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Synthesis of Angularly Fused Carbocycles via Tandem Radical Cyclization of α-Carbonyl Radicals

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An α-carbonyl radical cyclization approach towards the synthesis of angularly fused tricyclic systems is described. On reduction with tributyltin hydride, bromo ketones yield a α-carbonyl radical that undergoes successive 5-*exo*-*dig*/*trig* cyclizations, resulting in two or four contiguous stereocenters.

Introduction

Tandem-cyclization strategies for the synthesis of angularly fused carbocycles[1,2] have gained considerable prominence since these frameworks exist in many natural products. The tandem construction of the rings can provide an inherently efficient approach to the synthesis of an angularly fused tricyclic system if the stereochemistry is controlled. Thus, tandem radical cyclization[3] ranks among the most powerful methods to construct a tricyclic ring system in a single step from a monocyclic precursor. During the last fifteen years, Sha and co-workers exploited the α-carbonyl radical cyclization strategy to synthesize several natural products, including (±)-modhephene,[4a] (–)-dendrobine,[4b] (–)-5-oxosilphiperfol-6-ene,[4c] dimethyl gloiosphone A[4d] and (+)-paniculatine.[4e] The syntheses of these natural products were achieved by homolytic Bu_3SnH-mediated cleavage of the corresponding α-iodo cycloalkanones followed by intramolecular cyclization.

Results and Discussion

The angular tricyclic framework has received prominent attention among synthetic chemists. Several elegant strategies reported[5] for such ring systems are based on a tandem radical cyclization. Hence, a systematic study was undertaken to synthesize the angular tricyclic skeletons **1**–**3** of the natural products agariblazeispirol C,[6] dankasterone[7] and laurenene[8] following the α-carbonyl radical cyclization approach established by Sha and co-workers.[4]

Towards the realization of this objective, all our attempts to prepare the required α-iodo cycloalkanones were found to be cumbersome. Additionally, we found it difficult to reproduce the iodination of silyl enol ether when using the existing NaI/*m*CPBA protocol.[9] On the other hand, even though, in some cases the α-iodo cycloalkanones were prepared using Sha's procedure in reasonable yields, they are highly unstable and photo-labile. In particular, tertiary α-iodo ketone undergoes extensive decomposition even at room temperature (Figure 1).

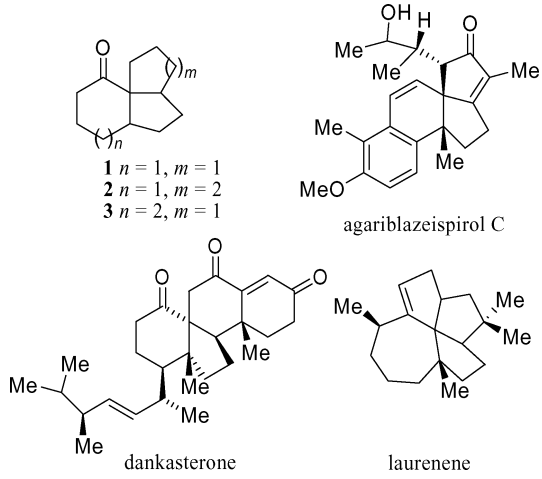

Figure 1. Natural products containing angular tricyclic units.

We believe that the labile nature of α-iodo cycloalkanones is a bottleneck for applying the α-carbonyl radical cyclization strategy to the synthesis of core skeleton of the above-mentioned natural products. In this regard, we have recently reported a facile preparation of α-bromo and α-iodo cycloalkanones using $NaX/FeCl_3$.[10] As expected, relatively, the α-bromo cycloalkanones were found to be more stable.

Initially, we tested the tandem radical cyclization approach with the synthesis of 6–5–5 angular tricyclic systems[4e] **7a** and **7b** (Scheme 1). A CuI-promoted 1,4-ad-

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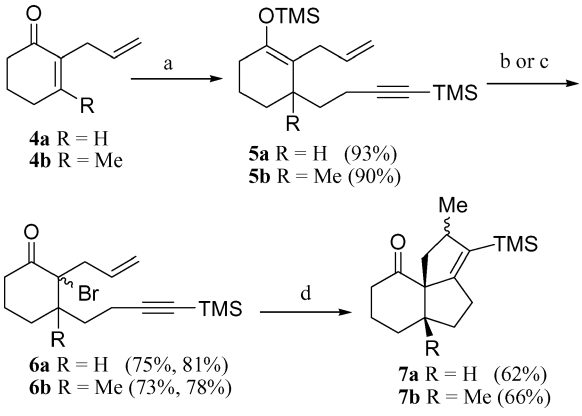
dition of 4-(trimethylsilyl)-3-butynylmagnesium bromide to enones[11,12] **4a** and **4b** followed by trapping of the resulting enolate with trimethylsilyl chloride afforded silyl enol ether **5a** and **5b**, which on bromination using KBr/*m*CPBA or $NaBr/FeCl_3$ delivered bromo compounds **6a** and **6b** in good yields. On treatment of **6a/6b** with tributyltin hydride and AIBN in benzene at reflux temperature through slow addition using a syringe pump technique (see Exp. Section), tandem radical cyclization occurred smoothly to afford angular 6–5–5 tricyclic systems **7a/7b** in 62 and 66% yields, respectively, through a combination of 5-*exo*-*dig* and 5-*exo*-*trig* cyclizations.

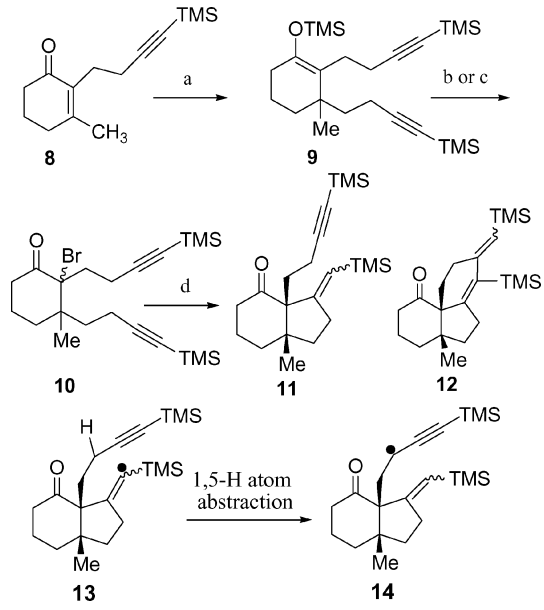


Scheme 1. Reagents and conditions: (a) (i) 4-(bromobut-1-ynyl)trimethylsilane; (ii) CuI, –78 °C; (iii) TMSCl, –78 °C; (iv) Et_3N, –78 °C to room temp.; (b) KBr/*m*CPBA (dry), THF, 0 °C to room temp., 8 h; (c) $NaBr/FeCl_3$, CH_3CN, 0 °C to room temp., 4 h; (d) Bu_3SnH/AIBN, syringe addition pump, 6 h, benzene, 80 °C.

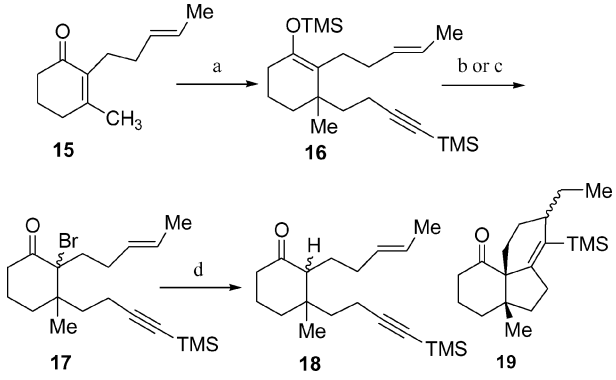
Next, the synthesis of the 6–5–6 angular tricyclic skeleton of dankasterone was planned. The required enone **8** was prepared using established procedure.[13] The CuI induced 1,4-addition of Grignard reagent to enone **8** followed by bromination using KBr/*m*CPBA or $NaBr/FeCl_3$ gave the bromo compound **10** in 68 and 74% yields, respectively. Tandem radical cyclization (TRC) of the bromo compound **10** using Bu_3SnH/AIBN under high dilution conditions via syringe addition pump at benzene reflux temperature afforded a bicyclic product **11**, instead of the expected tricyclic product **12** (Scheme 2). We presume that the bicyclic vinyl radical intermediate **13** might have formed a stable propargyl radical **14** via [1,5]-H abstraction as observed by Malacria and co-workers.[14]

We devised another synthetic route for the synthesis of 6–5–6 angular tricyclic system **19**. The required bromo compound **17** was prepared by using a known procedure.[13] However, tandem radical cyclization of bromo compound **17** also did not lead to the expected tricyclic product **19**; only reduction product **18** was isolated (Scheme 3). It should be noted that radical cyclization of **17** did not produce even the corresponding bicyclic product.

To generalize the approach, we undertook tandem radical cyclization in a seven-membered ring system. (Scheme 4). The required enone **20** was obtained from cy-



Scheme 2. Reagents and conditions: (a) (i) 4-(bromobut-1-ynyl)trimethylsilane; (ii) CuI, –78 °C; (iii) TMSCl, –78 °C; (iv) Et_3N, –78 °C to room temp., 86%; (b) KBr/*m*CPBA (dry), THF, 0 °C to room temp., 8 h, 68%; (c) $NaBr/FeCl_3$, CH_3CN, 0 °C to room temp., 4 h, 74%; (d) Bu_3SnH/AIBN, syringe addition pump, 6 h, benzene, 80 °C, 66%.

