Electronic Supplementary Material (ESI) for Green Chemistry.

Iron-catalysed chemo-selective oxidation of unprotected sugars: application for the competitive oxidation of pentoses from a sugar mixture

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General Experimental Information

Catalytic reactions were carried out in sealed tube (7 and 15 mL) equipped with a screw-top cap. D-ribose and D-galactose were purchased from Acros Organics, L-arabinose, L-rhamnose and D-mannose were purchased from Sigma-Aldrich, D-glucose from Merck, L-fucose from C. Rother and D-xylose from TCI; and were used as received. Ion exchange resin Ambersep 900 (OH) was purchased from Thermo-Fischer Scientific. Reagent grade acetone and *tert*-butanol from Acros were degassed by argon bubbling. Reactions were monitored by Thin Layer Chromatography (TLC) on silica plates (0.20 mm silica gel 60 with UV$_{254}$ indicator) and visualised using a combination of UV light and/or potassium permanganate (1.5 g $KMnO_4$, 10 g K_2CO_3, 1.25 mL 10% NaOH in 200 mL water) or vanillin (vanillin 15%, sulfuric acid 2.5% in ethanol) as staining solutions. Purifications were performed using an automated purification system Büchi C-815 puriflash, using 200-800 nm UV scan and ELSD as detector. Normal phase silica gel (50µm) were used as stationary phase for compounds **A, 1a** and **1b**. For carbohydrates purification, ion exchange resin ambersep 900 (OH) was used. (see page 22 for procedure)

NMR: ^{1}H NMR spectra were recorded at 300 MHz at 25°C on a Bruker 300 MHz FT-NMR spectrometer using the residual protic solvent defined as the internal standard. Chemical shifts are given in ppm, and are referenced to the internal solvent signal. Chemical shifts are quoted in ppm to the nearest 0.01 ppm using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet) defined as all multi-peak signals where overlap or complex coupling of signals make definitive descriptions of peaks difficult. ^{13}C{^{1}H} NMR spectra were recorded at 75 MHz at 25 °C using the stated solvent as standard. Chemical shifts are reported to the nearest 0.1 ppm. The coupling constants are defined as *J* and quoted in Hz. NMR yields and ratio of γ- and δ-lactones where determined on the crude mixture by ^{1}H NMR in DMSO-d6 after filtration trough a PTFE filter (0.2 µm) using 1 equivalent of 1-bromo-4-nitrobenzene as internal standard.

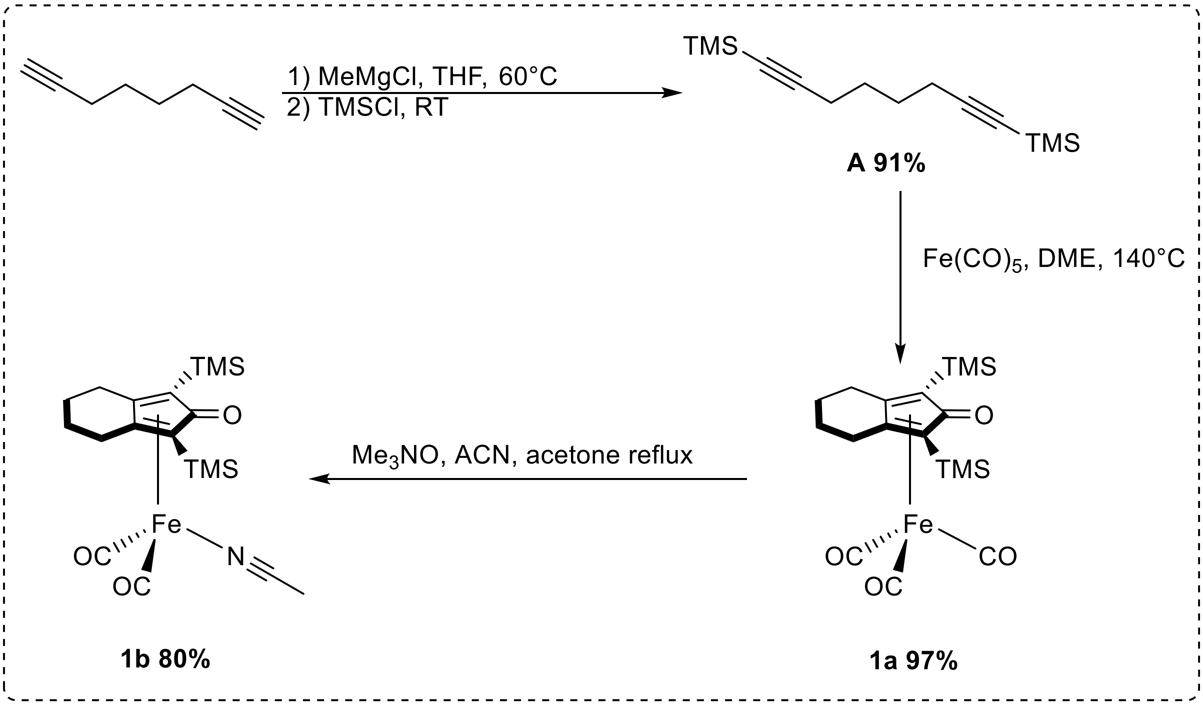
IR spectra were collected on a Perkin-Elmer Frontier operating in ATR mode.

Optical rotations were measured on a JASCO PTC-262 polarimeter at 568.6 nm with a path length of 10cm. [α] is expressed in deg.cm^3.g^{-1}.dm^{-1}, and c is expressed in g/100cm^3.

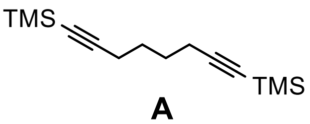
HRMS were measured on an Agilent 6530 QTOF-LC/MS mass-analyser in ESI+. LiCl dissolved in some samples to improve the ionization.

Solubility was estimated using a stability analyser Turbiscan™ Tower from Formulaction.

Synthesis of iron catalyst 1b



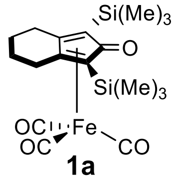
1,8-Bis(trimethylsilyl)-1,7-octadiyne A



A

A solution of 1,7-octadiyne (400 mg, 3.76 mmol, 1 equiv.) in THF (5.6 mL) was added dropwise over 1 hour to a solution of methyl magnesium chloride (5.3 mL, 3M in diethyl ether, 15.9 mmol, 4.2 equiv.) in THF (2 mL) at 60 °C. The solution was stirred at 65 °C for 3 hours and was allowed to cool down to room temperature. Trimethylsilyl chloride (2.22 g, 20.4 mmol, 5.4 equiv.) was then added slowly and the mixture was stirred at room temperature for 16 hours. The cloudy, white mixture was quenched with a saturated aqueous NH$_4$Cl solution (2 mL) and water was added until complete dissolution of the white precipitate. The organic layer was separated and the aqueous layer was extracted with cyclohexane (3 × 20 mL). The combined organic layers were dried over anhydrous MgSO$_4$ and evaporated under reduced pressure to give a colorless oil. Purification of the crude material by flash chromatography using cyclohexane as eluent, afforded **A** (858 mg, 3.42 mmol, 91% yield) as a white low melting point solid. **^{1}H NMR** (300 MHz, CDCl$_3$): δ 2.26 – 2.2 (m, 4H), 1.63 – 1.57 (m, 4H), 0.13 (s, 18H). **^{13}C{^{1}H} NMR** (75 MHz, CDCl$_3$): δ 106.8, 84.5, 27.5, 19.2, 0.0. Spectral data are in agreement with the data previously reported in the literature.[1]

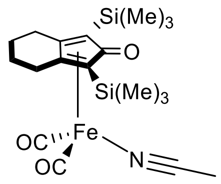
Tricarbonyl(1,3-bis(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one) iron 1a



1a

A solution of 1,8-bis(trimethylsilyl)-1,7-octadiyne **A** (350 mg, 1.39 mmol, 1 equiv.) and iron pentacarbonyl (363 µL, 544 mg, 2.78 mmol, 2 equiv.) in 1,2-dimethoxyethane (11.6 mL) was heated at 140 °C in a sealed tube for 24 hours. After cooling down, the mixture was evaporated under reduced pressure. Purification of the crude product was performed using flash chromatography using a gradient of cyclohexane:ethyl acetate (100:0 to 80:20) to afford **1a** (570 mg, 1.36 mmol, 97% yield) as a yellow solid. **^{1}H NMR** (300 MHz, CDCl$_3$): δ 2.49 – 2.62 (m, 4H), 1.76 – 1.87 (m, 4H), 0.26 (s, 18 H). **^{13}C{^{1}H} NMR** (75 MHz, CDCl$_3$): δ 209.3, 181.5, 111.3, 72.0, 25.1, 22.7, 0.0. Spectral data are in agreement with the data previously reported in the literature.[1]

Acetonitrile dicarbonyl(1,3-bis(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one) iron 1b



1b

A solution of iron compound **1a** (570 mg, 1.36 mmol, 1 equiv.), acetonitrile (144 µL, 113 mg, 2.75 mmol, 2 equiv.), and anhydrous trimethylamine *N*-oxide (123 mg, 1.63 mmol, 1.2 equiv.) in acetone (57 mL) was stirred at reflux for 24 hours. The orange/brown reaction was diluted with water (60mL) and was extracted with CH$_2$Cl$_2$ (3 x 30 mL). The combined organic layers were dried over MgSO$_4$, filtered, and the volatiles were removed under vacuum to afford a yellow/orange solid. Purification by flash chromatography on silica using a gradient of cyclohexane:ethyl acetate (100:0 to 0:100) afforded **1b** (479 mg, 1.11 mmol, 80 % yield. **IR** (neat): ν (cm^{-1}) 1983, 1926, 1584. **^{1}H NMR** (300 MHz, CDCl$_3$): δ 2.30 (q, J = 5.9, 4H), 2.22 (s, 3H), 1.44 – 1.60 (m, 4H), 0.23 (s, 18H). **^{13}C{^{1}H} NMR** (75 MHz, CDCl3): δ 212.9, 180.2, 126.2, 106.7, 70.0, 24.9, 22.4, 4.6, 0.0. Spectral data matched the literatures values already reported. **HRMS** (ESI+): m/z calculated for [M+H]$^+$ 432.1113, found 432.1119.[1]

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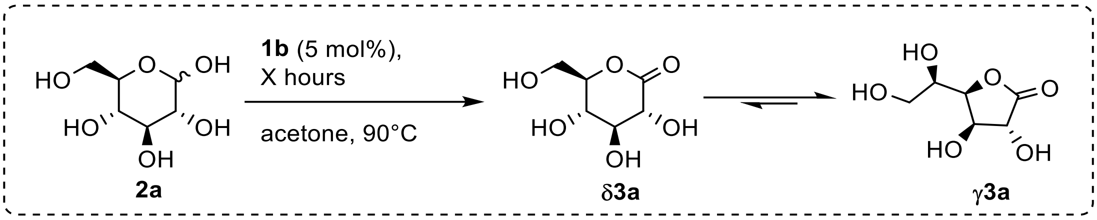
[1] **Plank, T. N.; Drake, J. L.; Kim, D. K.; Funk, T. W.** *Adv. Synth. Catal.* **2012**, *354* (4), 597–601.

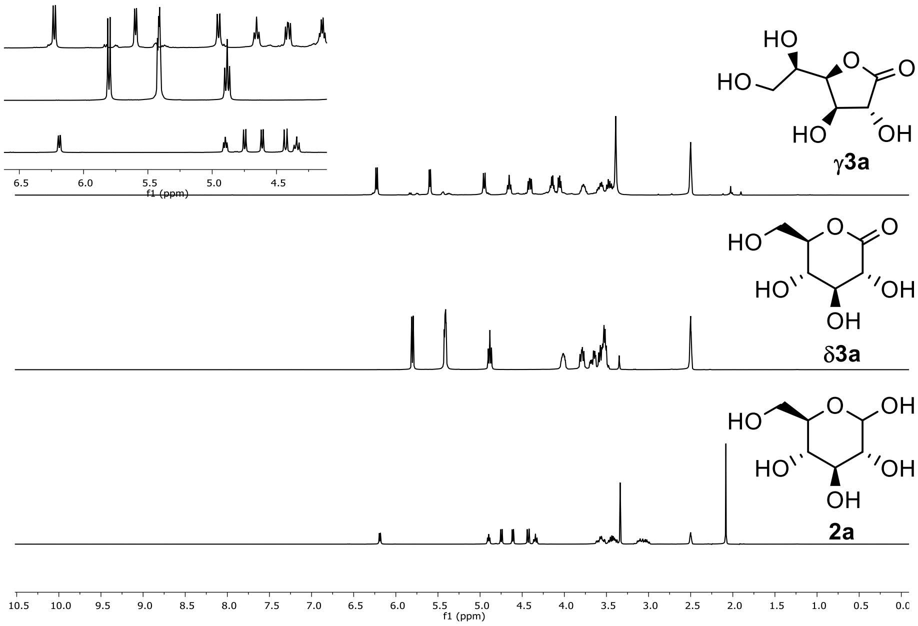
Preliminary work



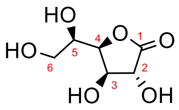
Acetone (0.8 mL) was degassed with argon for 15 min in a sealed tube after addition of glucose (50 mg, 0.277 mmol) and the catalyst 1b (X mg, X mol%). The reaction was stirred at 90 °C for X hours. The crude mixture was evaporated under reduced pressure. Yields and ratios where determined by ^{1}H NMR using 1-Bromo-4-nitrobenzene (1 equiv.) as internal standard in DMSO-d$_6$, after filtration trough a PTFE filter (0.2 µm).

Catalyst loading (mol%)	**Time (hours)**	**δ3a/γ3a ratio**	**NMR Yield (%)**
2.5	3	66:34	22
5	5	73:28	100

Table 1: Gluconolactones yield in acetone



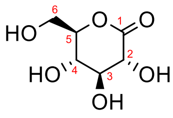
D-Glucono-1,4-lactone γ3a



γ3a

^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 6.22 (d, *J* = 5.3 Hz, OH-2), 5.59 (d, *J* = 4.3 Hz, OH-3), 4.95 (d, *J* = 5.4 Hz, OH-5), 4.65 (t, *J* = 4.6 Hz, OH-6), 4.41 (dd, *J* = 6.9, 4.8 Hz, H-4), 4.17-4.12 (dd, *J* = 4.18 Hz, 8.28 Hz , H-3), 4.08-4.03 (dd, *J* = 3.9 Hz, 5.0 Hz, H-2), 3.82-3.73 (m, H-5), 3.61-3.52 (m, CH$_2$). **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d$_6$) δ 176.0 (C-1), 80.5 (C-4), 73.6 (C-2), 73.1 (C-3), 69.7 (C-5), 63.2 (C-6). Spectral data matched the literatures values already reported.[2]

D-Glucono-1,5-lactone δ3a



δ3a

^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 5.80 (d, *J* = 5.6 Hz, 1H), 5.41 (m, 2H), 4.88 (t, *J* = 5.7 Hz, 1H), 4.01 (ddt, *J* = 6.7, 4.3, 2.2 Hz, 1H), 3.79 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.66 (ddd, *J* = 12.2, 5.3, 2.3 Hz, 1H), 3.61 – 3.49 (m, 3H). **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d$_6$) δ 172.4, 81.8, 74.3, 72.0, 68.4, 60.7. Spectral data matched the literatures values already reported.[2]

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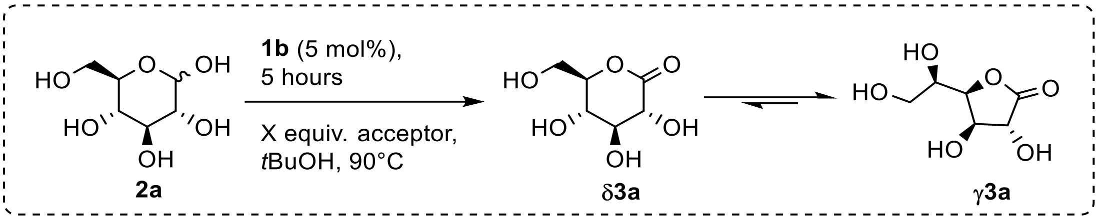
[2] **M. Bierenstiel, M. Schlaf** *Eur. J. Org. Chem*. **2004**, 1474-1481

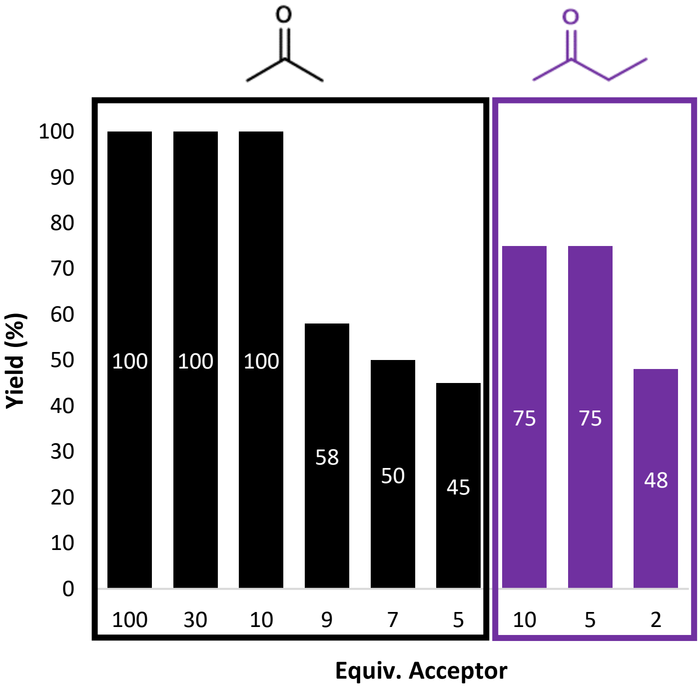
Optimization: acetone as solvent and acceptor



Tert-butanol (0.8 mL) was degassed with argon for 15 min in a sealed tube after addition of D-glucose (50 mg, 0.277 mmol) catalyst **1b** (6.0 mg, 5mol%) and acceptor (X mol, X equiv.). The reaction was stirred at 90 °C for 5 hours. 1-Bromo-4-nitrobenzene (1 equiv.) was added as an internal standard and the crude mixture was evaporated under reduced pressure. Conversion of D-glucose (see table 2) was determined by ^{1}H NMR in DMSO-d_6, after filtration trough a PTFE filter (0.2 µm).

Acceptor	Equiv. Acceptor	NMR Yield (%)
acetone	100	100
acetone	30	100
acetone	10	100
acetone	9	58
acetone	7	50
acetone	5	45
butanone	10	75
butanone	5	75
butanone	2	48

Table 2: Gluconolactones yield in t-BuOH with X eq acceptor



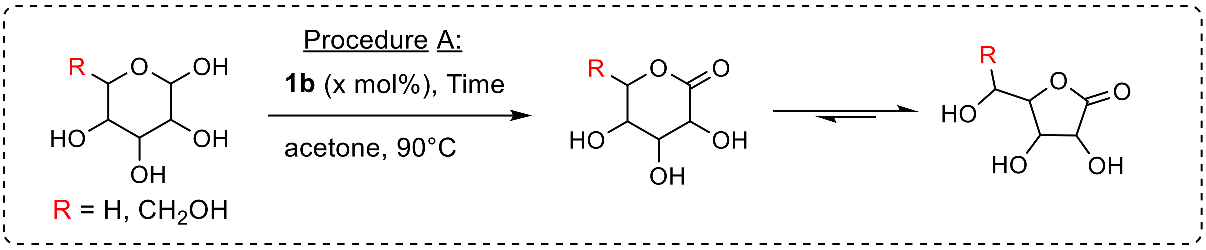
Solubility investigation

Various range of concentrations of carbohydrates were stirred vigorously during 1 hour in *tert*-butanol at 80°C in sealed vial. Solutions were immediately transferred into the stability analyser (Turbiscan Tower from Formulaction) at 80°C. The Turbiscan measures transmitted and backscattered intensities of an incident beam ($\lambda = 880$ nm) along the entire height of the sample (5 µm steps) every 2 minutes for 4 or 6 hours. Based on these parameters, the software calculates a Turbiscan Stability Index (TSI) which helps to detect flocculation/sedimentation.

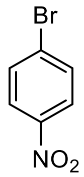
	galactose 2c	**galactose 2c + 1 eq xylose 2e**	**glucose 2a**	**glucose 2a + 1 eq xylose 2e**	**xylose 2e**
Solubility range (10^{-3} mmol/mL)	$0 < S < 5.31$	$4.31 < S < 6.31$	$29.809 < S < 32.309$	$29.809 < S < 32.309$	$87.31 < S < 107.107$

Table 3: Solubility range of monosaccharides in tert-butanol at 80°C

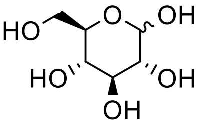
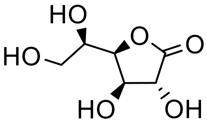
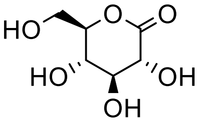
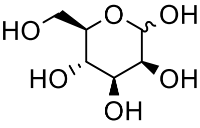
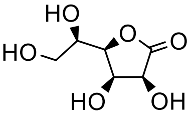
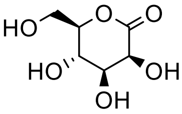
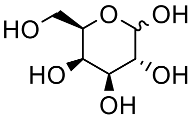
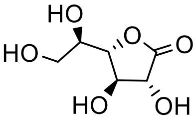
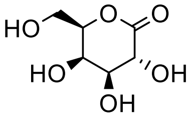
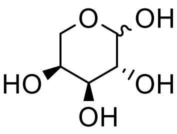
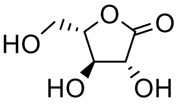
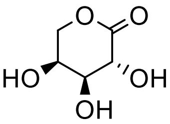
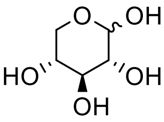
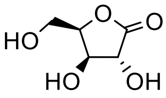
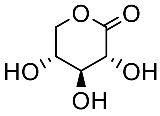
General Procedures of sugar C1-oxidation using catalyst 1b



Internal standard:
1-Bromo-4-nitrobenzene



Procedure A: Acetone (0.8 mL) was degassed with argon for 15 min in a sealed tube after addition of sugar (50 mg, X mmol) and the catalyst **1b** (X mg, X mol%). The reaction was stirred at 90 °C for X hours. Upon completion of the reaction (TLC), 1-bromo-4-nitrobenzene (1 equiv.) was added as an internal standard and the crude mixture was evaporated under reduced pressure. Yield of sugars lactones and ratios (see table 4) of 1,4-γ-, and 1,5-δ-lactones were determined by ^{1}H NMR in DMSO-d_6, after filtration trough a PTFE filter (0.2 µm).

Substrate	**Product (X)** **γ:δ**	**Catalyst loading (mol%)**	**Time (hours)**	**NMR Yield (%) Ratio γ:δ**
 **2a**	 γ**3a**  δ**3a**	5 2.5	5 3	> 98 (28 :72) 22 (34 :66)
 **2b**	 γ**3b**  δ**3b**	5	5	> 98 (47 :53)
 **2c**	 γ**3c**  δ**3c**	5 5 2.5	5 24 3	54 (ND) 98 (100 :0) 19 (100 :0)
 **2d**	 γ**3d**  δ**3d**	2.5	5	> 98 (23 :77)
 **2e**	 γ**3e**  δ**3e**	2.5 2.5	5 **3**	> 98 (66 :34) 98 (57 :43)

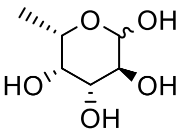
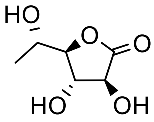
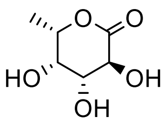
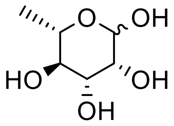
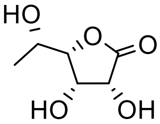
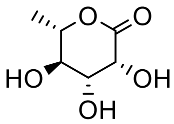
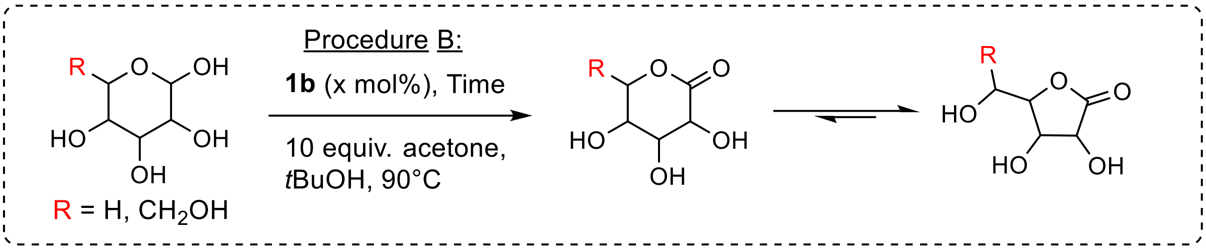
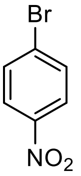
 **2f**	 γ**3f**  δ**3f**	2.5 2.5	5 5	> 98 (75 :25) 100 (ND)
 **2g**	 γ**3g**  δ**3g**	2.5	5	> 98 (57 :43)

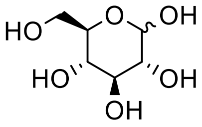
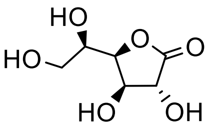
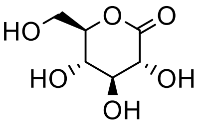
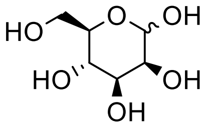
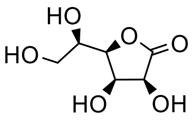
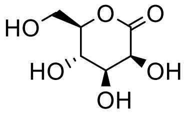
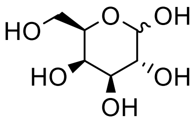
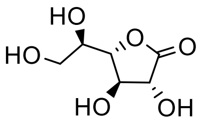
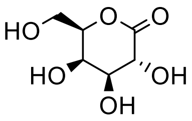
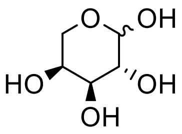
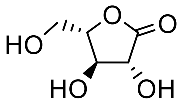
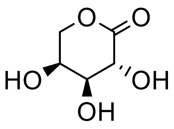
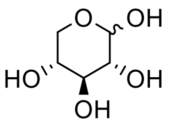
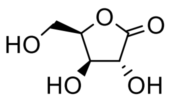
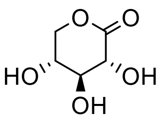
Table 4: Scope on hexoses and pentoses using procedure A



Internal standard:
1-Bromo-4-nitrobenzene



Procedure B: *Tert*-butanol (0.8 mL) was degassed with argon for 15 min in a sealed tube after addition of sugar (50 mg, X mmol) catalyst **1b** (X mg, X mol%) and acetone **4** (X mol, 10 equiv.). The reaction was stirred at 90 °C for X hours. Upon completion of the reaction (TLC), 1-bromo-4-nitrobenzene (1 equiv.) was added as an internal standard and the crude mixture was evaporated under reduced pressure. Yield of sugars lactones and ratios (see table 5) of 1,4-γ-, and 1,5-δ-lactones were determined by ^{1}H NMR in DMSO-d$_6$, after filtration trough a PTFE filter (0.2 µm).

