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Stereoselective Hydrogen Transfer Reactions of Vinyl Radicals: Cyclization of Alkynyl Iodides by Unimolecular Chain Transfer from Silicon Hydrides

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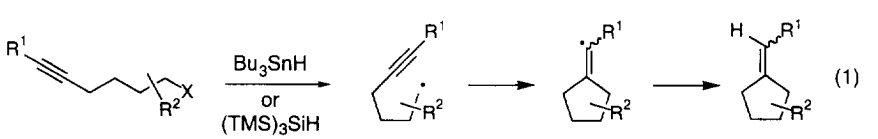
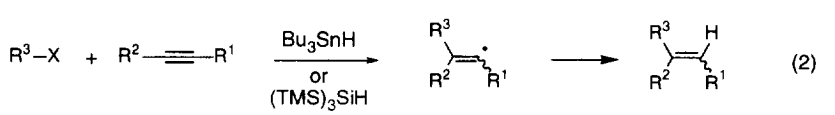
Abstract: The cyclization of several substituted hexynyl and heptynyl iodides proceeds stereoselectively to give either *E*- or *Z*-exocyclic double bonds depending on the type of precursor and radical chain used. In UniMolecular Chain Transfer (UMCT) reactions, the intramolecular abstraction of hydrogen by the intermediate vinyl radical leads exclusively to the *E*-isomer while the traditional tin hydride method usually provides the *Z*-isomer with good selectivity. © 1997 Elsevier Science Ltd.

INTRODUCTION

The control of the stereoselectivity in radical reactions is a rapidly moving area; however, the development of methods to selectively react sp^3-hybridized carbon radicals has rapidly outpaced methods for stereocontrolled reactions sp^2-hybridized radicals.[1] Over the last decade, a number of useful methods to make alkenes with concomitant carbon-carbon single-bond formation *via* intramolecular[2] (Scheme 1, eq 1) or intermolecular[3] (Scheme 1, eq 2) addition of carbon-centered radicals to triple bonds have been developed. The intermediate sp^2-hybridized vinyl radical in these processes is reactive compared to alkyl radicals, and it rapidly abstracts hydrogen bimolecularly from tributyltin hydride or *tris*(trimethyl)silicon hydride. Vinyl radicals also readily propagate iodine transfer addition and cyclization chains.[4] Significant exceptions notwithstanding, the stereoselectivity of these processes is often poor or moderate, and the resulting double bond is thus formed as a mixture of *E*-and *Z*-isomers.[5] Kinetic control in reactions of vinyl radicals is common and factors effecting kinetic stereoselection in the final hydrogen transfer reaction include the geometry of the vinyl radical,[6] the steric hindrance of the substituents,[7] and the type of hydrogen donor used.[8] In a few examples, stereocontrol by thermodynamic equilibration has been reported.[2c,9]

Scheme 1



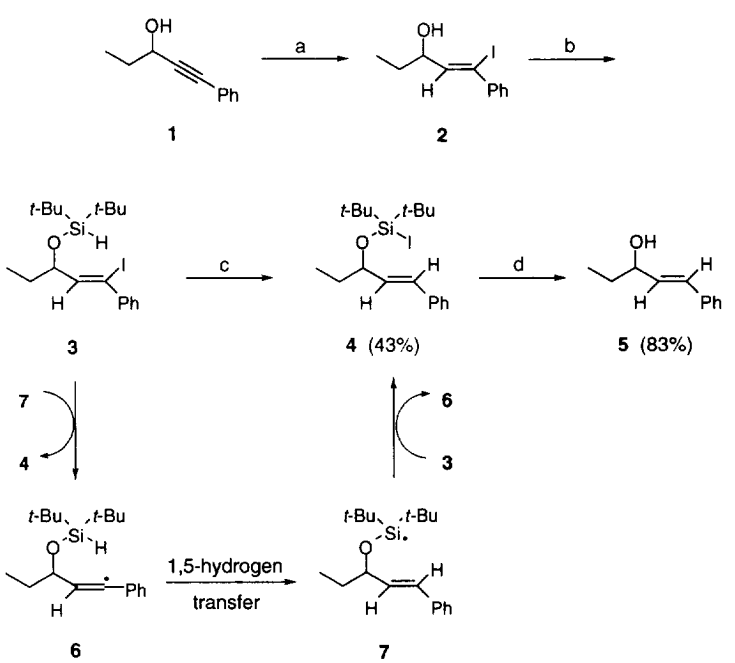


Although intramolecular 1,5-hydrogen atom transfer reactions of vinyl radicals are well known, these reactions are typically used not for stereocontrolled C–H bond formation[10] but for radical translocation prior to cyclization[11] or addition.[12] Recently, we have introduced the concept of UniMolecular Chain Transfer (UMCT) reactions of silicon hydrides[13] and demonstrated the advantages of the UMCT method for conducting bimolecular radical reactions.[14] An important yet heretofore unrealized feature of UMCT reactions of silicon hydrides is the stereoselectivity associated with the intramolecular hydrogen transfer step. Recently, we communicated preliminary results on the use of UMCT reactions of silicon hydrides to conduct intramolecular radical cyclizations to alkynes.[15] We now report the full details of this work along with additional examples and new observations. These UMCT reactions occur in the absence of tin hydride and they serve both to propagate the chain involving the radical cyclization and to rigorously control the geometry of the double bond in the final product.

RESULTS AND DISCUSSION

To demonstrate that UMCT reactions can be propagated from vinyl radicals, we first studied the isomerization reaction of the silicon hydride **3** (Scheme 2) as a simple model. Vinyl iodide **3** was prepared from propargylic alcohol **1** by the Denmark modification[16a,b] of the Corey reductive iodination[16c] and subsequent silylation of the γ-iodoallylic alcohol **2**. Isomerization was initiated by UV irradiation of a solution of **3** (0.1 M in benzene at 80°C) containing 10% of hexabutylditin. After 6 h, the starting vinyl iodide **3** was consumed, and the reaction mixture was concentrated and subjected to flash chromatography.

Scheme 2



Reagents: a) Red-Al, I_2; b) NaH, *t*-Bu_2SiHCl; c) $(Bu_3Sn)_2$, hv, benzene, 80°C; d) TBAF

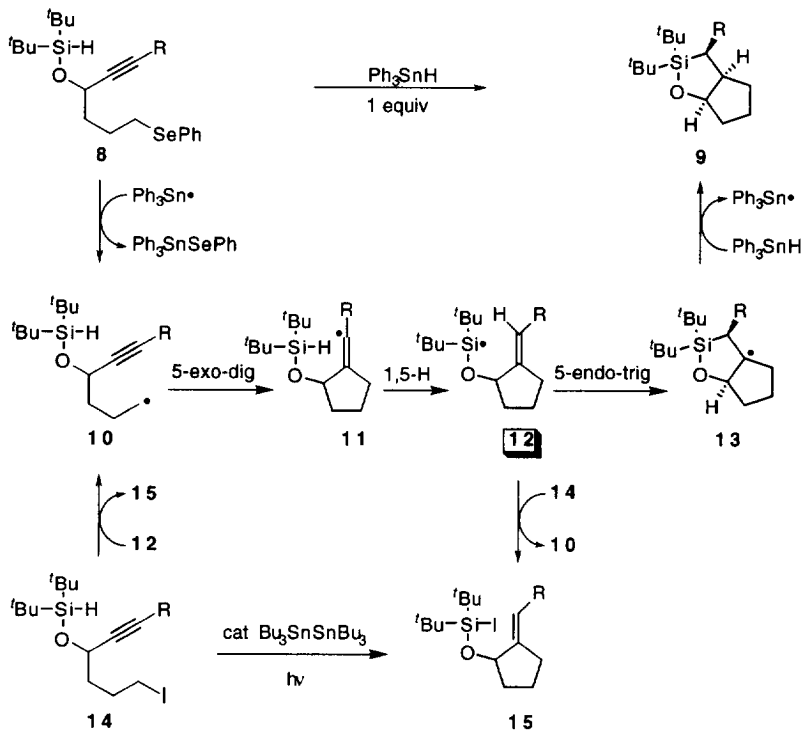
Expecting to isolate a silanol derived from hydrolysis of silicon iodide **4**, we were surprised to isolate instead **4** itself as an unstable oil in 43% yield. This compound decomposes to an intractable black oil over several hours at room temperature, and its instability may contribute in part to the modest yield. An elimination product [EtCH(OSi^{t}Bu$_2$H)C≡CPh] was also isolated in 23% yield. In earlier work,[13,14] we had used in situ trapping procedures to isolate derivatives of the silicon iodides, but in this work most of the alkoxy di-*tert*-butylsilyl iodides proved sufficiently stable for isolation and direct characterization. Only one isomer of the alkene **4** was obtained and this was identified as the *E*-isomer by its characteristic vicinal vinyl coupling constant (J = 16 Hz) in the ^{1}H NMR spectrum. After desilylation with TBAF, the allylic alcohol *E*-**5** was obtained in 83% yield.

We suggest that the isomerization of **3** to **4** proceeds by the mechanism shown in the lower part of Scheme 2. Iodine abstraction of the vinyl iodide **3** by silyl radical **7**[17] gives the silyl iodide **4** and the vinyl radical **6**. In turn, vinyl radical **6** undergoes intramolecular 1,5-hydrogen transfer to regenerate the silyl radical **7**. This is the key UMCT step. Although a radical chain based on bimolecular hydrogen transfer can be written, silicon hydrides like **3** are not known to participate in efficient chains based in bimolecular transfer.[18] Moreover, the formation of E-**4** provides sufficient experimental evidence to rule out chains based on bimolecular hydrogen transfer; such chains should produce predominately the Z-isomer (see below). Additional evidence is provided by the isolation of the elimination product [EtCH(OSi^{t}Bu$_2$H)C≡CPh] as exclusively the silicon hydride (not the silicon iodide); once HI is eliminated, there is no precursor for the UMCT reaction so the silicon hydride in this compound is inert.

While the simple experiment in Scheme 2 demonstrates the viability of vinyl-radical based UMCT chains of silicon hydrides, this type of reaction has relatively limited synthetic potential. More useful is the coupling of a UMCT process with a radical carbon-carbon bond forming reaction. However, this capability of the UMCT method was called into question at the outset of the work by an interesting report from Clive and coworkers.[19a] They observed that the slow addition of Ph_3SnH to phenylselenides like **8** (Scheme 3) provided cyclic silyl ethers **9** in good yield. Even though a radical cyclization (**10** → **11**) occurs and the resulting vinyl radical undergoes an intramolecular hydrogen transfer from the silicon hydride (**11** → **12**), this transformation is not a UMCT reaction because the subsequent 5-*endo-trig* cyclization of the silyl radical **12**[20] to give **13** is faster than the bimolecular abstraction of phenylselenium group from the precursor **8**. In effect, the cyclization of silyl radical **12** breaks the UMCT chain. The transformation of **8** into **9** is a standard radical reduction and requires 1 equiv of Ph_3SnH. As far as we know, this was the first published report of an intramolecular 1,5-hydrogen transfer reaction of a silicon hydride, and the subsequent work of Clive illustrates the generality and utility of the process.[19]

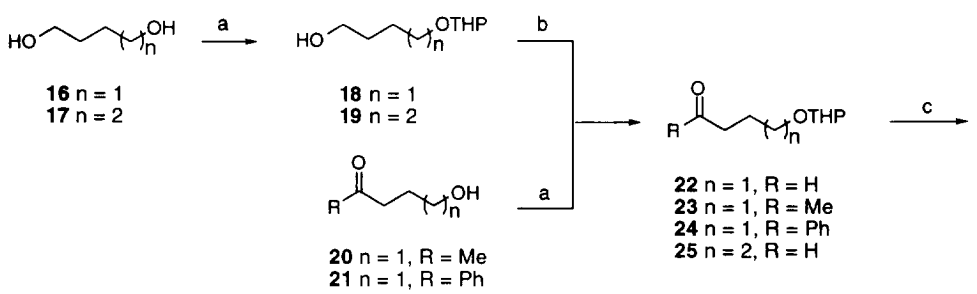
Silyl radicals **7** in Scheme 2 and **12** in Scheme 3 are structurally similar. Why then does one undergo 5-*endo-trig* cyclization and the other not? We hypothesized that this difference was due not to the structures of the radicals but to the nature of the radical precursor (I or PhSe). This influences the rate of the competing reaction (I or PhSe abstraction) that would propagate a UMCT process. If this is correct, then 5-*endo-trig* cyclization should be bypassed and a UMCT process should occur in Clive's systems simply by changing the radical precursor from a phenylselenium group to an iodine atom (Scheme 3, lower part). This transformation is not a reduction but an isomerization that requires only initiation and occurs by a sequence of: a) 5-*exo-dig* cyclization (**10** → **11**), b) intramolecular 1,5-hydrogen transfer from the Si–H bond (**11** → **12**), and c) bimolecular iodine abstraction by silyl radical (**12** → **15**). In this chain, no effort is made to retard the 5-*endo-trig* cyclization of the silyl radical **12**; we simply insert a more rapid competing process.

