), 7.22 (d, 1H, *J* = 7.6 Hz), 7.17 (td, 1H, *J* = 7.4 Hz, 1.1 Hz), 6.91 (td, 1H, *J* = 7.3 Hz, 0.8 Hz), 6.83 (d, 1H, *J* = 8.2 Hz), 5.06 (q, 1H, *J* = 3.9 Hz), 3.75 (s, 3H), 2.78−2.69 (m, 2H), 1.14 (t, 3H, *J* = 7.6 Hz), 0.62 (d, 1H, *J* = 3.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.4 (C_q), 150.4 (C_q), 136.6 (CH), 135.7 (CH), 133.9 (C_q) 131.4 (CH), 129.7 (CH), 127.7 (CH), 125.0 (CH), 124.1 (C_q), 120.7 (CH), 109.8 (CH), 55.2 (CH_3), 29.1 (CH_2), 16.0 (CH_3), −4.5 (CH_3). EI−MS *m*/*z*: 256 ($M^{+\bullet}$). HRMS (FAB) *m*/*z*: $[M]^{+\bullet}$ calcd for $C_{16}H_{20}OSi$ 256.1278; found 256.1283.

*(+)-(2-Methoxyphenyl)(methyl)(2-isopropylphenyl)silane (**4**).* Colorless solid (187 mg, 69%). Mp: 51.2−51.4 °C. HPLC (OZ-H, hexane, flow rate 1.0 mL/min, λ = 220 nm), t_r (minor, −) = 6.0 min, t_r (major, +) = 6.8 min, 35% ee. $[\alpha]_D^{19}$ +10.9 (*c* 1.0, hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (dd, 1H, *J* = 7.4 Hz, 1.1 Hz), 7.37 (dq, 2H, *J* = 7.7 Hz, 1.2 Hz), 7.31−7.28 (m, 2H), 7.17 (td, 1H, *J* = 7.3 Hz, 1.3 Hz), 6.91 (td, 1H, *J* = 7.3 Hz, 0.9 Hz), 6.83 (d, 1H, *J* = 8.2 Hz), 5.07 (q, 1H, *J* = 3.8 Hz), 3.75 (s, 3H), 3.18 (sept, 1H, *J* = 6.7 Hz), 1.19 (d, 3H, *J* = 7.0 Hz), 1.11 (d, 1H, *J* = 6.6 Hz), 0.62 (d, 3H, *J* = 3.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.3 (C_q), 155.2 (C_q), 136.6 (CH), 135.7 (CH), 133.4 (C_q), 131.4 (CH), 129.9 (CH), 125.2 (CH), 124.7 (CH), 124.2 (C_q), 120.6 (CH), 109.7 (CH), 55.2 (CH_3), 33.6 (CH), 24.4 (CH_3), 24.1 (CH_3), −4.3 (CH_3). EI−MS *m*/*z*: 270 ($M^{+\bullet}$). HRMS (FAB) *m*/*z*: $[M]^{+\bullet}$ calcd for $C_{17}H_{22}OSi$ 270.1434; found: 270.1441.

*(+)-(2-Methoxyphenyl)(methyl)(2-cyclohexylphenyl)silane (**5**).* Colorless solid (118 mg, 38%). $[\alpha]_D^{20}$ +7.1 (*c* 0.40, hexane). Mp: 59.6−60.5 °C. HPLC (OZ-H, hexane = 100%, flow rate 0.3 mL/min, λ = 220 nm), t_r (minor, −) = 23.3 min, t_r (major, +) = 25.1 min, 40% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (dd, 1H, *J* = 7.4 Hz, 1.1 Hz), 7.38−7.32 (m, 3H), 7.25 (d, 1H, *J* = 7.4 Hz), 7.16 (td, 1H, *J* = 7.4 Hz, 1.2 Hz), 6.93 (td, 1H, *J* = 7.3 Hz, 1.0 Hz), 6.82 (d, 1H, *J* = 8.2 Hz), 5.03 (q, 1H, *J* = 3.8 Hz), 3.71 (s, 3H), 2.76 (tt, 1H, *J* = 17.7 Hz, 9.1 Hz), 1.73−1.15 (m, 10H), 0.62 (d, 3H, *J* = 3.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.3 (C_q), 154.1 (C_q), 136.5 (CH), 135.7 (CH), 133.9 (C_q), 131.3 (CH), 129.6 (CH), 125.3 (CH), 125.1 (CH), 124.5 (C_q), 120.6 (CH), 109.8 (CH), 55.3 (CH_3), 44.3 (CH), 34.7 (CH_2), 34.5 (CH_2), 26.84 (CH_2), 26.79 (CH_2), 26.1 (CH_2), −4.2 (CH_3). EI−MS *m*/*z*: 310 ($M^{+\bullet}$). HRMS (FAB) *m*/*z*: $[M]^{+\bullet}$ calcd for $C_{20}H_{26}OSi$ 310.1747; found 310.1754.

