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β-Halovinylsilanes in oligoyne synthesis: a fluoride-catalysed unmasking of alkynes from β-fluorovinylsilanes

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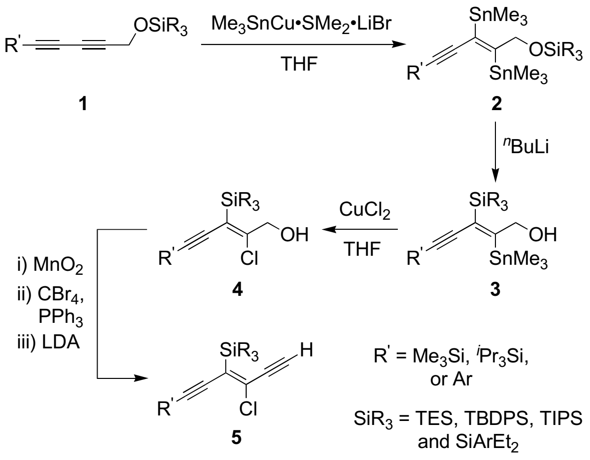
ABSTRACT

A stereoselective halodestannylation of (*E*)-β-stannylvinylsilane **6** has been used to access a range of (*E*)-β-halovinylsilanes. Most notably, the β-fluorovinylsilane **14** was accessed in high yield using the Selectfluor® reagent, and subsequently converted into a masked hexayne **22**. Release of the hexayne **25** was achieved by exposing **22** to sub-stoichiometric quantities of fluoride.

Oligoynes constitute an important class of highly π-conjugated organic molecule owing to their interesting physical properties and potential applications in advanced materials.[1] Whilst the Eglinton–Glaser–Hay oxidative coupling[2] of terminal alkynes provides the most established methodology for assembling this type of conjugated scaffold,[3] the instability of the terminal oligoynes, which are required as intermediates in this approach, has encouraged the development of other methodologies for oligoyne synthesis.[4–8] These alternative strategies generally involve the oligoyne being assembled first in a protected form. Unfortunately, many of these approaches are unsuitable for long-chain oligoyne assembly because the product is not particularly stable under the unmasking conditions.

Elimination strategies have been used widely for preparing alkynes,[9] although only rarely for synthesising oligoynes longer than the tetrayne.[10] We postulated that β-halovinylsilanes would be attractive alkyne precursors for oligoyne synthesis. Specifically, we envisaged a masked oligoyne containing one or more β-halovinylsilanes would undergo a highly chemoselective dehalosilylation reaction in the presence of fluoride. Significantly, we hoped this elimination approach would provide the corresponding oligoyne under sufficiently mild conditions which would leave the final product intact.[11] To this end, we have developed an efficient and flexible synthesis of a masked triyne **5** in which the internal alkynyl unit is protected as a (*E*)-β-chlorovinylsilane (Scheme 1).[12] Key steps in the synthesis of **5** include (i) a completely (*E*)-stereo- and regioselective Cu-mediated bis-stannylation of the unsymmetrically substituted internal buta-1,3-diyne **1** to afford bis-stannane **2**; (ii) a regioselective tin–lithium exchange on **2**, which initiates a 1,4-retro Brook rearrangement to install the vinylsilane in **3**; and (iii) a stereoselective chlorodestannylation of **3** to introduce the vinyl chloride motif in **4**, which can then be elaborated to masked triyne **5** in three straightforward steps. We have used this methodology to prepare long-chain oligoynes including the first aryl end-capped dodecayne.[13]



Scheme 1. Summary of our established route to a masked triyne containing an internal (*E*)-β-chlorovinylsilane.