Substrate	**Product (X) γ:δ**	**Catalyst loading (mol%)**	**Time (hours)**	**NMR Yield (%) Ratio γ:δ**
 **2a**	 γ**3a**  δ**3a**	5	5	> 98 (43 :57)
 **2b**	 γ**3b**  δ**3b**	5	5	> 98 (42 :58)
 **2c**	 γ**3c**  δ**3c**	5 5	5 24	35 (100 :0) 85 (100 :0)
 **2d**	 γ**3d**  δ**3d**	2.5	2 5	60 (66 :34) > 98 (100 :0)
 **2e**	 γ**3e**  δ**3e**	2.5	2 2	96 (52 :48) 96 (56 :44)

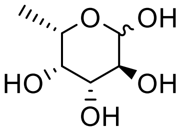
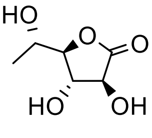
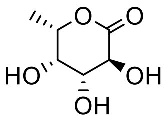
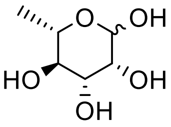
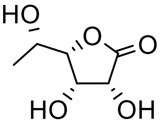
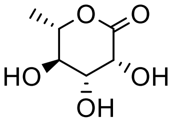
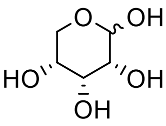
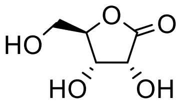
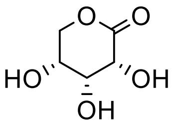
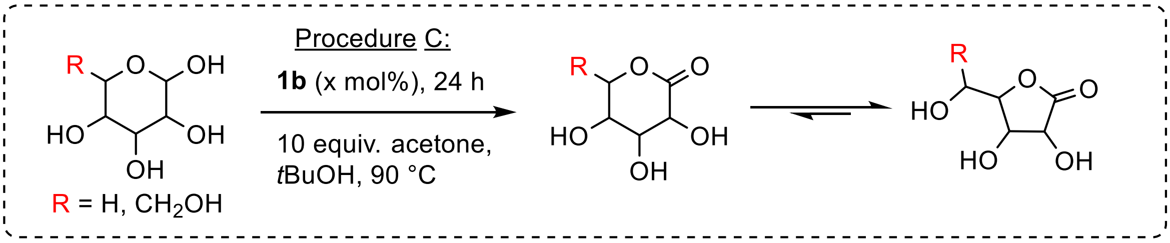
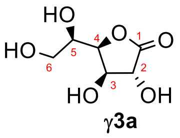
 **2f**	 γ**3f**  δ**3f**	2.5	5	> 98 (53 :47)
 **2g**	 γ**3g**  δ**3g**	2.5 5	5 5	85 (30 :70) 97 (34 :66)
 **2h**	 γ**3h**  δ**3h**	2.5	5	> 98 (87 :13)

Table 5: Scope on hexoses and pentoses using procedure B

<u>Procedure C:</u> A mixture of sugar (50mg) catalyst **1b** (2.5-5 mol%) and acetone **4** (X equiv.) in *tert*-butanol (0.8mL) in a sealed tube was degassed with argon for 15 min. The reaction was stirred at 90 °C for 24 hours, until total conversion of the monosaccharide and full isomerization of the resulting lactones. Purifications of the crude residue were carried out with successive diethyl ether sonication, or using flash chromatography on reverse phase (C18 Silica, 30 µm) as stationary phase; and a gradient of dichloromethane:methanol (100:0 to 60:40) as eluent.

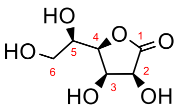


D-Glucono-1,4-lactone γ3a


γ**3a**

This product was prepared according to the general **<u>procedure C</u>**, using D-glucose (0.277mmol, 1 equiv.), catalyst **1b** (5.98mg, 0.013mmol, 5mol%) and acetone (205µL, 2.77mmol, 10 equiv.). $[\alpha]^{24}_{D}$ = +59 (c = 1.0g/100mL, H_2O). **IR** (neat): ν (cm^{-1}) 3288, 1772, 1733 (C=O). ^{1}**H NMR** (300 MHz, DMSO-*d*$_6$) δ 6.22 (d, *J* = 5.3 Hz, OH-2), 5.59 (d, *J* = 4.3 Hz, OH-3), 4.95 (d, *J* = 5.4 Hz, OH-5), 4.65 (t, *J* = 4.6 Hz, OH-6), 4.41 (dd, *J* = 6.9, 4.8 Hz, H-4), 4.17-4.12 (dd, *J* = 4.18 Hz, 8.28 Hz , H-3), 4.08-4.03 (dd, *J* = 3.9 Hz, 5.0 Hz, H-2), 3.82-3.73 (m, H-5), 3.61-3.52 (m, CH_2). ^{13}**C{^{1}H} NMR** (75 MHz, DMSO-d$_6$) δ 176.0 (C-1), 80.5 (C-4), 73.6 (C-2), 73.1 (C-3), 69.7 (C-5), 63.2 (C-6). **HRMS** (ESI+): m/z calculated for $[M+H]^+$ 179.0555, found 179.0553.

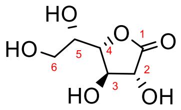
D-Manno-1,4-lactone γ3b



γ3b

This product was prepared according to the general **procedure C**, using D-mannose (0.277mmol, 1 equiv.), catalyst **1b** (5.98mg, 0.013mmol, 5mol%) and acetone (205µL, 2.77mmol, 10 equiv.). **[α]$^{24}_{\mathrm{D}}$** = +56 (c = 1.0g/100mL, H_2O). **IR** (neat): v (cm^{-1}) 3326, 1771 (C=O). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 5.77 (d, *J* = 7.5 Hz, OH-2), 5.31 (d, *J* = 3.8 Hz, OH-3), 4.84 (d, *J* = 6.0 Hz, OH-5), 4.60 (t, *J* = 5.2 Hz, OH-6), 4.46 (dd, *J* = 7.2, 4.3 Hz, CH-2), 4.23 (q, *J* = 3.8 Hz, CH-3), 4.13 (m, CH-4), 3.73 (m, CH-5), 3.55 (m, CH_2). **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6) δ 176.2 (C-1), 77.9 (C-4), 70.7 (C-2), 69.1 (C-3), 67.6 (C-5), 62.8 (C-6). **HRMS** (ESI+): m/z calculated for [M+H]$^+$ 179.0555, found 179.0552.

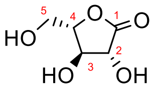
D-Galacto-1,4-lactone γ3c



γ3c

This product was prepared according to the general **procedure C**, using D-galactose (0.277mmol, 1 equiv.), catalyst **1b** (5.98mg, 0.013mmol, 5mol%) and acetone (205µL, 2.77mmol, 10 equiv.) **[α]$^{24}_{\mathrm{D}}$** = -63 (c = 1.0g/100mL, H_2O). **IR** (neat): v (cm^{-1}) 3234, 1709 (C=O). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 6.05 (d, *J* = 6.5 Hz, OH-2), 5.77 (d, *J* = 5.3 Hz, OH-3), 5.02 (d, *J* = 6.2 Hz, OH-5), 4.76 (t, *J* = 5.5 Hz, OH-6), 4.29-4.20 (dd, *J* = 6.5, 7.9 Hz, CH-2), 4.18-4.12 (m, CH-3), 4.10-4.07 (m, CH-4), 3.61 (ddd, *J* = 1.5 Hz, 6.2 Hz, 7.5 Hz, CH-5), 3.49-3.39 (m, CH_2). **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6) δ 174.7 (C-1), 79.1 (C-4), 74.0 (C-2), 72.4 (C-3), 68.0 (C-5), 61.8 (C-6). **HRMS** (ESI+): m/z calculated for [M+H]$^+$ 179.0555, found 179.0547.

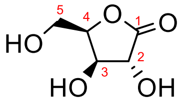
L-Arabino-1,4-lactone γ3d



γ3d

This product was prepared according to the general **procedure C**, using D-arabinose (0.333 mmol, 1 eq), catalyst **1b** (3.58mg, 0.0083mmol, 2.5mol%) and acetone (246µL, 3.33mmol, 10 equiv.). **[α]$^{24}_{\mathrm{D}}$** = +46 (c = 1.0g/100mL, H_2O). **IR** (neat): v (cm^{-1}) 3282, 1772 (C=O). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 6.05 (d, *J* = 6.6 Hz, OH-2), 5.81 (d, *J* = 5.1 Hz, OH-3), 5.04 (t, *J* = 5.6 Hz, OH-5), 4.23 (dd, *J* = 8.1, 6.5 Hz CH-2), 4.04-3.91 (m, CH-3, CH-4), 3.71 (ddd, *J* = 12.8, 5.2, 2 Hz, CH-5), 3.49 (ddd, *J* = 12.8, 5.9, 4.2 Hz, CH-5’). **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6) δ 174.7 (C-1), 81.2 (C-4), 73.8 (C-2), 59.2 (C-5), 54.9 (C-3). **HRMS** (ESI+): m/z calculated for [M+Li]$^+$ 155.0531, found 155.0529.

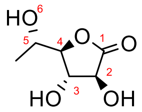
D-Xylono-1,4-lactone γ3e



γ3e

This product was prepared according to the general **procedure C**, using D-xylose (0.333 mmol, 1 equiv.), catalyst **1b** (3.58mg, 0.0083mmol, 2.5mol%) and acetone (246µL, 3.33mmol, 10 equiv.). **[α]$^{24}_{\mathrm{D}}$** = +78 (c = 1.0g/100mL, H_2O). **IR** (neat): v (cm^{-1}) 3251, 1755 (C=O). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 6.03 (d, *J* = 5.7 Hz, OH-2), 5.71 (d, *J* = 3.5 Hz, OH-3), 4.90 (t, *J* = 4.8 Hz, OH-5), 4.42 – 4.36 (m, CH-4), 4.22 (m, CH-2,3), 3.68 – 3.60 (m, CH_2). **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6) δ 175.6 (C-1), 80.0 (C-4), 73.2 (C-2), 72.4 (C-3), 58.6 (C-5). **HRMS** (ESI+): m/z calculated for [M+Li]$^+$ 155.0531, found 155.0530.

L-Fucono-1,4-lactone γ3f

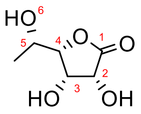


γ3f

This product was prepared according to the general **procedure C**, using L-fucose (0.274 mmol, 1 equiv.), catalyst **1b** (2.96mg, 0.0068mmol, 2.5mol%) and acetone (203µL, 2.744mmol, 10 equiv.). **[α]$^{24}_{\mathrm{D}}$** = +27 (c = 1.0g/100mL, H_2O). **IR** (neat): v (cm^{-1}) 3391, 3294, 1750 (C=O). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 6.05 (d, *J* = 6.3 Hz, OH-2), 5.79 (d, *J* = 5.1 Hz, OH-3), 4.94 (d, *J* = 5.2 Hz, OH-5), 4.21 (dd, *J* = 7.4, 6.8 Hz, CH-2), 4.09 (d, *J* = 6.4 Hz, CH-3), 4.00 (q, *J* = 7.9 Hz, CH-5), 3.82-3.75 (m, CH-4), 1.15 (d, *J* = 6.4 Hz, CH_3) **^{13}C{^{1}H} NMR** (75 MHz, DMSO-

d_6) δ 174.7 (C-1), 83.5 (C-2), 74.1 (C-4), 73.12 (C-3), 64.12 (C-5), 19.6 (C-6). **HRMS** (ESI+): m/z calculated for [M+Li]$^+$ 169.0688, found 169.0684.

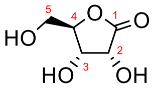
L-Rhamno-1,4-lactone γ3g



γ3g

This product was prepared according to the general **procedure C**, using L-rhamnose (0.274 mmol, 1 equiv.), catalyst **1b** (2.96mg, 0.0068mmol, 2.5mol%) and acetone (203µL, 2.744mmol, 10 equiv.). $[\alpha]_D^{24}$ = -17 (c = 1.0g/100mL, H_2O). **IR** (neat): v (cm^{-1}) 3377, 3319, 1722 (C=O). **^{1}H NMR** (300 MHz, DMSO-*d_6*) δ 5.59 (d, *J* = 5.7 Hz, OH-2), 5.35 (d, *J* = 6.4 Hz, OH-3), 5.30 (d, *J* = 3.6 Hz, OH-5), 4.47 (dd, *J* = 6.3, 3.5 Hz, CH-3), 4.20 – 4.08 (m, CH-4), 3.81 (t, *J* = 3.0 Hz, CH-5), 3.34 – 3.28 (m, CH-2), 1.29 (d, *J* = 6.2 Hz, CH_3). **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6) δ 172.9 (C-1), 76.0 (C-4), 75.3 (C-2), 75.2 (C-3), 68.3 (C-5), 18.9 (C-6). **HRMS** (ESI+): m/z calculated for [M+Li]$^+$ 169.0688, found 169.0685.

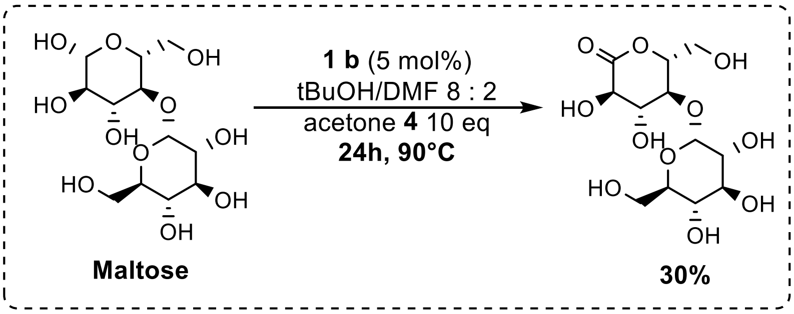
D-Ribono-1,4-lactone γ3h



γ3h

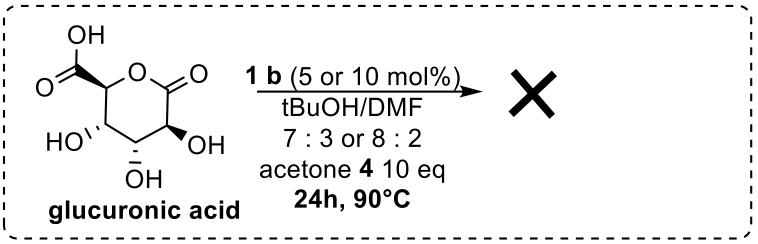
This product was prepared according to the general **procedure C**, using D-ribose (0.333 mmol, 1 equiv.), catalyst **1b** (3.58mg, 0.0083mmol, 2.5mol%) and acetone (246µL, 3.33mmol, 10 equiv.). $[\alpha]_D^{24}$ = +8 (c = 1.0g/100mL, H_2O). **IR** (neat): v (cm^{-1}) 3276, 1769 (C=O). **^{1}H NMR** (300 MHz, DMSO-*d_6*) δ 5.75 (d, *J* = 7.5 Hz, OH-2), 5.37 (d, *J* = 3.5 Hz, OH-3), 5.16 (t, *J* = 5.2 Hz, OH-5), 4.42 (dd, *J* = 5.6, 1.9 Hz, CH-2), 4.22 (t, *J* = 3.5 Hz, CH-4), 4.13-4.09 (m, CH-3), 3.55-3.58 (m, CH_2). **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6) δ 176.9 (C-1), 85.8 (C-4), 69.8 (C-3), 69.1 (C-2), 60.9 (C-5). **HRMS** (ESI+): m/z calculated for [M+Li]$^+$ 155.0531, found 155.0526.

Disaccharides oxidation



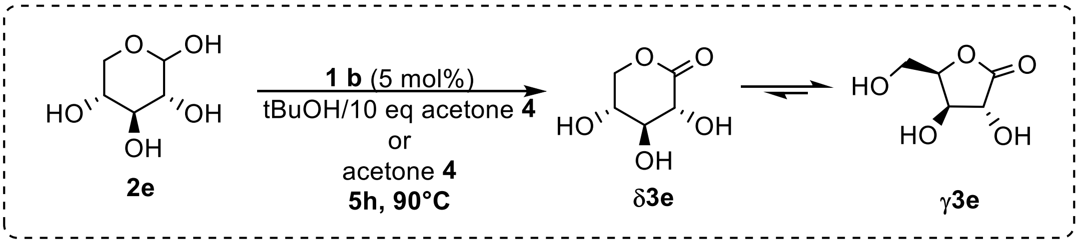
Tert-butanol-*N,N*-dimethylformamide mixture 8:2 (0.8 mL) was degassed with argon for 15 min in a sealed tube after addition of maltose (50 mg, 0.146 mmol) catalyst **1b** (3.1 mg, 5mol%) and acetone **4** (1.46 mol, 10 equiv.). The reaction was stirred at 90 °C for 24 hours. 1-bromo-4-nitrobenzene (1 equiv.) was added as an internal standard. Conversion of maltose was determined by ^{1}H NMR in DMSO-d_6, after filtration trough a PTFE filter (0.2 µm).

Alduronic acids oxidation



Tert-butanol-*N,N*-dimethylformamide mixture 7:3 or 8:2 (0.8 mL) was degassed with argon for 15 min in a sealed tube after addition of glucuronic acid (50 mg, 0.257 mmol) catalyst **1b** (5.5 mg, 5mol%) and acetone **4** (2.57 mol, 10 equiv.). The reaction was stirred at 90 °C for 24 hours. 1-Bromo-4-nitrobenzene (1 equiv.) was added as an internal standard and the crude mixture was evaporated under reduced pressure. Conversion of glucuronic acid was determined by ^{1}H NMR in DMSO-d_6, after filtration trough a PTFE filter (0.2 µm).

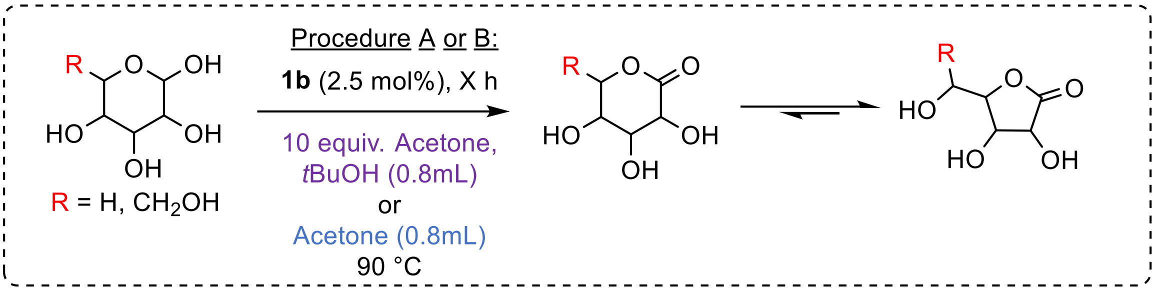
Scale-Up



A mixture of xylose **2e** (500mg) catalyst **1b** (71mg, 5 mol%) and acetone **4** (2.46mL, 10 equiv.) in *tert*-butanol (8mL) in a sealed tube was degassed with argon for 30 min. The reaction was stirred at 90 °C for 5 hours, until total conversion of the monosaccharide. Purifications of the crude residue were carried out with successive diethyl ether sonication and filtration, to afford xylonolactones **δ3e** and **γ3e** as a white solid in **quantitative yield**.

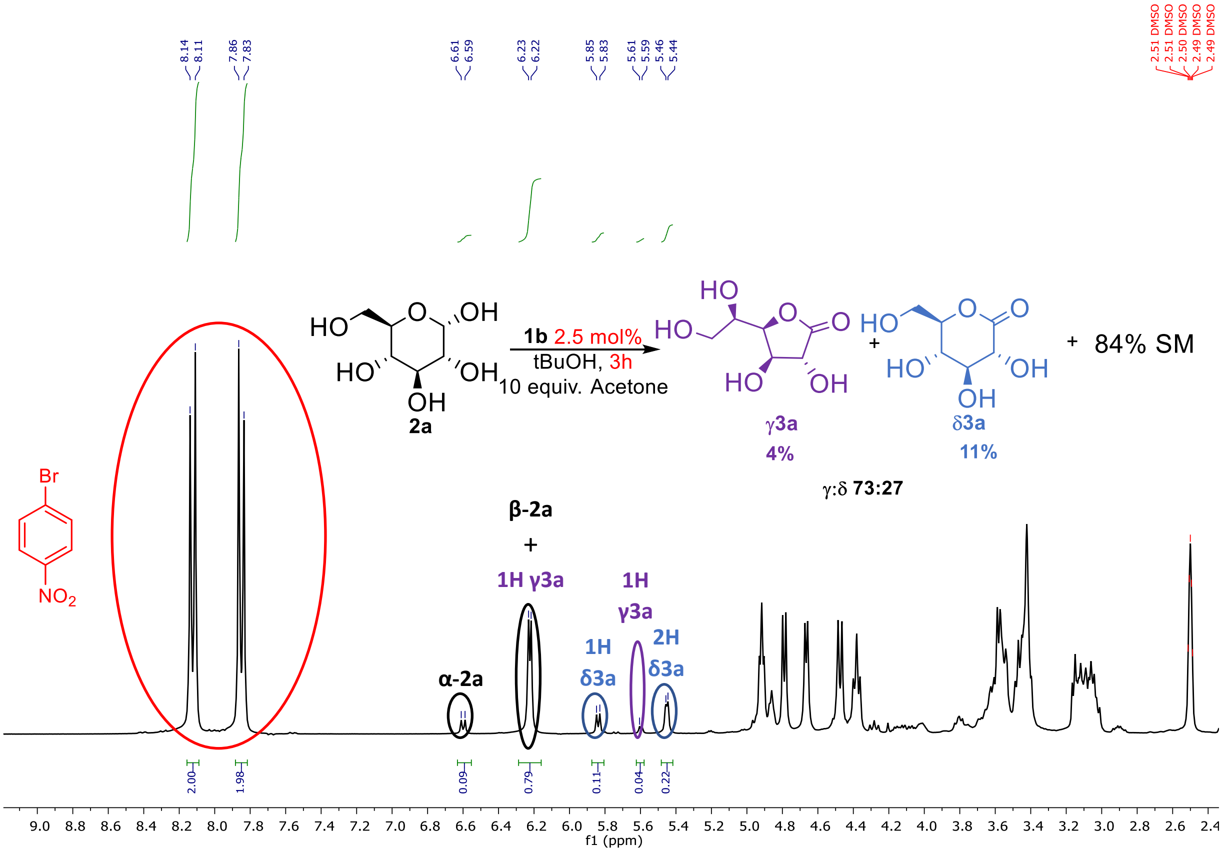
A mixture of xylose **2e** (500mg) catalyst **1b** (71mg, 5 mol%) and acetone **4** (8mL) in a sealed tube was degassed with argon for 30 min. The reaction was stirred at 90 °C for 5 hours, until total conversion of the monosaccharide. Purifications of the crude residue were carried out with successive diethyl ether sonication and filtration, to afford xylonolactones **δ3e** and **γ3e** as a white solid with **82% yield**.

Kinetics study:



A mixture of sugar (50 mg) catalyst **1b** (2.5 mol%), *tert*-butanol (0.8 mL) and acetone **4** (10eq) or only acetone **4** (0.8 mL) in a sealed tube was degassed with argon for 15 min. The reaction was stirred at 90 °C for X hours. 1-bromo-4-nitrobenzene (1 equiv.) was added as an internal standard and the crude mixture was evaporated under reduced pressure. Yields of lactones were determined by ^{1}H NMR in DMSO-d$_6$, after filtration through a PTFE filter (0.2 µm).

