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Triflimide-Catalysed Rearrangement of *N*-(1-Trimethylsilyl)allylhydrazones Results in the Formation of Vinylsilanes and Cyclopropanes

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A synthesis of terminal vinylsilanes by triflimide-catalysed rearrangement of *N*-(1-trimethylsilyl)allylhydrazones is reported. This protocol provides a convenient access to versatile olefinic building blocks through a traceless bond construction. Hydrazones derived from aromatic aldehydes give *cis*-cyclopropanes in an unexpected side-reaction.

Introduction

The [3,3]-sigmatropic rearrangement is a powerful tool for the construction of carbon–carbon bonds, and it has been used many times in organic synthesis.[1] The Stevens rearrangement of *N*-allylhydrazones leads to a new carbon–carbon bond with loss of dinitrogen, but due to the very high temperatures required (up to 300 °C), this reaction is limited in its applications.[2] Thomson and coworkers made significant improvements in 2010 when they introduced two modifications: the stability of the reaction substrates was greatly enhanced by using *N*-Boc-*N*-allylhydrazones (**A**; Boc = *tert*-butoxycarbonyl); and by using catalytic amounts (10 mol-%) of the Brønsted acid triflimide ($HNTf_2$) to trigger the rearrangement, the reaction temperature could be lowered to 125 °C.[3] Numerous olefins with vicinal disubstitution (**B**) were obtained using this "traceless bond construction" protocol by Thomson, and recently our group extended this approach to the synthesis of geminally disubstituted olefins (Figure 1).[4] Thomson[5] and Tantillo[6] have also described and calculated related rearrangements under different reaction conditions.

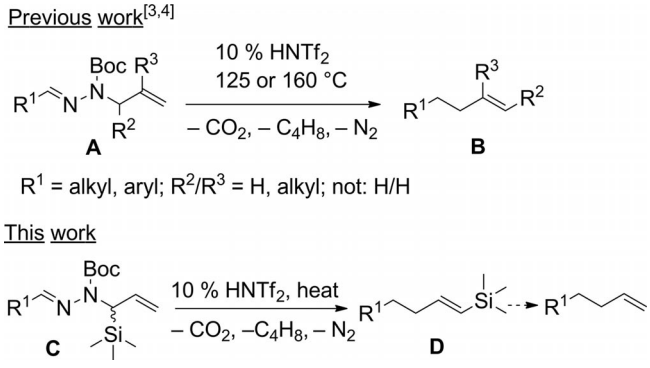
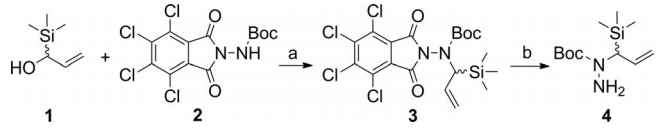


Figure 1. Olefin synthesis through "traceless bond construction" starting from Boc-protected *N*-allylhydrazones.

However, this method is not applicable to the synthesis of terminal monosubstituted olefins ($R^2 = R^3 = H$). To remedy this shortcoming, we planned to substitute one proton in the newly generated olefinic group with an easily removable, but also stable functional group.

Results and Discussion

The required hydrazine building block (i.e., **4**) was prepared starting from known 1-(trimethylsilyl)allyl alcohol (**1**) [7] by coupling with easily available *tert*-butyl 4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-ylcarbamate (**2**) under Mitsunobu conditions, followed by removal of the tetrachlorophthalimide protective group under standard conditions (Scheme 1).[8] The structure of intermediate **3** was confirmed by X-ray crystallography.



Scheme 1. Synthesis of hydrazine **4**. a) PPh_3, DIAD (diisopropyl azodicarboxylate), THF, 0 °C to room temp., 16 h, 77%. b) 1,2-ethylenediamine, THF, 50 °C, 30 min, 97%.

The subsequent condensations of **4** with various aldehydes gave the required hydrazones (i.e., **5a**–**5q**) in very high, up to quantitative, yields. The choice of an appropriate reaction temperature is a crucial factor in triflimide-catalysed [3,3]-sigmatropic rearrangements, and this is heavily dependent on the structure of the hydrazine building block used.[9] We first determined the optimum temperature for model hydrazone **5a** (R = cyclohexyl). Surprisingly, the best results were obtained at relatively low temperature (100 °C

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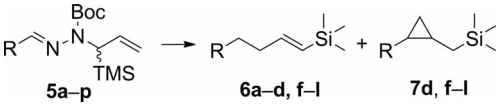
for 1 h). At 125 °C (for 1 h), the yield dropped, presumably due to decomposition of the product. We went on to investigate alternative solvents (1,4-dioxane, THF), but we found that anhydrous diglyme gave the best results. Varying amounts of the starting materials were recovered under the optimized conditions.

Hydrazones **5a**–**5c** derived from aliphatic aldehydes gave the desired vinylsilanes (i.e., **6a**–**6c**) with yields ranging from 28 to 65%; these products had an *E* configuration predominantly (*E*/*Z* ratios >20:1, determined by ^{1}H NMR spectroscopy; Scheme 2, Table 1).



Scheme 2. Products of the triflimide-catalysed rearrangements of *N*-Boc-*N*-allylhydrazones **5a**–**5p**. For residues R, see Table 1. Reaction conditions: $HNTf_2$ (10 mol-%), diglyme, 100 °C, 1 h. TMS = trimethylsilyl.

Table 1. Products obtained from rearrangement [using triflimide (10 mol-%), 100 °C for 1 h] of *N*-Boc-hydrazones **5a**–**5p**. For general structures, see Scheme 2.

Starting material	Product(s)	Yield [%]	Product ratio[a]
5a R = cyclohexyl	**6a**	65	*E*/*Z* > 22:1
5b R = 2-(phenyl)ethyl	**6b**	28	*E*/*Z* > 20:1
5c R = nonyl	**6c**	40	*E*/*Z* > 22:1
5d R = phenyl	**6d** and **7d**	13[b]	**6d/7d** = 1:9.3
5e R = 4-hydroxyphenyl	–	0	–
5f R = 3-hydroxyphenyl	**6f** and **7f**	39	**6f/7f** = 23:1
5g R = 4-cyanophenyl	**6g** and	40	**6g/7g** = 1:2.8
5h R = 3-cyanophenyl	**6h** and **7h**	18	**6h/7h** = 1:10
5i R = 4-bromophenyl	**6i** and **7i**	36	**6i/7i** = 1.1:1
5j R = 3-bromophenyl	**6j** and **7j**	21	**6j/7j** = 1:1.2
5k R = 3-methoxyphenyl	**6k** and **7k**	28	**6k/7k** = 12:1
5l R = 3-(trifluoromethyl)phenyl	**6l** and **7l**	22	**6l/7l** = 1:5
5m R = 4-(methoxycarbonyl)phenyl	–	(traces)	–
5n R = 4-nitrophenyl	–	0	–
5o R = 3-indolyl	–	0	–
5p R = ethoxycarbonyl	–	0	–

[a] *E*/*Z* ratios of vinylsilanes **6**, or ratio vinylsilane **6**/cyclopropane **7**. [b] Yield diminished due to the volatility of the product.

Some unexpected results were obtained in the rearrangements of hydrazones **5d**–**5n**, derived from substituted benzaldehydes, yields of successful rearrangements ranged from 18 to 40%, but hydrazones **5e**, **5m**, and **5n** did not give identifiable products. The outcome of these reactions was obviously strongly dependent on the electronic properties of the substituents on the phenyl ring. Some analogues bearing electron-donating functional groups (3-hydroxy **5f**, 3-methoxy **5k**) underwent smooth rearrangement, but the 4-hydroxyphenyl compound (i.e., **5e**) did not give any vinylsilane. For this latter compound, we hypothesize that the hydroxy group in the *para* position stabilizes the intermediate protonated hydrazone cation, and that the resulting mesomeric system does not undergo rearrangement.

In contrast, the *meta*-hydroxy analogue (i.e., **5f**) cannot show this type of stabilization, so vinylsilane **6f** was formed in an acceptable yield (39%).

With 4-nitro precursor **5n**, we did not observe any rearrangement. Probably the very strong electron-withdrawing effect of the nitro group prevents *N*-protonation of the hydrazone by triflimide. The typical change in colour of the solution, indicative of the initial *N*-protonation, was not observed in this experiment. Aldehyde hydrazones bearing acid-labile substituents (nitriles **5g** and **5h**, methoxy compound **5k**, ester **5m**, and indole **5o**) showed significant decomposition under the reaction conditions.

Although the aliphatic hydrazones (i.e., **5a**–**5c**) gave *E*-configured vinylsilanes containing minor amounts of the *Z* isomers, the aromatic rearrangement products were obtained as pure *E* isomers (see Table 1).

An unexpected side-reaction was observed with hydrazones derived from substituted benzaldehydes. The vinylsilane products contained cyclopropanes **7** (Scheme 2) as a new type of poorly separable by-product (<10% for products containing electron-rich phenyl rings **6f** and **6k**, but significant amounts for electron-poor products). In the rearrangements of hydrazones **5g**, **5h**, and **5l**, bearing cyano and trifluoromethyl groups, the cyclopropanes were formed as the major products. Careful reinvestigation of the NMR spectra of aliphatic vinylsilanes **6a**–**6c** confirmed that this side-reaction is exclusive to the aromatic series.

The relevant peaks of cyclopropanes **7** were clearly separated, due to their typical high-field shifts (δ = 2.1 ppm for benzylic protons, 1.2 to 1.0 and about 0.6 ppm for the others),[10] from the peaks of the vinylsilanes in the ^{1}H NMR spectra. Thus, the structures of the cyclopropanes could be solved unambiguously by NMR spectroscopic analysis (DEPT, HMQC, and HMBC experiments) of the product mixtures. The vinylsilane/cyclopropane ratios were determined by ^{1}H NMR spectroscopy, and ranged from 23:1 (**6f/7f**) to 1:10 (**6h/7h**). For the benzylic proton of the arylcyclopropane products, we always found almost identical coupling constants, with ^3J = 8.6, 8.6, and 6.0 Hz. Typical values resulting from ^3J coupling with the neighbouring methylene protons in cyclopropanes are about 8.6 and 6.0 Hz.[10a] The second 8.6 Hz coupling constant can be attributed to a coupling with the other methine proton in the 1,2-disubstituted cyclopropane rings, as this is known to be a typical value for *cis* stereochemistry. Since we did not observe the other cyclopropane isomer in any of the spectra, this side-reaction can be described as diastereoselective, giving the *cis* cyclopropanes only.

