

Vinylidisiloxanes: their synthesis, cross coupling and applications†

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During the studies towards the development of pentafluorophenyldimethylsilanes as a novel organosilicon cross coupling reagent it was revealed that the active silanolate and the corresponding disiloxane formed rapidly under basic conditions. The discovery that disiloxanes are in equilibrium with the silanolate led to the use of disiloxanes as cross coupling partners under fluoride free conditions. Our previous report focused on the synthesis and base induced cross coupling of aryl substituted vinylidisiloxanes with aryl halides; good yields and selectivities were achieved. As a continuation of our research, studies into the factors which influence the successful outcome of the cross coupling reaction with both alkyl and aryl substituted vinylidisiloxanes were examined and a proposed mechanism discussed. Further investigation into expanding the breadth and diversity of substituted vinylidisiloxanes in cross coupling was explored and applied to the synthesis of unsymmetrical *trans*-stilbenes and cyclic structures containing the *trans*-alkene architecture.

Introduction

The synthesis of carbon–carbon bonds by transition metal catalysed cross coupling has developed over the past 40 years into arguably one of the most utilised and important classes of reactions within organic chemistry.¹ Numerous organometallic species have been developed as suitable cross coupling partners, two of the most significant being organotin (Stille)² and organoboron reagents (Suzuki).³ To expand on the scope, breadth and application of cross coupling reactions even further, ongoing research into alternative coupling species and conditions are being developed that offer the possibility of milder reaction conditions, greater functional group tolerance, reduced toxicity, ease of reagent synthesis, trouble-free isolation and increased reagent stability. Consequently, the pioneering discovery by Hiyama and Hatanaka that organosilicon reagents could effectively participate in palladium catalysed cross coupling aroused interest.⁴ The addition of fluoride ions was required to activate the Si–C bond by formation of a pentacoordinate silyl species which facilitates transmetalation with palladium(II).^{5,6} Since these pioneering reports, significant advances in the cross coupling of organosilicon reagents have been made, the most prominent being the coupling of silanols under fluoride free (base induced) conditions.^{7,8}

The high reactivity and suitability of organosilanols for cross coupling; consequently, can hinder their progression as a functional group through multistep syntheses.^{9,10} As a result, more stable ‘masked’ forms of silanols have been

developed: examples include silacyclobutanes,^{10,11} triallylsilanes,¹² phenyldimethylsilanes,¹³ benzyldimethylsilanes,¹⁴ 2-pyridylsilanes,¹⁵ 2-thienylsilanes,^{16,17} [2-(hydroxymethyl)-phenyl]dimethylsilanes¹⁸ and disiloxanes.^{9,19–22} When subjected to the appropriate reactions conditions these ‘masked’ silanols are deprotected *in situ* to reveal the active silanol in preparation for the subsequent coupling reaction. Drawbacks of existing ‘masked’ silanols include loss of double bond configuration upon coupling, protodesilylation, the wrong group transferring (benzyl migration with benzyldimethylsilanes specifically) and high sensitivity to reaction conditions and variations in the coupling partners.^{11,13,23}

Disiloxanes offer the advantage of increased stability relative to the silanol and the potential to be carried through multi-step synthesis; moreover, they are highly atom efficient compared to alternative ‘masked’ silanols.^{9,19,20} In addition, aryl substituted vinylidisiloxanes are readily prepared from inexpensive starting materials, show good levels of functional group tolerance and can react under mild basic conditions with retention of stereochemistry.¹⁹ As a continuation from our previous research, herein, we aim to highlight and expand on our initial discoveries to include alkyl substituted vinylidisiloxanes and exemplify possible applications of this novel vinylidisiloxane methodology. On examination of the experimental data, a mechanism was proposed and influential factors identified to account for the observed isomerisation of the double bond geometry in particular coupling reactions.

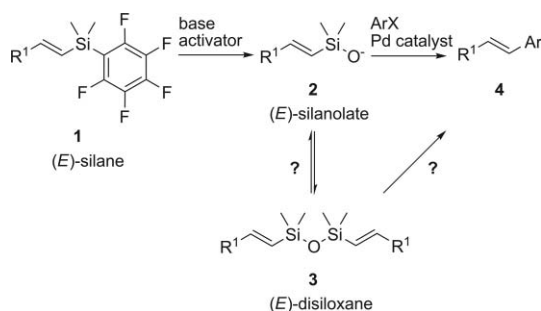
Results and Discussion

The transition to disiloxanes

In our quest to develop pentafluorophenyldimethylvinylsilanes (**1**, Scheme 1) into new class of ‘masked’ silanols, the necessary

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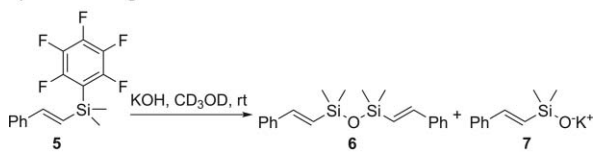
Scheme 1 Potential intermediates in the fluoride free coupling.

regio- and stereoselective synthesis of (*E*)-, (*Z*)- and α -vinylsilanes was successfully achieved; however, the development of fluoride free cross coupling conditions proved challenging.²⁴ Excellent yields and selectivities were obtained under fluoride induced cross coupling procedures;²⁴ but, on applying base activated coupling conditions, the selectivity and yields acquired were inconsistent and sometimes disappointing. Consequently, a detailed examination into the reaction profile was undertaken.

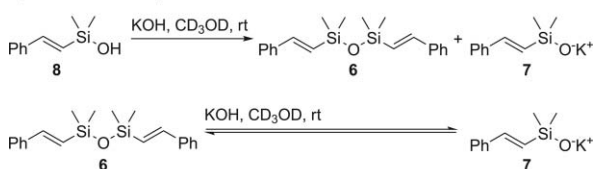
On considering the potential intermediates in the reaction pathway (Scheme 1), three fundamental questions arose: 1) how facile is the deprotection of the pentafluorophenyl group with base to reveal the active silanolate (transformation **1** to **2**); 2) under the reaction conditions is the silanolate (**2**) in an equilibrium with the more stable disiloxane (**3**), or is the corresponding disiloxane acting as a silicon sink removing the silyl reagent from the active reaction mixture; and 3) are disiloxanes able to directly participate in fluoride free cross coupling with aryl halides (conversion of **3** to produce **4**)?

A series of ¹H-NMR experiments were conducted in an attempt to answer these key questions (Scheme 2). On treating pentafluorophenyldimethylvinylsilane **5** with KOH in deuterated methanol, no starting material was observed after immediate inspection by ¹H-NMR spectroscopy. The pentafluorophenyl group had been displaced within seconds under the basic reaction conditions, producing a mixture of the corresponding disiloxane (**6**) and presumably the silanolate (**7**). To determine if the disiloxane (**6**) and active silanolate (**7**) are in equilibrium under base

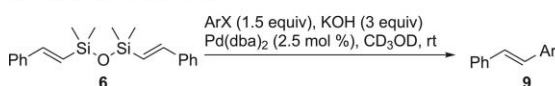
1) Unmasking?



2) Disiloxane Equilibrium?



3) Disiloxane Coupling?



Scheme 2 ¹H-NMR experiments.

induced conditions, two similar experiments were conducted. One experiment started from the disiloxane (**6**), the other from the respective silanol (**8**). Treatment of the two silicon reagents with KOH in CD₃OD resulted in identical ¹H-NMR spectra, indicating an equilibrium had been established in both incidences, ultimately resulting in the indistinguishable spectra. Building on these prior NMR experiments, we were optimistic that the disiloxane (**6**) would participate in fluoride free cross coupling with 4-iodoacetophenone. The ratio of disiloxane to aryl halide used was 1:1.5, making the aryl halide the limiting reagent, assuming that the disiloxane acts as two equivalents. Monitoring the coupling reaction over time saw complete consumption of the aryl halide and formation of the (*E*)-disubstituted alkene (**9**).

Development of substituted vinylsiloxanes

After the interesting results from the ¹H-NMR studies, the aim was to develop and optimise the synthesis and cross coupling of substituted vinylsiloxanes, with the intention of creating: 1) an attractive atom efficient alternative to existing 'masked' silanols that was able to partake in cross coupling under base induced conditions; 2) a protocol that utilised cheap reagents and was operationally simple; 3) a process that created and then maintained excellent geometrical purity of the disubstituted double bond; and 4) the products in good yields and under mild conditions.

To evaluate the scope of the cross coupling reaction, it was first necessary to prepare a variety of substituted vinylsiloxanes. Exceptional (*E*)-selectivity can be achieved for the hydrosilylation of terminal alkynes with Pt-catalysts.²⁵ In agreement with a report by Denmark²² it was found that the hydrosilylation of terminal alkynes with 1,1,3,3-tetramethyl-disiloxane (**11**) produced the corresponding (*E*)-vinylsiloxanes (**3**) in excellent yields and selectivity when the catalytic complex (^tBu₃P)Pt(DVDS) was employed (Table 1). Pleasingly, the high yields and selectivity were maintained when a wide variety of terminal alkynes were surveyed. Alkyl substituted terminal alkynes containing functionalities such as a free alcohol, a silyl protected alcohol and a bulky *tert*-butyl group and aryl substituted terminal alkynes containing electron rich, electron poor and heterocyclic rings were all well tolerated; the products were formed in good yields, with only the (*E*)-disiloxanes observed by crude ¹H-NMR spectroscopy.

The scope of the fluoride free cross coupling was explored by coupling a variety of differentially substituted (*E*)-vinylsiloxanes (**3**) with a selection of aryl iodides (Table 2). Firstly, the impact of the aryl iodide on the yield and regioselectivity (*i.e.* (*E*)-, (*Z*)- or (α)- product alkene geometry) of the reaction was investigated. In no case was there evidence for the formation of any of the undesired (*Z*)-product isomer. Electron deficient aryl iodides, including those with bulky *ortho*-substituents and heteroaryls, coupled in good yields and with excellent regioselectivity, only the desired (*E*)-isomer was observed by crude ¹H-NMR spectroscopy (entries 1 to 4).¹⁹ Interestingly, the cross coupling of electron rich aryl iodides proved to be more challenging, with poor yields and regioselectivities for the desired (*E*)-isomer being obtained on employment of the standard reaction conditions (entries 5 & 6). Mixtures of the α - and (*E*)-stilbenes were observed by crude ¹H-NMR; consequently, the isolated yields of the desired (*E*)-isomers were only modest. Simply elevating the reaction temperature did not assist in improving the regioselectivity for the (*E*)-isomer.