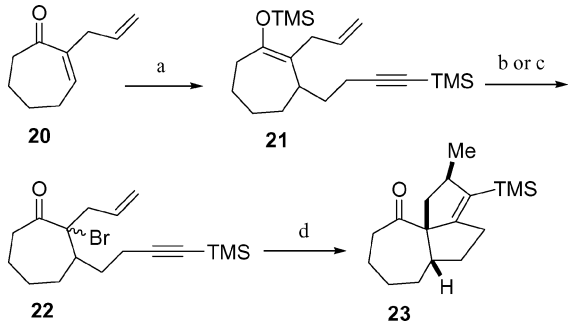


Scheme 3. Reagents and conditions: (a) (i) 4-(bromobut-1-ynyl)trimethylsilane; (ii) CuI, –78 °C; (iii) TMSCl, –78 °C; (iv) Et_3N, –78 °C to room temp., 87%; (b) KBr/*m*CPBA (dry), THF, 0 °C to room temp., 8 h, 65%; (c) $NaBr/FeCl_3$, CH_3CN, 0 °C to room temp., 4 h, 71%; (d) Bu_3SnH/AIBN, syringe addition pump, 6 h, benzene, 80 °C, 56%.

clohept-2-enone by means of a thioketone protocol[15] published for a six-membered ring system. A customary 1,4-addition, followed by bromination, afforded the bromo compound **22**, which underwent successive 5-*exo*-*dig* and 5-*exo*-*trig* radical cyclizations to give the angular tricycle **23** in 68% yield.

The stereochemistry of **23** was confirmed by X-ray crystallography analysis, Figure 2.

Since the natural product laurenene possesses an angular methyl group, the required α-bromo ketone **26** was prepared by using an established procedure. Surprisingly, the tandem radical cyclization of bromo compound **26** also



Scheme 4. Reagents and conditions: (a) (i) 4-(bromobut-1-ynyl)trimethylsilane; (ii) CuI, –78 °C; (iii) TMSCl, –78 °C; (iv) Et_3N, –78 °C to room temp., 95%; (b) KBr/*m*CPBA (dry), THF, 0 °C to room temp., 8 h, 67%; (c) NaBr/$FeCl_3$, CH_3CN, 0 °C to room temp., 4 h, 74%; (d) Bu_3SnH/AIBN, syringe addition pump, 6 h, benzene, 80 °C, 68%.

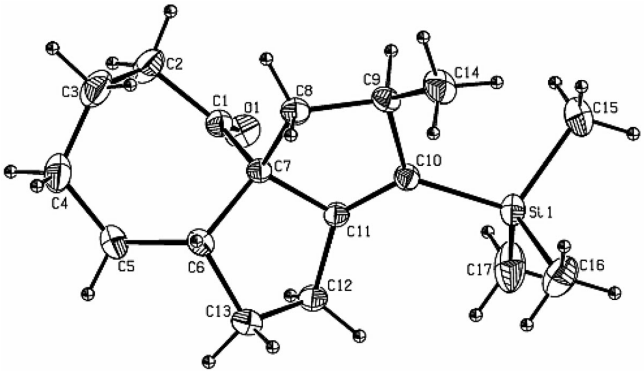
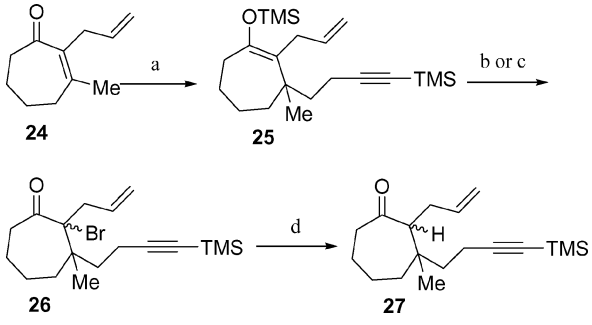


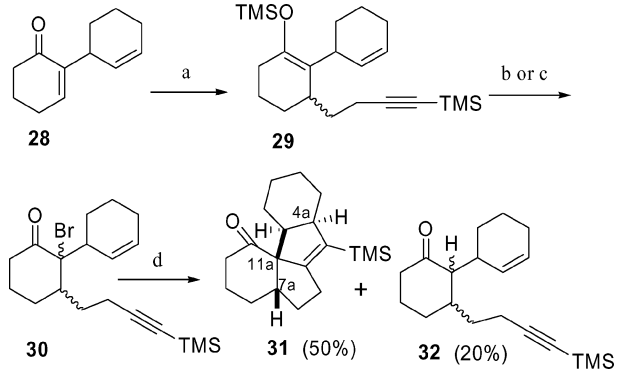
Figure 2. ORTEP view of tricyclic compound **23**.

did not afford the expected tricyclic product; always the corresponding radical-quenched product **27** was isolated (Scheme 5).



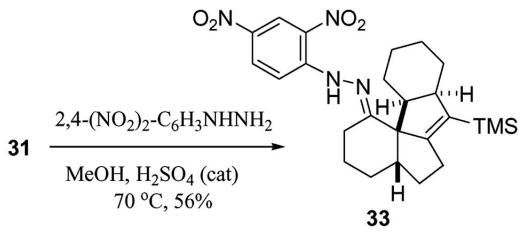
Scheme 5. Reagents and conditions: (a) (i) 4-(bromobut-1-ynyl)trimethylsilane; (ii) CuI, –78 °C; (iii) TMSCl, –78 °C; (iv) Et_3N, –78 °C to room temp., 95%; (b) KBr/*m*CPBA (dry), THF, 0 °C to room temp., 8 h, 63%; (c) NaBr/$FeCl_3$, CH_3CN, 0 °C to room temp., 4 h, 71%; (d) Bu_3SnH/AIBN, syringe addition pump, 6 h, benzene, 80 °C, 57%.

Finally, synthesis of angular tetracycle possessing four contiguous stereocenters was planned (Scheme 6). The CuI-mediated conjugate addition of 4-(trimethylsilyl)-3-butynylmagnesium bromide to enone **28** followed by trapping of the resulting enolate **29** with TMSCl and bromination with KBr/*m*CPBA or NaBr/$FeCl_3$ yielded bromo ketone **30** in good yields. When the latter was treated with tributyltin hydride and AIBN in benzene using the syringe-pump technique, tandem radical cyclization occurred smoothly to afford tetracycle **31** possessing four contiguous stereocenters in 50% yield along with the reduction product **32** in 20% yield.



Scheme 6. Reagents and conditions: (a) (i) 4-(bromobut-1-ynyl)trimethylsilane; (ii) CuI, –78 °C; (iii) TMSCl, –78 °C; (iv) Et_3N, –78 °C to room temp., 92%; (b) KBr/*m*CPBA (dry), THF, 0 °C to room temp., 8 h, 65%; (c) NaBr/$FeCl_3$, CH_3CN, 0 °C to room temp., 4 h, 70%; (d) Bu_3SnH/AIBN, syringe addition pump, 6 h, benzene, 80 °C.

Treatment of compound **31** with 2,4-dinitrophenyl hydrazine in the presence of sulfuric acid in catalytic proportion afforded hydrazone **33** as orange crystals suitable for X-ray



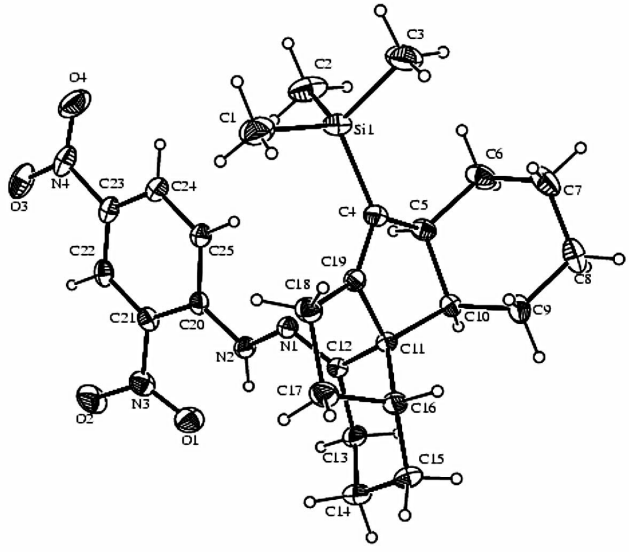


Figure 3. ORTEP view of tetracyclic compound **33**.

crystallography. The stereostructure of the tetracyclic compound **33** was confirmed by the single-crystal X-ray diffraction analysis, Figure 3.

Conclusions

In conclusion, an efficient α-carbonyl radical-initiated tandem cyclization for stereo-controlled synthesis of angularly fused tricyclic/tetracyclic systems starting from the respective α-bromo cycloalkanones was described. Attempts to prepare 6–5–6 angular tricyclic systems were unsuccessful. The synthesis of inaccessible 6–5–6 angular tricyclic system[16] and other angularly fused polycyclic systems using various silyl enol ethers and the respective α-bromo cycloalkanones involving a RCM approach is under investigation.

Experimental Section

General Methods: All melting points are uncorrected. IR spectra were recorded on a Shimadzu FT-IR 8300 instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on a JEOL 400 or 500 spectrometer at 400 and 100 or 125 MHz and Bruker-300 and 75 MHz, respectively. Mass spectra were recorded on a JEOL DX 303 HF spectrometer. Elemental analyses were carried out on a Perkin–Elmer 240 B instrument. High resolution mass analyses were performed using electrospray ionization (ESI) technique. Single-crystal X-ray analysis was performed on a Bruker Axs Kappa Apex 2 SMART CCD diffractometer.