*(+)-(2-Methoxyphenyl)(methyl)(2-phenylphenyl)silane (**6**).* Colorless oil (126 mg, 41%). HPLC (OJ-H, hexane/ethanol = 50:1, flow rate 1.0 mL/min, λ = 220 nm), t_r (minor, −) = 5.1 min, t_r (major, +) = 6.0 min, 86% ee. $[\alpha]_D^{19}$ +10.4 (*c* 1.4, hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (dd, 1H, *J* = 7.3 Hz, 1.0 Hz), 7.41 (td, 1H, *J* = 7.5 Hz, 1.5 Hz), 7.37−7.22 (m, 9H), 6.90 (td, 1H, *J* = 7.4 Hz, 1.0 Hz), 6.80 (d, 1H, *J* = 8.2 Hz), 4.72 (q, 1H, *J* = 3.8 Hz), 3.71 (s, 3H), 0.23 (d, 3H, *J* = 4.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2 (C_q), 149.4 (C_q), 143.6 (C_q), 136.7 (CH), 136.2 (CH), 134.6 (C_q), 131.2 (CH), 129.3 (CH), 129.1 (CH), 129.0 (CH), 127.7 (CH), 126.9 (CH), 126.1 (CH), 124.6 (C_q), 120.6 (CH), 109.7 (CH), 55.2 (CH_3), −4.7 (CH_3). EI−MS *m*/*z*: 304 ($M^{+\bullet}$). HRMS (FAB) *m*/*z*: $[M]^{+\bullet}$ calcd for $C_{20}H_{20}OSi$ 304.1278; found 304.1281.

*(+)-(S)-(2-Methoxyphenyl)(methyl)(2,6-dimethylphenyl)silane (**7**).* Colorless solid (131 mg, 51%). Mp: 51.5−52.9 °C. HPLC (OJ-H, hexane/ethanol = 100:1, flow rate 1.0 mL/min, λ = 220 nm), t_r (major, +) = 4.6 min, t_r (minor, −) = 5.4 min, 89% ee. $[\alpha]_D^{18}$ +35.0 (*c* 0.91, hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (td, 1H, *J* = 7.8 Hz, 1.8 Hz), 7.31 (dd, 1H, *J* = 7.3 Hz, 1.6 Hz), 7.16 (t, 1H, *J* = 7.6 Hz), 6.99 (d, 2H, *J* = 7.6 Hz), 6.92 (td, 1H, *J* = 7.3 Hz, 0.7 Hz), 6.82 (d, 1H, *J* = 8.2 Hz), 5.24 (q, 1H, *J* = 4.2 Hz), 3.74 (s, 3H), 2.42 (s, 6H), 0.66 (d, 3H, *J* = 4.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.4 (C_q), 144.8 (C_q), 136.2 (CH), 133.3 (C_q), 131.2 (CH), 129.2 (CH), 127.5 (CH), 124.0 (C_q), 120.7 (CH), 109.8 (CH), 55.2 (CH_3), 24.0 (CH_3), −3.5 (CH_3). EI−MS *m*/*z*: 256 ($M^{+\bullet}$). HRMS (FAB) *m*/*z*: $[M]^{+\bullet}$ calcd for $C_{16}H_{20}OSi$ 256.1278; found 256.1264.

