A Collective Domino Approach Towards the Core of Molecules Isolated from the Genus *Schisandra*

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Supporting Information

- **General Experimental**

$^1$H nuclear magnetic resonance (NMR) spectra were recorded using an internal deuterium lock at ambient temperatures on the following instruments: Bruker AC400 (400 MHz). An internal reference of $\delta_H$ 7.26 ppm was used for the residual protons in CDCl$_3$ and $\delta_H$ 7.16 ppm in the case of C$_6$D$_6$. Data are presented as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br means the signal is broad), coupling constant ($J$ in Hz), integration and interpretation. $^{13}$C NMR spectra were recorded on a Bruker AC300(75 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the internal solvent signal (peak at 77.16 ppm in the case of CDCl$_3$; peak at 128.06 ppm in the case of C$_6$D$_6$). Infra-red spectra were recorded on a FTIR spectrometer equipped with a single reflection diamond ATR Bruker A222 accessory. The measurements were done for pure samples. For each individual spectrum, about 30 scans were averaged at 4 cm$^{-1}$ resolution. The diamond crystal without sample served as reference. All the system was purged with dry air. The identification of peaks was done with the standard method proposed in OPUS 6.0 software. Wavelengths of maximum absorbance ($\nu_{\text{max}}$) are quoted in cm$^{-1}$.

High-resolution mass spectra (HRMS) were performed on a QStar Elite (Applied Biosystems SCIEX) spectrometer equipped with atmospheric pressure ionization source (API) pneumatically assisted. Samples were ionized by positive electrospray mode as follows: electrospray tension (ISV): 5500 V ; opening tension (OR): 50 V ; nebulization gas pression (air): 20 psi. Low resolution mass spectra were recorded on ion trap Bruker Esquire 6000, equipped with an electrospray source (methanolic sodium chloride solution). The parent ion (M$^+$, [M+H]$^+$, [M+Na]$^+$ or [M+NH$_4$]$^+$) is quoted.

Analytical thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 F254 plates. Flash column chromatography was carried out on Merck Kieselgel 60 (230-400 mesh) according to W. C. Still method.\(^1\)

Anhydrous THF, dichloromethane and Et$_2$O were obtained from a solvent purification system. Reagents and solvents were purified by standard means.\(^2\) All experiments were performed under anhydrous conditions and an inert atmosphere of argon and, except where stated, using dried apparatus and employing standard techniques for handling air-sensitive materials. All reagents were weighed and handled in air at room temperature.

Preparation of key domino precursor:

Preparation of ethyl 2-oxo-1-((trimethylsilyl)ethynyl)bicyclo[4.1.0] heptane-7-carboxylate (16):

To a solution of (2-ethoxy-2-oxoethyl)dimethylsulfonium bromide (0.596g, 2.60 mmol, 2.5 equiv) in DCM (10 mL) was slowly added DBU (0.47 mL, 3.12 mmol, 3 equiv) at rt. After 45 min, enyne 14 (0.200 g, 1.04 mmol, 1 equiv) was added and the resulting mixture was stirred at room temperature for 3 h. After evaporation of the solvent under reduced pressure, the residue was diluted with ethyl acetate and water. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated in vacuo. The residue was purified by flash chromatography (10 % Et₂O-PE, + 1% Et₃N) to give product 16 as an orange oil (0.289 g, quantitative yield).

Orange oil  

Rf (EP / Et₂O : 9 / 1) = 0.11

¹H NMR (C₆D₆, 300 MHz): 4.15-3.98 (m, 2H, H12), 2.62-2.48 (m, 1H, H6), 2.19 (d, J = 6.2 Hz, 1H, H10), 1.78-1.69 (m, 1H, H3’), 1.62-1.50 (m, 1H, H3), 1.24-1.09 (m, 2H, H5), 1.03 (t, J = 7.2 Hz, 3H, H13), 0.89-0.78 (m, 1H, H4’), 0.73-0.58 (m, 1H, H4), 0.20 (s, 9H, H9).

¹³C NMR (C₆D₆, 75 MHz): 198.1 (C, C2), 167.4 (C, C11), 101.5 (C, C8), 87.7 (C, C7), 61.3 (CH₂, C12), 36.6 (CH₂, C3), 33.5 (C, C1), 31.5 (CH, C10), 31.2 (CH, C6), 19.9 (CH₂, C5), 18.5 (CH₂, C4), 14.4 (CH₃, C13), 0.1 (CH₃, 3 x C9).

HRMS (EI) m/z 296.1677 [calc’d for C₁₅H₂₆O₃Si (M+NH₄⁺) 296.1676].

IR νmax: 3053, 2962-2896, 2171, 1726, 1697, 1246, 1202, 1176, 839, 757 cm⁻¹.
Preparation of \((\pm)-(1S,2R,6S,7S)\)-ethyl-2-hydroxy-1-(((trimethylsilyl)ethynyl)bicyclo[4.1.0]heptane-7-carboxylate and \((\pm)-(1S,2S,6S,7S)\)-ethyl 2-hydroxy-1-(((trimethylsilyl)ethynyl)bicyclo[4.1.0]heptane-7-carboxylate (17):

To a cooled (0°C) solution of ester 16 (1.410 g, 5.06 mmol, 1 equiv) in MeOH (3 mL) was slowly added sodium borohydride (0.191 g, 5.06 mmol, 1 equiv). The reaction mixture was stirred at that temperature for 2 hours and subsequently quenched with an aqueous solution of sodium bicarbonate. The aqueous phase was extracted with Et₂O and the combined organic layers were washed with water twice. The organic layer was dried over magnesium sulfate, filtered and concentrated in vacuo. The residue was purified by flash chromatography (10% Et₂O–PE, + 1% Et₃N) to give alcohol 17a (0.653 g, 46 %) and 17b (0.653 g, 46 %).

17a

**White solid**

Rf (EP / Et₂O : 4 / 1) = 0.43

Mp = 102.2°C

\(^1\text{H NMR (C}_6\text{D}_6, 300 \text{ MHz):}\) 4.13-3.99 (m, 2H, H9), 3.91 (br t, J = 3.9 Hz, 1H, H2), 2.74 (br s, 1H, OH), 2.26-2.21 (m, 1H, H6), 1.66-1.58 (m, 1H, H5), 1.56 (d, J = 6.2 Hz, 1H, H7), 1.52-1.37 (m, 2H, H3 et H4), 1.05 (t, J = 7.2 Hz, 3H, H10), 1.01-0.87 (m, 2H, H3’ and H5’), 0.76-0.64 (m, 1H, CH₂, H4’), 0.15 (s, 9H, H13).

