Supporting Information

Synthesis of Highly Oxygenated Carbocycles by Stereoselective Coupling of Alkynes to 1,3- and 1,4-Dicarbonyl Systems

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1. General Methods

a. Compound Names and Stereochemistry

Compound names were generated using ChemDraw Professional 15.0 (Cambridgesoft) software. Relative stereochemistry is drawn for all reported compounds.

b. Chemicals and Solvents

All chemicals were purchased from commercial sources and used as received unless otherwise stated. For flash chromatography, technical grade solvents were used without further purification. For reactions, dichloromethane (CH$_2$Cl$_2$), diethyl ether (Et$_2$O), dimethylformamide (DMF), tetrahydrofuran (THF), and toluene (PhMe) were purified by passage over activated alumina under an atmosphere of nitrogen using a Glass Contour Solvent System built by Pure Process Technology, LLC. Diisopropylamine was distilled under nitrogen from calcium hydride (CaH$_2$). Titanium(IV) isopropoxide (Ti(O-i-Pr)$_4$) was distilled under vacuum before use. Solutions of n-BuLi were purchased from Aldrich and titrated against N-benzylbenzamide according to Chong’s procedure. Solutions of isopropylmagnesium chloride (i-PrMgCl) were purchased from Aldrich and titrated against salicylaldehyde phenylhydrazone according to Love’s procedure.

c. Reactions

All reactions were carried out in flame-dried glassware under an atmosphere of nitrogen, magnetically stirred, and monitored by thin-layer chromatography (TLC) unless otherwise stated. TLC was performed on Merck silica gel 60 F$_{254}$ TLC glass-backed plates, visualized with UV light, and stained with an aqueous solution of p-anisaldehyde. Chromatographic purification was performed by flash column chromatography on a Biotage $^\text{®}$ Automated Liquid Chromatography Isolera™ One System using Biotage $^\text{®}$ SNAP KP-Sil 10–100 g, or Biotage $^\text{®}$ SNAP Ultra 25 μm HP-Sphere 10–25 g silica gel cartridges or by using Sorbent Technologies™ silica gel, 60 Å (40–63 μm particle size) as stated. The yields given refer to chromatographically purified and spectroscopically pure compounds unless otherwise stated.

d. Analysis

$^1$H NMR spectra were recorded on a Bruker Avance III 500 MHz (TBI probe) or a 600 MHz (BBFO probe) spectrometer in chloroform-$d$ (CDCl$_3$) or benzene-$d_6$ (C$_6$D$_6$) as indicated. All signals are reported in parts per million (ppm) and calibrated to the residual protium signal of chloroform (CHCl$_3$, 7.26 ppm) or benzene (C$_6$H$_6$, 7.16 ppm). Signals are reported as $\delta$ chemical shift(s) in ppm (multiplicity, coupling constant(s) in Hz, integration). $^{13}$C NMR spectra were recorded on a Bruker Avance III 600 MHz (BBFO probe) spectrometer.
measured at 150 MHz or a Bruker Avance III 500 MHz (TBI probe) spectrometer measured at 125 MHz. All signals are reported in ppm and are calibrated to the central line of the residual solvent signal of CHCl₃ (77.16 ppm) or benzene (128.06 ppm). Signals are reported as δ chemical shift(s) in ppm with substitution on the carbon atom indicated as; (C), fully substituted; (CH), methine; (CH₂), methylene; or (CH₃), methyl. Two-dimensional NMR spectra, including COSY, HSQC, HMBC, and NOESY were recorded on a Bruker Avance III 600 MHz spectrometer (BBFO probe), or a Bruker Avance III 500 MHz spectrometer (TBI probe). Infrared spectra were recorded on a JASCO FT/IR-4100 Fourier Transform Infrared Spectrometer. IR absorption is reported as very strong (vs), strong (s), medium (m), weak (w), very weak (vw), or broad (br). High-resolution mass spectroscopy (HRMS) analyses were performed at the mass spectrometry laboratory of the University of Illinois at Urbana-Champaign.

e. Structure Determination

Where appropriate, diagnostic ¹H NMR chemical shifts for new compounds are correlated to a structure in a figure in which signals are reported as letters in alphabetical order (A–Z), where A is the farthest downfield signal and Z the farthest upfield signal. Similarly, diagnostic ¹³C NMR chemical shifts for annulation products are correlated to a structure in a figure in which signals are reported as positive integers (1, 2, 3…) in numerical order, where 1 is the farthest downfield signal and the highest integer the farthest upfield signal.

¹H NMR (600 MHz, C₆D₆, δ): 2.78 s (br s, 1H), 2.23–2.09 m (2H), 1.96 (app dtd, J = 10.4, 7.0, 3.8 Hz, 1H), 1.70 (ddd, J = 14.5, 9.2, 7.2 Hz, 1H), 1.62 (ddd, J = 14.4, 8.2, 4.2 Hz, 1H), 1.54 (m, 1H), 1.21–1.13 (m, 7H), 0.96 (s, 3H), 0.84–0.74 (m, 1H), 0.54–0.44 (m, 1H).

¹³C NMR (150 MHz, CDCl₃, δ): 84.4 (C), 83.7 (C), 82.9 (C), 73.2 (C), 53.7 (C), 43.7 (CH), 32.9 (CH₂), 31.3 (CH₂), 26.6 (CH₂), 23.6 (CH₂), 18.9 (CH₃), 18.7 (CH₃), 14.1 (CH₃), 13.8 (CH₃).
2. Experimental Procedures

a. Synthesis of Intermolecular Coupling Partners (Compounds 5, 7, 11)

Methyl 4-hydroxybutanoate (S2). Following a modified literature procedure, \( \gamma \)-butyrolactone (2.29 mL, 30.0 mmol) was added to a solution of NaOMe (162 mg, 3.00 mmol) in anhydrous MeOH (27 mL). The mixture was refluxed overnight (18 h), then cooled to rt and filtered through a plug of silica, washing with Et\(_2\)O. The filtrate was concentrated \textit{in vacuo} to afford the crude isolate, which was purified by flash column chromatography (silica gel, 1:1:2 CH\(_2\)Cl\(_2\)-Et\(_2\)O-hexanes) to afford compound S2 (2.04 g, 58%) as a clear, colorless oil.

Analytical Data for S2:

\textbf{TLC:} \( R_f = 0.28 \) (2:2:1 CH\(_2\)Cl\(_2\)-Et\(_2\)O-hexanes).

\textbf{\(^1\)H NMR} (500 MHz, CDCl\(_3\), d): 3.72–3.67 (m, 5H), 2.45 (t, \( J = 7.2 \) Hz, 2H), 1.89 (quintet, \( J = 6.6 \) Hz, 2H), 1.65 (br s, 1H).

\textbf{\(^{13}\)C NMR} (150 MHz, CDCl\(_3\), d): 174.5 (C), 61.7 (CH\(_2\)), 51.7 (CH\(_3\)), 30.7 (CH\(_2\)), 27.7 (CH\(_2\)).

\textbf{Structure Determination:} Analytical data agrees with the literature data.

Methyl 4-oxobutanoate (5). Following a modified procedure, a solution of DMSO (0.781 mL, 11.0 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added dropwise via cannula to a stirred solution of oxalyl chloride (0.465 mL, 5.50 mmol) in CH\(_2\)Cl\(_2\) (55 mL) at \(-78 \) °C. The mixture was stirred at that temperature for 2 min, and then a solution of compound S2 (590 mg, 5.00 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added dropwise via cannula. After 45 min at \(-78 \) °C, NE\(_3\) (3.48 mL, 25.0 mmol) was added dropwise. After 15 min at \(-78 \) °C, the cooling bath was removed and the mixture was warmed to room temperature. Upon reaching room temperature, the reaction was quenched with deionized water (50 mL). The layers were separated, and the aqueous layer
extracted with CH₂Cl₂ (3 × 50 mL). The combined organic extracts were washed once with water, then brine, dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo, to afford 5 (448 mg, 77%) as a light-orange oil, which was used without further purification.

Analytical data for 5:

**TLC:** \( R_f = 0.36 \) (1:1 EtOAc–hexanes).

**\(^1\)H NMR** (500 MHz, CDCl₃, δ): 9.81 (s, 1H), 3.70 (s, 3H), 2.80 (t, \( J = 6.6 \) Hz, 2H) 2.64 (t, \( J = 6.8 \) Hz, 2H).

**\(^{13}\)C NMR** (150 MHz, CDCl₃, δ): 200.0 (CH), 172.7 (C), 51.8 (CH₃), 38.5 (CH₂), 26.3 (CH₂).

**Structure Determination:** Analytical data agrees with the literature data.\(^vi\)

2-(3-Bromopropoxy)tetrahydro-2H-pyran (S5). Following a literature procedure,\(^vi\) pyridinium \( p \)-toluenesulfonate (40 mg, 0.16 mmol) was added in one portion to a stirring solution of \( S_4 \) (14.4 mL, 158 mmol) and \( S_3 \) (12.7 mL, 138 mmol) in CH₂Cl₂ (200 mL) and the reaction mixture stirred for 5 h at room temperature. After this time, solid NaHCO₃ (2 g) and MgSO₄ (20 g) were added to the flask and the mixture was stirred for 15 min before being filtered through a pad of 4:1 silica gel–Celite\(^o\). The filter cake was washed with additional CH₂Cl₂ (2 × 50 mL) and the filtrate was concentrated in vacuo to afford the crude isolate which was purified by distillation under vacuum (bp 66 °C at 10 mbar) to yield S5 (23.7g, 78%) as a clear, colorless oil.

Analytical data for S5:

**TLC:** \( R_f = 0.30 \) (10% EtOAc in hexanes).

**\(^1\)H NMR** (600 MHz, CDCl₃, δ): 4.60 (app t, \( J = 7.1 \) Hz, 1H), 3.88–3.84 (m, 3H), 3.56–3.50 (m, 2H), 2.13 (app q, \( J = 12.5 \) Hz, 2H), 1.84–1.78, (m, 1H), 1.74–1.69 (m, 1H), 1.61–1.50 (m, 4H).

**\(^{13}\)C NMR** (150 MHz, CDCl₃, δ): 99.0 (CH), 65.0 (CH₂), 62.4 (CH₂), 33.0 (CH₂), 30.8 (CH₂), 30.7 (CH₂), 25.6 (CH₂), 19.6 (CH₂).

**Structure Determination:** Analytical data agrees with literature data.\(^vi\)
6-Phenylhexane-1,4-diol (S7). Following a modified literature procedure,\textsuperscript{vii} magnesium turnings (3.93 g, 162 mmol) and THF (54 mL) were added to a flame-dried 500 mL 3-neck round bottom flask equipped with a reflux condenser, addition funnel, and a stir bar. 1,2-Dibromoethane (0.50 mL) was added, and heat was applied with a heat gun until the magnesium had been activated (indicated visually by the evolution of ethylene at the metal surface). At this point, a solution of S5 (12.0 g, 53.8 mmol) in THF (81 mL) was added dropwise over 1.5 h through an addition funnel. After complete addition, the reaction mixture was stirred for 30 min at room temperature, then cooled to 0 °C in an ice–water bath, and hydrocinnamaldehyde (S6, 5.32 mL, 40.4 mmol) was added dropwise. The reaction mixture was then warmed to room temperature while stirring for 5 h. The reaction was quenched by carefully decanting the supernatant into a solution of saturated aqueous NH\textsubscript{4}Cl that was stirring at 0 °C. The reaction flask was rinsed with EtOAc (3 × 10 mL) and the rinsings were also added to the quench. Volatile organic solvents were removed from the quenched reaction mixture \textit{in vacuo}, and the remaining aqueous layer was extracted with EtOAc (3 × 100 mL). The combined organic extracts were dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered, and concentrated \textit{in vacuo} to afford the crude isolate which was used in the next step without further purification.

Following a modified procedure,\textsuperscript{viii} the crude residue was taken up in MeOH (200 mL) and \textit{p}-toluenesulfonic acid monohydrate (1.02 g, 5.37 mmol) was added in one portion. The mixture was stirred at room temperature for 12 h, before quenching with saturated aqueous NaHCO\textsubscript{3} (30 mL). MeOH was removed \textit{in vacuo}, and the remaining aqueous layer was diluted with water (50 mL), and then extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered, and concentrated \textit{in vacuo} to afford the crude isolate, which was purified by flash chromatography (silica gel, 50–100% EtOAc in hexanes, then 10% MeOH in EtOAc), to afford compound S7 (3.04 g, 39% over two steps) as a viscous pale-yellow oil.

Analytical Data for S7:

\textbf{TLC}: \textit{R}_{f} = 0.17 (60% EtOAc in hexanes).
$^1$H NMR (600 MHz, CDCl$_3$, δ): 7.30–7.26 (m, 2H), 7.22–7.16 (m, 3H), 3.71–3.62 (m, 3H), 2.82–2.75 (m, 1H), 2.71–2.61 (m, 3H), 1.81–1.76 (m, 2H), 1.72–1.64 (m, 3H), 1.57–1.49 (m, 1H).

$^{13}$C NMR (150 MHz, CDCl$_3$, δ): 142.2 (C), 128.5 (CH), 125.9 (CH), 71.3 (CH), 63.0 (CH$_2$), 39.3 (CH$_2$), 34.7 (CH$_2$), 32.3 (CH$_3$), 29.1 (CH$_2$).

**Structure Determination:** Analytical data agrees with the literature data.$^i$

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4-Oxo-6-phenylhexanal (7). Following a modified literature procedure,$^v$ a solution of DMSO (2.15 mL, 30.3 mmol) in CH$_2$Cl$_2$ (30 mL) was added dropwise via cannula to a stirred solution of oxalyl chloride (1.27 mL, 15.1 mmol) in CH$_2$Cl$_2$ (145 mL) at −78 °C. The mixture was reacted at that temperature for 2 min, then a solution of S7 (1.47 g, 7.57 mmol) in CH$_2$Cl$_2$ (30 mL) was added dropwise via cannula. After 45 min at −78 °C, NEt$_3$ (5.28 mL, 37.9 mmol) was added dropwise. After 15 more min at −78 °C, the cooling bath was removed and the mixture was warmed to room temperature. Upon reaching room temperature, the reaction was quenched with water (100 mL). The phases were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 100 mL). The combined organic extracts were washed with water, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated *in vacuo*, to afford keto-aldehyde 7 as a yellow-orange oil (942 mg, 93%), which was used without further purification.

