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Supporting Information

Furanosyl Oxocarbenium Ion Conformational Energy Landscape Maps as a Tool to Study the Glycosylation Stereoselectivity of 2-Azidofuranoses, 2-Fluorofuranoses and Methyl Furanosyl Uronates

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Supporting Information

Conformational Energy Landscapes as a tool to study the glycosylation stereoselectivity of 2-azidofuranoses, 2-fluorofuranoses, and methyl furanosyl urinates

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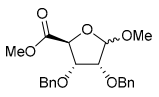
General procedure for the synthesis furanosyl methyl uronates by TEMPO/BAIB oxidation and methylation (17-20). The primary alcohol was dissolved in DCM/H_2O (2/1, v/v, 0.17 M) and the mixture was cooled to 0°C. TEMPO (0.2 eq.) and BAIB (2.5 eq.) were added and the reaction mixture was stirred vigorously overnight. A 10 % aq. NaS_2O_3 solution was added and the mixture stirred for 15 min at room temperature. The mixture was diluted with 0.01 M aq. HCl and DCM and phase separated and the aqueous layer extracted three times with DCM. The combined DCM layers were washed with H_2O and brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude carboxylic acid was dissolved in DMF (0.2 M) and K_2CO_3 (3 eq.) and MeI (3 eq.) were added at 0°C. The reaction was stirred for 3 h and then quenched with AcOH (5 eq). The solution was diluted with H_2O and extracted three times with Et_2O. The combined organic layers were washed with sat. aq. $NaHCO_3$ and brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (19/1 to 7/3) to give the uronic acid methyl ester.

General procedure for the formation of 2-*O*-trifluoromethanesulfonyl-furanosides (29-32). A 0.2M solution of the alcohol (1 eq.) in DCM was cooled to 0°C followed by the addition of pyridine (2 eq.) and Tf_2O (1.2 eq.). After stirring for 40 min the reaction mixture was poured into cold 1 M aq. HCl and extracted twice with DCM. The combined organic layers were washed with cold H_2O, cold sat. aq. $NaHCO_3$, and brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. After coevaporated with toluene the crude triflated furanoside was dissolved in the solvent required for the next synthetic step.

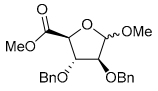
General procedure for the inversion of 2-*O*-trifluoromethanesulfonyl-furanosides (33-40). Conditions **A**: The triflate (1 eq.) was dissolved in *tert*-amyl alcohol (0.35 M) and CsF (4 eq.) was added. The reaction mixture was heated overnight at 90°C, followed by aqueous work up. Conditions **B**: The triflate (1 eq.) was dissolved in THF (0.2 M) and TBAF (1 M in THF, 2.5 eq.) was added at 0°C. The reaction mixture was allowed to reach room temperature and stirred overnight, followed by aqueous work up. Conditions **C**: The triflate (1 eq.) was dissolved in DMF (0.2 M) and NaN_3 (5 eq.) was added. The reaction mixture was heated for 2 h at 80°C, followed by aqueous work up. Work up conditons: the reaction mixture was diluted with H_2O (volume×10) and extracted with Et_2O three times. The combined organic layers were washed with H_2O, sat .aq. $NaHCO_3$, and brine. The organic layer was dried (MgSO4), filtered and concentrated *in vacuo*. Flash column chromatography (1/0 to 9/1 pentane/EtOAc) provided the target inverted furanosides as colourless oils.

General procedure for the hydrolysis of methyl furanosides (21-24, 41-48). Conditions **A**: The methyl glycoside was mixed with 80% aq. formic acid to a concentration of 0.05 M and stirred at 60-65°C for 6-64 h as mentioned for each experiment. After the reaction mixture was cooled to room temperature and transferred to a seperatory funnel, it was diluted 5× with H_2O and extracted three times with DCM. The combined DCM layers were washed with sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (pentane/EtOAc mixtures) to provide the target lactol as a mixture of anomers. Conditions **B**: The methyl glycoside was dissolved in 90% aq. TFA at 0°C and stirred for 4-8 h. The reaction was diluted with DCM and washed with H_2O three times. The aqueous layers were extracted twice with DCM and the combined organic layers were washed with sat. aq. $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residu was purified by flash column chromatography (19/1 to 6/4 pentane/EtOAc) to provide the target lactol as a mixture of anomers.

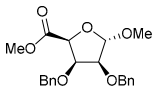
General procedure for the installation of the trifluoro-*N*-phenylacetimidoyl group (1-12). Conditions **A**: The furanose lactol was dissolved in acetone/H_2O (0.2 M, 9/1 v,v) and cooled to 0°C. Cs_2CO_3 (1.1 eq.) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (0.95 eq.) were added and the reaction mixture stirred until TLC-analysis showed complete conversion (1-4 days). The reaction mixture was reduced in volume under reduced pressure and H_2O was added. The aqueous phase was extracted twice with DCM and the combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Flash column chromatography (0-15% Et_2O/pentane) of the residue provided the target imidate donors. Conditions **B**: The furanose lactol was dissolved in DCM (0.25 M) and cooled to 0°C. 2,2,2-Trifluoro-*N*-phenylacetimidoyl chloride (0.95 eq.) was added followed bu DBU (1 eq.). The reaction mixture was stirred for 1 h and then concentrated under reduced pressure. Flash column chromatography (1/0 to 85/15 pentane/Et_2O) of the residue provided the target imidate donors.



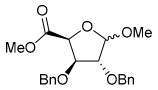
Methyl (methyl 2,3-di-*O*-benzyl-α/β-D-ribofuranosyl uronate) (17). The title compound was generated from **13**[1] (13.3 g, 38.7 mmol) by the general procedure for TEMPO/BAIB oxidation. Yield: 87% (12.5 g, 33.7 mmol) as a yellow oil. R*f*: 0.73 (7/3 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[2] Data for the β-anomer: IR (thin film): 698, 739, 957, 1026, 1063, 1111, 1136, 1205, 1358, 1454, 1738, 1753, 2930, 3030; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HH-NOESY, HSQC): δ 7.38 – 7.26 (m, 10H, CH_{arom}), 4.97 (s, 1H, H-1), 4.68 – 4.62 (m, 3H, CH_2 Bn, H-4), 4.61 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.57 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.35 (dd, 1H, *J* = 6.4, 4.7 Hz, H-3), 3.85 (d, 1H, *J* = 4.6 Hz, H-2), 3.74 (s, 3H, CH_3 CO_2Me), 3.38 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 172.0 (C=O), 137.6, 137.5 (C_q), 128.5, 128.4, 128.0, 127.9, 127.9 (CH_{arom}), 107.1 (C-1), 80.6 (C-3), 79.8 (C-2), 79.6 (C-4), 72.8, 72.7 (CH_2 Bn), 55.3 (CH_3 OMe), 52.3 (CH_3 CO_2Me); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$: +0.3 Hz, $^2J_{C2,H1}$: -0.6 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{21}H_{28}NO_6$ 390.19111, found 390.19105.



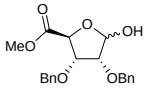
Methyl (methyl 2,3-di-*O*-benzyl-α/β-D-arabinofuranosyl uronate) (18). The title compound was generated from **14**[3] (28.2 g, 78.8 mmol) by the general procedure for TEMPO/BAIB oxidation. Yield: 70% (20.6 g, 55.3 mmol) as a yellow oil. R*f*: 0.75 (7/3 pentane/EtOAc). IR (thin film): 698, 737, 1028, 1059, 1099, 1207, 1360, 1454, 1734, 1755, 2874, 2916, 2949, 3030. Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.44 – 7.21 (m, 10H, CH_{arom}), 5.09 (s, 1H, H-1), 4.63 (d, 1H, *J* = 4.8 Hz, H-4), 4.67 – 4.54 (m, 2H, CH_2 Bn), 4.47 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.41 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.15 (dd, 1H, *J* = 4.8, 1.8 Hz, H-3), 3.96 (dd, 1H, *J* = 1.8, 0.8 Hz, H-2), 3.73 (s, 3H, CH_3 CO_2Me), 3.41 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.6 (C=O), 137.2, 137.2 (C_q), 128.4, 128.2, 128.0, 127.9, 127.9, 127.9 (CH_{arom}), 108.0 (C-1), 86.5 (C-2), 84.9 (C-3), 80.9 (C-4), 72.1, 71.7 (CH_2 Bn), 55.5 (CH_3 OMe), 52.4 (CH_3 CO_2Me); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.22 (m, 10H, CH_{arom}), 4.76 (d, 1H, *J* = 4.2 Hz, H-1), 4.73 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.67 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.64 – 4.58 (m, 2H, CH_2 Bn), 4.53 (dd, 1H, *J* = 6.6, 4.9 Hz, H-3), 4.42 (d, 1H, *J* = 4.9 Hz, H-4), 4.01 (dd, 1H, *J* = 6.6, 4.2 Hz, H-2), 3.73 (s, 3H, CH_3 CO_2Me), 3.42 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 171.5 (C=O), 137.7, 137.4 (C_q), 128.4, 128.4, 128.3, 128.1, 127.9, 127.7 (CH_{arom}), 102.3 (C-1), 83.8, 83.8 (C-2, C-3), 79.4 (C-4), 72.5, 72.5 (CH_2 Bn), 55.5 (CH_3 OMe), 52.2 (CH_3 CO_2Me); HRMS: $[M+NH_4]^+$ calcd for $C_{21}H_{28}NO_6$ 390.19111, found 390.19094.



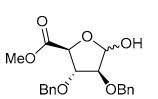
Methyl (methyl 2,3-di-*O*-benzyl-α-D-lyxofuranosyl uronate) (19). The title compound was generated from **15**[4] (9.91 g, 28.8 mmol) by the general procedure for TEMPO/BAIB oxidation. Yield: 89% (9.5 g, 25.5 mmol) as a white solid. R*f*: 0.70 (7/3 pentane/EtOAc). m.p. 76-80 °C. $[\alpha]_D^{20}$ = +29.7° (*c* = 0.92, $CHCl_3$); IR (thin film): 698, 739, 1028, 1065, 1145, 1211, 1454, 1734, 1767, 2949; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.38 – 7.23 (m, 10H, CH_{arom}), 5.23 (d, 1H, *J* = 3.6 Hz, H-1), 4.76 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.72 (d, 1H, *J* = 4.7 Hz, H-4), 4.69 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.63 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.59 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.35 (t, 1H, *J* = 4.7 Hz, H-3), 3.93 (dd, 1H, *J* = 4.6, 3.6 Hz, H-2), 3.72 (s, 3H, CH_3 CO_2Me), 3.43 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 169.1 (C=O), 138.0, 137.8 (C_q), 128.5, 128.4, 127.9, 127.9, 127.8, 127.8 (CH_{arom}), 108.0 (C-1), 83.3 (C-2), 79.0 (C-3), 78.5 (C-4), 73.9, 72.8 (CH_2 Bn), 56.5 (CH_3 OMe), 52.3 (CH_3 CO_2Me); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$ = -2.8 Hz, $^2J_{C2,H1}$ = -1.6 Hz; HRMS: $[M+H]^+$ calcd for $C_{21}H_{25}O_6$ 373.16456, found 373.16471.



Methyl (methyl 2,3-di-*O*-benzyl-α/β-D-xylofuranosyl uronate) (20). The title compound was generated from **16**[5] (34.4 g, 100 mmol) by the general procedure for TEMPO/BAIB oxidation. Yield: 88% (30.8 g, 88.2 mmol) as a yellow oil. R*f*: 0.65 (7/3 pentane/EtOAc). IR (thin film): 698, 739, 1063, 1119, 1207, 1454, 1738, 1765, 2916, 2949, 3030. Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.39 – 7.21 (m, 10H, CH_{arom}), 4.94 (d, 1H, *J* = 4.3 Hz, H-1), 4.79 (d, 1H, *J* = 7.4 Hz, H-4), 4.64 – 4.57 (m, 4H, 2xCH_2 Bn), 4.47 (dd, 1H, *J* = 7.4, 6.2 Hz, H-3), 4.11 (dd, 1H, *J* = 6.2, 4.3 Hz, H-2), 3.73 (s, 3H, CH_3 CO_2Me), 3.40 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 169.7 (C=O), 137.6, 137.4 (C_q), 128.5, 128.4, 128.2, 128.1, 127.7, 127.5 (CH_{arom}), 101.6 (C-1), 82.5 (C-2), 81.8 (C-3), 76.5 (C-4), 73.0, 72.9 (CH_2 Bn), 55.7 (OMe), 52.2 (CO_2Me); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.23 (m, 10H, CH_{arom}), 5.04 (s, 1H, H-1), 4.90 (d, 1H, *J* = 6.2 Hz, H-4), 4.61 – 4.56 (m, 1H, C*H*H Bn) 4.53 (d, 1H, *J* = 12.5 Hz, C*H*H Bn), 4.43 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.39 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.23 (dd, 1H, *J* = 6.2, 1.4 Hz, H-2), 3.98 – 3.97 (m, 1H, H-2), 3.77 (s, 3H, CH_3 CO_2Me), 3.53 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 169.7 (C=O), 137.2, 137.2 (C_q), 128.5, 128.5, 128.1, 128.0, 127.7, 127.5 (CH_{arom}), 108.8 (C-1), 85.1 (C-2), 81.2 (C-3), 81.1 (C-4), 72.7, 71.9 (CH_2 Bn), 56.0 (OMe), 52.1 (CO_2Me); HRMS: $[M+H]^+$ calcd for $C_{21}H_{25}O_6$ 373.16456, found 373.16448.

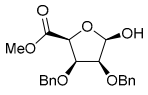


Methyl (2,3-di-*O*-benzyl-α/β-D-ribofuranosyl uronate) (21). The title compound was generated from **17** (8.33 g, 22.38 mmol) by the general procedure for methyl furanoside hydrolysis, conditions B (7.5 h). Yield: 73% α:β = 1.1:1 (5.87 g, 16.4) as a colourless oil. R*f*: 0.54 (7/3 pentane/EtOAc). IR (thin film): 698, 739, 1026, 1070, 1209, 1358, 1454, 1740, 2870, 2951, 3030, 3441; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.25 (m, 10H, CH_{arom}), 5.45 (dd, 1H, *J* = 11.1, 4.3 Hz, H-1), 4.82 – 4.44 (m, 5H, 2xCH_2Bn, H-4), 4.19 (d, 1H, *J* = 11.5 Hz, OH), 4.16 – 4.06 (m, 1H, H-3), 3.89 (d, 1H, *J* = 4.5 Hz, H-2), 3.71 (d, 3H, *J* = 4.2 Hz, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.6 (C=O), 137.11, 136.74 (C_q), 128.5 – 127.9 (CH_{arom}), 96.8 (C-1), 80.2 (C-2), 79.1 (C-4), 77.5 (C-3), 72.5, 72.4 (CH_2Bn), 52.6 (CH_3 CO_2Me); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.25 (m, 10H, CH_{arom}), 5.55 (s, 1H, H-1), 5.07 – 4.88 (m, 1H, OH), 4.78, (d, *J* = 1.4 Hz, H-4), 4.82 – 4.44 (m, 4H, 2xCH_2Bn), 4.38 (dd, 1H, *J* = 6.5, 4.5 Hz, H-3), 3.93 (t, 1H, *J* = 4.6 Hz, H-2), 3.71 (d, 3H, *J* = 4.2 Hz, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 173.3 (C=O), 137.6, 137.4 (C_q), 128.5 – 127.9 (CH_{arom}), 101.1 (C-1), 80.4 (C-3), 80.2 (C-2), 79.7 (C-4), 73.0, 72.7 (CH_2Bn), 52.6 (CH_3 CO_2Me); HRMS: $[M+Na]^+$ calcd for $C_{20}H_{22}O_6Na$ 381.13086, found 381.13084.

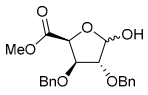


Methyl (2,3-di-*O*-benzyl-α/β-D-arabinofuranosyl uronate) (22). The title compound was generated from **18** (11.9 g, 32 mmol) by the general procedure for methyl furanoside hydrolysis, conditions B (8 h). Yield: 60% α:β = 2:1 (6.87 g, 19.2 mmol) as a yellow oil. R*f*: 0.38 (7/3 pentane/EtOAc). IR (thin film): 698, 739, 1028, 1076, 1090, 1207, 1454, 1740. Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.22 (m, 10H, CH_{arom}), 5.51 (d, 1H, *J* = 10.2 Hz, H-1), 4.86 (d, 1H, *J* = 1.7 Hz, H-4), 4.70 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.59 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.53 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.46 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.38 – 4.34 (m, 1H, H-3), 3.94 (d, 1H, *J* = 0.9 Hz,

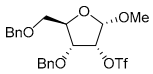
H-2), 3.69 (s, 3H, CH_3 CO_2Me), 3.41 (d, 1H, *J* = 10.3 Hz, OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.5 (C=O), 137.1, 136.7 (C_q), 128.6, 128.5, 128.4, 128.0, 128.0, 127.7 (CH_{arom}), 102.1 (C-1), 84.6 (C-2), 84.1 (C-3), 81.1 (C-4), 72.3, 71.6 (CH_2 Bn), 52.4 (CH_3 CO_2Me); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.22 (m, 10H, CH_{arom}), 5.55 (dd, 1H, *J* = 10.0, 3.9 Hz, H-1), 4.66 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.57 – 4.54 (m, 1H, CH*H* Bn), 4.53 (d, 1H, *J* = 2.2 Hz, H-4), 4.38 – 4.34 (m, 1H, H-3), 3.91 (dd, 1H, *J* = 3.9, 2.7 Hz, H-2), 3.85 (d, 1H, *J* = 10.0 Hz, OH), 3.72 (s, 3H, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 171.8 (C=O), 137.2, 136.9 (C_q), 128.5, 128.2, 128.2, 128.0, 127.9, 127.8 (CH_{arom}), 98.2 (C-1), 84.2 (C-3), 81.5 (C-2), 79.7 (C-4), 72.7, 72.1 (CH_2 Bn), 52.5 (CH_3 CO_2Me); HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{26}NO_6$ 376.17546, found 376.17566.



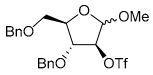
Methyl (2,3-di-*O*-benzyl-β-D-lyxofuranosyl uronate) (23). The title compound was generated from **19** (1.0 g, 2.7 mmol) by the general procedure for methyl furanoside hydrolysis, conditions B (6 h). Yield: 85% β only (818 mg, 2.28 mmol) as a white solid. R*f*: 0.35 (1/1 pentane/EtOAc). IR (thin film): 698, 739, 1026, 1065, 1141, 1211, 1360, 1437, 1454, 1738, 1763, 2874, 2951, 3466. ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.43 – 7.22 (m, 10H, CH_{arom}), 5.40 (dd, 1H, *J* = 12.6, 4.3 Hz, H-1), 4.85 (d, 1H, *J* = 11.2 Hz, C*H*H Bn), 4.80 (d, 1H, *J* = 11.6 Hz, C*H*H Bn), 4.63 – 4.59 (m, 3H, 2xCH*H* Bn, H-4), 4.37 (t, 1H, *J* = 4.4 Hz, H-3), 4.33 (d, 1H, *J* = 12.6 Hz, OH), 3.91 (t, 1H, *J* = 4.2 Hz, H-2), 3.73 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 169.5 (C=O), 137.3, 137.2 (C_q), 128.7, 128.5, 128.2, 128.2, 128.1, 127.9 (CH_{arom}), 97.0 (C-1), 78.8 (C-4), 78.5, 78.4 (C-2, C-3), 74.8, 72.2 (CH_2 Bn), 52.4 (CH_3 CO_2Me); HRMS: $[M+Na]^+$ calcd for $C_{20}H_{22}O_6Na$ 376.17546, found 376.17580.



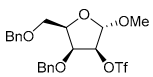
Methyl (2,3-di-*O*-benzyl-α/β-D-xylofuranosyl uronate) (24). The title compound was generated from **20** (17.7 g, 47.6 mmol) by the general procedure for methyl furanoside hydrolysis, conditions B (4 h). Yield: 90% α:β = 1:1.3 (15.3 mg, 42.7 mmol) as a light yellow oil. R*f*: 0.2 (8/2 pentane/EtOAc). IR (thin film): 698, 739, 1028, 1061, 1072, 1209, 1366, 1437, 1454, 1738, 1759, 2951, 3030, 3430; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.45 – 7.21 (m, 17.5H, CH_{arom}), 5.65 (dd, 0.75H, *J* = 10.1, 4.0 Hz, H-1α), 5.39 (d, 1H, *J* = 11.3 Hz, H-1β), 4.90 (d, 1H, *J* = 5.9 Hz, H-4β), 4.83 (d, 0.75H, *J* = 5.2 Hz, H-4α), 4.61 – 4.49 (m, 7H, CH_2 Bn), 4.28 (ddd, 1H, *J* = 5.9, 2.4, 0.8 Hz, H-3β), 4.25 (ddd, 1H, *J* = 5.2, 2.5, 0.4 Hz, H-3α), 4.00 (d, 1H, *J* = 11.6 Hz, 1-OHβ), 4.00 (dt, 1H, *J* = 2.4, 0.8 Hz, H-2β), 3.94 (dd, 0.75H, *J* = 3.9, 2.6 Hz, H-2α), 3.84 (d, 0.75H, *J* = 10.1 Hz, 1-OHα), 3.77 (s, 3H, CH_3 CO_2Meβ), 3.74 (s, 2.25H, CH_3 CO_2Meα); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 171.2, 169.7 (C=O), 137.1, 136.7 (C_q), 128.7, 128.6, 128.5, 128.5, 128.3, 128.1, 128.1, 127.9, 127.8 (CH_{arom}), 102.8 (C-1β), 97.4 (C-1α), 85.2 (C-2β), 82.1 (C-3β), 81.7 (C-3α), 80.8 (C-4β), 80.4 (C-2α), 77.9 (C-4α), 73.2, 73.0, 72.8, 72.1 (CH_2 Bn), 52.5 (CO_2Meβ), 52.1 (CO_2Meα); HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{26}NO_6$ 376.17546, found 376.17564.



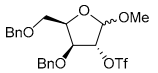
Methyl 3,5-di-*O*-benzyl-2-*O*-trifluoromethanesulfonate-α-D-ribofuranoside (29). The title compound was generated from **25**[6] by the general procedure for triflate formation and used crude. Spectroscopic data were in accord with those previously reported.[7] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.21 (m, 10H, CH_{arom}), 5.09 (d, 1H, *J* = 4.3 Hz, H-1), 5.01 (dd, 1H, *J* = 6.5, 4.3 Hz, H-2), 4.75 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.53 – 4.44 (m, 2H, CH*H* Bn, C*H*H Bn), 4.40 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.19 (dt, 1H, *J* = 5.8, 3.1 Hz, H-4), 4.07 (dd, 1H, *J* = 6.5, 5.0 Hz, H-3), 3.53 (dd, 1H, *J* = 10.9, 2.9 Hzm H-5), 3.51 (s, 3H, CH_3 OMe), 3.33 (dd, 1H, *J* = 10.8, 3.3 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.7, 137.1 (C_q), 128.7, 128.6, 128.4, 128.3, 128.0, 127.9 (CH_{arom}), 118.7 (d, *J* = 319.6 Hz), 101.1 (C-1), 81.4 (C-2), 81.1 (C-4), 74.6 (C-3), 73.7, 73.5 (CH_2 Bn), 68.5 (C-5), 56.4 (OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{21}H_{27}F_3NO_7S$ 494.14548, found 494.14526.



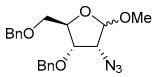
Methyl 3,5-di-*O*-benzyl-2-*O*-trifluoromethanesulfonate-α/β-D-arabinofuranoside (30). The title compound was generated from **26**[8] by the general procedure for triflate formation and used crude. Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.38 – 7.23 (m, 10H, CH_{arom}), 5.20 (s, 1H, H-2), 5.10 (s, 1H, H-1), 4.70 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.55 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.52 – 4.45 (m, 2H, 2x CH*H* Bn), 4.22 – 4.18 (m, 1H, H-4), 4.13 (ddd, 1H, *J* = 5.9, 1.7, 0.9 Hz, H-3), 3.61 (dd, 1H, *J* = 10.9, 3.6 Hz, H-5), 3.54 (dd, 1H, *J* = 10.9, 4.6 Hz, H-5), 3.42 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.8, 136.7 (C_q), 128.7, 128.5, 128.3, 128.1, 127.9, 127.9 (CH_{arom}), 118.5 (q, *J* = 319.8 Hz), 105.9 (C-1), 92.7 (C-2), 82.6 (C-3), 81.8 (C-4), 73.7, 72.8 (CH_2 Bn), 68.6 (C-5), 55.2 (OMe); Diagnostic peaks β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.11 – 5.07 (m, 1H, H-1), 5.00 (d, 1H, *J* = 4.4 Hz, H-2), 4.62 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.57 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.55 – 4.48 (m, 2H, CH_2 Bn), 4.29 (dd, 1H, *J* = 6.5, 5.4 Hz, H-3), 4.17 – 4.12 (m, 1H, H-4), 3.57 – 3.53 (m, 1H, H-5), 3.47 (dd, 1H, *J* = 9.9, 6.2 Hz, H-5), 3.39 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 100.4 (C-1), 88.3 (C-2), 80.9 (C-3), 79.8 (C-4), 73.5, 72.6 (CH_2 Bn), 71.4 (C-5), 55.5 (OMe).



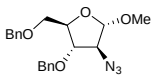
Methyl 3,5-di-*O*-benzyl-2-*O*-trifluoromethanesulfonate-α-D-lyxofuranoside (31). The title compound was generated from **27**[9] by the general procedure for triflate formation and used crude. ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.43 – 7.13 (m, 10H, CH_{arom}), 5.08 (s, 1H, H-1), 5.05 (d, 1H, *J* = 4.3 Hz, H-2), 4.73 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.63 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.51 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.50 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.46 – 4.37 (m, 2H, H-3, H-4), 3.74 (dd, 1H, *J* = 10.5, 4.1 Hz, H-5), 3.64 (dd, 1H, *J* = 10.5, 7.3 Hz, H-5), 3.38 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.0, 136.9 (C_q), 128.7, 128.5, 128.3, 128.0, 128.0, 127.8 (CH_{arom}), 118.6 (q, *J* = 319.6 Hz, CF_3), 104.0 (C-1), 86.2 (C-2), 77.5 (C-4), 76.4 (C-3), 73.9, 73.7 (CH_2 Bn), 69.6 (C-5), 55.7 (OMe).



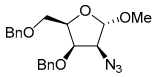
Methyl 3,5-di-*O*-benzyl-2-*O*-trifluoromethanesulfonate-α/β-D-xylofuranoside (32). The title compound was generated from **28**[10] by the general procedure for triflate formation (anomers were treated separately) and used crude. Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.21 (m, 10H, CH_{arom}), 5.18 (t, 1H, *J* = 5.1 Hz, H-2), 5.06 (d, 1H, *J* = 4.4 Hz, H-1), 4.66 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.57 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.55 – 4.50 (m, 2H, 2xCH*H* Bn), 4.44 (dd, 1H, *J* = 6.9, 5.8 Hz, H-3), 4.33 (dt, 1H, *J* = 7.0, 4.6 Hz, H-4), 3.67 (dd, 1H, *J* = 10.5, 4.2 Hz, H-5), 3.59 (dd, 1H, *J* = 10.5, 5.1 Hz, H-5), 3.44 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.9, 136.9 (C_q), 128.7, 128.5, 128.3, 127.9, 127.8, 127.8 (CH_{arom}), 118.6 (q, *J* = 319.6 Hz), 99.6 (C-1), 87.9 (C-2), 79.3 (C-3), 75.7 (C-4), 73.7, 73.3 (CH_2 Bn), 68.4 (C-5), 56.0 (OMe); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.42 – 7.23 (m, 10H, CH_{arom}), 5.17 (s, 1H, H-2), 5.05 (s, 1H, H-1), 4.71 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.59 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.54 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.53 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.48 (dt, 1H, *J* = 6.7, 5.5 Hz, H-4), 4.21 (dd, 1H, *J* = 5.9, 1.8 Hz, H-3), 3.74 (dd, 1H, *J* = 10.3, 5.1 Hz, H-5), 3.69 (dd, 1H, *J* = 10.3, 7.0 Hz, H-5), 3.42 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.0, 136.6, 128.7, 128.5, 128.4, 128.1, 128.0, 127.9, 106.4, 91.2, 80.6, 80.4, 73.7, 72.8, 69.2, 56.1; HRMS: $[M+NH_4]^+$ calcd for $C_{21}H_{27}F_3NO_7S$ 494.14548, found 494.14515.



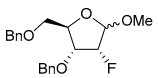
Methyl 2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-ribofuranoside (33). Employing conditions **C** of the general experimental for inversion of furanosyl triflates gave **33** as an α:β = 1:2 mixture from *arabino*-triflate **30**, and as a 4:1 mixture of **33** and **51**, combined yield 86% (4.3 mmol). IR (thin film): 698, 740, 1028, 1066, 1107, 1271, 1452, 2108, 2918; Data for the α-anomer (intermixed with **51**, *vide infra*): ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.35 – 7.20 (m, 10H, CH_{arom}), 5.03 (d, 1H, *J* = 4.6 Hz, H-1), 4.76 (d, 1H, *J* = 12.5 Hz, C*H*H Bn), 4.58 (d, 1H, *J* = 12.5 Hz, CH*H* Bn), 4.47 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.40 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.30 – 4.22 (m, 1H, H-4), 3.99 (dd, 1H, *J* = 7.2, 3.7 Hz, H-3), 3.49 (s, 3H, OMe), 3.45 (dd, 1H, *J* = 10.5, 3.7 Hz, H-5), 3.36 – 3.28 (m, 2H, H-2, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.8, 137.6 (C_q), 128.4, 128.4, 128.0, 128.0, 127.7 (CH_{arom}), 104.5 (C-1), 82.5 (C-4), 77.8 (C-3), 73.5, 72.9 (CH_2 Bn), 69.5 (C-5), 61.0 (C-2), 55.7 (OMe); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.38 – 7.23 (m, 10H, CH_{arom}), 4.83 (s, 1H, H-1), 4.63 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.56 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.51 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.51 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.28 – 4.21 (m, 2H, H-3, H-4), 3.80 (d, 1H, *J* = 3.8 Hz, H-2), 3.59 – 3.54 (m, 1H, H-5), 3.52 – 3.47 (m, 1H, H-5), 3.29 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1, 137.3 (C_q), 128.5, 128.4, 128.1, 127.9, 127.6 (CH_{arom}), 106.6 (C-1), 80.7 (C-4), 79.8 (C-3), 73.2, 73.0 (CH_2 Bn), 71.2 (C-5), 64.6 (C-2), 55.0 (OMe); HRMS: $[M-N_2+H]^+$ calcd for $C_{20}H_{24}NO_4$ 387.20268, found 387.20275.



Methyl 2-azido-3,5-di-*O*-benzyl-2-deoxy-α-D-arabinofuranoside (34). Employing conditions **C** of the general experimental for inversion of furanosyl triflates gave **34** in 93% yield (5.37 mmol) from *ribo*-triflate **29**. $[\alpha]_D^{20}$ = +76.4° (*c* = 1.0, $CHCl_3$). IR (thin film): 698, 714, 1026, 1070, 1097, 1107, 1271, 1452, 2104, 2932; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.35 – 7.23 (m, 10H, CH_{arom}), 4.88 (d, 1H, *J* = 1.5 Hz, H-1), 4.61 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.56 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.49 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 4.49 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.23 – 4.15 (m, 1H, H-4), 3.92 – 3.85 (m, 2H, H-2, H-3), 3.60 (dd, 1H, *J* = 10.8, 3.6 Hz, H-5), 3.54 (dd, 1H, *J* = 10.8, 4.8 Hz, H-5), 3.39 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.9, 137.2 (C_q), 128.5, 128.4, 128.0, 128.0, 127.8, 127.7 (CH_{arom}), 107.0 (C-1), 83.1 (C-3), 81.2 (C-4), 73.5, 72.6 (CH_2 Bn), 70.8 (C-2), 69.0 (C-5), 55.3 (OMe); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^{2}J_{C1,H2}$ = -2.1 Hz, $^{2}J_{C2,H1}$ = -0.3 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{27}N_4O_4$ 387.20268, found 387.20271.

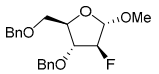


Methyl 2-azido-3,5-di-*O*-benzyl-2-deoxy-α-D-lyxofuranoside (35). Employing conditions **C** of the general experimental for inversion of furanosyl triflates, with additional 16 h stirring, gave **35** in 67% yield (3.36 mmol) from *xylo*-triflate **32α**, and side products **53α** (12%) and **55** (7%). Spectroscopic data were in accord with those previously reported.[11] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.34 – 7.27 (m, 10H, CH_{arom}), 4.95 (d, 1H, *J* = 2.1 Hz, H-1), 4.69 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.60 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.52 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.49 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.38 – 4.31 (m, 2H, H-3, H-4), 3.79 – 3.66 (m, 3H, H-2, H-5, H-5), 3.36 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1, 137.4 (C_q), 128.5, 128.4, 128.0, 127.9, 127.8, 127.7 (CH_{arom}), 105.9 (C-1), 79.0 (C-3), 78.2 (C-4), 73.9, 73.6 (CH_2 Bn), 69.2 (C-5), 65.9 (C-2), 55.6 (OMe); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^{2}J_{C1,H2}$ = -3.2 Hz, $^{2}J_{C2,H1}$ = -0.1 Hz, $^{3}J_{C1,H3}$ = +2.3 Hz, $^{3}J_{C3,H1}$ = +2.4 Hz; HRMS: $[M+Na]^+$ calcd for $C_{20}H_{23}N_3O_4$ 392.15808, found 392.15787.

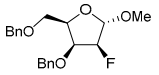


Methyl 3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α/β-D-ribofuranoside (37). Employing conditions **A** of the general experimental for inversion of furanosyl triflates gave **37** in 63% yield (3.2 mmol), as two anomers (R*f*: 0.47, and Rf: 0.15, 9/1 pentane/EtOAc) and two anomers of **52** (17% yield) from *arabino*-triflate **30**. Spectroscopic data were in accord with those previously reported for the β-anomer.[8] Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.41 – 7.27 (m, 10H, CH_{arom}), 5.09 (dd, 1H, *J* = 4.1, 3.5 Hz, H-1), 4.88 (ddd, 1H, *J* = 51.1, 6.1, 4.2 Hz), 4.82 (d, 1H, *J* = 12.4 Hz, C*H*H Bn), 4.59 (d, 1H, *J* = 12.4 Hz, CH*H* Bn), 4.58 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.49 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.30 (dt, 1H, *J* = 5.3, 3.4 Hz, H-4), 4.00 (ddd, 1H, *J* = 7.6, 6.0, 5.2 Hz, H-3), 3.63 (dd, 1H, *J* = 10.9, 2.9 Hz, H-5), 3.56 (s, 3H, CH3 OMe), 3.49 (dd, 1H, *J* = 10.8, 3.7 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.9, 137.8 (C_q), 128.5, 128.5, 128.0, 128.0, 127.8, 127.7 (CH_{arom}), 101.8 (d, *J* = 15.9 Hz, C-1), 88.2 (d, *J* = 202.7 Hz, C-2), 80.9 (d, *J* = 2.1 Hz, C-4), 74.6 (d, *J* = 14.8 Hz, C-3), 73.6 (CH_2 5-OBn), 72.9 (d, *J* = 2.2 Hz, CH_2 3-OBn), 69.1 (C-5), 56.1 (OMe); ^{19}F NMR ($CDCl_3$, 470 MHz): δ -216.73 (ddd, *J* = 51.2, 7.6, 3.3 Hz);

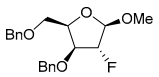
^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1\text{-}H2}$: +2.4 Hz, $^2J_{C2\text{-}H1}$: -+3.2 Hz; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.35 – 7.26 (m, 10H, CH_{arom}), 5.00 (d, 1H, *J* = 10.6 Hz, H-1), 4.76 (dd, 1H, *J* = 53.2, 3.7 Hz, H-2), 4.66 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.59 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.54 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.54 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.30 (ddd, 1H, *J* = 8.0, 5.7, 3.4 Hz, H-4), 4.07 (ddd, 1H, *J* = 24.6, 7.7, 3.7 Hz, H-3), 3.64 (dd, 1H, *J* = 10.6, 3.4 Hz, H-5), 3.53 (dd, 1H, *J* = 10.6, 5.7 Hz, H-5), 3.32 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.3, 137.4 (C_q), 128.6, 128.4, 128.1, 128.0, 127.7 (CH_{arom}), 105.7 (d, *J* = 29.3 Hz, C-1), 91.2 (d, *J* = 185.1 Hz, C-2), 80.1 (C-4), 77.8 (d, *J* = 15.6 Hz, C-3), 73.3, 72.8 (CH_2 Bn), 71.0 (C-5), 55.1 (OMe); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -209.71 (ddd, *J* = 53.2, 24.6, 10.6 Hz); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1\text{-}H2}$: +1.6 Hz, $^2J_{C2\text{-}H1}$: -1.6 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{24}FNO_4$ 364.19186, found 364.19205.



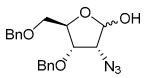
Methyl 3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α-D-arabinofuranoside (38). Employing conditions **A** of the general experimental for inversion of furanosyl triflates gave **38** in 86% yield (0.95 mmol) from *ribo*-triflate **29**. Spectroscopic data were in accord with those previously reported.[12] IR (thin film): 696, 737, 947, 988, 1039, 1055, 1098, 1193, 1364, 1454, 2862, 2922; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.25 (m, 10H, CH_{arom}), 5.06 (d, 1H, *J* = 12.0 Hz, H-1), 4.94 (dd, 1H, *J* = 51.3, 1.8 Hz, H-2), 4.67 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.58 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.56 – 4.51 (m, 2H, 2xCH*H* Bn), 4.21 (ddd, 1H, *J* = 6.4, 5.2, 3.8 Hz, H-4), 3.99 (dddd, 1H, *J* = 24.7, 6.4, 1.9, 1.0 Hz, H-3), 3.63 (dd, 1H, *J* = 10.8, 3.8 Hz, H-5), 3.58 (dd, 1H, *J* = 10.8, 5.1 Hz, H-5), 3.40 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.0, 137.2 (C_q), 128.5, 128.4, 128.0, 127.7, 127.7 (CH_{arom}), 106.5 (d, *J* = 36.0 Hz, C-1), 99.6 (d, *J* = 181.3 Hz, C-2), 83.0 (d, *J* = 25.6 Hz, C-3), 81.3 (d, *J* = 4.0 Hz, C-4), 73.4, 72.5 (CH_2 Bn), 69.3 (C-5), 54.9 (OMe); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -188.39 (ddd, *J* = 51.3, 24.6, 12.0 Hz); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1\text{-}H2}$ = -0.7 Hz, $^2J_{C2\text{-}H1}$ = -2.0 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{27}NFO_4$ 364.19186, found 364.19196.



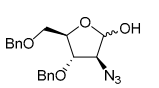
Methyl 3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α-D-lyxofuranoside (39). Employing conditions **B** of the general experimental for inversion of furanosyl triflates, with an additional 70°C reflux for 7 h, gave **39** in 44% yield (2.19 mmol) from *xylo*-triflate **32α**. Conditions **A** yielded 57% **54α** and 21% **55**. IR (thin film): 698, 739, 1056, 1452, 2932; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.40 – 7.24 (m, 10H, CH_{arom}), 5.08 (dd, 1H, *J* = 10.0, 1.0 Hz, H-1), 4.80 (ddd, 1H, *J* = 52.8, 4.1, 1.0 Hz, H-2), 4.68 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.65 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.53 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.52 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.42 (ddd, 1H, *J* = 8.0, 7.1, 3.8 Hz, H-4), 4.30 (ddd, 1H, *J* = 20.9, 7.1, 4.1 Hz, H-3), 3.77 (dd, 1H, *J* = 10.5, 3.8 Hz, H-5), 3.67 (ddd, 1H, *J* = 10.5, 8.0, 1.4 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.4, 137.5 (C_q), 128.6, 128.5, 128.1, 128.0, 127.8, 127.7 (CH_{arom}), 105.0 (d, *J* = 29.8 Hz, C-1), 92.4 (d, *J* = 187.9 Hz, C-2), 77.7 (C-4), 77.1 (d, *J* = 14.9 Hz, C-3), 73.6, 73.3 (CH_2 Bn), 70.3 (C-5), 55.5 (OMe); ^{19}F NMR ($CDCl_3$, 471 MHz, HH-COSY, HSQC): δ -207.58 (dddd, *J* = 52.8, 20.9, 10.0, 1.0 Hz); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C2,H1}$ = -2.5 Hz; HRMS: $[M+Na]^+$ calcd for $C_{20}H_{23}FO_4Na$ 369.14726, found 369.14734.



Methyl 3,5-di-*O*-benzyl-2-deoxy-2-fluoro-β-D-xylofuranoside (40). Employing conditions **A** of the general experimental for inversion of furanosyl triflates gave **40β** in 10% yield (0.52 mmol) as the minor product from *xylo*-triflate **32β**. IR (thin film): 698, 712, 978, 1068, 1107, 2929; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.37 – 7.26 (m, 10H, CH_{arom}), 5.02 (d, 1H, *J* = 14.8 Hz, H-1), 4.93 (d, 1H, *J* = 50.6 Hz, H-2), 4.68 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.60 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.55 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.54 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.52 – 4.48 (m, 1H, H-4), 4.15 (ddd, 1H, *J* = 18.2, 6.1, 1.7 Hz, H-3), 3.76 (dd, 1H, *J* = 10.3, 4.9 Hz, H-5), 3.70 (dd, 1H, *J* = 10.3, 7.3 Hz, H-5), 3.41 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.3, 137.4 (C_q), 128.6, 128.5, 128.1, 127.9, 127.9, 127.8 (CH_{arom}), 107.1 (d, *J* = 35.2 Hz, C-1), 98.4 (d, *J* = 181.0 Hz, C-2), 80.9 (d, *J* = 25.9 Hz, C-3), 80.7 (d, *J* = 1.9 Hz, C-4), 73.6, 72.7 (CH_2 Bn), 69.7 (C-5), 55.8 (OMe); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -192.85 (ddd, *J* = 50.6, 18.1, 14.9 Hz); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$ = -2.6 Hz, $^2J_{C2,H1}$ = -0.2 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{27}FNO_4$ 364.19186, found 364.19192.

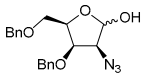


2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-ribofuranose (41). The title compound was generated from a 4:1 mixture of **33** and **51** by the general procedure for methyl furanoside hydrolysis, conditions A (65°C, 6 h). Combined yield: 89%, Yield of **41** was 70% over two steps (from **26**), α:β = 33:67 (0.29 mmol) as a colourless oil. IR (thin film): 696, 741, 1094, 1454, 2105, 2866, 3330; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.22 (m, 15H, CH_{arom}), 5.35 (bs, 0.5H, H-1α), 5.23 (s, 1H, H-1β), 4.68 – 4.58 (m, 2H, CH2 Bnα, C*H*H Bnβ), 4.53 (d, 1H, *J* = 11.8 Hz, C*H*H Bnβ), 4.49 – 4.35 (m, 4.5H, 2xCH*H* Bnβ, CH_2 Bnα, H-3β, H-4α), 4.21 (dt, 1H, *J* = 6.4, 3.1 Hz, H-4β), 4.13 (bs, 1H, 1-OHβ), 4.09 (dd, 0.5H, *J* = 5.4, 2.7 Hz, H-3α), 3.96 (bs, 0.5H, 1-OHα), 3.78 (d, 1H, *J* = 5.1 Hz, H-2β), 3.66 (dd, 0.5H, *J* = 5.4, 4.4 Hz, H-2α), 3.62 (dd, 1H, *J* = 10.4, 2.9 Hz, H-5β), 3.49 – 3.40 (m, 1.5H, H-5β, 2xH-5α); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.6, 137.2, 137.0, 136.8 (C_q), 128.6, 128.6, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.7 (CH_{arom}), 100.8 (C-1β), 97.6 (C-1α), 81.6 (C-4α), 80.9 (C-4β), 78.8 (C-3α), 78.4 (C-3β), 73.6, 73.6, 73.1, 73.0 (CH_2 Bn), 69.6 (C-5α), 69.3 (C-5β), 65.9 (C-2β), 62.1 (C-2α); HRMS: $[M+NH_4]^+$ calcd for $C_{19}H_{25}N_4O_4$ 373.18703, found 373.18699.

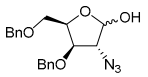


2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-arabinofuranose (42). The title compound was generated from **34** (554 mg, 1.50 mmol) by the general procedure for methyl furanoside hydrolysis, conditions A (60°C, 64 h). Yield: 76% α:β = 1:1 (1.1 mmol) as a colourless oil. IR (thin film): 696, 735, 1070, 1454, 2108, 3320; ^{1}H NMR ($CDCl_3$,

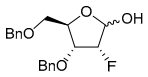
400 MHz, HH-COSY, HSQC): δ 7.45 – 7.10 (m, 20H), 5.33 (d, 1H, *J* = 7.0 Hz, H-1α), 5.30 (dd, 1H, *J* = 9.1, 4.6 Hz, H-1β), 4.68 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.62 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.58 – 4.54 (m, 4H, 2x CH_2 Bn), 4.52 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.50 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.45 – 4.38 (m, 1H, H-4α), 4.24 (dd, 1H, *J* = 7.0, 5.2 Hz, H-3β), 4.16 (dt, 1H, *J* = 5.2, 3.0 Hz, H-4β), 3.98 – 3.94 (m, 2H, H-2α, OHβ), 3.91 (ddd, 1H, *J* = 4.3, 2.6, 0.6 Hz, H-3α), 3.80 (dd, 1H, *J* = 6.9, 4.5 Hz, H-2β), 3.59 (dd, 1H, *J* = 10.3, 3.2 Hz, H-5β), 3.60 – 3.50 (m, 2H, 2xH-5α), 3.41 (dd, 1H, *J* = 10.3, 3.0 Hz, H-5β), 3.30 (d, 1H, *J* = 6.9 Hz, OHα); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.9, 137.4, 136.9, 136.8 (C_q), 128.8, 128.7, 128.7, 128.6, 128.4, 128.3, 128.3, 128.1, 128.1, 128.1, 127.9 (CH_{arom}), 101.0 (C-1α), 97.4 (C-1β), 82.9 (C-3α), 82.2 (C-4α), 81.8 (C-4β), 80.3 (C-3β), 73.9, 73.6, 72.7, 72.6 (CH_2 Bn), 70.2 (C-2α), 69.9 (C-5β), 69.6 (C-5α), 68.7 (C-2β); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): α-anomer: $^2J_{C1\text{-}H2}$ = -2.2 Hz, $^2J_{C2\text{-}H1}$ = -0.1 Hz. β-anomer: $^2J_{C1\text{-}H2}$ = -2.1 Hz, $^2J_{C2\text{-}H1}$ = +2.2 Hz; HRMS: $[M+Na]^+$ calcd for $C_{19}H_{26}N_3O_4Na$ 378.14243, found 378.14248.



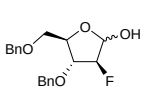
2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-lyxofuranose (43). The title compound was generated from **35** (620 mg, 1.68 mmol) by the general procedure for methyl furanoside hydrolysis, conditions A (60°C, 18 h). Yield: 62% α:β = 60:40 (1.04 mmol) as a colourless oil. IR (thin film): 696, 734, 1026, 1070, 1269, 1454, 2110, 2868, 2924, 3400; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.28 (m, 10H, CH_{arom}), 5.45 (t, 0.6H, *J* = 2.7 Hz, H-1α), 5.28 (dd, 0.4H, *J* = 12.2, 4.6 Hz, H-1β), 4.80 (d, 0.4H, *J* = 11.0 Hz, C*H*H Bnβ), 4.72 (d, 0.6H, *J* = 11.7 Hz, C*H*H Bnα), 4.65 (d, 0.4H, *J* = 11.0 Hz, CH*H* Bnβ), 4.62 – 4.47 (m, 3.2H, CH_2 Bnα, CH_2 Bnβ, CH*H* Bnα, H-4α), 4.41 (t, 0.6H, *J* = 5.5 Hz, H-3α), 4.22 (t, 0.4H, *J* = 4.0 Hz, H-3β), 4.17 (ddd, 0.4H, *J* = 7.2, 5.5, 3.8 Hz, H-4β), 3.84 – 3.76 (m, 1.4H, H-2α, H-5β, OHβ), 3.74 – 3.67 (m, 1.6H, H-5β, H-5α, H-5α), 3.63 (t, 0.4H, *J* = 4.4 Hz, H-2β), 3.06 (d, 0.6H, *J* = 3.1 Hz, OHα); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.2, 128.1, 128.0, 128.0, 127.8 (CH_{arom}), 99.8 (C-1α), 97.3 (C-1β), 79.6 (C-4α), 79.0 (C-3), 78.5, 78.4 (C-3β, C-4β), 75.0, 74.0, 73.9, 73.7 (CH_2 Bn), 69.4 (C-5α), 68.8 (C-5β), 66.6 (C-2α), 63.0 (C-2β); HRMS: $[M+Na]^+$ calcd for $C_{19}H_{21}N_3O_4Na$ 378.14243, found 378.14233.



2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-xylofuranose (44). Selenoglycoside **50** (360 mg, 0.72 mmol, 1 eq.) was dissolved in THF/H_2O/acetone (3/2/3 v/v/v, 8 mL) and cooled to 0°C, followed by addition of NIS (180 mg, 0.8 mmol, 1.1 eq.). After 1 h the reaction mixture was quenched by addition of 10% $Na_2S_2O_3$, diluted with H_2O and extracted with DCM three times. The combined organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash column chromatography (19/1 to 8/2 pentane/EtOAc) gave the title compound as a colourless oil (222 mg, 0.62 mmol, 87%). IR (thin film): 696, 737, 1053, 1255, 1454, 2102, 2866, 2924, 3390; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, NOESY, HSQC): δ 7.37 – 7.25 (m, 20H, CH_{arom}), 5.48 (dd, 1H, *J* = 5.4, 4.6 Hz, H-1α), 5.15 (dd, 1H, *J* = 11.4, 1.7 Hz, H-1β), 4.66 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.65 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.61 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.59 – 4.54 (m, 4H, C*H*H Bn, 3xCH*H* Bn), 4.52 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.47 (td, 1H, *J* = 6.1, 4.5 Hz, H-4α), 4.29 (dt, 1H, *J* = 5.6, 4.5 Hz, H-4β), 4.23 (dd, 1H, *J* = 5.9, 5.2 Hz, H-3α), 4.15 (d, 1H, *J* = 11.4 Hz, 1-OHβ), 4.03 (dd, 1H, *J* = 5.6, 3.7 Hz, H-3β), 3.99 (dd, 1H, *J* = 4.1, 1.7 Hz, H-2β), 3.89 – 3.85 (m, 1H, H-2α), 3.73 (dd, 1H, *J* = 10.1, 4.7 Hz, H-5β), 3.70 (dd, 1H, *J* = 10.1, 4.3 Hz, H-5β), 3.68 (dd, 1H, *J* = 10.3, 4.6 Hz, H-5α), 3.61 (dd, 1H, *J* = 10.3, 6.2 Hz, H-5α), 3.61 (d, 1H, *J* = 5.6 Hz, 1-OHα); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.9, 137.3, 136.9 (C_q), 128.7, 128.6, 128.5, 128.4, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8 (CH_{arom}), 101.2 (C-1β), 96.2 (C-1α), 81.6 (C-3β), 80.8 (C-3α), 79.5 (C-4β), 77.1 (C-4α), 73.9, 73.6, 73.2, 73.0 (CH_2 Bn), 70.5 (C-2β), 68.8 (C-5α), 68.5 (C-5β), 66.9 (C-2α); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): α-anomer: $^2J_{C1,H2}$ = -0.5 Hz, $^2J_{C2,H1}$ = +3.9 Hz, β-anomer: $^2J_{C1,H2}$ = -2.4 Hz, $^2J_{C2,H1}$ = -0.2 Hz; As additional confirmation of the xylo-configuration: α -anomer: $^2J_{C2,H3}$ = -2.8 Hz, $^2J_{C3,H2}$ = -5.0 Hz, β -anomer: $^2J_{C2,H3}$ = -3.3 Hz, $^2J_{C3,H2}$ = -4.6 Hz). HRMS: $[M+Na]^+$ calcd for $C_{19}H_{21}N_3O_4Na$ 378.14243, found 378.14235.

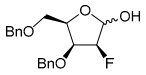


3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α/β-D-ribofuranose (45). The title compound was generated from **37** (205 mg, 0.59 mmol) by the general procedure for methyl furanoside hydrolysis, conditions A (60°C, 18 h). Yield: 78% α:β = 25:75 (0.46 mmol). Spectroscopic data were in accord with those previously reported.[8] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.21 (m, 10H, CH_{arom}), 5.35 (dd, 0.75H, *J* = 8.5, 6.7 Hz, H-1β), 5.33 (dt, 0.25H, *J* = 11.7, 3.6 Hz, H-1α), 4.91 (dt, 0.25H, *J* = 51.8, 4.3 Hz, H-2α), 4.76 (dd, 0.75H, *J* = 53.3, 3.4 Hz, H-2β), 4.72 (d, 0.25H, *J* = 11.8 Hz, C*H*H Bnα), 4.66 (d, 0.75H, *J* = 11.7 Hz, C*H*H Bnβ), 4.60 – 4.42 (m, 3H, CH*H* Bnα, CH*H* Bnβ, CH_2 Bnα, CH_2 Bnβ), 4.34 (qd, 0.25H, *J* = 3.4, 1.0 Hz, H-4α), 4.31 – 4.21 (m, 1.5H, H-3β, H-4β), 4.09 – 4.01 (m, 0.5H, H-3α, 1-OHα), 3.89 (dd, 0.75H, *J* = 6.7, 0.9 Hz, 1-OHβ), 3.66 (dd, 0.75H, *J* = 10.4, 2.4 Hz, H-5β), 3.54 (dd, 0.25H, *J* = 10.7, 3.3 Hz, H-5α), 3.51 – 3.45 (m, 1H, H-5α, H-5β); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.8, 137.3, 137.1 (C_q), 128.6, 128.6, 128.5, 128.2, 128.1, 128.1, 128.0, 127.9, 127.7 (CH_{arom}), 99.8 (d, *J* = 29.2 Hz, C-1β), 95.9 (d, *J* = 18.5 Hz, C-1α), 91.9 (d, *J* = 187.5 Hz, C-2β), 88.8 (d, *J* = 197.2 Hz, C-2α), 80.7 (d, *J* = 3.5 Hz, C-4α), 76.8 (C-4β), 76.8 (d, *J* = 14.7 Hz, C-3α), 76.5 (d, *J* = 15.5 Hz, C-3β), 73.6 (CH_2 Bnα), 73.6 (CH_2 Bnβ), 73.2 (d, *J* = 2.2 Hz, CH_2 Bnα), 72.8 (CH_2 Bnβ), 69.4 (C-5α), 69.1 (C-5β); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): α-anomer: $^2J_{C1\text{-}H2}$: +1.8 Hz, $^2J_{C2\text{-}H1}$: -+2.0 Hz, β-anomer: $^2J_{C2\text{-}H1}$: -0.3 Hz; HRMS: $[M+Na]^+$ calcd for $C_{19}H_{21}FO_4Na$ 355.13161, found 355.13147.

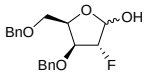


3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α/β-D-arabinofuranose (46). The title compound was generated from **38** (470 mg, 1.36 mmol) by the general procedure for methyl furanoside hydrolysis, conditions A (65°C, 64 h). Yield: 63% α:β = 70:30 (0.85 mmol) as a colourless oil**.** Spectroscopic data were in accord with those previously

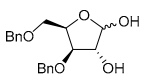
reported.[12] Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.37 – 7.23 (m, 10H, CH_{arom}), 5.45 (dd, 1H, *J* = 10.7, 2.9 Hz, H-1), 4.93 (d, 1H, *J* = 50.2 Hz, H-2), 4.62 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.57 – 4.47 (m, 3H, CH_2 Bn, CH*H* Bn), 4.43 (q, 1H, *J* = 5.2 Hz, H-4), 3.98 (dd, 1H, *J* = 21.0, 4.8 Hz, H-3), 3.76 (d, 1H, *J* = 4.1 Hz, OH), 3.58 – 3.54 (m, 1H, H-5), 3.51 (dd, 1H, *J* = 10.3, 5.1 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 137.9, 137.0 (C_q), 128.6, 128.4, 128.1, 128.0, 127.8, 127.8 (CH_{arom}), 100.4 (d, *J* = 34.5 Hz, C-2), 98.4 (d, *J* = 182.7 Hz, C-1), 82.6 (d, *J* = 25.6 Hz, C-3), 81.9 (d, *J* = 2.0 Hz, C-4), 73.5, 72.4 (CH_2 Bn), 69.7 (C-5); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -189.12 (ddd, *J* = 50.7, 21.0, 10.8 Hz); ^{13}C HSQC-HECADE NMR: $^2J_{C1\text{-}H2}$ = +1.8 Hz, $^2J_{C2\text{-}H1}$ = +3.9 Hz; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.36 – 7.23 (m, 10H, CH_{arom}), 5.32 – 5.24 (m, 1H, H-1), 5.00 – 4.85 (m, 1H, H-2), 4.66 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.57 – 4.47 (m, 3H, CH*H* Bn, CH_2 Bn), 4.28 (dt, 1H, *J* = 17.8, 4.9 Hz, H-3), 4.22 (d, 1H, *J* = 9.5 Hz, OH), 4.09 (q, 1H, *J* = 3.8 Hz, H-4), 3.58 – 3.54 (m, 1H, H-5), 3.47 (dd, 1H, *J* = 10.3, 3.8 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 137.3, 137.1 (C_q), 128.6, 128.6, 128.1, 128.1, 128.0, 127.9 (CH_{arom}), 95.8 (d, *J* = 194.1 Hz, C-2), 95.4 (d, *J* = 18.8 Hz, C-1), 80.6 (d, *J* = 22.8 Hz, C-3), 80.1 (d, *J* = 8.2 Hz, C-4), 73.7, 72.2 (CH_2 Bn), 70.0 (C-5); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -202.72 (dd, *J* = 52.7, 17.8 Hz); HRMS: $[M+Na]^+$ calcd for $C_{19}H_{21}FO_4Na$ 355.13161, found 355.13160.



3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α/β-D-lyxofuranose (47). The title compound was generated from **39** (340 mg, 0.98 mmol) by the general procedure for methyl furanoside hydrolysis, conditions A (65°C, 6 h). Yield: 75% α:β = 1:1 (0.73 mmol). IR (thin film): 696, 735, 1027, 1045, 1454, 2864, 2926, 3410; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.42 – 7.29 (m, 20H, CH_{arom}), 5.58 (dd, 1H, *J* = 9.8, 2.6 Hz, H-1α), 5.28 (dd, 1H, *J* = 12.5, 4.5 Hz, H-1β), 4.94 (dt, 1H, *J* = 50.3, 4.4 Hz, H-2α), 4.87 (d, 1H, *J* = 11.3 Hz, C*H*H Bn), 4.87 (ddd, 1H, *J* = 52.6, 4.1, 1.0 Hz, H-2β), 4.73 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.68 – 4.61 (m, 3H, CH*H* Bn 2xC*H*H Bn), 4.60 – 4.53 (m, 4H, 3xCH*H* Bn, H-4α), 4.40 (ddd, 1H, *J* = 20.3, 7.1, 4.1 Hz, H-3α), 4.25 (td, 1H, *J* = 4.2, 1.8 Hz, H-3β), 4.23 – 4.18 (m, 1H, H-4β), 4.17 (dd, 1H, *J* = 12.6, 1.0 Hz, 1-OHβ), 3.85 (dd, 1H, *J* = 9.7, 6.6 Hz, H-5β), 3.79 (dd, 1H, *J* = 10.5, 3.6 Hz, H-5α), 3.76 – 3.67 (m, 2H, H-5α, H-5β), 3.43 (t, 1H, *J* = 2.9 Hz, 1-OHα); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1, 137.8, 137.4, 137.0 (C_q), 128.7, 128.6, 128.6, 128.5, 128.4, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7 (CH_{arom}), 99.0 (d, *J* = 30.5 Hz, C-1α), 95.1 (d, *J* = 19.2 Hz, C-1β), 92.9 (d, *J* = 187.9 Hz, C-2α), 89.5 (d, *J* = 202.2 Hz, C-2β), 77.7 (C-4α), 77.4 (d, *J* = 5.9 Hz, C-4β), 76.9 (d, *J* = 15.0 Hz, C-3α), 76.3 (d, *J* = 14.6 Hz, C-3β), 74.5 (d, *J* = 3.1 Hz, CH_2 Bn), 73.8, 73.6 (CH_2 Bn), 73.2 (d, *J* = 1.3 Hz, CH_2 Bn), 70.3 (d, *J* = 1.2 Hz, C-5α), 68.9 (C-5β); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -207.67 (ddd, *J* = 52.6, 20.1, 9.3 Hz, C2-Fα), -214.36 (d, *J* = 50.4 Hz, C2-Fβ); HRMS: $[M+Na]^+$ calcd for $C_{19}H_{21}FO_4Na$ 355.13161, found 355.13164.

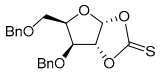


3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α/β-D-xylofuranose (48). The title compound was generated from **40** (181 mg, 0.52 mmol) by the general procedure for methyl furanoside hydrolysis, conditions A (60°C, 6 h). Yield: 75% α:β = 30:70 (0.40 mmol) as a colourless oil**.** Spectroscopic data were in accord with those previously reported for the L-enantiomer.[13] IR (thin film): 696, 735, 1026, 1047, 1454, 2868, 2924, 3400; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.37 – 7.24 (m, 10H), 5.48 (td, 0.3H, *J* = 8.3, 3.7 Hz, H-1α), 5.29 (dd, 0.7H, *J* = 13.9, 11.6 Hz, H-1β), 4.95 (ddd, 0.7H, *J* = 52.2, 3.2, 0.8 Hz, H-2β), 4.90 (dt, 0.3H, *J* = 52.1, 3.4 Hz, H-2α), 4.68 (d, 0.7H, *J* = 11.7 Hz, C*H*H Bnβ), 4.65 (d, 0.3H, *J* = 11.9 Hz, C*H*H Bnα), 4.60 – 4.50 (m, 3H, CH*H* Bnα, CH*H* Bnβ, CH_2 Bnα, CH_2 Bnβ), 4.50 – 4.46 (m, 0.3H, H-4α), 4.39 (dt, 0.7H, *J* = 6.1, 4.2 Hz, H-4β), 4.27 (ddd, 0.3H, *J* = 13.2, 5.3, 3.1 Hz, H-3α), 4.23 (dddd, 0.7H, *J* = 17.8, 6.1, 3.0, 0.7 Hz, H-3β), 4.14 (d, 0.7H, *J* = 11.6 Hz, 1-OHβ), 3.73 (ddd, 0.7H, *J* = 10.1, 4.6, 1.2 Hz, H-5β), 3.71 – 3.67 (m, 1H, H-5α, H-5β), 3.64 (dd, 0.3H, *J* = 10.2, 5.9 Hz, H-5α), 3.57 (dd, 0.3H, *J* = 8.5, 3.2 Hz, 1-OHα); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.1, 137.4, 137.3, 137.0 (C_q), 128.7, 128.6, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7 (CH_{arom}), 101.0 (d, *J* = 34.4 Hz, C-1β), 99.1 (d, *J* = 185.0 Hz, C-2β), 95.6 (d, *J* = 17.1 Hz, C-1α), 93.8 (d, *J* = 191.1 Hz, C-2α), 80.9 (d, *J* = 24.6 Hz, C-3β), 80.3 (d, *J* = 24.1 Hz, C-3α), 80.0 (d, *J* = 3.4 Hz, C-4β), 77.2 (d, *J* = 4.1 Hz, C-4α), 73.9 (CH_2 Bnβ), 73.6 (CH_2 Bnα), 73.0 (CH_2 Bnβ), 72.7 (CH_2 Bnα), 68.4 (C-5α), 68.4 (C-5β); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -189.88 (ddd, 0.7F, *J* = 52.2, 17.7, 14.1 Hz, F-2β), -204.74 (dt, 0.3F, *J* = 52.2, 9.7 Hz, F-2α); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): α-anomer: $^2J_{C1,H2}$ = +3.1 Hz, $^2J_{C2,H1}$ = +5.6 Hz, β-anomer: $^2J_{C2,H1}$ = -2.3 Hz; HRMS: $[M+Na]^+$ calcd for $C_{19}H_{21}FO_4Na$ 355.1322, found 355.1326.

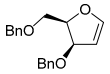


3,5-di-*O*-benzyl-α/β-D-xylofuranose (S1). Xyloside **27**[10] (7.6 g, 22 mmol) was dissolved in 20 mL THF and 40 mL H_2O and cooled to 0°C, followed by the slow addition of 100 mL TFA. After stirring overnight, the reaction mixture was partitioned between DCM and H_2O, and the aqueous layer was extracted three times with DCM. The combined DCM layers were washed with sat. aq. $NaHCO_3$ and brine, dried with $MgSO_4$, filtered and concentrated *in vacuo*. Flash column chromatography (9/1 to 1/1 pentane/EtOAc) afforded the title compound (6.1 g, 18.5 mmol, 84%) as a waxy material of a α:β = 70:30 anomeric composition. Spectroscopic data were in accord with those previously reported.[14] ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.34 – 7.23 (m, 10H, CH_{arom}), 5.44 (t, 0.7H, *J* = 4.8 Hz, H-1α), 5.11 (d, 0.3H, *J* = 10.9 Hz, H-1β), 4.87 (d, 0.7H, *J* = 5.5 Hz, 1-OHα), 4.66 – 4.53 (m, 2H, 2xC*H*H Bnα, 2xC*H*H Bnβ), 4.52 – 4.43 (m, 2.7H, 2xCH*H* Bnα, 2xCH*H* Bnβ, H-4α), 4.40 (q, 0.3H, *J* = 5.2 Hz, H-4β), 4.19 (t, 0.3H, *J* = 2.9 Hz, H-2β), 4.13 – 4.08 (m, 1H, H-2α, 1-OHβ), 3.98 – 3.93 (m, 1H, H-3α, H-3β), 3.77 – 3.70 (m, 0.6H, H-5β, H-5β), 3.66 – 3.64 (m, 1.4H, H-5α, H-5α), 3.30 (d, 0.7H, *J* = 5.8 Hz, 2-OHα), 3.14 (d, 0.3H, *J* = 4.3 Hz, 2-OHβ); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 137.9, 137.7, 137.4 (C_q), 128.6, 128.5, 128.5, 128.5, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.6 (CH_{arom}), 103.5 (C-1β), 96.1 (C-1α), 83.6 (C-3α), 82.9 (C-3β), 80.0 (C-4β), 79.2 (C-2β), 77.5 (C-

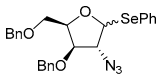
4α), 75.6 (C-2α), 73.7 (CH_2 Bnα), 73.6 (CH_2 Bnβ), 72.7 (CH_2 Bnα), 72.0 (CH_2 Bnβ), 69.2 (C-5), 69.1 (C-5α); HRMS: $[M+Na]^+$ calcd for $C_{19}H_{22}O_5Na$ 353.13594, found 353.13594.



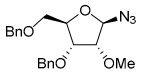
1,2-*O*-thiocarbonate-3,5-di-*O*-benzyl-α/β-D-xylofuranose (S2). Diol **S1** (1.65 g, 5 mmol, 1 eq.) was dissolved in 25 mL DCM and cooled to 0°C. DiPEA (7 ml, 40 mmol, 8 eq.) and DMAP (122 mg, 1 mmol, 0.2 eq.) were added, followed by the addition of thiophosgene (0.5 mL, 6.25 mmol, 1.25 eq., dissolved in 25 mL DCM). After 15 min the reaction was complete as concluded from TLC analysis. The reaction mixture was diluted with DCM and washed with 1 M aq. HCl, sat. aq. NH_4Cl, sat. aq. $NaHCO_3$, and brine. The organic layer was dried with Na_2SO_4, filtered and concentrated *in vacuo*. Flash column chromatography (19/1 to 8/2 pentane/EtOAc) afforded the title compound (1.45 g, 3.9 mmol, 78%) as a light orange oil. Spectroscopic data were in accord with those previously reported.[15,16] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.38 – 7.25 (m, 10H, CH_{arom}), 6.40 (d, 1H, *J* = 4.7 Hz, H-1), 5.08 (d, 1H, *J* = 4.7 Hz, H-2), 4.65 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.60 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.56 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.52 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.35 (td, 1H, *J* = 5.8, 3.5 Hz, H-4), 4.20 (d, 1H, *J* = 3.5 Hz, H-3), 3.78 (d, 2H, *J* = 5.8 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 189.8 (C=S), 137.6, 136.3 (C_q), 128.9, 128.7, 128.6, 128.1, 128.1, 127.9 (CH_{arom}), 107.8 (C-1), 86.0 (C-2), 80.7 (C-4), 79.4 (C-3), 73.8, 73.0 (CH_2 Bn), 66.5 (C-5).



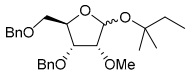
3-benzyloxy-2-(benzyloxy)methyl-2,3-dihydrofuran (49). Thionocarbonate **S2** (330 mg, 0.89 mmol, 1 eq.) was dissolved in toluene (1.8 mL) and heated to 70°C. When the target temperature was reached 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (0.18 mL, 0.98 mmol, 1.1 eq.) was added, and the reaction was continued to stir for 20 min. The reaction mixture was concentrated *in vacuo* and flash column chromatography (1/0 to 85/15 pentane/Et_2O) afforded the title compound (191 mg, 0.68 mmol, 76%) as a colourless oil. Spectroscopic data were in accord with those previously reported.[17] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.38 – 7.23 (m, 10H, CHarom), 6.61 (d, 1H, *J* = 2.8 Hz, H-1), 5.24 (t, 1H, *J* = 2.6 Hz, H-2), 4.64 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.61 (ddd, 2H, *J* = 7.1, 2.5, 0.7 Hz, H-3), 4.55 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.50 – 4.44 (m, 2H, C*H*H Bn, H-4), 4.42 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 3.96 (dd, 1H, *J* = 10.6, 4.6 Hz, H-5), 3.85 (dd, 1H, *J* = 10.6, 7.7 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 150.6 (C-1), 138.5, 138.1 (C_q), 128.4, 128.4, 127.8, 127.7, 127.6, 127.5 (CH_{arom}), 101.4 (C-2), 83.3 (C-4), 79.5 (C-3), 73.6, 70.7 (CH_2 Bn), 67.8 (C-5).



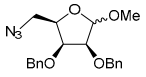
Phenyl 2-azido-3,5-di-*O*-benzyl-2-deoxy-1-seleno-α/β-D-xylofuranoside (50). Glycal **49** (314 mg, 1.11 mmol, 1 eq.) was dissolved in DCM (5.5 mL) followed by the subsequent addition of $TMSN_3$ (295 µL, 2.22 mmol, 2 eq.), TBAF (1M solution in THF, 220 µL, 0.22 mmol, 0.2 eq.), and *N*-(phenylseleno)phthalimide (671 mg, 2.22 mmol, 2 eq.). The reaction was stirred overnight, diluted with DCM and washed with sat. aq. $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (1/0 to 85/15 pentane/Et_2O) to give the still impure title compound (360 mg, 0.72 mmol, <65%) and was used direct in the subsequent hydrolysis (*vide infra*, **44**). The major product was confirmed as the trans-*xylo* isomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, NOESY, HSQC): δ 7.66 – 7.59 (m, 2H, CH_{arom}), 7.36 – 7.27 (m, 13H, CH_{arom}), 5.46 (d, 1H, *J* = 3.7 Hz, H-1), 4.66 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.62 – 4.53 (m, 3H, CH*H* Bn, CH_2 Bn), 4.34 (q, 1H, *J* = 5.4 Hz, H-4), 4.27 (t, 1H, *J* = 3.4 Hz, H-2), 4.01 (dd, 1H, *J* = 5.4, 3.2 Hz, H-3), 3.78 (dd, 1H, *J* = 10.2, 5.2 Hz, H-5), 3.73 (dd, 1H, *J* = 10.2, 6.0 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1, 137.1 (C_q), 134.3 (CH_{arom}), 130.0 (C_q), 129.2, 128.7, 128.6, 128.4, 128.1, 127.9, 127.9, 127.8, 127.8, 127.7 (CH_{arom}), 85.7 (C-1), 81.6 (C-3), 81.1 (C-4), 73.6, 72.7 (CH_2 Bn), 70.1 (C-2), 68.6 (C-5); ^{13}C HSQC-HECADE NMR: $^2J_{C1,H2}$ = -1.1 Hz, $^2J_{C2,H1}$ = -3.1 Hz, $^2J_{C2,H1}$ = -4.0 Hz. And minor products are identified as cis-xylo (^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$ = +0.9 Hz, $^2J_{C2,H1}$ = +1.3 Hz), and trans-lyxo (^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz):$^2J_{C1,H2}$ = -0.7 Hz, $^2J_{C2,H1}$ = -3.0 Hz).



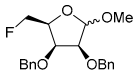
1-Azido 3,5-di-*O*-benzyl-1-deoxy-2-methyl-β-D-ribofuranoside (51). Intermixed with **33**. (*vide supra).* ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.34 – 7.20 (m, 10H, CH_{arom}), 5.32 (d, 1H, *J* = 1.9 Hz, H-1), 4.60 – 4.56 (m, 2H, 2xC*H*H Bn), 4.53 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.51 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 4.29 – 4.22 (m, 1H, H-4), 4.08 (dd, 1H, *J* = 6.9, 4.6 Hz, H-3), 3.64 (dd, 1H, *J* = 10.8, 3.3 Hz, H-5), 3.52 (dd, 1H, *J* = 10.9, 4.6 Hz, H-5), 3.50 – 3.47 (m, 1H, H-2), 3.40 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1, 137.5 (C_q), 128.4, 128.4, 128.0, 127.9, 127.8, 127.6 (CH_{arom}), 92.2 (C-1), 82.5 (C-2), 81.3 (C-4), 77.1 (C-3), 73.4, 72.7 (CH_2 Bn), 69.8 (C-5), 58.3 (OMe); After hydrolysis of the mixture of **51** and **33**, **3,5-di-*O*-benzyl-2-*O*-methyl-α/β-D-ribofuranose** could be isolated as a α:β = 1:0.7 anomeric mixture. Spectroscopic data were in accord with those previously reported.[18] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.39 – 7.22 (m, 17H), 5.32 (dd, 1H, *J* = 11.2, 4.1 Hz, H-1α), 5.28 (d, 0.7H, *J* = 6.4 Hz, H-1β), 4.68 (d, 1H, *J* = 11.9 Hz, C*H*H Bnα), 4.63 (d, 0.7H, *J* = 12.0 Hz, C*H*H Bnβ), 4.61 (d, 1H, *J* = 11.9 Hz, CH*H* Bnα), 4.59 – 4.42 (m, 4.1H, CH_2 Bnα,β, CH*H* Bnβ), 4.35 (td, 1H, *J* = 4.2, 2.4 Hz, H-4α), 4.27 – 4.17 (m, 1.4H, H-3β, H-4β), 4.12 (d, 1H, *J* = 11.2 Hz, 1-OHα), 4.01 (dd, 1H, *J* = 5.0, 2.4 Hz, H-3α), 3.78 (dd, 1H, *J* = 4.9, 4.3 Hz, H-2α), 3.67 – 3.59 (m, 2.1H, H-2β, H-5β, 1-OHβ), 3.52 – 3.43 (m, 7.8H, CH_3 OMeα,β, H-5β, 2xH-5α); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.9, 137.8, 137.5, 137.4 (C_q), 128.6, 128.6, 128.5, 128.5, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7 (CH_{arom}), 99.7 (C-1β), 96.1 (C-1α), 83.4 (C-2β), 81.0 (C-4α), 80.7 (C-3β), 80.2 (C-2β), 77.4 (C-3α), 77.2 (C-4β), 73.6, 73.5, 72.8, 72.7 (CH_2 Bn), 70.0 (C-5α), 69.6 (C-5β), 58.6, 58.4 (OMe); HRMS: $[M+Na]^+$ calcd for $C_{20}H_{24}O_5Na$ 367.15160, found 367.15164.



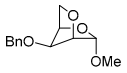
(2-Methyl-2-butyl) 3,5-di-*O*-benzyl-2-methyl-α/β-D-ribofuranoside (52). Formed as an 88:12 α:β anomeric mixture. Data for the isolated α-anomer: $[\alpha]_D^{20}$ = +86.3° (*c* = 0.35, $CHCl_3$).IR (thin film): 698, 739, 1026, 1042, 1109, 1211, 1454, 2928, 2970; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HH-NOESY, HSQC, HMBC): δ 7.37 – 7.20 (m, 10H, CH_{arom}), 5.34 (d, 1H, *J* = 4.1 Hz, H-1), 4.70 (d, 1H, *J* = 12.6 Hz, C*H*H Bn), 4.55 – 4.49 (m, 2H, C*H*H Bn, CH*H* Bn), 4.42 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.22 (q, 1H, *J* = 3.9 Hz, H-4), 3.91 (dd, 1H, *J* = 6.5, 4.5 Hz, H-3), 3.57 (dd, 1H, *J* = 6.5, 4.2 Hz, H-2), 3.50 – 3.44 (m, 4H, CH_3 OMe, H-5), 3.36 (dd, 1H, *J* = 10.6, 3.9 Hz, H-5), 1.60 (q, 2H, *J* = 7.5 Hz, C*H*$_2$CH$_3$ *t*-amyl), 1.26 (s, 3H, CH_3 *t*-amyl), 1.24 (s, 3H, CH_3 *t*-amyl), 0.93 (t, 3H, *J* = 7.5 Hz, CH_2C*H*$_3$ *t*-amyl); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.5, 138.2 (C_q), 128.3, 128.2, 128.0, 127.6, 127.5, 127.5 (CH_{arom}), 95.9 (C-1), 80.6, 80.5 (C-2, C-4), 77.0 (C_q t-amylOH)75.7 (C-3), 73.3, 72.2 (CH_2 Bn), 70.0 (C-5), 58.8 (OMe), 34.5 (CH_2 *t*-amyl), 26.1, 25.9 (C_q*C*H$_3$ *t*-amyl), 8.6 (CH_2*C*H$_3$ *t*-amyl); HRMS: $[M+Na]^+$ calcd for $C_{25}H_{34}O_5Na$ 437.22985, found 437.22953.



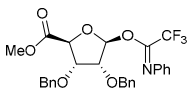
Methyl 5-azido-2,5-di-*O*-benzyl-5-deoxy-α/β-D-lyxofuranoside (53). Data for the α-anomer: IR (thin film):695, 734, 923, 1047, 1101, 1145, 1270, 1454, 2095; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.38 – 7.24 (m, 10H, CH_{arom}), 4.98 (d, 1H, *J* = 1.6 Hz, H-1), 4.71 – 4.63 (m, 2H, 2xC*H*H Bn), 4.59 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.47 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.29 – 4.19 (m, 2H, H-3, H-4), 3.88 (dd, 1H, *J* = 4.3, 1.7 Hz, H-2), 3.62 (dd, 1H, *J* = 12.8, 7.6 Hz, H-5), 3.45 (dd, 1H, *J* = 12.9, 3.8 Hz, H-5), 3.34 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 137.8 (C_q), 128.5, 128.0, 127.9, 127.9, 127.8 (CH_{arom}), 106.1 (C-1), 81.5 (C-2), 77.9, 77.8 (C-3, C-4), 73.2, 72.8 (CH_2 Bn), 55.5 (OMe), 52.1 (C-5); ^{13}C HSQC-HECADE NMR: $^2J_{C1,H2}$ = -0.9 Hz, $^2J_{C2,H1}$ = -1.0 Hz, $^2J_{C3,H2}$ = +0.7 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{27}N_4O_4$ 387.20268, found 387.20275. Data for the β-anomer: $[\alpha]_D^{20}$ = -58.5° (*c* = 0.48, $CHCl_3$); IR (thin film): 698, 737, 999, 1053, 1105, 1157, 1454, 2096, 2874, 2914, 3030; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.41 – 7.27 (m, 10H, CH_{arom}), 4.89 – 4.83 (m, 2H, C*H*H Bn, H-1), 4.72 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.62 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 4.58 (d, 1H, *J* = 12.3 Hz, CH*H* Bn), 4.13 (ddd, 1H, *J* = 8.7, 5.9, 4.3 Hz, H-4), 4.05 (t, 1H, *J* = 5.9 Hz, H-3), 3.83 (dd, 1H, *J* = 5.8, 4.5 Hz, H-2), 3.66 (dd, 1H, *J* = 13.0, 8.7 Hz, H-5), 3.47 (s, 3H, CH_3 OMe), 3.29 (dd, 1H, *J* = 13.0, 4.3 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1, 137.7 (C_q), 128.6, 128.5, 128.3, 128.1, 128.0, 127.9 (CH_{arom}), 102.0 (C-1), 79.3 (C-4), 79.0 (C-2), 75.0 (C-3), 73.8, 72.8 (CH_2 Bn), 55.9 (OMe), 52.8 (C-5); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$ = +1.0 Hz, $^2J_{C2,H1}$ = +2.5 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{27}N_4O_4$ 387.20268, found 387.20272.



Methyl 2,5-di-*O*-benzyl-5-deoxy-5-fluoro-α/β-D-lyxofuranoside (54). Data for the α-anomer: m.p. 62-64 °C. $[\alpha]_D^{20}$ = +16.6° (*c* = 0.62, $CHCl_3$); IR (thin film): 698, 737, 1009, 1026, 1069, 1107, 1150, 1454, 2922, 3032; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HH-NOESY, HSQC): δ 7.36 – 7.28 (m, 10H, CH_{arom}), 5.00 (d, 1H, *J* = 1.6 Hz, H-1), 4.74 – 4.62 (m, 4H, 2xC*H*H Bn, H-5, H-5), 4.60 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.50 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.44 (dtd, 1H, *J* = 15.6, 6.8, 4.4 Hz, H-4), 4.30 (dd, 1H, *J* = 6.6, 4.6 Hz, H-3), 3.88 (dt, 1H, *J* = 4.6, 1.6 Hz, H-2), 3.36 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 137.8, 137.7 (C_q), 128.5, 128.5, 128.0, 127.9, 127.8, 127.8 (CH_{arom}), 106.2 (C-1), 84.0 (d, *J* = 164.8 Hz, C-5), 81.1 (C-2), 77.8 (d, *J* = 7.1 Hz, C-3), 77.3 (d, *J* = 20.2 Hz, C-4), 73.2, 72.7 (CH_2 Bn), 55.5 (OMe); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -228.75 (td, *J* = 47.6, 15.7 Hz); ^{13}C HSQC-HECADE NMR: $^2J_{C1,H2}$ = -0.8 Hz, $^2J_{C2,H1}$ = -0.8 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{27}NFO_4$ 364.19186, found 364.19199. Data for the β-anomer: $[\alpha]_D^{20}$ = -100.5° (*c* = 0.95, $CHCl_3$); IR (thin film): 698, 737, 1003, 1066, 1109, 1163, 1348, 1454, 2910, 2924; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HH-NOESY, HSQC): δ 7.37 – 7.27 (m, 10H, CH_{arom}), 4.84 (dd, 1H, *J* = 4.5, 1.2 Hz, H-1), 4.82 (d, 1H, *J* = 12.5 Hz, C*H*H Bn), 4.70 – 4.64 (m, 2H, C*H*H Bn, H-5), 4.63 – 4.59 (m, 2H, 2xCH*H* Bn), 4.59 – 4.52 (m, 1H, H-5), 4.28 (dddd, 1H, *J* = 14.4, 7.0, 6.0, 5.1 Hz, H-4), 4.11 (t, 1H, *J* = 6.0 Hz, H-3), 3.80 (dd, 1H, *J* = 5.9, 4.5 Hz, H-2), 3.46 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.2, 137.7 (C_q), 128.6, 128.5, 128.3, 128.1, 128.0, 127.9 (CH_{arom}), 101.7 (C-1), 83.8 (d, *J* = 165.6 Hz, C-5), 79.1 (d, *J* = 0.9 Hz, C-2), 78.5 (d, *J* = 21.4 Hz, C-4), 74.7 (d, *J* = 6.0 Hz, C-3), 73.9, 72.7 (CH_2 Bn), 55.8 (OMe); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -227.76 (td, *J* = 47.5, 14.4 Hz); HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{27}NFO_4$ 364.19186, found 364.19178.

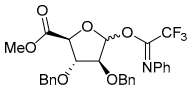


Methyl 2,5-anhydro-3-*O*-benzyl-α-D-lyxofuranoside (55). $[\alpha]_D^{20}$ = +88.3° (*c* = 0.41, $CHCl_3$); IR (thin film): 698, 741, 880, 989, 1028, 1051, 1107, 11998, 1454, 2882, 2940; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.38 – 7.28 (m, 5H, CH_{arom}), 4.74 (s, 1H, H-1), 4.66 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.55 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.25 (d, 1H, *J* = 2.7 Hz, H-4), 4.23 (d, 1H, *J* = 2.6 Hz, H-3), 4.10 (s, 1H, H-2), 3.99 (d, 1H, *J* = 7.8 Hz, H-5), 3.70 (d, 1H, *J* = 7.8 Hz, H-5), 3.36 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.7 (C_q), 128.6, 128.1, 127.9 (CH_{arom}), 106.2 (C-1), 78.6 (C-3), 76.7 (C-2), 75.0 (C-4), 72.5, 70.9 (CH_2 Bn), 55.5 (OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{13}H_{20}NO_4$ 254.13868, found 254.13878.

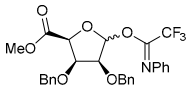


Methyl (2,3-di-*O*-benzyl-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-β-D-ribofuranosyl uronate) (1). The title compound was generated from **21** (1.0 g, 2.8 mmol) by the general procedure for imidate donor synthesis, conditions A. Yield: 85% β only (1.26 g, 2.38 mmol) as a white solid. R*f*: 0.54 (7/3 pentane/Et_2O). $[\alpha]_D^{20}$ = +18.6° (*c* = 0.90, $CHCl_3$); IR (thin film): 696, 1090, 1146, 1206, 1456, 1717, 1740; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.35 – 7.25 (m, 12H, CH_{arom}), 7.08 (t, 1H, *J* = 7.5 Hz, NPh), 6.81 (d, 2H, *J* = 7.5 Hz, NPh), 6.29 (bs, 1H, H-1), 4.72 (d, 1H, *J* = 6.4 Hz, H-4), 4.68 – 4.63 (m, 3H, CH_2 Bn, C*H*H Bn), 4.62 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.43 (dd, 1H, *J* = 6.3, 4.7 Hz, H-3), 4.09 (d, 1H, *J* = 4.5 Hz, H-2), 3.76 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 170.9 (C=O), 143.9 (C_q NPh), 137.5, 137.4 (C_q Bn), 128.9, 128.7, 128.6, 128.2, 128.2, 128.1, 128.1, 124.5, 119.7 (CH_{arom}), 116.11 (q, *J* = 285.8 Hz,

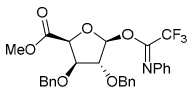
CF_3), 102.6 (C-1), 81.2 (C-4), 80.3 (C-3), 79.7 (C-2), 73.3, 73.0 (CH_2 Bn), 52.5 (CH_3 CO_2Me); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -66.62; HRMS: $[M+H]^+$ calcd for $C_{28}H_{27}F_3NO_6$ 530.17850, found 530.17802.



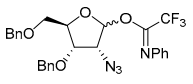
Methyl (2,3-di-*O*-benzyl-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-arabinofuranosyl uronate) (2). The title compound was generated from **22** (466 mg, 1.3 mmol) by the general procedure for imidate donor synthesis, conditions A. Yield: 97%, α:β = 1:1.2 (670 mg, 1.27 mmol) as a white solid. R*f*: 0.51 (8/2 pentane/Et_2O). IR (thin film): 696, 1074, 1105, 1318, 1712, 1769; ^{1}H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.35 – 7.20 (m, 24H, CH_{arom}), 7.10 – 7.02 (m, 2H, NPh), 6.79 (d, 2H, *J* = 7.7 Hz, NPh), 6.77 – 6.74 (m, 2H, NPh), 6.41 (bs, 1H, H-1β), 6.29 (bs, 1H, H-1α), 4.82 (d, 1H, *J* = 3.8 Hz, H-4β), 4.76 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.72 – 4.61 (m, 4H, CH_2 Bn, CH*H* Bn, C*H*H Bn), 4.60 – 4.53 (m, 4H, CH_2 Bn, H-3α, H-4α), 4.50 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.29 (d, 1H, *J* = 3.1 Hz, H-3β), 4.24 – 4.18 (m, 2H, H-2α, H-2β), 3.74 (s, 3H, CH_3 CO_2Me), 3.73 (s, 3H, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 170.7, 169.6 (C=O), 144.0, 143.8, 137.8, 137.5, 137.4, 137.1 (C_q), 128.8, 128.7, 128.6, 128.6, 128.5, 128.5, 128.2, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 124.5, 124.2, 119.8, 119.6 (CH_{arom}), 116.1 (q, *J* = 286.7 Hz, CF_3), 116.1 (q, *J* = 286.5 Hz, CF_3), 104.0 (C-1α), 97.3 (C-1β), 85.2, 85.2 (C-2β, C-3α), 84.0 (C-2α), 83.7 (C-3β), 83.3 (C-4α), 80.9 (C-4β), 73.4, 73.0, 72.4, 72.2 (CH_2 Bn), 52.5 (OMe); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -66.18; HRMS: $[M+Na]^+$ calcd for $C_{28}H_{26}F_3NO_6Na$ 552.16044, found 552.16010.



Methyl (2,3-di-*O*-benzyl-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-lyxofuranosyl uronate) (3). The title compound was generated from **23** (1.05 g, 2.90 mmol) by the general procedure for imidate donor synthesis, conditions A. Yield: 85% as two separate anomers (487 mg, 0.92 mmol α and 105 mg, 0.20 mmol β respectively) as colourless oils. R*f*: 0.24 and 0.69 (8/2 pentane/Et_2O). Data for the α-anomer: $[\alpha]_D^{20}$ = -5.5° (*c* = 1.23, $CHCl_3$); IR (thin film): 696, 1026, 1101, 1159, 1207, 1327, 1707, 1734, 1770; ^{1}H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.33 – 7.22 (m, 12H, CH_{arom}), 7.10 – 7.02 (m, 1H, NPh), 6.80 (d, 2H, *J* = 7.5 Hz, NPh), 6.49 (bs, 1H, H-1), 4.81 (d, 1H, *J* = 5.3 Hz, H-4), 4.71 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.66 (s, 2H, CH_2 Bn), 4.61 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.43 (t, 1H, *J* = 5.1 Hz, H-3), 4.20 (dd, 1H, *J* = 4.6, 2.7 Hz, H-2), 3.68 (s, 3H, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 167.9 (C=O), 143.7 (C_q NPh), 143.1 (q, *J* = 36.2 Hz, CF_3-*C*=N), 137.7, 137.3 (C_q Bn), 128.8, 128.5, 128.4, 128.1, 127.9, 127.8, 124.5, 119.7, (CH_{arom}), 116.1 (q, *J* = 285.8 Hz, CF_3), 103.5 (C-1), 82.0 (C-2), 79.7 (C-4), 78.4 (C-3), 73.9, 73.0 (CH_2 Bn), 52.1 (CH_3 CO_2Me); HRMS: $[M+NH_4]^+$ calcd for $C_{28}H_{30}F_3N_2O_6$ 547.20505, found 547.20459. Data for the β-anomer: $[\alpha]_D^{20}$ = -66.4° (*c* = 0.70, $CHCl_3$); IR (thin film): 696, 1074, 1086, 1144, 1327, 1715, 1769; ^{1}H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.35 – 7.25 (m, 10H, CH_{arom}), 7.25 – 7.19 (m, 3H, NPh), 7.09 – 6.99 (m, 1H, NPh), 6.79 (d, 2H, *J* = 7.7 Hz, NPh), 6.40 (bs, 1H, H-1), 4.89 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.74 (d, 1H, *J* = 5.5 Hz, H-4), 4.69 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.66 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.62 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.39 (t, 1H, *J* = 5.3 Hz, H-3), 3.98 (t, 1H, *J* = 4.6 Hz, H-2), 3.64 (s, 3H, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 168.3 (C=O), 144.4 (C_q NPh), 138.4, 137.4 (C_q Bn), 128.7, 128.7, 128.2, 128.2, 127.7, 127.4, 127.3, 124.0, 119.8 (CH_{arom}), 116.3 (q, *J* = 286.8 Hz, CF_3), 96.4 (C-1), 81.1 (C-4), 79.9 (C-2), 76.4 (C-3), 74.2, 73.3 (CH_2 Bn), 52.0 (CH_3 CO_2Me); HRMS: $[M+H]^+$ calcd for $C_{28}H_{27}F_3NO_6$ 530.17850, found 530.17835.

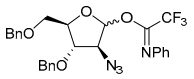


Methyl (2,3-di-*O*-benzyl-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-β-D-xylofuranosyl uronate) (4). The title compound was generated from **24** (1.20 g, 3.0 mmol) by the general procedure for imidate donor synthesis, conditions A. Yield: 81% β only (561 mg, 1.06 mmol) as a colourless oil. R*f*: 0.28 (8/2 pentane/Et_2O). $[\alpha]_D^{20}$ = +10.2° (*c* = 0.55, $CHCl_3$); IR (thin film): 696, 1105, 1159, 1207, 1325, 1717, 1732, 1771; ^{1}H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.34 – 7.22 (m, 12H, CH_{arom}), 7.15 – 7.02 (m, 1H, NPh), 6.82 (d, 1H, *J* = 7.5 Hz, NPh), 6.32 (bs, 1H, H-1), 5.00 (d, 1H, *J* = 6.0 Hz, H-4), 4.57 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.55 – 4.50 (m, 3H, CH_2 Bn, CH*H* Bn), 4.32 (dd, 1H, *J* = 6.0, 1.2 Hz, H-3), 4.23 (s, 1H, H-2), 3.72 (s, 3H, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 168.6 (C=O), 144.1 (C_q NPh), 137.5, 137.1 (C_q Bn), 128.8, 128.7, 128.5, 128.3, 128.0, 127.9, 127.6, 124.2, 119.8 (CH_{arom}), 116.1 (q, *J* = 286.8 Hz, CF_3), 103.3 (C-1), 84.0 (C-2), 82.9 (C-4), 82.0 (C-3), 73.1, 72.5 (CH_2 Bn), 52.0 (CH_3 CO_2 Me); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{26}F_3NO_6Na$ 552.16044, found 552.15999.

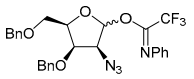


2-azido-3,5-di-*O*-benzyl-2-deoxy-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-ribofuranoside (5). The title compound was generated from **41** by the general procedure for imidate donor synthesis, conditions A. Yield: 77% α:β = 1:8 as separate anomers (0.085 mmol and 0.69 mmol respectively) as a white soild. Data for the α-anomer: $[\alpha]_D^{20}$ = +52.4° (*c* = 0.46, $CHCl_3$); IR (thin film): 696, 1101, 1144, 1161, 1207, 1319, 1713, 2114, 2864; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.36 – 7.25 (m, 10H, CH_{arom}), 7.25 – 7.21 (m, 2H, CH_{arom}), 7.11 – 7.05 (m, 1H, NPh), 6.87 (d, 2H, *J* = 7.7 Hz, NPh), 6.45 (bs, 1H, H-1), 4.74 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.61 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 4.49 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.45 – 4.40 (m, 2H, CH*H* Bn, H-4), 4.18 (dd, 1H, *J* = 6.6, 3.1 Hz, H-3), 3.63 – 3.58 (m, 1H, H-2), 3.51 (dd, 1H, *J* = 10.8, 3.7 Hz, H-5), 3.45 (dd, 1H, *J* = 10.7, 3.3 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 144.0 (C_q NPh), 137.8, 137.7 (C_q Bn), 128.9, 128.6, 128.6, 128.0, 127.8, 124.5, 119.9 (CH_{arom}), 99.9 (C-1), 84.8 (C-4), 78.3 (C-3), 73.9, 73.1 (CH_2 Bn), 69.6 (C-5), 61.4 (C-2); HRMS: $[M+Na]^+$ calcd for $C_{27}H_{25}F_3N_4O_4Na$ 549.17201, found 549.17174. Data for the β-anomer: $[\alpha]_D^{20}$ = -1.6° (*c* = 0.70, $CHCl_3$); IR (thin film): 696, 1090, 1144, 1159, 1207, 1331, 1715, 2108, 2862; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.35 – 7.24 (m, 12H, CH_{arom}), 7.08 (t, 1H, *J* = 7.4 Hz, NPh), 6.80 (d, 2H, *J* = 7.7 Hz, NPh), 6.18 (bs, 1H, H-1), 4.64 (d, 1H, *J* = 11.6

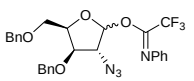
Hz, C*H*H Bn), 4.58 (d, 1H, *J* = 11.6 Hz, CH*H* Bn), 4.56 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.53 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.39 (dd, 1H, *J* = 7.0, 5.0 Hz, H-3), 4.33 (dt, 1H, *J* = 7.0, 4.3 Hz, H-4), 4.03 (d, 1H, *J* = 5.0 Hz, H-2), 3.64 (dd, 1H, *J* = 10.9, 4.0 Hz, H-5), 3.57 (dd, 1H, *J* = 10.9, 4.7 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 143.7 (C_q NPh), 138.1, 137.2 (C_q Bn), 128.9, 128.7, 128.5, 128.3, 128.1, 127.8, 127.8, 124.6, 119.7 (CH_{arom}), 116.06 (q, *J* = 286.0 Hz, CF_3), 102.5 (C-1), 82.6 (C-4), 79.0 (C-3), 73.6, 73.6 (CH_2 Bn), 70.0 (C-5), 64.8 (C-2); HRMS: $[2M+NH_4]^+$ calcd for $C_{54}H_{54}F_6N_9O_8$ 1070.39941, found 1070.40023.



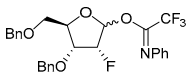
2-azido-3,5-di-*O*-benzyl-2-deoxy-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-arabinofuranoside (6). The title compound was generated from **42** by the general procedure for imidate donor synthesis, conditions B. Yield: 71% α:β = 1.6:1 as separate anomers (0.31 mmol and 0.19 mmol respectively) as colourless oils. Data for the α-anomer: $[\alpha]_D^{20}$ = +5.4° (*c* = 0.50, $CHCl_3$); IR (thin film): 696, 929, 1103, 1161, 1207, 1329, 1456, 1700, 1717, 2106, 2866, 3032; ^{1}H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.38 – 7.22 (m, 12H, CH_{arom}), 7.08 (t, 1H, *J* = 7.5 Hz, NPh), 6.82 (d, 2H, *J* = 7.7 Hz, NPh), 6.18 (bs, 1H, H-1), 4.63 – 4.56 (m, 2H, CH_2 Bn), 4.56 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.51 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.42 (q, 1H, *J* = 4.6 Hz, H-4), 4.17 (d, 1H, *J* = 2.2 Hz, H-2), 4.00 (dd, 1H, *J* = 6.0, 3.1 Hz, H-3), 3.64 (dd, 1H, *J* = 11.0, 4.2 Hz, H-5), 3.61 (dd, 1H, *J* = 11.0, 4.8 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 143.7 (C_q NPh), 138.0, 137.4 (C_q Bn), 128.9, 128.7, 128.5, 128.2, 127.9, 127.9, 127.9, 124.6, 119.8 (CH_{arom}), 116.1 (q, *J* = 286.7 Hz, CF_3), 104.0 (C-1), 84.2 (C-4), 83.4 (C-3), 73.7, 73.0 (CH_2 Bn), 70.8 (C-5), 68.9 (C-2); HRMS: $[2M+NH_4]^+$ calcd for $C_{54}H_{54}F_6N_9O_8$ 1070.39941, found 1070.40019. Data for the β-anomer: $[\alpha]_D^{20}$ = -56.1° (*c* = 1.30, $CHCl_3$); IR (thin film): 696, 1024, 1094, 1144, 1161, 1207, 1317, 1713, 2110, 2864; ^{1}H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.36 – 7.22 (m, 12H, CH_{arom}), 7.12 – 7.03 (m, 1H, NPh), 6.81 (d, 2H, *J* = 7.5 Hz, NPh), 6.43 (bs, 1H, H-1), 4.67 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.63 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.59 – 4.52 (m, 2H, CH_2 Bn), 4.26 (q, 1H, *J* = 5.6 Hz, H-4), 4.21 (dd, 1H, *J* = 7.5, 6.0 Hz, H-3), 4.04 (dd, 1H, *J* = 7.5, 4.5 Hz, H-2), 3.63 – 3.53 (m, 2H, H-5); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 143.8 (C_q NPh), 138.0, 137.5 (C_q Bn), 128.9, 128.7, 128.6, 128.2, 128.0, 127.9, 127.9, 124.5, 119.6 (CH_{arom}), 116.1 (d, *J* = 286.6 Hz, CF_3), 98.6 (C-1), 82.9 (C-4), 81.5 (C-3), 73.7, 73.1 (CH_2 Bn), 70.9 (C-5), 67.4 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{27}H_{29}F_3N_5O_4$ 544.21662, found 544.21623.



2-azido-3,5-di-*O*-benzyl-2-deoxy-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-lyxofuranoside (7). The title compound was generated from **43** by the general procedure for imidate donor synthesis, conditions B. Yield: 67% α:β = 1:1.2 (0.30 mmol and 0.37 mmol respectively) as colourless oils. Data for the α-anomer: $[\alpha]_D^{20}$ = -57.5° (*c* = 0.69, $CHCl_3$); IR (thin film): 696, 1045, 1098, 1144, 1207, 1323, 1714, 2112, 2866, 2926; ^{1}H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.37 – 7.22 (m, 12H, CH_{arom}), 7.11 – 7.03 (m, 1H, NPh), 6.82 (d, 2H, *J* = 7.5 Hz, NPh), 6.27 (bs, 1H, H-1), 4.71 (d, 1H, *J* = 11.5 Hz, C*H*H Bn), 4.59 (d, 1H, *J* = 11.6 Hz, CH*H* Bn), 4.56 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.53 – 4.47 (m, 2H, CH*H* Bn, H-4), 4.41 (t, 1H, *J* = 5.5 Hz, H-3), 4.02 (dd, 1H, *J* = 5.1, 1.9 Hz, H-1), 3.81 (dd, 1H, *J* = 10.4, 5.4 Hz, H-5), 3.71 (dd, 1H, *J* = 10.4, 6.5 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 143.7 (C_q NPh), 138.2, 137.2 (C_q Bn), 128.9, 128.7, 128.5, 128.2, 127.9, 127.9, 127.8, 124.6, 119.7 (CH_{arom}), 116.2 (q, *J* = 286.9 Hz, CF_3), 102.3 (C-1), 80.7 (C-4), 78.6 (C-3), 74.4, 73.7 (CH_2 Bn), 68.7 (C-5), 66.2 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{27}H_{29}F_3N_5O_4$ 544.21662, found 544.21667. Data for the β-anomer: $[\alpha]_D^{20}$ = +24.9° (*c* = 0.68, $CHCl_3$); IR (thin film): 696, 1094, 1144, 1153, 1207, 1319, 1717, 2110, 2926; ^{1}H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.37 – 7.21 (m, 12H, CH_{arom}), 7.10 – 7.02 (m, 1H, NPh), 6.84 (d, 2H, *J* = 7.5 Hz, NPh), 6.41 (bs, 1H, H-1), 4.83 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.66 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.51 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.46 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.36 (q, 1H, *J* = 6.3 Hz, H-4), 4.26 (t, 1H, *J* = 5.4 Hz, H-3), 3.82 (dd, 1H, *J* = 9.9, 6.7 Hz, H-5), 3.70 (dd, 1H, *J* = 9.9, 6.2 Hz, H-5), 3.51 (t, 1H, *J* = 4.9 Hz, H-2); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 143.9 (C_q NPh), 138.1, 137.6 (C_q Bn), 128.8, 128.5, 128.5, 127.9, 127.8, 127.5, 124.4, 119.7 (CH_{arom}), 116.2 (q, *J* = 286.3 Hz, CF_3), 98.5 (C-1), 82.2 (C-4), 77.7 (C-3), 74.7, 73.8 (CH_2 Bn), 69.0 (C-5), 62.2 (C-2); HRMS: $[2M+NH_4]^+$ calcd for $C_{54}H_{54}F_6N_9O_8$ 1070.39941, found 1070.39931.

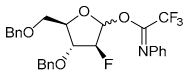


2-azido-3,5-di-*O*-benzyl-2-deoxy-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-xylofuranoside (8). The title compound was generated from **44** by the general procedure for imidate donor synthesis, conditions A. Yield: 100% α:β = 1:1 (0.33 mmol) as a colourless oil. IR (thin film): 696, 1044, 1099, 1143, 1207, 1321, 1712, 2114; ^{1}H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.36 – 7.23 (m, 24H, CH_{arom}), 7.10 – 7.06 (m, 2H, NPh), 6.84 (d, 2H, *J* = 7.7 Hz, NPh), 6.80 (d, 2H, *J* = 7.6 Hz, NPh), 6.43 (bs, 1H, H-1α), 6.15 (bs, 1H, H-1β), 4.69 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.64 – 4.57 (m, 4H, CH_2 Bn, CH*H* Bn, C*H*H Bn), 4.56 – 4.50 (m, 4H, CH_2 Bn, CH*H* Bn, H-4β), 4.50 – 4.45 (m, 1H, H-4α), 4.32 (t, 1H, *J* = 6.7 Hz, H-3α), 4.22 (bs, 1H, H-2β), 4.17 – 4.11 (m, 1H, H-2α), 4.08 (dd, 1H, *J* = 5.8, 2.8 Hz, H-3β), 3.85 (dd, 1H, *J* = 10.5, 5.3 Hz, H-5β), 3.76 (dd, 1H, *J* = 10.5, 6.5 Hz, H-5β), 3.71 (dd, 1H, *J* = 10.7, 4.4 Hz, H-5α), 3.61 (dd, 1H, *J* = 10.7, 4.9 Hz, H-5α); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 143.8, 143.8 (C_q NPh), 138.3, 138.2, 137.4, 137.4 (C_q Bn), 128.9, 128.9, 128.7, 128.5, 128.5, 128.3, 128.3, 127.9, 127.9, 127.8, 127.8, 127.8, 127.8, 124.5, 119.8, 119.7 (CH_{arom}), 103.2 (C-1β), 98.4 (C-1α), 82.7 (C-4β), 81.6 (C-3β), 79.1 (C-3α), 73.8 (C-4α), 73.8, 73.6, 73.3 (CH_2 Bn), 69.1 (C-2β), 69.0 (C-5β), 68.5 (C-5α), 66.7 (C-2α); HRMS: only mass of hydrolysis found $[M+Na]^+$ calcd for $C_{19}H_{21}N_3O_4Na$ 378.1430, found 378.1433.

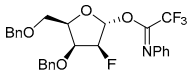


3,5-di-*O*-benzyl-2-deoxy-2-fluoro-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-ribofuranoside (9). The title compound was generated from **45** by the general procedure for imidate donor synthesis, conditions A.

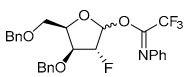
Yield: 98% β only (0.45 mmol) as a white solid, includes ~10% acetamide. IR (thin film): 694, 1092, 1151, 1207, 1712, 2869; ^{1}H NMR ($CDCl_3$, *T* = 328 K, 400 MHz, HH-COSY, HSQC): δ 7.36 – 7.21 (m, 12H, CH_{arom}), 7.11 – 7.04 (m, 1H, NPh), 6.79 (d, 2H, *J* = 8.2 Hz, NPh), 6.36 (d, 1H, *J* = 9.1 Hz, H-1), 4.95 (dd, 1H, *J* = 52.3, 3.5 Hz, H-2), 4.66 (d, 1H, *J* = 11.6 Hz, C*H*H Bn), 4.60 – 4.49 (m, 3H, CH_2 Bn, CH*H* Bn), 4.38 (dt, 1H, *J* = 7.6, 3.9 Hz, H-4), 4.24 (ddd, 1H, *J* = 23.6, 7.6, 3.6 Hz, H-3), 3.69 (dd, 1H, *J* = 11.1, 3.1 Hz, H-5), 3.58 (dd, 1H, *J* = 11.1, 4.4 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, *T* = 328 K, 101 MHz, HSQC): δ 143.6 (C_q NPh), 138.2, 137.3 (C_q Bn), 129.4, 128.8, 128.6, 128.5, 128.2, 128.0, 127.8, 127.7, 124.6, 119.6 (CH_{arom}), 116.0 (q, *J* = 286.1 Hz, CF_3), 101.2 (d, *J* = 32.4 Hz, C-1), 91.0 (d, *J* = 188.6 Hz, C-2), 82.0 (C-4), 77.0 (d, *J* = 15.7 Hz, C-3), 73.5, 73.2 (CH_2 Bn), 69.7 (C-5); ^{19}F NMR ($CDCl_3$, *T* =298 K, 471 MHz): δ -65.81 (bs, 3F, CF_3), -209.42 (ddd, 1F, *J* = 52.3, 23.9, 9.4 Hz); HRMS: $[M+H]^+$ calcd for $C_{27}H_{26}F_4NO_4$ 504.17925, found 504.17889.



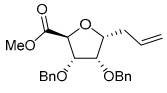
3,5-di-*O*-benzyl-2-deoxy-2-fluoro-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-arabinofuranoside (10). The title compound was generated from **46** by the general procedure for imidate donor synthesis, conditions A. Yield: 85% α:β = 5:1 as separate anomers (0.14 mmol and 0.60 mmol respectively) as colourless oils. Data for the α-anomer: $[\alpha]_D^{20}$ = +67.7° (*c* = 1.39, $CHCl_3$); IR (thin film): 696, 933, 1101, 1153, 1159, 1207, 1327, 1454, 1714, 2866, 3032; ^{1}H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.35 – 7.24 (m, 12H, CH_{arom}), 7.11 – 7.06 (m, 1H, NPh), 6.83 (d, 2H, *J* = 7.5 Hz, NPh), 6.37 (d, 1H, *J* = 8.3 Hz, H-1), 5.17 (dd, 1H, *J* = 50.5, 1.6 Hz, H-2), 4.65 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.61 – 4.55 (m, 2H, CH*H* Bn, C*H*H Bn), 4.53 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.44 (q, 1H, *J* = 4.9 Hz, H-4), 4.16 (dddd, 1H, *J* = 23.1, 5.8, 1.8, 0.9 Hz, H-3), 3.64 (d, 2H, *J* = 4.7 Hz, H-5, H-5); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 143.8 (C_q NPh), 138.1, 137.4 (C_q Bn), 128.9, 128.7, 128.6, 128.2, 127.9, 127.9, 124.6, 119.8 (CH_{arom}), 116.2 (q, *J* = 286.8 Hz, CF_3), 102.7 (d, *J* = 38.8 Hz, C-1), 98.9 (d, *J* = 184.9 Hz, C-2), 84.3 (d, *J* = 3.4 Hz, C-4), 82.9 (d, *J* = 25.7 Hz, C-3), 73.8, 72.8 (CH_2 Bn), 69.2 (C-5); ^{19}F NMR ($CDCl_3$, *T* = 323 K, 471 MHz, HH-COSY, HSQC): δ -66.34 (bs, 3F, CF_3), -188.59 (ddd, 1F, *J* = 50.5, 23.1, 11.0 Hz, F-2); Data for the β-anomer: $[\alpha]_D^{20}$ = -43.0° (*c* = 0.6, $CHCl_3$); IR (thin film): 696, 1026, 1072, 1092, 1153, 1159, 1207, 1319, 1717, 2864; ^{1}H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.35 – 7.24 (m, 12H, CH_{arom}), 7.10 – 7.05 (m, 1H, NPh), 6.80 (dd, 2H, *J* = 8.4, 1.1 Hz, NPh), 6.46 (bs, 1H, H-1), 5.17 (ddd, 1H, *J* = 52.0, 5.8, 4.5 Hz, H-2), 4.69 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.60 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.57 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.54 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.32 (dt, 1H, *J* = 16.7, 5.9 Hz, H-3), 4.25 (q, 1H, *J* = 5.7 Hz, H-4), 3.63 (dd, 1H, *J* = 10.4, 5.6 Hz, H-5), 3.60 (dd, 1H, *J* = 10.5, 5.5 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, *T* = 323 K, 126 MHz, HSQC): δ 143.8 (C_q NPh), 138.1, 137.5 (C_q Bn), 128.9, 128.6, 128.6, 128.1, 127.9, 127.9, 127.9, 124.4, 119.7 (CH_{arom}), 116.1 (q, *J* = 285.9 Hz, CF_3), 96.9 (d, *J* = 18.1 Hz, C-1), 95.1 (d, *J* = 201.9 Hz, C-2), 81.9 (d, *J* = 9.0 Hz, C-4), 81.2 (d, *J* = 21.4 Hz, C-3), 73.7, 72.7 (CH_2 Bn), 70.9 (C-5); ^{19}F NMR ($CDCl_3$, *T* = 323 K, 471 MHz, HH-COSY, HSQC): δ -66.45 (bs, 3F, CF_3), -203.20 (dd, 1F, *J* = 52.1, 16.7 Hz, F-2); HRMS: $[M+H]^+$ calcd for $C_{27}H_{26}F_4NO_4$ 504.17925, found 504.17933.



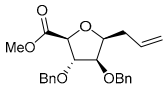
3,5-di-*O*-benzyl-2-deoxy-2-fluoro-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-lyxofuranoside (11). The title compound was generated from **47** by the general procedure for imidate donor synthesis, conditions A. Yield: 82% α only (0.54 mmol) as a colourless oil. $[\alpha]_D^{20}$ = +50.2° (*c* = 1.30, $CHCl_3$); IR (thin film): 694, 737, 931, 1086, 1097, 1150, 1207, 1321, 1715, 2872, 3032; ^{1}H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.36 – 7.22 (m, 12H, CH_{arom}), 7.11 – 7.04 (m, 1H, NPh), 6.82 (d, 2H, *J* = 7.5 Hz, NPh), 6.41 (bs, 1H, H-1), 5.02 (dd, 1H, *J* = 51.7, 3.8 Hz, H-2), 4.69 (d, 1H, *J* = 11.6 Hz, C*H*H Bn), 4.60 – 4.53 (m, 3H, C*H*H Bn, CH*H* Bn, H-4), 4.50 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.34 (ddd, 1H, *J* = 17.6, 6.4, 4.3 Hz, H-3), 3.83 (dd, 1H, *J* = 10.7, 4.5 Hz, H-5), 3.68 (dd, 1H, *J* = 9.8, 7.3 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 143.6 (C_q NPh), 142.9 (q, *J* = 36.4 Hz, F_3CC=N), 138.3, 137.4 (C_q Bn), 128.9, 128.6, 128.5, 128.2, 127.9, 127.7, 124.6, 119.7 (CH_{arom}), 116.2 (q, *J* = 285.9 Hz, CF_3), 101.3 (d, *J* = 33.4 Hz, C-1), 92.6 (d, *J* = 192.3 Hz, C-2), 80.2 (C-4), 76.6 (d, *J* = 15.0 Hz, C-3), 73.7, 73.7 (CH_2 Bn), 69.5 (C-5); ^{19}F NMR ($CDCl_3$, *T* = 323 K, 471 MHz): δ -66.49 (bs, 3F, CF_3), -207.43 (ddd, 1F *J* = 51.8, 17.6, 9.5 Hz, C2-F); HRMS: $[2M+NH_4]^+$ calcd for $C_{54}H_{54}F_8N_3O_8$ 1024.37777, found 1024.37849.



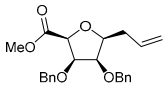
3,5-di-*O*-benzyl-2-deoxy-2-fluoro-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-xylofuranoside (12). The title compound was generated from **48** by the general procedure for imidate donor synthesis, conditions A. Yield: 91% α:β = 37:63 (0.36 mmol) as a colourless oil. IR (thin film): 694, 1086, 1153, 1207, 1323, 1715; ^{1}H NMR ($CDCl_3$, *T* = 323 K, 500 MHz, HH-COSY, HSQC): δ 7.35 – 7.22 (m, 12H, CH_{arom}), 7.11 – 7.04 (m, 1H, NPh), 6.84 – 6.78 (m, 2H, NPh), 6.46 (bs, 0.37H, H-1α), 6.34 (d, 0.63H, *J* = 12.5 Hz, H-1β), 5.23 (dt, 0.37H, *J* = 51.9, 4.0 Hz, H-2α), 5.18 (dd, 0.63H, *J* = 49.8, 1.6 Hz, H-2β), 4.71 (d, 0.37H, *J* = 11.8 Hz, C*H*H Bnα), 4.68 – 4.50 (m, 3.63H, CH*H* Bnα, CH_2 Bnα, 2xCH_2 Bnβ, H-4α, H-4β), 4.41 (ddd, 0.37H, *J* = 15.7, 6.5, 4.8 Hz, H-3α), 4.26 (ddd, 0.63H, *J* = 16.2, 5.8, 1.6 Hz, H-3β), 3.85 (dd, 0.63H, *J* = 10.5, 5.4 Hz, H-5β), 3.75 (dd, 0.63H, *J* = 10.4, 6.6 Hz, H-5β), 3.72 (dd, 0.37H, *J* = 10.7, 4.5 Hz, H-5α), 3.65 (dd, 0.37H, *J* = 10.6, 5.0 Hz, H-5α); ^{13}C-APT NMR ($CDCl_3$, *T* = 323K, 126 MHz, HSQC): δ 143.9, 143.8 (C_q NPh), 138.4, 138.2, 137.4, 137.4 (C_q Bn), 128.9, 128.9, 128.7, 128.5, 128.5, 128.2, 128.1, 127.8, 127.8, 127.8, 127.6, 124.5, 124.4, 119.7 (CH_{arom}), 116.1 (q, *J* = 286.3 Hz, CF_3), 102.1 (d, *J* = 37.5 Hz, H-1β), 97.0 (d, *J* = 16.8 Hz, H-1α), 97.0 (d, *J* = 184.5 Hz, H-2β), 94.1 (d, *J* = 200.0 Hz, H-2α), 83.1 (C-4β), 80.5 (d, *J* = 25.6 Hz, C-3β), 79.9 (d, *J* = 22.9 Hz, C-3α), 79.0 (d, *J* = 6.8 Hz, C-4α), 73.8 (CH_2 Bnα), 73.7, 73.2 (CH_2 Bnβ), 72.9 (CH_2 Bnα), 68.9 (C-5β), 68.2 (C-5α); ^{19}F NMR ($CDCl_3$, *T* = 323 K, 471 MHz): δ -66.32 (s, 3F, CF_3), -193.57 (dt, 0.63F, *J* = 49.8, 14.1 Hz, F-2β), -202.33 (dd, 0.37F, *J* = 52.1, 15.6 Hz, F-2α); HRMS: $[2M+NH_4]^+$ calcd for $C_{54}H_{54}F_8N_3O_8$ 1024.37777, found 1024.37842.



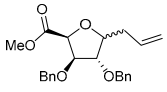
Methyl (1-allyl-2,3-di-*O*-benzyl-1-deoxy-α-D-ribofuranosyl uronate) (65). Donor **1** and allyltrimethylsilane (4 eq.) were condensed using the general procedure for furanosyl imidate glycosylations at -20°C for 100 h with TfOH as the promotor. Yield = 30.5 mg, 79 µmol, 79% as a white solid. R_f: 0.57 (4/1 pentane/EtOAc). $[\alpha]_D^{20}$ = +28.3° (*c* = 0.60, $CHCl_3$); IR (thin film): 698, 737, 916, 1026, 1099, 1144, 1206, 1275, 1356, 1454, 1748, 2868, 2922, 3030; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.38 – 7.27 (m, 10H, CH_{arom}), 5.77 (ddt, 1H, *J* = 17.1, 10.2, 6.9 Hz, CH allyl), 5.11 (dq, 1H, *J* = 17.2, 1.6 Hz, C*H*H allyl), 5.04 (ddt, 1H, *J* = 10.2, 2.0, 1.1 Hz, CH*H* allyl), 4.82 (d, 1H, *J* = 11.6 Hz, C*H*H Bn), 4.67 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.63 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.59 (d, 1H, *J* = 6.0 Hz, H-4), 4.56 (d, 1H, *J* = 11.6 Hz, CH*H* Bn), 4.22 (dd, 1H, *J* = 6.0, 4.5 Hz, H-3), 4.17 (td, 1H, *J* = 7.0, 4.1 Hz, H-1), 3.99 (t, 1H, *J* = 4.3 Hz, H-2), 3.73 (s, 3H, CH_3CO_2Me), 2.56 – 2.48 (m, 2H, CH_2 allylic); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 172.7 (C=O), 138.2, 137.6 (C_q), 134.6 (CH allyl), 128.6, 128.5, 128.1, 128.0, 127.9 (CH_{arom}), 117.3 (CH_2 allyl), 82.7 (C-3), 81.1 (C-1), 79.3 (C-4), 77.8 (C-2), 73.6, 72.8 (CH_2 Bn), 52.4 (CH_3CO_2Me), 34.0 (CH_2 allylic); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C2,H1}$: +1.5 Hz, $^3J_{Callyl,H2}$: +0.7 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{23}H_{30}NO_5$ 400.21185, found 400.21173.



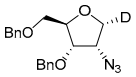
Methyl (1-allyl-2,3-di-*O*-benzyl-1-deoxy-β-D-arabinofuranosyl uronate) (66). Donor **2** and allyltrimethylsilane (4 eq.) were condensed using the general procedure for furanosyl imidate glycosylations at -20°C for 100 h with TfOH as the promotor. Yield = 29 mg, 76 µmol, 76% as a white solid (α:β = 5:95). R_f: 0.64 (4/1 pentane/EtOAc). $[\alpha]_D^{20}$ = +32.4° (*c* = 0.38, $CHCl_3$); IR (thin film): 698, 737, 916, 1028, 1101, 1207, 1279, 1454, 1726, 1761, 2920; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.44 – 7.18 (m, 10H, CH_{arom}), 5.79 (ddt, 1H, *J* = 17.1, 10.2, 7.0 Hz, CH allyl), 5.14 (dq, 1H, *J* = 17.1, 1.5 Hz, C*H*H allyl), 5.08 – 5.02 (m, 1H, CH*H* allyl), 4.66 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.56 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.51 (d, 1H, *J* = 1.7 Hz, H-4), 4.49 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.39 – 4.34 (m, 2H, CH*H* Bn, H-3), 4.21 (td, 1H, *J* = 7.2, 3.5 Hz, H-1), 3.81 (dd, 1H, *J* = 3.5, 0.8 Hz, H-2), 3.68 (s, 3H, CH_3CO_2Me), 2.64 – 2.50 (m, 2H, CH_2 allylic); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 171.4 (C=O) 137.7, 137.5 (C_q), 134.7 (CH allyl), 128.6, 128.5, 128.1, 127.9, 127.9, 127.8 (CH_{arom}), 117.3 (CH_2 allyl), 85.2 (C-3), 82.4 (C-1), 81.6 (C-4), 81.3 (C-2), 71.9, 71.8 (CH_2 Bn), 52.3 (CO_2Me), 33.3 (CH_2 allylic); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$ = +2.5 Hz, $^2J_{C2,H1}$ = +2.5 Hz, $^3J_{Callyl,H2}$ = +0.3 Hz; HRMS: $[M+Na]^+$ calcd for $C_{23}H_{26}O_5Na$ 405.16725, found 405.16656.



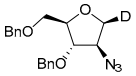
Methyl (1-allyl-2,3-di-*O*-benzyl-1-deoxy-β-D-lyxofuranosyl uronate) (67). Donor **3** and allyltrimethylsilane (4 eq.) were condensed using the general procedure for furanosyl imidate glycosylations at -20°C for 100 h with TfOH as the promotor. Yield = 29 mg, 76 µmol, 76% as a white solid. R_f: 0.32 (4/1 pentane/EtOAc). $[\alpha]_D^{20}$ = +3.6° (*c* = 0.58, $CHCl_3$); IR (thin film): 698, 737, 1028, 1072, 1084, 1099, 1152, 1207, 1356, 1437, 1454, 1732, 1763, 2870, 2920, 2949. ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.39 – 7.21 (m, 10H, CH_{arom}), 5.92 (ddt, 1H, *J* = 17.2, 10.2, 7.0 Hz, CH allyl), 5.15 (dq, 1H, *J* = 17.2, 1.4 Hz, C*H*H allyl), 5.09 – 5.04 (m, 1H, CH*H* allyl), 4.76 – 4.67 (m, 3H, CH_2 Bn, C*H*H Bn), 4.62 (d, 1H, *J* = 6.0 Hz, H-4), 4.56 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.34 (dd, 1H, *J* = 6.0, 4.4 Hz, H-3), 4.13 (dt, 1H, *J* = 8.8, 5.4 Hz, H-1), 4.04 (dd, 1H, *J* = 6.0, 4.4 Hz, H-2), 3.66 (s, 3H, CH_3CO_2Me), 2.75 – 2.64 (m, 1H, C*H*H allylic), 2.58 – 2.48 (m, 1H, CH*H* allylic); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 170.3 (C=O), 138.2, 138.2 (C_q), 135.8 (CH allyl), 128.5, 128.4, 127.8, 127.7, 127.6 (CH_{arom}), 116.8 (CH_2 allyl), 80.5 (C-1), 80.1 (C-3), 79.2 (C-2), 78.3 (C-4), 73.9, 73.2 (CH_2 Bn), 51.9 (CO_2Me), 35.0 (CH_2 allylic); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C2,H1}$ = -0.25 Hz, $^3J_{Callyl,H2}$ = +2.9 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{23}H_{30}NO_5$ 400.21185, found 400.21167.



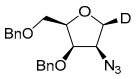
Methyl (1-allyl-2,3-di-*O*-benzyl-1-deoxy-α/β-D-xylofuranosyl uronate) (68). Donor **4** and allyltrimethylsilane (4 eq.) were condensed using the general procedure for furanosyl imidate glycosylations at -20°C for 100 h with TfOH as the promotor. Four fractions were isolated: amide **80** (1 mg, R_f: 0.66), mixed fraction (22 mg, product **68**, α:β = 35:65 as 68 wt%, and amide **80** as 32 wt%), title product **68** (7 mg, α:β = 69:33), cyclized product **81** (2 mg, R_f: 0.38) Calculated total title product yield = 22 mg, 57 µmol, 57%, (α:β = 45:55). R_f: 0.61 and 0.57 (4/1 pentane/EtOAc). Reported as a 1:1 mixture. IR (thin film): 698, 737, 1028, 1078, 1094, 1206, 1290, 1454, 1732, 1765, 2862, 2949. ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.38 – 7.24 (m, 20H, CH_{arom}), 5.88 – 5.72 (m, 2H, CH allyl), 5.16 – 5.03 (m, 4H, CH_2 allyl), 4.82 (d, 1H, *J* = 5.1 Hz, H-4α), 4.69 (d, 1H, *J* = 4.8 Hz, H-4β), 4.54 – 4.38 (m, 8H, 4xCH_2 Bn), 4.36 (ddd, 1H, *J* = 7.9, 6.5, 3.3 Hz, H-1α), 4.27 (dd, 1H, *J* = 5.1, 1.0 Hz, H-3α), 4.24 (dd, 1H, *J* = 4.8, 1.7 Hz, H-3β), 4.01 (td, 1H, *J* = 6.9, 3.3 Hz, H-1β), 3.82 (d, 1H, *J* = 3.5 Hz, H-2α), 3.82 (d, 1H, *J* = 3.4 Hz, H-2β), 3.76 (s, 3H, CH_3CO_2Meβ), 3.73 (s, 3H, CH_3CO_2Meα), 2.64 – 2.41 (m, 4H, CH2 allylic); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 170.6 (C=Oα), 169.6 (C=Oβ), 137.7 (C_qα), 137.7 (C_qβ), 137.6 (C_qβ), 137.5 (C_qα), 134.5 (CH allylα), 134.4 (CH allylβ), 128.6, 128.6, 128.6, 128.6, 128.1, 128.1, 128.1, 127.9, 127.9, 127.9 (CH_{arom}), 117.6 (CH_2 allylicβ), 117.3 (CH_2 allylicα), 84.7 (C-2β), 84.0 (C-1β), 83.9 (C-3β), 82.9 (C-3α), 81.6 (C-1α), 81.4 (C-2α), 80.4 (C-4β), 80.0 (C-4α), 73.0, 72.5, 72.3, 72.0 (CH_2 Bn), 52.1 (CO_2Meβ), 52.0 (CO_2Meα), 38.1 (CH_2 allylicβ), 33.1 (CH_2 allylicα); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): α-anomer: $^2J_{C1,H2}$ = +1.5 Hz, $^2J_{C2,H1}$ = +2.4 Hz, $^3J_{Callyl,H2}$ = +0.2 Hz, β-anomer: $^2J_{C1,H2}$ = -1.5 Hz, $^2J_{C2,H1}$ = -4.5 Hz, $^3J_{Callyl,H2}$ = +2.9 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{23}H_{30}NO_5$ 400.21185, found 400.21153.



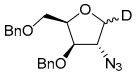
1-[^{2}H]-1,4-anhydro-2-azido-3,5-di-*O*-benzyl-2-deoxy-α-D-ribitol (69). Donor **5** and triethylsilane-*d* (4 eq.) were condensed using the general procedure for furanosyl imidate glycosylations at 0-5°C for 100 h with TfOH as the promotor. Yield = 23 mg, 68 µmol, 68% as a colourless oil. Inseparable mixture of **74** and amide **98** (in a 95:5 ratio). R_f: 0.26 (9/1 pentane/EtOAc). $[\alpha]_D^{20}$ = +88° (*c* = 0.77, $CHCl_3$) IR (thin film): 698, 738, 1028, 1089, 1269, 1454, 2104, 2864; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HH-NOESY, HSQC): δ 7.38 – 7.26 (m, 10H, CH_{arom}), 4.69 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.57 – 4.52 (m, 2H, C*H*H Bn, CH*H* Bn), 4.48 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.14 (dd, 1H, *J* = 6.1, 5.5 Hz, H-3), 4.09 – 4.02 (m, 2H, H-1, H-4), 3.89 (t, 1H, *J* = 5.4 Hz, H-2), 3.61 (dd, 1H, *J* = 10.7, 3.3 Hz, H-5), 3.50 (dd, 1H, *J* = 10.7, 4.0 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.1, 137.4 (C_q), 128.6, 128.5, 128.2, 128.1, 127.8, 127.8 (CH_{arom}), 80.9 (C-4), 79.9 (C-3), 73.6, 73.0 (CH_2 Bn), 70.2 (t, *J* =22.8 Hz, C-1), 69.8 (C-5), 60.8 (C-2); ^{2}H NMR ($CHCl_3$, 77 MHz): δ 3.90; ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1\text{-}H2}$: +1.5 Hz, $^2J_{C2\text{-}H1}$: +1.3 Hz; HRMS: $[M+Na]^+$ calcd for $C_{19}H_{20}DN_3O_3Na$ 363.1543, found 363.1546.



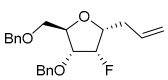
1-[^{2}H]-1,4-anhydro-2-azido-3,5-di-*O*-benzyl-2-deoxy-β-D-arabitol (70). Donor **6** and triethylsilane-*d* (4 eq.) were condensed using the general procedure for furanosyl imidate glycosylations at 0-5°C for 100 h with TfOH as the promotor. Yield = 19.5 mg, 57 µmol, 57% as a colourless oil. R_f: 0.38 (9/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported for the non-deuterated compound.[19] $[\alpha]_D^{20}$ = -14.6° (*c* = 0.98, $CHCl_3$); IR ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.37 – 7.26 (m, 10H, CH_{arom}), 4.59 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.56 (s, 2H, CH_2 Bn), 4.54 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.02 (td, 1H, *J* = 5.3, 4.3 Hz, H-4), 4.00 (bs, 1H, H-1), 3.98 (dd, 1H, *J* = 5.0, 1.9 Hz, H-2), 3.92 (dd, 1H, *J* = 4.3, 1.9 Hz, H-3), 3.59 (dd, 1H, *J* = 10.3, 5.5 Hz, H-5), 3.57 (dd, 1H, *J* = 10.3, 5.2 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.1, 137.4 (C_q), 128.7, 128.5, 128.2, 128.0, 127.9, 127.8 (CH_{arom}), 85.0 (C-3), 83.4 (C-4), 73.6, 72.4 (CH_2 Bn), 70.7 (t, *J* = 23.0 Hz, C-1), 70.5, 70.0 (C-5), 65.9 (C-2); ^{2}H NMR ($CHCl_3$, 77 MHz): δ 4.02; ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1\text{-}H2}$: +1.1 Hz, $^2J_{C2\text{-}H1}$: +2.3 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{19}H_{24}DN_4O_3$ 358.19839, found 358.19858.



1-[^{2}H]-1,4-anhydro-2-azido-3,5-di-*O*-benzyl-2-deoxy-β-D-lyxitol (71). Donor **7** and triethylsilane-*d* (4 eq.) were condensed using the general procedure for furanosyl imidate glycosylations at 0-5°C for 100 h with TfOH as the promotor. Yield = 20 mg, 59 µmol, 59% as a colourless oil. R_f: 0.13 (9/1 pentane/EtOAc). $[\alpha]_D^{20}$ = -37° (*c* = 1.0, $CHCl_3$); IR (thin film): 698, 738, 1984, 1269, 1452, 2104, 2868, 2922, 3032; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.36 – 7.26 (m, 10H, CH_{arom}), 4.77 (d, 1H, *J* = 11.6 Hz, C*H*H Bn), 4.61 – 4.56 (m, 2H, C*H*H Bn, CH*H* Bn), 4.50 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.20 (t, 1H, *J* = 5.2 Hz, H-3), 4.15 (dt, 1H, *J* = 6.9, 5.2 Hz, H-4), 3.92 (d, 1H, *J* = 6.4 Hz, H-1), 3.86 (dd, 1H, *J* = 6.3, 5.1 Hz, H-2), 3.73 (dd, 1H, *J* = 10.1, 5.0 Hz, H-5), 3.68 (dd, 1H, *J* = 10.1, 7.0 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.2, 137.5 (C_q), 128.6, 128.5, 128.1, 128.0, 127.9, 127.8 (CH_{arom}), 79.6, 79.6 (C-3, C-4), 74.0, 73.7 (CH_2 Bn), 69.0 (C-5), 68.7 (t, *J* = 22.8 Hz, C-1), 61.3 (C-2); ^{2}H NMR ($CHCl_3$, 77 MHz): δ 3.95; ^{13}C HSQC-HECADE NMR: $^2J_{C2,H1}$ = +0.2 Hz; HRMS: $[M+Na]^+$ calcd for $C_{19}H_{20}DN_3O_3Na$ 363.1543, found 363.1551.

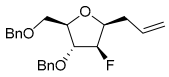


1-[^{2}H]-1,4-anhydro-2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-xylitol (72). Donor **8** and triethylsilane-*d* (4 eq.) were condensed using the general procedure for furanosyl imidate glycosylations at 0-5°C for 100 h with TfOH as the promotor. Yield = 23 mg, 68 µmol, 68% as a colourless oil (α:β = 85:15). Inseparable mixture of **72** and amide **79** (in a 73:27 ratio) R_f: 0.30 (85/15 pentane/Et_2O). IR (thin film): 696, 735, 1061, 1088, 1207, 1454, 1494, 1690, 2106, 2916; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.38 – 7.24 (m, 10H, CH_{arom}), 4.65 – 4.58 (m, 2H, 2xC*H*H Bn), 4.54 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.52 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.21 – 4.15 (m, 1.85H, H-1α, H-4), 4.04 (dd, 1H, *J* = 5.5, 1.9 Hz, H-2), 3.99 (dd, 1H, *J* = 4.4, 1.9 Hz, H-3), 3.74 – 3.70 (m, 1.15H, H-1β, H-5), 3.68 (dd, 1H, *J* = 10.0, 6.4 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.2, 137.4 (C_q), 128.7, 128.5, 128.2, 127.9, 127.8, 127.8 (CH_{arom}), 82.9 (C-3), 79.7 (C-4), 73.7, 72.6 (CH_2 Bn), 70.0 (t, *J* = 22.7 Hz C-1β), 70.0 (t, *J* = 22.7, C-1α) 68.4 (C-5), 65.0 (C-2); ^{2}H NMR ($CHCl_3$, 77 MHz): δ 4.19 (s, 0.15H), 3.75 (s, 0.85H);^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): α-anomer: $^2J_{C2,H1}$ = +0.7 Hz; β-anomer: $^2J_{C2,H1}$ = -4.3 Hz; HRMS: $[M+Na]^+$ calcd for $C_{19}H_{20}DN_3O_3Na$ 363.1543, found 363.1549.

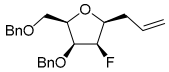


Allyl 3,5-di-*O*-benzyl-1,2-dideoxy-2-fluoro-α-D-ribofuranoside (73). Donor **9** and allyltrimethylsilane (4 eq.) were condensed using the general procedure for furanosyl imidate glycosylations at -20°C for 100 h with TfOH as the promotor. Yield = 27 mg, 76 µmol, 76% as a white solid. R_f: 0.52 (8/2 pentane/Et_2O). Spectroscopic data were in accord with those previously reported.[8] ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.40 – 7.19 (m, 10H, CH_{arom}), 5.80 (ddtd, 1H, *J* = 17.3, 10.2, 7.0, 0.8 Hz, CH allyl), 5.20 – 5.14 (m, 1H, C*H*H allyl), 5.09 (ddt, 1H, *J* = 10.2, 2.1, 1.1 Hz, CH*H* allyl), 4.89 (dt, 1H, *J* = 55.2, 2.9 Hz, H-2), 4.69 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.59 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.52 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.49 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.21 – 4.16 (m, 1H, H-4), 4.11 (ddd, 1H, *J* = 8.6, 3.5, 0.5 Hz, H-3), 4.05 (dtd, 1H, *J* = 29.3, 7.4, 2.4 Hz, H-1), 3.71 (dd, 1H, *J* = 10.8, 2.4 Hz, H-5), 3.56 (dd, 1H, *J* = 10.9, 3.4 Hz, H-5), 2.49 (ddt, 2H, *J* = 7.0, 5.6, 1.4 Hz, CH_2 allylic); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.3, 137.6 (C_q), 133.6 (CH allyl), 128.6, 128.5, 128.1, 128.0, 127.8, 127.7 (CH_{arom}), 118.0 (CH allyl), 90.1 (d, *J* = 191.0 Hz, C-2), 80.0 (d, *J* = 18.3 Hz, C-1), 79.2 (C-4), 78.6 (d, *J* = 16.5 Hz, C-3), 73.6, 72.5 (CH_2 Bn), 69.6 (C-5), 33.7 (d, *J* = 9.3 Hz, CH allylic); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -215.30 (ddd, *J* = 53.7, 29.4,

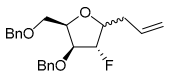
23.5 Hz, F-2); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C2,H1}$ = +4.9 Hz, $^3J_{Callyl,H2}$ = +0.2 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{22}H_{29}FNO_3$ 374.21260, found 374.21252.



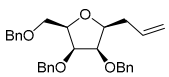
Allyl 3,5-di-*O*-benzyl-1,2-dideoxy-2-fluoro-β-D-arabinofuranoside (74). Donor **10** and allyltrimethylsilane (4 eq.) were condensed using the general procedure for furanosyl imidate glycosylations at -20°C for 100 h with TfOH as the promotor. Yield = 28 mg, 79 µmol, 79% as a colourless oil. R_f: 0.80 (9/1 pentane/EtOAc). $[\alpha]_D^{20}$ = -29.7° (*c* = 0.93, $CHCl_3$); IR (thin film):700, 712, 1026, 1070, 1096, 1269, 1452, 2924; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HH-NOESY, HSQC): δ 7.36 – 7.25 (m, 10H, CH_{arom}), 5.84 (ddtd, 1H, *J* = 17.2, 10.2, 7.1, 0.7 Hz, CH allyl), 5.17 (dq, 1H, *J* = 17.1, 1.5 Hz, C*H*H allyl), 5.10 (ddt, 1H, *J* = 10.2, 2.0, 1.1 Hz, CH*H* allyl), 4.88 (dd, 1H, *J* = 52.0, 2.8 Hz, H-2), 4.66 – 4.53 (m, 4H, 2xCH_2 Bn), 4.04 – 3.98 (m, 2.5H, H-1, H-3, H-4), 3.95 (td, 0.5H, *J* = 7.2, 2.8 Hz, H-3), 3.65 – 3.59 (m, 1H, H-5), 3.56 – 3.51 (m, 1H, H-5), 2.55 – 2.42 (m, 2H, CH_2 allylic);^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.2, 137.4 (C_q), 133.8 (CH allyl), 128.6, 128.5, 128.1, 127.9, 127.9, 127.8 (CH_{arom}), 117.8 (CH_2 allyl), 95.89 (d, *J* = 186.6 Hz, C-2), 84.71 (d, *J* = 27.3 Hz, C-3), 82.5 (C-4), 80.70 (d, *J* = 20.9 Hz, C-1), 73.6, 72.2 (CH_2 Bn), 70.2 (C-5), 32.63 (d, *J* = 8.1 Hz, CH_2 allylic); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -198.80 (ddd, *J* = 50.6, 29.6, 20.2 Hz); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$ = +4.2 Hz, $^2J_{C2,H1}$ = +5.6 Hz, $^3J_{Callyl,H2}$ = 0.1 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{22}H_{29}FNO_3$ 374.21260, found 374.21280.



Allyl 3,5-di-*O*-benzyl-1,2-dideoxy-2-fluoro-β-D-lyxofuranoside (75). Donor **11** and allyltrimethylsilane (4 eq.) were condensed using the general procedure for furanosyl imidate glycosylations at -20°C for 100 h with TfOH as the promotor. Yield = 32 mg, 90 µmol, 90% as a white solid. R_f: 0.28 (9/1 pentane/EtOAc). $[\alpha]_D^{20}$ = -10.5° (*c* = 1.07, $CHCl_3$); IR (thin film): 696, 711, 737, 1026, 1070, 1271, 1452, 2870, 2922; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.42 – 7.21 (m, 10H, CH_{arom}), 5.82 (ddt, 1H, *J* = 17.2, 10.2, 7.0 Hz, CH allyl), 5.17 (dd, 1H, *J* = 17.1, 1.5 Hz, C*H*H allyl), 5.12 – 5.06 (m, 1H, CH*H* allyl), 4.89 (ddd, 1H, *J* = 54.6, 4.0, 2.9 Hz, H-2), 4.69 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.62 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.58 – 4.51 (m, 2H, 2xCH*H* Bn), 4.28 (td, 1H, *J* = 7.7, 3.6 Hz, H-4), 4.19 (ddd, 1H, *J* = 22.8, 7.8, 4.0 Hz, H-3), 3.84 (dtd, 1H, *J* = 27.3, 7.2, 2.8 Hz, H-1), 3.80 (dd, 1H, *J* = 10.6, 3.7 Hz, H-5), 3.65 (ddd, 1H, *J* = 10.6, 7.7, 1.7 Hz, H-5), 2.51 (t, 2H, *J* = 7.1 Hz, CH_2 allylic); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.6, 137.5 (C_q), 133.7 (CH allyl), 128.6, 128.4, 128.1, 127.9, 127.8, 127.6 (CH_{arom}), 117.9 (CH_2 allyl), 90.2 (d, *J* = 193.1 Hz, C-2), 79.3 (d, *J* = 18.8 Hz, C-1), 78.6 (d, *J* = 15.7 Hz, C-3), 78.2 (C-4), 73.5, 72.8 (CH_2 Bn), 70.6 (d, *J* = 2.7 Hz, C-5), 33.9 (d, *J* = 8.1 Hz, CH_2 allylic); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -213.57 (ddd, *J* = 54.5, 27.2, 22.9 Hz); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$ = +1.2 Hz, $^2J_{C2,H1}$ = +5.2 Hz, $^3J_{Callyl,H2}$ = +0.4 Hz; HRMS: $[M+NH_4]^+$ calcd for $C_{22}H_{29}FNO_3$ 374.21260, found 374.21295.

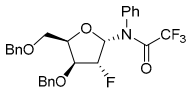


Allyl 3,5-di-*O*-benzyl-1,2-dideoxy-2-fluoro-α/β-D-xylofuranoside (76). Donor **12** and allyltrimethylsilane (4 eq.) were condensed using the general procedure for furanosyl imidate glycosylations at -20°C for 100 h with TfOH as the promotor. Yield = 22 mg, 62 µmol, 62% as a colourless oil (α:β = 70:30), and 12 mg (24%) of the anomeric amide (**78**). R_f: 0.53 and 0.40 (9/1 pentane/Et_2O). IR (thin film): 696, 735, 1028, 1076, 1088, 1454, 2868, 2922; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.37 – 7.25 (m, 10H, CH_{arom}), 5.88 – 5.77 (m, 1H, CH allyl), 5.19 – 5.07 (m, 2H, CH_2 allyl), 4.91 (ddd, 0.7H, *J* = 51.4, 2.8, 1.3 Hz, H-2α), 4.79 (ddd, 0.3H, *J* = 52.6, 2.9, 1.4 Hz, H-2β), 4.65 (d, 0.3H, *J* = 11.9 Hz, C*H*H Bnβ), 4.65 – 4.58 (m, 1.7H, 2xC*H*H Bnα, C*H*H Bnβ), 4.56 (d, 0.7H, *J* = 11.9 Hz, CH*H* Bnα), 4.53 – 4.49 (m, 1.3H, 2xCH*H* Bnβ, CH*H* Bnα), 4.42 – 4.36 (m, 0.7H, H-4α), 4.26 – 4.12 (m, 1.7H, H-1α, H-3α, H-4β), 4.08 (ddd, 0.3H, *J* = 8.9, 4.3, 1.3 Hz, H-3β), 4.02 (dddd, 0.3H, *J* = 13.9, 7.3, 6.5, 2.8 Hz, H-1β), 3.76 (dd, 0.3H, *J* = 10.0, 5.3 Hz, H-5β), 3.73 – 3.69 (m, 1H, H-5α, H-5β), 3.67 (dd, 0.7H, *J* = 9.8, 6.4 Hz, H-5α), 2.54 – 2.36 (m, 2H, CH_2 allylic); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 138.3, 138.2, 137.6 (C_q), 134.0 (CH allylα), 133.8 (CHallylβ), 128.6, 128.6, 128.5, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.7 (CH_{arom}), 117.8 (CH_2 allylβ), 117.7 (CH_2 allylα), 97.7 (d, *J* = 182.9 Hz, C-2β), 94.4 (d, *J* = 187.9 Hz, C-2α), 82.4 (d, *J* = 35.5 Hz, C-3β), 82.4 (d, *J* = 13.9 Hz, C-1β), 81.8 (d, *J* = 25.8 Hz, C-3α), 79.8 (d, *J* = 1.6 Hz, C-4β), 79.6 (d, *J* = 19.0 Hz, C-1α), 78.9 (C-4α), 73.6 (CH_2 Bnβ), 73.6, 72.9 (CH_2 Bnα), 72.1 (CH_2 Bnβ), 68.3 (C-5β), 68.2 (C-5α), 37.4 (d, *J* = 7.6 Hz, CH_2 allylicβ), 33.1 (d, *J* = 10.3 Hz, CH_2 allylicα); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -183.53 (dddd, 0.3F, *J* = 52.6, 28.0, 13.2, 1.8 Hz), -201.43 (dddd, 0.7F, *J* = 51.4, 31.9, 9.9, 2.5 Hz); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): α-anomer: $^2J_{C1,H2}$ = +5.0 Hz, $^2J_{C2,H1}$ = +4.5 Hz, $^3J_{Callyl,H2}$ = +0.3 Hz, β-anomer: $^2J_{C1,H2}$ = +1.3 Hz, $^2J_{C2,H1}$ = -5.4 Hz, $^3J_{Callyl,H2}$ = +2.8 Hz; HRMS: $[M+Na]^+$ calcd for $C_{22}H_{25}FO_3Na$ 379.1685, found 379.1685.

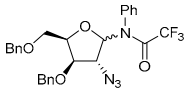


Allyl 2,3,5-tri-*O*-benzyl-1-deoxy-β-D-lyxofuranoside (77). R_f: 0.47 (9/1 pentane/EtOAc). ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.36 – 7.24 (m, 15H, CH_{arom}), 5.82 (ddt, 1H, *J* = 17.1, 10.2, 7.0 Hz, CH allyl), 5.07 (dq, 1H, *J* = 17.1, 1.5 Hz, C*H*H allyl), 5.02 (ddt, 1H, *J* = 10.2, 2.2, 1.2 Hz, CH*H* allyl), 4.76 (d, 1H, *J* = 11.8 Hz, C*H*H Bn), 4.68 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.61 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.59 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.54 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.52 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.24 – 4.19 (m, 1H, H-4), 4.17 (dd, 1H, *J* = 6.1, 3.9 Hz, H-3), 4.01 – 3.94 (m, 2H, H-1, H-2), 3.83 (dd, 1H, *J* = 10.1, 4.8 Hz, H-5), 3.72 (dd, 1H, *J* = 10.1, 6.6 Hz, H-5), 2.53 – 2.46 (m, 2H, CH_2 allylic); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.6, 138.5, 138.4 (C_q Bn), 135.6 (CH allyl), 128.5, 128.4, 128.4, 127.9, 127.7, 127.7, 127.6, 127.5 (CH_{arom}), 116.7 (CH_2 allyl), 79.6 (C-3), 79.1 (C-1), 78.9 (C-2), 78.0 (C-4), 73.4, 73.3, 73.3 (CH_2 Bn), 70.5 (C-5), 35.4 (CH

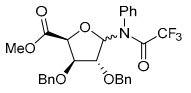
allylic); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 101 MHz): $^2J_{C1,H2}$ = +1.0 Hz, $^2J_{C2,H1}$ = +1.5 Hz, $^3J_{H2,C\text{-}allyl}$ = +1.6 Hz; HRMS: $[M+H]^+$ calcd for $C_{29}H_{33}O_4$ 445.23709, found 445.23704.