\(^{13}\text{C NMR (C}_6\text{D}_6, 75 \text{ MHz):}\) 169.3 (C, C8), 105.1 (C, C12), 87.9 (C, C11), 65.7 (CH, C2), 60.7 (CH₂, C9), 32.5 (CH, C7), 29.1 (C, C1), 27.9 (CH₂, C3), 27.6 (CH, C6), 21.3 (CH₂, C5), 14.9 (CH₂, C4), 14.5 (CH₃, C10), 0.1 (CH₃, 3 x C13).

HRMS (EI) m/z 281.1570 [calc’d for C₁₅H₂₅O₃Si (M+H\(^+\)) 281.1567].

IR \(\nu_{\max}:\) 3217, 2984-2871, 2164, 1734, 1244, 1203-1157, 835, 755 cm\(^{-1}\).
Pale yellow oil

$^1$H NMR (C$_6$D$_6$, 300 MHz): 4.22-4.14 (m, 1H, H2), 4.12-4.04 (dq, $J = 2.2$ Hz, 7.2 Hz, 2H, H9), 2.31-2.26 (m, 1H, H6), 2.10 (d, $J = 6.4$ Hz, 1H, H7), 1.92 (br s, 1H, OH), 1.47-1.29 (m, 2H, H3' and H5'), 1.05 (t, $J = 7.2$ Hz, H10), 0.9-0.90 (m, 2H, H4' and H5), 0.88-0.71 (m, 2H, H3 and H4), 0.23 (s, 9H, H13).

$^{13}$C NMR (C$_6$D$_6$, 75 MHz): 169.9 (C, C8), 108.1 (C, C12), 84.3 (C, C11), 70.1 (CH, C2), 60.7 (CH$_2$, C9), 30.1 (CH, C6 or C7), 29.9 (CH, C6 or C7), 29.5 (C, C1), 29.2 (CH$_2$, C3), 21.5 (CH$_2$, C5), 18.7 (CH$_2$, C4), 14.5 (CH$_3$, C10), 0.3 (CH$_3$, 3 x C13).

HRMS (EI) m/z 281.1571 [calc'd for C$_{15}$H$_{24}$O$_3$Si (M+H$^+$) 281.1567].

IR $\nu_{max}$: 3433, 2939-2868, 2162, 1733, 1192-1160, 838, 758 cm$^{-1}$. 

C$_{15}$H$_{24}$O$_3$Si
MW = 280.43 g mol$^{-1}$
Preparation of (±)-(1S,2R,6S,7S)-ethyl 2-(tert-butyldimethylsilyloxy)-1-((trimethylsilyl) ethynyl)bicyclo[4.1.0]heptane-7-carboxylate (18a):

To a solution of alcohol 17a (1.550 g, 5.52 mmol, 1 equiv) in dry CH$_2$Cl$_2$ (24 mL) were added imidazole (0.790 g, 11.61 mmol, 2.1 equiv) followed by tert-butyldimethylsilyl chloride (1.25 g, 8.3 mmol, 1.5 equiv) 10 min later. The reaction was stirred at room temperature for several hours. The reaction mixture was then diluted with water and extracted with Et$_2$O. The combined organic layers were washed with water, dried over MgSO$_4$, filtered and concentrated in vacuo. Purification by flash chromatography (10 % Et$_2$O-PE, + 1% Et$_3$N) afforded 2.12 g (quantitative yield) of silylated ether 18a as a colorless oil.

Colorless oil

**Rf** (EP / Et$_2$O : 9 / 1) = 0.48

$^1$H NMR (C$_6$D$_6$, 300 MHz): 4.22-4.12 (m, 1H, H9'), 4.08-3.97 (m, 2H, H2 and H9), 2.26 (br t, J = 6.3 Hz, 1H, H6), 1.70-1.44 (m, 2H, H4 and H5), 1.57 (d, J = 6.3 Hz, 1H, H7), 1.30-1.18 (m, 2H, H3 and H4'), 1.07 (t, J = 7.0 Hz, 3H, H10), 1.04 (s, 9H, H16), 0.94-0.83 (m, 1H, H3'), 0.81-0.70 (m, 1H, H5'), 0.26 (s, 3H, H14), 0.25 (s, 9H, H13), 0.07 (s, 3H, H14).

$^{13}$C NMR (C$_6$D$_6$, 75 MHz): 169.2 (C, C8), 107.2 (C, C12), 84.3 (C, C11), 67.8 (CH, C2), 60.6 (CH$_2$, C9), 33.1 (CH, C7), 29.3 (CH$_2$, C3), 28.9 (C, C1), 27.5 (CH, C6), 26.3 (CH$_3$, 3 x C16), 22.8 (C, C15), 20.8 (CH$_2$, C4), 14.7 (CH$_2$, C5), 14.6 (CH$_3$, C10), 0.4 (CH$_3$, 3 x C13), -4.1 (CH$_3$, C14'), -4.5 (CH$_3$, C14).

HRMS (EI) m/z 395.2437 [calc'd for C$_{21}$H$_{39}$O$_3$Si$_2$ (M+H$^+$) 395.2432].

IR $\nu_{max}$: 2952-2859, 2168, 1739, 1249, 1179-1156, 1098-1074, 836, 775-761 cm$^{-1}$.
Preparation of (±)-(1S,2S,6S,7S)-ethyl2-(tert-butyldimethylsilyloxy)-1-((trimethylsilyl) ethynyl)bicyclo[4.1.0]heptane-7-carboxylate (18b):

Same procedure as described for 18a.

Silylated ester 18b was obtained as a colorless oil in a quantitative manner.

