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DOI
10.1007/s11244-018-0967-5

Publication date
2018

Document Version
Final published version

Published in
Topics in Catalysis

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Citation for published version (APA):
van der Boon, L. J. P., Fuku-en, S., Slootweg, J. C., Lammertsma, K., & Ehlers, A. W. (2018). Toward Asymmetric Synthesis of Pentaorganosilicates. Topics in Catalysis, 61(7-8), 674-684. https://doi.org/10.1007/s11244-018-0967-5
Toward Asymmetric Synthesis of Pentaorganosilicates

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Published online: 20 April 2018 © The Author(s) 2018

Abstract
Introducing chiral silicon centers was explored for the asymmetric Rh-catalyzed cyclization of dihydrosilanes to enantiomerically enriched spirosilanes as targets to enable access to enantio-stable pentacoordinate silicates. The steric rigidity required in such systems demands the presence of two naphthyl or benzo[b]thiophene groups. The synthetic approach to the expanded spirosilanes extends Takai’s method (Kuninobu et al. in Angew Chem Int Ed 52(5):1520–1522, 2013) for the synthesis of spirosilabifluorenes in which both a Si–H and a C–H bond of a dihydrosilane are activated by a rhodium catalyst. The expanded dihydrosilanes were obtained from halogenated aromatic precursors. Their asymmetric cyclization to the spirosilanes were conducted with [Rh(cod)Cl]2 in the presence of the chiral bidentate phosphane ligands (R)-BINAP, (R)-MeO-BIPHEP, and (R)-SEGPHOS, including derivatives with P-(3,5-t-Bu-4-MeO)-phenyl (DTBM) groups. The highest enantiomeric excess of 84% was obtained for 11,11′-spirobi[benzo[b]-naphtho[2,1-d]silole] with the DTBM-SEGPHOS ligand.

Keywords Asymmetric catalysis · Silicates · Spirosilanes

1 Introduction
Chirality is a cornerstone in chemistry, crucial to live, and increasingly important to materials science. The synthesis of chiral organic molecules has become commonplace [1]. Simple examples of the numerous ones available are Knowles’s synthesis of L-DOPA and Sharpless’ asymmetric epoxidation resulting in compounds of high enantiomeric excess (ee) [2, 3]. Common approaches to introduce chirality are nucleophilic substitution of pro-chiral systems and asymmetric catalysis [4]. Once a chiral carbon center is formed, it retains its chirality in the absence of competing associative/dissociative reactions.

In strong contrast to compounds having chiral carbon centers, those with a chiral silicon center are not found in nature. Kipping reported the first optically active silicon compounds early in the previous century [5], and the first examples of chiral resolution on a practical scale were presented much later [6]. Extensive pioneering work on stereospecific reactions towards chiral silicon compounds was done by the group of Sommer [7]. During the same period, Corriu and coworkers laid the foundation of much that we know today about stereoselectivity in substitution reactions on silicon [8]. It is evident that chiral silicon compounds can only be acquired synthetically, some of the more recent methods towards these compounds are excellently reviewed elsewhere [9–11].

Chirality in tetracoordinate silicon derivatives has become a topic of recent interest and is driven by asymmetric catalysis using rhodium complexes carrying chiral diphosphate or diene ligands [12]. Examples include chiral silicon-ferrocenes by enantioselective activation of C–H bonds, enantioselective 1,4-silicon shifts from aryl to alkyl groups, and the chiral silylation using iridium complexes [13–15]. Here, we describe our synthetic approach toward chiral silanes for which we have a need in our program on chiral pentacoordinate silicon compounds.
It is important to recognize that the synthesis of enantiostable tetracoordinate silicon compounds is inherently more challenging than their carbon counterparts due to the tendency to form pentacoordinate intermediates or products, which readily undergo racemization [16]. The bigger atomic radius of silicon stabilizes such species, termed silicates, whereas the pentacoordinate carbon ones are instead transition structures [17]. Before proceeding with our synthesis on tetracoordinate silicon compounds, it is relevant to highlight the potential involvement and characteristics of silicates.

Pentacoordinate Si-intermediates are well documented for SN2 reactions. Racemization at the Si-center occurs readily via Berry pseudorotations (BPR),[18–20] causing isomerization between different trigonal bipyramid conformations via a low energy square pyramidal transition state. This change of geometry underlies the racemization process and can only be inhibited by increasing the barriers for isomerization. Recently, Strohman’s group provided such an example of selective inhibition for an SN2-type substitution at a prochiral silicon center [21]. They were able to obtain a chiral compound by selectively hampering one of the BPRs of the five coordinate Si-intermediate.

Earlier, we have shown computationally how to impede Berry pseudorotations to obtain chiral, enantiostable pentaorganosilicate salts and presented a synthetic method to accomplish this [22]. Silicate anions with five carbon substituents are usually short-lived species, observable only by mass spectrometry or low temperature NMR, but their stabilization increases substantially when four of the five Si–C bonds are formed by two bidentate ligands, such as biphenyls [23–25]. Such stable pentaorganosilicates, but with larger aromatic ligands, prevent formation of a square pyramidal conformation, thus hampering the BPR and preventing racemization. NMR spectroscopy revealed for ethyl, bis([2] naphthylpyrrol) silicate (Fig. 1) a BPR barrier of over 21 kcal mol⁻¹ and showed two diastereotopic ethylene hydrogens [22]. However, demonstrating unequivocally the inhibition of BPRs also demands an enantiomERICally pure silicate to be isolable. It is in this context that we pursue the synthesis of chiral silanes, because these are the starting point to generate silicates. Therefore, we seek an enantioselective synthetic approach to symmetrical pentaorganosilicates with large aromatic groups.

Conventionally, spiroxilanes are obtained from the reaction of SiCl4 with a dilithiated biaryl system generated from its dihalide (Scheme 1) [22]. Obtaining the chiral products than requires separation into the enantiomers by, e.g., chiral HPLC [23]. We envisioned that it might be advantageous to explore an enantioselective synthesis. Our approach is based on recent work by Takai and coworkers, who (a) reported on the synthesis of 9H-9sila-fluorennes using a rhodium catalyst for Si–H and C–H bond activation [26] and (b) showed that spiroxilanes could be obtained in high enantiomeric excess from dihydrosilanes on using a Rh-catalyst with a chiral (R)-BINAP diphosphane ligand (Scheme 2) [27]. The mechanism proposed for the reaction involves sequential oxidative additions of the Rh-catalyst at an aromatic C–H bond and a Si–H bond, followed by H₂-elimination and reductive elimination to a monohydrosilane, which undergoes the same catalytic cycle to give the spiroxilane [28].