Scheme 3

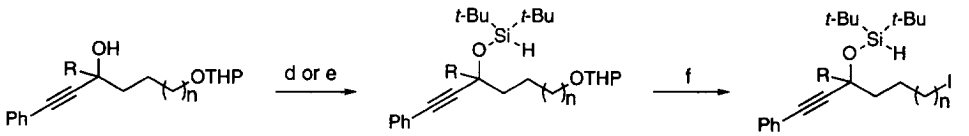


To test this hypothesis, we prepared a series of substituted alkynyl iodides and studied their isomerizations. The radical precursors **34-37** were synthesized as shown in Scheme 4. Compounds **23**[21] and **24** were prepared by protection of the alcohols **20** and **21**[22] with DHP. Compounds **22**[23] and **25**[24] were obtained from the diols **16** and **17** after monoprotection with DHP and Swern oxidation of the resulting tetrahydropyranyloxyalcohols **18** and **19**. Subsequent reaction of compounds **22-25** with lithium phenylacetylide gave the propargylic alcohols **26-27**[25] and **28-29**. Silylation[26] and iodination[27] under standard conditions provided the radical precursors **34-37**. Similiar reactions were used to synthesize the other precursors described later (see Experimental Section for details).

Scheme 4



Scheme 4 (cont.)



26 n = 1, R = H
27 n = 1, R = Me
28 n = 1, R = Ph
29 n = 2, R = H

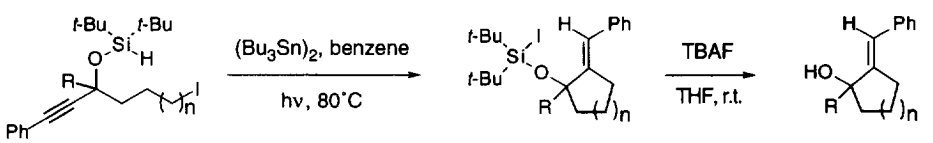
30 n = 1, R = H
31 n = 1, R = Me
32 n = 1, R = Ph
33 n = 2, R = H

34 n = 1, R = H
35 n = 1, R = Me
36 n = 1, R = Ph
37 n = 2, R = H

Reagents: a) DHP, PPTS, CH_2Cl_2, r.t; b) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; c) Ph-C≡CH, BuLi, THF, –78°C; d) *t*-Bu_2SiHCl, Et_3N, DMAP, ether, r.t.; e) *t*-Bu_2SiHCl, imidazole, DMAP, NaI, DMF, r.t.; f) I_2, dppe, CH_2Cl_2

Cyclative isomerizations of **34-37** are shown in Scheme 5; **37** is poised to undergo 6-*exo* cyclization while the other compounds are all precursors for 5-*exo* cyclizations. UV Irradiation of a benzene solution of **34**, **35**, and **37** in the presence of hexabutylditin (0.1 equiv) afforded a single isomer of the corresponding iodosilanes **38**, **39** and **41** in good yield (70-80%). However, **36** provided only traces of **40** (identified by GC-MS) under the same conditions. The reasons for the failure with **36** are not currently clear.[28] The iodosilanes **38-39** and **41** were stable to flash chromatography, and were isolated as white solids that could be stored in the dark under argon for several days in a freezer. An X-ray diffraction crystal structure was solved for **38**,[29] and this showed that the exocyclic double bond was E. After treatment of the silyl iodides **38**, **39** and **41** with TBAF, the alcohols **42-44** were obtained in good yields. The assignment of the double bond geometry was confirmed by comparison of ^1H NMR spectra with the data for the known alcohols *E*-**42**[30] and *E*-**44**.[31]

Scheme 5



34 n = 1, R = H
35 n = 1, R = Me
36 n = 1, R = Ph
37 n = 2, R = H

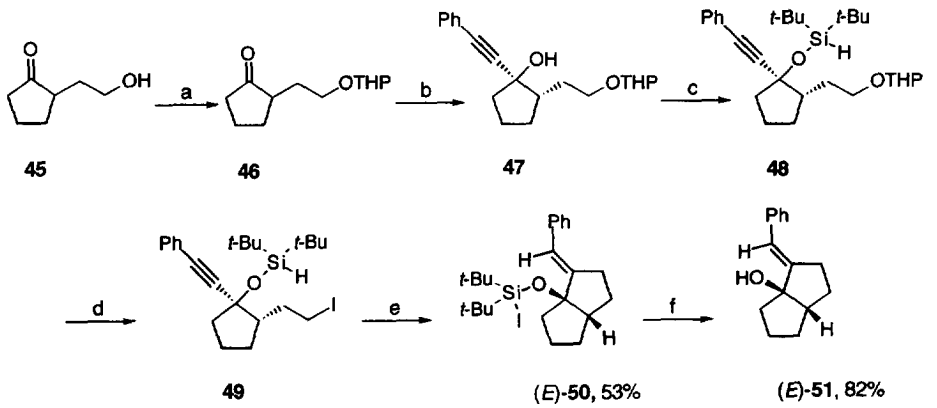
(*E*)-**38** n = 1, R = H 80%
(*E*)-**39** n = 1, R = Me 70%
(*E*)-**40** n = 1, R = Ph (traces)
(*E*)-**41** n = 2, R = H 76%

(*E*)-**42** n = 1, R = H 88%
(*E*)-**43** n = 1, R = Me 73%
(*E*)-**44** n = 2, R = H 50%

The radical precursor **49** (Scheme 6) was prepared from the known alcohol **45**[32] by protection with DHP (→ **46**), addition of lithium phenylacetylene (→ **47**), silylation (→ **48**) and iodination (→ **49**). After purification by chromatography, a single diastereomer of **49** was obtained. The relative configuration of **49** is determined in the addition of phenylacetylene to the ketone **46**, and we assume that a *cis* attack occurs to provide the *trans*-alcohol **47** by analogy with the previous studies on the stereochemistry of the addition of lithium acetylides to α-substituted cyclopentanones.[33]

Irradiation of a benzene solution of **49** with a UV lamp as usual (10% of hexabutylditin) provided a single (*E*)-isomer of the silicon iodide **50** in 53% yield. Subsequent treatment of **50** with TBAF led to the bicyclic alcohol **51** in 82% yield.

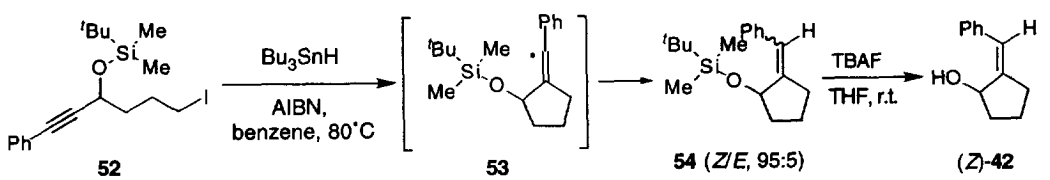
Scheme 6



Reagents: a) DHP, PPTS, CH_2Cl_2, r.t.; b) Ph-C≡CH, BuLi, THF, –78°C; c) *t*-Bu_2SiHCl, imidazole, DMAP, NaI, DMF, r.t.; d) I_2, dppe, CH_2Cl_2; e) $(Bu_3Sn)_2$, benzene, hv, 80°C; f) TBAF, THF, r.t.

To compare the outcome of these intramolecular hydrogen abstraction reactions with the usual bimolecular hydrogen transfer reactions of vinyl radicals, we studied the tin hydride mediated cyclization of the *t*-butyldimethylsilyl ether **52** (Scheme 7). This was prepared by a route analogous to that for synthesis of **34** (Scheme 4), and since it lacks a silicon hydride, cyclization by a UMCT process cannot occur. Standard reductive cyclization of **53** with 1.0 equiv of tributyltin hydride (slow addition over 2 h) provided a 95/5 mixture of *Z*/*E* isomers **54** according to GC analysis of the crude mixture. The major *Z*-isomer was isolated by flash chromatography, and treatment with TBAF gave the alcohol *Z*-**42**. This is the stereoisomer of alcohol E-**42** produced in the UMCT process in Scheme 5.

Scheme 7



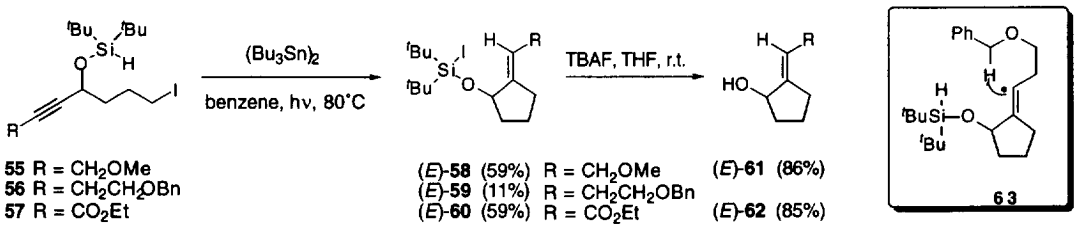
Spectroscopic[34] and chemical[35] evidence suggests that the α-phenyl substituted vinyl radicals are π-type. Therefore, under kinetic control, alkene geometry is determined by the direction of hydrogen transfer to the linear vinyl radical. In the case of silicon hydrides, the delivery of the hydrogen to the neighboring side by intramolecular hydrogen transfer leads exclusively to the *E* alkene. In contrast, bimolecular hydrogen transfer to radical **53** from tributyltin hydride occurs predominately away from the *t*-butyldimethylsilyl ether to give the less stable *Z*-alkene.

Alkyl- and ester-substituted vinyl radicals are generally thought to be bent rather than linear. In order to investigate the behavior of the σ-bent vinyl radicals towards both types of hydrogen abstraction, we synthesized the radical precursors **55**-**57** (Scheme 8). The syntheses of these

precursors are related to the prior precursor syntheses (Scheme 4), and they are described in the Experimental Section.

Irradiation of **55** with a UV lamp as usual provided a single isomer of **58** that was isolated in 59% yield after flash chromatography. After treatment with TBAF, one isomer of the alcohol **61** was obtained and the geometry of the exocyclic double bond was confirmed as E by comparison of the ^{13}C NMR spectrum with published data.[36] However, irradiation of **56** in the presence of 0.2 equiv of hexabutylditin led to a complex mixture from which the silicon iodide **59** was isolated in a only 11% yield. Other components of the mixture were not characterized. Although there is no firm experimental evidence, the difference between **55** and **56** may be due to the presence of the benzylic hydrogens in **56**. 1,5-Hydrogen transfer from these benzylic hydrogens (see **63**) may compete with hydrogen transfer from the silicon hydride.

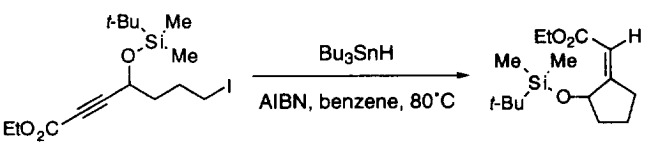
Scheme 8



Ester substituted iodide **57** was cyclized under the standard procedure to give the *E*-isomer of the silicon iodide **60** (Scheme 8). As with the other silicon iodides, this compound was stable to the flash chromatography and could be kept under argon in the dark for several days. The configuration of the double bond was confirmed after desilylation with TBAF by comparison of the ^1H NMR spectra of the alcohol **62** with the previously reported data.[37]

To provide an additional comparison to bimolecular hydrogen transfer, we prepared the analogous TBS ether **64** (Scheme 9) in which intramolecular hydrogen transfer is not possible. Slow addition of Bu_3SnH to a 0.07 M solution of **64** in benzene gave only the *Z*-isomer of the compound **65**. The configuration of the double bond was assigned by comparison of the ^1H NMR spectra with the reported data for this compound.[38] As with phenyl-substituted vinyl radicals, the UMCT and standard tin hydride methods exhibit stereochemical complementary.

Scheme 9



CONCLUSIONS

These results show that the UMCT method can be used to conduct radical cyclizations to alkynes provided that a good radical precursor (iodide) is used. The results nicely complement those of Clive and coworkers who observed that by choosing a poorer radical precursor (PhSe), the UMCT chain did not propagate and an interesting 5-*endo-trig* cyclization occurred instead.[19] The complementarity provides a striking example of how radical reaction products are dictated not by the structures of intermediate radicals but the nature of the radical precursors. This can happen whenever one of the steps in a chain involves the reaction of an intermediate radical with its own precursor.[39] In retrospect, the choice of radical precursors was probably fortuitous; had we chosen a less reactive precursor, we probably would have accidentally discovered the reaction that Clive was seeking to develop. And had Clive chosen a more reactive precursor, he probably would have accidentally discovered the reaction that we were seeking to develop.

