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

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[§]Graduate School of Science and Engineering, University of Toyama, 3190 Gofuku, Toyama 930-8555, Japan **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_{hum} : +0.008, $\sigma_{\rm F}$: 0.42). This simple molecular design opens up new strategies for developing small organic CPL dyes.

Introduction

There has been growing interest in the applications 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 complexes³ and aggregates with organic fluorophores⁴ often exhibit CPL. Although simple (small, nonaggregated, nonpolymeric) 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 σ - π 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 functionalization have been much less explored, and enantioselective synthesis of tertiary silanes remains a considerable challenge.

In our previous paper, we reported that $Pd(P(t-Bu)_3)_2$ 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 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, phenylmethylsilane reacted with 2-iodoanisole in the presence of (*R*,*R*)-A and Pd₂(dba)₃ to give (*S*)-phenyl(2-methoxyphenyl)methylsilane (1) in 57% yield and 61%ee (Scheme 1).

Scheme 1. Previous work



In our previous paper, we only examined mono-arylation 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: 64% 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. : 60%ee. and : 63%ee). Arylation of 2,3,4,5,6-pentamethylsilane 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: 85%ee). In contrast with the arylation of

methylphenylsilane, (cyclohexyl)phenylsilane exhibited good enantioselectivity (16: 64%ee). Phenyl(2-methylphenyl)silane also 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. Di-substituted 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.



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), trimethylamine (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 comparison with the reported data or X-ray analysis. ^{*d*}Results when reaction was carried out at -60 °C. ^{*e*}*dl/meso* ratio was determined by ¹³C NMR.

The Journal of Organic Chemistry

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 (Figures 1, S1, S2, and 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



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 have been removed for clarity except for Si–H.

19 and 21.

Construction of chiral quaternary silanes. To explore the synthetic utility of the current arylation reaction 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 (*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 silicon-stereogenic quaternary silane from secondary one



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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 di-substituted derivatives (19 and 21) displayed red-shifted absorption and emission compared with the mono-substituted derivatives (18 and 20), indicating an extended conjugation in the mono-substituted 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 ($\Phi_{\rm F}$: 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 CH₂Cl₂ (0.01 mM) showed fluorescence bands from 380 nm to 480 nm, which were attributed to the π - π * 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 (Figures 2(a) and (b)). The asymmetric factor, g_{abs} , at the π - π * transition showed values of ca. 10⁻⁴ for all compounds.

Compound	$\lambda_{\rm abs}({\rm nm})^a$	$\varepsilon (\mathrm{dm^3mol^{-1}cm^{-1}})^b$	$\lambda_{\mathrm{ex}} \left(\mathrm{nm} \right)$	$\lambda_{\rm em} ({\rm nm})$	${\it \Phi_{ m F}}^c$	τ (ns)	$g_{ m abs}$	$g_{ m lum}$
(<i>S</i>) -18	<u>367,</u> 387	9,700	367	395, 416	0.55	7.5	-1.2×10 ⁻⁴	$+0.00085^{d}$
							(386 nm)	(427 nm)
(<i>S</i> , <i>S</i>)- 19	<u>381,</u> 402	11,900	402	417, 436	0.97	9.1	-2.2×10 ⁻⁴	-0.0014^{d}
							(401 nm)	(416 nm)
(S) -20	279, 331, <u>348</u>	41,300	348	376, 394 ^e	0.13 ^e	23.4 ^e	+2.3×10 ⁻⁴	_ <i>e</i> , <i>f</i>
				393, 478 ^g	0.13 ^g	44.5 ^g	(347 nm)	-0.0016 (490 nm) ^g
(<i>S</i> , <i>S</i>) -21	283, 341, <u>358</u>	46,200	358	382, 402 ^e	0.45 ^e	30.4 ^e	+1.3×10 ⁻⁴	e,f
				402, 500 ^g	0.42 ^g	73.2 ^g	(356 nm)	+0.008 (500 nm) ^g

Table 2. Optical properties of optically pure 18–21 in CH₂Cl₂

^{*a*}Underlined values are wavelengths which 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*}No CPL signal was observed. ^{*g*}Concentration: 4.0×10^{-3} M.

