

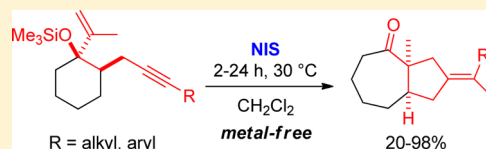
NIS-Mediated Electrophilic Cyclization of 3-Silyloxy-1,*n*-enynes

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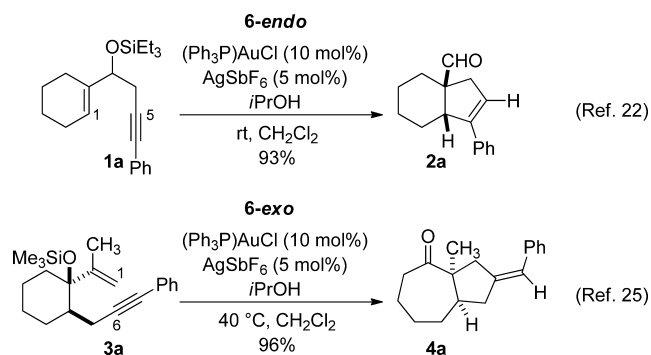
S Supporting Information

ABSTRACT: The electrophilic cyclization of 3-silyloxy-1,5-enynes and 3-silyloxy-1,6-enynes was investigated. In the presence of *N*-iodosuccinimide (NIS), the title compounds are transformed under metal-free conditions into five-membered carbocycles with all-carbon stereogenic centers following a sequence of iodonium activation of the triple bond, carbocyclization, and pinacol-type 1,2-shift.



The creation of all-carbon quaternary stereogenic centers is a major challenge in contemporary synthetic chemistry.^{1–3} In particular when these structural elements shall be embedded in cyclic frameworks, domino reactions^{4–6} consisting of carbocyclization and subsequent 1,2-shift have emerged as a powerful strategy to form the desired quaternary centers.^{7–13} In most cases, the 1,2-shift is designed as an integral part of a cationic reaction cascade; the key question then is how to initiate the cationic cyclization step. To this end, we and others^{14–18} focused on the activation of alkynes to initiate a carbocyclization/1,2-migration sequence. For examples, we showed in 2007 that, under gold catalysis,^{19–21} 3-silyloxy-1,5-enynes (e.g., **1a**) smoothly convert into cyclopentenyls via an initial 6-*endo* cyclization pathway (Scheme 1).^{22–24} The corresponding 3-silyloxy-1,6-enynes (e.g., **3a**) give the related products of an initial 6-*exo* cyclization having an exocyclic double bond.^{25,26}

Scheme 1. Gold-Catalyzed Reactivities of 3-Silyloxy-1,*n*-enynes

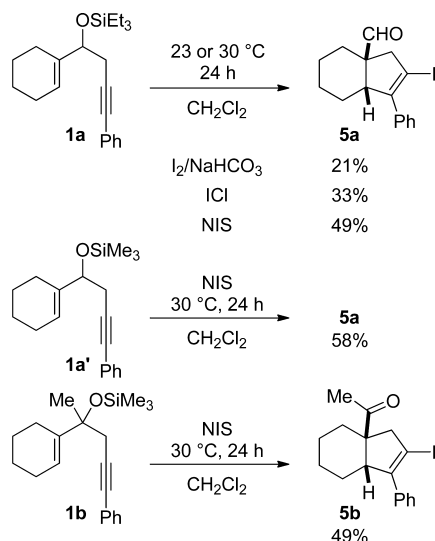


In the majority of the processes that are initiated by a nucleophilic attack onto a gold-activated alkyne, the final step to regenerate the catalytic species is a protodeauration of a vinylgold intermediate.^{27,28} In an analogous way, several reactions were described where vinylgold intermediates were successfully trapped by iodine electrophiles to incorporate iodine rather than hydrogen at the final product.^{29–31} Even

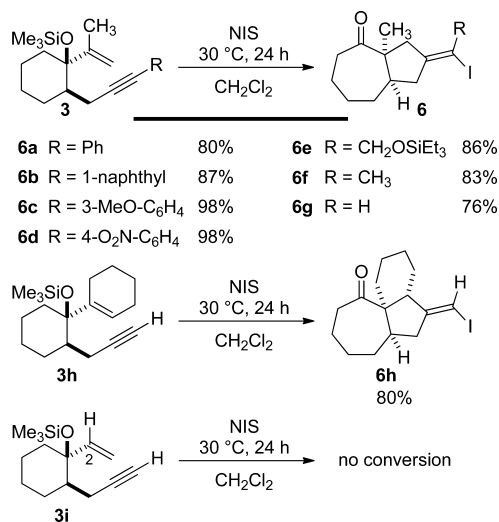
though both processes catalyzed by gold give rise to the same scaffolds, iodine incorporation allows for further functionalizations of the scaffold by use of, for example, traditional cross-coupling reactions; therefore, tetrasubstituted olefinic moieties are accessible instead of only trisubstituted ones. Over the past years it also became evident that, if classical cationic intermediates are assumed, quite a number of processes that were previously shown to be possible with gold catalysis can be triggered by direct iodonium activation in the absence of gold catalysts.^{32–45} As a logical extension, we speculated about the realization of the carbocyclization/1,2-migration cascades shown in Scheme 1 by using simple iodine electrophiles under metal-free conditions. To investigate the iodonium-triggered cyclization of 3-silyloxy-1,5-enynes and 3-silyloxy-1,6-enynes,^{46,47} we started a research program, the results of which are presented herein.

