Visible-Light-Mediated Z-Stereoselective Monoalkylation of β,β -Dichlorostyrenes by Photoredox/Nickel Dual Catalysis

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Visible-light mediated (Z)-stereoselective mono-alkylation of β,β -dichlorostyrenes by photoredox/Nickel dual catalysis

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Abstract Metal-catalyzed alkylation of 1,1-dihalovinyl moiety commonly suffers from both a lack of stereoselectivity and the overreaction leading to the dialkylation product. The methodology described herein features a new pathway to alkylate stereoselectively β,β -dichloro-styryl substrates to provide the (Z)-trisubstituted olefin only with fair to good yields. This cross-coupling reaction bears on the smooth and photo-induced formation of a C-centered radical that engages in a nickel-catalyzed organometallic cycle to form the key $C_{sp^2}-C_{sp^3}$ bond.

Key words Cross-coupling, stereoselective alkylation, radical, dichlorostyrenes, bis(catecholato)silicates, dual catalysis, counterion, nickel

The substitution of the carbon-chlorine bond of β,β -dichlorostyryl derivatives^{1,2} was firstly approached by Minato and Tamao^{3,4} who developed a palladium-catalyzed arylation that advantageously provided the (Z)-mono-arylated product (Scheme 1, eq. a). Later, Negishi and co-workers developed a palladium-catalyzed alkynylation^{5,6} employing zinc acetylides as nucleophilic partners to afford the (Z)-mono-substituted product with high yields and stereoselectively (Scheme 1, eq. b). However, the formation of the side di-alkynylated product remains the main weakness of this methodology. Concerning the alkylation attempts of β,β -dichlorostyryl substrates, they also suffered from overreaction and the disubstituted product were often observed.^{7,8} An alternative was considered by Figadère and Alami and consisted in the iron-catalyzed version of the Kumada cross-coupling but the formation of the dialkylated compound remained competitive (Scheme 1, eq. c).⁹ It was not until the work of Roulland and co-workers¹⁰ that a promising answer to the problem of a stereoselective mono-alkylation was provided. Indeed, Roulland designed a Suzuki-type reaction with 9-BBN alkyl boranes that relies on the use of a bidentate phosphine ligand for palladium with a large bite angle to achieve the mono alkylation in a high stereo-selectivity and excellent yields. However, once again, they observed traces of the (E) stereoisomer and/or of the dialkylated side product, that proved difficult to separate (Scheme 1, eq. d).

In contrast, to the best of our knowledge, nickel-catalyzed monoalkylation of such electrophiles has not yet been reported in the literature. Indeed, the closest example was the enantioselective alkylation of (Z)- β -bromo-styryl derivatives

developed by Reisman¹¹ to afford the mono-alkylated (Z)-trisubstituted alkene with retention of the stereochemistry of the double bond. However, this methodology, did not involve the substitution of dihalogenated styryl derivatives.

a) Minato & Tamao, 1987: arylation of dichlorostyrenes

b) Negishi, 2004: alkynylation of dichlorostyrenes

c) Figadère & Alami, 2004; Fe-catalyzed alkylation of dichlorostyrenes

d) Roulland, 2007: alkylation of dichlorostyrenes with alkyl boranes

e) This work:

Scheme 1 Literature on metal-catalyzed arylation, alkynylation and alkylation of β,β -dichloro-styrenes

Considering those elements and based on our continuing interest in photoredox catalysis^{12–15} and in photoredox/Ni dual catalysis,^{16–20} we considered involving bis(catecholato)silicates in a photoredox/Ni catalyzed vinylation reaction.²¹ Indeed, thanks to their low oxidation potential (between 0.3 and 0.9 V vs SCE) bis(catecholato)silicates are known as efficient radical precursors.²² Their uses in dual catalysis were investigated by our group^{22,23} and the group of Molander for the alkylation of aryl and alkenyl halides.^{24,25} To illustrate the versatility of this methodology, our group also investigated the C_{sp3}-C_{sp3} bond formation,²⁶ the formation of ketones through cross-coupling with acyl chlorides²⁷ and the alkylation of alkenyl halides including one preliminary example of alkylation of *p*-methoxy β,β -dichloro-styrene.²⁸ We wished to further investigate this valuable transformation and examined the reactivity of various dichlorostyryl substrates **1** towards silicates **2** to furnish cross coupling (Z)-styrylchloride products **3** (Scheme 1, eq. e).²⁹

[18-C-6]-Potassium silicates **2a** (R = Bn), **2b** (R = -(CH₂)₂OAc), **2c** (R = cyclohexyl) and **2d** (R = -CH₂NHPh) were prepared as in previously described procedures.^{22,30} At the occasion of this study, we also introduced the previously unknown sodium silicates **2-Na** since they could result in altered reactivity. Sodium salts as additives have indeed resulted in optimized reactivity in some nickel-catalyzed cross coupling reactions.^{11,31}

Sodium silicates **2-Na** were prepared as previously for potassium silicates (scheme 2).²² The desired alkoxy silane is reacted with catechol (2 equiv.) and with 1 equiv. of sodium methoxide in methanol. 15-Crown-5 (1 equiv.) can also be added in the reaction mixture to provide sodium silicates **2'**. Gram quantities of **2a-Na** (55% yield), **2b-Na** (64%) and **2c-Na** (55%) were obtained. Similarly, 15-C-5 chelated sodium silicates **2a'** was isolated in 45% yield. All these sodium silicates can be kept several months without degradation if stored under air and moisture free conditions.

Scheme 2 Synthesis of sodium silicate **2-Na** and **2'**

Suitable crystals of the sodium bis(catecholato)benzyl silicate **2a-Na** were obtained by vapor diffusion using an acetone/diethyl ether mixture. [C₂₂H₂₁NaO₅Si] crystallized in a tetragonal crystal system with *a* = 19.0046(7) Å, *b* = 19.0046(7) Å, *c* = 11.5788(5) Å, α , β , γ = 90° (*Z* = 8).³² Sodium ions are coordinated to one oxygen atom of four catechol ligands and one acetone molecule completes the coordination sphere. The O₁₋₅-Na₁ bond lengths are spanning from 2.288(3) Å to 2.355(2) Å. Finally, an intramolecular π -cation interaction between the centroid of the benzyl and Na₁ can be observed with a distance of 3.2712(9) Å.

Figure 1 X-ray crystal structure of **2a-Na**, thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Dashed lines denote bonds between neighbouring silicates.

The Si-coordination of **2a-Na** can be described as a slightly distorted square pyramid (SP) structure with the benzyl group occupying the apical site (Si-C₁₃ bond length = 1.879(2) Å). The four basal positions are occupied by the two oxygen atoms of two catechol ligands. We can notice that Si atom is located just a little above the plane defined by these fourth atoms (distance Si-plane centroid = 0.4517(6) Å). For **2a-Na**, the dihedral angle method permits to calculate a displacement of 89.3% (TBP $\rightarrow$ SP, TBP: trigonal bipyramidal).³³ This is also underlined by the close values of all the 4 basal bond Si-O distances from 1.735(2) to 1.759(2) Å. Compared to an idealized SP with four angles of 86°, a slight distortion is observed with an angle deviations from -2.5° to 2.1°. Interestingly, **2a-Na** forms a polymeric assembly along the *c*-axis that originates from multiple interactions between Na and oxygen atoms of the catechols of two silicates (see supporting information). Sodium cyclohexyl silicate **2c-Na** also crystallized and a XRD structure analysis was obtained³⁴ and proved to be very similar to the corresponding potassium one.²²

Finally, oxidation potentials of sodium silicates were determined by cyclic voltammetry and proved consistent with the low values we already observed for the potassium ones²² ie E_{ox} = + 0.77 V vs SCE for **2a-Na**, + 0.88 V for **2b-Na** and + 0.81 V for **2c-Na**.

