Supporting Information

Editing Sugars: Decatungstate Photocatalyzed Site- and Stereoselective C-H Functionalization in β-Fucosides

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1. Variation from the standard conditions of Figure 4 and optimization

Variation from the standard conditions described in Figure 4 were performed on **1-βCN** and **2a** as the benchmark. A brief survey of the few solvents that ensure solubility of TBADT and are compatible with the reaction conditions showed that the reaction does not occur in dimethylacetamide (DMA). In acetone the reaction was slow and the conversion lower than in acetonitrile, which therefore remained the solvent of choice (Table S1). The reaction time and amount of catalyst were screened next (Table S1, entries 6-10). First, we observed that reducing the reaction time from 7 h (entry 1) to 3 h only reduced the conversion to 90%, when the catalyst loading was 5 mol% (entry 6) and to 85% (73% isolated yields), when the loading was also reduced to 2 mol% (entry 7). Running the reaction for 7 h with 2 mol% catalyst (entry 8) restored full conversion and afforded **3-βCN** in 93% isolated yields. The catalyst loading could be reduced to 1 mol%, but with some erosion of conversion (7 h, 65%, entry 9), which could be compensated by longer reaction time (24 h, 82%, entry 10). This result shows that, for highly reactive partners, such as **1-βCN** and **2a,** the amount of catalyst can be reduced without sacrificing yields. No **1-βCN** conversion was observed when the reaction was run in the absence of light or TBADT.

Table S1. Reaction of nitrile **1-βCN** and **2a**.[a]

Entry	**Solvent**	**TBADT (mol%)**	**Time (h)**	**Yield %** ***(conv. %)***
1	CH_3CN	5	7	90 *(100)*
2	CH_3CN	-	7	0
3	CH_3CN	5 (no light)	7	0
4	DMA	5	7	0
5	Acetone	5	7	*(60)*
6	CH_3CN	5	3	*(90)*
7	CH_3CN	2	3	86 *(85)*
8	CH_3CN	2	7	93 *(100)*
9	CH_3CN	1	7	*(65)*
10	CH_3CN	1	24	*(82)*

[a]. **1-βCN** (0.1 M), **2a** (1.1 equiv), room temperature, irradiating at 370 nm. Isolated yields % and (*Conversion %*) are shown.

For alkenes that were found to be less reactive in standard conditions, such as **2c** and **2d** we explored the use of longer reaction times and higher catalyst loading (Table S2). For acrylonitrile **2c**, a moderate variation was observed both by increasing the reaction time up to 20 h (conversion from 35% to 40%) and by increasing the catalytic loading to 8 mol% (conversion from 40% to 45%). The outcome of the reaction for vinylpyridine **2d** proved to be more dependent on the amount of catalyst over time, showing a significant increase in conversion when using 8 mol% catalyst (from 48% to 66%)

Table S2. Reaction of nitrile **1-βCN** with alkenes **2c** and **2d.**[a]

Entry	**Alkene**	**TBADT (mol%)**	**Time (h)**	**Yield %** ***(conv. %)***
1	**2c**	5	7	87 *(35)*
2	**2c**	5	24	*(40)*
3	**2c**	8	7	*(40)*
4	**2c**	8	24	*(45)*
5	**2d**	5	7	95 *(47)*
6	**2d**	5	24	*(52)*
7	**2d**	5	48	*(57)*
8	**2d**	8	7	*(48)*
9	**2d**	8	24	*(60)*
10	**2d**	8	48	*(66)*

[a] **1-βCN** (0.1 M), **2c,d** (1.1 equiv), room temperature, irradiating at 370 nm in MeCN. Isolated yields % and (*Conversion %*) are shown.

2. General Methods and Materials

The catalytic tests were performed in septum-sealed 2-5 mL microwave vials (borosilicate glass 3.3 acc. to ISO 3585). Irradiation was performed using Kessil PR160L lamps of the specified wavelength while cooling down with a fan (unless otherwise specified). Reactions were monitored by analytical thin-layer chromatography (TLC) performed on Silica Gel 60 F254 plates (Merck) with UV detection (254 nm and 366 nm) and/or staining with ceric ammonium molybdate reagent. Flash chromatography was performed using silica gel (60 Å, particle size 40-64 μm) as stationary phase. Automated flash chromatography was performed with a Biotage Isolera Prime system, and SNAP ULTRA cartridges were employed. ^{1}H NMR experiments were recorded on a Bruker Avance 400 MHz instruments at 298 K. The signal shapes (^{1}H-NMR) are abbreviated as s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, ddt = doublet of doublet of triplets, dq = doublet of quartets, td = triplet of doublet. ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer operating at 100.56 MHz, with complete proton decoupling. ^{13}C NMR spectra are attached to the proton test J-modulated spin−echo (APT). Chemical shifts (δ) are expressed in ppm relative to tetramethylsilane with the respective solvent residual peak employed as the internal standard (^{1}H: $CDCl_3$, δ = 7.26 ppm, ^{13}C: $CDCl_3$, δ = 77.36 ppm). COSY and HSQC experiments were used to assist the ^{1}H and ^{13}C resonance assignments. NOESY experiments were used to confirm the stereochemistry. UV-Vis spectra were recorded on a Jasco V-630 spectro-photometer (Jasco, Easton, Maryland, USA). Low resolution mass spectrometry (MS) was performed on a ThermoFisherLCQ apparatus using ESI source. High resolution mass spectrometry (HRMS) was performed on Synapt G2-Si QTof HR-MS instrument (Waters) & ZsprayTM probe for electrospray ionization (Waters), Software: MassLynxTM V4.2 (Waters), analyte solution flow injection - full scan mode.

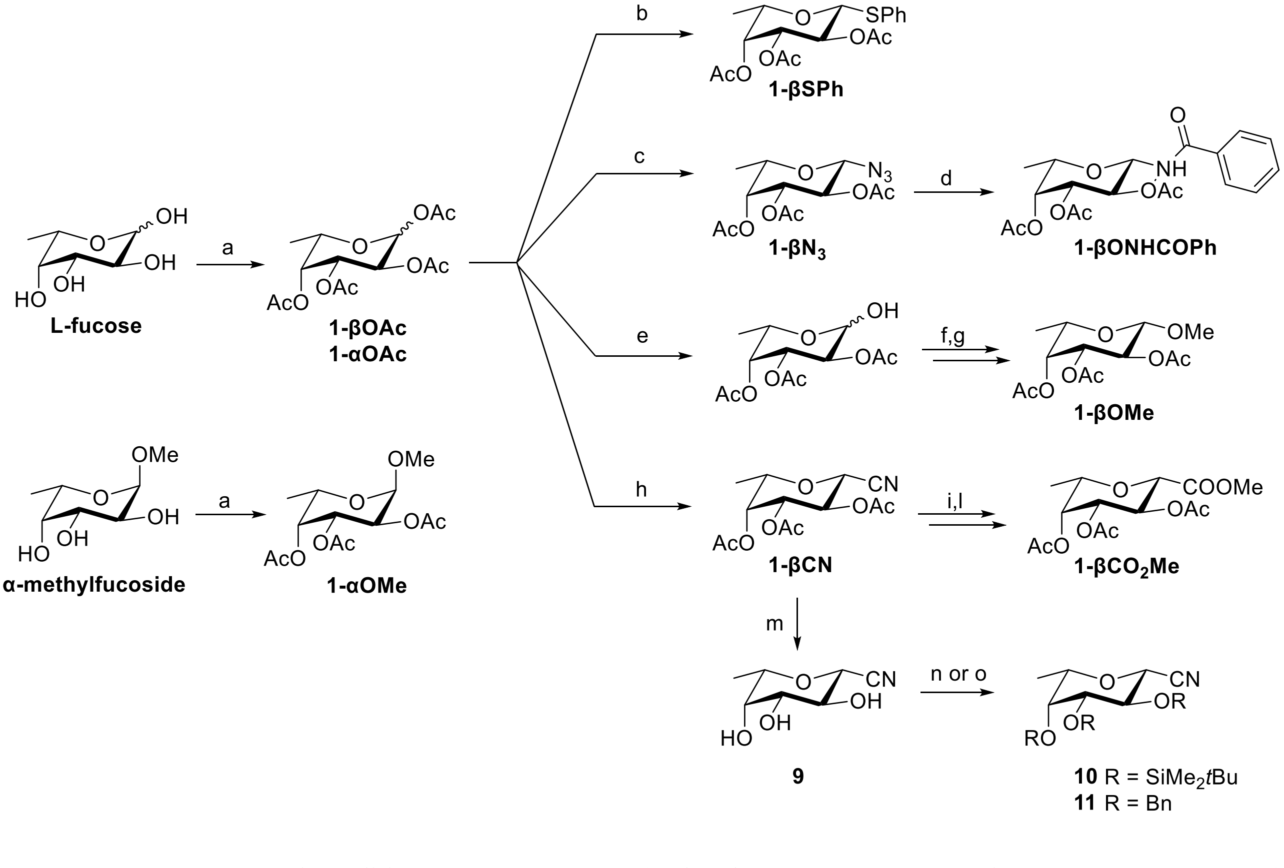
Materials

All commercial reagents (Abcr, Carbosynth, Merck) were used without further purification, unless otherwise indicated. Anhydrous solvents were either purchased from Merck (water content ≤ 0.0005%) or freshly distilled under nitrogen atmosphere over calcium hydride (CH_3CN). Deuterated solvents were purchased from EurisoTop, Sigma-Aldrich or VWR. All the fucoside substrates were synthesised following procedures reported in literature. TBADT photocatalyst was prepared following a reported procedure with slight modifications (see below).

2.1. Synthesis of TBADT Photocatalyst

Tetrabutylammonium bromide (TBAB) (2.4 g, 7.40 mmol, 1 equiv.) and sodium tungstate dihydrate $Na_2WO_4 \bullet 2H_2O$ (5 g, 15.2 mmol, 2 equiv.) were put in separate flasks. Water (HPLC grade, 150 mL) was added to each flask. Both solutions were rapidly stirred and heated to 90°C. When both solutions reached 90°C, HCl conc. was added dropwise to each flask to stabilize pH at 2. When pH was stable, the TBAB solution was added to the tungstate flask and the reaction mixture was stirred at 90°C for 30 min (white precipitate). After cooling to room temperature, the mixture was filtered on a Büchner funnel, washed with water. The solid was dried at 110°C for 4 h, then under high vacuum overnight. The yellow pale solid was suspended in CH_2Cl_2 (90 mL) and stirred for 4h, then the suspension was filtered on a Büchner funnel, giving TBADT as a white solid (y = 70%). UV-Vis characterization showed characteristic peak at ε_{330} nm as reported in literature.[1]

2.2. Synthesis of fucosides (1-αR, 1-βR, 9-11)

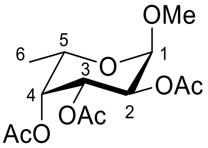


Scheme S1. Reagents and conditions: a) Ac_2O, $La(OTf)_3$; b) PhSH, $BF_3 \bullet OEt_2$, CH_2Cl_2; c) TMS-N_3, TMSOTf, CH_2Cl_2; d) PMe_3, PhCOOH, EDCI, HOBt, CH_2Cl_2; e) $MeNH_2$, THF, -10 °C; f) CCl_3CN, DBU CH_2Cl_2; g) MeOH, TMSOTf, CH_2Cl_2;h) TMS-CN, CH_3NO_2, $BF_3 \bullet OEt_2$; i) AcCl, MeOH; l) Ac_2O, Pyr; m) MeONa, MeOH; n) *tert*-butyl-dimethylsilyl triflate, CH_2Cl_2, TEA; o) $PhCH_2Br$, NaH, DMF.

General Procedure for acetylation

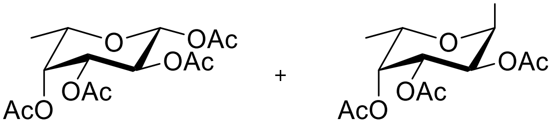
Commercially available L-fucose or methyl-α-L- fucopyranoside (1 equiv.) was suspended in Ac_2O (4 equiv.) under N_2 atmosphere, then $La(OTf)_3$ (4 equiv.) was added and mixture was stirred overnight. The mixture was diluted with CH_2Cl_2 and washed with $NaHCO_3$ ss.; the organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford desired product.

*Synthesis of methyl-2,3,4-tetra-O-acetyl α-L-fucopyranoside (**1-αOMe**)*



The product was obtained from methyl-α-L-fucopyranoside (400 mg, 2.24 mmol) following the general procedure (white solid, Y = 75%). Rf (*n*-hexane/ EtOAc 1:1) = 0,7. MS (ESI): m/z calcd for $[C_{13}H_{20}O_8\,Na]^+$: 304.12; found: 327.19 $[M+Na]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) : 5.34 (dd, $J_{3\text{-}2}$ = 11.7 Hz, $J_{3\text{-}4}$ = 3.4 Hz, 1H, H3), 5.29 (d, $J_{4\text{-}3}$ = 3.5 Hz, 1H, H4), 5.14 (dd, $J_{2\text{-}3}$ = 11.7 Hz, $J_{2\text{-}1}$ = 3.6 Hz, 1H, H2), 4.93 (d, $J_{1\text{-}2}$ = 3.6 Hz, 1H, H1), 4.12 (q, $J_{5\text{-}6}$ = 6.6 Hz, 1H, H5), 3.39 (s, 3H, OMe), 2.16 (s, 3H, OAc), 2.08 (s, 3H, OAc), 1.97 (s, 3H, OAc), 1.14 (d, $J_{6\text{-}5}$ = 6.6 Hz, 3H, H6). ^{13}C-NMR (400 MHz, $CDCl_3$), extrapolated from HSQC exp. δ (ppm): 98.0 (C1), 71.2 (C4), 68.2 (C2), 67.5 (C3), 64.3 (C5), 55.4 (OMe), 20.7 (OAc), 20.6 (OAc), 20.5 (OAc), 15.6 (OAc).

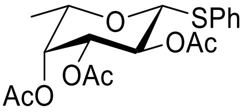
*Synthesis of 1,2,3,4-tetra-O-acetyl-β-L-fucopyranoside (**1-βOAc**) and 1,2,3,4-tetra-O-acetyl-α-L-fucopyranoside (**1-αOAc**)*



The product was obtained from L-fucose (1.003 g, 9.63 mmol) following the general procedure as anomeric mixture (α:β = 60:40) with traces of furanose form. The crude was purified by flash chromatography (n-hexane/AcOEt 7:3), obtaining the pure anomers as colorless oils (Y (tot) = 95%; Y (β-anomer) = 20%). Rf (n-hexane/AcOEt 1:2) = 0.52. Characterization data in agreement with those reported in literature.[2] ^{1}H-NMR (400 MHz, CDCl3) δ (ppm) α anomer: 6.33 (d, $J_{1\text{-}2}$ = 2.6 Hz, 1H, H1), 5.37 - 5.28 (m, 3H, H2 + H3 + H4), 4.26 (q, $J_{5\text{-}6}$ = 6.6 Hz, 1H, H5), 2.20 – 1.97 (s, 12H, OAc), 1.15 (d, $J_{6\text{-}5}$ = 6.6 Hz, 3H, H6). β anomer: 5.67 (d, $J_{1\text{-}2}$ = 8.3 Hz, 1H, H1), 5.26 (d, $J_{4\text{-}3}$ = 3.4

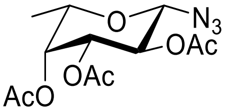
Hz, 1H, H4), 5.06 (dd, $J_{3\text{-}2}$ = 10.4 Hz, $J_{3\text{-}4}$ = 3.4 Hz, 1H, H3), 3.99-3.91 (m, 1H, H5), 2.20 – 1.97 (s, 12H, OAc), 1.22 (d, $J_{5\text{-}6}$ = 6.4 Hz, 3H, H6).

*Synthesis of phenyl 2,3,4-tri-O-acetyl-1-thio-β-L-fucopyranoside (**1-βSPh**)*



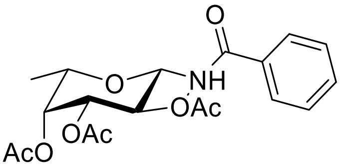
The anomeric mixture of *1,2,3,4-tetra-O-acetyl -L-fucopyranoside* (250 mg, 0.75 mmol, 1 equiv.) was dissolved in anhydrous CH_2Cl_2 (0.2 M), then PhSH (85 µL, 0.82 mmol, 1.1 equiv.) was added. The mixture was cooled to 0°C and BF_3•OEt_2 (1.3 equiv.) was added dropwise. The reaction was stirred overnight (solution was left in the ice bath to reach room temperature slowly) and then a saturated solution of $NaHCO_3$ was added. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude contained a mixture of β/α anomers (9:1), which was purified by flash chromatography providing the pure β-anomer product as yellow pale oil (Y = 70%). Rf (*n*-hexane/ EtOAc 85:15) = 0,2. Characterization data in agreement with those reported in literature.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.54 – 7.49 (m, 2H, ArHo), 7.34 – 7.28 (m, 3H, ArHm + ArHp), 5.26 (d, $J_{4\text{-}3}$ = 3.4 Hz, 1H, H4), 5.23 (t, $J_{2\text{-}1}$ = $J_{2\text{-}3}$ = 9.9 Hz, 1H, H2), 5.05 (dd, $J_{3\text{-}2}$ = 9.9 Hz, $J_{3\text{-}4}$ = 3.4 Hz, 1H, H3), 4.70 (d, $J_{1\text{-}2}$ = 9.9 Hz, 1H, H1), 3.83 (q, $J_{5\text{-}6}$ = 6.4 Hz, 1H, H5), 2.15 (s, 3H, OAc), 2.08 (s, 3H, OAc), 1.97 (s, 3H, OAc), 1.24 (d, $J_{6\text{-}5}$ = 6.4 Hz, 3H, H6).

*Synthesis of 2,3,4-tri-O-acetyl β-L-fucopyranosyl azide (**1-βN₃**)*



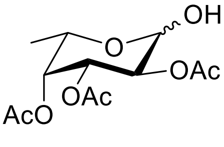
The anomeric mixture of *1,2,3,4-tetra-O-acetyl L-fucopyranoside* (1.4 g, 4.26 mmol, 1 eq.) was dissolved in anhydrous CH_2Cl_2 (10.7 mL) under N_2 atmosphere and cooled to 0°C. TMS-N_3 (1.13 mL, 8.52 mmol, 2 eq.) and TMS-OTf (310 µL, 1.7 mmol, 0.4 eq.) were added and the reaction mixture was stirred at room temperature overnight. The mixture was diluted with CH_2Cl_2 and washed with $NaHCO_3$ ss. and water; the organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was suspended in isopropylether and the yellow solid was filtered and dried in vacuo (Y = 60%). Rf (n-hexane/AcOEt 7:3) = 0.52. Characterization data in agreement with those reported in literature.[2] ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 5.27 (dd, $J_{3\text{-}4}$ = 3.4 Hz, $J_{4\text{-}5}$ = 0.8 Hz, 1H, H4), 5.14 (dd, $J_{2\text{-}3}$ = 10.3 Hz, $J_{1\text{-}2}$ = 8.7 Hz, 1H, H2) 5.03 (dd, $J_{2\text{-}3}$ = 10.3 Hz, $J_{3\text{-}4}$ = 3.4 Hz, 1H, H3), 4.58 (d, $J_{1\text{-}2}$ = 8.7 Hz, 1H, H1), 3.91 (dq, $J_{5\text{-}6}$ = 6.0 Hz, $J_{4\text{-}5}$ = 0.8 Hz, 1H, H5), 2.19 (s, 3H, OAc), 2.09 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.25 (d, $J_{5\text{-}6}$ = 6.0 Hz, 3H, H6).

*Synthesis of N-(2,3,4-tri-O-acetyl-β-L-fucopyranosyl)benzamide (**1-βNHCOPh**)*



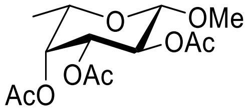
Benzoic acid (17 mg, 0.14 mmol, 1 eq.), EDC.HCl (30 mg, 0.16 mmol, 1.1 eq.) and HOBt (22 mg, 0.16 mmol, 1.1 eq.) were dissolved in anhydrous CH_2Cl_2 (0.1M) under N_2 atmosphere and then *N,N*-Diisopropylethylamine (2.5 eq.) was added. The mixture was stirred at room temperature until TLC showed complete activation of the acid (1h). Meanwhile, ***1*-β*N₃*** (50 mg, 0.16 mmol, 1.1 eq.) was dissolved in anhydrous CH_2Cl_2 (0.15 M) under N_2 atmosphere, cooled to 0°C and then PMe_3 (280 µL, 0.28 mmol, 2 eq.) was added dropwise. The mixture was stirred at room temperature until TLC showed complete reduction of the azide (20mins). The acid containing solution was then added to the reduced azide solution and the reaction mixture was stirred at room temperature overnight. Reaction mixture was diluted with CH_2Cl_2 and washed with NH_4Cl ss., $NaHCO_3$ ss. and brine, dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The crude was then purified by flash column chromatography (n-hexane/AcOEt 8:2), obtaining the compound as white foam (Y = 48%). Rf (n-hexane/AcOEt 6:4) = 0.36. Characterization data in agreement with those reported in literature.[4]
^{1}H-NMR (400 MHz, CDCl3) δ (ppm): 7.77 (d, $J_{6\text{-}7}$ = 7.3 Hz, 2H, ArH*o*), 7.53 (t, $J_{7\text{-}8}$ = 7.3 Hz, 1H, ArH*p*), 7.45 (t, $J_{7\text{-}6/9}$ = 7.3 Hz, 2H, ArH*m*), 7.03 (d, $J_{1\text{-NH}}$ = 8.6 Hz, 1H, NH), 5.39 (t, $J_{1\text{-}2/\text{NH}}$ = 8.6 Hz, 1H, H1), 5.34 (d, $J_{3\text{-}4}$ = 2.1 Hz, 1H, H4), 5.24-5.21 (m, 2H, H2 + H3), 4.02 (q, $J_{5\text{-}6}$ = 6.4 Hz, 1H, H5), 2.19 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.22 (d, $J_{5\text{-}6}$ = 6.4 Hz, 3H, H6).

Synthesis of 2,3,4-tri-O-acetil-L-fucopyranoside



The anomeric mixture of *1,2,3,4-tetra-O-acetyl -L-fucopyranoside* (211 mg, 0.63 mmol, 1 eq) was dissolved in anhydrous THF (0.63 mL, 1M) under a nitrogen atmosphere, and the resulting solution was cooled to -10°C. A 2M solution of $MeNH_2$ in THF (0.95 mL, 1.90 mmol, 3 eq) was slowly added to the flask. The reaction was stirred at 0°C for two hours. Complete conversion of the starting substrate was monitored by TLC. The solvent was evaporated under reduced pressure, and the crude product was purified by flash chromatography (toluene/EtOAc 7:3) to obtain the compound as a white foam, containing a mixture of α/β anomers (2:1)(Y = 68%). Rf (*n*-hexane/EtOAc 7:3) = 0.13. Characterizations in accordance with literature.[5] MS (ESI): m/z calcd for $[C_{12}H_{18}O_8\,Na]^+$: 290.10; found: 313.25 $[M+Na]^+$. ^{1}H-NMR ($CDCl_3$ / 400 MHz): α isomer: δ (ppm) = 5.48 (t, $J_{1\text{-}OH} = J_{1\text{-}2}$ = 3.4 Hz, 1H, H_1); 5.42 (dd, $J_{3\text{-}2}$ = 10.8 Hz, $J_{3\text{-}4}$ = 3.4 Hz, 1H, H_3); 5.32 (dd. $J_{4\text{-}3}$ 0 3.4 Hz, $J_{4\text{-}5}$ = 1.3 Hz, 1H, H_4); 5.172 (dd, $J_{2\text{-}1}$ = 3.4 Hz, $J_{2\text{-}3}$ = 10.8 Hz, 1H, H_2); 4.42 (q, $J_{5\text{-}6}$ = 6.5 Hz, 1H, H_5); 2.69 (dd, $J_{OH\text{-}1}$ = 3.4 Hz, $J_{OH\text{-}2}$ = 1 Hz, 1H, -OH); 2.17, 2.09, 1.996 (3s, 9H, -OAc); 1.15 (d, $J_{6\text{-}5}$ = 6.5 Hz, 3H, H_6). β isomer: δ (ppm) = 5.25 (dd, $J_{4\text{-}3}$ = 3.1 Hz, $J_{4\text{-}5}$ = 1.1 Hz, 1H, H_4); 5.08-5.05 (m, 2H, H_2, H_3); 4.69-4.63 (m, 1H, H_1); 3.85 (q, $J_{5\text{-}6}$ = 6.4 Hz, 1H, H_5); 3.36 (d, $J_{OH\text{-}1}$ = 9.1 Hz, 1H, -OH); 2.18, 2.10, 2.00 (3s, 9H, -OAc); 1.24 (d, $J_{6\text{-}5}$ = 6.4 Hz, 3H, H_6).

*Synthesis of methyl-2,3,4-tetra-O-acetyl-β-L-fucopyranoside (**1-βOMe**)*

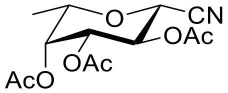


The anomeric mixture of *2,3,4-tri-O-acetil-L-fucopyranoside* (1.0 g, 3.5 mmol, 1 equiv.) was dissolved in anhydrous CH_2Cl_2 (0.1 M), CCl_3CN (2.1 mL, 21 mmol, 6 equiv.) and DBU (156 µL, 1.05 mmol, 0.3 equiv.) were added. The mixture was stirred until TLC confirmed completion of the reaction (2h), then it was concentrated under reduced pressure. The crude was purified by automatic chromatography (from *n*-hexane/AcOEt 8:2 to 1:1), affording the desired *2,3,4-tri-O-acetyl-L-fucopyranosyltrichloroacetimidate* as a white foam (Y = 90 %). Rf (*n*-hexane/AcOEt 8:2) ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.61 (s, 1H, NH), 6.54 (d, $J_{1\text{-}2}$ = 3.5 Hz, 1H, H1), 5.44 – 5.40 (m, 1H, H3), 5.39 (dd, $J_{4\text{-}3}$ = 3.3 Hz, $J_{4\text{-}5}$ = 1.2 Hz, 1H, H4), 5.34 (dd, $J_{2\text{-}3}$ = 10.6 Hz, $J_{2\text{-}1}$ = 3.5 Hz, 1H, H2), 4.43 – 4.31 (q, $J_{5\text{-}6}$ = 6.5 Hz, 1H, H5), 2.18 (s, 3H, OAc), 2.01 (s, 6H, OAc), 1.18 (d, $J_{6\text{-}5}$ = 6.5 Hz, 3H, H6).^{13}C-NMR (400 MHz, $CDCl_3$), extrapolated from HSQC exp. δ (ppm): 93.9 (C1), 71.3 (C4), 67.9 (C3), 67.5 (C5), 67.1 (C2), 20.8 (OAc), 20.6 (OAc), 16.1 (C6).

2,3,4-tri-O-acetyl-L-fucopyranosyltrichloroacetimidate (1.37 g, 3.15 mmol, 1 equiv.) was dissolved in anhydrous CH_2Cl_2 with molecular sieves (0.16 M) under Ar atmosphere. Anhydrous methanol (1.1 mL, 26.1 mmol, 8.3 equiv.) was added to the solution. The reaction mixture was left stirring at room temperature for 2h, then it was cooled to 0°C and TMSOTf (149 µL, 0.82 mmol, 0.26 equiv.) was added. After 2h stirring at 0°C, TLC confirmed consumption of starting material and 2mL of triethylamine were. The mixture was concentrated under reduced pressure and purified by automatic chromatography (from *n*-hexane/AcOEt 8:2 to 1:1), affording desired *methyl β-L-tri-O-acetylfucopyranoside* as white foam (Y = 97.3 %). Rf (*n*-hexane/AcOEt 1:1) = 0.6. MS (ESI): m/z calcd for $[C_{13}H_{20}O_8\,Na]^+$: 304.12; found: 327.19 $[M+Na]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):

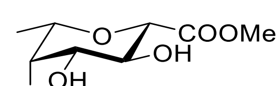
5.24 (d, $J_{4\text{-}3}$ = 3.4 Hz, 1H, H4), 5.18 (t, $J_{2\text{-}1}$ = $J_{2\text{-}3}$ = 10.4 Hz, 1H, H2), 5.02 (dd, $J_{3\text{-}2}$ = 10.4 Hz, J3-4 = 3.4 Hz, 1H, H3), 4.37 (d, $J_{1\text{-}2}$ = 10.4 Hz, 1H, H1), 3.81 (q, $J_{5\text{-}6}$ = 6.4 Hz, 1H, H5), 2.17 (s, 3H, OAc), 2.06 (s, 3H, OAc), 1.98 (s, 3H, OAc), 1.24 (d, $J_{6\text{-}5}$ = 6.4 Hz, 3H, H6). ^{13}C-NMR (400 MHz, $CDCl_3$), extrapolated from HSQC exp. δ (ppm): 101.8 (C1), 71.8 (C3), 70.6 (C4), 68.8 (C2), 69.6 (C5), 57.2 (OMe), 20.5 (OAc), 20.4 (OAc), 20.3 (OAc), 16.3 (C6).

*Synthesis of 2,3,4-tri-O-acetyl-β-L-fucopyranosyl cyanide (**1-βCN**)*



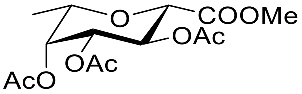
Following a reported procedure employed for galactose,[6] the anomeric mixture of *1,2,3,4-tetra-O-acetyl L-fucopyranoside* (500 mg, 1.5 mmol, 1 eq.) was dissolved in nitromethane (5 mL) under Ar atmosphere TMSCN (600 µL, 4.5 mmol, 3eq) and $BF_3.Et_2O$ (0.28 mL, 2.25 mmol, 1.5 eq.) were added dropwise. The solution was stirred at room temperature overnight, until TLC showed completion. The solvent was then evaporated, and the residue was diluted with CH_2Cl_2 and washed with H_2O. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (from *n*-hexane/AcOEt 8:2 to 7:3) to afford a yellow solid (Y = 78%). Rf (AcOEt/MeOH 9:1) = 0.87 Characterization data in agreement with those reported in literature.[7] ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.51 (t, $J_{2\text{-}3/1}$ = 10.2 Hz, 1H, H2), 5.27 (d, $J_{3\text{-}4}$ = 3.0 Hz, H4), 5.00 (dd, $J_{2\text{-}3}$ = 10.2 Hz, $J_{3\text{-}4}$ = 3.0 Hz, 1H, H3), 4.25 (d, $J_{1\text{-}2}$ = 10.2 Hz, 1H, H1), 3.82 (q, $J_{5\text{-}6}$ = 6.4 Hz, 1H, H5), 2.21 (s, 3H, OAc), 2.11 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.23 (d, $J_{5\text{-}6}$ = 6.4 Hz, 3H, H6).

Synthesis of methyl-β-L-fucopyranosyl carboxylate



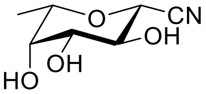
1-βCN (998 mg, 3.34 mmol, 1 eq.) was dissolved in a 3 M solution of acetyl chloride in dry MeOH (6.7 mL) under N_2 atmosphere. The solution was stirred at reflux temperature for 4h. The mixture was then evaporated to dryness and the residue was purified by flash chromatography (AcOEt/MeOH 95:5), affording a colourless oil (Y = 75%). Rf (AcOEt/MeOH 9:1) = 0.33. MS (ESI): m/z calcd for $[C_8H_{14}O_6Na]^+$: 206.08; found: 228.96 $[M+Na]^+$. ^{1}H-NMR (400 MHz, MeOD): δ (ppm) = 3.80 (t, $J_{2\text{-}1/3}$ = 9.4 Hz, 1H, H2), 3.76 (s, 3H, OMe) 3.72-3.64 (m, 3H, H1 + H4 + H5), 3.47 (dd, $J_{2\text{-}3}$ = 9.4 Hz, $J_{3\text{-}4}$ = 3.3 Hz, 1H, H3), 1.25 (d, $J_{5\text{-}6}$ = 6.5 Hz, 3H, H6). ^{13}C-NMR (400 MHz, MeOD), extrapolated from HSQC exp. δ (ppm): 79.4 (C1), 75.1 (C5), 74.5 (C3), 71.9 (C4), 68.1 (C2), 51.0 (OMe), 15.5 (C6).

*Synthesis of methyl-2,3,4-tri-O-acetyl-β-L-fucopyranosyl carboxylate (**1-βCO₂Me**)*



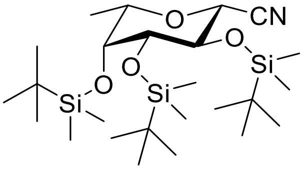
methyl-β-L-fucopyranosyl carboxylate (185 mg, 0.9 mmol, 1 eq.) was dissolved in pyridine (0.85 mL) and cooled to 0 °C. Ac_2O (0.85 mL, 9 mmol, 10 eq.) was slowly added and the solution was allowed to return to room temperature. The reaction was stirred overnight, until TLC showed completion. The reaction mixture was co-evaporated with toluene and the residue diluted with AcOEt and washed with 1M HCl, $NaHCO_3$ ss. and brine. It was dried over Na_2SO_4, filtered and concentrated under reduced pressure to give the product as yellow foam (Y = 92%). Rf (*n*-hexane/AcOEt 7:3) = 0.42. MS (ESI): m/z calcd for $[C_{14}H_{20}O_9 Na]^+$: 332.11; found: 355.14 $[M+Na]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 5.36 (t, $J_{2\text{-}1/3}$ = 10.1 Hz, 1H, H2), 5.30 (d, $J_{3\text{-}4}$ = 3.4 Hz, 1H, H4), 5.10 (dd, $J_{2\text{-}3}$ = 10.1 Hz, $J_{3\text{-}4}$ = 3.4 Hz, 1H, H3), 3.98 (d, $J_{1\text{-}2}$ = 10.1 Hz, 1H, H1), 3.84 (q, $J_{5\text{-}6}$ = 6.5 Hz, 1H, H5), 3.75 (s, 3H, OMe), 2.19 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.25 (d, $J_{5\text{-}6}$ = 6.5 Hz, 3H, H6). ^{13}C-NMR (400 MHz, CDCl3), extrapolated from HSQC exp. δ (ppm): 76.9 (C1), 73.4 (C5), 71.7 (C3), 70.3 (C4), 66.5 (C2), 52.7 (OMe), 20.7 (OAc), 16.4 (C6).

*Synthesis of methyl-β-L-fucopyranosyl cyanide (**9**)*



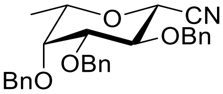
1*-β*CN (200 mg, 0.67 mmol, 1 eq.) was dissolved in anhydrous methanol (0.2M) under Ar and a solution of NaOMe in MeOH (0.025M) was slowly added. The reaction mixture was stirred at room temperature for 1.5h, then Amberlite™ IR-120H+ was added until pH 7. The mixture was filtered and evaporated to dryness. The crude was purified by flash chromatography (AcOEt/MeOH 90:10), affording the product as a colourless oil (Y = 30%). Rf (AcOEt/MeOH 9:1) = 0.45. MS (ESI): m/z calcd for $[C_7H_{11}NO_4 Na]^+$: 196.16; found: 196.65 $[M+Na]^+$. ^{1}H-NMR (400 MHz, MeOD) δ (ppm): 4.08 (d, $J_{1\text{-}2}$ = 10.4 Hz, 1H, H1), 3.80 (t, $J_{2\text{-}1/3}$= 9.7 Hz, 1H, H3), 3.72-3.65 (m, 2H, H4 + H5), 3.44 (dd, $J_{2\text{-}3}$ = 9.7 Hz, $J_{3\text{-}4}$=3.4 Hz, 1H, H3), 1.28 (d, $J_{6\text{-}5}$= 6.5 Hz). ^{13}C-NMR (400 MHz, CDCl3), extrapolated from HSQC exp. δ (ppm): 75.7 (C5), 74.0 (C3), 71.4 (C4), 69.4 (C1), 68.1 (C2), 15.5 (C6).

*Synthesis of 2,3,4-tri-O-tert-butyl(dimethyl)silyl -β-L-fucopyranosyl cyanide (**10**)*



*Compound **9*** (65 mg, 0.37 mmol, 1 equiv.) was suspended in CH_2Cl_2 (1 mL, 0.4 M), then Et_3N (410 µL, 2.96 mmol, 8 eq.) was added at 0°C. *tert*-Butyl-dimethylsilyl triflate (300 µL, 1.3 mmol, 3.5 eq.) was added dropwise and the solution was left stirring at 0°C for 3h. the crude mixture was washed with HCl 1 M and then with sat. $NaHCO_3$. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-hexane/AcOEt 9:1) to afford a yellow solid (Y = 20 %). Rf (AcOEt/MeOH 9:1) = 0.37. MS (ESI): m/z calcd for $[C_{25}H_{53}NO_4Si_3Na]^+$: 538.32; found: 538.60 $[M+Na]^+$. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.99 (m, 1H, H1), 3.83 (s, 1H, H4), 3.68 (q, $J_{5\text{-}6}$ = 6.1 Hz, 1H, H5), 3.65 – 3.59 (m, 2H, H2 + H3), 1.21 (d, $J_{6\text{-}5}$ = 6.1 Hz, 3H, H6), 0.97 – 0.81 (m, 27H, Si*t*Bu), 0.17 – -0.09 (m, 18H, Si CH_3). ^{13}C-NMR (400 MHz, $CDCl_3$), extrapolated from HSQC exp. δ (ppm): 176.3 ($SiCH_3$), 79.7 (C2), 77.4 (C3), 74.5 (C5), 74.0 (C4), 71.0 (C1), 26.5 (Si*t*Bu), 18.0 (C6).

*Synthesis of 2,3,4-tri-O-benzyl-β-L-fucopyranosyl cyanide (**11**)*



*Compound **9*** (20 mg, 0.17 mmol, 1 eq.) was dissolved in anhydrous DMF (500 µL, 0.3M) under N_2 and cooled to 0°C. NaH 90%$_w$ (27mg, 1mmol, 6 eq.) was added into the cold solution and the reaction mixture was left to stir at 0°C for 30 min. Benzyl bromide (100 µL, 0.86 mmol, 5 eq.) was slowly added and the mixture was stirred for 3h at room temperature. The reaction was quenched by slow addition of water and then extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The crude was purified by flash chromatography (*n*-hexane/AcOEt 9:1), affording product **11** as colorless oil (Y = 40%). Rf (*n*-hexane/AcOEt 8:2) = 0.49. MS (ESI): m/z calcd for $[C_{28}H_{29}NO_4Na]^+$: 466.20; found: 466.86 $[M+Na]^+$. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.35-7.19 (m,15H, ArH), 4.91 (d, J = 11.8 Hz, 1H, CH_2), 4.83 (s, 2H, CH_2), 4.68 (s, 2H, CH_2), 4.59 (d, J = 11.8 Hz, 1H, CH_2), 4.09 (t, $J_{2\text{-}1/3}$ = 9.9 Hz, 1H, H2), 3.93 (d, $J_{1\text{-}2}$ = 9.9 Hz, 1H, H1), 3.54 (d, $J_{3\text{-}4}$ = 2.6 Hz, 1H, H4), 3.45-3.35 (m, 2H, H3 + H5), 1.12 (d, $J_{6\text{-}5}$ = 6.6 Hz, 1H, H6). ^{13}C-NMR (400 MHz, $CDCl_3$), extrapolated from HSQC exp. δ (ppm): 128.2 (Ar*C*H), 83.5 (C3), 76.1 (C4), 76.0 (C2), 75.9 (*C*H_2), 75.8 (C5), 75.2 (*C*H_2), 73.0 (*C*H_2), 67.9 (C1), 16.9 (C6).

2.3. Photocatalyzed Giese-type alkylation

Reaction set up

Catalytic tests were run in 2-5 mL microwave vials sealed with a septum cap under irradiation by 40 W Kessil PR160L lamp (λ = 370 nm; distance between lamp and vial(s): 5 cm). Two fans were used to dissipate the heat generated by the lamp. The reaction setup is shown in Figure S1.

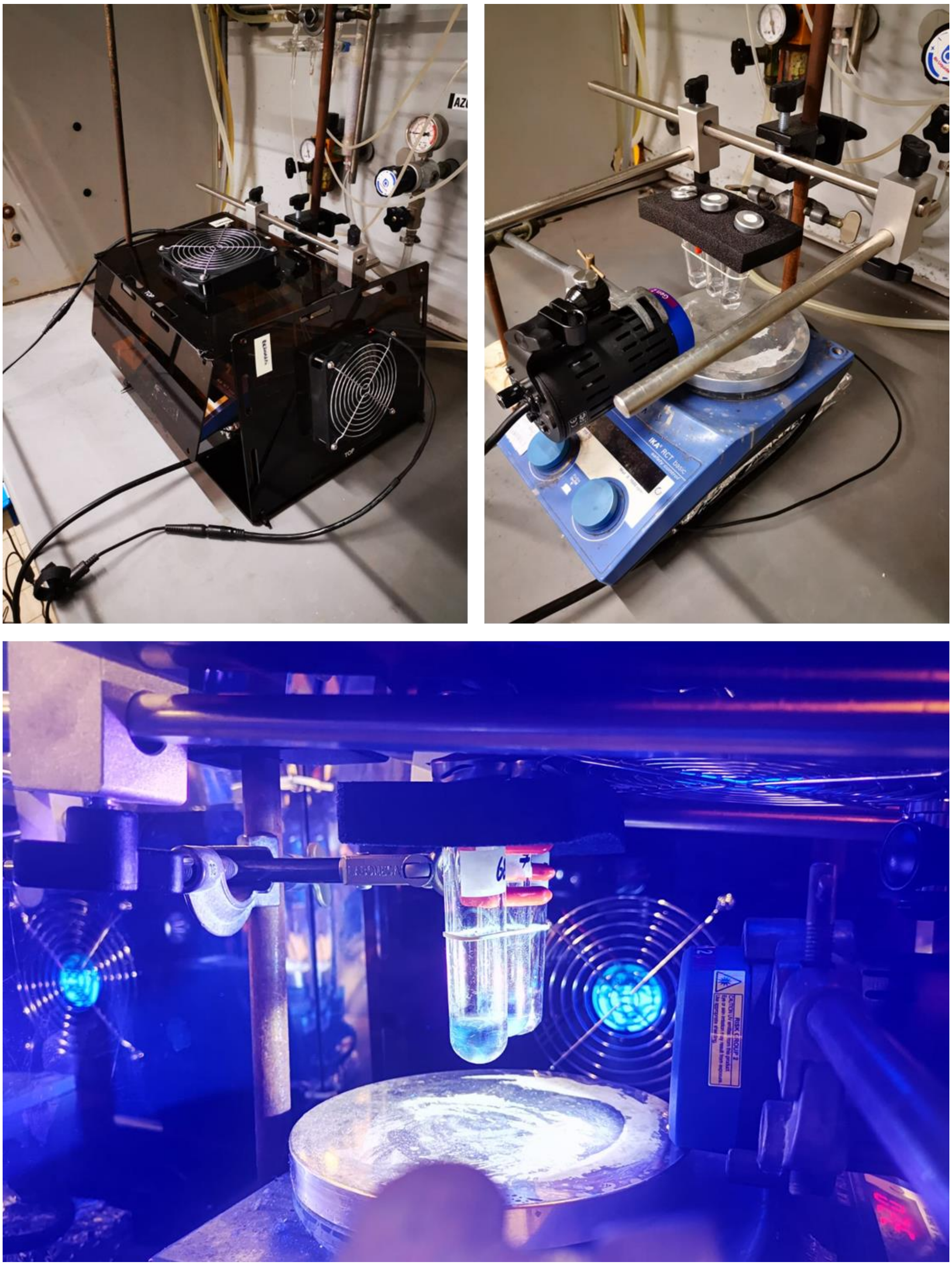
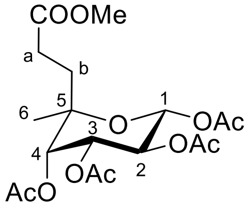


Figure S1. Reaction setup.

General procedure

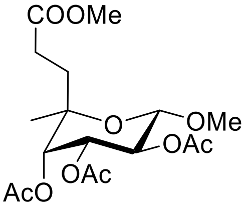
In a sealed 2-5 mL-microwave glass vial equipped with a magnetic stir bar, the fucoside (**1-βR**, 1 equiv.), TBADT (5 mol %) and the olefin (1.1 equiv.) were dissolved in anhydrous acetonitrile (0.1 M) under Ar atmosphere. Deoxygenation was performed by 3 freeze-pump-thaw cycles under Ar atmosphere. The reaction was irradiated at ca. 5 cm distance with a 370 nm Kessil lamp at 100% light intensity. Two fans were used for dissipating heat from the lamp. The reaction mixture was stirred for 7h, then it was quenched by air and concentrated to dryness. The residue was purified by flash column chromatography with a proper eluent, giving the desired C-5 alkylated product **3-βR** with full stereoselectivity.

*Synthesis of **3-βOAc***

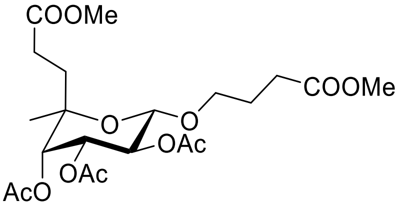


The product was obtained from ***1-βOAc*** (50 mg, 0.15 mmol) and methyl acrylate (15 µL, 0.16 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (7:3) as eluent, obtaining compound ***3-βOAc*** as colourless oil. (Y = 52%, Y brsm = 97%). Rf (*n*-hexane/AcOEt 6:4) = 0.45. HRMS (ESI) *m/z* calcd for $[C_{18}H_{26}O_{11}Na]^+$: 441.1373; found: 441.1374 $[M+Na]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.76 (d, $J_{1\text{-}2}$ = 7.9 Hz, 1H, H1), 5.40 (dd, $J_{3\text{-}2}$ = 7.9 Hz, $J_{3\text{-}4}$ = 2.8 Hz, 1H, H3), 5.32 (t, $J_{2\text{-}1}$ = $J_{2\text{-}3}$ = 7.9 Hz, 1H, H2), 5.19 (d, $J_{4\text{-}3}$ = 2.8 Hz, 1H, H4), 3.67 (s, 3H, OMe), 2.74- 2.65 (m, 1H, Ha), 2.54 – 2.45 (m, 1H, Ha'), 2.45 – 2.38 (m, 1H, Hb), 2.18 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.98 (s, 3H, OAc), 1.89 – 1.77 (m, 1H, Hb'), 1.16 (s, 3H, H6).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm)*:* 173.3 (*C*OOMe), 170.2 (OAc quat.), 169.8 (OAc quat.), 169.4 (OAc quat.), 169.4 (OAc quat.), 89.2 (C1), 77.3 (C5), 71.8 (C4), 69.1 (C3), 68.1 (C2), 51.9 (COO*Me*), 28.9 (CH_2b), 27.1 (CH_2a), 21.3 (C6), 20.8 (OAc), 20.7 (OAc), 20.6 (OAc), 20.5 (OAc).

*Synthesis of **3-βOMe***

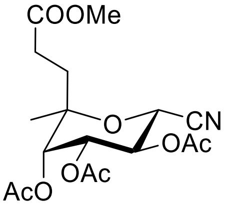


The product was obtained from ***1-βOMe*** (55 mg, 0.16 mmol) and methyl acrilate (15 µL, 0.18 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (7:3) as eluent, obtaining compound ***3-βOMe*** as white foam. (Y= 54%, Y brsm =64%). Rf (*n*-hexane/AcOEt 2:1) = 0.39. HRMS (ESI) *m/z* calcd for $[C_{17}H_{26}O_{10}Na]^+$: 413.1424; found: 413.1419 $[M+Na]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.31 (dd, $J_{3\text{-}2}$ = 10.3 Hz, $J_{3\text{-}4}$ = 3.4 Hz, 1H, H3), 5.23 – 5.17 (m, 1H, H2), 5.16 (d, $J_{4\text{-}3}$ = 3.2 Hz, 1H, H4), 4.55 (d, $J_{1\text{-}2}$ = 8.1 Hz, 1H, H1), 3.71 (s, 3H, COO*Me*), 3.47 (s, 3H, OMe), 2.56 – 2.35 (m, 2H, Ha), 2.34 – 2.21 (m, 1H, Hb), 2.16 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.97 (s, 3H, OAc), 1.92 – 1.77 (m, 1H, Hb'), 1.17 (s, 3H, H6). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.1 (*C*OOMe), 170.4 (OAc quat.), 170.1 (OAc quat.), 169.5 (OAc quat.), 98.1 (C1), 75.8 (C5), 72.0 (C4), 69.2 (C3), 69.1 (C2), 56.3 (OMe), 51.9 (COO*Me*), 29.1 (*C*H$_2$b), 27.6 (*C*H$_2$a), 21.5 (C6), 20.8 (OAc), 20.6 (OAc), 20.6 (OAc).



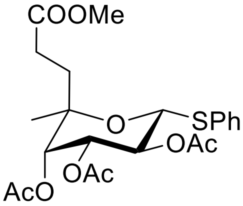
The product was obtained from ***1-βOMe*** (55 mg, 0.16 mmol) and methyl acrilate (15 µL, 0.18 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (7:3) as eluent, obtaining dialkylated derivative as a white foam. (Y= 8%, Y brsm = 10%). Rf (*n*-hexane/AcOEt 2:1) = 0.34. MS (ESI) *m/z* calcd for $[C_{21}H_{32}O_{12}Na]^+$: 499.18; found: 499.24 $[M+Na]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.25 (dd, $J_{3\text{-}2}$ = 10.1 Hz, $J_{3\text{-}4}$ = 2.8 Hz, 1H, H3), 5.16 – 5.07 (m, 2H, H2 + H4), 4.54 (d, $J_{1\text{-}2}$ = 7.8 Hz, 1H, H1), 3.87-3.78 (m, 1H, C*H$_2$*O), 3.65 (s, 3H, COO*Me*), 3.59 (s, 3H, COO*Me*), 3.40-3.35 (m, 1H, C*H$_2$*O) 2.43-2.21 (m, 4H, Ha), 2.10 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.91 (s, 3H, OAc), 1.87 – 1.63 (m, 2H, Hb), 1.17 (s, 3H, H6). ^{13}C-NMR (400 MHz, $CDCl_3$), extrapolated from HSQC exp.: δ (ppm): 94.4 (C1), 71.9 (C4), 69.5 (C2), 69.1 (C3), 68.6 (*C*H$_2$O), 52.1 (COO*Me*), 51.6 (COO*Me*), 31.7 (*C*H$_2$a), 30.1 (*C*H$_2$b), 29.3 (*C*H$_2$a), 25.2 (*C*H$_2$b), 21.9 (C6), 20.9 (OAc), 20.8 (OAc), 20.6 (OAc).

*Synthesis of **3-βCN***



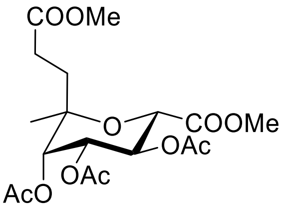
The product was obtained from ***1-βCN*** (40 mg, 0.13 mmol) and methyl acrylate (13 µL, 0.14 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (6:4) as eluent, obtaining compound ***3-βCN*** as white foam. (Y= 90%, Y brsm =90%). Rf (*n*-hexane/AcOEt 6:4) = 0.30. HRMS (ESI) *m/z* calcd for $[C_{17}H_{23}NO_9Na]^+$: 408.1271; found: 408.1271 $[M+Na]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.45 (t, $J_{2\text{-}1} = J_{2\text{-}3} = 10.0$ Hz, 1H, H2), 5.25 (dd, $J_{3\text{-}2} = 10$ Hz, $J_{3\text{-}4} = 3.2$ Hz, 1H, H3), 5.14 (d, $J_{4\text{-}3} = 3.3$ Hz, 1H, H4), 4.51 (d, $J_{1\text{-}2} = 10.0$ Hz 1H, H1), 3.69 (s, 3H, OMe), 2.45 – 2.36 (m, 2H, Ha), 2.35 – 2.25 (m, 1H, Hb), 2.16 (s, 3H, OAc), 2.08 (s, 3H, OAc), 1.96 (s, 3H, OAc), 1.84 – 1.74 (m, 1H, Hb'), 1.16 (s, 3H, H6).^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm): 173.0 (*C*OOMe), 170.0 (OAc quat.), 169.7 (OAc quat.), 168.9 (OAc quat.), 115.3 (CN), 78.8 (C5), 71.5 (C4), 68.6 (C3), 66.4 (C2), 62.1 (C1), 52.0, 27.8 (*C*H_2b), 27.5 (*C*H_2a), 20.8 (C6), 20.5 (OAc), 20.47 (OAc), 20.4 (OAc).

*Synthesis of **3-βSPh***



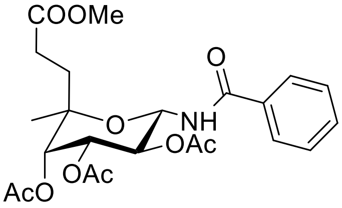
The product was obtained from ***1-βSPh (***40 mg, 0.11 mmol) and methyl acrylate (10 µL, 0.116 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (85:15) as eluent, obtaining compound ***3-βSPh*** as white foam. (Y= 67%, Y brsm = 70%). Rf (*n*-hexane/AcOEt 85:15) = 0.1. HRMS (ESI) *m/z* calcd for $[C_{22}H_{28}O_9SNa]^+$: 491.1352; found: 491.1349 $[M+Na]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.60 – 7.52 (m, 2H, ArH*o*), 7.36 – 7.28 (m, 3H, ArH*m* + ArH*p*), 5.34 (dd, $J_{3\text{-}2} = 10.0$ Hz, $J_{3\text{-}4} = 3.2$ Hz, 1H, H3), 5.20 (t, $J_{2\text{-}1} = J_{2\text{-}3} = 10.0$ Hz, 1H, H2), 5.14 (d, $J_{4\text{-}3} = 3.2$ Hz, 1H, H4), 4.78 (d, $J_{1\text{-}2} = 10.0$ Hz, 1H, H1), 3.64 (s, 3H, COOMe), 2.34 – 2.21 (m, 2H, Ha), 2.10 – 2.07 (m, 6H, OAc), 2.07 – 1.98 (m, 1H, Hb), 1.95 (s, 3H, OAc), 1.81 – 1.73 (m, 1H, Hb'), 1.13 (s, 3H, H6). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.0 (*C*OOMe), 170.3 (OAc quat.), 170.0 (OAc quat.), 169.4 (OAc quat.), 134.2 (ArC*o*), 131.7 (ArC quat.), 128.7 (ArC*m*), 128.5 (ArC*p*), 81.8 (C1), 77.7 (C5), 72.1 (C4), 69.9 (C3), 67.6 (C2), 51.8 (COO*Me*), 27.9 (*C*H_2b), 27.2 (*C*H_2a), 21.4 (C6), 20.8 (OAc), 20.6 (OAc).

Synthesis of ***3*-β*CO_2Me***



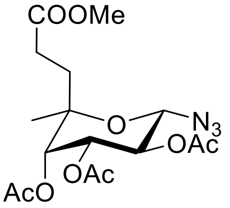
The product was obtained from ***1*-β*CO_2Me*** (40 mg, 0.12 mmol) and methyl acrylate (11 µL, 0.13 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (6:4) as eluent, obtaining compound ***3*-β*CO_2Me*** as white foam. (Y= 70%, Y brsm =80%). Rf (*n*-hexane/AcOEt 6:4) = 0.24. HRMS (ESI) *m/z* calcd for $[C_{18}H_{26}O_{11}Na]^+$: 441.1373; found: 441.1373 $[M+Na]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.40 – 5.33 (m, 2H, H2 + H3), 5.21 – 5.17 (m, 1H, H4), 4.16 – 4.08 (m, 1H, H1), 3.72 (s, 3H, COOMe), 3.69 (s, 3H, COOMe), 2.52 – 2.37 (m, 2H, Ha), 2.37 – 2.28 (m, 1H, Hb), 2.17 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.96 (s, 3H, OAc), 1.89 – 1.79 (m, 1H, Hb’), 1.17 (s, 3H, H6). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 173.0 (*C*OOMe), 170.4 (*C*OOMe), 170.0 (OAc quat.), 169.6 (OAc quat.), 168.1 (OAc quat.), 77.3 (C5), 72.0 (C4), 71.3 (C1), 69.3 (C2), 66.6 (C3), 52.7 (*C*OOMe), 51.9 (COOMe), 27.8 (*C*H_2b), 27.5 (*C*H_2a), 21.3 (C6), 20.6 (OAc), 20.6 (OAc), 20.5 (OAc).

Synthesis of ***3*-β*NHCOPh***

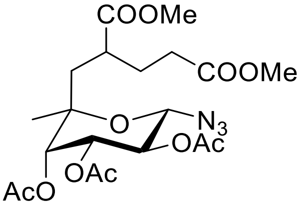


The product was obtained from ***1*-β*NHCOPh*** *(*25 mg, 0.065 mmol) and methyl acrylate (7 µL, 0.07 mmol) following the general procedure. The product ***3*-β*NHCOPh*** could not be chromatographically separated from the starting material (Y = 40% estimated by ^{1}H-NMR analysis of the crude reaction mixture). Rf (*n*-hexane/AcOEt 1:1) = 0.48. MS (ESI) *m/z* calcd for $[C_{23}H_{30}NO_{10}]^+$: 480.19; found: 480.24 $[M+H]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) of detectable peaks from the crude: 7.77 (m, 2H, ArH*o*), 7.53 (m, 1H, ArH*p*), 7.44 (m, 2H, ArH*m*), 7.02 (m,1H, N*H*), 5.60 – 5.53 (m, 1H, H3), 5.46 (t, $J_{1\text{-N}H/2}$ = 9.0 Hz, 1H, H1), 5.32 – 5.18 (m, 2H, H2 + H4), 3.74 (s, 3H, -COOC*H*$_3$), 3.07 – 2.85 (m, 1H, Ha’), 2.59 – 2.35 (m, 2H, Ha + Hb’), 2.18 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.92 – 1.80 (m, 1H, Hb), 1.15 (s, 3H, H6).

*Synthesis of **3-βN₃***

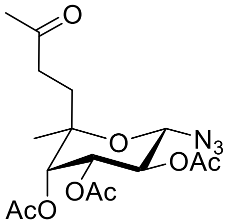


The product was obtained from ***1*-β*N₃*** (30 mg, 0.10 mmol) and methyl acrylate (9 μL, 0.11 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (7:3) as eluent, obtaining compound ***3*-β*N₃*** as white foam. (Y= 50%, Y brsm = 56%). Rf (*n*-hexane/AcOEt 6:4) = 0.35. HRMS (ESI) *m/z* calcd for $[C_{16}H_{23}N_3O_9Na]^+$: 424.1332; found: 424.1337 $[M+Na]^+$. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.33 (dd, $J_{3\text{-}2}$ = 10.4 Hz, $J_{3\text{-}4}$ = 3.3 Hz, 1H, H3), 5.18 (d, $J_{4\text{-}3}$ = 3.3 Hz, 1H, H4), 5.15 (t, $J_{2\text{-}1}$ = $J_{2\text{-}3}$ = 10.4 Hz, 1H, H2), 4.78 (d, $J_{1\text{-}2}$ = 10.4 Hz, 1H, H1), 3.72 (s, 3H, OMe), 2.50 – 2.40 (m, 2H, Ha), 2.40 – 2.32 (m, 1H, Hb), 2.18 (s, 3H, OAc), 2.08 (s, 3H, OAc), 1.98 (s, 3H, OAc), 1.90 – 1.79 (m, 1H, Hb'), 1.19 (s, 3H, H6) ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.0 (*C*OOMe), 170.2 (OAc quat.), 169.9 (OAc quat.), 169.4 (OAc quat.), 84.3 (C1), 77.6 (C5), 71.8 (C4), 68.8 (C3), 68.3 (C2), 52.0 (OMe), 28.4 (*C*H_2b), 27.6 (*C*H_2a), 21.1 (C6), 20.6 (OAc), 20.5 (OAc), 20.5 (OAc).



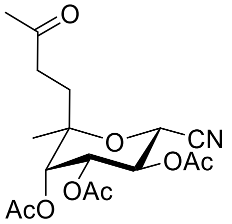
The product was obtained from ***1*-β*N₃*** (30 mg, 0.10 mmol) and methyl acrylate (9 μL, 0.11 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (7:3) as eluent, obtaining polyconjugate product as white foam. (Y= 10%, Y brsm = 12%). Rf (*n*-hexane/AcOEt 6:4) = 0.30. MS (ESI) *m/z* calcd for $[C_{20}H_{29}N_3O_{11}Na]^+$: 510.17; found: 510.57 $[M+Na]^+$. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.29 (dd, $J_{3\text{-}2}$ = 10.8 Hz, $J_{3\text{-}4}$ = 3.1 Hz, 1H, H3), 5.18-5.11 (m, 2H, H2 + H4), 4.90 (d, $J_{1\text{-}2}$ = 9.1 Hz, 1H, H1), 3.75 (s, 3H, OMe), 3.71 (s, 3H, OMe), 2.83 – 2.70 (m, 1H, C*H*a), 2.66 – 2.42 (m, 4H, 2xC*H_2*), 2.19 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.94-1.86 (m, 2H, C*H_2*), 1.18 (s, 3H, H6). ^{13}C-NMR (400 MHz, $CDCl_3$), extrapolated from HSQC exp.: δ (ppm): 84.4 (C1), 72.2 (C4), 69.1 (C3), 68.3 (C2), 52.4 (OMe), 51.7 (OMe), 31.7 (*C*H_2CO), 29.4 (*C*H_2CH), 21.0 (C6), 20.6 (OAc), 20.5 (OAc), 20.5 (OAc).

Synthesis of ***4-β**N_3*



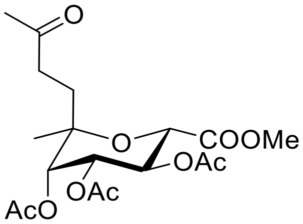
The product was obtained from ***1-β**CO$_2$**Me*** (40 mg, 0.13 mmol) and methyl vinyl ketone (9 μL, 0.14 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (7:3) as eluent, obtaining compound ***4-β**CO$_2$**Me*** as colourless oil. (Y= 43%, Y brsm = 55%). Rf (*n*-hexane/AcOEt 7:3) = 0.21. HRMS (ESI) *m/z* calcd for $[C_{16}H_{23}N_3O_8Na]^+$: 408.1383; found: 408.1385 $[M+Na]^+$. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 5.31 (dd, $J_{3\text{-}2}$ = 9.7 Hz, $J_{3\text{-}4}$ = 3.3 Hz, 1H, H3), 5.18 (d, $J_{4\text{-}3}$ = 3.3 Hz, 1H, H4), 5.13 (t, $J_{2\text{-}1}$ = $J_{2\text{-}3}$ = 9.7 Hz, 1H, H2), 4.69 (d, $J_{1\text{-}2}$ = 9.7 Hz, 1H, H1), 2.67 – 2.49 (m, 2H, Ha), 2.34 – 2.24 (m, 1H, Hb), 2.21 (s, 3H, CO*CH*$_3$), 2.17 (s, 3H, OAc), 2.07 (s, 3H, OAc), 1.96 (s, 3H, OAc), 1.84 – 1.74 (m, 1H, Hb’), 1.16 (s, 3H, H6). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm)*:* 206.7 (*C*OCH$_3$), 170.2 (OAc quat.), 169.9 (OAc quat.), 169.5 (OAc quat.), 84.3 (C1), 77.7 (C5), 71.8 (C4), 68.9 (C3), 68.4 (C2), 36.6 (*C*H$_2$b), 30.2 (CO*CH*$_3$), 26.9 (*C*H$_2$a), 21.6 (C6), 20.7 (OAc), 20.6 (OAc), 20.5 (OAc).

Synthesis of ***4-β**CN*



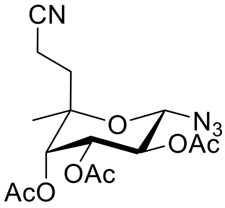
The product was obtained from ***1-β**CN* (40 mg, 0.13 mmol) and methyl vinyl ketone (12 μL, 0.14 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (7:3) as eluent, obtaining compound ***4-β**CN* as white foam. (Y= 78%, Y brsm = 99%). Rf (*n*-hexane/AcOEt 6:4) = 0.3. HRMS (ESI) *m/z* calcd for $[C_{17}H_{23}NO_8Na]^+$: 392.1321; found: 392.1324 $[M+Na]^+$. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 5.46 (t, $J_{2\text{-}1}$ = $J_{2\text{-}3}$ = 9.8 Hz, 1H, H2), 5.26 (dd, $J_{3\text{-}2}$ = 9.8 Hz, $J_{3\text{-}4}$ = 3.2 Hz, 1H, H3), 5.16 (d, $J_{4\text{-}3}$ = 3.2 Hz, 1H, H4), 4.45 (d, $J_{1\text{-}2}$ = 9.8 Hz, 1H, H1), 2.65 – 2.45 (m, 2H, Ha), 2.30 – 2.21 (m, 1H, Hb), 2.20 (s, 3H, CO*CH*$_3$), 2.17 (s, 3H, OAc), 2.09 (s, 3H, OAc), 1.97 (s, 3H, OAc), 1.82 – 1.67 (m, 1H, Hb’), 1.14 (s, 3H, H6). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 206.6 (COCH$_3$), 170.2 (OAc quat.), 169.7 (OAc quat.), 168.9 (OAc quat.), 115.4 (CN), 78.8 (C5), 71.5 (C4), 68.6 (C3), 66.4 (C2), 62.1 (C1), 36.5 (*C*H$_2$b), 30.2 (COCH$_3$), 26.2 (*C*H$_2$a), 21.3 (C6), 20.5 (OAc), 20.5 (OAc), 20.5 (OAc).