Our studies began with the reaction of silyl ether **1a** with several electrophilic iodine sources in the absence of transition-metal additives. To our pleasure, we found that aldehyde **5a** containing the desired vinyl iodide moiety could be formed in dichloromethane at room temperature in low yields ($I_2/NaHCO_3$, 21%; ICl , 33%); in all cases, quite long reaction times around 24 h were required to obtain full conversion of the starting material (Scheme 2).⁴⁸ After careful optimization, best yields (i.e., 49%) for iodide **5a** were obtained when using *N*-iodosuccinimide (NIS) at 30 °C in dichloromethane. As also shown in Scheme 2, the yield was further increased up to 58% by switching the silyl group from triethylsilyl to the more labile trimethylsilyl. We note that this observation is not analogous to the gold-catalyzed transformations where trimethylsilyl ether **1a'** resulted in significantly lower yields than triethylsilyl ether **1a**. As shown by the transformation of silyl ether **1b** derived from a tertiary alcohol, ketones (as **5b**) are also produced in moderate yield. However, it can be concluded that 3-silyloxy-1,5-enynes can indeed undergo iodonium-triggered carbocyclization/1,2-migration cascades under metal-free conditions, albeit not as rapid and high-yielding as under the gold-catalyzed conditions.

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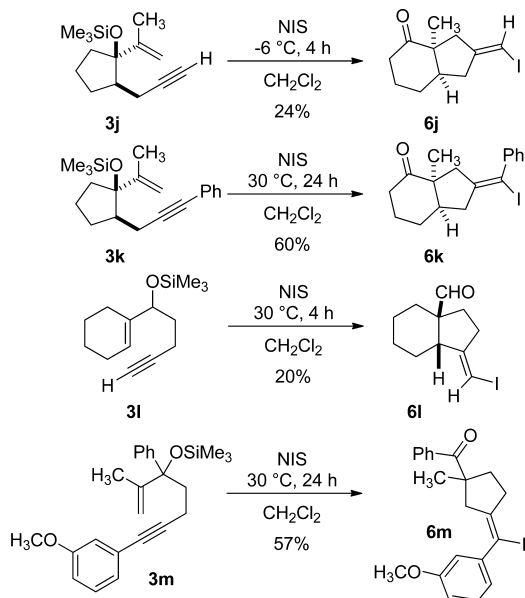
Scheme 2. Transformation of 3-Silyloxy-1,5-enynes 1a, 1a', and 1b

After this proof of concept regarding 3-silyloxy-1,5-enynes, we focused on the electrophilic conversion of 3-silyloxy-1,6-enynes into five-membered carbocycles with an exocyclic double bond; due to the two possible double bond isomers that can be formed in the course of the reaction, this transformation was believed to be more challenging. As summarized in Scheme 3, it was found that 3-silyloxy-1,6-

Scheme 3. Transformation of 3-Silyloxy-1,6-enynes (1)

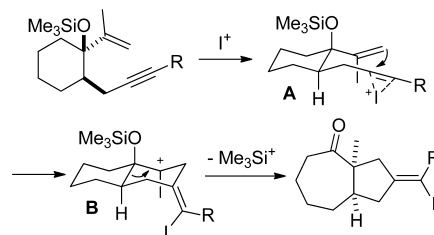
enynes are smoothly converted into the iodine-containing carbocycles under the reaction conditions (3 equiv of NIS, 30 °C, CH_2Cl_2). Reactions of enynes having aryl substituents at the alkyne terminus were high-yielding with both electron-rich and electron-poor aryls reacting equally well. Alkyl-substituted alkynes and terminal alkynes are also converted into the bicyclic products, although yields are slightly lower in these cases. As exemplified by the failed attempt to convert enyne **3i**, the starting 1,6-enynes require a substituent at the olefinic C2-position. This observation might point to a classical cationic mechanism where the stabilization of cationic intermediates is crucial (*vide infra*).

To our surprise, cyclopentanol derived silyl ether **3j** fully decomposed under the conditions at 30 °C (Scheme 4). The

Scheme 4. Transformation of 3-Silyloxy-1,6-enynes (2)

expected product could be obtained only when the reaction temperature was decreased to -6 °C, albeit in low yield. The phenyl-substituted product **6k** was obtained in 60% yield upon reaction with NIS at 30 °C. Acyclic substrates as **3l** and **3m** also gave the products where the initial 6-*exo* cyclization is followed by a 1,2-alkyl migration that proceeds with ring contraction. Notably, in the case of **3m** the alternative migration of the phenyl group was not observed.

Scheme 5 summarizes a plausible mechanism. Coordination of the iodine electrophile to the triple bond produces iodonium

Scheme 5. Plausible Mechanism

intermediate **A**, which after nucleophilic attack of the olefinic carbon produces cyclic carbenium ion **B**. The *anti*-mode of the initial 6-*exo* cyclization explains well why the exocyclic double bond is exclusively formed with *E*-configuration.⁴⁹ Subsequent 1,2-shift then creates the quaternary stereogenic center under ring contraction.

In conclusion, 3-silyloxy-1,5-enynes and 3-silyloxy-1,6-enynes with an alkyl substituent at the olefinic C2-position were transformed into polyfunctional five-membered carbocycles by use of NIS as a simple iodine electrophile under metal-free conditions. The reaction likely proceeds by a mechanism involving cyclization and subsequent 1,2-shift of the cationic intermediate. This protocol represents a synthetically valuable alternative to the previously reported ones on gold catalysis

since it, for the first time, provides a general access to iodinated carbocyclic products containing tri- and tetrasubstituted olefins.

EXPERIMENTAL SECTION

General. All reactions were carried out in sealed reaction vials. All commercial reagents were used as received. Thin-layer chromatography (TLC) was conducted with precoated glass-backed plates and visualized by exposure to UV light (254 nm) or stained with ceric ammonium molybdate (CAM). Flash chromatography was performed with silica gel (43–60 μm); the eluent used is reported in parentheses. ^1H NMR spectra were recorded on 600 MHz FT-NMR, 500 MHz FT-NMR, 400 MHz FT-NMR, 360 MHz FT-NMR, and 250 MHz FT-NMR spectrometers. ^{13}C NMR spectra were recorded at 151, 126, 101, 91, or 63 MHz. Chemical shifts are reported in ppm relative to solvent signal. Multiplicity is indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublets). Low resolution mass spectra were recorded applying GC–MS, EI or ESI techniques. High resolution mass spectra were obtained using ESI or APCI ionization methods on a MicroTOF. The compounds **1a**, **1a'**, **3a**, **3b**, **3f**, and **3g** were reported earlier.^{23,25} The remaining substrates **1** and **3** were synthesized in a fully analogous way.