All β,β -dichloro-styrenes **1** were synthesized by a common Corey-Fuchs-Ramirez olefination from the corresponding aldehydes³⁵ and were obtained with good yields. For our catalytic system, we considered the same as in our previous studies,²⁸ namely nickel(II).dme in the presence of 2,6-di-*tert*-butyl bipyridine as catalytic system and 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN)³⁶ as photocatalyst. 4CzIPN is endowed with a very high reduction potential after photoexcitation (+1.59 V. vs SCE)³⁷ and a long-lived excited state (5.1 μ s) which enables the efficient oxidation of the silicate (E_{ox} < 0.9 V. vs SCE) to afford the corresponding C-centered radical.

We first concentrated on the cross coupling of 1-vinylnaphtalene derivatives **1a** as electrophiles with benzyl silicates **2a** (see Table 1). We began our investigation by delineating the range of dihalogeno-styrenes that could handle this approach (Table 1, entries 1-3). The difluorinated reagent **1a-F** did not react despite the presence of silicon on the radical precursor likely to establish a strong interaction with a fluoride. In contrast, the dibrominated reagent **1a-Br** led in our

conditions to a complex mixture in which only a marginal amount of mono was detected. Interestingly, only the presumably less reactive dichlorinated substrate **1a** positively reacted in this dual catalysis reaction (44% of adduct **3aa**) and was then chosen as model substrate for the optimization of the reaction conditions. To our delight, the alkylation occurred selectively without any formation of side products such as the dialkylated product or the (*E*)-stereoisomer. The (*Z*)-stereochemistry of **3aa** was assigned by analogy with subsequent findings (*vide infra*).

Table 1 Optimization of the cross-coupling reaction

Entry	React. time (h)	X	[Si] counter ion	Silicate equiv.	Yield (%), 3aa ^a
1	48	F, 1a-F	K[18-C-6], 2a	1.5	NR ^b
2	48	Br, 1a-Br	K[18-C-6], 2a	1.5	Mixture
3	48	Cl, 1a	K[18-C-6], 2a	1.5	44
4	48	Cl, 1a	K, 2a-K	1.5	39
5	48	Cl, 1a	Na[15-C-5], 2a'	1.5	39
6	48	Cl, 1a	Na, 2a-Na	1.5	42
7	48	Cl, 1a	K[18-C-6], 2a	3	47
8 ^c	48	Cl, 1a	K[18-C-6], 2a	3	51
9	72	Cl, 1a	K[18-C-6], 2a	1.5	50
10	72	Cl, 1a	K[18-C-6], 2a	3	70
11 ^d	48	Cl, 1a	K[18-C-6], 2a	1.5	0

^aNMR Yield determined using 1,3,5-trimethoxybenzene as internal standard; ^b NR: no reaction detected; ^c Variation of the concentration (from 0.1 M to 0.2 M); ^d Reaction performed without nickel catalyst.

We then examined the effect of the cation in this reaction. No improvement of yield was observed from free potassium silicate **2a-K** (39% of **3a**, entry 4), sodium silicates with 15-C-5 (**2a'**, 39%, entry 5) or without 15-C-5 (**2a-Na**, 42%, entry 6). Nevertheless, the fact that the plain sodium silicate **2a-Na** could be engaged successfully opened interesting perspectives. Focusing on silicate **2a**, we then investigated other possibilities to increase the yield of **3aa** (Table 1). While doubling the loading in silicate (entry 7) or its concentration (entry 8) did not have a significant impact on the yield, a longer reaction time (72 h) with double amount of **2a** provided the best yield of **3a** (70%, entry 10). We also checked that nickel catalysis was necessary for this transformation: no radical addition – β -elimination of a chlorine radical takes place²² to deliver **3aa** (entry 11)

Based on all the results from Table 1, the standard conditions (48h and 1.5 equivalents of silicate) appear to be a good compromise in terms of reaction time and cost to reach a decent yield in this cross-coupling reaction. Subsequently, we engaged in those conditions various [18-C-6]-potassium and sodium silicates **2** and **2-Na** with β,β -dichlorostyrenes **1** in the Ni/4CzIPN dual catalysis conditions to explore the scope of this reactivity (Scheme 2).

The results of Table 2 illustrate a certain versatility of this cross-coupling reaction between the gem-dichloro-styryl precursors **1** and the silicates **2**. Indeed, the reaction occurs with an alkyl-silicate (primary and secondary), a benzylic one and even the α -methyl-anilino-silicate with various dichloro-styrenes **1** and provides previously unknown coupling products with fair to good yields. In some cases, the use of the sodium silicates **2-Na**

compared to the potassium ones **2** proved more rewarding in terms of yields for coupling products **3** (products **3ab** and **3dc**). The coupling does not depend on the electron-withdrawing or electron-donating character of the substituent of the dichloro-styrene. Indeed, substrates that own a methoxy group or a trifluoromethyl group in para position react similarly with the primary alkyl acetoxypentyl radical (**2b**) or the more nucleophilic α -methyl-anilino one (**2d**) (Table 2).

Table 2 Reaction of gem-dichlorostyrenes **1** with various silicates **2** (isolated yields)

we investigated the possibility of the post-functionalization of our alkylated adducts by using our methodology.

NR: no reaction detected, we only recovered starting material; ^a NMR yield determined using 1,3,5-trimethoxybenzene as internal standard; ^b See also ref. 28.

Of note, the more touchy precursors, piperonal and nitro substrates failed to give any adducts (**3fb** and **3gb**) and it is also important to specify that only the *Z* isomer, as determined by NOESY experiments, of each adduct **3** was isolated and that no dialkylation product was observed. In the reactions of amino silicate **2d**, some (*Z*)-chlorostyrene was formed as side product in 15-20% yield that was highly suggestive of a protodienickelation based on the proposed mechanism of Scheme 3.

Because, we know that nickel is necessary in these reactions to obtain products **3** and based on the literature mechanism proposals of related Ni/photoredox dual catalysis reactions,^{18-20,38} it appears reasonable to invoke the trapping by nickel of a C-centered radical originating from the photo-induced oxidation of the silicates **2**. The nickel intermediate that would be involved is the nickel(II) complex **I** that originates from the oxidative addition into the a C-Cl bond of the substrates **1** (Scheme 3). The observed (*Z*)-selectivity might be ascribed to the presence of the bidentate ligand on nickel that would generate a significant steric hindrance around the metallic

center and that possibly orients the oxidative addition on the more accessible C-Cl bond, with no aryl group in *syn*. Even though the effect of the bulkiness around the metallic center seems clear, the insensitivity of the coupling to the substituent on the aryl moiety might appear strange but is reminiscent of previous findings in arylative couplings.^{23,24} This would be consistent with a radical addition on nickel(II) that is rather insensitive to electronic effects.³⁹⁻⁴² The resulting nickel(III) complex **II** then undergoes reductive elimination to provide products **3** and a nickel(I) salt that would be reduced by the photoredox cycle to Ni(0).

Scheme 3 Plausible mechanism for the cross-coupling reaction

Based on the clean but inefficient conversion of some of these reactions, we also wished to explore other conditions to run them. Notably we used an in-house flow^{43,44} setting (see SI for details) in order to reduce the reaction times. We tested silicate **2c** and naphthyl electrophile **1a** as a model reaction based on its efficiency in batch after 48h of irradiation (70 % of **3ac**, Table 2). Interestingly, within a residence time of 50 min, we reached 32% yield in **3ac** and 50% within 90 min. Therefore, the flow conditions open promising perspectives for this methodology.

Finally, we investigated the possibility of the post-functionalization of the alkylated adducts **3** by using our methodology. We engaged different mono-alkylated products **3** with silicates **2** (**3bb** with benzyl silicate and **3bd** with acetoxypropyl silicate) and we only recovered the starting material after 2 days of irradiation. All in all, this absence of reactivity confirms that our methodology is inoperative to achieve the substitution of the two C-Cl bonds. Nevertheless, Roulland's and Tamao's works showed that the post functionalization of the mono-substituted product was effective by engaging them in their palladium-catalyzed alkylation or arylation sequences.^{2,3}

To conclude, we have developed an innovative way to alkylate gem-dichloro-styrenes with fair to good yields. Contrary to most of the previous methodologies employing palladium catalysts, this cross-coupling reaction advantageously combines the earth-abundant nickel metal with a cheap organic dye to achieve

smoothly the substitution at room temperature (where all the previous methods mentioned are performed under reflux). Furthermore, the main advantages of this reaction are its total (*Z*)-stereoselectivity and the absence of overreaction to widen the scope of this methodology. Otherwise, one of the aims of the study was the approach of the silicate's counterion and its effect on the photoredox catalysis. The second interest of this study is the introduction of sodium silicates **2-Na** improves atom economy compared to the [18-C-6] chelated potassic silicates analogs **2**. If this work provided interesting and promising insights, the influence of the counterion remains non exhaustive and will be pursued by our group.

