Supporting Information

Gold(I)-Catalyzed Stereoselective Cyclization of 1,3-Enyne Aldehydes by 1,3-Acyloxy Migration/Nazarov/Aldol Cascade

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1. Materials and Methods

1.1. General Methods. All non-aqueous reactions were performed under an inert atmosphere of dry nitrogen or argon in flame dried glassware sealed with a rubber septum unless otherwise noted. The protecting gas was passed over a column of CaCl\textsubscript{2} and supplied through a glass manifold. Reactions were stirred magnetically and monitored by thin layer chromatography (TLC). Analytical thin layer chromatography was performed using MERCK SILICA GEL F254 TLC glass plates and visualized by ultraviolet light (UV). Additionally, TLC plates were stained with aqueous potassium permanganate (KMnO\textsubscript{4}) \[1.5 \text{ g KMnO}_4, 200 \text{ mL H}_2\text{O}, 10 \text{ g K}_2\text{CO}_3, 2.5 \text{ mL 1 M NaOH aq.}\] or ethanolic p-anisaldehyde \[3.7 \text{ mL p-anisaldehyde, 135 mL EtOH, 5 mL conc. H}_2\text{SO}_4, 1.5 \text{ mL AcOH}\]. Concentration under reduced pressure (= \textit{in vacuo}) was performed by rotator evaporation at 40 °C at the appropriate pressure. Chromatographic purification was performed as flash chromatography\textsuperscript{1} on FLUKA silica gel 60 Å (230-400 mesh) at 0.3 – 0.5 bar over-pressure. Yields refer to the purified compound.

1.2. Chemicals. All chemicals and solvents were purchased from ABCR, ACROS, ALDRICH, COMBI-BLOCKS, FLUOROCHEM, J. T. BAKER, FLUKA, MERCK, FISHER-SCIENTIFIC, TCI, STREM or LANCASTER and were used as received from the commercial supplier without further purification unless mentioned otherwise. THF, Et\textsubscript{2}O, CH\textsubscript{2}Cl\textsubscript{2}, MeCN and toluene were dried on a LC TECHNOLOGY SOLUTIONS SP-1 solvent purification system under N\textsubscript{2}. (H\textsubscript{2}O content < 30 ppm, Karl–Fischer titration).\textsuperscript{2} Deuterated solvents were obtained from ARMAR CHEMICALS, Döttingen, Switzerland. Diisopropylamine and pyridine were distilled from KOH, DMPU and NEt\textsubscript{3} were distilled from calcium hydride under an atmosphere of dry nitrogen or high vacuum. BF\textsubscript{3}·OEt\textsubscript{2} was purified by a quick, heat gun promoted “bulb-to-bulb” distillation under an atmosphere of nitrogen prior to use. Aqueous buffer solutions were prepared according to the Sørensen’s phosphate buffer table from 0.067 M aqueous solutions of Na\textsubscript{2}HPO\textsubscript{4} and KH\textsubscript{2}PO\textsubscript{4}.

1.3. Analytics. Nuclear Magnetic Resonance (NMR) spectra were recorded on VARIAN MERCURY(300 MHz), BRUKER AV and DRX (400 MHz), BRUKER DRX and DRXII (500 MHz) or BRUKER AVIII (600 MHz with cryoprobe) spectrometers. Measurements were carried out at ambient temperature (ca. 22 °C). Chemical shifts (\(\delta\)) are reported in ppm with the residual solvent signal as internal standard (CHCl\textsubscript{3} at 7.26 and 77.16 ppm for \textsuperscript{1}H- and \textsuperscript{13}C NMR spectroscopy, respectively; DMSO at 2.50 and 39.52 ppm), unless otherwise noted. The data is reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved,

b = broad signal, app = apparent, coupling constant(s) in Hz, integration. $^{13}$C NMR spectra were recorded with broadband $^1$H-decoupling. Service measurements were performed by the NMR service team of the Laboratorium für Organische Chemie at ETH Zürich by Mr. René Arnold, Mr. Rainer Frankenstein and Mr. Philipp Zumbrunnen under direction of Dr. Marc-Olivier Ebert. Infrared (IR) spectra were recorded on a PERKIN ELMER TWO-FT-IR (UATR) as thin films. Absorptions are given in wavenumbers (cm$^{-1}$). Supercritical fluid chromatography (SFC) was performed on a JASCO 2080 PLUS system under the conditions given for each measurement. Optical rotations were measured with JASCO P-2000 POLARIMETER, 10 cm, 1.5 mL cell (c = 1.00 corresponds to 10.0 mg·mL$^{-1}$). Mass spectrometry (MS) analyses were performed as high resolution El measurements on a WATERS MICROMASS AUTOSPEC ULTIMA at 70 eV, as high resolution ESI measurements on a BRUKER DALTONICS MAXIS (UHR-TOF) instrument or as MALDI on a BRUKER SOLARIX – MALDI-FTICR-MS instrument by the mass spectrometry service of the Laboratorium für Organische Chemie at ETH Zürich by Mr. Louis Bertschi, Mr. Oswald Greter and Mr. Rolf Häfliger under direction of Dr. Xiangyang Zhang.
2. Optimization Studies

Selected Preliminary Results:

Aldehyde 1a was dissolved in a solvent in an oven-dried 10 mL one-neck flask and water was added. The resulting solution was cooled to –10 °C and Au-catalyst was added in one portion. The resulting slightly yellow solution was stirred at –10 °C for 24 h. The reaction mixture was filtered through a short pad of silica gel with EtOAc, concentrated in vacuo, and purified by flash column chromatography. Diastereomeric ratio was determined by $^1$H NMR and enantiomeric excess was determined by SFC on a chiral stationary phase.

**Effect of water amount**

Standard Conditions: 5 mol% [JohnPhosAu(MeCN)]SbF$_6$, x vol% H$_2$O, THF (0.05M), RT

Table S1

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<th>Entry</th>
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<th>Yield (2a)</th>
<th>Yield (11a)</th>
<th>$dr$ (2a)</th>
<th>ee (2a)</th>
<th>Ratio 2:11a</th>
</tr>
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<tr>
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<td>0.0%</td>
<td>33%</td>
<td>49%</td>
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<td>92%</td>
<td>1.8:1</td>
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<tr>
<td>2</td>
<td>0.1%</td>
<td>59%</td>
<td>19%</td>
<td>81:19</td>
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</tr>
<tr>
<td>3</td>
<td>0.2%</td>
<td>71%</td>
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<td>85:15</td>
<td>91%</td>
<td>5.7:1</td>
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<td>4</td>
<td>0.4%</td>
<td>76%</td>
<td>4%</td>
<td>85:15</td>
<td>85%</td>
<td>18.9:1</td>
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Solvent screening

Standard Conditions: 5 mol% [JohnPhosAu(MeCN)]SbF$_6$, 0.2 vol% H$_2$O, solvent (0.05 M), RT

Table S2

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<td>2</td>
<td>THF</td>
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<td>85:15</td>
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<td>18%</td>
<td>60:40</td>
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<td>Et$_2$O</td>
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<td>23%</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>6</td>
<td>CH$_2$Cl$_2$</td>
<td>36%</td>
<td>42%</td>
<td>61:39</td>
<td>92%</td>
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<td>19%</td>
<td>74%</td>
<td>-</td>
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*a dry CH$_2$Cl$_2$ was used as solvent

Catalyst screening

Standard Conditions: 5 mol% catalyst, 0.2 vol% H$_2$O, THF (0.05 M), RT

Table S3

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<td>JohnPhos Au(MeCN)SbF$_6$</td>
<td>71%</td>
<td>6%</td>
<td>85:15</td>
<td>91%</td>
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<tr>
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<td>tBuXPhos Au(MeCN)SbF$_6$</td>
<td>51%</td>
<td>9%</td>
<td>65:35</td>
<td>96%</td>
<td>5.6:1</td>
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<tr>
<td>4</td>
<td>Ipr AuCl + AgSbF$_6$</td>
<td>61%</td>
<td>-</td>
<td>81:19</td>
<td>67%</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>AuCl(PPh$_3$) + AgSbF$_6$</td>
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<td>-</td>
<td>81:19</td>
<td>44%</td>
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Effect of Temperature

Standard Conditions: 5 mol% [JohnPhosAu(MeCN)]SbF₆, 0.2 vol% H₂O, THF (0.05 M), Temperature

Table S4

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<th>dr (2a)</th>
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<td>15 min</td>
<td>71%</td>
<td>6%</td>
<td>85:15</td>
<td>91%</td>
<td>3.1:1</td>
</tr>
<tr>
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<td>0 °C</td>
<td>60 min</td>
<td>73%</td>
<td>-</td>
<td>88:12</td>
<td>92%</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>~10 °C</td>
<td>24 h</td>
<td>76%</td>
<td>-</td>
<td>89:11</td>
<td>93%</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>~30 to 10 °C</td>
<td>72 h</td>
<td>69%</td>
<td>-</td>
<td>92:8</td>
<td>93%</td>
<td>-</td>
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3. Synthesis and Characterization of Substrates

2.1 Synthesis of Aryl Substrates

General Procedures for Aryl-Substrate Synthesis

Reagents and conditions: a) Aryl iodide (1.3 equiv), PdCl$_2$(PPh$_3$)$_2$ (5 mol%), Cul (10 mol%), Et$_3$N/THF (2:1), RT; b) Pd(PPh$_3$)$_4$ (5 mol%), nBu$_3$SnH (1.5 equiv), THF; c) I$_2$ (1.1 equiv), CH$_2$Cl$_2$, 0°C to RT; d) (R)-3-butyln-2-ol (1.3 equiv), PdCl$_2$(PPh$_3$)$_2$ (5 mol%), Cul (10 mol%), Et$_3$N/THF (2:1); e) Ac$_2$O (1.1 equiv), DMAP (0.1 equiv), pyridine (1.5 equiv), CH$_2$Cl$_2$; f) TBAF (8 equiv), THF; g) (COCl)$_2$ (1.2 equiv), DMSO (2.4 equiv), NEt$_3$ (5 equiv), –78 °C to –30 °C CH$_2$Cl$_2$.

Alkyne S1. To a degassed solution of 1-(tert-butyldimethylsilyloxy)-4-pentyne (1.0 equiv) and aryl iodide (1.0 equiv) in NEt$_3$/THF (2:1, 0.15 M) was added PdCl$_2$(PPh$_3$)$_2$ (0.05 equiv) and Cul (0.1 equiv) and the resulting mixture was stirred at RT for 18 h before it was filtered through a short plug of silica gel eluting with EtOAc and concentrated in vacuo. Purification by column chromatography afforded alkyne S1.

Vinyl iodide S2. To a degassed solution of alkyne S1 (1.0 equiv) in THF (0.1 M) was added dropwise nBu$_3$SnH (1.5 equiv) and Pd(PPh$_3$)$_4$ (0.1 equiv) at ambient temperature. After 60 min, the solution was partially concentrated under reduced pressure until a solid phase started to crush out and was then directly loaded onto a silica gel column. Purification by flash column chromatography afforded the corresponding vinyl stannane (hexane/EtOAc 40:1). To a solution of the vinyl stannane (1.0 equiv) in CH$_2$Cl$_2$ (0.1 M) was added I$_2$ (1.2 equiv) at 0 °C. After 30 min, the reaction was quenched with sat. aq. Na$_2$S$_2$O$_3$ solution and stirred vigorously for 5 min. The phases were separated and the aqueous phase was extracted with Et$_2$O (3x). The combined organic phases were washed with brine, dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography afforded vinyl iodide S2.
**Propargyl alcohol S3.** To a degassed solution of S2 (1.0 equiv) and (R)-but-3-yn-2-ol (1.2 equiv) in NEt$_3$/THF (2:1, 0.15 M) was added PdCl$_2$(PPh$_3$)$_2$ (0.05 equiv) and CuI (0.1 equiv) and the resulting mixture was stirred at RT for 2h before it was filtered through a short plug of silica gel eluting with EtOAc and concentrated *in vacuo*. Purification by column chromatography afforded enyne S3.

**Propargyl acetate S4.** To a stirred solution of enyne S3 (1.0 equiv) dissolved in CH$_2$Cl$_2$ (0.1 M) at ambient temperature was added pyridine (5.0 equiv), DMAP (0.2 equiv), and Ac$_2$O (1.5 equiv). The resulting solution was stirred for 1h before it was quenched with H$_2$O. The aqueous phase was extracted with Et$_2$O (3x). The combined organic phases were washed with sat. aq. CuSO$_4$ solution, H$_2$O (1x), and brine, dried over MgSO$_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography provided propargyl acetate S4.

**Primary alcohol S5.** To a stirred solution of propargyl acetate S4 (1.0 equiv) in dry THF (0.1 M) in at 0 °C was added TBAF (1.0 M in THF, 2 equiv). After the addition, the solution was allowed to warm to ambient temperature and stirred for another 90 min. The mixture was quenched by the addition of sat. aq. NaHCO$_3$ solution. EtOAc was added to the mixture and the phases separated. The aqueous phase was extracted with EtOAc (3x). The combined organic phases were dried over MgSO$_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography provided primary alcohol S5.

**Aldehyde 1.** To a solution of oxalyl chloride (1.2 equiv) in CH$_2$Cl$_2$ (0.15 M) at −78 °C was added DMSO (2.4 equiv) dropwise and stirred for 15 min. Then a solution of alcohol S5 in CH$_2$Cl$_2$ (0.05-0.1M) was added dropwise and stirred for 30min. After that time, NEt$_3$ (5 equiv) was added and stirred for another 30min at −78 °C and then slowly warmed to −30 °C over 30 min and then quenched by the addition of sat. aq. NaHCO$_3$ solution. The phases were separated and the aqueous phase was extracted with CH$_2$Cl$_2$ (3x), dried over MgSO$_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography provided aldehyde 1.$^3$

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$^3$ Aldehyde 1 was found to decompose when stored in commercial CD$_3$Cl. Thus, filtration through basic Al$_2$O$_3$ or the use of CD$_2$Cl$_2$ is advised.
tert-Butyldimethyl(5-phenylpent-4-yn-1-yl)oxy)silane (S1a). General procedure for S1 was followed on a 3.64 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, yellow oil (1.86 g, 3.29 mmol, 90%). The characterization was consistent with reported values in the literature.  

Methyl 4-(5-((tert-butyldimethylsilyl)oxy)pent-1-yn-1-yl)benzoate (S1c). General procedure for S1 was followed on a 3.02 mmol scale. The crude product was isolated as clear, yellow oil (988 mg, 2.97 mmol, 98%).

**tert-Butyl((5-(4-chlorophenyl)pent-4-yn-1-yl)oxy)dimethylsilane (S1d).** General procedure for S1 was followed on a 2.10 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, yellow oil (630 mg, 2.04 mmol, 97%).

1H NMR (400 MHz, CDCl₃) δ 7.32 – 7.28 (m, 2H), 7.27 – 7.23 (m, 3H), 3.75 (t, J = 6.0 Hz, 2H), 2.48 (t, J = 7.0 Hz, 2H), 1.88 – 1.76 (m, 2H), 0.91 (s, 9H), 0.07 (s, 6H). 13C NMR (101 MHz, CDCl₃) δ 133.57, 132.89, 128.64, 122.67, 91.16, 79.79, 61.72, 31.79, 26.10, 18.52, 15.97, -5.16. IR (neat) 2953, 2929, 2896, 2857, 2230, 2048, 1899, 1646, 1594, 1490, 1472, 1464, 1430, 1389, 1361, 1350, 1326, 1287, 1255, 1189, 1104, 1093, 1071, 1015, 1007, 983, 951, 828, 775, 751, 719, 663, 582, 524, 498 cm⁻¹. HRMS (MALDI): m/z calcd for C₁₇H₂₅OSi [M-Cl]⁺ 273.1669, found 273.1672.

**tert-Butyl((5-(4-fluorophenyl)pent-4-yn-1-yl)oxy)dimethylsilane (S1e).** General procedure for S1 was followed on a 3.60 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, yellow oil (982 mg, 3.36 mmol, 93%).

1H NMR (400 MHz, CDCl₃) δ 7.41 – 7.32 (m, 1H), 7.08 – 6.84 (m, 1H), 3.75 (t, J = 6.0 Hz, 1H), 2.48 (t, J = 7.0 Hz, 1H), 2.01 – 1.74 (m, 1H), 0.91 (s, 9H), 0.08 (s, 6H). 13C NMR (101 MHz, CDCl₃) δ 162.2 (d, J = 248.1 Hz), 133.4 (d, J = 8.2 Hz), 120.2 (d, J = 3.5 Hz), 115.5 (d, J = 21.9 Hz), 89.7 (d, J = 1.5 Hz), 79.8, 61.8, 31.9, 26.1, 18.5, 15.9, -5.2. IR (neat) 3050, 2953, 2930, 2897, 2858, 2232, 2037, 1888, 1645, 1603, 1507, 1472, 1464, 1444, 1431, 1388, 1361, 1350, 1328, 1294, 1256, 1231, 1189, 1155, 1104, 1070, 1007, 983, 952, 940, 833, 775, 721, 664, 634, 575, 527 cm⁻¹. HRMS (MALDI): m/z calcd for C₁₇H₂₅FNaOSi [M+Na]⁺ 315.1551, found 315.1551.

**tert-Butyl((5-(3-fluorophenyl)pent-4-yn-1-yl)oxy)dimethylsilane (S1f).** General procedure for S1 was followed on a 4.03 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, yellow oil (1.06 g, 3.61 mmol, 89%). Purification by standard column chromatography proofed difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.
**1H NMR** (400 MHz, CDCl₃) δ 7.27 – 7.18 (m, 1H), 7.16 (dt, J = 7.7, 1.3 Hz, 1H), 7.07 (ddd, J = 9.6, 2.6, 1.4 Hz, 1H), 7.02 – 6.92 (m, 1H), 3.75 (t, J = 6.0 Hz, 2H), 2.49 (t, J = 7.0 Hz, 2H), 1.95 – 1.72 (m, 2H), 0.91 (s, 9H), 0.08 (s, 6H). **13C NMR** (101 MHz, CDCl₃) δ 162.5 (d, J = 245.9 Hz), 129.8 (d, J = 8.8 Hz), 127.5 (d, J = 3.0 Hz), 126.1 (d, J = 9.6 Hz), 118.5 (d, J = 22.5 Hz), 115.0 (d, J = 21.2 Hz), 91.2, 79.8 (d, J = 3.3 Hz), 61.7, 31.8, 26.1, 18.5, 15.9, -5.2. **IR** (neat) 2953, 2929, 2896, 2857, 2231, 1571, 1482, 1472, 1462, 1361, 1326, 1258, 1217, 1189, 1103, 1070, 1032, 986, 955, 832, 816, 775, 753, 677, 661, 572 cm⁻¹. **HRMS (MALDI):** m/z calcd for C₁₇H₂₅FNaOSi [M+Na]⁺ 315.1551, found 315.1551.

**tert-Butyl(5-(2-fluorophenyl)pent-4-yn-1-yl)oxy)dimethylsilane (S1g).** General procedure for S1 was followed on a 4.59 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, yellow oil (976 mg, 3.34 mmol, 73%). Purification by standard column chromatography proved difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

**1H NMR** (400 MHz, CDCl₃) δ 7.38 (td, J = 7.6, 1.8 Hz, 1H), 7.27 – 7.21 (m, 1H), 1.89 – 1.77 (m, 2H), 0.91 (s, 9H), 0.08 (s, 6H). **13C NMR** (101 MHz, CDCl₃) δ 164.2, 161.7, 133.6 (d, J = 1.6 Hz), 129.2 (d, J = 7.9 Hz), 123.9 (d, J = 3.7 Hz), 115.5 (d, J = 21.2 Hz), 95.5 (d, J = 3.3 Hz), 74.2 (d, J = 1.1 Hz), 61.7, 31.77, 26.1, 18.5, -5.2. **IR** (neat) 2953, 2929, 2896, 2857, 2235, 1574, 1493, 1472, 1463, 1454, 1389, 1361, 1326, 1255, 1217, 1189, 1103, 1070, 1032, 1006, 983, 954, 939, 833, 818, 775, 753, 677, 661, 577, 509 cm⁻¹. **HRMS (MALDI):** m/z calcd for C₁₇H₂₅FNaOSi [M+Na]⁺ 315.1551, found 315.1551.

**tert-Butyldimethyl((5-(naphthalen-2-yl)pent-4-yn-1-yl)oxy)silane (S1h).** General procedure for S1 was followed including heating at 70 °C for 7h on a 3.62 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, yellow oil (600 mg, 1.85 mmol, 51%). Purification by standard column chromatography proved difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

**1H NMR** (400 MHz, CDCl₃) δ 7.93 – 7.86 (m, 1H), 7.84 – 7.71 (m, 3H), 7.53 – 7.38 (m, 3H), 3.80 (t, J = 6.0 Hz, 2H), 2.55 (t, J = 7.0 Hz, 2H), 1.93 – 1.80 (m, 2H), 0.93 (d, J = 0.5 Hz, 9H), 0.10 (s, 6H). **13C NMR** (101 MHz, CDCl₃) δ 133.3, 132.7, 131.3, 129.0, 128.0, 127.9, 127.8, 126.6, 126.5, 121.6, 90.6, 81.3, 61.9, 32.1, 26.2, 16.2, -5.0. **IR** (neat) 3059, 2953, 2928, 2896, 2856, 1628, 1598, 1502, 1471, 1463, 1431, 1388, 1361, 1324,
4-(5-((tert-Butyldimethylsilyl)oxy)pent-1-yn-1-yl)phenyl acetate (S1i). General procedure for S1 was followed on a 4.03 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, yellow oil (1.32 g, 3.97 mmol, 98%). Purification by standard column chromatography proved difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

\[ \text{IR (neat)}: 2953, 2929, 2896, 2857, 1768, 1602, 1505, 1472, 1431, 1369, 1255, 1191, 1164, 1102, 1070, 1009, 983, 951, 909, 834, 775, 719, 688, 663, 593, 532, 501 \text{ cm}^{-1}. \]

HRMS (MALDI): \text{m/z calcd for C}_{21}H_{28}NaOSi [M+Na]^+ 347.1802, found 347.1802.

\[ \text{1H NMR (400 MHz, CDCl}_3\text{)}: 7.38 (d, J = 8.7 \text{ Hz}, 1H), 7.01 (d, J = 8.7 \text{ Hz}, 1H), 3.75 (t, J = 6.0 \text{ Hz}, 1H), 2.48 (t, J = 7.0 \text{ Hz}, 1H), 2.29 (s, 2H), 1.95 – 1.75 (m, 1H), 0.91 (s, 9H), 0.08 (s, 6H). \]

\[ \text{13C NMR (101 MHz, CDCl}_3\text{)}: 169.34, 150.03, 132.76, 121.90, 121.62, 90.14, 80.03, 61.74, 31.86, 26.11, 21.27, 18.52, 15.94, -5.15. \]

\[ \text{IR (neat)}: 2954, 2931, 2858, 1740, 1712, 1510, 1473, 1462, 1429, 1394, 1370, 1282, 1255, 1156, 1098, 1028, 1016, 983, 947, 922, 836, 775, 719, 688, 663, 593, 532, 501 \text{ cm}^{-1}. \]

HRMS (MALDI): \text{m/z calcd for C}_{19}H_{26}NaO_{2}Si [M+Na]^+ 355.1700, found 355.1700.

tert-Butylacetyl(4-((tert-butyldimethylsilyl)oxy)pent-1-yn-1-yl)phenylcarbamate (S1j). General procedure for S1 was followed on a 2.77 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, yellow oil (1.04 g, 2.41 mmol, 87%). Purification by standard column chromatography proved difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

\[ \text{1H NMR (400 MHz, CDCl}_3\text{)}: 7.42 – 7.37 (m, 2H), 7.10 – 6.93 (m, 2H), 3.75 (t, J = 6.0 \text{ Hz}, 2H), 2.56 (s, 3H), 2.49 (t, J = 7.0 \text{ Hz}, 2H), 1.85 – 1.70 (m, 2H), 1.37 (s, 9H), 0.91 (s, 9H), 0.08 (s, 6H). \]

\[ \text{13C NMR (101 MHz, CDCl}_3\text{)}: 172.99, 152.68, 138.16, 132.27, 128.21, 123.84, 90.81, 83.49, 80.28, 61.74, 31.84, 27.97, 26.59, 26.11, 18.51, 15.97, -5.16. \]

\[ \text{IR (neat)}: 2954, 2931, 2858, 1740, 1712, 1510, 1473, 1462, 1429, 1394, 1370, 1304, 1282, 1255, 1156, 1098, 1028, 1016, 983, 947, 922, 836, 775, 719, 688, 663, 545, 486, \text{ cm}^{-1}. \]

HRMS (ESI): \text{m/z calcd for C}_{24}H_{38}NFO_{2}Si [M+H]^+ 432.2565, found 432.2566.
(E)-tert-Butyl((5-iodo-5-phenylpent-4-en-1-yl)oxy)dimethylsilane (S2a). General procedure for S2 was followed on a 13.81 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (4.6 g, 11.43 mmol, 97%). The characterization was consistent with reported values in the literature.