**Analytical Data for 7:**

**TLC:** $R_f$ = 0.45 (40% EtOAc in hexanes).

$^1$H NMR (600 MHz, CDCl$_3$, δ): 9.80 (s, 1H), 7.28 (t, $J = 7.5$ Hz, 2H), 7.22–7.16 (m, 3H), 2.92 (t, $J = 7.4$ Hz, 2H), 2.80 (t, $J = 7.6$ Hz, 2H), 2.76 (t, $J = 6.2$ Hz, 2H), 2.70 (t, $J = 6.0$ Hz, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$, δ): 207.7 (CH), 200.4 (C), 140.9 (C), 128.5 (CH), 128.3 (CH), 126.2 (CH), 44.2 (CH$_2$), 37.4 (CH$_3$), 34.8 (CH$_2$), 29.8 (CH$_2$).

**Structure Determination:** Analytical data agrees with the literature data.$^x$
Trimethyl(3-methylbut-1-yn-1-yl)silane (11). Following a modified literature procedure,\textsuperscript{xi} n-BuLi (2.42 M in hexanes, 16.2 mL, 39.3 mmol) was added dropwise over 15 min to a solution of 3-methylbut-1-yne (S8) (3.75 mL, 36.7 mmol) in THF (50 mL) at \(-78 \, ^\circ\text{C}\). The reaction mixture was stirred at that temperature for 30 minutes, then TMSCl (5.00 mL, 39.3 mmol) was added dropwise. The reaction mixture was stirred for 30 min at \(-78 \, ^\circ\text{C}\) before being allowed to warm to room temperature. Upon reaching room temperature, the reaction was quenched with a 5\% aqueous NaHCO\textsubscript{3} solution, transferred to a separatory funnel and then extracted with pentane (3 \times 75 mL). The combined organic extracts were washed with water, dried over anhydrous NaN\textsubscript{2}SO\textsubscript{4}, filtered, and carefully concentrated \textit{in vacuo} (85 mbar, 34 \, ^\circ\text{C}) to afford alkyne 11 as an 85 wt \% solution in THF (3.90 g, 76\%) which was used without further purification.

Analytical Data for 11.

\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}, \(\delta\)): 2.57 (septet, \(J = 6.9 \, \text{Hz}, 1\text{H}\)), 1.16 (d, \(J = 6.9 \, \text{Hz}, 6\text{H}\)), 0.14 (s, 9H).

\textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}, \(\delta\)): 113.3 (C), 82.9 (C), 23.1 (CH\textsubscript{3}), 21.6 (CH), 0.4 (CH\textsubscript{3}).

\textbf{Structure Determination:} Analytical data agrees with the literature data.\textsuperscript{xii}
b. Intermolecular Couplings of Alkynes to Dicarbonyl Systems (Compounds 6, 8, 10, 12, and 15)

(E)-5-(1-Phenyl-2-(trimethylsilyl)vinyl)dihydrofuran-2(3H)-one (6). To a solution of 1-phenyl-2-trimethylsilylacetylene (0.492 mL, 2.50 mmol) in toluene (14 mL) was added Ti(Oi-Pr)$_4$ (0.592 mL, 2.00 mmol) dropwise at room temperature. The mixture was cooled to $-78 \degree$C in a dry ice–acetone bath, and n-BuLi (2.42 M in hexanes, 1.65 mL, 4.00 mmol) was added dropwise. After 5 min, the cooling bath was removed and the mixture warmed to room temperature. Upon reaching room temperature the reaction was placed in an oil bath that had been preheated to 50 $\degree$C and stirred at this temperature for 1.5 h. The mixture was then re-cooled to $-78 \degree$C and a solution of 5 (65 mg, 0.56 mmol) in toluene (2.75 mL) was added dropwise via syringe. The reaction was warmed to room temperature and stirred overnight (~12 h). After this time, the reaction was quenched with saturated aqueous NaHCO$_3$ while still under an atmosphere of nitrogen. This biphasic solution was filtered through Celite®, and the filter cake was washed with Et$_2$O. The filtrate was extracted with Et$_2$O (3 x 50 mL) and the combined organic extracts were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuo to afford the crude isolate. The crude product was purified by two flash column chromatography events on a Biotage® SNAP Ultra HP-Sphere 10 g cartridge with gradient elution (5–35% EtOAc in hexanes the first time, then 0–100% CH$_2$Cl$_2$ in hexanes the second time), to afford 6 (63 mg, 43%) as a pale-yellow oil.

Analytical data for 6:

TLC: $R_f = 0.21$ (15% EtOAc in hexanes).

$^1$H NMR (600 MHz, CDCl$_3$, $\delta$): 7.35–7.29 (m, 3 H), 7.17–7.13 (m, 2H), 5.95 (br s, 1H), 5.12 (app t, $J = 7.1$ Hz, 1H), 2.42 (app quint, $J = 8.7$ Hz, 1H) 2.37–2.30 (m, 1H), 2.30–2.22 (m, 1H), 2.02–1.94 (m, 1H), $-0.19$ (s, 9H).

$^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$): 177.2 (C), 154.4 (C), 139.0 (C), 129.4 (CH), 129.2 (CH), 128.3 (CH), 128.0 (CH), 84.1 (CH), 28.3 (CH$_3$), 27.4 (CH$_3$), $-0.2$ (CH$_3$).

IR (thin film, cm$^{-1}$): 3079 (w), 3057 (w), 3021 (w), 2953 (m), 2897 (w), 1781 (s), 1248 (m), 1176 (m), 1142 (m), 875 (m), 854 (m), 838 (m), 774 (w), 760 (w), 705 (m).
HRMS (ESI-TOF) (m/z): [M + H]⁺ calcd for C_{15}H_{21}O_{2}Si, 261.1311; found, 261.1306.

**Structure Determination:** The structure of 6 was determined by analysis of ¹H and ¹³C NMR shifts, and was supported by HSQC analysis.

![Figure S1. ¹H and ¹³C correlations for compound 6.](image)

5-Phenethyl-6-(trimethylsilyl)-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2,5-diol (8). To a solution of trimethyl(phenylethynyl)silane (4) (0.388 mL, 1.97 mmol) in toluene (10 mL) was added Ti(O-i-Pr)₄ (0.469 mL, 1.58 mmol) at room temperature. The mixture was cooled to −78 °C in a dry ice–acetone bath, and n-BuLi (2.51 M in hexanes, 1.25 mL, 3.15 mmol) was added dropwise. After 5 min, the cooling bath was removed and the mixture warmed to room temperature. Upon reaching room temperature the reaction was placed in an oil bath that had been preheated to 50 °C and was stirred at this temperature for 1.5 h. The mixture was then re-cooled to −78 °C and a solution of 7 (75 mg, 0.39 mmol) in toluene (2 mL) was added dropwise. The reaction stirred overnight (~13 hours) while warming to room temperature. After this time, the reaction was quenched with saturated aqueous NaHCO₃ while still under nitrogen. This reaction mixture was filtered through Celite®, and the filter cake washed with Et₂O. The aqueous filtrate was extracted with Et₂O (3 × 50 mL) and the combined organic extracts were dried over Na₂SO₄, filtered, and concentrated *in vacuo* to afford the crude isolate. The crude product was purified by flash chromatography on a Biotage® SNAP Ultra HP-Sphere 10 g cartridge with gradient elution (6 to 55% EtOAc in hexanes) to afford 8 as a white solid (65 mg, 45%).
Analytical Data for 8:

**TLC:** $R_f = 0.24$ (25% EtOAc in hexanes).

$^1$H NMR (600 MHz, CDCl$_3$, δ): 7.39–7.38 (m, br, 1H), 7.33–7.25 (m, 4 H), 7.24–7.20 (br m, 1H), 7.18 (t, $J = 7.4$ Hz, 1H), 7.14 (d, $J = 7.4$ Hz, 2H), 7.08–7.00 (br m, 1H), 4.37–4.32 (m, br, 1H), 2.72–2.62 (m, 1H), 2.09–2.00 (m, 2H), 2.00–1.91 (m, 3H), 1.86–1.79 (m, 1H), 1.66 (br s, 1H), 1.45 (br s, 1H), −0.22 (s, 9H).

$^{13}$C NMR (150 MHz, CDCl$_3$, δ): 156.3 (C), 142.4 (C), 138.8 (C), 138.4 (C), 131.4 (CH), 130.8 (CH), 128.54 (CH), 128.46 (CH), 128.0 (CH), 127.71 (CH), 127.67 (CH), 125.9 (CH), 73.0 (C), 67.2 (CH), 40.2 (CH$_2$), 29.9 (CH$_2$), 29.6 (CH$_2$), 28.0 (CH$_2$), 0.6 (CH$_3$).

IR (thin film, cm$^{-1}$): 3388 (br, s), 3058 (w), 3025 (w), 2949 (s), 2891 (m), 2861 (w), 1602 (w), 1585 (w), 1493 (m), 1455 (m), 1438 (m), 1246 (s), 1058 (w), 1015 (m), 1005 (w), 855 (s), 837 (s), 754 (m), 704 (s).

HRMS (ESI-TOF) (m/z): [M + Na]$^+$ calcd for C$_{23}$H$_{30}$O$_2$SiNa, 389.1913; found 389.1908.

**Structure Determination:** The structure of 8 was determined by $^1$H and $^{13}$C NMR shifts, and was supported by HSQC analysis.

![Figure S2. $^1$H and $^{13}$C correlations for compound 8.](image)

Relative stereochemistry for compound 8 was determined after protodesilylation and directed epoxidation to obtain S8 according to the following procedure:
5-Phenethyl-1-phenyl-7-oxabicyclo[4.1.0]heptane-2,5-diol (S9). Following a modified literature procedure, Tetrabutylammonium fluoride (1M in THF, 0.714 mL, 0.714 mmol) was added to a stirring solution of 8 (130 mg, 0.357 mmol) in THF (10 mL), and the resulting mixture reacted at 60 °C for 5 h. After this time, the mixture was cooled to room temperature and filtered through a plug of silica gel with a solution of 2.5% NEt₃ in EtOAc (the silica had also been pre-treated with this solvent mixture). The filtrate was concentrated in vacuo to afford the crude isolate (162 mg), of which a portion (27% by mass) was taken on to the next step without further purification.

Following a modified literature procedure, the crude residue (44 mg) was taken up in toluene (1 mL) and vanadyl acetylacetonate (2.7 mg, 0.010 mmol) was added. The vessel was purged with nitrogen and then heated to 80 °C. tert-Butyl hydroperoxide (70 wt. % in H₂O, 0.25 mL) was added dropwise and the resulting mixture was stirred at 80 °C for 2.5 h. The mixture was cooled to room temperature, diluted with EtOAc and poured into a separatory funnel that contained saturated aqueous sodium bisulfate (15 mL). The phases were separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic extracts were dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo to afford the crude isolate, which was purified by flash column chromatography on a Biotage® SNAP Ultra HP-Sphere 10g cartridge with gradient elution (25–100% EtOAc in hexanes) to afford S9 (24 mg, 80% over two steps) as a white solid.

Analytical Data for S9:

**TLC:** \( R_f = 0.42 \) (90% EtOAc in hexanes).

**¹H NMR** (600 MHz, CDCl₃, δ): 7.41–7.37 (m, 2H), 7.34–7.30 (m, 3H), 7.19 (app t, \( J = 7.4 \) Hz, 2H), 7.12 (app t, \( J = 7.4 \) Hz, 1H), 6.97 (app d, \( J = 7.4 \) Hz, 2H), 4.23–4.17 (br m, 1H), 3.67 (app d, \( J = 2.6 \) Hz “w-coupling”, 1H), 2.67 (br s, 1H), 2.60 (app ddd, \( J = 18.5, 13.4, 5.0 \) Hz, 1H), 2.55 (ddd, \( J = 18.6, 13.5, 5.5 \) Hz, 1H).
Hz, 1H), 2.27 (br s, 1H), 1.90 (app ddd, $J = 13.7, 8.5, 3.0$ Hz, 1H), 1.84–1.77 (m, 1H), 1.77–1.70 (m, 1H), 1.70–1.60 (m, 2H) 1.56 (app td, $J = 13.0, 5.4$ Hz, 1H).

**$^{13}$C NMR** (150 MHz, CDCl$_3$, δ): 142.2 (C), 137.2 (C), 128.8 (CH), 128.6 (CH), 128.54 (CH), 128.48 (CH), 128.3 (CH), 126.0 (CH), 72.2 (C), 71.3 (C), 66.6 (CH), 65.4 (CH), 40.8 (CH$_2$), 31.9 (CH$_2$), 29.8 (CH$_2$), 26.5 (CH$_2$).

**IR** (thin film in CH$_2$Cl$_2$, cm$^{-1}$): 3411 (s), 3060 (w), 3026 (w), 2951 (m), 2867 (w), 1601 (w), 1496 (m), 1448 (m), 1433 (w), 1413 (w), 1390 (w), 1384 (w), 1291 (w), 1282 (w), 1266 (w), 1061 (s), 1029 (m), 953 (m), 934 (m), 866 (m), 756 (s), 734 (m), 700 (s)

**HRMS** (ESI-TOF) (m/z): [M+Na]$^+$ calcld for C$_{20}$H$_{22}$O$_3$Na, 333.1467; found 333.1466.

**Structure Determination:** The structure of S8 was determined by $^1$H and $^{13}$C NMR shifts, and was supported by HSQC analysis. Individual proton signals were assigned using COSY and HSQC analysis. The following nOe interactions were observed in 1D nOe experiments, indicating presence of the syn-diasatereomer.

![Figure S3](image-url)

**Figure S3.** $^1$H and $^{13}$C, and selected nOe correlations for compound S9.

1-Phenethyl-3-(thiophen-2-yl)-2-(trimethylsilyl)cyclohex-2-ene-1,4-diol (10). To a solution of 2-(phenylethynyl)thiophene (9, 0.300 mL, 1.81 mmol) in toluene (10 mL) was added Ti(Oi-Pr)$_4$ (0.429 mL,
1.45 mmol) at room temperature. The mixture was cooled to −78 °C in a dry ice–acetone bath, and n-BuLi (2.42 M in hexanes, 1.20 mL, 2.90 mmol) was added dropwise. After 5 min, the cooling bath was removed and the mixture was warmed to room temperature. Upon reaching room temperature the reaction was placed in an oil bath that had been preheated to 50 °C and was stirred at that temperature for 1.5 h. The mixture was then re-cooled to −78 °C and a solution of 7 (69 mg, 0.36 mmol) in toluene (2 mL) was added dropwise. The reaction was warmed to room temperature and stirred overnight (~15 hours). After this time, the reaction was quenched with saturated aqueous NaHCO₃ while still under an atmosphere of nitrogen.

The reaction mixture was filtered through Celite®, and the filter cake was washed with Et₂O. The filtrate was extracted with Et₂O (3 × 50 mL) and the combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo to afford the crude isolate. The crude product was purified by flash column chromatography on a Biotage® SNAP Ultra HP-Sphere 25 g cartridge with gradient elution (7–60% EtOAc in hexanes) to afford 10 (71 mg, 53%) as an orange solid.