Another side-reaction was observed with the cinnamaldehyde hydrazone (i.e., **5q**) (Figure 2). With this substrate, the rearrangement did not give the expected 1,5-diene structure, but diene **6q**, bearing three nonconjugated π systems, was obtained in very low yield (10%). In contrast to our previous experiments on triflimide-catalysed rearrangements of cinnamaldehyde hydrazones, we did not observe the formation of a pyrazoline with this hydrazone.[4] We speculate that after successful triflimide-catalysed rearrangement and cleavage of the *N*-Boc group, the elimination of dinitrogen takes place through an allylic diazene rearrangement (ADR) to give the *E*-configured internal olefin (Figure 2).[11] The vinylsilane residue was formed as a >15:1 *E*/*Z* mixture. But we cannot exclude an alternative pathway in which a styrylcyclopropane is formed first, followed by an acid-catalysed retro-ene reaction.[12] A thermal retro-ene reaction can be excluded, since this would give a *Z*-configured internal olefin.[13]

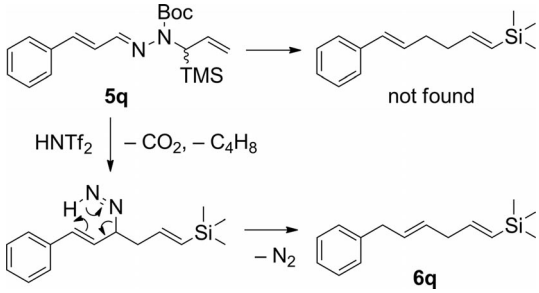


Figure 2. Rearrangement of cinnamaldehyde hydrazone **5q** with double-bond migration.

Since the reaction conditions [triflimide (10 mol-%), 100 °C, 1 h] that had been optimized with an aliphatic hydrazone (**5a**; R = cyclohexyl) gave (partial) decomposition with acid-labile substrates on the one hand, and formation of vinylsilane/cyclopropane mixtures on the other, we tested some variations of the reaction conditions to try to improve the yield and/or modify the product ratios (Table 2). We found that the yield of acid-sensitive methoxy compound **6k** could be enhanced from 28 to 51% by shortening the reaction time to 10 min. The relative amount of the cyclopropane by-product (i.e., **7k**) was almost unchanged. Surprisingly, the rearrangement of the cinnamaldehyde hydrazone (i.e., **5q**) could be significantly improved (yield rising from 10 to 49%) by slightly increasing the amount of acid, increasing the reaction temperature, and shortening the reaction time. Once again, only the 1,4-diene (i.e., **6q**; Figure 2) was formed.

Table 2. Rearrangement results with different reaction parameters; differences from standard conditions are underlined.

Starting material	Temp. [°C]	Catalyst amount [mol-%]	Time [min]	Yield [%]	Ratio of products
5k	100	10	10	51	**6k/7k** = 16:1
5q	125	30	10	49	**6q**, *E*/*Z* > 15:1
5i	100	0	60	0[a]	–
5i	100	30	10	38	**6i/7i/8** = 3.8:1:0.8
5i	160	10	5	30	**6i/7i** = 1:1[b]
5i	160	100	4	28	**6i/7i/8** = 12.7:1:6.3

[a] 91% starting material recovered. [b] Numerous side-products formed.

The influence of the reaction conditions on the vinylsilane/cyclopropane ratio was examined, using hydrazone **5i** (R = 4-bromophenyl) (Table 2) as a test compound, since this substrate gave an almost 1:1 mixture (36% yield) under the standard conditions (Table 1). A slightly lower yield (30%) was obtained at a higher reaction temperature (160 °C) with a dramatically shorter reaction time (5 min); no difference in the product ratio was found, but the formation of numerous by-products complicated the work-up. Increasing the amount of triflimide from 10 mol-% to 30 or 100 mol-% led to an increase of the vinylsilane/cyclopropane ratio in the product mixture, and the products were also contaminated with significant amounts of a new by-product **8** (Figure 3). Compound **8** obviously arises from protodesilylation of vinylsilane **6i**. In an acid-free control experiment (diglyme, 100 °C) no rearrangement or cyclopropane formation was observed.

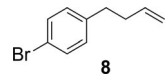


Figure 3. Desilylated by-product product **8** (see Table 2) formed when higher amounts of acid were used for the rearrangement of hydrazone **5i**.

The results shown in Table 2 demonstrate that the outcome of the rearrangements can be improved by tedious optimization of the reaction conditions for the individual substrates.

Thus, we can conclude that acid is necessary for cyclopropane formation, but that higher amounts of acid lower the yields of this by-product, and changing the reaction temperature has no significant effect. The substituents on the phenyl ring and the TMS group that is present in our compounds, but not in those investigated previously, have a major influence on the reaction outcome.

Thomson and Tantillo calculated that the free-energy barrier for the rearrangement of aliphatic hydrazones should be lower than that for aromatic derivatives, and stated that this may be the result of the decrease in conjugation during the rearrangement.[9] Our various results for the aliphatic and aromatic compounds are in accordance with these calculations. We suppose that for the aromatic derivatives, the hydrazone cation that is initially formed in the protonation step undergoes a stabilization reaction instead of the [3,3]sigmatropic rearrangement (Figure 4). The outcome of the reaction is heavily dependent on the substituents on the phenyl ring, and this pathway was found to be most prevalent when cyano and trifluoromethyl substituents were present in the *meta* position. The highest relative amounts of cyclopropanes were found for these examples. TMS groups are known for their ability to stabilize cations in the β position by hyperconjugation.[14] For the hyperconjugation to take place, the empty orbital has to be parallel to the TMS group. Probably, this orientation determines the observed stereoselectivity of the reaction. In the next step,

bicyclic cation **E** is formed. A similar structure was already calculated by Thomson and Tantillo as a possible intermediate in the rearrangement.[9] For the next step, we suggest the formation of a 1-pyrazoline. It is known that these compounds undergo thermal decomposition to give cyclopropanes, the observed reaction products.[15] When higher amounts of acid were used, less cyclopropane formation was observed, and we think that this is the result of an increased cleavage of the *N*-Boc group. As a result, the sp^3-hybridized nitrogen next to the TMS group can be protonated, and the rearrangement to the vinyl silane takes place.[9]

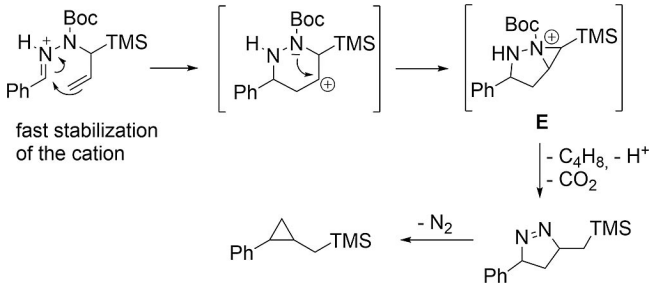


Figure 4. Proposed mechanism for *cis*-cyclopropane formation.

Conclusions

In conclusion, we have developed an extension of Thomson's protocol for the triflimide-catalysed Stevens rearrangement of *N*-Boc-*N*-allylhydrazones. This method opens a new route to terminal vinylsilanes through a traceless bond construction approach. The resulting vinylsilanes should be versatile building blocks for the synthesis of diversely substituted olefins. Moreover, we detected two unprecedented side-reactions, leading to *cis*-cyclopropanes from benzaldehyde hydrazones, and deconjugated double bonds from a cinnamaldehyde hydrazone.

Experimental Section

General Information: All chemicals were purchased at high grade, and were used without further purification. Bis(trifluoromethane)-sulfonimide ("triflimide") was purchased as colourless crystals in 1 g quantities. Diglyme was purchased in 100 mL quantities as 99+% extra-dry solvent packaged under nitrogen in a septum-sealed bottle, and was used as supplied. All reaction flasks were dried in a WTC Binder drying oven for at least 2 h at 200 °C. Thin-layer chromatography was carried out on Polygram Sil G/UV_{254} from Machery-Nagel. Plates were visualized using UV light (254 nm), phosphomolybdic acid hydrate (10 wt.-% in 99% ethanol) spray, and Ehrlich's reagent. Flash column chromatography was carried out with pentane and diethyl ether, using Geduran Si 60 (Merck) silica gel. Melting points were determined using a Büchi B-540 melting-point apparatus. Every substance (or product mixture) was fully characterized by nuclear magnetic resonance spectroscopy, including ^{1}H, ^{13}C, DEPT, COSY, HSQC, and HMBC spectra, recorded with JEOL J NMR-GX 500 (500 MHz), Bruker BioSpin Avance III HD (400 MHz), and Bruker BioSpin Avance III HD (500 MHz) instruments. Unless otherwise stated, spectra were recorded at ambient temperature (298 K), using $CDCl_3$ as solvent. Chemical shifts (δ) are quoted in ppm, and spectra were calibrated using solvent signals [$CHCl_3$: δ = 7.26 ppm (^{1}H NMR) and δ = 77.16 ppm (^{13}C NMR)]. Coupling constants (^2J, ^3J, ^4J) are given with numbers indicating the number of bonds between the coupling nuclei. Multiplicities are abbreviated as: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br. s = broad singlet; dd = doublet of doublets; dt = doublet of triplets, and so on. Infrared spectra were recorded with a Perkin–Elmer Paragon 1000 spectrometer using KBr pellets. High-resolution mass spectra (HRMS) were recorded with a JEOL GCmate instrument in EI mode, and with Finnigan MAT95 and MAT90 instruments operating in EI and ESI modes. The crystal structure was recorded and calculated with an Oxford XCalibur diffractometer by Dr. Peter Mayer.

