Catalytic Asymmetric trans-Selective Hydrosilylation of Bisalkynes to Access AIE and CPL-Active Silicon-Stereogenic Benzosiloles

Ren-He Tang, Zheng Xu, Yi-Xue Nie, ..., Guan-Wu Yin, Xue-Min Yang, Li-Wen Xu

HIGHLIGHTS
- Precise and facile construction of silicon-stereogenic center by desymmetrization
- Highly enantioselective Rh-catalyzed hydrosilylation controlled by MFMC P,O,O-ligand
- Catalytic asymmetric synthesis of AIE- and CPL-active chiral Si-center benzosiloles
- The proposed mechanism is supported by NMR and kinetic studies

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Catalytic Asymmetric trans-Selective Hydrosilylation of Bisalkynes to Access AIE and CPL-Active Silicon-Stereogenic Benzosiloles

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SUMMARY
Chirality widely exists in a diverse array of biologically active molecules and life forms, and the catalytic constructions of chiral molecules have triggered a heightened interest in the fields of chemistry and materials and pharmaceutical sciences. However, the synthesis of silicon-stereogenic organosilicon compounds is generally recognized as a much more difficult task than that of carbon-stereogenic centers because of no abundant organosilicon-based chiral sources in nature. Herein, we reported a highly enantioselective rhodium-catalyzed trans-selective hydrosilylation of silicon-tethered bisalkynes to access chiral benzosiloles bearing a silicon-stereogenic center. This protocol featured with chiral Ar-BINMOL-Phos bearing hydrogen-bond donors as a privileged P-ligand for catalytic asymmetric hydrosilylation that is operationally simple and has 100% atom-economy with good functional group tolerability as well as high enantioselectivity (up to >99:1 er). Benefiting from the trans-selective hydrosilylation with the aid of Rh/Ar-BINMOL-Phos-based asymmetric catalysis, the Si-stereogenic benzosiloles exhibited pronounced aggregation-induced emission (AIE) and circularly polarized luminescence (CPL) activity.

INTRODUCTION
Silacycles are considered as a new kind of σ*-π* conjugated organic material with low-lying lowest unoccupied molecular orbital (LUMO) energy levels (Chen and Cao, 2007; Fu and Cheng, 2012; Zhao et al., 2015; Pop et al., 2019; Dhibabi et al., 2019), deriving from the interaction between the σ* orbital of two exocyclic silicon-carbon σ-bonds and the π* orbital of the butadiene moiety (Yamaguchi and Tamao, 1996). As one of the most important types of silacycles, siloles exhibit unique electronic structure with low-lying LUMO level with intriguing optical and electronic properties due to high electron affinity and fast electron mobility, enabling them to function as luminescent core and electron transporters in optoelectronic devices (Tamao et al., 1996a, 1996b; Uchida et al., 2001, Son et al., 2009), such as organic light-emitting diodes (Chen et al., 2002; Cai et al., 2017 Nie et al., 2018), fluorescent bioprobes (Wu et al., 2010; Zhuang et al., 2017), chemosensors (Toal et al., 2005; Li et al., 2009; Dedeoglu et al., 2014), and circular polarized luminescence (CPL) (Liu et al., 2012; Ng et al., 2014a and 2014b; Li et al., 2016). Therefore, the development of practical methods for the synthesis of silole scaffolds is highly important in both synthetic and materials chemistry, which has attracted increasing attention (Ohmura et al., 2008; Matsuda et al., 2007; Ureshino et al., 2010; Liang et al., 2011; Shimizu et al., 2008; Zhao et al., 2012; Liang et al., 2012; Zhang et al., 2014 and 2015; Ilies et al., 2008; Tobisu et al., 2009; Onoe et al., 2012; Minami et al., 2017; Gimferrer et al., 2018; Yang et al., 2018). Especially, the construction of a stereogenic Si-center of siloles in a catalytic enantioselective manner is an appealing yet challenging task, although there have been some efforts for the catalytic synthesis of chiral Si-centers (Oestreich, 2007; Weickgenannt et al., 2010; Xu et al., 2011; Xu, 2012; Shintani, 2015; Tamao et al., 1996a, 1996b; Igawa et al., 2012; Nagamori et al., 2015; Zhan et al., 2018; Wen et al., 2018; Guo et al., 2019). In this regard, the catalytic enantioselective synthesis of silicon-stereogenic heterocycles have been achieved via Pd-catalyzed C-H arylation (Shintani et al., 2012) or amination (Sato et al., 2017) of prochiral 2-(aryl)silyl)aryl triflates or Rh-catalyzed aromatic C-H silylation (Scheme 1A) (Kuninobu et al., 2013; Zhang et al., 2016, 2017). Moreover, the rhodium-catalyzed [2 + 2 + 2] cycloadition of silicon-containing prochiral triynes with internal alkynes was also a facile approach to the construction of
silicon-stereogenic DBS (Shintani et al., 2015). All these methods mentioned above provided complementary processes to the preparation of enantio-enriched chiral DBS bearing a silicon-stereogenic center. However, the construction of Si-chirality on unsymmetrical benzosiloles (BS) via catalytic hydrosilylation is still unknown to date.

Very recently, we reported the catalytic asymmetric synthesis of sila-bicyclo[4.1.0]heptanes via palladium-catalyzed [4 + 2] annulation of cyclopentenes with benzosilacyclobutanes (Wang et al., 2020), in which a variety of chiral bicyclic sila-heterocycle derivatives could be achieved with good enantioselectivity (up to 95.5:4.5 ee). However, the construction of corresponding silacycles bearing a Si-stereogenic center is not successful in this reaction. Considering the powerful potential of rhodium catalysts for hydrosilylation of alkynes that can provide E- and Z-isomers depending on the precise nature of catalyst systems, substrates, and reaction conditions (Takeuchi and Tanouchi, 1993, 1994; Faller and D’Alliessi, 2002; Sato et al., 2004; Mori et al., 2004; Huckaba et al., 2013; Mancano et al., 2014; Diachenko et al., 2015), we envisioned that the Rh-catalyzed intramolecular and trans-type hydrosilylation might open the door to the enantioselective Si-C bond-forming construction of silicon-stereogenic benzosiloles. Although the desymmetrizing hydrosilylation of alkenes has been achieved to construct silicon-stereogenic center (Naganawa et al., 2015), this reaction suffered limited substrate scope and imperfect enantioselectivity.
Comparably, the intramolecular hydrosilylation of Si-tethered bisalkynes is much challenging. This lack of available trans-selective methods with high enantioselectivity is presumably due to the difficulty in the chirality induction during desymmetrization of dihydrosilanes (R1R2SiH2) or silicon-tethered bulky bisalkynes in catalytic asymmetric hydrosilylation. Herein, we reported such a trans-selective intramolecular hydrosilylation reaction with our strategy with Rh/Ar-BINMOL-Phos-based MFMC ligand catalysis (MFMC is multi-functional and multi-center) that can generate silicon-stereogenic siloles with good enantioselectivity (Scheme 1B). This P,O,O-ligand (Ar-BINMOL-Phos) -controlled approach affords a range of alkyne-substituted silicon-stereogenic siloles as potentially useful fluorescent probes from easily available alkynes and hydrosilanes. In addition, it should be noted that the extra alkynyl group on benzosiloles offered a potential functionalization with group transformations.

RESULTS

To construct the silicon-stereogenic BS via catalytic asymmetric hydrosilylation, we are confident that the Rh-catalyzed intramolecular and trans-type hydrosilylation would provide a robust and practical method to the synthesis of this type of alkyne benzosiloles. Then we began our studies by examining the model hydrosilylation of Si-tethered bisalkyne 1a using Rh catalysts. At 80°C in toluene, various phosphine ligands were evaluated in the [Rh(cod)Cl]2-catalyzed intramolecular hydrosilylation (see Figure 1 and Table S1). Gratifyingly, most of our MFMC Ar-BINMOL-Phos (Song et al., 2014) gave silicon-stereogenic benzosilole 2a in promising conversion (up to >99%) with moderate enantioselectivity (80:20 to 91:9 er in most cases) in the absence of any additives, demonstrating the good feasibility of this Rh-catalyzed hydrosilylation reaction with the aid of chiral P,O,O-ligand; especially, our Tao-Phos (Song et al., 2015) gave the desired product 2a with 89.5:10.5 er and 91:9 er, respectively. Notably, other phosphine ligands evaluated in this work, such as BINAP and Segphos, exhibited relatively low enantioselectivity (70:30 er as the best). Then with Tao-Phos in hand, we continued to optimize the reactions by changing rhodium precursors, additives, solvents, and temperature (for representative experimental data, see Tables S2–S4). And finally, the optimized reaction conditions were determined as follows (see Table 1, entry 1): [Rh(cod)Cl]2 (5 mol%), Ar-BINMOL-Phos (o-Me) (12 mol %), simplified as L8 in Supplemental Information), KOTBu (5 mol %), at 70°C. The corresponding product 2a could be obtained in 95.5:4.5 er, albeit the decrease of isolated yield because of low and almost same polarity in comparison with that of starting material 1a. As shown in Table 1, representative reaction results were also important to understand the challenging Rh-catalyzed intramolecular hydrosilylation. The effect of temperature (70°C or 80°C) on enantioselectivity is not obvious as imagined (entry 2). Under the optimized reaction conditions, other rhodium sources did not give better results in term of conversion and enantioselectivity (entry 3). To support the importance of three functional groups (P atom, chiral secondary alcohol, and phenol moiety) on the MFMC P,O,O-ligand (Ar-BINMOL-Phos), we investigated the effect of four representative ligands (CL1-CL4) on the conversion and enantioselectivity (entries 5–9). In sharp contrast, these P-ligands without additional chirality at the carbon of secondary alcohol (CL1 and CL4) gave inferior enantioselectivity (88:12 er for CL1 and 67:33 er for CL4, respectively, entries 6, 9). And more importantly, ligands CL2 and CL4 without secondary alcohol or phenol were not effective in the Rh-catalyzed hydrosilylation because of only moderate conversion (entries 7 and 9). Replacing two OHS (both secondary alcohol and phenol) with MOM and OBn, respectively, deactivated the catalyst (entry 8), probably because of strong hydrogen-bonding interaction between Rh/ligand and substrate. It is easy to understand that Ar-BINMOL without phosphine center is not suitable ligand, which supports the importance of P-atom in the coordination with Rh catalyst. In addition, KOTBu was proved to be an effective additive to promote the intramolecular hydrosilylation. As shown in Table 1 (entries 10–16), the use of other additives, including similar inorganic bases, resulted in inferior results in terms of conversion and enantioselectivity. In fact, we have also investigated the effect of the amount of KOTBu on the Rh-catalyzed intramolecular hydrosilylation of 1a (Table S5). The experimental results showed that the hydrogen-bonding activation from free chiral secondary alcohol is beneficial to the activation of Rh catalyst because large amount of KOTBu could inhibit the hydrosilylation. To our delight, when cobalt and palladium catalysts instead of rhodium catalyst were used in this reaction under the same conditions, only a trace amount of product 2a was detected, and poor enantioselectivity was observed in these experiments (entries 17–19).

With the optimized reaction conditions in hand, the substrate scope was next explored with respect to the variation of the silicon-tethered bisalkynes (Scheme 2). Si-linked bisalkynes with varied substitution patterns (Me, OMe, F, t-Pr, or t-Bu, etc.) could be smoothly converted to their corresponding hydrosilylation products in moderate to good yields (up to 87%) with high enantioselectivities (up to >99:1 er). Notably, this
potassium-assisted Rh-catalyzed hydrosilylation reaction worked well with various types of substrates with electron-neutral, electron-withdrawing or electron-donating groups, having little influence on the Si-centered stereochemistry. When small ring or S-containing heterocycle-substituted bisalkynes were employed, the reaction also worked well under Rh/Ar-BINMOL-Phos catalyst system. For example, the hydrosilylation of 1r proved to be highly enantioselective (93.5:6.5 er) with good yield (75%), and the cyclopropanyl group linked with the terminal position of alkyne on substrate 1q or 1t resulted in the corresponding alkynyl benzosilole 2q or 2t in good yield with high er value, respectively. In addition, the ortho-substituted group did not block the intramolecular hydrosilylation, as evidenced by the reaction of 1n to
"Standard reaction conditions" are as follows: [Rh(cod)Cl]₂ (5 mol%), Ligand (12 mol%), KOtBu (5 mol%), Toluene, 70 °C or 80 °C.

**Table 1. Optimization of Reaction Conditions for Rh-catalyzed Desymmetric Hydrosilylation of Bisalkyne 1a**

| Entry | Variation from Standard Conditions | T (°C/h) | 2a/1a | er |
|-------|-----------------------------------|----------|-------|----|
| 1     | None                              | 70/72    | >99:1 (50) | 95.5:4.5 |
| 2     | None                              | 80/34    | >99:1 | 94.5:5.5 |
| 3     | [Rh(cod)₂]BF₄ instead of [Rh(cod)Cl]₂ | 80/34 | n.r | – |
| 4     | [Rh(OAc)₂]Cl₂ instead of [Rh(cod)Cl]₂ | 80/34 | n.r | – |
| 5     | Tao-Phos instead of L8 | 80/22 | 80.20 | 92.5:7.5 |
| 6     | CL-1 instead of L8 | 70/72 | >99:1 | 88:12 |
| 7     | CL-2 instead of L8 | 70/72 | 54:46 | 60:40 |
| 8     | CL-3 instead of L8 | 70/72 | n.r | – |
| 9     | CL-4 instead of L8 | 70/72 | 34:66 | 67:33 |
| 10    | NaHBEt₃ instead of KOtBu | 80/34 | 98.2 | 92.5:7.5 |
| 11    | NaOEt instead of KOtBu | 80/34 | >99:1 | 90:10 |
| 12    | NaSbF₅ instead of KOtBu | 80/34 | n.r | – |
| 13    | CuI instead of KOtBu | 80/34 | 46:54 | 90:10 |
| 14    | Ag₃PO₄ instead of KOtBu | 80/34 | 90:10 | 92.5:7.5 |
| 15    | K₂CO₃ instead of KOtBu | 80/34 | 58:42 | 90:59.5 |
| 16    | NaOEt instead of KOtBu | 80/34 | 98.2 | 53:54.65 |
| 17    | OIP Co instead of [Rh] | 80/14 | 10:90 | 50:50 |
| 18    | Pd₂(dba)₃ | 80/14 | 10:90 | 62.5:37.5 |
| 19    | (η₅-C₅H₅)₂PdCl₂ | 80/14 | n.r | – |

*Unless otherwise noted, the standard reaction conditions were as follows: 1a (0.2 mmol), and solvent (2.0 mL). The structure of Tao-Phos with o-trimethylsilyl group is different from that of o-methyl substituent on phenyl ring (L8), the conversion is >99% for a family of Ar-BINMOL-Phos.