2-Allyl-3-methylcyclohex-2-enone (4b): To a stirred suspension of cyclohexane-1,3-dione (5 g, 44.59 mmol) in 20% KOH solution (30 mL) at 0 °C containing Cu powder (150 mg), allyl bromide (4.23 mL, 49.05 mmol) was slowly added. The reaction temperature was gradually raised to room temperature and stirred for 8 h. Then NaOH (2 g) was added to re-dissolve the precipitate and washed with diethyl ether (100 mL). The acidification of aqueous layer (dil. aqueous HCl, 20 mL) gave the 2-allylcyclohexane-1,3-dione. The crude product was recrystallized from benzene (4.41 g, 65%; m.p. 124 °C). Then 2-allylcyclohexane-1,3-dione was converted into the respective isobutyl ether using isobutyl alcohol (10 mL) and PTSA (500 mg) in benzene (80 mL) at reflux involving Dean–Stark for 5 h. A solution of isobutyl ether (2.26 g, 7.71 mmol) was treated with ethereal solution of CH_3MgI (2.5 M, 6.5 mL) in dry ether (50 mL) at 0 °C, raised to room temperature and stirred for 3 h. It was then quenched with saturated NH_4Cl solution and extracted with diethyl ether (2 × 30 mL). To a solution of the resulting alcohol (2.16 g, 9.64 mmol) in diethyl ether (15 mL) were added PTSA (2 g) and water (15 mL) with vigorous stirring for 6 h at room temperature. Extraction with diethyl ether (2 × 20 mL), followed by flash column chromatographic purification (silica gel, 3% ethyl acetate in hexane) afforded **4b** (838 mg, 58%) as a pale yellow liquid. IR (film): $\tilde{\nu}$ = 1665, 1631, 1428, 909, 751 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.68–5.61 (m, 1 H, $CH_2CH{=}CH_2$), 4.86–4.81 (m, 2 H, $CH_2CH{=}CH_2$), 2.96 (d, J = 6.0 Hz, 2 H, $CH_2CH{=}CH_2$), 2.30–2.26 (m, 4 H, $CH_2CH_2CH_2$), 1.88–1.82 (m, 5 H, $CH_2CH_2CH_2CH$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 197.9, 156.6, 135.5, 132.8, 114.0, 37.4, 32.6, 28.9, 22.0, 20.9 ppm. MS (EI): m/z (%) = 150 (67) $[M]^+$, 149 (68), 134 (100). $C_{10}H_{14}O$ (150.10): calcd. C 79.96, H 9.39; found C 79.87, H 9.27.

{2-Allyl-3-[4-(trimethylsilyl)but-3-ynyl]cyclohex-1-enyloxy}trimethylsilane (5a): To a stirred suspension of Mg turnings (705 mg, 29.41 mmol) in THF (10 mL) was added a solution of 4-bromo-1-trimethylsilyl-1-butyne (3.01 g, 14.70 mmol) and 1,2-dibromoethane (0.1 mL) in dry THF (10 mL) with a syringe pump (1 h). After the addition, the reaction mixture was heated to reflux for 1 h to ensure the completion of the Grignard formation; it was then diluted with dry THF (30 mL) and cooled to –78 °C. CuI (2.80 g, 14.70 mmol) was added. The reaction mixture was stirred for 30 min. To this mixture was added **4a** (800 mg, 5.88 mmol) in dry THF (5 mL) dropwise, followed by chlorotrimethylsilane (0.89 mL, 7.05 mmol) and triethylamine (1.06 mL, 7.64 mmol). The reaction mixture was warmed to room temperature, stirred for 12 h and quenched with saturated $NaHCO_3$ solution (10 mL). The resulting black precipitate was filtered off and washed with hexane (40 mL). The combined organic layer was washed with $NaHCO_3$ solution (2 × 20 mL) and dried (K_2CO_3). Filtration followed by removal of the solvent gave crude **5a** (1.82 g, 93%) as a pale yellow liquid. IR (film): $\tilde{\nu}$ = 2174, 1612, 845, 760 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.78–5.71 (m, 1 H, $CH_2CH{=}CH_2$), 5.13–4.93 (m, 2 H, $CH_2CH{=}CH_2$), 2.87 (dd, J = 7.3, 15.7 Hz, 1 H, $CHCH{=}CH_2$), 2.64 (dd, J = 7.3, 15.7 Hz, 1 H, $CHCH{=}CH_2$), 2.47–2.35 (m, 1 H, CH_2CHCH_2), 2.21–2.04 (m, 4 H, CH_2CH_2), 1.65–1.52 (m, 6 H, $CH_2CH_2CH_2$), 0.17 (s, 9 H, $SiMe_3$), 0.14 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 144.9, 136.9, 116.6, 114.4, 107.5, 84.2, 34.7, 32.2, 31.2, 30.2, 26.0, 19.2, 17.8, 0.60, 0.07 ppm. MS (EI): m/z (%) = 334 (16) $[M]^+$, 318 (13), 260 (18), 221 (19), 209 (30), 208 (100). HRMS: calcd. for $C_{19}H_{34}OSi_2$ $[M]^+$ 334.2148; found 334.2153. Crude **5a** was used for the next step without further purification.

{4-[2-Allyl-1-methyl-3-(trimethylsilyloxy)cyclohex-2-enyl]but-1-ynyl}trimethylsilane (5b): The 1,4-addition was performed using enone **4b** (850 mg, 5.66 mmol), Grignard reagent [prepared from Mg (680 mg, 28.33 mmol), 4-bromo-1-trimethylsilyl-1-butyne (2.90 g, 14.16 mmol)], CuI (2.69 g, 14.16 mmol), TMSCl (0.86 mL, 6.80 mmol) and Et_3N (1.03 mL, 7.36 mmol) following the same procedure as for **5a** to afford crude **5b** (1.77 g, 90%) as a pale yellow liquid. IR (film): $\tilde{\nu}$ = 2174, 1616, 847, 760 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.72–5.68 (m, 1 H, $CH_2CH{=}CH_2$), 4.99–4.85 (m, 2 H, $CH_2CH{=}CH_2$), 2.79 (dd, J = 6.5, 14.4 Hz, 1 H, $CHCH{=}CH_2$), 2.55 (dd, J = 6.5, 14.4 Hz, 1 H, $CHCH{=}CH_2$), 2.04–1.92 (m, 4 H, CH_2CH_2), 1.58–1.46 (m, 6 H, $CH_2CH_2CH_2$), 0.96 (s, 3 H, Me), 0.16 (s, 9 H, $SiMe_3$), 0.13 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 146.2, 138.2, 119.3, 113.5, 108.1, 83.6, 39.2, 37.6, 34.5, 30.6, 30.5, 26.6, 19.0, 15.1, 0.71, 0.08 ppm. MS (EI): m/z (%) = 348 (13) $[M]^+$, 333 (15), 274 (27), 223 (42), 222 (99). HRMS: calcd. for $C_{20}H_{36}OSi_2$ $[M]^+$ 348.2305; found 348.2311. Crude product **5b** was used for the next step without further purification.

2-Allyl-2-bromo-3-[4-(trimethylsilyl)but-3-ynyl]cyclohexanone (6a): To a stirred suspension of KBr (1.82 g, 15.26 mmol) in dry THF (15 mL) at 0 °C, a solution of dry *m*-CPBA (72.5% purity, 2.63 g, 15.26 mmol) in dry THF (10 mL) was added (5 min). The mixture was warmed to room temp. (10 min) and stirred for 5 min. The resulting dark brown solution was slowly added to a solution of silyl enol ether **5a** (1.7 g, 5.08 mmol) in THF (5 mL) at 0 °C for 10 min. It was then quenched (consumption of starting material indicated by TLC) with a solution of $Na_2S_2O_3$ and reaction mixture was extracted with Et_2O (3 × 30 mL). The combined organic layer was washed with $NaHCO_3$ solution (20 mL), brine and dried ($MgSO_4$). Removal of solvent followed by flash column chromatographic purification (silical gel, 0.5% ethyl acetate in hexane to 1% ethyl acetate in hexane) afforded **6a** (1.29 g, 75%) as a pale yellow

liquid. IR (film): $\tilde{\nu}$ = 2171, 1712, 1610, 845, 759 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.71–5.66 (m, 1 H, $CH_2CH{=}CH_2$), 5.20–5.08 (m, 2 H, $CH_2CH{=}CH_2$), 3.32 (dd, J = 5.6, 5.6 Hz, 1 H, $CHCH{=}CH_2$), 3.18 (m, 1 H, CH_2CHCH_2), 2.78 (dd, J = 8.4, 8.4 Hz, 1 H, $CHCH{=}CH_2$), 2.42–2.21 (m, 2 H, CH_2CH_2), 2.02–1.89 (m, 4 H, $CH_2CH_2CH_2$), 1.68–1.51 (m, 4 H, $CH_2CH_2CH_2$), 0.15 and 0.12 (2s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 203.2, 202.9, 133.4, 132.3, 119.8, 119.3, 107.1, 106.1, 76.7, 75.0, 46.4, 43.3, 41.1, 39.9, 37.1, 36.6, 29.8, 27.7, 26.5, 25.9, 24.4, 24.2, 22.0, 19.4, 17.9, 17.3, 0.16, 0.07 ppm. MS (EI): m/z (%) = 342 (15) $[M]^{+2}$, 340 (15) $[M]^+$, 308 (12), 261 (78), 170 (65), 129 (82), 73 (100). $C_{16}H_{25}BrOSi$ (340.08): calcd. C 56.30, H 7.38; found C 56.42, H 7.29.