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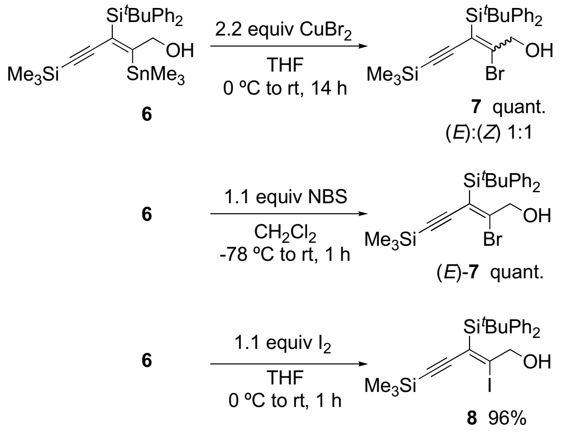
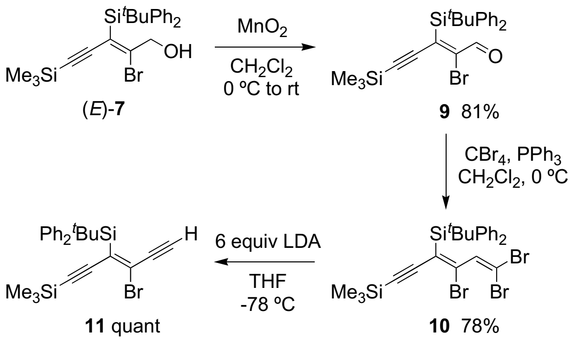
Our synthetic strategy allows a range of end-capping groups and silyl substituents to be introduced into masked triyne **5**. The vinylstannane **3** potentially also allows the halogen in the internal masked alkyne to be varied. To-date, however, we have focused exclusively on β-chlorovinylsilanes, rather than other halogens, since we thought that this motif would provide the right level of reactivity to ensure that the unit is not prone to premature dechlorosilylation but can still be effected when desired under mild conditions upon treatment with fluoride.[11] We recently postulated that changing the chloro substituent in **5** for other halogen leaving groups might impart useful properties on the masked oligoyne products. We were particularly keen to investigate whether the corresponding β-fluorovinylsilanes could be accessed, since β-elimination might proceed under fluoride *catalysis* on account of a fluoride anion being regenerated as the by-product in the elimination step. Although fluoride is only rarely used as a leaving group in elimination reactions,[14] and β-fluorovinylsilanes have not been used in elimination routes to alkynes, we envisaged that if successful, a fluoride-catalysed elimination would represent an exceptionally mild and chemoselective unmasking strategy for oligoyne synthesis. Herein, we report the synthesis and chemical behaviour of the iodo-, bromo- and fluoro-analogues of vinyl chloride **4** and show that β-fluorovinylsilanes are indeed very attractive alternatives to β-chlorovinylsilanes for oligoyne synthesis.

Vinylstannane **3** serves as our starting material for the synthesis of a range of β-halovinylsilanes. Ordinarily we treat **3** with CuCl$_2$ to provide vinyl chloride **4** in excellent yield and complete (*E*)-stereoselectivity.[12] In contrast, when vinylstannane **6** was treated with CuBr$_2$ under similar conditions,[15] the desired β-bromovinylsilane **7** was obtained in quantitative yield, but as a 1:1 mixture of (*E*)/(*Z*) stereoisomers (Scheme 2).[16] Much better results were obtained using N-bromosuccinimide (NBS): addition of NBS to a solution of **6** in CH$_2$Cl$_2$ at −78 °C, and warming to room temperature, provided vinyl bromide **7**,[17] again in excellent yield, but now as a single stereoisomer, which was later confirmed to have the (*E*)-geometry (vide infra).[18] The formation of the corresponding vinyl iodide **8** was achieved by treating **6** with molecular iodine (Scheme 2).[19,20] Although we were unable to confirm the stereochemistry of the olefin in **8**, we tentatively assign an (*E*)-configuration by analogy with the examples of this reaction elsewhere in the literature.[19]

β-Bromovinylsilane (*E*)-**7** was elaborated to the masked triyne **11** using the same reaction sequence as that used to access the corresponding β-chlorovinylsilanes (Scheme 3). Thus, allylic oxidation of (*E*)-**7** with MnO$_2$ provided aldehyde **9**, and subsequent dibromoolefination gave tribromide **10** in good yield (Scheme 3). A crystal structure of tribromide **10** confirmed that the bromodestannylation of **6** had proceeded with retention of configuration (Fig. 1).[21] Treatment of **10** with an excess of LDA at −78 °C effected a Fritsch–Buttenberg–Wiechell reaction to provide triyne **11** after aqueous work-up. Triyne **11** was used directly in the next step and exposed to our modified Hay coupling conditions in which we employ a copper salt (Cu(OTf)$_2$) which possesses a non-nucleophilic counteranion to minimise premature dehalosilylation.[12b,13] Unfortunately, in spite of taking this precautionary measure, triyne **11** decomposed rapidly under the reaction conditions. ^{1}H NMR analysis of the crude product upon work-up showed only signals corresponding to the *tert*-butyldiphenylsilyl group, which was most likely present as its corresponding silanol. The β-bromovinylsilane moiety in triyne **11** is clearly much more labile than its chloro analogue under the oxidative coupling conditions. In light of these results, we elected not to pursue any further derivatives of vinyl iodide **8**, as we expected these would exhibit reduced stability; however, we note that vinyl iodides are excellent substrates in metal-catalysed cross-coupling processes, and this substrate class might have application in the preparation of heavily substituted olefins,[22] since the residual vinylsilane can also serve as a masked vinyl halide to allow further elaboration.[23]