![Chemical Structure](image)

C₂₁H₃₈O₃Si₂

MW = 394.70 g mol⁻¹

**Colorless oil**

Rf (EP / Et₂O : 9 / 1) = 0.76

¹H NMR (C₆D₆, 400 MHz): 4.36 (t, J = 5.5 Hz, 1H, H2), 4.24-4.16 (m, 1H, H9'), 4.01-3.93 (m, 1H, H9), 2.30 (dt, J = 1.5 Hz and 6.8 Hz, 1H, H6), 2.21 (d, J = 6.8 Hz, 1H, H7), 1.47-1.37 (m, 1H, H5'), 1.27-1.13 (m, 2H, H3' and H5'), 1.09 (t, J = 7.3 Hz, 3H, H10), 1.06 (s, 9H, H16), 1.03-0.94 (m, 2H, H4' and H3), 0.87-0.76 (m, 1H, H4), 0.32 (s, 3H, H14), 0.24 (s, 9H, H13), 0.16 (s, 3H, H14).

¹³C NMR (C₆D₆, 100 MHz): 169.7 (C, C8), 109.1 (C, C12), 84.0 (C, C11), 70.4 (CH, C2), 60.4 (CH₂, C9), 31.4 (CH₂, C3), 29.7 (CH, C6 or C7), 29.6 (CH, C6 or C7), 29.0 (C, C1), 26.2 (CH₃, 3 x C16), 21.7 (CH₂, C5), 18.4 (C, C15), 17.0 (CH₂, C4), 14.7 (CH₃, C10), 0.3 (CH₃, 3 x C13), -4.1 (CH₃, C14'), -4.5 (CH₃, C14).

HRMS (EI) m/z 395.2438 [calc'd for C₂₁H₃₉O₃Si₂ (M+H⁺) 395.2432].

IR νmax: 2936-2856, 2164, 1736, 1248, 1191-1160, 1096, 834, 775-760 cm⁻¹.
Preparation of the (±)-(E)-ethyl 3-((1S,2R,6S,7S)-2-(tert-butylidimethylsilyloxy)-1-((trimethylsilyl)ethynyl)bicyclo[4.1.0]heptan-7-yl)acrylate (20a):

To a cooled (-78°C) solution of ester 18a (1.450 g, 3.67 mmol, 1 equiv) in THF (51 mL) was slowly added diisobutylaluminium hydride (8.45 mL, 8.45 mmol, 2.3 equiv, 1M in hexane). The reaction mixture was stirred at that temperature for several hours until completion of the reaction by TLC. The solution was quenched with successive addition of 2 M HCl and ethyl acetate. The aqueous phase was extracted with ethyl acetate and the combined organic layers were washed with brine. The organic layers were dried over sodium sulfate, filtered and concentrated in vacuo. The crude alcohol (c. 100 %) was used without further purification.

Colorless oil

1H NMR (C6D6, 300 MHz): 3.99 (dd, J = 3.2 and 4.7 Hz, 1H, H2), 3.87 (br dd, J = 5.3 and 11.7 Hz, 1H, H8), 3.64 (dd, J = 8.1 and 11.7 Hz, 1H, H8), 1.90 (br s, 1H, OH), 1.74-1.49 (m, 2H, H3 and H5), 1.36-1.17 (m, 3H, H4, H5’ and H7), 1.06 (s, 9H, H14), 1.00-0.95 (m, 1H, H4’), 0.90-0.81 (m, 2H, H3’ and H6), 0.27 (s, 3H, H12), 0.18 (s, 9H, H11), 0.11 (s, 3H, H12).

13C NMR (C6D6, 75 MHz): 111.6 (C, C10), 82.9 (C, C9), 71.2 (CH, C2), 64.2 (CH2, C8), 31.2 (CH2, C4), 29.8 (CH, C6), 29.2 (CH, C7), 26.2 (CH3, 3 x C14), 24.3 (C, C1), 22.6 (CH2, C5), 19.0 (CH2, C3), 18.4 (C, C13), 0.2 (CH3, 3 x C11), -4.0 (CH3, C12’), -4.3 (CH3, C12).
To a stirred solution of the crude alcohol (3.67 mmol, 1 equiv) in dry CH₂Cl₂ (60 mL) were added sodium bicarbonate (0.802 g, 9.55 mmol, 2.6 equiv) and then Dess Martin periodinane (2.337 g, 5.51 mmol, 1.5 equiv). After 2 h at room temperature, the reaction mixture was quenched with a 1:1 mixture of an aqueous saturated solution of sodium thiosulfate and an aqueous saturated solution of sodium bicarbonate. The aqueous phase was extracted with Et₂O and the combined organic layers were washed with brine, dried over MgSO₄, filtered and concentrated in vacuo to give the aldehyde 19a (c. quant.) as a colourless oil.

Colorless oil

\[
\text{Rf (EP} \text{/ Et}_2\text{O : 9 / 1) = 0.36}
\]

\(^1\text{H NMR (C}_6\text{D}_6, 300 MHz):\) 9.30 (d, \(J = 6.2\) Hz, 1H, H8), 3.80 (br t, \(J = 3.6\) Hz, 1H, H2), 1.74-1.78 (m, 1H, H6), 1.63-1.43 (m, 2H, H5), 1.40 (t, \(J = 6.0\) Hz, 1H, H7), 1.23-1.13 (m, 1H, H3'), 1.02 (s, 9H, H14), 0.98-0.92 (m, 1H, H4), 0.66-0.80 (m, 2H, H3 and H4'), 0.22 (s, 3H, H12), 0.15 (s, 9H, H11), 0.05 (s, 3H, H12).

\(^{13}\text{C NMR (C}_6\text{D}_6, 75 MHz):\) 199.0 (C, C8), 106.7 (C, C10), 86.0 (C, C9), 67.1 (CH, C2), 39.4 (CH, C7), 28.9 (CH₂, C4), 28.4 (CH, C6), 28.1 (C, C1), 26.2 (CH₃, 3 x C14), 20.9 (CH₂, C5), 18.5 (C, C13), 14.5 (CH₂, C3), 0.1 (CH₃, 3 x C11), -4.2 (CH₃, C12), -4.5 (CH₃, C12).
To a cooled (0°C) solution of triethylphosphonoacetate (2.19 mL, 11.02 mmol, 3 equiv) in THF (30 mL) was slowly added sodium hydride (0.441 g, 11.02 mmol, 3 equiv, 60% in oil). The reaction was stirred at room temperature for 1 h and thereafter cooled down to -78°C. A solution of the crude aldehyde 19a (3.67 mmol, 1 equiv) in THF (30 mL) was then transferred via canula and the resulting mixture was stirred at -78°C for 1 h. The solution was slowly allowed to stir at room temperature for several hours, until completion of the reaction by TLC. The mixture was quenched with a saturated aqueous solution of NH₄Cl, and diluted with ethyl acetate. The layers were separated. The combined organic layers were washed with water followed by brine, dried over magnesium sulfate, filtered and concentrated in vacuo. The residue was purified by flash chromatography (5% Et₂O–PE, +1% Et₃N) to give ester 20a (1.51 g, 98% over 3 steps, E/Z: 100/0) as a colorless oil.