Extension of the UMCT strategy to conduct alkene (as opposed to alkyne) cyclizations should be straightforward provided that the 1,5-hydrogen transfer succeeds. In these cases, 5-*endo* cyclization of the cyclized radical is not possible. We are currently studying substituent effects on 1,5-hydrogen transfer reactions of silicon hydrides to learn more about what types of systems will succeed. For the moment, vinyl radicals look like especially good intermediates for 1,5-hydrogen transfer from silyl hydrides, and this is to be expected since vinyl radicals are highly reactive in general.

A key feature of the UMCT chains is stereocontrol in hydrogen atom delivery. In general, high and predictable selectivity in alkene formation is expected from the UMCT process, while stereoselectivity in intermolecular hydrogen transfer reactions can vary depending on the radical and the hydrogen donor. In this work, the intra- and intermolecular hydrogen transfer reactions were designed to provide complementary results, but this will not always be the case due to the variable selectivities in the bimolecular process.

A remarkable and unexpected feature of the work is the stability of the UMCT products, which are di-*tert*-butylsilyl iodide derivatives of allylic alcohols. Some of these are crystalline, and although none are stable to long term storage at 0°C, all were sufficiently stable for purification and characterization. This stability, which can probably be attributed to the presence of the two *tert*-butyl groups, is remarkable because allylic alcohols are well known to react with silyl iodides.[40]

In summary, we have shown that UMCT reactions of silicon hydrides can be used to conduct radical cyclizations to triple bonds and that the geometry of the resulting alkene is strictly controlled by the intramolecular hydrogen transfer step independent of the type of intermediate vinyl radical.

EXPERIMENTAL

General. All reactions were performed under a nitrogen atmosphere. Methylene chloride, *N*,*N*-dimethylformamide and triethylamine were distilled from CaH_2. Benzene, diethyl ether and THF were distilled from sodium/benzophenone. NMR spectra were recorded at the following frequencies: 300 MHz for ^1H, 75 MHz for ^{13}C, and 100 MHz for ^{29}Si.

Synthesis of 1-iodo-1-phenylpent-1-en-3-ol (2): Ether (3.0 mL) was added to a solution of sodium *bis*(methoxyethoxy)aluminum hydride (0.96 mL, 3.2 mmol, 1.6 equiv, 65% in toluene). The solution was cooled to 0°C and treated, dropwise with a solution of the alcohol **1** (320 mg, 2.0 mmol, 1.0 equiv) in ether (3.0 mL). After 10 min, the reaction was warmed to room temperature, stirred for 30 min, and cooled to –78°C.

A solution of I_2 (4.06 g, 16.0 mmol, 8.0 equiv) in THF (10 mL) was added dropwise. The mixture was warmed to room temperature, stirred for 30 min, diluted with ether and washed three times with a saturated aqueous solution of $NaHSO_3$. The organic layer was dried over $MgSO_4$ and filtered. The compound obtained was used in the next step without any purification. ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (m, 2 H, aromatics), 7.30 (m, 3 H, aromatics), 5.97 (d, 1 H, J = 7.4 Hz, HC=C), 4.42 [q, 1 H, C(OH)H], 2.07 (s, 1 H, OH), 1.72 (m, 2 H, CH_2), 1.04 (t, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4, 128.6, 128.5, 128.2 (aromatics), 140.3 (H*C*=C), 105.2 (HC=*C*), 78.2 [C(OH)H], 29.18 (CH_2), 9.58 (CH_3); MS *m/z* 288 (M^+, 19), 270 (43), 259 (28), 241 (11), 165 (31), 143 (14), 131 (20), 103 (75), 91 (18), 77 (22), 57 (100).

Synthesis of 3-di-*tert*-butylsilyloxy-1-iodo-1-phenyl1-pentene (3): To a suspension of NaH (44 mg, 1.1 mmol, 1.1 equiv, 65% w) in THF (4 mL), was added a solution of the alcohol **2** (288 mg, 1.0 mmol, 1.0 equiv) in THF (5 mL). After 5 min, di-*tert*-butylchlorosilane (214 mg, 1.2 mmol, 1.2 equiv) was added and the mixture was stirred overnight at room temperature. Water was added and the aqueous layer was extracted twice with ether. The organic layer was dried over $MgSO_4$. The crude mixture was submitted to flash chromatography (hexane) and the compound **3** (172 mg, 40 % yield) was obtained as an unstable oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.49-7.23 (m, 5 H, aromatics), 5.94 (d, 1 H, J = 7.6 Hz, HC=C), 4.49 [q, 1 H, C(OH)H], 4.15 (s, 1 H, SiH), 1.70 (m, 2 H, CH_2), 1.04 [s, 9 H, $C(CH_3)_3$], 1.01 (t, 3 H, CH_3), 1.00 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 131.5, 128.5, 128.2 (aromatics), 141.0 (H*C*=C), 103.0 (HC=*C*), 81.7 [C(OSi)H], 30.1 (CH_2), 27.4 [$C(CH_3)_3$], 20.2, 19.8 [$C(CH_3)_3$], 9.2 (CH_3).

General Procedure for the Synthesis of the Tetrahydropyranyloxy Derivatives. A solution of the alcohol (1.0 equiv), 3,4-dihydro-2*H*-pyran (1.0 equiv) and pyridinium *p*-toluenesulfonate (0.1 equiv) in CH_2Cl_2 (1.5 ml/mmol) was stirred for 18-24 h at room temperature. The solution was washed with brine to remove the catalyst. The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude mixture was submitted to flash chromatography.

2-[2-(Tetrahydropyran-2-yloxy)ethyl]-cyclopentanone (46): Following the General Procedure from the alcohol **45**[32] (2.56 g, 20.0 mmol), after stirring for 18 h and flash chromatography (hexane/ethyl acetate, 4:1), compound **46** (3.101 g, 73% yield) was obtained as an oil: FT-IR (CCl_4) 2944, 2871, 1737, 1453, 1441, 1352, 1323, 1136, 1077, 1032 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (diastereomeric mixture) 4.59 [m, 1 H, OCH(O)], 3.88-3.75 (m, 2 H, CH_2O), 3.55-3.43 (m, 2 H, CH_2O), 2.35-1.50 (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (diastereomeric mixture) 221.2 (CO), 98.7, 98.6 [OCH(O)], 65.5, 65.2 (CH_2O), 62.2 (CH_2O), 46.4, 46.3 (CH), 37.8, 37.7 (*C*H_2CO), 30.5, 30.5, 29.5, 29.5 (3 CH_2), 25.3 (CH_2), 20.6 (CH_2), 19.4 (CH_2); MS *m/z* 212 (M^+, 1), 184 (11), 168 (28), 127 (36), 111 (92), 85 (100); HRMS calcd. for $C_{10}H_{16}O_3$ (M^+ – 28) 184.1099, found 184.1094.

General Procedure for the Synthesis of the Alcohols such as 28, 29, 47. BuLi (1.6 M in hexane) was added dropwise at -78°C, to a solution of the alkyne (1.0 equiv) in THF (4 mL/3 mmol). The mixture was stirred for 15 min and a solution of the aldehyde or ketone in THF (0.5 mL/mmol) was added. After 2 h, the reaction mixture was allowed to warm to room temperature and quenched by addition of saturated solution of ammonium chloride. The aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude mixture was purified by flash chromatography (hexane/ethyl acetate, 4:1).

1,3-Diphenyl-6-(tetrahydropyran-2-yloxy)hex-1-yn-3-ol (28): Following the General Procedure, using phenylacetylene (1.029 g, 10.08 mmol, 1.1 mL) and the ketone **24** (2.5 g, 10.08 mmol), the alcohol **28** (2.369 g, 67% yield) was obtained as an oil: FT-IR (CCl_4) 3390, 3059, 3027, 2943, 2871, 1598, 1489, 1446, 1383, 1352, 1322, 1118, 1023 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (diastereomeric mixture) 7.71-7.18 (m, 10 H, aromatics), 4.58 [m, 1 H, OCH(O)], 3.80 (m, 2 H, CH_2O), 3.44 (m, 2 H, CH_2O), 2.09 (m, 2 H), 1.91 (m, 1 H), 1.80-1.46 (m, 7 H), 1.26 (br s, 1 H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (diastereomeric mixture) 144.9, 131.6, 128.3, 128.2, 128.0, 127.9, 127.5, 122.6 (aromatics), 98.3 [OCH(O)], 91.7 (Ph-*C*≡C), 85.8, 85.7 (Ph-C≡*C*), 73.1, 73.1 [C(OH)H], 67.2 (CH_2O), 61.9 (CH_2O), 42.9 (CH_2), 31.5, 30.4 (CH_2), 25.3, 25.1 (CH_2), 22.5 (CH_2), 19.2 (CH_2); MS *m/z* 350 (M^+, 11), 332 (18), 291 (63), 248 (29), 217 (40), 207 (94), 183 (76), 147 (23), 129 (33), 115 (20), 105 (60), 85 (100), 77 (30); HRMS calcd. for $C_{23}H_{26}O_3$ 350.1882, found 350.1868.

1-Phenyl-7-(tetrahydropyran-2-yloxy)hept-1-yn-3-ol (29): Following the General Procedure, using phenylacetylene (1.345 g, 13.17 mmol, 1.45 mL) and the aldehyde **25**[24] (2.45 g, 13.17 mmol), the alcohol **29** (3.221 g, 85% yield) was obtained as an oil: FT-IR (CCl_4) 3401, 3059, 2942, 2867, 2200, 1598, 1489, 1442, 1383, 1352, 1119, 1074, 1024 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (diastereomeric mixture) 7.41 (m, 2 H, aromatics), 7.29 (m, 3 H, aromatics), 4.59 [m, 2 H, C(OH)H and OCH(O)], 3.92-3.73 (m, 2 H), 3.56-3.48 (m, 2 H), 2.14 (br s, 1 H, OH), 1.81-1.48 (m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (diastereomeric mixture) 131.6, 128.3, 128.2, 122.6 (aromatics), 98.8 [OCH(O)], 90.1 (Ph-*C*≡C), 84.8 (Ph-C≡*C*), 67.3 (CH_2O), 62.8 [C(OH)H], 62.3 (CH_2O), 37.6 (CH_2), 30.7 (CH_2), 29.3 (CH_2), 25.4 (CH_2), 21.9 (CH_2), 19.5 (CH_2); MS *m/z* 288 (M^+, 16), 242 (6), 230 (19), 215 (20), 203 (55), 187 (23), 131 (43), 115 (18), 103 (24), 85 (100); HRMS calcd. for $C_{18}H_{24}O_3$ 288.1725, found 288.1726.

1-Phenylethynyl-2-[2-(tetrahydropyran-2-yloxy)ethyl]cyclopentanol (47): Following the General Procedure, using phenylacetylene (1.325 g, 12.97 mmol, 1.42 mL) and the ketone **46** (2.75 g, 12.97 mmol), the alcohol **47** (2.672 g, 66% yield) was obtained as an oil: FT-IR (CCl_4) 3416, 3060, 2944, 2871, 1597, 1489, 1442, 1383, 1119, 1076, 1030 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (diastereomeric mixture) 7.41 (m, 2 H, aromatics), 7.29 (m, 3 H, aromatics), 4.73 (m, 1 H), 4.68 (m, 1 H), 4.03 (m, 1 H), 3.95-3.74 (m, 2 H), 3.51 (m, 2 H), 2.35-1.50 (m, 14 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (diastereomeric mixture) 131.4, 128.1, 127.9, 123.2 (aromatics), 98.1, 97.7 [OCH(O)], 91.4, 91.2 (Ph-*C*≡C), 85.8 (Ph-C≡*C*), 77.2 [C(OH)H], 66.7 (CH_2O), 61.9, 61.7 (CH_2O), 51.1, 50.9 (CH), 41.2, 41.0 (CH_2), 31.2, 30.6, 30.4, 30.2, 30.0 (3 CH_2), 25.3, 25.2 (CH_2), 20.1, 19.9, 19.1, 18.8 (2 CH_2); MS *m/z* 314 (M^+, 14), 296 (10), 286 (7), 269 (21), 241 (16), 229 (40), 213 (60), 186 (49), 157 (12), 144 (15), 129 (45), 115 (17), 105 (15), 85 (100), 77 (8); HRMS calcd. for $C_{20}H_{26}O_3$ 314.1882, found 314.1874.

1-Methoxy-7-(tetrahydropyran-2-yloxy)hept-2-yn-4-ol: Following the General Procedure, using methyl propargyl ether (1.997 g, 28.5 mmol, 2.4 mL) and the aldehyde **22**[23] (4.9 g, 28.5 mmol), the alcohol (6.221 g, 90% yield) was obtained as an oil: FT-IR (CCl_4) 3400, 2943, 2873, 2215, 1451, 1442, 1376, 1355, 1322, 1102, 1034 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (diastereomeric mixture) 4.61 [m, 1 H, OCH(O)], 4.48 [m, 1 H, C(OH)H], 3.80 (d, 2 H, *J*=1.4 Hz, CH_2C≡C), 3.82 (m, 2 H), 3.53 (m, 2 H), 3.38 (s, 3 H, OCH_3), 1.90-1.48 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (diastereomeric mixture) 98.5 [OCH(O)], 87.5, 79.9 (CH_2-*C*≡C, CH_2-C≡*C*), 67.0 (CH_2O), 62.0 (CH_2O), 61.7 [C(OH)H], 59.6 (CH_2O), 57.3 (CH_3O), 34.8 (CH_2), 30.3 (CH_2), 25.3 (CH_2), 25.2 (CH_2), 19.2 (CH_2); MS *m/z* 225 (M^+ – 17, 12), 209 (15), 169 (20), 139 (45), 123 (27), 109 (74), 101 (100); HRMS calcd. for $C_{13}H_{21}O_3$ (M^+ – 17) 225.1491, found 225.1482.