***N*-*tert*-Butyloxycarbonylamino-*N*-(2-trimethylsilylprop-2-en-1-yl)-4,5,6,7-tetrachlorophthalimide (3):** DIAD (650 μL, 3.21 mmol) was added to a solution of PPh_3 (900 mg, 3.43 mmol) in THF (12 mL) at 0 °C. After a white solid had formed, *tert*-butyl *N*-(4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl) carbamate (**2**; 1.2 g, 3.0 mmol) and a solution of 1-(trimethylsilyl)prop-2-en-1-ol (**1**; 500 mg, 3.83 mmol) in THF (3 mL) were added. The mixture was stirred at room temperature for 3 h, during which time the colour changed to dark green. The solvent was then evaporated, and the residue was purified by flash chromatography (pentane/diethyl ether, 9.5:0.5) to give **3** (1.19 g, 2.32 mmol, 77%) as a white solid. R_f = 0.50 (pentane/diethyl ether, 9.5:0.5), m.p. 170–171 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 323 K): δ = 5.98 (ddd, ^3J = 16.7, 9.9 Hz, 1 H, HC=C), 5.25–4.84 (m, 2 H, C=CH_2), 3.47 (s, 1 H, HCSi), 1.37 (s, 9 H, CCH_3), 0.16 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 323 K): δ = 160.9 (CC=O), 152.8 (OC=O), 141.0 (CCl), 135.0 (H*C*=CH_2), 130.5 (CCl), 125.9 (*C*CCl), 114.8 (C=*C*H_2), 82.7 (*C*CH_3), 59.9 (HCSi), 28.2 (C*C*H_3), –1.5 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 2979, 1798, 1749, 1721, 1371, 1247, 1146, 913, 846 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{15}Cl_4N_2O_2Si$ [M – $C_5H_7O_2$]$^+$ 412.9627; found 412.9624.

To obtain crystals for the crystal structure, the compound was heated in isohexane to reflux, and chloroform was added dropwise through the reflux condenser until the sample was dissolved. This mixture was then cooled, and stored in the fridge for several days, after which slightly yellow crystals were obtained.

CCDC-1055944 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

***tert*-Butyl 1-(2-Trimethylsilylprop-2-en-1-yl)hydrazinecarboxylate (4):** Compound **3** (800 mg, 1.56 mmol) was dissolved in THF (5 mL), and ethylenediamine (150 μL, 135 mg, 2.25 mmol, 1.44 equiv.) was added at 50 °C. The solution was stirred for 30 min at 50 °C. The mixture was cooled to room temperature, then isohexane was added, and the mixture was filtered. The filtrate was collected, and the solvent was removed with a rotary evaporator. The resulting residue was purified by gradient flash chromatography (pentane/diethyl ether, 9.5:0.5 to 8:2) to give **4** (370 mg, 1.51 mmol, 97%) as a pale yellow oil. R_f = 0.15 (pentane/diethyl ether, 9.5:0.5). ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 5.86 (ddd, ^3J = 17.1, 10.5, 6.5 Hz, 1 H, HC=C), 4.91 (d, ^3J = 10.5 Hz, 1 H, C=CH_2), 4.83 (d, ^3J = 17.2 Hz, 1 H, C=CH_2), 4.54 (s, 2 H, NH_2), 3.92 (s, 1 H, HCSi), 1.38 (s, 9 H, CCH_3), 0.05 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (125 MHz, [D_6]DMSO): δ = 157.2 (OC=O), 136.48 (H*C*=CH_2), 110.7 (C=*C*H_2), 78.8 (*C*CH_3), 56.8 (HCSi), 28.1 (C*C*H_3), –1.8 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 3329, 2977, 1690, 1630, 1367,

1247, 1170, 842 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{25}N_2O_2Si$ [M + H]$^+$ 245.1685; found 245.1681.

General Procedure for the Synthesis of the Hydrazones: The required aldehyde and hydrazine **4** were stirred in anhydrous ethanol (1.5 mL per mmol aldehyde) at room temperature until TLC showed that the conversion was complete. The ethanol was evaporated, and the residue was purified by flash chromatography with a mixture of pentane and diethyl ether as eluent to give the hydrazone.

***tert*-Butyl 2-(Cyclohexylmethylene)-1-[3-(trimethylsilyl)prop-1-en-3-yl]hydrazinecarboxylate (5a):** Cyclohexanecarbaldehyde (80 mg, 0.71 mmol) and **4** (220 mg, 0.90 mmol) gave **5a** (241 mg, 0.71 mmol, 100%) as a colourless oil. R_f = 0.56 (pentane/diethyl ether, 9.5:0.5). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (br. s, 1 H, N=CH), 5.83 (ddd, ^3J = 17.1, 10.5, 6.6 Hz, 1 H, HC=C), 4.95 (d, ^3J = 10.5 Hz, 1 H, C=CH_2), 4.85 (d, ^3J = 17.3 Hz, 1 H, C=CH_2), 4.11 (d, ^3J = 6.7 Hz, 1 H, HCSi), 2.30–2.20 (m, 1 H, CH), 1.88–1.79 (m, 2 H, CH_2), 1.80–1.72 (m, 2 H, CH_2), 1.70–1.63 (m, 1 H, CH_2), 1.46 (s, 9 H, CCH_3), 1.38–1.14 (m, 5 H, CH_2), 0.08 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.9 (N=CH), 154.0 (OC=O), 135.7 (H*C*=CH_2), 111.7 (C=*C*H_2), 80.7 (*C*CH_3), 56.3 (HCSi), 41.8 (CH), 30.3 (CH_2), 28.5 (C*C*H_3), 26.2 (CH_2), 25.7 (CH_2), –1.3 (Si*C*H_3) ppm. IR: $\tilde{\nu}$ = 2977, 2929, 2854, 1697, 1630, 1366, 1247, 842 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{34}N_2NaO_2Si$ [M + Na]$^+$ 361.2287; found 361.2283.

***tert*-Butyl 2-(3-Phenylprop-1-ylidene)-1-[3-(trimethylsilyl)prop-1-en-3-yl]hydrazinecarboxylate (5b):** Hydrocinnamaldehyde (95% purity; 94 mg, 0.66 mmol) and **4** (240 mg, 0.98 mmol) gave **5b** (206 mg, 0.57 mmol, 86%) as a colourless oil. R_f = 0.58 (pentane/diethyl ether, 9.5:0.5). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88 (br. s, 1 H, N=CH), 7.35–7.24 (m, 2 H, CH), 7.26–7.10 (m, 3 H, CH), 5.79 (ddd, ^3J = 17.1, 10.5, 6.5 Hz, 1 H, HC=C), 4.94 (ddd, ^3J = 10.5, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH_2), 4.81 (ddd, ^3J = 17.2, ^2J = 1.6, ^4J = 1.6 Hz, 1 H, C=CH_2), 4.04 (d, ^3J = 6.5 Hz, 1 H, HCSi), 2.86 (t, ^3J = 7.1 Hz, 2 H, CH_2), 2.61 (td, ^3J = 7.0, 6.0 Hz, 2 H, CH_2), 1.48 (s, 9 H, CCH_3), 0.06 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.0 (N=CH), 153.2 (OC=O), 141.3 (C), 135.4 (H*C*=C), 128.6 (CH), 128.5 (CH), 126.2 (CH), 111.8 (C=*C*H_2), 81.0 (*C*CH_3), 56.2 (HCSi), 35.3 (HC*C*H_2), 33.0 (C*C*H_2), 28.5 (C*C*H_3), –1.3 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 2977, 2953, 1696, 1630, 1366, 1283, 1247, 1168, 1147, 900, 842 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{25}N_2O_2Si$ [M – C_4H_7]$^+$ 305.1680; found 305.1680.

***tert*-Butyl 2-Decylidene-1-[3-(trimethylsilyl)prop-1-en-3-yl]-hydrazinecarboxylate (5c):** Decanal (109 mg, 0.70 mmol) and **4** (240 mg, 0.98 mmol) gave **3c** (230 mg, 0.60 mmol, 86%) as a colourless oil. R_f = 0.59 (pentane/diethyl ether, 9.5:0.5). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84 (br. s, 1 H, N=CH), 5.83 (ddd, ^3J = 17.1, 10.5, 6.6 Hz, 1 H, HC=C), 4.95 (ddd, ^3J = 10.5, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH_2), 4.84 (ddd, ^3J = 17.1, ^2J = 1.7, ^4J = 1.7 Hz, 1 H, C=CH_2), 4.07 (ddd, ^3J = 6.6, 1.6 Hz, 1 H, HCSi), 2.27 (td, ^3J = 7.5, 5.5 Hz, 2 H, NCCH_2), 1.56–1.40 (m, 11 H, CCH_3, CH_2), 1.41–1.13 (m, 12 H, CH_2), 0.88 (t, ^3J = 6.9 Hz, 3 H, CH_3), 0.08 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.9 (N=CH), 154.0 (OC=O), 135.6 (H*C*=C), 111.7 (C=*C*H_2), 80.8 (*C*CH_3), 56.4 (HCSi), 33.5 (NC*C*H_2), 32.0 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 28.5 (CH_2), 26.7 (CH_2), 22.8 (CH_2), 14.3 (CH_3), –1.3 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 2955, 2926, 2856, 1697, 1630, 1366, 1282, 1247, 1151, 867, 842 cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{35}N_2O_2Si$ [M – C_4H_7]$^+$ 327.2462; found 327.2462.

***tert*-Butyl 2-(Benzylidene)-1-[3-(trimethylsilyl)prop-1-en-3-yl]-hydrazinecarboxylate (5d):** Benzaldehyde (84 mg, 0.79 mmol) and **4** (220 mg, 0.90 mmol) gave **5d** (263 mg, 0.79 mmol, 100%) as a colourless oil. R_f = 0.59 (pentane/diethyl ether, 9.5:0.5). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.57 (br. s, 1 H, N=CH), 7.81–7.46 (m, 2 H, CH), 7.47–7.28 (m, 3 H, CH), 5.92 (ddd, ^3J = 17.1, 10.5, 6.5 Hz, 1 H, HC=C), 5.00 (ddd, ^3J = 10.5, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH_2), 4.91 (ddd, ^3J = 17.1, ^2J = 1.6, ^4J = 1.6 Hz, 1 H, C=CH_2), 4.22 (ddd, ^3J = 6.5, ^4J = 1.6, 1.6 Hz, 1 H, HCSi), 1.53 (s, 9 H, CCH_3), 0.15 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.9 (OC=O), 147.8 (N=CH), 135.7 (C), 135.3 (H*C*=CH_2), 129.5 (CH), 128.7 (CH), 127.3 (CH), 112.1 (C=*C*H_2), 81.4 (*C*CH_3), 56.5 (HCSi), 28.5 (C*C*H_3), –1.2 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 2977, 1667, 1414, 1367, 1292, 1278, 1249, 1156, 1139, 972, 898, 867, 843, 749, 690 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{23}N_2O_2Si$ [M + H]$^+$ 333.1993; found 333.1995.