Analysis:



Xylose 2e

Kinetics-xylose oxidation (2.5mol%) in acetone (0.8mL)

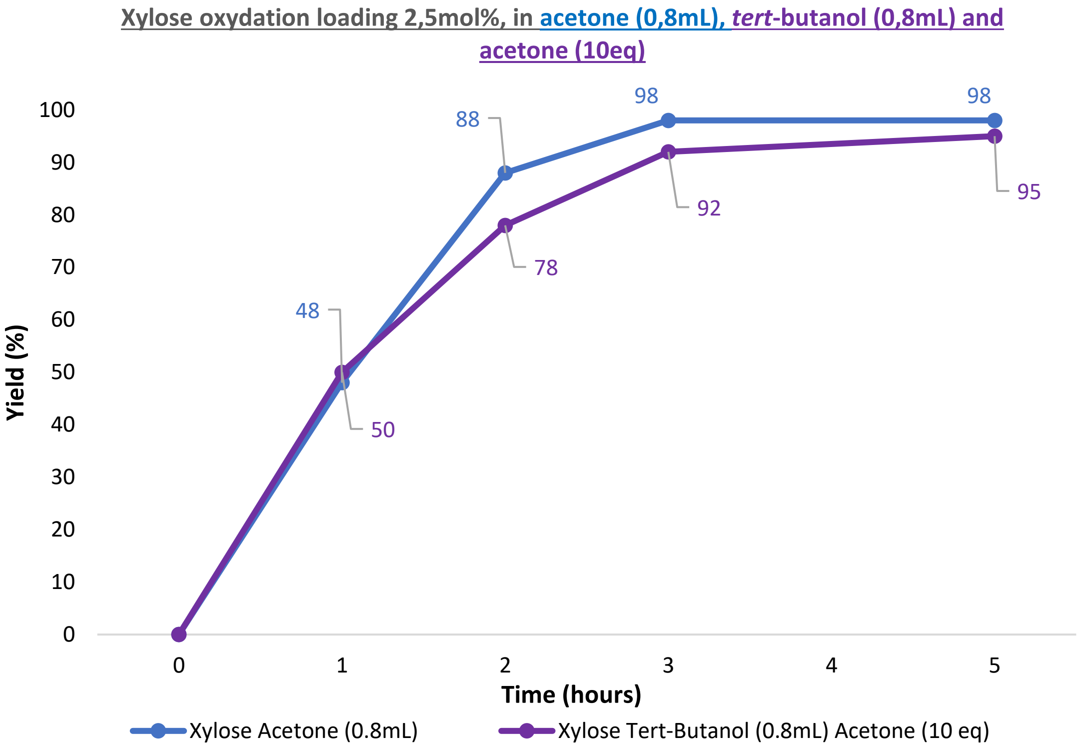
Time (hours)	Yield (%)
1	48
2	88
3	98
4	
5	98

Table 6: NMR yield of xylonolactones using procedure A

Kinetics-xylose oxidation (2.5mol%) in *tert*-butanol (0.8mL), and acetone (10 eq)

Time (hours)	Yield (%)
1	50
2	78
3	92
4	
5	95

Table 7: NMR yield of xylonolactones using procedure B



Arabinose 2d

Kinetics-arabinose oxidation (2.5mol%) in acetone (0.8mL)

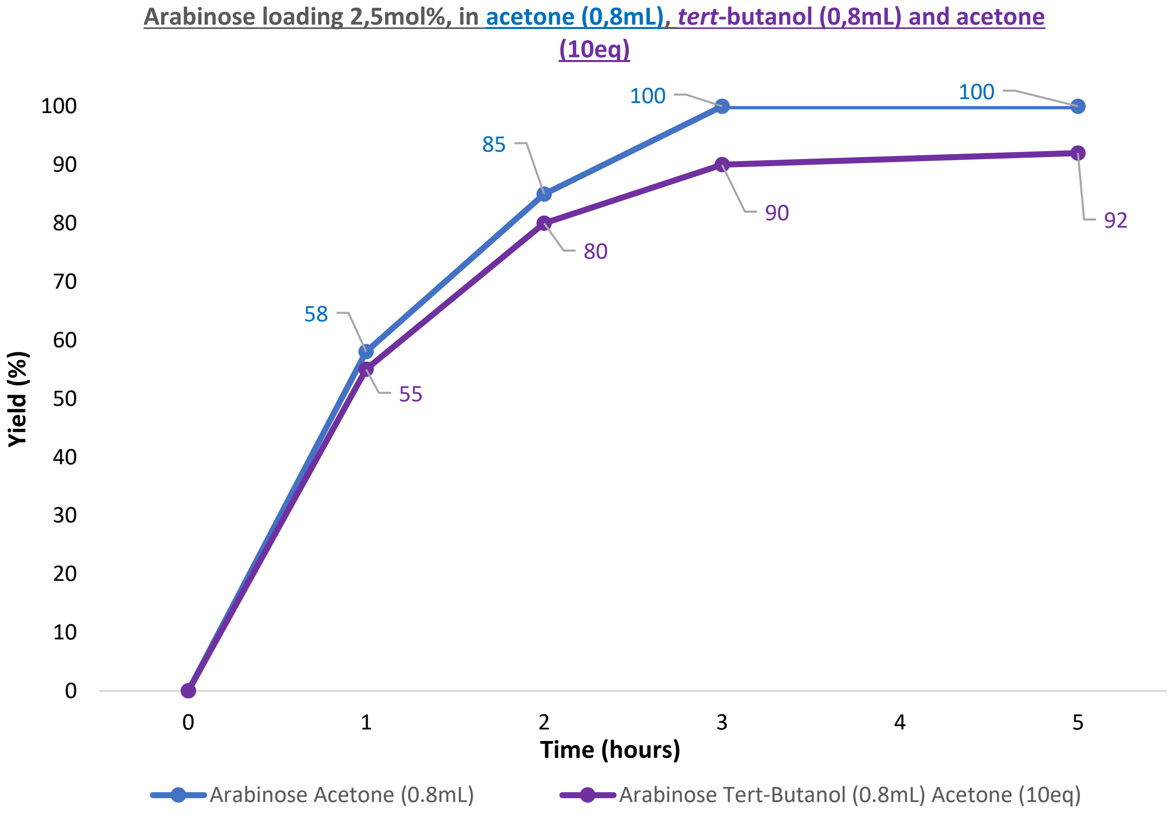
Time (hours)	Yield (%)
1	58
2	85
3	100
4	
5	100

Table 8: NMR yield of arabinolactones using procedure A

Kinetics-arabinose oxidation (2.5mol%) in *tert*-butanol (0.8mL), and acetone (10 eq)

Time (hours)	Yield (%)
1	55
2	80
3	90
4	
5	92

Table 9: NMR yield of arabinolactones using procedure B



Glucose 2a

Kinetics-glucose oxidation (2.5mol%) in acetone (0.8mL)

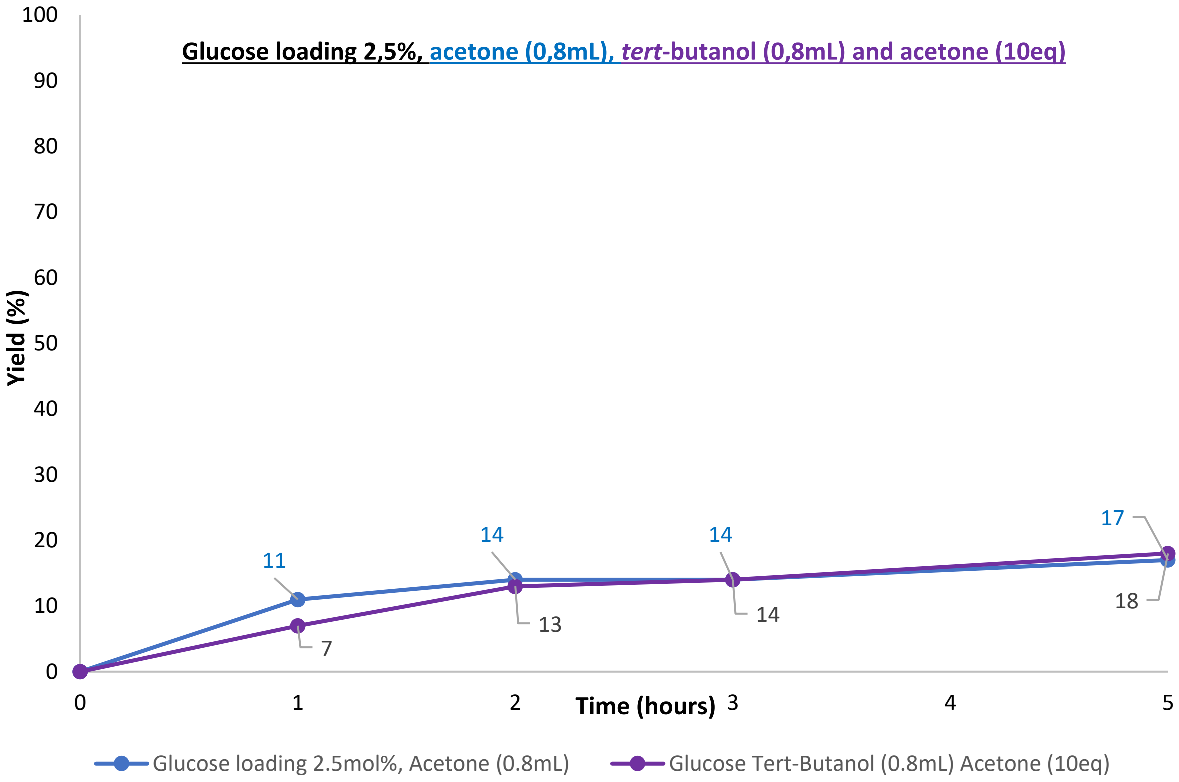
Time (hours)	Yield (%)
1	11
2	14
3	14
4	
5	17

Table 10: NMR yield of gluconolactones using procedure A

Kinetics-glucose oxidation (2.5mol%) in *tert*-butanol (0.8mL), and acetone (10 eq)

Time (hours)	Yield (%)
1	7
2	13
3	14
4	
5	18

Table 11: NMR yield of gluconolactones using procedure B



Galactose 2c

Kinetics-galactose oxidation (2.5mol%) in acetone (0.8mL)

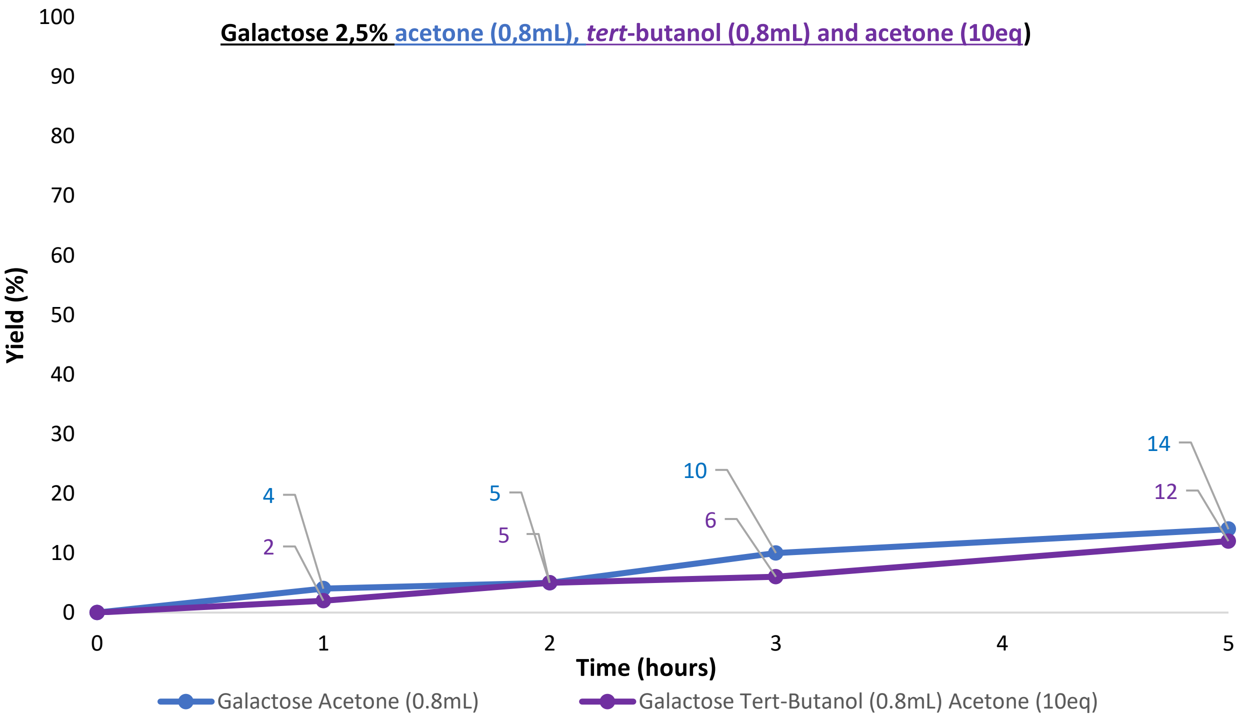
Time (hours)	Yield (%)
1	4
2	5
3	10
4	
5	14

Table 12: NMR yield of galactolactones using procedure A

Kinetics-Galactose oxidation (2.5mol%) in *tert*-butanol (0.8mL), and acetone (10 eq)

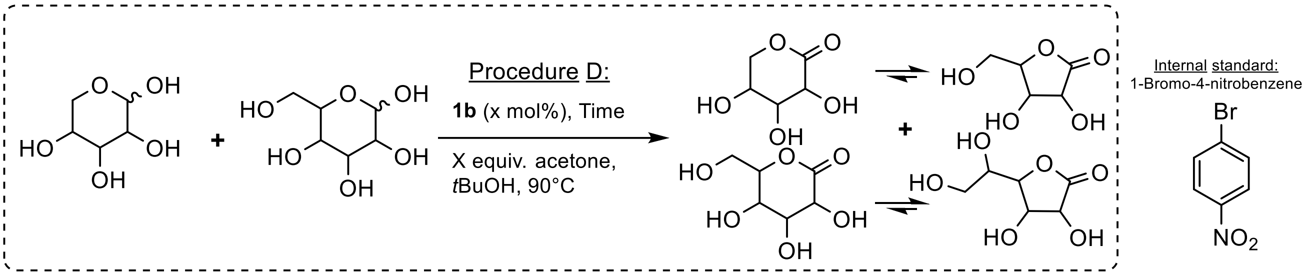
Time (hours)	Yield (%)
1	2
2	5
3	6
4	
5	12

Table 13: NMR yield of galactolactones using procedure B

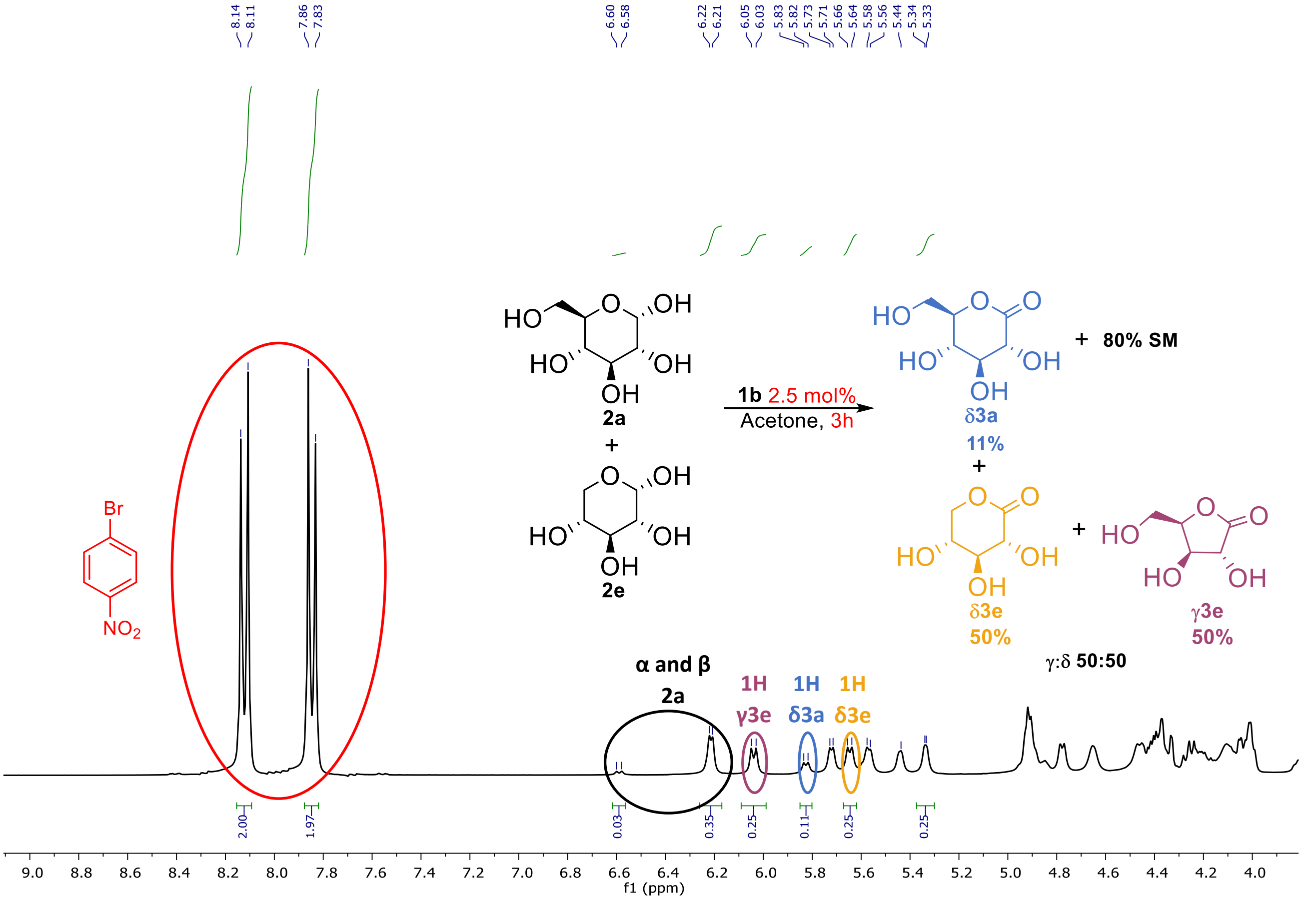


Mixtures-kinetics:

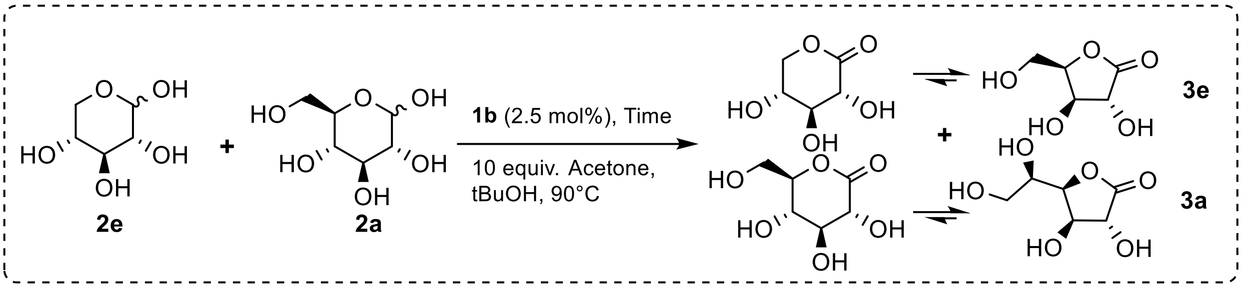
Procedure D: *Tert*-butanol (X mL) was degassed with argon for 15 min in a sealed tube after addition of sugars (X mg, X mmol, and X mg, X mmol; 1:1 mol or 1:1:1) catalyst **1b** (X mg, X mol%) and acceptor (X mol, X equiv.). The reaction was stirred at 90 °C for X hours. 1-bromo-4-nitrobenzene (1 equiv.) was added as an internal standard and the crude mixture was evaporated under reduced pressure. Yield of sugars lactones was determined by ^{1}H NMR in DMSO-d$_6$, after filtration trough a PTFE filter (0.2 µm).



Analysis:



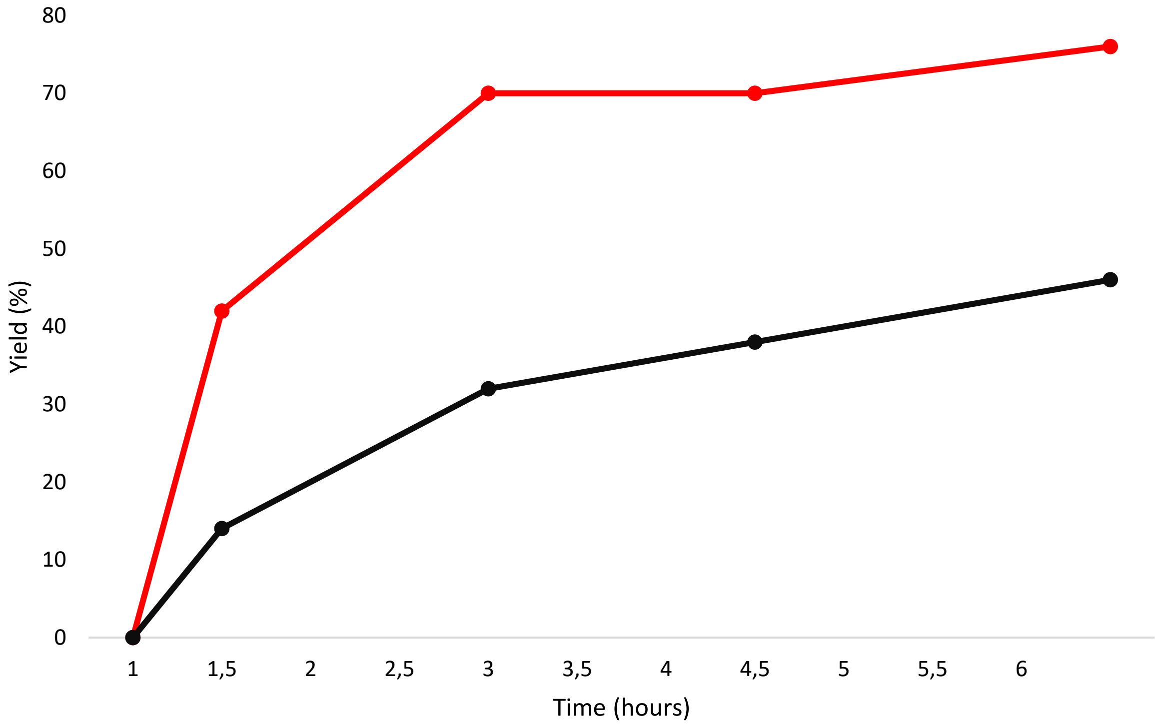
1 : 1 xylose/glucose mixture, acetone as acceptor



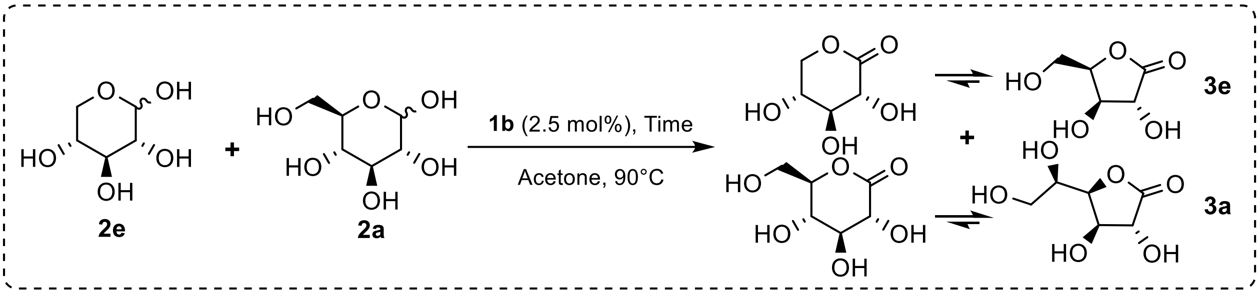
Reaction was carried out according to the general **procedure D**, using D-xylose **2e** (25 mg, 0.166 mmol, 1 equiv.) and D-glucose **2a** (30 mg, 0.166 mmol, 1 equiv.), catalyst **1b** (1.8 mg, 0.004 mmol, 2.5 mol%) and acetone **4** (246 µL, 3.333 mmol, 10 equiv.) as acceptor in *tert*-butanol (0.9 mL).

Time (hours)	*3e Yield (%)*	*3a Yield (%)*
0	*0*	*0*
1	*42*	*14*
2.5	*70*	*32*
4	*70*	*38*
6	*76*	*46*
24	*80*	*66*

Table 14: NMR yield of xylono- and gluconolactones using procedure D in tert-butanol



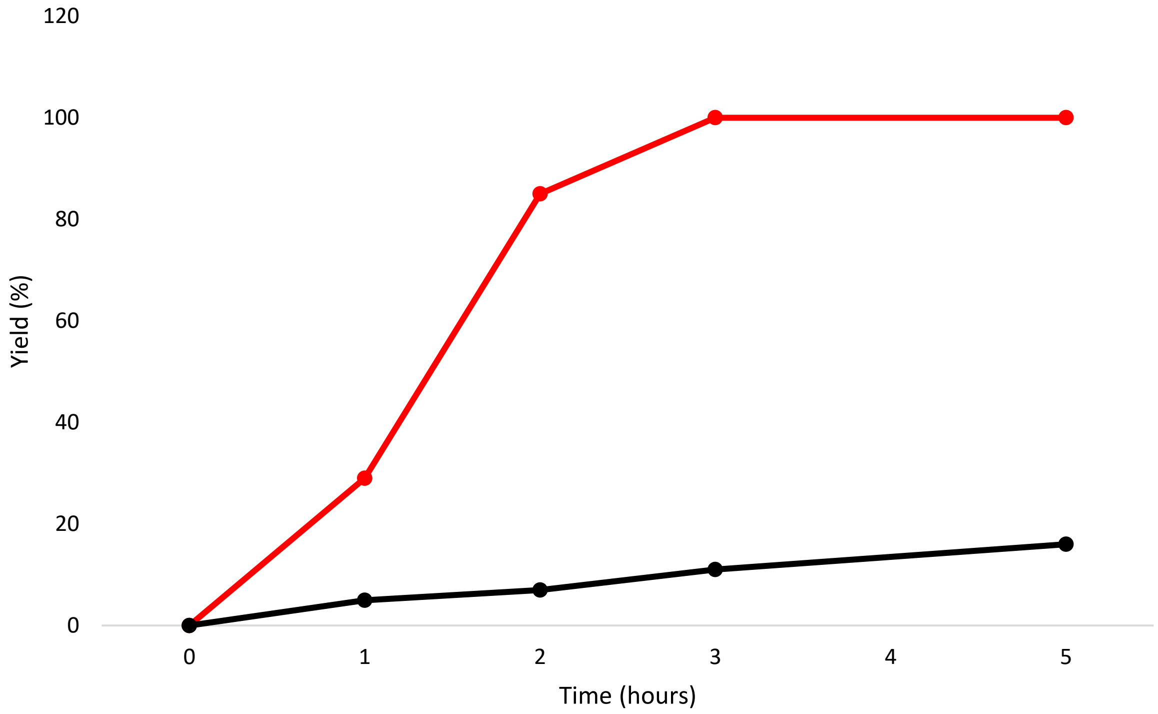
1 : 1 xylose/glucose mixture, acetone as acceptor/solvent



Reaction was carried out according to the general **procedure D**, using D-xylose **2e** (25mg, 0.166 mmol, 1 equiv.) and D-glucose **2a** (30 mg, 0.166 mmol, 1 equiv.) catalyst **1b** (1.8 mg, 0.004 mmol, 2.5 mol%) in acetone **4** (0.9mL) as solvent and acceptor.