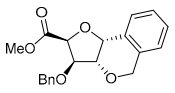
3,5-di-*O*-benzyl-1,2-dideoxy-2-fluoro-1-*N*-[phenyl]trifluoroacetyl-α/β-D-xylofuranoside (78). IR (thin film): 698, 737, 1070, 1153, 1188, 1207, 1454, 1495, 1595, 1690, 2862, 2922; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.43 – 7.19 (m, 15H, CH_{arom}), 6.31 (dd, 1H, *J* = 11.0, 5.1 Hz, H-1), 5.45 (ddd, 1H, *J* = 52.9, 5.0, 3.8 Hz, H-2), 4.65 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.47 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.40 (s, 2H, CH_2 Bn), 3.91 (dt, 1H, *J* = 14.3, 4.1 Hz, H-3), 3.77 (qd, 1H, *J* = 4.7, 1.7 Hz, H-4), 3.56 (ddd, 1H, *J* = 10.5, 4.4, 0.7 Hz, H-5), 3.49 (dd, 1H, *J* = 10.6, 4.8 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.0, 137.1 (C_q), 134.2, 132.0, 130.5, 129.6, 128.6, 128.5, 128.2, 127.9, 127.8, 127.7 (CH_{arom}), 93.5 (d, *J* = 194.8 Hz, C-2), 87.2 (d, *J* = 17.4 Hz, C-1), 80.1 (d, *J* = 23.2 Hz, C-3), 79.1 (d, *J* = 3.5 Hz, C-4), 73.4, 72.6 (CH_2 Bn), 68.0 (C-5); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -68.17 (s, 3F, CF_3), -196.37 (dt, 1F, *J* = 53.1, 12.7 Hz, F-2).



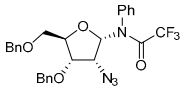
2-azido-3,5-di-*O*-benzyl-1,2-dideoxy-1-*N*-[phenyl]trifluoroacetyl-α/β-D-xylofuranoside (79). Intermixed with **76**. The anomeric amide was formed in an α:β = 93:7 ratio. Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.17 (dd, 2H, *J* = 6.6, 2.6 Hz, NPh), 6.33 (d, 1H, *J* = 6.6 Hz, H-1), 4.59 (t, 1H, *J* = 6.6 Hz, H-2), 4.50 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.46 – 4.40 (m, 3H, CH_2 Bn, CH*H* Bn), 3.66 (t, 1H, *J* = 4.3 Hz, H-4), 3.59 (t, 1H, *J* = 6.8 Hz, H-3), 3.49 (dd, 1H, *J* = 10.7, 4.0 Hz, H-5), 3.41 (dd, 1H, *J* = 10.7, 4.5 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 157.0 (q, *J* = 36.4 Hz, F_3C-*C*=O), 138.0, 137.0 (C_q), 132.0, 130.7, 129.6, 129.5, 128.7, 128.3, 128.1, 127.8, 127.8, 127.7, 126.5, 120.6 (CH_{arom}), 116.0 (q, *J* = 288.7 Hz, CF_3), 86.9 (C-1), 80.9 (C-3), 78.6 (C-4), 73.5, 73.3 (CH_2 Bn), 68.6 (C-5), 67.1 (C-2); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -68.04 (s, $CF_{3,}\alpha$), -68.18 (s, $CF_{3,}\beta$); ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): α-anomer: $^2J_{C1,H2}$ = -0.2 Hz, $^2J_{C2,H1}$ = +1.1 Hz; Diagnostic peaks for the β-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): 5.98 (d, 0.07H, *J* = 6.2 Hz, H-1), 4.28 (td, 0.07H, *J* = 6.3, 4.6 Hz, H-4); ^{13}C HSQC-HECADE NMR: $^2J_{C1,H2}$ = -4.0 Hz, $^2J_{C2,H1}$ = -2.1 Hz.



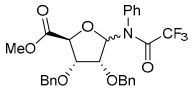
Methyl (2,3-di-*O*-benzyl-1-deoxy-1-*N*-[phenyl]trifluoroacetyl-α/β-D-xylofuranosyl uronate) (80). ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HH-NOESY, HSQC, HMBC): δ 7.41 – 7.28 (m, 18H, CH_{arom}), 7.15 (dd, 2H, *J* = 7.3, 2.0 Hz, CH_{arom}), 6.59 (d, 1H, *J* = 6.1 Hz, H-1), 4.70 (d, 1H, *J* = 11.2 Hz, C*H*H Bn), 4.58 (d, 1H, *J* = 11.2 Hz, CH*H* Bn), 4.51 (t, 1H, *J* = 6.1 Hz, H-2), 4.44 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.38 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.15 (d, 1H, *J* = 6.5 Hz, H-4), 3.77 – 3.72 (m, 1H, H-3), 3.67 (s, 3H, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC, HMBC): δ 169.5 (C=O), 137.3, 137.1 (C_q), 129.6, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9 (CH_{arom}), 87.6 (C-1), 81.9 (C-2), 81.1 (C-3), 78.2 (C-4), 74.3, 72.9 (CH_2 Bn), 52.3 (CO_2Me); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -68.09; ^{13}C HSQC-HECADE NMR ($CDCl_3$, 126 MHz): $^2J_{C1,H2}$ = +1.5 Hz.



Methyl (2*S*,3*R*,3a*S*,9b*R*)-3-(benzyloxy)-3,3a,5,9b-tetrahydro-2*H*-furo[3,2-*c*]isochromene-2-carboxylate (81). ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HH-NOESY, HSQC): δ 7.61 – 7.57 (m, 1H, CH_{arom}), 7.37 – 7.28 (m, 7H, CH_{arom}), 7.08 – 7.04 (m, 1H, CH_{arom}), 5.16 (d, 1H, *J* = 2.8 Hz, H-1), 4.92 (d, 1H, *J* = 4.9 Hz, H-4), 4.78 (d, 1H, *J* = 14.6 Hz, C*H*H Bn $_{(C\text{-}2)}$), 4.72 (d, 1H, *J* = 11.9 Hz, C*H*H Bn $_{(C\text{-}3)}$), 4.65 (d, 1H, *J* = 14.8 Hz, CH*H* Bn $_{(C\text{-}2)}$), 4.64 (d, 1H, *J* = 12.0 Hz, CH*H* Bn $_{(C\text{-}3)}$), 4.44 (d, 1H, *J* = 5.1 Hz, H-3), 4.26 (d, 1H, *J* = 3.0 Hz, H-2), 3.76 (s, 3H, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 170.2 (C=O), 134.4, 130.9, 130.3 (C_q), 128.7, 128.6, 128.1, 127.7, 127.7, 124.2 (CH_{arom}), 85.2 (C-3), 80.4 (C-4), 79.5 (C-2), 74.9 (C-1), 73.2 (CH_2 $Bn_{(C\text{-}3)}$), 67.2 (CH_2 $Bn_{(C\text{-}2)}$), 52.1 (CO_2Me).



3,5-di-*O*-benzyl-1,2-dideoxy-2-fluoro-1-*N*-[phenyl]trifluoroacetyl-α-D-ribofuranoside (98). Intermixed with **74**. Diagnostic peaks: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.04 (d, 1H, *J* = 5.1 Hz, H-1), 4.61 (t, 1H, *J* = 5.5 Hz, H-2), 4.44 (d, 1H, *J* = 11.6 Hz, C*H*H Bn), 4.41 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.30 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 3.44 (dd, 1H, *J* = 11.3, 2.5 Hz, H-5), 3.32 (dd, 1H, *J* = 11.3, 3.5 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 88.1 (C-1), 80.3 (C-4), 77.0 (C-3), 73.4, 73.3 (CH_2 Bn), 68.0 (C-5), 62.9 (C-2).



Methyl (2,3-di-*O*-benzyl-1-deoxy-1-*N*-[phenyl]trifluoroacetyl-α-D-ribofuranosyl uronate) (99). ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.43 – 7.16 (m, 14H, CH_{arom}), 7.09 – 7.00 (m, 1H, NPh), 6.44 (d, 1H, *J* = 5.8 Hz, H-1), 4.75 (d, 1H, *J* = 11.1 Hz, C*H*H Bn), 4.65 (d, 1H, *J* = 11.0 Hz, CH*H* Bn), 4.48 – 4.39 (m, 2H, C*H*H Bn, H-2), 4.35 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.02 – 3.99 (m, 2H, H-3, H-4), 3.67 (s, 3H, CH_3 CO_2Me); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.5 (C=O), 137.4, 137.0, 133.5 (C_q), 132.1, 131.8, 129.1, 128.6, 128.5, 128.3, 128.2, 128.2, 128.1 (CH_{arom}), 88.5 (C-1), 79.9, 79.0 (C-3, C-4), 77.2 (C-2), 74.5, 72.8 (CH_2 Bn), 52.7 (CO_2Me); ^{19}F NMR ($CDCl_3$, 471 MHz): δ -68.03.

Conformational energy landscape calculations

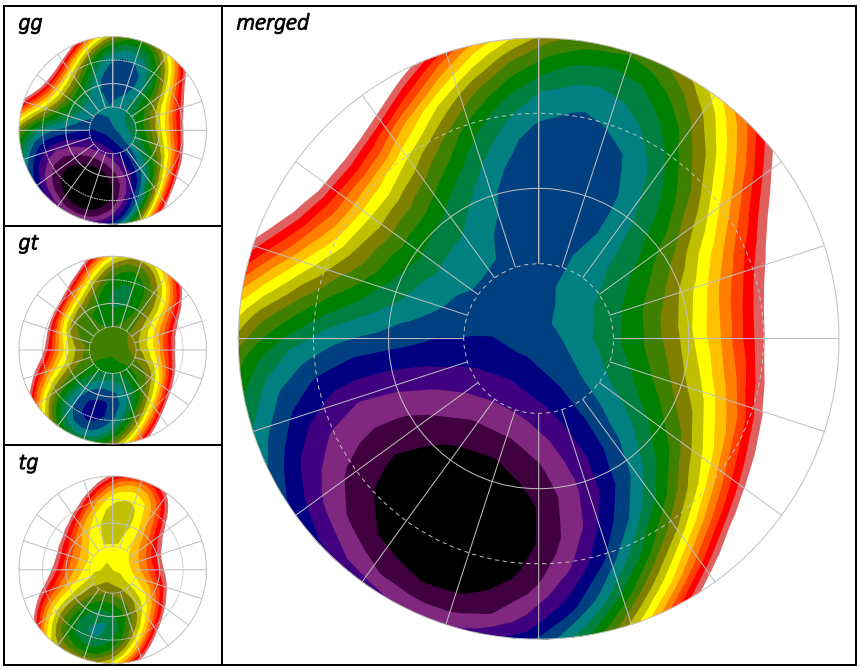
In an adaptation of our previous work,[20] all calculations were performed with Density Functional Theory calculations with the B3LYP hybrid functional. The starting conformer for the Conformational Energy Landscapes (CEL) was obtained by a conformer distribution search in the Spartan 10 program in the gas phase,[21] with a 6-31G(d) basis set. All resulting geometries were further optimized at the 6-311G(d,p) level in the Gaussian 03 program,[22] with a polarized continuum model (PCM) to correct for solvation in dichloromethane, and further corrected for their zero-point energy (ZPE). The geometry with the lowest, ZPE corrected solvated energy, was selected and used as the starting geometry for the CEL. Two dihedral angles of the five-membered ring were constrained: C4-O4-C1-C2 (D3) and C1-C2-C3-C4 (D1) by scanning with 10° per step, over 9 steps (-40° to 40°), totaling 81 conformations spanning the entire pseudo rotational sphere with a maximum puckering amplitude (τ_m) of 40°. All other internal coordinates were unconstrained. Three separate staggered rotamers (*gg*, *gt*, *tg*) of the O4-C4-C5-O5 dihedral angle (-65°, 65°, 175°) were considered and their CEL maps were calculated separately by pre-rotating the C4-C5 bond (not constrained), bringing the total conformations for each configuration to 243 geometries. The final denoted free Gibbs energy was calculated using Equation (1) in which ΔE_{gas} is the gas-phase energy (electronic energy), $\Delta G^{T}_{gas,QH}$ (T = reaction temperature and pressure = 1 atm.) is the sum of corrections from the electronic energy to free Gibbs energy in the quasi-harmonic oscillator approximation also including zero-point-vibrational energy, and ΔG_{solv} is their corresponding free solvation Gibbs energy. The $\Delta G^{T}_{gas,QH}$ were computed using the quasi-harmonic approximation in the gas phase according to the work of Truhlar. The quasi-harmonic approximation is the same as the harmonic oscillator approximation except that vibrational frequencies lower than 100 cm^{-1} were raised to 100 cm^{-1} as a way to correct for the breakdown of the harmonic oscillator model for the free energies of low-frequency vibrational modes.

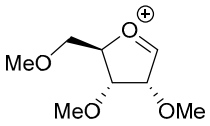
$$\Delta G^{T}_{in\ solution} = \Delta E_{gas} + \Delta G^{T}_{gas,QH} + \Delta G_{solv} \quad (1)$$

$$= \Delta G^{T}_{gas} + \Delta G_{solv}$$

All found minima were checked for negative frequencies. The CEL was visualized as a polar contour plot by the Origin pro 9 software, with the energy plotted as 0.5 $kcal \cdot mol^{-1}$ colored intervals, the phase angle P as the azimuth angle and the puckering amplitude (τ_m) as the radius, with a smoothing factor of 0.001.

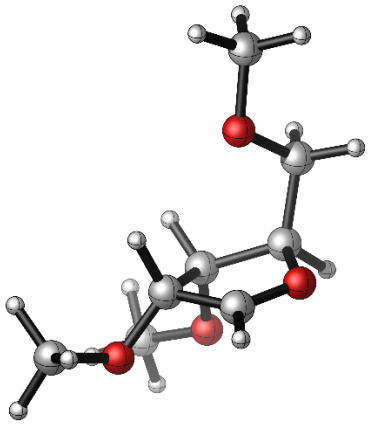
D-ribose oxocarbenium ion (82)





Local minima

E_3 conformation (0.0 kcal / mol)



D1 = -20° P = 198.6°
D3 = 0° τ_m = 21.1

E_{gas}(B3LYP) = -614.607960713 a.u.
E_{solv}(B3LYP) = -614.675828735 a.u.
Zero-point energy correction = 0.229998 a.u.

Atom coordinates

C	-0.855997	0.953000	0.769794
C	0.320121	0.791380	-0.205010
C	0.753193	-0.706461	-0.002357
C	0.165063	-1.021303	1.334185
O	-0.664237	-0.192684	1.762579
C	-2.233284	0.771095	0.178814
O	1.315697	1.694532	0.185101
O	2.133069	-0.901065	-0.014193
O	-2.211561	-0.420133	-0.578461
C	-3.470746	-0.737647	-1.170811
C	2.233164	2.068239	-0.850705
C	2.567677	-2.140795	-0.596569
H	-0.774275	1.853992	1.381129
H	-0.004608	0.953240	-1.239309
H	0.213697	-1.324694	-0.736824
H	0.407039	-1.873970	1.980230
H	-2.982553	0.725800	0.981170
H	-2.448243	1.652558	-0.444003
H	-3.336636	-1.671607	-1.714639
H	-4.241515	-0.870054	-0.402633
H	-3.784287	0.048290	-1.867705
H	2.874636	2.837234	-0.422757
H	2.840704	1.217328	-1.164607
H	1.693210	2.481296	-1.710585
H	2.202423	-2.231047	-1.625181
H	3.655486	-2.110234	-0.590732
H	2.226025	-2.998372	-0.007815

$^4T_3$ conformation (1.1 kcal / mol)

E_{gas}(B3LYP) = -614.606333411 a.u.
E_{solv}(B3LYP) = -614.674656437 a.u.
Zero-point energy correction = 0.230540 a.u.

Atom coordinates

C	-0.808253	0.938588	0.838045
C	0.326053	0.843801	-0.195014
C	0.691229	-0.690242	-0.199781
C	-0.079824	-1.202261	0.980021
O	-0.652655	-0.322710	1.663978
C	-2.199576	0.833776	0.250076
O	1.368825	1.665039	0.248234
O	2.033907	-0.929485	0.138872
O	-2.180761	-0.294625	-0.600110
C	-3.462563	-0.661659	-1.113732
C	2.315703	2.018837	-0.763812
C	2.625835	-2.074518	-0.500188
H	-0.687838	1.768274	1.535461
H	-0.031634	1.138384	-1.188815
H	0.385410	-1.170439	-1.136620
H	-0.031634	-2.212164	1.401461
H	-2.943679	0.724534	1.050012
H	-2.409485	1.761242	-0.301648
H	-3.312106	-1.547560	-1.728793
H	-4.156886	-0.894088	-0.298501
H	-3.878422	0.143490	-1.729311
H	3.003854	2.726477	-0.303615
H	2.873624	1.144960	-1.109826
H	1.812887	2.498358	-1.612142
H	2.569355	-1.971314	-1.588549
H	3.665327	-2.090892	-0.178285
H	2.135082	-3.002940	-0.192301

^4E conformation (1.1 kcal / mol)

E_{gas}(B3LYP) = -614.607154588 a.u.
E_{solv}(B3LYP) = -614.674729958 a.u.
Zero-point energy correction = 0.230406 a.u.

Atom coordinates

C	0.777119	-1.170163	0.589800
C	-0.417084	-0.844042	-0.317812
C	-0.604048	0.703948	-0.094560
C	0.112932	0.900437	1.211712
O	0.619366	-0.137511	1.699774
C	2.157694	-0.938825	0.018661
O	-1.503413	-1.599348	0.133711
O	-1.938046	1.064606	0.136699
O	2.173776	0.360826	-0.532147
C	3.470084	0.794945	-0.952045
C	-2.548253	-1.785087	-0.828736
C	-2.310148	2.360271	-0.363321
H	0.678634	-2.140431	1.078467
H	-0.176227	-1.048153	-1.369130
H	-0.129389	1.266490	-0.903776
H	0.070039	1.787813	1.852986
H	2.906327	-1.044398	0.815686
H	2.346135	-1.711821	-0.740315
H	3.352272	1.806485	-1.337437
H	4.169544	0.801426	-0.108786
H	3.857124	0.144868	-1.744057
H	-3.267660	-2.460103	-0.367386
H	-3.037162	-0.838763	-1.068703
H	-2.151734	-2.244094	-1.741885
H	-2.129591	2.417736	-1.441707
H	-3.373016	2.468001	-0.155652
H	-1.758531	3.157464	0.145195

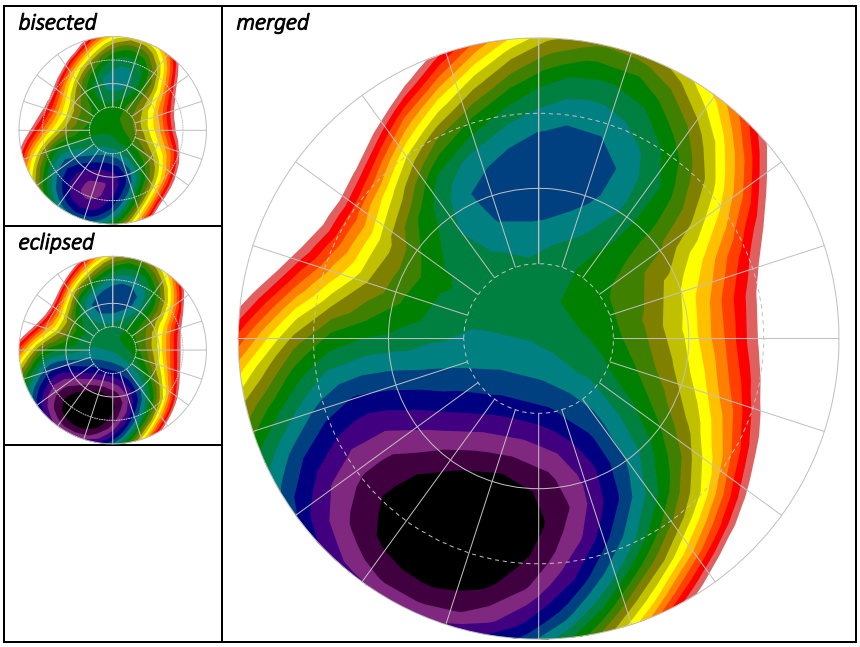
^3E conformation (1.9 kcal / mol)

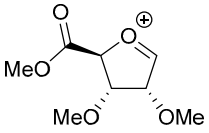
E_{gas}(B3LYP) = -614.605473408 a.u.
E_{solv}(B3LYP) = -614.672694683 a.u.
Zero-point energy correction = 0.229720 a.u.

Atom coordinates

C	0.713766	-1.309936	0.275273
C	-0.517851	-0.755006	-0.440311
C	-0.574225	0.683325	0.164313
C	-0.214560	0.352467	1.579411
O	0.466301	-0.691783	1.695841
C	2.107338	-0.959935	-0.177701
O	-1.617243	-1.536966	-0.080001
O	-1.815532	1.302811	0.047171
O	2.233311	0.427666	-0.392994
C	3.552340	0.816115	-0.780448
C	-2.731827	-1.488402	-0.984830
C	-1.764591	2.708529	-0.240536
H	0.629638	-2.382314	0.464521
H	-0.360141	-0.713490	-1.526956
H	0.262559	1.261855	-0.252190
H	-0.493300	0.891112	2.493291
H	2.821188	-1.310662	0.581537
H	2.288462	-1.535269	-1.099597
H	3.537174	1.897515	-0.906926
H	4.279982	0.548533	-0.005706
H	3.836382	0.341120	-1.726369
H	-3.438081	-2.236743	-0.628655
H	-3.198973	-0.502866	-0.978952
H	-2.410134	-1.745509	-2.000176
H	-1.214414	2.892993	-1.169527
H	-2.797281	3.032011	-0.355951
H	-1.300099	3.264956	0.580483

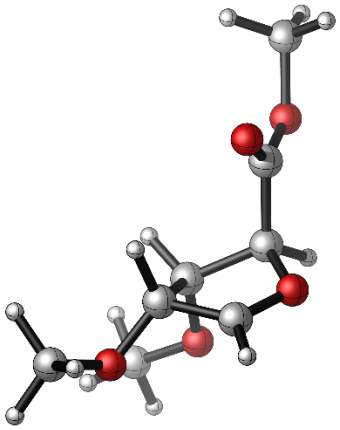
4-CO_2Me-D-ribose oxocarbenium ion (83)





Local minima

E_3 conformation (0.0 kcal / mol)



D1 = -30° P = 198.1°
D3 = 0° τ_m = 31.6

E_{gas}(B3LYP) = -688.657855795 a.u.
E_{solv}(B3LYP) = -688.728244100 a.u.
Zero-point energy correction = 0.211450 a.u.

Atom coordinates

C	0.430113	0.730224	-0.129081
C	1.193014	-0.647608	-0.167617
C	0.823447	-1.199659	1.169368
O	-0.197359	-0.682018	1.682133
C	-0.765612	0.373934	0.772094
C	-1.932093	-0.285629	0.036350
O	-2.895223	0.592539	-0.169479
C	-4.059873	0.121027	-0.905839
O	-1.911938	-1.439883	-0.310068
O	1.158901	1.722830	0.517772
O	2.567040	-0.502678	-0.318247
C	1.987486	2.538435	-0.327875
C	3.217322	-1.539280	-1.073274
H	0.110653	1.020945	-1.139098
H	0.724538	-1.291775	-0.933040
H	1.349731	-1.962434	1.755698
H	-1.077691	1.188197	1.427553
H	-3.755809	-0.231886	-1.891013
H	-4.541118	-0.682613	-0.349144
H	-4.711427	0.986422	-0.984544
H	2.797426	1.951439	-0.762637
H	1.386200	2.999429	-1.119017
H	2.396574	3.314353	0.316746
H	4.261921	-1.244479	-1.148572
H	3.147068	-2.504516	-0.561550
H	2.777736	-1.618062	-2.073037

$^4T_3$ conformation (0.3 kcal / mol)

E_{gas}(B3LYP) = -688.657512962 a.u.
E_{solv}(B3LYP) = -688.728181859 a.u.
Zero-point energy correction = 0.211760 a.u.

Atom coordinates

C	0.413742	0.715390	-0.119144
C	1.225335	-0.635968	-0.256855
C	0.728197	-1.409359	0.921555
O	-0.221620	-0.879221	1.547491
C	-0.758241	0.287521	0.785735
C	-1.935811	-0.273127	-0.014378
O	-2.954159	0.562526	-0.005468
C	-4.125468	0.170733	-0.778254
O	-1.863878	-1.333177	-0.585834
O	1.118653	1.703446	0.561566
O	2.602536	-0.458568	-0.127958
C	1.931268	2.554864	-0.260029
C	3.411502	-1.316550	-0.953354
H	0.065270	1.048113	-1.106135
H	0.927467	-1.150690	-1.185395
H	1.176220	-2.308021	1.360874
H	-1.042734	1.035727	1.525851
H	-3.847546	0.031088	-1.822578
H	-4.537482	-0.751792	-0.370189
H	-4.824217	0.994491	-0.665638
H	2.753453	1.995638	-0.710140
H	1.323371	3.026276	-1.040315
H	2.328573	3.320669	0.403872
H	4.440724	-1.004426	-0.788427
H	3.297381	-2.365786	-0.664147
H	3.144112	-1.192354	-2.007663
H	0.076210	0.624128	1.378812
H	-2.152560	-0.253865	1.524948
H	-1.721199	-2.702233	0.395833
H	0.446418	-0.268486	-1.529653
H	4.140908	0.729214	0.919800
H	4.614363	-0.259441	-0.491298
H	4.407031	1.512538	-0.671680
H	-2.105071	2.517529	0.731109
H	-0.471438	2.918283	1.342704
H	-1.049522	3.606208	-0.199492
H	-4.440129	-0.073256	-1.204547
H	-4.210018	-1.287191	0.080501
H	-4.210593	0.455890	0.48995

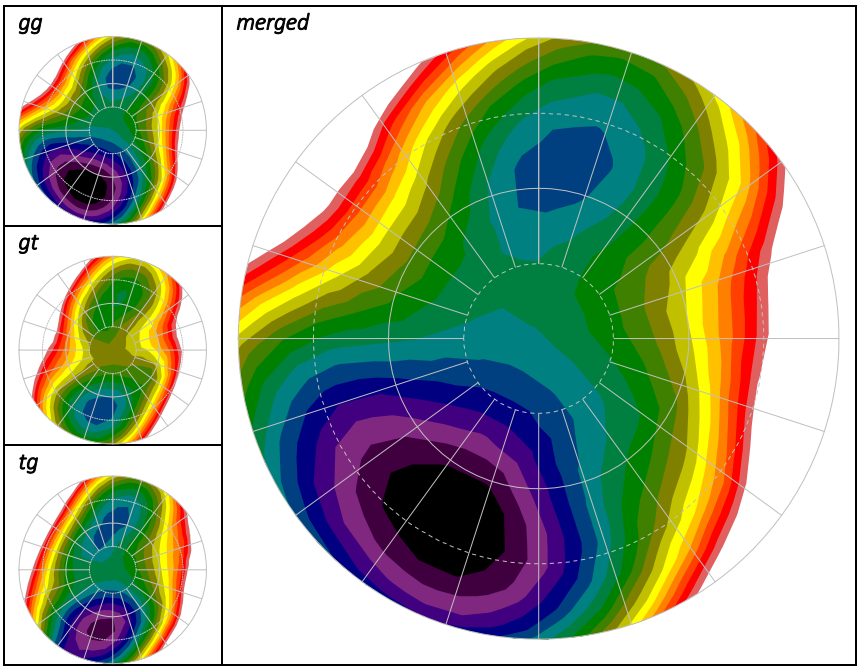
^3E conformation (2.5 kcal / mol)

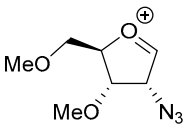
E_{gas}(B3LYP) = -688.648674301 a.u.
E_{solv}(B3LYP) = -688.723230292 a.u.
Zero-point energy correction = 0.211721 a.u.

Atom coordinates

C	-0.356994	0.468650	0.377262
C	-1.660920	-0.376980	0.553145
C	-1.171957	-1.760545	0.282157
O	-0.031698	-1.822524	-0.240297
C	0.546043	-0.462668	-0.456862
C	1.999428	-0.529932	-0.009858
O	2.662702	0.485792	-0.541563
C	4.059558	0.618723	-0.161445
O	2.430982	-1.365571	0.740028
O	-0.509969	1.658124	-0.322883
O	-2.525543	-0.195287	-0.554164
C	-1.069496	2.728862	0.444257
C	-3.935026	-0.286706	-0.264649

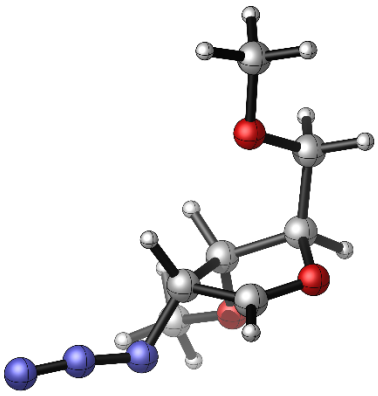
2-N_3-D-ribose oxocarbenium ion (84)





Local minima

$^4T_3$ conformation (0.0 kcal / mol)



D1 = -20° P = 219.4°
D3 = 10° τ_m = 25.9

E_{gas}(B3LYP) = -663.673787863 a.u.
E_{solv}(B3LYP) = -663.748259231 a.u.
Zero-point energy correction = 0.200834 a.u.

Atom coordinates

C	0.063291	0.936029	-0.289757
C	0.632750	-0.478967	0.097998
C	-0.032965	-0.727458	1.413184
O	-0.894361	0.113897	1.745930
C	-1.200030	1.045344	0.577445
C	-2.484441	0.535855	-0.032500
O	0.913863	1.984137	0.074741
O	-2.223556	-0.747512	-0.556699
C	-3.386832	-1.403334	-1.064500
C	1.824649	2.415159	-0.944666
N	2.081586	-0.482658	0.298269
N	2.690712	-1.464562	-0.154261
N	3.376264	-2.283223	-0.515480
H	-0.193333	0.956506	-1.355664
H	0.287584	-1.239772	-0.615911
H	0.225080	-1.510255	2.135851
H	-1.311143	2.032808	1.028625
H	-3.272743	0.506407	0.732342
H	-2.787626	1.248629	-0.813970
H	-4.135755	-1.534469	-0.275097
H	-3.825317	-0.833720	-1.891566
H	-3.065124	-2.378682	-1.426397
H	2.314566	3.305908	-0.554513
H	2.576208	1.650812	-1.156458
H	1.281577	2.668982	-1.861933

E_3 conformation (0.1 kcal / mol)

E_{gas}(B3LYP) = -663.673443200 a.u.
E_{solv}(B3LYP) = -663.747948953 a.u.
Zero-point energy correction = 0.200716 a.u.

Atom coordinates

C	0.034408	0.890613	-0.248171
C	0.696042	-0.475298	0.164618
C	0.081970	-0.730165	1.497753
O	-0.900920	-0.015862	1.779188
C	-1.216619	0.956245	0.643632
C	-2.508218	0.477976	0.026983
O	0.831977	1.993943	0.074106
O	-2.255525	-0.772071	-0.576126
C	-3.418004	-1.358351	-1.162733
C	1.692563	2.458252	-0.974604
N	2.151045	-0.419593	0.258431
N	2.770303	-1.383848	-0.216087
N	3.469398	-2.178553	-0.604439
H	-0.239216	0.866905	-1.309038
H	0.331906	-1.276898	-0.499906
H	0.415088	-1.462532	2.243053
H	-1.321804	1.923258	1.139880
H	-3.285234	0.404687	0.800559
H	-2.825569	1.234235	-0.707328
H	-4.193455	-1.528145	-0.406775
H	-3.819292	-0.719046	-1.957559
H	-3.109671	-2.312982	-1.586479
H	2.149508	3.374981	-0.605217
H	2.473212	1.728352	-1.200902
H	1.112204	2.677421	-1.877843

^4E conformation (1.4 kcal / mol)

E_{gas}(B3LYP) = -663.672509788 a.u.
E_{solv}(B3LYP) = -663.746300564 a.u.
Zero-point energy correction = 0.200954 a.u.

Atom coordinates

C	0.100966	1.001271	-0.332367
C	0.573346	-0.469939	-0.027097
C	-0.141680	-0.747309	1.263181
O	-0.857599	0.190608	1.685032
C	-1.168760	1.125735	0.522267
C	-2.456033	0.604480	-0.075370
O	1.002255	1.971322	0.115112
O	-2.206147	-0.703299	-0.543060
C	-3.385920	-1.416633	-0.925102
C	1.966676	2.399309	-0.854590
N	2.006874	-0.541653	0.270815
N	2.594345	-1.567878	-0.108252
N	3.265783	-2.426653	-0.395153
H	-0.133270	1.107582	-1.398978
H	0.253556	-1.165123	-0.811019
H	0.030232	-1.600042	1.929886
H	-1.278842	2.116401	0.965337
H	-3.246508	0.613870	0.687114
H	-2.748529	1.284435	-0.888730
H	-4.079599	-1.498506	-0.081162
H	-3.884677	-0.917439	-1.762687
H	-3.065070	-2.410382	-1.233407
H	2.532683	3.201248	-0.383198
H	2.645833	1.587640	-1.126920
H	1.465533	2.783075	-1.750313

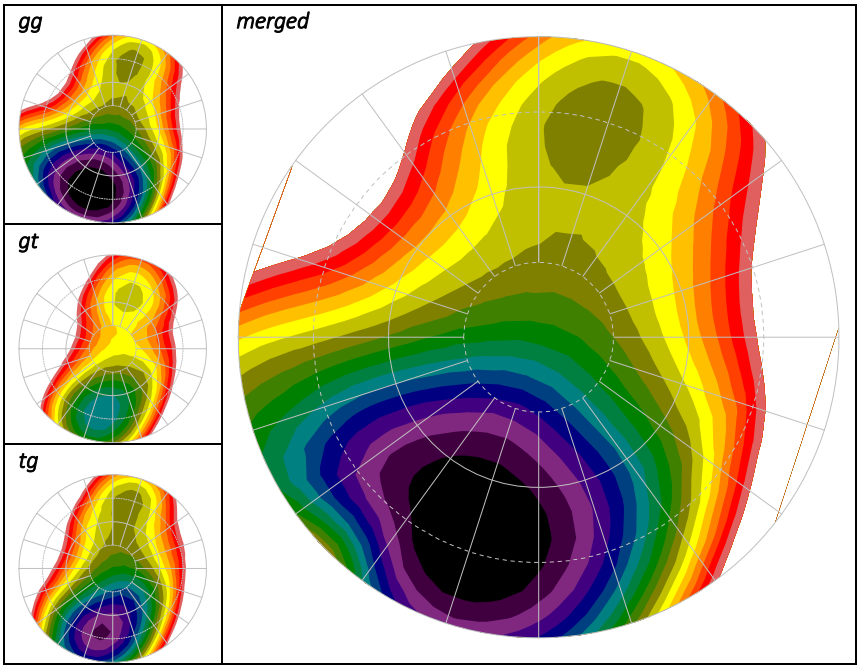
^3E conformation (2.8 kcal / mol)

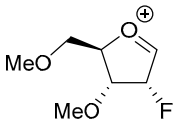
E_{gas}(B3LYP) = -663.668454842 a.u.
E_{solv}(B3LYP) = -663.743609461 a.u.
Zero-point energy correction = 0.200842 a.u.

Atom coordinates

C	-0.064156	0.624060	-0.092643
C	1.072452	-0.343050	-0.557249
C	0.490147	-1.678510	-0.228832
O	-0.519971	-1.649432	0.508671
C	-0.894704	-0.223064	0.883522
C	-2.393329	-0.107708	0.792690
O	0.351252	1.763628	0.592553
O	-2.773820	-0.288665	-0.551221
C	-4.181183	-0.177128	-0.752475
C	0.825478	2.820779	-0.247501
N	2.216551	-0.276201	0.378688
N	3.332578	-0.541019	-0.102941
N	4.403982	-0.730544	-0.394179
H	-0.668058	0.867123	-0.975470
H	1.362994	-0.244035	-1.609508
H	0.890308	-2.659950	-0.508543
H	-0.539783	-0.114244	1.913546
H	-2.860658	-0.854521	1.449816
H	-2.662201	0.891922	1.169881
H	-4.722096	-0.937998	-0.177041
H	-4.542670	0.817590	-0.464663
H	-4.360412	-0.333294	-1.815412
H	1.030820	3.663577	0.410128
H	1.747623	2.536779	-0.766027
H	0.064438	3.104873	-0.982782

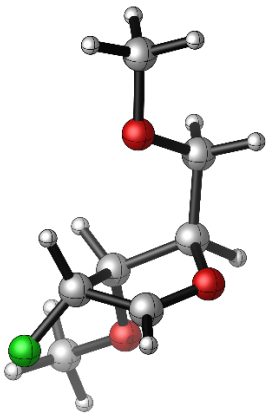
2-F-D-ribose oxocarbenium ion (85)





Local minima

E_3 conformation (0.0 kcal / mol)



D1 = -30° P = 198.1°
D3 = 0° τ_m = 31.6

E_{gas}(B3LYP) = -599.309735677 a.u.
E_{solv}(B3LYP) = -599.383496458 a.u.
Zero-point energy correction = 0.190013 a.u.

Atom coordinates

C	-0.713537	-0.533413	-0.189527
C	-0.606203	0.993354	-0.469373
C	-0.166341	1.510503	0.862487
O	0.339719	0.645323	1.602439
C	0.355412	-0.728468	0.894496
C	1.774392	-0.975382	0.449953
O	-1.952600	-0.864726	0.368650
O	2.101647	-0.011976	-0.525483
C	3.450282	-0.103400	-0.987687
C	-2.971373	-1.223813	-0.577927
F	-1.785082	1.581733	-0.857111
H	-0.476504	-1.120054	-1.086389
H	0.185551	1.217248	-1.197267
H	-0.250301	2.538522	1.236986
H	0.035828	-1.425439	1.672193
H	2.446138	-0.916816	1.317849
H	1.817718	-2.000802	0.051860
H	3.633963	-1.073000	-1.464130
H	3.586158	0.692023	-1.718766
H	4.155183	0.035744	-0.160110
H	-3.834644	-1.526081	0.012416
H	-3.240427	-0.377617	-1.213548
H	-2.638840	-2.064581	-1.196484

$^4T_3$ conformation (0.5 kcal / mol)

E_{gas}(B3LYP) = -599.308567619 a.u.
E_{solv}(B3LYP) = -599.382833168 a.u.
Zero-point energy correction = 0.190254 a.u.

Atom coordinates

C	-0.712835	-0.540374	-0.149087
C	-0.626817	0.970289	-0.540936
C	0.022648	1.581432	0.664363
O	0.416475	0.764180	1.517977
C	0.338366	-0.659432	0.965530
C	1.743116	-0.983051	0.511201
O	-1.955092	-0.864928	0.407451
O	2.046389	-0.089397	-0.537873
C	3.394023	-0.181348	-1.005980
C	-2.958681	-1.252396	-0.542206
F	-1.850268	1.571223	-0.735891
H	-0.451885	-1.178409	-1.002468
H	0.009826	1.131054	-1.420998
H	0.099319	2.651668	0.893737
H	0.002726	-1.270693	1.805089
H	2.443360	-0.875550	1.350586
H	1.754495	-2.031828	0.179697
H	3.594722	-1.176971	-1.416433
H	3.504583	0.564753	-1.791237
H	4.101388	0.030108	-0.196347
H	-3.824725	-1.556755	0.043109
H	-3.233060	-0.419884	-1.194272
H	-2.609425	-2.098063	-1.145191

^4E conformation (1.4 kcal / mol)

E_{gas}(B3LYP) = -599.305963072 a.u.
E_{solv}(B3LYP) = -599.380668173 a.u.
Zero-point energy correction = 0.190278 a.u.

Atom coordinates

C	-0.667707	-0.521031	-0.055428
C	-0.757723	0.913200	-0.679910
C	0.002416	1.761113	0.297043
O	0.475065	1.147452	1.270136
C	0.358140	-0.361098	1.080126
C	1.759319	-0.799749	0.717015
O	-1.876513	-0.923748	0.525449
O	2.042964	-0.199516	-0.529120
C	3.370290	-0.439779	-1.000768
C	-2.806456	-1.521772	-0.387329
F	-2.041919	1.408615	-0.749438
H	-0.308938	-1.233949	-0.806176
H	-0.289025	0.969799	-1.671551
H	0.091637	2.854780	0.278963
H	0.006414	-0.744547	2.039621
H	2.471189	-0.485266	1.491738
H	1.764925	-1.898248	0.660435
H	3.540604	-1.511277	-1.153573
H	3.463927	0.082137	-1.951810
H	4.110963	-0.049305	-0.293863
H	-3.644762	-1.864337	0.217078
H	-3.162697	-0.798559	-1.125680
H	-2.348747	-2.377557	-0.896448

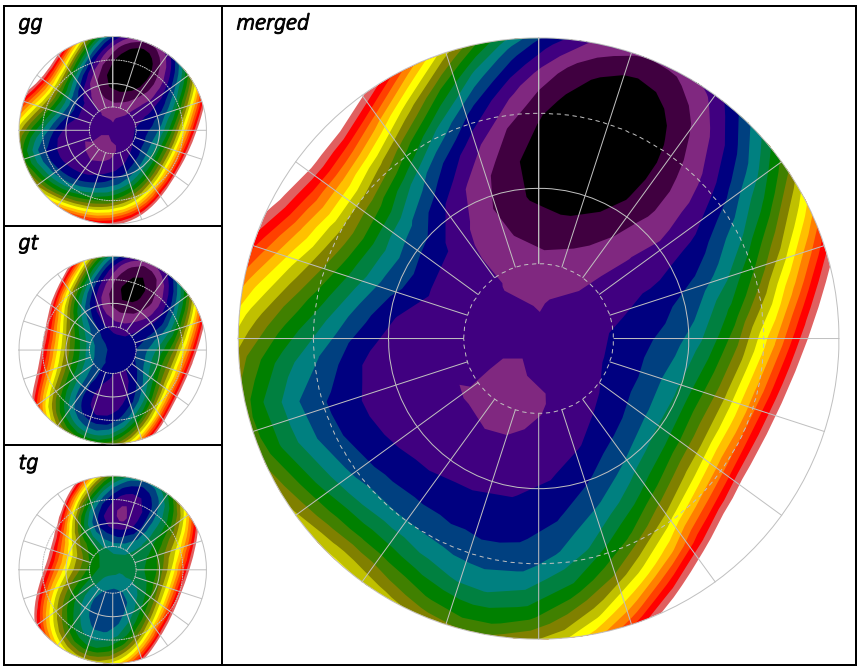
^3E conformation (5.2 kcal / mol)

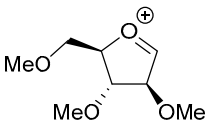
E_{gas}(B3LYP) = -599.297953875 a.u.
E_{solv}(B3LYP) = -599.374549517 a.u.
Zero-point energy correction = 0.190081 a.u.

Atom coordinates

C	0.609740	0.395296	-0.177045
C	1.595127	-0.699624	-0.647516
C	0.721561	-1.929480	-0.550735
O	-0.267921	-1.778234	0.189058
C	-0.305709	-0.361450	0.793074
C	-1.746872	0.054376	0.873156
O	1.193741	1.449514	0.520750
O	-2.261965	0.129430	-0.434250
C	-3.629856	0.531588	-0.472963
C	1.815202	2.442789	-0.304877
F	2.589647	-0.907240	0.303268
H	0.027945	0.727620	-1.048525
H	2.055923	-0.558759	-1.629005
H	0.883577	-2.914153	-1.007513
H	0.149395	-0.480743	1.782069
H	-2.304358	-0.663917	1.491098
H	-1.767499	1.029265	1.387059
H	-3.758598	1.531231	-0.040606
H	-3.922260	0.550835	-1.521917
H	-4.264186	-0.180381	0.068533
H	2.137433	3.235888	0.367260
H	2.687525	2.037047	-0.827745
H	1.102280	2.844575	-1.033152

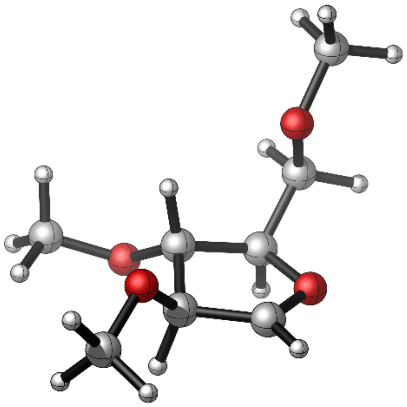
D-arabinose oxocarbenium ion (86)





Local minima

^{3}E conformation (0.0 kcal / mol)



D1 = 20° P = 18.0°
D3 = 0° τ_m = 21.0

E_{gas}(B3LYP) = -614.604741498 a.u.
E_{solv}(B3LYP) = -614.674465019 a.u.
Zero-point energy correction = 0.229580 a.u.

Atom coordinates

C	0.867804	0.086242	-1.077616
C	-0.260693	0.621400	-0.180951
C	-1.370602	-0.464939	-0.283823
C	-0.598217	-1.650299	-0.760272
O	0.554470	-1.403215	-1.174459
O	-1.995300	-0.718825	0.941643
C	2.277308	0.207031	-0.565591
O	-0.620309	1.883509	-0.662355
O	2.317559	-0.319270	0.739491
C	3.608245	-0.235804	1.338076
C	-1.370156	2.676331	0.265486
C	-3.378324	-1.099929	0.862040
H	0.768732	0.459309	-2.101997
H	0.068832	0.658342	0.864415
H	-2.075722	-0.177461	-1.089439
H	-0.914715	-2.700633	-0.748657
H	2.962883	-0.325036	-1.240532
H	2.538930	1.277323	-0.591179
H	3.522163	-0.669178	2.333603
H	4.348126	-0.800945	0.758309
H	3.937027	0.807283	1.422142
H	-1.472238	3.660983	-0.187516
H	-2.365151	2.253726	0.440337
H	-0.840224	2.762002	1.220353
H	-3.723336	-1.193681	1.889842
H	-3.958897	-0.330157	0.342352
H	-3.499954	-2.059652	0.349319

Flat-E_3 conformation (1.2 kcal / mol)

E_{gas}(B3LYP) = -614.604880013 a.u.
E_{solv}(B3LYP) = -614.673300847 a.u.
Zero-point energy correction = 0.229857 a.u.

Atom coordinates

C	0.578887	-1.186059	0.649564
C	-0.620759	-0.765857	-0.212175
C	-1.083362	0.602972	0.371069
C	-0.288368	0.705117	1.635437
O	0.564962	-0.188293	1.807916
O	-0.695551	1.704240	-0.415545
C	1.954062	-1.086979	0.039763
O	-1.602235	-1.764677	-0.059405
O	2.090098	0.201106	-0.507039
C	3.375171	0.444546	-1.071097
C	-2.626685	-1.734267	-1.055440
C	-1.629600	2.795892	-0.447460
H	0.407304	-2.154969	1.124505
H	-0.328558	-0.623244	-1.259509
H	-2.159527	0.585462	0.594384
H	-0.331370	1.510463	2.378081
H	2.712846	-1.287386	0.809944
H	2.029550	-1.876114	-0.725664
H	3.361426	1.464208	-1.453506
H	4.162227	0.350195	-0.312852
H	3.583411	-0.249640	-1.894478
H	-3.270677	-2.590161	-0.860232
H	-3.226423	-0.817761	-0.996022
H	-2.194598	-1.817966	-2.059061
H	-1.210407	3.524152	-1.139138
H	-2.604874	2.454454	-0.810311
H	-1.744600	3.257108	0.538486
H	0.083489	-2.353816	0.760186
H	-0.503370	-0.533212	-1.374231
H	-2.009986	0.946945	0.498848
H	-0.293669	1.162813	2.563098
H	2.459899	-1.715393	0.666944
H	1.788993	-1.976264	-0.960115
H	3.532379	1.226560	-1.171334
H	4.159431	-0.151598	-0.227636
H	3.522494	-0.411261	-1.877760
H	-3.739074	-1.940085	-0.885422
H	-3.352124	-0.210854	-1.029770
H	-2.569187	-1.392746	-2.119105
H	-0.295745	3.698838	-0.867676
H	-1.879421	2.872557	-0.912813
H	-1.196954	3.431378	0.645531

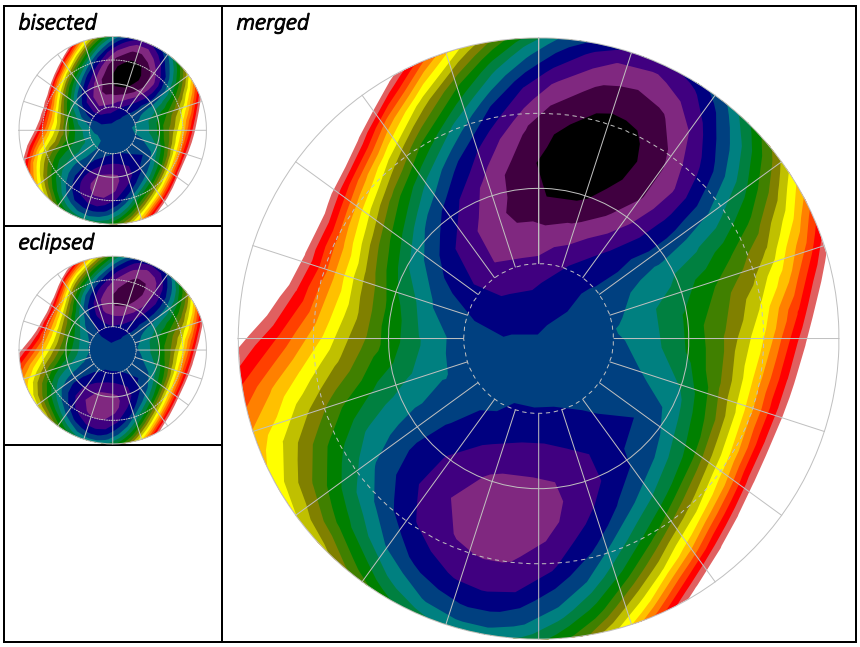
E_3 conformation (2.2 kcal / mol)

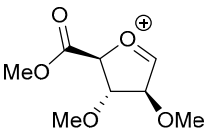
E_{gas}(B3LYP) = -614.603563697 a.u.
E_{solv}(B3LYP) = -614.671733582 a.u.
Zero-point energy correction = 0.229791 a.u.

Atom coordinates

C	0.365811	-1.342467	0.457969
C	-0.767594	-0.665852	-0.317067
C	-0.943782	0.723161	0.365583
C	-0.296163	0.487420	1.699838
O	0.380457	-0.558234	1.782945
O	-0.235110	1.779432	-0.227486
C	1.770139	-1.305203	-0.085674
O	-1.916841	-1.461765	-0.139199
O	2.088821	0.018268	-0.423365
C	3.401327	0.167529	-0.953740
C	-2.945874	-1.226914	-1.103690
C	-0.958156	3.016414	-0.338538

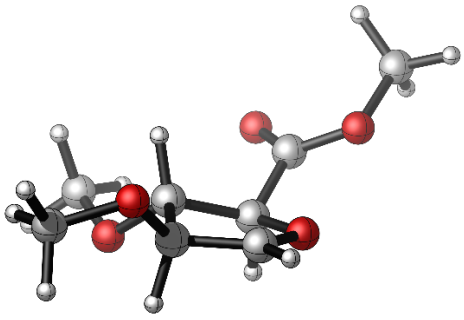
4-CO_2Me-D-arabinose oxocarbenium ion (87)





Local minima

^3E conformation (0.0 kcal / mol)



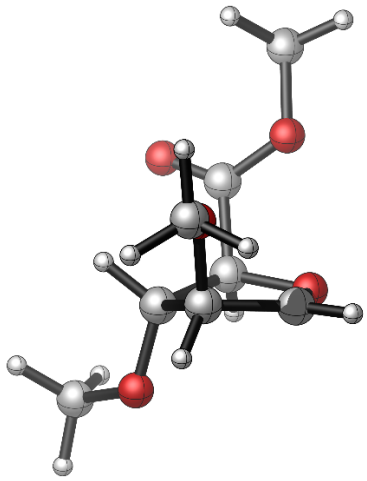
D1 = 20° P = 18.0°
D3 = 0° τ_m = 21.0

E_{gas}(B3LYP) = -688.651725363 a.u.
E_{solv}(B3LYP) = -688.726623078 a.u.
Zero-point energy correction = 0.210926 a.u.

Atom coordinates

C	-0.688150	0.438614	-0.010363
C	-1.674119	-0.738530	-0.241807
C	-0.780001	-1.870116	-0.573071
O	0.402151	-1.551252	-0.839895
C	0.594005	-0.060659	-0.747500
C	1.923872	0.245114	-0.076333
O	2.645024	-0.832209	0.173853
C	3.939655	-0.610835	0.800754
O	2.219176	1.387075	0.168994
O	-1.245037	1.595739	-0.554209
O	-2.536525	-1.062232	0.793862
C	-0.727491	2.837999	-0.047802
C	-3.800682	-0.371614	0.764479
H	-0.493821	0.537701	1.068200
H	-2.203974	-0.525242	-1.201329
H	-1.042424	-2.934105	-0.606477
H	0.611756	0.293278	-1.785439
H	4.561560	0.004457	0.151004
H	3.802718	-0.120711	1.764389
H	4.365625	-1.602424	0.923727
H	-1.344797	3.617225	-0.491022
H	-0.816926	2.872931	1.043226
H	0.317405	2.977142	-0.331395
H	-4.353985	-0.729793	1.630037
H	-3.656380	0.708834	0.835679
H	-4.347599	-0.616101	-0.151586

E_3 conformation (1.2 kcal / mol)



D1 = -20° P = 198.2°
D3 = 0° τ_m = 21.0

E_{gas}(B3LYP) = -688.654490261 a.u.
E_{solv}(B3LYP) = -688.726938637 a.u.
Zero-point energy correction = 0.211547 a.u.

Atom coordinates

C	-1.077442	-0.508004	-0.259524
C	-1.345046	0.955287	0.140411
C	-0.650176	1.074763	1.457211
O	0.130412	0.128378	1.718768
C	0.148886	-0.886173	0.606909
C	1.487873	-0.835473	-0.123131
O	2.315199	0.076898	0.354427
C	3.611092	0.179225	-0.299587
O	1.684689	-1.588545	-1.040947
O	-2.215617	-1.241195	0.108903
O	-0.552789	1.840285	-0.637164
C	-2.305734	-2.532658	-0.504722
C	-1.169106	3.103081	-0.962152
H	-0.849922	-0.579983	-1.330393
H	-2.415456	1.189036	0.154536
H	-0.678679	1.916590	2.157819
H	0.050266	-1.852009	1.108327
H	4.140046	-0.769742	-0.216366
H	3.473048	0.442647	-1.347955
H	4.134913	0.966408	0.235060
H	-3.238081	-2.972116	-0.155071
H	-2.325247	-2.438752	-1.595808
H	-1.470452	-3.178792	-0.211038
H	-0.444966	3.631561	-1.578785
H	-2.092389	2.931556	-1.522781
H	-1.380321	3.686729	-0.061922

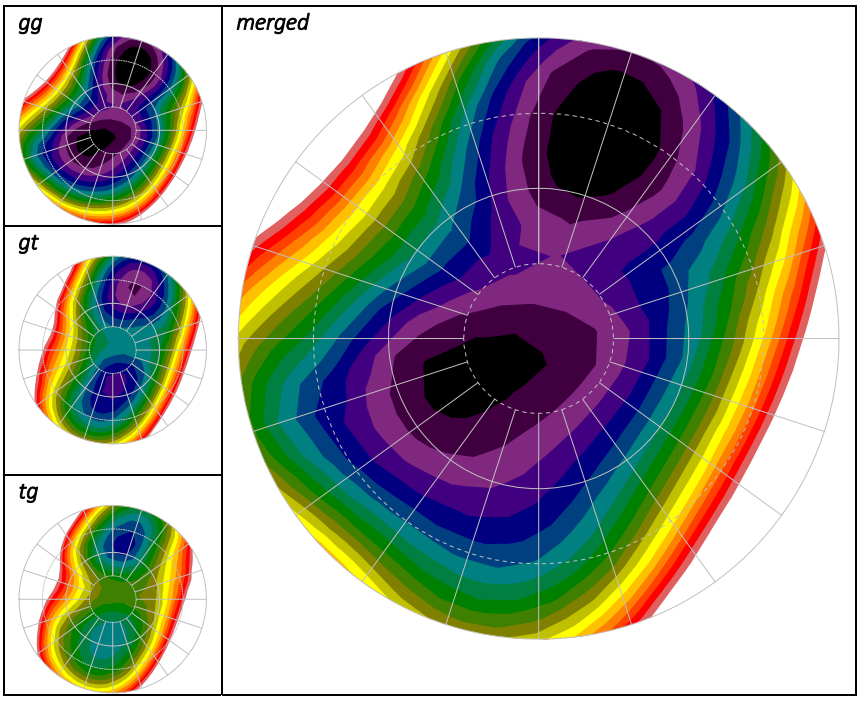
$^3T_4$ conformation (0.9 kcal / mol)

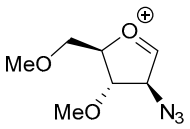
E_{gas}(B3LYP) = -688.654180078 a.u.
E_{solv}(B3LYP) = -688.726491044 a.u.
Zero-point energy correction = 0.211589 a.u.

Atom coordinates

C	-1.001965	-0.607168	-0.250505
C	-1.479110	0.809119	0.119735
C	-0.844906	1.035891	1.454479
O	0.130251	0.281808	1.687651
C	0.241316	-0.808000	0.655036
C	1.579427	-0.706023	-0.066725
O	2.291934	0.346938	0.292837
C	3.579124	0.511230	-0.364089
O	1.875715	-1.541706	-0.881239
O	-2.040454	-1.486738	0.091154
O	-0.775619	1.794037	-0.619007
C	-1.934440	-2.780469	-0.515263
C	-1.547017	2.949582	-1.009520
H	-0.736261	-0.656625	-1.314108
H	-2.569381	0.900259	0.084645
H	-1.030000	1.856211	2.156885
H	0.213746	-1.735301	1.232222
H	4.218132	-0.342488	-0.139612
H	3.434136	0.599319	-1.440548
H	3.992133	1.426549	0.050168
H	-2.813954	-3.338646	-0.199618
H	-1.921934	-2.693238	-1.607066
H	-1.033321	-3.309141	-0.183693
H	-0.864213	3.576203	-1.579524
H	-2.389290	2.638261	-1.633425
H	-1.908989	3.498967	-0.136388

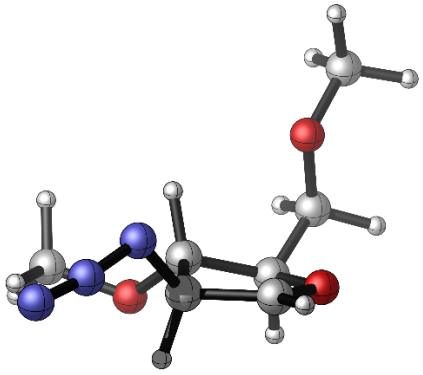
2-N_3-D-arabinose oxocarbenium ion (88)





Local minima

^3E conformation (0.0 kcal / mol)



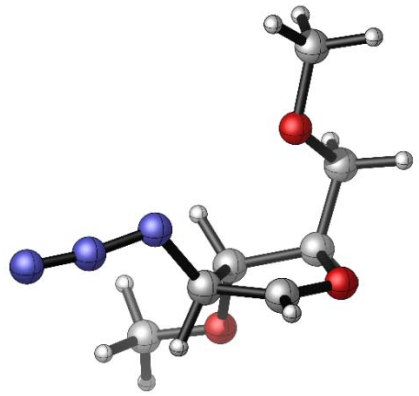
D1 = 20° P = 18.3°
D3 = 0° τ_m = 21.1

E_{gas}(B3LYP) = -663.669685310 a.u.
E_{solv}(B3LYP) = -663.745302055 a.u.
Zero-point energy correction = 0.200297 a.u.

Atom coordinates

C	-0.023596	0.635430	-0.222194
C	-1.148999	-0.427157	-0.425990
C	-0.378434	-1.613715	-0.887977
O	0.801246	-1.382595	-1.224167
C	1.143256	0.095017	-1.065990
C	2.520063	0.166209	-0.463430
O	-0.327179	1.912532	-0.700030
O	2.460995	-0.393205	0.827250
C	3.714111	-0.369872	1.506612
C	-1.075901	2.730850	0.207007
N	-1.903953	-0.729126	0.788208
N	-3.139955	-0.725846	0.685805
N	-4.265555	-0.742338	0.746139
H	0.247777	0.646543	0.839776
H	-1.789751	-0.119836	-1.277798
H	-0.736138	-2.649750	-0.940716
H	1.115924	0.496641	-2.084254
H	3.233147	-0.368486	-1.106935
H	2.810873	1.229061	-0.444216
H	3.552063	-0.826382	2.482127
H	4.469879	-0.944336	0.957396
H	4.070652	0.658721	1.640734
H	-1.104738	3.725669	-0.234127
H	-2.100356	2.363169	0.328434
H	-0.586588	2.775731	1.185874

Flat-^4E conformation (0.3 kcal / mol)



D1 = -10° P = 232.8°
D3 = 10° τ_m = 16.5

E_{gas}(B3LYP) = -663.670483626 a.u.
E_{solv}(B3LYP) = -663.744837496 a.u.
Zero-point energy correction = 0.200374 a.u.

Atom coordinates

C	0.206076	0.991091	-0.283747
C	0.888475	-0.109913	0.600312
C	-0.033409	-0.207179	1.769322
O	-1.025545	0.546674	1.736869
C	-1.165752	1.212869	0.365142
C	-2.342577	0.527286	-0.281992
O	0.898037	2.212695	-0.230006
O	-1.976937	-0.817039	-0.475464
C	-2.997937	-1.615042	-1.070511
C	2.031071	2.280938	-1.100260
N	1.045206	-1.427596	-0.017747
N	2.208108	-1.850180	-0.102570
N	3.201689	-2.360087	-0.261545
H	0.099171	0.619387	-1.308953
H	1.839185	0.279137	1.006448
H	0.101371	-0.845211	2.650865
H	-1.352943	2.266072	0.584190
H	-3.231549	0.625413	0.357151
H	-2.543125	1.046666	-1.232438
H	-2.595664	-2.623197	-1.156548
H	-3.897235	-1.632210	-0.443471
H	-3.257599	-1.239434	-2.067152
H	2.417580	3.295594	-1.022011
H	2.818394	1.578251	-0.800187
H	1.737285	2.075640	-2.135653

Flat conformation (0.4 kcal / mol)

E_{gas}(B3LYP) = -663.670577856 a.u.
E_{solv}(B3LYP) = -663.744990888 a.u.
Zero-point energy correction = 0.200428 a.u.

Atom coordinates

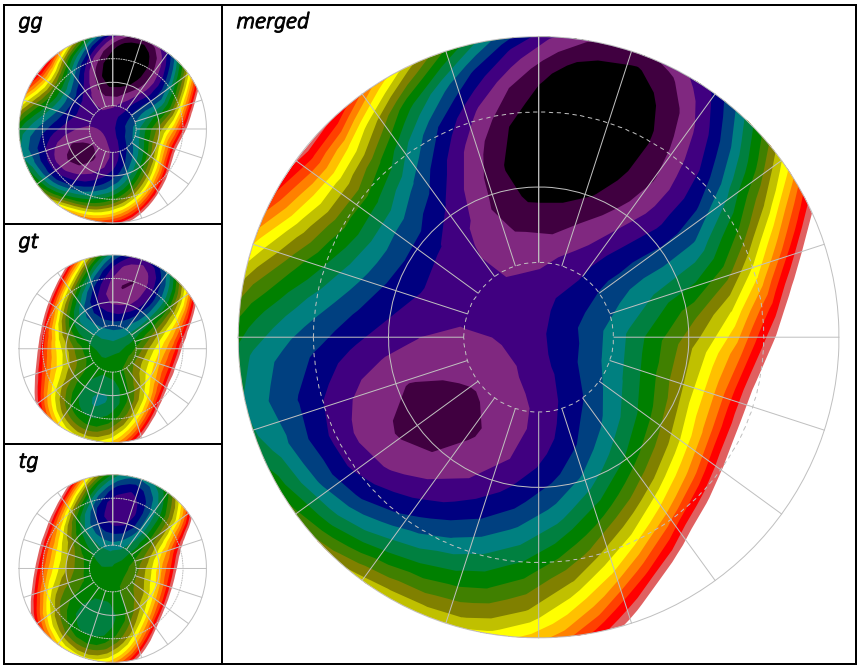
C	0.049595	0.970242	-0.105382
C	1.083862	-0.018772	0.520944
C	0.330643	-0.616688	1.661708
O	-0.836941	-0.207738	1.811787
C	-1.214376	0.831315	0.761671
C	-2.448429	0.298053	0.080740
O	0.453059	2.312192	-0.029928
O	-2.080458	-0.884384	-0.588979
C	-3.163974	-1.509183	-1.273127
C	1.380670	2.702551	-1.046821
N	1.439726	-1.115172	-0.392838
N	2.621432	-1.495843	-0.364480
N	3.653524	-1.938054	-0.464617
H	-0.150032	0.656075	-1.134930
H	1.959386	0.521486	0.917157
H	0.693333	-1.393683	2.345740
H	-1.409095	1.741348	1.335259
H	-3.236184	0.117933	0.825782
H	-2.804610	1.077356	-0.612006
H	-2.763055	-2.406772	-1.741797
H	-3.961070	-1.787954	-0.573496
H	-3.575854	-0.848036	-2.045100
H	1.532901	3.773855	-0.927544
H	2.343880	2.190790	-0.933835
H	0.974401	2.495418	-2.043125

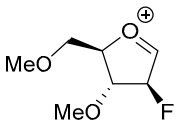
Flat-E_3 conformation (0.9 kcal / mol)

E_{gas}(B3LYP) = -663.670961102 a.u.
E_{solv}(B3LYP) = -663.745204890 a.u.
Zero-point energy correction = 0.200530 a.u.

C	0.148935	1.027398	-0.236751
C	1.037144	-0.024885	0.501769
C	0.262048	-0.289864	1.751384
O	-0.861717	0.245896	1.811121
C	-1.168029	1.060419	0.554316
C	-2.376203	0.414421	-0.073439
O	0.699835	2.318977	-0.166813
O	-1.998085	-0.871888	-0.497437
C	-3.054842	-1.601739	-1.114818
C	1.711254	2.578320	-1.144819
N	1.148856	-1.310541	-0.203616
N	2.278982	-1.824418	-0.223114
N	3.238386	-2.405069	-0.339141
H	-0.017795	0.701651	-1.269586
H	2.015002	0.401747	0.770388
H	0.567805	-0.935578	2.583292
H	-1.382059	2.063895	0.930478
H	-3.198113	0.381353	0.656120
H	-2.691332	1.055404	-0.912395
H	-2.643375	-2.569484	-1.397917
H	-3.889261	-1.749751	-0.418622
H	-3.419444	-1.084905	-2.010774
H	1.990350	3.623931	-1.026888
H	2.598651	1.953212	-0.987941

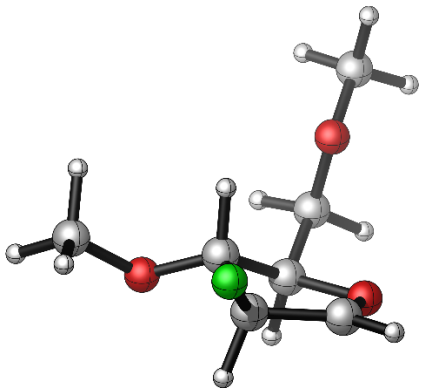
2-F-D-arabinose oxocarbenium ion (89)





Local minima

^3E conformation (0.0 kcal / mol)



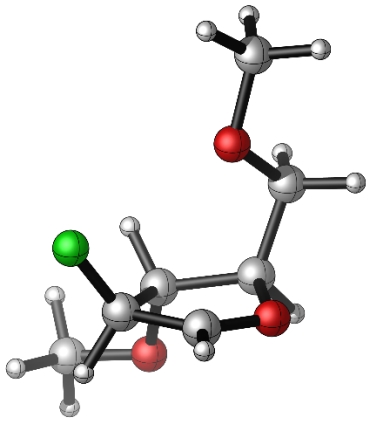
D1 = 30° P = 18.0°
D3 = 0° τ_m = 31.5

E_{gas}(B3LYP) = -599.303899915 a.u.
E_{solv}(B3LYP) = -599.380563768 a.u.
Zero-point energy correction = 0.189574 a.u.

Atom coordinates

C	-0.661357	0.350470	-0.077910
C	-1.648658	-0.833110	0.058478
C	-0.738940	-2.004620	-0.059544
O	0.355283	-1.742062	-0.599731
C	0.425255	-0.260300	-0.983257
C	1.841892	0.196422	-0.780980
O	-1.164802	1.476571	-0.723054
O	2.145414	0.102886	0.589445
C	3.465405	0.544377	0.900516
C	-1.923227	2.355351	0.121342
F	-2.371214	-0.867232	1.225915
H	-0.251077	0.578336	0.915758
H	-2.340245	-0.849765	-0.806906
H	-0.922583	-3.030056	0.286745
H	0.125887	-0.229392	-2.036638
H	2.517320	-0.418507	-1.393194
H	1.898841	1.232923	-1.151305
H	3.589705	0.429964	1.976434
H	4.215789	-0.063492	0.380876
H	3.602293	1.597757	0.627606
H	-2.172943	3.220844	-0.489353
H	-2.843885	1.874673	0.467153
H	-1.327546	2.671099	0.984436

Flat-^4E conformation (0.6 kcal / mol)



D1 = -10° P = 232.8°
D3 = 10° τ_m = 16.5

E_{gas}(B3LYP) = -599.305030720 a.u.
E_{solv}(B3LYP) = -599.379865593 a.u.
Zero-point energy correction = 0.189772 a.u.

Atom coordinates

C	-0.886163	-0.367565	-0.153666
C	-0.841882	1.183372	-0.086054
C	-0.026052	1.449915	1.146963
O	0.372239	0.433254	1.740755
C	0.121987	-0.832083	0.903204
C	1.488114	-1.215030	0.390033
O	-2.146561	-0.866529	0.218445
O	1.903608	-0.169470	-0.456276
C	3.204353	-0.353683	-1.013185
C	-3.111252	-0.852529	-0.839214
F	-0.253000	1.803245	-1.165770
H	-0.580791	-0.693291	-1.157147
H	-1.846803	1.605768	0.066702
H	0.218713	2.431671	1.572149
H	-0.301070	-1.552978	1.605455
H	2.180677	-1.369497	1.229033
H	1.379303	-2.168755	-0.149859
H	3.403502	0.518739	-1.633573
H	3.961833	-0.422579	-0.223802
H	3.240188	-1.257607	-1.631989
H	-4.018246	-1.295492	-0.431687
H	-3.330624	0.168118	-1.175075
H	-2.758599	-1.445729	-1.690154

Flat-$^4T_3$ conformation (1.1 kcal / mol)

E_{gas}(B3LYP) = -599.304860928 a.u.
E_{solv}(B3LYP) = -599.379368612 a.u.
Zero-point energy correction = 0.189835 a.u.

Atom coordinates

C	-0.921301	-0.301453	-0.280061
C	-0.719928	1.126587	0.303615
C	0.160436	0.883460	1.494511
O	0.366645	-0.320695	1.746712
C	0.076119	-1.165146	0.496630
C	1.438243	-1.315457	-0.138813
O	-2.209513	-0.796642	-0.017131
O	1.845385	-0.014074	-0.493982
C	3.190463	0.081362	-0.966551
C	-3.206205	-0.332572	-0.933774
F	-0.176589	2.054823	-0.548803
H	-0.683217	-0.291566	-1.352677
H	-1.671741	1.521124	0.698666
H	0.538064	1.637645	2.196164
H	-0.351455	-2.099520	0.862576
H	2.135961	-1.790707	0.563990
H	1.327020	-1.967523	-1.018322
H	3.366990	1.132729	-1.187201
H	3.897538	-0.259507	-0.202095
H	3.322334	-0.510905	-1.878372
H	-4.137646	-0.815265	-0.643231
H	-3.334436	0.755231	-0.878033
H	-2.947206	-0.614543	-1.960378

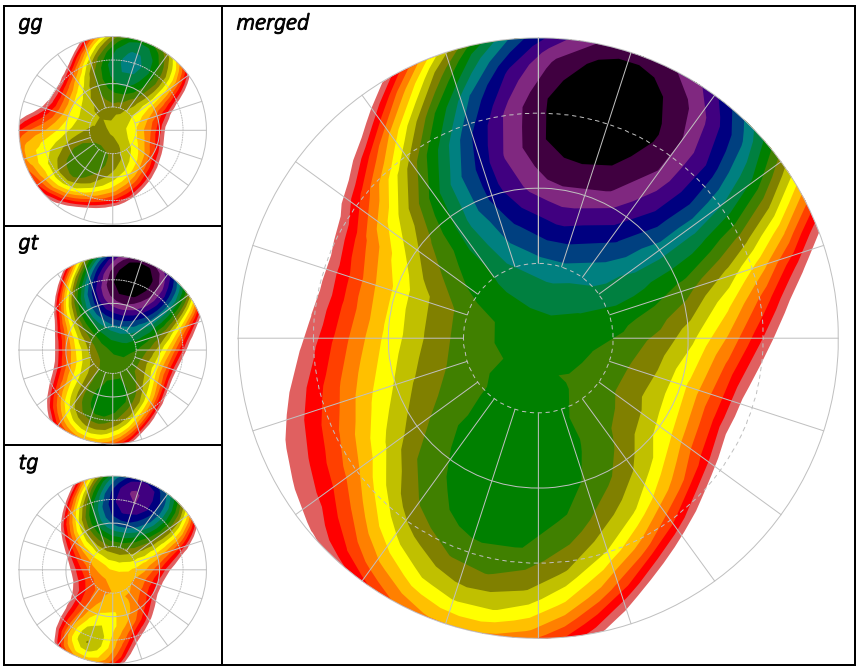
Flat-$^4T_3$ conformation (1.2 kcal / mol)

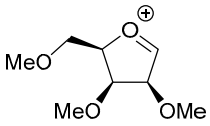
E_{gas}(B3LYP) = -599.304258277 a.u.
E_{solv}(B3LYP) = -599.378943699 a.u.
Zero-point energy correction = 0.189846 a.u.

Atom coordinates

C	-0.870313	-0.382142	-0.105445
C	-0.959718	1.157553	-0.262248
C	-0.185524	1.668926	0.921799
O	0.392937	0.794189	1.585669
C	0.160214	-0.611280	1.009768
C	1.526572	-1.088798	0.588196
O	-2.087668	-0.924202	0.345121
O	1.953505	-0.241821	-0.451731
C	3.265895	-0.535959	-0.927133
C	-3.053898	-1.136327	-0.689740
F	-0.337658	1.655661	-1.391373
H	-0.534737	-0.820493	-1.053935
H	-1.995645	1.518846	-0.230225
H	-0.048997	2.718490	1.212470
H	-0.256789	-1.179104	1.844931
H	2.212180	-1.064023	1.446971
H	1.424093	-2.135832	0.261406
H	3.481761	0.184883	-1.714279
H	4.005265	-0.432865	-0.124092
H	3.316479	-1.551050	-1.338335
H	-3.917756	-1.593861	-0.210897
H	-3.361209	-0.193862	-1.158351
H	-2.655285	-1.809253	-1.456954

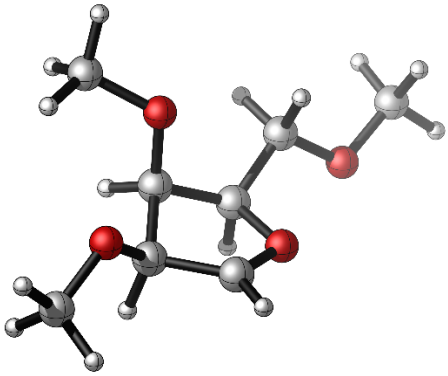
D-lyxose oxocarbenium ion (90)





Local minima

^{3}E conformation (0.0 kcal / mol)



D1 = 30° P = 18.5°
D3 = 0° τ_m = 31.6

E_{gas}(B3LYP) = -614.601741093 a.u.
E_{solv}(B3LYP) = -614.675167100 a.u.
Zero-point energy correction = 0.229442 a.u.

Atom coordinates

C	-0.839987	-0.331030	0.564493
C	0.453449	0.483932	0.602649
C	1.528020	-0.627922	0.328328
C	0.749548	-1.579046	-0.518496
O	-0.490711	-1.460949	-0.427783
C	-2.083633	0.347977	0.061088
O	0.416725	1.447718	-0.406428
O	2.678371	-0.162884	-0.296344
O	-3.168240	-0.524842	0.275786
C	-4.400908	0.004574	-0.203414
C	1.252849	2.594903	-0.194923
C	3.906876	-0.762649	0.147737
H	-1.026159	-0.868128	1.499847
H	0.598849	0.918625	1.600192
H	1.719455	-1.151800	1.288136
H	1.144036	-2.333023	-1.210284
H	-2.195246	1.286892	0.626764
H	-1.968571	0.612336	-0.998217
H	-5.166967	-0.740995	0.006285
H	-4.655780	0.940650	0.309477
H	-4.359161	0.188205	-1.284277
H	1.022249	3.287273	-1.002974
H	1.019900	3.065845	0.766606
H	2.308089	2.320349	-0.232874
H	4.702642	-0.250348	-0.389255
H	4.035096	-0.622277	1.226163
H	3.935129	-1.830375	-0.092210

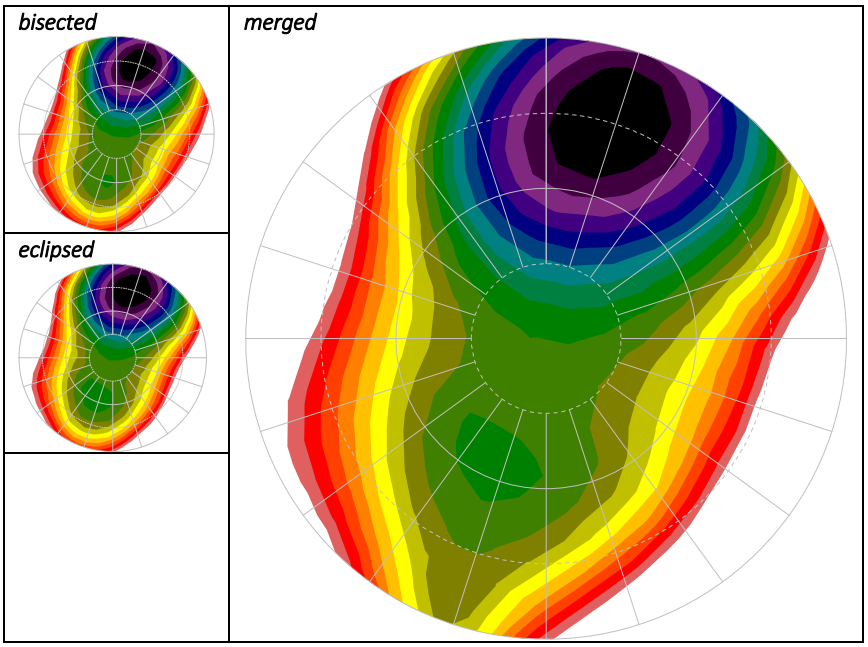
E_3 conformation (4.2 kcal / mol)

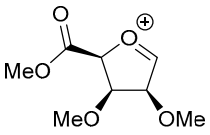
E_{gas}(B3LYP) = -614.596154162 a.u.
E_{solv}(B3LYP) = -614.668959666 a.u.
Zero-point energy correction = 0.230126 a.u.

Atom coordinates

C	0.801932	0.177142	-0.939456
C	-0.644015	0.703655	-0.860105
C	-1.493563	-0.563421	-0.516557
C	-0.576620	-1.667376	-0.934899
O	0.604421	-1.318346	-1.158180
C	1.662579	0.349342	0.290480
O	-0.710789	1.729257	0.080568
O	-1.569276	-0.765052	0.882676
O	2.946539	-0.146638	-0.013798
C	3.869741	0.034302	1.055311
C	-1.930043	2.474103	0.055660
C	-2.787192	-1.369058	1.357548
H	1.341516	0.488044	-1.835973
H	-0.953062	1.045552	-1.859804
H	-2.469673	-0.592034	-1.014711
H	-0.801974	-2.739069	-0.979237
H	1.677800	1.424890	0.514680
H	1.219313	-0.166917	1.153702
H	4.822432	-0.376334	0.722769
H	3.995875	1.098059	1.293500
H	3.541460	-0.497353	1.957397
H	-1.806661	3.286684	0.769468
H	-2.114037	2.887357	-0.942654
H	-2.782661	1.857747	0.359669
H	-2.702673	-1.387518	2.442380
H	-3.649072	-0.764889	1.057941
H	-2.902669	-2.390131	0.982849

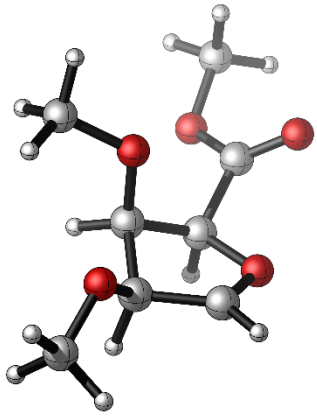
4-CO_2Me-D-lyxose oxocarbenium ion (91)





Local minima

^3E conformation (0.0 kcal / mol)



D1 = 30° P = 18.0°
D3 = 0° τ_m = 31.5

E_{gas}(B3LYP) = -688.652417408 a.u.
E_{solv}(B3LYP) = -688.729998238 a.u.
Zero-point energy correction = 0.211213 a.u.

Atom coordinates

C	0.400033	0.359248	0.550907
C	1.760943	-0.411169	0.407603
C	1.321062	-1.628120	-0.331734
O	0.092787	-1.867015	-0.251260
C	-0.583248	-0.818565	0.594135
C	-1.944051	-0.556675	-0.038943
O	-2.615180	0.277810	0.743377
C	-3.929296	0.685428	0.275685
O	-2.314645	-1.041869	-1.071712
O	0.114189	1.130500	-0.573870
O	2.750826	0.306632	-0.246160
C	0.517500	2.506888	-0.498874
C	4.081001	0.143120	0.276371
H	0.367123	0.930358	1.486680
H	2.050837	-0.760777	1.422213
H	1.929249	-2.307376	-0.941150
H	-0.674287	-1.261715	1.592084
H	-3.837976	1.187578	-0.687291
H	-4.575290	-0.187459	0.183554
H	-4.302083	1.366337	1.035648
H	0.145732	2.976939	-1.407615
H	0.066418	2.989458	0.374744
H	1.604728	2.590645	-0.457619
H	4.712537	0.819703	-0.295615
H	4.112267	0.411482	1.337471
H	4.433273	-0.884568	0.142994

$^3T_4$ conformation (1.4 kcal / mol)

E_{gas}(B3LYP) = -688.650429648 a.u.
E_{solv}(B3LYP) = -688.728063024 a.u.
Zero-point energy correction = 0.211393 a.u.

Atom coordinates

C	0.392508	0.350988	0.648346
C	1.772659	-0.390758	0.474239
C	1.351299	-1.703695	-0.100054
O	0.114033	-1.896024	-0.140519
C	-0.599094	-0.826639	0.635081
C	-1.911863	-0.556835	-0.089135
O	-2.651236	0.247014	0.662537
C	-3.925183	0.663199	0.101609
O	-2.196444	-1.016909	-1.160276
O	0.097195	1.177338	-0.435600
O	2.653160	0.248984	-0.391311
C	0.513116	2.542326	-0.294492
C	4.038691	0.208655	-0.003131
H	0.351767	0.878330	1.608771
H	2.193489	-0.576814	1.481403
H	1.990261	-2.450155	-0.586429
H	-0.762361	-1.258333	1.628125
H	-3.758458	1.198967	-0.832767
H	-4.554394	-0.209232	-0.073648
H	-4.365426	1.315429	0.850586
H	0.140065	3.062614	-1.174946
H	0.074836	2.985022	0.606668
H	1.602009	2.617336	-0.259407
H	4.571196	0.809300	-0.737640
H	4.166655	0.636242	0.996557
H	4.423905	-0.815375	-0.020696

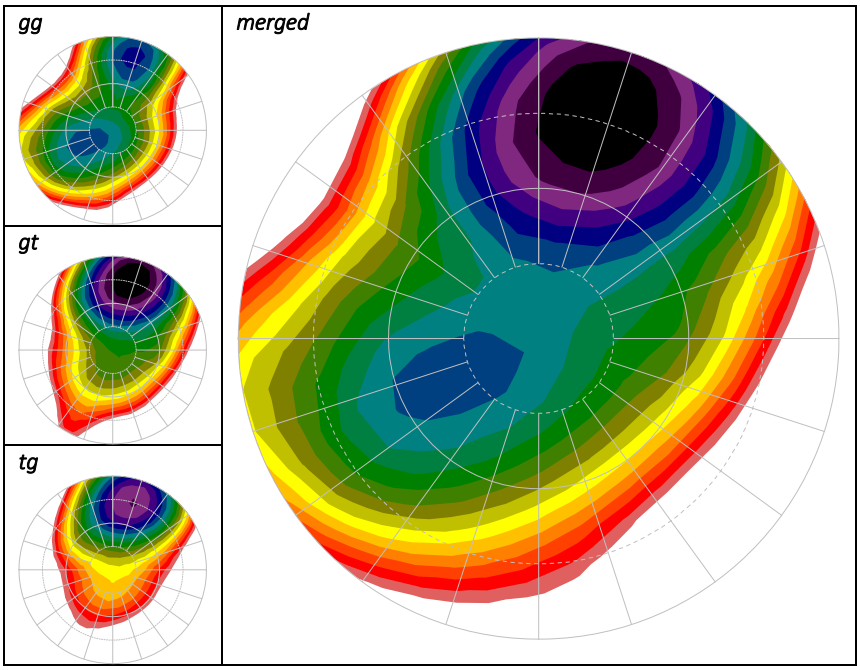
E_3 conformation (4.4 kcal / mol)

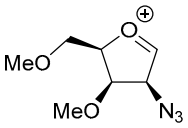
E_{gas}(B3LYP) = -688.648076709 a.u.
E_{solv}(B3LYP) = -688.723410595 a.u.
Zero-point energy correction = 0.211763 a.u.

Atom coordinates

C	-0.487938	0.536141	-1.051056
C	-1.715890	-0.229650	-0.450538
C	-1.341674	-1.651204	-0.722194
O	-0.145123	-1.827794	-1.059810
C	0.615516	-0.543994	-1.104770
C	1.555282	-0.561352	0.105072
O	2.608958	0.195844	-0.153589
C	3.557871	0.369342	0.931483
O	1.332528	-1.179380	1.111436
O	-0.028849	1.604666	-0.290664
O	-1.734704	-0.173346	0.957496
C	-0.845870	2.775782	-0.356509
C	-3.042397	-0.159443	1.559932
H	-0.746064	0.833553	-2.078727
H	-2.668949	0.055782	-0.913513
H	-1.955042	-2.548231	-0.579504
H	1.171468	-0.570538	-2.043575
H	3.061470	0.834416	1.783163
H	3.970766	-0.597211	1.220018
H	4.331343	1.018548	0.530806
H	-0.323688	3.543076	0.212013
H	-0.968513	3.106948	-1.393916
H	-1.829027	2.603303	0.093305
H	-2.870659	-0.038167	2.627650
H	-3.627537	0.681251	1.174300
H	-3.577443	-1.096381	1.380503

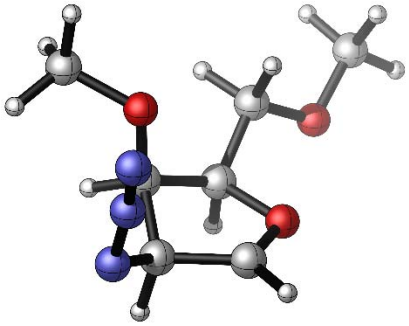
2-N_3-D-lyxose oxocarbenium ion (92)





Local minima

^3E conformation (0.0 kcal / mol)



D1 = 30° P = 18.0°
D3 = 0° τ_m = 31.5

E_{gas}(B3LYP) = -663.664855053 a.u.
E_{solv}(B3LYP) = -663.745117164 a.u.
Zero-point energy correction = 0.200229 a.u.

Atom coordinates

C	-0.339629	0.287244	-0.904115
C	-1.298786	-0.949130	-0.800812
C	-0.558277	-1.824099	0.151728
O	0.657242	-1.559463	0.253371
C	1.021240	-0.372588	-0.668202
C	2.084743	0.432967	0.024907
O	-0.634294	1.206913	0.107903
O	3.273382	-0.321178	0.012165
C	4.348488	0.336751	0.676958
C	-1.144024	2.477900	-0.330785
N	-2.698936	-0.711658	-0.525525
N	-2.988578	-0.195737	0.570252
N	-3.442076	0.248346	1.501918
H	-0.379894	0.724276	-1.908175
H	-1.260778	-1.490724	-1.766888
H	-0.962107	-2.649867	0.751343
H	1.405194	-0.868375	-1.565895
H	2.195030	1.375675	-0.535937
H	1.765972	0.686225	1.044614
H	5.210148	-0.326646	0.614149
H	4.589104	1.291001	0.191615
H	4.107889	0.521087	1.731339
H	-1.338545	3.052307	0.572913
H	-0.404731	2.999516	-0.945907
H	-2.073324	2.354419	-0.895280

$^3T_4$ conformation (1.4 kcal / mol)

E_{gas}(B3LYP) = -663.663724900 a.u.
E_{solv}(B3LYP) = -663.743244896 a.u.
Zero-point energy correction = 0.200449 a.u.

Atom coordinates

C	-0.355770	0.320770	-0.987239
C	-1.353129	-0.895834	-0.887347
C	-0.564656	-1.902273	-0.118786
O	0.624199	-1.591816	0.096198
C	1.001436	-0.342901	-0.723297
C	2.018343	0.438093	0.062950
O	-0.625317	1.272198	0.002821
O	3.224793	-0.288901	0.043066
C	4.259795	0.346004	0.788455
C	-1.309106	2.452078	-0.450275
N	-2.683674	-0.651942	-0.362399
N	-2.770657	-0.232882	0.809641
N	-3.052102	0.134539	1.837003
H	-0.372641	0.747192	-1.996379
H	-1.500926	-1.317518	-1.897987
H	-0.949487	-2.822940	0.338089
H	1.437844	-0.778089	-1.627675
H	2.125857	1.419635	-0.425311
H	1.655839	0.612495	1.084507
H	5.139217	-0.292472	0.713808
H	4.494239	1.335726	0.376497
H	3.978256	0.454363	1.843300
H	-1.436294	3.083067	0.427384
H	-0.709172	2.979087	-1.198635
H	-2.288585	2.203986	-0.870757
H	2.304942	-1.224835	-1.023461
H	0.236451	-1.709478	-2.617959
H	-0.499837	-2.500626	1.167425
H	-2.577077	-1.320556	0.952609
H	-1.529307	-0.303338	1.979482
H	-2.737824	2.020024	-0.526877
H	-3.754627	0.811426	0.303073
H	-2.581890	1.790686	1.234310
H	1.914071	1.660121	2.480603
H	2.534504	-0.010308	2.591237
H	2.844635	0.970846	1.126241

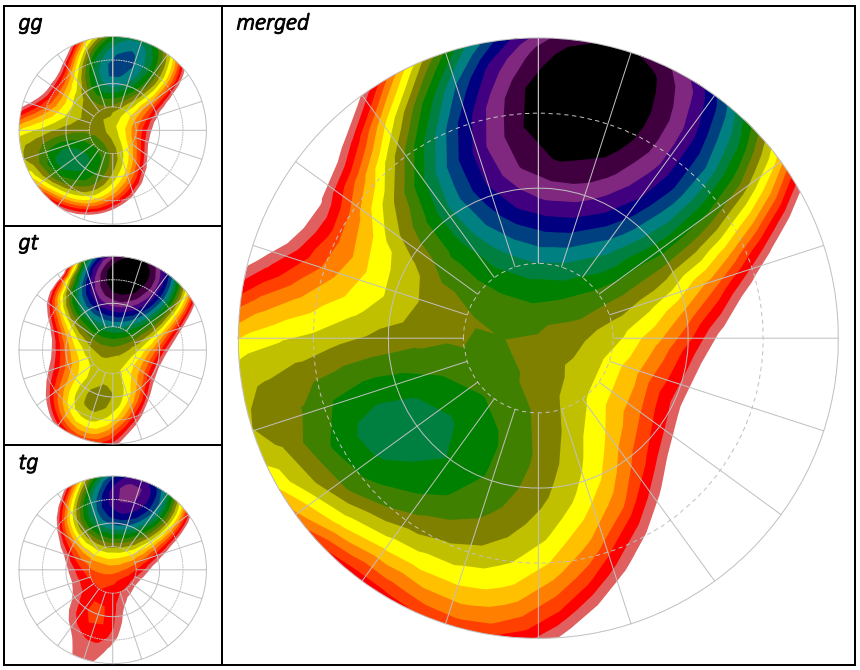
Flat-E_3 conformation (3.2 kcal / mol)

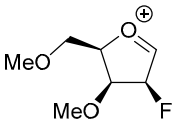
E_{gas}(B3LYP) = -663.665621486 a.u.
E_{solv}(B3LYP) = -663.741970436 a.u.
Zero-point energy correction = 0.201372 a.u.

Atom coordinates

C	0.929958	-0.885596	0.678364
C	1.343314	-0.725075	-0.835727
C	0.292954	-1.516660	-1.539979
O	-0.635547	-1.945372	-0.824964
C	-0.469845	-1.547175	0.634947
C	-1.673734	-0.694804	0.963117
O	0.868153	0.319766	1.376672
O	-1.748274	0.330113	0.001353
C	-2.766929	1.287380	0.278074
C	2.122867	0.750848	1.919807
N	1.506279	0.602227	-1.414921
N	0.669407	1.494602	-1.179682
N	0.062106	2.438911	-1.095393
H	1.635250	-1.583712	1.147173

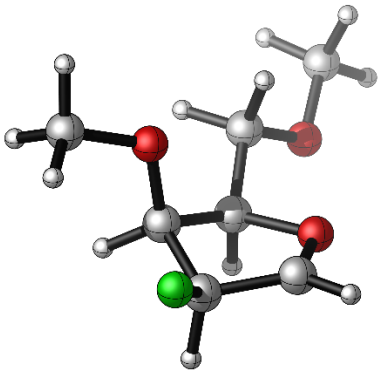
2-F-D-lyxose oxocarbenium ion (93)





Local minima

^{3}E conformation (0.0 kcal / mol)



D1 = 30° P = 18.0°
D3 = 0° τ_m = 31.5

E_{gas}(B3LYP) = -599.301489062 a.u.
E_{solv}(B3LYP) = -599.381342125 a.u.
Zero-point energy correction = 0.189563 a.u.

Atom coordinates

C	0.867450	0.325310	0.639593
C	1.792402	-0.903875	0.400869
C	0.939121	-1.786110	-0.445278
O	-0.276542	-1.524630	-0.377249
C	-0.512411	-0.336932	0.589578
C	-1.659258	0.471401	0.050964
O	0.972970	1.253083	-0.398925
O	-2.836637	-0.276131	0.243969
C	-3.992763	0.377635	-0.272404
C	1.938962	2.296171	-0.190982
F	2.992673	-0.622809	-0.191376
H	1.041572	0.766862	1.629694
H	1.961279	-1.444023	1.354178
H	1.270144	-2.601588	-1.101001
H	-0.772714	-0.837580	1.527867
H	-1.678303	1.420576	0.610743
H	-1.490044	0.713187	-1.006541
H	-4.838708	-0.281174	-0.080436
H	-4.160806	1.339317	0.228575
H	-3.901913	0.546857	-1.352508
H	1.848766	2.962506	-1.046890
H	1.714308	2.847352	0.728361
H	2.953022	1.892818	-0.146054

$^3T_4$ conformation (2.1 kcal / mol)

E_{gas}(B3LYP) = -599.297992637 a.u.
E_{solv}(B3LYP) = -599.377924089 a.u.
Zero-point energy correction = 0.189703 a.u.

Atom coordinates

C	0.878818	0.322230	0.665781
C	1.826736	-0.888341	0.380491
C	0.921211	-1.885382	-0.273017
O	-0.280307	-1.564891	-0.283024
C	-0.510391	-0.329473	0.613499
C	-1.635536	0.474479	0.023409
O	0.963855	1.287217	-0.341650
O	-2.825942	-0.252215	0.219564
C	-3.964337	0.399560	-0.336732
C	1.953667	2.303650	-0.123791
F	2.882337	-0.608390	-0.447758
H	1.064260	0.735596	1.665413
H	2.201904	-1.322575	1.324518
H	1.228675	-2.791187	-0.811294
H	-0.798139	-0.785694	1.565763
H	-1.653749	1.442914	0.547884
H	-1.443020	0.675850	-1.038432
H	-4.822617	-0.240420	-0.135895
H	-4.125985	1.380037	0.128696
H	-3.854783	0.530663	-1.420425
H	1.850243	3.005430	-0.949437
H	1.768624	2.821681	0.823488
H	2.961696	1.881994	-0.127421

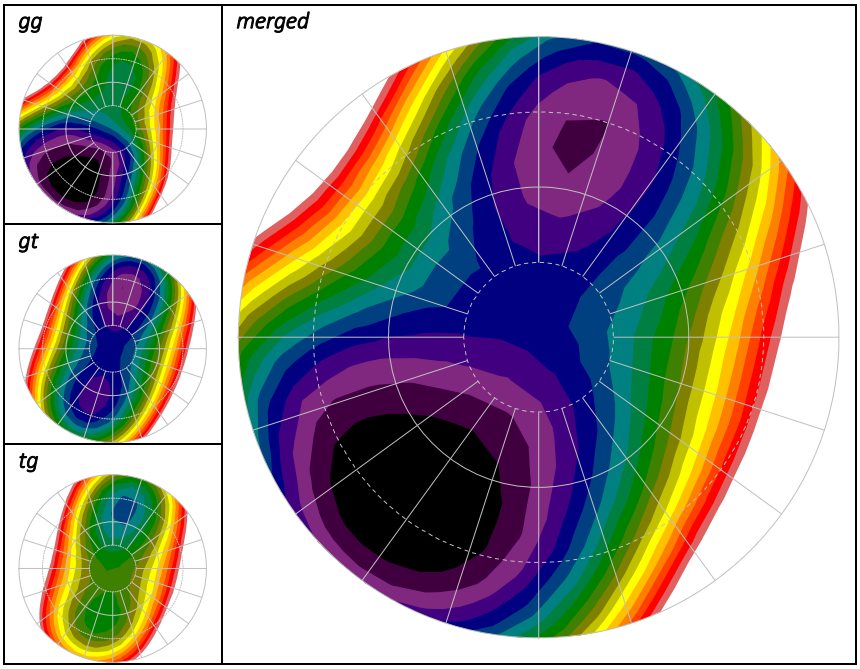
E_3 conformation (4.7 kcal / mol)

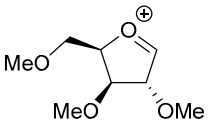
E_{gas}(B3LYP) = -599.296869616 a.u.
E_{solv}(B3LYP) = -599.374149207 a.u.
Zero-point energy correction = 0.190376 a.u.

Atom coordinates

C	1.060217	0.186001	-0.648366
C	1.102045	1.002463	0.677423
C	0.081627	2.077595	0.394057
O	-0.634747	1.869498	-0.602329
C	-0.290629	0.554208	-1.295810
C	-1.459964	-0.370685	-1.039448
O	1.139018	-1.195005	-0.498111
O	-1.677724	-0.407894	0.348395
C	-2.462142	-1.514048	0.781639
C	2.443430	-1.681391	-0.165511
F	0.680478	0.304462	1.787986
H	1.868425	0.577317	-1.286948
H	2.084676	1.440011	0.891562
H	-0.124799	2.970799	0.996735
H	-0.212082	0.828207	-2.350181
H	-2.344741	-0.009337	-1.581629
H	-1.173756	-1.350779	-1.445389
H	-2.548098	-1.430857	1.864272
H	-3.463729	-1.488914	0.335231
H	-1.974383	-2.462235	0.527098
H	2.375245	-2.767638	-0.181872
H	3.182984	-1.349244	-0.903027
H	2.746082	-1.355141	0.834745

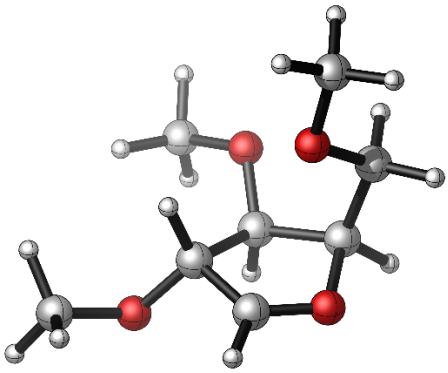
D-xylose oxocarbenium ion (94)





Local minima

$^4T_3$ conformation (0.0 kcal / mol)



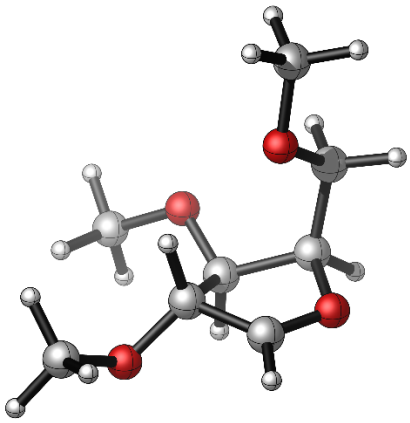
D1 = -20° P = 219.6°
D3 = 10° τ_m = 26.0

E_{gas}(B3LYP) = -614.607621849 a.u.
E_{solv}(B3LYP) = -614.674769993 a.u.
Zero-point energy correction = 0.230333 a.u.

Atom coordinates

C	0.881193	-0.012355	-1.359097
C	-0.371466	0.667528	-0.763149
C	-0.999319	-0.437608	0.135164
C	-0.374775	-1.671954	-0.438404
O	0.510295	-1.476907	-1.302917
C	2.147010	0.126518	-0.538657
O	0.002772	1.839263	-0.109593
O	-2.391460	-0.524778	-0.039076
O	1.872995	-0.383754	0.747636
C	2.976684	-0.290554	1.645905
C	-3.121573	-0.988068	1.108034
C	-1.081461	2.731935	0.161788
H	1.051303	0.195995	-2.416254
H	-1.090864	0.868287	-1.572718
H	-0.692889	-0.298764	1.179375
H	-0.682794	-2.710063	-0.268146
H	2.963892	-0.426611	-1.022120
H	2.404656	1.193697	-0.514041
H	2.655733	-0.734095	2.587445
H	3.842441	-0.841935	1.260407
H	3.256816	0.755802	1.812430
H	-4.173846	-0.941211	0.834206
H	-2.858626	-2.020361	1.361385
H	-2.930195	-0.339943	1.969922
H	-0.636970	3.636007	0.574334
H	-1.626566	2.973883	-0.757407
H	-1.776668	2.306077	0.893285

^4E conformation (0.4 kcal / mol)



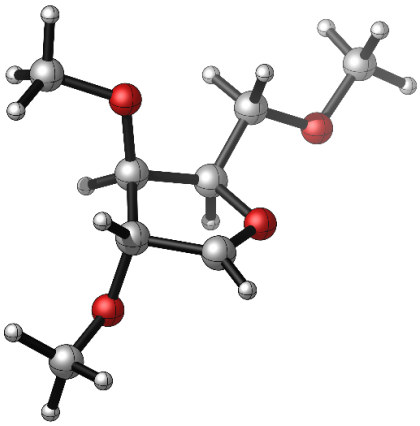
D1 = -20° P = 232.0°
D3 = 20° τ_m = 33.3

E_{gas}(B3LYP) = -614.607890375 a.u.
E_{solv}(B3LYP) = -614.674459414 a.u.
Zero-point energy correction = 0.230535 a.u.

Atom coordinates

C	0.875110	0.283383	-1.334999
C	-0.430122	0.780922	-0.677700
C	-0.920481	-0.461497	0.122583
C	-0.171045	-1.561595	-0.572071
O	0.580556	-1.183781	-1.507563
C	2.111824	0.350561	-0.460106
O	-0.157978	1.920723	0.075504
O	-2.285739	-0.718104	-0.114563
O	1.824947	-0.364762	0.722985
C	2.958468	-0.575629	1.566732
C	-2.979105	-1.373756	0.959678
C	-1.317503	2.673549	0.442250
H	1.054589	0.670828	-2.338283
H	-1.176743	0.976928	-1.462967
H	-0.664708	-0.379241	1.182982
H	-0.350960	-2.638461	-0.483236
H	2.964913	-0.088094	-0.994394
H	2.318565	1.409479	-0.258437
H	2.611772	-1.159013	2.418379
H	3.741257	-1.129203	1.035981
H	3.360741	0.380208	1.919059
H	-4.018281	-1.449332	0.645233
H	-2.581123	-2.377437	1.141236
H	-2.907260	-0.780240	1.877091
H	-0.955026	3.572071	0.938632
H	-1.898934	2.950257	-0.444294
H	-1.955971	2.113024	1.133920

^3E conformation (1.0 kcal / mol)



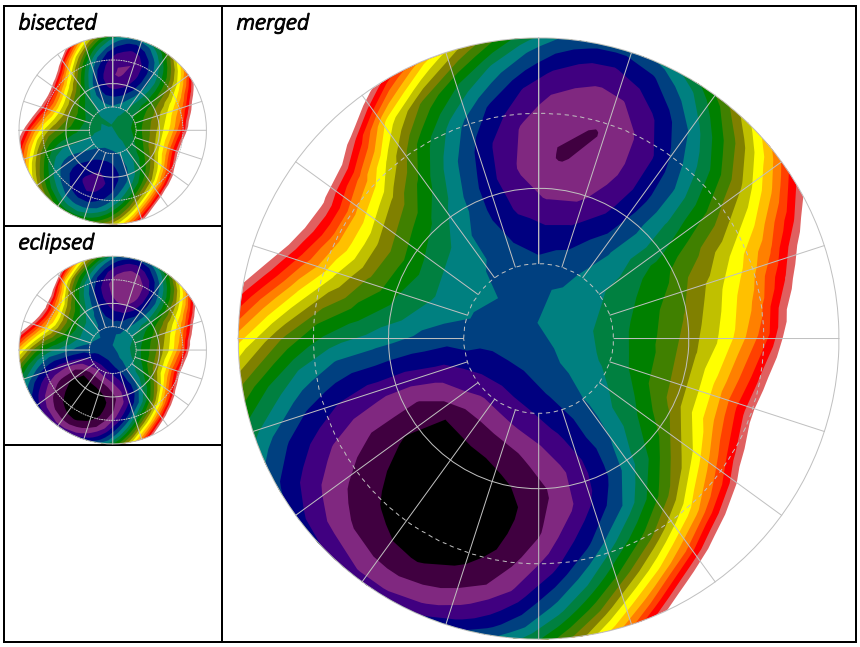
D1 = 20° P = 18.0°
D3 = 0° τ_m = 21.0

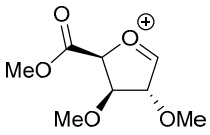
E_{gas}(B3LYP) = -614.601682902 a.u.
E_{solv}(B3LYP) = -614.672404985 a.u.
Zero-point energy correction = 0.229832 a.u.

Atom coordinates

C	0.659420	-0.310701	-0.428394
C	-0.516122	0.668304	-0.390786
C	-1.648471	-0.136073	0.299345
C	-0.893347	-1.220150	1.006663
O	0.298920	-1.340410	0.658364
C	2.031748	0.233231	-0.131540
O	-0.147471	1.784189	0.383694
O	-2.383963	-0.889706	-0.653222
O	2.959058	-0.806788	-0.340817
C	4.298636	-0.406835	-0.069354
C	-3.782247	-1.072330	-0.359535
C	-0.918771	2.961124	0.125762
H	0.668855	-0.932657	-1.328211
H	-0.819355	0.941160	-1.410635
H	-2.273250	0.472074	0.961394
H	-1.292958	-1.952197	1.718004
H	2.199634	1.076888	-0.819000
H	2.077514	0.625862	0.892218
H	4.930717	-1.274543	-0.254554
H	4.608292	0.414489	-0.728114
H	4.413681	-0.090539	0.975045
H	-4.188191	-1.633666	-1.198822
H	-3.928046	-1.640207	0.563860
H	-4.279163	-0.100457	-0.281638
H	-0.498182	3.746086	0.751927
H	-0.843385	3.249153	-0.928445
H	-1.973575	2.820858	0.389844

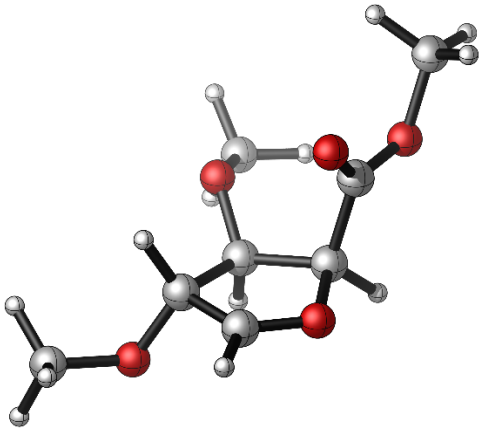
4-CO_2Me-D-xylose oxocarbenium ion (95)





Local minima

Flat-^4E conformation (0.0 kcal / mol)



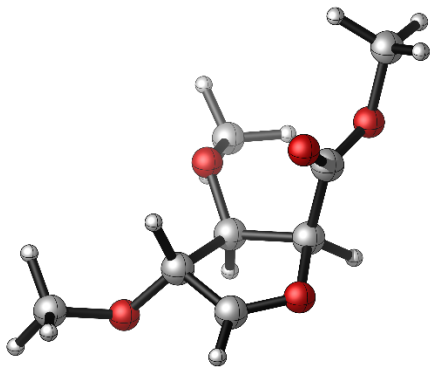
D1 = -10° P = 232.4°
D3 = 10° τ_m = 16.5

E_{gas}(B3LYP) = -688.655714009 a.u.
E_{solv}(B3LYP) = -688.727673410 a.u.
Zero-point energy correction = 0.211641 a.u.

Atom coordinates

C	-0.514223	0.628408	-0.471114
C	-1.655601	-0.128388	0.251050
C	-1.384226	-1.557501	-0.086913
O	-0.373077	-1.756018	-0.801912
C	0.443258	-0.517368	-0.937048
C	1.602347	-0.691461	0.050679
O	2.679300	-0.068653	-0.394027
C	3.837288	-0.069546	0.488264
O	1.481152	-1.287770	1.088742
O	0.083693	1.539659	0.402156
O	-2.913913	0.184243	-0.290031
C	0.686843	2.677403	-0.236156
C	-3.998475	0.225692	0.655665
H	-0.940308	1.119903	-1.356260
H	-1.584821	0.041595	1.338352
H	-2.024786	-2.422209	0.121577
H	0.765444	-0.490028	-1.978686
H	4.589500	0.515818	-0.032647
H	3.573787	0.387692	1.441635
H	4.176844	-1.093340	0.642676
H	1.052757	3.313133	0.568048
H	1.523944	2.379901	-0.874414
H	-0.055928	3.222412	-0.827338
H	-4.873279	0.538404	0.089027
H	-4.182330	-0.759162	1.095916
H	-3.781325	0.950751	1.446139

E$_3$ conformation (0.2 kcal / mol)



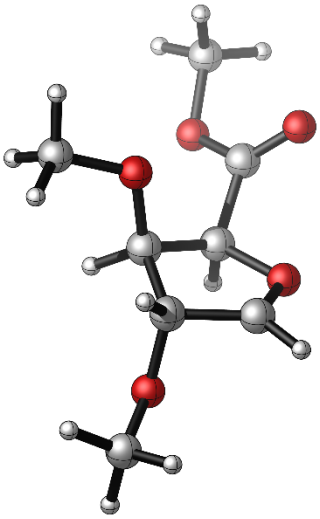
D1 = -20° P = 198.2°
D3 = 0° τ_m = 21.0

E_{gas}(B3LYP) = -688.655814018 a.u.
E_{solv}(B3LYP) = -688.728454663 a.u.
Zero-point energy correction = 0.211566 a.u.

Atom coordinates

C	-0.521804	0.576244	-0.571132
C	-1.625765	-0.221404	0.165242
C	-1.394304	-1.609856	-0.325455
O	-0.302650	-1.793302	-0.914018
C	0.502664	-0.534663	-0.970215
C	1.597268	-0.687457	0.087441
O	2.672496	-0.008278	-0.272305
C	3.768857	0.022090	0.684510
O	1.437996	-1.315580	1.101587
O	0.000293	1.552953	0.274350
O	-2.906618	0.228649	-0.158964
C	0.578707	2.684175	-0.397501
C	-3.846869	0.263872	0.928581
H	-0.962189	1.004920	-1.482640
H	-1.410149	-0.206618	1.251742
H	-2.074052	-2.467608	-0.253205
H	0.895805	-0.493026	-1.987019
H	4.530372	0.643142	0.221689
H	3.425405	0.455961	1.623294
H	4.137238	-0.989976	0.849673
H	0.875745	3.378504	0.386326
H	1.458586	2.394509	-0.979324
H	-0.160080	3.159877	-1.050177
H	-4.754294	0.706773	0.522950
H	-4.066145	-0.742896	1.297996
H	-3.460903	0.882895	1.744665

^3E conformation (1.1 kcal / mol)



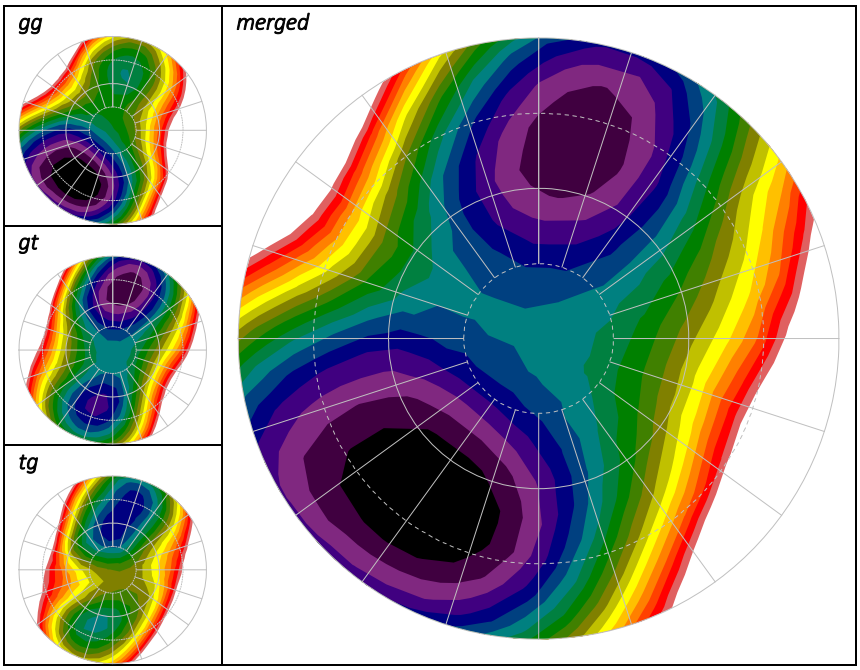
D1 = 20° P = 18.0°
D3 = 0° τ_m = 21.0

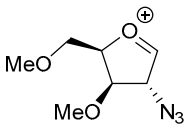
E_{gas}(B3LYP) = -688.653100738 a.u.
E_{solv}(B3LYP) = -688.727214809 a.u.
Zero-point energy correction = 0.211584 a.u.

Atom coordinates

C	0.428301	0.568540	0.286601
C	1.793532	0.091466	-0.270539
C	1.464650	-1.261900	-0.817833
O	0.353747	-1.713858	-0.456876
C	-0.355232	-0.743042	0.448897
C	-1.809692	-0.680209	-0.004220
O	-2.504852	-0.023559	0.913856
C	-3.911583	0.193767	0.623688
O	-2.221912	-1.158570	-1.024618
O	-0.248891	1.360301	-0.656829
O	2.667102	-0.273015	0.788284
C	0.026173	2.762675	-0.562769
C	4.067879	-0.016640	0.560345
H	0.561023	1.066600	1.255645
H	2.234631	0.777311	-1.000956
H	2.109187	-1.921342	-1.410393
H	-0.261316	-1.190982	1.443414
H	-4.295085	0.746372	1.476772
H	-4.012896	0.773151	-0.293902
H	-4.419612	-0.764821	0.520017
H	-0.596294	3.245419	-1.313903
H	-0.233475	3.139234	0.432163
H	1.078756	2.982407	-0.775062
H	4.574618	-0.330105	1.470787
H	4.447346	-0.593369	-0.287687
H	4.227397	1.051789	0.387560

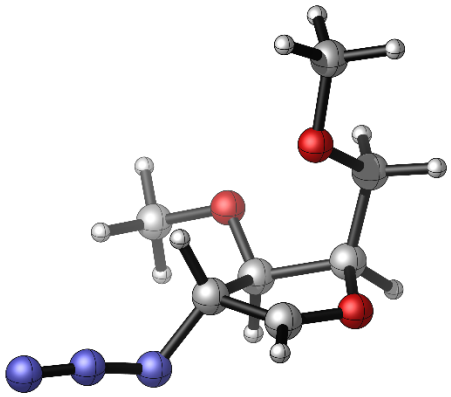
2-N_3-D-xylose oxocarbenium ion (96)





Local minima

$^4T_3$ conformation (0.0 kcal / mol)



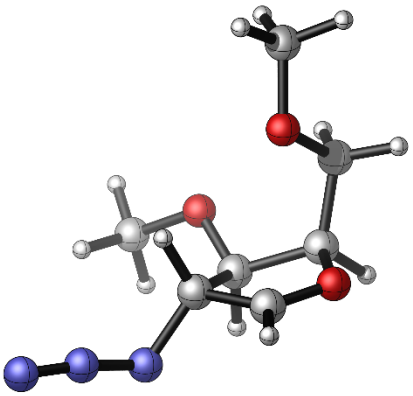
D1 = -20° P = 219.4°
D3 = 10° τ_m = 25.9

E_{gas}(B3LYP) = -663.672575796 a.u.
E_{solv}(B3LYP) = -663.746133264 a.u.
Zero-point energy correction = 0.200985 a.u.

Atom coordinates

C	-0.041453	0.798806	-0.791994
C	-0.849177	-0.329530	-0.076754
C	-0.258271	-1.554043	-0.696648
O	0.730880	-1.360402	-1.438140
C	1.215996	0.066837	-1.312898
C	2.388390	0.019475	-0.355432
O	0.350499	1.866790	0.008889
O	1.934881	-0.576338	0.839526
C	2.942625	-0.676092	1.844435
C	-0.678956	2.826469	0.267570
N	-2.277747	-0.279772	-0.419110
N	-3.069327	-0.622868	0.474544
N	-3.900652	-0.890668	1.187126
H	-0.640542	1.136541	-1.651871
H	-0.653911	-0.331525	1.004890
H	-0.654517	-2.574534	-0.634292
H	1.519236	0.353038	-2.321003
H	3.208596	-0.557283	-0.804459
H	2.723635	1.053675	-0.200662
H	3.793481	-1.267868	1.486972
H	3.291596	0.317934	2.146102
H	2.487651	-1.175624	2.698584
H	-0.202479	3.647214	0.800779
H	-1.111841	3.195731	-0.668682
H	-1.471823	2.403929	0.893858

E$_3$ conformation (0.1 kcal / mol)



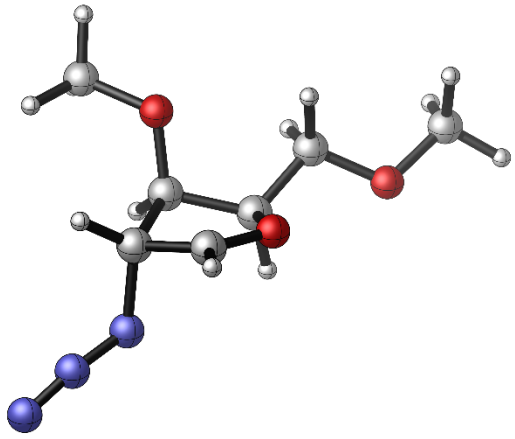
D1 = -20° P = 198.2°
D3 = 0° τ_m = 21.0

E_{gas}(B3LYP) = -663.670727128 a.u.
E_{solv}(B3LYP) = -663.745199693 a.u.
Zero-point energy correction = 0.200744 a.u.

Atom coordinates

C	-0.038726	0.639228	-0.870798
C	-0.893499	-0.389496	-0.065386
C	-0.339172	-1.685072	-0.551675
O	0.732407	-1.608925	-1.187497
C	1.206555	-0.171475	-1.303307
C	2.410207	-0.057994	-0.394077
O	0.363881	1.770502	-0.167414
O	2.006374	-0.475020	0.890863
C	2.999077	-0.267576	1.892120
C	-0.624056	2.802108	-0.076837
N	-2.321312	-0.291038	-0.386047
N	-3.112438	-0.468274	0.553747
N	-3.944660	-0.590131	1.304573
H	-0.617268	0.909480	-1.767656
H	-0.675094	-0.314709	1.012336
H	-0.780895	-2.679804	-0.415156
H	1.473715	-0.058840	-2.355545
H	3.227328	-0.682843	-0.780378
H	2.730160	0.992404	-0.408329
H	3.917309	-0.818255	1.654999
H	3.232055	0.798461	1.996803
H	2.586367	-0.641821	2.828104
H	-0.126426	3.660062	0.371902
H	-0.999540	3.071015	-1.070319
H	-1.462450	2.500160	0.559465

^{3}*E* conformation (0.8 kcal / mol)



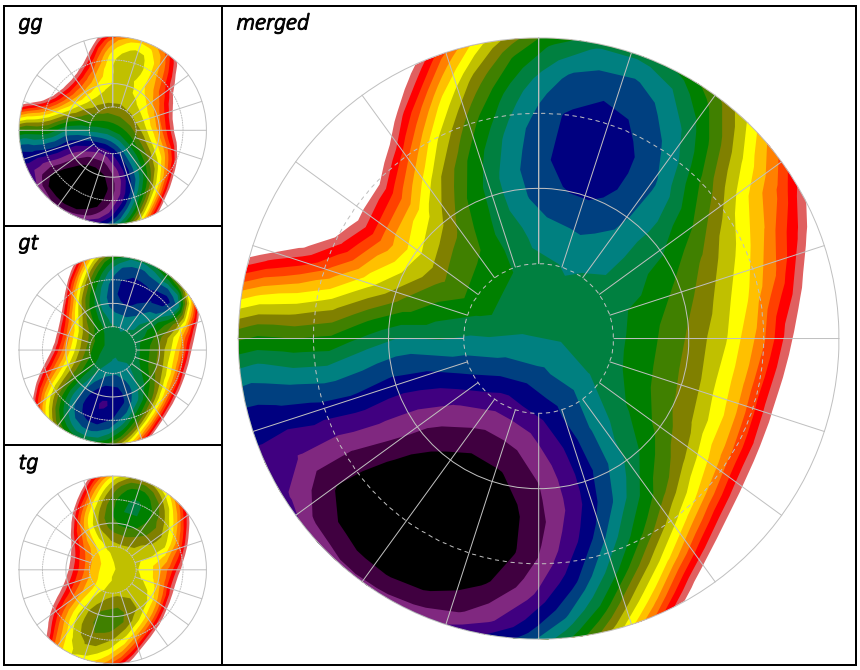
D1 = 30° P = 18.0°
D3 = 0° τ_m = 31.5

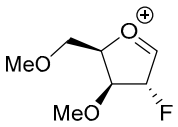
E_{gas}(B3LYP) = -663.668124678 a.u.
E_{solv}(B3LYP) = -663.744734611 a.u.
Zero-point energy correction = 0.200464 a.u.

Atom coordinates

C	-0.257663	0.787467	-0.397852
C	-1.473068	0.143169	0.319603
C	-0.784806	-0.781987	1.281214
O	0.395694	-1.050669	0.976938
C	0.786465	-0.321499	-0.336293
C	2.233064	0.076953	-0.237673
O	0.215485	1.886627	0.335699
O	3.008962	-1.094681	-0.327581
C	4.405366	-0.837724	-0.212139
C	-0.396418	3.138259	0.001508
N	-2.162775	-0.808380	-0.578041
N	-3.389117	-0.930618	-0.411536
N	-4.496662	-1.131738	-0.391989
H	-0.502595	1.034259	-1.439991
H	-2.145290	0.859249	0.802504
H	-1.224128	-1.284721	2.151102
H	0.631837	-1.100650	-1.088637
H	2.434620	0.767557	-1.072855
H	2.415969	0.623793	0.695986
H	4.754664	-0.179232	-1.017485
H	4.644829	-0.378730	0.755223
H	4.910107	-1.799958	-0.289316
H	0.091102	3.889464	0.620165
H	-0.239968	3.372200	-1.056740
H	-1.470036	3.133875	0.220345

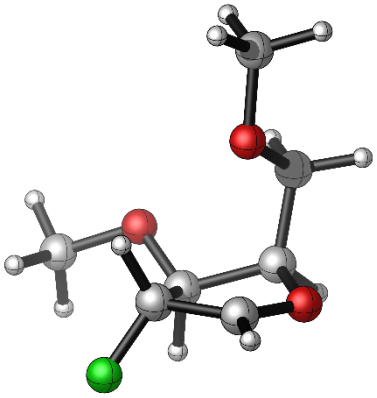
2-F-D-xylose oxocarbenium ion (97)





Local minima

$^4T_3$ conformation (0.0 kcal / mol)



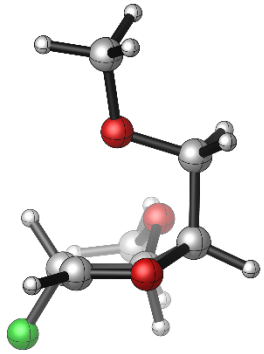
D1 = -20° P = 219.4°
D3 = 10° τ_m = 25.9

E_{gas}(B3LYP) = -599.307105502 a.u.
E_{solv}(B3LYP) = -599.381056097 a.u.
Zero-point energy correction = 0.190330 a.u.

Atom coordinates

C	0.917655	0.195379	0.570953
C	0.996466	-0.739495	-0.660243
C	0.146983	-1.897360	-0.232196
O	-0.459013	-1.735055	0.846517
C	-0.352082	-0.295948	1.307479
C	-1.641511	0.362047	0.859765
O	0.796026	1.553428	0.296221
O	-1.741616	0.160259	-0.532325
C	-2.894333	0.761682	-1.121966
C	2.027471	2.187020	-0.069104
F	2.271718	-1.212167	-0.920845
H	1.799305	-0.019133	1.197499
H	0.587110	-0.274915	-1.565006
H	0.082144	-2.877750	-0.719766
H	-0.261564	-0.349473	2.393109
H	-2.491963	-0.083426	1.393074
H	-1.571105	1.426222	1.120989
H	-2.870476	1.849922	-0.997933
H	-2.868880	0.516060	-2.182542
H	-3.812946	0.362710	-0.676719
H	1.800659	3.243993	-0.194863
H	2.777643	2.060366	0.719422
H	2.417528	1.785916	-1.011081

^4E conformation (0.0 kcal / mol)



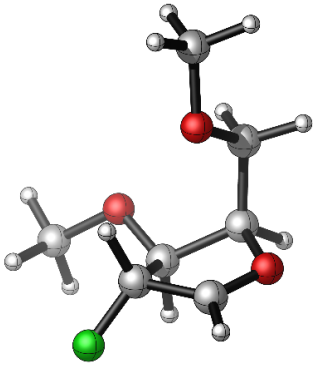
D1 = -20° P = 232.8°
D3 = 20° τ_m = 33.1

E_{gas}(B3LYP) = -599.307199314 a.u.
E_{solv}(B3LYP) = -599.380553495 a.u.
Zero-point energy correction = 0.190433 a.u.

Atom coordinates

C	-0.990414	-0.133978	0.533723
C	-0.792302	0.857461	-0.641124
C	0.262317	1.775236	-0.087064
O	0.654390	1.482048	1.068168
C	0.312861	0.043386	1.347593
C	1.501398	-0.738183	0.815130
O	-1.133592	-1.471371	0.182298
O	1.650667	-0.365167	-0.539381
C	2.894976	-0.754103	-1.132145
C	-2.450825	-1.822613	-0.258969
F	-1.910896	1.644314	-0.884392
H	-1.838507	0.233352	1.135011
H	-0.481342	0.368354	-1.568162
H	0.581016	2.734491	-0.512764
H	0.197296	-0.037737	2.428860
H	2.396728	-0.493996	1.400640
H	1.273539	-1.805970	0.921258
H	2.985388	-1.844743	-1.145502
H	2.884761	-0.376459	-2.153181
H	3.737187	-0.319184	-0.583726
H	-2.435143	-2.895534	-0.440767
H	-3.192038	-1.587830	0.512827
H	-2.710609	-1.300900	-1.186498

E_3 conformation (0.1 kcal / mol)



D1 = -30° P = 198.1°
D3 = 0° τ_m = 31.6

E_{gas}(B3LYP) = -599.306785301 a.u.
E_{solv}(B3LYP) = -599.381040096 a.u.
Zero-point energy correction = 0.190108 a.u.

Atom coordinates

C	0.924546	0.162361	0.576201
C	0.940381	-0.769935	-0.660921
C	0.226597	-1.964714	-0.123603
O	-0.467862	-1.738179	0.889452
C	-0.379029	-0.267318	1.289294
C	-1.653559	0.399737	0.829152
O	0.872820	1.524206	0.308555
O	-1.783625	0.189950	-0.558513
C	-2.948496	0.798706	-1.115456
C	2.139850	2.115706	-0.009268
F	2.205465	-1.117246	-1.088144
H	1.790090	-0.105607	1.204710
H	0.365492	-0.346181	-1.494489
H	0.270565	-2.992430	-0.506254
H	-0.307691	-0.290155	2.378275
H	-2.506053	-0.021493	1.379864
H	-1.562773	1.465457	1.082467
H	-2.915823	1.887159	-0.992598
H	-2.955199	0.552840	-2.176273
H	-3.856970	0.405948	-0.644145
H	1.958533	3.184021	-0.110234
H	2.862181	1.937499	0.794871
H	2.536058	1.723081	-0.951248

^3E conformation (2.3 kcal / mol)

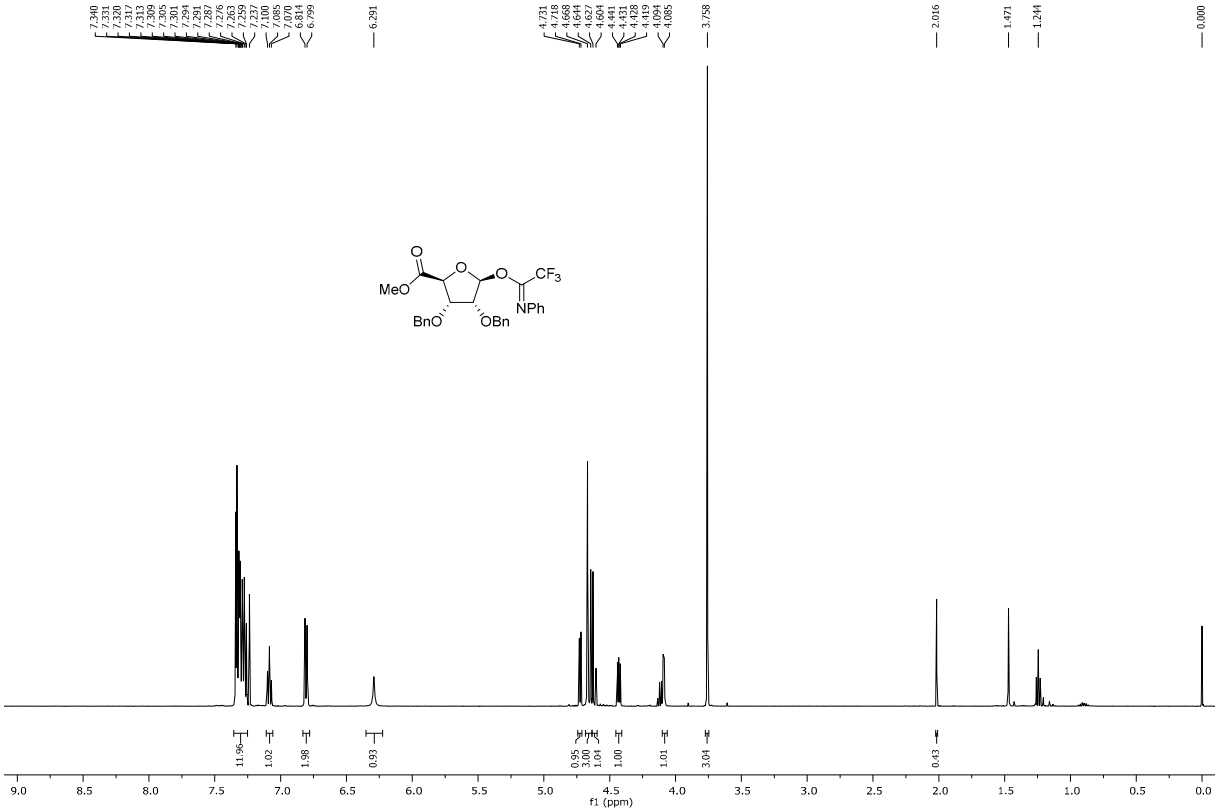
E_{gas}(B3LYP) = -599.298277566 a.u.
E_{solv}(B3LYP) = -599.376251453 a.u.
Zero-point energy correction = 0.189647 a.u.