*(+)-(2-Methoxyphenyl)(methyl)(3-methylphenyl)silane (**8**).* Colorless oil (169 mg, 70%). $[\alpha]_D^{19}$ +8.5 (*c* 0.32, hexane). HPLC (OZ-H, hexane = 100%, flow rate 0.5 mL/min, λ = 220 nm), t_r (major, +) = 18.0 min, t_r (minor, −) = 19.8 min, 65% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41−7.35 (m, 4H), 7.24 (t, 1H, *J* = 7.3 Hz), 7.18 (d, 1H, *J* = 7.6 Hz), 6.93 (td, 1H, *J* = 7.3 Hz, 1.0 Hz), 6.84 (d, 1H, *J* = 7.9 Hz), 4.89 (q, 1H, *J* = 3.8 Hz), 3.78 (s, 3H), 2.34 (s, 3H), 0.60 (d, 3H, *J* = 3.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.3 (C_q), 137.0 (C_q), 136.7 (CH), 135.7 (C_q), 135.5 (CH), 131.9 (CH), 131.5 (CH), 130.0 (CH), 127.6 (CH), 123.9 (C_q), 120.6 (CH), 109.7 (CH), 55.2 (CH_3), 21.5 (CH_3), −5.0 (CH_3). EI−MS *m*/*z*: 242 ($M^{+\bullet}$). HRMS (FAB) *m*/*z*: $[M]^{+\bullet}$ calcd for $C_{15}H_{18}OSi$ 242.1127; found 242.1145.

*(+)-(2-Methoxyphenyl)(methyl)(4-methylphenyl)silane (**9**).* Colorless oil (52 mg, 22%). $[\alpha]_D^{19}$ +10.6 (*c* 0.18, hexane). HPLC (OD-H, hexane = 100%, flow rate 1.0 mL/min, λ = 220 nm), t_r (minor, −) = 8.6 min, t_r (major, +) = 9.5 min, 60% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, 2H, *J* = 8.2 Hz), 7.37 (dd, 1H, *J* = 7.3 Hz, 2.2 Hz), 7.35 (d, 1H, *J* = 7.3 Hz), 7.17 (d, 2H, *J* = 7.3 Hz), 6.92 (td, 1H, *J* = 7.3 Hz, 0.6 Hz), 6.84 (d, 1H, *J* = 7.9 Hz), 4.90 (q, 1H, *J* = 3.8 Hz), 3.78 (s, 3H), 2.35 (s, 3H), 0.59 (d, 3H, *J* = 3.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.3 (C_q), 139.0 (C_q), 136.6 (CH), 134.9 (CH), 132.2 (C_q), 131.4 (CH), 128.6 (CH), 124.0 (C_q), 120.6 (CH), 109.7 (CH), 55.2 (CH_3), 21.5 (CH_3), −5.0 (CH_3). EI−MS *m*/*z*: 242 ($M^{+\bullet}$). HRMS (FAB) *m*/*z*: $[M]^{+\bullet}$ calcd for $C_{15}H_{18}OSi$ 242.1121; found 242.1114.

*(+)-(2-Methoxyphenyl)(methyl)(3,5-dimethylphenyl)silane (**10**).* Colorless oil (142 mg, 55%). $[\alpha]_D^{19}$ +5.8 (*c* 0.70, hexane). HPLC (OZ-H, hexane = 100%, flow rate 0.3 mL/min, λ = 220 nm), t_r (minor, −) = 26.2 min, t_r (major, +) = 28.8 min, 62% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38−7.35 (m, 2H), 7.21 (s, 2H), 7.01 (s, 1H), 6.93 (td, 1H, *J* = 7.3 Hz, 0.6 Hz), 6.84 (d, 1H, *J* = 7.9 Hz), 4.87 (q, 1H, *J* = 3.8 Hz), 3.78 (s, 3H), 2.30 (d, 6H, *J* = 0.6 Hz), 0.59 (d, 3H, *J* = 3.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.3 (C_q), 137.0 (C_q), 136.7 (CH), 135.5 (C_q), 132.6 (CH), 131.4 (CH), 131.0 (CH), 124.0 (C_q), 120.6 (CH), 109.7 (CH), 55.2 (CH_3), 21.3 (CH_3), −5.0 (CH_3). EI−MS *m*/*z*: 256 ($M^{+\bullet}$). HRMS (FAB) *m*/*z*: $[M]^{+\bullet}$ calcd for $C_{16}H_{20}OSi$ 256.1278; found 256.1309.