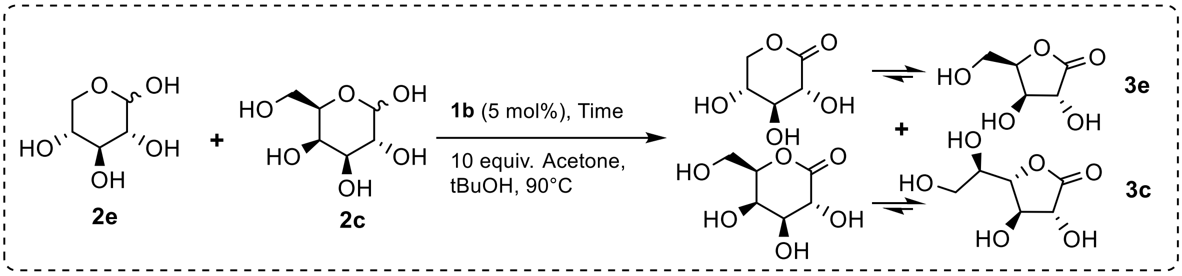
Time (hours)	***3e Yield (%)***	***3a Yield (%)***
0	*0*	*0*
1	*29*	*5*
2	*85*	*7*
3	*100*	*11*
5	*100*	*16*

Table 15: NMR yield of xylono- and gluconolactones using procedure D in acetone



1 : 1 xylose/galactose

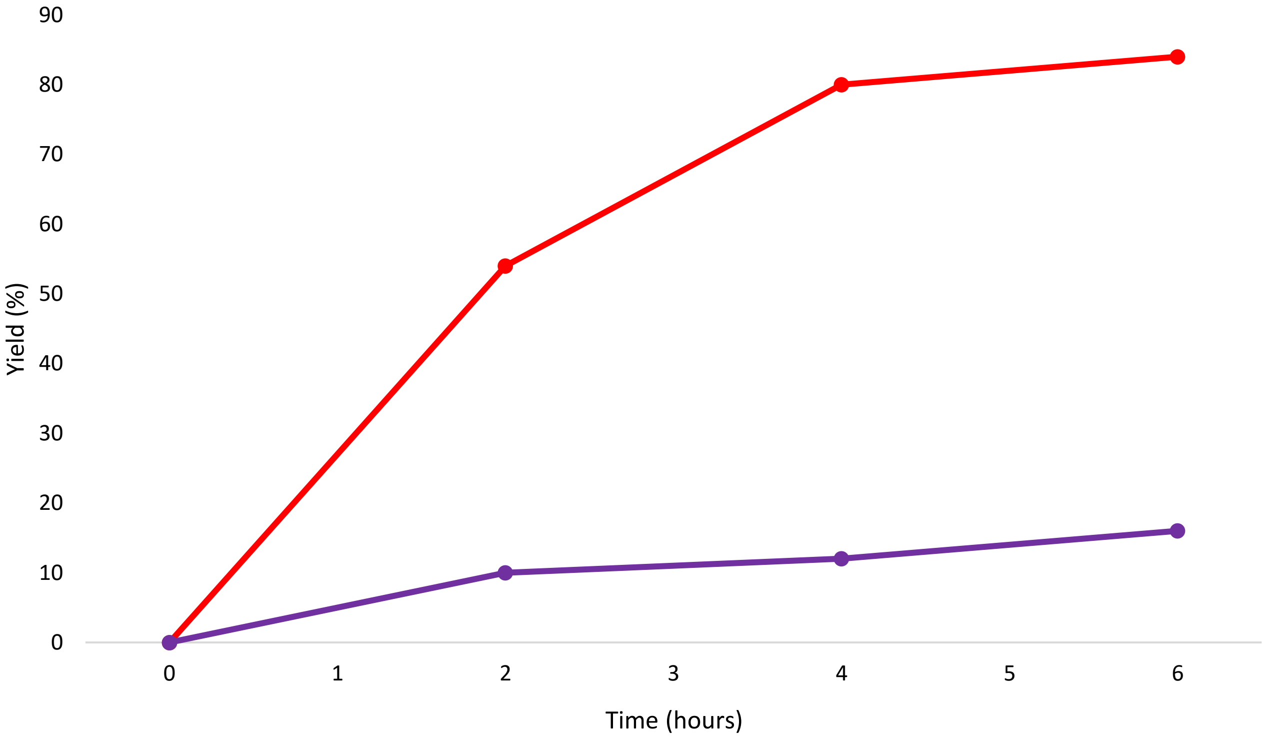
1 : 1 xylose/galactose mixture, acetone as acceptor



Reaction was carried out according to **procedure D**, using D-xylose **2e** (75 mg, 0.499 mmol, 1 equiv.) and D-galactose **2c** (90 mg, 0.499 mmol, 1 equiv.), catalyst **1b** (10.7 mg, 0.025 mmol, 5mol%) and acetone **4** (370 µL, 4.995 mmol, 10 equiv.) as acceptor in *tert*-butanol (2.6 mL).

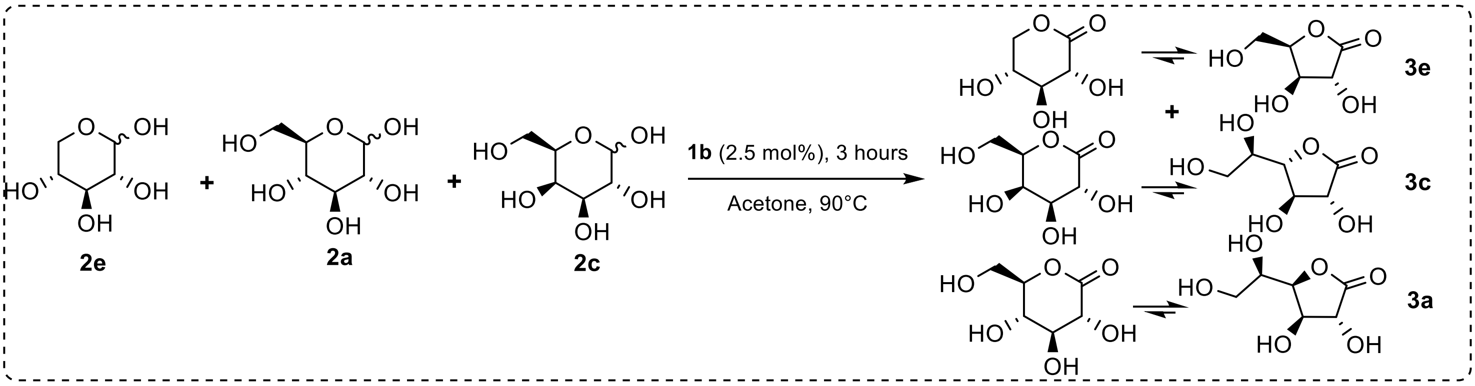
Time (hours)	3e Yield (%)	3c Yield (%)
0	0	0
2	54	10
4	80	12
6	84	16

Table 16: NMR yield of xylono- and galactolactones using procedure D in tert-butanol



1 : 1 : 1 xylose/glucose/galactose

1 : 1 : 1 xylose/glucose/galactose mixture, acetone as acceptor



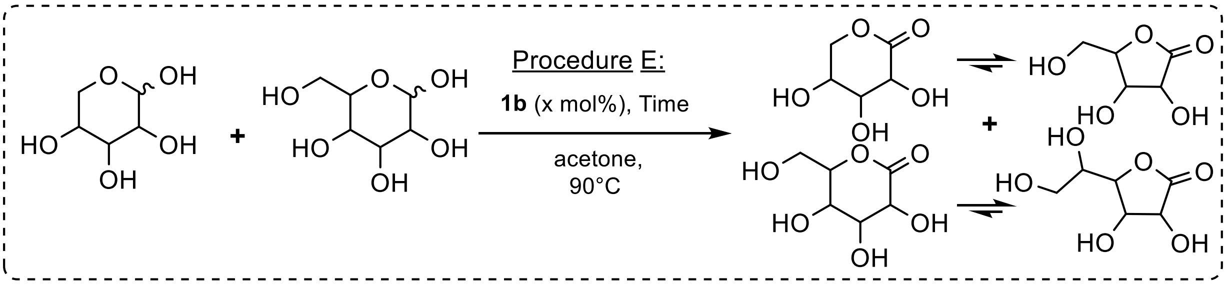
Reaction was carried out according to **procedure D**, using D-xylose **2e** (50 mg, 0.333 mmol, 1 equiv.) D-glucose **2a** (60 mg, 0.333 mmol, 1 equiv.) D-galactose **2c** (60 mg, 0.333 mmol, 1 equiv.) catalyst **1b** (3.6 mg, 0.008 mmol, 2.5 mol%) in acetone **4** (2.7 mL).

Time (hours)	3e Yield (%)	3a Yield (%)	3c Yield (%)
3	Quant.	16	8

Table 17: NMR yield of xylono-, glucono- and galactolactones using procedure D in acetone

Scale-up Mixtures:

Procedure E: *Tert*-butanol (X mL) was degassed in a sealed tube after addition of sugars (X mg, X mmol, and X mg, X mmol, 1:1 mol) catalyst **1b** (X mg, X mol%) and acceptor (X mol, X equiv.). The reaction was stirred at 90 °C for X hours and the solvent was evaporated under reduced pressure. The crude mixture was purified using the resin procedure or on silica gel.

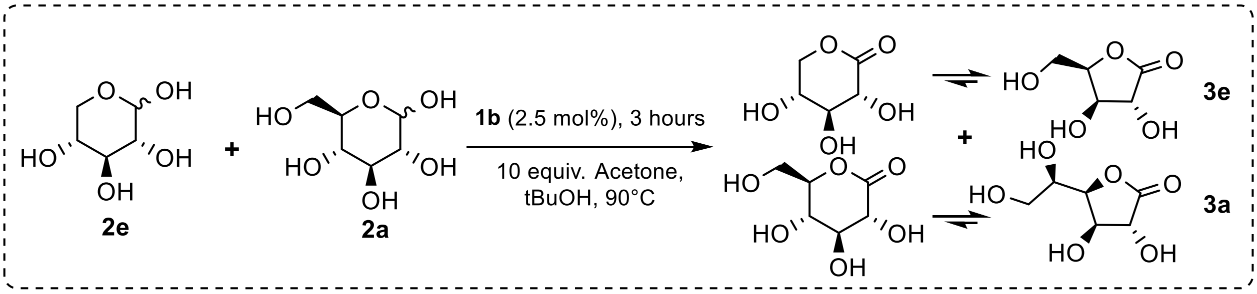


Two purification procedures were used:

Normal phase chromatography procedure I (gradient of toluene:acetone:acetic acid (60:40:0 to 0:90:10) or cyclohexane:acetone (100:0 to 0:100)) or resin.

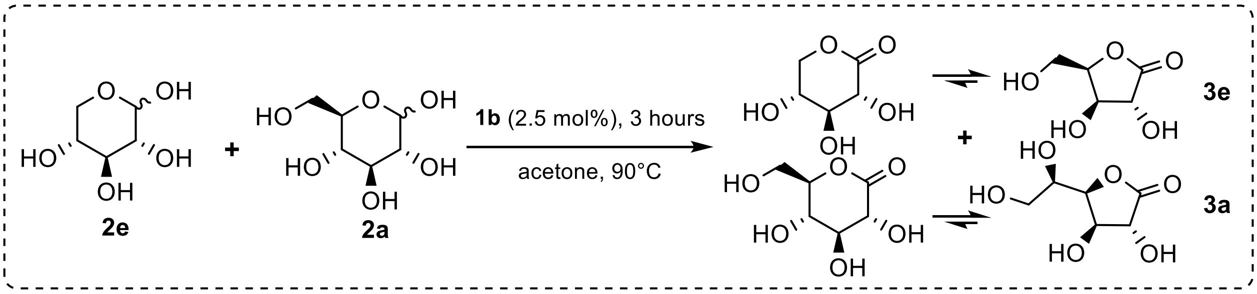
Resin purification procedure II The ambersep 900 (OH) ion exchange resin was first washed with water, methanol, diethyl ether and dried. The volatiles from the crude were evaporated under reduced pressure, then the residue was washed three times with diethyl ether. The crude was then stirred overnight with the resin in water (20 mL). Then the first 20mL where removed and the resin was washed again 3 times for 5 min with 20mL distilled water. The resin was then extracted with 2/1 M HCl solution (10mL). The solution was then freeze dried several times (the residue was dissolved each time in distilled water prior to freeze drying) affording the product as a brown/white solid.

1:1 xylose/glucose mixture with acetone as acceptor



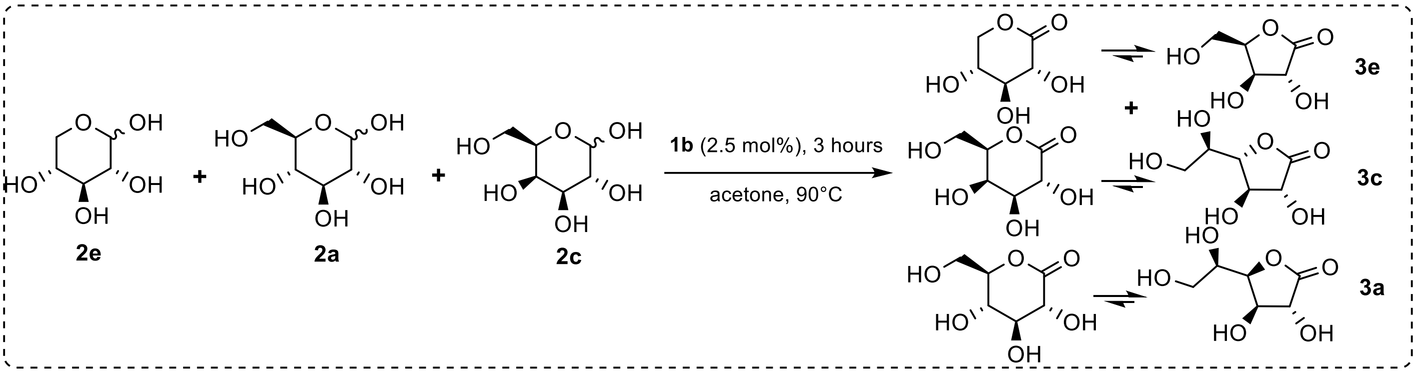
Reaction was carried out according to the general **procedure E**, using D-xylose **2e** (125 mg, 0.832 mmol, 1 equiv.), D-glucose **2a** (150 mg, 0.832 mmol, 1 equiv.), catalyst **1b** (8.9 mg, 0.020 mmol, 2.5 mol%) and acetone **4** (615 µL, 8.32 mmol, 10 equiv.) as acceptor in *tert*-butanol (4 mL). Purification using the ***resin procedure II*** afforded xylonolactone **3e** (114 mg, 0.773 mmol, **93%** isolated yield).

1:1 xylose/glucose mixture with acetone as acceptor



Reaction was carried out according to the general **procedure E**, using D-xylose **2e** (125 mg, 0.832 mmol, 1 equiv.), D-glucose **2a** (150 mg, 0.832 mmol, 1 equiv.), catalyst **1b** (8.9 mg, 0.020 mmol, 2.5 mol%) and acetone **4** (4 mL) as acceptor and solvent. Purification using the ***resin procedure II*** afforded xylonolactone **3e** (117 mg, 0.790 mmol, **95%** isolated yield).

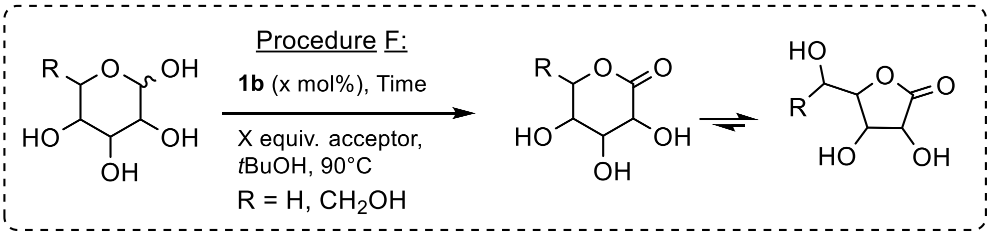
1:1:1 xylose/glucose/galactose mixture with acetone as acceptor



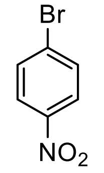
Reaction was carried out according to the general **procedure E**, using D-xylose **2e** (200 mg, 1.333 mmol, 1 equiv.), D-galactose **2c** (240 mg, 1.333 mmol, 1 equiv.) D-glucose **2a** (240 mg, 1.333 mol, 1 equiv.) catalyst **1b** (14 mg, 0.033 mmol, 2.5 mol%) and acetone (X mL) as acceptor and solvent. Purification using the ***resin procedure II*** afforded xylonolactone **3e** (122 mg, 0.826 mmol, **62%** isolated yield).

Acceptor Screening

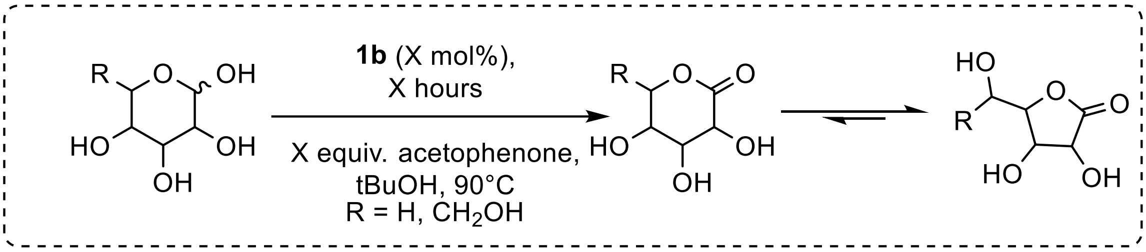
Procedure F: A mixture of sugar (50mg) catalyst **1b** (2.5-10 mol%) and acceptor (X equiv.) in *tert*-butanol (0.8mL) in a sealed tube was degassed with argon for 15 min. The reaction was stirred at 90 °C for X hours. 1-bromo-4-nitrobenzene (1 equiv.) was added as an internal standard and the crude mixture was evaporated under reduced pressure. Yields of lactones were determined by ^{1}H NMR in DMSO-d$_6$, after filtration through a PTFE filter (0.2 µm).



Internal standard:
1-Bromo-4-nitrobenzene



Acetophenone as acceptor

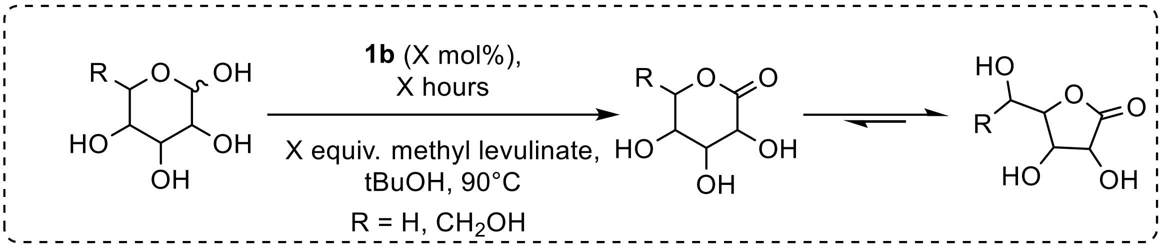


Reaction was carried out according to the general **procedure F**, using a mixture of sugar (50 mg) catalyst **1b** (X mg, X mol%), acetophenone (X mol, X equiv.) and *tert*-butanol (0.8 mL).

Substrat	**Catalyst loading (mol%)**	**Equiv. acetophenone**	**Time (hours)**	**NMR Yield (%)**
2a	5	10	5	30
2e	5	10	5	100

Table 18: NMR yield of xylono- and gluconolactones using procedure C and acetophenone as acceptor

Methyl Levulinate as acceptor

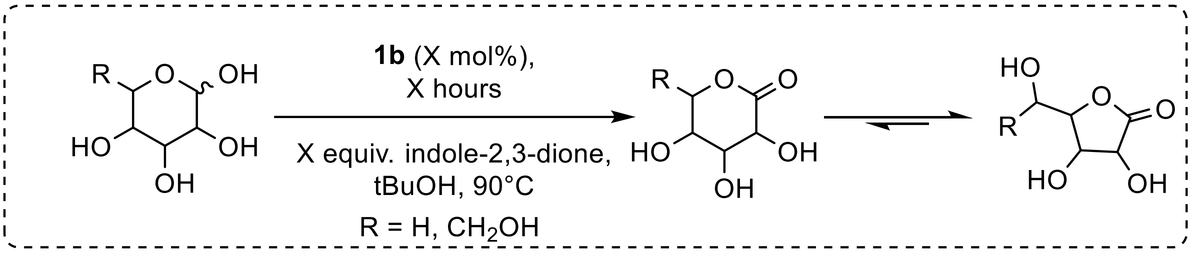


Reaction was carried out according to the general **procedure F** using a mixture of sugar (50 mg) catalyst **1b** (X mg, X mol%), methyl levulinate **7** (X mol, X equiv.) and *tert*-butanol (0.8 mL).

Substrate	Catalyst loading (mol%)	Equiv. Methyl Levulinate	Time (hours)	NMR Yield (%)
2a	5	10	5	40
2e	5	10	5	90
2e	2.5	1	24	80
2e	5	1	24	70

Table 19: NMR yield of xylono- and gluconolactones using procedure C and methyl levulinate as acceptor

Indole-2,3-dione as acceptor

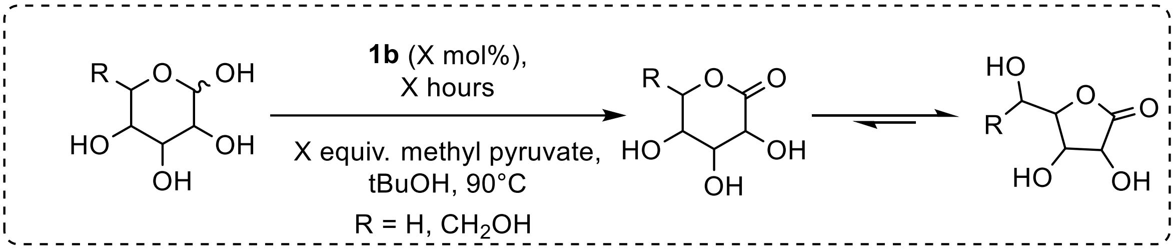


Reaction was carried out according to the general **procedure F** using a mixture of sugar (50 mg) catalyst **1b** (X mg, X mol%), Isatine **8** (X mol, X equiv.) and *tert*-butanol (0.8 mL).

Substrate	Catalyst loading (mol%)	Equiv. Indole-2,3-dione	Time (hours)	NMR Yield (%)
2a	5	10	5	35
2e	5	1	24	100
2e	2.5	1	24	100

Table 20: NMR yield of xylono- and gluconolactones using procedure C and indole-2,3-dione as acceptor

Methyl pyruvate as acceptor

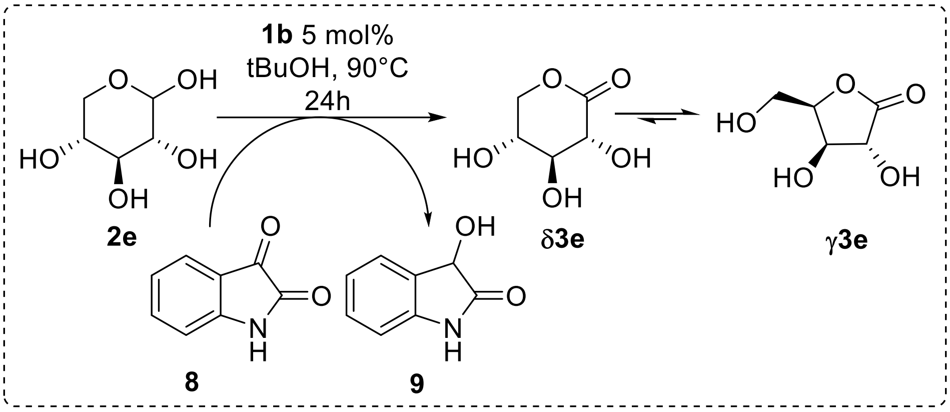


Reaction was carried out according to the general **procedure F** using a mixture of sugar (50 mg) catalyst **1b** (X mg, X mol%), methyl pyruvate **6** (X mol, X equiv.) and *tert*-butanol (0.8 mL).

Substrate	Catalyst loading (mol%)	Equiv. Methyl Pyruvate	Time (hours)	NMR Yield (%)
2a	5	10	5	30
2e	5	10	5	78

Table 21: NMR yield of xylono- and gluconolactones using procedure C and methyl pyruvate as acceptor

1:1 Donnor : Acceptor experiment

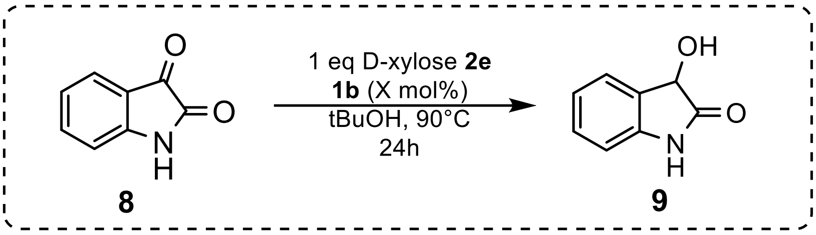


Tert-butanol (0.8 mL) was degassed with argon for 15 min in a sealed tube after addition of D-xylose **2e** (50 mg, 0.333 mmol, 1 equiv.) catalyst **1b** (7.8 mg, 0.016 mmol, 5 mol%) and isatin **8** (49 mg, 0.333 mmol, 1 equiv.). The reaction was stirred at 90 °C for 24 hours. Yields of xylonolactones **3e** were determined by ^{1}H NMR in DMSO-d$_6$, after filtration trough a PTFE filter (0.2 µm).