We sought to expand the scope of the chiral synthesis by using sterically more demanding substituents than...
the biphenyl group to obtain in high enantiomeric excess ‘bisligated’ spiroisilanes carrying naphthalene or benzo[b] thiophene groups (Scheme 3). Such systems would ideally confirm the ability to control the chirality of silicates and potentially reduce racemization of chiral silanes by the contaminating presences of silicates. At the same time, we realized that the increased steric bulk might affect the cyclization reaction unfavorably.

Derivatives of the larger aromatic substituents 2-phenylnaphthalene and 2-phenylbenzo[b]thiophene that were examined in this study are shown in Scheme 4. The selection of the two aromatic cores (naphthalene and benzo[b] thiophene) was derived from silicates that have been shown to be configurationally rigid. Double ring closure of dihydrosilanes 3a with two 2-phenylnaphthyl groups and 3c with two 2-phenylbenzothio[b]thiophenyl groups will result into the two targeted spiroisilanes. Additional t-butyl groups increase the sterics of 3d. Dihydrosilanes 3b and 3e were selected to resemble more the noted examples where the silicon atom is substituted on the phenyl ring. The methoxy-group on 3b would also hinder unwanted reactions of the rhodium catalyst with the 3-CH bond of the naphthalene ring.

Scheme 3 Asymmetric route towards optically pure pentaorganosilicates

Scheme 4 Dihydrosilanes containing bulky ring systems

2 Results and Discussion

To explore the increased size of the substituents on the synthesis of dihydrosilanes and the subsequent enantioselective cyclization to spiroisilanes by using the procedure of Takai and coworkers [23], we felt it important to be able to reproduce their result as benchmark.

The synthesis of the dihydrosilanes with larger aromatic groups proved to be more difficult than those with the biphenyl groups and could only be accomplished by introducing a silyl group on the larger rings, i.e., the naphthalene and benzo[b]thiophene groups. The most productive synthetic approach was to lithiate the bromo precursors with either t-BuLi or iPr-MgCl·LiCl, followed by treatment with SiCl4 to obtain the dichlorosilane and treatment with LiAlH4 to form the dihydrosilanes, which could only be obtained in poor yields. Illustrative is the synthesis of silane 3a from 1-bromo-2-phenylnapthalene with a yield of only 4% with trihydrosilane 6 as major isolated product in 33% yield (Scheme 5). Evidently, steric congestion plays a significant role and hampers the second nucleophilic addition at SiCl4. The naphthyl crowding effect is even more pronounced on introducing a silyl group at the phenyl group, as in 3c, which we were unable to obtain. For 2-phenylbenzo[b]thiophene the synthetic access proved to be more favorable than for 2-phenylnaphthalene. (Scheme 6). Thus, 3c could be prepared in 53% yield by reacting the Grignard reagent of bromide 7c with subsequently HSiCl3 and LiAlH4. The product showed the expected Si–H interaction using 1H-NMR spectroscopy. Steric factors do have an influence on the accessibility of the benzo-[b]thiophene group, which became evident.
In contrast to 2-phenylnaphthalene access silylation of the phenyl substituent ring of 2-phenylbenzo[b]thiophene (8) proved feasible, giving 3e, be it in only 8% of impure material, besides trihydrosilane 9 as major product (Scheme 7). This again illustrates that steric congestion hampers the second nucleophilic addition at silicon.

### 2.1 Asymmetric Catalysis

To assess the rhodium catalyzed asymmetric synthesis of dihydrosilanes, we re-examined the intramolecular cyclization of dihydrosilane 1a using (R)-BINAP and [Rh(cod)Cl]₂ to obtain the 2,2′-dimethoxy-9,9′-spiro-9-silabifluorene 2a in 84% yield and 79% ee (Table 1), which is in excellent agreement with the reported 81% ee. We note that lower ee’s were obtained if the reaction was not executed under inert conditions and degassed solvents.

The intramolecular double cyclization of the bulkier dihydrosilanes 3a and 3c using (R)-BINAP and [Rh(cod)Cl]₂ yielded the corresponding spirosilanes 4a (< 10%) and 4c (8.1%) in 52 and 54% ee, respectively. Whereas we had expected higher ee’s, anticipating that steric congesting would positively influence the distinction between the formation of both enantiomers [29], the ee’s were, in fact,
lower than that obtained for 2a. This effect must be due to the larger ring substituents, which apparently reduces the enantioselectivity. Also the fact that minor impurities were obtained, which could be removed by washing with n-pentane to significantly reduce the yields (e.g., to 8.1% for 4c), is also indicative for the steric sensitivity for cyclization.

In searching to improve the enantioselectivity, we explored other chiral ligands for the Rh-catalyzed bicyclization of 3c (Table 1). Formation of spirosilane 4c from 3c using the chiral methoxy-phenyl ligand MeO-BIPHEP and the bulkier 3,5-t-Bu-4-MeO-MeO-BIPHEP gave still lower ee's of 45% and even 13%, respectively. Apparently, the bulkier phenyl rings around the coordinating phosphorus ligand reduce the enantioselectivity of the reaction. It is than most intriguing that we found a much higher ee of 84% on using the quite large DTBM-SEGPHOS ligand, albeit with an expected lower yield of 31%. Clearly, with this bulky chiral ligand the transfer of chirality is effectively transferred in the Rh-catalyzed cyclization reaction. On removing the tBu and OMe substituents of the ligand's two P-phenyl groups, i.e., SEGPHOS, the steric bulk of the ligand reduces and so does the ee to 27%, while also reducing the yield (to 24%). Evidently, the bidentate ligand systems BIPHEP and SEGPHOS have significant effects on the enantioselective cyclization, whereas they merely differ in carrying OMe versus 1,3-dioxole groups.

3 Conclusion

This research has expanded the scope of the asymmetric Rh-catalyzed cyclization of dihydrosilanes to spirosilanes with more bulky ring systems. The successful synthesis of the naphthalene and benzo[b]thiophene silanes with more bulky ring systems. The successful Rh-catalyzed cyclization of dihydrosilanes to spiro-silicates. Our survey also reveals limitations such as the synthetic access of the required dihydrosilane precursors where the increased steric congestion has a debilitating effect, inhibiting the second nucleophilic substitution at silicon, thereby rendering trihydrosilanes; formation of byproducts also hampers product purification.

