

Supporting information

Diastereoselective sp^2 - sp^3 coupling of sugar enol ethers with unactivated cycloalkenes: new entries to C-branched sugars

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<u>Table of Contents</u>	<u>Page no.</u>
General Information	S2
Experimental procedures.	S2
General procedure for the preparation of 3a-3p, 4a-4c, 5a-5c, 6a, 7a.	S2
General procedure for the preparation of 8a, 8b.	S2
Spectral data of respective compounds (3a-3p, 4a-4c, 5a-5c, 6a, 7a, 8a-8b).	S3-S12
¹ H and ¹³ C NMR Spectra of compounds (3a-3p, 4a-4c, 5a-5c, 6a, 7a, 8a-8b).	S13-S34

General information

^1H and ^{13}C NMR spectra were recorded on 400 and 500 MHz spectrometers with TMS as internal standard. Chemical shifts are expressed in parts per million (δ ppm). Silica gel coated aluminium plates were used for TLC. The products were purified by column chromatography on silica gel (60-120 mesh) using petroleum ether–ethyl acetate as the eluent to obtain the pure products. Exact mass of all products were analysed by using HRMS having QTOF analyser. Reagents used were mostly purchased from Sigma Aldrich. Diastereoisomeric ratio of each compound is calculated on the basis of ^1H NMR.

Experimental procedures:-

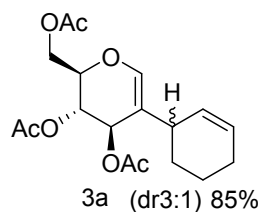
a) General procedure for the preparation of 3a-3p, 4a-4c, 5a-5c, 6a-7a.

TO a solution glycal (1equiv.), palladium diacetate (0.1equiv) and silver acetate(2.5equiv) in dimethylformamide(DMF) and dimethylsulphoxide(DMSO)(10:1) at 80 °C, under open air condition add cycloalkene (1.5equiv) drop wise. The mixture was allowed to stir at 80 °C for 24 hrs. Then the mixture was diluted with ethyl acetate (2 mL), filtered, washed with water (5 mL) and brine (5 mL). The organic layer was evaporated and the residue was purified by flash column chromatography (Hexane/EtOAc) (6:1) to afford the product as colorless oil.

b) General procedure for the preparation of 8a, 8b.

To a solution of **8** (1 equiv.), palladium diacetate (0.1equiv) and silver acetate(2.5equiv) in dimethylformamide (2 mL) and dimethylsulphoxide (0.2 mL) at 80 °C, under open air conditions add cycloalkene (1.5equiv) dropwise. The mixture was allowed to stir at 80 °C for 24 hrs. Then the mixture was diluted with ethyl acetate (2 mL), filtered nad washed with water (5 mL) followed by brine (5 mL). The organic layer was evaporated and the residue was purified by flash column chromatography (Hexane/EtOAc)(7:1) to afford the product as white solid.

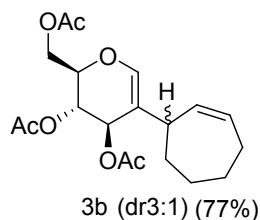
Spectral data of respective compounds (3a-3p, 4a-4c, 5a-5c, 6a,7a, 8a-8b).



¹H NMR (400 MHz, CDCl₃): δ 6.37 (s, H1 minor isomer), 6.27 (s, H1 major isomer), 5.85 – 5.79 (m, 1H), 5.73 – 5.66 (m, 1H), 5.60 – 5.47 (m, 1H), 5.23 – 5.15 (m, 1H), 4.44 – 4.37 (m, 1H), 4.22 – 4.15 (m, 2H), 2.71 (m, 1H), 2.09 (s, 3H), 2.06 (s, 6H), 1.73 (dd, *J* = 9.0, 2.6 Hz, 1H), 1.64 (m, 1H), 1.41 (m, 1H), 1.29 (m, 1H), 1.25 (m, 2H).

¹³C NMR (126 MHz, CDCl₃): δ 170.8, 170.7, 169.8, 143.1, 129.5, 127.5, 113.8, 73.6, 73.4, 68.1, 67.5, 61.6, 33.1, 29.7, 29.6, 27.6, 27.8, 25.1, 21.0, 20.9, 20.8, 20.8, 19.3.