Synthesis of ***4-βCO_2Me***



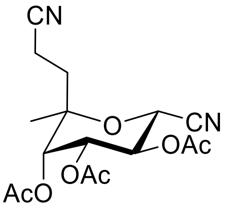
The product was obtained from sugar ***1-βCO_2Me*** (40 mg, 0.12 mmol) and methyl vinyl ketone (8 µL, 0.13 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (6:4) as eluent, obtaining compound ***4-βCO_2Me*** as white foam. (Y= 60%, Y brsm =97%). Rf (*n*-hexane/AcOEt 6:4) = 0.27. HRMS (ESI) *m/z* calcd for $[C_{18}H_{26}O_{10}Na]^+$: 425.1424; found: 425.1423 $[M+Na]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.36 (s, 1H, H2), 5.35 (s, 1H, H3), 5.19 (s, 1H, H4), 4.10 – 4.03 (m, 1H, H1), 3.72 (s, 3H, OMe), 2.66 – 2.54 (m, 1H, Ha), 2.54 – 2.44 (m, 1H, Ha'), 2.32 – 2.22 (m, 1H, Hb), 2.18 (s, 3H, CO$\mathit{CH_3}$), 2.16 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.96 (s, 3H, OAc), 1.87 – 1.74 (m, 1H, Hb'), 1.14 (s, 3H, H6). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 206.8 ($\mathit{C}OCH_3$), 170.4 (*C*OOMe), 169.9 (OAc quat.), 169.6 (OAc quat.), 168.2 (OAc quat.), 77.4 (C5), 72.0 (C4), 71.2 (C1), 69.3 (C2), 66.6 (C3), 52.7 (COO*Me*), 36.6 ($\mathit{C}H_2$b), 30.1 (CO$\mathit{CH_3}$), 26.2 ($\mathit{C}H_2$a), 21.7 (C6), 20.6 (OAc), 20.6 (OAc), 20.5 (OAc).

Synthesis of ***5-βN_3***



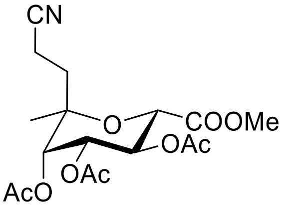
The product was obtained from ***1-βN_3*** (40 mg, 0.13 mmol) and acrylonitrile (10 µL, 0.14 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (7:3) as eluent, obtaining compound ***5-βN_3*** as colourless oil. (Y = 37%, Y brsm = 92%). Rf (*n*-hexane/AcOEt 6:4) = 0.3. HRMS (ESI) *m/z* calcd for $[C_{15}H_{20}N_4O_7Na]^+$: 391.1230; found: 391.1227 $[M+Na]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.26 (dd, J_{3-2} = 10.0 Hz, J_{3-4} = 3.2 Hz, 1H, H3), 5.18 (d, J_{4-3} = 3.2 Hz, 1H, H4), 5.17 (m, 1H, H2), 4.74 (d, J_{1-2} = 8.2 Hz, 1H), 2.55 – 2.42 (m, 2H, Ha), 2.39 – 2.27 (m, 1H, Hb), 2.19 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.97 – 1.88 (m, 1H, Hb'), 1.26 (s, 3H, H6). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.1 (OAc quat.), 169.9 (OAc quat.), 169.3 (OAc quat.), 118.6 (CN), 84.5 (C1), 77.1 (C5), 71.0 (C4), 68.4 (C3), 68.1 (C2), 29.9 ($\mathit{C}H_2$b), 21.0 (C6), 20.6 (OAc), 20.5 (OAc), 20.5 (OAc), 11.1 ($\mathit{C}H_2$a).

*Synthesis of **5-βCN***



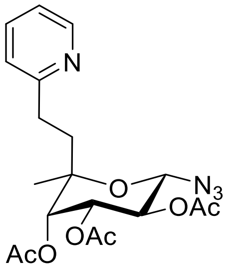
The product was obtained from ***1-βCN*** (40 mg, 0.13 mmol) and acrylonitrile (10 µL, 0.14 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (7:3) as eluent, obtaining compound ***5-βCN*** as colourless oil. (Y= 30%, Y brsm = 87%). Rf (*n*-hexane/AcOEt 7:3) = 0.38. HRMS (ESI) *m/z* calcd for $[C_{16}H_{20}N_2O_7Na]^+$: 375.1168; found: 375.1174 $[M+Na]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 5.44 (t, $J_{2\text{-}1} = J_{2\text{-}3} = 8.7$ Hz, 1H, H2), 5.23 (dd, $J_{3\text{-}2} = 8.7$ Hz, $J_{3\text{-}4} = 3.2$ Hz, 1H, H3), 5.16 (d, $J_{4\text{-}3} = 3.2$ Hz, 1H, H4), 4.50 (d, $J_{1\text{-}2} = 8.7$ Hz, 1H, H1), 2.59 – 2.38 (m, 2H, Ha), 2.30 – 2.20 (m, 1H, Hb), 2.19 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.02 – 1.86 (m, 1H, Hb'), 1.33 (s, 3H, H6). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm): 169.9 (OAc quat.), 169.7 (OAc quat.), 168.9 (OAc quat.), 118.7 (CN), 78.0 (C5), 70.3 (C4), 68.0 (C3), 66.8 (C2), 62.1 (C1), 30.1 (*C*H$_2$b), 20.5 (OAc), 20.5 (OAc), 20.4 (OAc), 11.1 (*C*H$_2$a).

*Synthesis of **5-βCO₂Me***



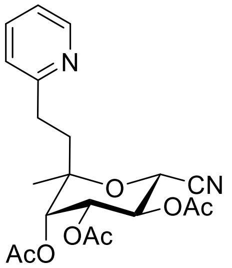
The product was obtained from ***1-βCO₂Me*** (30 mg, 0.09 mmol) and acrylonitrile (6 µL, 0.1 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (8:2) as eluent, obtaining compound ***5-βCO₂Me*** as white foam. (Y= 20%, Y brsm = 94%). Rf (*n*-hexane/AcOEt 7:3) = 0.43. HRMS (ESI) *m/z* calcd for $[C_{17}H_{23}NO_9Na]^+$: 408.1271; found: 408.1272 $[M+Na]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.40 (t, $J_{2\text{-}1} = J_{2\text{-}3} = 10.6$ Hz, 1H, H2), 5.33 – 5.26 (dd, $J_{3\text{-}2} = 10.6$ Hz, $J_{3\text{-}4} = 4.4$ Hz, 1H, H3), 5.18 (d, $J_{4\text{-}3} = 4.4$ Hz, 1H, H4), 4.05 (d, $J_{1\text{-}2} = 10.6$ Hz, 1H, H1), 3.76 (s, 3H, OMe), 2.56 – 2.43 (m, 2H, Ha), 2.42 – 2.36 (m, 1H, Hb), 2.19 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.97 – 1.84 (m, 1H, Hb'), 1.22 (s, 3H, H6). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.3 (*C*OOMe), 170.0 (OAc quat.), 169.4 (OAc quat.), 167.6 (OAc quat.), 118.7 (CN), 76.9 (C5), 71.6 (C1), 71.3 (C4) , 69.0 (C3), 66.3 (C2), 52.9 (COO*Me*), 28.8 (*C*H$_2$b), 27.9 (C6), 21.1 (OAc), 20.6 (OAc), 20.5 (OAc), 11.0 (*C*H$_2$a).

Synthesis of ***6-β**N$_3$*



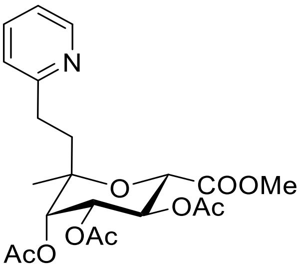
The product was obtained from ***1-β**N$_3$* (40 mg, 0.13 mmol) and 2-vinylpyridine (15 μL, 0.14 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (1:1) as eluent, obtaining compound ***6-β**N$_3$* as white foam. (Y= 38%, Y brsm =77%). Rf (*n*-hexane/AcOEt 6:4) = 0.3. HRMS (ESI) *m/z* calcd for $[C_{19}H_{24}N_4O_7Na]^+$: 443.1543; found: 443.1543 $[M+Na]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm)*:* 8,58 (d, $J_{ArHm\text{-}ArHp}$ = 4.9 Hz, 1H*,* ArH*m*), 7.66 (td, , $J_{ArHm'\text{-}ArHo} = J_{ArHm'\text{-}ArHp}$ = 7.7 Hz, $J_{ArHm'\text{-}ArHm}$ = 1.9 Hz 1H, ArH*m'*), 7.24 – 7.20 (m, 1H, ArH*o*), 7.20 – 7.16 (m, 1H, ArHp), 5.38 (dd, $J_{3\text{-}2}$ = 10.4 Hz, $J_{3\text{-}4}$ = 3.3 Hz, 1H, H3), 5.25 (d, $J_{4\text{-}3}$ = 3.3 Hz, 1H, H4), 5.16 (dd, $J_{2\text{-}1}$ = 8.8 Hz, $J_{2\text{-}3}$ = 10.4 Hz, 1H, H2), 4.87 (d, $J_{1\text{-}2}$ = 8.8 Hz, 1H, H1), 3.02 – 2.82 (m, 2H, Ha), 2.45 – 2.33 (m, 1H, Hb), 2.21 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.06 – 1.98 (m, 1H, Hb'), 1.99 (s, 3H, OAc), 1.32 (s, 3H, H6).^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.4 (OAc quat.), 170.0 (OAc quat.), 169.5 (OAc quat.), 160.1 (ArC quat.), 149.2 (ArCm), 136.9 (ArC*m'*), 123.1 (ArC*o*), 121.6 (ArC*p*), 84.2 (C1), 78.2 (C5), 72.0 (C4), 69.0 (C3), 68.6 (C2), 33.5 (*C*H_2b), 31.3 (*C*H_2a), 21.6 (C6), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc).

Synthesis of ***6-β**CN*



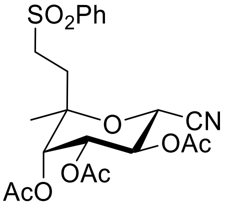
The product was obtained from ***1-β**CN* (40 mg, 0.13 mmol) and 2-vinylpyridine (15 μL, 0.14 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (1:1) as eluent, obtaining compound ***6-β**CN* as white foam. (Y= 45%, Y brsm =95%). Rf (*n*-hexane/AcOEt 1:1) = 0.5. HRMS (ESI) *m/z* calcd for $[C_{20}H_{25}N_2O_7]^+$: 405.1662; found: 405.1661 $[M+H]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.55 (d, $J_{ArHm\text{-}ArHp}$ = 5.1 Hz, 1H, ArH*m*), 7.61 (t, $J_{ArHm'\text{-}ArHo} = J_{ArHm'\text{-}ArHp}$ = 7.6 Hz, 1H, ArH*m'*), 7.24- 712 (m, 2H, ArH*o* + ArH*p*), 5.48 (t, $J_{2\text{-}1} = J_{2\text{-}3}$ = 10.0 Hz, 1H, H2), 5.32 (dd, $J_{3\text{-}2}$ = 10.0 Hz, $J_{3\text{-}4}$ = 3.2 Hz, 1H, H3), 5.20 (d, $J_{4\text{-}3}$ = 3.2 Hz, 1H, H4), 4.58 (d, $J_{1\text{-}2}$ = 10.0 Hz, 1H, H1), 2.97 – 2.77 (m, 2H, Ha), 2.45 – 2.34 (m, 1H, Hb), 2.19 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.05 – 1.97 (m, 1H, Hb’) 1.97 (s, 3H, OAc), 1.28 (s, 3H, H6). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)*:* 170.2 (OAc quat.), 169.8 (OAc quat.), 169.0 (OAc quat.), 159.9 (ArC quat.), 149.5 (ArC*m*), 136.7 (ArC*m’*), 123.0 (ArC*o*), 121.6 (ArC*p*), 115.5, 79.4 (C5), 71.8 (C4), 68.8 (C3), 66.6 (C2), 62.1 (C1), 32.3 (CH_2b), 31.3 (CH_2a), 21.3 (C6), 20.6 (OAc), 20.6 (OAc), 20.5 (OAc).

Synthesis of ***6-βCO₂Me***



The product was obtained from ***1-βCO₂Me*** (30 mg, 0.09 mmol) and 2-vinylpyridine (11 µL, 0.1 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (1:1) as eluent, obtaining compound ***6-βCO₂Me*** as white foam. (Y= 38%, Y brsm = 93%). Rf (*n*-hexane/AcOEt 6:4) = 0.1. HRMS (ESI) *m/z* calcd for $[C_{22}H_{28}NO_9]^+$: 438.1764; found: 438.1566 $[M+H]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.54 (dd, $J_{ArHm\text{-}ArHp}$ = 4.9 Hz, $J_{ArHm\text{-}ArHm'}$= 1.9 Hz 1H, ArH*m*), 7.60 (td, $J_{ArHm'\text{-}ArHo}$ = $J_{ArHm'\text{-}ArHp}$ = 7.6 Hz, $J_{ArHm'\text{-}ArHm}$ = 1.9 Hz, 1H, ArH*m’*), 7.17 (d, $J_{ArHo\text{-}ArHm'}$ = 7.6 Hz, 1H, ArH*o*), 7.13 (dd, $J_{ArHp\text{-}ArHm'}$ = 7.6 Hz, $J_{ArHp\text{-}ArHm}$ = 4.9 Hz, 1H, ArH*p*), 5.46 – 5.41 (m, 1H, H2), 5.41 – 5.35 (m, 1H, H3), 5.24 (d, $J_{4\text{-}3}$ = 2.8 Hz, 1H, H4), 4.22 (d, $J_{1\text{-}2}$ = 9.5 Hz, 1H, H1), 3.73 (s, 3H, OMe), 2.97 – 2.76 (m, 2H, Ha), 2.42- 2.37 (m, 1H, Hb), 2.19 (s, 3H, OAc), 2.07 – 1.98 (m, 1H, Ha’), 2.02 (s, 4H, OAc), 1.97 (s, 3H, OAc), 1.30 (s, 3H, H6). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.5 (*C*OOMe), 170.0 (OAc quat.), 169.6 (OAc quat.), 168.3 (OAc quat.), 160.4 (ArC quat.), 149.5 (ArC*m*), 136.5 (ArC*m’*), 122.9 (ArC*o*), 121.3 (ArC*p*), 78.0 (C5), 72.2 (C4), 71.3 (C1), 69.4 (C2), 66.8 (C3), 52.7 (COOMe), 32.8 (CH_2b), 31.4 (CH_2a), 21.7 (C6), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc).

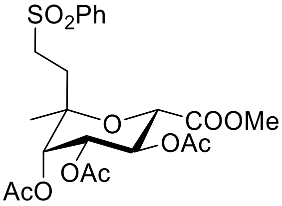
Synthesis of ***7-βCN***



The product was obtained from ***1-βCN*** (40 mg, 0.13 mmol) and phenyl vinylsulfone (23,5 µL, 0.14 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (7:3) as eluent, obtaining compound ***7-βCN*** as colourless oil. (Y= 14%, Y brsm

=78%). Rf (*n*-hexane/AcOEt 7:3) = 0.15. HRMS (ESI) *m/z* calcd for $[C_{21}H_{25}NO_9SNa]^+$: 490.1148; found: 490.1147 $[M+Na]^+$. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.95 (d, $J_{ArHo\text{-}ArHm}$ = 7.8 Hz, 2H, ArH*o*), 7.72 (t, $J_{ArHp\text{-}ArHm}$ = 7.8 Hz, 1H, ArH*p*), 7.63 (t, $J_{ArHm\text{-}ArHp}$ = $J_{ArHm\text{-}ArHo}$ = 7.8 Hz, 2H, ArH*m*), 5.45 (t, $J_{2\text{-}1}$ = $J_{2\text{-}3}$ = 9.4 Hz, 1H, H2), 5.22 (dd, $J_{3\text{-}2}$ = 9.4 Hz, $J_{3\text{-}4}$ = 3.2 Hz, 1H, H3), 5.14 (d, $J_{4\text{-}3}$ = 3.2 Hz, 1H, H4), 4.37 (d, $J_{1\text{-}2}$ = 9.4 Hz, 1H, H1), 3.26 – 3.15 (m, 1H, Ha), 3.15 – 3.04 (m, 1H, Ha'), 2.47 – 2.35 (m, 1H, Hb), 2.16 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.98 – 1.86 (m, 1H, Hb'), 1.16 (s, 3H, H6). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 169.9 (OAc quat.), 169.6 (OAc quat.), 168.9 (OAc quat.), 138.6 (ArC quat.), 134. (ArC*p*), 129.6 (ArC*m*), 128.0 (ArC*o*), 115.1 (CN), 77.9 (C5), 70.8 (C4), 68.2 (C3), 66.3 (C2), 61.9 (C1), 50.1 (*C*H_2b), 26.0 (*C*H_2a), 21.0 (C6), 20.5 (OAc), 21.05 (OAc).

*Synthesis of **7-βCO₂Me***

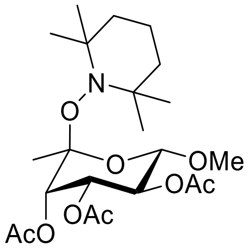


The product was obtained from ***1-βCO₂Me*** (30 mg, 0.9 mmol) and phenyl vinylsulfone (16,8 mg, 0.1 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (6:4) as eluent, obtaining compound ***7-βCO₂Me*** as colourless oil. (Y= 12%, Y brsm = 90%). Rf (*n*-hexane/AcOEt 6:4) = 0.21. HRMS (ESI) *m/z* calcd for $[C_{22}H_{28}O_{11}SNa]^+$: 523.1250; found: 523.1258 $[M+Na]^+$. ^1H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.95 (d, $J_{ArHo\text{-}ArHm}$ = 7.7 Hz, 2H, ArH*o*), 7.70 (t, $J_{ArHp\text{-}ArHm}$ = 7.7 Hz, 1H, ArH*p*), 7.62 (t, $J_{ArHm\text{-}ArHp}$ = $J_{ArHm\text{-}ArHo}$ = 7.7 Hz, 2H, ArH*m*), 5.38 (t, $J_{2\text{-}1}$ = $J_{2\text{-}3}$ = 9.8 Hz, 1H, H2), 5.28 (m, 1H, H3), 5.15 (s, 1H, H4), 3.99 (d, $J_{1\text{-}2}$ = 9.8 Hz, 1H, H1), 3.74 (s, 3H, OMe), 3.24 – 3.07 (m, 2H, Ha), 2.56 – 2.45 (m, 1H, Hb), 2.17 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.97 (s, 3H, OAc), 1.93 – 1.81 (m, 1H, Hb'), 1.10 (s, 3H, H6). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm): 170.3 (*C*OOMe), 169.9 (OAc quat.), 169.5 (OAc quat.), 167.7 (OAc quat.), 138.7 (ArC quat.), 134.0 (ArC*p*), 129.5 (ArC*m*), 128.1 (ArC*o*), 71.5 (C4), 71.2 (C1), 69.1 (C3), 66.1 (C2), 52.8 (COO*Me*), 50.2 (*C*H_2b), 25.6 (*C*H_2a), 21.5 (C6), 20.6 (OAc), 20.6 (OAc), 20.5 (OAc).

General procedure for the reactions in the presence of TEMPO

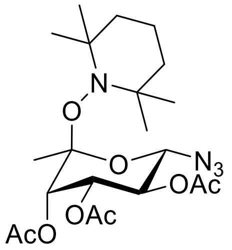
In a sealed 2-5 mL-microwave glass vial equipped with a magnetic stir bar, the fucoside substrate (1 equiv.), TBADT (5 mol %) and TEMPO (2 equiv.) were dissolved in anhydrous acetonitrile (0.1 M) under Ar atmosphere. Deoxygenation was performed by 3 freeze-pump-thaw cycles under Ar atmosphere. The reaction was irradiated for 7 h at ca. 5 cm distance with a 370 nm Kessil lamp at 100% light intensity. Two fans were used for dissipating heat from the lamp. The reaction was quenched by air and concentrated to dryness. The residue was purified by flash column chromatography with a proper eluent, giving the desired C-5 adduct.

Synthesis of ***10-βOMe***



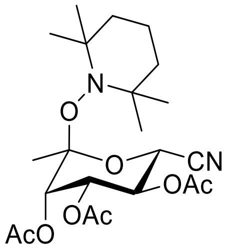
The product was obtained from ***1-βOMe*** (40 mg, 0.13 mmol) and TEMPO (40 mg, 0.26 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (7:3) as eluent, obtaining compound ***10-βOMe*** as white foam. (Y= 30%, Y brsm = 88%). Rf (*n*-hexane/AcOEt 6:4) = 0.5. HRMS (ESI) *m/z* calcd for $[C_{22}H_{37}NO_9Na]^+$: 482.2366; found: 482.2365 $[M+Na]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.52 (d, $J_{4\text{-}3}$ = 3.5 Hz, 1H, H4), 5.52 (dd, $J_{3\text{-}2}$ = 10.0 Hz, $J_{3\text{-}4}$ = 3.5 Hz, 1H, H3), 5.29 (t, $J_{2\text{-}1}$ = $J_{2\text{-}3}$ = 10.0 Hz, 1H, H2), 4.95 (d, $J_{1\text{-}2}$ = 10.0 Hz, 1H, H1), 3.44 (s, 3H, OMe), 2.16 (s, 3H, OAc), 2.08 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.64 – 1.42 (m, 9H, CH_2 + CH_3), 1.31 (s, 3H, CH_3), 1.27-1.18 (m, 6H, H6 + CH_3), 1.13 (s, 3H, CH_3): ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.4 (OAc quat.), 169.7 (OAc quat.), 104.8 (TEMPO C quat.), 98.5 (C1), 71.4 (C4), 69.2 (C3), 68.8 (C2), 60.8 (C5), 59.9, 57.1 (OMe), 40.9 (CH_2), 40.6 (CH_2), 33.7 (CH_3), 33.4 (CH_3), 21.7 (CH_3), 20.9 (C6), 20.8 (OAc), 20.8 (OAc), 20.7 (OAc), 19.6 (CH_3), 16.8 (CH_2).

*Synthesis of **10-βN_3***



The product was obtained from ***1-βN_3*** (50 mg, 0.16 mmol) and TEMPO (50 mg, 0.32 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (6:4) as eluent, obtaining compound ***10-βN_3*** as white foam. (Y= 24%, Y brsm = 65%). Rf (*n*-hexane/AcOEt 7:3) = 0.56. MS (ESI) *m/z* calcd for $[C_{21}H_{34}N_4O_8Na]^+$: 493.22; found: 493.21 $[M+Na]^+$. alfaD___ ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.43 (d, J_{4-3} = 3.2 Hz, 1H, H4), 5.40 (dd, J_{3-2} = 10.2 Hz, J_{2-1} = 3.2 Hz, 1H, H3), 5.16 (t, J_{2-1} = J_{2-3} = 10.2 Hz, 1H, H2), 4.98 (d, J = 8.9 Hz, 1H, H1), 2.10 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.93 (s, 3H, OAc), 1.55 – 1.45 (m, 4H, CH_2), 1.42 – 1.34 (m, 2H, CH_2), 1.20 – 1.14 (m, 6H, CH_3), 1.11 (s, 3H, H6), 1.09 – 1.03 (m, 7H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.1 (OAc quat.), 169.6 (OAc quat.), 105.4 (TEMPO C quat.), 84.2 (C1), 71.1 (C4), 69.1 (C3), 68.0 (C2), 61.0, 59.9 (C5), 40.8 (CH_2), 40.4 (CH_2), 33.8 (CH_3), 33.4, 21.8 (C6), 20.8 (OAc), 20.6 (OAc), 19.4 (CH_3), 16.8 (CH_2).

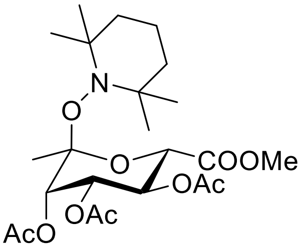
*Synthesis of **10-βCN***



The product was obtained from ***1-βCN*** (40 mg, 0.13 mmol) and TEMPO (40 mg, 0.26 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (7:3) as eluent, obtaining compound ***10-βCN*** as colourless oil (Y= 12%, Y brsm = 14%) and the corresponding amide ***10-β$CONH_2$*** (Y = 20%). Rf (*n*-hexane/AcOEt 6:4) = 0.82. MS (ESI) *m/z* calcd for $[C_{22}H_{34}N_2O_8Na]^+$: 477.22; found: 477.11 $[M+Na]^+$. alfaD___. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.57 (t, J_{2-1} = J_{2-3} = 10.4 Hz, 1H, H2), 5.47 (d, J_{4-3} = 3.5 Hz, 1H, H4), 5.39 (dd, J_{3-2} = 10.4 Hz, J_{3-4} = 3.5 Hz, 1H, H3), 4.81 (d, J_{4-3} = 10.4 Hz, 1H, H4), 2.19 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.57 – 1.49 (m, 4H, CH_2), 1.44 – 1.41 (m, 2H. CH_2), 1.23 – 1.17 (m, 12H, CH_3), 1.10 (s, 3H, H6). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.1 (OAc quat.), 169.9 (OAc quat.), 169.0 (OAc quat.), 115.6 (TEMPO C quat.), 105.6 (TEMPO C quat.), 70.9 (C4), 69.1

(C3), 65.9 (C2), 61.1 (C1), 61.0 (C5), 40.8 (CH_2), 40.44 (CH_2), 33.77 (CH_3), 33.40 (CH), 21.93 (C6), 20.86 (OAc), 20.81 (OAc), 20.59 (OAc), 19.36, 16.77.

Synthesis of ***10-βCO₂Me***



The product was obtained from ***1-βCO₂Me*** (30 mg, 0.09 mmol) and TEMPO (28 mg, 0.18 mmol) following the general procedure. The crude was purified by flash chromatography using *n*-hexane/AcOEt (6:4) as eluent, obtaining compound ***10-βCO₂Me*** as colourless oil. (Y= 22%, Y brsm = 95%). Rf (*n*-hexane/AcOEt 6:4) = 0.66. MS (ESI) *m/z* calcd for $[C_{23}H_{37}NO_{10}Na]^+$: 510.23; found: 510.12 $[M+Na]^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.50 (m, 2H, H3 + H4), 5.45 (t, J_{2-1} = J_{2-3} = 1H, H2), 4.54 (d, J_{1-2} = 11.0 Hz, 1H, H1), 3.75 (s, 3H, OMe), 2.17 (s, 3H, OAc), 2.06 (m, 3H, OAc), 2.00 (s, 3H, OAc), , 1.44 (m, 2H, CH_2), 1.20 (s, 3H, H6), (m, 13H, CH_3), 1.13, 1.60 – 1.51 (m, 4H, CH_2), 1.47 – 1.33 (m, 2H, CH_2), 1.27 – 1.22 (m, 6H, CH_3), 1.21 (s, 3H, H6), 1.19 – 1.10 (m, 8H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.4 (*C*OOMe), 170.1 (OAc quat.), 169.7 (OAc quat.), 168.5 (OAc quat.), 104.9 (TEMPO C quat.), 71.3 (C4), 70.5 (C1), 69.7 (C2), 66.4 (C3), 60.9, 59.9 (C5), 52.7 (OMe), 40.9 (CH_2), 40.5 (CH_2), 33.8 (CH_3), 33.2 (CH_3), 31.5 (CH_2), 22.6 (CH_2), 21.8 (C6), 20.9 (CH_3), 20.8 (OAc), 20.7 (OAc), 20.7 (OAc), 19.6 (CH_3), 16.8 (CH_2), 14.1.

3. Spectroscopical Study

3.1. General information

Nanosecond Laser Flash Photolysis profiles were measured by means of a photolysis apparatus. The minimum response time of the detection system was about 10 ns. The laser beam (a Nd/YAG operated at $\lambda = 355$ nm) was focused on a 3 mm wide circular area of the cell and the first 5 mm in depth were analyzed at a right-angle geometry. The incident pulse energies used were 5-7 mJ per pulse. The sample absorbance at 355 nm was typically 0.6-0.8 over 1 cm. The temperature was kept constant at 295±2 K.

3 mL of an air-equilibrated $2.0 \cdot 10^{-4}$ M CH_3CN solution of TBADT, $(n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$, were placed in a 1x1 cm quartz cell and excited with single pulses (5-7 mJ) delivered from the laser and analyzed with a pulsed Xe arc lamp.

Acquisition and processing of the absorption signals were performed by LP900 7.0.2 (Build 0) Software. Non-linear fitting procedures by the least square method were used to judge the goodness of the fit. Lifetimes of the reactive transient ***wO*** were obtained by fitting the first order decay profiles recorded at 780 nm by using the following equation:

$$y = y_0 + A \cdot e^{-\frac{x}{\tau}}$$

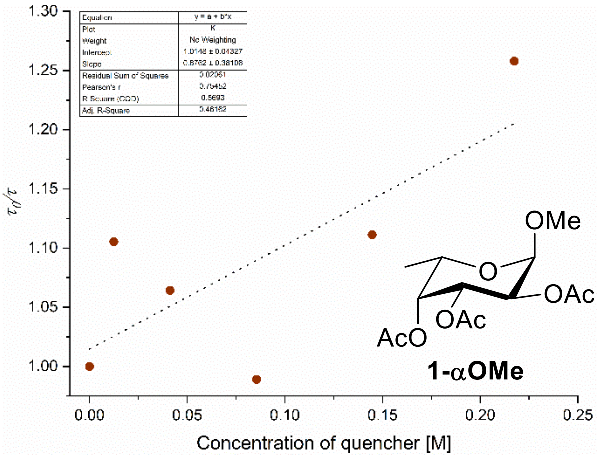
The lifetime of TBADT was monitored in the presence of different concentrations of the quencher and Stern-Volmer plots were obtained from the following equation:

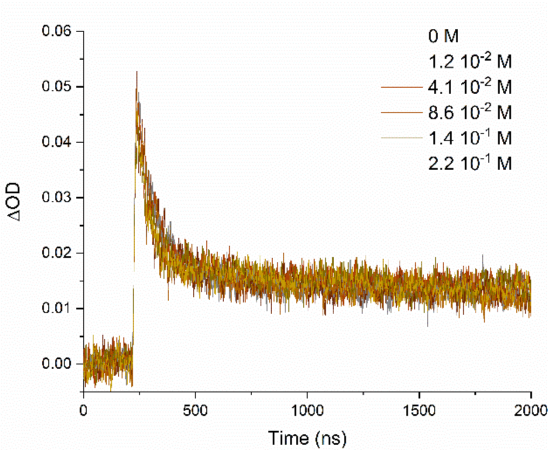
$$\frac{\tau_0}{\tau} = 1 + k_Q \tau_0 [Q]$$

Stock solutions of quenchers in CH_3CN were prepared (5 M for **1-αOMe** and **1-βOMe**, 2.5 M for **1-βN$_3$** and **1-βCN**) so that it was only necessary to add microliter volumes to the sample cell to obtain appropriate concentrations of the quencher.

3.2. LFP Experiments

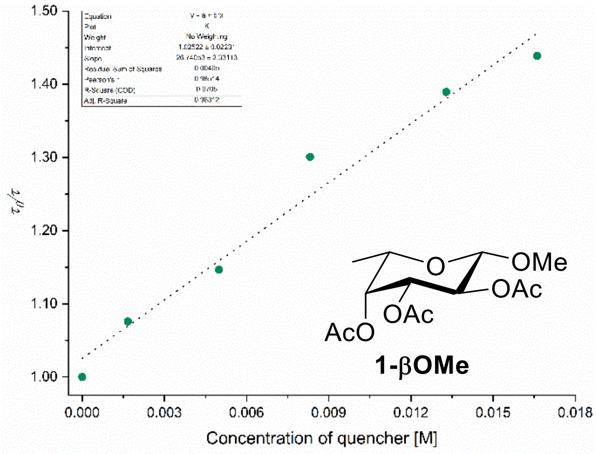
1-αOMe

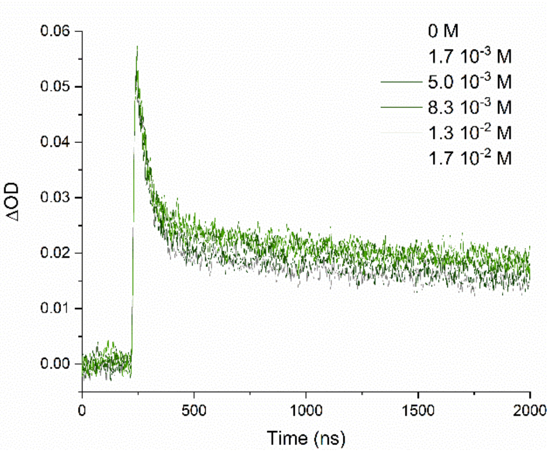




$t_0 = 63\times10^{-9}$ s $\quad$ $k_Q = 1.4\times10^{7}$ $M^{-1}\cdot s^{-1}$

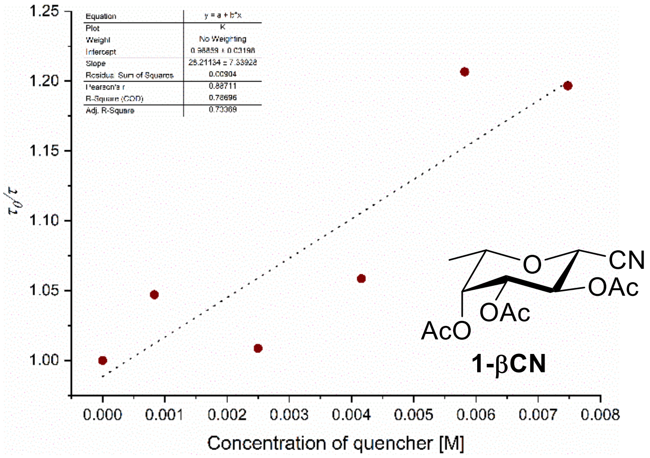
1-βOMe





$t_0 = 61\times10^{-9}$ s $\quad$ $k_Q = 4.4\times10^{8}$ $M^{-1}\cdot s^{-1}$

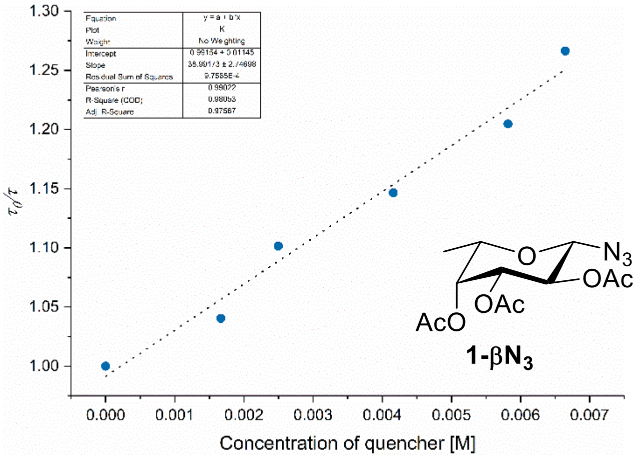
1-βCN



Equation	y = a + b*x
Plot	K
Weight	No Weighting
Intercept	0.98859 ± 0.03198
Slope	28.21134 ± 7.33928
Residual Sum of Squares	0.00904
Pearson's r	0.88711
R-Square (COD)	0.78696
Adj. R-Square	0.73369

$t_0 = 58\times10^{-9}$ s $k_Q = 4.9\times10^{8}\ M^{-1}\cdot s^{-1}$

1-βN₃



Equation	y = a + b*x
Plot	K
Weight	No Weighting
Intercept	0.99154 ± 0.01145
Slope	38.99173 ± 2.74698
Residual Sum of Squares	9.7555E-4
Pearson's r	0.99022
R-Square (COD)	0.98053
Adj. R-Square	0.97567

$t_0 = 62\times10^{-9}$ s $k_Q = 6.3\times10^{8}\ M^{-1}\cdot s^{-1}$

4. Experiments in deuterated media

General procedure

Method A (without olefin): In a sealed 2-5 mL-microwave glass vial equipped with a magnetic stir bar, **1-βCN** (40 mg, 0.1 mmol, 1 equiv.) and TBADT (5 mol%) were dissolved in CD_3CN or $CH_3CN:D_2O$ 95:5 (0.1 M) under Ar atmosphere. Deoxygenation was performed by 3 freeze-pump-thaw cycles under Ar atmosphere. The reaction was irradiated at *ca*. 5 cm distance with a 370 nm Kessil lamp at 100% light intensity. Two fans were used for dissipating heat from the lamp. The reaction mixture was stirred for 7h, then it was quenched by air and concentrated to dryness.

- *Experiment 1: $CH_3CN:D_2O$ medium*

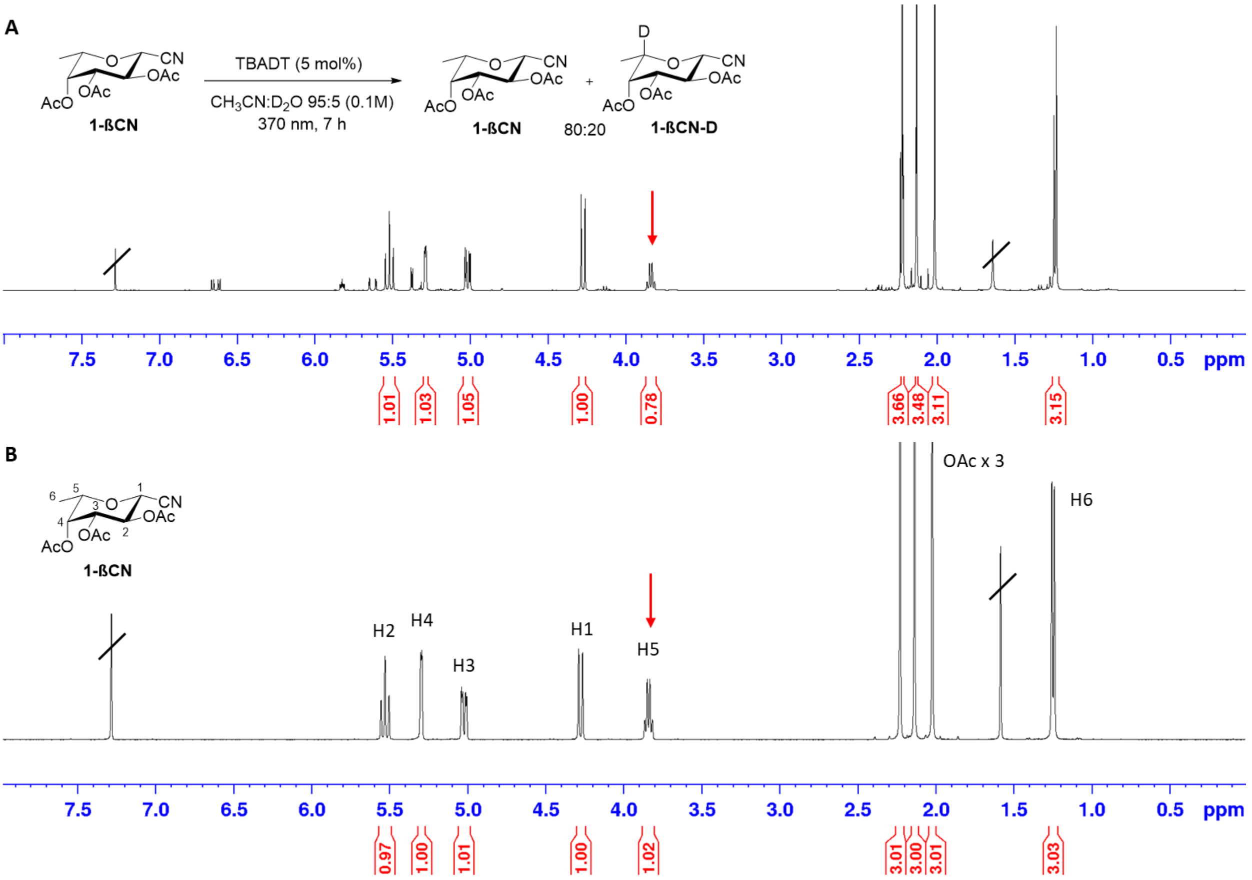


Figure S2. A) ^1H-NMR spectrum of the obtained product mixture, containing **1-βCN** and **1-βCN-D** (80:20). The presence and position of the deuterium can be confirmed by observing the signal corresponding to proton H5 at 3.82 ppm, which shows reduced integration relative to the anomeric proton (H1, 4.25 ppm). B) ^1H-NMR spectrum of the starting material **1-βCN**, taken as a reference.

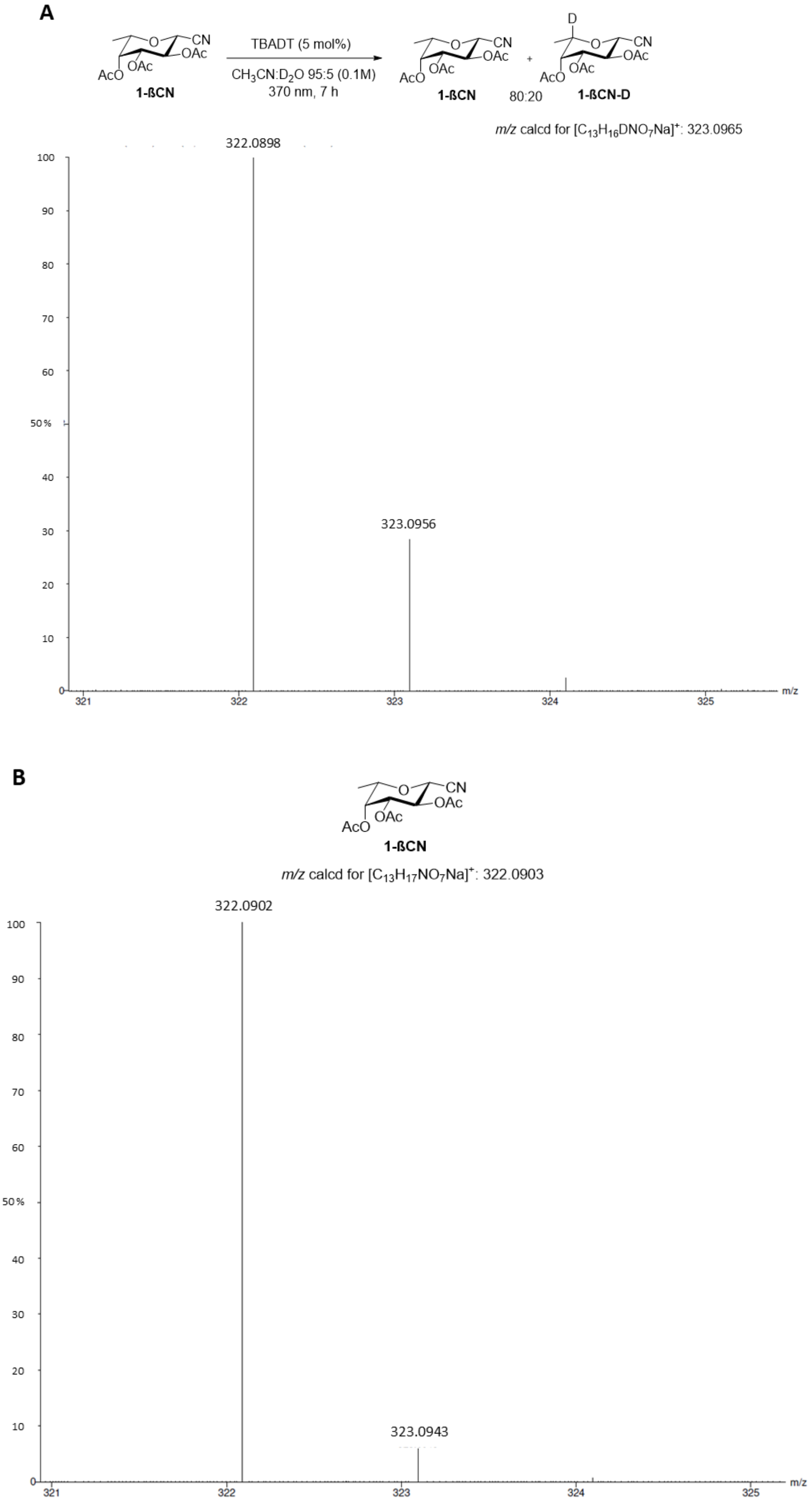


Figure S3. HRMS analysis of: A) the product mixture containing **1-βCN** and **1-βCN-D** and B) the starting material **1-βCN**, taken as a reference. An increase in intensity can be observed for the peak of the monodeuterated derivative (*m/z* 323.09) by comparing the two analyses.

- *Experiment 2: CD_3CN medium*

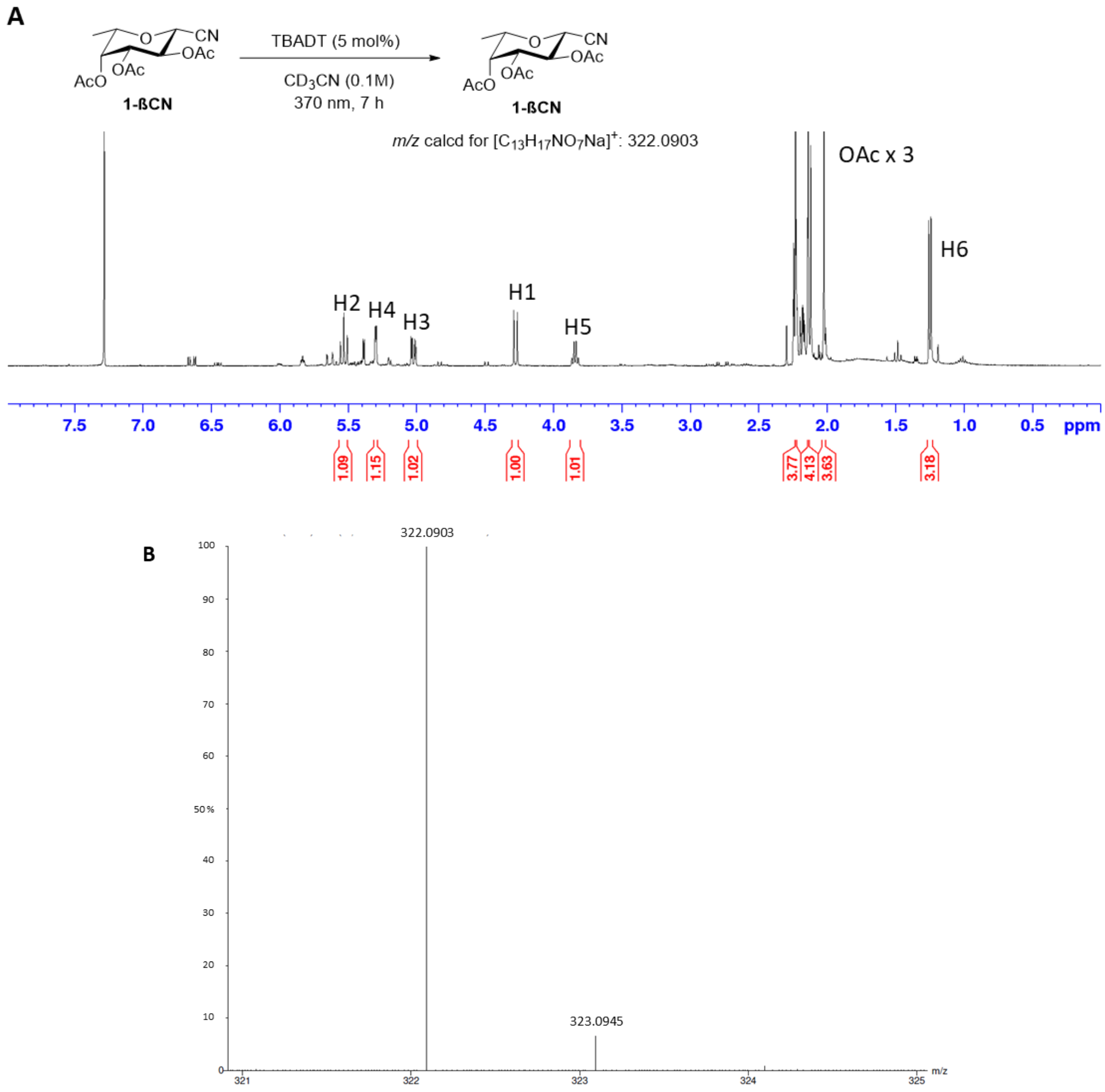


Figure S4. A) ^{1}H-NMR spectrum and B) HRMS analysis of the mixture after 6h irradiation: no deuteration observed compared to the starting material (Figures S2B and S3B)

Method B (with olefin): In a sealed 2-5 mL-microwave glass vial equipped with a magnetic stir bar, **1-βCN** (40 mg, 0.1 mmol, 1 equiv.), TBADT (5 mol%) and the olefin (**2a**, 13 µL, 0.14 mmol, 1.1 equiv.) were dissolved in CD_3CN or CH_3CN:D_2O 95:5 (0.1 M) under Ar atmosphere. Deoxygenation was performed by 3 freeze-pump-thaw cycles under Ar atmosphere. The reaction was irradiated at ca. 5 cm distance with a 370 nm Kessil lamp at 100% light intensity. Two fans were used for dissipating heat from the lamp. The reaction mixture was stirred for 7h, then it was quenched by air and concentrated to dryness.

- *Experiment 1: CH_3CN:D_2O medium*

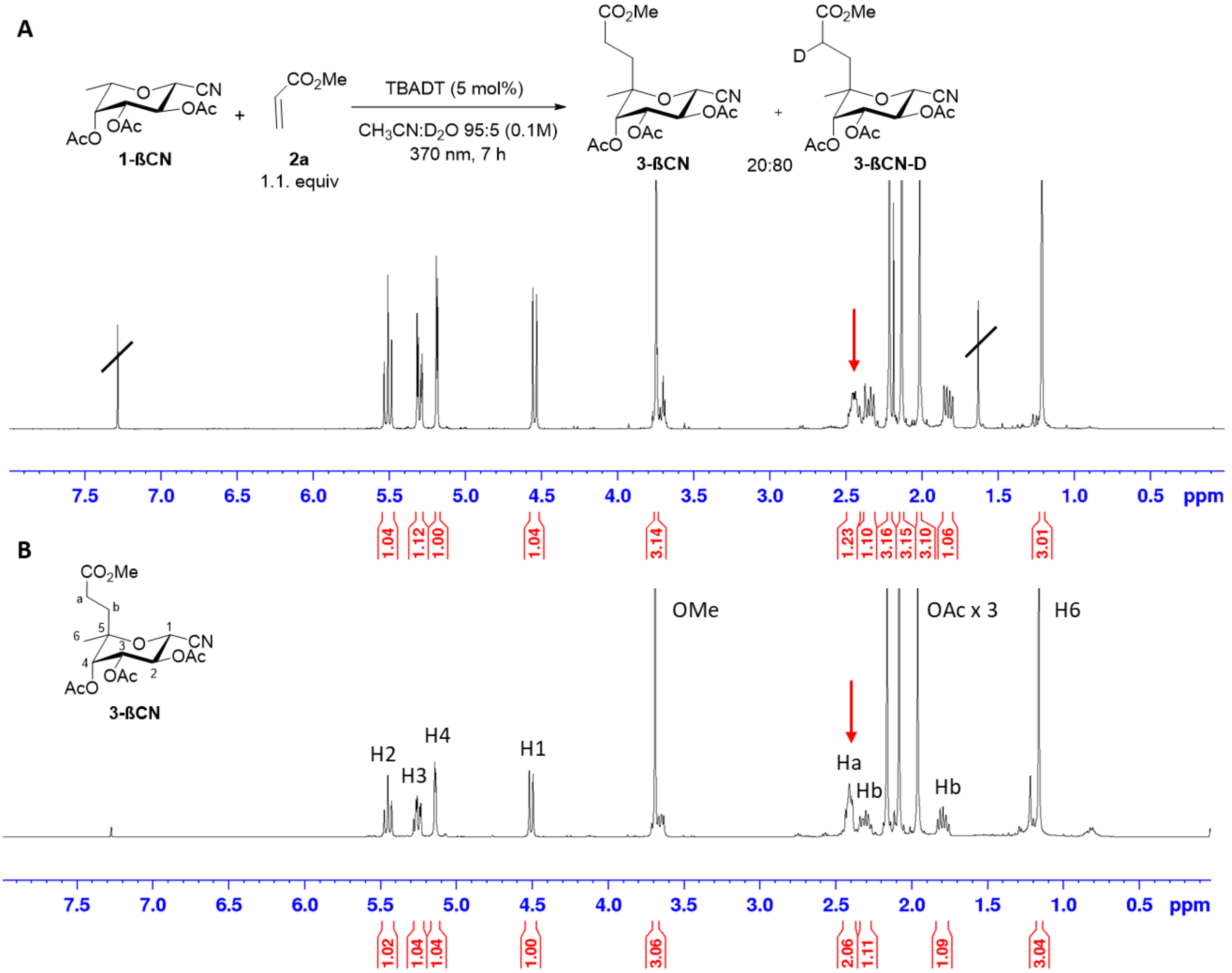


Figure S5. A) ^{1}H-NMR spectrum of the obtained product mixture, containing **3-βCN** and **3-βCN-D** (20:80). The presence and position of deuterium can be confirmed by observing the signal corresponding to protons Ha (2H, m, 2.46 – 2.34), which shows reduced integration, compared to the anomeric proton at 4.52 ppm. B) ^{1}H-NMR spectrum of the reference product **3-βCN**, taken as a reference.

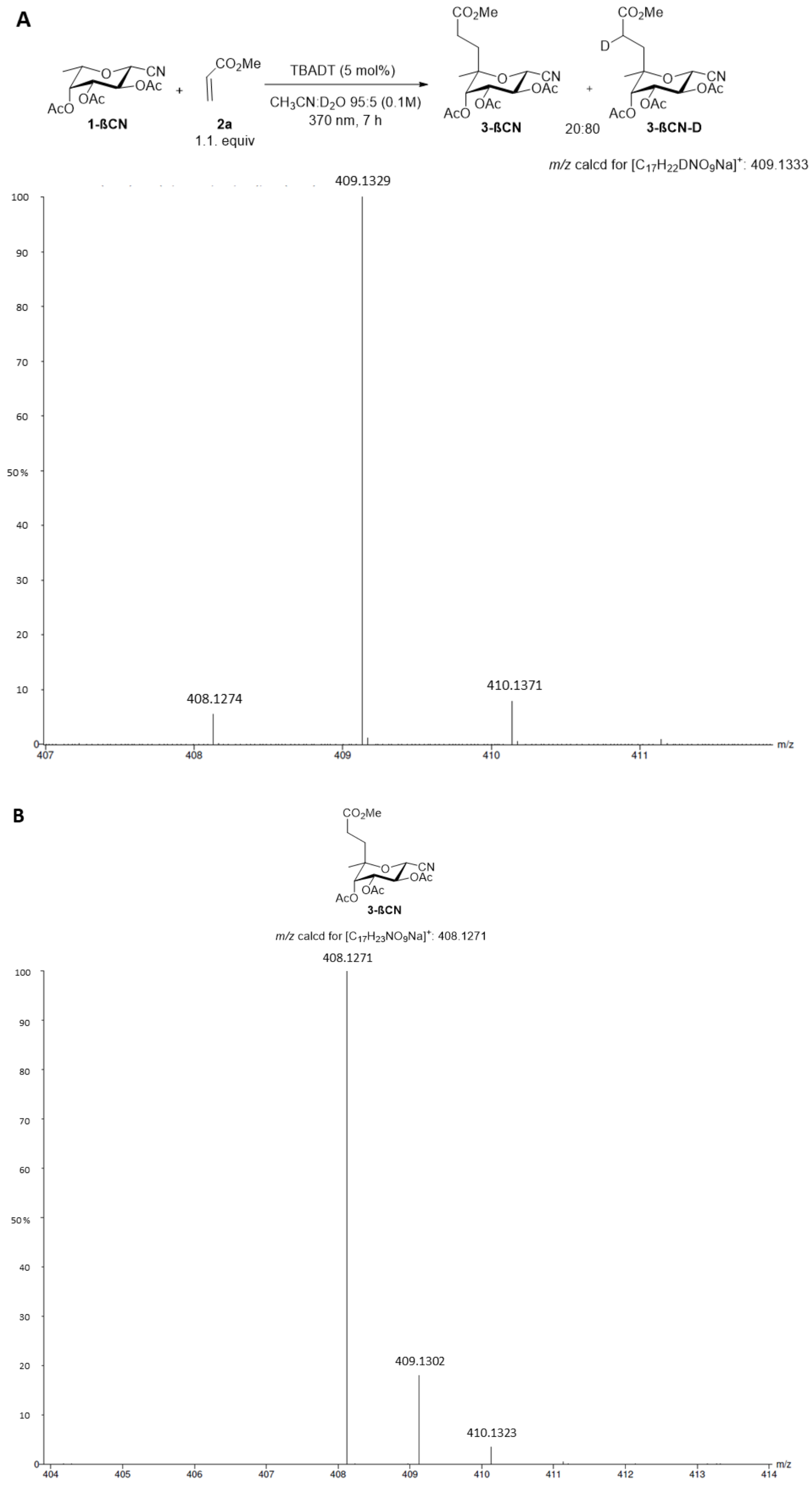
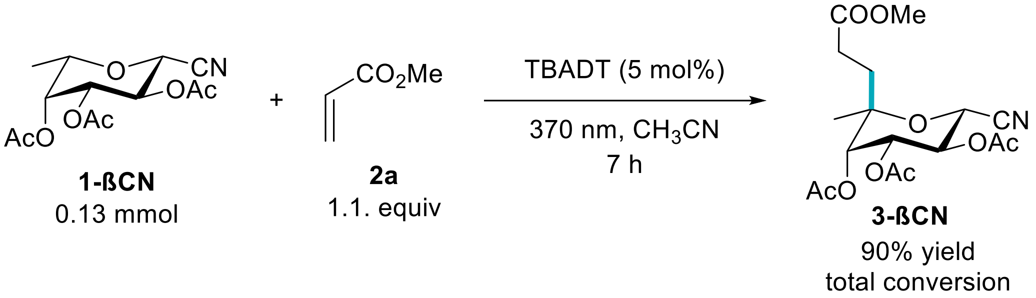


Figure S6. HRMS analysis of: A) the product mixture containing **3-βCN** and **3-βCN-D** and B) the reference product **3-βCN**, taken as a reference. From the spectrum A, it can be observed that the most intense peak corresponds to the deuterated product, in contrast to the spectrum of the reference product B.

5. Green metrics

The Process Mass Intensity (PMI), E-factor, Atom Economy (AE) and EcoScale were calculated for selected reactions herein reported: An Eco Scale of above 75 is considered an excellent green method, above 50 is acceptable, while scores below 50 indicate inadequate eco-friendliness. Eco Scale can be calculated as: Eco Scale = 100 - sum of the individual penalties.[8]

*Synthesis of **3-βCN***



$$AE = \frac{MM_{3\beta CN}}{MM_{1\beta CN} + MM_{2a}} \times 100 = \frac{385.37\ {}^{g}/_{mol}}{299.30\ {}^{g}/_{mol} + 86.09\ {}^{g}/_{mol}} \times 100 = 100\%$$

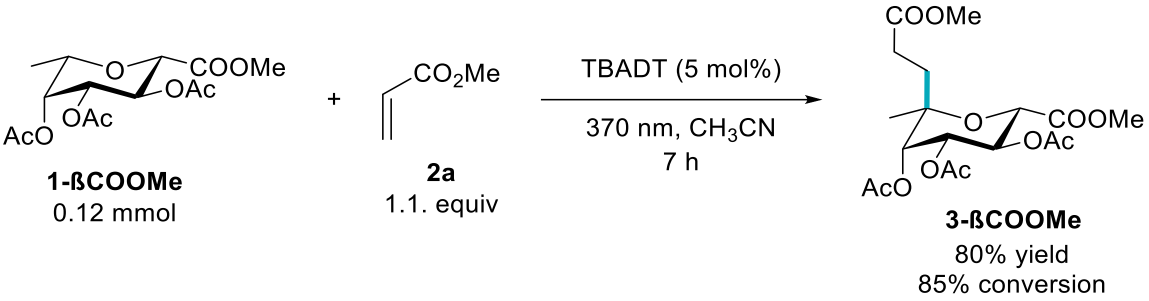
$$PMI = \frac{Mass_{1\mathrm{CN}} + Mass_{2a} + Mass_{TBADT} + Mass_{MeCN}}{Mass_{3\mathrm{CN}}} = \frac{40.0\ mg + 12.4\ mg + 21.6\ mg + 1021.8\ mg}{45.1\ mg} = \frac{1095.8\ mg}{45.1\ mg} = 24.3\ {}^{Kg}/_{Kg}$$

$$E_{factor} = PMI - 1\ = 23.3\,{}^{Kg}/_{Kg}$$

Entry	Parameter	Value	Penalty Points
1	Yield	(100-90)/2	5
2	Price of substrates	not commercially avaliable	5
3	Safety[a]	flammable, toxic	10
4	Technical Setup	Photochemical apparatus	2
5	Temperature/Time	r.t. ; < 24 h	1
6	Workup and purification	column chromatography	10
[a] Based on the hazard warning symbols		**Total Penalty Points**	**33**

$$EcoScale = 100 - Penalty\ Points\ = 67$$

Synthesis of ***3-βCO₂Me***



$$AE = \frac{MM_{3\beta COOMe}}{MM_{1\beta COOMe} + MM_{2a}} \times 100 = \frac{418.40\ ^{g}/_{mol}}{332.30\ ^{g}/_{mol} + 86.09\ ^{g}/_{mol}} \times 100 = 100\%$$

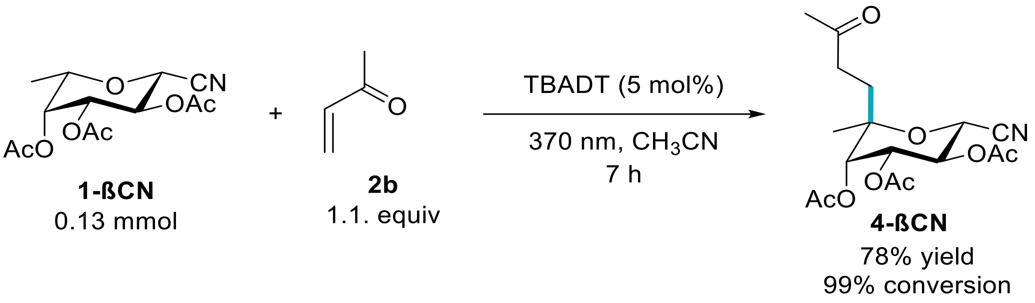
$$PMI = \frac{Mass_{1\beta COOMe} + Mass_{2a} + Mass_{TBADT} + Mass_{MeCN}}{Mass_{3\beta COOMe}} = \frac{40.0\ mg + 10.5\ mg + 20.0\ mg + 943.2\ \ mg}{29.8\ mg} = \frac{1013.7\ mg}{29.8\ mg} = 34.0\ ^{Kg}/_{Kg}$$

$$E_{factor} = PMI - 1\ = 34.0\ ^{Kg}/_{Kg}$$

Entry	Parameter	Value	Penalty Points
1	Yield	(100-68)/2	16
2	Price of substrates	not commercially avaliable	5
3	Safety[a]	flammable, toxic	10
4	Technical Setup	Photochemical apparatus	2
5	Temperature/Time	r.t. ; < 24 h	1
6	Workup and purification	column chromatography	10
[a] Based on the hazard warning symbols		**Total Penalty Points**	**44**

$$EcoScale = 100 - Penalty\ Points\ = 56$$

Synthesis of ***4-βCN***



1-ßCN
0.13 mmol

2b
1.1. equiv

4-ßCN
78% yield
99% conversion

$$AE = \frac{MM_{4\beta CN}}{MM_{1\beta CN} + MM_{2b}} \times 100 = \frac{369.37\ {}^{g}/_{mol}}{299.28\ {}^{g}/_{mol} + 70.09\ {}^{g}/_{mol}} \times 100 = 100\%$$

$$PMI = \frac{Mass_{1\beta CN} + Mass_{2b} + Mass_{TBADT} + Mass_{MeCN}}{Mass_{4\beta CN}} = \frac{40.0\ mg + 10.0\ mg + 21.6\ mg + 1021.8\ mg}{37.1\ mg} = \frac{1093.4\ mg}{37.1\ mg} = 29.5\ {}^{Kg}/_{Kg}$$

$$E_{factor} = PMI - 1\ = 28.5\,{}^{Kg}/_{Kg}$$

Entry	Parameter	Value	Penalty Points
1	Yield	(100-77)/2	11.5
2	Price of substrates	not commercially avaliable	5
3	Safety[a]	flammable, toxic	10
4	Technical Setup	Photochemical apparatus	2
5	Temperature/Time	r.t. ; < 24 h	1
6	Workup and purification	column chromatography	10
		Total Penalty Points	**39.5**

[a] Based on the hazard warning symbols

$$EcoScale = 100 - Penalty\ Points\ = 60.5$$

6. Computational Details

6.1. General Information

All the calculations were carried out using the Gaussian 16 program package, revision C.01,[9] installed on Galileo100 at CINECA facility (Italy) and on EOS facility at the University of Pavia (Italy). The level of theory chosen for the optimization of the reported stationary points was DFT (Density Functional Theory) by using the ωB97xD functional and the def2TZVP basis set in the gas phase. When appropriate, an unrestricted formalism (U prefix) has been adopted via the UωB97xD/def2TZVP keyword. No symmetry constraint was applied to the structures investigated and a thorough conformers search has been performed to locate the most stable species for each reacting situation. The structures and data used for this work correspond to those of the most stable located stationary point. Frequency calculations were performed in the gas phase to check that minima and transition states (TS) had 0 or 1 imaginary frequencies, respectively.

Solvent effect was included by single-point calculations at the same level of theory (ωB97xD/def2TZVP) adopting the standard implicit solvent model implemented in Gaussian 16 via the keyword SCRF=(SOLVENT=ACETONITRILE) on the optimized geometries obtained in vacuo.

The DFT Gibbs free energies reported in the main text have been calculated by means of Eq. S1 reported below:

$$G_{\mathrm{DFT}} = E_{0(\mathrm{DFT,MeCN})} + \Delta G_{\mathrm{CORR(vacuo)}} \qquad \text{(S1)}$$

where:

- $E_{0(\mathrm{DFT,MeCN})}$ is the total electronic energy calculated at the SCRF-wB97xD/def2TZVP level (acetonitrile bulk);

- $\Delta G_{\mathrm{CORR(vacuo)}}$ is the unscaled thermal correction to Gibbs Free Energy as from the output of the frequency calculation in vacuo, also including the zero-point vibrational energy (ZPVE).

