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# Carbopalladation of bromoene-alkynylsilanes: mechanistic insights and synthesis of fused-ring bicyclic silanes and phenols†

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The palladium-catalyzed cascade cyclization of silylated bromoenynes and alkenylstannanes provides a straightforward route to a range of bicyclic silylated cyclohexadienes. Mechanistic insights into aspects of carbopalladation and unusual palladium-mediated isomerizations have been obtained through the detection of reaction intermediates, the isolation of byproducts, and reaction monitoring by VT NMR spectroscopy. The utility of the bicyclic products is illustrated through oxidation to bicyclic enones and phenols.

## Introduction

Phenols represent one of the most important aromatic functional groups, featuring in numerous natural products and drugs.[1] Polycyclic phenols are of particular interest, as illustrated by highly bioactive compounds such as the anthracycline antibiotics, estrone, and morphine (Fig. 1).[2] As traditional methods for phenol preparation require harsh conditions that may not be compatible with sensitive functional groups,[3] phenols are usually incorporated at an early stage of a synthesis, thus restricting synthetic planning.

Late-stage phenolation is therefore an attractive prospect that has driven the development of transition metal-catalyzed aryl halide hydroxylation and aryl C–H activation/oxidation methods.[4] An alternative that avoids the prolonged heating often required by these processes is the use of a phenol surrogate, which could be revealed at a late stage of a synthetic route, but is stable to intermediate transformations. Here, arylboron derivatives have met with some success, particularly due to Molander's elegant work on the oxidation of aryl trifluoroborate salts,[5] although the synthetic processability of these remains to be proven. In contrast, organosilanes – stalwarts of the protecting group field – display unrivalled tolerance towards multistep synthesis, and in recent work we have reported the use of arylsilanes as a source of phenols through Tamao-type oxidation.[6,7]

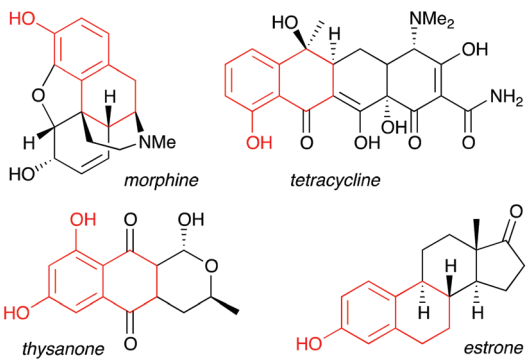


Fig. 1 Fused-ring phenols in bioactive natural products.

We have also disclosed a palladium-catalyzed cascade cyclization which prepares bi- or tricyclic products (**1**, Scheme 1) from the coupling of bromoenynes **2** with alkenyl- and dienylstannanes **3**,[8] a reaction pioneered and impressively explored by Suffert *et al.* for the synthesis of various polycycles.[9] A feature of this work is the requirement for an internal alkyne (*i.e.* $R^1 \neq H$, Scheme 1) to avoid the formation of undesired triene isomers **4**, which cannot undergo electrocyclization. One solution is to employ trimethylsilyl alkynes,[10] and although this functionality indeed enables the desired cascade, it was clear that the resultant TMS-substituted cyclohexadienes would be of limited synthetic utility.

We realized that the use of a more functional silane would lead to a silicon-containing product capable of undergoing a range of further transformations, such as the aforementioned Tamao oxidation or Hiyama coupling.[11] Indeed, we have illus-

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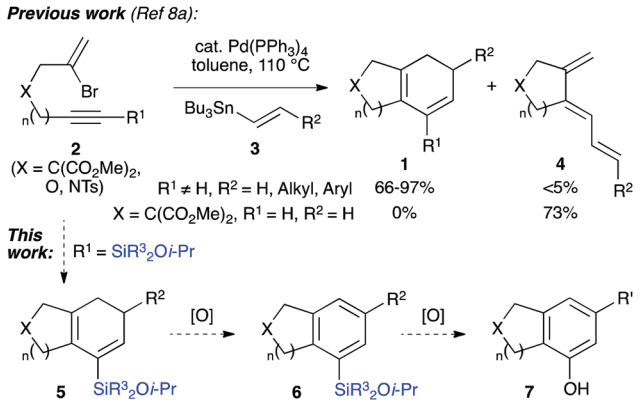
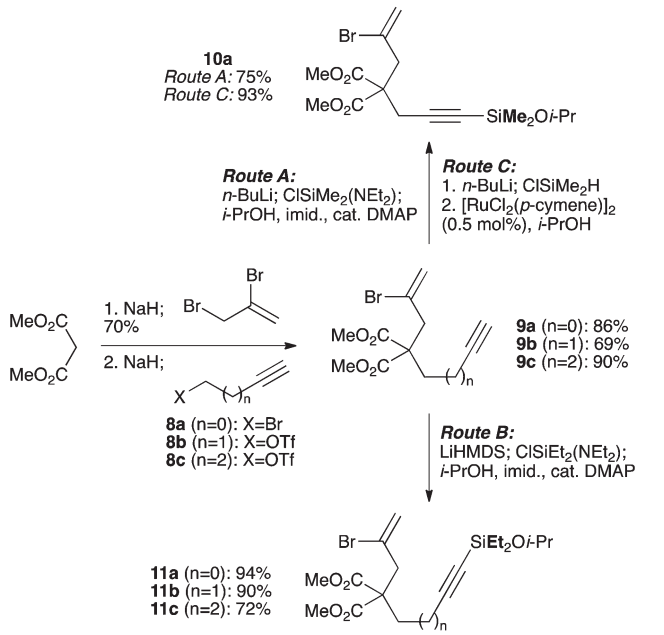
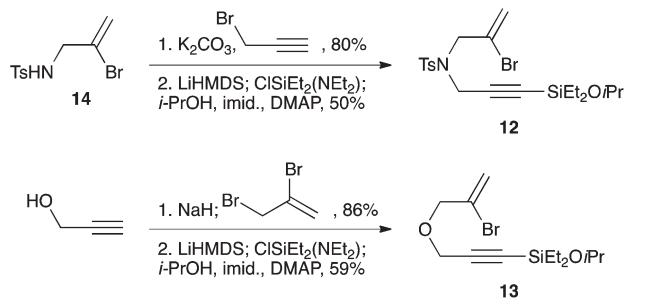
†Electronic supplementary information (ESI) available: Copies of $^1$H and $^{13}$C NMR spectra, and experimental details for NMR experiments. See DOI: 10.1039/c4qo00123k




Scheme 1 Proposed synthesis of bicyclic phenols.




Scheme 2 Synthesis of malonate-derived silylbromoenynes.




Scheme 3 Synthesis of heteroatom-tethered silylbromoenynes.

trated this principle in approaches to the CDE rings of rubriflordilactone A, where arylsilanes formed from the cyclizations of bromoenynes could be oxidized to give specific tricyclic phenols.[8b,12] In this paper we wish to report methods for the synthesis of a range of silylated bromoenynes, and their intermolecular coupling with alkenylstannanes to provide bicyclic silylcyclohexadienes **5**. The oxidation of these dienes and silane substituents leads to bicyclic arylsilanes (**6**) and phenols (**7**) that would be challenging to prepare by other routes, and offers a *de novo* approach to ring systems of this type.[13] Alongside this synthetic work, we expand on the mechanistic pathways operative in the cascade cyclization, including two unusual palladium-mediated isomerization processes. The unexpected observation of an unprecedented formal 4-*endo*-*trig* cyclization to afford fused ring cyclobutenes is also described.

## Results and discussion

### Synthesis of cascade cyclization substrates

We selected a range of linkers to connect the bromoalkene and silylalkyne, such that bicyclic products containing 5- to 7-membered rings, and heterocycles, could be obtained. Synthesis of carbon-tethered bromoenynes began with dimethylmalonate (Scheme 2), which following monoallylation with 2,3-dibromopropene (70%) was alkylated with alkynyl electrophiles **8a–c** to give bromoenynes **9a–c** (69–90%). The silylation of these alkynes was initially attempted using conditions employed in our arylsilane work.[6a] Thus, deprotonation of **9a** with *n*-butyllithium followed by trapping of the resultant alkynyllithium species with the moisture-sensitive (diethylamino)chlorodimethylsilane ($Et_2NMe_2SiCl$) gave an intermediate aminosilane which was not isolated, but immediately converted to the dimethylisopropoxysilane **10a** (Route A, Scheme 2).[14] Perhaps unsurprisingly, this silane proved to be rather unstable towards chromatography, however through rapid chromatographic purification using a solvent system buffered with triethylamine, **10a** could be isolated in 75% yield. In order to address the chromatographic instability of this dimethylisopropoxysilane, we employed the analogous diethylsilane reagent $(Et_2N)SiEt_2SiCl$,[15] which gave the alkynyl isopropoxydiethylsilanes **11a–c** in much improved yields following chromatographic purification (Route B). An alternative solution to the synthesis of **10a** proved to be the use of dimethylchlorosilane ($HMe_2SiCl$) as the acetylide trapping agent (Route C); the ensuing hydrolytically stable intermediate alkynylhydrosilane could be easily purified, and then smoothly oxidized to **10a** using Lee and Chang's elegant ruthenium-catalyzed dehydrogenative silylation methodology,[16] which improved the yield of **10a** to 93%.

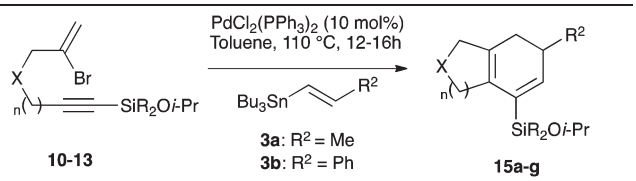
The syntheses of heteroatom-tethered silylbromoenynes could be achieved uneventfully using equivalent chemistry, with sulfonamide-tethered enyne **12** and ether-linked enyne **13** being prepared in reasonable yields over two steps from known sulfonamide **14** and propargyl alcohol, respectively (Scheme 3).