Table 1 Synthesis of substituted (*E*)-vinylsiloxanes^a

$\text{R}^1\text{—C}\equiv\text{C—H} + \text{H—Si}(\text{R}^2)_2\text{—O—Si}(\text{R}^3)_2\text{—H} \xrightarrow[\text{Toluene, rt}]{(\text{tBu}_3\text{P})\text{Pt}(\text{DVDS}) (0.2 \text{ mol } \%)} \text{R}^1\text{—CH=CH—Si}(\text{R}^2)_2\text{—O—Si}(\text{R}^3)_2\text{—R}^1$				
Entry	Product		(<i>E</i>) (%) ^b	Yield (%) ^c
1		3a	≥99	96
2		3b	≥99	90
3		3c	≥99	91
4 ^d		3d	≥99	94
5		3e	≥99	89
6		3f	≥99	89
7		3g	≥99	84
8		3h	≥99	94

^a Reaction conditions: alkyne (**10**) (1 equiv), silane (**11**) (2 equiv), (tBu₃P)Pt(DVDS) (0.2 mol%), toluene, rt. ^b Determined by ¹H-NMR spectroscopy. ^c Isolated yield after flash silica chromatography. ^d Heated at 60 °C.

Although complete consumption of the aryl iodide was seen with raised temperatures, this also resulted in an increased percentage of the reduced aryl iodide and homo-coupled impurities. The homo-coupled product results from an Ullmann coupling of the starting aryl iodide.

Investigation into the effect the vinylsiloxane substituent has on the successful outcome of the reaction was then explored. Our previous research found that the electronic nature of the aryl vinylsiloxane did not appear to significantly affect either the reactivity or regioselectivity of the cross coupling reaction; consequently, the corresponding (*E*)-stilbenes were all isolated in good yields and with excellent levels of regioselectivity (Table 2, entries 7 to 9).¹⁹ Unfortunately, on examining the base induced cross coupling of straight chain alkyl substituted (*E*)-vinylsiloxanes, only moderate levels of regioselectivity for the desired product isomers (*E*)-**4j** and (*E*)-**4k** was observed (entries 10 & 11). Isomerisation of the alkene geometry of the disiloxane starting materials had occurred, leading to a mixture of the *ipso* and *cine* substituted products by crude ¹H-NMR spectroscopy. The desired *ipso* products were isolated by flash silica chromatography, although typically only low yields were obtained because of the difficult separation of the isomers.

Interestingly, the sterically bulky alkyl substituted disiloxanes displayed excellent regioselectivity, only producing the *ipso* substituted product on coupling with 4-iodoacetophenone, albeit in modest yields (entries 12 & 13). In these incidences where

Table 2 Fluoride free cross coupling of substituted (*E*)-vinylsiloxanes (**3**) with a selection of aryl iodides^a

$\text{Ar—I} + \left(\text{R}^1\text{—CH=CH—Si}(\text{R}^2)_2\text{—O—Si}(\text{R}^3)_2\text{—R}^1\right)_2 \xrightarrow[\text{MeOH, rt}]{\text{KOH (3 equiv), Pd(dba)}_2 (2.5 \text{ mol } \%)} \text{Ar—CH=CH—R}^1 + \text{Ar—C}(\text{R}^1)=\text{CH—R}^1$				
Entry	ArI	Desired (<i>E</i>)- isomer of product	Crude isomeric ratio (<i>E</i>) : α ^b	Yield (%) ^c
1			100 : 0	91
2			100 : 0	91
3			100 : 0	75
4 ^d			100 : 0	56
5			62 : 38	37
6			57 : 43	33
7			100 : 0	70
8			100 : 0	83
9			100 : 0	61
10			58 : 42	19
11 ^e			79 : 21	8
12 ^e			100 : 0	24
13			100 : 0	39

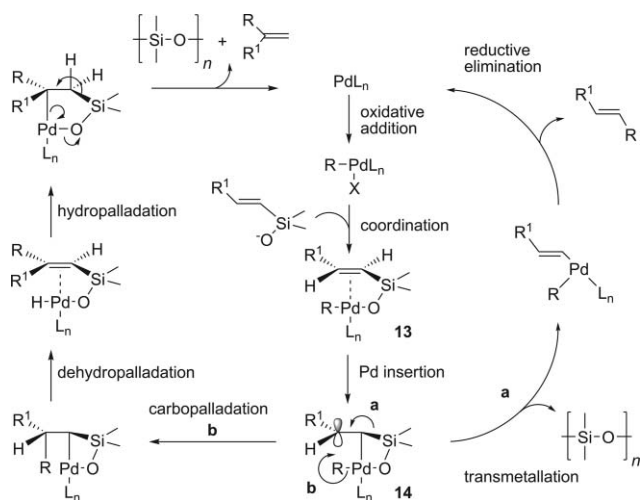
^a Reaction conditions: aryl halide (**12**) (1.5 equiv), disiloxane (**3**), KOH (3 equiv), Pd(dba)₂ (2.5 mol%), MeOH, rt. ^b Determined by analysis of ¹H-NMR spectrum of crude product material. ^c Isolated yield of pure (*E*)-isomer after flash silica chromatography. ^d Heated at 70 °C. ^e Heated at 50 °C.

transmetalation is potentially slower, the aryl halide is consumed by reduction or homo-coupling in preference to reacting with the active silanolate, resulting in reduced yields of the coupled products.

Isomerisation – the influential factors

On examining these results two factors appear to be critical for achieving high yields and levels of regioselectivity for the desired *trans*-isomer when cross coupling substituted (*E*)-vinylsiloxanes. Firstly, the electronic nature of the aryl halide has a significant effect, with electron withdrawing substituents producing the desired *trans*-isomer (*ipso* substituted product) whereas electron donating groups lead to the unexpected α -isomer (*cine* substituted product). Secondly, the vinyl substituent (R^1) is also highly influential, with good yields and maintained *trans* double bond geometry only being achieved with aryl substituted vinylsiloxanes. The reaction of alkyl substituted vinylsiloxanes only produced the desired *trans* coupled products in disappointing yields and regioselectivity; however, good regioselectivity was obtained with bulky alkyl groups.

A similar isomerisation phenomenon has been described by Hiyama for the palladium catalysed cross coupling of α -alkenylfluorodimethylsilanes under fluoride activation.^{26,27} Hiyama noted that the relative proportions of *ipso* vs. *cine* substituted products were closely related to the electronic nature of the aryl iodides used, with electron rich aryl iodides yielding the highest percentage of the *cine* substituted product.²⁶ A mechanism to account for the observed isomerisation with *trans* substituted vinylsiloxanes is proposed which amalgamates the mechanism suggested by Hiyama to explain the isomerisation phenomenon under fluoride activation,²⁶ the base induced cross coupling mechanism^{8,28} and the experimental observations reported here (Scheme 3). The base induced cross coupling process is believed to proceed *via* a tetracoordinate palladium intermediate rather than the pentacoordinate species described for the fluoride activated reaction.^{5,8,28}



Scheme 3 Proposed mechanism for the base induced cross coupling of substituted vinylsiloxanes with aryl halides which aims to account for the observed trends in isomerisation.

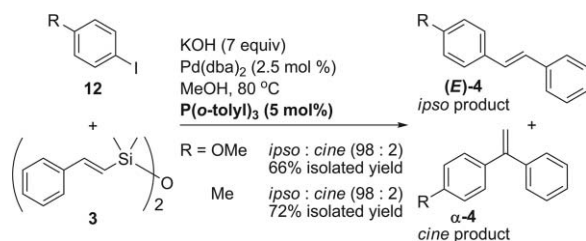
Initially the mechanism is similar to the base induced catalytic cycle, with oxidative addition of the aryl halide ($R-X$) to the palladium(0) species, followed by formation of the covalent $Pd-O-Si$ bond on reaction with the active silanolate group, generated *in situ* from the disiloxane under the basic reaction conditions (Scheme 3, intermediate **13**). Further coordination of the double bond within the tetracoordinate intermediate, facilitates Pd insertion, forming the $C-Pd$ bond and subsequently generating a β -cationic silicon species (Scheme 3, intermediate **14**). Progression through pathway **a** results in formation of the expected *ipso* substituted product. In order to promote this pathway and hence elimination, it is necessary that the $C-Si$ σ bond is sufficiently electron rich; consequently, stabilisation of the intermediate carbocation is advantageous. The presence of an aryl group at R^1 stabilises the adjacent cation and in addition the use of an electron rich silyl reagent enhances the silicon β -effect: the combination of these two factors assists in promoting pathway **a** when electron deficient aryl halides are employed. However, when electron rich aryl halides are used, the enhanced nucleophilicity of the aryl group now facilitated a 1,3-migration of the R group from Pd to the β -carbon *via* pathway **b**, eventually leading to the *cine* substituted products after a series of carbopalladation, dehydropalladation, hydropalladation and reductive elimination steps.

It can also be postulated therefore, that the absence of a carbocation stabilising group at R^1 leads to the observed moderate levels of regioselectivity for the *trans* substituted products on cross coupling straight chain alkyl substituted *trans* vinylsiloxanes, even when electron deficient aryl iodides are employed as the electrophilic partner. High levels of regioselectivity for the *trans* substituted product were maintained when bulky alkyl substituted vinylsiloxanes were cross coupled, which may be due to the steric hindrance of the alkyl group leading to formation of the more thermodynamically stable (*E*)-isomer. Alternatively, these high levels of *trans* selectivity may be rationalised on the basis of kinetic considerations; a bulky group would be expected to undergo slower transfer to carbon (Scheme 3, pathway **b**) meaning that reaction *via* pathway **a** is favoured.

Combating isomerisation

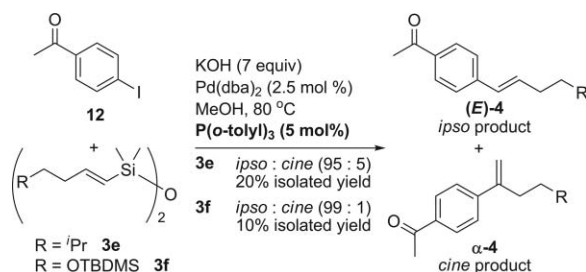
In an endeavour to improve the regioselectivity for the (*E*)-isomer (*ipso* substitution product) over the α -product, when cross coupling electron rich aryl halides with aryl substituted vinylsiloxanes, a variety of ligands were investigated. It was anticipated that increasing the steric bulk around the palladium would block the ability of the aryl group to attack the β -cation, thus preventing progression through pathway **b** (Scheme 3). An increased bite angle around the palladium (*i.e.*, the angle of $P-Pd-P$), would decrease the vinyl- $Pd-Ar$ angle, thus assisting in rapid reductive elimination and the potential for reduced isomerisation of the double bond geometry on coupling. A total of ten ligands were explored, including monodentate, bidentate and biaryl phosphine ligands, in the coupling of 4-iodoanisole with phenyl substituted vinylsiloxane. A clean reaction profile and excellent regioselectivity for the (*E*)-isomer was observed with tri(*o*-tolyl)phosphine as the ligand when the reaction was heated at 80 °C. The impact of the ligand on the regioselectivity for the (*E*)-isomer was highly pronounced as on applying the optimised reaction conditions, both 4-iodoanisole and 4-iodotoluene were

coupled in good yields with excellent levels of selectivity for the *ipso* substituted products (Scheme 4).