4 Experimental Section

General

All reagents were bought from Sigma–Aldrich and used as received unless specified otherwise. Pyridine was dried using activated molecular sieves (3 Å). Tetrahydrofuran (THF) was distilled subsequently from LiAlH4 and sodium/potassium alloy and diethyl ether from sodium/potassium alloy. n-Butyllithium was purchased as 1.6 M solutions in hexanes. Tetrachlorosilane was distilled and refluxed before use to remove HCl. Syntheses were performed using standard Schlenk techniques. NMR spectra were recorded on a Bruker Avance 400 (1H, 13C, 29Si, 2D spectra). NMR chemical shifts are internally referenced to the solvent for 1H (CHCl3: 7.26, THF: 3.58, CH2Cl2: 5.32) and 13C (CHCl3: 77.16, THF: 67.58, CH2Cl2: 53.84), and externally for 29Si to TMS. Melting points were measured on samples in sealed capillaries and are uncorrected. HR-ESI-MS measurements of silicates were measured on a Varian IonSpec FT-ICR mass spectrometer, for LR-MS a Bruker microOTF system was used. Separation of enantiomers was performed on a Chiralpak IA column.

4.1 Synthesis of 2-Bromo-4′-methoxy-biphenyl 10

[27]

\[
\text{OMe}
\]

\(\text{t-BuLi} \ (1.6 \text{ M in pentane, 4.0 mL, 6.4 mmol, 2.1 eq.})\) was added to a solution of p-methoxyiodobenzene (936 mg, 4.0 mmol, 1.3 eq.) in THF (5.0 mL) at −78 °C. After 1 h, a solution of ZnBr2 (1.1 g, 4.8 mmol, 1.5 eq.) was added at −78 °C. After stirring at room temperature for 30 min, a solution of Pd2(dba)3 (100 mg, 0.109 mmol, 3.5 mol%), PPh3 (173 mg, 0.660 mmol, 21 mol%), and ortho-iodobromobenzene (0.40 mL, 3.11 mmol, 1.00 eq.) in THF (3.0 mL) was added. Stirring was maintained overnight. The reaction was quenched by NH4Cl aq., and the mixture was extracted into Et2O. The organic layer was dried over MgSO4 and concentrated under reduced pressure. Purification by column chromatography (silica gel, DCM: c-Hex = 1:5) afforded 2-bromo-4′-methoxy-biphenyl 10 (287 mg, 1.09 mmol, 35%) as a white solid. 1H NMR (CDCl3, 400.13 MHz): δ 7.65 (d, \(J(H,H)=8.0\) Hz, 1H), 7.36–7.31 (m, 4H), 7.19–7.15 (m, 1H), 6.96 (d, \(J(H,H)=8.8\) Hz, 1H), 3.86 (s, 3H).
4.2 Synthesis of Bis(4′-methoxybiphenyl-2-yl)silane 1a [27]

2.2 mmol, 2.0 eq.) was added to a solution of 2-bromo-4′-methoxybiphenyl 10 (287 mg, 1.09 mmol, 1.0 eq.) in Et₂O (5.0 mL) at −78 °C and the mixture was stirred for 1 h at r.t.. The pale brown solution was added to a solution of tetrachlorosilane (0.06 mL, 0.5 mmol, 0.46 eq.) in Et₂O (0.5 mL) at −78 °C and stirred for 3 h at r.t.. The resulting pale orange suspension was added to a solution of LiAlH₄ (1 M in Et₂O, 2.2 mL, 2.2 mmol, 2.0 eq.) at 0 °C and stirred overnight at r.t.. The orange suspension was quenched with H₂O and 10% aq. NaOH, filtered through Celite, extracted into Et₂O and dried over MgSO₄. After removing solvents, purification by column chromatography (silica gel, c-Hex:EtOAc:NEt₃ = 50:1:0.1) afforded bis(4′-methoxybiphenyl-2-yl)silane 1a (49 mg, 0.12 mmol, 11%) as a white solid. 1H NMR (CDCl₃, 250 MHz): δ 7.42–7.34 (m, 4H), 7.26–7.17 (m, 4H), 7.08 (d, 3J(H,H) = 8.8 Hz, 4H), 6.78 (d, 3J(H,H) = 8.8 Hz, 4H), 4.59 (s, 2H), 3.82 (s, 6H).

4.3 Synthesis of 2,2′-Dimethoxy-9,9′-spiro-9-silabifluorene 2a [27]

A solution of [Rh(cod)Cl]₂ (5 mg, 0.01 mmol, 9.8 mol%) and (R)-BINAP (16 mg, 0.026 mmol, 25 mol%) in 1,4-dioxane (2.0 mL) was stirred for 30 min at r.t.. A portion of the red mixture (0.1 mL) was transferred to a solution of bis(4′-methoxybiphenyl-2-yl)silane 1a (41 mg, 0.10 mmol, 1.0 eq.) in a separate Schlenk vessel, and heated at 135 °C for 3 h. Afterwards, solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, c-Hex:EtOAc:NEt₃ = 50:1:0.1) to afford 2,2′-dimethoxy-9,9′-spiro-9-silabifluorene 2a (33 mg, 0.084 mmol, 84%) as a white solid. 1H NMR (CDCl₃, 250 MHz): δ 7.46–7.37 (m, 4H), 7.29–7.17 (m, 4H), 7.08 (d, 3J(H,H) = 8.8 Hz, 4H), 6.78 (d, 3J(H,H) = 8.8 Hz, 4H), 4.59 (s, 2H), 3.82 (s, 6H).

4.4 Synthesis of 1-Bromonaphthalen-2-yl trifluoromethanesulfonate 11 [30]

Br OTf Pyridine (2.8 mL, 35 mmol, 1.2 eq.) was added to a mixture of 1-bromonaphthalen-2-ol (6.7 g, 30 mmol, 1.0 eq.) in dichloromethane (40 mL) at −10 °C. Triflic anhydride (5.6 mL, 33 mmol, 1.1 eq.) was gradually added to the reaction mixture and stirred for 30 min at −10 °C. After stirring at r.t. for 2 h, water was added to the mixture at −10 °C. The mixture was extracted into dichloromethane, the organic layer was washed with 1M HCl and brine, then dried over MgSO₄ and filtered. Purification by column chromatography (silica gel, c-Hex:EtOAc = 50:1) afforded 1-bromonaphthalen-2-yl trifluoromethanesulfonate 11 (9.17 g, 0.0258 mmol, 85%) as a white solid. 1H NMR (CDCl₃, 250 MHz): δ 8.32 (d, 3J(H,H) = 8.3 Hz, 1H), 7.70 (d, 3J(H,H) = 8.5 Hz, 2H), 7.74–7.59 (m, 2H), 7.44 (d, 3J(H,H) = 9.0 Hz, 1H).