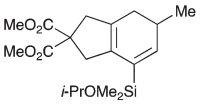
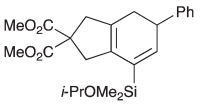
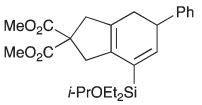
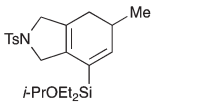
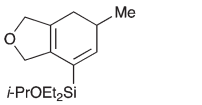
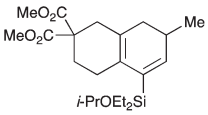
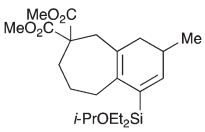
### Cascade cyclizations of silylated bromoenynes

With a selection of silylated alkynes in hand, their palladium-catalyzed cascade cyclizations were examined. These reactions

**Table 1** Cascade cyclizations of silylated bromoenynes **10–13**




| Entry | Silane | Stannane | Product | | Yield[a] [%] |
|---|---|---|---|---|---|
| 1 | **10a** | **3a** |  | **15a** | 92 |
| 2 | **10a** | **3b** |  | **15b** | 97 |
| 3 | **11a** | **3b** |  | **15c** | 77 |
| 4 | **12** | **3a** |  | **15d** | 63 |
| 5 | **13** | **3a** |  | **15e** | 23 |
| 6 | **11b** | **3a** |  | **15f** | 75[b] |
| 7 | **11c** | **3a** |  | **15g** | 58[c] |

[a] Isolated yield. [b] Isolated as an 80 : 13 : 7 ratio of **15f** : **16a** : **17a**. [c] Isolated as a 63 : 19 : 18 ratio of **15g** : **16b** : **17b**. See text for discussion.

were carried out according to our previously optimized conditions,[8a] using $PdCl_2(PPh_3)_2$ as precatalyst in refluxing toluene (Table 1). For the purposes of this work, the propenyl and styrenyl stannanes **3a** and **3b** were selected as generic cross-coupling partners. The reaction of dimethylsilane **10a** was first investigated, which in spite of the relative instability of the alkynylsilane cyclized in excellent yields with both stannanes (92–97%, entries 1, 2). Notably, the hydrolytic stability of the silane increases markedly upon cyclization owing to the increased steric bulk of the cyclohexadienyl substituent in **15a** compared to the alkyne substituent of the starting material. The cyclizations of the (more robust) diethylsilane substrates proved more challenging (entries 3–5), with these reactions requiring longer reaction times, likely due to steric hindrance

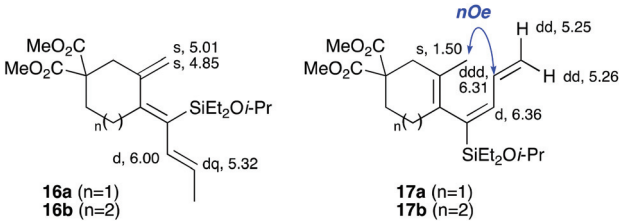
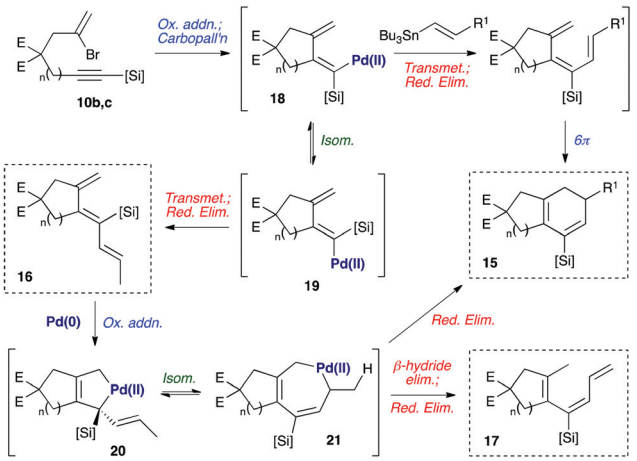



**Fig. 2** Cyclization byproducts **16a/b** and **17a/b**. Selected key $^1$H NMR chemical shifts/multiplicities (in $CDCl_3$) for **16a** and **17a** are shown.

of the key transmetallation step following carbopalladation. This resulted in lower isolated yields, as exemplified by the malonate and sulfonamide tethered enynes **11a** and **12** which gave the corresponding bicycles **15c** and **15d** in 77 and 63% yields respectively. The oxygen-tethered substrate **13** proved particularly troublesome, delivering the dihydrofuran product **15e** in low yield, possibly due to instability of the allyl propargyl ether. Reaction of substrates featuring a longer tether also proved effective, giving the 6,6- and 7,6-bicyclic products **15f** and **15g** in good yields (entries 6, 7).

In the latter two cases, the desired bicyclic products were contaminated with significant quantities of partially separable isomeric byproducts **16a**, **b** and **17a**, **b** (Fig. 2), which were identified by careful analysis of $^1$H–$^1$H COSY, and $^1$H–$^{13}$C HSQC and HMBC 2D NMR spectra;[17] the assignment of one of these sets of byproducts (**16a** and **17a**) is discussed here. Byproduct **16a** contains an *exo*-methylene unit ($\delta_H$ 5.01 and 4.85 ppm), and two vicinal alkene protons ($\delta_H$ 6.00 ppm, dd, $J$ = 15.5, 1.5 Hz; and 5.32 ppm, dq, $J$ = 15.5 and 6.5 Hz), the latter being characteristic of the *trans*-alkene of the propenyl unit. These data, together with key HMBC correlations, are strongly suggestive of the formal *anti*-carbopalladation/cross-coupling product **16a**, the formation of which is entirely consistent with our earlier results.[8a] The identification of the second byproduct proved less straightforward. Key signals in the $^1$H NMR spectrum at $\delta_H$ 6.36 (d, $J$ = 10.6 Hz), 6.31 (ddd, $J$ = 16.5, 10.6 and 9.7 Hz), 5.26 (dd, $J$ = 16.5 and 2.0 Hz) and 5.25 ppm (dd, $J$ = 9.8 and 2.0 Hz) revealed a connectivity between four alkene protons and thus the surprising presence of a 1,3-butadienyl unit. A further significant piece of evidence was the detection of a methyl singlet at 1.50 ppm, to which the proton at 6.33 ppm showed an nOe enhancement. These combined observations, and $^1$H–$^{13}$C correlations, led us to propose structure **17a**, which features an (*E*)-alkenylsilane as part of a conjugated triene.

A mechanistic hypothesis for the formation of these byproducts is depicted in Scheme 4. The formation of byproduct **16** is consistent with our earlier observation[8a] that such undesired *anti*-trienes form in the course of the cyclization reaction, potentially *via* isomerization of the intermediate dienylpalladium complex **18** to its isomer **19**.[18] The rate of transmetallation of complex **19** is likely to exceed that of **18**, so even small amounts of **19** may lead to significant quantities of *anti*-triene **16** (*i.e.*, a Curtin–Hammett situation). The formation of increased quantities of this triene for substrates **11b** and **11c**




**Scheme 4** Mechanistic proposal for byproduct formation. E = $CO_2Me$, [Si] = $SiEt_2Oi$-Pr.

may reflect the increased flexibility of the larger tethering ring, which can distort to alleviate 1,3-allylic strain between the silyl substituent and *exo*-methylene in **19** – and therefore reduce the steric cost of placing a silane in this more hindered position. The formation of **17** may be explained by our second previous observation[8a] that *anti*-trienes can isomerize to bicyclic products on prolonged exposure to the reaction conditions. We suggest that this process may proceed *via* oxidative addition of Pd(0) with diene **16** to give a palladacyclopentene **20**.[19] This could undergo a 1,3-allylic migration of the palladium atom to the 7-membered palladacycle **21**, reductive elimination from which would afford the cyclohexadiene product **15**.[20] The formation of byproduct **17** could be rationalised by β-hydride elimination from this common palladacycle intermediate **21**, followed by reductive elimination of the resultant palladium(II) hydride species. We presume that the steric hindrance imposed by the methyl group in **17** prevents a 6π-electrocyclization of this compound.

As [4 + 1] oxidative additions of Pd(0) to dienes are rare,[19] more concrete evidence to support these pathways was sought. Firstly, the formation of **16** *via* the intermediacy of dienylpalladium complex **19** was probed through the exposure of alkynylsilane **22** to one equivalent of $Pd(PPh_3)_4$ in $d_8$-toluene at 110 °C (Fig. 3). The characteristic methylene signals of **22** at $\delta_H$ 5.41 and 5.71 ppm were rapidly converted (10 min) to two new sets of peaks: a prominent (apparent) singlet at 4.60 ppm, and two smaller singlets at 4.58 and 4.78 ppm. These were tentatively assigned as the *exo*-methylene peaks of the *syn*- and *anti*-dienylpalladium complexes **23** and **24** respectively, based on analysis by COSY and HSQC experiments. Support for this assignment was gained through the addition of 1.5 equivalents of tributylvinyltin to the NMR tube; further heating for 10 minutes led to exclusive formation of cyclohexadiene **25** and triene **26** in a ratio mirroring that of these intermediate species (84 : 16).

To explore the isomerization of **26** to **25**, a 1 : 0.32 mixture of these compounds, formed from reaction of silane **22** with

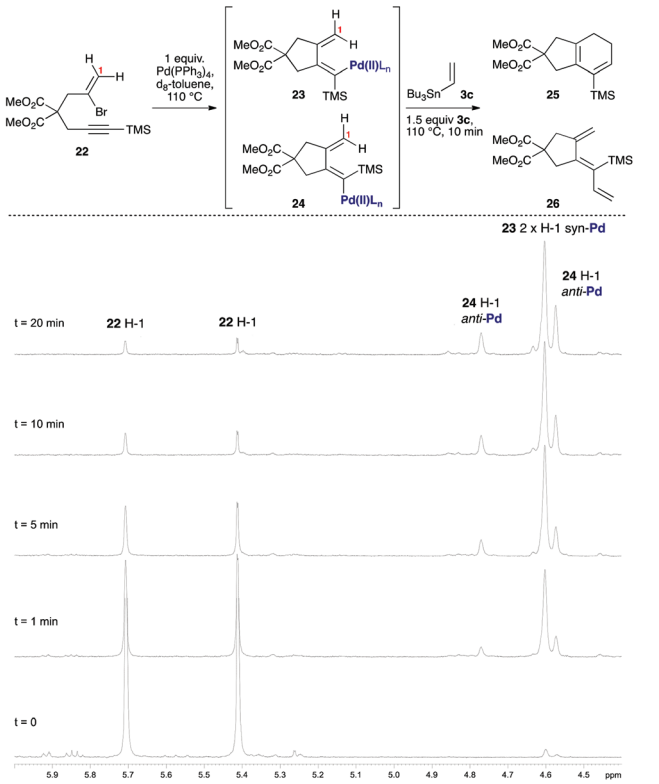
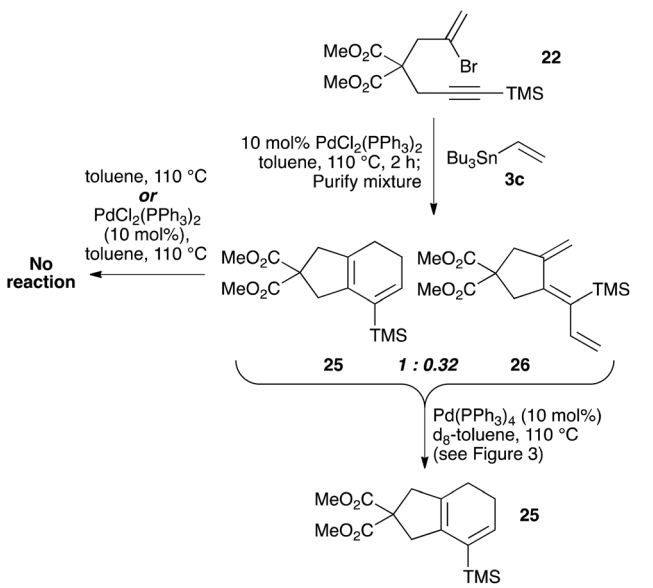



**Fig. 3** Use of stoichiometric $Pd(PPh_3)_4$/VT $^1H$ NMR spectroscopy to probe the putative dienylpalladium(II) intermediates.