8-Benzyloxy-1-(tetrahydropyran-2-yloxy)oct-5-yn-4-ol: Following the General Procedure, using 4-benzyloxybut-1-yne (3.632 g, 22.7 mmol) and the aldehyde **22**[23] (3.9 g, 22.7 mmol), the alcohol (6.093 g, 81% yield) was obtained as an oil: FT-IR (CCl_4) 3400, 3060, 3020, 2942, 2871, 2213, 1453, 1355, 1323, 1117, 1030 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (diastereomeric mixture) 7.30 (m, 5 H, aromatics), 4.60 [m, 1 H, OCH(O)], 4.54 (s, 2 H, CH_2Ph), 4.40 [m, 1 H, C(OH)H], 3.80 (m, 2 H, CH_2O), 3.57 (t, 2 H, CH_2OBn), 3.49 (m, 2 H, CH_2O), 2.52 (t, 2 H, CH_2C≡C), 1.82-1.45 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (diastereomeric mixture) 137.9, 128.3, 127.6 (aromatics), 98.6, 98.5 [OCH(O)], 82.2, 81.6 (CH_2-*C*≡C, CH_2-C≡*C*), 72.8 (CH_2O), 68.3 (CH_2O), 67.1, 67.0 (CH_2O), 62.1 (CH_2O), 53.3 [C(OH)H], 35.1 (CH_2), 30.4 (CH_2), 25.4 (CH_2), 25.3 (CH_2), 20.0 (CH_2), 19.3 (CH_2); MS *m/z* 332 (M^+, 11), 314 (8), 264 (13), 247 (13), 230 (51), 200 (47), 85 (100); HRMS calcd. for $C_{20}H_{28}O_4$ 332.1987, found 332.1981.

Silylation of Alcohols. Procedure A. To a solution of the alcohol (1.0 equiv) in ether (30 mL/8 mmol), triethylamine (2.0 equiv) and dimethylaminopyridine (0.2 equiv) were added. After 5 min, di-*tert*-butylchlorosilane (1.2 equiv) was added and the mixture was stirred overnight at room temperature. Water was added and the aqueous layer was extracted twice with ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude mixture was submitted to flash chromatography (hexane/ethyl acetate, 19:1).

Procedure B. To a solution of the alcohol (1.0 equiv) in DMF (2 mL/mmol), imidazole (2.0 equiv) and dimethylaminopyridine (0.5 equiv) were added. After stirring for 5 min, di-*tert*-butylchlorosilane (1.5 equiv) and sodium iodide (1.5 equiv) were added and the mixture was stirred overnight at room temperature. Water was added and the aqueous layer was extracted twice with ethyl acetate. The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude mixture was submitted to flash chromatography (hexane/ethyl acetate, 19:1).

Di-*tert*-butyl-{3-phenyl-1-[3-(tetrahydropyran-2-yloxy)propyl]prop-2-ynyloxy}silane (30): Following the Procedure A, from the alcohol **26**[25] (2.5 g, 9.12 mmol) the silane **30** (3.73 g, 98% yield) was obtained as an oil: FT-IR (CCl_4) 2942, 2927, 2882, 2858, 2359, 2097, 1470, 1443, 1386, 1363, 1344, 1064 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 (m, 2 H, aromatics), 7.29 (m, 3 H, aromatics), 4.73 [m, 1 H, C(OSi)H], 4.60 [m, 1 H, OCH(O)], 4.15 (s, 1 H, SiH), 3.83 (m, 2 H, CH_2O), 3.47 (m, 2 H, CH_2O), 1.80-1.45 (m, 10 H), 1.06 [s, 9 H, $C(CH_3)_3$], 1.02 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.5, 128.0, 123.1 (aromatics), 98.7 [OCH(O)], 90.2 (Ph-*C*≡C), 84.8 (Ph-C≡*C*), 67.2 (CH_2O), 66.5 [C(OSi)H], 62.2 (CH_2O), 35.2 (CH_2), 30.7 (CH_2), 27.3 [C(*C*H_3)$_3$], 25.5 (CH_2), 25.3 (CH_2), 20.1 [*C*$(CH_3)_3$], 19.5 (CH_2); MS *m/z* 359 (M^+ – 57, 25), 331 (44), 315 (9), 289 (14), 273 (57), 257 (37), 229 (37), 217 (15), 189 (17), 171 (53), 155 (55), 141 (19), 129 (100), 115 (48), 105 (34); HRMS calcd. for $C_{21}H_{31}O_3Si$ (M^+ – 57) 359.2042, found 359.2030.

Di-*tert*-butyl-{1-methyl-3-phenyl-1-[3-(tetrahydropyran-2-yloxy)propyl]prop-2-ynyloxy}silane (31): Following the Procedure B, from the alcohol **27**[25] (2.189 g, 7.60 mmol) the silane **31** (2.125 g, 65% yield) was obtained as an oil: FT-IR (CCl_4) 2932, 2891, 2856, 2103, 1489, 1470, 1443, 1385, 1364, 1118, 1069 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (m, 2 H, aromatics), 7.29 (m, 3 H, aromatics), 4.61 [m, 1 H, OCH(O)], 4.33 (s, 1 H, SiH), 3.94-3.75 (m, 2 H, CH_2O), 3.49 (m, 2 H, CH_2O), 1.97-1.53 (m, 10 H), 1.59 (s, 3 H, CH_3), 1.04 [s, 9 H, $C(CH_3)_3$], 1.01 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.4, 128.1, 127.9, 123.1 (aromatics), 98.7 [OCH(O)], 93.1 (*C*H≡C), 84.2 (CH≡*C*), 70.8 [C(OSi)], 67.5 (CH_2O), 62.2 (CH_2O), 41.9 (CH_2), 30.7 (CH_3), 30.3 (CH_2), 27.7 [C(*C*H_3)$_3$], 25.4 (CH_2), 25.2 (CH_2), 19.7 [*C*$(CH_3)_3$], 19.5 (CH_2); MS *m/z* 373 (M^+–57, 28), 287 (39), 187 (28), 169 (21), 115 (11), 85 (100); HRMS calcd. for $C_{22}H_{33}O_3Si$ (M^+ – 57) 373.2199, found 373.2183.

Di-*tert*-butyl-{1,3-diphenyl-1-[3-(tetrahydropyran-2-yloxy)propyl]prop-2-ynyloxy}silane (32): Following the Procedure B, from the alcohol **28** (2.0 g, 5.71 mmol) the silane **32** (2.512 g, 89% yield) was obtained as an oil: FT-IR (CCl_4) 3066, 3031, 2934, 2856, 2112, 1490, 1469, 1446, 1385, 1257, 1211, 1168, 1146 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.68 (m, 2 H, aromatics), 7.52 (m, 2 H, aromatics), 7.27 (m, 6 H, aromatics), 4.48 [m, 1 H, OCH(O)], 4.40 (s, 1 H, SiH), 3.80 (m, 1 H), 3.65 (m, 1 H), 3.44 (m, 1 H), 3.32 (m, 1 H), 2.15 (m, 2 H), 1.84-1.44 (m, 8 H), 1.09 [s, 9 H, $C(CH_3)_3$], 0.84 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 131.5, 128.3, 128.2, 127.7, 127.3, 126.1, 122.8 (aromatics), 98.5 [OCH(O)], 90.7 (*C*H≡C), 88.5 (CH≡*C*), 76.2 [C(OSi)], 67.1 (CH_2O), 62.1 (CH_2O), 44.1 (CH_2), 30.6 (CH_2), 27.8 [C(*C*H_3)$_3$], 27.5 [C(*C*H_3)$_3$], 25.4 (CH_2), 25.2 (CH_2), 19.8 [*C*$(CH_3)_3$], 19.7 [*C*$(CH_3)_3$], 19.4 (CH_2); MS *m/z* 435 (M^+ – 57, 42), 349 (61), 289 (9), 249 (30), 217 (29), 204 (27), 191 (9), 147 (10), 115 (15), 85 (100); HRMS calcd. for $C_{27}H_{35}O_3Si$ (M^+ – 57) 435.2355, found 435.2339.

Di-*tert*-butyl-{3-phenyl-1-[4-(tetrahydropyran-2-yloxy)butyl]prop-2-ynyloxy}silane (33): Following the Procedure A, from the alcohol **29** (2.5 g, 8.68 mmol) the silane **33** (3.53 g, 95% yield) was obtained as an oil: FT-IR (CCl_4) 2932, 2891, 2856, 2102, 1470, 1443, 1385, 1360, 1118, 1035 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (m, 2 H, aromatics), 7.29 (m, 3 H, aromatics), 4.69 [t, 1 H, C(OSi)H], 4.60 [m, 1 H, OCH(O)], 4.16 (s, 1 H, SiH), 3.94-3.73 (m, 2 H, CH_2O), 3.47-3.38 (m, 2 H, CH_2O), 1.80-1.46 (m, 12 H), 1.06 [s, 9 H, $C(CH_3)_3$], 1.02 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.4, 128.1, 127.9, 123.0 (aromatics), 98.6 [OCH(O)], 90.2 (Ph-*C*≡C), 84.7 (Ph-C≡*C*), 67.3 (CH_2O), 66.6 [C(OSi)H], 62.0 (CH_2O), 38.2 (CH_2), 30.6 (CH_2), 29.4 (CH_2), 27.2 [C(*C*H_3)$_3$], 25.4 (CH_2), 21.8 (CH_2), 20.0 [*C*$(CH_3)_3$], 19.4 (CH_2); MS *m/z* 373 (M^+ – 57, 17), 287 (24), 187 (17), 169 (10), 159 (7), 145 (17), 85 (100); HRMS calcd. for $C_{22}H_{33}O_3Si$ (M^+ – 57) 373.2198, found 373.2172.

Di-*tert*-butyl-{1-phenylethynyl-2-[2-(tetrahydropyran-2-yloxy)ethyl-1-cyclopentyloxy}silane (48): Following the Procedure B, from the alcohol **47** (1.3 g, 4.14 mmol) the silane **48** (1.8 g, 95% yield) was obtained as an oil: FT-IR (CCl_4) 2960, 2939, 2892, 2856, 2103, 1489, 1470, 1443, 1385, 1363, 1119, 1077, 1033 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (diastereomeric mixture) 7.41 (m, 2 H, aromatics), 7.30 (m, 3 H, aromatics), 4.60 [m, 1 H, OCH(O)], 4.31 (s, 1 H, SiH), 3.85 (m, 2 H, CH_2O), 3.50 (m, 2 H, CH_2O), 2.28-1.40 (m, 15 H), 1.05 [s, 9 H, C(*C*H_3)$_3$], 1.01 [s, 9 H, C(*C*H_3)$_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ (diastereomeric mixture) 131.4, 128.1, 127.9, 123.3 (aromatics), 98.8 [OCH(O)], 90.7 (Ph-*C*≡C), 86.9 (Ph-C≡*C*), 80.8 [*C*(C≡C)OSi], 66.8, 66.3 (CH_2O), 62.2, 62.1 (CH_2O), 49.4, 49.1 (CH), 41.5 (CH_2), 31.7, 31.5 (CH_2), 30.7 (CH_2), 28.3, 28.2 (CH_2), 27.6 [C(*C*H_3)$_3$], 25.5 (CH_2), 20.4, (CH_2), 19.8, 19.2

[$C(CH_3)_3$], 19.5 (CH_2); MS *m/z* 399 (M^+ – 57, 7), 371 (27), 327 (10), 313 (33), 298 (8), 213 (44), 171 (25), 85 (100); HRMS calcd. for $C_{24}H_{35}O_3Si$ (M^+ – 57) 399.2355, found 399.2350.