4.5 Synthesis of 1-Bromo-2-phenylnaphthalene 5 [31]

A solution of PhMgBr (3 M in Et₂O, 10 mL, 29 mmol, 1.2 eq.) was added to a mixture of 1-bromonaphthalen-2-yl trifluoromethanesulfonate 11 (8.6 g, 24 mmol, 1.0 eq.), lithium bromide (2.1 g, 13 mmol, 0.54 eq.), Pd₂(dba)₃ (334 mg, 0.365 mmol, 1.5 mol%) and 1,3-(diphenylphosphino)propane (301 mg, 0.730 mmol, 3.0 mol%) at 0 °C. After stirring the brown solution overnight at r.t., NH₄Cl aq. was added at 0 °C. The organic layer was separated and the aqueous layer was extracted into EtOAc. The combined organic layers were dried over MgSO₄, filtered and concentrated in vacuo. Purification by column chromatography (silica gel, c-Hex:CH₂Cl₂ = 3:1) afforded 1-bromo-2-phenylnaphthalene (5.6 g, 20 mmol, 81%) as a white solid. 1H NMR (CDCl₃, 250 MHz): δ 8.43 (d, 3J(H,H) = 8.5 Hz, 1H), 7.90–7.84 (m, 2H), 7.68–7.41 (m, 8H).

4.6 Reaction of (2-Phenylnaphthalen-1-yl)lithium with 0.5 Equivalents of SiCl₄

n-BuLi (1.6 M in hexanes, 1.6 mL, 2.6 mmol, 1.1 eq.) was added to a solution
of 1-bromo-2-phenyl-naphthalene 5 (700 mg, 2.47 mmol, 1.0 eq.) in Et₂O (10 mL) at −78 °C and the mixture was stirred for 1 h at −78 °C. The pale yellow suspension was added to a solution of tetrachlorosilane (0.14 mL, 1.2 mmol, 0.49 eq.) in Et₂O (6.0 mL) at −78 °C and stirred for 3 h at r.t.. The reaction mixture was added to a solution of LiAlH₄ (1 M in Et₂O, 2.5 mL, 2.5 mmol, 1.0 eq.) at 0 °C and stirred for 7 h at r.t.. The resulting yellow suspension was quenched with H₂O and 10% aq. NaOH, filtered through Celite, extracted into Et₂O, dried over MgSO₄ and filtered. After removing solvents in vacuo, purification by column chromatography (silica gel, hexane/gluco= 40:1) afforded bis(2-phenyl-naphthalen-1-yl)silane 3a (19 mg, 0.044 mmol, 4%) as a white solid and (2-phenyl-naphthalen-1yl)silane 6 (116 mg, 0.410 mmol, 33%) as a colorless oil. Data of bis(2-phenyl-naphthalen-1-yl)silane: 1H NMR (CDCl₃, 400.13 MHz): δ 8.00 (d, 3J(H,H) = 8.5 Hz, 2H), 8.13 (d, 3J(H,H) = 7.6 Hz, 2H; H12), 7.81 (d, 3J(H,H) = 8.2 Hz, 2H; H6), 7.60 (t, 3J(H,H) = 7.7 Hz, 2H; 13H), 7.43 (d, 3J(H,H) = 6.9 Hz, 2H; H15), 7.29-7.23 (m, 4H; H7 and H14), 7.16 (d, 3J(H,H) = 8.2 Hz, 2H; H9), 7.06 (t, 3J(H,H) = 7.6 Hz, 2H; H8); 13C{1H} NMR (125.78 MHz, CDCl₃): δ 150.42 (C11), 149.81 (C2), 137.47 (C10), 136.24 (C13), 131.90 (C13), 131.40 (C1), 128.88 (C6), 128.66 (C9), 128.55 (C14), 127.43 (C8), 126.23 (C7), 122.09 (C12), 120.43 (C3); 1H-29Si-HMBC NMR (400.13, 79.49 MHz, CDCl₃): δ 145.2 (q), 142.0 (q), 140.4 (q), 138.2 (CH), 130.5 (CH), 130.2 (CH), 129.2 (q), 127.9 (CH), 124.7 (CH), 124.6 (CH), 123.9 (CH), 123.2 (CH), 122.3 (CH). HR-MS (FD): calcd for C₃₂H₂₄Si 436.1647, found 436.1638.

4.7 Reaction of (2-Phenyl-naphthalen-1-yl)lithium with 0.9 Equivalents of SiCl₄

![Image of reaction](image)

$t$-BuLi (1.7 M in pentane, 1.2 mL, 2.0 mmol, 2.0 eq.) was added to a solution of 1-bromo-2-phenyl-naphthalene 5 (283 mg, 1.00 mmol, 1.0 eq.) in Et₂O (5.0 mL) at −78 °C, the mixture was stirred for 1 h at −78 °C. The pale yellow suspension was added to a solution of tetrachlorosilane (0.10 mL, 0.87 mmol, 0.87 eq.) in Et₂O (0.5 mL) at −78 °C and stirred overnight at r.t.. The yellow suspension was added to a solution of LiAlH₄ (1 M in Et₂O, 3.0 mL, 3.0 mmol, 3.0 eq.) at 0 °C and stirred for 6 h at r.t.. The mixture was quenched with H₂O and 10% aq. NaOH, filtered through Celite, extracted with Et₂O, dried over MgSO₄ and filtered. After removing solvents in vacuo, purification by column chromatography (silica gel, hexane) afforded (2-phenyl-naphthalen-1-yl) silane 6 (111 mg, 0.474 mmol, 47%) as a colorless oil. 1H NMR (CDCl₃, 400.13 MHz): δ 8.21 (d, 3J(H,H) = 8.4 Hz, 2H), 7.96 (d, 3J(H,H) = 8.4 Hz, 1H), 7.91 (d, 3J(H,H) = 8.4 Hz, 1H), 7.39-7.62 (m, 8H), 4.20 (s, 3H). 13C NMR (CDCl₃, 126 MHz): δ 145.4 (q), 144.2 (q), 138.1 (q), 132.0 (q), 130.4 (CH), 129.6 (CH), 128.9 (CH), 128.3 (CH), 128.2 (CH), 127.9 (CH), 127.6 (CH), 126.8 (CH), 125.8 (CH), 125.1 (q). GC-MS (LR-EI) m/z: calcd for C₁₅H₁₄Si 234.1, found 234.1.

