Supporting Information
for
Design and synthesis of propellane derivatives and oxa-bowls via ring-rearrangement metathesis as a key step

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Detailed experimental procedures, characterization data and copies of $^1$H and $^{13}$C NMR for all new compounds

Contents
Experimental procedures and characterization data ................................................................. S2
Copies of $^1$H and $^{13}$C NMR spectra of the all new compounds ........................................ S11
Experimental procedures and characterization data

General methods

All reactions were monitored by thin-layer chromatography (TLC) using an appropriate mixture of EtOAc and petroleum ether for development. Reactions involving oxygen-sensitive reagents or catalysts were performed in degassed solvents. Transfer of moisture-sensitive materials was carried out using standard syringe–septum techniques and the reactions were maintained under nitrogen or argon atmosphere until work-up. Dry dichloromethane (CH₂Cl₂) was obtained by distillation from P₂O₅ and anhydrous tetrahydrofuran (THF) was obtained by distillation from sodium benzophenone directly prior to use. All commercial grade reagents were used without further purification.

Techniques

Melting points were recorded on a Veego melting point apparatus and are uncorrected. Nuclear Magnetic Resonance (NMR) spectra were generally recorded on a Bruker (Avance™ 400 or Avance™ III 500) spectrometer operating at 400 or 500 MHz for ¹H and 100.6 or 125.7 MHz for ¹³C nuclei. NMR samples were generally made in deuterio chloroform as the solvent and chemical shifts (δ values) are reported in parts per million (ppm) using tetramethylsilane (TMS) as an internal standard. Coupling constants (J) are reported in hertz (Hz). The standard abbreviations s, d, t, q, m, dd, dt, dq, td and br refer to singlet, doublet, triplet, quartet, multiplet, doublet of doublet, doublet of triplet, doublet of quartet, triplet of doublet and broadened, respectively. The high-resolution mass spectrometric (HRMS) measurements were carried out using a Bruker (Maxis Impact) or Micromass Q-ToF spectrometer. Infrared (IR) spectra were recorded on a Nicolet Impact-400 FT IR spectrometer.

General procedure for the allylation of Diels–Alder adducts 3a–c and diols 8a,b: To a stirred suspension of sodium hydride (10 equiv) in THF, a solution of the DA adducts 3a–c,
8a or 8b in 5 mL of THF was added at 0 °C under nitrogen atmosphere and the reaction mixture was stirred at room temperature (rt) for 10 min. Afterwards, allyl bromide (3 equiv) was added and the resulting reaction mixture was refluxed (70–80 °C) for 2–19 h. After completion of the reaction (TLC), the reaction mixture was quenched with saturated NH₄Cl solution (5–15 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated in vacuo. The crude products were purified by silica gel column chromatography using an appropriate mixture of EtOAc and petroleum ether (1–3% EtOAc–petroleum ether) or pure petroleum ether to obtain compounds 2a–c in 41–70%, 4a,b in 7–28% and 6a,b in 67–79% yield.

**Compound 2a:** Obtained from 3a (100 mg, 0.57 mmol), THF (15 mL); yellow liquid (62 mg, 42%); ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 6.85 (t, J = 1.8 Hz, 2H), 6.51 (s, 2H), 6.13–6.04 (m, 2H), 5.42 (dq, J = 17.2, 1.5 Hz, 2H), 5.28 (dd, J = 10.5, 1.4 Hz, 2H) 4.51 (dt, J = 5.2, 1.3 Hz, 4H), 4.22–4.21 (m, 2H), 2.26–2.20 (m, 2H); ¹³C NMR (100.6 MHz, CDCl₃): δ (ppm) = 148.1 (s), 143.1 (d), 141.2 (s), 134.2 (d), 117.2 (t), 111.7 (d), 70.5 (t), 70.0 (t), 47.2 (d); HRMS (ESI, Q-ToF) m/z: calculated for C₁₇H₁₈NaO₂ [M+Na]+: 277.1199, found: 277.1195; IR (neat): vₘₐₓ = 3077, 2937, 2871, 1492, 1258, 1011, 915 cm⁻¹.