Analytical Data for 10:

**TLC:** Rᵣ = 0.18 (30% EtOAc in hexanes).

**¹H NMR** (600 MHz, CDCl₃, δ): 7.31 (app dd, J = 5.1, 1.0 Hz, 1H), 7.27 (app t, J = 7.7 Hz, 2H), 7.18 (app t, J = 8.0 Hz, 3H), 7.00 (app dd, J = 5.1, 3.4 Hz, 1H), 6.84 (app d, J = 3.4 Hz, 1H), 4.35–4.30 (br m, 1H), 2.75–2.61 (m, 2H), 2.05–1.94 (m, 5H), 1.94–1.88 (m, 1H), 1.61 (br s, 1H), 1.55 (br s, 1H), −0.11 (s, 9H).

**¹³C NMR** (150 MHz, CDCl₃, δ): 148.7 (C), 145.2 (C), 142.2 (C), 139.0 (C), 129.5 (CH), 128.6 (CH), 128.5 (CH), 126.7 (CH), 126.4 (CH), 126.0 (CH), 72.7 (C), 68.0 (CH), 40.7 (CH₂), 30.3 (CH₂), 29.5 (CH₂), 28.8 (CH₂), 0.5 (CH₃).

**IR** (thin film, cm⁻¹): 3388 (br, s), 3062 (w), 3026 (w), 2949 (s), 2894 (m), 2861 (m), 1603 (m), 1496 (m), 1454 (m), 1426 (m), 1403 (m), 1327 (w), 1246 (s), 1059 (w), 1016 (m), 840 (s), 743 (w), 698 (s), 666 (m).

**HRMS** (ESI-TOF) (m/z): [M+Na]⁺ calcd for C₂₁H₂₈O₂NaSiS, 395.1477; found 395.1470.

**Structure Determination:** The structure of 10 was determined by ¹H and ¹³C NMR shifts, and was supported by HSQC analysis. Relative stereochemistry was assigned by analogy to compound 8.
Figure S4. $^1$H and $^{13}$C correlations for compound 10.

3-Isopropyl-1-phenethyl-2-(trimethylsilyl)cyclohex-2-ene-1,4-diol (12). To a solution of trimethyl(3-methylbut-1-yn-1-yl)silane (11, 163 mg, 1.00 mmol) in toluene (5 mL) was added Ti(Oi-Pr)$_4$ (0.237 mL, 0.800 mmol) at room temperature. The mixture was cooled to $-78 \, ^\circ\text{C}$ in a dry ice–acetone bath, and $n$-BuLi (2.51 M in hexanes, 0.637 mL, 1.60 mmol) was added dropwise. After 5 minutes, the cooling bath was removed and the mixture warmed to room temperature. Upon reaching room temperature the reaction was placed in an oil bath that had been preheated to 50 $^\circ\text{C}$ and reacted at this temperature for 1.5 h. The mixture was then re-cooled to $-78 ^\circ\text{C}$ and 7 (38 mg, 0.20 mmol) in toluene (1 mL) was added dropwise. The reaction was stirred overnight (~15 hours) after warming to room temperature. After this time, the reaction was quenched with saturated aqueous NaHCO$_3$ while still under an atmosphere of nitrogen. The reaction mixture was filtered through Cellite®, and the filter cake was washed with Et$_2$O. The filtrate was extracted with Et$_2$O (3 x 50 mL) and the combined organic extracts were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuo to afford the crude isolate. The crude product was purified by flash chromatography on a Biotage® SNAP Ultra HP-Sphere 10 g cartridge with gradient elution (6–60% EtOAc in hexanes) to afford 12 (31 mg, 47%) as a white solid.

Analytical Data for 12:

TLC: $R_f = 0.30$ (30% EtOAc in hexanes).
\(^1\)H NMR (500 MHz, CDCl\(_3\), \(\delta\)): 7.30−7.26 (m, 2H), 7.21−7.16 (m, 3H), 4.19 (app d, \(J = 3.1\) Hz, 1H), 2.81 (septet, \(J = 8.5\) Hz, 1H), 2.75 (app td, \(J = 12.8, 4.8\) Hz, 1H), 2.54 (app td, \(J = 12.9, 5.3\) Hz, 1H), 2.16 (app td, \(J = 13.6, 4.4\) Hz, 1H), 2.01−1.92, (m, 1H), 1.91−1.86 (m, 2H), 1.81−1.70 (m, 2H), 1.31 (app d, \(J = 7.1\) Hz, 3H), 1.29 (app d, \(J = 7.1\) Hz, 3H), 1.24 (br s, 2H), −0.18 (s, 9H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\), \(\delta\)): 163.2 (C), 142.6 (C), 134.3 (C), 128.6 (CH), 128.5 (CH), 126.0 (CH), 76.4 (C), 66.7 (CH), 41.3 (CH\(_2\)), 37.4 (CH), 31.2 (CH\(_2\)), 30.09 (CH\(_2\)), 25.3 (CH\(_3\)), 21.9 (CH\(_3\)), 1.1 (CH\(_3\)).

IR (thin film, cm\(^{-1}\)): 3418 (s), 2949 (s), 2868 (m) 1602 (w), 1572 (w), 1454 (m), 1353 (w), 1248 (s), 1196 (w), 1094 (w), 1065 (w), 1032 (w), 989 (m), 954 (w), 856 (s), 832 (s), 753 (w), 700 (m).

HRMS (ESI-TOF) \([m/z]\): [M+Na]\(^+\) calcd for C\(_{20}\)H\(_{32}\)O\(_2\)NaSi, 355.2069; found 355.2063.

Structure Determination: The structure of 12 was determined by \(^1\)H and \(^{13}\)C NMR shifts, and was supported by HSQC analysis. Relative stereochemistry for 12 was assigned by analogy to compound 8.

![Figure S5. \(^1\)H and \(^{13}\)C correlations for compound 12.](image)

1,2,2,3,4-Pentamethyl-5-(trimethylsilyl)cyclopent-4-ene-1,3-diol (15). A solution of Ti(O-i-Pr)\(_4\) (1.44 mL, 4.88 mmol) in THF (20 mL) was cooled to −78 \(^\circ\)C and i-PrMgCl (1.96 M in THF, 4.97 mL, 9.75 mmol) was added dropwise. The solution was stirred at that temperature for 30 min prior to the addition of a solution of 13 (577 \(\mu\)L, 3.90 mmol) and 14 (256 \(\mu\)L, 1.95 mmol) in THF (20 mL) dropwise through a Teflon™ cannula. The resulting mixture was warmed to room temperature and stirred overnight. The reaction was quenched
with half-saturated aqueous NH$_4$Cl (40 mL) and stirred at room temperature for 30 min. The mixture was filtered to remove solid material and the resulting biphasic mixture was separated. The aqueous layer was extracted with Et$_2$O and the combined organic layers were dried over anhydrous MgSO$_4$, filtered, and concentrated to obtain a crude oil. The crude material was purified by flash column chromatography (Biotage$^\circledR$ SNAP KP-Sil 25 g cartridge, 5–40% EtOAc in hexanes) to obtain spectroscopically pure 15 (175 mg, 37%) as a white solid.

**Analytical Data for 15:**

**TLC:** $R_f = 0.22$ (8:2 Hexanes–EtOAc, p-Anisaldehyde).

$^1$H NMR (600 MHz, C$_6$D$_6$, $\delta$): 2.21 (s, 1H), 1.91 (s, 1H), 1.73 (s, 3H), 1.17 (s, 3H), 0.98 (s, 3H), 0.97 (s, 3H), 0.63 (s, 3H), 0.26 (s, 9H).

$^{13}$C (150 MHz, C$_6$D$_6$, $\delta$): 156.9 (C), 140.7 (C), 88.5 (C), 86.4 (C), 50.2 (C), 23.5 (CH$_3$), 22.4 (CH$_3$), 19.6 (CH$_3$), 15.7 (CH$_3$), 13.2 (CH$_3$), 1.6 (CH$_3$).

IR (NaCl, dry film, cm$^{-1}$): 3409 (br, s), 2997 (m), 2968 (m), 2952 (m), 1644 (m), 1413 (w), 1385 (w), 1247 (w), 1090 (w), 838 (m).

HRMS–ESI ($m/z$): [M + Na]$^+$ calcd for C$_{13}$H$_{26}$O$_2$NaSi, 265.1600; found, 265.1602.

**Structure Determination:** The structure was determined by analysis of the 1D $^1$H NMR and $^{13}$C NMR chemical shifts, and were supported by 2D HMBC and NOESY correlations.

*Figure S6. $^1$H, $^{13}$C, and nOe correlations for compound 15.*
c. Synthesis of Substrates for Intramolecular Annulation of Alkynes to Dicarbonyl Systems
(Compounds 16, 18, 21, 24, and 28)

4,4-Dimethylundec-9-yne-3,5-dione (16). Following a modified literature procedure, a solution of 2-butanone (S10, 2.68 g, 37.2 mmol) in THF (62 mL) was cooled to –78 °C and lithium bis(trimethylsilyl)amide (1.0 M in THF, 34.1 mL, 34.1 mmol) was added dropwise. The solution was stirred at –78 °C for 1 h prior to the dropwise addition of S11 (4.00 g, 15.5 mmol). The solution was stirred at this temperature for 20 min, then warmed to 0 °C for 10 min, room temperature for 30 min, then 60 °C for 30 min. The resulting solution was cooled to room temperature and quenched with half-saturated aqueous NH4Cl. The layers were separated and the aqueous layer washed with Et2O. The combined organic layers were washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated to obtain a crude oil. The crude material was purified by flash column chromatography (Biotage® SNAP KP Sil 100 g cartridge, 0–5% Et2O in hexanes) to obtain a mixture of tautomers of undec-9-yne-3,5-dione (1.47 g, 53%, Rf = 0.24 in 20:1 hexanes–Et2O, p-anisaldehyde) as a pale-yellow, clear oil.

Following a modified literature procedure, undec-9-yne-3,5-dione (0.645 g, 3.58 mmol) was dissolved in 2:1 DMSO–THF (3.6 mL) and K2CO3 (1.24 g, 8.94 mmol) was added to the solution. The resulting suspension was stirred at room temperature for 15 min prior to the dropwise addition of iodomethane (557 µL, 8.94 mmol), and then stirred for 48 h at room temperature. The mixture was partitioned between Et2O and water and the layers separated. The organic layer was washed with water, then with brine, and the solution dried over anhydrous magnesium sulfate, filtered, and concentrated to obtain a crude oil. The crude material was purified by flash column chromatography (Biotage® SNAP Ultra 25 g cartridge, 10% EtOAc in hexanes) to obtain spectroscopically pure 16 (0.681 g, 91%) as a clear, colorless oil.

Analytical Data for 16:

TLC: Rf = 0.33 (9:1 Hexanes–EtOAc, p-anisaldehyde).
\(^1\)H NMR (500 MHz, CDCl\(_3\), \(\delta\)): 2.51 (t, \(J = 7.1\) Hz, 2H), 2.42 (q, \(J = 7.2\) Hz, 2H), 2.14 (tq, \(J = 6.8,\ 2.5\) Hz, 2H), 1.76 (t, \(J = 2.5\) Hz, 3H), 1.72 (quintet, \(J = 7.0\) Hz, 2H), 1.34 (s, 6H), 1.05 (t, \(J = 7.2\) Hz, 3H).

\(^1^3\)C (150 MHz, CDCl\(_3\), \(\delta\)): 210.5 (C), 209.7 (C), 78.1 (C), 76.6 (C), 62.3 (C), 37.1 (CH\(_2\)), 31.8 (CH\(_2\)), 23.0 (CH\(_2\)), 21.5 (CH\(_3\)), 18.0 (CH\(_2\)), 8.2 (CH\(_3\)), 3.5 (CH\(_3\)).

IR (NaCl, thin film, cm\(^{-1}\)): 2977 (s), 2939 (s), 2921 (s), 2879 (s), 2231 (vw), 1719 (s), 1699 (s), 1466 (s), 1367 (s), 1103 (s), 1084 (s).

HRMS–EI (m/z): [M]+ calcd for C\(_{13}\)H\(_{20}\)O\(_2\), 208.1463; found, 208.1463.

**Structure Determination:** The structure of compound 16 was determined by analysis of \(^1\)H and \(^1^3\)C NMR data, see spectral data.

\[
\begin{align*}
S11 & \quad \text{1. LiHMDS, THF, then} \\
S12 & \quad 1. \text{LiHMDS, THF, then} \\
& \quad \text{2. K}_2\text{CO}_3, \text{CH}_3\text{I, 2:1 DMSO–THF} \\
18 & \quad \text{62% (2 steps)} \\
\end{align*}
\]

1-Cyclopropyl-2,2-dimethylnon-7-yne-1,3-dione (18). Following a modified literature procedure\(^{xv}\), a solution of cyclopropyl methyl ketone (S12, 3.7 mL, 37 mmol) in THF (62 mL) was cooled to –78 °C and lithium bis(trimethylsilyl)amide (1.0 M in THF, 34.1 mL, 34.1 mmol) was added dropwise. The solution was stirred at –78 °C for 30 min prior to the dropwise addition of S11 (4.00 g, 15.5 mmol). The solution was stirred at this temperature for 10 min, then warmed to 0 °C for 10 min, room temperature for 30 min, then 60 °C for 30 min. The resulting solution was cooled to room temperature and quenched with half-saturated aqueous NH\(_4\)Cl. The layers were separated and the aqueous layer washed with Et\(_2\)O. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered, and concentrated to obtain a crude oil. The crude material was purified by flash column chromatography (silica gel, 9:1 hexanes–EtOAc) to obtain a mixture of tautomers of 1-cyclopropylnon-7-yne-1,3-dione (2.58 g, 86%, \(R_f = 0.40\) in 9:1 hexanes–EtOAc, \(p\)-anisaldehyde) as a pale-yellow, clear oil.

Following a modified literature procedure\(^{xvi}\), 1-cyclopropylnon-7-yne-1,3-dione (2.00 g, 10.4 mmol) was dissolved in 2:1 DMSO–THF (9.0 mL) and K\(_2\)CO\(_3\) (3.59 g, 26.0 mmol) was added to the solution. The resulting suspension was stirred at room temperature for 10 min prior to the dropwise addition of
iodomethane (1.62 mL, 26.0 mmol), and then stirred for 72 h at room temperature. The mixture was partitioned between Et<sub>2</sub>O and water and the layers separated. The organic layer was washed with water, then with brine, and the solution dried over anhydrous magnesium sulfate, filtered, and concentrated to obtain a crude oil. The crude material was purified by flash column chromatography (silica gel, 5–7% EtOAc in hexanes) to obtain spectroscopically pure 18 (1.64 g, 72%) as a clear, colorless oil.