**It was difficult to isolate the product 2a from the reaction mixture if the reaction was not completed because of the same polarity of 2a and the starting material 1a. The ratio of 2a/1a was determined by HPLC. n.r = no reaction.

**The er value of 3a was determined by chiral HPLC analysis.

**The catalyst OIP Co complex was used instead of [Rh(cod)Cl]₂/Ar-BINMOL-Phos catalyst system.
with 60% yield and 95:5 er. The same level of experimental result was also provided by the intramolecular hydrosilylation reaction of Si-linked bisalkyne 1s, giving the corresponding 2s with 50% yield and 97.5:2.5 er. When the methyl group on silicon atom was replaced by ethyl group, the reaction was also proven to be enantioselective and gave the desired benzosilole 2p in 97.5:2.5 er, albeit with some yield loss in comparison with that of methyl-substituted 2h (80% yield, 94:6 er). Unfortunately, it was found that another bulky group on silicon center, such as t-Bu and phenyl, was not suitable for the construction of their corresponding benzosiloles because of the steric hindrance. Notably, the configuration of the silicon-stereogenic alkynyl benzosiloles 2r was confirmed by X-ray diffraction pattern (Figure S1). Notably, these compounds were very stable for a long period of time (0.5 year), and its ee value was not changed after reflux in toluene for several days.

Scheme 2. Scope of MFMC Ar-BINMOL-Phos (L8)-controlled Rh-catalyzed Intramolecular Hydrosilylation of Si-Tethered Bisalkynes

(A) The optimized reaction conditions for the Ar-BINMOL-Phos-based MFMC ligand catalysis based on the experimental results.

(B) Substrate scope for the trans-selective hydrosilylation driven by the MFMC Ar-BINMOL-Phos ligand-controlled desymmetrization of bisalkynes.

2n with 60% yield and 95:5 er. The same level of experimental result was also provided by the intramolecular hydrosilylation reaction of Si-linked bisalkyne 1s, giving the corresponding 2s with 50% yield and 97.5:2.5 er. When the methyl group on silicon atom was replaced by ethyl group, the reaction was also proven to be enantioselective and gave the desired benzosilole 2p in 97.5:2.5 er, albeit with some yield loss in comparison with that of methyl-substituted 2h (80% yield, 94:6 er). Unfortunately, it was found that another bulky group on silicon center, such as t-Bu and phenyl, was not suitable for the construction of their corresponding benzosiloles because of the steric hindrance. Notably, the configuration of the silicon-stereogenic alkynyl benzosiloles 2r was confirmed by X-ray diffraction pattern (Figure S1). Notably, these compounds were very stable for a long period of time (0.5 year), and its ee value was not changed after reflux in toluene for several days.
Then, the further investigation of such alkylnyl benzosiloles as optical material was highly attractive. The fluorescence property of benzosiloles (BS) was subsequently evaluated using 2c, 2g, 2r, 2t, 2q, 2s, and 2l as candidates. As shown in Figure 2, the BS emission was enhanced by the introduction of electron-donating group (-OMe) on the aromatic ring, and p-OMe substituted BS 2g exhibited a very distinctive behavior. The highest occupied molecular orbital (HOMO)-LUMO data might be useful information to distinguish the structural difference. Thus, we then checked the aggregation-induced emission (AIE) property of 2g according to the standard method (Zhou et al., 2019). As expected, the benzosilole 2g showed a blue fluorescence color when the water fraction was above 30% in the THF-water mixture (Figure S7 of Supporting Information). Notably, the relationship of AIE and chirality was also evaluated and it was found that there is no obvious effect for the fluorescence intense.

The phenomenon of circularly polarized luminescence (CPL) has attracted considerable attention owing to its wide applications in various research fields (Gao et al., 2019). Therefore, the circular dichroism (CD) and CPL analyses were next performed at 300 nm to evaluate the Si-centered chirality. To our delight, in the test of benzosilole 2g, intensive CPL signs were observed in this case (Figure S8). We anticipated that CPL effect of benzosilole augments its great potential of enantioselective Rh-catalyzed intramolecular hydrosilylation of bisalkynes in the development of a CPL-active material linked with silole backbone.

**DISCUSSION**

In metal-catalyzed hydrosilylation (Zaranek and Pawluc, 2018; Wen et al., 2019), including the Rh catalysts (Sakaki et al., 2002; Wu et al., 2013 and 2014; Doyle et al., 1991; Sanada et al., 2006; Morales-Ceron et al., 2017) employed for alkyne hydrosilylation, cationic metal complexes usually give predominately (E)-isomer depending on the precise nature of substrates and reaction conditions (Ojima et al., 1990; Trost and Ball, 2005; Ding et al., 2013). In this work, we believed the Rh-catalyzed alkyne trans-hydrosilylation reactions are similar to that of previous reports (Ojima et al., 1990; Matsuda and Ichikawa, 2012; Crabtree, 2003) on the isomerization of the M-vinyl complex intermediate to the less sterically congested isomer via an η2-vinyl metal species. In addition, to understand what makes Rh/Ar-BINMOL-Phos (L8) a successful catalyst in
the desymmetrization of Si-linked bisalkynes via hydrosilylation, its structure was examined by $^{31}$P-NMR and ESI-MS (see Figure 3, for $^{31}$P-NMR analysis, see Figure 3B, and others see Figures S3–S5). And these experimental results indicate that the various types of Rh/L8 complexes might be in situ formed in this reaction, and a dimeric Rh catalyst comprising a dirhodium core is a possible and active species in the pre-activation process (Meiñner et al., 2015a, 2015b; Mannu et al., 2018), which generated through dissociation of cod (1,5-cyclooctadiene) with two coordinating phosphorous centers from Ar-BINMOL-Phos ligands. It is generally accepted that treatment of [Rh(cod)Cl]$_2$ with diphosphine ligands smoothly affords neutral $\mu_2$-bridged dimeric/dinuclear rhodium complexes (Meiñner et al., 2015a, 2015b); thus, accordingly, the $\mu_2$-bridged dimeric Rh complex is formed probably in the reaction mixtures (the double peaks appeared probably at 33–34 ppm with $^{1}J_{P-Rh} = 204$ or 220 Hz in Figure 3B). However, it is difficult to confirm the true structure of dimeric Rh/L8 complex that formed in the pre-activation stage by NMR analysis. Furthermore, the in situ analysis of reaction mixtures with ESI-MS and NLE (Satyanarayana et al., 2009) and kinetic study (Figure 4) showed the mononuclear complex with single Rh(I) catalytic center with one ligand acted probably as majorly active species during the full reaction process. In addition, the stable

Figure 3. The Structural Analysis of the Active Rh Species by $^{31}$P NMR

(A) The illustrative view of the in situ formed dimeric Rh complex and mononuclear Rh complex from [Rh(cod)Cl]$_2$ and Ar-BINMOL-Phos L8 in CDCl$_3$.

(B) Comparison of $^{31}$P NMR of ligand and Rh complex. (a) only L8, a single peak at $-14.83$ ppm; (b) mixture of [Rh(cod)Cl]$_2$ and L8 (5 min), two double peaks for the Rh/Ar-BINMOL-Phos complex appeared at 22.16 ppm with $^{1}J_{P-Rh} = 183$ Hz and 34.40 ppm with $^{1}J_{P-Rh} = 204$ Hz, and another single peak appeared at 37.69 ppm, respectively; (c) mixture of L8 and [Rh(cod)Cl]$_2$ (20 min), the double peak at 22.16 ppm disappeared, and another single peak appeared at 45.11 ppm; (d) mixture of substrate 1a, L8 and [Rh(cod)Cl]$_2$ (20 min), a new and single peak appeared at 39.50 ppm; (e) mixture of L8, KOtBu, and [Rh(cod)Cl]$_2$ (5 min); (f) mixture of L8, KOtBu, and [Rh(cod)Cl]$_2$ (20 min); (g) mixture of L8, KOtBu, and [Rh(cod)Cl]$_2$, and substrate 1a (20 min), a double peak appeared at 33.72 ppm with $^{1}J_{P-Rh} = 220$ Hz and a single peak with 45.27 ppm.
P/O-coordination of Ar-BINMOL-Phos with [Rh(cod)Cl]₂ to give mononuclear Rh complex is supported by ³¹P-NMR spectra data in which the related ³¹P signal of such stable mononuclear Rh complex was observed at 41 ppm (Rani et al., 2008).

It should be noted that the potassium tert-butoxide (KOtBu) played an important role in the in situ formation of the active Rh species to promote the catalytic asymmetric hydrosilylation. As shown in Figure 4, the absence of KOtBu led to decreased enantioselectivity (only 75:25 er), in which the negative result revealed reaction between KOtBu and chiral ligand L₈ could form a more stable mononuclear rhodium catalyst that is responsible for the high level of enantioselective induction shown in Figure 4C. When the reaction was performed without KOtBu, enantioselectivity (ee value of 2a) of the same intramolecular hydrosilylation was gradually decreased with time because of irreversible reactions of the active dimeric Rh catalyst with substrate in the catalytic cycle. And notably, excess amount of KOtBu (>24 mol%) decreased the enantioselectivity and much more amount of KOtBu (>36 mol%) inhibited the catalytic activities of all the Rh species reaction to result in almost no reaction. These results provided an indirect evidence for the importance of the chiral secondary alcohol of Ar-BINMOL-Phos (L₈) in the enhancement of enantioselectivity and catalytic activity of Rh complex.

Therefore, based on the experimental results and related NMR and ESI-MS analysis, we proposed a reaction mechanism for the asymmetric Rh-catalyzed hydrosilylation (Figure 5). It is expected that the dirhodium core in the chlorine-bridged dimeric rhodium precursor is easily broken by a proton abstraction reaction with ligand L₈, releasing HCl with the aid of KOtBu and generating mononuclear precursor complex M₀. The cod ligand in the four-coordinated neutral Rh(I) complex will further be replaced by the substrate and leads to an Rh intermediate, in which the alkenyl group and Si-H group of substrate is

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**Figure 4. Experimental Results for Relationship of eₑₚₑᵣₒᵈ/eₑᵓₑᵓₐᵣ₈ and the Reaction Rate and Enantioselectivity Data with or without KOtBu**

(A) The model reaction with intramolecular hydrosilylation of 1a under the optimized reaction conditions.

(B) The NLE result revealed that a mononuclear complex structure with single Rh(I) catalytic center with one ligand acted probably as the true active species.

(C) KOtBu-activated Rh catalysis. There are two stages (before and after 5 h, respectively) for catalytic cycles in the Rh-catalyzed hydrosilylation that detected by ee values and reaction rate under the optimized reaction conditions.

(D) Without KOtBu as additive. When no use of KOtBu for this reaction, the corresponding ee value gradually decreases with reaction time.
coordinated to the Rh center in $\eta^2$ and $\eta^1$ manner. Then the Rh intermediate underwent Si-H oxidative addition to form a five-coordinated Rh(III) intermediate A. The pre-coordinated alkynyl group is exactly the one to proceed migratory insertion, followed by the Si-H oxidative addition. That is, the two symmetric alkynyl groups in $1a$ have already been discriminated during the formation of this precursor complex B, in which the reactive alkynyl group and Si-H group linked to the Rh center in enantioselective manner. And then the subsequent process is only related to the Z/E-selectivity but not the enantioselectivity. Similarly to previous Ru catalysis for the trans-selective hydrosilylation of alkynes (Ding et al., 2013), B can be further isomerized to the more stable C (metallacyclohexene intermediate). At this time, the H atom is completely inverted to the trans position, and the alkenyl group is at the trans position of the O-ligand. For the origin of stereoselective induction of such rhodium catalyst, more theoretic studies would be continuously undergoing in our laboratory to gain much more accurate understanding of the hydrosilylation reaction mechanism.

Conclusion

In summary, we accomplished a highly enantioselective Rh-catalyzed intramolecular and trans-type hydrosilylation of silicon-tethered bisalkynes, which provided a practical approach to the construction of AIE and CPL-active benzosiloles bearing silicon-stereogenic center. For this purpose, our chiral Ar-BINMOL-Phos bearing hydrogen-bond donors could be efficiently used as a privileged MFMC P,O,O-ligand in the desymmetrization process of silicon-tethered bisalkynes. The reaction is operationally robust and atom-economic with good functional group tolerability as well as high enantioselectivity (up to >99:1 er) with the aid of Rh/Ar-BINMOL-Phos-based MFMC ligand catalysis. More specially, the use of the basic additive KOtBu is crucial to maintaining of high level of enantioselectivity in this reaction because the catalytic amount KOtBu is responsible for the formation of active Rh/L8 complex. Although the true reaction mechanism for the stereoselective induction of Rh catalyst system is still unclear, the highly enantioselective synthesis of chiral benzosiloles and corresponding construction of silicon-stereogenic center by desymmetric hydrosilylation opens a great opportunity to create the next generation of organosilicon material or possibly better targeted Si-containing biologically active molecules that bring silicon to material and life (Kan et al., 2016). At present, the DFT calculation studies are undergoing in our laboratory to gain a more accurate understanding of the mechanism of trans-selective hydrosilylation and will be reported elsewhere. In addition, the reactive alkyne groups as side chains in the silicon-stereogenic benzosiloles are expected to undergo further functionalization and hold promise for synthesis of conjugate polymers or cross-linked materials.

Limitations of the Study

Terminal alkynes were not applicable in the construction of silicon-stereogenic benzosiloles by the intramolecular hydrosilylation. And the reaction mechanism and the origin of enantioselectivity that is controlled by the Ar-BINMOL-Phos need to be clarified in more reliable manner.
Resource Availability
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Material Availability
No unique reagents or no restrictions to the availability of chemicals.