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Supporting Information

Is there **Supporting Information** to be published? Click here, then the arrow, and choose YES or NO.

Primary Data

No

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Supporting Information

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I. General informations

Unless otherwise noted, reactions were carried out under an argon atmosphere in oven-dried glassware. Methanol was distilled over CaH_2 and DMF was dried with a PureSolv solvent purification system from Innovative Technology. Catechol was purchased from commercial source and purified by crystallization from chloroform. Reagents and chemicals were purchased from commercial sources and used as received. Infrared (IR) spectra were recorded on a Bruker Tensor 27 (ATR diamond) spectrophotometer. Melting points were determined on a melting point apparatus SMP3 (Stuart scientific). Electrochemical measurements were carried out on an Origaflex (Origalys) electrochemical workstation. ^1H , ^{13}C and ^{19}F NMR spectra were recorded at room temperature at 400, 100 and 376 MHz respectively, on 400 MHz Bruker AVANCE I spectrometer and at 300, 75 and 282 MHz respectively, on 300 MHz Bruker AVANCE II spectrometer. ^{29}Si NMR spectra were recorded at room temperature at 79 MHz on 400 MHz Bruker AVANCE I spectrometer. Chemical shifts (δ) are reported in ppm and coupling constants (J) are given in Hertz (Hz). Abbreviations used for peak multiplicity are: s (singlet); bs (broad singlet); d (doublet); t (triplet); q (quartet); quint (quintet); sept (septet); m (multiplet) etc. Thin layer chromatographies (TLC) were performed on Merck silica gel 60 F 254 and revealed with a UV lamp ($\lambda = 254 \text{ nm}$) and KMnO_4 staining. Flash Column Chromatographies were conducted on Silica gel 60 M, 0.04–0.063 mm, from Macherey Nagel. High resolution mass spectrometries were performed on a microTOF (ESI). All the solvents used in flash chromatography (toluene, petroleum ether, pentane and Et_2O) were distilled.

II. General procedures

General procedure 1. Synthesis of the silicates

1. Synthesis of [18-crown-6] bis(catecholato)-alkylsilicate

To a stirred solution of catechol (2 equiv) in dry methanol (0.25 M) was added 18-Crown-6 [18-C-6] (1 equiv). After dissolution of the crown ether, the trialkoxyorganosilane (1 equiv) was added followed by a solution of potassium methoxide in methanol (1 equiv). The reaction mixture was stirred for 3 hours and the solvent was removed under reduced pressure. The residue was dissolved in a minimum volume of acetone and diethyl ether was added until a cloudy solution was obtained (scrapping on the edge of the flask could be done to induce crystallization). The flask was placed at -20°C overnight. The crystals were collected by filtration under air, washed with diethyl ether and dried under vacuum to afford [18-C-6] potassium silicate.¹

2. Synthesis of sodium or potassium bis(catecholato)-alkyl silicate

All manipulations were performed following the conventional Schlenk techniques.

In a dry Schlenk tube under argon covered with aluminium foil was added catechol (2 equiv) and the Schlenk was purged. Degassed MeOH (0.25 M) was added followed by the alkyltriethoxysilane (1 equiv.). A solution of sodium or potassium methoxide in methanol (1 equiv) was added dropwise and the reaction was stirred 3 hours at room temperature. Solvent was removed directly on the Schlenk line and the crude was dry under high vacuum until a powder was obtained. Silicate was purified by recrystallisation as mentioned for each silicate. The crystals were collected by filtration under argon flux, washed with degassed diethyl ether and dried under vacuum to afford the desired silicate.

General procedure 2. Synthesis of β,β -dihalostyryls

1. Synthesis of β,β -dichlorostyryl derivatives

In a round-bottom-flask was added the aldehyde (1.0 equiv) in MeCN (0.125 M). The reaction mixture was cooled with an ice bath to 0°C and $BrCCl_3$ (1.5 equiv) was added, followed by addition of a solution of triphenylphosphine (3.0 equiv) in a minimum amount of MeCN. The reaction mixture was stirred at room temperature for 3 hours then the solvent was removed under reduced pressure to afford a crude residue. This residue was dissolved in dichloromethane (0.25 M) and the organic phase was washed with water, brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue purified on a pad of silica (elution with a mixture $Et_2O:n\text{-pent}$ (1:9)), giving the pure material.

¹ Corcé, V.; Chamoreau, L. M.; Derat, E.; Goddard, J.-P.; Ollivier, C.; Fensterbank, L. *Angew. Chem. Int. Ed.* **2015**, *54*, 11414.

2. Synthesis of β,β -dibromostyryl derivatives

In a round-bottom-flask was added the aldehyde (1.0 equiv) in MeCN (0.125 M). The reaction mixture was cooled with an ice bath to 0°C and CBr₄ (1.5 equiv) was added, followed by addition of a solution of triphenylphosphine (3.0 equiv) in a minimum amount of MeCN. The reaction mixture was stirred at room temperature for 3 hours then the solvent was removed under reduced pressure to afford a crude residue. This residue was dissolved in dichloromethane (0.25 M) and the organic phase was washed with water, brine and dried over MgSO₄. The solvent was removed under reduced pressure and the residue purified on a pad of silica (Et₂O:*n*-pentane), giving the pure material.

3. Synthesis of β,β -difluorostyryl derivatives

In a two-neck round-bottom-flask was added the aldehyde (1.0 equiv), NaI (2 equiv) and PPh₃ (3.0 equiv) in MeCN (0.5 M). The reaction mixture was heated at 70°C for 30 minutes then methyl 2,2-difluoro-2-(fluorosulfonyl)acetate (1.75 equiv) was added over 10 minutes. The reaction mixture was stirred at 70°C for 3 hours then water was added and the resulting solution was extracted with Et₂O (3 times), dried over MgSO₄, filtered and concentrated *in vacuo*. The obtained residue was purified by column chromatography (*n*-pentane).

General procedure 3. Photoredox/nickel cross-coupling dual catalysis with the β,β -dihalogenostyryl derivative

To a Schlenk tube was added the β,β -dihalogenostyryl derivative (1 equiv.), the appropriate silicate (1.5 equiv.), 4CzIPN (1 mol %) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (2 mol %). The Schlenk tube was then charged with NiCl₂.dme (2 mol %) into a glovebox, sealed with a rubber septum, removed from the glovebox, and evacuated/purged with vacuum/argon three times. Degassed DMF (0.1 M) was introduced (with the β,β -dihalogenostyryl derivative if it is a liquid) and the reaction mixture was irradiated with blue LEDs (477 nm) for 48 hours. The reaction mixture was diluted with diethyl ether, washed with saturated NaHCO₃ (2 times), brine (2 times), dried over MgSO₄ and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the cross-coupling product.