4.8 Synthesis of 11,11′-Spirobi[benzo[b]naphtho[2,1-d]silole] 4a

![Structural diagram](image)

The solution of [Rh(cod)Cl]₂ (2 mg, 0.004 mmol, 17 mol%) and (R)-BINAP (10 mg, 0.016 mmol, 70 mol%) in 1,4-dioxane (0.8 mL) was stirred for 30 min at r.t.. A portion of the red mixture (0.03 mL) was transferred to bis(2-phenyl-naphthalen-1-yl)silane 3a (10 mg, 0.023 mmol, 1.0 eq.), and heated at 135 °C for 3 h. After solvents were removed in vacuo, purification by column chromatography (silica gel, hexane/EtOAc= 50:1) afforded 11,11′-spirobi[benzo[b]naphtho[2,1-d]silole] 4a as a white solid, which was confirmed by 1H NMR measurements. 1H NMR (500.23 MHz, CD₂Cl₂, 296 K): δ 8.21 (d, 3J(H,H) = 8.8 Hz, 2H; 3H), 8.13 (d, 3J(H,H) = 7.6 Hz, 2H; H12), 8.09 (d, 3J(H,H) = 8.5 Hz, 2H; 4H), 7.81 (d, 3J(H,H) = 8.2 Hz, 2H; 6H), 7.60 (t, 3J(H,H) = 7.7 Hz, 2H; 13H), 7.43 (d, 3J(H,H) = 6.9 Hz, 2H; H15), 7.29-7.23 (m, 4H; H7 and H14), 7.16 (d, 3J(H,H) = 8.2 Hz, 2H; H9), 7.06 (t, 3J(H,H) = 7.6 Hz, 2H; H8); 13C{1H} NMR (125.78 MHz, CD₂Cl₂, 296 K): δ 150.42 (C11), 149.81 (C2), 137.47 (C10), 136.24 (C13), 131.90 (C13), 131.40 (C1), 128.88 (C6), 128.66 (C9), 128.55 (C14), 127.43 (C8), 126.23 (C7), 122.09 (C12), 120.43 (C3); 1H-29Si-HMBC NMR (400.13, 79.49 MHz, CD₂Cl₂, 296 K): δ = −8.64; HR-MS (EI): calcd for C₁₅H₁₄Si 342.1334, found 342.1330. Mp 275-277 °C (decomp.). The ee was determined on a Chiracel OD-H column with n-hexane/isopropanol = 90/10, flow = 0.7 mL/min, oven temp. = 40 °C; 52% ee.

4.9 Synthesis of 3-Bromo-2-phenylbenzo[b]thiophene 12 [32]

![Structural diagram](image)

Benz[b]thiophene (9.6 g, 71.5 mmol, 1.0 eq.) was dissolved in DCM (286 mL) and acetic acid (286 mL), to this solution N-bromosuccinimide (31.8 g, 178.8 mmol, 2.5 eq.) was added in small portions over the course of an hour at 0 °C. After 70 min, the ice bath was removed and the mixture was warmed to room temperature. After 9 days of stirring at r.t., the red mixture was quenched with 10% aq. KOH (200 mL), 5% aq. NaHCO₃ (300 mL) and 5% aq. Na₂S₂O₃ (300 mL). The organic phase was dried over MgSO₄, filtered and concentrated in vacuo. Purification by
column chromatography (silica gel, c-Hex) afforded 12 as a white solid (15.4 g, 73%). $^1$H NMR (500.23 MHz, (CD$_2$)$_2$SO, 296 K): $\delta$ 8.23 (d, $^3$J(H,H) = 8.51 Hz, 1H), 8.19 (d, $^3$J(H,H) = 9.14 Hz, 1H), 8.12 (d, $^3$J(H,H) = 7.88 Hz, 1H), 7.81 (t, $^3$J(H,H) = 7.73 Hz, 1H), 7.73 (t, $^3$J(H,H) = 7.57 Hz, 1H), 7.66 (d, $^3$J(H,H) = 9.14 Hz, 1H).

### 4.10 Synthesis of 2-Phenylbenzo[b]thiophene 7c

(4.5 g, 15.3 mmol, 1.0 eq.), phenylboronic acid (1.866 g, 16.5 mmol, 1.0 eq.). Pd(PPh$_3$)$_4$ (0.354 g, 0.306 mmol, 400 mol%) in 1,4-dioxane (1.0 mL) was stirred for 1 h at r.t.. A portion of the red mixture (0.1 mL) was transferred to bis(2-Maisch chiral AM column with $n$-propanol = 95/5, iso-propanol = 95/5, -hexane/iso-pentane = 95/5) and added dropwise at $-78^\circ$C. The product was isolated via column chromatography (silica gel, hexane:EtOAc = 50:1) afforded spirosilane 3c as a white solid (635.8 mg, 0.0051 mmol, 5.1 mol%). $^1$H NMR (500.23 MHz, THF-$d_8$, 294 K): $\delta$ = 7.89 (d, $^3$J(H,H) = 7.5 Hz, 2H, H4), 7.64 (d, $^3$J(H,H) = 8.0 Hz, 2H, H7), 7.52–7.38 (m, 2H, H5), 6.34 (d, $^3$J(H,H) = 7.5 Hz, 2H, H7) 7.34–7.19 (m, 14H, H5, H6, H10, H11, H12), 5.14 (s, 2H, Si–H); $^{13}$C-$^1$H NMR (125.78 MHz, CDCl$_3$, 293 K): $\delta$ 155.0 (C1), 145.1 (C3), 141.0 (C8), 135.2 (C9), 129.8 (C10), 128.5 (C12), 128.1 (C11), 124.7 (C7), 124.5 (CH, C5), 124.2 (CH, C7), 123.5 (C2), 121.8 (C4). $^{29}$Si-HMBC NMR (400.13, 79.49 MHz, CDCl$_3$, 296 K): $\delta$ = −62.3 (Si). HR-MS (FD): calcd for C$_{28}$H$_{20}$S$_2$Si 448.0786, found 448.0788.