**Scheme 5** Exploration of conditions to effect the isomerization of *anti*-triene **26** to bicycle **25**.

vinyltributyltin for two hours, was purified by silica gel chromatography (Scheme 5); the triene **26** in this mixture would be expected to isomerize to give the **25** upon resubmission to the reaction conditions. Heating the mixture in toluene overnight at 110 °C in the absence of catalyst led to no conversion

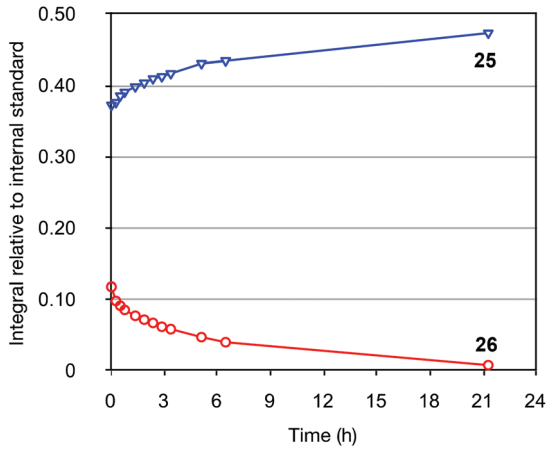



**Fig. 4** $^1$H NMR spectroscopic monitoring of the conversion of **26** to **25** catalyzed by $Pd(PPh_3)_4$. 1,4-Dimethoxybenzene was used as internal standard.

of **26** to the bicyclic product **25**, with both compounds recovered unchanged after this period (thus ruling out a purely thermal process). Palladium(II) salts have previously been shown to promote alkene isomerisation,[21] but subjection of the *anti*-triene to $PdCl_2(PPh_3)_2$ at 110 °C also led to no reaction. However, heating the mixture in the presence of $Pd(PPh_3)_4$ for 20 h led to complete consumption of *anti*-triene, and by performing this isomerization in $d_8$-toluene with monitoring by $^1$H NMR spectroscopy in the presence of an internal standard (1,4-dimethoxybenzene), a smooth conversion of **26** to **25** was observed (Fig. 4). This clearly demonstrates that the isomerization of *anti*-triene to product is not a thermal process, and in fact requires a Pd(0) catalyst, thus offering some support to our proposed mechanism. At no point do we detect the formation of *syn*-triene, which lends some weight to our mechanistic hypothesis for the direct conversion of *anti*-trienes to bicyclic products (Scheme 4, although we recognise that any *syn*-triene formed could electrocyclize rapidly).

### Cyclization to 7,4-fused ring cyclobutenes

In the course of cyclization reactions to form seven-membered rings (including **11c**), we had noticed the occasional formation of a different byproduct to those discussed thus far, the production of which seemed highly dependent on the reaction concentration, and quantity of stannane coupling partner. Although this byproduct was not observed under our optimized conditions, the use of <1.5 equivalents of stannane, or more dilute reaction conditions (*i.e.* such that transmetallation would be slowed) increased its formation. In fact, we had first observed such a species in the attempted 8π-electrocyclic coupling of bromoenyne **27** with stannane **28** (Fig. 5), which resulted in a surprising degree of apparent protodestannylation of **28** (leading to the known diene **29**).[22] We assigned the product formed in this reaction as the 7,4-fused cyclobutene **30** based on detailed analysis by 2D NMR experiments. Specifically, a complete set of HMBC correlations (Fig. 5) was observed between protons H1, H3 and H7, and carbons C2, C8

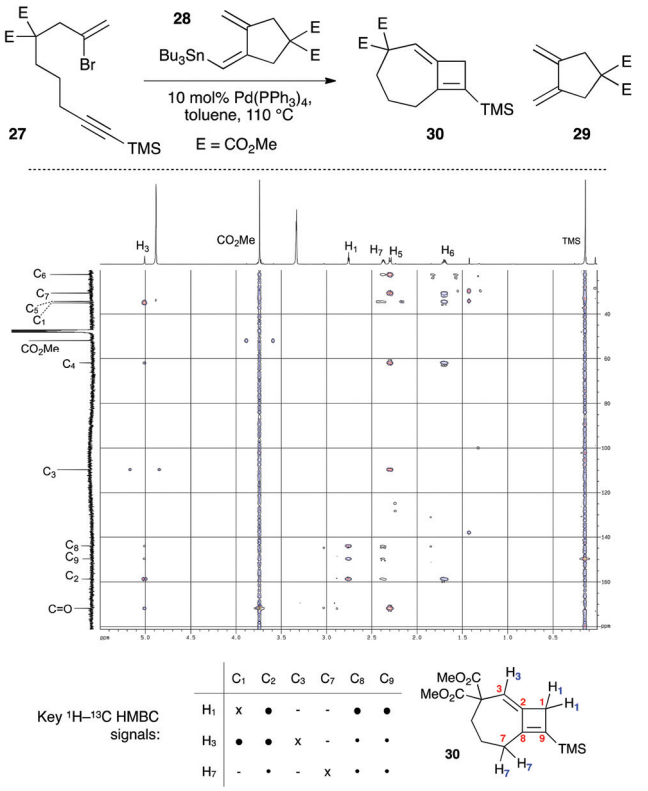
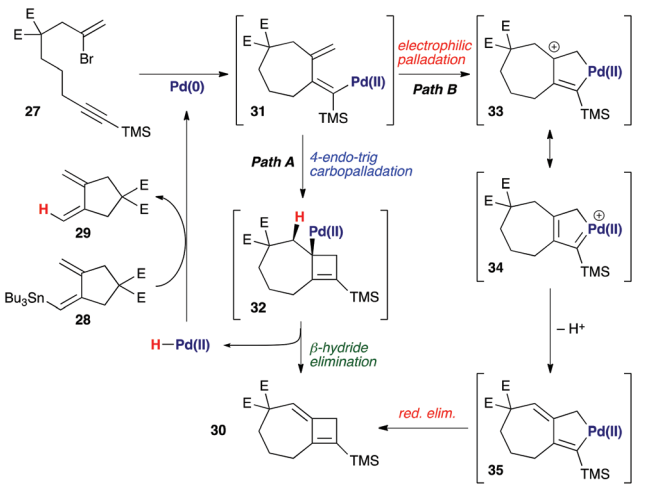


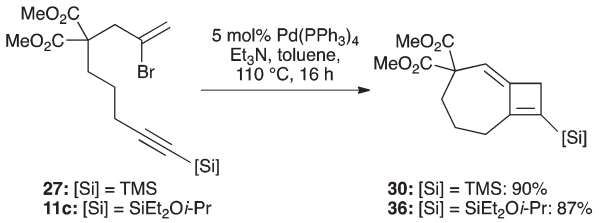

**Fig. 5** Initial synthesis of 7,4-fused cyclobutene **30**, and key HMBC spectra correlations. E = $CO_2Me$. ● = strong correlation; • = weak correlation.




**Scheme 6** Possible mechanisms for the formation of 7,4-fused cyclobutene **30**. E = $CO_2Me$.

and C9, together with long-range coupling between H1 and H7 ($^5J$ = 2.7 Hz; this coupling was also observed in a $^1$H–$^1$H COSY spectrum).

The formation of this product is not unreasonable if potential mechanisms for its formation are considered (Scheme 6). Following carbopalladation (**31**), one possibility would involve a 4-*endo-trig* carbopalladation (Path A), leading to cyclobutene



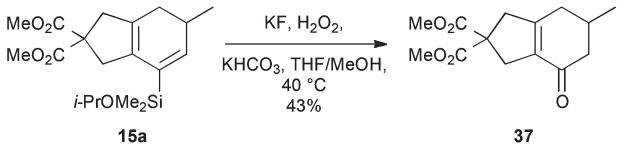

Scheme 7 Heck conditions for formation of 7,4-fused cyclobutenes.

**32** – a pathway that might be favoured, in spite of ring strain, due to the formation of an allylpalladium intermediate. β-Hydride elimination would afford the observed product **30**, and liberate a palladium(II) hydride species that could be reduced to palladium(0) by transmetallation with **28**, thus leading to the 'protodestannylated' product **29**. However, due to a lack of precedent for this mode of carbopalladation, we also consider an electrophilic palladation route feasible (Path B), in which attack by the *exo*-methylene on the proximal palladium(II) atom leads to palladacycle **33** – which may again be rendered possible by the formation of an allyl cation in this process. Now, loss of a proton generates palladacyclopentene **35**, reductive elimination from which leads to **30**.[23] The resemblance of intermediate **35** to those proposed in enyne cycloisomerization processes is clear;[24] the proton lost from this pathway could then effect protodestannylation of the coupling partner **28** to afford **29**.

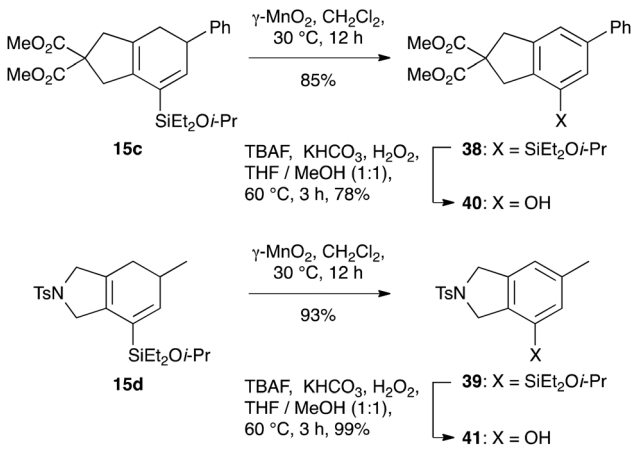
Whatever mechanism is operational, it was clear to us that this process overall corresponds to a Heck reaction in which regeneration of the palladium(0) catalyst is mediated by the stannane reagent. This suggested that an amine base might perform a similar role, and to our delight, the use of common Heck conditions (toluene, triethylamine) at just 5 mol% catalyst loading indeed led to a high-yielding cyclization of **27** to **30** (90%, Scheme 7). The more functional bromoenyne **11c** was also tested in this chemistry, which gave the corresponding 7,4-fused silylcyclobutene **36** in excellent yield (86%). This efficient process offers an alternative entry to this type of fused cyclobutene ring system.[25]

### Oxidations of silylcyclohexadienes

To illustrate the potential utility of this chemistry, we subjected the product dienylsilanes to a selection of oxidative transformations. Firstly, a direct Tamao oxidation of the dienylsilane was carried out,[26] which we hoped would deliver a bicyclic enone. In the case of the isopropoxydimethylsilane **15a**, this met with some success (Scheme 8), delivering **37** in moderate yield (43%). The successful formation of this product, which lacks any olefinic protons, could be confirmed by $^{13}$C NMR ($\delta_C$ 194.9, 158.7, 134.8 ppm for the enone region) and IR spectroscopy ($\nu_{max}$ 1667 cm$^{-1}$). Attempted oxidation of the equivalent diethylisopropoxysilanes proved unsuccessful, potentially due to competing nucleophilic epoxidation of the product enone, which highlights a reactivity benefit of the less-hindered dimethylalkoxysilane group.




Scheme 8 Bicyclic enone formation.




Scheme 9 Oxidation of the silylcyclohexadiene framework.