General procedure 4. Continuous flow photoredox/nickel cross-coupling dual catalysis

A solution of 1-(2,2-dichlorovinyl)naphthalene **1a** (0.21 mmol, 47.3 mg) with potassium [18-C-6] bis(catecholato)-cyclohexylsilicate **2b** (0.32 mmol, 193 mg), 4CzIPN (1 mol %, 0.002 mmol, 1.73 mg), 2,2'-di-tert-butyl-bipyridine (2 mol %, 0.004 mmol, 1 mg) and NiCl₂.dme (2 mol %, 0.004 mmol, 0.93 mg) prepared in glovebox in degassed DMF (1 mL) was pumped by a syringe pump (KDSscience, model KDS-100-CE) with a flow rate of 1.2 mL/h for the experiment with a residence time of 50 min (Experiment in Red) and 0.67 mL/h for a residence time of 90 min (Experiment in Blue). The mixture was mixed within a glass milli-mixer (LTF-MX, 0.2 mL at room temperature, Little Things Factory, Germany) under blue LED irradiation (477 nm) and then flowed through a PTFE tubing (1/16" tubing, 2 m, 1 mL at room temperature) under blue LED irradiation (477 nm). The mixer and the PTFE tubing were rinsed with degassed DMF prior to use. The residence time was calculated with the total reaction volume and the total flow rate. The reaction mixture was then collected, diluted with diethyl ether, washed with an aqueous saturated K₂CO₃ solution (2 times), brine (2 times), dried over MgSO₄ and evaporated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel to afford the product.

III. Compound characterizations

1. Synthesis and characterisation of the silicates

Potassium [18-Crown-6] bis(catecholato)-benzylsilicate **2a**

The silicate **2a** was synthesized as described in General procedure 1.1. The spectroscopic data are in agreement with those reported in the literature.¹

¹H NMR (400 MHz, Methanol-d₄): δ 7.09 – 6.75 (m, 5H), 6.66 – 6.60 (m, 4H), 6.56 – 6.49 (m, 4H), 3.55 (s, 24H), 2.14 (s, 2H). ¹³C NMR (100 MHz, Methanol-d₄): δ 150.9 (4 C), 142.8, 129.8 (2 C), 128.2 (2 C), 123.9, 119.3 (4 C), 111.5 (4 C), 71.3 (12 C), 27.9.

Potassium [18-Crown-6] bis(catecholato)-acetoxypropylsilicate **2b**

The silicate **2b** was synthesized as described in General procedure 1.1. The spectroscopic data are in agreement with those reported in the literature.²

¹H NMR (400 MHz, Methanol-d₄): δ 6.68 (dd, J = 5.6, 3.5 Hz, 4H), 6.56 (dd, J = 5.6, 3.5 Hz, 4H), 3.88 (t, J = 7.0 Hz, 2H), 1.92 (s, 3H), 1.66 – 1.56 (m, 2H), 0.70 – 0.65 (m, 2H). ¹³C NMR (100 MHz, Methanol-d₄): δ 173.1, 150.9 (4 C), 119.3 (4 C), 111.5 (4 C), 71.2 (12 C), 68.6, 24.9, 20.8, 13.9.

Potassium [18-Crown-6] bis(catecholato)-cyclohexylsilicate **2c**

The silicate **2c** was synthesized as described in General procedure 1.1. The spectroscopic data are in agreement with those reported in the literature and the X-ray crystal structure was previously determined.

² Lvque, C.; Chennberg, L.; Corc, V.; Goddard, J.-P.; Ollivier, C.; Fensterbank, L. *Org. Chem. Front.* **2016**, *3*, 462.

¹H NMR (400 MHz, Methanol-d₄): δ 6.72 – 6.60 (m, 4H), 6.57 – 6.49 (m, 4H), 3.53 (s, 24H), 1.69 – 1.48 (m, 5H), 1.34 – 1.02 (m, 5H), 0.84 (tt, J = 12.2, 3.1 Hz, 1H). **¹³C NMR** (100 MHz, Methanol-d₄): δ 151.5 (4 C), 119.0 (4 C), 111.2 (4 C), 71.2 (12 C), 31.4, 29.6 (2 C), 29.4 (2 C), 28.3.

Potassium [18-Crown-6] bis(catecholato)-anilinomethylsilicate **2d**

The silicate **2d** was synthesized as described in General procedure 1.1. The spectroscopic data are in agreement with those reported in the literature.¹

¹H NMR (400 MHz, Methanol-d₄): δ 7.27 – 6.90 (m, 2H), 6.87 – 6.71 (m, 4H), 6.70 – 6.54 (m, 4H), 6.55 – 6.39 (m, 3H), 3.56 (s, 24H), 2.52 (s, 2H), NH is missing. **¹³C NMR** (100 MHz, Methanol-d₄): δ 152.2, 150.8 (4 C), 129.8 (2 C), 119.7 (4 C), 117.0, 113.4 (2 C), 111.9 (4 C), 71.3 (12 C), 34.1.

Sodium bis(catecholato)-benzylsilicate **2a-Na**

The silicate **2a-Na** was synthesized as described in General procedure 1.2 with catechol (5 mmol, 0.55 g), benzyltriethoxysilane (2.5 mmol, 0.64 g), MeOH (10 mL), NaOMe in MeOH (2.5 mmol, 1.66M). Recrystallisation was done from acetone using diethyl ether as anti-solvent affording 1.37 mmol (0.49 g, 55%) of the desired silicate **2a-Na** as a white powder.

¹H NMR (400 MHz, Methanol-d₄): δ 7.00 – 6.93 (m, 2H), 6.92–6.83 (m, 3H), 6.73 – 6.66 (m, 4H), 6.62 – 6.52 (m, 4H), 2.18 (s, 2H). **¹³C NMR** (100 MHz, Methanol-d₄): δ 150.6 (4 C), 142.7, 129.7 (2 C), 128.2 (2 C), 123.9, 119.4 (4 C), 111.6 (4 C), 27.5. **²⁹Si NMR** (79 MHz, Methanol-d₄): δ -80.90. **HRMS**: calc. for C₁₉H₁₅O₄SiNa₂ 381.0530; found 381.0529. **M.p.** >350°C.

Potassium bis(catecholato)-benzylsilicate **2a-K**

The silicate **2a-K** was synthesized as described in General procedure 1.2. with catechol (5 mmol, 0.55 g), benzyltriethoxysilane (2.5 mmol, 0.64 g), MeOH (10 mL), KOMe in MeOH (2.5 mmol, 3.56 M). Recrystallisation

was done from acetone using diethyl ether as anti-solvent affording 1.35 mmol (0.5 g, 54%) of the desired silicate **2a-K** as a grey powder. *Note: Exposing the silicate to air before drying turn the powder darker.*

¹H NMR (400 MHz, Methanol-d₄): δ 7.01 – 6.95 (m, 2H), 6.91–6.84 (m, 3H), 6.73 – 6.67 (m, 4H), 6.62 – 6.57 (m, 4H), 2.18 (s, 2H). ¹³C NMR (100 MHz, Methanol-d₄): δ 150.7 (4 C), 142.9, 129.7 (2 C), 128.2 (2 C), 123.9, 119.4 (4 C), 111.5 (4 C), 71.3 (12 C), 27.5. ²⁹Si NMR (79 MHz, Methanol-d₄): δ -80.90. HRMS: calc. for C₁₉H₁₅O₄Si 335.0745; found 335.0741. M.p. >350°C.

Sodium [15-crown-5] bis(catecholato)-benzylsilicate **2a'**

The silicate **2a'** was synthesized as described in General procedure 1.2. with catechol (8 mmol, 0.88 g), benzyltriethoxysilane (4 mmol, 1 g), MeOH (16 mL), 15-C-5 (4 mmol, 790 µL) that was added before NaOMe in MeOH (4 mmol, 1.66 M). Recrystallisation was done from acetone affording 1.6 mmol (0.92 g, 45%) of the desired silicate **2a'** as a white powder.

¹H NMR (400 MHz, Methanol-d₄): δ 6.98 – 6.80 (m, 5H), 6.68 – 6.62 (m, 4H), 6.59 – 6.53 (m, 4H), 3.65 (s, 20H), 2.17 (s, 2H). ¹³C NMR (100 MHz, Methanol-d₄): δ 150.9 (4 C), 142.7, 129.8 (2 C), 128.2 (2 C), 123.9, 119.3 (4 C), 111.5 (4 C), 69.9 (10 C), 27.8. ²⁹Si NMR (79 MHz, Methanol-d₄): δ -80.80. HRMS: calc. for C₁₉H₁₅O₄Si 335.0745; found 335.0743. M.p. 238°C (decomp.).