The size and type of substituents on the silicon atoms affected the CPL properties substantially. The CPL strength increased as the acene unit lengthened (anthracene < pyrene) and as the number of chiral silicon stereogenic groups increased (mono-substituted \leq di-substituted). Figures 2, S7, and S8 show the UV-vis, circular dichroism (CD), total luminescence (TL), and CPL spectra for the CH₂Cl₂ solution of (S,S)-21. The CD spectrum showed positive Cotton effects at 356 nm (g_{abs} : +1.3×10⁻⁴). 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 element chiral center exhibit a large g_{lum} value near the order of 10^{-2} . The absolute g_{lum} values of single molecules are generally 1×10^{-3} to 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 conventional CD-active materials.



Figure 2. (a) UV-vis absorption (solid line) and CD spectra (dotted line) of (S,S)-**21** in CH₂Cl₂. (b) TL (solid line) and CPL (dotted line) of (S,S)-**21** in CH₂Cl₂ (4.0 mM) upon excitation at 300–380 nm. Inset: Photograph of (S,S)-**21** in CH₂Cl₂ (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.

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 \rightarrow LUMO transition was predominant in the lowest-energy transitions (S_1 state). The longest wavelength peaks in the absorption spectra were assigned to the π - π * S₁ 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. Based on 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 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 in 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-CH₃ 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.



Figure 3. Proposed transition state for the stereoselective arylation of the secondary silane. Hydrogen atoms have been removed for clarity except for Si-H and Pd-H

Conclusion

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 Bruker US-500 spectrometer using CDCl₃ as the solvent at ambient temperature. Chemical shifts are reported in ppm with TMS (0.00 ppm) as the reference for ¹H NMR spectra and CDCl₃ (77.0 ppm) as the reference for ¹³C NMR spectra. ¹³C 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) as stated in the experimental section. 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 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 by 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 and phenyl(2-methylphenyl)silane²⁴ 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 rotating-anode generator system equipped with а X-ray producing graphite-monochromated MoK α radiation ($\lambda = 0.7107$ Å). X-ray diffraction data for 21 were collected at 93 K on a Rigaku Saturn 724 (Varimax dual) diffractometer with a multi-layer mirror monochromated ΜοΚα 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-92²⁵ 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 calculation. DFT and TD-DFT calculations were executed by 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-MeC₆H₄MgBr (2 M, 20 mL, diethyl ether solution) at -78 °C. The mixture was stirred for 2 h and the temperature allowed to rise to room temperature. After overnight stirring, to the mixture was added LiAlH₄ (1.651 g, 40.8 mmol) at 0 °C and additionally stirred for overnight. To the reaction mixture was sequentially added 1.6 mL of water,

1.6 mL of 4 N aqueous NaOH, and 4.8 mL of water carefully. 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 Na₂SO₄ 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%). ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 144.0 (C_q), 135.7 (C_q), 132.7 (CH), 130.0 (CH), 129.3 (CH), 125.2 (CH), 22.3 (CH₃), -7.8 (CH₃). EI–MS *m/z*: 136 (M⁺⁺). HRMS (FAB) *m/z*: [M–H]⁺ Calcd for C₈H₁₁Si 135.0630; Found 135.0634.

Methyl(2-*ethylphenyl*)*silane*. Colorless oil (11.20 g, 56%). ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): δ 150.4 (C_q), 135.9 (CH), 132.0 (C_q), 130.2 (CH), 127.7 (CH), 125.2 (CH),

29.3 (CH₂), 16.0 (CH₃), −7.2 (CH₃). EI–MS *m/z*: 150 (M⁺⁺). Elemental analysis: Calcd (%) for C₉H₁₄Si: C 71.92, H 9.39. Found: C 71.78, H 9.57.