The silylcyclohexadiene frameworks could also be readily oxidized to the corresponding arylsilanes using manganese dioxide, conditions that we had successfully employed in other work[27] and which proved superior to the use of other oxidants such as DDQ. The resultant arylsilanes could generally be isolated in excellent yield; two examples are shown in Scheme 9 (**38**: 88%; **39**: 93%). These arylsilanes show potential for a range of transformations – but here, in keeping with our interests in the synthesis of phenols from arylsilanes,[6] we chose to investigate Tamao oxidation. Under Tamao conditions (TBAF, $KHCO_3$, $H_2O_2$, 60 °C),[28] good yields of the corresponding phenols **40** and **41** were obtained, thus validating this approach to the synthesis of bi/polycyclic phenols.

## Conclusions

In summary, we have developed efficient routes for the synthesis of functional alkynylsilanes and demonstrated their application in bicyclization cascade reactions. The resultant silylated bicyclic cyclohexadienes are substrates for oxidation to bicyclic enones, arylsilanes, and phenols; the latter process thus affords bicyclic phenols from acyclic precursors in just three steps. Investigations into the mechanism of the cascade cyclization have revealed some unusual palladium-mediated isomerization pathways. Finally, 7,4-fused cyclobutene ring systems, arising from cyclization of a 7-membered exocyclic dienylpalladium complex, could be formed under standard 'Heck' type conditions. Together, these processes underline the rich reactivity – both expected and unexpected – that can be harvested from carbopalladation chemistry.

# Experimental

## General

Reagents were used as purchased, or purified by standard laboratory techniques. Reaction solvents were purified using an alumina column drying system, and reactions were performed under inert atmosphere unless otherwise stated.

**Dimethyl 2-(2-bromoallyl)malonate.** To a suspension of NaH (60% dispersion in mineral oil, 2.32 g, 58.0 mmol) in THF (50 mL) at 0 °C was added dropwise dimethyl malonate (5.52 mL, 48.4 mmol), and the mixture was stirred for 1 h. 2,3-dibromopropene (80% tech. grade, 5.52 mL, 48.4 mmol) was added to the milky yellow mixture, and stirring was continued for 3 h until completion of the reaction as monitored by TLC. The reaction was quenched with $NH_4Cl$ (sat., aq.). The aqueous phase was extracted with $Et_2O$ and the combined organic extracts washed with brine and dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the crude product purified by distillation at (101–106 °C, 1 mmHg) to afford the product as a colourless oil (8.50 g, 33.9 mmol, 70%). $R_f$ 0.22 (5 : 1 pet. ether–ether); $^1$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 5.69 (1H, dt, $J$ = 2.0, 1.0 Hz), 5.48 (1H, d, $J$ = 2.0 Hz), 3.89 (1H, t, $J$ = 7.5 Hz), 3.76 (6H, s), 3.03 (2H, dd, $J$ = 7.5, 1.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 168.7, 129.2, 119.9, 52.7, 50.4, 40.5. Data in accordance with the literature.[29]

## General procedure 1: alkylation of dimethyl 2-(2-bromoallyl)-malonate

A solution of dimethyl 2-(2-bromoallyl)malonate (1 equiv.) in THF (2 mL mmol$^{-1}$) was added to a stirred suspension of NaH (60% dispersion in mineral oil, 1.2 equiv.) and the alkyne electrophile (1.2 equiv.) in THF (2 mL mmol$^{-1}$). The resulting mixture was stirred at room temperature under argon until completion of the reaction as monitored by TLC. The reaction was quenched by addition of $NH_4Cl$ (sat., aq.). The aqueous layer was extracted with $Et_2O$ and the combined organic extracts washed with brine, and dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the crude product purified by flash chromatography to afford the bromoenyne product.

**Dimethyl 2-(2-bromoallyl)-2-(prop-2-ynyl)malonate (9a).** Synthesised from dimethyl 2-(2-bromoallyl)malonate (2.90 g, 11.7 mmol) and propargyl bromide (1.60 mL, 14.0 mmol) using general procedure 1. The crude product was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **9a** as a colourless oil (2.91 g, 10.1 mmol, 86%). $R_f$ 0.31 (5 : 1 pet. ether–ether); IR (thin film) $\nu_{max}$/cm$^{-1}$ 3289, 2954, 1737; $^1$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 5.83 (1H, t, $J$ = 0.6 Hz), 5.63 (1H, d, $J$ = 1.6 Hz), 3.77 (6H, s), 3.31 (2H, br s), 2.93 (2H, d, $J$ = 2.7 Hz), 2.05 (1H, t, $J$ = 2.7 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 169.5, 126.1, 122.9, 78.6, 72.1, 56.0, 53.0, 42.9, 22.2; HRMS ($ES^+$) calcd for $C_{11}H_{13}BrO_4$ $[M + H]^+$ 289.0074, found 289.0070. Data in accordance with the literature.[8a]

**Dimethyl 2-(2-bromoallyl)-2-(but-3-ynyl)malonate (9b).** Synthesised from dimethyl 2-(2-bromoallyl)malonate (876 mg, 3.49 mmol) and but-3-ynyl trifluoromethanesulfonate (847 mg, 4.19 mmol) using general procedure 1. The crude product was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **9b** as a colourless oil (730 mg, 2.41 mmol, 69%). $R_f$ 0.26 (5 : 1 pet. ether–ether); IR (thin film) $\nu_{max}$/cm$^{-1}$ 3285, 2954, 1730, 1624, 1433, 1201, 1150, 959, 649; $^1$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 5.70–5.68 (1H, m), 5.61 (1H, d, $J$ = 1.8 Hz), 3.75 (6H, s), 3.19 (2H, d, $J$ = 0.5 Hz), 2.30–2.28 (2H, m), 2.21–2.19 (2H, m), 1.97 (1H, t, $J$ = 2.8 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 170.4, 126.7, 122.2, 82.8, 68.9, 56.4, 52.8, 43.3, 30.7, 14.0; HRMS ($ES^+$) calcd for $C_{12}H_{15}BrNaO_4$ $[M + Na]^+$ 325.0070, found 325.0062.

**Dimethyl 2-(2-bromoallyl)-2-(pent-4-ynyl)malonate (9c).** Synthesised from dimethyl 2-(2-bromoallyl)malonate (200 mg, 0.796 mmol) and pent-4-ynyl trifluoromethanesulfonate (207 mg, 0.957 mmol) using general procedure 1. The crude product was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **9c** as a colourless oil (227 mg, 0.716 mmol, 90%). $R_f$ 0.26 (5 : 1 pet. ether–ether); IR (thin film) $\nu_{max}$/cm$^{-1}$ 3291, 2952, 1731, 1625, 1434, 1278, 1150, 901, 640; $^1$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 5.69–5.67 (1H, m), 5.59 (1H, d, $J$ = 1.7 Hz), 3.75 (6H, s), 3.17 (2H, s), 2.21 (2H, dt, $J$ = 7.0, 2.6 Hz), 2.12–2.10 (2H, m), 1.96 (1H, t, $J$ = 2.6 Hz), 1.44–1.42 (2H, m); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 170.8, 126.9, 121.9, 83.5, 68.8, 56.8, 52.7, 43.1, 30.8, 23.4, 18.5; HRMS ($ES^+$) calcd for $C_{13}H_{17}BrNaO_4$ $[M + Na]^+$ 339.0202, found 339.0200.

**Dimethyl 2-(2-bromoallyl)-2-(3-(isopropoxydimethylsilyl)-prop-2-ynyl)malonate (10a). Method A.** To a solution of **9a** (150 mg, 0.519 mmol) in dry THF (5 mL) at −78 °C was added *n*-BuLi (1.6 M in hexanes, 405 μL, 0.649 mmol, 1.25 equiv.), and the mixture was stirred for 20 min. Chloro(diethylamino)-dimethylsilane (130 μL, 0.649 mmol, 1.25 equiv.) was added, and the reaction mixture was allowed to warm to rt. When complete as judged by TLC, the reaction was concentrated, diluted with dry pentane, and stirred for 15 min, then filtered through oven-dried Celite. The clear filtrate was evaporated to give the intermediate aminosilane. This was dissolved in $CH_2Cl_2$ (3 mL) and cooled to 0 °C, then imidazole (71 mg, 1.04 mmol, 2 equiv.), isopropanol (80 μL, 1.04 mmol, 2 equiv.) and DMAP (cat.) were added to the mixture, which was stirred at rt for 2 h. The reaction was quenched with $NaHCO_3$ (aq., sat.), the aqueous layer was extracted with $CH_2Cl_2$, and the combined organic extracts were washed with brine, and dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the product was purified by flash chromatography (10 : 1 pet. ether–ether with 1% $Et_3N$) to afford the **10a** as a colourless oil (158 mg, 0.39 mmol, 75%). $R_f$ 0.38 (5 : 1 pet. ether–ether); IR (thin film) $\nu_{max}$/cm$^{-1}$ 2360, 1658, 1568, 1382, 1369, 1290, 1030; $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ 5.83–5.81 (1H, m), 5.63 (1H, d, $J$ = 1.5 Hz), 4.09 (1H, septet, $J$ = 6.1 Hz), 3.76 (6H, s), 3.30 (2H, s), 2.97 (2H, s), 1.18 (6H, d, $J$ = 6.1 Hz), 0.22 (6H, s); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 169.4, 126.2, 122.7, 100.8, 87.4, 65.9, 56.0, 53.0, 43.0, 25.4, 23.4, 0.6; HRMS ($ES^+$) calcd for $C_{16}H_{25}BrNaO_5Si$ $[M + Na]^+$ 427.0533, found 427.0547.

**Dimethyl 2-(2-bromoallyl)-2-(3-(isopropoxydimethylsilyl)-prop-2-ynyl)malonate (10a). Method B.** To a solution of **9a** (200 mg, 0.691 mmol) in THF (2 mL) at −78 °C was added LiHMDS (1 M in hexanes, 830 μL, 0.83 mmol) and the mixture

was stirred for 30 min. $ClSiMe_2H$ (116 μL, 1.038 mmol) was then added, and the reaction was allowed to warm to rt, then stirred until completion as monitored by TLC. The reaction was quenched with $H_2O$, and the aqueous layer was extracted with ether. The combined organic extracts washed with brine and dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the crude product was purified by flash chromatography (10 : 1 pet. ether–ether), to afford the intermediate alkynyl hydrosilane as a colourless oil (224 mg, 0.645 mmol, 93%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ 5.65–5.58 (1H, m), 5.43 (1H, d, $J$ = 1.5 Hz), 3.87 (1H, septet, $J$ = 3.7 Hz), 3.56 (6H, s), 3.10 (2H, s), 2.76 (2H, s), 0.01 (6H, d, $J$ = 3.7 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$ 169.4, 126.1, 122.8, 102.5, 86.0, 56.0, 53.0, 42.9, 23.6, −3.0; HRMS ($ES^+$) calcd for $C_{13}H_{19}BrNaO_4Si$ $[M + Na]^+$ 369.0128, found 369.0128. To a solution of this hydrosilane (30 mg, 0.086 mmol) in i-PrOH (100 μL) was added $[RuCl_2(p\text{-cymene})]_2$ (0.3 mg, 0.0004 mmol). The reaction was stirred at rt for 10 min, then concentrated. Pentane (1 mL) was added, and the crude product was filtered through Celite (ether eluent). Concentration of the filtrate gave **10a** as a pale pink oil (35 mg, 0.086 mmol, 99%).

