Supporting Information

Domino Enyne Metathesis en Route to Skeletally Diverse, Privileged Scaffolds: Synthesis of Tricyclic Core of Pseudolaric Acid F

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1. General Information

All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise stated. All the chemicals were purchased commercially and used without further purification, unless otherwise stated. The boiling point of petroleum ether (PE) is between 60-90 °C. Tetrahydrofuran (THF) was distilled from sodium-benzophenone; Dichloromethane (CH₂Cl₂) was distilled from calcium hydride. Toluene was distilled from sodium under argon atmosphere. HMPA was distilled in vacuo from calcium hydride; Diisopropylamine (DIPA) was distilled from calcium hydride under argon atmosphere; 1,2-Dichloroethane (DCE) was distilled from calcium hydride under argon atmosphere. Super-dry N,N-Dimethylformamide (DMF) were purchased from Innochem Science & Technology Co., Ltd. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25mm Qingdao silica gel plates (60F-254) using UV lights as the visualizing agent and KMnO₄. Flash column chromatography was performed over Qingdao silica gel (200-300 mesh). Infrared spectra were recorded on a Nicolet AVATER FTIR330 spectrometer as thin film and are reported in reciprocal centimeter (cm⁻¹). High resolution mass spectra (HRMS) were recorded on a Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization. NMR spectra were recorded on Bruker AV-400 and Bruker AV-500 instruments and were calibrated using residual undeuterated solvents (CHCl₃, δH = 7.26 ppm) and deuterated solvents (CDCl₃, δC = 77.0 ppm) as internal references. The data for ¹H NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet), coupling constants (Hz) and integration.
2. General Procedures for the Synthesis of Substrates

2.1) Procedures for the preparation of enyne-I

To a solution of DIPA (31.8 mL, 226.2 mmol) in THF (300 mL) at 0 °C was added n-BuLi (68 mL, 2.5 M in hexane). After being stirred for 30 min, the reaction was cooled to –78 °C, and then a solution of α,β-unsaturated ester S1 (17.4 g, 113.1 mmol) in THF (50 mL) was added slowly and the stirring was continued for another 1 h. The distilled HMPA (118.1 mL, 678.6 mmol) was added slowly. The mixture was stirred for another 30 min and the bromide (21.0 mL, 170.0 mmol) in THF (50 mL) was added dropwise. The reaction was stirred for 2 days, and the saturated NH₄Cl solution (150 mL) was
added and the resulting mixture was extracted with Et$_2$O. The combined organic layers were washed with brine, dried over MgSO$_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 100:1) afforded 1b (22.63 g, 97%) as a colorless oil. The product contained 6.6 mol% of S2.

**Ethyl 2-(cyclopent-1-en-1-yl)hex-5-ynoate (1b).** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.60 – 5.56 (m, 1H), 4.14 (q, $J = 7.1$ Hz, 2H), 3.36 (t, $J = 7.4$ Hz, 1H), 2.35 – 2.24 (m, 4H), 2.20 – 2.14 (m, 2H), 2.07 – 1.98 (m, 1H), 1.96 (t, $J = 2.6$ Hz, 1H), 1.90 – 1.77 (m, 3H), 1.25 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.2, 140.3, 127.9, 83.4, 68.9, 60.5, 46.3, 32.8, 32.3, 28.9, 23.2, 16.4, 14.2. IR (KBr, cm$^{-1}$): 2956, 1732, 1157, 1043, 634. HRMS (ESI, m/z) calc for C$_{13}$H$_{18}$O$_2$ [M+H]$^+$: 207.1380, found: 207.1377.

To a suspension of ester 1b (1.0 g, 4.9 mmol) and NH(OMe)Me•HCl (0.71 g, 7.3 mmol) in THF (50 mL) at 0 °C was added $i$-PrMgCl (7.3 mL, 14.7 mmol, 2 M in THF) over 15 min. The reaction mixture was stirred at 0 °C for 0.5 h before being quenched with a saturated NH$_4$Cl solution (20 mL). The mixture was extracted with Et$_2$O. The combined organic layers were washed with brine, dried over MgSO$_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 10:1) afforded 1c (0.77 g, 72%) as a colorless oil.

**2-(Cyclopent-1-en-1-yl)-N-methoxy-N-methylhex-5-ynamide (1c).** $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.53 – 5.49 (m, 1H), 3.92 – 3.79 (brs, 1H), 3.66 (s, 3H), 3.16 (s, 3H), 2.32 – 2.24 (m, 4H), 2.22 – 2.10 (m, 2H), 2.04 – 1.95 (m, 1H), 1.93 (t, $J = 2.63$ Hz, 1H), 1.86 – 1.72 (m, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 173.9, 141.3, 127.2, 83.9, 68.7, 61.3, 41.8, 33.1, 32.2, 29.1, 23.1, 16.4. IR (KBr, cm$^{-1}$): 2937, 1660, 1383, 992, 629. HRMS (ESI, m/z) calc for C$_{13}$H$_{19}$NO$_2$ [M+Na]$^+$: 244.1308, found: 244.1310.
To a stirred suspension of LiAlH4 (0.20 g, 5.3 mmol) in THF (10 mL) at 0 °C was added dropwise a solution of ester 1b (1.0 g, 4.9 mmol) in THF (20 mL), and the mixture was stirred for 10 min. The reaction was quenched with saturated NH4Cl solution (10 mL). The mixture was extracted with Et2O. The organic phase was washed with brine, dried over MgSO4, and concentrated in vacuo. Purification of the residue by flash chromatography (PE/EtOAc = 10:1) afforded the desired alcohol S3 (0.63 g, 80%) as a colorless oil.

2-(Cyclopent-1-en-1-yl)hex-5-yn-1-ol (S3). 1H NMR (500 MHz, CDCl3) δ 5.56 (dq, J = 3.4, 1.9 Hz, 1H), 3.59 – 3.46 (m, 2H), 2.62 – 2.53 (m, 1H), 2.37 – 2.29 (m, 2H), 2.24 – 2.15 (m, 3H), 2.15 – 2.06 (m, 1H), 1.94 (t, J = 2.7 Hz, 1H), 1.90 – 1.83 (m, 2H), 1.70 – 1.55 (m, 2H), 1.45 (t, J = 4.7 Hz, 1H). 13C NMR (125 MHz, CDCl3) δ 143.2, 128.1, 84.2, 68.4, 63.9, 43.1, 32.2, 31.8, 28.4, 23.1, 16.3. IR (KBr, cm⁻¹): 3291, 2936, 1433, 1039, 639. HRMS (ESI, m/z) calc for C11H16O [M+H]⁺: 165.1274, found: 165.1273.

To a stirred solution of alcohol S3 (0.10 g, 0.61 mmol) in THF at 0 °C was added TsNHBoc (0.22 g, 0.82 mmol), Diisopropyl azodicarboxylate (DIAD) (0.19 mL, 0.92 mmol) and PPh3 (0.32 g, 1.22 mmol) successively. The mixture was stirred at 0 °C for 1 h before being quenched with H2O and extracted with Et2O. The combined organic phases were washed with brine, dried over MgSO4 and concentrated in vacuo. Purification of the residue by flash chromatography (PE/EtOAc = 20:1) afforded 1d (0.18 g, 71%) as a colorless oil.

tert-Butyl (2-(cyclopent-1-en-1-yl)hex-5-yn-1-yl)(tosyl)carbamate (1d). 1H NMR (500 MHz, CDCl3) δ 7.79 – 7.76 (d, J = 8.4 Hz, 2H), 7.30 – 7.27 (d, J = 8.4 Hz, 2H),
5.54 – 5.51 (m, 1H), 3.92 – 3.86 (dd, J = 14.1, 8.0 Hz, 1H), 3.81 – 3.75 (dd, J = 14.1, 7.0 Hz, 1H), 3.00 – 2.90 (m, 1H), 2.43 (s, 3H), 2.35 – 2.25 (m, 3H), 2.25 – 2.15 (m, 2H), 2.11 – 2.03 (m, 1H), 1.96 – 1.93 (t, J = 2.6 Hz, 1H), 1.89 – 1.82 (m, 2H), 1.77 – 1.69 (m, 1H), 1.65 – 1.57 (m, 1H), 1.31 (s, 9H). 13C NMR (125 MHz, CDCl3) δ 151.1, 144.0, 142.5, 137.6, 129.1, 128.8, 127.9, 84.2, 84.0, 68.4, 49.7, 40.9, 32.2, 31.0, 29.3, 27.8, 23.2, 21.6, 16.4. IR (KBr, cm⁻¹): 3286, 2933, 2847, 1728, 1355, 1088, 545. HRMS (ESI, m/z) calc for C23H31NO4S [M+Na]⁺: 440.1866, found: 440.1870.

![chemical structure](image1)

To a stirred solution of alcohol S3 (0.54 g, 3.29 mmol) in CH₂Cl₂ (30 mL) at rt was added DIPEA (2.17 mL, 13.2 mmol) and MOMCl (0.75 mL, 9.88 mmol). The reaction mixture was stirred at rt for 2 h before being quenched with saturated NaHCO₃ solution (10 mL) and extracted with CH₂Cl₂. The combined organic phases were washed with brine, dried over MgSO₄ and concentrated in vacuo. Purification of the residue by flash chromatography (PE/EtOAc = 50:1) afforded 1e (0.64 g, 94%) as a colorless oil.

1-(1-(Methoxymethoxy)hex-5-yn-2-yl)cyclopent-1-ene (1e). ¹H NMR (400 MHz, CDCl₃) δ 5.49 – 5.45 (m, 1H), 4.59 (s, 2H), 3.51 (dd, J = 9.6, 6.6 Hz, 1H), 3.45 (dd, J = 9.6, 6.6 Hz, 1H), 3.33 (s, 3H), 2.68 – 2.59 (m, 1H), 2.32 – 2.26 (m, 2H), 2.23 – 2.09 (m, 4H), 1.92 (t, J = 2.7 Hz, 1H), 1.86 – 1.73 (m, 3H), 1.62 – 1.52 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 143.5, 126.4, 96.4, 84.3, 69.9, 68.2, 55.1, 40.3, 32.1, 32.0, 28.9, 23.1, 16.2. IR (KBr, cm⁻¹): 3312, 2925, 2852, 1463, 1045, 630. HRMS (ESI, m/z) calc for C₁₃H₂₀O₂ [M+Na]⁺: 231.1356, found: 231.1356.

![chemical structure](image2)
To a stirred solution of alcohol S3 (0.4 g, 2.4 mmol) in CH2Cl2 (20 mL) at rt was added Et3N (0.68 mL, 4.9 mmol) and DMAP (0.03 g, 0.24 mmol) and acetic anhydride (0.35 mL, 3.7 mmol) in sequence. The reaction mixture was stirred at rt for 3 h before being quenched with saturated NaHCO3 solution (10 mL), and extracted with CH2Cl2. The combined organic phases were washed with brine, dried over MgSO4 and concentrated in vacuo. Purification of the residue by flash chromatography (PE/EtOAc = 100:1) afforded 1f (0.40 g, 80%) as a colorless oil.

2-(Cyclopent-1-en-1-yl)hex-5-yn-1-yl acetate (1f). 1H NMR (400 MHz, CDCl3) δ 5.48 (s, 1H), 4.07 (dd, J = 10.8, 6.6 Hz, 1H), 3.99 (dd, J = 10.8, 6.9 Hz, 1H), 2.77 – 2.59 (m, 1H), 2.32 – 2.25 (m, 2H), 2.24 – 2.05 (m, 4H), 2.02 (s, 3H), 1.93 (t, J = 2.6 Hz, 1H), 1.87 – 1.78 (m, 2H), 1.76 – 1.54 (m, 2H). 13C NMR (100 MHz, CDCl3) δ 170.9, 142.5, 127.1, 84.0, 68.5, 66.2, 39.4, 32.2, 32.2, 28.9, 23.2, 20.9, 16.2. IR (KBr, cm⁻¹): 2950, 1741, 1365, 1240, 1037, 634. HRMS (ESI, m/z) calc for C13H18O2 [M+Na]⁺: 229.1199, found: 229.1196.

To a stirred solution of alcohol S3 (0.63 g, 3.8 mmol) in CH2Cl2 (20 mL) was treated with TBDPSCl (1.31 mL, 5.0 mmol), imidazole (0.53 g, 7.7 mmol), and a catalytic amount of DMAP. The reaction mixture was stirred at rt for 0.5 h before being quenched with H2O (20 mL). The resulting mixture was extracted with CH2Cl2. The combined organic layer was washed with brine, dried over MgSO4 and concentrated in vacuo. Purification of the residue by column chromatography (PE/EtOAc = 100:1) afforded 1g (1.45 g, 94%) as a colorless oil.

tert-Butyl((2-(cyclopent-1-en-1-yl)hex-5-yn-1-yl)oxy)diphenylsilane (1g). 1H NMR (500 MHz, CDCl3) δ 7.70 – 7.66 (m, 4H), 7.45 – 7.38 (m, 6H), 5.47 – 5.43 (m, 1H), 3.63 (qd, J = 9.9, 6.3 Hz, 2H), 2.61 – 2.54 (m, 1H), 2.33 – 2.28 (m, 2H), 2.24 – 2.07 (m, 4H), 1.95 (t, J = 2.6 Hz, 1H), 1.92 – 1.79 (m, 3H), 1.68 – 1.59 (m, 1H), 1.07 (s, 9H).
$^{13}$C NMR (125 MHz, CDCl$_3$) δ 143.8, 135.6, 135.6, 133.9, 133.9, 129.5, 129.5, 127.6, 126.2, 84.8, 68.1, 66.1, 42.8, 32.6, 32.2, 28.8, 26.8, 23.2, 19.3, 16.4. IR (KBr, cm$^{-1}$): 2930, 1427, 1111, 701, 504. HRMS (ESI, m/z) calc for C$_{27}$H$_{34}$OSi [M+Na]$^+$: 425.2271, found: 425.2274.