### 4.11 Synthesis Bis(2-phenylbenzo[b]thiophen-3-yl) silane 3c

Magnesium (0.28 g, 11.5 mmol, 2.3 eq.) was added to an oven dried reflux setup and dry THF (3 mL) was added. 3-bromo-2-(3,5-dimethylphenyl)benzo[b]thiophene 7c (1.44 g, 5 mmol, 1 eq.) was dissolved in THF (6 mL) and slowly added to the reflux setup. 1,2-dibromoethane (0.02 mL, 0.23 mmol, 0.046 eq.) was then added and the suspension was refluxed at 66 °C for 2.5 h. Trichlorosilane (0.338 g, 2.5 mmol, 0.5 eq.) was dissolved in dry THF (3 mL) in a separate flame dried Schlenk flask and then added to the yellow solution. The mixture was stirred for 15 min at 60 °C. Next, LiAlH$_4$ (1 M in Et$_2$O, 1.56 mL, 3.75 mmol, 0.75 eq.) was added dropwise at $-78^\circ$C and the solution was stirred overnight. The blue clear solution was quenched by adding saturated aqueous Rochelle salt dropwise at $-78^\circ$C. The white suspension was extracted using DCM (3x), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The product was isolated via column chromatography (silica gel, c-Hex:DCM = 100/0 / 90/10 / 50/50) and washed with n-pentane to obtain 3c as a white solid (635.8 mg, 56.8%). $^1$H NMR (500.23 MHz, CDCl$_3$, 293 K): $\delta$ 7.82 (d, $^3$J(H,H) = 7.5 Hz, 2H, H4), 7.64 (d, $^3$J(H,H) = 8.0 Hz, 2H, H7) 7.34–7.19 (m, 14H, H5, H6, H10, H11, H12), 5.14 (s, 2H, Si–H); $^{13}$C-$^1$H NMR (125.78 MHz, CDCl$_3$, 293 K): $\delta$ 155.0 (C1), 145.1 (C3), 141.0 (C8), 135.2 (C9), 129.8 (C10), 128.5 (C12), 128.1 (C11), 124.7 (C7), 124.5 (CH, C5), 124.2 (CH, C7), 123.5 (C2), 121.8 (C4). $^{29}$Si-HMBC NMR (400.13, 79.49 MHz, CDCl$_3$, 296 K): $\delta$ = −62.3 (Si). HR-MS (FD): calcd for C$_{28}$H$_{20}$S$_2$Si 448.0786, found 448.0788.

### 4.12 Synthesis of 10,10'-Spirobi[benzo[b]benzo [4,5] silolo[2,3-d]thiophene] Using (R)-BINAP 4c

A solution of [Rh(cod)Cl]$_2$ (2.5 mg, 0.0051 mmol, 5.1 mol%) and (R)-BINAP (10 mg, 0.016 mmol, 16 mol%) in 1,4-dioxane (1.0 mL) was stirred for 1 h at r.t. A portion of the red mixture (0.1 mL) was transferred to bis(2-phenylbenzo[b]thiophen-3-yl)silane 3c (45 mg, 0.10 mmol, 1.0 eq.), and heated at 135 °C for 3 h. After solvents were removed in vacuo, purification by column chromatography (silica gel, hexane:EtOAC = 50:1) afforded spirosilane 4c (4 mg, 0.008 mmol, 8.8%) after washing with n-pentane as a white solid, which was confirmed by $^1$H NMR measurements. $^1$H NMR (500.23 MHz, THF-$d_8$, 294 K): $\delta$ = 7.89 (d, $^3$J(H,H) = 8.0 Hz, 2H, H4), 7.68 (d, $^3$J(H,H) = 7.5 Hz, 2H, H14), 7.52 (t, $^3$J(H,H) = 7.5 Hz, 2H, H13), 7.39 (d, $^3$J(H,H) = 7.0 Hz, 2H, H11), 7.25–7.21 (m, 6H, H4, H6, H12), 7.11 (t, $^3$J(H,H) = 7.5 Hz, 2H; H15); $^{13}$C-$^1$H NMR (125.78 MHz, CD$_2$Cl$_2$, 296 K): $\delta$ 161.26 (C1), 145.76 (C9), 143.46 (C8), 141.55 (C3), 143.23 (C11), 134.57 (C10), 131.93 (C13), 129.81 (C2), 128.58 (C12), 125.36 (C5), 124.77 (C6), 124.66 (C4), 123.38 (C7), 122.43 (C14); $^1$H-$^{29}$Si-HMBC NMR (400.13, 79.49 MHz, THF-$d_8$, 296 K): $\delta$ = −24.1 (Si); HR-MS (FD): calcd for C$_{28}$H$_{20}$S$_2$Si 448.0776, found 448.0788.
4.13 Synthesis of 10,10′-Spirobi[benzo[b]benzo [4,5] silolo[2,3-d]thiophene] Using (R)-SEGPHEROS 4c

A solution of [Rh(cod)Cl]2 (2.5 mg, 0.0051 mmol, 5.1 mol%) and (R)-SEGPHEROS (7.3 mg, 0.012 mmol, 12 mol%) in 1,4-dioxane (1.0 mL) was stirred for 30 min at r.t. A portion of the red mixture (0.1 mL) was transferred to bis(2-phenylbenzo[4,5]silolo[2,3-d])silane 3c (45 mg, 0.10 mmol, 1.0 eq.) and heated at 135 °C for 3 h. After all volatiles were removed in vacuo, purification by column chromatography (silica gel, hexane:EtOAc = 50:1) afforded the desired spirosilane (10.8 mg, 0.024 mmol, 24.0%) as a white solid, which was confirmed by 1H NMR measurements. 1H NMR (CDCl3, 400.13 MHz): δ 7.90 (d, J(H,H) = 8.0 Hz, 2H), 7.68 (d, J(H,H) = 7.6 Hz, 2H), 7.52 (td, J(H,H) = 7.6 Hz, 2H), 7.42 (d, J(H,H) = 7.2 Hz, 2H), 7.29 (td, J(H,H) = 7.6 Hz, 2H), 7.26–7.22 (m, 4H), 7.14 (td, J(H,H) = 8.0 Hz, 4J(H,H) = 0.8 Hz, 2H). The ee was determined on a Chiral OD-H column with n-hexane/isopropanol = 90/10, flow = 0.7 mL/min, oven temp. = 40 °C; 45% ee.