**(Diethylamino)diethylchlorosilane.** To a solution of dichlorodiethylsilane (20 mL, 134 mmol) and anhydrous triethylamine (20.6 mL, 147 mmol) in THF at 0 °C was added a solution of anhydrous diethylamine (13.8 mL, 137 mmol) in THF (6 mL) over 2 h. The resulting beige suspension was warmed to rt overnight with vigorous stirring maintained. The mixture was then filtered through Celite under $N_2$, the filter cake washed with anhydrous pentane, and the filtrate concentrated *in vacuo* to give an orange oil. This residue was purified by vacuum distillation (bp 92–94 °C, 36 mbar) to afford (diethylamino) diethylchlorosilane as a colourless oil (17.6 g, 90.8 mmol, 68%). $^1$H NMR (250 MHz, $CDCl_3$) $\delta_H$ 2.88 (4H, q, $J$ = 7.0 Hz), 1.07–0.99 (12H, m), 0.90 (4H, q, $J$ = 6.5 Hz). Data in accordance with literature.[30]

### General procedure 2: alkyne silylation with (diethylamino)-diethylchlorosilane

To a solution of bromoenyne (1 equiv.) in THF (4.5 mL $mmol^{-1}$) at −78 °C under Ar was added LiHMDS (1 M in THF, 1.5 equiv.). The pale yellow solution was stirred at −78 °C for 20 min and (diethylamino)diethylchlorosilane (1.5 equiv.) was added dropwise to the reaction mixture. After stirring for 30 min, after which time the starting material had been consumed (as monitored by TLC), i-PrOH (4 equiv.), DMAP (cat.) and imidazole (4 equiv.) were added and the reaction was allowed to warm to rt. The reaction was quenched by addition of water, and the aqueous layer was extracted with ether. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by flash chromatography to afford the silylated bromoenyne.

**Dimethyl 2-(2-bromoallyl)-2-(3-(diethyl(isopropoxy)silyl)-prop-2-ynyl)malonate (11a).** Synthesised from **9a** (500 mg, 1.73 mmol), LiHMDS (2.60 mL, 2.60 mmol), $ClSiEt_2(NEt_2)$ (606 μL, 2.60 mmol), i-PrOH (530 μL, 6.90 mmol) and imidazole (471 mg, 6.92 mmol) using general procedure 2. The product was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **11a** as a colourless oil (701 mg, 1.62 mmol, 94%). $R_f$ 0.26 (5 : 1 pet. ether–ether); Anal. calcd for $C_{18}H_{29}BrO_5Si$: C, 49.88; H, 6.74, found: C, 49.96; H, 6.72; IR (thin film) $\nu_{max}/cm^{-1}$ 2956, 2178, 1742, 1626, 1025, 733; $^1$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 5.84–5.82 (1H, m), 5.63 (1H, d, $J$ = 1.7 Hz), 4.10 (1H, septet, $J$ = 6.1 Hz), 3.76 (6H, s), 3.32 (2H, s), 3.00 (2H, s), 1.18 (6H, d, $J$ = 6.1 Hz), 0.98 (6H, t, $J$ = 7.9 Hz), 0.62 (4H, app. qd, $J$ = 7.9 Hz, 2.2 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 169.3, 126.2, 122.7, 101.6, 85.5, 66.0, 56.1, 53.0, 42.9, 25.4, 23.5, 6.8, 6.6; HRMS ($ES^+$) calcd for $C_{18}H_{29}NaBrO_5Si$ $[M + Na]^+$ 455.0860, found 455.0862.

**Dimethyl 2-(2-bromoallyl)-2-(4-(diethyl(isopropoxy)silyl)but-3-ynyl)malonate (11b).** Synthesised from **9b** (545 mg, 1.80 mmol), LiHMDS (2.70 mL, 2.70 mmol), $ClSiEt_2(NEt_2)$ (634 μL, 2.70 mmol), i-PrOH (550 μL, 7.20 mmol) and imidazole (490 mg, 7.20 mmol) using general procedure 2. The product was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **11b** as a colourless oil (723 mg, 1.62 mmol, 90%); $R_f$ 0.26 (5 : 1 Pet. ether–ether); Anal. calcd for $C_{19}H_{31}BrO_5Si$: C, 51.00; H, 6.98, found: C, 50.92, H; 7.02; IR (thin film) $\nu_{max}/cm^{-1}$ 2956, 2173, 1735, 1625, 1435, 1088, 1027, 732; $^1$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 5.84–5.82 (1H, m), 5.63 (1H, d, $J$ = 1.7 Hz), 4.10 (1H, septet, $J$ = 6.1 Hz), 3.76 (6H, s), 3.18 (2H, s), 2.31–2.29 (2H, m), 2.23–2.24 (2H, m), 1.18 (6H, d, $J$ = 6.1 Hz), 0.98 (6H, t, $J$ = 7.9 Hz), 0.62 (4H, app. qd, $J$ = 7.9 Hz, 2.2 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 170.4, 126.6, 122.2, 106.0, 81.9, 65.9, 56.5, 52.8, 43.4, 30.9, 25.5, 15.3, 6.8, 6.5; HRMS ($ES^+$) calcd for $C_{19}H_{31}BrNaO_5Si$ $[M + Na]^+$ 469.1016, found 469.1015.

**Dimethyl 2-(2-bromoallyl)-2-(5-(diethyl(isopropoxy)silyl)-pent-4-ynyl)malonate 11c).** Synthesised from **9c** (320 mg, 1.01 mmol), LiHMDS (1.50 mL, 1.50 mmol), $ClSiEt_2(NEt_2)$ (355 μL, 1.50 mmol), i-PrOH (306 μL, 4.00 mmol) and imidazole (272 mg, 4.00 mmol) using general procedure 2. The product was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **11c** as a colourless oil (337 mg, 0.730 mmol, 72%); $R_f$ 0.26 (5 : 1 pet. ether–ether); Anal. calcd for $C_{20}H_{33}BrO_5Si$: C, 52.05; H, 7.21, found: C, 51.94; H, 7.30; IR (thin film) $\nu_{max}/cm^{-1}$ 2955, 2172, 1735, 1625, 1434, 1278, 1026, 732; $^1$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 5.68–5.66 (1H, m), 5.59 (1H, d, $J$ = 1.5 Hz), 4.14 (1H, septet, $J$ = 6.4 Hz), 3.75 (6H, s), 3.18 (2H, s), 2.29 (2H, t, $J$ = 7.3 Hz), 2.14–2.12 (2H, m), 1.49–1.47 (2H, m), 1.20 (6H, d, $J$ = 3.4 Hz), 1.00 (6H, t, $J$ = 6.4 Hz), 0.65–0.62 (4H, m); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 170.8, 127.0, 121.9, 106.8, 81.8, 65.9, 56.9, 52.9, 43.2, 30.9, 25.5, 23.4, 19.9, 6.9, 6.6; HRMS ($ES^+$) calcd for $C_{20}H_{33}BrNaO_5Si$ $[M + Na]^+$ 483.1173, found 483.1179.

***N*-(2-Bromoallyl)-4-methyl-*N*-(prop-2-ynyl)benzene sulfonamide.** To a mixture of *N*-(2-bromoallyl)-4-methylbenzenesulfonamide (1.00 g, 3.45 mmol) and $K_2CO_3$ (953 mg, 6.89 mmol) in acetone (10 mL) was added propargyl bromide (80% in toluene, 460 μL, 4.14 mmol). The reaction mixture was stirred at 60 °C for 12 h, then it was cooled to rt and quenched with water. The aqueous layer was extracted with $Et_2O$, then the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by

flash chromatography (2 : 1 pet. ether–ether) to afford the title compound as a colourless oil (903 mg, 2.75 mmol, 80%); $R_f$ 0.35 (2 : 1 pet. ether–ether); IR (thin film) $\nu_{max}/cm^{-1}$ 3280, 1629, 1344, 1181, 1150, 892, 679; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta_H$ 7.75 (2H, d, $J$ = 8.1 Hz), 7.31 (2H, d, $J$ = 8.1 Hz), 5.97–5.95 (1H, m), 5.69–5.67 (1H, m), 4.13 (2H, d, $J$ = 2.3 Hz), 4.08 (2H, s), 2.44 (3H, s), 2.05 (1H, t, $J$ = 2.3 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta_C$ 143.9, 135.8, 129.6, 127.7, 126.9, 120.5, 76.0, 74.2, 53.8, 36.1, 21.6; HRMS ($ES^+$) calcd for $C_{14}H_{18}BrNNaO_3S$ $[M + MeOH + Na]^+$ 382.0083, found 382.0077.

***N*-(2-Bromoallyl)-*N*-(3-(diethyl(isopropoxy)silyl)prop-2-ynyl)-4-methylbenzene sulfonamide (12).** Synthesised from *N*-(2-bromoallyl)-4-methyl-*N*-(prop-2-ynyl)benzene sulfonamide (150 mg, 0.457 mmol), LiHMDS (686 μL, 0.686 mmol), $ClSiEt_2(NEt_2)$ (160 μL, 0.686 mmol), i-PrOH (140 μL, 1.80 mmol) and imidazole (125 mg, 1.84 mmol) using general procedure 2. The product was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **12** as a colourless oil (107 mg, 0.226 mmol, 50%); $R_f$ 0.26 (5 : 1 pet. ether–ether); Anal. calcd for $C_{20}H_{30}BrNO_3SSi$: C, 50.84; H, 6.40; N, 2.96, found: C, 50.90; H, 6.32; N, 2.95. IR (thin film) $\nu_{max}/cm^{-1}$ 2960, 1353, 1163, 1119, 1092, 1002, 899, 734, 661; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta_H$ 7.77 (2H, d, $J$ = 8.1 Hz), 7.33 (2H, d, $J$ = 8.1 Hz), 5.98 (1H, d, $J$ = 1.8 Hz), 5.72 (1H, d, $J$ = 1.8 Hz), 4.23 (2H, s), 4.11 (2H, s), 3.95 (1H, sept, $J$ = 6.0 Hz), 2.45 (3H, s), 1.14 (6H, d, $J$ = 6.0 Hz), 0.89 (6H, t, $J$ = 7.8 Hz), 0.51 (4H, q, $J$ = 7.8 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta_C$ 144.0, 136.3, 130.4, 130.1, 128.1, 119.7, 98.9, 66.5, 45.4, 41.0, 38.6, 26.2, 25.8, 7.8, 7.0; HRMS ($ES^+$) calcd for $C_{20}H_{30}BrNNaO_3SSi$ $[M + Na]^+$ 494.0791, found 494.0789.