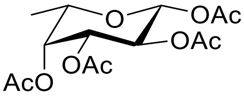
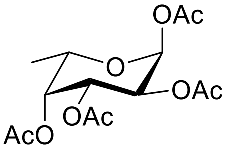
The two terms from Eq. S1 have been reported in blue color for all the stationary points reported below.

As for TSs, Intrinsic Reaction Coordinate (IRC) calculations were performed in both directions (30 steps each) at the same level of theory adopted for optimizations (ωB97xD/def2TZVP in the gas phase) in order to investigate the process in detail and to confirm the nature of the TS itself. The "LQA" option for the IRC keyword has been consistently specified, in order to adopt the local quadratic approximation for the predictor step.

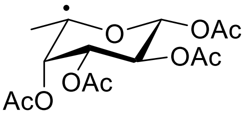
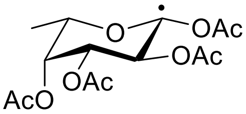
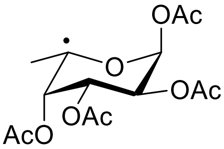
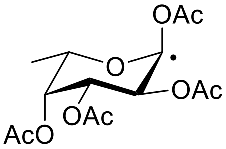
Optimized geometry listed in cartesian format (coordinates are given in Å), minimum energies and thermochemical data (in Hartree; the default options were adopted in the latter case, *viz.* temperature: 298.150 K and pressure: 1.00000 atm) are reported below.

The conversion factor adopted between Hartree and kcal mol^{-1} is: 1 Hartree = 627.509 kcal·mol^{-1}.

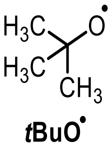
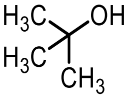
FUCOSE derivatives

SPECIES	G_{DFT} [Hartree]	SPECIES	G_{DFT} [Hartree]
 **1-βOAc**	-1222.460157	 **1-αOAc**	-1222.459555

RADICAL Intermediates

SPECIES	G_{DFT} [Hartree]	SPECIES	G_{DFT} [Hartree]
 **1-βOAc**$^{C5\bullet}$	-1221.812598	 **1-βOAc**$^{C1\bullet}$	-1221.809048
 **1-αOAc**$^{C5\bullet}$	-1221.812818	 **1-αOAc**$^{C1\bullet}$	-1221.804022

OTHERS Species

SPECIES	G_{DFT} [Hartree]	SPECIES	G_{DFT} [Hartree]
 ***t*BuO**$^{\bullet}$	-232.932223	 ***t*BuOH**	-233.595761

TRANSITION States

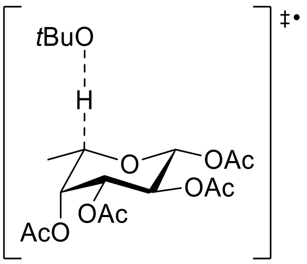
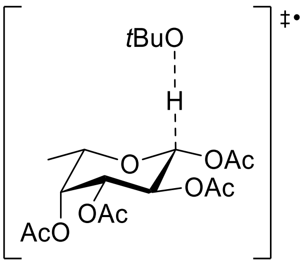
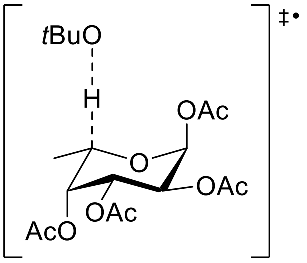
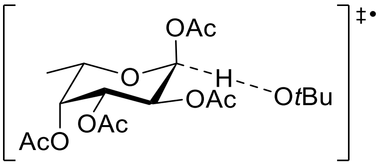
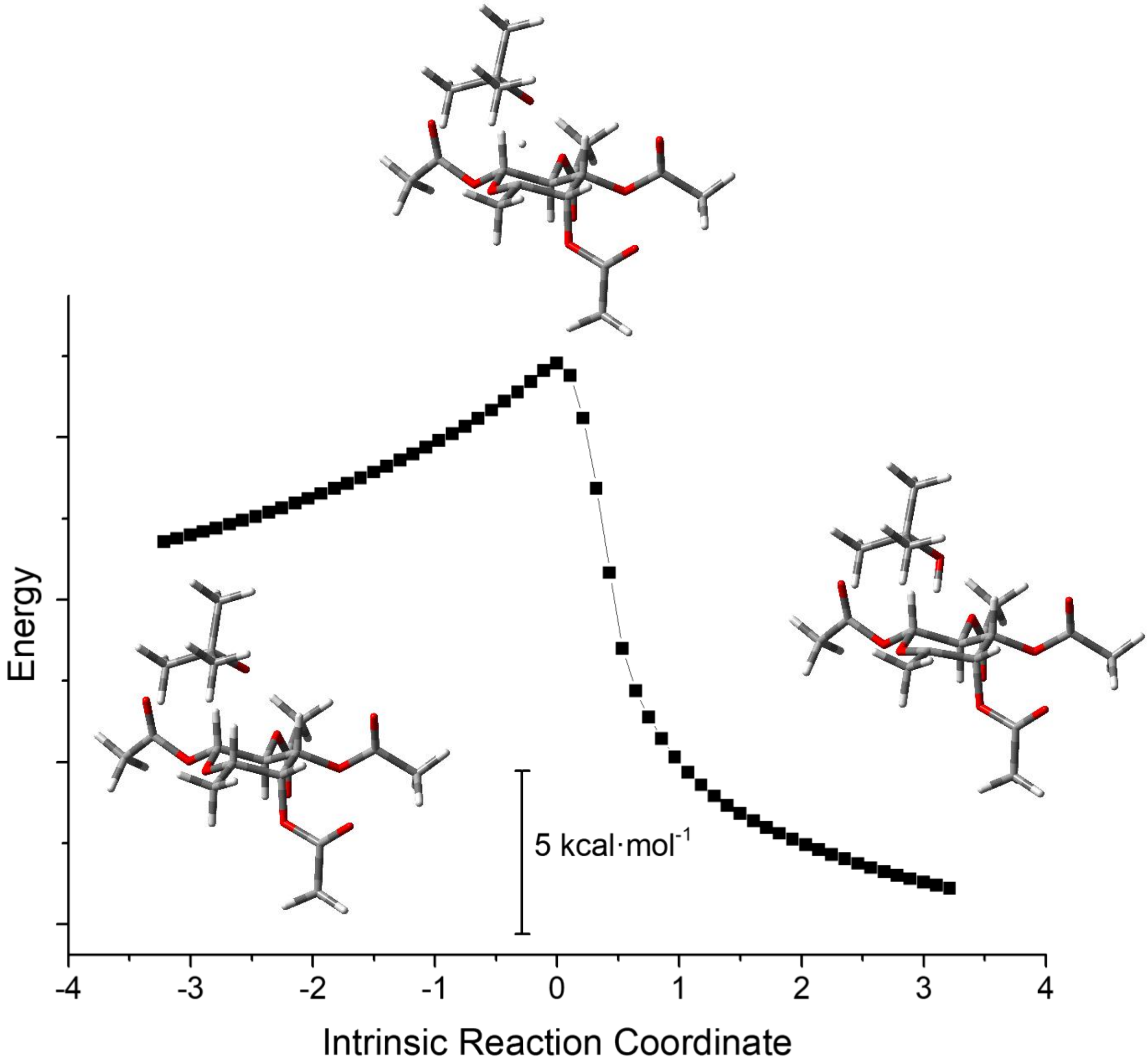
SPECIES	G_{DFT} [Hartree]	SPECIES	G_{DFT} [Hartree]
 **TS(1-βOAc^{C5})**	-1455.371821	 **TS(1-βOAc^{C1})**	-1455.361081
 **TS(1-αOAc^{C5})**	-1455.369776	 **TS(1-αOAc^{C1})**	-1455.363971

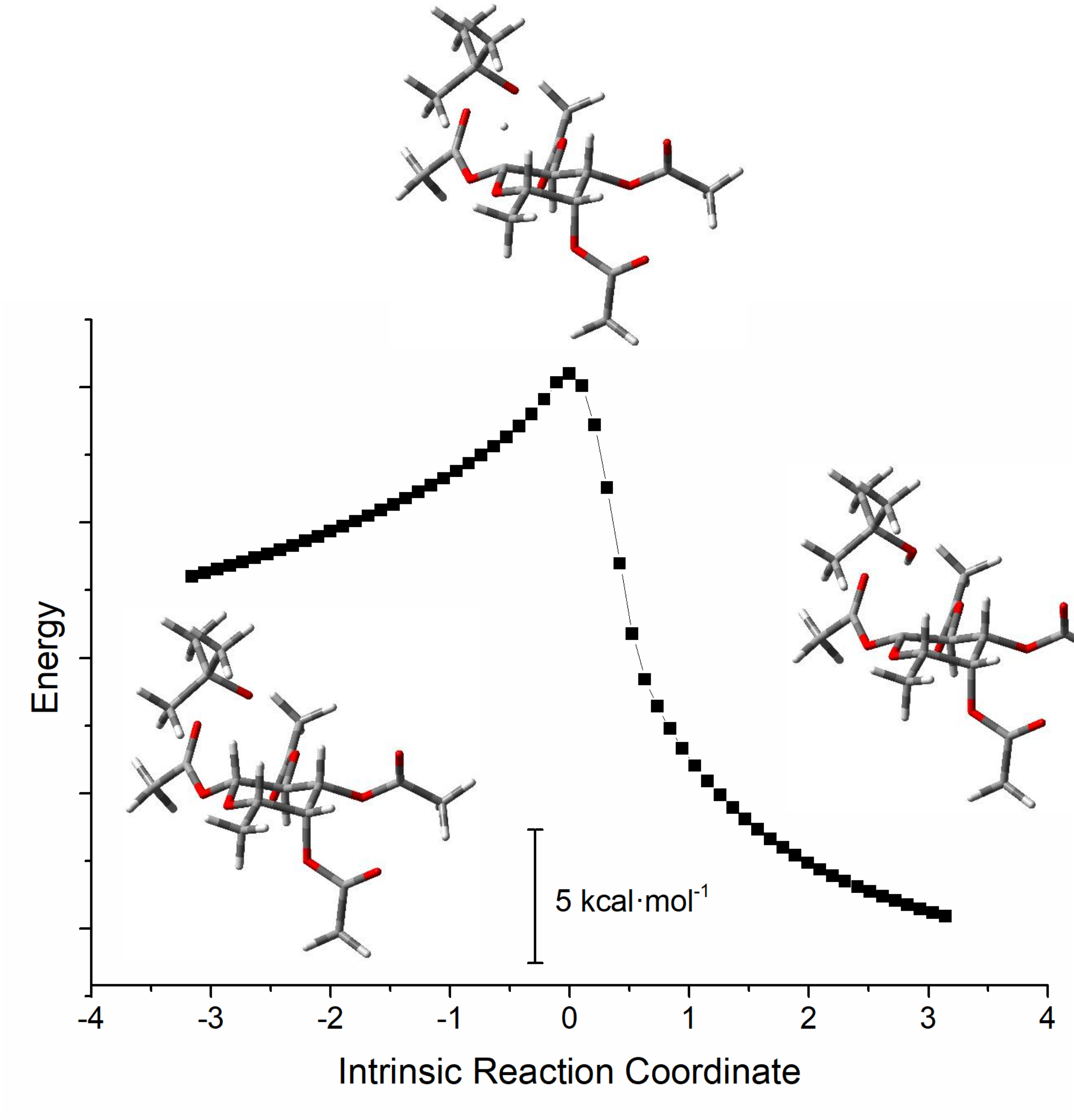
Table S3. Gibbs free energies (shown in Hartree) of the species optimized to model the hydrogen abstraction processes adopted in our computational study (see Figure 6 in the main text), as determined from ωB97xD/def2TZVP calculations in bulk acetonitrile.

6.2. IRC plots for located transition states (TS)

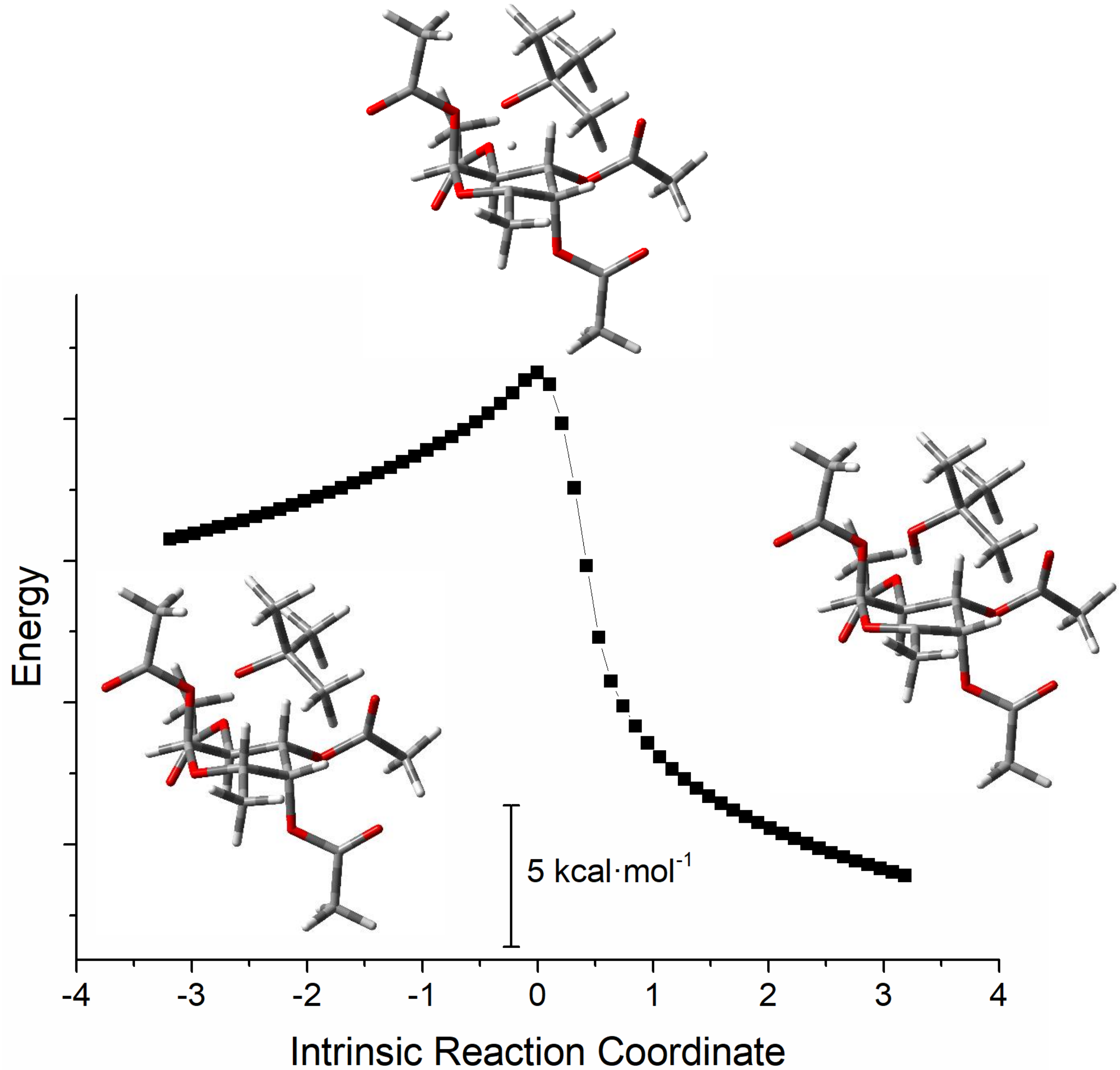
TS(1-βOAc^{C5})



TS(1-βOAc^{C1})


Energy
5 kcal·mol-1
-4
-3
-2
-1
0
1
2
3
4
Intrinsic Reaction Coordinate

TS(1-αOAc^{C5})


Energy
5 kcal·mol-1
-4
-3
-2
-1
0
1
2
3
4
Intrinsic Reaction Coordinate

TS(1-αOAc^{C1})

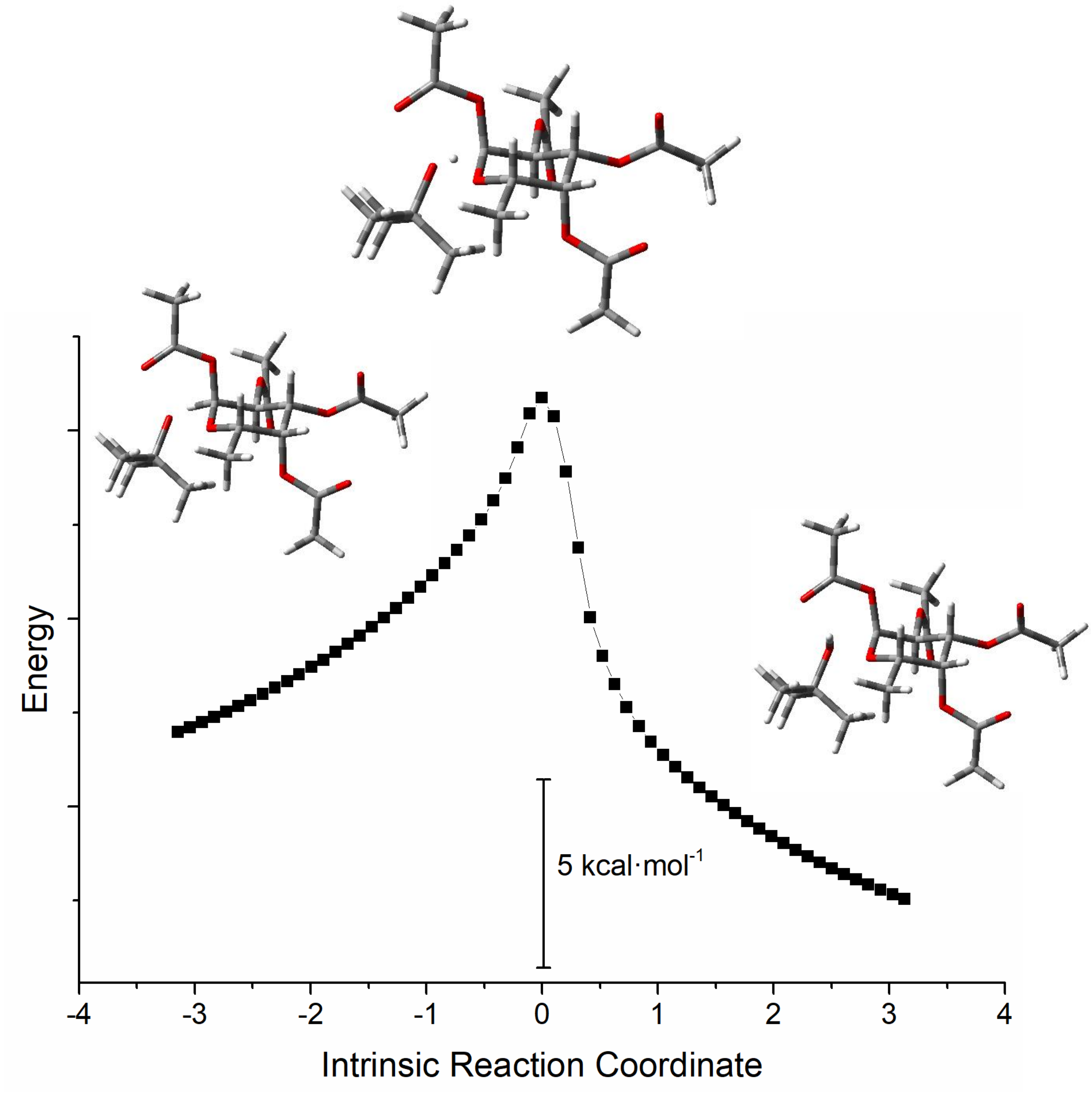
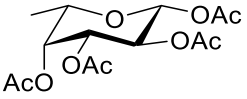


Figure S7. Intrinsic Reaction Coordinate (IRC) profile associated with transition states: **TS(1-bOAc^{C5})**, **TS(1-bOAc^{C1})**, **TS(1-aOAc^{C5})** and **TS(1-aOAc^{C1})** at the ωB97xD/def2TZVP level of theory. The three structures reported in the graph refer, respectively, to those of the first point (left), the transition state (center) and the last point (right) along the reaction coordinate.

6.3. Optimized Structures



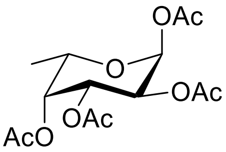
1-βOAc

C	1.61625300	-0.54855300	-0.40321200
O	1.14250900	-1.84242500	-0.19120500
C	0.58038800	0.48525300	0.02452200
C	-0.70799400	0.23331200	-0.73576700
O	1.06868500	1.77228100	-0.32217900
C	-1.15827500	-1.21586800	-0.57712900
O	0.91321800	2.50037200	1.80326600
C	-0.01150800	-2.14954000	-0.95409500
O	-1.69018800	1.12762200	-0.23832200
C	-0.33191300	-3.61016300	-0.73661400
O	-2.70900900	1.13979600	-2.23884600
O	-1.50766300	-1.45528800	0.78475000
C	1.18848400	2.69683600	0.65536100
O	-3.69373100	-1.13600700	0.36757100
C	1.70718600	3.98500700	0.08772600
C	-2.68710900	1.46810200	-1.08676500
C	-3.73671000	2.26713000	-0.38065200
C	-2.80098300	-1.35556300	1.13894100
C	-2.95575800	-1.54636300	2.61794500
O	2.74512300	-0.38235900	0.40734700
C	3.94445300	-0.74405200	-0.11423400
H	1.89274800	-0.40612200	-1.45550600
H	0.42037200	0.42117500	1.09991200
H	-0.54975500	0.42774700	-1.79918400
H	-2.02358700	-1.39911700	-1.21440300
H	0.20189700	-1.97511100	-2.01908800
H	-1.21742100	-3.89056300	-1.30828800
H	0.50565400	-4.22494700	-1.06282400
H	-0.51747700	-3.80238400	0.31933300
H	2.66182700	3.81266100	-0.40963600
H	1.01018300	4.36095600	-0.66186600
H	1.82480900	4.71249400	0.88538800
H	-3.29049700	2.95738800	0.33307800
H	-4.34365900	2.79724300	-1.10930900
H	-4.36719100	1.56558800	0.16948300
H	-2.51810700	-0.68783800	3.13004400
H	-4.00989000	-1.62373600	2.86778900
H	-2.41736300	-2.43471400	2.94591200
C	5.02513700	-0.58290500	0.91095700
H	5.99215300	-0.76925100	0.45321600
H	4.99024400	0.41852700	1.33927700
H	4.85541400	-1.29228100	1.72202200
O	4.08977400	-1.13192900	-1.23578700

Zero-point correction= 0.345195
Thermal correction to Energy= 0.370217

Thermal correction to Enthalpy= 0.371161
Thermal correction to Gibbs Free Energy= 0.286831

E(UwB97XD, MeCN) -1222.746988



1-αOAc

O	-0.49181700	-2.18887800	-0.63440900
O	-2.09974000	-1.21839100	0.66380300
O	-1.48435500	1.28755100	-0.29075100
O	-1.85602200	1.51122300	-2.49460600
O	1.23316800	1.41227400	0.43123000
O	1.66478100	1.36576600	2.63369100
O	2.08788100	-0.91651300	-0.82134400
O	3.91191700	-0.11282200	0.21887600
C	-1.34064700	-1.10791700	-0.54791100
H	-2.01869400	-1.14858100	-1.39743500
C	-0.58005700	0.22432700	-0.53826300
H	-0.11491900	0.35122700	-1.51526900
C	0.46769400	0.22254400	0.55146100
H	-0.00700900	0.19274000	1.53292900
C	1.36212600	-1.00567700	0.40498600
H	2.06263700	-1.04615400	1.23917500
C	0.51079000	-2.26835100	0.37749000
H	0.02306500	-2.34230800	1.35574800
C	1.31100500	-3.52251100	0.11336300
H	0.65876200	-4.39382800	0.15273100
H	2.09166000	-3.63512500	0.86679900
H	1.77414500	-3.47708700	-0.87144900
C	-3.40618800	-0.89726000	0.63956300
C	-2.10520100	1.82517600	-1.36606700
C	-3.13813000	2.82058000	-0.93910600
H	-2.77953600	3.42419400	-0.10710000
H	-4.01544600	2.26277400	-0.60554900
H	-3.41135900	3.44679300	-1.78370200
C	1.83515900	1.86007100	1.55520300
C	2.74144100	3.01178900	1.25216900
H	2.29584000	3.67772900	0.51526200
H	3.66310100	2.60315600	0.83282400
H	2.97172800	3.54594400	2.16971200
C	3.34170800	-0.43185900	-0.78763700
C	3.90782200	-0.34437100	-2.17339900
H	4.96346100	-0.09445600	-2.12121400
H	3.37292900	0.43017500	-2.72527500
H	3.76261100	-1.28502300	-2.70335300
C	-4.02059300	-1.08430500	1.99493300
H	-3.55791300	-0.39007000	2.69778300
H	-5.08875000	-0.89609100	1.93928400
H	-3.83195000	-2.09491600	2.35641500

```
O                  -3.98280700   -0.50827200   -0.33762000

Zero-point correction=                          0.345641
Thermal correction to Energy=                   0.370433
Thermal correction to Enthalpy=                 0.371377
Thermal correction to Gibbs Free Energy=        0.288687

E(UwB97XD, MeCN)                            -1222.748242
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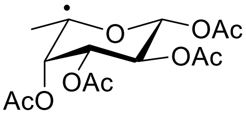

1-βOAc$^{C5\bullet}$

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O                   0.94696300    2.52746800   -0.30929400
O                   2.03971700   -0.11802300    0.62637300
O                   3.21446000   -1.87554800   -0.14411900
O                  -0.03079400   -1.50489100   -0.31294600
O                  -1.61276400   -1.99702100   -1.83093300
O                  -2.12040500    0.61106700   -0.18077400
O                  -2.36078700   -0.75896900    1.58431300
C                   1.78700200    1.65364800   -0.94314500
C                   1.56870100    0.20263100   -0.70360500
C                   0.09488900   -0.17485400   -0.78273500
C                  -0.73638100    0.77753200    0.06654100
C                  -0.42591700    2.21755100   -0.37084600
C                   3.15398600    2.19465200   -1.12499000
C                   2.81389400   -1.21309200    0.77101200
C                   3.08702600   -1.47188000    2.22248100
C                  -0.92500300   -2.32352200   -0.90448600
C                  -0.93574200   -3.65588600   -0.22267700
C                  -2.83481000   -0.19287300    0.64179800
C                  -4.25488500   -0.27596300    0.17873100
H                   2.13903200   -0.39003500   -1.41709400
H                  -0.24368400   -0.11681200   -1.81971700
H                  -0.51365800    0.63244600    1.12393400
H                  -0.78934000    2.34461900   -1.39836000
H                   3.75023200    1.51724300   -1.73585300
H                   3.12190000    3.17301200   -1.60574900
H                   3.66289200    2.31563100   -0.16049400
H                   2.15763500   -1.77818500    2.70519500
H                   3.82886200   -2.25920100    2.31983300
H                   3.42832600   -0.56107200    2.71314500
H                  -1.34139200   -3.52458300    0.78195900
H                  -1.55448700   -4.34931000   -0.78457900
H                   0.08021600   -4.03769000   -0.12687000
H                  -4.27494900   -0.79072000   -0.78329200
H                  -4.84332600   -0.82585800    0.90713800
H                  -4.66340900    0.72336900    0.03272200
C                  -1.13986600    3.17756000    0.47706900
N                  -1.72476300    3.90877800    1.13660700

Zero-point correction=                          0.331367
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Thermal correction to Energy=                    0.356736
Thermal correction to Enthalpy=                  0.357680
Thermal correction to Gibbs Free Energy=         0.271530

E(UwB97XD, MeCN)                             -1222.084128
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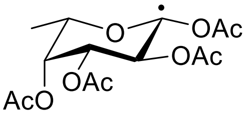
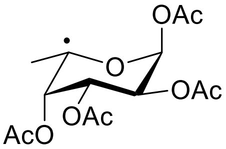


1-βOAc$^{C1\bullet}$

C	1.55684700	-0.58443400	-0.21299400
O	1.11869900	-1.85950700	-0.17495000
C	0.56571000	0.50517800	0.08437800
C	-0.69976000	0.26871100	-0.71855000
O	1.12142400	1.75462400	-0.30275600
C	-1.17264200	-1.17271400	-0.56628800
O	1.12453500	2.50440500	1.82143200
C	-0.04925600	-2.12544900	-0.95268200
O	-1.68359400	1.17698100	-0.24927700
C	-0.39793700	-3.58165800	-0.75737000
O	-2.68711500	1.13820900	-2.25665800
O	-1.52473400	-1.41371400	0.79532400
C	1.35158400	2.67391400	0.65789300
O	-3.70703000	-1.07344000	0.37631300
C	1.92492300	3.92109800	0.05239000
C	-2.67146700	1.50039300	-1.11472500
C	-3.72079400	2.32704900	-0.44055300
C	-2.81868000	-1.30334700	1.14890500
C	-2.97709300	-1.49833600	2.62679000
O	2.74444700	-0.43391200	0.44707700
C	3.88166800	-0.85192900	-0.18787200
H	0.33499800	0.53451800	1.15404700
H	-0.50204200	0.45715400	-1.77504200
H	-2.03968400	-1.34037000	-1.20526000
H	-1.27435600	-3.83737200	-1.35389100
H	0.43519100	-4.20736100	-1.07398400
H	-0.61238200	-3.78534000	0.29101100
H	2.84369100	3.68202000	-0.48348000
H	1.22160400	4.33326900	-0.67170900
H	2.12384400	4.64718100	0.83508900
H	-3.27464900	3.04054800	0.25000800
H	-4.32269100	2.83381900	-1.18967800
H	-4.35635100	1.64800600	0.13148700
H	-2.52970400	-0.64771200	3.14360300
H	-4.03236400	-1.56389300	2.87505800
H	-2.45032400	-2.39489000	2.95137800
C	5.06353300	-0.68074600	0.71662300
H	5.97366300	-0.91213900	0.17123700
H	5.09688400	0.33807300	1.10218700
H	4.96269700	-1.35135200	1.57102500
O	3.89233200	-1.28440100	-1.29826600
H	0.19043200	-1.93449400	-2.00466700

Zero-point correction= 0.331725
Thermal correction to Energy= 0.356897
Thermal correction to Enthalpy= 0.357842
Thermal correction to Gibbs Free Energy= **0.272210**

E(UwB97XD, MeCN) **-1222.081258**



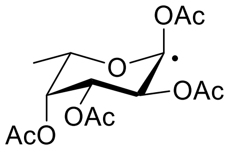
1-αOAc$^{C5•}$

O	0.56540200	2.21562700	-0.67838800
O	2.09323400	1.20539400	0.66377100
O	1.45663000	-1.29253200	-0.30687200
O	1.88355800	-1.48943000	-2.50262600
O	-1.24807000	-1.35153300	0.43842300
O	-1.60490000	-1.28493600	2.65504200
O	-2.14374300	0.87357400	-0.88278800
O	-3.91744300	0.17732100	0.31077200
C	1.37841200	1.09504000	-0.56384300
H	2.07858900	1.11530100	-1.39534900
C	0.57878000	-0.21113700	-0.56501300
H	0.11646400	-0.33026900	-1.54482700
C	-0.47083200	-0.16842100	0.52048200
H	-0.00113200	-0.10553200	1.50180000
C	-1.34795900	1.06525000	0.32086600
H	-2.02789300	1.17522200	1.16411700
C	-0.53147400	2.29085900	0.14130000
C	-1.14344200	3.63799200	0.17213700
H	-0.39122200	4.39743300	0.39023800
H	-1.92268200	3.68279200	0.93276300
H	-1.59925700	3.89201100	-0.79360900
C	3.39837000	0.86860000	0.68098500
C	2.09467600	-1.82856400	-1.37369900
C	3.09103700	-2.85514100	-0.93502000
H	2.69359500	-3.46496400	-0.12552500
H	3.97067100	-2.32479800	-0.56483800
H	3.37507100	-3.47212800	-1.78280100
C	-1.81417600	-1.78628800	1.58756500
C	-2.73555800	-2.93594200	1.32419700
H	-2.32034300	-3.60760600	0.57484300
H	-3.67092100	-2.52579600	0.93806800
H	-2.93348900	-3.46432900	2.25258200
C	-3.39532500	0.40766600	-0.74599000
C	-4.03611900	0.21157000	-2.08881700
H	-5.09017700	-0.01708200	-1.96003900
H	-3.54012600	-0.61562100	-2.59910600
H	-3.90975900	1.10130300	-2.70445400
C	3.97047100	1.05863100	2.05324500
H	3.47781900	0.37390700	2.74494300

H	5.03790400	0.85968900	2.03302700
H	3.77856300	2.07305200	2.40186300
O	3.99747500	0.46610600	-0.27659100

Zero-point correction= 0.331530
Thermal correction to Energy= 0.356759
Thermal correction to Enthalpy= 0.357703
Thermal correction to Gibbs Free Energy= **0.272432**

E(UwB97XD, MeCN) **-1222.085250**



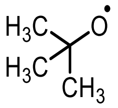
1-αOAc$^{C1\bullet}$

O	1.24337900	-1.81054300	0.56951600
O	2.62018300	-0.32286600	-0.52388200
O	1.10899600	1.78444500	0.25104900
O	0.09651800	2.60123100	2.09011900
O	-1.52865400	1.05776300	-0.49707700
O	-1.95915700	0.82747900	-2.68812000
O	-1.61214200	-1.40196800	0.80289400
O	-3.60902800	-1.19773700	-0.20903100
C	1.66193800	-0.54023400	0.44781900
C	0.57527500	0.49464900	0.47935300
H	0.08546000	0.46082400	1.45291800
C	-0.44024800	0.15626200	-0.60933000
H	0.02187400	0.26137100	-1.59271800
C	-0.91437700	-1.28647400	-0.43558800
H	-1.58245100	-1.54922700	-1.25664600
C	0.27617900	-2.23572700	-0.41602400
H	0.74986500	-2.17839000	-1.40296400
C	-0.08912800	-3.66480700	-0.09946800
H	0.80014600	-4.29222600	-0.13693900
H	-0.81223900	-4.03601900	-0.82699200
H	-0.52325600	-3.73241800	0.89691900
C	3.91275600	-0.65900400	-0.23600300
C	0.78412300	2.76383900	1.12416900
C	1.41056800	4.05995700	0.70341100
H	1.06311200	4.32867100	-0.29451300
H	2.49374600	3.94608000	0.65551400
H	1.14760300	4.83804100	1.41383200
C	-2.25555400	1.27528000	-1.61688000
C	-3.46107100	2.10826800	-1.31471500
H	-3.22963800	2.88342700	-0.58633800
H	-4.21543400	1.44740400	-0.88277000
H	-3.84748300	2.53872300	-2.23436500
C	-2.95443500	-1.30252800	0.79097800
C	-3.49440000	-1.33018100	2.18866300
H	-4.57612100	-1.42334900	2.16064600
H	-3.21805900	-0.39974400	2.68772500

H	-3.05227900	-2.15024300	2.75300600
C	4.78090700	-0.44035800	-1.43822100
H	4.66544500	0.58149700	-1.79949300
H	5.81674400	-0.63511800	-1.17667200
H	4.46894900	-1.11014400	-2.24062700
O	4.26350600	-1.05940700	0.82971900

Zero-point correction= 0.331258
Thermal correction to Energy= 0.356484
Thermal correction to Enthalpy= 0.357428
Thermal correction to Gibbs Free Energy= **0.271379**

E(UwB97XD, MeCN) **-1222.075401**

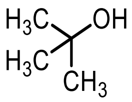


***t*BuO$^\bullet$**

C	0.00013500	-0.02519500	0.08411900
C	1.27145700	-0.78386400	-0.30948200
H	2.15536800	-0.21230500	-0.02597500
H	1.30487000	-1.74745100	0.20109300
H	1.29646800	-0.96591600	-1.38552300
C	-1.26422300	-0.79531600	-0.30954000
H	-1.28888900	-1.75943600	0.20054100
H	-2.15326100	-0.23195000	-0.02556300
H	-1.28781700	-0.97705000	-1.38565000
C	-0.00625800	1.37544600	-0.58197100
H	-0.89737900	1.93163900	-0.29437800
H	0.87943100	1.94001100	-0.29389800
H	-0.00524500	1.23357100	-1.66361800
O	-0.00127600	0.27030700	1.42177600

Zero-point correction= 0.122952
Thermal correction to Energy= 0.129414
Thermal correction to Enthalpy= 0.130359
Thermal correction to Gibbs Free Energy= **0.093462**

E(UwB97XD, MeCN) **-233.025685**



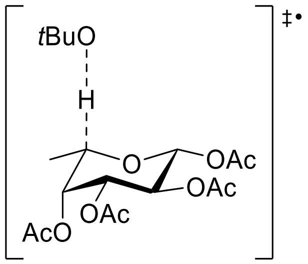
***t*BuOH**

C	-0.00618500	-0.00007600	0.01827100
C	0.67893600	-1.25505300	-0.51783700
H	1.73644300	-1.26609500	-0.23962600

H	0.20607300	-2.14723800	-0.10530300
H	0.62024300	-1.30070200	-1.60703600
C	-1.48573100	-0.00169200	-0.33477000
H	-1.97081500	-0.88652600	0.07924100
H	-1.97264300	0.88203000	0.07941000
H	-1.62318600	-0.00182200	-1.41716500
C	0.67601900	1.25655900	-0.51801300
H	0.20094300	2.14758100	-0.10557500
H	1.73348600	1.27006100	-0.23976400
H	0.61727400	1.30181100	-1.60722400
O	0.03939100	0.00011100	1.44483700
H	0.95882300	0.00158500	1.71843600

Zero-point correction= 0.136405
Thermal correction to Energy= 0.143061
Thermal correction to Enthalpy= 0.144006
Thermal correction to Gibbs Free Energy= **0.107490**

E(wB97XD, MeCN) **-233.703251**



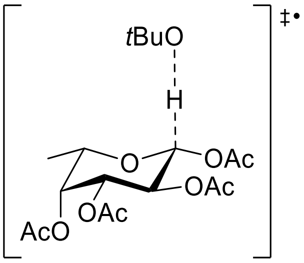
TS(1-βOAc^{C5})

C	0.96340700	1.01490100	0.46453200
O	1.07659500	0.02023900	1.45169400
C	-0.47572300	1.16264400	-0.01324900
C	-0.99117400	-0.17680200	-0.50063100
O	-0.47473900	2.07735100	-1.09825900
C	-0.81292500	-1.23463700	0.58279400
O	-1.89378700	3.47154200	-0.04205100
C	0.62464600	-1.23976900	1.07990800
O	-2.36480200	-0.01406000	-0.81812100
C	0.91120900	-2.22149800	2.18074600
O	-2.22306900	-1.62942000	-2.37271100
O	-1.65749400	-0.92151600	1.69480600
C	-1.23000900	3.19231600	-0.99816100
O	-3.24288600	-2.35782200	1.00177400
C	-1.11210100	4.00914400	-2.25089900
C	-2.88229900	-0.84881900	-1.74973900
C	-4.36505100	-0.66918200	-1.85436700
C	-2.86009700	-1.52090300	1.77092600
C	-3.63906000	-0.98554300	2.93499900
O	1.33152800	2.21870200	1.07529200
C	2.60993600	2.64665800	0.93080500
H	1.63173900	0.78620700	-0.36974600
H	-1.09450900	1.54642900	0.79727100

H	-0.43701900	-0.49613500	-1.38504400
H	-1.07422800	-2.21457600	0.18524900
H	0.60672800	-3.22324300	1.87821900
H	1.97499800	-2.22947300	2.41428300
H	0.36149700	-1.94308100	3.08169300
H	-0.06537400	4.24567900	-2.44257400
H	-1.47689300	3.42908300	-3.09916400
H	-1.69187200	4.92145800	-2.14638700
H	-4.64115400	0.37998700	-1.76444300
H	-4.71697100	-1.08565400	-2.79409800
H	-4.82175400	-1.21597200	-1.02690100
H	-3.92320100	0.04615200	2.72105600
H	-4.53067400	-1.58735200	3.08512900
H	-3.02496200	-0.97829100	3.83465600
C	3.01339200	-3.68979700	-0.52174100
C	3.05195400	-2.25248700	-1.03847300
H	2.63575000	-3.71791000	0.50198000
H	2.35773500	-4.29659100	-1.14738400
H	4.01075000	-4.13376300	-0.52399200
C	3.56513900	-2.22175900	-2.48412100
C	3.92697200	-1.36793900	-0.15215800
H	3.58418700	-1.19786600	-2.85719500
H	4.57723500	-2.62911100	-2.51991400
H	2.92149500	-2.81975700	-3.12953900
H	4.95329400	-1.73936600	-0.13356000
H	3.93202100	-0.33975400	-0.51335700
H	3.55375800	-1.35860900	0.87377800
O	1.74981000	-1.72972100	-1.14095700
H	1.23612100	-1.57774600	0.05746200
C	2.82021400	3.91128700	1.70609100
H	2.06363800	4.64671200	1.43313300
H	2.70390900	3.70212200	2.77024400
H	3.81622400	4.29734000	1.51069100
O	3.43221300	2.08172900	0.27164400

Zero-point correction= 0.464365
Thermal correction to Energy= 0.497045
Thermal correction to Enthalpy= 0.497989
Thermal correction to Gibbs Free Energy= **0.395602**

E(wB97XD, MeCN) **-1455.767423**



TS(1-βOAc^{C1})

C	-0.90181800	-0.04172400	-0.79808200

O	-0.39109800	-1.07841700	-1.52465000
C	0.18066800	0.82232300	-0.12468200
C	1.16304100	-0.06293500	0.61861000
O	-0.39215600	1.69501600	0.83080200
C	1.67836500	-1.17986500	-0.27837700
O	-0.47931900	3.39367300	-0.63647500
C	0.49990900	-1.95856800	-0.83807700
O	2.23172300	0.76782700	1.04848600
C	0.89300000	-3.03915700	-1.81663700
O	2.63927700	-0.63058600	2.75698500
O	2.41437900	-0.61837000	-1.36589700
C	-0.68776600	2.95415000	0.46173900
O	4.37972300	-0.98492000	-0.33734000
C	-1.33305100	3.69167000	1.59235600
C	2.93429800	0.34134900	2.12259100
C	4.11810800	1.22382900	2.36874000
C	3.75375700	-0.55219200	-1.26479000
C	4.33686200	0.13885200	-2.46122200
O	-1.65582100	0.67810100	-1.72376100
C	-2.72695600	1.41607400	-1.35932900
H	0.68361900	1.39744900	-0.90472300
H	0.66753700	-0.51069600	1.48135800
H	2.32429200	-1.84033200	0.29967000
H	1.57113000	-3.74539500	-1.33630000
H	0.00750100	-3.57880500	-2.15066900
H	1.38847200	-2.60828400	-2.68578600
H	-2.33590500	3.28262000	1.72718600
H	-0.78095800	3.53555200	2.51790000
H	-1.39519600	4.74910500	1.35206400
H	3.87067700	2.27000700	2.19752800
H	4.48132500	1.07120800	3.38119900
H	4.89729600	0.93436400	1.66073000
H	4.05400100	1.19235400	-2.43289300
H	5.41913100	0.04988900	-2.44224300
H	3.93349500	-0.28541200	-3.37992700
C	-3.28552300	-2.35340600	-0.38374400
C	-3.01818700	-1.97380800	1.07415900
H	-3.45638600	-1.46105100	-0.98790900
H	-2.44002700	-2.89873600	-0.80542400
H	-4.17431400	-2.98260100	-0.45033000
C	-2.80885400	-3.24464800	1.90752200
C	-4.16947700	-1.14482400	1.63779300
H	-2.54621400	-2.98465200	2.93331000
H	-3.72685600	-3.83540000	1.92269500
H	-2.00616300	-3.85151400	1.48615400
H	-5.10976100	-1.69903900	1.59047500
H	-3.96852700	-0.89178000	2.67985400
H	-4.27560500	-0.21832000	1.07532900
O	-1.80337600	-1.27220700	1.19404500
C	-3.22399800	2.21032200	-2.52559900
H	-2.52583800	3.03452300	-2.68489500
H	-3.24280500	1.60375100	-3.42945700
H	-4.21037400	2.60639300	-2.30208900
O	-3.18272000	1.43368300	-0.25239900
H	-1.56907900	-0.50152800	0.15567400
H	-0.03363500	-2.38871600	0.01532600

```
Zero-point correction=                           0.464840
Thermal correction to Energy=                    0.497033
Thermal correction to Enthalpy=                  0.497977
Thermal correction to Gibbs Free Energy=         0.399476

E(wB97XD, MeCN)                              -1455.760557
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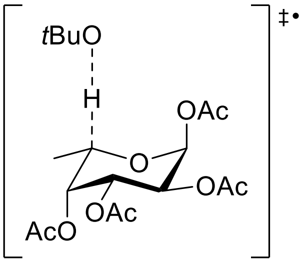


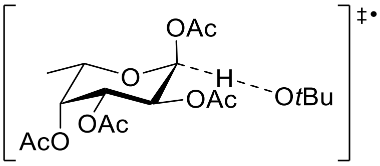
TS(1-αOAc^{C5})

O	-0.57536100	0.64190800	-1.93243100
O	-1.14233000	1.87115000	-0.05997300
O	1.47624100	2.20727700	0.64511900
O	2.66323100	3.32725600	-0.89665800
O	2.11652500	-0.48781000	0.99416400
O	1.00814000	-1.59283400	2.60336200
O	1.48487500	-1.43534900	-1.48604800
O	2.02871600	-3.29623400	-0.34843000
C	-0.16035800	1.63596900	-1.04445300
H	-0.00522400	2.52882100	-1.64591900
C	1.11818200	1.22587500	-0.31379500
H	1.91173300	1.12328300	-1.05339900
C	0.88755100	-0.08211900	0.40837400
H	0.13293200	0.04894800	1.18295800
C	0.40986800	-1.13771600	-0.58599900
H	0.13152100	-2.04520600	-0.05131000
C	-0.75818800	-0.64146400	-1.42177800
C	-1.15973000	-1.55183700	-2.55091700
H	-2.09511100	-1.20096500	-2.98344900
H	-1.30480200	-2.56699300	-2.18273700
H	-0.38976100	-1.55803800	-3.32339800
C	-2.17644500	2.68893700	-0.38960800
C	2.26928300	3.21570200	0.22970400
C	2.56929400	4.15145700	1.36197200
H	1.63913400	4.57906200	1.73740800
H	3.22844200	4.94159600	1.01495300
H	3.03393400	3.60365000	2.18188600
C	2.04153400	-1.29260500	2.07582500
C	3.40080600	-1.76550900	2.48662900
H	4.14473900	-0.98040700	2.36479500
H	3.66928500	-2.59917000	1.83447800
H	3.36904900	-2.11528800	3.51473100
C	2.23088200	-2.52894800	-1.24855000
C	3.33676900	-2.63825900	-2.25504600
H	4.03939300	-1.81799500	-2.10046800

H	2.93969400	-2.54478700	-3.26526600
H	3.84817600	-3.58858300	-2.13312200
C	-2.44586600	-1.18361800	2.01118500
C	-3.25772300	-1.50161700	0.75817500
H	-1.38350900	-1.37680900	1.85765300
H	-2.57250500	-0.13476700	2.28386100
H	-2.76570300	-1.80317000	2.85111300
C	-4.75729600	-1.32161600	1.03971700
C	-2.98949200	-2.92837100	0.28024300
H	-5.33909900	-1.50297400	0.13600400
H	-5.07122700	-2.02667400	1.81126700
H	-4.96205400	-0.30962600	1.39096100
H	-3.29411400	-3.65422500	1.03607000
H	-3.53746000	-3.12825600	-0.64152200
H	-1.92455000	-3.07869100	0.09250000
O	-3.00880800	-0.57005100	-0.26225200
H	-1.76651500	-0.61154500	-0.69418700
O	-2.21818100	3.31516300	-1.40660900
C	-3.21649900	2.66566800	0.68462900
H	-2.75725500	2.79820600	1.66384600
H	-3.95646100	3.43838900	0.49770200
H	-3.68249800	1.67883300	0.66281800

Zero-point correction= 0.464827
Thermal correction to Energy= 0.497171
Thermal correction to Enthalpy= 0.498115
Thermal correction to Gibbs Free Energy= **0.397951**

E(wB97XD, MeCN) **-1455.767727**



TS(1-αOAc^{C1})

O	-0.76553000	-1.66376200	0.00460200
O	-1.27602000	-0.52319200	1.95633900
O	-0.24739900	1.77609700	0.97007000
O	-0.11834100	2.92463400	-0.96446000
O	2.41337300	0.93322000	0.45606300
O	3.67818200	0.19458700	2.15673700
O	1.75533100	-1.15482100	-1.26609600
O	4.00117900	-1.14004300	-1.17326800
C	-1.02712300	-0.45479600	0.57899000
H	-2.05679800	0.05487700	0.03048300
C	0.07015400	0.56685300	0.31699800
H	0.12089300	0.73397400	-0.75758400
C	1.39528900	0.01156400	0.80779100
H	1.37810500	-0.12023900	1.89059900
C	1.64095700	-1.34338300	0.14329400
H	2.56145300	-1.78028500	0.53141000

C	0.46749900	-2.27732200	0.40832300
C	0.56382300	-3.59640900	-0.31916300
H	-0.28778700	-4.22404900	-0.06088400
H	1.48133200	-4.11368600	-0.03582500
H	0.56707700	-3.43590700	-1.39636500
C	-2.40788400	-1.14774600	2.39143300
C	-0.37960200	2.88251100	0.20291400
C	-0.91025600	4.01941900	1.02091700
H	-1.97009200	3.83673000	1.20736700
H	-0.79401500	4.94987500	0.47270900
H	-0.40438200	4.07175800	1.98381100
C	3.54785100	0.89145300	1.19041000
C	4.58954900	1.79610800	0.61171800
H	4.14629300	2.72151900	0.24828100
H	5.04058000	1.27645400	-0.23615500
H	5.35436800	1.99582800	1.35701300
C	2.98433800	-1.02262100	-1.79871900
C	2.88784000	-0.70180800	-3.25948800
H	3.87342600	-0.75731900	-3.71234800
H	2.48769200	0.30770800	-3.36888100
H	2.19842200	-1.38421800	-3.75515600
C	-3.85296800	-1.06500000	-1.69260600
C	-3.19074800	0.30652100	-1.79299000
H	-3.16518600	-1.78506000	-1.24752000
H	-4.73820900	-1.01116700	-1.05864300
H	-4.14484300	-1.42553600	-2.68138000
C	-4.17459800	1.34572100	-2.34330200
C	-1.94009100	0.25328700	-2.67157800
H	-3.69724100	2.32394100	-2.40780900
H	-4.50039500	1.04543000	-3.34084500
H	-5.04911100	1.42038400	-1.69656900
H	-2.20636700	0.00101700	-3.69987300
H	-1.43271000	1.21916100	-2.66475300
H	-1.25023700	-0.51139600	-2.30806300
O	-2.88246500	0.80216200	-0.50869600
H	0.43388100	-2.45101500	1.49000400
C	-2.48147200	-1.08559800	3.88755800
H	-2.51318300	-0.04340400	4.20656300
H	-3.37066900	-1.60799700	4.22774700
H	-1.58970100	-1.53562400	4.32466600
O	-3.20430500	-1.65441800	1.66408500

Zero-point correction= 0.464479
Thermal correction to Energy= 0.496809
Thermal correction to Enthalpy= 0.497753
Thermal correction to Gibbs Free Energy= **0.397788**

E(wB97XD, MeCN) **-1455.761759**

7. References

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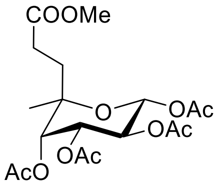
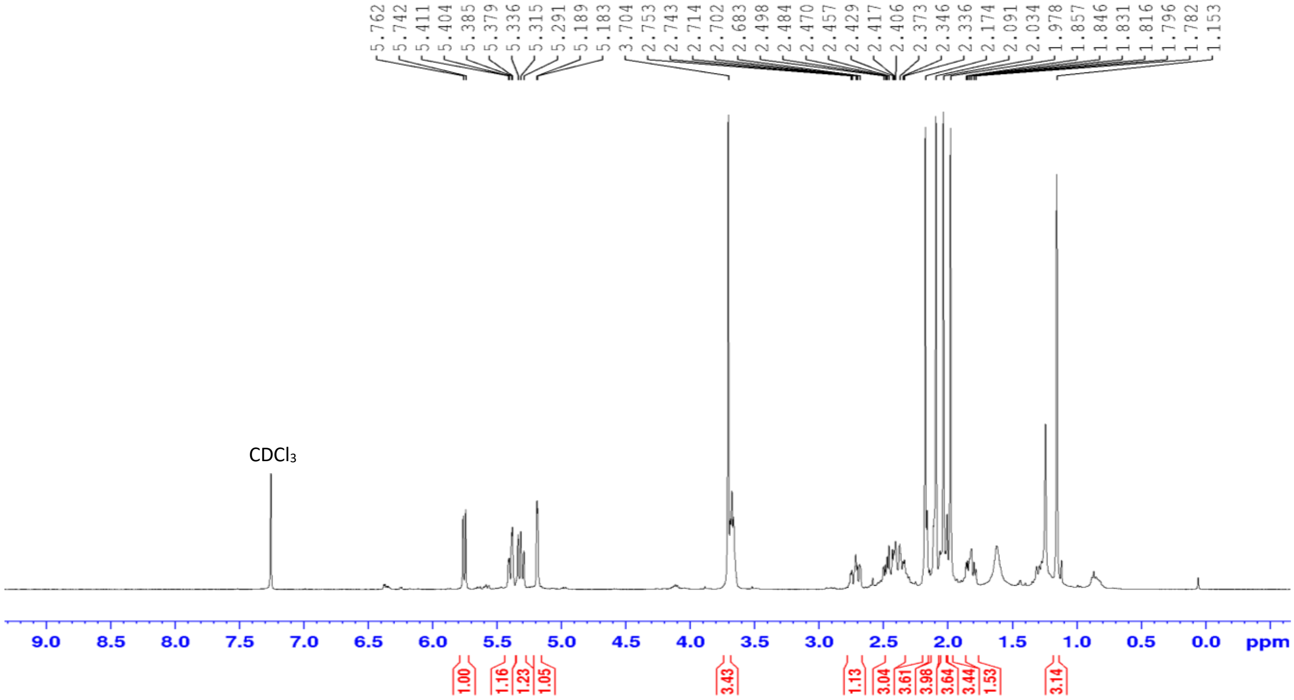
8. NMR Spectra of New Compounds



3-βOAc

3-βOAc: ^{1}H NMR (400 MHz, CDCl$_3$)



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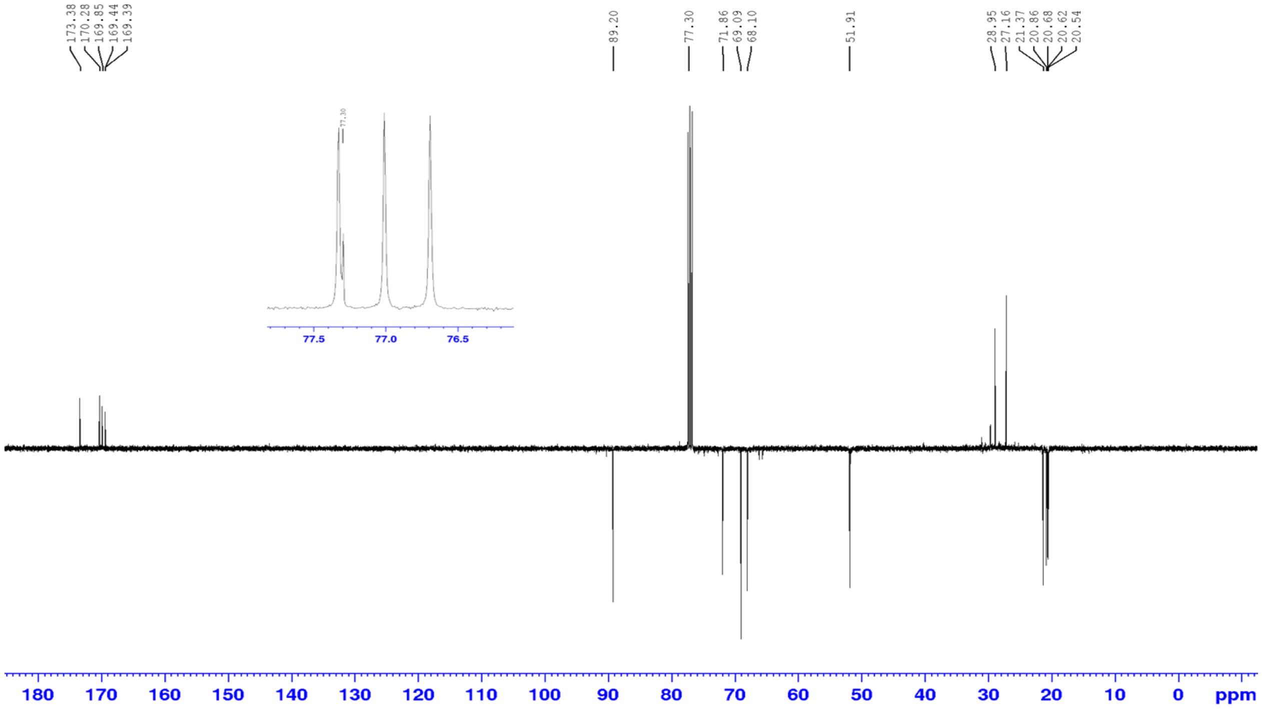
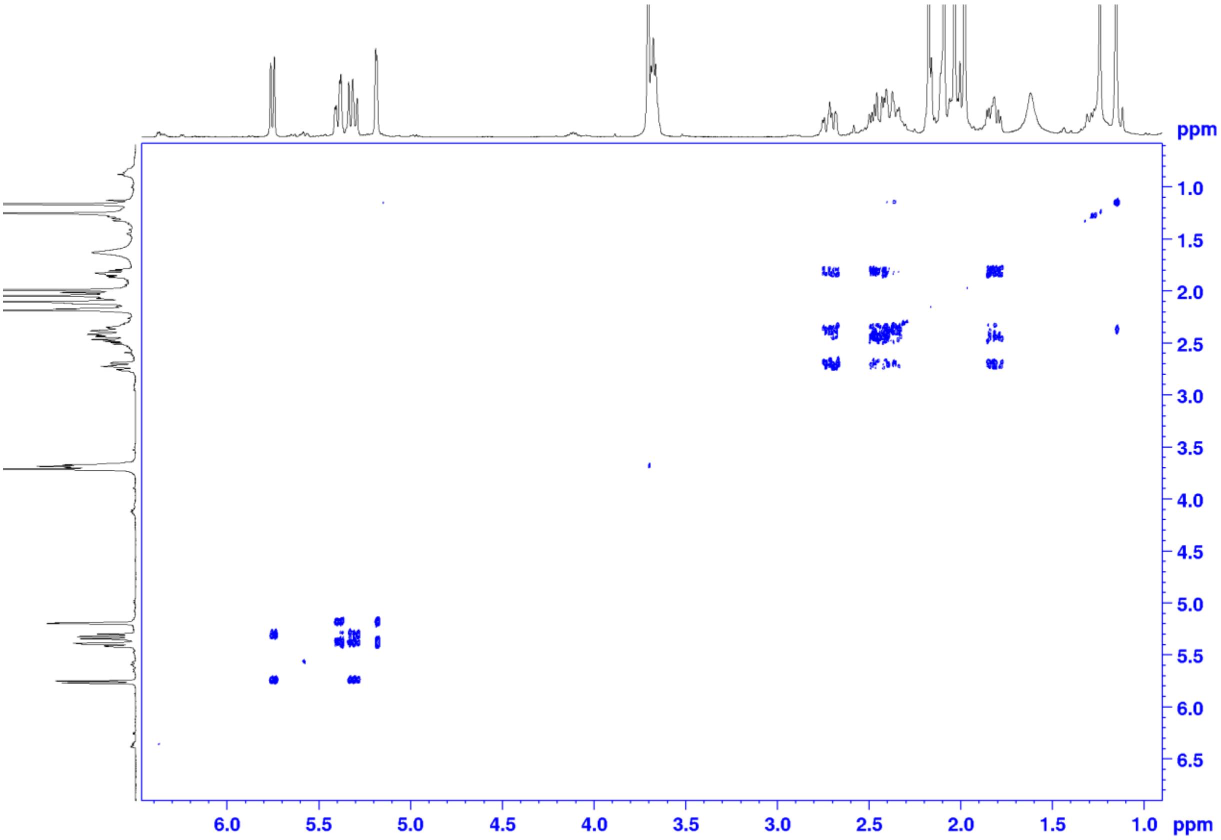
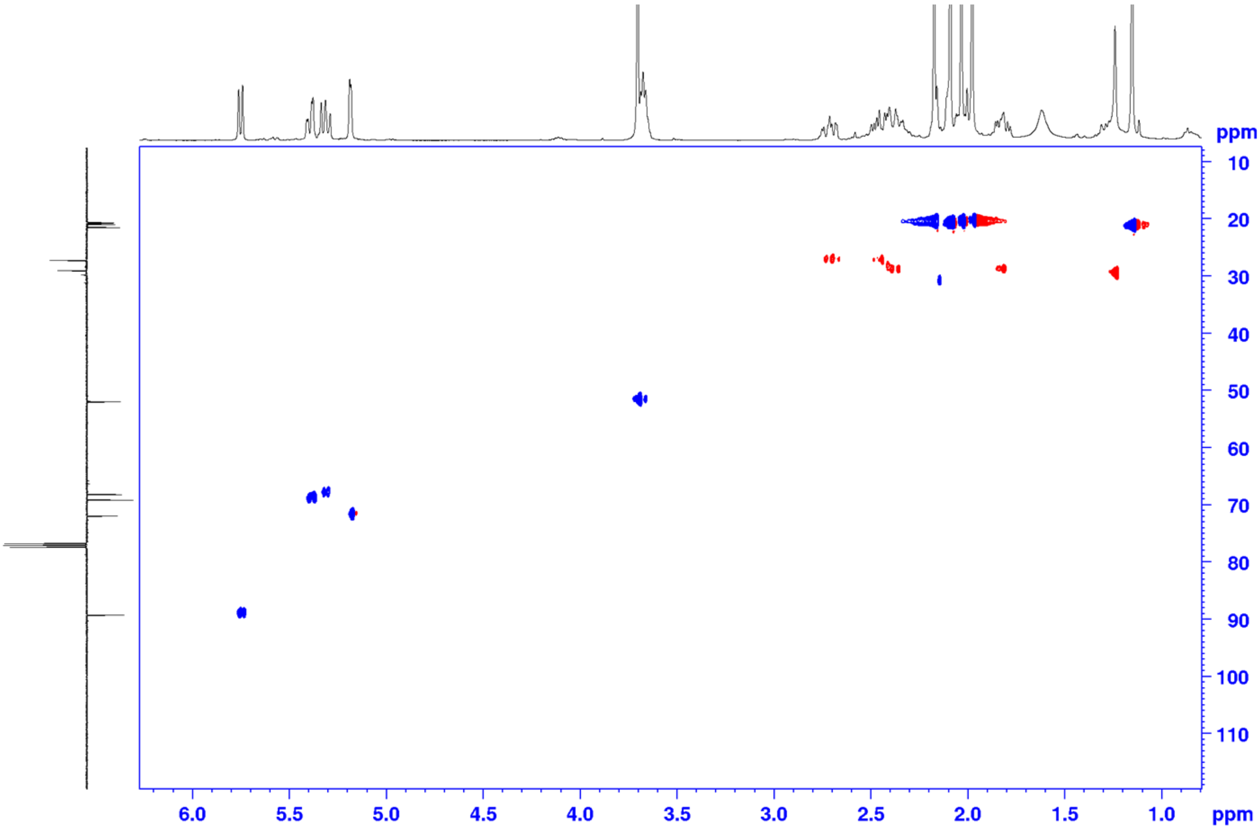