2-Allyl-2-bromo-3-methyl-3-[4-(trimethylsilyl)but-3-ynyl]cyclohexanone (6b): Bromination using compound **5b** (1.70 g, 4.88 mmol), KBr (1.74 g, 14.65 mmol) and dry *m*-CPBA (72.5% purity, 2.52 g, 14.65 mmol) following the same procedure as for **6a** to afford **6b** (1.26 g, 73%) as a yellow liquid. IR (film): $\tilde{\nu}$ = 2173, 1712, 1613, 848, 762 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.58–5.52 (m, 1 H, $CH_2CH{=}CH_2$), 5.09–5.00 (m, 2 H, $CH_2CH{=}CH_2$), 3.89 (d, J = 15.0 Hz, 1 H, $CHCH{=}CH_2$), 2.41 (dd, J = 8.3, 5.4 Hz, 1 H, $CHCH{=}CH_2$), 2.39–2.07 (m, 2 H, CH_2CH_2), 1.96–1.60 (m, 4 H, $CH_2CH_2CH_2$), 1.32–1.19 (m, 4 H, $CH_2CH_2CH_2$), 1.01 and 0.77 (2s, 3 H, Me), 0.13 and 0.11 (2s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 204.6, 203.1, 132.1, 131.9, 118.5, 118.0, 107.8, 107.1, 84.3, 84.1, 61.3, 58.3, 45.1, 38.9, 38.5, 37.4, 37.3, 36.4, 33.7, 31.4, 31.2, 25.0, 21.8, 21.6, 19.4, 17.7, 15.0, 14.4, 0.16, 0.07 ppm. MS (EI): m/z (%) = 356 (18) $[M]^{+2}$, 354 (18) $[M]^+$, 341 (14), 278 (23), 253 (65), 190 (35), 116 (76), 82 (100). $C_{17}H_{27}BrOSi$ (354.10): calcd. C 57.45, H 7.66; found C 57.56, H 7.74.

Representative Procedure for Bromination with NaBr/$FeCl_3$. 2-Allyl-2-bromo-3-[4-(trimethylsilyl)but-3-ynyl]cyclohexanone (6a): To a solution of $FeCl_3$ (1.55 g, 9.58 mmol) in acetonitrile (20 mL), NaBr (488 mg, 4.79 mmol) was added and stirred at 0 °C for 15 min. To this, a solution of silyl enol ether **5a** (1.6 g, 4.79 mmol) in acetonitrile (10 mL) was added dropwise at 0 °C. The reaction mixture was warmed to room temperature and stirred for 4 h. It was then quenched (consumption of starting material indicated by TLC) with saturated NH_4Cl solution and reaction mixture was extracted with Et_2O (2 × 20 mL). The organic layer was separated and washed with saturated $Na_2S_2O_3$ (2 × 10 mL) solution, water (20 mL) and dried (Na_2SO_4). Removal of solvent followed by flash column chromatographic purification (silical gel, 0.5% ethyl acetate in hexane to 1% ethyl acetate in hexane) afforded **6a** (1.31 g, 81%) as a pale yellow liquid.

(9^1*S)-2-Methyl-3-(trimethylsilyl)-4,5,5a,6,7,8-hexahydro-1*H*-cyclopenta[*c*]inden-9(2*H*)-one (7a):** To a refluxing solution of bromo compound **6a** (1.3 g, 3.82 mmol) in dry benzene (200 mL) under N_2 was added a solution of Bu_3SnH (1.2 mL, 4.58 mmol) in dry benzene (20 mL) containing AIBN (94 mg, 0.57 mmol) with a syringe pump over 6 h. After addition, the reaction mixture was heated at reflux for 1 h to ensure the completion of radical cyclization and then cooled to room temperature. Benzene was removed in vacuo and the residue was dissolved in Et_2O (20 mL), then saturated aqueous KF solution was added. The resulting mixture was stirred at room temperature for 6 h. Then the organic layer was separated and washed with saturated aqueous $NaHCO_3$ solution (20 mL) followed by brine and dried ($MgSO_4$). Removal of solvent followed by flash column chromatographic purification (silica gel, 1% EtOAc in hexane to 2% EtOAC in hexane) afforded **7a** (621 mg, 62%) as a viscous liquid. IR (film): $\tilde{\nu}$ = 1704, 1612, 848, 760 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.18–3.04 (m, 1 H, CH_2CH), 2.59–2.48 (m, 1 H, CH_2CH), 2.29–2.23 (m, 2 H, CH_2CH_2), 2.16–2.11 (m, 3 H, CH_2CHCH_2), 1.92–1.90 (m, 3 H, CH_2CHCH_2), 1.65 (d, J = 12.0 Hz, 2 H, CH_2CH_2), 1.32–1.25 (m, 2 H, CH_2CH_2), 1.05 (d, J = 7.2 Hz, 3 H, Me), 0.12 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 213.2, 161.1, 137.4, 74.0, 49.1, 48.0, 45.2, 40.0, 30.7, 24.7, 24.2, 23.1, 21.8, 0.09 ppm. MS (EI): m/z (%) = 262 (30) $[M]^+$, 247 (44), 219 (36), 137 (40), 105 (70), 73 (100). HRMS: calcd. for $C_{16}H_{26}OSi$ $[M]^+$ 262.1753; found 262.1747.

(5a*S, 9^1*S**)-2,5a Dimethyl-3-(trimethylsilyl)-4,5,5a,6,7,8-hexahydro-1*H*-cyclopenta[c]inden-9(2*H*)-one (7b):** The radical cyclization of **6b** (1.20 g, 3.38 mmol) was performed using Bu_3SnH (1.1 mL, 4.06 mmol) and AIBN (83 mg, 0.51 mmol) following the same procedure that of **7a** to afford **7b** (617 mg, 66%) as a viscous liquid. IR (film): $\tilde{\nu}$ = 1706, 1615, 846, 760 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.15–3.02 (m, 1 H, CH_2CH), 2.53–2.42 (m, 1 H, CH_2CH), 2.32–1.63 (m, 5 H, $CH_2CH_2CHCH_2$), 1.52–1.45 (m, 2 H, CH_2CH_2), 1.29–1.10 (m, 4 H, $CH_2CH_2CH_2$), 0.92 (d, J = 6.8 Hz, 3 H, Me), 0.75 (s, 3 H, Me), 0.06 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 212.9, 159.4, 137.7, 77.6, 48.7, 43.5, 39.3, 38.3, 37.2, 33.1, 25.1, 22.6, 22.5, 21.8, 0.07 ppm. MS (EI): m/z (%) = 276 (16) $[M]^+$, 261 (14), 204 (15), 186 (18), 133 (11), 118 (10), 73 (100). HRMS: calcd. for $C_{17}H_{28}OSi$ $[M]^+$ 276.1909; found 276.1915.

3-Methyl-2-[4-(trimethylsilyl)but-3-ynyl]cylohex-2-enone (8): To a solution of *t*BuLi (1.5 M, 16 mL) in dry THF (80 mL) at –78 °C was added 1,5-dimethoxy-1,4-cyclohexadiene (3 g, 21.4 mmol) and the resultant solution was stirred at the same temperature for 1 h. To this, HMPA (5.6 mL, 32.14 mmol) was added. After 10 min, (4-bromobut-1-ynyl)trimethylsilane (6.6 g, 32.14 mmol) was added. The reaction mixture was slowly raised to room temperature and stirred for 2 h. It was then quenched with saturated NH_4Cl solution (50 mL) and extracted with hexane (3 × 50 mL). The crude product (4.58 g) was dissolved in dry acetone (30 mL, previously purged with a stream of N_2 for 15 min). With vigorous stirring, 1 N hydrochloric acid (10 mL, previously purged with a stream of N_2 for 15 min) was added. The resultant solution was stirred for 1 h. Usual work up followed by flash column chromatographic purification (silica gel, 30% ethyl acetate in hexane) afforded a white solid (2.12 g, 52%), m.p. 140 °C. This was converted into the respective isobutyl ether with isobutyl alcohol (15 mL), PTSA (500 mg) in benzene (80 mL) at reflux using a Dean–Stark apparatus for 5 h. To a solution of isobutyl ether (2.32 g, 7.94 mmol) was treated with ethereal solution of CH_3MgI (2.5 M, 4.8 mL) in dry ether (50 mL) at 0 °C, raised to room temperature and stirred for 3 h. It was then quenched with saturated NH_4Cl solution and extracted with diethyl ether (2 × 30 mL). The crude product (2.22 g, 91%) in diethyl ether (15 mL) was added PTSA (2 g, 15 mL of H_2O) with vigorous stirring for 6 h at room temperature. Extraction of the product using ether (2 × 20 mL), followed by flash column chromatographic purification (silica gel, 3% ethyl acetate in hexane) afforded **8** (1.21 g, 72%) as a pale yellow liquid. IR (film): $\tilde{\nu}$ = 2172, 1668, 859, 758 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.45–2.43 (m, 2 H, CH_2CH_2), 2.29–2.23 (m, 6 H, $CH_2CH_2CH_2CH_2$), 1.94–1.18 (m, 5 H, $CH_2CH_2CH_2CH$), 0.05 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.5, 157.1, 133.6, 107.1, 84.4, 37.6, 32.8, 24.2, 22.1, 21.7, 19.2, 0.13 ppm. MS (EI): m/z (%) = 234 (34) $[M]^+$, 219 (46), 195 (27), 163 (52), 127 (71), 98 (33), 57 (100). $C_{14}H_{22}OSi$ (234.14): calcd. C 71.73, H 9.46; found C 71.80, H 9.57.