Methyl(2-*isopropylphenyl*)*silane*. Colorless oil (11.39 g, 56%). ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), -6.9 (CH₃). EI–MS *m/z*: 164 (M⁺⁺). Elemental analysis: Calcd (%) for C₁₀H₁₆Si: C 73.09, H 9.81. Found: C 72.92, H 9.94.

Methyl(2-cyclohexylphenyl)silane. Colorless oil (3.76 g, 45%). ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): δ 154.2 (Cq), 136.0 (CH), 131.9 (Cq), 130.2 (CH), 125.4 (CH), 125.3 (CH), 45.1 (CH), 34.6 (CH₂), 26.9 (CH₂), 26.1 (CH₂), -6.8 (CH₃). EI–MS *m/z*: 204 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₁₃H₂₀Si: 204.1329; Found 204.1339.

The Journal of Organic Chemistry

Methyl(2-*phenylphenyl*)*silane*. Colorless oil (21.43 g, 73%). ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃). EI–MS *m/z*: 198 (M⁺⁺). Elemental analysis: Calcd (%) for C₁₃H₁₄Si: C 78.72, H 7.12. Found: C 78.88, H 7.09.

Methyl(3,5-dimethylphenyl)silane. Colorless oil (4.77 g, 54%). ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): δ 137.3 (C_q), 133.1 (C_q), 132.6 (CH), 131.3 (CH), 21.2 (CH₃), -7.6 (CH₃). EI–MS *m/z*: 150 (M⁺⁺). Elemental analysis: Calcd (%) for C₉H₁₄Si: 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. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): δ 139.6 (C_q), 137.0 (C_q), 132.5 (CH), 129.8 (C_q), 21.3 (CH₃), 16.9 (CH₃), 16.5 (CH₃), -6.7 (CH₃). EI-MS m/z: 192 (M⁺⁺). HRMS (FAB) m/z: [M]⁺⁺ Calcd for C₁₂H₂₀Si 192.1329; Found 192.1311.

(9-Anthracenyl)(methyl)silane. Pale yellow solid (5.73 g, 86%). Mp: 46.1–46.9 °C.
¹H NMR (500 MHz, CDCl₃): 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).
¹³C NMR (125 MHz, CDCl₃): δ 137.0 (Cq), 131.1 (Cq), 130.2 (CH), 129.4 (CH),
128.0 (CH), 125.8 (CH), 124.8 (CH), -6.5 (CH₃). EI–MS *m/z*: 222 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₁₅H₁₄Si 222.0859; Found 222.0880.

9,10-Bis(methylsilyl)anthracene. Yellow solid (1.52 g, 39%). Mp: 69.9–71.6 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.55 (dd, 4H, J = 6.8 Hz, 3.3 Hz), 7.54 (dd, 4H, J = 6.9Hz, 3.2 Hz), 5.13 (q, 4H, J = 4.2 Hz), 0.59 (t, 6H, J = 4.3 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 136.3 (C_q), 133.7 (C_q), 129.2 (CH), 125.2 (CH), -6.5 (CH₃). EI–MS *m/z*: 266 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₁₆H₁₈Si₂: 266.0942; Found 266.0928.

(1-Pyrenyl)(methyl)silane. Colorless oil (0.92 g, 30%). ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃). EI–MS *m/z*: 246 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₁₇H₁₄Si 246.0859; Found 246.0848.

1,6-Bis(methylsilyl)pyrene. Colorless solid (1.86 g, 43%). Mp: 153.9–156.0 °C. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): δ 136.1 (Cq), 133.6 (CH), 132.2 (Cq), 129.5 (Cq), 127.8 (CH), 124.6 (CH), 124.4 (Cq), -6.9 (CH₃). EI–MS *m/z*: 290 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₁₈H₁₈Si₂ 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 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 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 colorless oil (131 mg, 51%). Enantiomeric excess value was determined as 86%ee 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, $\lambda = 220$ nm) t_r (minor, -) = 8.9 min, t_r (minor, +) = 10.1 min. ee = 64%. [α]_D¹⁸ = +9.9 (c = 0.81, hexane). ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): δ 164.4 (Cq), 144.0 (Cq), 136.5 (Cq), 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 (Cq), 55.2 (CH₃),