*(+)-(2-Methoxyphenyl)(methyl)(2,3,4,5,6-pentamethylphenyl)-silane (**11**).* Colorless solid (103 mg, 34%). $[\alpha]_D^{20}$ +11.9 (*c* 0.81, hexane). Mp: 76.1−77.5 °C. HPLC (OD-H, hexane = 100%, flow rate 0.5 mL/min, λ = 220 nm), t_r (major, +) = 18.0 min, t_r (minor, −) = 21.3 min, 85% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36−7.33 (m, 2H), 6.90 (t, 1H, *J* = 7.3 Hz), 6.83 (d, 1H, *J* = 7.9 Hz), 5.29 (q, 1H, *J* = 4.1 Hz), 3.80 (s, 3H), 2.38 (s, 6H), 2.26 (s, 3H), 2.21 (s, 6H), 0.64 (d, 3H, *J* = 4.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.3 (C_q), 140.3 (C_q), 136.6 (C_q), 136.5 (CH), 132.5 (C_q), 131.3 (C_q), 131.0 (CH), 124.7 (C_q), 120.6 (CH), 109.7 (CH), 55.3 (CH_3), 21.8 (CH_3), 17.0 (CH_3), 16.5 (CH_3), −2.4 (CH_3). EI−MS *m*/*z*: 298 ($M^{+\bullet}$). HRMS (FAB) *m*/*z*: $[M]^{+\bullet}$ calcd for $C_{19}H_{26}OSi$ 298.1747; found 298.1754.

*(+)-(3-Methoxyphenyl)(methyl)(2,6-dimethylphenyl)silane (**12**).* Colorless oil (63 mg, 24%). $[\alpha]_D^{19}$ +20.4 (*c* 0.41, hexane). HPLC (OZ-H, hexane = 100%, flow rate 0.7 mL/min, λ = 220 nm), t_r (major, +) = 15.9 min, t_r (minor, −) = 18.0 min, 77% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (t, 1H, *J* = 7.7 Hz), 7.19 (t, 1H, *J* = 7.6 Hz), 7.07 (d,

DOI: 10.1021/acs.joc.7b00583
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1H, J = 7.3 Hz), 7.03 (d, 1H, J = 2.5 Hz), 7.00 (d, 2H, J = 7.6 Hz), 6.89 (dd, 1H, J = 7.7 Hz, 2.3 Hz), 5.24 (q, 1H, J = 4.2 Hz), 3.77 (s, 3H), 2.39 (s, 6H), 0.68 (d, 3H, J = 4.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1 (C_q), 144.9 (C_q), 137.8 (C_q), 132.3 (C_q), 129.7 (CH), 129.2 (CH), 127.7 (CH), 116.7 (CH), 120.0 (CH), 114.3 (CH), 55.0 (CH_3), 24.3 (CH_3), −4.2 (CH_3). EI−MS m/z: 256 ($M^{+\bullet}$). HRMS (FAB) m/z: $[M]^{+\bullet}$ calcd for $C_{16}H_{20}OSi$ 256.1278; found 256.1284.

(+)-(4-Methoxyphenyl)(methyl)(2,6-dimethylphenyl)silane (**13**). Colorless oil (103 mg, 40%). $[\alpha]_D^{20}$ +30.8 (c 0.65, hexane). HPLC (OJ-H, hexane = 100%, flow rate 1.0 mL/min, λ = 220 nm), t_r (major, +) = 13.8 min, t_r (minor, −) = 21.5 min, 70% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, 2H, J = 8.5 Hz), 7.19 (t, 1H, J = 7.6 Hz), 7.00 (d, 2H, J = 7.6 Hz), 6.88 (d, 2H, J = 8.5 Hz), 5.24 (q, 1H, J = 4.1 Hz), 3.80 (s, 3H), 2.39 (s, 6H), 0.66 (d, 3H, J = 4.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.6 (C_q), 144.9 (C_q), 135.8 (CH), 132.8 (C_q), 129.6 (CH), 127.6 (CH), 126.6 (C_q), 113.8 (CH), 55.0 (CH_3), 24.2 (CH_3), −4.0 (CH_3). EI−MS m/z: 256 ($M^{+\bullet}$). HRMS (FAB) m/z: $[M]^{+\bullet}$ calcd for $C_{16}H_{20}OSi$ 256.1278; found 256.1279.