Compound 9: The 1,4-addition was performed using enone **8** (840 mg, 3.58 mmol), Grignard reagent [prepared from Mg (430 mg, 17.94 mmol), 4-bromo-1-trimethylsilyl-1-butyne (1.84 g,

8.97 mmol)], CuI (1.71 g, 8.97 mmol), TMSCl (0.54 mL, 4.31 mmol) and Et_3N (0.65 mL, 4.66 mmol) following the same procedure as for **5a** to afford crude **9** (1.33 g, 86%) as a pale yellow liquid. IR (film): $\tilde{\nu}$ 2171), 1612, 845, 759 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.46–2.37 (m, 2 H, CH_2CH_2), 2.34–2.28 (m, 6 H, $CH_2CH_2CH_2CH_2$), 2.23–1.62 (m, 6 H, $CH_2CH_2CH_2CH_2$), 1.23 (s, 3 H, Me), 0.17 (s, 9 H, $SiMe_3$), 0.13 (s, 9 H, $SiMe_3$), 0.10 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.6, 122.8, 107.6, 106.2, 85.8, 84.2, 38.4, 32.8, 31.3, 29.6, 26.5, 23.2, 19.8, 19.1, 15.4, 0.86, 0.21 ppm. MS (EI): *m*/*z* (%) = 432 (22) $[M]^+$, 386 (37), 341 (19), 284 (42), 192 (61), 95 (45), 64 (100). $C_{24}H_{44}OSi_3$ (432.27): calcd. C 66.59, H 10.25; found C 66.67, H 10.36. Crude **9** was used for the next step without further purification.

2-Bromo-3-methyl-2,3-bis[4-(trimethylsilyl)but-3-ynyl]cyclohexanone (10): Bromination using compound **9** (1.20 g, 2.77 mmol), KBr (991 mg, 8.33 mmol) and dry *m*-CPBA (72.5% purity, 1.43 g, 8.33 mmol) following the same procedure as for **6a** to afford **10** (827 mg, 68%) as a yellow liquid. IR (film): $\tilde{\nu}$ = 2173, 1710, 1616, 845, 760 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.38–2.26 (m, 2 H, CH_2CH_2), 2.25–2.06 (m, 6 H, $CH_2CH_2CH_2CH_2$), 2.03–1.55 (m, 6 H, $CH_2CH_2CH_2CH_2$), 1.15 and 1.01 (2s, 3 H, Me), 0.14 (s, 9 H, $SiMe_3$), 0.11 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.5, 106.9, 106.7, 106.4, 106.2, 85.1, 84.5, 82.4, 72.6, 71.2, 46.2, 45.7, 39.5, 38.8, 36.2, 36.1, 32.6, 32.0, 27.6, 27.3, 25.6, 21.3, 21.1, 19.2, 15.6, 15.4, 0.07, 0.05 ppm. MS (EI): *m*/*z* (%) = 440 (13) [M + 2], 438 (13) $[M]^+$, 383 (21), 356 (26), 262 (35), 197 (36), 135 (64), 82 (100). $C_{21}H_{35}BrOSi_2$ (438.14): calcd. C 57.38, H 8.03; found C 57.45, H 8.14.

(3a*S,7a*S**)-7a-Methyl-3a-[4-(trimethylsilyl)but-3-ynyl]-3-[(trimethylsilyl)methylene]octahydro-4*H*-inden-4-one (11):** Radical cyclization of **10** (800 mg, 1.82 mmol) was performed using Bu_3SnH (0.59 mL, 2.19 mmol) and AIBN (44 mg, 0.27 mmol) following the same procedure as for **7a** to afford **11** (433 mg, 66%) as a viscous liquid. IR (film): $\tilde{\nu}$ = 2173, 1705, 1610, 760 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.79–5.62 (m, 1 H, vinyl CH), 2.44–2.01 (m, 6 H, CH_2 $CH_2CH_2CH_2$), 1.87–1.63 (m, 4 H, $CH_2CH_2CH_2$), 1.46–1.24 (m, 4 H, $CH_2CH_2CH_2$), 0.91 (s, 3 H, Me), 0.14 (s, 9 H, $SiMe_3$), 0.06 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 214.1, 132.0, 128.2, 107.9, 84.4, 67.6, 45.6, 37.4, 36.6, 32.6, 26.8, 22.0, 17.4, 16.6, 15.0, 0.22, 0.04 ppm. MS (EI): *m*/*z* (%) = 360 (16) $[M]^+$, 283 (37), 231 (52), 188 (56), 74 (100). HRMS: calcd. for $C_{21}H_{36}OSi_2$ $[M]^+$ 360.2305; found 360.2310.

3-Methyl-2-(pent-3-enyl)cyclohex-2-enone (15): Following the same experimental procedure as for **8** to afford **15** as a pale yellow liquid in 63% yield. IR (film): $\tilde{\nu}$ = 1667, 1628, 963, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.34–5.31 (m, 2 H, $CH_2CH{=}CHCH_3$), 2.30–2.23 (m, 6 H, $CH_2CH_2CH_2CH_2$), 1.91–1.81 (m, 7 H, $CH_2CH_2CH_2CH_2CH$), 1.55 (d, *J* = 4.3 Hz, 3 H, Me) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 199.8, 156.5, 136.1, 131.9, 125.9, 38.8, 33.8, 32.9, 26.3, 23.2, 22.2, 18.9 ppm. MS (EI): *m*/*z* (%) = 178 (46) $[M]^+$, 127 (46), 125 (58), 123 (71), 55 (100). $C_{12}H_{18}O$ (178.13): calcd. C 80.85, H 10.18; found C 80.93, H 10.30.

Trimethyl{3-methyl-2-(pent-3-enyl)-3-[4-(trimethylsilyl)but-3-ynyl]cyclohex-1-enyloxy}silane (16): The 1,4-addition was performed using enone **15** (730 mg, 4.10 mmol), Grignard reagent [prepared from Mg (492 mg, 20.50 mmol), 4-bromo-1-trimethylsilyl-1-butyne (2.10 g, 10.25 mmol)], CuI (1.95 g, 10.25 mmol), TMSCl (0.62 mL, 4.92 mmol) and Et_3N (0.74 mL, 5.33 mmol) following the same procedure as for **5a** to afford crude **16** (1.34 g, 87%) as a pale yellow liquid. IR (film): $\tilde{\nu}$ = 2174, 1616, 847, 760 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 5.43–5.41 (m, 2 H, $CH_2CH{=}CHCH_3$), 2.23–1.93 (m, 8 H, $CH_2CH_2CH_2CH_2CH_2$), 1.78–1.64 (m, 4 H, $CH_2CH_2CH_2$) 1.59–1.20 (m, 5 H, $CH_2CH_2CH_2CH$), 0.96 (s, 3 H, Me), 0.15 (s, 9 H, $SiMe_3$), 0.12 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 146.0, 132.3, 124.2, 121.6, 108.5, 84.7, 39.6, 34.7, 32.5, 30.9, 27.7, 26.7, 19.4, 19.3, 18.0, 15.4, 0.91, 0.24 ppm. MS (EI): *m*/*z* (%) = 376 (33) $[M]^+$, 348 (25), 284 (39), 242 (46), 193 (64), 78 (100). Found: C, 70.21; H, 10.81. $C_{22}H_{40}OSi_2$ (376.26) calcd. C 70.14, H 10.70; found C 70.21, H 10.81. Crude product **16** was used for the next step without further purification.

2-Bromo-3-methyl-2-(pent-3-enyl)-3-[4-(trimethylsilyl)but-3-ynyl]-cyclohexanone (17): Bromination using compound **16** (1.25 g, 3.32 mmol), KBr (1.18 g, 9.97 mmol) and dry *m*-CPBA (72.5% purity, 1.72 g, 9.97 mmol) following the same procedure as for **6a** to afford **17** (827 mg, 65%) as a yellow liquid. IR (film): $\tilde{\nu}$ = 2173, 1710, 1616, 845, 760 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.54–5.37 (m, 2 H, $CH_2CH{=}CHCH_3$), 2.48–1.93 (m, 8 H, $CH_2CH_2CH_2CH_2CH_2$), 1.84–1.72 (m, 4 H, $CH_2CH_2CH_2$), 1.70–1.24 (m, 5 H, $CH_2CH_2CH_2CH$), 1.06 and 1.01 (2s, 3 H, Me), 0.13 and 0.07 (2s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.8, 139.2, 116.1, 115.4, 107.7, 107.3, 86.7, 86.5, 73.1, 72.2, 47.8, 47.0, 40.6, 38.3, 38.1, 36.9, 33.6, 25.2, 23.5, 23.1, 20.4, 16.7, 16.4, 15.8, 0.09, 0.06 ppm. MS (EI): *m*/*z* (%) = 384 (16) $[M]^{+2}$, 382 (16) $[M]^+$, 278 (34), 213 (27), 184 (42), 158 (57), 114 (52), 73 (100). $C_{19}H_{31}BrOSi$ (382.13) calcd. C 59.51, H 8.15; found C 59.60, H 8.23.