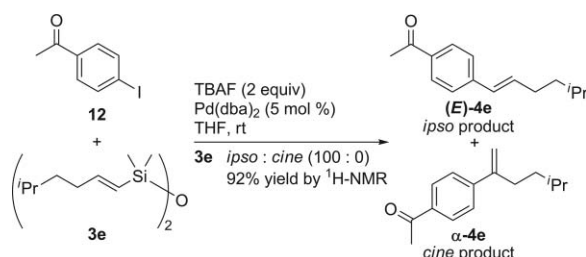
Scheme 4 Fluoride free cross coupling of electron rich aryl iodides with phenyl substituted vinyldisiloxane.

Application of these modified conditions to the coupling of alkyl substituted vinyldisiloxanes did result in an improvement in the regioselectivity for the *trans* coupled products; however, the isolated yields remained low (Scheme 5). Vinyldisiloxanes **3e** and **3f** were cross coupled with 4-iodoacetophenone using the modified reaction conditions: KOH (7 equiv), Pd(dba)₂ (2.5 mol%), P(*o*-tolyl)₃ (5 mol%), MeOH, 80 °C. Only the (*E*)-isomers were observed on inspecting the crude ¹H-NMR spectra; however, extensive reduction and homo-coupling of the starting aryl iodide was also seen. This resulted in poor isolated yields of the desired coupled products.



Scheme 5 Fluoride free cross coupling of 4-iodoacetophenone with alkyl substituted vinyldisiloxanes.

The high level of regioselectivity for the *ipso* coupled product was maintained during the cross coupling of alkyl substituted vinyldisiloxanes when fluoride induced conditions were employed (TBAF) (Scheme 6).²² In the coupling of vinyldisiloxane **3e** with 4-iodoacetophenone under fluoride activation conditions excellent selectivity was observed for the *ipso* coupled product on examining the ¹H-NMR spectra of the crude reaction mixture. No *cine* product was visible. It has emerged that the coupling reaction is highly dependent upon the activation source: with better selectivity

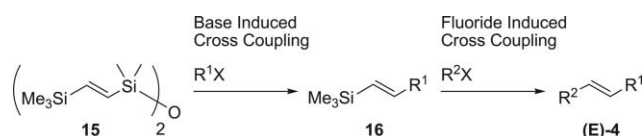


Scheme 6 Fluoride induced cross coupling of an alkyl vinyldisilane.

and yields for the *ipso* substituted product being observed under fluoride activation rather than base induced conditions. It can be postulated therefore, that the fluoride induced coupling of substituted vinyldisiloxanes proceeds *via* an alternative pathway to the mechanism proposed in Scheme 3.

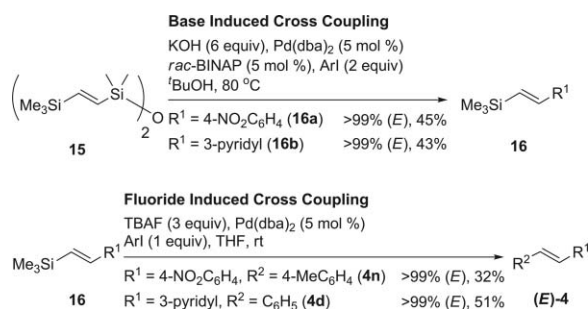
Synthesis of unsymmetrical *trans*-stilbenes

Unsymmetrical *trans*-stilbenes display a range of biological activities. For example, Resveratrol, a hydroxylated *trans*-stilbene and more recently one of its analogues DMU-212 have emerged as interesting anticancer agents.²⁹ The regio and stereoselective formation of the double bond is key to the generation of these (*E*)-stilbenes. As an extension of the disiloxane methodology, the development of an efficient method for the synthesis of unsymmetrical *trans*-stilbenes by reacting differentially substituted bissilyl olefins (**15**) under sequential palladium cross couplings with aryl halides using fluoride free conditions followed by fluoride induced activation conditions was investigated (Scheme 7). In a similar strategy, Denmark *et al.* synthesised a selection of unsymmetrical 1,4-disubstituted 1,3-butadienes from the sequential cross coupling of 1,4-bissilylbutadienes using a silanol and thienylsilane as the two distinct silicon sources.²³ Likewise, Hiyama *et al.* performed a fluoride induced double cross coupling of a 1,2-bissilylated alkene to generate a *trans*-stilbene.¹⁷ Herein, the unique feature of our bissilyl olefin (**15**) is that one silicon substituent cross couples readily under base activation whilst the other silyl group requires the presence of fluoride to enable coupling to occur. Selection of the appropriate reaction conditions allows the silyl substituents to be distinguished. Most significantly, by following this procedure disubstituted stilbenes are generated from readily available aryl halides, mitigating the use of acetylene gas or the requirement for terminal alkynes which have limited commercial availability.



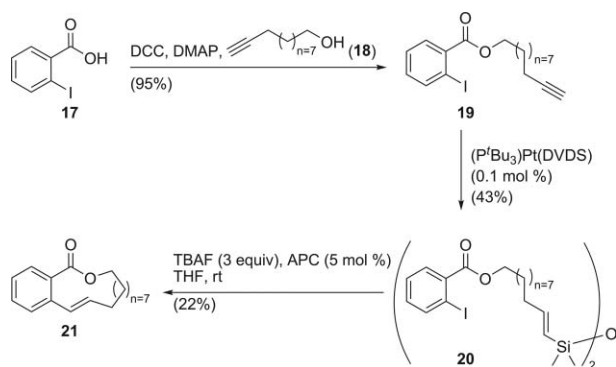
Scheme 7 Bissilyl strategy for the synthesis of unsymmetrical alkenes.

The bissilyl olefin (**15**) was generated by (^tBu₃P)Pt(DVDS) catalysed hydrosilylation of the commercially available trimethylsilylacetylene with tetramethyldisiloxane. The bissilyl disiloxane (**15**) was produced in a 70% yield, with excellent regioselectivity, only the (*E*)-isomer being observed by ¹H-NMR spectroscopy. Initial base activated cross coupling with the bissilyl disiloxane were disappointing, with loss of (*E*)-selectivity being observed (*E*/*Z*, 2/1). After a broad optimisation screen of the reaction conditions and the introduction of ligands, excellent selectivity for the (*E*)-isomer (Scheme 8, **16a** & **16b**) was achieved. Good (*E*)-selectivity was maintained in the subsequent fluoride activated palladium catalysed cross coupling of the (*E*)-vinyltrimethylsilanes. The unsymmetrical disubstituted olefins (Scheme 8, **4n** & **4d**) were generated with excellent (*E*)-selectivity.

Scheme 8 Synthesis of unsymmetrical (*E*)-stilbenes.

Intramolecular cyclisation

To expand on the disiloxane methodology further, the potential to form lactones *via* an intramolecular Hiyama cross coupling reaction was explored (Scheme 9). Cyclic structures containing the vinyl-aryl-lactone motif are common architectures found in natural products and are typically constructed *via* a Stille or Suzuki cross coupling.³⁰ The development of methodology to construct these synthetically challenging scaffolds from inexpensive and readily synthesised vinylidisiloxanes would be appealing, mitigating the use of toxic or unstable reagents.



Scheme 9 Intra-molecular Hiyama cross coupling of disiloxanes.

Using standard reaction conditions for ester formation, the substituted terminal alkyne (19) was isolated in an excellent yield. Hydrosilylation of the alkyne proceeded with excellent selectivity for the (*E*)-isomer when catalysed by the Pt-complex; even in the presence of an aryl iodide within the molecule. The (*E*)-disiloxane was isolated in a moderate yield. In the initial cyclisation attempts 10 equivalents of TBAF were used; however, this predominately led to protodesilylation, with only trace amounts of the desired product being observed. Additionally, at higher concentrations, cyclic dimer formation was also observed. Reducing the equivalents of TBAF and increasing the dilution resulted in a modest yield of desired product being isolated. Pleasingly, these early results highlight the potential of disiloxanes to participate in intramolecular cross coupling reactions. With further investigation we envisage that this approach will offer an attractive alternative to existing methods commonly used to construct these difficult scaffolds.

Conclusions

The synthesis and cross coupling of vinylidisiloxanes has been developed creating an attractive atom efficient alternative to existing

'masked' silanols; which, were able to cross couple under base or fluoride induced conditions with retention of the double bond geometry. The developed protocol utilised inexpensive reagents and was operationally simple. The hydrosilylation/coupling process offers an effective method for obtaining disubstituted double bonds with excellent geometrical purity; ultimately, generating the products in good yields and under mild conditions.

The disiloxane methodology has successfully been applied to the synthesis of unsymmetrical stilbenes and cyclic structures. The sequential palladium catalysed cross coupling of the bisilyl alkene has enabled the functionalisation of both groups around a (*E*)-disubstituted alkene. The unsymmetrical (*E*)-alkenes were generated with excellent selectivity from easy to handle and readily available starting materials avoiding the use of acetylene gas or terminal alkynes with limited commercial availability. Synthesis of the synthetically challenging vinyl-aryl-lactone macrocyclic scaffold was achieved with excellent selectivity *via* a palladium catalysed intramolecular cyclisation of the intermediate vinylidisiloxane.

The development of disiloxanes as effective cross coupling partners has continued to build the Hiyama reaction into a viable and practical alternative to the existing strategies for making disubstituted double bonds. This methodology could find applications in natural product synthesis and in the synthesis of biologically active compounds within the pharmaceutical industry. To expand upon the disiloxane-mediated methodology, exploration into the efficient and mild coupling of aryl and heteroaryl disiloxanes is ongoing and results will be reported in due course.