Scheme 2. Formation of a β-bromovinylsilane and a β-iodovinylsilane from vinylstannane **6**.



Scheme 3. Conversion of β-bromovinylsilane (*E*)-**7** to the masked triyne **11**.

We next turned our attention to the more attractive β-fluorovinylsilane analogues. Although fluorine atoms have been incorporated into a diverse range of organic molecules, there are very few examples of β-fluorovinylsilanes in the literature.[24–27] Our desired approach, in which we sought to effect fluorodestannylation of vinylstannane **6** has literature precedent. Fluorodestannylation

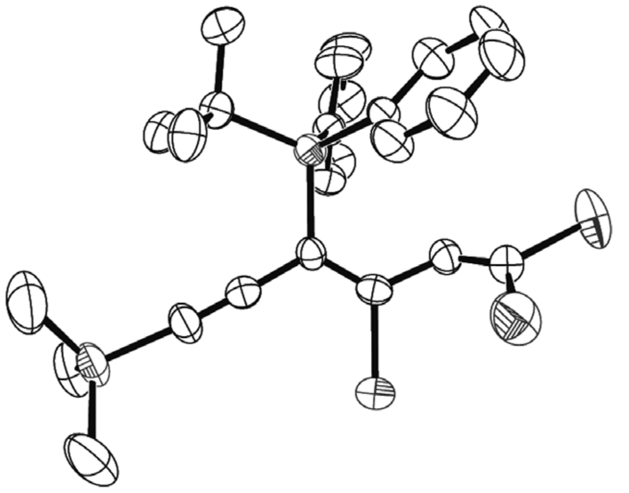
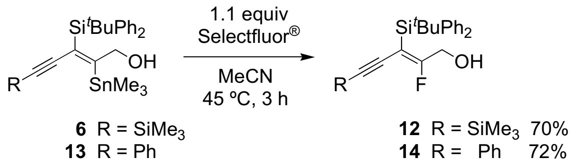


Figure 1. ORTEP plot of **10** confirming the (*E*)-stereochemistry of the internal olefin. Atomic displacement parameters at 296 K.

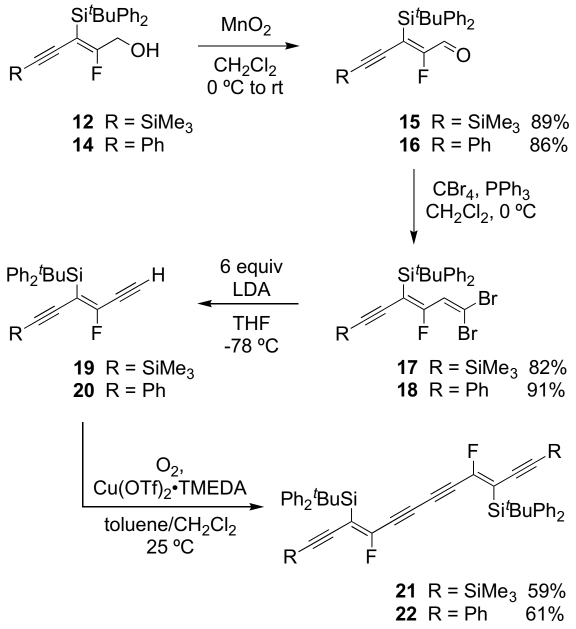


Scheme 4. Synthesis of β-fluorovinylsilanes using Selectfluor®.

has been accomplished using XeF_2 in the presence of a silver(I) salt.[28] Selectfluor® (1-chloromethyl-4-fluoro-1,4-diazonia-bicyclo-[2.2.2]octane bis(tetrafluoroborate)[29]) has also been used to effect the electrophilic fluorination of vinylstannanes.[30] In our hands, we found that treatment of (*E*)-vinylstannane **6** with Selectfluor® in acetonitrile at 45 °C led to clean consumption of the starting material and the formation of β-fluorovinylsilane **12** in 70% yield (Scheme 4).[31] The product was obtained as a single stereoisomer, which we have assigned as (*E*) in analogy with literature reports.[30] A similar result was obtained when the trimethylsilyl group of **6** was replaced by a phenyl residue (**13**→**14**) (Scheme 4).