Data and Code Availability
The related figures and data in this article can be found at the Supplemental Information.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.101268.

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AUTHOR CONTRIBUTIONS
R.-H.T., Z.X., and Y.-X.N. are co-first authors. L.-W.X. conceived the concept. R.-H.T. carried out experiments, including the preparation of chiral ligands and the rhodium-catalyzed hydrosilylation. Y.-X.N. and Z.X. carried out the experiments for the proposed reaction mechanism. X.-Q.X. carried the X-ray analysis. K.-F.Y. and J.-L.X. carried out partial reactions and the NMR analysis for the products and reaction intermediates. G.-W.Y., B.G., and X.-M.Y. synthesized the substrates and conducted the structural analysis of unknown compounds. L.-W.X wrote the manuscript, and all authors discussed the results and participated in revising the manuscript. L.-W.X. supervised the project.

DECLARATION OF INTERESTS
The authors declare no competing financial interests.

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Supplemental Information

Catalytic Asymmetric trans-Selective Hydrosilylation of Bisalkynes to Access AIE and CPL-Active Silicon-Stereogenic Benzosiloles

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More details for reaction condition optimization:

Table S1. Optimization of reaction conditions by screening of chiral ligands. \(^{[a]}\) Related to Figure 1.

| Entry | Rh (X mol%) | Ligand | Temp (°C) | Time (h) | \(2a/1a^{[b]}\) | er (%)\(^{[c]}\) |
|-------|-------------|--------|-----------|----------|-----------------|----------------|
| 1     | 2.5         | L1     | 80        | 36       | >99:1           | 85:15          |
| 2     | 2.5         | L2     | 80        | 34       | 60:40           | 80:20          |
| 3     | 10          | L3     | 60        | 24       | 80:20           | 90:10          |
| 4     | 2.5         | L4     | 80        | 34       | 62:38           | 80:20          |
| 5     | 2.5         | L5     | 80        | 34       | 94:6            | 70:40          |
| 6     | 2.5         | L6     | 80        | 36       | 54:46           | 85:15          |
| 7     | 2.5         | L7     | 80        | 36       | 60:40           | 50:50          |
| 8     | 2.5         | L8     | 80        | 34       | 60:40           | 85:15          |
| 9     | 2.5         | L9     | 80        | 34       | 70:30           | 87.5:12.5      |
| 10    | 2.5         | L10    | 80        | 36       | 60:40           | 50:50          |
| 11    | 10          | L11    | 60        | 24       | -               | 65:35          |
| 12    | 10          | L12    | 60        | 24       | -               | 50:50          |
| 13    | 2.5         | L13    | 80        | 36       | 20:80           | 50:50          |
| 14    | 10          | L14    | 60        | 24       | -               | 50:50          |
| 15    | 10          | L15    | 60        | 24       | -               | 50:50          |
| 16    | 10          | L16    | 60        | 24       | -               | 59:41          |
| 17    | 10          | L17    | 60        | 24       | -               | 56:44          |
| 18    | 10          | L18    | 60        | 24       | -               | 70:30          |
| 19    | 10          | L19    | 60        | 24       | -               | 65:35          |
| 20    | 10          | L20    | 60        | 24       | -               | 65:35          |
| 21    | 2.5         | L21    | 80        | 24       | 10:90           | 55:45          |
| 22    | 5           | L9     | 80        | 24       | 76:24           | 90:10          |
| 23    | 5           | L8     | 80        | 24       | 82:18           | 91:9           |

\(^{[a]}\) Reaction conditions: \(1a\) (0.2 mmol), \([\text{Rh}(\text{cod})\text{Cl}]_2\) (10 mol%), and solvent (1 mL) at 60-80 °C. \(^{[b]}\) The ratio of \(2a/1a\) was determined by HPLC. \(^{[c]}\) The er value was determined by chiral HPLC.
Table S2. Optimization of reaction conditions by screening of solvents.^[a] Related to Figure 1.

[Ph][SiH][Ph] \[\text{[Rh(cod)Cl]}_2 (2.5 \text{ mol%}) \quad \text{L3} (6 \text{ mol%}) \quad \text{Solvent} \rightarrow \text{Ph} \quad [\text{Si}] \quad \text{Ph} \]

| Entry | Solvent      | Temp (°C) | Time (h) | 2a/1a^[b] | er (%)^[c] |
|-------|--------------|-----------|----------|-----------|------------|
| 1     | Dioxane      | 70        | 36       | NR        | -          |
| 2     | CH$_3$CN     | 70        | 36       | -         | 50:50      |
| 3     | Ethanol      | 70        | 36       | NR        | -          |
| 4     | THF          | 70        | 36       | -         | 77.5:25.5  |
| 5     | DCE          | 70        | 36       | NR        | 50:50      |
| 6     | Benzene      | 80        | 22       | >99:1     | 91.9       |
| 7     | m-Xylene     | 80        | 22       | >99:1     | 90:10      |
| 8     | p-Xylene     | 80        | 22       | 80:20     | 85:15      |
| 9     | o-Xylene     | 80        | 22       | 94:6      | 82.5:17.5  |
| 10    | Toluene      | 70        | 24       | 80:20     | 90:10      |
| 11    | 1,2,4-Trimethylbenzene | 80 | 22       | 88:12     | 90:10      |

[a] Reaction conditions: 1a (0.2 mmol), [Rh(cod)Cl]$_2$ (10 mol%), and solvent (1 mL) at 70–80 °C. [b] Determined by HPLC. [c] The er value was determined by chiral HPLC with a chiral stationary phase.
Table S3. Evaluation of catalytic activity of transition-metal catalysts. \(^{[a]}\) Related to Table 1.

| Entry | Catalyst       | Ligand | Time (h) | \(2a/1a^{[b]}\) | er (%) \(^{[c]}\) |
|-------|----------------|--------|----------|-----------------|-----------------|
| 1     | [RhCl(C\(_2\)H\(_2\))]\(_2\) | L3     | 34       | NR              | -               |
| 2     | [(C\(_6\)H\(_5\))\(_3\)P]\(_2\)RhCl | L3     | 34       | NR              | -               |
| 3     | Rh\(_2\)(OOCCH\(_3\))\(_4\) | L3     | 34       | NR              | -               |
| 4     | [Rh(cod)]\(_2\)BF\(_4\) | L3     | 34       | NR              | -               |
| 5     | [Rh(OAc)]\(_2\)\(_2\) | L3     | 34       | NR              | -               |
| 6     | [Rh(nbd)]\(_2\)Cl\(_2\) | L3     | 34       | NR              | -               |
| 7     | Rh(CO)\(_2\)(C\(_2\)H\(_2\)O\(_2\)) | L3     | 34       | NR              | -               |
| 8     | RhCl\(_2\)(CO)\(_4\) | L3     | 34       | NR              | -               |
| 9     | (η\(_3\)-C\(_3\)H\(_5\))\(_2\)Pd\(_2\)Cl\(_2\) | L8     | 14       | NR              | -               |
| 10    | PdCl\(_2\) | L8     | 14       | 10:90           | 62.5:37.5       |
| 11    | Pd\(_3\)(dba)\(_3\) | L8     | 14       | 14:86           | 50:50           |
| 12    | PdCl\(_2\)(dppb) | L8     | 14       | 22:78           | 65:35           |
| 13    | Pd(PPPh\(_3\))Cl\(_2\) | L8     | 14       | 10:90           | 50:50           |
| 14    | OIP Co | -      | 14       | 20:80           | 90:10           |
| 15\(^{[d]}\) | [Rh(cod)]Cl\(_2\) | L8     | 14       | 8:92            | 95.5:4.5        |

\(^{[a]}\) Reaction conditions: 1a (0.2 mmol), [Rh(cod)Cl]\(_2\) (10 mol%), and solvent (1 mL) at 80 °C. \(^{[b]}\) Determined by HPLC. \(^{[c]}\) The er value was determined by chiral HPLC with a chiral stationary phase. \(^{[d]}\) At 80 °C. \(^{[e]}\) At 60 °C.
Table S4. Optimization of reaction conditions by screening of additives.\(^{[a]}\) Related to Table 1.

![Chemical structure](image)

Table: Optimization of reaction conditions by screening of additives.

| Entry | Additive   | \(2a/1a^{[b]}\) | er (%)\(^{[c]}\) |
|-------|------------|-----------------|-----------------|
| 1     | AlCl\(_3\) | NR              |                 |
| 2     | NaHBEt\(_3\) | >99:1           | 92.5:7.5        |
| 3     | NaSbF\(_6\) | NR              |                 |
| 4     | K\(_2\)CO\(_3\) | 60:40         | 90.5:9.5        |
| 5     | AlCl\(_3\) | 30:70           | 85:15           |
| 6     | CuI        | 60:40           | 90:10           |
| 7     | KOtBu      | >99:1           | 95:5            |
| 8     | Ag\(_3\)PO\(_4\) | 90:10     | 92:8            |
| 9     | NEt\(_3\)  | 90:10           | 92:8            |
| 10    | NaO'Bu     | >99:1           | 90:10           |
| 11    | NaOEt      | >99:1           | 85:15           |

\(^{[a]}\) Reaction conditions: \(1a\) (0.2 mmol), \([\text{Rh} \text{(cod)Cl}]_2\) (5 mol%), and solvent (1 mL) at 70 °C. \(^{[b]}\) Determined by HPLC. NR is no reaction. \(^{[c]}\) The er value was determined by chiral HPLC with a chiral stationary phase.
Table S5. The effect of KOtBu on the Rh-catalyzed intramolecular hydrosilylation.\textsuperscript{[a]} Related to Table 1.

![Diagram of reaction](image)

| Entry | KOtBu (X mol\%) | \(2a/1a\)\textsuperscript{[b]} | \(\text{er} \%)\textsuperscript{[c]} |
|-------|----------------|---------------------|-----------------|
| 1     | 6              | >99:1               | 95.5:4.5        |
| 2     | 12             | >99:1               | 95.5:4.5        |
| 3     | 24             | >99:1               | 95.5:4.5        |
| 4     | 36             | >99:1               | 75:25           |
| 5     | 48             | NR                  | -               |
| 6     | 60             | NR                  | -               |

\textsuperscript{[a]} Reaction conditions: 1a (0.2 mmol), [Rh(cod)Cl]\textsubscript{2} (5 mol\%), and solvent (1 mL) at 70 °C. \textsuperscript{[b]} Determined by HPLC. \textsuperscript{[c]} The \(\text{er}\) value was determined by chiral HPLC with a chiral stationary phase.
Table S6a. Kinetic studies on the Rh-catalyzed intramolecular hydrosilylation: a) with KOtBu.\(^\text{[a]}\) Related to Figure 4.

![Reaction Mechanism]

| Entry | Catalyst       | Temp (°C) | Time (h) | 2a/1a\(^{[b]}\) | er (%)\(^{[c]}\) |
|-------|----------------|-----------|----------|----------------|----------------|
| 1     | [Rh(cod)Cl\(_2\)] | 70        | 1        | 18:82          | >99:1          |
| 2     | [Rh(cod)Cl\(_2\)] | 70        | 2        | 18:82          | >99:1          |
| 3     | [Rh(cod)Cl\(_2\)] | 70        | 4        | 28:72          | 95.5:4.5      |
| 4     | [Rh(cod)Cl\(_2\)] | 70        | 14       | 30:70          | 95.5:4.5      |
| 5     | [Rh(cod)Cl\(_2\)] | 70        | 40       | 54:46          | 95.5:4.5      |
| 6     | [Rh(cod)Cl\(_2\)] | 70        | 70       | >99:1          | 95.5:4.5      |

\(^{[a]}\) Reaction conditions: 1a (0.2 mmol), [Rh(cod)Cl\(_2\)] (5 mol%), and solvent (1 mL) at 70 °C. \(^{[b]}\) Determined by HPLC. \(^{[c]}\) The er value was determined by chiral HPLC with a chiral stationary phase.

Table S6b. Kinetic studies on the Rh-catalyzed intramolecular hydrosilylation: b) without KOtBu.\(^\text{[a]}\) Related to Figure 4.

| Entry | Catalyst       | Temp (°C) | Time (h) | er (%)\(^{[b]}\) |
|-------|----------------|-----------|----------|-----------------|
| 1     | [Rh(cod)Cl\(_2\)] | 70        | 2        | 97.5:2.5        |
| 2     | [Rh(cod)Cl\(_2\)] | 70        | 10       | 91:9            |
| 3     | [Rh(cod)Cl\(_2\)] | 70        | 22       | 91:9            |
| 4     | [Rh(cod)Cl\(_2\)] | 70        | 34       | 85:15           |
| 5     | [Rh(cod)Cl\(_2\)] | 70        | 50       | 75:25           |

\(^{[a]}\) Reaction conditions: 1a (0.2 mmol), [Rh(cod)Cl\(_2\)] (5 mol%), and solvent (1 mL) at 70 °C. \(^{[b]}\) The er value was determined by chiral HPLC with a chiral stationary phase.
**Figure S1.** X-ray structures of 2r (CCDC 1954490). Related to Scheme 2.