(+)-(Phenyl)(methyl)(2,6-dimethylphenyl)silane (**14**). Colorless oil (105 mg, 46%). $[\alpha]_D^{18}$ +31.4 (c 0.81, hexane). HPLC (OJ-H, hexane = 100%. flow rate 1.0 mL/min, λ = 220 nm), t_r (major, +) = 6.3 min, t_r (minor, −) = 7.8 min, 83% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (dd, 2H, J = 7.7 Hz, 1.7 Hz), 7.36−7.31 (m, 3H), 7.20 (t, 1H, J = 7.6 Hz), 7.01 (d, 2H, J = 7.6 Hz), 5.26 (q, 1H, J = 4.1 Hz), 2.39 (s, 6H), 0.69 (d, 3H, J = 4.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.9 (C_q), 136.1 (C_q), 134.4 (CH), 132.5 (C_q), 129.7 (CH), 129.1 (CH), 127.9 (CH), 127.7 (CH), 24.3 (CH_3), −4.2 (CH_3). EI−MS m/z: 226 ($M^{+\bullet}$). HRMS (FAB) m/z: $[M]^{+\bullet}$ calcd for $C_{15}H_{18}Si$ 226.1172; found 226.1158.

(+)-(3-Cyanophenyl)(methyl)(2,6-dimethylphenyl)silane (**15**). Colorless oil (129 mg, 51%). $[\alpha]_D^{18}$ +39.0 (c 0.31, hexane). HPLC (OZ-H, hexane = 100%, flow rate 1.5 mL/min, λ = 220 nm), t_r (minor, −) = 28.8 min, t_r (major, +) = 34.7 min, 82% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.69 (d, 1H, J = 7.6 Hz), 7.63 (d, 1H, J = 7.6 Hz), 7.42 (t, 1H, J = 7.7 Hz), 7.23 (t, 1H, J = 7.6 Hz), 7.03 (d, 2H, J = 7.6 Hz), 5.26 (q, 1H, J = 4.1 Hz), 2.37 (s, 6H), 0.72 (d, 3H, J = 4.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.8 (C_q), 138.6 (C_q), 138.4 (CH), 137.8 (CH), 132.5 (CH), 130.7 (C_q), 130.3 (CH), 128.5 (CH), 127.9 (CH), 119.0 (C_q), 112.3 (C_q), 24.2 (CH_3), −4.4 (CH_3). EI−MS m/z: 251 ($M^{+\bullet}$). HRMS (FAB) m/z: $[M]^{+\bullet}$ calcd for $C_{16}H_{17}NSi$ 251.1125; found 251.1121.

(+)-(2-Methoxyphenyl)(cyclohexyl)(phenyl)silane (**16**). Yellow oil (184 mg, 62%). $[\alpha]_D^{18}$ +9.5 (c 0.71, hexane). HPLC (OJ-H, methanol = 100%, flow rate 0.5 mL/min, λ = 220 nm), t_r (major, +) = 12.1 min, t_r (minor, −) = 13.0 min, 64% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (td, 2H, J = 3.8 Hz, 2.1 Hz), 7.45 (dd, 1H, J = 7.3 Hz, 1.9 Hz), 7.38−7.30 (m, 4H), 6.93 (td, 1H, J = 7.3 Hz, 0.6 Hz), 6.84 (d, 1H, J = 8.5 Hz), 4.60 (d, 1H, J = 4.5 Hz), 3.79 (s, 3H), 1.75−1.68 (m, 5H), 1.41−1.24 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.1 (C_q), 137.5 (CH), 135.5 (CH), 134.8 (C_q), 133.9 (C_q), 131.4 (CH), 129.0 (CH), 127.6 (CH), 122.6 (C_q), 120.6 (CH), 109.6 (CH), 55.1 (CH_3), 28.7 (CH), 28.6 (CH_2), 28.0 (CH_2), 27.9 (CH_2), 26.8 (CH_2), 23.2 (CH_2). EI−MS m/z: 296 ($M^{+\bullet}$). HRMS (FAB) m/z: $[M]^{+\bullet}$ calcd for $C_{19}H_{24}OSi$ 296.1591; found 296.1569.