Colorless oil

Rf (EP / Et₂O : 9 / 1) = 0.81

¹H NMR (C₆D₆, 300 MHz): 7.17 (dd, J = 9.9 Hz and 15.6 Hz, H8), 6.02 (d, J = 15.6 Hz, H9), 4.16-4.06 (m, 2H, H11), 3.94 (br t, J = 3.8 Hz, 1H, H2), 1.65-1.49 (m, 2H, H4 and H5), 1.44-1.38 (m, 1H, H6), 1.33-1.24 (m, 1H, H3), 1.19-1.14 (m, 1H, H5'), 1.12 (br s, 1H, H7), 1.05 (s, 9H, C18), 1.04 (t, J = 7.2 Hz, 3H, H12), 0.99-0.76 (m, 2H, H3' and H4'), 0.27 (s, 3H, H16), 0.26 (s, 9H, H15), 0.10 (s, 3H, H16).

¹³C NMR (C₆D₆, 75 MHz): 165.8 (C10), 149.6 (CH, C8), 121.1 (CH, C9), 108.8 (C, C14), 85.2 (C, C13), 67.4 (CH, C2), 60.0 (CH₂, C11), 32.6 (CH, C7), 31.2 (CH, C6), 29.7 (C, C1), 29.3 (CH₂, C3), 26.2 (CH₃, 3 x C18), 21.5 (CH₂, C5), 18.6 (C, C17), 14.8 (CH₂, C4), 14.5 (CH₃, C12), 0.3 (CH₃, 3 x C15), -4.0 (CH₃, C16'), -4.4 (CH₃, C16).

HRMS (EI) m/z 421.2590 [calc'd for C₂₃H₄₁O₃Si₂ (M+H') 421.2589].

IR νmax: 2951-2853, 2159, 1706, 1261-1247, 1087, 1053-1046, 835, 781-757 cm⁻¹.
Preparation of the \((\pm)-(E)\)-ethyl 3-\(((1S,2S,6S,7S)-2-((\text{tert-butyl})\text{dimethyl}silyloxy)-1-((\text{trimethyl}silyl)\text{ethynyl})\text{bicyclo}[4.1.0]\text{heptan-7-yl})\text{acrylate (20b)}:

Same procedure as described for 20a.
Ester 20b was obtained in 96% yield over 3 steps.

\[
\begin{align*}
\text{Colorless oil} & \quad \text{Rf (EP / Et}_2\text{O : 9 / 1) = 0.17} \\
\text{1H NMR (C}_6\text{D}_6, 300 MHz):} & \quad 4.27 (\text{dd}, J = 5.5 \text{ Hz and 7.2 Hz, 1H, H2}), 3.85-3.93 (\text{m, 1H, H8}), 3.65-3.73 (\text{m, 1H, H8’}), 1.69 (\text{s, 1H, OH}), 1.36-1.55 (\text{m, 2H, H3 and H4}), 1.32-1.36 (\text{m, 1H, H7}), 1.25-1.30 (\text{m, 1H, H6}), 1.09-1.18 (\text{m, 2H, H4’ and H5}), 1.03 (\text{s, 9H, H14}), 0.81-0.95 (\text{m, 2H, H3’ and H5’}), 0.27 (\text{s, 3H, H12}), 0.19 (\text{s, 9H, H11}), 0.14 (\text{s, 3H, H12}).
\end{align*}
\]

\[
\begin{align*}
\text{13C NMR (C}_6\text{D}_6, 75 MHz):} & \quad 111.6 (\text{C, C10}), 82.9 (\text{C, C9}), 71.2 (\text{CH, C2}), 64.2 (\text{CH}_2, \text{C8}), 31.2 (\text{CH}_2, \text{C3}), 29.8 (\text{CH, C7}), 29.2 (\text{CH, C6}), 26.2 (\text{CH}_3, 3 \times \text{C14}), 24.3 (\text{C, C1}), 22.6 (\text{CH}_2, \text{C4}), 19.0 (\text{CH}_2, \text{C5}), 18.4 (\text{C, C13}), 0.2 (\text{CH}_3, 3 \times \text{C11}), -4.0 (\text{CH}_3, \text{C12}), -4.3 (\text{CH}_3, \text{C12’}).
\end{align*}
\]
Colorless oil  

**Rf (EP / Et₂O : 9 / 1) = 0.51**

**1H NMR (C₆D₆, 300 MHz):** 9.36 (d, J = 6.0 Hz, 1H, H8), 4.24 (br t, J = 5.6 Hz, 1H, H2), 2.09 (br t, J = 6.0 Hz, 1H, H7), 1.84 (dt, J = 1.5 and 6.8 Hz, 1H, H6), 1.30-1.39 (m, 1H, H5'), 1.12-1.20 (m, 1H, H5), 1.02-1.06 (m, 1H, H3'), 1.00 (s, 9H, H14), 0.87-0.97 (m, 2H, H4' and H3), 0.74-0.82 (m, 1H, H4), 0.25 (s, 3H, H12), 0.16 (s, 9H, H11), 0.12 (s, 3H, H12).