Experimental Section

General information

All experiments were carried out under an atmosphere of nitrogen, using anhydrous solvents, unless otherwise stated. All chemicals were purchased from Sigma-Aldrich, Strem or Fluorochem. Room temperature refers to 20–25 °C. Analytical thin layer chromatography was carried out on Merck Kieselgel 60 F₂₅₄ plates with visualisation by ultraviolet light or staining with potassium permanganate made using a standard procedure. Retention factors (*R_f*) are quoted to 0.01. Flash column chromatography was performed using Merck Kieselgel 60 (230–400 mesh) or biotage silica columns under a positive pressure of nitrogen. Infra-red spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer fitted with an Attenuated Total Reflectance (ATR) sampling accessory as neat films. Maximum absorbance (*v*_{max}) are quoted in wavenumbers (cm⁻¹) and the abbreviations used to describe the absorbance intensity are: w, weak; m, medium; s, strong. Proton nuclear magnetic resonance (¹H-NMR) and carbon nuclear magnetic resonance (¹³C-NMR) were recorded using ambient probe temperatures on the following instruments: Bruker DXP 400, Bruker Avance DXP 400, Bruker Avance 500 BB-ATM, Bruker Avance Cyro 500. The following deuterated solvents were used: chloroform (CDCl₃) and methanol (CD₃OD). ¹H-NMR chemical shifts (δ) are quoted in ppm relative to the residual non-deuterated solvent peak and coupling constants (*J*) are quoted to the nearest 0.1 Hertz (Hz). Spectral data is reported as follows: chemical shift, integration, multiplicity [s, singlet; d, doublet; t, triplet; q, quartet; sept, septuplet; m, multiplet; br, broad; or as a combination of these, *e.g.* br s, dd *etc.*], coupling constant(s) and

assignment. Proton assignment is supported by COSY (2D ^1H – ^1H) spectra where necessary. Carbon assignment is supported by DEPT editing and HMQC (2D one bond ^1H – ^{13}C) correlations where necessary. High resolution mass spectrometry (HRMS) was carried out with a Micromass Q-TOF or a Micromass LCT premier spectrometer using electrospray ionisation (ESI) or electron ionisation (EI) and the calculated mass value relative to found mass value is within the error limits of ± 5 ppm mass units. Low resolution mass spectrometry (LCMS) was carried out using either method LCMS (A) or LCMS (B). LCMS (A): Acquity UPLC BEH C18 column (50mmx2.1mm i.d. 1.7 μm packing diameter) at 40 $^\circ\text{C}$. Solvent A = 0.1% v/v solution of formic acid in water. Solvent B = 0.1% v/v solution of formic acid in acetonitrile. The gradient employed was over 2 min going from 100% A to 100% B at a flow rate of 1 ml min $^{-1}$. LCMS (B): ABZ++ column. Solvent A = 1% v/v solution of formic acid and 10 mM ammonium acetate in water. Solvent B = 0.05% v/v solution of formic acid and 5% water in acetonitrile. The gradient was employed over 8 min going from 100% A to 100% B at a flow rate of 5 ml min $^{-1}$. The UV detection was an averaged signal from wavelength of 210 nm to 350 nm and mass spectra were recorded on a mass spectrometer using alternate-scan positive and negative mode electrospray ionisation. Melting points were carried out using a Buchi melting point B545 apparatus and are uncorrected.

General method A, for the hydrosilylation of terminal alkynes

A solution of tri-*tert*-butylphosphine (0.1 mol%, 1.0 M in toluene) was added to a solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (0.1 mol%, 0.1 M in xylenes) under N_2 and stirred for 5 min. On cooling the reaction to 0 $^\circ\text{C}$, 1,1,3,3-tetramethyldisiloxane (**11**) (1 equiv) in anhydrous toluene (~0.13 ml per mmol disiloxane) was added followed by terminal alkyne (**10**) (2 equiv) in anhydrous toluene (~0.07 ml per mmol alkyne). The reaction mixture was stirred at room temperature for 16 h. Solvent was removed and crude residue purified by flash silica chromatography to yield vinylidisiloxane (**3**).

(*E*)- β -Distyryltetramethyldisiloxane (**3a**)³¹

Following general method A, the crude product was purified by flash silica column chromatography eluting with a gradient of dichloromethane:cyclohexane (0:100 \rightarrow 50:50) to yield the product as a colourless oil (96%). R_f 0.39 [petroleum ether 40–60]. ν_{max} (neat)/cm $^{-1}$ 2944 (m, C–H), 2867 (m, C–H), 1641 (w, C=C), 1516 (s, C=C). δ_{H} (400 MHz, CDCl_3) 7.44 (4H, d, J = 7.3 Hz, o-Ar CH), 7.33 (4H, t, J = 7.4 Hz, m-Ar CH), 7.24–7.30 (2H, m, p-Ar CH), 6.97 (2H, d, J = 19.3 Hz, SiCH=CHAr), 6.46 (2H, d, J = 19.1 Hz, SiCH=CH), 0.27 (12H, s, Si(CH $_3$) $_2$). δ_{C} (101 MHz, CDCl_3) 144.3 (SiCH=CH), 138.2 (Ar C), 128.6 (Ar CH), 128.5 (SiCH=CH), 128.2 (Ar CH), 126.5 (Ar CH), 0.9 (Si(CH $_3$) $_2$).

(*E*)- β -Di-(4-nitrostyryl)-tetramethyldisiloxane (**3b**)

Following general method A, the crude residue was purified by flash silica column chromatography eluting with a gradient of dichloromethane:cyclohexane (0:100 \rightarrow 50:50) to yield product as a colourless oil (90%). R_f 0.13 [dichloromethane:cyclohexane (30:70)]. ν_{max} (neat)/cm $^{-1}$ 2961 (w, C–H), 1589 (m, C=C), 1512

(s, C=C). δ_{H} (400 MHz, CDCl_3) 8.20 (4H, d, J = 8.8 Hz, Ar CH), 7.56 (4H, d, J = 8.8 Hz, Ar CH), 7.00 (2H, d, J = 19.1 Hz, SiCH=CHAr), 6.65 (2H, d, J = 19.1 Hz, SiCH=CHAr), 0.31 (12H, s, Si(CH $_3$) $_2$). δ_{C} (101 MHz, CDCl_3) 147.7 (Ar CNO $_2$), 144.4 (Ar C), 142.3 (SiCH=CH), 134.8 (SiCH=CH), 127.4 (Ar CH), 124.3 (Ar CH). LCMS (A) R_t 1.65 min, $[\text{M}+\text{H}_2\text{O}]^+$ 445.9. HRMS (ESI) m/z found 429.1314, $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_5\text{Si}_2$ (MH $^+$) requires 429.1302 (Δ = 2.8 ppm).

(*E*)- β -Di-(4-methoxystyryl)-tetramethyldisiloxane (**3c**)

Following general method A, the crude residue was purified by flash silica column chromatography eluting with a stepped gradient of dichloromethane:petroleum ether 40–60 (0:100 \rightarrow 20:80) to yield product as a white solid (91%). R_f 0.46 [dichloromethane:petroleum ether 40–60 (50:50)]. ν_{max} (neat)/cm $^{-1}$ 2959 (m, C–H), 2839 (w, C–H), 1602 (s, C=C), 1571 (w, C=C), 1506 (s, C=C). δ_{H} (500 MHz, CDCl_3) 7.36 (4H, d, J = 8.8 Hz, Ar CH), 6.90 (2H, d, J = 19.2 Hz, SiCH=CHAr), 6.85 (4H, d, J = 8.8 Hz, Ar CH), 6.28 (2H, d, J = 19.2 Hz, SiCH=CHAr), 3.82 (6H, s, OCH $_3$), 0.23 (12H, s, Si(CH $_3$) $_2$). δ_{C} (125 MHz, CDCl_3) 159.7 (Ar COCH $_3$), 143.7 (SiCH=CH), 131.1 (Ar C), 127.8 (Ar CH), 125.9 (Ar CH), 113.9 (SiCH=CH), 55.3 (OCH $_3$), 0.9 (Si(CH $_3$) $_2$). m.p. 58.0–58.6 $^\circ\text{C}$. HRMS (ESI) m/z found 421.1626, $\text{C}_{22}\text{H}_{30}\text{O}_3\text{Si}_2\text{Na}$ (MNa $^+$) requires 421.1621 (Δ = 1.1 ppm).

(*E*)- β -Di-(3-pyridylvinyl)-tetramethyldisiloxane (**3d**)

Following general method A except heated reaction at 60 $^\circ\text{C}$, the crude residue was purified by flash silica column chromatography eluting with a gradient of ethyl acetate:cyclohexane (25:75 \rightarrow 100:0) to yield product as a colourless oil (94%). R_f 0.21 [ethyl acetate]. ν_{max} (neat)/cm $^{-1}$ 2957 (w, C–H), 1606 (m, C=C), 1566 (w, C=C). δ_{H} (400 MHz, CDCl_3) 8.63 (2H, d, J = 2.0 Hz, Ar CH), 8.49 (2H, dd, J = 4.8, 1.5 Hz, Ar CH), 7.74 (2H, ddd, J = 7.9, 2.0, 1.9 Hz, Ar CH), 7.23–7.28 (2H, m, Ar CH), 6.94 (2H, d, J = 19.1 Hz, SiCH=CHAr), 6.54 (2H, d, J = 19.3 Hz, SiCH=CHAr), 0.28 (12H, s, Si(CH $_3$) $_2$). δ_{C} (101 MHz, CDCl_3) 149.2 (Ar CH), 148.7 (Ar CH), 140.8 (SiCH=CH), 133.4 (Ar C), 132.8 (Ar CH), 131.5 (SiCH=CH), 123.5 (Ar CH), 0.8 (Si(CH $_3$) $_2$). LCMS (A) R_t 0.96 min, $[\text{M}+\text{H}]^+$ 340.9. HRMS (ESI) m/z found 341.1494, $\text{C}_{18}\text{H}_{25}\text{N}_2\text{O}_2\text{Si}_2$ (MH $^+$) requires 341.1505 (Δ = –3.2 ppm).

(*E*)- β -Di-(5-methylhex-1-enyl)-tetramethyldisiloxane (**3e**)

Following general method A, the crude residue was purified by flash silica column chromatography eluting with cyclohexane (100%) to yield product as a colourless oil (89%). R_f 0.42 [cyclohexane]. ν_{max} (neat)/cm $^{-1}$ 2956 (m, C–H), 2928 (w, C–H), 2849 (w, C–H), 1619 (m, C=C). δ_{H} (400 MHz, CDCl_3) 6.10 (2H, dt, J = 18.6, 6.3 Hz, SiCH=CHCH $_2$), 5.57–5.65 (2 H, m, SiCH=CH), 2.07–2.15 (4H, m, SiCH=CHCH $_2$), 1.51–1.62 (2H, m, CH(CH $_3$) $_2$), 1.25–1.33 (4H, m, CH $_2$ CH(CH $_3$) $_2$), 0.90 (12H, d, J = 6.5 Hz, CH(CH $_3$) $_2$), 0.12 (12H, s, Si(CH $_3$) $_2$). δ_{C} (101 MHz, CDCl_3) 148.6 (SiCH=CH), 129.5 (SiCH=CH), 38.1 (CH $_2$ CH(CH $_3$) $_2$), 34.8 (SiCH=CHCH $_2$), 28.0 (CH(CH $_3$) $_2$), 22.9 (CH(CH $_3$) $_2$), 1.2 (Si(CH $_3$) $_2$). HRMS (ESI) m/z found 349.2347, $\text{C}_{18}\text{H}_{38}\text{OSi}_2\text{Na}$ (MNa $^+$) requires 349.2353 (Δ = 1.9 ppm).