Atom coordinates

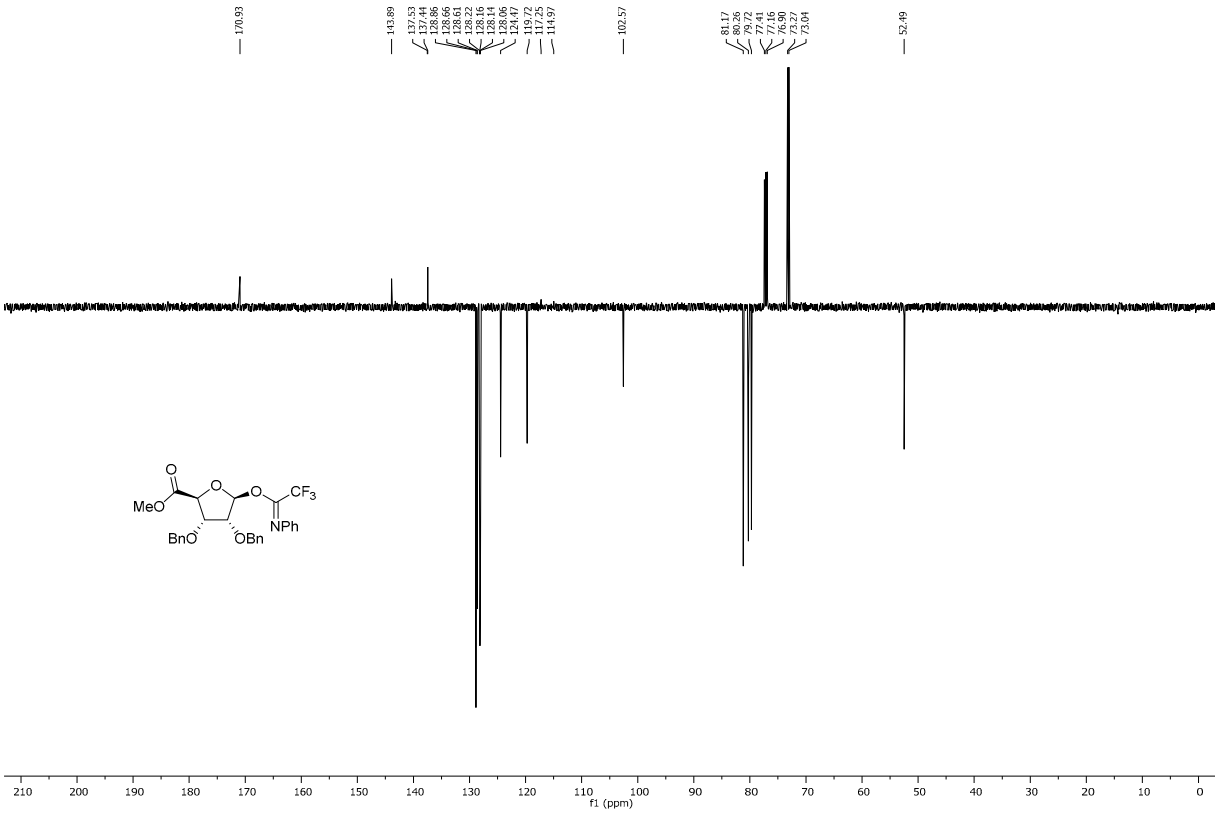
C	-0.959849	0.405511	-0.439196
C	-1.937987	-0.623413	0.171626
C	-1.010937	-1.592675	0.867406
O	0.183398	-1.468749	0.557913
C	0.380988	-0.326921	-0.478363
C	1.616051	0.440618	-0.093043
O	-0.839123	1.522802	0.405515
O	2.724560	-0.397966	-0.313852
C	3.958374	0.216754	0.047600
C	-1.808927	2.550954	0.167033
F	-2.574000	-1.392106	-0.798088
H	-1.280088	0.668835	-1.457644
H	-2.685227	-0.189656	0.842895
H	-1.293805	-2.399502	1.555856
H	0.537586	-0.897483	-1.399036
H	1.643062	1.338857	-0.730424
H	1.551434	0.777047	0.949725
H	3.972233	0.479222	1.112727
H	4.743148	-0.510995	-0.154782
H	4.139290	1.120761	-0.547306
H	-1.576883	3.354446	0.863580
H	-1.733233	2.918209	-0.861908
H	-2.828477	2.195543	0.354120

Methyl (2,3-di-*O*-benzyl-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-β-D-ribofuranosyl uronate) (1β). [*T* =328 K]

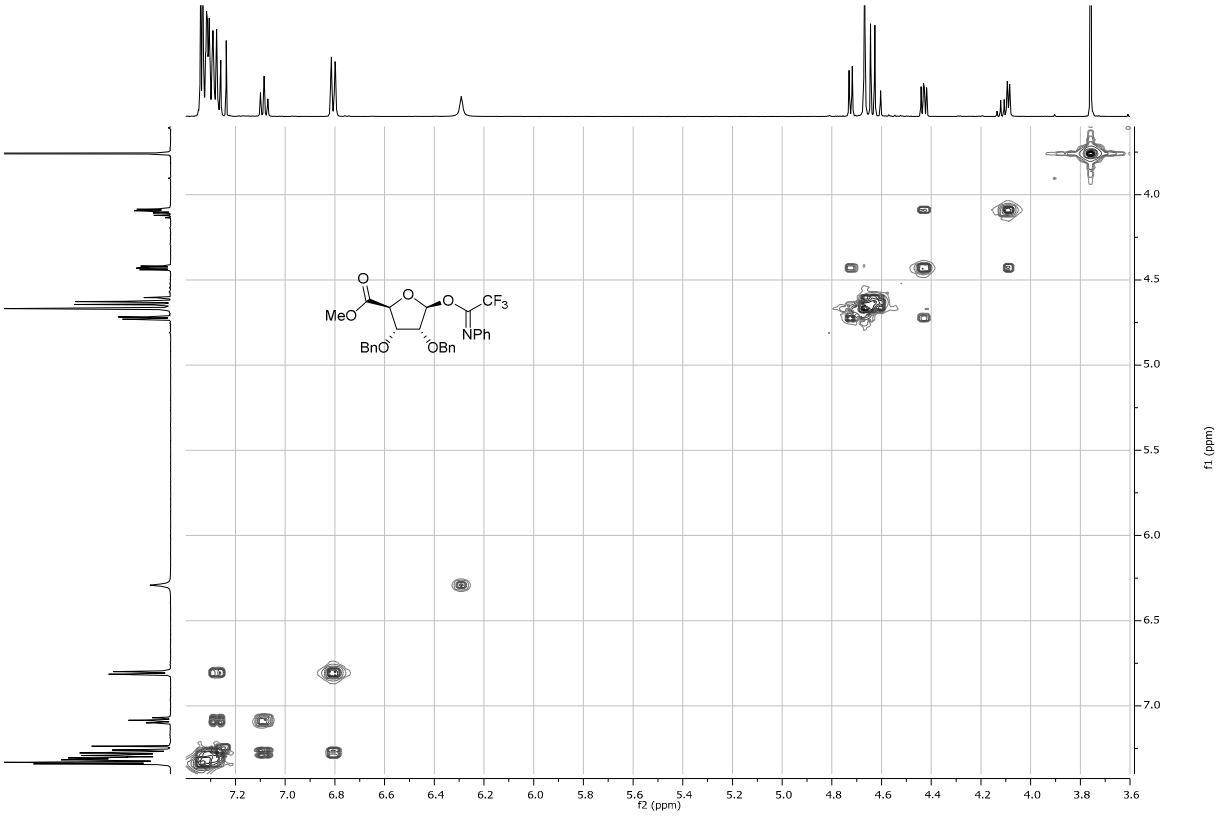
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **1β**



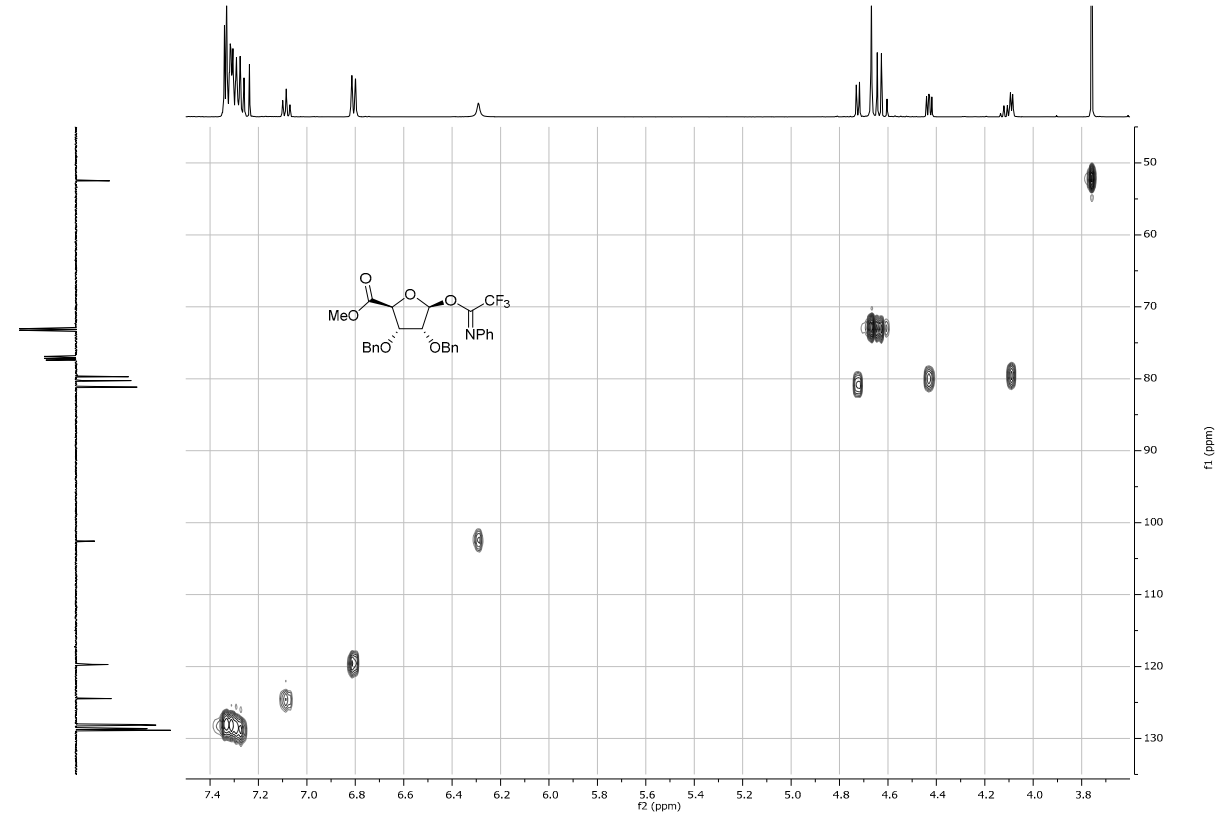
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **1β**



^{1}H-^{1}H COSY of compound **1β**

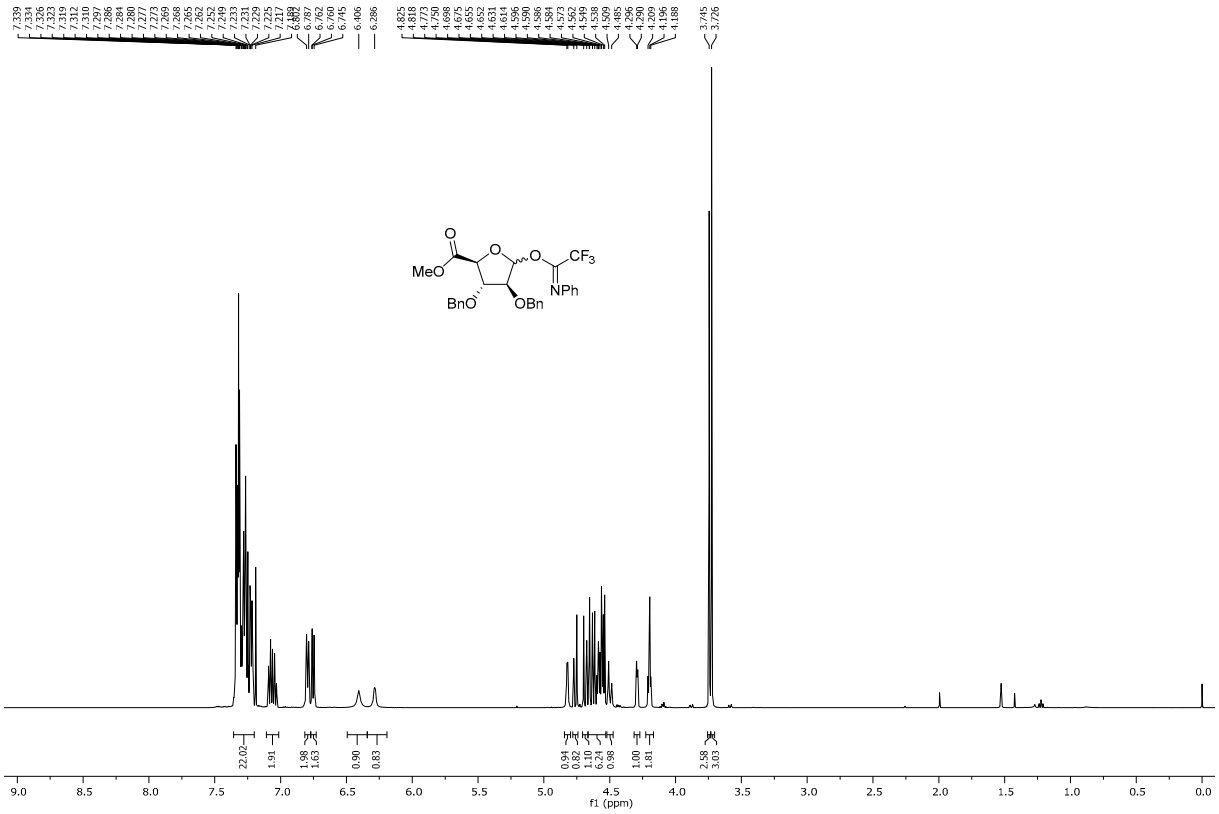


^{1}H-^{13}C HSQC of compound **1β**

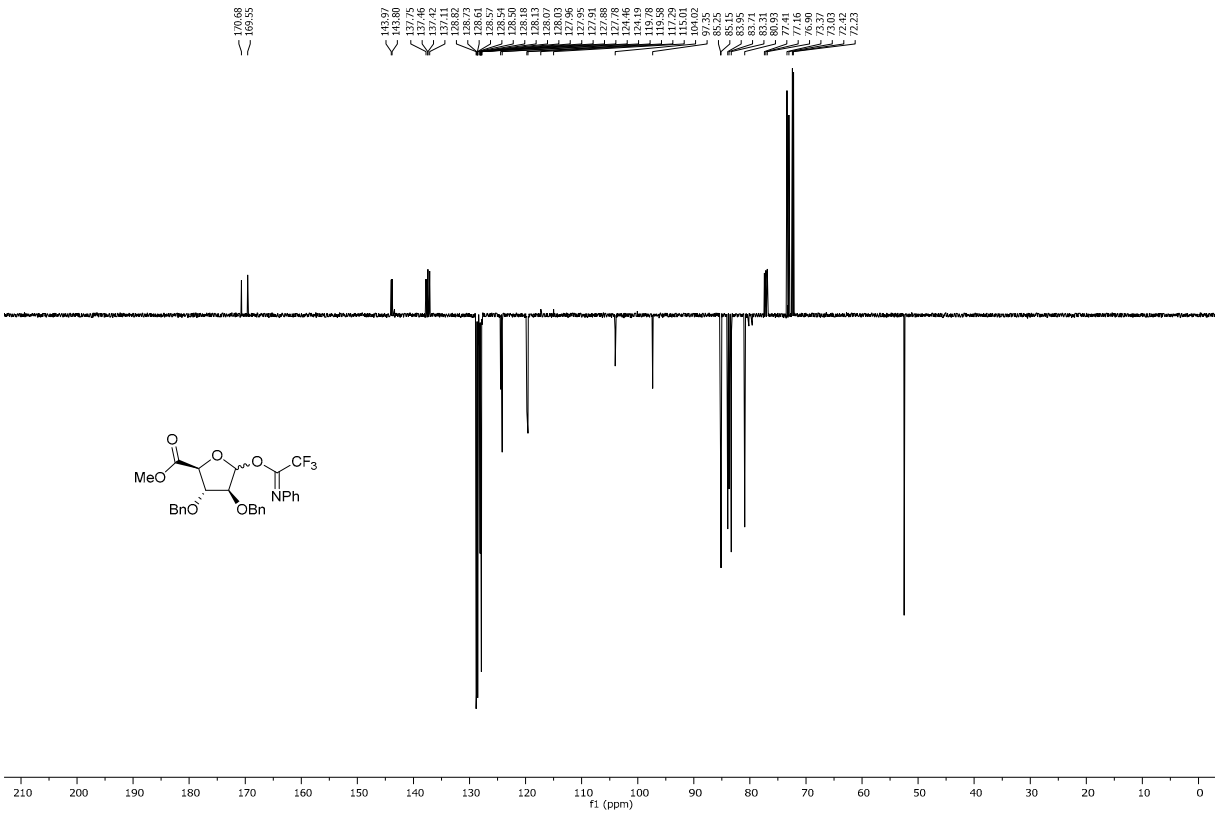


Methyl (2,3-di-*O*-benzyl-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-arabinofuranosyl uronate) (2) [*T* = 323 K]

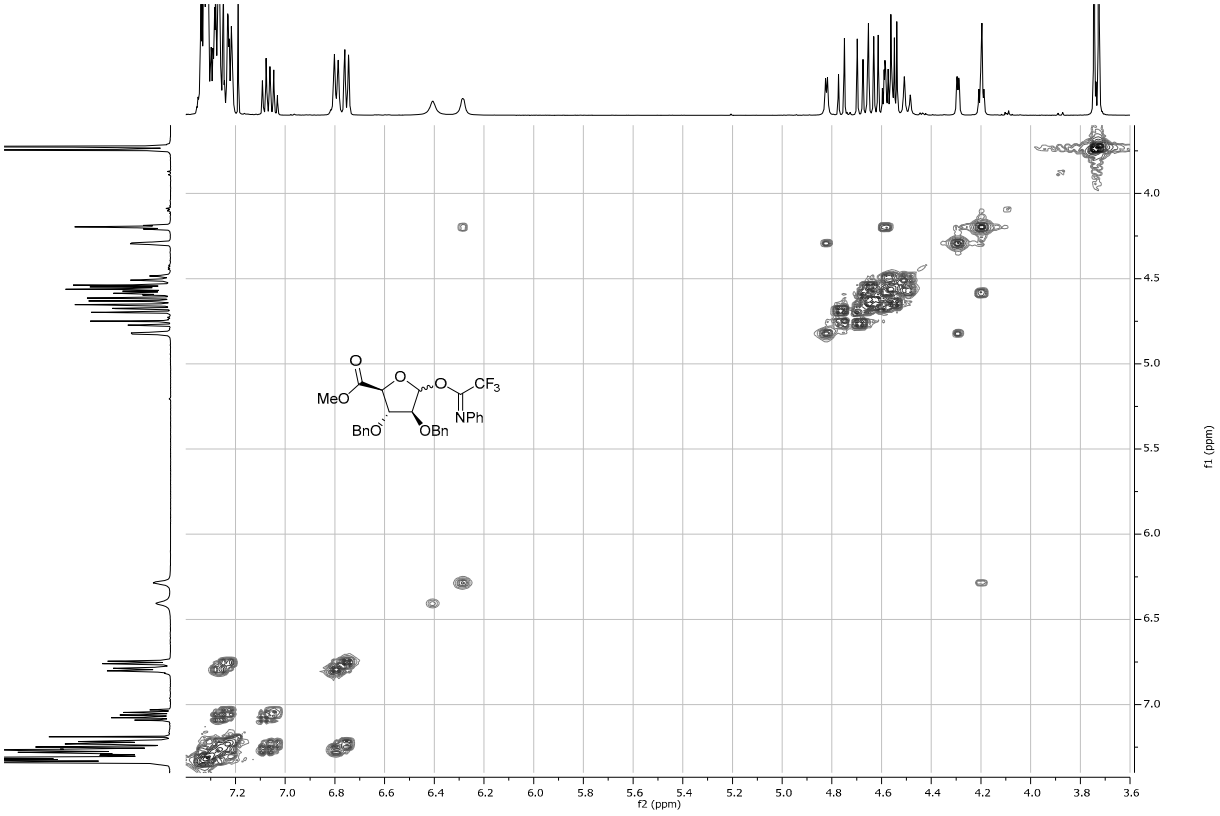
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **2**



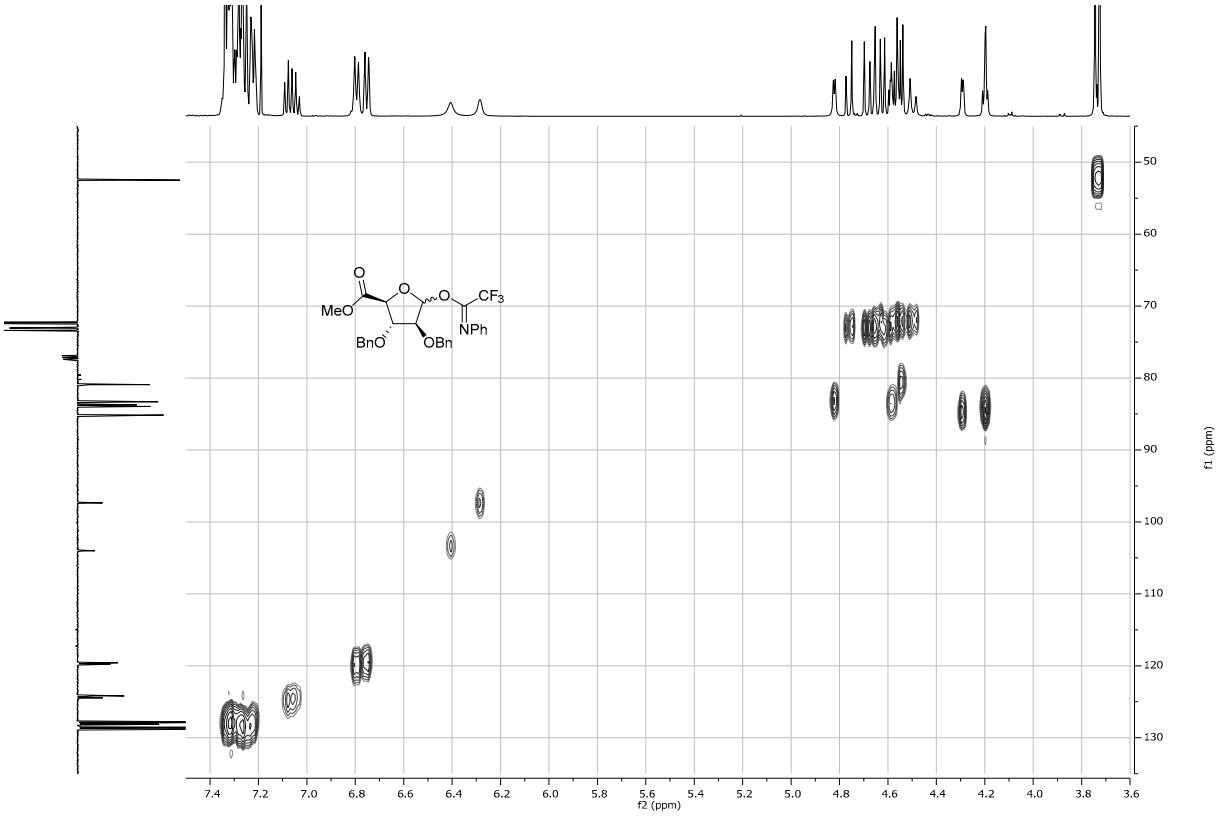
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **2**



^{1}H-^{1}H COSY of compound **2**

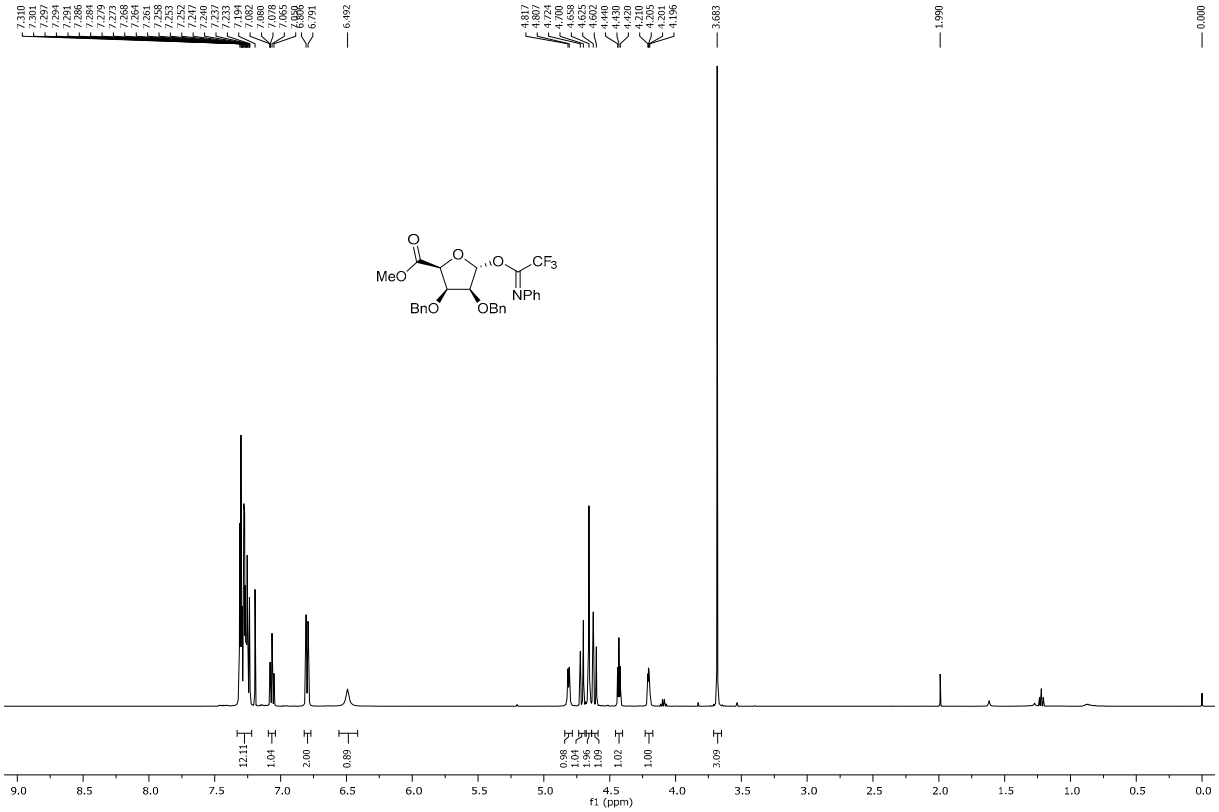


^{1}H-^{13}C HSQC of compound **2**

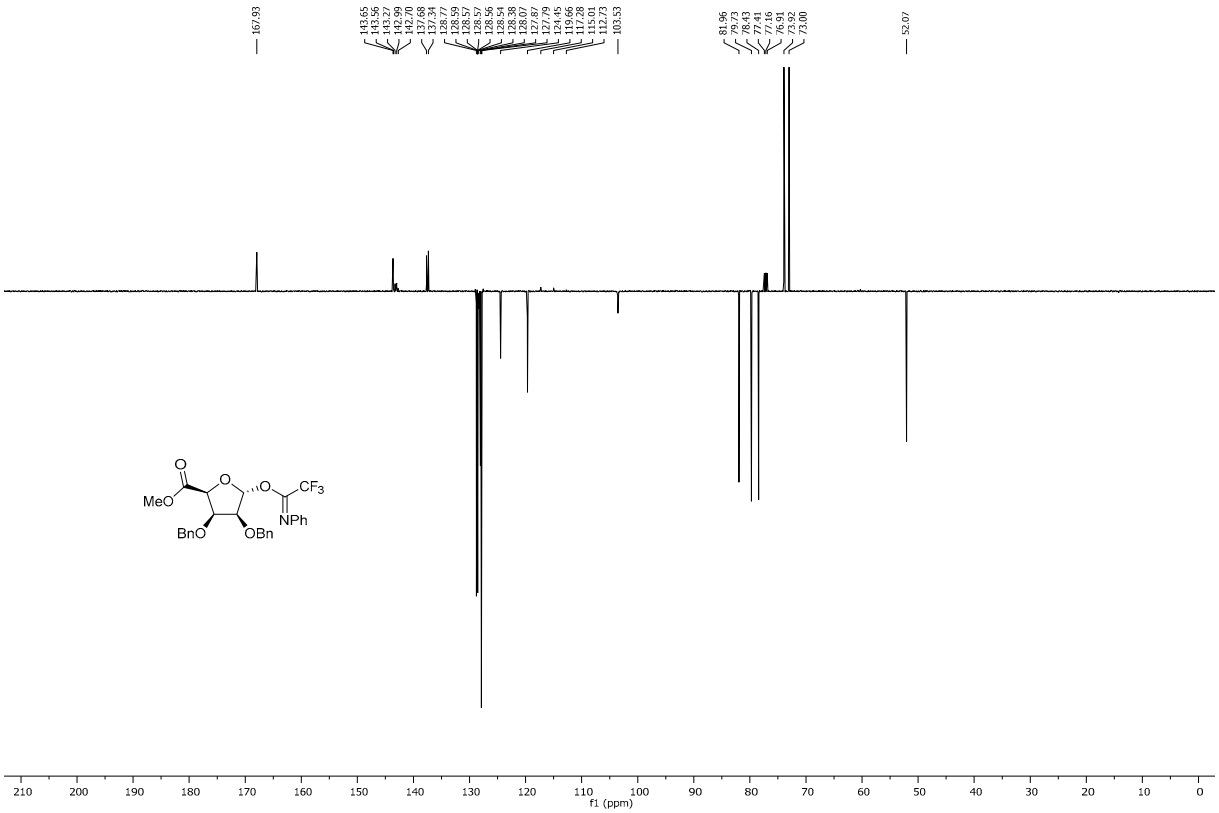


Methyl (2,3-di-*O*-benzyl-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α-D-lyxofuranosyl uronate) (3α). [*T* = 323 K]

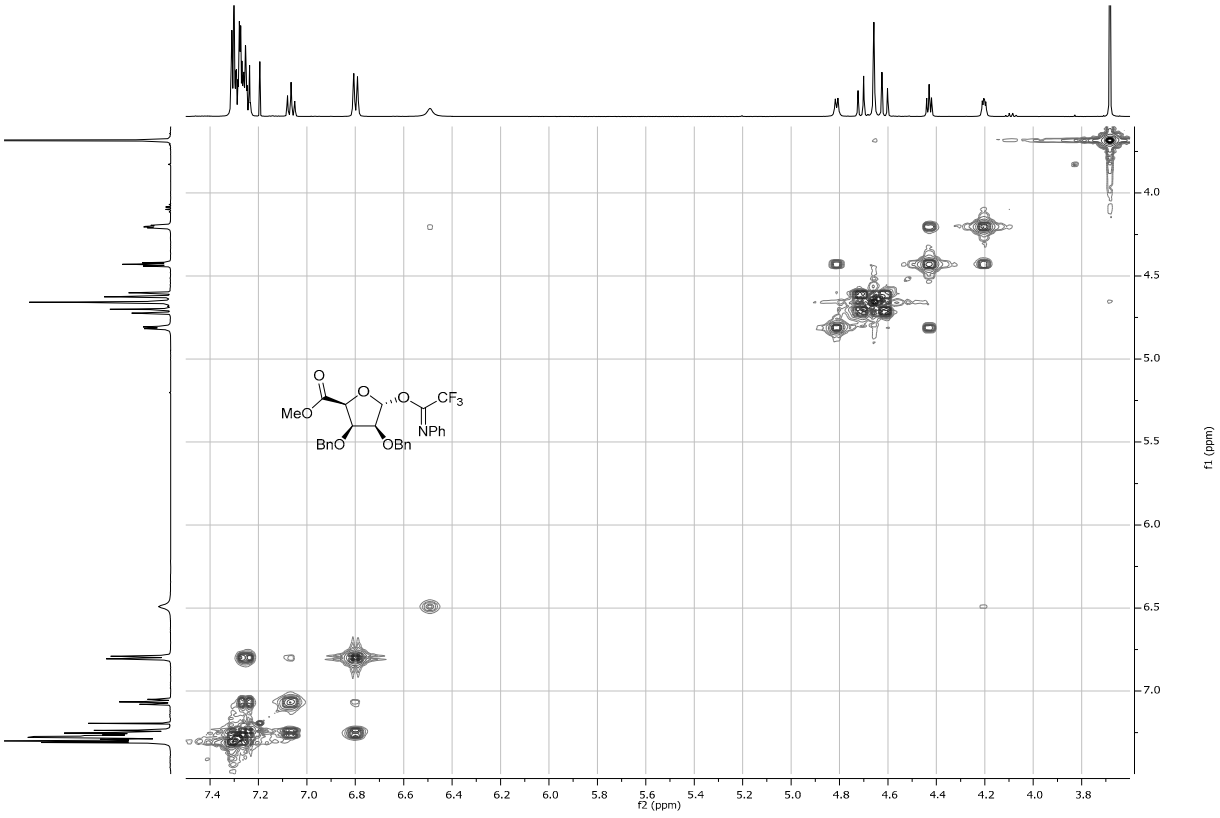
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **3α**



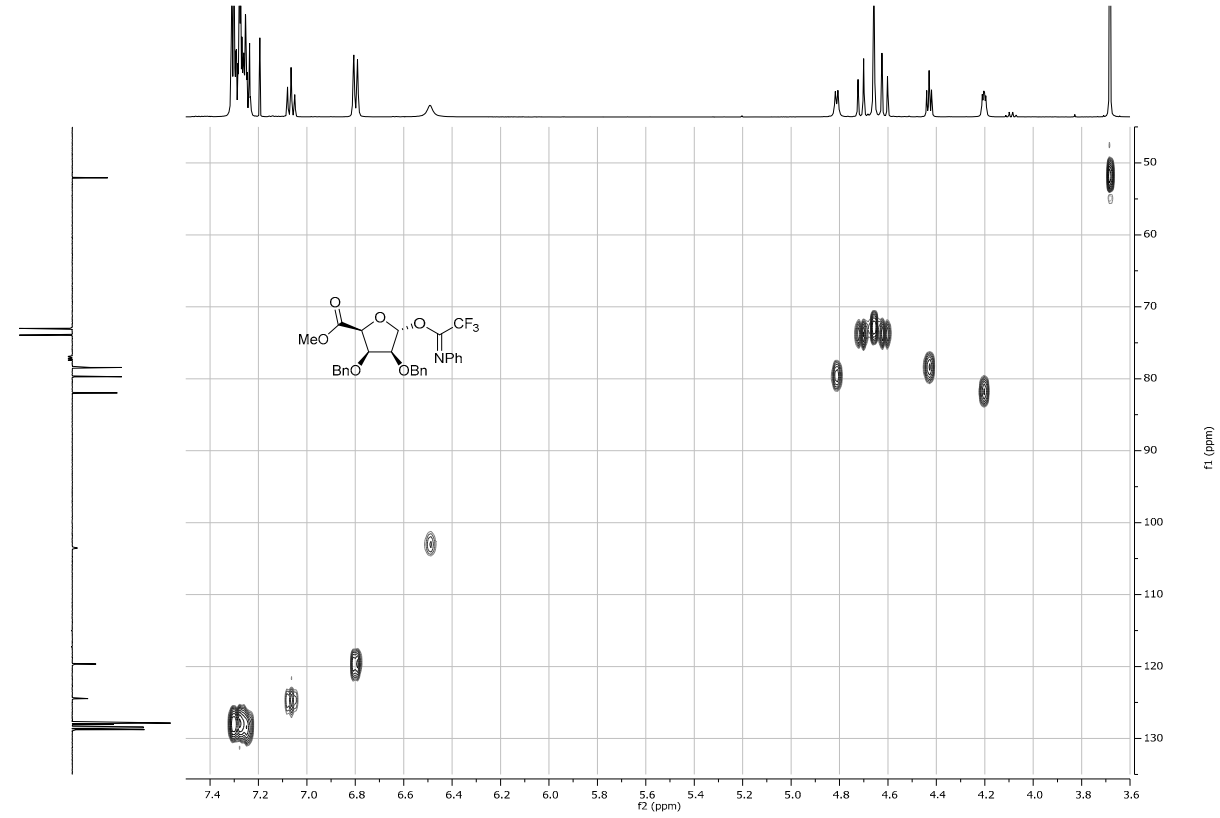
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **3α**



^{1}H-^{1}H COSY of compound **3α**

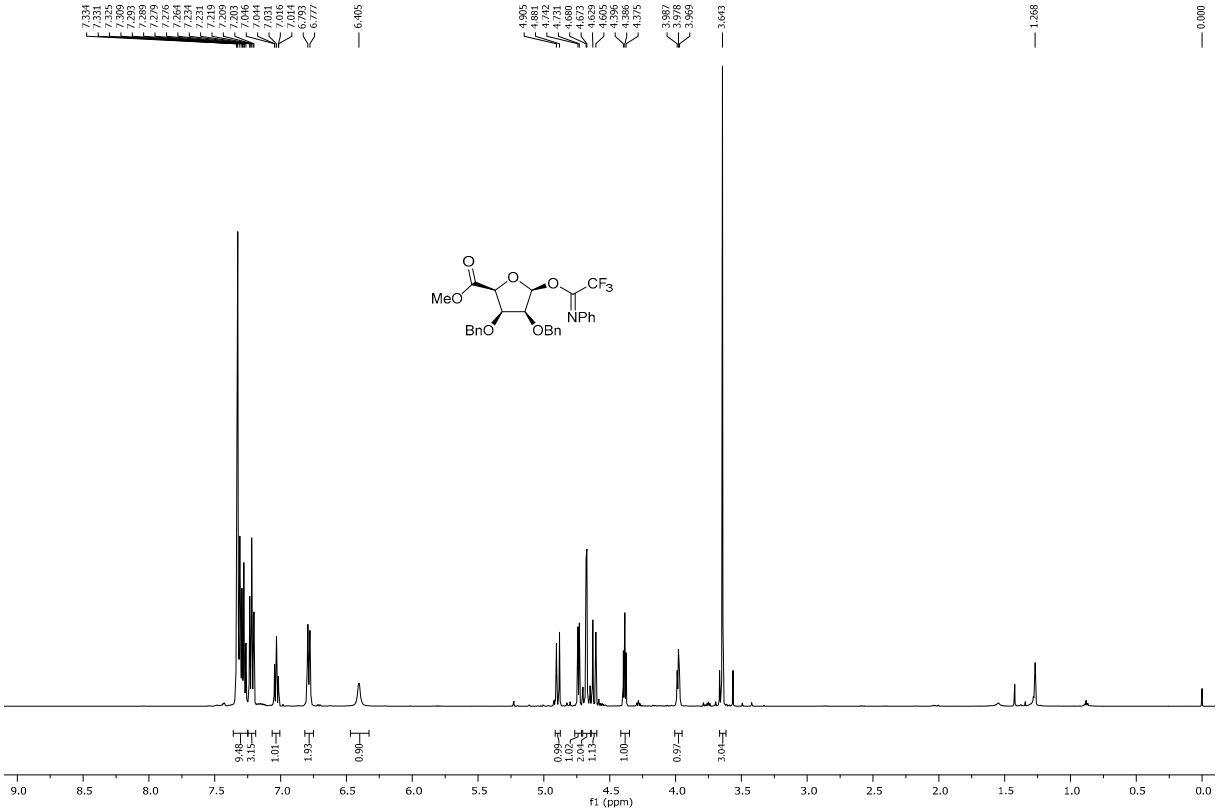


^{1}H-^{13}C HSQC of compound **3α**

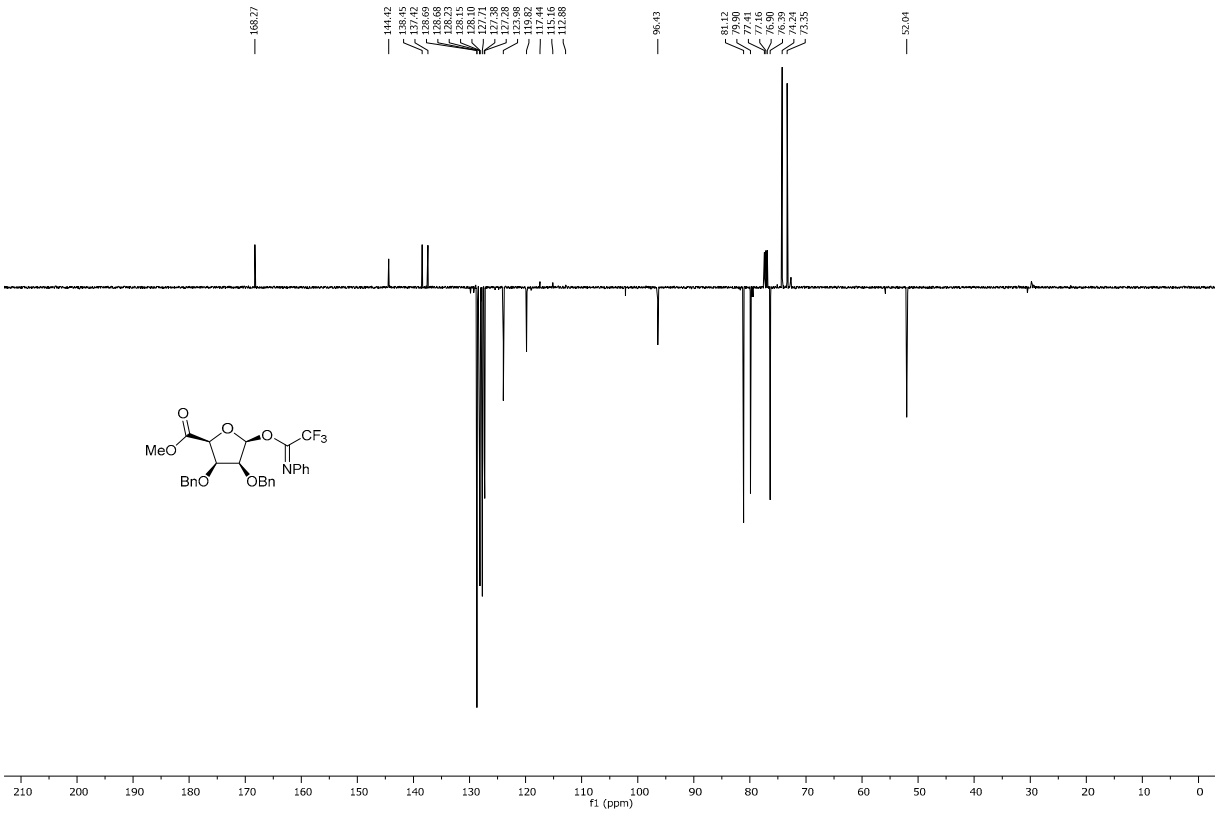


Methyl (2,3-di-*O*-benzyl-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-β-D-lyxofuranosyl uronate) (3β). [*T* = 323 K]

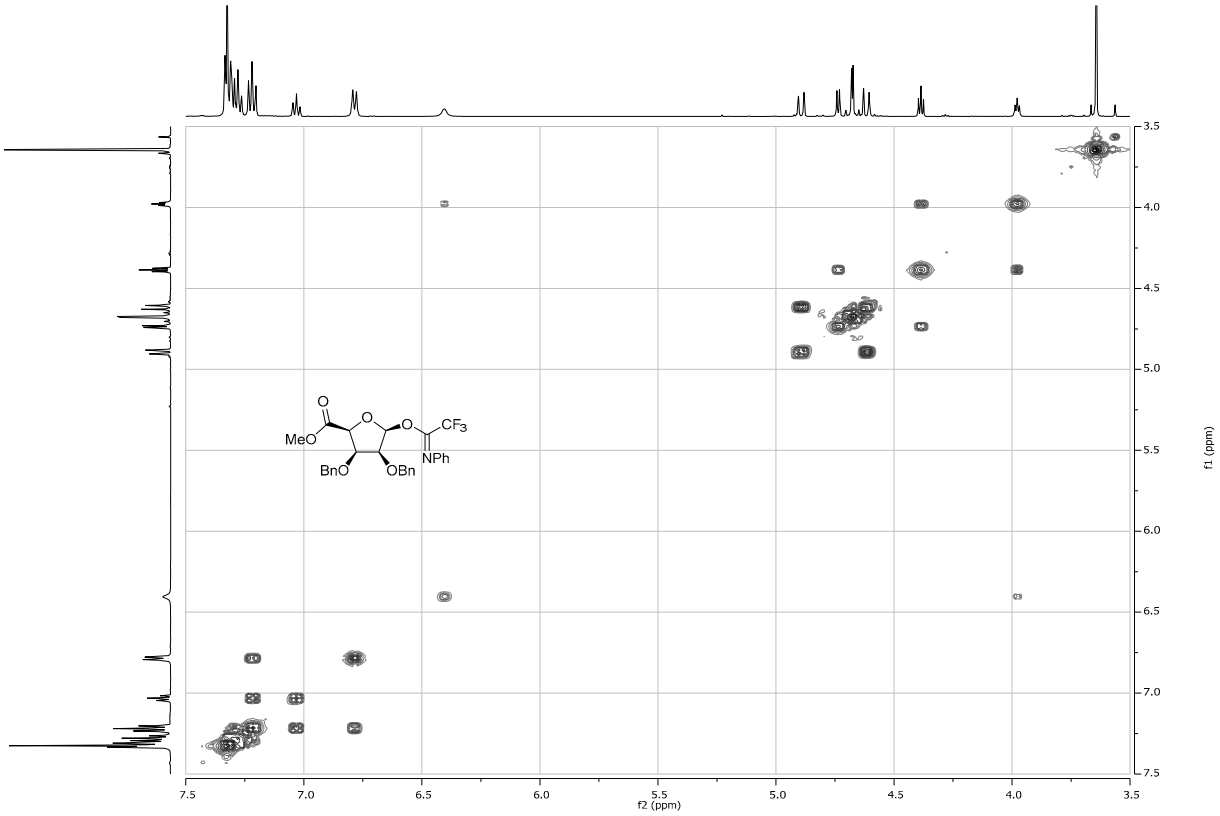
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **3β**



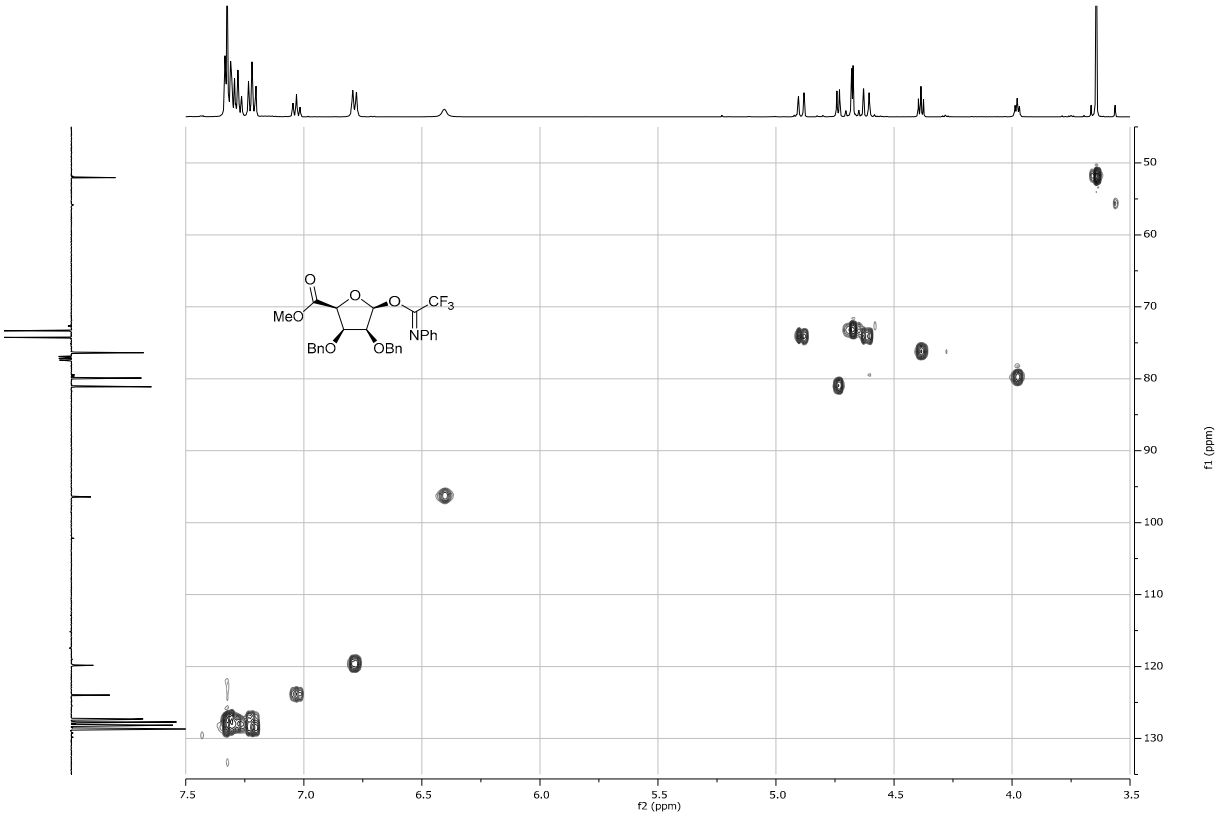
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **3β**



^{1}H-^{1}H COSY of compound **3β**

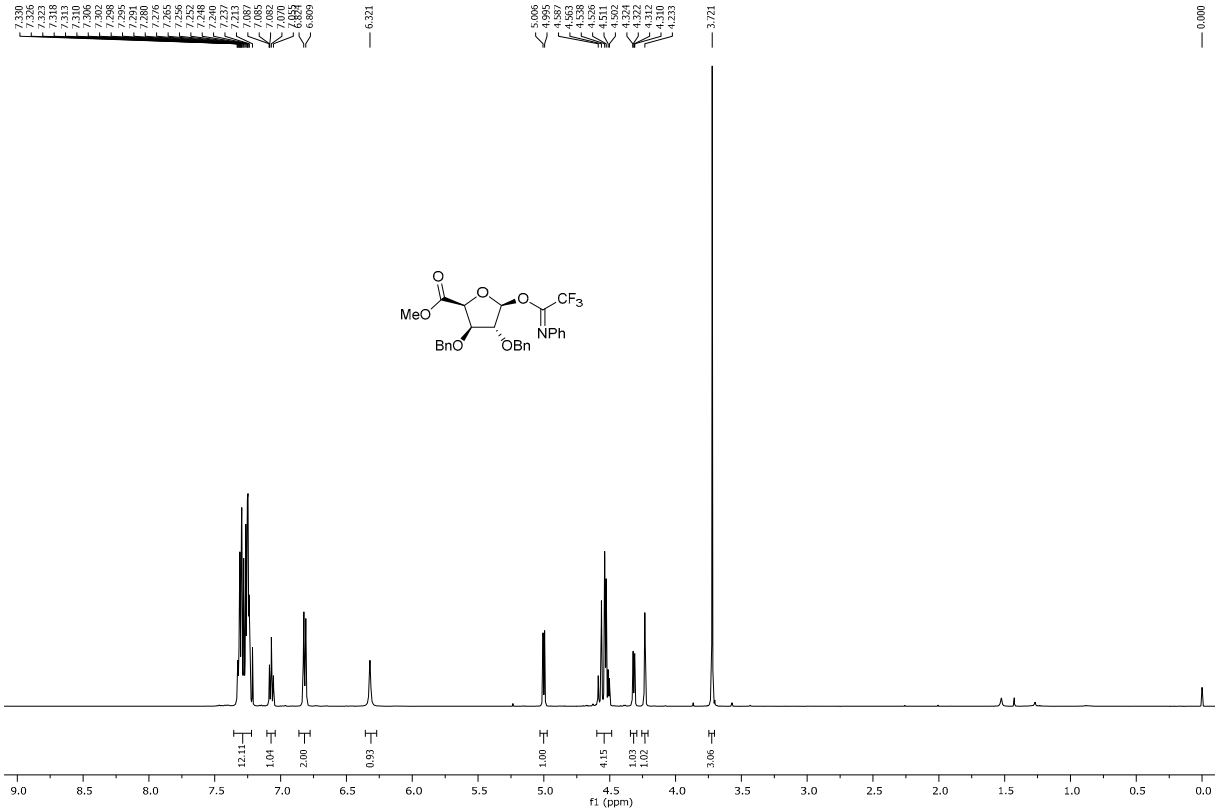


^{1}H-^{13}C HSQC of compound **3β**

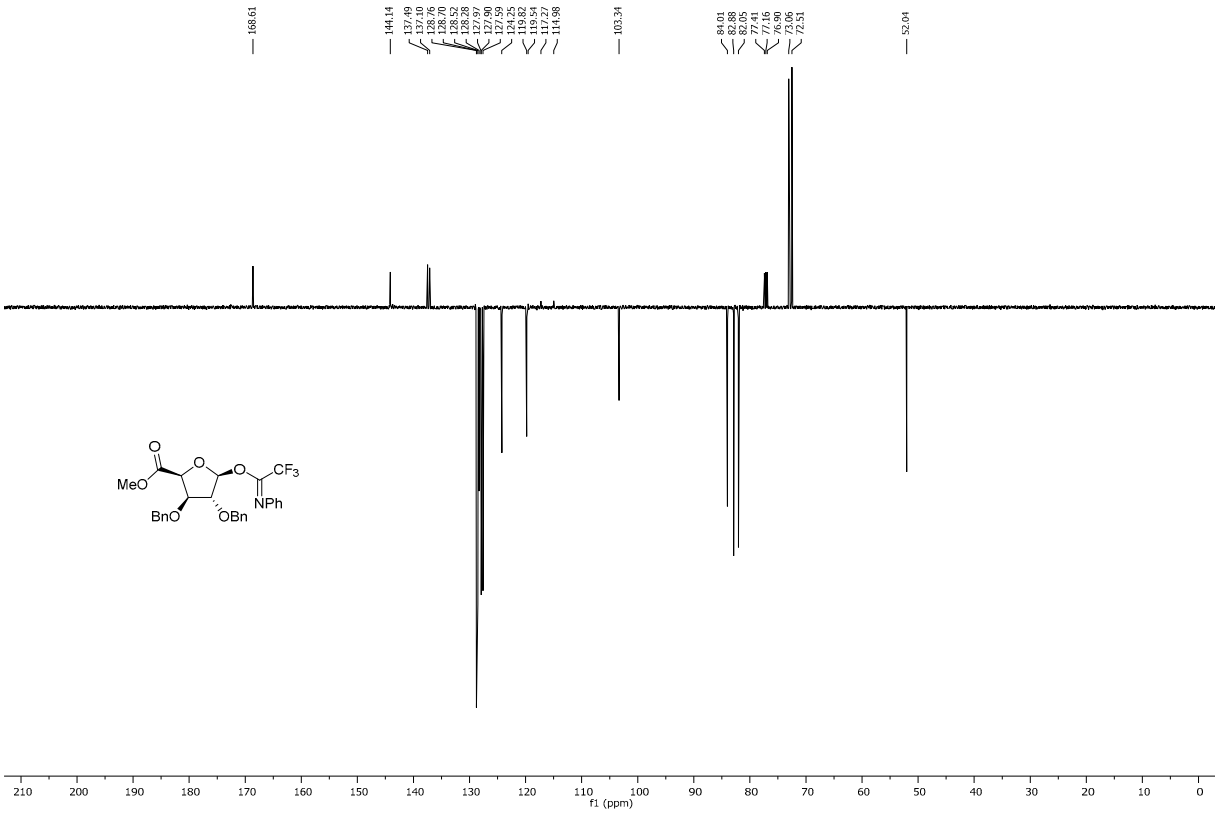


Methyl (2,3-di-*O*-benzyl-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-β-D-xylofuranosyl uronate) (4α) [*T* = 323 K]

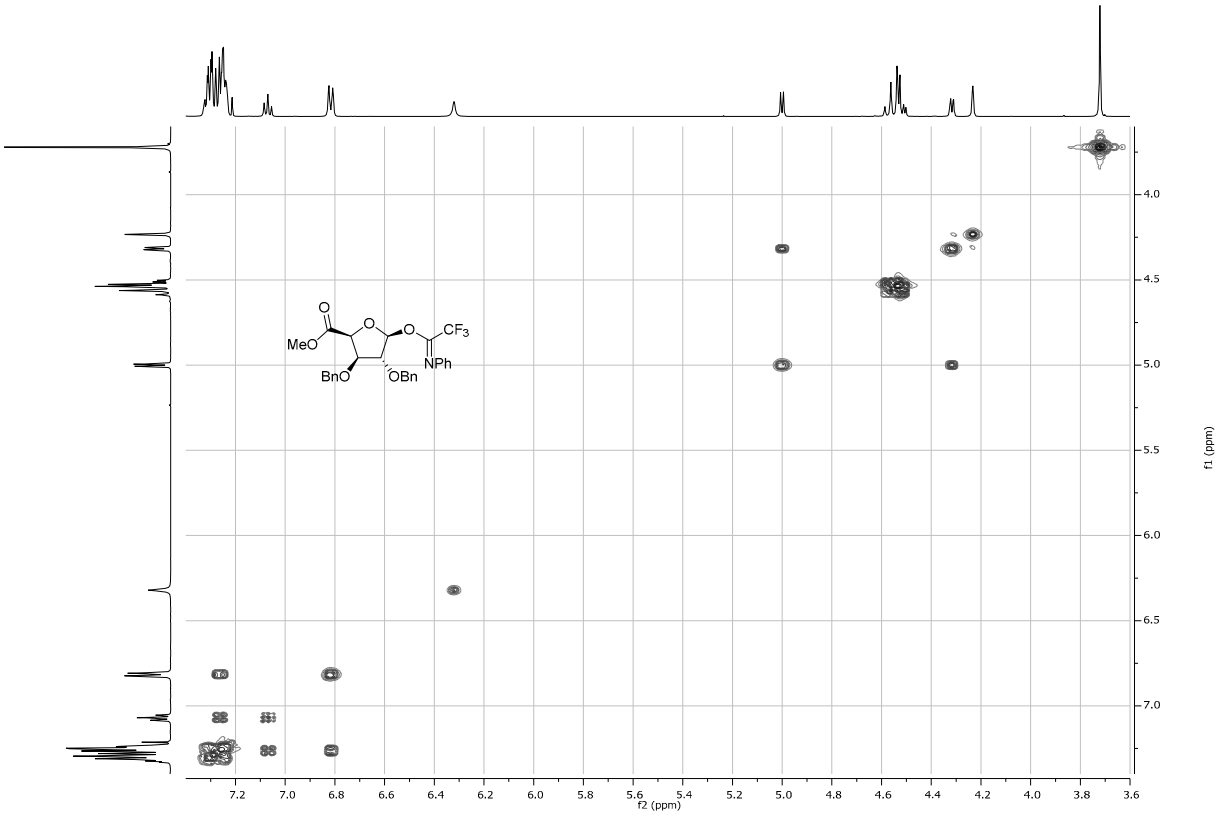
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **4α**



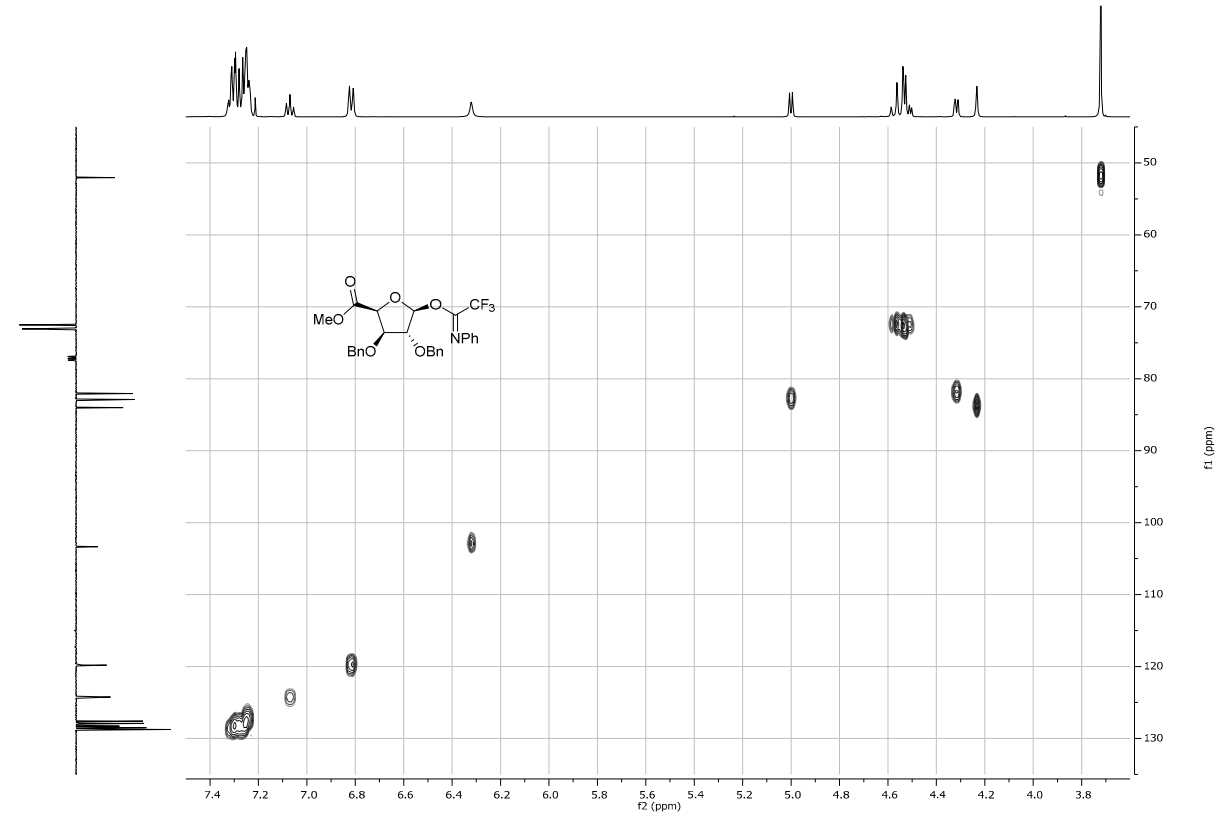
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **4α**



^{1}H-^{1}H COSY of compound **4α**

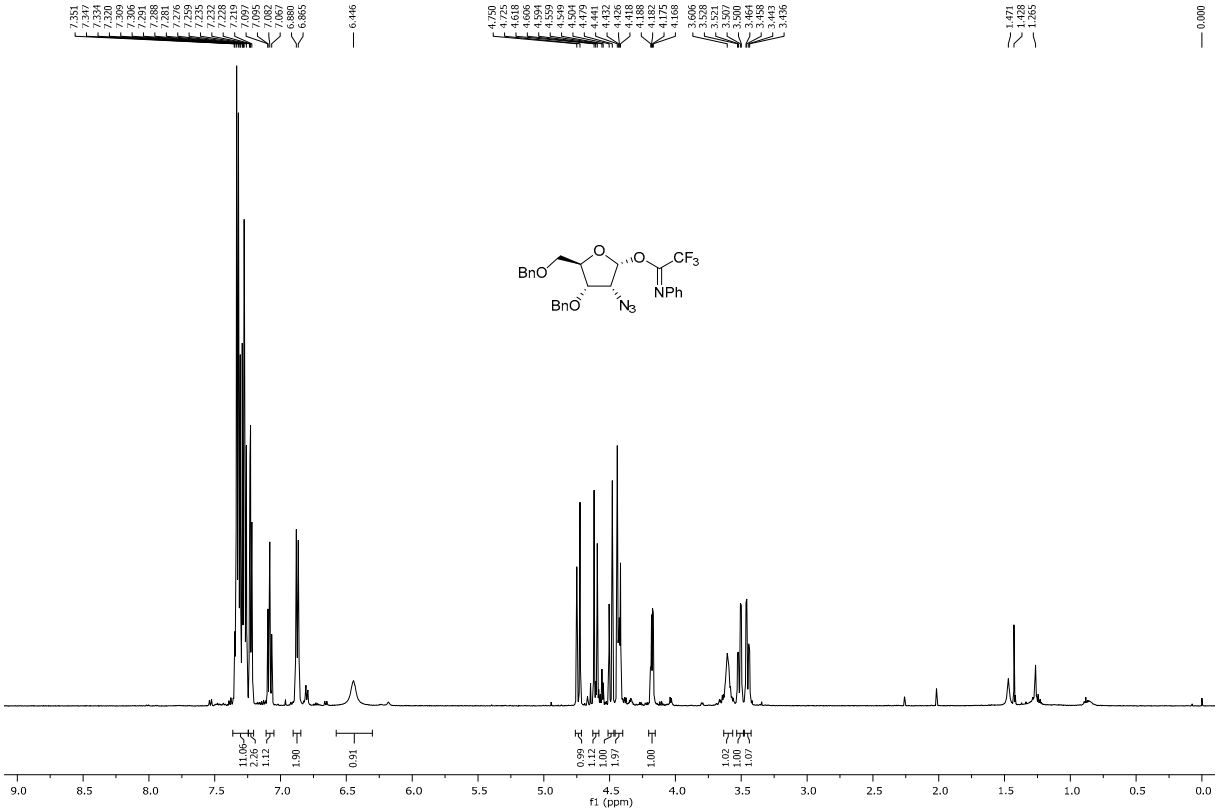


^{1}H-^{13}C HSQC of compound **4α**

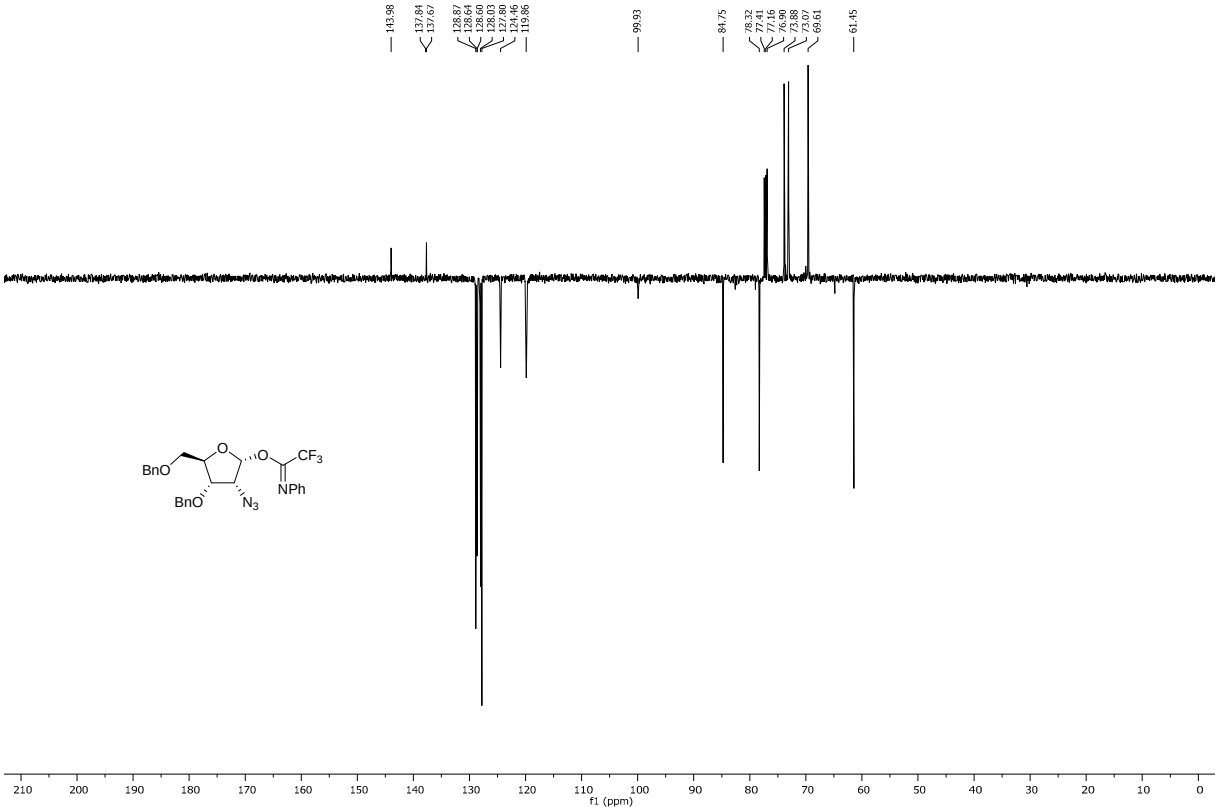


2-azido-3,5-di-*O*-benzyl-2-deoxy-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α-D-ribofuranoside (5α) [*T* = 323 K]

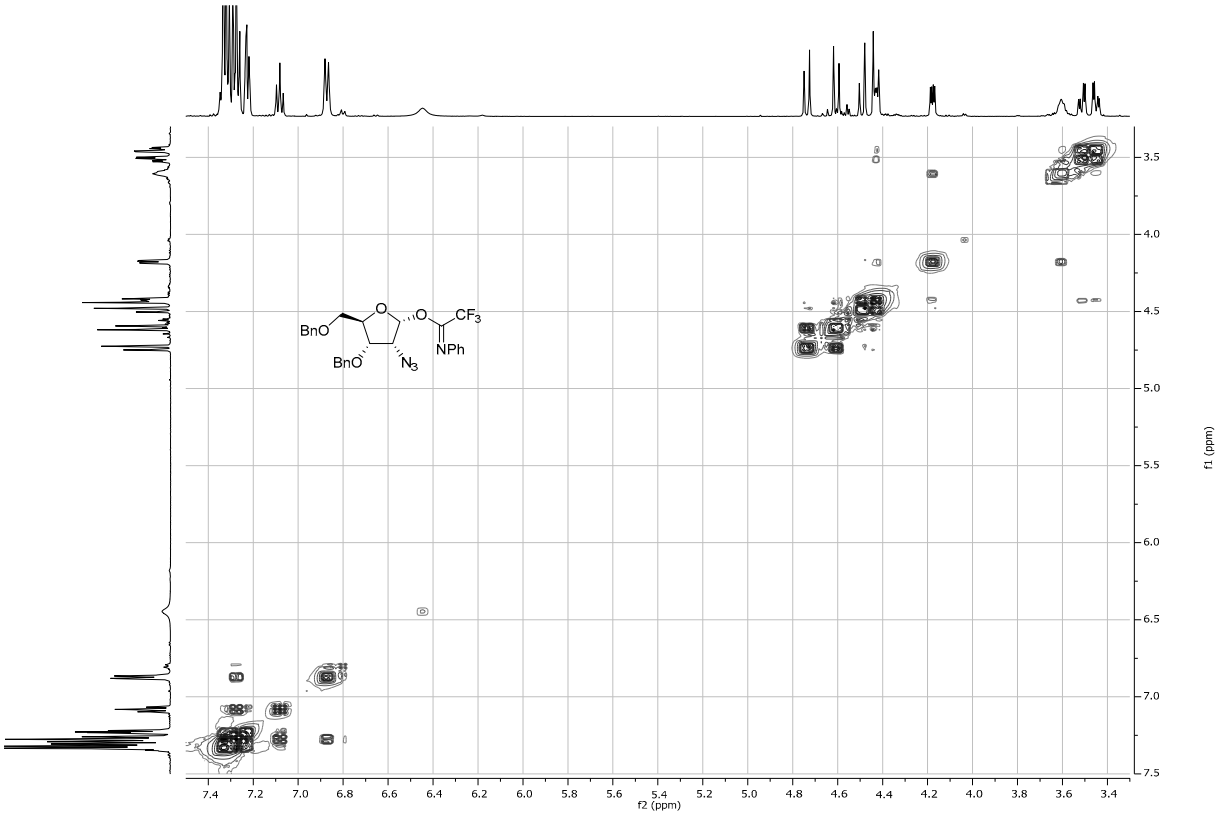
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **5α**



^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **5α**



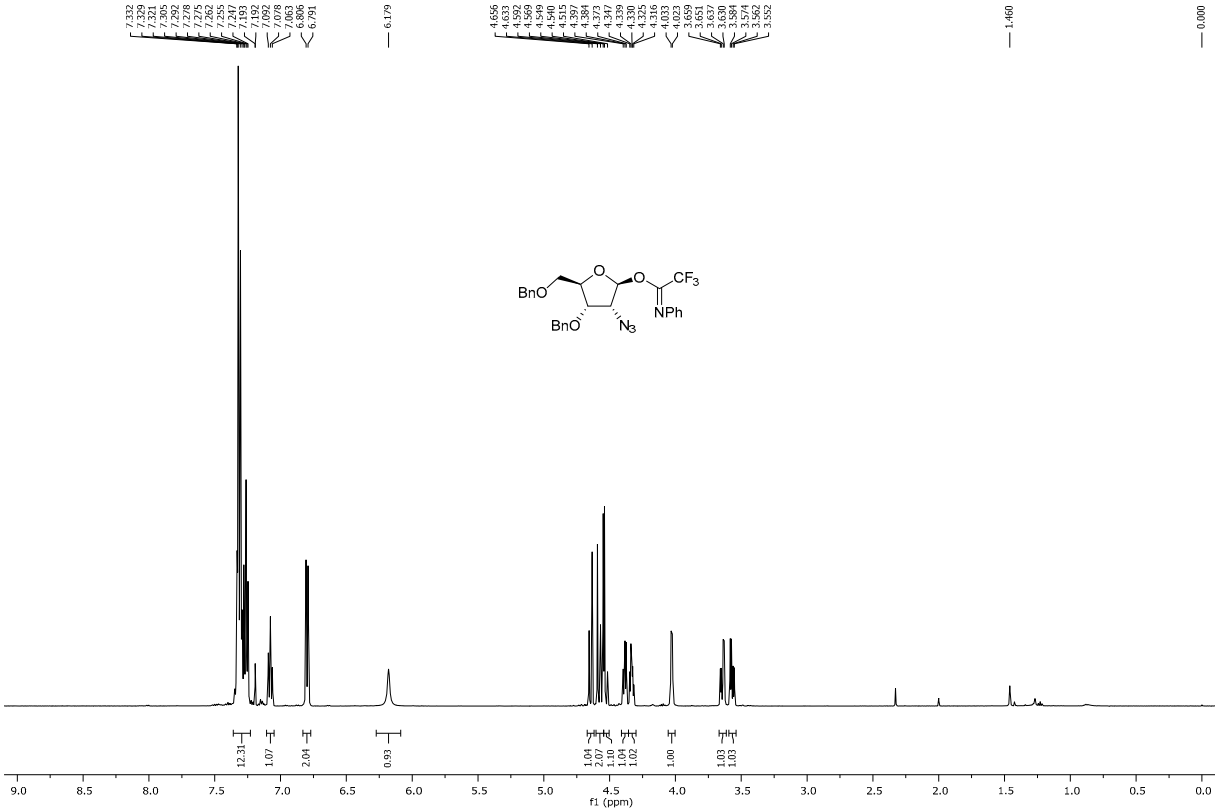
^{1}H-^{1}H COSY of compound **5α**



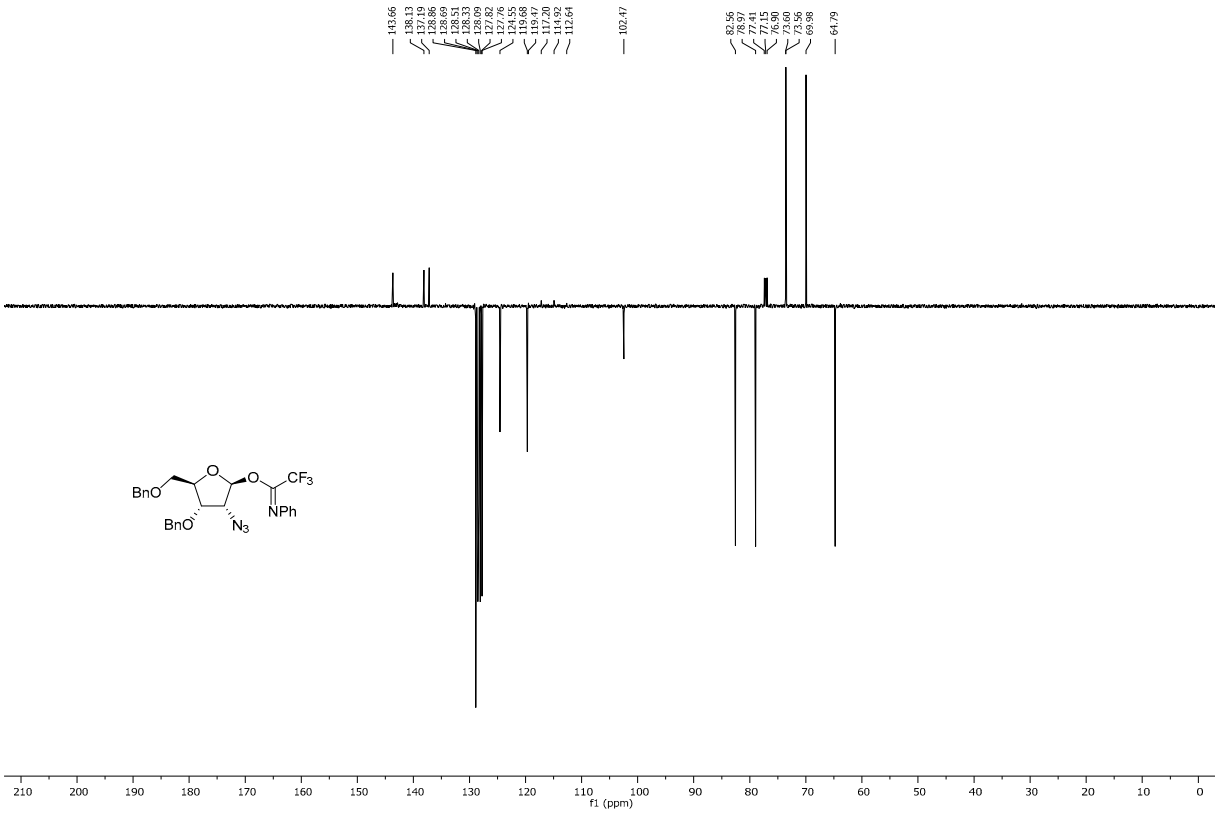
^{1}H-^{13}C HSQC of compound **5α**

2-azido-3,5-di-*O*-benzyl-2-deoxy-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-β-D-ribofuranoside (5β) [*T* = 323 K]

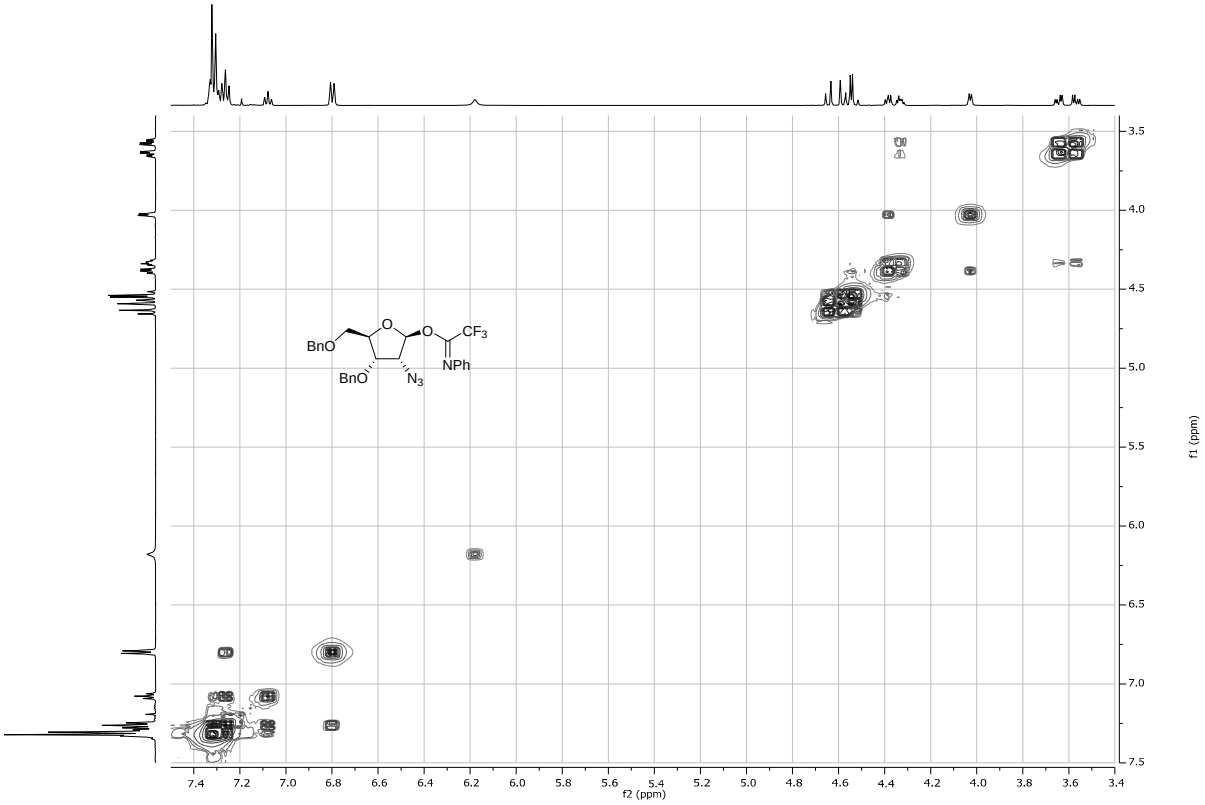
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **5β**



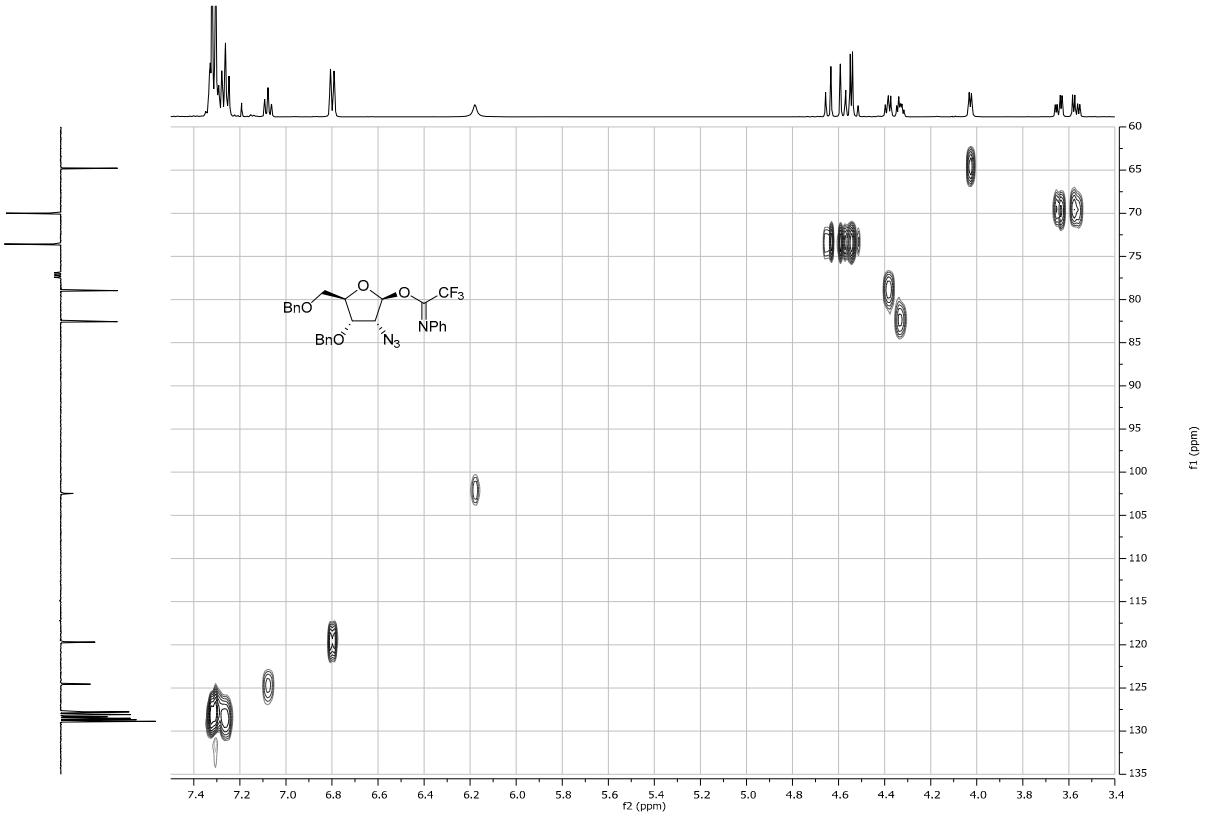
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **5β**



^{1}H-^{1}H COSY of compound **5β**

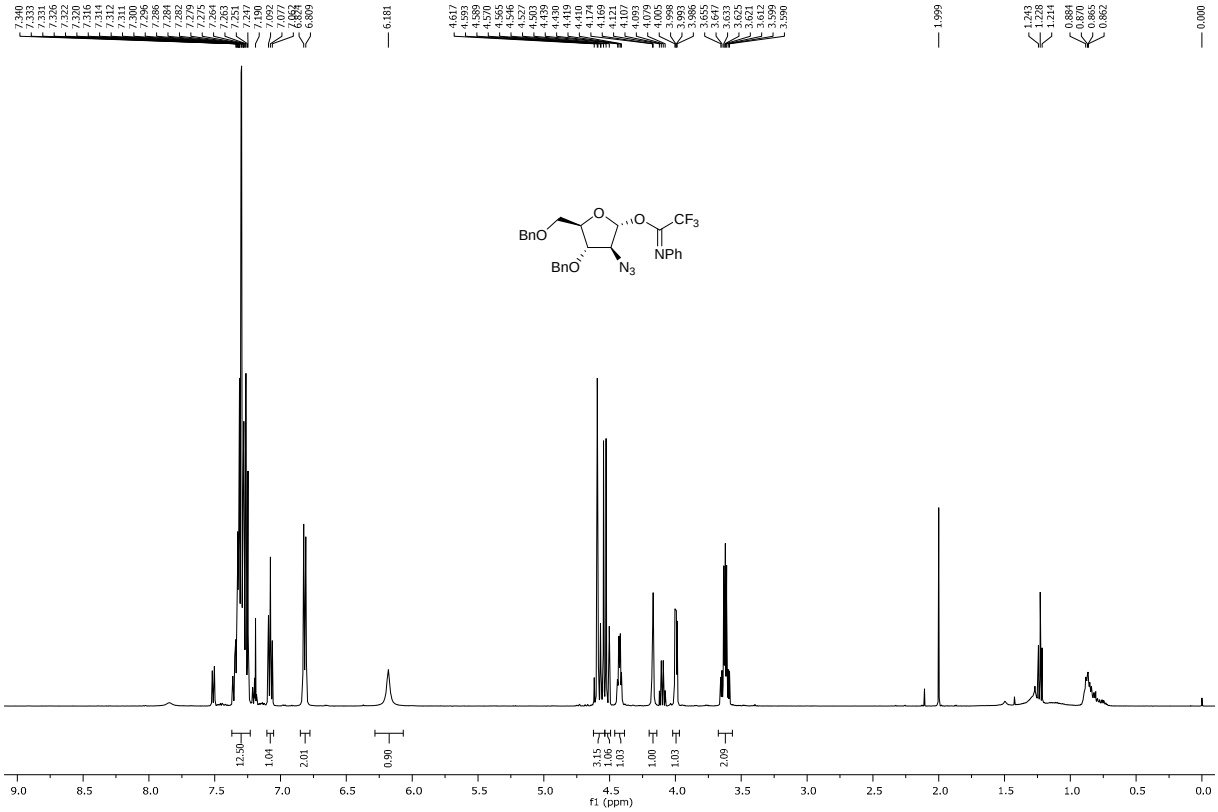


^{1}H-^{13}C HSQC of compound **5β**

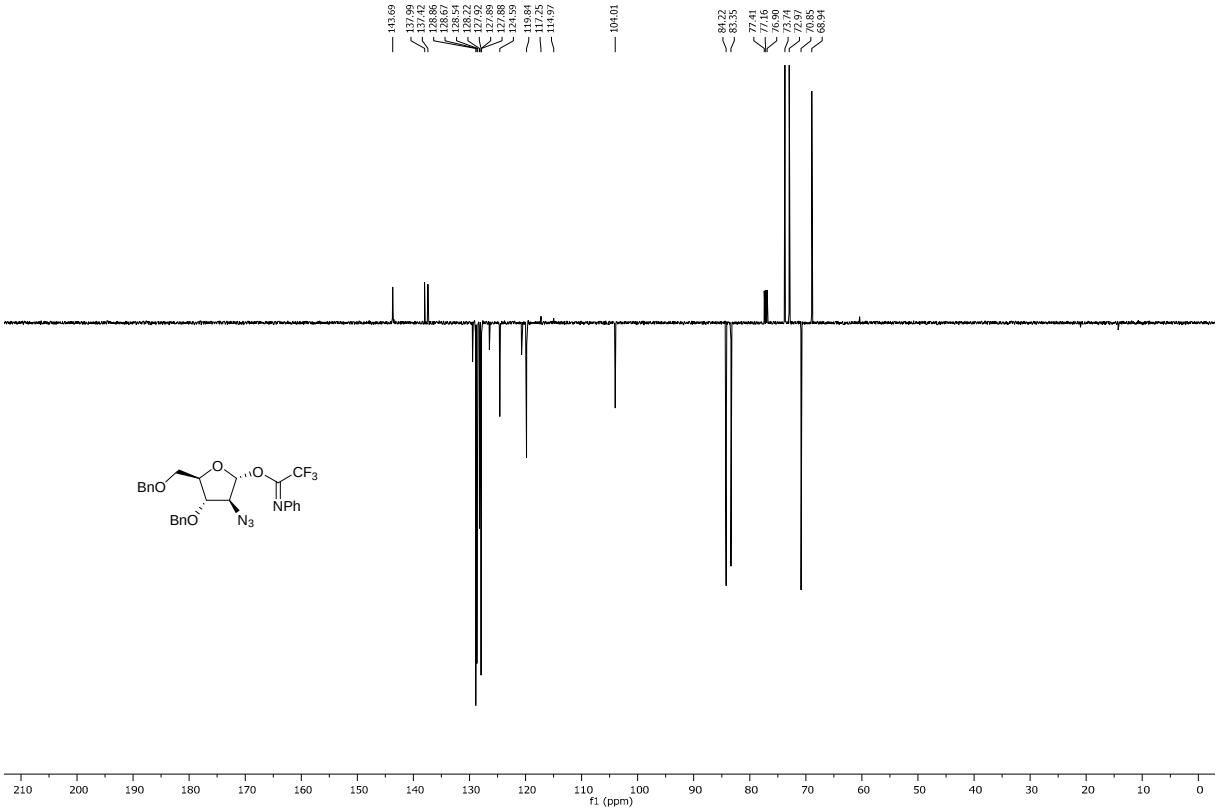


2-azido-3,5-di-*O*-benzyl-2-deoxy-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α-D-arabinofuranoside (6α) [*T* = 323 K]

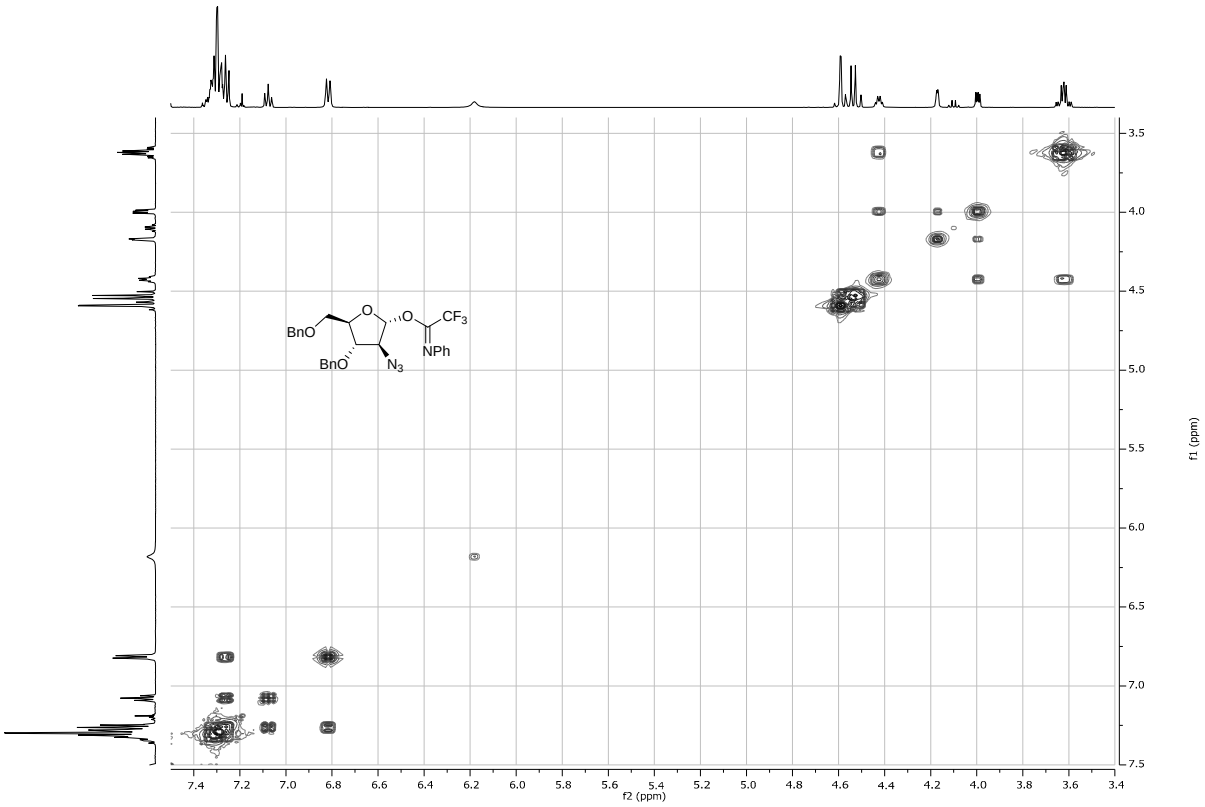
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **6α**



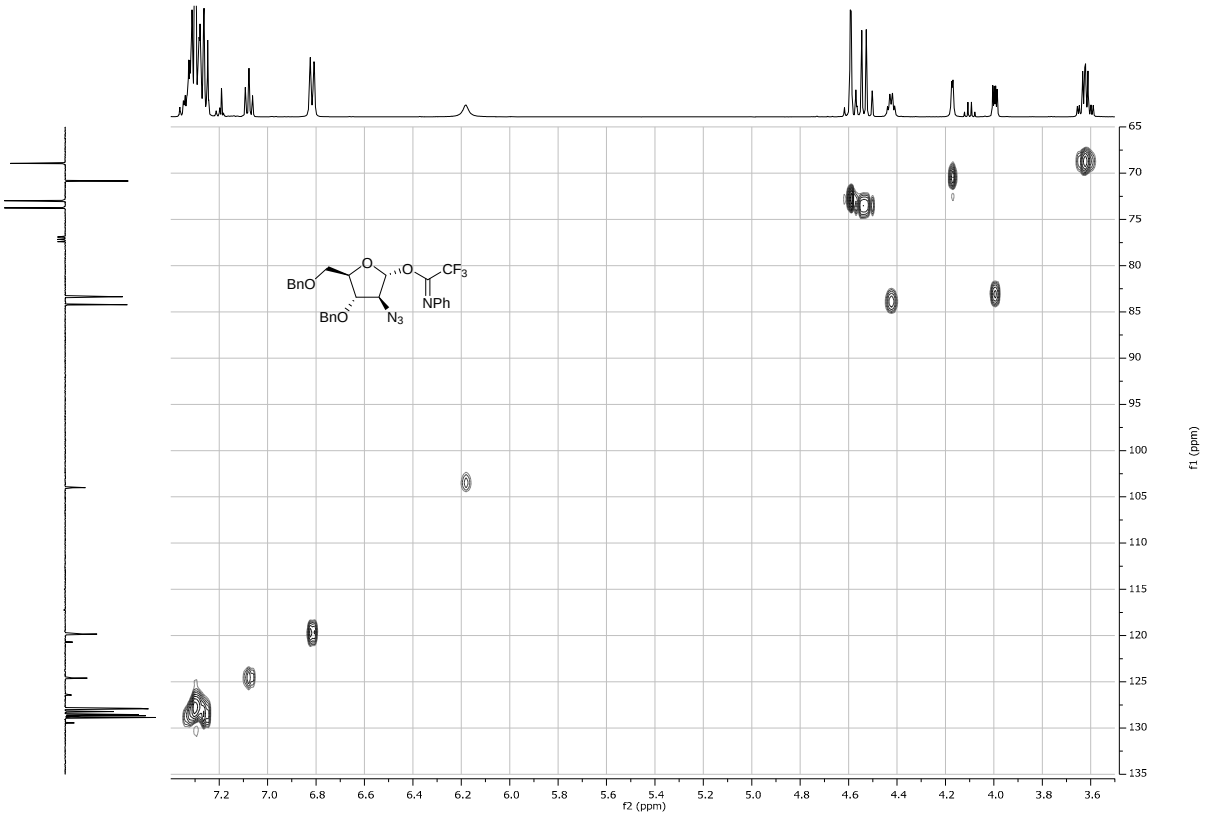
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **6α**



^{1}H-^{1}H COSY of compound **6α**

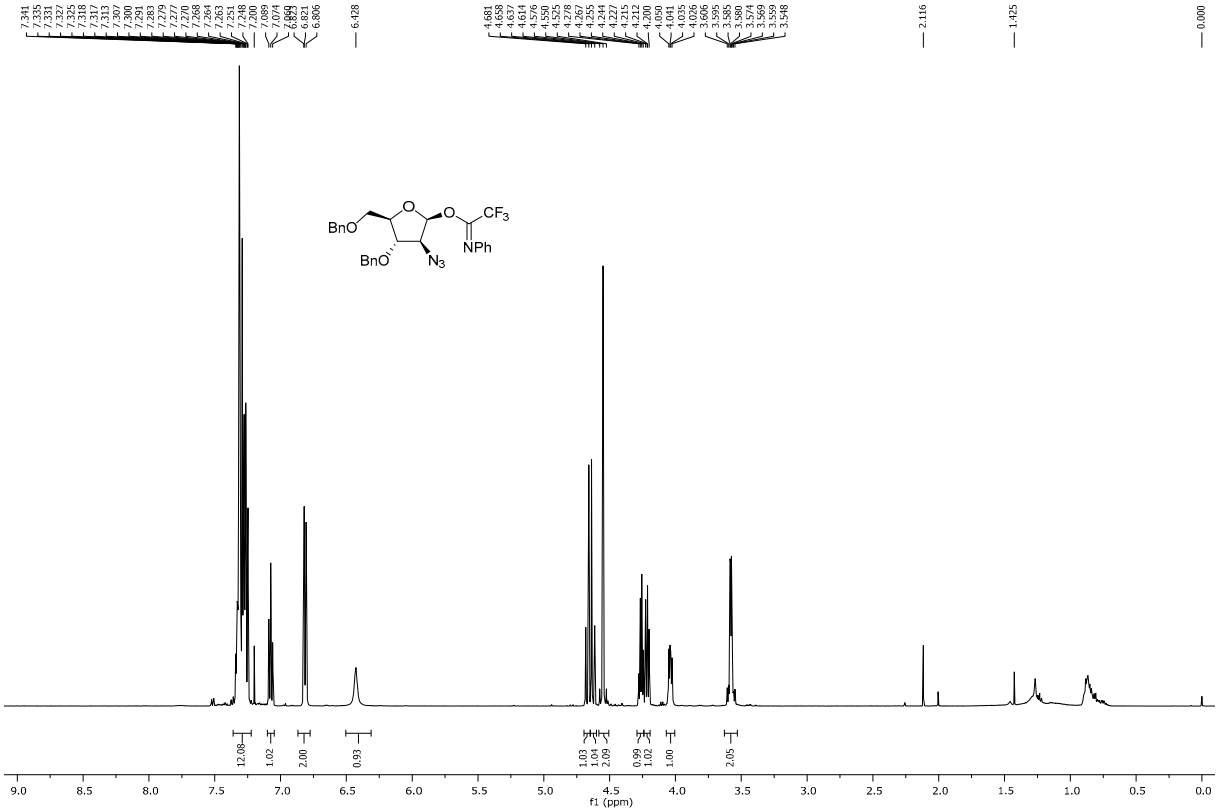


^{1}H-^{13}C HSQC of compound **6α**

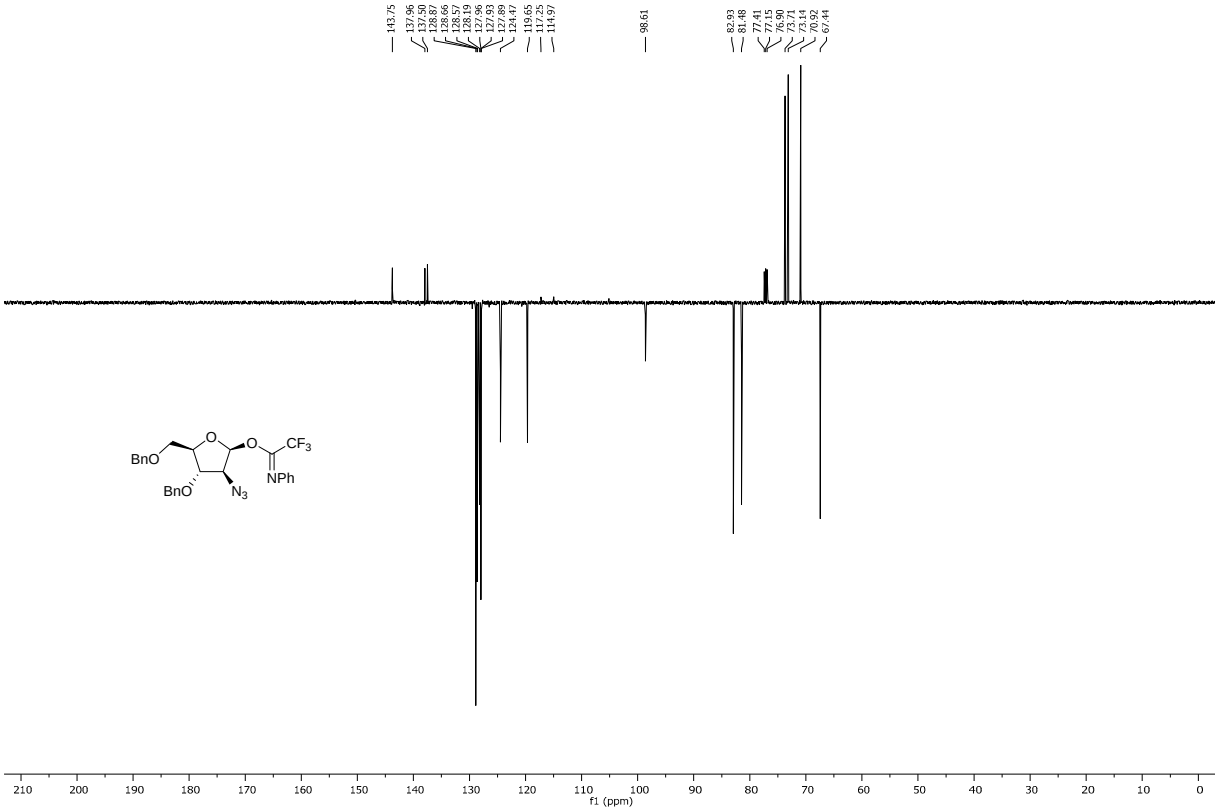


2-azido-3,5-di-*O*-benzyl-2-deoxy-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-β-D-arabinofuranoside (6β) [*T* = 323 K]

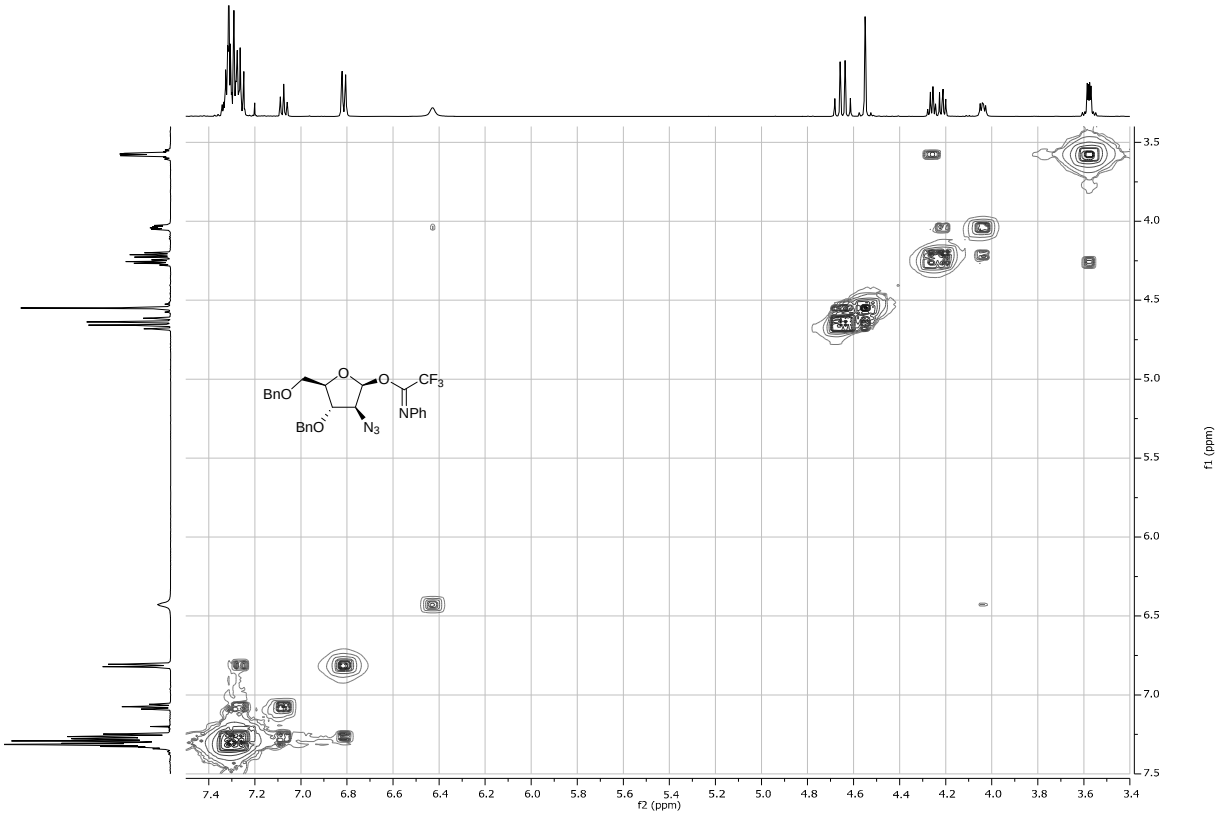
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **6β**



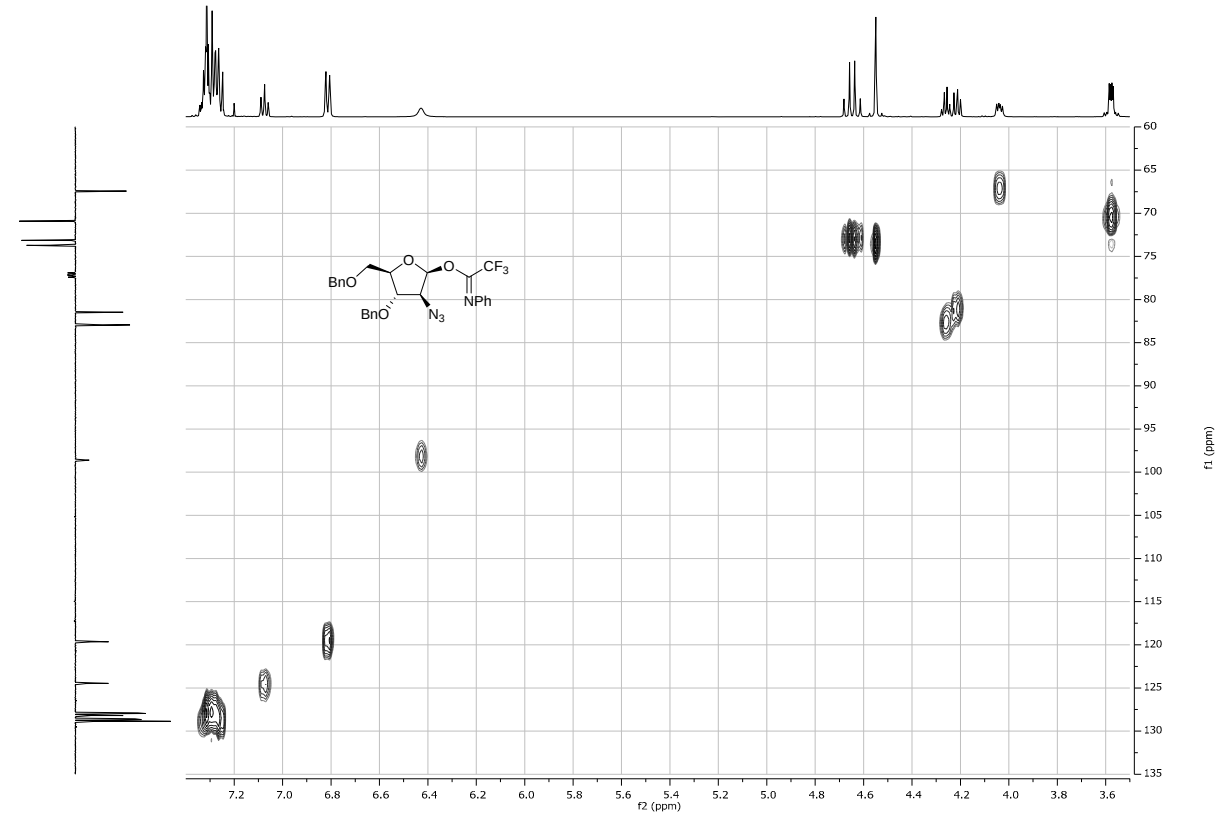
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **6β**



^{1}H-^{1}H COSY of compound **6β**

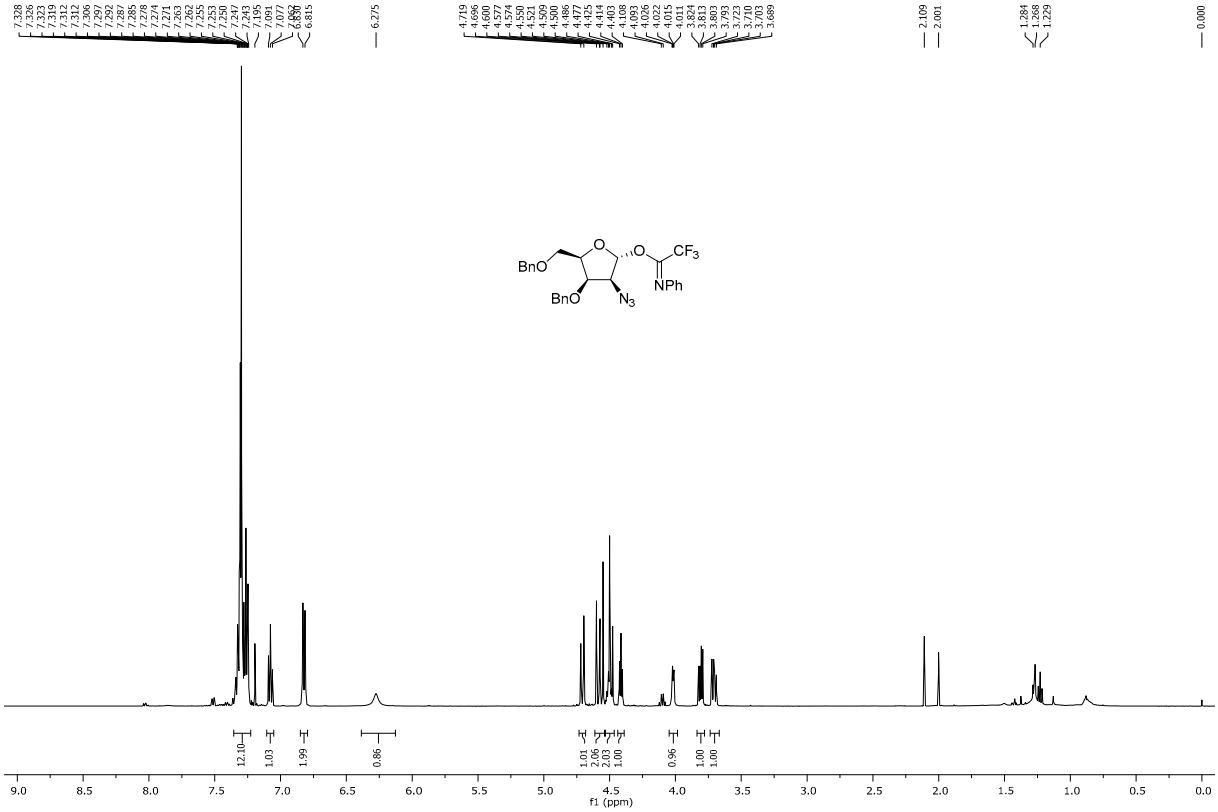


^{1}H-^{13}C HSQC of compound **6β**

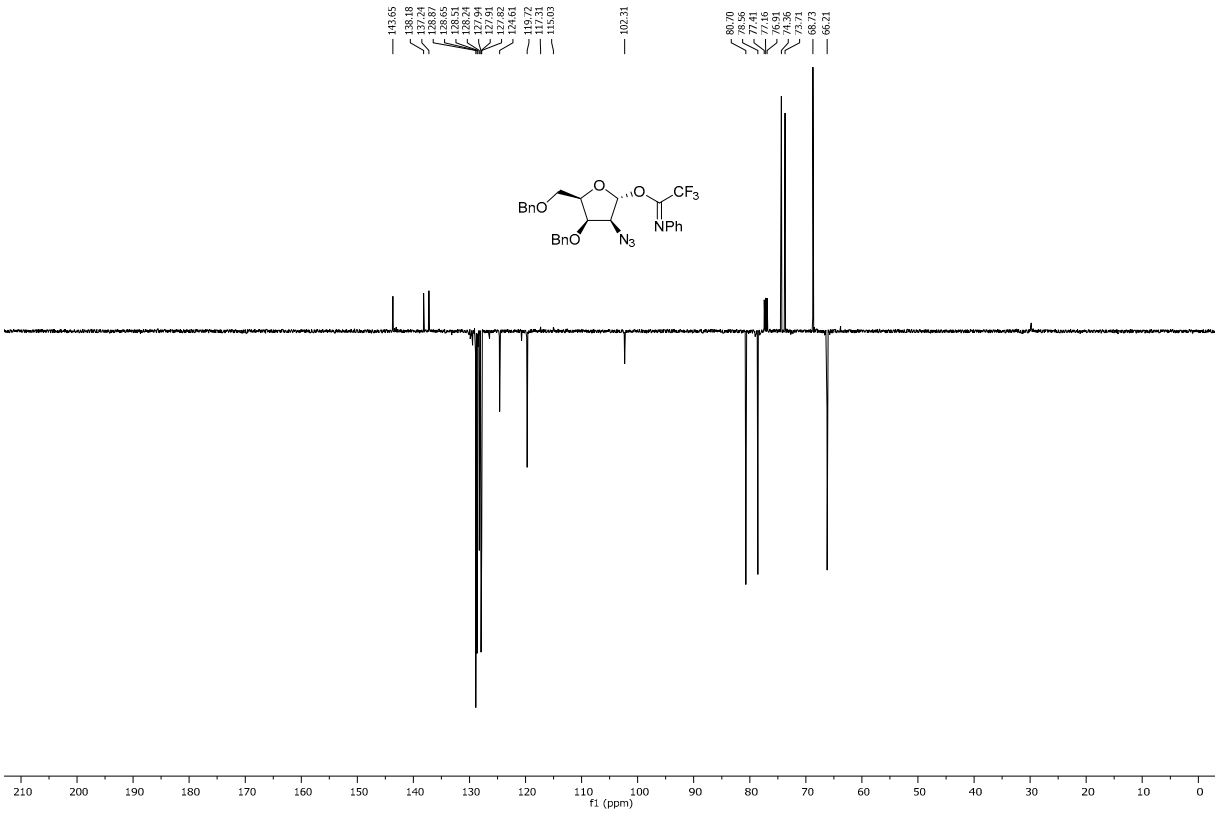


2-azido-3,5-di-*O*-benzyl-2-deoxy-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α-D-lyxofuranoside (7α) [*T* = 323 K]

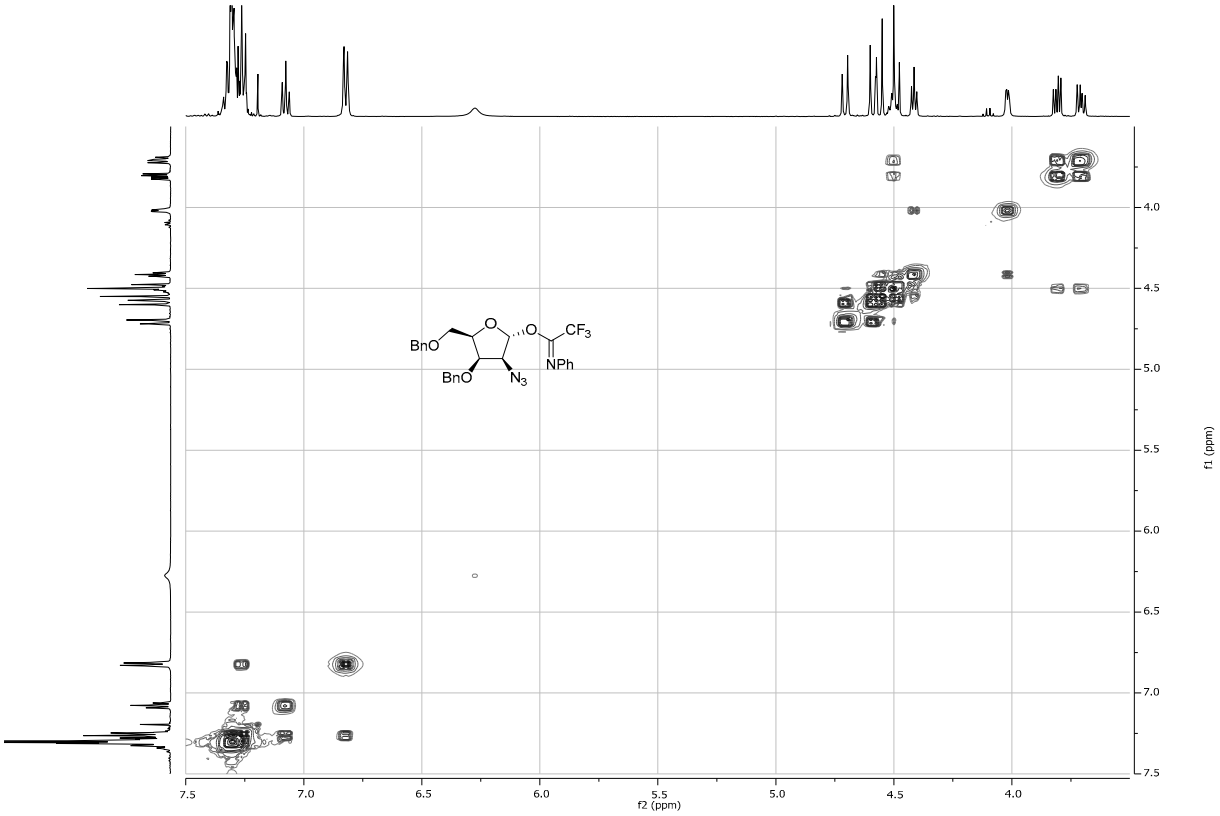
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **7α**



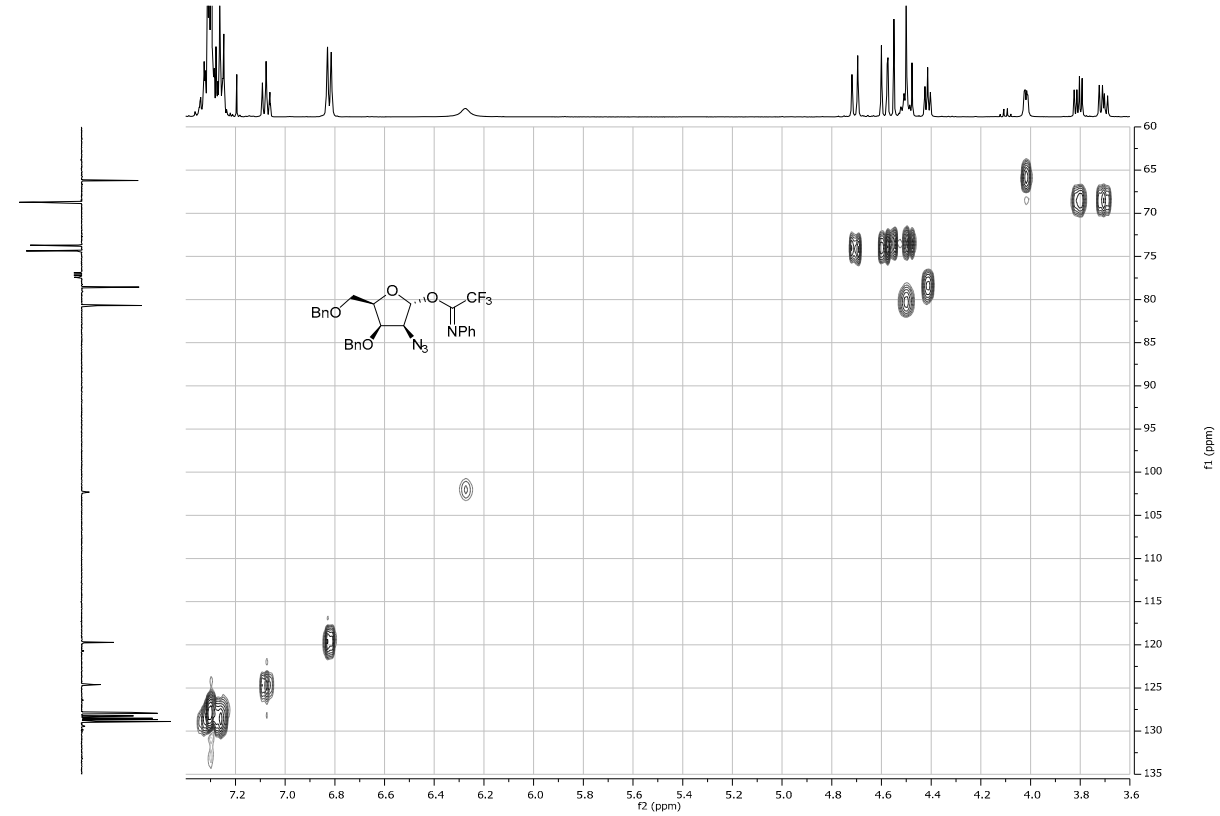
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **7α**



^{1}H-^{1}H COSY of compound **7α**

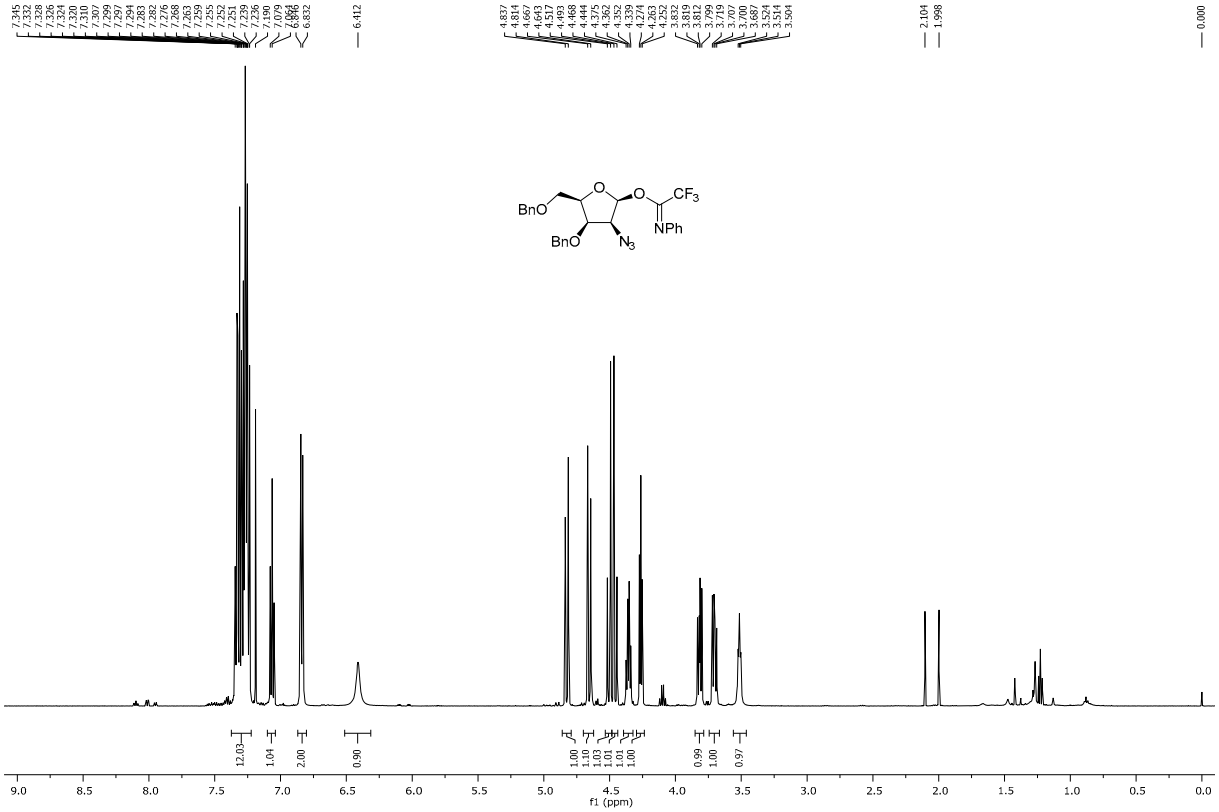


^{1}H-^{13}C HSQC of compound **7α**

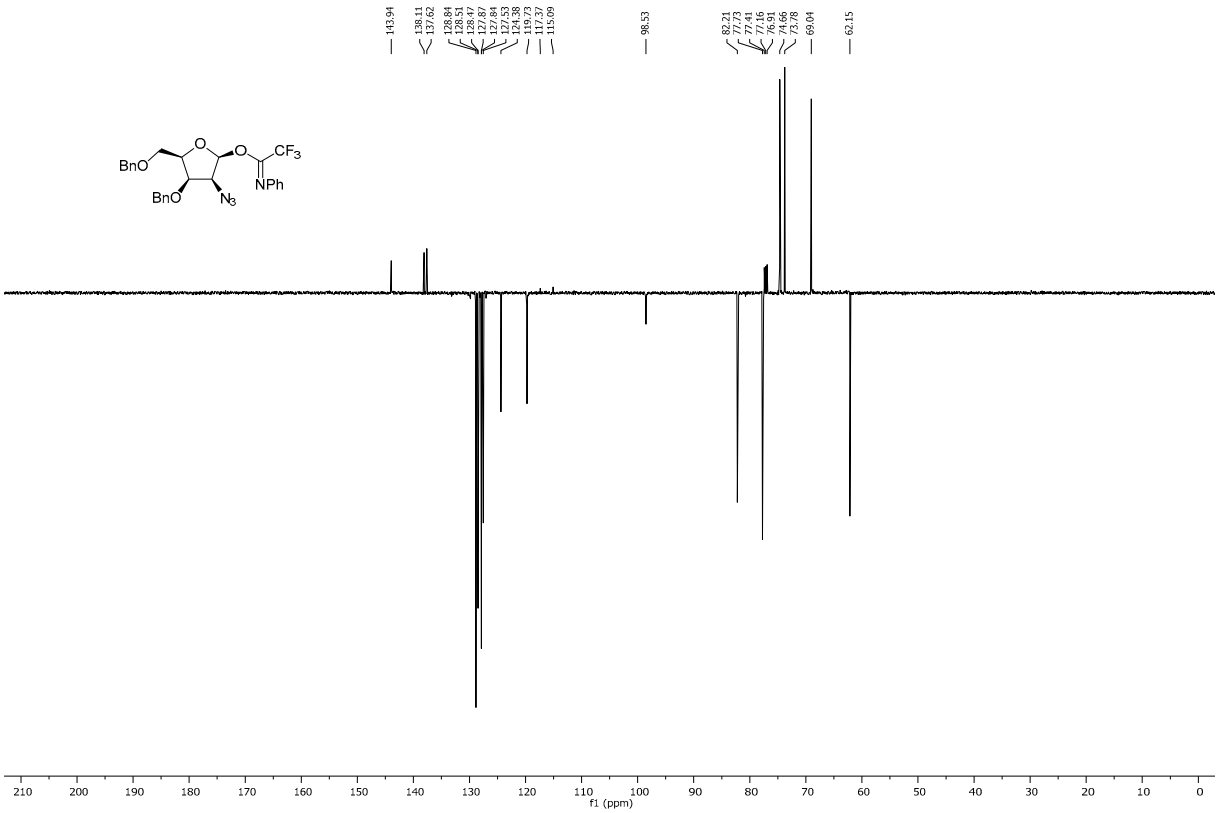


2-azido-3,5-di-*O*-benzyl-2-deoxy-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-β-D-lyxofuranoside (7β) [*T* = 323 K]

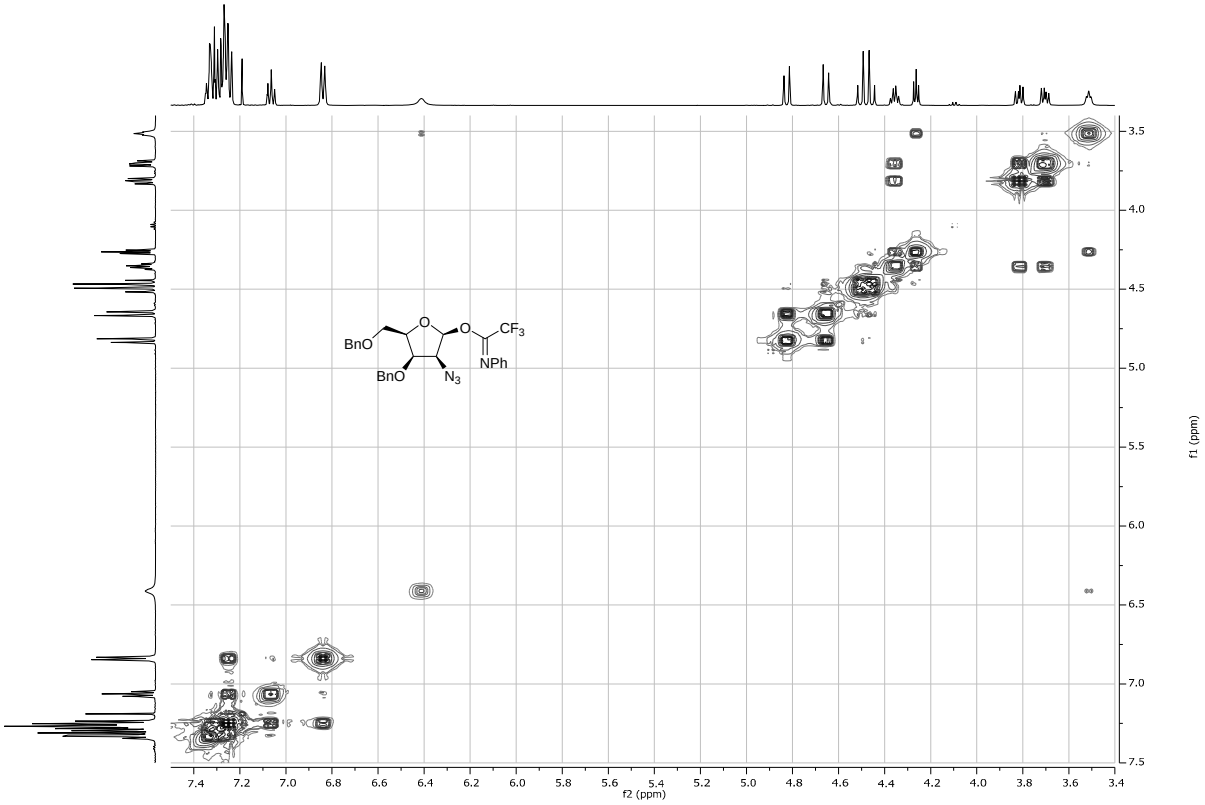
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **7β**



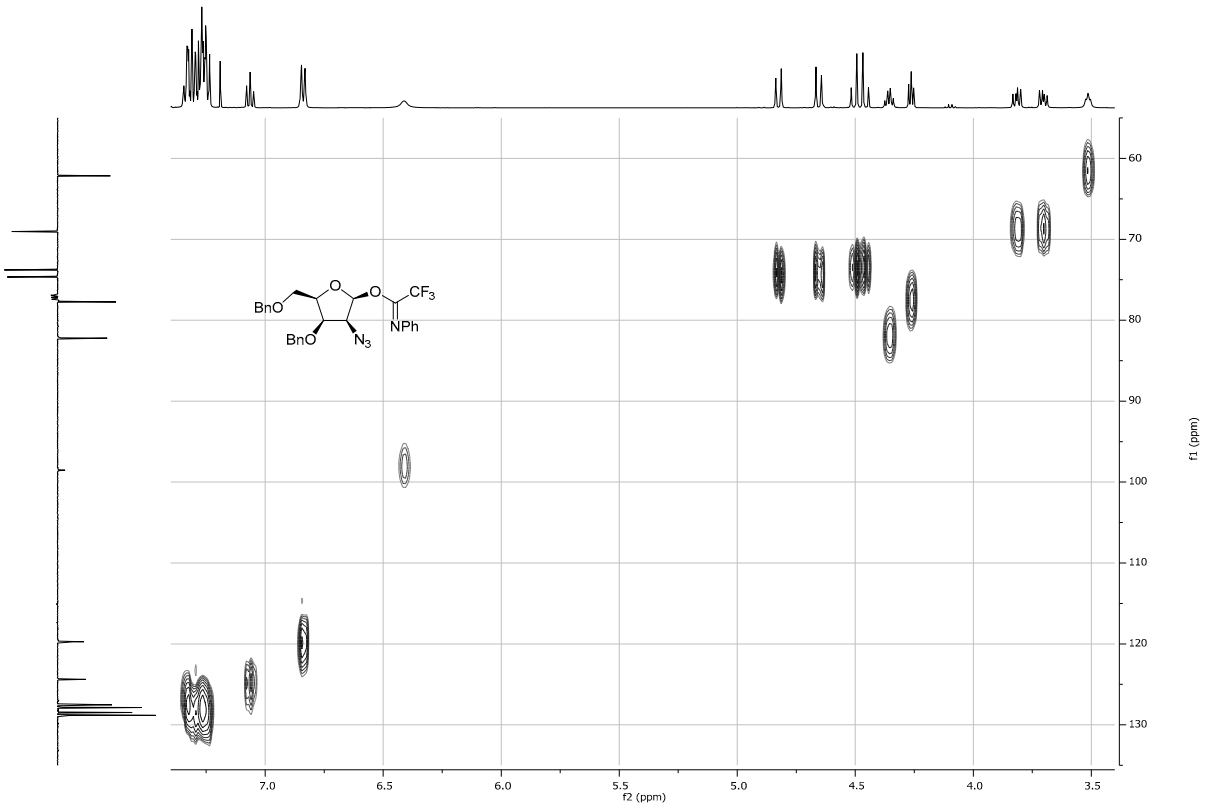
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **7β**



^{1}H-^{1}H COSY of compound **7β**

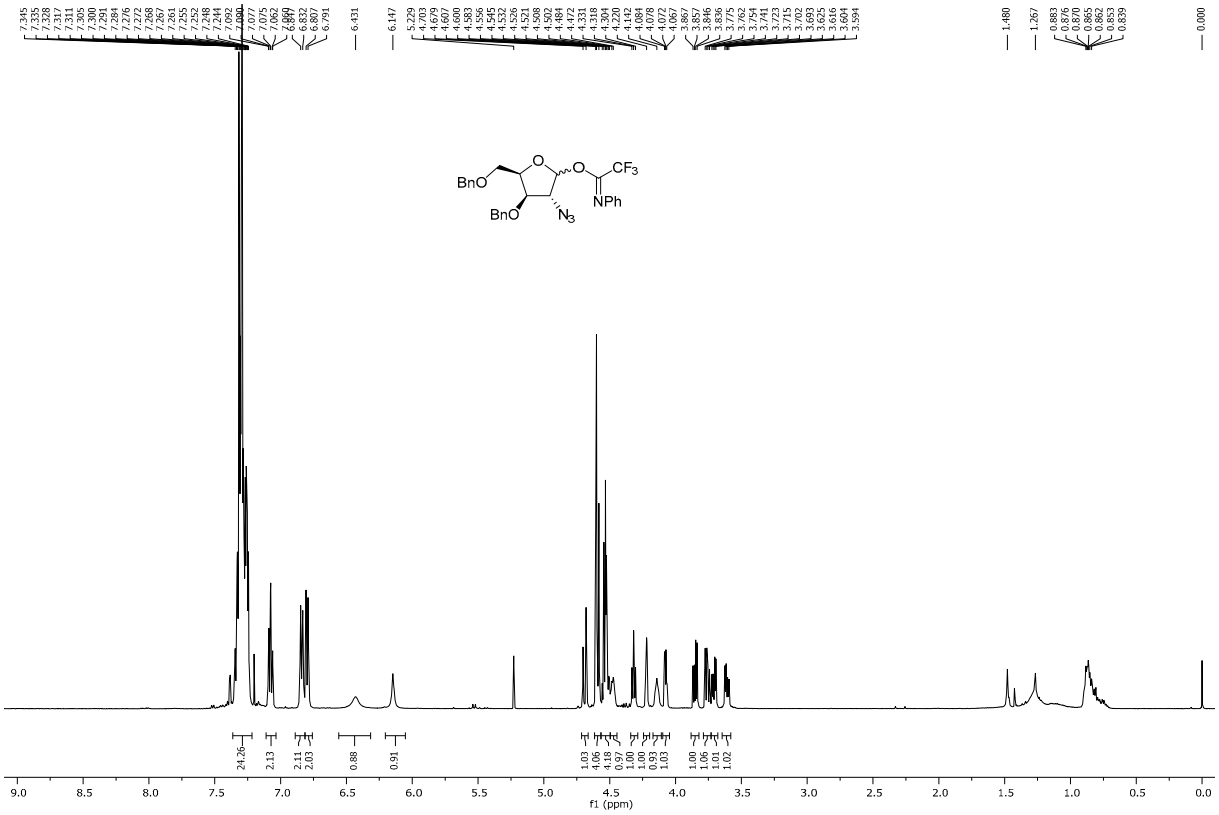


^{1}H-^{13}C HSQC of compound **7β**

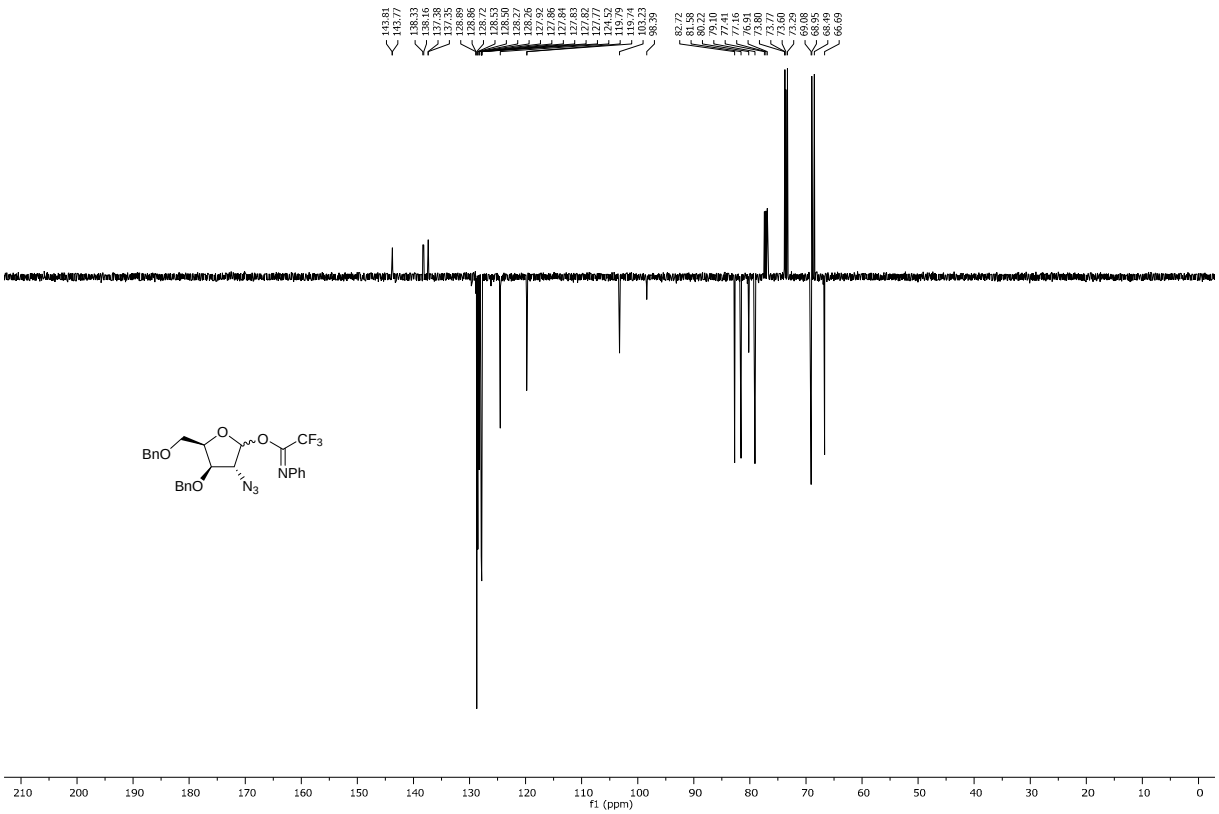


2-azido-3,5-di-*O*-benzyl-2-deoxy-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-xylofuranoside (8). [*T* = 323 K]

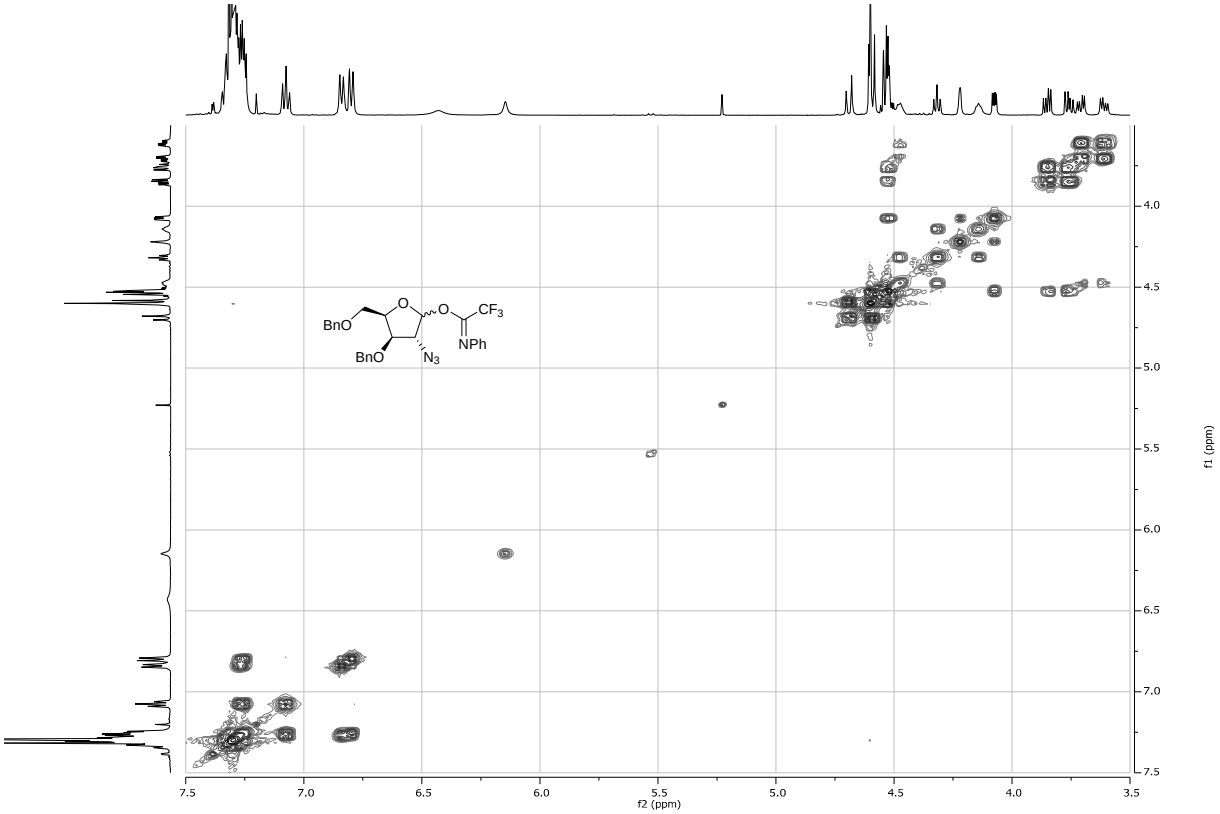
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **8**



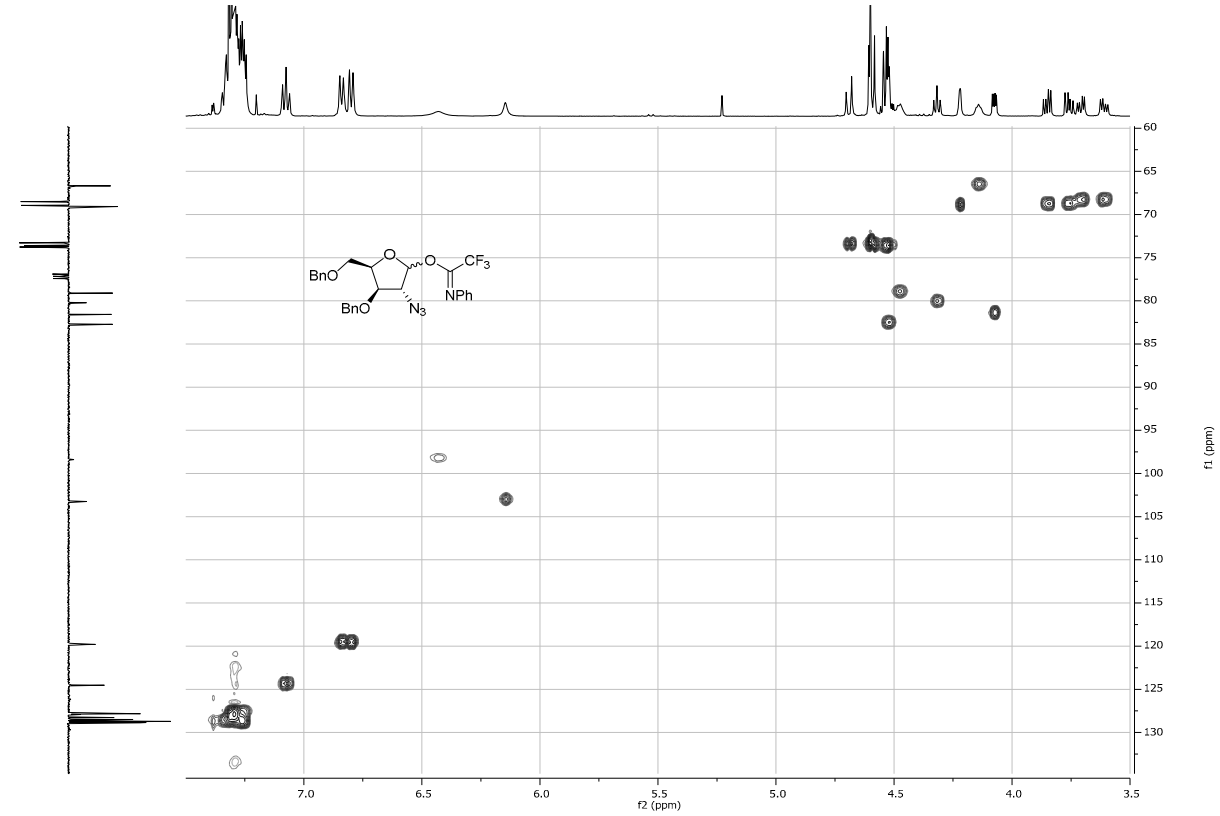
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **8**



^{1}H-^{1}H COSY of compound **8**

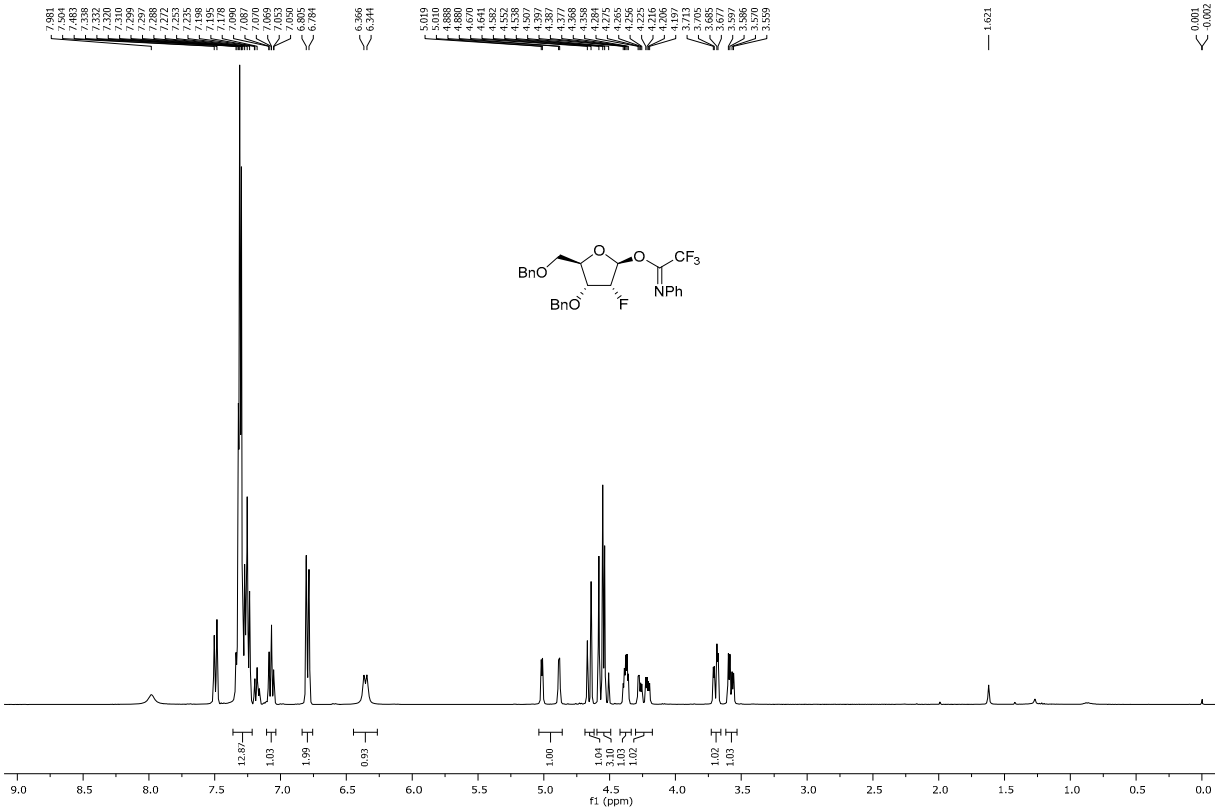


^{1}H-^{13}C HSQC of compound **8**

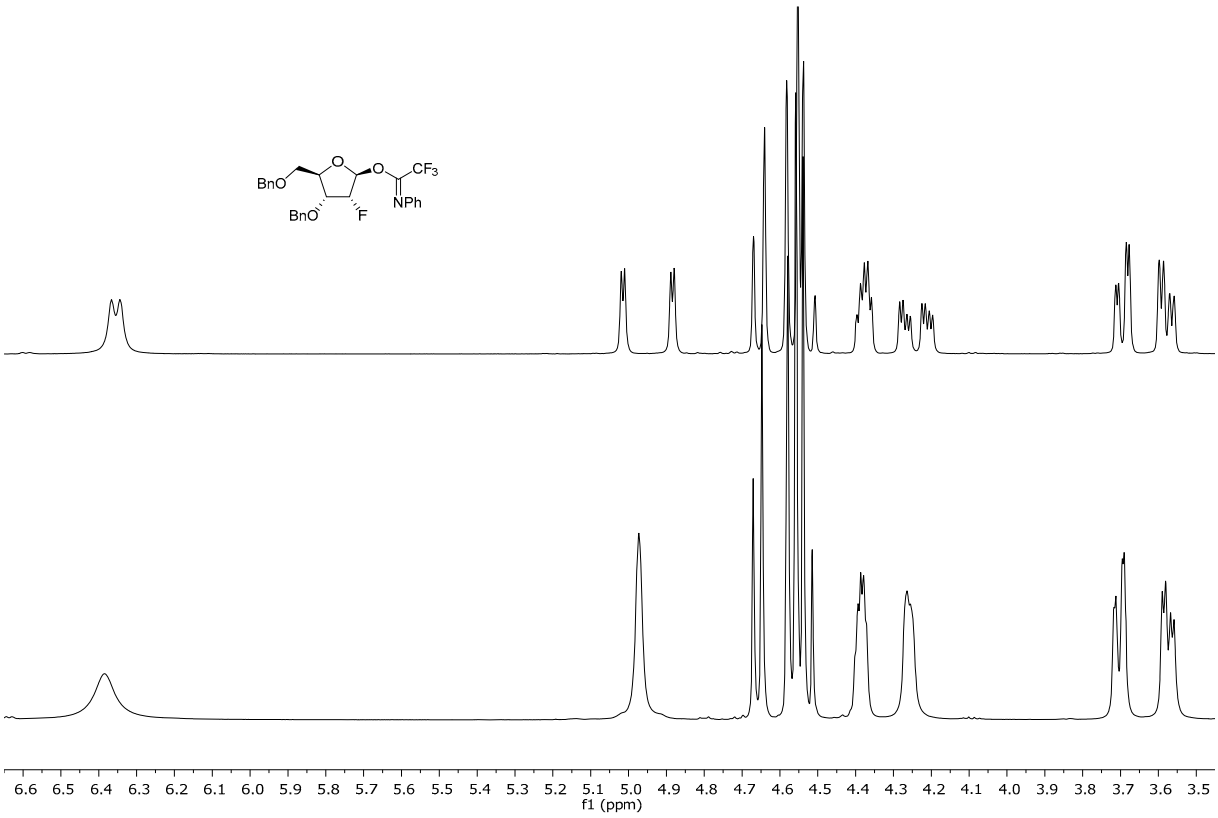


3,5-di-*O*-benzyl-2-deoxy-2-fluoro-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-β-D-ribofuranoside (9β). [*T* = 323 K]

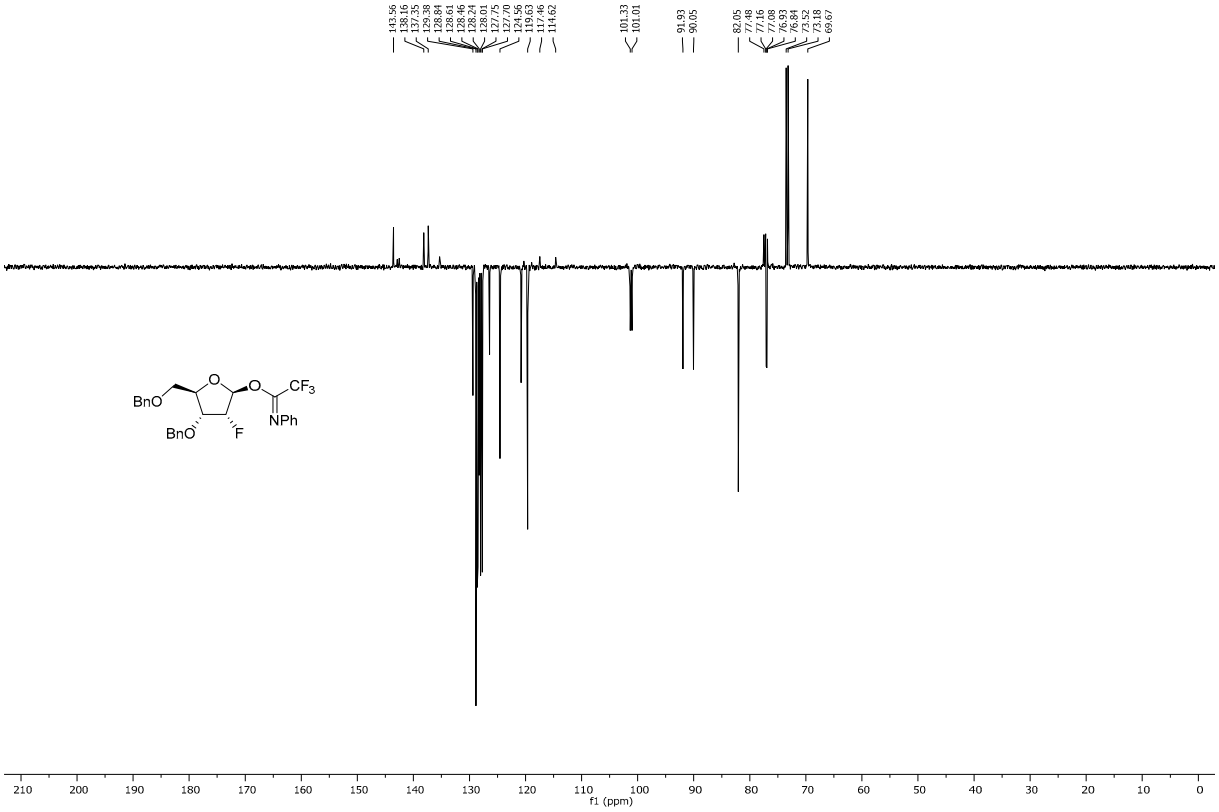
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **9β**



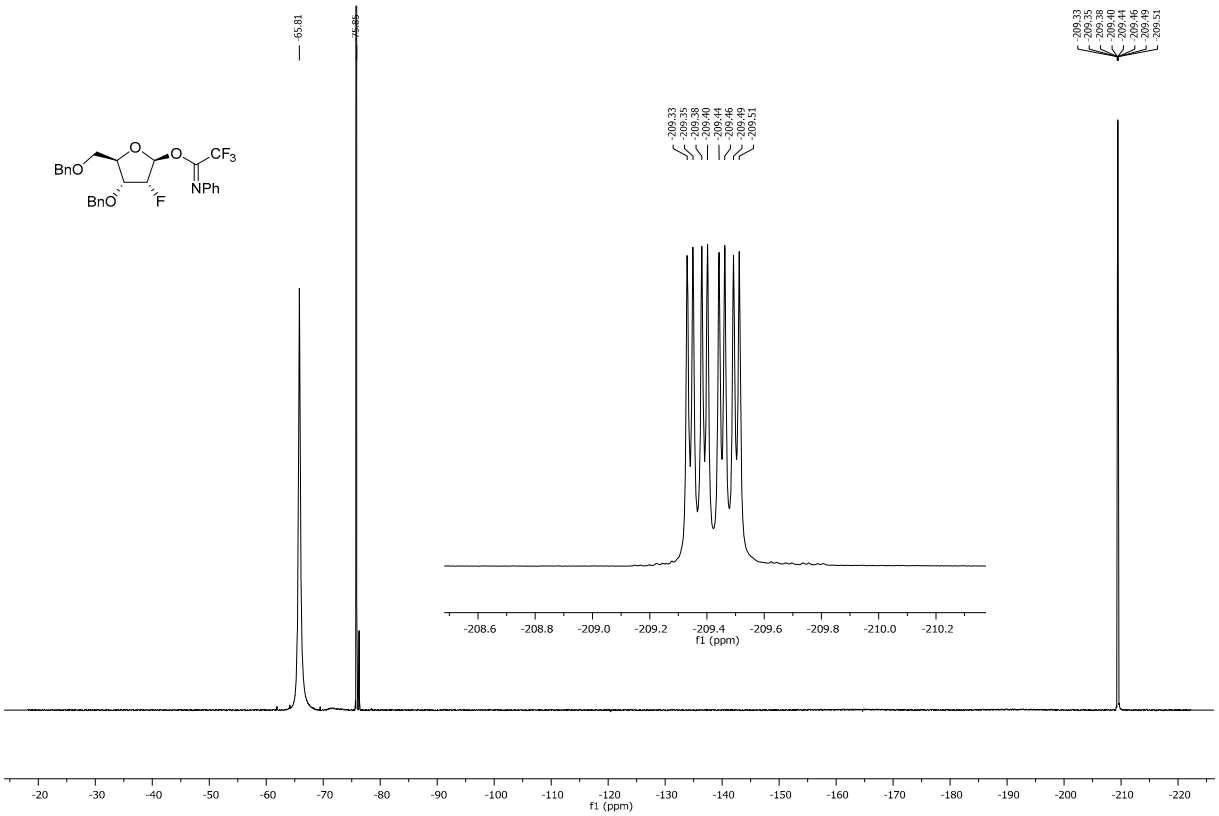
^{19}F-decoupled ^{1}H NMR, (-200 ppm), T = 298 K



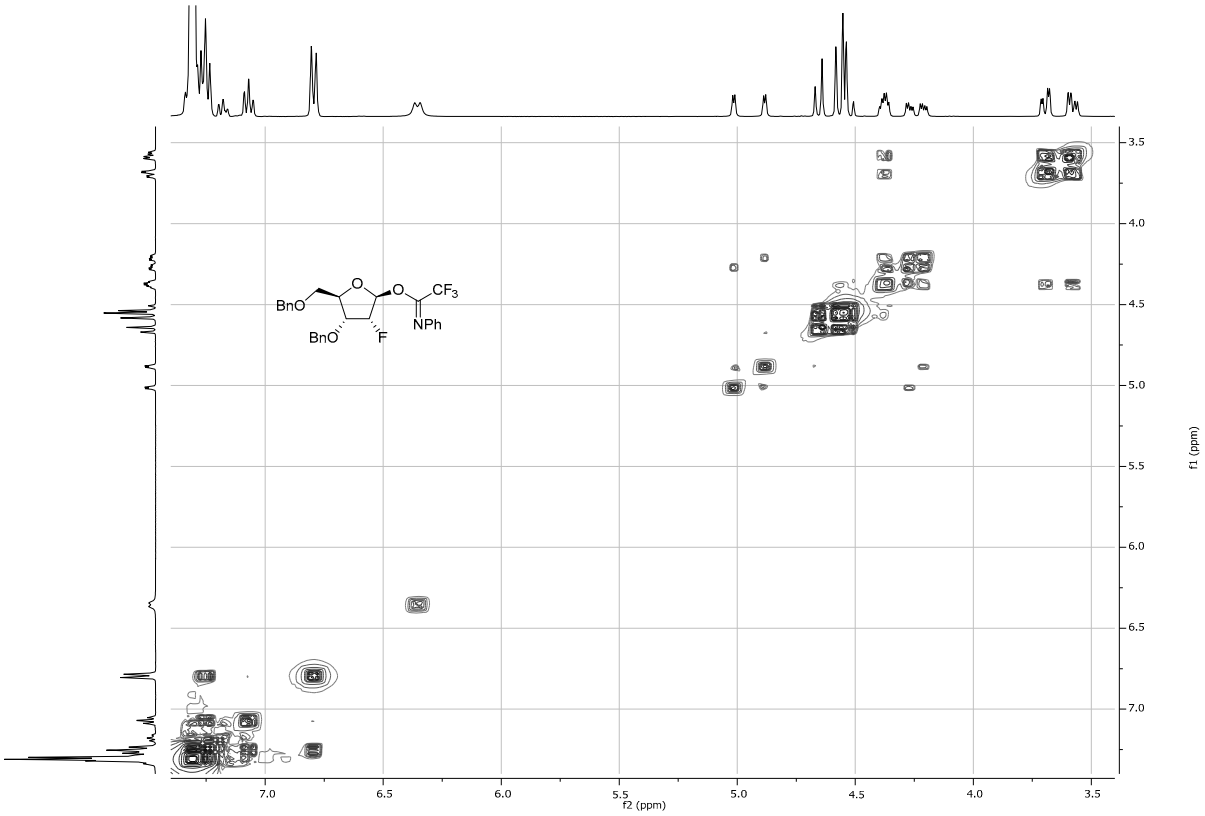
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **9β**