(E)-tert-Butyl((5-iodo-5-(4-(trifluoromethyl)phenyl)pent-4-en-1-yl)oxy)dimethylsilane (S2b). General procedure for S2 was followed on a 2.86 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (962 mg, 2.05 mmol, 72%).

1H NMR (400 MHz, CDCl3) δ 7.57 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.0, 2H), 6.57 (t, J = 7.8 Hz, 1H), 3.55 (t, J = 6.1 Hz, 2H), 2.15 – 1.98 (m, 2H), 1.66 – 1.51 (m, 2H), 0.82 (s, 9H), -0.01 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 144.7, 129.4, 125.5 (q, J = 3.7 Hz), 125.4, 125.4, 92.4, 62.2, 32.3, 29.1, 26.1, 18.4, -5.1. IR (neat) 2954, 2930, 2896, 2858, 2087, 1923, 1613, 1576, 1472, 1464, 1405, 1388, 1361, 1322, 1256, 1167, 1129, 1107, 1066, 1019, 1007, 955, 939, 865, 834, 775, 742, 715, 681, 662, 604, 506, 486 cm⁻¹. HRMS (MALDI): m/z calcd for C18H26F3INaOSi [M+Na]+ 493.0642, found 493.0638.

(E)-Methyl 4-(5-((tert-butyldimethylsilyl)oxy)-1-iodopent-1-en-1-yl)benzoate (S2c). General procedure for S2 was followed on a 2.97 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (1.10 g, 2.39 mmol, 80%). Purification by standard column chromatography proved difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

1H NMR (400 MHz, CDCl3) δ 8.04 – 7.89 (m, 2H), 7.42 – 7.31 (m, 2H), 6.55 (t, J = 7.7 Hz, 1H), 3.92 (s, 3H), 3.54 (t, J = 6.2 Hz, 2H), 2.05 (q, J = 7.6 Hz, 2H), 1.66 – 1.50 (m, 2H), 0.83 (s, 9H), -0.01 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 166.7, 146.3, 144.3, 129.6, 129.0, 93.1, 62.2, 52.3, 32.3, 29.0, 26.0, 18.4, -5.2. IR (neat)

2952, 2928, 2856, 1725, 1309, 1273, 1255, 1179, 1102, 1020, 1006, 966, 939, 834, 809, 771, 712, 682, 662, 560, 478 cm\(^{-1}\). **HRMS (MALDI):** m/z calcd for C\(_{19}\)H\(_{29}\)NaO\(_3\)Si \([M+Na]^+\) 483.0823, found 483.0822.

![Diagram](image)

**(E)-**tert-Butyl((5-(4-chlorophenyl)-5-iodopent-4-en-1-yl)oxy)dimethylsilane (S2d). General procedure for S2 was followed on a 1.94 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (650 mg, 1.49 mmol, 77%). Purification by standard column chromatography proved difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32 – 7.28 (m, 2H), 7.28 – 7.24 (m, 2H), 6.54 (t, \(J = 7.7\) Hz, 1H), 3.57 (t, \(J = 6.2\) Hz, 2H), 2.08 (q, \(J = 7.6\) Hz, 2H), 0.95 (t, \(J = 7.2\) Hz, 2H), 0.87 (s, 9H), 0.03 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 144.0, 140.3, 133.9, 130.2, 128.5, 93.2, 62.2, 32.3, 28.9, 26.0, 18.4, -5.2. **IR** (neat) 2954, 2928, 2856, 1590, 1486, 1471, 1463, 1394, 1361, 1255, 1193, 1092, 1015, 940, 834, 814, 774, 729, 662, 581, 557, 483 cm\(^{-1}\). **HRMS (MALDI):** m/z calcd for C\(_{17}\)H\(_{27}\)ClOSi \([M+H]^+\) 437.0559, found 437.0558.

![Diagram](image)

**(E)-**tert-Butyl((5-(4-fluorophenyl)-5-iodopent-4-en-1-yl)oxy)dimethylsilane (S2e). General procedure for S2 was followed on a 3.21 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, light brown oil (750 mg, 1.78 mmol, 55%). Purification by standard column chromatography proved difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.30 – 7.22 (m, 2H), 7.03 – 6.94 (m, 2H), 6.50 (t, \(J = 7.7\) Hz, 1H), 3.55 (t, \(J = 6.2\) Hz, 2H), 2.05 (q, \(J = 7.6\) Hz, 2H), 0.92 (t, \(J = 7.3\) Hz, 2H), 0.84 (s, 9H), 0.00 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 163.4, 160.9, 130.7 (d, \(J = 8.3\) Hz), 115.3 (d, \(J = 21.7\) Hz), 93.6, 62.2, 32.3, 28.9, 26.0, 18.4, -5.2. **IR** (neat) 2954, 2928, 2856, 1770, 1598, 1505, 1471, 1463, 11387, 1361, 1253, 1232, 1174, 1157, 1099, 1006, 939, 834, 774, 719, 661, 623, 558, 511 cm\(^{-1}\). **HRMS (MALDI):** m/z calcd for C\(_{17}\)H\(_{26}\)FNaO\(_4\)Si \([M+Na]^+\) 443.0674, found 443.0673.
**S2f.** General procedure for S2 was followed on a 3.56 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (1.04 g, 2.47 mmol, 63%). Purification by standard column chromatography proved difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

\[ \text{1H NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.31 – 7.22 \text{ (m, 1H)}, \ 7.06 \text{ (ddd, } J = 7.7, 1.6, 1.0 \text{ Hz, 1H}), \ 7.03 – 6.89 \text{ (m, 2H), 6.51 (t, } J = 7.7 \text{ Hz, 1H, 3.55 (t, } J = 6.2 \text{ Hz, 2H), 2.07 (q, } J = 7.6 \text{ Hz, 2H, 1.63 – 1.51 (m, 2H), 0.84 (s, 9H), -0.00 (s, 6H).} \]

\[ \text{13C NMR} \ (101 \text{ MHz, CDCl}_3) \delta 163.5, 161.1, 144.1, 129.8 (d, } J = 8.4 \text{ Hz), 124.6 (d, } J = 2.9 \text{ Hz, 116.0 (d, } J = 22.1 \text{ Hz), 115.1 (d, } J = 21.1 \text{ Hz), 92.7 (d, } J = 2.3 \text{ Hz, 62.2, 32.3, 29.0, 26.0, 18.4, -5.2. IR (neat) 2953, 2928, 2895, 2856, 1608, 1582, 1472, 1463, 1431, 1388, 1361, 1286, 1254, 1232, 1191, 1134, 1101, 1028, 1006, 966, 939, 875, 834, 814, 774, 698, 681, 662, 572, 521 \text{ cm}^{-1}. \]

HRMS (MALDI): m/z calcd for C_{17}H_{26}NaFIOSi [M+H]^+ 420.0776, found 420.0766.

**S2g.** General procedure for S2 was followed on a 3.16 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (1.20 g, 2.85 mmol, 90%). Purification by standard column chromatography proved difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

\[ \text{1H NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.26 – 7.20 \text{ (m, 2H), 7.15 – 7.07 \text{ (m, 1H)}, 7.05 – 6.97 \text{ (m, 1H), 6.61 (t, } J = 7.7 \text{ Hz, 1H, 3.53 (t, } J = 6.3 \text{ Hz, 2H), 1.95 (dd, } J = 15.1, 7.7 \text{ Hz, 1H), 1.62 – 1.55 \text{ (m, 2H), 0.83 (s, 9H), -0.01 (s, 6H).} \]

\[ \text{13C NMR} \ (101 \text{ MHz, CDCl}_3) \delta 159.7, 157.3, 146.1, 131.0 (d, } J = 2.5 \text{ Hz), 130.1 (d, } J = 8.2 \text{ Hz, 124.2 (d, } J = 3.7 \text{ Hz), 116.0 (d, } J = 21.8 \text{ Hz), 84.9, 62.3, 31.9, 29.3, 26.0, 18.4, -5.2. IR (neat) 2953, 2928, 2856, 1608, 1582, 1472, 1463, 1431, 1388, 1361, 1286, 1254, 1232, 1191, 1134, 1101, 1028, 1006, 966, 939, 875, 834, 814, 774, 698, 681, 662, 572, 521 \text{ cm}^{-1}. \]

HRMS (MALDI): m/z calcd for C_{17}H_{26}NaFIOSi [M+H]^+ 420.0776, found 420.0765.
(E)-tert-Butyl((5-iodo-5-(naphthalen-2-yl)pent-4-en-1-yl)oxy)dimethylsilane (S2h). General procedure for S2 was followed on a 1.85 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (670 mg, 1.48 mmol, 80%). Purification by standard column chromatography proofed difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

\[ ^{1}H \text{ NMR} (400 \text{ MHz, CDCl}_3) \delta 7.87 – 7.76 (m, 3H), 7.73 (d, J = 1.8 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.41 (dd, J = 8.5, 1.8 Hz, 1H), 6.59 (t, J = 7.7 Hz, 1H), 3.54 (t, J = 6.3 Hz, 2H), 2.11 (q, J = 7.6 Hz, 2H), 1.64 – 1.57 (m, 2H), 0.80 (s, 9H), -0.02 (s, 6H). \]

\[ ^{13}C \text{ NMR} (101 \text{ MHz, CDCl}_3) \delta 143.5, 139.2, 133.0, 132.9, 128.3, 128.1, 127.8, 127.5, 127.0, 126.6, 126.5, 95.2, 62.4, 32.4, 29.0, 26.0, 18.4, -5.2. \]

\[ \text{IR (neat)} 3056, 2954, 2928, 2856, 1770, 1596, 1503, 1471, 1463, 1387, 1361, 1251, 1189, 1100, 1006, 961, 834, 816, 774, 754, 714, 663, 597, 563, 476 \text{ cm}^{-1}. \]

\[ \text{HRMS (MALDI): m/z calcd for C}_{22}H_{29}INaOSi [M+Na]^+ 475.0925, found 475.0924. \]

(E)-4-((tert-Butyldimethylsilyl)oxy)-1-iodopent-1-en-1-yl)phenyl acetate (S2i). General procedure for S2 was followed on a 3.61 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (826 mg, 1.79 mmol, 50%). Purification by standard column chromatography proofed difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

\[ ^{1}H \text{ NMR} (400 \text{ MHz, CDCl}_3) \delta 7.33 – 7.27 (m, 2H), 7.06 – 7.01 (m, 2H), 6.51 (t, J = 7.7 Hz, 1H), 3.54 (t, J = 6.3 Hz, 2H), 2.30 (s, 3H), 2.07 (q, J = 7.6 Hz, 2H), 1.66 – 1.51 (m, 2H), 0.85 (s, 9H), 0.01 (s, 6H). \]

\[ ^{13}C \text{ NMR} (101 \text{ MHz, CDCl}_3) \delta 169.3, 150.2, 143.8, 139.3, 130.1, 121.4, 93.8, 62.3, 32.4, 28.9, 26.1, 21.3, 18.4, -5.2. \]

\[ \text{IR (neat)} 2953, 2928, 2894, 2856, 2101, 1765, 1598, 1499, 1471, 1463, 1432, 1405, 1368, 1254, 1193, 1165, 1100, 1017, 1008, 940, 911, 834, 814, 774, 736, 714, 683, 663, 640, 605, 593, 521 \text{ cm}^{-1}. \]

(E)-tert-Butyl-acetyl(4-((tert-butyldimethylsilyl)oxy)-1-iodopent-1-en-1-yl)phenyl)-carbamate (S2j). General procedure for S2 was followed on a 0.95 mmol scale. The crude product was purified by flash
column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (450 mg, 0.80 mmol, 84%). Purification by standard column chromatography proved difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

^1H NMR (400 MHz, CDCl$_3$) δ 7.35 – 7.28 (m, 2H), 7.08 – 6.95 (m, 2H), 6.52 (t, $J$ = 7.6 Hz, 1H), 3.55 (t, $J$ = 6.4 Hz, 2H), 2.57 (s, 3H), 2.18 – 1.98 (m, 2H), 1.66 – 1.53 (m, 2H), 1.38 (s, 9H), 0.87 (s, 9H), 0.07 (s, 6H). ^13C NMR (101 MHz, CDCl$_3$) δ 172.9, 152.7, 143.8, 141.1, 138.7, 129.5, 128.0, 93.8, 83.5, 62.4, 32.3, 28.9, 27.9, 26.6, 26.1, 18.4, -5.2. IR (neat) 2929, 2857, 1739, 1711, 1504, 1472, 1393, 1370, 1338, 1300, 1272, 1254, 1156, 1097, 1028, 936, 836, 774, 748, 690, 662, 619 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{24}$H$_{39}$NNaO$_4$Si $\text{[M+Na]}^+$ 582.1507, found 582.1498.

(R,E)-9-((tert-Butyldimethylsilyl)oxy)-5-phenylnon-5-en-3-yn-2-ol (S3a). General procedure for S3 was followed on a 11.43 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, yellow oil (3.1 g, 9.00 mmol, 79%).

^1H NMR (400 MHz, CDCl$_3$) δ 7.38 – 7.27 (m, 5H), 6.19 (t, $J$ = 7.7 Hz, 1H), 4.66 (q, $J$ = 6.6 Hz, 1H), 3.58 (t, $J$ = 6.2 Hz, 2H), 2.28 (q, $J$ = 7.6 Hz, 2H), 1.86 (s, 1H), 1.68 – 1.56 (m, 2H), 1.48 (d, $J$ = 6.6 Hz, 3H), 0.85 (s, 9H), 0.01 (s, 6H). ^13C NMR (101 MHz, CDCl$_3$) δ 140.4, 137.5, 128.8, 128.3, 127.6, 123.1, 88.9, 86.1, 62.5, 59.0, 32.7, 26.2, 26.0, 24.6, 18.4, -5.2. IR (neat) 3508, 3059, 3023, 2854, 2929, 2885, 2857, 2215, 1673, 1600, 1494, 1472, 1463, 1444, 1388, 1362, 1295, 1186, 1144, 1095, 1031, 1007, 964, 939, 920, 907, 891, 835, 813, 775, 662, 589, 527 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{21}$H$_{32}$NaO$_2$Si $\text{[M+Na]}^+$ 367.2064, found 367.2064. $[\alpha]_D^{26} = +11.3$ (c = 1.0, CHCl$_3$).

(R,E)-9-((tert-Butyldimethylsilyl)oxy)-5-(4-(trifluoromethyl)phenyl)non-5-en-3-yn-2-ol (S3b). General procedure for S3 was followed on a 0.79 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, yellow oil (244 mg, 0.59 mmol, 75%).

^1H NMR (400 MHz, CDCl$_3$) δ 7.60 (d, $J$ = 8.0 Hz, 2H), 7.46 (d, $J$ = 8.0 Hz, 2H), 6.26 (t, $J$ = 7.8 Hz, 1H), 4.65 (t, $J$ = 6.6 Hz, 1H), 3.58 (t, $J$ = 6.1 Hz, 2H), 2.27 (q, $J$ = 7.6 Hz, 2H), 1.80 (s, 1H), 1.71 – 1.56 (m, 2H), 1.48 (d, $J$ = 6.6 Hz, 3H), 0.83 (s, 9H), -0.01 (s, 6H). ^13C NMR (101 MHz, CDCl$_3$) δ 141.8, 129.2, 125.3 (q, $J$ = 3.8 Hz), 122.1, 189.6, 85.3, 62.3, 59.0, 32.6, 26.3, 26.0, 24.6, 18.4, -5.2. IR (neat) 3339, 2955, 2931, 2887, 2859, 1618, 1472,
1464, 1408, 1389, 1362, 1325, 1256, 1167, 1128, 1110, 1066, 1020, 940, 911, 36, 814, 776, 710, 662, 622, 493, 469 cm\(^{-1}\). HRMS (ESI): \(m/z\) calcd for C\(_{22}\)H\(_{31}\)FNaO\(_2\)Si [M+Na]+ 435.1938, found 435.1934. \([\alpha]_D^{26} = +10.2\) (c = 1.0, CHCl\(_3\)).

(R,E)-Methyl4-(9-((tert-butyldimethylsilyl)oxy)-2-hydroxynon-5-en-3-yn-5-yl)-benzoate (S3c). General procedure for S3 was followed on a 1.13 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, yellow oil (330 mg, 0.82 mmol, 73%).

\[^1H\] NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.23 – 7.86 (m, 2H), 7.68 – 7.37 (m, 2H), 6.25 (t, \(J = 7.8\) Hz, 1H), 4.66 (q, \(J = 6.6\) Hz, 1H), 3.92 (s, 3H), 3.57 (t, \(J = 6.2\) Hz, 2H), 2.27 (q, \(J = 7.6\) Hz, 2H), 1.88 (s, 1H), 1.71 – 1.56 (m, 2H), 1.48 (d, \(J = 6.6\) Hz, 3H), 0.84 (s, 9H), -0.00 (s, 6H).

\[^13C\] NMR (101 MHz, CDCl\(_3\)) \(\delta\) 167.0, 142.2, 141.7, 129.6, 129.2, 128.8, 122.4, 89.5, 85.3, 62.4, 59.0, 52.3, 32.6, 26.3, 26.0, 24.5, 18.4, -5.2. IR (neat) 3426, 2953, 2930, 2886, 2857, 1724, 1609, 1565, 1472, 1463, 1436, 1405, 1389, 1362, 1311, 1278, 1256, 1191, 1144, 1104, 1021, 966, 911, 892, 835, 775, 707, 663, 591, 498 cm\(^{-1}\). \([\alpha]_D^{26} = +11.1\) (c = 1.0, CHCl\(_3\)).

(R,E)-9-((tert-Butyldimethylsilyl)oxy)-5-(4-chlorophenyl)non-5-en-3-yn-2-ol (S3d). General procedure for S3 was followed on a 1.26 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, yellow oil (350 mg, 0.92 mmol, 73%).

\[^1H\] NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35 – 7.26 (m, 4H), 6.19 (t, \(J = 7.7\) Hz, 1H), 4.66 (q, \(J = 6.6\) Hz, 1H), 3.58 (t, \(J = 6.2\) Hz, 2H), 2.25 (q, \(J = 7.6\) Hz, 2H), 1.81 (s, 1H), 1.69 – 1.55 (m, 2H), 1.48 (d, \(J = 6.6\) Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H).

\[^13C\] NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.9, 135.9, 133.4, 130.2, 128.5, 122.1, 89.3, 85.6, 62.4, 59.0, 32.6, 26.3, 26.0, 24.6, 18.4, -5.2. IR (neat) 3347, 2954, 2930, 2886, 2858, 1594, 1491, 1472, 1396, 1362, 1329, 1256, 1144, 1094, 1016, 940, 910, 835, 776, 720, 663, 590, 511 cm\(^{-1}\). \([\alpha]_D^{26} = +10.8\) (c = 1.0, CHCl\(_3\)).
(R,E)-9-((tert-Butyldimethylsilyl)oxy)-5-(4-fluorophenyl)non-5-en-3-yn-2-ol (S3e). General procedure for S3 was followed on a 1.31 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, yellow oil (330 mg, 0.91 mmol, 70%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.35 – 7.29 (m, 2H), 7.09 – 6.93 (m, 2H), 6.18 (t, $J$ = 7.7 Hz, 1H), 4.77 – 4.58 (m, 1H), 3.58 (t, $J$ = 6.2 Hz, 2H), 2.26 (q, $J$ = 7.6 Hz, 2H), 1.78 (s, 1H), 1.68 – 1.57 (m, 2H), 1.48 (d, $J$ = 6.6 Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.2 (d, $J$ = 246.8 Hz), 140.5, 133.4 (d, $J$ = 3.5 Hz), 130.5 (d, $J$ = 8.1 Hz), 122.1, 115.2 (d, $J$ = 21.5 Hz), 89.1, 85.9, 62.4, 59.0, 32.7, 26.2, 26.0, 24.6, 18.4, -5.2. IR (neat) 3333, 2955, 2930, 2858, 1603, 1509, 1472, 1362, 1256, 1159, 1143, 1100, 1007, 940, 837, 776, 725, 662, 573, 526, 484, 464, 695, 613, 504, 487, 460 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{21}$H$_{31}$NaFO$_2$Si [M+Na]$^+$ 385.1970, found 385.1969. $[^{[\alpha]}]_{D}^{26}$ = +11.8 (c = 1.0, CHCl$_3$).

(R,E)-9-((tert-Butyldimethylsilyl)oxy)-5-(3-fluorophenyl)non-5-en-3-yn-2-ol (S3f). General procedure for S3 was followed on a 0.95 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, yellow oil (265 mg, 0.73 mmol, 77%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.27 (m, 2H), 7.16 – 7.09 (m, 2H), 6.10 (dd, $J$ = 9.9, 2.6, 1.6 Hz, 1H), 6.97 (tdd, $J$ = 8.4, 2.6, 1.0 Hz, 1H), 6.21 (t, $J$ = 7.7 Hz, 1H), 4.78 – 4.58 (m, 1H), 3.58 (t, $J$ = 6.2 Hz, 2H), 2.28 (q, $J$ = 7.6 Hz, 2H), 1.81 (s, 1H), 1.70 – 1.58 (m, 2H), 1.48 (d, $J$ = 6.6 Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.7 (d, $J$ = 245.8 Hz), 141.2, 139.6 (d, $J$ = 7.7 Hz), 129.7 (d, $J$ = 8.3 Hz), 124.6 (d, $J$ = 2.9 Hz), 122.1 (d, $J$ = 2.3 Hz), 115.8 (d, $J$ = 22.0 Hz), 114.5 (d, $J$ = 21.1 Hz), 89.3, 85.5, 62.4, 59.0, 32.6, 26.3, 26.0, 24.6, 18.4, -5.2. IR (neat) 3343, 2955, 2930, 2886, 2858, 1611, 1581, 1486, 1472, 1463, 1438, 1388, 1362, 1329, 1256, 1209, 1158, 1095, 1007, 964, 924, 884, 835, 814, 776, 704, 662, 594, 520, 460 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{21}$H$_{31}$FNaO$_2$Si [M+Na]$^+$ 385.1970, found 385.1969. $[^{[\alpha]}]_{D}^{26}$ = +11.8 (c = 1.0, CHCl$_3$).
(R,Z)-9-((tert-Butyldimethylsilyl)oxy)-5-(2-fluorophenyl)non-5-en-3-yn-2-ol (S3g) General procedure for S3 was followed on a 1.19 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, yellow oil (308 mg, 0.85 mmol, 71%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31 – 7.23 (m, 2H), 7.15 – 7.10 (m, 1H), 7.09 – 7.02 (m, 1H), 6.29 (t, $J$ = 7.7 Hz, 1H), 4.63 (q, $J$ = 6.6 Hz, 1H), 3.55 (t, $J$ = 6.3 Hz, 2H), 2.14 – 1.99 (m, 2H), 1.63 – 1.53 (m, 2H), 1.46 (d, $J$ = 6.6 Hz, 3H), 0.83 (s, 9H), -0.01 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.4 (d, $J$ = 247.7 Hz), 143.1, 131.1 (d, $J$ = 3.5 Hz), 129.6 (d, $J$ = 8.1 Hz), 125.1 (d, $J$ = 16.0 Hz), 124.1 (d, $J$ = 3.6 Hz), 116.8, 115.9 (d, $J$ = 22.3 Hz), 88.9, 85.0, 62.6, 59.0, 32.1, 26.6 (d, $J$ = 2.2 Hz), 26.0, 24.5, 18.4, -5.2. IR (neat) 3354, 2954, 2930, 2886, 2857, 1611, 1579, 1491, 1472, 1463, 1450, 1388, 1361, 1329, 1255, 1220, 1143, 1100, 1032, 1007, 940, 911, 836, 776, 757, 662, 593, 521 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{21}$H$_{31}$FNaO$_2$Si [M+Na]$^+$ 385.1970, found 385.1970. $\left[\alpha\right]_{D}^{26} = +12.5$ (c = 1.0, CHCl$_3$).