(+)-(2-Methoxyphenyl)(phenyl)(o-tolyl)silane (**17**). Colorless oil (104 mg, 34%). $[\alpha]_D^{18}$ +0.7 (c 0.68, hexane). HPLC (OZ-H, hexane = 100%, flow rate 1.0 mL/min, λ = 220 nm), t_r (minor, −) = 14.9 min, t_r (major, +) = 23.1 min, 21% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (dd, 2H, J = 7.9 Hz, 1.3 Hz), 7.42−7.37 (m, 2H), 7.35−7.29 (m, 4H), 7.25 (dd, 1H, J = 7.4 Hz, 1.7 Hz), 7.18 (d, 1H, J = 8.2 Hz), 7.11 (t, 1H, J = 7.4 Hz), 6.93 (t, 1H, J = 7.3 Hz), 6.88 (d, 1H, J = 8.2 Hz), 5.58 (s, 1H), 3.67 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.5 (C_q), 144.5 (C_q), 137.6 (CH), 136.7 (CH), 135.7 (CH), 133.9 (C_q), 132.6 (C_q), 131.9 (CH), 129.8 (CH), 129.4 (CH), 129.3 (CH), 127.8 (CH), 124.9 (CH), 121.7 (C_q), 120.8 (CH), 110.0 (CH), 55.3 (CH_3), 22.6 (CH_3). EI−MS m/z: 304 ($M^{+\bullet}$). HRMS (FAB) m/z: $[M]^{+\bullet}$ calcd for $C_{20}H_{20}OSi$ 304.1278; found 304.1271.

(S)-(+)-(9-Anthracenyl)(2-methoxyphenyl)(methyl)silane (**18**). Colorless solid (332 mg, 50%). Mp: 108.1−108.7 °C. $[\alpha]_D^{20}$ +92.2 (c 0.5, CH_2Cl_2). HPLC (OJ-H, hexane/i-PrOH = 95:5, flow rate 1.0 mL/min, λ = 220 nm), t_r (major, −) = 8.8 min, t_r (minor, +) = 12.9 min, 82% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.56 (d, 2H, J = 9.2 Hz), 8.47 (s, 1H), 7.98−7.97 (m, 2H), 7.41−7.37 (m, 5H), 7.33−7.30 (m, 1H), 6.85 (t, 1H, J = 7.3 Hz), 6.79 (d, 1H, J = 8.2 Hz), 5.96 (q, 1H, J = 3.8 Hz), 3.64 (s, 3H), 0.86 (d, 3H, J = 4.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): 164.4 (C_q), 137.3 (C_q), 136.6 (C_q), 131.6 (CH), 131.5 (CH), 131.3 (CH), 130.1 (CH), 129.3 (CH), 128.9 (CH), 125.2 (CH), 124.7 (CH), 123.9 (CH), 120.8 (C_q) 109.8 (C_q), 55.2 (CH_3), −2.7 (CH_3). EI−MS m/z: 328 ($M^{+\bullet}$). HRMS (FAB) m/z: $[M]^{+\bullet}$ calcd for $C_{22}H_{20}OSi$ 328.1278; found 328.1263.

(S,S)-(+)-9,10-Bis((2-methoxyphenyl)(methyl)silyl)anthracene (**19**). Colorless needles (125 mg, 35%). Mp: 177.4−180.3 °C. $[\alpha]_D^{15}$ +97.1 (c 1.0, CH_2Cl_2). HPLC (OJ-H, MeOH, flow rate 1.0 mL/min, λ = 220 nm), t_r (major, +) = 13.2 min, t_r (minor, −) = 16.2 min, >99% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.58 (dd, 4H, J = 6.9 Hz, 3.5 Hz), 7.43−7.36 (m, 8H), 6.91−6.87 (m, 4H), 5.92 (q, 2H, J = 4.1 Hz), 3.76 (s, 6H), 0.85 (d, 6H, J = 3.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.4 (C_q), 136.8 (CH), 136.7 (C_q), 135.4 (C_q), 131.5 (CH), 129.8 (CH), 124.4 (CH), 124.0 (C_q), 120.9 (CH), 109.7 (CH), 55.3 (CH_3), −2.4 (CH_3). EI−MS m/z: 478 ($M^{+\bullet}$). HRMS (FAB) m/z: $[M]^{+\bullet}$ calcd for $C_{30}H_{30}O_2Si_2$ 478.1779; found 478.1773.