Sodium bis(catecholato)-acetoxypropylsilicate **2b-Na**

Following general procedure 1.2. with catechol (10 mmol, 1.1 g), acetoxypropyltrimethoxysilane (5 mmol, 1.1 g), MeOH (20 mL), NaOMe in MeOH (5 mmol, 1.66 M). Recrystallisation was done from acetone using diethyl ether as anti-solvent affording 3.2 mmol (1.17 g, 64%) of the desired silicate **2b-Na** as a white powder.

¹H NMR (400 MHz, Methanol-d₄): δ 6.77 – 6.69 (m, 4H), 6.63 – 6.57 (m, 4H), 3.91 (t, J = 7.0 Hz, 2H), 1.95 (s, 3H), 1.69 – 1.59 (m, 2H), 0.73 – 0.65 (m, 2H). ¹³C NMR (100 MHz, Methanol-d₄): δ 173.3, 150.6 (4 C), 119.4 (4 C), 111.6 (4 C), 68.5, 24.7, 20.8, 13.5. ²⁹Si NMR (79 MHz, Methanol-d₄): δ -76.36. HRMS: calc. for [C₁₇H₁₇O₆SiNa₂] 391.0584; found 345.0584. M.p. 300°C (decomp.).

Sodium bis(catecholato-)cyclohexylsilicate 2c-Na

Following general procedure 1.2. with catechol (10 mmol, 1.1 g), cyclohexyltrimethoxysilane (5 mmol, 1.02 g), MeOH (20 mL), NaOMe in MeOH (5 mmol, 1.66 M). Recrystallisation was done from acetone affording 2.75 mmol (0.96 g, 55%) of the desired silicate **2c-Na** as a white powder.

¹H NMR (300 MHz, Methanol-d₄): δ 6.73 – 6.69 (m, 4H), 6.60 – 6.55 (m, 4H), 1.68 – 1.54 (m, 5H), 1.30 – 1.05 (m, 5H), 0.87 (tt, J = 12.0, 3.0 Hz, 1H). **¹³C NMR** (100 MHz, Methanol-d₄): δ 151.3 (4 C), 119.1 (4 C), 111.2 (4 C), 31.2, 29.6 (2 C), 29.3 (2 C), 28.2. **²⁹Si NMR** (79 MHz, Methanol-d₄): δ -77.75. **HRMS**: calc. for C₁₈H₁₉O₄SiNa₂ 373.0843; found 373.0842. **M.p.** > 350°C.

2. Synthesis of the dihalostyryl derivatives

1-(2,2-Difluorovinyl)naphthalene (1a-F)

The difluoro-styryl derivative **1a-F** was synthesized as described in General procedure 2.3. The spectroscopic data are in agreement with those reported in the literature.³

¹H NMR (300 MHz, CDCl₃): δ 8.01 – 7.76 (m, 3H), 7.64 – 7.44 (m, 4H), 5.88 (dd, J = 24.3, 3.0 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 156.8 (dd, J = 7.7 and 286.5 Hz), 133.8, 131.6 (d, J = 3.4 Hz), 128.8, 128.1, 126.5–126.7 (m, 2C), 126.4, 125.6, 125.1, 123.9, 78.8 (dd, J = 286.7 and 294.3 Hz). ¹⁹F NMR (282 MHz, CDCl₃): δ -84.9 – -85.1 (m), -83.1 – -83.3 (m).

1-(2,2-dibromovinyl)naphthalene (1a-Br)

The gem-dibromo-styryl derivative **1a-Br** was synthesized as described in General procedure 2.2. The spectroscopic data are in agreement with those reported in the literature.⁴

¹H NMR (300 MHz, CDCl₃): 7.99-7.84 (m, 4H), 7.64 (d, J = 6.9 Hz, 1H), δ 7.60-7.46 (m, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 136.0, 133.6, 133.3, 130.8, 129.0, 128.7, 126.9, 126.7, 126.3, 125.4, 124.3, 93.0.

1-(2,2-dichlorovinyl)naphthalene (1a)

The gem-dichloro-styryl derivative **1a** was synthesized as described in General procedure 2.1. The spectroscopic data are in agreement with those reported in the literature.⁵

¹H NMR (400 MHz, CDCl₃): δ 7.89-7.84 (m, 2H), 7.65-7.63 (m, 1H), 7.54-7.49 (m, 3H), 7.36 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 133.4, 131.1, 130.8, 128.9, 128.6, 127.0, 126.9, 126.6, 126.2, 125.2, 124.0, 123.5.

³ Zhang, B.; Zhang, X.; Hao, J.; Yang, C. *Eur. J. Org. Chem.* **2018**, 5007.

⁴ Ma, X.; Herzon, S. B. *J. Org. Chem.* **2016**, *81*, 8673.

⁵ Ranu, B. C.; Samanta, S.; Das, A. *Tetrahedron Lett.* **2002**, *43*, 5993.

1-(2,2-dichlorovinyl)-3-methoxybenzene (1b)

The gem-dichloro-styryl derivative **1b** was synthesized as described in General procedure 2.1. The spectroscopic data are in agreement with those reported in the literature.⁵

¹H NMR (400 MHz, CDCl₃): δ 7.29-7.26 (m, 1H), 7.12-7.08 (m, 2H), 6.89-6.86 (m, 1H), 6.84 (s, 1H), 3.82 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 159.5, 134.6, 129.5, 128.5, 128.5, 121.3, 114.2, 114.0, 55.3.

2,2-dichlorostyrene (1c)

The gem-dichloro-styryl derivative **1c** was synthesized as described in General procedure 2.1. The spectroscopic data are in agreement with those reported in the literature.⁵

¹H NMR (400 MHz, CDCl₃): δ 7.61 – 7.51 (m, 2H), 7.48 – 7.34 (m, 4H), 6.89 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 133.4, 128.6 (2C), 128.6, 128.5, 128.4 (2C).

1-(2,2-dichlorovinyl)-4-(trifluoromethyl)benzene (1d)

The gem-dichloro-styryl derivative **1d** was synthesized as described in General procedure 2.1. The spectroscopic data are in agreement with those reported in the literature.⁶

¹H NMR (400 MHz, CDCl₃): δ 7.63 (m, 4H), 6.90 (s, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 137.0 (q, J = 1.5 Hz, 1C), 130.4 (q, J = 32.5 Hz, 1C), 129.0 (2C), 127.5 (1C), 125.5 (q, J = 3.5 Hz, 2C), 123.7 (1C), 123.0 (q, J = 270.4 Hz, 1C).

¹⁹F NMR (376 MHz, CDCl₃): δ -62.8.

1-(2,2-dichlorovinyl)-4-methoxybenzene (1e)

The gem-dichloro-styryl derivative **1e** was synthesized as described in General procedure 2.1. The spectroscopic data are in agreement with those reported in the literature.⁵

⁶ Semba, K.; Kameyama, R.; Nakao, Y. *Chem. Lett.* **2018**, 47, 213.

¹H NMR (400 MHz, CDCl₃): δ 7.50 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 6.79 (s, 1H), 3.83 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃): δ 159.7, 130.2 (2C), 128.2, 126.1, 118.9, 114.0 (2C), 55.4.

5-(2,2-dichlorovinyl)benzo[d][1,3]dioxole (**1f**)

The gem-dichloro-styryl derivative **1f** was synthesized as described in General procedure 2.1 The spectroscopic data are in agreement with those reported in the literature.⁷

1-(2,2-dichlorovinyl)-4-nitrobenzene (**1g**)

The gem-dichloro-styryl derivative **1g** was synthesized as described in General procedure 2.1 The spectroscopic data are in agreement with those reported in the literature.⁸

¹H NMR (400 MHz, CDCl₃): δ 6.95 (s, 1H), 7.71 (d, J = 8.0 Hz, 2H), 8.25 (d, J = 8.0 Hz, 2H) ppm. **¹³C NMR** (75 MHz, CDCl₃): δ 123.9 (2C), 125.4, 126.9, 129.5 (2C), 139.7, 147.3.