(R,E)-9-((tert-Butyldimethylsilyl)oxy)-5-(naphthalen-2-yl)non-5-en-3-yn-2-ol (S3h). General procedure for S3 was followed on a 0.55 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, yellow oil (131 mg, 0.33 mmol, 60%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 – 7.79 (m, 3H), 7.79 – 7.76 (m, 1H), 7.54 – 7.43 (m, 3H), 6.28 (t, $J$ = 7.7 Hz, 1H), 4.69 (q, $J$ = 6.6 Hz, 1H), 3.58 (t, $J$ = 6.3 Hz, 2H), 2.34 (q, $J$ = 7.6 Hz, 2H), 1.84 (s, 1H), 1.72 – 1.60 (m, 2H), 1.50 (d, $J$ = 6.6 Hz, 3H), 0.82 (s, 9H), -0.01 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.8, 135.0, 133.2, 132.8, 128.2, 127.9, 127.8, 126.9, 126.3, 126.2, 123.1, 89.2, 86.0, 62.6, 59.1, 32.8, 26.4, 26.0, 24.6, 18.4, -5.2. IR (neat) 3346, 3057, 2953, 2929, 2885, 2857, 1599, 1504, 1471, 1463, 1435, 1388, 1361, 1329, 1255, 1185, 1141, 1096, 1007, 940, 899, 835, 776, 747, 662, 568, 524, 478 cm$^{-1}$. HRMS (ESI): m/z calcd for C$_{25}$H$_{34}$NaO$_2$Si [M+Na]$^+$ 417.2220, found 417.2221. $\left[\alpha\right]_{D}^{16} = +10.9$ (c = 1.0, CHCl$_3$).
(R,E)-4-[(tert-Butyldimethylsilyl)oxy]-2-hydroxynon-5-en-3-yn-5-yl)phenyl acetate (S3i). General procedure for S3 was followed on a 0.95 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, yellow oil (252 mg, 0.63 mmol, 66%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J = 8.6$ Hz, 2H), 7.06 (d, $J = 8.6$ Hz, 2H), 6.19 (t, $J = 7.7$ Hz, 1H), 4.91 – 4.53 (m, 1H), 3.59 (t, $J = 6.2$ Hz, 2H), 2.32 – 2.22 (m, 5H), 1.80 (s, 1H), 1.66 – 1.60 (m, 2H), 1.48 (d, $J = 6.6$ Hz, 3H), 0.86 (s, 9H), 0.01 (s, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.6, 150.0, 140.6, 135.0, 129.9, 122.2, 121.4, 89.1, 85.9, 62.5, 59.0, 32.7, 26.3, 26.1, 24.6, 21.3, 18.4, -5.2. IR (neat) 3415, 2954, 2930, 2886, 2857, 1761, 1506, 1473, 1369, 1329. HRMS (MALDI): m/z calcd for C$_{23}$H$_{34}$NaO$_4$Si [M+Na]$^+$ 425.2119, found 425.2119. $[\alpha]_{D}^{26} = +8.6$ (c = 1.0, CHCl$_3$).

(R,E)-tert-Butylacetyl(4-[(tert-butyldimethylsilyl)oxy]-2-hydroxynon-5-en-3-yn-5-yl)phenyl carbamate (S3j). General procedure for S3 was followed on a 0.63 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, yellow oil (192 mg, 0.38 mmol, 61%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.29 (m, 2H), 7.05 (d, $J = 8.4$ Hz, 2H), 6.21 (t, $J = 7.7$ Hz, 1H), 4.84 – 4.45 (m, 1H), 3.59 (t, $J = 6.3$ Hz, 2H), 2.57 (s, 6H), 2.28 (q, $J = 7.6$ Hz, 2H), 1.80 (d, $J = 5.3$ Hz, 1H), 1.68 – 1.58 (m, 2H), 1.48 (d, $J = 6.6$ Hz, 3H), 1.39 (s, 9H), 0.87 (s, 9H), 0.02 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 173.0, 152.8, 140.9, 138.1, 136.9, 129.5, 128.0, 122.4, 89.1, 85.8, 83.5, 62.6, 59.0, 32.7, 28.0, 26.7, 26.3, 26.1, 24.6, 18.5, -5.2. IR (neat) 3419, 2954, 2931, 2887, 2858, 1740, 1712, 1606, 1510, 1473, 1462, 1394, 1370, 1303, 1272, 1255, 1156, 1097, 1029, 1016, 947, 923, 837, 775, 749, 662, 629, 529, 489 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{28}$H$_{43}$NNaO$_5$Si [M+Na]$^+$ 524.2803, found 524.2803. $[\alpha]_{D}^{26} = +8.0$ (c = 1.0, CHCl$_3$).
(R,E)-9-((tert-Butyldimethylsilyl)oxy)-5-phenylnon-5-en-3-yn-2-yl acetate (S4a). General procedure for S4 was followed on a 5.78 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (2.23 g, 5.77 mmol, 99%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.41 – 7.27 (m, 5H), 6.22 (t, J = 7.7 Hz, 1H), 5.60 (q, J = 6.7 Hz, 1H), 3.58 (t, J = 6.2 Hz, 2H), 2.29 (q, J = 7.6 Hz, 2H), 2.07 (s, 3H), 1.66 – 1.57 (m, 2H), 1.51 (d, J = 6.7 Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.1, 141.1, 137.2, 128.8, 128.3, 127.6, 122.9, 86.6, 85.3, 62.6, 61.1, 32.7, 26.3, 26.1, 21.7, 21.3, 18.4, -5.2. IR (neat) 2954, 2930, 2886, 2857, 2226, 1743, 1600, 1495, 1472, 1463, 1445, 1371, 1340, 1232, 1154, 1098, 1068, 1030, 948, 835, 814, 775, 699, 662, 610, 567, 526 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{23}$H$_{34}$NaO$_3$Si [M+Na]$^+$ 409.2169, found 409.2171. $\left[\alpha\right]_D^{26} = +73.0$ (c = 1.0, CHCl$_3$).

( R,E)-9-((tert-Butyldimethylsilyl)oxy)-5-(4-(trifluoromethyl)phenyl)non-5-en-3-yn-2-yl acetate (S4b). General procedure for S4 was followed on a 0.58 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (259 mg, 0.57 mmol, 98%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 – 7.51 (m, 2H), 7.46 (dt, J = 7.7, 0.9 Hz, 2H), 6.30 (t, J = 7.8 Hz, 1H), 5.58 (q, J = 6.7 Hz, 1H), 3.58 (t, J = 6.1 Hz, 2H), 2.28 (q, J = 7.7 Hz, 2H), 2.07 (s, 3H), 1.62 (m, 2H), 1.51 (d, J = 6.7 Hz, 3H), 0.83 (s, 9H), -0.01 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.1, 142.5, 140.9, 129.2, 121.9, 86.1, 85.8, 62.3, 61.0, 32.5, 26.3, 26.0, 21.6, 21.3, 18.4, -5.2. IR (neat) 2954, 2932, 2887, 2858, 1745, 1618, 1473, 1408, 1371, 1325, 1234, 1167, 1127, 1109, 1066, 1019, 948, 836, 776, 711, 662, 622, 528, 495, 471 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{24}$H$_{33}$F$_3$NaO$_3$Si [M+Na]$^+$ 477.2043, found 477.2043. $\left[\alpha\right]_D^{26} = +70.7$ (c = 1.0, CHCl$_3$).
(R,E)-Methyl 4-(2-acetoxy-9-((tert-butyldimethylsilyl)oxy)non-5-en-3-yn-5-yl)benzoate (S4c). General procedure for S4 was followed on a 0.82 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (337 mg, 0.76 mmol, 92%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11 – 7.97 (m, 2H), 7.47 – 7.34 (m, 2H), 6.29 (t, $J = 7.8$ Hz, 1H), 5.59 (q, $J = 6.6$ Hz, 1H), 3.92 (s, 3H), 3.57 (t, $J = 6.2$ Hz, 2H), 2.28 (q, $J = 7.6$ Hz, 2H), 2.07 (s, 3H), 1.70 – 1.55 (m, 2H), 1.50 (d, $J = 6.7$ Hz, 3H), 0.84 (s, 9H), 0.00 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.1, 167.0, 142.4, 141.9, 129.6, 128.9, 122.2, 85.93, 85.89, 62.4, 61.0, 52.3, 32.6, 26.4, 26.0, 21.6, 21.3, 18.4, -5.2. IR (neat) 2953, 2931, 2857, 1744, 1725, 1609, 1472, 1436, 1405, 1371, 1340, 1278, 1233, 1191, 1154, 1103, 1071, 1021, 948, 836, 776, 708, 662, 610, 502 cm$^{-1}$. $[\alpha]_D^{26} = +73.4$ (c = 1.0, CHCl$_3$).

(R,E)-9-((tert-Butyldimethylsilyl)oxy)-5-(4-chlorophenyl)non-5-en-3-yn-2-yl acetate (S4d). General procedure for S4 was followed on a 0.92 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (368 mg, 0.87 mmol, 95%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 – 7.26 (m, 4H), 6.22 (t, $J = 7.7$ Hz, 1H), 5.58 (q, $J = 6.7$ Hz, 1H), 3.57 (t, $J = 6.1$ Hz, 2H), 2.26 (q, $J = 7.6$ Hz, 2H), 2.07 (s, 3H), 1.65 – 1.55 (m, 2H), 1.50 (d, $J = 6.7$ Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.1, 141.5, 135.7, 133.4, 130.2, 128.5, 128.1, 86.1, 85.7, 62.4, 61.0, 32.6, 26.3, 26.0, 21.7, 21.3, 18.4, -5.2. IR (neat) 2954, 2930, 2886, 2857, 2226, 1744, 1594, 1491, 1472, 1463, 1370, 1340, 1307, 1233, 1153, 1095, 1071, 1016, 948, 835, 776, 721, 662, 607, 569, 506 cm$^{-1}$. $[\alpha]_D^{26} = +74.5$ (c = 1.0, CHCl$_3$).

(R,E)-9-((tert-Butyldimethylsilyl)oxy)-5-(4-fluorophenyl)non-5-en-3-yn-2-yl acetate (S4e). General procedure for S4 was followed on a 0.88 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil...
(342 mg, 0.85 mmol, 96%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.35 – 7.28 (m, 2H), 7.06 – 6.98 (m, 2H), 6.20 (t, J = 7.2 Hz, 1H), 5.59 (q, J = 6.9 Hz, 1H), 3.58 (t, J = 6.1 Hz, 2H), 2.26 (q, J = 7.6 Hz, 2H), 2.07 (d, J = 0.6 Hz, 3H), 1.66 – 1.57 (m, 2H), 1.50 (d, J = 6.7 Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 170.1, 162.2 (d, J = 246.7 Hz), 141.1, 133.2 (d, J = 3.3 Hz), 130.5 (d, J = 8.1 Hz), 121.9, 115.2 (d, J = 21.5 Hz), 86.4, 85.5, 62.4, 61.0, 32.6, 26.3, 26.0, 21.7, 21.3, 18.4, -5.2. IR (neat) 2954, 2931, 2887, 2224, 1743, 1604, 1509, 1472, 1464, 1405, 1371, 1340, 1307, 1232, 1152, 1099, 1071, 1023, 948, 836, 776, 726, 661, 582, 525 cm\textsuperscript{-1}. \([\alpha]\)\textsubscript{D}\textsuperscript{26} = +78.5 (c = 1.0, CHCl\textsubscript{3}).

\textbf{(R,E)-9-((tert-Butyldimethylsilyloxy)-5-(3-fluorophenyl)non-5-en-3-yn-2-yl acetate (S4f).} General procedure for S4 was followed on a 0.72 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (280 mg, 0.69 mmol, 97%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.30 (td, J = 8.0, 5.9 Hz, 1H), 7.12 (dt, J = 7.7, 1.2 Hz, 1H), 7.09 – 7.03 (m, 1H), 6.97 (tdd, J = 8.4, 2.6, 1.0 Hz, 1H), 6.24 (t, J = 6.1 Hz, 2H), 5.59 (q, J = 6.7 Hz, 1H), 3.58 (t, J = 6.1 Hz, 2H), 2.29 (q, J = 7.6 Hz, 2H), 2.07 (s, 3H), 1.67 – 1.57 (m, 2H), 1.51 (d, J = 6.7 Hz, 3H), 0.84 (s, 9H), 0.00 (s, 6H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 169.9, 162.5 (d, J = 245.7 Hz), 141.8, 139.2 (d, J = 7.7 Hz), 129.6 (d, J = 8.4 Hz), 124.4 (d, J = 2.9 Hz), 121.7 (d, J = 2.2 Hz), 115.7 (d, J = 22.0 Hz), 114.4 (d, J = 21.1 Hz), 85.9, 85.6, 62.3, 60.9, 32.4, 26.2, 25.9, 21.5, 21.1, 18.3, -5.4. IR (neat) 2954, 2931, 2887, 2858, 1743, 1612, 1582, 1487, 1472, 1441, 1371, 1256, 1234, 1137, 1103, 1024, 949, 909, 879, 836, 813, 777, 704, 662, 609, 522, 488, 461 cm\textsuperscript{-1}. HRMS (MALDI): m/z calcd for C\textsubscript{23}H\textsubscript{33}FNaO\textsubscript{3}Si [M+Na]\textsuperscript{+} 427.2075, 427.2076. \([\alpha]\)\textsubscript{D}\textsuperscript{26} = +79.6 (c = 1.0, CHCl\textsubscript{3}).

\textbf{(R,Z)-9-((tert-Butyldimethylsilyloxy)-5-(2-fluorophenyl)non-5-en-3-yn-2-yl acetate (S4g).} General procedure for S4 was followed on a 0.84 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (324 mg, 0.80 mmol, 95%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.31 – 7.24 (m, 2H), 7.15 – 7.10 (m, 1H), 7.09 – 7.02 (m, 1H), 6.32 (t, J = 7.7 Hz, 1H), 5.58 (q, J = 6.6 Hz, 1H), 3.55 (t, J = 6.3 Hz, 2H), 2.13 – 2.03 (m, 5H), 1.62 – 1.55 (m, 2H), 1.48 (d, J = 6.6 Hz, 3H), 0.83 (s, 9H), -0.01 (s, 6H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 170.1, 159.4 (d, J = 247.8 Hz), 143.9, 131.1 (d, J = 3.4 Hz), 129.6 (d, J = 8.1 Hz), 124.9 (d, J = 16.0 Hz), 124.1 (d, J = 3.6 Hz), 116.6, 115.9 (d, J = 7.7 Hz).
22.3 Hz), 85.6, 85.2, 62.6, 61.0, 32.1, 26.6 (d, J = 2.4 Hz), 26.0, 21.7, 21.3, 18.4, -5.2. IR (neat) 2931, 2857, 1743, 1492, 1450, 1371, 1233, 1100, 948, 836, 776, 759 cm⁻¹. HRMS (MALDI): m/z calcd for C_{23}H_{33}FNaO_{3}Si [M+Na]⁺ 427.2075, 427.2075. \[\alpha\] _D^26 = +80.3 (c = 1.0, CHCl₃).

\((R,E)-9-((\text{tert-Butyldimethylsilyl})oxy)-5-(naphthalen-2-yl)non-5-en-3-yn-2-yl\) acetate (S4h). General procedure for S4 was followed on a 0.33 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (133 mg, 0.31 mmol, 92%).

H NMR (400 MHz, CDCl₃) δ 7.86 – 7.79 (m, 3H), 7.79 – 7.75 (m, 1H), 7.51 – 7.45 (m, 3H), 6.31 (t, J = 7.7 Hz, 1H), 5.63 (q, J = 6.6 Hz, 1H), 3.58 (t, J = 6.3 Hz, 2H), 2.35 (q, J = 7.6 Hz, 2H), 2.08 (s, 3H), 1.64 (m, 2H), 1.52 (d, J = 6.7 Hz, 3H), 0.82 (s, 9H), -0.01 (s, 6H). IR (neat) 2954, 2931, 2858, 1743, 1603, 1506, 1472, 1470, 1371, 1234, 1198, 1167, 1154, 1101, 1071, 1018, 947, 912, 836, 776, 663, 609, 525 cm⁻¹. HRMS (MALDI): m/z calcd for C_{25}H_{36}FNaO_{5}Si [M+Na]⁺ 467.2224, 467.2224. \[\alpha\] _D^26 = +66.3 (c = 1.0, CHCl₃).

\((R,E)-4-(2-Acetoxy-9-((\text{tert-Butyldimethylsilyl})oxy)non-5-en-3-yn-5-yl)phenyl\) acetate (S4i). General procedure for S4 was followed on a 0.62 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (262 mg, 0.59 mmol, 95%).

H NMR (400 MHz, CDCl₃) δ 7.44 – 7.31 (m, 2H), 7.16 – 7.02 (m, 2H), 6.21 (t, J = 7.7 Hz, 1H), 5.59 (q, J = 6.6 Hz, 1H), 3.58 (t, J = 6.2 Hz, 2H), 2.33 – 2.25 (m, 5H), 2.07 (s, 3H), 1.70 – 1.56 (m, 2H), 1.50 (d, J = 6.6 Hz, 3H), 0.85 (s, 9H), 0.01 (s, 6H). IR (neat) 2954, 2931, 2858, 1743, 1603, 1506, 1472, 1370, 1234, 1198, 1167, 1154, 1101, 1071, 1018, 947, 912, 836, 776, 663, 609, 525 cm⁻¹. HRMS (MALDI): m/z calcd for C_{25}H_{36}NaO_{5}Si [M+Na]⁺ 467.2224, found 467.2224. \[\alpha\] _D^26 = +66.3 (c = 1.0, CHCl₃).
(R,E)-5-(4-(N-(tert-Butoxycarbonyl)acetamido)phenyl)-9-((tert-butyldimethylsilyl)oxy)non-5-en-3-yn-2-yl acetate (S4j). General procedure for S4 was followed on a 0.49 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (253 mg, 0.47 mmol, 95%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 – 7.32 (m, 2H), 7.08 – 7.00 (m, 2H), 6.23 (t, $J$ = 7.7 Hz, 1H), 5.59 (q, $J$ = 6.7 Hz, 1H), 3.59 (t, $J$ = 6.3 Hz, 2H), 2.57 (s, 3H), 2.29 (q, $J$ = 7.6 Hz, 2H), 2.07 (s, 3H), 1.67 – 1.59 (m, 2H), 1.50 (d, $J$ = 6.7 Hz, 3H), 1.39 (s, 9H), 0.87 (s, 9H), 0.02 (s, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 173.0, 170.1, 152.8, 141.5, 138.1, 136.7, 129.5, 128.0, 122.2, 86.3, 85.5, 83.5, 62.6, 61.0, 32.7, 28.0, 26.7, 26.4, 26.1, 21.7, 21.3, 18.5, -5.2. IR (neat) 2932, 2857, 1739, 1712, 1607, 1510, 1473, 1462, 1370, 1337, 1302, 1271, 1254, 1234, 1155, 1096, 1072, 1017, 948, 923, 836, 775, 738, 662, 614, 529 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{30}$H$_{45}$NNaO$_6$Si [M+Na]$^+$ 566.2908, found 566.2906. $[\alpha]_D^{26}$ = +57.1 (c = 1.0, CHCl$_3$).

(R,E)-9-Hydroxy-5-phenylnon-5-en-3-yn-2-yl acetate (S5a). General procedure for S5 was followed on a 1.95 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (457 mg, 1.68 mmol, 86%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.27 (m, 5H), 6.21 (t, $J$ = 7.7 Hz, 1H), 5.60 (q, $J$ = 6.6 Hz, 1H), 3.61 (t, $J$ = 6.4 Hz, 2H), 2.31 (q, $J$ = 7.6 Hz, 2H), 2.07 (s, 3H), 1.75 – 1.58 (m, 2H), 1.50 (d, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.1, 140.4, 137.1, 128.8, 128.4, 127.7, 123.4, 86.4, 85.6, 62.3, 61.1, 32.5, 26.0, 21.7, 21.3. IR (neat) 2419, 2988, 2937, 2872, 2211, 1740, 1599, 1494, 1444, 1371, 1234, 1153, 1067, 1028, 947, 857, 768, 700, 611, 567, 526, 477 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{30}$H$_{20}$NaO$_3$ [M+Na]$^+$ 295.1305, 295.1305. $[\alpha]_D^{26}$ = +112.6 (c = 1.0, CHCl$_3$).

(R,E)-9-Hydroxy-5-(4-(trifluoromethyl)phenyl)non-5-en-3-yn-2-yl acetate (S5b). General procedure for S5 was followed on a 0.55 mmol scale. The crude product was purified by flash column chromatography
on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (96 mg, 0.28 mmol, 51%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.72 – 7.56 (m, 2H), 7.52 – 7.37 (m, 2H), 6.28 (t, \(J = 7.7\) Hz, 1H), 5.58 (q, \(J = 6.7\) Hz, 1H), 3.62 (t, \(J = 6.4\) Hz, 2H), 5.58 (q, \(J = 6.6\) Hz, 1H), 3.60 (t, \(J = 6.4\) Hz, 2H), 2.29 (q, \(J = 7.6\) Hz, 2H), 2.07 (s, 3H), 1.78 – 1.62 (m, 2H), 1.50 (d, \(J = 6.7\) Hz, 3H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.1, 141.8, 140.8 (d, \(J = 1.4\) Hz), 129.8 (d, \(J = 32.5\) Hz), 129.2, 127.5, 125.4 (q, \(J = 3.8\) Hz), 122.3, 86.3, 85.6, 62.2, 60.9, 32.3, 26.1, 21.6, 21.3.

IR (neat) 3422, 2939, 1741, 1618, 1448, 1408, 1372, 1233, 116, 1018, 947, 848, 708, 621, 527, 496, 471 cm\(^{-1}\).

HRMS (MALDI): m/z calcd for C\(_{18}\)H\(_{17}\)F\(_3\)NaO\(_3\) [M+Na]\(^+\) 361.1022, found 361.1022. \([\alpha]\)\(_D\)^{26} = +86.7 (c = 1.0, CHCl\(_3\)).

\((R,E)-methyl\ 4-(2-acetoxy-9-hydroxynon-5-en-3-yn-5-yl)benzoate (S5c).\) General procedure for S5 was followed on a 0.74 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (175 mg, 0.53 mmol, 72%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.21 – 7.86 (m, 2H), 7.44 – 7.38 (m, 2H), 6.27 (t, \(J = 7.7\) Hz, 1H), 5.58 (q, \(J = 6.6\) Hz, 1H), 3.91 (s, 3H), 3.60 (t, \(J = 6.4\) Hz, 2H), 2.30 (q, \(J = 7.6\) Hz, 2H), 2.06 (s, 3H), 1.74 – 1.58 (m, 2H), 1.50 (d, \(J = 6.7\) Hz, 3H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.1, 166.9, 141.8, 141.7, 129.7, 129.3, 128.8, 122.6, 86.2, 85.7, 62.2, 60.9, 52.3, 32.3, 26.1, 21.6, 21.2.

IR (neat) 3443, 2990, 2939, 1721, 1609, 1565, 1436, 1405, 1372, 1338, 1279, 1233, 1192, 1153, 1105, 1070, 1020, 947, 869, 777, 708, 610, 498 cm\(^{-1}\). \([\alpha]\)\(_D\)^{26} = +93.8 (c = 1.0, CHCl\(_3\)).

\((R,E)-5-(4-Chlorophenyl)-9-hydroxynon-5-en-3-yn-2-yl acetate (S5d).\) General procedure for S5 was followed on a 0.86 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (238 mg, 0.78 mmol, 91%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.34 – 7.29 (m, 2H), 7.29 – 7.25 (m, 2H), 6.20 (t, \(J = 7.7\) Hz, 1H), 5.57 (q, \(J = 6.7\) Hz, 1H), 3.60 (t, \(J = 6.4\) Hz, 2H), 2.28 (q, \(J = 7.6\) Hz, 2H), 2.06 (s, 3H), 1.65 (m, 2H), 1.49 (d, \(J = 6.7\) Hz, 3H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.1, 140.9, 135.6, 133.6, 130.2, 128.6, 122.3, 85.9, 62.2, 61.0, 32.4, 26.1, 21.6, 21.3.