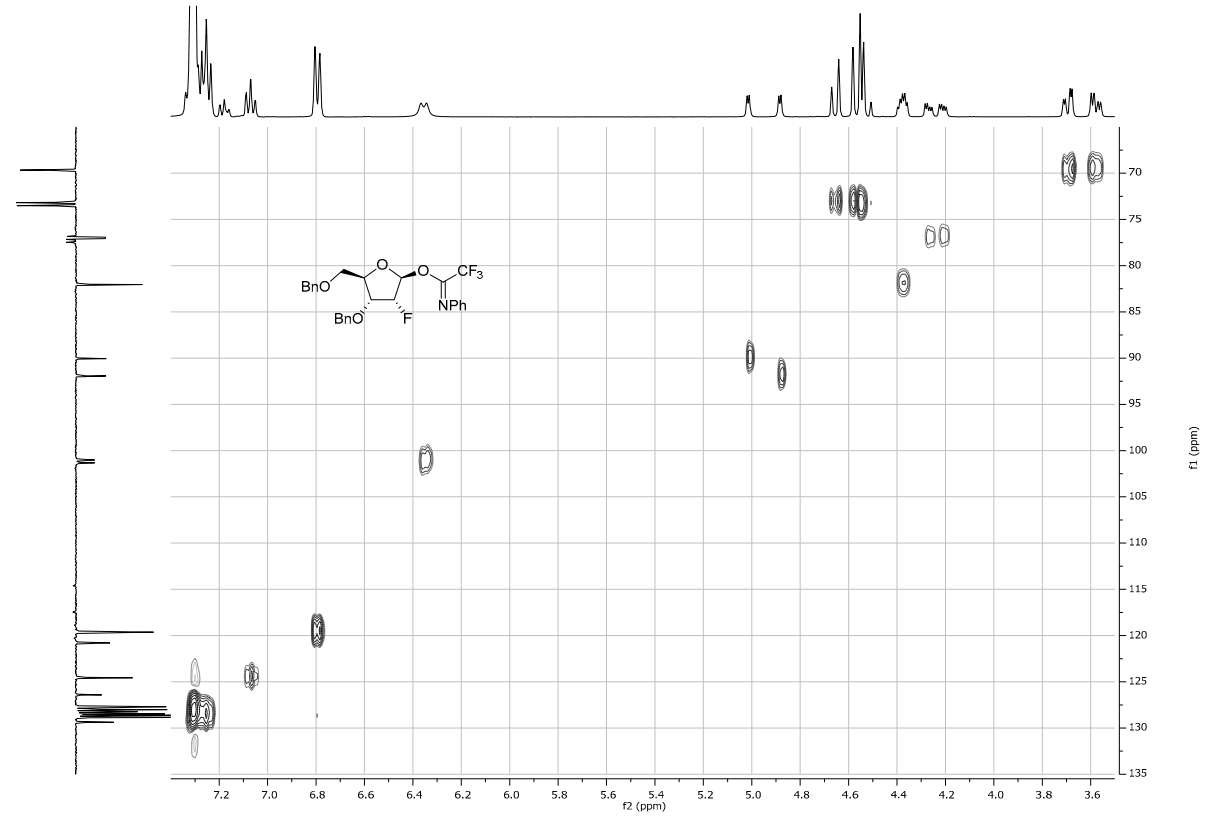
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **9β**



^{1}H-^{1}H COSY of compound **9β**

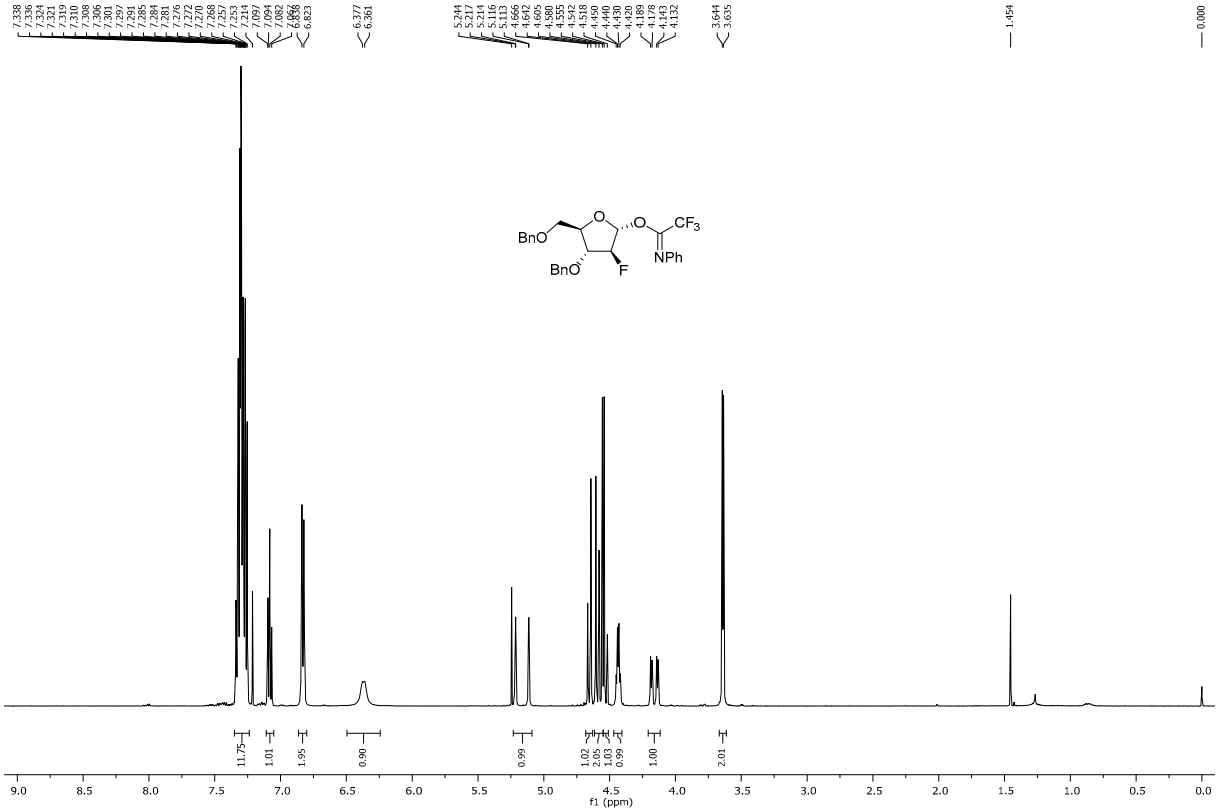


^{1}H-^{13}C HSQC of compound **9β**

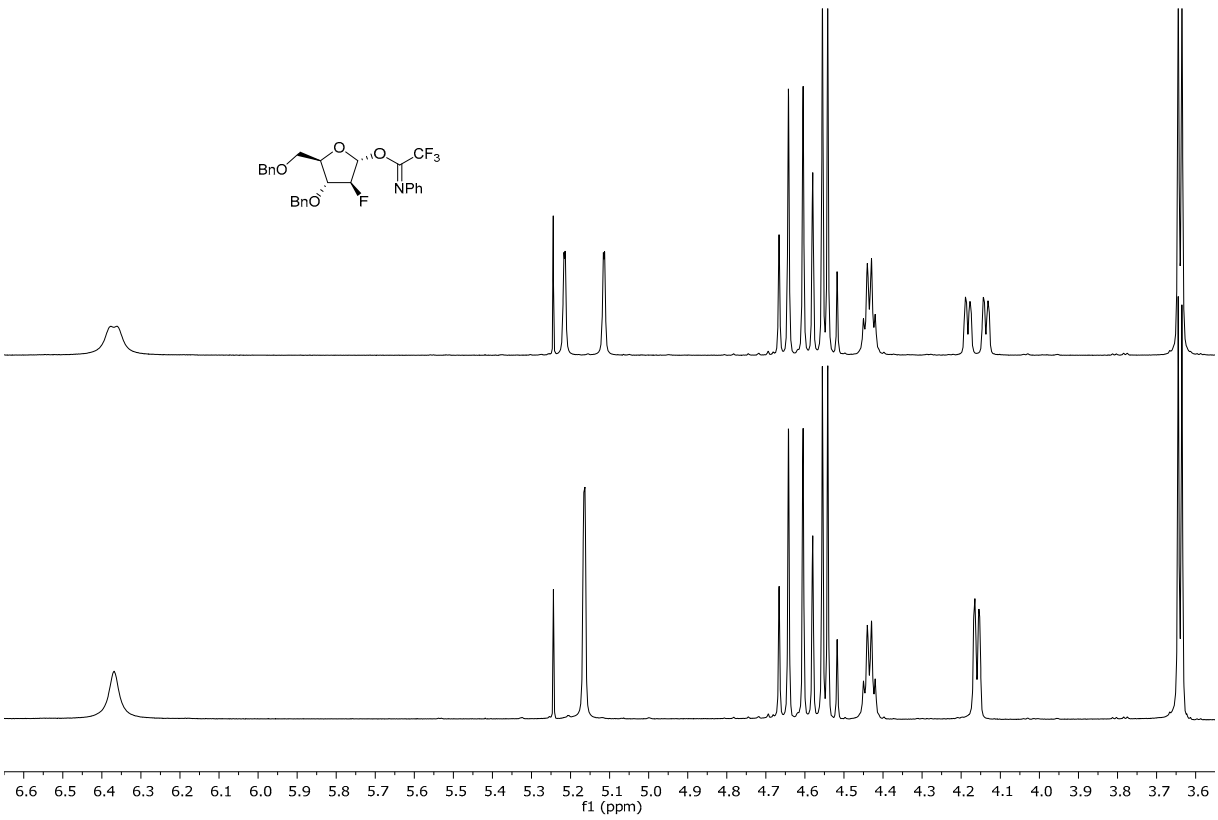


3,5-di-*O*-benzyl-2-deoxy-2-fluoro-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α-D-arabinofuranoside (10α) [*T* = 323 K]

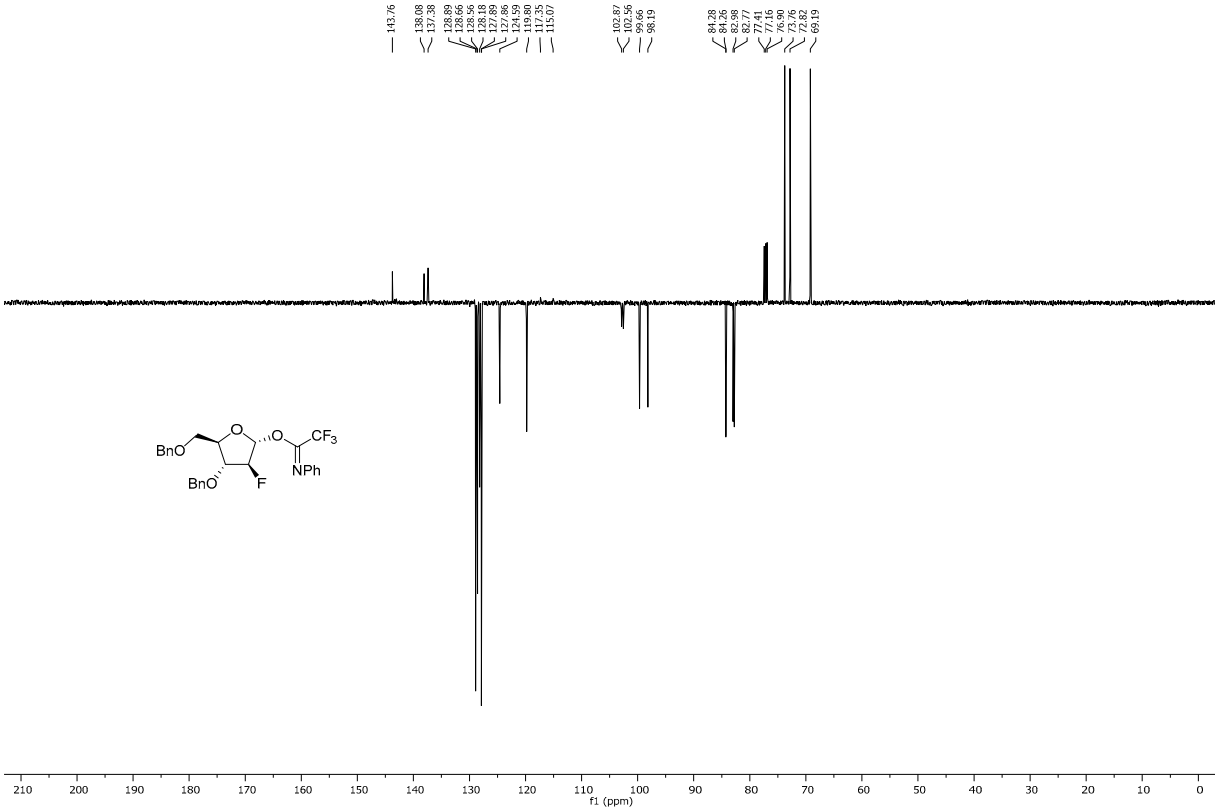
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **10α**



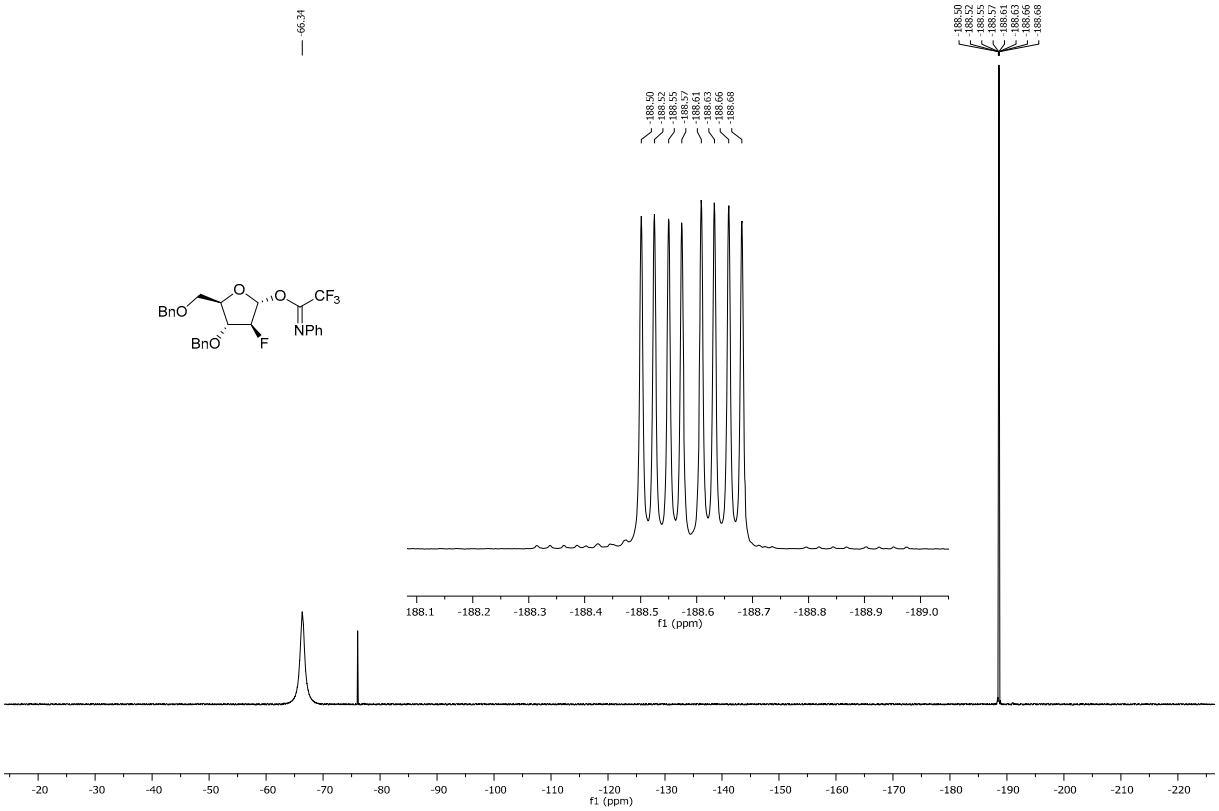
^{19}F-decoupled ^{1}H NMR, (-188 ppm)



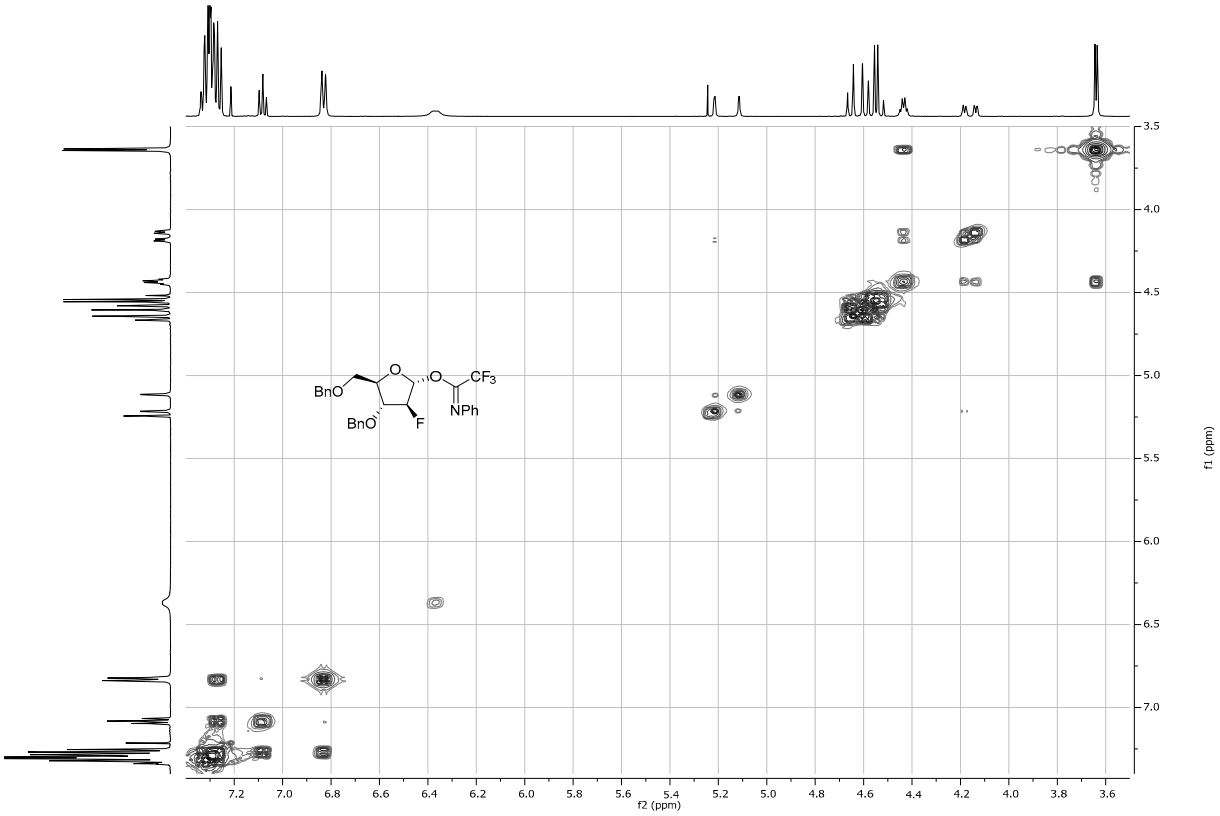
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **10α**



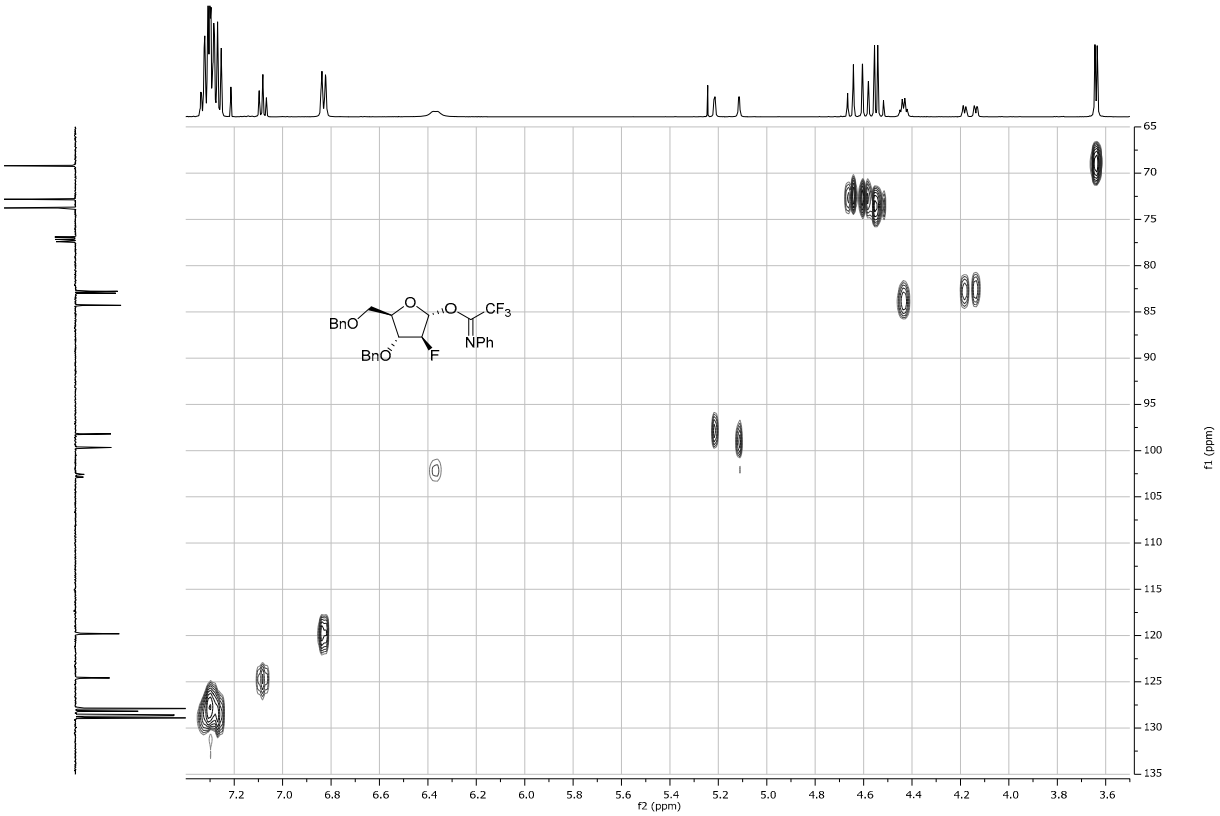
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **10α**



^{1}H-^{1}H COSY of compound **10α**

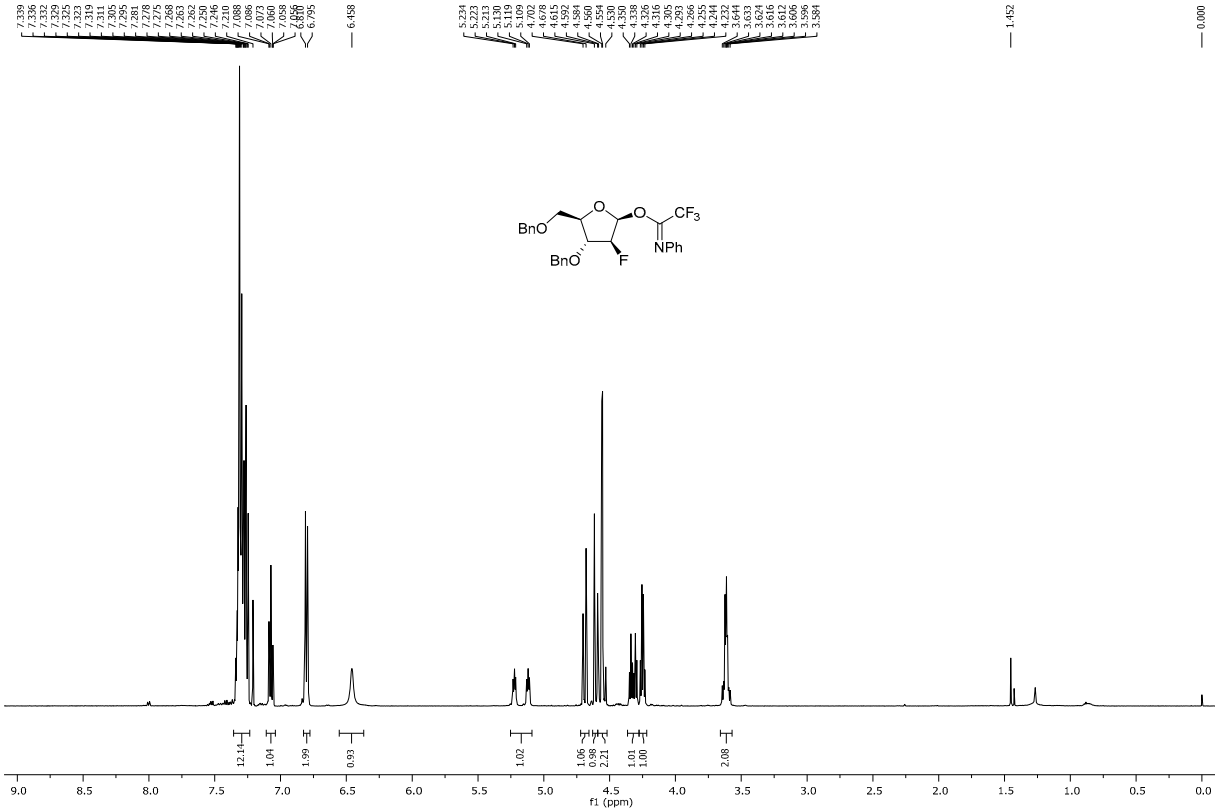


^{1}H-^{13}C HSQC of compound **10α**

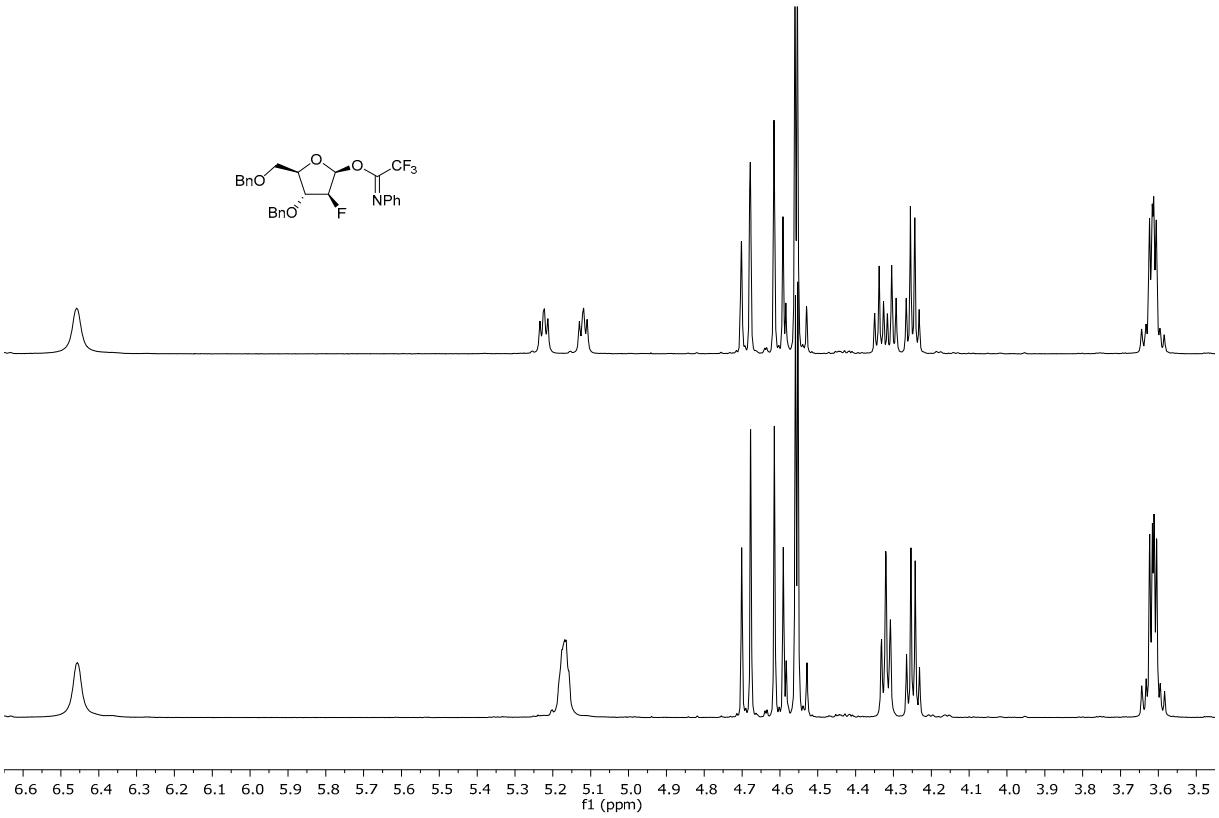


3,5-di-*O*-benzyl-2-deoxy-2-fluoro-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-β-D-arabinofuranoside (10β) [*T* = 323 K]

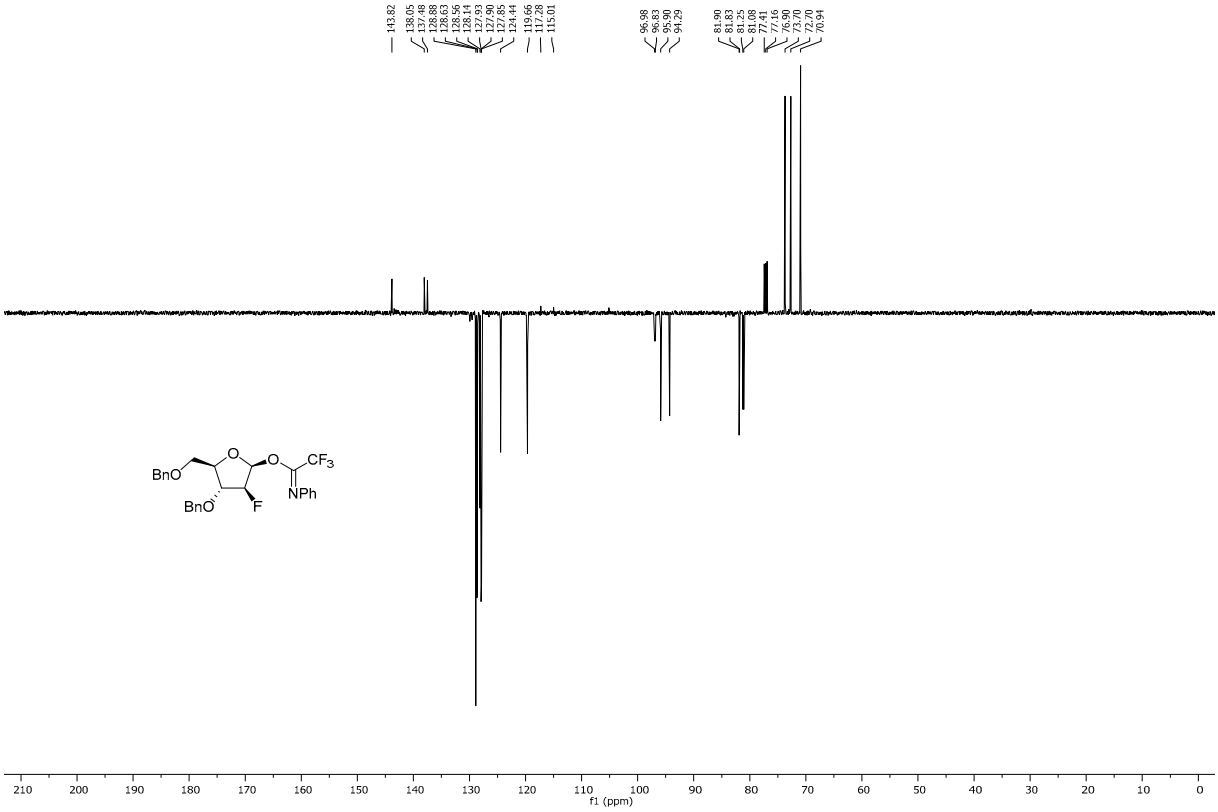
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **10β**



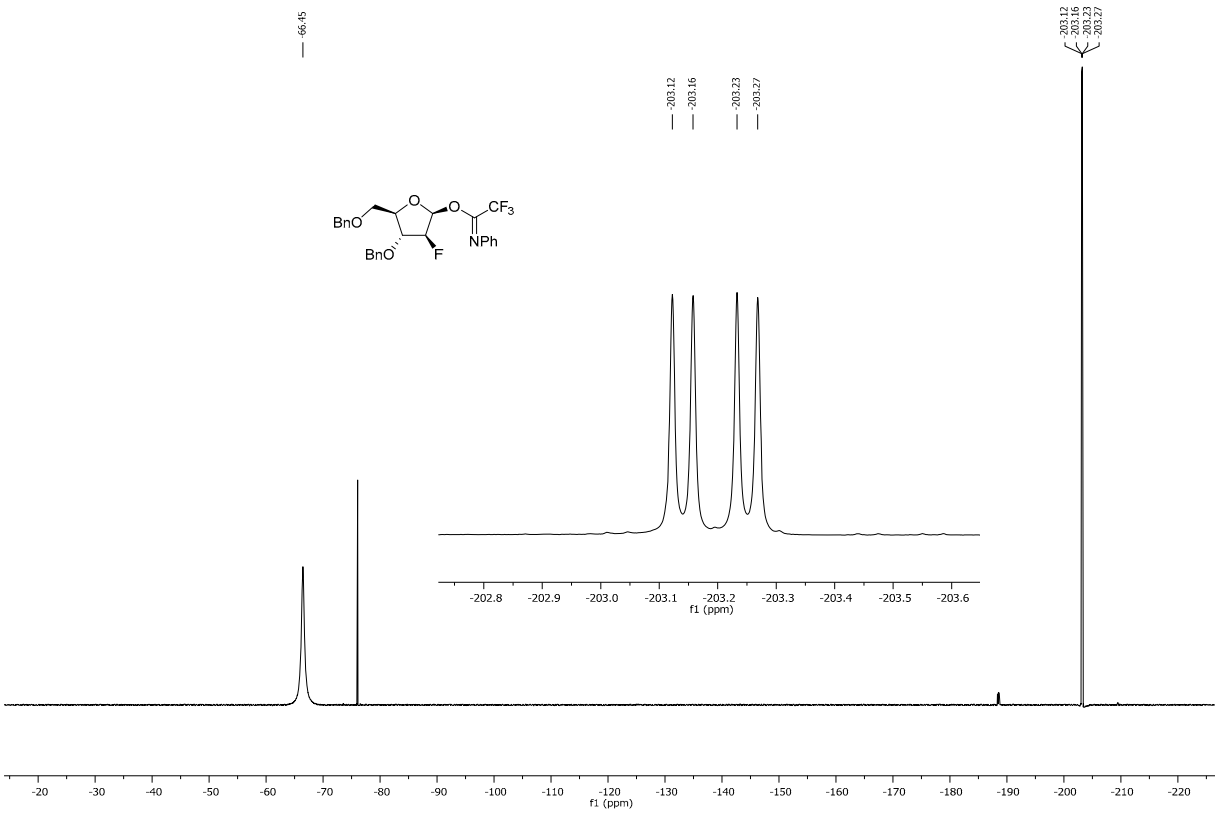
^{19}F-decoupled ^{1}H NMR, (-200 ppm)



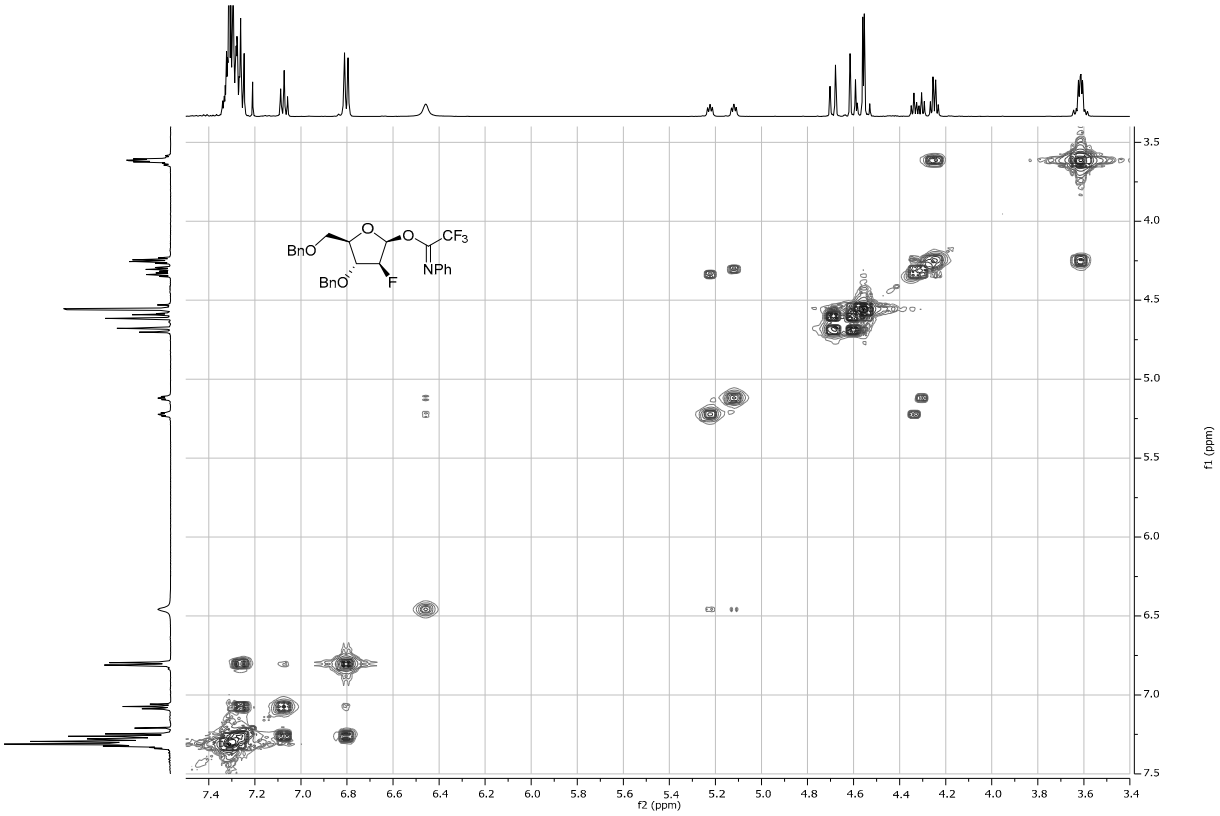
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **10β**



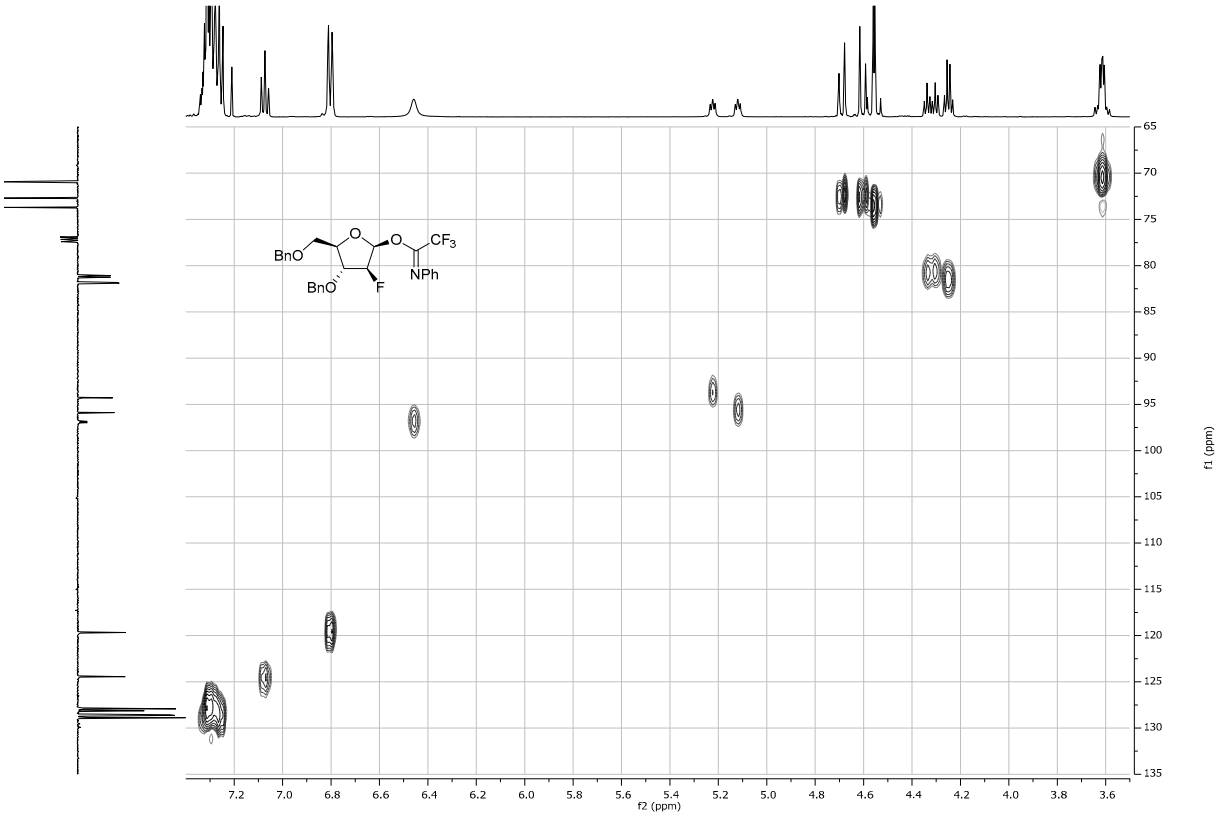
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **10β**



^{1}H-^{1}H COSY of compound **10β**

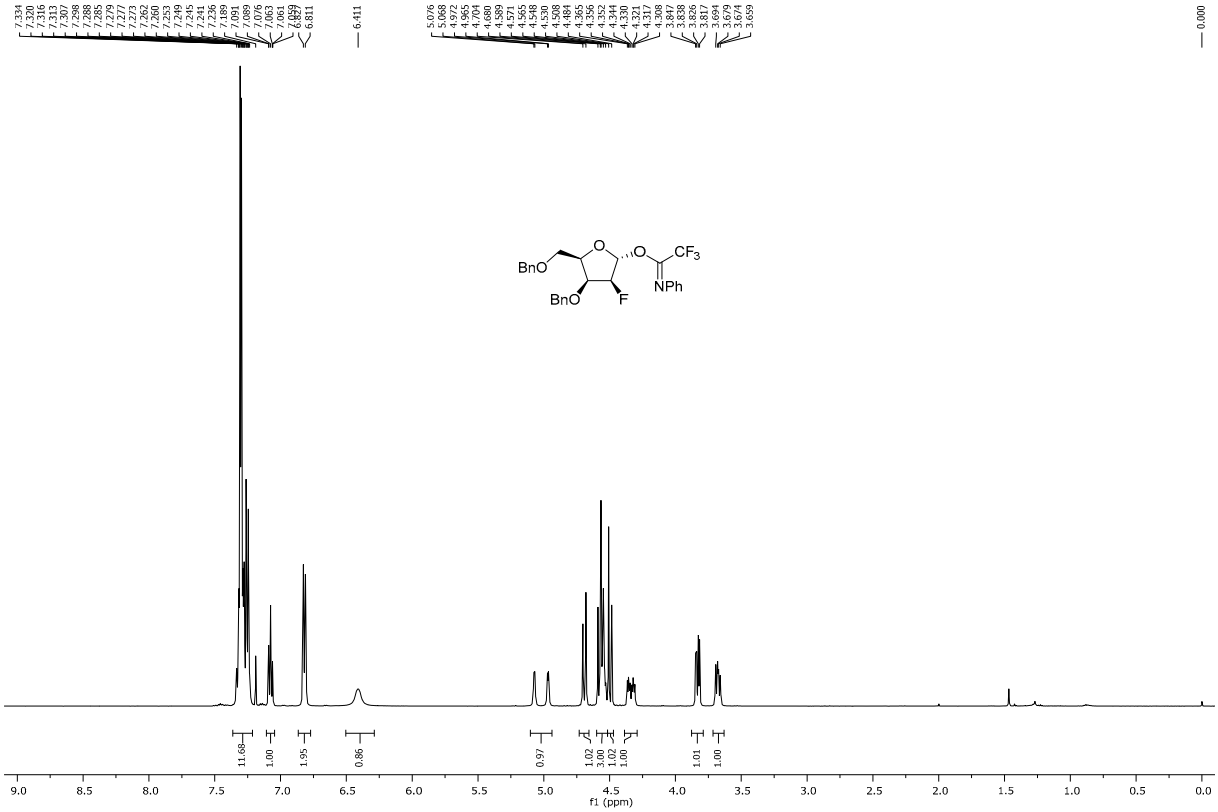


^{1}H-^{13}C HSQC of compound **10β**

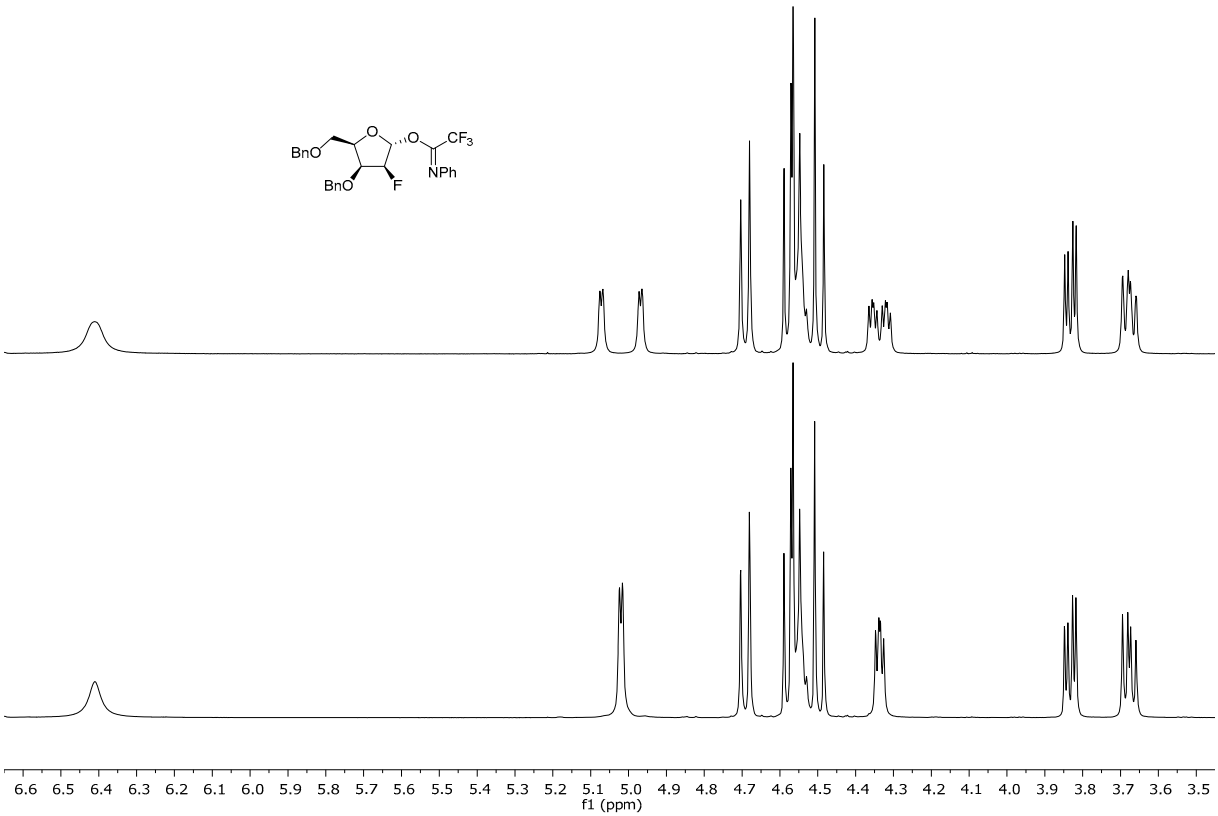


3,5-di-*O*-benzyl-2-deoxy-2-fluoro-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α-D-lyxofuranoside (11α) [*T* = 323 K]

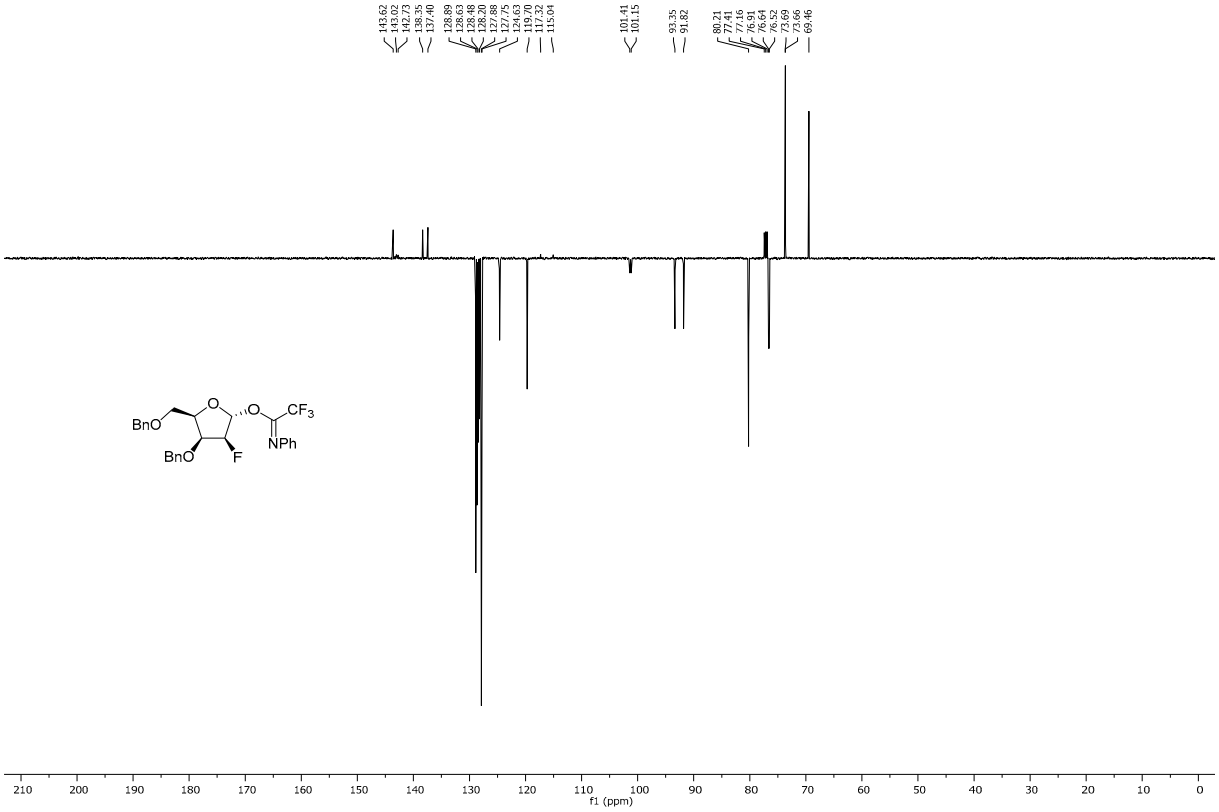
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **11α**



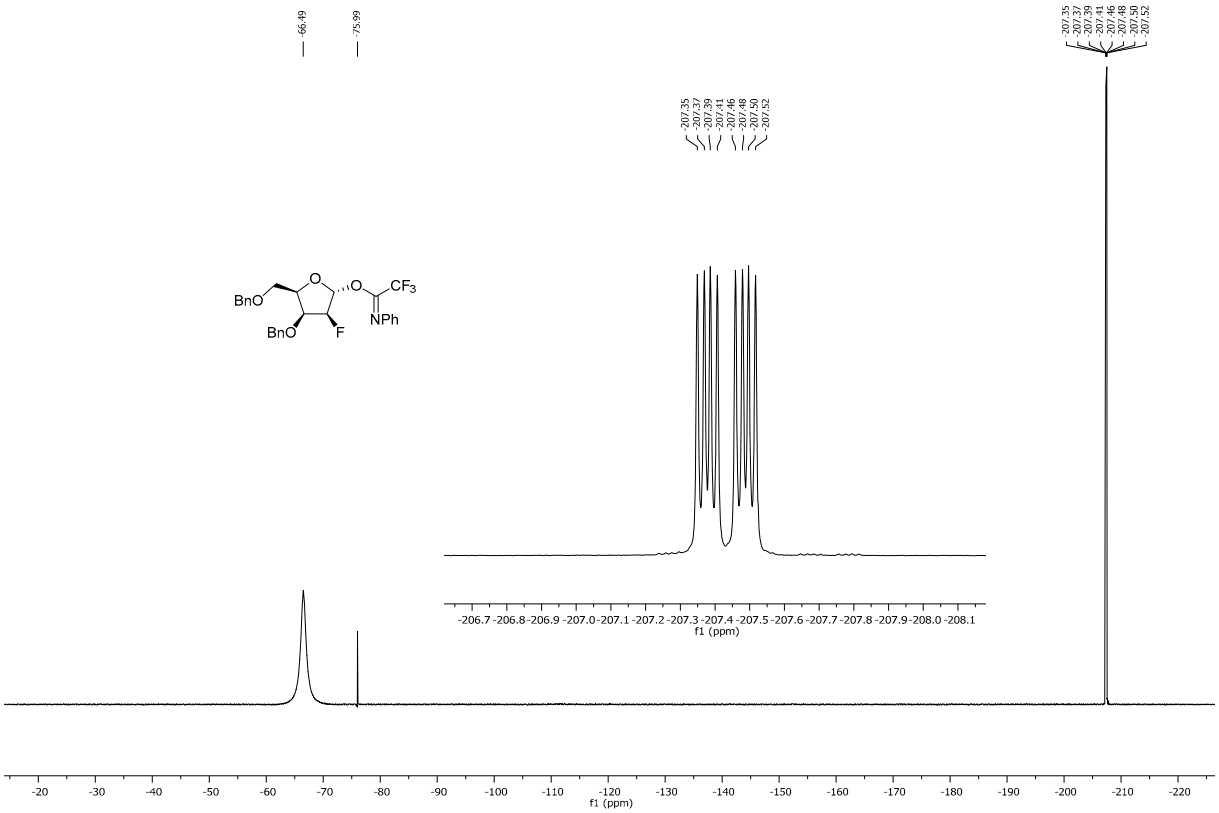
^{19}F-decoupled ^{1}H NMR, (-207 ppm)



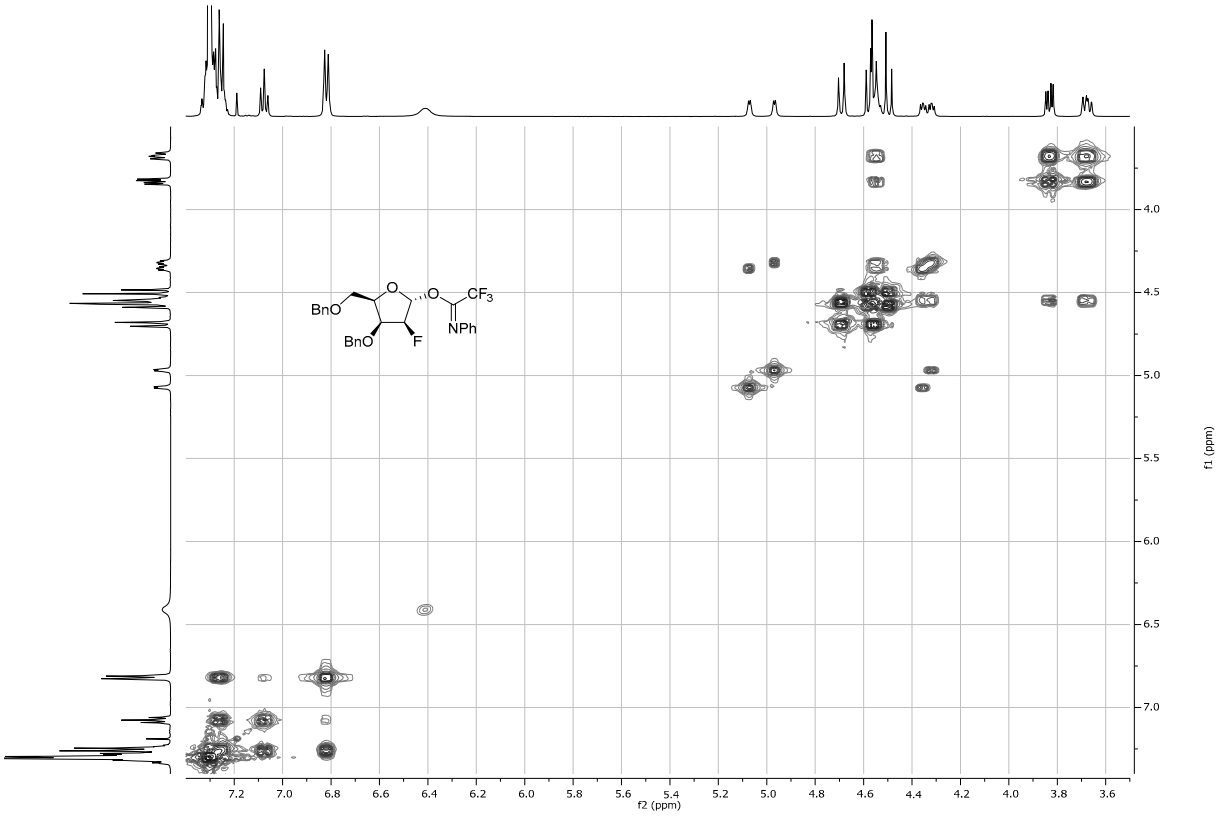
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **11α**



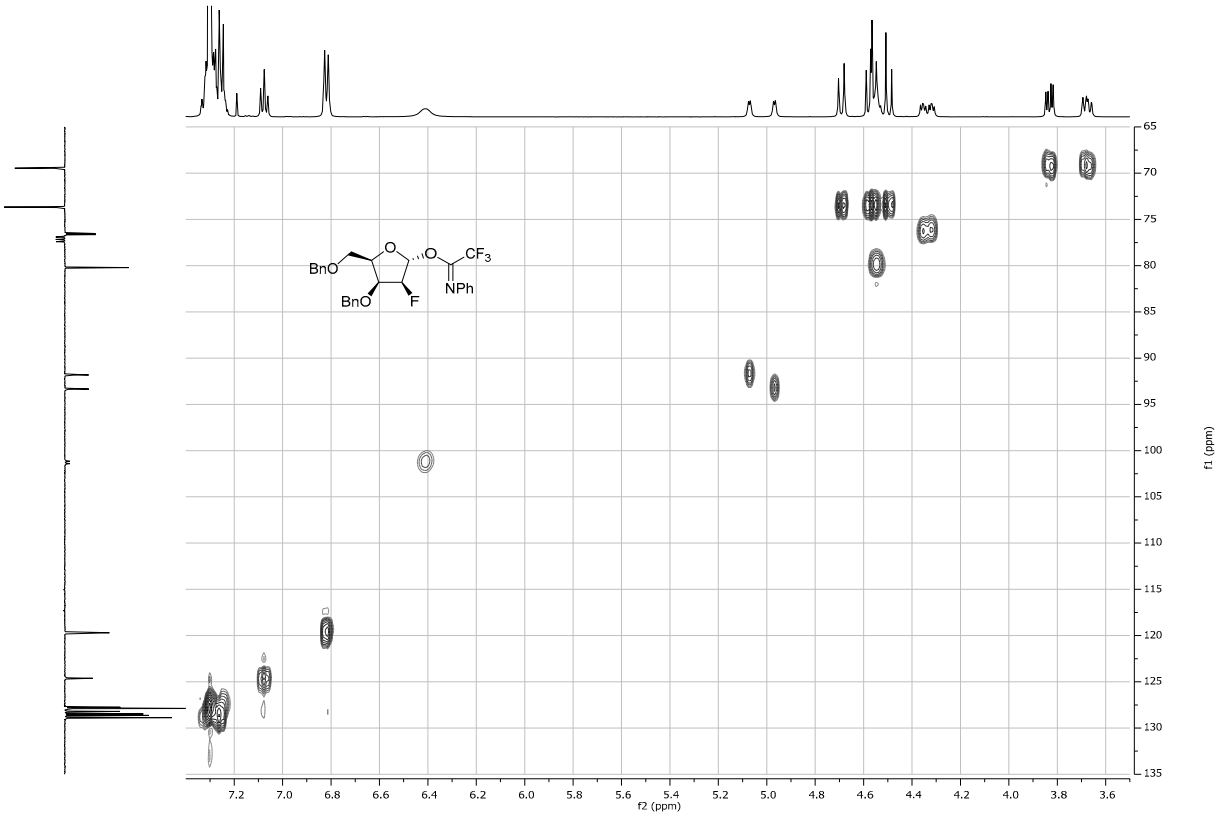
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **11α**



^{1}H-^{1}H COSY of compound **11α**

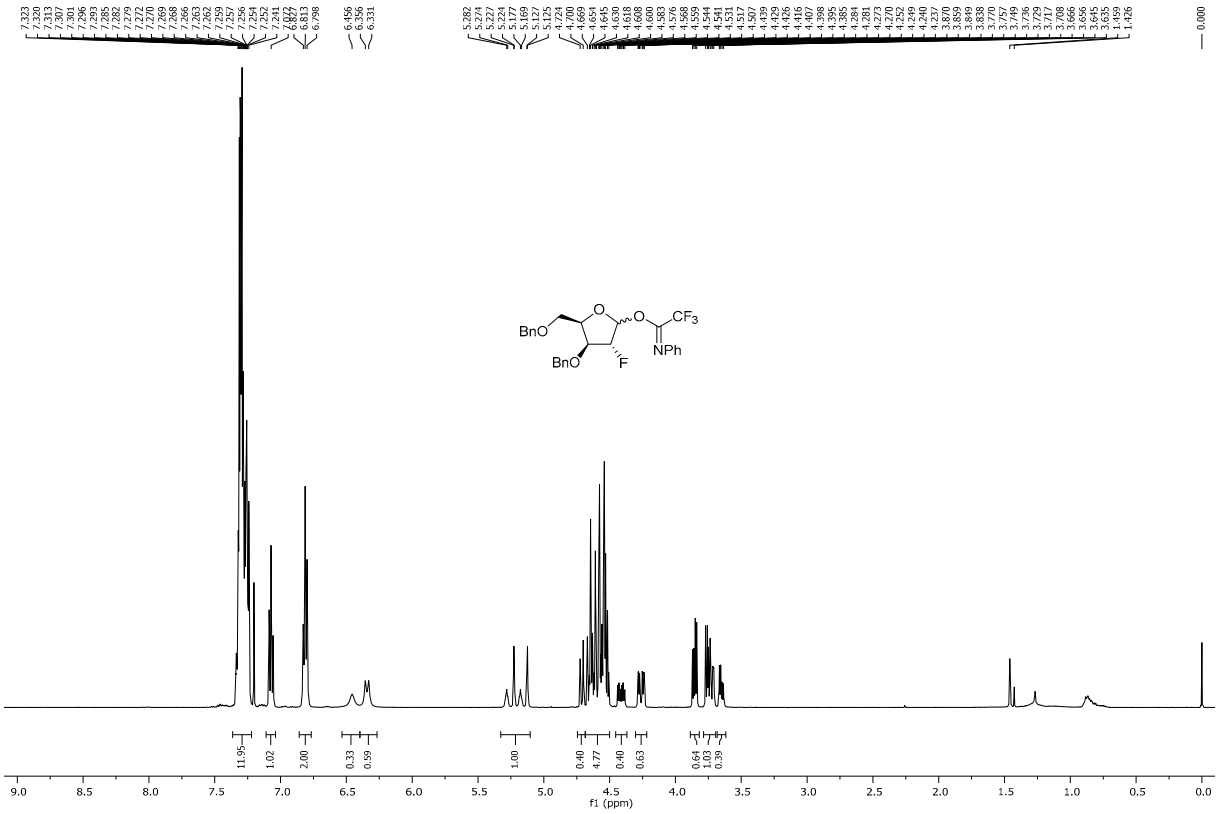


^{1}H-^{13}C HSQC of compound **11α**

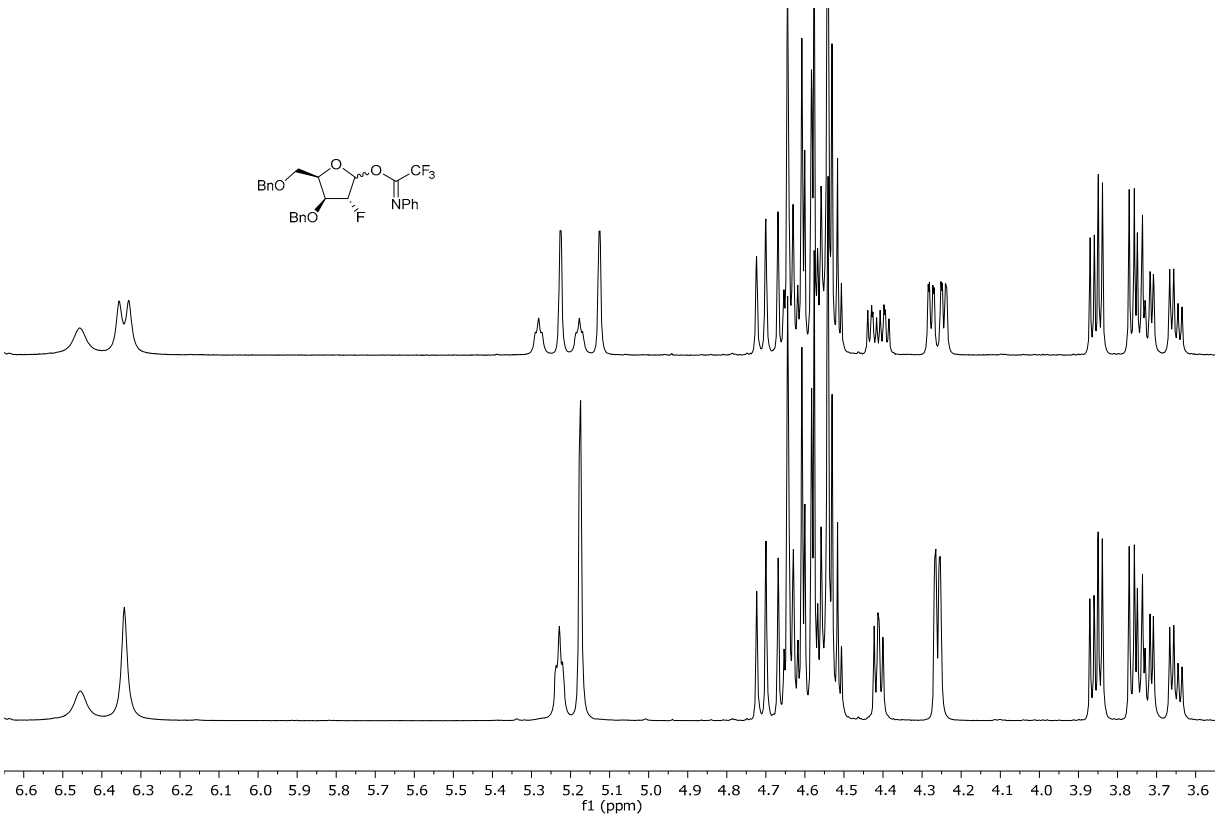


3,5-di-*O*-benzyl-2-deoxy-2-fluoro-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-xylofuranoside (12) [*T* = 323 K]

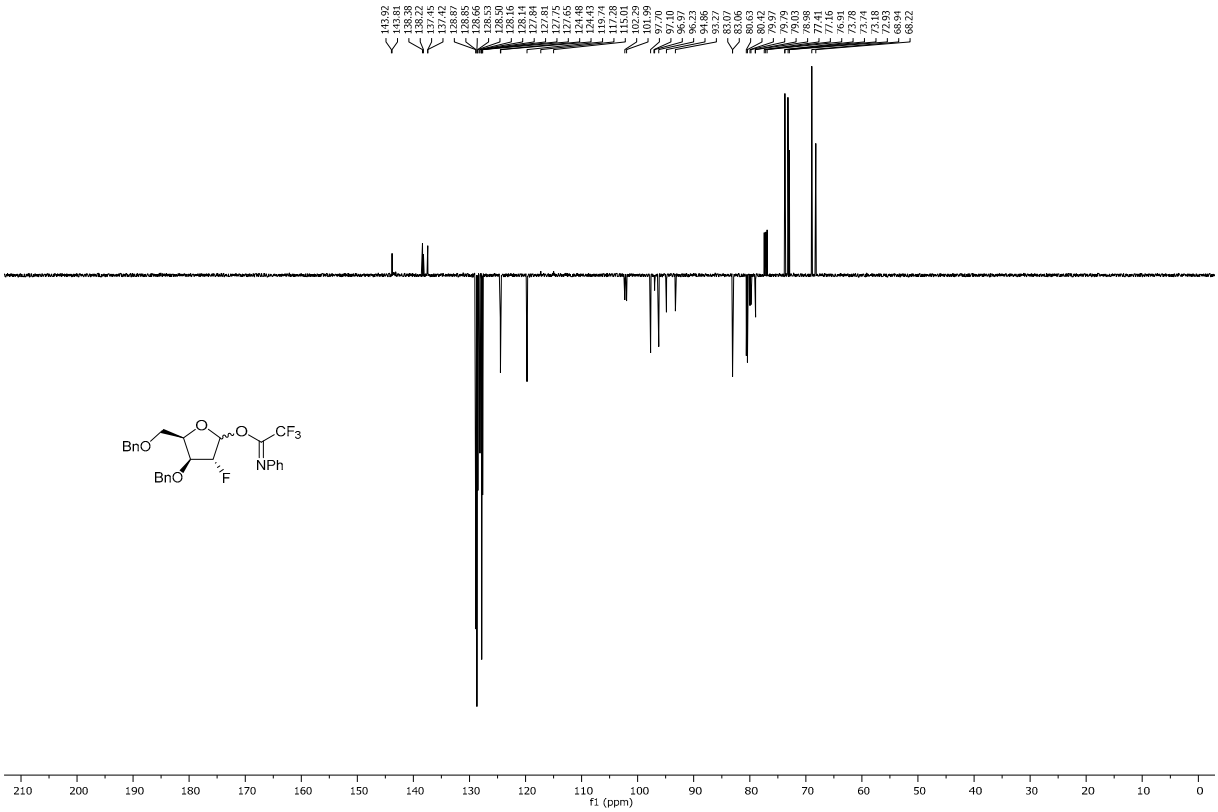
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **12**



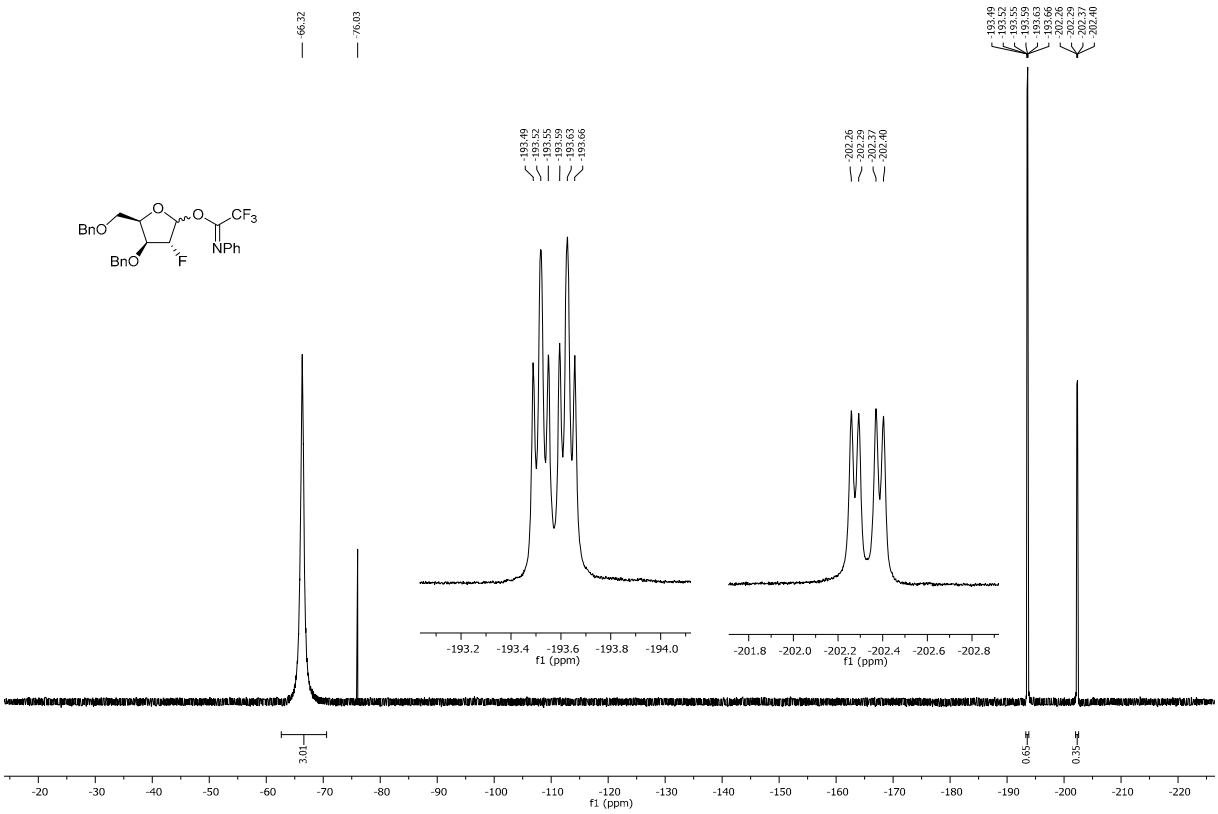
^{19}F-decoupled ^{1}H NMR, (-200 ppm)



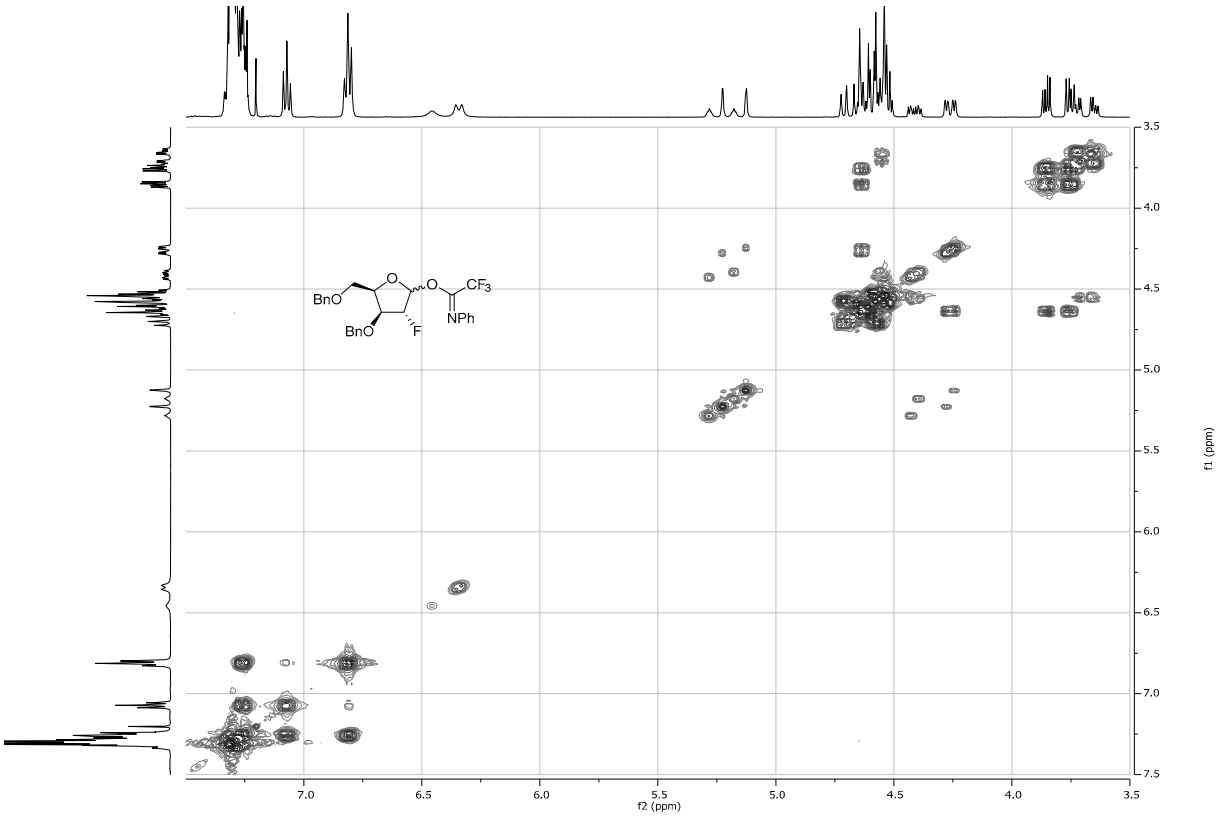
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **12**



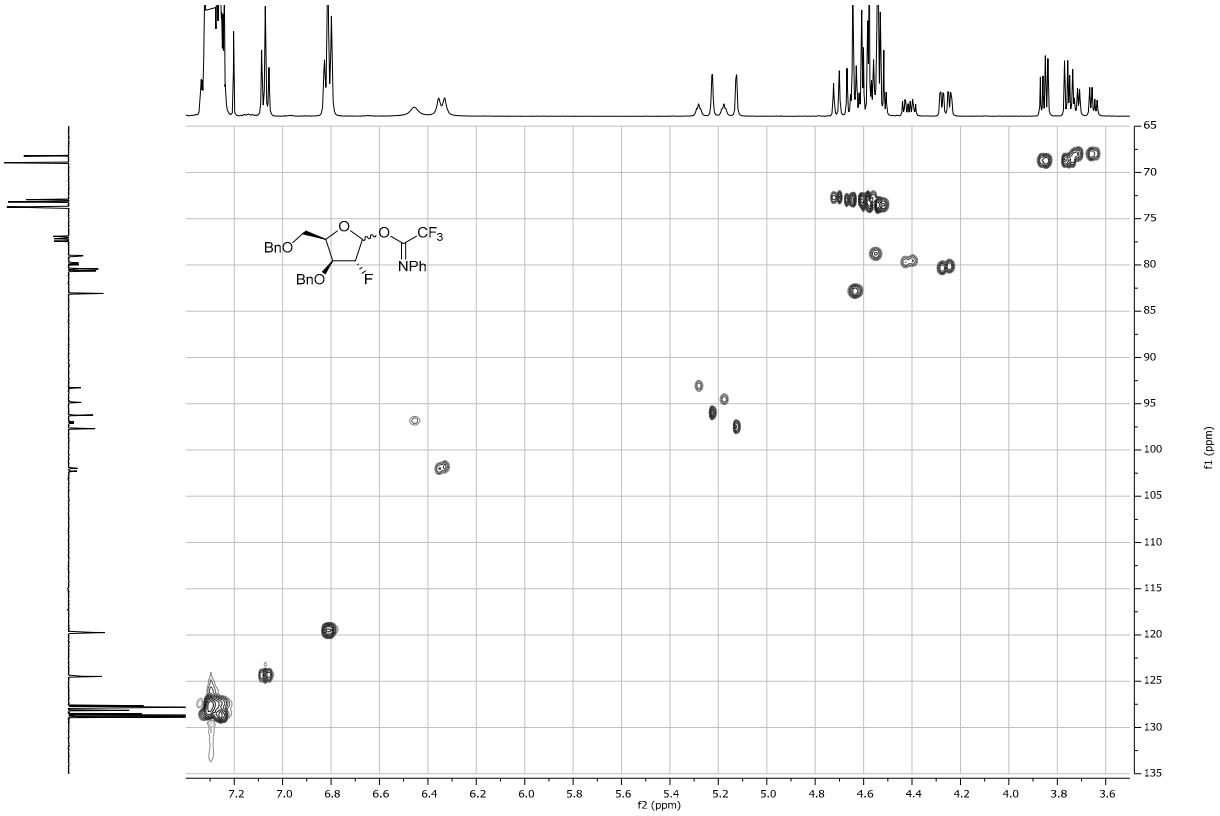
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **12**



^{1}H-^{1}H COSY of compound **12**

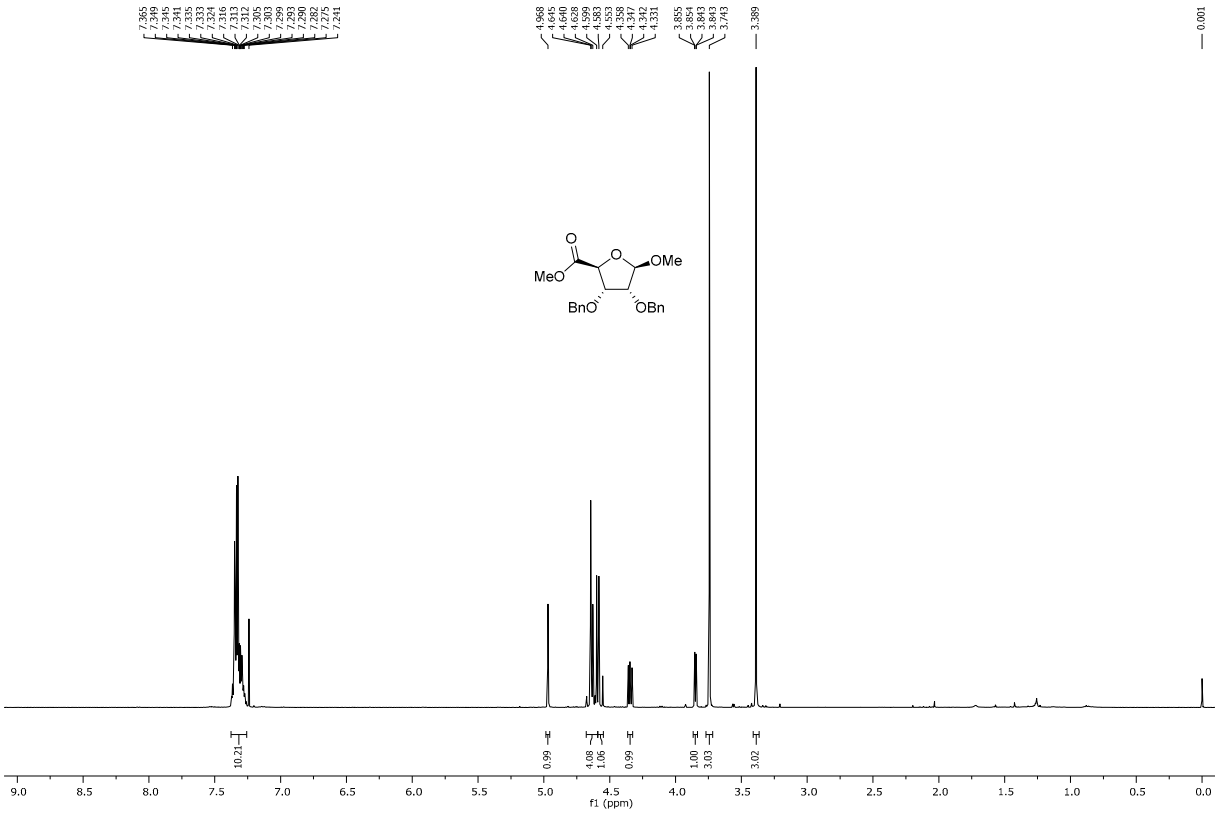


^{1}H-^{13}C HSQC of compound **12**

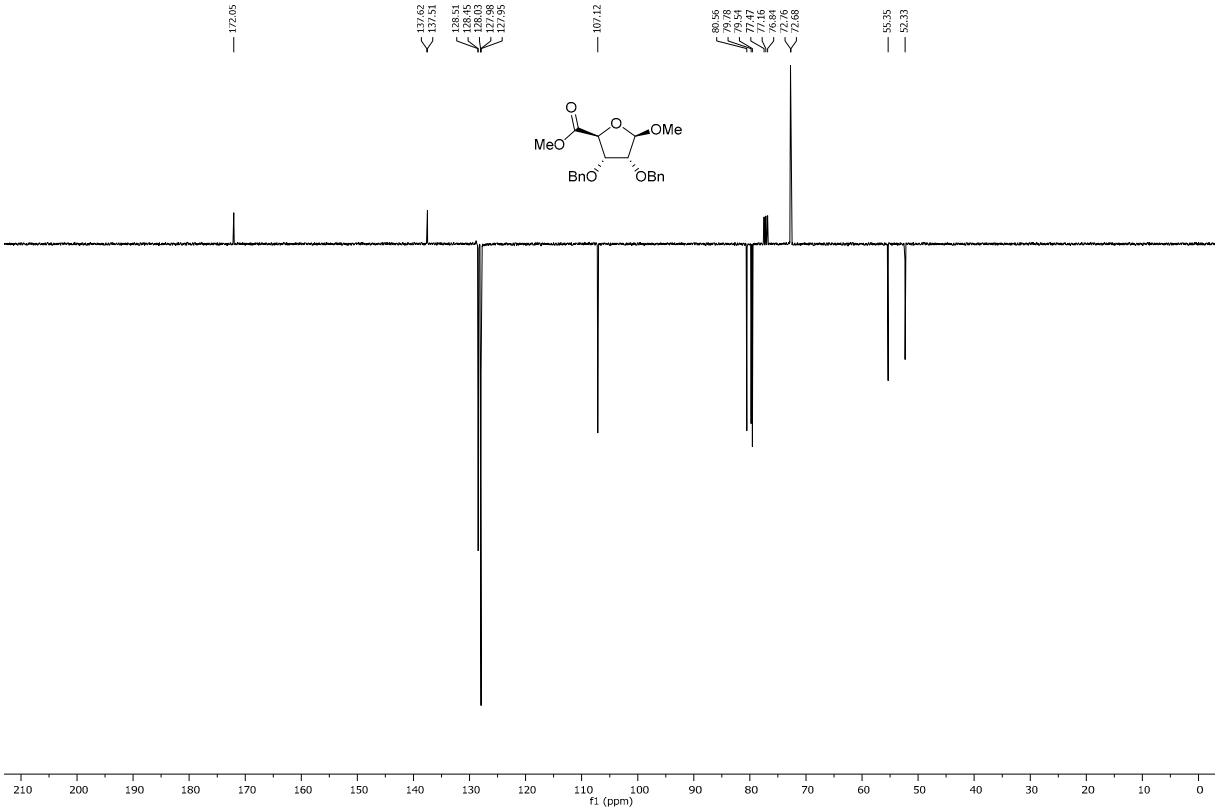


Methyl (methyl 2,3-di-*O*-benzyl-β-D-ribofuranosyl uronate) (17)

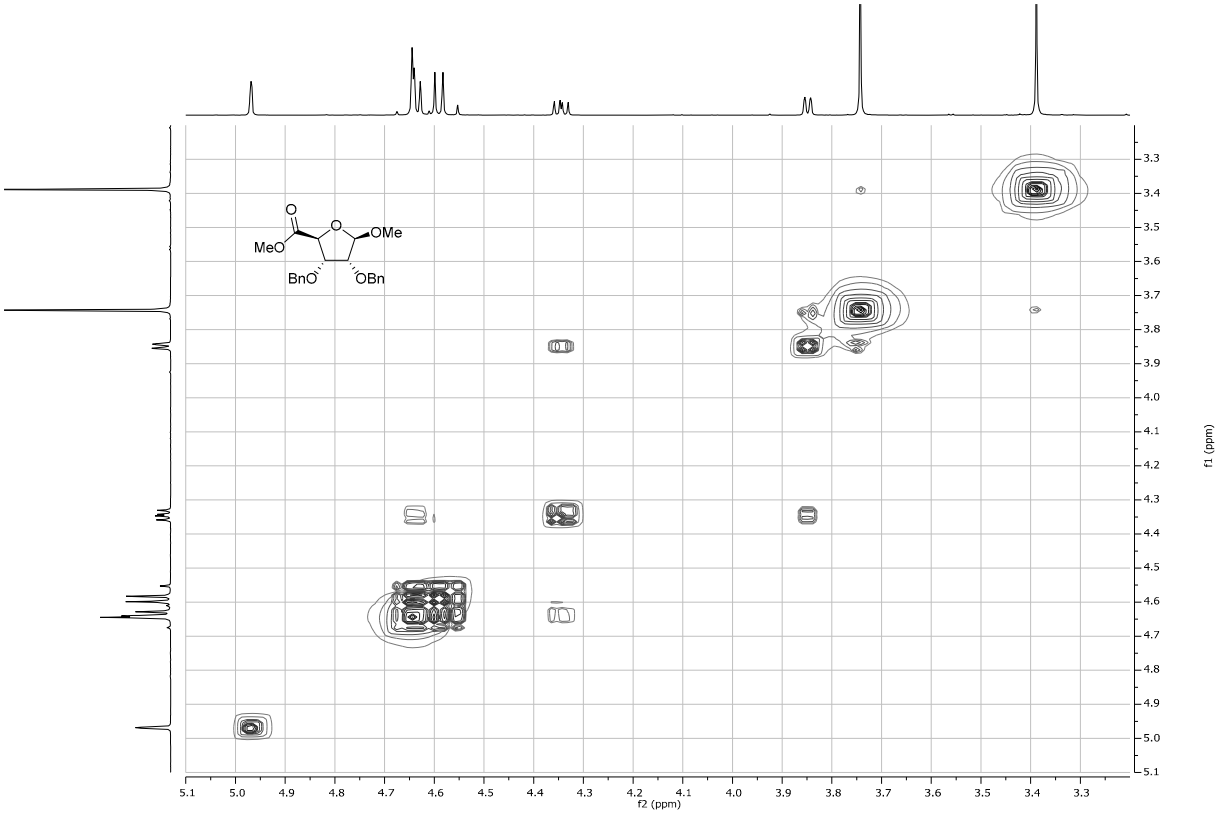
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **17**



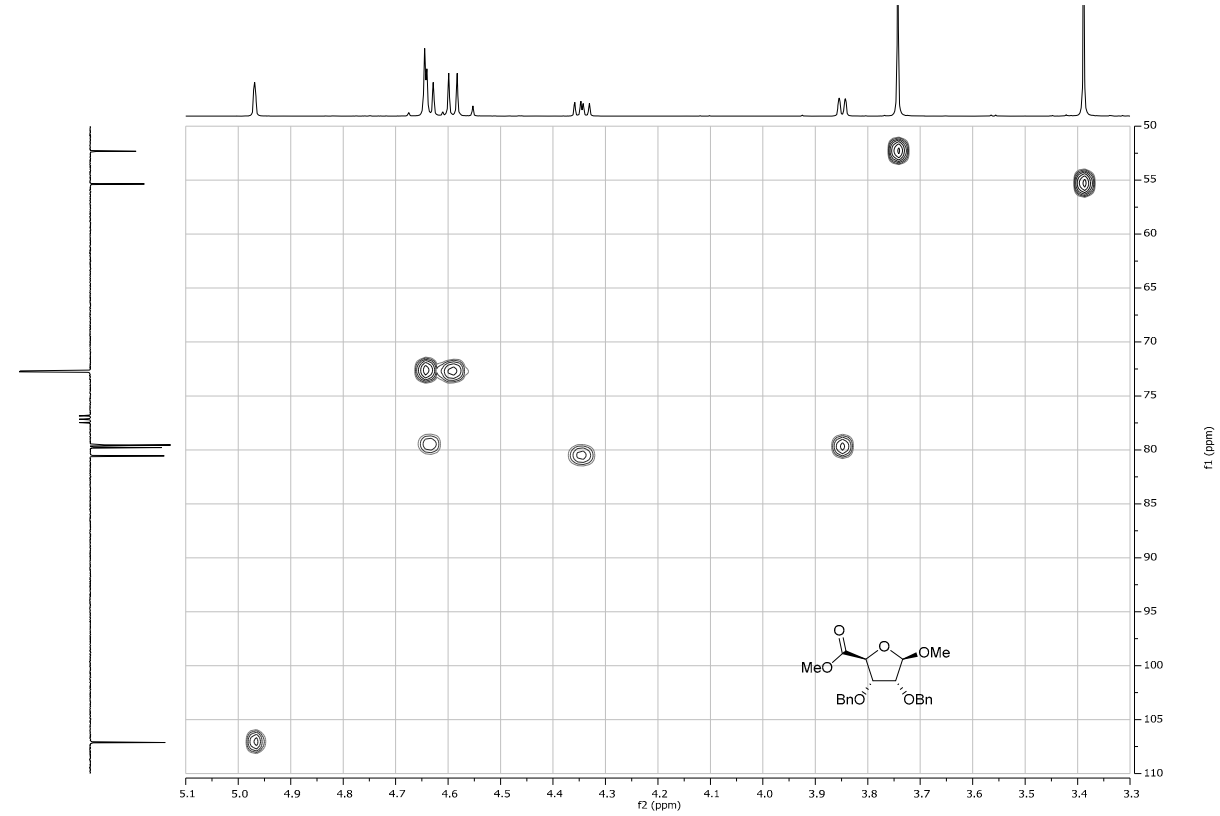
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **17**



^{1}H-^{1}H COSY of compound **17**

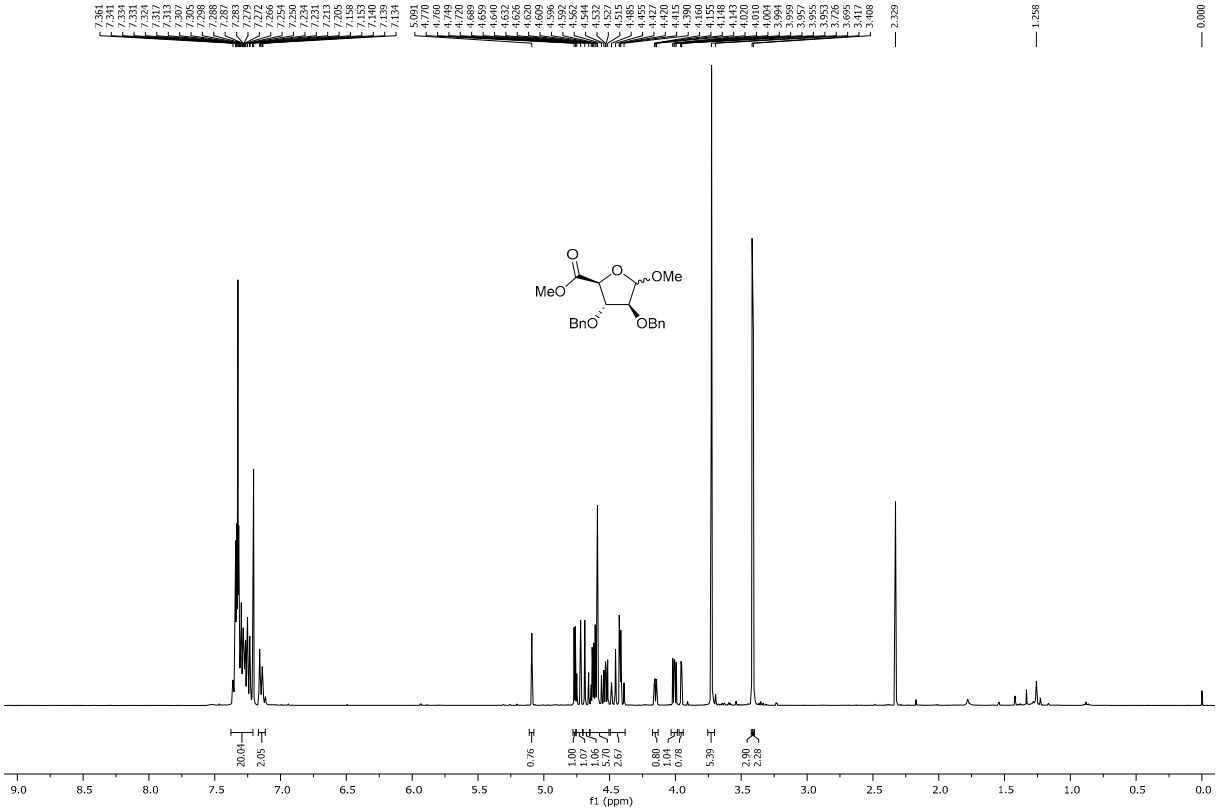


^{1}H-^{13}C HSQC of compound **17**

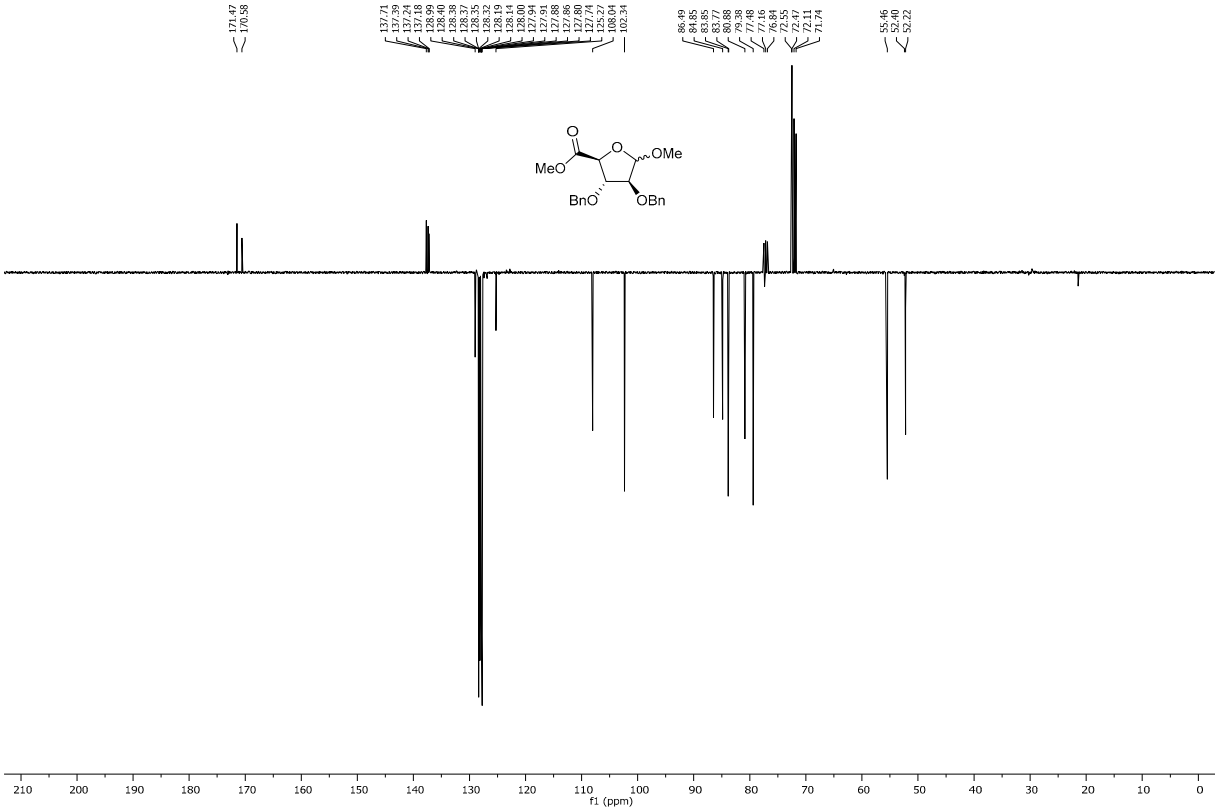


Methyl (methyl 2,3-di-*O*-benzyl-α/β-D-arabinofuranosyl uronate) (18)

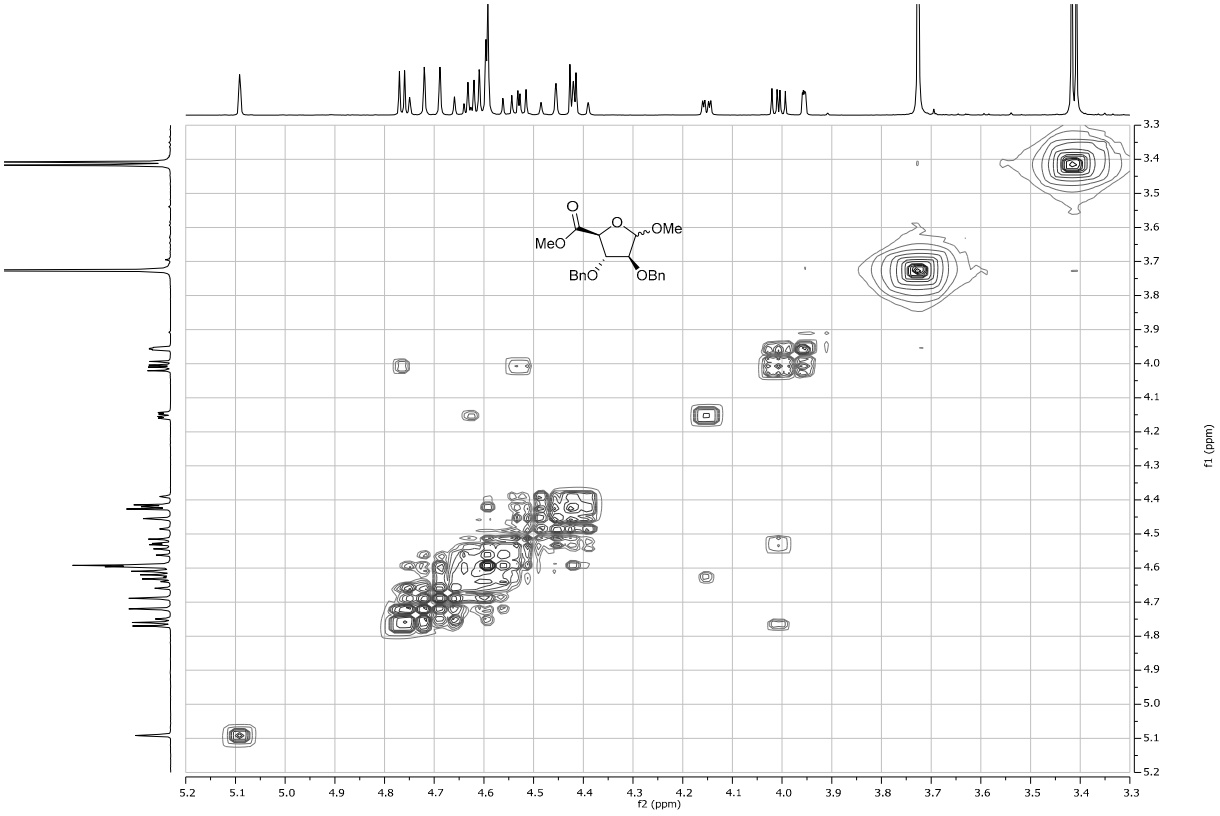
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **18**



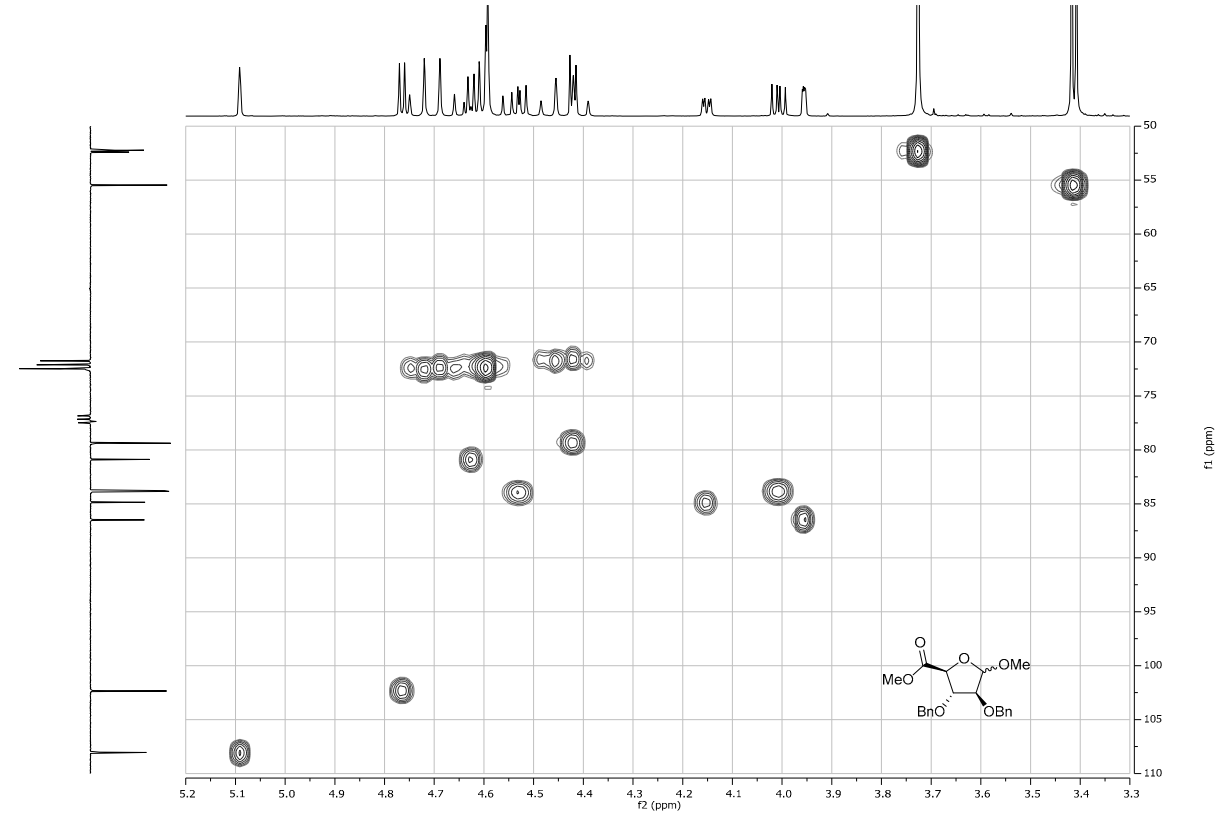
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **18**



^{1}H-^{1}H COSY of compound **18**

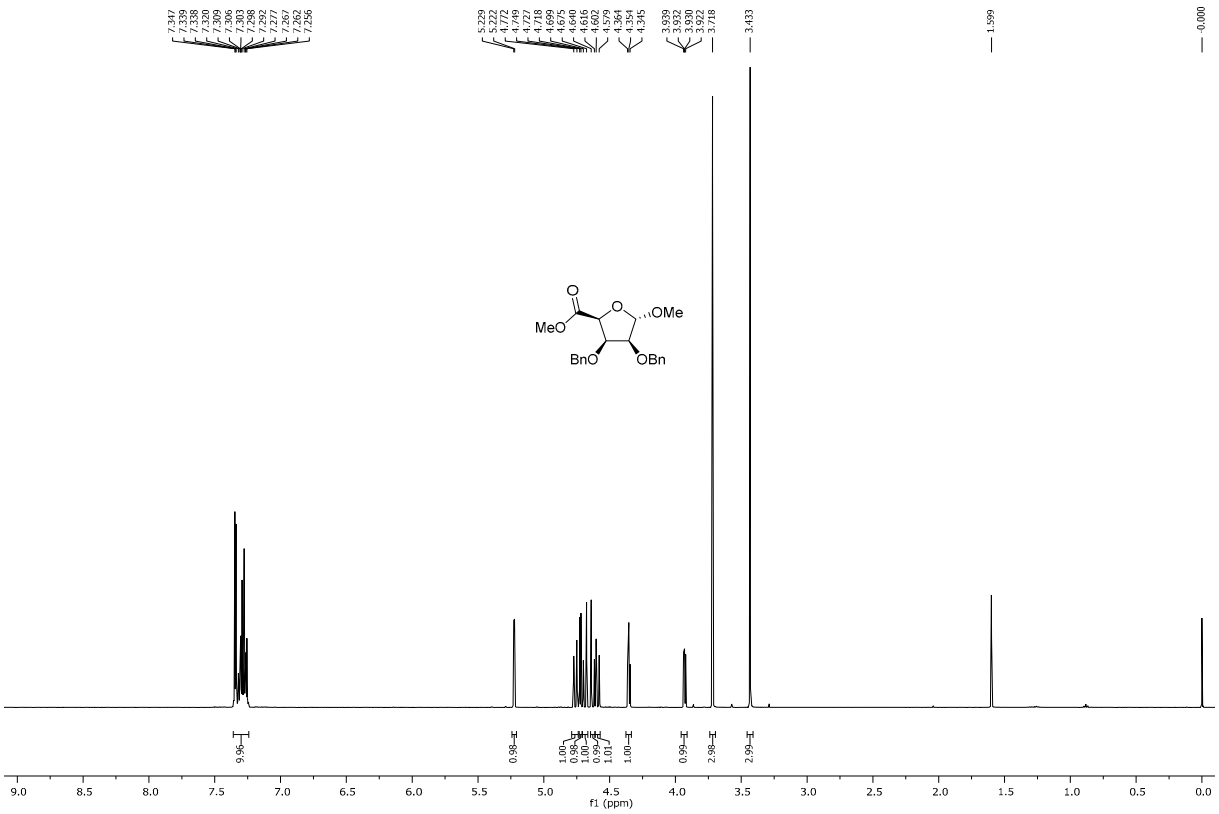


^{1}H-^{13}C HSQC of compound **18**

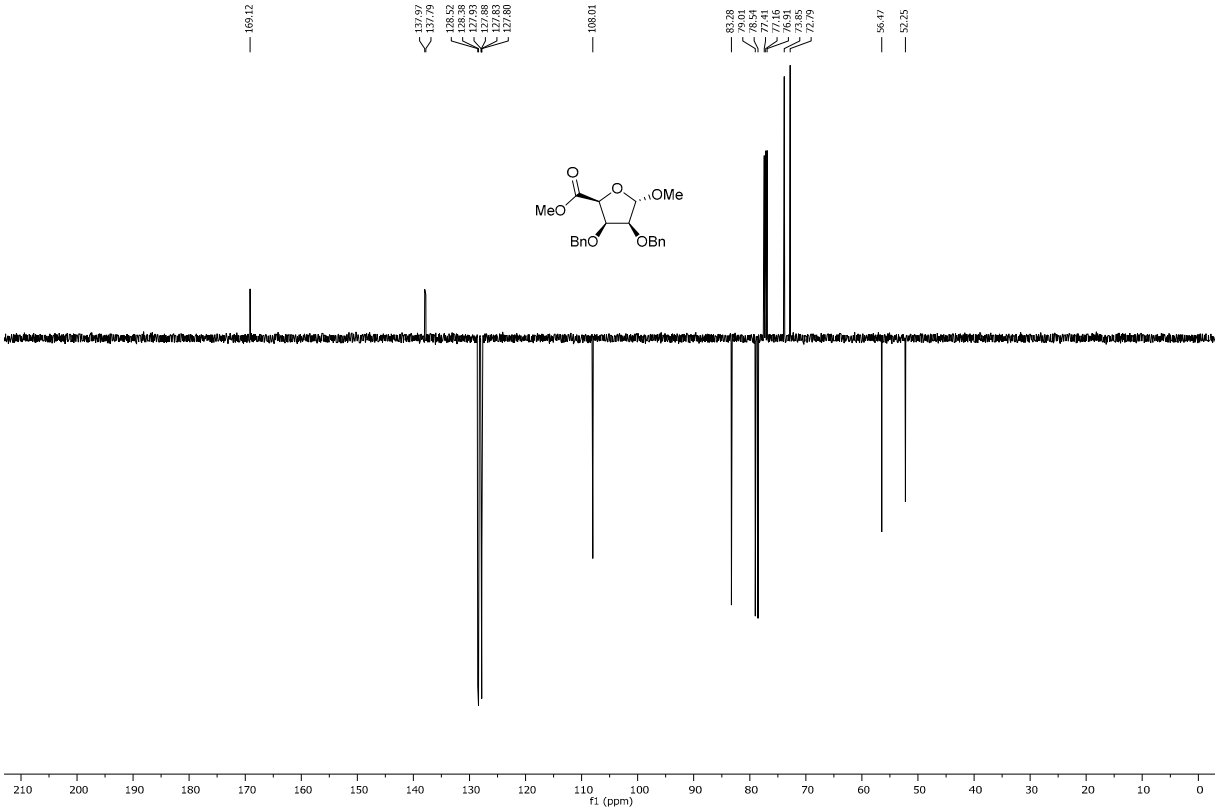


Methyl (methyl 2,3-di-*O*-benzyl-α-D-lyxofuranosyl uronate) (19)

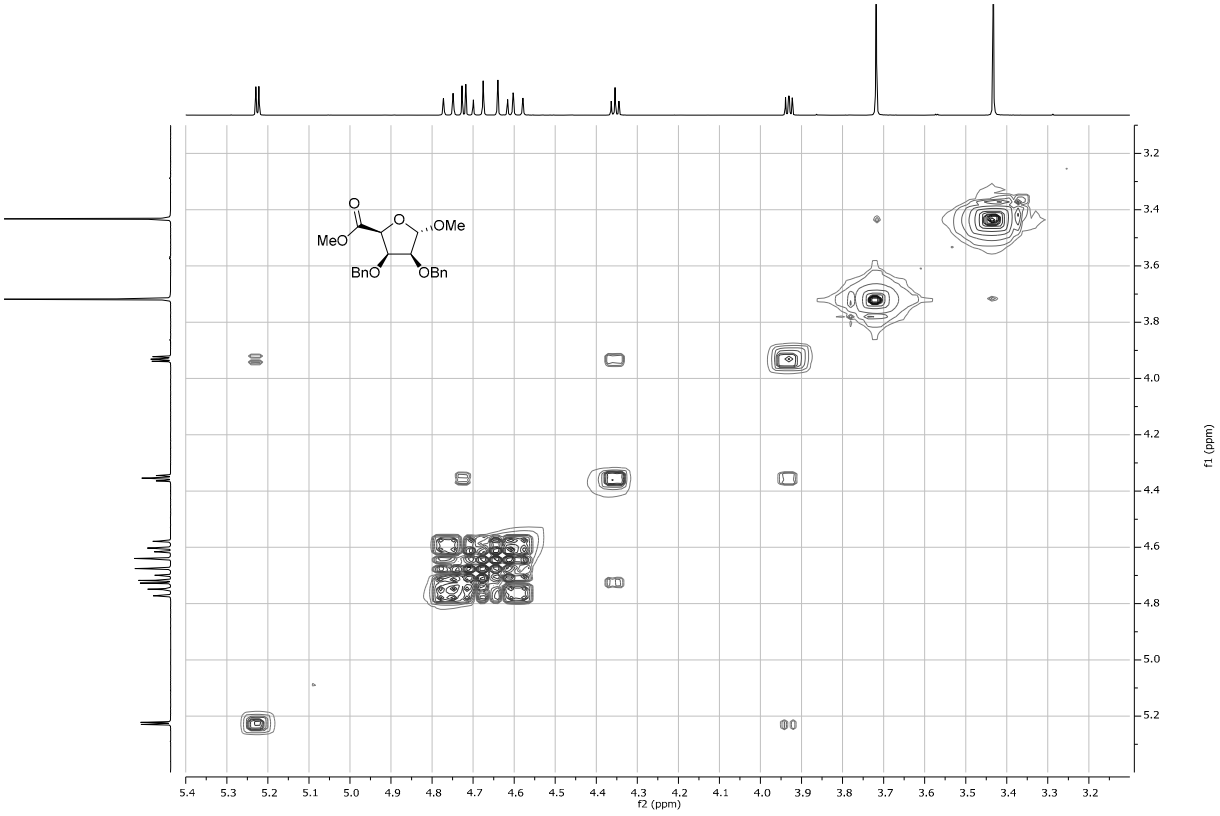
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **19**



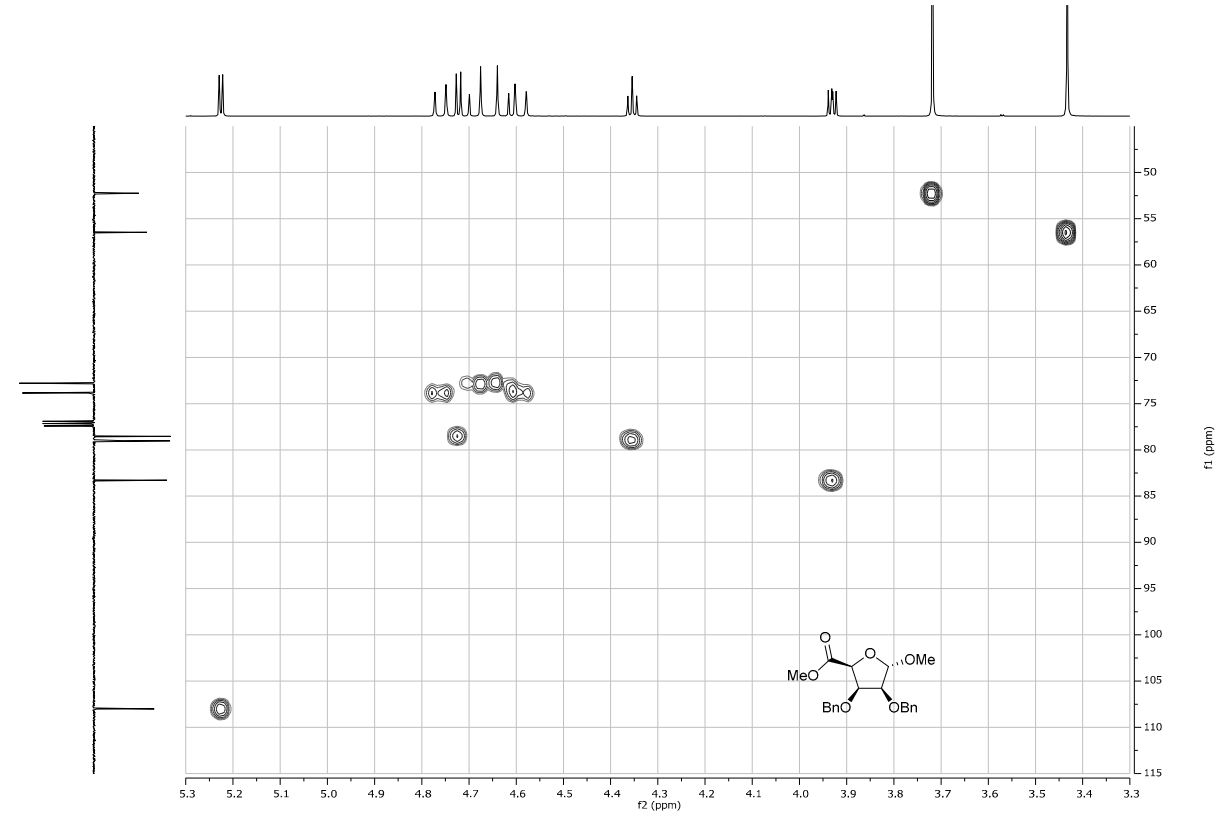
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **19**



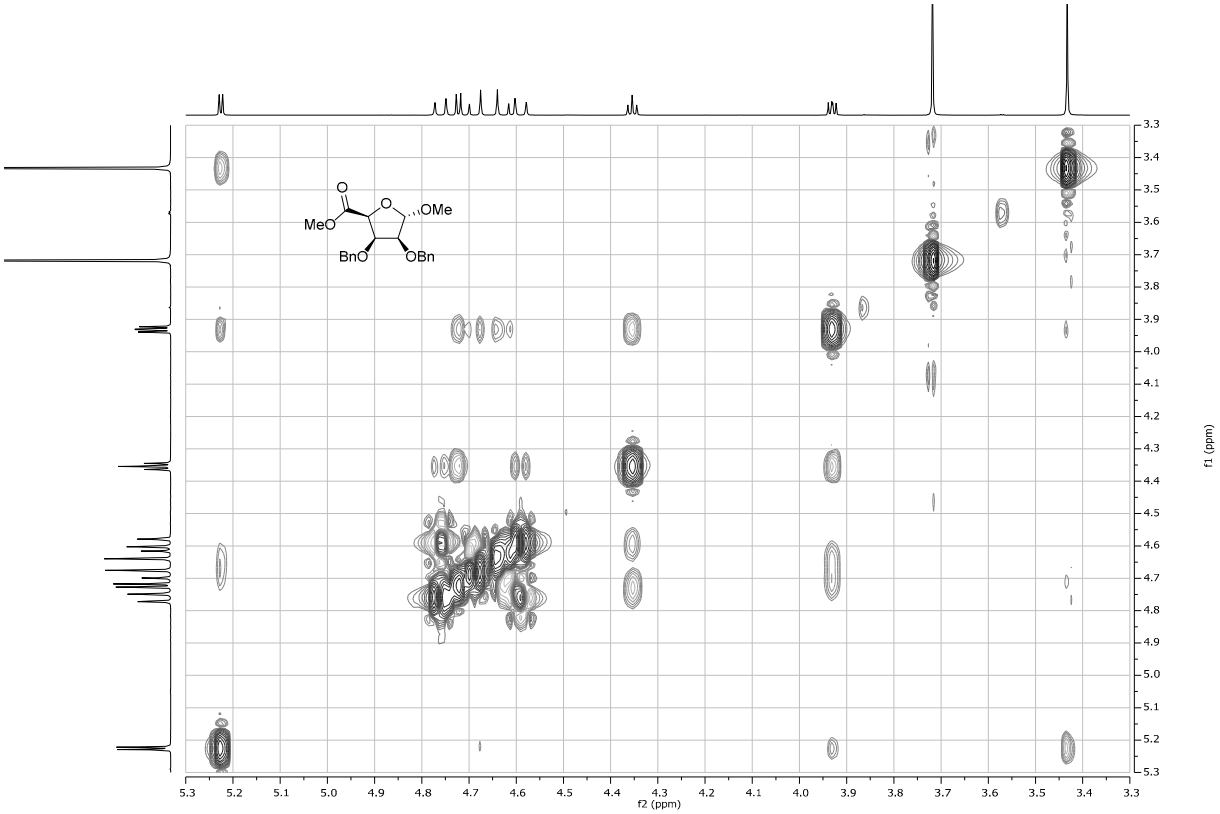
^{1}H-^{1}H COSY of compound **19**



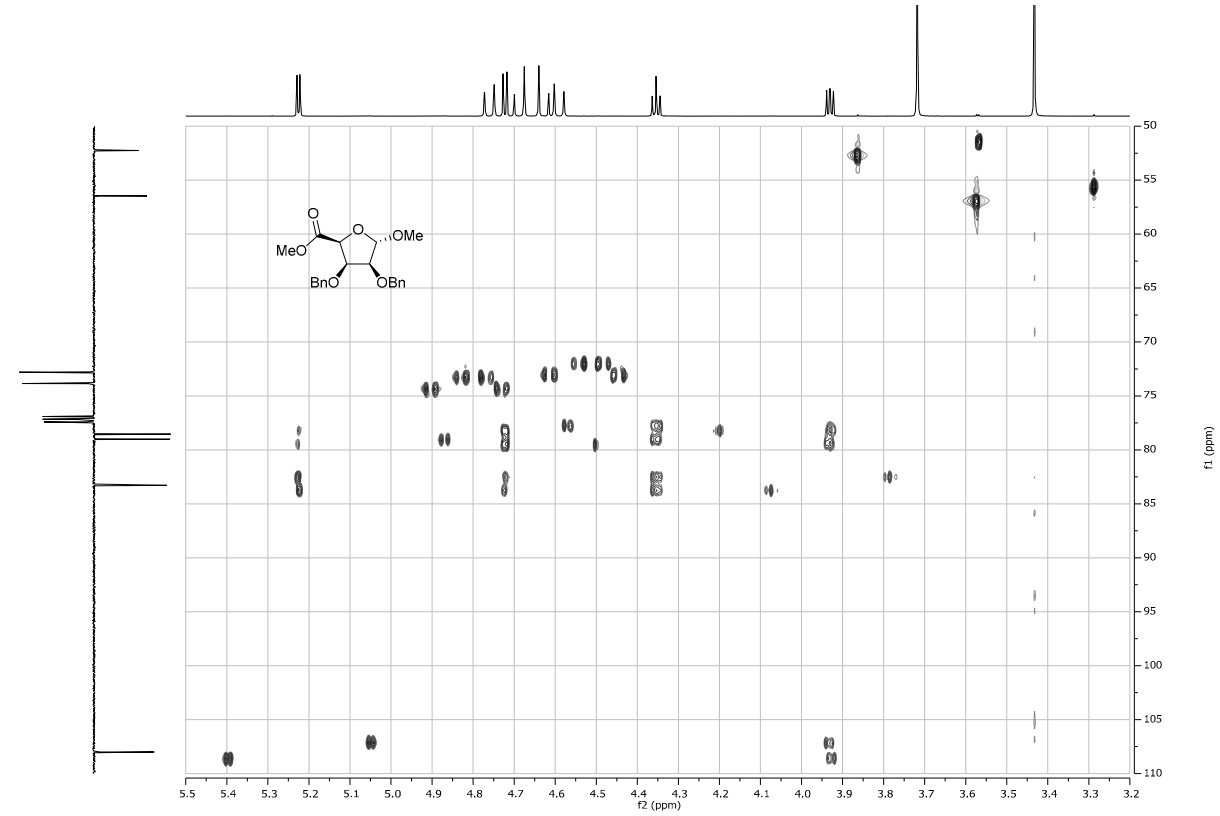
^{1}H-^{13}C HSQC of compound **19**



^{1}H-^{1}H NOESY of compound **19**

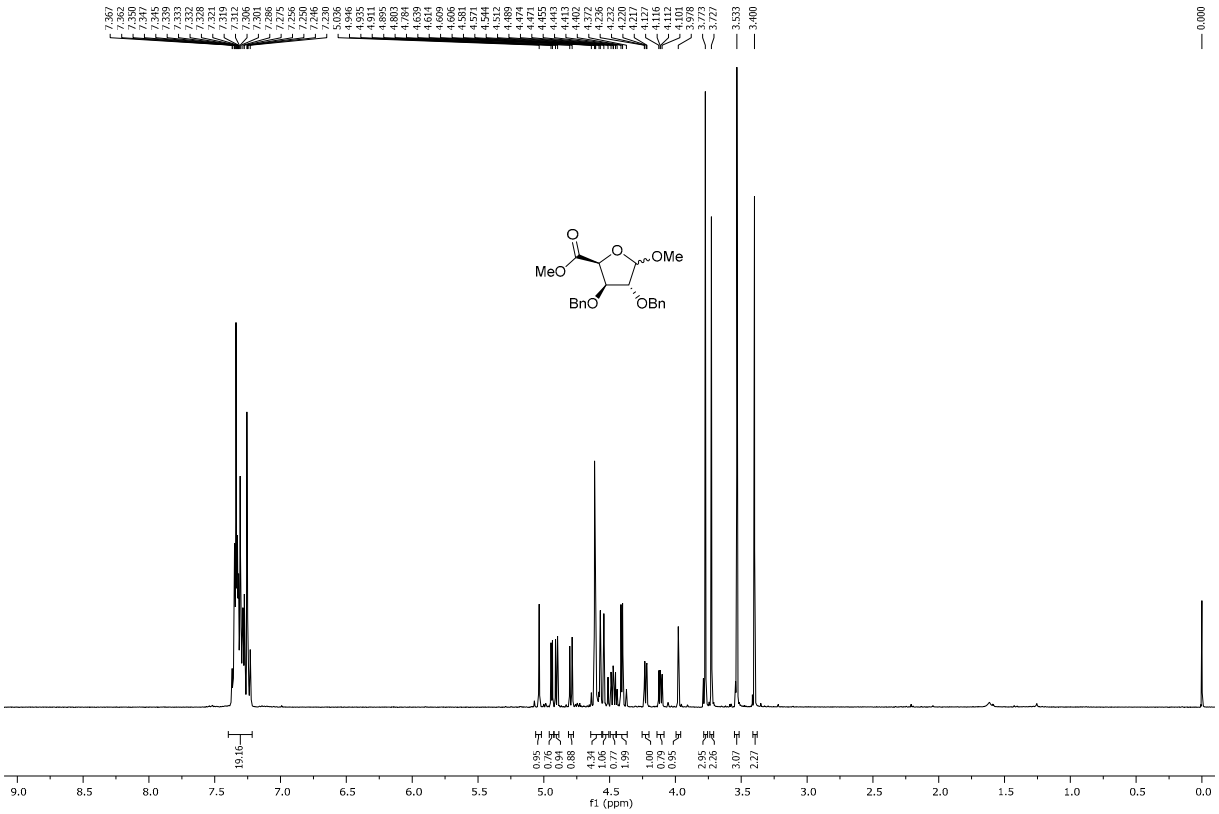


^{1}H-^{13}C HSQC-HECADE of compound **19**

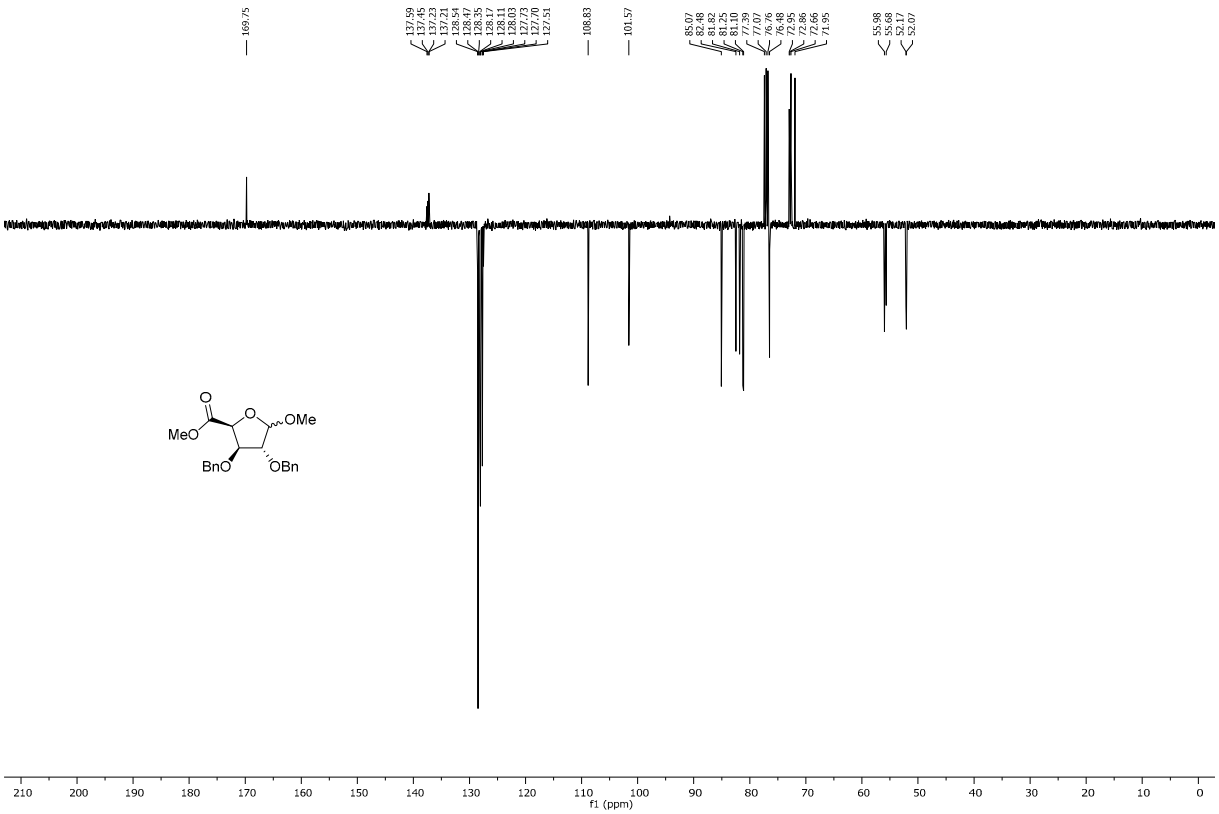


Methyl (methyl 2,3-di-*O*-benzyl-α/β-D-xylofuranosyl uronate) (20)

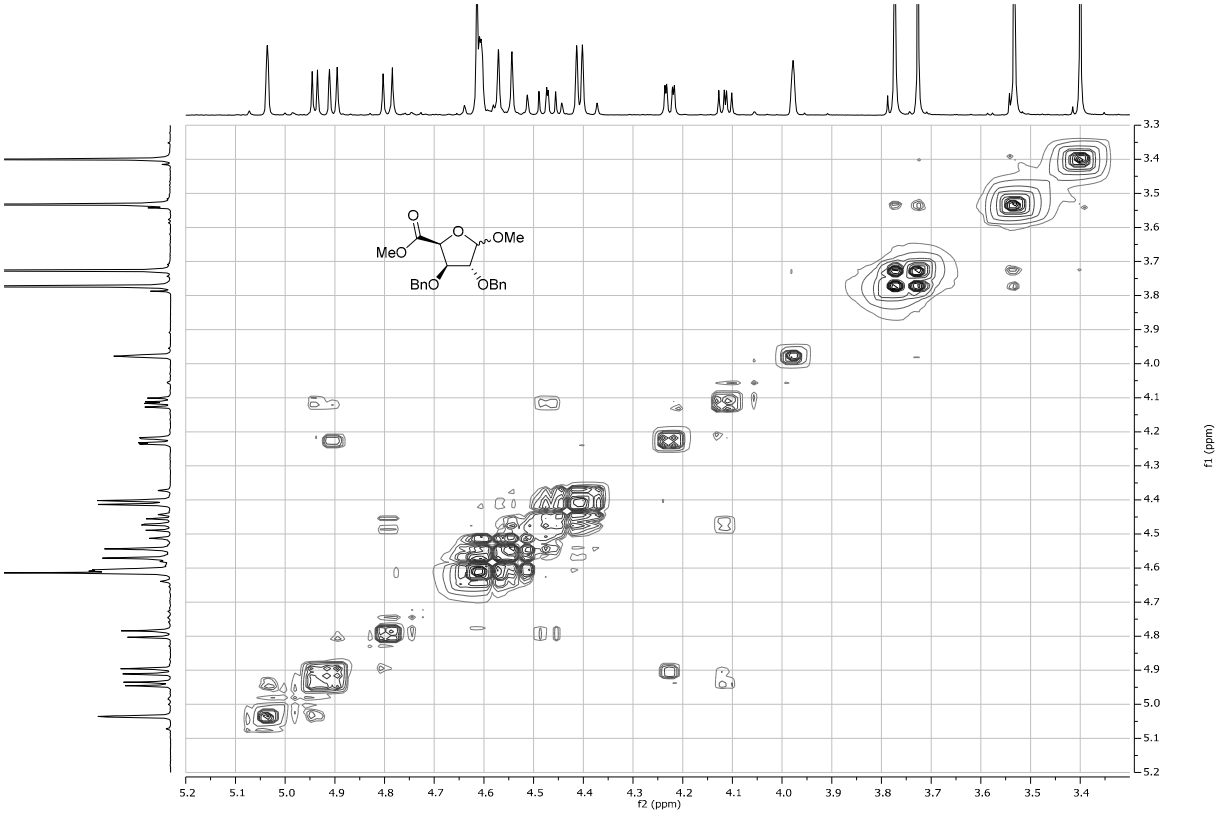
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **20**



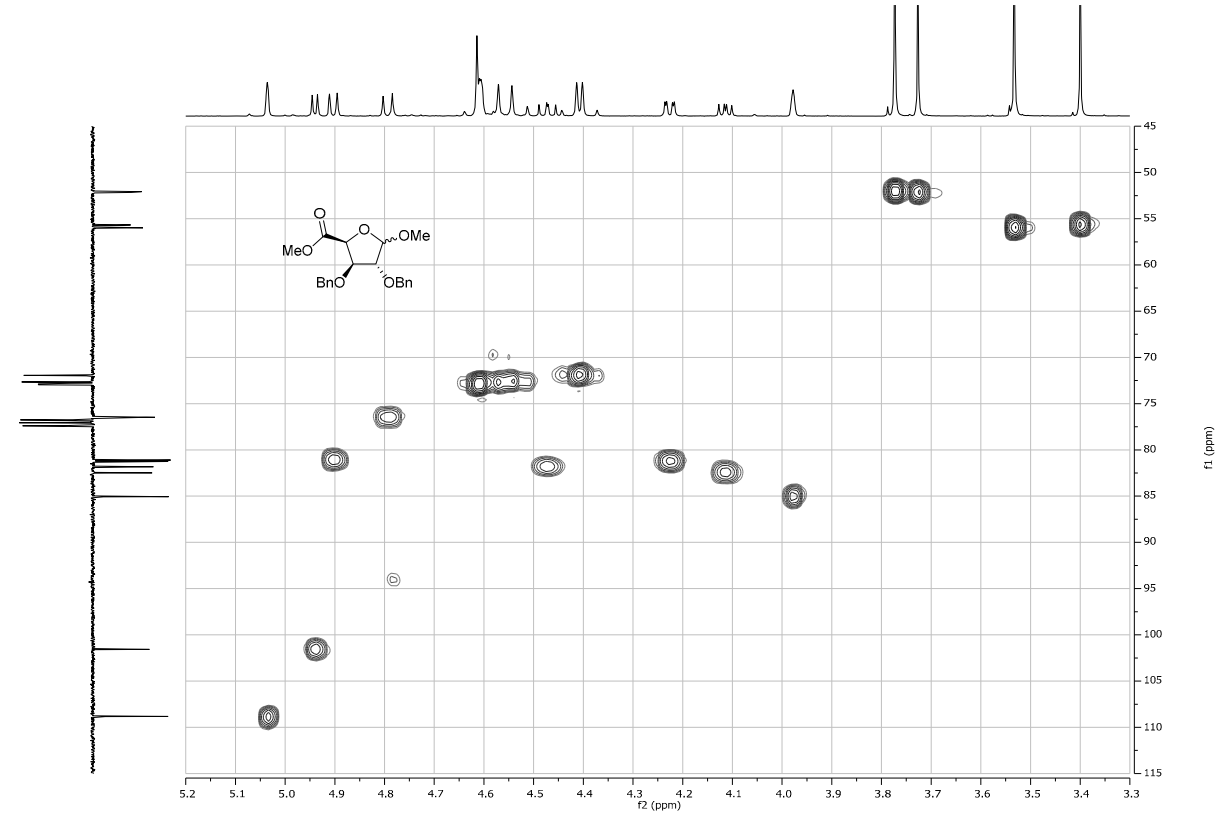
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **20**



^{1}H-^{1}H COSY of compound **20**

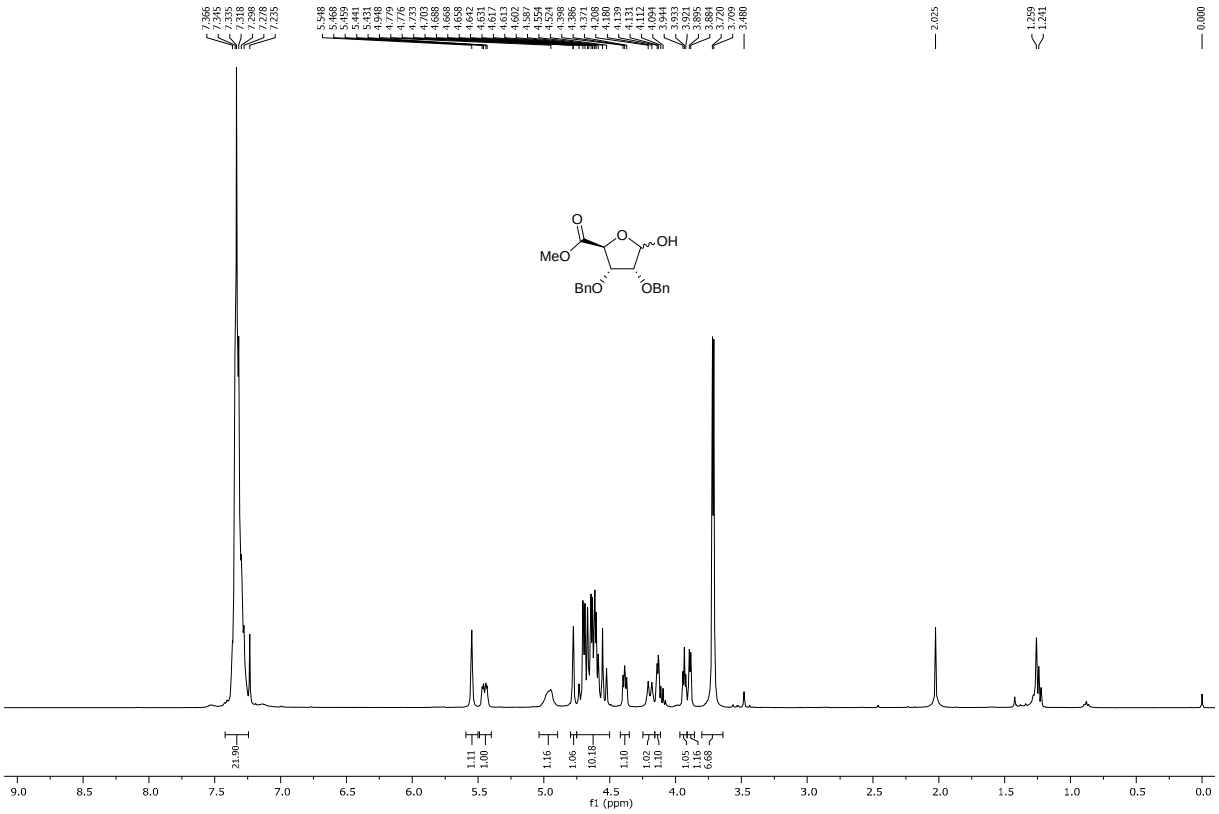


^{1}H-^{13}C HSQC of compound **20**

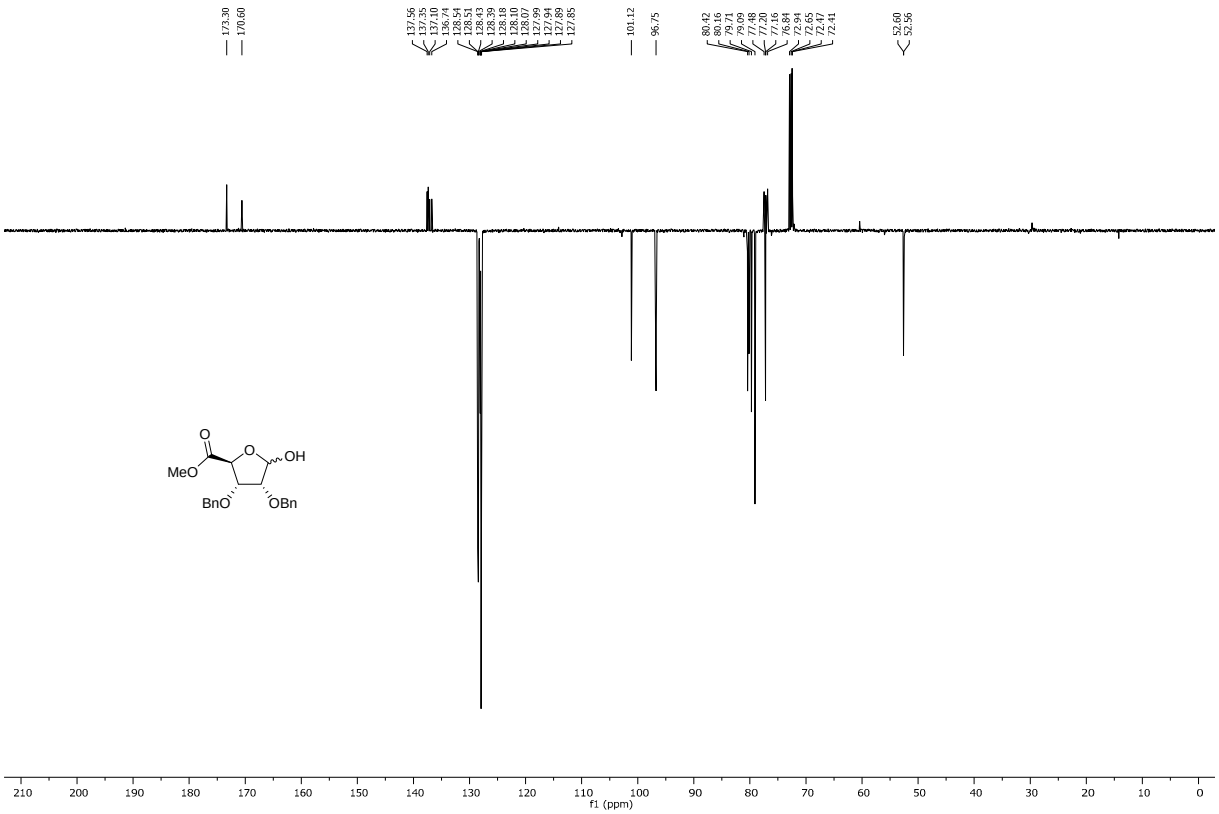


Methyl (2,3-di-*O*-benzyl-α/β-D-ribofuranosyl uronate) (21)

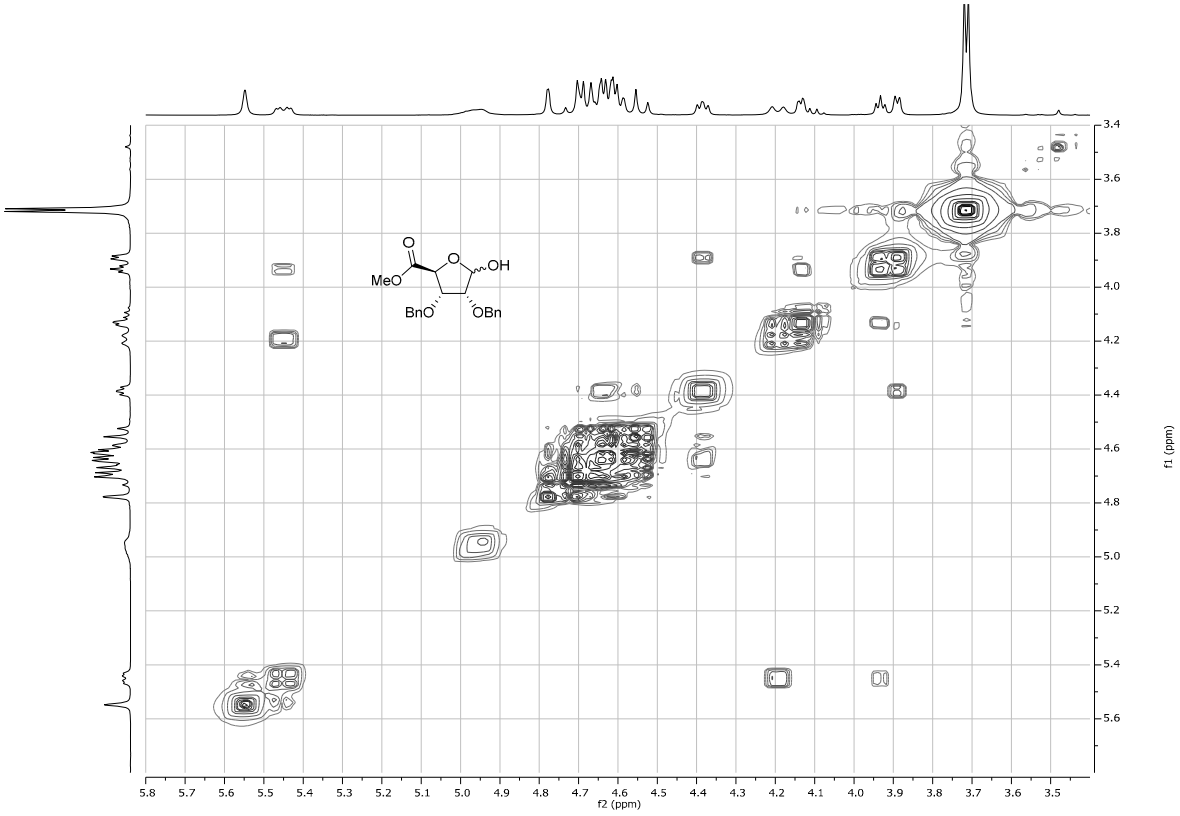
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **21**



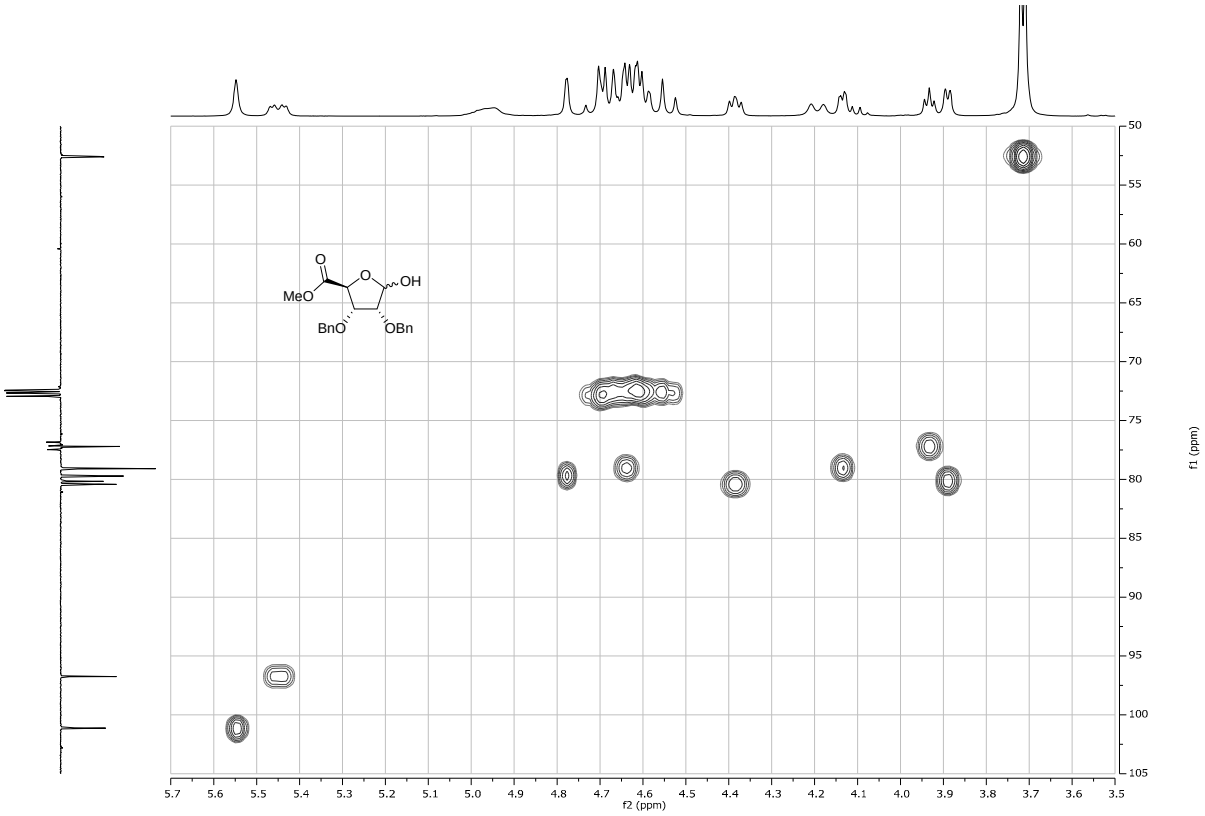
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **21**