The Journal of Organic Chemistry

22.5 (CH₃), -5.0 (CH₃). EI–MS *m/z*: 242 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₁₅H₁₈OSi 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, $\lambda = 220$ nm) t_r (minor, -) = 38.9 min, t_r (major, +) = 42.2 min. ee = 71%. [α]_D¹⁹ = +5.0 (c = 0.41, hexane). ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), 29.1 (CH₂), 16.0 (CH₃), -4.5 (CH₃). EI–MS m/z: 256 (M⁺⁺). HRMS (FAB) m/z: [M]⁺⁺ Calcd for C₁₆H₂₀OSi 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, $\lambda = 220$ nm) t_r (minor, –) = 6.0 min, t_r (major, +) = 6.8 min. ee = 35%. $[\alpha]_D^{19}$ = +10.9 (c = 1.0, hexane). ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), 33.6 (CH), 24.4 (CH₃), 24.1 (CH₃), -4.3 (CH₃). EI–MS *m/z*: 270 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₁₇H₂₂OSi: 270.1434; Found: 270.1441.

(+)-(2-Methoxyphenyl)(methyl)(2-cyclohexylphenyl)silane (**5**). Colorless solid (118 mg, 38%). [α]_D²⁰ = +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. ee = 40%. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), 44.3 (CH), 34.7 (CH₂), 34.5 (CH₂), 26.84 (CH₂), 26.79 (CH₂), 26.1 (CH₂), -4.2 (CH₃). EI−MS *m/z*: 310 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₂₀H₂₆OSi 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. ee = 86%. [α]_D¹⁹ = +10.4 (c = 1.4, hexane). ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): δ 164.2 (Cq), 149.4 (Cq), 143.6 (Cq), 136.7 (CH), 136.2 (CH), 134.6 (Cq), 131.2 (CH), 129.3 (CH), 129.1 (CH), 129.0 (CH), 127.7 (CH), 126.9 (CH), 126.1 (CH), 124.6 (Cq), 120.6 (CH), 109.7 (CH), 55.2 (CH₃), -4.7 (CH₃). EI–MS m/z: 304 (M⁺⁺). HRMS (FAB) m/z: [M]⁺⁺ Calcd for C₂₀H₂₀OSi 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, $\lambda = 220$ nm) t_r (major, +) = 4.6 min, t_r (minor, -) = 5.4 min. ee = 89%. [α]_D¹⁸ = +35.0 (c = 0.91, hexane). ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), 24.0 (CH₃), -3.5 (CH₃). EI–MS *m/z*: 256 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₁₆H₂₀OSi 256.1278; Found 256.1264.

(+)-(2-Methoxyphenyl)(methyl)(3-methylphenyl)silane (8). Colorless oil (169 mg, 70%). [α]_D¹⁹ = +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. ee = 65%. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), 21.5 (CH₃), -5.0 (CH₃). EI–MS m/z: 242 (M⁺⁺). HRMS (FAB) m/z: [M]⁺⁺ Calcd for C₁₅H₁₈OSi 242.1127; Found 242.1145.

The Journal of Organic Chemistry

(+)-(2-Methoxyphenyl)(methyl)(4-methylphenyl)silane (9). Colorless oil (52 mg, 22%). [α]_D¹⁹ = +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. ee = 60%. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), 21.5 (CH₃), -5.0 (CH₃). EI–MS m/z: 242 (M⁺⁺). HRMS (FAB) m/z: [M]⁺⁺ Calcd for C₁₅H₁₈OSi 242.1121; Found 242.1114.