IR (neat) 3421, 2937, 22224, 1740, 1594, 1491, 1447, 1397, 1371, 1339, 1233, 1152, 1093, 1069, 1015, 948, 839, 721, 608, 507 cm\(^{-1}\). \([\alpha]\)\(_D\)^{26} = +98.1 (c = 1.0, CHCl\(_3\)).
(R,E)-5-(4-Fluorophenyl)-9-hydroxynon-5-en-3-yn-2-yl acetate (S5e). General procedure for S5 was followed on a 0.76 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (182 mg, 0.63 mmol, 82%).

H NMR (400 MHz, CDCl₃) δ 7.35 – 7.27 (m, 2H), 7.07 – 7.00 (m, 2H), 6.19 (t, J = 7.6 Hz, 1H), 5.58 (q, J = 6.7 Hz, 1H), 3.61 (t, J = 6.4 Hz, 2H), 2.28 (q, J = 7.5 Hz, 2H), 2.07 (s, 3H), 1.67 (dt, J = 8.4, 6.7 Hz, 2H), 1.50 (d, J = 6.7 Hz, 3H). C NMR (101 MHz, CDCl₃) δ 170.01, 162.2 (d, J = 247.0 Hz), 140.4, 133.1 (d, J = 3.3 Hz), 130.5 (d, J = 8.1 Hz), 122.3, 115.3 (d, J = 21.6 Hz), 86.2, 85.8, 62.3, 61.0, 32.4, 26.0, 21.6, 21.3. IR (neat) 3408, 2989, 2938, 2874, 2222, 1739, 1603, 1508, 1447, 1405, 1372, 1340, 1308, 1232, 1152, 1097, 1070, 1025, 948, 843, 726, 610, 580, 525 cm⁻¹. HRMS (MALDI): m/z calcd for C₁₇H₁₉FNaO₃ [M+Na]⁺ 313.1210, found 313.1211. [α]D₂⁶ = +110.0 (c = 1.0, CHCl₃).

(R,E)-5-(3-Fluorophenyl)-9-hydroxynon-5-en-3-yn-2-yl acetate (S5f). General procedure for S5 was followed on a 0.69 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (188 mg, 0.65 mmol, 94%).

H NMR (400 MHz, CDCl₃) δ 7.31 (td, J = 8.0, 5.9 Hz, 1H), 7.11 (dt, J = 7.7, 1.2 Hz, 1H), 7.05 (dd, J = 9.9, 2.6, 1.6 Hz, 1H), 6.98 (tdd, J = 8.5, 2.7, 1.0 Hz, 1H), 6.22 (t, J = 7.7 Hz, 1H), 5.58 (q, J = 6.6 Hz, 1H), 3.61 (t, J = 6.4 Hz, 2H), 2.30 (q, J = 7.6 Hz, 2H), 2.07 (s, 3H), 1.71 – 1.62 (m, 2H), 1.50 (d, J = 6.6 Hz, 3H). C NMR (101 MHz, CDCl₃) δ 170.1, 162.7 (d, J = 246.0 Hz), 141.2, 139.3 (d, J = 7.7 Hz), 129.8 (d, J = 8.4 Hz), 124.5 (d, J = 2.9 Hz), 122.3 (d, J = 2.2 Hz), 115.8 (d, J = 22.0 Hz), 114.6 (d, J = 21.1 Hz), 86.0, 85.8, 62.2, 61.0, 32.3, 26.1, 21.6, 21.2. IR (neat) 3416, 1989, 2937, 2874, 2223, 1739, 1611, 1581, 1486, 1440, 1371, 1339, 1308, 1233, 1207, 1160, 1135, 1064, 1024, 948, 908, 879, 848, 787, 703, 645, 610, 574, 521, 497, 465 cm⁻¹. HRMS (MALDI): m/z calcd for C₁₈H₂₄FO₄ [M+H]⁺ 323.1653, found 323.1644. [α]D₂⁶ = +107.3 (c = 1.0, CHCl₃).
(R,E)-5-(2-Fluorophenyl)-9-hydroxynon-5-en-3-yn-2-yl acetate (S5g). General procedure for S5 was followed on a 0.76 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (195 mg, 0.67 mmol, 89%).

\[^{1}H\] NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32 – 7.24 (m, 2H), 7.14 (ddd, \(J = 7.8, 7.2, 1.2\) Hz, 1H), 7.11 – 7.04 (m, 1H), 6.31 (t, \(J = 7.6\) Hz, 1H), 5.57 (q, \(J = 6.6\) Hz, 1H), 2.16 – 2.07 (m, 3H), 3.59 (t, \(J = 6.4\) Hz, 2H), 2.14 – 2.08 (m, 2H), 2.06 (s, 3H), 1.70 – 1.60 (m, 2H), 1.48 (d, \(J = 6.7\) Hz, 3H). \[^{13}C\] NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.1, 159.3 (d, \(J = 247.6\) Hz), 143.2, 131.0 (d, \(J = 3.4\) Hz), 129.7 (d, \(J = 8.1\) Hz), 124.8 (d, \(J = 16.0\) Hz), 124.2 (d, \(J = 3.6\) Hz), 117.0, 116.0 (d, \(J = 22.2\) Hz), 85.5, 85.4, 62.4, 61.0, 31.8, 26.4 (d, \(J = 2.4\) Hz), 21.6, 21.3. IR (neat) 3419, 2989, 2938, 2873, 1739, 1579, 1491, 1450, 1372, 1340, 1233, 1159, 1148, 1095, 1069, 1026, 948, 893, 838, 809, 760, 612, 527, 480 cm\(^{-1}\). \([\alpha]_{D}^{26}\) = +108.4 (c = 1.0, CHCl\(_3\)).

(R,E)-9-Hydroxy-5-(naphthalen-2-yl)non-5-en-3-yn-2-yl acetate (S5h). General procedure for S5 was followed on a 0.30 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (66 mg, 0.20 mmol, 68%).

\[^{1}H\] NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.87 – 7.79 (m, 3H), 7.78 (d, \(J = 1.8\) Hz, 1H), 7.52 – 7.45 (m, 3H), 6.29 (t, \(J = 7.7\) Hz, 1H), 5.62 (q, \(J = 6.7\) Hz, 1H), 3.61 (t, \(J = 6.4\) Hz, 2H), 2.37 (q, \(J = 7.6\) Hz, 2H), 2.07 (s, 3H), 1.78 – 1.64 (m, 2H), 1.52 (d, \(J = 6.7\) Hz, 3H). \[^{13}C\] NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.1, 140.7, 134.6, 133.2, 132.8, 128.2, 128.0, 127.82, 127.76, 126.8, 126.4, 126.3, 123.4, 86.4, 85.9, 62.3, 61.1, 32.5, 26.1, 21.7, 21.3. IR (neat) 3410, 2936, 1738, 1504, 1445, 1371, 139, 1233, 1147, 1070, 1024, 952, 900, 862, 823, 750, 526, 478 cm\(^{-1}\). HRMS (MALDI): m/z calcd for C\(_{21}\)H\(_{22}\)NaO\(_3\) [M+Na]\(^{+}\) 345.1461, found 345.1461. \([\alpha]_{D}^{26}\) = +95.0 (c = 1.0, CHCl\(_3\)).

(R,E)-4-(2-Acetoxy-9-hydroxynon-5-en-3-yn-5-yl)phenyl acetate (S5i). General procedure for S5 was followed on a 0.59 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (260 mg, 0.44 mmol, 76%).
\[1^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \delta \ 7.45 - 7.29 \ (m, 2H), \ 7.13 - 7.02 \ (m, 2H), \ 6.20 \ (t, J = 7.6 \text{ Hz, 1H}), \ 5.58 \ (q, J = 6.6 \text{ Hz, 1H}), \ 3.67 - 3.49 \ (m, 2H), \ 2.37 - 2.26 \ (m, 5H), \ 2.07 \ (s, 3H), \ 1.72 - 1.62 \ (m, 2H), \ 1.50 \ (d, J = 6.6 \text{ Hz, 3H}).\]

\[1^3\text{C NMR} \ (101 \text{ MHz, CDCl}_3) \delta \ 170.1, \ 169.6, \ 150.1, \ 140.6, \ 134.7, \ 129.9, \ 122.5, \ 121.5, \ 86.2, \ 85.8, \ 62.3, \ 61.0, \ 32.4, \ 26.1, \ 21.6, \ 21.3.\]

\[\text{IR (neat) 3456, 2989, 2938, 2874, 2223, 1740, 1603, 1506, 1432, 1407, 1370, 1339, 1307, 1232, 1197, 1167, 1153, 1103, 1070, 1018, 947, 913, 852, 703, 609, 574, 526, 494 \text{ cm}^{-1}.\]

\[\text{HRMS (MALDI)}: m/z \ \text{calcd for C}_{19}\text{H}_{22}\text{NaO}_5 \ [M+Na]^+ 353.1359, \ \text{found 353.1360.} \ \ [\alpha]_{D}^{26} = +83.6 \ (c = 1.0, \text{CHCl}_3).\]

\((R, E)-5-(4-(\text{N-(tert-Butoxycarbonyl)acetamido})\text{phenyl})-9\text{-hydroxynon-5-en-3-yn-2-yl acetate (S5j).}\)

General procedure for S5 was followed on a 0.46 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (80 mg, 0.19 mmol, 41%).

\[\text{IR (neat) 3456, 2982, 2937, 1737, 1708, 1509, 1370, 1339, 1304, 1272, 1234, 1154, 1097, 1070, 1016, 948, 924, 848, 774, 737, 615, 530, 490, 474 \text{ cm}^{-1}.}\]

\[\text{HRMS (MALDI)}: m/z \ \text{calcd for C}_{24}\text{H}_{31}\text{NNaO}_6 \ [M+Na]^+ 452.2044, \ 452.2043. \ \ [\alpha]_{D}^{26} = +64.7 \ (c = 1.0, \text{CHCl}_3).\]

\((R, E)-9\text{-Oxo-5-phenylnon-5-en-3-yn-2-yl acetate (1a).}\)

General procedure for 1 was followed on a 0.55 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, colorless oil (131 mg, 0.49 mmol, 88%).

\[\text{IR (neat) 3058, 2892, 2938, 2896, 2728, 2223, 2095, 2018, 1958, 1738, 1616, 1599, 1575, 1494, 1444, 1409, 1371, 1340, 1307, 1232, 1153, 1067, 1048, 1022, 946, 923, 856, 701, 657, 610, 589, 563, 525 \text{ cm}^{-1}.}\]

\[\text{HRMS (MALDI)}: m/z \ \text{calcd for C}_{17}\text{H}_{19}\text{O}_3 \ [M+H]^+ 271.1329, \ \text{found 271.1327.} \ \ [\alpha]_{D}^{26} = +105.8 \ (c = 1.0, \text{CH}_2\text{Cl}_2).\]
(R,E)-9-Oxo-5-(4-(trifluoromethyl)phenyl)non-5-en-3-yn-2-yl acetate (1b). General procedure for 1 was followed on a 0.15 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, slightly yellow oil (40 mg, 0.12 mmol, 80%).

\[ ^1H\text{ NMR}\ (400\text{ MHz, } CD_2Cl_2) \delta 9.71 (t, J = 1.1\text{ Hz}, 1H), 7.69 - 7.61 (m, 1H), 7.58 - 7.35 (m, 1H), 6.22 (t, J = 7.4\text{ Hz}, 1H), 5.53 (q, J = 6.7\text{ Hz}, 1H), 2.59 - 2.53 (m, 2H), 2.52 - 2.46 (m, 3H), 2.04 (s, 4H), 1.48 (d, J = 6.7\text{ Hz}, 4H). \]

\[ ^{13}C\text{ NMR}\ (101\text{ MHz, } CD_2Cl_2) \delta 201.0, 170.1, 141.1 (d, J = 1.5\text{ Hz}), 140.3, 129.5, 125.7 (q, J = 3.8\text{ Hz}), 123.2, 87.2, 85.3, 60.9, 43.4, 22.6, 21.6, 21.2. \]

\[ \text{IR (neat) 2991, 2939, 2829, 2729, 2225, 1739, 1617, 1448, 1408, 1372, 1323, 1231, 1165, 1154, 1122, 1109, 1064, 1017, 946, 848, 777, 712, 645, 620, 527 cm}^{-1}.\]

\[ \text{HRMS (MALDI): } m/z \text{ calcd for C}_{18}H_{17}F_3NaO_3 [M+Na]^+ 361.1022, \text{ found 361.1022. } [\alpha]^{26}_{D} = +94.0 (c = 1.0, CH_2Cl_2). \]

(R,E)-Methyl 4-(2-acetoxy-9-oxonon-5-en-3-yn-5-yl)benzoate (1c). General procedure for 1 was followed on a 0.26 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (72 mg, 0.22 mmol, 84%).

\[ ^1H\text{ NMR}\ (400\text{ MHz, } CD_2Cl_2) \delta 9.70 (s, 1H), 8.02 (d, J = 8.5\text{ Hz}, 2H), 7.43 (d, J = 8.4\text{ Hz}, 2H), 6.21 (t, J = 7.3\text{ Hz}, 1H), 5.54 (q, J = 6.7\text{ Hz}, 1H), 3.90 (s, 3H), 2.61 - 2.44 (m, 4H), 2.04 (s, 3H), 1.49 (d, J = 6.7\text{ Hz}, 3H). \]

\[ ^{13}C\text{ NMR}\ (101\text{ MHz, } CD_2Cl_2) \delta 201.0, 170.1, 166.9, 141.8, 140.1, 129.9, 129.1, 123.5, 87.1, 85.4, 61.0, 52.4, 43.4, 22.6, 21.6, 21.2. \]

\[ \text{IR (neat) 2991, 2953, 2842, 2728, 1721, 1609, 1565, 1507, 1436, 1406, 1372, 1339, 1309, 1279, 1233, 1192, 1181, 1153, 1113, 1070, 1019, 947, 869, 818, 776, 708, 658, 611, 529 cm}^{-1}. \]

\[ \text{HRMS (MALDI): } m/z \text{ calcd for C}_{19}H_{20}NaO_5 [M+Na]^+ 351.1203, \text{ found 351.1202. } [\alpha]^{26}_{D} = +91.3 (c = 1.0, CH_2Cl_2). \]

(R,E)-5-(4-Chlorophenyl)-9-oxonon-5-en-3-yn-2-yl acetate (1d). General procedure for 1 was followed on a 0.35 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, slightly yellow oil (82 mg, 0.27 mmol, 76%).
\( ^1H \) NMR (400 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 9.70 (t, \( J = 1.1 \text{ Hz}, 1\text{H} \)), 7.39 – 7.33 (m, 2H), 7.32 – 7.28 (m, 2H), 6.14 (t, \( J = 7.4 \text{ Hz}, 1\text{H} \)), 5.53 (q, \( J = 6.7 \text{ Hz}, 1\text{H} \)), 2.67 – 2.42 (m, 4H), 2.04 (s, 3H), 1.48 (d, \( J = 6.7 \text{ Hz}, 3\text{H} \)). \( ^{13}C \) NMR (101 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 200.7, 169.7, 138.9, 135.3, 133.5, 130.0, 128.4, 122.7, 86.4, 85.2, 60.6, 43.1, 22.1, 21.2, 20.8. IR (neat) 3453, 2989, 2938, 2895, 2827, 2727, 2225, 1738, 1593, 1491, 1446, 1397, 1371, 1339, 1307, 1231, 1152, 1092, 1070, 1015, 947, 839, 747, 722, 654, 608, 570, 507 cm\(^{-1}\). HRMS (MALDI): m/z calcd for C\(_{17}\)H\(_{18}\)FNaO\(_3\) [M+Na]\(^+\) 327.0758, found 327.0758. \( [\alpha]_D^{26} = +99.8 \) (c = 1.0, CH\(_2\)Cl\(_2\)).

(R,E)-5-(4-Fluorophenyl)-9-oxonon-5-en-3-yn-2-yl acetate (1e). General procedure for 1 was followed on a 0.23 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, colorless oil (60 mg, 0.21 mmol, 90%).

\( ^1H \) NMR (400 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 9.70 (t, \( J = 1.1 \text{ Hz}, 1\text{H} \)), 7.44 – 7.24 (m, 2H), 7.19 – 6.98 (m, 2H), 6.13 (t, \( J = 7.1 \text{ Hz}, 1\text{H} \)), 5.54 (q, \( J = 6.7 \text{ Hz}, 1\text{H} \)), 2.59 – 2.41 (m, 4H), 2.04 (s, 3H), 1.48 (d, \( J = 6.7 \text{ Hz}, 3\text{H} \)). \( ^{13}C \) NMR (101 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 203.2, 169.0 (d, \( J = 631.3 \text{ Hz} \)), 163.4, 141.0, 135.3 (d, \( J = 3.3 \text{ Hz} \)), 132.8 (d, \( J = 8.1 \text{ Hz} \)), 125.2, 117.6 (d, \( J = 21.6 \text{ Hz} \)), 88.7, 87.9, 63.0, 45.5, 24.5, 23.6, 23.2. IR (neat) 2990, 2938, 2829, 2728, 2225, 2086, 1736, 1508, 1447, 1407, 1341, 1307, 1230, 1152, 1098, 1070, 1048, 1023, 947, 843, 727, 654, 609, 568, 524 cm\(^{-1}\). HRMS (MALDI): m/z calcd for C\(_{17}\)H\(_{17}\)FNaO\(_3\) [M+Na]\(^+\) 311.1054, found 311.1053. \( [\alpha]_D^{26} = +103.4 \) (c = 1.0, CH\(_2\)Cl\(_2\)).

(R,E)-5-(3-Fluorophenyl)-9-oxonon-5-en-3-yn-2-yl acetate (1f). General procedure for 1 was followed on a 0.22 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, colorless oil (58 mg, 0.20 mmol, 93%).

\( ^1H \) NMR (400 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 9.71 (d, \( J = 1.1 \text{ Hz}, 1\text{H} \)), 7.36 (td, \( J = 8.0, 6.0 \text{ Hz}, 1\text{H} \)), 7.16 – 7.12 (m, 1H), 7.11 – 6.98 (m, 2H), 6.16 (t, \( J = 7.2 \text{ Hz}, 1\text{H} \)), 5.54 (q, \( J = 6.7 \text{ Hz}, 1\text{H} \)), 2.63 – 2.43 (m, 4H), 2.04 (s, 3H), 1.48 (d, \( J = 6.7 \text{ Hz}, 3\text{H} \)). \( ^{13}C \) NMR (101 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 201.1, 170.1, 163.0 (d, \( J = 245.5 \text{ Hz} \)), 139.7, 139.4 (d, \( J = 7.7 \text{ Hz} \)), 130.3 (d, \( J = 8.4 \text{ Hz} \)), 124.8 (d, \( J = 2.9 \text{ Hz} \)), 123.2 (d, \( J = 2.2 \text{ Hz} \)), 115.9 (d, \( J = 22.1 \text{ Hz} \)), 115.0 (d, \( J = 21.1 \text{ Hz} \)), 86.9, 85.5, 61.0, 43.5, 22.6, 21.6, 21.2. IR (neat) 2990, 2938, 2929, 2729, 2224, 2082, 1736, 1612, 1581, 1487, 1439, 1410, 1371, 1339, 1306, 1231, 1208, 1260, 1136, 1072, 1048, 1023, 948, 907, 880, 849, 788, 699, 645, 610 521 cm\(^{-1}\). HRMS (MALDI): m/z calcd for C\(_{17}\)H\(_{18}\)FO\(_3\) [M+H]\(^+\) 289.1234, found 289.1236. \( [\alpha]_D^{26} = +100.5 \) (c = 1.0, CH\(_2\)Cl\(_2\)).
(R,Z)-5-(2-Fluorophenyl)-9-oxonon-5-en-3-yn-2-yl acetate (1g). General procedure for 1 was followed on a 0.18 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, colorless oil (46 mg, 0.16 mmol, 89%).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 9.69 (t, $J = 1.2$ Hz, 1H), 7.37 – 7.27 (m, 2H), 7.18 (td, $J = 7.5, 1.2$ Hz, 1H), 7.11 (ddd, $J = 9.6, 8.2, 1.2$ Hz, 1H), 6.26 (t, $J = 7.6$ Hz, 1H), 5.52 (q, $J = 6.6$ Hz, 1H), 2.58 – 2.46 (m, 2H), 2.36 – 2.26 (m, 2H), 2.03 (s, 3H), 1.47 (d, $J = 6.6$ Hz, 3H). $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) $\delta$ 201.2, 170.1, 159.5 (d, $J = 246.9$ Hz), 141.7, 131.2 (d, $J = 3.3$ Hz), 130.3 (d, $J = 8.1$ Hz), 124.8, 124.7 (d, $J = 3.6$ Hz), 117.9, 116.2 (d, $J = 22.1$ Hz), 86.4, 85.0, 61.0, 22.9 (d, $J = 2.6$ Hz), 21.6, 21.2. IR (neat) 3444, 2989, 2939, 2730, 1738, 1610, 1580, 1491, 1451, 1372, 1340, 1307, 1232, 1149, 1095, 1069, 1045, 1024, 947, 907, 858, 838, 810, 761, 610, 529 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{17}$H$_{17}$FNaO$_3$ [M+Na]$^+$ 311.1054, found 311.1052. $\left[\alpha\right]_{D}^{26} = +106.1$ (c = 1.0, CH$_2$Cl$_2$).

(R,E)-5-(Naphthalen-2-yl)-9-oxonon-5-en-3-yn-2-yl acetate (1h). General procedure for 1 was followed on a 0.24 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, colorless oil (71 mg, 0.22 mmol, 93%).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 9.69 (t, $J = 1.1$ Hz, 1H), 7.89 – 7.83 (m, 3H), 7.79 (s, 1H), 7.54 – 7.46 (m, 3H), 6.30 – 6.11 (m, 1H), 5.57 (q, $J = 6.7$ Hz, 1H), 2.69 – 2.47 (m, 4H), 2.04 (s, 3H), 1.50 (d, $J = 6.7$ Hz, 3H). $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) $\delta$ 201.2, 170.1, 139.2, 134.7, 133.5, 133.1, 128.4, 128.3, 128.00, 127.97, 126.9, 126.7, 124.3, 86.8, 86.1, 61.1, 43.6, 22.7, 21.7, 21.3. IR (neat) 3056, 2989, 2937, 2826, 2726, 2225, 1738, 1598, 1504, 1434, 1408, 1371, 1339, 1307, 1233, 1199, 1148, 1127, 1070, 1023, 951, 901, 863, 847, 823, 751, 705, 667, 611, 524 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{21}$H$_{20}$NaO$_3$ [M+Na]$^+$ 343.1305, found 343.1303. $\left[\alpha\right]_{D}^{26} = +93.6$ (c = 1.0, CH$_2$Cl$_2$).
(R,E)-4-(2-Acetoxy-9-oxonon-5-en-3-yn-5-yl)phenyl acetate (1i). General procedure for 1 was followed on a 0.12 mmol scale. The crude product was purified by a quick flash column chromatography on silica gel (hexane/EtOAc 1:1). The title compound was isolated as clear, colorless oil (35 mg, 0.11 mmol, 90%). Aldehyde 1i was found to be extremely instable when concentrated and even short term storage was not possible. Thus, the freshly isolated product was immediately used in the subsequent gold(I)-catalyzed cyclization.

(R,E)-5-(4-((N-(tert-Butoyxcarbonyl)acetamido)phenyl)-9-oxonon-5-en-3-yn-2-yl acetate (1j). General procedure for 1 was followed on a 0.15 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 2:1). The title compound was isolated as clear, colorless oil (54 mg, 0.13 mmol, 85%).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 9.70 (d, $J = 0.9$ Hz, 1H), 7.49 – 7.26 (m, 2H), 7.18 – 7.00 (m, 2H), 6.28 – 6.09 (m, 1H), 5.55 (q, $J = 6.7$ Hz, 1H), 2.56 (s, 3H), 2.55 – 2.50 (m, 4H), 2.04 (s, 3H), 1.49 (d, $J = 6.7$ Hz, 3H), 1.38 (s, 9H).