General Procedure A for the Electrophilic Cyclization. *rel*-(3*aR*,7*aS*)-2-iodo-3-phenyl-3*a*,4,5,6,7,7*a*-hexahydro-1*H*-indene-7*a*-carbaldehyde (5a**).** Compound **1a'** (32.8 mg, 0.11 mmol) was dissolved in 1.1 mL of dichloromethane, and *N*-iodosuccinimide (NIS; 74.2 mg, 0.33 mmol) was added at once. The mixture was stirred at the given temperature (30 °C, 24 h) until TLC indicated full conversion. The reaction was quenched by addition of 20 mL of a saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution. The reaction mixture was extracted with Et_2O (3 \times 20 mL). The combined organic phases were washed with brine and dried over MgSO_4 . The solvent was evaporated, and the residue was purified by flash chromatography on silica (pentanes/ Et_2O 98:2) to give compound **5a** (22.6 mg, 64.2 μmol , 58%) as a colorless oil; R_f = 0.32 (pentanes/ Et_2O 95:5), [UV]. ^1H NMR (400 MHz, CDCl_3 , ppm) δ = 1.23–1.36 (m, 2 H), 1.44–1.53 (m, 3 H), 1.64–1.71 (m, 2 H), 1.82–1.88 (m, 1 H), 2.73 (dd, J = 16.0, 1.7 Hz, 1 H), 3.04 (dd, J = 16.0, 1.9 Hz, 1 H), 3.27 (t, J = 6.2 Hz, 1 H), 7.34–7.42 (m, 5 H), 9.66 (s, 1 H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 21.6, 21.7, 26.4, 27.6, 47.1, 50.1, 57.0, 89.0, 127.9, 128.0, 128.2, 136.5, 151.3, 203.5. The analytical data are in accordance with those previously reported.²³

***rel*-1-(3*aR*,7*aS*)-(2-iodo-3-phenyl-3*a*,4,5,6,7,7*a*-hexahydro-1*H*-inden-7*a*-yl)ethanone (**5b**).** Compound **1b** (31.4 mg, 100 μmol) was converted following the general procedure A (30 °C, 24 h). After flash chromatography on silica (pentanes/ Et_2O 95:5), **5b** (18.0 mg, 49.1 μmol , 49%) was obtained as a colorless oil; R_f = 0.21 (pentanes/ Et_2O 95:5), [CAM/UV]. ^1H NMR (400 MHz, CDCl_3 , ppm) δ = 1.13–1.17 (m, 3 H), 1.48–1.56 (m, 2 H), 1.63–1.71 (m, 1 H), 1.80 (ddd, J = 14.2, 10.5, 3.8 Hz, 1 H), 1.94–1.99 (m, 1 H), 2.24 (s, 3 H), 2.73 (dd, J = 15.7, 1.8 Hz, 1 H), 3.01 (dd, J = 15.7, 2.8 Hz, 1 H), 3.53–3.55 (m, 1 H), 7.31–7.35 (m, 3 H), 7.38–7.42 (m, 2 H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 21.8, 21.9, 25.2, 25.8, 31.0, 47.3, 53.4, 58.9, 88.2, 127.7, 128.0, 128.2, 136.9, 151.8, 210.6. LRMS (GC–MS) m/z [%]: 254 (7), 239 (14) [$\text{M}^+ - \text{I}$], 197 (8), 165 (11), 127 (100), 115 (16), 77 (10). HRMS m/z : 389.0358 [389.0373 calculated for $\text{C}_{17}\text{H}_{19}\text{OINa}$ ($\text{M} + \text{Na}^+$)].

***rel*-(3*aR*,8*aS*,*E*)-2-(iodo(phenyl)methylene)-3*a*-methyl-octahydroazulen-4(2*H*)-one (**6a**).** Compound **3a** (30.0 mg, 91.9 μmol) was converted following the general procedure A (30 °C, 24 h). After flash chromatography on silica (pentanes/ Et_2O 95:5), **6a** (28.2 mg, 74.2 μmol , 80%) was obtained as a colorless oil; R_f = 0.35 (pentanes/ Et_2O 9:1), [CAM/UV]. ^1H NMR (500 MHz, CDCl_3 , ppm) δ = 1.13 (s, 3 H), 1.31–1.53 (m, 3 H), 1.66–1.70 (m, 1 H), 1.90–1.93 (m, 2 H), 2.02–2.06 (m, 1 H), 2.23–2.33 (m, 3 H), 2.68–2.76 (m, 2 H), 2.99–3.05 (m, 1 H), 7.19–7.22 (m, 1 H), 7.26–7.29 (m, 4 H). ^{13}C NMR (63 MHz, CDCl_3 , ppm) δ = 24.8, 27.9, 30.4, 35.8, 39.3, 40.7, 46.0, 49.2, 60.7, 91.8, 127.7, 128.3, 129.0, 143.6, 148.3, 216.6. LRMS (GC–MS) m/z [%]: 380 (100) [M^+], 323 (10), 253

(73), 235 (13), 211 (65), 195 (15), 167 (23), 153 (17), 128 (17), 115 (27). HRMS m/z : 380.0628 [380.0632 calculated for $\text{C}_{18}\text{H}_{21}\text{OI}$ (M^+)].