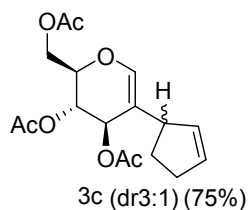
HRMS (ESI⁺): *m/z* calcd. for C₁₈H₂₄NaO₇ (M+Na)⁺ 375.1414, found 375.1424.



¹H NMR (400 MHz, CDCl₃): δ 6.40 (s, H1 minor isomer), 6.37 (s, H1 major isomer), 5.85 – 5.72 (m, 1H), 5.62 – 5.49 (m, 2H), 5.17 (m, 1H), 4.44 – 4.36 (m, 1H), 4.21 (m, 2H), 2.88 (m, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 2.05 (m, 3H), 1.70 (m, 2H), 1.60 – 1.53 (m, 2H), 1.27 (m, 4H).

¹³C NMR (126 MHz, CDCl₃): δ 170.6, 170.4, 169.7, 142.6, 141.7, 136.1, 133.2, 132.6, 131.2, 114.7, 114.1, 112.8, 68.0, 67.9, 67.6, 67.3, 61.5, 61.4, 40.5, 39.2, 32.4, 31.9, 31.6, 30.2, 29.7, 29.6, 29.3, 28.4, 28.2, 27.8, 26.9, 26.6, 22.7, 20.9, 20.9, 20.8, 20.7, 14.1.

HRMS (ESI⁺): *m/z* calcd. for C₁₉H₂₆NaO₇ (M+Na)⁺ 389.1571, found 389.1560.

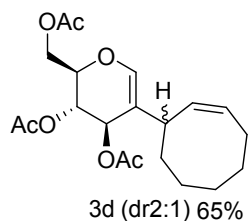


¹H NMR (400 MHz, CDCl₃): δ 6.33 (s, H1 minor isomer), 6.28 (s, H1 major isomer), 5.90 – 5.72 (m, 1H), 5.58 – 5.48 (m, 2H), 5.20 – 5.13 (m, 1H), 4.41 – 4.37 (m, 1H), 4.24 – 4.13 (m,

2H), 3.27 – 3.20 (m, 1H), 2.39 – 2.24 (m, 2H), 2.10 – 2.08 (m, 3H), 2.07 – 2.06 (m, 6H), 2.04 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 170.6, 170.5, 169.7, 141.4, 140.9, 132.9, 131.5, 131.0, 113.9, 73.5, 68.0, 61.54, 43.8, 31.8, 30.7, 20.9, 20.8, 20.7.

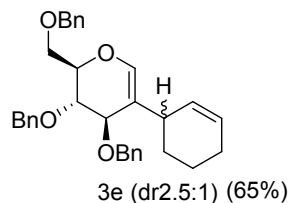
HRMS (ESI⁺): m/z calcd. for C₁₇H₂₂Na O₇ (M+Na)⁺ 361.1263, found 361.1267.



¹H NMR (400 MHz, CDCl₃) : δ 6.34 (s, H1 major isomer), 6.29 (s, H1 minor isomer), 5.62 (m, 1H), 5.47 (m, 1H), 5.28 – 5.20 (m, 1H), 5.16 – 5.05 (m, 1H), 4.37 – 4.28 (m, 1H), 4.17 – 4.11 (m, 1H), 4.10 – 4.03 (m, 1H), 3.06 (m, 1H), 2.02 (m, 4H), 2.00 (s, 3H), 1.99 – 1.97 (s, 6H), 1.95 (m, 2H), 1.64 – 1.57 (m, 2H), 1.55 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) : δ 170.6, 170.3, 169.6, 141.5, 140.8, 132.7, 132.3, 131.1, 129.2, 114.5, 114.3, 73.4, 68.4, 68.2, 61.5, 35.7, 34.6, 32.5, 31.6, 29.7, 29.6, 29.5, 26.7, 26.6, 26.5, 26.4, 25.6, 25.4, 22.6, 20.9, 20.8, 20.7, 14.0.

