Aza-Peterson Olefinations: Rapid Synthesis of (*E*)-Alkenes

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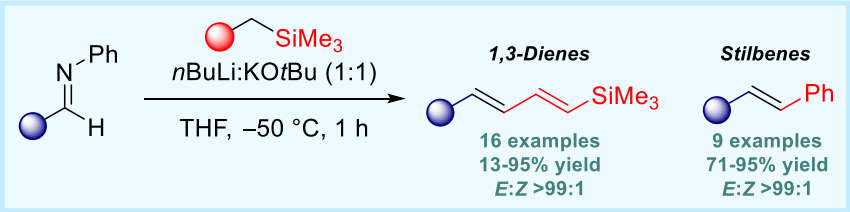

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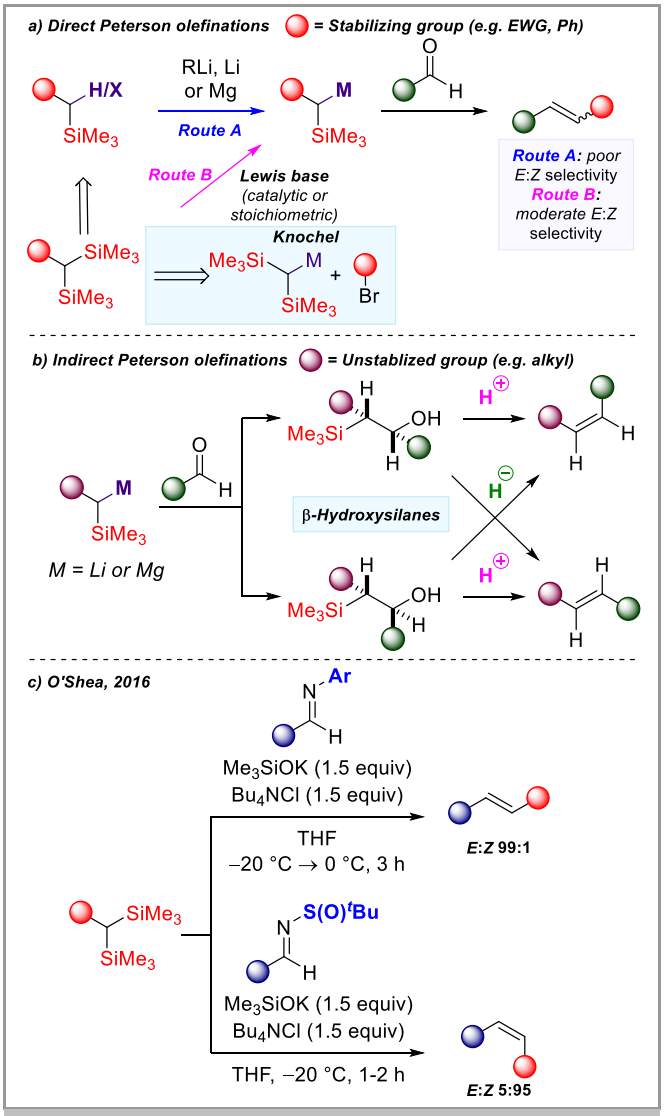
Abstract An aza-Peterson olefination methodology to access 1,3-dienes and stilbene derivatives from the corresponding allyl- or benzyl trimethylsilanes is described. Silanes can be deprotonated using Schlosser's base and added into *N*-phenyl imines or ketones to directly give the desired products in high yields.

Key words Peterson olefination, imines, allyl silanes, Schlosser's base, 1,3-dienes, stilbenes

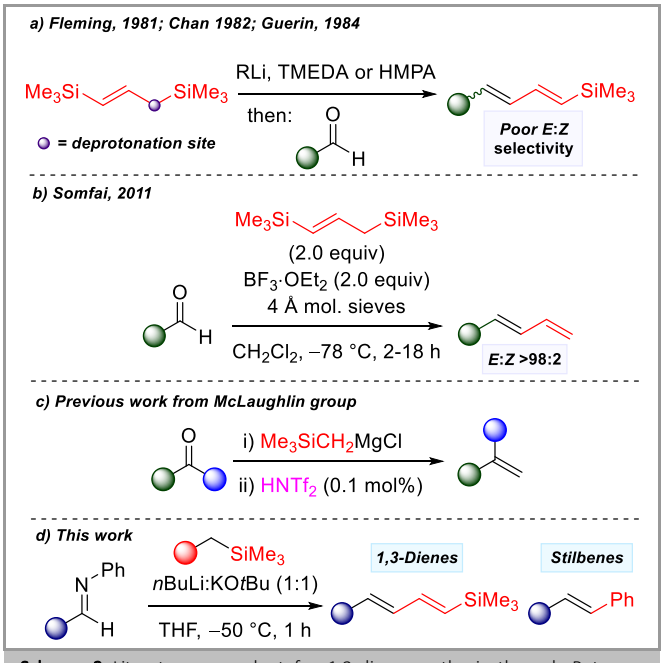
The Peterson olefination, first reported in 1968,[1] is a silicon variant of the Wittig reaction that involves the reaction of α-silyl carbanions with carbonyl-containing compounds to provide the requisite alkene in one or two-steps (via β-hydroxysilanes). Olefination reactions are an important tool for the synthetic chemistry community and a key advantage of the Peterson olefination over the Wittig reaction is the easy removal of volatile silicon by-products vs solid phosphine oxides.[2] α-Silyl carbanions are commonly accessed through deprotonation using a strong base or metal-halogen exchange from the corresponding α-halosilanes (Scheme 1a).[3,4] Bench stable bis(trimethylsilane) reagents have emerged as a milder method to access α-silyl carbanions by activation with catalytic or stoichiometric amounts of Lewis bases (nBu$_4$NF, nBu$_4$NSiF$_2$Ph$_3$, CsF, KOSiMe$_3$/nBu$_4$NCl).[5–10] In most examples, strong bases are still required to synthesise these reagents.[5,8–10] Alternatively, Knochel and co-workers have reported a palladium(0)-catalyzed cross coupling reaction from bis(trimethylsilyl)organometallic reagents and aryl bromides.[6,7] Dependent on the electronics of the silicon reagent, alkenes can either be accessed directly (one step, Scheme 1a) or indirectly (two steps, Scheme 1b) – through isolation of β-hydroxysilanes (Scheme 1b) and treatment under acidic (*anti*-elimination promoted by the β-silicon effect)[11] or basic conditions (*syn*-elimination) to selectively give either the *E* or *Z*-alkene. A long-standing issue for direct Peterson olefinations – using stabilised α-silyl carbanions – is the lack of control over the stereoselectivity of the resulting olefin.[3–5,12,13] O'Shea and co-workers have addressed this problem through replacement of



Scheme 1 Controlling *E*/*Z*-selectivity of direct Peterson olefinations

carbonyl compounds with *N*-aryl or *N*-sulfinyl imines to give *E*- and *Z*-alkenes, respectively (Scheme 1c). [8,10]