***tert*-Butyl 2-(4-Hydroxybenzylidene)-1-[3-(trimethylsilyl)prop-1-en-3-yl]hydrazinecarboxylate (5e):** 4-Hydroxybenzaldehyde (85 mg, 0.70 mmol) and **4** (220 mg, 0.90 mmol) gave **5e** (232 mg, 0.67 mmol, 96%) as a white solid. R_f = 0.41 (pentane/diethyl ether, 6:4), m.p. 81–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (br. s, 1 H, N=CH), 7.56–7.43 (m, 2 H, CH), 6.86–6.75 (m, 2 H, CH), 5.91 (ddd, ^3J = 17.1, 10.5, 6.6 Hz, 1 H, HC=C), 5.69 (s, 1 H, OH), 4.99 (ddd, ^3J = 10.5, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH_2), 4.92 (ddd, ^3J = 17.2, ^2J = 1.6, ^4J = 1.6 Hz, 1 H, C=CH_2), 4.23 (ddd, ^3J = 6.6, ^4J = 1.6, 1.6 Hz, 1 H, HCSi), 1.52 (s, 9 H, CCH_3), 0.13 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4 (COH), 154.1 (OC=O), 151.1 (N=CH), 135.5 (H*C*=C), 129.2 (CH), 128.0 (C), 115.8 (CH), 112.1 (C=*C*H_2), 81.5 (*C*CH_3), 56.6 (HCSi), 28.5 (C*C*H_3), –1.3 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 3355, 2977, 1696, 1655, 1608, 1516, 1368, 1248, 1161, 1147, 903, 840, 755 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{21}N_2O_3Si$ [M – C_4H_7]$^+$ 293.1316; found 293.1315.

***tert*-Butyl 2-(3-Hydroxybenzylidene)-1-[3-(trimethylsilyl)prop-1-en-3-yl]hydrazinecarboxylate (5f):** 3-Hydroxybenzaldehyde (85 mg, 0.70 mmol) and **4** (240 mg, 0.98 mmol) gave **5f** (229 mg, 0.66 mmol, 94%) as a colourless oil. R_f = 0.52 (pentane/diethyl ether, 6:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (br. s, 1 H, N=CH), 7.22 (dd, ^3J = 8.0 Hz, 1 H, CH), 7.18–7.12 (m, 2 H, CH), 6.82 (ddd, ^3J = 7.9, ^4J = 2.5, 1.3 Hz, 1 H, CH), 5.90 (ddd, ^3J = 17.0, 10.5, 6.5 Hz, 1 H, HC=C), 5.44 (s, 1 H, OH), 5.00 (ddd, ^3J = 10.5, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH_2), 4.90 (ddd, ^3J = 17.2, ^2J = 1.6, ^4J = 1.6 Hz, 1 H, C=CH_2), 4.23 (ddd, ^3J = 6.5, ^4J = 1.6, 1.6 Hz, 1 H, HCSi), 1.53 (s, 9 H, CCH_3), 0.14 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1 (COH), 153.9 (OC=O), 148.0 (N=CH), 137.1 (C), 135.1 (H*C*=C), 129.9 (CH), 120.4 (CH), 116.9 (CH), 113.4 (CH), 112.2 (C=*C*H_2), 81.7 (*C*CH_3), 56.4 (HCSi), 28.5 (C*C*H_3), –1.2 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 3381, 2978, 1698, 1664, 1603, 1579, 1453, 1368, 1249, 1145, 900, 842 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{29}N_2O_3Si$ [M + H]$^+$ 349.1942; found 349.1944.

***tert*-Butyl 2-(4-Cyanobenzylidene)-1-[3-(trimethylsilyl)prop-1-en-3-yl]hydrazinecarboxylate (5g):** 4-Formylbenzonitrile (92 mg, 0.70 mmol) and **4** (220 mg, 0.90 mmol) gave **5g** (247 mg, 0.69 mmol, 99%) as a white solid. R_f = 0.62 (pentane/diethyl ether, 9.5:0.5), m.p. 101–102 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.60 (br. s, 1 H, N=CH), 7.77–7.68 (m, 2 H, CH), 7.68–7.56 (m, 2 H, CH), 5.89 (ddd, ^3J = 17.1, 10.5, 6.5 Hz, 1 H, HC=C), 5.02 (ddd, ^3J = 10.5, ^2J = 1.4, ^4J = 1.4 Hz, 1 H, C=CH_2), 4.88 (ddd, ^3J = 17.2, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH_2), 4.20 (ddd, ^3J = 6.5, ^4J = 1.6, 1.6 Hz, 1 H, HCSi), 1.54 (s, 9 H, CCH_3), 0.15 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.6 (OC=O), 143.3 (N=CH), 140.3 (C), 134.8 (H*C*=C), 132.5 (CH), 127.4 (CH), 119.0 (CN), 112.4 (C=*C*H_2), 112.3 (*C*CN), 82.1 (*C*CH_3), 56.6 (HCSi), 28.4 (C*C*H_3), –1.2 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 2980, 2223, 1698, 1597, 1418, 1246, 1148, 1062, 852, 768 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{20}N_3O_2Si$ [M – C_4H_7]$^+$ 302.1319; found 302.1319.

***tert*-Butyl 2-(3-Cyanobenzylidene)-1-[3-(trimethylsilyl)prop-1-en-3-yl]hydrazinecarboxylate (5h):** 3-Formylbenzonitrile (89 mg, 0.68 mmol) and **4** (240 mg, 0.98 mmol) gave **5h** (236 mg, 0.66 mmol, 97%) as a colourless oil. R_f = 0.48 (pentane/diethyl ether, 9.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (br. s, 1 H, N=CH), 7.91 (dd, ^4J = 1.7, 1.7 Hz, 1 H, CH), 7.84 (ddd, ^3J = 7.9, ^4J = 1.5, 1.5 Hz, 1 H, CH), 7.59 (ddd, ^3J = 7.7, ^4J = 1.4, 1.4 Hz, 1 H, CH), 7.47 (dd, ^3J = 7.9 Hz, 1 H, CH), 5.89 (ddd, ^3J = 17.0, 10.5, 6.4 Hz, 1 H, HC=C), 5.02 (ddd, ^3J = 10.5, ^2J = 1.4, ^4J = 1.4 Hz, 1 H, C=CH), 4.88 (ddd, ^3J = 17.2, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH), 4.19 (ddd, ^3J = 6.6, ^4J = 1.6, 1.6 Hz, 1 H, HCSi), 1.54 (s, 9 H, CCH_3), 0.15 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7 (OC=O), 143.1 (N=CH), 137.3 (C), 134.8 (H*C*=C), 132.3 (CH), 131.1 (CH), 130.5 (CH), 129.5 (CH), 118.7 (CN), 113.0 (*C*CN), 112.4 (C=*C*H$_2$), 82.0 (*C*CH$_3$), 56.5 (HCSi), 28.4 (C*C*H$_3$), –1.2 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 2977, 2231, 1702, 1404, 1367, 1277, 1248, 1151, 842, 685 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{20}N_3O_2Si$ [M – C_4H_7]$^+$ 302.1319; found 302.1319.

***tert*-Butyl 2-(4-Bromobenzylidene)-1-[3-(trimethylsilyl)prop-1-en-3-yl]hydrazinecarboxylate (5i):** 4-Bromobenzaldehyde (129 mg, 0.70 mmol) and **4** (240 mg, 0.98 mmol) gave **5i** (270 mg, 0.66 mmol, 94%) as a colourless oil. R_f = 0.38 (pentane/diethyl ether, 9.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (br. s, 1 H, N=CH), 7.50 (m, 4 H, CH), 5.90 (ddd, ^3J = 17.1, 10.5, 6.5 Hz, 1 H, HC=C), 5.00 (ddd, ^3J = 10.5, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH$_2$), 4.89 (ddd, ^3J = 17.2, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH$_2$), 4.19 (dt, ^3J = 6.6, ^4J = 1.6, 1.6 Hz, 1 H, HCSi), 1.52 (s, 9 H, CCH_3), 0.14 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8 (OC=O), 145.8 (N=CH), 135.2 (H*C*=C), 134.8 (CBr), 131.9 (CH), 128.6 (CH), 123.5 (C), 112.2 (C=*C*H$_2$), 81.6 (*C*CH$_3$), 56.6 (HCSi), 28.4 (CCH_3), –1.2 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 2978, 1700, 1412, 1367, 1279, 1249, 1147, 843 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{28}BrN_2O_2Si$ [M + H]$^+$ 411.1098; found 411.1102.

***tert*-Butyl 2-(3-Bromobenzylidene)-1-[3-(trimethylsilyl)prop-1-en-3-yl]hydrazinecarboxylate (5j):** 3-Bromobenzaldehyde (145 mg, 0.78 mmol) and **4** (240 mg, 0.98 mmol) gave **5j** (317 mg, 0.77 mmol, 99%) as a colourless oil. R_f = 0.38 (pentane/diethyl ether, 9.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (br. s, 1 H, N=CH), 7.81 (dd, ^4J = 1.8 Hz, 1 H, CH), 7.54 (ddd, ^3J = 7.8, ^4J = 1.3, 1.3 Hz, 1 H, CH), 7.44 (ddd, ^3J = 8.0, ^4J = 2.1, 1.1 Hz, 1 H, CH), 7.23 (dd, ^3J = 7.9, 7.9 Hz, 1 H, CH), 5.90 (ddd, ^3J = 17.0, 10.5, 6.5 Hz, 1 H, HC=C), 5.01 (ddd, ^3J = 10.5, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH$_2$), 4.89 (ddd, ^3J = 17.2, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH$_2$), 4.19 (ddd, ^3J = 6.6, ^4J = 1.6, 1.5 Hz, 1 H, HCSi), 1.53 (s, 9 H, CCH_3), 0.15 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8 (OC=O), 144.7 (N=CH), 138.0 (C), 135.0 (H*C*=C), 132.2 (CH), 130.2 (CH), 129.9 (CH), 125.9 (CH), 122.9 (CBr), 112.3 (C=*C*H$_2$), 81.8 (*C*CH$_3$), 56.5 (HCSi), 28.4 (C*C*H$_3$), –1.2 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 2978, 1702, 1403, 1367, 1278, 1249, 1148, 863, 842, 781, 684 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{28}BrN_2O_2Si$ [M + H]$^+$ 411.1103; found 411.1103.