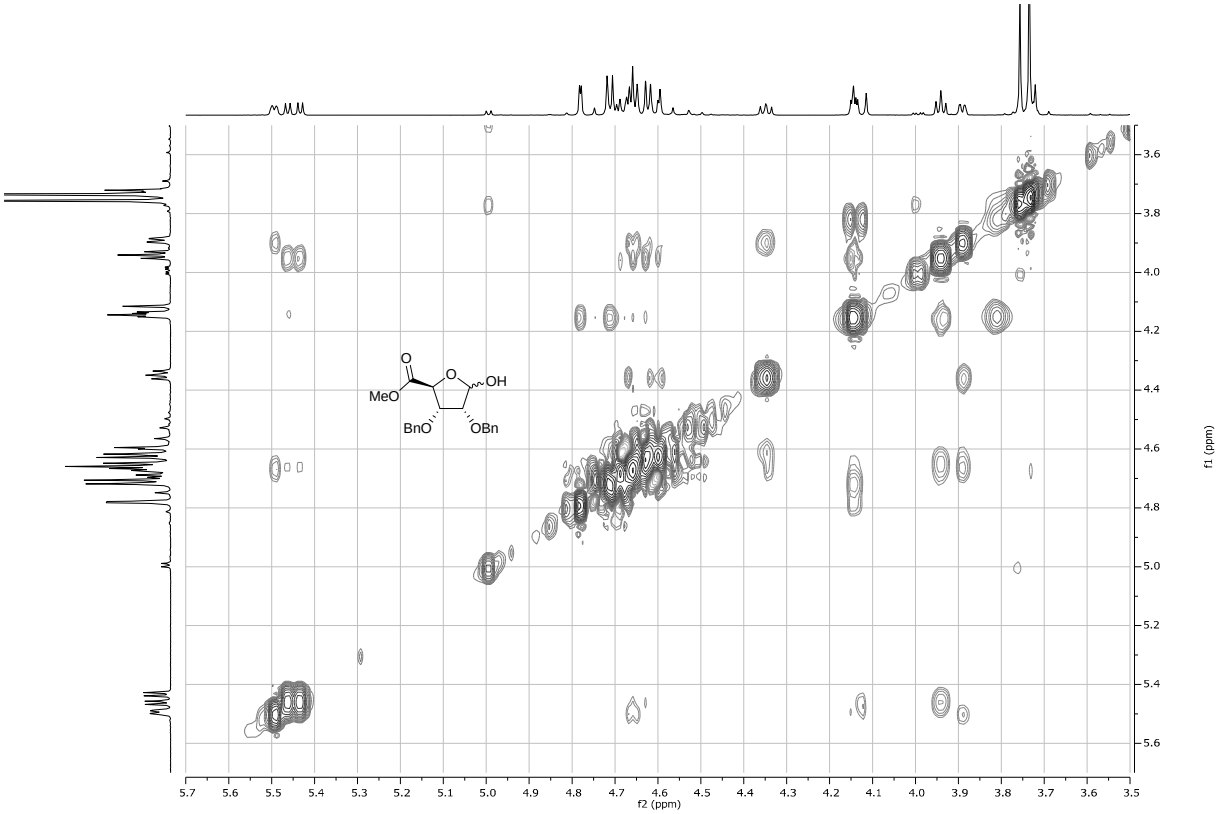
^{1}H-^{1}H COSY of compound **21**



^{1}H-^{13}C HSQC of compound **21**

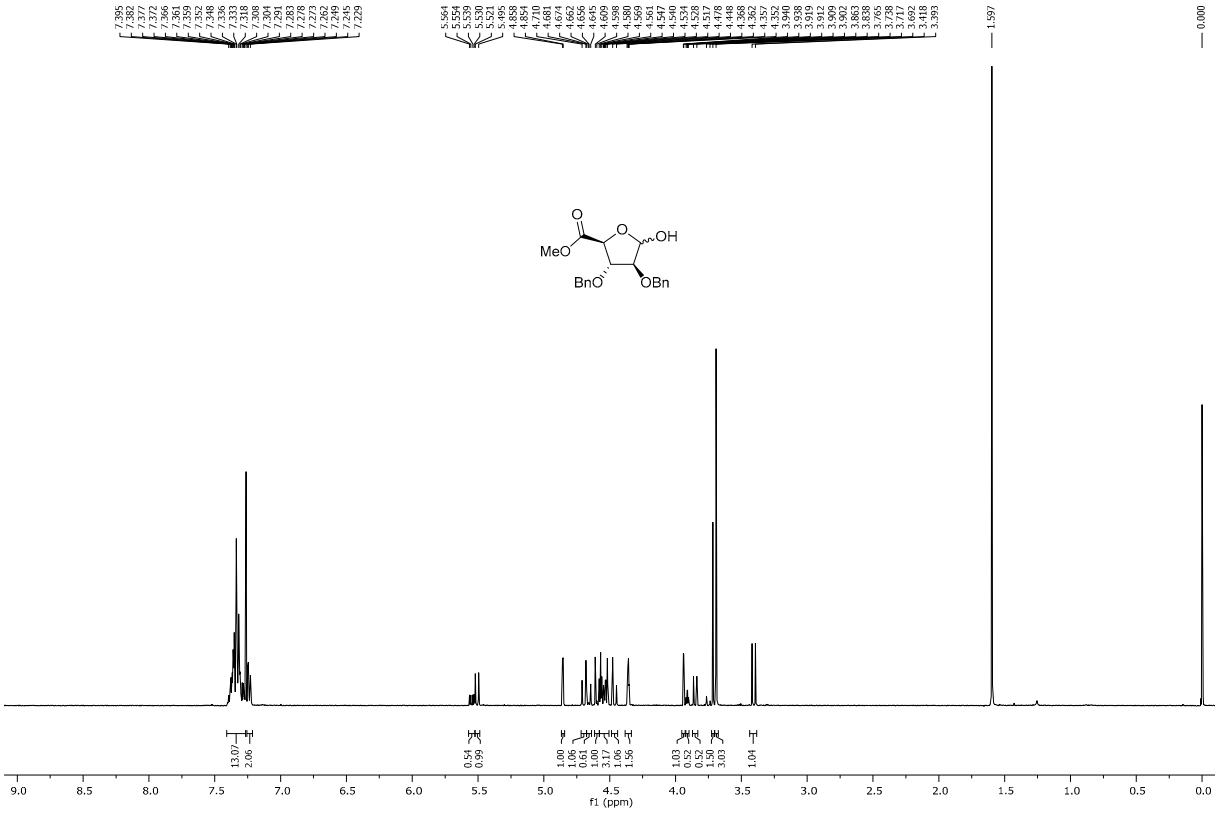


^{1}H-^{1}H NOESY of compound **21**

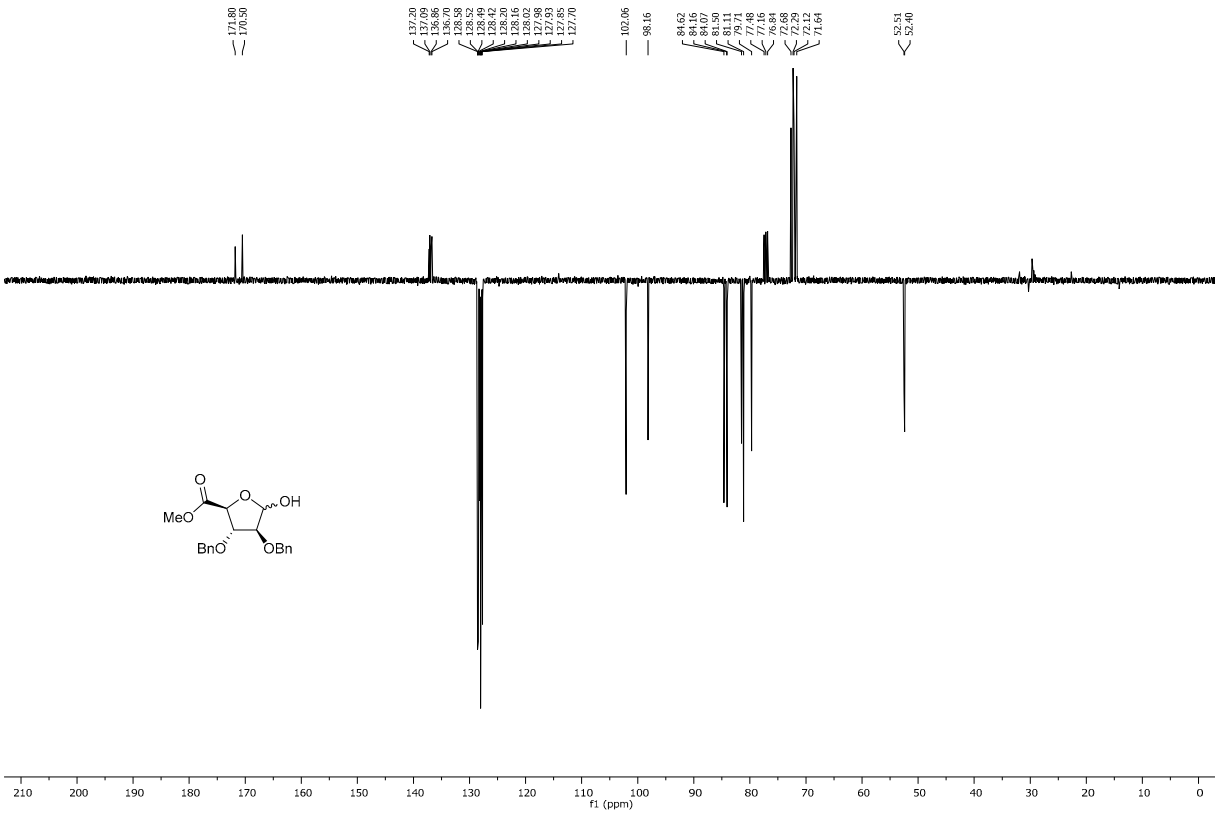


Methyl (2,3-di-*O*-benzyl-α/β-D-arabinofuranosyl uronate) (22)

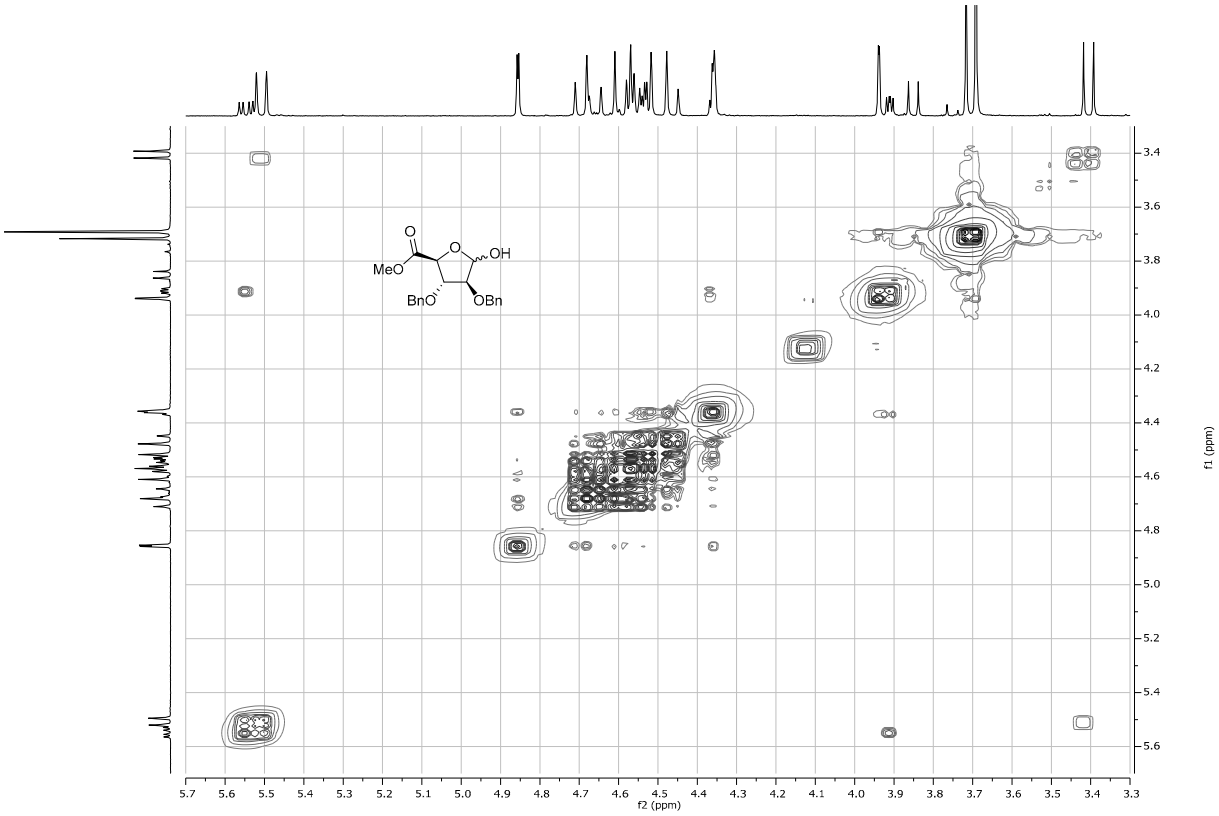
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **22**



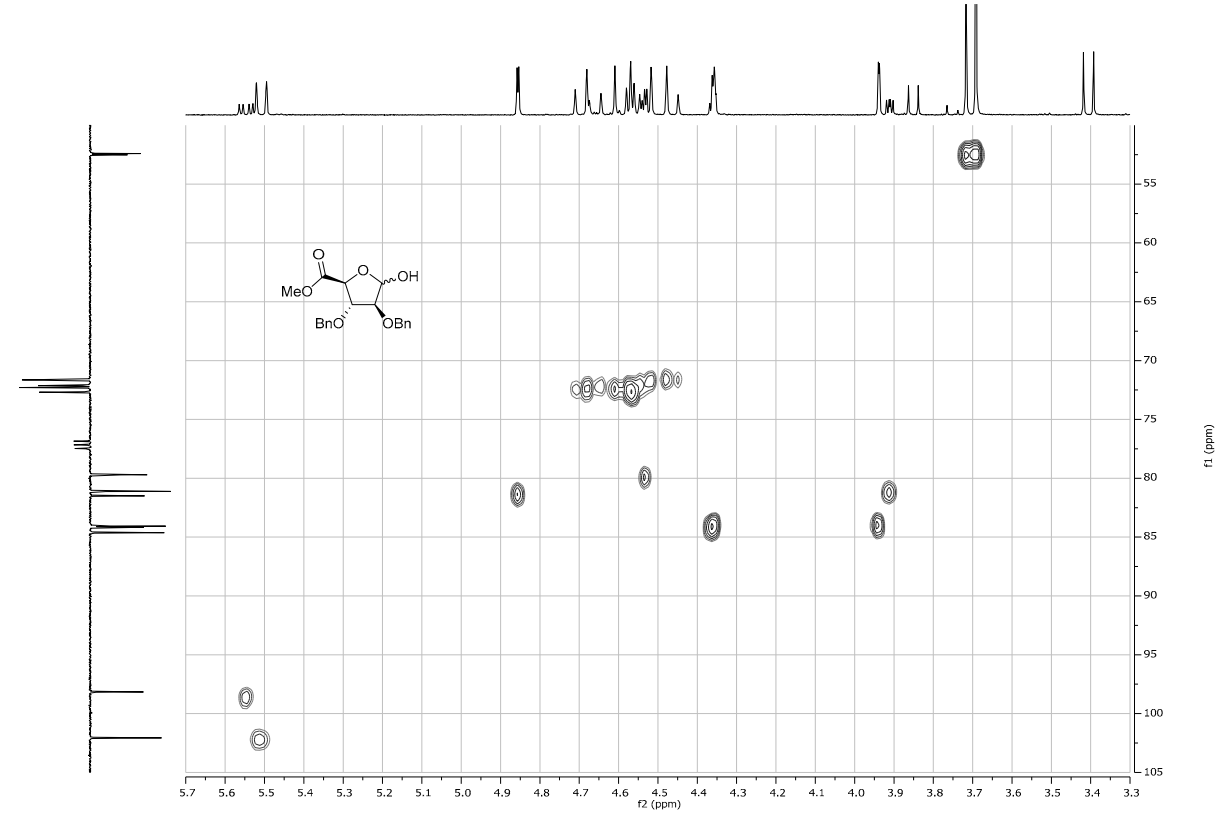
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **22**



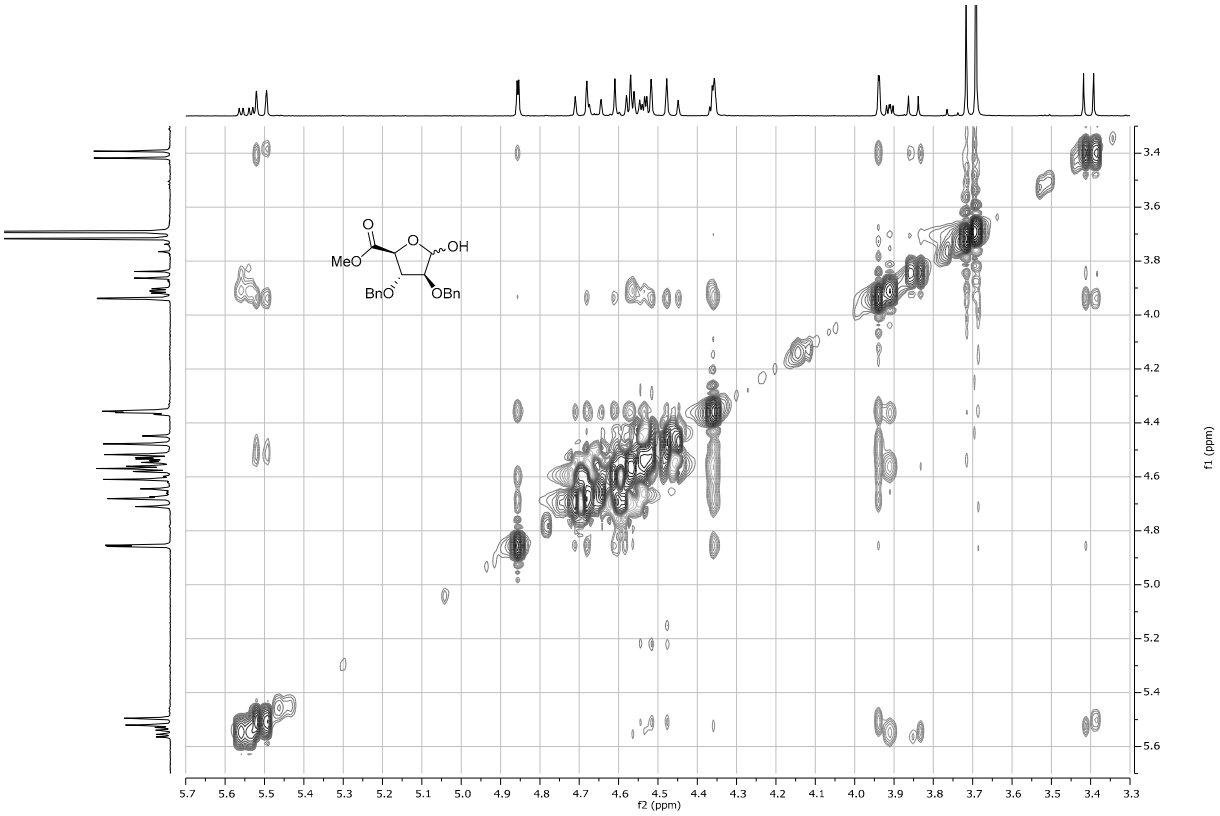
^{1}H-^{1}H COSY of compound **22**



^{1}H-^{13}C HSQC of compound **22**

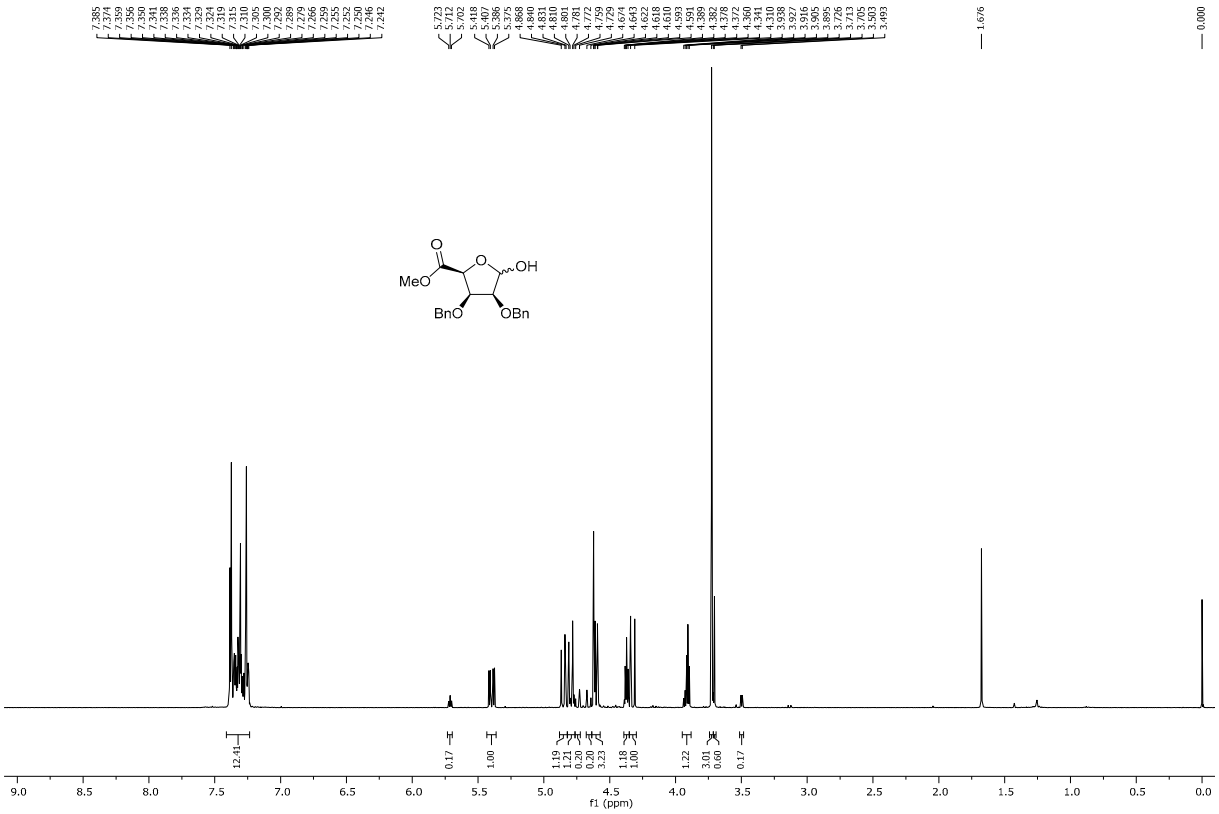


^{1}H-^{1}H NOESY of compound **22**

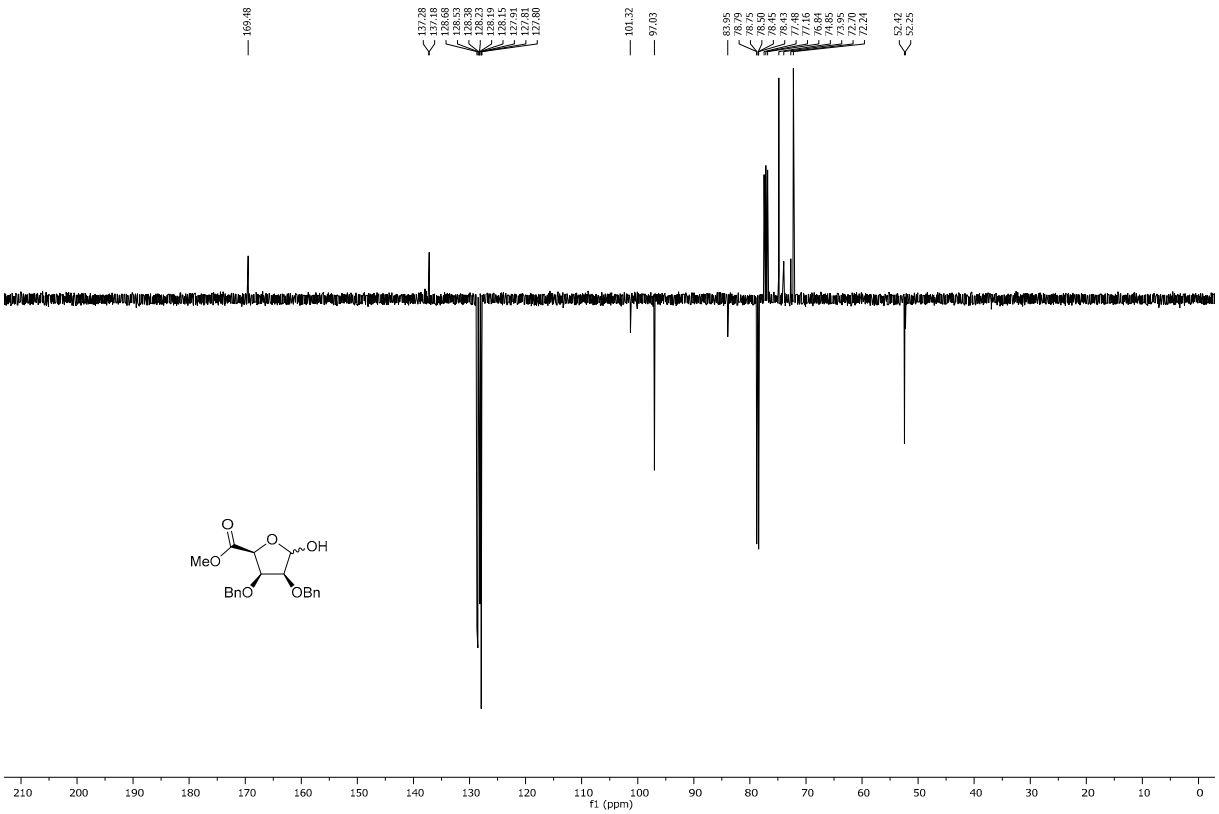


Methyl (2,3-di-*O*-benzyl-α/β-D-lyxofuranosyl uronate) (23)

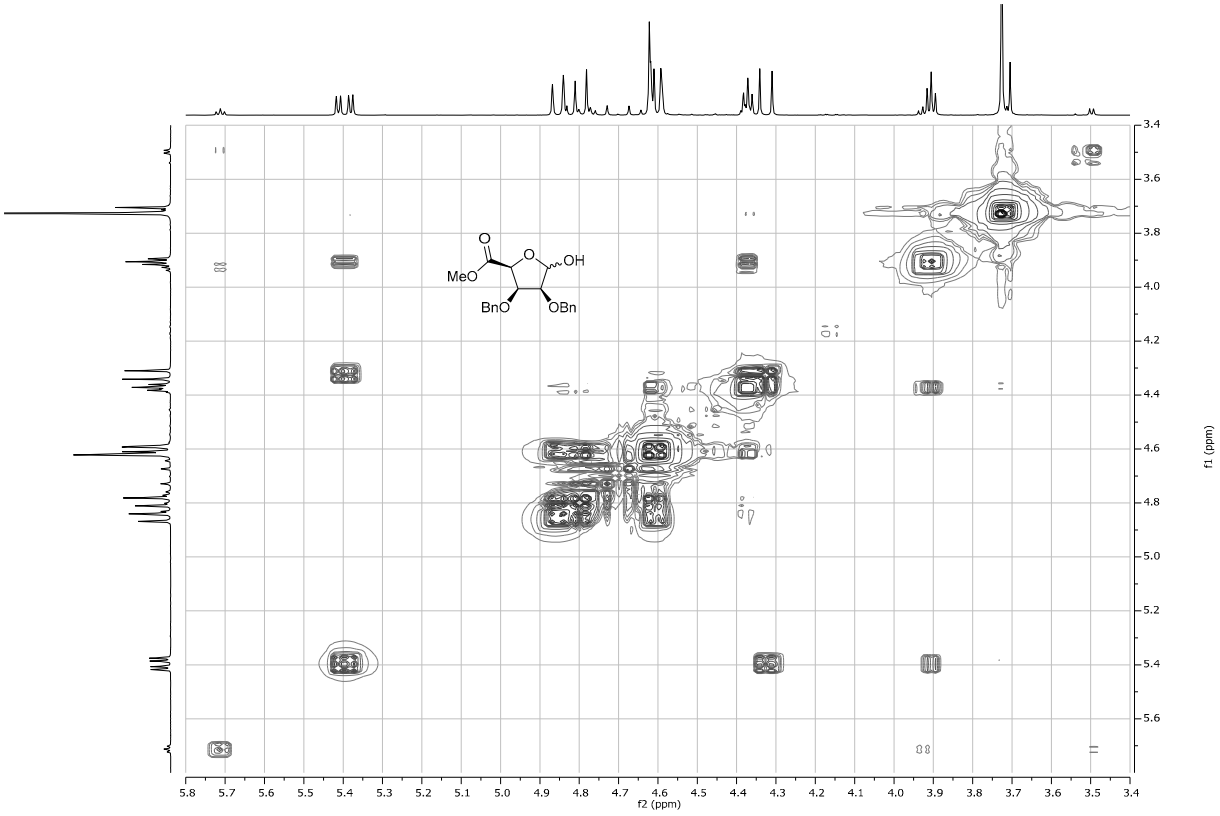
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **23**



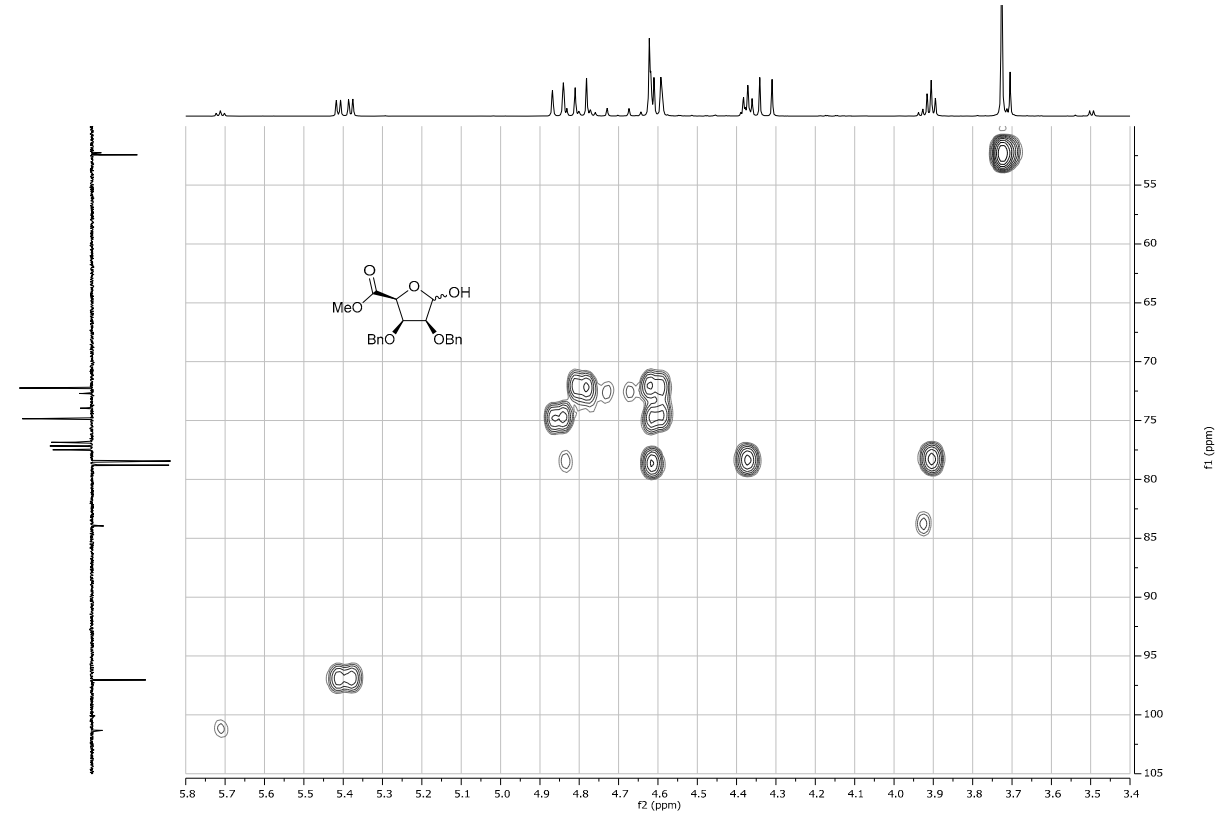
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **23**



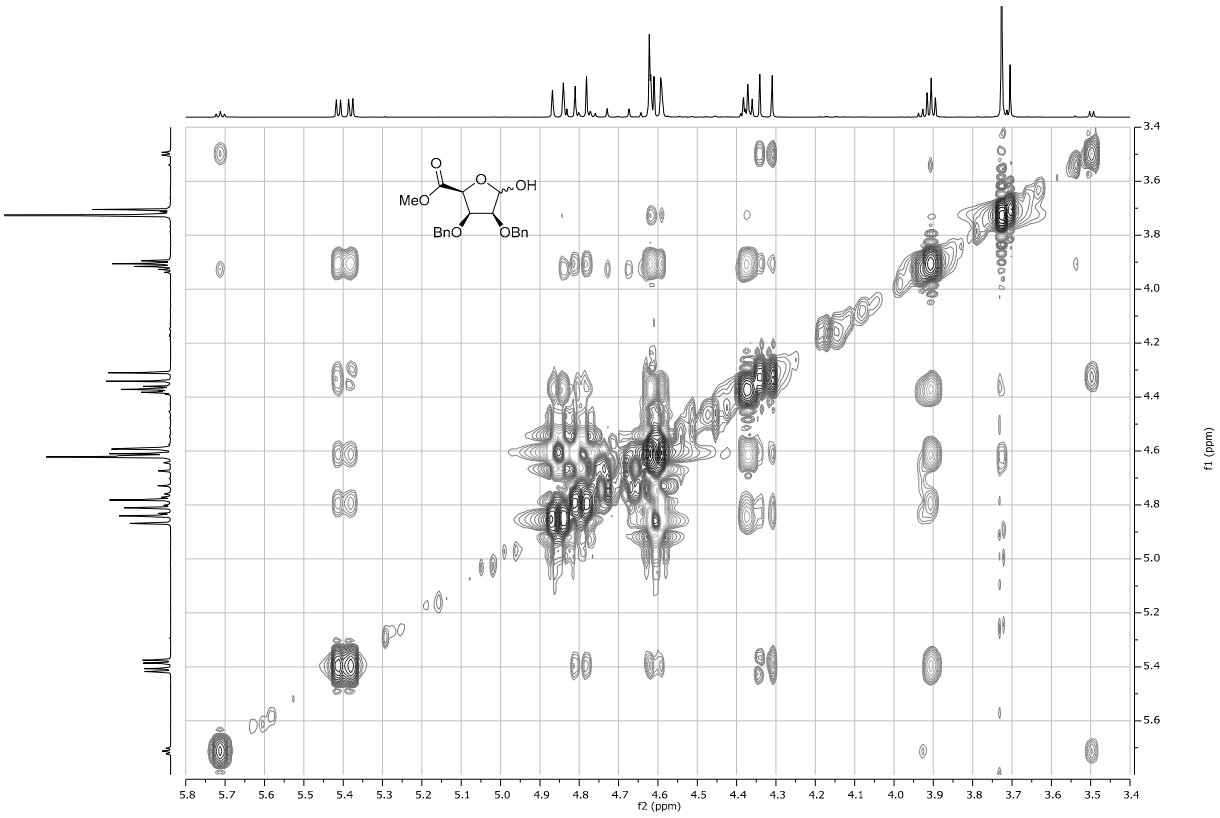
^{1}H-^{1}H COSY of compound **23**



^{1}H-^{13}C HSQC of compound **23**

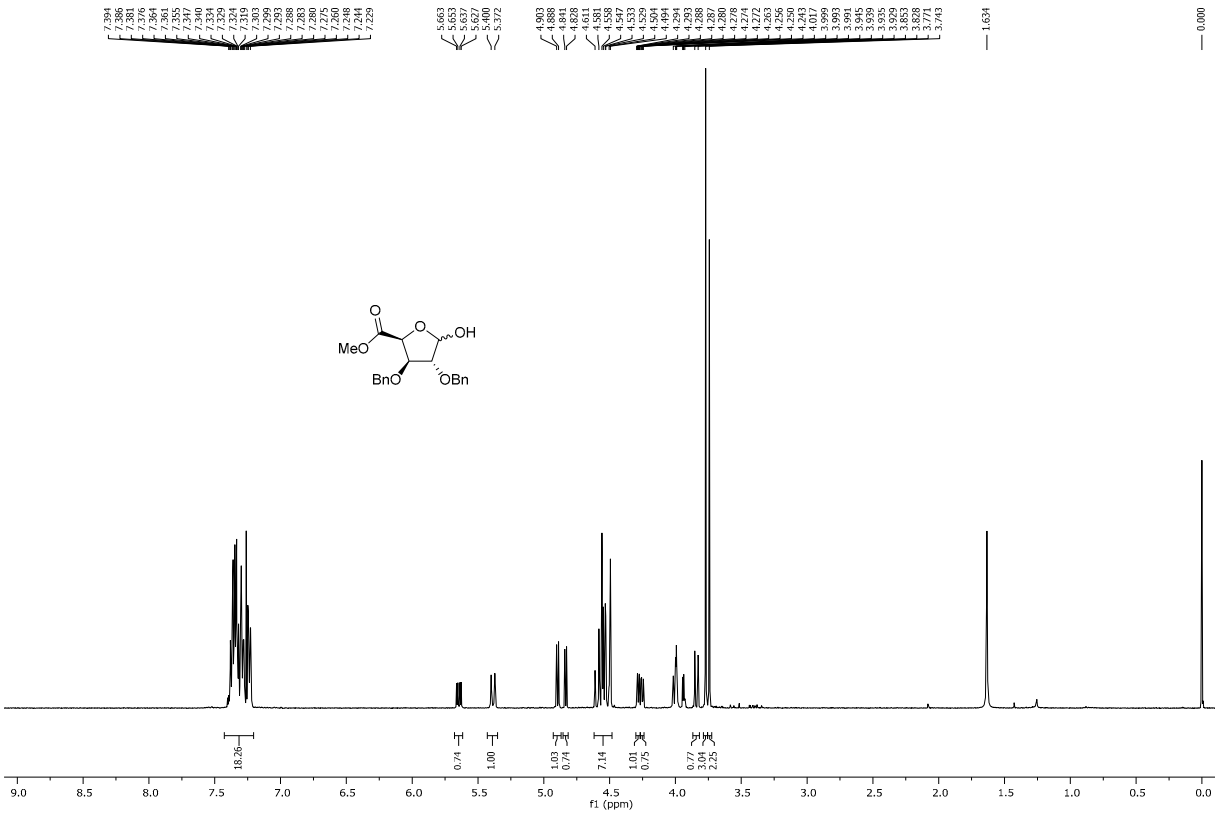


^{1}H-^{1}H NOESY of compound **23**

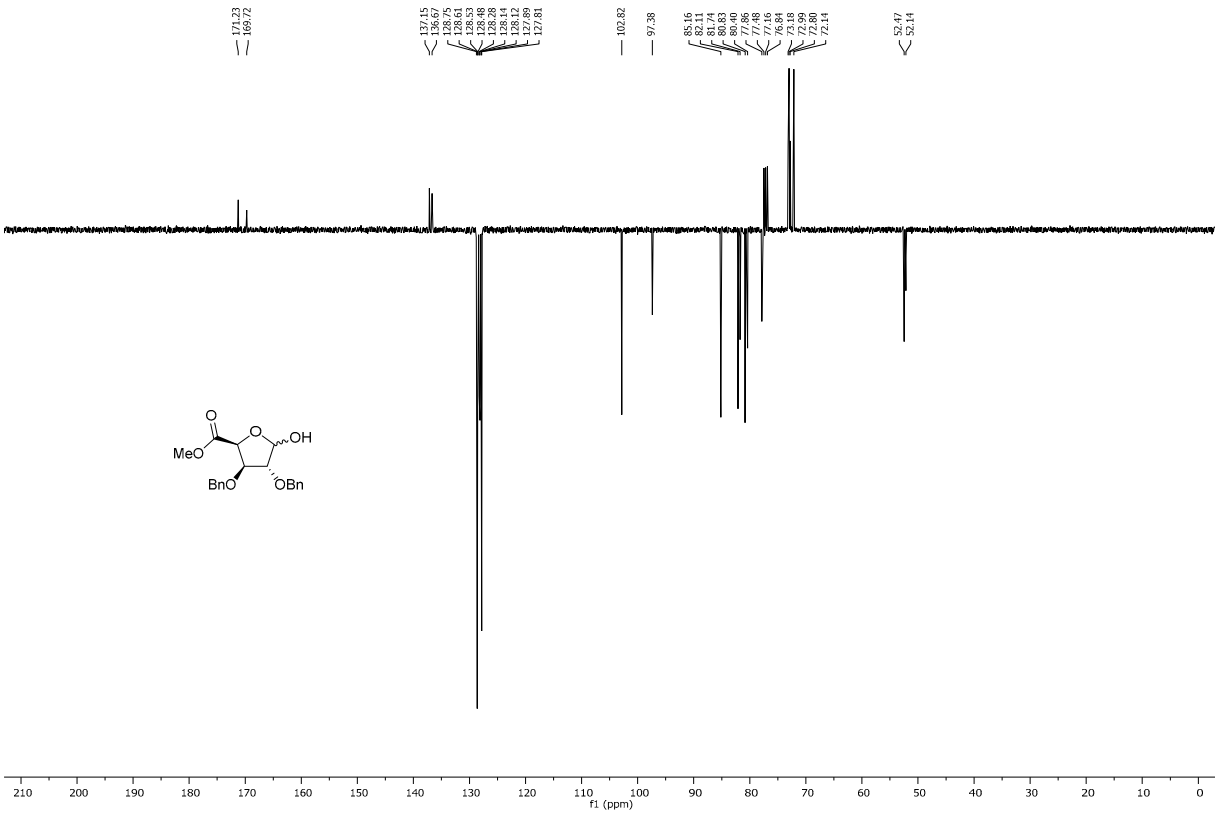


Methyl (2,3-di-*O*-benzyl-α/β-D-xylofuranosyl uronate) (24)

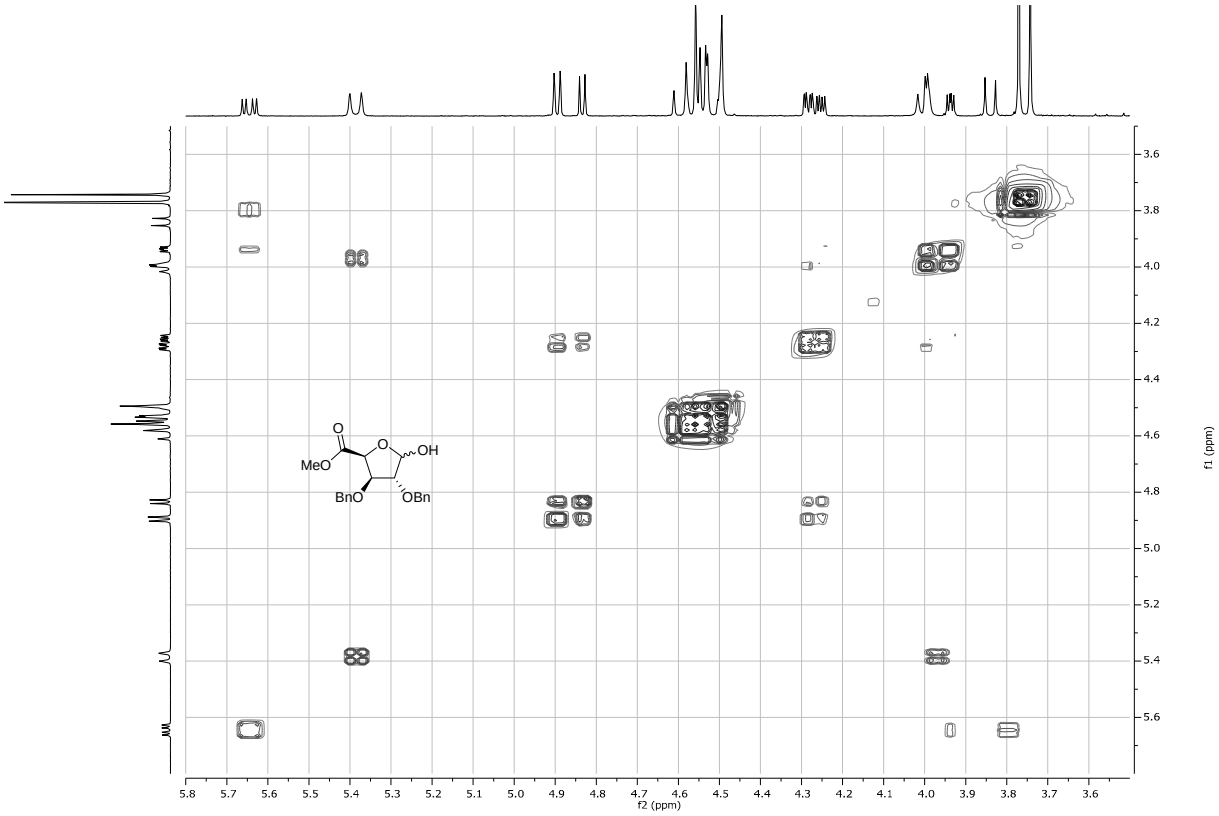
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **24**



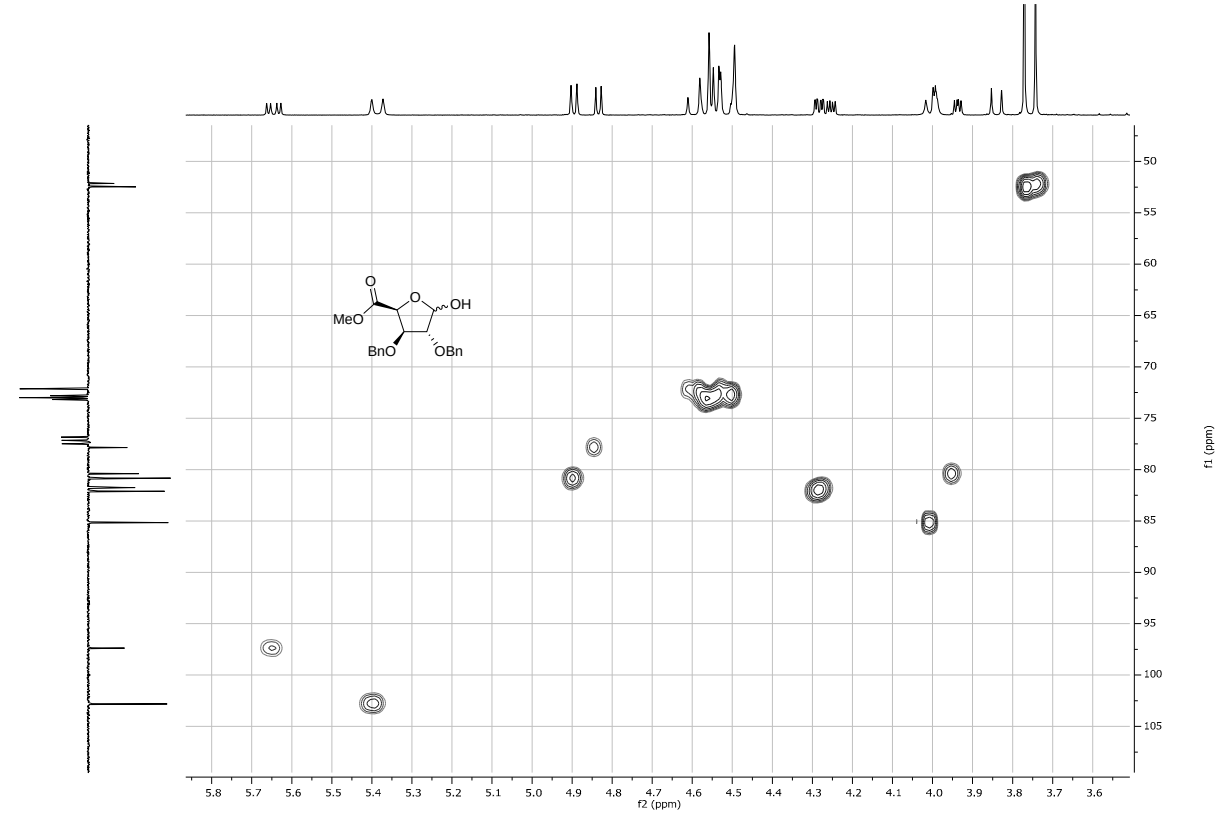
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **24**



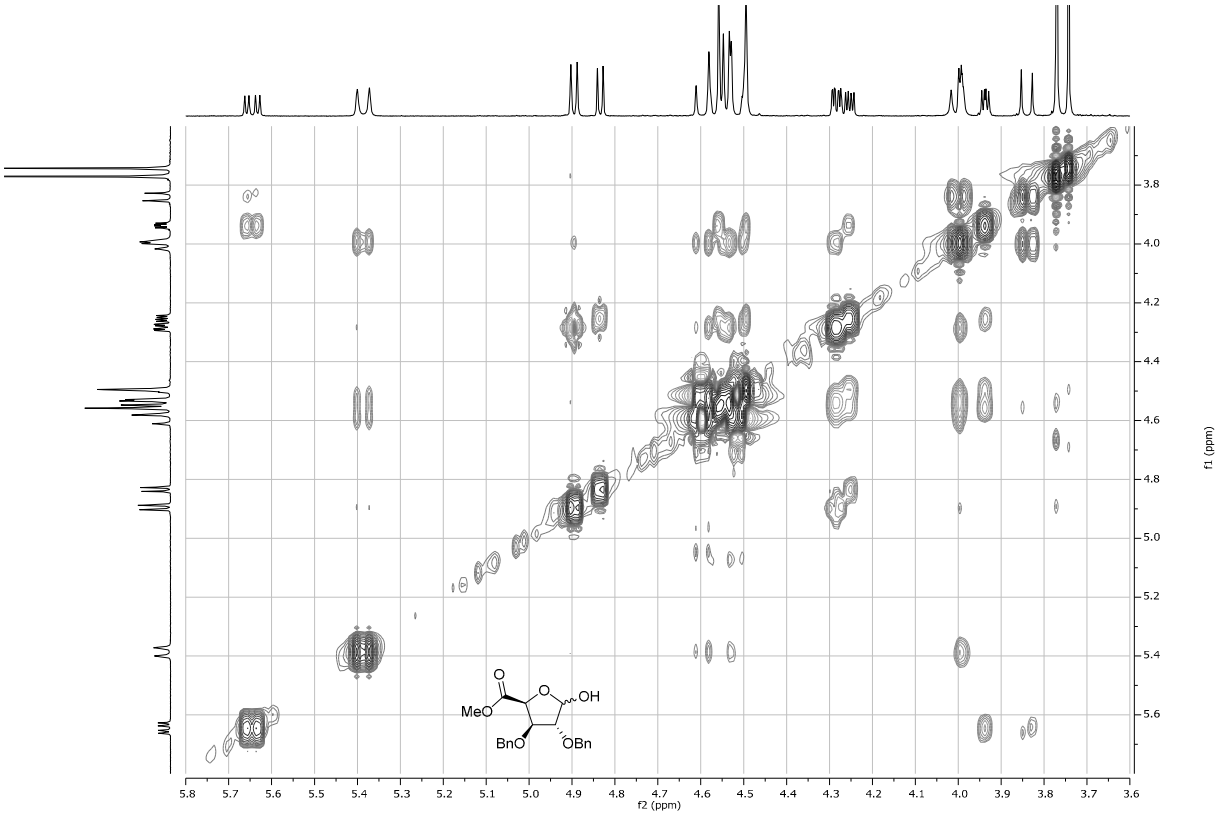
^{1}H-^{1}H COSY of compound **24**



^{1}H-^{13}C HSQC of compound **24**

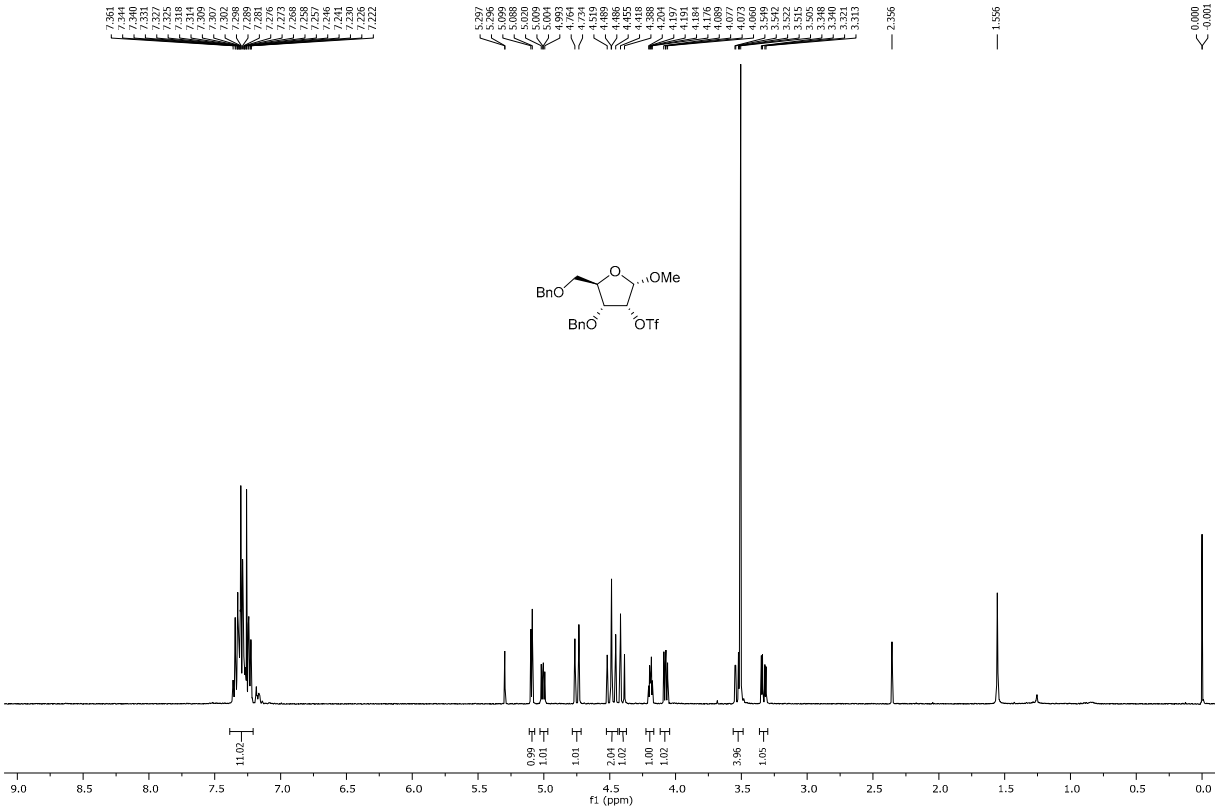


^{1}H-^{1}H NOESY of compound **24**

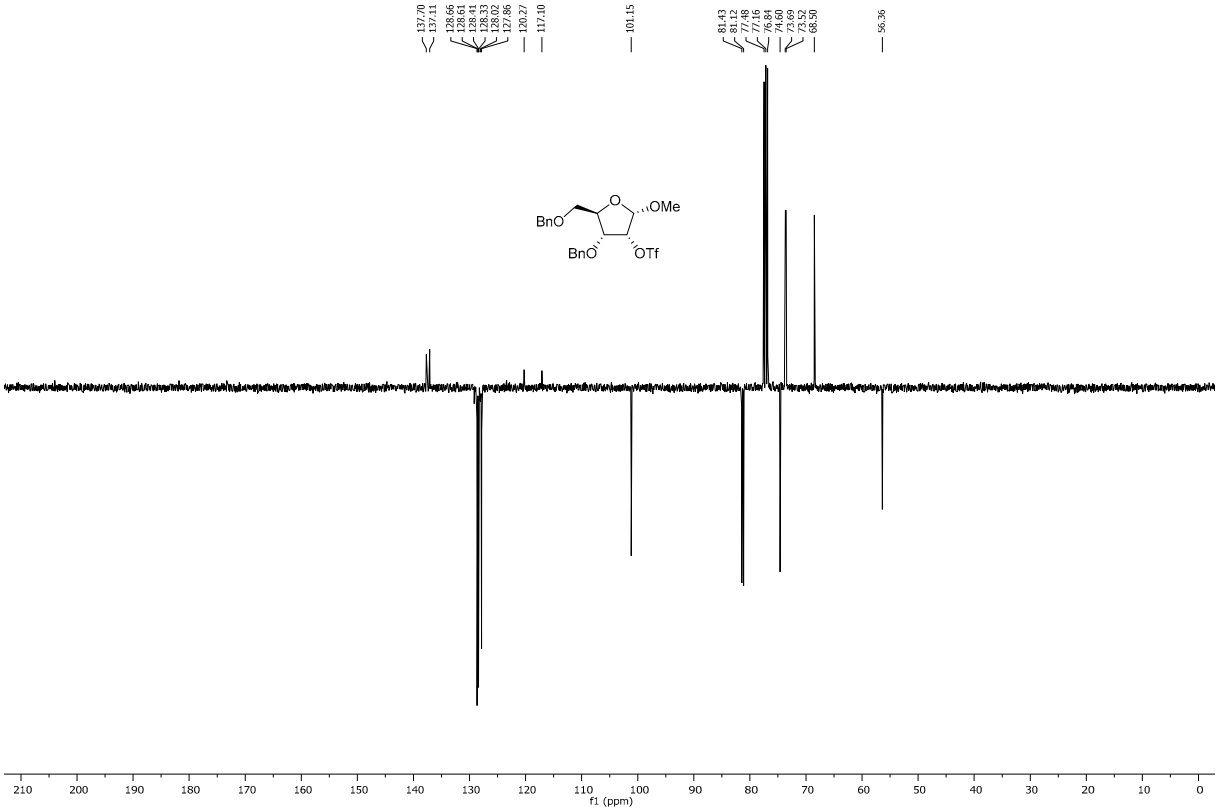


Methyl 3,5-di-*O*-benzyl-2-*O*-trifluoromethanesulfonate-α-D-ribofuranoside (29).

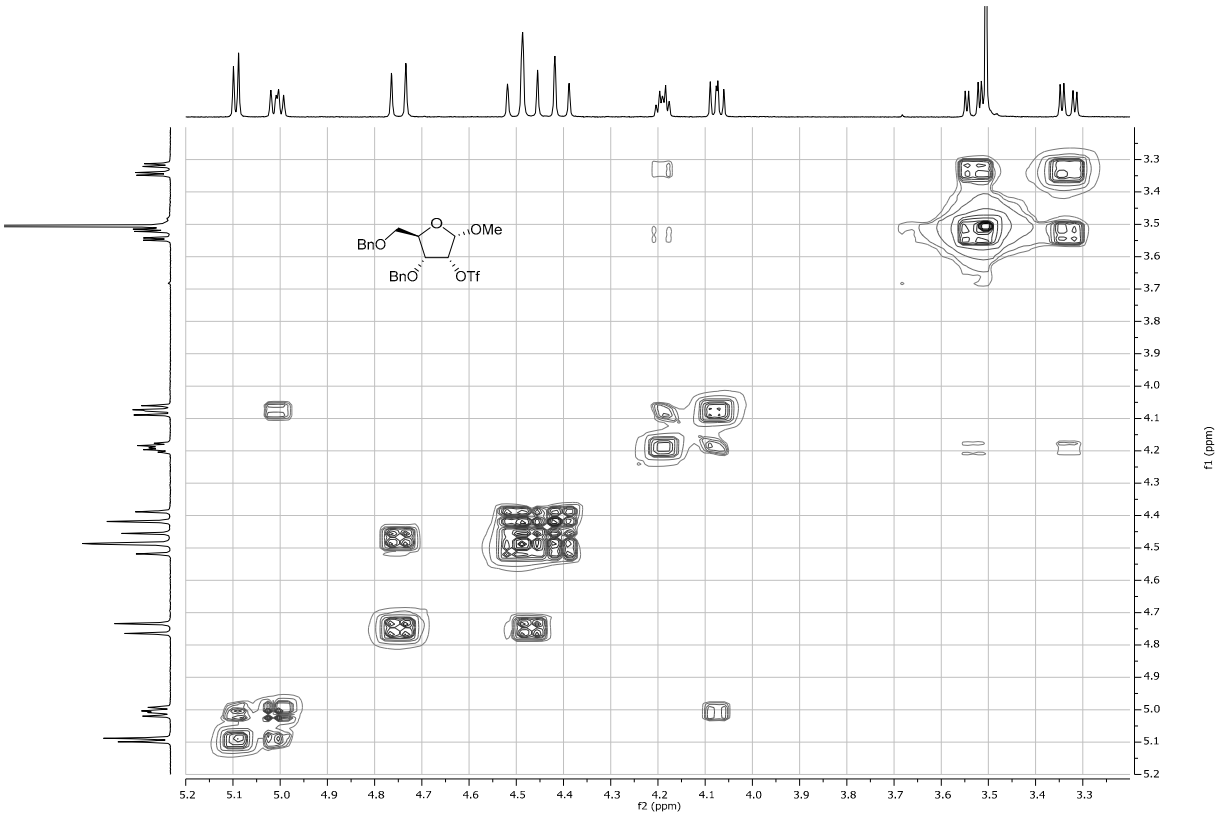
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **29**



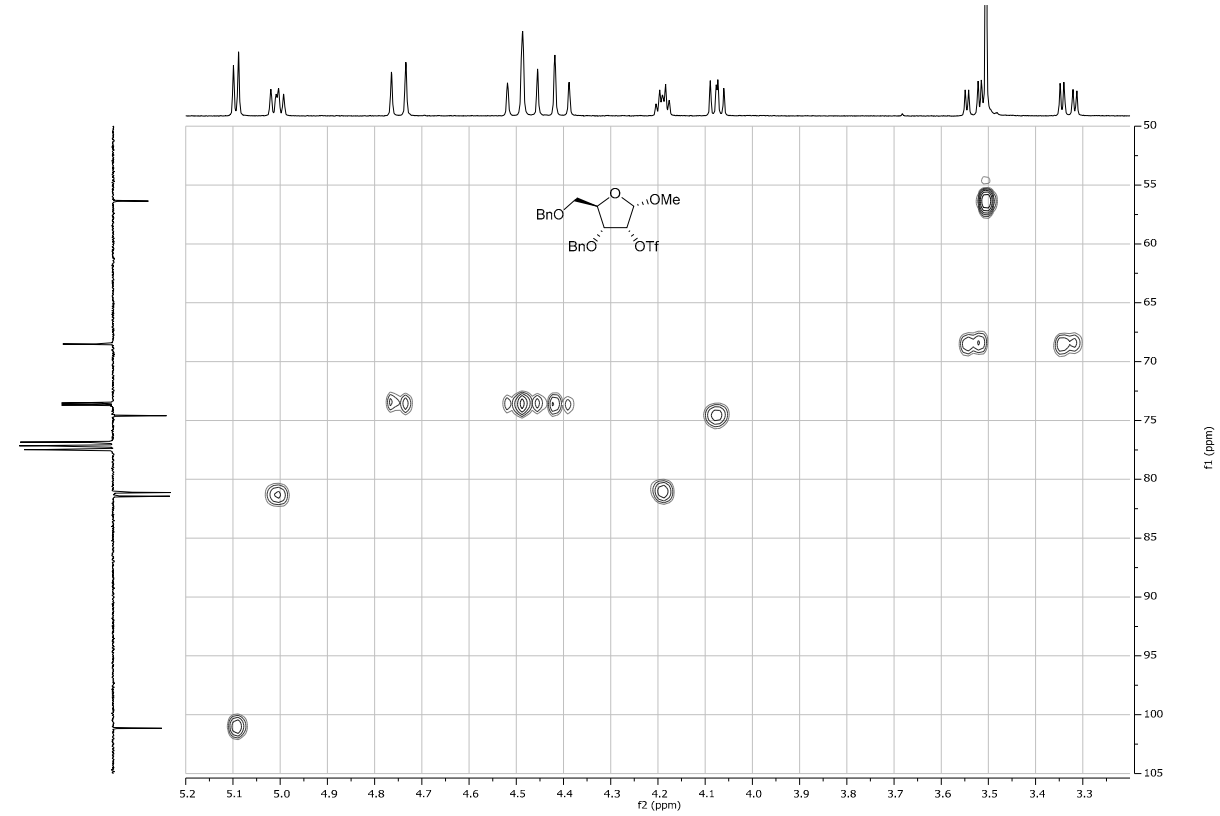
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **29**



^{1}H-^{1}H COSY of compound **29**

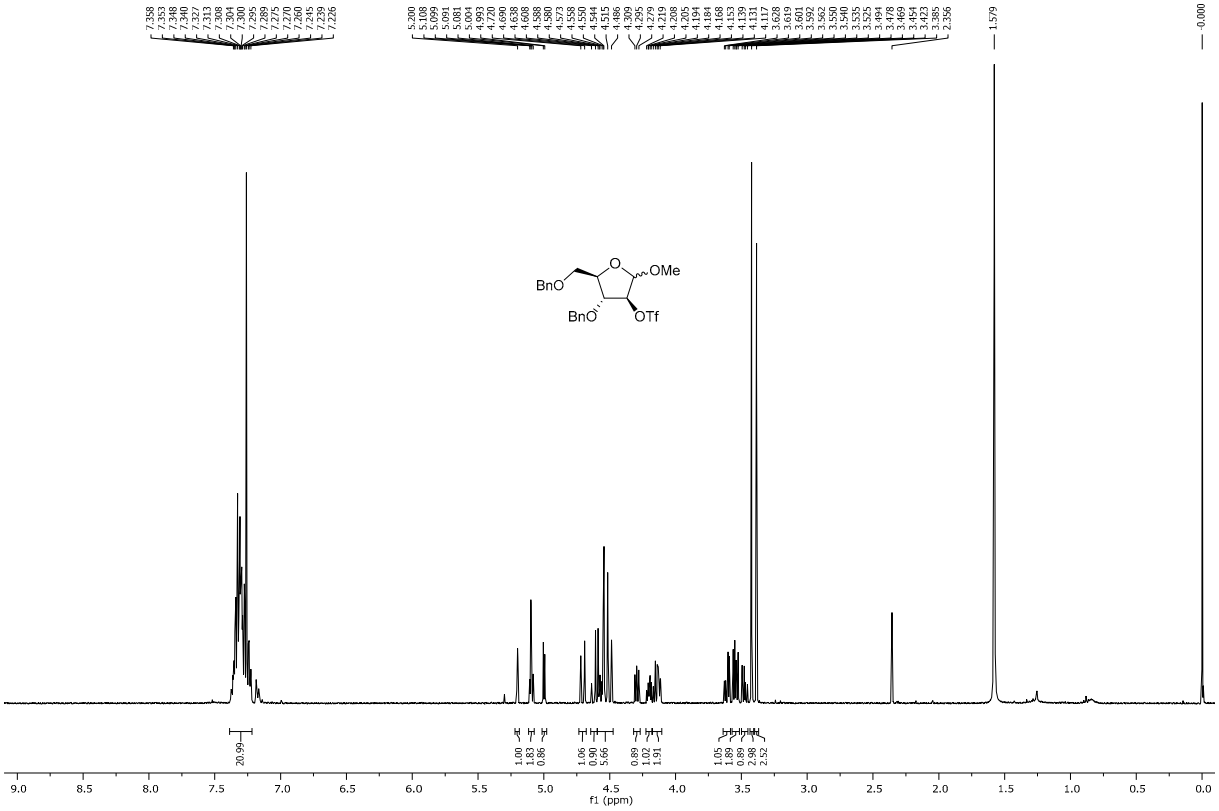


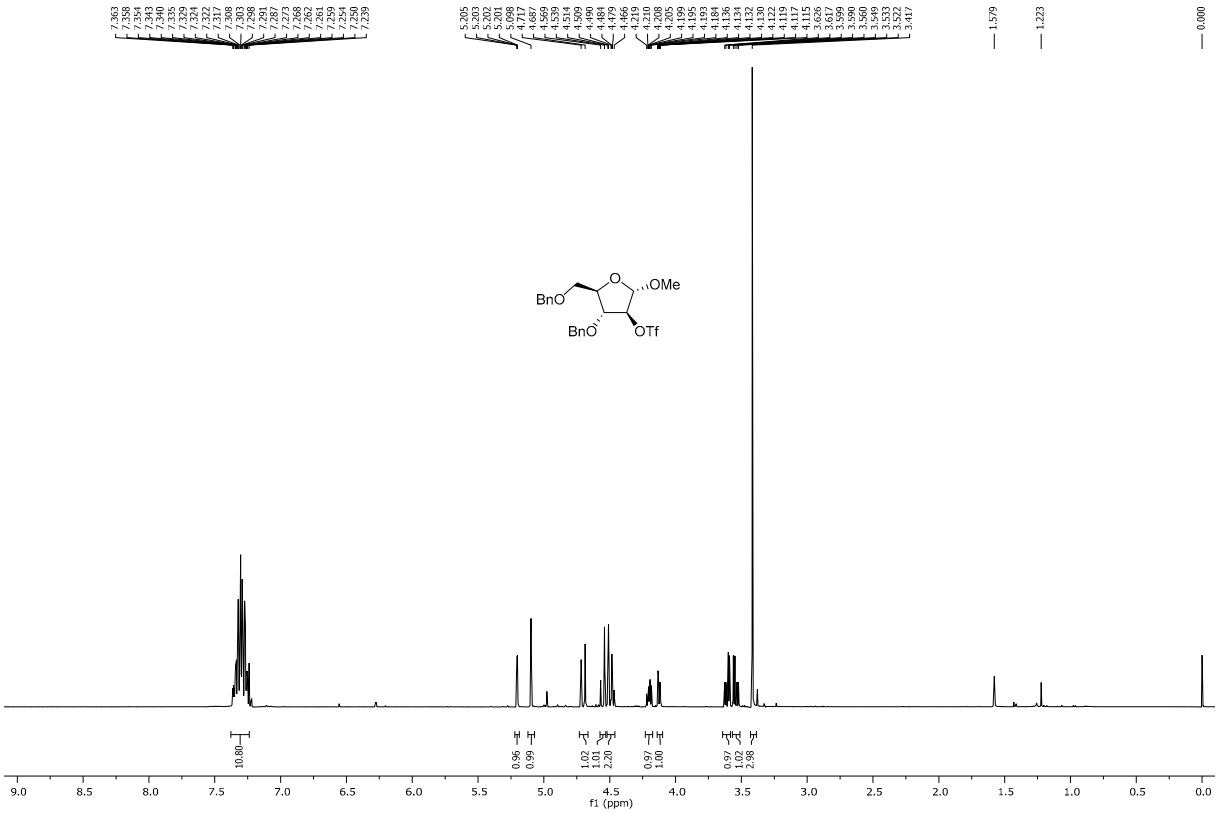
^{1}H-^{13}C HSQC of compound **29**



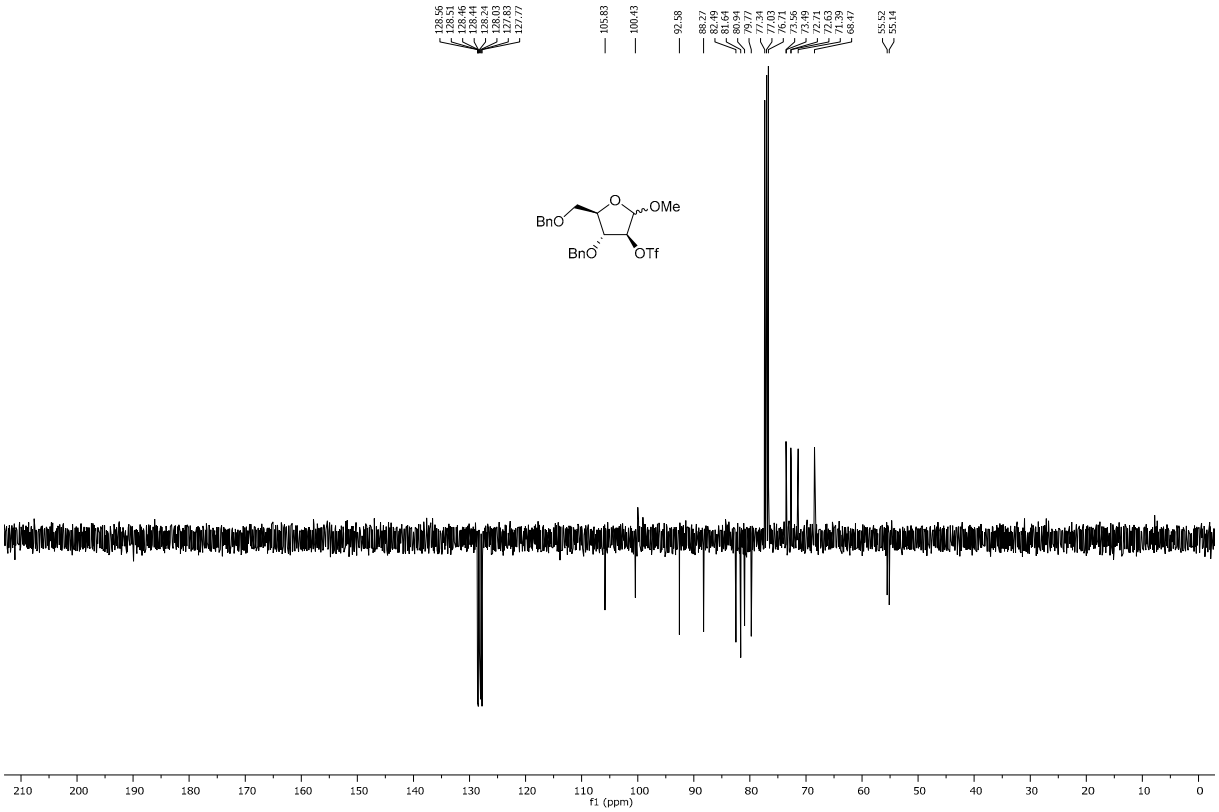
Methyl 3,5-di-*O*-benzyl-2-*O*-trifluoromethanesulfonate-α/β-D-arabinofuranoside (30).

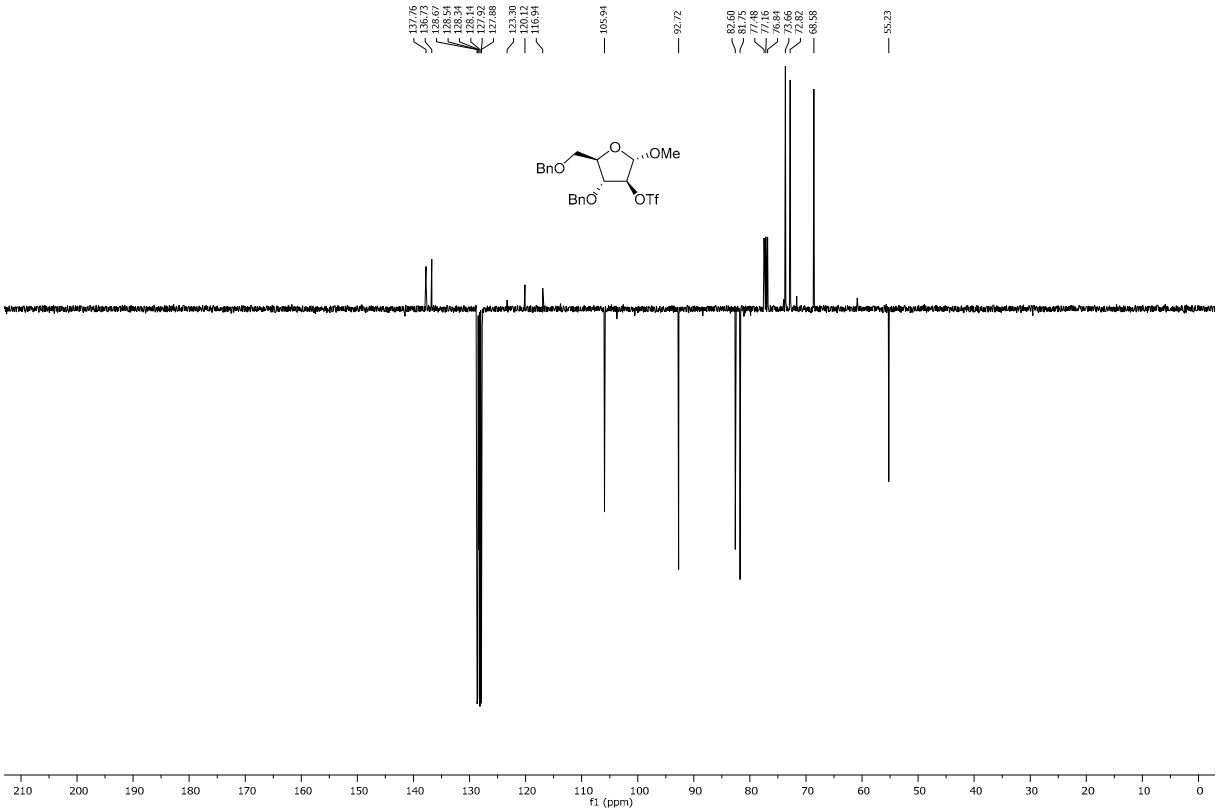
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **30**



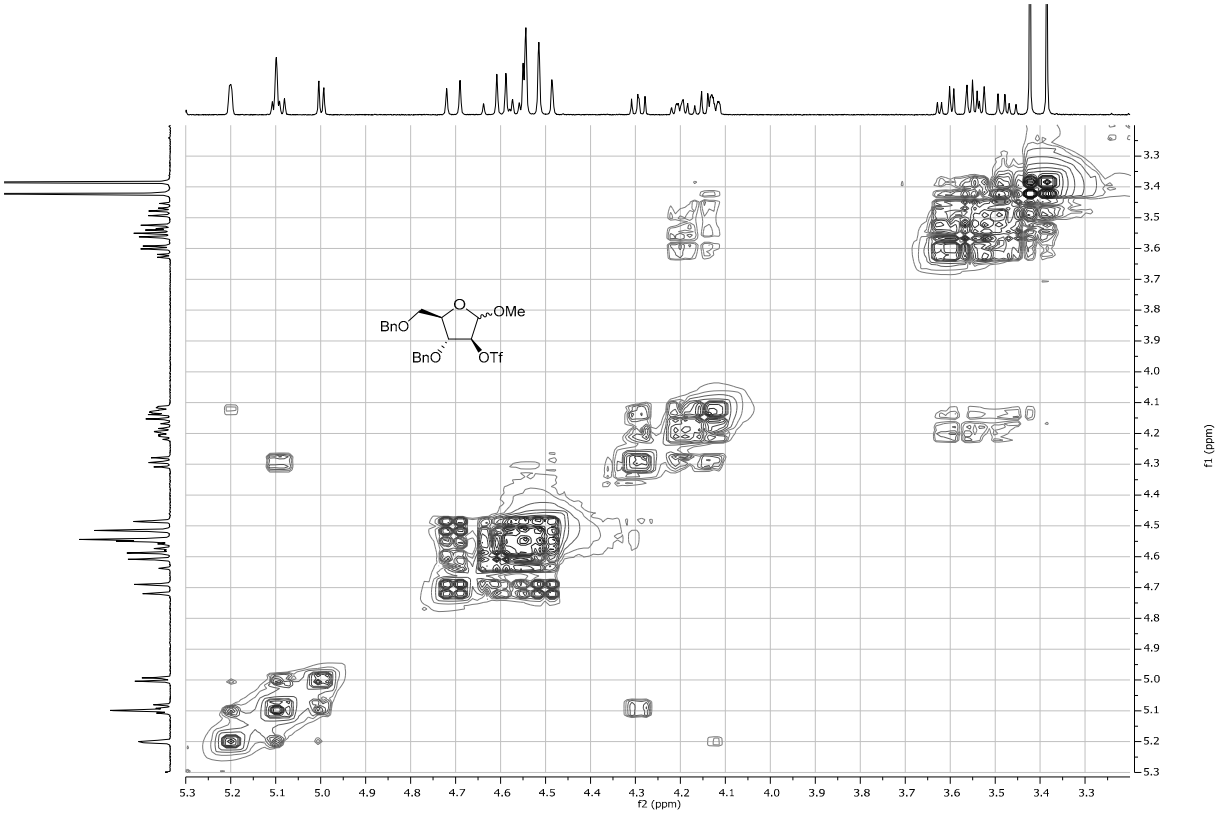


^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **30**

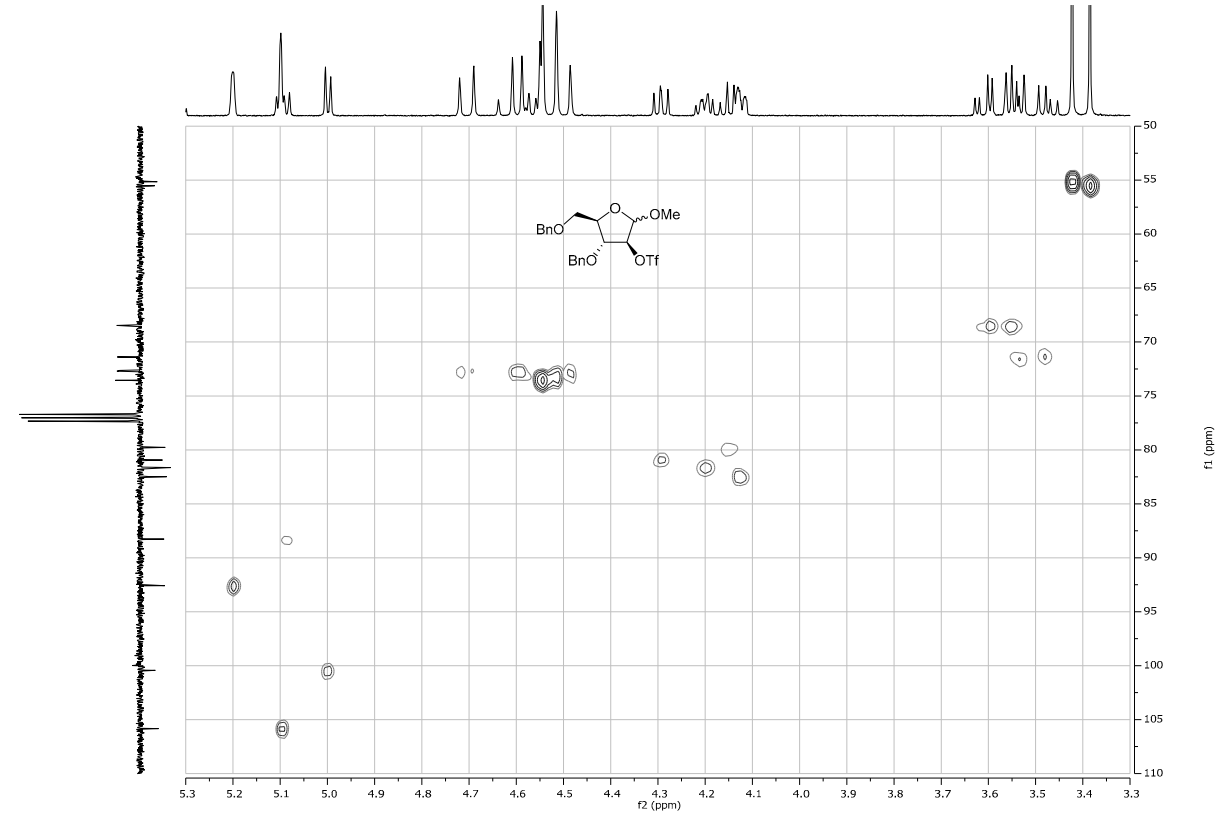




^{1}H-^{1}H COSY of compound **30**

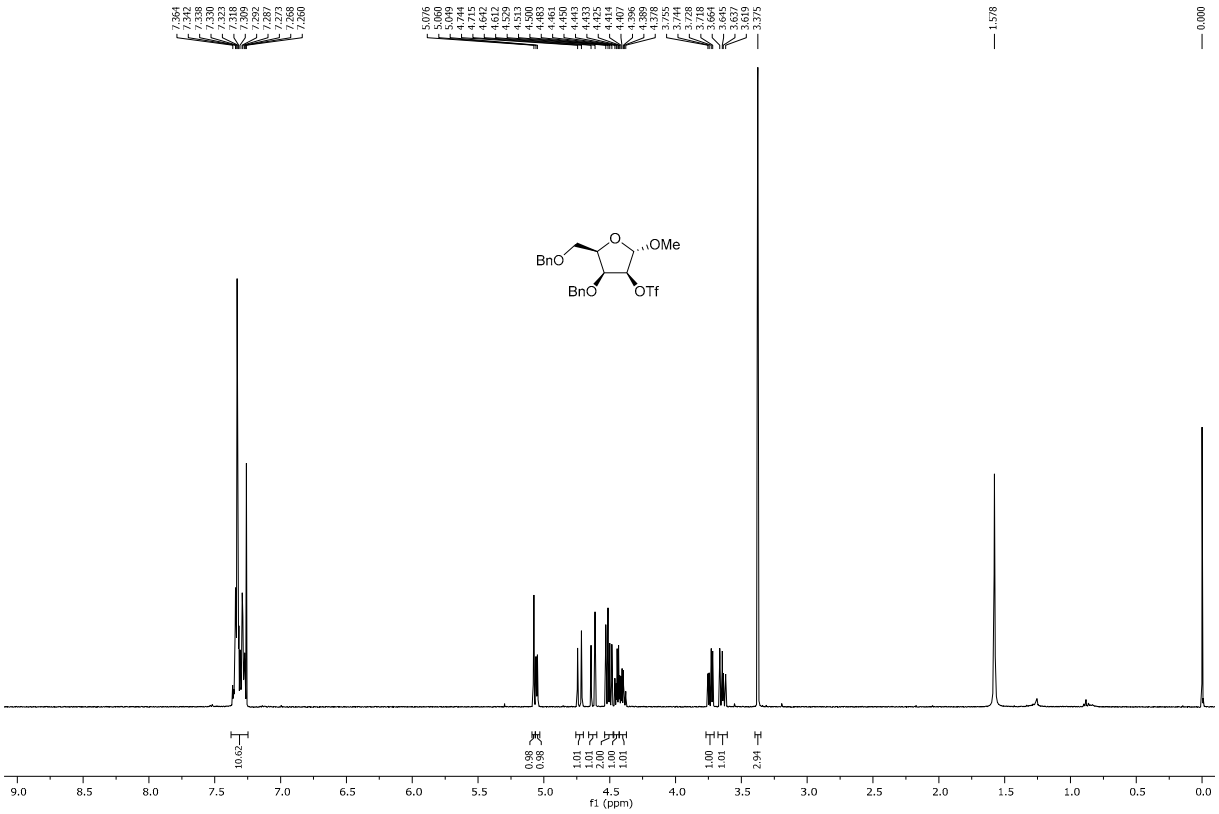


^{1}H-^{13}C HSQC of compound **30**

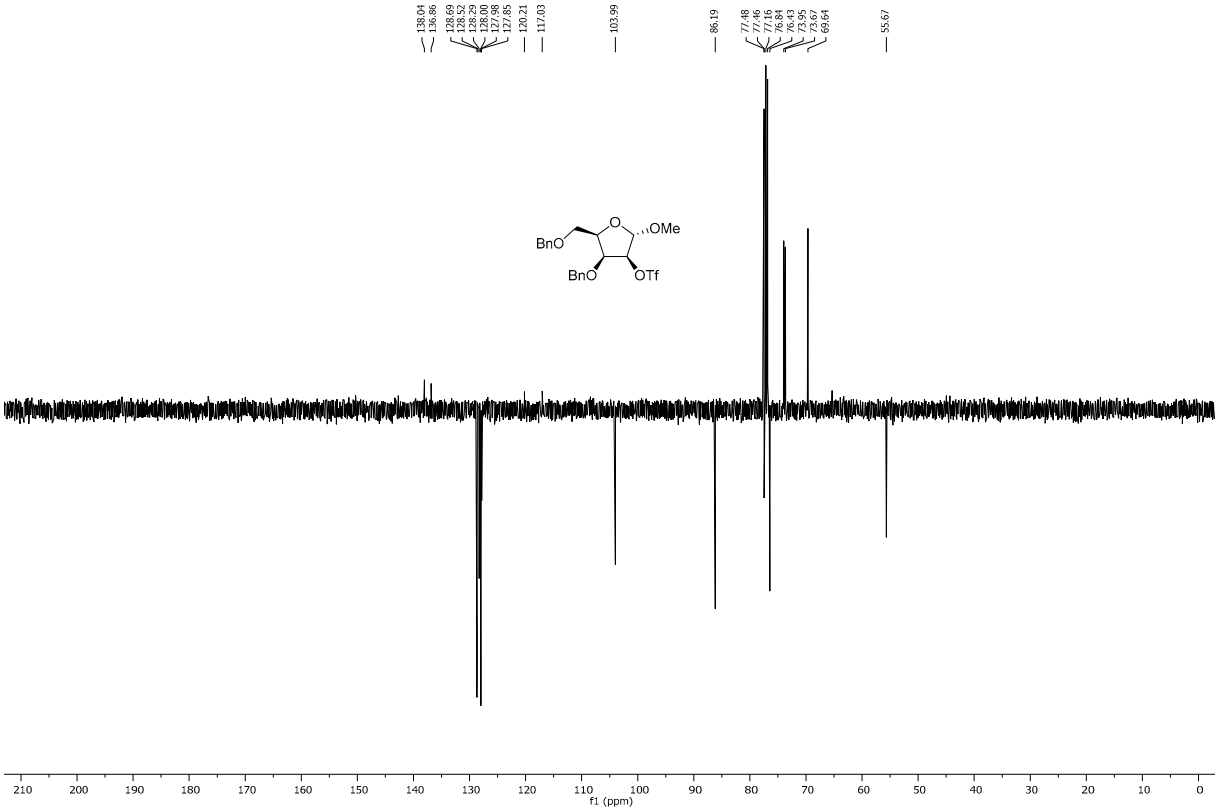


Methyl 3,5-di-*O*-benzyl-2-*O*-trifluoromethanesulfonate-α-D-lyxofuranoside (31).

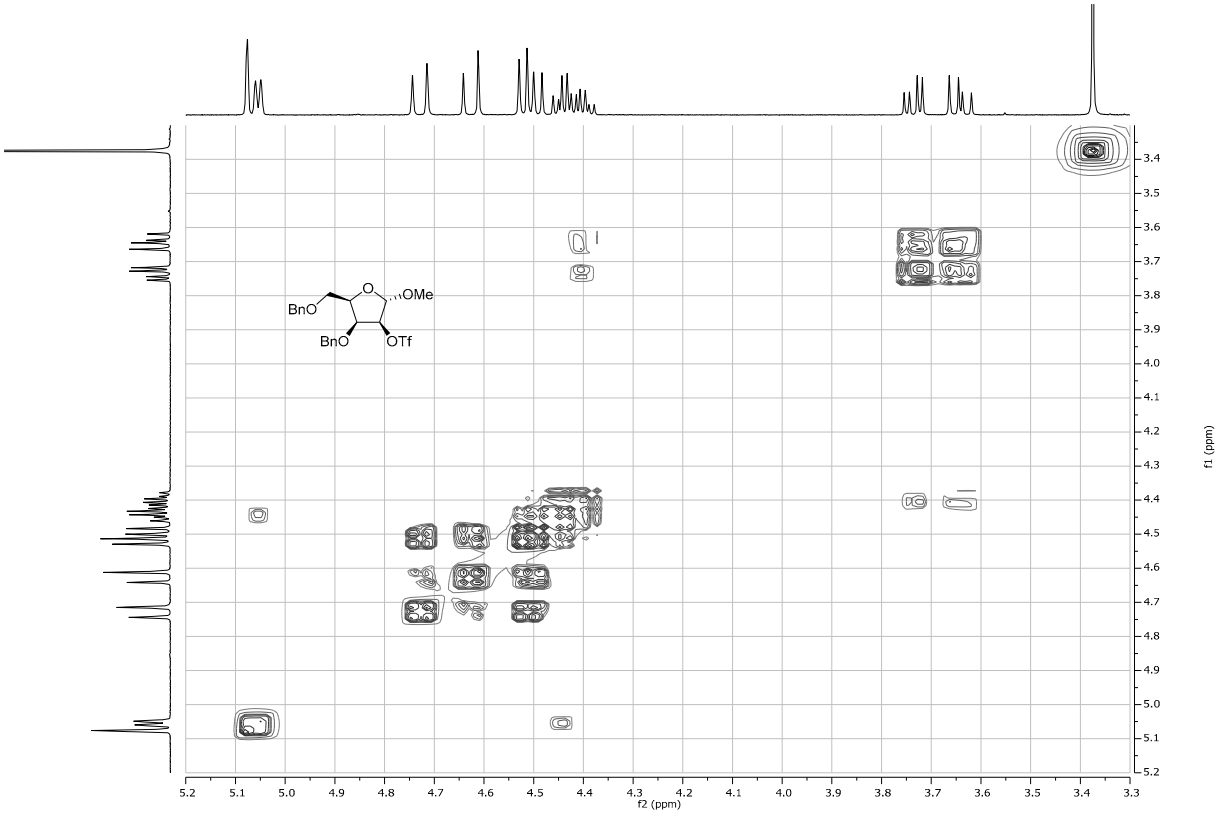
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **31**



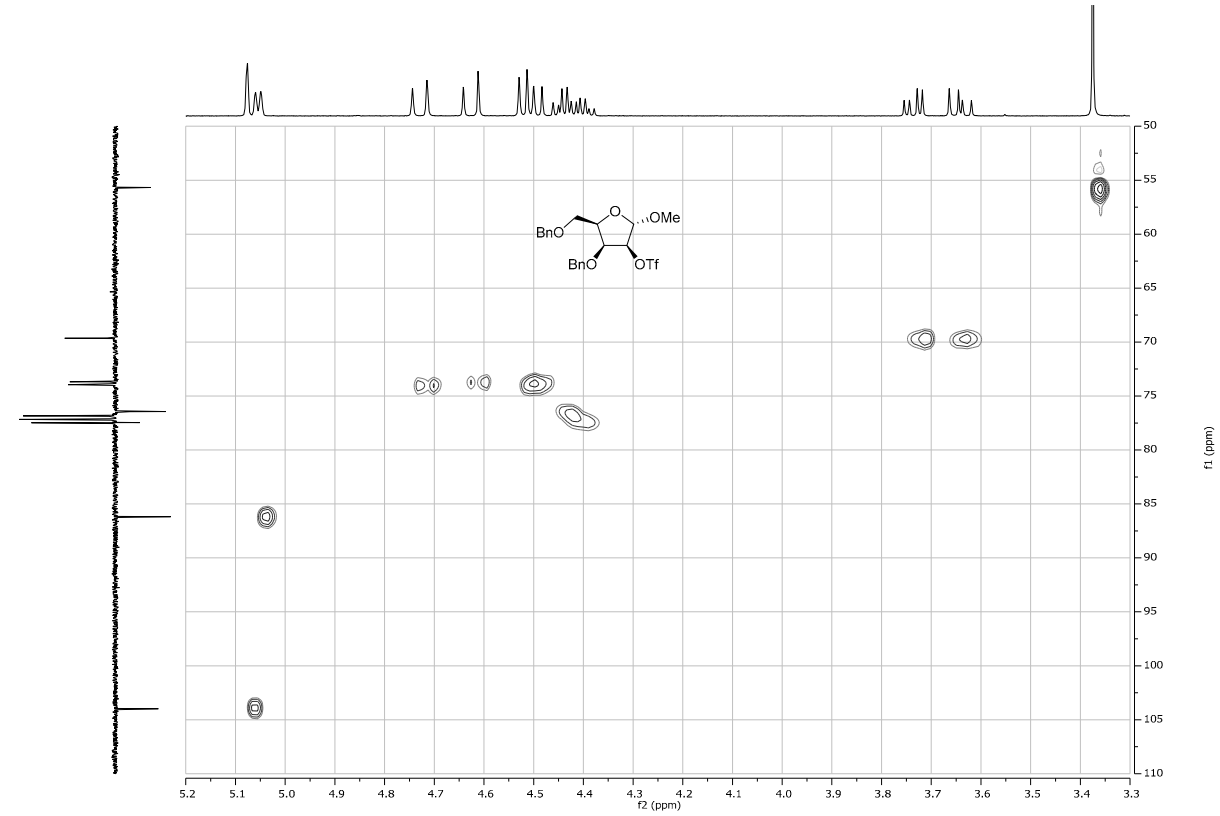
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **31**



^{1}H-^{1}H COSY of compound **31**

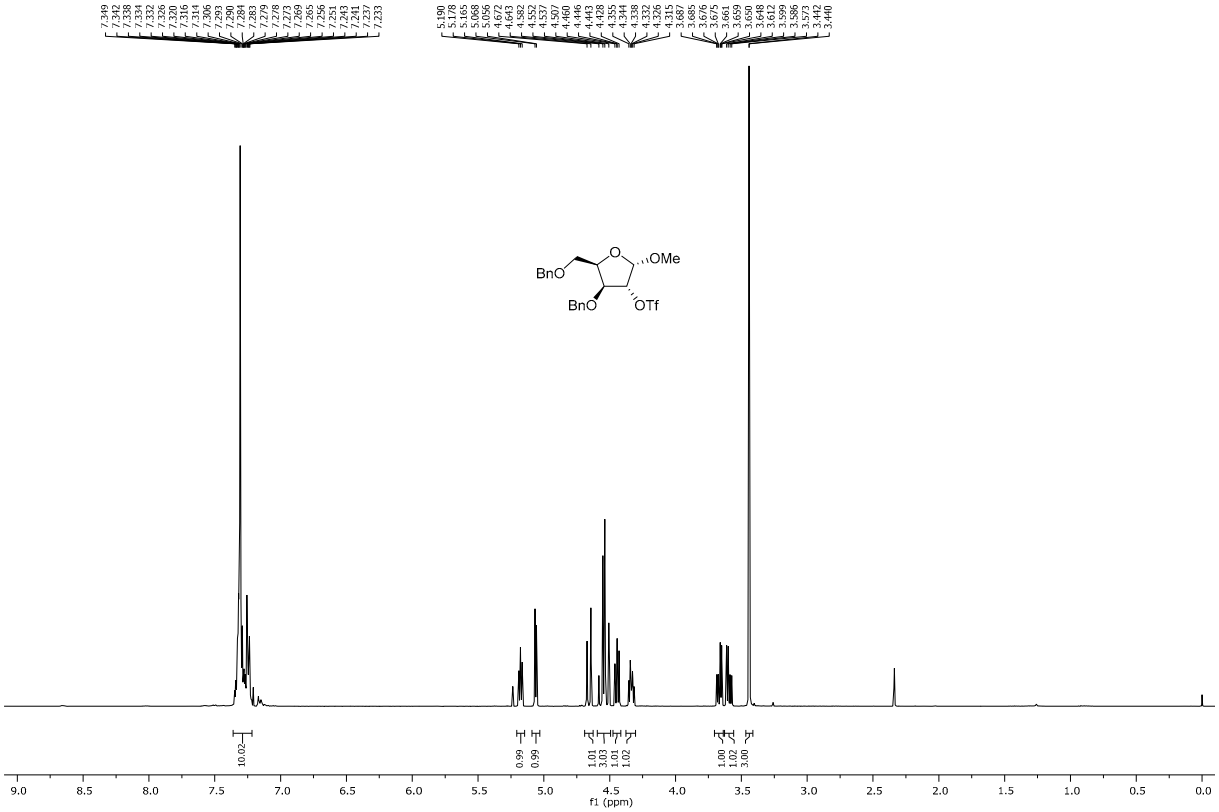


^{1}H-^{13}C HSQC of compound **31**

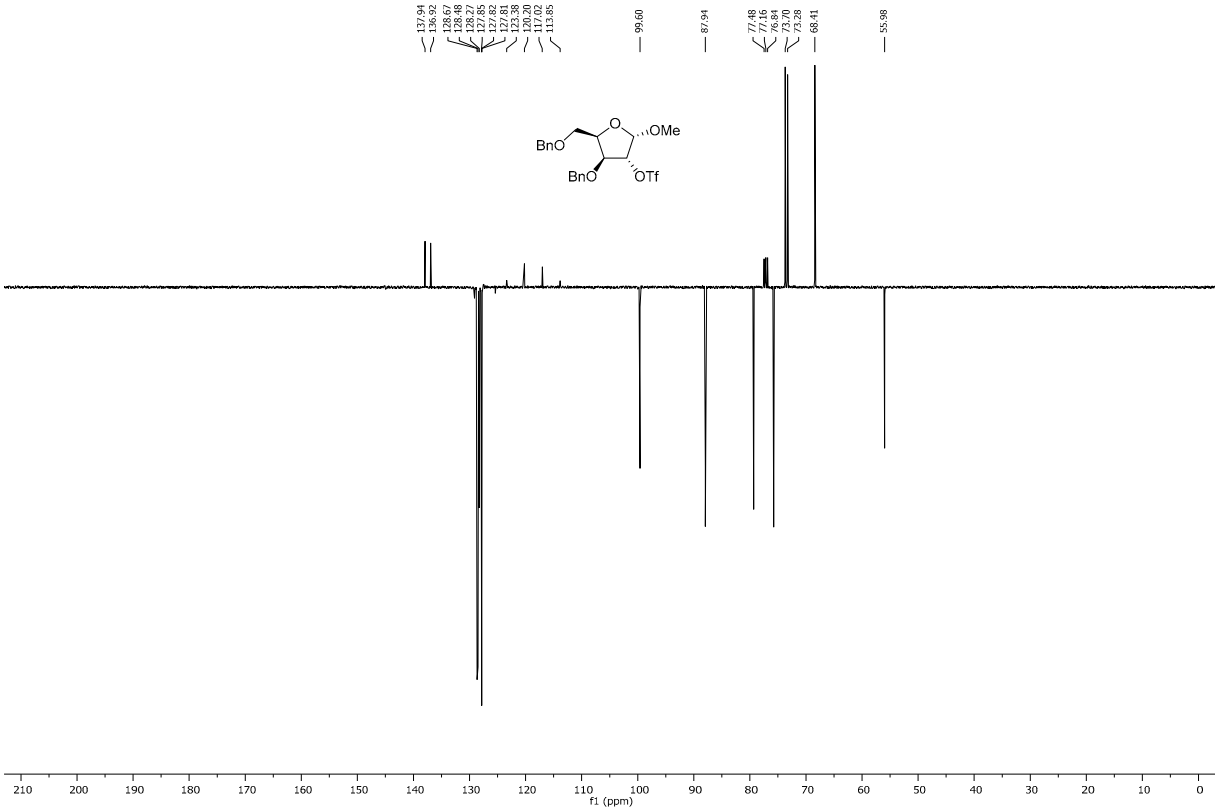


Methyl 3,5-di-*O*-benzyl-2-*O*-trifluoromethanesulfonate-α -D-xylofuranoside (32α).

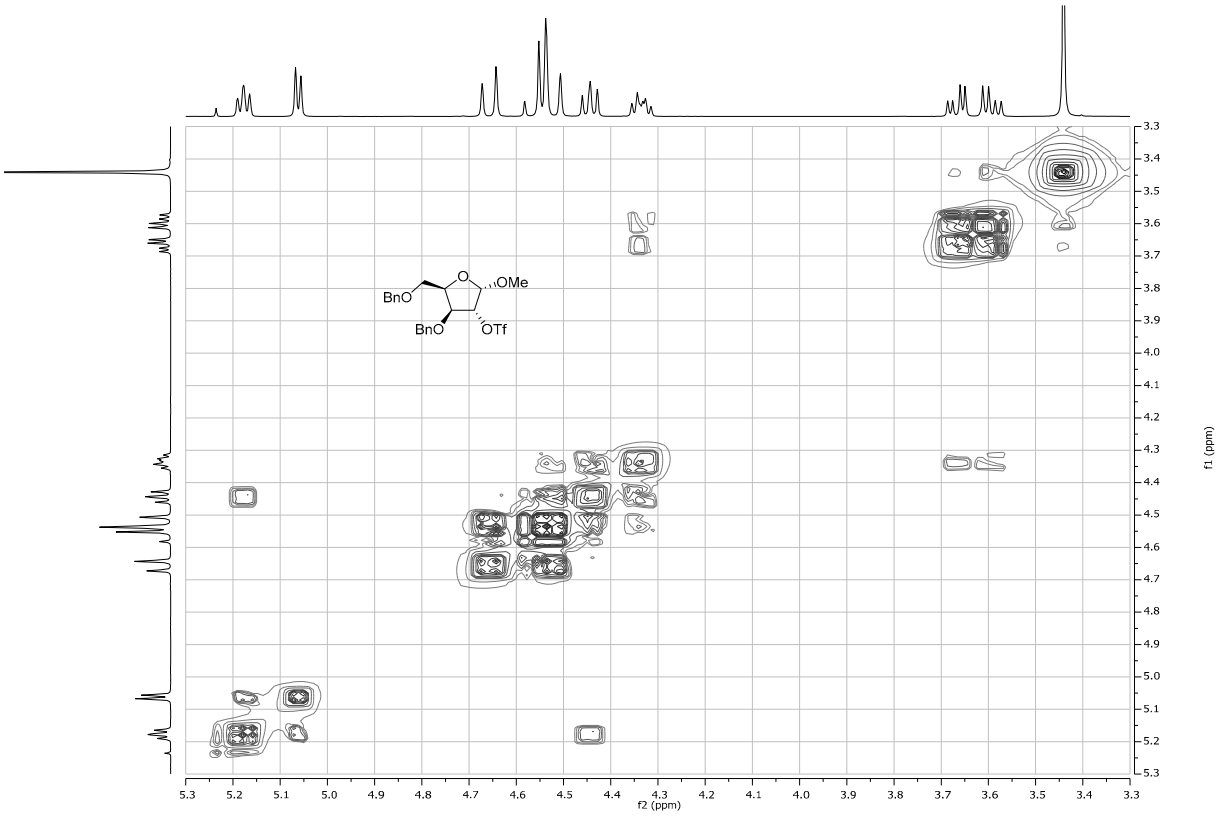
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **32α**



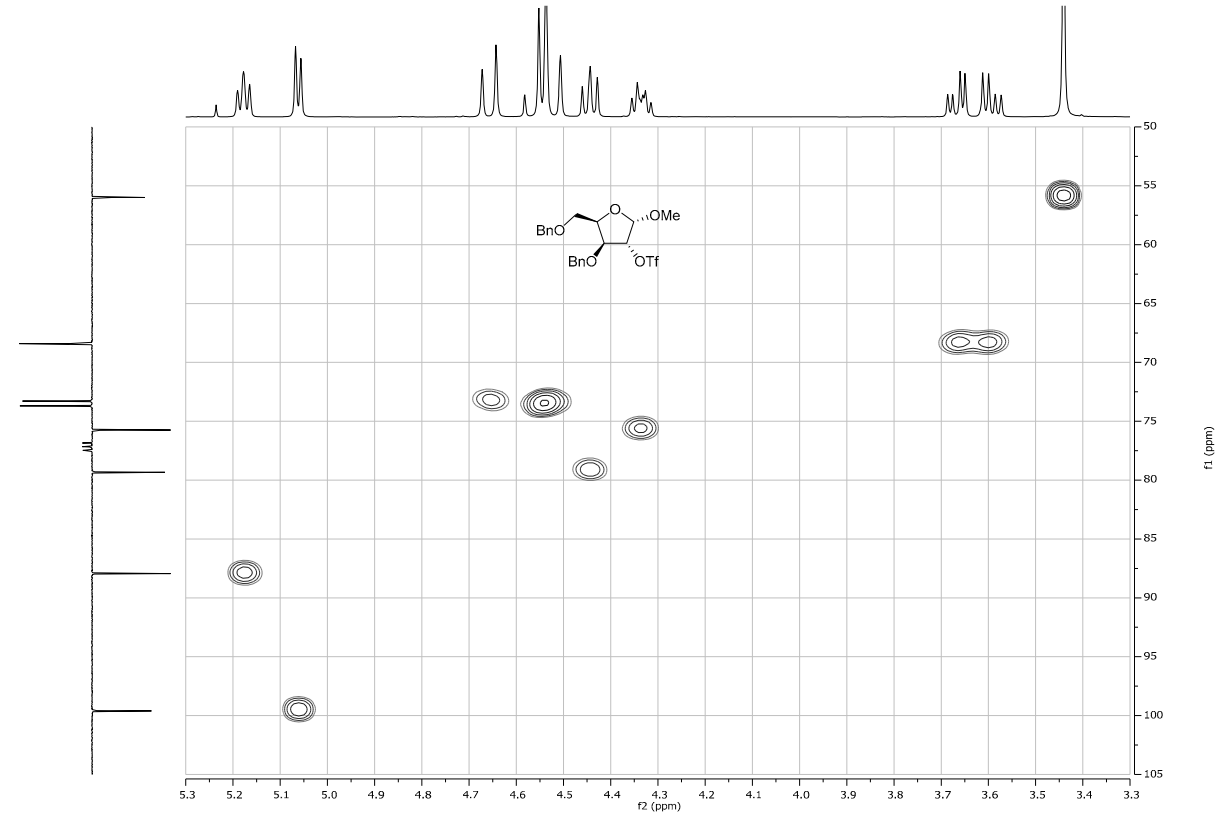
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **32α**



^{1}H-^{1}H COSY of compound **32α**

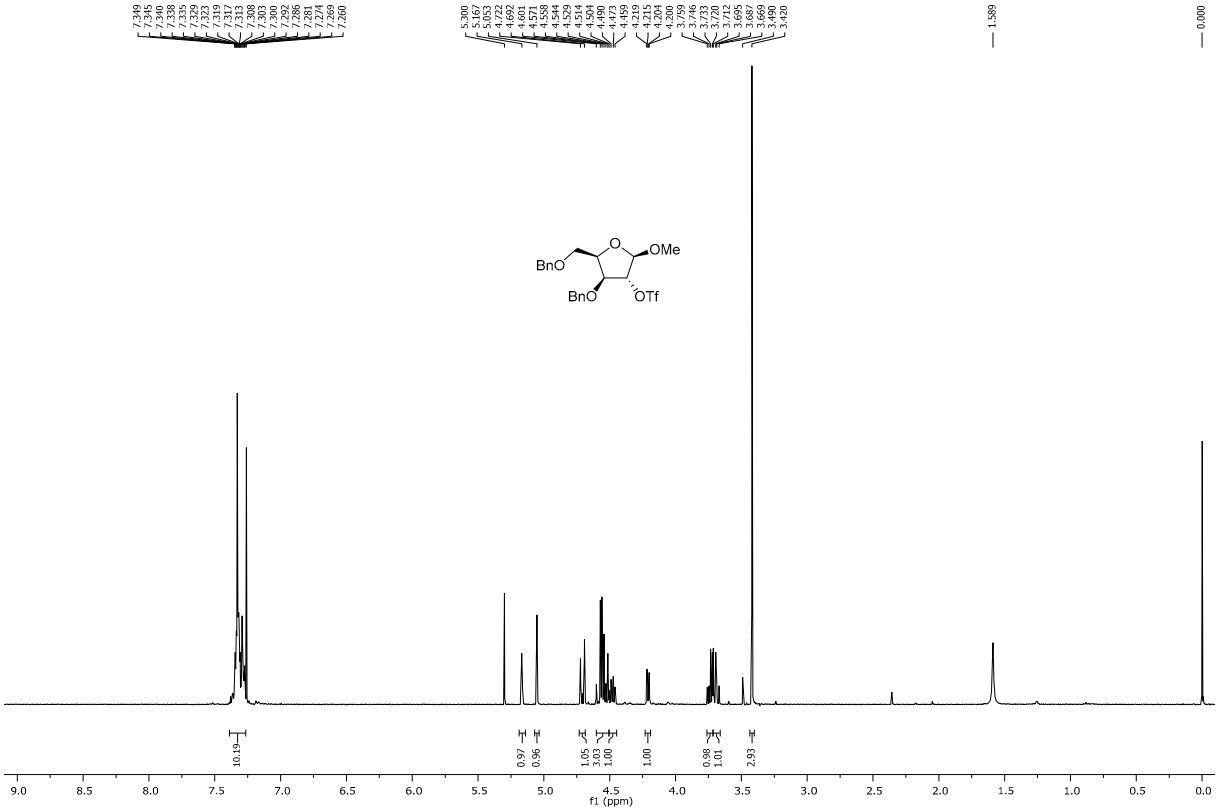


^{1}H-^{13}C HSQC of compound **32α**

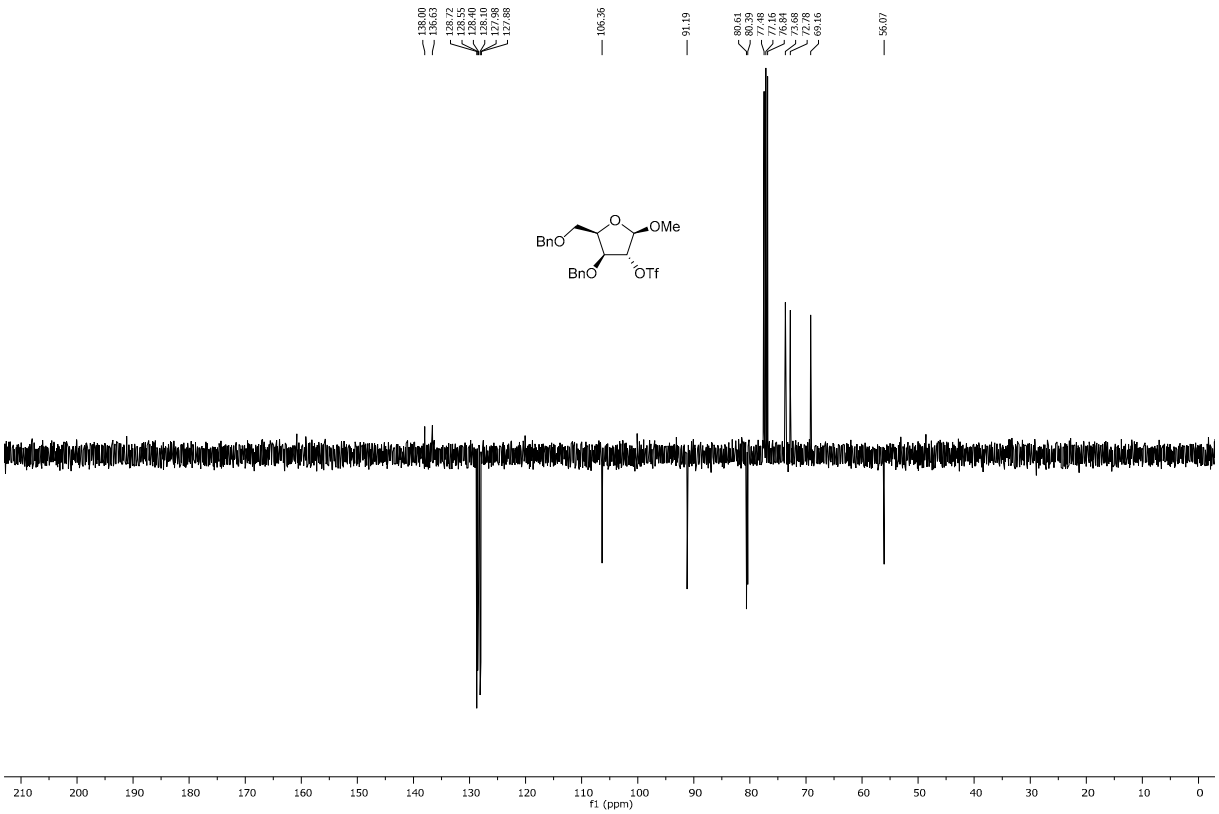


Methyl 3,5-di-*O*-benzyl-2-*O*-trifluoromethanesulfonate-β-D-xylofuranoside (32β).

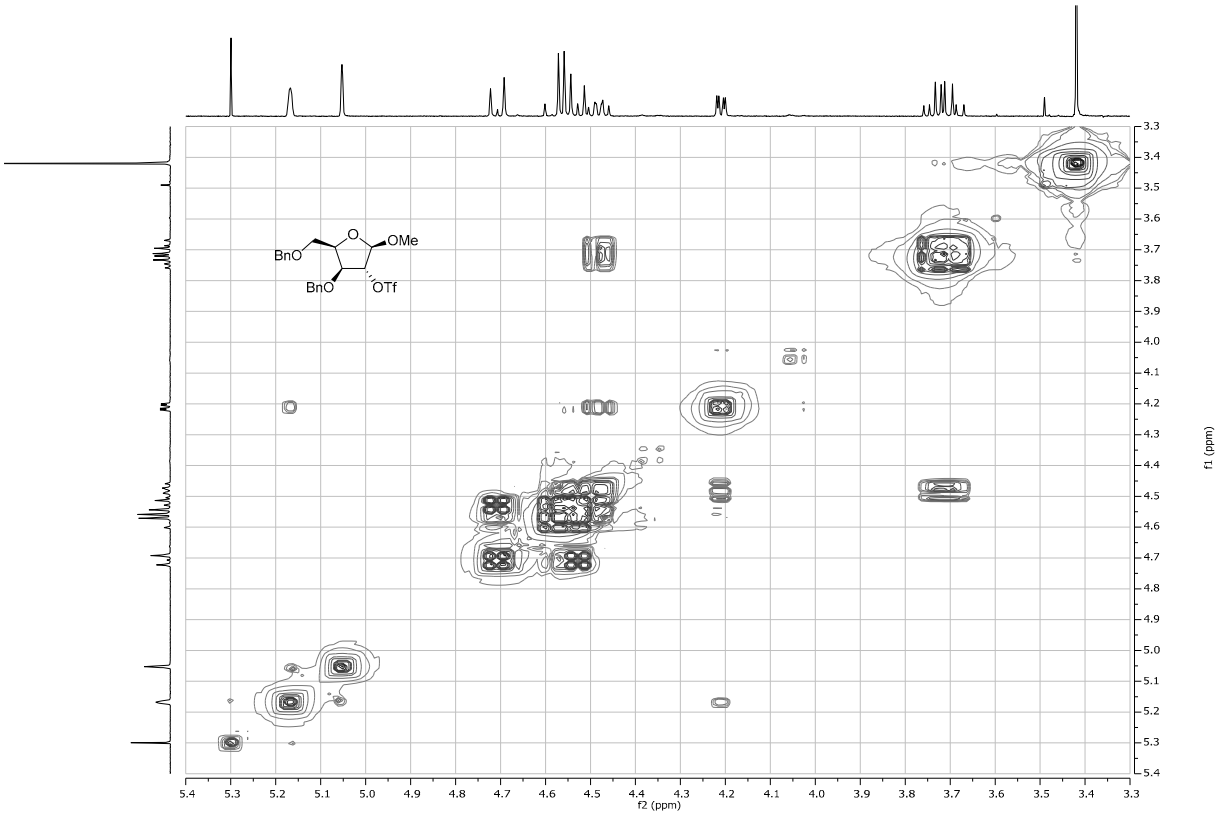
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **32β**



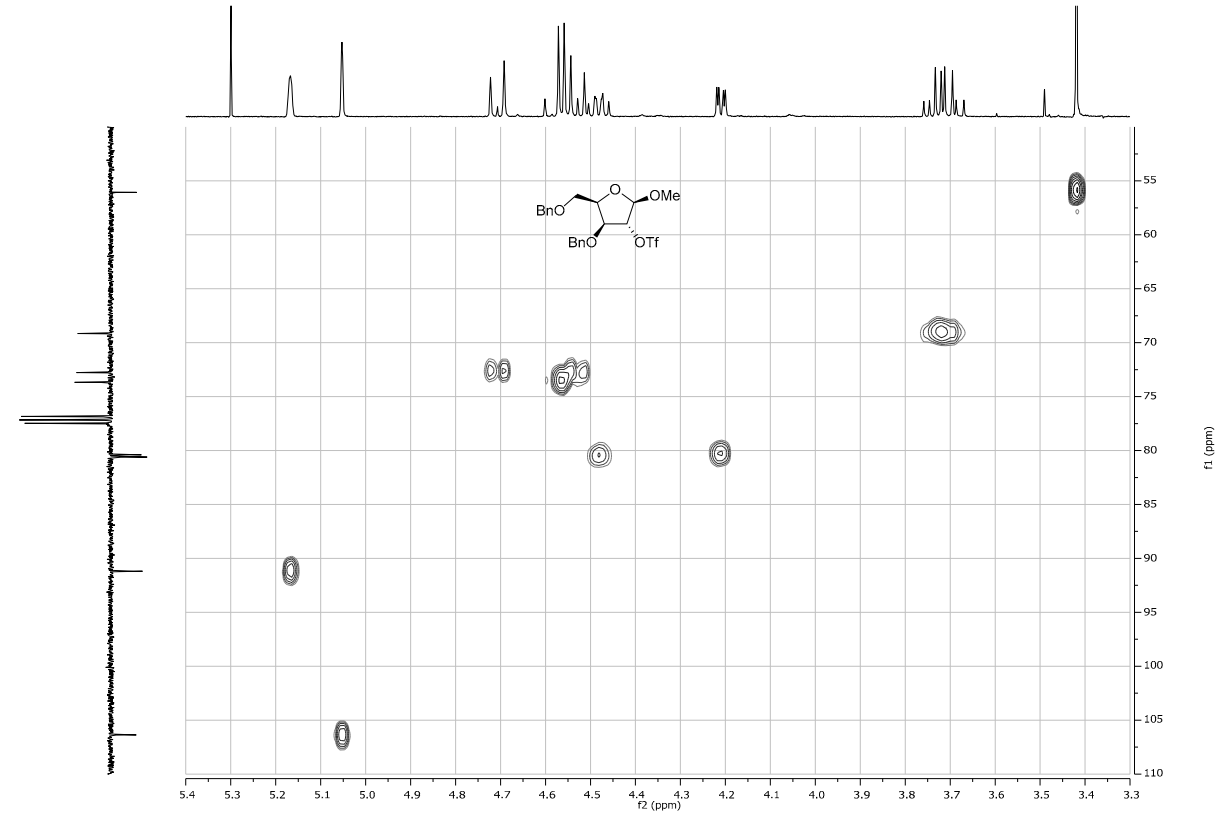
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **32β**



^{1}H-^{1}H COSY of compound **32β**

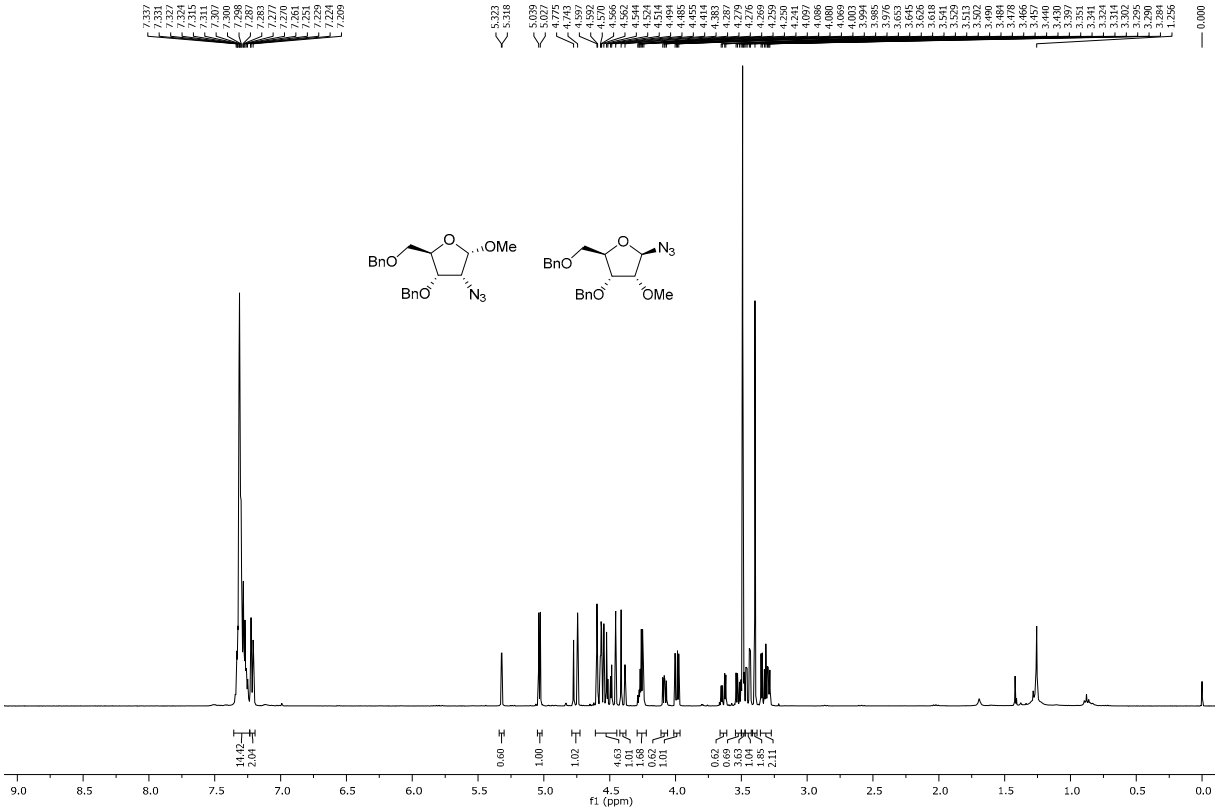


^{1}H-^{13}C HSQC of compound **32β**

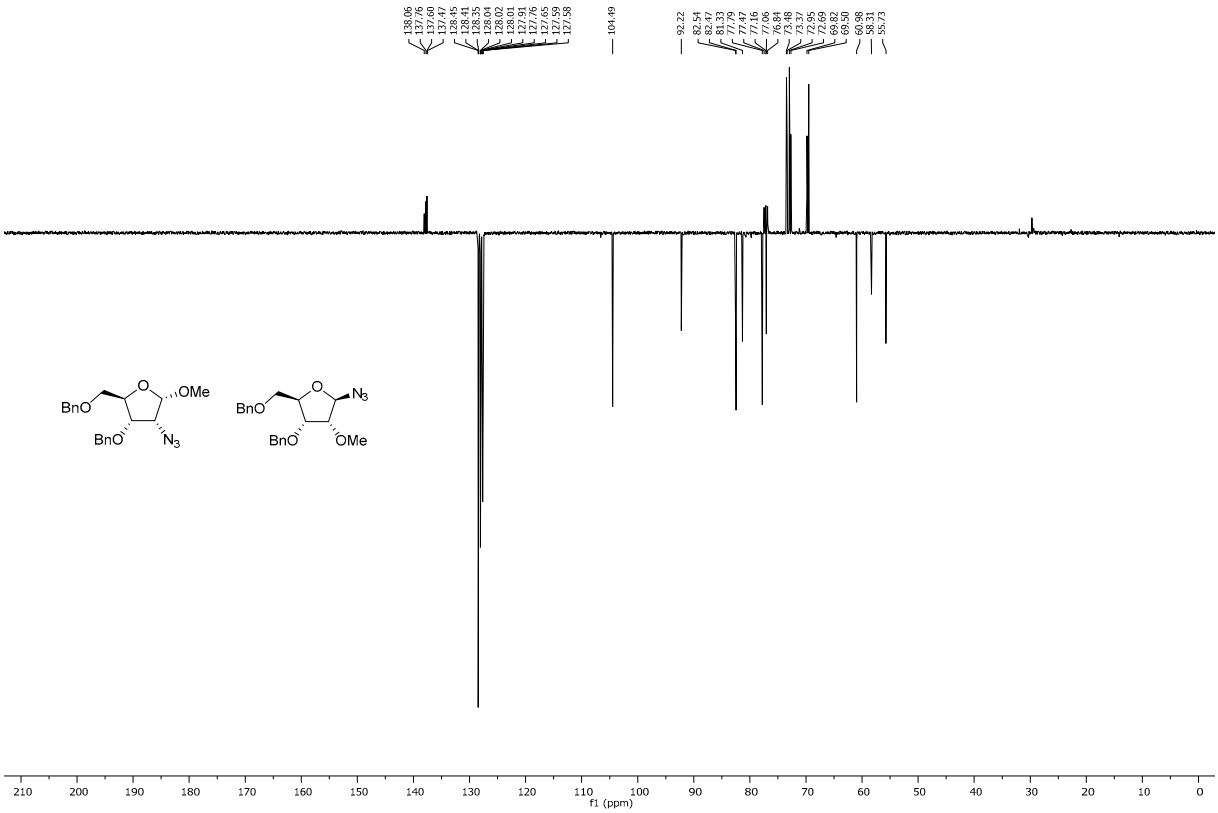


Methyl 2-azido-3,5-di-*O*-benzyl-2-deoxy-α-D-ribofuranoside (33α)

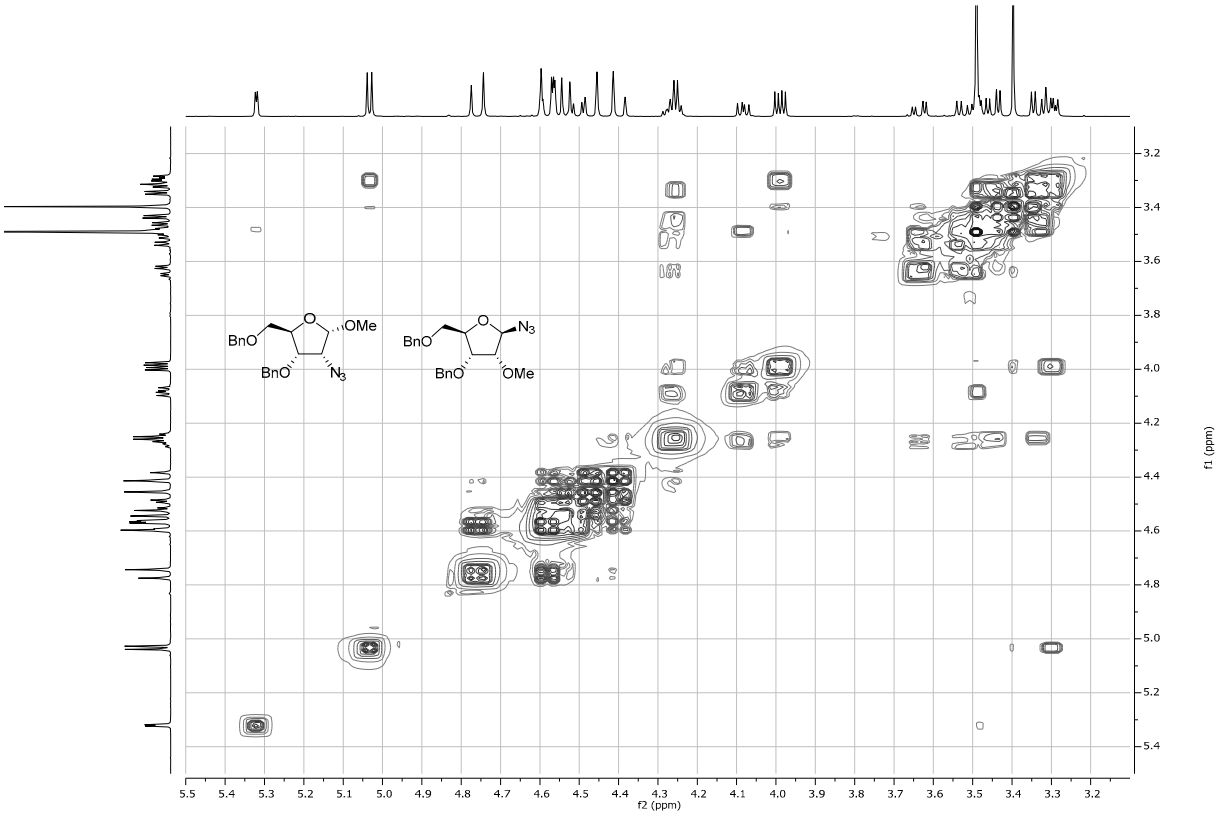
^{1}H NMR, 400 MHz, $CDCl_3$ of compounds **33α** and **51**



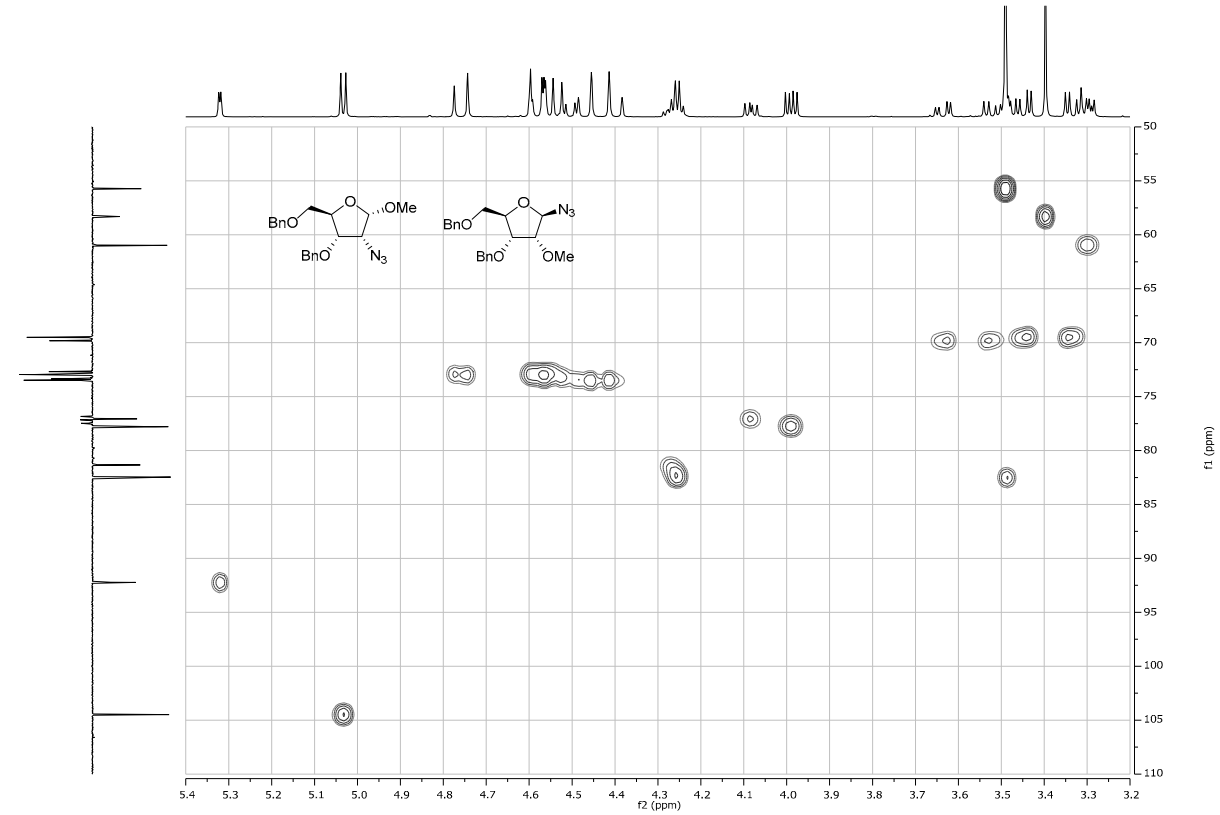
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compounds **33α** and **51**



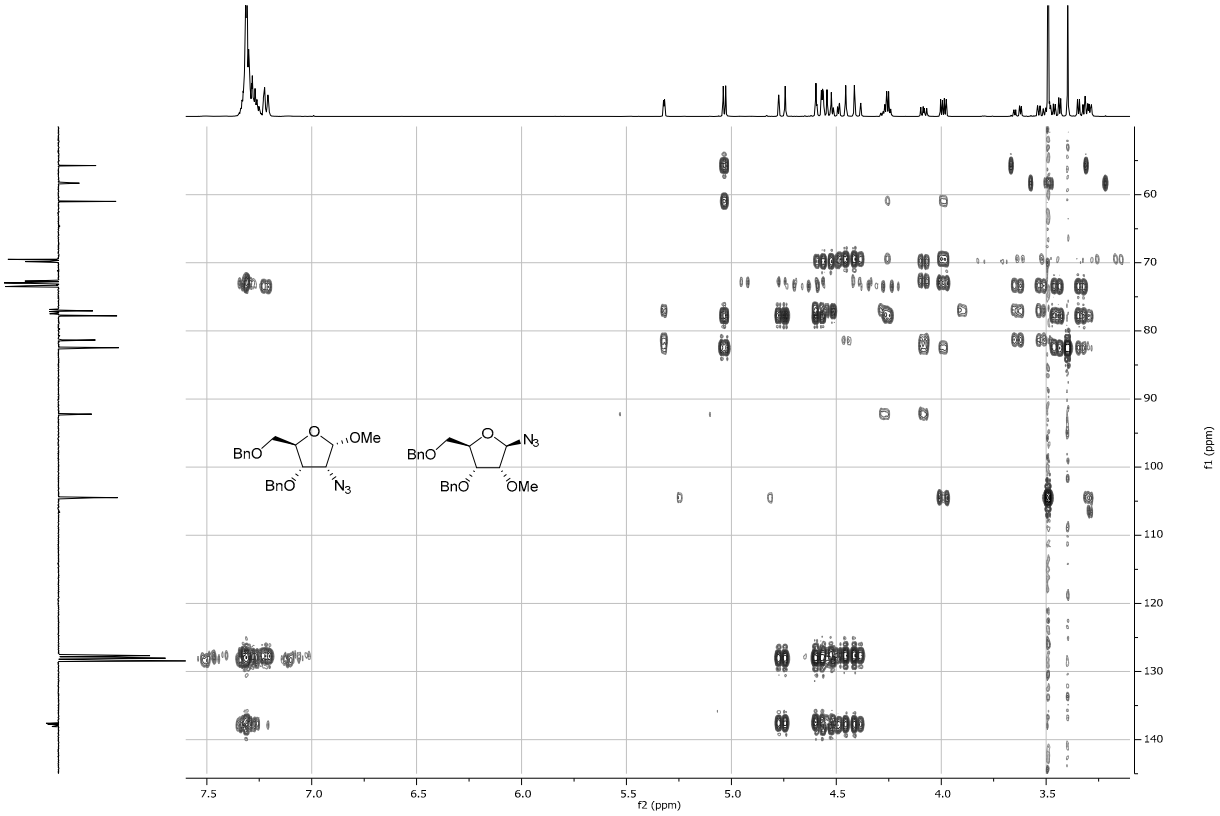
^{1}H-^{1}H COSY of compound compounds **33α** and **51**



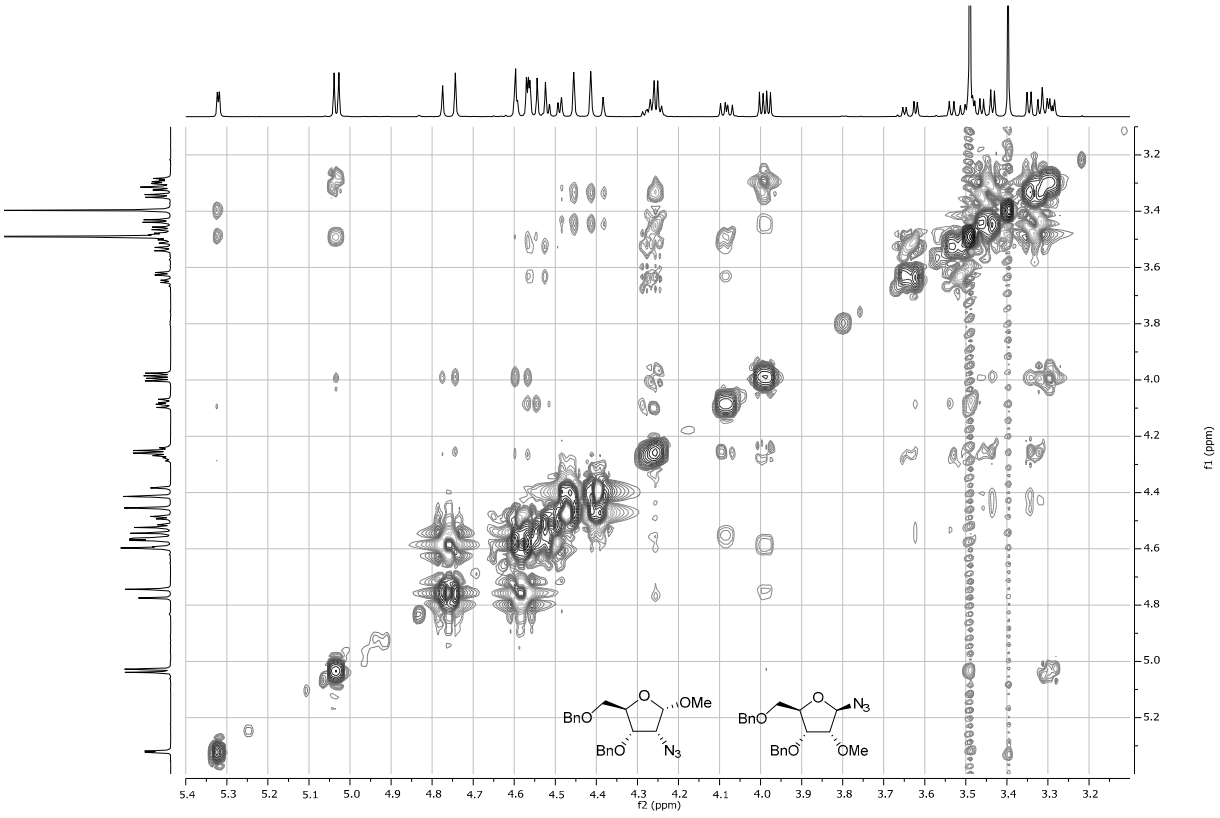
^{1}H-^{13}C HSQC of compound compounds **33α** and **51**



^{1}H-^{13}C HMBC of compound compounds **33α** and **51**

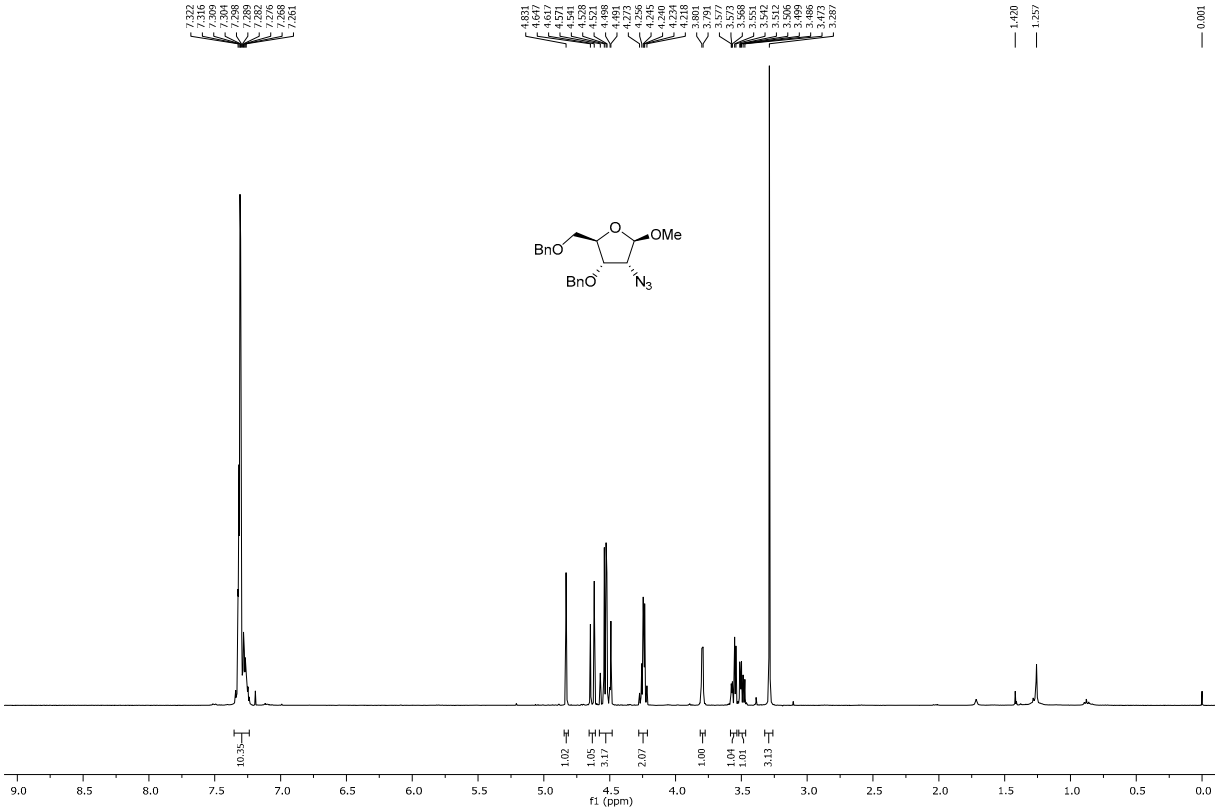


^{1}H-^{1}H NOESY of compound compounds **33α** and **51**

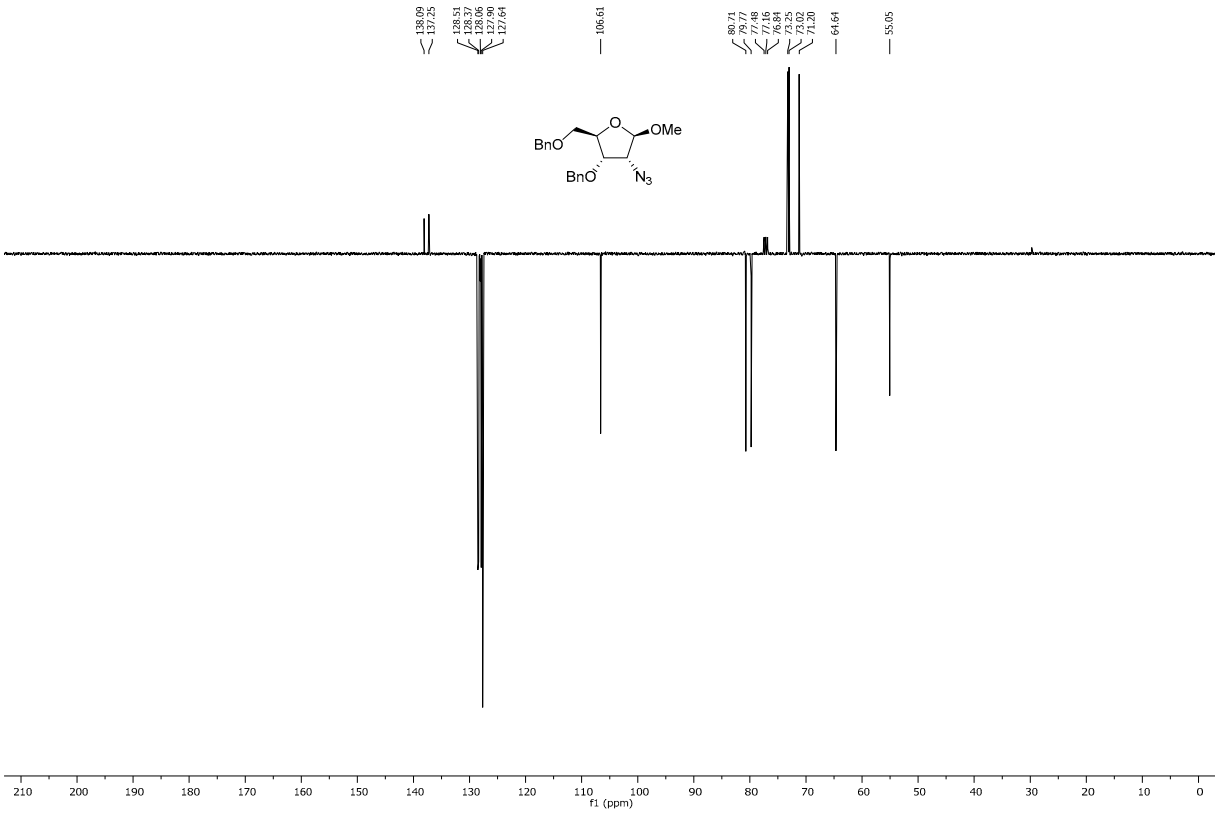


Methyl 2-azido-3,5-di-*O*-benzyl-2-deoxy-β-D-ribofuranoside (33β)