The Peterson olefination has been applied to a wide-variety of alkenes, yet the synthesis of 1,3-dienes, an important building block within the synthetic community,[14] is relatively underexplored[15–17]. Common routes to access 1,3-dienes include olefination reactions (Wittig and Horner-Wadsworth-Emmons),[18–20] enyne metathesis,[21,22] and transition metal-catalyzed cross coupling reactions.[23–26] Various groups have reported the synthesis of 1,3-dienes through a Peterson olefination starting from 1,3-bis(trimethylsilyl)propene (Scheme 2a).[27–31] Deprotonation with organolithium bases, in combination with diamine or phosphoramide additives, and addition into carbonyl compounds produces 1,3-diene products in one step, albeit in low yields and poor stereoselectivity.[27,28] Chan and co-workers found that the addition of $MgBr_2$ to the organometallic reagent enabled the isolation of the β-hydroxysilane intermediate, which could be treated under acidic or basic conditions to stereoselectively form (1*E*, 3*E*)- or (1*E*, 3*Z*)-dienes.[28] Guerin and co-workers investigated various aldehydes and symmetrical ketones to give a mixture of 1,3-dienes and the β-hydroxysilane intermediates, which could be converted into the 1,3-diene by treatment with silica gel.[29] Somfai and co-workers reported a Lewis acid mediated Hosomi-Sakurai-type reaction employing aliphatic aldehydes, which provided the terminal (*E*)-1,3-dienes with high geometric selectivity (Scheme 2b).[30] However, strict anhydrous conditions were required to prevent protodesilylation. To date, there are no general set of conditions to access stereodefined 1,3-dienes via a Peterson olefination. Given our groups interest in expanding the utility of the Peterson olefination (Scheme 2c),[32] we wanted to carry out a two-step (indirect) procedure, to access these important structural motifs. β-Hydroxysilanes were prepared via addition of Grignard reagents, to carbonyl compounds, followed by treatment of the β-hydroxysilanes with catalytic Brønsted acids.

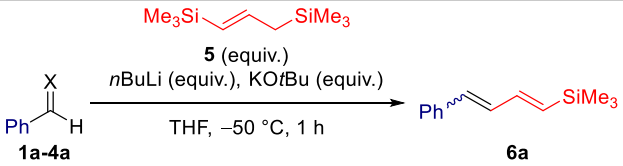


Scheme 2 Literature precedent for 1,3-diene synthesis through Peterson olefinations

The latter step provided alkenes with excellent *E*/*Z* selectivity, though low to moderate yields (20-50%) of β-hydroxysilanes were obtained, which after extensive optimization could not be improved. Addition of the organometallic reagent into carbonyls was accompanied by a background direct Peterson olefination reaction to give *E*/*Z* mixture of alkenes. Herein we report a rapid *E*-selective synthesis of 1,3-butadiene and stilbene derivatives using *N*-phenyl imines to control the *E*/*Z*-selectivity (Scheme 2d).

Inspired by work from the O'Shea group on the synthesis of stilbenes,[8,10] we chose to investigate the use of *N*-phenyl imines **2** to control the *E*/*Z* selectivity. We opted not to use bis(trimethylsilane) reagents and instead focused on the deprotonation conditions used by O'Shea to synthesize these reagents (*n*BuLi, KO*t*Bu and 2,2,6,6-tetramethylpiperidine).[33] To our surprise, there have been no reports of using these conditions to access α-silyl carbanions for Peterson olefinations directly. We started by looking at the synthesis of 1,3-dienes using allyltrimethylsilane derivative **5** (Table 1), which was accessed in one step on a multigram scale from allyltrimethylsilane.[34]

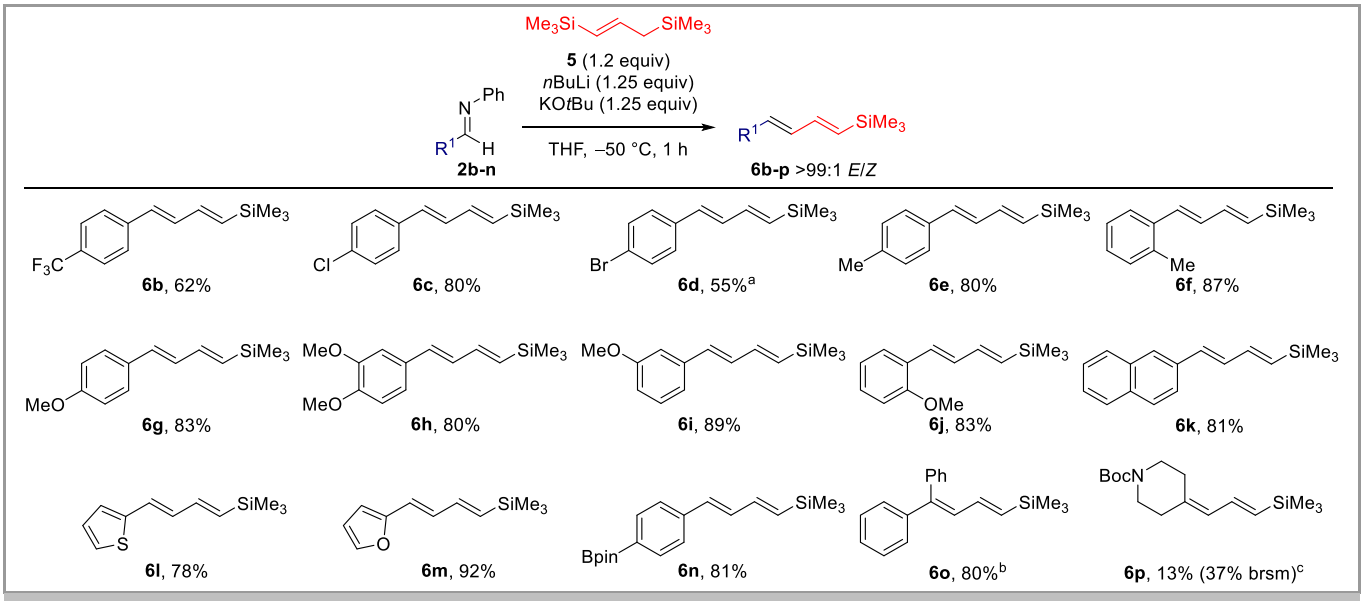
Table 1 Optimisation of aza-Peterson olefination to access 1,3-dienes



Entry	X	5 (equiv.)	*n*BuLi (equiv.)	KO*t*Bu (equiv.)	Yield 6a (%)[a]	*E*/*Z*[b]
1	O **1a**	1.50	1.55	1.55	54[c]	41:59
2	O[d] **1a**	1.50	1.55	1.55	49[c]	39:61
3	NPh **2a**	1.50	1.55	1.55	84	>99:1
4	NPh **2a**	1.20	1.25	1.25	84 (95)[e]	>99:1
5	NS(O)^{t}Bu **3a**	1.20	1.25	1.25	-	-
6	NTs **4a**	1.20	1.25	1.25	-	-

[a] Isolated yields; [b] Determined by ^{1}H NMR; [c] Yield was determined through ^{1}H NMR of the crude product using 1,3,5-trimethoxybenzene as an internal standard; [d] Aldehyde addition at −78 °C; [e] 1 Gram scale yield in parentheses.