3e Yield (%)	9 Yield (%)
>98	>98

Table 22: NMR yield of xylonolactones and 3-hydroxyindolin-2-one using indol-2,3-dione in a 1:1 ratio as acceptor

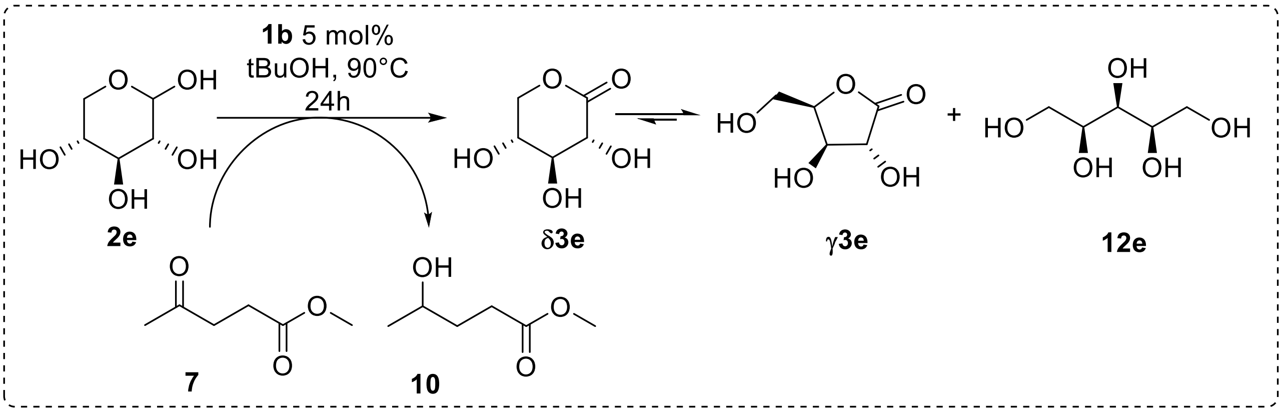
Acceptor reduction:



Tert-butanol (0.8 mL) was degassed with argon for 15 min in a sealed tube after addition of isatin **8** (100 mg, 0.679 mmol) catalyst **1b** (X mg, X mol%) and D-xylose **2e** as donor (0.679 mol, 1 equiv.). The reaction was stirred at 90 °C for 24 hours. 1-Bromo-4-nitrobenzene (1 equiv.) was added as an internal standard and the crude mixture was evaporated under reduced pressure. Yield of 3-hydroxyindolin-2-one was determined by ^{1}H NMR in DMSO-d$_6$, after filtration trough a PTFE filter (0.2 µm). The purification was performed on silica gel using a cyclohexane/ethyl acetate gradient starting from 100:0 to 33:67 affording 3-hydroxyindolin-2-one **9** (85.8 mg, 0.579 mmol, **85%**) as a light-yellow solid. **^{1}H NMR** (300 MHz, DMSO-*d*$_6$) δ 10.23 (s, 1H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.16 (d, *J* = 7.6 Hz, 1H), 4.82 (d, *J* = 7.6 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d$_6$) δ 177.9, 142.1, 129.3, 128.9, 124.7, 121.5, 109.4, 69.1, 40.3, 40.0, 39.8, 39.5, 39.2, 38.9, 38.6. Spectral data are in agreement with the data previously reported in literature.[2]

Loading (mol%)	Time (hours)	NMR Yield (%)	Isolated Yield (%)
5	24	100	/
2.5	24	100	85

Table 23: NMR and isolated yields of 3-hydroxyindolin-2-one using D-xylose in a 1:1 ratio as donor

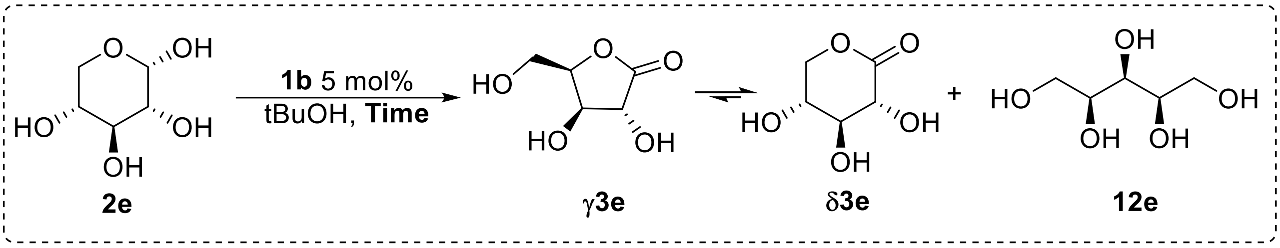


Tert-butanol (0.8 mL) was degassed with argon for 15 min in a sealed tube after addition of D-xylose **2e** (50 mg, 0.333 mmol, 1 equiv.) catalyst **1b** (7.8 mg, 0.016 mmol, 5 mol%) and methyl levulinate **7** (43 mg, 0.333 mmol, 1 equiv.). The reaction was stirred at 90 °C for 24 hours. Yields of xylonolactones **3e**, xylitol **12e** and methyl 4-hydroxypentanoate **10** were determined by ^{1}H NMR in DMSO-d$_6$, after filtration trough a PTFE filter (0.2 µm).

3e Yield (%)	12e Yield (%)	10 Yield (%)
70	30	30

Table 24: NMR yield of xylonolactones, xylitol and 4-hydroxypentanoate using methyl levulinate in a 1:1 ratio as acceptor

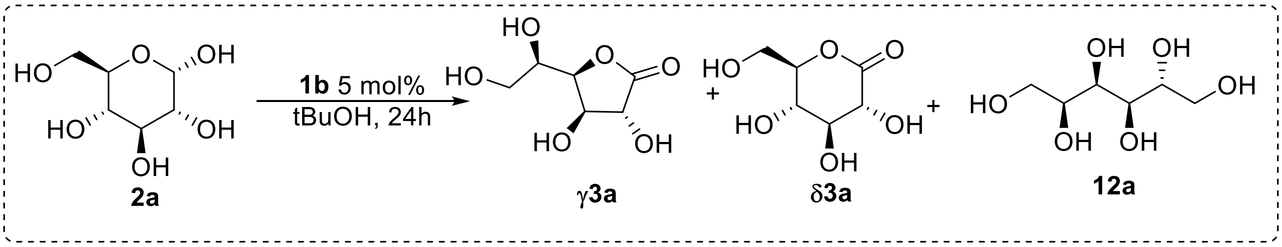
Disproportionation experiment



Tert-butanol (0.8 mL) was degassed with argon for 15 min in a sealed tube after addition of D-xylose **2e** (50 mg, 0.333 mmol, 1 equiv.) catalyst **1b** (7.8 mg, 0.016 mmol, 5 mol%) with no acceptor. The reaction was stirred at 90 °C for X hours. Yield and ratios of xylonolactones **3e** and xylitol **12e** were determined by ^{1}H NMR in DMSO-d$_6$ using an internal standard (1,4-bromonitrobenzene) after filtration trough a PTFE filter (0.2 µm).

Time (hours)	**3e Yield (%)**	**γ-δ ratio**	**12 Yield (%)**
5	55	90:10	45
24	55	95:5	45

Table 25: NMR yield of xylonolactones and xylitol in acceptor free conditions

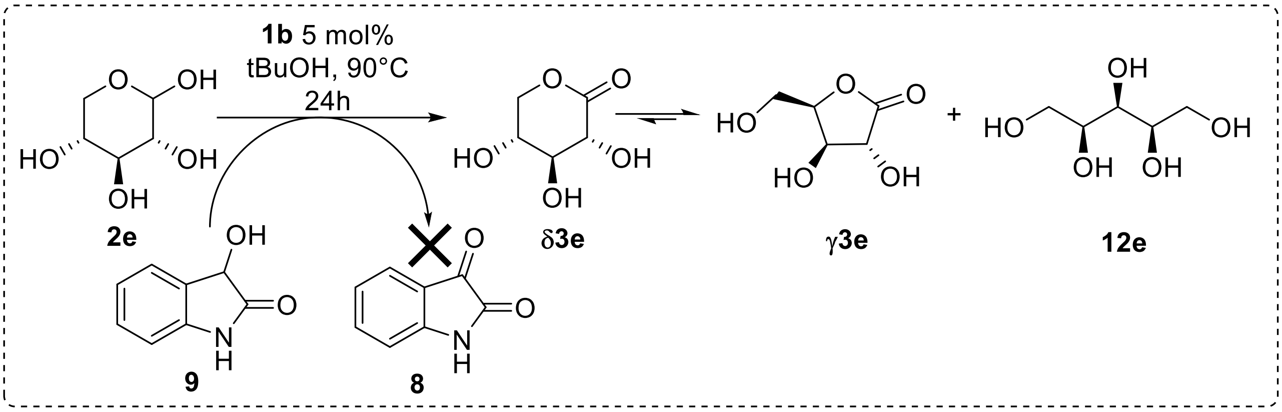


Tert-butanol (0.8 mL) was degassed with argon for 15 min in a sealed tube after addition of D-glucose (50 mg, 0.277 mmol, 1 equiv.) catalyst **1b** (5.9 mg, 0.014 mmol, 5 mol%) with no acceptor. The reaction was stirred at 90 °C for 24 hours. Yield and ratios of gluconolactones **3a** and sorbitol **12a** were determined by ^{1}H NMR in DMSO-d$_6$ using an internal standard (1,4-bromonitrobenzene) after filtration trough a PTFE filter (0.2 µm).

3a Yield (%)	**γ-δ ratio**	**12a Yield (%)**
25	80:20	~30

Table 26: NMR yield of gluconolactones and sorbitol in acceptor free conditions

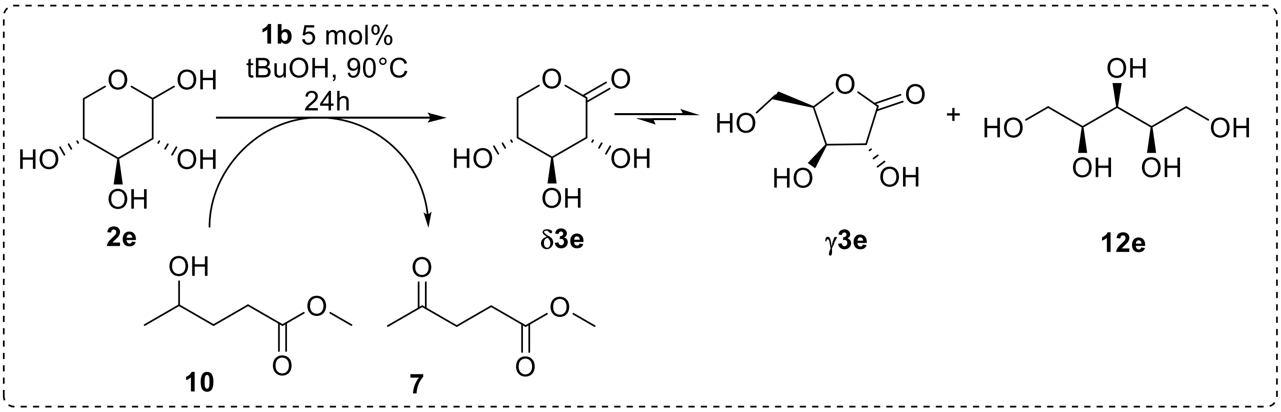
Reversibility experiments



Tert-butanol (0.8 mL) was degassed with argon for 15 min in a sealed tube after addition of D-xylose **2e** (50 mg, 0.333 mmol, 1 equiv.) catalyst **1b** (7.8 mg, 0.016 mmol, 5 mol%) and 3 hydroxyindolin-2-one **9** (49 mg, 0.333 mmol, 1 equiv.). The reaction was stirred at 90 °C for 24 hours. Yields and ratios of xylonolactones **3e**, xylitol **12e** and isatin **8** were determined by ^{1}H NMR in DMSO-d$_6$, after filtration trough a PTFE filter (0.2 μm).

3e Yield (%)	γ-δ ratio	12e Yield (%)	8 Yield (%)
50	90:10	50	/

Table 27: NMR yield of xylonolactones and xylitol using 3-hydroxyindolin-2-one



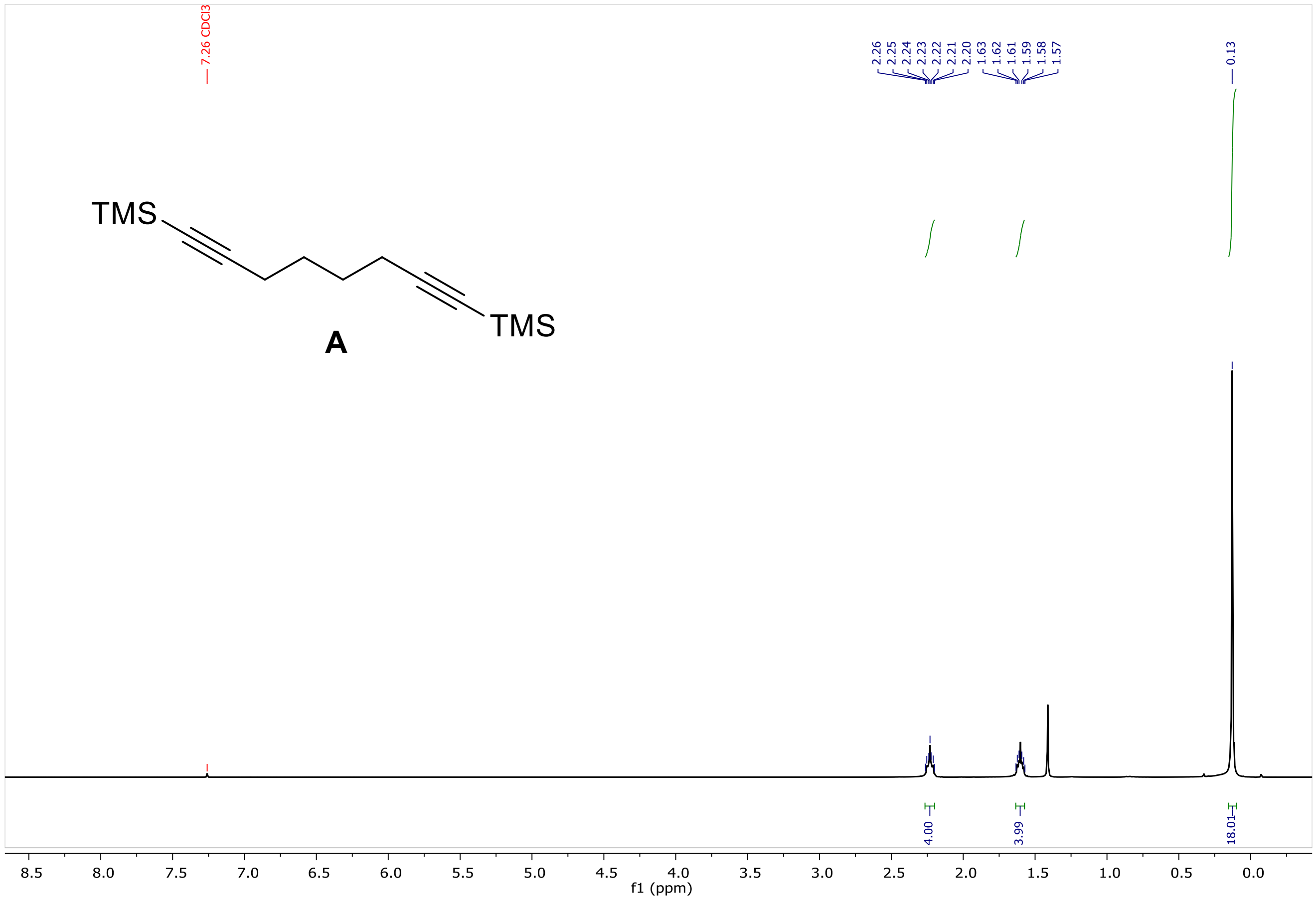
Tert-butanol (0.8 mL) was degassed with argon for 15 min in a sealed tube after addition of D-xylose **2e** (50 mg, 0.333 mmol, 1 equiv.) catalyst **1b** (7.8 mg, 0.016 mmol, 5 mol%) and methyl 4-hydroxypentanoate **10** (44 mg, 0.333 mmol, 1 equiv.). The reaction was stirred at 90 °C for 24 hours. Yields and ratios of xylonolactones **3e**, xylitol **12e** and methyl levulinate **7** were determined by ^{1}H NMR in DMSO-d$_6$, after filtration trough a PTFE filter (0.2 μm).

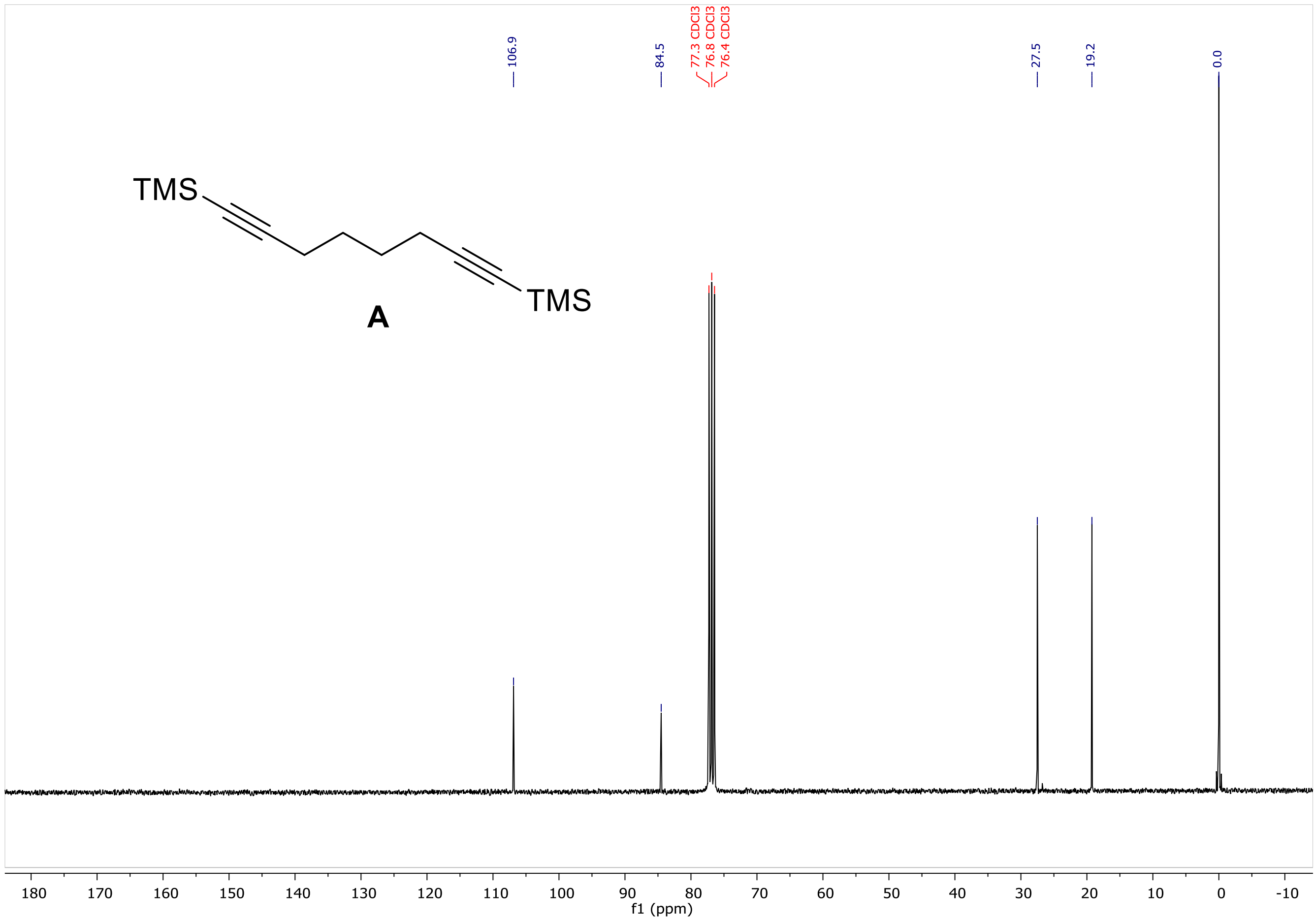
3e Yield (%)	γ-δ ratio	12e Yield (%)	7 Yield (%)
57	9:1	43	10

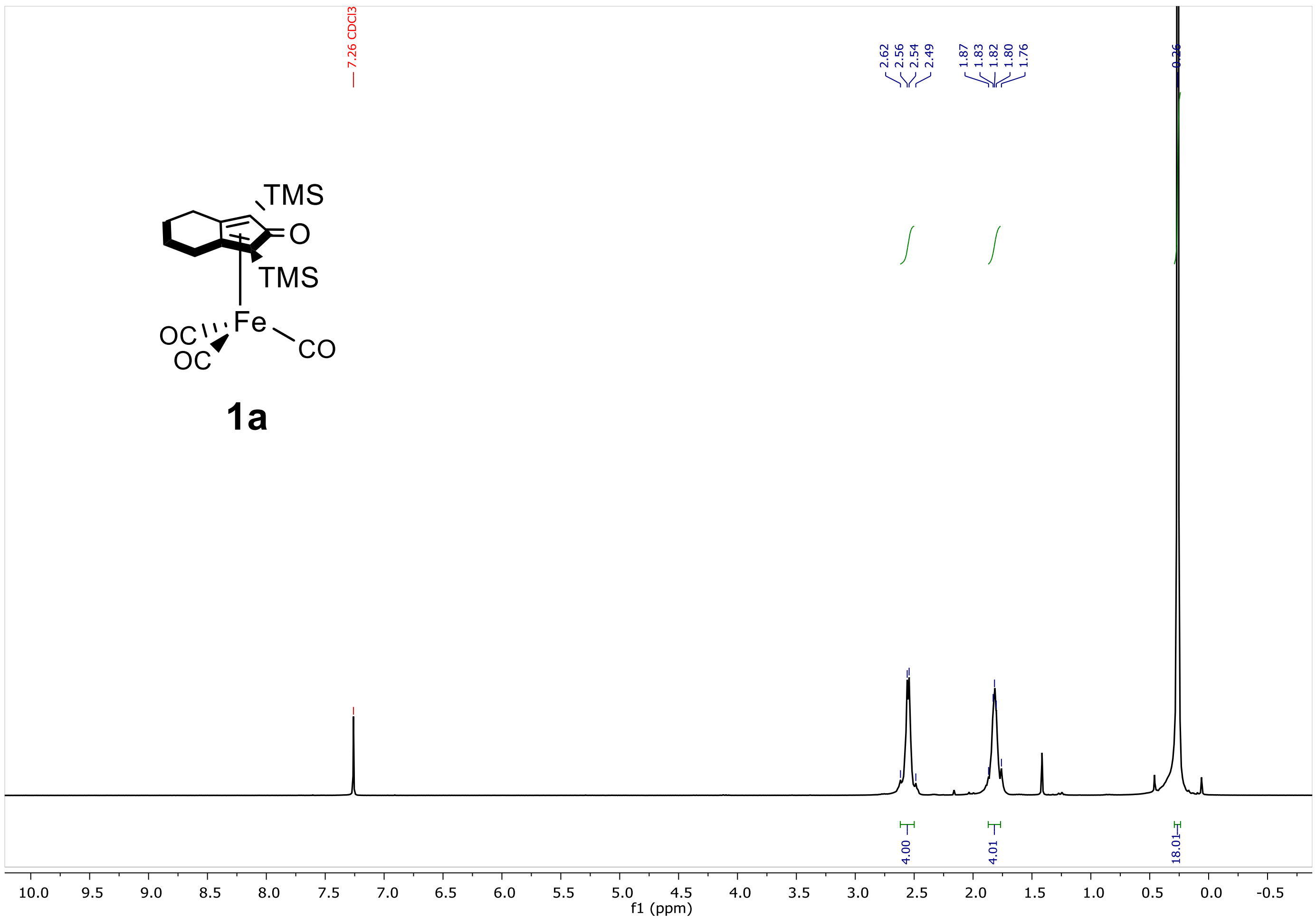
Table 28: NMR yield of xylonolactones and xylitol using 4-hydroxypentanoate

[2] ***Rui, H.; Shanchao, W.; Haoming, T.; Xiaohang, H.; Zhenliang, S.; Waubin, Z.;*** *Org. Lett.* **2018**, 20, 19, 6183–6187