4.14 Synthesis of 10,10′-Spirobi[benzo[b]benzo [4,5] silolo[2,3-d]thiophene] Using (R)-DTBM-SEGPHEROS 4c

A solution of [Rh(cod)Cl]2 (2.5 mg, 0.0051 mmol, 5.1 mol%) and (R)-DTBM-SEGPHEROS (14 mg, 0.012 mmol, 12 mol%) in 1,4-dioxane (1.0 mL) was stirred for 30 min at r.t. A portion of the red mixture (0.1 mL) was transferred to bis(2-phenylbenzo[4,5]silolo[2,3-d])silane 3c (45 mg, 0.10 mmol, 1.0 eq.) and heated at 135 °C for 3 h. After all volatiles were removed in vacuo, purification by column chromatography (silica gel, c-Hex:EtOAc = 50:1) afforded the desired spirosilane (14 mg, 0.031 mmol, 31.1%) as a white solid, which was confirmed by 1H NMR measurements. 1H NMR (CDCl3, 400.13 MHz): δ 7.90 (d, J(H,H) = 8.0 Hz, 2H), 7.68 (d, J(H,H) = 7.6 Hz, 2H), 7.52 (td, J(H,H) = 7.6 Hz, 2H), 7.42 (d, J(H,H) = 7.2 Hz, 2H), 7.29 (td, J(H,H) = 7.6 Hz, 2H), 7.26–7.22 (m, 4H), 7.14 (td, J(H,H) = 8.0 Hz, 4J(H,H) = 0.8 Hz, 2H). The ee was determined on a Chiral OD-H column with n-hexane/isopropanol = 90/10, flow = 0.7 mL/min, oven temp. = 40 °C; 84% ee.

4.15 Synthesis of 10,10′-Spirobi[benzo[b]benzo [4,5] silolo[2,3-d]thiophene] Using (R)-(+-)-MeO-BIPHEP 4c

A solution of [Rh(cod)Cl]2 (2.5 mg, 0.0051 mmol, 5.1 mol%) and (R)-(+-)-MeO-BIPHEP (14 mg, 0.024 mmol, 24 mol%) in 1,4-dioxane (1.0 mL) was stirred for 30 min at r.t. A portion of the red mixture (0.1 mL) was transferred to bis(2-phenylbenzo[4,5]silolo[2,3-d])silane 3c (45 mg, 0.10 mmol, 1.0 eq.) and heated at 135 °C for 3 h. After solvents were removed in vacuo, purification by column chromatography (silica gel, hexane:EtOAc = 50:1) afforded the desired spirosilane (33 mg, 0.073 mmol, 73.3%) as a white solid, which was confirmed by 1H NMR measurements. 1H NMR (CDCl3, 400.13 MHz): δ 7.90 (d, J(H,H) = 8.0 Hz, 2H), 7.68 (d, J(H,H) = 7.6 Hz, 2H), 7.52 (td, J(H,H) = 7.6 Hz, 2H), 7.42 (d, J(H,H) = 7.2 Hz, 2H), 7.29 (d, J(H,H) = 7.2 Hz, 2H), 7.26–7.22 (m, 4H), 7.14 (td, J(H,H) = 8.0 Hz, 4J(H,H) = 0.8 Hz, 2H). The ee was determined on a Chiral OD-H column with n-hexane/isopropanol = 90/10, flow = 0.7 mL/min, oven temp. = 40 °C; 84% ee.

4.16 Synthesis of 10,10′-Spirobi[benzo[b]benzo [4,5] silolo[2,3-d]thiophene] Using (R)-3,5-tBu-4-MeO-MeO-BIPHEP 4c

A solution of [Rh(cod)Cl]2 (2.5 mg, 0.0051 mmol, 5.1 mol%) and (R)-3,5-tBu-4-MeO-MeO-BIPHEP (14 mg, 0.012 mmol, 12 mol%) in 1,4-dioxane (1.0 mL) was stirred for 30 min at r.t. A portion of the red mixture (0.1 mL) was transferred to bis(2-phenylbenzo[b]silolo[3,4-d])silane 3c (45 mg, 0.10 mmol, 1.0 eq.) and heated at 135 °C for 3 h. After solvents were removed in vacuo, purification by column chromatography (silica gel, iso-propanol = 90/10, flow = 0.7 mL/min, oven temp. = 40 °C; 84% ee.)
NH₄Cl, extracted into Et₂O, dried over MgSO₄, filtered and concentrated in vacuo. Purification by column chromatography (silica gel, 1st column; hexane:CH₂Cl₂ = 10:1, 2nd column; hexane) afforded 2-(2-bromophenyl)benzo[b]thiophene 8 (1.4 g, 4.8 mmol, 48%) as a white solid. 

1H NMR (CDCl₃, 250 MHz): δ 7.89–7.80 (m, 2H), 7.71 (d, 3J(H,H) = 8.0 Hz, 1H), 7.56 (dd, 3J(H,H) = 7.5 Hz, 3J(H,H) = 1.5 Hz, 1H), 7.32–7.42 (m, 3H), 7.50 (s, 1H), 7.22 (dd, 3J(H,H) = 7.5 Hz, 4J(H,H) = 1.8 Hz, 1H). GC-MS m/z calcd for C₁₄H₉BrS 288.0 (79Br), found 287.9 (79Br).

4.18 Synthesis of Bis(2-(benzo[b]thiophen-2-yl)phenyl)silane 3e

n-BuLi (1.6 M in hexanes, 2.3 mL, 3.6 mmol, 1.0 eq.) was added to a solution of 2-(2-bromophenyl)benzo[b]thiophene 8 (1.0 g, 3.5 mmol, 1.0 eq.) in Et₂O (10 mL) at −78 °C and the mixture was stirred for 1 h at r.t.. Tetrachlorosilane (0.2 mL, 1.7 mmol, 0.49 eq.) was added to the yellow solution at −78 °C and stirred for 21.5 h at r.t.. Afterwards, LiAlH₄ (1 M in Et₂O, 3.5 mL, 3.5 mmol, 1.0 eq.) was added at 0 °C and stirred for 5 h at r.t.. The brown suspension was quenched with H₂O and 10% aq. NaOH, filtered through Celite and volatiles were removed in vacuo. Purification by column chromatography (silica gel, hexane) afforded bis(2-(benzo[b]thiophen-2-yl)phenyl)silane 3e (120 mg, 0.267 mmol, 8%) as a white solid, which still contains minor impurities that could not be separated. The product was used without further purification. 