Analytical Data for 18:

**TLC:** \( R_f = 0.34 \) (7% EtOAc in hexanes, p-anisaldehyde).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>, \( \delta \)): 2.53 (t, \( J = 7.2 \) Hz, 2H), 2.12 (tq, \( J = 7.0, 2.5 \) Hz, 2H), 1.86 (tt, \( J = 7.7, 4.5 \), 1H), 1.76–1.69 (m, 5H), \( ^{xvi} \) 1.35 (s, 6H), 1.03 (m, 2H), 0.89 (m, 2H).

**<sup>13</sup>C** (150 MHz, CDCl<sub>3</sub>, \( \delta \)): 209.66 (C), 209.65 (C), 78.2 (C), 76.5 (C), 62.6 (C), 37.5 (CH<sub>2</sub>), 23.2 (CH<sub>2</sub>), 21.1 (CH<sub>3</sub>), 18.1 (CH<sub>2</sub>), 17.8 (CH), 12.2 (CH<sub>2</sub>), 3.5 (CH<sub>3</sub>).

**IR** (NaCl, thin film, cm\(^{-1}\)): 2979 (s), 2936 (s), 2921 (s), 2871 (m), 2232 (vw), 1716 (s), 1690 (s), 1465 (s), 1444 (s), 1198 (m), 1059 (s), 1004 (s).

**HRMS–ES** (m/z): [M + Na]+ calcld for C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>Na, 243.1361; found, 243.1369.

**Structure Determination:** The structure of compound 18 was determined by analysis of <sup>1</sup>H and <sup>13</sup>C NMR data, see spectral data.

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**Hept-5-yn-1-ol (S14).** Following a literature procedure,\(^{xviii}\) n-BuLi (2.42 M in hexanes, 62.0 mL, 152 mmol) was added dropwise over 15 min to a solution of hex-5-yn-1-ol (S13, 8.43 mL, 76.0 mmol) in THF (200 mL) at \(-78 \)°C. The reaction mixture was stirred at that temperature for 30 min, then methyl iodide (5.20 mL, 83.6 mmol) was added dropwise. The reaction mixture was stirred for 30 more min at \(-78 \)°C before warming to room temperature. Upon reaching room temperature, the reaction was quenched with water.
The mixture was transferred to a separatory funnel and extracted with CH₂Cl₂ (3 × 100 mL). The combined organic extracts were washed with water and dried over anhydrous MgSO₄, filtered, and concentrated in vacuo to obtain the crude isolate, which was purified by distillation under vacuum (49 °C, 1 mbar) to afford alkynyl alcohol S₁₄ (3.75 g, 44 %) as a clear colorless oil. Analytical data agreed with the literature data.¹⁹

Analytical Data for S₁₄:

**TLC:** $R_f = 0.59$ (60% EtOAc in hexanes).

**¹H NMR** (600 MHz, CDCl₃, δ): 3.67 (app dd, $J = 7.0, 6.3$ Hz, 2H), 2.20–2.15 (m, 2H), 1.78 (t, $J = 2.2$ Hz, 3H), 1.70–1.64 (m, 2H), 1.59–1.53 (m, 2H), 1.35–1.27 (br m, 1H).

**¹³C NMR** (150 MHz, CDCl₃, δ): 79.0 (C), 76.0 (C), 62.6 (CH₂), 32.0 (CH₂), 25.4 (CH₂), 18.6 (CH₂), 3.6 (CH₃).

**Structure Determination:** Analytical data agrees with the literature data.¹⁹

**Hept-5-ynal (S₁₅).** Following a modified literature procedure,⁴ a solution of DMSO (2.19 mL, 30.8 mmol) in CH₂Cl₂ (25 mL) was added dropwise via cannula to a stirred solution of oxalyl chloride (1.30 mL, 15.4 mmol) in CH₂Cl₂ (132 mL) at −78 °C. The mixture was reacted at that temperature for 2 min, then a solution of compound S₁₄ (1.57 g, 14.0 mmol) in CH₂Cl₂ (25 mL), was added dropwise via cannula. After 45 min at −78 °C, NEt₃ (9.76 mL, 70.0 mmol) was added dropwise. After 15 more min at −78 °C, the cooling bath was removed and the mixture was warmed to room temperature. Upon reaching room temperature, the reaction was quenched with water (100 mL). The phases were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 100 mL). The combined organic extracts were washed with water, dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo, to afford the crude isolate, which was purified by flash chromatography on a Biotage® SNAP Ultra HP-Sphere 25 g cartridge (50% CH₂Cl₂ in hexanes) to afford aldehyde S₁₅ (1.00 g, 65%) as a clear colorless oil.

Analytical Data for S₁₅:

**TLC:** $R_f = 0.45$ (1:1 CH₂Cl₂–pentane).
$^1$H NMR (600 MHz, CDCl$_3$, $\delta$): 9.83–9.81 (m, 1H), 2.56 (t, $J = 7.2$ Hz, 2H), 2.22–2.18 (m, 2H), 1.81 (quintet, $J = 7.2$ Hz, 2H), 1.77 (t, $J = 2.5$ Hz, 3 H).

$^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$): 202.2 (CH), 77.9 (C), 76.8 (C), 42.8 (CH$_2$), 21.5 (CH$_2$), 18.2 (CH$_2$), 3.4 (CH$_3$).

**Structure Determination:** Analytical data agreed with the literature data.$^{xx}$

2-Methylidodec-10-yn-3,6-dione (21). Following a modified literature procedure,$^{xxi}$ to a 20 mL scintillation vial containing S15 (352 mg, 3.00 mmol) and a stir bar was added 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazol-3-ium chloride (S17, 78 mg, 0.30 mmol) and S16 (382 mg, 3.00 mmol). A rubber septum was placed on the vial and the vessel was purged with $N_2$. NEt$_3$ (0.25 mL) was added, and the septum was removed and replaced with a screw cap. The vial was sealed with electrical tape and placed in an oil bath that had been preheated to 60 °C, and the reaction mixture was stirred at this temperature for 12 h. The reaction mixture was then cooled to room temperature, diluted with CH$_2$Cl$_2$ (10 mL) and poured into a separatory funnel containing 1% aqueous H$_2$SO$_4$ (15 mL). The layers were separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 30 mL). The combined organic extracts were washed with saturated aqueous NaHCO$_3$, then water, and dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuo to afford the crude isolate. The crude product was purified by flash chromatography on a Biotage$^\text{®}$ SNAP Ultra HP-Sphere 25 g cartridge with gradient elution (0–35% EtOAc in hexanes) to afford 21 (264 mg, 42%) as a pale-yellow oil.

**Analytical Data for 21:**

**TLC:** $R_f = 0.31$ (20% EtOAc in hexanes).

$^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 2.75–2.61 (m, 5H), 2.58 (t, $J = 7.3$ Hz, 2H) 2.18–2.12 (m, 2H), 1.78–1.71 (m, 5H), 1.11 (d, $J = 7.0$ Hz, 6 H).
\[^{13}\text{C}\ \text{NMR}\ (150\ \text{MHz},\ \text{CDCl}_3,\ \delta):\ 213.3\ (\text{C}),\ 209.1\ (\text{C}),\ 78.3\ (\text{C}),\ 76.3\ (\text{C}),\ 41.6\ (\text{CH}_2),\ 40.8\ (\text{CH}),\ 36.2\ (\text{CH}_2),\ 33.8\ (\text{CH}_2),\ 23.0\ (\text{CH}_2),\ 18.3\ (\text{CH}_3),\ 18.2\ (\text{CH}_2),\ 3.5\ (\text{CH}_3).\]

\[^{\text{IR}}\ \text{(thin\ film,\ cm}^{-1}\text{)}:\ 2969\ (s),\ 2930\ (s),\ 2915\ (s),\ 2875\ (m),\ 1710\ (s),\ 1467\ (s),\ 1405\ (m),\ 1379\ (m),\ 1365\ (m),\ 1284\ (w),\ 1218\ (w),\ 1200\ (w),\ 1102\ (m),\ 1085\ (m),\ 1038\ (m).\]

\[^{\text{HRMS–ESI\ (m/z):\ [M+H]^+\ calcd\ for\ C_{13}H_{21}O_2,\ 209.1542;\ found\ 209.1537.}\]

\[^{\text{Structure\ Determination:}}\ \text{The\ structure\ of\ compound\ 21\ was\ determined\ by\ analysis\ of\ }^1\text{H}\ \text{and\ }^{13}\text{C\ NMR\ data,\ see\ spectral\ data.}\]

\[^{\text{Undec-9-yno-2,5-dione\ (23).}}\ \text{Following\ a\ modified\ literature\ procedure,}\ ^{\text{xxi}}\ \text{to\ a\ 20\ mL\ scintillation\ vial\ containing\ S15\ (83\ mg,\ 0.76\ mmol)\ and\ a\ stir\ bar\ was\ added\ 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazol-3-ium\ chloride\ (S17,\ 39\ mg,\ 0.15\ mmol)\ and\ methyl\ vinyl\ ketone\ (S18,\ 74.0\ \mu\text{L,\ 0.907\ mmol).\ A\ rubber\}}\]

\[^{\text{septum\ was\ placed\ on\ the\ vial\ and\ the\ vessel\ was\ purged\ with\ }\text{N}_2.\ \text{NEt}_3\ (1\ mL)\ \text{was\ added,\ and\ the\ septum\}}\]

\[^{\text{was\ removed\ and\ replaced\ with\ a\ screw\ cap.\ The\ vial\ was\ sealed\ with\ electrical\ tape\ and\ placed\ in\ an\ oil}}\]

\[^{\text{bath\ that\ had\ been\ preheated\ to\ 60\ °C,\ and\ the\ reaction\ mixture\ was\ stirred\ at\ this\ temperature\ for\ 12\ h.\ The\ reaction\ mixture\ was\ then\ cooled\ to\ room\ temperature,\ dilute\ with\ CH}_2\text{Cl}_2\ (10\ mL)\ \text{and\ poured\ into\ a}}\]

\[^{\text{separatory\ funnel\ containing\ 15\ mL\ of\ 1%\ aqueous\ H}_2\text{SO}_4.\ The\ phases\ were\ separated\ and\ the\ aqueous}}\]

\[^{\text{layer\ was\ extracted\ with\ CH}_2\text{Cl}_2\ (3\ \times\ 30\ mL).\ Combined\ organic\ extracts\ were\ washed\ with\ saturated}}\]

\[^{\text{aqueous\ NaHCO}_3\ \text{and\ water,\ then\ dried\ over\ anhydrous\ Na}_2\text{SO}_4,\ filtered,\ and\ concentrated\ in\ vacuo\ to}}\]

\[^{\text{afford\ the\ crude\ isolate.\ The\ crude\ product\ was\ purified\ by\ flash\ chromatography\ on\ a\ Biotage®\ SNAP\ Ultra}}\]

\[^{\text{HP-Sphere\ 10\ g\ cartridge\ with\ gradient\ elution\ (0–60%\ EtOAc\ in\ hexanes)\ to\ afford\ 23\ (86\ mg,\ 43\ %)\ as\ a}}\]

\[^{\text{pale-yellow\ oil.}}\]

\[^{\text{Analytical\ Data\ for\ 23:\ }}\]

\[^{\text{TLC:\ }R_f = 0.53\ (60\%\ \text{EtOAc\ in\ hexanes).}}\]
\[ ^1H \text{ NMR} \ (500 \text{ MHz, CDCl}_3, \delta): \ 2.74-2.66 \ (m, 4H), \ 2.58 \ (t, \ J = 7.4 \text{ Hz, 2H}), \ 2.19 \ (s, 3H), \ 2.18-2.13 \ (m, \ 2H), \ 1.77 \ (t, \ ^5J = 2.6 \text{ Hz, 3H}), \ 1.74 \ (\text{quintet, } J = 7.1 \text{ Hz, 2H}) \]

\[ ^{13}C \text{ NMR} \ (150 \text{ MHz, CDCl}_3, \delta): \ 209.1 \ (C), \ 207.3 \ (C), \ 78.3 \ (C), \ 76.4 \ (C), \ 41.6 \ (\text{CH}_2), \ 40.0 \ (\text{CH}_2), \ 36.3 \ (\text{CH}_2), \ 30.0 \ (\text{CH}_3), \ 23.0 \ (\text{CH}_2), \ 18.2 \ (\text{CH}_2), \ 3.5 \ (\text{CH}_3). \]

IR (thin film, cm\(^{-1}\)): 2999 (w), 2919 (m), 2853 (w), 1717 (s), 1399 (m), 1363 (m), 1170 (m), 1100 (m).

HRMS–ESI (m/z): [M + H]\(^+\) calcd for C\(_{11}\)H\(_{17}\)O\(_2\), 181.1229; found 181.1225.

Structure Determination: The structure of compound 23 was determined by analysis of \(^1H\) and \(^{13}C\) NMR data, see spectral data.

2-cyclohexylidene-1,1-dimethylhydrazine (S19). Following a literature procedure,\(^{xxii}\) a mixture of cyclohexanone (26, 10.4 mL, 100 mmol), \(N,N\)-dimethylhydrazine (9.13 mL, 120 mmol), and trifluoroacetic acid (50 \(\mu\)L, 0.65 mmol) in benzene (40 mL) were refluxed under nitrogen for 5 h while using a Dean-Stark trap to remove water. The reaction mixture was cooled to room temperature and partitioned between diethyl ether (200 mL) and water (50 mL). The organic layer was separated and then washed with brine (50 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated to obtain a crude oil. The crude material was purified by distillation (67 °C, 20 mbar) to obtain spectroscopically pure S19 (12.0 g, 86%) as a clear, colorless oil.

Analytical Data for S19:

\[ ^1H \text{ NMR} \ (600 \text{ MHz, CDCl}_3, \delta): \ 2.49 \ (m, 2H), \ 2.41 \ (s, 6H), \ 2.22 \ (m, 2H), \ 1.68 \ (m, 2H), \ 1.65-1.56 \ (m, 4H). \]

\[ ^{13}C \text{ NMR} \ (150 \text{ MHz, CDCl}_3, \delta): \ 170.2 \ (C), \ 47.6 \ (\text{CH}_3), \ 36.1 \ (\text{CH}_2), \ 28.7 \ (\text{CH}_2), \ 27.5 \ (\text{CH}_2), \ 26.7 \ (\text{CH}_2), \ 26.1 \ (\text{CH}_2). \]
IR (NaCl, thin film, cm⁻¹): 2981 (s), 2931 (s), 2855 (s), 2666 (w), 1633 (s), 1468 (s), 1448 (s), 1021 (s), 995 (s), 964 (s).