HRMS (ESI⁺) : m/z calcd. for C₂₀H₂₈NaO₇ (M+Na)⁺ 403.1733, found 403.1730.

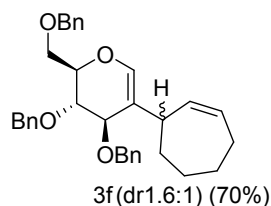


¹H NMR (400 MHz, CDCl₃) : δ 7.38 – 7.28 (m, 15H), 6.27 (s, H1 major isomer), 6.21 (s, H1 minor isomer), 5.70 (m, 1H), 5.56 (m, 1H), 4.72 (m, 1H), 4.65 (m, 2H), 4.56 (m, 2H major isomer), 4.47 (m, 2H minor isomer), 4.26 – 4.22 (m, 1H), 4.14 – 4.09 (m, 1H), 3.96 (m, 1H), 3.87 (m, 1H), 3.79 (m, 1H major isomer), 3.72 (m, 1H minor isomer), 3.68 – 3.64 (m, 1H), 2.95 (s, 1H major isomer), 1.96 (s, 2H), 1.79 (m, 1H), 1.57 (m, 2H), 1.25 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) : δ 142.1, 141.2, 139.3, 138.3, 138.0, 130.0, 128.6, 128.4, 128.4, 128.3, 128.3, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.1, 115.6, 115.0, 76.2, 75.5,

74.7, 73.9, 73.5, 73.4, 73.3, 72.9, 72.4, 71.4, 71.2, 68.3, 68.1, 36.5, 33.2, 31.9, 31.6, 29.7, 29.3, 29.0, 28.0, 25.2, 25.0, 22.7, 20.9, 19.4, 14.1.

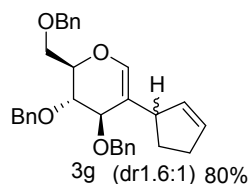
HRMS (ESI⁺) : m/z calcd. for C₃₃H₃₆NaO₄ (M+Na)⁺ 519.2506, found 519.2505.



¹H NMR (400 MHz, CDCl₃) : δ 7.30 (m, 6H), 7.27 (m, 9H), 6.32 (s, H1 major isomer), 6.29 (s, H1 minor isomer), 5.83 – 5.75 (m, 1H), 5.69 – 5.60 (m, 1H), 4.70 (s, 1H), 4.65 (m, 2H), 4.57 – 4.52 (m, 2H), 4.48 – 4.44 (m, 2H), 4.23 – 4.19 (m, 1H), 4.15 (m, 1H major isomer), 3.95 (m, 1H minor isomer), 4.00 (m, 1H major isomer), 3.90 (m, 1H minor isomer), 3.79 (m, 1H major isomer), 3.69 (m, 1H minor isomer), 3.08 – 2.99 (m, 1H), 2.11 (m, 2H), 1.73 – 1.64 (m, 2H), 1.56 – 1.50 (m, 2H), 1.28 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) : δ 141.8, 140.0, 138.4, 137.8, 134.4, 132.0, 131.2, 128.5, 128.4, 128.4, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 117.0, 114.9, 76.1, 75.7, 75.2, 74.8, 73.7, 73.6, 73.5, 73.4, 72.8, 72.1, 72.1, 71.1, 68.4, 68.2, 39.9, 39.3, 32.4, 32.1, 31.0, 29.8, 28.6, 28.4, 27.8, 27.2, 26.8.

HRMS (ESI⁺) : m/z calcd. for C₃₄H₃₈NaO₄ (M+Na)⁺ 533.2668, found 533.2663.