***tert*-Butyl 2-(3-Methoxybenzylidene)-1-[3-(trimethylsilyl)prop-1-en-3-yl]hydrazinecarboxylate (5k):** 3-Methoxybenzaldehyde (95 mg, 0.70 mmol) and **4** (240 mg, 0.98 mmol) gave **5k** (251 mg, 0.69 mmol, 99%) as a colourless oil. R_f = 0.48 (pentane/diethyl ether, 9.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (br. s, 1 H, N=CH), 7.31–7.23 (m, 2 H, CH), 7.17 (dt, ^3J = 7.5, ^4J = 1.1 Hz, 1 H, CH), 6.90 (ddd, ^3J = 8.2, ^4J = 2.7, 1.1 Hz, 1 H, CH), 5.91 (ddd, ^3J = 17.1, 10.5, 6.5 Hz, 1 H, HC=C), 5.00 (ddd, ^3J = 10.5, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH$_2$), 4.91 (ddd, ^3J = 17.1, ^4J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH$_2$), 4.22 (ddd, ^3J = 6.5, ^4J = 1.6, 1.6 Hz, 1 H, HCSi), 3.82 (s, 3 H, OCH_3), 1.53 (s, 9 H, CCH_3), 0.16 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9 (*C*OCH_3), 153.8 (OC=O), 147.5 (N=CH), 137.2 (C), 135.4 (H*C*=C), 129.6 (CH), 120.7 (CH), 116.3 (CH), 112.1 (C=*C*H$_2$), 110.7 (CH), 81.4 (*C*CH$_3$), 56.7 (HCSi), 55.4 (OCH_3), 28.5 (C*C*H$_3$), –1.2 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 2954, 1613, 1602, 1585, 1489, 1259, 1247, 1152, 1045, 990, 863, 837 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{31}N_2O_3Si$ [M + H]$^+$ 363.2104; found 363.2107.

***tert*-Butyl 2-(3-Trifluoromethylbenzylidene)-1-[3-(trimethylsilyl)-prop-1-en-3-yl]hydrazinecarboxylate (5l):** 3-Trifluoromethylbenzaldehyde (121 mg, 0.69 mmol) and **4** (200 mg, 0.82 mmol) gave **5l** (270 mg, 0.67 mmol, 97%) as a colourless oil. R_f = 0.36 (pentane/diethyl ether, 9.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66 (br. s, 1 H, N=CH), 7.94 (s, 1 H, CH), 7.79 (d, ^3J = 7.8 Hz, 1 H, CH), 7.57 (d, ^3J = 7.7 Hz, 1 H, CH), 7.48 (dd, ^3J = 7.7 Hz, 1 H, CH), 5.91 (ddd, ^3J = 17.1, 10.5, 6.5 Hz, 1 H, HC=C), 5.02 (ddd, ^3J = 10.5, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH$_2$), 4.90 (ddd, ^3J = 17.2, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH$_2$), 4.20 (ddd, ^3J = 6.5, ^4J = 1.6, 1.6 Hz, 1 H, HCSi), 1.54 (s, 9 H, CCH_3), 0.16 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8 (OC=O), 144.7 (N=CH), 136.8 (C), 135.1 (H*C*=C), 131.2 [q, ^2J(C,F) = 33.5 Hz, CF_3], 130.3 (CH), 129.2 (CH), 125.7 (CH), 125.5 [q, ^1J(C,F) = 272.2 Hz, CF_3], 123.8 (CH), 112.3 (C=*C*H$_2$), 81.8 (*C*CH$_3$), 56.8 (HCSi), 28.4 (C*C*H$_3$), –1.2 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 2979, 1704, 1406, 1368, 1328, 1275, 1250, 1166, 1148, 1131, 1070, 866, 842, 800, 697 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{28}F_3N_2O_2Si$ [M + H]$^+$ 401.1872; found 401.1872.

***tert*-Butyl 2-(4-Methoxycarbonylbenzylidene)-1-[3-(trimethylsilyl)-prop-1-en-3-yl]hydrazinecarboxylate (5m):** Methyl 4-formylbenzoate (115 mg, 0.70 mmol) and **4** (220 mg, 0.90 mmol) gave **5m** (268 mg, 0.69 mmol, 99%) as a colourless oil. R_f = 0.27 (pentane/diethyl ether, 9.5:0.5). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.69 (br. s, 1 H, HC=N), 8.18–7.94 (m, 2 H, CH), 7.81–7.60 (m, 2 H, CH), 5.90 (ddd, ^3J = 17.0, 10.5, 6.5 Hz, 1 H, HC=C), 5.01 (ddd, ^3J = 10.5, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH$_2$), 4.89 (ddd, ^3J = 17.2, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH$_2$), 4.20 (ddd, ^3J = 6.7, ^4J = 1.6, 1.6 Hz, 1 H, HCSi), 3.92 (s, 3 H, OCH_3), 1.54 (s, 9 H, CCH_3), 0.15 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.9 (C*C*=O), 153.7 (OC=O), 144.7 (N=CH), 140.1 (C), 134.9 (H*C*=C), 130.5 (*C*C=O), 130.0 (CH), 127.0 (CH), 112.3 (C=*C*H$_2$), 81.8 (*C*CH$_3$), 56.5 (HCSi), 52.3 (OCH_3), 28.4 (C*C*H$_3$), –1.2 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 2978, 1725, 1702, 1408, 1275, 1249, 1146, 1110, 843, 768 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{31}N_2O_4Si$ [M + H]$^+$ 391.2048; found 391.2052.

***tert*-Butyl 2-(4-Nitrobenzylidene)-1-[3-(trimethylsilyl)prop-1-en-3-yl]hydrazinecarboxylate (5n):** 4-Nitrobenzaldehyde (105 mg, 0.69 mmol) and **4** (220 mg, 0.90 mmol) gave **5n** (262 mg, 0.69 mmol, 100%) as a yellow solid. R_f = 0.41 (pentane/diethyl ether, 9.5:0.5), m.p. 105–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (br. s, 1 H, N=CH), 8.32–8.15 (m, 2 H, CH), 7.85–7.69 (m, 2 H, CH), 5.90 (ddd, ^3J = 17.0, 10.5, 6.4 Hz, 1 H, HC=C), 5.03 (ddd, ^3J = 10.5, ^2J = 1.4, ^4J = 1.4 Hz, 1 H, C=CH$_2$), 4.89 (ddd, ^3J = 17.2, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH$_2$), 4.21 (ddd, ^3J = 6.5, ^4J = 1.6, 1.6 Hz, 1 H, HCSi), 1.54 (s, 9 H, CCH_3), 0.16 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6 (OC=O), 148.0 (CNO_2), 142.6 (N=CH), 142.1 (C), 134.7 (H*C*=C), 127.5 (CH), 124.1 (CH), 112.5 (C=*C*H$_2$), 82.3 (*C*CH$_3$), 56.7 (HCSi), 28.4 (C*C*H$_3$), –1.2 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 2981, 1699, 1581, 1511, 1418, 1335, 1246, 1149, 1104, 902, 845, 694 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{20}N_3O_4Si$ [M – C_4H_7]$^+$ 322.1218; found 322.1217.

***tert*-Butyl 2-(Indol-3-ylmethylene)-1-[3-(trimethylsilyl)prop-1-en-3-yl]hydrazinecarboxylate (5o):** 3-Formylindole (117 mg, 0.81 mmol) and **4** (220 mg, 0.90 mmol) were stirred in a mixture of ethanol

(1 mL), chloroform (1 mL), and acetic acid (0.1 mL) to give **5o** (284 mg, 0.77 mmol, 95%) as a white solid after flash chromatography. R_f = 0.40 (pentane/diethyl ether, 1:1), m.p. 148–149 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.44 (d, ^3J = 5.2 Hz, 1 H, N=CH), 8.40 (s, 1 H, NH), 8.36 (br. s, 1 H, N=CH), 7.37 (d, ^3J = 7.4 Hz, 2 H, CH), 7.26 (ddd, ^3J = 8.1, 7.4, ^4J = 1.1 Hz, 1 H, CH), 7.21 (ddd, ^3J = 8.1, 7.4, ^4J = 1.1 Hz, 1 H, CH), 5.96 (ddd, ^3J = 17.0, 10.5, 6.6 Hz, 1 H, HC=C), 5.03 (ddd, ^3J = 10.5, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH_2), 4.98 (ddd, ^3J = 17.1, ^2J = 1.6, ^4J = 1.6 Hz, 1 H, C=CH_2), 4.18 (d, ^3J = 6.1 Hz, 1 H, HCSi), 1.58 (s, 9 H, CCH_3), 0.16 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.5 (OC=O), 136.9 (C), 134.8 (N=CH), 127.5 (CH), 125.0 (C), 123.5 (CH), 123.0 (NCH), 121.3 (CH), 114.2 (C), 112.3 (C=CH_2), 111.1 (CH), 80.8 (CCH_3), 53.8 (HCSi), 28.6 (CCH_3), –1.0 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 3264, 2972, 1701, 1534, 1416, 1248, 1143, 1131, 1113, 902, 849, 748 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{30}N_3O_2Si$ $[M + H]^+$ 372.2102; found 372.2103.