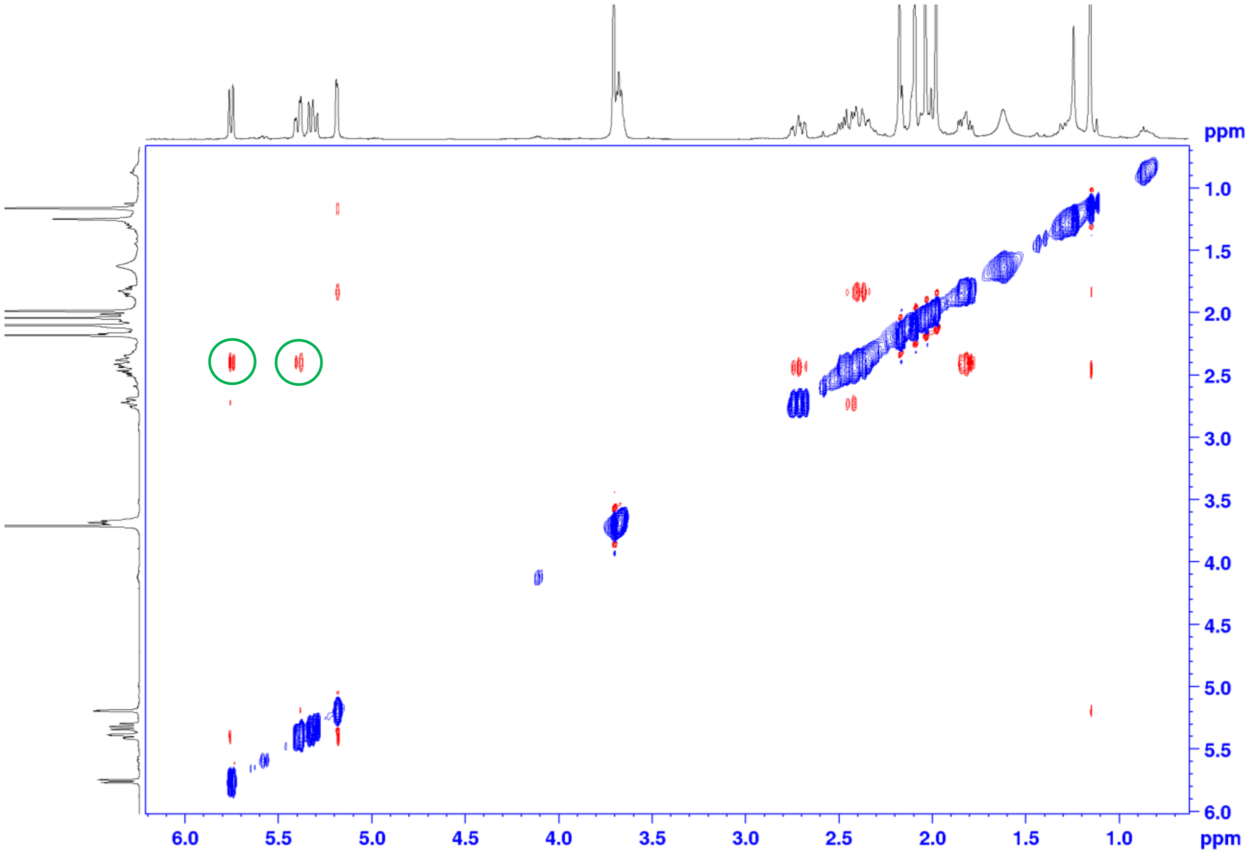
3-βOAc: COSY (400 MHz, CDCl₃)

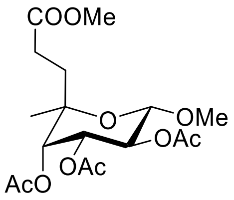


3-βOAc: HSQC (400 MHz, CDCl₃)



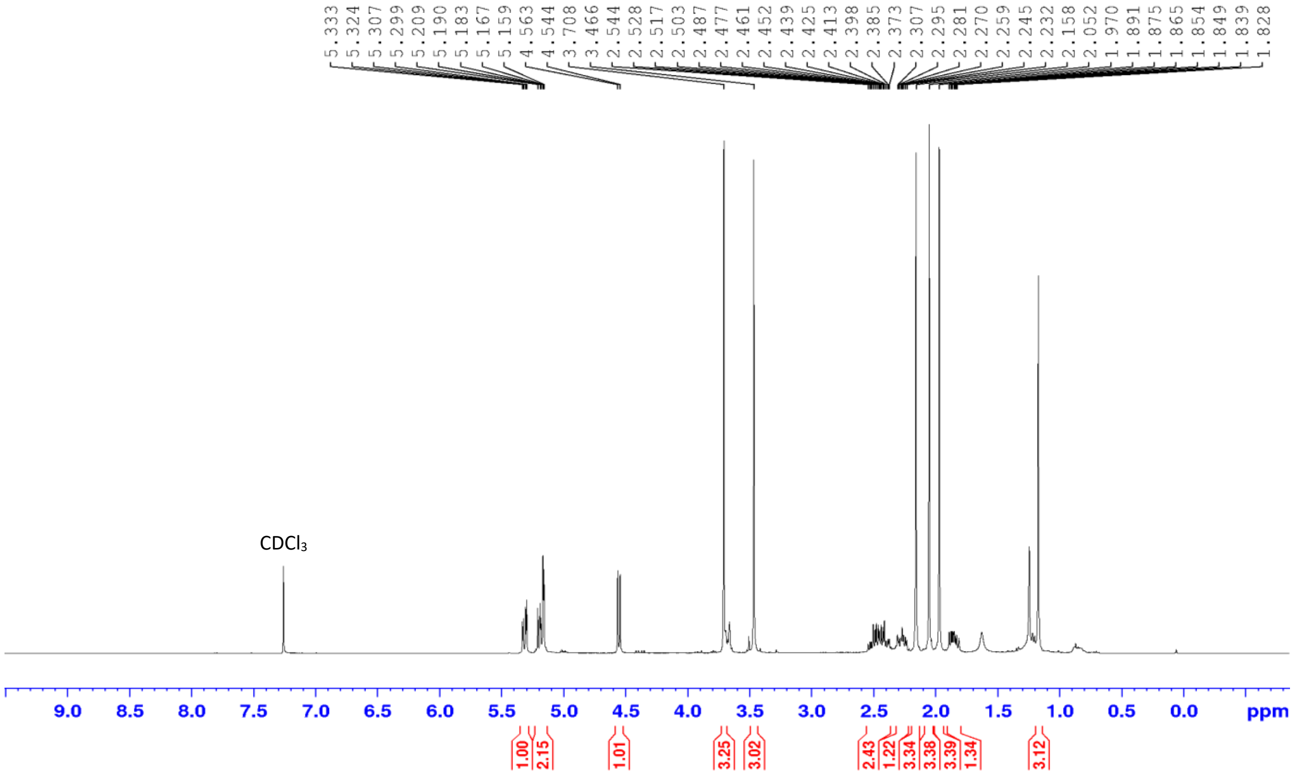
3-βOAc: NOESY (400 MHz, $CDCl_3$)



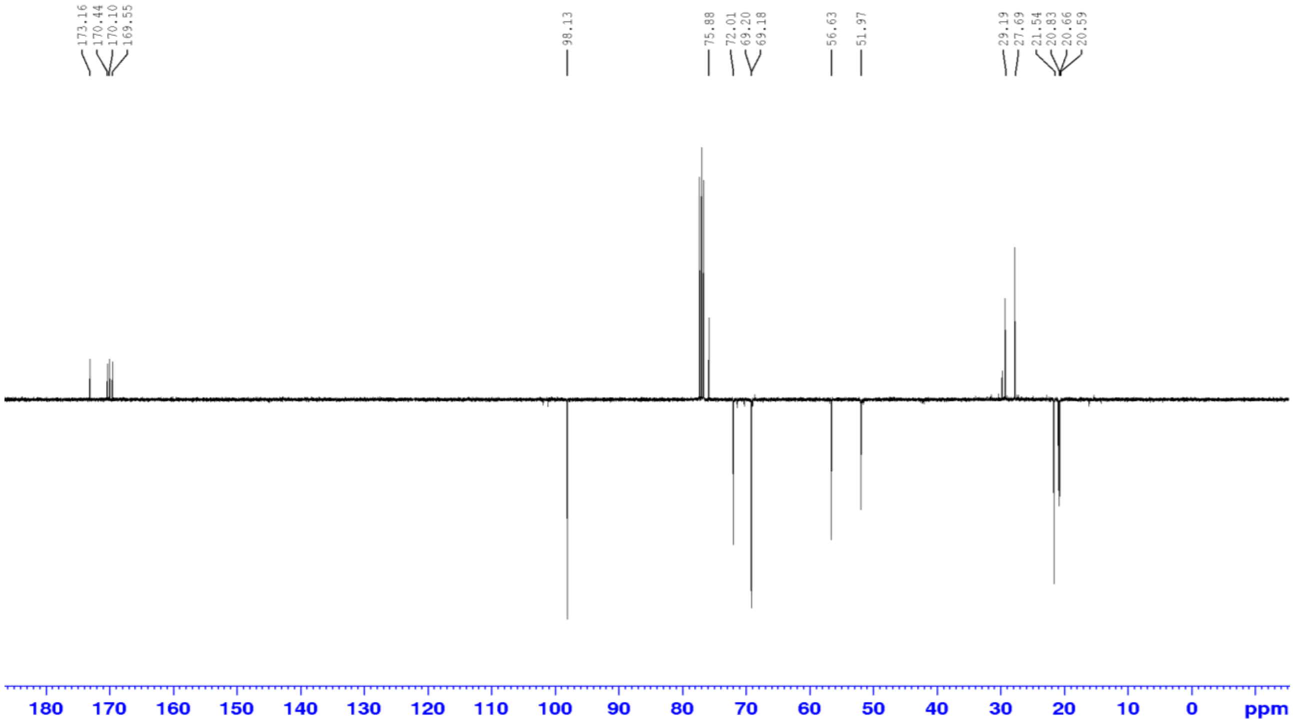


3-βOMe

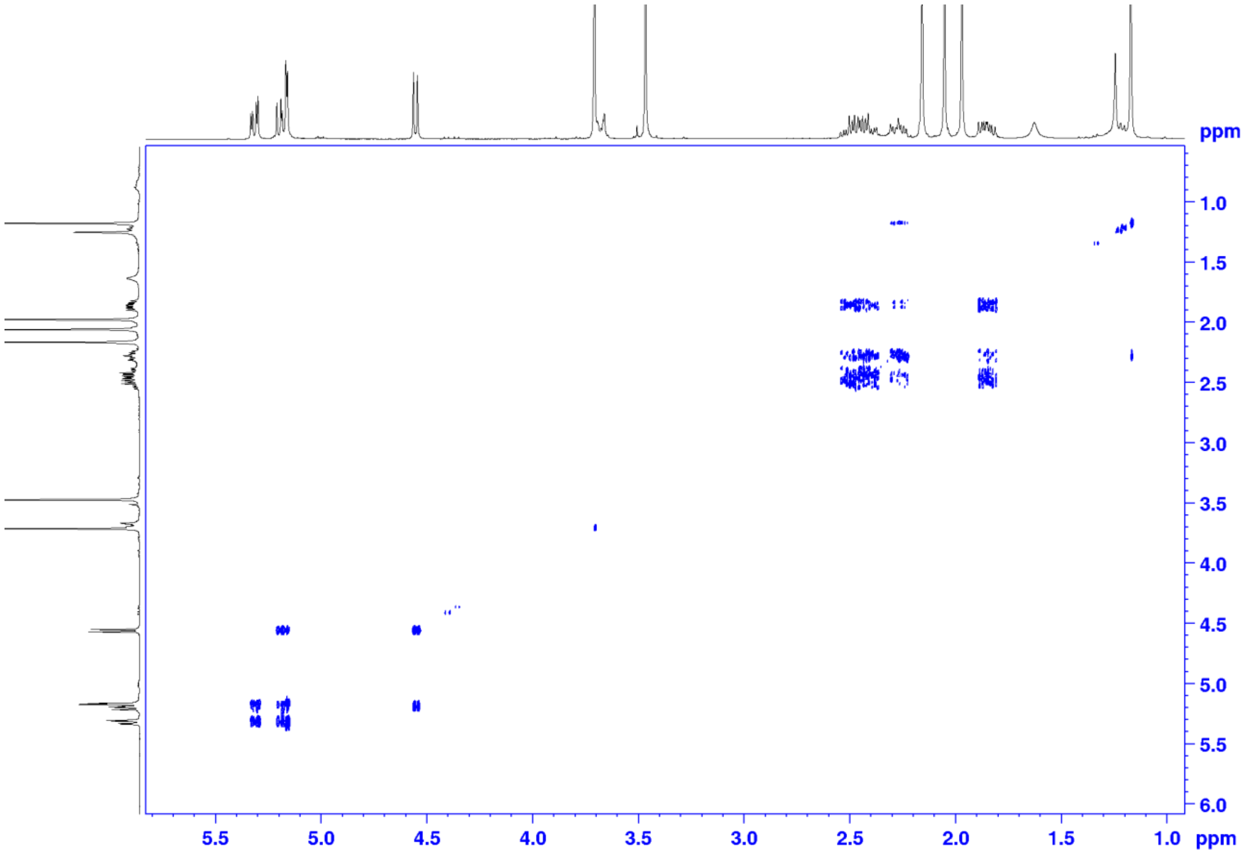
3-βOMe: ^{1}H NMR (400 MHz, CDCl$_3$)



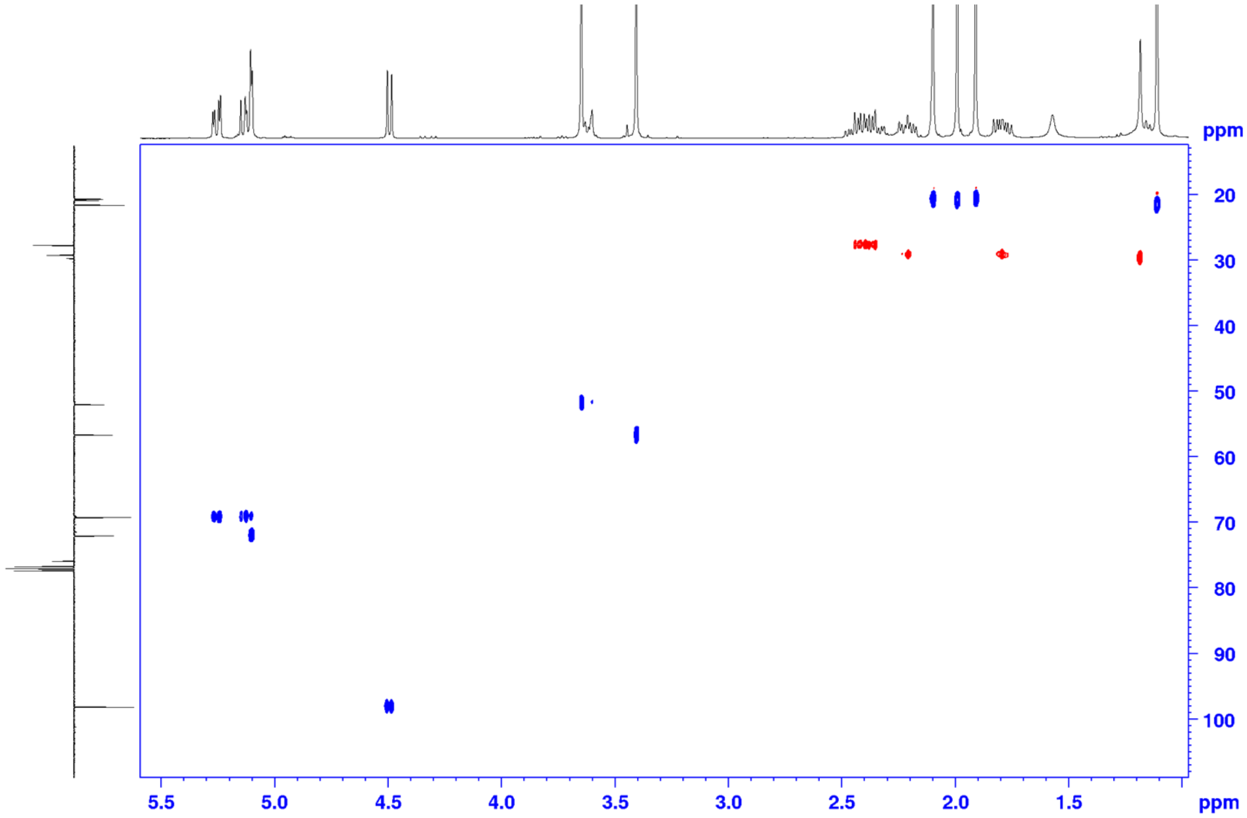
3-βOMe: ^{13}C NMR APT (100 MHz, CDCl$_3$)



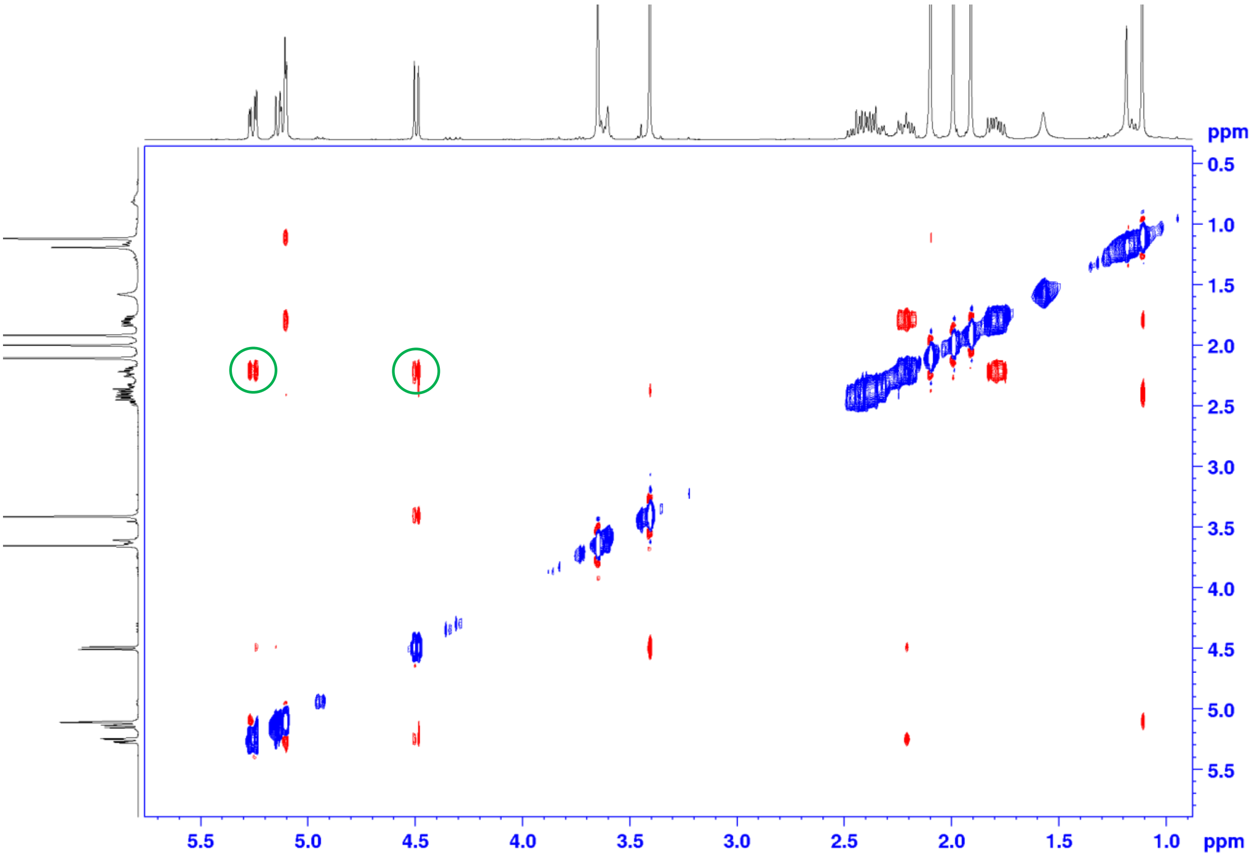
3-βOMe: COSY (400 MHz, $CDCl_3$)

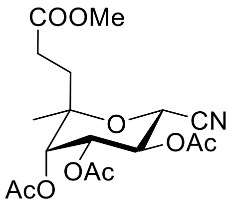


3-βOMe: HSQC (400 MHz, $CDCl_3$)



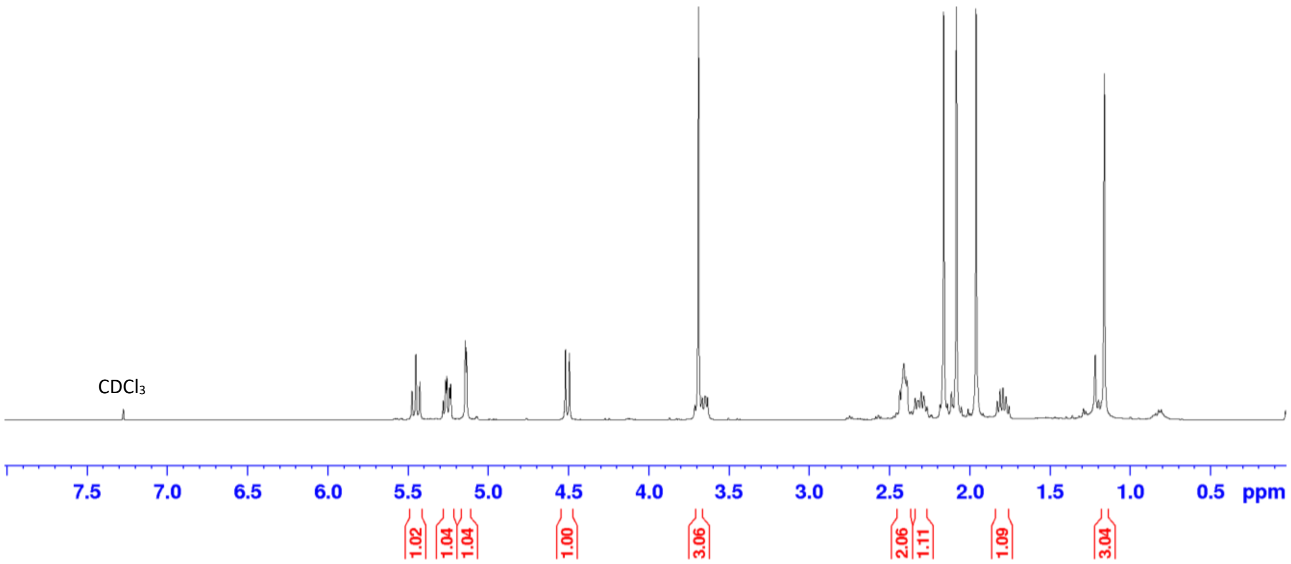
3-βOMe: NOESY (400 MHz, $CDCl_3$)



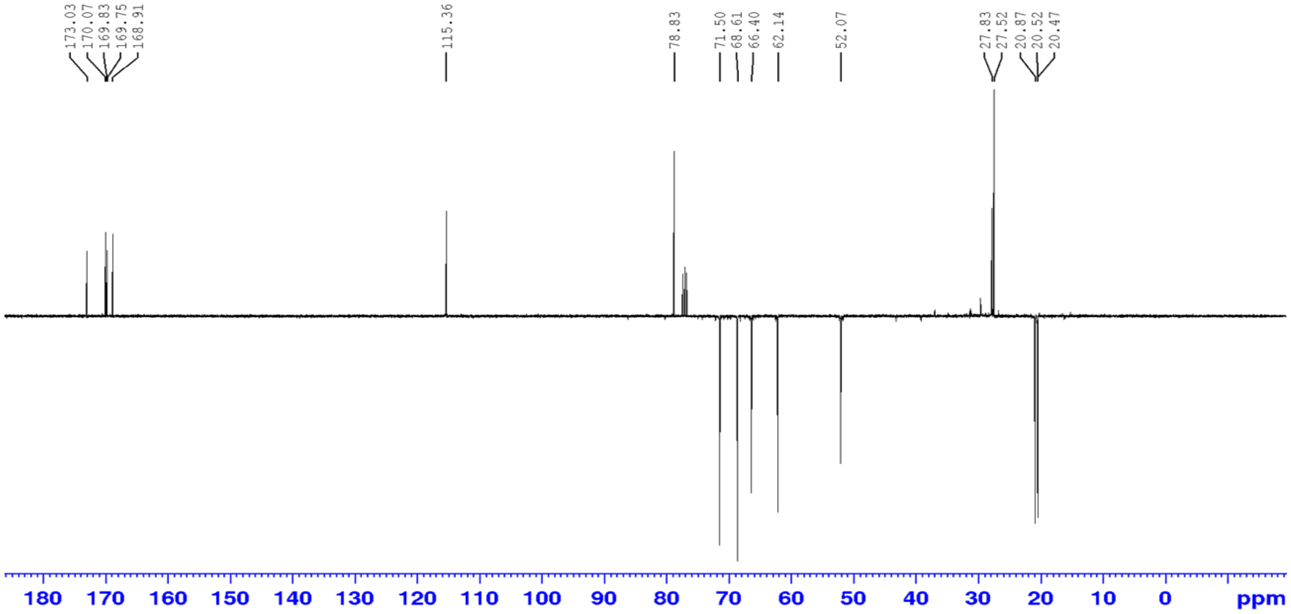


3-βCN

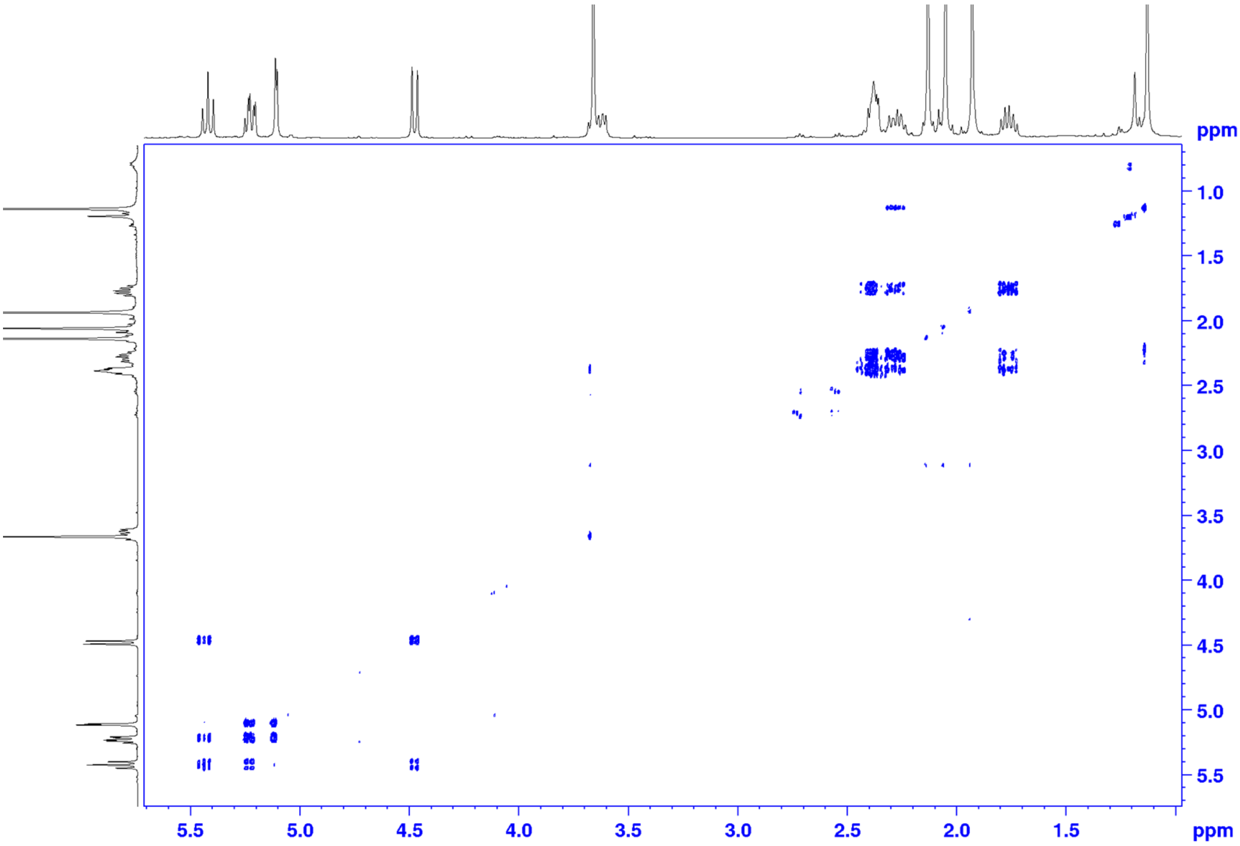
3-βCN: ^{1}H NMR (400 MHz, $CDCl_3$)



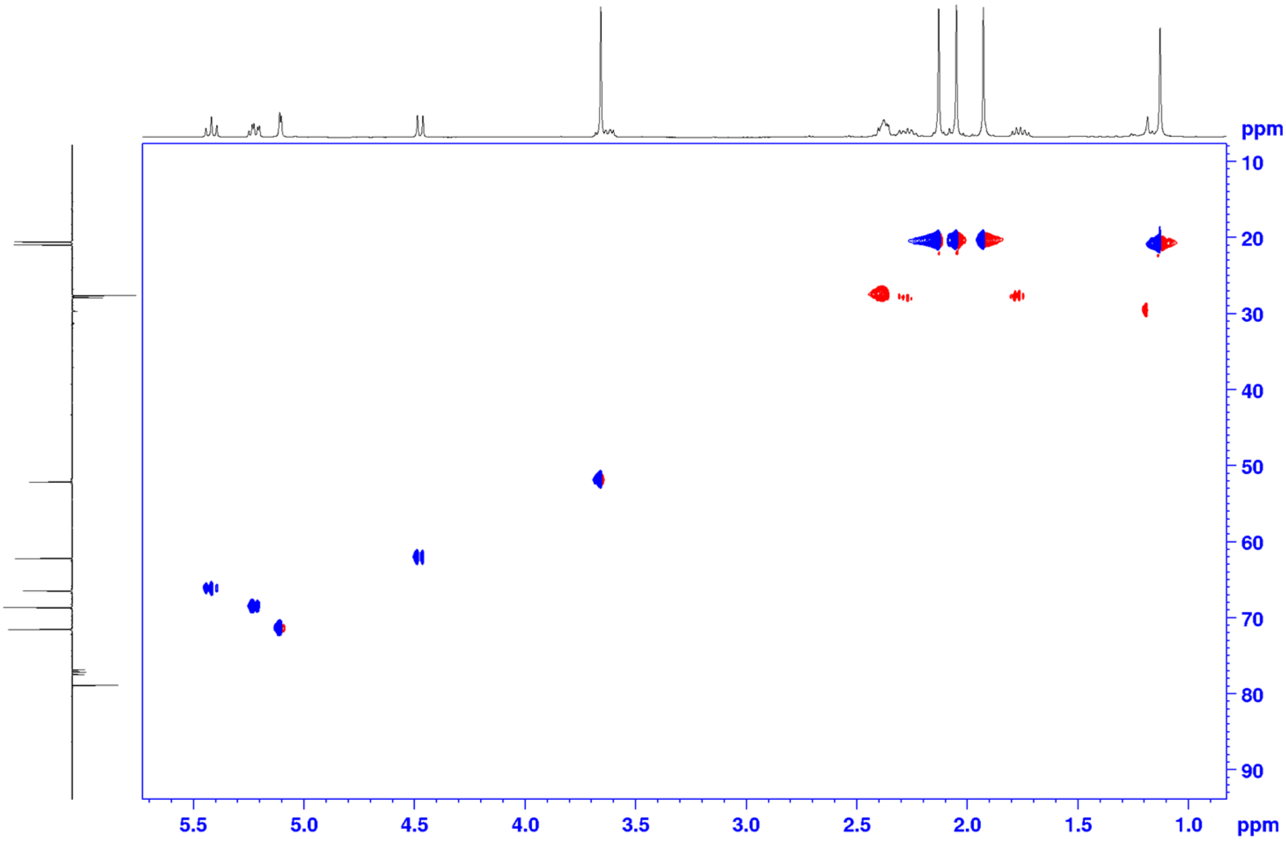
3-βCN: ^{13}C NMR APT (100 MHz, $CDCl_3$)



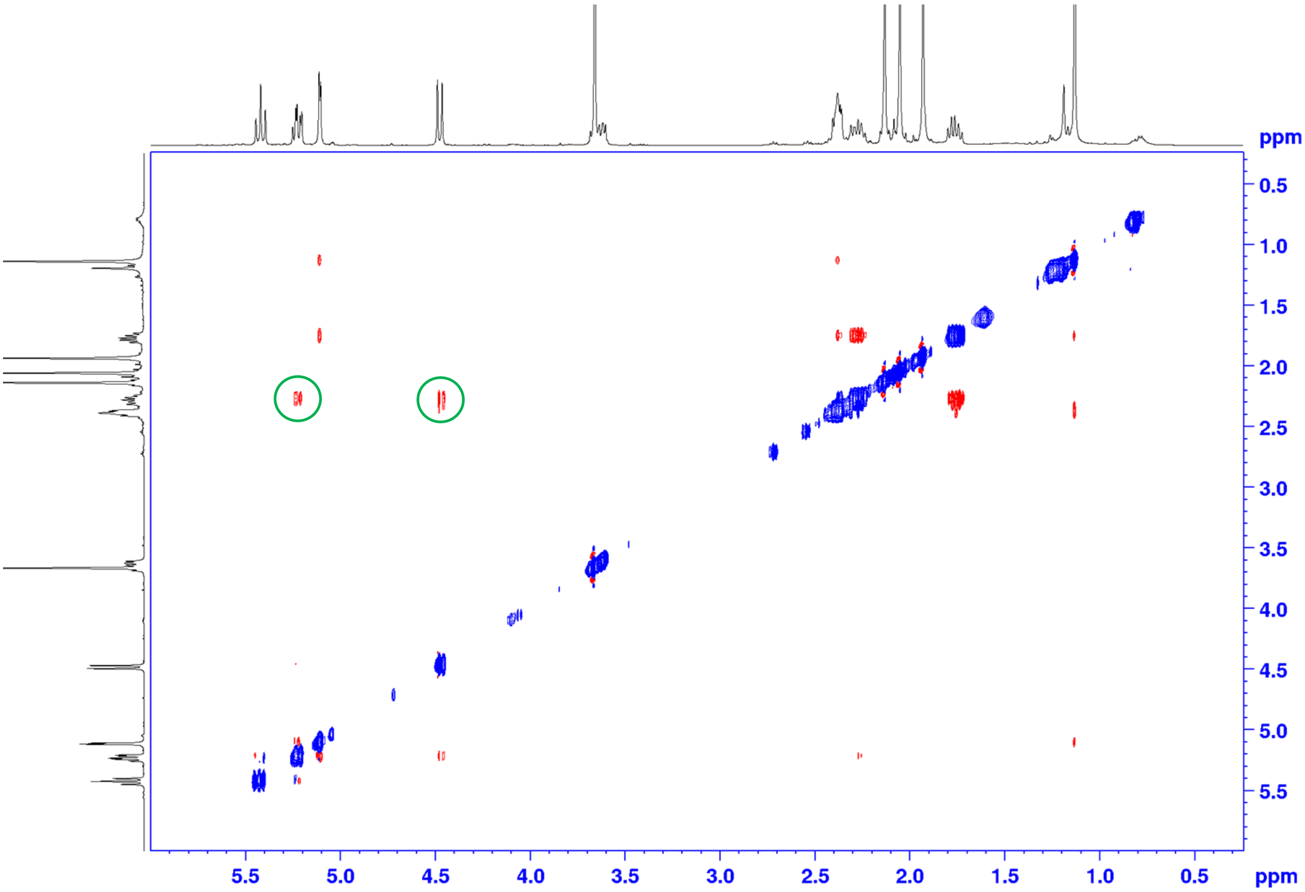
3-βCN: COSY (400 MHz, $CDCl_3$)



3-βCN: HSQC (400 MHz, $CDCl_3$)



3-βCN: NOESY (400 MHz, $CDCl_3$)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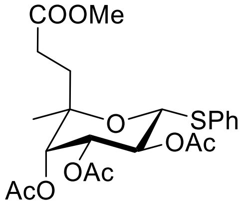
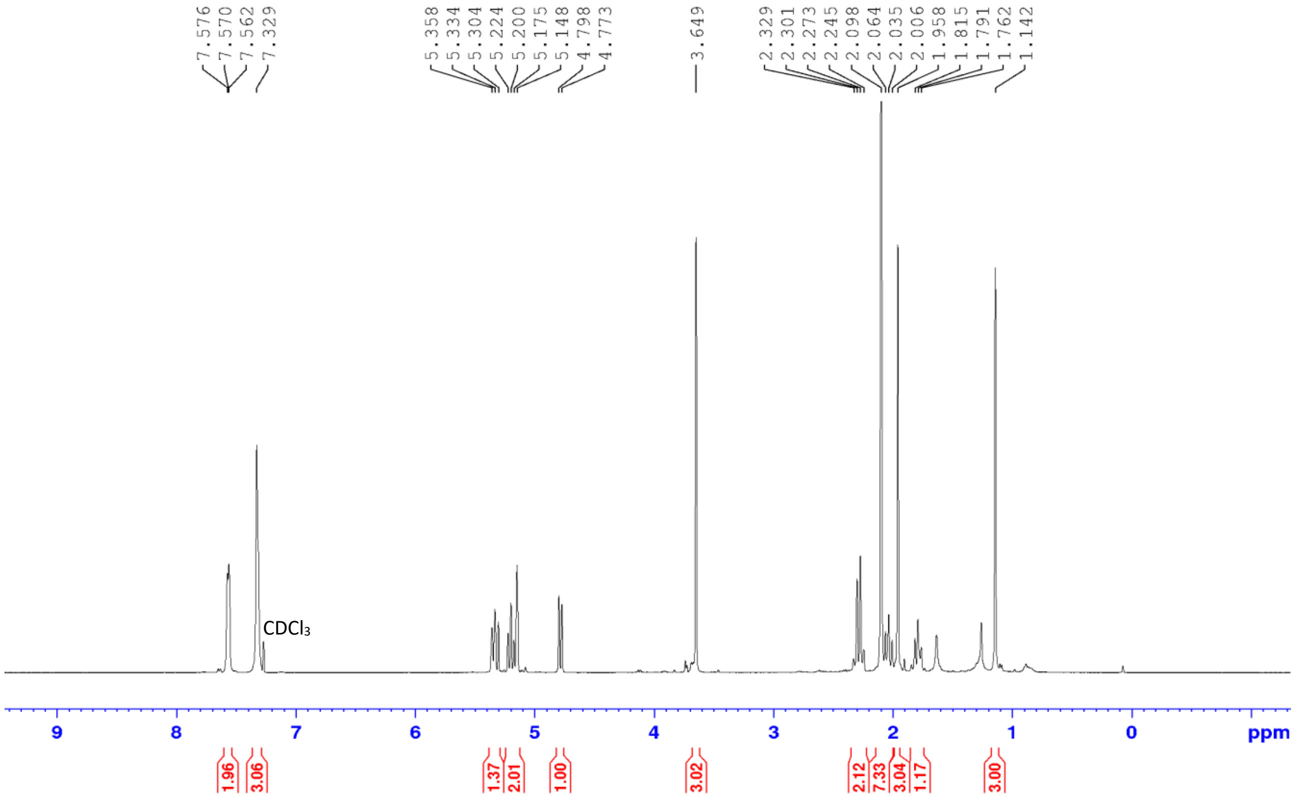
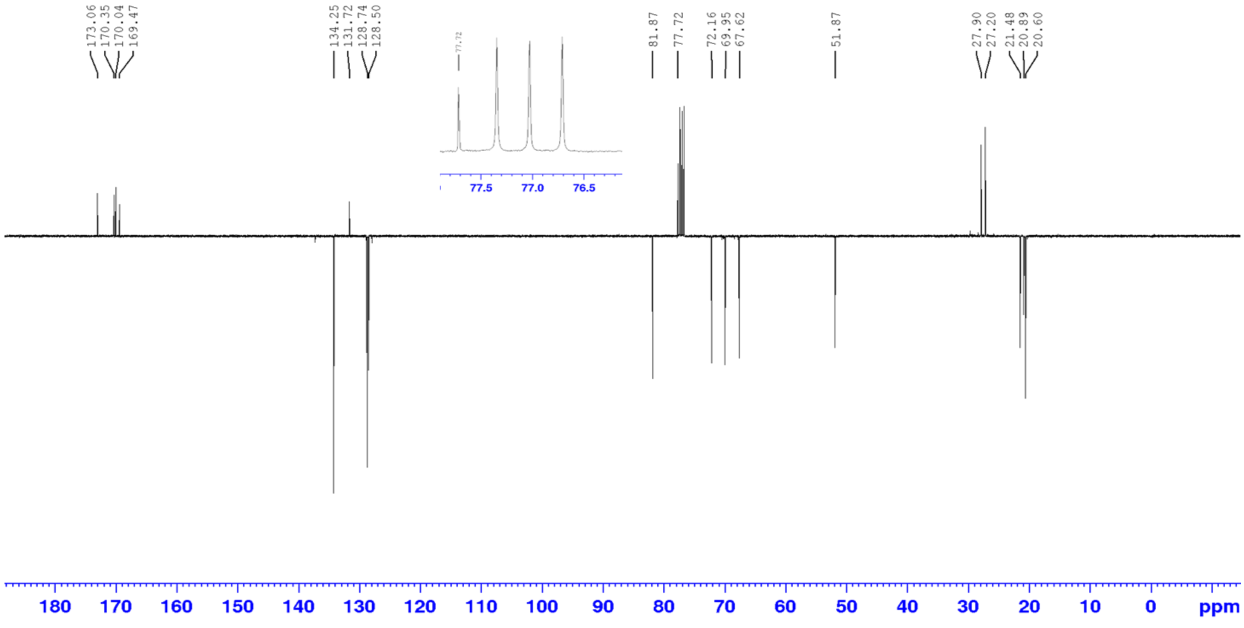


3-βSPh

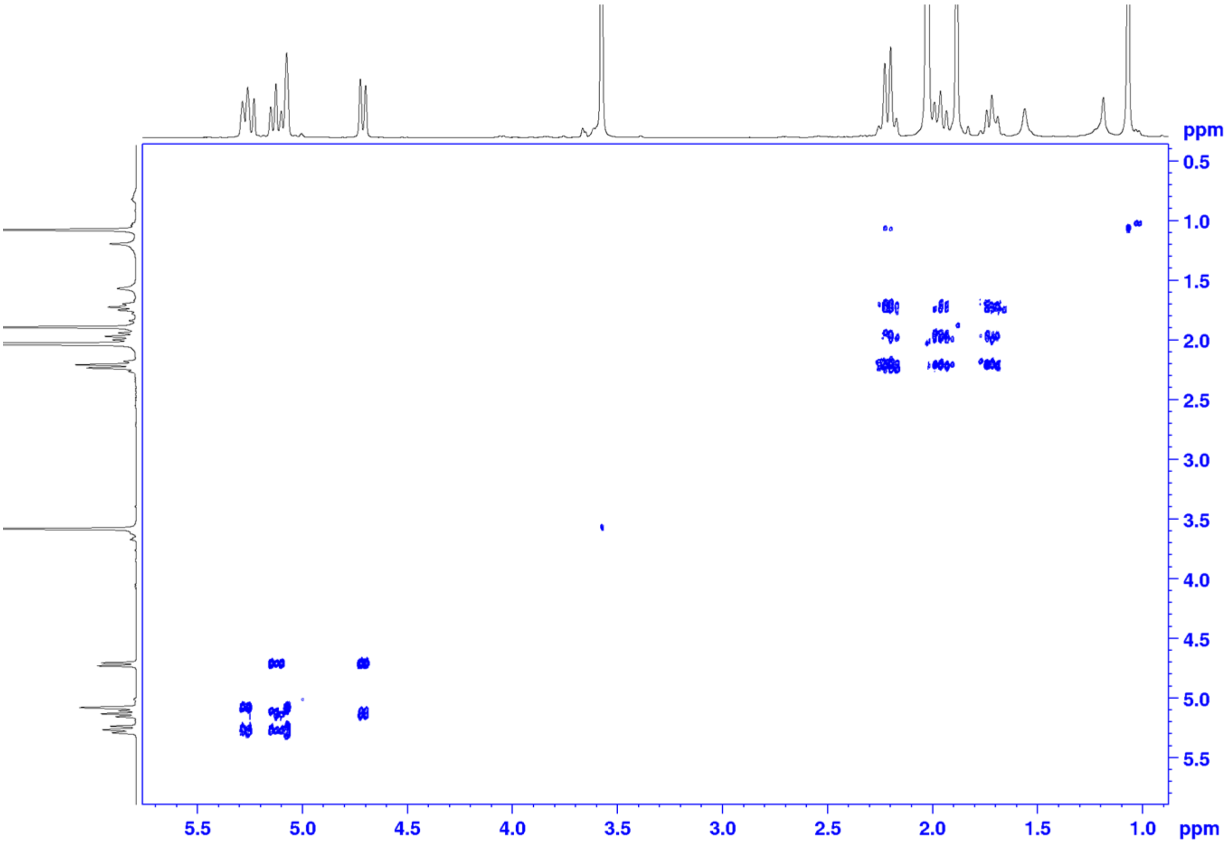
3-βSPh: ^{1}H NMR (400 MHz, CDCl$_3$)



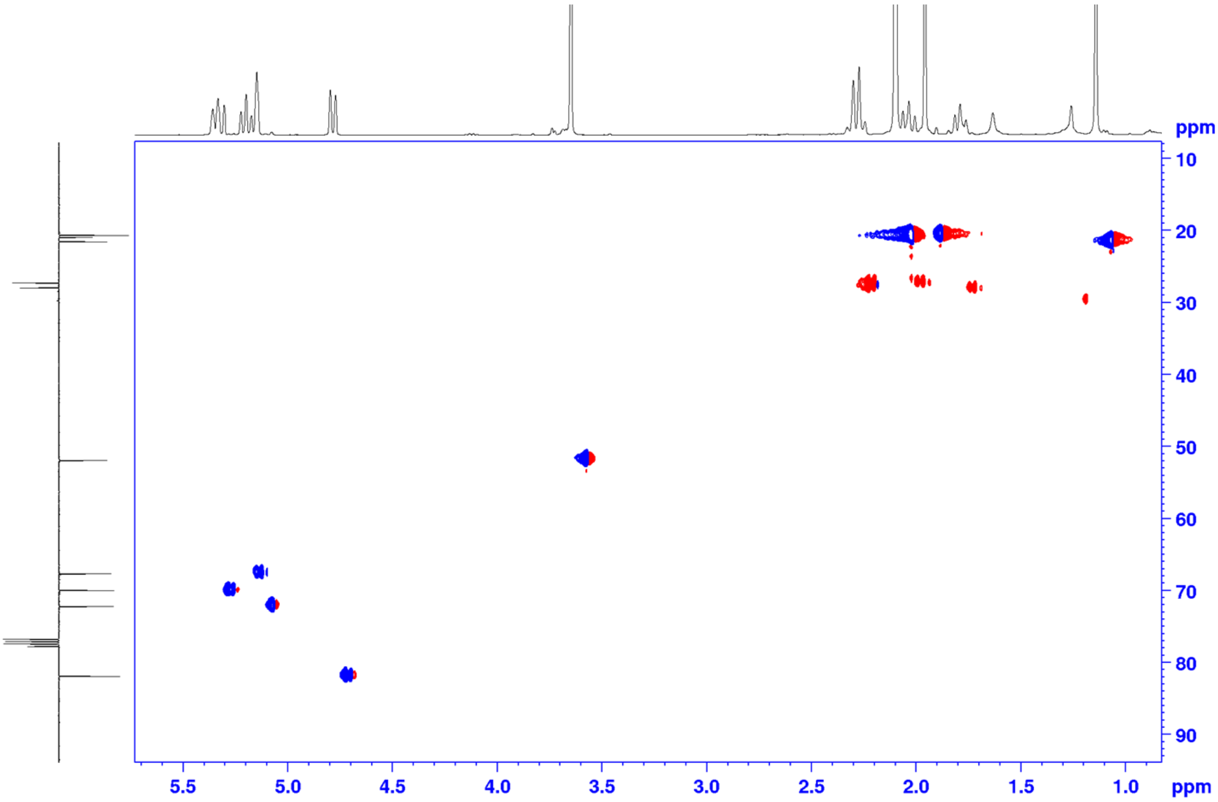
3-βSPh: ^{13}C NMR APT (100 MHz, CDCl$_3$)



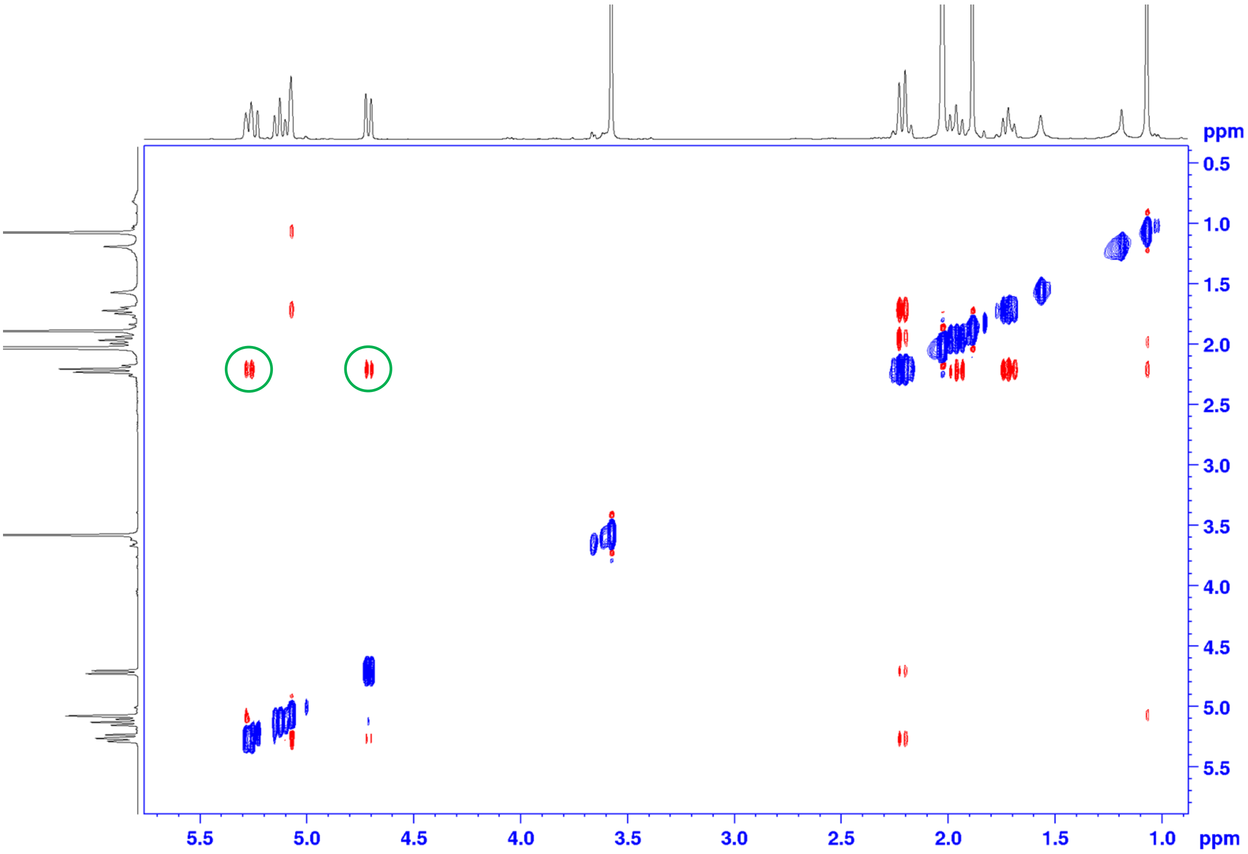
3-βSPh:COSY (400 MHz, $CDCl_3$)

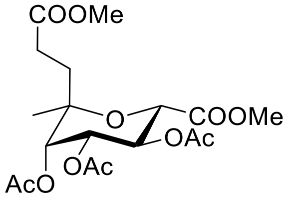


3-βSPh:HSQC (400 MHz, $CDCl_3$)



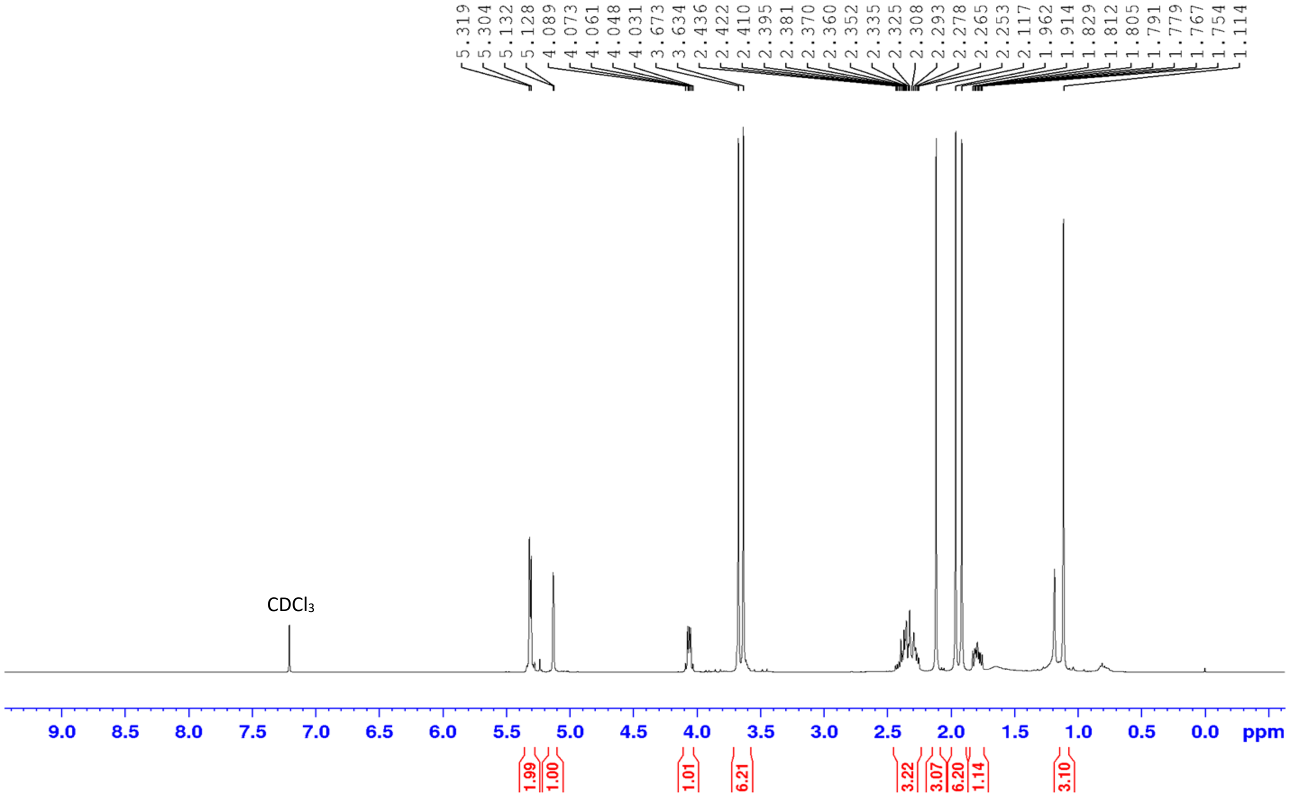
3-βSPh:NOESY (400 MHz, $CDCl_3$)



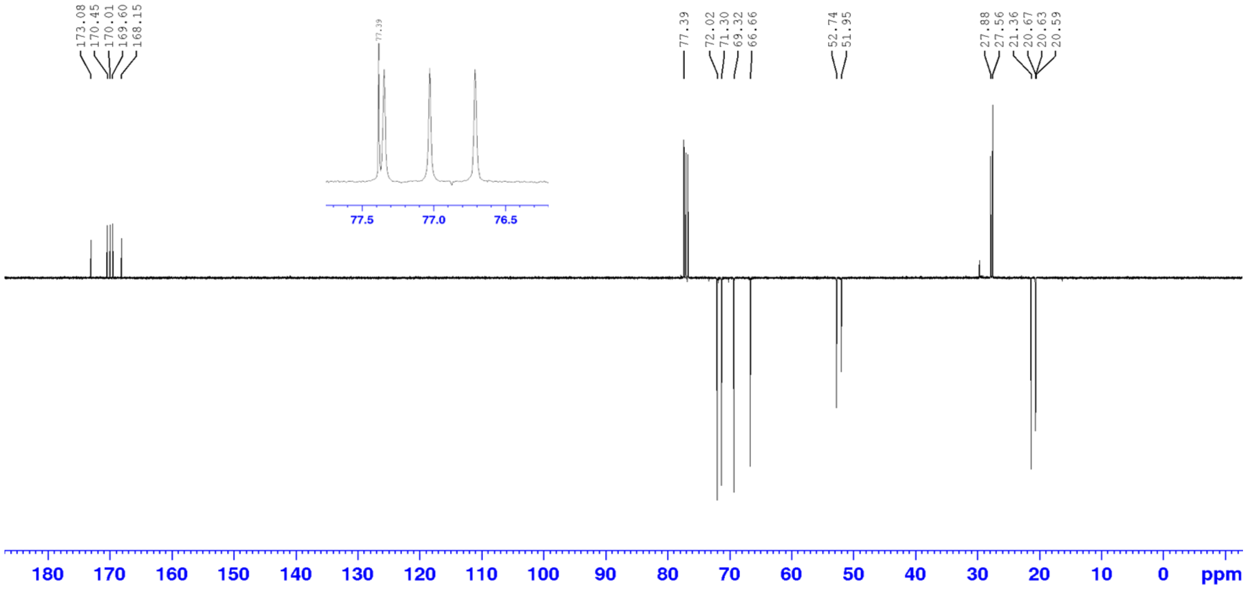


3-βCO$_2$Me

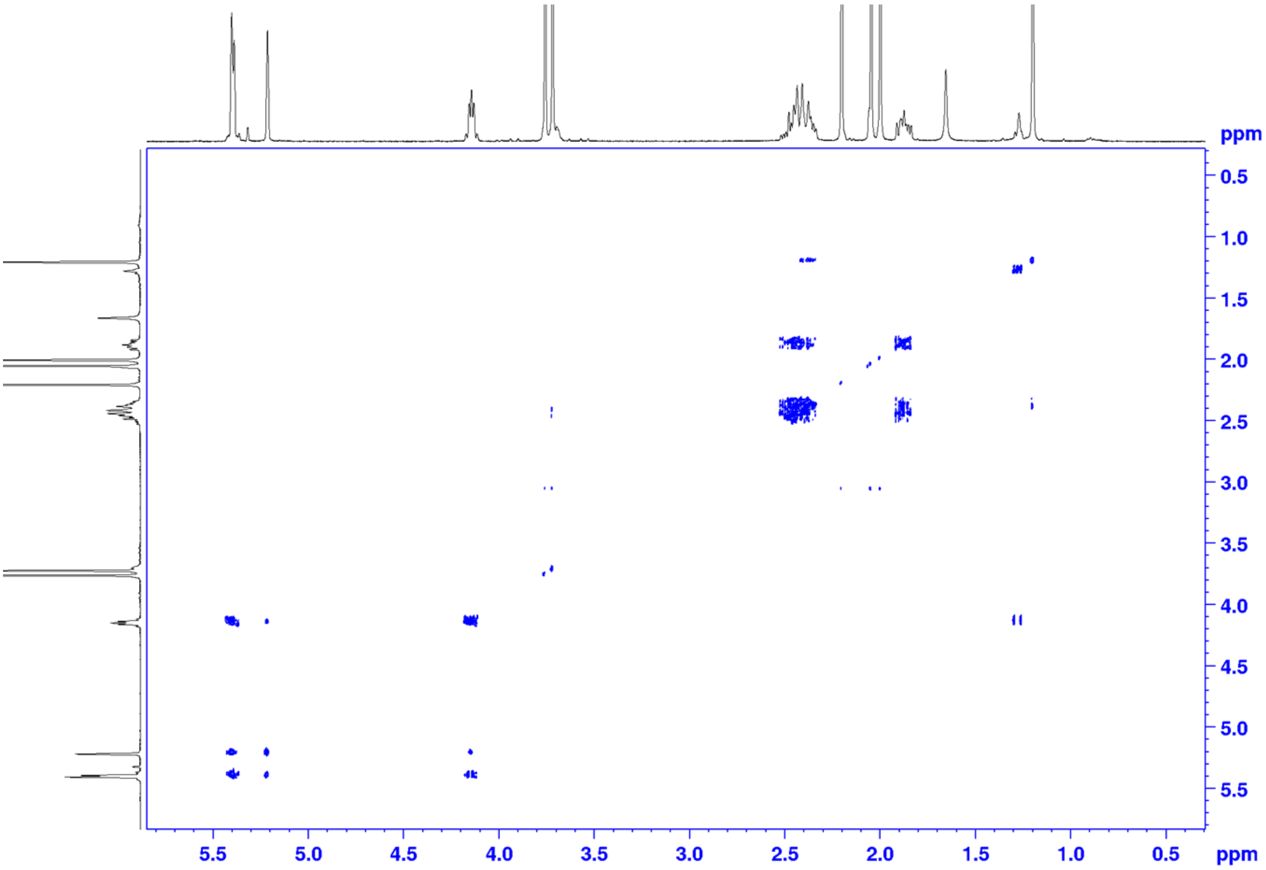
3-βCO$_2$Me: ^{1}H NMR (400 MHz, CDCl$_3$)



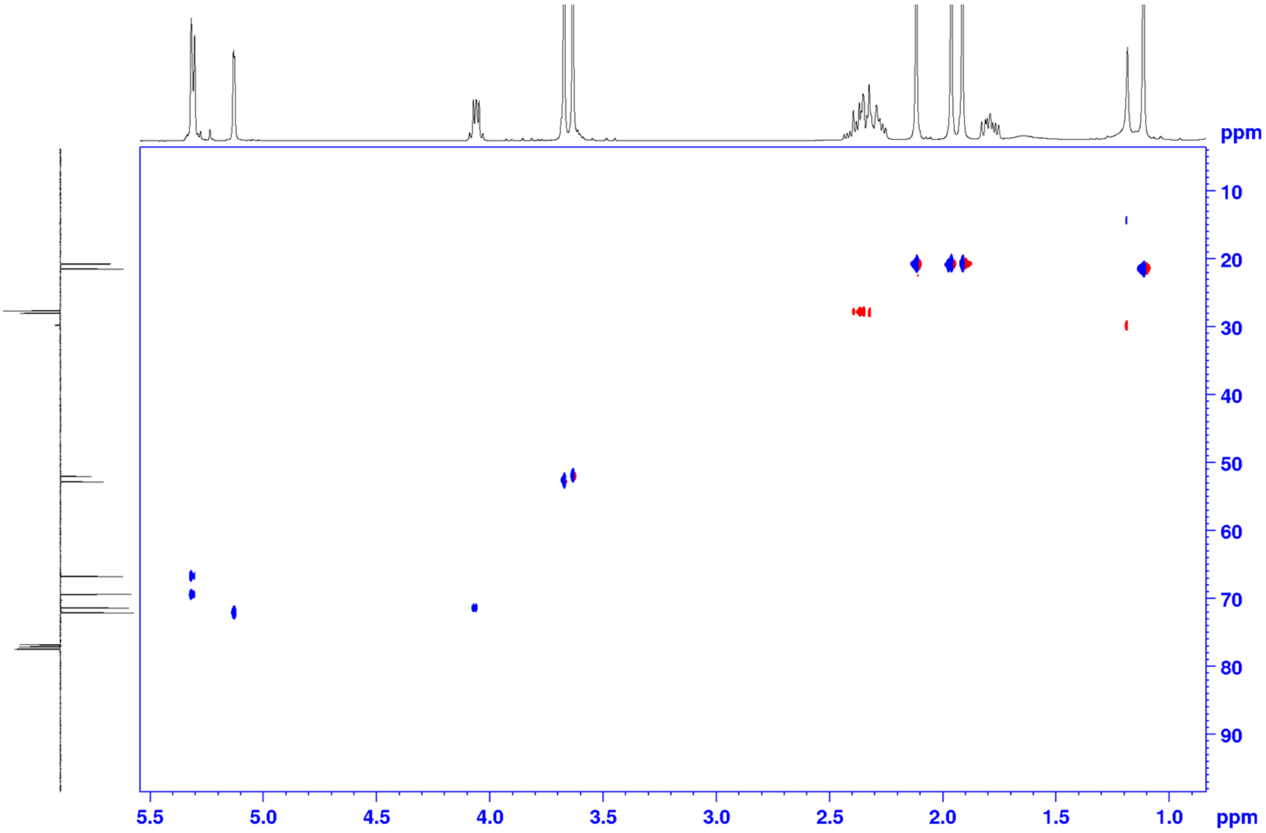
3-βCO$_2$Me: ^{13}C NMR APT (100 MHz, CDCl$_3$)



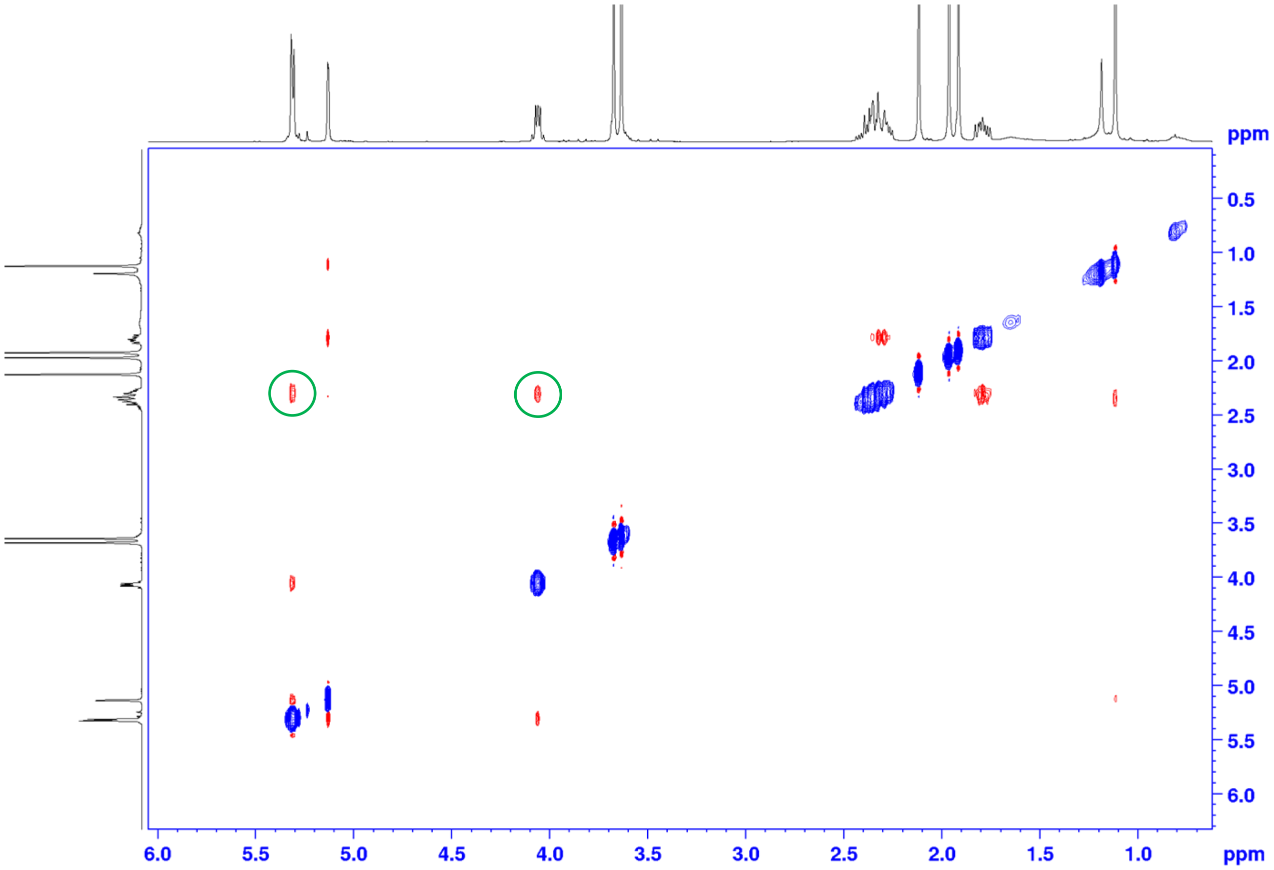
3-βCO₂Me: COSY (400 MHz, CDCl₃)