**Compound 2b:** Obtained from 3b (2 g, 8.92 mmol), THF (30 mL); yellow thick liquid (1.90 g, 70%); ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.04 (dd, J = 6.3, 3.3 Hz, 2H), 7.43 (dd, J = 6.3, 3.3 Hz, 2H), 6.76 (t, J = 1.7 Hz, 2H), 6.23–6.13 (m, 2H), 5.45 (dq, J = 17.1, 1.5 Hz, 2H), 5.30 (dq, J = 10.4, 1.2 Hz, 2H), 4.59 (qdt, J = 12.5, 5.6, 1.3 Hz, 4H), 4.28 (t, J = 1.8 Hz, 2H), 2.27 (dt, J = 7.5, 1.5 Hz, 1H), 2.17 (d, J = 7.5 Hz, 1H); ¹³C NMR (100.6 MHz, CDCl₃): δ (ppm) = 144.2, 141.9, 136.7, 134.4, 128.3, 125.6, 122.3, 117.7, 75.5, 65.4, 47.1; HRMS
(ESI, Q-ToF) m/z: calculated for C$_{21}$H$_{20}$NaO$_2$ [M+Na]$^+$: 327.1356, found: 327.1356; IR (neat): $\nu_{\max} = 3068, 2951, 2878, 1644, 1336, 1082, 769$ cm$^{-1}$.

**Compound 4a:** Orange thick liquid (758 mg, 28%)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 7.83 (dd, $J = 5.8$, 3.3 Hz, 2H), 7.68 (dd, $J = 5.7$, 3.3 Hz, 2H) 6.42 (t, $J = 1.9$ Hz, 2H), 5.79–5.69 (m, 2H), 5.04–5.01 (m, 2H), 4.94 (dq, $J = 16.9$, 1.4 Hz, 2H), 3.61–3.59 (m, 2H), 2.35–2.29 (m, 2H), 2.16 (dd, $J = 14.3$, 7.2 Hz, 2H), 1.51 (d, $J = 9.4$ Hz, 1H), 1.11 (d, $J = 9.4$ Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ (ppm) = 200.1, 137.5, 137.1, 134.2, 133.8, 126.6, 118.0, 61.5, 50.5, 47.5, 38.7; HRMS (ESI, Q-ToF) m/z: calculated for C$_{21}$H$_{20}$NaO$_2$ [M+Na]$^+$: 327.1356, found: 327.1358; IR (neat): $\nu_{\max} = 3073, 2929, 2869, 1682, 1450, 1270, 917$ cm$^{-1}$.

**Compound 2c:** Obtained from 3c (330 mg, 1.20 mmol), THF (30 mL); off-white solid (174 mg, 41%), mp: 90–92 ºC; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.56 (d, $J = 5.2$ Hz, 2H), 8.02–7.99 (m, 2H), 7.46–7.43 (m, 2H), 6.30–6.20 (m, 2H), 5.52–5.47 (m, 2H), 5.35–5.32 (m, 2H), 4.72–4.64 (m, 4H), 4.31 (br s, 2H), 2.27 (d, $J = 7.6$ Hz, 1H), 2.16 (d, $J = 7.5$ Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ (ppm) = 143.6 (s), 141.2 (d), 134.5 (d), 134.3 (s), 131.6 (s), 128.5 (d), 127.8 (s), 125.4 (d), 121.0 (d), 117.9 (t), 75.5 (t), 63.2 (t), 46.8 (d); HRMS (ESI, Q-ToF) m/z: calculated for C$_{25}$H$_{23}$O$_2$ [M+H]$^+$: 355.1693, found: 355.1694; IR (neat): $\nu_{\max} = 3050, 2991, 2863, 1655, 1447, 1319, 1010, 750$ cm$^{-1}$.