![Chemical reaction](image)

To a stirred solution of alcohol S3 (1.97 g, 12.0 mmol) in CH$_2$Cl$_2$ (40 mL) was added TBSCl (2.72 g, 18.1 mmol), imidazole (1.64 g, 24.1 mmol), and a catalytic amount of DMAP in sequence. The reaction mixture was stirred at rt for 0.5 h before being quenched with H$_2$O (40 mL). The resulting mixture was extracted with CH$_2$Cl$_2$. The combined organic layer was washed with brine, dried over MgSO$_4$ and concentrated in vacuo. Purification of the residue by column chromatography (PE/EtOAc = 100:1) afforded 1h (3.12 g, 93%) as a colorless oil.

**tert-Butyl((2-(cyclopent-1-en-1-yl)hex-5-yn-1-yl)oxy)dimethylsilane (1h).** $^1$H NMR (500 MHz, CDCl$_3$) δ 5.44 – 5.41 (m, 1H), 3.59 (dd, $J$ = 9.9, 5.7 Hz, 1H), 3.50 (dd, $J$ = 9.9, 7.1 Hz, 1H), 2.52 – 2.44 (m, 1H), 2.31 – 2.26 (m, 2H), 2.24 – 2.15 (m, 3H), 2.13 – 2.04 (m, 1H), 1.92 (t, $J$ = 2.7 Hz, 1H), 1.86 – 1.77 (m, 3H), 1.60 – 1.53 (m, 1H), 0.88 (s, 9H), 0.03 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 144.0, 126.0, 84.8, 68.0, 65.6, 43.0, 32.7, 32.2, 28.9, 25.9, 23.3, 18.3, 16.4, -5.4. IR (KBr, cm$^{-1}$): 2929, 2856, 1254, 1110, 836, 628. HRMS (ESI, m/z) calc for C$_{17}$H$_{30}$OSi [M+H]$^+$: 279.2139, found: 279.2136.

### 2.2) Procedures for the preparation of enynes-1r,1n,1s,1i,1k,1l,1m,1a

![Chemical reaction](image)
To a stirred solution of DIPA (0.58 mL, 4.11 mmol) in THF (40 mL) at 0 °C was added \textit{n}-BuLi (1.64 mL, 2.5 M in hexane). After 30 min, the reaction was cooled to \(-78 \, ^\circ\text{C}\), and then a solution of ethyl isobutyrate (0.48 g, 4.11 mmol) in THF was added slowly and the stirring was continued for another 1 h. The 1-(bromomethyl)cyclopent-1-ene (0.508 g, 3.16 mmol) in THF was added dropwise. The reaction was stirred for 2 h at this temperature before being quenched with saturated NH\textsubscript{4}Cl solution (20 mL) and extracted with Et\textsubscript{2}O. The combined organic layers were washed with brine, dried over MgSO\textsubscript{4} and concentrated \textit{in vacuo}. Purification of the residue by column chromatography (PE/EtOAc = 100:1) afforded S4 (0.50 g, 2.55 mmol).

\textbf{Ethyl 3-(cyclopent-1-en-1-yl)-2,2-dimethylpropanoate (S4).} All spectral data were in agreement with reported values.\textsuperscript{1}

\begin{center}
\includegraphics[width=\textwidth]{diagram.png}
\end{center}

\textbf{Step 1.} To a stirred solution of DIPA (1.3 equiv) in THF (0.2 M) at 0 °C was added \textit{n}-BuLi (1.3 equiv, 2.5 M in hexane). After 30 min, the reaction was cooled to \(-78 \, ^\circ\text{C}\), and then a solution of ethyl isobutyrate (1.3 equiv) in THF was added slowly and the stirring was continued for another 1 h. The ketone (1.0 equiv) in THF was added dropwise. The reaction was stirred for 2 h before being quenched with saturated NH\textsubscript{4}Cl solution and extracted with Et\textsubscript{2}O. The combined organic layers were washed with brine, dried over MgSO\textsubscript{4} and concentrated \textit{in vacuo} to afford the crude aldol products which was used
for next step without further purification.

**Step 2.** To a stirred solution of the alcohol (1.0 equiv) in CH₂Cl₂ (0.3 M) and pyridine (3.0 equiv) at 0 °C was added SOCl₂ (1.5 equiv). The mixture was stirred for 1 h at this temperature, then poured into ice water and stirred for an additional 20 min at rt. The two-phase system was extracted with CH₂Cl₂. The combined extracts were washed with brine, dried over MgSO₄ and concentrated *in vacuo* to afford the unsaturated ester.

**Step 3.** To a stirred suspension of LiAlH₄ (1.1 equiv) in THF at 0 °C was added a solution of above unsaturated ester (1.0 equiv) in THF (0.1 M) dropwise. The mixture was stirred for 10 min before being quenched with H₂O and extracted with Et₂O. The combined organic layers was washed with brine, dried over MgSO₄ and concentrated *in vacuo* to afford the reduction product alcohol.

**Step 4.** To alcohol (1.0 equiv) in EtOAc (0.3 M) was added IBX (1.5 equiv.). The resulting suspension was immersed in an oil bath preheated to 80 °C and stirred vigorously open to the air atmosphere. After being stirred for 4 h, the reaction was cooled to rt and filtered. The filter cake was washed with EtOAc, and the combined filtrates were concentrated *in vacuo*. Purification of the residue by column chromatography (PE/EtOAc = 100:1) afforded aldehyde.

**Step 5.** Epoxide formation method I: To a stirred solution of trimethylsulfonium iodide (2.5 equiv) in THF (0.1 M) was added sodium hydride (60% in mineral oil, 3.0 equiv) and the reaction mixture was heated to reflux for 1h. A solution of aldehyde (1.0 equiv) in THF was added dropwise. After 4 h, the reaction was cooled to rt and was quenched with saturated NH₄Cl solution and extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄ and concentrated *in vacuo*. Purification of the residue by column chromatography (PE/EtOAc = 100:1) afforded the epoxide.
Epoxide formation method II: To a stirred solution of aldehyde (1.0 equiv) and dibromomethane (1.3 equiv) in THF (0.1 M) at –78 °C was added dropwise n-BuLi (1.3 equiv, 2.5 M in hexane).³ The resulting pale yellow mixture was stirred for overnight while allowing the bath temperature to rise to rt. The reaction was then quenched with saturated NH₄Cl solution and extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄ and concentrated \textit{in vacuo}. Purification of the residue by column chromatography (PE/EtOAc = 100:1) afforded the epoxide.

\textbf{Step 6.} To a solution of trimethylsilylacetylene (2.5 equiv) and THF (0.1 M) at –78°C was added \textit{n}-BuLi (2.5 equiv, 2.5 M in hexane) dropwise. The resulting solution was stirred at the same temperature for 30 min before the addition of BF₃\textit{•}OEt₂ (1.0 equiv). After being stirring for an additional 10 min at –78 °C, a solution of epoxide (1.0 equiv) in THF was added dropwise via syringe. When TLC analysis indicated complete consumption of the epoxide, the reaction was quenched with saturated NaHCO₃ solution and extracted with Et₂O. The combined organic layers were washed with brine, dried with MgSO₄ and concentrated \textit{in vacuo} to give the crude enyne alcohol.

To a stirred solution of enyne (1.0 equiv) in THF (0.3 M) was added TBAF (1.5 equiv, 1.0 M in THF), and the resulting mixture was stirred at rt for 0.5 h. The reaction was quenched with H₂O and extracted with ether. The combined organic layers were washed with brine, dried over MgSO₄ and concentrated \textit{in vacuo}. Purification of the residue by column chromatography (PE/EtOAc = 20:1) afforded the alkyne alcohol.

\textbf{Step 7.} To a solution of above alcohol (1.0 equiv) CH₂Cl₂ (0.1 M) at 0 °C was added imidazole (2.5 equiv), DMAP (0.1 equiv) and TMSCl (2.0 equiv) in sequence. After being stirred for 0.5 h, the reaction mixture was poured into H₂O and extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried over MgSO₄ and concentrated \textit{in vacuo}. Purification of the residue by column chromatography (PE/EtOAc = 100:1) afforded the siloxane.
3-(Cyclobut-1-en-1-yl)-2,2-dimethylpropanal (S5). It was used without further purification immediately because it was instable.

2-(Cyclopent-1-en-1-yl)-2-methylpropanal (S6). 3.00 g (21.74 mmol) of S6 was prepared from 3.62 g (43.04 mmol) of cyclopentanone (51% yield). All spectral data were in agreement with reported values.²

2-(Cyclohex-1-en-1-yl)-2-methylpropanal (S7). 4.30 g (28.29 mmol) of S7 was prepared from 3.0 g (30.55 mmol) of cyclohexanone (93% yield). ¹H NMR (500 MHz, CDCl₃) δ 9.25 (s, 1H), 5.61 – 5.55 (m, 1H), 2.10 – 2.03 (m, 2H), 1.87 – 1.81 (m, 2H), 1.62 – 1.50 (m, 4H), 1.14 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 203.4, 137.0, 124.6, 51.6, 25.7, 25.2, 23.0, 22.1, 20.3. IR (KBr, cm⁻¹): 2930, 1727, 1137, 919, 555. HRMS (ESI, m/z) calc for C₁₀H₁₆O [M+H]⁺: 153.1274, found: 153.1274.

3-(Cyclopent-1-en-1-yl)-2,2-dimethylpropanal (S8). 0.68 g (4.47 mmol) of S8 was prepared from 1.33 g (6.79 mmol) from the corresponding ester (66% yield). All spectral data were in agreement with reported values.¹
2-(1H-Inden-2-yl)-2-methylpropanal (S9). 1.94 g (10.43 mmol) of S9 was prepared from 2.28 g (17.27 mmol) of 1,3-dihydro-2H-inden-2-one (60% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.47 (s, 1H), 7.46 – 7.41 (m, 1H), 7.38 (d, $J$ = 7.5 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.22 – 7.17 (m, 1H), 6.78 – 6.75 (m, 1H), 3.37 – 3.35 (m, 2H), 1.45 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.3, 148.9, 144.3, 143.2, 128.9, 126.4, 124.6, 123.6, 120.7, 49.1, 38.5, 21.7. IR (KBr, cm$^{-1}$): 2971, 1722, 1462, 913, 753. HRMS (ESI, m/z) calc for C$_{13}$H$_{14}$O $[M+Na]^+$: 209.0937, found: 209.0937.

2-(1H-Inden-3-yl)-2-methylpropanal (S10). 4.09 g (22.0 mmol) of S10 was prepared from 3.0 g (22.72 mmol) of 2,3-dihydro-1H-inden-1-one (97% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.58 (s, 1H), 7.49 (d, $J$ = 7.2 Hz, 1H), 7.32 (d, $J$ = 7.3 Hz, 1H), 7.29 – 7.19 (m, 2H), 6.48 (t, $J$ = 1.9 Hz, 1H), 3.41 (d, $J$ = 1.5 Hz, 2H), 1.51 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 203.1, 145.0, 144.3, 142.8, 130.6, 126.1, 124.8, 124.1, 121.0, 48.4, 37.7, 21.2. IR (KBr, cm$^{-1}$): 2972, 1731, 1459, 903, 766. HRMS (ESI, m/z) calc for C$_{13}$H$_{14}$O $[M+Na]^+$: 209.0937, found: 209.0938.

2-(7-Methoxy-1H-inden-3-yl)-2-methylpropanal (S11). 2.40 g (11.11 mmol) of S11 was prepared from 3.12 g (19.23 mmol) of 4-methoxy-2,3-dihydro-1H-inden-1-one (58% yield).
yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.57 (s, 1H), 7.26 (t, $J$ = 7.9 Hz, 1H), 6.97 (d, $J$ = 7.6 Hz, 1H), 6.78 (d, $J$ = 8.2 Hz, 1H), 6.48 (t, $J$ = 1.9 Hz, 1H), 3.90 (s, 3H), 3.37 (d, $J$ = 1.8 Hz, 2H), 1.50 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 203.2, 155.4, 144.9, 144.6, 131.8, 130.7, 127.8, 114.1, 107.2, 55.1, 48.4, 35.0, 21.2. IR (KBr, cm$^{-1}$): 2971, 1727, 1478, 1259, 776. HRMS (ESI, m/z) calc for C$_{14}$H$_{16}$O [M+Na]$^+$: 239.1043, found: 239.1041.