1H NMR (CDCl₃, 400.13 MHz): δ 7.74 (d, 3J(H,H) = 8.0 Hz, 2H), 7.64 (d, 3J(H,H) = 7.2 Hz, 2H), 7.45 (d, 3J(H,H) = 7.6 Hz, 2H), 7.46–7.28 (m, 8H) 7.13 (t, 3J(H,H) = 7.0 Hz, 2H), 6.99 (s, 2H), 4.87 (s, 2H). GC-MS m/z calcd for C₂₈H₂₀S₂Si 448.1, found 446.1.

4.19 Synthesis of (2-(Benzo[b]thiophen-2-yl)phenyl)silane 9

n-BuLi (1.6 M in hexanes, 0.70 mL, 1.1 mmol, 1.1 eq.) was added to a solution of 2-(2-bromophenyl)benzo-[b]thiophene 8 (289 g, 1.00 mmol, 1.0 eq.) in Et₂O (3.0 mL) at −78 °C, the mixture was stirred for 30 min at −78 °C and then for 30 min at r.t.. A solution of tetrachlorosilane (0.06 mL, 0.5 mmol, 0.5 eq.) in Et₂O (0.50 mL) was added to the yellow solution at 0 °C and stirred for 3 h at r.t.. Next, LiAlH₄ (1 M in Et₂O, 1.0 mL, 1.0 mmol, 1.0 eq.) was added to the yellow suspension at −78 °C and stirred overnight at r.t.. The mixture was quenched with water and 10% aq. NaOH, filtered through Celite and the solvent was removed in vacuo. Purification by column chromatography (silica gel, c-Hex) afforded (2-(benzo[b]thiophen-2-yl)phenyl)silane 9 (30 mg, 0.13 mmol, 13%) as a colorless oil.

1H NMR (CDCl₃, 400.13 MHz, 293 K): δ 7.86 (d, 3J(H,H) = 7.6 Hz, 1H), 7.82 (d, 3J(H,H) = 7.6 Hz, 1H), 7.57 (d, 3J(H,H) = 7.6 Hz, 1H), 7.50 (t, 3J(H,H) = 7.6 Hz, 1H), 7.41–7.32 (m, 4H), 4.22 (s, 3H). GC-MS m/z calcd for C₁₄H₁₂SSi 240.0, found 240.0.

4.20 Synthesis of 3-Bromo-2-(3,5-dimethylphenyl)benzo[b]thiophene 7d

2,3-Dibromobenzo[b]thiophene (4.0 g, 13.6 mmol, 1.0 eq.), (3,5-dimethylphenyl)boronic acid (2.04 g, 13.6 mmol, 1.0 eq.), Pd(PPh₃)₄ (0.31 g, 0.272 mmol, 0.02 eq.) and sodium carbonate (5.91 g, 55.76 mmol, 4.1 eq.) were dissolved in a mixture 1,4-dioxane (75 mL) and water (75 mL), after which the mixture was degassed. After reflux overnight at 115 °C, the yellow mixture was quenched with 2M HCl and filtered with Celite using 1,4-dioxane and concentrated in vacuo. The yellow mixture was extracted into EtOAc, dried over MgSO₄, filtered and concentrated in vacuo. 7d was isolated as a white powder using column chromatography (c-Hex) (2.33 g, 7.3 mmol, 54%). 

1H NMR (500.23 MHz, CDCl₃, 293 K): δ 7.87 (d, 3J(H,H) = 8.0 Hz, 1H, H₄), 7.81 (d, 3J(H,H) = 8.0 Hz, 1H, H₇), 7.48 (t, 3J(H,H) = 7.4 Hz, 1H, H₅), 7.42–7.38 (m, 3H, H₆, H₁₀) 7.08 (s, 1H, H₁₂), 2.41 (s, 6H, H₁₃); 13C{1H} NMR (125.78 MHz, CDCl₃, 293 K): δ 139.3 (C₃), 138.7 (C₁), 138.3 (C₉), 137.8 (C₈), 133.0 (C₁₁), 130.7 (CH, C₁₂), 127.5 (C₁₃), 125.5 (CH, C₆), 125.3 (CH, C₅), 123.7 (CH, C₄), 122.3 (CH, C₇), 104.8 (C₂), 21.5 (C₁₃).
4.21 Synthesis of Bis(2-(3,5-dimethylphenyl)benzo[b]thiophen-3-yl)silane 3d

\[ \text{Mg (0.28 g, 11.5 mmol, 2.3 eq.)} \]

dispersed in dry THF (3 mL) was added to an oven dried setup. 3-bromo-2-(3,5-dimethylphenyl)benzo-[b]thiophene 7d (1.58 g, 5 mmol, 1.0 eq.) was dissolved in THF (6 mL) and slowly added to the reflux setup followed by addition of 1,2-dibromoethane (0.02 mL, 0.23 mmol, 0.046 eq.) and the mixture was refluxed at 66 °C for 2.5 h. Trichlorosilane (0.338 g, 2.5 mmol, 0.5 eq.) was dissolved in dry THF (3 mL) in a separate flame dried Schlenk vessel, added to the yellow solution and the resulting mixture was stirred for 15 min at 60 °C. Next, LiAlH₄ (1 M in Et₂O, 1.56 mL, 3.75 mmol, 0.75 eq.) was added dropwise at − 78 °C and the solution was stirred overnight. The reaction was quenched by dropwise adding a saturated aqueous Rochelle salt at − 78 °C. It was extracted into DCM (3x) and dried over Na₂SO₄, filtered and concentrated in vacuo. The product isolated via column chromatography (c-Hex) was not the desired product, but 2-(3,5-dimethylphenyl)benzo-[b]thiophene was obtained instead (106.9 mg, 21%). 1H NMR (400.13 MHz, CDCl₃, 293 K): δ 7.82 (d, \(J(H,H) = 7.8 \) Hz, 1H), 7.70–7.69 (m, 2H), 7.26–7.19 (m, 4H), 6.88 (s, 1H), 2.20 (s, 1H). 1H-29Si-HMBC NMR (400.13, 79.49 MHz, CDCl₃, 295 K): δ − 62.51 (Si–H).

Acknowledgements This work was supported by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (NWO/CW).

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