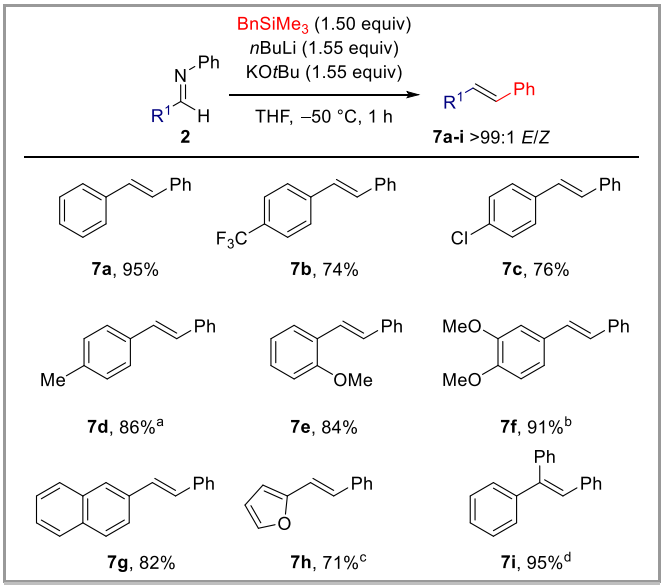
Deprotonation of **5** did not require 2,2,6,6-tetramethylpiperidine and Schlosser's base was sufficient to access the organometallic reagent. Schlosser's base is a superbase made using equimolar amounts of alkylithium (commonly *n*BuLi) and potassium *tert*-butoxide (KO*t*Bu) that has found widespread applications across the synthetic community,[35–39] The optimum temperature for the deprotonation step was −50 °C, however it can be completed at −78 °C with longer reaction times. Degradation was observed at warmer temperatures (0 °C). Deprotonation of **5** using *n*BuLi and tetramethylethylenediamine (TMEDA) or Turbo Grignard (^{i}PrMgCl•LiCl) were unsuccessful under the reaction conditions, highlighting the efficiency of Schlosser's base. Addition of benzaldehyde **1a** to the organometallic reagent of **5** (1.5 equiv.) successfully gave 1,3-diene **6a**, albeit in moderate yields and as a mixture of *E*/*Z*-isomers originating from the electrophilic partner. (entries 1 and 2). The amount of **5** could be reduced (1.25 equiv.) and the reaction was completed on a gram scale without any detrimental effect to the yield (entry 4). The O'Shea



Scheme 3 Substrate scope for aza-Peterson olefination to access 1,3-dienes. [a] Addition of imine **2d** at –78 °C; [b] Using benzophenone; [c] Using *N*-Boc-piperidone.

group has elegantly shown that *N*-sulfinyl imines **3a** (Ellman imines) can be used to access *Z*-stilbenes,[10] however, and rather interestingly, we observed no conversion to these scaffolds under our conditions (entry 5). Similar observations were found with *N*-sulfonyl imines **4a** (entry 6). The observed *E*-selectivity using imines is the result of a diastereoselective addition of the organometallic reagent into imine **2a** – driven by the increased steric hindrance of *N*-phenyl imines versus aldehydes –to give a *trans*-β-aminosilane intermediate, which undergoes elimination (either concerted or step-wise) to give the *E*-1,3-diene **6a**.

Next, we wanted to expand the 1,3-diene synthesis to a series of *N*-phenyl imines **2b-n** (Scheme 3). Electron deficient imines containing trifluoromethyl groups **2b** and halogen-containing aromatics **2c,d** were well tolerated under the reaction conditions. In general, electron-withdrawing groups gave lower yields and for other substrates (e.g. 4-NO_2 or 3,5-CF_3 substituted imines) no reaction was observed, even at elevated temperatures. We tentatively propose that metalation of the electron deficient aromatic ring is inhibiting the reaction. Lithium-halogen exchange of bromides **2d/6d** was minimized by lowering the reaction mixture temperature from −50 °C to −78 °C prior to the addition of imine **2d** to the organometallic reagent of **5**. However, 1,3-diene **6a** (product of lithium-halogen exchange of **6d**, followed by protonation) was isolated in low yields alongside 1,3-diene **6d**. *Ortho*, *meta* and *para*-electron rich aromatics **2e-j**, as well as fused aromatics **2k** gave 1,3-dienes **6e-j** in excellent yields. Imines **2l,m** containing electron rich heterocycles, such as furan and thiophene, were also successfully converted into 1,3-dienes **6l,m** in good yields. Finally, boron-containing imine **2n** gave 1,3-diene **6n** in high yields and possess a functional handle for palladium(0)-catalysed cross coupling reactions. The current methodology was unsuccessful using imines with nitrogen containing heterocycles, such as pyridines (no reaction) and *N*-Ts indoles (degradation). With symmetrical ketones, imines are not required to control any *E*/*Z* selectivity and benzophenone reacted smoothly to give 1,3-diene **6o** in good yield. Symmetrical ketones, e.g. *N*-Boc piperidone, with acidic α-hydrogens proved problematic, as competing deprotonation events can occur. Nevertheless, 1,3-diene **6p** was produced in low yield. We are currently investigating alternative approaches to these scaffolds, which will be reported in due course. The use of unsymmetrical ketones (e.g. acetophenone) gave 1,3-dienes in poor *E*/*Z*-selectivity. 1,3-Dienes **6** showed good stability over a prolonged period of time (6+ months) when stored in either the fridge (4°C) or freezer (−18°C). In terms of applications, Pawluć and coworkers have shown trimethylsilyl-containing 1,3-dienes can be used as a functional handle to form vinyl halides and ayclic dienones.[40] Similarly, Fleming and co-workers have outlined elegant transformations using cycloadducts formed through Diels-Alder reactions of **6** with carbon dienophiles.[27]



Scheme 4 Substrate scope for aza-Peterson olefination to access stilbene derivatives. [a] Reaction run for 3 hours; [b] Reaction run for 4 hours; [c] Crude treated with nBu_4NF (2.0 equiv.); [d] Using benzophenone.

We then moved our attention towards applying this methodology to the synthesis of *E*-stilbenes using commercially available benzyl trimethylsilane (Scheme 4). Using imine **2a** as our model substrate (see supplementary information for optimisation), *E*-stilbene **7a** was formed in excellent yields, though a larger quantity of benzyl trimethylsilane (1.50 equiv.) was required to obtain good reactivity. The reaction successfully gave *E*-stilbenes **7b-g** bearing electron-withdrawing groups **7b**, halogens **7c**, electron-donating groups **7d-f** and fused aromatic groups **7g**. Furan containing alkene **7h** was formed in good yields, but this reaction required further treatment with *n*Bu_4NF, as moderate amounts of silylation at the 2-position of the ring was observed under the olefination conditions. Symmetrical ketones are also tolerated, with benzophenone providing triphenylethylene **7i** in high yields.

In conclusion, we have developed an efficient and selective synthesis of 1*E*, 3*E*-dienes and *E*-stilbenes using Schlosser's base as rapid method to access α-silyl carbanions. Our new methodology provides an operationally simple route to 1,3-diene and stilbene building blocks that, compared to Wittig methodology (solid phosphine oxides), are easily purified and isolated due to volatile silicon by-products. Work is currently underway on expanding the substrate scope and the applications of this methodology in complex synthesis.

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Solvents and reagents

All solvents were purchased from commercial sources and used without purification (HPLC or analytical grade). Anhydrous solvent was obtained from a Pure Solv™ Solvent Purification System. Standard vacuum line techniques were used and glassware was oven dried prior to use. Organic solvents were dried during workup using anhydrous Na_2SO_4.

Purification and chromatography

Thin Layer Chromatography (TLC) was carried out using aluminum plates coated with 60 F254 silica gel. Plates were visualized using UV light (254 or 365 nm) or staining with 1% aq. $KMnO_4$. Normal-phase silica gel chromatography was carried out using either a Biotage Isolera One flash column chromatography system (LPLC) or traditional flash column chromatography using Geduran® Silica gel 60, 40–63 microns RE.