Di-*tert*-butyl-{4-methoxy-1-[3-(tetrahydropyran-2-yloxy)propyl]but-2-ynyloxy}silane: Following the Procedure A, from 1-methoxy-7-(tetrahydropyran-2-yloxy)-hept-2-yn-4-ol (1.2 g, 4.96 mmol), the silane (1.33 g, 70% yield) was obtained as an oil: FT-IR (CCl_4) 2935, 2886, 2858, 2099, 1471, 1387, 1363, 1200, 1103, 1077, 1035 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.59 [m, 2 H, C(OSi)H, OCH(O)], 4.13 (s, 2 H, CH_2-C≡C), 4.09 (s, 1 H, SiH), 3.84, (m, 2 H, CH_2O), 3.46 (m, 2 H, CH_2O), 3.37 (s, 3 H, OCH_3), 1.90-1.50 (m, 10 H), 1.03 [s, 9 H, $C(CH_3)_3$], 0.99 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 98.6 [OCH(O)], 87.2, 80.4 (CH_2-*C*≡C, CH_2-C≡*C*), 67.0 (CH_2O), 66.0 [C(OSi)H], 62.1 (CH_2O), 59.8 (CH_2O), 57.3 (OCH_3), 35.1 (CH_2), 30.6 (CH_2), 27.2 [$C(CH_3)_3$], 27.1 [$C(CH_3)_3$], 25.4 (CH_2), 25.1 (CH_2), 20.0 [$C(CH_3)_3$], 19.7 [$C(CH_3)_3$], 19.4 (CH_2); MS *m/z* 327 (M^+ – 57, 7), 283 (5), 255 (9), 241 (22), 211 (16), 145 (22), 131 (38), 85 (100); HRMS calcd. for $C_{17}H_{31}O_4Si$ 327.1992, found 327.2017.

{5-Benzyloxy-1-[3-(tetrahydropyran-2-yloxy)propyl]pent-2-ynyloxy}-di-*tert*-butylsilane: Following the Procedure A, from 8-benzyloxy-1-(tetrahydropyran-2-yloxy)-oct-5-yn-4-ol (2.5 g, 7.53 mmol) the silane (3.43 g, 96% yield) was obtained as an oil: FT-IR (CCl_4) 3065, 3030, 2928, 2886, 2857, 2094, 1469, 1386, 1363, 1100, 1076, 1035 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (diastereomeric mixture) 7.35-7.26 (m, 5 H, aromatics), 4.58 [m, 1 H, OCH(O)], 4.54 (s, 2 H, CH_2Ph), 4.48 [m, 1 H, C(OSi)H], 4.07 (s, 1 H, SiH), 3.86, 3.76 (m, 2 H, CH_2O), 3.58 (t, 2 H, *J*=7.1 Hz, CH_2OBn), 3.49 (m, 2 H, CH_2O), 2.52 (dt, 2 H, *J*=7.1 and 1.2 Hz, CH_2C≡C), 1.88-1.48 (m, 10 H), 1.01 [s, 9 H, $C(CH_3)_3$], 0.98 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ (diastereomeric mixture) 138.0, 128.3, 127.6 (aromatics), 98.5 [OCH(O)], 82.0, 81.7 (CH_2-*C*≡C, CH_2-C≡*C*), 72.8 (CH_2O), 68.5 (CH_2O), 67.1 (CH_2O), 66.2 [C(OSi)H], 62.1 (CH_2O), 35.3, 35.2 (CH_2), 30.6 (CH_2), 27.2 [$C(CH_3)_3$], 25.4 (CH_2), 25.2 (CH_2), 20.0 (CH_2), 19.9 [$C(CH_3)_3$], 19.7 [$C(CH_3)_3$], 19.4 (CH_2); MS *m/z* 417 (M^+ – 57, 9), 331 (10), 282 (14), 259 (8), 229 (8), 199 (8), 105 (26), 91 (100), 77 (90), 57 (55); HRMS calcd. for $C_{24}H_{37}O_4Si$ (M^+ – 57) 417.2461, found 417.2445.

Di-*tert*-butyl-{1-[3-(tetrahydropyran-2-yloxy)propyl]prop-2-ynyloxy}silane: Following the Procedure A, from 6-(tetrahydropyran-2-yloxy)-hex-1-yn-3-ol. (2.135 g, 10.78 mmol), the silane (2.86 g, 78% yield) was obtained as an oil: FT-IR (CCl_4) 2938, 2891, 2857, 2094, 1470, 1386, 1364, 1096, 1076 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (diastereomeric mixture) 4.59 [m, 1 H, OCH(O)], 4.51 [m, 1 H, C(OSi)H], 4.08 (s, 1 H, SiH), 3.83 (m, 2 H, CH_2O), 3.47 (m, 2 H, CH_2O), 2.43 (d, 1 H, *J* = 2.1 Hz, HC≡C), 1.88-1.50 (m, 10 H), 1.03 [s, 9 H, $C(CH_3)_3$], 0.99 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ (diastereomeric mixture) 98.5 [OCH(O)], 84.4 (HC≡*C*), 72.7 (H*C*≡C), 67.0 (CH_2O), 65.8 [C(OSi)H], 62.1 (CH_2O), 35.0, 35.0 (CH_2), 30.6 (CH_2), 27.2 [$C(CH_3)_3$], 27.1 [$C(CH_3)_3$], 25.4 (CH_2), 25.0 (CH_2), 20.1 [$C(CH_3)_3$], 19.4 (CH_2); MS *m/z* 283 (M^+ – 57, 12), 239 (11), 227 (7), 197 (7), 157 (5), 101 (6), 85 (100); HRMS calcd. for $C_{15}H_{27}O_3Si$ 283.1729, found 283.1718.

Synthesis of ethyl 4-di-*tert*-butylsilyloxy-7-(tetrahydropyran-2-yloxy)hept-2-ynoate: To a solution of *di-tert*-butyl-{1-[3-(tetrahydropyran-2-yloxy)propyl]prop-2-ynyloxy}silane (1.0 g, 2.94 mmol) in THF (25 mL), BuLi (1.6 M in hexane, 1.84 mL, 2.94 mmol, 1.0 equiv) was added at –50°C. The mixture was warmed to –20°C and after stirring for 15 min was cooled again at –50°C and ethyl chloroformate (0.56 mL, 0.64 g, 5.88 mmol, 2.0 equiv) was added dropwise. The reaction was allowed to warm to 0°C over 2 h and stirred at this temperature for 2 h. A solution of saturated ammonium chloride was added and the aqueous layer was extracted twice with ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude mixture was submitted to flash chromatography (hexane/ethyl acetate, 9:1) to provide the compound (0.885 g, 73% yield) as an oil. FT-IR (CCl_4) 2933, 2892, 2858, 2237, 2096, 1716, 1469, 1365, 1351, 1245, 1097, 1076 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.63 [m, 1 H, C(OSi)H], 4.58 [m, 1 H, OCH(O)], 4.21 (q, 2 H, $CO_2CH_2CH_3$), 4.08 (s, 1 H, SiH), 3.80 (m, 2 H, CH_2O), 3.46 (m, 2 H, CH_2O), 1.90-1.47 (m, 10 H), 1.29 (t, 3 H, $CO_2CH_2CH_3$), 1.02 [s, 9 H, $C(CH_3)_3$], 0.98 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4 (CO_2Et), 98.6 [OCH(O)], 87.5 (C≡*C*), 76.7 (*C*≡C), 66.8 (CH_2O), 65.7 [C(OSi)H], 62.1 (CH_2O), 61.8 (CH_2O), 34.4 (CH_2), 30.6 (CH_2), 27.1 [$C(CH_3)_3$], 25.4 (CH_2), 24.9 (CH_2), 20.0 [$C(CH_3)_3$], 19.4 (CH_2), 13.9 (OCH_2CH_3); MS *m/z* 355 (M^+ – 57, 11), 283 (10), 269 (34), 241 (25), 225 (27), 85 (100); HRMS calcd. for $C_{18}H_{31}O_5Si$ (M^+ – 57) 355.1941, found 355.1947.

General Procedure for the Synthesis of the TBS derivatives. Procedure A. To a solution of the alcohol (1.0 equiv) in ether (30 mL) triethylamine, (1.1 equiv) and dimethylaminopyridine (0.3 equiv) were added. After 5 min, *tert*-butyldimethylsilyl chloride (1.1 equiv) was added and the mixture was heated overnight at reflux. Water was added and the aqueous layer was extracted twice with ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude mixture was submitted to flash chromatography (hexane/ethyl acetate, 19:1).

Procedure B. To a solution of the alcohol (1.0 equiv) in DMF (2 mL/mmol) were added imidazole (2.0 equiv) and dimethylaminopyridine (0.5 equiv). After 5 min, *tert*-butyldimethylsilyl chloride (1.5 equiv) and sodium iodide (1.5 equiv) were added and the mixture was stirred overnight at room temperature. Water was added and the aqueous layer was extracted twice with ethyl acetate. The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude mixture was submitted to flash chromatography (hexane/ethyl acetate, 19:1).

***tert*-Butyldimethyl-{3-phenyl-1-[3-(tetrahydropyran-2-yloxy)propyl-1-prop-2-ynyloxy}silane:** Following the Procedure A, from the alcohol **26**[25] (1.2 g, 4.38 mmol) the silane (1.354 g, 80% yield) was obtained as an oil: FT-IR (CCl_4) 2952, 2883, 2856, 2202, 1451, 1277, 1174, 1070, 1036 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (diastereomeric mixture) 7.40 (m, 2 H, aromatics), 7.28 (m, 3 H, aromatics), 4.60 [m, 2 H, C(OSi)H, OCH(O)], 3.85 (m, 2 H, CH_2O), 3.49 (m, 2 H, CH_2O), 1.80-1.49 (m, 10 H), 0.94 [s, 9 H, $C(CH_3)_3$], 0.18 (s, 3 H, CH_3), 0.16 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (diastereomeric mixture) 131.4, 128.1, 128.0, 123.0 (aromatics), 98.7, 98.6 [OCH(O)], 90.8 (Ph-*C*≡C), 84.1 (Ph-C≡*C*), 67.1 (CH_2O), 63.2 [C(OSi)H], 62.1 (CH_2O), 35.4 (CH_2), 30.6 (CH_2), 25.7 [$C(CH_3)_3$], 25.6 [$C(CH_3)_3$], 25.4 (CH_2), 19.5 (CH_2), 18.2 [$C(CH_3)_3$], -4.42 (CH_3), -4.9 (CH_3).

***tert*-Butyldimethyl-{1-[3-(tetrahydropyran-2-yloxy)propyl]prop-2-ynyloxy}silane:** Following the Procedure B, from 6-(tetrahydropyran-2-yloxy)-hex-1-yn-3-ol (1.0 g, 5.0 mmol), the silane (1.325 g, 84% yield) was obtained as an oil: FT-IR (CCl_4) 3310, 2950, 2896, 2858, 2120, 1471, 1361, 1351, 1076, 1035 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (diastereomeric mixture) 4.56 [m, 1 H, OCH(O)], 4.37 [m, 1 H, C(OSi)H], 3.80 (m, 2 H, CH_2O), 3.44 (m, 2 H, CH_2O), 2.36 (d, 1 H, J = 2.1 Hz, HC≡C), 1.85-1.45 (m, 10 H), 0.88 [s, 9 H, $C(CH_3)_3$], 0.12 (s, 3 H, CH_3), 0.09 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (diastereomeric mixture) 98.6, 98.6 [OCH(O)], 85.4 (HC≡*C*), 72.0 (H*C*≡C), 67.0 (CH_2O), 62.5 [C(OSi)H], 62.1 (CH_2O), 35.3 (CH_2), 30.6 (CH_2), 25.7 [$C(CH_3)_3$], 25.4 (CH_2), 25.3 (CH_2), 19.5 (CH_2), 18.1 [$C(CH_3)_3$]; MS *m/z* 227 (M^+ – OTHP, 9), 211 (71), 169 (18), 159 (45), 141 (6), 129 (13), 115 (18), 103 (54), 85 (100); HRMS calcd. for $C_{12}H_{23}O_2Si$ (M^+ – OTHP) 227.1467, found 227.1468.

Synthesis of ethyl 4-*tert*-butyldimethylsilyloxy-7-(tetrahydropyran-2-yloxy)hept-2-ynoate: To a solution of *tert*-butyldimethyl-{1-[3-(tetrahydropyran-2-yloxy)-propyl]-prop-2-ynyloxy}-silane (1.275 g, 4.09 mmol) in THF (25 mL), BuLi (1.6 M in hexane, 2.55 mL, 4.09 mmol, 1.0 equiv) was added at –50°C. The mixture was warmed to –20°C and after 15 min was cooled again to –50°C and ethyl chloroformate (0.78 mL, 0.887 g, 8.17 mmol, 2.0 equiv) was added dropwise. The reaction was allowed to warm to 0°C in 2 h and stirred at this temperature for 3 h. A solution of saturated ammonium chloride was added and the aqueous layer was extracted twice with ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude mixture was submitted to flash chromatography (hexane/ethyl acetate, 19:1) to provide the compound (1.036 g, 66% yield) as an oil: FT-IR (CCl_4) 2952, 2938, 2897, 2858, 2236, 1715, 1471, 1365, 1248 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.56 [m, 1 H, OCH(O)], 4.50 [t, 1 H, C(OSi)H], 4.20 (q, 2 H, $CO_2CH_2CH_3$), 3.79 (m, 2 H, CH_2O), 3.43 (m, 2 H, CH_2O), 1.88-1.47 (m, 10 H), 1.28 (t, 3 H, $CO_2CH_2CH_3$), 0.88 [s, 9 H, $C(CH_3)_3$], 0.13 (s, 3 H, CH_3), 0.09 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4 (CO_2Et), 98.6 [OCH(O)], 88.3 (C≡*C*), 76.0 (*C*≡C), 66.8 (CH_2O), 62.4, 62.1, 61.8 [C(OSi)H, 2 CH_2O], 34.6 (CH_2), 30.6 (CH_2), 25.6 [$C(CH_3)_3$], 25.4 (CH_2), 24.2 (CH_2), 19.5 [$C(CH_3)_3$], 18.0 (CH_2), 13.9 (OCH_2CH_3), -4.6 (CH_3Si), -5.2 (CH_3Si); MS *m/z* 339 (M^+ – 45, 15), 327 (3), 299 (6), 283 (74), 243 (65), 197 (71), 159 (66), 123 (86), 85 (100); HRMS calcd. for $C_{16}H_{27}O_5Si$ (M^+ – 57) 327.1627, found 327.1637.