***rel*-(3*aR*,8*aS*,*E*)-2-(iodo(naphthalen-1-yl)methylene)-3*a*-methyl-octahydroazulen-4(2*H*)-one (**6b**).** Compound **3b** (30.2 mg, 80.2 μmol) was converted following the general procedure A (30 °C, 24 h). After flash chromatography on silica (pentanes/ Et_2O 9:1), **6b** (30.1 mg, 69.9 μmol , 87%) was obtained as a colorless oil; R_f = 0.2 (pentanes/ Et_2O 95:5), [CAM/UV]. ^1H NMR (500 MHz, CDCl_3 , ppm) δ = 1.13–1.19 (m, 3 H), 1.30–1.41 (m, 2 H), 1.47–1.55 (m, 1 H), 1.71–1.77 (m, 1 H), 1.83–2.05 (m, 3 H), 2.09–2.13 (m, 1 H), 2.26–2.29 (m, 1 H), 2.36–2.59 (m, 2 H), 2.67–2.71 (m, 1 H), 3.12–3.17 (m, 1 H), 7.37–7.54 (m, 4 H), 7.77–7.96 (m, 3 H). ^{13}C NMR (63 MHz, CDCl_3 , ppm) δ = 24.7/25.0, 27.8/27.9, 30.3/30.4, 35.7/35.8, 38.7/39.1, 40.7, 46.3, 47.8/48.1, 60.4/60.6, 88.1/88.1, 125.2/125.2, 125.7/125.8, 126.0/126.1, 126.2/126.3, 126.3/126.5, 128.4/128.5, 128.6, 129.9/130.1, 134.1/134.2, 140.9/141.27, 150.2/150.3, 216.5/216.6. LRMS (GC–MS) m/z [%]: 430 (4) [M^+], 304 (13), 303 (56), 220 (14), 205 (71), 179 (22), 164 (20), 125 (27), 86 (86), 84 (100), 57 (28). HRMS m/z : 430.0785 [430.0788 calculated for $\text{C}_{22}\text{H}_{23}\text{OI}$ (M^+)].

***rel*-(3*aR*,8*aS*,*E*)-2-(iodo(3-methoxyphenyl)methylene)-3*a*-methyl-octahydroazulen-4(2*H*)-one (**6c**).** Compound **3c** (31.0 mg, 86.9 μmol) was converted following the general procedure A (30 °C, 24 h). After flash chromatography on silica (pentanes/ Et_2O 9:1), **6c** (35.1 mg, 85.5 μmol , 98%) was obtained as a colorless oil; R_f = 0.12 (pentanes/ Et_2O 9:1), [CAM/UV]. ^1H NMR (250 MHz, CDCl_3 , ppm) δ = 1.14 (s, 3 H), 1.36–1.72 (m, 4 H), 1.90–2.08 (m, 3 H), 2.23–2.35 (m, 3 H), 2.67–2.76 (m, 2 H), 2.95–3.07 (m, 1 H), 3.80 (s, 3 H), 6.75–6.89 (m, 3 H), 7.17–7.26 (m, 1 H). ^{13}C NMR (91 MHz, CDCl_3 , ppm) δ = 24.8, 27.9, 30.4, 35.7, 39.4, 40.7, 46.0, 49.1, 55.4, 60.6, 91.4, 113.4, 114.7, 121.3, 129.3, 144.9, 148.4, 159.3, 216.6. LRMS (GC–MS) m/z [%]: 410 (21) [M^+], 304 (26), 303 (100), 283 (32), 179 (39), 165 (36), 125 (40). HRMS m/z : 410.0731 [410.0737 calculated for $\text{C}_{19}\text{H}_{23}\text{O}_2\text{I}$ (M^+)].

***rel*-(3*aR*,8*aS*,*E*)-2-(iodo(4-nitrophenyl)methylene)-3*a*-methyl-octahydroazulen-4(2*H*)-one (**6d**).** Compound **3d** (27.3 mg, 73.5 μmol) was converted following the general procedure A (30 °C, 24 h). After flash chromatography on silica (pentanes/ Et_2O 9:1), **6d** (30.6 mg, 72.0 μmol , 98%) was obtained as a colorless oil; R_f = 0.28 (pentanes/ Et_2O 8:2), [CAM/UV]. ^1H NMR (250 MHz, CDCl_3 , ppm) δ = 1.14 (s, 3 H), 1.35–1.48 (m, 2 H), 1.54–1.73 (m, 3 H), 1.89–1.98 (m, 2 H), 2.07 (t, J = 9.6 Hz, 1 H), 2.19 (d, J = 17.3 Hz, 1 H), 2.27–2.34 (m, 2 H), 2.66–2.82 (m, 2 H), 3.05 (ddd, J = 18.6, 8.5, 2.7 Hz, 1 H), 7.46 (d, J = 8.9 Hz, 2 H), 8.16 (d, J = 8.9 Hz, 2 H). ^{13}C NMR (63 MHz, CDCl_3 , ppm) δ = 24.8, 27.9, 30.3, 35.7, 39.7, 40.6, 45.9, 49.4, 60.8, 87.9, 123.7, 130.0, 146.9, 149.8, 151.5, 216.1. LRMS (GC–MS) m/z [%]: 425 (100) [M^+], 410 (15), 368 (38), 298 (27), 280 (13), 256 (94), 239 (17), 209 (15), 165 (29), 152 (23), 115 (13). HRMS m/z : 425.0475 [425.0482 calculated for $\text{C}_{18}\text{H}_{20}\text{O}_3\text{NI}$ (M^+)].

***rel*-(3*aR*,8*aS*,*E*)-2-(1-iodo-2-((triethylsilyl)oxy)ethylidene)-3*a*-methyl-octahydroazulen-4(2*H*)-one (**6e**).** Compound **3e** (30.1 mg, 76.3 μmol) was converted following the general procedure A (30 °C, 24 h). After flash chromatography on silica (pentanes/ Et_2O 98:2), **6e** (29.0 mg, 64.7 μmol , 86%) was obtained as a colorless oil; R_f = 0.14 (pentanes/ Et_2O 95:5), [CAM]. ^1H NMR (250 MHz, CDCl_3 , ppm) δ = 0.64 (q, J = 7.4 Hz, 6 H), 0.98 (t, J = 7.9 Hz, 9 H), 1.17 (s, 3 H), 1.37–1.62 (m, 4 H), 1.85–2.00 (m, 3 H), 2.16–2.47 (m, 3 H), 2.68–2.90 (m, 3 H), 4.31 (d, J = 12.2 Hz, 1 H), 4.22 (d, J = 12.6 Hz, 1 H). ^{13}C NMR (63 MHz, CDCl_3 , ppm) δ = 4.7, 7.0, 25.2, 27.9, 30.4, 35.5, 38.2, 40.8, 45.5, 48.5, 60.6, 67.5, 99.3, 146.9, 216.8. LRMS (GC–MS) m/z [%]: 419 (12) [$\text{M}^+ - \text{C}_2\text{H}_5$], 321 (7), 316 (22), 299 (8), 190 (15), 189 (100), 161 (22), 91 (18), 75 (19). HRMS m/z : 419.0895 [419.0898 calculated for $\text{C}_{17}\text{H}_{28}\text{O}_3\text{ISI}$ ($\text{M}^+ - \text{C}_2\text{H}_5$)].