Characterization

Infrared spectroscopy was carried out with a Nicolet® 380 FT/IR – Fourier Transform Infrared Spectrometer. Only the most significant frequencies have been considered during the characterization and selected absorption maxima (ν_{max}) recorded in wavenumbers (cm^{-1}). NMR spectra were recorded using a JEOL® ECS-400 MHz spectrometer using the deuterated solvent stated. Chemical shifts (δ) quoted in parts per million (ppm) and referenced to the residual $CHCl_3$ (δ_H = 7.26 ppm) and $CDCl_3$ (δ_C = 77.16 ppm) peak. Multiplicities are denoted as s- singlet, d- doublet, t- triplet, q- quartet and quin- quintet and derivatives thereof (br denotes a broad resonance peak). Coupling constants recorded as Hz and round to the nearest 0.1 Hz. High Resolution Mass Spectrometry (HRMS) was recorded using an Agilent Technologies® 6540 Ultra-High-Definition (UHD) AccurateMass equipped with a time of flight (Q-TOF) analyzer and the samples were ionized by ESI and APCI techniques and introduced through a high pressure oil chromatography (HPLC) model Agilent Technologies® 1260 Infinity Quaternary LC system.

General Procedure A: Synthesis of *N*-Phenyl Imines

Aniline (1.05 equiv.) was added in one portion to a stirred suspension of an aldehyde (1.0 equiv.) and $MgSO_4$ (1.0 equiv.) in MeOH (2-3 M) at room temperature under argon and then heated at reflux until no starting material remained (12-72 h, reaction monitored by ^{1}H NMR in DMSO-d_6). The reaction mixture was cooled, filtered through celite and the filtrate evaporated under reduced pressure to give the crude product. The crude product was purified by flash column chromatography on silica gel to give imines **2a-n**. *Note: NEt_3 (1-5%) added to column solvent systems to prevent degradation of imines during purification*. All analytical data was in accordance to previously published data.[41–46]

General Procedure B: Synthesis of 1,3-Dienes

*n*BuLi (2.2-2.3 M in hexane, 1.25 equiv.) was added dropwise to a stirred solution of allyl silane **5** (1.20 equiv.) in THF (0.4 M) at −50 °C under argon and stirred for 5 minutes. KO^{t}Bu (1 M solution in THF, 1.25 equiv.) was added dropwise at −50 °C and the reaction mixture stirred for 30 minutes. A solution of ketone/*N*-Ph imine (1.0 equiv.) in THF (0.2 M) was added dropwise at −50 °C, stirred for 30 minutes and then warmed to room temperature. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl. The aqueous phase was extracted three times with CH_2Cl_2, dried (Na_2SO_4) and evaporated under reduced pressure to give the crude product. The crude product was purified by flash column chromatography on silica gel using an appropriate solvent system, as described for each individual procedure. *Note: A commercially available solution of KO^{t}Bu in THF (1 M) was used, however solid KO^{t}Bu (dissolved in THF to make a 1 M solution) can be used without a noticeable decrease in efficiency.*

General Procedure C: Synthesis of Stilbenes

*n*BuLi (2.2-2.4 M in hexane, 1.55 equiv.) was added dropwise to a stirred solution of benzyl trimethylsilane (1.50 equiv.) in THF (0.4 M) at −50 °C under argon and stirred for 5 minutes. KO^{t}Bu (1 M solution in THF, 1.55 equiv.) was added dropwise at −50 °C and the reaction mixture stirred for 30 minutes. A solution of ketone/*N*-Ph imine (1.0 equiv.) in THF (0.2 M) was added dropwise at −50 °C, stirred for 30 minutes and then warmed to room temperature. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl. The aqueous phase was extracted three times with CH_2Cl_2, dried (Na_2SO_4) and evaporated under reduced pressure to give the crude product. The crude product was purified by flash column chromatography on silica gel using an appropriate solvent system, as described for each individual procedure. *Note: A commercially available solution of KO^{t}Bu in THF (1 M) was used, however solid KO^{t}Bu (dissolved in THF to make a 1 M solution) can be used without a noticeable decrease in efficiency.*

(*E*)-Prop-1-ene-1,3-diylbis(trimethylsilane) (**5**)

Using a modified procedure by Schlosser and co-workers,[34] *n*BuLi (2.2 M in hexane, 10.4 mL, 23.3 mmol, 1.1 equiv.) and allyltrimethylsilane (3.30 mL, 20.8 mmol, 1.0 equiv.) were sequentially added dropwise to a stirred solution of KO^{t}Bu (2.61 g, 23.3 mmol, 1.1 equiv.) in THF (21 mL) at −50 ºC under argon and then stirred for 1 hour at −50 ºC. Chlorotrimethylsilane (2.95 mL, 23.3 mmol, 1.1 equiv.) was added dropwise at −50 ºC and the reaction mixture stirred for another 30 minutes. The reaction mixture was warmed up to room temperature and quenched with a saturated aqueous solution of NH_4Cl (10 mL). The organic layer was separated, the aqueous phase was extracted with Et_2O (3 x 20 mL) and the combined organic layers were dried (Na_2SO_4). The solvent was removed under reduced pressure (product is volatile, temperature must be kept < 30 °C). The crude product was purified by flash column chromatography on silica gel (pentane) to give **5** as a colourless liquid (2.71 g, 14.5 mmol, 70%, *E*:*Z* 96:4). Spectral data in accordance to previously published data.[30,34]

R_f (hexane) = 0.87

^{1}H NMR (400 MHz, $CDCl_3$); δ 6.01 (dt, *J* = 18.4, 7.8 Hz, 1H), 5.42 (dt, *J* = 18.4, 1.3 Hz, 1H), 1.62 (dd, *J* = 7.8, 1.3 Hz, 2H), 0.03 (s, 9H), -0.01 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$); δ = 143.8, 128.1, 28.5, −0.8, −0.9.

Trimethyl[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]silane (**6a**).

Using general procedure B, **5** (1.17 g, 6.29 mmol), *n*BuLi (2.3 M in hexane, 2.9 mL, 6.55 mmol) and KO^{t}Bu (1M in THF, 6.6 mL, 6.55 mmol) in THF (18 mL) were treated with imine **2a** (950 mg, 5.24 mmol) in THF (26 mL) to give 1,3-diene **6a** (1.01 g, 4.99 mmol, 95%) as a colourless oil after purification by flash column chromatography (eluent: hexane). Spectral data in accordance to previously published data.[26]

R_f (hexane) = 0.51.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.43–7.39 (m, 2H), 7.35–7.29 (m, 2H), 7.25–7.21 (m, 1H), 6.83–6.65 (m, 2H), 6.58 (d, *J* = 15.4 Hz, 1H), 6.01 (d, *J* = 18.0 Hz, 1H), 0.12 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 144.2, 137.3, 135.1, 133.0, 131.8, 128.7, 127.8, 126.7, −1.1.

Trimethyl{(1*E*,3*E*)-4-[4-(trifluoromethyl)phenyl]buta-1,3-dien-1-yl}silane (**6b**)

Using general procedure B, **5** (118 mg, 0.63 mmol), *n*BuLi (2.2 M in hexane, 0.30 mL, 0.66 mmol) and KO^{t}Bu (1M in THF, 0.66 mL, 0.66 mmol) in THF (1.8 mL) were treated with imine **2b** (132 mg, 0.53 mmol) in THF (2.6 mL) to give 1,3-diene **6b** (88 mg, 0.33 mmol, 62%) as a colourless oil after purification by flash column chromatography (eluent: hexane). Spectral data in accordance to previously published data.[26]

R_f = 0.68.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 6.85 (dd, *J* = 15.6, 10.1 Hz, 1H), 6.69 (dd, *J* = 18.2, 10.1 Hz, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 6.10 (d, *J* = 18.2 Hz, 1H), 0.13 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 143.6, 140.8, 137.5, 134.1, 131.2, 129.4 (q, *J* = 32.1 Hz), 126.7, 125.7 (q, *J* = 3.8 Hz), 123.0, −1.2.