![S12](image)

2-(Cyclobut-1-en-1-yl)-2-methylhex-5-yn-3-ol (S12). 1.07 g (6.52 mmol) of S12 was prepared from 2.8 g (40.0 mmol) of cyclobutanone (16% yield) via step 5, method I, and the 2-(cyclobut-1-en-1-yl)-2-methylpropanal intermediate was unstable. $^1$H NMR (500 MHz, CDCl$_3$) δ 5.77 (t, $J$ = 0.8 Hz, 1H), 3.65 – 3.60 (m, 1H), 2.50 – 2.40 (m, 3H), 2.31 – 2.22 (m, 3H), 2.07 (d, $J$ = 3.6 Hz, 1H), 2.05 (t, $J$ = 2.6 Hz, 1H), 1.03 (s, 3H), 1.01 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 154.9, 127.9, 82.3, 75.2, 70.2, 40.5, 29.0, 25.7, 22.6, 21.5, 20.9. IR (KBr, cm$^{-1}$): 3308, 2920, 1362, 1061, 857, 632. HRMS (ESI, m/z) calc for C$_{11}$H$_{16}$O [M+Na]$^+$: 187.1093, found: 187.1092.

![S13](image)

2-(Cyclopent-1-en-1-yl)-2-methylhex-5-yn-3-ol (S13). 0.50 g (2.81 mmol) of S13 was prepared from 1.0 g (5.37 mmol) of the corresponding aldehyde (52% yield) via step 5, method I. $^1$H NMR (400 MHz, CDCl$_3$) δ 5.50 – 5.45 (m, 1H), 3.69 (dt, $J$ = 9.7, 3.0 Hz, 1H), 2.36 – 2.15 (m, 6H), 2.05 – 2.00 (m, 2H), 1.87 – 1.77 (m, 2H), 1.08 (s, 3H), 1.04 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.7, 125.1, 82.6, 74.9, 69.9, 40.6, 32.1, 31.8, 23.6, 23.0, 22.3, 21.9. IR (KBr, cm$^{-1}$): 3308, 2964, 1362, 1064, 958, 632. HRMS (ESI, m/z) calc for C$_{12}$H$_{18}$O [M+Na]$^+$: 201.1250, found: 201.1248.
2-(Cyclohex-1-en-1-yl)-2-methylhex-5-yn-3-ol (S14). 0.46 g (2.4 mmol) of S14 was prepared from 1.0 g (6.58 mmol) the corresponding aldehyde (36% yield) via step 5 method I. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.59 – 5.55 (m, 1H), 3.71 (dt, $J$ = 9.8, 2.7 Hz, 1H), 2.36 – 2.30 (m, 1H), 2.23 – 2.16 (m, 1H), 2.07 – 1.99 (m, 5H), 1.96 – 1.88 (m, 1H), 1.66 – 1.48 (m, 4H), 1.03 (s, 3H), 0.99 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.7, 122.5, 82.8, 74.5, 69.8, 43.1, 25.6, 24.7, 23.3, 22.3, 22.1, 21.5. IR (KBr, cm$^{-1}$): 3308, 2927, 1384, 1061, 921, 632. HRMS (ESI, m/z) calc for C$_{13}$H$_{20}$O $[\text{M}+$Na$]^+$: 215.1406, found: 215.1406.

1-(Cyclopent-1-en-1-yl)-2,2-dimethylhex-5-yn-3-ol (S15). 0.41 g (2.14 mmol) of S15 from 0.66 g (4.34 mmol) of the corresponding aldehyde (49% yield) via step 5, method I. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.44 – 5.40 (m, 1H), 3.55 – 3.50 (m, 1H), 2.46 – 2.41 (m, 1H), 2.31 – 2.24 (m, 5H), 2.21 (d, $J$ = 13.1 Hz, 1H), 2.15 (d, $J$ = 3.7 Hz, 1H), 2.06 – 2.00 (m, 2H), 1.88 – 1.80 (m, 2H), 0.91 (s, 3H), 0.88 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 141.6, 128.4, 82.5, 76.3, 70.3, 40.4, 38.1, 37.6, 32.4, 24.1, 23.8, 22.9, 22.3. IR (KBr, cm$^{-1}$): 3308, 2954, 1384, 1061, 844, 633. HRMS (ESI, m/z) calc for C$_{13}$H$_{20}$O $[\text{M}+$Na$]^+$: 215.1406, found: 215.1405.

2-(1H-Inden-2-yl)-2-methylhex-5-yn-3-ol (S16). 0.60 g (2.65 mmol) of S16 was prepared from 1.0 g (5.38 mmol) of the corresponding aldehyde (49% yield) via step 5, method I. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 (d, $J$ = 7.3 Hz, 1H), 7.33 (d, $J$ = 7.4 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.15 (td, $J$ = 7.4, 1.1 Hz, 1H), 6.64 (s, 1H), 3.83 (dd, $J$ =
9.8, 2.8 Hz, 1H), 3.45 (q, $J = 22.6$ Hz, 2H), 2.39 (dt, $J = 16.8, 2.7$ Hz, 1H), 2.28 – 2.11 (m, 2H), 2.04 (t, $J = 2.6$ Hz, 1H), 1.29 (d, $J = 5.5$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 155.1, 144.6, 143.2, 127.1, 126.3, 124.2, 123.5, 120.4, 82.1, 76.5, 70.5, 41.1, 38.8, 24.6, 23.2, 22.8. IR (KBr, cm$^{-1}$): 3292, 2966, 1390, 1066, 753, 718, 635. HRMS (ESI, m/z) calc for C$_{16}$H$_{18}$O [M+Na]$^+$: 249.1250, found: 249.1247.

![S17](image)

2-((1H-Inden-3-yl)-2-methylhex-5-yn-3-ol (S17). 0.62 g (2.74 mmol) of S17 was prepared from 2.0 g (10.57 mmol) of the corresponding aldehyde (26% yield) via step 5, method II. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.67 (d, $J = 7.7$ Hz, 1H), 7.51 – 7.46 (m, 1H), 7.32 – 7.27 (m, 1H), 7.21 (td, $J = 7.4, 0.9$ Hz, 1H), 6.35 (t, $J = 2.1$ Hz, 1H), 4.46 – 4.32 (m, 1H), 3.34 (d, $J = 1.5$ Hz, 2H), 2.33 – 2.28 (m, 2H), 2.15 (d, $J = 3.5$ Hz, 1H), 2.02 (t, $J = 2.6$ Hz, 1H), 1.45 (s, 3H), 1.38 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.7, 145.6, 143.1, 129.8, 125.8, 124.4, 124.1, 122.2, 82.3, 73.9, 70.3, 41.4, 37.4, 23.6, 22.7, 21.8. IR (KBr, cm$^{-1}$): 3292, 2971, 1391, 1065, 767, 722, 639. HRMS (ESI, m/z) calc for C$_{16}$H$_{18}$O [M+Na]$^+$: 249.1250, found: 249.1248.

![S18](image)

2-((7-Methoxy-1H-inden-3-yl)-2-methylhex-5-yn-3-ol (S18). 0.50 g (1.95 mmol) of S18 was prepared from 1.36 g (6.27 mmol) the corresponding aldehyde (31% yield) via step 5, method II. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.31 – 7.25 (m, 2H), 6.77 (dd, $J = 7.5, 1.2$ Hz, 1H), 6.34 (t, $J = 2.1$ Hz, 1H), 4.40 – 4.33 (m, 1H), 3.89 (s, 3H), 3.31 – 3.26 (m, 2H), 2.33 – 2.24 (m, 2H), 2.12 (d, $J = 3.4$ Hz, 1H), 2.01 (t, $J = 2.7$ Hz, 1H), 1.43 (s, 3H), 1.36 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 155.4, 149.7, 144.9, 132.7, 129.9, 127.5, 115.5, 106.9, 82.4, 74.0, 70.3, 55.2, 41.3, 34.6, 23.8, 22.7, 21.8. IR (KBr, cm$^{-1}$):
3290, 2969, 1477, 1256, 1020, 775. HRMS (ESI, m/z) calc for C_{17}H_{20}O_{2} [M+Na]^+: 279.1356, found: 279.1353.

((2-(Cyclobut-1-en-1-yl)-2-methylhex-5-yn-3-yl)oxy)trimethylsilane (1m). 1.15 g (4.87 mmol) of 1m was prepared from 1.07 g (6.52 mmol) of alcohol S14 (75% yield).

\[
\begin{align*}
\text{1m} & \quad \text{OTMS} \\
& \quad \text{≡} \\
& \quad \text{H} \\
& \quad \text{H} \\
& \quad \text{H} \\
& \quad \text{H} \\
& \quad \text{H} \\
\end{align*}
\]

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.69 (t, $J = 0.8$ Hz, 1H), 3.66 (dd, $J = 8.6, 2.8$ Hz, 1H), 2.44 – 2.37 (m, 3H), 2.29 – 2.25 (m, 2H), 2.20 – 2.13 (m, 1H), 1.96 (t, $J = 2.7$ Hz, 1H), 0.98 (s, 3H), 0.94 (s, 3H), 0.16 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 155.5, 127.0, 84.0, 77.7, 69.4, 41.3, 29.1, 25.7, 23.8, 23.8, 19.8, 0.7. IR (KBr, cm$^{-1}$): 2958, 1250, 1105, 929, 841, 635. HRMS (ESI, m/z) calc for C$_{14}$H$_{24}$OSi [M+Na]$^+$: 259.1489, found: 259.1486.

((2-(Cyclopent-1-en-1-yl)-2-methylhex-5-yn-3-yl)oxy)trimethylsilane (1a). 0.47 g (1.89 mmol) of 1a was prepared from 0.37 g (2.05 mmol) of alcohol S15 (92% yield).

\[
\begin{align*}
\text{1a} & \quad \text{OTMS} \\
& \quad \text{≡} \\
& \quad \text{H} \\
& \quad \text{H} \\
& \quad \text{H} \\
& \quad \text{H} \\
& \quad \text{H} \\
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.42 – 5.37 (m, 1H), 3.75 (dd, $J = 8.8, 2.5$ Hz, 1H), 2.35 – 2.16 (m, 5H), 2.15 – 2.04 (m, 1H), 1.94 (t, $J = 2.6$ Hz, 1H), 1.87 – 1.76 (m, 2H), 1.01 (d, $J = 6.2$ Hz, 6H), 0.16 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.2, 124.2, 84.3, 77.8, 69.3, 41.4, 32.1, 32.0, 25.5, 23.6, 23.6, 21.0, 0.7. IR (KBr, cm$^{-1}$): 2956, 1249, 1102, 841, 929, 634. HRMS (ESI, m/z) calc for C$_{15}$H$_{26}$OSi [M+Na]$^+$: 273.1645, found: 273.1642.
((2-(Cyclohex-1-en-1-yl)-2-methylhex-5-yn-3-yl)oxy)trimethylsilane (1r). 0.56 g (2.12 mmol) of 1r was prepared from 0.46 g (2.40 mmol) of alcohol S16 (88% yield). ¹H NMR (400 MHz, CDCl₃) δ 5.52 – 5.46 (m, 1H), 3.80 (dd, J = 8.9, 2.3 Hz, 1H), 2.30 (dt, J = 17.0, 2.5 Hz, 1H), 2.12 – 1.98 (m, 4H), 1.96 – 1.83 (m, 2H), 1.64 – 1.48 (m, 4H), 0.98 (s, 3H), 0.94 (s, 3H), 0.16 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 142.1, 121.3, 84.5, 77.4, 77.0, 69.2, 43.8, 25.6, 25.4, 25.0, 23.4, 22.4, 20.0, 0.8. IR (KBr, cm⁻¹): 2929, 1249, 1103, 840, 633. HRMS (ESI, m/z) calc for C₁₆H₂₈O₅Si [M+Na]⁺: 287.1802, found: 287.1800.

((1-(Cyclopent-1-en-1-yl)-2,2-dimethylhex-5-yn-3-yl)oxy)trimethylsilane (1n). 0.39 g (1.48 mmol) of 1n was prepared from 0.38 g (1.98 mmol) of alcohol S17 (75% yield). ¹H NMR (500 MHz, CDCl₃) δ 5.38 – 5.34 (m, 1H), 3.56 (dd, J = 8.5, 2.9 Hz, 1H), 2.48 – 2.43 (m, 1H), 2.31 – 2.24 (m, 4H), 2.22 – 2.16 (m, 1H), 2.08 – 1.99 (m, 2H), 1.96 (t, J = 2.7 Hz, 1H), 1.87 – 1.80 (m, 2H), 0.85 (s, 3H), 0.83 (s, 3H), 0.16 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 141.7, 127.9, 84.0, 79.5, 69.5, 39.6, 38.9, 37.8, 32.4, 24.1, 23.7, 23.3, 22.9, 0.7. IR (KBr, cm⁻¹): 2956, 1249, 1096, 841, 635. HRMS (ESI, m/z) calc for C₁₆H₂₈O₅Si [M+Na]⁺: 287.1802, found: 287.1799.