Crystallographic data and data collection for the product 2r

| Property                  | Value                        |
|---------------------------|------------------------------|
| Formula                   | C$_{25}$H$_{18}$S$_2$Si      |
| $D_{calc.}/g\ cm^3$       | 1.298                        |
| $\mu/mm^1$                | 2.887                        |
| Formula Weight            | 410.60                       |
| Colour                    | colourless                   |
| Shape                     | prism                        |
| Size/mm$^3$               | 0.15x0.12x0.10               |
| $T/K$                     | 296.15                       |
| Crystal System            | triclinic                    |
| Flack Parameter           | 0.101(7)                     |
| Hooft Parameter           | 0.103(5)                     |
| Space Group               | $P1$                         |
| $a/\AA$                   | 8.6621(2)                    |
| $b/\AA$                   | 11.3298(3)                   |
| $c/\AA$                   | 11.8647(3)                   |
| $\alpha/\degree$         | 73.2290(10)                  |
| $\beta/\degree$          | 70.5240(10)                  |
| $\gamma/\degree$         | 83.5540(10)                  |
| $V/\AA^3$                 | 1050.92(5)                   |

| Parameter                | Value                        |
|--------------------------|------------------------------|
| $Z$                      | 2                            |
| $Z'$                     | 2                            |
| Wavelength/Å              | 1.54178                      |
| Radiation type           | CuK                          |
| $\theta_{\min}\degree$  | 4.076                        |
| $\theta_{\max}\degree$  | 71.022                       |
| Measured Refl's.         | 33860                        |
| Ind't Refl's             | 7453                         |
| Refl's with I > 2(I)     | 7409                         |
| $R_{int}$                | 0.0342                       |
| Parameters               | 696                          |
| Restraints               | 195                          |
| Largest Peak             | 0.180                        |
| Deepest Hole             | -0.221                       |
| GooF                     | 1.050                        |
| $wR_2 (all\ data)$       | 0.0871                       |
| $wR_2$                   | 0.0870                       |
| $R_1 (all\ data)$        | 0.0315                       |
| $R_1$                    | 0.0314                       |
Supplemental Figures for NMR spectrums:

**Figure S2.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1a, related to Scheme 2

**Figure S3.** $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1a, related to Scheme 2
Figure S4. \(^1\)H NMR (400 MHz, CDCl\(_3\)) spectrum of compound 1b, related to Scheme 2

Figure S5. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) spectrum of compound 1b, related to Scheme 2
Figure S6. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1c, related to Scheme 2

Figure S7. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1c, related to Scheme 2
Figure S8. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1d, related to Scheme 2

Figure S9. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1d, related to Scheme 2
Figure S10. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1e, related to Scheme 2

Figure S11. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1e, related to Scheme 2
Figure S12. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1f, related to Scheme 2

Figure S13. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1f, related to Scheme 2
Figure S14. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1g, related to Scheme 2

Figure S15. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1g, related to Scheme 2
Figure S16. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1h, related to Scheme 2

Figure S17. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1h, related to Scheme 2
Figure S18. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1i, related to Scheme 2

Figure S19. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1i, related to Scheme 2
Figure S20. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1j, related to Scheme 2

Figure S21. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1j, related to Scheme 2
Figure S22. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1k, related to Scheme 2

Figure S23. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1k, related to Scheme 2
Figure S24. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 11, related to Scheme 2

Figure S25. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 11, related to Scheme 2
Figure S26. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1m, related to Scheme 2

Figure S27. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1m, related to Scheme 2
Figure S28. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1n, related to Scheme 2

Figure S29. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1n, related to Scheme 2
Figure S30. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1o, related to Scheme 2

Figure S31. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1o, related to Scheme 2
Figure S32. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1p, related to Scheme 2

Figure S33. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1p, related to Scheme 2
Figure S34. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1q, related to Scheme 2

Figure S35. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1q, related to Scheme 2
Figure S36. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1r, related to Scheme 2

Figure S37. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1r, related to Scheme 2
Figure S38. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1s, related to Scheme 2.

Figure S39. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1s, related to Scheme 2.
Figure S40. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 1t, related to Scheme 2

Figure S41. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1t, related to Scheme 2
5.2 NMR spectra of products 2 (benzosiloles)

Figure S42. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2a, related to Scheme 2

Figure S43. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2a, related to Scheme 2
Figure S44. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2b, related to Scheme 2.

Figure S45. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2b, related to Scheme 2.
Figure S46. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2c, related to Scheme 2

Figure S47. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2c, related to Scheme 2
Figure S48. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2d, related to Scheme 2.

Figure S49. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2d, related to Scheme 2.
Figure S50. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2e, related to Scheme 2

Figure S51. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2e, related to Scheme 2
Figure S52. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2f, related to Scheme 2.

Figure S53. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2f, related to Scheme 2.
Figure S54. $^1\text{H}$ NMR (400 MHz, CDCl$_3$) spectrum of compound 2g, related to Scheme 2

Figure S55. $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$) spectrum of compound 2g, related to Scheme 2
Figure S56. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2h, related to Scheme 2

Figure S57. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2h, related to Scheme 2
Figure S58. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2i, related to Scheme 2

Figure S59. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2i, related to Scheme 2
**Figure S60.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2j, related to Scheme 2.

**Figure S61.** $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2j, related to Scheme 2.
Figure S62. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2k, related to Scheme 2

Figure S63. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2k, related to Scheme 2
Figure S64. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2l, related to Scheme 2

Figure S65. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2l, related to Scheme 2
Figure S66. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2m, related to Scheme 2

Figure S67. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2m, related to Scheme 2
Figure S68. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2n, related to Scheme 2

Figure S69. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2n, related to Scheme 2
Figure S70. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2o, related to Scheme 2

Figure S71. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2o, related to Scheme 2
Figure S72. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2p, related to Scheme 2.

Figure S73. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2p, related to Scheme 2.
Figure S74. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2q, related to Scheme 2

Figure S75. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2q, related to Scheme 2
Figure S76. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2r, related to Scheme 2.

Figure S77. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2r, related to Scheme 2.
Figure S78. \(^1\)H NMR (400 MHz, CDCl\(_3\)) spectrum of compound 2s, related to Scheme 2.

Figure S79. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) spectrum of compound 1s, related to Scheme 2.
Figure S80. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2t, related to Scheme 2

Figure S81. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 1t, related to Scheme 2
React IR experiment for the detection of benzosilole backbone

IR analysis was carried out under the reaction conditions: Under N₂ atmosphere, [Rh(cod)Cl]₂ (4.9 mg, 5 mol%), L₈ (13.8 mg, 12 mol%), KOtBu (2.7 mg, 12 mol%) and evacuated under high vacuum and backfilled with N₂. Toluene (1 mL) was next added and stirred at room temperature for about 0.5 h. Then methylbis(2-(phenylethynyl)phenyl)silane 1a (79.6 mg, 0.2 mmol) were added sequentially. The mixture was stirred at 70 °C in a preheated oil. Then the IR probe was inserted and the IR data collection was started. The mixture was stirred at 70 °C for about 72 h.

**Figure S82.** IR spectra for detection of the formation of benzosilole 2a from the hydrosilylation of alkynyl C(sp)-C(sp) bond. Related to Figure 5
**Figure S83 (continued).** Possible Rh complex or intermediates in this reaction could be confirmed on the basis of the $^{31}$P-NMR and ESI-MS analysis. For the Rh complexes, B-D, the existence of couplings between Rh and P in the $^{31}$P NMR spectra. Related to Figure 5.
Supplemental Figures for ESI-MS spectrums:

**Figure S84.** ESI(+) - MS analysis for the mixture of only \([\text{Rh(cod)Cl}]_2\) and Ar-BINMOL-Phos (\(\text{o-Me}\)) in toluene. Related to Figure 5
Figure S85. ESI(+) -MS analysis for the mixture of [Rh(cod)Cl]_2, alkyne, Ar-BINMOL-Phos (o-Me) in toluene. Related to Figure 5.

Chemical Formula: C_{73}H_{61}O_2PRhSi
Exact Mass: 1131.3233
Molecular Weight: 1132.2533

(Int1)
Supplemental Figures for fluorescence spectra of product:

**Figure S86.** UV-vis absorption (down) and fluorescence emission (up) properties of seven compounds in DCM solvents ($10^{-5}$ M), related to Figure 2.
Figure S87. Fluorescence emission spectra of 2g (5 μM) in THF/water mixtures (fw = 0 to 90%). λ<sub>ex</sub>=300 nm, λ<sub>es</sub>=550 nm. related to Figure 2.
Figure S88. For racemic 2g (AIE) related to Figure 2.
**Figure S89.** The photography for the AIE phenomena of 2g. Related to Figure 2
Figure S90. The industrial method for preparation of silicon rubber with blue blue-fluorescence because of the additive of alkyne-substituted benzosilole 2g (10⁻⁴ w/w). Related to Figure 2

\[
\begin{align*}
\{ & \text{Si} \text{O} \text{SiH} \} \text{n} + \{ & \text{Si} \text{O} \text{Si} \} \text{n} + \text{SiO}_2 \\
\text{PMHS} & & \text{Vinyl-PMS} & & 10\text{g} \\
(1:1) & & & & \\
\end{align*}
\]

\[
\begin{align*}
+ & \text{Karstedt catalyst (Pt)} \\
\rightarrow & \text{Cross-linked rubber} \\
\end{align*}
\]
CPL spectra of product 2g:

**Figure S91.** CPL (upper panel) and DC (nether panel) spectra of (S) (black lines) and (R) (red lines) in CHCl₃ (1.0 × 10⁻³ M). Related to Figure 2.
Table S92. HOMO and LUMO energy computed for product. Related to Figure 2

| product | HOMO       | LUMO       | Δ (ev) |
|---------|------------|------------|--------|
| 2c      | -4.529 ev  | -1.795 ev  | 2.734  |
| 2g      | -4.570 ev  | -1.857 ev  | 2.713  |
| 2r      | -4.751 ev  | -2.174 ev  | 2.577  |
| 2t      | -4.867 ev  | -1.575 ev  | 3.292  |
| 2q      | -4.738 ev  | -1.480 ev  | 3.258  |
| 2S      | -4.640 ev  | -1.883 ev  | 2.757  |
| 2I      | -4.818 ev  | -1.920 ev  | 2.898  |
| Time/min | Area     | Height | Area% |
|---------|----------|--------|-------|
| 1       | 27.800   | 1075240| 13152 | 50    |
| 2       | 31.463   | 1075240| 9160  | 50    |

**Figure S93.** The HPLC spectrum of compound 2a, related to Scheme 2
| Time/min | Area    | Height | Area% |
|----------|---------|--------|-------|
| 1        | 46.485  | 291019 | 4784  | 49.38 |
| 2        | 48.690  | 298330 | 4768  | 50.62 |

| Time/min | Area    | Height | Area% |
|----------|---------|--------|-------|
| 1        | 46.575  | 35478  | 739   | 3.86  |
| 2        | 48.474  | 883685 | 14102 | 96.14 |

**Figure S94**, the HPLC spectrum of compound 2b, related to **Scheme 2**
| Time/min | Area  | Height | Area% |
|---------|-------|--------|-------|
| 1       | 18.712| 199777 | 6793  | 50.03 |
| 2       | 27.235| 199505 | 2981  | 49.97 |

| Time/min | Area  | Height | Area% |
|---------|-------|--------|-------|
| 1       | 19.268| 1979257| 64815 | 96.69 |
| 2       | 26.547| 68054  | 1716  | 3.32  |

Figure S95, the HPLC spectrum of compound 2c, related to Scheme 2
| Time/min | Area    | Height | Area% |
|----------|---------|--------|-------|
| 1        | 11.445  | 585900 | 18153 | 47.25 |
| 2        | 12.877  | 654006 | 18480 | 52.75 |

| Time/min | Area    | Height | Area% |
|----------|---------|--------|-------|
| 1        | 10.038  | 17535  | 673   | 0.68  |
| 2        | 11.121  | 2578652| 64490 | 99.32 |

Figure S96, the HPLC spectrum of compound 2d, related to Scheme 2
| Time/min | Area   | Height  | Area% |
|----------|--------|---------|-------|
| 1        | 10.612 | 628213  | 21274 | 50.39 |
| 2        | 24.909 | 618583  | 6286  | 49.61 |

| Time/min | Area   | Height  | Area% |
|----------|--------|---------|-------|
| 1        | 10.227 | 793482  | 27894 | 5.4   |
| 2        | 21.087 | 13896236| 115139| 94.6  |

*Figure S97*, the HPLC spectrum of compound 2e, related to *Scheme 2*
| Time/min | Area  | Height | Area% |
|----------|-------|--------|-------|
| 1        | 8.538 | 504871 | 22886 | 50.72 |
| 2        | 14.625| 490480 | 5420  | 49.28 |

Figure S98, the HPLC spectrum of compound 2f, related to Scheme 2
| Time/min | Area    | Height | Area% |
|---------|---------|--------|-------|
| 1       | 22.010  | 269297 | 3960  | 49.89 |
| 2       | 44.267  | 270455 | 1965  | 50.11 |

| Time/min | Area    | Height | Area% |
|---------|---------|--------|-------|
| 1       | 22.223  | 2515042| 70131 | 90.16 |
| 2       | 45.074  | 273306 | 3394  | 9.84  |

**Figure S99**, the HPLC spectrum of compound 2g, related to **Scheme 2**
| Time/min | Area  | Height | Area% |
|---------|-------|--------|-------|
| 1       | 11.286| 353752 | 20995 | 52.68 |
| 2       | 11.258| 317785 | 17791 | 47.32 |

| Time/min | Area  | Height | Area% |
|---------|-------|--------|-------|
| 1       | 8.647 | 7203931| 499663| 93.88 |
| 2       | 9.589 | 469848 | 31878 | 6.12  |

**Figure S100**, the HPLC spectrum of compound 2h, related to **Scheme 2**
| Time/min | Area     | Height | Area% |
|--------|----------|--------|-------|
| 1      | 10.341   | 174103 | 50.16 |
| 2      | 12.112   | 173006 | 49.84 |

| Time/min | Area     | Height | Area% |
|--------|----------|--------|-------|
| 1      | 9.768    | 7356783| 95.66 |
| 2      | 11.227   | 333700 | 4.34  |

Figure S101, the HPLC spectrum of compound 2i, related to Scheme 2
| Time/min | Area  | Height | Area% |
|---------|-------|--------|-------|
| 1       | 7.762 | 376725 | 35806 | 49.28 |
| 2       | 8.286 | 387792 | 29118 | 50.72 |

**Figure S102.** The HPLC spectrum of compound 2j related to Scheme 2
Figure S10, the HPLC spectrum of compound 2k, related to Scheme 2
| Time/min | Area     | Height  | Area%  |
|----------|----------|---------|--------|
| 1        | 26.429   | 558438  | 12010  | 50.01  |
| 2        | 28.422   | 558275  | 11269  | 49.99  |

| Time/min | Area     | Height  | Area%  |
|----------|----------|---------|--------|
| 1        | 26.164   | 22488323| 466399 | 95.46  |
| 2        | 28.709   | 1070176 | 19025  | 4.54   |