^{19}F (376 MHz, $CDCl_3$) δ -62.4 (s).

Trimethyl[(1*E*,3*E*)-4-(4-chlorophenyl)buta-1,3-dien-1-yl]silane (**6c**)

Using general procedure B, **5** (112 mg, 0.60 mmol), *n*BuLi (2.2 M in hexane, 0.28 mL, 0.63 mmol) and KO^{t}Bu (1M in THF, 0.63 mL, 0.63 mmol) in THF (1.7 mL) were treated with imine **2c** (108 mg, 0.50 mmol) in THF (2.4 mL) to give 1,3-diene **6c** (95 mg, 0.40 mmol, 80%) as a yellow solid after purification by flash column chromatography (eluent: hexane). Spectral data in accordance to previously published data.[40]

R_f (hexane) = 0.60.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.34–7.26 (m, 4H), 6.78–6.62 (m, 2H), 6.52 (d, *J* = 15.2 Hz, 1H), 6.02 (d, *J* = 17.5 Hz, 1H), 0.11 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 143.8, 136.0, 135.8, 133.3, 132.3, 131.6, 128.9, 127.8, −1.2.

Trimethyl[(1*E*,3*E*)-4-(4-bromophenyl)buta-1,3-dien-1-yl]silane (**6d**)

Using general procedure B, **5** (114 mg, 0.61 mmol), *n*BuLi (2.2 M in hexane, 0.28 mL, 0.63 mmol) and KO^{t}Bu (1M in THF, 0.63 mL, 0.63 mmol) in THF (1.8 mL) was cooled from −50 °C to −78 °C after deprotonation step and treated with imine **2d** (132 mg, 0.51 mmol) in THF (2.5 mL) to give 1,3-diene **6d** (143 mg, 0.28 mmol, 55%) as a colourless solid and 1,3-diene **6a** (8.0 mg, 0.04 mmol, 8%) after purification by flash column chromatography (eluent: hexane). Spectral data in accordance to previously published data.[47]

R_f (hexane) = 0.56.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.45–7.41 (m, 2H), 7.28–7.24 (m, 2H), 6.76 (dd, *J* = 15.4, 10.1 Hz, 1H), 6.65 (dd, *J* = 18.0, 10.1 Hz, 1H), 6.50 (d, *J* = 15.4 Hz, 1H), 6.03 (d, *J* = 18.0 Hz, 1H), 0.11 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 143.8, 136.3, 136.1, 132.4, 131.9, 131.6, 128.1, 121.5, −1.2.

Trimethyl[(1*E*,3*E*)-4-(4-methylphenyl)buta-1,3-dien-1-yl]silane (**6e**)

Using general procedure B, **5** (112 mg, 0.60 mmol), *n*BuLi (2.2 M in hexane, 0.28 mL, 0.63 mmol) and KO^{t}Bu (1M in THF, 0.63 mL, 0.63 mmol) in THF (1.7 mL) were treated with imine **2e** (98 mg, 0.50 mmol) in THF (2.4 mL) to give 1,3-diene **6e** (87 mg, 0.40 mmol, 80%) as a colourless oil after purification by flash column chromatography (eluent: hexane). Spectral data in accordance to previously published data.[48]

R_f (hexane) = 0.48.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.78–6.64 (m, 2H), 6.55 (d, *J* = 15.0 Hz, 1H), 5.97 (d, *J* = 17.4 Hz, 1H), 2.34 (s, 3H), 0.11 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 144.4, 137.7, 134.5, 134.4, 133.0, 130.9, 129.5, 126.6, 21.4, −1.1.

Trimethyl[(1*E*,3*E*)-4-(2-methylphenyl)buta-1,3-dien-1-yl]silane (**6f**)

Using general procedure B, **5** (148 mg, 0.79 mmol), *n*BuLi (2.2 M in hexane, 0.37 mL, 0.83 mmol) and KO^{t}Bu (1M in THF, 0.83 mL, 0.83 mmol) in THF (2.3 mL) were treated with imine **2f** (129 mg, 0.66 mmol) in THF (3.2 mL) to give 1,3-diene **6f** (125 mg, 0.58 mmol, 87%) as a colourless oil after purification by flash column chromatography (eluent: hexane).

R_f (hexane) = 0.47.

IR (ATR): 2954, 1246, 998, 865, 832 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.51–7.48 (m, 1H), 7.20–7.14 (m, 3H), 6.84–6.66 (m, 3H), 6.06–5.95 (m, 1H), 2.37 (s, 3H), 0.13 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 144.6, 136.2, 135.9, 135.0, 132.9, 130.7, 130.5, 127.7, 126.2, 125.3, 20.0, −1.1.

HRMS (ESI and APCI): target not found.

Trimethyl[(1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl]silane (**6g**)

Using general procedure B, **5** (112 mg, 0.60 mmol), *n*BuLi (2.2 M in hexane, 0.28 mL, 0.63 mmol) and KO^{t}Bu (1M in THF, 0.63 mL, 0.63 mmol) in THF (1.7 mL) were treated with imine **2g** (106 mg, 0.50 mmol) in THF (2.4 mL) to give 1,3-diene **6g** (96 mg, 0.41 mmol, 83%) as a cream solid after purification by flash column chromatography (eluent: hexane-EtOAc, 99:1). Spectral data in accordance to previously published data.[48]

R_f (hexane-EtOAc, 90:10) = 0.43.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.36–7.32 (m, 2H), 6.88–6.84 (m, 2H), 6.70–6.62 (m, 2H), 6.57–6.50 (m, 1H), 5.97–5.89 (m, 1H), 3.81 (s, 3H), 0.11 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 159.4, 144.5, 133.6, 132.6, 130.1, 129.9, 127.9, 114.2, 55.4, −1.1.

Trimethyl[(1*E*,3*E*)-4-(3,4-dimethoxyphenyl)buta-1,3-dien-1-yl]silane (**6h**)

Using general procedure B, **5** (145 mg, 0.78 mmol), *n*BuLi (2.2 M in hexane, 0.36 mL, 0.81 mmol) and KO^{t}Bu (1M in THF, 0.81 mL, 0.81 mmol) in THF (2.2 mL) were treated with imine **2h** (156 mg, 0.65 mmol) in THF (3.1 mL) to give 1,3-diene **6h** (136 mg, 0.52 mmol, 80%) as a colourless oil that became a sticky colourless solid upon standing after purification by flash column chromatography (eluent: hexane-EtOAc, 95:5 to 90:10).

R_f (hexane-EtOAc, 80:20) = 0.45.

IR (ATR): 2954, 1510, 1230, 1138, 1024, 994, 832 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$); δ 6.96–6.93 (m, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.69– 6.63 (m, 2H), 6.56–6.49 (m, 1H), 6.00–5.92 (m, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 0.11 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 149.1, 149.1, 144.3, 133.9, 132.8, 130.4, 130.1, 120.1, 111.2, 108.7, 56.0, 55.9, −1.1.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{15}H_{22}O_2Si$: 263.1462; found: 263.1459.