(+)-(2-*Methoxyphenyl*)(*methyl*)(3,5-*dimethylphenyl*)silane (10). Colorless oil (142 mg, 55%). [α]_D¹⁹ = +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. ee = 62%. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), 21.3 (CH₃), -5.0 (CH₃). EI–MS m/z: 256 (M^{+•}). HRMS (FAB) m/z: [M]^{+•} Calcd for C₁₆H₂₀OSi 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, $\lambda = 220$ nm), t_r (major, +) = 18.0 min, t_r (minor, -) = 21.3 min. ee = 85%. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), 21.8 (CH₃), 17.0 (CH₃), 16.5 (CH₃), -2.4 (CH₃). EI–MS m/z: 298 (M⁺⁺). HRMS (FAB) m/z: [M]⁺⁺ Calcd for C₁₉H₂₆OSi 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, $\lambda = 220$ nm), t_r (major, +) = 15.9 min, t_r (minor, -) = 18.0 min. ee = 77%. ¹H NMR (500 MHz, CDCl₃): δ 7.26 (t, 1H, J = 7.7 Hz), 7.19 (t, 1H, J = 7.6 Hz), 7.07 (d, 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 = 7.6 Hz)

 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), 24.3 (CH₃), -4.2 (CH₃). EI–MS *m/z*: 256 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₁₆H₂₀OSi 256.1278; Found 256.1284.

(+)-(4-Methoxyphenyl)(methyl)(2,6-dimethylphenyl)silane (13). Colorless oil (103 mg, 40%). $[\alpha]_D^{20} = +30.8 \ (c = 0.65, \text{ hexane}). \text{ HPLC (OJ-H, hexane} = 100\%, \text{ flow rate}$ 1.0 mL/min, $\lambda = 220 \text{ nm}$), t_r (major, +) = 13.8 min, t_r (minor, -) = 21.5 min. ee = 70%. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), 24.2 (CH₃), -4.0 (CH₃). EI–MS *m/z*: 256 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₁₆H₂₀OSi 256.1278; Found 256.1279.

(+)-(Phenyl)(methyl)(2, 6-dimethylphenyl)silane (14). Colorless oil (105 mg, 46%). $[\alpha]_D^{18} = +31.4 \ (c = 0.81, \text{ hexane})$. HPLC (OJ-H, hexane = 100%. flow rate 1.0 mL/min, $\lambda = 220 \text{ nm}$), t_r (major, +) = 6.3 min, t_r (minor, -) = 7.8 min. ee = 83%. ¹H NMR (500

 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), -4.2 (CH₃). EI–MS *m/z*: 226 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₁₅H₁₈Si 226.1172; Found 226.1158.

(+)-(3-Cyanophenyl)(methyl)(2,6-dimethylphenyl)silane (15). Colorless oil (129 mg, 51%). $[\alpha]_D^{18} = +39.0 \ (c = 0.31, \text{ hexane})$. HPLC (OZ-H, hexane = 100%, flow rate 1.5 mL/min, $\lambda = 220 \text{ nm}$), t_r (minor, -) = 28.8 min, t_r (major, +) = 34.7 min. ee = 85%. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), -4.4 (CH₃). EI–MS *m/z*: 251 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₁₆H₁₇NSi 251.1125; Found 251.1121.

(+)-(2-Methoxyphenyl)(cyclohexyl)(phenyl)silane (16). Yellow oil (184 mg, 62%). $[\alpha]_D^{18} = +9.5 \ (c = 0.71, \text{ hexane}). \text{ HPLC} \ (\text{OJ-H, methanol} = 100\%, \text{ flow rate } 0.5 \text{ mL/min}, \lambda = 220 \text{ nm}), t_r \ (\text{major}, +) = 12.1 \text{ min}, t_r \ (\text{minor}, -) = 13.0 \text{ min}. \text{ ee} = 64\%.$ ¹H

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 NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), 28.7 (CH), 28.6 (CH₂), 28.0 (CH₂), 27.9 (CH₂), 26.8 (CH₂), 23.2 (CH₂). EI–MS *m/z*: 296 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₁₉H₂₄OSi 296.1591; Found 296.1569.