(*E*)- β -Di-(4-*tert*-butyldimethylsilanyloxy)but-1-enyl)tetramethyldisiloxane (3f)

Following general method A, the crude residue was purified by flash silica column chromatography eluting with a gradient of dichloromethane : cyclohexane (0 : 100 \rightarrow 25 : 75) to yield product as a colourless oil (89%). R_f 0.48 [dichloromethane : cyclohexane (50 : 50)]. ν_{\max} (neat)/cm⁻¹ 2955 (w, C–H), 2930 (w, C–H), 2858 (w, C–H), 1620 (w, C=C). δ_H (400 MHz, CDCl₃) 6.09 (2H, dt, J = 18.8, 6.3 Hz, SiCH=CHCH₂), 5.68 (2H, d, J = 18.6 Hz, SiCH=CH), 3.68 (4H, t, J = 6.8 Hz, CH₂CH₂O), 2.34 (4H, q, J = 6.5 Hz, SiCH=CHCH₂), 0.90 (18H, s, Si(CH₃)₂C(CH₃)₃), 0.12 (12H, s, Si(CH₃)₂), 0.06 (12H, s, Si(CH₃)₂C(CH₃)₃). δ_C (101 MHz, CDCl₃) 144.3 (SiCH=CH), 131.9 (SiCH=CH), 62.6 (CH₂CH₂O), 40.1 (SiCH=CHCH₂), 26.0 (Si(CH₃)₂C(CH₃)₃), 18.4 (Si(CH₃)₂C(CH₃)₃), 0.8 (Si(CH₃)₂), -5.2 (Si(CH₃)₂C(CH₃)₃). HRMS (ESI) m/z found 525.3069, C₂₄H₅₄O₃Si₄Na (MNa⁺) requires 525.3048 (Δ = 4.0 ppm).

(*E*)- β -Di-(3,3-dimethylbut-1-enyl)-tetramethyldisiloxane (3g)

Following general method A, the crude residue was purified by flash silica column chromatography eluting with cyclohexane (100%) to yield product as a colourless oil (84%). R_f 0.48 [cyclohexane]. ν_{\max} (neat)/cm⁻¹ 2958 (m, C–H), 1615 (m, C=C). δ_H (400 MHz, CDCl₃) 6.10 (2H, d, J = 19.1 Hz, SiCH=CH), 5.51 (2H, d, J = 19.1 Hz, SiCH=CH), 1.01 (18H, s, C(CH₃)₃), 0.12 (12H, s, Si(CH₃)₂). δ_C (101 MHz, CDCl₃) 158.1 (SiCH=CH), 122.6 (SiCH=CH), 34.9 (C(CH₃)₃), 29.0 (C(CH₃)₃), 0.9 (Si(CH₃)₂). HRMS (ESI) m/z found 321.2044, C₁₆H₃₄O₂Si₂Na (MNa⁺) requires 321.2040 (Δ = -1.2 ppm).

(*E*)- β -Di-(3-hydroxy-3-methylbut-1-enyl)-tetramethyldisiloxane (3h)

Following general method A, the crude residue was purified by flash silica column chromatography eluting with a stepped gradient of diethyl ether : petroleum ether 40–60 (0 : 100 \rightarrow 10 : 90 \rightarrow 20 : 80 \rightarrow 30 : 70 \rightarrow 40 : 60) to yield product as a colourless oil (94%). R_f 0.17 [diethyl ether : petroleum ether 40–60 (50 : 50)]. ν_{\max} (neat)/cm⁻¹ 3352 (br m, O–H), 2971 (m, C–H), 1620 (w, C=C). δ_H (400 MHz, CDCl₃) 6.20 (2H, d, J = 19.1 Hz, SiCH=CH), 5.78 (2H, d, J = 18.9 Hz, SiCH=CH), 1.30 (12H, s, COH(CH₃)₂), 0.14 (12H, s, Si(CH₃)₂). δ_C (101 MHz, CDCl₃) 153.9 (SiCH=CH), 124.3 (SiCH=CH), 71.9 (COH(CH₃)₂), 29.3 (COH(CH₃)₂), 0.7 (Si(CH₃)₂). HRMS m/z found 325.1631, C₁₄H₃₀O₃Si₂Na (MNa⁺) requires 325.1642 (Δ = 3.4 ppm).

General method B, for Cross Coupling of Aryl Iodides

Vinylsiloxane (**3**) (1 equiv), aryl iodide (**12**) (1.5 equiv), potassium hydroxide (3 equiv) and Pd(dba)₂ (2.5 mol%) in methanol (~ 7 ml per mmol disiloxane) were stirred for 2–16 h. Reaction mixture was partitioned between water and dichloromethane, separated, aqueous extracted further with dichloromethane. Organic extracts were combined, dried (MgSO₄), concentrated and crude residues purified by flash silica chromatography to yield coupled product (**4**).

(*E*)-1-(4-Styrylphenyl)ethanone (4a)³²

Following general method B, the crude residue purified by flash silica chromatography eluting with a gradient of dichloromethane : hexane (0 : 100 \rightarrow 10 : 90 \rightarrow 20 : 80 \rightarrow 30 : 70) to yield the product as a white solid (91%). R_f 0.17 [dichloromethane : hexane (30 : 70)]. ν_{\max} (neat)/cm⁻¹ 3083 (w, C–H), 3022 (w, C–H), 2956 (w, C–H), 2922 (C–H), 1676 (s, C=O), 1594 (w, C=C), 1577 (w, C=C), 1558 (w, C=C). δ_H (400 MHz, CDCl₃) 7.95 (2H, d, J = 8.4 Hz, Ar CH), 7.58 (2H, d, J = 8.4 Hz, Ar CH), 7.55–7.53 (2H, m, Ar CH), 7.40–7.37 (2H, m, Ar CH), 7.32–7.29 (1H, m, Ar CH), 7.22 (1H, d, J = 16.3 Hz, ArCH=CHAr), 7.12 (1H, d, J = 16.3 Hz, ArCH=CHAr), 2.60 (3H, s, C=OCH₃). δ_C (101 MHz, CDCl₃) 197.8 (C=O), 142.4 (Ar CCOCH₃), 137.1 (Ar C), 136.4 (Ar C), 131.9 (ArCH=CHAr), 129.3 (Ar CH), 129.2 (Ar CH), 128.7 (Ar CH), 127.9 (ArCH=CHAr), 127.2 (Ar CH), 126.9 (Ar CH), 30.1 (C=OCH₃). m.p. 143.2–144.5 °C (lit. value 139–141 °C).³² LCMS (A) R_t 1.24 min, [M+H]⁺ 222.9.

(*E*)-1-Styryl-3-(trifluoromethyl)benzene (4b)³³

Following general method B, the crude residue was purified by flash silica column chromatography eluting with cyclohexane (100%) to yield the product as a white solid (91%). R_f 0.45 [cyclohexane]. ν_{\max} (neat)/cm⁻¹ 3038 (w, C–H), 1575 (w, C=C). δ_H (400 MHz, CDCl₃) 7.84 (1H, s, Ar CH), 7.73 (1H, d, J = 7.8 Hz, Ar CH), 7.58–7.64 (3H, m, Ar CH), 7.51–7.57 (1H, m, Ar CH), 7.46–7.50 (2H, m, Ar CH), 7.36–7.43 (1H, m, Ar CH), 7.25 (1H, d, J = 16.0 Hz, ArCH=CHAr), 7.18 (1H, d, J = 16.0 Hz, ArCH=CHAr). δ_F (376 MHz, CDCl₃) -63.14 (3F, s). δ_C (101 MHz, CDCl₃) 138.1 (Ar C), 136.6 (Ar C), 131.1 (q, J = 31.9 Hz, Ar CCF₃), 130.5 (ArCH=CHAr), 129.5 (Ar CH), 129.1 (Ar CH), 128.8 (Ar CH), 128.2 (Ar CH), 127.1 (ArCH=CHAr), 126.7 (Ar CH), 124.2 (q, J = 273.7 Hz, CF₃), 124.0 (q, J = 4.0 Hz, Ar CH), 123.1 (q, J = 3.7 Hz, Ar CH). m.p. 66.6–67.4 °C (lit. value 67–68 °C).³⁴

(*E*)-1-Nitro-2-styrylbenzene (4c)³⁵

Following general method B, the crude residue was purified by flash silica column chromatography eluting with a gradient of dichloromethane : cyclohexane (0 : 100 \rightarrow 25 : 75) to yield the product as a yellow solid (75%). R_f 0.45 [dichloromethane : cyclohexane (50 : 50)]. ν_{\max} (neat)/cm⁻¹ 3076 (w, C–H), 3022 (w, C–H), 2918 (w, C–H), 2850 (w, C–H), 1625 (w, C=C), 1602 (w, C=C), 1569 (m, C=C). δ_H (400 MHz, CDCl₃) 7.98 (1H, d, J = 8.8 Hz, Ar CH), 7.78 (1H, d, J = 7.8 Hz, Ar CH), 7.58–7.65 (2H, m, Ar CH), 7.56 (2H, d, J = 7.5 Hz, Ar CH), 7.37–7.45 (3H, m, ArCH=CHAr and Ar CH), 7.31–7.36 (1H, m, Ar CH), 7.10 (1H, d, J = 16.1 Hz, ArCH=CHAr). δ_C (101 MHz, CDCl₃) 148.0 (Ar CNO₂), 136.5 (Ar C), 133.9 (Ar C), 133.0 (Ar CH), 133.0 (ArCH=CHAr), 128.8 (Ar CH), 128.6 (Ar CH), 128.1 (Ar CH), 127.9 (ArCH=CHAr), 127.1 (Ar CH), 124.7 (Ar CH), 123.5 (Ar CH). m.p. 72.1–72.9 (lit. value 70–72 °C).³⁶ LCMS (A) R_t 1.30 min, [M+H]⁺ 225.9.