***rel*-(3*aR*,8*aS*,*E*)-2-(1-iodoethylidene)-3*a*-methyl-octahydroazulen-4(2*H*)-one (**6f**).** Compound **3f** (30.7 mg, 116 μmol) was converted following the general procedure A (30 °C, 24 h). After flash chromatography on silica (pentanes/ Et_2O 98:2), **6f** (30.6 mg, 96.2 μmol , 83%) was obtained as a colorless oil; R_f = 0.45 (pentanes/ Et_2O 8:2), [CAM]. ^1H NMR (250 MHz, CDCl_3 , ppm) δ = 1.17–1.31 (m, 4

H), 1.37–1.62 (m, 3 H), 1.84–1.99 (m, 3 H), 2.10–2.17 (m, 1 H), 2.30–2.43 (m, 5 H), 2.65–2.88 (m, 3 H). ^{13}C NMR (63 MHz, CDCl_3 , ppm) δ = 25.3, 27.9, 30.3, 30.4, 35.5, 37.7, 40.8, 46.1, 48.3, 60.7, 89.6, 144.7, 217.1. LRMS (GC–MS) m/z [%]: 318 (100) [M^+], 303 (25), 261 (30), 191 (36), 148 (36), 147 (25), 105 (27), 91 (35), 44 (42). HRMS m/z : 318.0474 [318.0481 calculated for $\text{C}_{13}\text{H}_{19}\text{OI}$ (M^+)].

rel-(3a*R*,8a*S*,*E*)-2-(Iodomethylene)-3a-methyloctahydroazulen-4(2*H*)-one (6g). Compound **3g** (35.7 mg, 122 μmol) was converted following the general procedure A (30 $^\circ\text{C}$, 24 h). After flash chromatography on silica (pentanes/ Et_2O 95:5), **6g** (28.3 mg, 93.0 μmol , 76%) was obtained as a colorless oil: R_f = 0.1 (pentanes/ Et_2O 98:2), [CAM]. ^1H NMR (500 MHz, CDCl_3 , ppm) δ = 1.16 (s, 3 H), 1.21–1.30 (m, 1 H), 1.37–1.51 (m, 2 H), 1.58–1.62 (m, 1 H), 1.86–1.94 (m, 2 H), 2.01–2.05 (m, 1 H), 2.07–2.11 (m, 1 H), 2.26–2.29 (m, 1 H), 2.32–2.35 (m, 1 H), 2.70–2.78 (m, 3 H), 5.93 (m, 1 H). ^{13}C NMR (63 MHz, CDCl_3 , ppm) δ = 24.9, 27.9, 30.4, 35.7, 40.7, 41.2, 44.7, 46.2, 60.3, 70.4, 152.6, 216.4. LRMS (GC–MS) m/z [%]: 304 (33) [M^+], 247 (28), 177 (31), 159 (20), 105 (25), 91 (100), 77 (48). HRMS m/z : 305.0396 [305.0397 calculated for $\text{C}_{12}\text{H}_{18}\text{OI}$ ($\text{M} + \text{H}^+$)].

rel-(6a*S*,11a*S*,*E*)-5-(Iodomethylene)decahydro-1*H*-benzo[*c*]azulen-11(2*H*)-one (6h). Compound **3h** (29.8 mg, 103 μmol) was converted following the general procedure A (30 $^\circ\text{C}$, 24 h). After flash chromatography on silica (pentanes/ Et_2O 95:5), **6h** (28.2 mg, 81.9 μmol , 80%) was obtained as a colorless oil: R_f = 0.27 (petroleum ether/ Et_2O 95:5), [CAM]. ^1H NMR (400 MHz, CDCl_3 , ppm) δ = 0.96–1.08 (m, 1 H), 1.15–1.49 (m, 8 H), 1.84–1.94 (m, 5 H), 2.00–2.06 (m, 2 H), 2.21–2.25 (m, 1 H), 2.75–2.87 (m, 3 H), 5.86–5.88 (m, 1 H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 20.9, 22.7, 23.6, 28.3, 30.5, 31.7, 34.9, 39.7, 43.8, 44.4, 44.6, 62.4, 70.2, 154.9, 215.9. LRMS (GC–MS) m/z [%]: 344 (41) [M^+], 326 (16), 287 (47), 217 (100), 199 (21), 91 (20). HRMS m/z : 367.0527 [367.0529 calculated for $\text{C}_{15}\text{H}_{21}\text{OINa}$ ($\text{M} + \text{Na}^+$)].

rel-(3a*S*,7a*R*,*E*)-2-(Iodomethylene)-3a-methylhexahydro-1*H*-inden-4(2*H*)-one (6j). Compound **3j** (23.1 mg, 97.7 μmol) was converted following the general procedure A (–6 $^\circ\text{C}$, 24 h). After flash chromatography on silica (pentanes/ Et_2O 98:2), **6j** (6.8 mg, 23.4 μmol , 24%) was obtained as a colorless oil: R_f = 0.28 (pentanes/ Et_2O 9:1), [CAM]. ^1H NMR (500 MHz, CDCl_3 , ppm) δ = 1.20 (s, 3 H), 1.60–1.67 (m, 1 H), 1.80–1.87 (m, 1 H), 1.91–1.97 (m, 2 H), 2.00–2.03 (m, 1 H), 2.08–2.14 (m, 1 H), 2.26–2.31 (m, 1 H), 2.32–2.36 (m, 1 H), 2.42–2.50 (m, 2 H), 3.09 (d, J = 16.2 Hz, 1 H), 5.96–5.97 (m, 1 H). ^{13}C NMR (126 MHz, CDCl_3 , ppm) δ = 22.9, 23.6, 25.9, 38.1, 41.4, 43.6, 48.0, 56.5, 71.0, 152.0, 214.2. LRMS (GC–MS) m/z [%]: 290 (100) [M^+], 275 (42), 247 (15), 232 (27), 219 (4), 205 (6), 163 (19), 145 (8), 105 (19), 91 (21). HRMS m/z : 290.0161 [290.0162 calculated for $\text{C}_{11}\text{H}_{15}\text{OI}$ (M^+)].