HRMS–ESI (m/z): [M + H]^+ calcd for C₉H₁₇N₂, 141.1392; found, 141.1386.

Structure Determination: Analytical data agrees with the literature data.xiii

2-(Pent-3-yn-1-yl)cyclohexan-1-one (27). Following a modified literature procedure,xiii a solution of S19 (6.48 g, 46.2 mmol) in THF (90 mL) was cooled to −5 °C and n-BuLi (2.48 M in hexanes, 19.6 mL, 48.5 mmol) was added dropwise. The mixture was stirred at that temperature for 1 h prior to the dropwise addition of 1-iodo-3-pentyne (9.24 g, 47.6 mmol). The resulting mixture was warmed to room temperature and stirred overnight. An aqueous solution of 2 N HCl (90 mL) was added and the mixture stirred for 3 h at room temperature. The layers were separated and the aqueous layer extracted with EtOAc. The combined organic layers were washed with water, then brine, dried over anhydrous magnesium sulfate, filtered, and concentrated to obtain a crude oil. The crude material was purified by flash column chromatography (Biotage® SNAP KP-Sil 100 g cartridge, 2–17% EtOAc in hexanes) to obtain spectroscopically pure 27 (6.34 g, 84%) as a clear, orange oil.

Analytical Data for 27:
TLC: \( R_f = 0.38 \) (9:1 hexanes–EtOAc, \( p \)-anisaldehyde)

\(^1\)H NMR (500 MHz, CDCl₃, \( δ \)): 2.44 (app sextet, \( J = 6.1 \) Hz, 1H), 2.39–2.26 (m, 2H), 2.23–2.13 (m, 2H), 2.13–2.07 (m, 1H), 2.07–2.00 (m, 1H), 1.96 (app sextet, \( J = 7.0 \) Hz, 1H), 1.89–1.79 (m, 1H), 1.74 (t, \( J = 2.5 \) Hz, 3H), 1.72–1.58 (m, 2H), 1.38–1.25 (m, 2H).

\(^{13}\)C NMR (125 MHz, CDCl₃, \( δ \)): 213.1 (C), 78.8 (C), 75.9 (C), 49.3 (CH), 42.3 (CH₂), 34.0 (CH₂), 28.8 (CH₂), 28.2 (CH₂), 25.2 (CH₂), 16.5 (CH₂), 3.6 (CH₃).
IR (NaCl, thin film, cm⁻¹): 2933 (s), 2860 (s), 2051 (w), 1709 (s), 1448 (s), 1371 (s), 1338 (m), 1312 (s), 1228 (m), 1129 (s).

HRMS – ES (m/z): [M + H]⁺ calcd for C₁₃H₁₇O, 165.1279; found, 165.1279.

Structure Determination: Analytical data agrees with the literature data.xxiii

2-Acetyl-2-methyl-6-(pent-3-yn-1-yl)cyclohexan-1-one (28). Following a modified literature procedure,xxiv a solution of n-BuLi (2.54 M in hexanes, 6.57 mL, 16.7 mmol) was cooled to −78 °C. Diisopropylamine (2.38 mL, 17.0 mmol) was added dropwise, followed by the addition of THF (8.0 mL) to obtain an approximate 1 M solution of LDA in THF. The mixture was stirred for 40 min at −78 °C, prior to the dropwise addition of 27 (2.50 g, 15.2 mmol) as a solution in THF (23 mL). The resulting solution was stirred for 1 h at −78 °C, then slowly transferred dropwise to a pre-cooled (−78 °C) solution of acetyl chloride (1.29 mL, 18.2 mmol) in THF (15 mL). The mixture was stirred for 2 h and then quenched with saturated aqueous NH₄Cl (45 mL) at −78 °C. The mixture was warmed to room temperature and the layers separated. The aqueous layer was extracted with EtOAc, and the combined organic layers dried over anhydrous magnesium sulfate, filtered, and concentrated to obtain a crude oil. The crude material was purified by flash column chromatography (Biotage® SNAP KP-Sil 100 g cartridge, 10% EtOAc in hexanes) to obtain 2-acetyl-6-(pent-3-yn-1-yl)cyclohexan-1-one (2.70 g, 86%, Rf = 0.37 and 0.38 in 9:1 hexanesEtOAc, p-anisaldehyde) as a clear, yellow oil, a mixture of diastereomers and enol tautomers.

To a solution of 2-acetyl-6-(pent-3-yn-1-yl)cyclohexan-1-one (2.0 g, 9.7 mmol) in THF (120 mL) was added a solution of KHMDS (0.52 M in PhMe, 18.6 mL, 9.7 mmol) dropwise at room temperature, and the solution stirred for 30 min prior to the addition of methyl iodide (755 µL, 12.1 mmol). The suspension was stirred for 2 h at room temperature, then quenched by the addition of saturated aqueous NaHCO₃ (50 mL). The resulting layers were separated and the aqueous layer extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated to obtain a crude
oil. The crude material was purified by flash column chromatography (Biotage® SNAP KP-Sil 100 g cartridge, 2–20% EtOAc in hexanes) to obtain spectroscopically pure 28 (823 mg, 38%) as a clear, yellow oil.

Analytical Data for 28:

**TLC:** $R_f = 0.23$ (9:1 hexanes–EtOAc, $p$-anisaldehyde)

$^1$H NMR (600 MHz, CDCl$_3$, $\delta$): 2.72 (app sextet, $J = 6.2$ Hz, 1H), 2.27–2.07 (m, 7H), 1.92 (app sextet, $J = 6.9$ Hz, 1H), 1.89–1.80 (m, 2H), 1.75 (t, $J = 2.6$ Hz, 3H), 1.72–1.67 (m, 1H), 1.44–1.36 (m, 4H), 1.31 (app sextet, $J = 6.8$ Hz, 1H).

$^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$): 213.4 (C), 208.4 (C), 78.2 (C), 76.2 (C), 62.3 (C), 45.5 (CH), 35.1 (CH$_2$), 33.0 (CH$_2$), 28.4 (CH$_2$), 27.3 (CH$_3$), 20.6 (CH$_2$), 20.0 (CH$_3$), 16.3 (CH$_2$), 3.5 (CH$_3$).

IR (NaCl, thin film, cm$^{-1}$): 2938 (m), 2864 (m), 2229 (vw), 2052 (vw), 1714 (s), 1697 (s), 1620 (w), 1449 (m), 994 (w).

HRMS–ES (m/z): [M + H]$^+ \text{calcd for C}_{14}\text{H}_{21}\text{O}_2$, 221.1542; found, 221.1541.

**Structure Determination:** Structure was determined by analysis of the $^1$H, $^{13}$C, HMQC, HMBC, and NOESY data.

*Figure S7.* $^1$H, $^{13}$C, and nOe correlations for compound 28.
d. Intramolecular Annulation of Alkynes to Dicarbonyl Systems (Compounds 17, 19, 20, 22, 23, 25, 29, and 30)

![Diagram of reaction](image)

2-Ethyl-1,3,3-trimethyl-2,4,5,6-tetrahydropentalene-2,3a(3H)-diol (17). To a solution of Ti(i-Pr)$_4$ (284 µL, 0.960 mmol) in THF (4.8 mL) at $-78$ °C was added i-PrMgCl (2.03 M in THF, 946 µL, 1.92 mmol) dropwise. A solution of 16 (0.100 g, 0.480 mmol) in THF (4.8 mL) was added dropwise and the reaction solution warmed to $-20$ °C and stirred at that temperature for 1 h. The reaction mixture was quenched at $-20$ °C by the addition of half-saturated aqueous NaHCO$_3$ (9 mL). The mixture was stirred at rt for 1 h and then filtered to remove the solid material. The biphasic filtrate was separated and the aqueous layer extracted with Et$_2$O (3 x 5 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated to provide a crude mixture of 16 and 17. The crude material was purified by flash column chromatography (Biotage® SNAP Ultra 10 g cartridge, 20% EtOAc in hexanes) to obtain spectroscopically pure 17 (63 mg, 63%) as a white solid and 16 (35 mg, 35%) as a clear, colorless oil.

Analytical Data for 17:

**TLC:** $R_f = 0.17$ (8:2 hexanes–EtOAc, $p$-anisaldehyde)

$^1$H NMR (600 MHz, CDCl$_3$, δ): 2.45 (br s, 1H), 2.39 (br s, 1H), 2.32–2.23 (m, 1H), 2.20–2.11 (m, 1H), 2.10–2.03 (m, 1H), 1.90–1.82 (m, 1H), 1.64–1.53 (m, 6H), 1.42 (ddd, $J = 13.1, 7.0, 2.7$ Hz, 1H), 1.11 (s, 3H), 1.01 (t, $J = 7.5$ Hz, 3H), 0.82 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$, δ): 149.7 (C), 134.9 (C), 94.6 (C), 92.3 (C), 49.3 (C), 31.2 (CH$_2$), 26.8 (CH$_2$), 26.6 (CH$_2$), 23.3 (CH$_3$), 22.6 (CH$_2$), 18.2 (CH$_3$), 11.5 (CH$_3$), 8.2 (CH$_3$).

IR (NaCl, dry film, cm$^{-1}$): 3401 (br s), 2965 (s), 2878 (s), 1699 (m), 1447 (s), 1383 (s), 1201 (m), 1108 (s), 977 (s), 938 (s).

HRMS—ES ($m/z$): [M + Na]$^+$ calcd for C$_{13}$H$_{22}$O$_2$Na, 233.1517; found, 233.1516.

**Structure Determination:** The structure was determined by analysis of the 1D $^1$H NMR and $^{13}$C NMR chemical shifts, and were supported by 2D HMQC, COSY, HMBC, and NOESY correlations.
2-Cyclopropyl-1,3,3-trimethyl-2,4,5,6-tetrahydropentalene-2,3a(3H)-diol (19). To a solution of Ti(Oi-Pr)$_4$ (269 µL, 0.908 mmol) in THF (4.5 mL) at −78 °C was added i-PrMgCl (2.03 M in THF, 895 µL, 1.82 mmol) dropwise. A solution of 18 (0.100 g, 0.454 mmol) in THF (4.5 mL) was added dropwise and the reaction solution warmed to −20 °C and stirred at that temperature for 1 h. The reaction mixture was quenched at −20 °C by the addition of half-saturated aqueous NaHCO$_3$ (9 mL). The mixture was stirred at rt for 1 h and then filtered to remove the solid material. The biphasic filtrate was separated and the aqueous layer extracted with Et$_2$O (3 x 5 mL). The combined organic layers were dried over magnesium sulfate, filtered, and concentrated to provide a crude mixture of 18 and 19. The crude material was purified by flash column chromatography (Biotage® SNAP Ultra 10 g cartridge, 20% EtOAc in hexanes) to obtain spectroscopically pure 19 (66 mg, 65%) as a white solid and 18 (22 mg, 22%) as a clear, colorless oil.

Analytical Data for 19:

**TLC:** $R_f = 0.29$ (8:2 hexanes–EtOAc, p-anisaldehyde)

$^1$H NMR (600 MHz, C$_6$D$_6$, $\delta$): 2.24–2.16 (m, 2H), 2.16–2.07 (m, 1H), 2.01–1.87 (m, 2H), 1.77–1.68 (m, 1H), 1.64 (tt, $J = 1.6$ Hz, 3H), 1.50 (ddd, $J = 13.0, 9.9, 8.0$ Hz, 1H), 1.33 (ddd, $J = 12.6, 6.7, 2.3$ Hz, 1H), 1.15 (s, 3H), 0.87 (s, 3H), 0.71–0.06 (m, 2H), 0.52 (tt, $J = 8.3, 5.5$ Hz, 1H), 0.27–0.19 (m, 2H).

$^{13}$C NMR (150 MHz, C$_6$D$_6$, $\delta$): 149.2 (C), 135.6 (C), 94.5 (C), 89.9 (C), 50.3 (C), 31.8 (CH$_2$), 27.1 (CH$_2$), 23.8 (CH$_3$), 22.6 (CH$_2$), 17.9 (CH$_3$), 12.7 (CH), 11.4 (CH$_3$), −0.8 (CH$_2$), −1.1 (CH$_2$).
IR (KBr, pellet, cm\(^{-1}\)): 3420 (br s), 3343 (br s), 3001 (s), 2968 (m), 1377 (m), 1059 (s), 1025 (s), 987 (s), 940 (s).

HRMS–ESI (m/z): [M + Na]\(^+\) calcd for C\(_{22}\)H\(_{22}\)O\(_2\)Na, 245.1517; found, 245.1525.

**Structure Determination:** The structure was determined by analysis of the 1D \(^1\)H NMR and \(^{13}\)C NMR chemical shifts, and were supported by 2D HSQC, HMBC, and NOESY correlations.

**Figure S9.** \(^1\)H, \(^{13}\)C, and nOe correlations for compound 19.

2-Ethyl-1a,3,3-trimethyltetrahydro-3H-pentaleno[1,6a-b]oxirene-2,3a(4H)-diol (20). To a solution of Ti(O-i-Pr)\(_4\) (284 \(\mu\)L, 0.960 mmol) in THF (4.8 mL) at –78 °C was added i-PrMgCl (2.03 M in THF, 946 \(\mu\)L, 1.92 mmol) dropwise. A solution of 16 (0.100 g, 0.480 mmol) in THF (4.8 mL) was added dropwise and the reaction solution warmed to –20 °C and stirred at that temperature for 1 h. t-BuOOH (5.5 M in nonane, 873 \(\mu\)L, 4.80 mmol) was added at –20 °C and the solution warmed to rt and stirred at that temperature for 2 h. The solution was quenched by the addition of half-saturated aqueous NaHCO\(_3\) (9 mL) and the mixture was stirred at rt for 1 h and then filtered to remove the solid material. The biphasic filtrate was separated and the aqueous layer extracted with Et\(_2\)O (3 x 5 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated to provide crude 20. The crude material was purified by flash column chromatography (Biotage\textsuperscript{®} SNAP Ultra 10 g cartridge, 35% EtOAc in hexanes) to obtain spectroscopically pure 20 (86 mg, 79%) as a white solid.

**Analytical Data for 20:**
TLC: \( R_f = 0.30 \) (35% EtOAc in hexanes, \( p \)-anisaldehyde).

\(^1\)H NMR (600 MHz, \( \text{C}_6\text{D}_6 \), \( \delta \)): 2.97 (br s, 1H), 2.84 (br s, 1H), 1.87–1.77 (m, 2H), 1.63–1.52 (m, 2H), 1.44–1.37 (m, 2H), 1.29 (dq, \( J = 14.5, 7.3 \) Hz, 1H), 1.15–1.06 (m, 4H), 1.05 (s, 3H), 1.00 (t, \( J = 7.4 \) Hz, 3H), 0.52 (s, 3H).