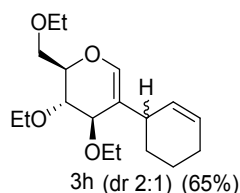


¹H NMR (400 MHz, CDCl₃) : δ 7.39 – 7.31 (m, 9H), 7.30 – 7.26 (m, 6H), 6.27 (s, H1 major isomer), 6.22 (s, H1 minor isomer), 5.85 – 5.75 (m, 1H), 5.69 – 5.60 (m, 1H), 4.71 – 4.64 (m, 1H), 4.59 – 4.51 (m, 2H), 4.47 (m, 2H), 4.30 – 4.17 (m, 2H), 3.92 (m, 1H, major isomer), 3.81 (m, 1H, minor isomer), 3.69 (m, 2H), 3.45 (m, 1H), 3.27 (m, 1H), 2.41 – 2.25 (m, 1H), 2.17 – 2.12 (m, 1H), 2.09 – 1.97 (m, 1H), 1.76 – 1.64 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) : δ 138.7, 138.6, 137.3, 137.1, 137.0, 132.6, 131.1, 129.9, 127.5, 127.4, 127.3, 127.3, 127.3, 126.9, 126.8, 126.8, 126.7, 126.7, 126.7, 126.6, 126.6, 114.6, 114.0,

74.8, 74.4, 74.0, 73.85, 72.4, 72.3, 72.3, 72.2, 71.7, 71.4, 70.8, 70.4, 67.2, 67.2, 45.3, 43.1, 31.1, 30.7, 30.24, 29.6, 28.7.

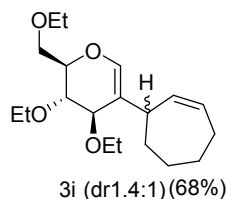
HRMS (ESI⁺) : m/z calcd. for C₃₂H₃₄Na O₄ (M+Na)⁺ 505.2355, found 505.2359.



¹H NMR (400 MHz, CDCl₃) : δ 6.20 (s, H1 major isomer), 6.14 (s, H1 minor isomer), 5.81 – 5.49 (m, 2H), 4.06 – 3.95 (m, 1H), 3.94 – 3.82 (m, 1H), 3.76 – 3.59 (m, 7H), 3.58 – 3.48 (m, 2H), 2.95 (m, 1H, minor isomer), 2.80 (m, 1H, major isomer), 2.09 – 1.91 (m, 2H), 1.85 – 1.68 (m, 2H), 1.61 – 1.48 (m, 2H), 1.26 (m, 5H), 1.23 – 1.17 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) : δ 142.0, 140.9, 130.2, 128.7, 128.6, 126.8, 116.2, 115.7, 76.2, 75.1, 74.9, 69.0, 68.8, 66.8, 66.6, 65.9, 36.0, 32.8, 29.7, 28.8, 25.1, 21.2, 19.3, 15.8, 15.8, 15.7, 15.2.

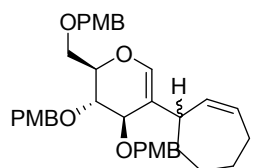
HRMS (ESI⁺) : m/z calcd. for C₁₈H₃₀NaO₄ (M+Na)⁺ 333.2036, found 333.2036.



¹H NMR (500 MHz, CDCl₃) : δ 6.24 (s, H1 minor isomer), 6.22 (s, H1 major isomer), 5.85 – 5.70 (m, 1H), 5.70 – 5.57 (m, 1H), 3.94 (s, 2H), 3.83 (m, 1H), 3.79 – 3.62 (m, 6H), 3.61 – 3.50 (m, 2H), 3.01 (m, 1H), 2.18 – 2.08 (m, 2H), 2.05 – 1.96 (m, 1H), 1.79 – 1.67 (m, 2H), 1.62 – 1.51 (m, 2H), 1.25 (m, 3H), 1.24 – 1.22 (m, 4H), 1.21 – 1.20 (m, 3H).

¹³C NMR (126 MHz, CDCl₃): δ 141.6, 139.6, 137.7, 131.9, 131.0, 117.7, 115.2, 76.6, 76.4, 76.3, 76.1, 75.1, 74.9, 69.0, 68.9, 66.9, 66.8, 66.7, 65.9, 64.8, 39.2, 32.0, 31.2, 29.8, 28.5, 26.8, 15.8, 15.8, 15.2.

HRMS (ESI⁺) : m/z calcd. for C₁₉H₃₂NaO₄ (M+Na)⁺ 347.2193, found 347.2195.