$^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) $\delta$ 201.1, 173.2, 170.1, 152.9, 139.2, 139.0, 136.5, 129.5, 128.7, 123.6, 86.8, 85.8, 83.7, 61.0, 43.5, 27.9, 26.8, 22.6, 21.6, 21.3. IR (neat) 2982, 2938, 2729, 1736, 1708, 1605, 1511, 1478, 1456, 1414, 1394, 1370, 1340, 1303, 1271, 1253, 1233, 1154, 1097, 1070, 1028, 1016, 947, 924, 848, 774, 743, 610 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{24}$H$_{29}$NaO$_6$ [M+Na]$^+$ 450.1887, found 450.1887. $[\alpha]^{26}_D = +85.4$ (c = 1.0, CH$_2$Cl$_2$).
2.2 Synthesis of Alkyl Substrates

General Procedures for Alkyl-Substrate Synthesis

Reagents and conditions: a) PhLi (1.0 equiv), LiBr (2.0 equiv), alkyltriphenylphosphonium bromide (1 equiv), –78°C; then PhLi, –78°C to RT; then I₂, –78°C to RT.; b) (R)-3-butyn-2-ol (1.3 equiv), PdCl₂(PPh₃)₂ (5 mol%), Cul (10 mol%), Et₃N/THF (2:1); c) Ac₂O (1.1 equiv), DMAP (0.1 equiv), pyridine (1.5 equiv), CH₂Cl₂; d) TBAF (2 equiv), THF; e) (COCl)₂ (1.2 equiv), DMSO (2.4 equiv), NEt₃ (5 equiv), –78 °C to –30 °C CH₂Cl₂.

Propargyl alcohol S7.⁶,⁷ (step 1) To a solution of anhydrous LiBr (1.0 equiv) in dry THF (0.4 M) at ambient temperature was added alkyltriphenylphosphonium bromide (1.0 equiv) and stirred for 10 min. The resulting suspension was cooled to –78°C and PhLi (1.9 M in Bu₂O, 1.0 equiv) was added dropwise. The solution was allowed to warm to RT over 15 min and then stirred for another 30 min at that temperature. Then the solution was recooled to –78°C and a solution of 4-(tert-butyldimethylsilyloxy)butanal (1.0 M in THF, 1.0 equiv) was added dropwise. After 10 min, PhLi (1.9M in Bu₂O, 1.1 equiv) was added dropwise and stirred for 30 min at –78°C, then allowed to warm to RT over 15 min. After 30 min at ambient temperature, the mixture was recooled to –78°C and transferred via cannula to a solution of I₂ (1.0 M in THF, 1.2 equiv) at –78°C and stirred for 30 min. Then the solution was allowed to warm to RT and stirred for another hour. The resulting mixture was quenched by the addition of sat. aq. Na₂S₂O₃ solution and stirred vigorously for 5 min. The phases were separated and the aqueous phase was extracted with Et₂O (3x). The combined organic phases were washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo. Purification by flash column chromatography afforded the corresponding vinyl iodide.

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(step 2) To a degassed solution of the vinyl iodide (1.0 equiv) and (R)-but-3-yn-2-ol (1.2 equiv) in NEt₃/THF (2:1, 0.15 M) was added PdCl₂(PPh₃)₂ (0.05 equiv) and CuI (0.1 equiv) and the resulting mixture was stirred at RT for 2h before it was filtered through a short plug of silica gel eluting with EtOAc and concentrated in vacuo. Purification by column chromatography afforded enyne S7.

Propargyl Acetate S8. To a stirred solution of enyne S7 (1.0 equiv) dissolved in CH₂Cl₂ (0.1 M) at ambient temperature was added pyridine (5.0 equiv), DMAP (0.2 equiv), and Ac₂O (1.5 equiv). The resulting solution was stirred for 1h before it was quenched with H₂O. The aqueous phase was extracted with Et₂O (3x). The combined organic phases were washed with sat. aq. CuSO₄ solution, H₂O (1x), and brine, dried over MgSO₄, filtered, and concentrated in vacuo. Purification by flash column chromatography provided propargyl acetate S8.

Primary alcohol S9. To a stirred solution of propargyl acetate S8 (1.0 equiv) in dry THF (0.1 M) at 0 °C was added TBAF (1.0 M in THF, 2 equiv). After the addition, the solution was allowed to warm to ambient temperature and stirred for another 90 min. The mixture was quenched by the addition of sat. aq. NaHCO₃ solution. EtOAc was added to the mixture and the phases separated. The aqueous phase was extracted with EtOAc (3x). The combined organic phases were dried over MgSO₄, filtered, and concentrated in vacuo. Purification by flash column chromatography provided primary alcohol S9.

Aldehyde 1. To a solution of oxalyl chloride (1.2 equiv) in CH₂Cl₂ (0.15 M) at –78 °C was added DMSO (2.4 equiv) dropwise and stirred for 15 min. Then a solution of alcohol S9 in CH₂Cl₂ (0.05-0.1 M) was added dropwise and stirred for 30 min. After that time, NEt₃ (5 equiv) was added and stirred for another 30 min at –78 °C and then slowly warmed to –30 °C over 30 min and then quenched by the addition of sat. aq. NaHCO₃ solution. The phases were separated and the aqueous phase was extracted with CH₂Cl₂ (3x), dried over MgSO₄, filtered, and concentrated in vacuo. Purification by flash column chromatography provided aldehyde 1.

(R,E)-9-((tert-butyldimethylsilyl)oxy)-5-methylnon-5-en-3-yn-2-ol (S7k). The general procedure for S7 (part b) was followed on a 1.76 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, orange oil (312 mg, 1.10 mmol, 75%).

1H NMR (400 MHz, CDCl₃) δ 5.91 – 5.75 (m, 1H), 4.70 – 4.49 (m, 1H), 3.60 (t, J = 6.2 Hz, 2H), 2.20 – 2.09 (m, 2H), 1.80 (d, J = 4.6 Hz, 1H), 1.77 (dd, J = 1.6, 0.9 Hz, 3H), 1.62 – 1.54 (m, 2H), 1.46 (d, J = 6.6 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H). 13C NMR (101 MHz, CDCl₃) δ 138.3, 117.5, 87.5, 87.2, 62.5, 59.0, 32.2, 26.1, 25.0,

8 Aldehyde 10 were found to decompose when stored in commercial CDCl₃. Thus, filtration through basic Al₂O₃ or the use of CD₂Cl₂ is advised.
24.7, 18.5, 17.2, -5.2. **IR (neat)** 3342, 2954, 2930, 2886, 2858, 2217, 1633, 1472, 1463, 1446, 1387, 1361, 1329, 1288, 1254, 1180, 1101, 1006, 859, 839, 916, 887, 835, 814, 775, 720, 680, 662, 573, 542, 494 cm\(^{-1}\).

**HRMS (MALDI):** \(m/z\) calcd for \(C_{16}H_{30}KO_2Si\) [M+K]\(^+\) 321.1647, found 321.1647. \([\alpha]^{26}_D = +14.9\) (c = 1.0, CHCl\(_3\)).

\(R,E\)-9-((tert-Butyldimethylsilyl)oxy)-5-isopropynon-5-en-3-yn-2-ol (S7l). General procedure for S7 was followed on a 4.94 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, orange oil (513 mg, 1.65 mmol, 33%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.76 (t, \(J = 7.6\) Hz, 1H), 4.82 – 4.55 (m, 1H), 3.60 (t, \(J = 6.3\) Hz, 2H), 2.88 – 2.62 (m, 1H), 2.18 (q, \(J = 7.6\) Hz, 2H), 1.76 (s, 1H), 1.62 – 1.53 (m, 2H), 1.48 (d, \(J = 6.6\) Hz, 3H), 1.03 (dd, \(J = 6.8, 0.9\) Hz, 6H), 0.89 (s, 9H), 0.04 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 136.4, 129.6, 89.9, 83.9, 62.5, 59.1, 32.7, 28.0, 26.1, 24.8, 24.4, 21.6, 8.9, -5.1. **IR (neat)** 3342, 2958, 2930, 2887, 2858, 2214, 2087, 1472, 1385, 1362, 1328, 1288, 1255, 1186, 1162, 1104, 1007, 960, 939, 922, 887, 835, 813, 775, 716, 662, 639, 573, 521 cm\(^{-1}\). **HRMS (MALDI):** \(m/z\) calcd for \(C_{18}H_{34}FO_3Si\) [M+Na]\(^+\) 333.2221, found 333.2221. \([\alpha]^{26}_D = +11.2\) (c = 1.0, CHCl\(_3\)).

\(R,E\)-5-(2-(Benzyloxy)ethyl)-9-((tert-butyldimethylsilyl)oxy)non-5-en-3-yn-2-ol (S7m). General procedure for S7 was followed on a 5.88 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 5:1). The title compound was isolated as clear, orange oil (555 mg, 1.38 mmol, 24%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 – 7.32 (m, 5H), 7.32 – 7.27 (m, 1H), 5.95 (t, \(J = 7.6\) Hz, 1H), 4.61 (t, \(J = 6.5\) Hz, 1H), 4.53 (d, \(J = 1.9\) Hz, 2H), 3.60 (q, \(J = 6.7\) Hz, 4H), 2.54 – 2.42 (m, 2H), 2.19 (q, \(J = 7.6\) Hz, 2H), 1.66 – 1.54 (m, 3H), 1.43 (d, \(J = 6.6\) Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.1, 138.6, 128.5, 127.8, 127.7, 119.2, 88.6, 85.7, 73.0, 68.7, 62.6, 59.0, 32.5, 31.3, 26.1, 25.0, 24.6, 18.5, -5.1. **IR (neat)** 2954, 2929, 2857, 1472, 1463, 1455, 1388, 1362, 1328, 1255, 1099, 1029, 1006, 964, 939, 912, 890, 835, 814, 776, 735, 697, 662, 498 cm\(^{-1}\). **HRMS (MALDI):** \(m/z\) calcd for \(C_{24}H_{39}O_3Si\) [M+H]\(^+\) 403.2663, found 403.2657. \([\alpha]^{26}_D = +9.8\) (c = 1.0, CHCl\(_3\)).
(R,E)-9-((tert-Butyldimethylsilyl)oxy)-5-methylnon-5-en-3-yn-2-yl acetate (S8k). General procedure for S8 was followed on a 1.1 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, yellow oil (331 mg, 1.02 mmol, 92%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.88 (td, $J = 7.5$, 1.6 Hz, 1H), 5.57 (q, $J = 6.6$ Hz, 1H), 3.59 (t, $J = 6.2$ Hz, 2H), 2.18 – 2.09 (m, 2H), 2.07 (s, 3H), 1.78 – 1.74 (m, 3H), 1.62 – 1.53 (m, 2H), 1.49 (d, $J = 6.6$ Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.1, 139.1, 117.3, 87.8, 83.9, 62.5, 61.1, 32.2, 26.1, 25.0, 21.8, 21.3, 18.4, 17.1, -5.2. IR (neat) 2989, 2954, 2930, 2887, 2858, 2219, 1745, 1472, 1463, 1446, 1371, 1341, 1308, 1231, 1099, 1040, 1008, 944, 889, 835, 814, 75, 721, 680, 662, 609, 543 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{18}$H$_{32}$KO$_3$Si [M+K]$^+$ 363.1752, found 363.1750. $\left[\alpha\right]_{D}^{26} = +96.8$ (c = 1.0, CHCl$_3$).

(R,E)-9-((tert-Butyldimethylsilyl)oxy)-5-isopropynon-5-en-3-yn-2-yl acetate (S8l). General procedure for S8 was followed on a 1.65 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, yellow oil (519 mg, 1.47 mmol, 89%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.79 (t, $J = 7.6$ Hz, 1H), 5.58 (q, $J = 6.7$ Hz, 1H), 3.60 (t, $J = 6.3$ Hz, 2H), 2.84 – 2.60 (m, 1H), 2.17 (q, $J = 7.6$ Hz, 2H), 2.07 (s, 3H), 1.57 (dt, $J = 8.3$, 6.5 Hz, 2H), 1.50 (d, $J = 6.7$ Hz, 3H), 1.02 (dd, $J = 6.8$, 2.9 Hz, 6H), 0.89 (s, 9H), 0.04 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.0, 136.8, 129.2, 86.1, 84.4, 62.3, 61.0, 32.5, 27.9, 25.9, 24.3, 21.7, 21.4, 21.2, 18.3, -5.3. IR (neat) 2958, 2930, 2896, 2858, 2219, 1744, 1472, 1464, 1371, 1339, 1308, 1231, 1164, 1099, 1056, 1018, 947, 889, 834, 814, 775, 718, 679, 662, 638, 609, 523, 469 cm$^{-1}$. $\left[\alpha\right]_{D}^{26} = +87.3$ (c = 1.0, CHCl$_3$).

(R,E)-5-(2-(Benzyloxy)ethyl)-9-((tert-butyldimethylsilyl)oxy)non-5-en-3-yn-2-yl acetate (S8m). General procedure for S8 was followed on a 1.19 mmol scale. The crude product was purified by flash column
chromatography on silica gel (hexane/EtOAc 8:1). The title compound was isolated as clear, yellow oil (485 mg, 1.09 mmol, 92%).

**1H NMR** (400 MHz, CDCl₃) δ 7.34 (d, J = 4.4 Hz, 5H), 7.32 – 7.25 (m, 1H), 5.98 (t, J = 7.7 Hz, 1H), 5.55 (q, J = 6.7 Hz, 1H), 4.53 (s, 2H), 3.60 (q, J = 6.7 Hz, 4H), 2.46 (td, J = 7.1, 1.1 Hz, 2H), 2.18 (q, J = 7.6 Hz, 2H), 2.06 (d, J = 1.2 Hz, 3H), 1.63 – 1.53 (m, 2H), 1.47 (d, J = 6.7 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H).

**13C NMR** (101 MHz, CDCl₃) δ 170.1, 140.8, 138.7, 128.5, 127.7, 127.6, 118.9, 86.3, 85.0, 73.06, 68.7, 62.6, 61.1, 32.4, 31.2, 26.1, 25.0, 21.8, 21.3, 18.5, -5.1. **IR** (neat) 2953, 2930, 2885, 2857, 1742, 1472, 1463, 1454, 1370, 1339, 1308, 1232, 1180, 1099, 1056, 1029, 948, 888, 844, 610, 542, 498 cm⁻¹. **HRMS (MALDI):** m/z calcd for C₂₆H₄₀NaO₄Si [M+Na]⁺ 467.2588, found 467.2588. [α]₂₆° = +70.6 (c = 1.0, CHCl₃).

**(R,E)-9-Hydroxy-5-methylnon-5-en-3-yn-2-yl acetate (S9k).** General procedure for S9 was followed on a 1.02 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as colorless oil (184 mg, 0.88 mmol, 86%).

**1H NMR** (400 MHz, CDCl₃) δ 5.92 – 5.83 (m, 1H), 5.56 (q, J = 6.6 Hz, 1H), 3.65 (t, J = 6.4 Hz, 2H), 2.21 – 2.13 (m, 2H), 2.07 (d, J = 1.4 Hz, 3H), 1.80 – 1.75 (m, 3H), 1.70 – 1.58 (m, 2H), 1.49 (d, J = 6.6 Hz, 3H). **13C NMR** (101 MHz, CDCl₃) δ 170.1, 140.8, 138.5, 117.7, 87.6, 84.1, 62.4, 61.1, 32.0, 24.9, 21.8, 21.3, 17.2. **IR** (neat) 3419, 2989, 2938, 2872, 2219, 1741, 1446, 1372, 1340, 1309, 1232, 1127, 1087, 1041, 948, 888, 844, 610, 542, 498 cm⁻¹. **HRMS (MALDI):** m/z calcd for C₁₂H₁₈NaO₃ [M+Na]⁺ 233.1148, found 233.1148. [α]₂₆° = +131.2 (c = 1.0, CHCl₃).

**(R,E)-9-Hydroxy-5-isopropylnon-5-en-3-yn-2-yl acetate (S9l).** General procedure for S9 was followed on a 0.85 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as colorless oil (169 mg, 0.71 mmol, 83%).

**1H NMR** (400 MHz, CDCl₃) δ 5.78 (t, J = 7.6 Hz, 1H), 5.57 (q, J = 6.6 Hz, 1H), 3.64 (t, J = 6.4 Hz, 2H), 2.81 – 2.64 (m, 1H), 2.20 (q, J = 7.5 Hz, 2H), 2.06 (s, 2H), 1.69 – 1.57 (m, 2H), 1.50 (dd, J = 6.6, 0.6 Hz, 3H), 1.03 (dd, J = 6.7, 2.8 Hz, 6H). **13C NMR** (101 MHz, CDCl₃) δ 170.1, 136.4, 129.7, 86.5, 84.4, 62.4, 61.1, 32.4, 28.1, 24.4, 21.9, 21.6, 21.3. **IR** (neat) 3425, 2964, 2936, 2871, 2218, 1740, 1448, 1371, 1339, 1309, 1232, 1161, 1131, 1095, 1055, 1019, 948, 888, 856, 638, 610, 523, 469 cm⁻¹. **HRMS (MALDI):** m/z calcd for C₁₄H₂₂NaO₃ [M+Na]⁺ 261.1461, found 261.1462. [α]₂₆° = +123.2 (c = 1.0, CHCl₃).
(R,E)-5-(2-(Benzyloxy)ethyl)-9-hydroxynon-5-en-3-yn-2-yl acetate (S9m). General procedure for S9 was followed on a 1.06 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 2:1). The title compound was isolated as clear, colorless oil (250 mg, 0.76 mmol, 72%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 – 7.31 (m, 5H), 7.30 – 7.26 (m, 1H), 6.02 – 5.92 (m, 1H), 5.53 (q, $J = 6.6$ Hz, 1H), 4.53 (s, 2H), 3.61 (t, $J = 6.4$ Hz, 2H), 3.56 (t, $J = 6.0$ Hz, 2H), 2.45 (t, $J = 6.4$ Hz, 2H), 2.25 (q, $J = 7.2$ Hz, 2H), 2.05 (s, 3H), 1.67 – 1.57 (m, 2H), 1.45 (d, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.2, 140.4, 138.3, 128.6, 128.0, 127.9, 119.8, 86.1, 85.3, 73.3, 68.2, 61.4, 61.1, 31.7, 31.3, 24.6, 21.8, 21.4. IR (neat) 3425, 2987, 2936, 2865, 1740, 1496, 1454, 1371, 1339, 1309, 1233, 1175, 1100, 1088, 1055, 1029, 947, 888, 844, 738, 699, 608, 524, 493, 459 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{20}$H$_{26}$NaO$_4$ [M+Na]$^+$ 353.1723, found 353.1723. $\left[\alpha\right]_{D}^{26} = +93.6$ (c = 1.0, CHCl$_3$).

(R,E)-5-Methyl-9-oxonon-5-en-3-yn-2-yl acetate (1k). General procedure for 1 was followed on a 0.57 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, colorless oil (99 mg, 0.48 mmol, 83%).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 9.74 (t, $J = 1.3$ Hz, 1H), 5.83 – 5.73 (m, 1H), 5.50 (q, $J = 6.7$ Hz, 1H), 2.57 – 2.48 (m, 3H), 2.43 – 2.33 (m, 3H), 2.03 (s, 4H), 1.83 – 1.75 (m, 4H), 1.45 (d, $J = 6.7$ Hz, 4H). $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) $\delta$ 201.5, 170.1, 137.0, 118.7, 87.3, 85.0, 61.0, 43.3, 21.8, 21.5, 21.3, 17.2. IR (neat) 3457, 2989, 2938, 2729, 2222, 1737, 1634, 1446, 1411, 1371, 1340, 1308, 1229, 1124, 1088, 1040, 1016, 948, 889, 844, 654, 609, 543, 526, 502 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{12}$H$_{17}$O$_3$ [M+H]$^+$ 209.1172, found 209.1171. $\left[\alpha\right]_{D}^{26} = +130.8$ (c = 1.0, CH$_2$Cl$_2$).

(R,E)-5-Isopropyl-9-oxonon-5-en-3-yn-2-yl acetate (1l). General procedure for 1 was followed on a 0.35 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, colorless oil (70 mg, 0.30 mmol, 85%).
$^1$H NMR (400 MHz, CDCl$_3$) δ 9.77 (s, 1H), 5.72 (t, $J = 7.4$ Hz, 1H), 5.56 (q, $J = 6.5$ Hz, 1H), 2.75 (p, $J = 6.7$ Hz, 1H), 2.52 (m, 2H), 2.49 – 2.39 (m, 2H), 2.07 (s, 3H), 1.50 (d, $J = 6.7$ Hz, 3H), 1.04 (dd, $J = 6.7$, 2.7 Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 201.4, 170.1, 134.3, 133.1, 130.7, 87.0, 84.0, 61.1, 43.5, 28.3, 21.8, 21.5, 21.3, 20.7. IR (neat) 3474, 2966, 2937, 2872, 2726, 2216, 2082, 2005, 1740, 1449, 1410, 1372, 1339, 1308, 1234, 1163, 1132, 1096, 1056, 1019, 948, 854, 640, 609, 576, 523, 498, 470 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{12}$H$_{17}$O$_3$ [M+H]$^+$ 259.1305, found 259.1304. $[\alpha]^D_{26}$ = +87.7 (c = 1.0, CHCl$_3$).

(R,E)-5-(2-(Benzyloxy)ethyl)-9-oxonon-5-en-3-yn-2-yl acetate (1m). General procedure for 1 was followed on a 0.55 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, colorless oil (140 mg, 0.43 mmol, 78%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.69 (t, $J = 1.2$ Hz, 1H), 7.35 – 7.31 (m, 5H), 7.30 – 7.25 (m, 1H), 5.91 (t, $J = 7.3$ Hz, 1H), 5.50 (q, $J = 6.6$ Hz, 1H), 4.50 (s, 2H), 3.62 (t, $J = 6.6$ Hz, 2H), 2.54 – 2.38 (m, 6H), 2.02 (s, 3H), 1.45 (d, $J = 6.7$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 203.0, 171.6, 140.6, 140.1, 130.1, 129.4, 129.3, 122.3, 87.5, 87.4, 74.8, 70.2, 62.5, 45.0, 33.1, 23.2, 22.9, 22.8. IR (neat) 3064, 3030, 2988, 2935, 2858, 2726, 2222, 1737, 1496, 1454, 1409, 1370, 1339, 1308, 1230, 1179, 1101, 1055, 1028, 946, 910, 842, 738, 699, 653, 608, 525 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{20}$H$_{24}$NaO$_4$ [M+Na]$^+$ 351.1567, found 351.1566. $[\alpha]^D_{26}$ = +96.5 (c = 1.0, CH$_2$Cl$_2$).
4. Synthesis and Characterization of Products

General Procedure for Au-Catalyzed Enantiospecific tandem Nazarov-Aldol Cyclization:

Aldehyde 1 (1.0 equiv) was dissolved in dry THF (0.05 M) and water (0.2 vol%) was added. The resulting clear solution was cooled to –10 °C and 3 (5 mol%) was added in one portion. The resulting faintly yellow solution was stirred at –10 °C for 16 hours and, if necessary, allowed to warm to ambient temperature to achieve full conversion. The reaction mixture was filtered through a short pad of silica gel washing with EtOAc, concentrated in vacuo, and subsequently subjected to silica gel flash chromatography to afford the product.

(3aR,6aR)-6-Hydroxy-3-methyl-6a-phenyl-4,5,6,6a-tetrahydropentalen-1(3aH)-one (2a). General procedure was followed on a 0.107 mmol scale. The solution was stirred at -10 °C for 24h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (18.5 mg, 0.081 mmol, 76%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.45 – 7.40 (m, 2H), 7.35 – 7.30 (m, 2H), 7.26 – 7.22 (m, 1H), 6.08 (t, \(J = 1.3\) Hz, 1H), 4.50 – 4.35 (m, 1H), 4.06 (d, \(J = 7.6\) Hz, 1H), 3.27 (d, \(J = 10.5\) Hz, 0H), 2.24 (dd, \(J = 1.3, 0.8\) Hz, 3H), 2.11 – 2.05 (m, 1H), 1.92 – 1.86 (m, 1H), 1.76 – 1.69 (m, 1H), 1.52 – 1.41 (m, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 211.36, 182.53, 140.47, 131.25, 128.85, 127.20, 126.56, 79.30, 63.37, 57.99, 32.35, 24.16, 18.08. IR (neat) 3459, 3060, 3026, 2958, 2873, 1679, 1618, 1581, 1497, 1433, 1378, 1296, 1250, 1188, 1104, 1091, 1050, 1018, 953, 932, 906, 856, 765, 738, 719, 699, 598, 572, 533, 497 cm\(^{-1}\). HRMS (MALDI): m/z calcd for C\(_{15}\)H\(_{17}\)O\(_2\) [M+H]** 229.1223, found 229.1223. \([\alpha]^{26}_{D} = -176.8\) (c = 0.5, CHCl\(_3\)). SFC Daicel Chiralcel OJ-H, 3% MeOH, 2.0 mL/min., 25 °C, 93% ee \(t_\beta\) (1, major enantiomer, major diastereomer) = 9.83 min, \(t_\alpha\) (2, minor enantiomer, major diastereomer) = 12.19 min, \(t_\alpha\) (3, minor enantiomer, minor diastereomer) = 15.96 min, \(t_\beta\) (4, major enantiomer, major diastereomer) = 17.38 min.