With two β-fluorovinylsilanes in hand, we directed our attention towards synthesising the corresponding masked hexaynes (Scheme 5). As before, allylic oxidation of **12** to the corresponding aldehyde **15** with MnO_2, followed by dibromoolefination afforded dibromoolefin **17** without incident. Treatment of **17** with 6 equiv of LDA at −78 °C afforded the masked triyne **19**, which was immediately subjected to our modified Hay coupling conditions. This time, the homocoupling reaction proceeded smoothly and was complete in 4–5 h, affording the masked hexayne **21** in good yield (Scheme 5).[32] Masked hexayne **22** was obtained in a similar fashion from **14** (Scheme 5).

We have previously synthesised masked hexaynes **23** and **24** (Fig. 2), which incorporate two β-chlorovinylsilanes into the conjugated framework.[13] The UV–vis absorption spectra for fluoro-substituted masked hexayne **21** and its chloro analogue **23** are shown in Figure 3. The two spectra display a similar overall shape, and the intensity of the peaks is also of the same order of magnitude; however, more interestingly, replacing the chloro substituents in **23** with fluoro substituents leads to a ~10 nm hypsochromic shift in λ_{max}. This suggests a larger HOMO–LUMO band gap for these oligoyne precursors, which should improve the stability of fluorinated masked oligoynes compared with their β-chlorovinylsilane analogues. Similar observations were made when the UV–vis spectra of **22** and **24** were compared, although in these two cases, the spectra exhibited a bathochromic shift owing to the conjugated π-electron system extending into the phenyl end-groups.



Scheme 5. Synthesis of masked hexaynes **21** and **22**.

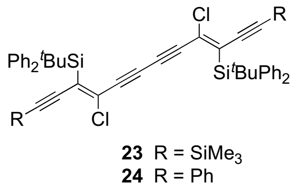


Figure 2. Chloro-substituted masked hexaynes **23** and **24**.[13]

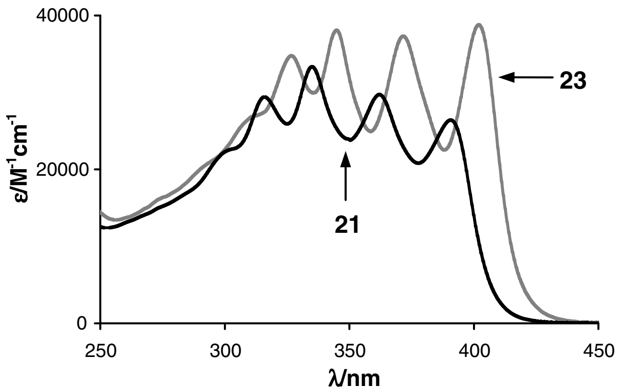
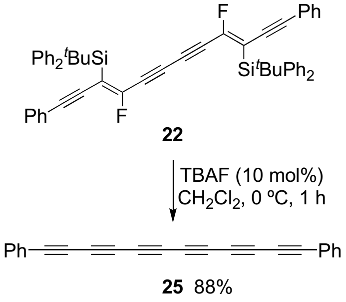


Figure 3. UV–vis spectra of masked hexaynes **21** (black line) and **23** (grey line).

Having shown that our synthetic approach could be extended to the synthesis of masked oligoynes containing β-fluorovinylsilanes in place of β-chlorovinylsilanes, we were now ready to investigate whether or not we could effect unmasking.[33] We have already shown that the elimination reaction of chloro-substituted masked hexayne **24** requires stoichiometric quantities (i.e., 2 equiv) of TBAF and proceeds rapidly at room temperature.[13] We were therefore delighted to observe that fluoro-substituted masked hexayne **22** underwent twofold defluorosilylation on exposure to a *sub-stoichiometric* quantity of TBAF (10 mol %) in 1 h at 0 °C, to provide known hexayne **25** in 88% isolated yield (Scheme 6). This result confirmed our hypothesis that the unmasking of β-fluorovinylsilanes is a fluoride-catalysed rather than a fluoride-mediated process.