***tert*-Butyl 2-(Ethoxycarbonylmethylene)-1-[3-(trimethylsilyl)prop-1-en-3-yl]hydrazinecarboxylate (5p):** Ethyl glyoxylate (50% in toluene; 0.5 mL, 2.52 mmol) and **4** (200 mg, 0.82 mmol) gave **5p** (268 mg, 0.82 mmol, 100%) as a white solid. R_f = 0.38 (pentane/diethyl ether, 9:1), m.p. 35–37 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (br. s, 1 H, N=CH), 5.80 (ddd, ^3J = 17.1, 10.5, 6.6 Hz, 1 H, HC=C), 5.00 (ddd, ^3J = 10.4, ^2J = 1.3, ^4J = 1.3 Hz, 1 H, C=CH_2), 4.82 (ddd, ^3J = 17.2, ^2J = 1.4, ^4J = 1.4 Hz, 1 H, C=CH_2), 4.26 (q, ^3J = 7.1 Hz, 2 H, CH_2), 4.06 (d, ^3J = 6.3 Hz, 1 H, HCSi), 1.51 (s, 9 H, CCH_3), 1.32 (t, ^3J = 7.1 Hz, 3 H, CH_3), 0.12 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.5 (CC=O), 153.0 (OC=O), 134.4 (H*C*=C), 133.3 (N=CH), 112.6 (C=CH_2), 83.0 (CCH_3), 61.1 (OCH_2), 58.0 (HCSi), 28.2 (CCH_3), 14.3 (CH_3), –1.5 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 2980, 1742, 1715, 1581, 1369, 1239, 1148, 845 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{32}N_3O_4Si$ $[M + NH_4]^+$ 346.2159; found 346.2157.

***tert*-Butyl 2-(3-Phenylprop-2-en-1-ylidene)-1-[3-(trimethylsilyl)prop-1-en-3-yl]hydrazinecarboxylate (5q):** Cinnamaldehyde (105 mg, 0.79 mmol) and **4** (220 mg, 0.90 mmol) gave **5q** (285 mg, 0.79 mmol, 100%) as a yellow oil. R_f = 0.59 (pentane/diethyl ether, 9.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (br. s, 1 H, N=CH), 7.50–7.41 (m, 2 H, CH), 7.38–7.31 (m, 2 H, CH), 7.31–7.22 (m, 1 H, CH), 6.95–6.75 (m, 2 H,CH), 5.88 (ddd, ^3J = 17.0, 10.5, 6.3 Hz, 1 H, HC=C), 5.00 (ddd, ^3J = 10.5, ^2J = 1.5, ^4J = 1.5 Hz, 1 H, C=CH_2), 4.87 (ddd, ^3J = 17.2, ^2J = 1.6, ^4J = 1.6 Hz, 1 H, C=CH_2), 4.13 (ddd, ^3J = 6.4, ^4J = 1.7, 1.7 Hz, 1 H, HCSi), 1.52 (s, 9 H, CCH_3), 0.13 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7 (OC=O), 148.8 (N=CH), 137.8 (CH), 136.6 (C), 135.1 (H*C*=CH_2), 128.9 (CH), 128.6 (CH), 127.1 (CH), 127.0 (CH), 112.0 (C=CH_2), 81.6 (CCH_3), 56.6 (HCSi), 28.4 (CCH_3), –1.1 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 2978, 1697, 1414, 1278, 1248, 1156, 1140, 972, 843 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{31}N_2O_2Si$ $[M + H]^+$ 359.2155; found 359.2152.

General Procedure for the Rearrangement: A solution of triflimide in diglyme was added by syringe to a septum-sealed and nitrogen-purged two-necked flask equipped with a reflux condenser. This solution was always freshly prepared as follows: triflimide crystals were put into a separate flask under nitrogen. The crystals were dissolved in diglyme, and an aliquot corresponding to 10 mol-% triflimide was added to the reaction flask. The solution in the reaction flask was then diluted with diglyme until 70% of the maximum solvent volume was reached. The remaining solvent volume was used to dissolve the desired hydrazone under nitrogen, and to rinse the flask properly. The final concentration of the hydrazone in diglyme was 0.05 M. After the hydrazone solution had been added to the reaction flask by syringe, the flask was put into a preheated oil bath, and the mixture was stirred at 100 °C. To prevent overpressure, a bubbler was added with a needle through the septum on the top of the reflux condenser. After 1 h, the flask was removed from the oil bath, and the mixture was cooled down to room temperature. Saturated aq. $NaHCO_3$ (10 mL) and water (100 mL) were added. The mixture was extracted with pentane (3 × 10 mL). The combined pentane phases were dried with $MgSO_4$, filtered, and concentrated in vacuo. Flash chromatography with pentane and diethyl ether as eluent was used to purify the products. Unless otherwise stated, the R_f values for the products are around 0.9 in pentane. All product ratios in the resulting mixtures were calculated from their ^{1}H NMR spectra.

4-Cyclohexyl-1-(trimethylsilyl)but-1-ene (6a): Prepared from hydrazone **5a** (171 mg, 0.51 mmol) according to the general procedure with $HNTf_2$ (14 mg) and diglyme (10 mL). Flash chromatography with pentane gave **6a** (70 mg, 0.33 mmol, 65%, *E*/*Z* > 22:1) as a colourless liquid, a mixture of two olefin isomers. Starting material **5a** (39 mg, 23%) was also recovered. Data for **6a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.02 (dt, ^3J = 18.5, 6.2 Hz, 1 H, C=CH), 5.61 (dt, ^3J = 18.5, ^4J = 1.5 Hz, 1 H, SiCH), 2.10 (dtd, ^3J = 7.9, 6.2, ^4J = 1.4 Hz, 2 H, CH_2), 1.76–1.60 (m, 5 H), 1.34–1.08 (m, 6 H), 0.93–0.78 (m, 2 H), 0.04 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.9 (C=CH), 129.3 (SiCH), 37.5 (CH), 36.6 (CH_2), 34.3 (CH_2), 33.5 (CH_2), 26.9 (CH_2), 26.6 (CH_2), –1.0 (CH_3) ppm. IR: $\tilde{\nu}$ = 2923, 2852, 2359, 2342, 1617, 1449, 1247, 990, 862, 837 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{13}H_{26}Si$ $[M]^+$ 210.1804; found 210.1797.

6-Phenyl-1-(trimethylsilyl)hex-1-ene (6b): Prepared from hydrazone **5b** (179 mg, 0.50 mmol) according to the general procedure with $HNTf_2$ (15 mg) and diglyme (10 mL). Flash chromatography with pentane gave **5b** (32 mg, 0.14 mmol, 28%, *E*/*Z* > 11:1) as a colourless liquid, a mixture of two olefin isomers. Starting material **5b** (38 mg, 21%) was also recovered. Data for **6b**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32–7.23 (m, 2 H, CH), 7.24–7.13 (m, 3 H,CH), 6.01 (dt, ^3J = 18.5, 6.2 Hz, 1 H,CH), 5.63 (dt, ^3J = 18.5, ^4J = 1.6 Hz, 1 H, SiCH), 2.62 (t, ^3J = 7.8 Hz, 2 H, CH_2), 2.14 (tdd, ^3J = 7.7, 6.2, ^4J = 1.5 Hz, 2 H, CH_2), 1.60 (tt, ^3J = 7.9, 7.4 Hz, 2 H, CH_2), 1.45 (tt, ^3J = 7.9, 7.4 Hz, 2 H, CH_2), 0.04 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.1 (CH_2CH), 142.9 (C), 130.0 (SiCH), 128.6 (CH), 128.4 (CH), 125.8 (CH), 36.7 (CH_2CH), 36.0 (CCH_2), 31.1 (CH_2), 28.4 (CH_2), –1.0 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 3027, 2954, 2932, 2856, 1616, 1496, 1453, 1247, 998, 863, 837 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{15}H_{24}Si$ $[M]^+$ 232.1647; found 232.1647.

1-(Trimethylsilyl)tridec-1-ene (6c): Prepared from hydrazone **5c** (191 mg, 0.50 mmol) according to the general procedure with $HNTf_2$ (14 mg) and diglyme (10 mL). Flash chromatography with pentane gave **6c** (51 mg, 0.20 mmol, 40%, *E*/*Z* > 22:1) as a colourless liquid, a mixture of two olefin isomers. Starting material **5c** (75 mg, 39%) was also recovered. Data for **6c**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.02 (dt, ^3J = 18.5, 6.2 Hz, 1 H, CH), 5.61 (dt, ^3J = 18.5, ^4J = 1.5 Hz, 1 H, SiCH), 2.09 (dt, ^3J = 7.7, 6.3 Hz, 2 H, CH_2), 1.48–1.13 (m, 18 H, CH_2), 0.87 (t, ^3J = 6.7 Hz, 3 H, CH_3), 0.04 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.6 (CH_2CH), 129.6 (SiCH), 36.9 (CH_2CH), 32.1 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 28.9 (CH_2), 22.9 (CH_2), 14.3 (CH_3), –1.0 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 2923, 2852, 2359, 2342, 1617, 1449, 1247, 990, 862, 837 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{16}H_{34}Si$ $[M]^+$ 254.2430; found 254.2439.

4-Phenyl-1-(trimethylsilyl)but-1-ene (6d) and (±)-*cis*-1-(Trimethylsilyl)methyl-2-phenylcyclopropane (7d): Prepared from hydrazone **5d** (169 mg, 0.51 mmol) according to the general procedure with

$HNTf_2$ (14 mg) and diglyme (10 mL). Flash chromatography with pentane gave a mixture of **6d** and **7d** (13 mg, 0.064 mmol, 13%, **6d/7d** = 1:9.3) as a volatile colourless liquid. Starting material **5d** (69 mg, 43%) was also recovered.

NMR spectroscopic data for **6d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.22 (m, 2 H, CH), 7.19 (m, 3 H, CH), 6.09 (dt, ^3J = 18.6, 6.1 Hz, 1 H, CH), 5.68 (dt, ^3J = 18.6, ^4J = 1.5 Hz, 1 H, SiCH), 2.72 (t, ^3J = 8.6 Hz, 2 H, CCH_2), 2.42 (dtd, ^3J = 9.3, 6.3, ^4J = 1.5 Hz, 2 H, CH_2CH), 0.05 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.3 (CH_2CH), 142.2 (C), 130.6 (SiCH), 128.6 (CH), 128.4 (CH), 125.9 (CH), 38.6 (CHCH_2), 35.4 (CCH_2), –1.0 ($SiCH_3$) ppm.

NMR spectroscopic data for **7d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.22 (m, 2 H, CH), 7.19 (m, 3 H, CH), 2.06 (ddd, ^3J = 8.7, 5.9, 5.9 Hz, 1 H, CCH), 1.17–1.07 (m, 1 H, CH), 1.06–0.98 (m, 1 H, CH_2), 0.56 (dd, ^3J = 5.6 Hz, 1 H, CH_2), 0.51 (dd, ^2J = 14.7 Hz, ^3J = 4.3 Hz, 1 H, $SiCH_2$), –0.02 (s, 9 H, $SiCH_3$), –0.07 (dd, ^2J = 14.9 Hz, ^3J = 10.4 Hz, 1 H, $SiCH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.0 (C), 129.3 (CH), 127.9 (CH), 125.6 (CH), 21.4 (CCH), 15.3 (CH), 15.0 ($SiCH_2$), 11.6 (CH_2), –1.3 ($SiCH_3$).