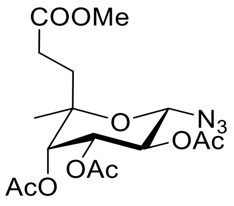


3-βCO₂Me: HSQC (400 MHz, CDCl₃)



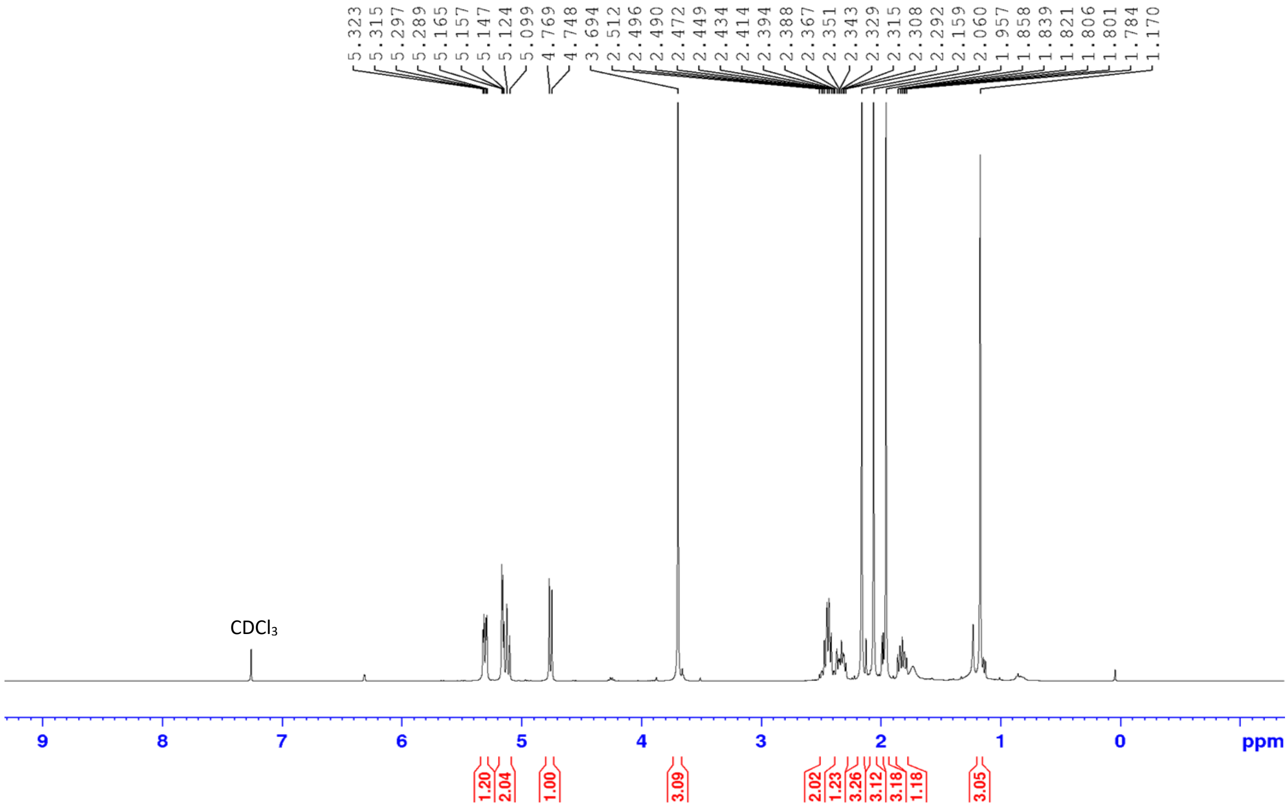
3-βCO$_2$Me: NOESY (400 MHz, CDCl$_3$)



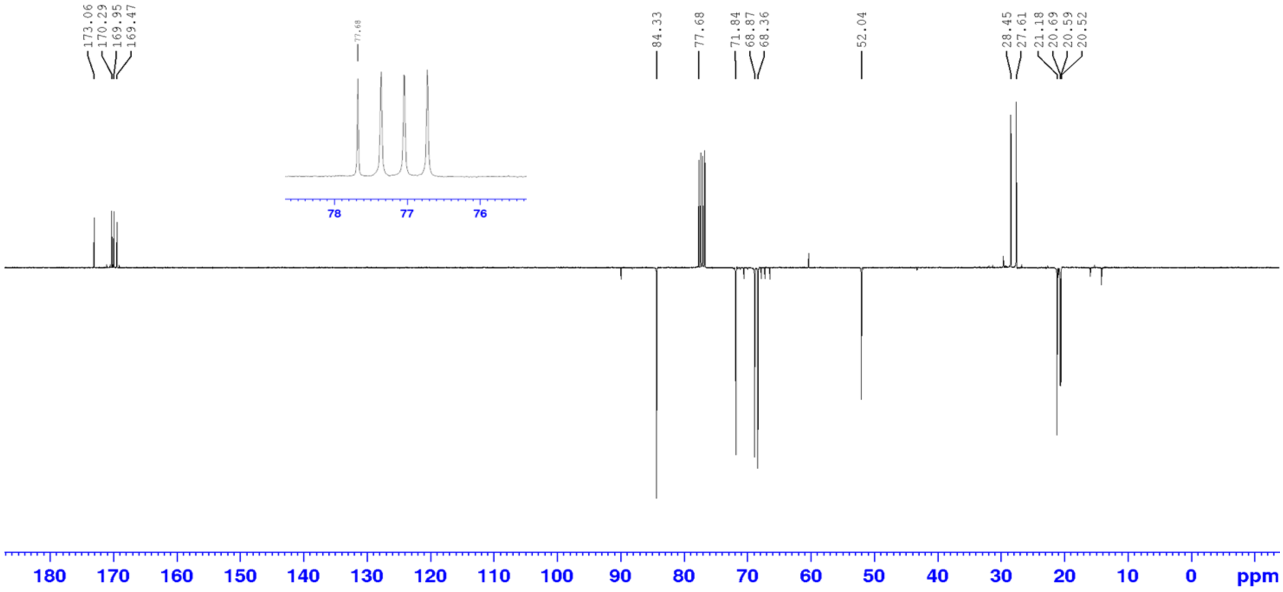


3-βN$_3$

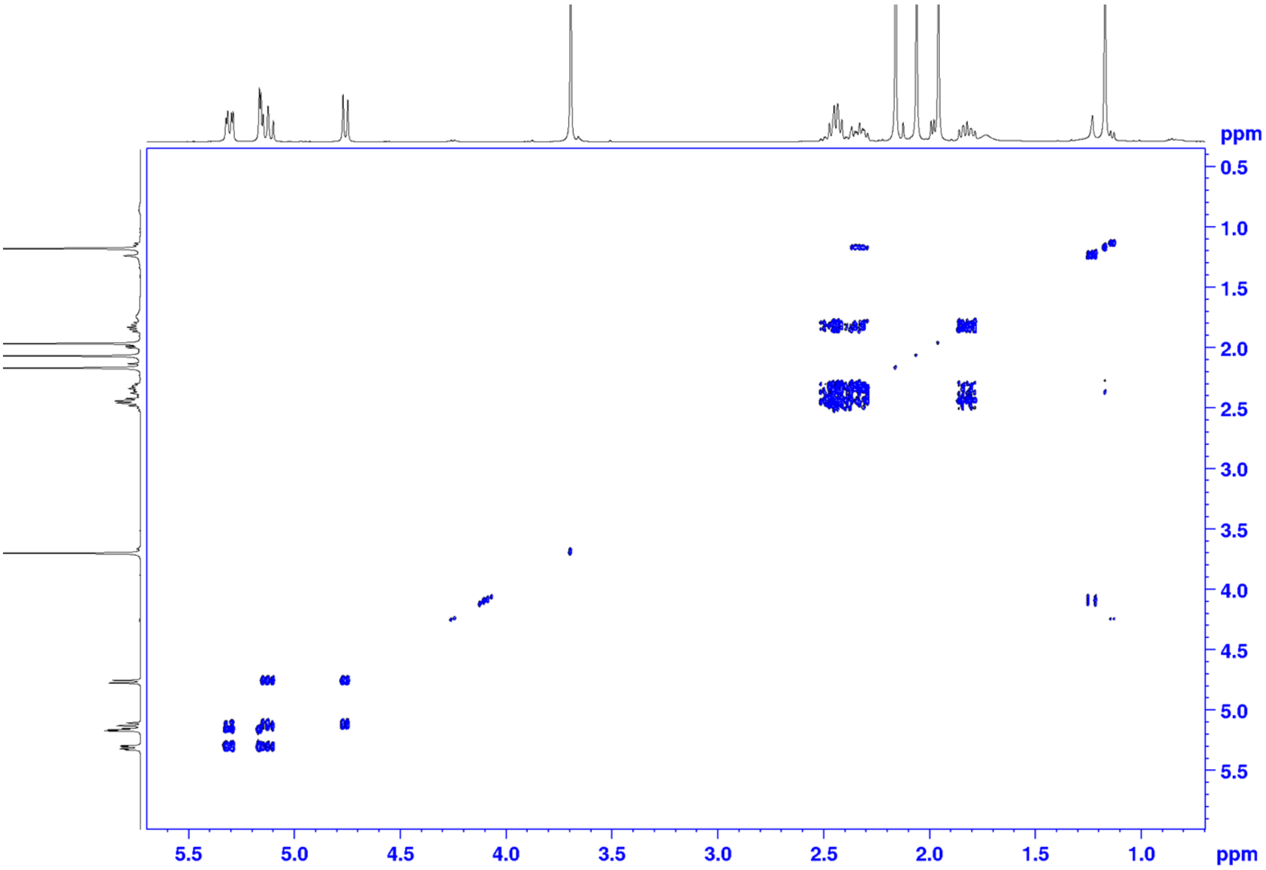
3-βN$_3$: ^{1}H NMR (400 MHz, CDCl$_3$)



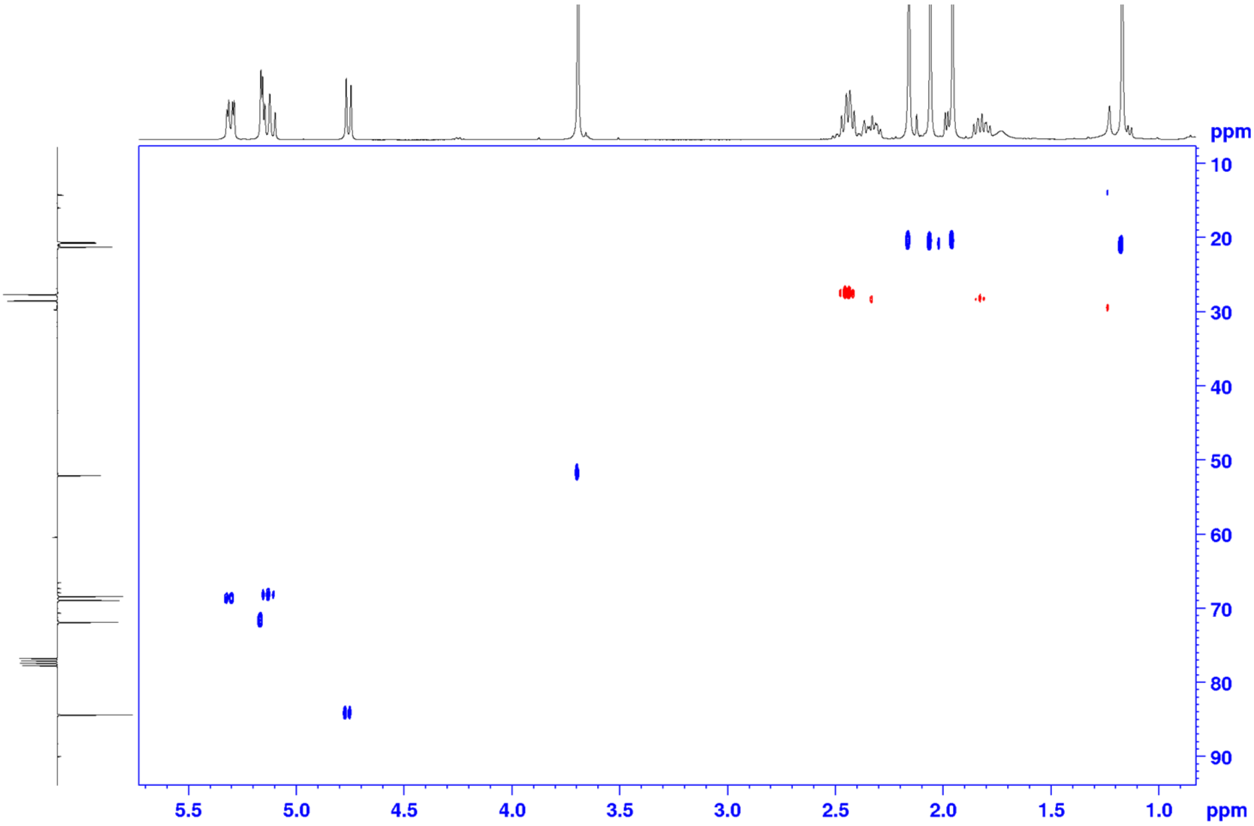
3-βN$_3$: ^{13}C NMR APT (100 MHz, CDCl$_3$)



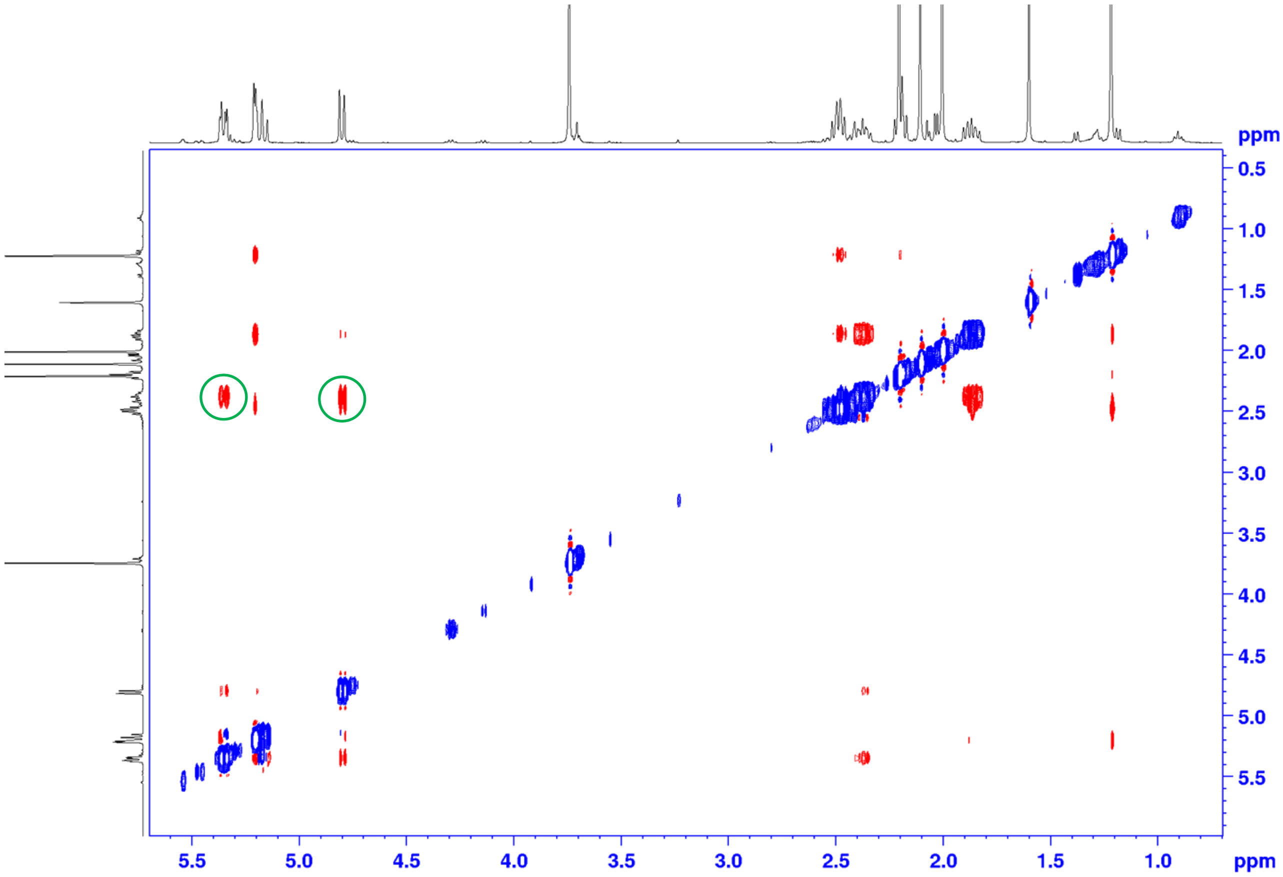
3-βN$_3$: COSY (400 MHz, CDCl$_3$)

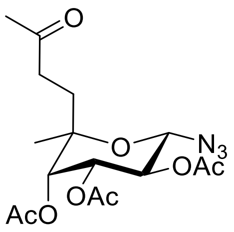


3-βN$_3$: HSQC (400 MHz, CDCl$_3$)



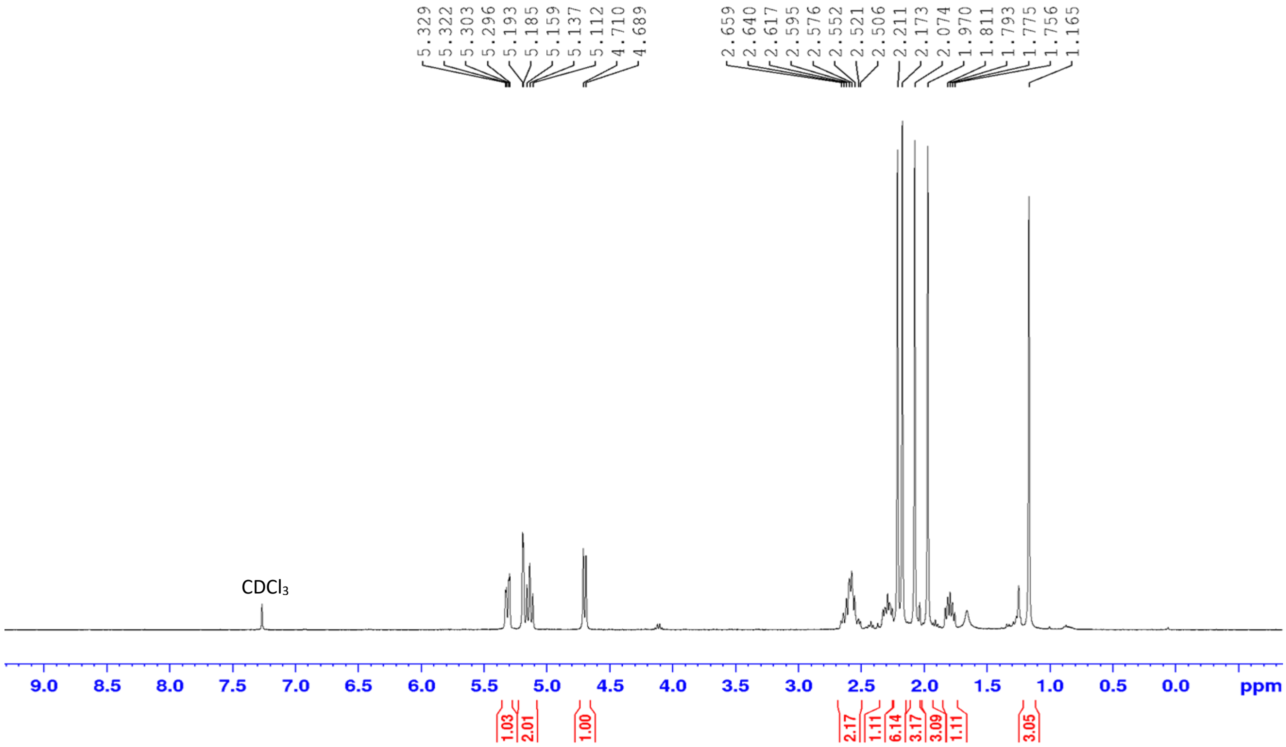
3-βN$_3$: NOESY (400 MHz, CDCl$_3$)



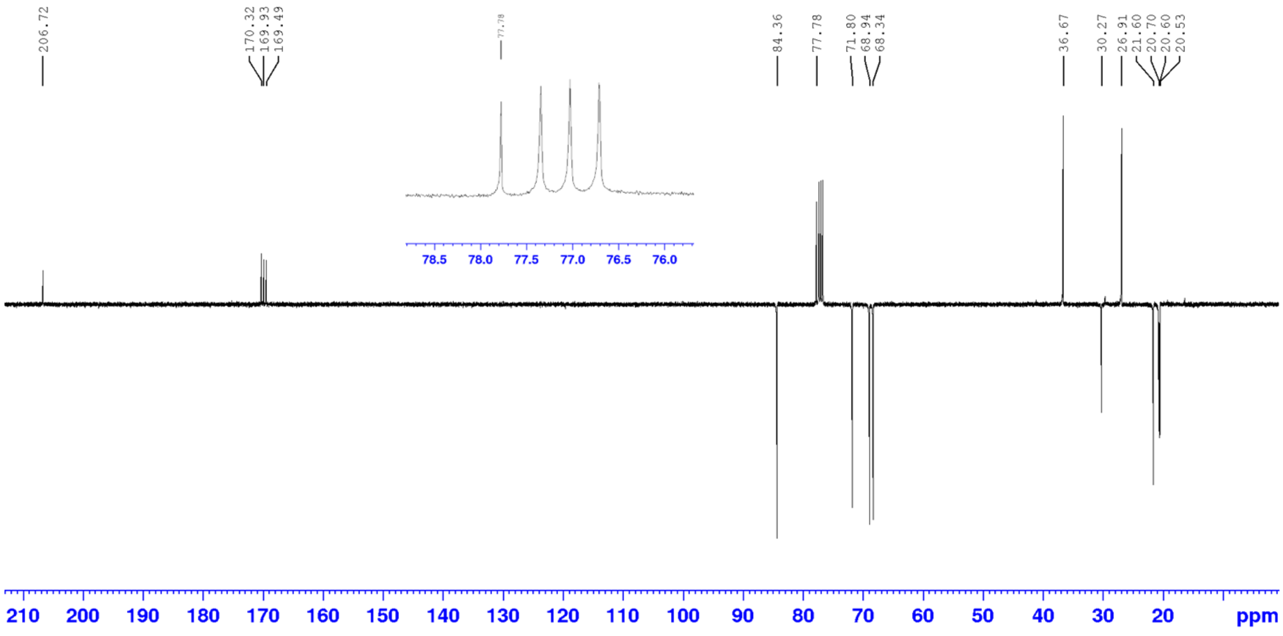


4-βN_3

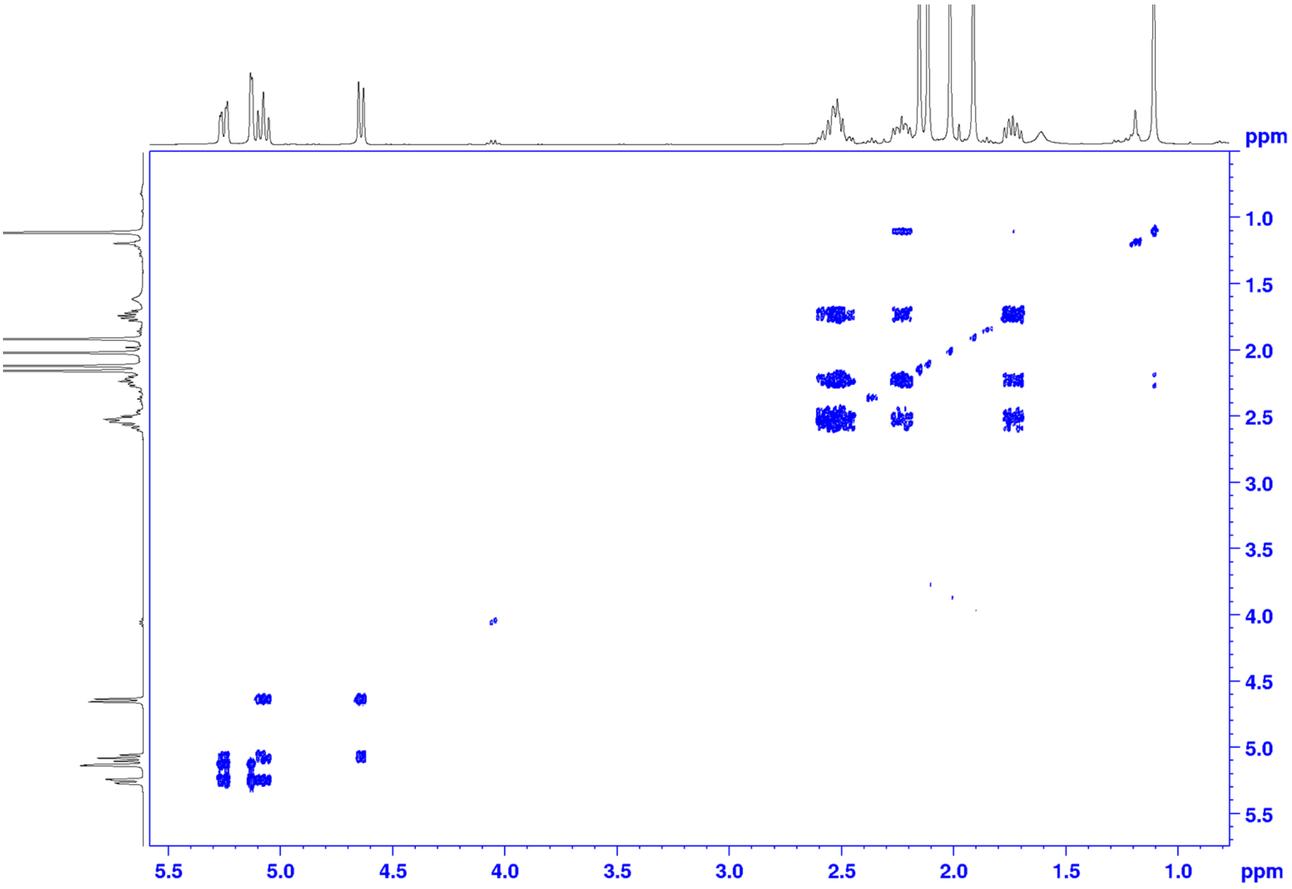
4-βN_3: ^{1}H NMR (400 MHz, $CDCl_3$)



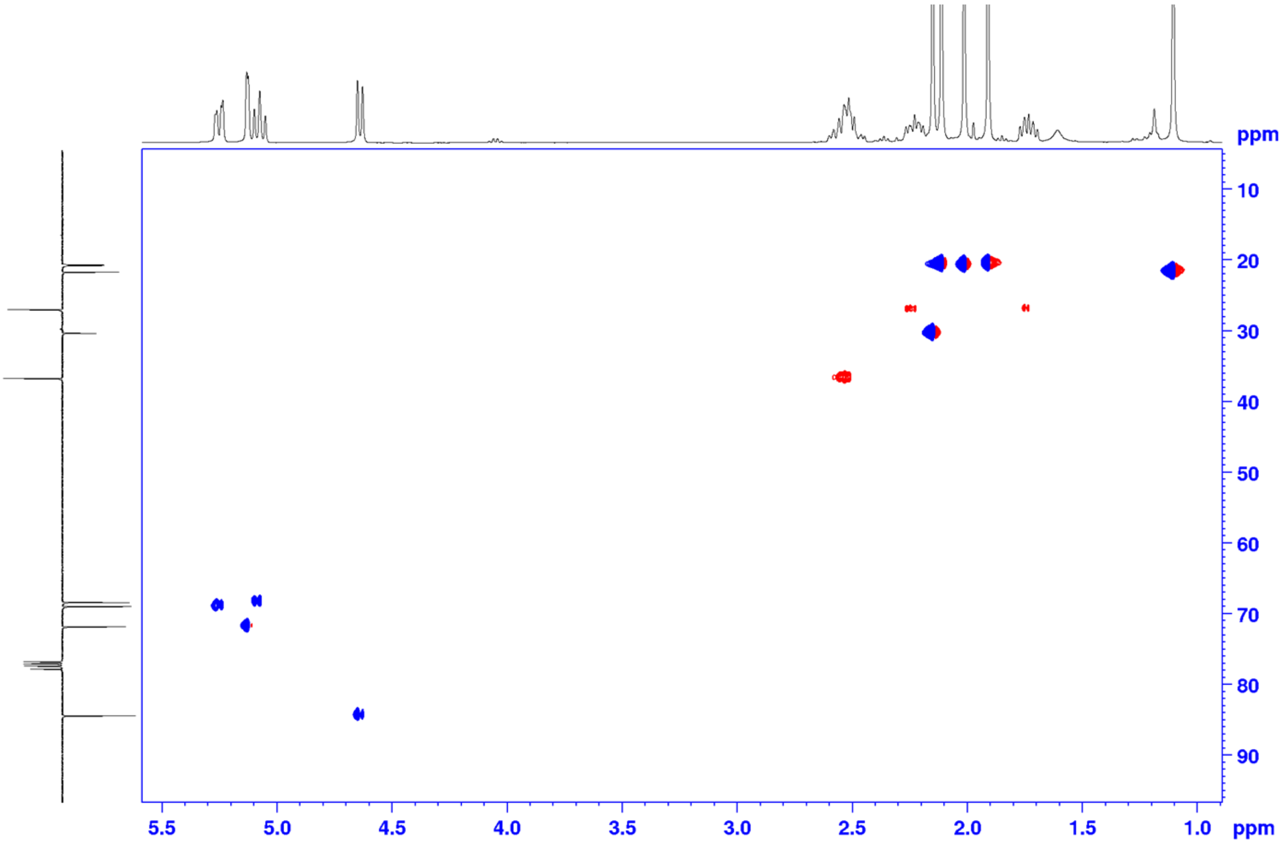
4-βN_3: ^{13}C NMR APT (100 MHz, $CDCl_3$)



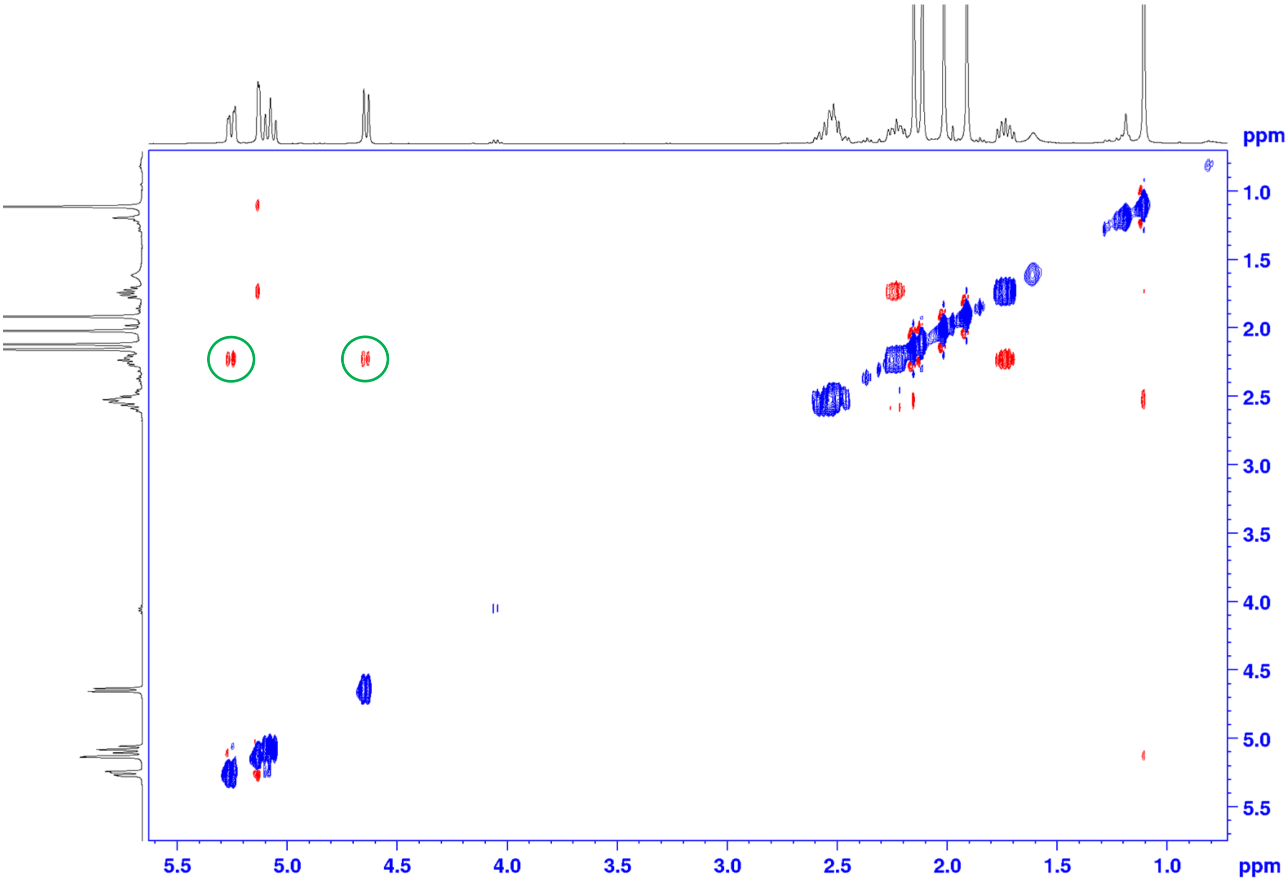
4-βN$_3$: COSY (400 MHz, CDCl$_3$)

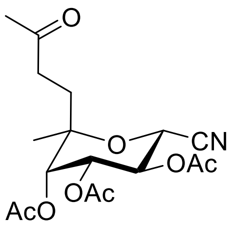


4-βN$_3$: HSQC (400 MHz, CDCl$_3$)



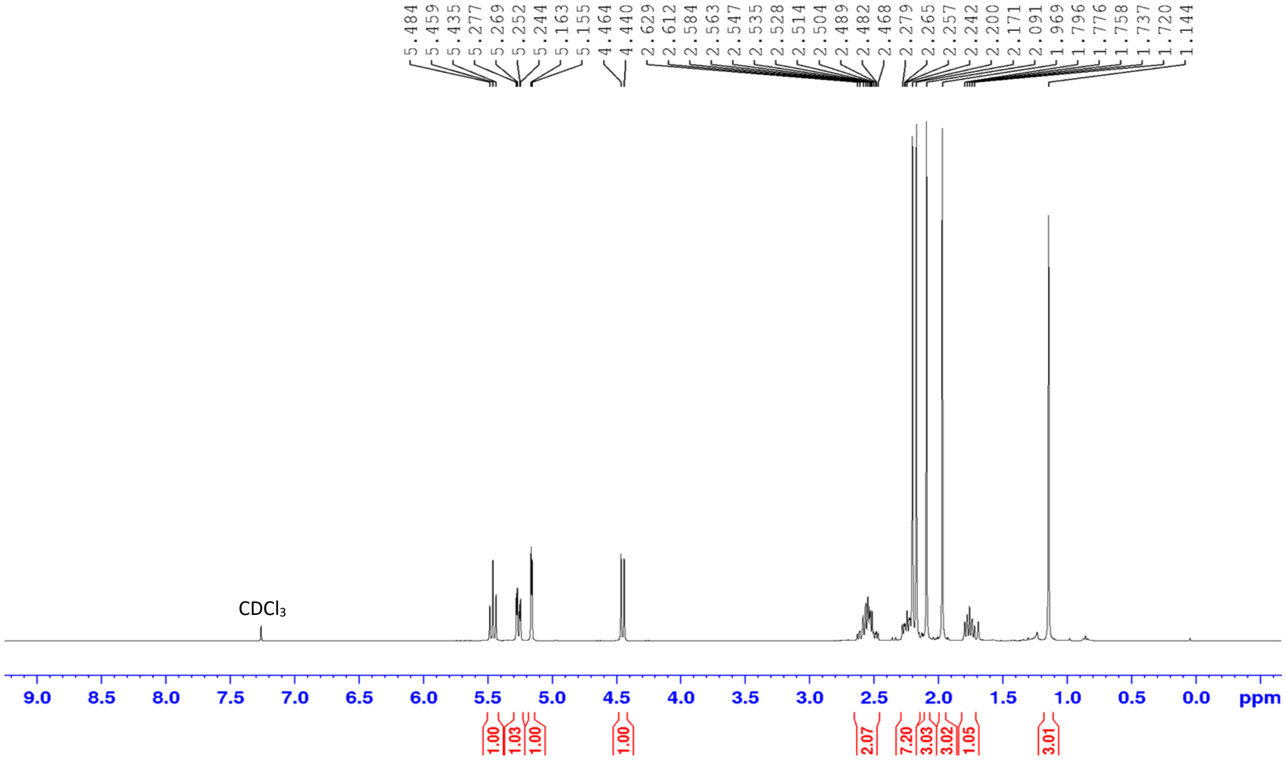
4-βN_3: NOESY (400 MHz, $CDCl_3$)



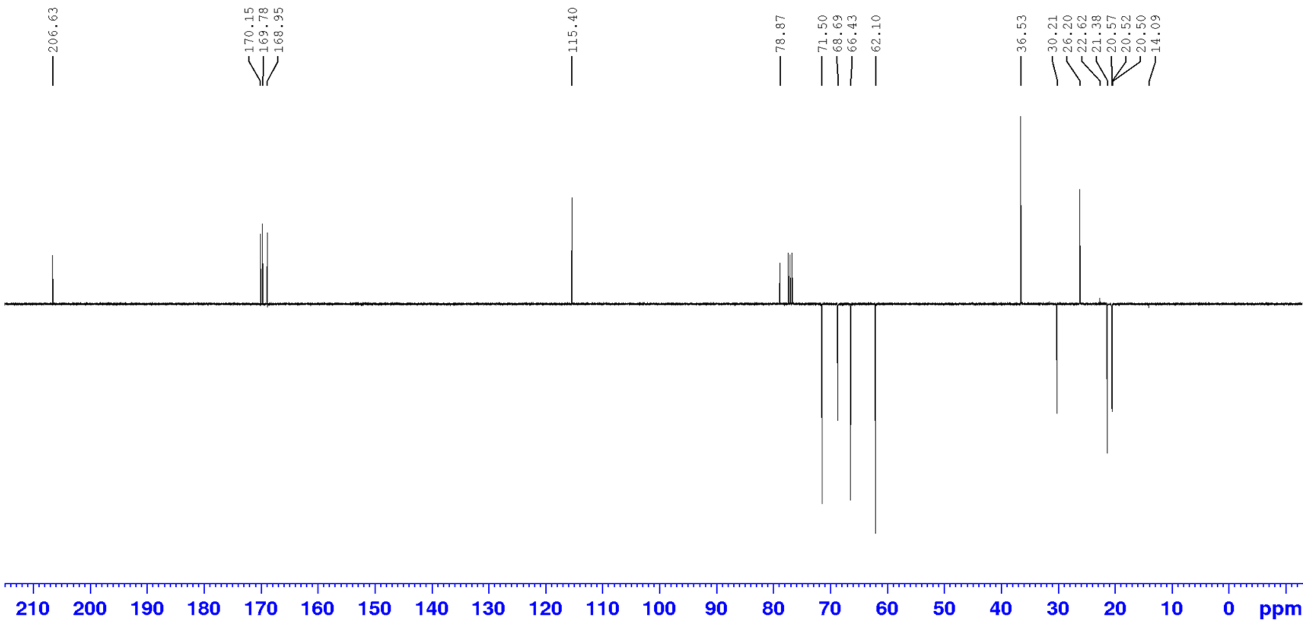


4-βCN

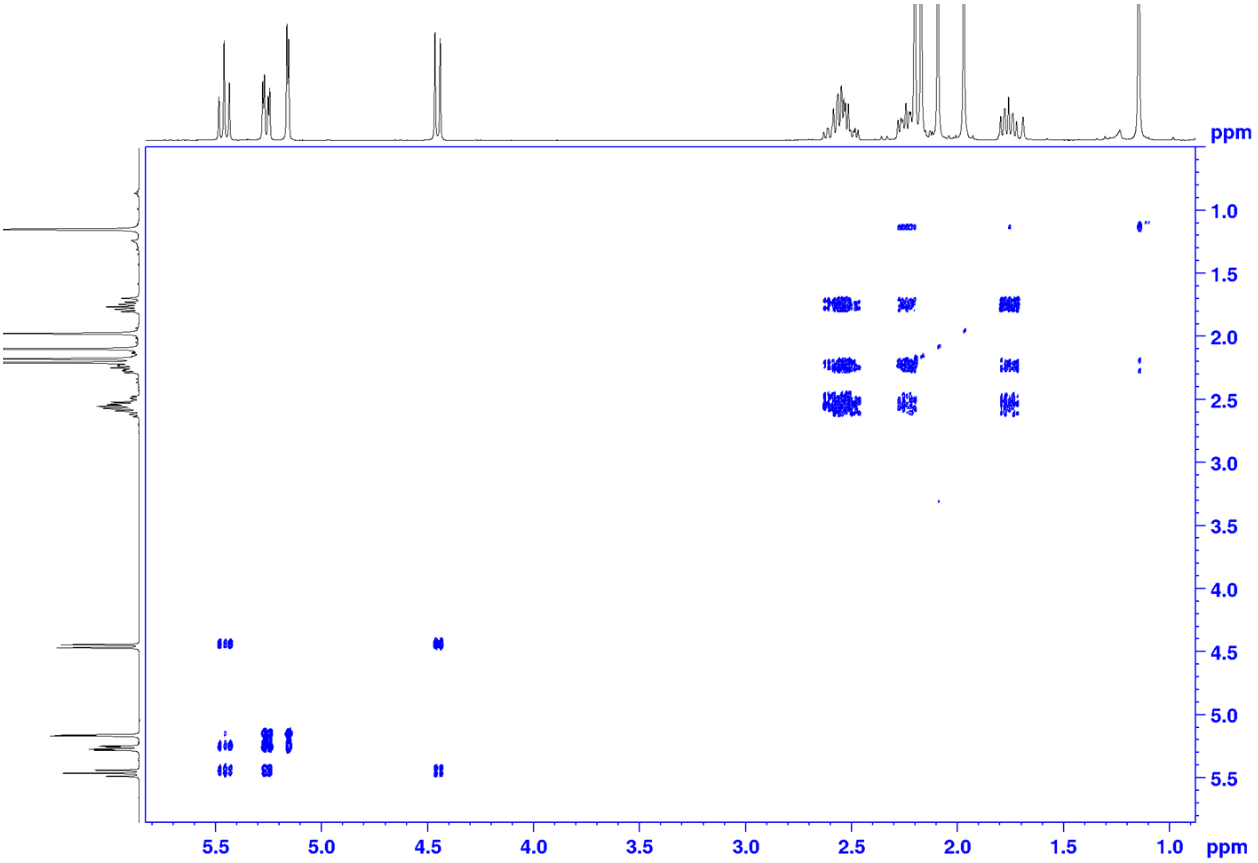
4-βCN: ^{1}H NMR (400 MHz, $CDCl_3$)



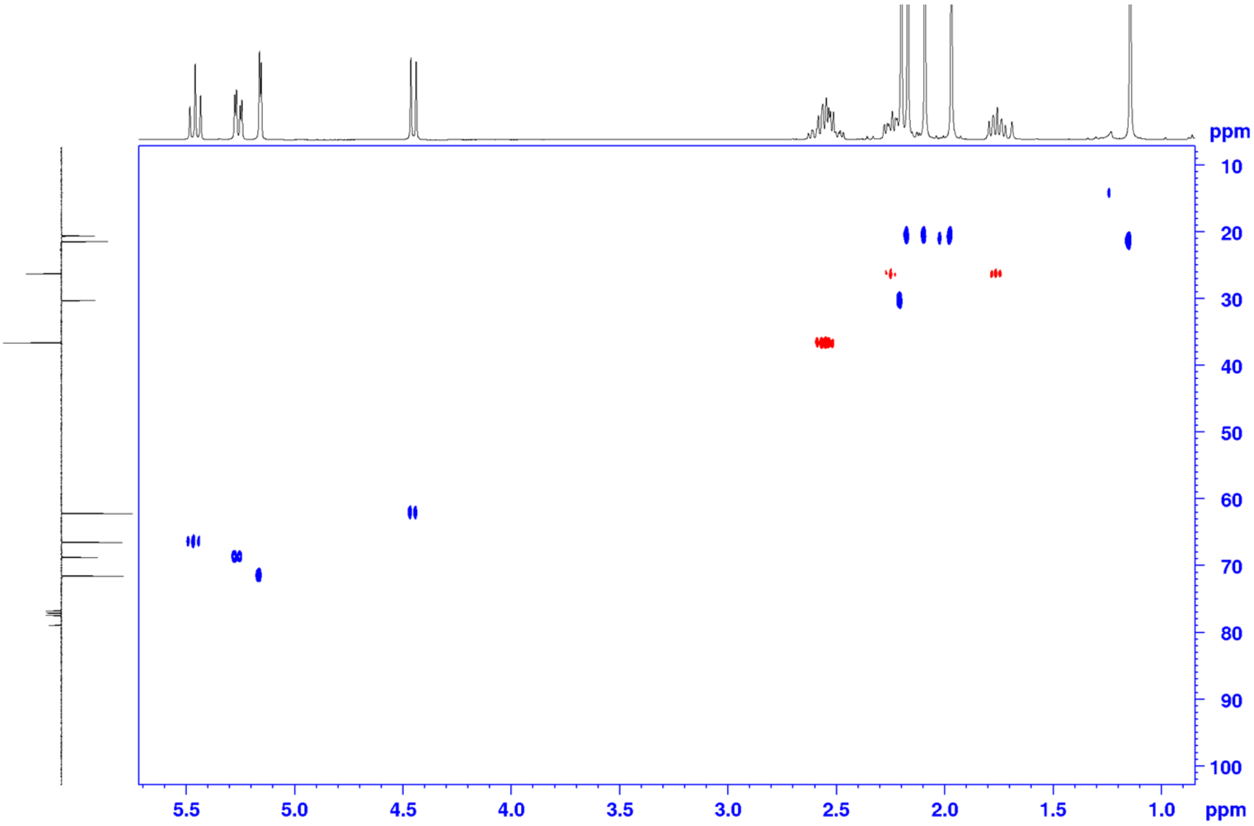
4-βCN: ^{13}C NMR APT (100 MHz, $CDCl_3$)



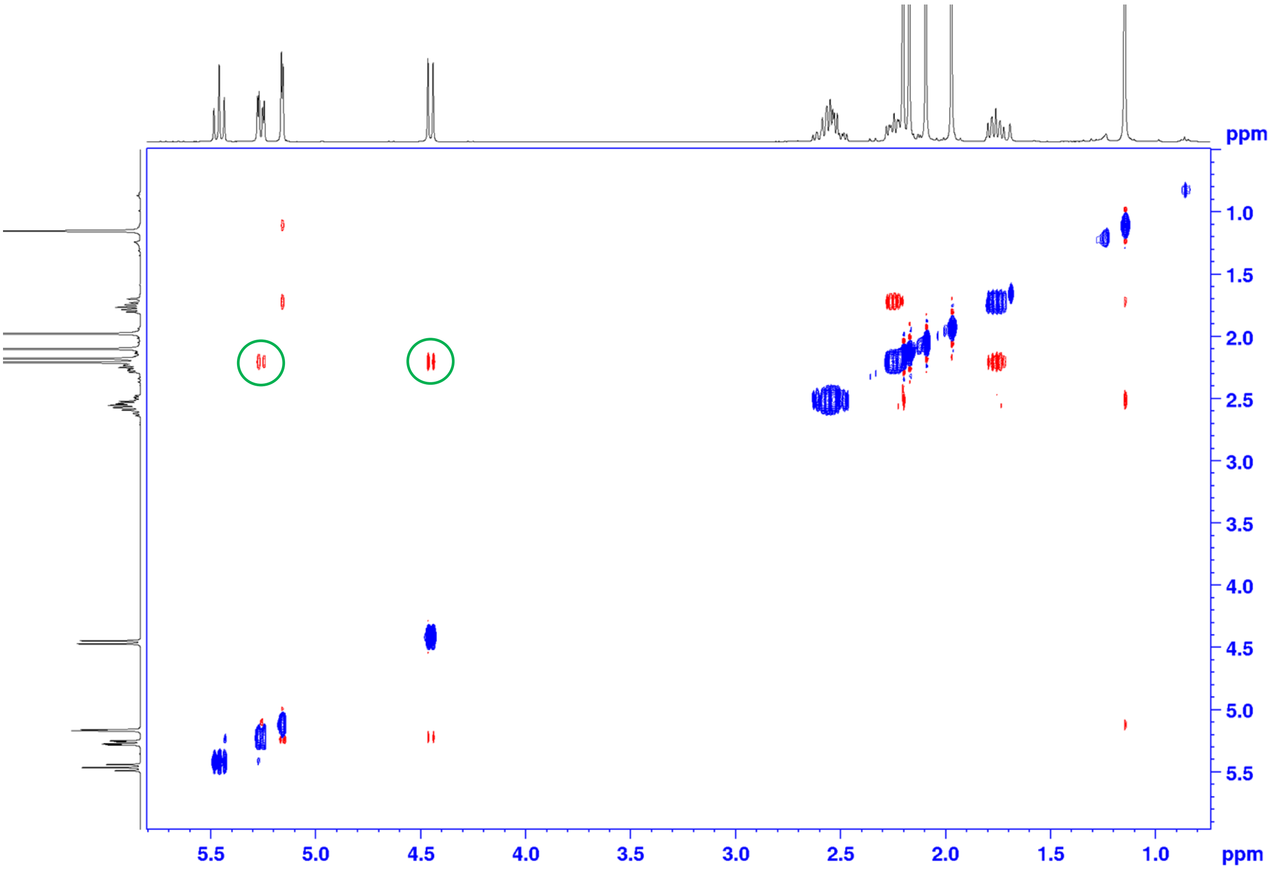
4-βCN: COSY (400 MHz, CDCl$_3$)

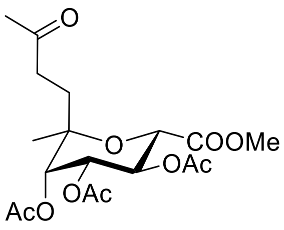


4-βCN: HSQC (400 MHz, CDCl$_3$)



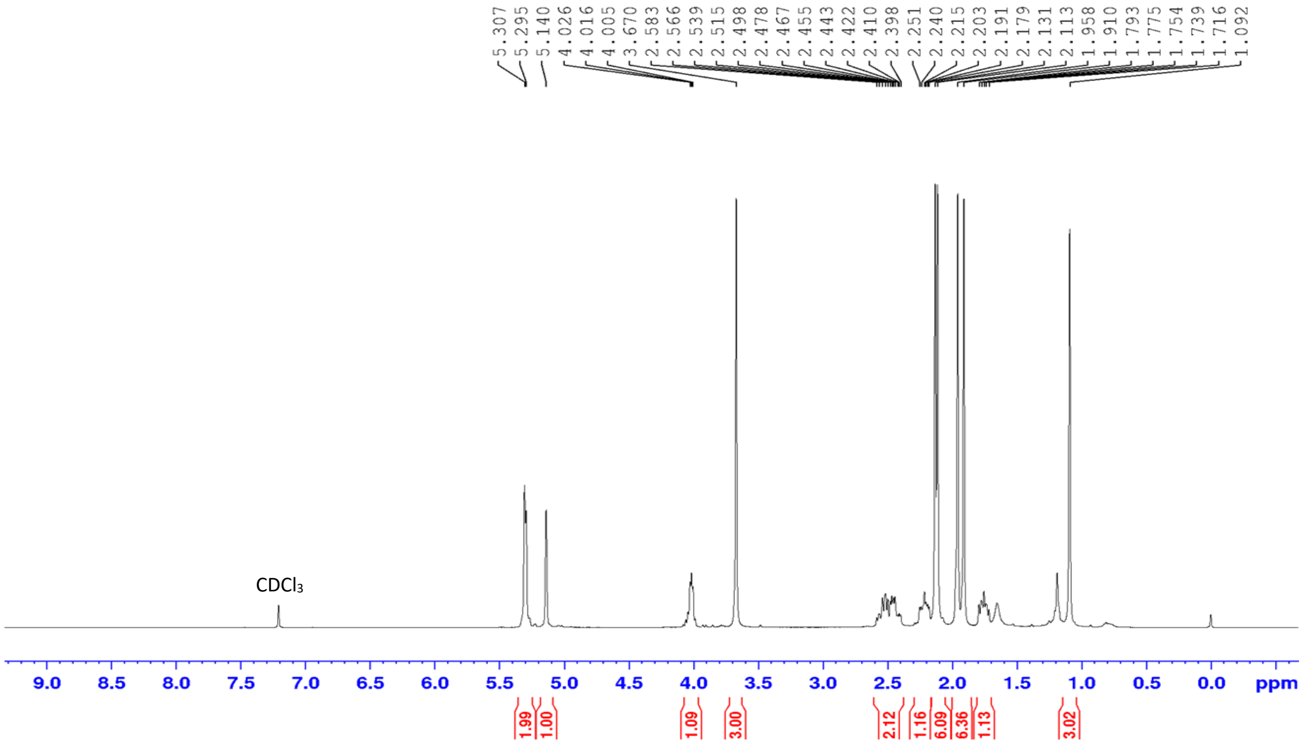
4-βCN: NOESY (400 MHz, $CDCl_3$)



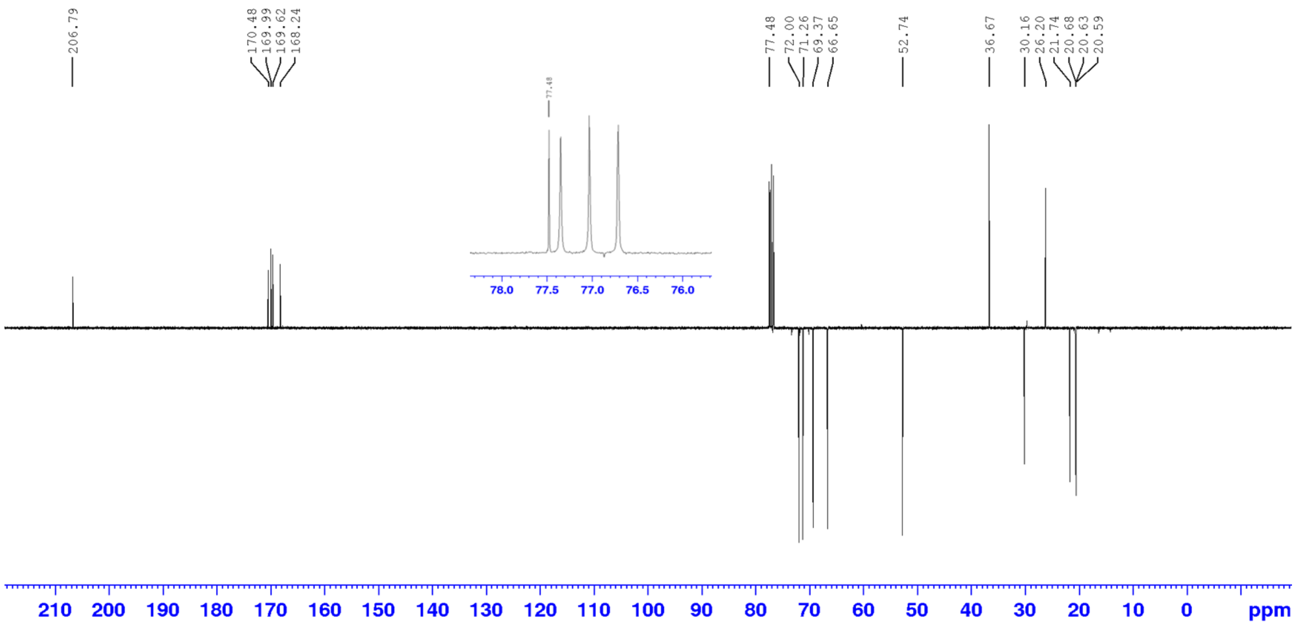


4-βCO$_2$Me

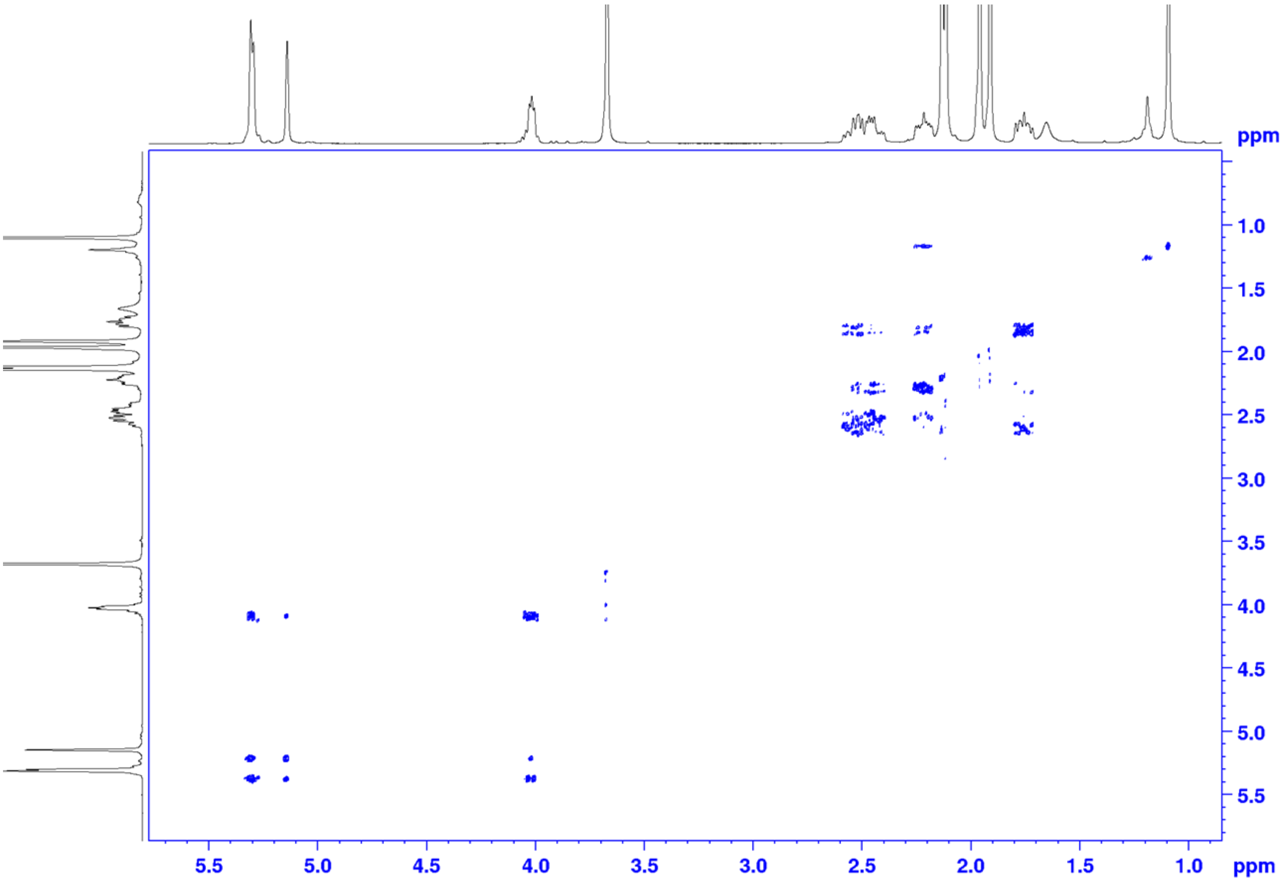
4-βCO$_2$Me: ^{1}H NMR (400 MHz, CDCl$_3$)



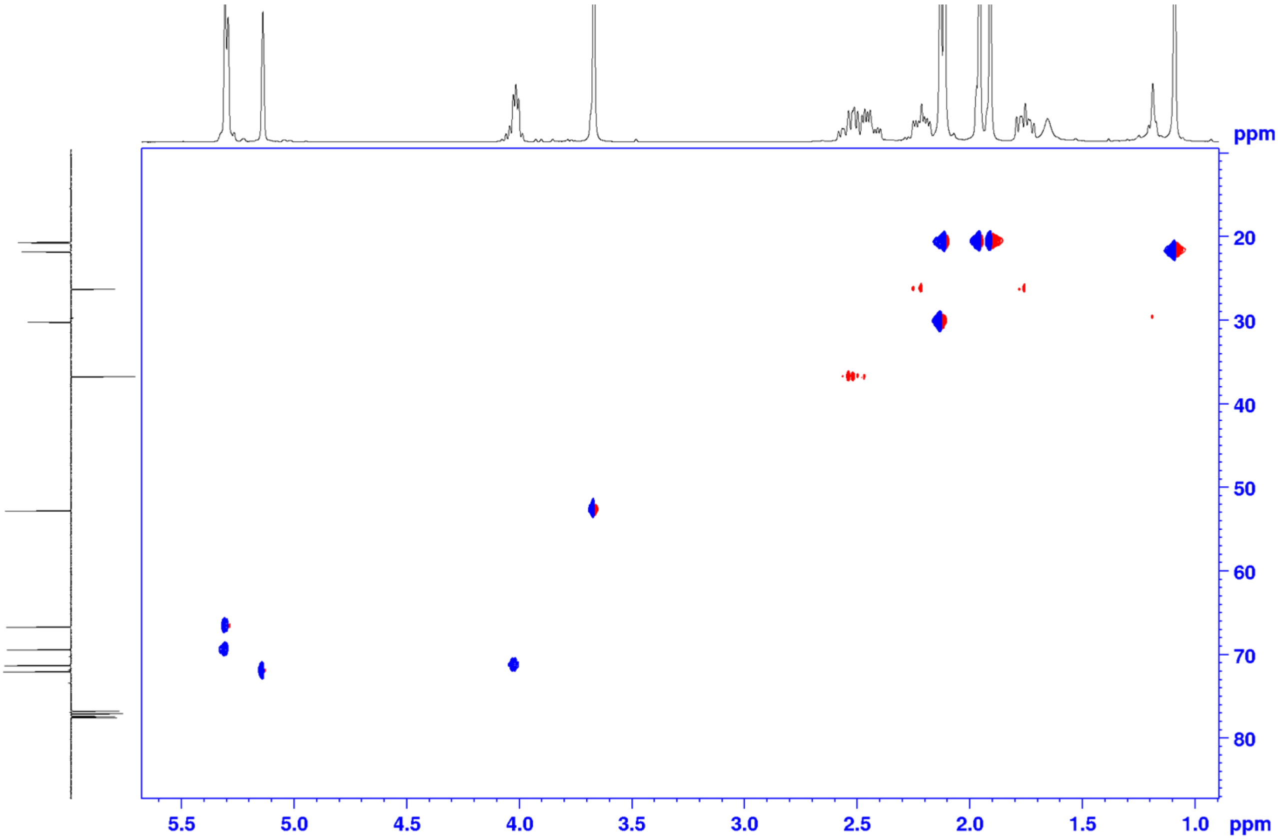
4-βCO$_2$Me: ^{13}C NMR APT (100 MHz, CDCl$_3$)