3-Methyl-2-(pent-3-enyl)-3-[(4-trimethylsilyl)but-3-ynyl]cyclohexanone (18): Radical cyclization of **17** (820 mg, 2.14 mmol) was performed using Bu_3SnH (0.69 mL, 2.56 mmol) and AIBN (52 mg, 0.32 mmol) following the same procedure that of **7a** to afford the radical-quenched product **18** (364 mg, 56%) as a viscous liquid. IR (film): $\tilde{\nu}$ = 2173, 1706, 1615, 846, 760 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 5.38–5.36 (m, 2 H, $CH_2CH{=}CHCH_3$), 2.38–2.07 (m, 7 H, $CH_2CH_2CH_2CH_2CH$), 2.02–1.67 (m, 4 H, $CH_2CH_2CH_2$), 1.64–1.23 (m, 5 H, $CH_2CH_2CH_2CH$), 1.02–0.95 (m, 2 H, CH_2CH_2), 0.73 (s, 3 H, Me), 0.12 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 213.3, 130.8, 125.6, 107.2, 84.6, 60.7, 57.7, 41.6, 34.3, 33.9, 31.5, 25.0, 24.1, 22.6, 17.9, 14.2, 0.19 ppm. MS (EI): *m*/*z* (%) = 304 (27) $[M]^+$, 279 (18), 232 (35), 197 (43), 158 (54), 82 (100). HRMS: calcd. for $C_{19}H_{32}OSi$ $[M]^+$ 304.2222; found 304.2217.

2-Allylcyclohept-2-en-1-one (20): To a solution of NaOMe (prepared from Na, 1.25 g, 5.43 mmol and CH_3OH, 30 mL) in methanol (20 mL) was stirred at 0 °C. To this, a solution of methyl thioglycolate (4.28 g, 45.45 mmol) in methanol (20 mL) was added. After 5 min, cyclohepten-1-one (5 g, 45.45 mmol) dissolved in methanol (20 mL) was added drop wise at the same temperature. The reaction mixture was slowly raised to room temperature and refluxed for 10 h. Then the solvent was removed in vacuo. Orange residue was dissolved in diethyl ether (50 mL) and extracted with 2 N NaOH (2 × 30 mL). The combined aqueous layer was acidified with dilute aqueous HCl (60 mL), extracted with diethyl ether (2 × 50 mL) and dried (Na_2SO_4). Removal of solvent followed by flash column chromatographic purification (silica gel, 10% EtOAC in hexane) afforded tetrahydro-cyclohepta[*b*]thiophene-3,4-dione as an orange-yellow liquid (4.93 g, 59%). To a solution of the latter (3 g, 16.30 mmol) in dry acetone (70 mL), powdered K_2CO_3 (11.25 g, 81.52 mmol) was added. Then allyl bromide (5.64 mL, 65.21 mmol) was added. The reaction mixture was refluxed for 4 h. After completion of the reaction, the solvent was removed in vacuo. The residue was poured onto ice/water and the crude product was extracted with diethyl ether (2 × 100 mL) and dried (Na_2SO_4). The solvent was removed and the crude product (2.37 g) dissolved in diethyl ether (50 mL), then aqueous 5% NaOH (50 mL) was added.

The reaction mixture was stirred for 4 h at room temperature. Then the organic layer was separated and washed with saturated $NaHCO_3$ solution followed by brine solution (2 × 50). Removal of solvent followed by flash column chromatographic purification (silica gel, 5% ethyl acetate in hexane) afforded **20** (761 mg, 48%) as a pale yellow liquid. IR (film): $\tilde{\nu}$ = 1661, 1622, 859, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.43 (t, J = 6.4 Hz, 1 H, $CH_2CH{=}CH$), 5.75–5.67 (m, 1 H, $CH_2CH{=}CH_2$), 5.05–4.91 (m, 2 H, $CH_2CH{=}CH_2$), 2.91–2.89 (m, 2 H, CH_2CH_2), 2.52–2.49 (m, 2 H, CH_2CH_2), 2.34–2.2.28 (m, 2 H, CH_2CH_2), 1.72–1.64 (m, 4 H, $CH_2CH_2CH_2$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 204.1, 142.3, 141.6, 136.2, 115.7, 42.4, 36.6, 27.4, 24.9, 21.2 ppm. MS (EI): m/z (%) = 150 (35) $[M]^+$, 127 (38), 111 (33), 93 (57), 85 (100). $C_{10}H_{14}O$ (150.10) calcd. C 79.96, H 9.39; found C 80.05, H 9.51.

Compound 21: The 1,4-addition was performed using enone **20** (650 mg, 4.33 mmol), Grignard reagent [prepared from Mg (520 mg, 2.16 mmol), 4-bromo-1-trimethylsilyl-1-butyne (2.22 g, 10.83 mmol)], CuI (2.06 g, 10.83 mmol), TMSCl (0.66 mL, 5.20 mmol) and Et_3N (0.79 mL, 5.63 mmol) following the same procedure as for **5a** to afford crude **21** (1.43 g, 95%) as a viscous oil. IR (film): $\tilde{\nu}$ = 2174, 1616, 847, 760 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 5.72–5.66 (m, 1 H, $CH_2CH{=}CH_2$), 5.04–4.92 (m, 2 H, $CH_2CH{=}CH_2$), 3.04 (dd, J = 5.7, 5.7 Hz, 1 H, $CHCH{=}CH_2$), 2.48–2.40 (m, 2 H, CH_2CH_2), 2.26–2.07 (m, 4 H, $CH_2CH_2CH_2$), 1.75–1.55 (m, 6 H, $CH_2CH_2CH_2CH_2$), 1.50–1.35 (m, 2 H, CH_2CH_2), 0.15 (s, 9 H, $SiMe_3$), 0.13 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 148.6, 137.1, 121.4, 115.1, 107.5, 84.6, 37.7, 37.1, 34.9, 29.7, 29.4, 26.0, 24.9, 18.5, 0.81, 0.26 ppm. MS (EI): m/z (%) = 348 (6) $[M]^+$, 307 (6), 223 (22), 185 (4), 147 (13), 73 (100). $C_{20}H_{36}OSi_2$ (348.23) calcd. C 68.89, H 10.41; found C 68.76, H 10.33. Crude product **21** was used for the next step without further purification.

2-Allyl-2-bromo-3-[4-(trimethylsilyl)but-3-ynyl]cycloheptanone (22): Bromination using compound **21** (1.30 g, 3.73 mmol), KBr (1.33 g, 11.20 mmol) and dry *m*-CPBA (72.5% purity, 1.93 g, 11.01 mmol) following the same procedure as for **6a** to afford **22** (886 mg, 67%) as a yellow liquid. IR (film): $\tilde{\nu}$ = 2175, 1708, 1612, 845, 760 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.88–5.77 (m, 1 H, $CH_2CH{=}CH_2$), 5.12–4.98 (m, 2 H, $CH_2CH{=}CH_2$), 3.34 (dt, J = 2.6, 11.8 Hz, 1 H, $CHCH{=}CH_2$), 3.12 (dd, J = 7.8, 14.8 Hz, 1 H, $CHCH{=}CH_2$), 2.75 (dd, J = 7.8, 14.5 Hz, 1 H, $CHCH{=}CH_2$), 2.61–2.34 (m, 4 H, $CH_2CH_2CH_2$), 2.32–2.14 (m, 2 H, CH_2CH_2), 1.97–1.76 (m, 2 H, CH_2CH_2), 1.63–1.29 (m, 4 H, $CH_2CH_2CH_2$), 0.15 and 0.12 (2s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.2, 138.5, 119.7, 106.1, 87.4, 71.7, 49.5, 43.3, 38.7, 35.2, 31.5, 30.8, 28.5, 18.7, 0.17, 0.10 ppm. HRMS: calcd. for $C_{17}H_{27}BrOSi$ $[M]^+$ 354.1015; found 354.1021.

(2*R, 5a*S**, 10[1]*S**)-2-Methyl-3-(trimethylsilyl)-1,2,5,5a,6,7,8,9-octahydrocylopenta[*c*]azulen-10(4*H*)-one (23):** Radical cyclization of bromo compound **22** (820 mg, 2.31 mmol) was performed using Bu_3SnH (0.75 mL, 2.77 mmol) and AIBN (57 mg, 0.34 mmol) following the same procedure as for **7a** to afford **23** (434 mg, 68%) as white crystals; m.p. 56–57 °C. IR (KBr): $\tilde{\nu}$ = 1701, 1610, 842, 760 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.05–3.04 (m, 1 H, CH_2CH), 2.81–2.74 (m, 1 H, CH_2CH), 2.65 (dd, J = 5.6, 5.6 Hz, 1 H, CH_2CH), 2.44–2.32 (m, 4 H, $CH_2CH_2CH_2$), 2.07–1.96 (m, 2 H, CH_2CH_2), 1.89–1.77 (m, 5 H, $CH_2CH_2CH_2CH$), 1.71–1.62 (m, 2 H, CH_2CH_2), 1.14 (d, J = 6.8 Hz, 3 H, Me), 0.06 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 213.9, 163.0, 135.9, 75.6, 47.9, 47.5, 44.9, 41.5, 33.6, 31.3, 26.5, 24.3, 23.3, 21.6, 0.16 ppm. MS (EI): m/z (%) = 276 (17) $[M]^+$, 261 (7), 233 (10), 191 (11), 175 (40), 73 (100). HRMS: calcd. for $C_{17}H_{28}OSi$ $[M]^+$ 276.1909; found 276.1914. For single-crystal X-ray analysis of **23**, all calculations were made with SHELXL-97 program.[17] Crystal data of **23**: $C_{17}H_{28}OSi$, MW = 276.48 g/mol, triclinic crystal system, space group $P\bar{1}$, Z = 2, a = 7.3877(2) Å, b = 10.4954(3) Å, c = 11.4520(3) Å, α = 91.7610(10)°, β = 105.7330(10)°, γ = 98.2520(10)°, V = 843.57(4) $Å^3$ and D_x = 1.088 Mg/m^3. In total, 4552 independent reflections were collected of which 3244 were considered as observed [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least-squares procedures to final R value of 5.10%.