⁷ Saputra, M. A.; Ngo, L.; Kartika, R. *J. Org. Chem.* **2015**, *80*, 8815.

⁸ Newman, S. G.; Brian, C. S.; Perez, D.; Lautens, M. *Synthesis* **2011**, *2*, 342.

3. Photoredox/nickel cross-coupling dual catalysis with the β,β -dichlorostyryl

(Z)-1-(2-chloro-2-benzyl)naphthalene (3aa)

Following General procedure 3 with 1-(2,2-dichlorovinyl)naphthalene (0.32 mmol, 71 mg), potassium [18-Crown-6] bis(catecholato)-benzylsilicate (0.45 mmol, 280 mg). The crude product was purified by flash column chromatography (Et_2O :*n*-pentane From 0/100 to 2/98) to afford (Z)-1-(2-chloro-2-benzyl)naphthalene (**3aa**) (33.5 mg, 40%) as a colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.93–7.84 (m, 2H), 7.81 (d, J = 8.2 Hz, 1H), 7.67 (dt, J = 7.1 Hz, 1.2 Hz, 1H), 7.53–7.45 (m, 3H), 7.44–7.40 (m, 4H), 7.36–7.30 (m, 1H), 7.00 (s, 1H), 3.95 (s, 2H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 137.3, 136.3, 133.5, 132.4, 131.5, 129.2 (2C), 128.7 (2C), 128.6, 128.1, 127.2, 127.1, 126.1, 125.8, 125.2, 124.4, 124.3, 46.7. **HRMS**: calc. for $\text{C}_{19}\text{H}_{15}\text{Cl}$ 279.0935; found 279.0933.

(Z)-4-chloro-5-(3-methoxyphenyl)benzyl (3ba)

Following General procedure 3 with 1-(2,2-dichlorovinyl)-3-methoxybenzene (0.32 mmol, 64.2 mg) and potassium [18-Crown-6] bis(catecholato)-benzyl silicate (0.45 mmol, 280 mg). The crude product was purified by flash column chromatography (Et_2O :*n*-pentane 2/98) to afford (Z)-4-chloro-5-(3-methoxyphenyl)benzyl (**3ba**) (38 mg, 48%) as a pale brown oil.

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.43–7.27 (m, 6H), 7.24 (t, J = 2.1 Hz, 1H), 7.18 (d, J = 7.7 Hz, 1H), 6.89–6.81 (m, 1H), 6.55 (s, 1H), 3.84 (s, 3H), 3.82 (s, 2H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 159.4, 137.3, 136.2, 133.7, 129.1 (d, J = 1.9 Hz), 128.6, 127.0, 125.8, 121.8, 114.3, 113.6, 55.3, 47.4. **HRMS**: calc. for $\text{C}_{16}\text{H}_{15}\text{ClO}$ 259.0884; found 259.0883.

Z-[2-chloro-1-propene-1,3-diyl]bisbenzene (3ca)

Following General procedure 3 with (2,2-dichlorovinyl)-benzene (0.32 mmol, 55.4 mg) and potassium [18-Crown-6] bis(catecholato)-benzyl silicate (0.45 mmol, 280 mg). The crude product was purified by flash column chromatography (Toluene) to afford the cross-coupling product Z-[2-chloro-1-propene-1,3-diyl]bisbenzene

(3ca) (35.7 mg, 54 %). Geometry of the double bond was determined by NOESY experiment. All the spectroscopic data agree with the literature.⁷

¹H NMR (400 MHz, CDCl₃): δ 7.62 (dd, J = 7.5, 1.7 Hz, 2H), 7.42 – 7.23 (m, 7H), 6.56 (s, 1H), 3.82 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 137.3, 135.0, 133.4, 129.1 (2C), 129.1 (2C), 128.6 (2C), 128.2 (2C), 127.7, 127.0, 125.9, 47.3. HRMS: Calc. for C₁₅H₁₃Cl 228.0700; found 228.0699.

(Z)-1-(2-chloro-3-phenylprop-1-en-1-yl)-4-(trifluoromethyl)benzene (3da)

Following General procedure 3 with 1-(2,2-dichlorovinyl)-3-(trifluoromethyl)benzene (0.32 mmol, 76 mg) and potassium [18-Crown-6] bis(catecholato)-benzylsilicate (0.45 mmol, 288 mg). The crude product was purified by flash column chromatography (Toluene:*n*-pentane From 0/100 to 10/90) to afford (Z)-1-(2-chloro-3-phenylprop-1-en-1-yl)-4-(trifluoromethyl)benzene (**3ad**) (64.3 mg, 70%) as a pale oil.

¹H NMR (CDCl₃, 400 MHz): δ 7.70-7.66 (d, J = 8 Hz, 2H), 7.61-7.59 (d, J = 8 Hz, 2H), 7.40-7.35 (m, 2H), 7.32-7.27 (m, 3H), 6.55 (s, 1H), 3.83 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ 138.5, 136.8, 136.0, 129.3 (2C), 129.1 (2C), 128.7 (2C), 128.3, 127.2, 125.1 (q, J = 3.7 Hz, 2C), 124.7, 124.2 (q, J = 270.3 Hz), 47.3 ppm. ¹⁹F NMR (CDCl₃, 376 MHz): δ -62.6 ppm. HRMS: calc for C₁₆H₁₂ClF₃: 291.0578; found: 291.2006.

(Z)-4-chloro-5-(naphthalen-1-yl)pent-4-en-1-yl acetate (3ab)

Following General procedure 3 with 1-(2,2-dichlorovinyl)naphthalene (0.30 mmol, 66.7 mg) and potassium [18-Crown-6] bis(catecholato)-acetoxypentylsilicate (0.45 mmol, 231 mg). The crude product was purified by flash column chromatography (Et₂O:*n*-pentane From 2/98 to 10/90) to afford (Z)-4-chloro-5-(naphthalen-1-yl)pent-4-en-1-yl acetate (**3ab**) (40 mg, 45%) as a pale brown oil.

¹H NMR (400 MHz, CDCl₃): δ 7.92-7.79 (m, 3H), 7.65-7.59 (m, 1H), 7.55-7.42 (m, 3H), 6.98 (s, 1H), 4.24 (t, J = 6 Hz, 2H), 2.71 (t, J = 7.5 Hz, 2H), 2.1 (s, 3H), 2.13-2.08 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 171.1, 136.3, 133.5, 132.3, 131.4, 128.6, 128.0, 127.2, 126.1, 125.8, 125.2, 124.3, 123.7, 63.2, 37.0, 26.7, 21.0. HRMS: calc. for [C₁₇H₁₇ClO₂]⁺Na 311.0809; found 311.0811.

(Z)-4-chloro-5-(3-methoxyphenyl)pent-4-en-1-yl acetate (3bb)

Following General procedure 3 with 1-(2,2-dichlorovinyl)-3-methoxybenzene (0.32 mmol, 64.2 mg) and potassium [18-Crown-6] bis(catecholato)-acetoxypentylsilicate (0.45 mmol, 293 mg). The crude product was purified by flash column chromatography (Et₂O:*n*-pentane 2/98) to afford (Z)-4-chloro-5-(3-methoxyphenyl)pent-4-en-1-yl acetate (**3bb**) (47.9 mg, 64%) as a pale oil.

¹H NMR (400 MHz, CDCl₃): δ 7.24-7.28 (m, 1H), 7.02-7.19 (m, 1H), 7.14-7.12 (m, 1H), 6.85-6.81 (m, 1H), 6.48 (s, 1H), 4.16-4.13 (t, *J* = 6.4 Hz, 2H), 3.82 (s, 3H), 2.59-2.55 (td, *J* = 0.52 Hz and 6.7 Hz, 2H), 2.06 (s, 3H), 2.05-1.94 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 171.1, 159.4, 136.2, 133.7, 129.1, 125.1, 121.7, 114.3, 113.4, 63.2, 55.2, 37.8, 26.7, 20.9 ppm. HRMS: calc for [C₁₄H₁₇ClO₃]⁺Na: 291.0759; found: 291.0760.