rel-(3a*S*,7a*R*,*E*)-2-(Iodo(phenyl)methylene)-3a-methylhexahydro-1*H*-inden-4(2*H*)-one (6k). Compound **3k** (32.5 mg, 104 μmol) was converted following the general procedure A (30 $^\circ\text{C}$, 24 h). After flash chromatography on silica (pentanes/ Et_2O 9:1), **6k** (22.8 mg, 62.3 μmol , 60%) was obtained as a colorless oil: R_f = 0.32 (petroleum ether/ Et_2O 8:2), [CAM/UV]. ^1H NMR (600 MHz, CDCl_3 , ppm) δ = 1.19 (s, 3 H), 1.71–1.74 (m, 1 H), 1.88–1.92 (m, 1 H), 1.96–2.04 (m, 3 H), 2.33–2.39 (m, 2 H), 2.47–2.51 (m, 1 H), 2.64–2.73 (m, 1 H), 3.11 (dd, J = 16.6, 1.7 Hz, 1 H), 7.23–7.36 (m, 5 H). ^{13}C NMR (151 MHz, CDCl_3 , ppm) δ = 22.9, 23.4, 25.6, 38.0, 41.8, 45.4, 47.7, 56.7, 91.5, 127.6, 128.2, 128.7, 143.7, 147.8, 213.8. LRMS (GC–MS) m/z [%]: 366 (25) [M^+], 240 (62), 239 (100), 197 (34), 181 (47), 155 (30), 115 (49), 91 (42). HRMS m/z : 389.0372 [389.0373 calculated for $\text{C}_{17}\text{H}_{19}\text{OINa}$ ($\text{M} + \text{Na}^+$)].

rel-(3a*S*,7a*R*,*E*)-1-(Iodomethylene)octahydro-1*H*-indene-3a-carbaldehyde (6l). **3l** (31.5 mg, 133 μmol) was converted following the general procedure A (30 $^\circ\text{C}$, 4 h). After flash chromatography on silica (pentanes/ Et_2O 95:5), **6l** (7.9 mg, 27.2 μmol , 20%) was obtained as a colorless oil: R_f = 0.33 (pentanes/ Et_2O 95:5), [CAM]. ^1H NMR (500 MHz, CDCl_3 , ppm) δ = 1.28–1.38 (m, 4 H), 1.49–1.55 (m, 2 H), 1.59–1.64 (m, 1 H), 1.76–1.85 (m, 3 H), 2.39–2.43 (m, 2 H), 2.81 (s, 1 H), 5.95 (q, J = 2.5 Hz, 1 H), 9.49 (s, 1 H). ^{13}C NMR (63 MHz, CDCl_3 , ppm) δ = 21.0, 22.4, 25.1, 26.5, 29.8, 34.9, 46.6, 57.9,

71.0, 155.2, 204.6. LRMS (GC–MS) m/z [%]: 290 (79) [M^+], 272 (4), 261 (6), 248 (4), 233 (4), 219 (4), 163 (100), 145 (23), 135 (15), 91 (50). HRMS m/z : 290.0157 [290.0162 calculated for $\text{C}_{11}\text{H}_{15}\text{OI}$ (M^+)].

(*E*)-(3-(Iodo(3-methoxyphenyl)methylene)-1-methylcyclopentyl)(phenyl)methanone (6m). Compound **3m** (30.6 mg, 80.8 μmol) was converted following the general procedure A (30 $^\circ\text{C}$, 24 h). After flash chromatography on silica (pentanes/ Et_2O 95:5), **6m** (20.0 mg, 46.3 μmol , 57%) was obtained as a colorless oil: R_f = 0.21 (pentanes/ Et_2O 95:5), [CAM/UV]. ^1H NMR (500 MHz, CDCl_3 , ppm) δ = 1.39 (s, 3 H), 1.98–2.04 (m, 1 H), 2.35–2.39 (m, 1 H), 2.41–2.45 (m, 1 H), 2.54–2.66 (m, 2 H), 3.01 (d, J = 16.6 Hz, 1 H), 3.80 (s, 3 H), 6.76–6.78 (m, 1 H), 6.83–6.84 (m, 1 H), 6.85–6.87 (m, 1 H), 7.20 (t, J = 7.9 Hz, 1 H), 7.39–7.42 (m, 2 H), 7.47–7.50 (m, 1 H), 7.76–7.78 (m, 2 H). ^{13}C NMR (63 MHz, CDCl_3 , ppm) δ = 24.6, 36.1, 39.6, 44.2, 55.4, 56.6, 91.2, 113.5, 114.5, 121.2, 128.4, 128.7, 129.3, 132.0, 136.9, 145.1, 149.4, 159.4, 205.7. LRMS (GC–MS) m/z [%]: 432 (34) [M^+], 327 (4), 305 (88), 287 (8), 263 (20), 200 (8), 185 (12), 145 (16), 105 (100), 77 (21). HRMS m/z : 432.0574 [432.0581 calculated for $\text{C}_{21}\text{H}_{21}\text{O}_2\text{I}$ (M^+)].