\(^{13}\)C NMR (150 MHz, \( \text{C}_6\text{D}_6 \), \( d \) ): 84.9 (C), 82.6 (C), 81.7 (C), 73.7 (C), 56.5 (C), 34.7 (CH\(_2\)), 26.4 (CH\(_2\)), 24.2 (CH\(_2\)), 23.1 (CH\(_2\)), 21.0 (CH\(_3\)), 16.9 (CH\(_3\)), 14.6 (CH\(_3\)), 8.6 (CH\(_3\)).

IR (NaCl, dry film, cm\(^{-1}\)): 3434 (br s), 2970 (s), 2884 (m), 1467 (s), 1381 (s), 1311 (m), 1213 (m), 1117 (s), 982 (s), 863 (s).

HRMS–ESI (\( m/z \)): [M + Na]\(^+\) calcd for \( \text{C}_{13}\text{H}_{22}\text{O}_3\text{Na} \), 249.1467; found, 249.1462.

Structure Determination: The structure was determined by analysis of the 1D \(^1\)H NMR and \(^{13}\)C NMR chemical shifts, and were supported by 2D HSQC, HMBC, and NOESY correlations.

Figure S10. \(^1\)H, \(^{13}\)C, and nOe correlations for compound 20.

2-Isopropyl-1a-methylhexahydroindeno[3a,4-\( b \)]oxirene-2,4a(\( 5\)\( H \))-diol (22). To a stirring solution of 21 (61 mg, 0.29 mmol) in THF (6 mL) was added Ti(Oi-Pr)\(_4\) (0.173 mL, 0.586 mmol). The solution was cooled to –78 °C in a dry ice–acetone bath, and i-PrMgCl (1.86 M in THF, 0.619 mL, 1.17 mmol) was added dropwise. The reaction mixture was stirred at –78 °C for 20 min, and the cooling bath was removed. Upon reaching room temperature, the reaction mixture was cooled to 0 °C and t-BuOOH (5.5 M in nonane, 0.600 mL, 3.30 mmol) was added. After stirring at 0 °C for 10 min the reaction was quenched with saturated aqueous NaHCO\(_3\) while still under an atmosphere of nitrogen. This biphasic solution was filtered and the
filter cake was washed with Et₂O. The filtrate was extracted with Et₂O (3 × 50 mL). The combined organic extracts were dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo to afford the crude isolate. The crude product was purified by flash chromatography on a Biotage® SNAP Ultra HP-Sphere 10 g cartridge (60% EtOAc in hexanes) to afford 22 as an amorphous white solid (32.3 mg, 49%).

Analytical Data for 22:

**TLC:** \( R_f = 0.21 \) (60% EtOAc in hexanes)

**\(^1\)H NMR** (600 MHz, C₆D₆, \( \delta \)): 2.82 (br s, 1H), 2.18–2.05 (m, 2H), 1.90 (app septet d, \( J = 7.1, 1.5 \) Hz, 1H), 1.69–1.63 (m, 2H), 1.62–1.55 (m, 2H), 1.45–1.34 (m, 2H), 1.26 (app td, \( J = 14.7, 3.1 \) Hz, 1H), 1.21 (s, 3H), 1.17 (app tdd, \( J = 14.5, 3.3, 1.6 \) Hz, 1H), 1.12–1.06 (m, 1H), 1.05 (app d, \( J = 6.9 \) Hz, 3H), 0.61 (app d, \( J = 7.3 \) Hz, 3H).

**\(^{13}\)C NMR** (150 MHz, CDCl₃, \( \delta \)): 79.2 (C), 76.0 (C), 73.8 (C), 70.8 (C), 39.8 (CH₂), 34.1 (CH), 33.6 (CH₂), 29.3 (CH₂), 25.6 (CH₂), 22.3 (CH₂), 19.6 (CH₃), 17.0 (CH₃), 14.7 (CH₃).

**IR** (thin film, cm⁻¹): 3425 (br, s), 2962 (m), 2879 (w), 2853 (w), 1641 (m), 1463 (w), 1444 (w), 1379 (w), 1361 (w), 1034 (w), 1008 (w), 983 (w), 895 (w).

**HRMS–ESI** (m/z): [M + Na]⁺ calcld for C₁₃H₂₂O₃Na, 249.1467; found 249.1465.

**Structure Determination:** The structure of 22 was determined by \(^1\)H and \(^{13}\)C NMR shifts, and was supported by HSQC analysis. Individual proton signals were assigned using COSY and HSQC analysis. Relative stereochemistry was assigned by analogy to 20.

\[
\begin{align*}
\text{Me} & \quad \text{Ti(Oi-Pr)}_4, \quad i\text{-PrMgCl, THF } \\
23 & \quad \text{58% (2:1 22–23)} \quad \text{22} & \quad \text{S20} \quad \text{S21}
\end{align*}
\]

6,7-Dimethyl-1,2,3,4,5,6-hexahydro-3aH-indene-3a,6-diol and (E)-2-ethylidene-1-(3-hydroxy-3-methylhexyl)cyclopentan-1-ol (S20 and S21). To a stirring solution of 23 (83 mg, 0.46 mmol) in THF (9 mL) was added Ti(Oi-Pr)₄ (0.273 mL, 0.929 mmol). The solution was cooled to −78 °C in a dry ice/acetone bath, and i-PrMgCl (1.89 M in THF, 0.974 mL, 1.84 mmol) was added dropwise. The reaction mixture stirred overnight (~15 h) while slowly warming to room temperature. After this time, the reaction was quenched with saturated aqueous NaHCO₃ while still under a nitrogen atmosphere. This biphasic solution was filtered...
through Celite®, and the filter cake was washed with Et₂O. The filtrate was extracted with Et₂O (3 x 50 mL). The combined organic extracts were dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo to afford the crude isolate. The crude product was purified by flash chromatography on a Biotage® SNAP Ultra HP-Sphere 10 g cartridge with gradient elution (20–100% EtOAc in hexanes) to afford S20 as a white solid (33 mg, 39%), and S21 as an inseparable mixture of diastereomers, a clear, colorless oil (combined 19 mg, 19%).

Analytical Data for S20:

**TLC:** $R_f = 0.11$ (60% EtOAc in hexanes).

**$^1$H NMR** (500 MHz, CDCl₃, δ): 2.43–2.34 (app dd, $J = 17.5, 10.0$ Hz, 1H), 2.20 (app dt, $J = 17.5, 8.8$ Hz, 1H), 2.11–2.04 (app td, $J = 13.9, 3.4$ Hz, 1H), 2.03–1.92 (m, 2H), 1.87 (app dd, $J = 13.5, 7.0$ Hz, 1H), 1.83 (app dt, $J = 13.1, 3.4$ Hz, 1H), 1.80–1.72 (m, 1H), 1.71 (br s, 1H), 1.66 (br s, 1H), 1.64 (s, 3H), 1.54 (app td, $J = 14.0, 3.4$ Hz, 1H), 1.37 (app td, $J = 12.2, 8.0$ Hz, 1H), 1.24 (s, 3H).

**$^{13}$C NMR** (150 MHz, CDCl₃, δ): 140.3 (C), 133.3 (C), 76.4 (C), 72.9 (C), 41.0 (CH₂), 36.7 (CH₂), 34.1 (CH₂), 27.4 (CH₂), 25.9 (CH₃), 21.8 (CH₃), 12.8 (CH₃).

**IR** (thin film, cm⁻¹): 3306 (s), 2941 (s), 2852 (m), 1442 (m), 1403 (m), 1364 (s), 1334 (s), 1275 (w), 1208 (s), 1143 (s), 1116 (m), 1063 (m), 1046 (m), 995 (m), 983 (s), 930 (m), 890 (m), 854 (w).

**HRMS–ESI (m/z):** [M + Na]$^+$ calcd for C₁₁H₁₈O₂Na, 205.1204; found 205.1198.

**Structure Determination:** The structure of S20 was determined by $^1$H and $^{13}$C NMR shifts, and was supported by HSQC analysis. Relative stereochemistry was assigned by analogy to compound 22.

![Figure S11. $^1$H and $^{13}$C correlations for compound S20.](image)

Analytical Data for S21:
**TLC**: $R_f = 0.22$ (60% EtOAc in hexanes)

**$^1$H NMR** (600 MHz, CDCl$_3$, $\delta$): 5.56–5.50 (m, 1H), 2.51–2.43 (m, 1H), 2.22–2.14 (m, 1H), 1.80–1.65 (m, 5H), 1.67–1.63 (m, 1H), 1.63 (app dt, $J$ = 6.7, 1.4 Hz, 3H), 1.60–1.56 (m, 3H), 1.46–1.41 (m, 2H), 1.40–1.30 (m, 2H), 1.169 (s, major 3H), 1.167 (s, minor, 3H), 0.93 (app t, $J$ = 7.2 Hz, 3H).

**$^{13}$C NMR** (150 MHz, CDCl$_3$, $\delta$): [149.2 (C, minor), 149.1 (C, major)], [116.40 (CH, major), 116.39 (CH, minor)], 80.7 (C, both), [72.61 (C, major), 72.56 (C, minor)], [44.9 (CH$_2$, minor), 44.3 (CH$_2$, major)], [39.70 (CH$_2$, major), 39.67 (CH$_2$, minor)], [36.21 (CH$_2$, major), 36.20 (CH$_2$, minor)], [33.7 (CH$_2$, minor), 33.6 (CH$_2$, major)], 28.2 (CH$_2$, both), [27.3 (CH$_3$, major), 26.9 (CH$_3$, minor)], 21.6 (CH$_2$, both), 17.4 [(CH$_2$, major), 17.3 (CH$_2$, minor)], 14.8 (CH$_3$, both), 14.6 (CH$_3$, both)

**IR** (thin film, cm$^{-1}$): 3378 (s), 2955 (s), 2871 (s), 1711 (w), 1682 (w), 1467 (m), 1456 (m), 1376 (m), 1274 (w), 1069 (w), 1015 (w), 993 (w), 931 (w), 822 (w), 665 (w).

**HRMS–ESI** ($m/z$): [M + Na]$^+$ calcd for C$_{14}$H$_{26}$O$_2$Na, 249.1831; found 249.1838.

**Structure Determination:** The structure of S21 was determined by $^1$H and $^{13}$C NMR shifts. DEPT edited HSQC confirmed that an $n$-propyl, rather than an isopropyl group was added to the methyl ketone. $^{13}$C NMR suggests S21 was isolated as a mixture of diastereomers. The stereochemistry of the major and minor diastereomers were not determined.

![Reaction Scheme](image)

3,4,4a-Trimethyl-1,2,4,4a,5,6,7,7a-octahydro-2a1H-cyclopenta[cd]inden-2a1,4-diol (29). To a solution of Ti(O-i-Pr)$_4$ (269 $\mu$L, 0.908 mmol) in THF (4.5 mL) at $-78$ °C was added i-PrMgCl (2.03 M in THF, 895 $\mu$L, 1.82 mmol) dropwise. A solution of 28 (0.100 g, 0.454 mmol) in THF (4.5 mL) was added dropwise and the reaction solution warmed to $-20$ °C and stirred at that temperature for 1 h. The reaction mixture was quenched at $-20$ °C by the addition of half-saturated aqueous NaHCO$_3$ (9 mL). The mixture was stirred at rt for 1 h and then filtered to remove the solid material. The biphasic filtrate was separated and the aqueous layer extracted with Et$_2$O (3 x 5 mL). The combined organic layers were dried over anhydrous
magnesium sulfate, filtered, and concentrated to provide crude 29. The crude material was purified by flash column chromatography (Biotage® SNAP Ultra 10 g cartridge, 30% EtOAc in hexanes) to obtain spectroscopically pure 29 (40 mg, 40%) as a white solid.

Analytical Data for 29:

**TLC:** $R_f = 0.24$ (30% EtOAc in hexanes, $p$-anisaldehyde)

$^1$H NMR (600 MHz, C$_6$D$_6$, $\delta$): 2.44 (app dtd, $J = 12.4, 9.7, 6.2$ Hz, 1H), 2.36 (br s, 1H), 2.18 (app ddt, $J = 17.7, 10.1, 1.4$ Hz, 1H), 2.13 (br s, 1H), 1.98 (app quintet, $J = 8.8$ Hz, 1H), 1.65 (app quintet, $J = 6.3$ Hz, 1H), 1.53 (t, $J = 1.4$ Hz, 3H), 1.51 (app dd, $J = 12.6, 8.9$ Hz, 1H), 1.46–1.39 (m, 1H), 1.26–1.20 (m, 1H), 1.20–1.16 (m, 1H), 1.16–1.10 (m, 4H), 0.97 (s, 3H), 0.75 (app td, $J = 13.0, 2.7$ Hz, 1H), 0.58 (app qd, $J = 13.0, 2.7$ Hz, 1H).

$^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$): 148.6 (C), 135.2 (C), 92.7 (C), 92.5 (C), 48.5 (C), 41.8 (CH), 36.2 (CH$_2$), 33.6 (CH$_2$), 29.8 (CH$_2$), 21.8 (CH$_2$), 19.9 (CH$_2$), 17.5 (CH$_3$), 14.4 (CH$_3$), 11.0 (CH$_3$).

IR (NaCl, dry film, cm$^{-1}$): 3407 (br s), 2927 (s), 2856 (m), 2728 (vw), 1643 (m), 1446 (m), 1375 (m), 1095 (m), 1032 (m), 1020 (m).

HRMS–ESI ($m/z$): [M + Na]$^+$ calcd for C$_{14}$H$_{22}$O$_2$Na, 245.1517; found 245.1518.

Structure Determination: The structure was determined by analysis of the 1D $^1$H NMR and $^{13}$C NMR chemical shifts, and were supported by 2D HSQC, HMBC, COSY, and NOESY correlations.

![Figure S12. $^1$H, nOe, and $^{13}$C correlations for compound 29.](image_url)
6α,7,7α-Trimethyloctahydrocyclopenta[7,1]indenol[1,2-b]oxirene-1α,7(2H)-diol (30). To a solution of Ti(Oi-Pr)$_4$ (269 µL, 0.908 mmol) in THF (4.5 mL) at −78 °C was added i-PrMgCl (2.03 M in THF, 895 µL, 1.82 mmol) dropwise. A solution of 28 (0.100 g, 0.454 mmol) in THF (4.5 mL) was added dropwise and the reaction solution warmed to −20 °C and stirred at that temperature for 1 h. t-BuOOH (5.5 M in nonane, 825 µL, 4.54 mmol) was added at −20 °C and the solution warmed to rt and stirred at that temperature for 2 h. The reaction solution was quenched by the addition of half-saturated aqueous NaHCO$_3$ (9 mL). The mixture was stirred at rt for 1 h and then filtered to remove the solid material. The biphasic filtrate was separated and the aqueous layer extracted with Et$_2$O (3 x 5 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated to provide crude 30. The crude material was purified by flash column chromatography (Biotage® SNAP Ultra 10 g cartridge, 40% EtOAc in hexanes) to obtain spectroscopically pure 30 (67 mg, 62%) as a white solid.