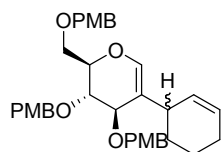


3j (dr2:1) (70%)

^1H NMR (400 MHz, CDCl_3) : δ 7.24 (m, 2H), 7.19 (m, 3H), 6.90 – 6.81 (m, 7H), 6.29 (s, H1 minor isomer), 6.26 (s, H1 major isomer), 5.84 – 5.57 (m, 2H), 4.68 – 4.52 (m, 2H), 4.52 – 4.37 (m, 5H), 4.0 (m, 4H), 3.79 (s, 9H), 3.11 – 2.95 (m, 1H), 2.20 – 1.88 (m, 2H), 1.79 – 1.62 (m, 4H), 1.58 – 1.45 (m, 2H).

^{13}C NMR (126 MHz, CDCl_3) : δ 159.3, 159.2, 159.1, 141.7, 139.8, 137.9, 134.4, 131.9, 131.1, 130.6, 130.2, 129.5, 129.5, 129.5, 117.2, 113.9, 113.8, 113.8, 75.9, 75.0, 73.5, 73.5, 73.1, 73.0, 72.5, 72.3, 71.82, 70.7, 68.0, 67.9, 55.3, 55.26, 39.7, 32.0, 31.1, 28.6, 28.4, 27.2, 26.7.

HRMS (ESI⁺) : m/z calcd. for $\text{C}_{37}\text{H}_{44}\text{NaO}_4$ ($\text{M}+\text{Na}$)⁺ 575.3137, found 575.3142.

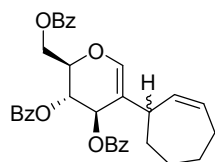


3k (dr 1.3:1) (68%)

^1H NMR (400 MHz, CDCl_3) : δ 7.34 – 7.11 (m, 6H), 6.98 – 6.74 (m, 6H), 6.23 (s, H1 major isomer), 6.18 (s, H1 minor isomer), 5.72 (m, 1H), 5.54 (m, 1H), 4.69 – 4.55 (m, 2H), 4.54 – 4.38 (m, 5H), 4.19 – 4.05 (m, 2H), 3.92 (m, 2H), 3.80 (s, 9H), 2.83 (m, 1H), 1.92 (m, 2H), 1.84 – 1.62 (m, 4H).

^{13}C NMR (101 MHz, CDCl_3) : δ 159.1, 142.0, 141.1, 129.5, 129.5, 129.4, 128.6, 127.0, 113.9, 113.8, 113.8, 113.7, 75.3, 74.5, 72.9, 71.6, 70.9, 67.9, 55.3, 36.5, 29.7, 29.0, 25.0, 20.9.

HRMS (ESI⁺) : m/z calcd. for $\text{C}_{36}\text{H}_{42}\text{NaO}_4$ ($\text{M}+\text{Na}$)⁺ 561.2981, found 561.2985.



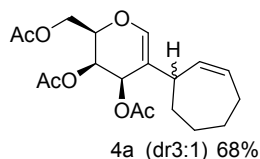
3l (dr2:1) (75%)

^1H NMR (400 MHz, CDCl_3) : δ 8.18 – 7.84 (m, 7H), 7.54 (dt, $J = 6.8, 5.6$ Hz, 2H), 7.41 (m, 6H), 6.58 (s, H1 minor isomer), 6.56 (s, H1 major isomer), 5.86 (m, 2H), 5.67 (m, 2H), 4.85 –

4.65 (m, 2H), 4.61 – 4.49 (m, 1H), 3.09 – 2.95 (m, 1H), 2.18 – 1.92 (m, 2H), 1.91 – 1.74 (m, 2H), 1.63 – 1.47 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 167.6, 167.3, 166.6, 144.1, 143.4, 137.3, 135.0, 134.9, 134.8, 134.7, 134.6, 134.2, 133.2, 131.4, 131.3, 131.2, 131.2, 131.1, 130.9, 130.7, 130.7, 129.9, 129.8, 115.2, 113.7, 74.2, 74.2, 69.6, 69.6, 68.6, 68.2, 67.6, 63.5, 63.4, 47.7, 41.5, 34.2, 33.6, 31.41, 29.8, 29.4, 28.3, 28.0.