**13C NMR (C₆D₆, 75 MHz):** 198.4 (C, C8), 108.3 (C, C10), 85.5 (C, C9), 70.7 (CH, C2), 36.5 (CH, C7), 31.1 (CH₂, C4), 30.2 (CH, C6), 28.5 (C, C1), 26.1 (CH₃, 3 x C14), 21.7 (CH₂, C5), 18.3 (C, C13), 17.0 (CH₂, C3), 0.1 (CH₃, 3 x C11), -4.0 (CH₃, C12), -4.6 (CH₃, C12).
Colorless oil

\[ \text{Rf (EP / Et}_2\text{O : 9 / 1) = 0.86} \]

\[ \text{1H NMR (C}_6\text{D}_6, 300 MHz): 7.17 (dd, } J = 10.0 \text{ Hz and 15.5 Hz, H8), 6.12 (d, } J = 15.5 \text{ Hz, H9), 4.33 (br t, } J = 5.5 \text{ Hz, 1H, H2), 4.10-3.98 (m, 2H, H11), 1.92 (dd, } J = 5.8 \text{ Hz and 10.0 Hz, 1H, H7), 1.49-1.36 (m, 2H, H5 and H6), 1.26-1.16 (m, 2H, H3 and H5'), 1.11-1.04 (m, 2H, H4 and H3'), 0.99 (t, } J = 7.0 \text{ Hz, 3H, H12), 0.98 (s, 9H, C18), 0.90-0.77 (m, 1H, H4'), 0.25 (s, 9H, H15), 0.23 (s, 3H, H16), 0.13 (s, 3H, H16).} \]

\[ \text{13C NMR (C}_6\text{D}_6, 75 MHz): 165.9 (C10), 149.7 (CH, C8), 121.3 (CH, C9), 110.3 (C, C14), 84.6 (C, C13), 70.5 (CH, C2), 60.0 (CH₂, C11), 33.1 (CH, C6), 31.4 (CH₂, C3), 30.2 (C, C1), 29.5 (CH, C7), 26.1 (CH₃, 3 x C18), 22.3 (CH₂, C5), 18.3 (C, C17), 17.1 (CH₂, C4), 14.4 (CH₃, C12), 0.3 (CH₃, 3 x C15), -3.9 (CH₃, C16), 4.6 (CH₃, C16').} \]

\[ \text{HRMS (EI) m/z 421.2593 [calc'd for C}_{23}\text{H}_{41}\text{O}_3\text{Si}_2 (M+H') 421.2589].} \]

\[ \text{IR } \nu_{\text{max}}: 2956-2835, 2160, 1717, 1646, 1249, 1088, 834, 775-758 \text{ cm}^{-1}.} \]
Preparation of the (±)-(E)-3-((1S,2R,6S,7S)-2-(tert-butylidimethylsilyloxy)-1-((trimethylsilyl)ethynyl)bicyclo[4.1.0]heptan-7-yl)prop-2-en-1-ol (21a):

To a cooled (-78°C) solution of ester 20a (1.33 g, 3.16 mmol, 1 equiv) in THF (41 mL) was slowly added diisobutylaluminium hydride (7.27 mL, 7.27 mmol, 2.3 equiv, 1M in hexane). The reaction mixture was stirred at that temperature for several hours, until completion of the reaction by TLC. The solution was quenched with successive addition of 2 M HCl and ethyl acetate. The aqueous phase was extracted with ethyl acetate and the combined organic layers were washed with brine. The organic layers were dried over sodium sulfate, filtered and concentrated in vacuo. The crude alcohol (c. 100 %) was used without further purification.

Colorless oil

1H NMR (C6D6, 400 MHz): 5.76-5.62 (m, 2H, H8 and H9), 4.04 (br t, J = 4.0 Hz, 1H, H2), 3.98 (d, J = 4.3 Hz, 2H, H10), 1.81-1.69 (m, 1H, H5), 1.67-1.56 (m, 1H, H4), 1.39-1.32 (m, 2H, H3 and H6), 1.29-1.23 (m, 1H, H5’), 1.22-1.17 (m, 1H, H7), 1.08 (s, 9H, H16), 1.03-0.99 (m, 1H, H3’), 0.93-0.85 (m, 1H, H4’), 0.75 (br s, 1H, OH), 0.29 (s, 3H, H14), 0.24 (s, 9H, H13), 0.13 (s, 3H, H14’).

13C NMR (C6D6, 100 MHz): 132.2 (CH, C8), 130.2 (CH, C9), 110.0 (C, C12), 84.1 (C, C11), 67.8 (CH, C2), 63.7 (CH2, C10), 32.5 (CH, C7), 29.6 (CH, C6), 29.5 (CH2, C3), 27.7 (C, C1), 26.3 (CH3, 3 x C16), 21.7 (CH2, C5), 18.7 (C, C15), 15.1 (CH2, C4), 0.5 (CH3, 3 x C13), -4.1 (CH3, C14), -4.4 (CH3, C14’).

IR νmax: 3312, 3003-2857, 2162, 1664, 1249, 1089, 1012, 836, 774-759 cm⁻¹.
To a solution of the crude alcohol (3.16 mmol, 1 equiv) in dry CH₂Cl₂ (9 mL) were added imidazole (0.452 g, 6.64 mmol, 2.1 equiv) followed by tert-butyldimethylsilyl chloride (0.715 g, 4.74 mmol, 1.5 equiv) 10 min later. The reaction was stirred at room temperature for several hours. The reaction mixture was then diluted with water and extracted with Et₂O. The combined organic layers were washed with water, dried over MgSO₄, filtered and concentrated in vacuo. Purification by flash chromatography (10 % Et₂O-PE, + 1% Et₃N) afforded 1.37 g (88% over 2 steps) of silylated ether 21a as a colorless oil.

**Colorless oil**

Rf (EP / Et₂O : 9 / 1) = 0.94

**¹H NMR** (C₆D₆, 300 MHz): 5.85-5.72 (m, 2H, H₈ and H₉), 4.30-4.18 (m, 2H, H₁₀), 4.01 (dd, J = 3.0 Hz and 4.5 Hz, 1H, H₂), 1.79-1.67 (m, 1H, H₅), 1.64-1.53 (m, 1H, H₄), 1.39-1.34 (m, 2H, H₆), 1.33-1.28 (m, 1H, H₃), 1.26-1.21 (m, 2H, H₇ and H₅‘), 1.07 (s, 9H, H₁₆ or H₁₉), 1.06-1.04 (m, 1H, H₃‘), 1.01 (s, 9H, H₁₆ or H₁₉), 0.92-0.82 (m, 1H, H₄‘), 0.29 (s, 3H, H₁₄ or H₁₇), 0.26 (s, 9H, H₁₃), 0.13 (s, 6H, H₁₄ or H₁₇), 0.12 (s, 3H, H₁₄‘ or H₁₇‘).