In summary, we have further demonstrated the synthetic versatility of our approach to oligoynes through the stereoselective



Scheme 6. Fluoride-catalysed unmasking of **22**.

synthesis of β-fluoro-, β-bromo- and β-iodovinylsilanes from intermediate vinylstannane **6**. Whilst the bromo derivative proved too labile for further application, the corresponding vinyl fluorides were elaborated uneventfully into masked hexaynes. In contrast to the analogous masked hexayne, which contains β-chlorovinylsilane units and requires the use of stoichiometric quantities of fluoride to effect unmasking, the new scaffold containing a β-fluorovinylsilane can be unmasked using sub-stoichiometric quantities of fluoride. This bodes well for the application of this novel class of masked alkyne in the assembly of longer-length oligoynes, where exceptionally mild reaction conditions will be invaluable.

Acknowledgements

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17. (*E*)-β-Bromovinylsilane **7**: NBS (23 mg, 0.13 mmol) was added in one portion to a solution of vinylstannane **6** (66 mg, 0.11 mmol) in CH_2Cl_2 (2 mL) at −78 °C. The reaction mixture was warmed to rt and after 1 h, satd aq NH_4Cl solution (10 mL) was added. The layers were separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with H_2O (3 × 10 mL), brine (3 × 10 mL), and dried (Na_2SO_4). The solvent was removed under reduced pressure and purification of the residue by flash column chromatography (20% Et_2O in hexane) gave vinyl bromide (*E*)-**7** as a white solid (53 mg, quant.); $R_f = 0.11$ (10% Et_2O in hexane); mp = 82–84 °C; ν_{max} ($CHCl_3$)/cm^{-1} 3398br (O–H), 3073w, 2960m, 2897w, 2860m, 2127w ($C{\equiv}C$), 1713m, 1659s ($C{=}C$), 1541w, 1429m, 1391w, 1343m, 1286m, 1249m, 1216s, 1106m, 1030m, 845s, 819m, 758s, 703s, 666m, 648m; δ_H (300 MHz, $CDCl_3$) 0.25 (9H, s, $Si(CH_3)_3$), 1.01 (1H, t, *J* 7.0, CH_2OH), 1.14 (9H, s, $C(CH_3)_3$), 3.80 (2H, d, *J* 7.0, CH_2OH), 7.33–7.49 (6H, m, Ph*H*), 7.68–7.81 (4H, m, Ph*H*); δ_C (75 MHz, $CDCl_3$) −0.3 (CH_3, $Si(CH_3)_3$), 19.3 (quat. C, $C(CH_3)_3$), 27.2 (CH_3, $C(CH_3)_3$), 67.3 (CH_2, CH_2OH), 106.5 (quat. C), 106.6 (quat. C), 124.0 (quat. C), 128.1 (CH, Ph), 129.9 (CH, Ph), 133.4 (quat. C, *ipso*Ph), 135.6 (CH, Ph), 148.4 (quat. C); *m*/*z* (TOF ES+) 493.1 ($[M+Na]^+$, 100%); HRMS *m*/*z* (TOF ES+). Found $(M+Na)^+$ 493.0980. $C_{24}H_{31}{}^{79}BrOSi_2Na$ requires 493.0995.
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31. (*E*)-β-Fluorovinylsilane **12**: Selectfluor® (246 mg, 0.69 mmol) was added in one portion to a solution of vinylstannane **6** (350 mg, 0.63 mmol) in MeCN (10 mL) at 45 °C. After stirring at 45 °C for 3 h, the reaction mixture was cooled to rt and diluted with Et_2O (10 mL). The suspension was filtered through a short silica plug, eluting with Et_2O (30 mL). The solvent was removed under reduced pressure and purification of the residue by flash column chromatography (20% Et_2O in hexane) gave vinyl fluoride **12** as a colourless oil (180 mg, 70%); $R_f = 0.14$ (10% Et_2O in hexane); ν_{max} ($CHCl_3$)/cm^{-1} 3583w (O–H), 3424br w (O-H), 3073w, 3052w, 3017w, 2962m, 2898m, 2861m, 2133m ($C{\equiv}C$), 1602m ($C{=}C$), 1429m, 1250s, 1217m, 1174w, 1106s, 1028w, 845vs, 820w, 758vs, 703vs, 609s; δ_H (300 MHz, $CDCl_3$) 0.25 (9H, s, $Si(CH_3)_3$), 1.01 (1H, t, *J* 6.8, CH_2OH), 1.19 (9H, s, $C(CH_3)_3$), 3.58 (2H, dd, ${}^3J_{H-F}$ 21.3, ${}^3J_{H-H}$ 6.8, CH_2OH), 7.34–7.55 (6H, m, Ph*H*), 7.71–7.90 (4H, m, Ph*H*); δ_F (282 MHz, $CDCl_3$) −67.2 (s); δ_C (75 MHz, $CDCl_3$) −0.2 (CH_3, $Si(CH_3)_3$), 19.1 (d, ${}^4J_{C-F}$ 1.7, quat. C, $C(CH_3)_3$), 27.3 (CH_3, $C(CH_3)_3$), 60.3 (d, ${}^2J_{C-F}$ 29.6, CH_2, CH_2OH), 97.1 (d, J_{C-F} 4.6, quat. C), 100.5 (d, J_{C-F} 12.4, quat. C), 104.1 (d, J_{C-F} 6.3, quat. C), 128.1 (CH, Ph), 129.9 (CH, Ph), 133.5 (d, ${}^4J_{C-F}$ 1.4, quat. C, *ipso*Ph), 135.7 (CH, Ph), 172.1 (d, ${}^1J_{C-F}$ 290.8, quat. C); *m*/*z* (TOF ES+) 433.2 ($[M+Na]^+$, 100%); HRMS *m*/*z* (TOF ES+). Found $(M+Na)^+$ 433.1808. $C_{24}H_{31}FOSi_2Na$ requires 433.1795.