(+)-(2-Methoxyphenyl)(phenyl)(o-tolyl)silane (17). Colorless oil (104 mg, 34%). [α]_D¹⁸ = +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. ee = 21%. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), 22.6 (CH₃). EI-MS *m/z*: 304 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₂₀H₂₀OSi 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, CH₂Cl₂). HPLC (OJ-H, hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 220$ nm), t_r (major, –) = 8.8 min, t_r (minor, +) = 12.9 min. ee = 82%. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 164.4 (Cq), 137.3 (Cq), 136.6 (Cq), 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 (Cq) 109.8 (Cq), 55.2 (CH₃), –2.7 (CH₃). EI–MS m/z: 328 (M⁺⁺). HRMS (FAB) m/z: [M]⁺⁺ Calcd for C₂₂H₂₀OSi 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, CH₂Cl₂). 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. ee = >99%. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), -2.4 (CH₃). EI–MS *m/z*: 478 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₃₀H₃₀O₂Si₂ 478.1779; Found 478.1773.

(*S*)-(+)-(*1*-*Pyrenyl*)(2-methoxyphenyl)(methyl)silane (20). Colorless solid (177 mg, 50%). Mp: 102.5–103.4 °C. [α]_D¹⁹ +126.0 (c = 1.0, CH₂Cl₂). HPLC (MeOH, flow rate 0.5 mL/min, $\lambda = 220$ nm), t_r (major, +) = 27.5 min, t_r (minor, -) = 30.1 min. ee = 61%. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (CH₃), -4.3 (CH₃). EI–MS *m/z*: 352 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₂₄H₂₀OSi 352.1278; Found 352.1280.

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(*S*,*S*)-(+)-1,6-*Bis*((2-methoxyphenyl)(methyl)silyl)pyrene (**21**). Colorless solid (276 mg, 11%). Mp: 135.1–137.6 °C. [α]_D²⁶ +128.7 (c = 1.0, CH₂Cl₂). 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. ee = 90%. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): δ 164.4 (Cq), 136.8 (CH), 136.2 (Cq), 133.3 (CH), 131.9 (Cq), 131.6 (CH), 131.4 (Cq), 128.3 (CH), 127.4 (CH), 124.6 (Cq), 124.4 (CH), 123.7 (Cq), 120.8 (CH), 109.8 (CH), 55.2 (CH₃), –4.3 (CH₃). FAB–MS m/z: 503 ([M+H]⁺). HRMS (FAB) m/z: [M]⁺⁺ Calcd for C₃₂H₃₀O₂Si₂ 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

 μ L, 2.0 mmol). After stirring for 3 d at -40 °C, the temperature was allowed to rise to room temperature and 2-iodothiophene (195 μ L, 1.0 mmol) was added to the reaction mixture. After stirring for 8 d at room temperature, the reaction mixture was quenched with water, extracted with dichloromethane three times, and the extracts dried over sodium sulfate. The solvent was evaporated under reduced pressure and purification of crude TLC gel) (*R*)product by preparative (silica afforded (2-methoxyphenyl)(phenyl)(2-thiophenyl)(methyl)silane (22) as a colorless solid (138 mg, 45%). Enantiomeric excess of the arylated product was determined as 71% ee by HPLC analysis with a chiral stationary phase.

(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, $\lambda = 280$ nm), t_r (minor, -) = 20.1 min, t_r (major, +) = 21.9 min. ee = 71%. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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 (Cq), 120.6 (CH), 110.0 (CH), 55.0 (CH₃), −2.0 (CH₃).
EI-MS *m/z*: 310 (M⁺⁺). HRMS (FAB) *m/z*: [M]⁺⁺ Calcd for C₁₈H₁₈OSSi 310.0842;
Found 310.0845.

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Notes

The authors declare no competing financial interest.

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ASSOCIATED CONTENT

SUPPORTING INFORMATION

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

X-ray crystallographic files (CIF) for molecules (*S*)-7, (*S*,*S*)-19, (*S*,*S*)-21, and (*R*)-22, copies of ¹H and ¹³C NMR, MS, HPLC analysis for all new compounds, and photophysical data and theoretical calculation of 18-21 (PDF)

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