((2-(1H-Inden-2-yl)-2-methylhex-5-yn-3-yl)oxy)trimethylsilane (1i). 0.74 g (2.49 mmol) of 1i was prepared from 0.60 g (2.66 mmol) of alcohol S19 (94% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.42 (d, J = 7.4 Hz, 1H), 7.32 (d, J = 7.4 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.17 – 7.12 (m, 1H), 6.63 – 6.58 (m, 1H), 3.88 (dt, J = 11.2, 5.6 Hz, 1H), 3.50 (d, J = 22.6 Hz, 1H), 3.36 (d, J = 22.6 Hz, 1H), 2.35 (dt, J = 17.1, 2.8 Hz, 1H), 2.13 (ddd, J = 17.1, 8.5, 2.7 Hz, 1H), 1.93 (t, J = 2.7 Hz, 1H), 1.24 (d, J = 3.9 Hz,
6H), 0.21 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 155.5, 144.8, 143.3, 126.7, 126.2, 123.9, 123.4, 120.3, 83.7, 79.1, 69.7, 42.1, 39.0, 26.5, 23.8, 22.9, 0.7. IR (KBr, cm$^{-1}$): 2961, 1249, 1102, 928, 841, 751, 717, 635. HRMS (ESI, m/z) calc for C$_{19}$H$_{26}$OSi [M+Na]$^+$: 321.1645, found: 321.1643.

![Image of 1k](image)

((2-(1H-Inden-3-yl)-2-methylhex-5-yn-3-yl)oxy)trimethylsilane (1k). 0.81 g (2.72 mmol) of 1k was prepared from 0.62 g (2.74 mmol) of alcohol S20 (99% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.61 (d, $J = 7.8$ Hz, 1H), 7.47 (d, $J = 7.2$ Hz, 1H), 7.31 – 7.27 (m, 1H), 7.20 (td, $J = 7.4$, 0.8 Hz, 1H), 6.28 (t, $J = 2.1$ Hz, 1H), 4.46 (dd, $J = 8.7$, 3.0 Hz, 1H), 3.30 (d, $J = 2.0$ Hz, 2H), 2.28 (dt, $J = 16.9$, 2.9 Hz, 1H), 2.21 (ddd, $J = 16.9$, 8.7, 2.7 Hz, 1H), 1.89 (t, $J = 2.7$ Hz, 1H), 1.37 (s, 3H), 1.31 (d, $J = 3.7$ Hz, 3H), 0.15 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 150.5, 145.4, 132.7, 129.2, 125.7, 124.2, 124.1, 122.2, 83.9, 76.1, 69.5, 42.2, 37.3, 24.6, 23.6, 21.7, 0.7. IR (KBr, cm$^{-1}$): 2956, 1249, 1104, 928, 841, 755, 722, 632. HRMS (ESI, m/z) calc for C$_{19}$H$_{26}$OSi [M+Na]$^+$: 321.1645, found: 321.1638.

![Image of 1l](image)

((2-(7-Methoxy-1H-inden-3-yl)-2-methylhex-5-yn-3-yl)oxy)trimethylsilane (1l). 0.50 g (1.52 mmol) of 1l was prepared from 0.46 g (1.74 mmol) of alcohol S21 (87% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31 – 7.22 (m, 2H), 6.76 (d, $J = 7.5$ Hz, 1H), 6.30 – 6.25 (m, 1H), 4.46 (dd, $J = 8.5$, 3.1 Hz, 1H), 3.90 (s, 3H), 3.26 (d, $J = 1.8$ Hz, 2H), 2.32 – 2.15 (m, 2H), 1.89 (t, $J = 2.6$ Hz, 1H), 1.36 (s, 3H), 1.30 (s, 3H), 0.15 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.4, 150.4, 145.4, 132.7, 129.3, 127.3, 115.5, 106.7, 83.9, 76.2, 69.5, 55.2, 42.2, 34.6, 24.8, 23.6, 21.7, 0.7. IR (KBr, cm$^{-1}$): 2956,
2.3) Procedures for the preparation of enynes-1o,1p,1j,1q

To a suspension of NaH (0.11 g, 2.64 mmol, 60% dispersion in mineral oil) in DMF (5 mL) at 0 °C was added dropwise a solution of diethyl 2-(prop-2-yn-1-yl)malonate (0.5 g, 2.52 mmol) in DMF (5 mL). The reaction mixture was stirred for 1 h. A solution of 1-(2-iodoethyl)cyclopent-1-ene (0.67 g, 3.03 mmol) in DMF (5 mL) was added dropwise, and then the reaction mixture was heated to 80 °C for 2 h. After being cooled to rt, the reaction was quenched with saturated NH₄Cl solution (5 mL) and extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄ and concentrated in vacuo. Purification of the residue by flash chromatography (PE/EtOAc = 100:1) afforded 1o (0.58 g, 82%) as a colorless oil.

**Diethyl 2-(2-(cyclopent-1-en-1-yl)ethyl)-2-(prop-2-yn-1-yl)malonate (1o).** ¹H NMR (400 MHz, CDCl₃) δ 5.39 – 5.35 (m, 1H), 4.22 – 4.15 (m, 4H), 2.82 (d, J = 2.7 Hz, 2H), 2.30 – 2.17 (m, 6H), 1.99 – 1.92 (m, 3H), 1.87 – 1.78 (m, 2H), 1.24 (t, J = 7.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 143.2, 123.9, 78.9, 71.2, 61.5, 56.6, 35.1, 32.4, 30.0, 25.5, 23.3, 22.6, 14.0. IR (KBr, cm⁻¹): 2936, 1733, 1195, 1022, 643. HRMS (ESI, m/z) calc for C₁₇H₂₄O₄ [M+Na]^+: 315.1567, found: 315.1568.
To a solution of 1-bromo-2-[(trimethylsilyl)ethynyl]benzene (1.10 g, 4.34 mmol) in THF (30 mL) was dropped n-BuLi (1.74 mL, 2.5 M in hexane) at −78 °C. The mixture was stirred for 1 h before the addition of aldehyde S6 (0.5 g, 3.62 mmol) in THF (10 mL). The resulting mixture was stirred for another 2 h at this temperature before being quenched with saturated NH₄Cl solution and extracted with Et₂O. And the combined organic layers were washed with brine, dried with MgSO₄ and concentrated in vacuo to give the crude enyne.

To a stirred solution of the crude enyne in THF (15 mL) was added TBAF (5.4 mL, 1.0 M in THF), and the resulting mixture was stirred at rt for 0.5 h. The reaction was quenched with H₂O and extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄ and concentrated in vacuo. Purification of the residue by flash chromatography (PE/EtOAc = 20:1) afforded alcohol (0.69 g, 80%) as a colorless oil.

To a stirred solution of the alcohol (0.25 g, 1.04 mmol) in CH₂Cl₂ (20 mL) at 0 °C was added DMAP (13 mg, 0.036 mmol), imidazole (0.176 g, 2.59 mmol), and TMSCl (0.26 mL, 2.07 mmol) in sequence. After being stirred for 0.5 h, the reaction mixture was poured into H₂O and extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried over MgSO₄ and concentrated in vacuo. Purification of the residue by flash chromatography (PE/EtOAc = 100:1) afforded 1p (0.31 g, 95%) as a colorless oil.

(2-(Cyclopent-1-en-1-yl)-1-(2-ethynylphenyl)-2-methylpropoxy)trimethylsilane (1p). ¹H NMR (500 MHz, CDCl₃) δ 7.44 – 7.39 (m, 2H), 7.30 – 7.26 (m, 1H), 7.17 (td,
\[ J = 7.5, 1.3 \text{ Hz, 1H}, 5.28 - 5.25 (m, 1H), 5.16 (s, 1H), 3.27 (s, 1H), 2.42 - 2.33 (m, 2H), 2.32 - 2.20 (m, 2H), 1.90 - 1.75 (m, 2H), 1.07 (s, 3H), 1.02 (s, 3H), -0.08 (s, 9H) \].

\[ ^{13} \text{C NMR (125 MHz, CDCl}_3) \delta 150.0, 145.4, 132.0, 128.6, 127.8, 126.5, 124.9, 121.1, 82.8, 81.0, 77.3, 42.3, 33.1, 32.4, 24.3, 23.6, 22.5, -0.2. \]

IR (KBr, cm\(^{-1}\)): 2955, 1382, 1251, 1067, 885, 760, 607. HRMS (ESI, m/z) calc for C\(_{20}\)H\(_{28}\)OSi [M+Na]\(^{+}\): 335.1802, found: 335.1796.

To a solution of 1H-indene (1.1 equiv) in THF (0.1 M) at \(-78^\circ\text{C}\) was added \(n\)-BuLi (1.2 equiv, 2.5 M in hexane) dropwise. The reaction mixture was stirred for 1 h before the addition of BF\(_3\)•OEt\(_2\) (1.0 equiv). The mixture was stirred for 0.5 h before the addition of epoxide (1.0 equiv) in THF and then stirred for another 2 h. The reaction was quenched with saturated NH\(_4\)Cl solution and extracted with Et\(_2\)O. The combined organic layers were washed with brine, dried with MgSO\(_4\) and concentrated \textit{in vacuo} to give the crude enyne.

To a stirred solution of crude enyne in THF (0.3 M) was added TBAF (1.5 equiv, 1.0 M in THF), and the resulting mixture was stirred at rt for 0.5 h. H\(_2\)O was added, and the mixture was extracted with Et\(_2\)O. The combined organic layers were washed with brine, dried over MgSO\(_4\) and concentrated \textit{in vacuo}. Purification of the residue by flash chromatography (PE/EtOAc = 20:1) afforded the alcohol S\(_{19}\) or S\(_{20}\).
Alcohol **S19** or **S20** (1 equiv) was dissolved in CH$_2$Cl$_2$ (0.1 M), and then treated with imidazole (2.5 equiv), DMAP (0.1 equiv) and TMSCl (2.0 equiv) at 0°C. After being stirred for 0.5 h, the reaction mixture was poured into H$_2$O and extracted with CH$_2$Cl$_2$. The combined organic layers were dried over MgSO$_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 100:1) afforded the **1j** or **1q** as a colorless oil.

![Image of S19](image)

**1-(1H-Inden-3-yl)pent-4-yn-2-ol (S19).** 0.48 g (2.44 mmol) of **S19** was prepared from 0.72 g (4.69 mmol) of the corresponding epoxide (52% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 (d, $J = 7.3$ Hz, 1H), 7.42 (d, $J = 7.5$ Hz, 1H), 7.32 (t, $J = 7.4$ Hz, 1H), 7.23 (t, $J = 7.4$ Hz, 1H), 6.39 (s, 1H), 4.22 – 4.09 (m, 1H), 3.39 (s, 2H), 2.98 – 2.89 (m, 1H), 2.82 (dd, $J = 14.4$, 7.6 Hz, 1H), 2.58 – 2.41 (m, 2H), 2.16 – 2.09 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.8, 144.4, 140.3, 131.0, 126.1, 124.8, 123.8, 119.1, 80.6, 71.0, 68.4, 38.0, 34.7, 26.8. IR (KBr, cm$^{-1}$): 3293, 2916, 1460, 1077, 770, 722, 644. HRMS (ESI, m/z) calc for C$_{14}$H$_{14}$O [M+Na]$^+$: 221.0937, found: 221.0935.

![Image of S20](image)

**1-(1H-Inden-3-yl)-3,3-dimethylhex-5-yn-2-ol (S20).** 0.28 g (1.17 mmol) of **S20** was prepared from 0.5 g (2.55 mmol) of the corresponding epoxide (46% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 (d, $J = 7.3$ Hz, 1H), 7.42 (d, $J = 7.5$ Hz, 1H), 7.32 (t, $J = 7.4$ Hz, 1H), 7.27 – 7.21 (m, 1H), 6.40 (s, 1H), 3.83 (dd, $J = 8.7$, 2.2 Hz, 1H), 3.39 (s, 2H), 2.94 – 2.84 (m, 1H), 2.61 – 2.52 (m, 1H), 2.44 – 2.24 (m, 2H), 2.03 (t, $J = 2.7$ Hz, 1H), 1.79 (d, $J = 3.1$ Hz, 1H), 1.15 (s, 3H), 1.12 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ
144.8, 144.5, 141.6, 130.8, 126.1, 124.8, 123.9, 119.1, 82.3, 74.5, 70.2, 37.9, 37.5, 30.4, 29.1, 23.5, 22.0. IR (KBr, cm\(^{-1}\)): 3300, 2963, 1427, 1056, 770, 722, 632. HRMS (ESI, m/z) calc for C\(_{17}\)H\(_{20}\)O [M+Na]^+: 263.1406, found: 263.1403.