General Procedure for Iodination. A solution of iodine (1.2 equiv) in CH_2Cl_2 (10 mL/mmol) was added dropwise with stirring to a solution of 1,2-bis(diphenylphosphino)ethane (1.2 equiv) in CH_2Cl_2 (6 mL/mmol) at 0°C and the mixture was stirred for 30 min. A solution of the corresponding silane (1.0 equiv) in CH_2Cl_2 (4 mL/mmol) was added and the reaction mixture was warmed to room temperature. After stirring for 1-2 h, ether/pentane (1:2) was added to precipitate the undesired byproducts. The mixture was quickly filtered over

Celite 526 and the solid was washed with ether/pentane 1:2. The filtrate was evaporated and the residue was submitted to flash chromatography (hexane/ethyl acetate, 98:2).

Di-*tert*-butyl-[1-(3-iodopropyl)-3-phenylprop-2-ynyloxy]silane (34): Following the General Procedure, from the silane **30** (0.5 g, 1.2 mmol) the iodide **34** (0.315 g, 59% yield) was obtained as a very unstable oil: FT-IR (CCl_4) 3065, 3020, 2929, 2856, 2250, 2095, 1653, 1489, 1469, 1443, 1387, 1361, 1341, 1070 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (m, 2 H, aromatics), 7.30 (m, 3 H, aromatics), 4.74 [t, 1 H, C(OSi)H], 4.15 (s, 1 H, SiH), 3.28 (t, 2 H, CH_2I), 2.12 (m, 2 H, CH_2), 1.81 (m, 2 H, CH_2), 1.06 [s, 9 H, $C(CH_3)_3$], 1.02 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.5, 128.2, 122.8 (aromatics), 89.6 (Ph-*C*H≡C), 85.1 (Ph-CH≡*C*), 65.6 [C(OSi)H], 38.9 (CH_2), 29.0 (CH_2), 27.2 [$C(CH_3)_3$], 20.1 [$C(CH_3)_3$], 19.7 [$C(CH_3)_3$], 6.7 (CH_2I); ^{29}Si NMR (99 MHz, $CDCl_3$) δ 16.3 (d, *J*=197.2 Hz, SiH); MS *m/z* 385 (M^+ – 57, 18), 343 (26), 271 (4), 229 (7), 187 (6), 173 (9), 159 (29), 145 (18), 128 (44), 115 (37), 84 (100); HRMS calcd. for $C_{16}H_{22}IOSi$ (M^+ – 57) 385.0485, found 385.0488.

Di-*tert*-butyl-[1-(3-iodopropyl)-1-methyl-3-phenylprop-2-ynyloxy]silane (35): Following the General Procedure, from the silane **31** (0.5 g, 1.16 mmol) the iodide **35** (0.36 g, 68% yield) was obtained as a very unstable oil: FT-IR (CCl_4) 3055, 2930, 2856, 2230, 2103, 1489, 1470, 1443, 1386, 1363, 1068 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (m, 5 H, aromatics), 4.32 (s, 1 H, SiH), 3.24 (t, 2 H, CH_2I), 2.13 (m, 2 H), 1.88 (m, 2 H), 1.60 (s, 3 H, CH_3), 1.04 [s, 9 H, $C(CH_3)_3$], 1.01 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.4, 128.2, 128.1, 122.9 (aromatics), 92.6 (*C*H≡C), 84.5 (CH≡*C*), 70.3 [C(OSi)], 46.1 (CH_2), 30.5 (CH_3), 29.1 (CH_2), 27.7 [$C(CH_3)_3$], 19.8 [$C(CH_3)_3$], 19.5 [$C(CH_3)_3$], 7.2 (CH_2I); MS *m/z* 399 (M^+–57, 100), 357 (46), 313 (9), 271 (11), 229 (22), 187 (50), 159 (49), 145 (57), 129 (38), 115 (33), 85 (59); HRMS calcd. for $C_{17}H_{24}IOSi$ (M^+ – 57) 399.0641, found 399.0653.

Di-*tert*-butyl-[1-(3-iodopropyl)-1,3-diphenylprop-2-ynyloxy]silane (36): Following the General Procedure, from the silane **32** (1.0 g, 2.03 mmol) the iodide **36** (0.42 g, 40% yield) was obtained as a very unstable oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, 2 H, aromatics), 7.54 (m, 2 H, aromatics), 7.32 (m, 6 H, aromatics), 4.41 (s, 1 H, SiH), 3.11 (t, 2 H, CH_2I), 2.33-1.72 (m, 4 H), 1.12 [s, 9 H, $C(CH_3)_3$], 0.85 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 131.5, 128.5, 128.3, 127.9, 127.6, 126.0, 122.6 (aromatics), 90.2 (*C*H≡C), 88.9 (CH≡*C*), 75.7 [C(OSi)], 48.2 (CH_2), 29.0 (CH_2), 27.8 [$C(CH_3)_3$], 27.5 [$C(CH_3)_3$], 19.7 [$C(CH_3)_3$], 6.4 (CH_2I).

Di-*tert*-butyl-[1-(4-iodobutyl)-3-phenylprop-2-ynyloxy]silane (37): Following the General Procedure, from the silane **33** (1.5 g, 3.49 mmol) the iodide **37** (1.172 g, 74% yield) was obtained as a very unstable oil: FT-IR (CCl_4) 2928, 2856, 2257, 2093, 1489, 1469, 1443, 1387, 1363, 1343, 1086 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (m, 2 H, aromatics), 7.29 (m, 3 H, aromatics), 4.68 [t, 1 H, C(OSi)H], 4.15 (s, 1 H, SiH), 3.21 (t, 2 H, CH_2I), 1.90 (m, 2 H, CH_2), 1.80 (m, 2 H, CH_2), 1.65 (m, 2 H, CH_2), 1.06 [s, 9 H, $C(CH_3)_3$], 1.02 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.5, 128.2, 128.1, 122.9 (aromatics), 89.9 (*C*H≡C), 85.0 (CH≡*C*), 66.4 [C(OSi)H], 37.2 (CH_2), 33.2 (CH_2), 27.3 [$C(CH_3)_3$], 27.2 [$C(CH_3)_3$], 26.0 (CH_2), 20.0 [$C(CH_3)_3$], 19.7 [$C(CH_3)_3$], 6.7 (CH_2I); MS *m/z* 399 (M^+ – 57, 94), 343 (73), 271 (13), 229 (32), 187 (29), 159 (98), 145 (67), 115 (100); HRMS calcd. for $C_{17}H_{24}IOSi$ (M^+ – 57) 399.0641, found 399.0657.

Di-*tert*-butyl-[2-(2-iodoethyl)-1-phenylethynylcyclopentyloxy]silane (49): Following the General Procedure, from the silane **48** (1.0 g, 2.19 mmol) the iodide **49** (0.603 g, 57% yield) was obtained as a very unstable oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (m, 5 H, aromatics), 4.29 (s, 1 H, SiH), 3.34 (m, 1 H, CH_2I), 3.25 (m, 1 H, CH_2), 2.50-1.70 (m, 8 H), 1.39 (m, 1 H), 1.06 [s, 9 H, $C(CH_3)_3$], 1.02 [s, 9 H, $C(CH_3)_3$]; MS *m/z* 322 (20), 195 (71), 178 (35), 165 (100), 152 (42), 141 (30), 115 (98), 77 (50), 63 (37).

***tert*-Butyl-[1-(3-iodopropyl)-3-phenylprop-2-ynyloxy]dimethylsilane (52):** Following the General Procedure, from the silane (1.2 g, 3.1 mmol) the iodide **52** (0.837 g, 65% yield) was obtained as a very unstable oil: FT-IR (CCl_4) 3079, 3032, 2952, 2927, 2893, 2855, 2202, 1489, 1470, 1442, 1360, 1340, 1252, 1091 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 (m, 2 H, aromatics), 7.30 (m, 3 H, aromatics), 4.62 [t, 1 H, C(OSi)H], 3.26 (t, 2 H, CH_2I), 2.08 (m, 2 H, CH_2), 1.87 (m, 2 H, CH_2), 0.93 [s, 9 H, $C(CH_3)_3$], 0.18 (s, 3 H, CH_3), 0.15 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.4, 128.2, 122.8 (aromatics), 90.3 (Ph-*C*H≡C), 84.4 (Ph-CH≡*C*), 62.3 [C(OSi)H], 39.1 (CH_2), 29.3 (CH_2), 25.8 [$C(CH_3)_3$], 18.2 [$C(CH_3)_3$], 6.7

(CH_2I), -4.3 (CH_3), -4.9 (CH_3); MS *m/z* 357 (M^+ – 57, 80), 315 (8), 255 (38), 229 (5), 185 (18), 159 (100), 128 (35), 115 (28), 75 (72); HRMS calcd. for $C_{14}H_{18}IOSi$ (M^+ – 57) 357.0173, found 357.0168.

Di-*tert*-butyl-[1-(3-iodopropyl)-4-methoxy-but-2-ynyloxy]silane (55): Following the General Procedure, from the silane (0.6 g, 1.56 mmol) the iodide **55** (0.602 g, 94% yield) was obtained as a very unstable oil: FT-IR (CCl_4) 2959, 2929, 2888, 2856, 2093, 1469, 1363, 1343, 1099 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.57 [m, 1 H, C(OSi)H], 4.14 (d, 2 H, *J*=1.5 Hz, $CH_2C{\equiv}C$), 4.08 (s, 1 H, SiH), 3.38 (s, 3 H, OCH_3), 3.24 (t, 2 H, *J*=6.9 Hz, CH_2I), 2.04 (m, 2 H, CH_2), 1.84 (m, 2 H, CH_2), 1.02 [s, 9 H, $C(CH_3)_3$], 1.00 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 86.7, 80.8 (CH_2-*C*≡C, CH_2-C≡*C*), 65.1 [C(OSi)H], 59.8 (CH_2), 57.5 (OCH_3), 38.8 (CH_2), 28.8 (CH_2), 27.2 [C(*C*H_3)$_3$], 27.1 [C(*C*H_3)$_3$], 20.0 [*C*(CH_3)$_3$], 19.7 [*C*(CH_3)$_3$], 6.5 (CH_2I); MS *m/z* 353 (M^+ – 57, 25), 311 (5), 201 (100), 141 (13), 115 (12), 91 (67), 75 (63), 57 (60); HRMS calcd. for $C_{12}H_{22}IO_2Si$ (M^+ – 57) 353.0434, found 353.0439.

[5-Benzyloxy-1-(3-iodopropyl)-pent-2-ynyloxy]-di-*tert*-butylsilane (56): Following the General Procedure, from the silane (1.0 g, 2.11 mmol) the iodide **56** (0.97 g, 92% yield) was obtained as a very unstable oil: FT-IR (CCl_4) 3060, 3015, 2930, 2895, 2860, 2095, 1597, 1506, 1489, 1468, 1441, 1387, 1361, 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.25 (m, 5 H, aromatics), 4.58 (s, 2 H, CH_2Ph), 4.51 [m, 1 H, C(OSi)H], 4.09 (s, 1 H, SiH), 3.60 (t, 2 H, *J*=7.0 Hz, CH_2OBn), 3.24 (t, 2 H, *J*=7.0 Hz, CH_2I), 2.55 (dt, 2 H, *J*=7.0 and 1.8 Hz, C*H*$_2$-C≡C), 2.04 (qt, 2 H, CH_2), 1.81 (m, 2 H, CH_2), 1.04 [s, 9 H, $C(CH_3)_3$], 1.01 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 128.3, 127.6 (aromatics), 82.2, 81.5 (CH_2-*C*≡C, CH_2-C≡*C*), 73.0 (CH_2O), 68.4 (CH_2O), 65.1 [C(OSi)H], 39.0 (CH_2), 28.9 (CH_2), 27.3 [C(*C*H_3)$_3$], 27.2 [C(*C*H_3)$_3$], 19.9, 19.7 [CH_2, *C*(CH_3)$_3$], 6.8 (CH_2I); MS *m/z* 443 (M^+ – 57, 23), 401 (4), 337 (3), 225 (16), 167 (8), 91 (100); HRMS calcd. for $C_{19}H_{28}IO_2Si$ (M^+ – 57) 443.0905, found 443.0901.