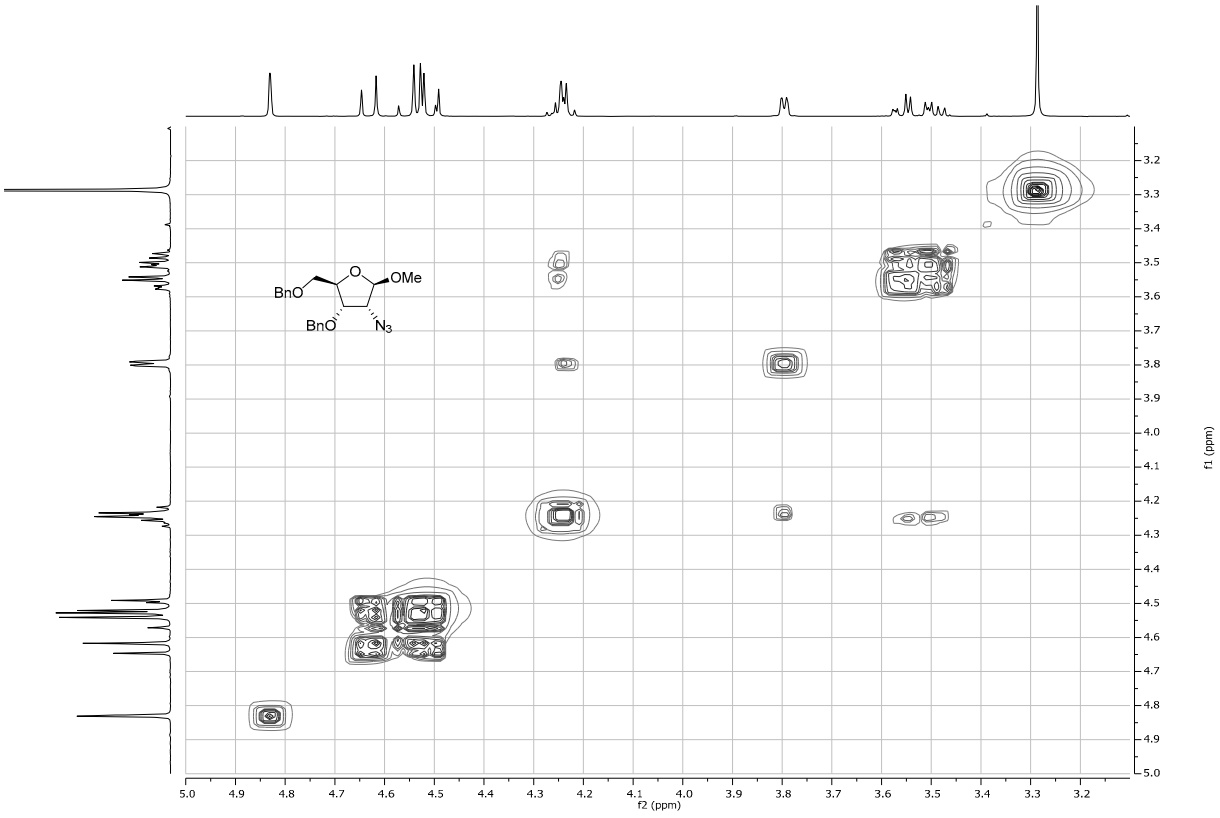
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **33β**



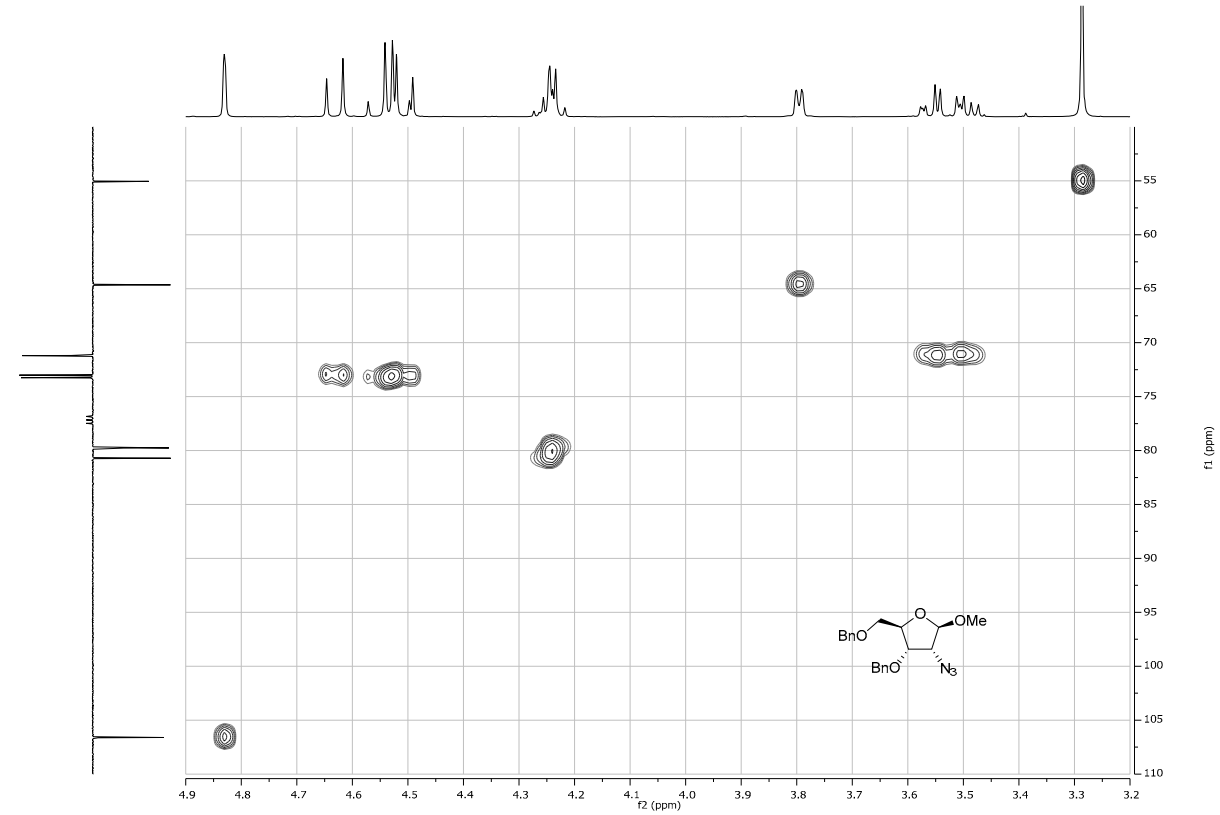
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **33β**



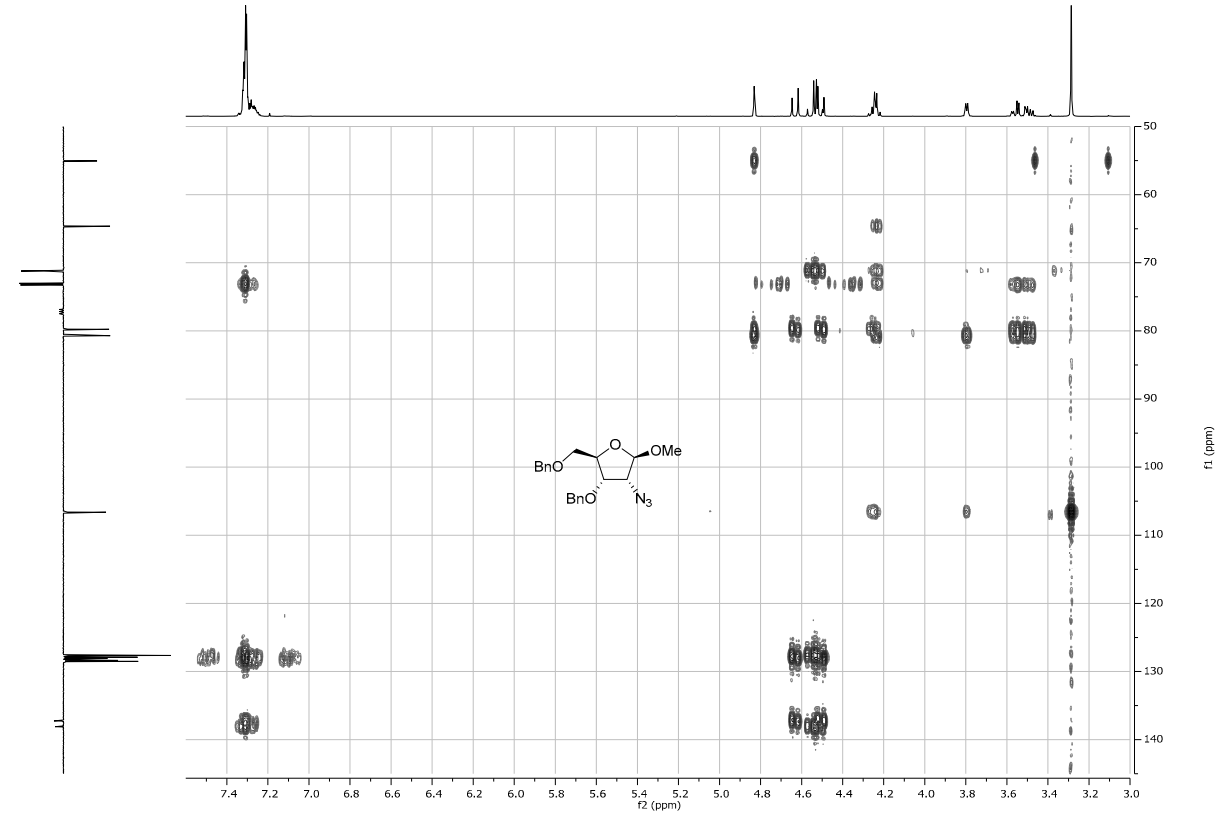
^{1}H-^{1}H COSY of compound **33β**



^{1}H-^{13}C HSQC of compound **33β**

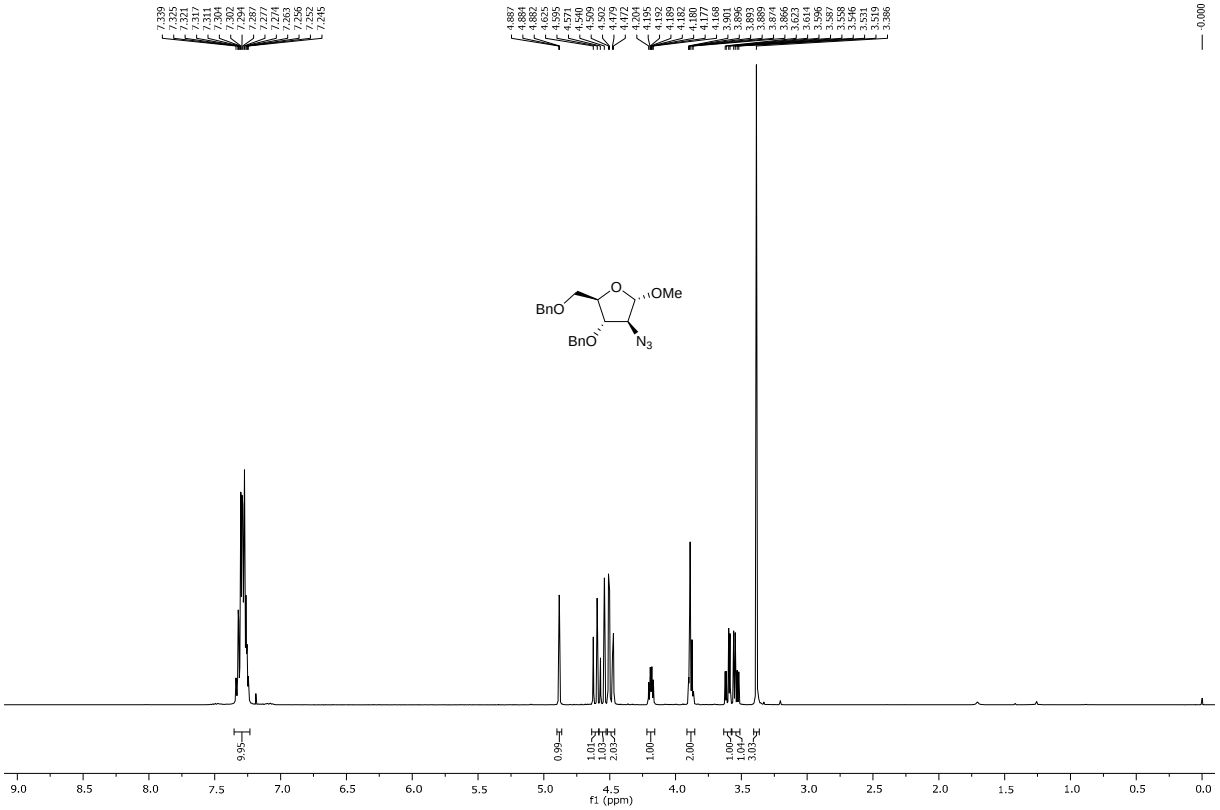


^{1}H-^{13}C HMBC of compound **33β**

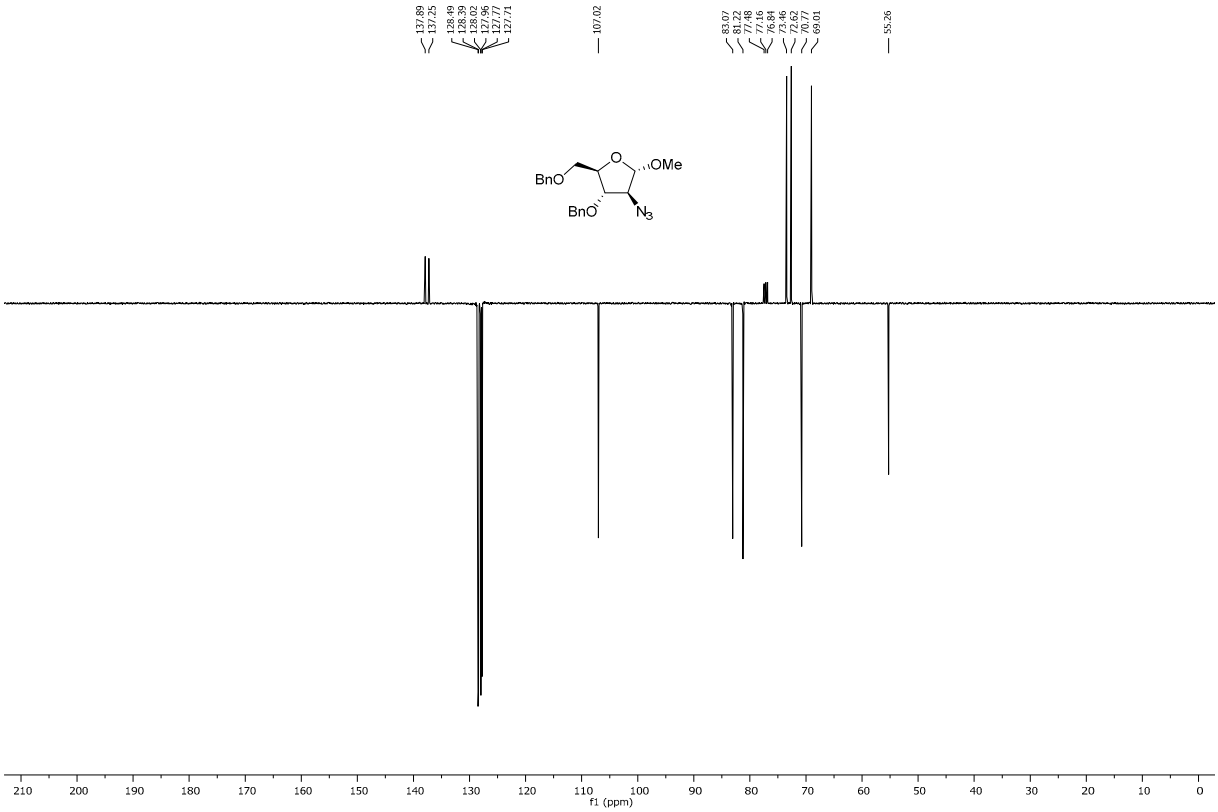


Methyl 2-azido-3,5-di-*O*-benzyl-2-deoxy-α-D-arabinofuranoside (34)

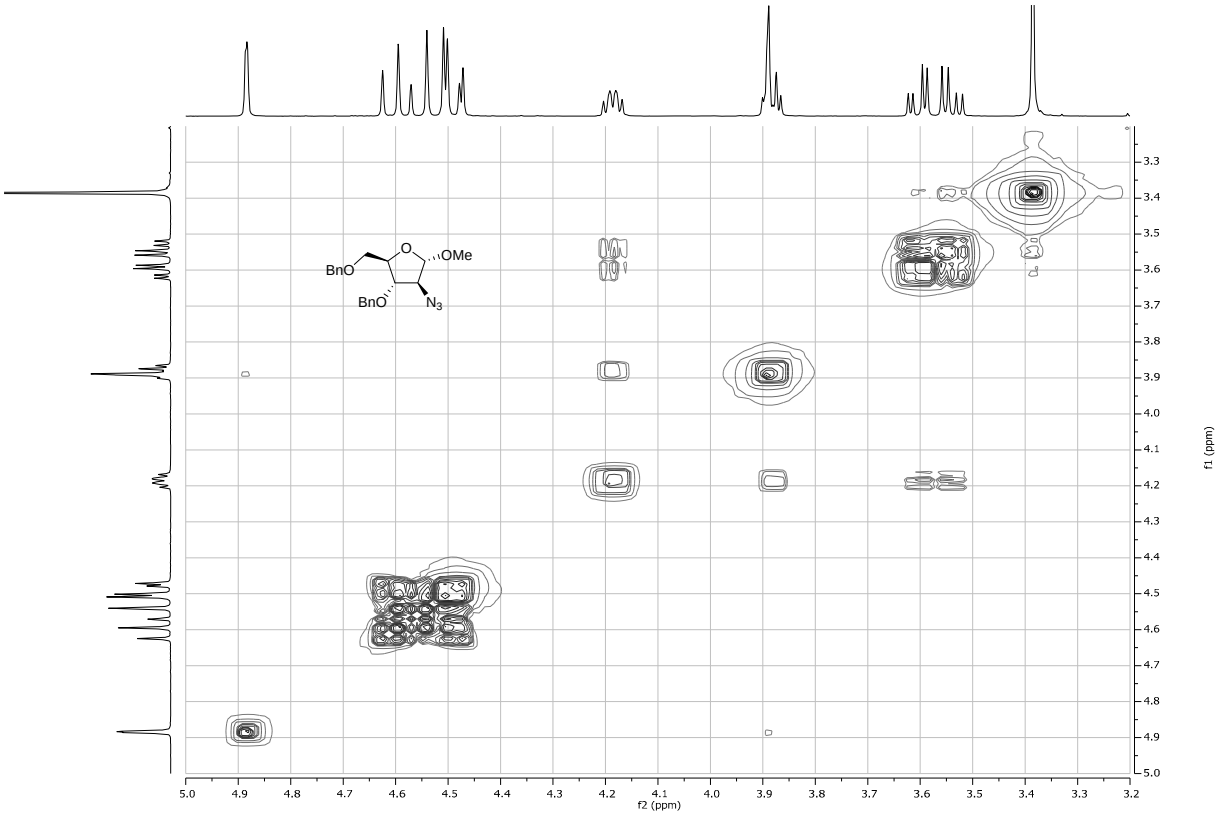
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **34**



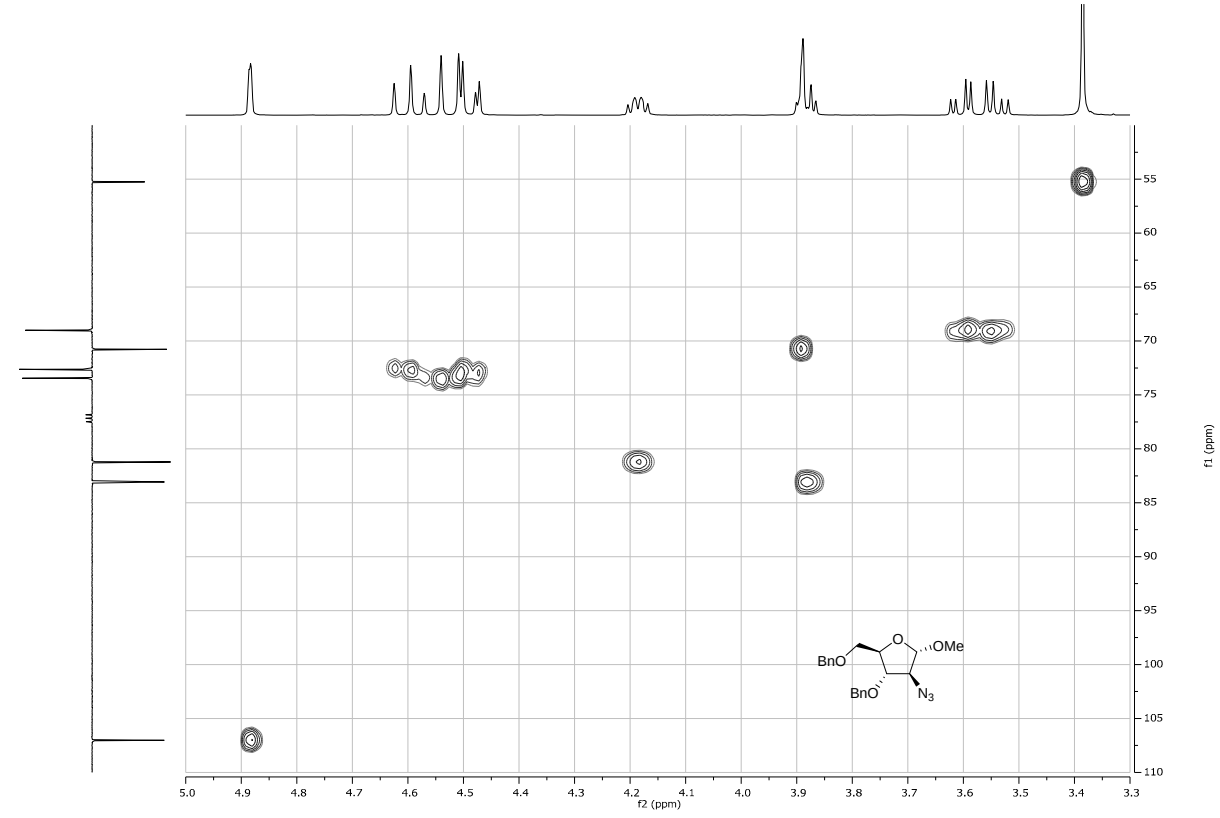
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **34**



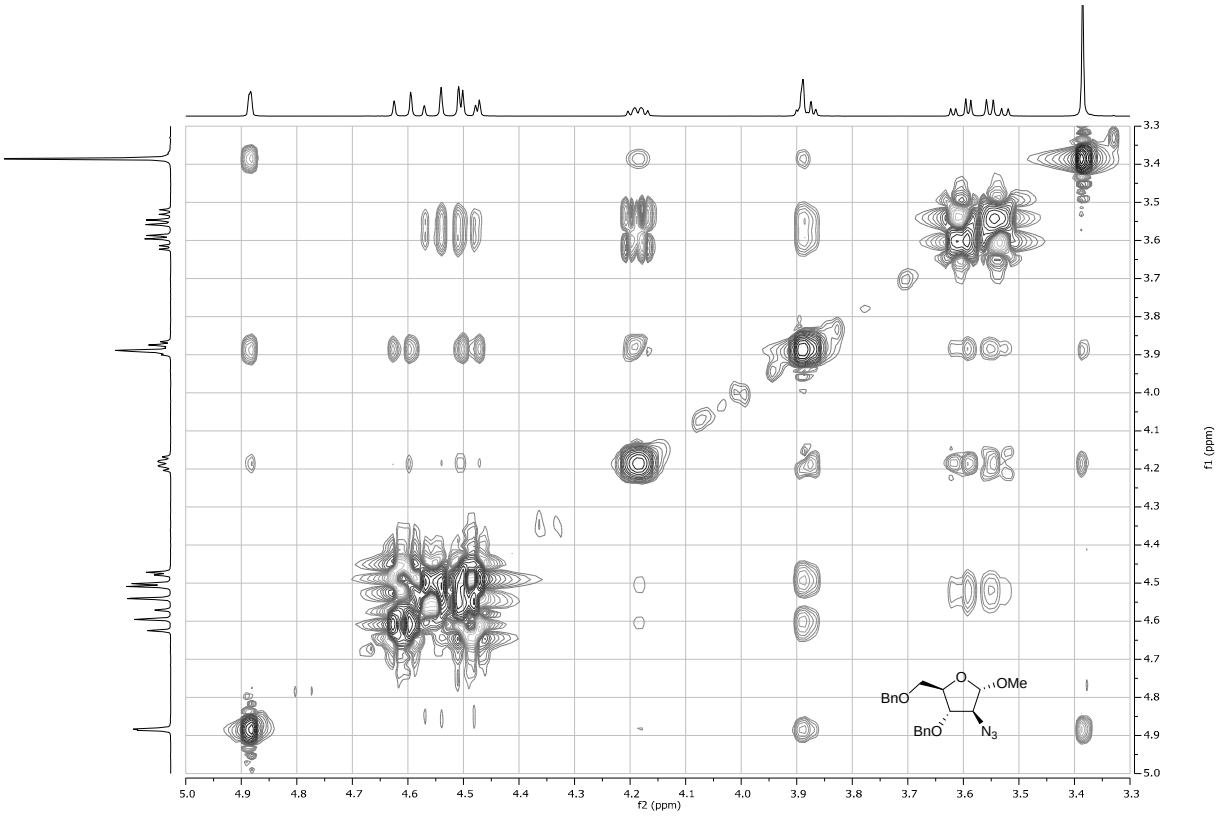
^{1}H-^{1}H COSY of compound **34**



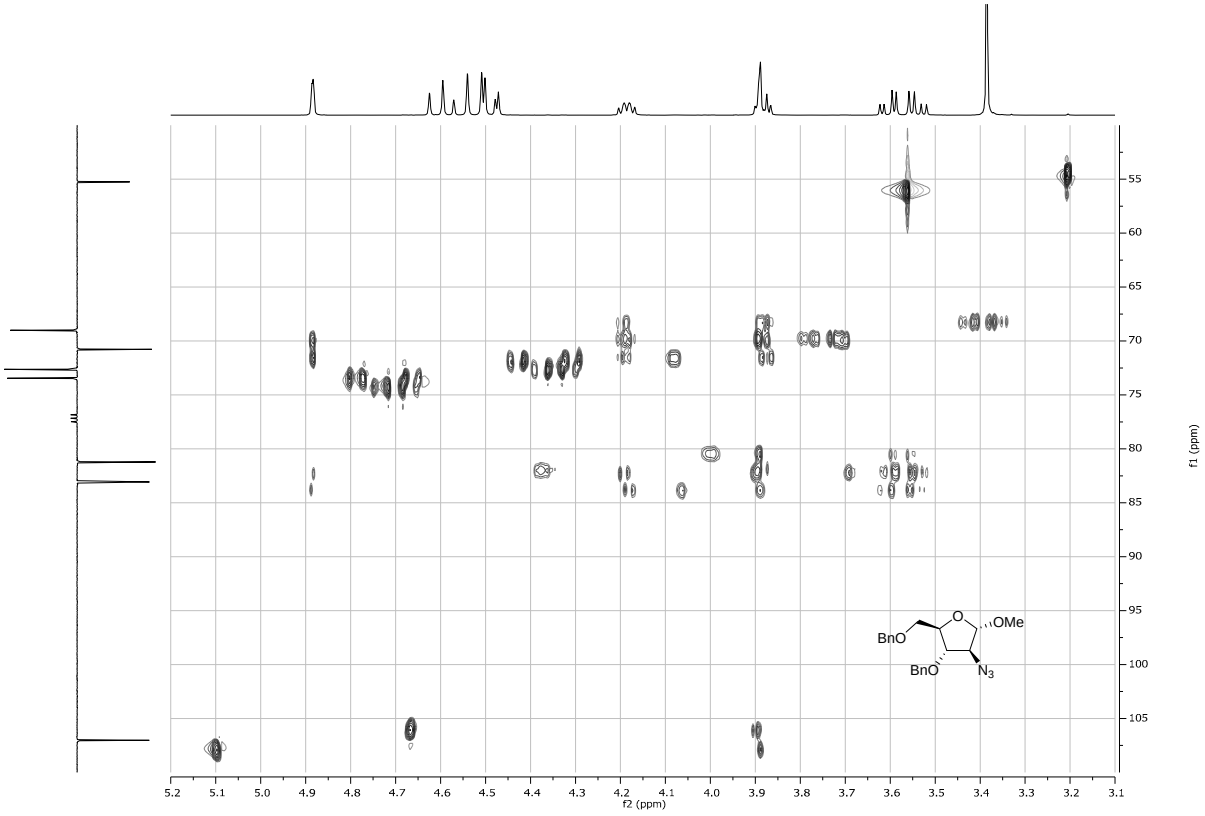
^{1}H-^{13}C HSQC of compound **34**



^{1}H-^{1}H NOESY of compound **34**

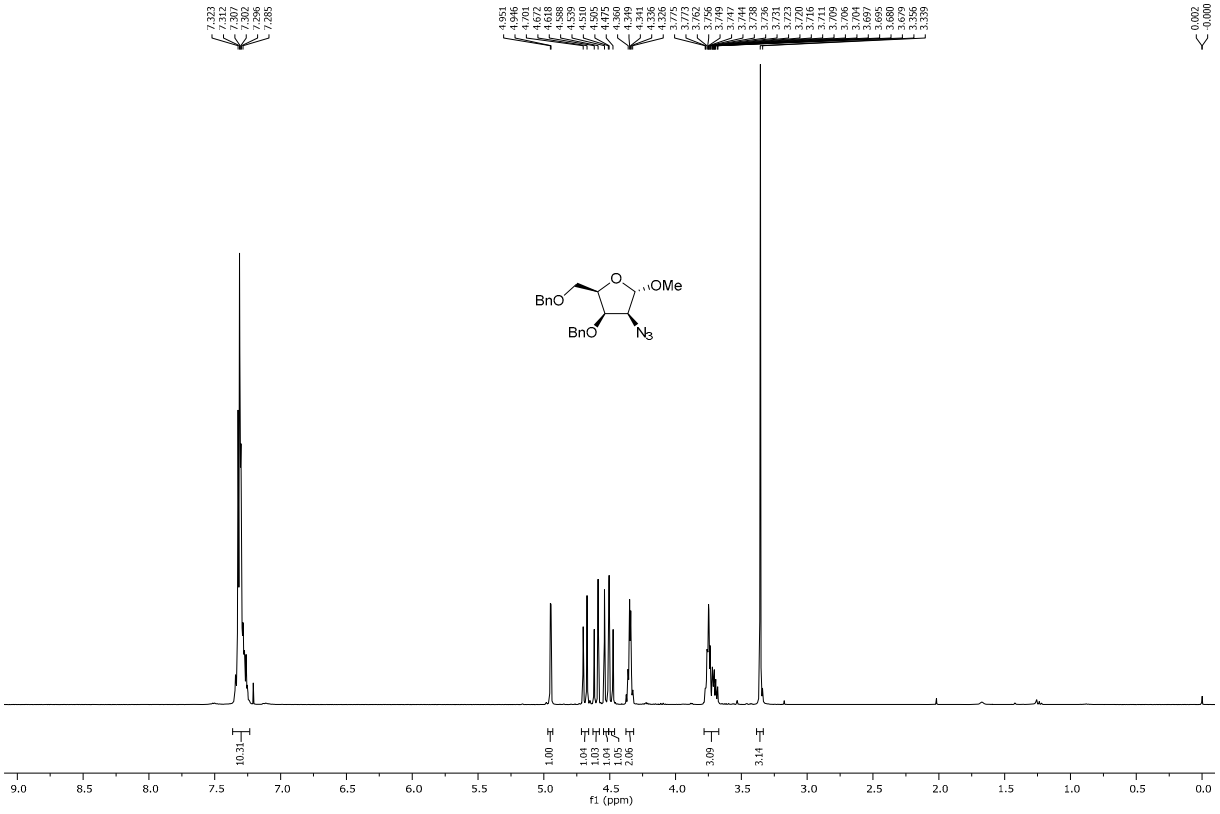


^{1}H-^{13}C HSQC-HECADE of compound **34**

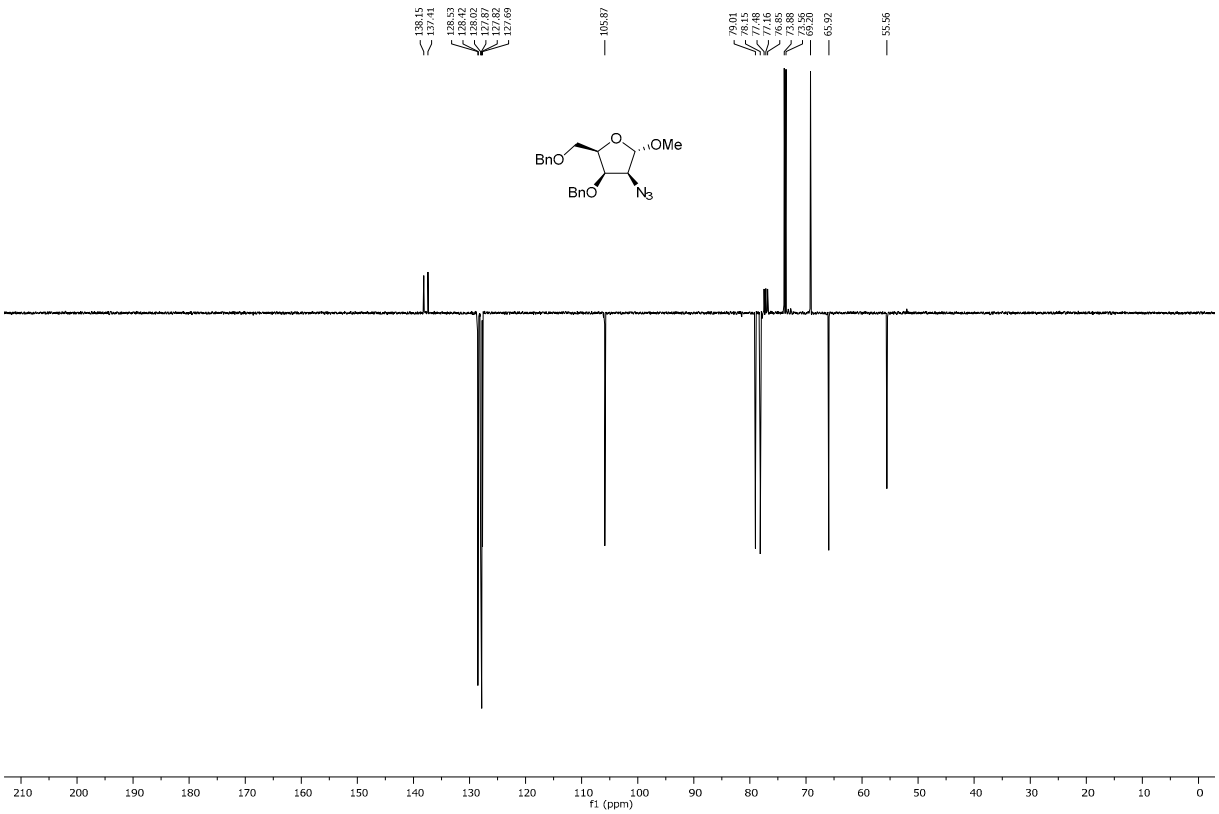


Methyl 2-azido-3,5-di-*O*-benzyl-2-deoxy-α-D-lyxofuranoside (35)

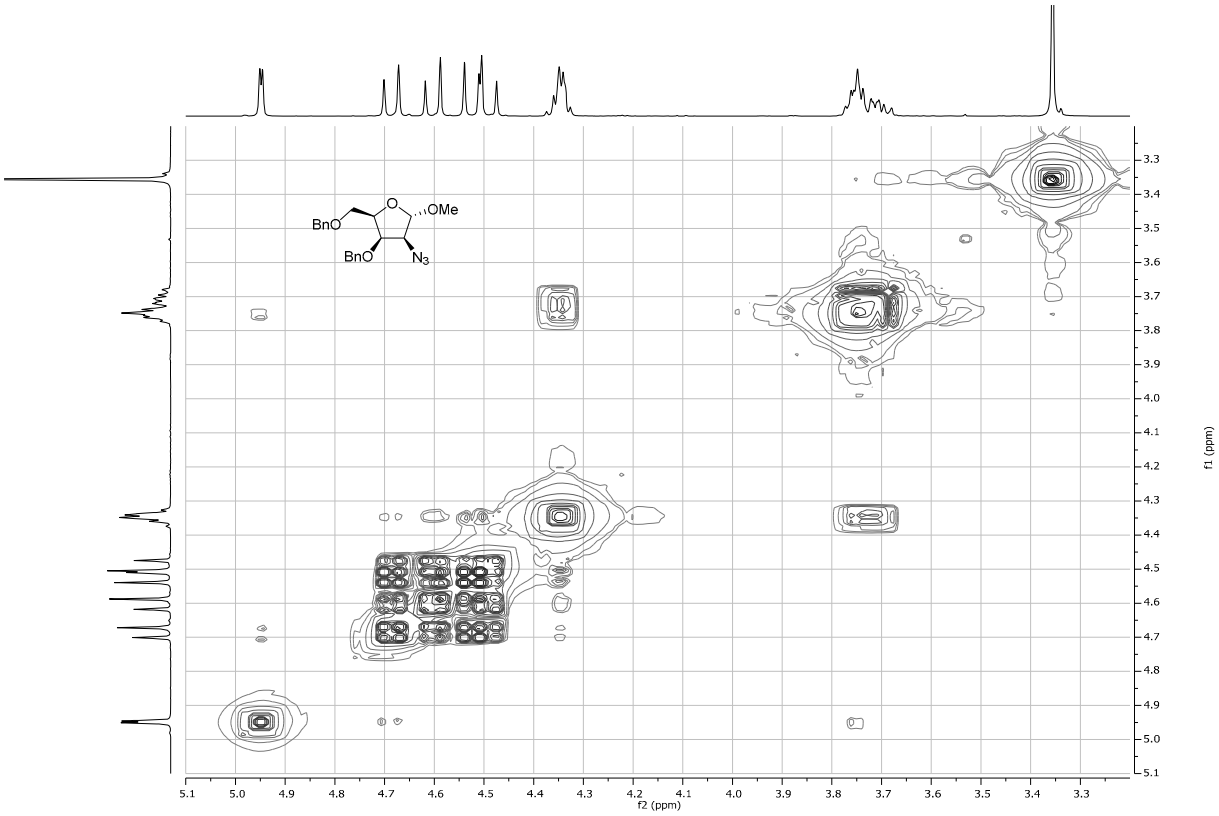
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **35**



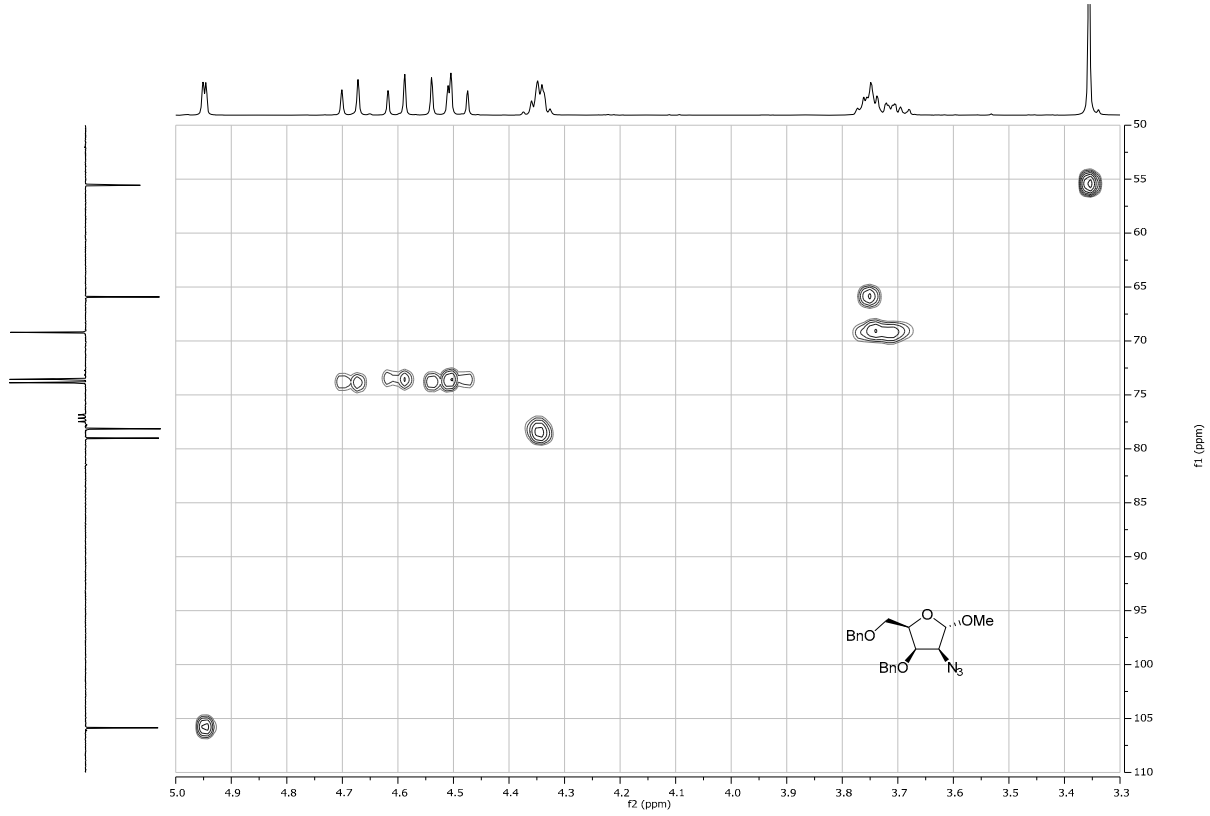
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **35**



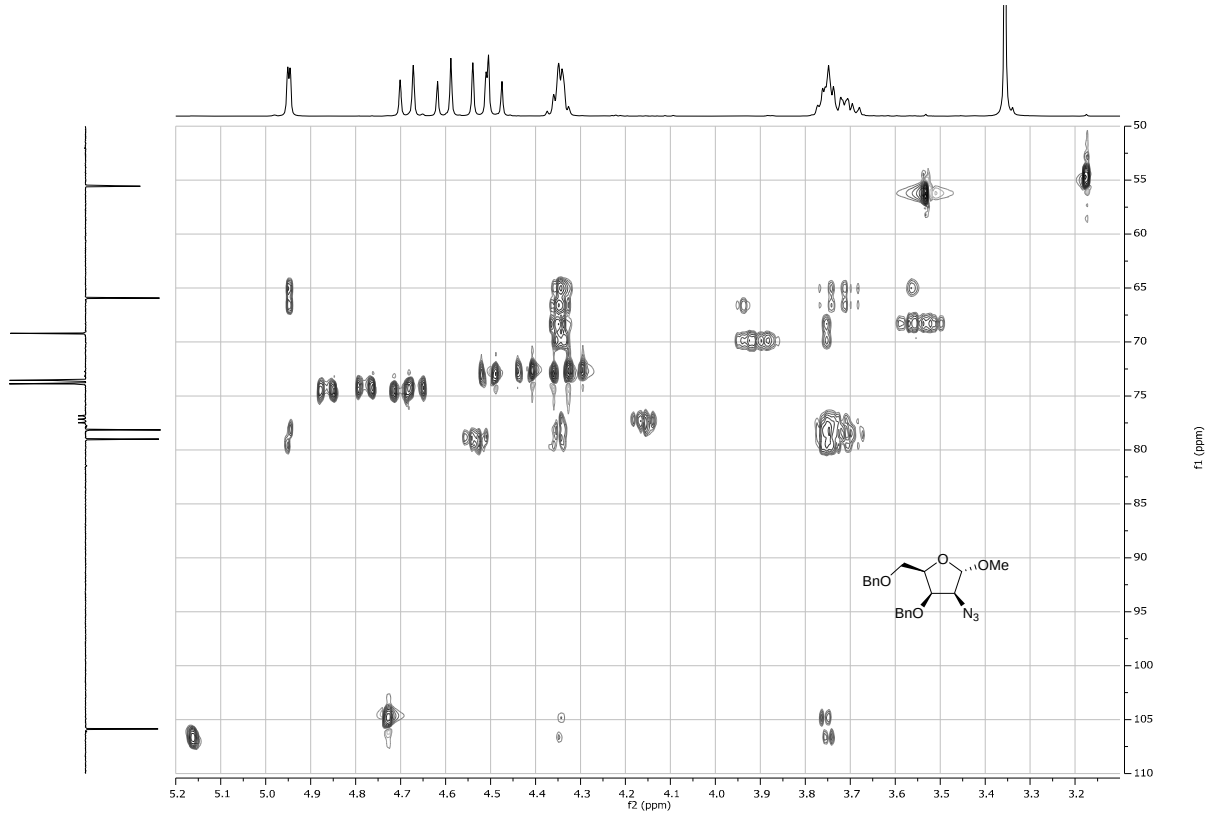
^{1}H-^{1}H COSY of compound **35**



^{1}H-^{13}C HSQC of compound **35**

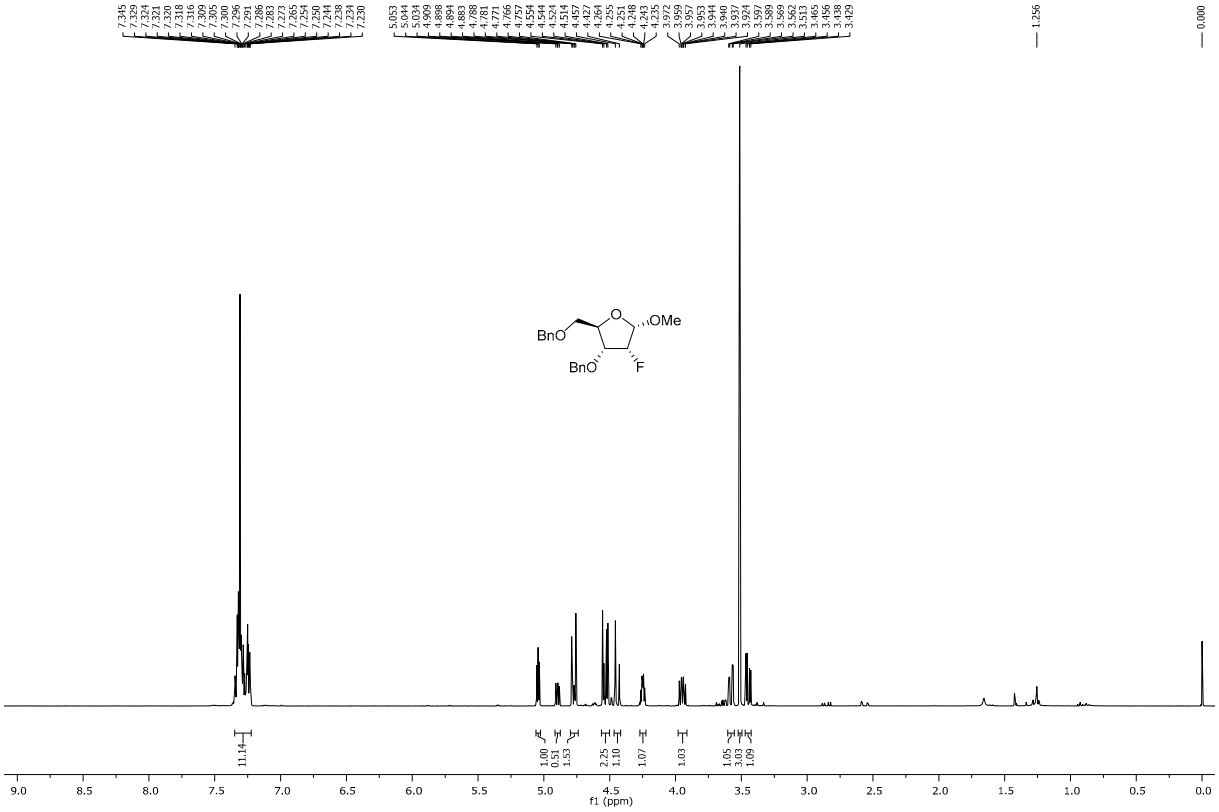


^{1}H-^{13}C HSQC-HECADE of compound **35**

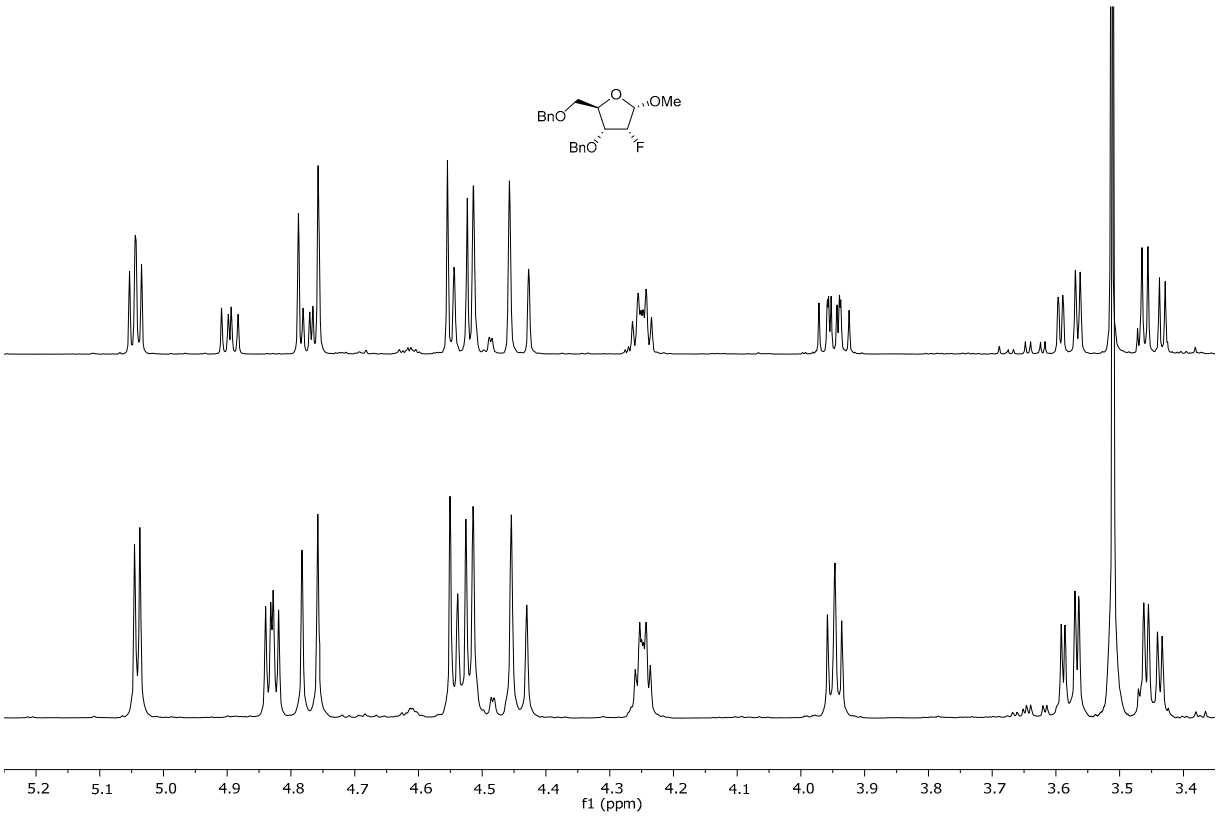


Methyl 3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α-D-ribofuranoside (37α)

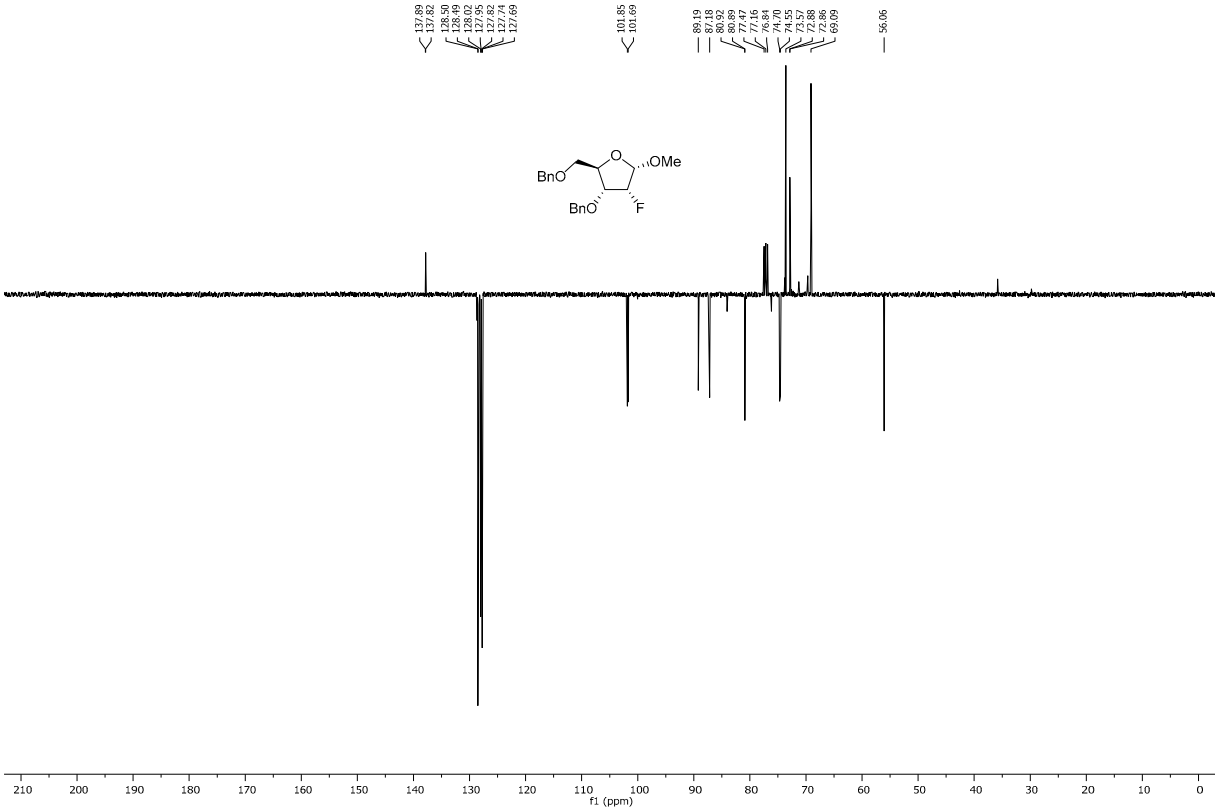
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **37α**



^{19}F-decoupled ^{1}H NMR, (-210 ppm)

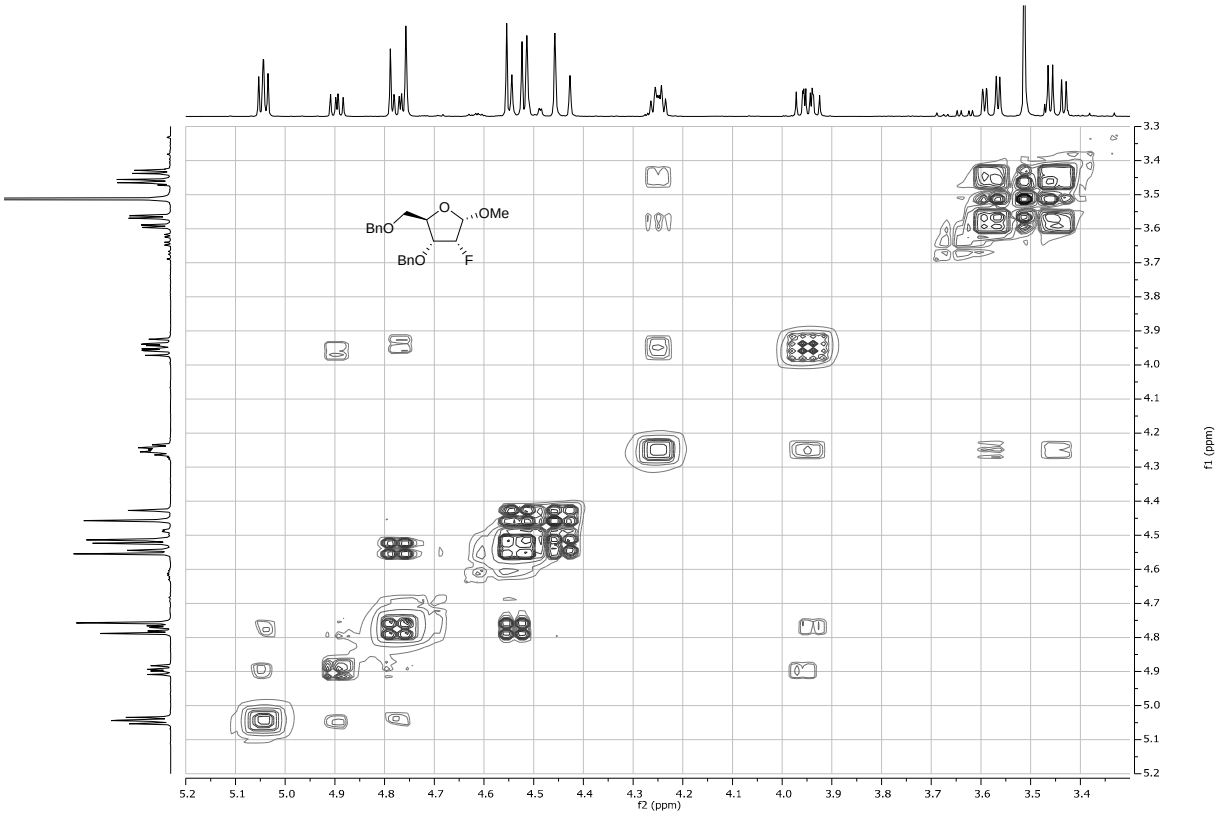


^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **37α**

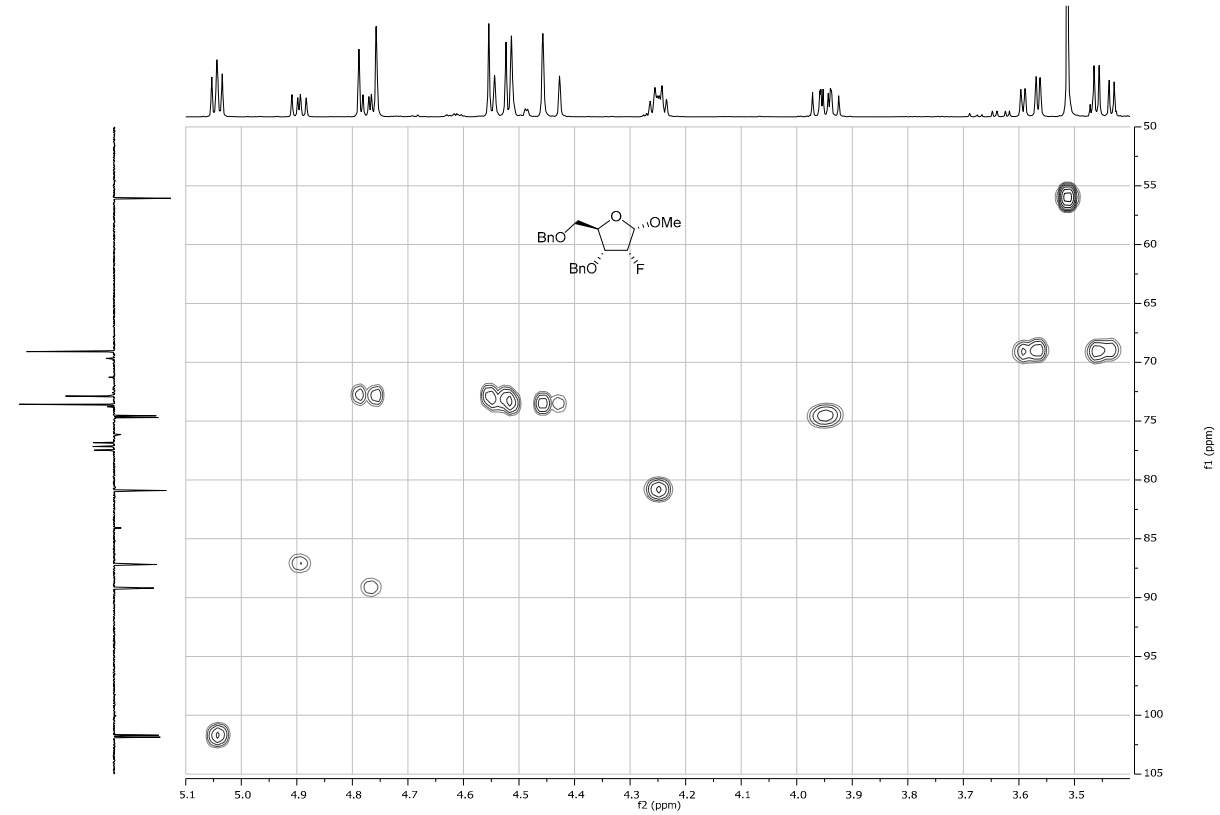


^{19}F NMR, 471 MHz, $CDCl_3$ of compound **37α**

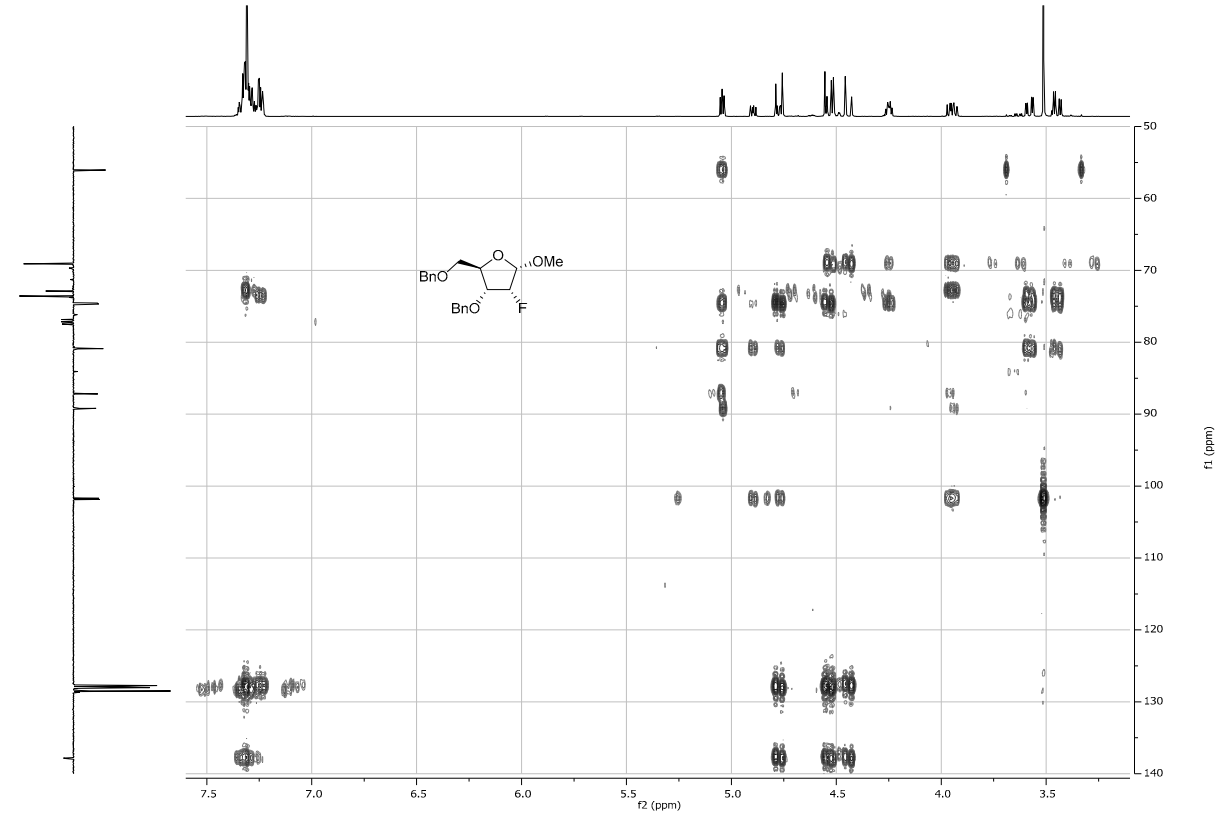
^{1}H-^{1}H COSY of compound **37α**



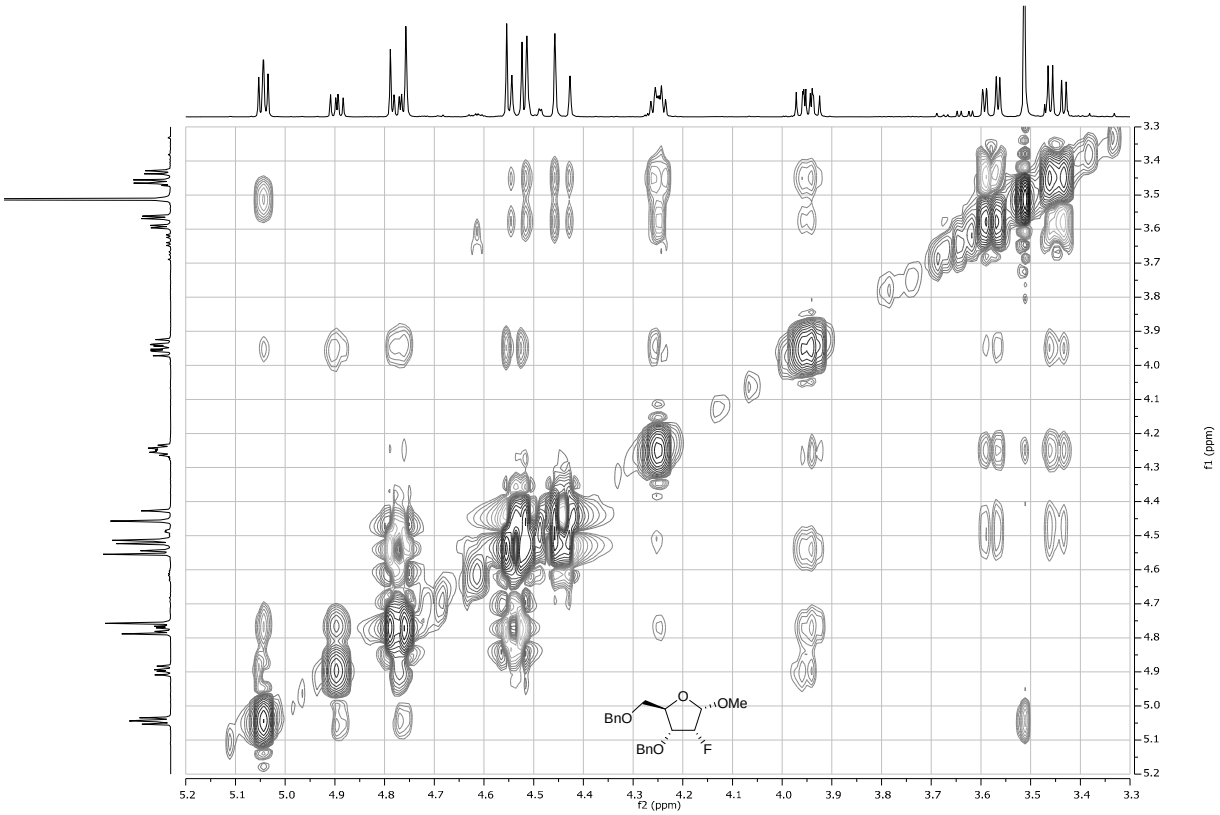
^{1}H-^{13}C HSQC of compound **37α**



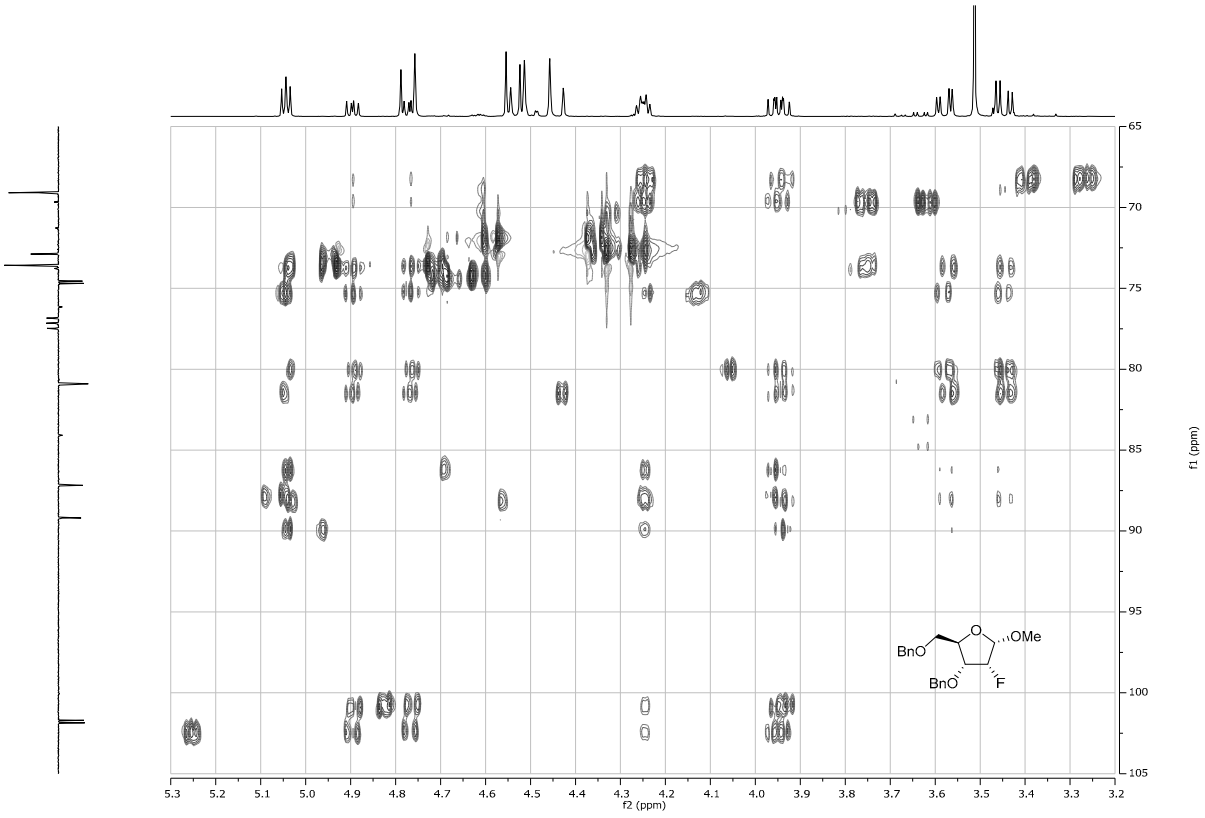
^{1}H-^{13}C HMBC of compound **37α**



^{1}H-^{1}H NOESY of compound **37α**

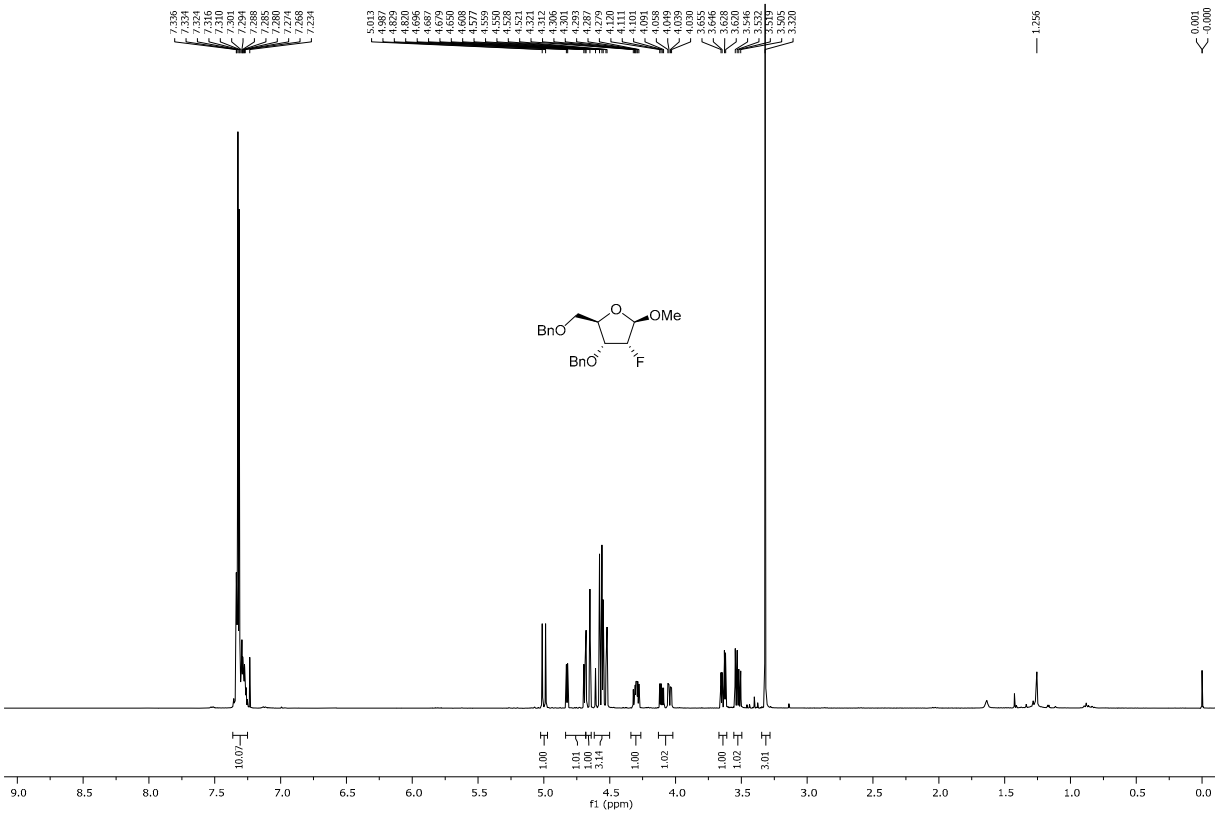


^{1}H-^{13}C HSQC-HECADE of compound **37α**

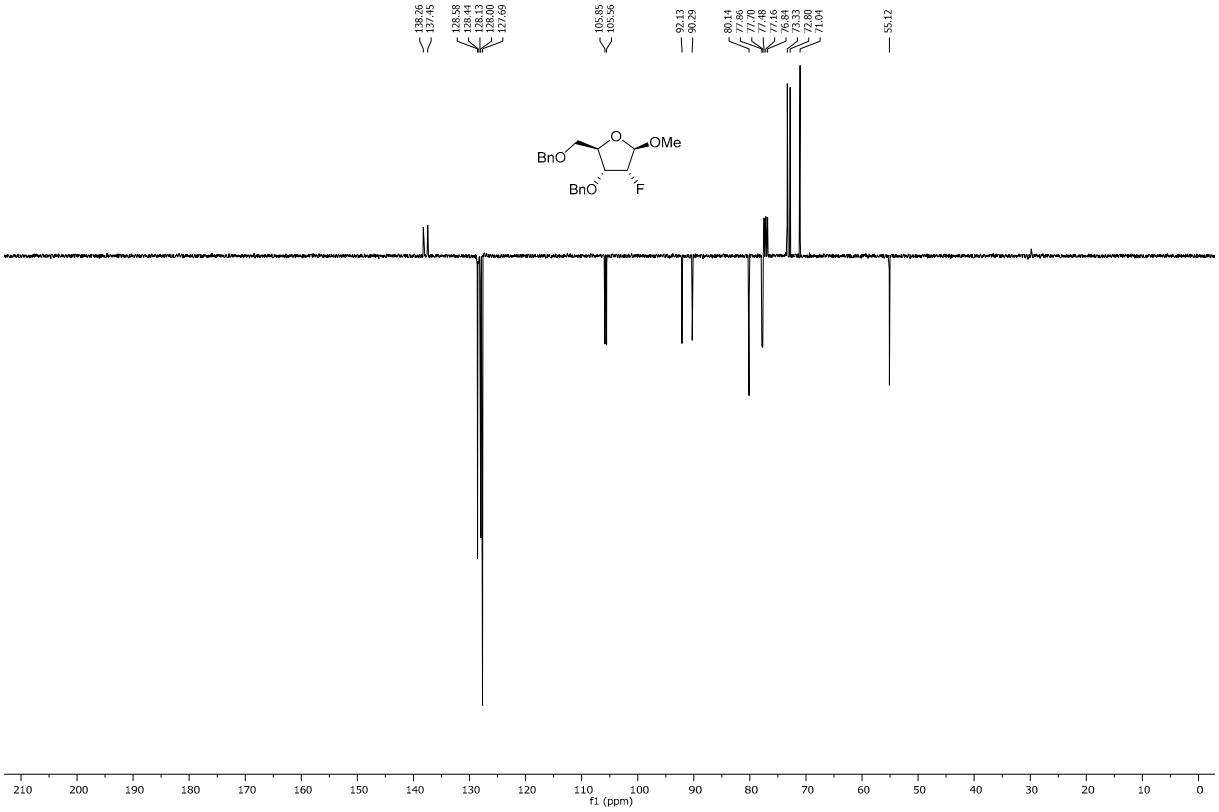


Methyl 3,5-di-*O*-benzyl-2-deoxy-2-fluoro-β-D-ribofuranoside (37β)

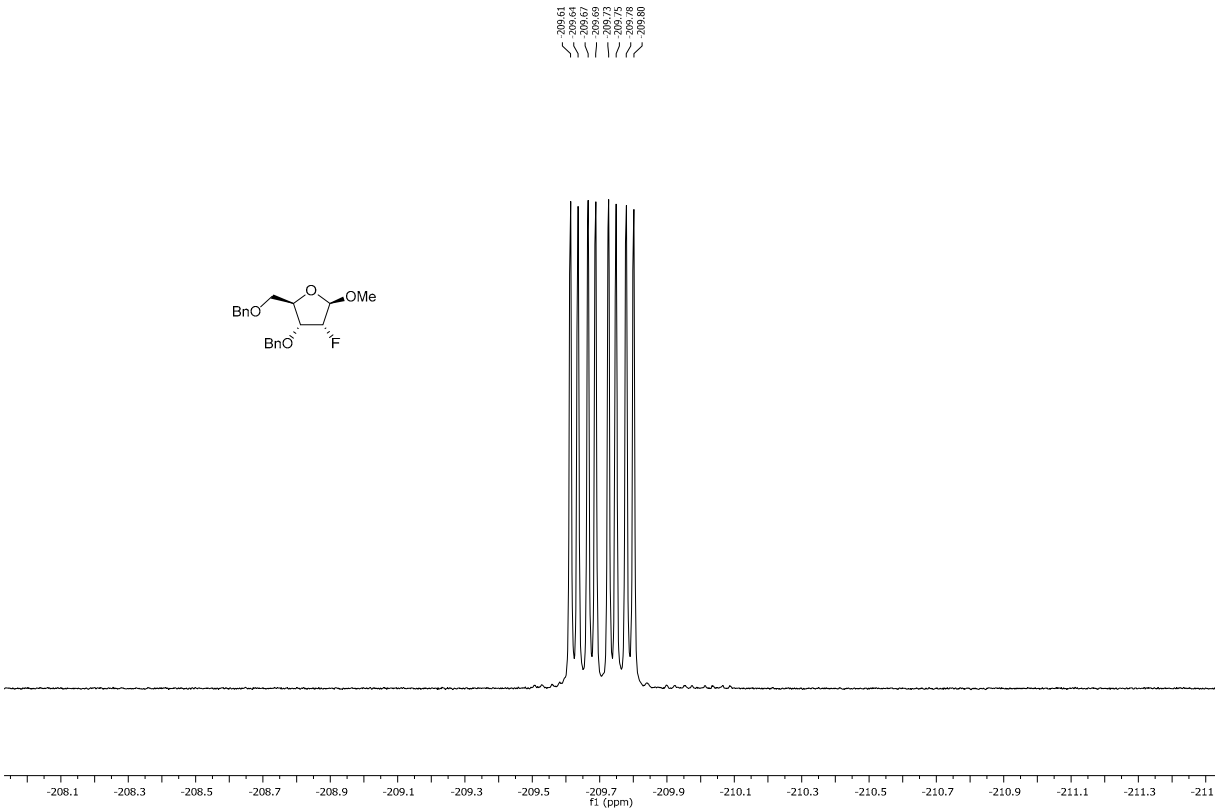
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **37β**



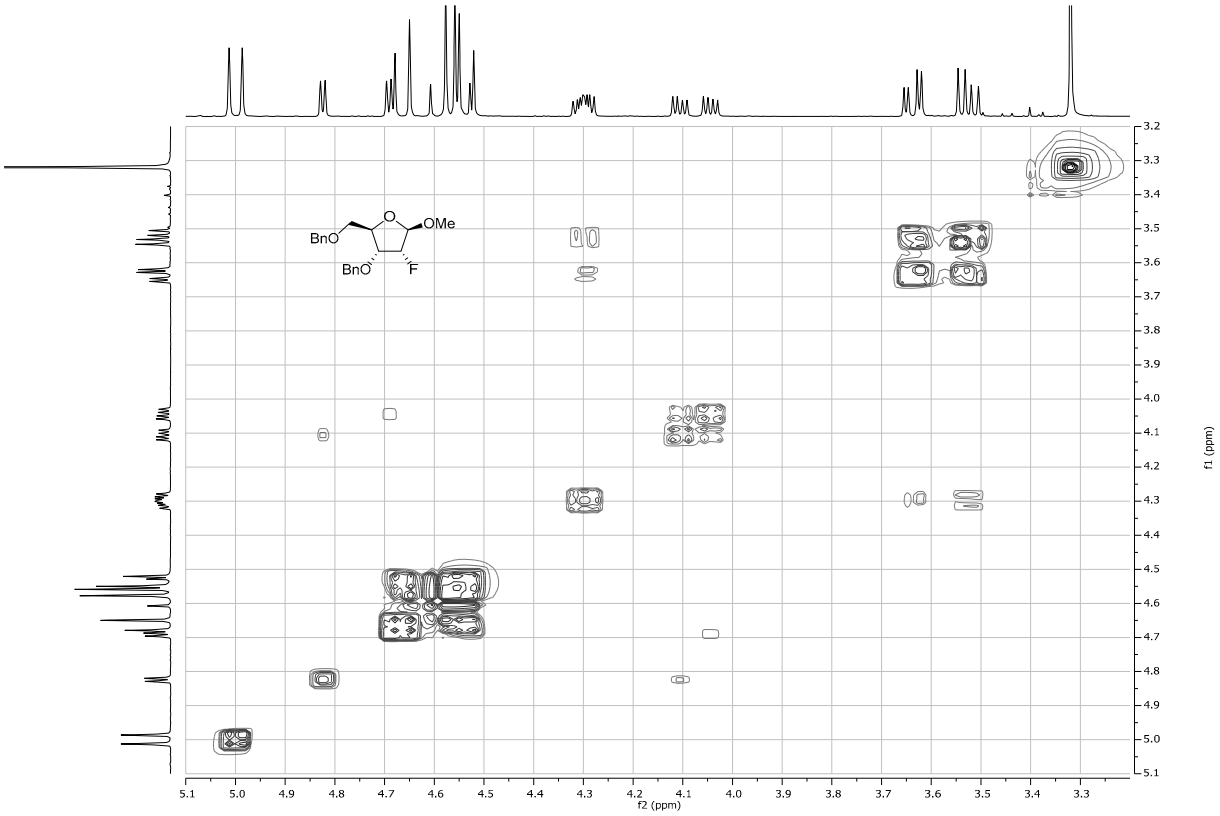
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **37β**



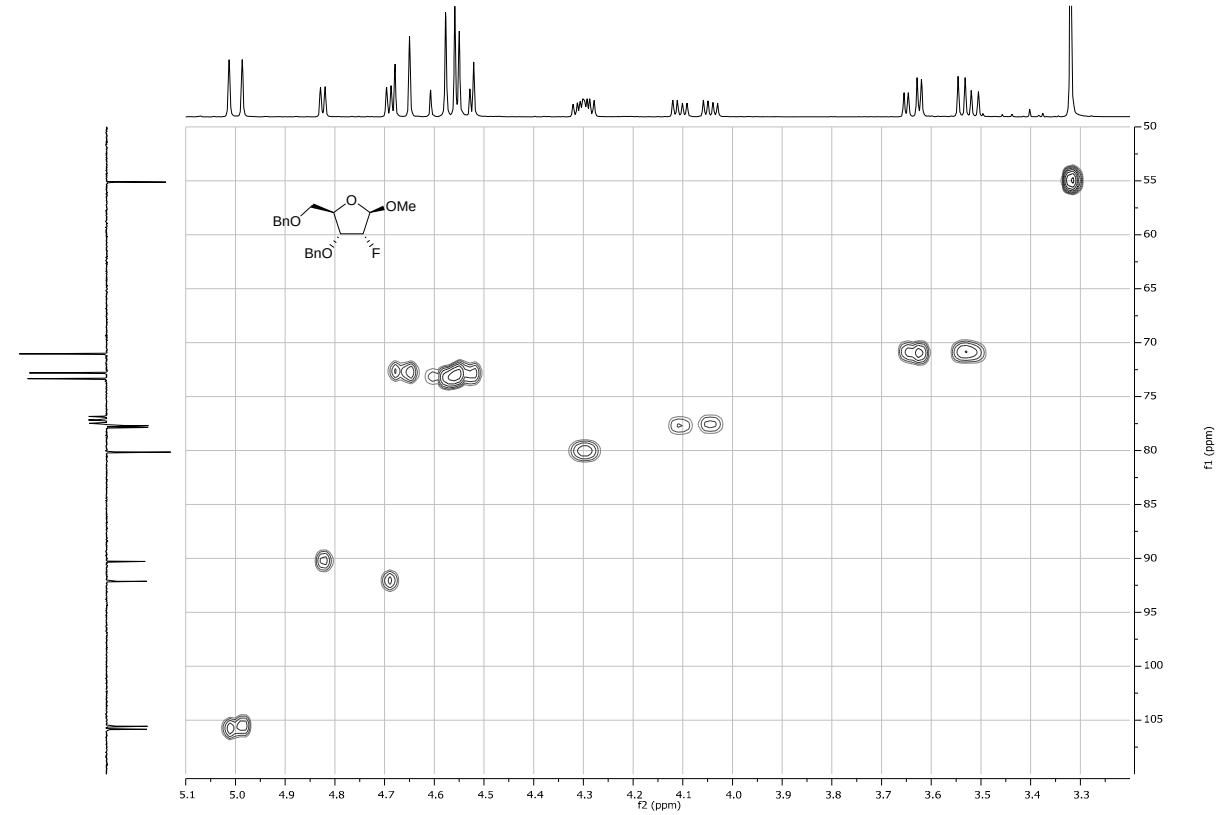
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **37β**



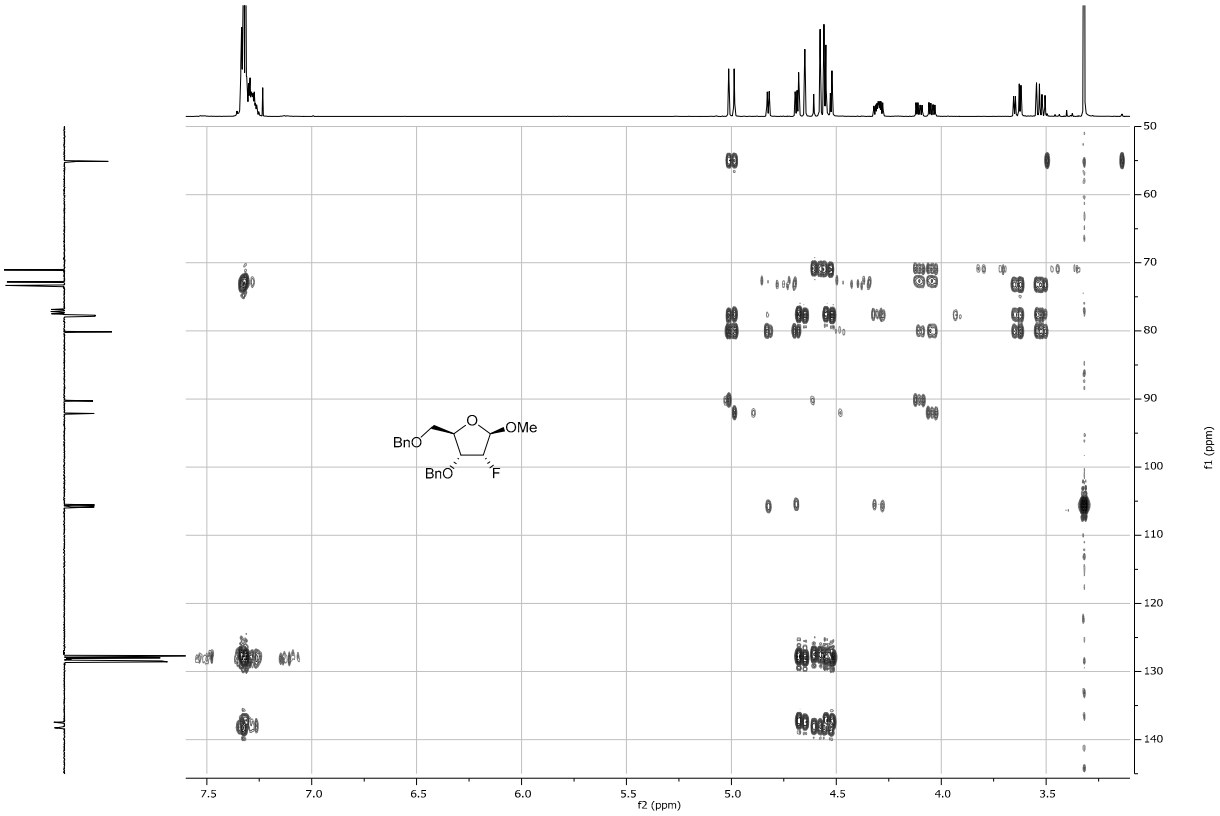
^{1}H-^{1}H COSY of compound **37β**



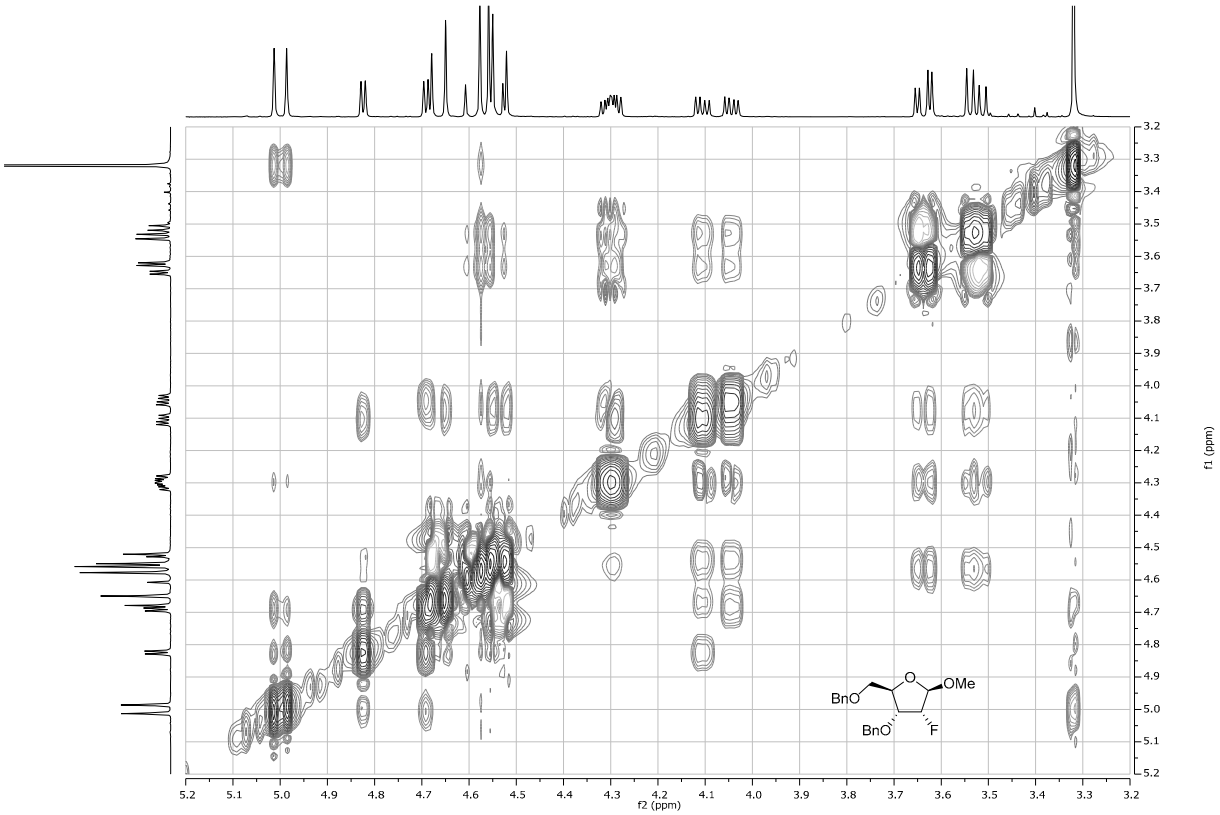
^{1}H-^{13}C HSQC of compound **37β**



^{1}H-^{13}C HMBC of compound **37β**

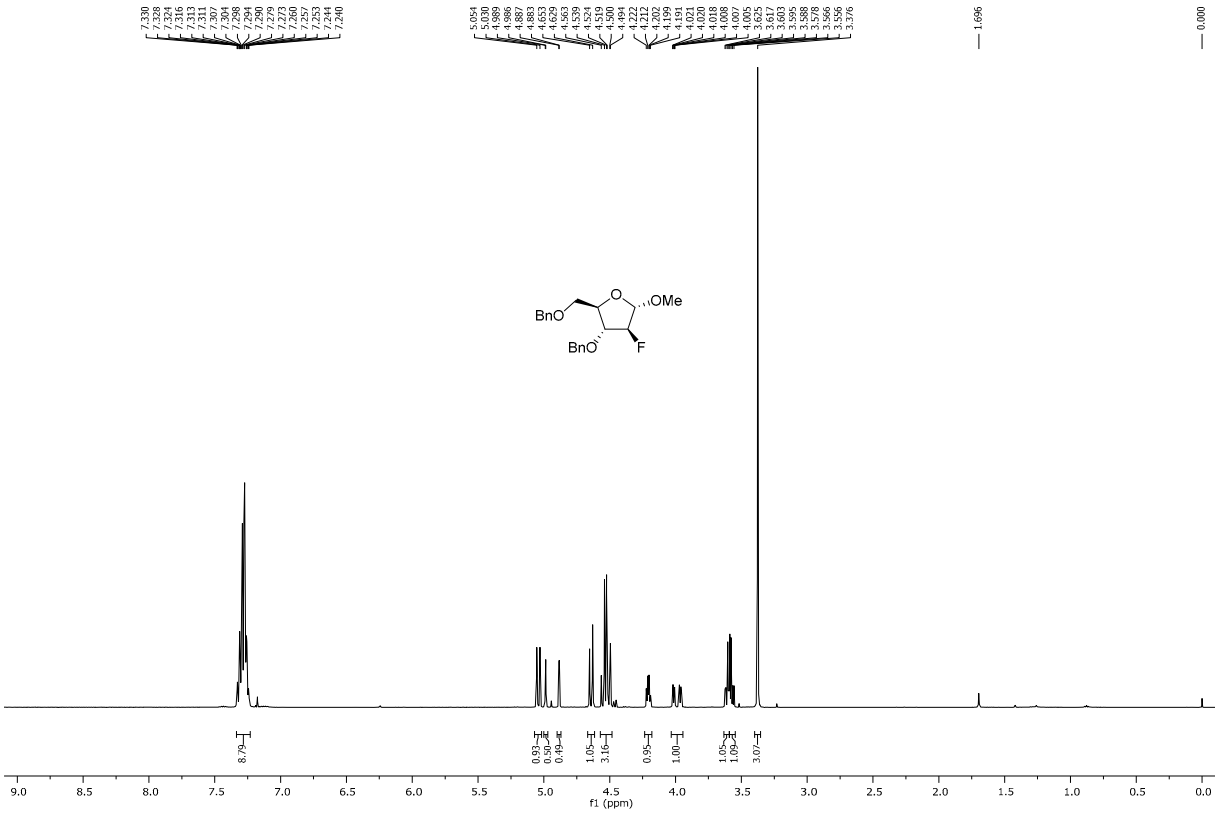


^{1}H-^{1}H NOESY of compound **37β**

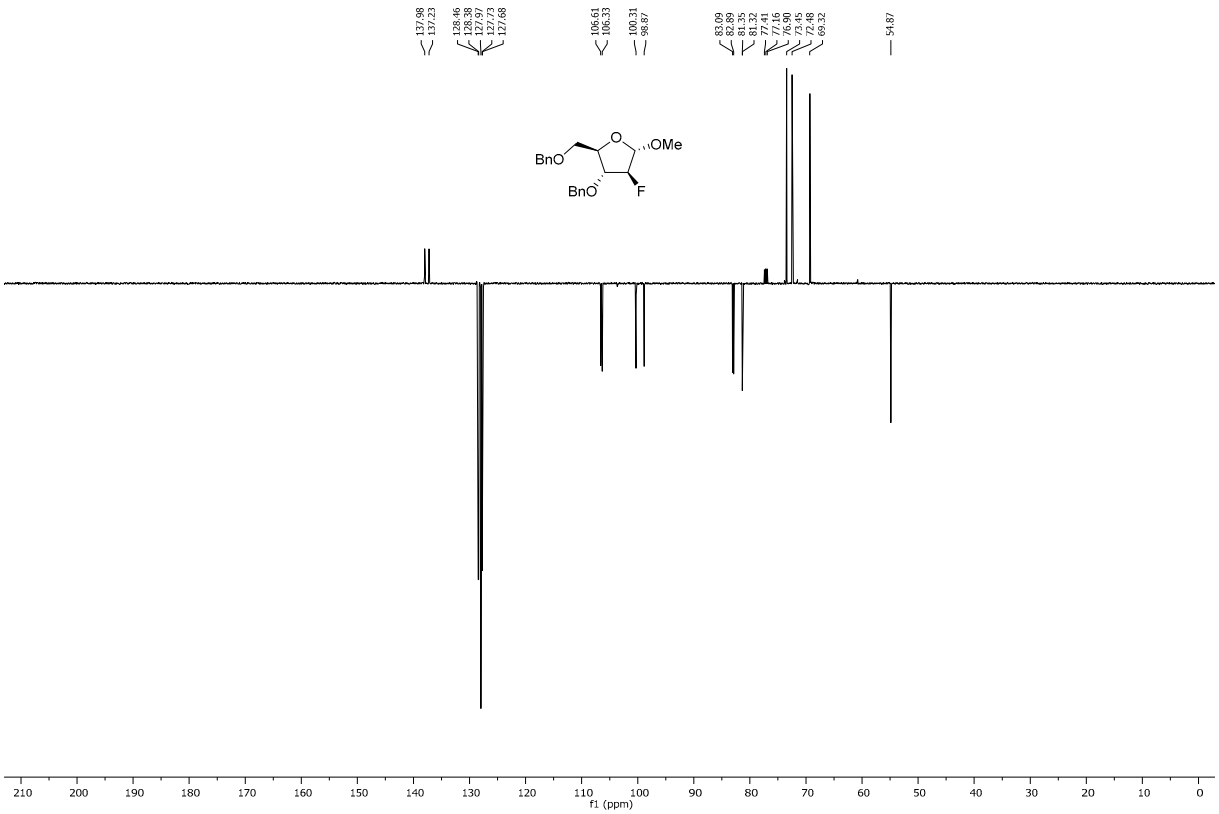


Methyl 3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α-D-arabinofuranoside (38)

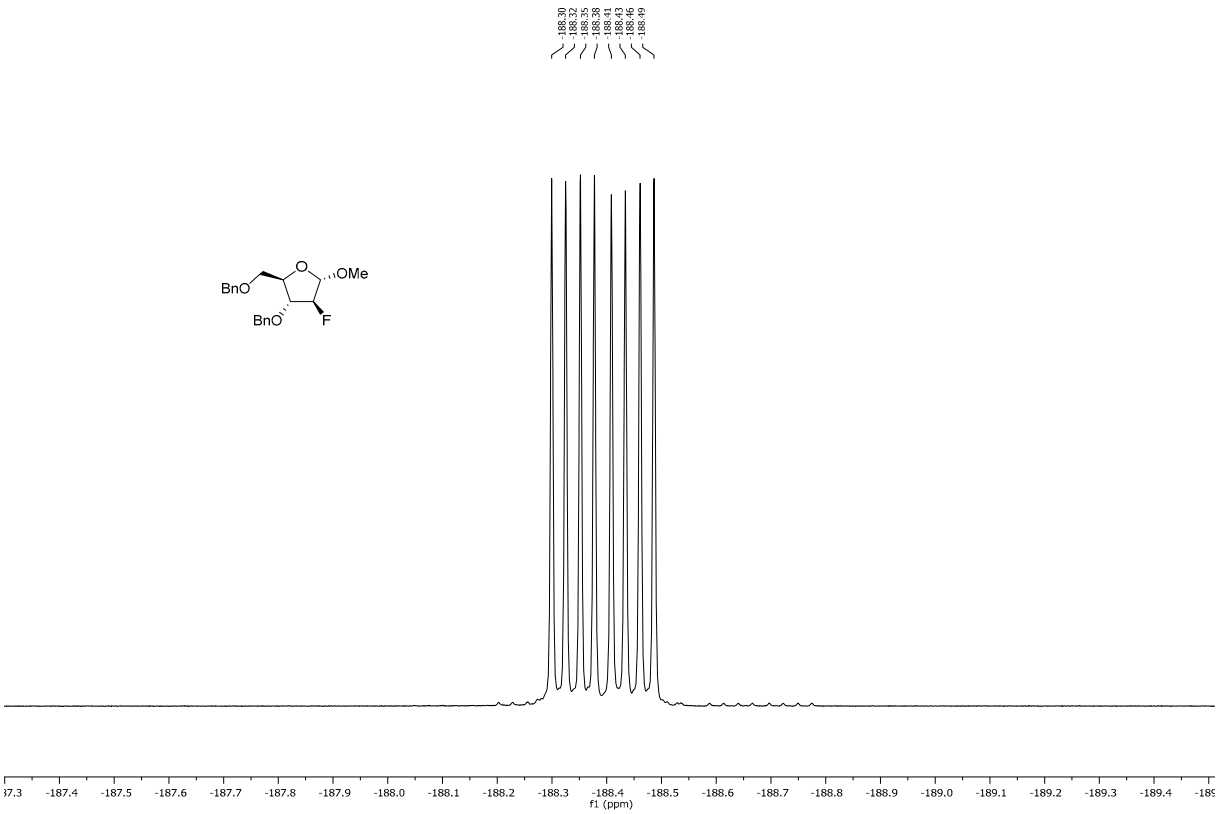
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **38**



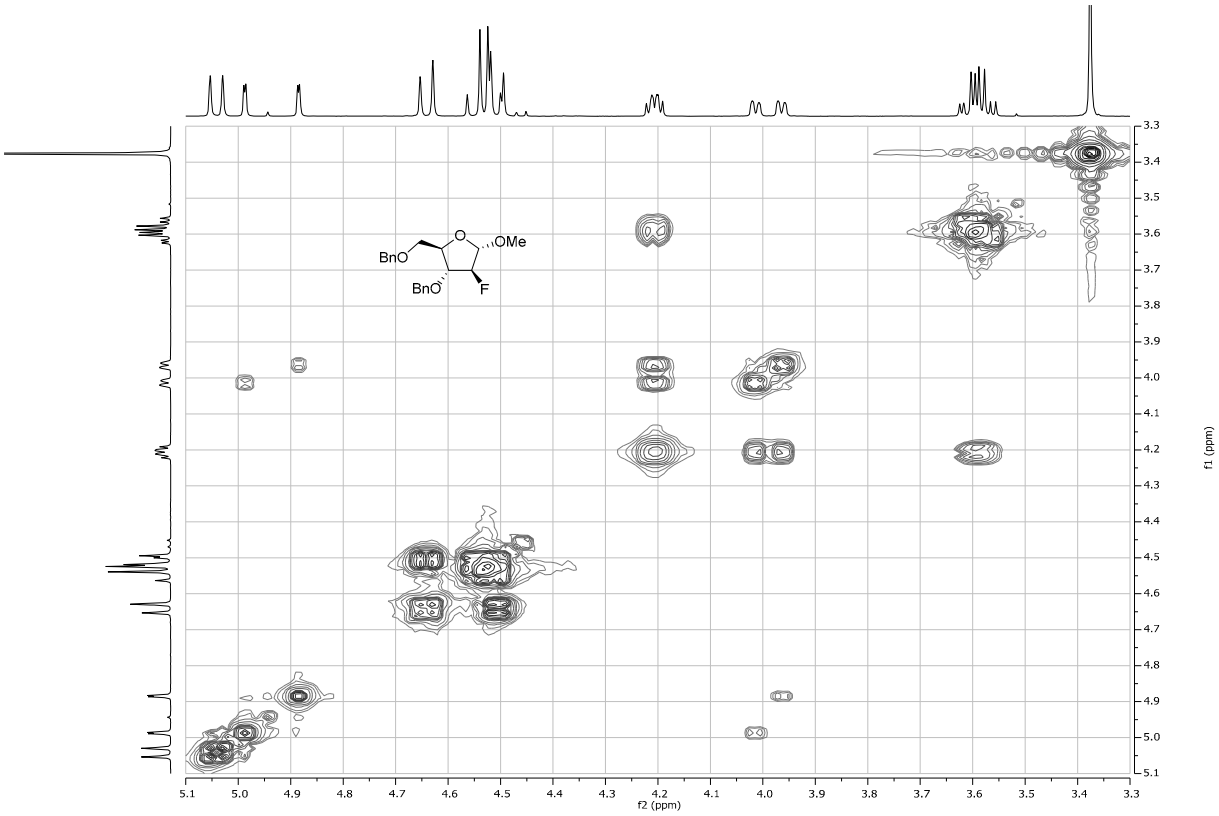
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **38**



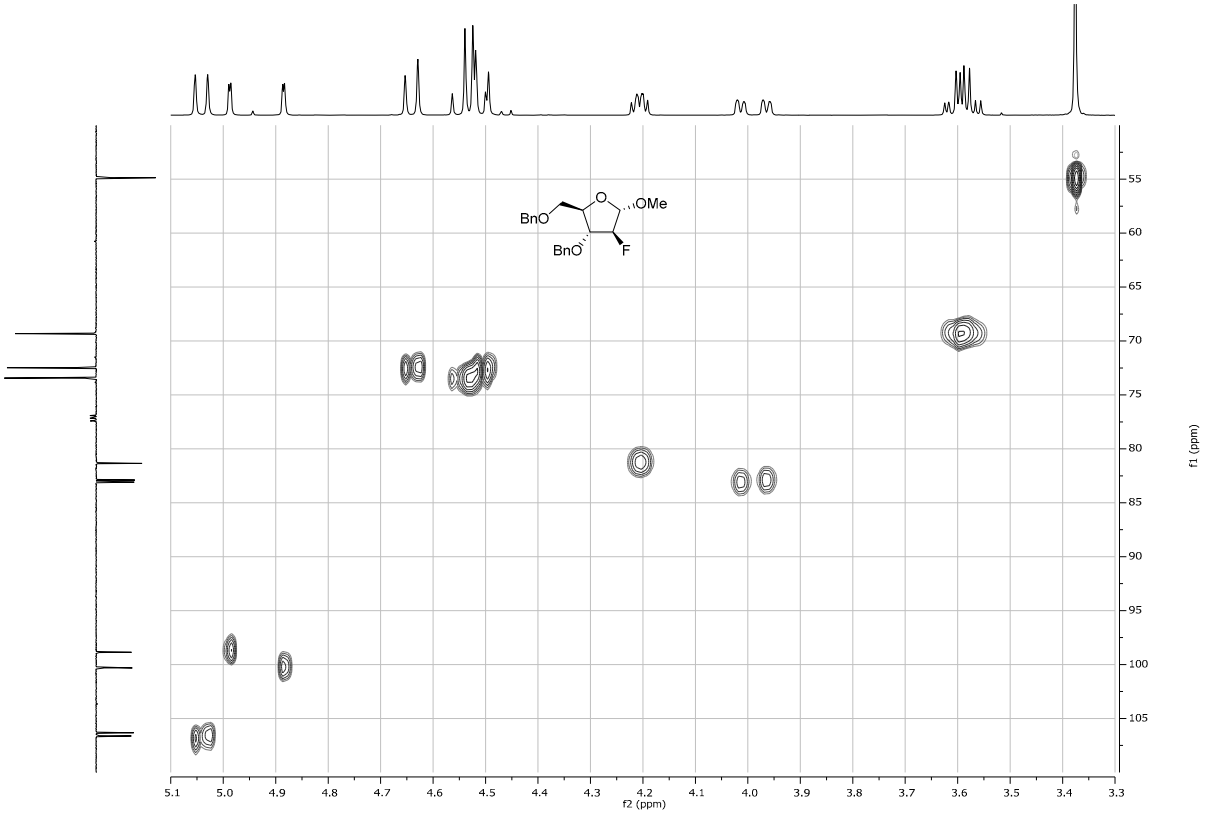
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **38**



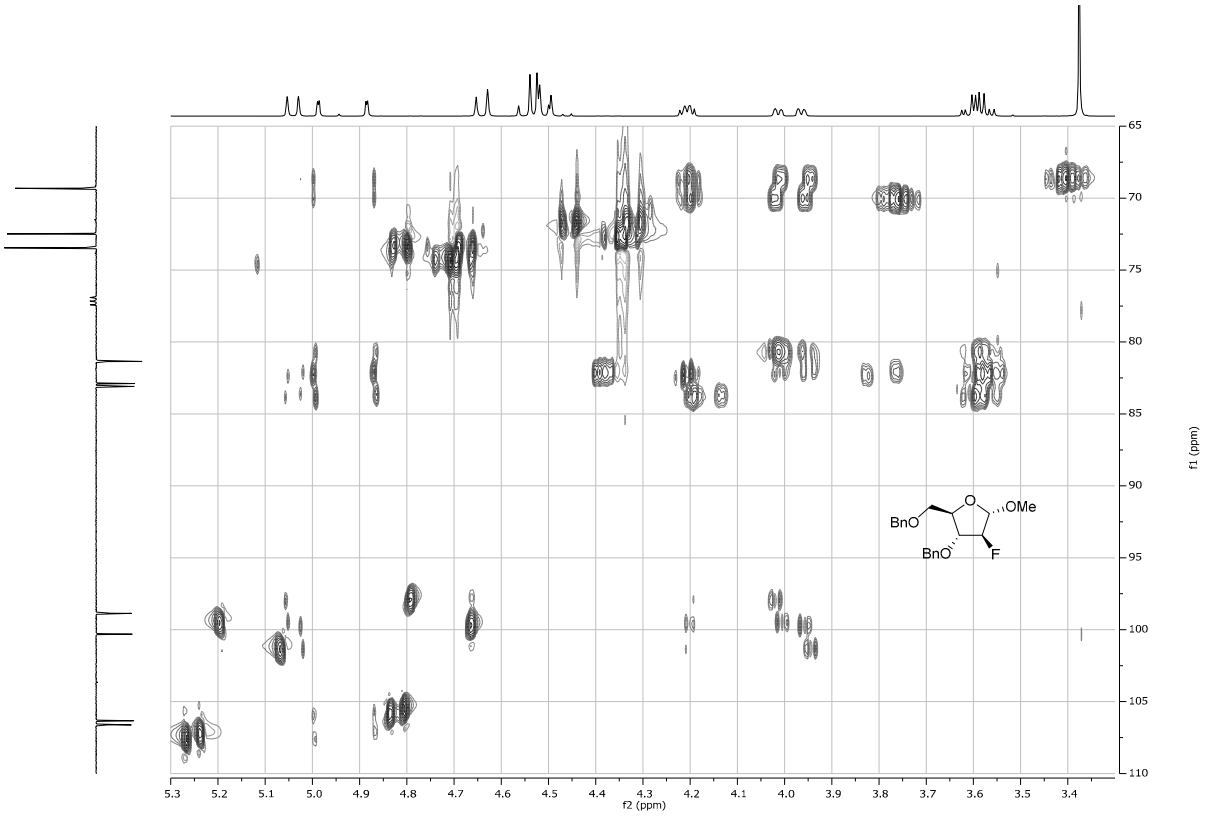
^{1}H-^{1}H COSY of compound **38**



^{1}H-^{13}C HSQC of compound **38**

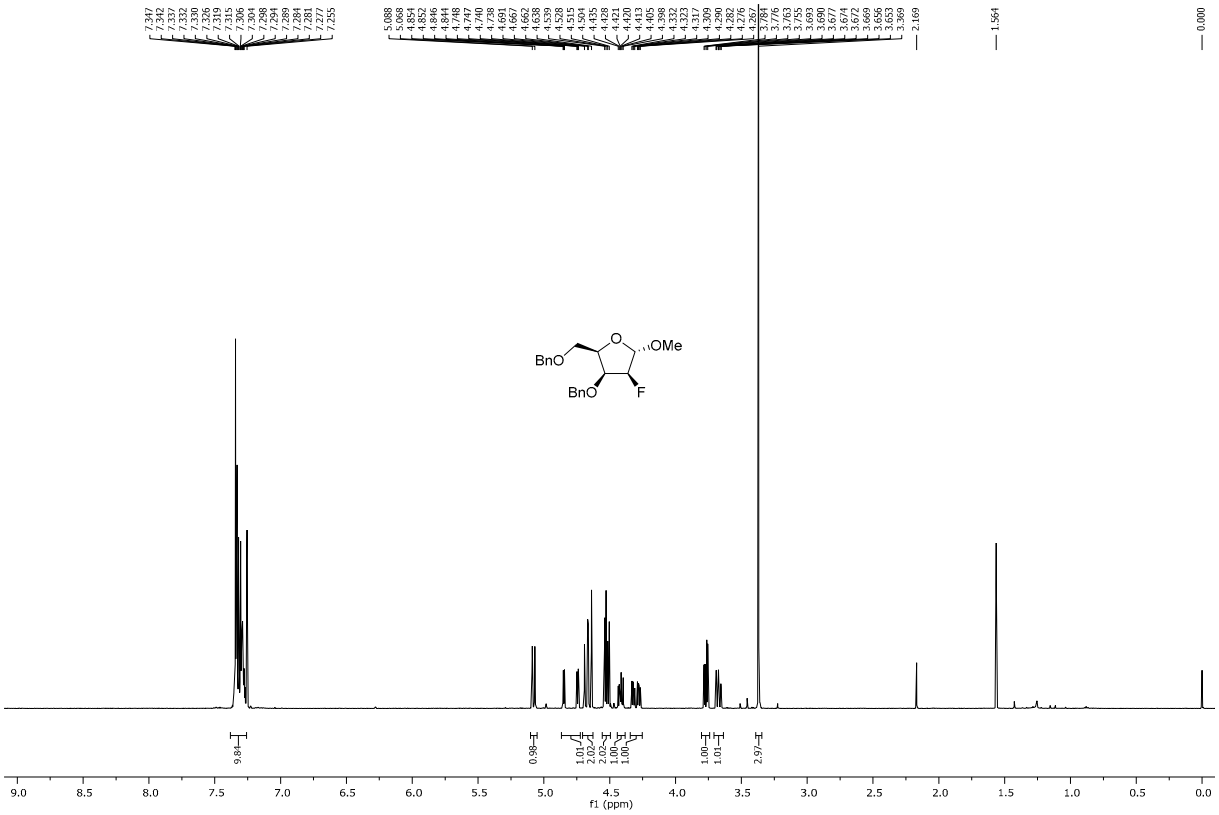


^{1}H-^{13}C HSQC-HECADE of compound **38**

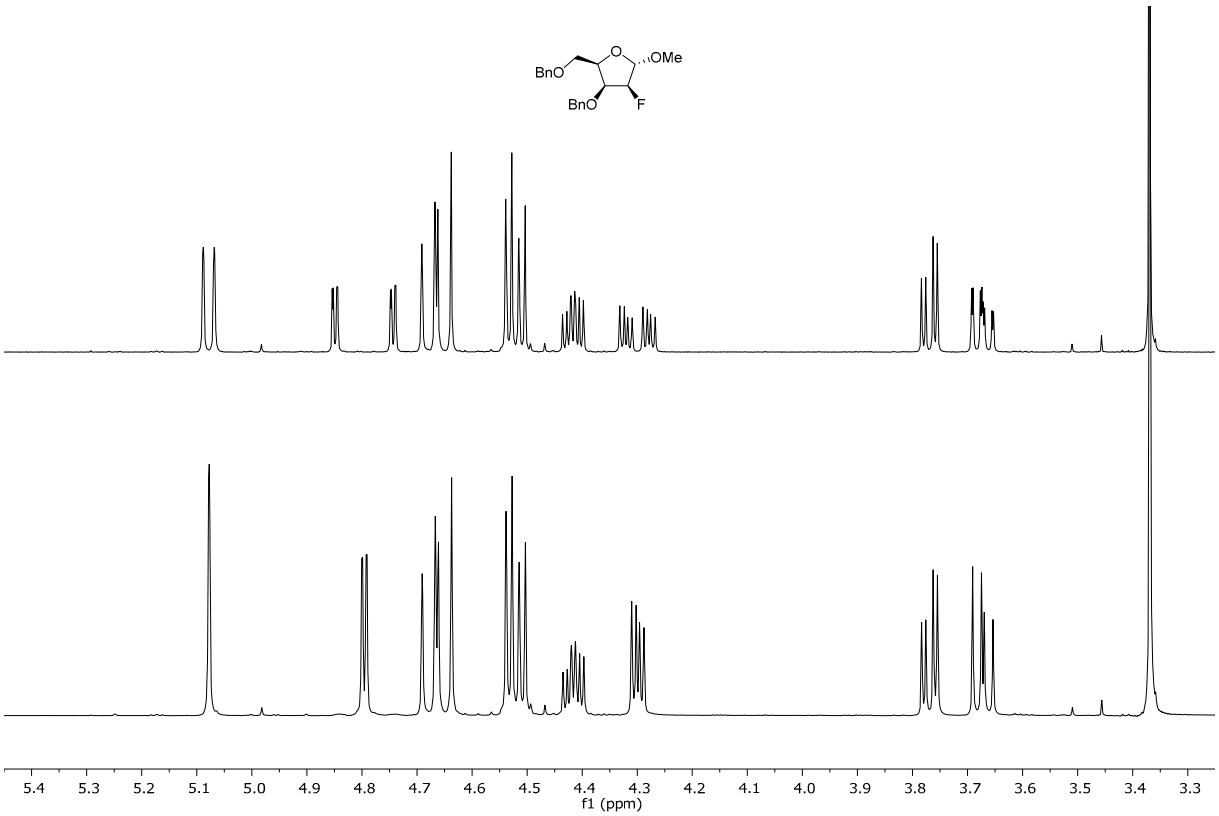


Methyl 3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α-D-lyxofuranoside (39)

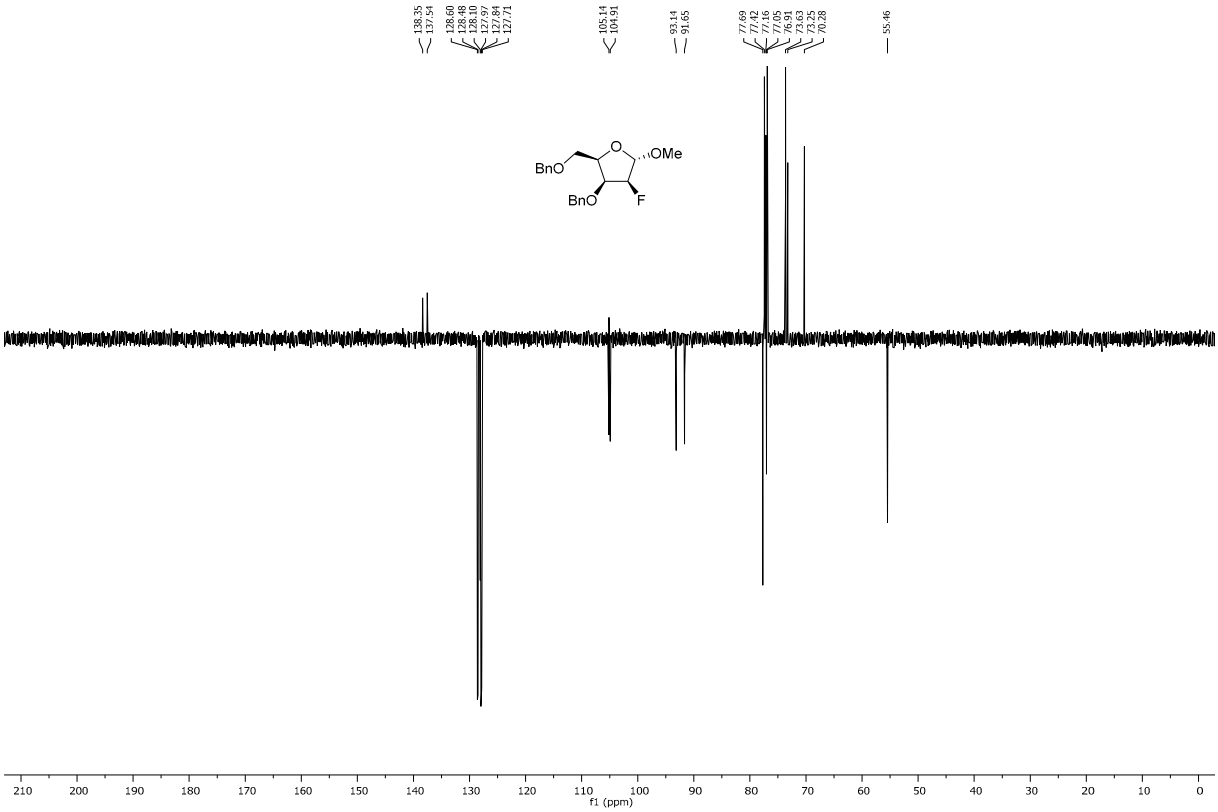
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **39**



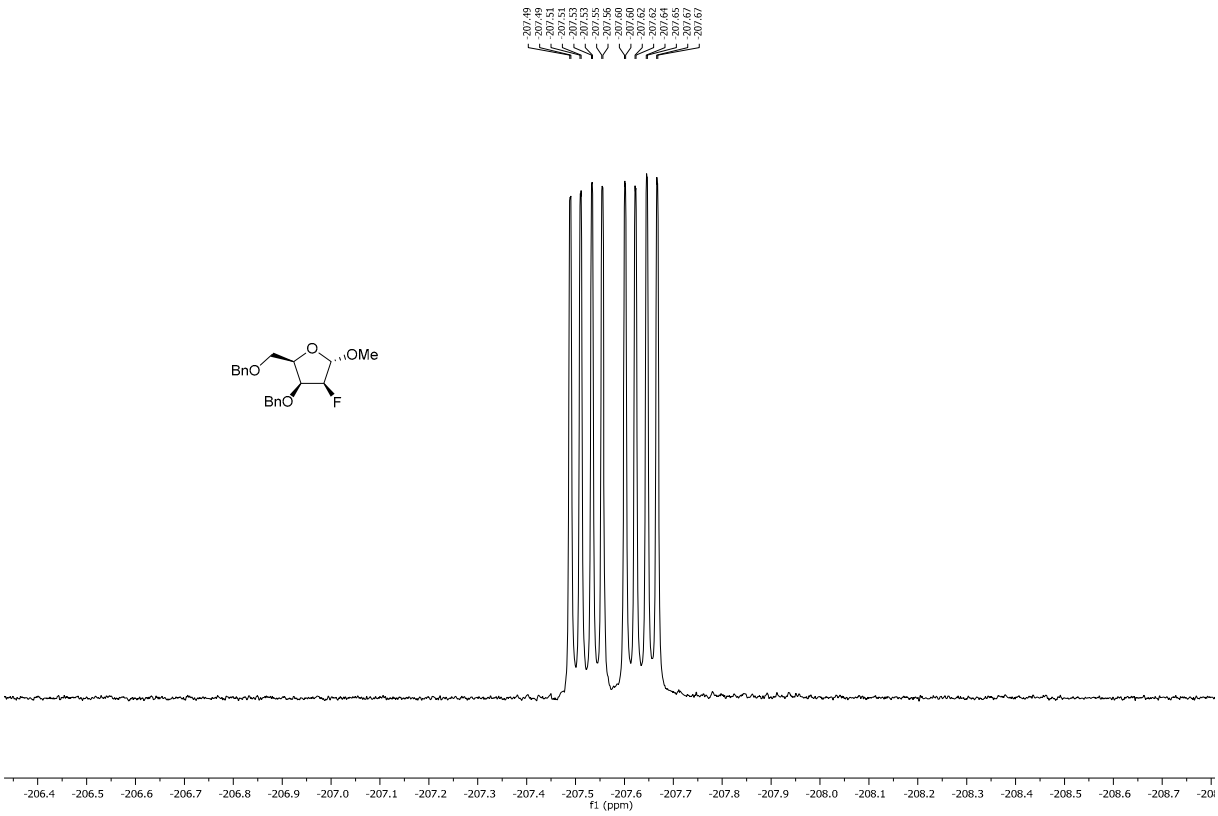
^{19}F-decoupled ^{1}H NMR, (-208 ppm)



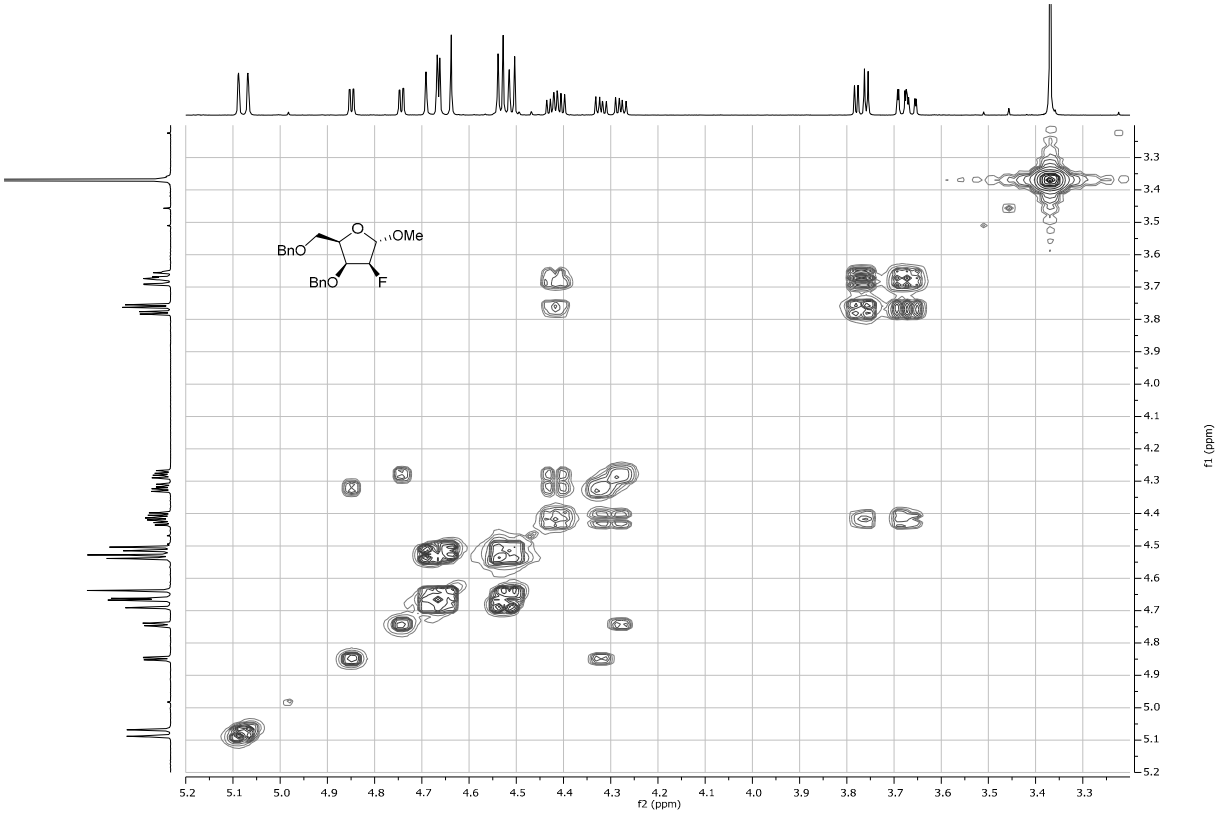
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **39**



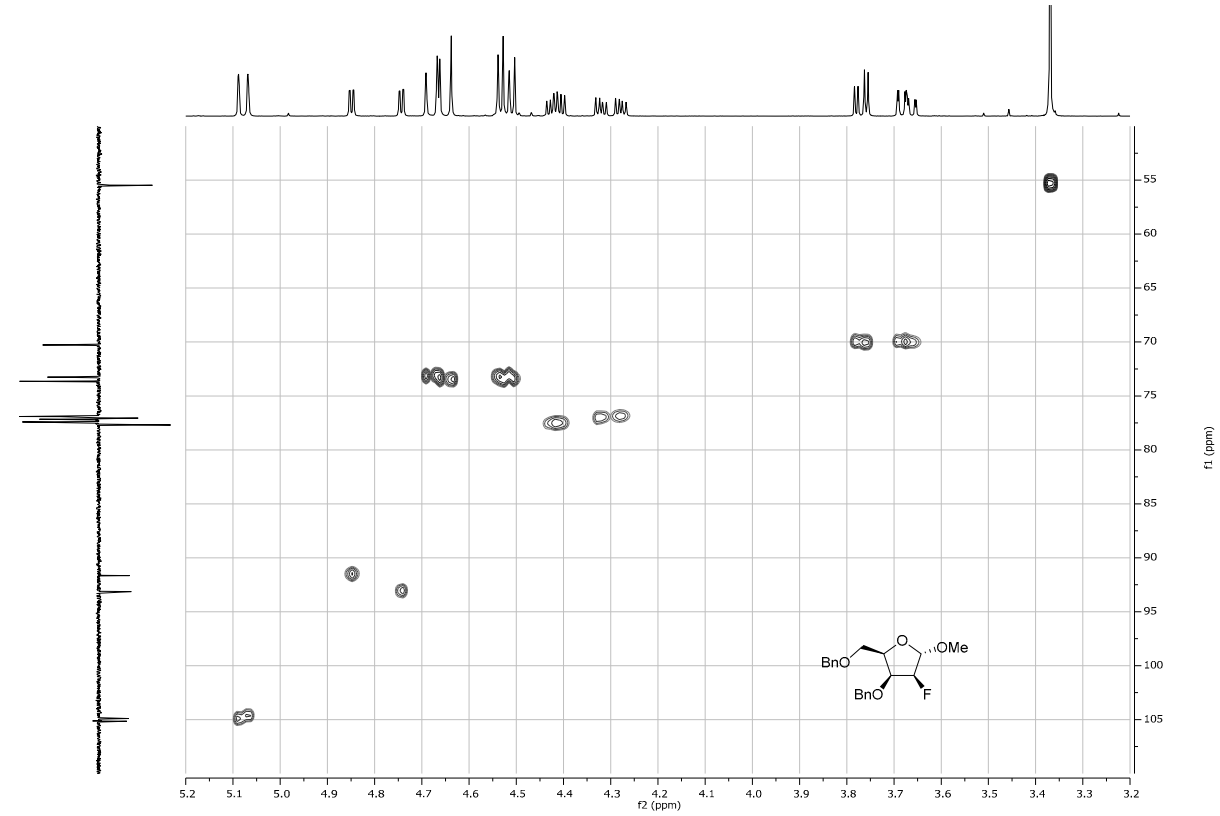
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **35**



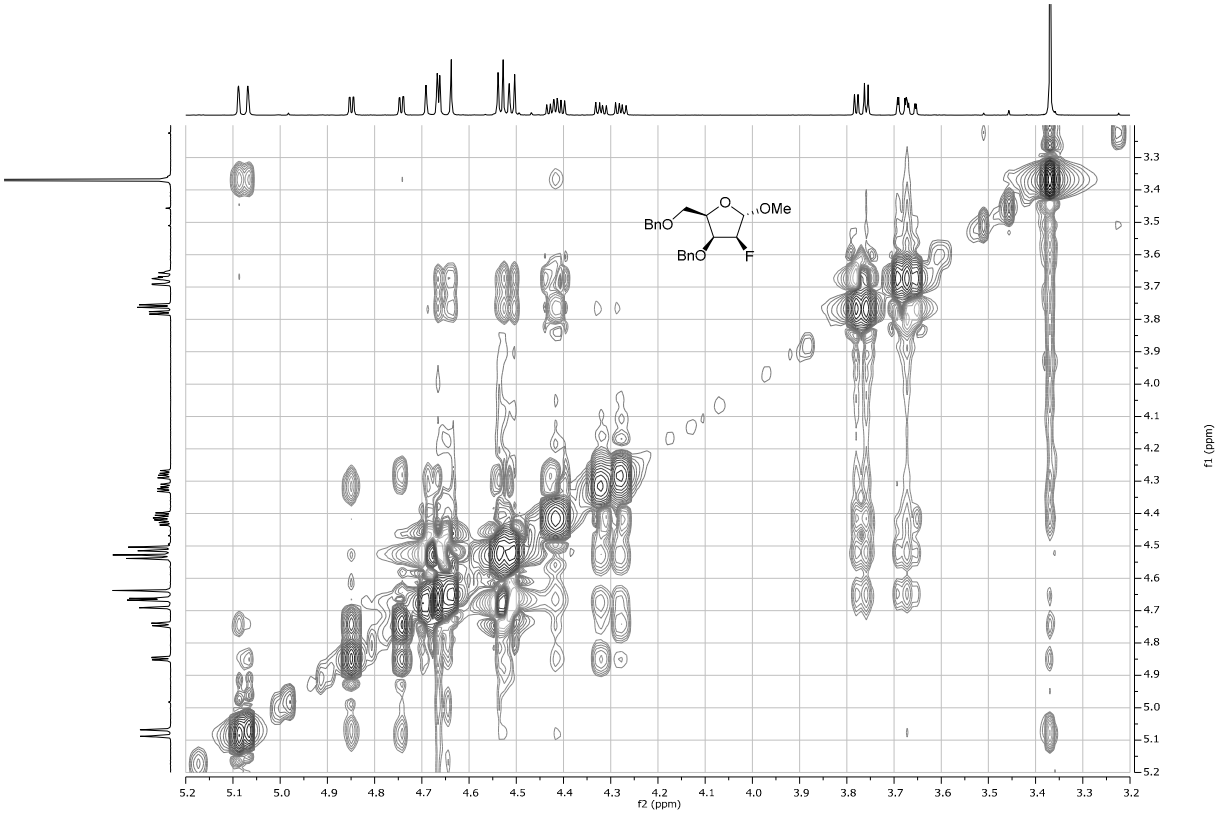
^{1}H-^{1}H COSY of compound **39**



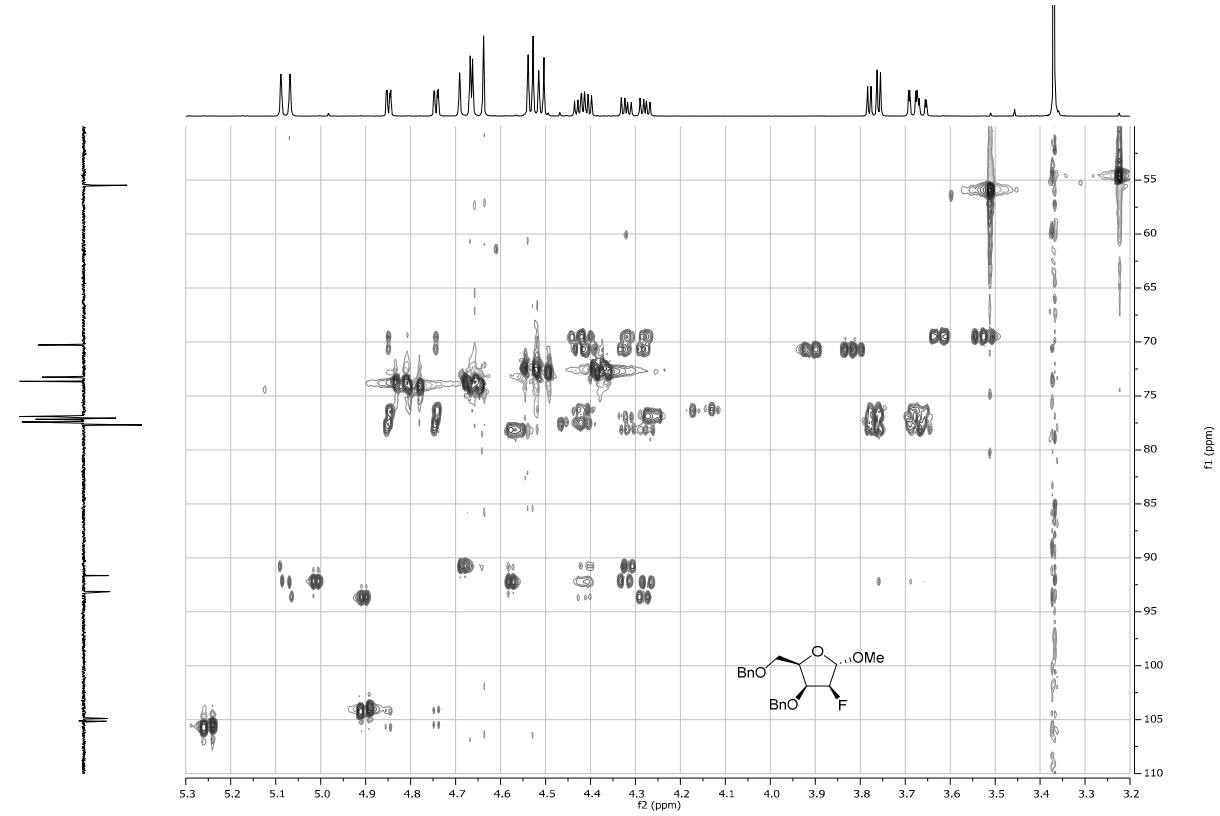
^{1}H-^{13}C HSQC of compound **39**



^{1}H-^{1}H NOESY of compound **39**

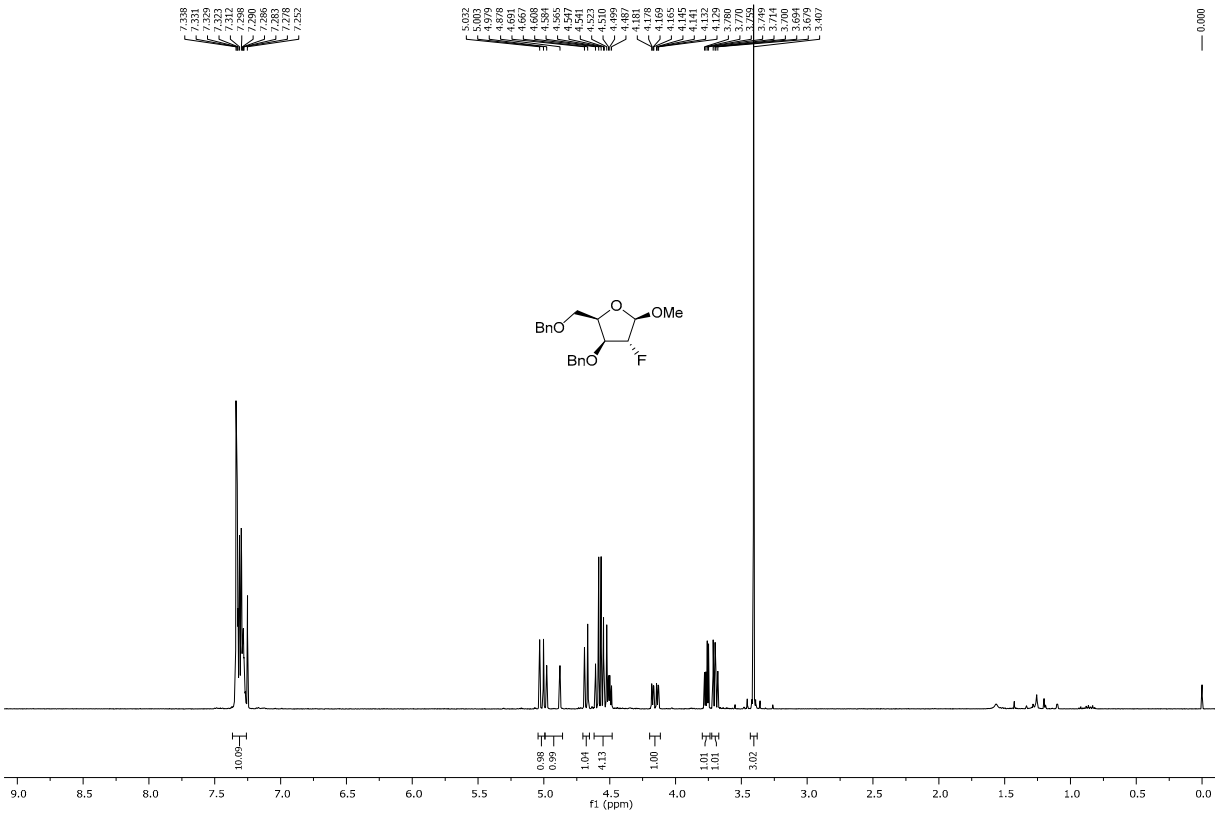


^{1}H-^{13}C HSQC-HECADE of compound **39**

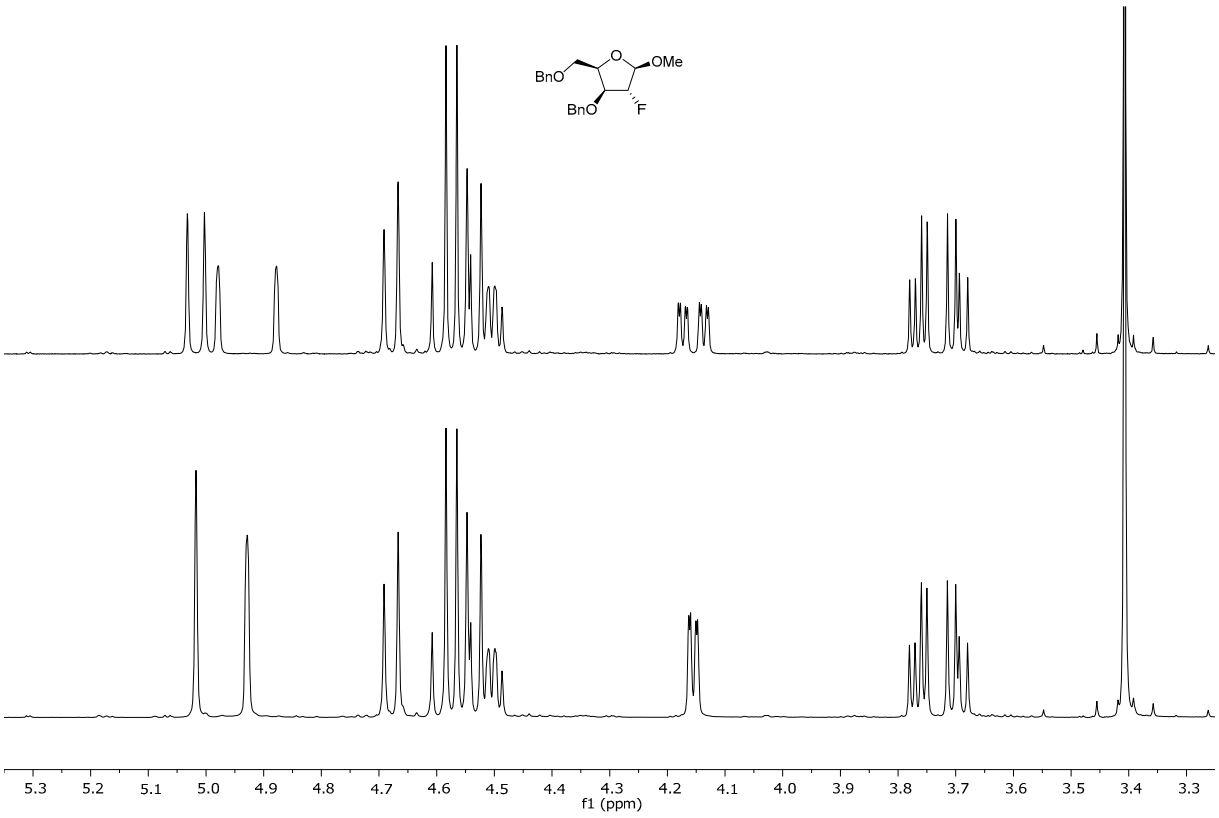


Methyl 3,5-di-*O*-benzyl-2-deoxy-2-fluoro-β-D-xylofuranoside (40β)

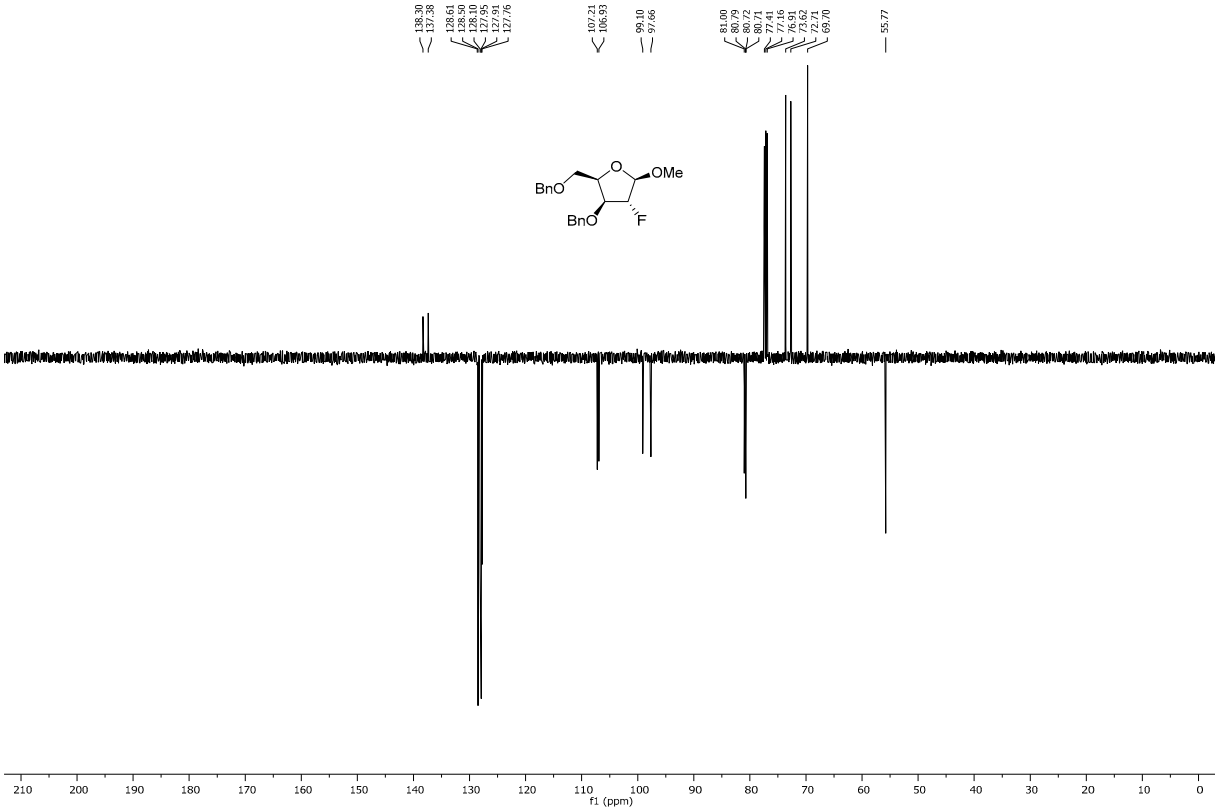
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **40β**



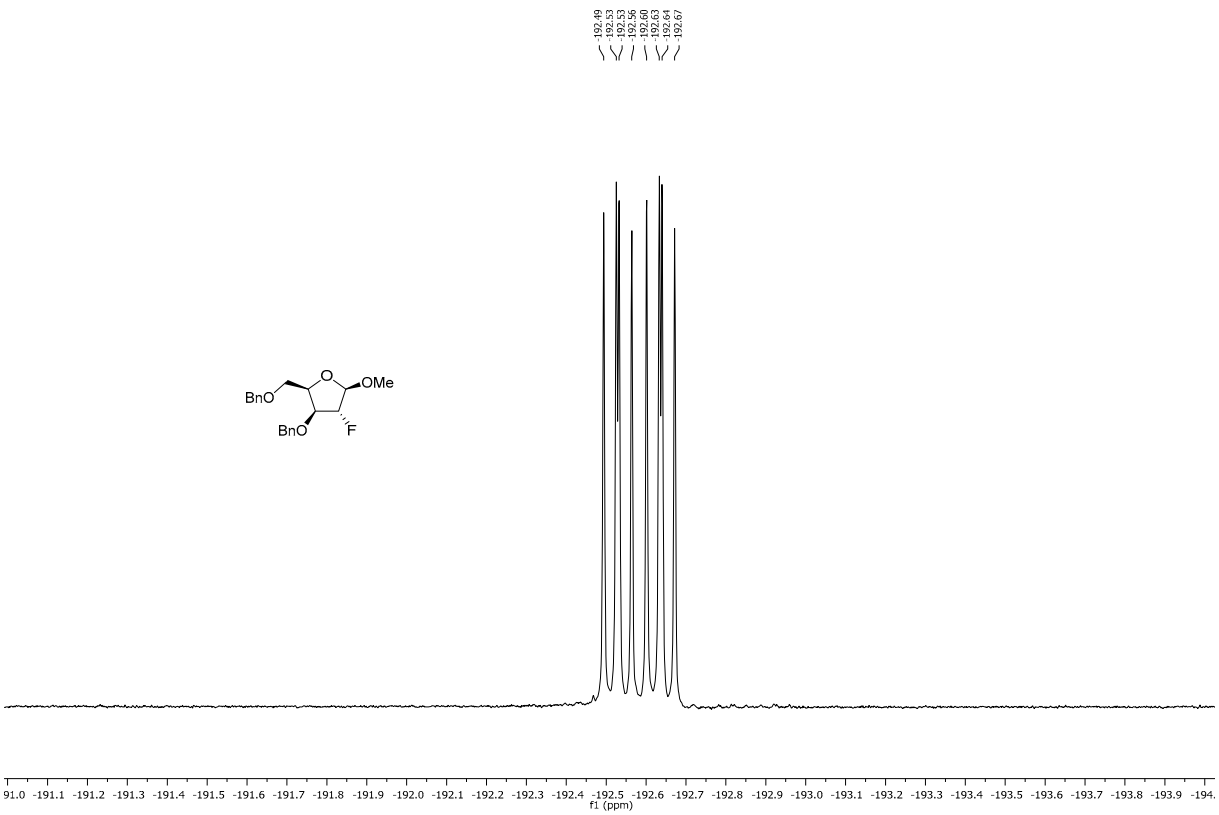
^{19}F-decoupled ^{1}H NMR, (-190 ppm)