(((1-(1H-Inden-3-yl)pent-4-yn-2-yl)oxy)trimethylsilane (1j). 0.55 g (2.04 mmol) of 1j was prepared from 0.46 g (2.34 mmol) of S19 (87% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.47 (d, \(J = 7.3\) Hz, 1H), 7.42 (d, \(J = 7.5\) Hz, 1H), 7.31 (t, \(J = 7.4\) Hz, 1H), 7.21 (t, \(J = 7.4\) Hz, 1H), 6.33 (s, 1H), 4.18 – 4.10 (m, 1H), 3.35 (s, 2H), 3.01 – 2.94 (m, 1H), 2.76 (dd, \(J = 14.0, 7.2\) Hz, 1H), 2.50 – 2.33 (m, 2H), 2.10 – 2.05 (m, 1H), 0.02 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 145.4, 144.2, 140.9, 131.0, 125.9, 124.5, 123.7, 119.3, 81.6, 70.3, 70.2, 37.8, 35.3, 27.6, 0.0. IR (KBr, cm\(^{-1}\)): 2954, 1251, 1098, 842, 758, 639. HRMS (ESI, m/z) calc for C\(_{17}\)H\(_{22}\)Si [M+Na]^+: 293.1332, found: 293.1334.

(((1-(1H-Inden-3-yl)-3,3-dimethylhex-5-yn-2-yl)oxy)trimethylsilane (1q). 0.29 g (0.93 mmol) of 1q was prepared from 0.26 g (1.10 mmol) of S20 (85% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.47 (d, \(J = 7.3\) Hz, 1H), 7.40 (d, \(J = 7.5\) Hz, 1H), 7.33 – 7.27 (m, 1H), 7.21 (td, \(J = 7.4, 1.0\) Hz, 1H), 6.31 – 5.27 (m, 1H), 4.01 (dd, \(J = 9.9, 2.2\) Hz, 1H), 3.34 (s, 2H), 2.85 – 2.78 (m, 1H), 2.59 (dd, \(J = 13.9, 9.9\) Hz, 1H), 2.33 – 2.19 (m, 2H), 2.05 (t, \(J = 2.7\) Hz, 1H), 1.11 (d, \(J = 6.0\) Hz, 3H), 1.09 (s, 3H), -0.20 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 145.4, 144.3, 142.1, 131.0, 125.9, 124.4, 123.8, 119.2, 82.7, 77.1, 70.3, 38.6, 37.6, 31.2, 29.2, 23.7, 22.6, 0.4. IR (KBr, cm\(^{-1}\)): 2960, 1249, 1092, 839, 771, 719, 634. HRMS (ESI, m/z) calc for C\(_{20}\)H\(_{28}\)OSi [M+Na]^+: 335.1802, found: 335.1798.
3. Optimization of EYM Conditions

3.1) Table S1. Optimization of EYM Reaction Conditionsa.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>T(°C)</th>
<th>t [h]</th>
<th>Yield [%] (2a:3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>PtCl₂ (5)</td>
<td>Toluene</td>
<td>80</td>
<td>1</td>
<td>66 (1:2.4)c</td>
</tr>
<tr>
<td>2d</td>
<td>A (5)</td>
<td>DCE</td>
<td>reflux</td>
<td>1.5</td>
<td>86 (1:1.2)f</td>
</tr>
<tr>
<td>3</td>
<td>B (5)</td>
<td>CH₂Cl₂</td>
<td>reflux</td>
<td>4</td>
<td>30 (2a)</td>
</tr>
<tr>
<td>4</td>
<td>C (5)</td>
<td>CH₂Cl₂</td>
<td>reflux</td>
<td>24</td>
<td>30 (2a)</td>
</tr>
<tr>
<td>5</td>
<td>E (5)</td>
<td>CH₂Cl₂</td>
<td>reflux</td>
<td>1</td>
<td>81 (2a)</td>
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<tr>
<td>6</td>
<td>D (5)</td>
<td>CH₂Cl₂</td>
<td>reflux</td>
<td>1</td>
<td>93 (2a)</td>
</tr>
<tr>
<td>7</td>
<td>D (5)</td>
<td>Toluene</td>
<td>80</td>
<td>1</td>
<td>79 (2a)</td>
</tr>
<tr>
<td>8</td>
<td>D (3)</td>
<td>CH₂Cl₂</td>
<td>reflux</td>
<td>1</td>
<td>90 (2a)</td>
</tr>
</tbody>
</table>

Catalysts:

Catalysts: aReactions were performed with 0.5 mmol of 1a, 3–5 mol% of catalyst under ethylene in specified solvent (0.03 M) unless otherwise stated. b NMR yield with anthracene as an internal standard. cIsolated yield, the ratio was determined by 1H NMR. d5 mol% A, 5 mol% P(OPh)₃, DMAD (1.0 equiv), DCE, 80 °C, 1.5 h. eReaction was run under argon atmosphere. fWith a 40% yield of recycling starting material 1a. gWith a 10% yield of recycling starting material 1a.
3.2) Proposed mechanism of the formation of byproduct 3

Scheme S1. Proposed mechanism of the formation of byproduct 3
3.3) Typical procedure for EYM reaction

**Method I:** To a solution of enyne (1.0 equiv) in CH$_2$Cl$_2$ (0.03 M) was added G-II (3 mol%), and the solution was refluxed under an atmosphere of ethylene for 4 h. Then the solvent was removed *in vacuo*. Purification of the residue by flash chromatography afforded the corresponding diene.

**Method II:** To a solution of enyne (1.0 equiv) in CH$_2$Cl$_2$ (0.03 M) was added G-II (3 mol%), and the solution was refluxed under an atmosphere of ethylene for 4 h. After the solvent was removed, the residue was redissolved in THF (0.5 M), and then treated with TBAF (1.5 equiv, 1 M in THF). After 0.5 h, water was added, and the mixture was extracted with Et$_2$O. The combined organic layers were washed with brine, dried over MgSO$_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography afforded the corresponding diene.

**Method III:** To a solution of enyne (1.0 equiv) in CH$_2$Cl$_2$ (0.03 M) was added G-II (3 mol%), and the solution was refluxed under an atmosphere of ethylene for 4 h. Then the second portion of G-II (3 mol%) was added again, and then the reaction was run for another 12 h. Then the solvent was removed in vacuo. Purification of the residue by flash chromatography afforded the corresponding diene.

**Method IV:** To a solution of enyne (1.0 equiv) in CH$_2$Cl$_2$ (0.005 M) was added G-II (5 mol%), and the solution was refluxed under an atmosphere of ethylene for 12 h. After the solvent was removed, the residue was redissolved in THF (0.5 M), and then treated with TBAF (1.5 equiv, 1 M in THF). After stirred for 0.5 h, the mixture was quenched with H$_2$O and extracted with Et$_2$O. The combined organic layers were washed with brine, dried over MgSO$_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography afforded the corresponding diene.
4. Characterization of Bicyclic Dienes 2a-2r

(3,3-Dimethyl-1,2,3,4,5,6-hexahydroazulen-2-yl)oxy)trimethylsilane (2a).

Following the typical procedure method I, diene 2a (0.81 g, 3.23 mmol) was obtained from enyne 1a (0.93 g, 3.69 mmol) as a colorless oil in 87% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 5.75 – 5.63 (m, 2H), 3.86 (t, $J$ = 7.3 Hz, 1H), 2.44 – 2.20 (m, 6H), 1.90 – 1.70 (m, 2H), 0.96 (s, 3H), 0.88 (s, 3H), 0.12 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.0, 132.0, 127.1, 125.3, 79.5, 50.3, 43.3, 31.4, 28.5, 24.7, 24.6, 18.9, 0.2. IR (KBr, cm$^{-1}$): 2956, 1250, 1090, 898, 840, 748. HRMS (ESI, m/z) calc for C$_{15}$H$_{26}$O$_2$Si [M+Na]$^+$: 273.1645, found: 273.1644.

Ethyl 1,2,3,6,7,8-hexahydroazulene-1-carboxylate (2b).

Following the typical procedure method I, diene 2b (2.01 g, 9.95 mmol) was obtained from enyne 1b (3.0 g, 14.85 mmol) as a colorless oil in 67% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 5.82 – 5.71 (m, 2H), 4.18 – 4.11 (m, 2H), 3.46 (t, $J$ = 6.9 Hz, 1H), 2.65 – 2.56 (m, 1H), 2.45 – 2.28 (m, 5H), 2.10 – 2.04 (m, 2H), 1.90 – 1.72 (m, 2H), 1.28 – 1.22 (m, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 175.1, 137.6, 135.4, 133.3, 124.3, 60.3, 56.7, 37.5, 31.1, 30.9, 26.9, 24.2, 14.3. IR (KBr, cm$^{-1}$): 2935, 1728, 1182, 1038, 840. HRMS (ESI, m/z) calc for C$_{13}$H$_{18}$O$_2$ [M+Na]$^+$: 229.1199, found: 229.1196.

N-Methoxy-N-methyl-1,2,3,6,7,8-hexahydroazulene-1-carboxamide (2c).
Following the typical procedure method I, diene 2c (1.20 g, 5.43 mmol) was obtained from enyne 1c (1.54 g, 6.97 mmol) as a colorless oil in 78% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.79 – 5.68 (m, 2H), 3.99 (s, 1H), 3.67 (s, 3H), 3.19 (s, 3H), 2.63 – 2.52 (m, 1H), 2.50 – 2.40 (m, 1H), 2.35 – 2.24 (m, 3H), 2.23 – 2.03 (m, 2H), 2.00 – 1.91 (m, 1H), 1.87 – 1.70 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.5, 138.5, 135.4, 132.8, 124.5, 61.3, 52.7, 37.7, 32.4, 31.0, 27.4, 24.3. IR (KBr, cm$^{-1}$): 2936, 1657, 1384, 1177, 992, 842, 733. HRMS (ESI, m/z) calc for C$_{13}$H$_{19}$NO$_2$ [M+Na]$^+$: 244.1308, found: 244.1304.

**tert-Butyl ((1,2,3,6,7,8-hexahydroazulen-1-yl)methyl)(tosyl)carbamate (2d).**

Following the typical procedure method I, diene 2d (0.11 g, 0.26 mmol) was obtained from enyne 1d (0.18 g, 0.43 mmol) as a colorless oil in 60% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.79 – 7.75 (d, $J = 8.3$ Hz, 2H), 7.31 – 7.27 (d, $J = 8.3$ Hz, 2H), 5.80 – 5.72 (m, 2H), 3.91 – 3.86 (dd, $J = 14.0$, 4.1 Hz, 1H), 3.82 – 3.76 (dd, $J = 14.0$, 10.1 Hz, 1H), 3.12 – 3.04 (m, 1H), 2.61 – 2.49 (m, 1H), 2.43 (s, 3H), 2.42 – 2.37 (m, 2H), 2.37 – 2.27 (m, 3H), 1.99 – 1.90 (m, 1H), 1.89 – 1.76 (m, 3H), 1.32 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 151.3, 144.0, 140.8, 137.7, 134.1, 132.6, 127.9, 124.8, 84.1, 51.9, 49.4, 36.2, 31.3, 30.9, 27.0, 24.4, 21.6. IR (KBr, cm$^{-1}$): 2978, 2933, 1727, 1354, 1154, 674, 545. HRMS (ESI, m/z) calc for C$_{23}$H$_{31}$NO$_4$S [M+Na]$^+$: 440.1866, found: 440.1867.

**3-((Methoxymethoxy)methyl)-1,2,3,4,5,6-hexahydroazulene (2e).**

Following the typical procedure method I, diene 2e (0.255 g, 1.23 mmol) was obtained from enyne 1e (0.416 g, 2.0 mmol) as a colorless oil in 62% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.77 – 5.69 (m, 2H), 4.65 – 4.60 (m, 2H), 3.59 (dd, $J = 9.4$, 4.5 Hz, 1H), 3.43
(dd, $J = 9.4, 7.4$ Hz, 1H), 3.36 (s, 3H), 2.84 (brs, 1H), 2.46 – 2.28 (m, 6H), 2.04 – 1.93 (m, 1H), 1.86 – 1.67 (m, 3H). $^{13}$C NMR (100 MHz, CDCl3) $\delta$ 140.7, 133.7, 132.2, 125.0, 96.6, 70.2, 55.1, 51.5, 36.6, 31.1, 30.8, 26.7, 24.4. IR (KBr, cm$^{-1}$): 3360, 2925, 1439, 1044, 811. HRMS (ESI, m/z) calc for C$_{13}$H$_{20}$O$_2$ [M+Na]$^+$: 231.1356, found: 231.1355.

![2f]

(1,2,3,6,7,8-Hexahydroazulen-1-yl)methyl acetate (2f).