Analytical Data for 30:

**TLC:** $R_f = 0.33$ (40% EtOAc in hexanes, p-anisaldehyde)

**$^1$H NMR** (600 MHz, C$_6$D$_6$, δ): 2.78 (br s, 1H), 2.23–2.09 (m, 2H), 1.96 (app dtd, $J = 10.4$, 7.0, 3.8 Hz, 1H), 1.70 (ddd, $J = 14.5$, 9.2, 7.2 Hz, 1H), 1.62 (ddd, $J = 14.4$, 8.2, 4.2 Hz, 1H), 1.54 (m, 1H), 1.21–1.13 (m, 3H), 1.11–1.02 (m, 7H), 0.96 (s, 3H), 0.84–0.74 (m, 1H), 0.54–0.44 (m, 1H).

**$^{13}$C NMR** (150 MHz, CDCl$_3$, δ): 84.4 (C), 83.7 (C), 82.9 (C), 73.2 (C), 53.7 (C), 43.7 (CH), 32.9 (CH$_2$), 31.3 (CH$_2$), 26.6 (CH$_2$), 23.6 (CH$_2$), 18.9 (CH$_3$), 18.7 (CH$_2$), 14.1 (CH$_3$), 13.8 (CH$_3$).

**IR** (NaCl, dry film, cm$^{-1}$): 3464 (s), 2934 (s), 2866 (m), 1709 (w), 1643 (w), 1462 (m), 1379 (m), 1122 (m), 1090 (m), 1039 (m).

**HRMS–ESI** (m/z): [M + Na]$^+$ calcd for C$_{14}$H$_{22}$O$_3$Na, 261.1467; found 261.1459.

**Structure Determination:** The structure was determined by analysis of the 1D $^1$H NMR and $^{13}$C NMR chemical shifts, and were supported by 2D HSQC, HMBC, COSY, and NOESY correlations.
Note that these are two overlapping peaks that could not be integrated separately; however, J-values were still determined while integrals can be estimated to give: 1.73 (t, J = 2.5 Hz, 3H), 1.72 (app quintet, J = 7.0 Hz, 2H).

Figure S13. $^1$H, nOe, and $^{13}$C correlations for compound 30.

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3. X-Ray Diffraction Data for 22

![ORTEP representation of 22](image)

**Note:** Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge, CB2 1EZ, United Kingdom and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 1556519.

**Table S1.** Crystal data and structure refinement for 22 (CCDC 1556519).

| Property                      | Value                                      |
|-------------------------------|--------------------------------------------|
| Empirical formula             | C₁₃H₂₂O₃                                   |
| Formula weight                | 226.30                                     |
| Temperature                   | 100.15 K                                   |
| Wavelength                    | 1.54178 Å                                  |
| Crystal system                | Triclinic                                  |
| Space group                   | P-1                                        |
| Unit cell dimensions          |                                            |
| a                             | 8.5418(3) Å                               |
| b                             | 11.8408(5) Å                              |
| c                             | 14.1682(6) Å                              |
| β                             | 104.764(3)°                               |
| γ                             | 105.210(2)°                               |
| β                             | 107.082(2)°                               |
| Volume                        | 1233.26(9) Å                              |
| Z                             | 4                                          |
| Density (calculated)          | 1.219 Mg/m³                                |
| Absorption coefficient        | 0.680 mm⁻¹                                 |
| F(000)                        | 496                                        |
| Crystal size                  | 0.28 x 0.28 x 0.26 mm³                     |
| Theta range for data collection | 3.465 to 68.380°                  |
| Index ranges                  | -10<=h<=10, -13<=k<=14, -17<=l<=17          |
| Reflections collected         | 15547                                      |
| Independent reflections       | 4428 [R(int) = 0.0417]                     |
| Completeness to theta = 67.679° | 98.2 %                                    |
| Absorption correction         | Semi-empirical from equivalents           |
| Max. and min. transmission    | 0.3201 and 0.2261                          |
| Refinement method             | Full-matrix least-squares on F²           |
| Data / restraints / parameters| 4428 / 0 / 299                             |
| Goodness-of-fit on F²         | 1.064                                      |
| Final R indices [I>2sigma(I)] | R1 = 0.0431, wR2 = 0.1199                 |
| R indices (all data)          | R1 = 0.0500, wR2 = 0.1267                 |
| Extinction coefficient        | n/a                                        |
| Largest diff. peak and hole   | 0.337 and -0.184 e.Å⁻³                    |
Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 22 (CCDC 1556519). U(eq) is defined as one third of the trace of the orthogonalized U^ij tensor.

|          | x      | y      | z      | U(eq) |
|----------|--------|--------|--------|-------|
| O(2')    | 5536(1)| 1287(1)| 1739(1)| 22(1) |
| O(2)     | 9259(1)| 3848(1)| 3322(1)| 23(1) |
| O(1')    | 4206(1)| 2537(1)| 3141(1)| 24(1) |
| O(3')    | 8605(1)| 1302(1)| 2898(1)| 26(1) |
| O(1)     | 10961(1)| 2526(1)| 2065(1)| 24(1) |
| O(3)     | 6289(1)| 4091(1)| 2130(1)| 29(1) |
| C(7')    | 5494(2)| 118(1) | 1888(1)| 21(1) |
| C(8')    | 7079(2)| 303(1) | 2827(1)| 21(1) |
| C(8)     | 7935(2)| 4832(1)| 2123(1)| 21(1) |
| C(4')    | 4231(2)| 1328(1)| 3124(1)| 20(1) |
| C(7)     | 9427(2)| 4998(1)| 3101(1)| 21(1) |
| C(4)     | 10675(2)| 3650(1)| 1980(1)| 21(1) |
| C(9)     | 8170(2)| 4263(1)| 1105(1)| 24(1) |
| C(5')    | 4122(2)| 599(1) | 2022(1)| 20(1) |
| C(5)     | 10757(2)| 4440(1)| 3048(1)| 21(1) |
| C(2')    | 2630(2)| 604(1) | 3363(1)| 23(1) |
| C(11')   | 7378(2)| -920(1)| 2486(1)| 26(1) |
| C(9')    | 6761(2)| 624(1) | 3846(1)| 23(1) |
| C(2)     | 12256(2)| 4355(1)| 1720(1)| 25(1) |
| C(10')   | 6023(2)| 1662(1)| 3964(1)| 23(1) |
| C(12)    | 8329(2)| 6657(1)| 3530(1)| 29(1) |
| C(6')    | 2348(2)| 40(1)  | 1136(1)| 25(1) |
| C(6)     | 12495(2)| 4978(1)| 3960(1)| 27(1) |
| C(3')    | 2483(2)| -727(1)| 3341(1)| 28(1) |
| C(10)    | 8852(2)| 3211(1)| 1134(1)| 24(1) |
| C(11)    | 9771(2)| 6203(1)| 3978(1)| 25(1) |
| C(13)    | 7954(2)| 6172(1)| 2349(1)| 26(1) |
| C(1)     | 12234(2)| 3609(2)| 658(1) | 32(1) |
| C(12')   | 6875(2)| -1291(1)| 1299(1)| 30(1) |
| C(1')    | 2557(2)| 1362(1)| 4388(1)| 29(1) |
| C(13')   | 5205(2)| -1020(1)| 970(1) | 26(1) |
| C(3)     | 12513(2)| 5721(1)| 1795(1)| 32(1) |
Table S3. Bond lengths [Å] and angles [°] for 22 (CCDC 1556519).

| Bond  | Length [Å] | Angle [°] |
|-------|------------|-----------|
| O(2')-C(7') | 1.4445(15) | C(11')-H(11B) | 0.9900 |
| O(2')-C(5') | 1.4577(15) | C(11')-C(12') | 1.530(2) |
| O(2)-C(7) | 1.4488(15) | C(9')-H(9'A) | 0.9900 |
| O(2)-C(5) | 1.4665(16) | C(9')-H(9'B) | 0.9900 |
| O(1')-H(1') | 0.8400 | C(9')-C(10') | 1.5310(18) |
| O(1')-C(4') | 1.4314(15) | C(2)-H(2) | 1.0000 |
| O(3')-H(3') | 0.8400 | C(2)-C(1) | 1.530(2) |
| O(3')-C(8') | 1.4399(15) | C(2)-C(3) | 1.5379(19) |
| O(1)-H(1) | 0.8400 | C(10')-H(10A) | 0.9900 |
| O(1)-C(4) | 1.4509(15) | C(10')-H(10B) | 0.9900 |
| O(3)-H(3) | 0.8400 | C(12)-H(12C) | 0.9900 |
| O(3)-C(8) | 1.4258(16) | C(12)-H(12D) | 0.9900 |
| C(7')-C(8') | 1.5439(18) | C(12)-C(11) | 1.537(2) |
| C(7')-C(5') | 1.4790(18) | C(12)-C(13) | 1.5341(19) |
| C(7')-C(13) | 1.5211(19) | C(6')-H(6'A) | 0.9800 |
| C(8')-C(11') | 1.5229(18) | C(6')-H(6'B) | 0.9800 |
| C(8')-C(9') | 1.5129(18) | C(6')-H(6'C) | 0.9800 |
| C(8)-C(7) | 1.5400(18) | C(6)-H(6A) | 0.9800 |
| C(8)-C(9) | 1.5198(18) | C(6)-H(6B) | 0.9800 |
| C(8)-C(13) | 1.5307(18) | C(6)-H(6C) | 0.9800 |
| C(4')-C(5') | 1.5428(18) | C(3')-H(3'A) | 0.9800 |
| C(4')-C(2') | 1.5564(18) | C(3')-H(3'B) | 0.9800 |
| C(4')-C(10') | 1.5381(17) | C(3')-H(3'C) | 0.9800 |
| C(7)-C(5) | 1.4808(18) | C(10)-H(10C) | 0.9900 |
| C(7)-C(11) | 1.5245(19) | C(10)-H(10D) | 0.9900 |
| C(4)-C(5) | 1.5344(18) | C(11)-H(11C) | 0.9900 |
| C(4)-C(2) | 1.5529(18) | C(11)-H(11D) | 0.9900 |
| C(4)-C(10) | 1.5349(18) | C(13)-H(13C) | 0.9900 |
| C(9)-H(9A) | 0.9900 | C(13)-H(13D) | 0.9900 |
| C(9)-H(9B) | 0.9900 | C(1)-H(1A) | 0.9800 |
| C(9)-C(10) | 1.5283(18) | C(1)-H(1B) | 0.9800 |
| C(5')-C(6') | 1.5160(18) | C(1)-H(1C) | 0.9800 |
| C(5)-C(6) | 1.5155(18) | C(12')-H(12A) | 0.9900 |
| C(2')-H(2') | 1.0000 | C(12')-H(12B) | 0.9900 |
| C(2')-C(3') | 1.5356(19) | C(12')-C(13') | 1.533(2) |
| C(2')-C(1') | 1.5286(19) | C(1')-H(1'A) | 0.9800 |
| C(11')-H(11A) | 0.9900 | C(1')-H(1'B) | 0.9800 |
| Bond                  | Angle (°) | Bond                  | Angle (°) |
|-----------------------|-----------|-----------------------|-----------|
| C(12')-C(11')-H(11B) | 110.9     | C(2')-C(3')-H(3'C)   | 109.5     |
| C(8')-C(9')-H(9'A)   | 109.4     | H(3'A)-C(3')-H(3'B)  | 109.5     |
| C(8')-C(9')-H(9'B)   | 109.4     | H(3'A)-C(3')-H(3'C)  | 109.5     |
| C(8')-C(9')-C(10')   | 111.06(11)| H(3'B)-C(3')-H(3'C)  | 109.5     |
| H(9'A)-C(9')-H(9'B)  | 108.0     | C(4)-C(10)-H(10C)   | 108.7     |
| C(10')-C(9')-H(9'A)  | 109.4     | C(4)-C(10)-H(10D)   | 108.7     |
| C(10')-C(9')-H(9'B)  | 109.4     | C(9)-C(10)-C(4)     | 114.25(11)|
| C(4)-C(2)-H(2)      | 106.1     | C(9)-C(10)-H(10C)   | 108.7     |
| C(1)-C(2)-C(4)      | 112.63(11)| C(9)-C(10)-H(10D)   | 108.7     |
| C(1)-C(2)-H(2)      | 106.1     | H(10C)-C(10)-H(10D) | 107.6     |
| C(1)-C(2)-C(3)      | 109.80(12)| C(7)-C(11)-C(12)    | 104.77(11)|
| C(3)-C(2)-C(4)      | 115.40(11)| C(7)-C(11)-H(11C)   | 110.8     |
| C(3)-C(2)-H(2)      | 106.1     | C(7)-C(11)-H(11D)   | 110.8     |
| C(4')-C(10')-H(10A) | 108.4     | C(12)-C(11)-H(11C)  | 110.8     |
| C(4')-C(10')-H(10B) | 108.4     | C(12)-C(11)-H(11D)  | 110.8     |
| C(9')-C(10')-C(4')  | 115.63(11)| H(11C)-C(11)-H(11D) | 108.9     |
| C(9')-C(10')-H(10A) | 108.4     | C(8)-C(13)-C(12)    | 103.32(11)|
| C(9')-C(10')-H(10B) | 108.4     | C(8)-C(13)-H(13C)   | 111.1     |
| H(10A)-C(10')-H(10B)| 107.4     | C(8)-C(13)-H(13D)   | 111.1     |
| H(12C)-C(12)-H(12D) | 109.1     | C(12)-C(13)-H(13C)  | 111.1     |
| C(11)-C(12)-H(12C)  | 111.1     | C(12)-C(13)-H(13D)  | 111.1     |
| C(11)-C(12)-H(12D)  | 111.1     | H(13C)-C(13)-H(13D) | 109.1     |
| C(13)-C(12)-H(12C)  | 111.1     | C(2)-C(1)-H(1A)     | 109.5     |
| C(13)-C(12)-H(12D)  | 111.1     | C(2)-C(1)-H(1B)     | 109.5     |
| C(13)-C(12)-C(11)   | 103.07(11)| C(2)-C(1)-H(1C)     | 109.5     |
| C(5')-C(6')-H(6'A)  | 109.5     | H(1A)-C(1)-H(1B)    | 109.5     |
| C(5')-C(6')-H(6'B)  | 109.5     | H(1B)-C(1)-H(1C)    | 109.5     |
| C(5')-C(6')-H(6'C)  | 109.5     | H(1B)-C(1)-H(1C)    | 109.5     |
| H(6'A)-C(6')-H(6'B) | 109.5     | C(11')-C(12')-H(12A)| 111.2     |
| H(6'A)-C(6')-H(6'C) | 109.5     | C(11')-C(12')-H(12B)| 111.2     |
| H(6'B)-C(6')-H(6'C) | 109.5     | C(11')-C(12')-C(13')| 102.69(11)|
| C(5)-C(6)-H(6A)    | 109.5     | H(12A)-C(12')-H(12B)| 109.1     |
| C(5)-C(6)-H(6B)    | 109.5     | C(13')-C(12')-H(12A)| 111.2     |
| C(5)-C(6)-H(6C)    | 109.5     | C(13')-C(12')-H(12B)| 111.2     |
| H(6A)-C(6)-H(6B)   | 109.5     | C(2')-C(1')-H(1'A)  | 109.5     |
| H(6A)-C(6)-H(6C)   | 109.5     | C(2')-C(1')-H(1'B)  | 109.5     |
| H(6B)-C(6)-H(6C)   | 109.5     | C(2')-C(1')-H(1'C)  | 109.5     |
| C(2')-C(3')-H(3'A) | 109.5     | H(1'A)-C(1')-H(1'B) | 109.5     |
| C(2')-C(3')-H(3'B) | 109.5     | H(1'A)-C(1')-H(1'C) | 109.5     |
| Bond                                        | Distance | Bond                                        | Distance |
|---------------------------------------------|----------|---------------------------------------------|----------|
| H(1'B)-C(1')-H(1'C)                        | 109.5    | C(2)-C(3)-H(3A)                             | 109.5    |
| C(7')-C(13')-C(12')                       | 104.54(11) | C(2)-C(3)-H(3B)                             | 109.5    |
| C(7')-C(13')-H(13A)                        | 110.8    | C(2)-C(3)-H(3C)                             | 109.5    |
| C(7')-C(13')-H(13B)                        | 110.8    | H(3A)-C(3)-H(3B)                            | 109.5    |
| C(12')-C(13')-H(13A)                       | 110.8    | H(3A)-C(3)-H(3C)                            | 109.5    |
| C(12')-C(13')-H(13B)                       | 110.8    | H(3B)-C(3)-H(3C)                            | 109.5    |
| H(13A)-C(13')-H(13B)                       | 108.9    |                                             |          |