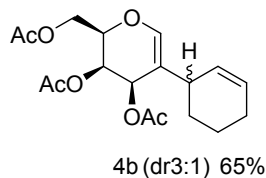
HRMS (ESI⁺) : m/z calcd. for C₃₄H₃₂NaO₇ (M+H)⁺ 575.2046, found 575.2050.



¹H NMR (400 MHz, CDCl₃) : δ 6.34 (s, H1 major isomer), 6.33 (s, H1 minor isomer), 5.87 – 5.81 (m, 1H), 5.72 (dt, *J* = 10.0, 5.0 Hz, 1H, major isomer), 5.67 (d, *J* = 3.9 Hz, 1H), 5.57 (t, *J* = 9.0 Hz, 1H, minor isomer), 5.42 – 5.39 (m, 1H), 4.36 – 4.26 (m, 2H), 4.21 (dd, *J* = 10.6, 3.3 Hz, 1H), 2.96 – 2.85 (m, 1H), 2.10 (s, 6H), 2.04 (s, 3H), 1.71 – 1.66 (m, 2H), 1.59 – 1.51 (m, 2H), 1.43 (m, 1H), 1.27 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) : δ 170.7, 170.5, 170.1, 142.0, 141.0, 136.1, 133.0, 132.6, 131.1, 114.1, 112.3, 72.3, 64.9, 64.8, 64.3, 61.9, 61.9, 40.4, 32.3, 30.1, 29.6, 28.4, 28.3, 26.7, 20.8, 20.8, 20.7.

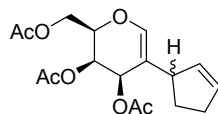
HRMS (ESI⁺) : m/z calcd. for C₁₉H₂₆NaO₇ (M+Na)⁺ 389.1571, found 389.1574.



¹H NMR (400 MHz, CDCl₃) : δ 6.30 (s, H1 major isomer), 6.23 (s, H1 minor isomer), 5.74 – 5.64 (m, 2H), 5.49 (m, 1H), 5.44 – 5.36 (m, 1H), 4.36 (m, 1H), 4.31 – 4.26 (m, 1H), 4.21 (m, 1H), 2.73 (s, 1H), 2.09 (s, 6H), 2.03 (s, 3H), 1.73 (m, 2H), 1.54 (m, 2H), 1.25 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) : δ 170.8, 170.5, 170.1, 142.4, 142.0, 129.5, 129.3, 127.6, 127.5, 113.3, 113.2, 72.5, 72.3, 65.1, 64.9, 64.7, 63.9, 62.0, 61.8, 36.2, 33.1, 28.4, 27.6, 25.2, 24.8, 20.9, 20.9, 20.9, 20.8, 20.7.

HRMS (ESI⁺) : m/z calcd. for C₁₈H₂₄NaO₇ (M+Na)⁺ 375.1414, found 375.1410.

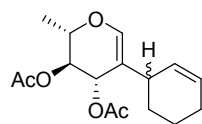


4c (dr3.5:1) 70%

¹H NMR (500 MHz, CDCl₃) : δ 6.26 (s, H1 major isomer), 6.23 (s, H1 minor isomer), 5.87 (m, 1H), 5.75 (m, 1H), 5.63 (m, 1H), 5.52 (m, 1H), 5.39 – 5.34 (m, 1H), 4.40 – 4.31 (m, 1H, major isomer), 4.30 – 4.24 (m, 1H, minor isomer), 4.23 – 4.18 (m, 1H), 3.22 (m, 1H), 2.40 – 2.33 (m, 1H), 2.31 – 2.22 (m, 1H), 2.08 (s, 3H), 2.08 (s, 3H), 2.01 (s, 3H), 1.81 (m, 1H), 1.66 – 1.54 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) : δ 169.7, 169.4, 168.9, 139.6, 139.3, 131.8, 131.4, 130.5, 130.0, 112.2, 89.6, 89.5, 71.3, 71.2, 64.2, 63.7, 63.6, 60.8, 60.8, 44.6, 42.8, 31.0, 30.7, 29.3, 28.6, 19.8, 19.6, 19.6, 19.6.

HRMS (ESI⁺) : m/z calcd. for C₁₇H₂₂NaO₇ (M+Na)⁺ 361.1263, found 361.1267.