**Figure S104**, the HPLC spectrum of compound 2l, related to Scheme 2
| Time/min | Area     | Height | Area% |
|---------|----------|--------|-------|
| 1       | 28.190   | 1993930| 39346 | 49.06 |
| 2       | 31.599   | 2070135| 29805 | 50.94 |

**Figure S105**, the HPLC spectrum of compound 2m, related to **Scheme 2**
| Time/min | Area    | Height  | Area%  |
|----------|---------|---------|--------|
| 1        | 17.498  | 202433  | 48.76  |
| 2        | 20.321  | 212717  | 51.24  |

| Time/min | Area    | Height  | Area%  |
|----------|---------|---------|--------|
| 1        | 17.353  | 3337311 | 92.24  |
| 2        | 20.000  | 204123  | 5.76   |

Figure S106, the HPLC spectrum of compound 2n, related to Scheme 2
### Table 1

| Time/min | Area   | Height | Area%  |
|----------|--------|--------|--------|
| 1        | 17.027 | 164795 | 5122   | 50.30  |
| 2        | 19.334 | 162811 | 3939   | 49.70  |

### Table 2

| Time/min | Area    | Height | Area%  |
|----------|---------|--------|--------|
| 1        | 18.401  | 7131377| 184341 | 97.26  |
| 2        | 21.860  | 200971 | 4212   | 2.74   |

**Figure S10**, the HPLC spectrum of compound 2o, related to **Scheme 2**
| Time/min | Area    | Height | Area% |
|----------|---------|--------|-------|
| 1        | 15.1117 | 410167 | 49.22 |
| 2        | 20.148  | 423245 | 50.78 |

**Figure S108.** the HPLC spectrum of compound 2p, related to Scheme 2
| Time/min | Area  | Height | Area% |
|----------|-------|--------|-------|
| 1        | 8.268 | 200472 | 17266 | 49.74 |
| 2        | 9.225 | 202602 | 15387 | 50.26 |

| Time/min | Area  | Height | Area% |
|----------|-------|--------|-------|
| 1        | 7.831 | 1527382| 135633| 92.00 |
| 2        | 8.445 | 132880 | 11364 | 8.00  |

**Figure S109.** The HPLC spectrum of compound 2q, related to **Scheme 2**
| Time/min | Area       | Height   | Area% |
|----------|------------|----------|-------|
| 1        | 18.571     | 1716021  | 43100 | 50.95 |
| 2        | 26.626     | 1652184  | 26019 | 49.05 |

| Time/min | Area       | Height   | Area% |
|----------|------------|----------|-------|
| 1        | 17.897     | 16892981 | 465377 | 93.60 |
| 2        | 26.132     | 1154284  | 21004 | 6.40  |

**Figure S110**, the HPLC spectrum of compound 2r, related to **Scheme 2**
| Time/min | Area | Height | Area% |
|----------|------|--------|-------|
| 1        | 20.208 | 202251 | 5635  | 51.22 |
| 2        | 22.060 | 192607 | 4481  | 48.78 |

| Time/min | Area     | Height  | Area% |
|----------|----------|---------|-------|
| 1        | 21.295   | 980883  | 191494| 97.19 |
| 2        | 24.207   | 283094  | 7215  | 2.81  |

*Figure S111*, the HPLC spectrum of compound 2s, related to Scheme 2
| Time/min | Area   | Height | Area% |
|----------|--------|--------|-------|
| 1        | 11.972 | 284419 | 16853 | 49.77 |
| 2        | 17.445 | 287023 | 11358 | 50.23 |

Figure S112, the HPLC spectrum of compound 2t, related to Scheme 2
Transparent Methods

1. General information:

Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. For example, all the aldehydes recrystallized or distilled prior to use. Dichloromethane, toluene, were freshly distilled from CaH2, Ether (Et2O), tetrahydrofuran (THF) and 1, 4-dioxane were dried and distilled from metal sodium and benzophenone. Alcohol solvents were dried and distilled from metal magnesium. Other commercially available reagents and solvents were used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (300 - 400 mesh). 1H, 13C, 31P, 19F and 29Si NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in CDCl3. Multiplicities were given as: s (singlet); d (doublet); dd (doublets of doublet); t (triplet); q (quartet); td (triplet of doublets); tt (triplet of triplets) ddd (doublet of doublet of doublets) or m (multiplets). High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer. HPLC was carried out with a Agilent 1260 infinity or Waters AcQuity UPLC using a chiralcel IA column, a chiral INA column (from Phenomenex) and a Chiralcel OD-H column.

2. General procedure for the synthesis of Si-tethered bisalkynes (Substrate 1)
The synthesis of S3: A 50 mL single-necked, round-bottomed flask equipped with an egg-shaped magnetic stir bar is flame-dried under vacuum. After cooling to 23 °C, Pd(PPh₃)₂Cl₂ (140 mg, 0.2 mmol, 2 mol %) and CuI (75 mg, 0.4 mmol, 4 mol %) is added, the reaction flask is put under an atmosphere of N₂, and S1 (10 mmol), Et₃N (18 mL, 120 mmol, 1.8 equiv), and S2 (10.2 g, 11 mmol, 1.1 equiv) is added via syringe resulting in a clear solution with a brown color. The reaction mixture is stirred at rt for 4 h. The solution was then diluted with EA (20 mL), and washed with water (2 × 20 mL) and brine (2 × 20 mL). The organics were then passed through a hydrophobic frit and concentrated under reduced pressure to give a yellow oil, which was purified by flash chromatography (silica gel, petroleum ether) to afford S3.

The synthesis of S4 (substrate 1 in the text): A 50 mL single-necked, round-bottomed flask equipped with an egg-shaped magnetic stir bar is flame-dried under vacuum. After cooling to 23 °C, S3 is added, the reaction flask is put under an atmosphere of N₂, 5 ml (2.5 mmol) of a 2.5 M solution n-BuLi in hexanes was added at -78 °C. The resulting solution was stirred at -78 °C for 1 h, and then 0.6 mL of MeHSiCl₂ (6 mmol, 0.6 equiv) was added slowly to the above mixture at the same temperature. The reaction mixture was stirred for 4 hours at rt. When the reaction is complete, it was quenched with saturated aqueous NH₄Cl (10 mL) and stirred vigorously for 5 minutes. The aqueous phase was extracted with ethyl acetate (3×40 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. Which was purified by flash chromatography (silica gel, petroleum ether) to afford S4.

![Methylbis(2-(phenylethynyl)phenyl)silane (1a)](image)

Methylbis(2-(phenylethynyl)phenyl)silane (1a)

White solid. mp 75.4-77.6 °C.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J = 7.5$ Hz, 3H), 7.42 $-$ 7.32 (m, 6H), 7.32 $-$ 7.22 (m, 9H), 5.36 (q, $J = 3.8$ Hz, 1H), 0.82 (d, $J = 3.8$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.9, 136.2, 132.1, 131.5, 129.6, 129.4, 128.4, 128.3, 127.7, 123.4, 93.0, 90.4, -5.0.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{29}$H$_{22}$NaSi, 421.1383; found 421.1390.

Bis(5-fluoro-2-(phenylethynyl)phenyl)(methyl)silane (1b)

White solid. mp 112.0$-$112.4 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (dd, $J = 8.4$, 5.2 Hz, 2H), 7.35 (dd, $J = 6.7$, 3.0 Hz, 4H), 7.30 (d, $J = 5.3$ Hz, 2H), 7.24 (s, 1H), 7.22 (d, $J = 2.6$ Hz, 1H), 7.06 (m, $J = 8.5$, 2.7 Hz, 2H), 5.30 (q, $J = 3.6$ Hz, 1H), 0.81 (d, $J = 3.8$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 139.5, 136.2, 134.5, 132.7, 131.5, 129.2, 128.67, 128.4, 128.2, 123.6, 92.5, 90.6, 21.4, -4.7.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{29}$H$_{20}$F$_2$NaSi, 457.1195; found 457.1215.

Bis(5-methoxy-2-(phenylethynyl)phenyl)(methyl)silane (1c)

White solid. mp 102.9-104.2 °C.
**Methylbis(5-methyl-2-(phenylethynyl)phenyl)silane (1d)**

Yellow oil.

**1H NMR (400 MHz, CDCl₃)** δ 7.38 (s, 1H), 7.36 (s, 1H), 7.34 (d, J = 1.2 Hz, 2H), 7.28 – 7.24 (m, 3H), 7.22 – 7.20 (m, 3H), 7.19 (s, 4H), 7.08 (dd, J = 7.8, 1.2 Hz, 2H), 5.19 (q, J = 3.8 Hz, 1H), 2.12 (s, 6H), 0.73 (d, J = 3.9 Hz, 3H).

**13C NMR (100 MHz, CDCl₃)** δ 137.8, 137.4, 137.1, 132.0, 131.5, 130.3, 128.3, 128.1, 126.2, 123.7, 92.1, 90.5, 21.5, -5.1.

**HRMS (ESI-TOF) m/z:** [M+Na]⁺ Calcd for C₃₁H₂₆NaO₂Si, 481.1594; found 481.1611.

**Methylbis(2-(p-tolylethynyl)phenyl)silane (1e)**

Yellow solid. mp 88.1-92.2 °C.

**1H NMR (400 MHz, CDCl₃)** δ 7.55 (dd, J = 5.1, 3.6 Hz, 4H), 7.36 (td, J = 7.6, 1.2 Hz, 2H), 7.26 – 7.21 (m, 6H), 7.09 (d, J = 8.0 Hz, 4H), 5.34 (q, J = 3.8 Hz, 1H), 2.34 (s, 6H), 0.81 (d, J = 3.9 Hz, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 138.5, 137.8, 136.2, 131.9, 131.4, 129.6, 129.5, 129.2, 127.5, 120.4, 93.2, 89.8, 21.6, -5.0.

HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{31}$H$_{27}$Si, 427.1877; found 427.1861.

Methylbis(2-((4-propylphenyl)ethynyl)phenyl)silane (1f)

Yellow solid. mp 65.5-68.6 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.56 (d, $J = 7.9$ Hz, 4H), 7.36 (t, $J = 7.7$ Hz, 2H), 7.26 (t, $J = 4.0$ Hz, 6H), 7.09 (d, $J = 8.1$ Hz, 4H), 5.34 (q, $J = 3.8$ Hz, 1H), 2.61 – 2.52 (m, 4H), 1.62 (dd, $J = 15.1$, 7.5 Hz, 4H), 0.93 (t, $J = 7.3$ Hz, 6H), 0.81 (d, $J = 3.8$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.2, 137.8, 136.2, 132.0, 131.4, 129.6, 129.5, 128.6, 127.5, 120.6, 93.2, 89.9, 38.1, 24.5, 13.9, -4.9.

HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{35}$H$_{35}$Si, 483.2503; found 483.2509.

Bis(2-((4-methoxyphenyl)ethynyl)phenyl)(methyl)silane (1g)

White solid. mp 118.5-120.7 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.61 – 7.52 (m, 4H), 7.36 (td, $J = 7.6$, 1.3 Hz, 2H), 7.28 (d, $J = 2.0$ Hz, 1H), 7.26 (s, 4H), 7.24 (d, $J = 1.0$ Hz, 1H), 6.81 (d, $J = 8.9$ Hz, 4H), 5.33 (q, $J = 3.8$ Hz, 1H), 3.80 (s, 6H), 0.80 (d, $J = 3.9$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.7, 137.7, 136.2, 133.0, 131.8, 129.7, 129.5, 127.3, 115.6, 114.1, 93.0, 89.2, 55.4, -5.0.
HRMS (ESI-TOF) m/z: [M+H]+ Calcd for C$_{31}$H$_{27}$O$_2$Si, 459.1775; found 459.1781.

Methylbis(5-methyl-2-((4-propylphenyl)ethynyl)phenyl)silane (1h)
White solid. mp 105.5-106.3 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (s, 1H), 7.41 (s, 3H), 7.25 (s, 2H), 7.23 (s, 2H), 7.15 (d, $J = 1.5$ Hz, 1H), 7.13 (d, $J = 1.3$ Hz, 1H), 7.09 (d, $J = 8.1$ Hz, 4H), 5.24 (q, $J = 3.8$ Hz, 1H), 2.63 – 2.52 (m, 4H), 2.18 (s, 6H), 1.62 (d, $J = 7.6$ Hz, 4H), 0.93 (t, $J = 7.3$ Hz, 6H), 0.79 (d, $J = 3.8$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.0, 137.7, 137.2, 137.1, 131.9, 131.4, 130.3, 128.5, 126.4, 120.9, 92.3, 89.9, 38.1, 24.5, 21.5, 13.9, -5.0.

HRMS (ESI-TOF) m/z: [M+H]+ Calcd for C$_{37}$H$_{39}$Si, 511.2816; found 511.2821.

Methylbis(5-methyl-2-((p-tolylethynyl)phenyl)silane (1i)
Yellow solid. mp 126.0-130.1 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (s, 1H), 7.33 (d, $J = 2.4$ Hz, 3H), 7.15 (d, $J = 8.3$ Hz, 4H), 7.10 – 7.03 (m, 2H), 7.01 (d, $J = 7.9$ Hz, 4H), 5.17 (q, $J = 3.7$ Hz, 1H), 2.25 (s, 6H), 2.12 (s, 6H), 0.71 (d, $J = 3.8$ Hz, 3H).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 138.2, 138.0, 137.7, 137.2, 137.0, 135.4, 131.9, 131.8, 131.4, 131.1, 130.3, 130.1, 129.1, 127.2, 126.3, 125.6, 120.6, 96.1, 92.2, 91.6, 89.9, 21.6, 21.6, 21.5, -5.0.

HRMS (ESI-TOF) \(m/z\): [M+N\(^+\)] Calcd for C\(_{19}\)H\(_{30}\)N\(_{12}\)NaSi, 477.2378; found 477.2360.