CCDC-643499 contains the supplementary crystallographic data for **23**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2-Allyl-3-methylcyclohept-2-enone (24): To a stirred solution of 2-allylcyclohept-2-enone (**20**) (2.5 g, 16.66 mmol) in 20 mL of anhydrous ether at –78 °C, ethereal solution of methyllithium (1.56 M, 13 mL) was added dropwise. The resulting solution was warmed to room temperature, stirred for 2 h and quenched by drop wise addition of water (10 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined ethereal solution was dried (Na_2SO_4), and solvent was removed under reduced pressure to afford the corresponding alcohol (2.62 g, 95%) as viscous oil. The solution of this alcohol (2.6 g, 15.66 mmol) in dry DCM (20 mL) was added to a magnetically stirred slurry of pyridinium chlorochromate (6.75 g, 31.32 mmol) and celite (10 g) in dry DCM (30 mL). The reaction mixture was stirred at room temperature for 2 h. Usual work up, followed by flash column chromatographic purification (silica gel, 3% ethyl acetate in hexane) afforded **24** (1.59 g, 62%) as a pale yellow liquid. IR (film): $\tilde{\nu}$ = 1658, 1625, 855, 758 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 5.70–5.65 (m, 1 H, $CH_2CH{=}CH_2$), 4.88–4.83 (m, 2 H, $CH_2CH{=}CH_2$), 2.99 (d, J = 5.7 Hz, 2 H, $CH_2CH{=}CH_2$), 2.48–2.46 (m, 2 H, CH_2CH_2), 2.34–2.32 (m, 2 H, CH_2CH_2), 1.86 (s, 3 H, Me), 1.76–1.59 (m, 4 H, $CH_2CH_2CH_2$) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 205.8, 152.0, 136.0, 118.1, 114.3, 41.7, 34.5, 33.0, 24.0, 23.2, 21.5 ppm. MS (EI): m/z (%) = 164 (42) $[M]^+$, 163 (23), 150 (19), 131 (44), 79 (100). $C_{11}H_{16}O$ (164.12) calcd. C 80.44, H 9.82; found C 80.52, H 9.95.

Compound 25: The 1,4-addition was performed using enone **24** (680 mg, 4.14 mmol), Grignard reagent [prepared from Mg (496 mg, 20.7 mmol), 4-bromo-1-trimethylsilyl-1-butyne (2.15 g, 10.36 mmol)], CuI (1.97 g, 10.36 mmol), TMSCl (0.63 mL, 4.97 mmol) and Et_3N (0.75 mL, 5.39 mmol) following the same procedure as for **5a** to afford crude **25** (1.42 g, 95%) as a viscous oil. IR (film): $\tilde{\nu}$ = 2172, 1614, 844, 760 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 5.81–5.77 (m, 1 H, $CH_2CH{=}CH_2$), 5.16–4.98 (m, 2 H, $CH_2CH{=}CH_2$), 2.57–2.48 (m, 2 H, CH_2CH_2), 2.34–2.12 (m, 4 H, $CH_2CH_2CH_2$), 1.85–1.61 (m, 6 H, $CH_2CH_2CH_2CH_2$), 1.57–1.48 (m, 2 H, CH_2CH_2), 0.96 (s, 3 H, Me), 0.18 (s, 9 H, $SiMe_3$), 0.13 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 149.4, 138.6, 122.1, 117.3, 107.8, 85.3, 39.4, 38.7, 36.3, 30.8, 30.3, 27.6, 25.2, 19.6, 15.7, 0.86, 0.31 ppm. MS (EI): m/z (%) = 362 (13) $[M]^+$, 325 (16), 246 (31), 194 (9), 153 (21), 73 (100). $C_{21}H_{38}OSi_2$ (362.24) calcd. C 69.54, H 10.56; found C 69.66, H 10.70. Crude **25** was used for the next step without further purification.

2-Allyl-2-bromo-3-methyl-3-[4-(trimethylsilyl)but-3-ynyl]cycloheptanone (26): Bromination of **25** (1.25 g, 3.45 mmol) with KBr (1.23 g, 10.35 mmol) and dry *m*-CPBA (72.5% purity, 1.78 g, 10.35 mmol), following the same procedure as for **6a**, afforded **26** (802 mg, 63%) as a yellow liquid. IR (film): $\tilde{\nu}$ = 2174, 1710, 1614, 843, 760 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.76–5.64 (m, 1

H, $CH_2CH=CH_2$), 5.03–4.87 (m, 2 H, $CH_2CH=CH_2$), 3.25 (dt, J = 3.2, 12.5 Hz, 1 H, $CHCH=CH_2$), 3.06 (dd, J = 8.4, 15.2 Hz, 1 H, $CHCH=CH_2$), 2.56–2.34 (m, 2 H, CH_2CH_2), 2.27–2.09 (m, 4 H, $CH_2CH_2CH_2$), 1.84–1.62 (m, 2 H, CH_2CH_2), 1.56–1.18 (m, 4 H, $CH_2CH_2CH_2$), 1.02 and 0.88 (2s, 3 H, Me), 0.13 and 0.10 (2s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.6, 136.5, 117.2, 106.4, 85.8, 71.3, 48.4, 42.6, 36.2, 34.5, 30.7, 29.5, 28.5, 17.6, 15.3, 0.15, 0.11 ppm. HRMS: calcd. for $C_{18}H_{29}BrOSi$ $[M]^+$ 368.1171; found 368.1176.

2-Allyl-3-methyl-3-[4-(trimethylsilyl)but-3-ynyl]cycloheptanone (27): Radical cyclization of bromo compound **26** (750 mg, 2.03 mmol) was performed using Bu_3SnH (0.66 mL, 2.43 mmol) and AIBN (50 mg, 0.30 mmol) following the same procedure that of **7a** to afford the radical-quenched product **27** (336 mg, 57%) as a viscous liquid. IR (film): $\tilde{\nu}$ = 2175, 1701, 1643, 1247, 842, 756 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 5.74–5.64 (m, 1 H, $CH_2CH=CH_2$), 5.02–4.95 (m, 2 H, $CH_2CH=CH_2$), 2.52–2.43 (m, 2 H, CH_2CH_2), 2.34–2.19 (m, 2 H, CH_2CH_2), 2.10–1.88 (m, 4 H, $CH_2CH_2CH_2$), 1.83–1.34 (m, 7 H, $CH_2CH_2CH_2CH_2CH$), 1.17 (s, 3 H, Me), 0.11 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 214.1, 136.9, 116.5, 106.2, 85.0, 54.7, 44.1, 36.2, 33.1, 32.9, 26.3, 24.2, 23.6, 18.2, 15.3, 0.18 ppm. HRMS: calcd. for $C_{18}H_{30}OSi$ $[M]^+$ 290.2066; found 290.2073.

2-(Cyclohex-2-enyl)cyclohex-2-enone (28): To a solution of NaOMe (prepared from Na, 1.25 g, 5.43 mmol and CH_3OH, 30 mL) in methanol (20 mL) was stirred at 0 °C. To this, a solution of methyl thioglycolate (5.52 g, 5.21 mmol) in methanol (20 mL) was added. After 5 min, cyclohexen-1-one (5 g, 5.21 mmol) dissolved in methanol (20 mL) was added drop wise at the same temperature. The reaction mixture was slowly raised to room temperature and refluxed for 10 h. Then, the solvent was removed in vacuo. Resulting orange residue was dissolved in diethyl ether (50 mL) and extracted with 2 N NaOH (2 × 30 mL). The combined aqueous layer was acidified with dilute aqueous HCl (60 mL), extracted with diethyl ether (2 × 50 mL) and dried (Na_2SO_4). Removal of solvent followed by flash column chromatographic purification (silica gel, 10% EtOAc in hexane) afforded hexahydro-benzothiophene-3,4-dione as an orange-yellow liquid (5.66 g, 64%). To a solution of hexahydro-benzothiophene-3,4-dione (3 g, 17.64 mmol) in dry acetone (70 mL), powdered K_2CO_3 (12.2, 88.23 mmol) was added. Then 3-bromocyclohex-1-ene (11.3 g, 70.58 mmol) was added. The reaction mixture was refluxed for 4 h. After completion of the reaction, the solvent was removed in vacuo. The residue was poured onto ice/water and the crude product was extracted with diethyl ether (2 × 100 mL) and dried (Na_2SO_4). The solvent was removed and the crude product (2.37 g) dissolved in diethyl ether (50 mL) and an aqueous solution of NaOH (5%, 50 mL) was added. The reaction mixture was stirred for 4 h at room temperature. Then the organic layer was separated and washed with saturated $NaHCO_3$ solution followed by brine solution (2 × 50 mL). Removal of solvent followed by flash column chromatographic purification (silica gel, 5% ethyl acetate in hexane) afforded **28** (800 mg, 48%) as a pale yellow liquid. IR (film): $\tilde{\nu}$ = 1668, 1615, 859, 758 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 6.67 (t, J = 3.8 Hz, 1 H, $CH_2CH=CH$), 5.82–5.80 (m, 1 H, $CHCH=CHCH_2$), 5.40–5.38 (m, 1 H, $CHCH=CHCH_2$), 3.39–3.42 (m, 1 H, CHCH=CH), 2.40–2.34 (m, 4 H, $CH_2CH_2CH_2$), 1.96–1.79 (m, 4 H, $CH_2CH_2CH_2$), 1.53–1.24 (m, 4 H, $CH_2CH_2CH_2$) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 198.9, 145.7, 143.0, 129.1, 128.9, 38.8, 33.3, 28.9, 26.1, 25.1, 23.1, 20.0 ppm. MS (EI): m/z (%) = 176 (34) $[M]^+$, 156 (41), 132 (23), 112 (54), 73 (100). $C_{12}H_{16}O$ (176.12) calcd. C 81.77, H 9.15; found C 81.85, H 9.28.