NMR Spectra

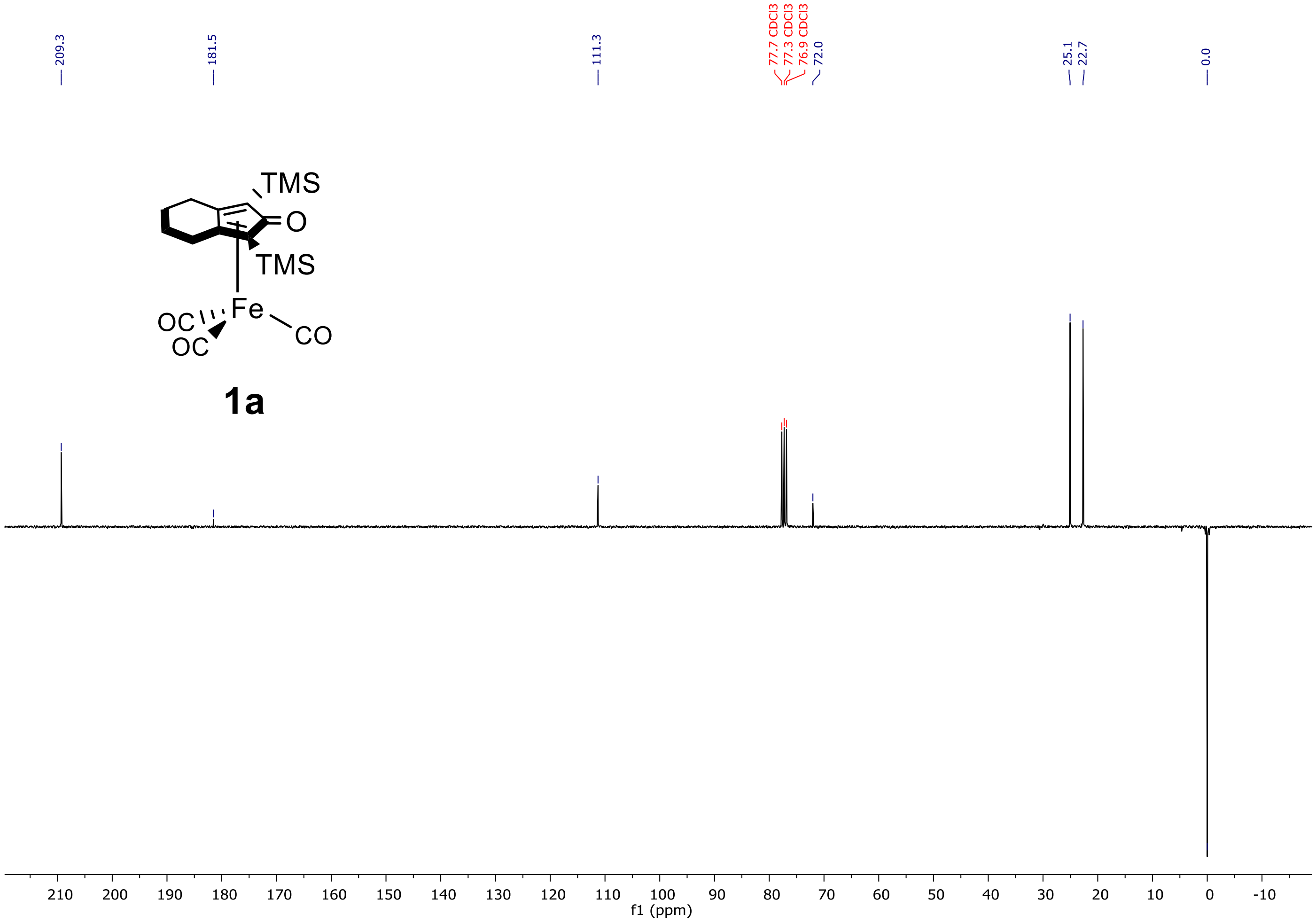

TMS
TMS
A
7.26 CDCl3
2.26
2.25
2.24
2.23
2.22
2.21
2.20
1.63
1.62
1.61
1.59
1.58
1.57
0.13
4.00
3.99
18.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


TMS
TMS
A
106.9
84.5
77.3 CDCl3
76.8 CDCl3
76.4 CDCl3
27.5
19.2
0.0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



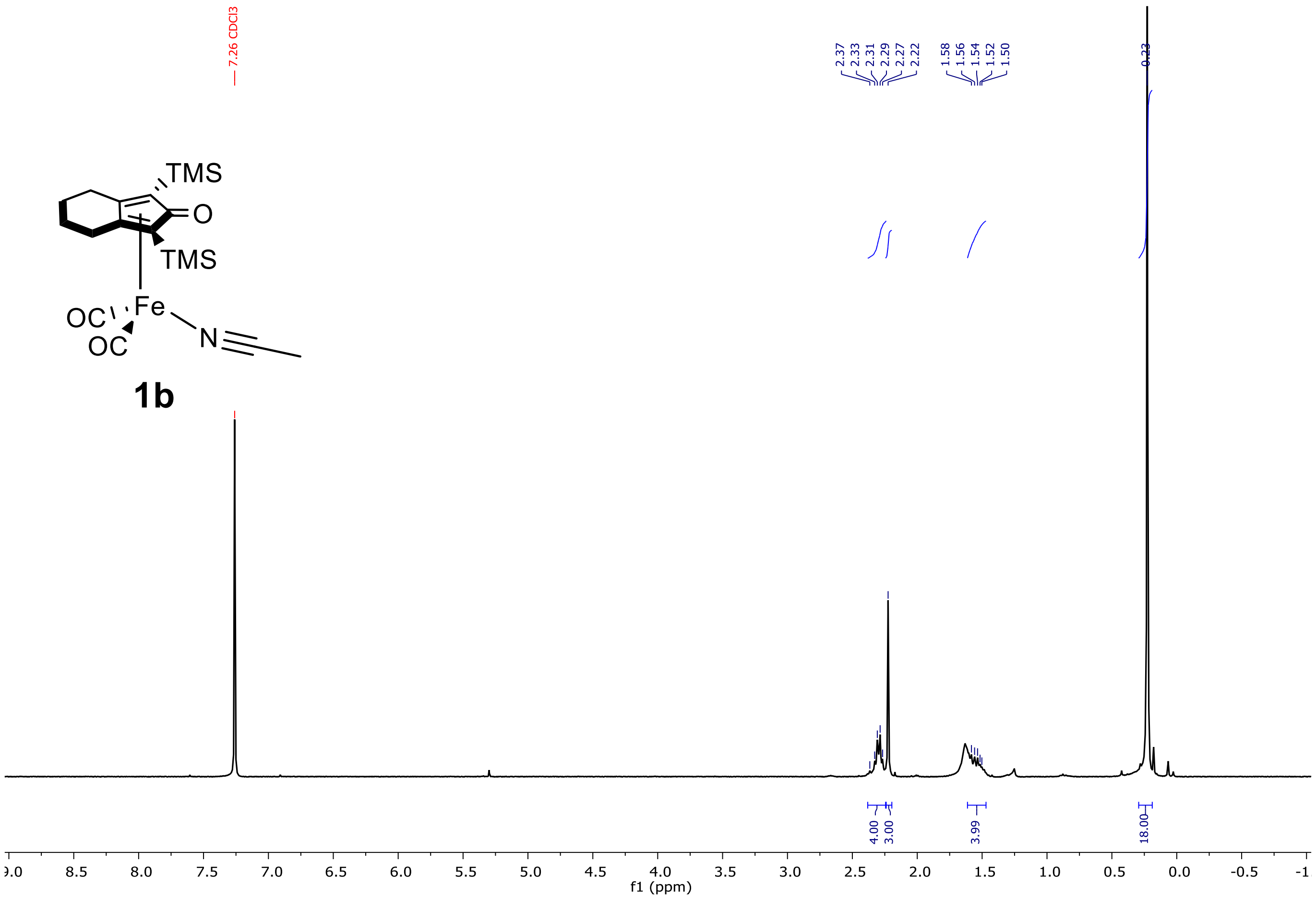
1a

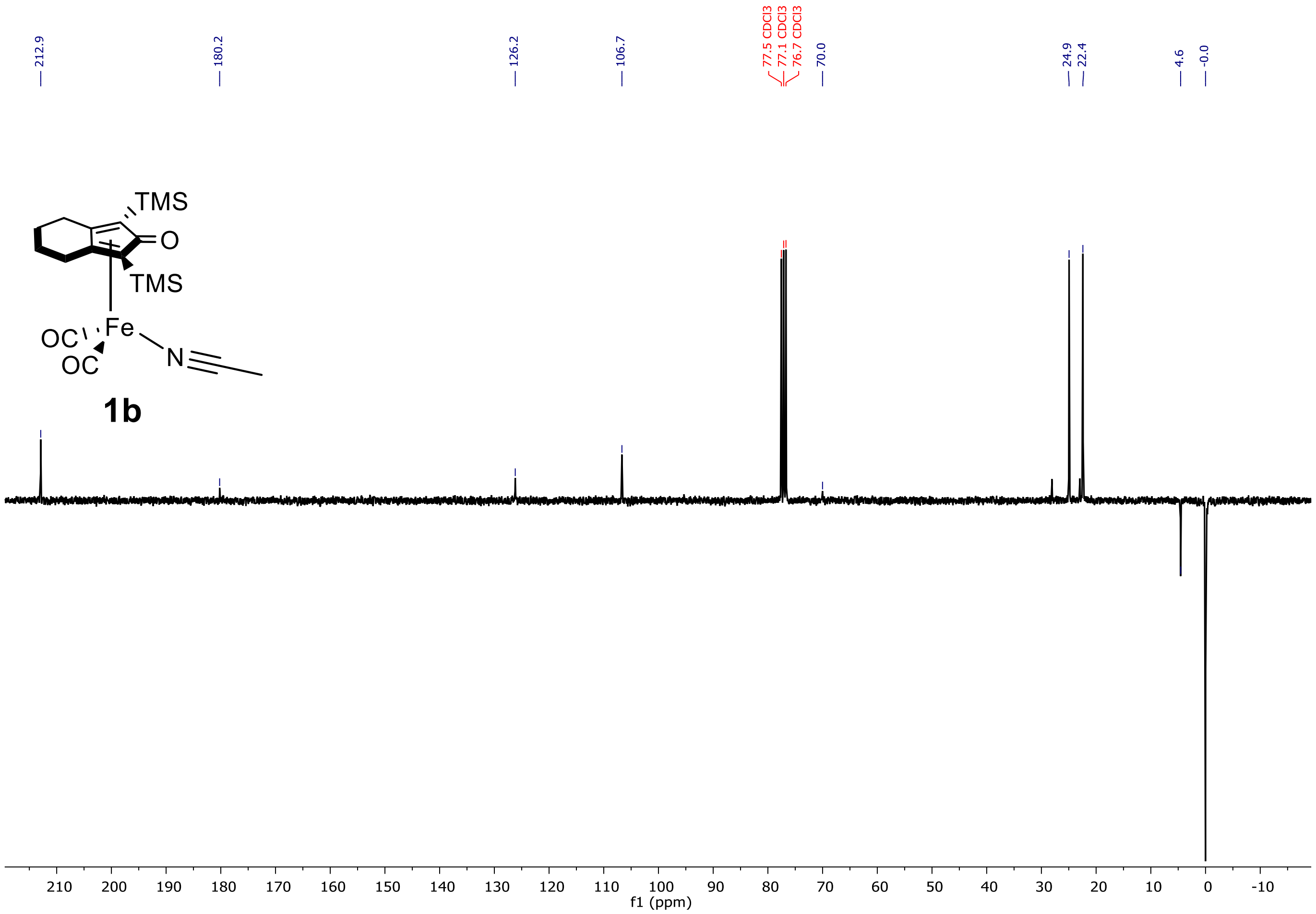
7.26 CDCl3
2.62
2.56
2.54
2.49
1.87
1.83
1.82
1.80
1.76
0.26
TMS
O
TMS
Fe
OC
OC
CO
4.00
4.01
18.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

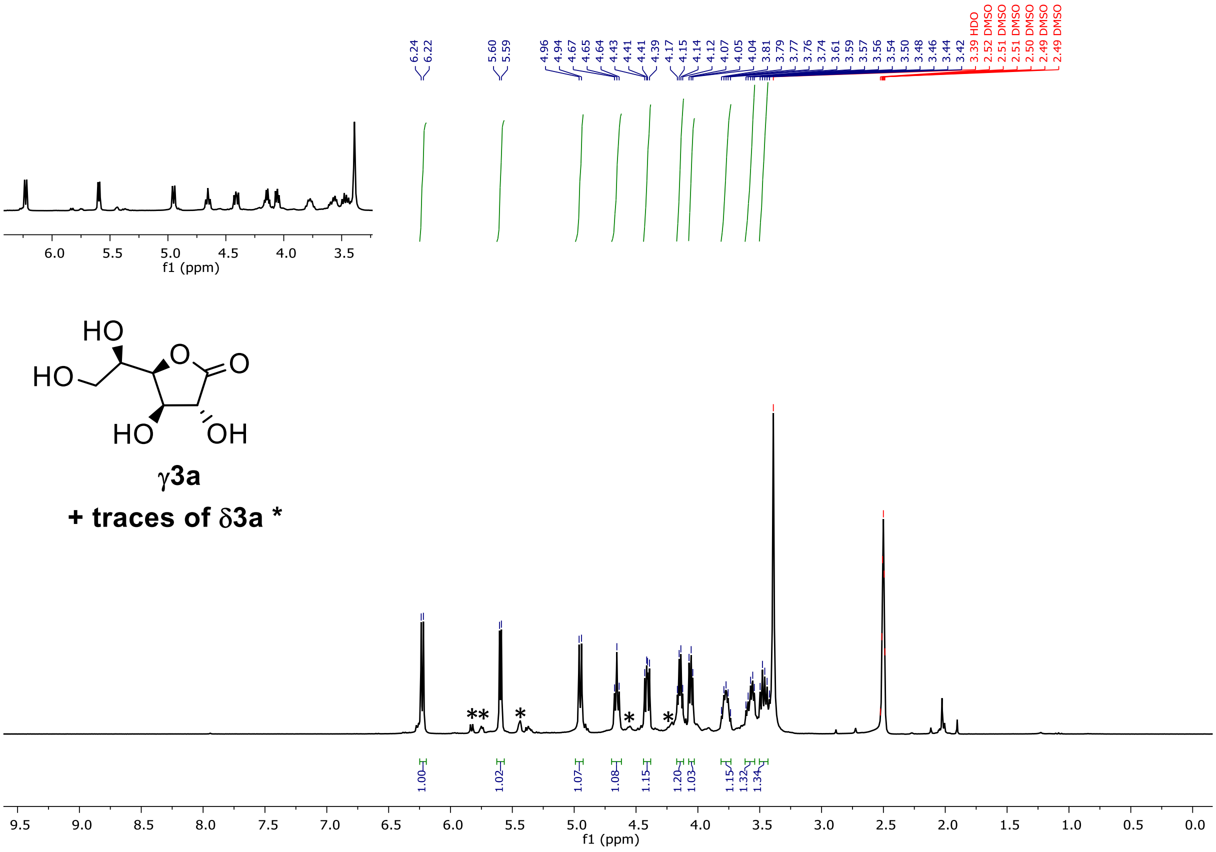


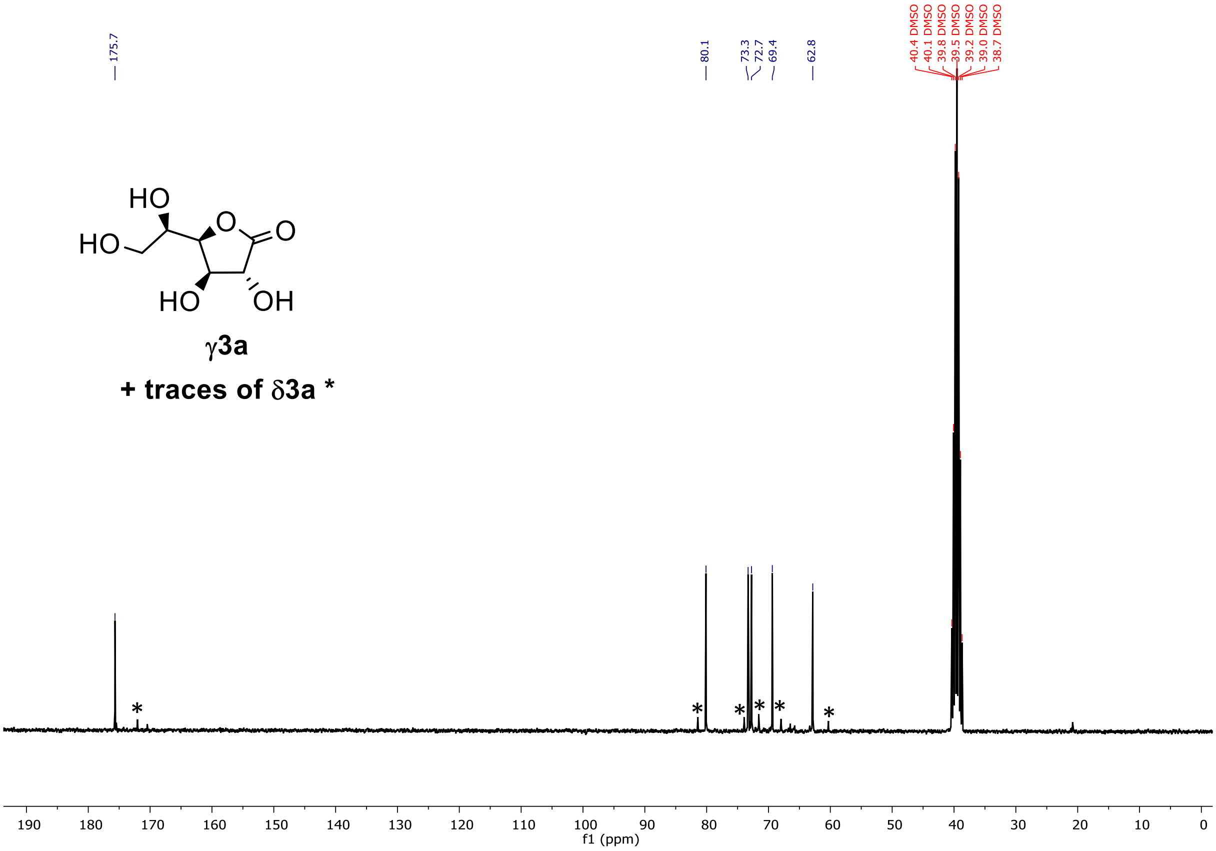
1a

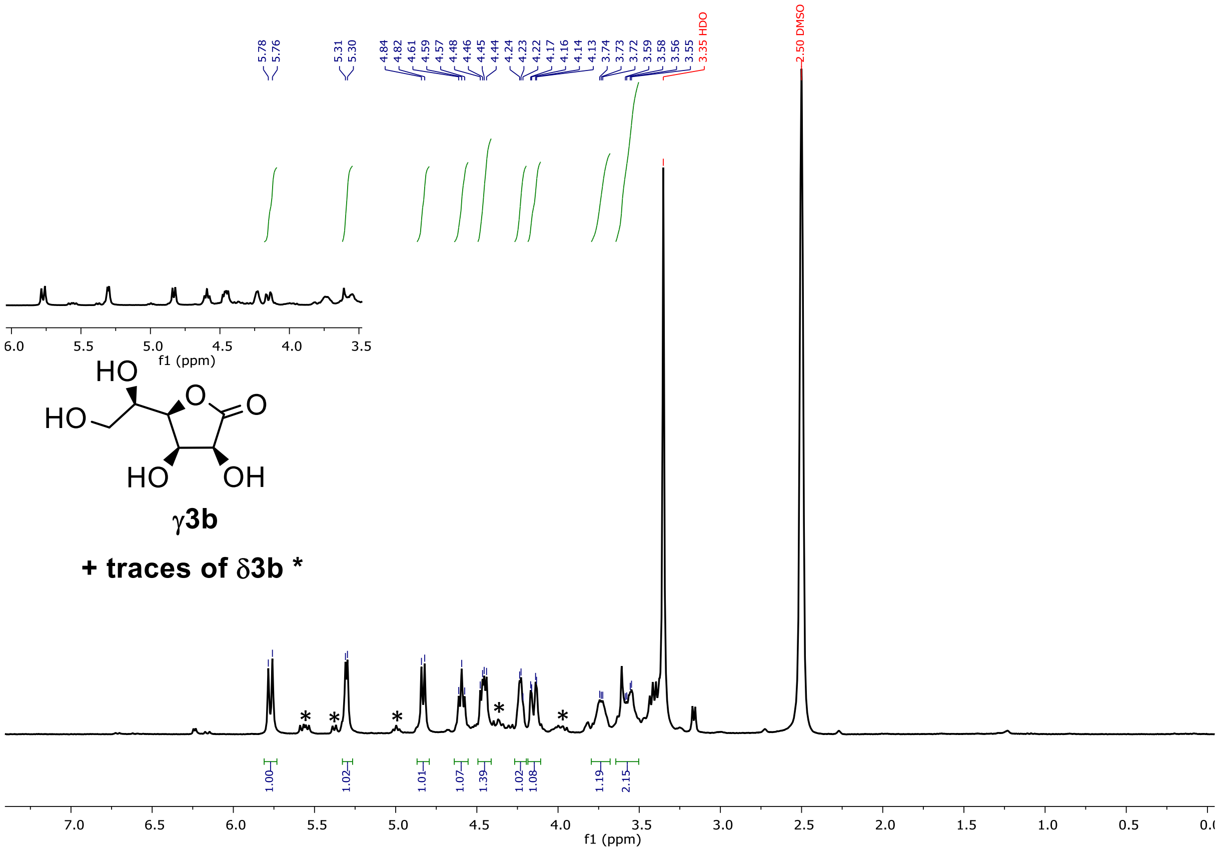
209.3
181.5
111.3
77.7 CDCl3
77.3 CDCl3
76.9 CDCl3
72.0
25.1
22.7
0.0
TMS
O
TMS
Fe
OC
OC
CO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TMS
O
TMS
OC
Fe
OC
N
1b
7.26 CDCl3
2.37
2.33
2.31
2.29
2.27
2.22
1.58
1.56
1.54
1.52
1.50
0.23
4.00
3.00
3.99
18.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


212.9
180.2
126.2
106.7
77.5 CDCl3
77.1 CDCl3
76.7 CDCl3
70.0
24.9
22.4
4.6
-0.0
TMS
O
TMS
OC
Fe
OC
N
1b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

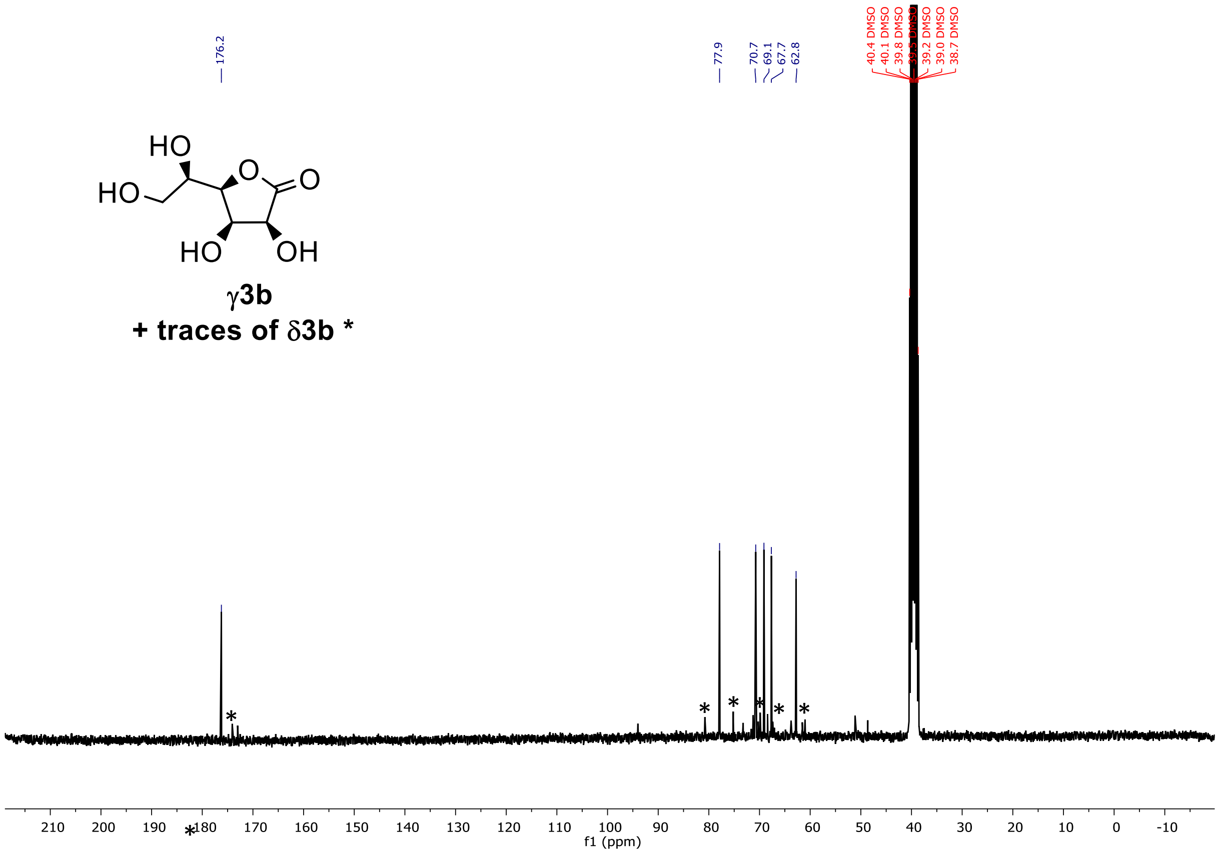

6.24
6.22
5.60
5.59
4.96
4.94
4.67
4.65
4.64
4.43
4.41
4.41
4.39
4.17
4.15
4.14
4.12
4.07
4.05
4.04
3.81
3.79
3.77
3.76
3.74
3.61
3.59
3.57
3.56
3.54
3.50
3.48
3.46
3.44
3.42
3.39 HDO
2.52 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.49 DMSO
2.49 DMSO
HO
HO
O
O
HO
OH
γ3a
+ traces of δ3a *
**
*
*
*
1.00
1.02
1.07
1.08
1.15
1.20
1.03
1.15
1.32
1.34
f1 (ppm)


175.7
80.1
73.3
72.7
69.4
62.8
40.4 DMSO
40.1 DMSO
39.8 DMSO
39.5 DMSO
39.2 DMSO
39.0 DMSO
38.7 DMSO
HO
HO
O
O
HO
OH
γ3a
+ traces of δ3a *
*
*
*
*
*
*
f1 (ppm)