(S)-(+)-(1-Pyrenyl)(2-methoxyphenyl)(methyl)silane (**20**). Colorless solid (177 mg, 50%). Mp: 102.5−103.4 °C. $[\alpha]_D^{19}$ +126.0 (c 1.0, CH_2Cl_2). HPLC (MeOH, flow rate 0.5 mL/min, λ = 220 nm), t_r (major, +) = 27.5 min, t_r (minor, −) = 30.1 min, 61% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (d, 1H, J = 9.2 Hz), 8.25 (d, 1H, J = 8.2 Hz), 8.16 (t, 3H, J = 6.9 Hz), 8.08 (q, 2H, J = 8.2 Hz), 8.05 (d, 1H, J = 9.2 Hz), 7.99 (t, 1H, J = 7.6 Hz), 7.37 (td, 1H, J = 7.7, 1.9 Hz), 7.32 (dd, 1H, J = 7.1, 1.9 Hz), 6.89−6.85 (m, 2H), 5.57 (q, 1H, J = 3.8 Hz), 3.75 (s, 3H), 0.87 (d, 3H, J = 3.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.4 (C_q), 136.8 (CH), 136.0 (C_q), 133.4 (CH), 132.3 (C_q), 131.6 (CH), 131.4 (C_q), 131.3 (C_q), 130.8 (C_q), 128.0 (CH), 127.7 (CH), 127.5 (CH), 127.2 (CH), 125.8 (CH), 125.2 (CH), 125.0 (CH), 124.8 (C_q), 124.4 (C_q), 124.2 (CH), 123.7 (C_q), 120.8 (CH), 109.8 (CH), 55.3 (CH_3), −4.3 (CH_3). EI−MS m/z: 352 ($M^{+\bullet}$). HRMS (FAB) m/z: $[M]^{+\bullet}$ calcd for $C_{24}H_{20}OSi$ 352.1278; found 352.1280.

(S,S)-(+)-1,6-Bis((2-methoxyphenyl)(methyl)silyl)pyrene (**21**). Colorless solid (276 mg, 11%). Mp: 135.1−137.6 °C. $[\alpha]_D^{26}$ +128.7 (c 1.0, CH_2Cl_2). HPLC (OJ-H, MeOH, flow rate 2.0 mL/min, λ = 220 nm), t_r (minor + meso, −) = 9.2 min, t_r (major, +) = 12.0 min, 90% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.42 (d, 2H, J = 9.1 Hz), 8.23 (d, 2H, J = 7.6 Hz), 8.14 (d, 2H, J = 7.6 Hz), 8.02 (d, 2H, J = 8.8 Hz), 7.35 (t, 2H, J = 7.9 Hz), 7.29 (d, 2H, J = 7.3 Hz), 6.87−6.82 (m, 4H), 5.58 (q, 2H, J = 3.8 Hz), 3.72 (s, 6H), 0.86 (d, 6H, J = 3.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.4 (C_q), 136.8 (CH), 136.2 (C_q), 133.3 (CH), 131.9 (C_q), 131.6 (CH), 131.4 (C_q), 128.3 (CH), 127.4 (CH), 124.6 (C_q), 124.4 (CH), 123.7 (C_q), 120.8 (CH), 109.8 (CH), 55.2 (CH_3), −4.3 (CH_3). FAB−MS m/z: 503 ([M + H]$^+$). HRMS (FAB) m/z: $[M]^{+\bullet}$ calcd for $C_{32}H_{30}O_2Si_2$ 502.1779; found 502.1791.