{4-[2-(Cyclohex-2-enyl)-3-methylcyclohex-2-enyl]but-1-ynyl}trimethylsilane (29): The 1,4-addition was performed using enone **28** (760 mg, 4.31 mmol), Grignard reagent [prepared from Mg (518 mg, 21.59 mmol), 4-bromo-1-trimethylsilyl-1-butyne (2.21 g, 10.79 mmol)], CuI (2.05 g, 10.79 mmol), TMSCl (0.66 mL, 5.18 mmol) and Et_3N (0.78 mL, 5.61 mmol) following the same procedure as for **5a** to afford crude **29** (1.54 g, 92%) as a viscous oil. IR (film): $\tilde{\nu}$ = 2174, 1616, 847, 760 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.53–5.47 (m, 2 H, $CHCH=CHCH_2$), 3.17–3.15 (m, 1 H, CHCH=CH), 2.21–2.11 (m, 8 H, $CH_2CH_2CH_2CH_2CH_2$), 1.96–1.40 (m, 7 H, $CH_2CH_2CH_2CH_2CH$), 1.22–1.18 (m, 2 H, CH_2CH_2), 0.12 (s, 9 H, $SiMe_3$), 0.10 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 133.2, 125.6, 122.2, 107.7, 84.6, 37.0, 34.7, 31.4, 30.6, 29.6, 25.8, 24.9, 23.1, 19.3, 18.7, 0.83, 0.13 ppm. MS (EI): m/z (%) = 389 (13) $[M]^+$, 331 (17), 274 (24), 246 (8), 184 (17), 124 (100). $C_{23}H_{41}OSi_2$ (389.26) calcd. C 70.88, H 10.60; found C 70.97, H 10.71. Crude product **29** was used for the next step without further purification.

2-Bromo-2-(cyclohex-2-enyl)-3-[4-(trimethylsilyl)but-3-ynyl]cyclohexanone (30): Bromination using compound **29** (1.40 g, 3.59 mmol), KBr (1.28 g, 10.79 mmol) and dry m-CPBA (72.5% purity, 1.86 g, 10.79 mmol) following the same procedure as for **6a** to afford **30** (891 mg, 65%) as a yellow liquid. IR (film): $\tilde{\nu}$ = 2174, 1704, 1610, 842, 760 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.96 (d, J = 10.8 Hz, 1 H, $CHCH=CHCH_2$), 5.72–5.64 (m, 1 H, $CHCH=CHCH_2$), 3.59–3.50 (m, 1 H, CHCH=CH), 3.42–3.38 (m, 1 H, CH_2CHCH_2), 2.47–2.24 (m, 8 H, $CH_2CH_2CH_2CH_2CH_2$), 2.16–1.25 (m, 8 H, $CH_2CH_2CH_2CH_2CH_2$), 0.15 and 0.11 (2s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.3, 134.7, 129.5, 107.2, 84.6, 74.5, 45.2, 44.8, 38.2, 33.7, 29.4, 28.2, 27.6, 25.3, 24.7, 18.6, 0.05 ppm. MS (EI): m/z (%) = 382 (12) $[M]^{2+}$, 380 (12) $[M]^+$, 357 (16), 283 (26), 265 (47), 223 (32), 176 (63), 126 (66), 84 (100). $C_{19}H_{29}BrOSi$ (380.11) calcd. C 59.83, H 7.66; found C 59.91, H 7.78.

(4a*S,7a*R**,11a*S**)-7-Trimethylsilyl-2,3,4,4a,5,6,7a,8,9,10,11,11a-dodecahydro-1*H*-indeno[7a,1-*a*]inden-1-one (31):** Radical cyclization of **30** (880 mg, 2.31 mmol) was performed using Bu_3SnH (0.75 mL, 2.77 mmol) and AIBN (57 mg, 0.34 mmol) following the same procedure as for **7a** to afford **31** (349 mg, 50%) and also **32** (139 mg, 20%) as a viscous liquid.

31: IR (film): $\tilde{\nu}$ = 1704, 1610, 842, 760 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.11–3.04 (m, 1 H, CH_2CHCH_2), 2.58–2.50 (m, 1 H, CH_2CH), 2.33–2.20 (m, 4 H, $CH_2CH_2CH_2$), 1.96–1.63 (m, 6 H, $CH_2CH_2CH_2CH_2$), 1.61–1.53 (m, 5 H, $CH_2CH_2CH_2CH$), 1.51–1.38 (m, 2 H, CH_2CH_2), 1.31–1.16 (m, 2 H, CH_2CH_2), 0.08 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 211.7, 161.3, 133.5, 77.1, 51.7, 45.1, 40.1, 38.8, 31.1, 27.7, 24.8, 24.6, 24.5, 24.2, 22.6, 22.5, 0.07 ppm. HRMS: calcd. for $C_{19}H_{30}OSi$ $[M]^+$ 302.2066; found 302.2061.

32: IR (film): $\tilde{\nu}$ = 2174, 1704, 1610, 842, 760 cm^{-1}. ^1H NMR (300 MHz, CDCl3): δ = 5.66–5.26 (m, 2 H, $CH_2CH=CHCH_2$), 2.68–2.34 (m, 4 H, $CH_2CH_2CH_2$), 2.07–1.76 (m, 7 H, $CH_2CH_2CH_2CH_2CH$), 1.72–1.23 (m, 6 H, $CH_2CH_2CH_2CH_2$), 0.87 (t, J = 7.1 Hz, 2 H, CH_2CH), 0.09 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 214.2, 129.3, 128.8, 128.6, 107.1, 85.6, 61.3, 40.6, 40.1, 38.0, 37.6, 35.2, 34.8, 32.1, 28.5, 27.8, 27.6, 25.5, 24.8, 23.7, 22.8, 21.5, 21.2, 18.4, 18.1, 14.3, 0.08 ppm. HRMS: calcd. for $C_{19}H_{30}OSi$ $[M]^+$ 302.2066; found 302.2070.

Preparation of 2,4-Dinitrophenylhydrazone of 33: To a stirred suspension of 2,4-dinitrophenylhydrazine in CH_3OH (5 mL) was added concentrated H_2SO_4 (0.15 mL). To this solution was added a solution of **31** (50 mg, 0.17 mmol) in CH_3OH (2 mL) and the

reaction mixture was heated at 70 °C for 10 min. On cooling, hydrazone **33** (44 mg, 56%) was obtained as an orange-yellow solid; m.p. 191–192 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.97 (s, 1 H, NH), 8.92 (d, J = 2.4 Hz, 1 H, ArCH), 8.02 (dd, J = 2.1, 2.1 Hz, 1 H, ArCH), 7.68 (d, J = 9.6 Hz, 1 H, ArCH), 3.12–3.01 (m, 1 H, CH_2CHCH_2), 2.55–2.50 (m, 1 H, CH_2CHCH_2), 2.13–1.98 (m, 4 H, $CH_2CH_2CH_2$), 1.83–1.46 (m, 8 H, $CH_2CH_2CH_2CH_2CH_2$), 1.38–1.28 (m, 5 H, $CH_2CH_2CH_2CH$), 1.07–0.97 (m, 2 H, CH_2CH_2), 0.17 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.1, 159.8, 145.4, 137.2, 132.2, 129.5, 128.5, 123.3, 116.1, 70.3, 51.3, 45.6, 37.3, 31.8, 27.9, 25.5, 25.3, 24.7, 24.6, 24.5, 22.5, 21.1, 0.20 ppm. HRMS: calcd. for $C_{25}H_{34}N_4O_4Si$ $[M]^+$ 482.2349; found 482.2354. For single-crystal X-ray analysis of **33**, all calculations were made with the SHELXL-97 program.[17] Crystal data of **33**: $C_{25}H_{34}N_4O_4Si$, MW = 482.65 g/mol, triclinic crystal system, space group $P\bar{1}$, Z = 2, a = 10.1028(2) Å, b = 10.9354(2) Å, c = 12.9619(3) Å, α = 94.4180(10)°, β = 107.3150(10)°, γ = 110.6550(10)°, V = 1252.40(4) Å^3 and D_x = 1.280 Mg/m^3. In total, 6376 independent reflections were collected of which 4219 were considered as observed [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least-squares procedures to final R value of 5.26%.

CCDC-643500 contains the supplementary crystallographic data for **33**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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