(*E*)-3-Styrylpyridine (4d)³²

Following general method B except heating the reaction at 70 °C, the crude residue was purified by flash silica column

chromatography eluting with a gradient of dichloromethane : hexane (0 : 100 → 50 : 50 → 100 : 0) to yield the product as a white solid (56%). R_f 0.20 [ethyl acetate : cyclohexane (50 : 50)]. ν_{\max} (neat)/cm⁻¹ 3028 (w, C–H), 1687 (s, N=C), 1638 (w, C=C), 1568 (m, C=C). δ_H (400 MHz, CDCl₃) 8.73 (1H, s, Py CH), 8.50 (1H, d, J = 4.0 Hz, Py CH), 7.85 (1H, dt, J = 7.5, 4.0 Hz, Py CH), 7.54 (2H, d, J = 7.5 Hz, Ar CH), 7.39 (2H, t, J = 7.5 Hz, Ar CH), 7.25–7.34 (2H, m, Py CH and Ar CH), 7.18 (1H, d, J = 16.0 Hz, ArCH=CHAr), 7.08 (1H, d, J = 16.0 Hz, ArCH=CHAr). δ_C (101 MHz, CDCl₃) 148.5 (Py CH), 136.6 (Ar or Py C), 133.0 (Ar or Py C), 132.7 (Py CH), 130.8 (ArCH=CHAr), 128.8 (Ar CH), 128.2 (Ar CH), 126.6 (Ar CH and Py CH), 124.9 (ArCH=CHAr), 123.5 (Py CH). m.p. 77.6–79.9 °C (lit. value 81–83 °C).³² LCMS (A) R_t 0.73 min, [M+H]⁺ 182.0.

(E)-1-Methyl-4-styrylbenzene (4e)³⁵

Following general method B except using potassium hydroxide (7 equiv.), adding tri(*o*-tolyl)phosphine (5 mol%) and heating the reaction mixture at 80 °C, the crude residue was purified by flash silica column chromatography eluting with cyclohexane (100%) to yield the product as a white solid (72%). R_f 0.38 [cyclohexane]. ν_{\max} (neat)/cm⁻¹ 3023 (w, C–H), 2914 (w, C–H), 2856 (w, C–H), 1594 (w, C=C), 1576 (w, C=C). δ_H (400 MHz, CDCl₃) 7.60 (2H, d, J = 7.5 Hz, Ar CH), 7.51 (2H, d, J = 8.0 Hz, Ar CH), 7.44 (2H, t, J = 7.5 Hz, Ar CH), 7.31–7.36 (1H, m, Ar CH), 7.26 (2H, d, J = 8.0 Hz, Ar CH), 7.19 (1H, d, J = 16.0 Hz, ArCH=CHAr), 7.14 (1H, d, J = 16.0 Hz, ArCH=CHAr), 2.45 (3H, s, CH₃). δ_C (101 MHz, CDCl₃) 137.5 (Ar C), 134.5 (Ar C), 129.4 (Ar CH), 128.6 (Ar CH), 128.6 (Ar CH), 127.7 (ArCH=CHAr), 127.4 (ArCH=CHAr), 126.4 (Ar CH), 126.4 (Ar CH and Ar CMe), 21.3 (CH₃). m.p. 119.7–120.9 (lit. value 118–119 °C).³⁷

(E)-1-Methoxy-4-styrylbenzene (4f)³²

Following general method B except using potassium hydroxide (7 equiv.), adding tri(*o*-tolyl)phosphine (5 mol%) and heating the reaction mixture at 80 °C, the crude residue was purified by flash silica column chromatography eluting with a gradient of dichloromethane : cyclohexane (0 : 100 → 25 : 75) to yield the product as a white solid (66%). R_f 0.40 [dichloromethane : petroleum ether 40–60 (40 : 60)]. ν_{\max} (neat)/cm⁻¹ 3022 (w, C–H), 3003 (w, C–H), 2964 (w, C–H), 2838 (w, C–H), 1601 (w, C=C), 1593 (w, C=C), 1571 (w, C=C), 1509 (w, C=C). δ_H (400 MHz, CDCl₃) 7.41 (2H, d, J = 7.4 Hz, Ar CH), 7.38 (2H, d, J = 8.7 Hz, Ar CH), 7.28–7.24 (2H, m, Ar CH), 7.17–7.13 (1H, m, Ar CH), 6.99 (1H, d, J = 16.3 Hz, ArCH=CHAr), 6.89 (1H, d, J = 16.3 Hz, ArCH=CHAr), 6.82 (2H, d, J = 8.7 Hz, Ar CH), 3.75 (3H, s, OCH₃). δ_C (101 MHz, CDCl₃) 159.7 (Ar COCH₃), 138.1 (Ar C), 130.6 (Ar C), 129.0 (Ar CH), 128.6 (ArCH=CHAr), 128.1 (Ar CH), 127.6 (Ar CH), 127.0 (ArCH=CHAr), 126.7 (Ar CH), 114.6 (Ar CH), 55.7 (OCH₃). m.p. 130.5–132.2 °C (lit. value 134–136 °C).³² LCMS (A) R_t 1.39 min, [M+H]⁺ 211.0.

(E)-1-(4-(4-Nitrostyryl)phenyl)ethanone (4g)³⁸

Following general method B, the crude residue was purified by flash silica column chromatography eluting with a gradient of dichloromethane : cyclohexane (0 : 100 → 100 : 0) to yield the

product as a yellow solid (70%). R_f 0.25 [dichloromethane]. ν_{\max} (neat)/cm⁻¹ 2922 (w, C–H), 1671 (s, C=O ketone), 1598 (s, C=C), 1559 (m, C=C). δ_H (400 MHz, CDCl₃) 8.26 (2 H, d, J = 8.8 Hz, Ar CH), 8.00 (2 H, d, J = 8.3 Hz, Ar CH), 7.69 (2 H, d, J = 8.8 Hz, Ar CH), 7.65 (2 H, d, J = 8.3 Hz, Ar CH), 7.32 (1 H, d, J = 16.0 Hz, ArCH=CHAr), 7.26 (1 H, d, J = 16.0 Hz, ArCH=CHAr), 2.64 (3 H, s, C=OCH₃). δ_C (101 MHz, CDCl₃) 197.0 (C=O), 146.9 (Ar CNO₂), 142.8 (Ar CCOCH₃), 140.3 (Ar C), 136.6 (Ar C), 131.6 (ArCH=CHAr), 128.7 (Ar CH), 128.6 (ArCH=CHAr), 126.9 (Ar CH), 126.7 (Ar CH), 123.9 (Ar CH), 26.3 (C=OCH₃). m.p. 188.2–193.8 °C (lit. value 194–197 °C).³⁸ LCMS (A) R_t 1.22 min, [M – H][–] 265.0. HRMS (ESI) m/z found 290.0792, C₁₆H₁₃NO₃Na (MNa⁺) requires 290.0788 (Δ = –1.5 ppm).

(E)-1-(4-(4-methoxystyryl)phenyl)ethanone (4h)¹⁹

Following general method B, the crude residue was purified by flash silica column chromatography eluting with a gradient of dichloromethane : petroleum ether (50 : 50 → 70 : 30) to yield the product as a yellow solid (83%). R_f 0.49 [ethyl acetate : petroleum ether 40–60 (50 : 50)]. ν_{\max} (neat)/cm⁻¹ 3330–2842 (w, C–H), 1667 (s, C=O), 1595 (m C=C), 1559 (w, C=C). δ_H (400 MHz, CDCl₃) 7.93 (2 H, d, J = 8.4 Hz, Ar CH), 7.54 (2 H, d, J = 8.3 Hz, Ar CH), 7.47 (2 H, d, J = 8.7 Hz, Ar CH), 7.17 (1 H, d, J = 16.3 Hz, ArCH=CHAr), 6.99 (1 H, d, J = 16.3 Hz, ArCH=CHAr), 6.91 (2 H, d, J = 8.7 Hz, Ar CH), 3.83 (3 H, s, OCH₃), 2.59 (3 H, s, C=OCH₃). δ_C (100 MHz, CDCl₃) 197.9 (C=O), 160.3 (Ar C), 142.8 (Ar C), 136.0 (Ar C), 131.44 (CH), 129.9 (Ar C), 129.3 (CH), 128.8 (CH), 126.6 (CH), 125.7 (CH), 114.6 (CH), 55.7 (OCH₃), 26.9 (C=OCH₃). LCMS (B) R_t 4.78 min, [M+H]⁺ 253.2.

(E)-1-(4-(2-(Pyridin-3-yl)vinyl)phenyl)ethanone (4i)³⁹

Following general method B except heating the reaction at 50 °C, the crude residue was purified by flash silica column chromatography eluting with a gradient of ethyl acetate : cyclohexane (25 : 75 → 100 : 0) to yield the product as a white solid (40.0 mg, 61%). R_f 0.30 [ethyl acetate]. ν_{\max} (neat)/cm⁻¹ 3021 (w, C–H), 1671 (s, C=O ketone), 1599 (s, C=C), 1558 (w, C=C), 1583 (w, C=C), 1571 (w, C=C), 1561 (w, C=C). δ_H (400 MHz, CDCl₃) 8.83 (1 H, d, J = 1.8 Hz, Py CH), 8.60 (1 H, dd, J = 4.8, 1.5 Hz, Py CH), 8.05 (2 H, d, J = 8.4 Hz, Ar CH), 7.93 (1 H, ddd, J = 8.1, 1.8, 1.5 Hz, Py CH), 7.68 (2 H, d, J = 8.4 Hz, Ar CH), 7.39 (1 H, dd, J = 8.1, 4.8 Hz, Py CH), 7.27 (2 H, s, ArCH=CHAr), 2.69 (3 H, s, C=OCH₃). δ_C (101 MHz, CDCl₃) 197.4 (C=O), 149.2 (Py CH), 148.8 (Py CH), 141.2 (Ar CCOCH₃), 136.5 (Py C), 133.0 (Py CH), 132.4 (Ar C), 129.6 (ArCH=CHAr), 128.9 (Ar CH), 127.6 (ArCH=CHAr), 126.7 (Ar CH), 123.6 (Py CH), 26.6 (C=OCH₃). m.p. 106.5–108.5 °C (lit. value 99–101 °C).³⁹ LCMS (A) R_t 0.69 min, [M+H]⁺ 224.0.