**Compound 4b:** Yellow solid (32 mg, 7%), mp: 113–115 ºC

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) = 8.37 (s, 2H), 8.02 (dd, $J = 6.2$, 3.3 Hz, 2H), 7.65 (dd, $J = 6.3$, 3.2 Hz, 2H), 6.45 (t, $J = 1.7$ Hz, 2H), 5.83–5.75 (m, 2H), 5.04–5.02 (m, 2H), 4.96 (dd, $J = 16.9$, 1.5 Hz, 2H), 3.66 (t, $J = 1.6$ Hz, 2H), 2.34 (dd, $J = 14.4$, 7.0 Hz, 2H), 2.17 (dd, $J = 14.3$, 7.2 Hz,
2H), 1.55 (d, J = 9.5 Hz, 1H), 1.19 (d, J = 9.4 Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ (ppm) = 200.3 (s), 137.2 (d), 135.3 (s), 134.4 (d), 133.7 (s), 129.8 (d), 129.1 (d), 127.9 (d), 117.9 (t), 61.7 (s), 50.6 (d), 47.7 (t), 38.9 (t); HRMS (ESI, Q-ToF) m/z: calculated for C$_{25}$H$_{22}$NaO$_2$ [M+Na]$^+$: 377.1512, found: 377.1513; IR (neat): $\nu_{\text{max}}$ = 3061, 2975, 2867, 1682, 1455, 1265, 911 cm$^{-1}$.

**Compound 6a:** Obtained from 8a (255 mg, 0.83 mmol), THF (30 mL); colourless thick liquid (215 mg, 67%); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) = 7.36–7.34 (m, 2H), 7.24–7.23 (m, 2H), 6.26 (s, 2H), 6.07–5.99 (m, 2H), 5.96–5.88 (m, 2H), 5.40 (dd, J = 17.2, 1.3 Hz, 2H), 5.23 (dd, J = 10.5, 0.8 Hz, 2H), 4.78–4.71 (m, 4H), 4.53 (s, 2H), 4.35 (dd, J = 13.0, 4.7 Hz, 2H), 4.08 (dd, J = 13.0, 5.7 Hz, 2H), 3.04 (s, 2H), 2.25 (d, J = 9.6 Hz, 1H), 2.07 (dd, J = 14.9, 8.4 Hz, 2H), 1.75 (dd, J = 14.9, 5.2 Hz, 2H), 1.54 (d, J = 9.6 Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ (ppm) = 139.7 (d), 138.1 (s), 136.9 (d), 135.2 (d), 126.3 (d), 123.5 (d), 116.8 (t), 114.6 (t), 82.5 (d), 72.8 (t), 57.0 (s), 50.5 (d), 43.5 (t), 37.4 (t); HRMS (ESI, Q-ToF) m/z: calculated for C$_{27}$H$_{32}$NaO$_2$ [M+Na]$^+$: 411.2295, found: 411.2296; IR (neat): $\nu_{\text{max}}$ = 3072, 2964, 2856, 1635, 1456, 1117, 1067, 915 cm$^{-1}$.

**Compound 6b:** Obtained from 8b (79 mg, 0.22 mmol), THF (10 mL); colourless liquid (76 mg, 79%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 7.87 (dd, J = 6.2, 3.2 Hz, 2H), 7.79 (s, 2H), 7.47 (dd, J = 6.2, 3.2 Hz, 2H), 6.30 (t, J = 1.8 Hz, 2H), 6.16–5.98 (m, 4H), 5.46 (dq, J = 17.2, 1.7 Hz, 2H), 5.30 (dq, J = 10.5, 1.4 Hz, 2H), 4.80–4.72 (m, 6H), 4.48 (ddt, J = 13.0, 4.8, 1.6 Hz, 2H), 4.17 (ddt, J = 13.1, 5.8, 1.4 Hz, 2H), 3.14 (t, J = 1.6 Hz, 2H), 2.30 (d, J = 9.7 Hz, 1H), 2.30 (dd, J = 15.0, 8.5 Hz, 2H), 1.77 (dd, J = 14.9, 5.2 Hz, 2H), 1.61 (d, J = 9.7 Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ (ppm) = 139.8 (d), 136.8 (d), 136.5 (s), 135.2 (d), 132.5 (s), 128.0 (d), 125.6 (d), 122.3 (d), 117.0 (t), 114.5 (t), 82.5 (d), 73.0 (t), 56.4 (s), 55
50.2 (d), 43.4 (t), 37.0 (t); HRMS (ESI, Q-ToF) m/z: calculated for C_{31}H_{34}NaO_{2} [M+Na]^{+}: 461.2451, found: 461.2454; IR (neat): \nu_{\text{max}} = 3070, 2971, 2855, 1633, 1445, 1418, 1112, 1068, 901 \text{ cm}^{-1}.