Symmetry transformations used to generate equivalent atoms.
Table S4. Anisotropic displacement parameters (Å² x 10³) for 22 (CCDC 1556519). The anisotropic displacement factor exponent takes the form: 

\[-2\pi^2 [ h^2 a^*^2 U_{11} + \ldots + 2hk ab^* U_{12} ] \]

|       | U^{11} | U^{22} | U^{33} | U^{23} | U^{13} | U^{12} |
|-------|--------|--------|--------|--------|--------|--------|
| O(2')| 24(1)  | 21(1)  | 24(1)  | 11(1)  | 10(1)  | 9(1)   |
| O(2) | 25(1)  | 20(1)  | 24(1)  | 10(1)  | 9(1)   | 9(1)   |
| O(1')| 25(1)  | 18(1)  | 28(1)  | 7(1)   | 7(1)   | 9(1)   |
| O(3')| 22(1)  | 21(1)  | 33(1)  | 10(1)  | 10(1)  | 6(1)   |
| O(1) | 25(1)  | 20(1)  | 30(1)  | 10(1)  | 11(1)  | 10(1)  |
| O(3) | 21(1)  | 26(1)  | 39(1)  | 14(1)  | 9(1)   | 7(1)   |
| C(7')| 23(1)  | 19(1)  | 20(1)  | 8(1)   | 7(1)   | 7(1)   |
| C(8')| 19(1)  | 19(1)  | 23(1)  | 7(1)   | 6(1)   | 6(1)   |
| C(8) | 19(1)  | 19(1)  | 23(1)  | 7(1)   | 6(1)   | 7(1)   |
| C(4')| 20(1)  | 18(1)  | 21(1)  | 6(1)   | 6(1)   | 8(1)   |
| C(7) | 22(1)  | 18(1)  | 20(1)  | 6(1)   | 7(1)   | 7(1)   |
| C(4) | 22(1)  | 17(1)  | 23(1)  | 6(1)   | 7(1)   | 8(1)   |
| C(9) | 25(1)  | 26(1)  | 20(1)  | 6(1)   | 4(1)   | 10(1)  |
| C(5')| 22(1)  | 17(1)  | 20(1)  | 6(1)   | 6(1)   | 6(1)   |
| C(5) | 22(1)  | 18(1)  | 21(1)  | 7(1)   | 6(1)   | 6(1)   |
| C(2')| 22(1)  | 24(1)  | 23(1)  | 7(1)   | 8(1)   | 9(1)   |
| C(11')| 26(1)  | 21(1)  | 29(1)  | 8(1)   | 8(1)   | 11(1)  |
| C(9')| 22(1)  | 25(1)  | 20(1)  | 8(1)   | 5(1)   | 9(1)   |
| C(2) | 24(1)  | 24(1)  | 27(1)  | 9(1)   | 10(1)  | 9(1)   |
| C(10')| 21(1)  | 23(1)  | 19(1)  | 4(1)   | 4(1)   | 8(1)   |
| C(12) | 34(1)  | 24(1)  | 29(1)  | 6(1)   | 12(1)  | 15(1)  |
| C(6')| 24(1)  | 24(1)  | 21(1)  | 5(1)   | 4(1)   | 10(1)  |
| C(6) | 26(1)  | 25(1)  | 24(1)  | 6(1)   | 4(1)   | 10(1)  |
| C(3')| 26(1)  | 25(1)  | 34(1)  | 13(1)  | 12(1)  | 7(1)   |
| C(10) | 24(1)  | 23(1)  | 21(1)  | 2(1)   | 6(1)   | 9(1)   |
| C(11) | 30(1)  | 22(1)  | 21(1)  | 5(1)   | 9(1)   | 11(1)  |
| C(13) | 27(1)  | 21(1)  | 28(1)  | 8(1)   | 7(1)   | 11(1)  |
| C(1) | 35(1)  | 34(1)  | 30(1)  | 12(1)  | 16(1)  | 15(1)  |
| C(12')| 34(1)  | 27(1)  | 31(1)  | 6(1)   | 13(1)  | 15(1)  |
| C(1') | 31(1)  | 33(1)  | 27(1)  | 11(1)  | 14(1)  | 14(1)  |
| C(13')| 31(1)  | 24(1)  | 21(1)  | 4(1)   | 8(1)   | 11(1)  |
| C(3) | 31(1)  | 25(1)  | 39(1)  | 13(1)  | 16(1)  | 8(1)   |
Table S5. Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 22 (CCDC 1556519).

|     | x    | y    | z    | U(eq) |
|-----|------|------|------|-------|
| H(1') | 3193 | 2444 | 2780 | 37    |
| H(3') | 8424 | 1975 | 2990 | 38    |
| H(1)  | 10154| 2090 | 2212 | 36    |
| H(3)  | 6341 | 3431 | 2229 | 43    |
| H(9A) | 9009 | 4936 | 982  | 29    |
| H(9B) | 7028 | 3916 | 516  | 29    |
| H(2') | 1553 | 487  | 2790 | 28    |
| H(11A)| 6623 | -1585| 2660 | 31    |
| H(11B)| 8623 | -780 | 2830 | 31    |
| H(9'A)| 7880 | 913  | 4441 | 28    |
| H(9'B)| 5920 | -144 | 3863 | 28    |
| H(2)  | 13334| 4417 | 2259 | 30    |
| H(10A)| 6885 | 2426 | 3955 | 27    |
| H(10B)| 5912 | 1884 | 4659 | 27    |
| H(12C)| 7265 | 6286 | 3681 | 35    |
| H(12D)| 8751 | 7592 | 3820 | 35    |
| H(6'A)| 1838 | 682  | 1152 | 37    |
| H(6'B)| 1562 | -687 | 1220 | 37    |
| H(6'C)| 2499 | -237 | 464  | 37    |
| H(6A) | 12314| 5287 | 4617 | 40    |
| H(6B) | 13334| 5680 | 3879 | 40    |
| H(6C) | 12959| 4315 | 3973 | 40    |
| H(3'A)| 2674 | -1168| 2722 | 43    |
| H(3'B)| 1308 | -1204| 3311 | 43    |
| H(3'C)| 3372 | -659 | 3975 | 43    |
| H(10C)| 8905 | 2829 | 441  | 29    |
| H(10D)| 8003 | 2542 | 1255 | 29    |
| H(11C)| 10954| 6849 | 4162 | 31    |
| H(11D)| 9686 | 6024 | 4612 | 30    |
| H(13C)| 6806 | 6156 | 1944 | 31    |
| H(13D)| 8889 | 6707 | 2177 | 31    |
| H(1A) | 12049| 2736 | 609  | 47    |
| H(1B) | 13360| 4006 | 592  | 47    |
|        |       |       |       |       |
|--------|-------|-------|-------|-------|
| H(1C)  | 11279 | 3608  | 95    | 47    |
| H(12A) | 6634  | -2197 | 959   | 36    |
| H(12B) | 7815  | -770  | 1123  | 36    |
| H(1'A) | 3531  | 1434  | 4981  | 44    |
| H(1'B) | 1437  | 929   | 4447  | 44    |
| H(1'C) | 2656  | 2210  | 4394  | 44    |
| H(13A) | 5055  | -823  | 321   | 31    |
| H(13B) | 4152  | -1757 | 848   | 31    |
| H(3A)  | 11670 | 5708  | 1168  | 47    |
| H(3B)  | 13713 | 6175  | 1849  | 47    |
| H(3C)  | 12321 | 6151  | 2418  | 47    |
4. Spectral Data

Note: For 2D spectra, **Black** signals = positive phase, **Red** signals = negative phase
Figure S15: $^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (150 MHz, CDCl$_3$) of 6
Figure S16: HSQC (600 MHz, CDCl₃) of 6
Figure S17: $^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (150 MHz, CDCl$_3$) of 8
Figure S18: HSQC (600 MHz, CDCl₃) of 8
Figure S19: $^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (150 MHz, CDCl$_3$) of S9
Figure S20: HSQC (600 MHz, CDCl₃) of S9
Figure S21: COSY (600 MHz, C$_6$D$_6$) of S9
Figure S22: $^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (150 MHz, CDCl$_3$) of 6b
Figure S23: $^1$HSQC (600 MHz and 150 MHz, CDCl$_3$) of 6b
Figure S24: $^1$H NMR (500 MHz, CDCl$_3$) and $^{13}$C NMR (150 MHz, CDCl$_3$) NMR of 12
Figure S25: HSQC (600 MHz and 150 MHz, CDCl₃) of 12
Figure S26: $^1$H NMR (600 MHz, C$_6$D$_6$) and $^{13}$C NMR (150 MHz, C$_6$D$_6$) of 15
Figure S27: HMBC (600 MHz and 150 MHz, C₆D₆) and NOESY (600 MHz, C₆D₆) of 15
Figure S28: $^1$H NMR (500 MHz, CDCl$_3$) and $^{13}$C NMR (150 MHz, CDCl$_3$) of 16
Figure S29: $^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (150 MHz, CDCl$_3$) of 18
Figure S31: $^1$H NMR (500 MHz, CDCl$_3$) and $^{13}$C NMR (150 MHz, CDCl$_3$) of 21)
Figure S30: $^1$H NMR (500 MHz, CDCl$_3$) and $^{13}$C NMR (150 MHz, CDCl$_3$) of 23
Figure S32: $^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (150 MHz, CDCl$_3$) of 28
Figure S33: HMBC (600 MHz, and 150 MHz, CDCl₃) of 28
Figure S34: HMQC (600 MHz, and 150 MHz, CDCl₃) of 28
Figure S35: NOESY (600 MHz, CDCl₃) of 28
Figure S36: $^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (150 MHz, CDCl$_3$) of 17
Figure S37: COSY (600 MHz, CDCl₃) of 17
Figure S38: HMBC (600 MHz and 150 MHz, CDCl₃) of 17
Figure S39: HMQC (600 MHz and 150 MHz, CDCl$_3$) of 17
Figure S40: NOESY (600 MHz, CDCl₃) of 17
Figure S41: $^1$H NMR (600 MHz, C$_6$D$_6$) and $^{13}$C NMR (150 MHz, C$_6$D$_6$) of 19
Figure S42: HMBC (600 MHz and 150 MHz, C₆D₆) of 19
Figure S43: HSQC (600 MHz and 150 MHz, C₆D₆) of 19
Figure S44: NOESY (600 MHz, C₆D₆) of 19
Figure S45: $^1$H NMR (600 MHz, $C_6D_6$) and $^{13}$C NMR (150 MHz, $C_6D_6$) of 20
Figure S46: HMBC (600 MHz and 150 MHz, C₆D₆) of 20
Figure S47: HSQC (600 MHz and 150 MHz, C₆D₆) of 20
Figure S48: NOESY (600 MHz, C6D6) of 20
Figure S49: $^1$H NMR (500 MHz, CDCl$_3$) and $^{13}$C NMR (150 MHz, CDCl$_3$) of S20
Figure S50: HSQC (600 MHz and 150 MHz, CDCl₃) of S20
Figure S51: $^1$H NMR (500 MHz, CDCl$_3$) and $^{13}$C NMR (150 MHz, CDCl$_3$) of S21
Figure S52: HSQC (600 MHz and 150 MHz, CDCl$_3$) of S21
Figure S53: $^1$H NMR (600 MHz, C$_6$D$_6$) and $^{13}$C NMR (150 MHz, CDCl$_3$) of 22
Figure S54: HSQC (600 MHz, and 150 MHz, CDCl₃) of 22
Figure S55: COSY (600 MHz, C$_6$D$_6$) of 22
Figure S56: $^1$H NMR (600 MHz, C$_6$D$_6$) and $^{13}$C NMR (150 MHz, CDCl$_3$) of 29
Figure S57: COSY (600 MHz, C₆D₆) of 29
Figure S58: HMBC (600 MHz, C<sub>6</sub>D<sub>6</sub>) of 29
Figure S59: HSQC (600 MHz, CD$_6$) of 29
Figure S60: NOESY (600 MHz, C$_6$D$_6$) of 29
Figure S61: $^1$H NMR (600 MHz, C$_6$D$_6$) and $^{13}$C NMR (150 MHz, CDCl$_3$) of 30
Figure S62: COSY (600 MHz, C$_6$D$_6$) of 30
Figure S63: HMBC (600 MHz, C₆D₆) of 30
Figure S64: HSQC (600 MHz, C₆D₆) of 30
Figure S65: NOESY (600 MHz, C₆D₆) of 30