Following the typical procedure method I, diene 2f (0.14 g, 0.68 mmol) was obtained from enyne 1f (0.21 g, 1.02 mmol) as a colorless oil in 66% yield. $^1$H NMR (400 MHz, CDCl3) $\delta$ 5.78 – 5.68 (m, 2H), 4.12 (dd, $J = 10.8, 4.7$ Hz, 1H), 3.97 (dd, $J = 10.8, 7.4$ Hz, 1H), 2.86 (brs, 1H), 2.51 – 2.25 (m, 6H), 2.05 – 1.92 (m, 4H), 1.96 – 1.73 (m, 2H), 1.67 – 1.57 (m, 1H). $^{13}$C NMR (100 MHz, CDCl3) $\delta$ 171.2, 139.7, 134.2, 132.7, 124.6, 66.5, 50.4, 36.5, 31.1, 30.7, 26.6, 24.3, 20.9. IR (KBr, cm$^{-1}$): 2937, 1739, 1365, 1236, 1034, 802. HRMS (ESI, m/z) calc for C$_{13}$H$_{18}$O$_2$ [M+Na]$^+$: 229.1199, found: 229.1197.

![2g]

tert-Butyl((1,2,3,6,7,8-hexahydroazulen-1-yl)methoxy)diphenylsilane (2g).

Following the typical procedure method I, diene 2g (1.454 g, 3.61 mmol) was obtained from enyne 1g (0.90 g, 2.24 mmol) as a colorless oil in 62% yield. $^1$H NMR (400 MHz, CDCl3) $\delta$ 7.72 – 7.70 (m, 4H), 7.45 – 7.40 (m, 6H), 5.81 – 5.72 (m, 2H), 3.76 (dd, $J = 9.9, 4.7$ Hz, 1H), 3.61 (dd, $J = 9.9, 6.6$ Hz, 1H), 2.82 (brs, 1H), 2.55 – 2.45 (m, 1H), 2.40 – 2.24 (m, 5H), 2.04 – 1.94 (m, 1H), 1.88 – 1.75 (m, 3H), 1.09 (s, 9H). $^{13}$C NMR (100 MHz, CDCl3) $\delta$ 141.3, 135.6, 135.6, 135.5, 134.1, 134.0, 133.6, 132.0, 129.5, 127.5, 125.1, 66.2, 53.9, 36.8, 31.1, 31.0, 26.8, 26.4, 24.5, 19.3. IR (KBr, cm$^{-1}$): 2930, 1427, 1111, 822, 739, 702, 612, 504. HRMS (ESI, m/z) calc for C$_{27}$H$_{34}$OSi [M+Na]$^+$:
455.2271, found: 455.2277

**tert-Butyl((1,2,3,6,7,8-hexahydroazulen-1-yl)methoxy)dimethylsilane (2h).**

Following the typical procedure method I, diene 2h (2.30 g, 8.26 mmol) was obtained from enyne 1h (3.12 g, 11.2 mmol) as a colorless oil in 74% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.75 – 5.69 (m, 2H), 3.67 (dd, $J = 9.8$, 4.9 Hz, 1H), 3.47 (dd, $J = 9.8$, 7.2 Hz, 1H), 2.77 – 2.71 (m, 1H), 2.47 – 2.28 (m, 6H), 1.97 – 1.88 (m, 1H), 1.87 – 1.75 (m, 1H), 1.66 (ddd, $J = 13.5$, 9.4, 4.8 Hz, 1H), 0.89 (s, 9H), 0.04 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 141.5, 133.4, 132.0, 125.1, 65.6, 54.0, 36.6, 31.2, 31.1, 26.4, 25.9, 24.6, 18.3, -5.3, -5.3. IR (KBr, cm$^{-1}$): 2929, 1471, 1255, 1101, 836, 776. HRMS (ESI, m/z) calc for C$_{17}$H$_{30}$OSi [M+Na$^+$]: 301.1958, found: 301.1958.

**3,3-Dimethyl-1,2,3,4-tetrahydrobenzo[f]azulen-2-ol (2i).**

Following the typical procedure method II, diene 2i (0.15 g, 0.67 mmol) was obtained from enyne 1i (0.30 g, 1.0 mmol) as a white solid in 67% yield. M.P. 77 – 79 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 – 7.27 (m, 2H), 7.23 – 7.18 (m, 1H), 7.14 (d, $J = 7.5$ Hz, 1H), 6.94 (d, $J = 11.4$ Hz, 1H), 6.36 (d, $J = 11.4$ Hz, 1H), 3.96 (t, $J = 7.4$ Hz, 1H), 3.12 (d, $J = 13.7$ Hz, 1H), 2.99 (d, $J = 13.7$ Hz, 1H), 2.51 (dd, $J = 14.6$, 7.3 Hz, 1H), 2.36 (dd, $J = 14.6$, 7.5 Hz, 1H), 1.12 (s, 3H), 1.00 (s, 3H), 0.11 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.2, 136.4, 136.1, 131.5, 128.6, 128.6, 128.2, 127.7, 127.4, 125.3, 80.4, 49.6, 40.3, 32.4, 25.2, 19.6, 0.1. IR (KBr, cm$^{-1}$): 3375, 2953, 1461, 1060, 788, 738. HRMS (ESI, m/z) calc for C$_{16}$H$_{18}$O [M+Na$^+$]: 249.1250, found: 249.1245.
**1,2,3,6-Tetrahydrobenzo[e]azulen-2-ol (2j).**

Following the typical procedure method II, diene 2j (0.18 g, 0.91 mmol) was obtained from enyne 1j (0.27 g, 1.0 mmol) as a colorless oil in 91% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.38 – 7.32 (m, 2H), 7.29 – 7.24 (m, 1H), 7.21 (d, $J$ = 7.6 Hz, 1H), 6.09 (d, $J$ = 9.7 Hz, 1H), 5.76 (dt, $J$ = 9.6, 6.8 Hz, 1H), 4.67 – 4.59 (m, 1H), 3.42 – 3.30 (m, 1H), 3.12 – 2.97 (m, 4H), 2.74 (d, $J$ = 17.4 Hz, 1H), 2.08 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 137.6, 136.4, 135.7, 134.9, 128.5, 127.7, 125.7, 125.7, 125.5, 125.1, 70.3, 46.7, 45.5, 34.9. IR (KBr, cm$^{-1}$): 3340, 2924, 1487, 1035, 822, 758, 729, 628. HRMS (ESI, m/z) calc for C$_{14}$H$_{14}$O $[M+Na]^+$: 221.0937, found: 221.0935.

**1,1-Dimethyl-1,2,3,6-tetrahydrobenzo[e]azulen-2-ol (2k).**

Following the typical procedure method II, diene 2k (0.07 g, 0.31 mmol) was obtained from enyne 1k (0.145 g, 0.49 mmol) as a colorless oil in 63% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.66 (dd, $J$ = 7.9, 0.8 Hz, 1H), 7.31 (td, $J$ = 7.4, 1.3 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.21 (dd, $J$ = 7.5, 1.0 Hz, 1H), 6.02 (d, $J$ = 9.6 Hz, 1H), 5.80 (dt, $J$ = 9.5, 6.7 Hz, 1H), 3.98 (t, $J$ = 6.1 Hz, 1H), 3.05 – 2.84 (m, 3H), 2.61 (dd, $J$ = 15.7, 5.9 Hz, 1H), 1.83 (brs, 1H), 1.43 – 1.35 (m, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 146.2, 138.5, 136.0, 134.0, 127.8, 127.7, 127.1, 125.8, 125.1, 125.1, 80.6, 41.5, 35.0, 29.6, 25.8, 20.0. IR (KBr, cm$^{-1}$): 3390, 2927, 1461, 1081, 768, 728, 662. HRMS (ESI, m/z) calc for C$_{16}$H$_{18}$O $[M+Na]^+$: 249.1250, found: 249.1247.
7-Methoxy-1,1-dimethyl-1,2,3,6-tetrahydrobenzo[e]azulen-2-ol (2l).
Following the typical procedure method II, diene 2l (0.18 g, 0.70 mmol) was obtained from enyne 1l (0.33 g, 1.0 mmol) as a white solid in 70% yield. M.P. 119 – 121 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.29 (d, $J = 7.7$ Hz, 1H), 7.20 – 7.15 (m, 1H), 6.92 (d, $J = 7.9$ Hz, 1H), 6.05 (d, $J = 9.4$ Hz, 1H), 5.84 (dt, $J = 9.4, 6.9$ Hz, 1H), 4.00 – 3.95 (m, 1H), 3.86 (s, 3H), 2.86 (b.rs, 2H), 2.61 (dd, $J = 15.6, 5.6$ Hz, 1H), 1.83 (s, 1H), 1.46 – 1.31 (m, 7H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 155.2, 146.3, 136.4, 135.6, 127.5, 126.8, 126.3, 125.0, 117.6, 109.6, 80.7, 55.7, 41.6, 25.9, 25.2, 20.0. IR (KBr, cm$^{-1}$): 3410, 2931, 1471, 1265, 1107, 790, 726, 643. HRMS (ESI, m/z) calc for C$_{17}$H$_{20}$O$_2$ [M+Na]$^+$: 279.1356, found: 279.1356.

$^{(3,3}$-Dimethyl-2,3,4,5-tetrahydro-$1H$-inden-2-yl)oxy)trimethylsilane (2m).
Following the typical procedure method I, diene 2m (0.40 g, 1.69 mmol) was obtained from enyne 1m (0.47 g, 2.00 mmol) as a colorless oil in 85% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 5.84 (dt, $J = 9.5, 1.9$ Hz, 1H), 5.68 – 5.63 (m, 1H), 3.95 (t, $J = 7.0$ Hz, 1H), 2.43 (ddt, $J = 15.1, 7.1, 2.2$ Hz, 1H), 2.25 – 2.18 (m, 3H), 2.09 – 2.02 (m, 2H), 0.98 (s, 3H), 0.89 (s, 3H), 0.12 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 142.1, 127.6, 124.7, 123.9, 80.6, 47.8, 39.8, 24.7, 23.4, 19.6, 19.0, 0.1. IR (KBr, cm$^{-1}$): 2956, 1462, 1250, 1093, 840, 750. HRMS (ESI, m/z) calc for C$_{14}$H$_{24}$OSi [M+Na]$^+$: 259.1489, found: 259.1485.
3,3-Dimethyl-2,3,4,5,6,7-hexahydro-1H-benzo[7]annulen-2-ol (2n).

Following the typical procedure method II, diene 2n (0.105 g, 0.55 mmol) was obtained from enyne 1n (0.264 g, 1.00 mmol) as a colorless oil in 55% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 5.77 – 5.71 (m, 1H), 5.57 (d, $J = 11.9$ Hz, 1H), 3.50 (t, $J = 5.8$ Hz, 1H), 2.41 – 2.32 (m, 1H), 2.23 (dd, $J = 11.9$, 5.9 Hz, 2H), 2.14 – 1.94 (m, 5H), 1.86 – 1.79 (m, 2H), 1.42 (brs, 1H), 0.92 (s, 3H), 0.90 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 135.7, 131.3, 130.1, 123.5, 74.1, 45.1, 37.3, 35.4, 33.7, 32.1, 28.0, 26.2, 21.8. IR (KBr, cm$^{-1}$): 3404, 2924, 1448, 1043, 722. HRMS (ESI, m/z) calc for C$_{13}$H$_{20}$O $[M+Na]^+$: 215.1406, found: 215.1405.

![Diagram](image1.png)


Following the typical procedure method I, diene 2o (0.15 g, 0.54 mmol) was obtained from enyne 1o (0.28 g, 1.00 mmol) as a colorless oil in 54% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 5.78 – 5.72 (m, 1H), 5.61 (d, $J = 11.8$ Hz, 1H), 4.19 – 4.14 (m, 4H), 2.55 (s, 2H), 2.24 – 2.15 (m, 4H), 2.11 – 2.05 (m, 4H), 1.85 – 1.78 (m, 2H), 1.23 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 171.5, 135.6, 131.5, 130.0, 124.6, 61.1, 53.5, 35.9, 35.0, 31.0, 29.6, 28.2, 27.7, 14.0. IR (KBr, cm$^{-1}$): 2934, 1731, 1446, 1250, 1095, 864. HRMS (ESI, m/z) calc for C$_{17}$H$_{24}$O$_4$ [M+Na]$^+$: 315.1572, found: 315.1571.

![Diagram](image2.png)

6,6-Dimethyl-6,7,8,9-tetrahydro-5H-cyclohepta[a]naphthalen-5-ol (2p).

Following the typical procedure method II, diene 2p (0.083 g, 0.35 mmol) was obtained from enyne 1p (0.25 g, 0.80 mmol) as a colorless oil in 43% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.38 – 7.35 (m, 1H), 7.30 – 7.26 (m, 2H), 7.23 – 7.19 (m, 1H), 6.47 (d, $J =
11.0 Hz, 1H), 6.29 – 6.23 (m, 1H), 4.28 (d, J = 8.0 Hz, 1H), 2.34 – 2.24 (m, 2H), 2.16 – 2.05 (m, 4H), 1.70 (d, J = 8.1 Hz, 1H), 1.19 (s, 3H), 1.08 (s, 3H). 13C NMR (125 MHz, CDCl3) δ 147.1, 135.7, 134.1, 133.4, 128.2, 128.0, 127.6, 126.8, 126.6, 123.2, 77.8, 41.0, 36.1, 27.7, 27.6, 24.9, 21.0. IR (KBr, cm⁻¹): 3464, 2928, 1484, 1298, 1043, 739, 613. HRMS (ESI) m/z calc’d for C17H20O [M+Na]+: 263.1406, found: 263.1411

11. ((3,3-Dimethyl-2,3,4,7-tetrahydro-1H-dibenzo[a,c][7]annulen-2-yl)oxy)trimethylsilane (2q).