IR: $\tilde{\nu}$ = 2954, 2924, 2852, 1617, 1449, 1247, 990, 862, 837 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{12}H_{17}Si$ [M – CH_3]$^+$ 189.1100; found 189.1099.

4-(3-Hydroxyphenyl)-1-(trimethylsilyl)but-1-ene (6f) and (±)-*cis*-1-(Trimethylsilyl)methyl-2-(3-hydroxyphenyl)cyclopropane (7f): Prepared from hydrazone **5f** (188 mg, 0.54 mmol) according to the general procedure with $HNTf_2$ (15 mg) and diglyme (10.8 mL). Flash chromatography with pentane/diethyl ether (8:2) gave a mixture of **6f** and **7f** (46 mg, 0.21 mmol, 39%, **6f/7f** = 23:1) as a colourless liquid. Starting material **5f** (43 mg, 23%) was also recovered.

NMR spectroscopic data for **6f**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.15 (ddd, ^3J = 7.4, ^4J = 1.1, 1.1 Hz, 1 H, CH), 6.71 (ddd, ^3J = 7.3, ^4J = 1.2, 1.2 Hz, 1 H, CH), 6.69–6.63 (m, 2 H, CH), 6.07 (dt, ^3J = 18.6, 6.1 Hz, 1 H, CH), 5.67 (dt, ^3J = 18.6, ^4J = 1.5 Hz, 1 H, SiCH), 4.69 (d, ^4J = 1.5 Hz, 1 H, OH), 2.67 (dd, ^3J = 9.2, 6.7 Hz, 2 H, CH_2), 2.40 (dt, ^3J = 7.6, ^4J = 1.4 Hz, 2 H, CCH_2), 0.05 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.5 (COH), 146.1 (CH_2CH), 144.2 (C), 130.6 (SiCH), 129.6 (CH), 121.2 (CH), 115.5 (CH), 112.8 (CH), 38.4 (CCH_2), 35.2 (CH_2CH), –1.0 ($SiCH_3$) ppm.

The NMR spectroscopic data for **7f** could not be fully resolved. Relevant resonances were identified, and the relative amount of the by-product was calculated from the integrations.

IR: $\tilde{\nu}$ = 3330, 2954, 1615, 1589, 1455, 1247, 1155, 990, 864, 837 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{13}H_{20}OSi$ [M]$^+$ 220.1278; found 220.1250.

4-(4-Cyanophenyl)-1-(trimethylsilyl)but-1-ene (6g) and (±)-*cis*-1-(Trimethylsilyl)methyl-2-(4-cyanophenyl)cyclopropane (7g): Prepared from hydrazone **5g** (180 mg, 0.50 mmol) according to the general procedure with $HNTf_2$ (14 mg) and diglyme (10 mL). Flash chromatography with pentane gave a mixture of **6g** and **7g** (46 mg, 0.20 mmol, 40%, **6g/7g** = 1:2.8) as a colourless liquid. Starting material **5g** (40 mg, 22%) was also recovered.

NMR spectroscopic data for **6g**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60–7.54 (m, 2 H, CH), 7.32–7.18 (m, 2 H, CH), 6.01 (dt, ^3J = 18.5, 6.2 Hz, 1 H, CH), 5.64 (dd, ^3J = 18.6, ^4J = 1.5 Hz, 1 H, SiCH), 2.77 (t, ^3J = 7.8 Hz, 2 H, CCH_2), 2.41 (dtd, ^3J = 7.8, 6.2, ^4J = 1.6 Hz, 2 H, CH_2), 0.03 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.7 (C), 144.9 (CH_2CH), 132.2 (SiCH), 129.4 (CH), 119.3 (CN), 109.8 (*C*CN), 37.8 (CH_2CH), 35.4 (CCH_2), –1.1 ($SiCH_3$) ppm.

NMR spectroscopic data for **7g**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60–7.52 (m, 2 H, CH), 7.31–7.20 (m, 2 H, CH), 2.09 (ddd, ^3J = 8.6, 8.6, 6.0 Hz, 1 H, CCH), 1.23 (ddddd, ^3J = 10.2, 8.8, 8.8, 5.9, 4.4 Hz, 1 H, CH), 1.14 (ddd, ^3J = 8.4, 8.4, ^2J = 5.2 Hz, 1 H, CH_2), 0.63 (ddd, ^3J = 5.8, 5.7, ^2J = 5.7 Hz, 1 H, CH_2), 0.43 (dd, ^2J = 14.8, ^3J = 4.4 Hz, 1 H, $SiCH_2$), –0.03 (s, 9 H, $SiCH_3$), –0.08 (dd, ^2J = 14.8, ^3J = 10.2 Hz, 1 H, $SiCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.4 (C), 131.7 (CH), 129.7 (CH), 119.5 (CN), 109.2 (*C*CN), 22.0 (C*C*H), 16.4 (CH), 15.2 ($SiCH_2$), 12.5 (CH_2), –1.4 ($SiCH_3$) ppm.

IR: $\tilde{\nu}$ = 3068, 2954, 2899, 2227, 1608, 1505, 1248, 862, 839 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{14}H_{19}NSi$ [M]$^+$ 229.1287; found 229.1264.

4-(3-Cyanophenyl)-1-(trimethylsilyl)but-1-ene (6h) and *cis*-1-(Trimethylsilyl)methyl-2-(3-cyanophenyl)cyclopropane (7h): Prepared from hydrazone **5h** (177 mg, 0.49 mmol) according to the general procedure with $HNTf_2$ (14 mg) and diglyme (9.9 mL). Flash chromatography with pentane gave a mixture of **6h** and **7h** (21 mg, 0.09 mmol, 18%, **6h/7h** = 1:10) as a colourless liquid. Starting material **5h** (10 mg, 6%) was also recovered.

NMR spectroscopic data for **7h**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 (ddd, ^3J = 7.3, ^2J = 1.7 Hz, 1 H, CH), 7.43 (dd, ^3J = 1.7 Hz, 1 H, CH), 7.42–7.32 (m, 2 H, CH), 2.06 (ddd, ^3J = 8.6, 8.6, 5.9 Hz, 1 H, CCH), 1.18 (ddddd, ^3J = 10.2, 8.8, 8.8, 5.8, 4.2 Hz, 1 H, CH), 1.11 (ddd, ^3J = 8.4, 8.4, ^2J = 5.0 Hz, 1 H, CH_2), 0.56 (ddd, ^3J = 5.7, 5.7, ^2J = 5.7 Hz, 1 H, CH_2), 0.45 (dd, ^2J = 14.6, ^3J = 4.2 Hz, 1 H, $SiCH_2$), –0.02 (s, 9 H, $SiCH_3$), –0.17 (dd, ^2J = 14.7, ^3J = 10.4 Hz, 1 H, $SiCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.8 (C), 133.9 (CH), 132.7 (CH), 129.4 (CH), 128.7 (CH), 119.4 (CN), 112.0 (*C*CN), 21.1 (C*C*H), 15.5 (CH), 15.4 ($SiCH_2$), 12.0 (CH_2), –1.3 ($SiCH_3$) ppm.

The NMR spectroscopic data for **6h** could not be fully resolved. Relevant resonances were identified, and the relative amount of the by-product was calculated from the integrations.

IR: $\tilde{\nu}$ = 2954, 2229, 2227, 1601, 1580, 1484, 1248, 860, 840 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{14}H_{18}NSi$ [M]$^+$ 228.1203; found 228.1203.

4-(4-Bromophenyl)-1-(trimethylsilyl)but-1-ene (6i) and (±)-*cis*-1-(Trimethylsilyl)methyl-2-(4-bromophenyl)cyclopropane (7i): Prepared from hydrazone **5i** (212 mg, 0.51 mmol) according to the general procedure with $HNTf_2$ (14 mg) and diglyme (10.3 mL). Flash chromatography with pentane gave a mixture of **6i** and **7i** (52 mg, 0.18 mmol, 36%, **6i/7i** = 1.1:1) as a colourless liquid. Starting material **5i** (45 mg, 25%) was also recovered.

NMR spectroscopic data for **6i**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50–7.34 (m, 2 H, CH), 7.16–6.94 (m, 2 H, CH), 6.04 (dt, ^3J = 18.5, 6.1 Hz, 1 H, CH), 5.66 (dt, ^3J = 18.5, ^4J = 1.5 Hz, 1 H, SiCH), 2.67 (dt, ^3J = 9.0, 6.7 Hz, 2 H, CCH_2), 2.38 (dtd, ^3J = 7.6, 6.2, ^4J = 1.5 Hz, 2 H, CH_2), 0.05 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.66 (CH_2CH), 141.06 (C), 131.07 (SiCH), 131.03 (CH), 130.38 (CH), 119.61 (CBr), 38.35 (CH_2CH), 34.72 (CCH_2), –1.06 ($SiCH_3$) ppm.

NMR spectroscopic data for **7i**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50–7.33 (m, 2 H, CH), 7.16–6.86 (m, 2 H, CH), 1.99 (ddd, ^3J = 8.6, 8.6, 5.9 Hz, 1 H, CCH), 1.11 (ddddd, ^3J = 10.0, 8.7, 5.7, 5.6, 4.2 Hz, 1 H, CH), 1.05 (ddd, ^3J = 8.4, 8.4, ^2J = 4.9 Hz, 1 H, CH_2), 0.51 (ddd, ^3J = 5.7, 5.6, ^2J = 5.6 Hz, 1 H, CH_2), 0.47 (dd, ^2J = 14.8, ^3J = 4.2 Hz, 1 H, $SiCH_2$), –0.02 (s, 9 H, $SiCH_3$), –0.13 (dd, ^2J = 14.8, ^3J = 10.3 Hz, 1 H, $SiCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.11 (C), 131.41 (CH), 130.94 (CH), 119.31 (CBr),

20.95 (C*C*H), 15.37 (CH), 15.01 ($SiCH_2$), 11.82 (CH_2), –1.29 ($SiCH_3$) ppm.