(E)-1-(4-(5-Methylhex-1-enyl)phenyl)ethanone (4j)⁴⁰

Following general method B, the crude residue was purified by flash silica column chromatography eluting with a gradient of dichloromethane : cyclohexane (0 : 100 → 100 : 0) to yield the product as a colourless oil (19%). R_f 0.55 [dichloromethane]. ν_{\max} (neat)/cm⁻¹ 2955 (w, C–H), 2927 (w, C–H), 2869 (w, C–H), 2849 (w, C–H), 1679 (s, C=O ketone), 1648 (w, C=C),

1601 (s, C=C), 1563 (w, C=C). δ_{H} (400 MHz, CDCl_3) 7.89 (2H, d, $J = 8.3$ Hz, Ar CH), 7.41 (2H, d, $J = 8.6$ Hz, Ar CH), 6.33–6.47 (2H, m, ArCH=CHCH₂), 2.59 (3H, s, COCH₃), 2.25 (2H, td, $J = 7.7$, 5.8 Hz, ArCH=CHCH₂), 1.62 (1H, apparent sept, $J = 6.5$ Hz, CH(CH₃)₂), 1.34–1.42 (2H, m, CH₂CH(CH₃)₂), 0.93 (6H, d, $J = 6.8$ Hz, CH(CH₃)₂). δ_{C} (101 MHz, CDCl_3) 197.6 (C=O), 142.7 (Ar CCOCH₃), 135.3 (Ar C), 134.7 (CH=CH), 128.7 (CH=CH and Ar CH), 125.9 (Ar CH), 38.2 (CH₂CH(CH₃)₂), 31.0 (ArCH=CHCH₂), 27.6 (CH(CH₃)₂), 26.5 (C=OCH₃), 22.5 (CH(CH₃)₂). LCMS (B) R_{t} 5.20 min, $[\text{M}+\text{H}]^+$ 217.28.

(E)-1-(4-(4-(tert-Butyldimethylsilyloxy)but-1-enyl)phenyl)ethanone (4k)

Following general method B except heating the reaction at 50 °C, the crude residue was purified by flash silica column chromatography eluting with a gradient of dichloromethane:cyclohexane (0:100 → 100:0) to yield the product as a colourless oil (8%). R_{f} 0.35 [dichloromethane]. ν_{max} (neat)/cm⁻¹ 2955 (w, C–H), 2929 (w, C–H), 2857 (w, C–H), 1683 (s, C=O ketone), 1650 (w, C=C), 1603 (s, C=C), 1563 (w, C=C). δ_{H} (400 MHz, CDCl_3) 7.90 (2H, d, $J = 8.3$ Hz, Ar CH), 7.42 (2H, d, $J = 8.6$ Hz, Ar CH), 6.34–6.53 (2H, m, ArCH=CHCH₂), 3.76 (2H, t, $J = 6.5$ Hz, CH₂CH₂O), 2.60 (3H, s, COCH₃), 2.47 (2H, q, $J = 6.6$ Hz, ArCH=CHCH₂), 0.91 (9H, s, Si(CH₃)₂C(CH₃)₃), 0.07 (6H, s, Si(CH₃)₂C(CH₃)₃). δ_{C} (101 MHz, CDCl_3) 197.6 (C=O), 142.4 (Ar CCOCH₃), 135.5 (Ar C), 130.8 (CH=CH), 130.7 (CH=CH), 128.8 (Ar CH), 126.0 (Ar CH), 62.6 (CH₂CH₂O), 36.7 (ArCH=CHCH₂), 26.6 (C=OCH₃), 25.9 (Si(CH₃)₂C(CH₃)₃), 18.4 (Si(CH₃)₂C(CH₃)₃), –5.2 (Si(CH₃)₂C(CH₃)₃). LCMS (B) R_{t} 5.37 min, $[\text{M}+\text{H}]^+$ 305.20. HRMS (ESI) m/z found 305.1938, C₁₈H₂₉O₂Si (MH⁺) requires 305.1937 ($\Delta = 0.3$ ppm).

(E)-1-(4-(3,3-Dimethylbut-1-enyl)phenyl)ethanone (4l)⁴¹

Following general method B except heating the reaction at 50 °C, the crude residue was purified by flash silica column chromatography eluting with a gradient of dichloromethane:cyclohexane (0:100 → 50:50) to yield the product as a colourless oil (24%). R_{f} 0.50 [dichloromethane]. ν_{max} (neat)/cm⁻¹ 2960 (w, C–H), 2867 (w, C–H), 1682 (s, C=O ketone), 1645 (w, C=C), 1603 (s, C=C), 1563 (w, C=C). δ_{H} (400 MHz, CDCl_3) 7.90 (2H, d, $J = 8.3$ Hz, Ar CH), 7.44 (2H, d, $J = 8.3$ Hz, Ar CH), 6.31–6.45 (2H, m, CH=CH), 2.60 (3H, s, COCH₃), 1.14 (9H, s, C(CH₃)₃). δ_{C} (101 MHz, CDCl_3) 197.7 (C=O), 145.0 (CH=CH), 142.9 (Ar CCOCH₃), 135.4 (Ar C), 128.7 (Ar CH), 126.0 (Ar CH), 123.9 (CH=CH), 33.7 (C(CH₃)₃), 29.4 (C(CH₃)₃), 26.6 (C=OCH₃). LCMS (A) R_{t} 1.35 min, $[\text{M}+\text{H}]^+$ 203.1. HRMS (ESI) m/z found 203.1435, C₁₄H₁₉O (MH⁺) requires 203.1436 ($\Delta = -0.5$ ppm).

(E)-1-(4-(3-Hydroxy-3-methylbut-1-enyl)phenyl)ethanone (4m)

Following general method B, except using 5 equiv. of base and heating to 50 °C, the crude was purified by flash silica chromatography eluting with a gradient of petroleum ether 40–60:ethyl acetate (80:20 → 70:30 → 60:40) to yield the product as a colourless oil (39%). R_{f} 0.30 [dichloromethane:petroleum ether (40–60) (30:70)]. ν_{max} (neat)/cm⁻¹ 3472 (w, O–H), 3220–2930 (w,

C–H), 1668 (s, C=O, ketone), 1600 (m, C=C), 1563 (m, C=C). δ_{H} (400 MHz, CDCl_3) 7.90 (2H, d, $J = 8.4$ Hz, Ar CH), 7.45 (2H, d, $J = 8.3$ Hz, Ar CH), 6.64 (H, d, $J = 16.1$ Hz, CH=CH), 6.47 (1H, d, $J = 16.1$ Hz, CH=CH), 2.59 (3H, s, COCH₃), 1.44 (6H, s, C(CH₃)₂OH). δ_{C} (101 MHz, CDCl_3) 198.1 (C=O), 142.2 (Ar CCOCH₃), 140.9 (Ar CH), 136.3 (Ar CCH=CH), 129.2 (CH=CH), 126.9 (CH=CH), 125.9 (Ar CH), 71.5 (C(CH₃)₂OH), 30.3 (C(CH₃)₂OH), 27.0 (C=OCH₃).

1,1,3,3-Tetramethyl-1,3-bis[2-(trimethylsilyl)ethenyl]-, (E,E)-disiloxane (15)

Following general method A, except using ethynyl(trimethyl)silane (2.2 equiv.) as the acetylene, the crude residue was purified by flash silica column chromatography eluting with hexane (100%) to yield product as a volatile colourless oil (70%). R_{f} 0.54 [hexane]. ν_{max} (neat)/cm⁻¹ 2957 (w, C–H), 1407 (w, C=C). δ_{H} (400 MHz, CDCl_3) 6.64 (2H, d, $J = 22.6$ Hz, SiCH=CHSi(CH₃)₃), 6.53 (2H, d, $J = 22.6$ Hz, SiCH=CHSi(CH₃)₃), 0.13 (12H, s, Si(CH₃)₂), 0.07 (18H, s, Si(CH₃)₃). δ_{C} (101 MHz, CDCl_3) 153.0 (SiCH=CHSi(CH₃)₃), 151.5 (SiCH=CHSi(CH₃)₃), 2.1 (Si(CH₃)₂), 0.03 (Si(CH₃)₃). HRMS (ESI) m/z found 353.1572, C₁₄H₃₄OSi₄Na (MNa⁺) requires 353.1579 ($\Delta = 2.0$ ppm).

General method C, for the synthesis of (E)-vinyltrimethylsilanes

1,1,3,3-tetramethyl-1,3-bis[2-(trimethylsilyl)ethenyl]-, (E,E)-disiloxane (**15**) (1 equiv.), aryl iodide (1.8 equiv.) and potassium hydroxide (6 equiv.) were dissolved in 'butanol (~30 ml per mmol disiloxane). *Rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (5 mol%) followed by bis(dibenzylideneacetone)palladium(0) (5 mol%) were added and the reaction mixture was heated at 80 °C for 16–19 h. Reaction mixture was partitioned between water and dichloromethane, separated, aqueous extracted further with dichloromethane. Organic extracts were combined, dried (MgSO₄), concentrated and crude residue purified by flash silica chromatography to yield the product (**16**).

(E)-4-Nitrostyryltrimethylsilane (16a)⁴²

Following general method C, the crude residue was purified by flash silica column chromatography eluting with dichloromethane:petroleum ether 40–60 (20:80) to yield product as a bright yellow solid (45%). R_{f} 0.45 [dichloromethane:petroleum ether 40–60 (20:80)]. ν_{max} (neat)/cm⁻¹ 3645–3524 (w, C–H), 2958 (m, C–H), 1592 (m, C=C), 1520 (m, C=C). δ_{H} (400 MHz, CDCl_3) 8.19 (2H, d, $J = 8.8$ Hz, Ar CH), 7.55 (2H, d, $J = 8.7$ Hz, Ar CH), 6.92 (1H, d, $J = 19.1$ Hz, SiCH=CHAr), 6.71 (1H, d, $J = 19.1$ Hz, SiCH=CHAr), 0.19 (9H, s, Si(CH₃)₃). δ_{C} (101 MHz, CDCl_3) 147.1 (Ar CNO₂), 144.4 (Ar C), 141.2 (Ar CH), 136.2 (Ar CH), 126.9 (SiCH=CHAr), 123.9 (SiCH=CHAr), –1.5 (Si(CH₃)₃). m.p. 59 °C (lit. value 59–61 °C).⁴²

3-[(1E)-2-(trimethylsilyl)ethenyl]-pyridine (16b)⁴³

Following general method C, the crude residue was purified by flash silica column chromatography eluting with a gradient of dichloromethane:methanol (99:1 → 98:2 → 97:3) to yield

product as a brown oil (43%). R_f 0.38 [dichloromethane : methanol (98 : 2)]. ν_{\max} (neat)/cm⁻¹ 3549–3424 (w, C–H), 2949 (m, C–H), 2368 (s, C–H), 2313 (s, C–H), 1623 (w, C=C). δ_H (400 MHz, CDCl₃) 8.61 (1H, d, J = 1.7 Hz, Py CH), 8.45 (1H, dd, J = 4.7, 1.3 Hz, Py CH), 7.75–7.72 (1H, m, Py CH), 7.25–7.22 (1H, m, Py CH), 6.84 (1H, d, J = 19.2 Hz, SiCH=CHPy), 6.57 (1H, d, J = 19.2 Hz, SiCH=CHpy), 0.16 (9H, s, Si(CH₃)₃). δ_C (101 MHz, CDCl₃) 148.8 (Py CH), 148.5 (Py CH), 139.9 (Py C), 132.8 (Py CH), 132.6 (Py CH), 123.4 (SiCH=CHPy), 119.6 (SiCH=CHpy), –1.4 (Si(CH₃)₃). HRMS (ESI) m/z found 178.1052, C₁₀H₁₆NSi (MH⁺) requires 178.1059 (Δ = –3.9 ppm).