Trimethyl[(1*E*,3*E*)-4-(3-methoxyphenyl)buta-1,3-dien-1-yl]silane (**6i**)

Using general procedure B, **5** (112 mg, 0.60 mmol), *n*BuLi (2.2 M in hexane, 0.28 mL, 0.63 mmol) and KO^{t}Bu (1M in THF, 0.63 mL, 0.63 mmol) in THF (1.7 mL) were treated with imine **2i** (112 mg, 0.50 mmol) in THF (2.4 mL) to give 1,3-diene **6i** (103 mg, 0.44 mmol, 89%) as a colourless oil after purification by flash column chromatography (eluent: hexane-EtOAc, 95:5). Spectral data in accordance to previously published data.[26]

R_f (hexane-EtOAc, 90:10) = 0.77.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.23 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.95–6.93 (m, 1H), 6.81–6.74 (m, 2H), 6.67 (dd, *J* = 17.9, 10.1 Hz, 1H), 6.55 (d, *J* = 15.3 Hz, 1H), 6.01 (d, *J* = 17.9 Hz, 1H), 3.82 (s, 3H), 0.12 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 159.9, 144.1, 138.8, 135.4, 132.9, 132.1, 129.7, 119.4, 113.5, 111.8, 55.3, −1.1.

Trimethyl[(1*E*,3*E*)-4-(2-methoxyphenyl)buta-1,3-dien-1-yl]silane (**6j**)

Using general procedure B, **5** (112 mg, 0.60 mmol), *n*BuLi (2.2 M in hexane, 0.28 mL, 0.63 mmol) and KO^{t}Bu (1M in THF, 0.63 mL, 0.63 mmol) in THF (1.7 mL) were treated with imine **2j** (106 mg, 0.50 mmol) in THF (2.4 mL) to give 1,3-diene **6j** (97 mg, 0.42 mmol, 83%) as a colourless oil after purification by flash column chromatography (eluent: hexane-EtOAc, 95:5).

R_f (hexane-EtOAc, 90:10) = 0.65.

IR (ATR): 2954, 1242, 1000, 866, 833, 746 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.47 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.24–7.20 (m, 1H), 6.96–6.91 (m, 2H), 6.88–6.69 (m, 3H), 5.97 (d, *J* = 17.4 Hz, 1H), 3.86 (s, 3H), 0.11 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 157.0, 145.1, 134.2, 132.4, 128.8, 127.8, 126.6, 120.8, 111.0, 55.6, −1.1.

HRMS (APCI): *m/z* $[M+H]^+$ calcd for $C_{14}H_{20}OSi$: 233.1356; found: 233.1361.

Trimethyl[(1*E*,3*E*)-4-(naphthalen-2-yl)buta-1,3-dien-1-yl]silane (**6k**)

Using general procedure B, **5** (112 mg, 0.60 mmol), *n*BuLi (2.2 M in hexane, 0.28 mL, 0.63 mmol) and KO^{t}Bu (1M in THF, 0.63 mL, 0.63 mmol) in THF (1.7 mL) were treated with imine **2k** (116 mg, 0.50 mmol) in THF (2.4 mL) to give 1,3-diene **6k** (102 mg, 0.40 mmol, 81%) as a colourless solid after purification by flash column chromatography (eluent: hexane). Spectral data in accordance to previously published data.[26,47]

R_f (hexane) = 0.38.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.81–7.77 (m, 3H), 7.75 (s, 1H), 7.63 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.48–7.41 (m, 2H), 6.92 (dd, *J* = 15.5, 10.1 Hz, 1H), 6.78–6.71 (m, 2H), 6.06 (d, *J* = 18.3 Hz, 1H), 0.14 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 144.2, 135.4, 134.9, 133.8, 133.2, 133.1, 132.2, 128.4, 128.1, 127.8, 126.8, 126.4, 126.1, 123.6, −1.1.

Trimethyl[(1*E*,3*E*)-4-(thiophen-2-yl)buta-1,3-dien-1-yl]silane (**6l**)

Using general procedure B, **5** (179 mg, 0.96 mmol), *n*BuLi (2.2 M in hexane, 0.45 mL, 1.00 mmol) and KO^{t}Bu (1M in THF, 1.0 mL, 1.00 mmol) in THF (2.8 mL) were treated with imine **2l** (150 mg, 0.80 mmol) in THF (3.9 mL) to give 1,3-diene **6l** (131 mg, 0.63 mmol, 78%) as a colourless oil after purification by flash column chromatography (eluent: hexane). Spectral data in accordance to previously published data.[47]

R_f (hexane) = 0.53.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.17 (d, *J* = 4.6 Hz, 1H), 6.99–6.96 (m, 2H), 6.72–6.56 (m, 3H), 6.02– 5.93 (m, 1H), 0.11 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 143.6, 142.7, 135.1, 131.5, 127.7, 126.4, 125.8, 124.8, −1.1.

Trimethyl[(1*E*,3*E*)-4-(furan-2-yl)buta-1,3-dien-1-yl]silane (**6m**)

Using general procedure B, **5** (170 mg, 0.91 mmol), *n*BuLi (2.2 M in hexane, 0.43 mL, 0.95 mmol) and KO^{t}Bu (1M in THF, 0.95 mL, 0.95 mmol) in THF (2.6 mL) were treated with imine **2m** (130 mg, 0.76 mmol) in THF (3.7 mL) to give 1,3-diene **6m** (135 mg, 0.70 mmol, 92%) as a pale yellow oil after purification by flash column chromatography (eluent: hexane).

R_f (hexane) = 0.35.

IR (ATR): 2955, 1592, 1247, 996, 850, 833 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.37 (d, *J* = 1.7 Hz, 1H), 6.73–6.57 (m, 2H), 6.39–6.29 (m, 3H), 5.99 (d, *J* = 17.6 Hz, 1H), 0.11 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 153.2, 143.7, 142.4, 135.3, 130.3, 120.4, 111.8, 109.0, −1.1.

HRMS (ESI and APCI): target not found.

Trimethyl{(1*E*,3*E*)-4-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]buta-1,3-dien-1-yl}silane (**6n**)

Using general procedure B, **5** (47 mg, 0.25 mmol), *n*BuLi (2.2 M in hexane, 0.12 mL, 0.26 mmol) and KO^{t}Bu (1M in THF, 0.26 mL, 0.26 mmol) in THF (0.7 mL) were treated with imine **2n** (65 mg, 0.21 mmol) in THF (1.0 mL) to give 1,3-diene **6n** (56 mg, 0.17 mmol, 81%) as a yellow oil after purification by flash column chromatography (eluent: hexane).

R_f (hexane-EtOAc, 95:5) = 0.52.

IR (ATR): 2980, 2986, 1357, 834 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 6.85 (dd, *J* = 15.5, 10.1 Hz, 1H), 6.68 (dd, *J* = 18.2, 10.1 Hz, 1H), 6.58 (d, *J* = 15.5 Hz, 1H), 6.03 (d, *J* = 18.2 Hz, 1H), 1.34 (s, 12H), 0.11 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 144.1, 140.0, 136.0, 135.2, 132.9, 132.7, 125.9, 83.9, 25.0, −1.2.

HRMS (APCI): *m/z* $[M+H]^+$ calcd for $C_{19}H_{29}BO_2Si$: 328.2103; found: 328.2139.

Trimethyl[(1*E*)-4,4-diphenylbuta-1,3-dien-1-yl]silane (**6o**)

Using general procedure B, **5** (112 mg, 0.60 mmol), *n*BuLi (2.2 M in hexane, 0.28 mL, 0.63 mmol) and KO^{t}Bu (1M in THF, 0.63 mL, 0.63 mmol) in THF (1.7 mL) were treated with benzophenone (91 mg, 0.50 mmol) in THF (2.4 mL) to give 1,3-diene **6o** (111 mg, 0.40 mmol, 80%) as a yellow oil after purification by flash column chromatography (eluent: hexane-EtOAc, 99:1).