((2-(Cyclohex-1-en-1-yl)-5-phenylpent-4-yn-2-yl)oxy)trimethylsilane (1b). R_f = 0.83 (pentanes/ethylacetate 8:2), [CAM/UV]. ^1H NMR (400 MHz, CDCl_3 , ppm) δ = 0.16 (s, 9 H), 1.54 (s, 3 H), 1.58–1.69 (m, 4 H), 2.09–2.11 (m, 4 H), 2.61–2.72 (m, 2 H), 5.76–5.78 (m, 1 H), 7.28–7.31 (m, 3 H), 7.38–7.41 (m, 2 H). ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ = 2.3, 22.4, 23.1, 24.3, 25.3, 26.3, 33.9, 77.5, 82.4, 87.9, 121.3, 124.2, 127.4, 128.2, 131.5, 141.4. LRMS (GC–MS) m/z [%]: 312 (2) [M^+], 198 (17), 197 (100), 115 (8), 73 (57). HRMS m/z : 335.1799 [335.1802 calculated for $\text{C}_{20}\text{H}_{28}\text{OSiNa}$ ($\text{M} + \text{Na}^+$)].

rel-(1*R*,2*R*)-2-(3-(3-Methoxyphenyl)prop-2-yn-1-yl)-1-(prop-1-en-2-yl)cyclohexyl)oxy)trimethylsilane (3c). R_f = 0.35 (pentanes/ Et_2O 99:1), [CAM]. ^1H NMR (250 MHz, CDCl_3 , ppm) δ = 0.10 (s, 9 H), 1.48 (s, 3 H), 2.04–2.23 (m, 1 H), 2.32–2.52 (m, 3 H), 3.82 (s, 3 H), 5.03–5.04 (m, 1 H), 5.39 (m, 1 H), 6.83–6.88 (m, 1 H), 6.94–7.02 (m, 2 H), 7.18–7.43 (m, 6 H). ^{13}C NMR (63 MHz, CDCl_3 , ppm) δ = 1.9, 12.4, 19.5, 38.0, 55.4, 80.4, 81.0, 90.6, 111.6, 114.3, 116.6, 124.3, 125.2, 126.3, 127.0, 128.1, 129.3, 144.6, 148.8, 159.4. LRMS (GC–MS) m/z [%]: 378 (48) [M^+], 363 (81), 350 (15), 337 (56), 323 (40), 301 (29), 288 (19), 273 (29), 260 (21), 219 (92), 186 (23), 145 (56), 115 (25), 73 (100). HRMS (APCI) m/z : 357.2223 [357.2244 calculated for $\text{C}_{22}\text{H}_{33}\text{O}_2\text{Si}$ ($\text{M} + \text{H}^+$)].

rel-Trimethyl(((1*R*,2*R*)-2-(3-(4-nitrophenyl)prop-2-yn-1-yl)-1-(isopropenyl)-cyclohexyl)oxy)silane (3d). R_f = 0.68 (pentanes/ Et_2O 95:5), [CAM/UV]. ^1H NMR (250 MHz, CDCl_3 , ppm) δ = 0.17 (m, 9 H), 1.27–1.51 (m, 2 H), 1.55–1.78 (m, 9 H), 1.88–1.94 (m, 1 H), 2.20 (dd, J = 17.4, 10.3 Hz, 1 H), 2.53 (dd, J = 17.4, 3.6 Hz, 1 H), 4.93–4.94 (m, 1 H), 5.03–5.04 (m, 1 H), 7.49 (d, J = 8.9 Hz, 2 H), 8.14 (d, J = 8.9 Hz, 2 H). ^{13}C NMR (63 MHz, CDCl_3 , ppm) δ = 3.0, 20.6, 20.7, 21.9, 25.5, 27.0, 35.5, 42.7, 79.9, 81.3, 97.8, 112.2, 123.6, 131.7, 132.3, 146.6, 149.0. LRMS (GC–MS) m/z [%]: 371 (48) [M^+], 356 (54), 328 (75), 314 (29), 300 (17), 266 (17), 169 (23), 73 (100). HRMS m/z : 372.1995 [372.1990 calculated for $\text{C}_{21}\text{H}_{30}\text{O}_3\text{NSi}$ ($\text{M} + \text{H}^+$)].

rel-Triethyl((4-((1*R*,2*R*)-2-(isopropenyl)-2-((trimethylsilyl)oxy)cyclohexyl)but-2-yn-1-yl)oxy)silane (3e). R_f = 0.72 (pentanes/ Et_2O 98:2), [CAM]. ^1H NMR (250 MHz, CDCl_3 , ppm) δ = 0.13–0.16 (m, 9 H), 0.64 (q, J = 7.8 Hz, 6 H), 0.97 (t, J = 7.9 Hz, 9 H), 1.22–1.40 (m, 2 H), 1.50–1.72 (m, 9 H), 1.87–1.99 (m, 2 H), 2.28 (ddd, J = 17.0, 5.3, 2.3 Hz, 1 H), 4.28 (t, J = 2.2 Hz, 2 H), 4.88–4.89 (m, 1 H), 4.97 (m, 1 H). ^{13}C NMR (63 MHz, CDCl_3 , ppm) δ = 2.9, 4.7, 6.9, 19.7, 20.5, 22.1, 25.5, 26.8, 35.6, 42.7, 51.8, 79.0, 81.4, 85.9, 111.9, 149.2. LRMS (GC–MS) m/z [%]: 394 (6) [M^+], 379 (13), 351 (13), 337 (13), 262 (23), 247 (27), 233 (13), 219 (25), 197 (100), 169 (17), 147 (17), 73 (52). HRMS m/z : 417.2616 [417.2616 calculated for $\text{C}_{22}\text{H}_{42}\text{O}_2\text{NaSi}_2$ ($\text{M} + \text{Na}^+$)].

rel-Trimethyl(((1*R*,2*R*)-2-(prop-2-yn-1-yl)-[1,1'-bi(cyclohexan)]-1'-en-1-yl)oxy)silane (3h). R_f = 0.35 (petroleum ether), [CAM]. ^1H NMR (400 MHz, CDCl_3 , ppm) δ = 0.15 (s, 9 H), 1.34–1.72 (m, 12 H), 1.85–1.97 (m, 5 H), 2.06–2.11 (m, 2 H), 2.31