**2-Bromo-3-(prop-2-ynyloxy)prop-1-ene.** To a solution of NaH (60% in mineral oil, 1.50 g, 35.8 mmol) in THF (10 mL) at 0 °C was added propargyl alcohol (1.00 mL, 17.0 mmol) and the reaction mixture was stirred for 30 min. 2,3-Dibromopropene (1.50 mL, 14.3 mmol) was slowly added, then the reaction mixture was allowed to warm to rt and stirred for 12 h. The reaction was quenched by addition of water and the aqueous layer was extracted with $Et_2O$; the combined organic extracts were washed with brine and dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the crude product purified by flash chromatography (5 : 1 pet. ether–ether) to afford the 2-bromo-3-(prop-2-ynyloxy)prop-1-ene as a colourless oil (2.15 g, 12.3 mmol, 86%); $R_f$ 0.26 (5 : 1 pet. ether–ether); IR (thin film) $\nu_{max}/cm^{-1}$ 3300, 2923, 2130, 1639, 1443, 1l62, 1086, 899, 668; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta_H$ 5.97–5.95 (1H, m), 5.67–5.65 (1H, m), 4.23–4.19 (4H, m), 2.47 (1H, t, $J$ = 2.4 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta_C$ 128.4, 118.7, 78.8, 75.1, 73.3, 57.0; HRMS ($ES^+$) calcd for $C_6H_7BrO$ $[M + H]^+$ 173.9681, found 173.9679. Data in accordance with the literature.[31]

**(3-(2-Bromoallyloxy)prop-1-ynyl)diethyl(isopropoxy)silane (13).** Synthesised from 2-bromo-3-(prop-2-ynyloxy) prop-1-ene (500 mg, 2.86 mmol), LiHMDS (4.30 mL, 4.30 mmol), $ClSiEt_2(NEt_2)$ (1.00 mL, 4.30 mmol), i-PrOH (875 μL, 11.4 mmol) and imidazole (778 mg, 11.4 mmol) using general procedure 2. The product was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **13** as a colourless oil (537 mg, 1.68 mmol, 59%); $R_f$ 0.26 (5 : 1 pet. ether–ether); IR (thin film) $\nu_{max}/cm^{-1}$ 2969, 1461, 1380, 1240, 1122, 1088, 878, 734; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta_H$ 5.93 (1H, d, $J$ = 1.7 Hz), 5.64–5.62 (1H, m), 4.23 (2H, s), 4.21 (2H, s), 4.12 (1H, septet, $J$ = 6.1 Hz), 1.17 (6H, d, $J$ = 6.1 Hz), 0.96 (6H, t, $J$ = 7.8 Hz), 0.58 (4H, q, $J$ = 7.9 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta_C$ 128.7, 118.8, 101.3, 89.1, 73.3, 66.3, 57.9, 25.7, 6.8, 6.7; HRMS ($ES^+$) calcd for $C_{13}H_{23}BrNaO_2Si$ $[M + Na]^+$ 341.0543, found 341.0531.

### General procedure 3: cyclisation of bromoenynes to silylcyclohexyldienes

$PdCl_2(PPh_3)_2$ (0.1 equiv.) was added to a degassed solution of bromoenyne (1 equiv.) and vinyl stannane (1.5–1.7 equiv.) in toluene (20 mL $mmol^{-1}$) under argon. The reaction mixture was heated to reflux (110 °C) until completion as monitored by TLC and/or $^1H$ NMR spectroscopic analysis of an aliquot. After concentration, the crude mixture was purified by flash chromatography to obtain the bicyclic diene.

**Dimethyl 7-(isopropoxydimethylsilyl)-5-methyl-4,5-dihydro-1*H*-indene-2,2(3*H*)-dicarboxylate (15a).** Synthesised from **10a** (23.9 mg, 0.0590 mmol) and (*E*)-tributyl(prop-1-enyl)stannane **3a** (29.3 mg, 0.0885 mmol) using general procedure 3. The product was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **15a** as a colourless oil (20 mg, 0.0546 mmol, 92%); $R_f$ 0.33 (5 : 1 pet. ether–ether); IR (thin film) $\nu_{max}/cm^{-1}$ 2358, 1737, 1252, 1024, 890, 822, 781; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta_H$ 5.95 (1H, d, $J$ = 3.3 Hz, H6), 3.95 (1H, septet, $J$ = 6.3 Hz, C*H*$Me_2$), 3.74 (3H, s, $CO_2$*Me*), 3.74 (3H, s, $CO_2$*Me*), 3.67–3.65 (1H, m, H5), 3.20 (2H, br s, H3), 3.03–3.01 (1H, m, H4), 2.96–2.94 (1H, m, H′4), 2.46–2.44 (1H, m, H3), 2.20–2.18 (1H, m, H′3), 1.13 (3H, d, $J$ = 6.3 Hz, CH*Me*$_2$), 1.12 (3H, d, $J$ = 6.3 Hz, CH*Me*$_2$), 1.04 (3H, d, $J$ = 7.1 Hz, *Me*), 0.23 (6H, s, Si*Me*$_2$); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta_C$ 172.8, 172.8, 143.9, 132.1, 131.3, 131.1, 65.1, 58.5, 52.7, 52.7, 43.0, 41.7, 31.1, 30.0, 25.6, 20.1, −0.90; HRMS ($ES^+$) calcd for $C_{19}H_{30}NaO_5Si$ $[M + Na]^+$ 389.1743, found 389.1755.

**Dimethyl 7-(isopropoxydimethylsilyl)-5-phenyl-4,5-dihydro-1*H*-indene-2,2(3*H*)-dicarboxylate (15b).** Synthesised from **10a** (26.6 mg, 0.0656 mmol) and (*E*)-tributyl(styryl)stannane **3b** (38.8 mg, 0.0987 mmol) using general procedure 3. The product was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **15b** as a colourless oil (27.4 mg, 0.0639 mmol, 97%); $R_f$ 0.30 (5 : 1 pet. ether–ether); IR (thin film) $\nu_{max}/cm^{-1}$ 2391, 1737, 1434, 1367, 1252, 1023, 782; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta_H$ 7.30 (2H, m, ArH), 7.24 (3H, m, ArH), 6.10 (1H, d, $J$ = 3.1 Hz, H6), 3.99 (1H, septet, $J$ = 6.2 Hz, C*H*$Me_2$), 3.76 (3H, s, $CO_2$*Me*), 3.74 (3H, s, $CO_2$*Me*), 3.65–3.63 (1H, m, H5), 3.28–3.26 (2H, m, H1), 3.10 (1H, d, $J$ = 17.4 Hz, H4), 2.94 (1H, d, $J$ = 17.4 Hz, H′4), 2.45–2.43 (1H, m, H3), 2.29–2.27 (1H, m, H′3), 1.16 (3H, d, $J$ = 6.2 Hz, CH*Me*$_2$), 1.14 (3H, d, $J$ = 6.2 Hz, CH*Me*$_2$), 0.25 (6H, s, Si*Me*$_2$); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta_C$ 172.7, 145.4, 140.7, 133.4, 131.7, 131.1, 128.5, 127.6, 126.3, 65.2, 58.5, 52.7, 42.9, 41.2, 41.7, 32.0, 25.6, −0.9; HRMS ($ES^+$) calcd for $C_{24}H_{32}NaO_5Si$ $[M + Na]^+$ 451.1892, found 451.1911.

**Dimethyl 7-(diethyl(isopropoxy)silyl)-5-phenyl-4,5-dihydro-1*H*-indene-2,2(3*H*)-dicarboxylate (15c).** Synthesised from **11a**

(300 mg, 0.670 mmol) and (*E*)-tributyl(styryl)stannane **3b** (435 mg, 1.11 mmol) using general procedure 3. The crude product was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **15c** as a colourless oil (237 mg, 0.519 mmol, 77%); $R_f$ 0.42 (5 : 1 pet. ether–ether); IR (thin film) $\nu_{max}/cm^{-1}$ 2955, 1736, 1434, 1381, 1243, 1005, 874, 730, 699; $^1H$ NMR (400 MHz, CDCl3) $\delta_H$ 7.32–7.30 (2H, m, ArH), 7.27–7.23 (3H, m, ArH), 6.12–6.10 (1H, m, H6), 4.01 (1H, septet, $J$ = 6.2 Hz, C*H*Me$_2$), 3.76 (3H, s, CO$_2$*Me*), 3.73 (3H, s, CO$_2$*Me*), 3.64–3.62 (1H, m, H5), 3.25 (2H, br s, H3), 3.10 (1H, d, $J$ = 17.5 Hz, H1), 2.94 (1H, d, $J$ = 17.5 Hz, H′1), 2.45–2.43 (1H, m, H4), 2.27–2.25 (1H, m, H′4), 1.16 (3H, d, $J$ = 6.2 Hz, CH*Me*$_2$), 1.15 (3H, d, $J$ = 6.2 Hz, CH*Me*$_2$), 1.00–0.95 (6H, m, SiCH$_2$*Me*), 0.77–0.74 (4H, m, Si*C*$H_2$Me); $^{13}C$ NMR (125 MHz, CDCl$_3$) $\delta_C$ 172.8, 172.7, 145.5, 141.3, 131.8, 131.5, 130.9, 128.5, 127.6, 126.3, 65.2, 58.5, 52.7, 52.7, 42.9, 42.2, 41.8, 32.1, 25.7, 25.6, 6.8, 5.0, 4.9; HRMS (ES$^+$) calcd for $C_{27}H_{40}NaO_6Si$ [M + MeOH + Na]$^+$ 511.2486, found 511.2432.

**7-(Diethyl(isopropoxy)silyl)-5-methyl-2-tosyl-2,3,4,5-tetrahydro-1*H*-isoindole (15d).** Synthesised from **12** (50.0 mg, 0.106 mmol) and (*E*)-tributyl(prop-1-enyl)stannane **3a** (60.0 mg, 0.181 mmol) using general procedure 3. The product was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **15d** as a colourless oil (29.0 mg, 0.0670 mmol, 63%); $R_f$ 0.29 (5 : 1 pet. ether–ether); IR (thin film) $\nu_{max}/cm^{-1}$ 2958, 1436, 1378, 1230, 1015, 874, 730, 699; $^1H$ NMR (500 MHz, CDCl$_3$) $\delta_H$ 7.72 (2H, d, $J$ = 8.0 Hz, ArH), 7.31 (2H, d, $J$ = 8.0 Hz, ArH), 5.93 (1H, d, $J$ = 3.5 Hz, H6), 4.22–4.20 (2H, m, H1), 4.11–4.00 (2H, m, H3), 3.95 (1H, septet, $J$ = 5.9 Hz, C*H*Me$_2$), 2.42 (4H, s, H5, Ar*Me*), 2.15 (1H, dd, $J$ = 17.0, 8.5 Hz, H5), 1.81–1.73 (1H, m, H′5), 1.13 (3H, d, $J$ = 6.0 Hz, CH*Me*$_2$), 1.11 (3H, d, $J$ = 6.0 Hz, CH*Me*$_2$), 1.02 (3H, d, $J$ = 7.1 Hz, CH*Me*), 0.89 (6H, app. td, $J$ = 8.0, 1.7 Hz, SiCH$_2$*Me*), 0.68–0.65 (4H, m, Si*C*$H_2$Me); $^{13}C$ NMR (125 MHz, CDCl$_3$) $\delta_C$ 145.1, 143.2, 134.4, 129.9, 129.6, 128.1, 127.8, 127.5, 65.3, 56.3, 55.4, 29.8, 28.7, 25.7, 25.7, 21.5, 19.9, 6.8, 5.0, 5.0; HRMS (ES$^+$) calcd for $C_{23}H_{35}NNaO_3SSi$ [M + Na]$^+$ 456.1999, found 456.2000.