Bis(2-((4-(tert-butyl)phenyl)ethynyl)-5-methylphenyl)(methyl)silane (1j)

Yellow solid. mp 116.7-119.1 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.44 (s, 1H), 7.42 (s, 1H), 7.40 (s, 2H), 7.29 (q, \(J =\) 8.5 Hz, 8H), 7.13 (d, \(J = 7.8\) Hz, 2H), 5.25 (q, \(J = 3.7\) Hz, 1H), 2.16 (s, 6H), 1.30 (s, 18H), 0.80 (d, \(J = 3.8\) Hz, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 151.3, 137.8, 137.2, 137.1, 131.9, 131.3, 130.3, 126.4, 125.3, 120.7, 92.217, 879.927, 34.9, 31.3, 21.5, -5.0.

HRMS (ESI-TOF) \(m/z\): [M+N\(^+\)] Calcd for C\(_{39}\)H\(_{42}\)NaSi, 561.2948; found 561.2960.

Bis(5-methoxy-2-(p-tolylethynyl)phenyl)(methyl)silane (1k)

Yellow solid. mp 117.3-118.1 °C.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (s, 1H), 7.36 (s, 1H), 7.14 (s, 2H), 7.12 (s, 2H), 7.02 (d, $J = 2.7$ Hz, 2H), 6.96 (s, 2H), 6.94 (s, 2H), 6.75 (d, $J = 2.7$ Hz, 1H), 6.73 (d, $J = 2.7$ Hz, 1H), 5.20 (q, $J = 3.7$ Hz, 1H), 3.50 (s, 6H), 2.19 (s, 6H), 0.72 (d, $J = 3.8$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.8, 139.5, 138.0, 133.5, 131.2, 129.1, 121.6, 121.5, 120.6, 115.2, 91.6, 89.8, 55.1, 21.5, -5.1.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{33}$H$_{30}$NaO$_2$Si, 509.1907; found 509.1920.

Bis(2-((3-methoxyphenyl)ethynyl)phenyl)(methyl)silane (1l)

Yellow solid. mp 92.9-94.2 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.71 – 7.47 (m, 4H), 7.39 (dd, $J = 10.6$, 4.4 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 2H), 7.03 – 6.93 (m, 2H), 6.92 – 6.82 (m, 4H), 5.38 (dd, $J = 7.5$, 3.7 Hz, 1H), 3.77 (s, 6H), 0.83 (d, $J = 3.9$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.3, 137.8, 136.0, 131.9, 129.5, 129.1, 129.2 127.6, 124.2, 124.0, 115.9, 115.1, 92.8, 90.1, 55.3, -5.1.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{31}$H$_{28}$NaO$_2$Si, 481.1594; found 481.1611.

Methylbis(2-(m-tolylethynyl)phenyl)silane (1m)
Yellow oil

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 (d, $J = 7.9$ Hz, 4H), 7.41 (td, $J = 7.6, 1.1$ Hz, 2H), 7.31 (dd, $J = 11.0, 3.7$ Hz, 2H), 7.21 (d, $J = 6.1$ Hz, 4H), 7.15 (dd, $J = 8.3, 5.8$ Hz, 4H), 5.41 (q, $J = 3.8$ Hz, 1H), 2.34 (s, 6H), 0.85 (d, $J = 3.8$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.0, 137.9, 136.2, 132.1, 132.0, 129.6, 129.5, 129.2, 128.55, 128.3, 127.6, 123.2, 93.2, 90.1, 21.3, -5.0.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{31}$H$_{26}$NaSi, 449.1696; found 449.1710.

Bis(2-((2-methoxyphenyl)ethynyl)-5-methylphenyl)(methyl)silane (1n)

White solid. mp 102.3-103.8 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 – 7.52 (m, 4H), 7.41 (d, $J = 7.0$ Hz, 2H), 7.33 (t, $J = 7.3$ Hz, 2H), 7.23 (d, $J = 7.2$ Hz, 2H), 7.05 – 6.85 (m, 4H), 5.88 – 5.02 (m, 1H), 3.90 (s, 6H), 2.27 (s, 6H), 1.02 (d, $J = 2.1$ Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.9, 137.7, 137.1, 133.4, 132.0, 130.1, 129.5, 126.5, 120.4, 112.9, 110.6, 94.5, 88.5, 55.5, 21.3, -5.2.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{33}$H$_{30}$NaO$_2$Si, 509.1907; found 509.1919.

Methylbis(4-methyl-2-(phenylethynyl)phenyl)silane (1o)

Yellow oil.
\[ \text{Ethylbis(5-methyl-2-} \begin{array}{c} \text{((4-propylphenyl)ethynyl)} \text{phenyl)silane (1p)} \\
\end{array} \]

Yellow oil.

\[ \text{Bis(2-} \begin{array}{c} \text{(cyclopropylethynyl)-} \text{5-methylphenyl)(methyl)silane (1q)} \\
\end{array} \]

Yellow oil.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22 (d, $J = 7.5$ Hz, 4H), 7.05 – 7.00 (m, 2H), 4.94 (q, $J = 3.8$ Hz, 1H), 2.22 (s, 6H), 1.29 – 1.18 (m, 2H), 0.68 – 0.62 (m, 4H), 0.59 (d, $J = 3.8$ Hz, 3H), 0.55 – 0.48 (m, 2H), 0.48 – 0.41 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.7, 135.6, 135.3, 130.8, 129.1, 126.0, 95.2, 20.6, 7.3, 7.3, -0.7, -6.1.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{25}$H$_{26}$NaSi, 377.1696; found 377.1709.

![Methylbis(2-(thiophen-2-ylethynyl)phenyl)silane (1r)](image)

White solid. mp 70.5–72.3 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J = 7.3$ Hz, 2H), 7.45 (d, $J = 7.6$ Hz, 2H), 7.28 (dd, $J = 7.5$, 6.7 Hz, 2H), 7.18 (dd, $J = 13.9$, 6.2 Hz, 4H), 7.03 (d, $J = 3.6$ Hz, 2H), 6.88 (dd, $J = 5.0$, 3.7 Hz, 2H), 5.19 (q, $J = 3.6$ Hz, 1H), 0.73 (d, $J = 3.9$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.7, 136.2, 131.8, 129.6, 128.9, 127.8, 127.4, 127.2, 123.4, 94.1, 86.3, -5.1.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{25}$H$_{18}$NaS$_2$Si, 433.0511; found 433.0520.

![Bis(2-((2-methoxyphenyl)ethynyl)phenyl)(methyl)silane (1s)](image)

Yellow oil.
**Bis(2-(cyclopropylethynyl)phenyl)(methyl)silane (1t)**

Yellow oil.

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.48 (d, \( J = 7.3 \) Hz, 2H), 7.44 (d, \( J = 7.6 \) Hz, 2H), 7.34 (td, \( J = 7.5, 1.3 \) Hz, 2H), 7.29 – 7.22 (m, 2H), 5.11 (q, \( J = 3.8 \) Hz, 1H), 1.36 (m), \( J = 9.9, 6.6, 4.2 \) Hz, 2H), 0.78 (m, \( J = 5.8, 3.0 \) Hz, 4H), 0.73 (d, \( J = 3.9 \) Hz, 3H), 0.69 – 0.63 (m, 2H), 0.60 – 0.53 (m, 2H).

\[ ^13C \text{ NMR (100 MHz, CDCl}_3 \] \( \delta \) 137.8, 135.8, 131.8, 130.1, 129.3, 126.8, 97.2, 8.4, 0.3, -5.2.

**HRMS (ESI-TOF) m/z: [M+Na]^+** Calcd for C_{23}H_{22}NaSi, 349.1383; found 349.1400.

For the chiral Ligand (L8)^3:

3-(diphenylphosphanyl)-2'-(hydroxy(o-tolyl)methyl)-[1,1'-binaphthalen]-2-ol

Colorless solid.

**Optical rotation:** \( [\alpha]_D^{25} = +34.5 \) (c = 0.63, CHCl\(_3\)).

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.80 (dd, \( J = 8.3, 3.0 \) Hz, 2H), 7.60 (t, \( J = 7.0 \) Hz, 2H), 7.35 (ddd, \( J = 22.6, 12.3, 5.7 \) Hz, 12H), 7.25 (d, \( J = 8.7 \) Hz, 1H), 7.22 – 7.14 (m, 4H).
7.10 – 7.00 (m, 3H), 6.84 (dd, J = 13.6, 7.9 Hz, 2H), 6.61 (s, 1H), 5.81 (s, 1H), 1.56 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.00, 140.34, 139.76, 134.92, 134.44, 134.33, 134.14, 133.83, 133.64, 133.54, 133.10, 131.58, 130.14, 129.31, 128.82, 128.76, 128.75, 128.69, 128.24, 128.15, 127.27, 126.92, 126.65, 126.40, 126.35, 126.19, 125.94, 125.47, 124.91, 123.95, 71.45, 19.44.
3. General procedure for the synthesis of product 2

General procedure for the enantioselective synthesis of benzsilole 2 via Rh-catalyzed intramolecular hydrosilylation. A vial was charged with [Rh(cod)Cl]₂ (4.9 mg, 5 mol%), L₈ (13.8 mg, 12 mol%), KOᵗBu (2.7 mg, 12 mol%) and evacuated under high vacuum and backfilled with N₂. Then toluene (1 mL) was added and stirred at room temperature for about 0.5 h. Subsequently, the methylbis(2-(phenylethynyl)phenyl)silane 1a (79.6 mg, 0.2 mmol) were added to the reaction mixture and was stirred at 70 °C. Upon reaction completion (72 h, TLC, eluent: hexane), the mixture was filtered over a plug of silica gel (washed with 20 mL EtOAc), and the filtrate was concentrated. The crude was purified by column chromatography to give the products 2.

(S)-1-methyl-2-phenyl-1-(2-(phenylethynyl)phenyl)-1H-benzo[b]silole (2a)

The mobile phase for flash chromatography: hexane. Yellow oil. (40.1 mg, 50%).

Optical rotation: [α]_D³² = +221.5 (c = 0.63, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 6.9 Hz, 1H), 7.70 (s, 1H), 7.58 (t, J = 7.0 Hz, 3H), 7.51 (dd, J = 6.5, 3.1 Hz, 2H), 7.46 (d, J = 7.4 Hz, 1H), 7.35 (dd, J = 5.0, 1.6 Hz, 3H), 7.33 – 7.30 (m, 3H), 7.29 – 7.20 (m, 3H), 7.19 – 7.11 (m, 2H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.1, 143.4, 142.4, 138.8, 137.6, 137.4, 135.6, 132.8, 132.7, 132.6, 131.5, 131.3, 130.2, 129.8, 129.3, 128.8, 128.5, 128.2, 128.1, 127.8, 127.4, 127.2, 127.1, 127.0, 124.6, 123.2, 92.2, 91.3, -3.6.

HRMS: (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{29}$H$_{23}$Si, 399.1564; found 399.1567.

HPLC: Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column and a Phenomenex column (hexanes: 2-propanol = 99.5:0.5, 0.5 mL/min, 330 nm, 95.5:4.5 er); major enantiomer $t_r = 26.8$ min, minor enantiomer $t_r = 30.0$ min.

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 (s, 1H), 7.61 – 7.52 (m, 3H), 7.52 – 7.46 (m, 3H), 7.38 (dd, $J = 5.9, 2.6$ Hz, 3H), 7.34 (d, $J = 7.8$ Hz, 2H), 7.21 (dd, $J = 8.2, 4.8$ Hz, 1H), 7.14 (dd, $J = 8.7, 2.8$ Hz, 1H), 7.08 – 6.94 (m, 3H), 0.98 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.8, 163.4, 161.3, 160.9, 145.0, 142.4, 141.8, 140.0, 140.0, 139.9, 138.4, 135.0, 134.9, 131.6, 129.0, 128.8, 128.7, 127.6, 126.9, 125.9, 125.4, 123.0, 122.5, 122.2, 120.1, 119.9, 117.4, 117.2, 117.0, 116.8, 92.1, 90.0, -3.9.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{29}$H$_{20}$F$_2$NaSi, 457.1195; found 457.1120.

HPLC: Enantiomeric excess was determined by HPLC with a Phenomenex column and a Chiralcel OD-H column (hexanes: 2-propanol = 95.5:0.5, 0.5 mL/min, 330 nm, 96.1:3.9 er); major enantiomer $t_r = 46.6$ min, minor enantiomer $t_r = 48.5$ min.

(R)-6-fluoro-1-(5-fluoro-2-(phenylethynyl)phenyl)-1-methyl-2-phenyl-1H-benzo[b]silole (2b)

The mobile phase for flash chromatography: hexane. Yellow oil. (32.1 mg, 37%).

Optical rotation: $[\alpha]_D^{25} = +153.6$ (c = 0.33, CHCl$_3$).
(S)-6-methoxy-1-(5-methoxy-2-(phenylethynyl)phenyl)-1-methyl-2-phenyl-1H-benzo[b]silole (2c)

The mobile phase for flash chromatography: hexane/ethyl acetate = 100:1. White solid. mp 74-76 °C. (55 mg, 60%).

Optical rotation: $[\alpha]_D^{25} = +391.5$ (c = 1.63, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (s, 1H), 7.46 (t, $J = 8.1$ Hz, 6H), 7.24 (dd, $J = 11.0$, 7.3 Hz, 4H), 7.12 (dd, $J = 7.6$, 5.1 Hz, 3H), 6.88 (d, $J = 2.7$ Hz, 1H), 6.73 (ddd, $J = 13.7$, 8.4, 2.6 Hz, 2H), 3.45 (s, 3H), 3.42 (s, 3H), 0.93 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.3, 159.0, 142.5, 142.0, 140.0, 140.0, 139.3, 134.3, 131.5, 128.9, 128.6, 128.3, 126.9, 126.9, 125.6, 124.8, 123.6, 121.2, 120.9, 118.4, 116.0, 115.8, 91.8, 90.9, 77.5, 76.8, 55.2, 55.0, -3.3.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{31}$H$_{26}$NaO$_2$Si, 481.1592; found 481.1581.

HPLC: Enantiomeric excess was determined by HPLC with a Chiralpak IA column (hexanes: 2-propanol = 99.3:0.7, 0.6 mL/min, 330 nm, 96.7:3.3 er); major enantiomer $t_r = 19.3$ min, minor enantiomer $t_r = 26.5$ min.

(R)-1,6-dimethyl-1-(5-methyl-2-(phenylethynyl)phenyl)-2-phenyl-1H-benzo[b]silole (2d)

The mobile phase for flash chromatography: hexane. Yellow oil. (34.9 mg, 41%).