**¹³C NMR** (C₆D₆, 75 MHz): 131.3 (CH, C₈), 130.3 (CH, C₉), 110.0 (C, C₁₂), 83.9 (C, C₁₁), 67.9 (CH, C₂), 64.4 (CH₂, C₁₀), 32.7 (CH, C₇), 29.7 (CH, C₆), 29.6 (CH₂, C₃), 27.5 (C, C₁), 26.3 (CH₃, 3 x C₁₆ and 3 x C₁₉), 21.7 (CH₂, C₅), 18.7 (C, C₁₅ and C₁₈), 15.2 (CH₂, C₄), 0.6 (CH₃, 3 x C₁₃), -4.0 (CH₃, C₁₇), -4.4 (CH₃, C₁₇‘), -4.8 (CH₃, C₁₄ and C₁₄‘).

**HRMS** (EI) m/z 493.3350 [calc’d for C₂₇H₅₃O₂Si₃ (M+H⁺) 493.3348].

**IR** νₘₐₓ: 2953-2858, 2161, 1669, 1250, 1100, 1054, 834, 775-761 cm⁻¹.

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C₂₇H₅₂O₂Si₃

MW = 492.96 g mol⁻¹
Preparation of \((\pm)-(E)-3-\{(1S,2S,6S,7S)-2-\text{((tertiary-butyl)dihydroxysilyloxy)-1-((trimethylsilyl)ethynyl)}\}\text{bicyclo[4.1.0]heptan-7-yl})\text{prop-2-en-1-ol} \text{ (28b)}:

Same procedure as described for 21a.
Silylated ether 21b was obtained in 87\% yield over 2 steps.

\[
\text{Colorless oil} \quad \text{Rf (EP / Et}_2\text{O : 9 / 1) = 0.34}
\]

\(^1\text{H NMR (C}_6\text{D}_6, 300 \text{ MHz):} \quad 5.79-5.66 \text{ (m, 2H, H8 and H9)}, \quad 4.40 \text{ (t, } J = 5.3 \text{ Hz, 1H, H2)}, \quad 3.93 \text{ (d, } J = 5.2 \text{ Hz, 2H, H10}), \quad 1.89 \text{ (dd, } J = 6.6 \text{ Hz and 7.9 Hz, 1H, H7)}, \quad 1.60-1.49 \text{ (m, 1H, H5)}, \quad 1.43-1.24 \text{ (m, 3H, H4, H5' and H6)}, \quad 1.20-1.09 \text{ (m, 2H, H3 and H4')}, \quad 0.97-0.88 \text{ (m, 1H, H3')}, \quad 1.04 \text{ (s, 9H, H16)}, \quad 0.29 \text{ (s, 3H, H14)}, \quad 0.23 \text{ (s, 9H, H13)}, \quad 0.18 \text{ (s, 3H, H14)}.

\(^{13}\text{C NMR (C}_6\text{D}_6, 75 \text{ MHz):} \quad 131.9 \text{ (CH, C8)}, \quad 130.7 \text{ (CH, C9)}, \quad 111.7 \text{ (C, C12)}, \quad 83.5 \text{ (C, C11)}, \quad 70.9 \text{ (CH, C2)}, \quad 63.6 \text{ (CH2, C10)}, \quad 31.6 \text{ (CH2, C4)}, \quad 31.6 \text{ (CH, C6)}, \quad 29.2 \text{ (CH, C7)}, \quad 27.2 \text{ (C, C1)}, \quad 26.2 \text{ (CH3, 3 x C16)}, \quad 22.5 \text{ (CH2, C5)}, \quad 18.4 \text{ (C, C15)}, \quad 17.5 \text{ (CH2, C3)}, \quad 0.4 \text{ (CH3, 3 x C13)}, \quad -3.8 \text{ (CH3, C14')}, \quad -4.5 \text{ (CH3, C14')}.

\text{IR } \nu_{\text{max}}: 3340, 3009-2856, 2158, 1668, 1247, 1089, 1012, 833, 774-758 \text{ cm}^{-1}.
Colorless oil

$^1$H NMR (C$_6$D$_6$, 300 MHz): 5.87-5.72 (m, 2H, H8 and H9), 4.41 (t, $J = 5.6$ Hz, 1H, H2), 4.24-4.11 (m, 2H, H10), 1.91 (br t, $J = 7.0$ Hz, 1H, H7), 1.8-1.47 (m, 1H, H5), 1.42-1.24 (m, 3H, H4, H5' and H6), 1.20-1.09 (m, 1H, H3), 1.05 (s, 9H, H16 or H19), 1.02 (s, 9H, H16 or H19), 0.13 (s, 6H, H14 or H17), 0.93-0.87 (m, 2H, H3' and H4'), 0.31 (s, 3H, H14 or H17), 0.26 (s, 9H, H13), 0.19 (s, 3H, H14 or H17).

$^{13}$C NMR (C$_6$D$_6$, 75 MHz): 130.9 (CH, C8), 130.6 (CH, C9), 111.8 (C, C12), 83.3 (C, C11), 71.1 (CH, C2), 64.2 (CH$_2$, C10), 31.6 (CH$_2$, C4), 31.6 (CH, C6), 29.4 (CH, C7), 27.1 (C, C1), 26.2 (CH$_3$, 3 x C16 et 3 x C19), 22.5 (CH$_2$, C5), 18.5 (C, C15 and C18), 17.5 (CH$_2$, C3), 0.5 (CH$_3$, 3 x C13), -3.8 (CH$_3$, C17), -4.5 (CH$_3$, C17'), 4.8 (CH$_3$, C14 and C14').

HRMS (EI) m/z 510.3615 [calc'd for C$_{27}$H$_{56}$NO$_3$Si$_3$ (M+NH$_4^+$) 510.3613].

IR $\nu_{\text{max}}$: 2953-2856, 2157, 1667, 1249, 1086, 1050, 832, 773-759 cm$^{-1}$. 
Preparation of (±)-tert-butyl((E)-3-((1S,2R,6S,7S)-2-(tert-butyldimethylsilyloxy)-1-ethynylbicyclo[4.1.0]heptan-7-yl)allyloxy)dimethylsilane (22a):

To a solution of compound 21a (0.1 g, 0.02 mol, 1 equiv) in Et₂O (4 mL) was added at room temperature, a solution of KOH in MeOH (1.6 mL, 3M, 24 equiv). After 1 hour, a solution of KOH in MeOH (1.6 mL, 3M, 24 equiv) was added again. The mixture was stirred at this temperature overnight. The residue was treated with a saturated aqueous solution of NH₄Cl and extracted three times with diethylether. The combined organic layers were dried over magnesium sulfate filtered and concentrated in vacuo. The residue was purified by flash chromatography (PE) to give 74 mg (87 %) of 22a as a pale yellow oil.