32. *Characterisation data for* **21**: $R_f = 0.36$ (10% toluene in hexane); mp 118 °C (dec.); UV–vis (CH_2Cl_2): 304sh (22 240), 316 (28 770), 335 (32 610), 362 (29 080), 391 (25 840); ν_{max} ($CHCl_3$)/cm^{-1} 3071w, 2960m, 2933m, 2896m, 2859m, 2119m ($C{\equiv}C$), 1545m, 1462w, 1428m, 1392w, 1363w, 1251m, 1216w, 1192m, 1107m, 1029w, 843s, 758s, 738m, 697s, 666m, 648m, 622m, 606s; δ_H (300 MHz, benzene-d_6) 0.17 (18H, s, $Si(CH_3)_3$), 1.24 (18H, s, $C(CH_3)_3$), 7.00–7.17 (12H, m, Ph*H*), 7.57–7.75 (8H, m, Ph*H*); δ_F (282 MHz, benzene-d_6) −63.8 (s); δ_C (75 MHz, benzene-d_6) −0.4 (CH_3, $Si(CH_3)_3$), 19.8 (quat. C, $C(CH_3)_3$), 28.2 (CH_3, $C(CH_3)_3$), 78.3 (dd, J_{C-F} 42.2, 1.5, quat. C), 82.9 (app t, J_{C-F} 5.6, quat. C), 101.6 (d, J_{C-F} 6.5, quat. C), 109.8 (quat. C), 114.3 (d, J_{C-F} 6.9, quat. C), 128.2 (CH, Ph), 130.3 (CH, Ph), 132.6 (quat. C, *ipso*Ph), 136.5 (CH, Ph), 153.2 (dd, ${}^1J_{C-F}$ 265.7, ${}^6J_{C-F}$ 1.2, quat. C); *m*/*z* (TOF ES+) 915.4 ($[M+{}^{109}Ag]^+$, 100%), 603.2 (26, $[({}^tBuPh_2Si)_2O + {}^{109}Ag]^+$); HRMS *m*/*z* (TOF ES+). Found $(M+{}^{107}Ag)^+$ 913.2548. $C_{50}H_{56}F_2Si_4{}^{107}Ag$ requires 913.2478.
33. Unmasking was only performed on phenyl end-capped masked hexayne **22** and not on TMS end-capped analogue **21**. Under the conditions used to effect defluorosilylation, removal of the TMS end-caps in **21** would also occur to provide an extremely unstable free hexayne. Since the TMS protecting groups can be removed without inducing dehalosilylation, **21** represents a convenient monomer precursor for oligomerisation studies.