IR: $\tilde{\nu}$ = 2954, 1616, 1488, 1073, 1011, 839, 838 cm^{-1}. HRMS (EI^+): calcd. for $C_{13}H_{19}BrSi$ $[M]^+$ 282.0434; found 282.0427.

4-(3-Bromophenyl)-1-(trimethylsilyl)but-1-ene (6j) and (±)-*cis*-1-(Trimethylsilyl)methyl-2-(3-bromophenyl)cyclopropane (7j): Prepared from hydrazone **5j** (285 mg, 0.69 mmol) according to the general procedure with $HNTf_2$ (19 mg) and diglyme (13.8 mL). Flash chromatography with pentane gave a mixture of **6j** and **7j** (41 mg, 0.15 mmol, 21%, **6j/7j** = 1:1.2) as a colourless liquid. Starting material **5j** (129 mg, 45%) was also recovered.

NMR spectroscopic data for **6j**: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.28 (m, 2 H, CH), 7.18–7.11 (m, 1 H, CH), 7.11–7.04 (m, 1 H, CH), 6.03 (dt, ^3J = 18.6, 6.2 Hz, 1 H, CH), 5.65 (dt, ^3J = 18.6, ^4J = 1.5 Hz, 1 H, SiCH), 2.68 (dd, ^3J = 9.0, 6.7 Hz, 2 H, CCH_2), 2.39 (dtd, ^3J = 7.7, 6.2, ^4J = 1.5 Hz, 2 H, CH_2), 0.04 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.5 (CH_2CH), 144.5 (C), 131.7 (CH), 131.2 (SiCH), 129.9 (CH), 129.0 (CH), 127.3 (CH), 122.42 (CBr), 38.28 (CH_2CH), 34.95 (CCH_2), –1.07 ($SiCH_3$) ppm.

NMR spectroscopic data for **7j**: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.27 (m, 2 H, CH), 7.17–7.10 (m, 1 H, CH), 7.11–7.04 (m, 1 H, CH), 2.02 (ddd, ^3J = 8.6, 8.6, 5.9 Hz, 1 H, CCH), 1.12 (ddddd, ^3J = 10.1, 8.7, 5.7, 5.6, 4.2 Hz, 1 H, CH), 1.05 (ddd, ^3J = 8.4, 8.4, ^2J = 4.9 Hz, 1 H, CH_2), 0.53 (ddd, ^3J = 5.7, 5.6, ^2J = 5.7 Hz, 1 H, CH_2), 0.49 (dd, ^2J = 14.8, ^3J = 4.2 Hz, 1 H, $SiCH_2$), –0.02 (s, 9 H, $SiCH_3$), –0.12 (dd, ^2J = 14.7, ^3J = 10.3 Hz, 1 H, $SiCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.7 (C), 132.4 (CH), 129.4 (CH), 128.7 (CH), 128.0 (CH), 122.1 (CBr), 21.2 (C*C*H), 15.4 ($SiCH_2$), 15.2 (CH), 11.8 (CH_2), –1.3 ($SiCH_3$) ppm.

IR: $\tilde{\nu}$ = 2953, 1616, 1595, 1566, 1477, 1247, 862, 838 cm^{-1}. HRMS (EI^+): calcd. for $C_{13}H_{19}BrSi$ $[M]^+$ 282.0434; found 282.0406.

4-(3-Methoxyphenyl)-1-(trimethylsilyl)but-1-ene (6k) and (±)-*cis*-1-(Trimethylsilyl)methyl-2-(3-methoxyphenyl)cyclopropane (7k): Prepared from hydrazone **5k** (208 mg, 0.57 mmol) similarly to the general procedure, with triflime (16 mg, 0.057 mmol, 10 mol-%) at 100 °C, and with a 10 min reaction time. The total amount of diglyme used was 11.4 mL. The work-up procedure was the same as that described above. Flash chromatography with pentane gave a mixture of **6k** and **7k** (68 mg, 0.29 mmol, 51%, **6k/7k** = 16.5:1) as a colourless liquid.

NMR spectroscopic data for **6k**: ^1H NMR (400 MHz, $CDCl_3$): δ = 7.20 (dd, ^3J = 8.9, 7.6 Hz, 1 H, CH), 6.78 (d, ^3J = 7.9 Hz, 2 H, CH), 6.76–6.71 (m, 2 H, CH), 6.09 (dt, ^3J = 18.5, 6.1 Hz, 1 H, CH), 5.68 (dt, ^3J = 18.5, ^4J = 1.5 Hz, 1 H, SiCH), 3.80 (s, 3 H, OCH_3), 2.70 (dd, ^3J = 9.2, 6.7 Hz, 2 H, CCH_2), 2.42 (tdd, ^3J = 7.6, 6.3, ^4J = 1.6 Hz, 2 H, CH_2), 0.05 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8 ($COCH_3$), 146.3 (CH_2CH), 143.9 (C), 130.6 (SiCH), 129.4 (CH), 121.0 (CH), 114.3 (CH), 111.3 (CH), 55.3 (OCH_3), 38.5 (CH_2CH), 35.4 (CCH_2), –1.0 ($SiCH_3$) ppm.

The NMR spectroscopic data for **7k** could not be fully resolved. Relevant resonances were identified, and the relative content of the by-product was calculated from the integrations.

IR: $\tilde{\nu}$ = 2953, 1613, 1602, 1585, 1489, 1259, 1247, 1152, 1045, 990, 863, 837 cm^{-1}. HRMS (EI^+): calcd. for $C_{14}H_{22}OSi$ $[M]^+$ 234.1434; found 234.1431.

4-(3-Trifluoromethylphenyl)-1-(trimethylsilyl)but-1-ene (6l) and (±)-*cis*-1-(Trimethylsilyl)methyl-2-[3-(trifluoromethyl)phenyl]cyclopropane (7l): Prepared from hydrazone **5l** (188 mg, 0.46 mmol) according to the general procedure with $HNTf_2$ (13 mg) and diglyme (9.3 mL). Flash chromatography with pentane gave a mixture of **6l** and **7l** (28 mg, 0.10 mmol, 22%, **6l/7l** = 1:5) as a colourless liquid.

NMR spectroscopic data for **6l**: ^1H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.30 (m, 4 H, CH), 6.03 (dt, ^3J = 18.5, 6.2 Hz, 1 H, CH), 5.65 (dt, ^3J = 18.6, ^4J = 1.5 Hz, 1 H, SiCH), 2.78 (dd, ^3J = 8.8, 6.8 Hz, 2 H, CCH_2), 2.43 (dtd, ^3J = 7.5, 6.2, ^4J = 1.5 Hz, 2 H, CH_2), 0.04 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.3 (CH_2CH), 142.9 (C), 132.5, 132.1, 131.5, 130.5, 130.1, 128.8, 128.3, 126.1, 126.0, 126.0, 125.9, 123.2, 122.5, 122.4, 38.2 (CH_2CH), 35.1 (CCH_2), –1.1 ($SiCH_3$) ppm. Note: Unassigned ^{13}C signals given for both compounds.

NMR spectroscopic data for **7l**: ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.30 (m, 4 H, CH), 2.09 (ddd, ^3J = 8.6, 8.6, 5.9 Hz, 1 H, CCH), 1.22–1.13 (m, 1 H, CH), 1.13–1.05 (m, 1 H, CH_2), 0.59 (ddd, ^3J = 5.6, 5.6, 5.5 Hz, 1 H, CH_2), 0.46 (dd, ^2J = 14.7, ^3J = 4.3 Hz, 1 H, $SiCH_2$), –0.03 (s, 9 H, $SiCH_3$), –0.09 to –0.17 (m, ^2J = 14.7 Hz, 1 H, ^3J = 10.8 Hz, $SiCH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.1 (C), 132.5, 132.1, 131.5, 130.45, 130.1, 128.8, 128.3, 126.1, 126.0, 126.0, 125.9, 123.2, 122.5, 122.4, 122.4, 122.4, 21.4 (C*C*H), 15.4 ($SiCH_2$), 15.3 (CH_2), 11.9 (CH_2), –1.3 ($SiCH_3$) ppm.

IR: $\tilde{\nu}$ = 2955, 1441, 1326, 1248, 1164, 1127, 1074, 862, 840 cm^{-1}. HRMS (EI^+): calcd. for $C_{14}H_{18}F_3Si$ $[M - H]^+$ 271.1124; found 271.1123.

6-Phenyl-1-(trimethylsilyl)hexa-1,4-diene (6q): Prepared from hydrazone **5q** (100 mg, 0.29 mmol) similarly to the general procedure, but with triflime (25 mg, 0.089 mmol, 30 mol-%) at 125 °C, and with a 10 min reaction time. The total amount of diglyme used was 5.6 mL. The work-up procedure was the same as that described above. Flash chromatography with pentane gave a mixture of two olefin isomers **6q** (33 mg, 0.14 mmol, 49%, $E/Z > 15:1$) as a colourless liquid. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.28 (m, 2 H, CH), 7.24–7.18 (m, 3 H, CH), 6.04 (dt, ^3J = 18.6, 5.9 Hz, 1 H, CH), 5.68 (d, ^3J = 18.5 Hz, 1 H, SiCH), 5.62 (dt, ^3J = 15.5, 6.5 Hz, 1 H, CH), 5.54 (dt, ^3J = 15.5, 6.3 Hz, 1 H, CH), 3.38 (d, ^3J = 6.5 Hz, 2 H, C*C*H_2), 2.86 (dd, ^3J = 5.9 Hz, 2 H, CH*C*H_2), 0.07 (s, 9 H, CH_3) ppm. ^{13}C NMR (125 MHz $CDCl_3$): δ = 145.1 (CH), 141.0 (C), 130.8 (CH), 130.3 (CH), 129.4 (CH), 128.7 (CH), 128.5 (CH), 126.1 (CH), 39.7 (CH*C*H_2), 39.2 (C*C*H_2), –1.0 ($SiCH_3$) ppm. IR: $\tilde{\nu}$ = 2955, 1613, 1494, 1453, 1425, 1247, 988, 968, 861, 837, 744, 697 cm^{-1}. HRMS (EI^+): calcd. for $C_{15}H_{22}Si$ $[M]^+$ 230.1491; found 230.1481.

Supporting Information (see footnote on the first page of this article): Copies of ^1H and ^{13}C NMR spectra for all compounds, crystallographic data for compound **3**.

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