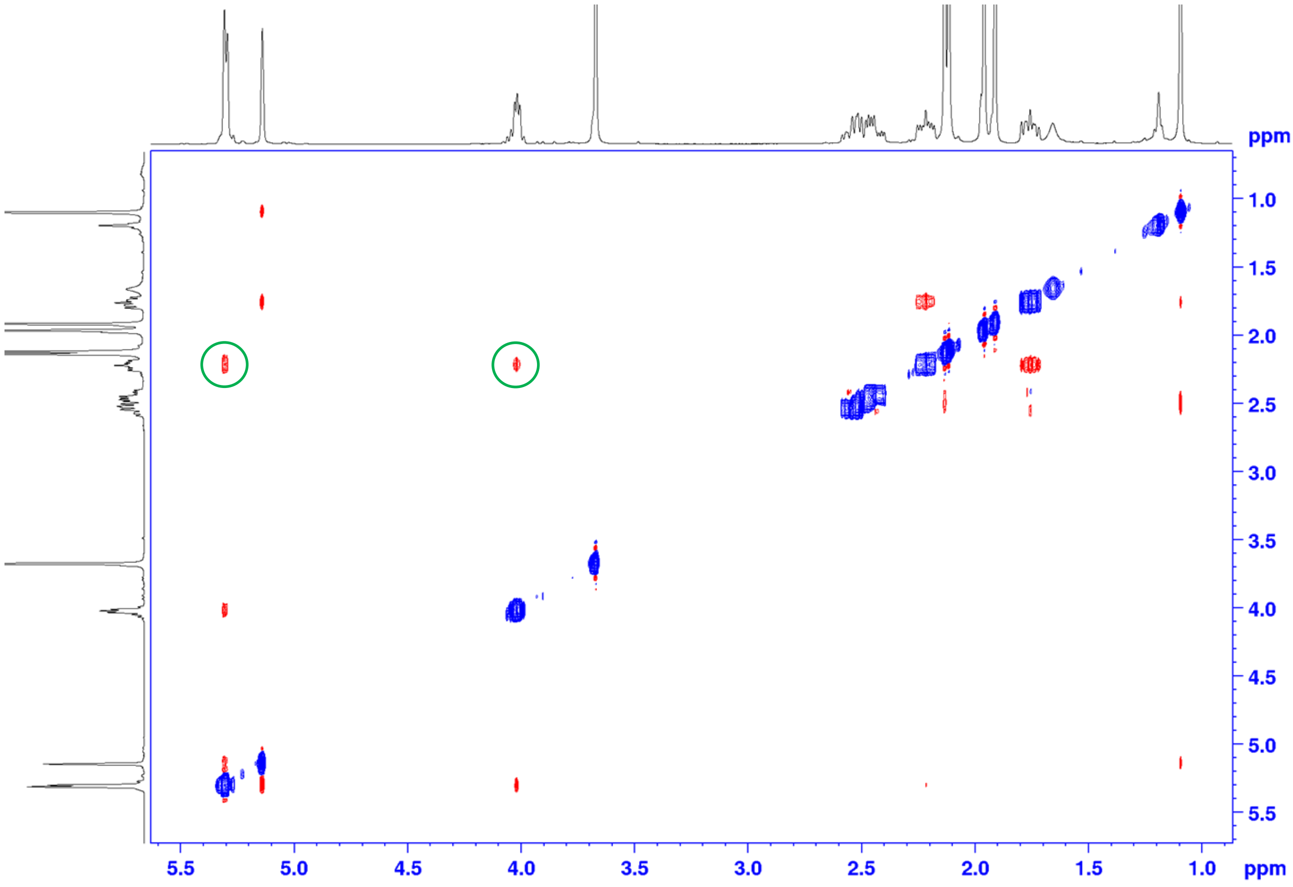
4-βCO₂Me: COSY (400 MHz, CDCl₃)

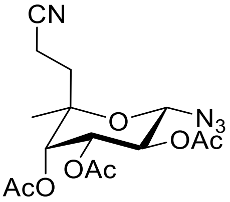


4-βCO₂Me: HSQC (400 MHz, CDCl₃)



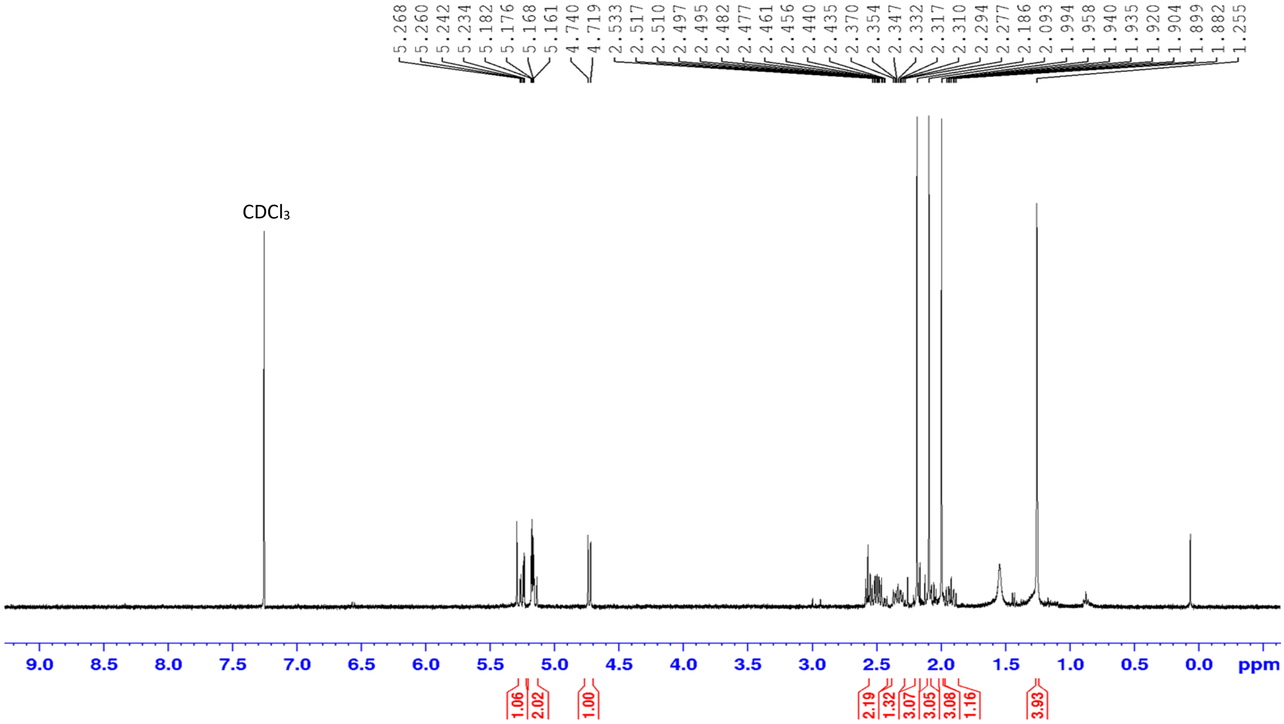
4-βCO$_2$Me: NOESY (400 MHz, CDCl$_3$)



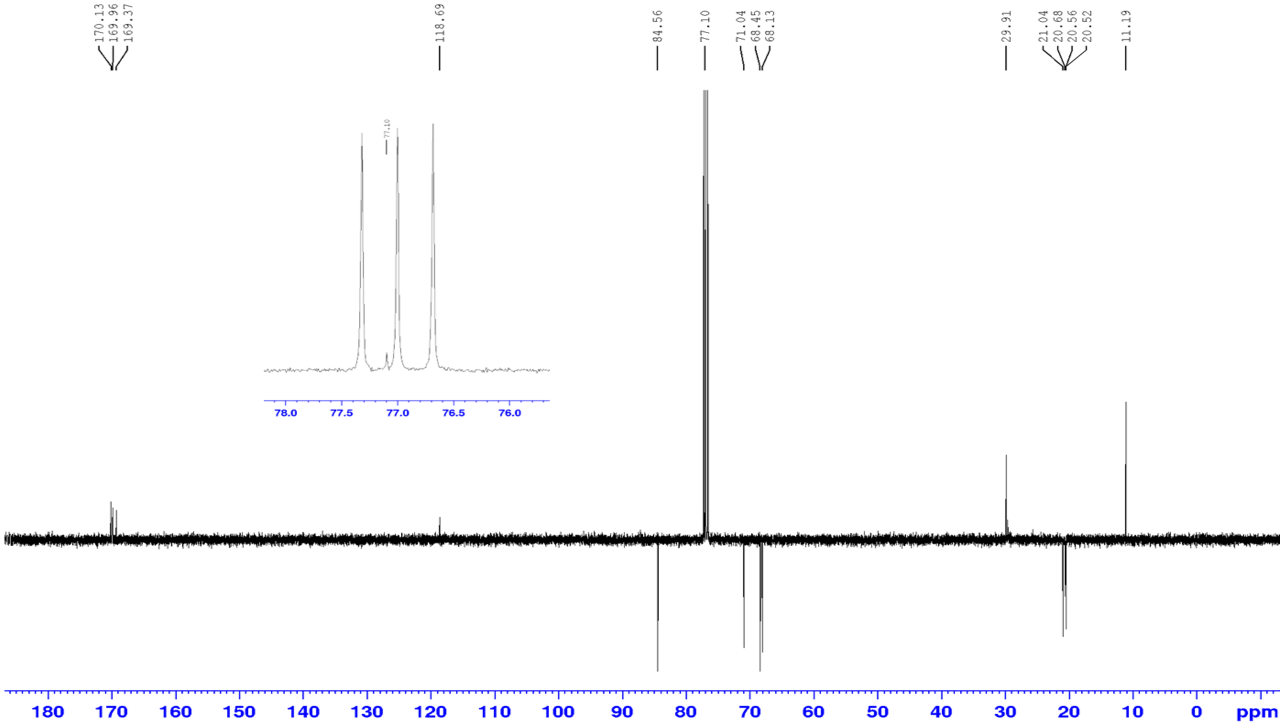


5-βN3

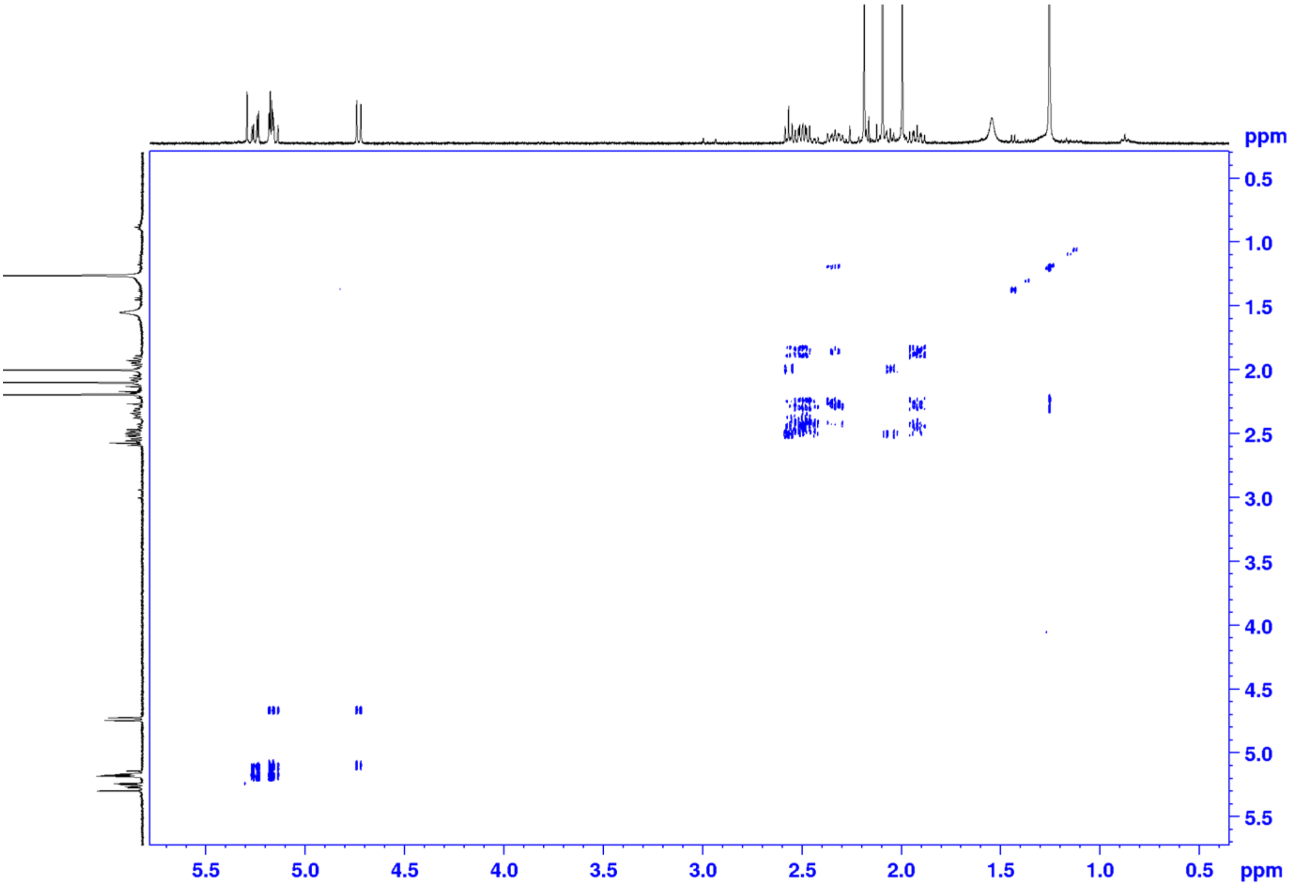
5-βN$_3$: ^{1}H NMR (400 MHz, CDCl$_3$)



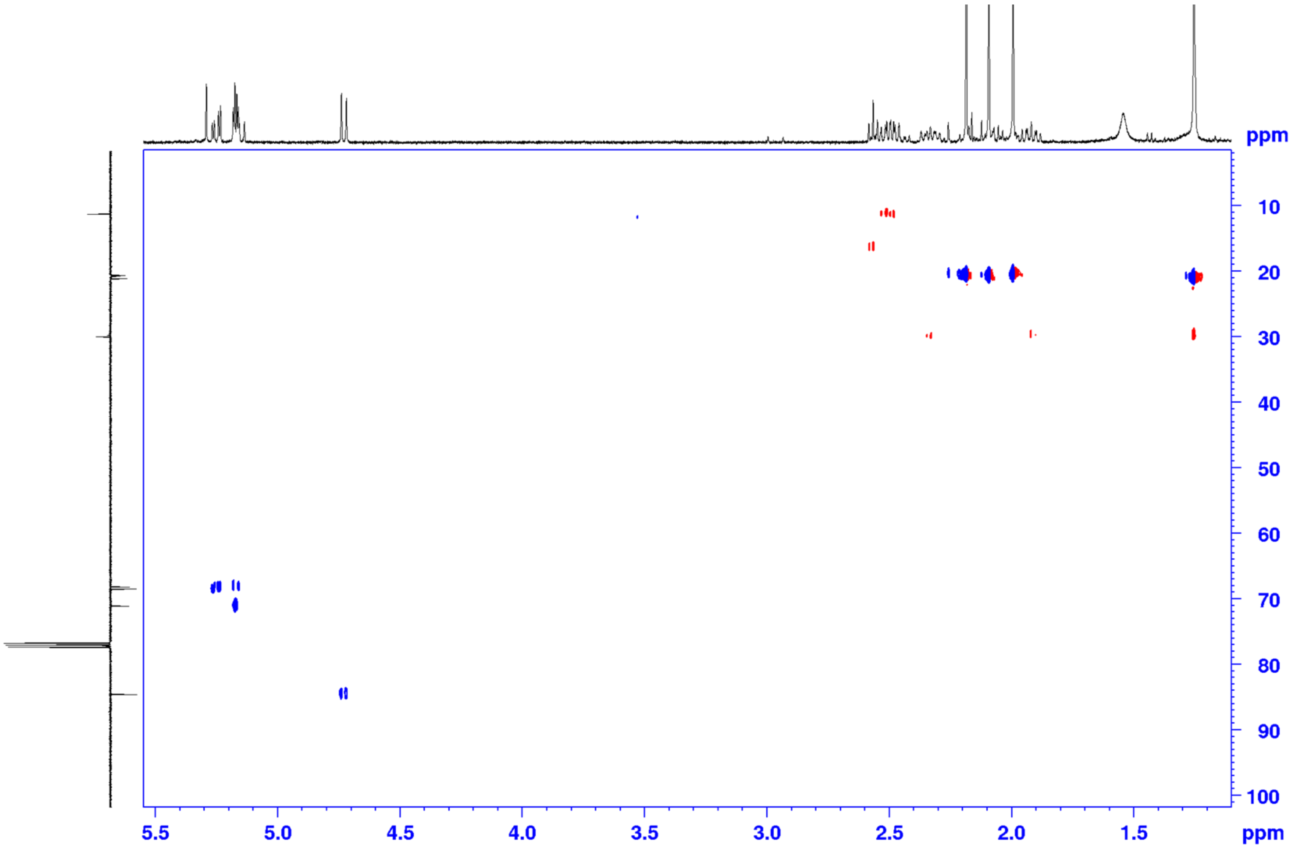
5-βN$_3$: ^{13}C NMR APT (100 MHz, CDCl$_3$)



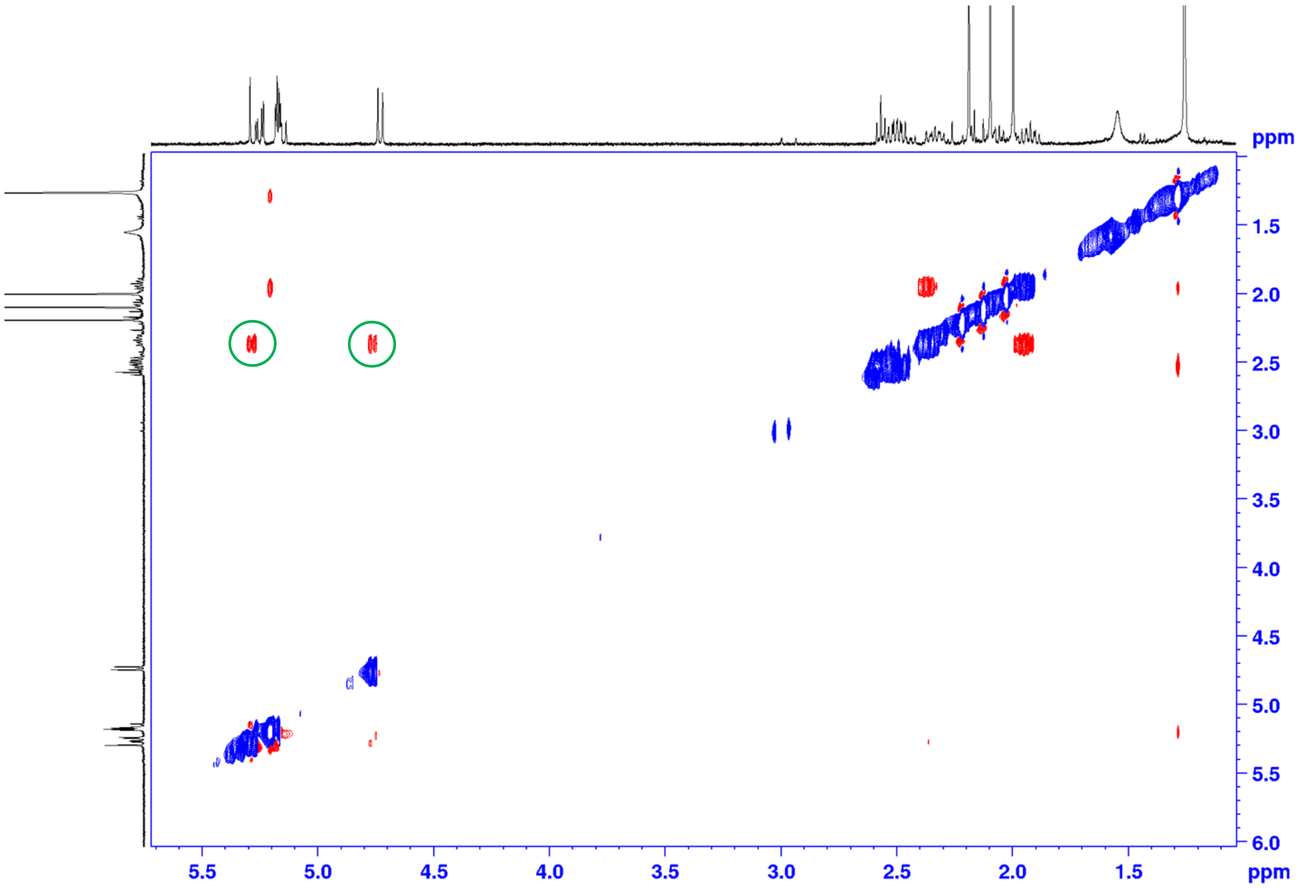
5-βN$_3$: COSY (400 MHz, CDCl$_3$)

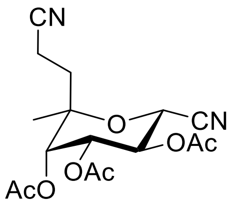


5-βN$_3$: HSQC (400 MHz, CDCl$_3$)



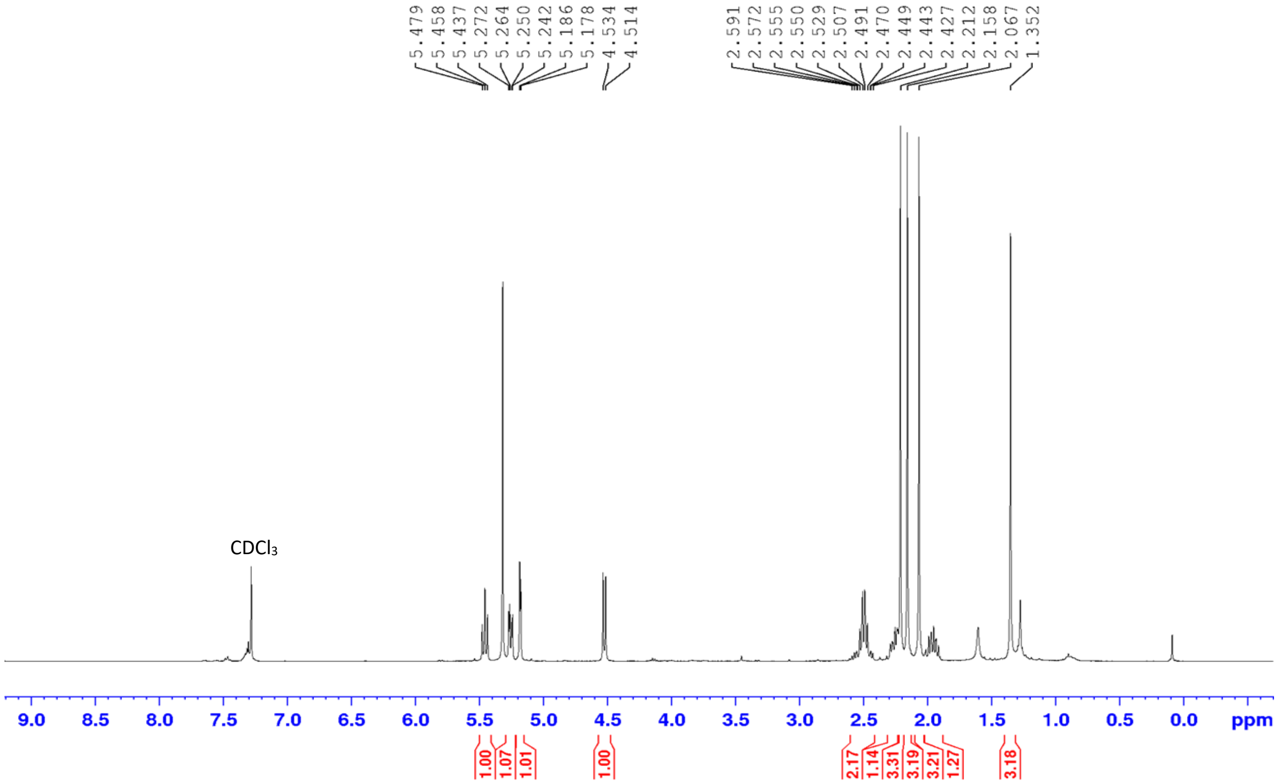
5-βN_3: NOESY (400 MHz, $CDCl_3$)



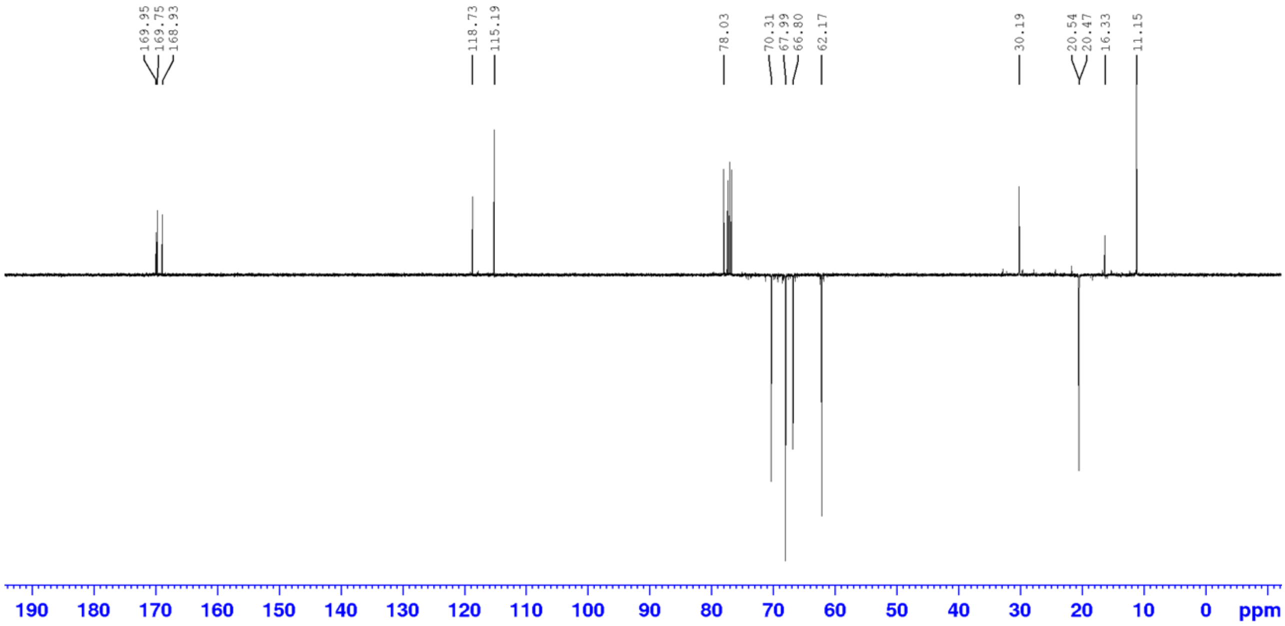


5-βCN

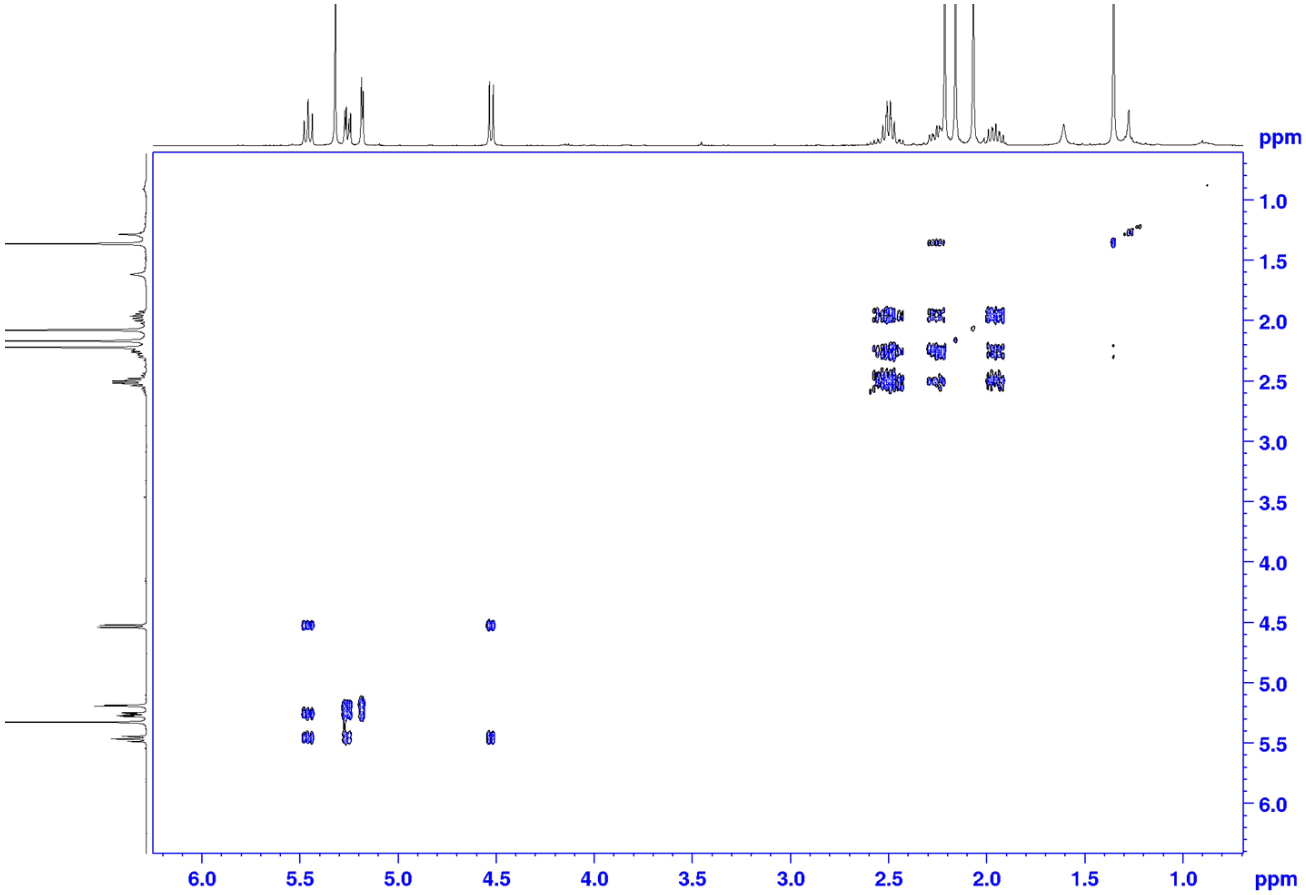
5-βCN: ^{1}H NMR (400 MHz, $CDCl_3$)



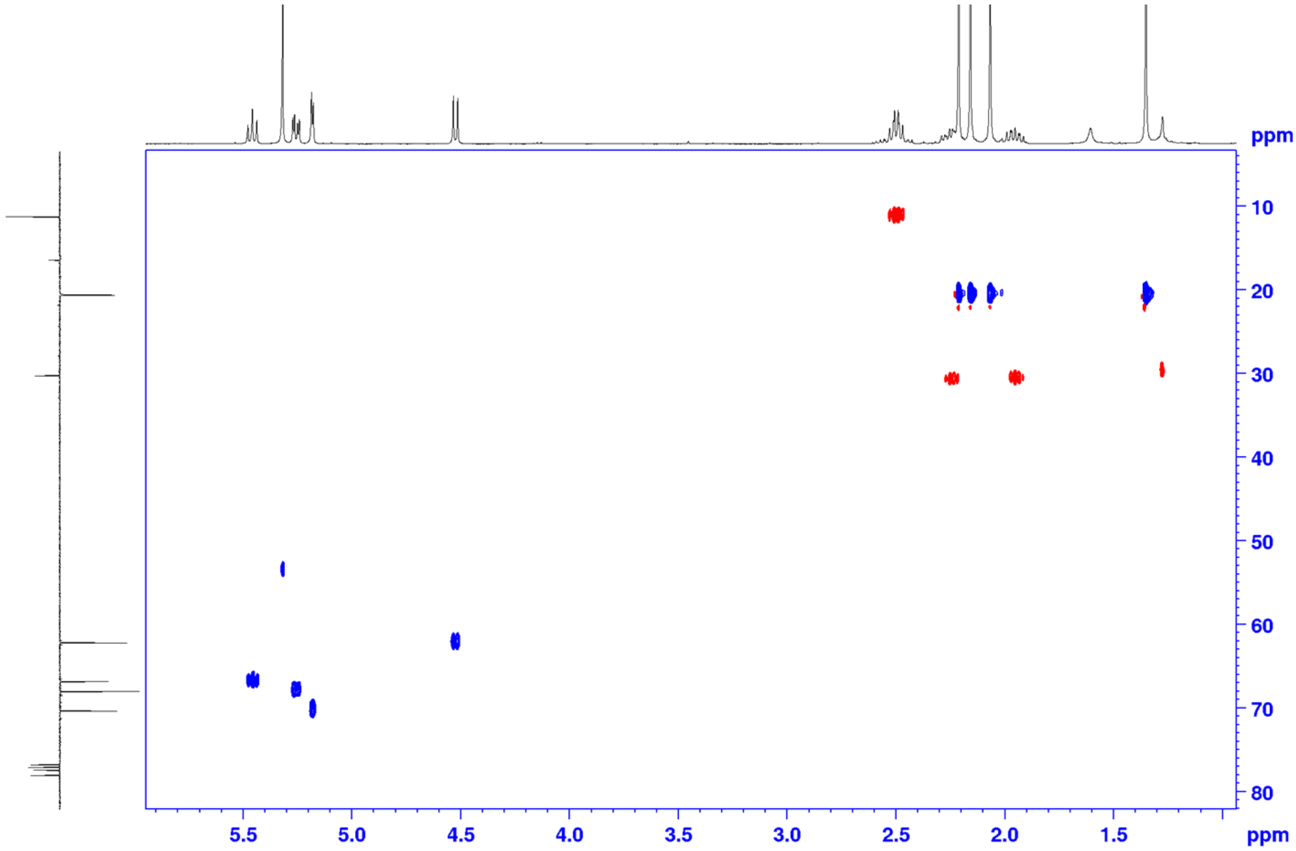
5-βCN: ^{13}C NMR APT (100 MHz, $CDCl_3$)



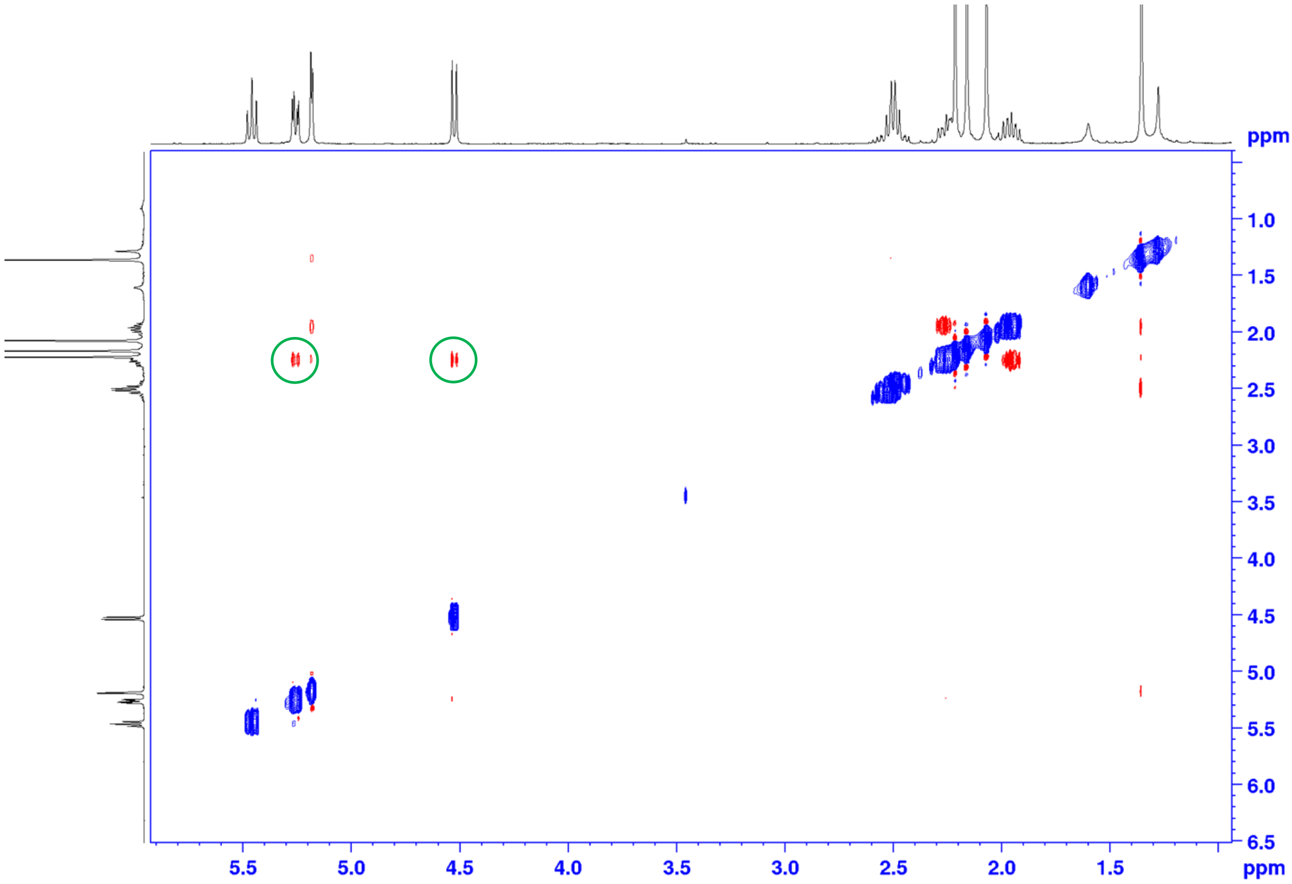
5-βCN: COSY (400 MHz, $CDCl_3$)

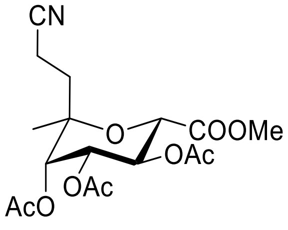


5-βCN: HSQC (400 MHz, $CDCl_3$)



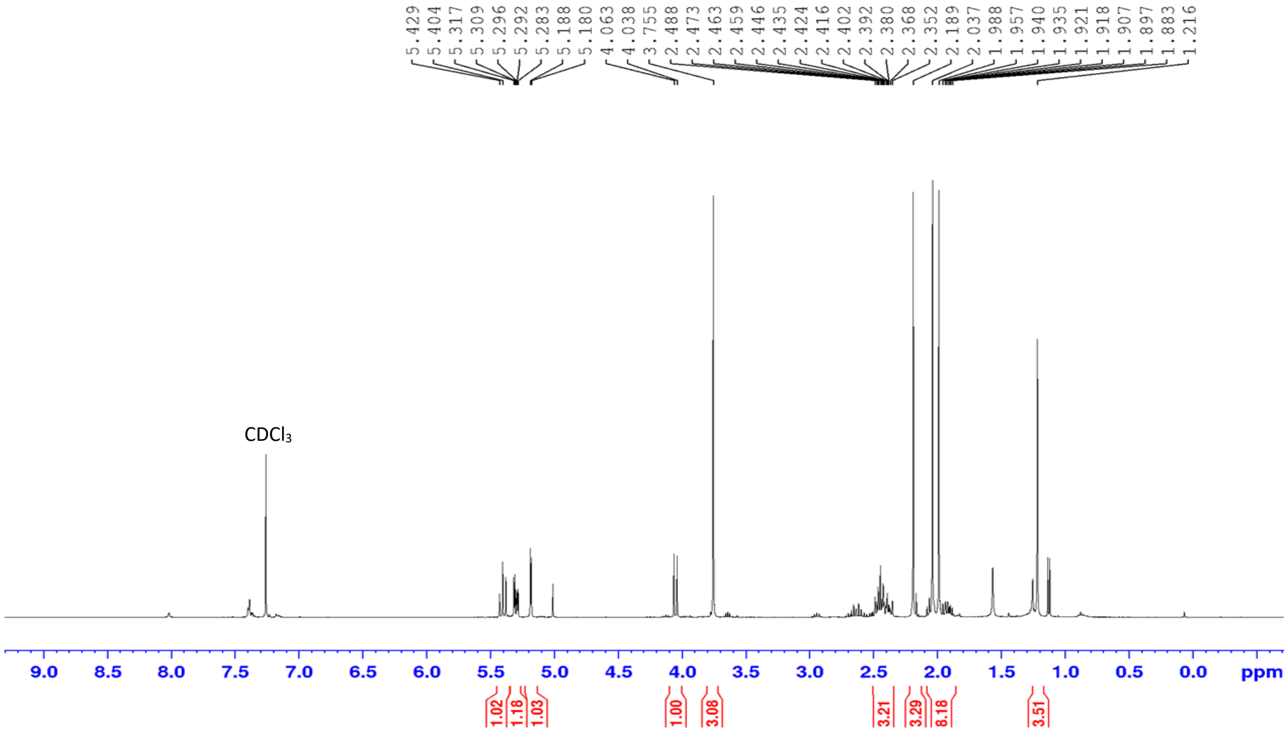
5-βCN: NOESY (400 MHz, $CDCl_3$)



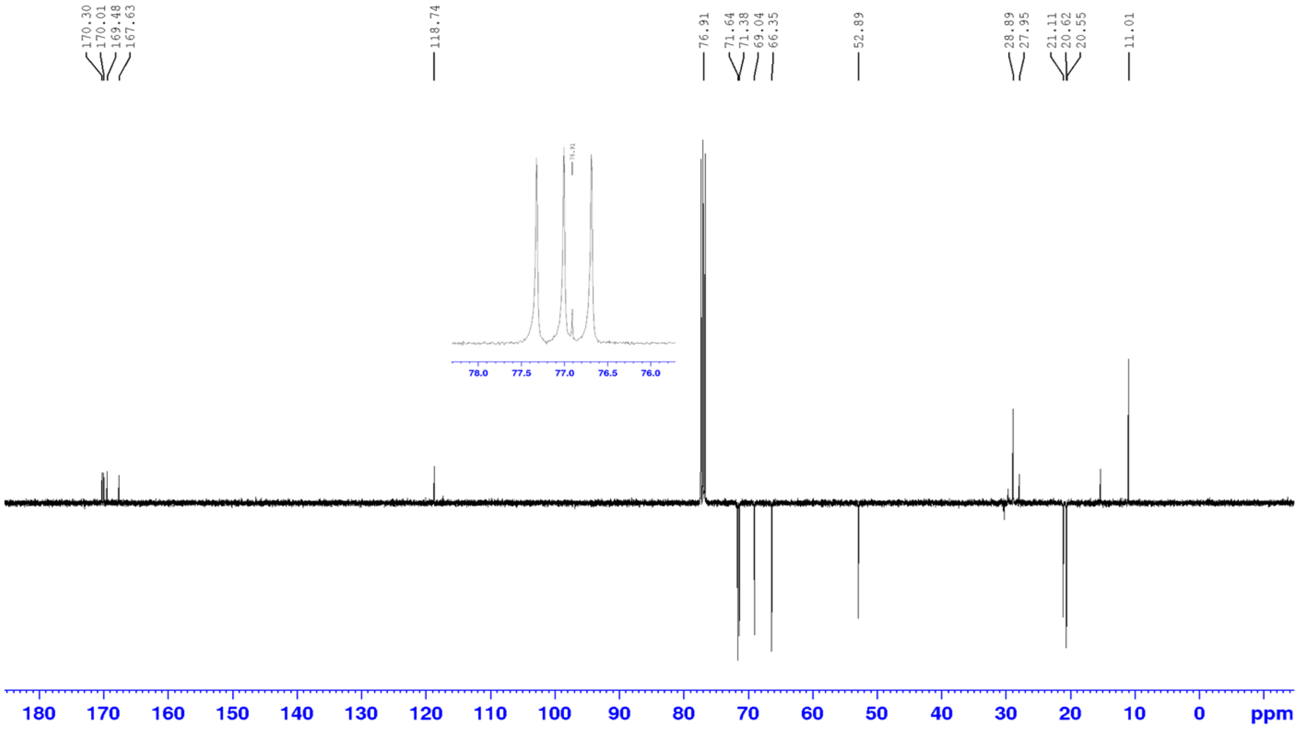


5-βCO$_2$Me

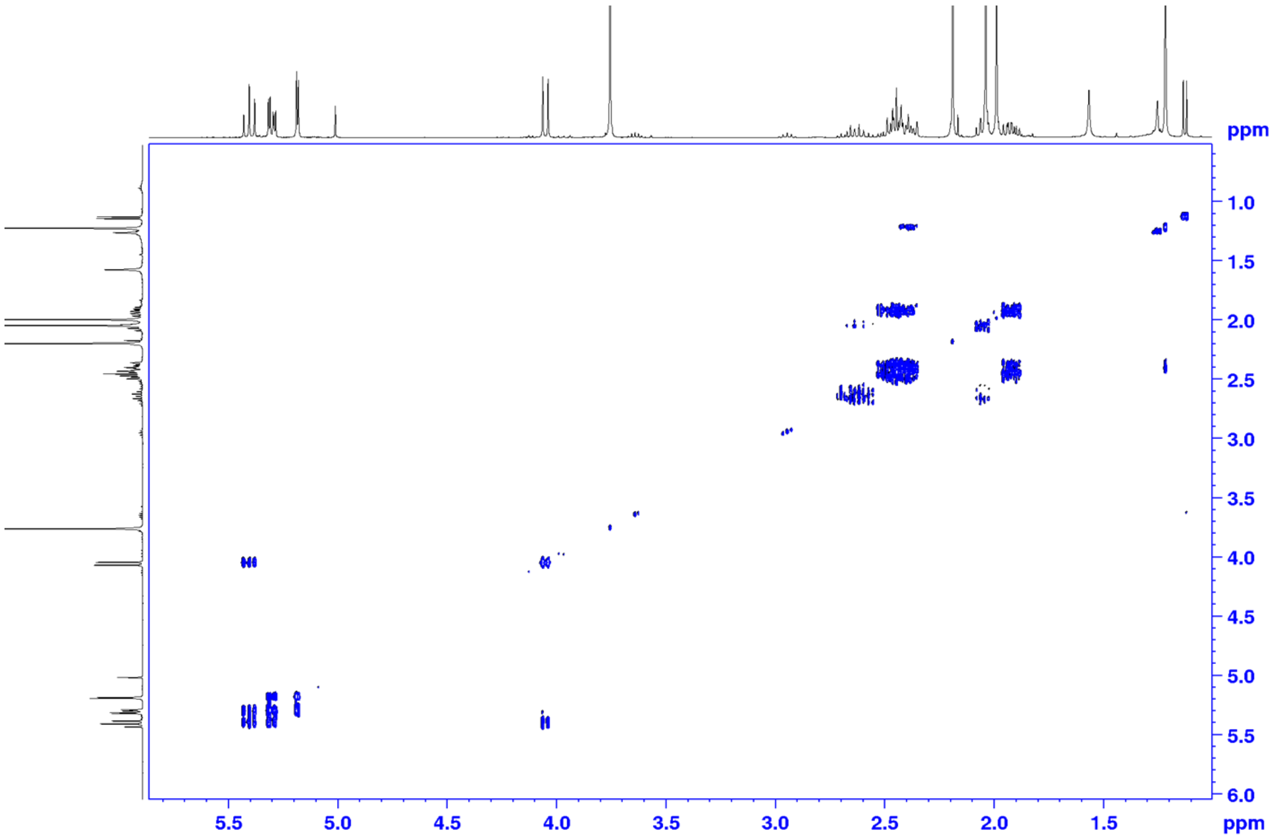
5-βCO$_2$Me: ^{1}H NMR (400 MHz, CDCl$_3$)



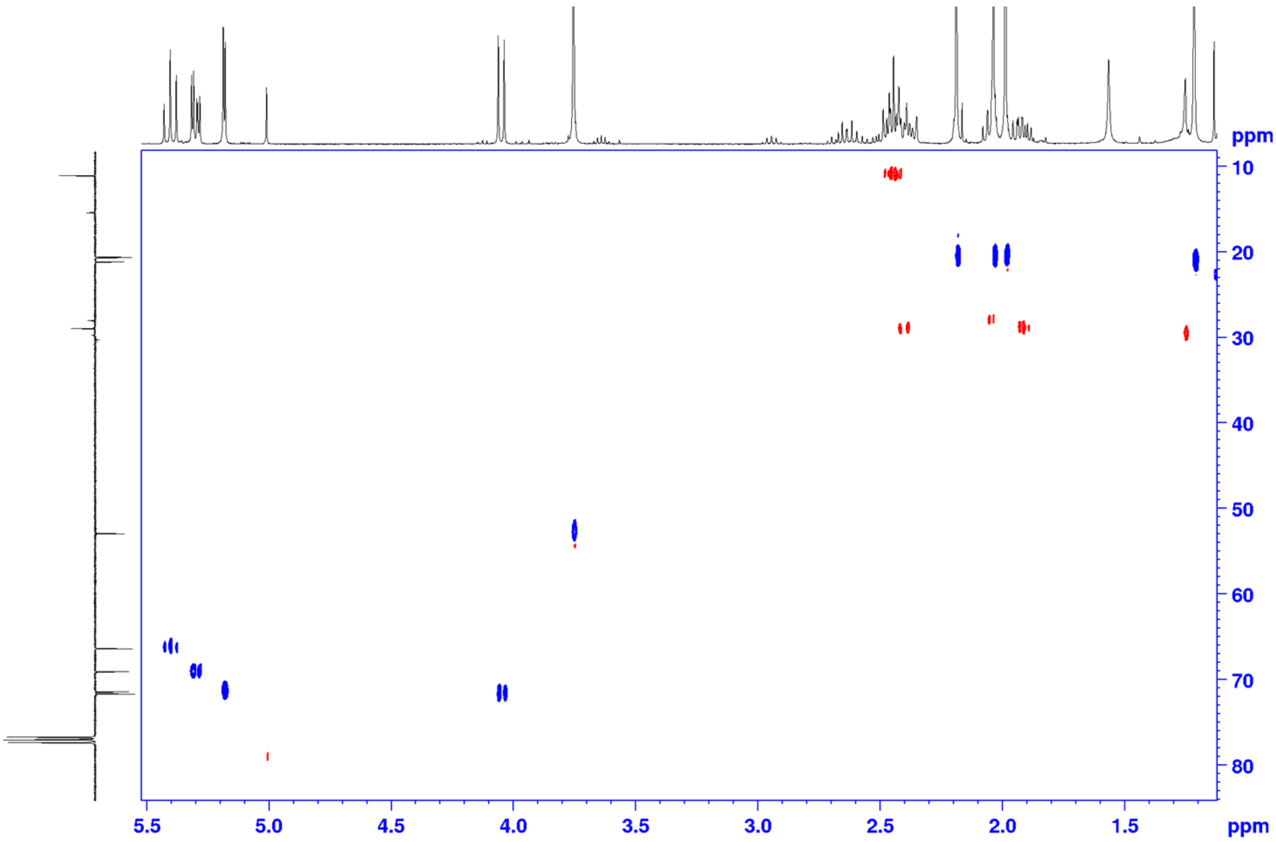
5-βCO$_2$Me: ^{13}C NMR APT (100 MHz, CDCl$_3$)



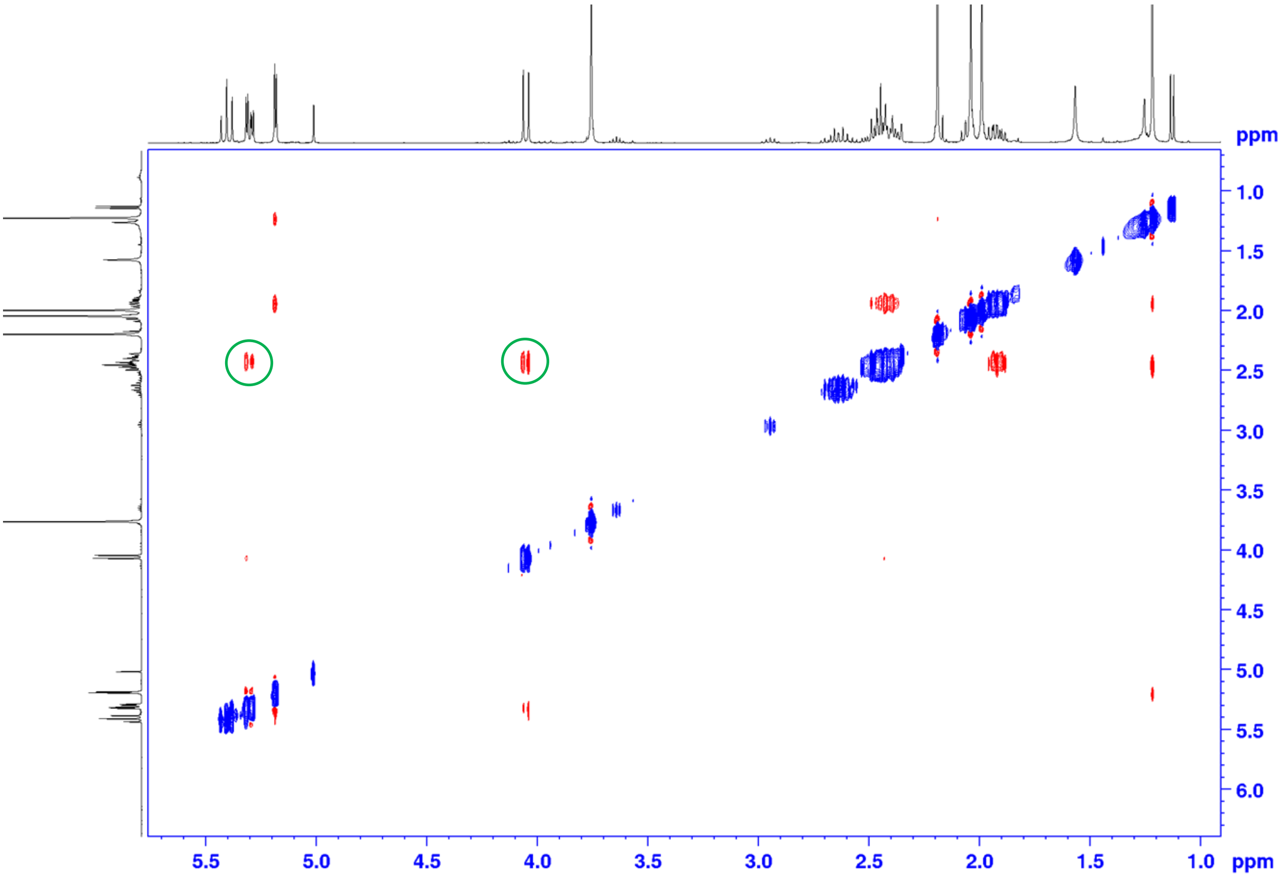
5-βCO₂Me: COSY (400 MHz, CDCl₃)

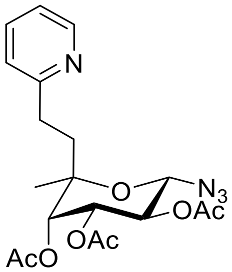


5-βCO₂Me: HSQC (400 MHz, CDCl₃)



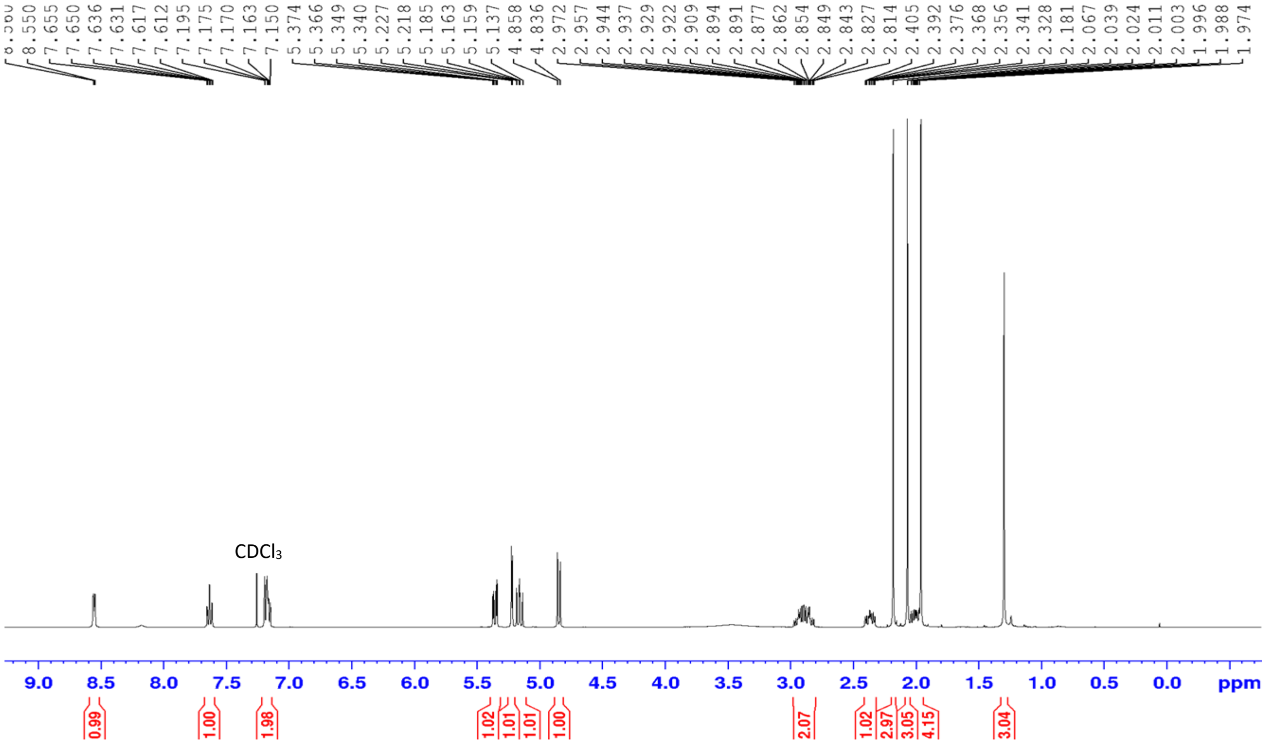
5-βCO$_2$Me: NOESY (400 MHz, CDCl$_3$)



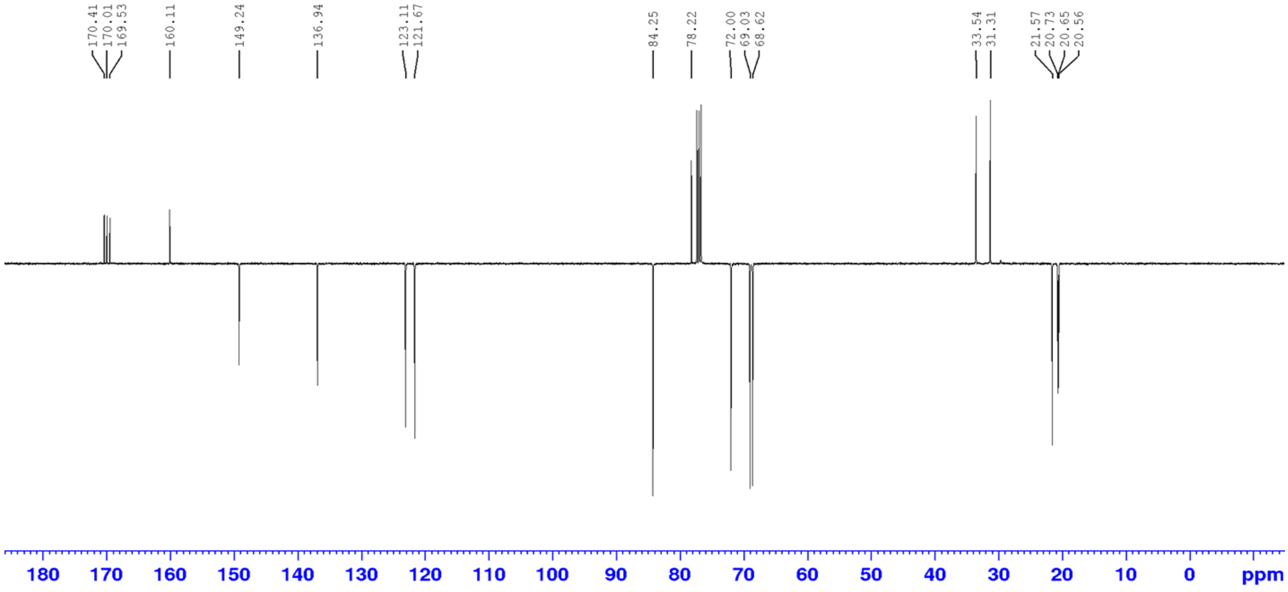


6-βN$_3$

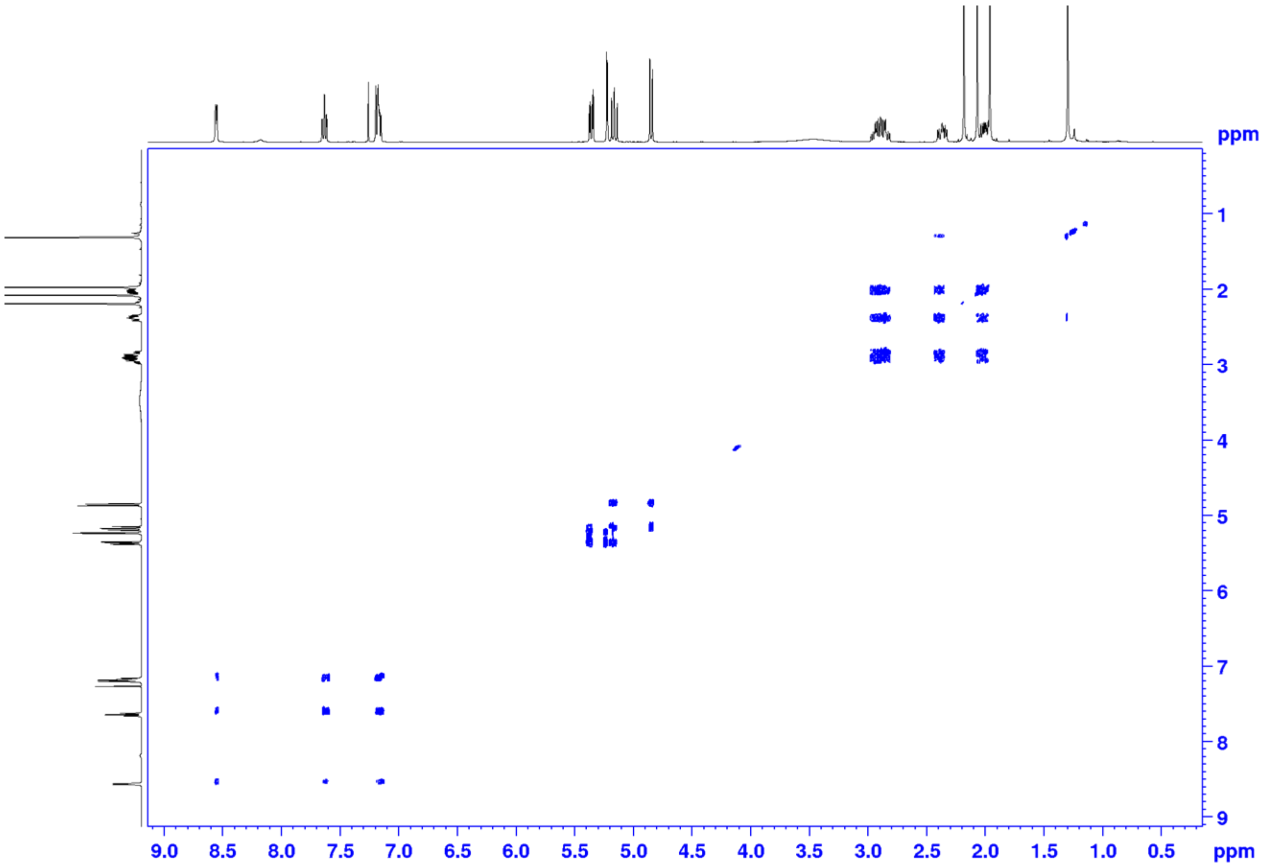
6-βN$_3$: ^{1}H NMR (400 MHz, CDCl$_3$)



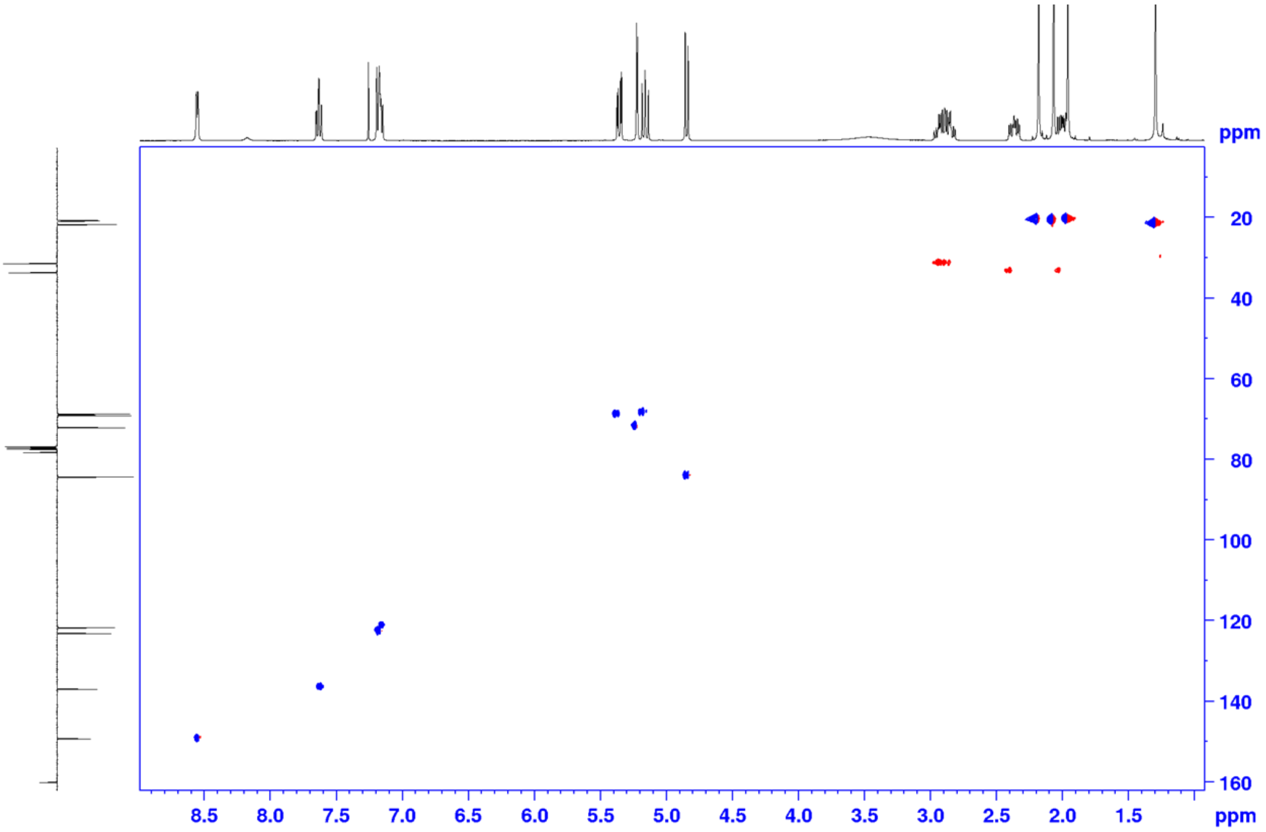
6-βN$_3$: ^{13}C NMR APT (100 MHz, CDCl$_3$)