(Z)-4-chloro-5-phenylpent-4-en-1-yl acetate (3cb)

Following General procedure 3 with 1-(2,2-dichlorovinyl)-benzene (0.32 mmol, 55 mg) and sodium bis(catecholato)-acetoxypentylsilicate (0.45 mmol, 166 mg). The crude product was purified by flash column chromatography (Et₂O:*n*-pentane 2/98) to afford (Z)-4-chloro-5-phenylpent-4-en-1-yl acetate (**3cb**) (25 mg, 35%) as a pale oil.

¹H NMR (400 MHz, CDCl₃): δ 7.58 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.35-7.27 (m, 3H), 6.51 (s, 1H), 4.15 (t, *J* = 6.4 Hz, 2H), 2.58 (t, *J* = 7.4 Hz, 2H), 2.07 (s, 3H), 2.04 – 1.97 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 171.0, 134.9, 133.4, 129.0 (2C), 128.1 (2C), 127.6, 125.2, 63.2, 37.7, 26.7, 21.0. HRMS: Calcd for C₁₃H₁₆O₂Cl 239.0834; found 239.0833.

(Z)-4-chloro-5-(4-(trifluoromethyl)phenyl)pent-4-en-1-yl acetate (3db)

Following General procedure 3 with 1-(2,2-dichlorovinyl)-4-(trifluoromethyl)benzene (0.31 mmol, 72.3 mg) and potassium [18-Crown-6] bis(catecholato)-acetoxypentylsilicate (0.45 mmol, 295 mg). The crude product was

purified by flash column chromatography (Et₂O:*n*-pentane 10/90) (Z)-4-chloro-5-(4-(trifluoromethyl)phenyl)pent-4-en-1-yl acetate (**3db**) (49 mg, 51%) as a pale brown oil.

¹H NMR (400 MHz, CDCl₃): δ 7.69-7.66 (d, J = 8 Hz, 2H), 7.62-7.59 (d, J = 8 Hz, 2H), 6.54 (s, 1H), 4.17-4.13 (t, J = 6.4 Hz, 2H), 2.62-2.58 (td, J = 0.5 Hz and 7 Hz, 2H), 2.06 (s, 3H), 2.04-1.98 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 171.1, 138.4, 135.9, 129.5, 129.2 (2C), 125.1 (q, J = 3.7 Hz, 2C), 124.3 (q, J = 283.7 Hz), 124.1, 63.1, 37.7, 26.6, 20.9. ¹⁹F NMR (376 MHz, CDCl₃): δ -62.7 ppm. HRMS: calc for [C₁₄H₁₄ClF₃O₂]⁺Na 329.9527; found 329.9527.

(Z)-1-(2-chloro-2-cyclohexylvinyl)naphthalene (**3ac**)

Following General procedure 3 with 1-(2,2-dichlorovinyl)naphthalene (0.32 mmol, 71 mg) and [18-Crown-6] bis(catecholato)-cyclohexylsilicate (0.45 mmol, 290 mg). The crude product was purified by flash column chromatography (Et₂O:*n*-pentane From 0/100 to 2/98) to afford (Z)-1-(2-chloro-2-cyclohexylvinyl)naphthalene (**3ac**) (58.5 mg, 70%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.95-7.74 (m, 4H), 7.54-7.45 (m, 3H), 7.62-7.58 (m, 1H), 6.93 (s, 1H), 2.54-2.54 (m, 1H), 2.14-2.03 (m, 2H), 1.94-1.85 (m, 2H), 1.62-1.19 (m, 5H). ¹³C NMR (100 MHz, CDCl₃): δ 143.4, 133.5, 132.9, 131.5, 128.5, 127.7, 127.1, 125.9, 125.7, 125.2, 124.5, 120.6, 48.2, 31.9 (2C), 26.2 (2C), 26.0. HRMS: calc for C₁₈H₁₉Cl 273.1174; found 273.6994.

(Z)-4-chloro-5-(3-methoxyphenyl)cyclohexane (**3bc**)

Following general procedure 3 with 1-(2,2-dichlorovinyl)-3-methoxybenzene (0.32 mmol, 60.9 mg) and potassium [18-Crown-6] bis(catecholato)-cyclohexyl silicate (0.45 mmol, 284 mg). The crude product was purified by flash column chromatography (Et₂O:*n*-pentane From 0/100 to 5/95) to afford (Z)-4-chloro-5-(3-methoxyphenyl)cyclohexane (**3bc**) as a yellow oil (23 mg, 30%).

¹H NMR (400 MHz, CDCl₃): δ 7.40 – 7.11 (m, 3H), 6.81 (dd, J = 8.2, 2.6 Hz, 1H), 6.45 (s, 1H), 3.82 (s, 3H), 2.33 (tt, J = 11.6, 3.3 Hz, 1H), 1.94 (d, J = 12.5 Hz, 2H), 1.84 (dt, J = 12.8, 3.1 Hz, 2H), 1.76 – 1.68 (m, 1H), 1.57 – 1.12 (m, 5H). ¹³C NMR (100 MHz, CDCl₃): δ 159.3, 140.8, 136.7, 129.0, 122.2, 121.8, 114.4, 113.1, 55.23, 48.8, 31.7 (2C), 26.2 (2C), 25.9. HRMS: Calc for C₁₅H₁₉ClO 251.1196; found 251.1197.

(Z)-(2-chloro-2-cyclohexylvinyl)benzene (**3cc**)

Following General procedure 3 with 1-(2,2-dichlorovinyl)-benzene (0.32 mmol, 55 mg) and potassium [18-Crown-6] bis(catecholato)-cyclohexyl silicate (0.45 mmol, 284 mg). The crude product was purified by flash column chromatography (toluene:cyclohexane From 0/100 to 5/95) to afford (Z)-(2-chloro-2-cyclohexylvinyl)benzene (**3cc**) (40 mg, 60%) as a pale oil. All the spectroscopic data agree with the literature.⁹

¹H NMR (300 MHz, CDCl₃): δ 7.61 (d, J = 7.3 Hz, 1H), 7.40 – 7.32 (m, 4H), 6.50 (s, 1H), 2.44 – 2.29 (m, 1H), 2.01 – 1.69 (m, 7H), 1.53 – 1.32 (m, 3H). **¹³C NMR** (75 MHz, CDCl₃): δ 129.2 (2C), 128.1 (2C), 127.3, 122.3, 48.8, 31.7 (2C), 29.7 (2C), 26.2, two carbons are missing.

(Z)-N-(2-chloro-3-(naphthalen-1-yl)allyl)aniline (**3ad**)

Following General procedure 3 with 1-(2,2-dichlorovinyl)naphthalene (0.32 mmol, 71 mg) and potassium [18-Crown-6] bis(catecholato)-anilinomethylsilicate (0.45 mmol, 294 mg). The crude product was purified by flash column chromatography (Et₂O:*n*-pentane From 2/98 to 10/90) to afford (Z)-N-(2-chloro-3-(naphthalen-1-yl)allyl)aniline (**3ad**) (39 mg, 43 %) as a pale brown oil.

¹H NMR (400 MHz, CDCl₃): δ 7.82-7.78 (m, 2H), 7.65-7.59 (m, 2H), 7.49-7.37 (m, 3H), 7.29-7.24 (m, 3H), 6.84-6.75 (m, 3H), 4.23 (s, 2H), NH is missing. **¹³C NMR** (100 MHz, CDCl₃): δ 133.7, 133.4, 131.8, 131.5, 129.4 (2C), 128.4, 128.1, 126.9, 126.1, 125.8, 125.2, 124.4, 123.3, 113.4 (2C), 118.5, 113.5, 51.5. **HRMS**: calc. for [C₁₉H₁₇ClN]⁺ 294.1044, found: 294.1055.