**Diethyl(isopropoxy)(6-methyl-1,3,6,7-tetrahydroisobenzofuran-4-yl)silane (15e).** Synthesised from **13** (50.0 mg, 0.157 mmol) and (*E*)-tributyl(prop-1-enyl)stannane **3a** (88.1 mg, 0.266 mmol) using general procedure 3. The crude product was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **15e** as a colourless oil (10.0 mg, 0.0356 mmol, 23%); $R_f$ 0.29 (5 : 1 pet. ether–ether); IR (thin film) $\nu_{max}/cm^{-1}$ 2955, 1732, 1463, 1210, 866; $^1H$ NMR (500 MHz, CDCl$_3$) $\delta_H$ 5.99 (1H, d, $J$ = 3.3 Hz, H5), 4.75–4.73 (2H, m, H1), 4.60–4.58 (2H, m, H3), 3.99 (1H, septet, $J$ = 6.0 Hz, C*H*Me$_2$), 2.59–2.48 (1H, m, H8), 2.26 (1H, dd, $J$ = 17.0, 9.0 Hz, H7), 1.92–1.84 (1H, m, H7), 1.16 (3H, d, $J$ = 6.0 Hz, CH*Me*$_2$), 1.15 (3H, d, $J$ = 6.0 Hz, CH*Me*$_2$), 1.09 (3H, d, $J$ = 7.0 Hz, CH*Me*), 0.94 (6H, t, $J$ = 7.9 Hz, SiCH$_2$*Me*), 0.75–0.65 (4H, m, Si*C*$H_2$Me); $^{13}C$ NMR (125 MHz, CDCl$_3$) $\delta_C$ 144.6, 131.3, 129.7, 127.4, 76.3, 75.7, 65.2, 29.9, 27.7, 25.7, 20.1, 6.7, 4.9; HRMS (ES$^+$) calcd for $C_{16}H_{28}NaO_2Si$ [M + Na]$^+$ 303.1751, found 303.1749.

**Dimethyl 5-(diethyl(isopropoxy)silyl)-7-methyl-3,4,7,8-tetrahydronaphthalene-2,2(1*H*)-dicarboxylate (15f).** Synthesised from **11b** (100 mg, 0.223 mmol) and (*E*)-tributyl(prop-1-enyl)-stannane **3a** (126 mg, 0.381 mmol) using general procedure 3. The product was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **15f** as a colourless oil (68.0 mg, 0.166 mmol, 75%); $R_f$ 0.52 (5 : 1 pet. ether–ether); IR (thin film) $\nu_{max}/cm^{-1}$ 2956, 1735, 1435, 1250, 1170, 1121, 1083, 1018, 872, 731; $^1H$ NMR (500 MHz, CDCl$_3$) $\delta_H$ 5.99 (1H, d, $J$ = 3.4 Hz, H6), 3.94 (1H, sept, $J$ = 6.1 Hz, OC*H*Me$_2$), 3.72 (3H, s, CO$_2$*Me*), 3.71 (3H, s, CO$_2$*Me*), 2.60 (2H, m, H1), 2.31–2.29 (3H, m, H4 and H7), 2.24–2.20 (1H, m, H3), 2.12 (1H, dt, $J$ = 13.4, 6.3 Hz, H3), 1.98 (1H, dd, $J$ = 16.0, 7.5 Hz, H8), 1.80–1.69 (1H, m, H8), 1.12 (6H, t, $J$ = 6.1 Hz, OCH*Me*$_2$), 1.01 (3H, d, $J$ = 6.8 Hz, C11), 0.95–0.90 (6H, m, SiCH$_2$*Me*), 0.75–0.72 (4H, m, Si*C*$H_2$Me); $^{13}C$ NMR (125 MHz, CDCl$_3$) $\delta_C$ 172.4, 172.0, 144.9, 134.1, 127.8, 125.7, 65.2, 53.5, 52.7, 52.7, 36.4, 36.1, 29.5, 28.5, 25.8, 25.8, 25.2, 19.6, 7.0, 7.0, 5.7, 5.6; HRMS (ES$^+$) calcd for $C_{22}H_{36}NaO_5Si$ [M + Na]$^+$ 431.2224, found 431.2236. NMR data for **16a** and **17a** was obtained from a purified mixture of **16a** and **17a** (2.8 : 1 ratio).

**Dimethyl (*Z*)-4-((*E*)-1-(diethyl(isopropoxy)silyl)but-2-en-1-ylidene)-3-methylenecyclohexane-1,1-dicarboxylate (16a).** $^1H$ NMR (500 MHz, CDCl$_3$) $\delta_H$ 6.00 (1H, dd, $J$ = 15.5, 1.5 Hz, H8), 5.32 (1H, dq, $J$ = 15.5, 6.5 Hz, H9), 5.01 (1H, d, $J$ = 2.3 Hz, H11), 4.87–4.83 (1H, m, H11), 4.00 (1H, sept, $J$ = 6.0 Hz, C*H*Me$_2$), 3.72 (6H, s, CO$_2$*Me*), 2.81 (2H, s, H2), 2.58–2.52 (2H, m, H5), 2.11–2.06 (2H, m, H6), 1.74 (3H, dd, $J$ = 6.5, 1.5 Hz, H10), 1.13 (6H, d, $J$ = 6.0 Hz, CH*Me*$_2$), 0.91 (6H, t, $J$ = 7.5 Hz, Si*C*$H_2$Me), 0.69 (4H, $J$ = 7.5 Hz, SiCH$_2$*Me*); $^{13}C$ NMR (126 MHz, CDCl$_3$) $\delta_C$ 171.2, 151.58, 146.1, 132.1, 132.1, 127.6, 115.1, 65.2, 57.1, 52.8, 41.2, 32.3, 30.3, 25.9, 18.7, 7.3, 6.7.

**Dimethyl (*E*)-3-(1-(diethyl(isopropoxy)silyl)buta-1,3-dien-1-yl)-4-methylcyclopent-3-ene-1,1-dicarboxylate (17a).** $^1H$ NMR (500 MHz, CDCl$_3$) $\delta_H$ 6.36 (1H, d, $J$ = 10.6 Hz, H8), 6.31 (1 H, ddd, $J$ = 16.5, 10.6, 9.7 Hz, H9), 5.26 (1H, dd, $J$ = 16.5, 2.0 Hz, H10), 5.13 (1H, dd, $J$ = 9.7, 2.0, H10), 4.00 (1H, sept, $J$ = 6.0 Hz, C*H*Me$_2$), 3.73 (6H, s, CO$_2$*Me*), 2.61 (1H, d, $J$ = 17.2 Hz, H2), 2.45 (1H, d, $J$ = 17.2 Hz, H2), 2.24–2.18 (2H, m, H6 and H5), 2.14–2.11 (1H, m, H6), 1.87–1.82 (1H, m, H5), 1.50 (3H, s, H11), 1.14 (6H, d, $J$ = 6.0 Hz, CH*Me*$_2$), 0.91 (6H, t, $J$ = 7.5 Hz, Si*C*$H_2$Me), 0.69 (4H, $J$ = 7.5 Hz, SiCH$_2$*Me*); $^{13}C$ NMR (126 MHz, CDCl$_3$) $\delta_C$ 172.4, 172.2, 144.5, 140.2, 134.4, 130.5, 123.2, 118.9, 65.2, 53.9, 52.7, 52.7, 36.3, 28.3, 27.7, 26.0, 25.9, 20.3, 7.0, 6.8, 5.5, 5.3.

**Dimethyl 4-(diethyl(isopropoxy)silyl)-2-methyl-5,6,7,9-tetrahydro-1*H*-benzo[7]annulene-8,8(2*H*)-dicarboxylate (15g).** Synthesised from **11c** (51.4 mg, 0.111 mmol) and (*E*)-tributyl-(prop-1-enyl)stannane **3a** (55.0 mg, 0.166 mmol) using general procedure 3. The crude product was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **15g** as a colourless oil (27.5 mg, 0.0651 mmol, 58%, mixture with **16b** and **17b**); $R_f$ 0.52 (5 : 1 pet. ether–ether); IR (thin film) $\nu_{max}/cm^{-1}$ 2954, 1736, 1455, 1228, 1172, 1007, 873, 729; $^1H$ NMR (500 MHz, CDCl$_3$) $\delta_H$ 5.98 (1H, d, $J$ = 3.2 Hz, H3), 3.95 (1H, septet, $J$ = 5.9 Hz, C*H*Me$_2$), 3.71 (3H, s, CO$_2$*Me*), 3.70 (3H, s, CO$_2$*Me*), 2.49–2.44 (2H, m, H9), 2.29–2.20 (2H, m, H5), 2.17–2.04 (3H, m, H5, H2, H1), 1.78–1.72 (1H, m, H1), 1.68–1.60 (2H, m, H7),

1.38–1.33 (2H, m, H6), 1.13 (3H, d, $J$ = 6.0, CH$Me_2$), 1.13 (3H, d, $J$ = 6.0, CH$Me_2$), 0.99 (3H, d, $J$ = 7.0 Hz, CH$Me$), 0.96–0.87 (6H, m, SiCH$_2$$Me$), 0.76–0.60 (4H, m, SiC$H_2$Me); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 172.3, 172.0, 145.3, 137.8, 135.6, 129.2, 65.1, 55.0, 52.3, 52.1, 39.7, 39.1, 37.2, 31.4, 29.8, 28.6, 26.7, 25.6, 25.4, 22.7, 19.4, 17.3, 13.6, 6.9, 6.8, 5.2, 5.1; HRMS (ES$^+$) calcd for $C_{23}H_{38}NaO_5Si$ $[M + Na]^+$ 445.2381, found 445.2386.

**Dimethyl 8-(trimethylsilyl)bicyclo[5.2.0]nona-1,7-diene-3,3-dicarboxylate (30).** To $Pd(PPh_3)_4$ (5.0 mg, 0.0045 mmol, 5 mol%) was added a degassed solution of bromoenyne **27**[8a] (35.0 mg, 0.0899 mmol) and $Et_3N$ (25.0 μl, 0.180 mmol) in toluene (1.2 mL) under Ar, and the mixture was refluxed in a preheated oil bath (110 °C) until completion of the reaction (16 h). The mixture was concentrated, and the residue purified by flash chromatography (10 : 1 pet. ether–$Et_2O$) to obtain **30** as a colourless oil (25.0 mg, 0.0811 mmol, 90%); $R_f$ 0.46 (2 : 1 pet. ether–$Et_2O$); IR (thin film) $\nu_{max}$/cm$^{-1}$ 2954, 1736, 1248, 840; $^1$H NMR (500 MHz, MeOD) $\delta_H$ 4.99 (1H, s, H2), 3.71 (6H, s, $CO_2Me$), 2.73 (2H, t, $J$ = 2.9 Hz, H9), 2.38–2.32 (2H, m, H6), 2.29–2.25 (2H, m, H4), 1.67 (2H, app. qd, $J$ = 6.0, 4.5 Hz, H5), 0.12 (9H, s, Si$Me$); $^{13}$C NMR (126 MHz, MeOD) $\delta_C$ 173.1, 159.9, 150.9, 145.3, 110.9, 63.2, 53.3, 36.4, 35.7, 31.9, 23.6, −1.7; HRMS (ES+) calcd for $C_{16}H_{24}NaO_4Si$ $[M + Na]^+$ 331.1336, found 331.1340.