(3aR,6aR)-6-Hydroxy-3-methyl-6a-(4-(trifluoromethyl)phenyl)-4,5,6,6a-tetrahydropentalen-1(3aH)-one (2b). General procedure was followed on a 0.092 mmol scale. The solution was stirred at -10 °C for 9...
24h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (19 mg, 0.064 mmol, 70%).

**1H NMR (400 MHz, CDCl₃)** δ 7.65 – 7.45 (m, 4H), 6.09 (p, J = 1.3 Hz, 1H), 4.48 – 4.32 (m, 1H), 3.96 (d, J = 8.0 Hz, 1H), 3.36 – 3.20 (m, J = 3.3 Hz), 2.26 (t, J = 1.1 Hz, 3H), 2.09 (dddd, J = 11.9, 5.8, 5.0, 1.4 Hz, 1H), 1.90 (dddd, J = 13.2, 9.6, 5.9 Hz, 1H), 1.76 (ddt, J = 13.4, 6.5, 1.5 Hz, 1H), 1.48 (tdd, J = 12.6, 11.1, 6.5 Hz, 1H).

**13C NMR (101 MHz, CDCl₃)** δ 210.3, 182.7, 144.4 (d, J = 1.5 Hz), 131.2, 128.3, 127.1, 125.7 (q, J = 3.7 Hz), 79.4, 63.3, 57.7, 54.0, 32.2, 24.2, 18.1.

**IR (neat)** 3465, 2961, 1684, 1618, 1518, 1435, 1411, 1379, 1326, 1300, 1285, 1248, 1165, 1120, 1070, 1018, 953, 859, 835, 776, 752, 738, 715, 688, 622, 610, 521 cm⁻¹. **HRMS (MALDI):** m/z calcd for C₁₆H₁₆F₃O₂ [M+H]+ 297.1097, found 297.1097. [α]²⁶一个 = –134.2 (c = 1.0, CHCl₃).

**SFC (of the corresponding 4-bromophenyl-carbamate) Daicel Chiralcel OJ-H, 3% MeOH, 2.0 mL/min., 25 °C, 96% ee** (tᵣ (1, major enantiomer, major diastereomer) = 8.13 min, tᵣ (2, minor enantiomer, major diastereomer) = 9.13 min).

**Methyl 4-((3R,3aR,6aR)-3-hydroxy-6-methyl-4-oxo-1,2,3,3a,4,6a-hexahydropentalen-3a-yl)benzoate (2c).** General procedure was followed on a 0.167 mmol scale. The solution was stirred at -10 °C for 24h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 4:1 to 2:1). The title compound was isolated as clear, colorless oil (33 mg, 0.115 mmol, 69%).

**1H NMR (400 MHz, CDCl₃)** δ 8.02 – 7.95 (m, 2H), 7.52 – 7.47 (m, 2H), 6.08 (s, 1H), 4.50 – 4.37 (m, 1H), 3.98 (d, J = 7.9 Hz, 1H), 3.89 (s, 3H), 3.28 (d, J = 9.5 Hz, 5H), 2.25 (s, 3H), 2.13 – 2.04 (m, 1H), 1.97 – 1.85 (m, 1H), 1.79 – 1.69 (m, 1H), 1.53 – 1.41 (m, 1H). **13C NMR (101 MHz, CDCl₃)** δ 210.4, 182.6, 166.9, 145.6, 131.2, 129.1, 126.7, 79.3, 63.6, 57.7, 52.2, 32.3, 24.2, 18.1. **IR (neat)** 3472, 2961, 2875, 2071, 1719, 1699, 1683, 1611, 1569, 1510, 1435, 1409, 1378, 1318, 1280, 1190, 1111, 1055, 1020, 964, 926, 861, 825, 774, 741, 727, 703, 617, 607, 574, 536 cm⁻¹. **HRMS (MALDI):** m/z calcd for C₁₇H₁₉O₄ [M+H]+ 287.1278, found 287.1278. [α]²⁶一个 = –163.8 (c = 1.0, CHCl₃). **SFC (of the corresponding 4-bromophenyl-carbamate) Daicel Chiralcel OJ-H, 15% MeOH, 2.0 mL/min., 25 °C, 95% ee** (tᵣ (1, minor enantiomer, major diastereomer) = 11.65 min, tᵣ (2, minor enantiomer, minor diastereomer) = 23.59 min, tᵣ (3, major enantiomer, major diastereomer) = 23.59 min, tᵣ (4, major enantiomer, minor diastereomer) = 28.47 min).
(3aR,6R,6aR)-6a-(4-Chlorophenyl)-6-hydroxy-3-methyl-4,5,6,6a-tetrahydropentalen-1(3aH)-one (2d).

General procedure was followed on a 0.174 mmol scale. The solution was stirred at -10 °C for 24h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (32 mg, 0.122 mmol, 70%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 – 7.24 (m, 4H), 6.06 (s, 1H), 4.43 – 4.31 (m, 1H), 3.97 (d, $J = 8.0$ Hz, 1H), 3.23 (d, $J = 9.2$ Hz, 7H), 2.24 (dd, $J = 1.3, 0.8$ Hz, 1H), 1.97 – 1.82 (m, 1H), 1.79 – 1.67 (m, 1H), 1.53 – 1.34 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 210.7, 182.4, 138.8, 131.1, 128.8, 128.5, 127.9, 79.3, 62.7, 57.6, 32.1, 24.0, 18.0.

IR (neat) 3462, 3070, 2959, 2873, 1679, 1618, 1593, 1493, 1451, 1433, 1401, 1378, 1296, 1250, 1185, 1093, 1054, 953, 858, 823, 742, 719, 705, 618, 608, 573, 536, 524, 507 cm$^{-1}$.

HRMS (MALDI): m/z calcd for C$_{15}$H$_{16}$ClO$_2$ [M+H]$^+$ 263.0833, found 263.0834. $[\alpha]_{D}^{26} = -142.1$ (c = 1.0, CHCl$_3$).

SFC Daicel Chiralcel OJ-H, 3% MeOH, 2.0 mL/min., 25 °C, 95% ee (t$_R$ (1, major enantiomer, major diastereomer) = 11.69 min, t$_R$ (2, minor enantiomer, major diastereomer) = 13.09 min).

(3aR,6aR)-6a-(4-Fluorophenyl)-6-hydroxy-3-methyl-4,5,6,6a-tetrahydropentalen-1(3aH)-one (2e).

General procedure was followed on a 0.191 mmol scale. The solution was stirred at -10 °C for 16h, and then allowed to warm to RT and stirred for another 8h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (35 mg, 0.142 mmol, 75%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.55 – 7.35 (m, 2H), 7.17 – 6.95 (m, 2H), 6.09 (s, 1H), 4.47 – 4.33 (m, 1H), 4.02 (d, $J = 7.9$ Hz, 1H), 3.26 (d, $J = 9.7$ Hz, 1H), 2.27 (s, 3H), 2.17 – 2.04 (m, 1H), 2.00 – 1.84 (m, 1H), 1.75 (dd, $J = 13.4, 6.5$ Hz, 1H), 1.57 – 1.41 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 211.1, 182.5, 162.0 (d, $J = 246.0$ Hz), 131.2, 129.5 (d, $J = 7.9$ Hz), 128.2 (d, $J = 7.9$ Hz), 115.6 (d, $J = 21.3$ Hz), 79.5, 62.7, 57.9, 32.3, 24.1, 18.1.

IR (neat) 3460, 3072, 2959, 2875, 1679, 1618, 1606, 1509, 1451, 1434, 1409, 1378, 1297, 1225, 1189, 1164, 1134, 1100, 1089, 1054, 1015, 995, 953, 852, 832, 812, 775, 743, 706, 647, 613, 576, 563, 526, 456 cm$^{-1}$.

HRMS (MALDI): m/z calcd for C$_{15}$H$_{16}$FO$_2$ [M+H]$^+$ 247.1129, found 247.1129. $[\alpha]_{D}^{26} = -180.5$ (c = 1.0, CHCl$_3$).

SFC Daicel Chiralcel OJ-H, 3% MeOH, 2.0 mL/min., 25 °C, 93% ee (t$_R$ (1, major enantiomer, major diastereomer) = 6.89 min, t$_R$ (2, minor enantiomer, major diastereomer) = 7.63 min, t$_R$ (3, minor enantiomer, minor diastereomer) = 11.61 min, t$_R$ (4, major enantiomer, minor diastereomer) = 13.61 min).
(3aR,6aR)-6a-(3-Fluorophenyl)-6-hydroxy-3-methyl-4,5,6,6a-tetrahydropentalen-1(3aH)-one (2f).

General procedure was followed on a 0.146 mmol scale. The solution was stirred at -10 °C for 16 h, and then allowed to warm to RT and stirred for another 8 h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (26 mg, 0.106 mmol, 73%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.34 – 7.24\) (m, 1H), \(7.23 – 7.13\) (m, 2H), \(6.97 – 6.91\) (m, 1H), \(6.07\) (p, \(J = 1.3\) Hz, 1H), \(4.40\) (ddd, \(J = 11.1, 7.9, 5.7\) Hz, 1H), \(3.97\) (d, \(J = 8.0\) Hz, 1H), \(3.31 – 3.16\) (m, 1H), \(2.24\) (t, \(J = 1.1\) Hz, 3H), \(2.16 – 2.01\) (m, 1H), \(2.01 – 1.80\) (m, 1H), \(1.80 – 1.66\) (m, 1H), \(1.55 – 1.37\) (m, 1H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 210.6, 182.6, 163.1\) (d, \(J = 245.9\) Hz), \(143.0\) (d, \(J = 7.3\) Hz), \(131.2, 130.2\) (d, \(J = 8.4\) Hz), \(122.2\) (d, \(J = 2.9\) Hz), \(114.2\) (d, \(J = 21.1\) Hz), \(113.9\) (d, \(J = 22.4\) Hz), \(79.3, 63.1\) (d, \(J = 1.9\) Hz), \(57.8, 32.3, 24.1, 18.1\).

IR (neat) 3461, 3072, 2959, 2874, 1680, 1614, 1586, 1488, 1436, 1379, 1296, 1262, 1189, 1166, 1128, 1105, 1090, 1059, 1018, 998, 953, 929, 892, 860, 785, 741, 693, 672, 625, 583, 558, 524, 511, 454 cm\(^{-1}\).

HRMS (MALDI): m/z calcd for C\(_{15}\)H\(_{16}\)NaFO\(_2\) [M+Na]\(^+\) 269.0948, found 269.0948. \(\Delta \alpha\) 26\(\Delta\) 

SFC Daicel Chiralcel OJ-H, 1% MeOH, 2.0 mL/min., 25 °C, 94% ee \(t_R\) (1, major enantiomer, major diastereomer) = 10.55 min, \(t_R\) (2, minor enantiomer, major diastereomer) = 11.62 min, \(t_R\) (3, minor enantiomer, minor diastereomer) = 17.65 min, \(t_R\) (4, minor enantiomer, major diastereomer) = 23.47 min.

(3aR,6R,6aR)-6a-(2-Fluorophenyl)-6-hydroxy-3-methyl-4,5,6,6a-tetrahydropentalen-1(3aH)-one (2g).

General procedure was followed on a 0.187 mmol scale. The solution was stirred at -10 °C for 16 h, and then allowed to warm to RT and stirred for another 8 h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (31 mg, 0.126 mmol, 67%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.64\) (td, \(J = 8.0, 1.8\) Hz, 1H), \(7.35 – 7.20\) (m, 1H), \(7.15\) (td, \(J = 7.6, 1.4\) Hz, 1H), \(7.03\) (ddd, \(J = 12.2, 8.1, 1.4\) Hz, 1H), \(4.80 – 4.53\) (m, 1H), \(3.92\) (d, \(J = 7.8\) Hz, 1H), \(3.40\) (d, \(J = 9.3\) Hz, 1H), \(2.11\) (t, \(J = 1.0\) Hz, 3H), \(2.13 – 2.05\) (m, 1H), \(2.04 – 1.94\) (m, 1H), \(1.75\) (dd, \(J = 13.1, 6.4\) Hz, 1H), \(1.52 – 1.38\) (m, 1H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 211.0, 182.5\) (d, \(J = 1.4\) Hz), \(161.5\) (d, \(J = 246.7\) Hz), \(131.1\) (d, \(J = 1.6\) Hz), \(129.5\) (d, \(J = 4.3\) Hz), \(129.0\) (d, \(J = 8.8\) Hz), \(127.7\) (d, \(J = 11.8\) Hz), \(124.4\) (d, \(J = 3.3\) Hz), \(116.3\) (d, \(J = 22.8\) Hz), \(78.2\) (d, \(J = 1.8\) Hz), \(60.8\) (d, \(J = 2.8\) Hz), \(56.9\) (d, \(J = 4.7\) Hz), \(31.5, 24.0\) (d, \(J = 1.0\) Hz), 18.0.

IR (neat) 3463, 2958, 1678, 1621, 1490, 1450, 1377, 1298, 1277, 1227, 1203, 1109, 1059, 1038, 923, 858, 807, 759,
663, 599, 543, 464 cm\(^{-1}\). **HRMS (MALDI):** m/z calcd for C\(_{15}H_{15}FNaO\_2\) [M+Na]\(^+\) 269.0948, found 269.0948. \([\alpha]_D^{26} = -53.7\) (c = 1.0, CHCl\(_3\)). **SFC** Daicel Chiralcel OJ-H, 3% MeOH, 2.0 mL/min., 25 °C, 86% ee (t\(_R\) 1, major enantiomer, major diastereomer) = 5.72 min, t\(_R\) 2, minor enantiomer, major diastereomer) = 6.35 min.

\((3aR,6R,6aR)-6\)-Hydroxy-3-methyl-6a-(naphthalen-2-yl)-4,5,6,6a-tetrahydropentalen-1(3aH)-one (2h).

General procedure was followed on a 0.109 mmol scale. The solution was stirred at -10 °C for 24h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (26 mg, 0.094 mmol, 86%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.96 (d, \(J = 1.8\) Hz, 1H), 7.84 – 7.80 (m, 3H), 7.51 – 7.40 (m, 3H), 6.14 (t, \(J = 1.4\) Hz, 1H), 4.58 (ddd, \(J = 11.0, 7.4, 5.7\) Hz, 1H), 4.12 (d, \(J = 7.6\) Hz, 1H), 3.37 (d, \(J = 9.6\) Hz, 1H), 2.27 (s, 3H), 2.13 (ddtd, \(J = 11.9, 5.7, 1.4\) Hz, 1H), 2.01 – 1.88 (m, 1H), 1.53 (tdd, \(J = 12.7, 11.2, 6.5\) Hz, 1H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 211.3, 182.5, 137.7, 133.5, 132.5, 131.5, 128.6, 128.2, 127.6, 126.4, 126.1, 125.5, 124.6, 79.3, 63.6, 58.0, 32.4, 24.2, 18.1.

IR (neat) 3459, 3055, 2956, 2927, 2871, 1677, 1599, 1506, 1450, 1432, 1377, 1329, 1293, 1247, 1215, 1187, 1137, 1102, 1087, 1059, 1018, 997, 951, 926, 886, 856, 816, 749, 666, 638, 576, 558, 528, 504, 477 cm\(^{-1}\).

**HRMS (MALDI):** m/z calcd for C\(_{19}H_{19}O\_2\) [M+H]\(^+\) 279.1380, found 279.1380. \([\alpha]_D^{26} = -206.6\) (c = 1.0, CHCl\(_3\)). **SFC** Daicel Chiralcel OJ-H, 10% MeOH, 2.0 mL/min., 25 °C, 91% ee (t\(_R\) 1, major enantiomer, major diastereomer) = 12.49 min, t\(_R\) 2, minor enantiomer, major diastereomer) = 14.41 min.

\(\text{OAc}\)

**4-((3R,3aR,6aR)-3-Hydroxy-6-methyl-4-oxo-1,2,3,3a,4,6a-hexahydropentalen-3a-yl)phenyl} acetate (2i).

General procedure was followed on a 0.107 mmol scale. The solution was stirred at -10 °C for 16h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 4:1 to 2:1). The title compound was isolated as clear, colorless oil (22 mg, 0.077 mmol, 72% over two steps (see 250i).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.53 – 7.34 (m, 2H), 7.12 – 6.96 (m, 2H), 6.06 (s, 1H), 4.45 – 4.34 (m, 1H), 4.02 (d, \(J = 7.9\) Hz, 1H), 3.25 (d, \(J = 9.2\) Hz, 6H), 2.28 (s, 3H), 2.12 – 2.01 (m, 8H), 1.99 – 1.81 (m, 1H), 1.76 – 1.69 (m, 1H), 1.52 – 1.39 (m, 1H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 211.1, 182.5, 169.7, 149.7, 138.0, 131.2, 127.7, 121.9, 79.4, 62.9, 57.9, 32.3, 24.1, 21.3, 18.1.

IR (neat) 3465, 2958, 2874, 1754, 1679, 1679, 1618, 1508, 1434, 1411, 1371, 1297, 1200, 1171, 1135, 1118, 1102, 1089, 1054, 1019, 951, 926, 846, 799, 745, 716,
684, 619, 610, 595, 575, 528 cm\(^{-1}\). **HRMS (MALDI):** m/z calcd for C\(_{17}H_{19}O_4\) [M+H]\(^+\) 287.1278, found 287.1278. \([\alpha]_D^{26} = -135.7\) (c = 1.0, CHCl\(_3\)). **SFC** Daicel Chiralcel OJ-H, 2% MeOH, 2.0 mL/min., 25 °C, 92\% ee (t\(_R\) 1, major enantiomer, major diastereomer) = 17.08 min, t\(_R\) 2, minor enantiomer, major diastereomer) = 20.53 min).

**tert-Butyl acetyl(4-((3aR,6aR)-3-hydroxy-6-methyl-4-oxo-1,2,3,3a,4,6a-hexahydropentalen-3a-yl)phenyl) carbamate (2j).** General procedure was followed on a 0.105 mmol scale. The solution was stirred at -10 °C for 16h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 4:1 to 2:1). The title compound was isolated as clear, colorless oil (30 mg, 0.078 mmol, 74\%).

\(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.51 – 7.45 (m, 2H), 7.09 – 7.04 (m, 2H), 6.09 (s, 1H), 4.45 (m, 1H), 4.06 (d, \(J = 7.8\) Hz, 1H), 3.30 (d, \(J = 9.5\) Hz, 1H), 2.58 (s, 3H), 2.26 (s, 3H), 2.15 – 2.06 (m, 1H), 1.99 – 1.85 (m, 1H), 1.75 (ddt, \(J = 13.3, 6.5, 1.5\) Hz, 1H), 1.57 – 1.44 (m, 1H), 1.40 (s, 9H).

\(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 210.9, 182.5, 173.1, 152.9, 140.1, 137.8, 131.3, 128.5, 127.3, 83.6, 79.4, 63.1, 57.9, 32.3, 28.0, 26.7, 24.2, 18.1. IR (neat) 3472, 2976, 1737, 1704, 1619, 1513, 1414, 1395, 1371, 1340, 1275, 1255, 1157, 1098, 1055, 1016, 923, 849, 774, 743, 612, 544 cm\(^{-1}\). **HRMS (MALDI):** m/z calcd for C\(_{22}H_{28}NO_5\) [M+H]\(^+\) 386.1962, found 386.1963. \([\alpha]_D^{26} = -101.1\) (c = 1.0, CHCl\(_3\)). **SFC** (of the corresponding 4-bromophenyl-carbamate) Daicel Chiralcel OJ-H, 1% MeOH, 2.0 mL/min., 25 °C, 93\% ee (t\(_R\) 1, major enantiomer, major diastereomer) = 11.68 min, t\(_R\) 2, minor enantiomer, major diastereomer) = 12.83 min.

**tert-Butyl acetyl(4-((3aR,6aR)-3-hydroxy-6-methyl-4-oxo-1,2,3,3a,4,6a-hexahydropentalen-3a-yl)phenyl) carbamate (2j).** General procedure was followed on a 0.105 mmol scale. The solution was stirred at -10 °C for 16h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 4:1 to 2:1). The title compound was isolated as clear, colorless oil (30 mg, 0.078 mmol, 74\%).

\(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.51 – 7.45 (m, 2H), 7.09 – 7.04 (m, 2H), 6.09 (s, 1H), 4.45 (m, 1H), 4.06 (d, \(J = 7.8\) Hz, 1H), 3.30 (d, \(J = 9.5\) Hz, 1H), 2.58 (s, 3H), 2.26 (s, 3H), 2.15 – 2.06 (m, 1H), 1.99 – 1.85 (m, 1H), 1.75 (ddt, \(J = 13.3, 6.5, 1.5\) Hz, 1H), 1.57 – 1.44 (m, 1H), 1.40 (s, 9H).

\(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 210.9, 182.5, 173.1, 152.9, 140.1, 137.8, 131.3, 128.5, 127.3, 83.6, 79.4, 63.1, 57.9, 32.3, 28.0, 26.7, 24.2, 18.1. IR (neat) 3472, 2976, 1737, 1704, 1619, 1513, 1414, 1395, 1371, 1340, 1275, 1255, 1157, 1098, 1055, 1016, 923, 849, 774, 743, 612, 544 cm\(^{-1}\). **HRMS (MALDI):** m/z calcd for C\(_{22}H_{28}NO_5\) [M+H]\(^+\) 386.1962, found 386.1963. \([\alpha]_D^{26} = -101.1\) (c = 1.0, CHCl\(_3\)). **SFC** (of the corresponding 4-bromophenyl-carbamate) Daicel Chiralcel OJ-H, 1% MeOH, 2.0 mL/min., 25 °C, 93\% ee (t\(_R\) 1, major enantiomer, major diastereomer) = 11.68 min, t\(_R\) 2, minor enantiomer, major diastereomer) = 12.83 min.

**(3aR,6aS)-6-Hydroxy-3,6a-dimethyl-4,5,6,6a-tetrahydropentalen-1(3aH)-one (2k).** General procedure was followed on a 0.125 mmol scale. The solution was stirred at -10 °C for 24h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (13 mg, 0.078 mmol, 63%).
**H NMR** (400 MHz, CDCl₃) Major Diastereomer: δ 5.91 (s, 1H), 3.90 – 3.73 (m, 1H), 3.33 (s, 1H), 2.71 – 2.66 (m, 1H), 2.12 (t, J = 1.1 Hz, 3H), 1.96 – 1.89 (m, 1H), 1.74 – 1.67 (m, 1H), 1.53 – 1.44 (m, 1H), 1.42 – 1.30 (m, 1H), 1.25 (s, 3H). Minor Diastereomer: 5.81 (s, 1H), 4.13 – 3.96 (m, 1H), 2.75 (d, J = 10.5 Hz, 1H), 2.22 – 2.13 (m, 1H), 2.10 (t, J = 1.1 Hz, 3H), 1.85 – 1.75 (m, 1H), 1.66 – 1.59 (m, 1H), 1.57 – 1.52 (m, 1H), 1.18 (s, 3H).

**13C NMR** (101 MHz, CDCl₃) Major diastereomer: δ 214.1, 181.2, 130.2, 79.6, 56.5, 42.9, 32.8, 32.7, 20.9, 17.9. Minor diastereomer: δ 212.9, 179.6, 128.6, 75.6, 61.4, 56.6, 32.8, 18.0, 17.9, 16.7. IR (neat) 3443, 2828, 2856, 1740, 1620, 1448, 1373, 1237, 1066, 967, 859, 604, 534, 496 cm⁻¹.

HRMS (MALDI): m/z calcd for C₁₀H₁₄NaO₂ [M+Na]⁺ 189.0886, found 189.0887. [α]²⁶_D = +4.7 (c = 0.33, CHCl₃) SFC Daicel Chiralcel OJ-H, 3% MeOH, 2.0 mL/min., 25 °C, 90% ee (tᵣ (1, major enantiomer, minor diastereomer) = 1.38 min, tᵣ (2, minor enantiomer, minor diastereomer) = 1.53 min, tᵣ (3, major enantiomer, major diastereomer) = 1.78 min, tᵣ (4, minor enantiomer, major diastereomer) = 2.25 min).