(dt, $J = 6.3$ Hz, 3.4 Hz, 1 H), 5.69 – 5.70 (m, 1 H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) $\delta = 2.8, 19.2, 22.0, 22.4, 23.3, 25.1, 25.2, 25.7, 26.6, 35.1, 42.5, 68.2, 80.8, 85.5, 122.04, 140.4$. LRMS (GC–MS) m/z [%]: 290 (18) [M^+], 247 (100), 233 (35), 209 (89), 181 (18), 91 (23), 73 (84). HRMS (APCI) m/z : 291.2111 [291.2139 calculated for $\text{C}_{18}\text{H}_{31}\text{OSi}$ ($\text{M} + \text{H}^+$)].

rel-Trimethyl(((1*R*,2*R*)-1-(isopropenyl)-2-(prop-2-yn-1-yl)-cyclopentyl)oxy)silane (3j). $R_f = 0.37$ (pentanes), [CAM]. ^1H NMR (360 MHz, CDCl_3 , ppm) $\delta = 0.09$ – 0.11 (m, 9 H), 1.50 – 1.69 (m, 2 H), 1.73 – 1.82 (m, 5 H), 1.86 – 2.09 (m, 5 H), 2.21 – 2.28 (m, 1 H), 4.87 – 4.97 (m, 2 H). ^{13}C NMR (63 MHz, CDCl_3 , ppm) $\delta = 2.1, 17.8, 19.9, 21.7, 29.5, 36.8, 47.7, 67.8, 85.4, 86.0, 111.8, 147.7$. LRMS (GC–MS) m/z [%]: 235 (4) [$\text{M}^+ - \text{H}$], 221 (46), 207 (25), 193 (63), 181 (25), 169 (25), 155 (15), 131 (19), 73 (100). HRMS (APCI) m/z : 237.1652 [237.1669 calculated for $\text{C}_{14}\text{H}_{25}\text{OSi}$ ($\text{M} + \text{H}^+$)].

rel-Trimethyl(((1*R*,2*R*)-2-(3-phenylprop-2-yn-1-yl)-1-(prop-1-en-2-yl)cyclopentyl)oxy)silane (3k). $R_f = 0.8$ (petrolether/ Et_2O), [CAM]. ^1H NMR (400 MHz, CDCl_3 , ppm) $\delta = 0.14$ (s, 9 H), 1.63 – 1.72 (m, 2 H), 1.79 (m, 3 H), 1.81 – 1.87 (m, 2 H), 1.98 – 2.18 (m, 3 H), 2.27 – 2.34 (m, 1 H), 2.49 (dd, $J = 17.1, 3.8$ Hz, 1 H), 4.92 – 5.03 (m, 2 H), 7.26 – 7.31 (m, 3 H), 7.38 – 7.41 (m, 2 H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) $\delta = 2.0, 18.6, 19.8, 21.6, 29.6, 36.7, 47.8, 80.2, 86.9, 91.0, 111.5, 124.4, 127.3, 128.1, 131.5, 147.7$. LRMS (GC–MS) m/z [%]: 312 (32) [M^+], 297 (45), 269 (30), 207 (46), 179 (28), 115 (39), 73 (100). HRMS m/z : 335.1782 [335.1802 calculated for $\text{C}_{20}\text{H}_{28}\text{OSiNa}$ ($\text{M} + \text{Na}^+$)].

((1-(Cyclohex-1-en-1-yl)pent-4-yn-1-yl)oxy)trimethylsilane (3l). $R_f = 0.15$ (pentanes), [CAM]. ^1H NMR (250 MHz, CDCl_3 , ppm) $\delta = 0.08$ – 0.10 (m, 9 H), 1.45 – 1.75 (m, 6 H), 1.77 – 1.88 (m, 1 H), 1.92 (t, $J = 2.7$ Hz, 1 H), 2.00 – 2.08 (m, 3 H), 2.15 – 2.22 (m, 2 H), 4.06 (dd, $J = 7.9, 5.2$ Hz, 1 H), 5.59 – 5.60 (m, 1 H). ^{13}C NMR (63 MHz, CDCl_3 , ppm) $\delta = 0.3, 15.2, 22.8, 22.9, 23.4, 25.2, 35.0, 68.3, 76.0, 84.7, 123.0, 139.5$. LRMS (GC–MS) m/z [%]: 236 (4) [M^+], 221 (2), 208 (6), 183 (100), 73 (25). HRMS (APCI) m/z : 235.1517 [235.1513 calculated for $\text{C}_{14}\text{H}_{23}\text{OSi}$ ($\text{M}^+ - \text{H}$)].

((7-(3-Methoxyphenyl)-2-methyl-3-phenylhept-1-en-6-yn-3-yl)oxy)trimethylsilane (3m). $R_f = 0.35$ (pentanes/ Et_2O 99:1), [CAM]. ^1H NMR (250 MHz, CDCl_3 , ppm) $\delta = 0.10$ (s, 9 H), 1.48 (s, 3 H), 2.04 – 2.23 (m, 1 H), 2.32 – 2.52 (m, 3 H), 3.82 (s, 3 H), 5.03 – 5.04 (m, 1 H), 5.39 (m, 1 H), 6.83 – 6.88 (m, 1 H), 6.94 – 7.02 (m, 2 H), 7.18 – 7.43 (m, 6 H). ^{13}C NMR (63 MHz, CDCl_3 , ppm) $\delta = 1.9, 12.4, 19.5, 38.0, 55.4, 80.4, 81.0, 90.6, 111.6, 114.3, 116.6, 124.3, 125.2, 126.3, 127.0, 128.1, 129.3, 144.6, 148.8, 159.4$. LRMS (GC–MS) m/z [%]: 378 (48) [M^+], 363 (81), 350 (15), 337 (56), 323 (40), 301 (29), 288 (19), 273 (29), 260 (21), 219 (92), 186 (23), 145 (56), 115 (25), 73 (100). HRMS m/z : 378.2003 [378.2010 calculated for $\text{C}_{24}\text{H}_{30}\text{O}_2\text{Si}$ (M^+)].

■ ASSOCIATED CONTENT

● Supporting Information

^1H and ^{13}C NMR spectra of all and 2D-NMR data of selected examples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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