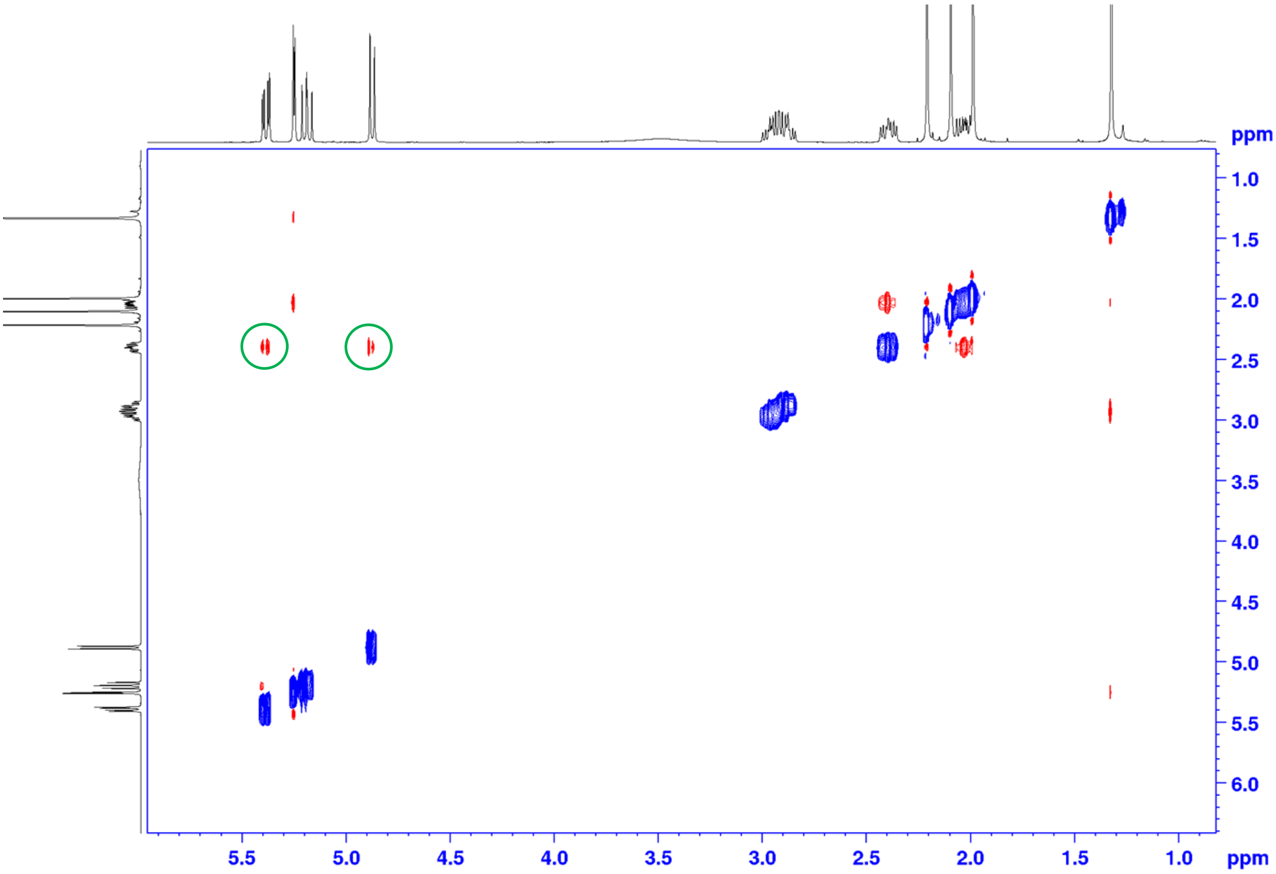
6-βN$_3$: COSY (400 MHz, CDCl$_3$)

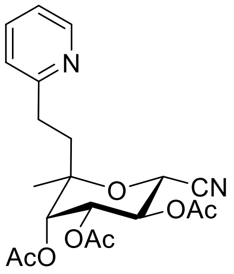


6-βN$_3$: HSQC (400 MHz, CDCl$_3$)



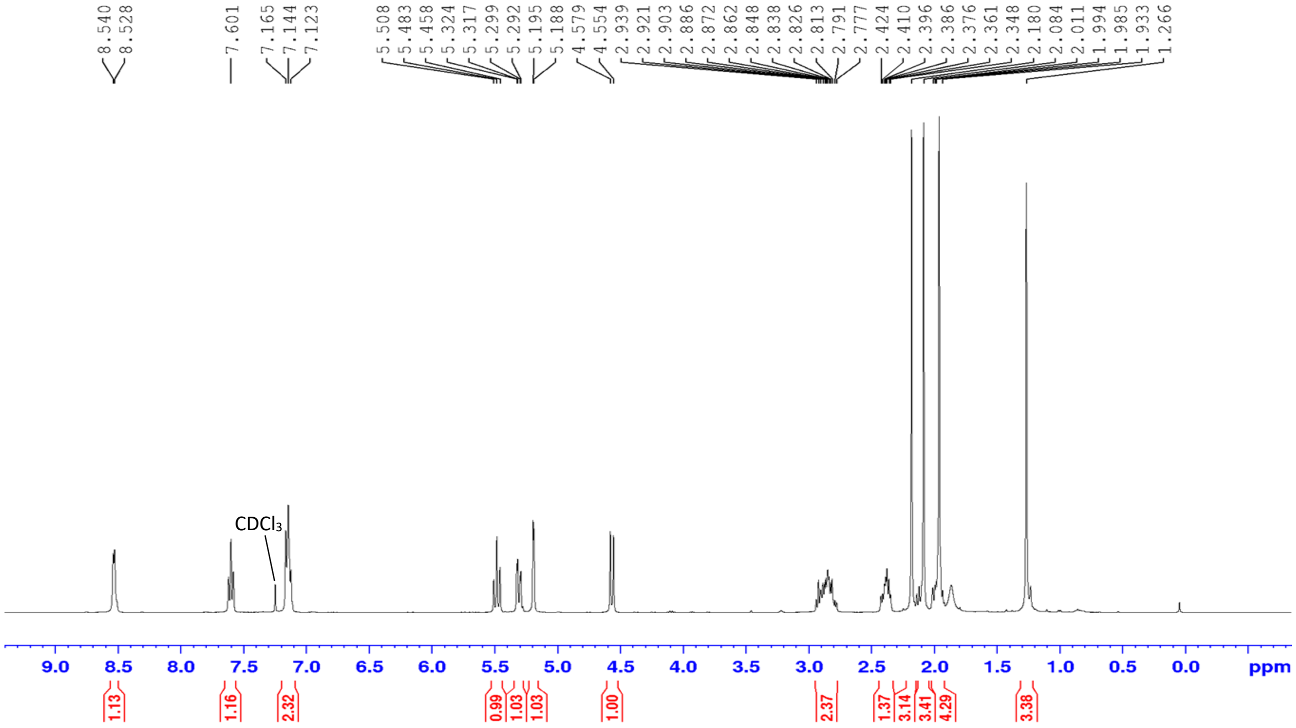
6-βN$_3$: NOESY (400 MHz, CDCl$_3$)



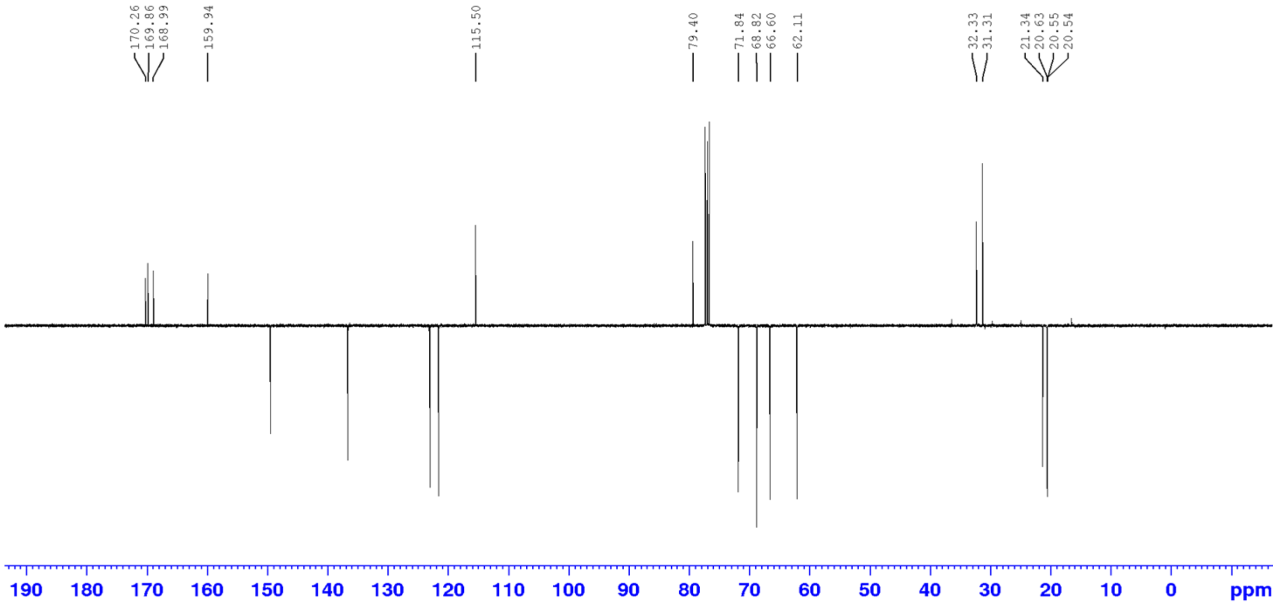


6-βCN

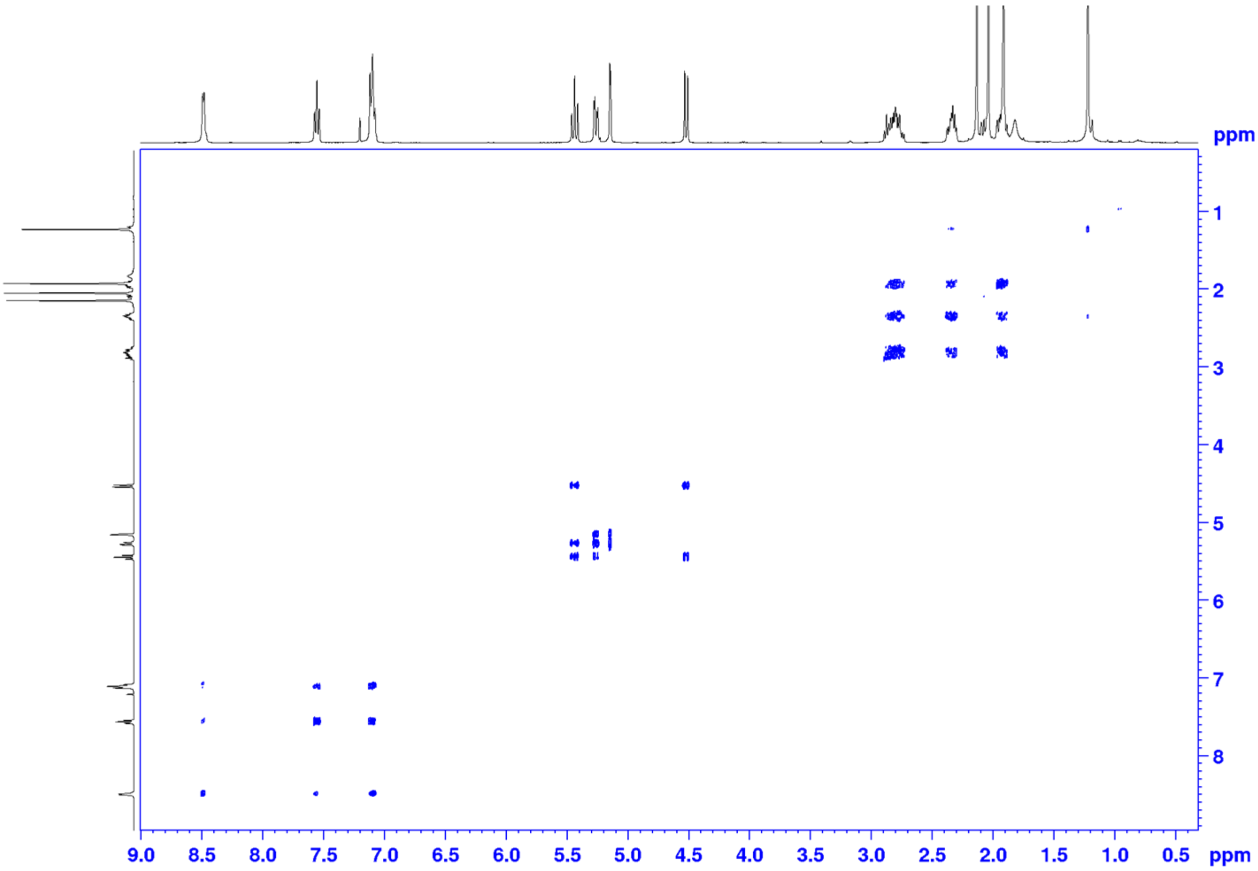
6-βCN: ^{1}H NMR (400 MHz, CDCl$_3$)



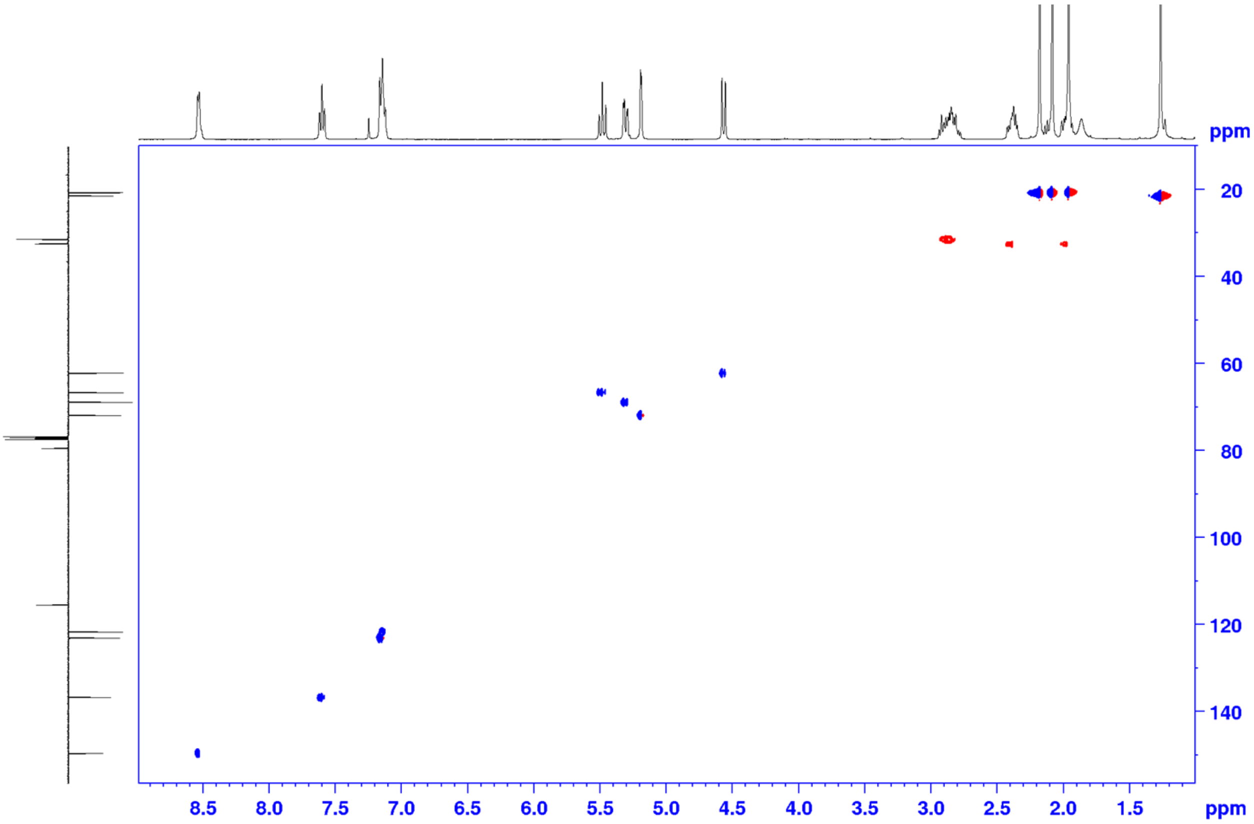
6-βCN: ^{13}C NMR APT (100 MHz, CDCl$_3$)



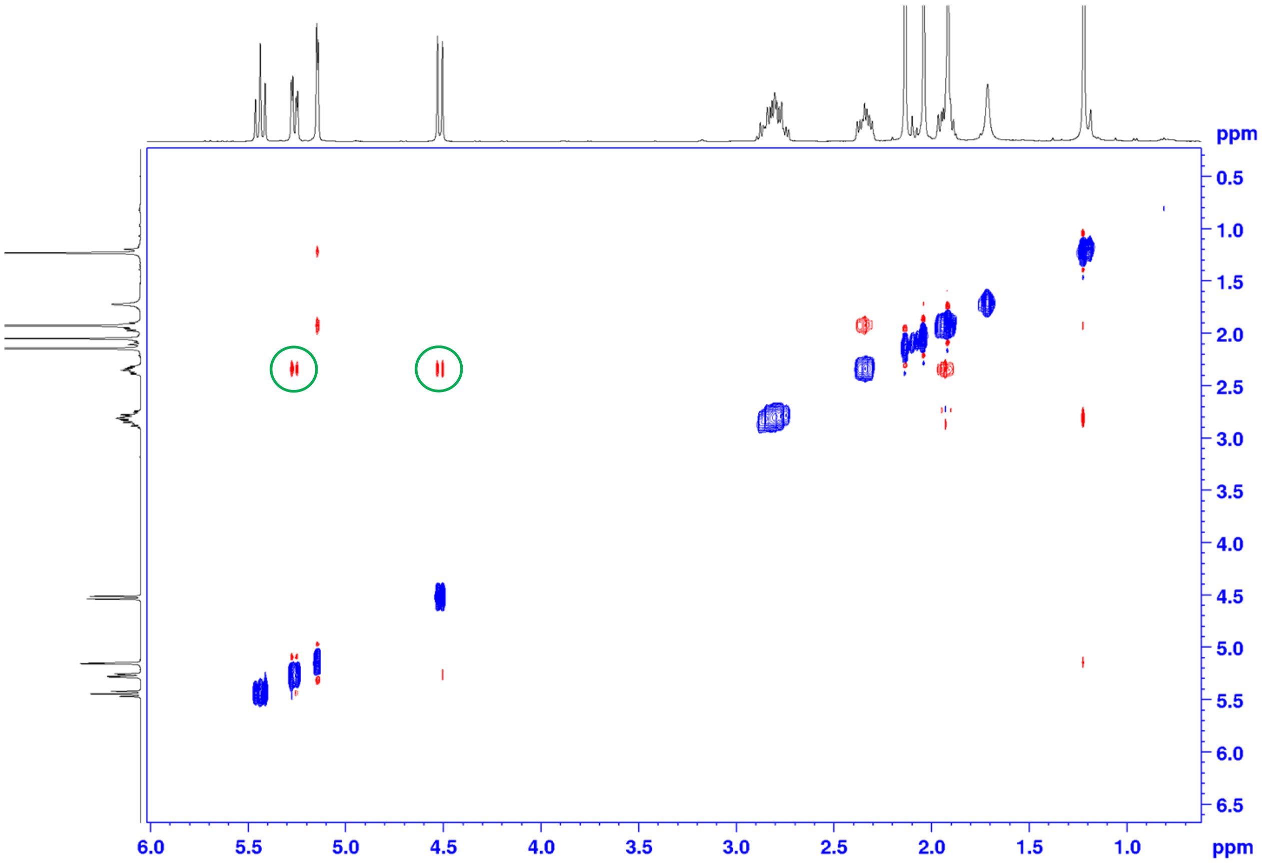
6-βCN: COSY (400 MHz, $CDCl_3$)

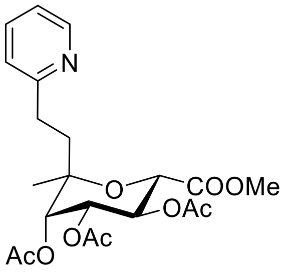


6-βCN: HSQC (400 MHz, $CDCl_3$)



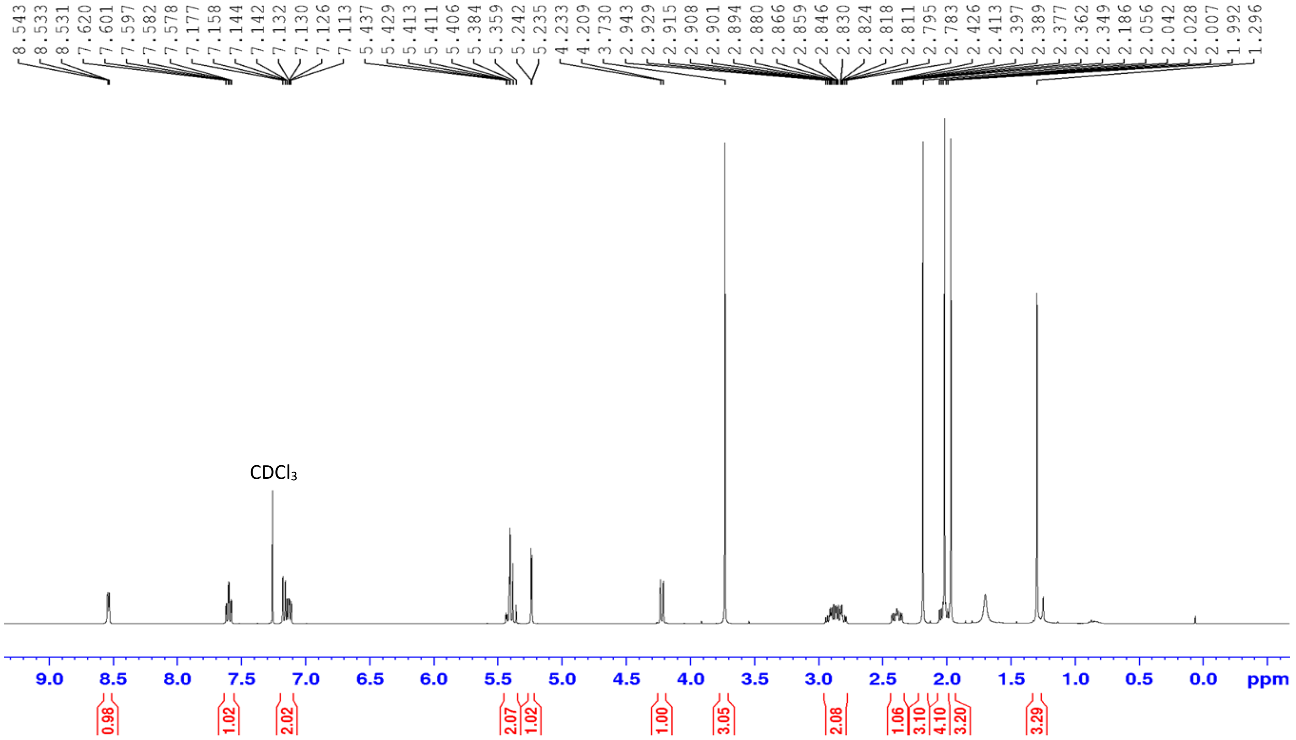
6-βCN: NOESY (400 MHz, $CDCl_3$)



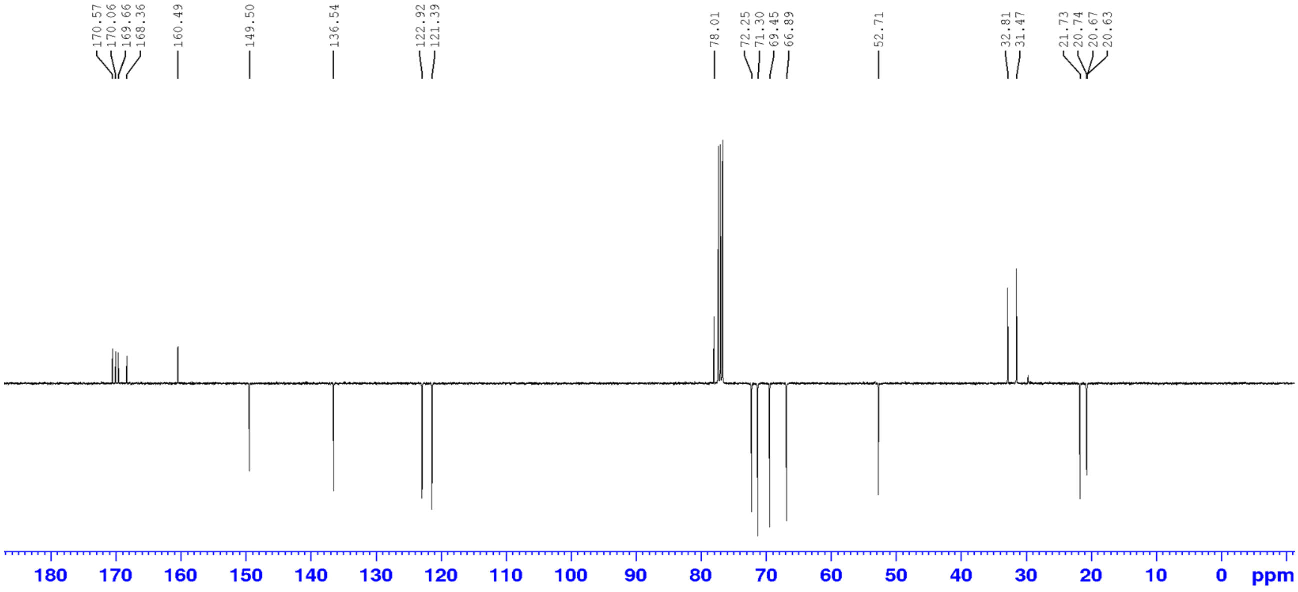


6-βCO$_2$Me

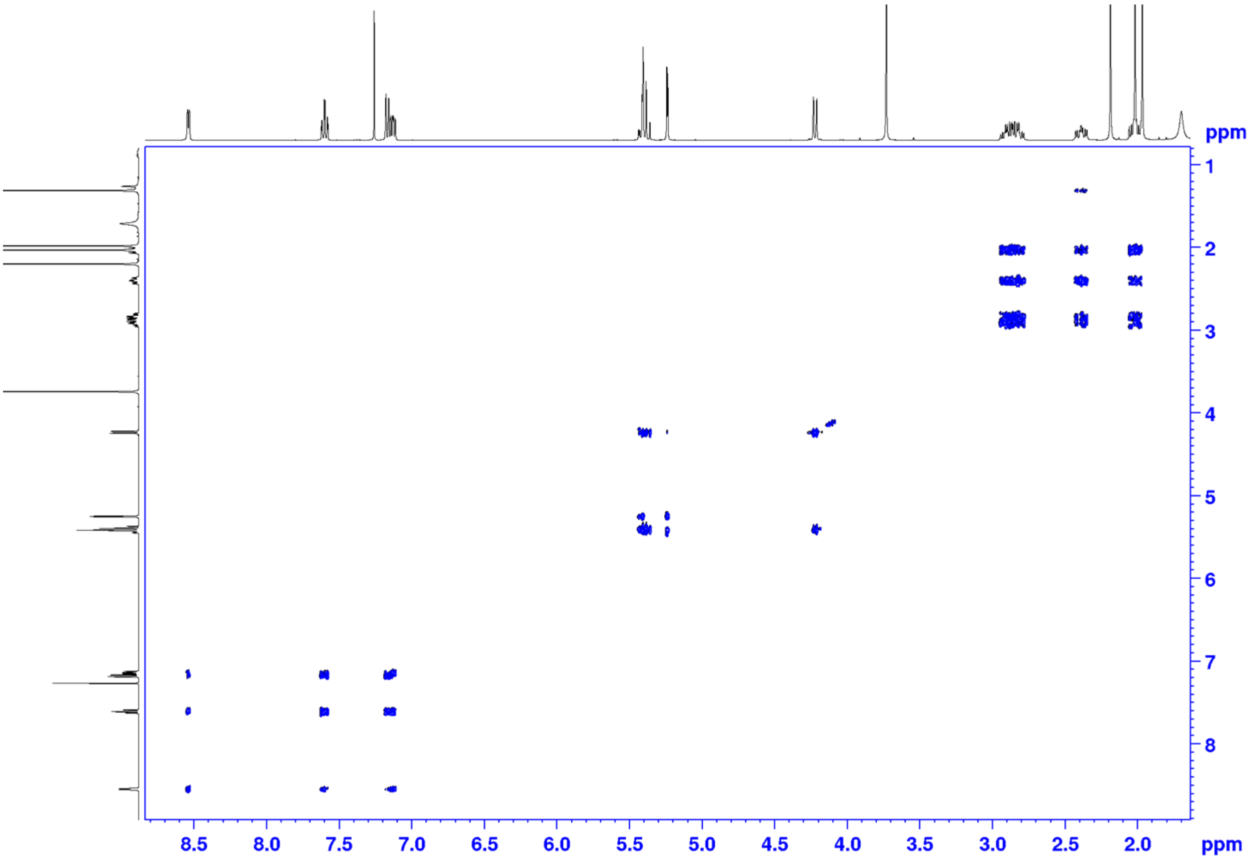
6-βCO$_2$Me: ^{1}H NMR (400 MHz, CDCl$_3$)



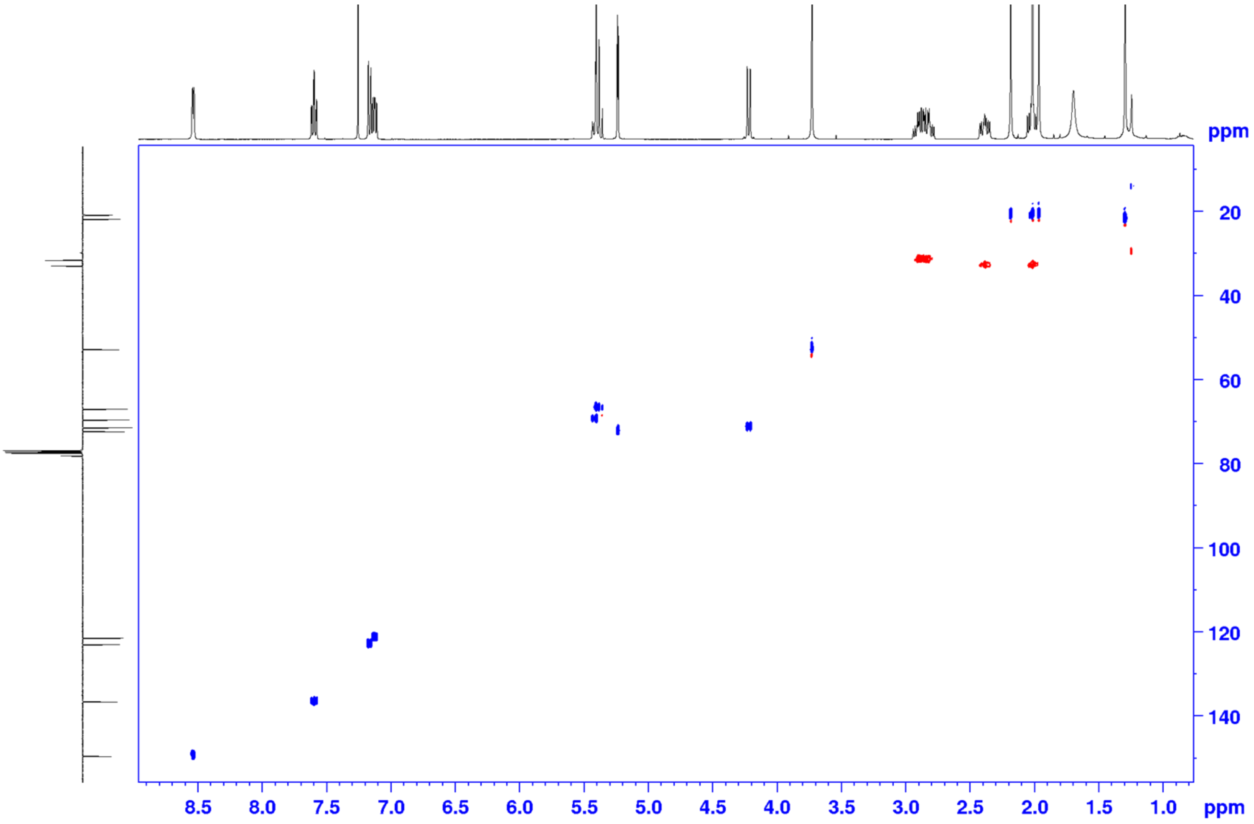
6-βCO$_2$Me: ^{13}C NMR APT (100 MHz, CDCl$_3$)



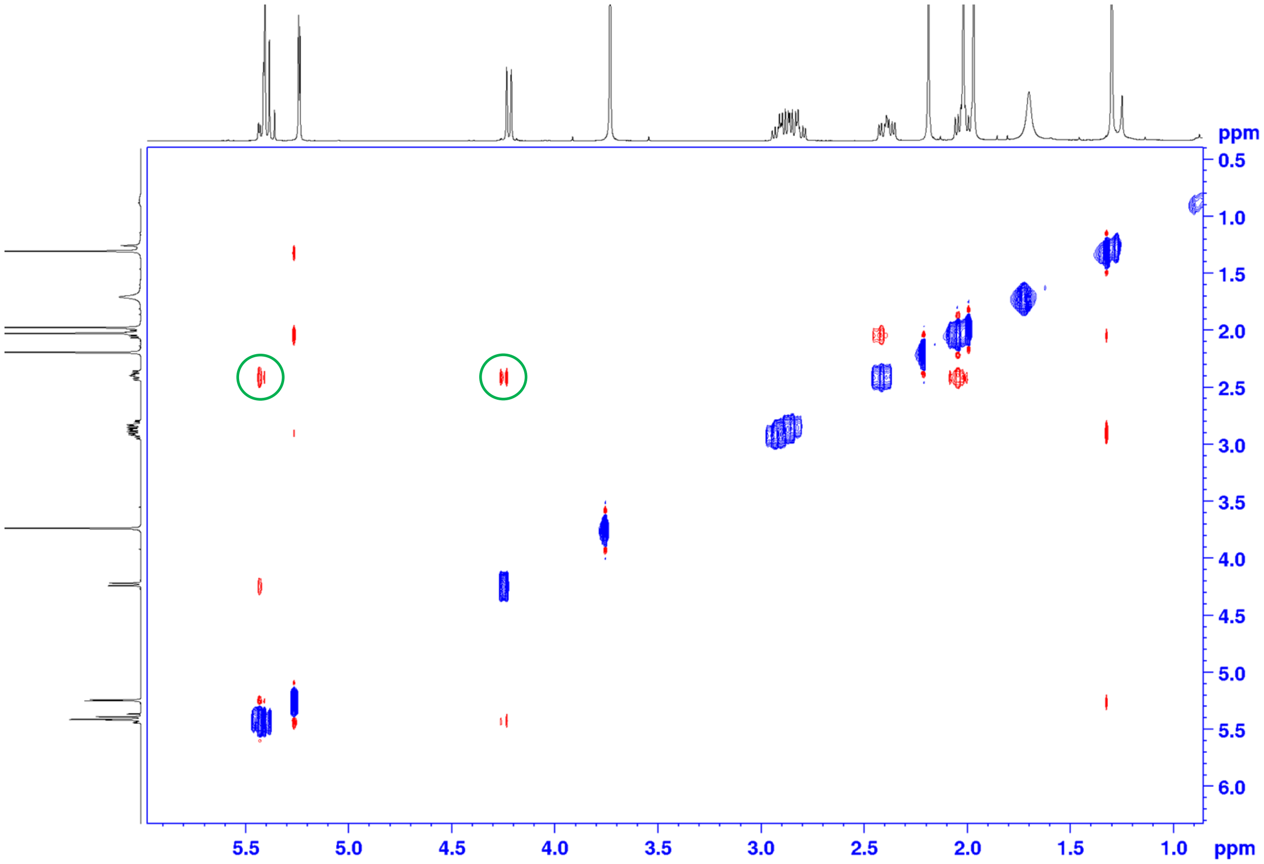
6-βCO$_2$Me: COSY (400 MHz, CDCl$_3$)

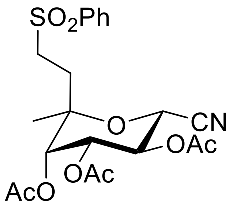


6-βCO$_2$Me: HSQC (400 MHz, CDCl$_3$)



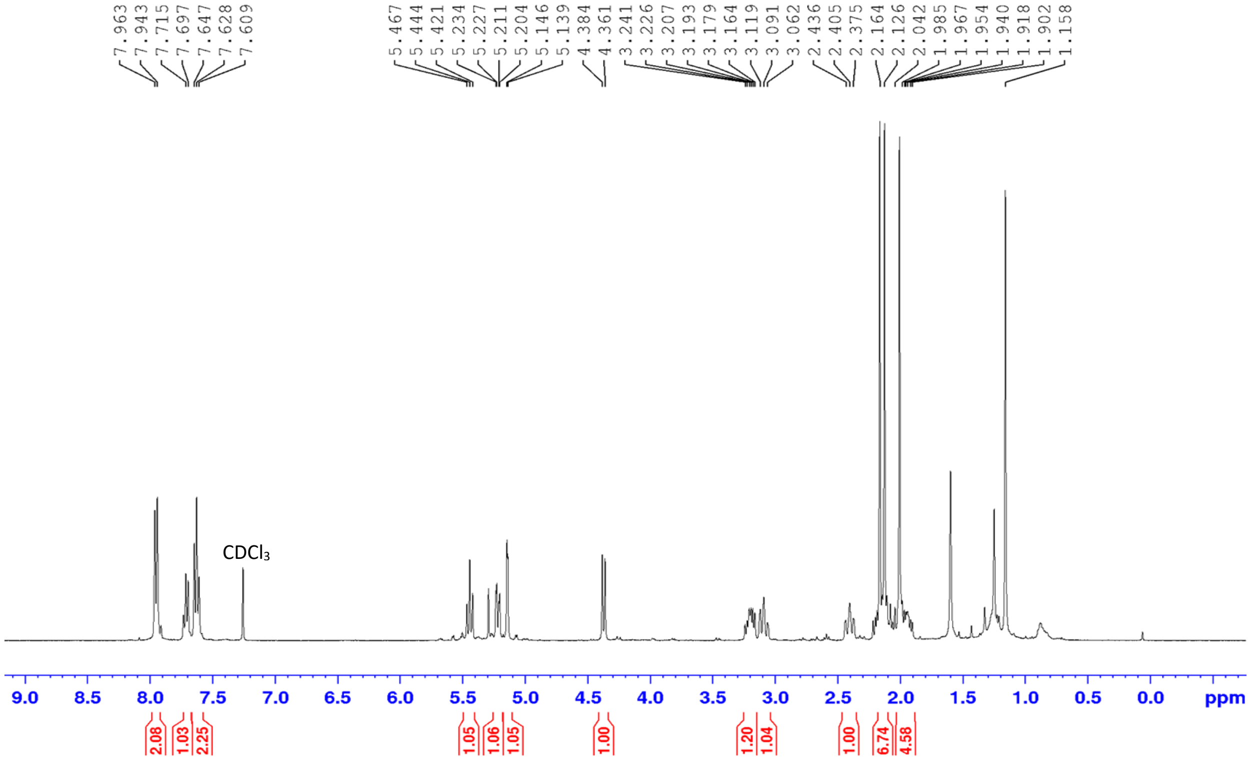
6-βCO$_2$Me: NOESY (400 MHz, CDCl$_3$)



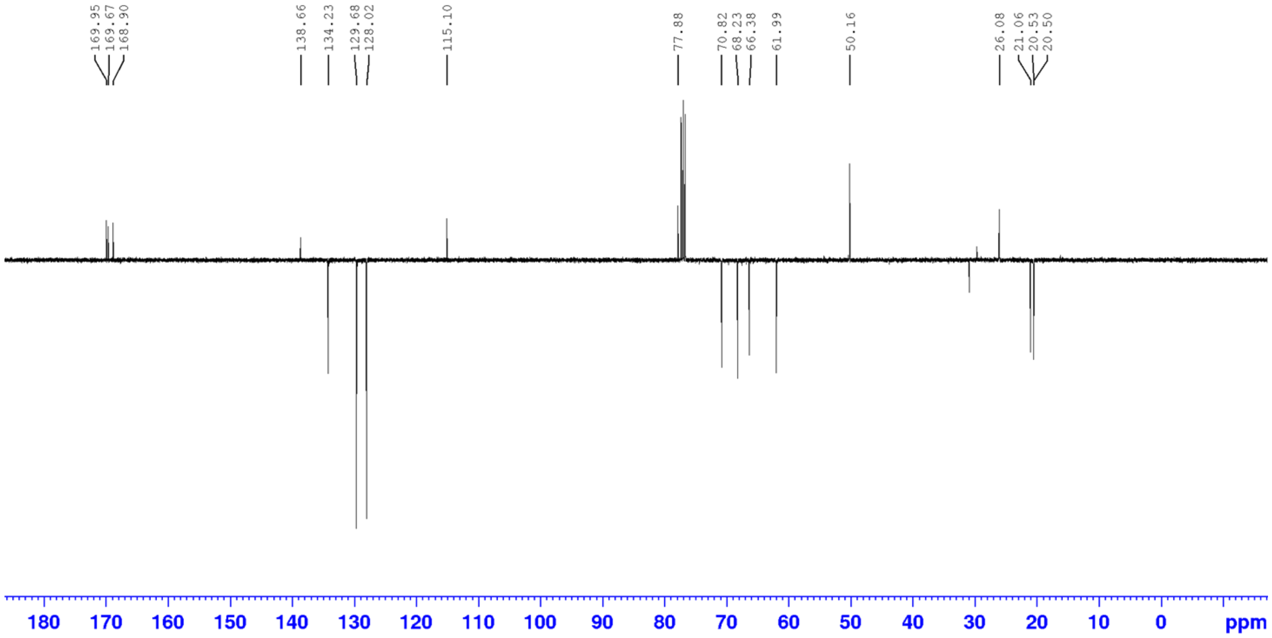


7-βCN

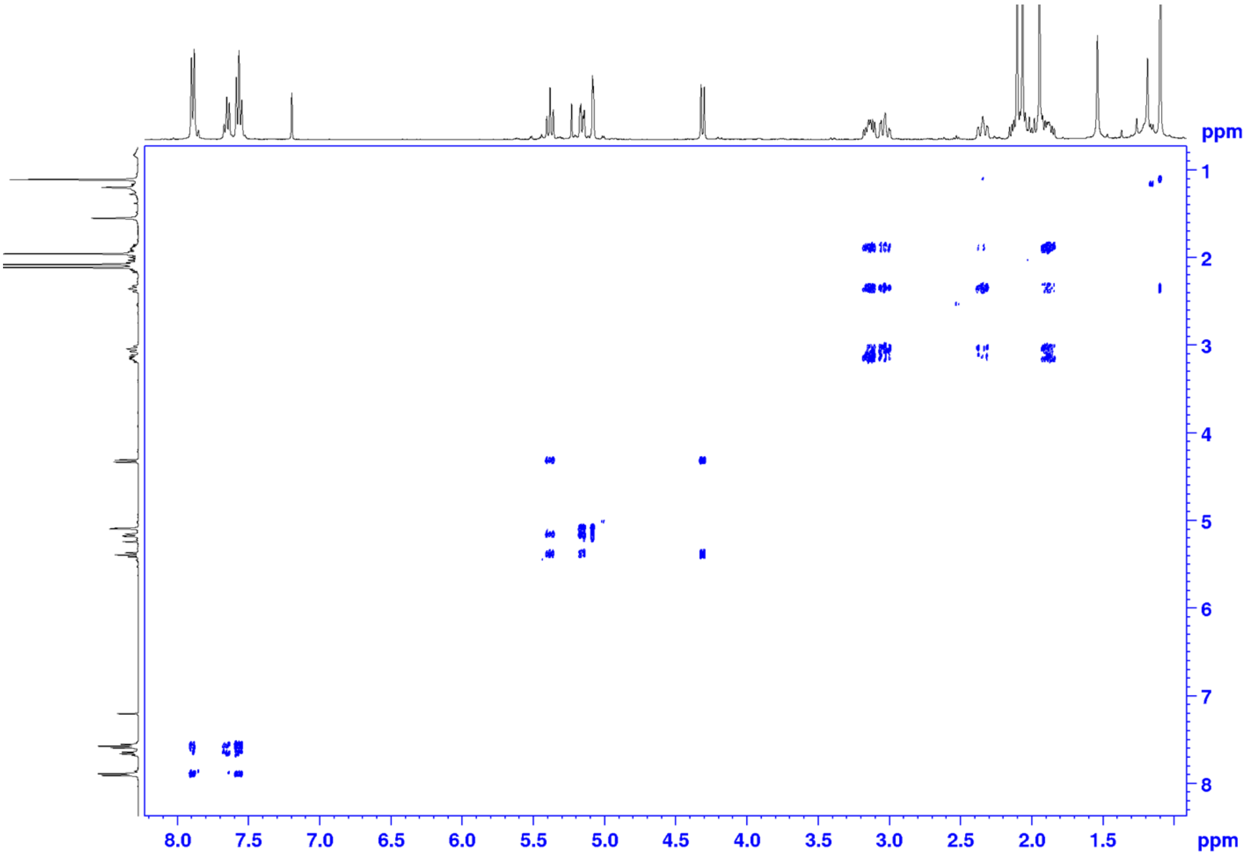
7-βCN: ^{1}H NMR (400 MHz, CDCl$_3$)



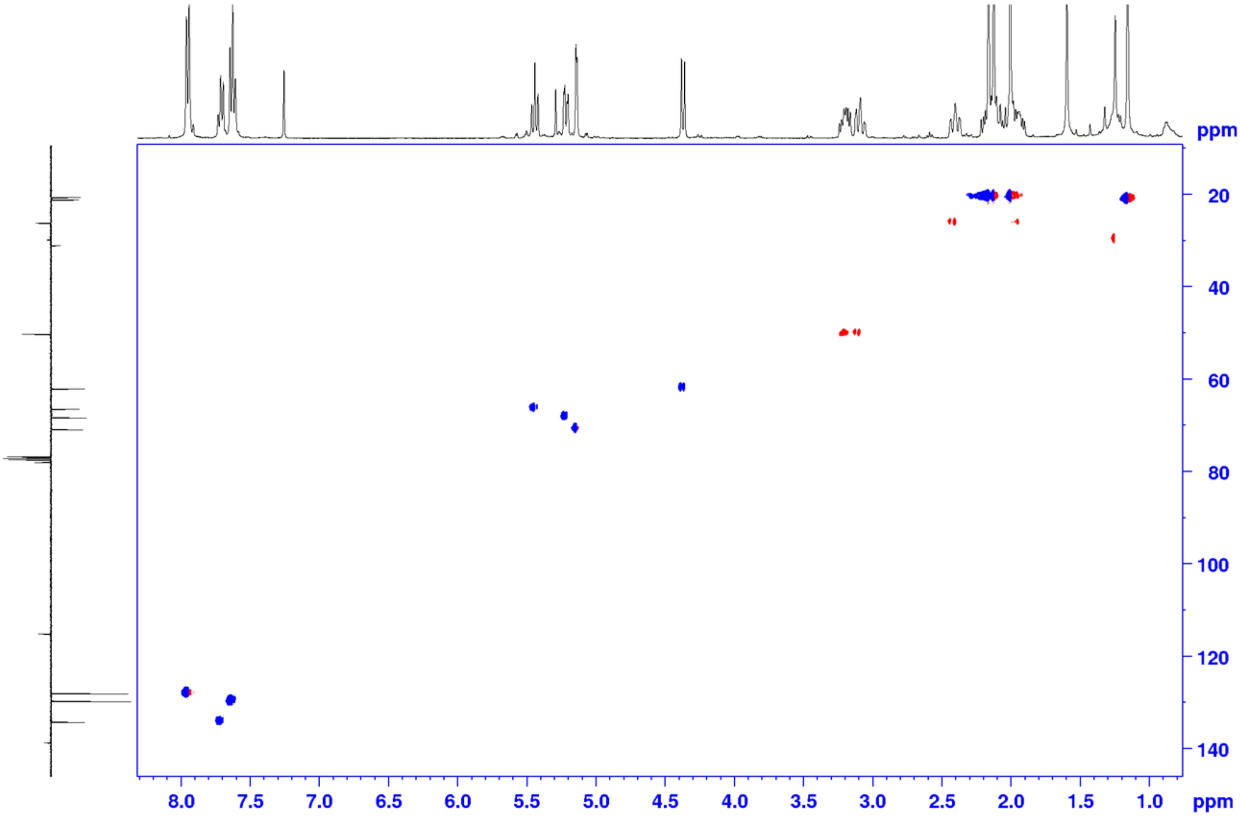
7-βCN: ^{13}C NMR APT (100 MHz, CDCl$_3$)



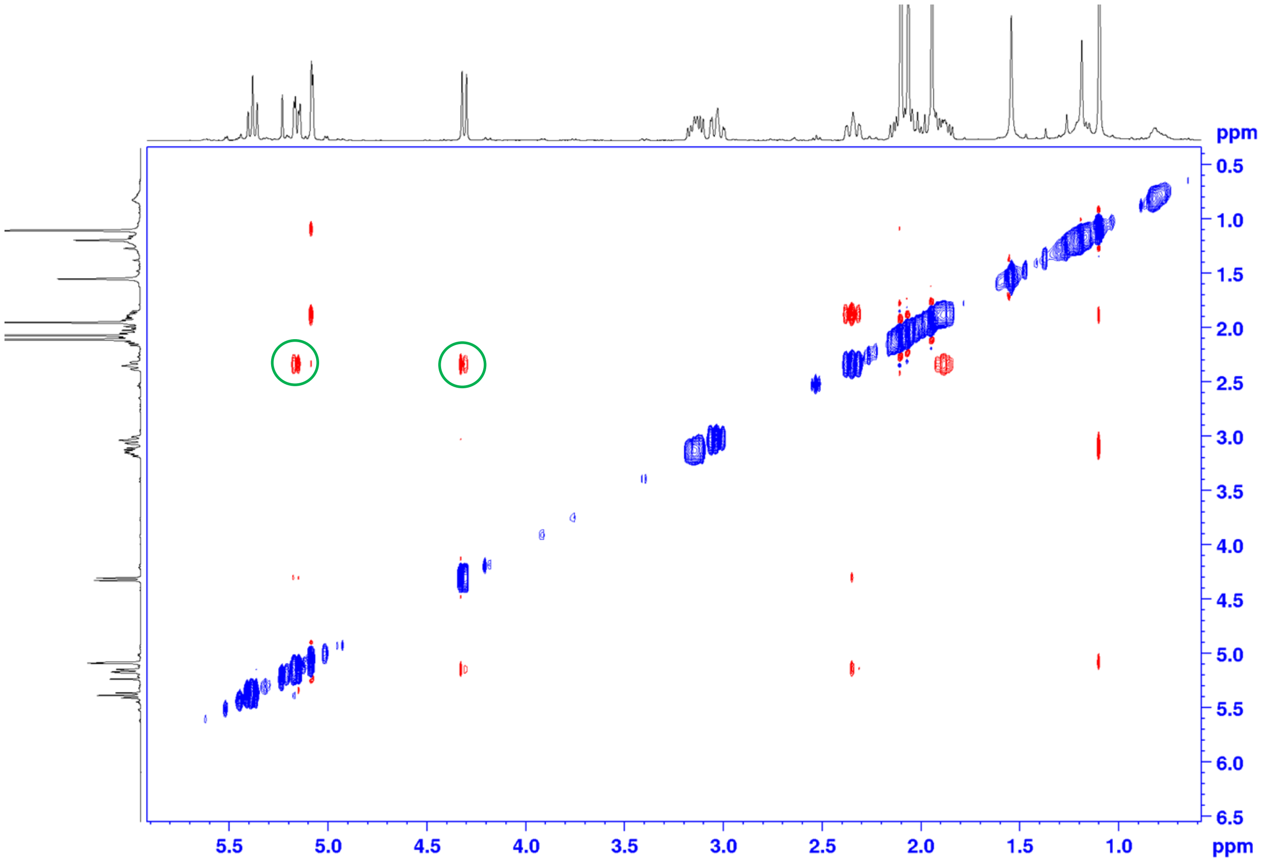
7-βCN: COSY (400 MHz, $CDCl_3$)

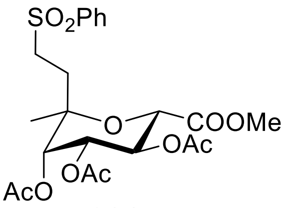


7-βCN: HSQC (400 MHz, $CDCl_3$)



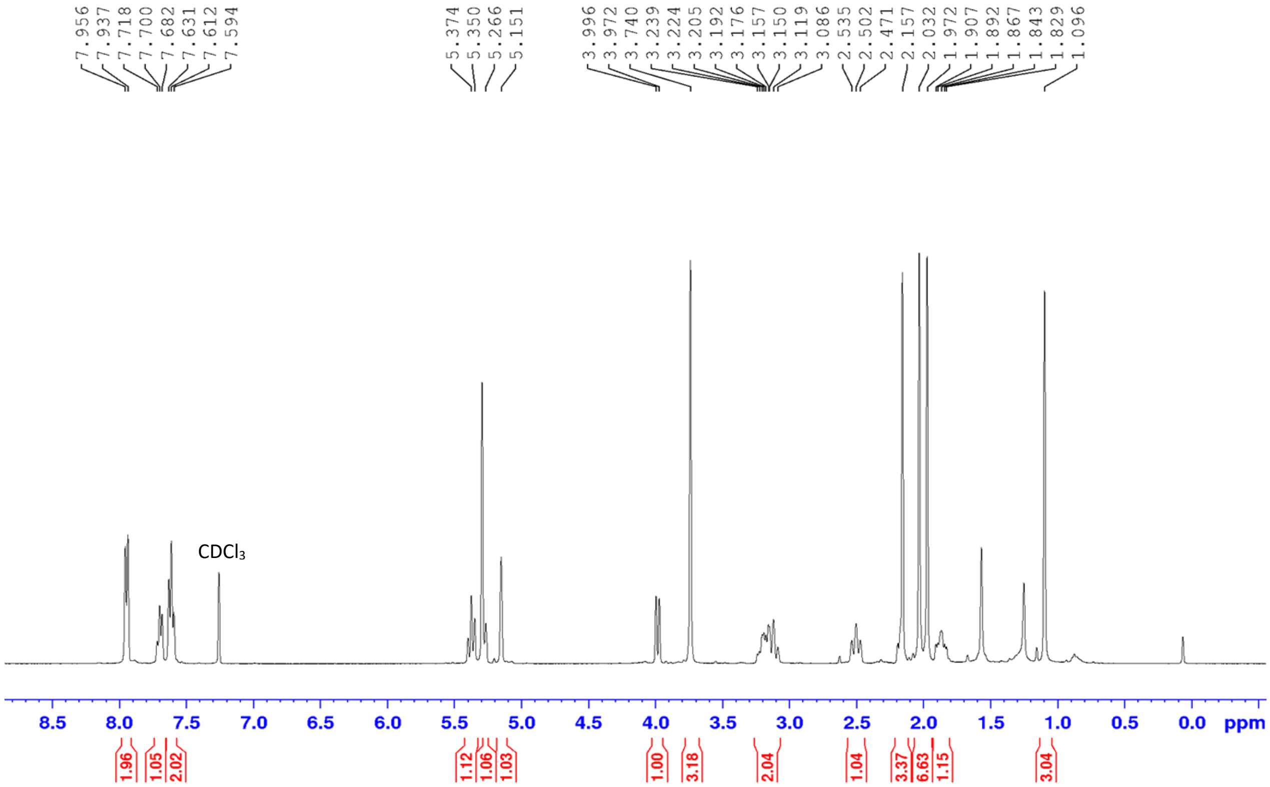
7-βCN: NOESY (400 MHz, $CDCl_3$)



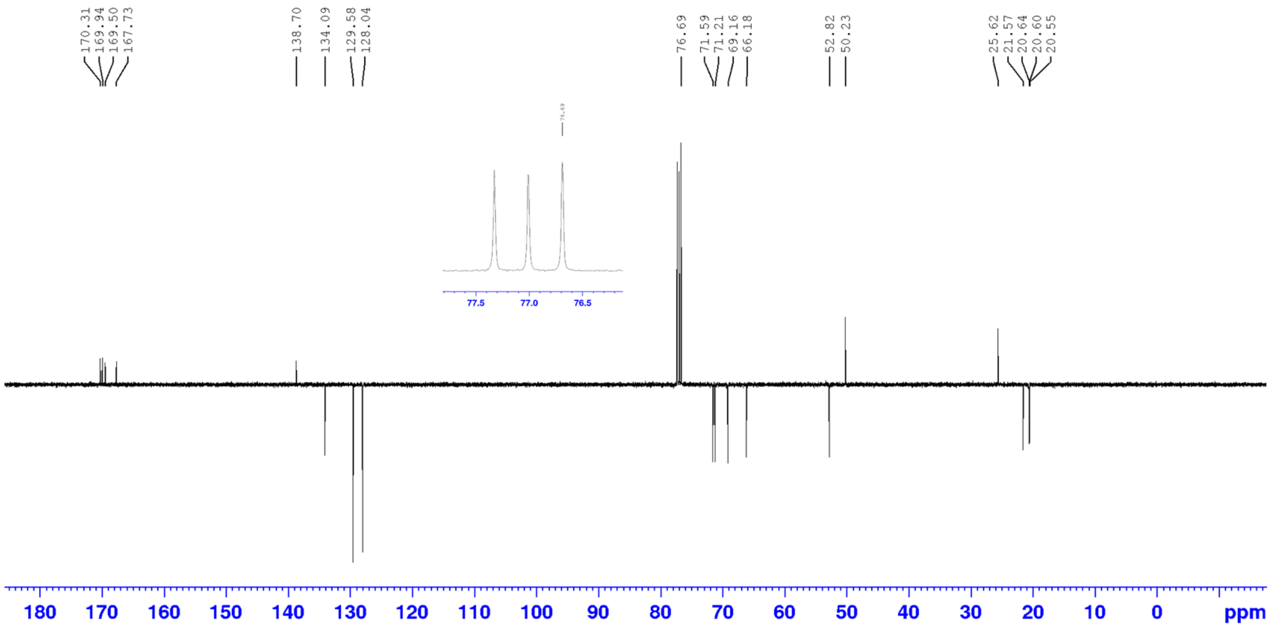


7-βCO$_2$Me

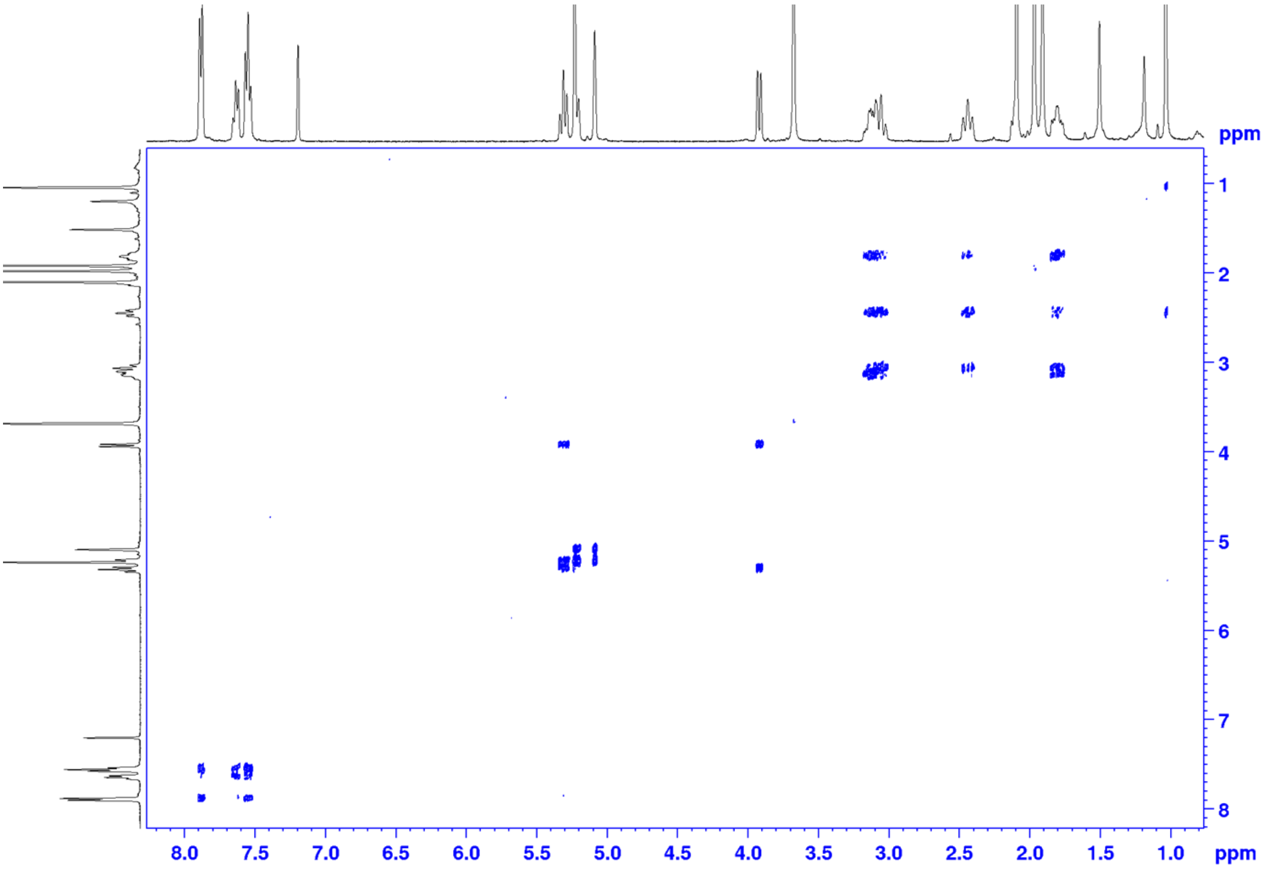
7-βCO$_2$Me: ^{1}H NMR (400 MHz, CDCl$_3$)



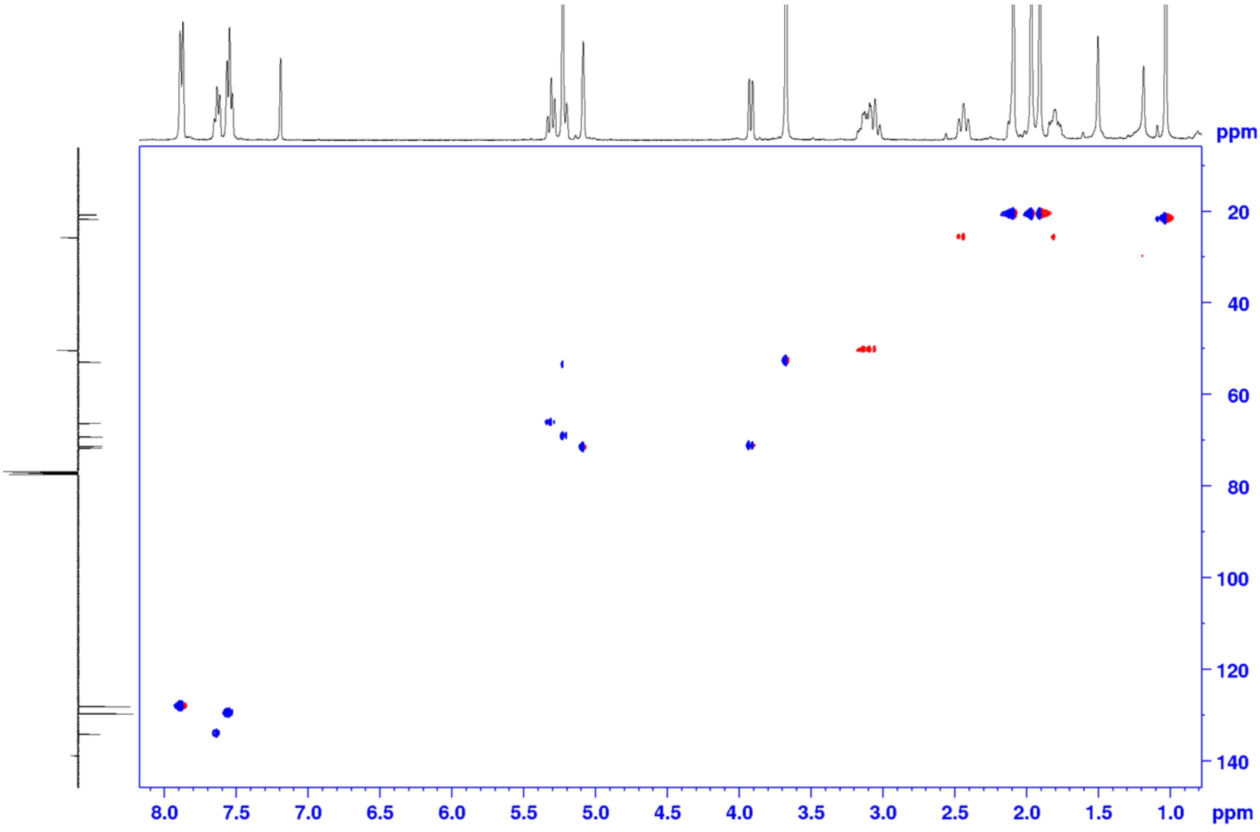
7-βCO$_2$Me: ^{13}C NMR APT (100 MHz, CDCl$_3$)