(3aR,6R,6aS)-6-Hydroxy-6a-isopropyl-3-methyl-4,5,6,6a-tetrahydropentalen-1(3aH)-one (2l). General procedure was followed on a 0.118 mmol scale. The solution was stirred at -10 °C for 16h, then warmed to RT and stirred for 8h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (13 mg, 0.067 mmol, 57%).

**H NMR** (400 MHz, CDCl₃) δ 5.95 (t, J = 1.4 Hz, 1H), 4.14 – 3.99 (m, 1H), 3.58 (d, J = 6.5 Hz, 1H), 2.87 – 2.69 (m, 1H), 2.15 – 2.07 (m, 4H), 1.96 – 1.87 (m, 1H), 1.73 – 1.60 (m, 2H), 1.38 – 1.26 (m, 1H), 1.21 – 1.09 (m, 1H), 0.93 (d, J = 6.8 Hz, 3H), 0.88 (d, J = 6.9 Hz, 3H). **13C NMR** (101 MHz, CDCl₃) δ 214.9, 182.2, 132.4, 75.9, 63.8, 51.6, 32.5, 31.4, 24.3, 18.7, 18.2, 17.8. IR (neat) 3472, 2962, 2874, 1984, 1744, 1677, 1620, 1464, 1436, 1372, 1299, 1240, 1208, 1085, 921, 893, 852, 744, 520, 464 cm⁻¹. HRMS (MALDI): m/z calcd for C₁₂H₁₈NaO₂ [M+Na]⁺ 217.1199, found 217.1199. [α]²⁶_D = +4.7 (c = 1.0, CHCl₃) SFC Daicel Chiralcel OJ-H, 3% MeOH, 2.0 mL/min., 25 °C, 90% ee (tᵣ (1, minor enantiomer, minor diastereomer) = 2.87 min, tᵣ (2, major enantiomer, minor diastereomer) = 3.13 min, tᵣ (3, major enantiomer, major diastereomer) = 3.57 min, tᵣ (4, minor enantiomer, major diastereomer) = 3.97 min).

(3aR,6R,6aS)-6a-(2-(Benzyloxy)ethyl)-6-hydroxy-3-methyl-4,5,6,6a-tetrahydropentalen-1(3aH)-one (251m). General procedure was followed on a 0.305 mmol scale. The solution was stirred at -10 °C for 24h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient...
from 6:1 to 4:1). The two diastereomers of the title compound could be separated and isolated to give 2m (51 mg, 0.178 mmol, 59%) and 2m' (12 mg, 0.042 mmol, 14%).

\[\text{\textsuperscript{1}H NMR (400 MHz, CD}_{2}\text{Cl}_{2}) \delta 7.37 – 7.31 (m, 2H), 7.30 – 7.24 (m, 3H), 5.90 (t, J = 1.4 Hz, 1H), 4.39 (d, J = 1.9 Hz, 2H), 3.84 (dd, J = 10.5, 5.6 Hz, 1H), 3.62 – 3.46 (m, 1H), 3.46 – 3.34 (m, 1H), 3.00 (d, J = 9.2 Hz, 2H), 2.19 (ddd, J = 14.2, 6.9, 5.8 Hz, 1H), 2.06 (t, J = 1.1 Hz, 3H), 1.89 – 1.79 (m, 2H), 1.78 – 1.65 (m, 1H), 1.60 (ddt, J = 13.2, 6.6, 2.0 Hz, 1H), 1.37 – 1.14 (m, 1H).\]

\[\text{\textsuperscript{13}C NMR (101 MHz, CD}_{2}\text{Cl}_{2}) \delta 213.7, 182.5, 138.9, 131.5, 128.6, 128.0, 127.9, 79.0, 73.4, 67.7, 59.1, 54.5, 35.0, 32.1, 24.3, 17.9. IR (neat) 3461, 3063, 3031, 2937, 2909, 2868, 1956, 1677, 1617, 1497, 1454, 1433, 1377, 1366, 1256, 1199, 1091, 1028, 1003, 948, 916, 882, 858, 734, 699, 666, 607, 581, 532 cm\textsuperscript{-1}. \text{HRMS (MALDI): m/z calcd for C}_{18}\text{H}_{22}\text{NaO}_{3} [M+Na]^+ 309.1461, found 309.1461. [\alpha]_{D}^{25} = -36.3 (c=1.0, CHCl\textsubscript{3}). \text{SFC Daicel Chiralcel OJ-H, 2% MeOH, 2.0 mL/min., 25 °C, 95% ee (t\textsubscript{R} (1, major enantiomer, major diastereomer) = 17.77 min, t\textsubscript{R} (2, minor enantiomer, major diastereomer) = 25.69 min).}\]

(3aR,6S,6aS)-6a-(2-(Benzyloxy)ethyl)-6-hydroxy-3-methyl-4,5,6,6a-tetrahydropentalen-1(3aH)-one (2m').

\[\text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 7.38 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 5.77 (t, J = 1.3 Hz, 1H), 4.65 (d, J = 11.6 Hz, 1H), 4.51 (d, J = 11.6 Hz, 1H), 4.20 (t, J = 2.9 Hz, 1H), 4.06 (ddd, J = 10.6, 9.5, 2.1 Hz, 1H), 3.81 (t, J = 2.3 Hz, 1H), 3.48 (ddd, J = 9.4, 4.6, 3.2 Hz, 1H), 2.73 (d, J = 9.8 Hz, 1H), 2.22 (ddd, J = 14.4, 9.4, 7.6, 3.4 Hz, 2H), 2.13 – 2.05 (m, 3H), 1.75 (dd, J = 13.4, 6.2 Hz, 1H), 1.65 (ddd, J = 15.2, 4.7, 2.1 Hz, 1H), 1.54 (dd, J = 12.7, 7.0 Hz, 1H), 1.47 – 1.33 (m, 1H). \text{\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \delta 211.9, 179.4, 137.7, 129.2, 128.6, 128.0, 127.9, 74.6, 73.7, 66.2, 64.8, 56.9, 32.1, 31.6, 25.3, 18.2. IR (neat) 3438, 3064, 3031, 2942, 2866, 1688, 1618, 1497, 1454, 1435, 1376, 1365, 1330, 1305, 1250, 1186, 1165, 1089, 1073, 1029, 989, 959, 943, 921, 860, 826, 738, 698, 637, 609, 566 cm\textsuperscript{-1}. [\alpha]_{D}^{26} = -11.7 (c = 1.0, CHCl\textsubscript{3}).}\]
5. Synthesis of Triquinane 12

Reagents and Conditions: a) (i) n-BuLi (1.05 equiv), 0 °C, THF, 60 min; then tert-butyl(3-iodopropoxy)dimethylsilane (1.05 equiv), –78 °C to RT, 20h (ii) O₃, CH₂Cl₂, –78 °C, 10min, then PPh₃ (1.3 equiv), RT, 18h, 70% over two steps; b) (i) LDA (1.1 equiv), –78 °C, 30 min; then TMSCl (1.1 equiv), –78 °C to –40 °C; (ii) MeLi (1.00 equiv), 0 °C, 30min; then Comin’s Reagent (1.3 equiv), –78 °C to RT, 2h, 80% over two steps; (iii) (S)-3-butyn-2-ol (1.3 equiv), PdCl₂(PPh₃)₂ (5 mol%), Cul (10 mol%), Et₃N/THF (2:1), 71%; c) Ac₂O (1.1 equiv), DMAP (0.1 equiv), pyridine (1.5 equiv), CH₂Cl₂, 93%; d) TBAF (2 equiv), THF, 94%; e) DMP (2.0 equiv), t-BuOH (2.0 equiv), CH₂Cl₂, 84%; f) Au(MeCN)(JohnPhos)SbF₆ (5 mol%), THF, 0.2% H₂O, –10 °C, 24h, 60%.
(S)-2-[(3-[(tert-Butyldimethylsilyl)oxy]propyl)cyclopentanone (S12). To a solution of S11 (2.00 g, 10.2 mmol, 1.0 equiv) in THF (51 ml) at 0 °C was added n-BuLi (1.6 M in hexanes, 6.69 ml, 10.7 mmol, 1.05 equiv) and stirred for 60 min. The solution was then cooled to −78 °C and a solution of tert-butyl(3-iodopropoxyl)dimethylsilane (3.21 g, 10.7 mmol, 1.05 equiv) in THF (10 ml) was added dropwise and then slowly warmed to RT. The reaction mixture was quenched by the addition of sat. aq. NH4Cl. EtOAc was added to the mixture and the phases separated. The aqueous phase was extracted with EtOAc (3x). The combined organic phases were dried over MgSO4, filtered, and concentrated in vacuo. Purification by flash column chromatography provided the alkylated hydrazone (3.70 g, 10.0 mmol, 98%) as a yellow oil.

1H NMR (400 MHz, CDCl3) δ 3.69 – 3.55 (m, 2H), 3.46 (d, J = 5.2 Hz, 1H), 3.34 (s, 3H), 3.30 – 3.16 (m, 3H), 2.40 (q, J = 9.0 Hz, 3H), 2.23 – 2.08 (m, 1H), 1.95 (dd, J = 11.9, 7.6, 5.2 Hz, 2H), 1.88 – 1.74 (m, 3H), 1.73 – 1.47 (m, 6H), 1.44 – 1.20 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H).

The alkylated hydrazone (3.70 g, 10.0 mmol, 1 equiv) was dissolved in CH2Cl2 (100 ml) and cooled to −78 °C. At that temperature, ozone was bubbled through the reaction mixture until the yellow reaction mixture turned green (TLC control). After bubbling through O2 for 5 min, PPh3 (7.90 g, 30.1 mmol, 3 equiv) was added and the mixture was allowed to warm to RT and stirred overnight. The reaction mixture was reduced to about 15ml and then pentane (100 ml) was added. The formed suspension was filtered through celite and concentrated in vacuo. Flash column chromatography (pentane to pentane–Et2O 25:1) furnished cyclopentone S12 (1.83 g, 7.14 mmol, 71%) as a colorless oil.

1H NMR (400 MHz, CD2Cl2) δ 3.61 (td, J = 6.4, 1.2 Hz, 2H), 2.31 – 2.15 (m, 2H), 2.13 – 1.92 (m, 3H), 1.84 – 1.67 (m, 2H), 1.60 – 1.44 (m, 3H), 1.35 – 1.20 (m, 1H), 0.89 (s, 9H), 0.04 (s, 6H). 13C NMR (101 MHz, CD2Cl2) δ 221.1, 63.5, 49.2, 38.5, 31.2, 30.1, 26.6, 26.1, 21.1, 18.6, -5.2. IR (neat) 2954, 2929, 2884, 2857, 1739, 1721, 1463, 1407, 1388, 1361, 1333, 1305, 1253, 1215, 1200, 1154, 1096, 1038, 1006, 955, 938, 887, 834, 813, 774, 72, 680, 662, 572, 544, 515 cm⁻¹. HRMS (MALDI): m/z calcd for C18H32NaO3Si [M+Na]+ 279.1751, found 279.1748. [α]D26 = −61.9 (c = 1.0, CH2Cl2).

(S)-4-[(S)-5-(3-[(tert-Butyldimethylsilyl)oxy]propyl)cyclopent-1-en-1-yl]but-3-yn-2-ol (S13). To a freshly prepared solution of LDA (0.2 M, 230 mg, 2.15 mmol, 1.1 equiv) was added a solution of S12 (500 mg, 2.15 mmol, 1.0 equiv) and stirred for 30 min. After that time, TMSCl (0.272 ml, 2.15 mmol, 1.1 equiv) was added dropwise and slowly warmed to −40 °C over 30 min. The reaction was quenched with Sorensen Buffer (pH = 7.0). Et2O was added to the mixture and the phases separated. The aqueous phase was

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extracted with Et<sub>2</sub>O (3x). The combined organic phases were dried over K<sub>2</sub>CO<sub>3</sub>, filtered, and concentrated in vacuo.

The crude mixture was dissolved in THF and at 0 °C MeLi (1.6 M in hexanes, 1.27 ml, 2.04 mmol, 1.1 equiv) was added dropwise and stirred for 30 min. The solution as then cooled to –78 °C. At that temperature, Comin’s reagent (948 mg, 2.41 mmol, 1.3 equiv) was added in one portion and the cooling bath was removed. After 60min, the reaction was quenched with sat. aq. NaHCO<sub>3</sub>. Et<sub>2</sub>O was added to the mixture and the phases separated. The aqueous phase was extracted with Et<sub>2</sub>O (3x). The combined organic phases were dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. Flash column chromatography (hexane/EtOAc 10:1) furnished the vinyl triflate as colorless oil (600 mg, 1.54 mmol, 80%).

To a degassed solution of the crude vinyl triflate (240 mg,0.62 mmol, 1.0 equiv) and (R)-but-3-yn-2-ol (0.06 ml, 0.74 mmol, 1.2 equiv) in NEt<sub>3</sub>/THF (1:1, 0.15 M) was added PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (21.7 mg, 0.03 mmol, 0.05 equiv) and CuI (11.8 mg, 0.06 mmol, 0.1 equiv) and the resulting mixture was stirred at RT for 2 h before it was filtered through a short plug of silica gel eluting with EtOAc and concentrated in vacuo. Purification by column chromatography (hexane/EtOAc 5:1) afforded enyne S13 (135 mg, 0.44 mmol, 71%).

1<sup>H</sup> NMR (400 MHz, CDCl<sub>3</sub>) δ 6.03 (q, J = 2.4 Hz, 1H), 4.66 (q, J = 6.6 Hz, 1H), 3.63 (t, J = 6.6 Hz, 2H), 2.74 – 2.59 (m, 1H), 2.45 – 2.28 (m, 2H), 2.15 – 2.02 (m, 1H), 1.82 – 1.69 (m, 1H), 1.66 – 1.49 (m, 3H), 1.47 (d, J = 6.6 Hz, 3H), 1.31 – 1.17 (m, 1H), 0.90 (s, 9H), 0.06 (s, 6H). 13<sup>C</sup> NMR (101 MHz, CDCl<sub>3</sub>) δ 137.9, 128.5, 93.2, 81.1, 63.6, 59.0, 47.8, 32.1, 30.7, 30.5, 29.8, 26.1, 24.6, 18.5, -5.1. IR (neat) 3357, 2953, 2930, 2893, 2857, 1472, 1388, 1361, 1327, 1255, 1102, 1039, 1006, 940, 910, 835, 775, 663 cm<sup>-1</sup>. HRMS (MALDI): m/z calcd for C<sub>18</sub>H<sub>32</sub>NaO<sub>3</sub>Si [M+Na]<sup>+</sup> 331.2064, found 331.2064. [α]<sub>D</sub><sup>26</sup> = −7.3 (c = 1.0, CHCl<sub>3</sub>).

(S)-4-((S)-5-(3-((tert-Butyldimethylsilyl)oxy)propyl)cyclopent-1-en-1-yl)but-3-yn-2-yl acetate (S14). To a stirred solution of enyne S13 (135 mg, 0.44 mmol, 1.0 equiv) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (4.5 ml) at ambient temperature was added pyridine (0.177 ml, 2.19 mmol, 5.0 equiv), DMAP (10.7 mg, 0.09 mmol, 0.2 equiv), and Ac<sub>2</sub>O (0.062 ml, 0.66 mmol, 1.5 equiv). The resulting solution was stirred for 1h before it was quenched with H<sub>2</sub>O. The aqueous phase was extracted with Et<sub>2</sub>O (3x). The combined organic phases were washed with sat. aq. CuSO<sub>4</sub> solution, H<sub>2</sub>O (1x), and brine, dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. Purification by flash column chromatography provided propargyl acetate S14 (142 mg, 0.41 mmol, 93%) as a colorless oil.

1<sup>H</sup> NMR (400 MHz, CDCl<sub>3</sub>) δ 6.07 (q, J = 2.5 Hz, 1H), 5.60 (q, J = 6.7 Hz, 1H), 3.62 (t, J = 6.6 Hz, 2H), 2.73 – 2.60 (m, 0H), 2.41 – 2.31 (m, 2H), 2.14 – 2.03 (m, 4H), 1.76 (ddddd, J = 12.9, 10.2, 6.1, 4.1 Hz, 1H), 1.62 – 1.44 (m, 6H), 1.31 – 1.17 (m, 1H), 0.90 (s, 9H), 0.05 (s, 6H). 13<sup>C</sup> NMR (101 MHz, CDCl<sub>3</sub>) δ 170.1, 138.8, 128.3, 89.5, 81.7, 63.5, 61.1, 47.8, 32.1, 30.7, 30.5, 29.7, 26.1, 21.8, 21.3, 18.5, -5.1. IR (neat) 2952, 2930, 2857, 2227, 1746, 1472, 1463, 1371, 1340, 1308, 1230, 1097, 1033, 1009, 953, 939, 835, 813, 775, 713,
(S)-4-((S)-5-(3-Hydroxypropyl)cyclopent-1-en-1-yl)but-3-yn-2-yl acetate (S15). To a stirred solution of propargyl acetate S14 (140 mg, 0.40 mmol, 1.0 equiv) in dry THF (3.3 ml) in 0 °C was added TBAF (1.0 M in THF, 0.799 ml, 0.80 mmol, 2.0 equiv). After the addition, the solution was allowed to warm to ambient temperature and stirred for another 90 min. The mixture was quenched by the addition of sat. aq. NaHCO$_3$ solution. EtOAc was added to the mixture and the phases separated. The aqueous phase was extracted with EtOAc (3x). The combined organic phases were dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography provided primary alcohol S15 (89 mg, 0.38 mmol, 94%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.08 (q, $J = 2.6$ Hz, 1H), 5.56 (q, $J = 6.7$ Hz, 1H), 3.66 (t, $J = 6.5$ Hz, 2H), 2.83 – 2.63 (m, 0H), 2.43 – 2.31 (m, 2H), 2.16 – 2.04 (m, 4H), 1.80 – 1.69 (m, 1H), 1.67 – 1.58 (m, 2H), 1.51 (d, $J = 6.7$ Hz, 4H), 1.40 – 1.27 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.3, 139.0, 128.0, 89.7, 81.7, 63.3, 61.2, 47.6, 32.1, 30.6, 30.3, 29.8, 21.6, 21.3. IR (neat) 3420, 3054, 2989, 2937, 2855, 2226, 2099, 1770, 1743, 1619, 1450, 1372, 1309, 1232, 1076, 1057, 1032, 956, 844, 810, 612, 533, 483 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{14}$H$_{20}$NaO$_3$ [M+Na]$^+$ 259.1305, found 259.1305. $[^{[\alpha]}_D] = -134.77$ (c = 1.0, CHCl$_3$).

(S)-4-((S)-5-(3-Oxopropyl)cyclopent-1-en-1-yl)but-3-yn-2-yl acetate (12). To a solution of S15 (85 mg, 0.36 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (3.6 ml) at RT was added t-BuOH (68 μl, 0.72 mmol, 2.0 equiv) and DMP (305 mg, 0.72 mmol, 2.0 equiv). The mixture was stirred for 15 min and then quenched by the addition of sat. aq. Na$_2$S$_2$O$_3$. The mixture was poured on sat. aq. NaHCO$_3$ solution and CH$_2$Cl$_2$ was added. The phases were separated and the aqueous phase was extracted with CH$_2$Cl$_2$ (3x), dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography provided aldehyde 12 (71 mg, 0.30 mmol, 84%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.79 (t, $J = 1.8$ Hz, 1H), 6.10 (q, $J = 2.5$ Hz, 1H), 5.57 (q, $J = 6.7$ Hz, 1H), 2.78 – 2.67 (m, 1H), 2.49 (td, $J = 7.8$, 1.8 Hz, 2H), 2.42 – 2.33 (m, 2H), 2.16 – 2.05 (m, 4H), 2.04 – 1.94 (m, 1H), 1.70 – 1.61 (m, 1H), 1.50 (d, $J = 6.7$ Hz, 3H), 1.48 – 1.43 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 202.7, 170.1, 139.6, 127.6, 90.1, 81.3, 61.0, 47.1, 41.7, 32.1, 29.6, 26.4, 21.7, 21.3. IR (neat) 2989, 2937, 2947, 2723, 2226, 2099, 1740, 1724, 1448, 1412, 1371, 1339, 1307, 1229, 1150, 1088, 1076, 1031, 954, 887, 843, 656, 611, 532, 497, 480 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{14}$H$_{19}$O$_3$ [M+H]$^+$ 235.1329, found 235.1328. $[^{[\alpha]}_D] = -117.6$ (c = 1.0, CHCl$_3$).
(3\textit{aS},8\textit{S},8\textit{aS})-8-Hydroxy-3-methyl-4,5,5\textit{a},6,7,8-hexahydrocyclopenta[c]pentalen-1(3\textit{a}H)-one (13). Enyne \textit{12} (53 mg, 0.23 mmol, 1.0 equiv) was dissolved in THF (4.5 ml) and \textit{H}_2\textit{O} (9.0 \mu l) was added at ambient temperature. \textit{3} (8.73 mg, 0.011 mmol, 0.05 equiv) was added in one portion and stirred for 16h. Then the reaction mixture was filtered through a short pad of silica gel washing with EtOAc, concentrated in vacuo, and subsequently subjected to silica gel flash chromatography to afford triquinine \textit{13} (26 mg, 0.135 mmol, 60%) as a colorless oil.

\textbf{\textit{1H NMR} (400 MHz, CDCl\textsubscript{3})} \delta 6.04 – 5.75 (m, 0H), 4.70 – 4.38 (m, 1H), 3.33 (d, \textit{J} = 8.9 Hz, 0H), 2.48 – 2.32 (m, 1H), 2.13 – 2.08 (m, 3H), 2.06 – 1.99 (m, 1H), 1.96 – 1.90 (m, 1H), 1.88 – 1.80 (m, 1H), 1.75 (ddt, \textit{J} = 13.1, 6.6, 2.1 Hz, 1H), 1.68 – 1.54 (m, 3H), 1.50 (ddt, \textit{J} = 12.9, 6.8, 2.1 Hz, 1H), 1.39 – 1.31 (m, 1H). \textbf{\textit{13C NMR} (101 MHz, CDCl\textsubscript{3})} \delta 212.8, 180.4, 130.8, 76.9, 71.7, 51.2, 46.6, 35.3, 32.1, 28.2, 27.2, 17.8. \textbf{IR (neat)} 3405, 3067, 2946, 2867, 1678, 1615, 1477, 1377, 1305, 1285, 1237, 1197, 1169, 1099, 1084, 1051, 1038, 1021, 979, 960, 925, 854, 810, 762, 650, 626, 603, 586, 571, 512 cm\textsuperscript{-1}. \textbf{HRMS (MALDI)}: m/z calcd for C_{12}H_{16}NaO_2 [M+Na]\textsuperscript{+} 215.1043, found 215.1042. \([\alpha]_{D}^{26} = +32.2 \text{ (c = 1.0, CHCl}_3)\).

Reagents and Conditions: a) PhLi (1.0 equiv), LiBr (2.0 equiv), S16 (1.0 equiv), –78°C; then PhLi (1.1 equiv), then S17 (1.0 equiv), 10 min, then PhLi (1.1 equiv), then –78°C to RT; then 1,2-diiodoethane (1.2 equiv), –78°C to RT; 47%, E/Z = 6:1; b) (R)-3-butyn-2-ol (1.3 equiv), PdCl₂(PPh₃)₂ (5 mol%), CuI (10 mol%), Et₃N/THF (2:1), 63%, E/Z = 6:1; c) Ac₂O (1.1 equiv), DMAP (0.1 equiv), pyridine (1.5 equiv), CH₂Cl₂, 82%, E/Z = 6:1; d) 9-BBN (1.8 equiv), THF, 0 °C to RT, then H₂O, NaBO₃·4H₂O (30.0 equiv), RT, 87%, E/Z = 6:1; e) DMP (2.0 equiv), t-BuOH (2.0 equiv), CH₂Cl₂, 89%, E/Z = 6:1.
(R,E)-5-Benzylidenenon-8-en-3-yn-2-ol (S19). To a solution of anhydrous LiBr (3.42 g, 39.4 mmol, 2.0 equiv) in dry THF (90 ml) at ambient temperature was added S16\(^\text{11}\) (8.10 g, 19.7 mmol, 1.0 equiv) and stirred for 10 min. The resulting suspension was cooled to −78°C and PhLi (1.9 M in Bu\(_2\)O, 10.37 ml, 19.7 mmol, 1.0 equiv) was added dropwise. The solution was allowed to warm to RT over 15 min and then stirred for another 30 min at that temperature. Then the solution was recooled to −78°C and benzaldehyde (2.0 ml, 19.7 mmol, 1.0 equiv) in THF (5 ml) was added dropwise. After 10 min, PhLi (1.9 M in Bu\(_2\)O, 11.40 ml, 21.7 mmol 1.1 equiv) was added dropwise and stirred for 30 min at −78°C, then allowed to warm to RT over 15 min. After 30 min at ambient temperature, the mixture was cooled to −78°C and transferred via cannula to a solution of 1,2-diiodoethane (1.0 M in THF, 1.2 equiv) at −78°C and stirred for 30 min. Then the solution was allowed to warm to RT and stirred for another hour. The resulting mixture was quenched by the addition of sat. aq. Na\(_2\)S\(_2\)O\(_3\) solution and stirred vigorously for 5 min. The phases were separated and the aqueous phase was extracted with Et\(_2\)O (3x). The combined organic phases were washed with brine, dried over MgSO\(_4\), filtered, and concentrated in vacuo. Purification by flash column chromatography (hexane/EtOAc 40:1) afforded the corresponding vinyl iodide S18 (2.60 g, 9.2 mmol, 47%) as a mixture of diastereomers (E/Z = 6:1) and a yellow oil, which contained impurities unseparable by silica gel chromatography and was used in the following step directly.