General method D, for the synthesis of unsymmetrical stilbenes

To a solution of (*E*)-vinyltrimethylsilane (**16**) (1 equiv.) and aryl iodide (1 equiv.) in tetrahydrofuran (~ 4.5 ml per mmol silane) was added a tetrabutylammonium fluoride solution (1.0 M in tetrahydrofuran, 3 equiv.) and bis(dibenzylideneacetone)-palladium(0) (5 mol%). The reaction mixture was stirred at room temperature for 16–19 h, then filtered through silica eluting with dichloromethane and the filtrate was concentrated under reduced pressure. The crude residue was purified by flash silica column chromatography to yield the product.

(*E*)-4-Methyl-4'-nitro-stilbene (**4n**)⁴⁴

Following general method D, the crude residue was purified by flash silica column chromatography eluting with a gradient of dichloromethane : petroleum ether (40–60) (0 : 100 → 10 : 90 → 20 : 80 → 30 : 70) to yield product as a yellow solid (32%). R_f 0.30 [dichloromethane : petroleum ether (40–60) (30 : 70)]. ν_{\max} (neat)/cm⁻¹ 3541–3472 (w, C–H), 1710 (s, C=O, ketone), 1594 (w, C=C), 1518 (m, C=C). δ_H (400 MHz, CDCl₃) 8.21 (2H, d, J = 8.9 Hz, Ar CH), 7.62 (2H, d, J = 8.7 Hz, Ar CH), 7.45 (2H, d, J = 8.1 Hz, Ar CH), 7.25 (1H, d, J = 16.4 Hz, CH=CH), 7.21 (2H, d, J = 8.0 Hz, Ar CH), 7.10 (1H, d, J = 16.3 Hz, CH=CH), 2.39 (3H, s, CH₃). δ_C (101 MHz, CDCl₃) 146.6 (Ar CNO₂), 142.7 (Ar C), 133.3 (Ar C), 129.6 (Ar CCH₃), 127.0 (Ar CH), 126.7 (Ar CH), 126.1 (Ar CH), 125.3 (Ar CH), 124.1 (ArCH=CHAr), 122.7 (ArCH=CHAr), 21.4 (CH₃). m.p. 150 °C (lit. value 150 °C).⁴⁵

Undec-10-yn-1-yl 2-iodobenzoate (**19**)⁴⁶

To a solution of 2-iodobenzoic acid (0.730 g, 2.97 mmol) in dichloromethane was added undec-10-yn-1-ol (0.5 g, 2.97 mmol), *N,N'*-dicyclohexylcarbodiimide (0.72 g, 3.5 mmol) and then 4-(dimethylamino)-pyridine (0.09 g, 0.75 mmol). The reaction was stirred at room temperature for 16 h. The reaction mixture was concentrated and purified by flash silica column chromatography eluting with dichloromethane to yield the product as a colourless oil (1.12 g, 95%). R_f 0.65 [ethyl acetate : petroleum ether (40–60) (5 : 95)]. ν_{\max} (neat)/cm⁻¹ 3303 (m, C–H alkyne), 2927 (m, C–H), 2855 (w, C–H), 2117 (w, C=C), 1726 (s, C=O, ester), 1584 (m, C=C), 1562 (w, C=C). δ_H (400 MHz, CDCl₃) 7.91 (1H, dd, J = 7.6, 0.8 Hz, Ar CH), 7.71 (1H, dd, J = 7.6, 1.6 Hz, Ar CH), 7.33 (1H, td, J = 7.6, 1.2 Hz, Ar CH), 7.07 (1H, td, J = 7.6, 1.6 Hz, Ar CH), 4.26 (2H, t, J = 6.4, OCH₂), 2.10 (2H, dt, J = 7.2, 2.8 Hz CH₂), 1.86 (1H, t, J = 2.4 Hz, C=CH), 1.70 (2H, m, CH₂), 1.44 (2H, m,

CH₂), 1.32 (10H, m, (CH₂)₅). δ_C (101 MHz, CDCl₃) 166.7 (C=O), 141.2 (Ar CH), 135.6 (Ar C), 132.4 (Ar CH), 130.8 (Ar CH), 127.8 (Ar CH), 93.9 (Ar CI), 84.7 (CH₂C=CH), 68.0 (CH₂C=CH), 65.8 (OCH₂), 29.3 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 28.7 (CH₂), 28.5 (CH₂), 28.4 (CH₂), 25.9 (CH₂), 18.4 (CH₂). HRMS (ESI) m/z found 421.0651, C₁₈H₂₃O₂INa (MNa⁺) requires 421.0641 (Δ = –3.9 ppm).

(*E*)-Di-(11-(2-iodobenzoyloxy)undec-1-enyl)tetramethyldisiloxane (**20**)

A solution of tri-*tert*-butylphosphine (4.0 μ L, 0.0024 mmol, 1.0 M in toluene) was added to a solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (60 μ L, 0.0024 mmol, 2% in xylenes) under N₂ and stirred for 5 min. On cooling the reaction to 0 °C, 1,1,3,3-tetramethyldisiloxane (0.085 mL, 0.5 mmol) in anhydrous toluene was added followed by 10-undecyn-1-ol (400 mg, 1.0 mmol) in anhydrous toluene. The reaction mixture was stirred at room temperature for 16 h. The solvent was removed under reduced pressure and the crude residue purified by flash silica column chromatography eluting with a gradient of ethyl acetate : petroleum ether (40–60) (0 : 100 → 5 : 95) to yield product as a colourless oil (0.2 g, 43%). R_f 0.55 [ethyl acetate : petroleum ether (40–60) (5 : 95)]. ν_{\max} (neat)/cm⁻¹ 2853 (m, C–H), 1729 (s, C=O ester), 1618 (w, C=C), 1584 (w, C=C). δ_H (400 MHz, CDCl₃) 7.98 (2H, dd, J = 8, 1.2 Hz, Ar CH), 7.77 (2H, dd, J = 7.6, 1.6 Hz, Ar CH), 7.39 (2H, td, J = 7.6, 1.2 Hz, Ar CH), 7.13 (2H, td, J = 7.6, 1.6 Hz, Ar CH), 6.08 (2H, dt, J = 18.4, 6.4 Hz, SiCH=CH), 5.59 (2H, d, J = 18.4 Hz, SiCH=CH), 4.33 (4H, t, J = 6.8 Hz, OCH₂), 2.06 (4H, m, CH₂), 1.77 (4H, m, CH₂), 1.31 (24H, m, (CH₂)₆), 0.12 (12H, s, Si(CH₃)₂). δ_C (101 MHz, CDCl₃) 166.7 (C=O), 148.0 (SiCH=CH), 141.2 (Ar CH), 135.6 (Ar C), 132.5 (Ar CH), 130.8 (Ar CH), 129.4 (SiCH=CH), 127.9 (Ar CH), 93.9 (Ar CI), 65.9 (OCH₂), 36.5 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 29.2 (CH₂), 28.6 (CH₂), 28.6 (CH₂), 26.0 (CH₂), 0.8 (Si(CH₃)₂). HRMS (EI) m/z found 930.8815, C₄₀H₆₀I₂O₅Si₂ (M⁺) requires 930.8813 (Δ = 0.7 ppm).

(*E*)-4,5,6,7,8,9,10,11-Octahydrobenzo[c][1]oxacyclopentadecin-1(3*H*)-one (**21**)⁴⁷

To a solution of anhydrous tetrahydrofuran and allyl palladium chloride (12 mg, 30 mol%) under N₂ at 0 °C, was added vinylsiloxane (**21**) (100 mg, 0.11 mmol) in tetrahydrofuran and tetrabutylammonium fluoride (0.25 mL, 0.25 mmol) dropwise. The reaction mixture was stirred at 0 °C for 5 h, and then warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure. The crude residue was purified by flash silica column chromatography eluting ethyl acetate : petroleum ether (40–60) (5 : 95) followed by preparative TLC eluting dichloromethane : petroleum ether (40–60) (40 : 60) to yield the product as a colourless oil (12 mg, 22%). R_f 0.40 [dichloromethane : petroleum ether (40–60) (40 : 60)]. ν_{\max} (neat)/cm⁻¹ 2928 (m, C–H), 2855 (m, C–H), 1710 (w, C=O ester), 1649 (m, C=C), 1601 (m, C=C), 1447 (m, C–H). δ_H (400 MHz, CDCl₃) 7.64 (1H, dd, J = 8.0, 1.6 Hz, Ar CH), 7.40 (1H, d, J = 8.0, Ar CH), 7.33 (1H, td, J = 8.0, 1.2 Hz, Ar CH), 7.17 (1H, td, J = 8.0, 1.2 Hz, Ar CH), 6.88 (1H, d, J = 15.6 Hz, CH=CHAr), 5.92 (1H, dt, J = 15.6, 7.6 Hz, CH=CHAr), 4.33 (2H, t, J = 5.2 Hz,

OCH₃), 1.64 (2H, m, CH₂), 2.19 (2H, m, CH₂), 1.33 (12H, m, (CH₂)₆). δ_c (101 MHz, CDCl₃) 167.8 (C), 137.4 (C), 135.0 (CH), 131.7 (CH), 130.4 (C), 130.3 (CH), 129.8 (CH), 127.8 (CH), 127.0 (CH), 65.5 (CH₂), 31.7 (CH₂), 29.3 (CH₂), 28.1 (CH₂), 27.5 (CH₂), 26.4 (CH₂), 25.7 (CH₂), 25.2 (CH₂), 24.5 (CH₂). HRMS (EI) *m/z* found 273.1857, C₁₈H₂₅O₂ (M⁺) requires 273.1855 (Δ = 0.7 ppm).

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