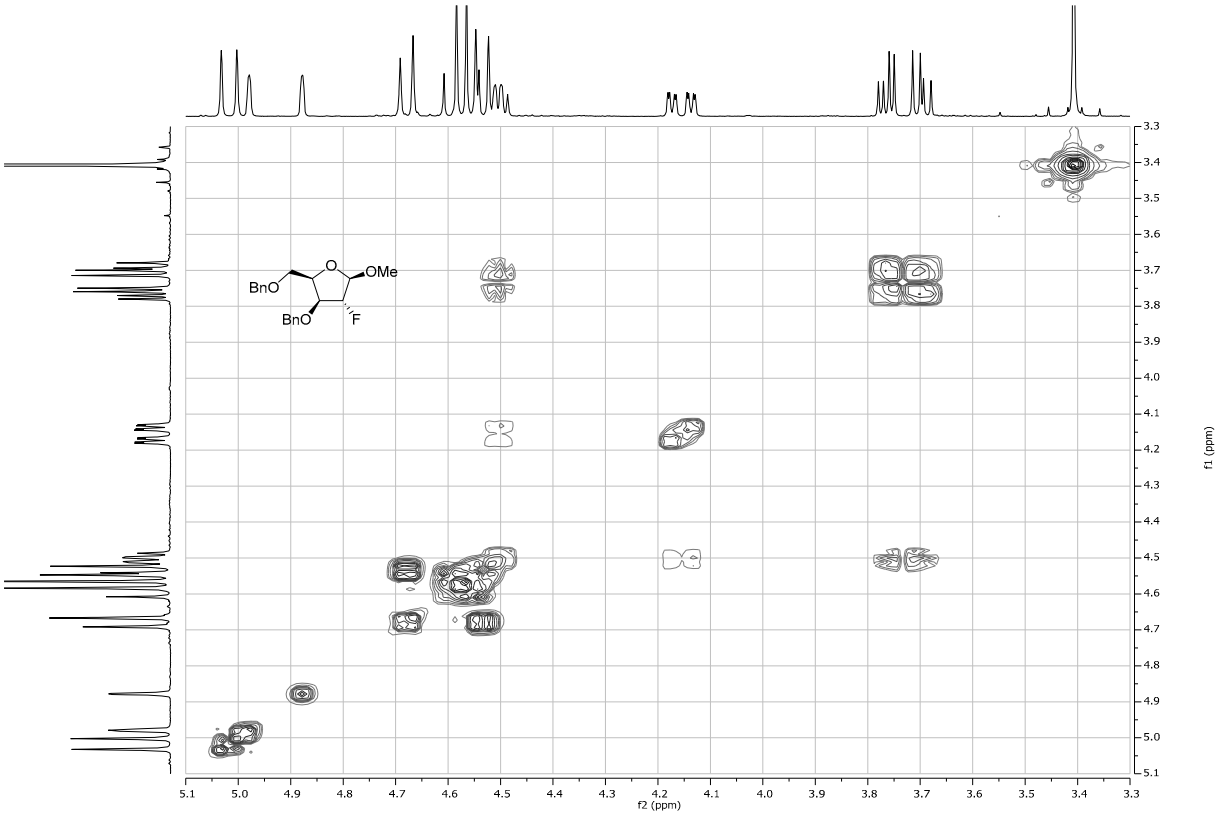
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **40β**



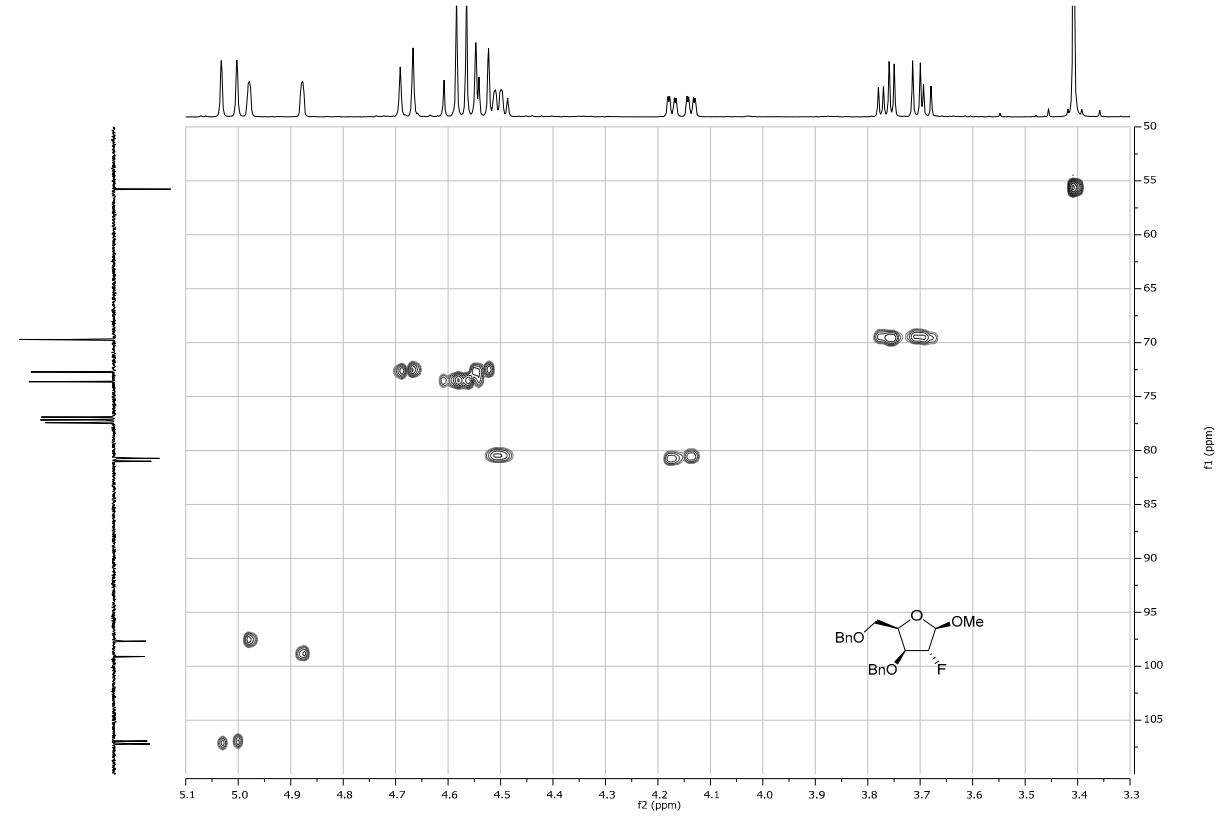
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **40β**



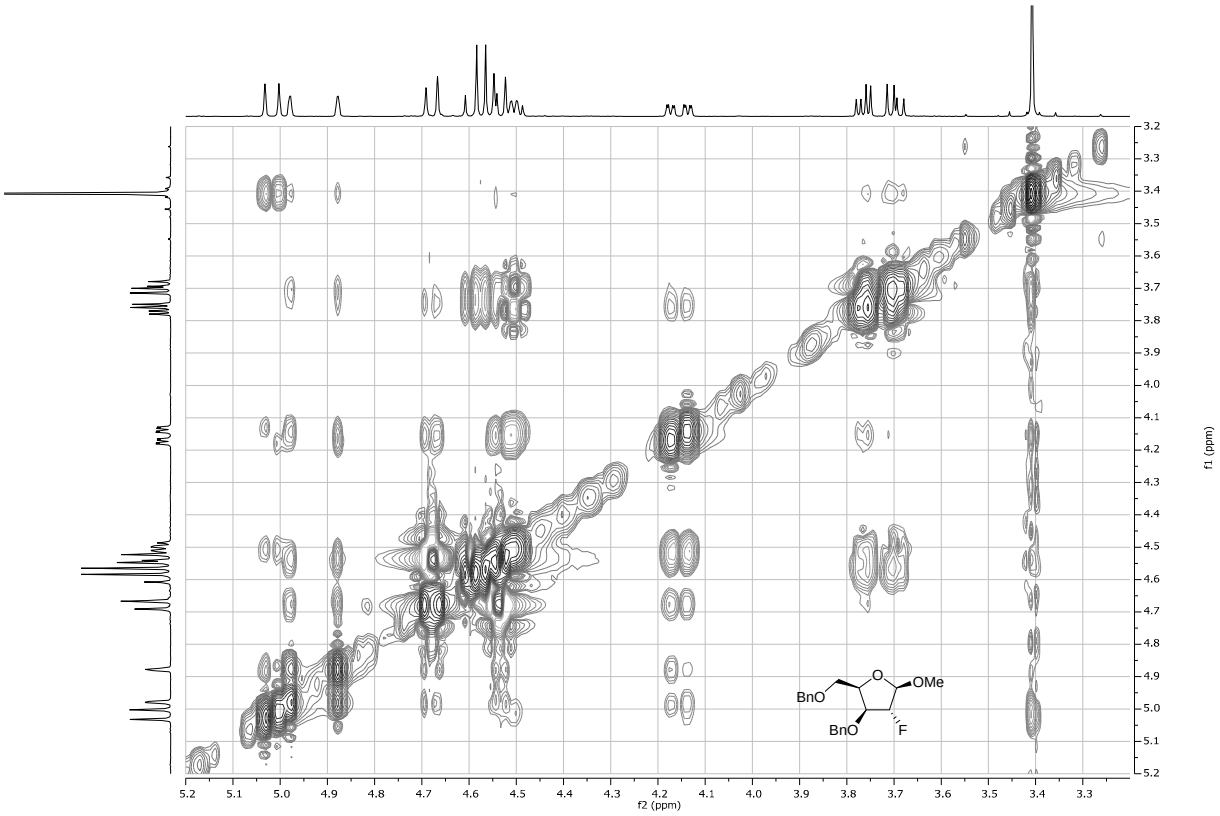
^{1}H-^{1}H COSY of compound **40β**



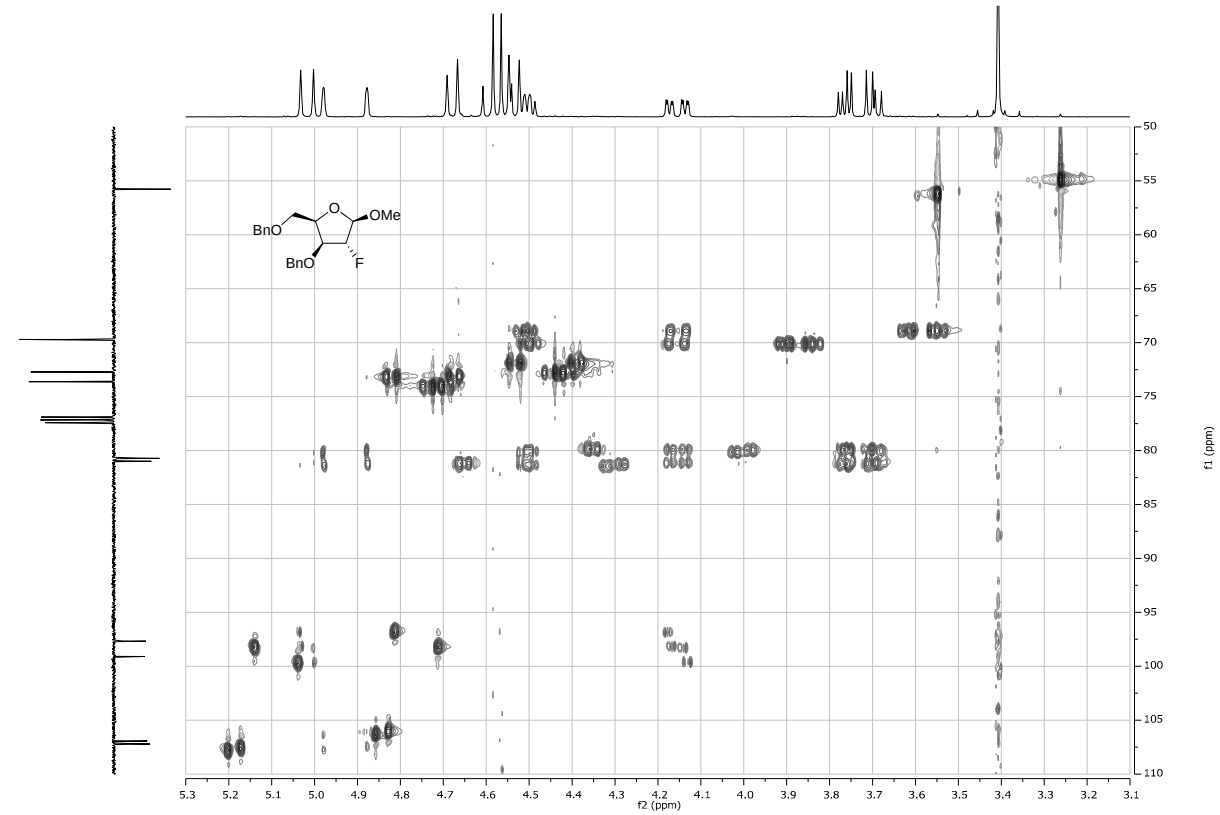
^{1}H-^{13}C HSQC of compound **40β**



^{1}H-^{1}H NOESY of compound **40β**

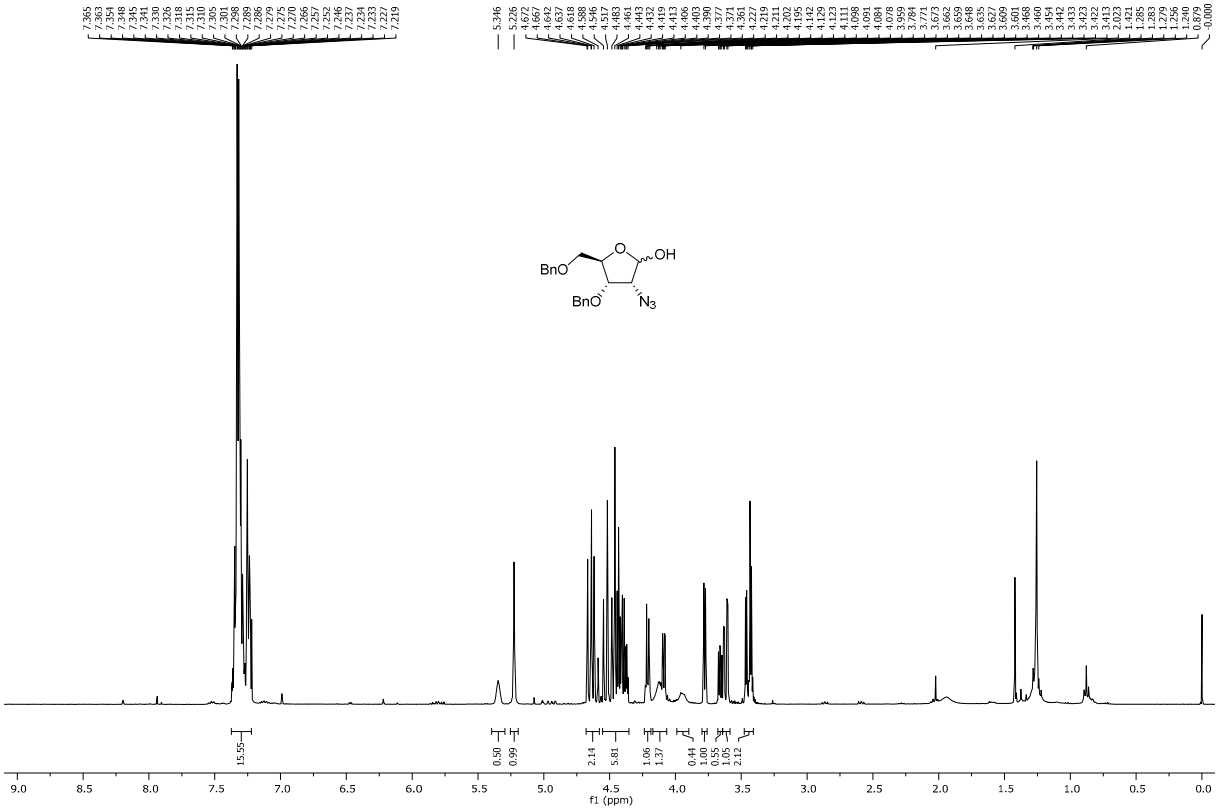


^{1}H-^{13}C HSQC-HECADE of compound **40β**

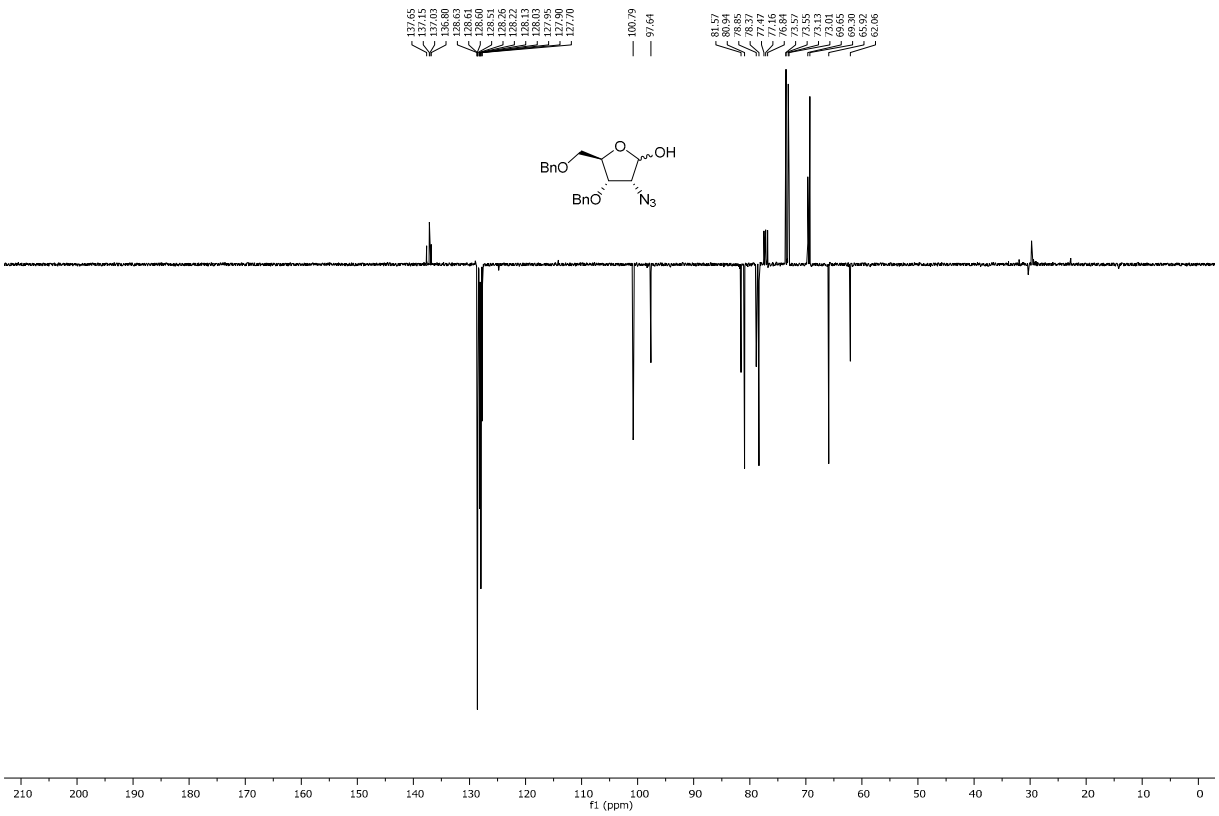


2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-ribofuranose (41)

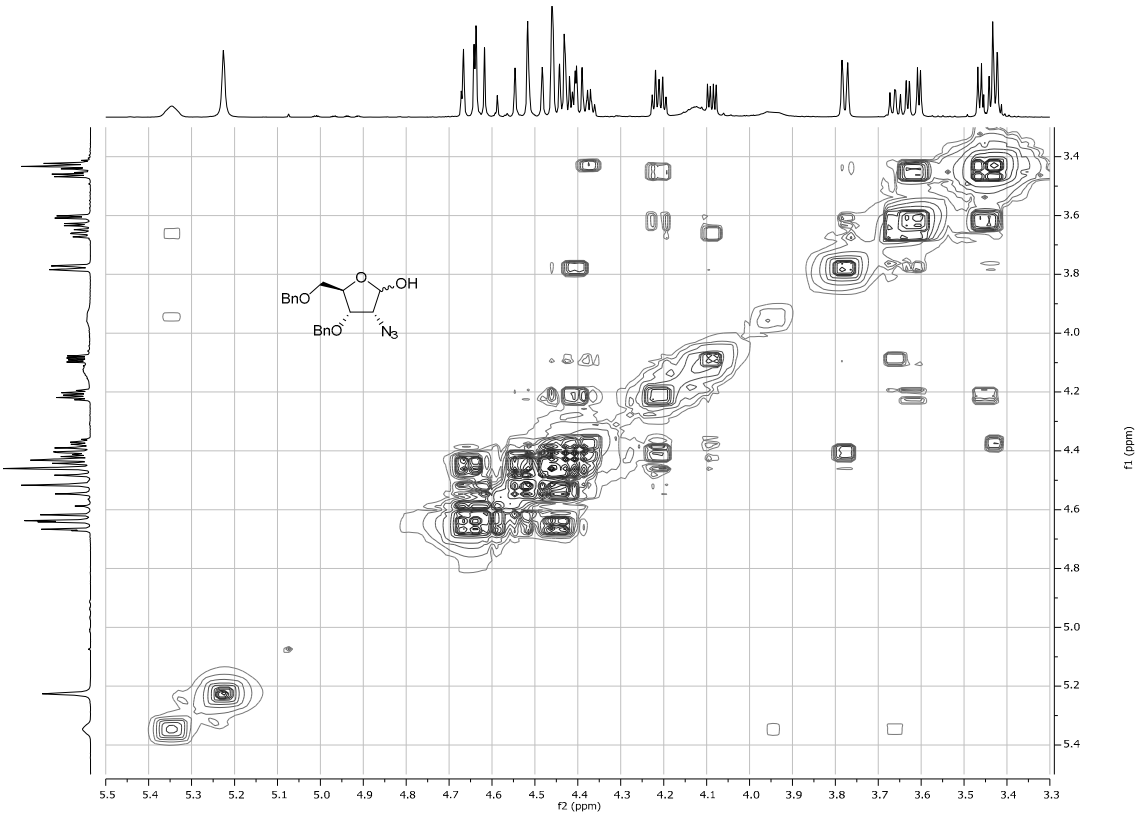
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **41**



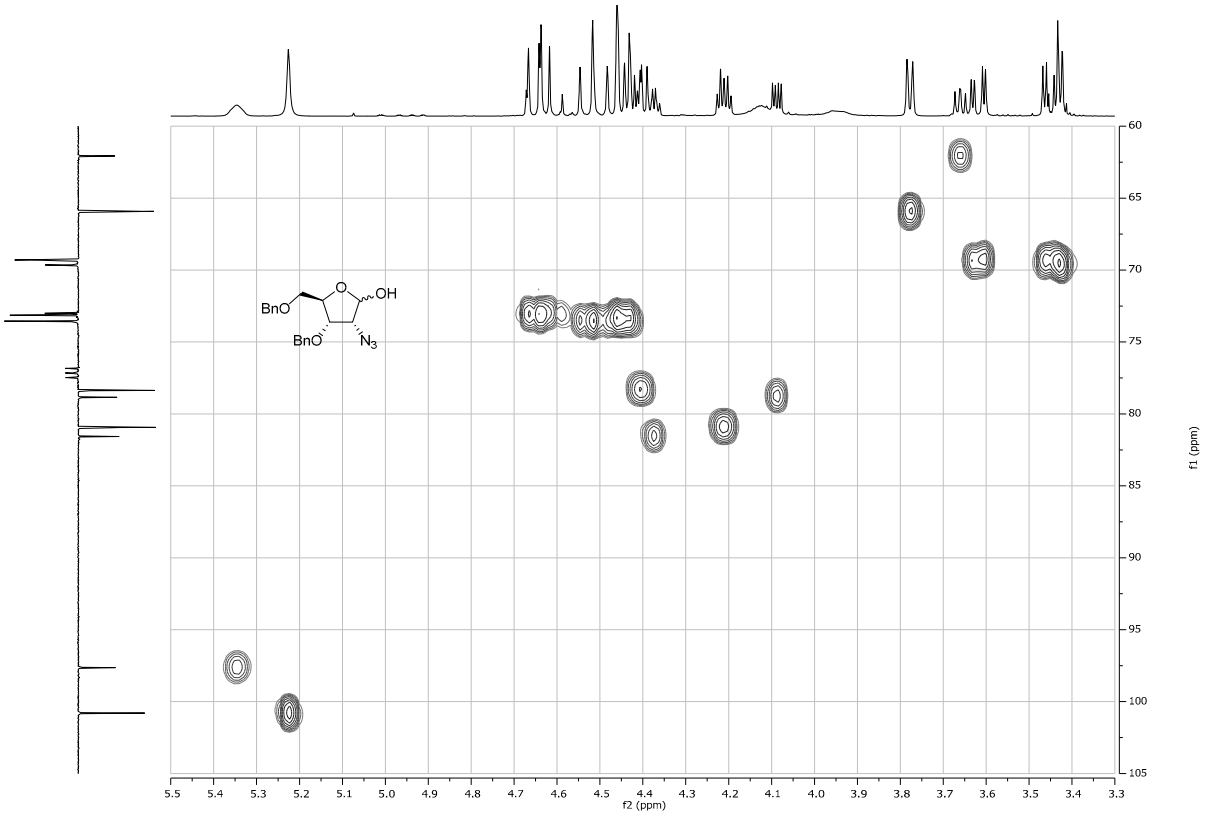
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **41**



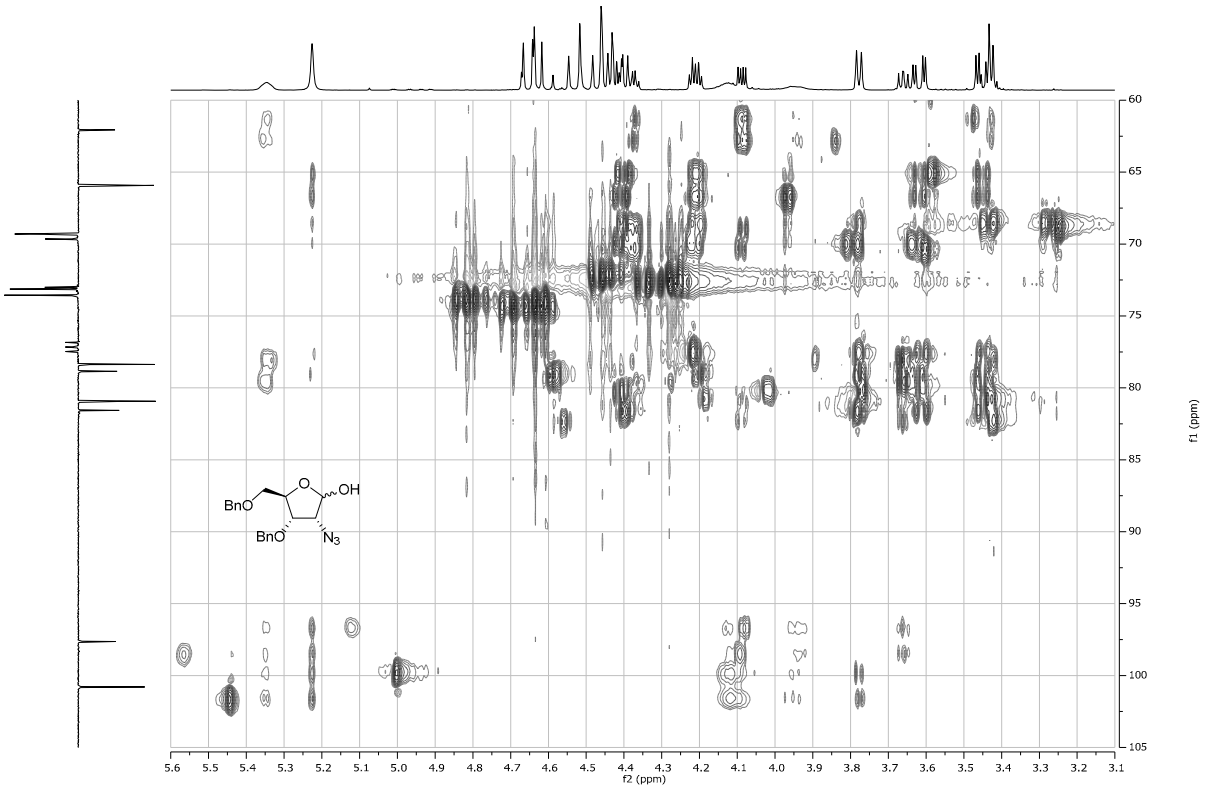
^{1}H-^{1}H COSY of compound **41**



^{1}H-^{13}C HSQC of compound **41**

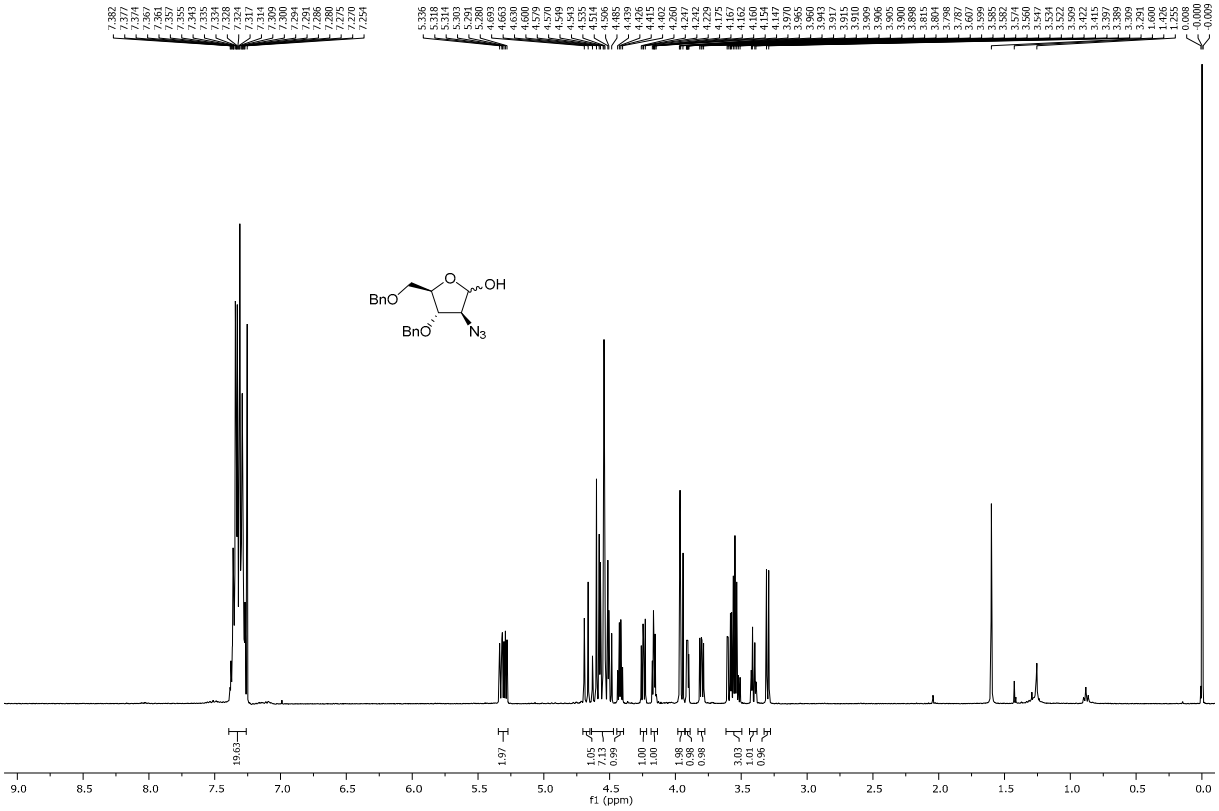


^{1}H-^{13}C HSQC-HECADE of compound **41**

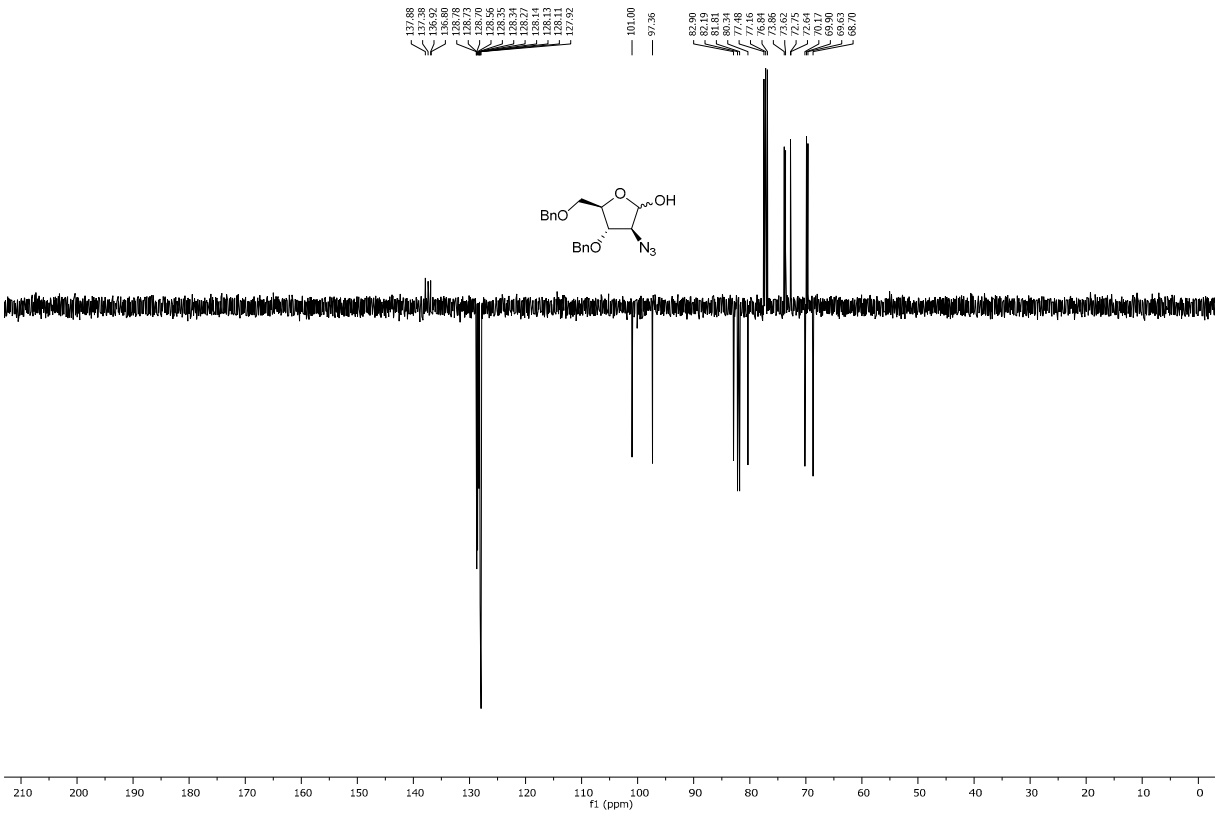


2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-arabinofuranose (42)

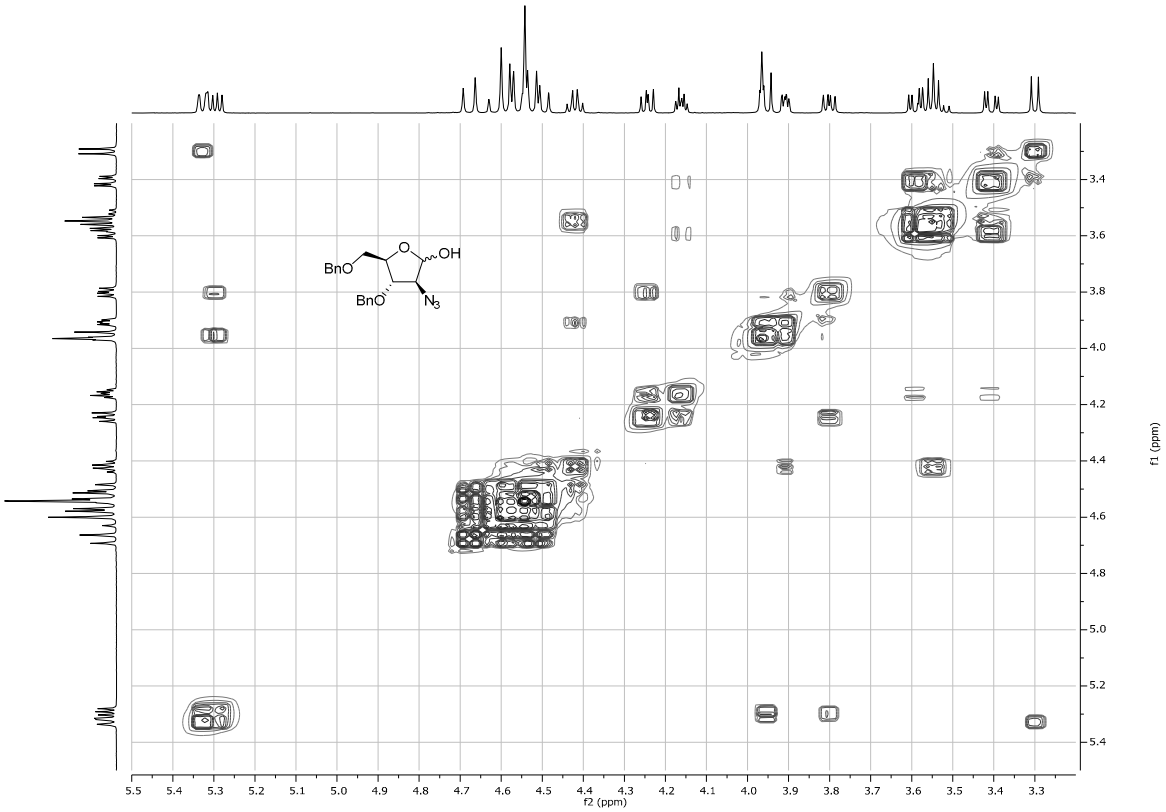
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **42**



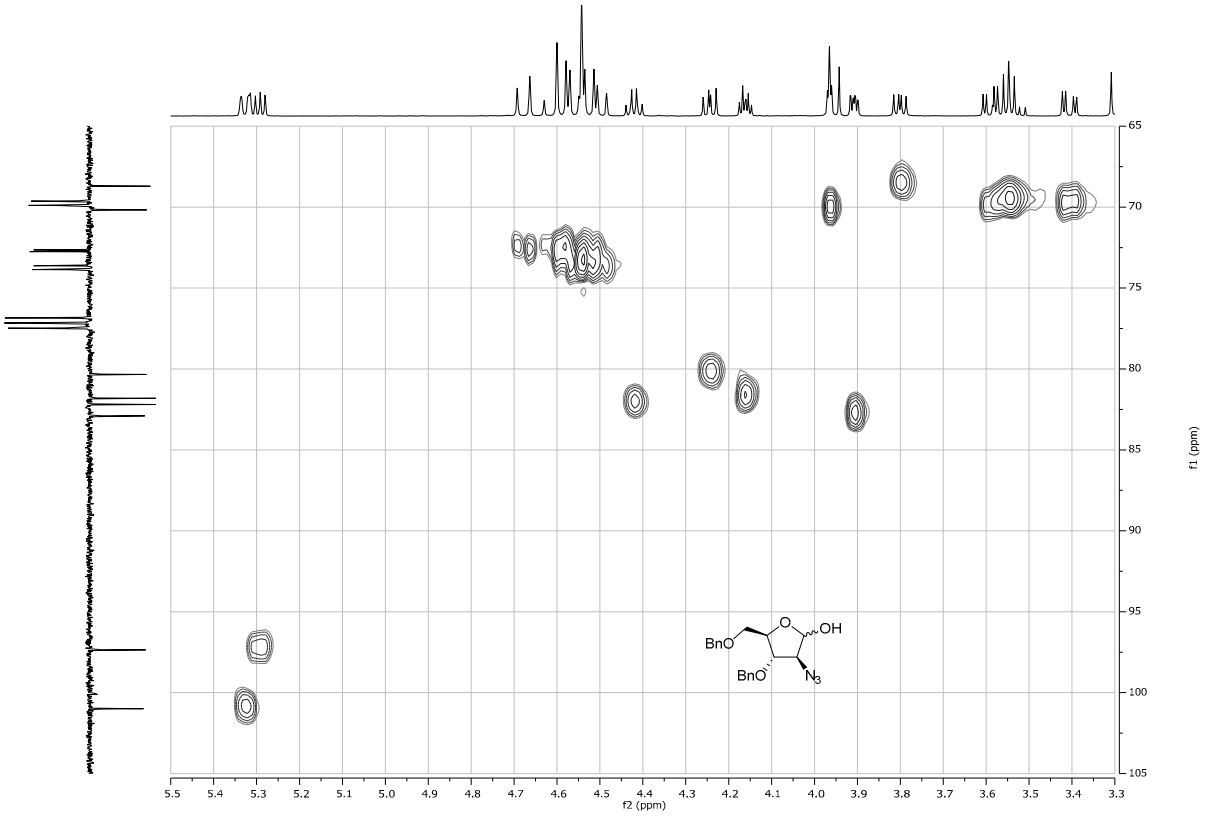
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **42**



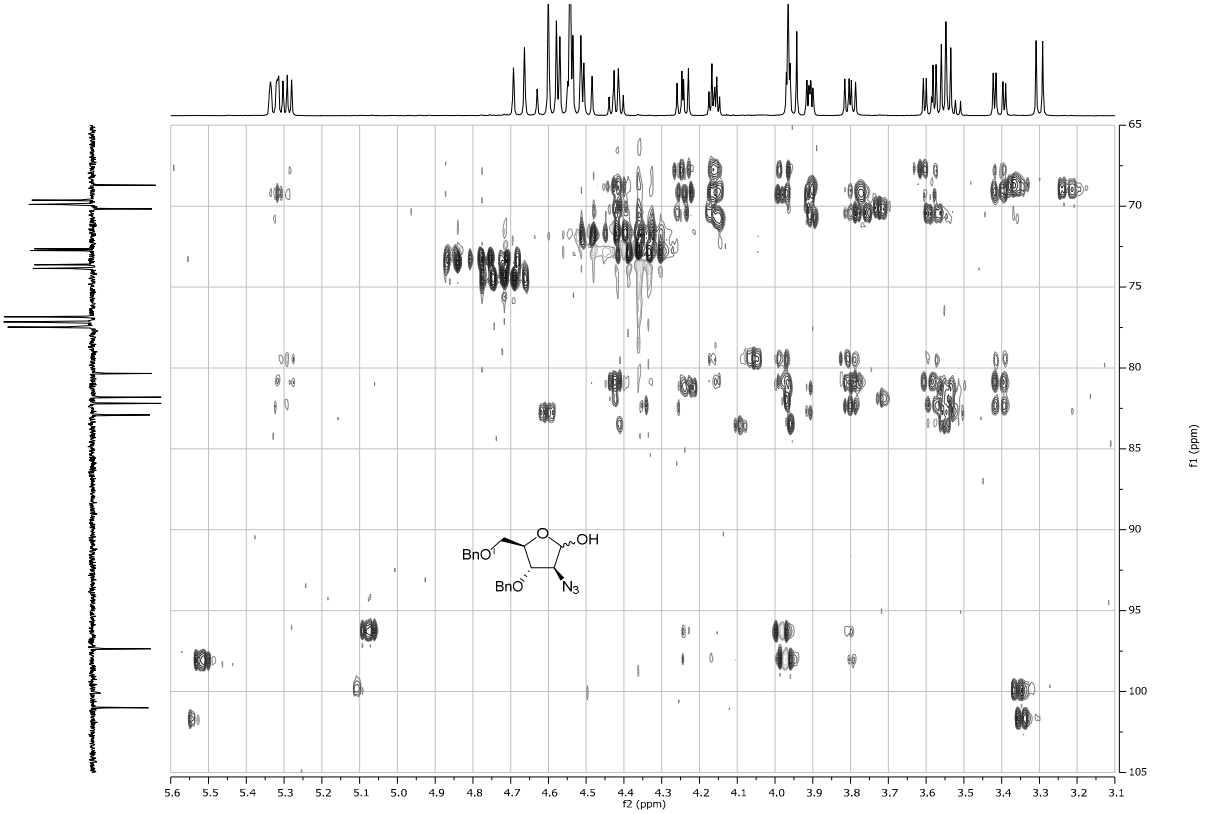
^{1}H-^{1}H COSY of compound **42**



^{1}H-^{13}C HSQC of compound **42**

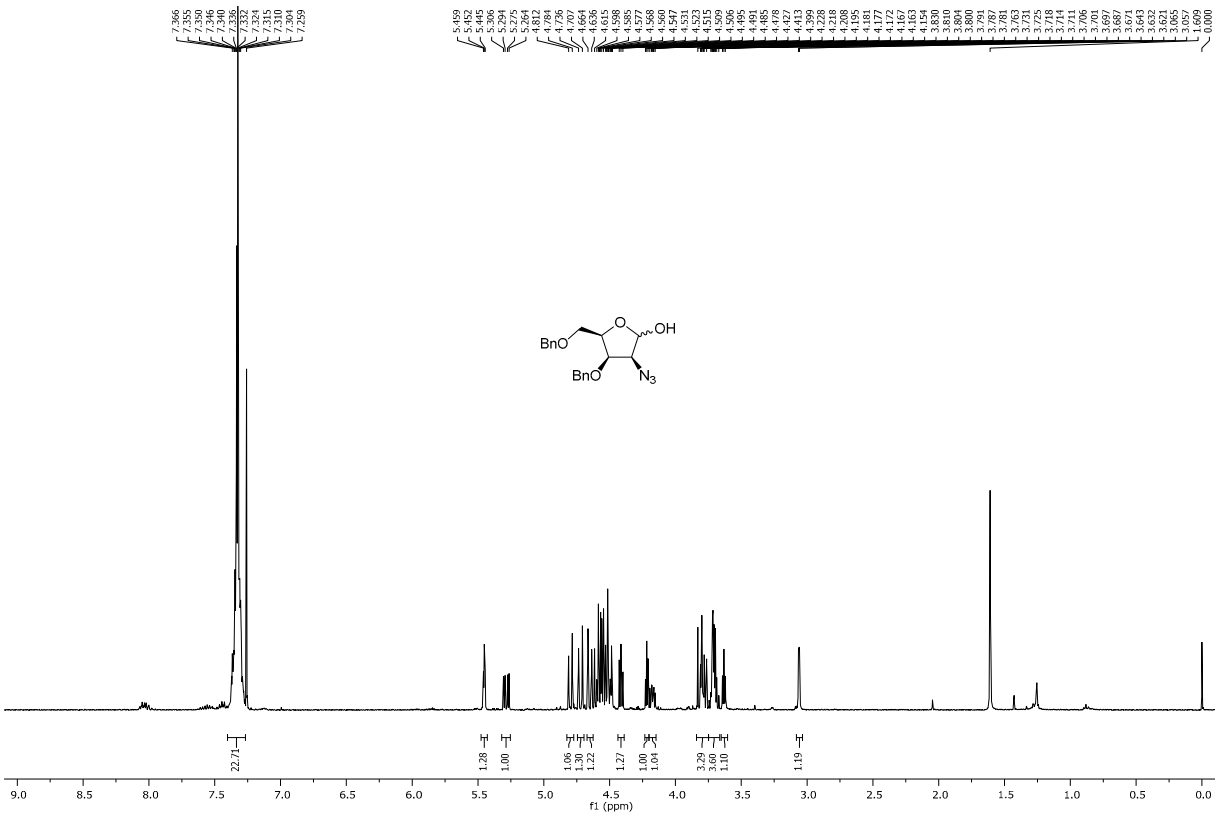


^{1}H-^{13}C HSQC-HECADE of compound **42**

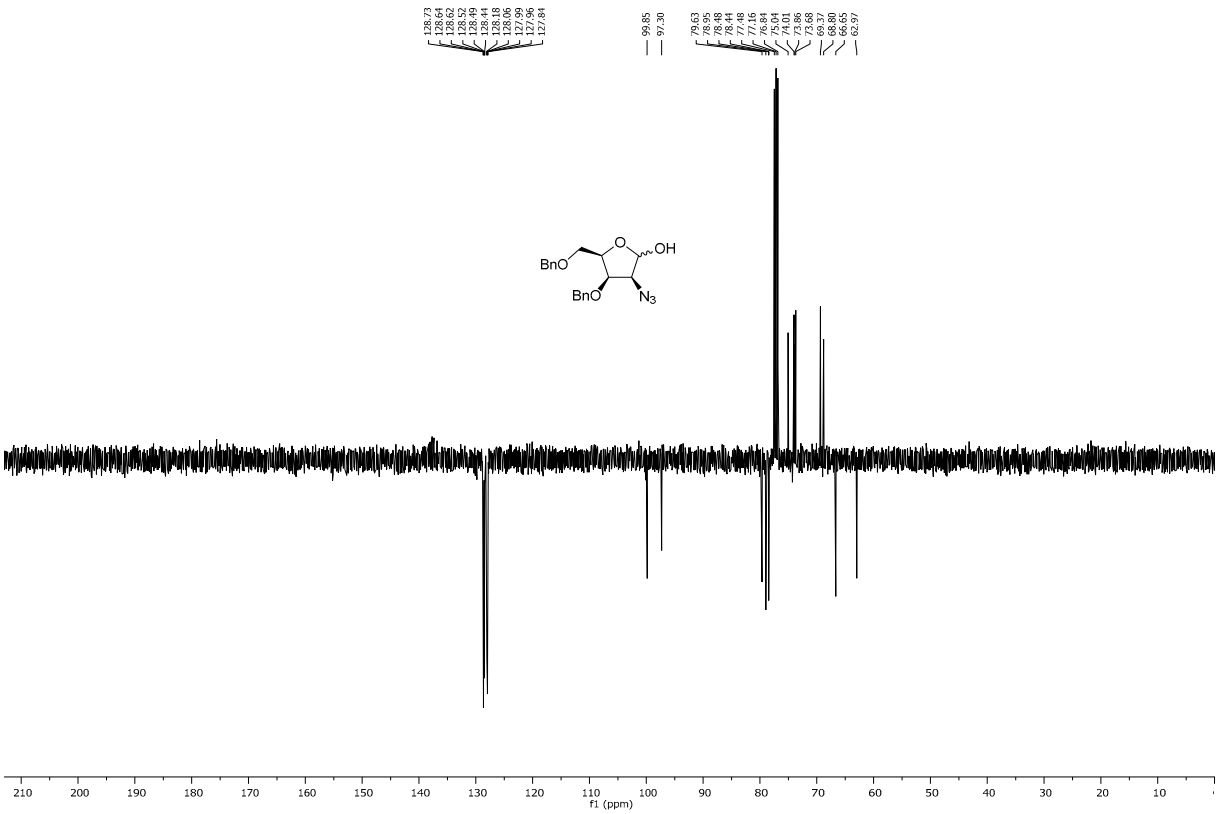


2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-lyxofuranose (43)

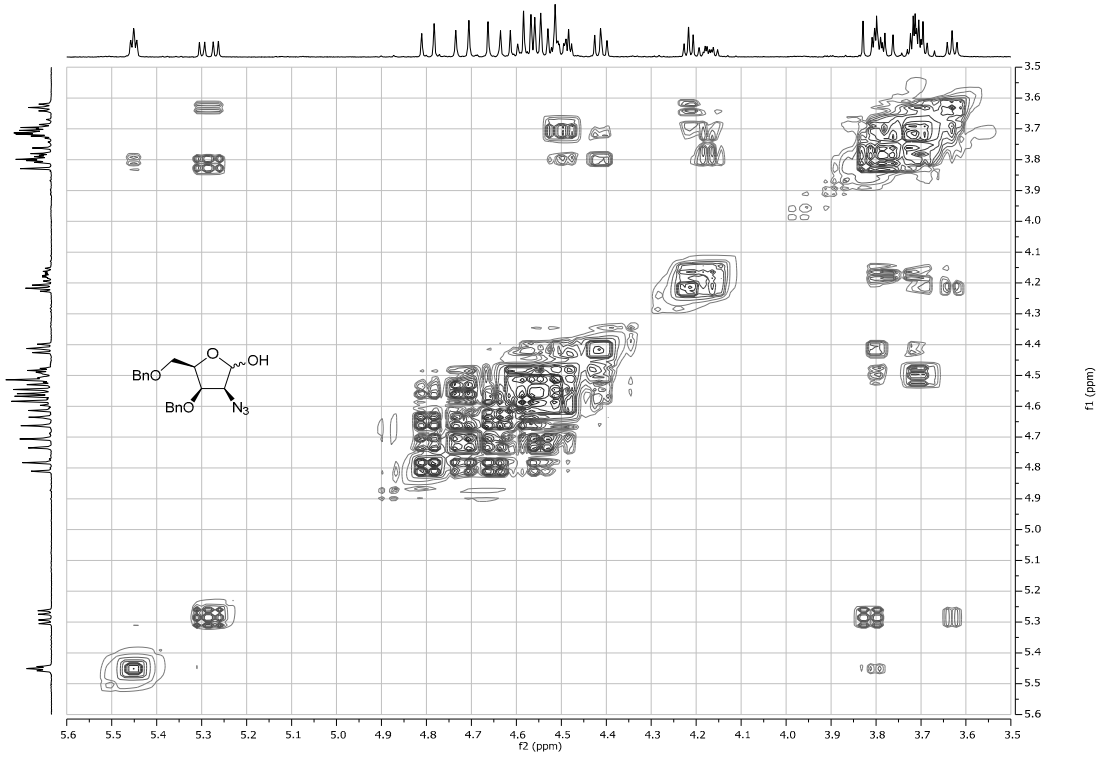
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **43**



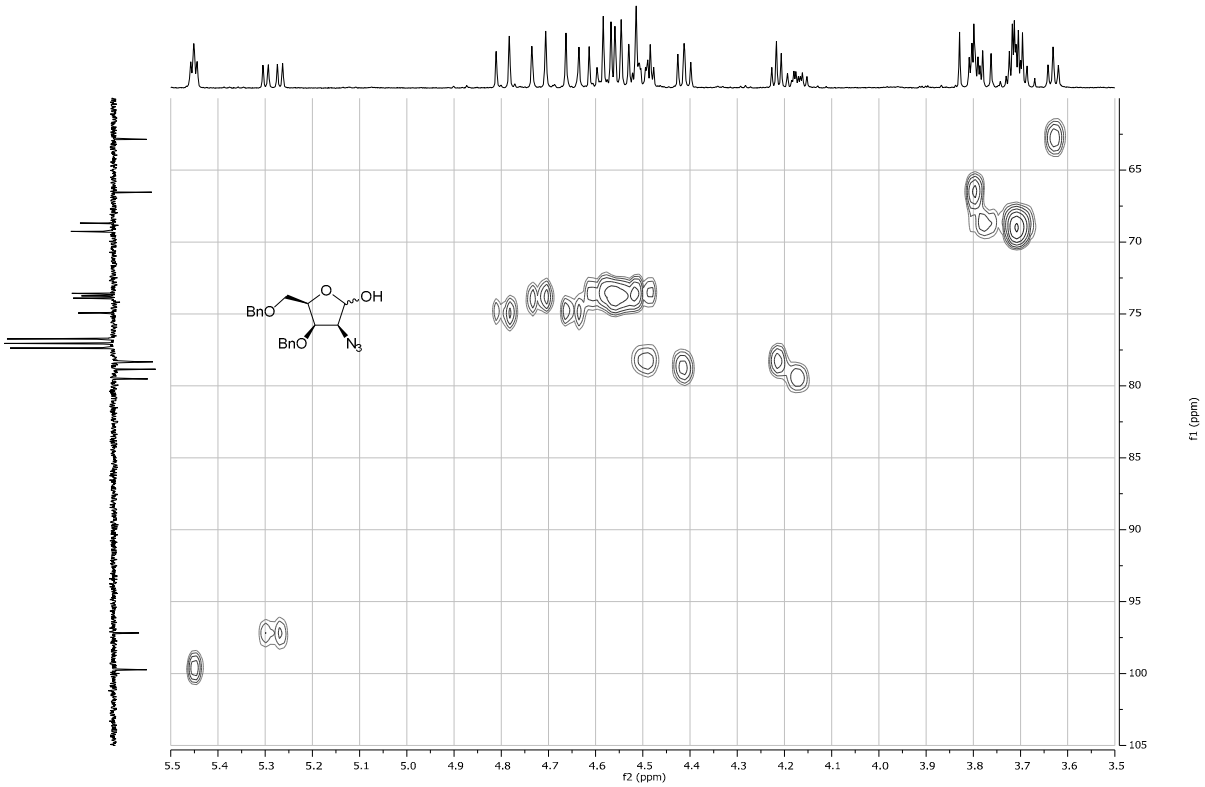
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **43**



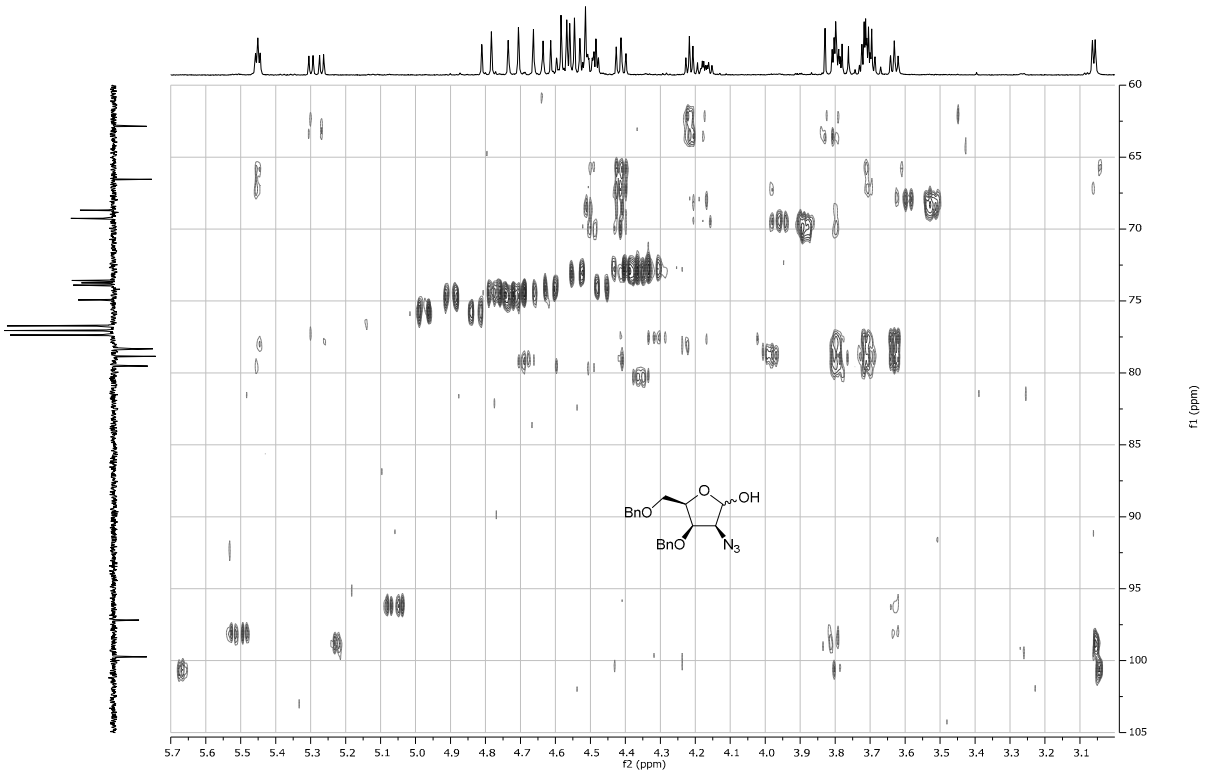
^{1}H-^{1}H COSY of compound **43**



^{1}H-^{13}C HSQC of compound **43**

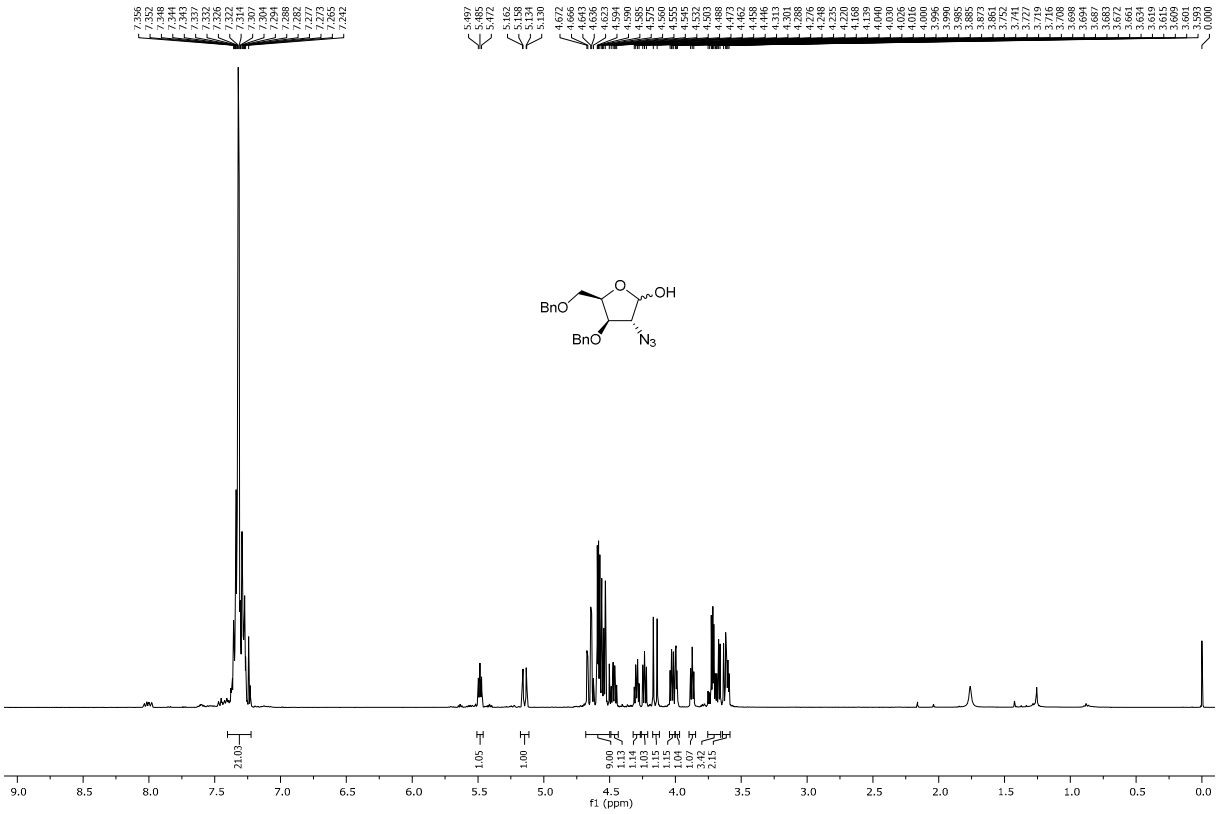


^{1}H-^{13}C HSQC-HECADE of compound **43**

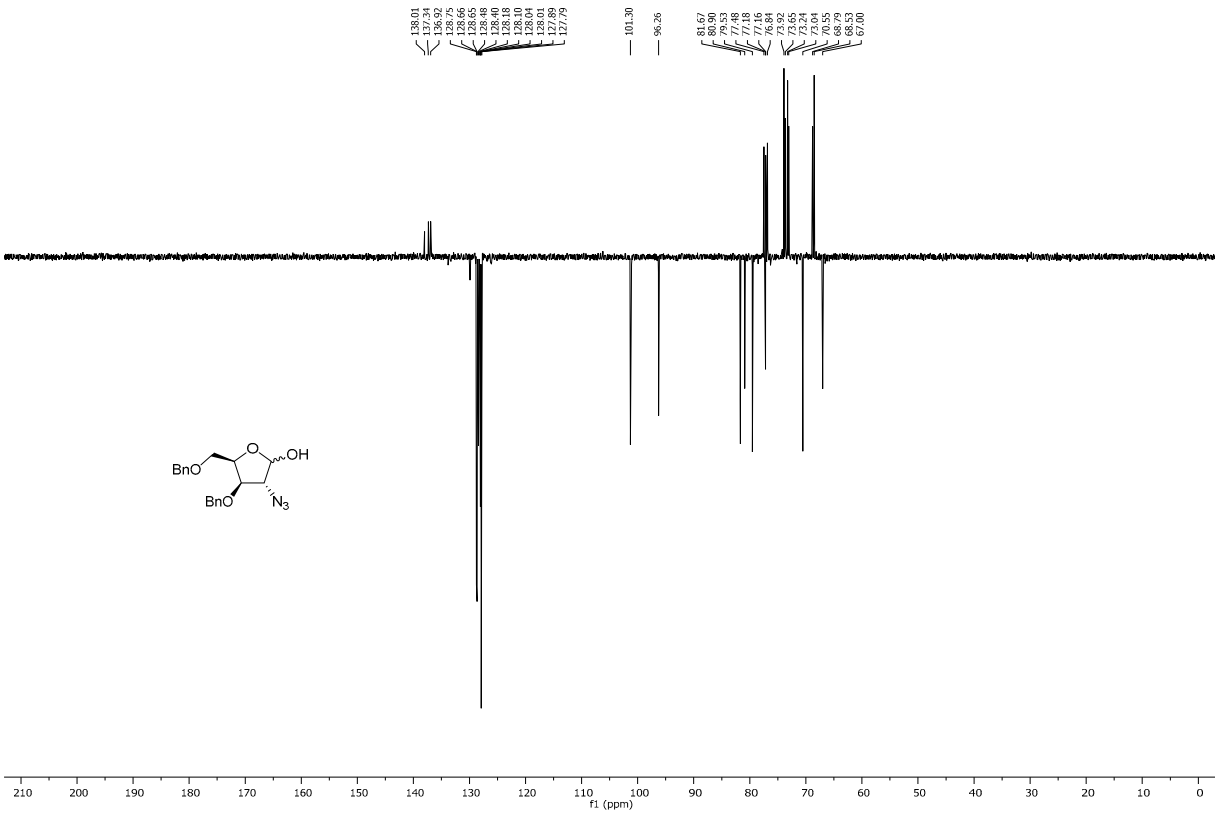


2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-xylofuranose (44)

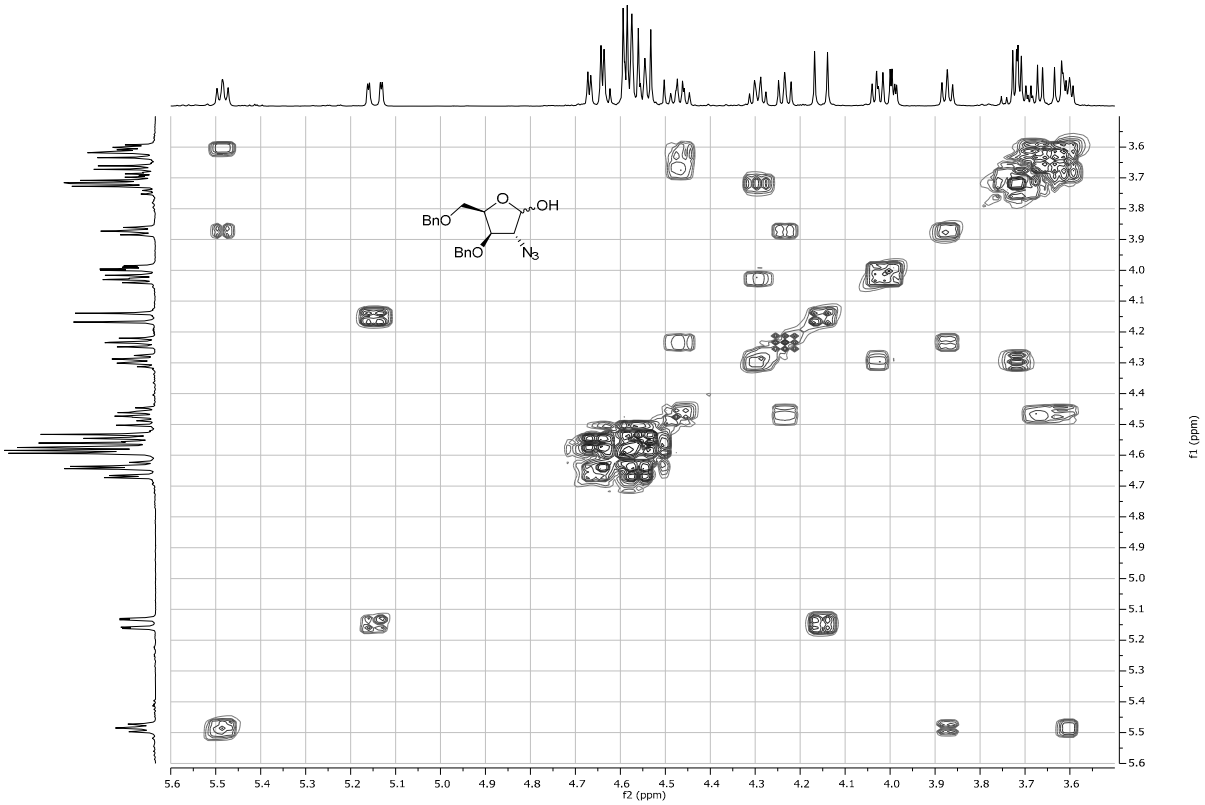
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **44**



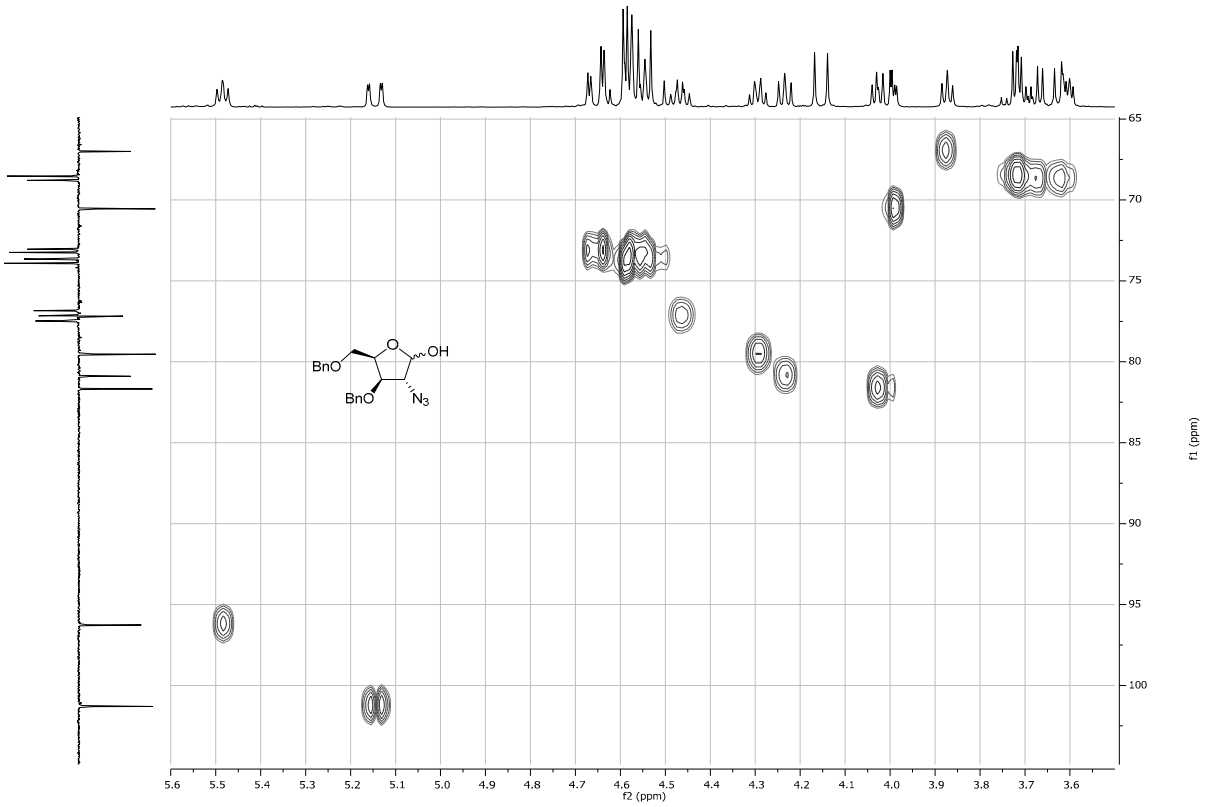
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **44**



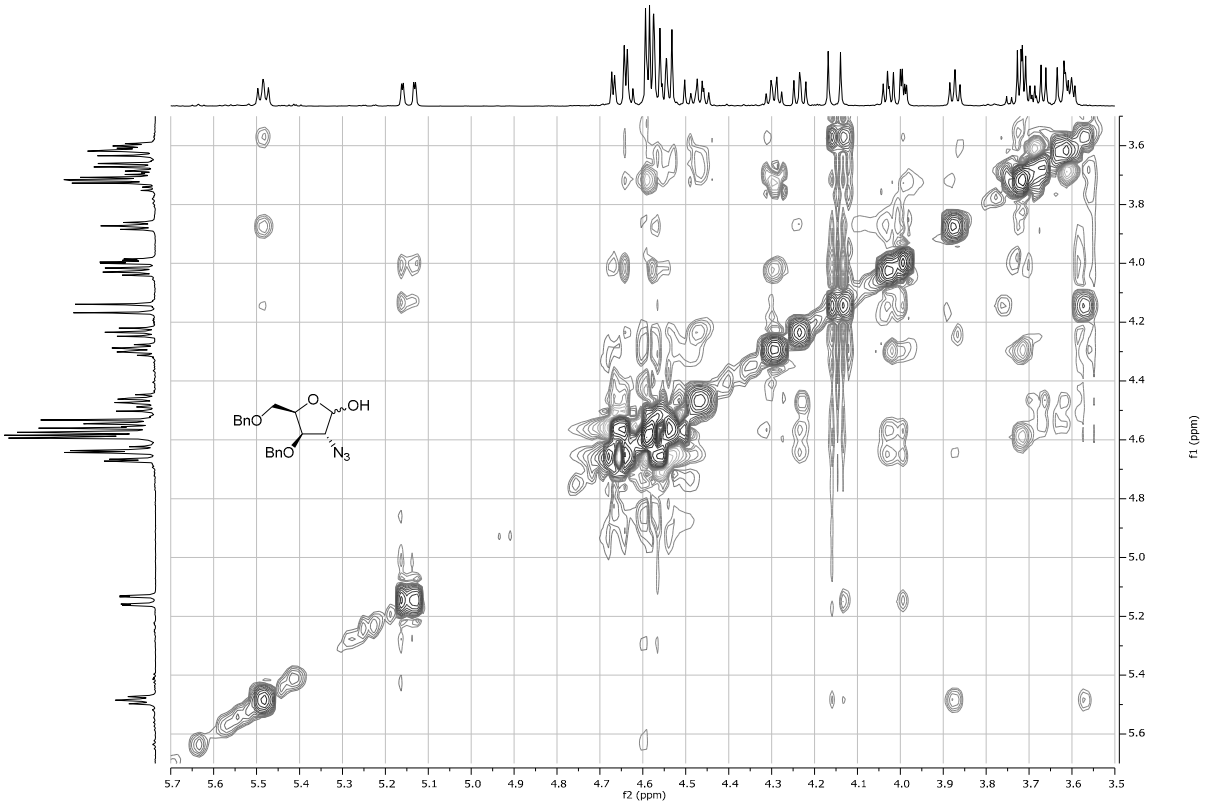
^{1}H-^{1}H COSY of compound **44**



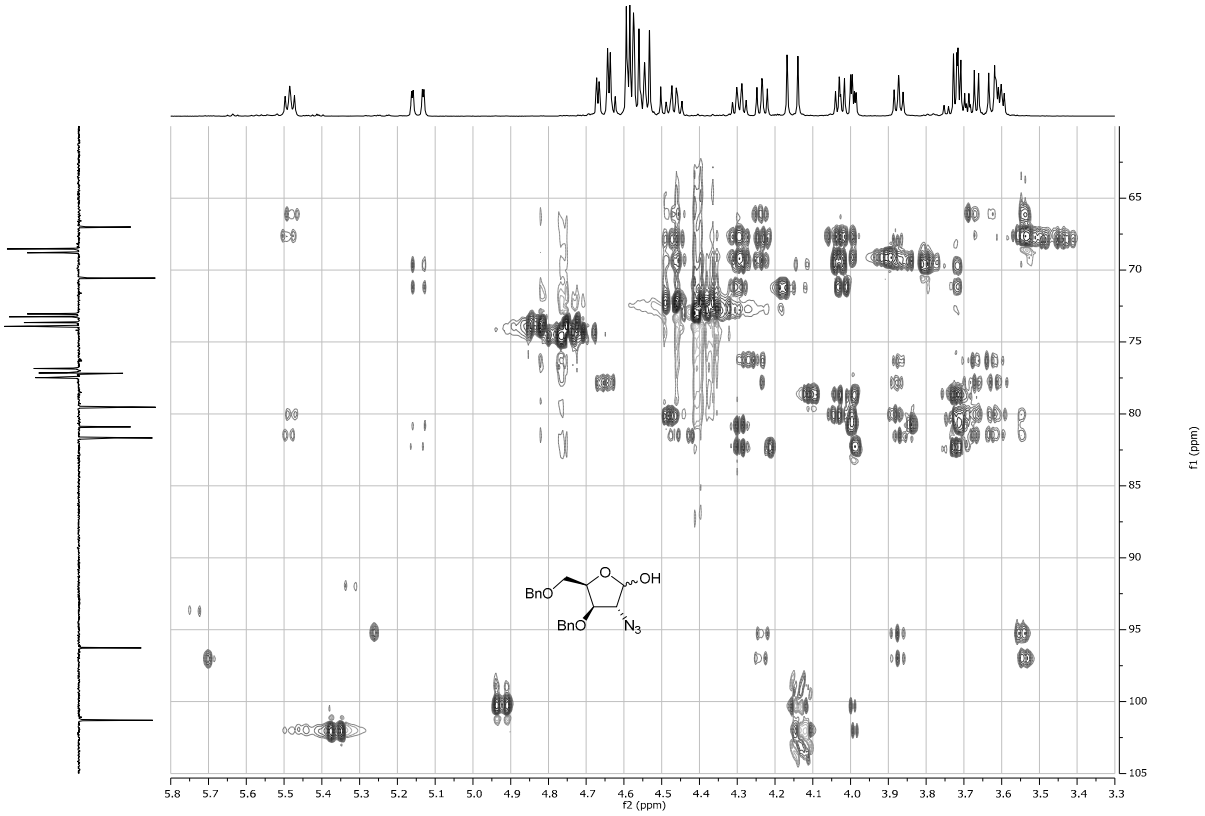
^{1}H-^{13}C HSQC of compound **44**



^{1}H-^{1}H NOESY of compound **44**

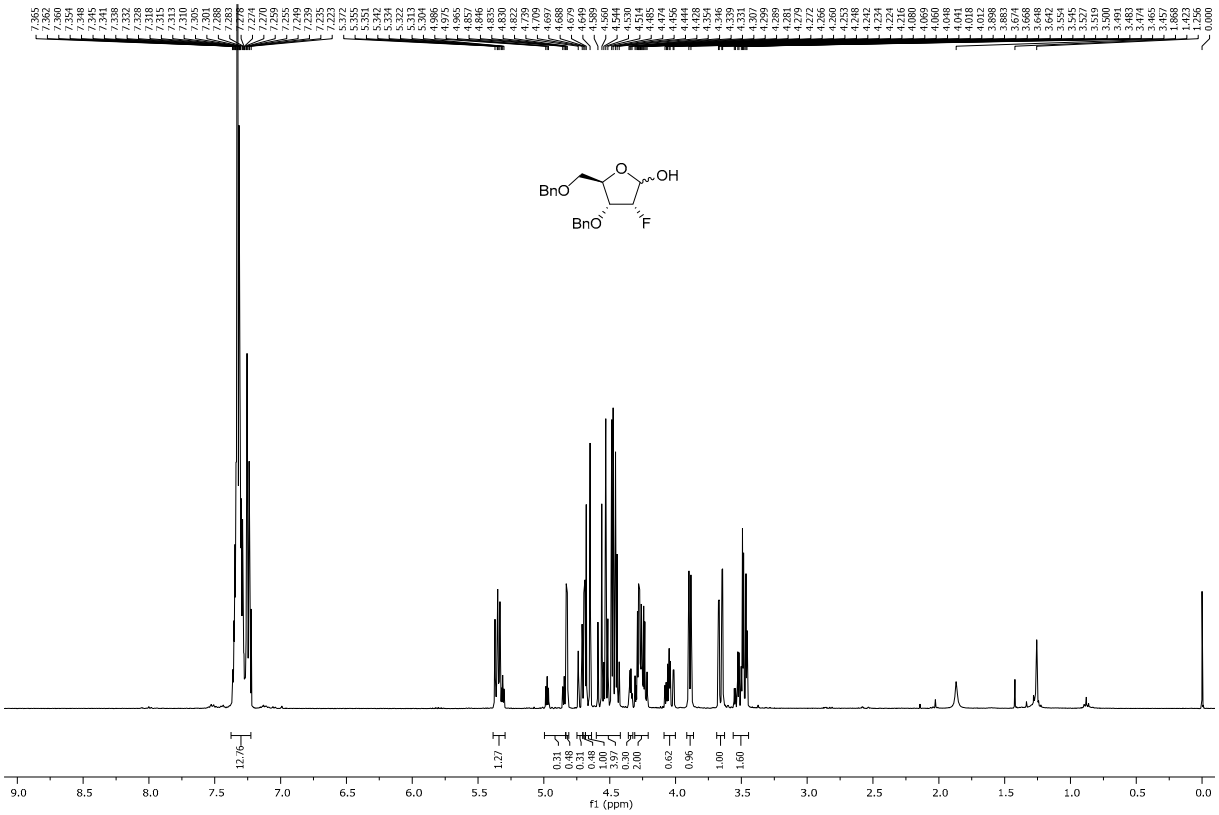


^{1}H-^{13}C HSQC-HECADE of compound **44**

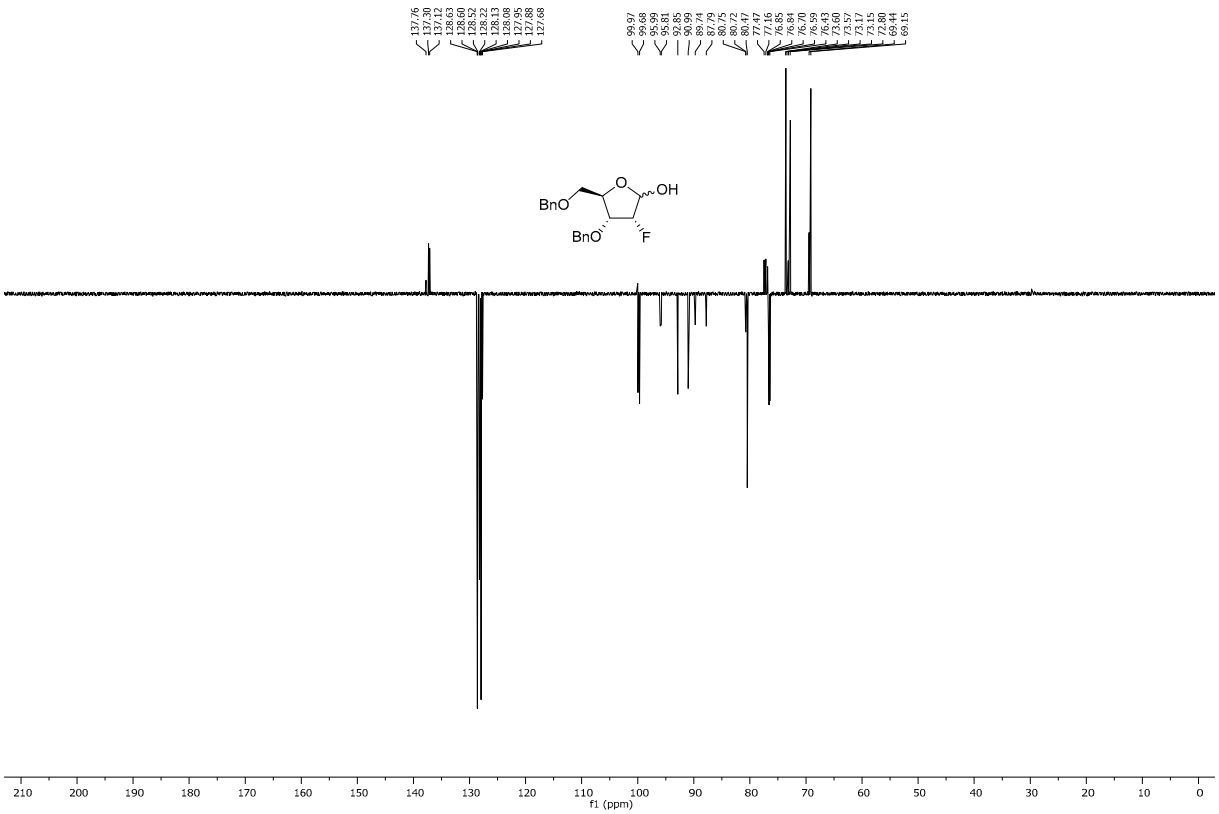


3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α/β-D-ribofuranose (45)

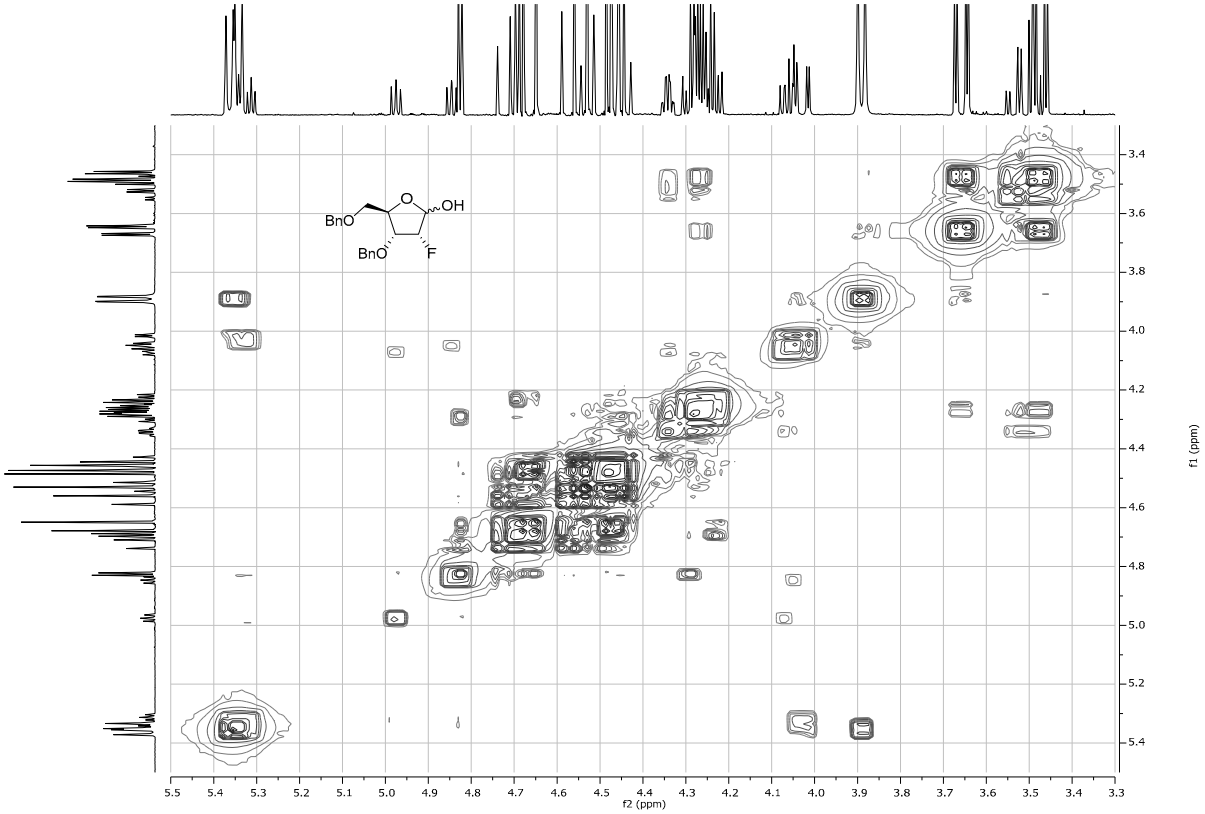
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **45**



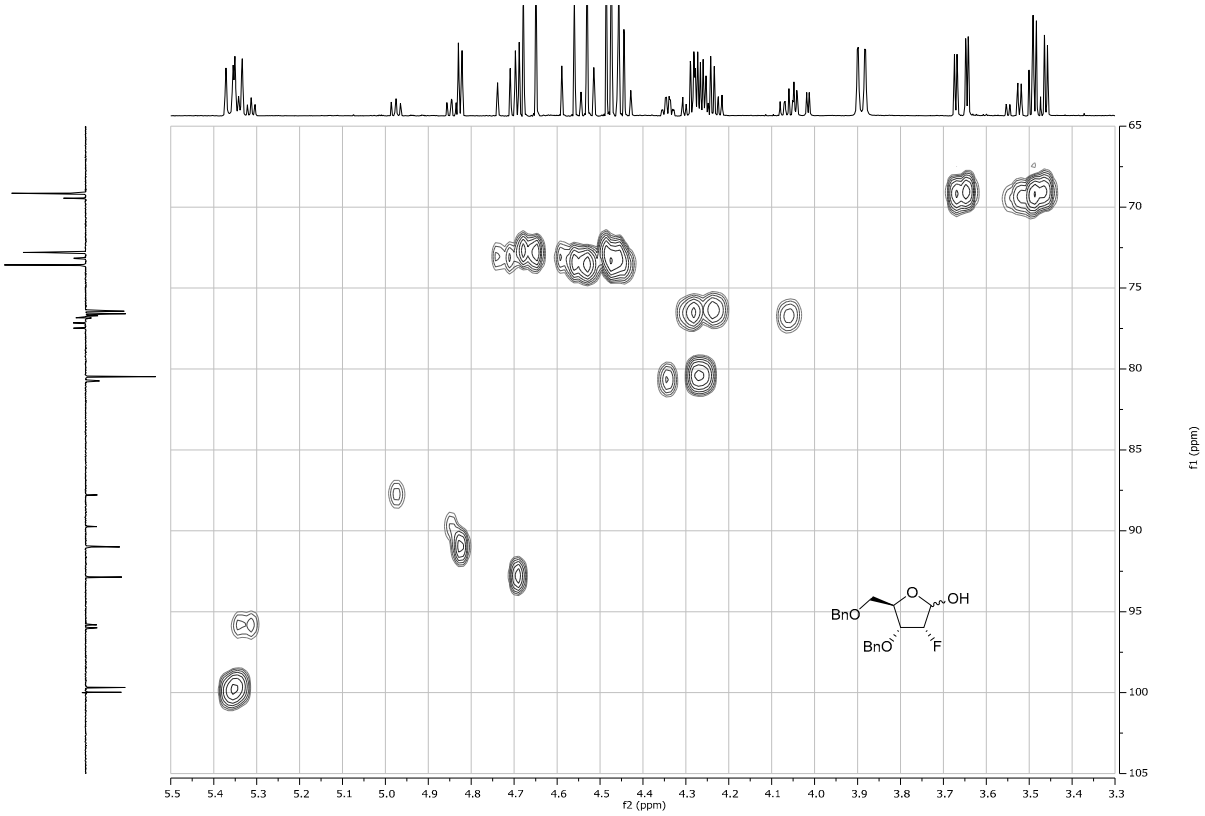
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **45**



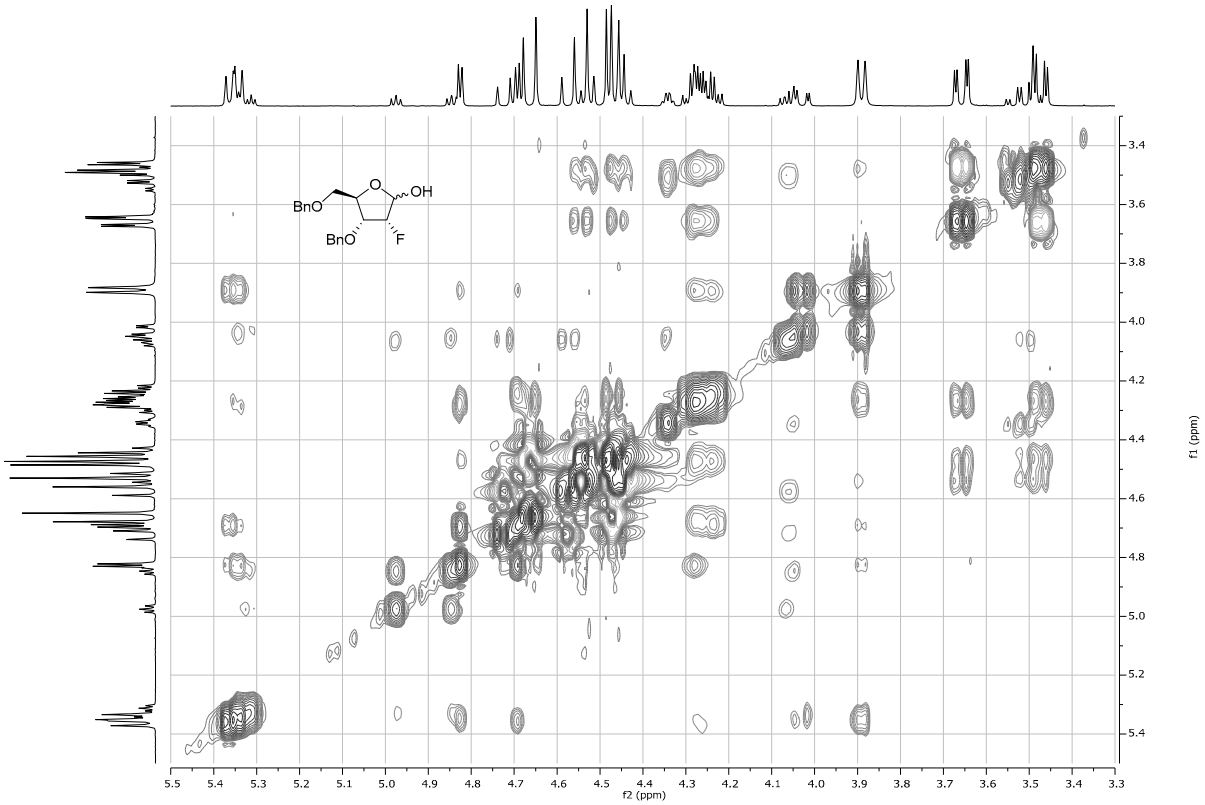
^{1}H-^{1}H COSY of compound **45**



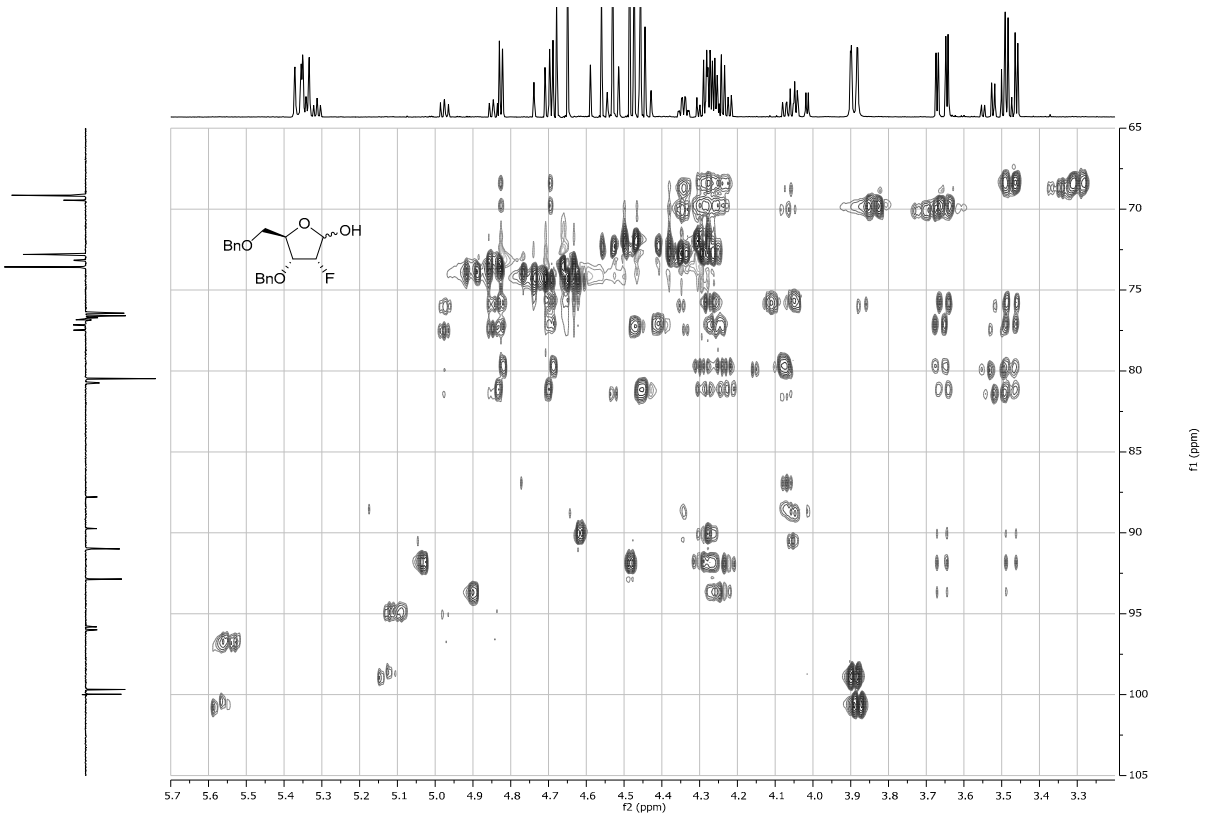
^{1}H-^{13}C HSQC of compound **45**



^{1}H-^{1}H NOESY of compound **45**

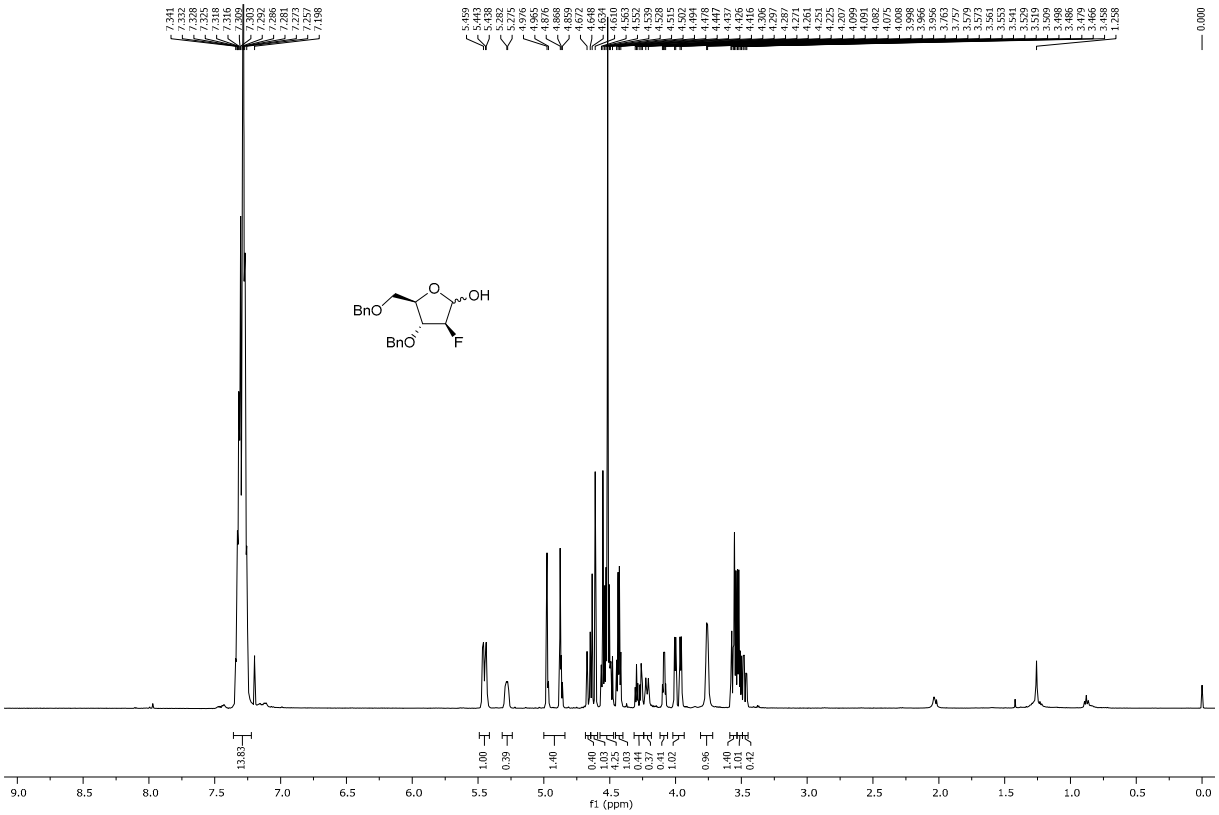


^{1}H-^{13}C HSQC-HECADE of compound **45**

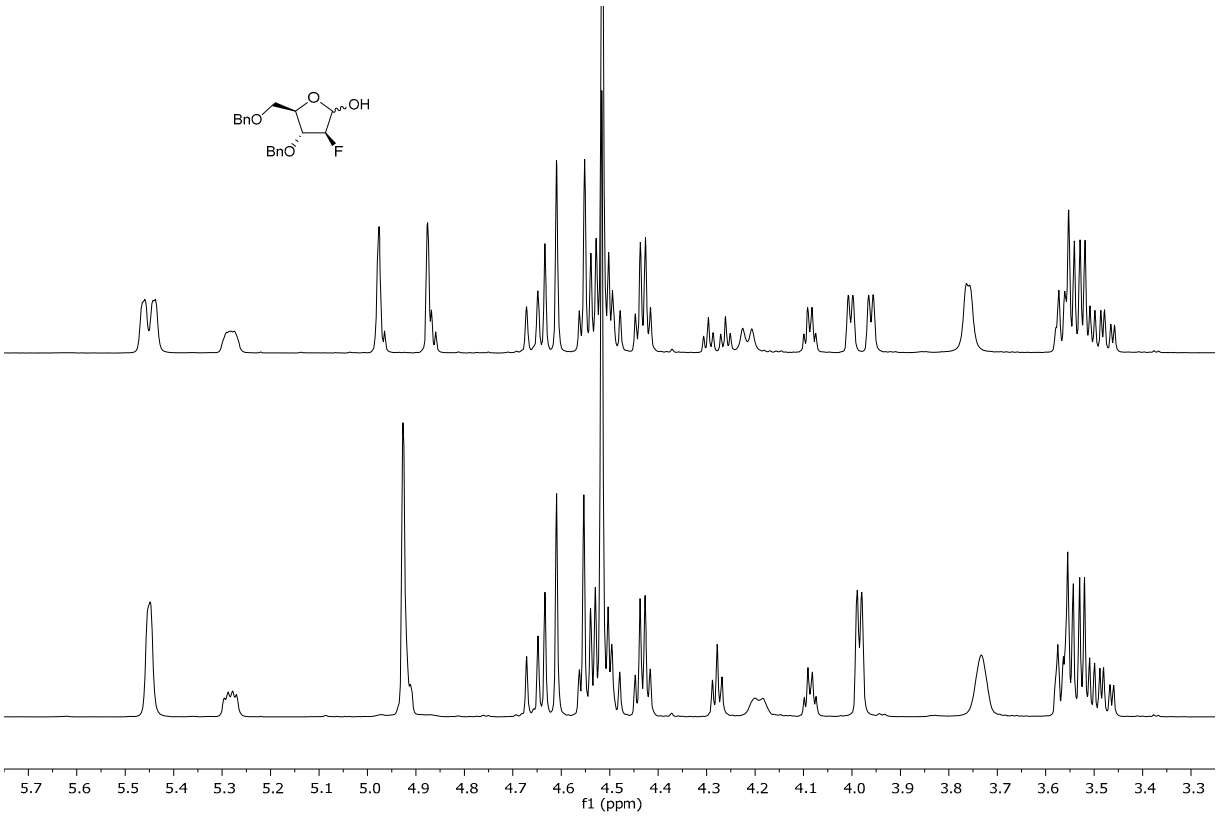


3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α/β-D-arabinofuranose (46)

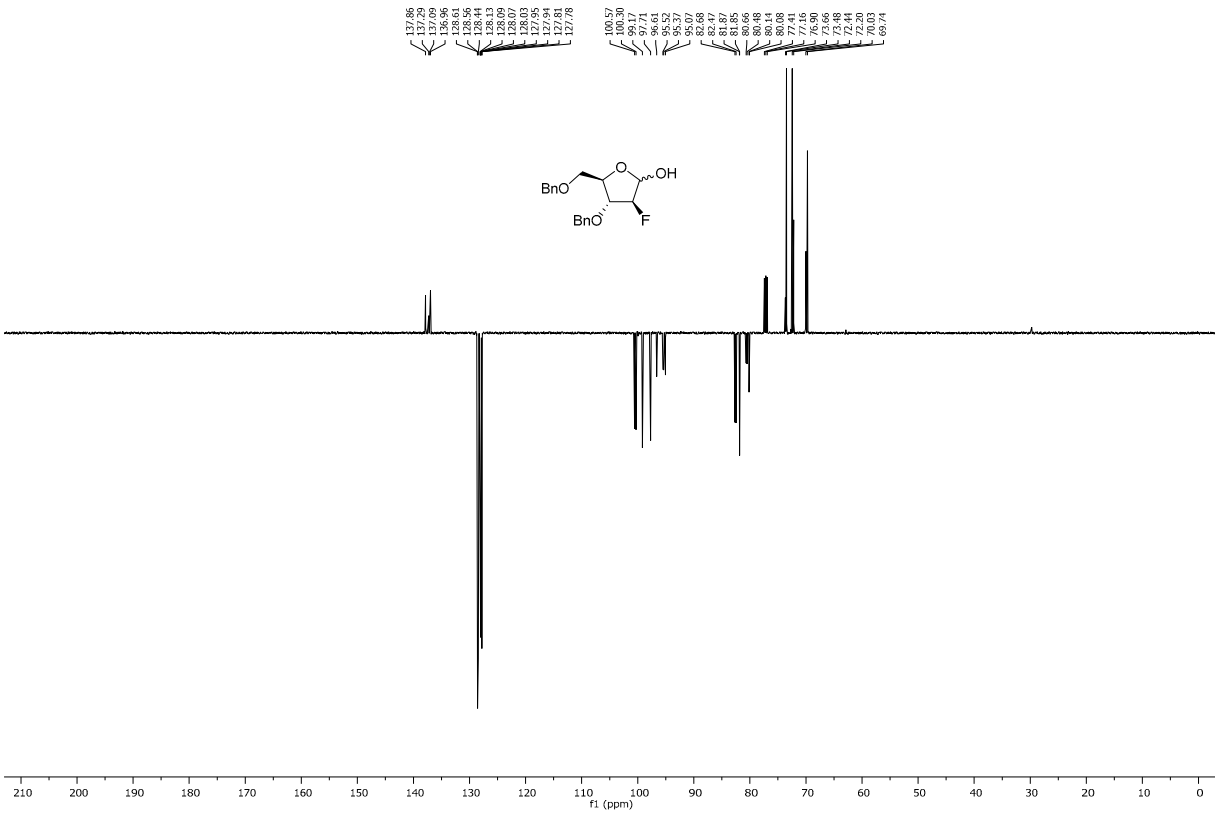
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **46**



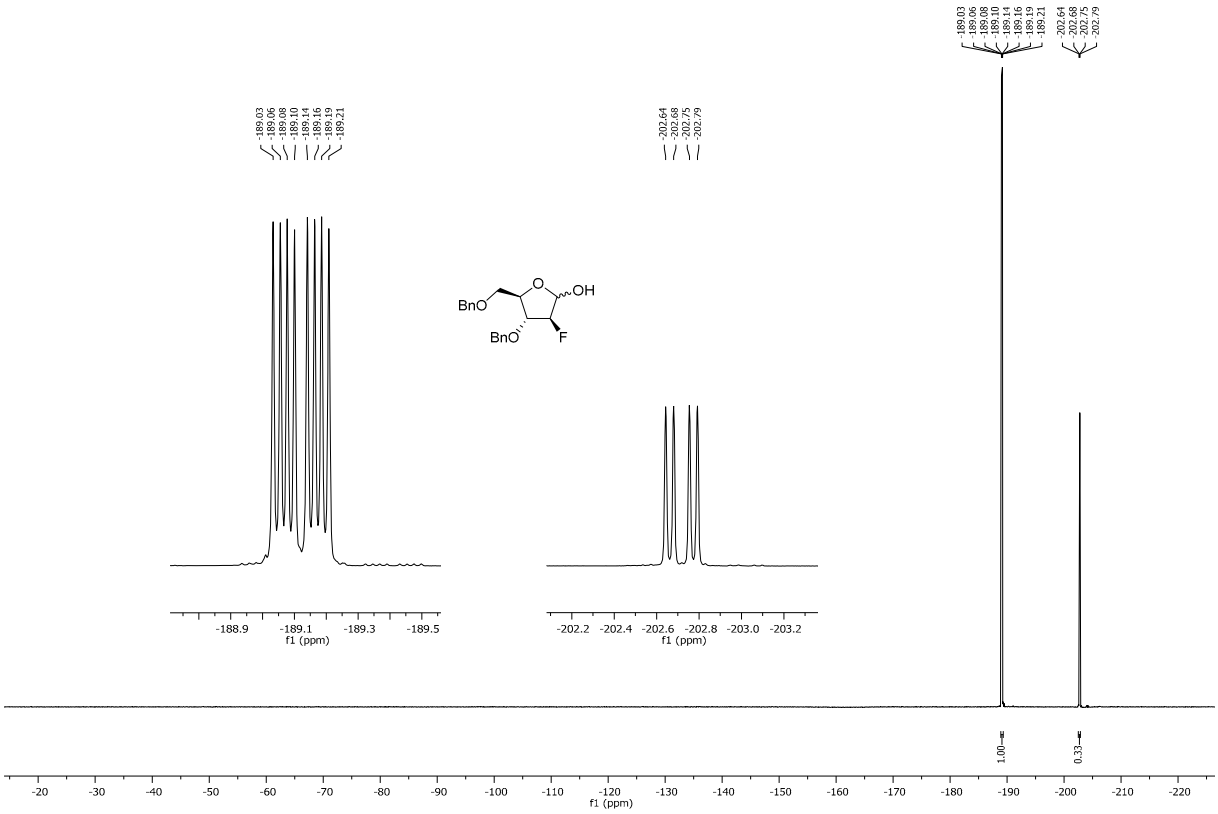
^{19}F-decoupled ^{1}H NMR, (-210 ppm)



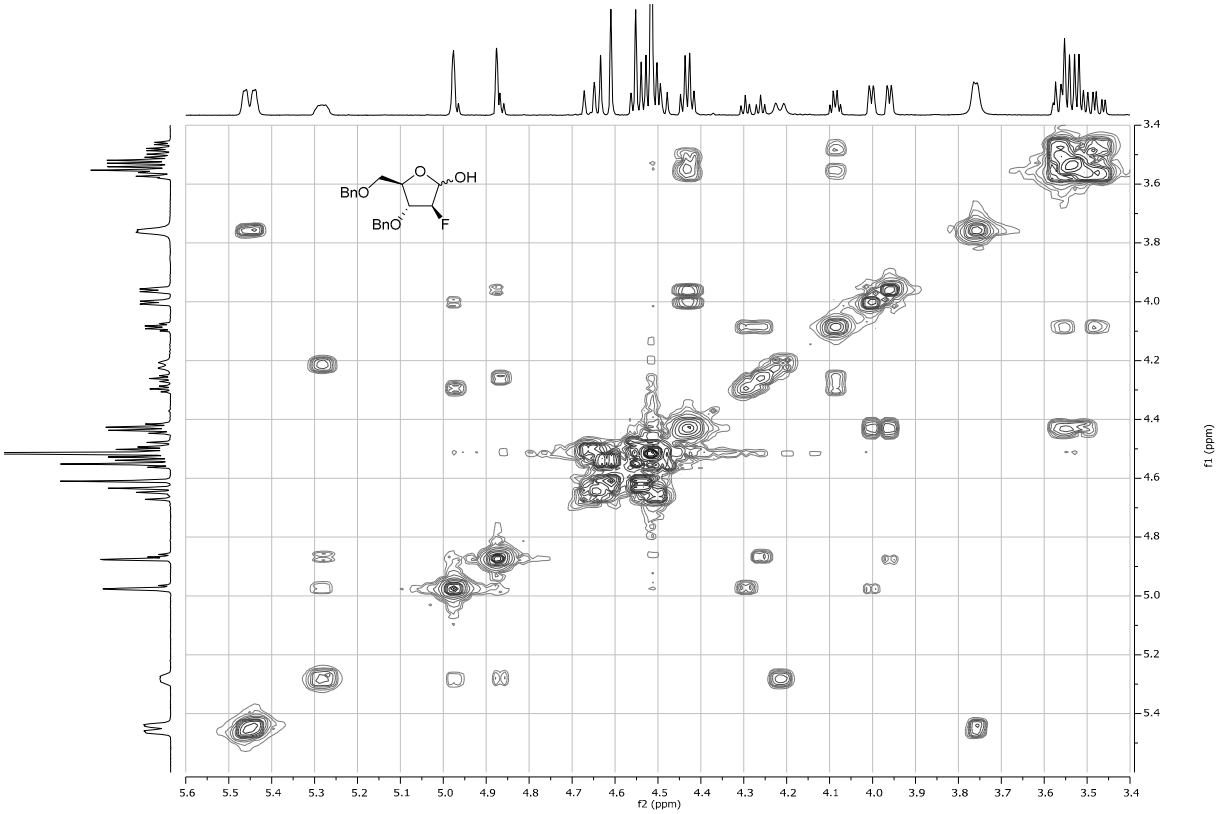
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **46**



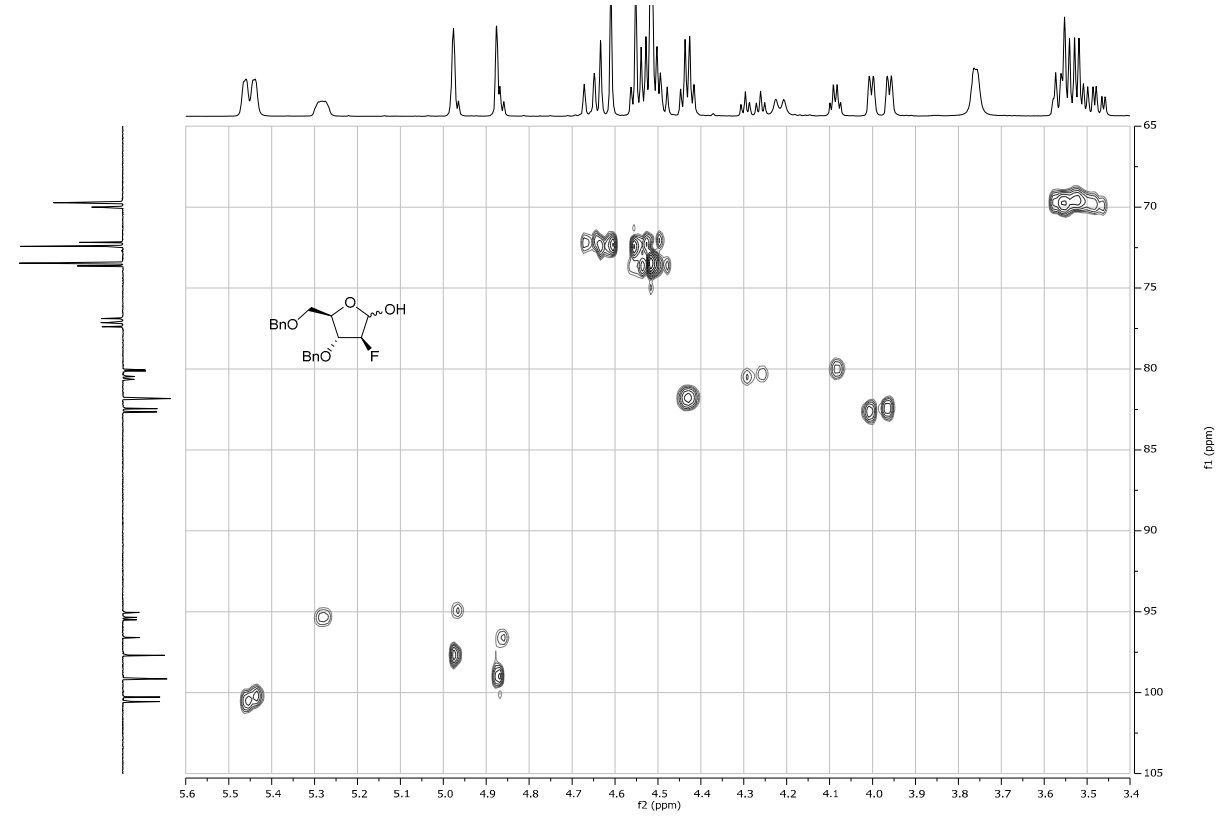
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **46**



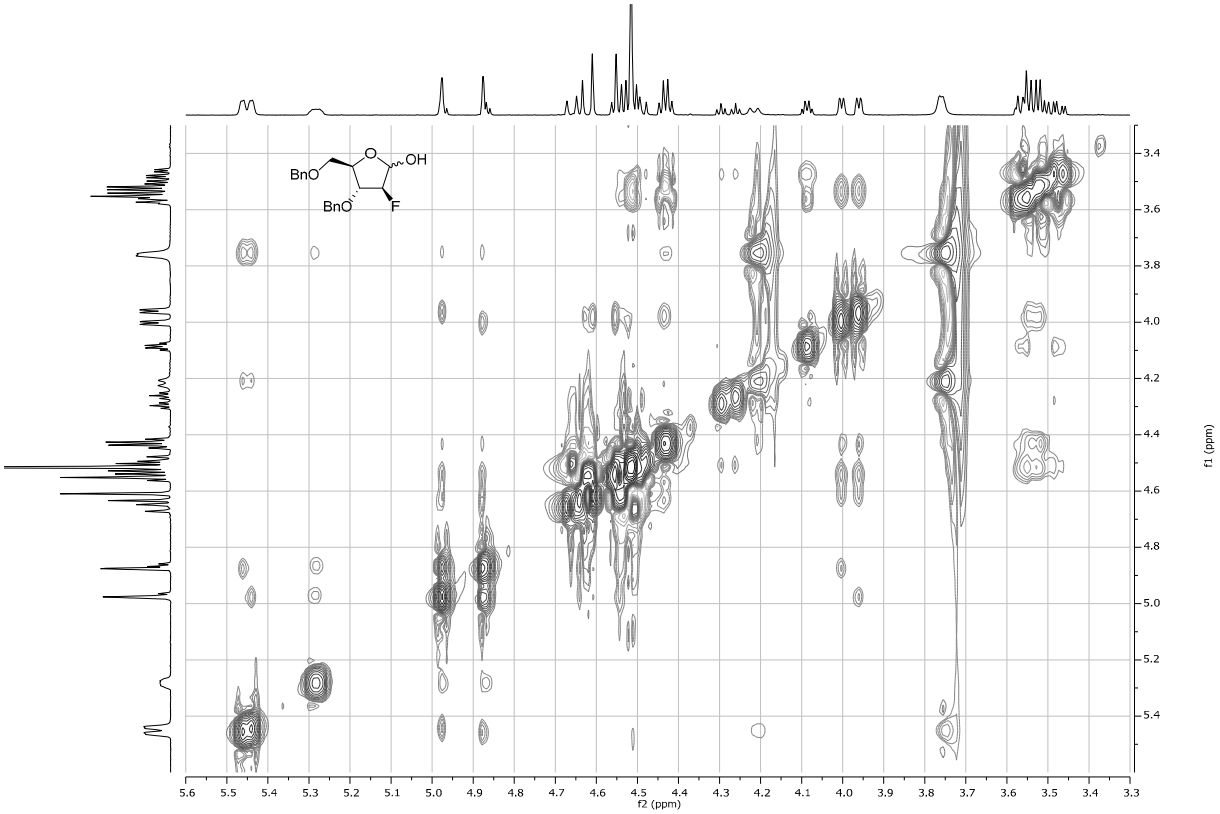
^{1}H-^{1}H COSY of compound **46**



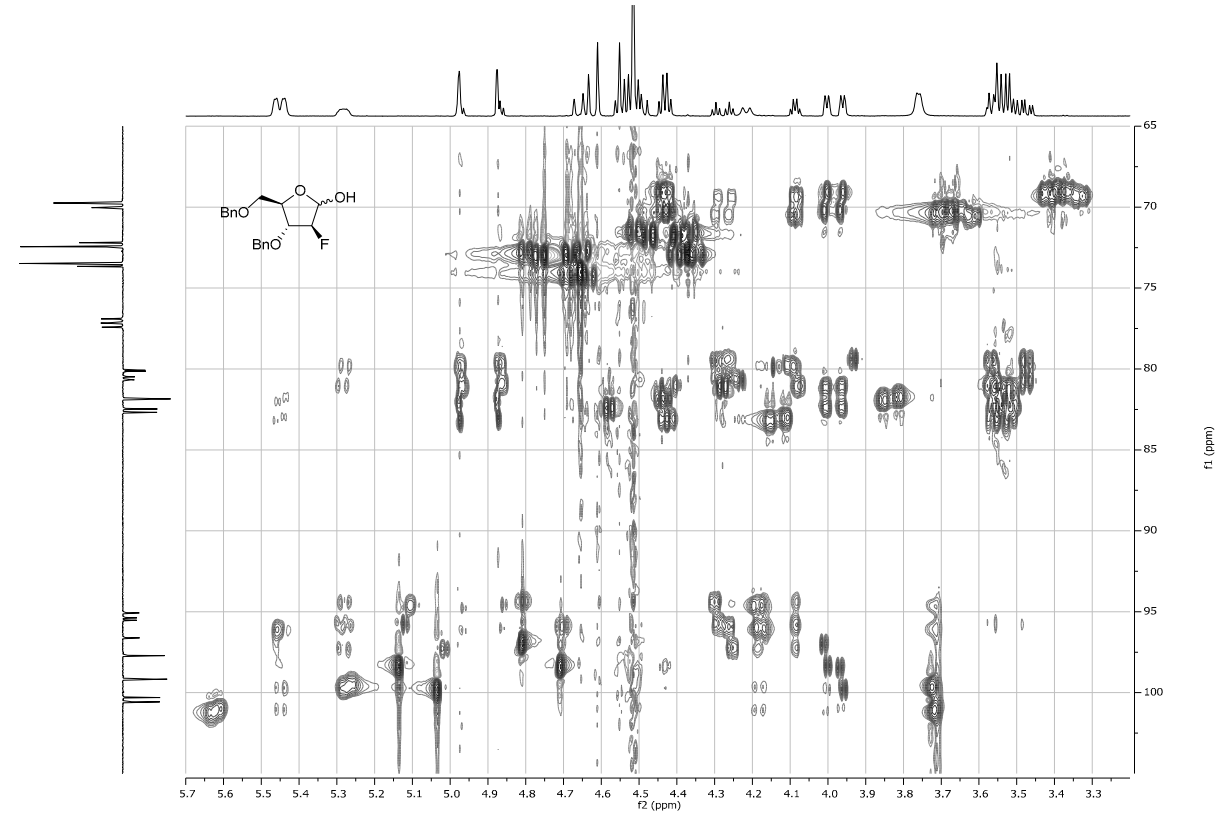
^{1}H-^{13}C HSQC of compound **46**



^{1}H-^{1}H NOESY of compound **46**

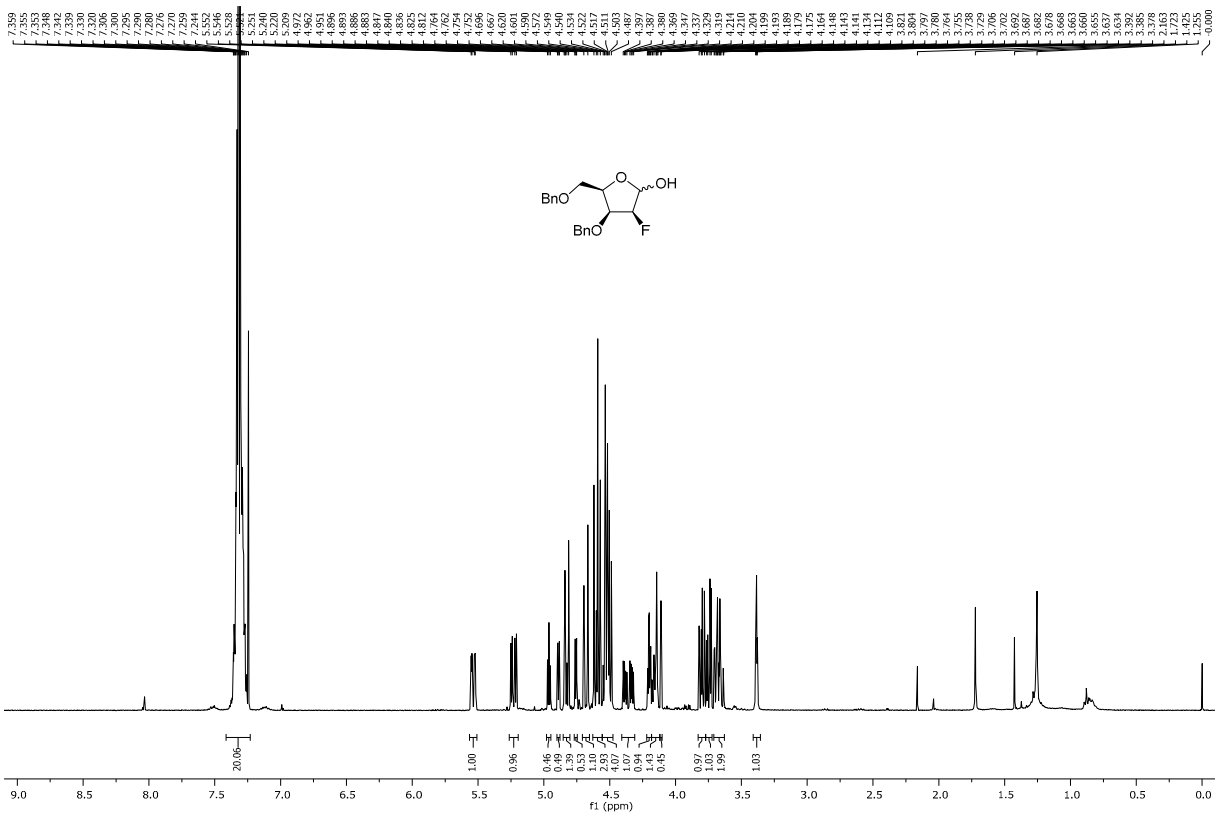


^{1}H-^{13}C HSQC-HECADE of compound **46**

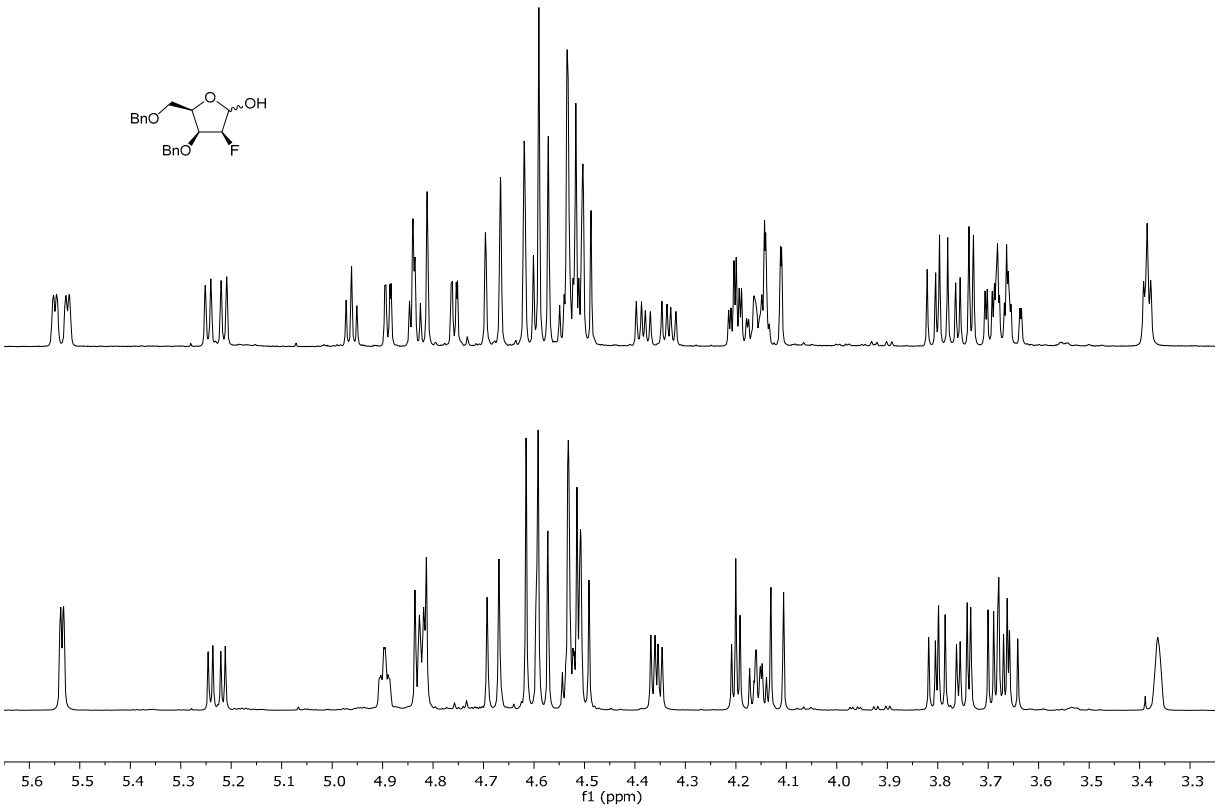


3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α/β-D-lyxofuranose (47)

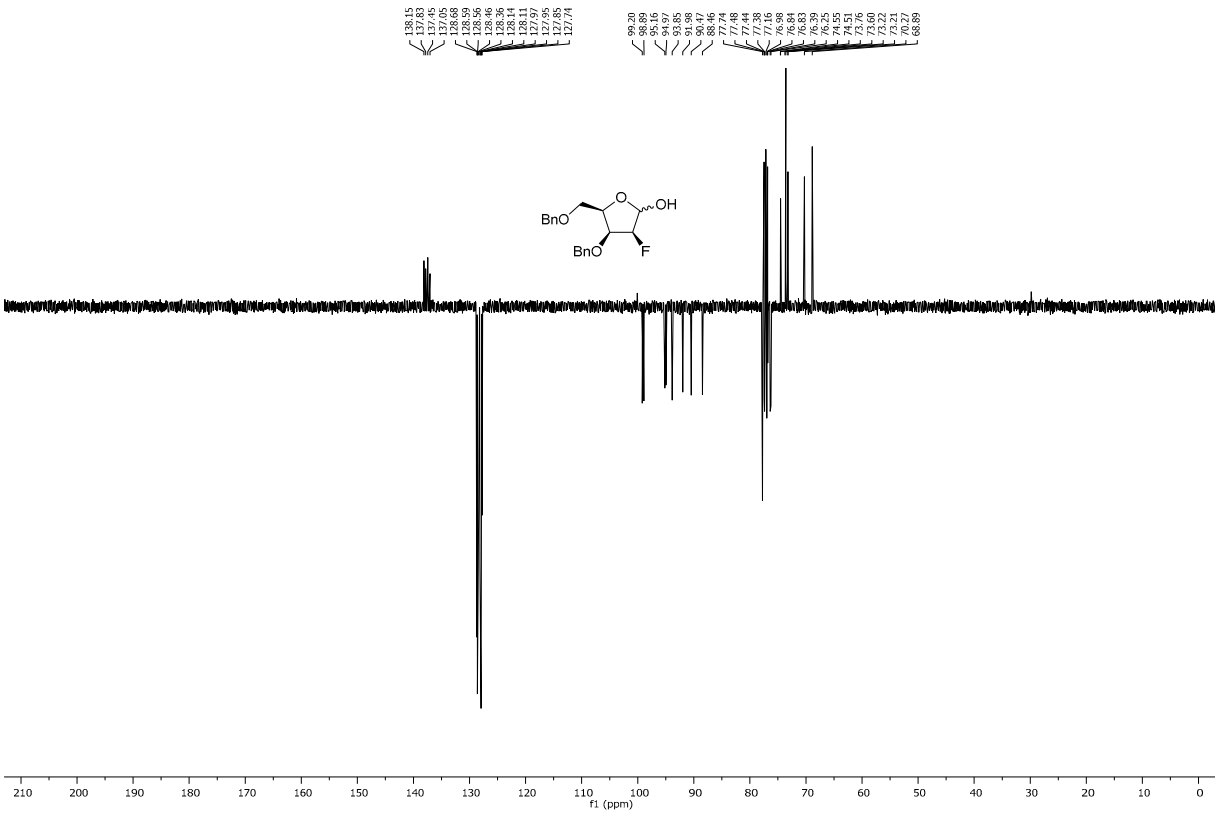
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **47**



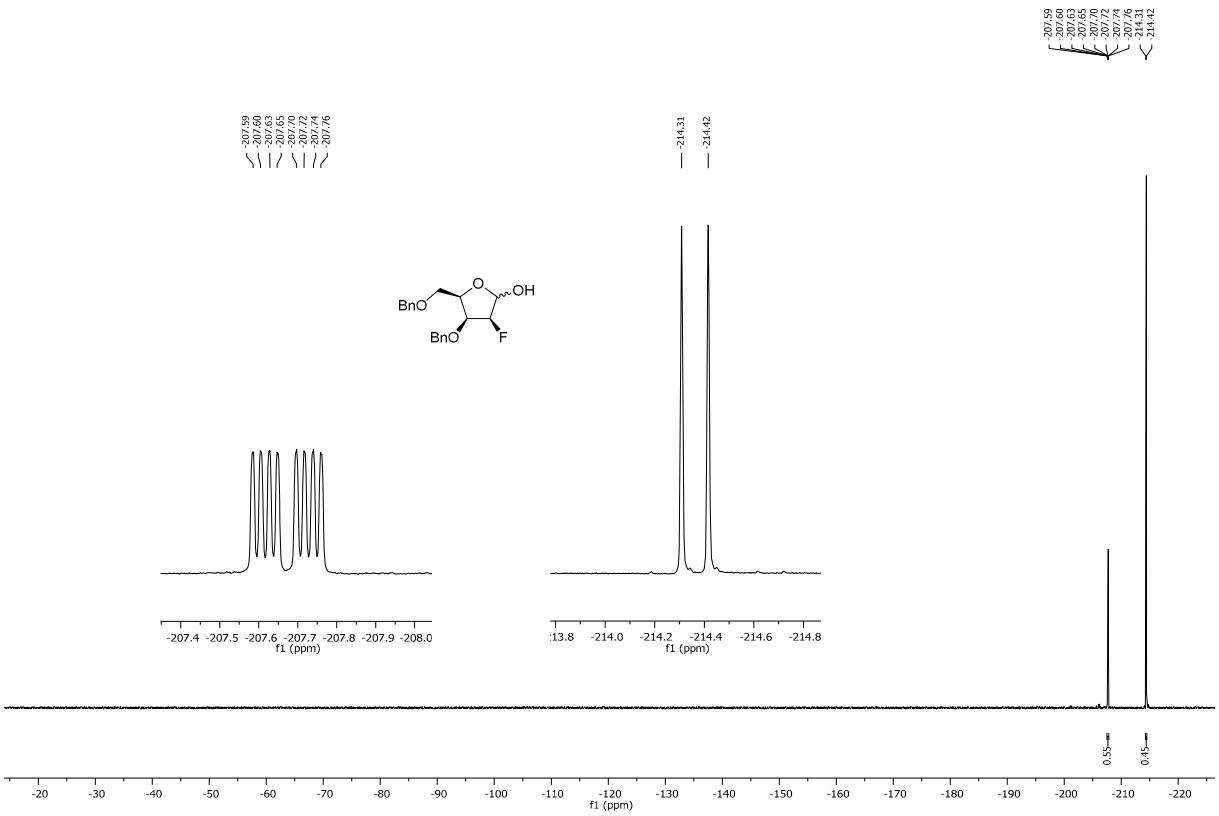
^{19}F-decoupled ^{1}H NMR, (-200 ppm)



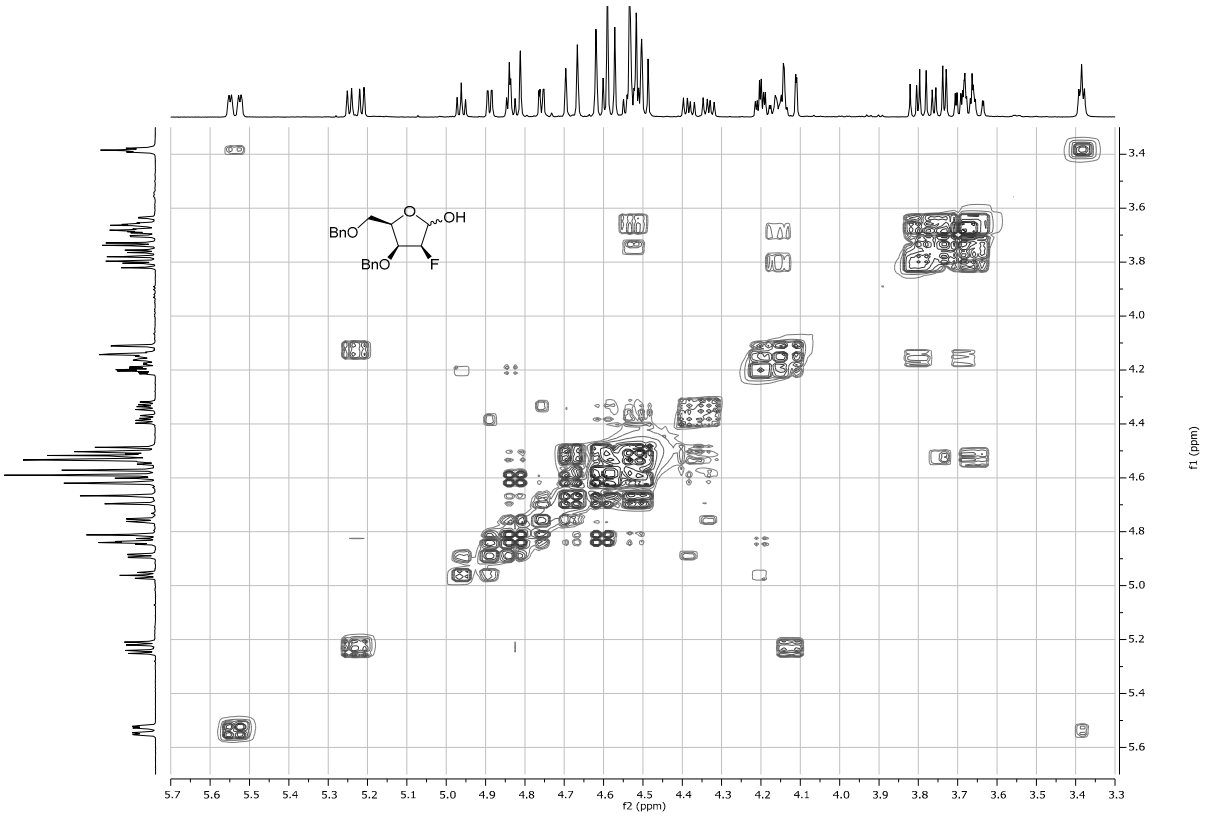
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **47**



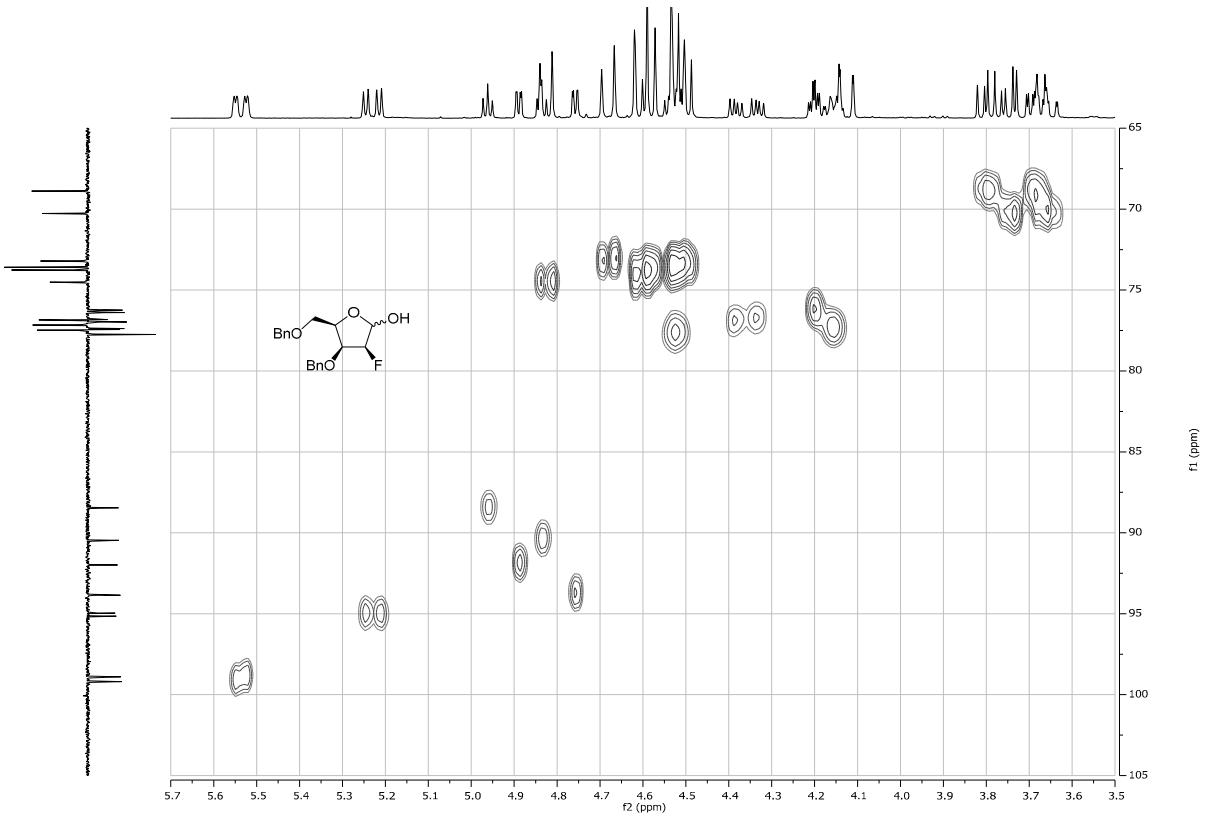
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **47**