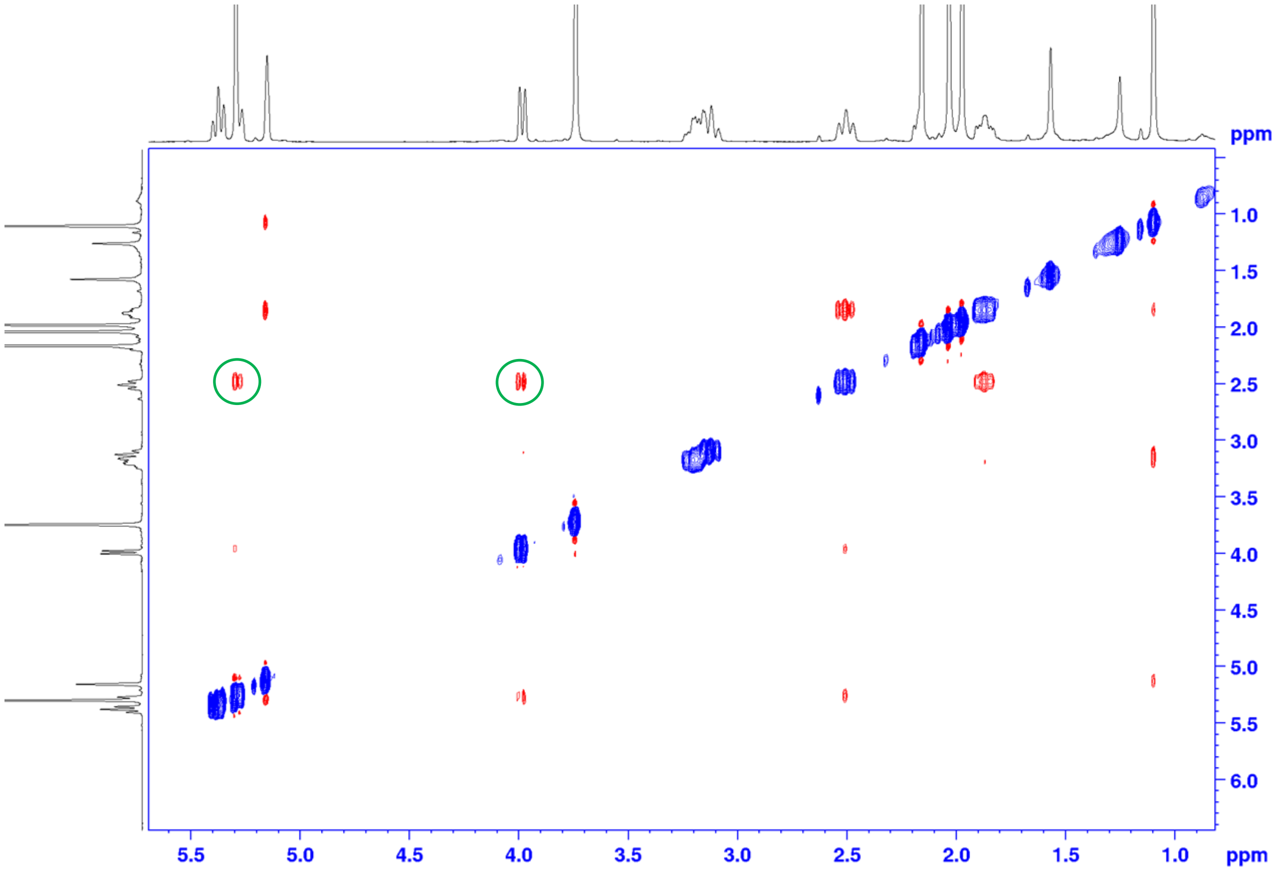
7-βCO$_2$Me: COSY (400 MHz, CDCl$_3$)

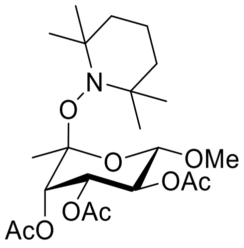


7-βCO$_2$Me: HSQC (400 MHz, CDCl$_3$)



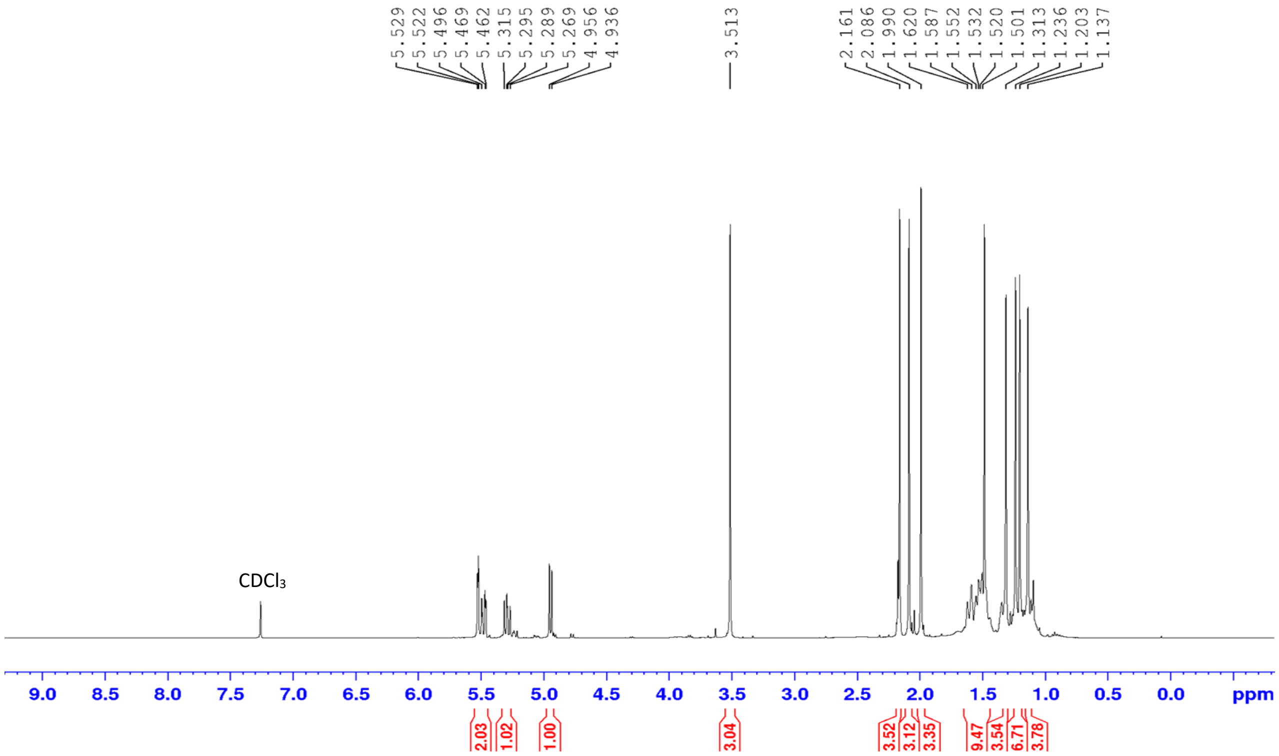
7-βCO$_2$Me: NOESY (400 MHz, CDCl$_3$)



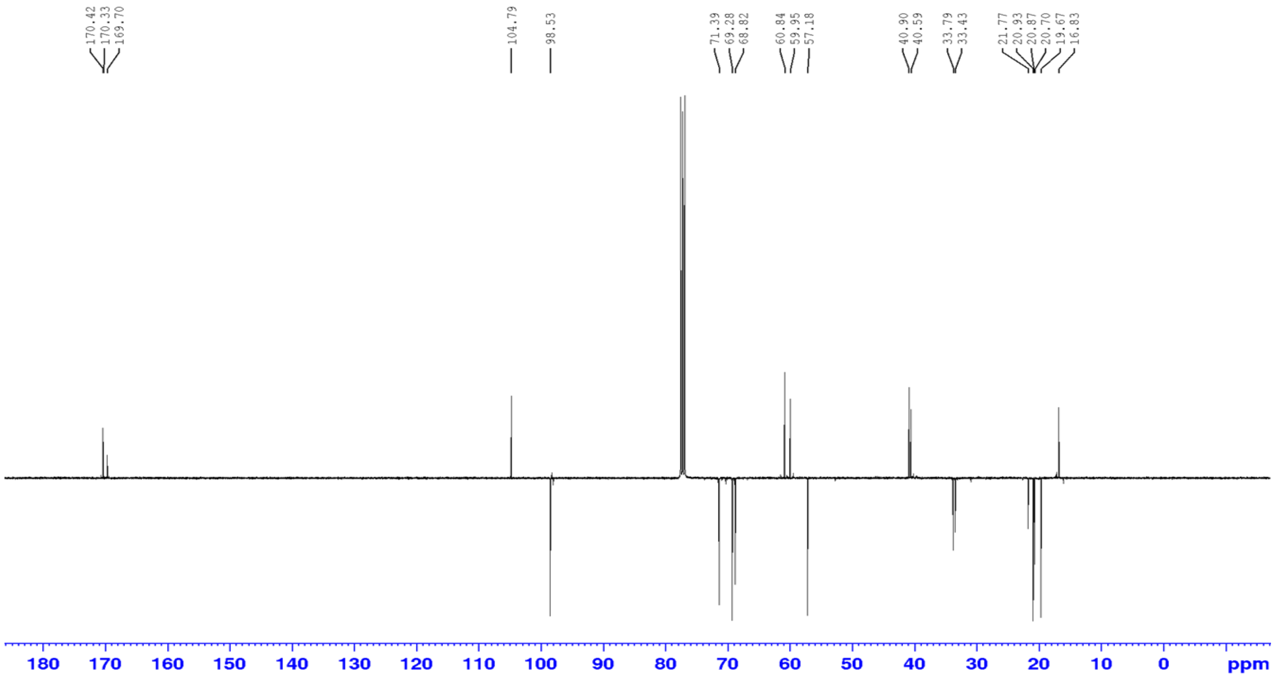


10-βOMe

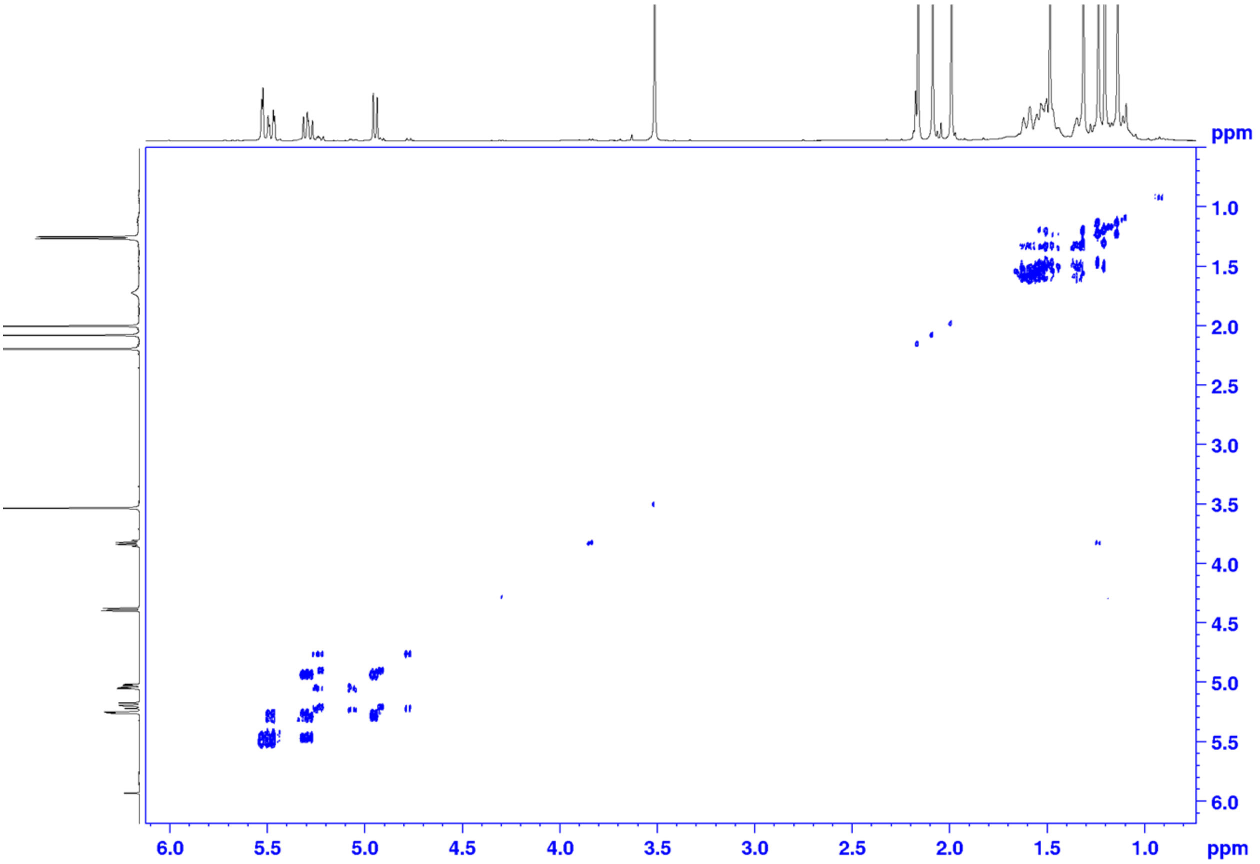
10-βOMe: ^{1}H NMR (400 MHz, $CDCl_3$)



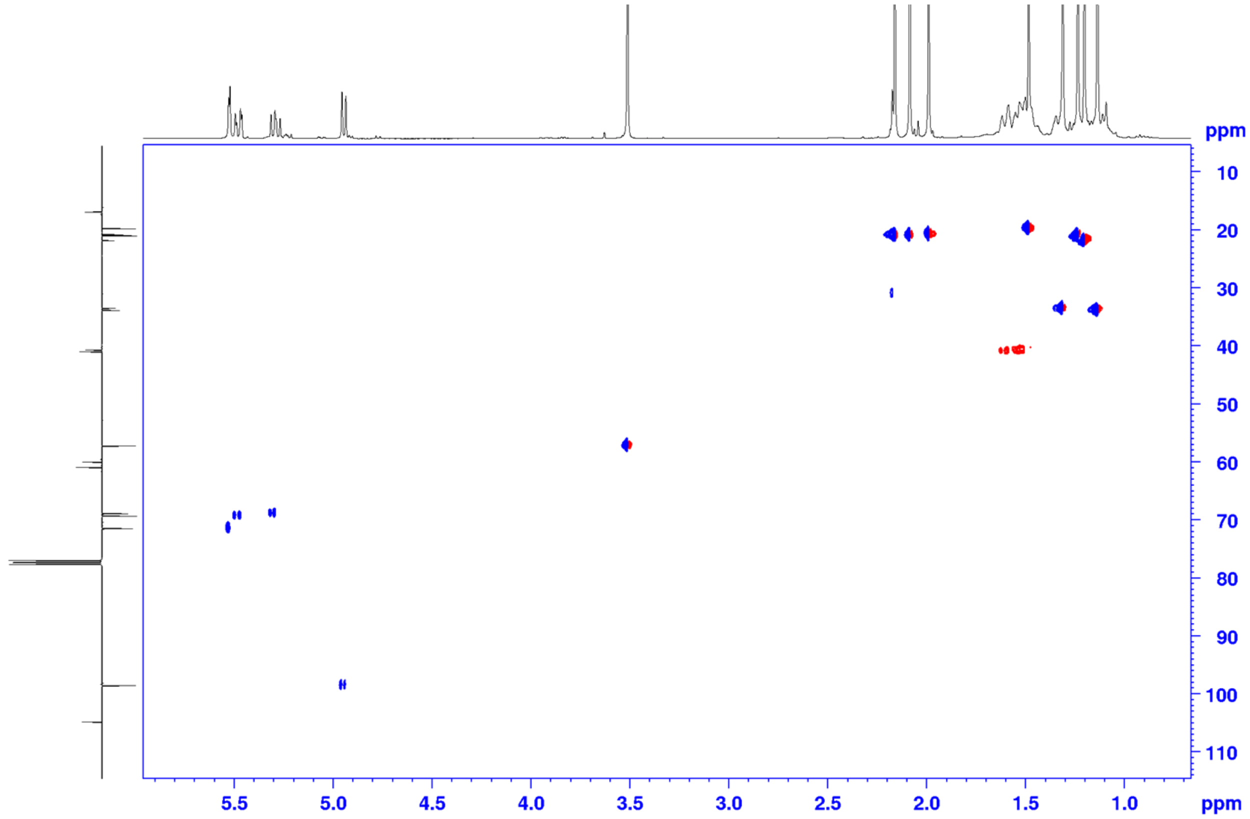
10-βOMe: ^{13}C NMR APT (100 MHz, $CDCl_3$)



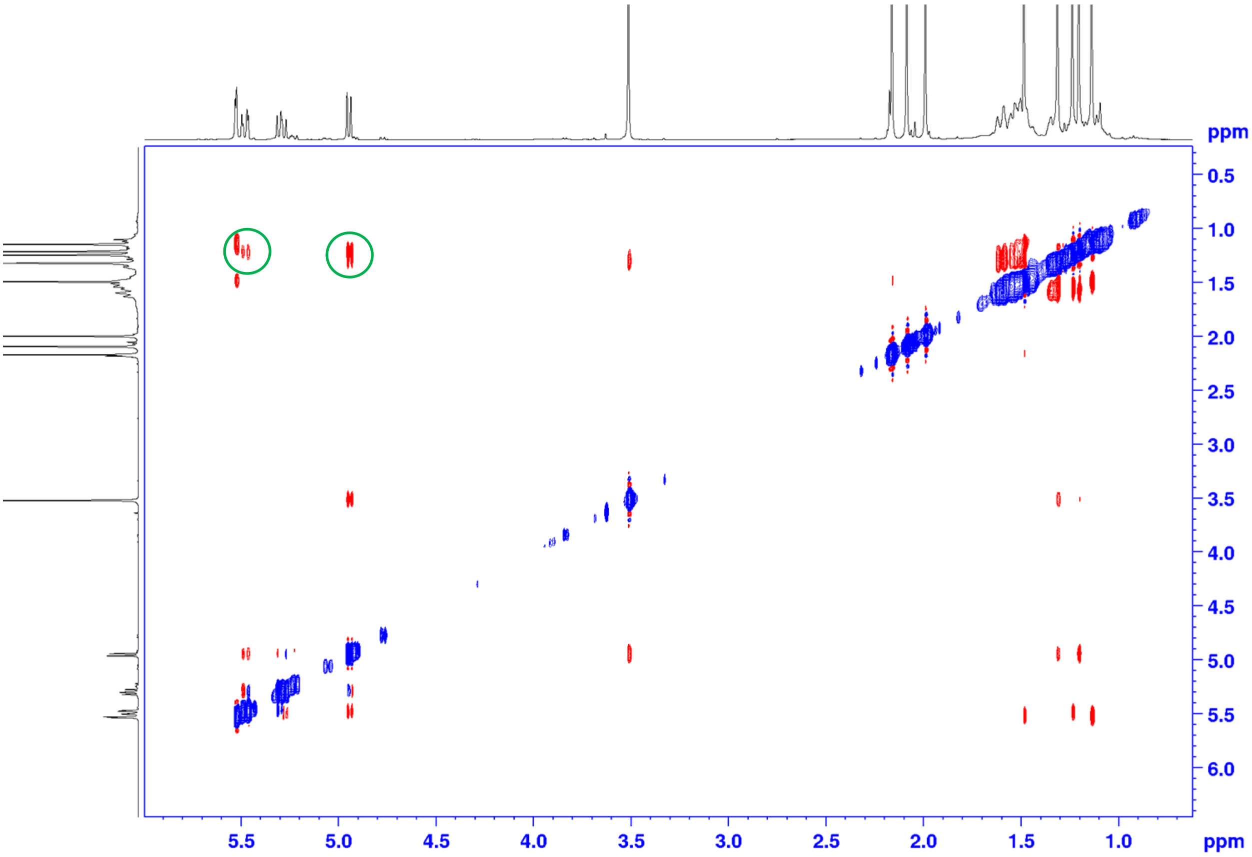
10-βOMe: COSY (400 MHz, $CDCl_3$)

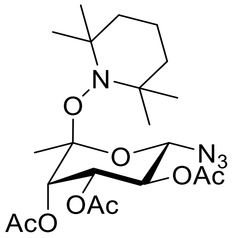


10-βOMe: HSQC (400 MHz, $CDCl_3$)



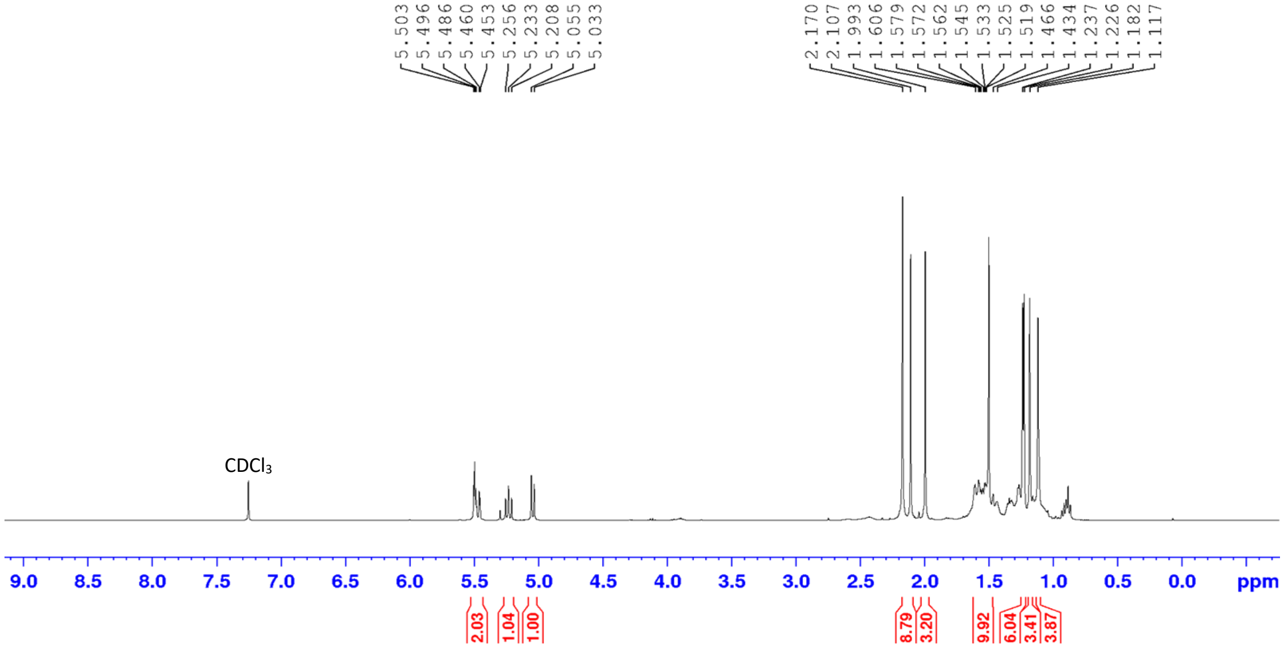
10-βOMe: NOESY (400 MHz, CDCl$_3$)



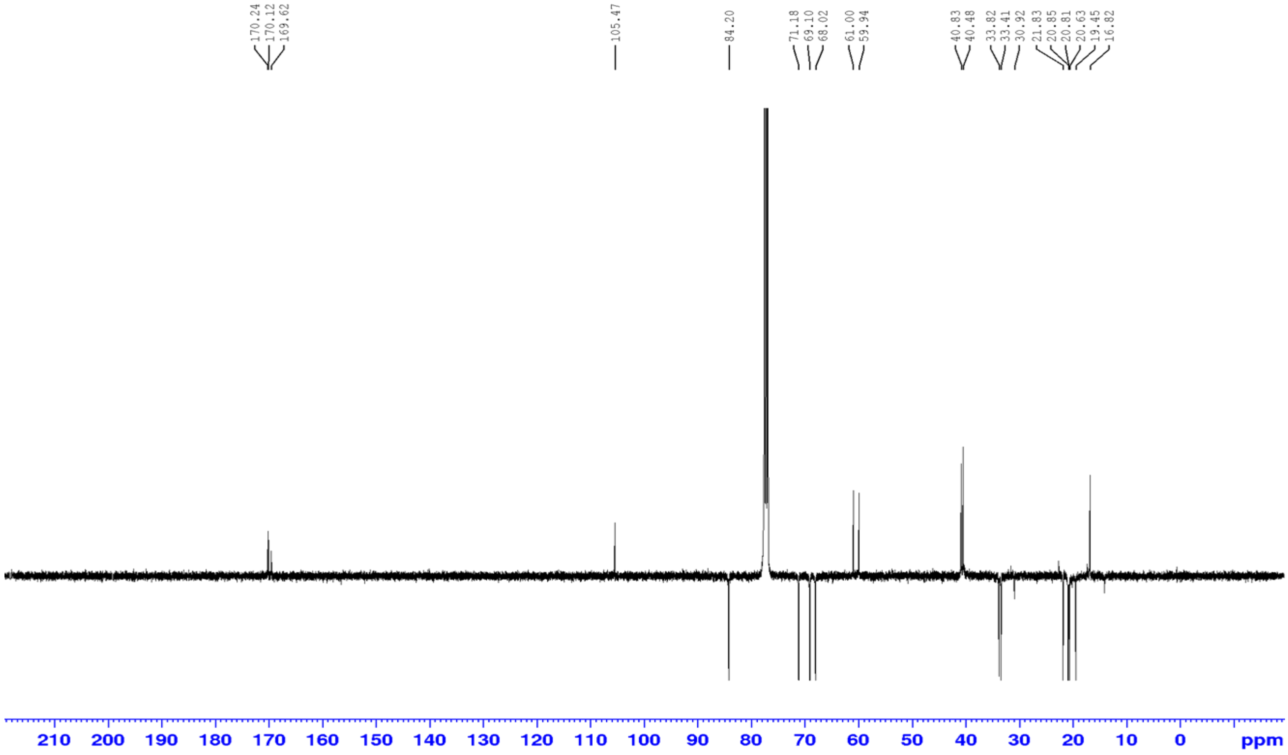


10-βN$_3$

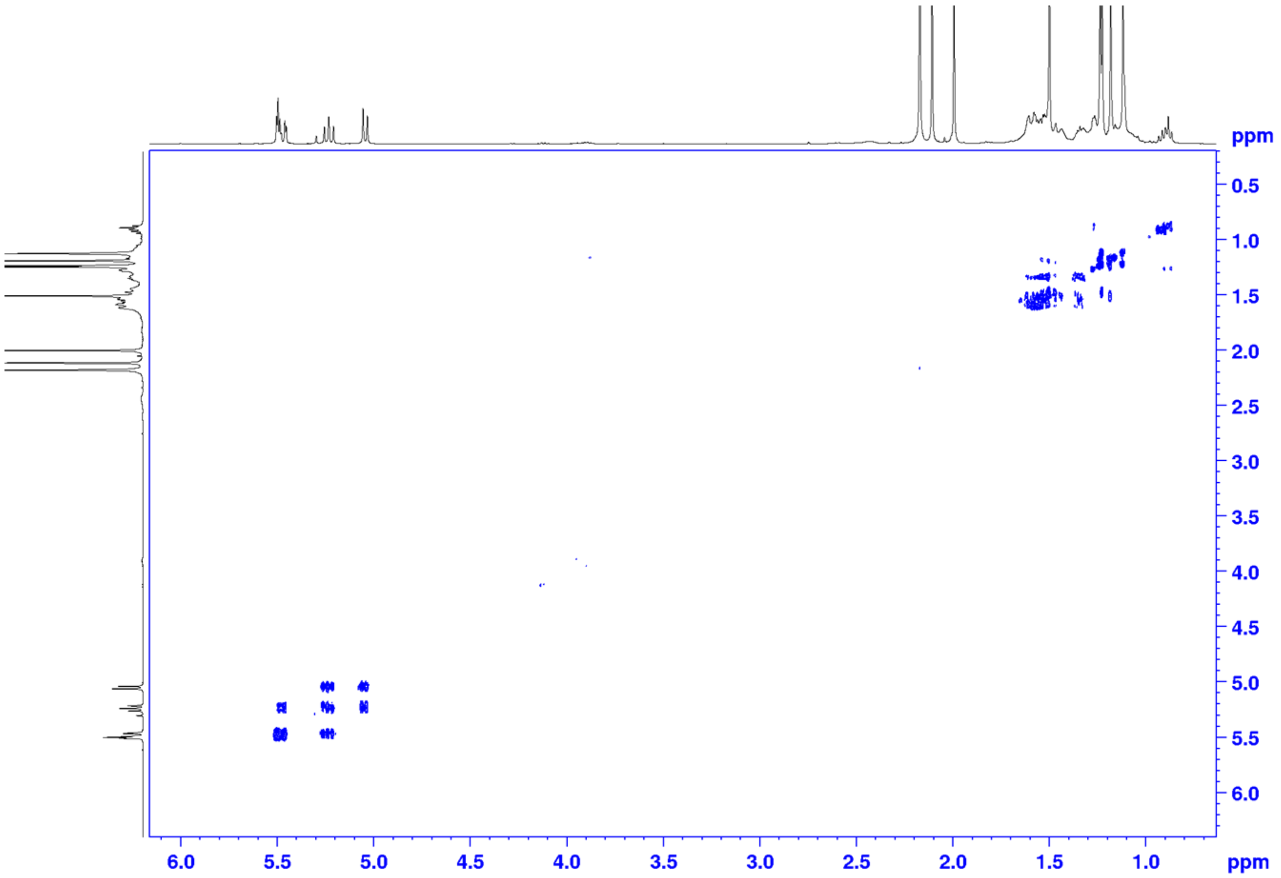
10-βN$_3$: ^{1}H NMR (400 MHz, CDCl$_3$)



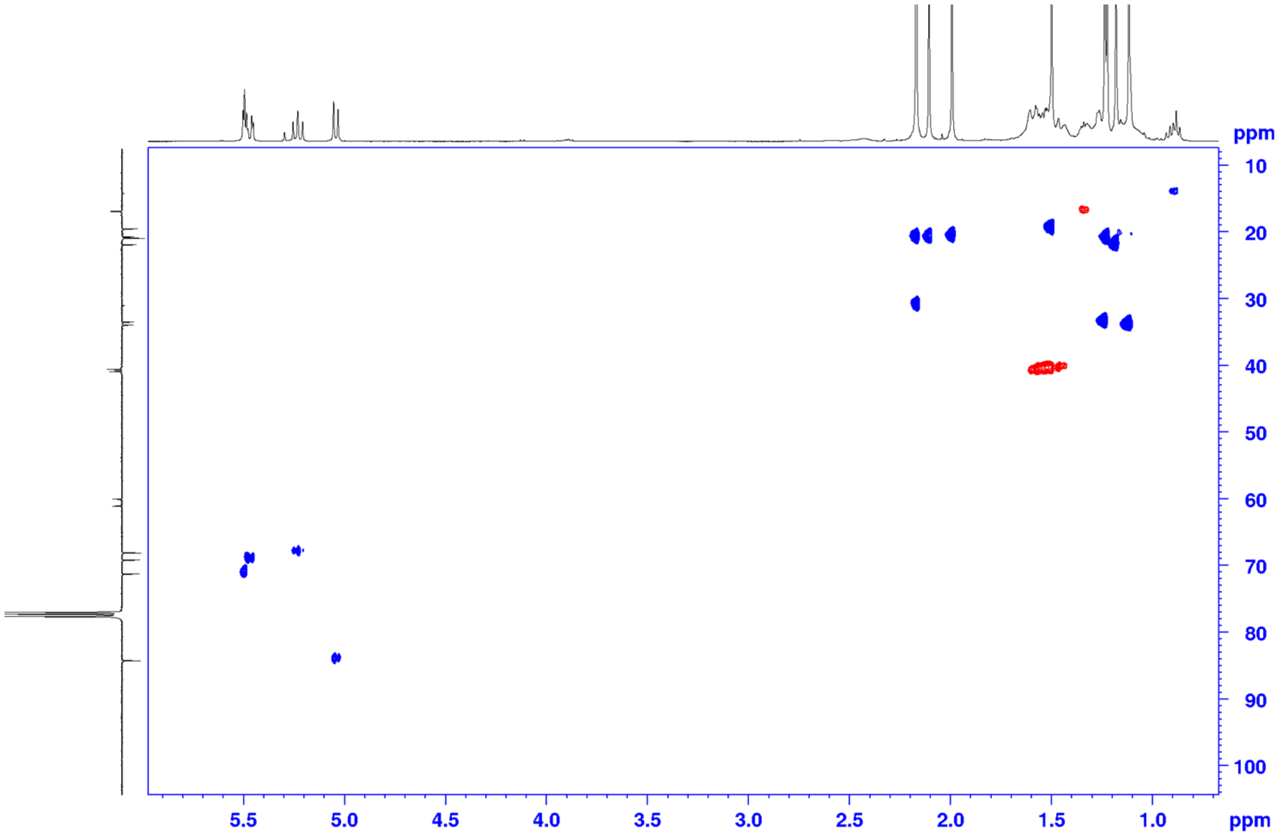
10-βN$_3$: ^{13}C NMR APT (100 MHz, CDCl$_3$)



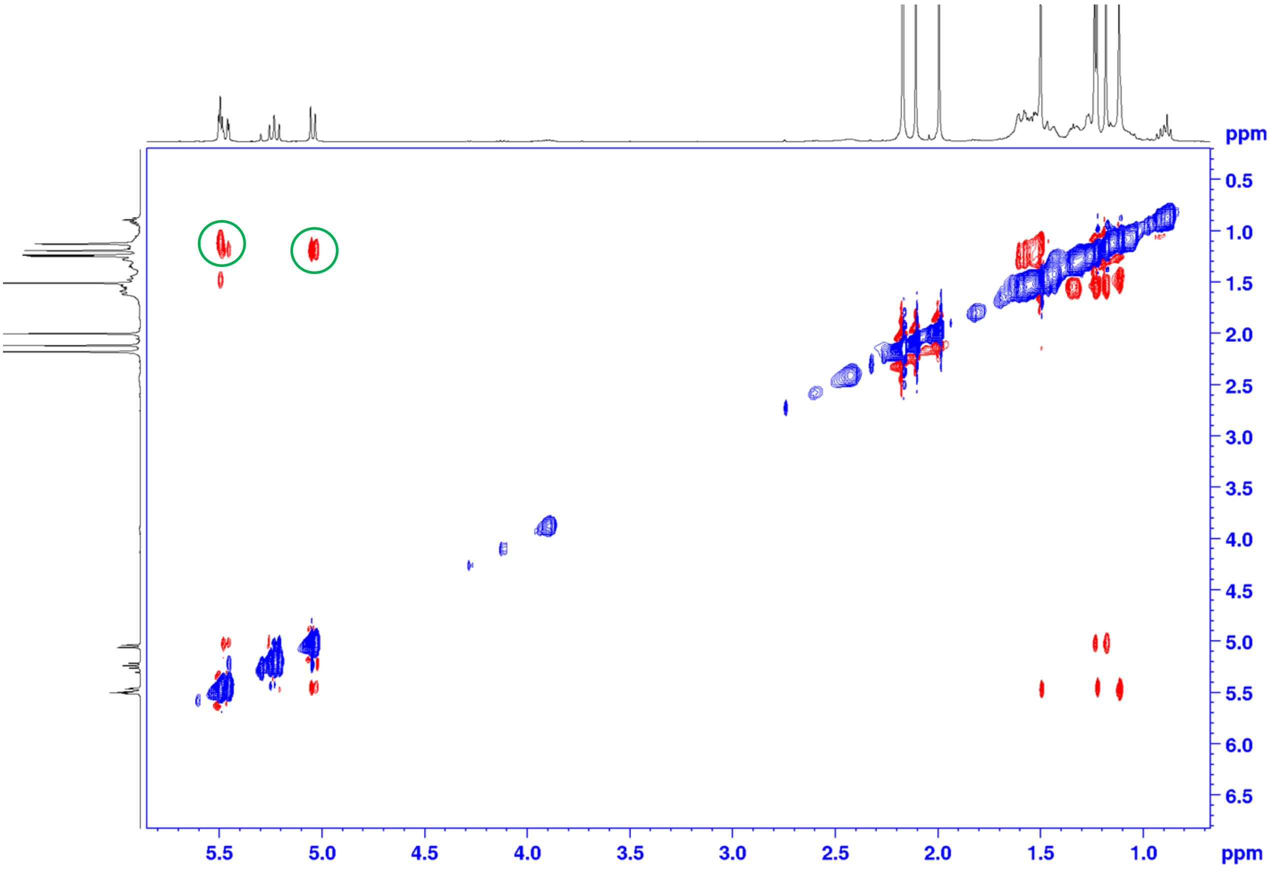
10-βN$_3$: COSY (400 MHz, CDCl$_3$)

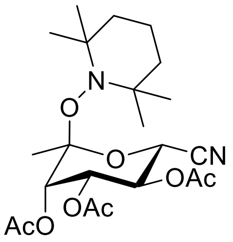


10-βN$_3$: HSQC (400 MHz, CDCl$_3$)



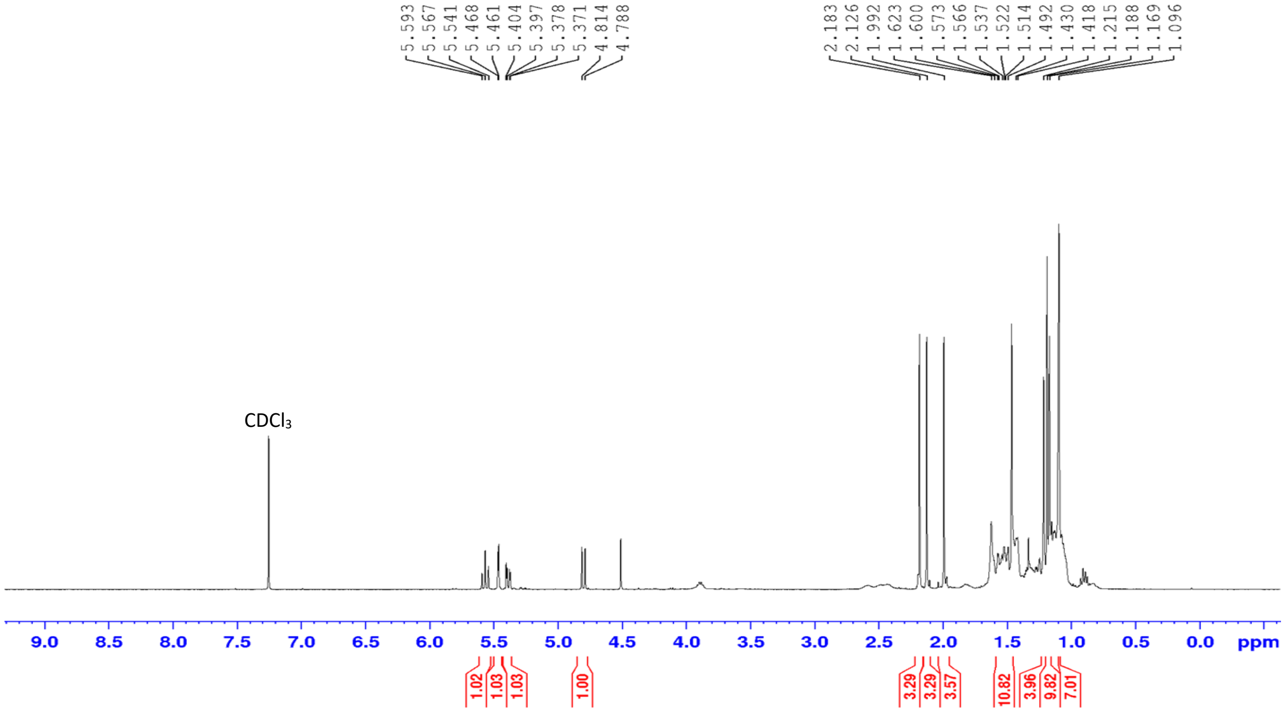
10-βN_3: NOESY (400 MHz, $CDCl_3$)



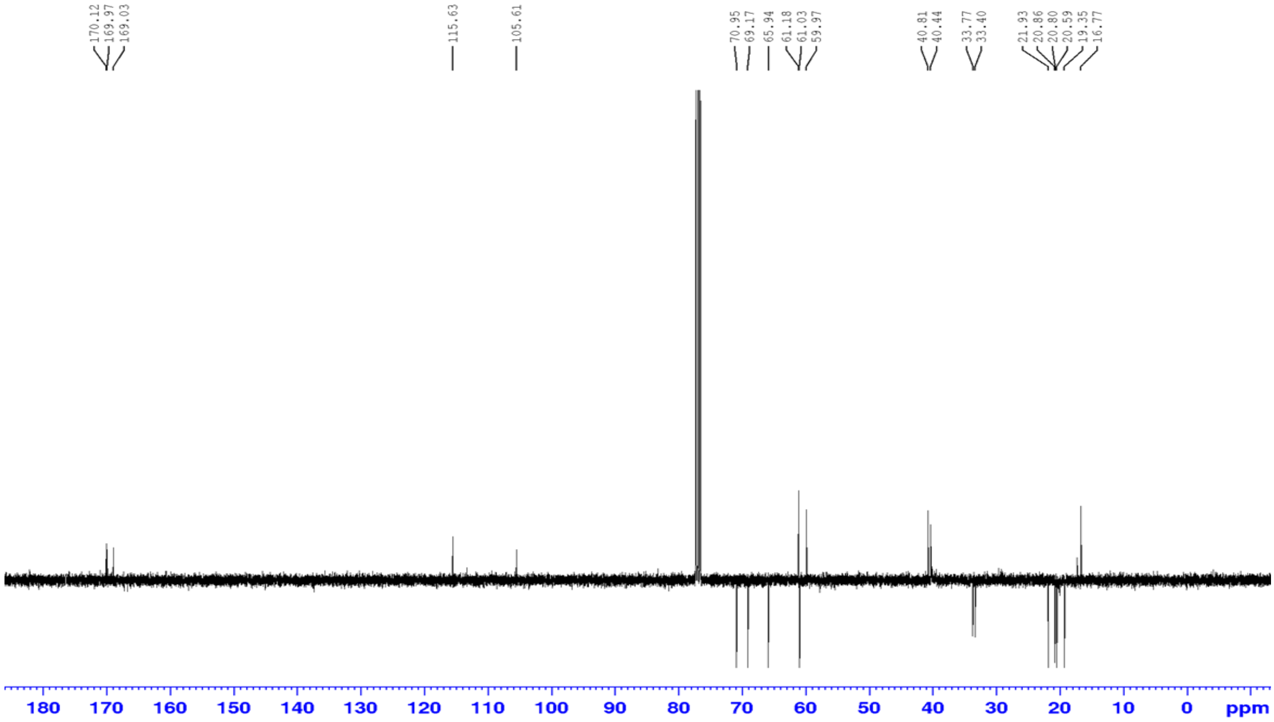


10-βCN

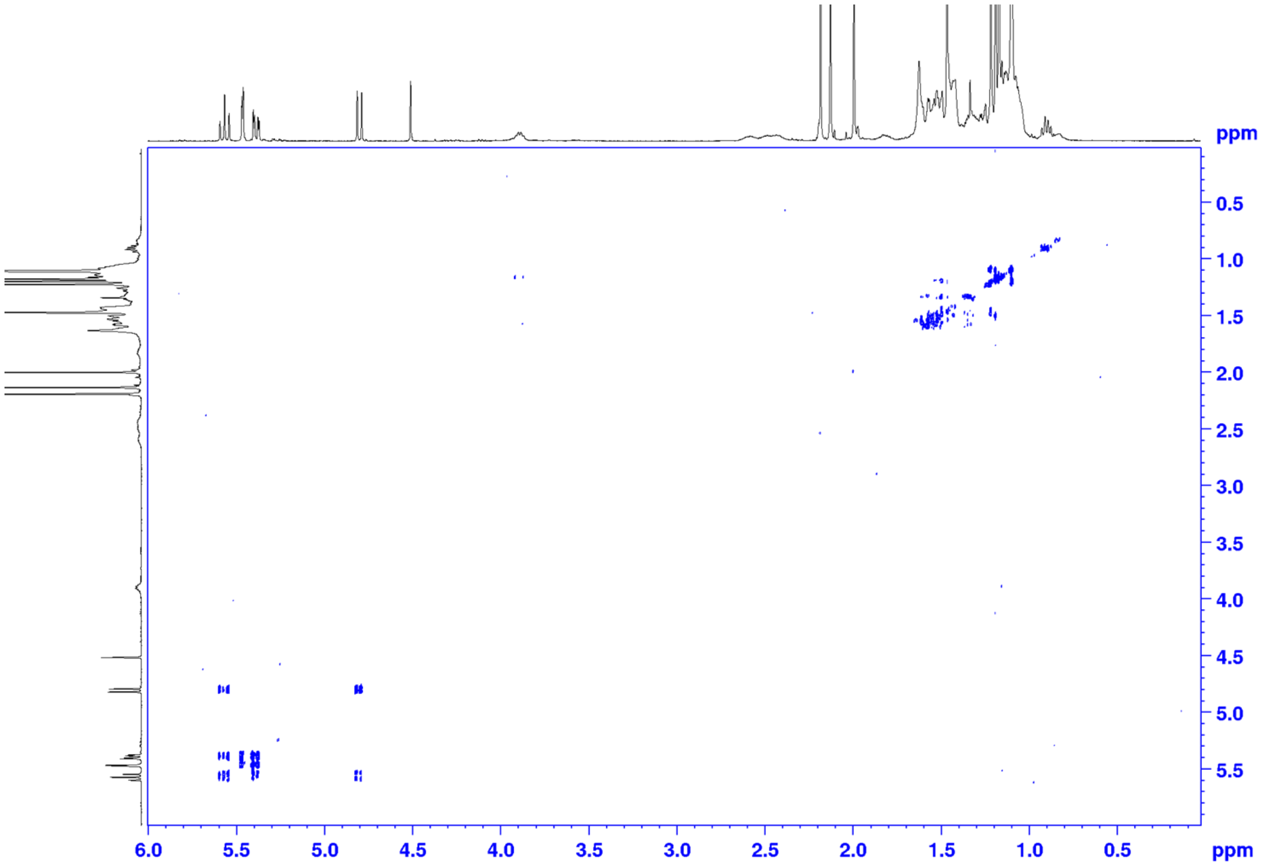
10-βCN: ^{1}H NMR (400 MHz, CDCl$_3$)



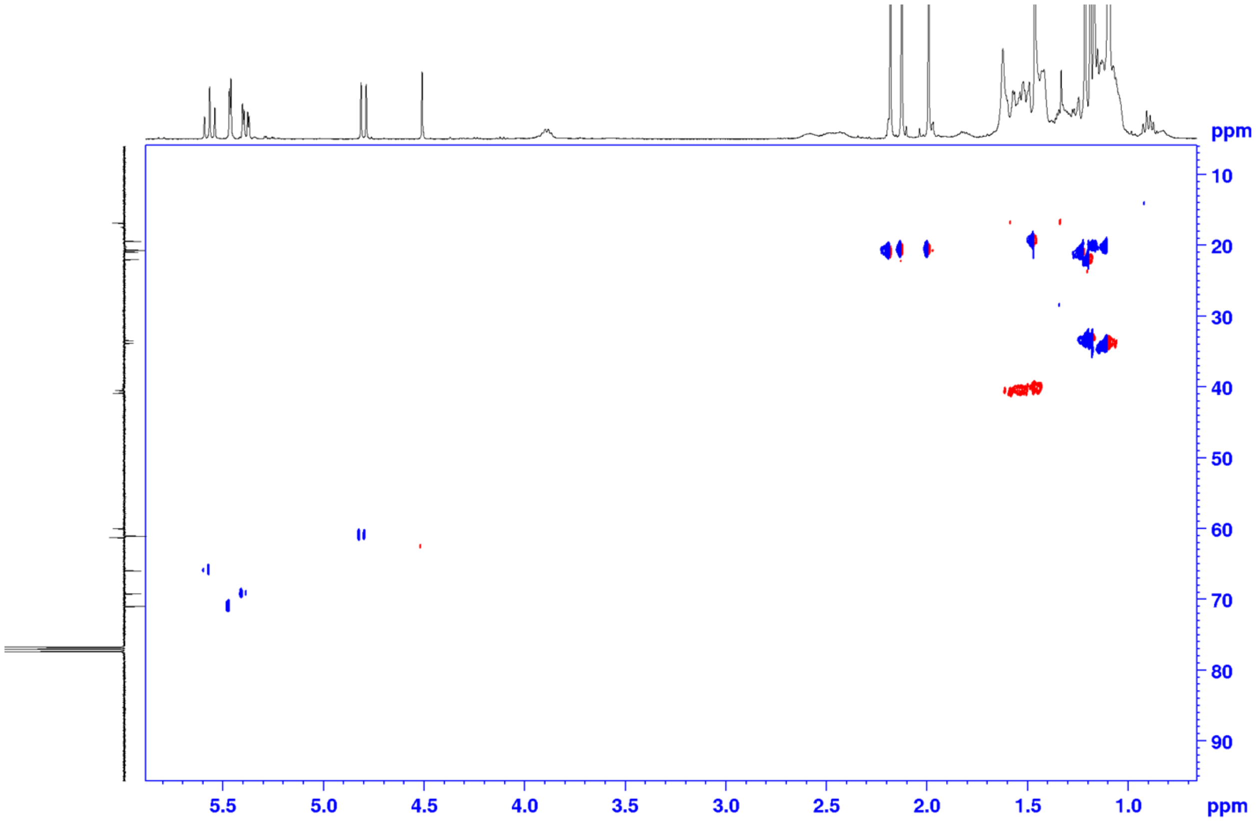
10-βCN: ^{13}C NMR APT (100 MHz, CDCl$_3$)



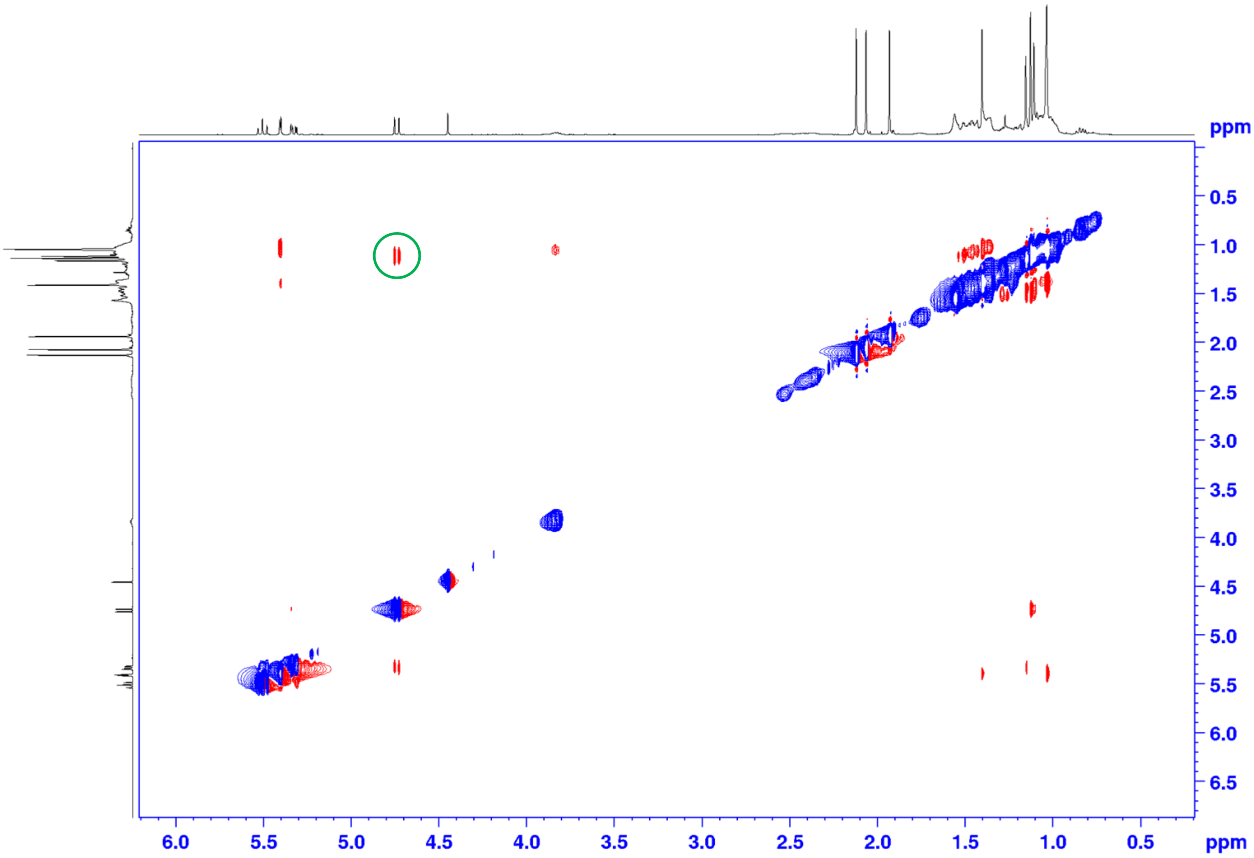
10-βCN: COSY (400 MHz, $CDCl_3$)

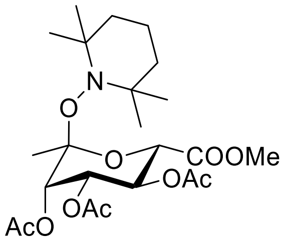


10-βCN: HSQC (400 MHz, $CDCl_3$)



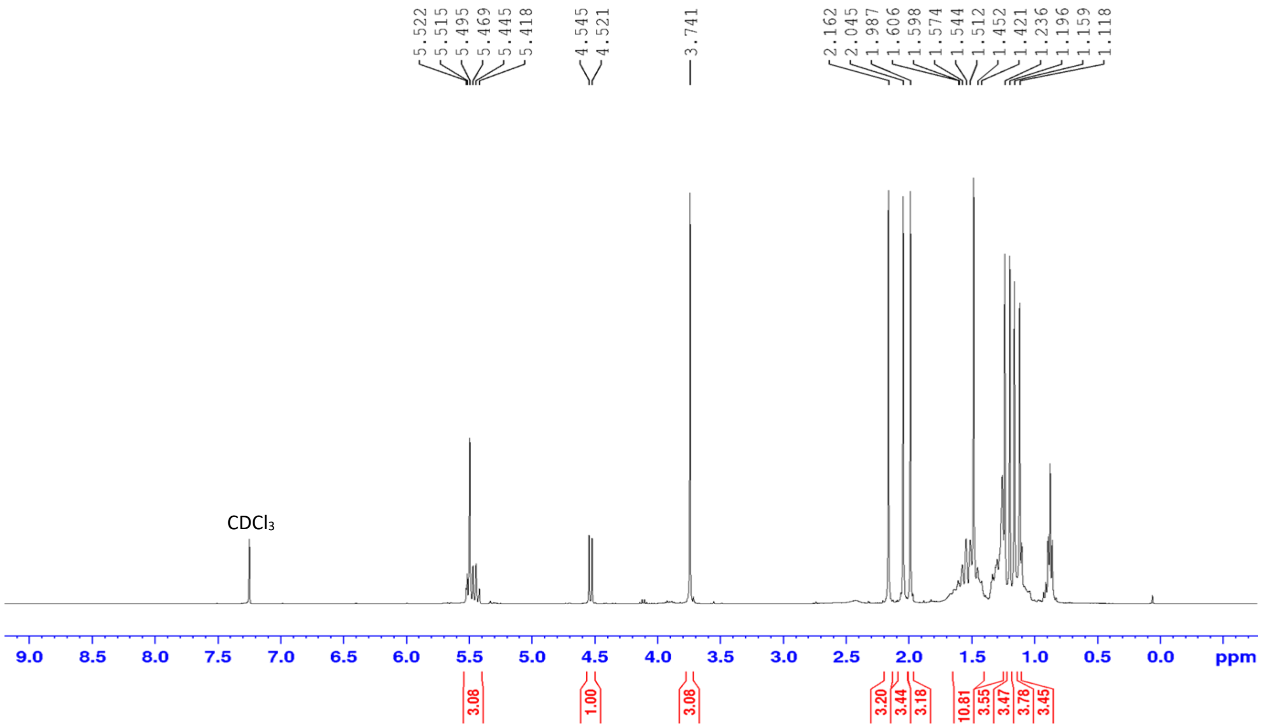
10-βCN: NOESY (400 MHz, $CDCl_3$)



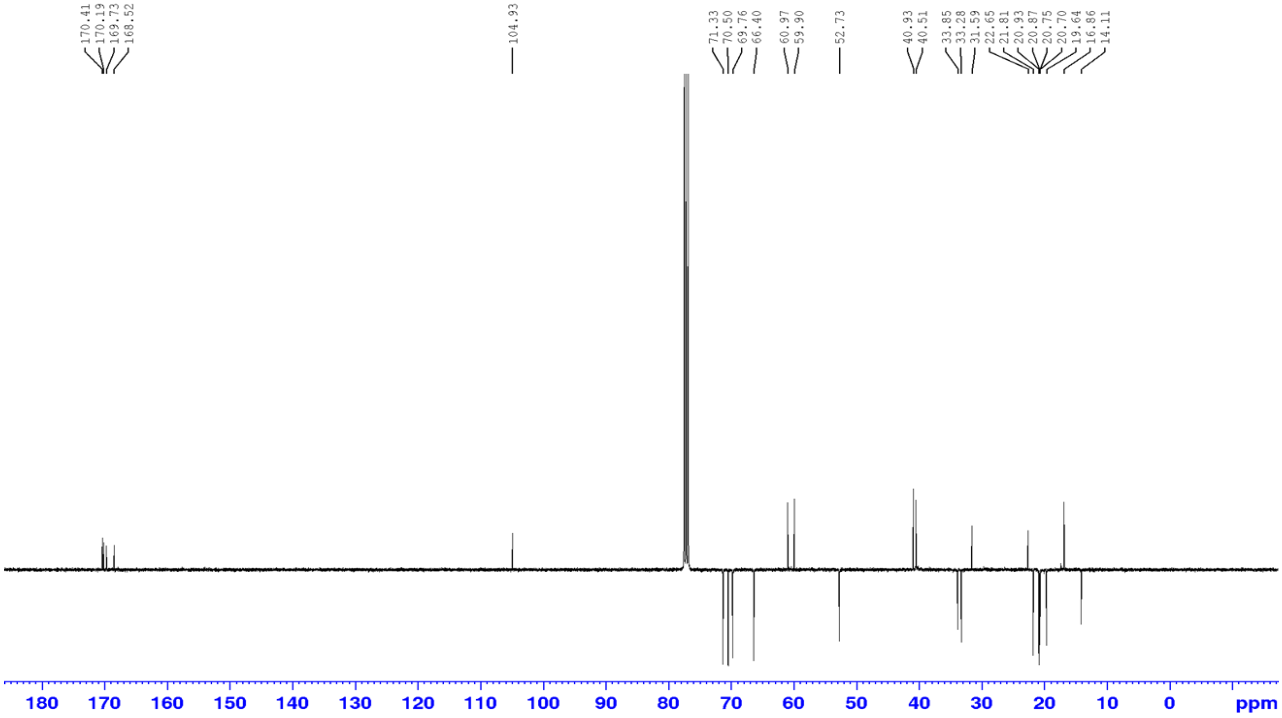


10-βCO₂Me

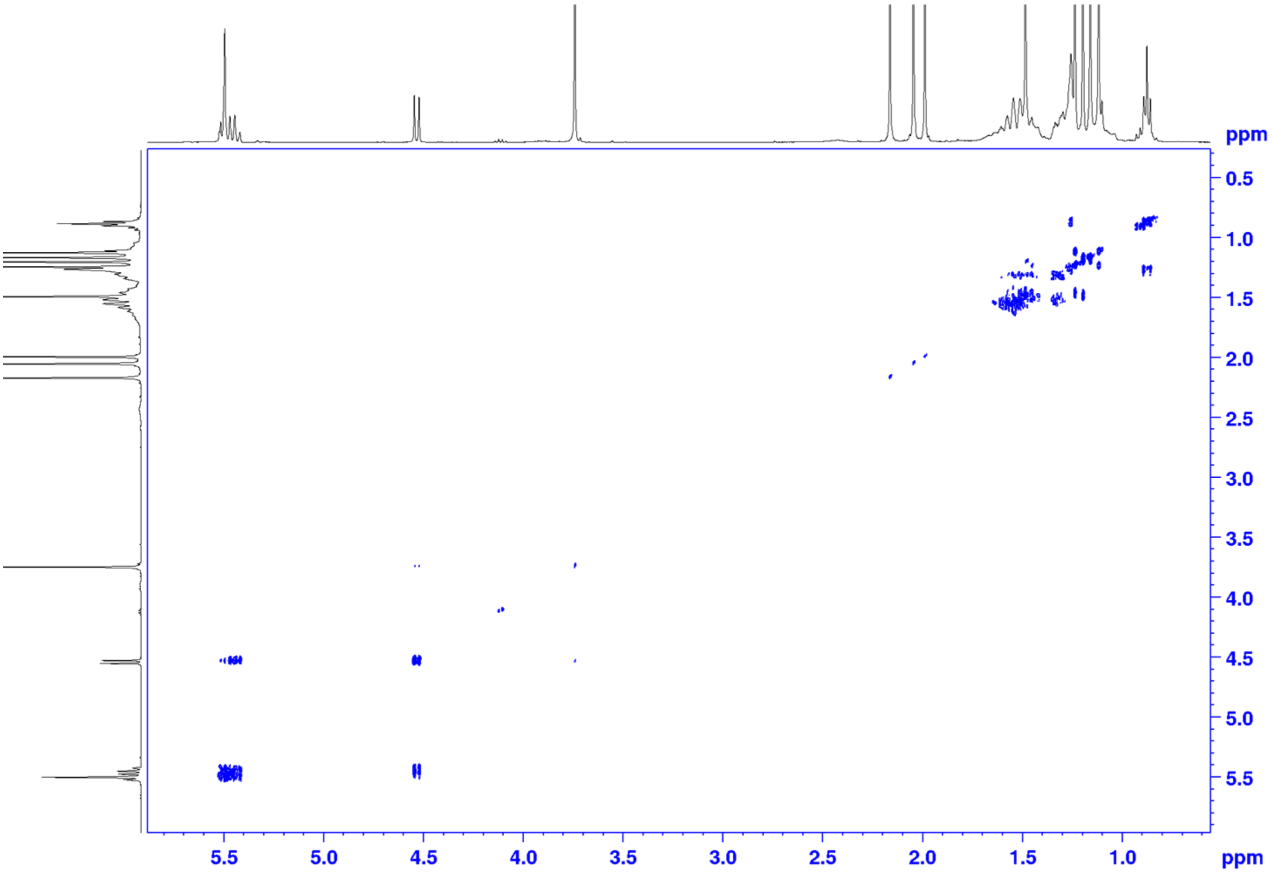
10-βCO2Me: ¹H NMR (400 MHz, CDCl3)



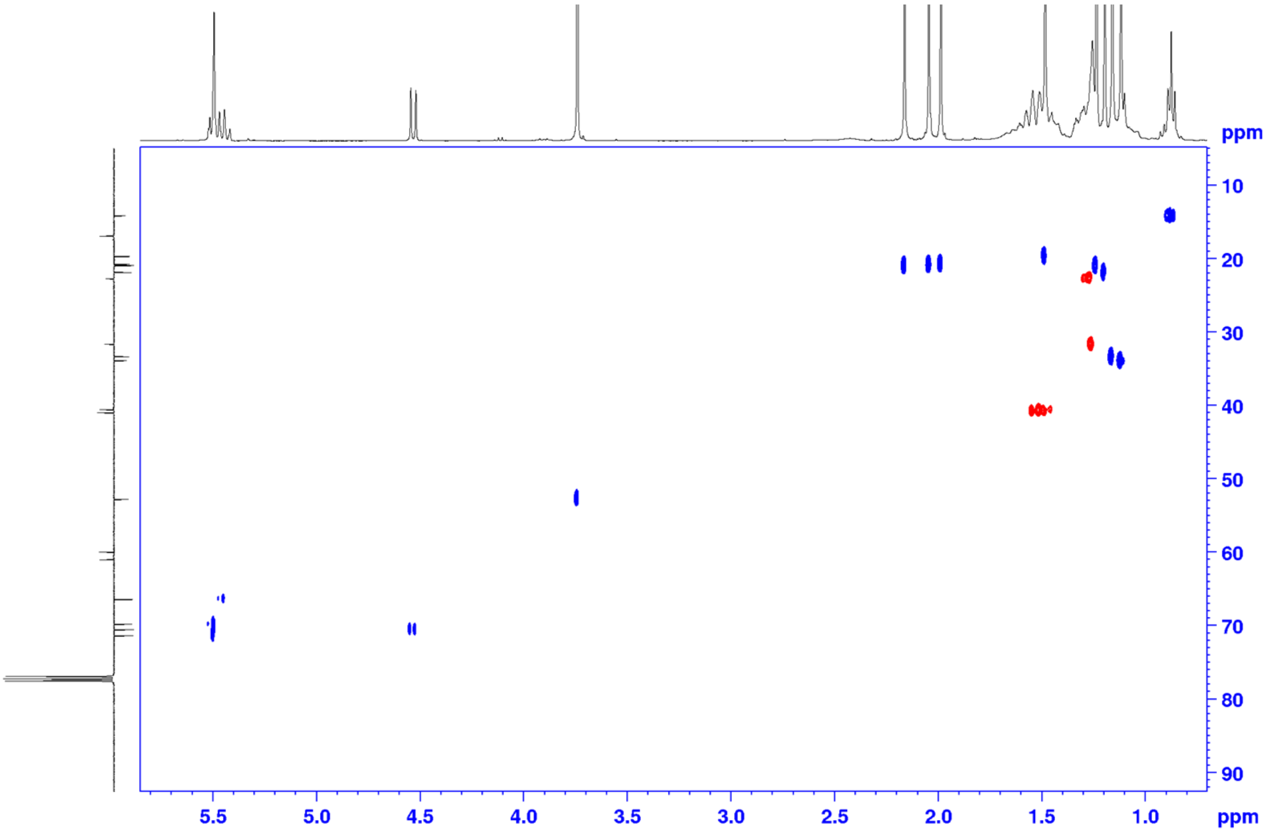
10-βCO2Me: ¹³C NMR APT (100 MHz, CDCl3)



10-βCO$_2$Me: COSY (400 MHz, CDCl$_3$)



10-βCO$_2$Me: HSQC (400 MHz, CDCl$_3$)



10-βCO$_2$Me: NOESY (400 MHz, CDCl$_3$)