R_f (hexane-CH_2Cl_2, 90:10) = 0.54.

IR (ATR): 2953, 1699, 1246, 834 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.40–7.20 (m, 10H), 6.69–6.59 (m, 2H), 6.06 (d, *J* = 16.9 Hz, 1H), 0.01 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 143.1, 142.5, 141.9, 139.8, 136.4, 130.8, 130.6, 128.3, 128.2, 127.9, 127.6, 127.6, −1.2.

HRMS (APCI): *m/z* $[M+H]^+$ calcd for $C_{19}H_{22}Si$: 279.1564; found: 279.1558.

tert-Butyl 4-[(2*E*)-3-(trimethylsilyl)prop-2-en-1-ylidene]piperidine-1-carboxylate (**6p**)

Using general procedure B, **5** (134 mg, 0.72 mmol), *n*BuLi (2.2 M in hexane, 0.34 mL, 0.75 mmol) and KO^{t}Bu (1M in THF, 0.75 mL, 0.75 mmol) in THF (2.1 mL) were treated with *N*-Boc piperidone (119 mg, 0.60 mmol) in THF (2.9 mL) at −78 °C to give 1,3-diene **6p** (23 mg, 0.08 mmol, 13%) as a pale yellow sticky solid and recovered *N*-Boc piperidone (77 mg, 0.39 mmol, 64%) after purification by flash column chromatography (eluent: hexane-EtOAc, 95:5).

R_f (hexane-EtOAc, 80:20) = 0.52.

IR (ATR): 2951, 1701 (C=O), 1422, 1234, 835 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$); δ 6.76 (dd, *J* = 18.2, 10.5 Hz, 1H), 5.92 (d, *J* = 10.5 Hz, 1H), 5.81 (d, *J* = 18.2 Hz, 1H), 3.46–3.40 (m, 4H), 2.42–2.37 (m, 2H), 2.22–2.17 (m, 2H), 1.46 (s, 9H), 0.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$, additional peaks due to rotamers denoted by an asterisk); δ 154.8, 139.1, 138.8, 133.1, 127.4, 79.7, 45.7*, 45.1 (br), 44.2*, 36.1, 29.8*, 29.0, 28.6, −1.1.

HRMS (ESI and APCI): target not found.

(*E*)-1,2-diphenylethene (**7a**)

Using general procedure C, benzyl trimethylsilane (0.17 mL, 0.87 mmol), *n*BuLi (2.2 M in hexane, 0.41 mL, 0.90 mmol) and KO^{t}Bu (1M in THF, 0.90 mL, 0.90 mmol) in THF (2.1 mL) were treated with imine **2a** (105 mg, 0.58 mmol) in THF (2.9 mL) to give stilbene **7a** (99 mg, 0.55 mmol, 95%) as a colourless solid after purification by flash column chromatography (eluent: hexane). Spectral data in accordance to previously published data.[49]

R_f (hexane) = 0.38.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.59–7.52 (m, 4H), 7.42–7.34 (m, 4H), 7.31–7.27 (m, 2H), 7.14 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 137.4, 128.8, 127.8, 126.6.

(*E*)-1-Trifluoromethyl-4-styrylbenzene (**7b**)

Using general procedure C, benzyl trimethylsilane (0.15 mL, 0.75 mmol), *n*BuLi (2.4 M in hexane, 0.33 mL, 0.78 mmol) and KO^{t}Bu (1M in THF, 0.78 mL, 0.78 mmol) in THF (1.7 mL) were treated with imine **2b** (125 mg, 0.50 mmol) in THF (2.5 mL) to give stilbene **7b** (92 mg, 0.37 mmol, 74%) as a colourless solid after purification by flash column chromatography (eluent: hexane). Spectral data in accordance to previously published data.[50]

R_f (hexane) = 0.34.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.61 (s, 4H), 7.56–7.53 (m, 2H), 7.41–7.37 (m, 2H), 7.33–7.28 (m, 1H), 7.20 (d, *J* = 16.4 Hz, 1H), 7.12 (d, *J* = 16.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 140.9, 136.7, 131.3, 129.5, 128.9, 128.4, 127.2, 126.9, 126.7, 125.8 (q, *J* = 3.7 Hz), 123.0.

^{19}F (376 MHz, $CDCl_3$) δ -62.3 (s).

(*E*)-1-Chloro-4-styrylbenzene (**7c**)

Using general procedure C, benzyl trimethylsilane (0.15 mL, 0.77 mmol), *n*BuLi (2.3 M in hexane, 0.34 mL, 0.79 mmol) and KO^{t}Bu (1M in THF, 0.79 mL, 0.79 mmol) in THF (1.8 mL) were treated with imine **2c** (110 mg, 0.51 mmol) in THF (2.6 mL) to give stilbene **7c** (83 mg, 0.39 mmol, 76%) as a colourless solid after purification by flash column chromatography (eluent: hexane). Spectral data in accordance to previously published data.[49,51]

R_f (hexane) = 0.30.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.53–7.49 (m, 2H), 7.47–7.42 (m, 2H), 7.40–7.27 (m, 5H), 7.07 (AB q, *J* = 16.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 137.1, 135.9, 133.3, 129.4, 129.0, 128.9, 128.0, 127.8, 127.5, 126.7.

(*E*)-1-Methyl-4-styrylbenzene (**7d**)

Using general procedure C, benzyl trimethylsilane (0.18 mL, 0.92 mmol), *n*BuLi (2.3 M in hexane, 0.41 mL, 0.95 mmol) and KO^{t}Bu (1M in THF, 0.95 mL, 0.95 mmol) in THF (2.1 mL) were treated with imine **2e** (120 mg, 0.62 mmol) in THF (3.1 mL) for 3 hours to give stilbene **7d** (103 mg, 0.53 mmol, 86%) as a colourless solid after purification by flash column chromatography (eluent: hexane). Spectral data in accordance to previously published data.[50,52]

R_f (hexane) = 0.24.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.54–7.50 (m, 2H), 7.46–7.42 (m, 2H), 7.39–7.35 (m, 2H), 7.29–7.24 (m, 1H), 7.21–7.17 (m, 2H), 7.10 (AB q, *J* = 16.4 Hz, 2H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 137.7, 137.6, 134.6, 129.5, 128.8, 128.7, 127.8, 127.5, 126.6, 126.5, 21.4.

(*E*)-1-Methoxy-2-styrylbenzene (**7e**)

Using general procedure C, benzyl trimethylsilane (0.17 mL, 0.89 mmol), *n*BuLi (2.3 M in hexane, 0.40 mL, 0.92 mmol) and KO^{t}Bu (1M in THF, 0.92 mL, 0.92 mmol) in THF (2.0 mL) were treated with imine **2j** (129 mg, 0.59 mmol) in THF (2.8 mL) to give stilbene **7e** (105 mg, 0.50 mmol, 84%) as a colourless solid after purification by flash column chromatography (eluent: hexane-EtOAc, 98:2). Spectral data in accordance to previously published data.[50,52]

R_f (hexane-EtOAc, 9:1) = 0.62.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.61 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.56–7.48 (m, 3H), 7.37–7.34 (m, 2H), 7.27–7.23 (m, 2H), 7.12 (d, *J* = 16.5 Hz, 1H), 7.00-6.95 (m, 1H), 6.91 (dd, *J* = 8.2, 0.6 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 157.0, 138.1, 128.8, 128.7, 126.7, 126.5, 123.6, 111.0, 55.6.