Pale yellow oil \[ \text{Rf (EP / Et}_2\text{O : 98 / 2) = 0.77} \]

Due to the poor stability of alkyne 22a, \(^1\)H NMR was the only analysis performed.

\(^1\)H NMR (C₆D₆, 400 MHz): 5.86-5.80 (m, 1H, H5 or H6), 5.74-5.68 (m, 1H, H5 or H6), 4.32-4.22 (m, 2H, H4), 3.94 (br t, \(J = 3.8\) Hz, 1H, H11), 1.73-1.52 (m, 2H, H13' and H7), 1.38 (s, 1H, H10), 1.36-1.20 (m, 4H, H12, H13 and H8), 1.12 (s, 9H, H33 or H36), 1.05 (s, 9H, H33 or H36), 1.01-0.95 (m, 1H, H14'), 0.90-0.81 (m, 1H, H14'), 0.38 (s, 3H, H31 or H34), 0.17 (s, 3H, H31 or H34), 0.17 (s, 3H, H31 or H34), 0.16 (s, 3H, H31 or H34).
Preparation of (±)-tert-butyl((E)-3-((1S,2S,6S,7S)-2-(tert-butyldimethylsilyloxy)-1-ethynylbicyclo[4.1.0]heptan-7-yl)allyloxy)dimethylsilane (22b):

Same procedure as described for 22a.
Alkyne 22b was obtained in a quantitative manner as a pale yellow oil.

Due to the poor stability of alkyne 22B, $^1$H NMR were the only analysis performed.

$^1$H NMR (C$_6$D$_6$, 400 MHz): 5.83-5.71 (m, 2H, H5 and H6), 4.38 (br t, $J = 5.3$ Hz, H11), 4.14 (br d, $J = 4.8$ Hz, H4), 1.93 (dd, $J = 6.5$ Hz and 8.3 Hz, 1H, H7), 1.85 (s, 1H, CH, H10), 1.55-1.48 (m, 1H, H13'), 1.38-1.25 (m, 4H, H12 or H14' and H13 and H12' and H6), 1.20-1.10 (m, 1H, H12 or H14'), 1.04 (s, 9H, H33 or H36), 1.02 (s, 9H, H33 or H36), 0.96-0.88 (m, 1H, H14), 0.40 (s, 6H, H31 or H34), 0.11 (s, 6H, H31 or H34).
**Key cascade reactions:**

**Preparation of 6-endo-dig product 24:**

Compound **22a** (0.088 g, 0.21 mmol, 1 equiv) and bromoacid **10** (0.063 g, 0.42 mmol, 2 equiv) were taken up in acetonitrile (2 mL) at 0 °C. After bubbling argon for 20 min, a solution of PdCl$_2$(PPh$_3$)$_2$ (0.007 g, 0.01 mmol, 0.05 equiv) and triphenylphosphine (0.005 g, 0.021 mmol, 0.1 equiv) in acetonitrile (2 mL) was added, followed by CuI (0.004 g, 0.021 mmol, 0.1 equiv) and triethylamine (0.12 mL, 0.84 mmol, 4 equiv). The resulting mixture was stirred at 25 °C for 2 days. The residue was diluted with ethyl acetate and a saturated aqueous solution of NH$_4$Cl. The layers were separated. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (10% AcOEt-PE) to afford 0.016 g (16 %) of the tricyclic compound **24** as an orange oil.

![Orange oil Rf (EP / AcOEt : 9 / 1) = 0.72](image)

**Orange oil**

**1H NMR** ($C_6D_6$, 300 MHz): 6.71 (d, $J = 10.0$ Hz, 1H, H1), 5.85 (dt, $J = 2.8$ and 11.7 Hz, 1H, H6), 5.68 (d, $J = 10.2$ Hz, 1H, H2), 5.32 (br d, $J = 2.5$, 4.0 and 11.7 Hz, 1H, H7), 5.09 (d, $J = 9.8$ Hz, 1H, H10), 4.59 (br s, 1H, H11), 4.01 (dd, $J = 5.3$, 9.8 Hz, 1H, H4), 3.80 (dd, $J = 3.2$ and 9.8 Hz, 1H, H4'), 3.50-3.63 (m, 1H, H8), 2.69-2.78 (m, 1H, H5), 1.63-1.95 (m, 4H, H12 and H13), 1.18-1.36 (m, 2H, H14), 0.99 (s, 9H, H33 or H36), 0.91 (s, 9H, H33 or H36), 0.19 (s, 3H, H31 or H34), 0.14 (s, 3H, H31 or H34), -0.03 (s, 3H, H31 or H34), -0.07 (s, 3H, H31 or H34).

**13C NMR** ($C_6D_6$, 75 MHz): 161.9 (C, C3), 149.8 (C, C19), 138.0 (CH, C1), 133.4 (CH, C7), 129.2 (CH, C6), 124.8 (C, C9), 116.7 (CH, C2), 78.3 (CH, C10), 68.8 (CH, C11), 62.8 (CH$_2$, C4), 45.9 (CH, C5), 40.6 (CH, C8), 36.7 (CH$_2$, C12 or C13), 35.6 (CH$_2$, C12 or C13), 26.2 (3 x CH$_3$, C33 or C36), 25.9 (3 x CH$_3$, C33 or C36), 20.9 (CH$_2$, C14), 18.6 (C, C32 or C35), 18.1 (C, C32 or C35), -4.4 (CH$_3$, C31 or C34), -4.7 (CH$_3$, C31 or C34), -5.2 (CH$_3$, C31 or C34), -5.3 (CH$_3$, C31 or C34).
HRMS (EI) m/z 508.3273 [calc’d for C_{27}H_{50}NO_4Si_2 (M+NH_4^+) 508.3273]

IR ν_{max}: 2955-2851, 1724, 1621, 1251, 1080, 1024-1004, 833, 773 cm^{-1}. 
Preparation of 5-exo-dig product 23:

Compound 22b (0.050 g, 0.12 mmol, 1 equiv) and acid 10 (0.036 g, 0.24 mmol, 2 equiv) were taken up in acetonitrile (2 mL) at 0 °C. After bubbling argon for 20 min, a solution of PdCl$_2$(PPh$_3$)$_2$ (0.004 g, 0.006 mmol, 0.05 equiv) and triphenylphosphine (0.003 g, 0.012 mmol, 0.1 equiv) in acetonitrile (2 mL) was added, followed by Cul (0.002 g, 0.012 mmol, 0.1 equiv), and triethylamine (0.066 mL, 0.47 mmol, 4 equiv). The resulting mixture was stirred at 25 °C for 2 days. The residue was diluted with ethyl acetate and an aqueous saturated solution of NH$_4$Cl. The different phases were separated and the aqueous layer extracted with ethyl acetate. The organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated in vacuo. The residue was purified by flash chromatography (10% AcOEt-PE) to afford 0.018 g (31%) of the spiro compound 23 as a pale orange oil.

![Image of chemical structure]

Pale orange oil

Rf (EP / AcOEt : 9 / 1) = 0.72

$^1$H NMR (C$_6$D$_6$, 400 MHz): 6.97 (d, $J = 5.5$ Hz, 1H, H1), 6.06 (s, 1H, H19), 5.72 (ddd, $J = 3.0$, 4.0 and 12.0 Hz, 1H, H6), 5.54 (d, $J = 5.3$ Hz, 1H, H2), 5.30 (dt, $J = 2.8$ and 12.0 Hz, 1H, H7), 3.82 (dd, $J = 4.4$ and 10.8 Hz, 1H, H11), 3.61 (d, $J = 5.0$ Hz, 2H, H4), 3.15-3.10 (m, 1H, H5), 2.43-2.40 (m, 1H, H8), 1.91-1.87 (m, 1H, H12), 1.52-1.45 (m, 2H, H13 and H14), 1.36-1.24 (m, 1H, H12'), 1.23-1.13 (m, 1H, H13'), 1.06-0.99 (m, 1H, H14'), 0.97 (s, 9H, H33 or H36), 0.89 (s, 9H, H33 or H36), 0.10 (s, 3H, H31 or H34), 0.04 (s, 3H, H31 or H34), -0.04 (s, 3H, H31 or H34), -0.05 (s, 3H, H31 or H34).

$^{13}$C NMR (C$_6$D$_6$, 100 MHz): 171.9 (C, C3), 157.5 (CH, C1), 144.8 (C, C9), 133.9 (CH, C7), 126.5 (CH, C6), 122.4 (CH, C19), 119.2 (CH, C2), 89.3 (C, C10), 74.4 (CH, C11), 62.1 (CH$_2$, C4), 47.4 (CH, C5), 43.0 (CH, C8), 38.4 (CH$_2$, C12 or C13), 36.3 (CH$_2$, C14), 26.1 (3 x CH$_3$, C33 or C36), 26.0 (3 x CH$_3$, C33 or C36), 24.3 (CH$_2$, C12 or C13), 18.5 (C, C32 or C35), 18.4 (C, C32 or C35), -4.7 (CH$_3$, C31 or C34), -4.8 (CH$_3$, C31 or C34), -5.5 (CH$_3$, C31 or C34), -5.6 (CH$_3$, C31 or C34).

HRMS (EI) m/z 508.3265 [calc’d for C$_{27}$H$_{50}$NO$_5$Si$_2$ (M+NH$_4^+$) 508.3273]
IR $\nu_{\text{max}}$: 2951-2856, 1755, 1598, 1251, 1116, 1074, 826, 773 cm$^{-1}$.
Preparation of the ABCD skeleton 25:

To a cooled (0°C) solution of compound 23 (0.061 g, 0.12 mmol, 1 equiv) in THF (3 mL) was added tetrabutylammonium fluoride (0.3 mL, 0.30 mmol, 1M in THF, 2.5 equiv). The solution was slowly allowed to warm to room temperature for three hours. The residue was treated with a saturated aqueous solution of NH₄Cl and extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over sodium sulfate, filtered and concentrated in vacuo. The residue was purified by flash chromatography (30% Et₂O-PE) to give 21 mg (64 %) of 25 as a pale yellow oil.

Pale yellow oil

\[ \text{Rf} \ (\text{EP} / \text{AcOEt} : 7 / 3) = 0.17 \]

\(^1\text{H NMR} \ (\text{C}_6\text{D}_6, 400 \text{ MHz}): \]

- 5.74 (s, 1H, H19), 5.18 (dt, \( J = 3.3 \) and 12.5 Hz, 1H, H7), 5.03 (dt, \( J = 2.5 \) and 12.5 Hz, 1H, H6), 4.14 (d, \( J = 4.5 \) Hz, 1H, H1), 3.91 (dd, \( J = 4.5 \) and 8.3 Hz 1H, H4), 3.53-3.49 (m, 1H, H4’), 3.47 (d, \( J = 8.5 \) Hz, 1H, H11), 2.90 (br s, 1H, H5), 2.41-2.21 (m, 3H, H8 and H2), 1.88-1.81 (m, 1H, H12), 1.42-1.36 (m, 3H, OH, H13), 1.15-1.04 (m, 2H, H12’ and H14), 0.97-0.87 (m, 1H, H14’).

\(^{13}\text{C NMR} \ (\text{C}_6\text{D}_6, 100 \text{ MHz}): \]

- 174.8 (C, C3), 146.3 (C, C9), 133.9 (CH, C7), 126.9 (CH, C6), 116.7 (CH, C19), 95.1 (C, C10), 83.5 (CH, C1), 76.1 (CH₂, C4), 73.0 (CH, C11), 47.9 (CH, C5), 42.6 (CH, C8), 37.1 (CH₂, C12), 36.7 (CH₂, C2), 35.1 (CH₂, C13), 23.9 (CH₂, C14).

\( \text{HRMS (EI) m/z 263.1279 [calc’d for C}_{13}\text{H}_{19}\text{O}_{4} (\text{M+H}^+) 263.1278] \)

\( \text{IR } \nu_{\text{max}}: \) 3396, 2957-2852, 1772, 1209-1193, 1041, 964-942, 842 cm\(^{-1}\).