Following the typical procedure method III, diene 2q (0.195 g, 0.23 mmol) was obtained from enyne 1q (0.231 g, 0.74 mmol) as a colorless oil in 84% yield. 1H NMR (500 MHz, CDCl3) δ 7.50 (dd, J = 7.6, 1.5 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.17 (dd, J = 7.2, 1.7 Hz, 1H), 5.84 (dt, J = 9.7, 6.7 Hz, 1H), 5.76 (d, J = 9.8 Hz, 1H), 3.78 – 3.70 (m, 1H), 3.20 – 2.60 (m, 4H), 2.26 (s, 2H), 1.03 (s, 3H), 1.02 (s, 3H), 0.17 (s, 9H). 13C NMR (125 MHz, CDCl3) δ 139.6, 138.5, 132.8, 132.2, 129.5, 127.5, 126.9, 126.4, 125.7, 125.5, 74.4, 37.1, 34.3, 34.1, 27.1, 0.4. IR (KBr, cm⁻¹): 2956, 1448, 1082, 839, 756, 718. HRMS (ESI, m/z) calc for C20H28OSi [M+Na]⁺: 335.1802, found: 335.1800.

(Z)-3,3-Dimethyl-2,3,4,5,6,7-hexahydro-1H-cyclopenta[8]annulen-2-ol (2r).

Following the typical procedure method IV, diene 2r (0.133 g, 0.69 mmol) was obtained from enyne 1r (0.528 g, 2.0 mmol) as a colorless oil in 34% yield. 1H NMR (500 MHz, CDCl3) δ 5.76 (d, J = 11.2 Hz, 1H), 5.55 (dt, J = 11.2, 7.2 Hz, 1H), 3.87 (q, J = 6.2 Hz, 1H), 2.57 (dd, J = 15.5, 6.6 Hz, 1H), 2.23 – 2.15 (m, 3H), 2.10 (t, J = 5.7 Hz, 2H), 1.65 – 1.48 (m, 5H), 1.01 (s, 3H), 0.98 (s, 3H). 13C NMR (125 MHz, CDCl3) δ 144.0, 130.0, 128.1, 126.5, 79.8, 50.3, 42.5, 27.8, 25.6, 25.0, 24.9, 23.2, 19.0. IR (KBr,
cm$^{-1}$): 3391, 2925, 1448, 1060, 745. HRMS (ESI, m/z) calc for C$_{13}$H$_{20}$O$^+ [M+Na]$: 215.1406, found: 215.1405

5. Syntheses of Skeletally Diverse, Privileged Scaffolds from 2g and 2h.

To a stirred solution of diene 2g (0.72 g, 1.79 mmol) in CH$_2$Cl$_2$ (300 mL) at 0 °C was treated methylene blue (0.050 g), and the mixture was irradiated with a 300 W tungsten lamp while bubbled with O$_2$ until no starting material left. Then Et$_3$N (1.24 mL, 9.0 mmol) was added and the mixture was stirred at rt overnight. The solvent was removed in vacuo. Purification of the residue by flash chromatography (PE/ EtOAc = 20:1~4:1) afforded the 5b (0.28 g, 0.65 mmol, 36%) as a white solid and 5a (0.19 g, 0.44 mmol, 24%) as a colorless oil.
rac-(1S,8aS)-1-(((tert-Butyldiphenylsilyl)oxy)methyl)-8a-hydroxy-2,3,6,7,8,8a-hexahydroazulen-5(1H)-one (5b). M.P. 103 – 105 °C. 1H NMR (500 MHz, CDCl3) δ 7.68 – 7.64 (m, 4H), 7.46 – 7.38 (m, 6H), 5.92 (s, 1H), 3.77 (dd, J = 10.4, 7.8 Hz, 1H), 3.70 (dd, J = 10.4, 5.9 Hz, 1H), 3.05 (ddd, J = 16.9, 10.7, 2.5 Hz, 1H), 2.74 – 2.65 (m, 1H), 2.53 (ddd, J = 18.1, 7.6, 3.8, 1.4 Hz, 1H), 2.46 – 2.38 (m, 1H), 2.35 – 2.25 (m, 1H), 2.08 – 2.00 (m, 2H), 1.95 – 1.87 (m, 1H), 1.83 – 1.70 (m, 2H), 1.44 – 1.34 (m, 1H), 1.06 (s, 9H). 13C NMR (125 MHz, CDCl3) δ 205.3, 163.0, 135.5, 135.5, 133.0, 133.0, 129.8, 127.8, 127.8, 125.5, 81.8, 63.4, 55.3, 41.7, 32.3, 31.7, 26.8, 24.8, 19.1. IR (KBr, cm-1): 3406, 2930, 1656, 1427, 1111, 832, 702, 504. HRMS (ESI, m/z) calc for C27H34O3Si [M+Na]+: 457.2169, found: 457.2168.

rac-(1S,8aR)-1-(((tert-Butyldiphenylsilyl)oxy)methyl)-8a-hydroxy-2,3,6,7,8,8a-hexahydroazulen-5(1H)-one (5a). 1H NMR (500 MHz, CDCl3) δ 7.70 – 7.66 (m, 4H), 7.47 – 7.40 (m, 6H), 5.91 (s, 1H), 4.04 (dd, J = 11.0, 3.4 Hz, 1H), 3.98 (brs, 1H), 3.87 (dd, J = 11.0, 4.0 Hz, 1H), 3.01 (ddd, J = 15.1, 8.4, 4.1 Hz, 1H), 2.78 (ddt, J = 18.3, 9.0, 2.0 Hz, 1H), 2.51 – 2.41 (m, 2H), 2.33 (ddd, J = 14.2, 5.9, 4.4 Hz, 1H), 2.27 – 2.13 (m, 2H), 1.85 – 1.71 (m, 3H), 1.67 (ddd, J = 14.3, 9.9, 4.5 Hz, 1H), 1.08 (s, 9H). 13C NMR (125 MHz, CDCl3) δ 203.1, 164.4, 135.5, 135.5, 132.4, 132.2, 123.0, 129.9, 127.8, 125.9, 81.1, 62.9, 51.5, 43.6, 36.9, 31.9, 26.7, 24.5, 19.0, 18.9. IR (KBr, cm-1): 3439, 2929, 1655, 1471, 1255, 1093, 837, 776. HRMS (ESI, m/z) calc for C27H34O3Si [M+Na]+: 457.2169, found: 457.2164.

To a stirred solution of diene 2h (1.0 g, 3.59 mmol) in CH2Cl2 (20 mL) at 0 °C was added NaHCO3 (0.60 g, 7.2 mmol) and m-CPBA (0.84 g, 3.66 mmol, contains ca. 25% water). After being stirred for 10 min, the mixture was filtered through a pad of basic aluminium oxide and washed with PE/EtOAc = 20:1. The filtrate was concentrated in
vacuo. Purification of the residue by column chromatography (aluminium oxide, basic PE/EtOAc = 100:1) afforded the α-epoxide 6a (0.19 g, 0.65 mmol, 18%) as a colorless oil and β-epoxide 6b (0.29 g, 0.99 mmol, 27%) as a colorless oil.

tert-butyl(dimethyl)((3S,3aR,8aR)-2,3,5,6-tetrahydro-1H,4H-3a,8a-epoxyazulen-3-yl)methoxy)silane (6a). $^1$H NMR (400 MHz, CDCl$_3$) δ 5.89 – 5.81 (ddd, $J$ = 11.6, 7.2, 2.8 Hz, 1H), 5.74 – 5.68 (dd, $J$ = 11.6, 2.8 Hz, 1H), 3.86 – 3.80 (dd, $J$ = 10.0, 7.2 Hz, 1H), 3.59 – 3.53 (dd, $J$ =10.0, 6.8 Hz, 1H), 2.47 – 2.38 (m, 1H), 2.35 – 2.25 (m, 1H), 2.22 – 2.16 (m, 1H), 2.07 – 1.89 (m, 4H), 1.75 – 1.62 (m, 3H), 1.09 – 0.98 (m, 1H), 0.92 (s, 9H), 0.08 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 136.5, 125.7, 75.2, 69.8, 63.7, 46.8, 31.8, 31.1, 30.4, 25.9, 23.2, 22.6, -5.4. IR (KBr, cm$^{-1}$): 2925, 2354, 1542, 810. HRMS (ESI, m/z) calc for C$_{17}$H$_{30}$O$_2$Si [M+Na]$^+$: 317.1907, found: 317.1913.

tert-butyl(dimethyl)((3S,3aS,8aS)-2,3,5,6-tetrahydro-1H,4H-3a,8a-epoxyazulen-3-yl)methoxy)silane (6b). $^1$H NMR (400 MHz, CDCl$_3$) δ 5.88 – 5.80 (ddd, $J$ = 11.6, 7.1, 2.6 Hz, 1H), 5.76 – 5.71 (dd, $J$ = 11.6, 2.8 Hz, 1H), 3.74 – 3.68 (dd, $J$ = 10.1, 4.6 Hz, 1H), 3.67 – 3.62 (dd, $J$ = 10.1, 3.8 Hz, 1H), 2.35 – 2.25 (m, 1H), 2.23 – 2.16 (m, 2H), 2.10 – 1.89 (m, 4H), 1.73 – 1.65 (m, 2H), 1.62 – 1.56 (m, 1H), 1.47 – 1.40 (m, 1H), 0.89 (s, 9H), 0.06 (s, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 136.8, 125.4, 75.8, 70.0, 64.2, 47.3, 32.9, 31.4, 29.2, 25.9, 23.8, 22.0, 18.1, -5.6. IR (KBr, cm$^{-1}$): 2925, 1577, 1031, 419. HRMS (ESI, m/z) calc for C$_{17}$H$_{30}$O$_2$Si [M+Na]$^+$: 317.1907, found: 317.1902.

To a stirred solution of β-epoxide 6b (0.294 g, 1.0 mmol) in CH$_2$Cl$_2$ (10 mL) at –78 °C was added BF$_3$•OEt$_2$ (0.16 mL, 48% boron fluoride in Et$_2$O) dropwise. After being stirred for 0.5 h, the mixture was quenched with aqueous NaOH solution (5 mL, 1 M) and then extracted with CH$_2$Cl$_2$. The combined organic layers were washed with brine, dried over MgSO$_4$ and concentrated in vacuo. Purification of the residue by column chromatography (PE/EtOAc = 50:1) afforded the spiro compound 7 (0.12 g, 40%) as a colorless oil.

rac-(2S,5S)-2-(((tert-Butyldimethylsilyl)oxy)methyl)spiro[4.5]dec-6-en-1-one (7). $^1$H NMR (500 MHz, CDCl$_3$) δ 5.92 (dt, $J$ = 10.0, 3.8 Hz, 1H), 5.29 (dt, $J$ = 10.0, 2.1 Hz, 1H), 3.93 (dd, $J$ = 9.9, 4.0 Hz, 1H), 3.68 (dd, $J$ = 9.9, 3.3 Hz, 1H), 2.31 – 2.25 (m,
1H), 2.08 – 1.98 (m, 4H), 1.89 (ddd, J = 12.8, 5.3, 3.2 Hz, 1H), 1.82 – 1.69 (m, 4H),
1.55 – 1.47 (m, 1H), 1.42 – 1.36 (m, 1H), 0.86 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H). 13C
NMR (125 MHz, CDCl3) δ 220.8, 130.1, 128.9, 61.3, 51.1, 51.0, 35.9, 28.6, 25.8, 24.7,
21.8, 18.4, 18.2, -5.5, -5.6. IR (KBr, cm⁻¹): 2927, 1737, 1463, 1255, 1092, 836, 775.
HRMS (ESI, m/z) calc for C17H30O2Si [M+Na]⁺: 317.1907, found: 317.1903.

A stirred solution of diene 2g (0.20 g, 0.50 mmol) in n-hexane equipped in quartz
reaction tube was degassed with argon for 5 min and then irradiated with 365 nm UV
lamp (8 W × 4) for 12 h. TLC showed no starting materials left, the solvent was removed
in vacuo. Purification of the residue by flash chromatography (PE/EtOAc = 100:1)
afforded two inseparable diastereoisomers 8 (0.12 g, 60%) as a colorless oil.

rac-tert-Butyl(((4aS,7aS)-2,3,4a,5,6,7-hexahydro-1H-
cyclobuta[1,2:1,4]di[5]annulen-1-yl)methoxy)diphenylsilane (8). 1H NMR (500
MHz, CDCl3) δ 7.75 – 7.60 (m, 4H), 7.50 – 7.30 (m, 6H), 5.54 – 5.48 (m, 1H), 3.74 –
3.64 (m, 1H), 3.64 – 3.40 (m, 1H), 2.84 – 2.54 (m, 1H), 2.20 – 2.12 (m, 1H), 2.12 – 1.9
(m, 3H), 1.75 – 1.54 (m, 5H), 1.28 – 1.14 (m, 2H), 1.06 (s, 9H). 13C NMR (125 MHz,
CDCl3) δ 158.8, 156.3, 135.6, 134.2, 134.1, 129.5, 127.6, 124.3, 123.6, 65.0, 64.7, 60.8,
60.5, 47.0, 45.4, 44.0, 42.5, 32.5, 32.0, 31.6, 26.9, 26.8, 26.6, 26.5, 24.6, 24.0, 23.8,
23.4, 23.1, 19.2. HRMS (ESI, m/z) cal for C27H34OSi [M+Na]⁺: 425.2271, found: 425.2276.
6. Construction of the Core Skeleton of Pseudolaric Acid F.