Optical rotation: $[\alpha]_D^{25} = +223.5$ (c = 0.67, CHCl$_3$).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 (s, 1H), 7.58 (s, 1H), 7.49 – 7.37 (m, 5H), 7.28 – 7.16 (m, 5H), 7.06 (ddd, $J = 22.1, 15.3, 7.3$ Hz, 5H), 2.14 (s, 3H), 2.08 (s, 3H), 0.86 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.6, 142.5, 142.4, 139.2, 137.9, 137.9, 137.4, 136.8, 136.4, 133.9, 132.8, 131.6, 130.8, 130.7, 128.8, 128.5, 128.4, 127.0, 126.3, 124.5, 123.6, 91.7, 91.6, 21.6, 21.5, -3.5.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{31}$H$_{26}$NaSi, 449.1696; found 449.1708.

HPLC: Enantiomeric excess was determined by HPLC with a Chiralpak IA column (hexanes: 2-propanol = 99.5:0.5, 0.8 mL/min, 330 nm, 99.3:0.7 er); major enantiomer $t_r = 10.0$ min, minor enantiomer $t_r = 11.1$ min.

(S)-1-methyl-2-(p-tolyl)-1-(2-(p-tolylethynyl)phenyl)-1H-benzo[b]silole (2e)

The mobile phase for flash chromatography: hexane. Yellow oil. (34.9 mg, 41%).

Optical rotation: $[\alpha]_D^{25} = +321.5$ (c = 1.33, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 7.0$ Hz, 1H), 7.60 (s, 1H), 7.50 (d, $J = 7.7$ Hz, 1H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 3H), 7.27 – 7.17 (m, 3H), 7.06 (ddd, $J = 14.5, 9.9, 4.9$ Hz, 6H), 2.31 (s, 3H), 2.27 (s, 3H), 0.89 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.4, 143.4, 141.5, 138.8, 137.7, 137.5, 137.2, 136.0, 135.7, 132.9, 132.7, 131.6, 130.3, 129.8, 129.6, 129.6, 129.4, 127.8, 127.1, 127.0, 124.5, 120.3, 92.5, 90.9, 21.7, 21.4, -3.5.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{31}$H$_{26}$NaSi, 449.1686; found 449.1696.
HPLC: Enantiomeric excess was determined by HPLC with a Chiralpak IA column (hexanes: 2-propanol = 99.5:0.5, 0.8 mL/min, 330 nm, 94.6:5.4 $er$); major enantiomer $t_r = 10.2$ min, minor enantiomer $t_r = 21.0$ min.

$\text{(S)}$-1-methyl-2-(4-propylphenyl)-1-(2-((4-propylphenyl)ethynyl)phenyl)-1H-benzo[b]silole (2f)

The mobile phase for flash chromatography: hexane. Yellow oil. (64.9 mg, 71%).

Optical rotation: $[\alpha]_D^{25} = +232.4$ (c = 0.63, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 7.0$ Hz, 1H), 7.60 (s, 1H), 7.50 (d, $J = 7.6$ Hz, 1H), 7.42 (d, $J = 8.1$ Hz, 2H), 7.37 (t, $J = 5.9$ Hz, 3H), 7.27 – 7.17 (m, 3H), 7.13 – 7.01 (m, 6H), 2.57 – 2.46 (m, 4H), 1.57 (dt, $J = 14.6$, 7.3 Hz, 4H), 0.94 – 0.82 (m, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.4, 143.5, 143.4, 142.1, 141.6, 137.7, 137.6, 136.3, 135.8, 132.9, 132.7, 131.6, 130.3, 129.8, 129.6, 129.0, 128.8, 127.7, 127.1, 127.0, 124.5, 120.6, 92.6, 90.9, 38.2, 38.0, 24.6, 24.5, 14.1, 13.9, -3.4.

HRMS (ESI-TOF) m/z: [M$+$Na]$^+$ Calcd for C$_{35}$H$_{34}$NaSi, 505.2322; found 505.2313.

HPLC: Enantiomeric excess was determined by HPLC with a Chiralpak IA column (hexanes: 2-propanol = 99.5:0.5, 0.8 mL/min, 330 nm, 93.6:6.5 $er$); major enantiomer $t_r = 7.5$ min, minor enantiomer $t_r = 13.1$ min.
(S)-2-(4-methoxyphenyl)-1-(2-((4-methoxyphenyl)ethynyl)phenyl)-1-methyl-1H-benzof[b]silole (2g)

The mobile phase for flash chromatography: hexane/ethyl acetate = 100:1. Yellow solid. (52.3 mg, 57%).

**Optical rotation:** $[\alpha]_D^{25} = +321.5$ (c = 1.67, CHCl$_3$). mp 64.9 $^\circ$C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 (d, $J = 6.9$ Hz, 1H), 7.61 – 7.41 (m, 8H), 7.33 – 7.24 (m, 2H), 7.17 – 7.09 (m, 2H), 6.89 (t, $J = 8.7$ Hz, 4H), 3.83 (s, 3H), 3.80 (s, 3H), 0.96 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.9, 159.1, 149.6, 143.0, 140.3, 137.4, 137.4, 135.8, 135.7, 133.1, 132.9, 132.8, 132.5, 132.5, 131.6, 130.3, 129.8, 129.7, 128.9, 128., 127.6, 127.2, 126.8, 124.3, 92.4, 90.2, 55.5, 55.4, -3.4.

**HRMS** (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{31}$H$_{26}$NaO$_2$Si, 481.1584; found 481.1594.

**HPLC:** Enantiomeric excess was determined by HPLC with a Chiralpak IA column (hexanes: 2-propanol = 99.5:0.5, 0.8 mL/min, 330 nm, 90.2:9.8 er); major enantiomer $t_r = 22.2$ min, minor enantiomer $t_r = 45.0$ min.

(R)-1,6-dimethyl-1-(5-methyl-2-((4-propylphenyl)ethynyl)phenyl)-2-(4-propylphenyl)-1H-benzof[b]silole (2h)

The mobile phase for flash chromatography: hexane. Yellow oil. (82.7 mg, 81%).

**Optical rotation:** $[\alpha]_D^{25} = +221.5$ (c = 0.63, CHCl$_3$).
\textbf{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})} \delta 7.65 (s, 1H), 7.57 (s, 1H), 7.43 – 7.34 (m, 5H), 7.17 (s, 1H), 7.11 – 6.99 (m, 7H), 2.67 – 2.41 (m, 4H), 2.15 (s, 3H), 2.09 (s, 3H), 1.63 – 1.50 (m, 4H), 0.87 (dt, J = 7.3, 3.0 Hz, 9H).

\textbf{\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3})} \delta 146.8, 143.3, 142.4, 141.7, 141.4, 137.9, 137.6, 137.5, 136.6, 136.5, 136.5, 134.0, 132.7, 131.5, 130.8, 130.6, 128.9, 128.7, 127.0, 126.5, 124.3, 120.8, 91.9, 91.1, 38.1, 37.9, 24.6, 24.5, 21.6, 21.5, 14.0, 13.9, -3.4.

\textbf{HRMS (ESI-TOF) m/z: [M+Na]\textsuperscript{+}} Calcd for C\textsubscript{37}H\textsubscript{38}NaSi, 533.2635; found 533.2623.

\textbf{HPLC}: Enantiomeric excess was determined by HPLC with a Phenomenex column (hexanes: 2-propanol = 99.5:0.5, 0.6 mL/min, 330 nm, 93.9:6.1 er); major enantiomer \(t_r = 8.6\) min, minor enantiomer \(t_r = 9.6\) min.

\begin{center}
(R)-1,6-dimethyl-1-(5-methyl-2-(p-tolylethynyl)phenyl)-2-(p-tolyl)-1\textit{H}-benzo[b]silole (2i)
\end{center}

The mobile phase for flash chromatography: hexane. Yellow oil. (54.5 mg, 60%).

\textbf{Optical rotation:} \([\alpha]_D^{25} = +231.1\) (c = 1.33, CHCl\textsubscript{3}).

\textbf{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})} \delta 7.65 (s, 1H), 7.56 (s, 1H), 7.41 – 7.33 (m, 5H), 7.18 (s, 1H), 7.14 – 6.99 (m, 8H), 2.29 (s, 3H), 2.26 (s, 3H), 2.15 (s, 3H), 2.09 (s, 3H), 0.84 (s, 3H).

\textbf{\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3})} \delta 146.8, 142.3, 141.4, 138.5, 137.9, 137.7, 137.5, 136.9, 136.5, 136.4, 136.3, 134.0, 132.7, 131.5, 130.8, 130.6, 129.5, 129.3, 127.0, 126.5, 124.3, 120.6, 91.8, 91.0, 21.7, 21.6, 21.5, 21.4, -3.5.

\textbf{HRMS (ESI-TOF) m/z: [M+Na]\textsuperscript{+}} Calcd for C\textsubscript{33}H\textsubscript{30}NaSi, 477.2009; found 477.2019.
**HPLC:** Enantiomeric excess was determined by HPLC with a Phenomenex column (hexanes: 2-propanol = 99.5:0.5, 0.6 mL/min, 330 nm, 95.7:4.3 *er*); major enantiomer *t*<sub>r</sub> = 9.7 min, minor enantiomer *t*<sub>r</sub> = 11.2 min.

![Chemical structure](image)

(R)-2-(4-(tert-butyl)phenyl)-1-(2-((4-(tert-butyl)phenyl)ethynyl)-5-methylphenyl)-1,6-dimethyl-1H-benzo[b]silole (2j)

The mobile phase for flash chromatography: hexane. Yellow oil. (54.8 mg, 51%).

**Optical rotation:** [α]<sub>D</sub> = +211.9 (c = 0.67, CHCl₃).

**1H NMR (400 MHz, CDCl₃)**: δ 7.65 (s, 1H), 7.59 (s, 1H), 7.46 – 7.37 (m, 4H), 7.29 (dd, *J* = 15.2, 8.3 Hz, 4H), 7.19 (s, 1H), 7.17 (s, 1H), 7.07 (dt, *J* = 23.2, 7.5 Hz, 3H), 2.17 (s, 3H), 2.11 (s, 3H), 1.26 (s, 9H), 1.24 (s, 9H), 0.85 (s, 3H).

**13C NMR (100 MHz, CDCl₃)**: δ 151.6, 150.1, 146.8, 142.4, 141.6, 141.6, 138.0, 137.7, 137.5, 136.6, 136.4, 136.3, 133.9, 132.7, 131.3, 130.8, 130.6, 126.8, 126.5, 125.7, 125.5, 124.3, 120.6, 91.9, 91.1, 35.9, 34.7, 31.5, 31.4, 21.6, 21.5, -3.4.

**HRMS (ESI-TOF) m/z:** [M+Na]<sup>+</sup> Calcd for C₃₀H₄₂NaSi, 561.2948; found 561.2934.

**HPLC:** Enantiomeric excess was determined by HPLC with a Chiralpak IA column (hexanes: 2-propanol = 99.5:0.5, 0.6 mL/min, 330 nm, 92.4:7.6 *er*); major enantiomer *t*<sub>r</sub> = 7.8 min, minor enantiomer *t*<sub>r</sub> = 8.2 min.

![Chemical structure](image)
(R)-6-methoxy-1-(5-methoxy-2-(p-tolylethynyl)phenyl)-1-methyl-2-(p-tolyl)-1H-b enzo[b]silole (2k)

The mobile phase for flash chromatography: hexane/ethyl acetate = 100:1. Yellow oil. (38.9 mg, 40%).

Optical rotation: $[\alpha]_{D}^{25} = +158.2$ (c = 0.67, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 (s, 1H), 7.49 (d, $J = 2.6$ Hz, 1H), 7.45 (d, $J = 8.5$ Hz, 1H), 7.39 (d, $J = 1.7$ Hz, 2H), 7.37 (d, $J = 1.7$ Hz, 2H), 7.14 – 7.09 (m, 2H), 7.09 – 7.04 (m, 3H), 6.89 (d, $J = 2.7$ Hz, 1H), 6.75 (ddd, $J = 15.4$, 8.4, 2.7 Hz, 2H), 3.49 (s, 3H), 3.46 (s, 3H), 2.30 (s, 3H), 2.27 (s, 3H), 0.91 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.1, 158.8, 142.2, 141.5, 140.4, 139.6, 139.6, 138.4, 136.7, 136.4, 134.2, 131.4, 129.6, 129.4, 126.8, 125.4, 121.5, 121.0, 120.6, 118.4, 116.0, 115.7, 91.1, 91.0, 55.2, 55.1, 21.7, 21.3, -3.4.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{33}$H$_{30}$NaO$_2$Si, 509.1907; found 509.1905.

HPLC: Enantiomeric excess was determined by HPLC with a Phenomenex column (hexanes: 2-propanol = 99.5:0.5, 0.8 mL/min, 330 nm, 94.0:6.0 er); major enantiomer $t_r = 19.7$ min, minor enantiomer $t_r = 25.4$ min.

(S)-2-(3-methoxyphenyl)-1-((3-methoxyphenyl)ethynyl)phenyl)-1-methyl-1H-b enzo[b]silole (2l)

The mobile phase for flash chromatography: hexane/ethyl acetate = 100:1. Yellow oil. (36.7 mg, 40%).

Optical rotation: $[\alpha]_{D}^{25} = +149.2$ (c = 1.33, CHCl$_3$).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J = 7.0$ Hz, 1H), 7.81 – 7.73 (m, 2H), 7.51 (d, $J = 7.7$ Hz, 1H), 7.42 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.26 (ddd, $J = 9.3$, 8.0, 2.4 Hz, 2H), 7.20 – 7.13 (m, 4H), 7.06 – 6.97 (m, 2H), 6.95 – 6.82 (m, 3H), 6.76 (d, $J = 7.7$ Hz, 1H), 3.80 (s, 3H), 3.38 (s, 3H), 0.87 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.2, 156.4, 148.1, 142.8, 140.5, 139.4, 137.3, 134.7, 133.6, 132.8, 132.7, 129.9, 129.6, 128.8, 128.5, 128.5, 127.3, 127.1, 126.0, 124.2, 121.0, 120.6, 112.9, 111.0, 110.8, 95.6, 88.3, 55.7, 54.3. -3.3.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{31}$H$_{26}$NaO$_2$Si, 481.1594; found 481.1584.