**General procedure for the RRM of the O-allyl compounds 2a–c and 6a,b:** The solution of 2a–c, 6a or 6b in dry CH_{2}Cl_{2} was degassed with nitrogen for 5 min and purged with ethylene gas for another 10 min. Afterwards, Grubbs 1\textsuperscript{st} generation (G-I) catalyst (10 mol \%) was added in the presence of ethylene gas and the resulting reaction mixture was stirred at rt for 3–24 h. After completion of the reaction (TLC), the solvent was removed and the crude product was purified by silica gel column chromatography using an appropriate mixture of EtOAc and petroleum ether (1–4\% EtOAc–petroleum ether) to obtain the desired oxa-bowls 1a–c or the propellane derivatives 7a,b in 71–100\% yield.

**Compound 1a:** Obtained from 2a (42 mg, 0.16 mmol), CH_{2}Cl_{2} (35 mL); pale yellow solid (28 mg, 75\%); mp: decomposed >95 \degree C; \textsuperscript{1}H NMR (400 MHz, CDCl_{3}): \delta (ppm) = 6.70 (s, 2H), 5.81 (d, \textit{J} = 11.1 \text{ Hz}, 2H), 5.75–5.69 (m, 2H), 4.77 (dd, \textit{J} = 15.3, 5.6 \text{ Hz}, 2H), 4.41 (d, \textit{J} = 15.2 \text{ Hz}, 2H), 4.23–4.19 (m, 2H) 2.67–2.60 (m, 1H), 1.66, 1.60 (ABq, \textit{J}_{AB} = 11.8 \text{ Hz}, 1H); \textsuperscript{13}C NMR (100.6 MHz, CDCl_{3}): \delta (ppm) = 152.3 (s), 135.2 (s), 133.6 (d), 126.6 (d), 119.4 (d), 68.8 (t), 42.7 (d), 41.2 (t); HRMS (ESI, Q-ToF) m/z: calculated for C_{15}H_{15}O_{2} [M+H]^{+}: 227.1067, found: 227.1072; IR (neat): \nu_{\text{max}} = 3015, 2980, 2866, 1485, 1228, 1052, 752 \text{ cm}^{-1}.

**Compound 1b:** Obtained from 2b (100 mg, 0.33 mmol), CH_{2}Cl_{2} (70 mL); yellow sticky solid (82 mg, 90\%); \textsuperscript{1}H NMR (400 MHz, CDCl_{3}): \delta (ppm) = 8.13 (dd, \textit{J} = 6.3, 3.4 \text{ Hz}, 2H), 7.45 (dd, \textit{J} = 6.4, 3.3 \text{ Hz}, 2H), 5.91–5.88 (m, 2H), 5.85–5.79 (m, 2H), 4.98 (dd, \textit{J} = 15.2, 5.0 \text{ Hz}, 2H), 4.57–4.53 (m, 2H), 4.38–4.32 (m, 2H), 2.72–2.66 (m, 1H), 1.72, 1.66 (ABq, \textit{J}_{AB} = 12.0 \text{ Hz}, 1H); \textsuperscript{13}C NMR (100.6 MHz, CDCl_{3}): \delta (ppm) = 146.9, 133.3, 130.2, 127.6, 126.8, 125.5, 121.7, 68.8, 42.5, 41.8;
HRMS (ESI, Q-ToF) m/z: calculated for C_{19}H_{17}O_{2} [M+H]^+: 277.1223, found: 277.1221; IR (neat): \( \nu_{\text{max}} = 3014, 2929, 1640, 1605, 1456, 1349, 1097 \text{ cm}^{-1} \).