To a degassed solution of the vinyl iodide (584 mg, 2.06 mmol) and (R)-but-3-yn-2-ol (0.18 ml, 1.1 equiv) in NEt\(_3\)/THF (2:1, 0.15 M) was added PdCl\(_2\)(PPh\(_3\))\(_2\) (72 mg, 0.10 mmol, 0.05 equiv) and CuI (39 mg, 0.21 mmol, 0.1 equiv) and the resulting mixture was stirred at RT for 2 h before it was filtered through a short plug of silica gel eluting with EtOAc and concentrated in vacuo. Purification by column chromatography (hexane/EtOAc 8:1) afforded enyne S19 (310 mg, 1.37 mmol, 67%, E/Z = 6:1) as an orange oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37 – 7.30 (m, 2H), 7.28 – 7.22 (m, 3H), 6.87 (s, 1H), 5.93 – 5.73 (m, 1H), 5.09 – 5.02 (m, 1H), 5.01 – 4.94 (m, 1H), 2.51 – 2.44 (m, 2H), 2.41 – 2.36 (m, 2H), 1.53 (d, \(J = 6.6\) Hz, 4H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 137.8, 136.7, 136.6, 128.9, 128.5, 127.5, 124.1, 115.2, 91.3, 86.2, 59.1, 32.6, 30.8, 24.7. IR (neat) 3342, 3079, 2980, 2929, 1641, 1598, 1493, 1446, 1370, 1328, 1182, 1117, 1076, 1032, 997, 943, 916, 871, 755, 696, 634, 542, 508, 414 cm\(^{-1}\). HRMS (ESI): m/z calcd for C\(_{16}\)H\(_{18}\)NaO [M+Na]\(^+\) 249.1250, found 249.1250. \([\alpha]\)\(^{26}\) = +23.0 (c = 0.5, CHCl\(_3\)).

(R,E)-5-Benzylidenenon-8-en-3-yn-2-yl acetate (S20). To a stirred solution of propargyl alcohol S19 (250 mg, 1.11 mmol) dissolved in CH₂Cl₂ (10 ml) at ambient temperature was added pyridine (0.45 ml, 5.52 mmol, 5.0 equiv), DMAP (27.0 mg, 0.22 mmol, 0.2 equiv), and Ac₂O (0.16 ml, 1.66 mmol, 1.5 equiv). The resulting solution was stirred for 1 h before it was quenched with H₂O. The aqueous phase was extracted with Et₂O (3x). The combined organic phases were washed with sat. aq. CuSO₄ solution, H₂O (1x), and brine, dried over MgSO₄, filtered, and concentrated in vacuo. Purification by flash column chromatography (hexane/EtOAc 20:1) provided propargyl acetate S20 (260 mg, 0.97 mmol, 88%, E/Z = 6:1) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.30 (m, 2H), 7.26 – 7.21 (m, 3H), 6.88 (s, 1H), 5.60 (q, J = 6.6 Hz, 1H), 3.63 (t, J = 6.4 Hz, 2H), 2.40 (td, J = 7.4, 1.2 Hz, 2H), 2.10 (d, J = 1.4 Hz, 3H), 1.74 – 1.63 (m, 2H), 1.63 – 1.56 (m, 2H), 1.55 (d, J = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.3, 137.2, 136.5, 135.6, 128.9, 128.5, 127.5, 124.4, 87.6, 86.8, 62.8, 61.1, 32.3, 30.9, 24.6, 21.6, 21.3. IR (neat) 2928, 2855, 1742, 1641, 1493, 1446, 1371, 1339, 1262, 1075, 756, 697, 611, 510 cm⁻¹. HRMS (ESI): m/z calcd for C₁₈H₂₀NaO₂ [M+Na]+ 291.1356, found 291.1360. [α]₂⁶° = +97.1 (c = 0.5, CHCl₃).

(R,E)-5-Benzylidene-9-hydroxynon-3-yn-2-yl acetate (S21). To a solution of 9-BBN (0.5 M in THF, 2.68 ml, 1.34 mmol, 1.8 equiv) was added THF (5.4 ml) and cooled to 0 °C. A solution of S20 (200 mg, 0.75 mmol, 1.0 equiv) in THF (0.9 ml) was added dropwise. The resulting mixture was stirred at RT for 2 h. The mixture was then cooled to 0 °C and diluted with H₂O (7 ml), THF (2 ml) and sodium perborate tetrahydrate (3.44 g, 22.4 mmol, 30.0 equiv) was added. The mixture was allowed to warm up to RT and was stirred at the same temperature for 2 h. The phases were separated and the aqueous phase was extracted with EtOAc (3x). The combined organic extracts were washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. Flash chromatography (hexane/EtOAc 15:1 to 2:1) provided the desired product S21 (186 mg, 0.65 mmol, 87%, E/Z = 6:1) as a faint yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.30 (m, 2H), 7.28 – 7.21 (m, 3H), 6.88 (s, 1H), 5.60 (q, J = 6.7 Hz, 1H), 3.63 (t, J = 6.3 Hz, 2H), 2.40 (t, J = 7.9 Hz, 2H), 2.10 (s, 3H), 1.74 – 1.63 (m, 2H), 1.63 – 1.56 (m, 2H), 1.55 (d, J = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.1, 137.0, 136.4, 135.4, 128.8, 128.3, 127.4, 124.2, 87.5, 86.7, 62.7, 61.0, 32.2, 30.8, 24.5, 21.5, 21.2. IR (neat) 3424, 2988, 2936, 2865, 2217, 1739, 1597, 1492, 1446, 1371, 1338, 1308, 1230, 1197, 1157, 1061, 1030, 954, 922, 874, 845, 756, 697, 611, 510, 415
(R,E)-5-Benzylidene-9-oxonon-3-yn-2-yl acetate (14). To a solution of S21 (60 mg, 0.21 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (2.1 ml) at RT was added t-BuOH (30 µl, 0.31 mmol, 2.0 equiv) and DMP (68 mg, 0.31 mmol, 2.0 equiv). The mixture was stirred for 30 min and then quenched by the addition of sat. aq. Na$_2$S$_2$O$_3$. The mixture was poured on sat. aq. NaHCO$_3$ solution and CH$_2$Cl$_2$ was added. The phases were separated and the aqueous phase was extracted with CH$_2$Cl$_2$ (3x), dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography (hexane/EtOAc 4:1) provided aldehyde 13 (50 mg, 0.18 mmol, 84%, E/Z = 6:1) as a colorless oil.

$\text{^1H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 9.74 (t, $J$ = 1.5 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.28 – 7.20 (m, 3H), 6.91 (s, 1H), 5.61 (q, $J$ = 6.7 Hz, 1H), 2.52 – 2.37 (m, 4H), 2.10 (s, 3H), 1.98 – 1.86 (m, 2H), 1.55 (d, $J$ = 6.7 Hz, 3H).

$\text{^13C NMR}$ (101 MHz, CDCl$_3$) $\delta$ 202.2, 170.0, 137.7, 136.1, 128.7, 128.4, 127.5, 123.2, 87.8, 86.2, 60.9, 43.1, 30.3, 21.5, 21.2, 20.7. IR (neat) 2989, 2937, 2724, 1739, 1492, 1446, 1371, 1339, 1307, 1232, 1092, 1063, 1033, 955, 923, 845, 758, 698, 608, 510, 417 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{18}$H$_{22}$NaO$_3$ [M+Na]$^+$ 307.1305, found 307.1307. $\alpha_D^{26} = +107.4$ (c = 1.0, CHCl$_3$).

(4S,5R,6R)-6-Hydroxy-3-methyl-4-phenylspiro[4.4]non-2-en-1-one (15). Enyne 14 (37 mg, 0.13 mmol, 1.0 equiv) was dissolved in THF (2.6 ml) and H$_2$O (5.2 µl) was added at ambient temperature. 3 (5.0 mg, 0.0065 mmol, 0.05 equiv) was added in one portion and stirred for 2 h. Then the reaction mixture was filtered through a short pad of silica gel washing with EtOAc, concentrated in vacuo, and subsequently subjected to silica gel flash chromatography (hexane/EtOAc 2:1) to afford triquinine 15 as a single diastereomer (24 mg, 0.10 mmol, 76%) as a whit solid.

$\text{^1H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 7.36 – 7.22 (m, 4H), 6.28 – 6.02 (m, 1H), 4.25 – 4.19 (m, 2H), 2.18 – 2.07 (m, 1H), 1.99 (s, 3H), 1.79 – 1.60 (m, 2H), 1.59 – 1.46 (m, 1H), 1.28 – 1.17 (m, 1H), 1.17 – 1.08 (m, 1H). $\text{^13C NMR}$ (101 MHz, CDCl$_3$) $\delta$ 213.0, 180.4, 139.0, 131.0, 128.8, 127.3, 80.0, 65.2, 55.6, 32.9, 29.3, 19.3, 18.6. IR (neat) 3396, 3061, 3027, 2956, 2875, 1681, 1623, 1601, 1493, 1454, 1435, 1375, 1309, 1208, 1079, 1017, 880, 851, 741, 703, 627, 556, 493, 458, 417 cm$^{-1}$. HRMS (MALDI): m/z calcd for C$_{16}$H$_{20}$NaO$_3$ [M+Na]$^+$ 265.1199, found 265.1198. $\alpha_D^{26} = -124.6$ (c = 1.0, CHCl$_3$). SFC Daicel Chiralcel OJ-H, 10% MeOH, 2.0 mL/min., 25 °C, 78% ee ($t_1$ (1, major enantiomer) = 3.35 min, $t_2$ (2, minor enantiomer) = 3.91 min).
7. NMR Spectra
CDCl₃, 400 MHz

CDCl₃, 101 MHz
d.r. 87.13
CDCl₃, 400 MHz
Synthesis of Triquinane 7

CD$_2$Cl$_2$, 400 MHz

[Chemical structure diagram]
8. SFC Traces

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**Chromatogram**

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<th>#</th>
<th>Peak Name</th>
<th>CH</th>
<th>tR [min]</th>
<th>Area [µV-sec]</th>
<th>Height [µV]</th>
<th>Area%</th>
<th>Height%</th>
<th>Quantity</th>
<th>NTP</th>
<th>Resolution</th>
<th>Symmetry Factor</th>
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<tbody>
<tr>
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<td>9</td>
<td>9.827</td>
<td>1736878</td>
<td>98577</td>
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<td>90.238</td>
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<td>7120</td>
<td>4.756</td>
<td>1.675</td>
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<td>31195</td>
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<td>2.855</td>
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<td>3</td>
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<td>10734</td>
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<td>0.987</td>
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<td>17.380</td>
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<td>8175</td>
<td>N/A</td>
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### Chromatogram

**MB5-021-carbamate-c1-97 - CH9**

![Chromatogram](image1)

<table>
<thead>
<tr>
<th>#</th>
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<th>CH</th>
<th>tR [min]</th>
<th>Area [μVsec]</th>
<th>Height [μV]</th>
<th>Area%</th>
<th>Height%</th>
<th>Quantity</th>
<th>NTP</th>
<th>Resolution</th>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>9</td>
<td>7.099</td>
<td>5463500</td>
<td>457468</td>
<td>50.308</td>
<td>53.210</td>
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<td>800</td>
<td>2.558</td>
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<tr>
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<td>2</td>
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<td>7.952</td>
<td>5317620</td>
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<td>46.790</td>
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### Chromatogram

**MB5-031-carbamate-c1-97 - CH9**

![Chromatogram](image2)

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<th>Area [μVsec]</th>
<th>Height [μV]</th>
<th>Area%</th>
<th>Height%</th>
<th>Quantity</th>
<th>NTP</th>
<th>Resolution</th>
<th>Symmetry Factor</th>
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<tr>
<td>1</td>
<td>1</td>
<td>9</td>
<td>8.127</td>
<td>9268815</td>
<td>622646</td>
<td>98.344</td>
<td>98.381</td>
<td>N/A</td>
<td>661</td>
<td>2.342</td>
<td>1.580</td>
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<tr>
<td>2</td>
<td>2</td>
<td>9</td>
<td>9.127</td>
<td>156418</td>
<td>10224</td>
<td>1.658</td>
<td>1.639</td>
<td>N/A</td>
<td>639</td>
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Chromatogram

![Chromatogram 1](image1)

<table>
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<th>#</th>
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<th>CH</th>
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<th>Area [nA·sec]</th>
<th>Height [µV]</th>
<th>Area%</th>
<th>Height%</th>
<th>Quantity</th>
<th>NTP</th>
<th>Resolution</th>
<th>Symmetry Factor</th>
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<td>9</td>
<td>11.567</td>
<td>92128.20</td>
<td>4056.1</td>
<td>41.50%</td>
<td>81.74%</td>
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<td>6342</td>
<td>7.964</td>
<td>1.417</td>
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<td>9</td>
<td>17.267</td>
<td>170178.3</td>
<td>5430.5</td>
<td>8.08%</td>
<td>8.26%</td>
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<td>6537</td>
<td>5.482</td>
<td>1.427</td>
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<td>23.491</td>
<td>932248.6</td>
<td>17156.1</td>
<td>42.06%</td>
<td>26.13%</td>
<td>N/A</td>
<td>4302</td>
<td>2.836</td>
<td>1.315</td>
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<tr>
<td>4</td>
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<td>9</td>
<td>28.260</td>
<td>183709.6</td>
<td>2540.2</td>
<td>8.28%</td>
<td>3.66%</td>
<td>N/A</td>
<td>3365</td>
<td>N/A</td>
<td>0.955</td>
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Chromatogram

![Chromatogram 2](image2)

<table>
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<th>CH</th>
<th>tR [min]</th>
<th>Area [nA·sec]</th>
<th>Height [µV]</th>
<th>Area%</th>
<th>Height%</th>
<th>Quantity</th>
<th>NTP</th>
<th>Resolution</th>
<th>Symmetry Factor</th>
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<td>9</td>
<td>11.653</td>
<td>237316</td>
<td>1180.5</td>
<td>2.14%</td>
<td>5.83%</td>
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<td>7118</td>
<td>6.838</td>
<td>1.575</td>
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<td>17.409</td>
<td>45600</td>
<td>2175.4</td>
<td>0.41%</td>
<td>1.07%</td>
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<td>3751</td>
<td>4.852</td>
<td>1.119</td>
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<tr>
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<td>893299.6</td>
<td>16287.3</td>
<td>80.81%</td>
<td>80.49%</td>
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<td>4429</td>
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<td>2548.9</td>
<td>16.62%</td>
<td>12.57%</td>
<td>N/A</td>
<td>3469</td>
<td>N/A</td>
<td>1.123</td>
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</table>
### Chromatogram 1

**Unknown**: 5.660, 435148, 50.246, 52.92, N/A, 7826, 2.249, 1.530

**Unknown**: 6.267, 431715, 387014, 49.768, 47.673, N/A, 7736, N/A, 1.518

### Chromatogram 2

**Unknown**: 5.720, 1107884, 100153, 93.12, 92.944, N/A, 6119, 2.198, 1.673

**Unknown**: 6.358, 876749, 8058, 6.87, 7.056, N/A, 7952, N/A, 1.517
**Chromatogram**

![Chromatogram](image)

### Table 1

<table>
<thead>
<tr>
<th>#</th>
<th>Peak Name</th>
<th>CH</th>
<th>tR [min]</th>
<th>Area [μV·sec]</th>
<th>Height [μV]</th>
<th>Area%</th>
<th>Height%</th>
<th>Quantity</th>
<th>NTP</th>
<th>Resolution</th>
<th>Symmetry Factor</th>
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<tr>
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<td>51275100</td>
<td>204578</td>
<td>51.368</td>
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<td>4730</td>
<td></td>
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<td>1.035</td>
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<td>52335000</td>
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<td>5495</td>
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**Chromatogram**

![Chromatogram](image)

### Table 2

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<th>Height [μV]</th>
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<th>Height%</th>
<th>Quantity</th>
<th>NTP</th>
<th>Resolution</th>
<th>Symmetry Factor</th>
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<tr>
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<td>65118787</td>
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<td>95.630</td>
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<td>4534</td>
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<td>4.370</td>
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Chromatogram

![Chromatogram Image]

### Peak Table 1

<table>
<thead>
<tr>
<th>#</th>
<th>Peak Name</th>
<th>CH</th>
<th>tR [min]</th>
<th>Area [(\mu V\cdot sec)]</th>
<th>Height [(\mu V)]</th>
<th>Area%</th>
<th>Height%</th>
<th>Quantity</th>
<th>NTP</th>
<th>Resolution</th>
<th>Symmetry Factor</th>
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</thead>
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<tr>
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<td>9061</td>
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<td>447</td>
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Chromatogram

![Chromatogram Image]

### Peak Table 2

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<th>Height [(\mu V)]</th>
<th>Area%</th>
<th>Height%</th>
<th>Quantity</th>
<th>NTP</th>
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<tbody>
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<td>11.680</td>
<td>14837890</td>
<td>551516</td>
<td>96.68</td>
<td>95.62</td>
<td>N/A</td>
<td>423</td>
<td>1.772</td>
<td>1.968</td>
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<td>3.31</td>
<td>4.37</td>
<td>N/A</td>
<td>765</td>
<td>N/A</td>
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Auto-Scaled Chromatogram

Processed Channel: PDA Ch2 214nm@1.2nm

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<th>Retention Time (min)</th>
<th>Area</th>
<th>% Area</th>
<th>Height</th>
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<tbody>
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<td>3.255</td>
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<td>373444</td>
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<tr>
<td>3</td>
<td>3.811</td>
<td>1107684</td>
<td>43.06%</td>
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<tr>
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<td>4.138</td>
<td>1105184</td>
<td>42.98%</td>
<td>1483420</td>
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</table>

Auto-Scaled Chromatogram

Processed Channel: PDA Ch2 214nm@1.2nm

<table>
<thead>
<tr>
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<th>Area</th>
<th>% Area</th>
<th>Height</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>2.895</td>
<td>44037</td>
<td>0.78%</td>
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<td>2</td>
<td>3.125</td>
<td>664729</td>
<td>11.37%</td>
<td>151009</td>
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<tr>
<td>3</td>
<td>3.571</td>
<td>483789</td>
<td>82.72%</td>
<td>900670</td>
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<tr>
<td>4</td>
<td>3.988</td>
<td>301670</td>
<td>5.16%</td>
<td>62114</td>
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</table>
9. X-Ray Crystallographic Data

9.1 X-Ray Crystallographic Data of 2e

Structure deposited at the Cambridge Crystallographic Data Centre (CCDC 1517155)

<table>
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<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>CCDC Deposit Number</td>
<td>CCDC 1517155</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{15}H_{15}FO_{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>246.27</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100.0(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_{1}</td>
</tr>
<tr>
<td>a/Å</td>
<td>7.4982(2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>8.0473(2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>20.6908(6)</td>
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<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>99.071(2)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>1232.87(6)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>ρ_{calc}/g/cm³</td>
<td>1.327</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.800</td>
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<tr>
<td>F(000)</td>
<td>520.0</td>
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<tr>
<td>Crystal size/mm³</td>
<td>0.2 × 0.15 × 0.03</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα (λ = 1.54178)</td>
</tr>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>------------------------------------------------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>4.324 to 133.278</td>
</tr>
<tr>
<td>Index ranges</td>
<td>(-7 \leq h \leq 8, -9 \leq k \leq 9, -24 \leq l \leq 24)</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>25303</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>4301 [(R_{int} = 0.0290, R_{sigma} = 0.0172)]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>4301/17/350</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.078</td>
</tr>
<tr>
<td>Final R indexes [(I \geq 2\sigma (I))]</td>
<td>(R_1 = 0.0301, wR_2 = 0.0773)</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>(R_1 = 0.0302, wR_2 = 0.0774)</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å(^3)</td>
<td>0.20/-0.25</td>
</tr>
<tr>
<td>Flack parameter</td>
<td>0.07(5)</td>
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</table>
9.2 X-Ray Crystallographic Data of $2j$

Structure deposited at the Cambridge Crystallographic Data Centre (CCDC 1517154)

<table>
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<tbody>
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<tr>
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<td>385.44</td>
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<tr>
<td>Temperature/K</td>
<td>100.0(2)</td>
</tr>
<tr>
<td>Crystal system</td>
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</tr>
<tr>
<td>Space group</td>
<td>$P2_1$</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>12.6297(2)</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>11.1898(2)</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>14.5794(3)</td>
</tr>
<tr>
<td>$\alpha$/°</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$/°</td>
<td>96.0660(10)</td>
</tr>
<tr>
<td>$\gamma$/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>2048.88(6)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$/cm$^3$</td>
<td>1.250</td>
</tr>
<tr>
<td>$\mu$/mm$^{-1}$</td>
<td>0.720</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>824.0</td>
</tr>
<tr>
<td>Crystal size/mm$^3$</td>
<td>$0.25 \times 0.17 \times 0.05$</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα ($\lambda = 1.54178$)</td>
</tr>
<tr>
<td>$2\Theta$ range for data collection/°</td>
<td>6.096 to 134.282</td>
</tr>
</tbody>
</table>
Index ranges \(-15 \leq h \leq 15, -13 \leq k \leq 13, -17 \leq l \leq 14\)

Reflections collected 31920

Independent reflections 7145 \([R_{int} = 0.0324, R_{sigma} = 0.0281]\)

Data/restraints/parameters 7145/499/643

Goodness-of-fit on \(F^2\) 1.036

Final R indexes \([I \geq 2\sigma (I)]\) \(R_1 = 0.0970, wR_2 = 0.2559\)

Final R indexes [all data] \(R_1 = 0.1005, wR_2 = 0.2603\)

Largest diff. peak/hole / e Å\(^3\) 0.84/-0.62

Flack parameter 0.03(8)
9.3 X-Ray Crystallographic Data of 14

Structure deposited at the Cambridge Crystallographic Data Centre (CCDC 1913669)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C\textsubscript{16}H\textsubscript{18}O\textsubscript{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>242.30</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100.0(1)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2</td>
</tr>
<tr>
<td>a/Å</td>
<td>14.76169(11)</td>
</tr>
<tr>
<td>b/Å</td>
<td>6.20905(4)</td>
</tr>
<tr>
<td>c/Å</td>
<td>14.27446(9)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>95.4272(6)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å\textsuperscript{3}</td>
<td>1302.475(16)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>(\rho_{\text{calc}})/cm\textsuperscript{3}</td>
<td>1.236</td>
</tr>
<tr>
<td>(\mu/\text{mm}^{-1})</td>
<td>0.632</td>
</tr>
<tr>
<td>F(000)</td>
<td>520.0</td>
</tr>
</tbody>
</table>
Crystal size/mm³: 0.234 × 0.214 × 0.139
Radiation: CuKα (λ = 1.54184)
2θ range for data collection/°: 6.22 to 158.98
Index ranges: -18 ≤ h ≤ 18, -7 ≤ k ≤ 7, -18 ≤ l ≤ 18
Reflections collected: 25439
Independent reflections: 2793 [Rint = 0.0297, Rsigma = 0.0126]
Data/restraints/parameters: 2793/4/170
Goodness-of-fit on F²: 1.075
Final R indexes [I>2σ (I)]: R₁ = 0.0305, wR₂ = 0.0773
Final R indexes [all data]: R₁ = 0.0308, wR₂ = 0.0775
Largest diff. peak/hole / e Å³: 0.15/-0.17
Flack parameter: 0.00(5)