Ethyl 4-di-*tert*-butylsilyloxy-7-iodo-hept-2-ynoate (57): Following the General Procedure, from the silane (0.825 g, 2.0 mmol) the iodide **57** (0.38 g, 44% yield) was obtained as a very unstable oil: FT-IR (CCl_4) 2962, 2931, 2892, 2858, 2240, 2097, 1715, 1469, 1388, 1365, 1341, 1246, 1094 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.62 [t, 1 H, C(OSi)H], 4.23 (q, 2 H, $CO_2CH_2CH_3$), 4.08 (s, 1 H, SiH), 3.23 (t, 2 H, *J*=6.9 Hz, CH_2I), 2.04 (m, 2 H, CH_2), 1.88 (m, 2 H, CH_2), 1.31 (t, 3 H, OCH_2CH_3), 1.03 [s, 9 H, $C(CH_3)_3$], 0.99 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2 (*C*O_2Et), 86.8, 76.9 (*C*≡C, C≡*C*), 64.9 [C(OSi)H], 61.9 (CH_2O), 38.1 (CH_2), 28.5 (CH_2), 27.1 [C(*C*H_3)$_3$], 27.1 [C(*C*H_3)$_3$], 20.0 [*C*(CH_3)$_3$], 19.7 [*C*(CH_3)$_3$], 13.9 (CH_3), 5.9 (CH_2I); MS *m/z* 381 (M^+ – 57, 100), 339 (79), 267 (22), 255 (7), 225 (9), 212 (18), 185 (34), 155 (21), 141 (22), 79 (95); HRMS calcd. for $C_{13}H_{22}IO_3Si$ (M^+ – 57) 381.0383, found 381.0402.

Ethyl 4-*tert*-butyldimethylsilyloxy-7-iodohept-2-ynoate (64): Following the General Procedure, from the silane (0.73 g, 1.9 mmol) the iodide **64** (519 mg, 67%) was obtained as a very unstable oil: FT-IR (CCl_4) 2954, 2931, 2895, 2858, 2238, 1714, 1471, 1445, 1385, 1365, 1248, 1097 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.52 [t, 1 H, C(OSi)H], 4.23 (q, 2 H, $CO_2CH_2CH_3$), 3.22 (t, 2 H, CH_2I), 2.00 (m, 2 H, CH_2), 1.85 (m, 2 H, CH_2), 1.32 (t, 3 H, $CO_2CH_2CH_3$), 0.91 [s, 9 H, $C(CH_3)_3$], 0.16 (s, 3 H, CH_3), 0.12 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3 (*C*O_2Et), 87.6 (C≡*C*), 76.3 (*C*≡C), 62.0, 61.6 [C(OSi)H, CH_2O], 38.3 (CH_2), 28.8 (CH_2), 25.6 [C(*C*H_3)$_3$], 18.1 [*C*(CH_3)$_3$], 13.9 (OCH_2CH_3), 6.0 (CH_2I), -4.6 (CH_3Si), -5.1 (CH_3Si); MS *m/z* 365 (M^+ – 45, 15), 353 (93), 325 (11), 311 (65), 257 (33), 241 (18), 197 (23), 185 (36), 155 (40), 103 (80), 75 (100); HRMS calcd. for $C_{11}H_{18}IO_3Si$ (M^+ – 57) 353.0070, found 353.0073.

General Procedure for Radical Cyclization and 1,5-Hydrogen Transfer. Bis(tributyltin) (0.1 equiv) was added to a solution of the corresponding iodide (1.0 equiv) in benzene (0.1 M solution). The mixture was heated to 80°C and irradiated with a UV lamp. After 5-12 h, the reaction was complete. The reaction was cooled to room temperature and the solvent was evaporated. Purification by flash chromatography (hexane) afforded the silicon iodide that, due to its instability, could only be kept in freezer under argon in dark for a few hours.

(*E*)-3-Di-*tert*-butyliodosilyloxy-1-phenyl-1-pentene (*E*-4): Following the General Procedure from the iodide **3** (120 mg, 0.28 mmol), after irradiation for 6 h using bis(tributyltin) (0.2 equiv), the iodosilane **(*E*)-4** (52 mg, 43% yield) was obtained as a very unstable oil: FT-IR (CCl_4) 3060, 3010, 2920, 2851, 1674, 1643, 1549, 1487, 1446, 1390, 1365, 1109 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.21 (m, 5 H, aromatics), 6.54 (d, 1 H, *J* = 16 Hz, HC(Ph)=C), 6.17 [dd, 1 H, *J* = 6.9 and 16.0 Hz, C(Ph)=C*H*], 4.54 [m, 1

H, C(OSi)H], 1.69 (m, 2 H, CH_2), 1.14 [s, 9 H, $C(CH_3)_3$], 1.08 [s, 9 H, $C(CH_3)_3$], 0.90 (t, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.5, 128.2, 123.2, 90.2, 84.7, 67.9, 31.5, 27.3, 20.1, 9.4.

(*E*)-1-Di-*tert*-butyliodosilyloxy-2-phenylmethylenecyclopentane (*E*-38): Following the General Procedure after irradiation for 5 h, from the iodide **34** (200 mg, 0.45 mmol) the iodosilane **(*E*)-38** (160 mg, 80% yield) was obtained as a very unstable solid; mp 103-105°C (hexane). FT-IR (CCl_4) 3070, 3025, 2924, 2865, 1655, 1595, 1466, 1387, 1363, 1346, 1076 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, 4 H, aromatics), 7.22 (m, 1 H, aromatics), 6.65 (m, 1 H, *J* = 2.4 Hz, HC=C), 4.85 [m, 1 H, C(OSi)H], 2.72-2.52 (m, 2 H), 1.97 (m, 2 H), 1.72 (m, 2 H), 1.14 [s, 9 H, $C(CH_3)_3$], 1.13 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5 (*C*=CH), 137.8, 128.4, 128.2, 126.3 (aromatics), 123.9 (C=*C*H), 81.0 [C(OSi)H], 34.1 (CH_2), 28.5 (CH_2), 27.6 [$C(CH_3)_3$], 27.5 [$C(CH_3)_3$], 24.9 [$C(CH_3)_3$], 24.6 [$C(CH_3)_3$], 21.9 (CH_2); ^{29}Si NMR (99 MHz, $CDCl_3$) δ 20.2 (s, SiI); MS *m/z* 442 (M^+, 66), 385 (32), 315 (18), 257 (17), 229 (25), 187 (97), 157 (100), 129 (56), 117 (35), 91 (57); HRMS calcd. for $C_{20}H_{31}IOSi$ *m/z* 442.1188, found 442.1168.

(*E*)-1-Di-*tert*-butyliodosilyloxy-1-methyl-2-phenylmethylenecyclopentane (*E*-39): Following the General Procedure after irradiation for 12 h, from the iodide **35** (150 mg, 0.33 mmol) the iodosilane **(*E*)-39** (105 mg, 70% yield) was obtained as a very unstable oil: FT-IR (CCl_4) 3060, 3020, 2928, 2856, 1495, 1469, 1446, 1385, 1361, 1153, 1088 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (m, 4 H, aromatics), 7.23 (m, 1 H, aromatics), 6.59 (t, 1 H, *J* = 2.5 Hz, HC=C), 2.80-2.60 (m, 2 H), 2.15-1.66 (m, 4 H), 1.62 (s, 3 H, CH_3), 1.10 [s, 9 H, $C(CH_3)_3$], 1.09 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1 (HC=*C*), 137.9, 128.4, 128.2, 126.3 (aromatics), 122.5 (H*C*=C), 85.6 [C(OSi)], 41.5 (CH_2), 29.6 (CH_2), 27.7 [$C(CH_3)_3$], 24.8 [$C(CH_3)_3$], 22.3 (CH_2), 13.0 (CH_3); MS *m/z* 456 (M^+, 4), 399 (14), 329 (3), 229 (17), 187 (100), 129 (23), 91 (42).

(*E*)-1-Di-*tert*-butyliodosilyloxy-2-phenylmethylenecyclohexane (*E*-41): Following the General Procedure after irradiation for 6 h, from the iodide **37** (250 mg, 0.55 mmol) the iodosilane **(*E*)-41** (190 mg, 76% yield) was obtained as a very unstable solid; mp 34-35°C. FT-IR (CCl_4) 3065, 3020, 2926, 2860, 1655, 1597, 1464, 1381, 1361, 1190, 1097 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.31 (m, 2 H, aromatics), 7.20 (m, 3 H, aromatics), 6.51 (s, 1 H, HC=C), 4.49 [m, 1 H, C(OSi)H], 2.56 (m, 1 H), 2.30 (m, 1 H), 2.0-1.7 (m, 3 H), 1.62-1.53 (m, 3 H), 1.15 [s, 9 H, $C(CH_3)_3$], 1.12 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5 (*C*=CH), 137.6, 128.8, 128.0, 126.2 (aromatics), 122.4 (C=*C*H), 78.4 [C(OSi)H], 36.2 (CH_2), 27.6 (CH_2), 27.5 [$C(CH_3)_3$], 26.6 (CH_2), 25.2 [$C(CH_3)_3$], 24.2 [$C(CH_3)_3$], 22.3 (CH_2); MS *m/z* 456 (M^+, 38), 399 (34), 329 (22), 229 (23), 187 (100), 129 (40), 91 (44).

(*E*)-3a-Di-*tert*-butyliodosilyloxy-3-(phenylmethylene)hexahydro-1*H*-pentalene (*E*-50): Following the General Procedure after irradiation for 6 h, from the iodide **49** (150 mg, 0.31 mmol) the iodosilane **(*E*)-50** (79 mg, 53% yield) was obtained as a very unstable oil: FT-IR (CCl_4) 3060, 3025, 2943, 2858, 1496, 1466, 1446, 1361, 1103, 1008 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.4 (m, 5 H, aromatics), 6.63 (s, 1 H, HC=C) , 2.8-1.2 (m, 11 H), 1.11 [s, 9 H, $C(CH_3)_3$], 1.07 [s, 9 H, $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 138.0, 128.6, 128.1, 126.4, 123.6, 77.2, 49.3, 41.4, 31.6, 30.9, 30.8, 27.6, 25.0, 24.7; MS *m/z* 482 (M^+, 1), 425 (8), 355 (1), 297 (1), 229 (5), 187 (62), 141 (24), 91 (77), 75 (100).

(*E*)-1-Di-*tert*-butyliodosilyloxy-2-(2-methoxyethylidene)cyclopentane (*E*-58): Following the General Procedure after irradiation for 6 h, from the iodide **55** (0.2 g, 0.48 mmol) the iodosilane **(*E*)-58** (0.118 g, 59% yield) was obtained as a very unstable oil: FT-IR (CCl_4) 3077, 3039, 2958, 2933, 2893, 2859, 1470, 1386, 1364, 1102 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.74 (m, 1 H, HC=C) , 4.69 [m, 1 H, C(OSi)H], 3.94 (dd, 2 H, *J* = 6.6 and 0.8 Hz, CH_2OMe), 3.33 (s, 3 H, OMe), 2.80-1.75 (m, 6 H), 1.11 [s, 9 H, $C(CH_3)_3$], 1.10 [s, 9 H, $C(CH_3)_3$]; MS *m/z* 365 ($M^+ - 45$, 5), 353 (3), 283 (4), 201 (49), 91 (74).

(*E*)-1-Di-*tert*-butyliodosilyloxy-2-(3-benzyloxypropylidene)cyclopentane (*E*-59): Following the General Procedure from the iodide **56** (250 mg, 0.5 mmol), after irradiation for 12 h using bis(tributyltin) (0.2 equiv), the iodosilane **(*E*)-59** (27 mg, 11% yield) was obtained as a very unstable oil: FT-IR (CCl_4) 3070, 3025, 2924, 2865, 1655, 1595, 1466, 1387, 1363, 1346, 1076 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (m, 5 H, aromatics), 5.64 (m, 1 H, HC=C) , 4.66 [m, 1 H, C(OSi)H], 4.50 (s, 2 H, OCH_2Ph), 3.49 (t, 2 H, CH_2OBn), 2.35 (q, 2 H, CH_2CH=C), 2.30-1.70 (m, 6 H), 1.09 [s, 18 H, 2 $C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.0 (*C*=CH), 138.5, 128.2, 127.6, 127.5 (aromatics), 120.3 (C=*C*H), 79.5 [C(OSi)H], 72.8

(CH_2O), 69.7 (CH_2O), 35.0 (CH_2), 29.9 (CH_2), 27.6 [C(CH_3)$_3$], 27.5 [C(CH_3)$_3$], 24.7 [C(CH_3)$_3$], 24.5 [C(CH_3)$_3$], 21.3 (CH_2), 16.3 (CH_2); MS *m/z* 373 (M^+ – 127, 2), 281 (3), 223 (10), 181 (4), 91 (100).