**Compound 1c:** Obtained from 2c (150 mg, 0.42 mmol), CH\(_2\)Cl\(_2\) (40 mL); yellow sticky solid (138 mg, 100%), mp: 152–154 \(^\circ\text{C}\) (decomposed); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 8.69 (s, 2H), 8.01 (dd, \( J = 6.4, 3.3 \text{ Hz}, 2\)H), 7.44 (dd, \( J = 6.5, 3.2 \text{ Hz}, 2\)H), 5.97–5.94 (m, 2H), 5.92–5.86 (m, 2H), 5.11–5.05 (m, 2H), 4.66–4.60 (m, 2H), 4.42–4.36 (m, 2H), 2.73–2.66 (m, 1H), 1.76, 1.70 (ABq, \( J_{\text{AB}} = 12.1 \text{ Hz}, 1\)H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 146.5 (s), 133.8 (d), 131.5 (s), 128.6 (d), 128.2 (s), 127.0 (s), 126.9 (d), 125.4 (d), 120.4 (d), 68.6 (t), 42.4 (d), 41.7 (t); HRMS (ESI, Q-ToF) m/z: calculated for C\(_{23}\)H\(_{18}\)KO\(_2\) [M+K]^+: 365.0938, found: 365.0936; IR (neat): \( \nu_{\text{max}} = 3013, 2941, 2862, 1643, 1451, 1344, 1304, 1087, 986 \text{ cm}^{-1} \).

**Compound 7a:** Obtained from 6a (27 mg, 0.07 mmol), CH\(_2\)Cl\(_2\) (30 mL); white solid (16.50 mg, 71%), mp: 162–163 \(^\circ\text{C}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 7.33‒7.30 (m, 2H), 7.20 (dd, \( J = 5.5, 3.4 \text{ Hz}, 2\)H), 6.12–6.08 (m, 2H), 6.05–5.99 (m, 2H), 5.28 (t, \( J = 3.4 \text{ Hz}, 2\)H), 4.60–4.55 (m, 4H), 4.27 (ddd, \( J = 14.3, 4.2, 2.0 \text{ Hz}, 2\)H), 3.20–3.16 (m, 2H), 2.07 (m, 1H), 1.95–1.83 (m, 5H); \(^{13}\)C NMR (125.7 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 138.0 (s), 137.5 (d), 128.4 (d), 127.8 (d), 126.3 (d), 121.8 (d), 88.9 (d), 68.7 (t), 54.8 (d), 52.3 (s), 34.5 (t), 27.2 (t); HRMS (ESI, Q-ToF) m/z: calculated for C\(_{23}\)H\(_{24}\)KO\(_2\) [M+K]^+: 371.1408, found: 371.1409; IR (neat): \( \nu_{\text{max}} = 3013, 2941, 2862, 1643, 1451, 1344, 1304, 1087, 986 \text{ cm}^{-1} \).