**Dimethyl 8-(diethyl(isopropoxy)-λ$^4$-sulfanyl)bicyclo[5.2.0]nona-1,7-diene-3,3-dicarboxylate (36).** To $Pd(PPh_3)_4$ (5.0 mg, 0.0045 mmol, 5 mol%) was added a degassed solution of bromoenyne **11c** (32.0 mg, 0.0693 mmol) and $Et_3N$ (20.0 μl, 0.144 mmol) in toluene (1.2 mL) under Ar, and the mixture was heated in a preheated oil bath (110 °C) until completion of the reaction (16 h). The mixture was concentrated, and the residue was purified by flash chromatography (10 : 1 pet. ether–$Et_2O$) to obtain **36** as a colourless oil (23.0 mg, 0.0604 mmol, 87%); $R_f$ 0.24 (9 : 1 pet. ether–$Et_2O$); IR (thin film) $\nu_{max}$/cm$^{-1}$ 2955, 1736, 1565, 1243, 1031; $^1$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 5.09 (1H, s, H2), 3.99 (1H, sept, $J$ = 6.0 Hz, SiOC$H$Me), 3.74 (6H, s, $CO_2Me$), 2.84 (2H, t, $J$ = 2.9 Hz, H9), 2.39–2.35 (2H, m, H6), 2.33–2.30 (2H, m, H4), 1.71 (2H, dt, $J$ = 10.8, 5.6 Hz, H5), 1.15 (6H, d, $J$ = 6.0 Hz, SiOCH$Me$), 0.96 (6H, t, $J$ = 7.9 Hz, SiCH$_2$$Me$), 0.68 (4H, q, $J$ = 7.9 Hz, SiC$H_2$Me); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta_C$ 171.8, 160.6, 146.9, 144.5, 110.5, 65.6, 62.0, 52.9, 36.9, 34.7, 31.5, 26.0, 22.6, 6.8, 5.7; HRMS (ESI$^+$) calcd for $C_{20}H_{32}NaO_5Si$ $[M + Na]^+$ 403.1911, found 403.1916.

**Dimethyl 6-methyl-4-oxo-4,5,6,7-tetrahydro-1*H*-indene-2,2-(3*H*)-dicarboxylate (37). 15a** (16.8 mg, 0.0458 mmol) was dissolved in THF–MeOH (1 : 1, 400 μL). KF (5.3 mg, 0.090 mmol), $KHCO_3$ (9.2 mg, 0.090 mmol), $H_2O_2$ (30% aq., 5.2 μL, 0.050 mmol) were added and the reaction mixture was heated to 40 °C for 3 h. The reaction was allowed to cool to rt, then it was diluted with $CH_2Cl_2$ and water. The organic extract was washed with water, dried ($MgSO_4$), and concentrated. The product was purified by flash chromatography (2 : 1 pet. ether–ether) to afford **37** as a colourless oil (5.3 mg, 0.020 mmol, 43%); $R_f$ 0.21 (2 : 1 pet. ether–ether); IR (thin film) $\nu_{max}$/cm$^{-1}$ 2349, 1734, 1667, 1434, 1262, 913, 745; $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ 3.75 (6H, s, $CO_2Me$), 3.23–3.21 (4H, m, H1, H3), 2.42 (1H, dd, $J$ = 17.0, 3.9 Hz, H5), 2.42–2.36 (1H, m, H7), 2.32–2.20 (1H, m, H6), 2.09 (1H, dd, $J$ = 17.0, 12.0 Hz, H5), 2.07–2.00 (1H, m, H7), 1.07 (3H, d, $J$ = 6.5 Hz, $Me$); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 194.9, 172.0 (2C), 158.7, 134.8, 57.8, 52.5 (2C), 45.8, 45.2, 38.6, 33.8, 31.0, 21.0; HRMS (ES$^+$) calcd for $C_{14}H_{19}O_5$ $[M + H]^+$ 267.1227, found 267.1225.

**Dimethyl 4-(diethyl(isopropoxy)silyl)-6-phenyl-1*H*-indene-2,2(3*H*)-dicarboxylate (38).** To a solution of **15c** (20.0 mg, 0.0438 mmol) in $CH_2Cl_2$ (1 mL) was added $MnO_2$ (19.0 mg, 0.220 mmol) and the reaction mixture was stirred at 30 °C for 12 h. The mixture was filtered through a pad of Celite and concentrated, and the residue was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **38** as a colourless oil (17.0 mg, 0.0374 mmol, 85%); $R_f$ 0.31 (5 : 1 pet. ether–ether); IR (thin film) $\nu_{max}$/cm$^{-1}$ 2923, 2853, 1740, 1460, 699; $^1$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 7.60–7.40 (6H, m, H5, H7, ArH), 7.33 (1H, t, $J$ = 7.3 Hz, ArH), 4.08 (1H, septet, $J$ = 6.1 Hz, C$H$Me$_2$), 3.76 (6H, s, $CO_2Me$), 3.74 (2H, s, H1 or H3), 3.63 (2H, s, H1 or H3), 1.19 (6H, d, $J$ = 6.1 Hz, CH$Me_2$), 1.03–0.93 (4H, m, SiC$H_2$Me); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 172.2, 144.6, 141.5, 139.9, 139.4, 132.7, 132.5, 128.7, 127.1, 127.0, 124.3, 65.5, 60.4, 52.9, 41.4, 40.1, 25.8, 6.8, 5.5; HRMS (ES$^+$) calcd for $C_{26}H_{34}NaO_5Si$ $[M + Na]^+$ 477.2068, found 477.2053.

**4-(Diethyl(isopropoxy)silyl)-6-methyl-2-tosylisoindoline (39).** To a solution of **15d** (29.0 mg, 0.0669 mmol) in $CH_2Cl_2$ (1 mL) was added $MnO_2$ (50.0 mg, 0.460 mmol) and the reaction mixture was stirred at 30 °C for 12 h. The mixture was filtered through a pad of Celite and concentrated, and the residue was purified by flash chromatography (5 : 1 pet. ether–ether) to afford **39** as a colourless oil (27.0 mg, 0.0625 mmol, 93%); $R_f$ 0.30 (5 : 1 pet. ether–ether); IR (thin film) $\nu_{max}$/cm$^{-1}$ 2958, 1733, 1596, 1433, 1259, 699; $^1$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 7.76 (2H, d, $J$ = 8.3 Hz, ArH), 7.29 (2H, d, $J$ = 8.3 Hz, ArH), 7.14 (1H, s, H5), 6.99 (1H, s, H7), 4.67 (2H, s, H3), 4.56 (2H, s, H1), 4.05 (1H, sept, $J$ = 6.3 Hz, C$H$Me$_2$), 2.40 (3H, s, Ts-$Me$), 2.31 (3H, s, $Me$), 1.18 (6H, d, $J$ = 6.3 Hz, CH$Me_2$), 0.92 (6H, t, $J$ = 6.8 Hz, SiCH$_2$$Me$), 0.88–0.82 (4H, m, SiC$H_2$Me); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 143.4, 138.8, 136.3, 135.6, 134.4, 133.7, 131.1, 129.7, 127.6, 124.2, 65.4, 54.6, 53.3, 25.7, 21.4, 21.2, 6.8, 5.5; HRMS (ES$^+$) calcd for $C_{23}H_{33}NNaO_3SSi$ $[M + Na]^+$ 454.1843, found 454.1845.

**Dimethyl 4-hydroxy-6-phenyl-1*H*-indene-2,2(3*H*)-dicarboxylate (40).** To a solution of **38** (17.0 mg, 0.0374 mmol) in THF–MeOH (1 : 1, 1 mL) was added and TBAF (1 M solution in THF, 13.0 μL, 0.013 mmol), $KHCO_3$ (7.5 mg, 0.080 mmol) and $H_2O_2$ (30% aq., 13 μL, 0.12 mmol). The reaction mixture was heated to 60 °C for 3 h, then it was cooled to rt, diluted with $CH_2Cl_2$ and water. The organic phase was washed with water, dried ($MgSO_4$), and concentrated. The residue was purified by flash chromatography (2 : 1 pet. ether–ether) to afford **40** (9.4 mg, 0.0288 mmol, 78%); $R_f$ 0.15 (2 : 1 pet. ether–ether); IR (thin film) $\nu_{max}$/cm$^{-1}$ 2954, 1733, 1596, 1434, 1260, 1165, 864, 699; $^1$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 7.52 (2H, d, $J$ = 7.5 Hz, ArH), 7.41 (2H, t, $J$ = 7.5 Hz, ArH), 7.32 (1H, t, $J$ = 7.5 Hz, ArH), 7.01 (1H, s, H7), 6.85 (1H, s, H5), 3.78 (6H, s, $CO_2Me$), 3.66 (2H, s,

H1), 3.60 (2H, s, H3); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 172.0, 151.8, 142.8, 142.5, 140.9, 128.7, 127.2, 127.1, 124.7, 115.6, 112.6, 60.3, 53.0, 40.9, 36.8; HRMS ($ES^-$) calcd for $C_{19}H_{17}O_5$ $[M]^-$ 325.1081, found 325.1081.

**6-Methyl-2-tosylisoindolin-4-ol (41).** To a solution of **39** (20.0 mg, 0.0463 mmol) in THF–MeOH (1 : 1, 1 mL) was added and TBAF (1 M solution in THF, 16.0 μL, 0.016 mmol), $KHCO_3$ (9.0 mg, 0.10 mmol) and $H_2O_2$ (30% aq., 17 μL, 0.15 mmol). The reaction mixture was heated to 60 °C for 3 h, then it was cooled to rt, diluted with $CH_2Cl_2$ and water. The organic phase was washed with water, dried ($MgSO_4$), and concentrated. The residue was purified by flash chromatography (2 : 1 pet. ether–ether) to afford **41** as a colourless oil (14.0 mg, 0.0461 mmol, 99%); $R_f$ 0.26 (2 : 1 pet. ether–ether); IR (thin film) $\nu_{max}/cm^{-1}$ 2954, 1733, 1596, 1434, 1260, 1165, 864, 699; $^1$H NMR (500 MHz, $CDCl_3$) $\delta_H$ 7.76 (2H, d, $J$ = 7.7 Hz, ArH), 7.31 (2H, d, $J$ = 7.7 Hz, ArH), 6.54 (1H, s, H7), 6.47 (1H, s, H5), 4.57 (4H, s, H1, H3), 2.40 (3H, s, Ts*Me*), 2.24 (3H, s, *Me*); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta_C$ 150.6, 143.6, 139.8, 138.2, 133.6, 129.8, 127.6, 119.7, 115.2, 114.8, 54.0, 51.4, 21.5, 21.2; HRMS ($ES^+$) calcd for $C_{16}H_{17}NNaO_3S$ $[M + Na]^+$ 326.0821, found 326.0824.

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