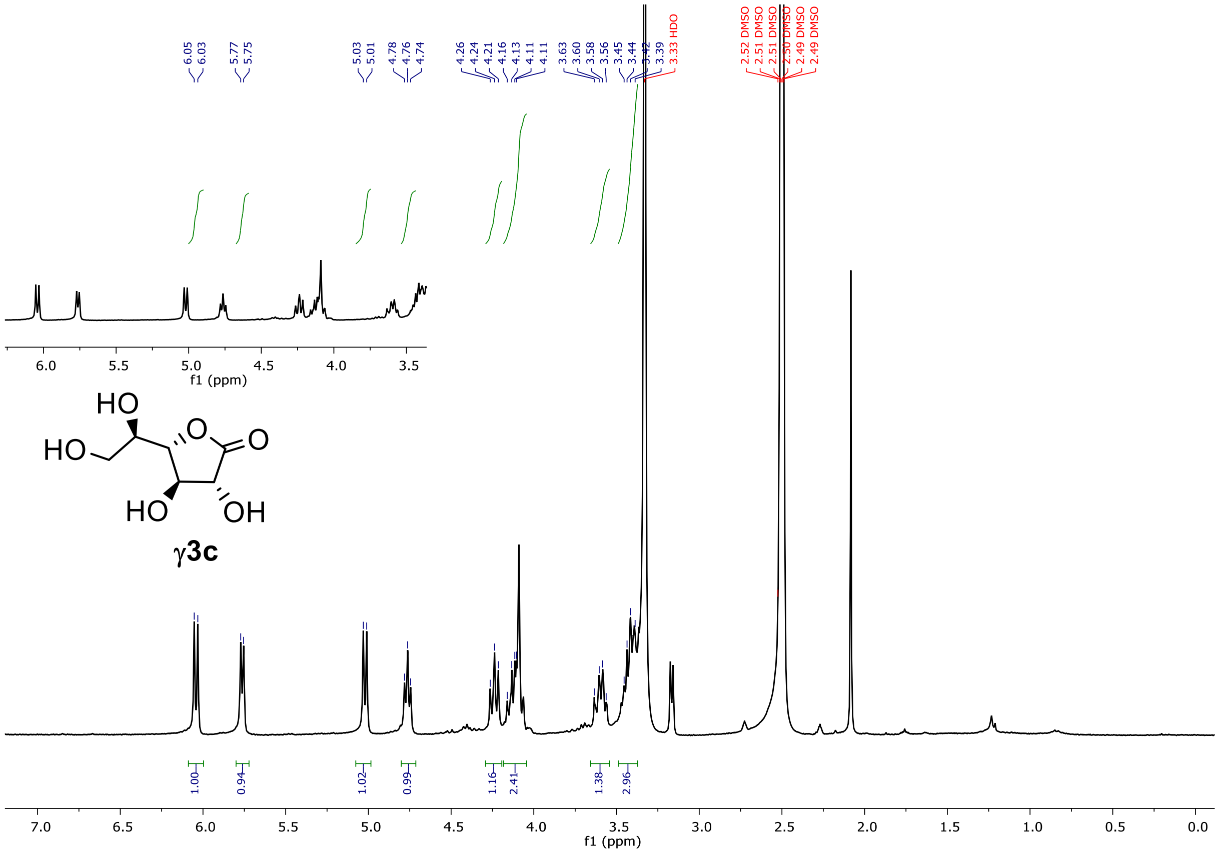
γ3b

+ traces of δ3b *

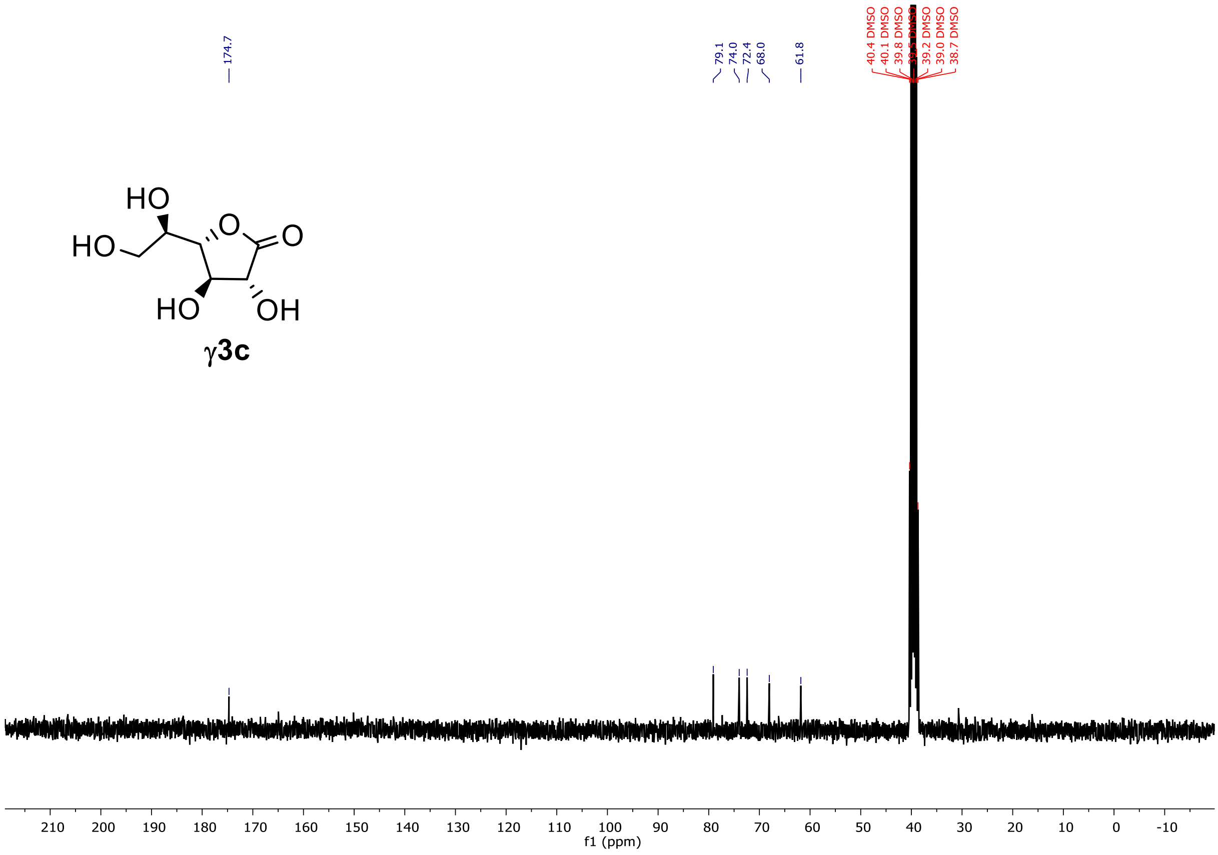


γ3b

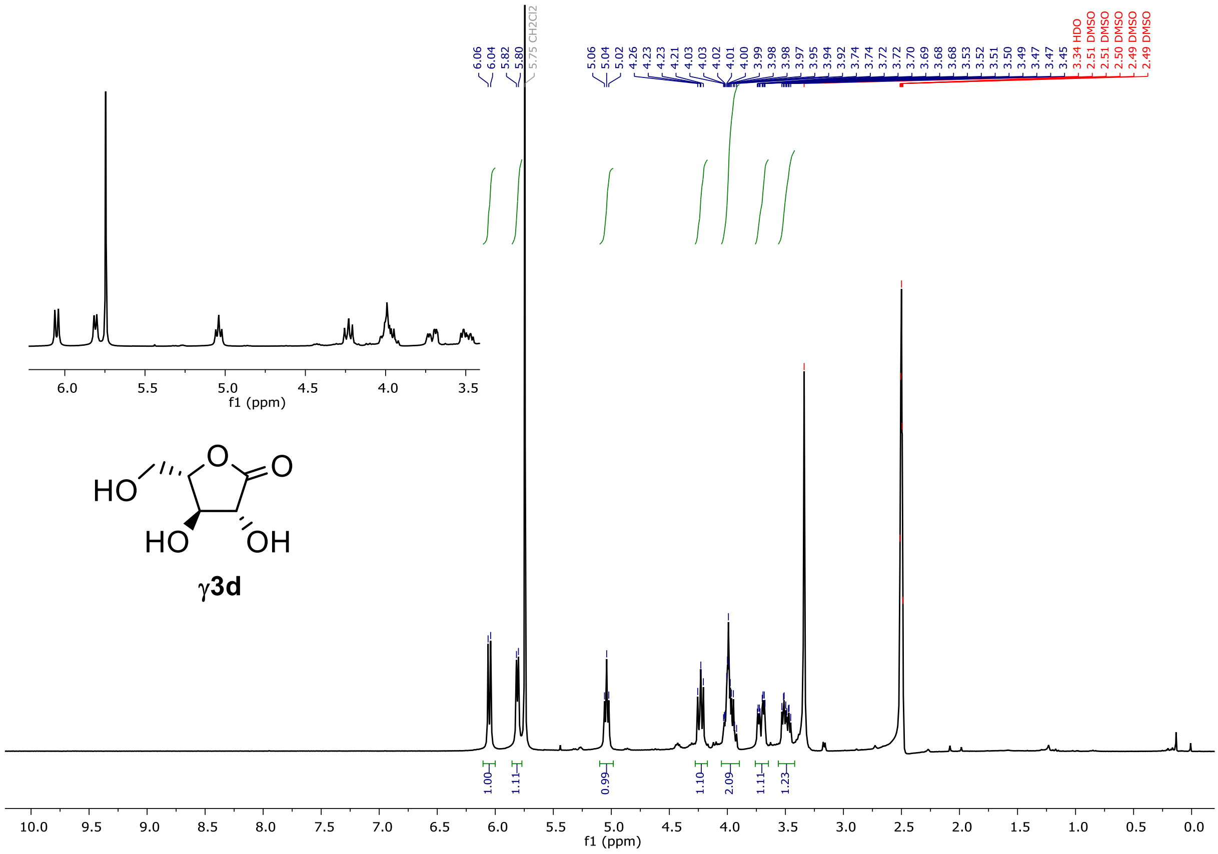
+ traces of δ3b *

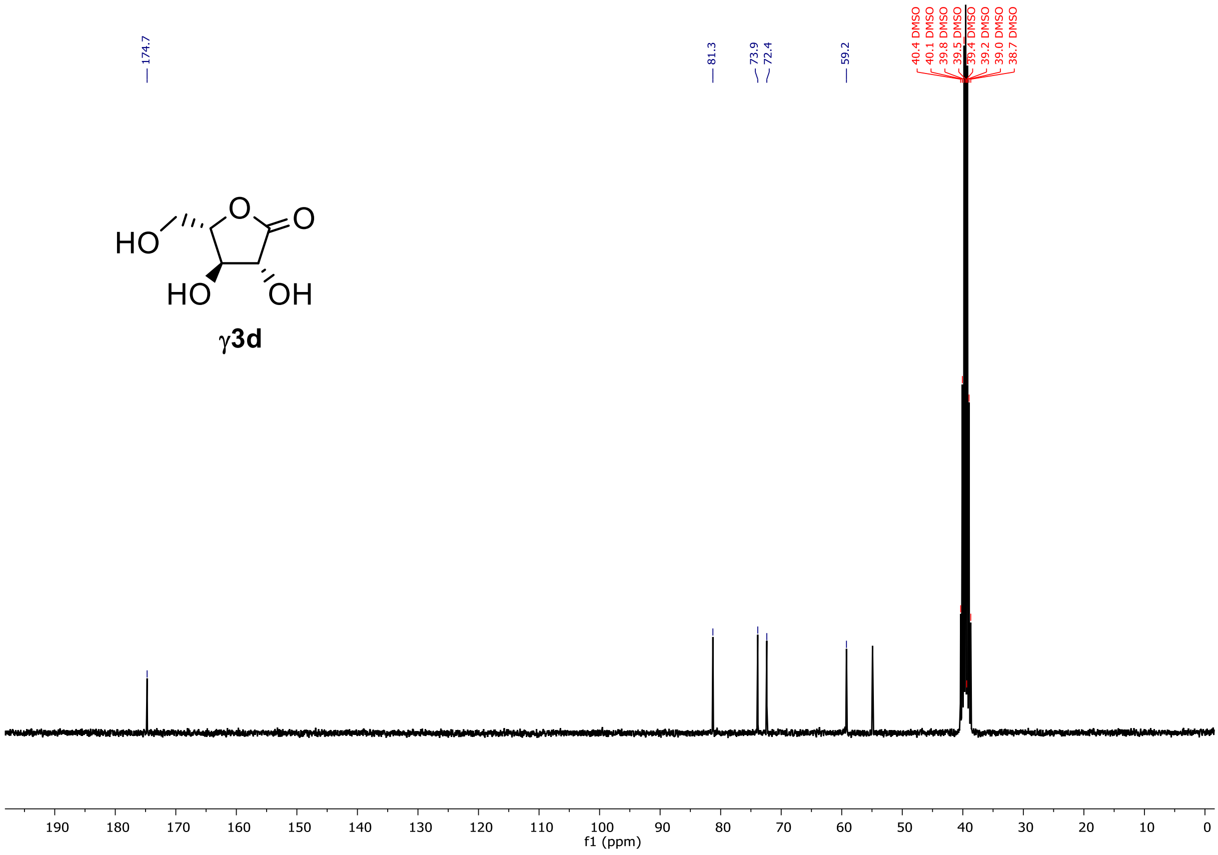

6.05
6.03
5.77
5.75
5.03
5.01
4.78
4.76
4.74
4.26
4.24
4.21
4.16
4.13
4.11
4.11
4.11
3.63
3.60
3.58
3.56
3.45
3.44
3.42
3.39
3.33 HDO
2.52 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.49 DMSO
2.49 DMSO
6.0
5.5
5.0
4.5
4.0
3.5
f1 (ppm)
HO
HO
O
O
HO
OH
1.00
0.94
1.02
0.99
1.16
2.41
1.38
2.96
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

γ3c


174.7
79.1
74.0
72.4
68.0
61.8
40.4 DMSO
40.1 DMSO
39.8 DMSO
39.5 DMSO
39.2 DMSO
39.0 DMSO
38.7 DMSO
HO
HO
O
O
HO
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