**Compound 7b:** Obtained from 6b (71 mg, 0.16 mmol), CH\(_2\)Cl\(_2\) (40 mL); white solid (60 mg, 97%), mp: 193–197 \(^\circ\text{C}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 7.81 (dd, \( J = 6.1, 3.3 \text{ Hz}, 2\)H), 7.73 (s, 2H), 7.41 (dd, \( J = 6.2, 3.2 \text{ Hz}, 2\)H), 6.15–6.11 (m, 2H), 6.08–6.02 (m, 2H), 5.17 (t, \( J = 3.5 \text{ Hz}, 2\)H), 4.65–4.58 (m, 1H), 2.72–2.64 (m, 1H), 1.74, 1.67 (ABq, \( J_{\text{AB}} = 12.1 \text{ Hz}, 1\)H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 146.5 (s), 133.8 (d), 128.4 (d), 128.2 (s), 127.9 (s), 126.9 (d), 125.7 (d), 120.4 (d), 68.6 (t), 42.4 (d), 41.7 (t); HRMS (ESI, Q-ToF) m/z: calculated for C\(_{23}\)H\(_{24}\)KO\(_2\) [M+K]^+: 371.1408, found: 371.1409; IR (neat): \( \nu_{\text{max}} = 3013, 2941, 2862, 1643, 1451, 1344, 1304, 1087, 986 \text{ cm}^{-1} \).
2H), 4.77 (s, 2H), 4.65 (ddd, \( J = 14.2, 6.8, 0.6 \) Hz, 2H), 4.37–4.32 (m, 2H), 3.26–3.23 (m, 2H), 2.13–1.93 (m, 4H), 1.83 (d, \( J = 2.8 \) Hz, 1H), 1.79 (d, \( J = 2.8 \) Hz, 1H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 137.5 (d), 136.7 (s), 132.4 (s), 128.4 (d), 128.0 (d), 127.7 (d), 125.5 (d), 120.6 (d), 88.6 (d), 68.7 (t), 54.8 (d), 52.1 (s), 34.2 (t), 27.0 (t); HRMS (ESI, Q-ToF) m/z: calculated for C\(_{27}\)H\(_{26}\)NaO\(_2\) [M+Na]\(^+\): 405.1825, found: 405.1826; IR (neat): \( \nu_{\text{max}} = 3023, 2952, 2833, 1456, 1444, 1366, 1091, 890, 729 \) cm\(^{-1}\).

**Synthesis of the propellane derivative 5a:** A solution of 4a (55 mg, 0.18 mmol) in dry CH\(_2\)Cl\(_2\) (50 mL) was degassed with nitrogen for 5 min. Afterwards, Grubbs 2\(^{nd}\) generation (G-II) catalyst (15.35 mg, 10 mol %) was added and the resulting mixture was stirred at rt for 24 h. After completion of the reaction (TLC), the solvent was removed and the crude product was purified by silica gel column chromatography (1% EtOAc–petroleum ether) to obtain propellane derivative 5a as a yellow liquid in 69% yield.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 8.09 (dd, \( J = 5.8, 3.3 \) Hz, 2H), 7.74 (dd, \( J = 5.8, 3.3 \) Hz, 2H), 5.77–5.70 (m, 2H), 5.66 (br s, 2H), 5.05–4.99 (m, 4H), 3.34, 3.30 (ABq, \( J_{AB} = 8.2 \) Hz, 2H), 2.62–2.58 (m, 2H), 2.35–2.29 (m, 1H), 2.00 (d, \( J = 16.3 \) Hz, 2H), 1.78–1.72 (m, 1H); \(^{13}\)C NMR (125.7 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 199.0, 138.2, 134.6, 132.3, 127.6, 125.4, 117.4, 61.0, 49.4, 34.3, 26.1; HRMS (ESI, Q-ToF) m/z: calculated for C\(_{21}\)H\(_{20}\)NaO\(_2\) [M+Na]\(^+\): 327.1356, found: 327.1359; IR (neat): \( \nu_{\text{max}} = 3073, 2929, 1683, 1639, 1595, 1426, 1262, 918 \) cm\(^{-1}\).

**General procedure for the reduction of the ketones 4a,b:** To a solution of the ketone 4a or 4b in dry CH\(_2\)Cl\(_2\) (10–20 mL) was added diisobutylaluminium hydride (DIBAL-H, 1 M solution in toluene) at \(-73\) to \(-74 \) \( ^\circ \)C and stirring was continued at the same temperature for 7–10 h. After completion of the reaction (TLC), the reaction was quenched by the addition of saturated sodium potassium tartrate solution (10–15 mL). Then, the reaction mixture was extracted with EtOAc (3 \( \times \) 20 mL), the combined organic layers were washed with brine (2 \( \times \)
20 mL) and dried over anhydrous Na₂SO₄. The solvent was evaporated in vacuo and the crude product was purified by silica gel column chromatography to obtain the desired diols 8a along with a minor amount of 9 (19 mg, 8%) or 8b in 81–88% yield.