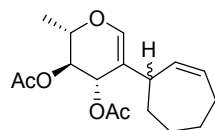


5a (dr4:1) 75%

¹H NMR (500 MHz, CDCl₃) δ 6.32 (s, H1 minor isomer), 6.22 (s, H1 major isomer), 5.85 – 5.78 (m, 1H), 5.69 – 5.59 (m, 1H), 5.50 (m, 1H), 5.03 – 4.95 (m, 1H), 4.15 – 4.01 (m, 1H), 2.69 (m, 1H), 2.08 – 2.05 (s, 6H), 1.98 – 1.93 (m, 2H), 1.72 (m, 1H), 1.60 – 1.45 (m, 3H), 1.32 – 1.21 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 171.0, 170.1, 146.0, 143.5, 143.0, 129.9, 129.3, 127.7, 127.0, 113.5, 98.8, 73.0, 72.8, 72.5, 72.2, 72.0, 68.8, 68.3, 32.9, 29.7, 29.6, 27.8, 25.2, 21.1, 21.0, 20.9, 19.3, 16.7.

HRMS (ESI⁺) : m/z calcd. for C₁₆H₂₂NaO₅ (M+Na)⁺ 317.1359 found 317.1359.

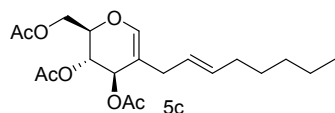


5b (dr2:1) 80%

¹H NMR (400 MHz, CDCl₃) : δ 6.37 (s, H1 minor isomer) 6.34 (s, H1 major isomer), 5.87 – 5.66 (m, 2H), 5.66 – 5.52 (m, 1H), 5.05 – 4.89 (m, 1H), 4.15 – 3.99 (m, 1H), 2.96 – 2.79 (m, 1H), 2.07 (s, 3H), 2.05 (s, 3H), 1.79 – 1.65 (m, 3H), 1.62 – 1.49 (m, 4H), 1.47 – 1.40 (m, 1H), 1.29 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) : δ 170.8, 170.0, 143.1, 142.0, 136.7, 133.5, 132.4, 130.8, 114.6, 112.5, 72.9, 72.8, 71.9, 71.9, 68.6, 68.3, 40.4, 39.0, 32.0, 28.4, 28.3, 27.8, 27.0, 26.7, 21.0, 20.91, 16.6, 16.5.

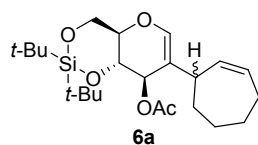
HRMS (ESI⁺) : m/z calcd. for C₁₇H₂₄NaO₅ (M+Na)⁺ 331.1516, found 331.1503.



¹H NMR (400 MHz, CDCl₃): δ 6.30 (s, 1H), 5.46 (d, J = 5.5 Hz, 1H), 5.42 (m, 1H), 5.29 (m, 1H), 5.17 (dd, J = 7.4, 5.4 Hz, 1H), 4.38 (dd, J = 12.0, 5.8 Hz, 1H), 4.23 – 4.14 (m, 2H), 2.58 (d, J = 6.6 Hz, 2H), 2.09 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 1.97 (m, 2H), 1.36 – 1.26 (m, 6H), 0.88 (t, J = 7.0 Hz, 3H).

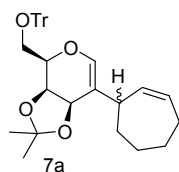
¹³C NMR (126 MHz, CDCl₃): δ 170.6, 170.5, 169.7, 141.6, 133.3, 126.0, 109.8, 73.5, 68.3, 68.1, 61.5, 32.4, 31.6, 31.4, 29.0, 22.5, 20.8, 20.7, 14.0.

HRMS (ESI⁺) : m/z calcd. for C₂₀H₃₀NaO₇ (M+Na)⁺ 405.1889, found 405.1893.