HPLC: Enantiomeric excess was determined by HPLC with a Phenomenex column (hexanes: 2-propanol = 99.6:0.4, 0.8 mL/min, 330 nm, 95.5:4.5 er); major enantiomer $t_r$ = 26.2 min, minor enantiomer $t_r$ = 28.7 min.

(S)-1-methyl-2-(m-tolyl)-1-(2-(m-tolylethynyl)phenyl)-1H-benzo[b]silole (2m)

The mobile phase for flash chromatography: hexane. Yellow oil. (46.9 mg, 55%).

Optical rotation: $[\alpha]_D^{25} = +272.7$ (c = 0.99, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 (d, $J = 7.0$ Hz, 1H), 7.70 (s, 1H), 7.58 (d, $J = 7.6$ Hz, 1H), 7.47 – 7.41 (m, 2H), 7.37 – 7.32 (m, 4H), 7.30 – 7.22 (m, 4H), 7.19 – 7.12 (m, 3H), 7.06 (d, $J = 7.5$ Hz, 1H), 2.36 (s, 3H), 2.34 (s, 3H), 0.98 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.3, 143.7, 142.4, 138.9, 138.4, 138.3, 137.8, 137.5, 135.7, 132.9, 132.8, 132.2, 130.3, 129.8, 129.5, 129.5, 128.5, 128.5, 128.2, 127.9, 127.5, 127.1, 124.7, 124.6, 123.2, 92.5, 91.1, 21.7, 21.4, -3.4.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{31}$H$_{26}$NaSi, 449.1696; found 449.1685.
HPLC: Enantiomeric excess was determined by HPLC with a Chiralpak IA column (hexanes: 2-propanol = 99.5:0.5, 0.6 mL/min, 330 nm, 92.0:8.0 er); major enantiomer \( t_r = 26.0 \) min, minor enantiomer \( t_r = 27.8 \) min.

\((R)\)-2-(2-methoxyphenyl)-1-(2-((2-methoxyphenyl)ethynyl)-5-methylphenyl)-1,6-dimethyl-1H-benzo[b]silole (2n)

The mobile phase for flash chromatography: hexane/ethyl acetate = 100:1. Yellow oil. (58.3 mg, 60%).

**Optical rotation:** \([\alpha]_D^{25} = +357.1 \) (c = 1.33, CHCl\(_3\)).

\(^1\text{H NMR (400 MHz, CDCl}_3\) \( \delta \) 7.82 – 7.65 (m, 3H), 7.42 (d, \( J = 8.1 \) Hz, 2H), 7.24 (td, \( J = 8.3, 1.7 \) Hz, 1H), 7.19 – 7.10 (m, 1H), 7.07 (d, \( J = 7.6 \) Hz, 2H), 6.98 (ddd, \( J = 6.7, 4.3, 1.1 \) Hz, 2H), 6.93 – 6.79 (m, 3H), 6.79 – 6.68 (m, 1H), 3.79 (s, 3H), 3.38 (s, 3H), 2.15 (s, 3H), 2.05 (s, 3H), 0.84 (s, 3H).

\(^{13}\text{C NMR (100 MHz, CDCl}_3\) \( \delta \) 160.1, 156.3, 145.6, 142.7, 140.6, 139.3, 137.1, 136.6, 136.4, 135.4, 133.7, 133.5, 132.7, 130.2, 129.7, 129.6, 128.2, 128.1, 126.1, 125.7, 124.0, 120.9, 120.6, 113.1, 110.9, 110.7, 95.9, 87.6, 55.7, 54.3, 21.6, -3.2.

**HRMS (ESI-TOF) m/z:** [M+Na]+ Calcd for C\(_{37}\)H\(_{38}\)NaSi, 509.1907; found 509.1899.

HPLC: Enantiomeric excess was determined by HPLC with a Phenomenex column (hexanes: 2-propanol = 99.5:0.5, 0.8 mL/min, 330 nm, 92.2:5.8 er); major enantiomer \( t_r = 17.3 \) min, minor enantiomer \( t_r = 20.0 \) min.
(S)-1,5-dimethyl-1-(4-methyl-2-(phenylethynyl)phenyl)-2-phenyl-1H-benzo[b]silole (2o)

The mobile phase for flash chromatography: hexane. Yellow oil. (41.7 mg, 49%).

**Optical rotation:** $[\alpha]^{25}_{D} = +201.6$ (c = 0.65, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J$ = 7.2 Hz, 1H), 7.66 (s, 1H), 7.57 (d, $J$ = 7.3 Hz, 2H), 7.50 (dd, $J$ = 6.6, 3.0 Hz, 2H), 7.43 (s, 1H), 7.36 (dd, $J$ = 6.3, 3.4 Hz, 4H), 7.34 – 7.30 (m, 2H), 7.23 (s, 1H), 7.11 (s, 1H), 6.99 (t, $J$ = 7.3 Hz, 2H), 2.31 (d, $J$ = 4.3 Hz, 6H), 0.94 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.6, 144.0, 142.4, 140.3, 139.9, 139.1, 135.8, 134.4, 134.1, 133.5, 132.8, 131.6, 129.3, 128.9, 128.9, 128.5, 128.5, 127.9, 127.2, 127.1, 125.7, 123.5, 91.9, 91.5, 21.7, 21.3, -3.3.

**HRMS (ESI-TOF) m/z:** [M+H]$^+$ Calcd for C$_{31}$H$_{27}$Si, 427.1877; found 427.1884.

**HPLC:** Enantiomeric excess was determined by HPLC with a Chiralpak IA column (hexanes: 2-propanol = 99.5:0.5, 0.5 mL/min, 330 nm, 97.3:2.7 er); major enantiomer $t_r$ = 18.4 min, minor enantiomer $t_r$ = 21.9 min.

(R)-1-ethyl-6-methyl-1-(5-methyl-2-((4-propylphenyl)ethynyl)phenyl)-2-(4-propylphenyl)-1H-benzo[b]silole (2p)

The mobile phase for flash chromatography: hexane. Yellow oil. (42.0 mg, 41%).

**Optical rotation:** $[\alpha]^{25}_{D} = +97.8$ (c = 0.67, CHCl$_3$).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J = 14.6$ Hz, 1H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.21 – 7.17 (m, 1H), 7.15 (s, 1H), 7.06 (ddd, $J = 15.3, 10.1, 4.2$ Hz, 6H), 6.97 – 6.91 (m, 1H), 6.88 – 6.81 (m, 1H), 2.57 – 2.45 (m, 4H), 2.16 (s, 3H), 2.10 (s, 2H), 1.56 (dd, $J = 15.9, 8.0$ Hz, 4H), 1.32 (dd, $J = 15.1, 7.8$ Hz, 2H), 0.90 – 0.83 (m, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.4, 143.2, 142.2, 141.6, 141.5, 137.6, 136.9, 136.9, 136.8, 136.7, 136.4, 134.2, 132.8, 131.5, 130.7, 130.6, 128.9, 128.8, 128.7, 128.6, 127.0, 126.6, 126.6, 124.2, 120.9, 91.6, 91.1, 38.1, 37.9, 24.6, 24.5, 21.6, 21.5, 14.0, 13.9, 7.7, 5.0, 1.2.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{38}$H$_{40}$NaSi, 547.2791; found 547.2781.

HPLC: Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (hexanes: 2-propanol = 99.5:0.5, 0.6 mL/min, 330 nm, 97.9:2.1 er); major enantiomer $t_r = 14.8$ min, minor enantiomer $t_r = 20.8$ min.

\begin{center}
\includegraphics[width=0.2\textwidth]{image.png}
\end{center}

(R)-2-cyclopropyl-1-(2-(cyclopropylethynyl)-5-methylphenyl)-1,6-dimethyl-1H-benzo[b]silole (2q)

The mobile phase for flash chromatography: hexane. Yellow oil. (31.9 mg, 45%).

Optical rotation: $[\alpha]_D^{25} = +162.2$ (c = 0.33, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (s, 1H), 7.28 (dd, $J = 1.2$, 0.5 Hz, 1H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.16 (s, 1H), 7.03 – 6.97 (m, 2H), 6.94 (d, $J = 7.6$ Hz, 1H), 6.84 (s, 1H), 2.22 (s, 3H), 2.19 (s, 3H), 1.79 – 1.69 (m, 1H), 1.42 – 1.30 (m, 1H), 0.81 – 0.69 (m, 6H), 0.61 (s, 3H), 0.59 – 0.43 (m, 2H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.2, 147.0, 140.3, 137.2, 137.1, 136.8, 135.9, 135.3, 133.5, 132.6, 130.5, 130.4, 127.0, 122.8, 95.3, 21.6, 21.5, 14.4, 8.6, 8.2, 8.1, 1.2, 0.6, -4.0.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{25}$H$_{26}$NaSi, 377.1696; found 377.1689.

HPLC: Enantiomeric excess was determined by HPLC with a Phenomenex column (hexanes: 2-propanol = 99.5:0.5, 0.6 mL/min, 330 nm, 92.0:8.0 er); major enantiomer $t_r = 7.8$ min, minor enantiomer $t_r = 8.4$ min.

![Chemical structure](image)

(R)-1-methyl-2-(thiophen-2-yl)-1-(2-(thiophen-2-ylylthynyl)phenyl)-1H-benzo[b]silole (2r)

The mobile phase for flash chromatography: hexane. colorless solid. (61.7 mg, 75%).

Optical rotation: $[\alpha]_{D}^{25} = +66.5$ (c = 0.33, CHCl$_3$ ). mp 143.5-146.4 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J = 7.0$ Hz, 1H), 7.47 (d, $J = 7.6$ Hz, 1H), 7.42 (d, $J = 5.8$ Hz, 2H), 7.26 – 7.14 (m, 5H), 7.12 – 7.09 (m, 2H), 7.04 (d, $J = 0.7$ Hz, 1H), 6.93 (dd, $J = 5.0$, 3.7 Hz, 1H), 6.90 – 6.83 (m, 2H), 0.84 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.1, 144.1, 141.3, 137.0, 136.8, 135.7, 133.0, 132.4, 132.2, 130.5, 130.0, 129.0, 128.1, 127.9, 127.8, 127.4, 127.1, 126.7, 124.6, 124.5, 123.3, 94.9, 85.9, -3.8.

HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{25}$H$_{16}$S$_2$Si, 411.0692; found 411.0678.

HPLC: Enantiomeric excess was determined by HPLC with a Phenomenex column (hexanes: 2-propanol = 99.5:0.5, 0.6 mL/min, 330 nm, 93.6:6.4 er); major enantiomer $t_r = 17.9$ min, minor enantiomer $t_r = 26.1$ min.
(R)-2-(2-methoxyphenyl)-1-(2-((2-methoxyphenyl)ethynyl)phenyl)-1-methyl-1H-benzo[b]silole (2s)

The mobile phase for flash chromatography: hexane/ethyl acetate = 100:1. Yellow oil (20.7 mg, 30%).

**Optical rotation:** $[\alpha]_{D}^{25} = +117.9$ (c = 0.67, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 7.0$ Hz, 1H), 7.60 (s, 1H), 7.51 (d, $J = 7.4$ Hz, 1H), 7.42 – 7.37 (m, 1H), 7.22 (ddd, $J = 20.7, 10.7, 6.3, 2.1$ Hz, 5H), 7.14 – 7.00 (m, 5H), 6.96 – 6.92 (m, 1H), 6.86 – 6.80 (m, 1H), 6.73 (dd, $J = 8.1, 2.0$ Hz, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 0.89 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.0, 159.5, 149.1, 143.5, 142.9, 140.4, 137.7, 137.4, 135.8, 132.9, 132.8, 130.3, 129.9, 129.8, 129.6, 129.3, 128.0, 127.3, 124.7, 124.3, 124.2, 120.1, 116.5, 115.1, 113.0, 112.2, 92.3, 91.1, 55.4, 55.3, -3.5.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{31}$H$_{26}$NaO$_2$Si, 481.1594; found 481.1609.

**HPLC:** Enantiomeric excess was determined by HPLC with a Phenomenex column (hexanes: 2-propanol = 99.3:0.7, 0.7 mL/min, 330 nm, 97.2:2.8 er); major enantiomer $t_r = 21.3$ min, minor enantiomer $t_r = 24.2$ min.
(R)-2-cyclopropyl-1-(2-(cyclopropylethynyl)phenyl)-1-methyl-1H-benzo[b]silole (2t)

The mobile phase for flash chromatography: hexane. Yellow oil. (44.4 mg, 68%).

**Optical rotation:** $[\alpha]_{D}^{25} = +77.8$ (c = 1.33, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 (d, $J$ = 6.9 Hz, 1H), 7.46 (dd, $J$ = 7.4, 0.8 Hz, 1H), 7.33 (d, $J$ = 7.6 Hz, 1H), 7.19 (tdd, $J$ = 8.1, 3.7, 1.6 Hz, 2H), 7.10 (td, $J$ = 7.4, 1.1 Hz, 1H), 7.03 (t, $J$ = 8.0 Hz, 2H), 6.86 (s, 1H), 1.82 – 1.69 (m, 1H), 1.35 (tt, $J$ = 8.2, 5.1 Hz, 1H), 0.80 – 0.69 (m, 6H), 0.64 – 0.61 (m, 3H), 0.59 (dd, $J$ = 8.9, 4.0 Hz, 1H), 0.50 – 0.44 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.6, 148.7, 139.4, 136.1, 135.8, 134.2, 131.7, 131.5, 129.2, 129.1, 128.7, 126.0, 124.9, 122.1, 95.3, 13.5, 7.9, 7.3, 7.2, -0.5, -5.2.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{23}$H$_{22}$NaSi, 349.1383; found 349.1369.

**HPLC:** Enantiomeric excess was determined by HPLC with a Phenomenex column (hexanes: 2-propanol = 99.5:0.5, 0.6 mL/min, 330 nm, 93.2:6.8 $er$); major enantiomer $t_r$ = 10.9 min, minor enantiomer $t_r$ = 15.8 min.