To a stirred solution of 5b (0.435 g, 1.0 mmol) in toluene (15 mL) was added DMAP (0.122 g, 1.0 mmol), Et₃N (0.56 mL, 4.0 mmol) and Ac₂O (0.28 mL, 3.0 mmol) successively, and the mixture was heated to reflux for 5 h. After being cooled to rt, the mixture was quenched with H₂O (20 mL) and extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄ and concentrated in vacuo to give the crude acetylation product.

The above crude acetylation product was dissolved with THF (10 mL), AcOH (0.17 mL, 3.0 mmol) and TBAF (1.5 mL, 1 M in THF) was added successively. The mixture was heated at 50 °C for 2 h. After being cooled to rt, the mixture was quenched with H₂O (10 mL) and extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄ and concentrated in vacuo. Purification of the residue by column chromatography (PE/EtOAc = 4:1~1:1) afforded the alcohol 9 (0.238 g, 99%) as a colorless oil.
rac-(3S,3aS)-3-(Hydroxymethyl)-7-oxo-2,3,4,5,6,7-hexahydroazulen-3a(1H)-yl acetate (9). $^1$H NMR (500 MHz, CDCl$_3$) δ 5.97 – 5.91 (m, 1H), 3.81 (dd, $J = 11.0$, 6.8 Hz, 1H), 3.62 (dd, $J = 11.0$, 6.7 Hz, 1H), 3.05 – 2.98 (m, 1H), 2.96 – 2.87 (m, 1H), 2.84 – 2.76 (m, 1H), 2.53 – 2.43 (m, 3H), 2.05 – 1.99 (m, 1H), 1.97 (s, 3H), 1.92 – 1.86 (m, 1H), 1.85 – 1.73 (m, 3H), 1.43 – 1.34 (m, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 204.1, 169.7, 161.0, 125.9, 89.0, 61.8, 50.2, 40.6, 32.4, 28.5, 25.9, 21.8, 18.6. IR (KBr, cm$^{-1}$): 3439, 2950, 1734, 1661, 1236, 1049, 960. HRMS (ESI, m/z) calc for C$_{13}$H$_{18}$O$_4$ [M+Na$^+$]: 261.1097, found: 261.1099.

To a stirred solution of alcohol 9 (0.219 g, 0.92 mmol) in THF (10 mL) at rt was added CDI (0.448 g, 2.76 mmol), and the mixture was stirred for 12 h. When TLC showed no starting material left, the solvent was removed in vacuo. Purification of the residue by flash chromatography (PE/EtOAc = 2:1~1:1) afforded the product 10 (0.246 g, 0.74 mmol, 81%) as a yellow oil.

rac-((1S,8aS)-8a-Acetoxy-5-oxo-1,2,3,5,6,7,8,8a-octahydroazulen-1-yl)methyl 1H-imidazole-1-carboxylate (10). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.10 (s, 1H), 7.38 (t, $J =$ 1.4 Hz, 1H), 7.07 (dd, $J =$ 1.5, 0.7 Hz, 1H), 5.94 (s, 1H), 4.54 (dd, $J =$ 11.1, 7.2 Hz, 1H), 4.46 (dd, $J =$ 11.1, 7.2 Hz, 1H), 3.43 – 3.35 (m, 1H), 3.06 – 2.96 (m, 1H), 2.83 – 2.75 (m, 1H), 2.55 (dd, $J =$ 17.2, 7.3 Hz, 1H), 2.50 – 2.43 (m, 1H), 2.40 – 2.31 (m, 1H), 2.12 – 2.05 (m, 1H), 1.98 – 1.94 (m, 1H), 1.92 (s, 3H), 1.85 – 1.77 (m, 2H), 1.43 (ddd, $J =$ 24.1, 11.8, 7.3 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 204.0, 169.2, 158.8, 148.3, 136.9, 130.8, 125.6, 116.9, 88.1, 67.0, 46.0, 39.9, 32.0, 28.6, 26.0, 21.5, 18.7. IR (KBr, cm$^{-1}$): 2921, 1762, 1736, 1665, 1377, 1239, 1004, 769. HRMS (ESI, m/z) calc for C$_{17}$H$_{20}$N$_2$O$_5$ [M+Na$^+$]: 355.1264, found: 355.1265.
To a stirred solution of (PhSe)$_2$ (188 mg, 0.60 mmol) in DMF (5 mL) at rt was added with NaBH$_4$ (23 mg, 0.62 mmol). The mixture was stirred for 10 min and then transferred to a stirred solution of starting material 10 (100 mg, 0.301 mmol) in DMF (5 mL). The reaction mixture was stirred for 0.5 h and TLC showed no starting material left. The mixture was diluted with Et$_2$O (10 mL) and then quenched with saturated NaHCO$_3$ solution (10 mL) and extracted with Et$_2$O. The combined organic layers were washed with brine, dried over MgSO$_4$ and concentrated in vacuo. Purification of the residue by column chromatography (PE/EtOAc = 8:1~4:1) afforded the product 11 (90 mg, 0.213 mmol, 71%) as a colorless oil.

\[ \text{rac-}(3S,3aS)-7\text{-Oxo-3-(((phenylselanyl)carbonyl)oxy)methyl}-2,3,4,5,6,7-\text{hexahydroazulen-3a(1H)-yl acetate (11).} \]

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.66 – 7.62 (m, 2H), 7.44 – 7.37 (m, 3H), 5.95 (s, 1H), 4.42 (dd, $J = 11.1, 6.8$ Hz, 1H), 4.35 (dd, $J = 11.1, 6.7$ Hz, 1H), 3.31 – 3.23 (m, 1H), 3.03 – 2.93 (m, 1H), 2.83 (ddd, $J = 17.0, 12.4, 3.2$ Hz, 1H), 2.55 – 2.46 (m, 2H), 2.35 – 2.29 (m, 1H), 2.04 – 1.99 (m, 4H), 1.97 – 1.91 (m, 1H), 1.84 – 1.67 (m, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 204.2, 169.2, 166.7, 159.6, 135.7, 129.3, 129.2, 125.7, 125.6, 88.1, 66.5, 46.2, 40.1, 32.1, 28.6, 25.8, 21.7, 18.7. IR (KBr, cm$^{-1}$): 2926, 1734, 1666, 1367, 1236, 1119, 1020, 741, 690. HRMS (ESI, m/z) calc for C$_{20}$H$_{22}$O$_5$Se [M+Na]$^+$: 445.0525, found: 445.0519.

To a stirred solution of compound 11 (90 mg, 0.213 mmol) in toluene (10 mL) at rt was added with AIBN (18 mg, 0.107 mmol) and (TMS)$_3$SiH (0.154 mL, 0.426 mmol) successively. The resulting mixture was heated to reflux for 12 h. After being cooled to rt, the mixture was concentrated in vacuo. Purification of the residue by flash...
chromatography (PE/EtOAc = 8:1~4:1) afforded the tricyclic compound 10 (26 mg, 0.098 mmol, 46%) as a white solid.

*rac-(4S,4aS,9aR)-1,8-Dioxohexahydro-1H-4,9a-ethanocyclohepta[c]pyran-4a(5H)-yl acetate (12).* M.P. 108 – 110 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 4.52 – 4.45 (m, 1H), 4.22 (d, $J = 11.4$ Hz, 1H), 3.42 (dd, $J = 6.2$, 2.9 Hz, 1H), 3.19 – 3.12 (m, 1H), 3.05 (d, $J = 17.4$ Hz, 1H), 2.77 (d, $J = 17.4$ Hz, 1H), 2.60 (dd, $J = 16.5$, 6.4 Hz, 1H), 2.38 – 2.28 (m, 1H), 2.23 – 2.05 (m, 5H), 2.00 – 1.91 (m, 1H), 1.85 – 1.76 (m, 2H), 1.72 – 1.63 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 209.2, 173.8, 169.5, 88.6, 73.0, 55.1, 44.3, 43.1, 42.5, 37.0, 30.8, 26.5, 21.7, 18.2. IR (KBr, cm$^{-1}$): 2921, 1736, 1697, 1229, 1180, 1028, 945. HRMS (ESI) $m/z$ calc’d for C$_{14}$H$_{18}$O$_5$ [M+Na]$^+$: 289.1046, found: 289.1039.
7. X-ray Crystal Structures

Fig. S1 X-ray crystallographic structure of 2i (CCDC 1907870).

Table 2. Crystal data and structure refinement for 2i.

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Fig. S2 X-ray crystallographic structure of 5b (CCDC 1907871).

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Fig. S3 X-ray crystallographic structure of 12 (CCDC 1907872).

Table 4. Crystal data and structure refinement for 12.

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8. Theoretical Calculations

8.1 Computational methods
All of the structures were optimized at the B3LYP/6-311++G(d,p) level of DFT. The frequency calculations were performed to confirm the characteristics of the calculated structures as minima. The Gibbs Free Energies (GFEs) are all calculated in gas phase without any solvent. All the optimizations were performed with the Gaussian 09 software package.

8.2 DFT calculated results

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Most Stable
8.3 Cartesian coordinates

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G

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\]
E = -389.5743570 (G = -389.394064)

I

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C 1.921174 1.392958 0.096120
C -0.513955 -0.665010 0.017883
C 2.587410 0.066654 0.345849
C 0.637401 -1.626896 0.081063
C 1.994788 -1.125482 -0.423504
9. References


(7) M. J. Frisch, et al. *Gaussian 09*, revision B.01; Gaussian, Inc.: Wallingford, CT, **2009**.
10. NMR Spectra Data

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{1}$H NMR
(400 MHz, CDCl$_3$)

$^{13}$C NMR
(100 MHz, CDCl$_3$)
$^1$H NMR
(400 MHz, CDCl$_3$)

$^{13}$C NMR
(100 MHz, CDCl$_3$)
S12

$^1$H NMR
(500 MHz, CDCl$_3$)

S12

$^{13}$C NMR
(125 MHz, CDCl$_3$)
$^{1}H$ NMR
(400 MHz, CDCl$_3$)

$^{13}C$ NMR
(100 MHz, CDCl$_3$)
$^1$H NMR
(500 MHz, CDCl$_3$)

$^{13}$C NMR
(125 MHz, CDCl$_3$)
$^1$H NMR
(400 MHz, CDCl$_3$)

$^{13}$C NMR
(100 MHz, CDCl$_3$)
$^{1}H$ NMR
(400 MHz, CDCl$_3$)

$^{13}C$ NMR
(100 MHz, CDCl$_3$)
$^1$H NMR
(500 MHz, CDCl$_3$)

$^{13}$C NMR
(125 MHz, CDCl$_3$)
$^1$H NMR
(400 MHz, CDCl$_3$)

$^{13}$C NMR
(100 MHz, CDCl$_3$)
$^1$H NMR
(400 MHz, CDCl$_3$)

$^{13}$C NMR
(100 MHz, CDCl$_3$)
$^1$H NMR  
(500 MHz, CDCl$_3$)

$^{13}$C NMR  
(125 MHz, CDCl$_3$)
$^1$H NMR
(400 MHz, CDCl$_3$)

$^{13}$C NMR
(100 MHz, CDCl$_3$)
$^1$H NMR
(400 MHz, CDCl$_3$)

$^{13}$C NMR
(100 MHz, CDCl$_3$)
$^{1}H$ NMR
$(400 \text{ MHz, CDCl}_3)$

$^{13}C$ NMR
$(100 \text{ MHz, CDCl}_3)$
$^{1}$H NMR
(500 MHz, CDCl$_3$)

$^{13}$C NMR
(125 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
$^1$H NMR  
(500 MHz, CDCl$_3$)

$^{13}$C NMR  
(125 MHz, CDCl$_3$)
$^1$H NMR
(500 MHz, CDCl$_3$)

$^{13}$C NMR
(125 MHz, CDCl$_3$)
$^1$H NMR
(500 MHz, CDCl$_3$)

$^{13}$C NMR
(125 MHz, CDCl$_3$)
$^1$H NMR
(500 MHz, CDCl$_3$)

$^{13}$C NMR
(125 MHz, CDCl$_3$)
$^{1}H\text{ NMR}$

(500 MHz, CDCl$_3$)

$^{13}C\text{ NMR}$

(125 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)