Experimental Procedure for the Preparation of Optically Active Quaternary Silane (22) from Phenylmethylsilane via Stepwise Arylation. A mixture of $Pd_2(dba)_3$ (46 mg, 0.050 mmol) and phosphoramidite ligand **A** (115 mg, 0.15 mmol) was stirred in THF (2.1 mL) for 2 h at room temperature. The reaction mixture was cooled to −40 °C and stirred for an additional 10 min. To the reaction mixture were added triethylamine (836 μL, 6.0 mmol), 2-iodoanisole (165 μL, 1.3 mmol), and phenylmethylsilane (275 μL, 2.0 mmol). After stirring for 3 d at −40 °C, the temperature was allowed to increase to room temperature, and 2-iodothiophene (195 μL, 1.0 mmol) was added to the reaction mixture. After stirring for 8 d at room temperature, the reaction mixture was quenched with water and extracted with dichloromethane three times, and the extracts were dried over sodium sulfate. The solvent was evaporated under reduced pressure, and purification of crude product by preparative TLC (silica gel) afforded (*R*)-(2-methoxyphenyl)(phenyl)(2-thiophenyl)(methyl)-silane (**22**) as a colorless solid (138 mg, 45%). The arylated product was determined to have 71% ee by HPLC analysis with a chiral stationary phase.

DOI: 10.1021/acs.joc.7b00583
J. Org. Chem. 2017, 82, 6108−6117

*(R)-(+)-(2-Methoxyphenyl)(phenyl)(2-thiophenyl)(methyl)silane (**22**).* Colorless solid (138 mg, 45%). $[\alpha]_D^{18}$ +2.3 (*c* 0.32, hexane). Mp: 71.2−72.6 °C. HPLC (OJ-H, hexane/EtOH = 1:1, flow rate 0.3 mL/min, λ = 280 nm), t_r (minor, −) = 20.1 min, t_r (major, +) = 21.9 min, 71% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, 1H, *J* = 4.7 Hz), 7.54 (dd, 2H, *J* = 7.6 Hz, 0.9 Hz), 7.41−7.30 (m, 5H), 7.25 (dd, 1H, *J* = 7.3 Hz, 1.6 Hz), 7.19 (dd, 1H, *J* = 3.7 Hz, 4.2 Hz), 6.91 (t, 1H, *J* = 7.3 Hz), 6.86 (d, 1H, *J* = 8.5 Hz), 3.68 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.5 (C_q), 136.9 (CH), 136.8 (C_q), 136.6 (CH), 136.4 (C_q), 134.8 (CH), 131.8 (CH), 131.4 (CH), 129.2 (CH), 128.0 (CH), 127.6 (CH), 123.9 (C_q), 120.6 (CH), 110.0 (CH), 55.0 (CH_3), −2.0 (CH_3). EI−MS *m*/*z*: 310 ($M^{+\bullet}$). HRMS (FAB) *m*/*z*: $[M]^{+\bullet}$ calcd for $C_{18}H_{18}OSSi$ 310.0842; found 310.0845.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00583.

Copies of ^{1}H and ^{13}C NMR, MS, HPLC analysis for all new compounds, and photophysical data and theoretical calculations of **18**−**21** (PDF)
X-ray crystallographic file for molecule (*S*)-**7** (CIF)
X-ray crystallographic file for molecule (*S*,*S*)-**19** (CIF)
X-ray crystallographic file for molecule (*S*,*S*)-**21** (CIF)
X-ray crystallographic file for molecule (*R*)-**22** (CIF)
(CIF)
(CIF)
(CIF)
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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Dr. Aiko Kamitsubo, the Elemental Analysis Center of The University of Tokyo, for the elemental analysis measurements. We also thank Ms. Hikaru Koike for the measurement of CPL spectrum of (*S*)-**18**. X-ray diffraction measurements of (*S*,*S*)-**21** were supported by "Nanotechnology Platform" (No. 12024046) of the Ministry of Education, Culture, Sports, Science and Technology, Japan. The present work was financially supported in part by CREST from JST (No. JPMJCR15F2; H.N.), Tokyo Kasei Chemical Promotion foundation (Y.Y.), Nippon Sheet Glass Foundation for Materials Science and Engineering (Y.Y.), Precise Measurement Technology Promotion Foundation (Y.Y.), Grant-in-Aids for Scientific Research (C) (No. 15K05604; Y.Y.), and Scientific Research on Innovative Areas "Molecular Architectonics: Orchestration of Single Molecules for Novel Functions" (area 2509, Nos. 26110505, 26110506, 16H00957, and 16H00958; H.N. and Y.Y.) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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DOI: 10.1021/acs.joc.7b00583
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