¹H NMR (400 MHz, CDCl₃) δ 6.16 (s, H1 minor isomer), 6.14 (s, H1 major isomer), 5.76 – 5.68 (m, 2H), 5.50 (m, 1H), 4.14 – 4.01 (m, 2H), 3.90 – 3.81 (m, 2H), 2.79 (m, 1H), 2.04 (s, 3H, major isomer), 2.02 (s, 3H, minor isomer), 1.99 (m, 2H), 1.65 (m, 2H), 1.52 (m, 2H), 1.45 – 1.39 (m, 2H), 0.97 (s, 18H, minor isomer), 0.92 (s, 18H, major isomer).

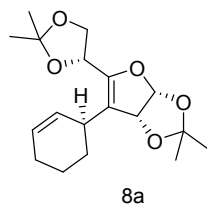
HRMS (ESI⁺) : m/z calcd. for C₂₃H₃₈NaO₅Si (M+Na)⁺ 445.2386, found 445.2390.



¹H NMR (400 MHz, CDCl₃) : δ 7.63 – 7.36 (m, 5H), 7.27 (m, 10H), 6.25 (s, 1H), 5.82 – 5.74 (m, 1H), 5.67 (dd, *J* = 11.1, 4.0 Hz, 1H), 4.63 (d, *J* = 6.3 Hz, 1H), 4.44 (d, *J* = 6.4 Hz, 1H), 3.92 (t, *J* = 6.3 Hz, 1H), 3.42 (d, *J* = 6.5 Hz, 2H), 3.02 (d, *J* = 7.9 Hz, 1H), 2.16 – 2.11 (m, 2H), 1.69 (m, 2H), 1.54 (m, 4H), 1.38 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 143.96, 140.75, 137.09, 131.37, 128.80, 127.80, 127.02, 119.18, 110.06, 86.84, 74.52, 73.29, 70.89, 63.01, 39.86, 31.96, 30.75, 29.70, 29.36, 28.61, 27.81, 26.78, 22.69, 14.09.

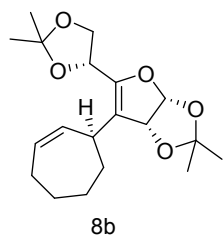
HRMS (ESI⁺) : *m/z* calcd. for C₃₅H₃₈NaO₄ (M+Na)⁺ 545.2668 found 545.2682



¹H NMR (400 MHz, CDCl₃) : δ 5.98 (d, *J* = 5.4 Hz, 1H), 5.88–5.61 (m, 2H), 5.20 (d, *J* = 5.3 Hz, 1H), 4.87–4.83 (m, 1H), 4.10–4.02 (m, 2H), 3.29 (m, 1H), 2.20–1.92 (m, 3H), 1.91 – 1.70 (m, 3H), 1.51 (s, 3H), 1.48 (s, 3H), 1.47 (s, 3H), 1.40 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) : δ 150.6, 129.9, 129.3, 127.4, 117.7, 112.2, 110.1, 104.3, 85.5, 69.5, 66.5, 32.6, 29.6, 28.2, 28.0, 25.9, 25.8, 24.6, 22.1.

HRMS (ESI⁺) : *m/z* calcd. for C₁₈H₂₆NaO₅ (M+Na)⁺ 345.1678, found 345.1685.



¹H NMR (500 MHz, CDCl₃) : δ 5.96 (d, *J* = 5.5 Hz, 1H), 5.87 – 5.75 (m, 2H), 5.23 (d, *J* = 5.5 Hz, 1H), 4.78 (t, *J* = 6.7 Hz, 1H), 4.10–4.05 (m, 1H), 4.02–3.97 (m, 1H), 3.44(m, 1H), 2.25–1.94 (m, 4H), 1.81 – 1.57 (m, 4H), 1.50 (s, 3H), 1.46 (s, 6H), 1.38 (s, 3H)

¹³C NMR (126 MHz, CDCl₃) : δ 150.7, 137.3, 132.8, 119.9, 113.7, 111.6, 105.8, 86.5, 71.2, 68.0, 37.9, 35.3, 32.6, 31.1, 30.1, 29.7, 29.4, 28.0, 27.3, 27.2.

HRMS (ESI⁺) : *m/z* calcd. for C₁₉H₂₈NaO₅ (M+Na)⁺ 359.1834, found 359.1838.

¹H and ¹³C NMR Spectra of compounds (3a-3p, 4a-4c, 5a-5c, 6a,7a, 8a-8b).