**Compound 8a**: Obtained from 4a (300 mg, 0.98 mmol), DIBAL-H (5.91 mL, 6 equiv); white solid (246 mg, 81%), mp: 140–142 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.32–7.29 (m, 2H), 7.26–7.24 (m, 2H), 6.37 (s, 2H), 6.16–6.07 (m, 2H), 5.25–5.16 (m, 4H), 4.60 (s, 2H), 2.71 (dd, J = 12.8, 7.7 Hz, 2H), 2.51 (s, 2H), 1.95 (dd, J = 12.9, 6.9 Hz, 2H), 0.65 (d, J = 9.5 Hz, 1H), 0.26 (d, J = 9.6 Hz, 1H); ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) = 141.0 (s), 138.7 (d), 136.4 (d), 129.0 (d), 128.1 (d), 117.5 (t), 75.4 (d), 51.5 (s), 50.7 (d), 44.0 (t), 37.9 (t); HRMS (ESI, Q-ToF) m/z: calculated for C₂₁H₂₄NaO₂ [M+Na]⁺: 331.1669, found: 331.1664; IR (neat): υₘₐₓ = 3177, 2960, 1636, 1456, 1252, 1006, 917 cm⁻¹.

**Compound 9**: Off-white solid (19 mg, 8%), mp: 94–96 °C

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.13–8.10 (m, 1H), 7.75–7.71 (m, 1H), 7.45–7.41 (m, 2H), 7.29 (s, 1H), 6.10–5.99 (m, 2H), 5.21–5.09 (m, 3H), 5.04–4.98 (m, 1H), 3.59 (dt, J = 5.7, 1.8 Hz, 2H), 3.54–3.53 (m, 2H); ¹³C NMR (100.6 MHz, CDCl₃): δ (ppm) = 150.2 (s), 137.3 (d), 137.1 (s), 135.9 (d), 133.4 (s), 127.3 (d), 126.1 (d), 124.9 (d), 123.9 (s), 121.4 (d), 120.9 (d), 117.9 (s), 116.6 (t), 116.3 (t), 38.4 (t), 31.0 (t); HRMS (ESI, Q-ToF) m/z: calculated for C₁₆H₁₇O [M+H]+: 225.1274, found: 225.1272; IR (neat): υₘₐₓ = 3495, 3076, 2924, 1660, 1596, 1293, 915, 752 cm⁻¹.

**Compound 8b**: Obtained from 4b (100 mg, 0.28 mmol), DIBAL-H (2.52 mL, 9 equiv); pale yellow liquid (89 mg, 88%); ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.78 (dd, J = 6.0, 3.2 Hz, 2H), 7.67 (s, 2H), 7.47 (dd, J = 6.0, 3.2 Hz, 2H), 6.37 (s, 2H), 6.20–6.09 (m, 2H), 5.27–5.19 (m, 4H)
4.76 (s, 2H), 3.32 (br s, 2H), 2.73 (dd, $J = 13.2, 7.6$ Hz, 2H), 2.54 (br s, 2H), 1.96 (dd, $J = 13.2, 7.2$ Hz, 2H), 0.60 (d, $J = 9.6$ Hz, 1H), 0.26 (d, $J = 10.0$ Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ (ppm) = 138.7 (d), 138.6 (d), 136.3 (s), 133.6 (s), 128.0 (d), 126.9 (d), 126.5 (d), 117.6 (t), 75.6 (d), 51.7 (s), 50.7 (d), 44.1 (t), 37.8 (t); HRMS (ESI, Q-ToF) $m/z$: calculated for C$_{25}$H$_{26}$NaO$_2$ [M+Na]$^+$: 381.1825, found: 381.1826; IR (neat): $\nu_{\text{max}}$ = 3328, 2963, 1637, 1451, 1266, 1007, 912 cm$^{-1}$. 
Copies of $^1$H and $^{13}$C NMR spectra of the all new compounds including DEPT-135

**Compound 2a**: $^1$H NMR (400 MHz, CDCl$_3$)

![1H NMR spectrum of Compound 2a](image)

**Compound 2a**: $^{13}$C NMR (100.6 MHz, CDCl$_3$)

![13C NMR spectrum of Compound 2a](image)
Compound 2a: DEPT-135 NMR (100.6 MHz, CDCl₃)