γ3c


6.06
6.04
5.82
5.80
5.75 CH2Cl2
5.06
5.04
5.02
4.26
4.23
4.23
4.21
4.03
4.03
4.02
4.01
4.00
3.99
3.98
3.98
3.97
3.95
3.94
3.92
3.74
3.72
3.72
3.70
3.69
3.68
3.68
3.53
3.52
3.51
3.50
3.49
3.47
3.45
3.34 HDO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.49 DMSO
2.49 DMSO
1.00
1.11
0.99
1.10
2.09
1.11
1.23
f1 (ppm)
HO
O
O
HO
OH
γ3d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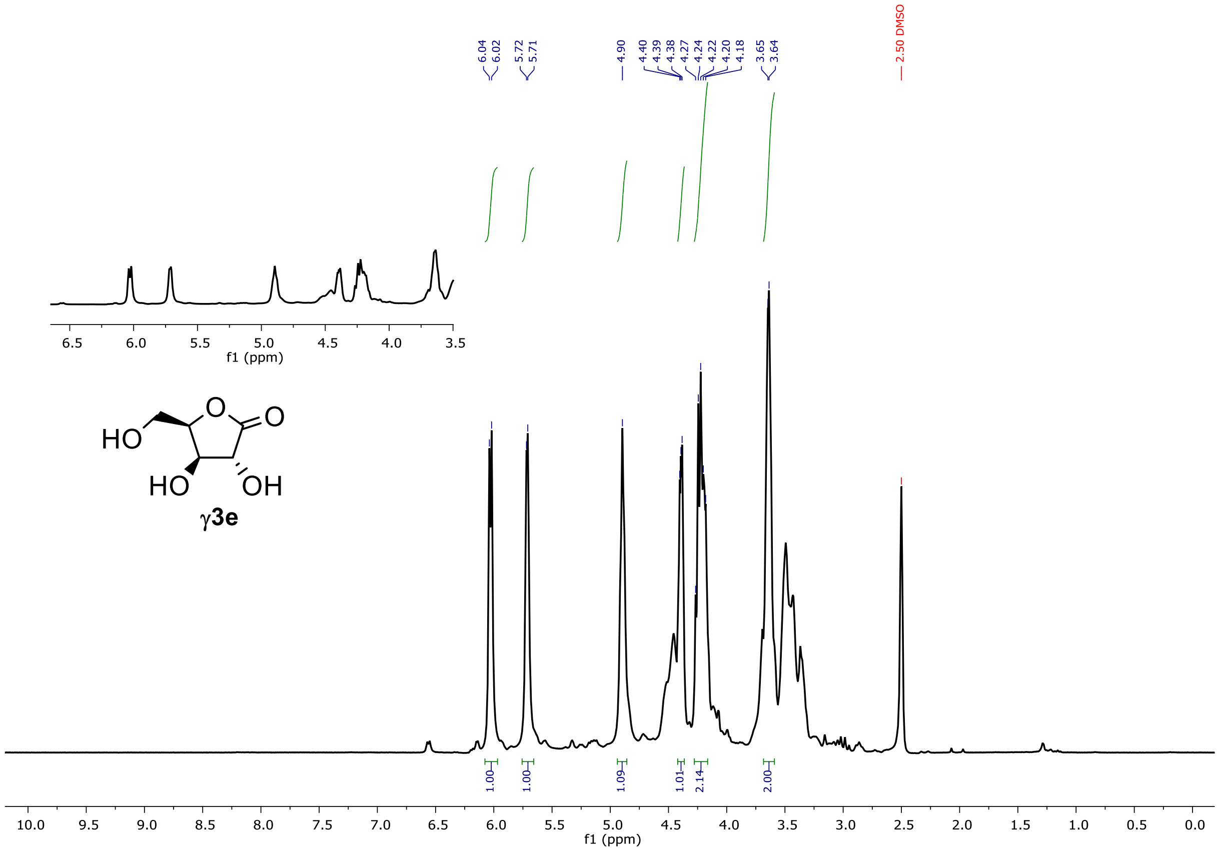
81.3
73.9
72.4
59.2
40.4 DMSO
40.1 DMSO
39.8 DMSO
39.5 DMSO
39.4 DMSO
39.2 DMSO
39.0 DMSO
38.7 DMSO
f1 (ppm)
HO
O
O
HO
OH
γ3d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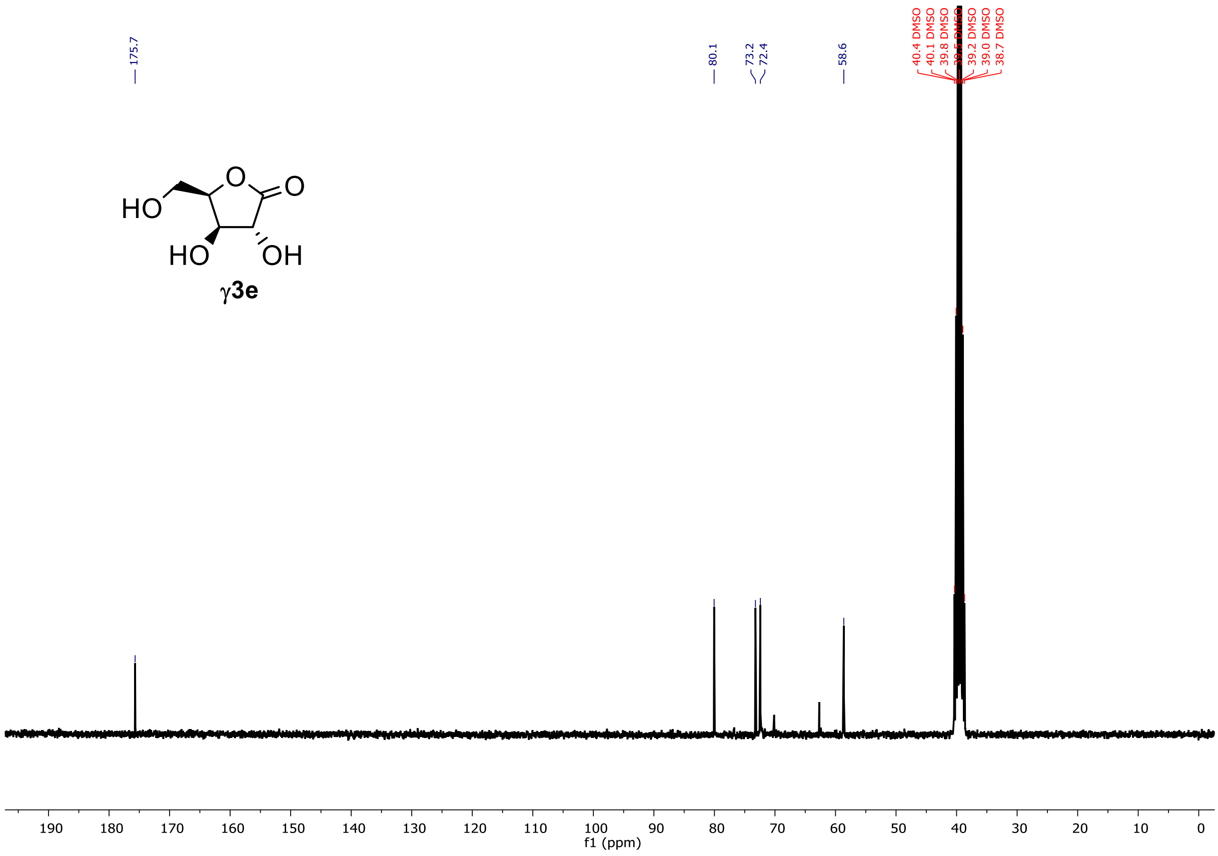
6.02
5.72
5.71
4.90
4.40
4.39
4.38
4.27
4.24
4.22
4.20
4.18
3.65
3.64
2.50 DMSO
6.5
6.0
5.5
5.0
4.5
4.0
3.5
f1 (ppm)
HO
O
O
HO
OH
γ3e
1.00
1.00
1.09
1.01
2.14
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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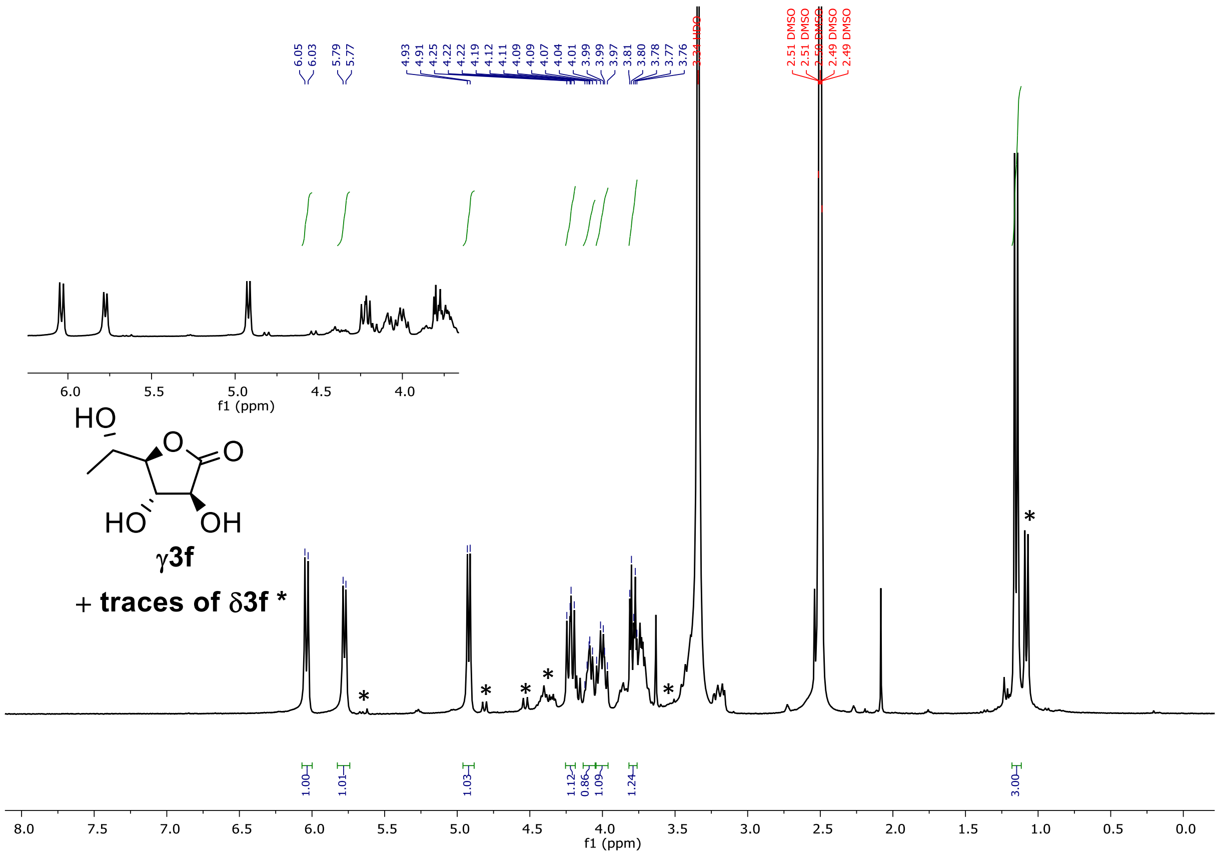
80.1
73.2
72.4
58.6
40.4 DMSO
40.1 DMSO
39.8 DMSO
39.5 DMSO
39.2 DMSO
39.0 DMSO
38.7 DMSO
HO
O
O
HO
OH
γ3e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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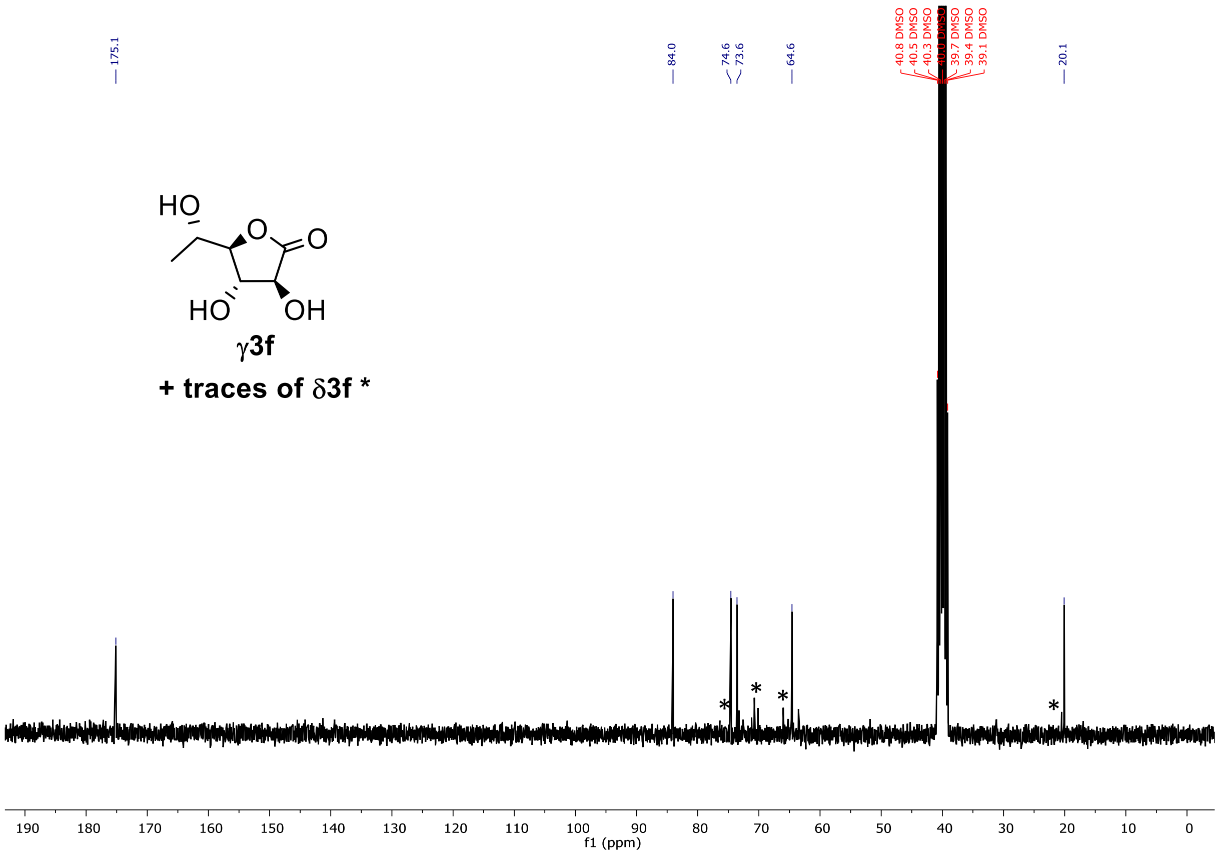
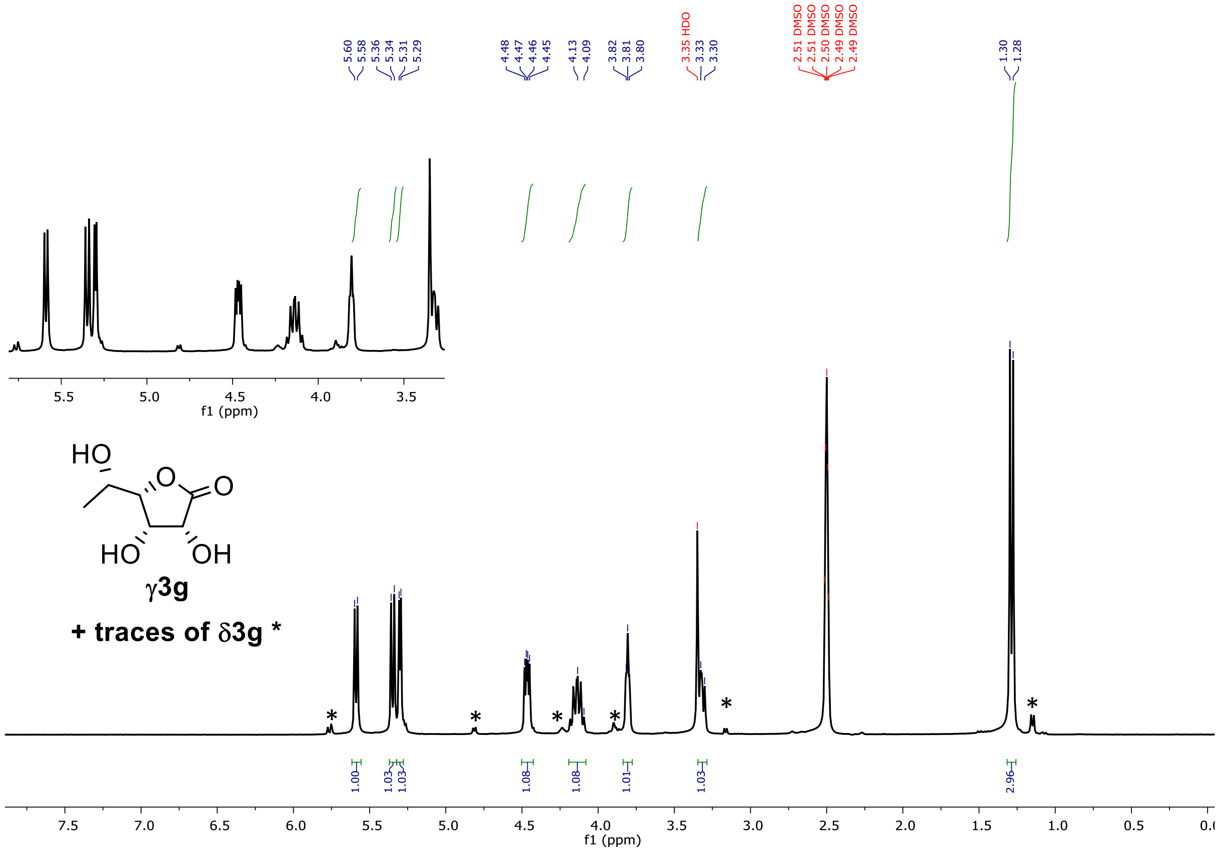
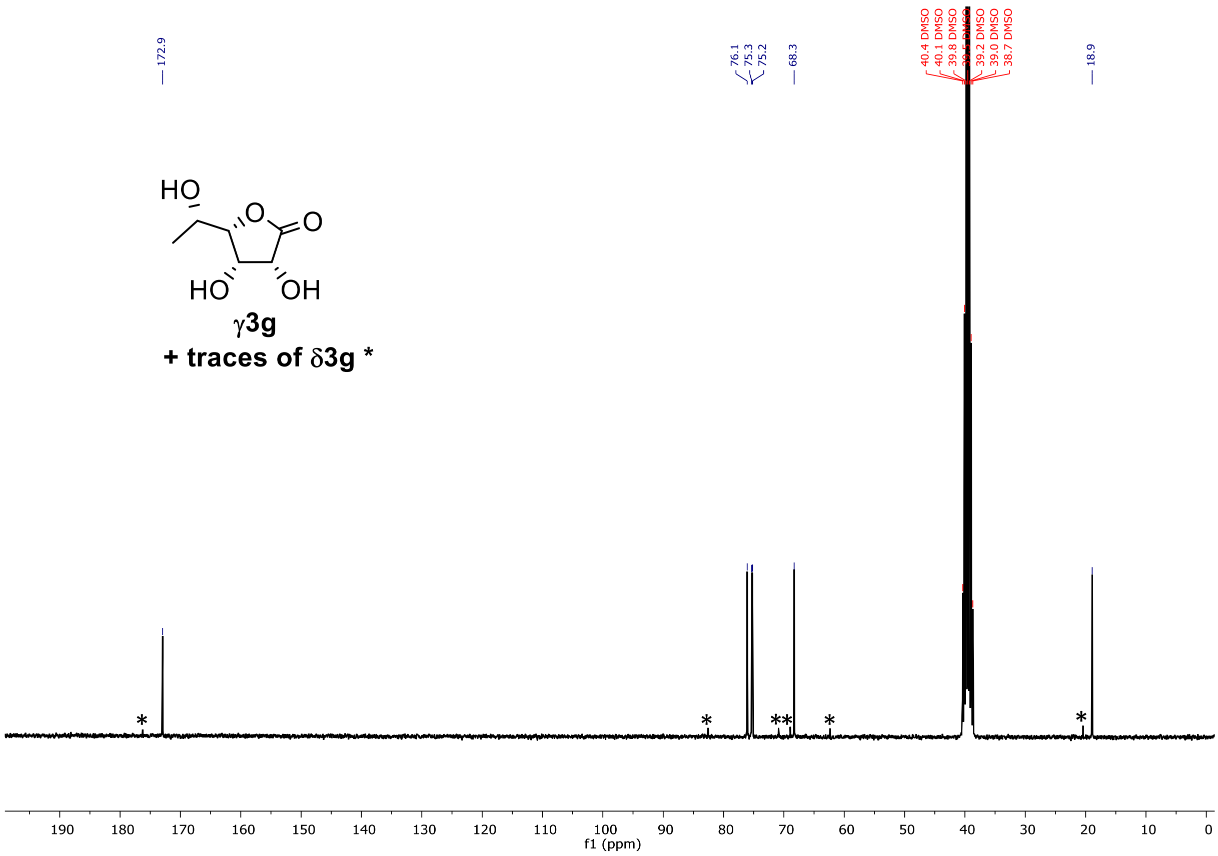
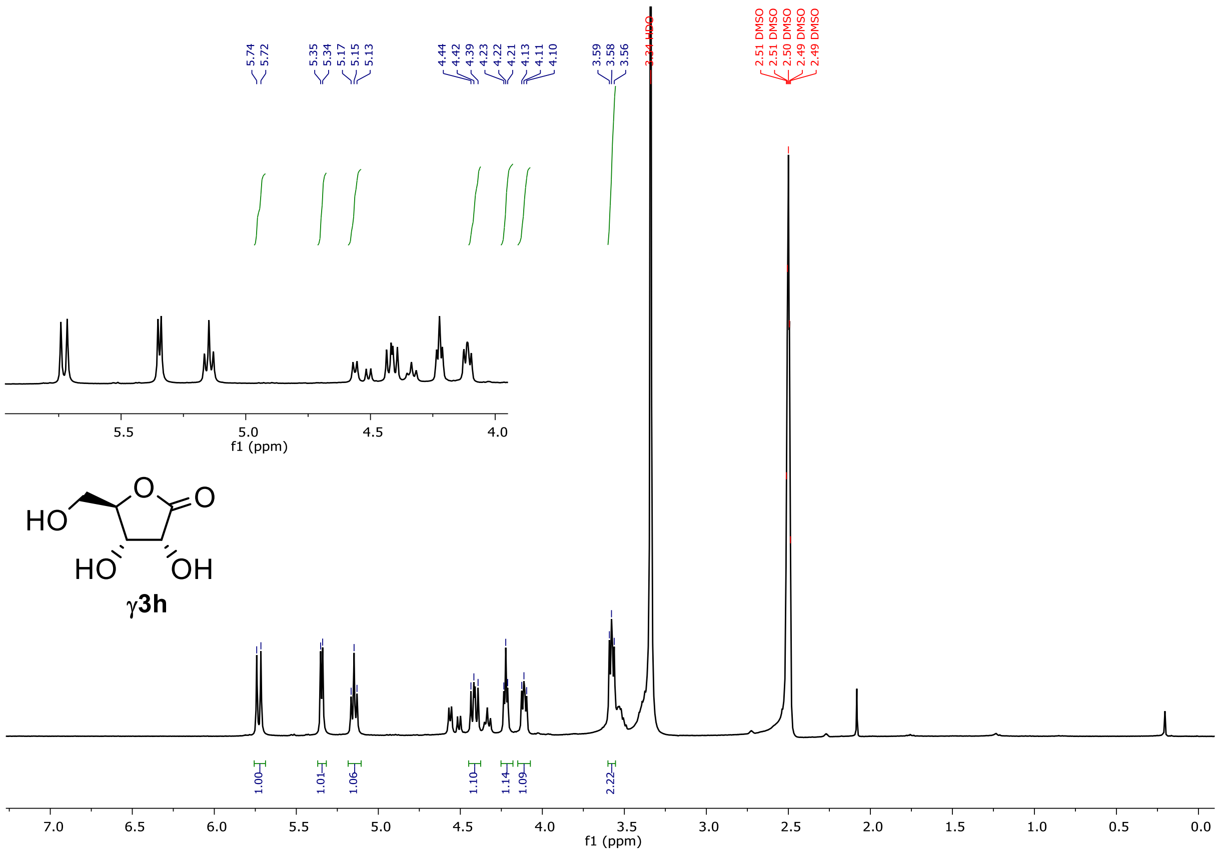
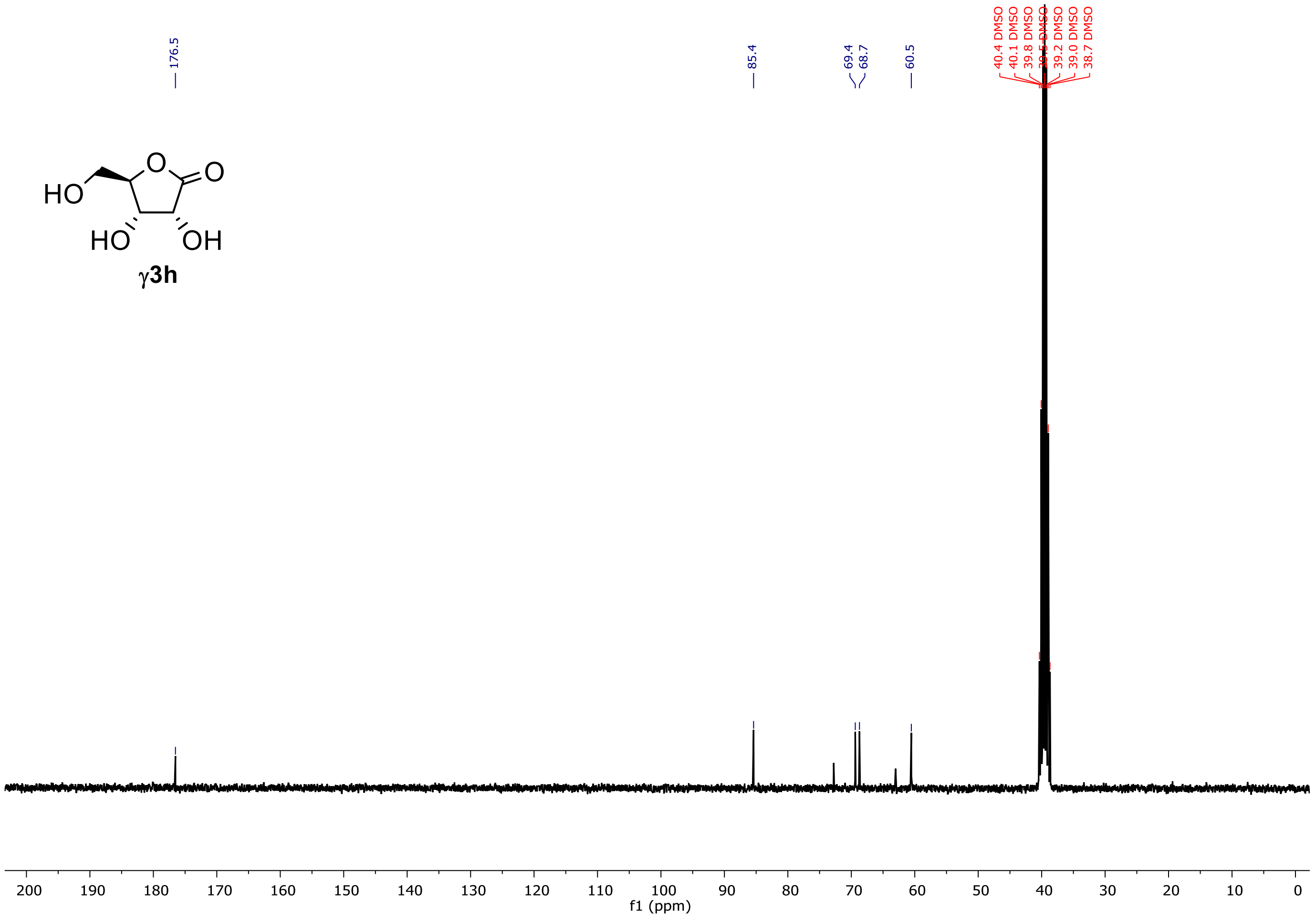
6.03
5.79
5.77
4.93
4.91
4.25
4.22
4.22
4.19
4.12
4.11
4.09
4.09
4.07
4.04
4.01
3.99
3.99
3.97
3.81
3.80
3.78
3.77
3.76
3.34 HDO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.49 DMSO
2.49 DMSO
1.00
1.01
1.03
1.12
0.86
1.09
1.24
3.00
f1 (ppm)
HO
O
O
HO
OH
γ3f
+ traces of δ3f *
*

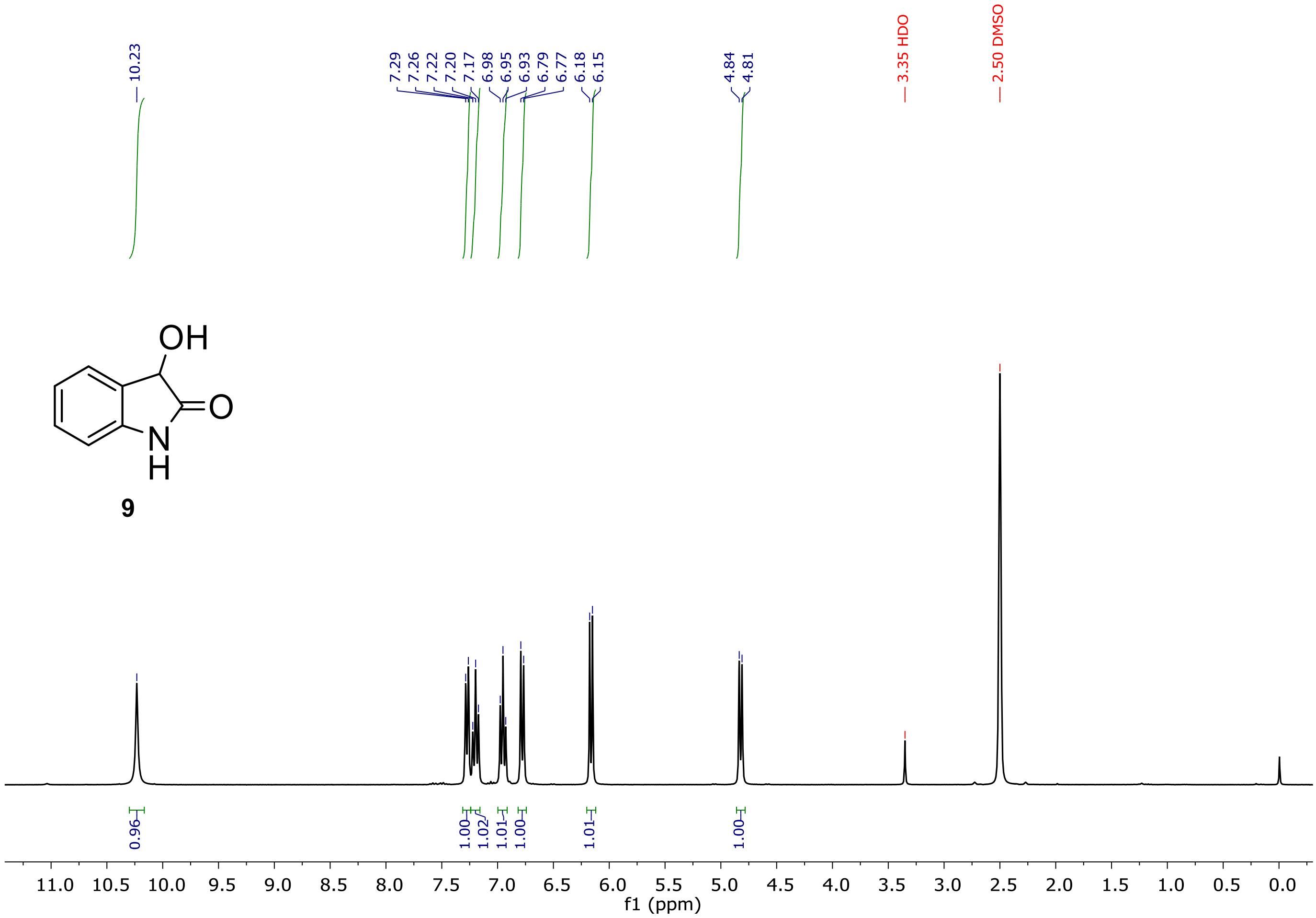

175.1
84.0
74.6
73.6
64.6
40.8 DMSO
40.5 DMSO
40.3 DMSO
40.0 DMSO
39.7 DMSO
39.4 DMSO
39.1 DMSO
20.1
f1 (ppm)
HO
O
O
HO
OH
γ3f
+ traces of δ3f *
*


5.60
5.58
5.36
5.34
5.31
5.29
4.48
4.47
4.46
4.45
4.13
4.09
3.82
3.81
3.80
3.35 HDO
3.33
3.30
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.49 DMSO
2.49 DMSO
1.30
1.28
5.5
5.0
4.5
4.0
3.5
f1 (ppm)
HO
O
O
HO
OH
γ3g
+ traces of δ3g *
*
1.00
1.03
1.03
1.08
1.08
1.01
1.03
2.96
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

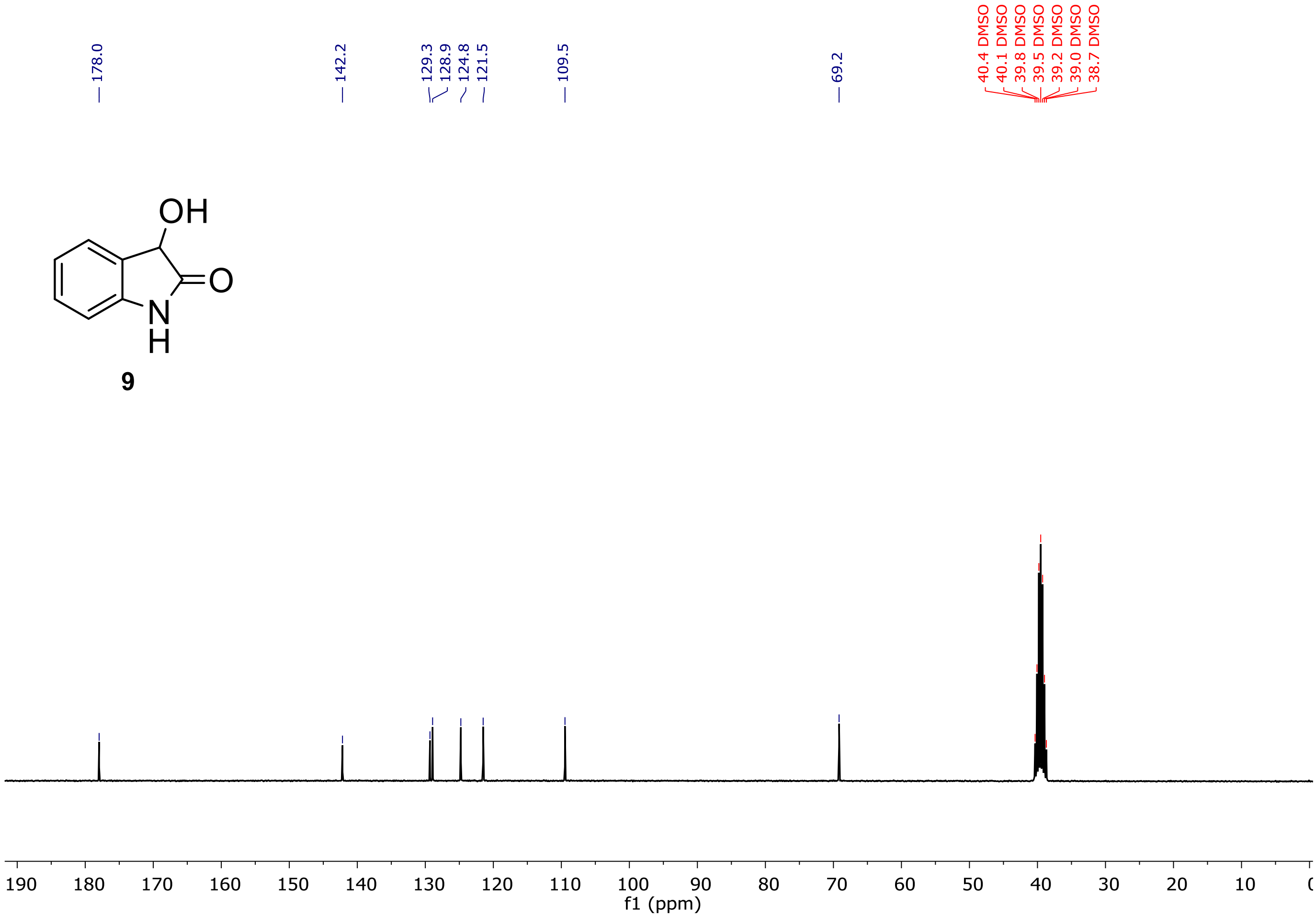

172.9
76.1
75.3
75.2
68.3
40.4 DMSO
40.1 DMSO
39.8 DMSO
39.6 DMSO
39.2 DMSO
39.0 DMSO
38.7 DMSO
18.9
HO
O
O
HO
OH
γ3g
+ traces of δ3g *
*
**
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


5.74
5.72
5.35
5.34
5.17
5.15
5.13
4.44
4.42
4.39
4.23
4.22
4.21
4.13
4.11
4.10
3.59
3.58
3.56
3.34 HDO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.49 DMSO
2.49 DMSO
1.00
1.01
1.06
1.10
1.14
1.09
2.22
HO
O
O
HO
OH
γ3h
f1 (ppm)


176.5
85.4
69.4
68.7
60.5
40.4 DMSO
40.1 DMSO
39.8 DMSO
39.5 DMSO
39.2 DMSO
39.0 DMSO
38.7 DMSO
HO
O
O
HO
OH
γ3h
f1 (ppm)



10.23
7.29
7.26
7.22
7.20
7.17
6.98
6.95
6.93
6.79
6.77
6.18
6.15
4.84
4.81
3.35 HDO
2.50 DMSO
OH
O
N
H
9
0.96
1.00
1.02
1.01
1.00
1.01
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



178.0
142.2
129.3
128.9
124.8
121.5
109.5
69.2
40.4 DMSO
40.1 DMSO
39.8 DMSO
39.5 DMSO
39.2 DMSO
39.0 DMSO
38.7 DMSO
OH
O
N
H
9
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)