Ethyl (*E*)-(2-di-*tert*-butyliodosilyloxycyclopentylidene)acetate (*E*-60): Following the General Procedure after irradiation for 6 h, from the iodide **57** (250 mg, 0.57 mmol) the iodosilane ***E*-60** (147 mg, 59% yield) was obtained as a very unstable oil: FT-IR (CCl_4) 2957, 2935, 2896, 2860, 1715, 1665, 1469, 1385, 1366, 1329, 1200 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.99 (m, 1 H, HC=C) , 4.74 [m, 1 H, C(OSi)H], 4.15 (q, 2 H, $CO_2CH_2CH_3$), 2.86-2.75 (m, 2 H), 2.20-1.82 (m, 4 H), 1.27 (t, 3 H, $CO_2CH_2CH_3$), 1.13 [s, 9 H, C(CH_3)$_3$], 1.10 [s, 9 H, C(CH_3)$_3$]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 165.8 (CO_2Et, *C*=CH), 113.4 (C=*C*H), 80.0 [C(OSi)H], 59.7 ($CO_2CH_2CH_3$), 33.9 (CH_2), 29.4 (CH_2), 27.6 [C(CH_3)$_3$], 27.5 [C(CH_3)$_3$], 25.1 [C(CH_3)$_3$], 24.4 [C(CH_3)$_3$], 20.6 (CH_2), 14.3 (CH_3); MS *m/z* 438 (M^+, 1), 381 (3), 353 (2), 311 (10), 254 (5), 215 (6), 187 (25), 107 (52), 41 (100).

General Procedure for the Radical Cyclization using Bu_3SnH. A solution of Bu_3SnH (1.0 equiv) and a catalytic amount of AIBN (0.2 equiv) were added slowly *via* syringe pump in 2 h to a solution of the corresponding iodide (1.0 equiv) in benzene (0.01 M solution) at 80 °C. After refluxing overnight, benzene was evaporated and the crude mixture was purified by flash chromatography (hexane).

(*Z*)-1-*tert*-Butyldimethylsilyloxy-2-phenylmethylenecyclopentane (*Z*-54): Following the General Procedure, from the iodide **52** (250 mg, 0.60 mmol) the compound **(*Z*)-54** (55 mg, 32% yield) was obtained as an oil: FT-IR (CCl_4) 3075, 3030, 2951, 2853, 1493, 1469, 1358, 1252, 1066, 1039 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (m, 2 H, aromatics), 7.28 (m, 2 H, aromatics), 7.18 (m, 1 H, aromatics), 6.40 (br s, 1 H, HC=C), 4.79 [m, 1 H, C(OSi)H], 2.68 (m, 1 H), 2.35 (m, 1 H), 1.88 (m, 2 H), 1.68 (m, 2 H), 0.87 [s, 9 H, C(CH_3)$_3$], 0.07 (s, 3 H, CH_3), 0.06 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7 (*C*=CH), 138.0, 128.4, 128.0, 126.3 (aromatics), 124.4 (C=*C*H), 72.1 [C(OSi)H], 36.9 (CH_2), 32.4 (CH_2), 25.9 [C(CH_3)$_3$], 21.6 (CH_2), 18.1 [C(CH_3)$_3$], -3.6 (CH_3), -4.3 (CH_3); MS *m/z* 231 (M^+ – 57, 9), 189 (2), 155 (6), 129 (10), 115 (9), 75 (100). HRMS calcd. for $C_{14}H_{19}OSi$ 231.1205, found 231.1212.

Ethyl (*Z*)-(2-*tert*-butyldimethylsilyloxycyclopentylidene)acetate (*Z*-65): Following the General Procedure, from the iodide **64** (200 mg, 0.49 mmol) in benzene (0.07 M solution), the compound **(*Z*)-65** (55 mg, 40% yield) was obtained as an oil: FT-IR (CCl_4) 2955, 2929, 2892, 2858, 1719, 1665, 1471, 1463, 1370, 1249, 1098 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.73 (s, 1 H, HC=C) , 5.39 [br s, 1 H, C(OSi)H], 4.14 (q, 2 H, $CO_2CH_2CH_3$), 2.70-1.60 (m, 6 H), 1.27 (t, 3 H, $CO_2CH_2CH_3$), 0.84 [s, 9 H, C(CH_3)$_3$], 0.13 (s, 3 H, CH_3), 0.05 (s, 3 H, CH_3); MS *m/z* 227 (M^+ – 57, 18), 199 (8), 181 (7), 137 (9), 107 (27), 75 (100).

General Procedure for Desilylation: The iodosilane (1.0 equiv) was dissolved in dry THF, and TBAF (1.0 M in THF, 1.5 equiv) was added dropwise. The reaction was stirred at room temperature until completion and water was added. After extraction with ether, the organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated. Purification by flash chromatography (hexane/ethyl acetate, 4:1) afforded the corresponding alcohol.

(*E*)-2-Benzylidenecyclopentanol (*E*-42): Following the General procedure, after stirring overnight, from the iodosilane **(*E*)-38** (120 mg, 0.27 mmol) the alcohol **(*E*)-42** (42 mg, 88% yield) was obtained as a solid; mp 82-84°C (lit.[30] mp 83°C); ^1H NMR (300 MHz, CDCl3) δ 7.36 (m, 4 H, aromatics), 7.23 (m, 1 H, aromatics), 6.57 (s, 1 H, HC=C), 4.59 [t, 1 H, C(OH)H], 2.77-2.52 (m, 2 H), 1.96 (m, 2 H), 1.70 (m, 2 H), 1.63 (br s, 1 H, OH);^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7 (*C*=CH), 137.7, 128.3, 128.3, 126.5 (aromatics), 123.6 (C=CH), 77.3 [C(OH)H], 34.8 (CH_2), 29.3 (CH_2), 22.5 (CH_2); MS *m/z* 174 (M^+, 98), 156 (16), 145 (41), 128 (34), 115 (66), 91 (100), 83 (36); HRMS calcd. for $C_{12}H_{14}O$ 174.1044, found 174.1052.

(*E*)-1-Methyl-2-phenylmethylenecyclopentanol (*E*-43): Following the General Procedure, after stirring for 6 h, from the iodosilane **(*E*)-39** (88 mg, 0.19 mmol) the alcohol **(*E*)-43** (27 mg, 73% yield) was obtained as an oil: FT-IR (CCl_4) 3400-3200 (br), 2949, 2865, 1498, 1450, 1377, 1163, 1107, 1047 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (m, 4 H, aromatics), 7.21 (m, 1 H, aromatics), 6.53 (m, 1 H, J = 2.5 Hz, HC=C), 2.79-2.57 (m, 2 H), 1.89-1.66 (m, 5 H), 1.46 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.9 (CH=*C*), 137.8, 128.4, 128.2, 126.4 (aromatics), 121.3 (*C*H=C), 80.1 [C(OH)], 41.4 (CH_2), 30.2 (CH_2), 22.2 (CH_2), 20.2 (CH_3); MS *m/z* 188 (M^+, 49), 171 (25), 159 (18), 141 (18), 128 (31), 115 (91), 105 (57), 91 (100), 77 (65), 63 (21); HRMS calcd. for $C_{13}H_{16}O$ 188.1201, found 188.1198.

(*E*)-2-Benzylidenecyclohexanol (*E*-44): Following the General procedure, after stirring overnight, from the iodosilane **(*E*)-41** (150 mg, 0.33 mmol) the alcohol **(*E*)-44** (49 mg, 50% yield) was obtained as a solid; mp 62-64°C (lit.[31b] mp 62.5-63.5°C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.22 (m, 5 H, aromatics), 6.54 (s, 1 H, HC=C), 4.26 [m, 1 H, C(OH)H], 2.76 (m, 1 H), 2.20-1.30 (m, 8 H);^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3, 137.6, 128.9, 128.0, 126.2 (*C*=CH, aromatics), 120.7 (C=*C*H), 73.7 [C(OH)H], 36.5 (CH_2), 27.3 (CH_2), 26.9 (CH_2), 23.1 (CH_2); MS *m/z* 188 (M^+, 92), 170 (10), 159 (58), 145 (50), 131 (63), 115 (74), 91 (100), 77 (44); HRMS calcd. for $C_{13}H_{16}O$ 188.1201, found 188.1203.

(*E*)-3-(Phenylmethylene)hexahydro-1*H*-pentalen[3a]ol (*E*-51): Following the General Procedure, after stirring for 2 h, from the iodosilane **(*E*)-50** (40 mg, 0.08 mmol) the alcohol **(*E*)-51** (15 mg, 82% yield) was obtained as an oil: FT-IR (CCl_4) 3530-3369 (br), 3065, 3025, 2945, 2895, 2859, 1650, 1610, 1472, 1449, 1370, 1060; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, 4 H, aromatics), 7.21 (m, 1 H, aromatics), 6.56 (m, 1 H, *J* = 2.4 Hz, HC=C), 2.14-1.43 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.5 (*C*=CH), 137.9, 128.5, 128.2, 126.4 (aromatics), 121.7 (C=*C*H), 92.0 [C(OH)], 51.4 (CH), 40.7 (CH_2), 31.4 (CH_2), 30.3 (CH_2), 29.9 (CH_2), 25.2 (CH_2); MS *m/z* 214 (M^+, 2), 196 (27), 167 (21), 153 (8), 128 (7), 115 (17), 91 (26), 77 (15); HRMS calcd. for $C_{15}H_{18}O$ 214.1357, found 214.1367.

(*E*)-2-(2-Methoxyethylidene)-cyclopentanol (*E*-61): Following the General procedure, from the iodosilane **(*E*)-58** (100 mg, 0.24 mmol) the alcohol **(*E*)-61**[36] (30 mg, 86% yield) was obtained as an oil: IR (CCl_4) 3400, 2958, 2928, 2872, 2822, 1451, 1431, 1382, 1097 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69 (m, 1 H, HC=C), 4.43 [m, 1 H, C(OH)H], 3.95 (dd, 2 H, *J* = 6.6 and 0.9 Hz, C*H*$_2$OCH$_3$), 3.35 (s, 3 H, OCH_3), 2.51-2.22 (m, 2 H), 2.00-1.80 (m, 2 H), 1.75-1.55 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.6 (*C*=CH), 119.8 (C=*C*H), 75.5 [C(OH)H], 70.0 (*C*H$_2$OCH$_3$), 58.1 (OCH_3), 35.2 (CH_2), 26.9 (CH_2), 21.7 (CH_2); MS *m/z* 124 (M^+ – 18, 7), 110 (41), 97 (100), 82 (47), 79 (36), 67 (82); HRMS calcd. for $C_8H_{12}O$ (M^+ – 18) 124.0888, found 124.0885.

(*E*)-Ethyl (2-hydroxycyclopentylidene)acetate (*E*-62): Following the General procedure, from the iodosilane **(*E*)-60** (120 mg, 0.27 mmol) the alcohol **(*E*)-62**[37] (39 mg, 85% yield) was obtained as an oil: IR (CCl_4) 3430 (br), 2962, 2932, 2873, 2855, 1712, 1662, 1466, 1452, 1416, 1371, 1348, 1202, 1140, 1034 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$) δ 5.96 (m, 1 H, *J* = 2.4 Hz, HC=C), 4.50 [m, 1 H, C(OH)H], 4.16 (q, 2 H, $CO_2CH_2CH_3$), 2.95-2.70 (m, 2 H), 2.12-1.03 (m, 5 H), 1.27 (t, 3 H, $CO_2CH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.7, 166.9 (CO_2Et, *C*=CH), 113.2 (C=*C*H), 76.3 [C(OH)H], 59.8 ($CO_2CH_2CH_3$), 34.6 (CH_2), 30.2 (CH_2), 21.1 (CH_2), 14.3 (CH_3); MS *m/z* 170 (M^+, 15), 152 (62), 141 (22), 124 (78), 114 (100), 107 (12), 97 (43), 86 (67), 79 (49), 68 (60); HRMS calcd. for $C_9H_{14}O_3$ 170.0943, found 170.0946. **(*Z*)-2-Benzylidenecyclopentanol (*Z*-42):** Following the General procedure, after stirring overnight, from the compound **(*Z*)-54** (50 mg, 0.17 mmol) the alcohol **(*Z*)-42** (26 mg, 87% yield) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (m, 2 H, aromatics), 7.34 (m, 2 H, aromatics), 7.22 (m, 1 H, aromatics), 6.49 (br s, 1 H, HC=C), 4.86 [br s, 1 H, C(OH)H], 2.65 (m, 1 H), 2.40 (m, 1 H), 1.95-1.56 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.0 (*C*=CH), 137.1, 128.5, 128.2, 126.8 (aromatics), 125.7 (C=*C*H), 71.5 [C(OH)H], 36.9 (CH_2), 33.2 (CH_2), 22.1 (CH_2); MS *m/z* 174 (M^+, 93), 156 (17), 145 (38), 128 (30), 115 (58), 91 (100), 83 (33); HRMS calcd. for $C_{12}H_{14}O$ 174.1044, found 174.1058.

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