Compound 2b: ¹H NMR (400 MHz, CDCl₃)
Compound 2b: $^{13}$C NMR (100.6 MHz, CDCl$_3$)

![Compound 2b NMR spectrum]

Compound 4a: $^1$H NMR (400 MHz, CDCl$_3$)

![Compound 4a NMR spectrum]
Compound 4a: $^{13}$C NMR (100.6 MHz, CDCl$_3$)

Compound 2c: $^1$H NMR (400 MHz, CDCl$_3$)
Compound 2c: $^{13}$C NMR (100.6 MHz, CDCl$_3$)

Compound 2c: DEPT-135 NMR (100.6 MHz, CDCl$_3$)
Compound 4b: $^1$H NMR (500 MHz, CDCl$_3$)

Compound 4b: $^{13}$C NMR (100.6 MHz, CDCl$_3$)
**Compound 4b:** DEPT-135 NMR (100.6 MHz, CDCl$_3$)

**Compound 6a:** $^1$H NMR (400 MHz, CDCl$_3$)
Compound 6a: $^{13}$C NMR (100.6 MHz, CDCl$_3$)

Compound 6a: DEPT-135 NMR (100.6 MHz, CDCl$_3$)
Compound 6b: $^1$H NMR (400 MHz, CDCl$_3$)

![NMR Spectrum Image]

Compound 6b: $^{13}$C NMR (100.6 MHz, CDCl$_3$)

![NMR Spectrum Image]
Compound 6b: DEPT-135 NMR (100.6 MHz, CDCl₃)

Compound 1a: ¹H NMR (400 MHz, CDCl₃)
**Compound 1a: $^{13}$C NMR (100.6 MHz, CDCl$_3$)**

![$^{13}$C NMR spectrum of Compound 1a]

**Compound 1a: DEPT-135 NMR (100.6 MHz, CDCl$_3$)**

![DEPT-135 NMR spectrum of Compound 1a]
Compound 1b: $^1$H NMR (400 MHz, CDCl$_3$)

Compound 1b: $^{13}$C NMR (100.6 MHz, CDCl$_3$)
Compound 1c: $^1$H NMR (400 MHz, CDCl$_3$)

Compound 1c: $^{13}$C NMR (100.6 MHz, CDCl$_3$)
**Compound 1c:** DEPT-135 NMR (100.6 MHz, CDCl₃)

**Compound 7a:** ^1^H NMR (400 MHz, CDCl₃)
Compound 7a: $^{13}$C NMR (125.7 MHz, CDCl$_3$)

![$^{13}$C NMR spectrum of Compound 7a](image)

Compound 7a: DEPT-135 NMR (125.7 MHz, CDCl$_3$)

![DEPT-135 NMR spectrum of Compound 7a](image)
**Compound 7b:** $^1$H NMR (400 MHz, CDCl$_3$)

**Compound 7b: $^{13}$C NMR (100.6 MHz, CDCl$_3$)**
Compound 7b: DEPT-135 NMR (100.6 MHz, CDCl$_3$)

Compound 5a: $^1$H NMR (400 MHz, CDCl$_3$)
Compound 5a: $^{13}$C NMR (100.6 MHz, CDCl$_3$)

Compound 8a: $^1$H NMR (400 MHz, CDCl$_3$)
Compound 8a: $^{13}$C NMR (125.7 MHz, CDCl$_3$)

Compound 8a: DEPT-135 NMR (125.7 MHz, CDCl$_3$)
Compound 9: $^1$H NMR (400 MHz, CDCl$_3$)

Compound 9: $^{13}$C NMR (100.6 MHz, CDCl$_3$)
Compound 9: DEPT-135 NMR (100.6 MHz, CDCl₃)

Compound 8b: ¹H NMR (400 MHz, CDCl₃)
Compound 8b: $^{13}$C NMR (100.6 MHz, CDCl$_3$)

Compound 8b: DEPT-135 NMR (100.6 MHz, CDCl$_3$)