(Z)-N-(2-chloro-3-(3-methoxyphenyl)allyl)aniline (**3bd**)

Following General procedure 3 with 1-(2,2-dichlorovinyl)-3-methoxybenzene (0.73 mmol, 149 mg) and potassium [18-Crown-6] bis(catecholato)-anilinomethylsilicate (1.09 mmol, 713 mg). The crude product was purified by flash column chromatography (Et₂O:*n*-pentane From 2/98 to 10/90) to afford (Z)-N-(2-chloro-3-(3-methoxyphenyl)allyl)aniline (**3bd**) (110 mg, 57 %) as a pale brown oil.

¹H NMR (400 MHz, CDCl₃): δ 7.19 – 7.05 (m, 5H), 6.77 – 6.58 (m, 5H), 4.15 (m, 1H), 4.01 (d, J = 2.6 Hz, 2H), 3.72 (s, 3H), NH is missing. **¹³C NMR** (100 MHz, CDCl₃): δ 159.4, 147.0, 135.7, 131.5, 129.3 (2C), 129.2, 124.4, 121.8, 118.3, 114.4, 113.9, 113.1 (2C), 55.3, 52.1. **HRMS**: calc. for [C₁₆H₁₇ClNO]⁺: 274.0993, found: 274.099.

⁹ Adak, T.; Hoffmann, M.; Witzel, S.; Rudolph, M.; Dreuw, A.; Hashmi, S. K. *Chem. Eur. J.* **2020**, *26*, 15573.

(Z)-N-(2-chloro-3-(4-(trifluoromethyl)phenyl)allyl)aniline (3dd)

Following General procedure 3 with 1-(2,2-dichlorovinyl)-4-(trifluoromethyl)benzene (0.30 mmol, 72.3 mg) and potassium [18-Crown-6] bis(catecholato)-anilinomethylsilicate (0.45 mmol, 294 mg). The crude product was purified by flash column chromatography (Et₂O:*n*-pentane 10/90) to afford (Z)-N-(2-chloro-3-(4-(trifluoromethyl)phenyl)allyl)aniline (**3dd**) (28 mg, 30%) as a pale brown oil.

¹H NMR (300 MHz, CDCl₃): δ 7.67 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.25 – 7.17 (m, 2H), 6.84 – 6.62 (m, 4H), 4.25 (s, 1H), 4.11 (s, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 146.9, 138.1 (d, J = 1.3 Hz, 1C), 133.9, 129.6 (d, J = 58.0 Hz, 1C), 129.5 (2C), 129.4 (2C), 125.2 (q, J = 3.75 Hz, 2C), 124.2 (q, J = 270.3 Hz, 1C), 123.2, 118.6, 113.2 (2C), 52.1. ¹⁹F NMR (376 MHz, CDCl₃): δ -62.7. HRMS: Calc. for [C₁₆H₁₃ClF₃N] 312.0761; found 312.0761.

IV. ^1H , ^{13}C , ^{19}F and ^{29}Si spectra

1. Bis-catecholato silicates

S20

Note: The silicate co-crystalizes with one equivalent of acetone

S21

Note: The silicate co-crystalizes with one equivalent of acetone

2c-Na

Note: The silicate co-crystalizes with one equivalent of acetone

2. Cross-coupling products

S31

S35

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3ac

3cc

3ad

S42

S43

3dd

The red correlation spots show the remote space couplings between the vinylic proton and the alkyl ones which confirms the configuration of the double bond

NOESY experiments permitted to confirm the configuration of the double bonds of the cross-coupling products. We adopted for all the coupling products the same methodology as for the example here under:

V. X-ray crystallographic details

The structures of **2a-Na** and **2c-Na** were determined by X-ray.

A single crystal of **2a-Na** was selected, mounted onto a cryoloop, and transferred in a cold nitrogen gas stream. Intensity data were collected with a BRUKER Kappa-APEXII diffractometer with graphite-monochromated Mo-K α radiation. Data collection was performed with APEX2 suite (BRUKER). Unit-cell parameters refinement, integration and data reduction were carried out with SAINT program (BRUKER). SADABS (BRUKER) was used for scaling and numerical absorption corrections. The structure was solved using the Olex2 (Dolomanov et al., 2009) software package and refined by full-matrix least-squares methods using SHELXL-14 (Sheldrick, 2014).

A single crystal of **2c-Na** was selected, mounted onto a cryoloop, and transferred in a cold nitrogen gas stream. Intensity data were collected with a BRUKER Kappa-APEXII diffractometer with micro-focused Cu-K α radiation. Data collections were performed with APEX3 suite (BRUKER). Unit-cell parameters refinement, integration and data reduction were carried out with SAINT program (BRUKER). SADABS (BRUKER) was used for scaling and multi-scan absorption corrections. The WinGX (Farrugia, 2012) suite of programs was used to solve the structure (cf cif files) and refined by full-matrix least-squares methods using SHELXL-15 (Sheldrick, 2015).

The figure 1 illustrates the polymeric unit of silicate **2a-Na** and figure 2 the one for **2c-Na**.

Figure 1. X-ray crystal packing of **2a-Na** (view along the b-axis), thermal ellipsoids are drawn at 25% probability level. Hydrogen atoms are omitted for clarity. Dashed lines denote bonds between neighbouring silicates.

Figure 2. X-ray crystal packing of **2c-Na** (view along the a-axis), thermal ellipsoids are drawn at 25% probability level. Hydrogen atoms are omitted for clarity. Dashed lines denote bonds between neighbouring silicates.

Table 1 gives some crystal information for the structures **2a-Na** and **2c-Na**. Other crystal and refinement information can be found in the CIF file of each structure, downloadable free of charge on www.ccdc.cam.ac.uk, with CCDC numbers 2058159 and 2050302 respectively.

Table 1. Crystal information

	2a-Na	2c-Na
CCDC number	2048159	2050302
Empirical formula	C ₂₂ H ₂₁ NaO ₅ Si	C ₂₄ H ₃₁ NaO ₆ Si
Temperature (K)	200(2)	200(1)
Space group	P4 ₂ ₁ c	Pbca
a (Å)	19.0046(7)	20.1599(19)
b (Å)	19.0046(7)	11.4841(11)
c (Å)	11.5788(5)	21.738(3)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Z	8	8

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VI. Cyclic voltammetries

CV performed towards oxidative potentials of DMF solution (10 ml) containing $n\text{-Bu}_4\text{NBF}_4$ (1 mmol) at room temperature, at a scan rate of $0.2 \text{ V}\cdot\text{s}^{-1}$ using steady glassy carbon disk electrode ($d = 3 \text{ mm}$) as working electrode, a SCE as reference and Pt wire as counter-electrode. CV with **2a-Na** (0.1 mmol).

CV performed towards oxidative potentials of DMF solution (10 ml) containing $n\text{-Bu}_4\text{NBF}_4$ (1 mmol) at room temperature, at a scan rate of $0.2 \text{ V}\cdot\text{s}^{-1}$ using steady glassy carbon disk electrode ($d = 3 \text{ mm}$) as working electrode, a SCE as reference and Pt wire as counter-electrode. CV with **2a-K** (0.1 mmol)

CV performed towards oxidative potentials of DMF solution (10 ml) containing $n\text{-Bu}_4\text{NBF}_4$ (1 mmol) at room temperature, at a scan rate of 0.2 V.s^{-1} using steady glassy carbon disk electrode ($d = 3 \text{ mm}$) as working electrode, a SCE as reference and Pt wire as counter-electrode. CV with **2a'** (0.1 mmol).

CV performed towards oxidative potentials of DMF solution (10 ml) containing $n\text{-Bu}_4\text{NBF}_4$ (1 mmol) at room temperature, at a scan rate of 0.2 V.s^{-1} using steady glassy carbon disk electrode ($d = 3 \text{ mm}$) as working electrode, a SCE as reference and Pt wire as counter-electrode. CV with **2b-Na** (0.1 mmol).

CV performed towards oxidative potentials of DMF solution (10 ml) containing $n\text{-Bu}_4\text{NBF}_4$ (1 mmol) at room temperature, at a scan rate of 0.2 V.s^{-1} using steady glassy carbon disk electrode ($d = 3 \text{ mm}$) as working electrode, a SCE as reference and Pt wire as counter-electrode. CV with **2c-Na** (0.1 mmol).