(*E*)-1,2-Dimethoxy-4-styrylbenzene (**7f**)

Using general procedure C, benzyl trimethylsilane (0.14 mL, 0.76 mmol), *n*BuLi (2.3 M in hexane, 0.34 mL, 0.78 mmol) and KO^{t}Bu (1M in THF, 0.78 mL, 0.78 mmol) in THF (2.4 mL) were treated with imine **2h** (122 mg, 0.51 mmol) in THF (1.7 mL) for 4 hours to give stilbene **7f** (110 mg, 0.46 mmol, 91%) as a colourless solid after purification by flash column chromatography (eluent: hexane-EtOAc, 90:10). Spectral data in accordance to previously published data.[52]

R_f (hexane-EtOAc, 80:20) = 0.29.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.39–7.33 (m, 2H), 7.27–7.23 (m, 1H), 7.10–7.04 (m, 3H), 6.98 (d, *J* = 16.3 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 3.96 (s, 3H), 3.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 149.2, 149.0, 137.6, 130.5, 128.8, 128.6, 127.4, 126.9, 126.6, 126.4, 120.0, 111.3, 108.8, 56.1, 56.0.

(*E*)-2-styrylnaphthalene (**7g**)

Using general procedure C, benzyl trimethylsilane (0.14 mL, 0.75 mmol), *n*BuLi (2.4 M in hexane, 0.40 mL, 0.78 mmol) and KO^{t}Bu (1M in THF, 0.78 mL, 0.78 mmol) in THF (1.7 mL) were treated with imine **2k** (116 mg, 0.50 mmol) in THF (2.5 mL) to give stilbene **7g** (94 mg, 0.41 mmol, 82%) as a colourless solid after purification by flash column chromatography (eluent: hexane). Spectral data in accordance to previously published data.[50,52]

R_f (hexane) = 0.13.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.87–7.81 (m, 4H), 7.76 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.60–7.56 (m, 2H), 7.49–7.38 (m, 4H), 7.32–7.22 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 137.5, 134.9, 133.8, 133.2, 129.1, 128.9, 128.4, 128.1, 127.8, 126.8, 126.7, 126.5, 126.0, 123.6.

(*E*)-2-Styrylfuran (**7h**)

*n*BuLi (2.2 M in hexane, 0.31 mL, 0.70 mmol, 1.55 equiv.) was added dropwise to a stirred solution of benzyl trimethylsilane (0.13 mL, 0.68 mmol, 1.50 equiv.) in THF (1.6 mL) at −50 °C under argon and stirred for 5 minutes. KO^{t}Bu (1 M solution in THF, 0.70 mL, 0.70 mmol, 1.55 equiv.) was added dropwise at −50 °C and the reaction mixture stirred for 30 minutes. A solution of imine **2m** (77 mg, 0.45 mmol, 1.0 equiv.) in THF (2.2 mL) was added dropwise at −50 °C, stirred for 30 minutes and then warmed to room temperature. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl. The aqueous phase was extracted three times with CH_2Cl_2, dried (Na_2SO_4) and evaporated under reduced pressure. TBAF (1M in THF, 0.90 mL, 0.90 mmol, 2.0 equiv.) was added dropwise to the crude product in CH_2Cl_2 (2 mL) at room temperature and stirred for 30 minutes. The reaction mixture was quenched with a

saturated aqueous solution of NH_4Cl. The aqueous phase was extracted three times with CH_2Cl_2, dried (Na_2SO_4) and evaporated under reduced pressure to give the crude product. The crude product was purified by flash column chromatography on silica gel (eluent: hexane) to give stilbene **7h** (54 mg, 0.32 mmol, 71%) as a colourless solid. Spectral data in accordance to previously published data.[52]

R_f (hexane) = 0.29.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.48–7.45 (m, 2H), 7.41–7.40 (m, 1H), 7.37–7.32 (m, 2H), 7.24– 7.22 (m, 1H), 7.04 (d, *J* = 16.3 Hz, 1H), 6.90 (d, *J* = 16.3 Hz, 1H), 6.43 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.36 (d, *J* = 3.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 153.4, 142.3, 137.1, 128.8, 127.7, 127.2, 126.4, 116.6, 111.8, 108.7.

Triphenylethylene (**7i**)

Using general procedure C, benzyl trimethylsilane (0.16 mL, 0.83 mmol), *n*BuLi (2.2 M in hexane, 0.39 mL, 0.86 mmol) and KO^{t}Bu (1M in THF, 0.86 mL, 0.86 mmol) in THF (1.9 mL) were treated with benzophenone (101 mg, 0.55 mmol) in THF (2.8 mL) to give alkene **7i** (134 mg, 0.52 mmol, 95%) as a clear oil after purification by flash column chromatography (eluent: hexane). Spectral data in accordance to previously published data.[50]

R_f (hexane-EtOAc, 90:10) = 0.92.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.36–7.27 (m, 8H), 7.24–7.19 (m, 2H), 7.16–7.02 (m, 5H), 6.97 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$); δ 143.6, 142.7, 140.5, 137.5, 130.5, 129.7, 128.8, 128.3, 128.3, 128.1, 127.7, 127.6, 127.5, 126.9.

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO (this text will be deleted prior to publication)

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Biosketches

	**Dr Tom Britten** Originally from Bournemouth, Tom graduated from Bangor University in 2015 with an MChem degree. After graduation, Tom moved to Lancaster University for his PhD under the supervision of Dr Susannah Coote, in collaboration with AstraZeneca. His PhD focused on the development of scalable photochemical methodologies to access functionalized four-membered rings. He subsequently moved to MMU in May 2019 as a postdoc within the McLaughlin group, working on a variety of organic methodology and medicinal chemistry projects. Outside of chemistry, he enjoys football, NFL and travelling.
	**Ashley Basson** Ashley, originally from Westhoughton, Bolton, graduated with an MChem degree from Manchester Metropolitan University in 2019 and was winner of the RSC John Leach Memorial Prize. He worked under the supervision of Dr Ryan Mewis for his undergraduate projects in which he focused on the synthesis of transition metal- NHC complexes for use in medical imaging. In summer 2019, he began his PhD within the McLaughlin group, focusing on the development of enantioselective alkaline earth metal catalysis. Outside the lab, Ashley enjoys hiking in the Lake District with friends, camping, and playing tennis for his local club.
	**Dean Roberts** Dean is originally from Manchester, and graduated from Manchester Metropolitan University with an MChem degree in 2019, having carried out his undergraduate project under the supervision of Dr Ryan Mewis on transition metal-macrocyclic complexes. He joined the McLaughlin group for his PhD in the summer of 2019, works on the development of novel transition metal catalyzed synthesis and applications of high value metalloid scaffolds. Outside of chemistry, his hobbies and interests include hiking, football and camping.
	**Dr Mark McLaughlin** Mark completed his undergraduate degree (MSci.) in 2010 and PhD (2014) at Queen's University Belfast under the supervision of Prof. Matthew Cook. His graduate studies concerned the development and application of transition metal catalyzed hydrometallation reactions followed by postdoctoral fellowships at the Institute of Cancer Research and University of Oxford. He was appointed as lecturer in synthetic and medicinal chemistry at Manchester Metropolitan University in 2018 and promoted to senior lecturer in 2020. His group are interested in the use of alkaline earth metals in synthesis, organosilicon chemistry and antibacterial and cardiovascular disease drug discovery.