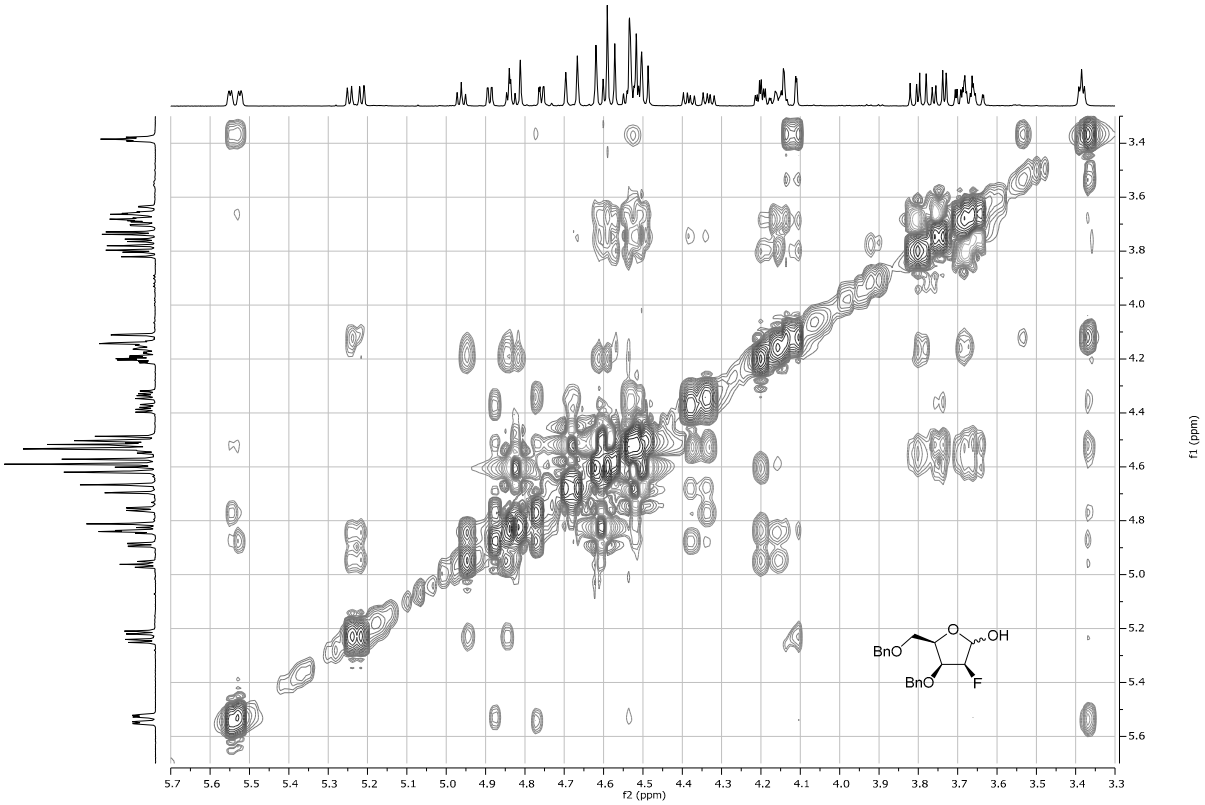
^{1}H-^{1}H COSY of compound **47**



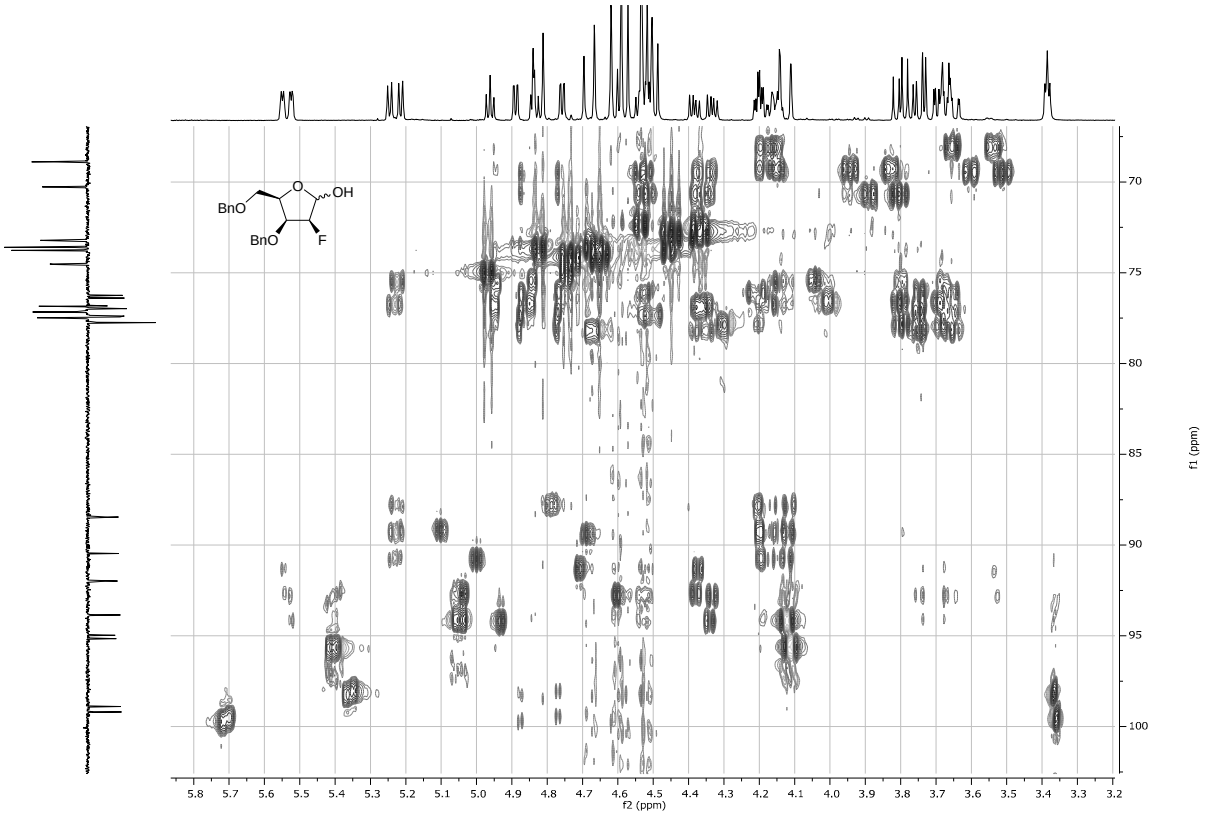
^{1}H-^{13}C HSQC of compound **47**



^{1}H-^{1}H NOESY of compound **47**

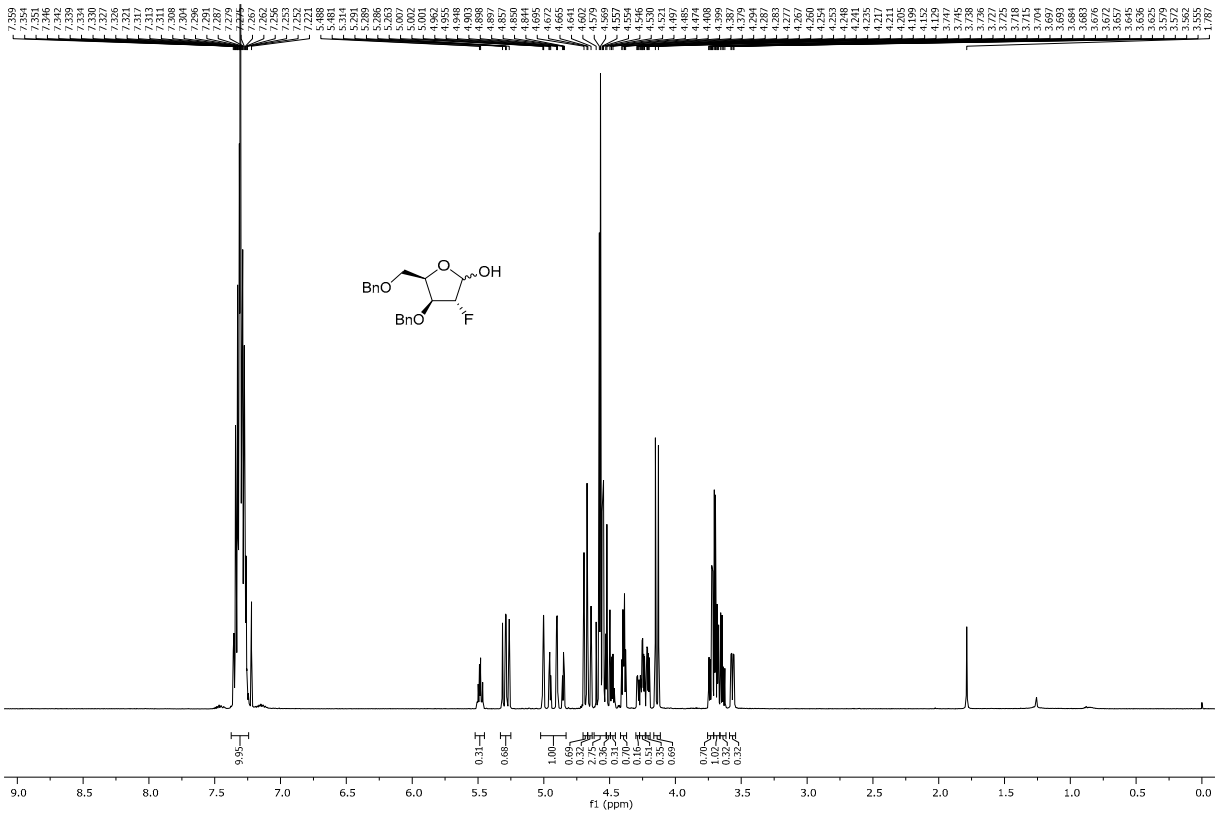


^{1}H-^{13}C HSQC-HECADE of compound **47**

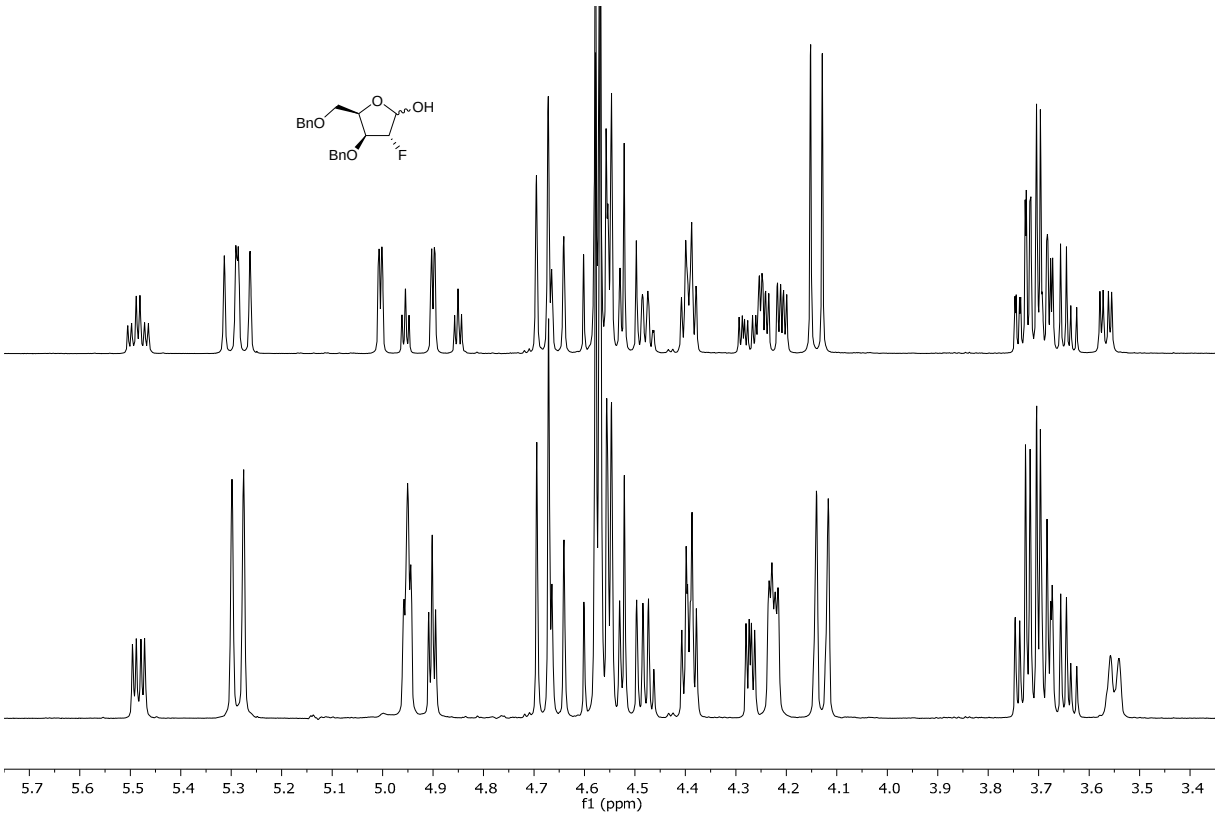


3,5-di-*O*-benzyl-2-deoxy-2-fluoro-α/β-D-xylofuranose (48)

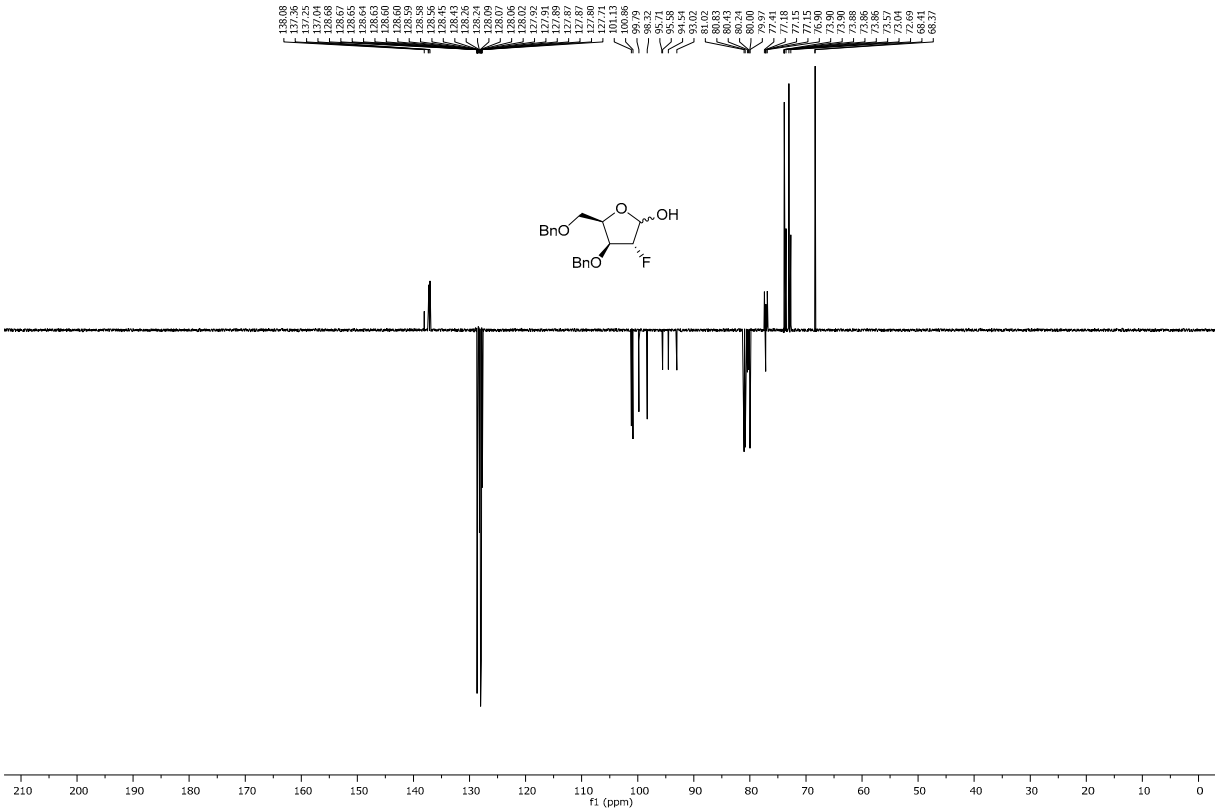
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **48**



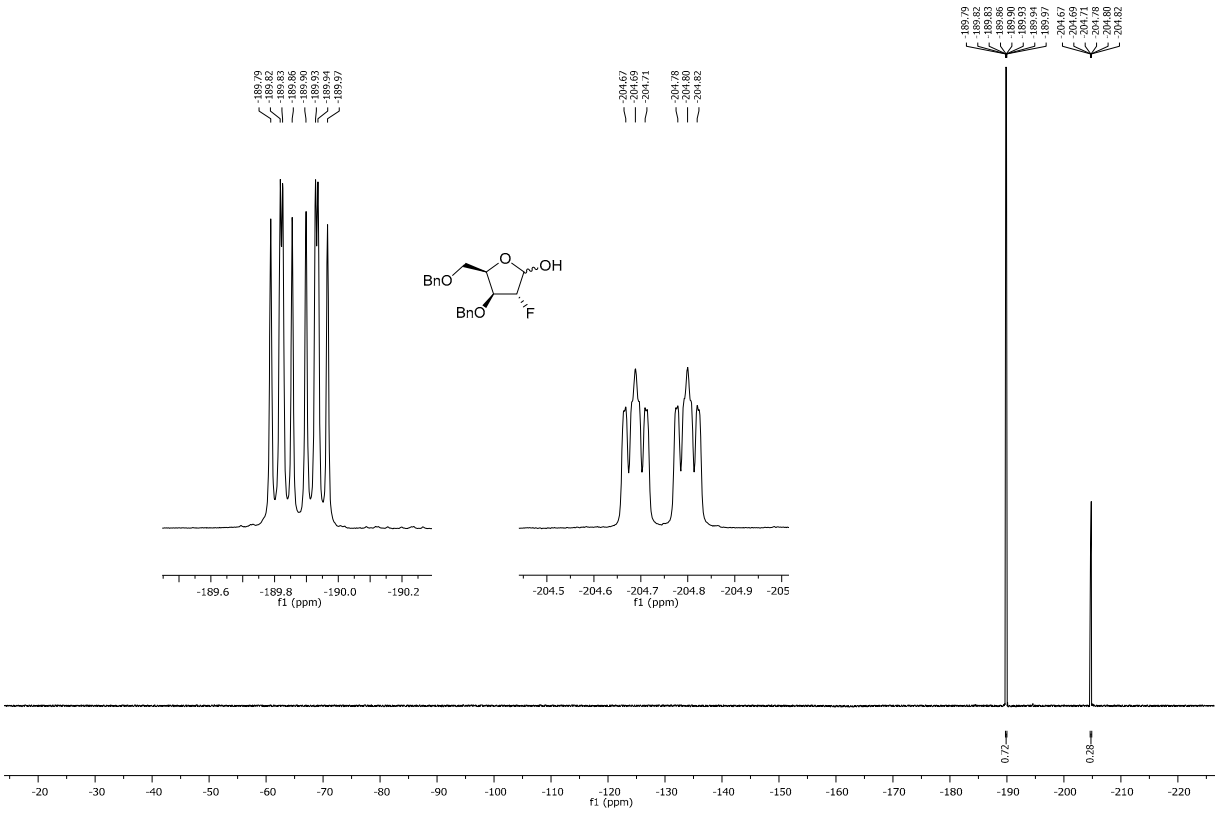
^{19}F-decoupled ^{1}H NMR, (-200 ppm)



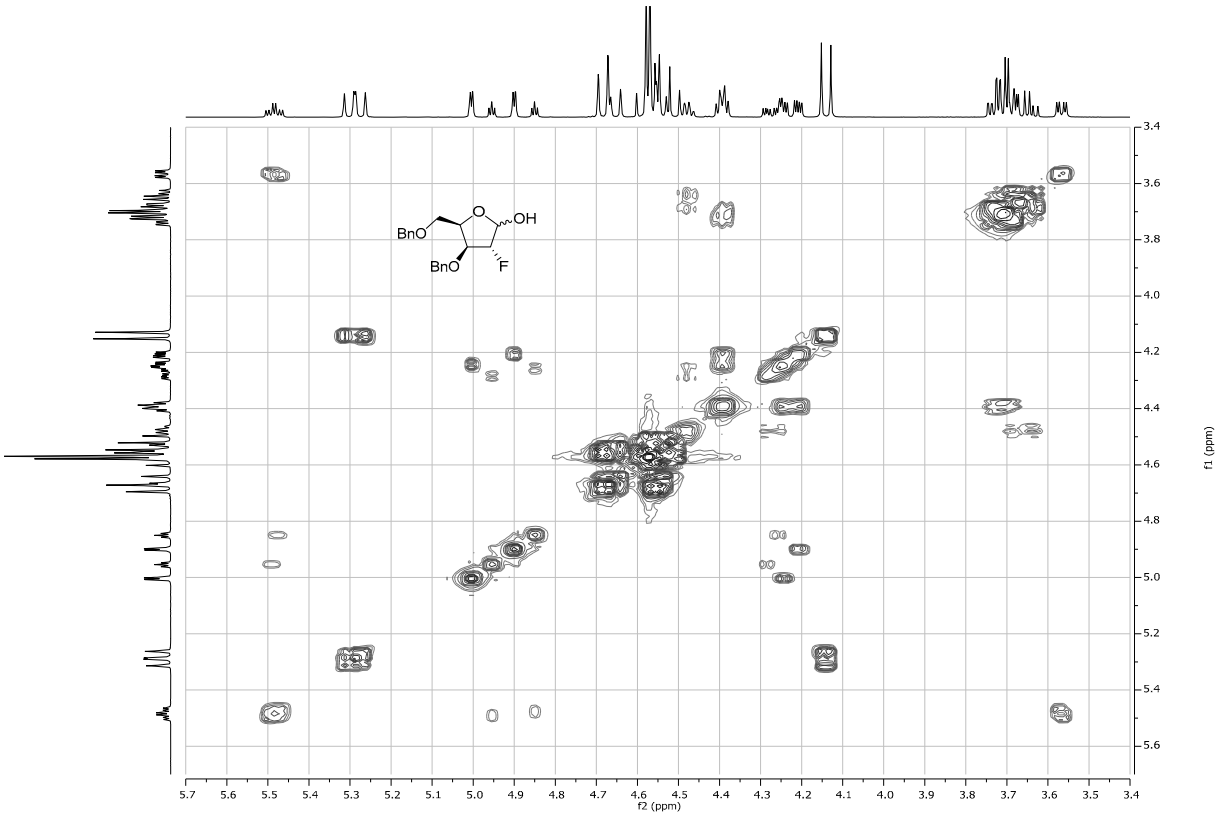
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **48**



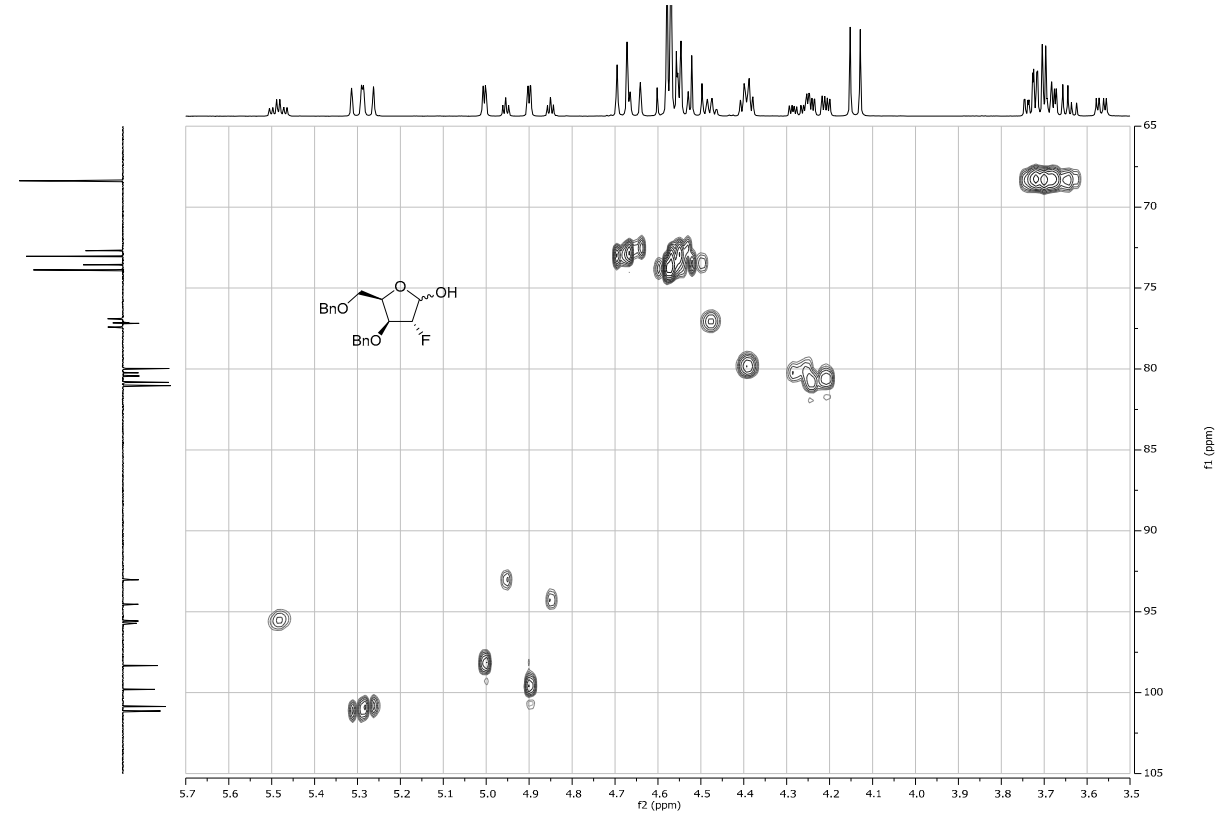
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **48**



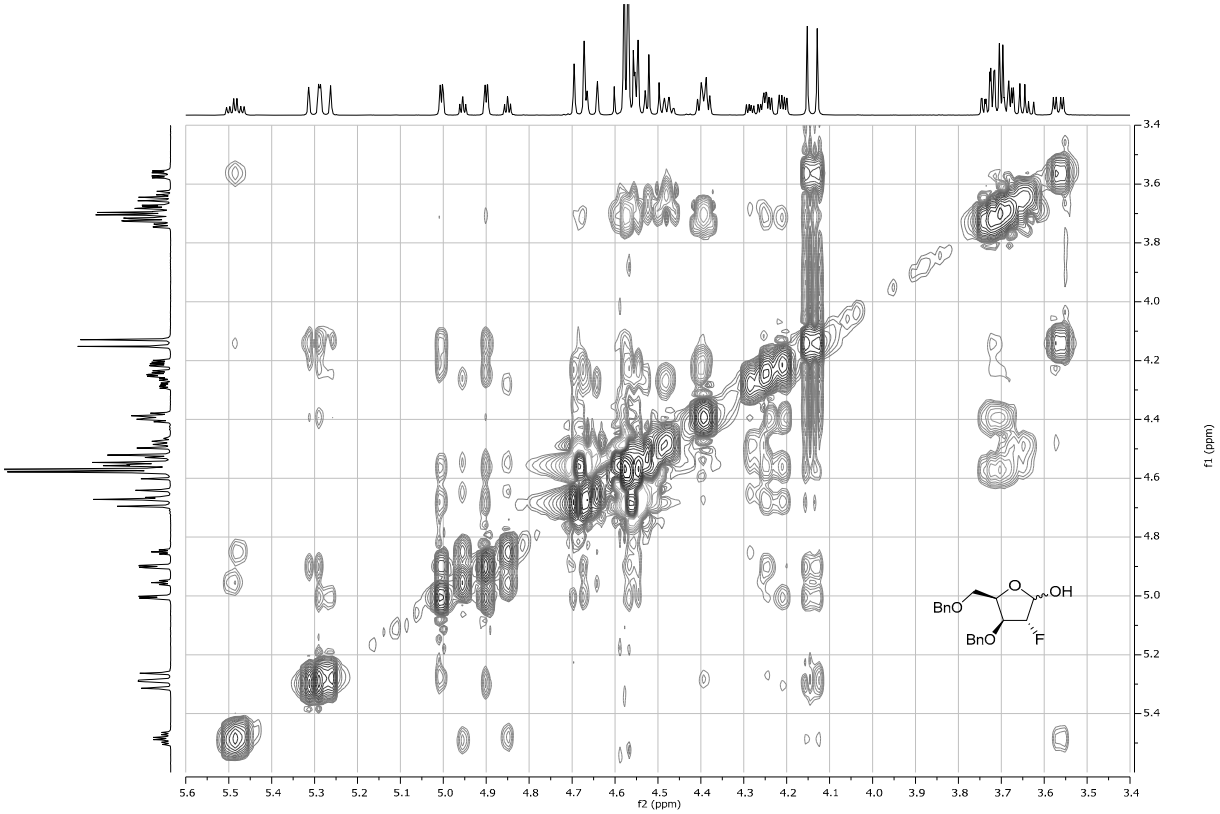
^{1}H-^{1}H COSY of compound **48**



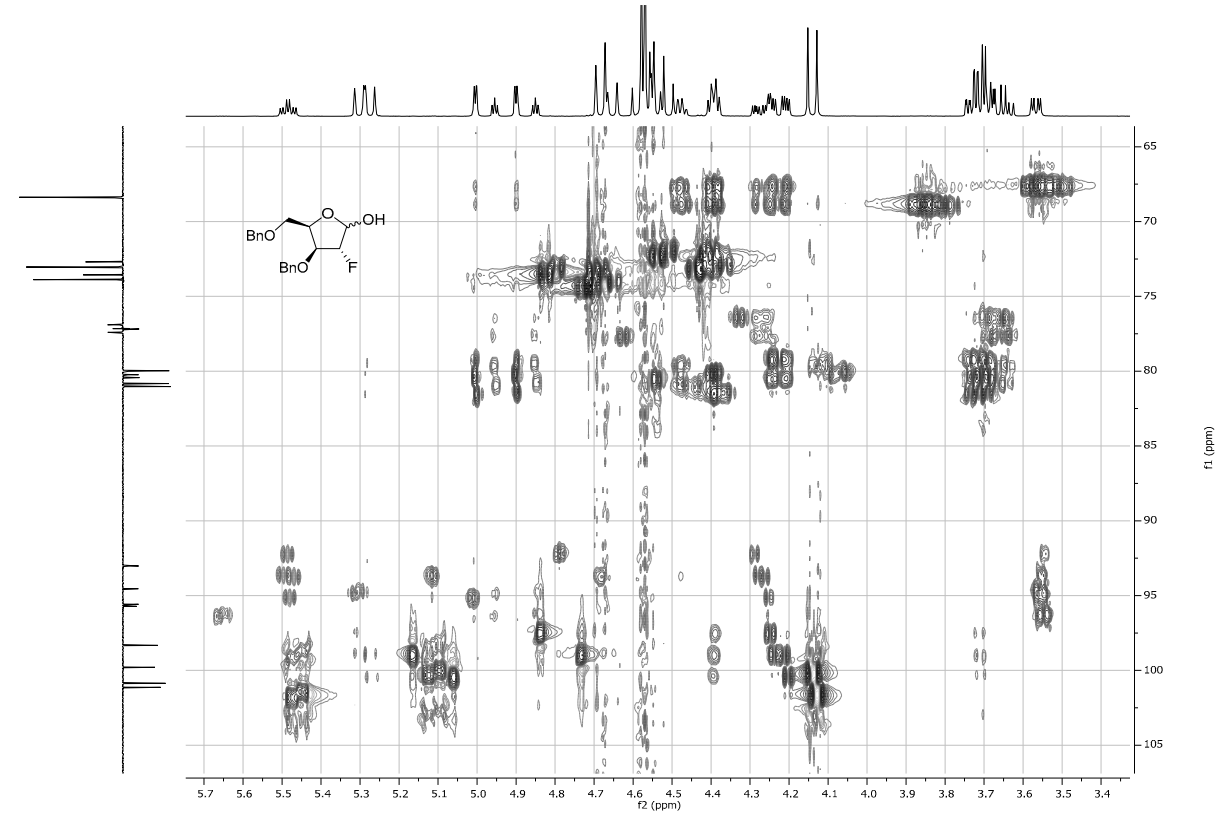
^{1}H-^{13}C HSQC of compound **48**



^{1}H-^{1}H NOESY of compound **48**

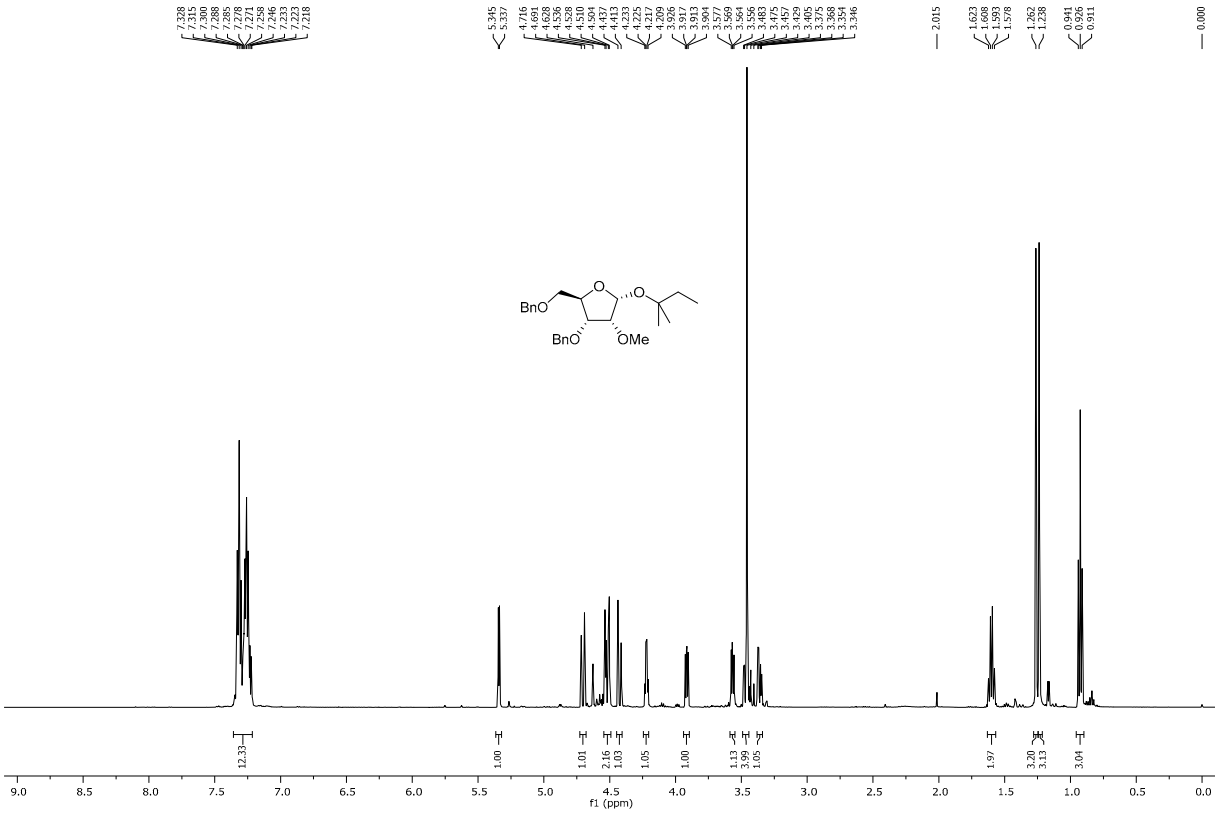


^{1}H-^{13}C HSQC-HECADE of compound **48**

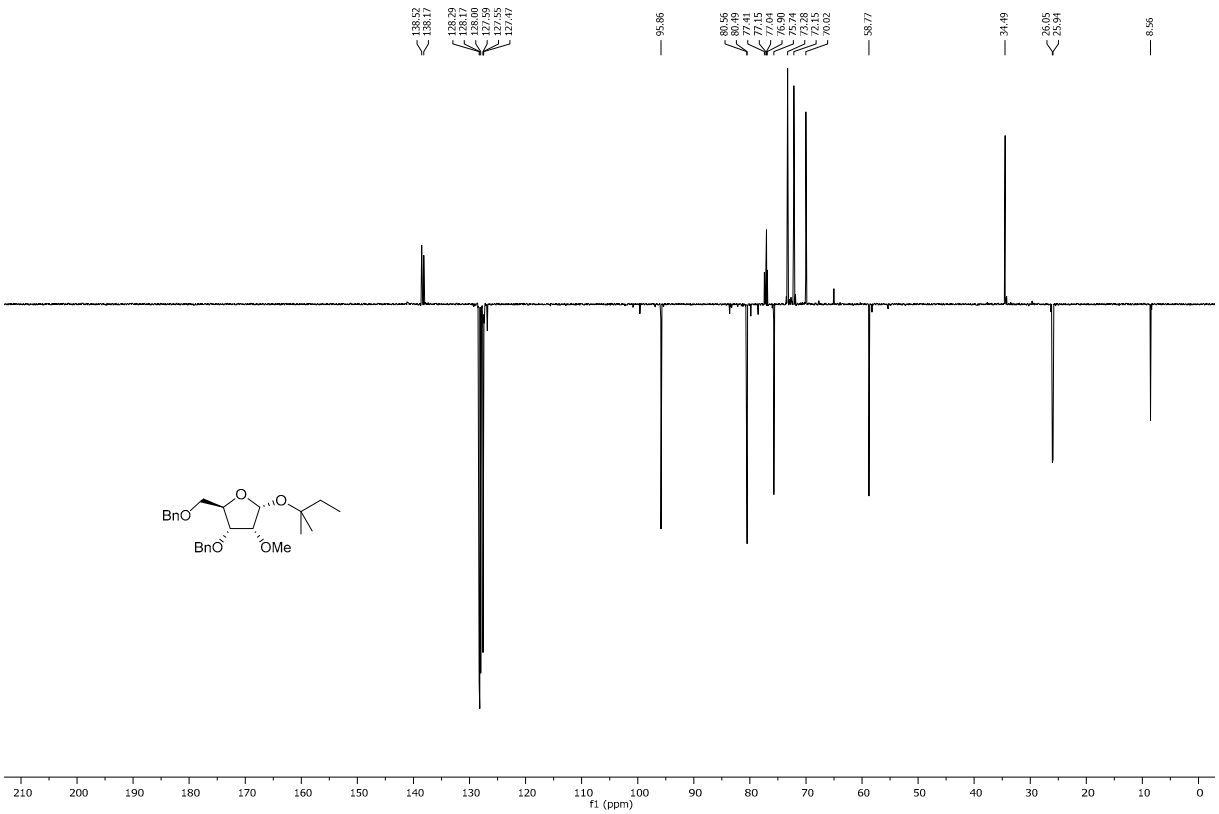


(2-Methyl-2-butyl) 3,5-di-*O*-benzyl-2-methyl-α-D-ribofuranoside (52)

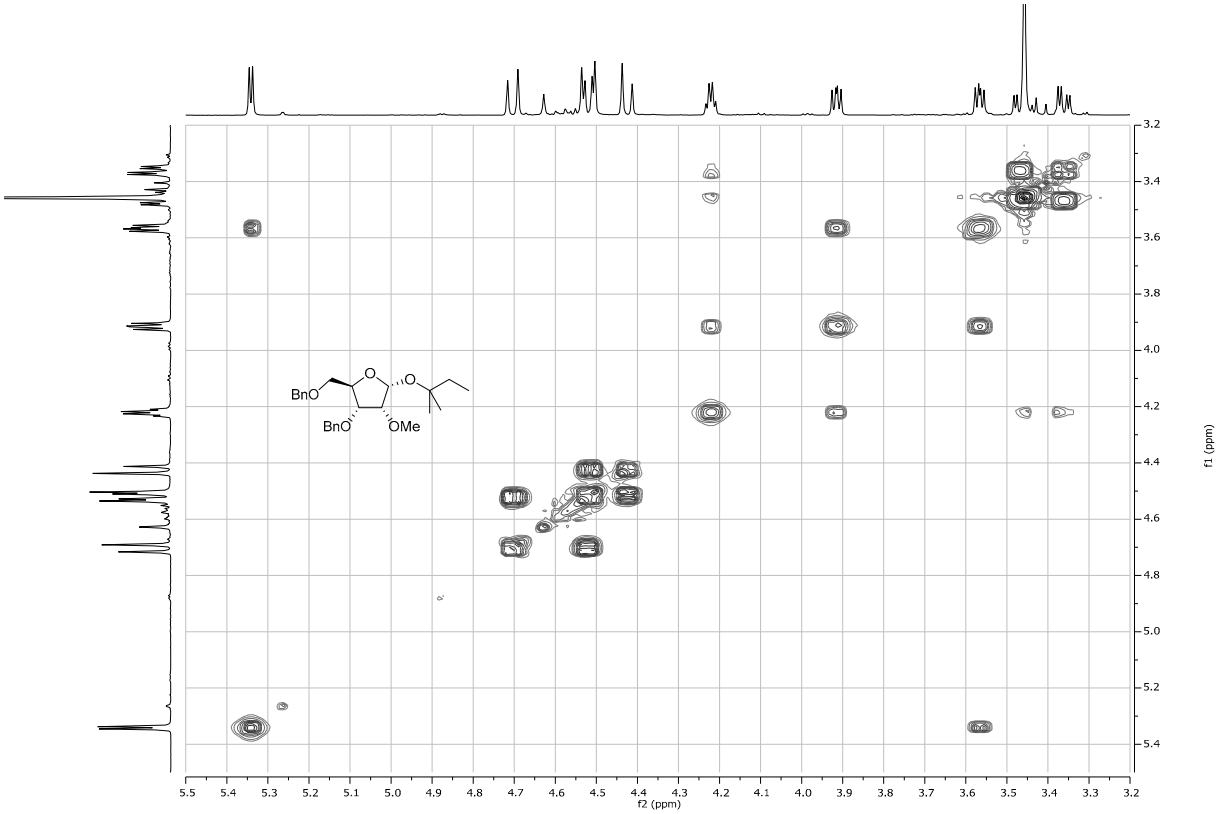
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **52**



^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **52**

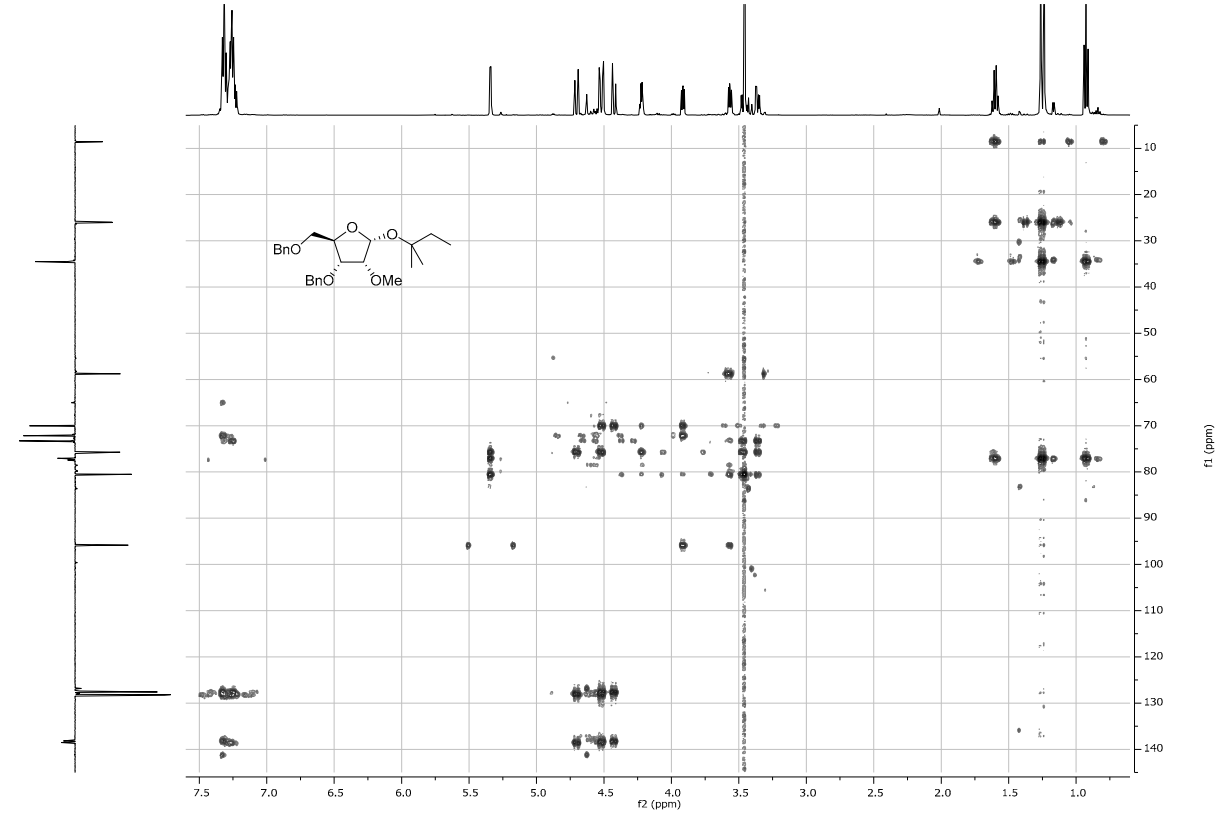


^{1}H-^{1}H COSY of compound **52**

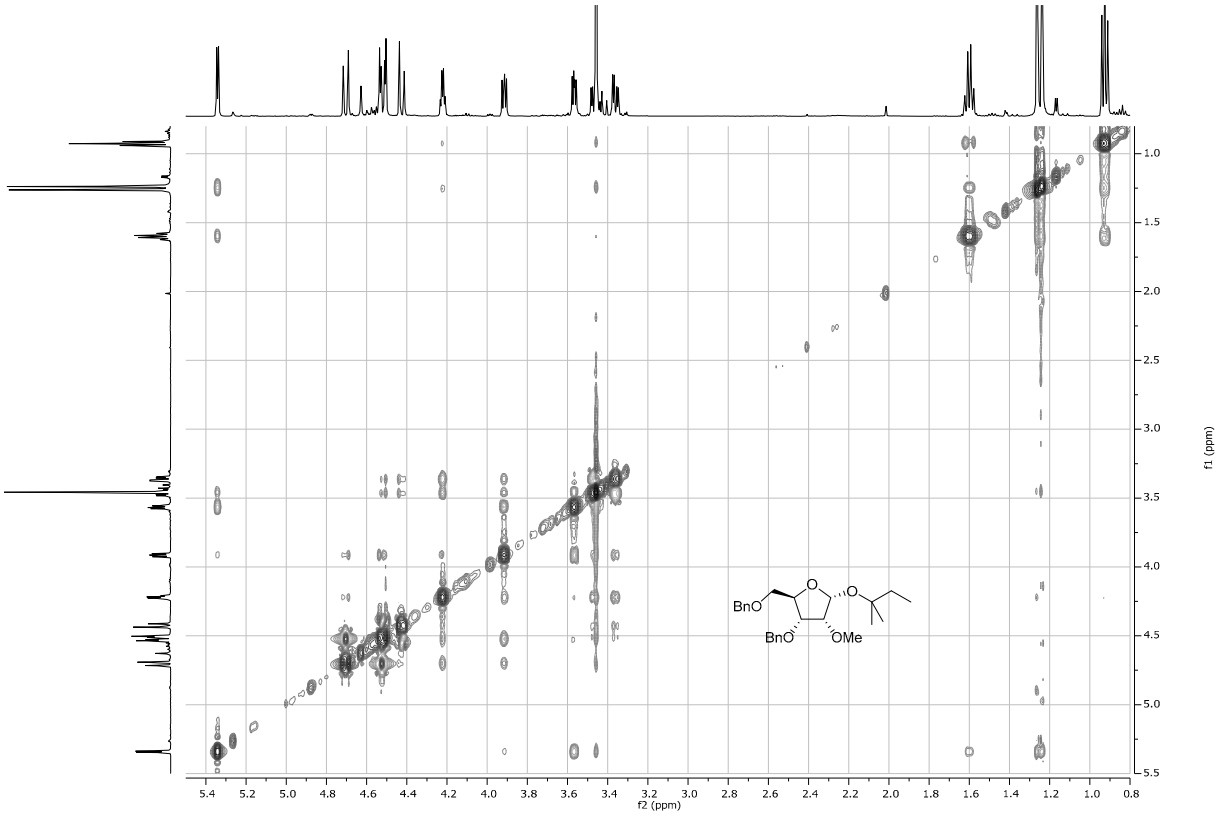


^{1}H-^{13}C HSQC of compound **52**

^{1}H-^{13}C HMBC of compound **52**

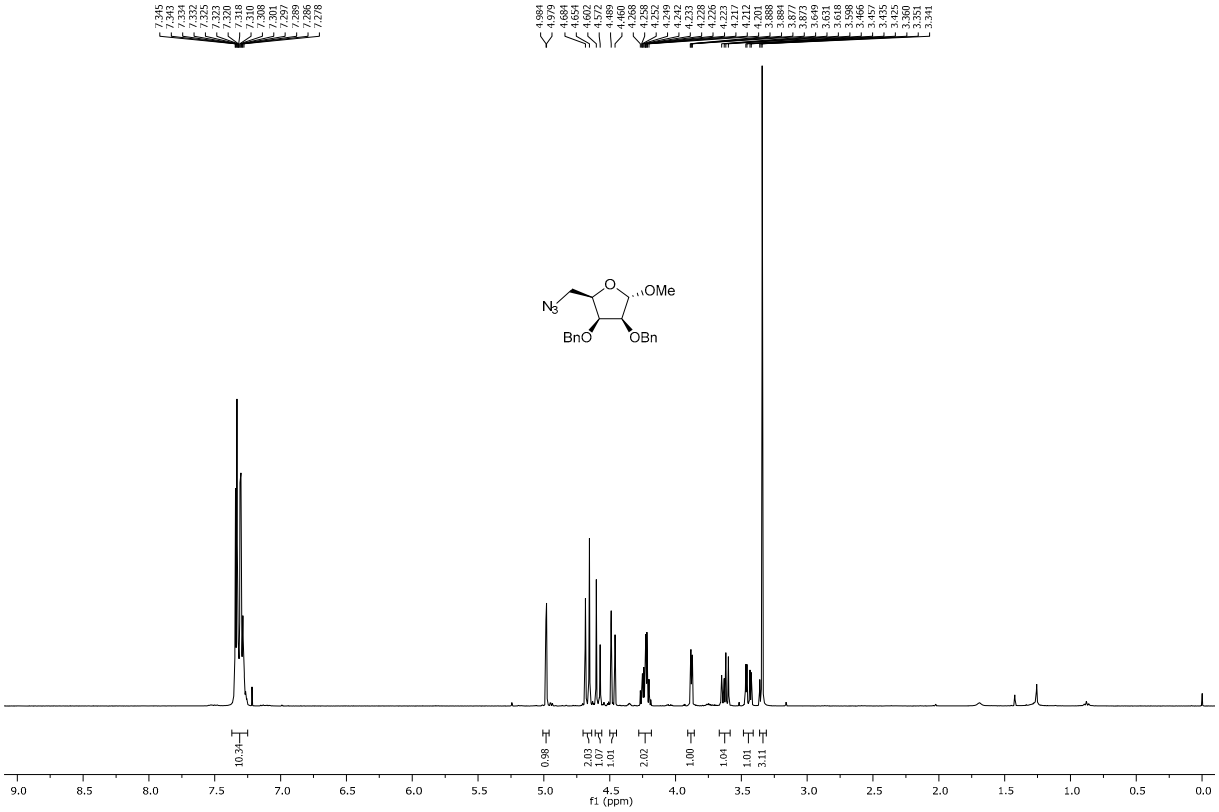


^{1}H-^{1}H NOESY of compound **52**

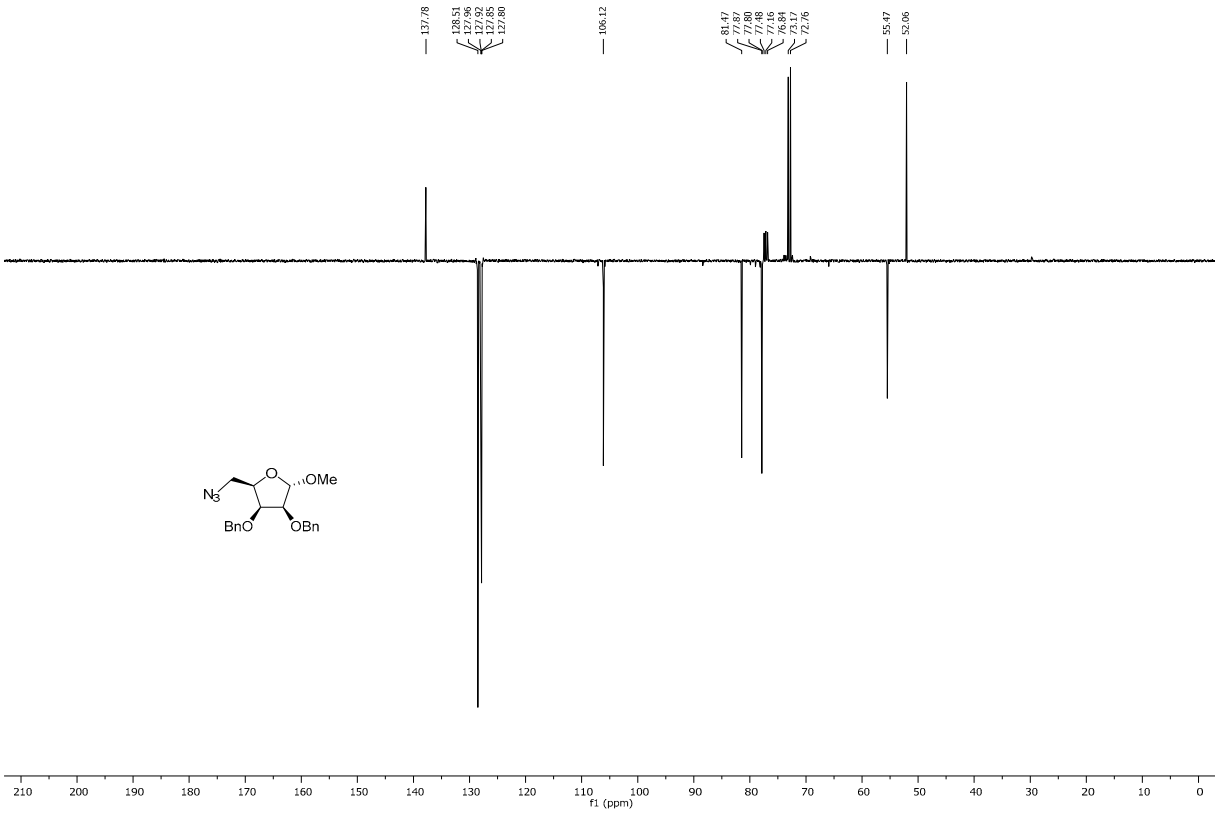


Methyl 5-azido-2,5-di-*O*-benzyl-5-deoxy-α-D-lyxofuranoside (53α)

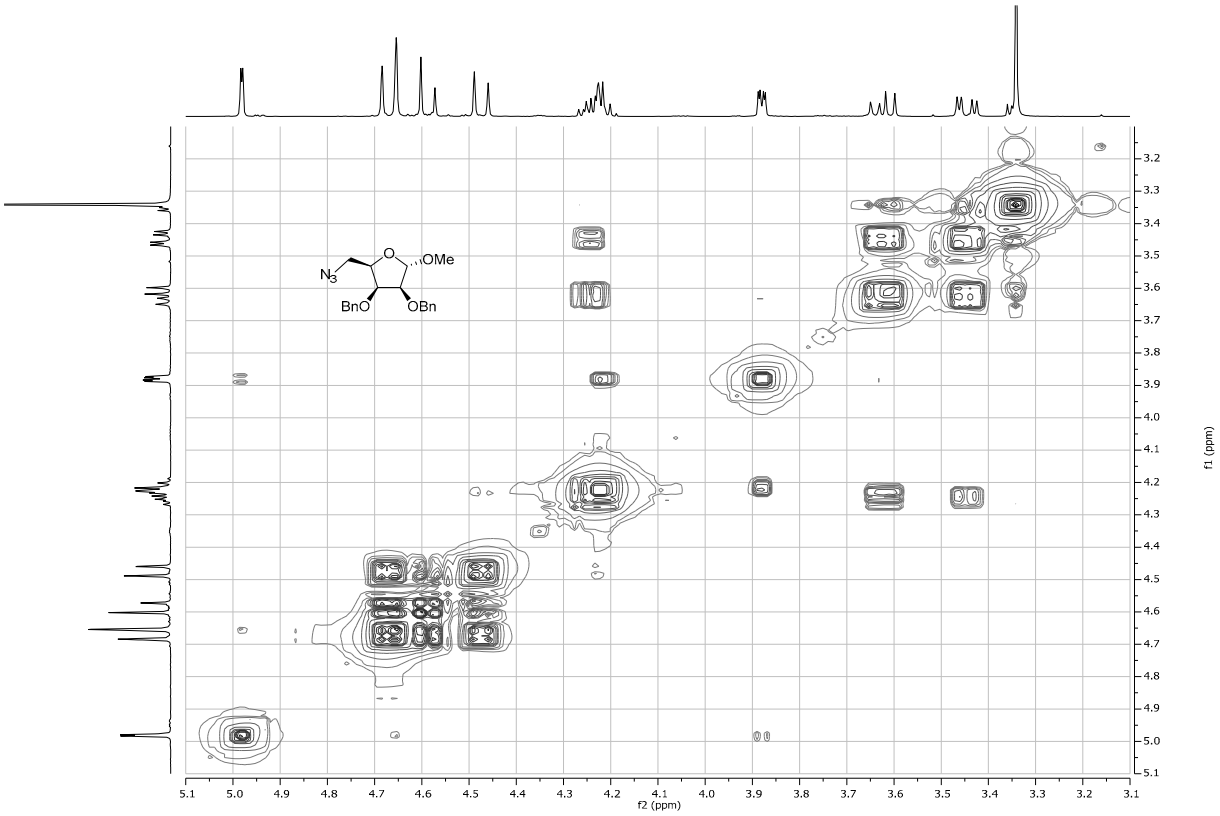
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **53α**



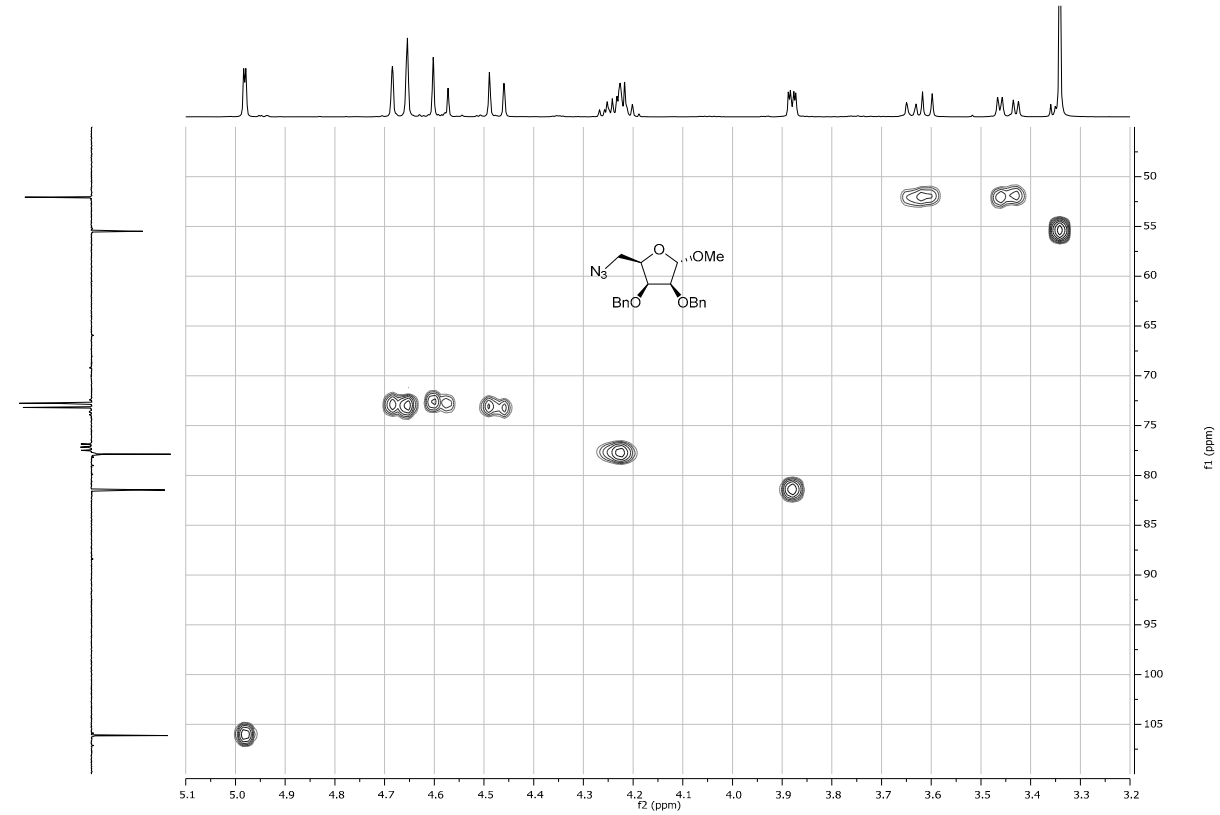
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **53α**



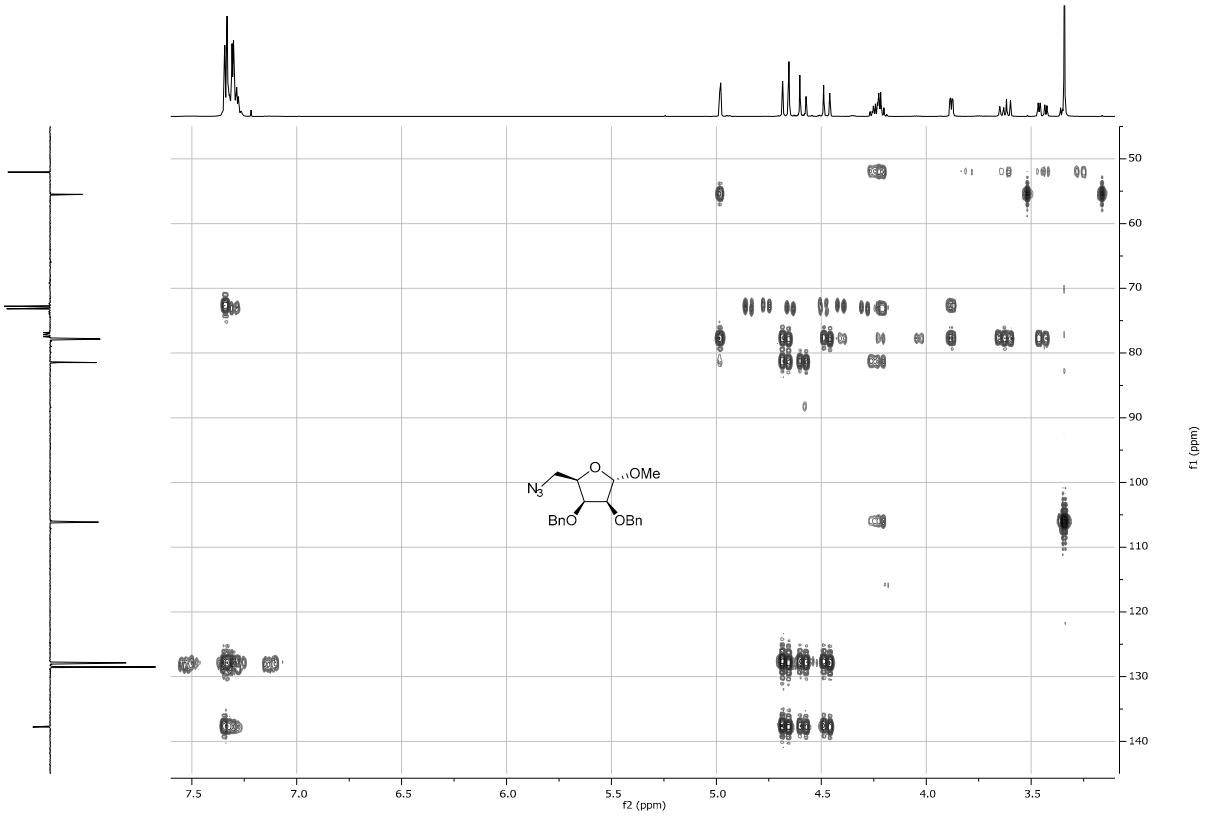
^{1}H-^{1}H COSY of compound **53α**



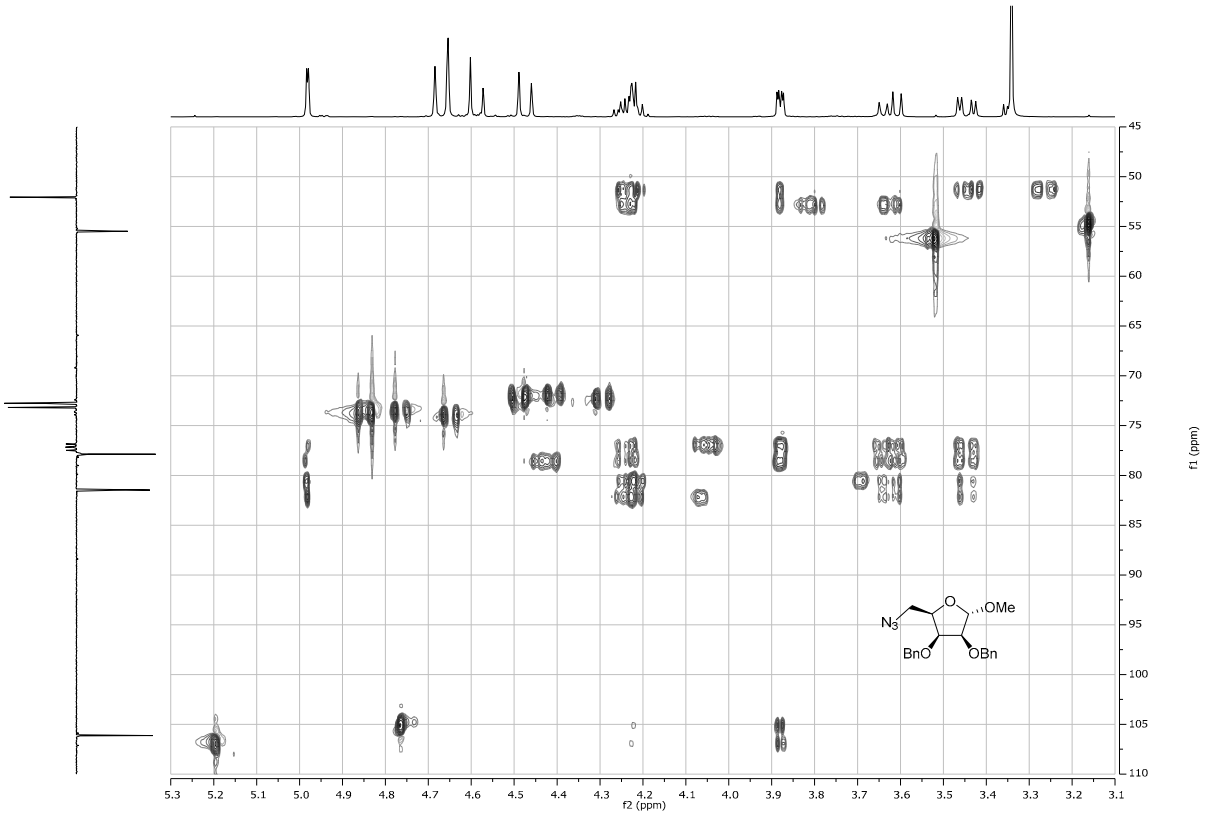
^{1}H-^{13}C HSQC of compound **53α**



^{1}H-^{13}C HMBC of compound **53α**

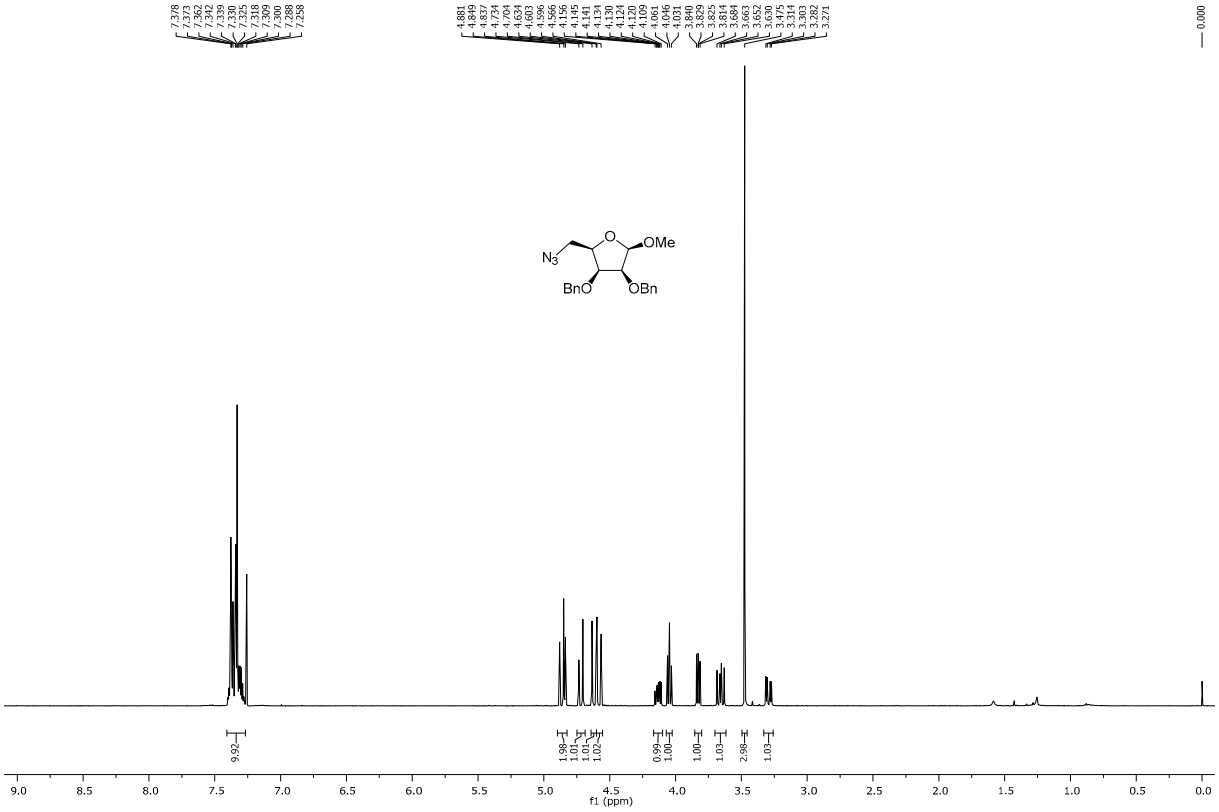


^{1}H-^{13}C HSQC-HECADE of compound **53α**

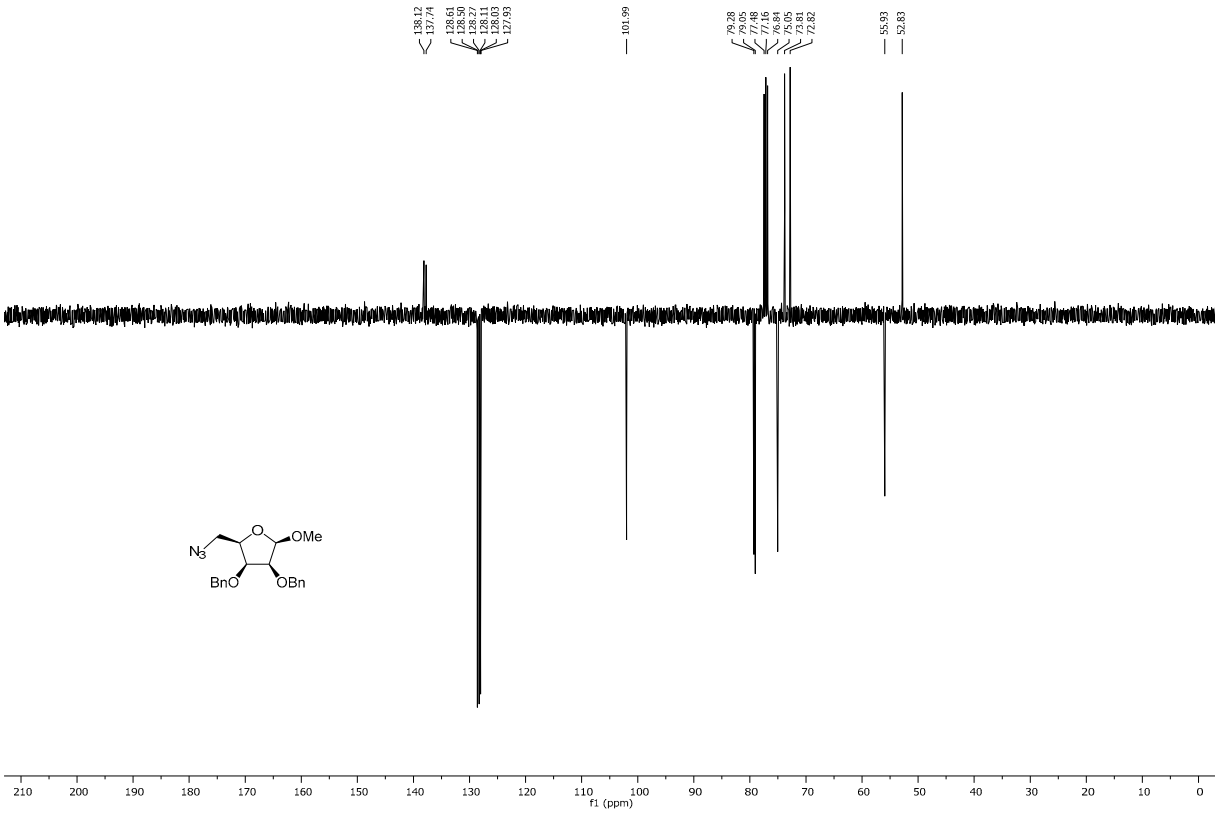


Methyl 5-azido-2,5-di-*O*-benzyl-5-deoxy-β-D-lyxofuranoside (53β)

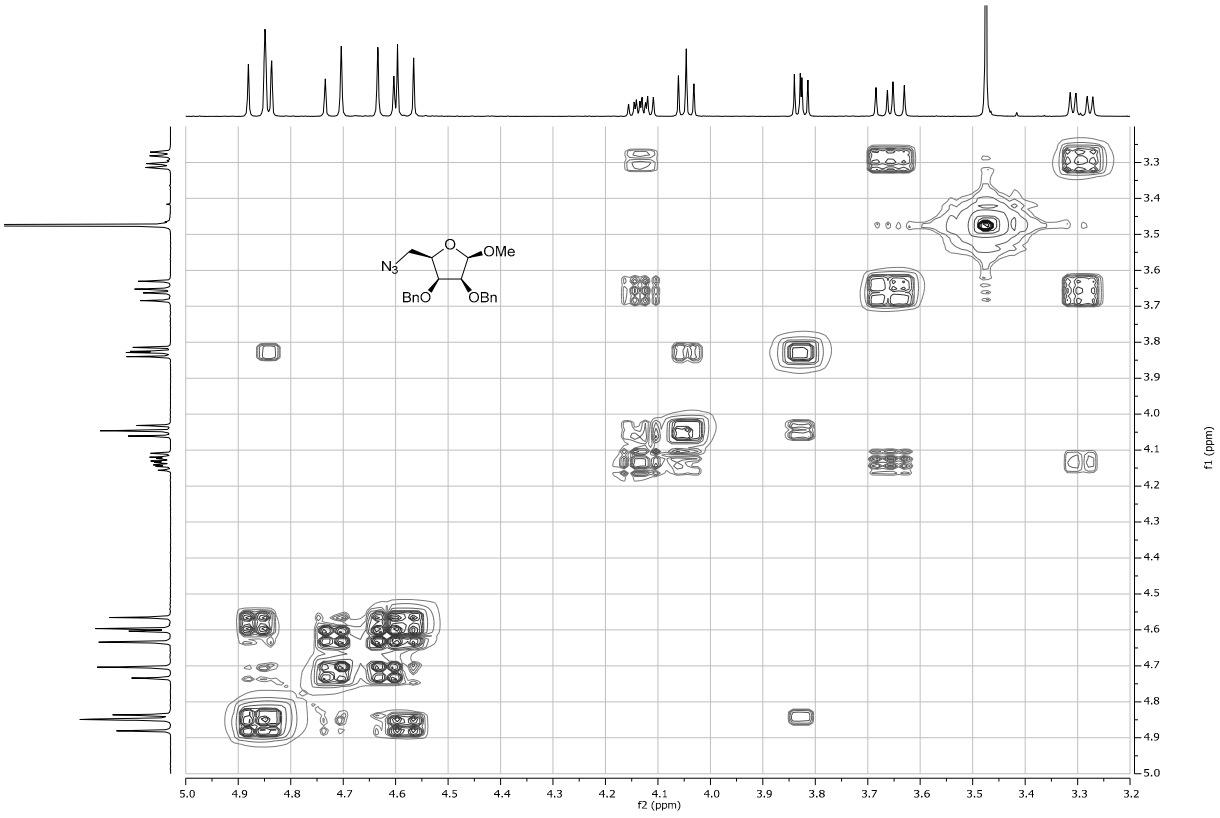
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **53β**



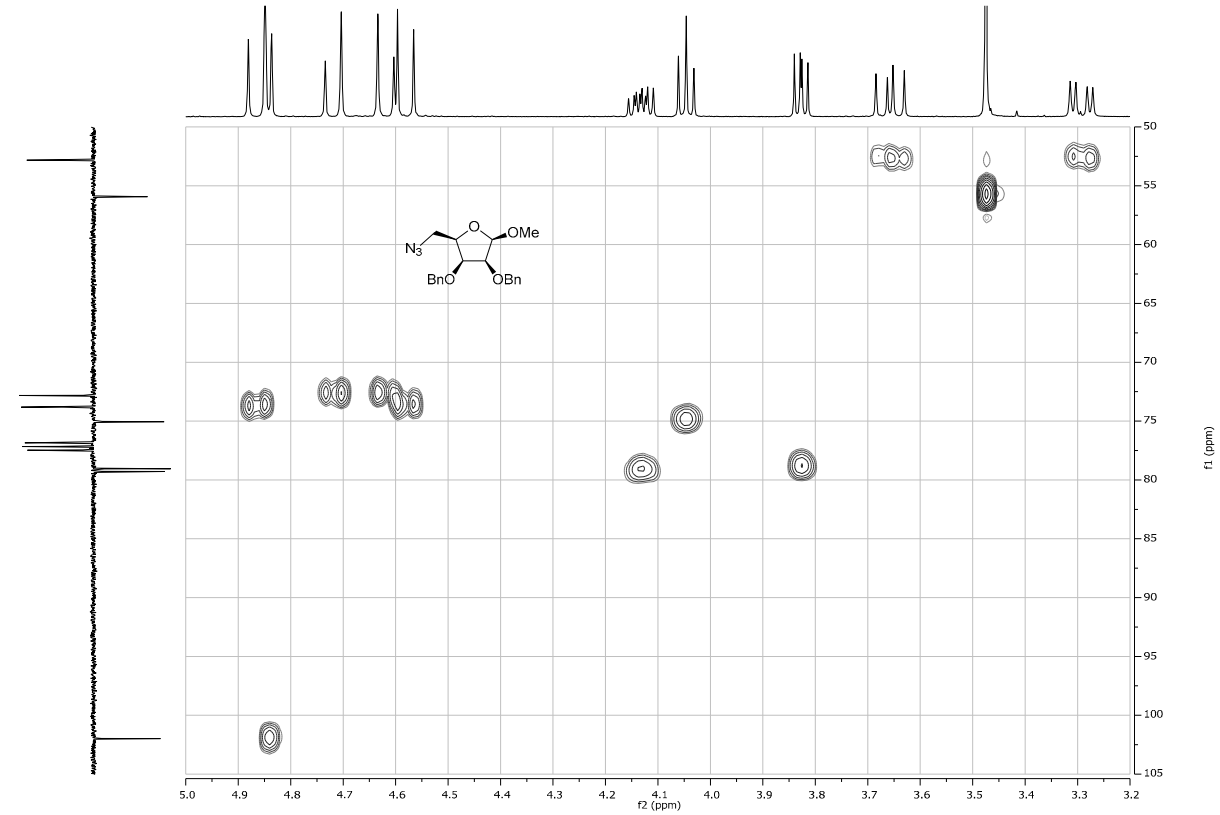
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **53β**



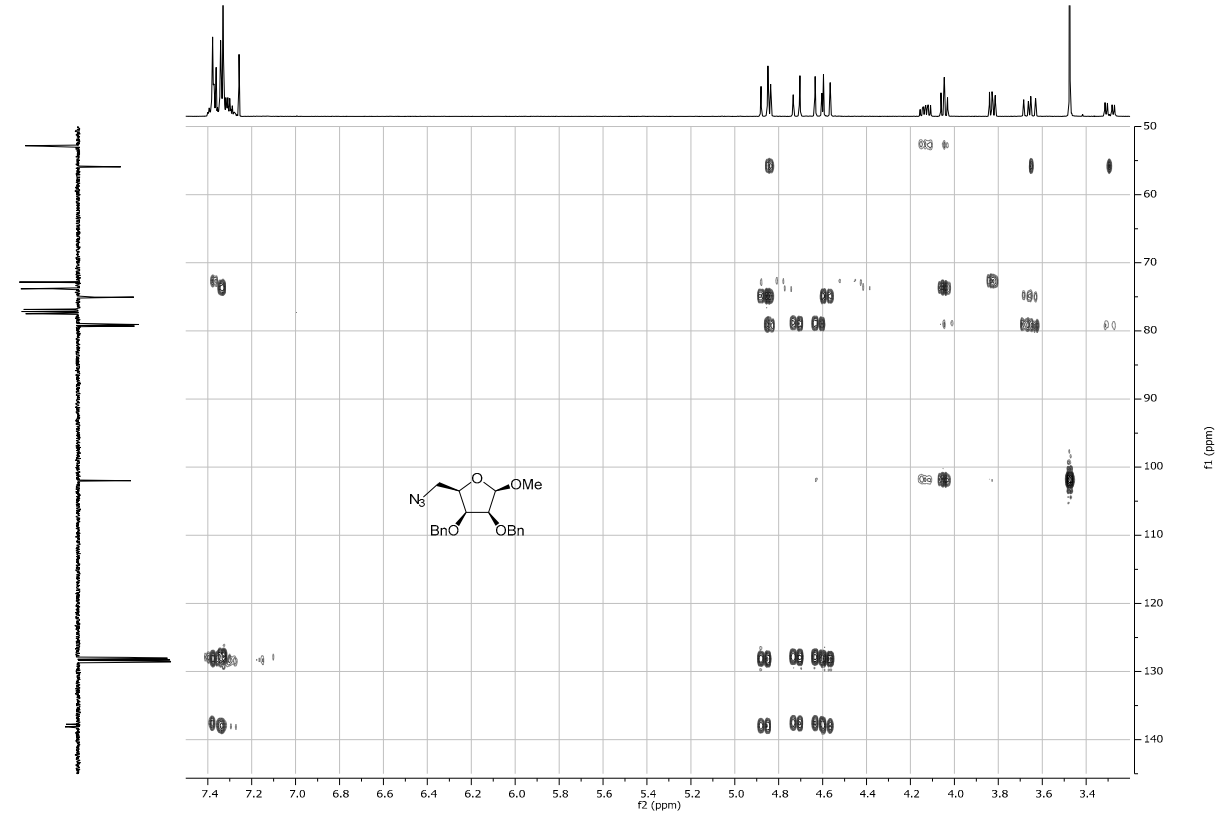
^{1}H-^{1}H COSY of compound **53β**



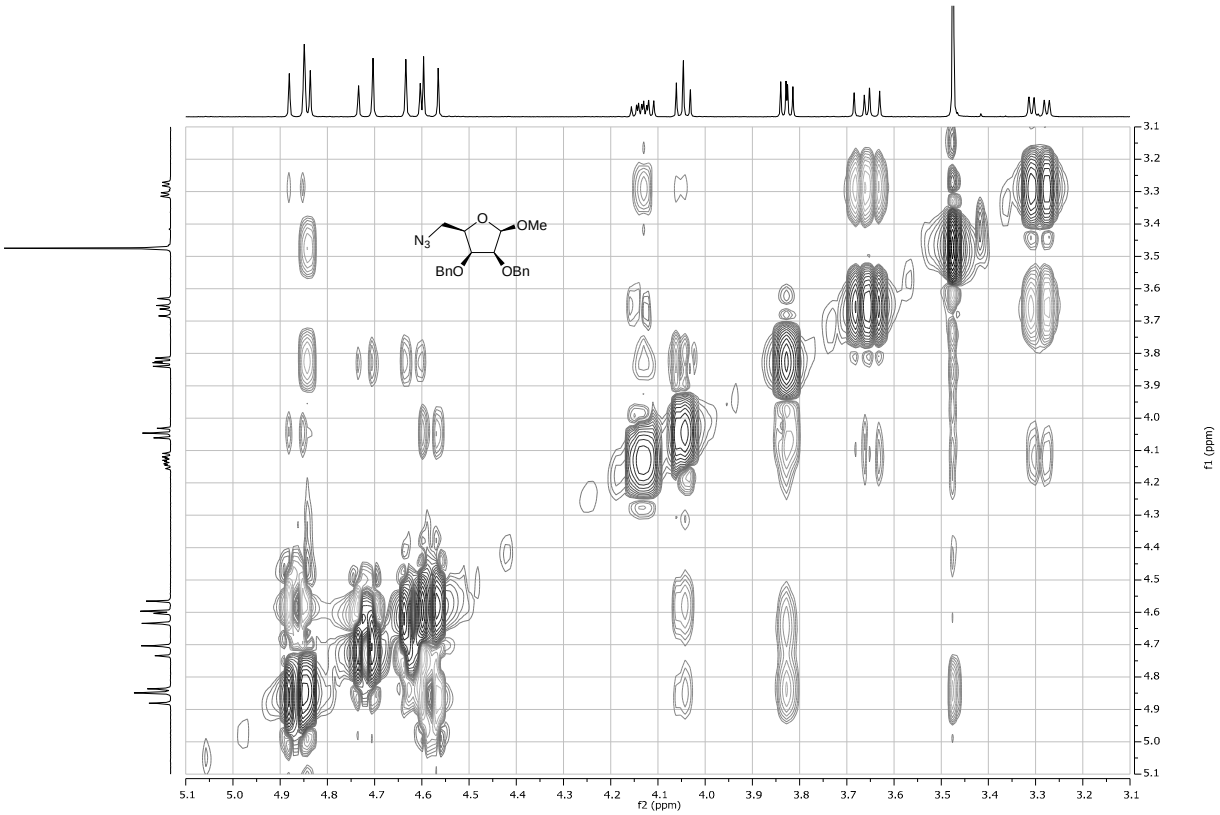
^{1}H-^{13}C HSQC of compound **53β**



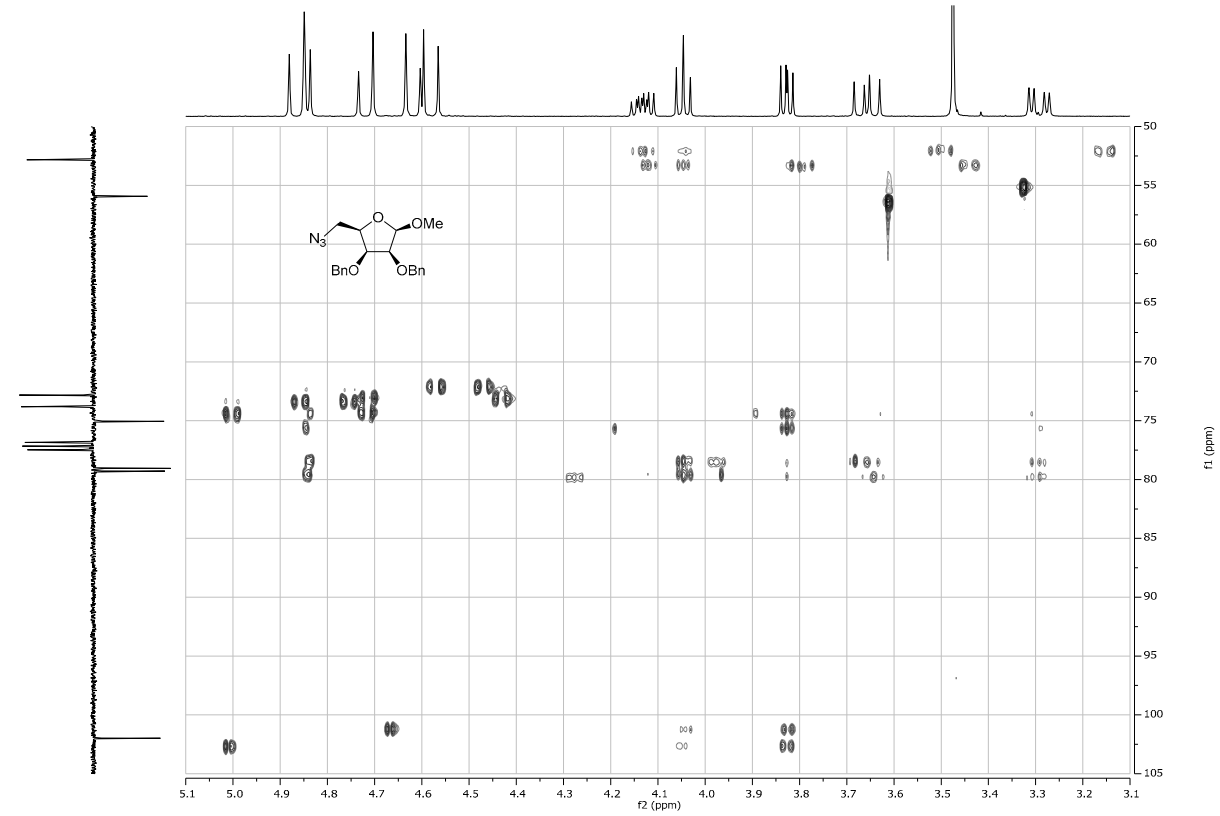
^{1}H-^{13}C HMBC of compound **53β**



^{1}H-^{1}H NOESY of compound **53β**

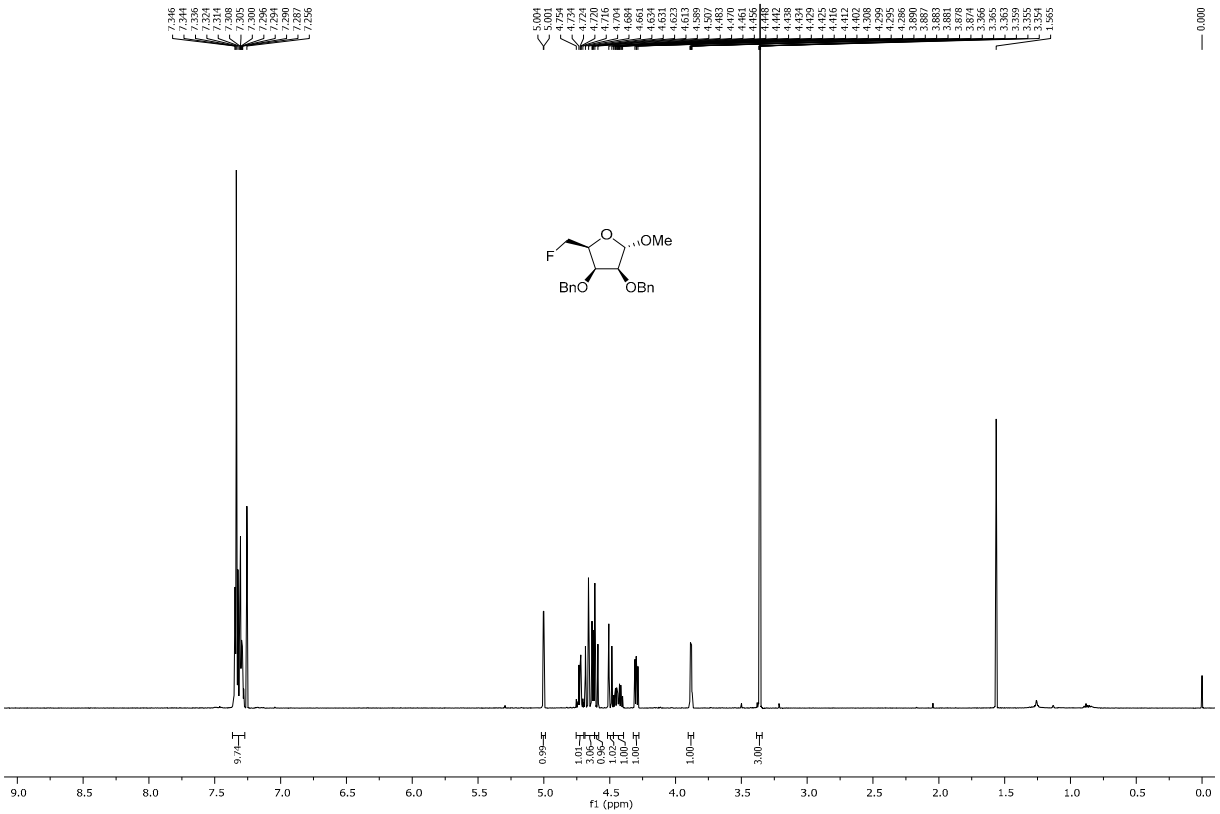


^{1}H-^{13}C HSQC-HECADE of compound **53β**

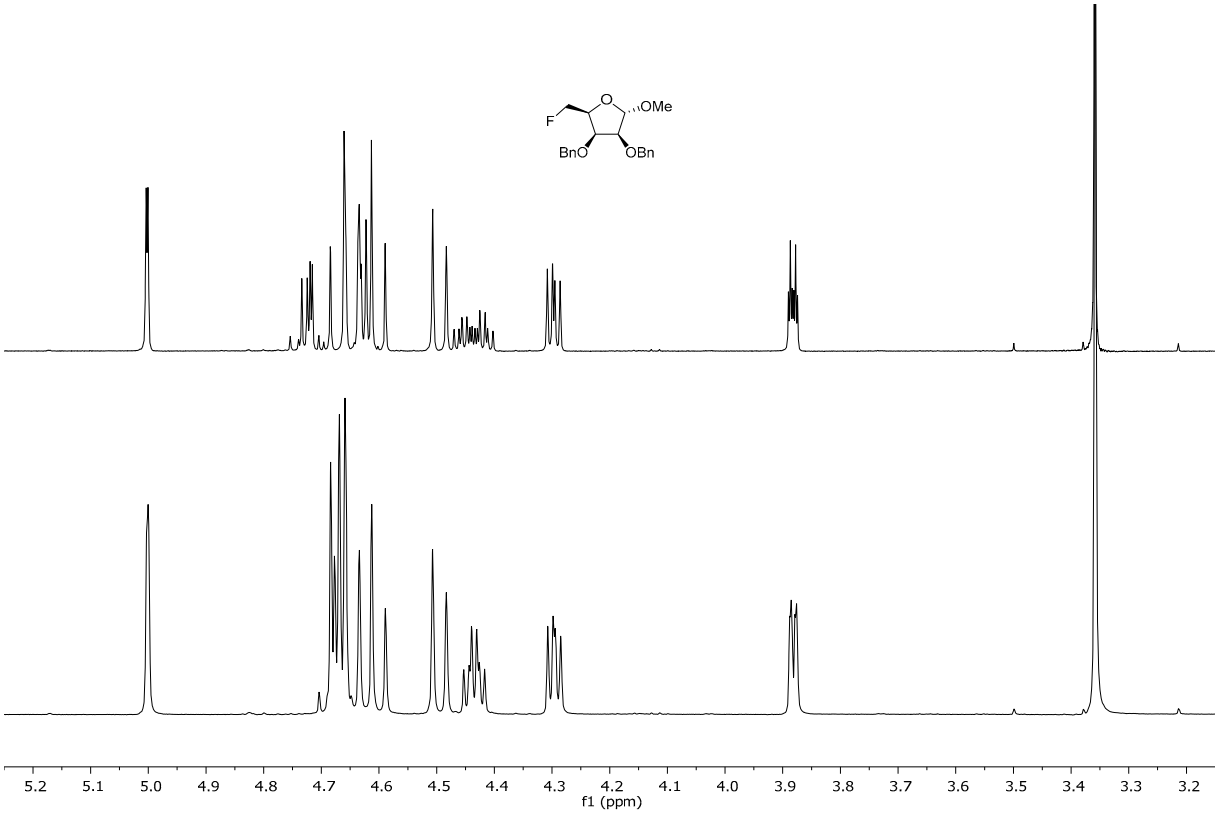


Methyl 2,5-di-*O*-benzyl-5-deoxy-5-fluoro-α-D-lyxofuranoside (54α)

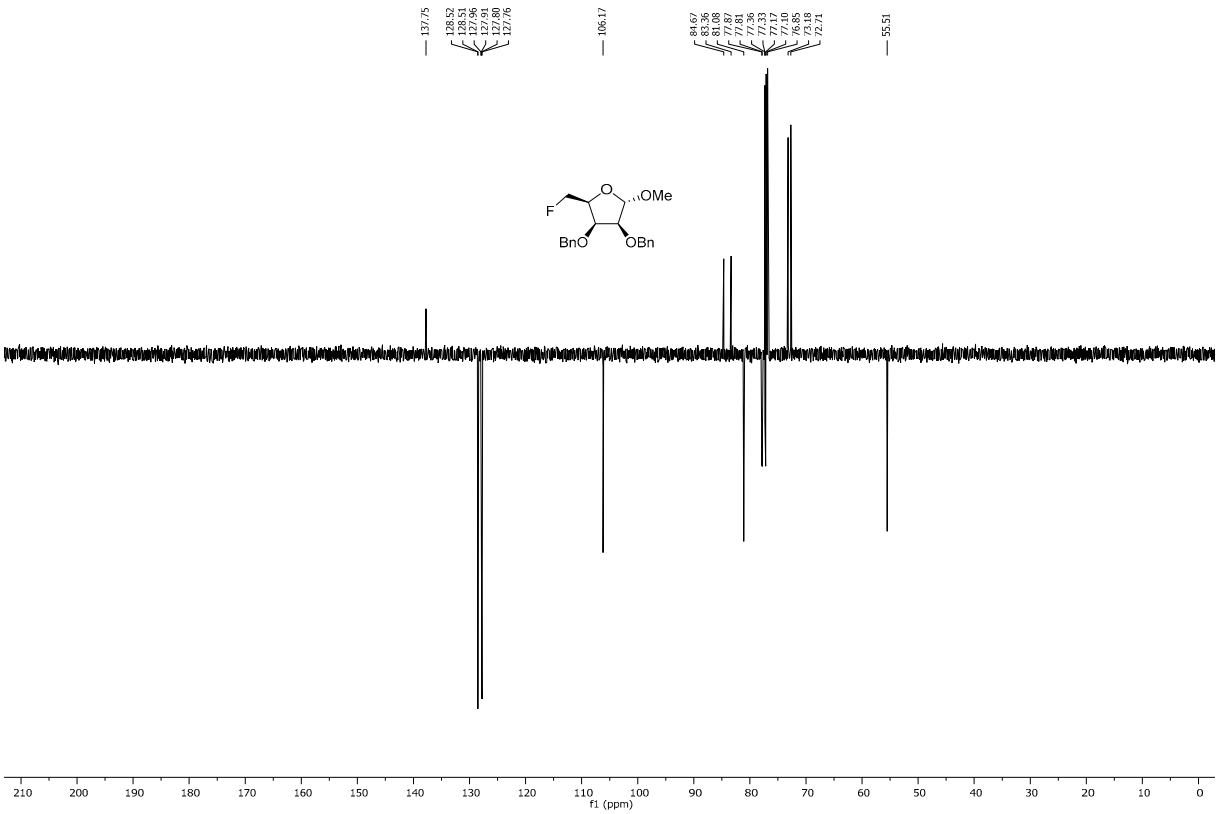
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **54α**



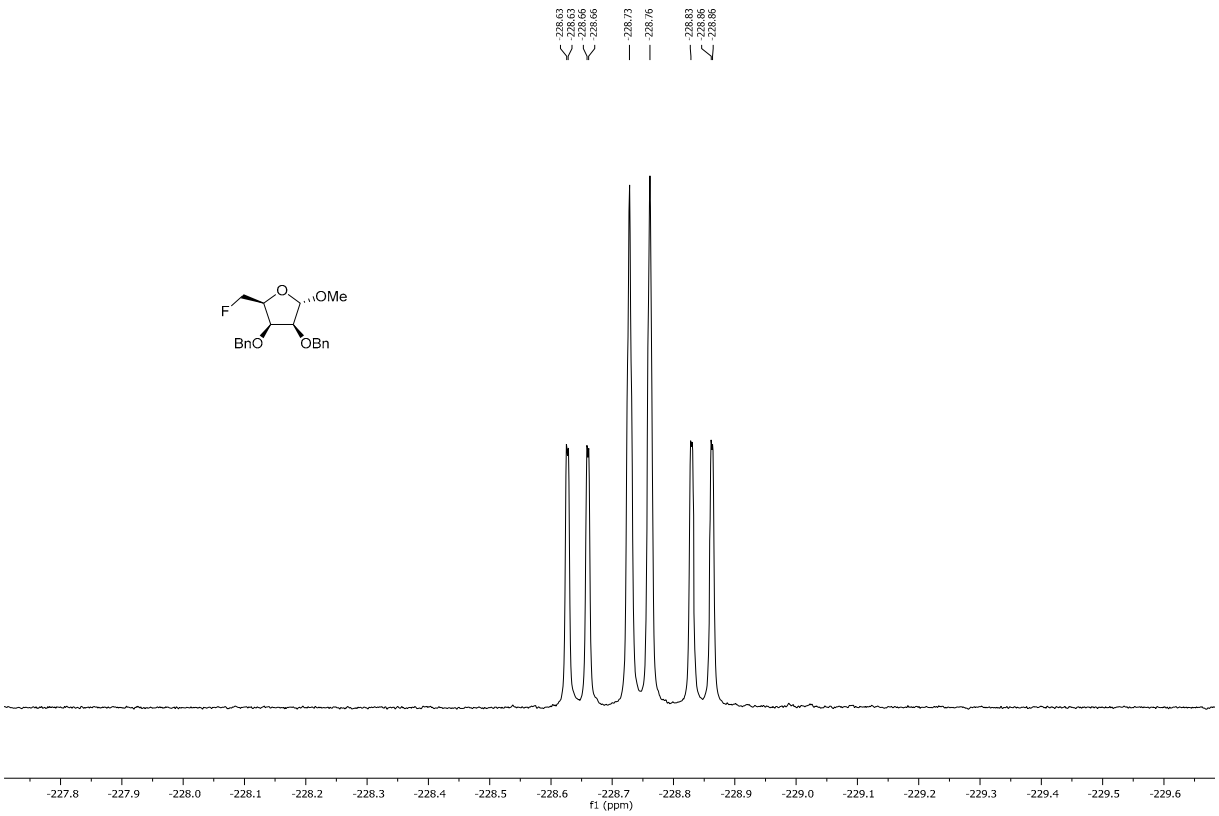
^{19}F-decoupled ^{1}H NMR, (-228 ppm)



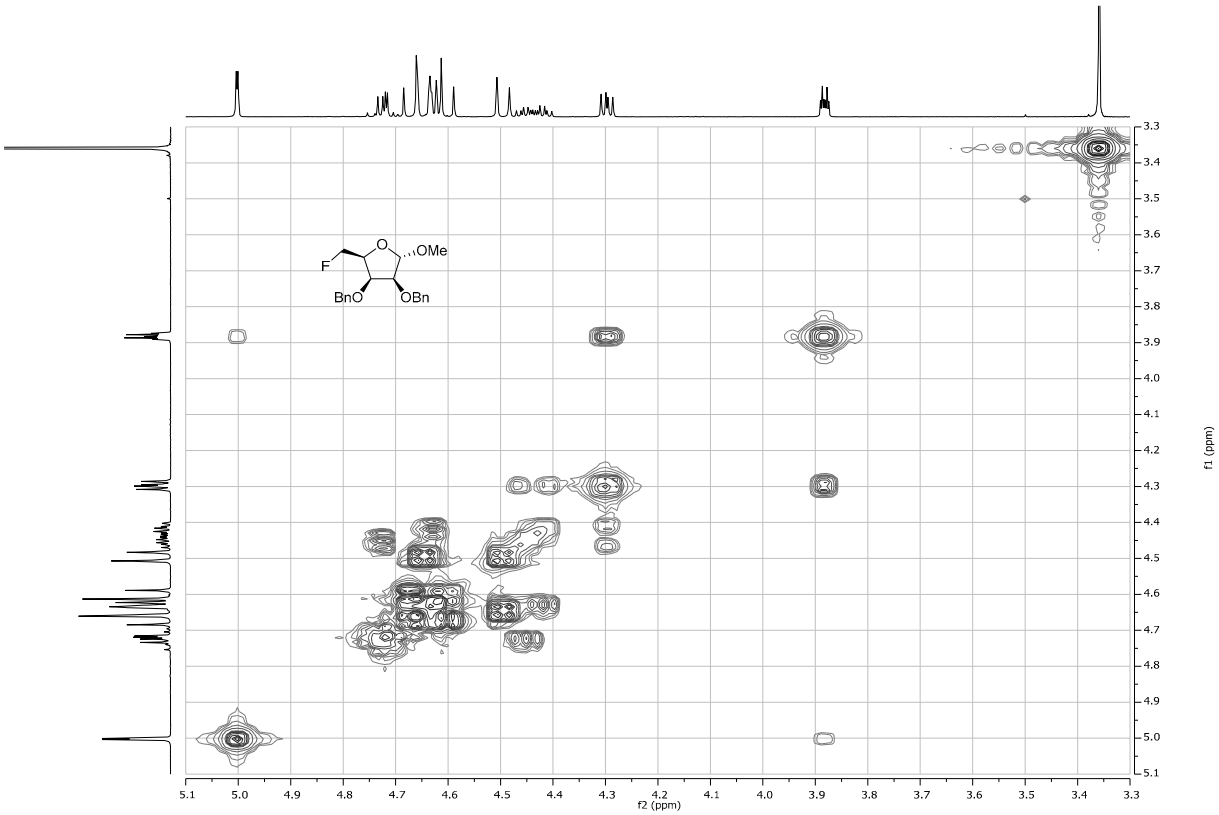
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **54α**



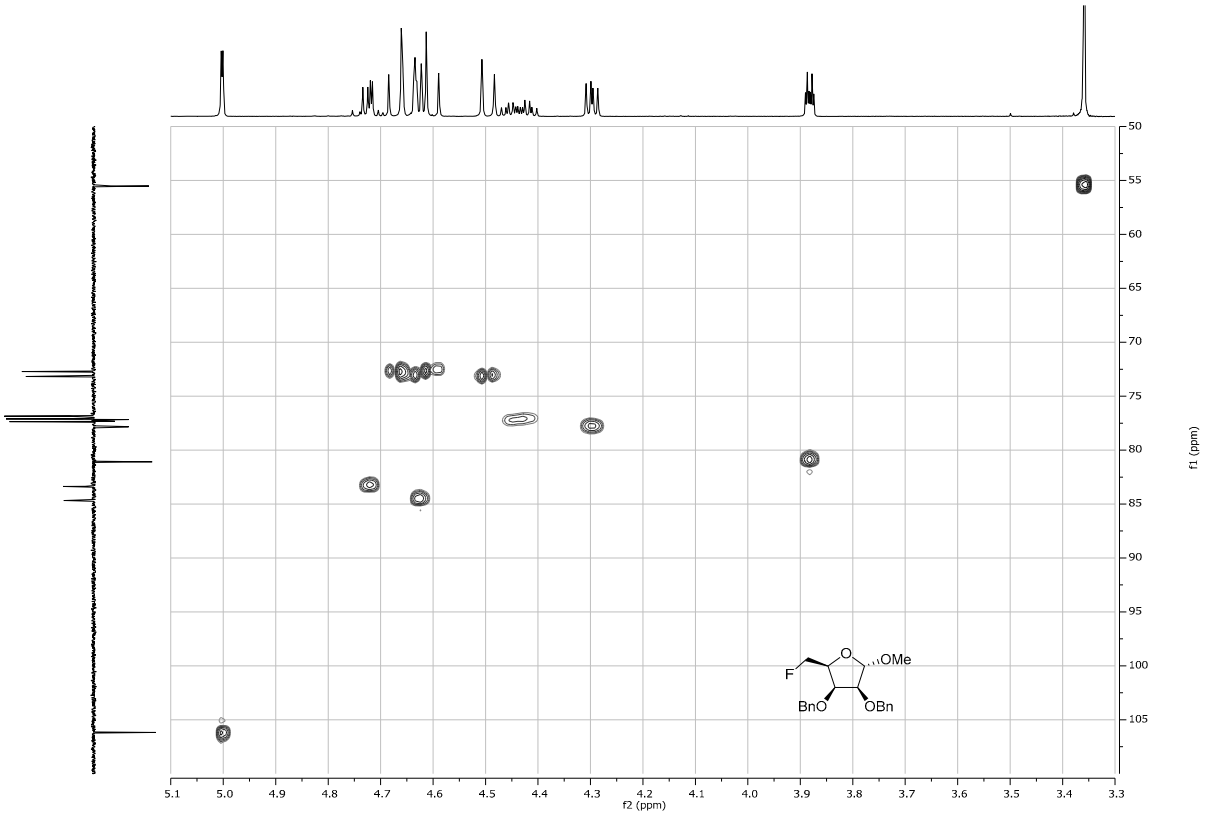
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **54α**



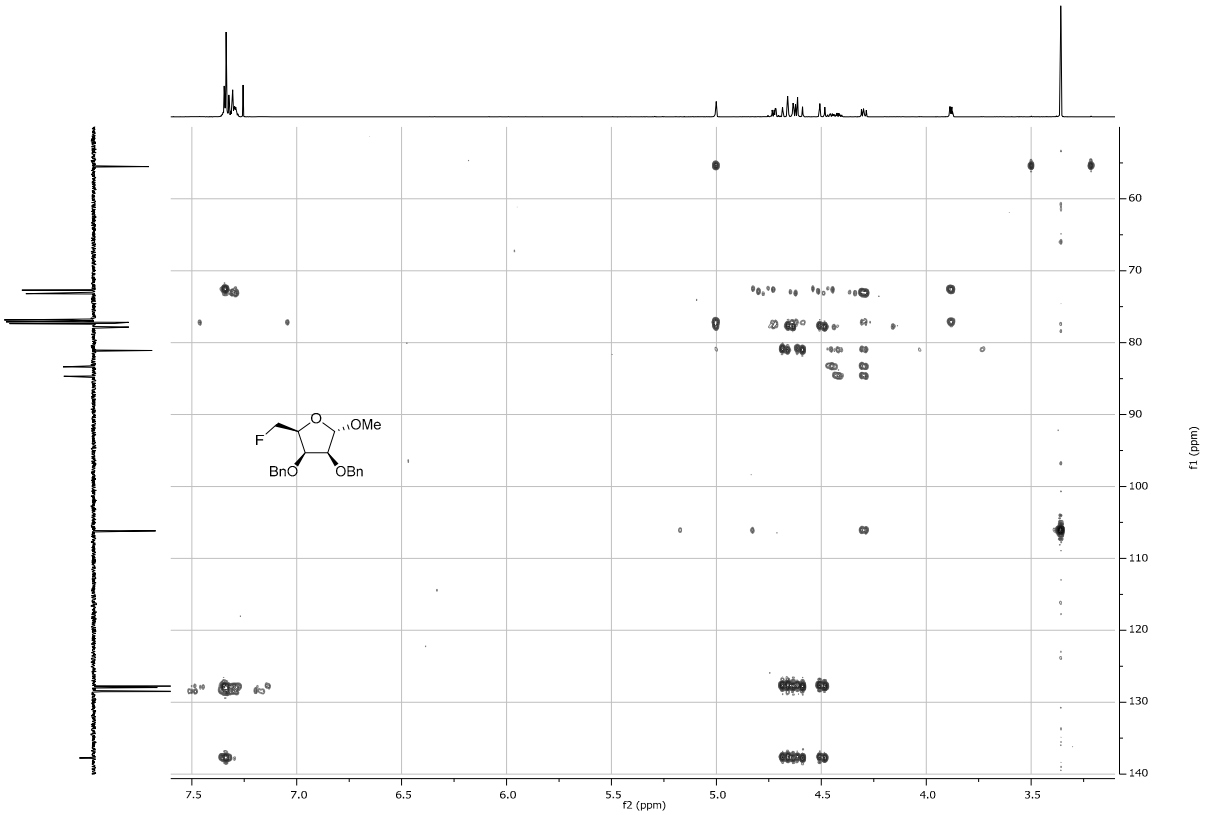
^{1}H-^{1}H COSY of compound **54α**



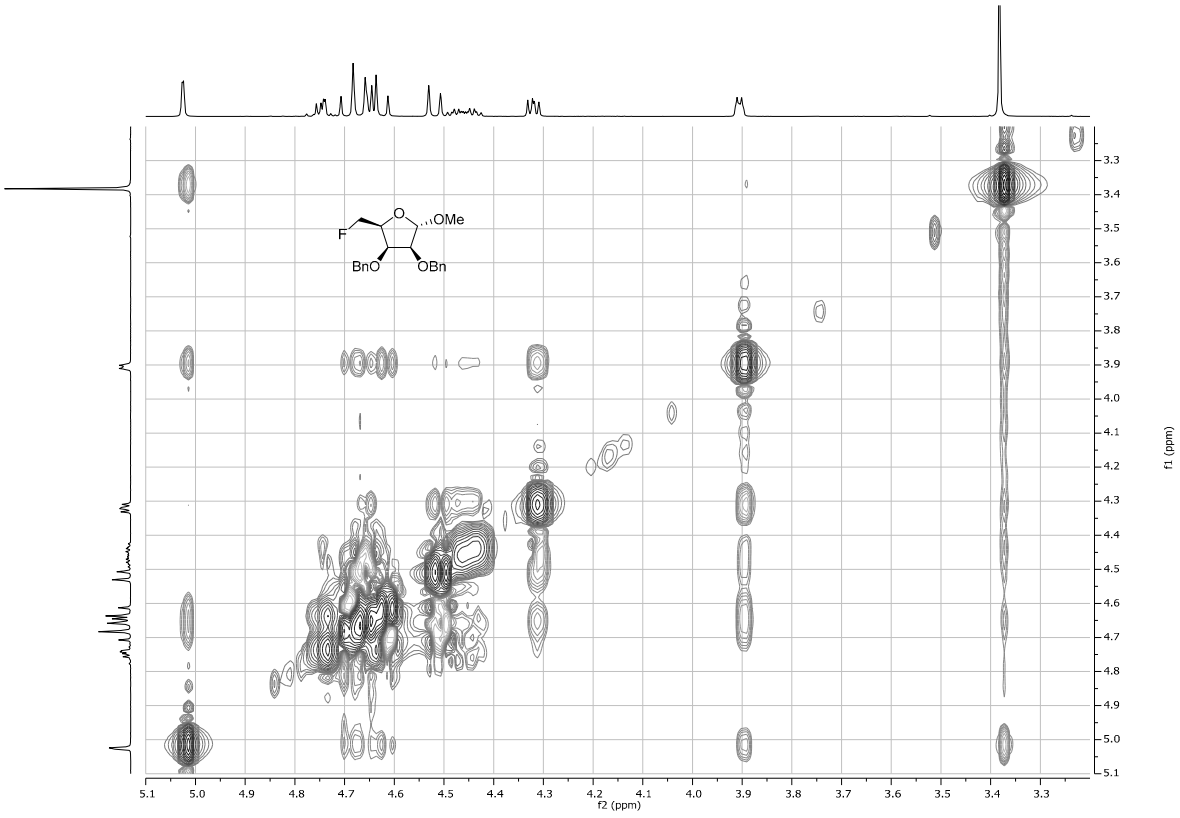
^{1}H-^{13}C HSQC of compound **54α**



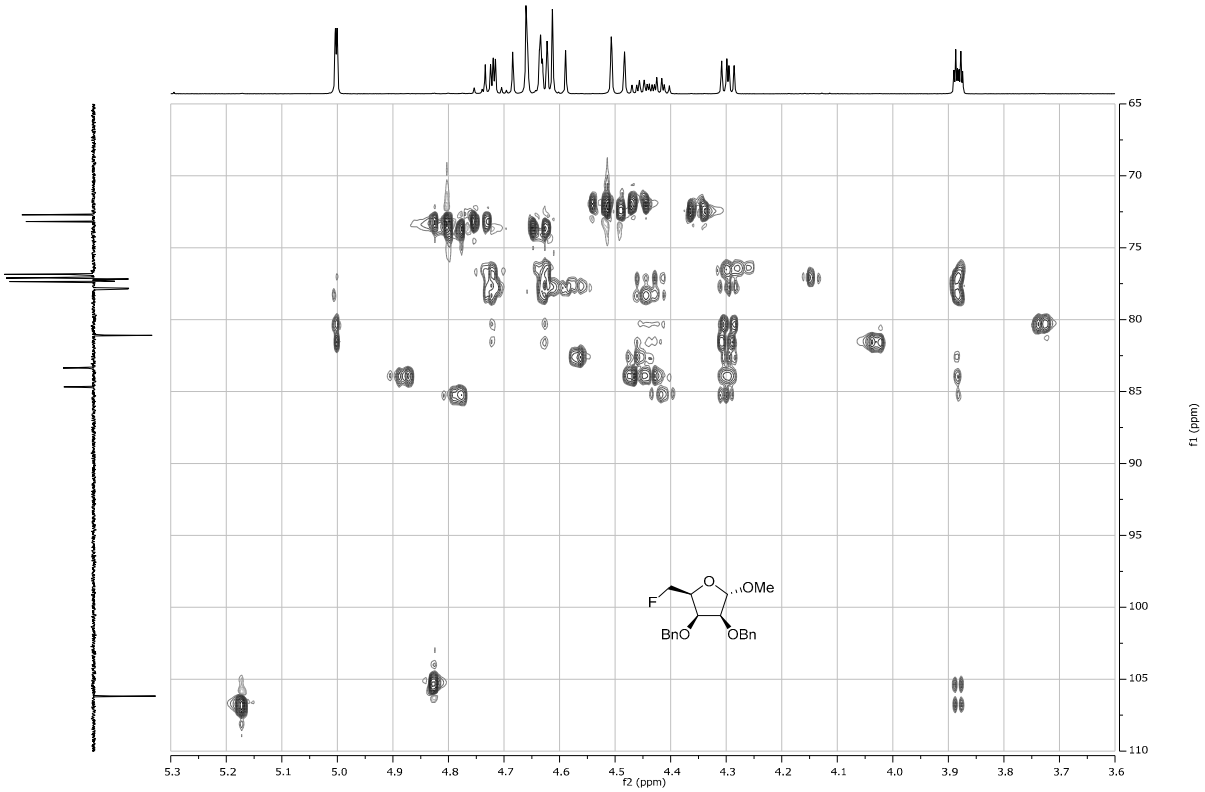
^{1}H-^{13}C HMBC of compound **54α**



^{1}H-^{1}H NOESY of compound **54α**

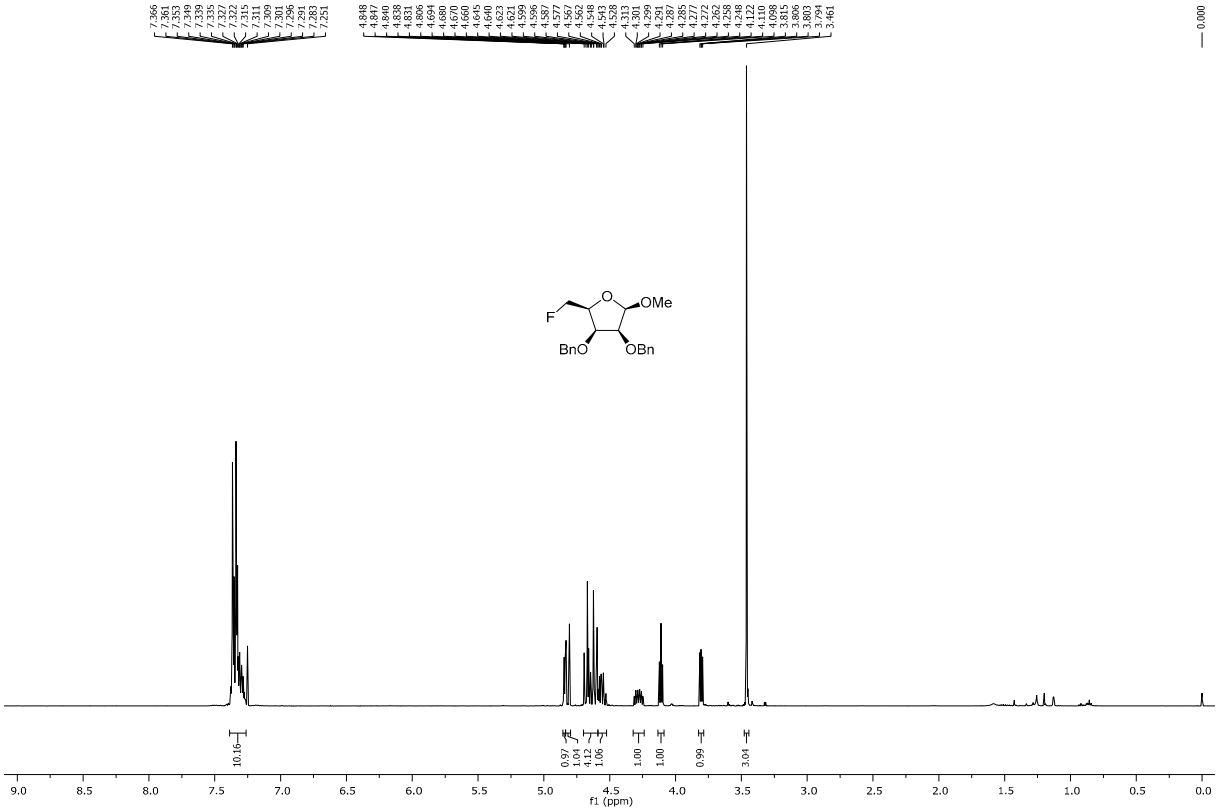


^{1}H-^{13}C HSQC-HECADE of compound **54α**

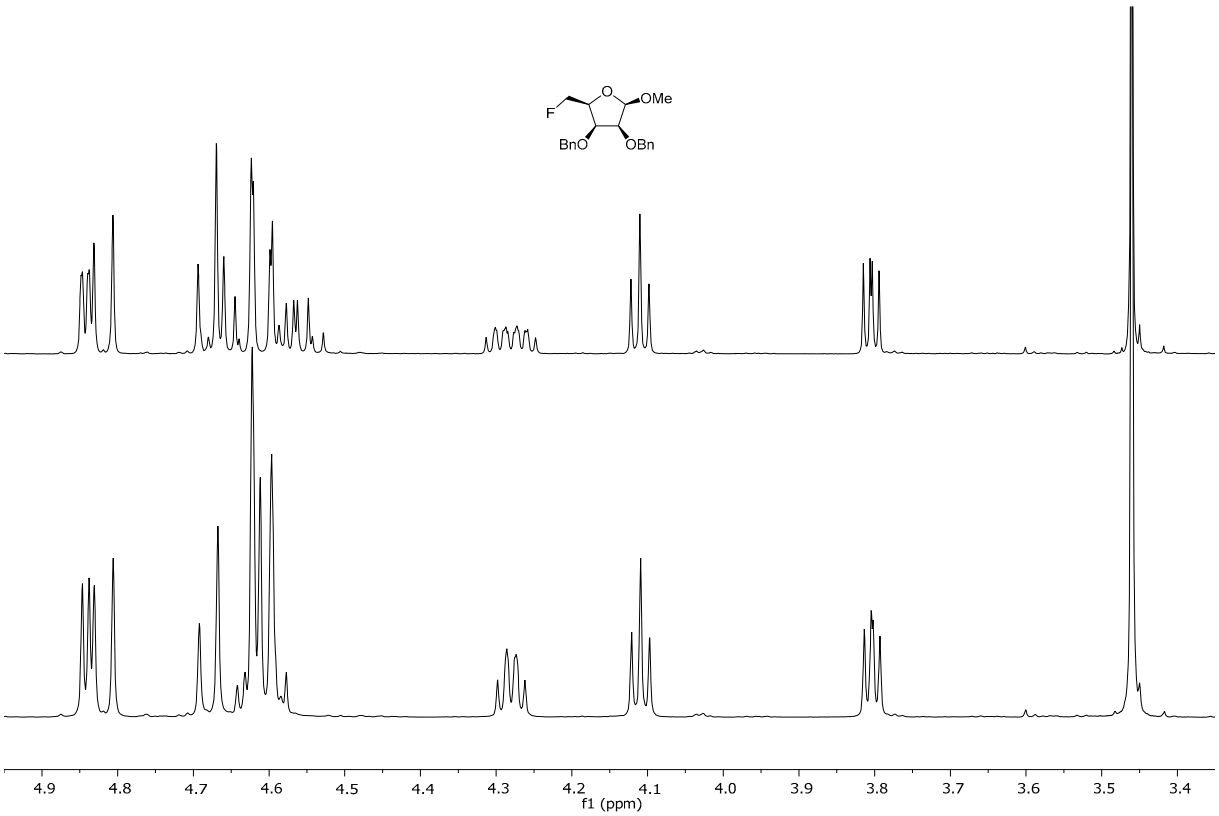


Methyl 2,5-di-*O*-benzyl-5-deoxy-5-fluoro-β-D-lyxofuranoside (54β)

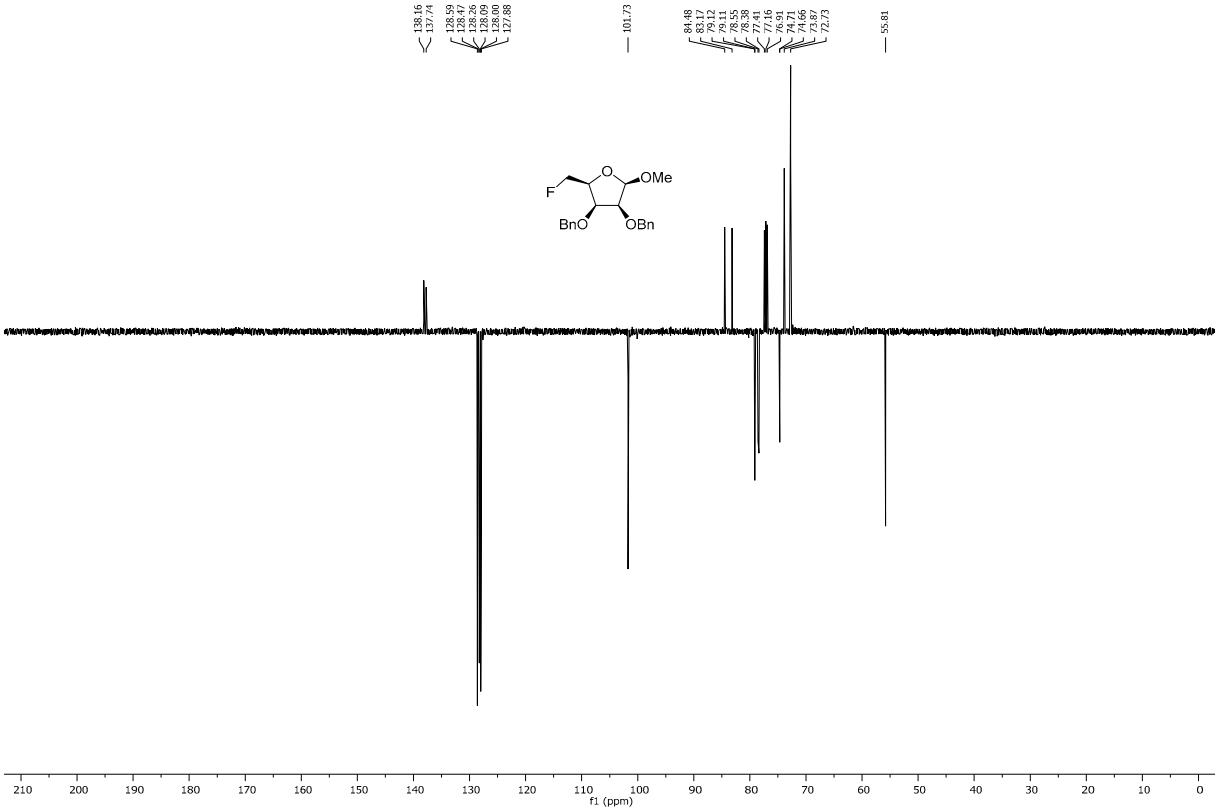
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **54β**



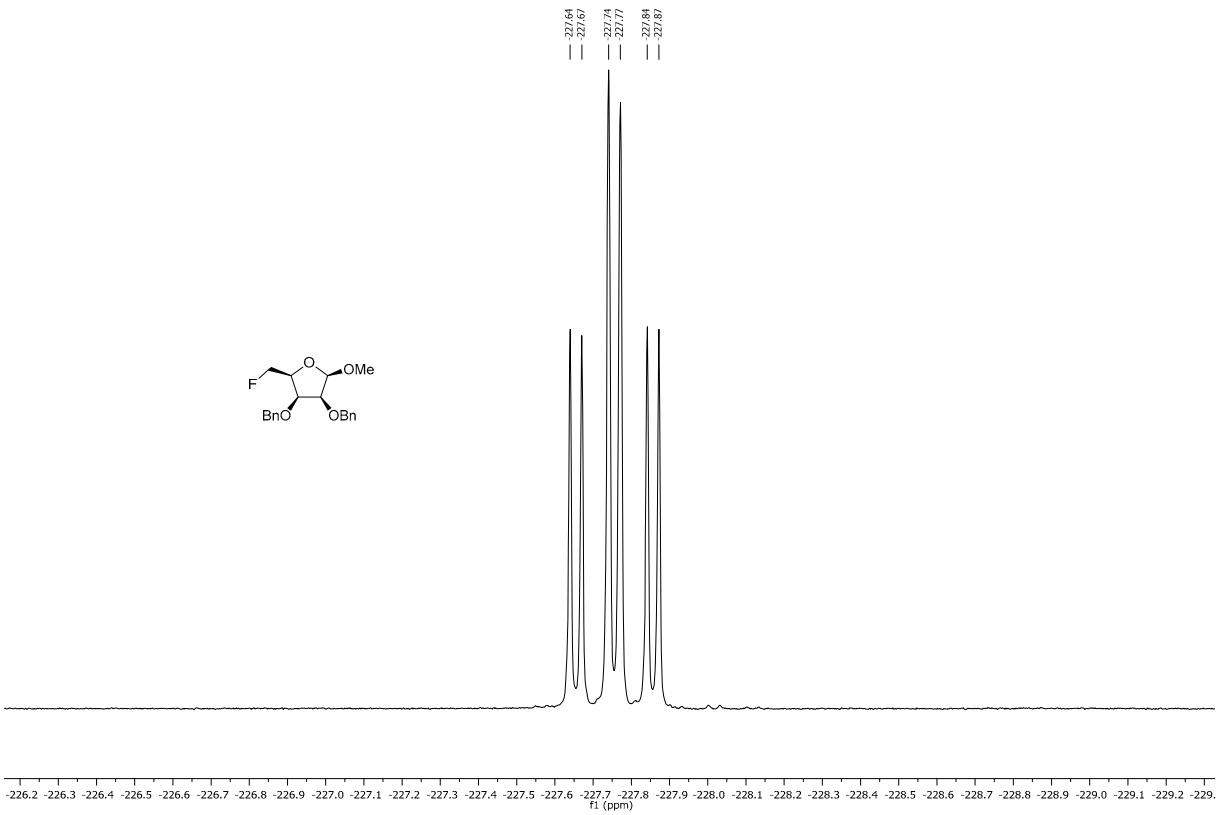
^{19}F-decoupled ^{1}H NMR, (-227 ppm)



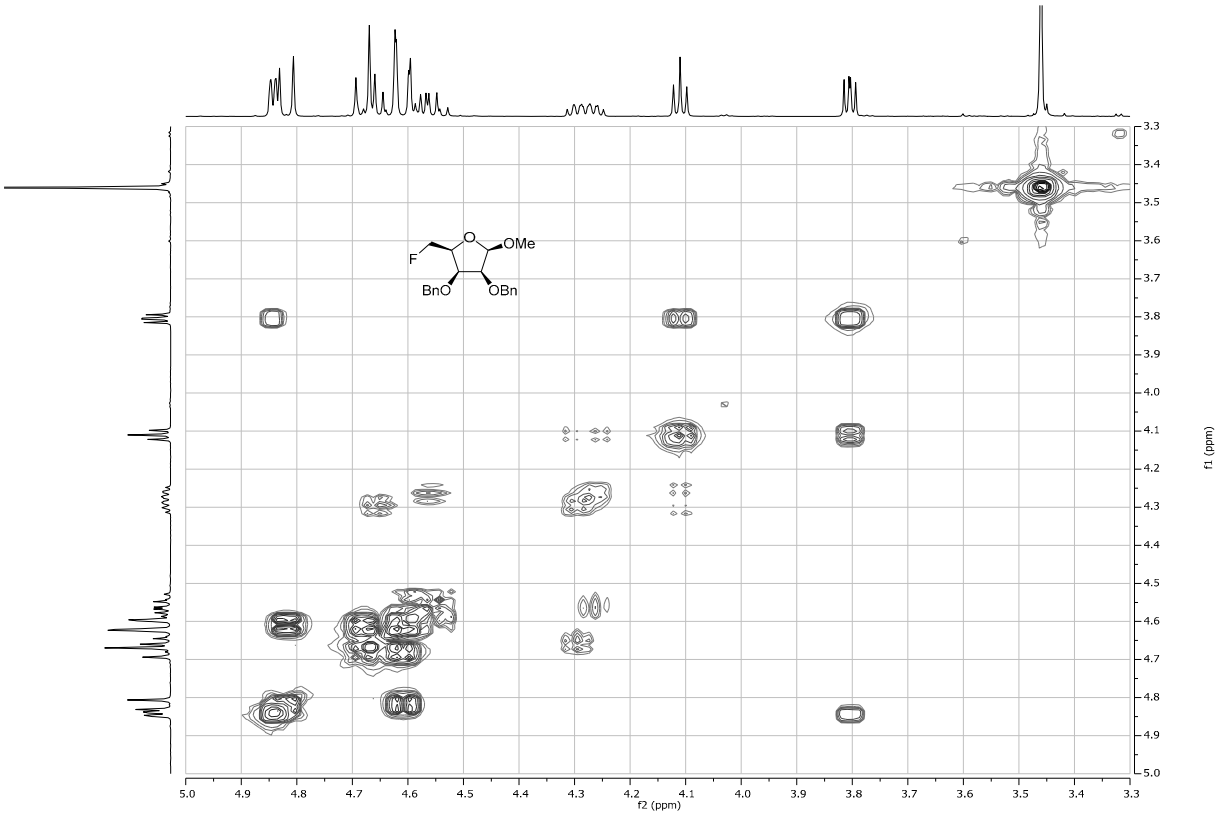
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **54β**



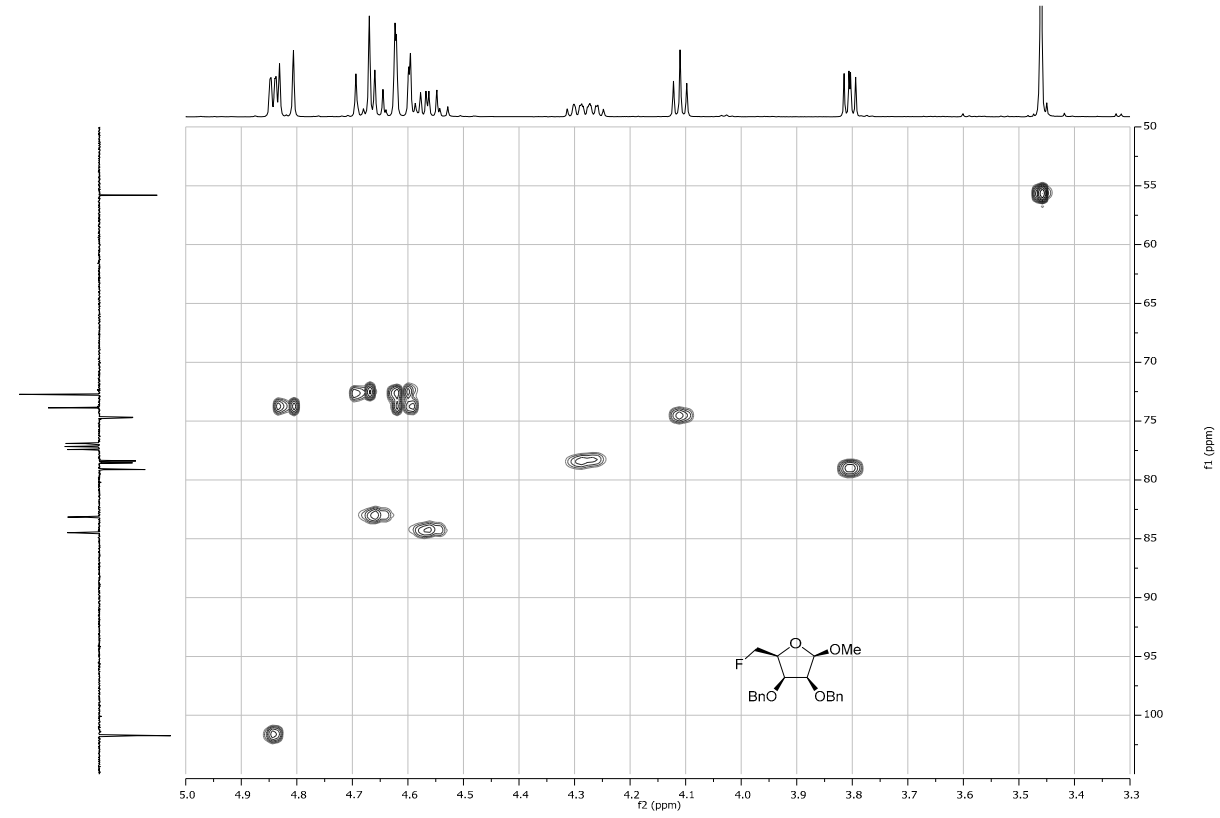
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **54β**



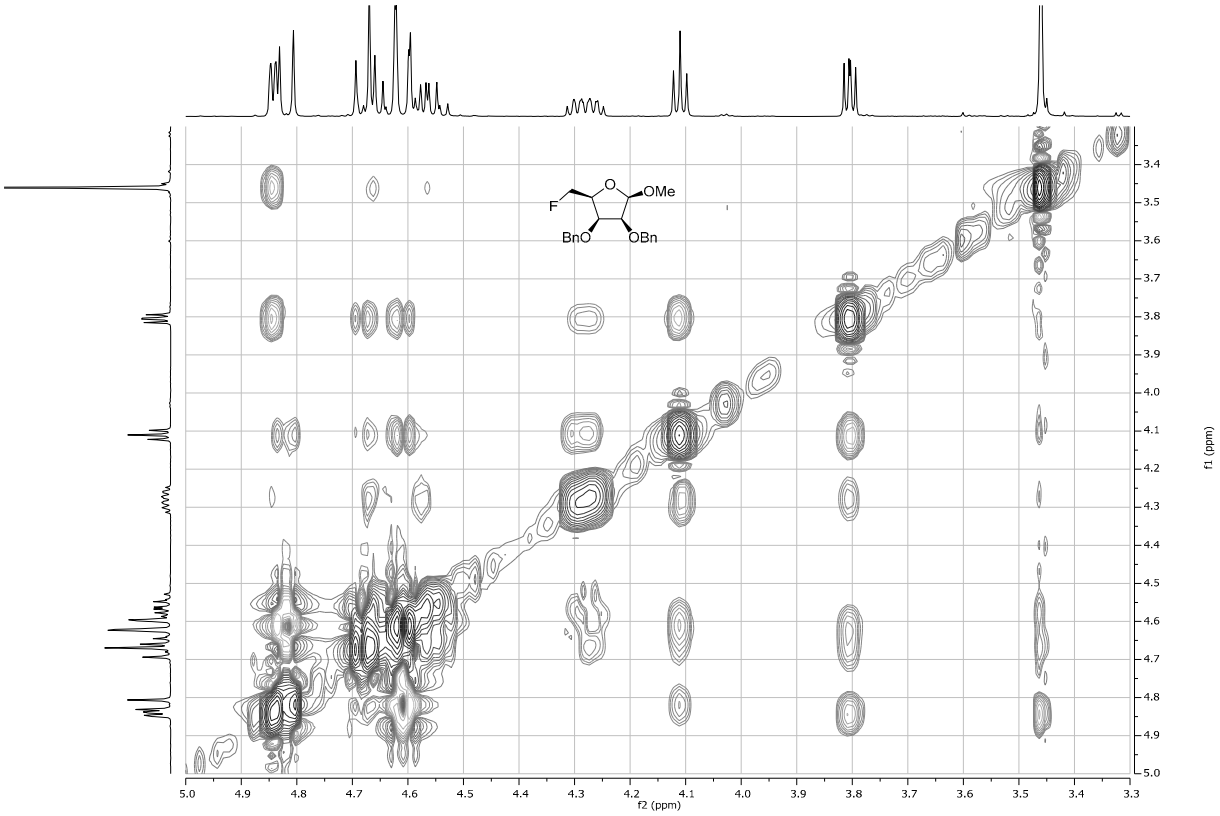
^{1}H-^{1}H COSY of compound **54β**



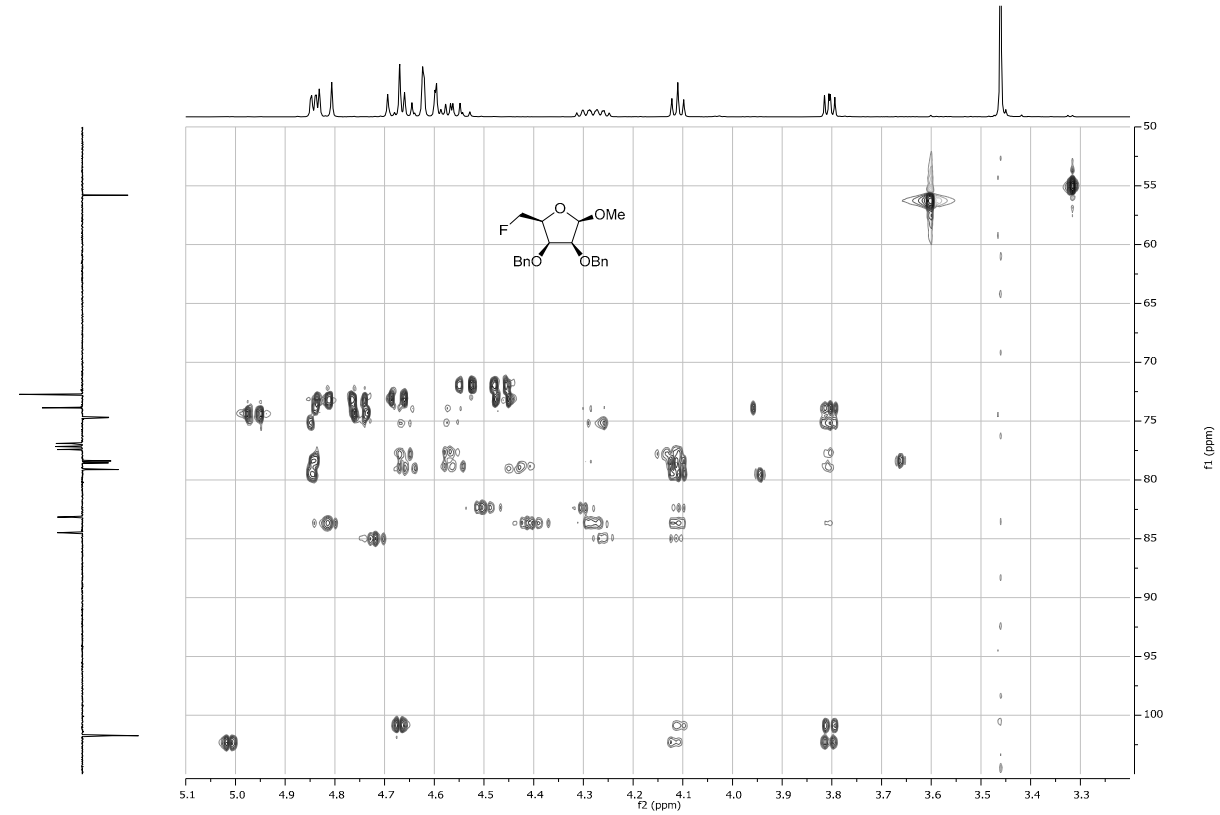
^{1}H-^{13}C HSQC of compound **54β**



^{1}H-^{1}H NOESY of compound **54β**

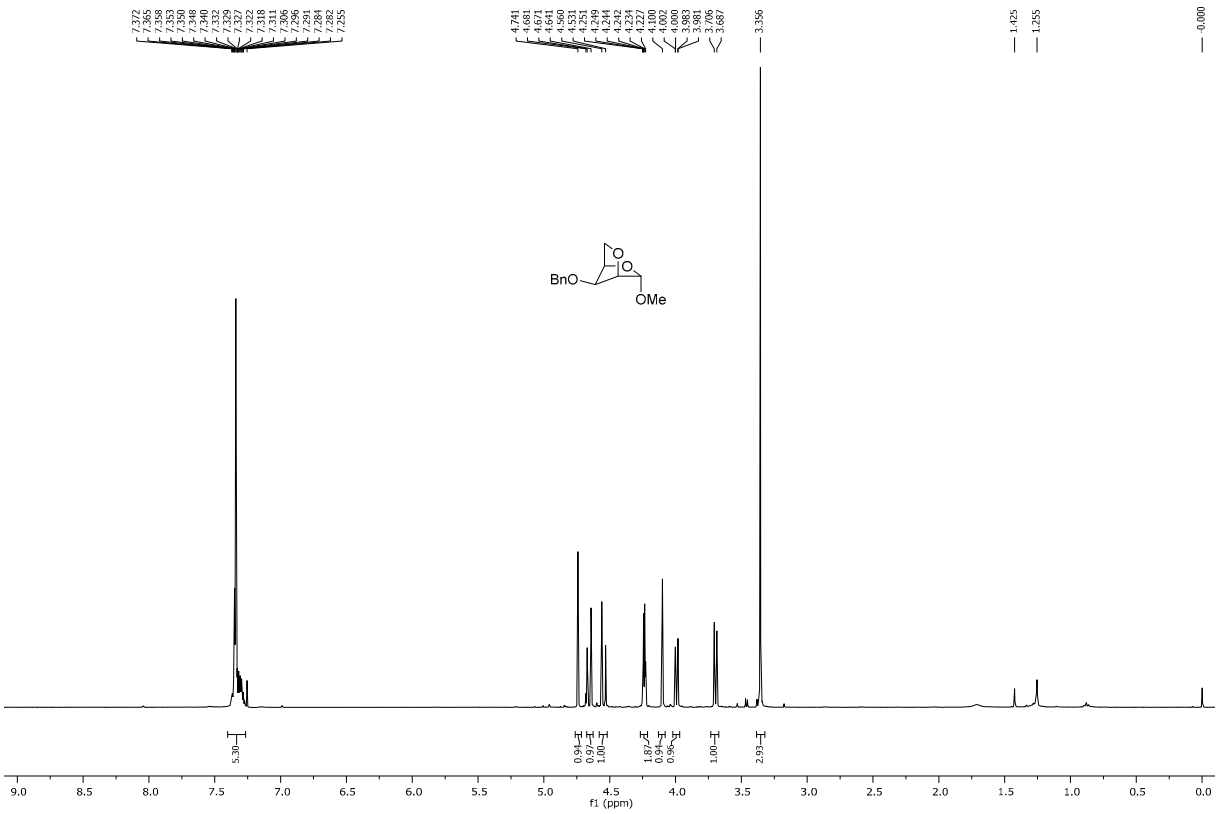


^{1}H-^{13}C HSQC-HECADE of compound **54β**

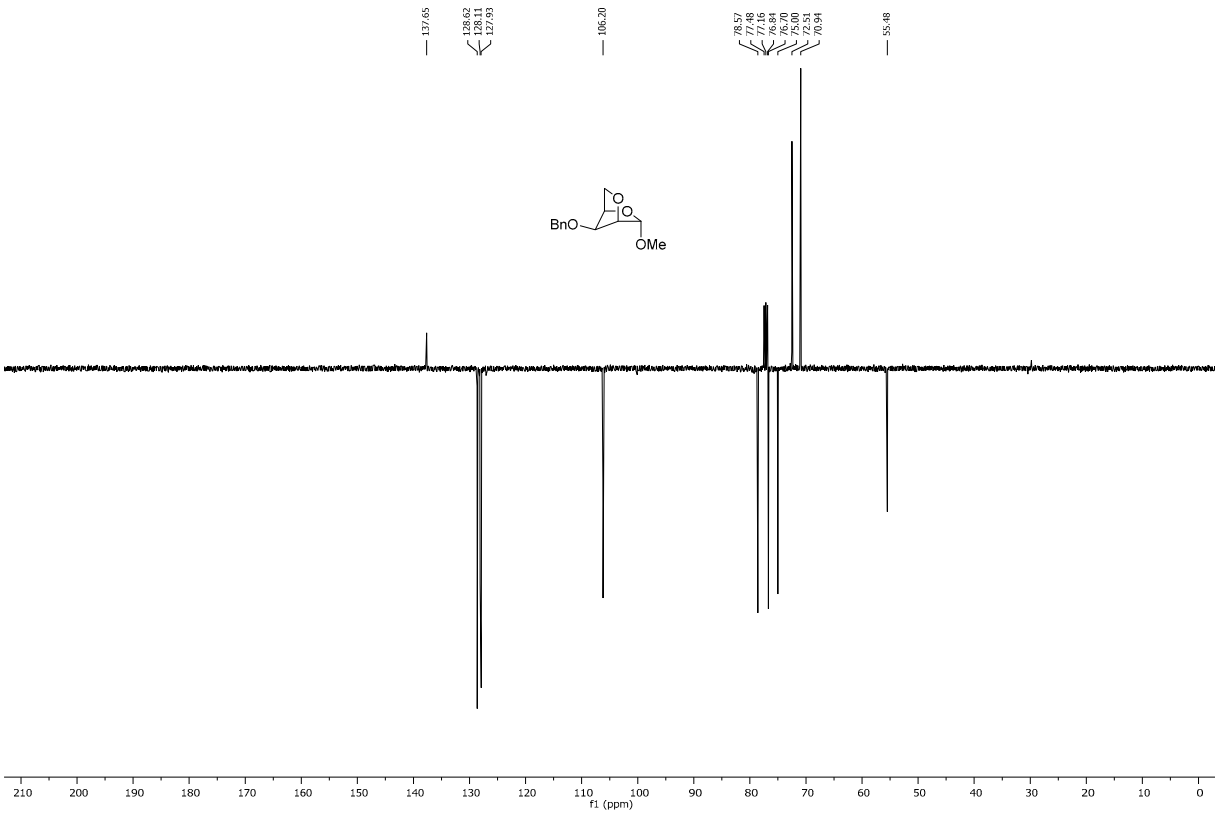


Methyl 2,5-anhydro-3-*O*-benzyl-α-D-lyxofuranoside (55)

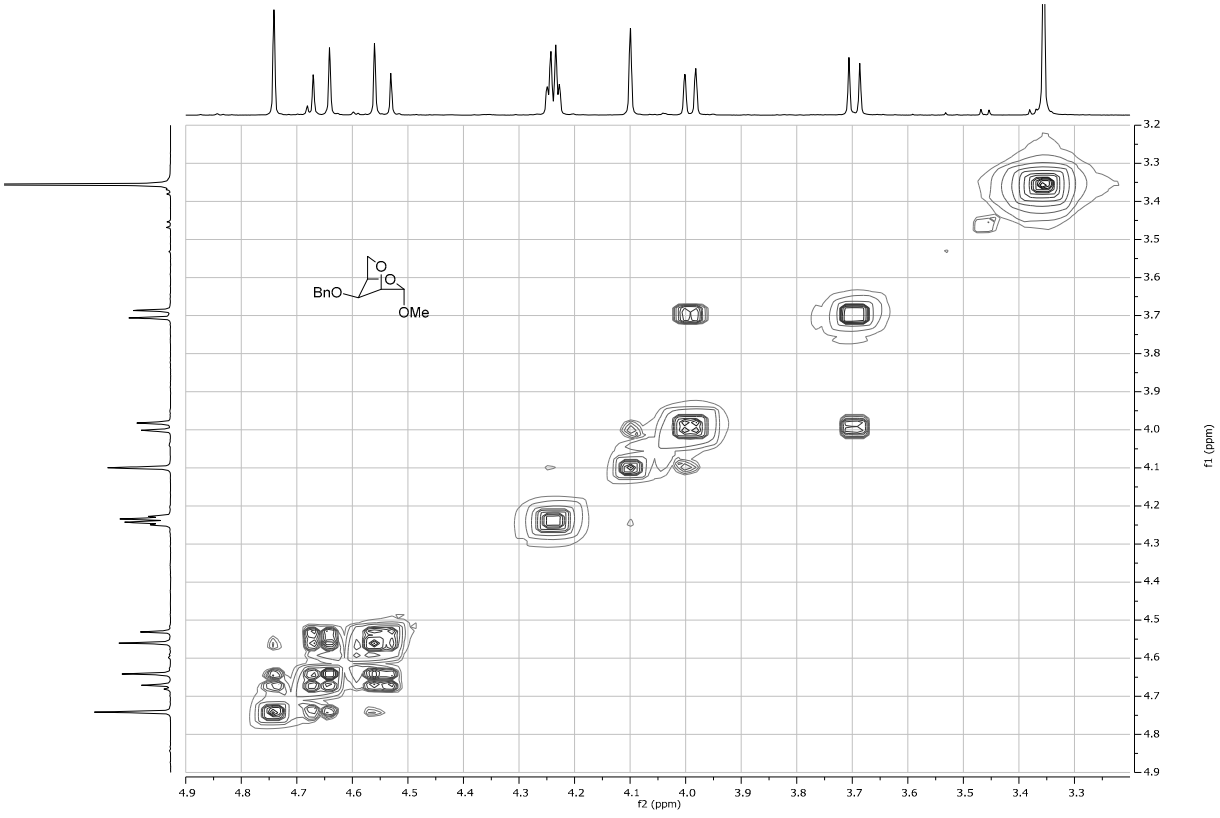
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **55**



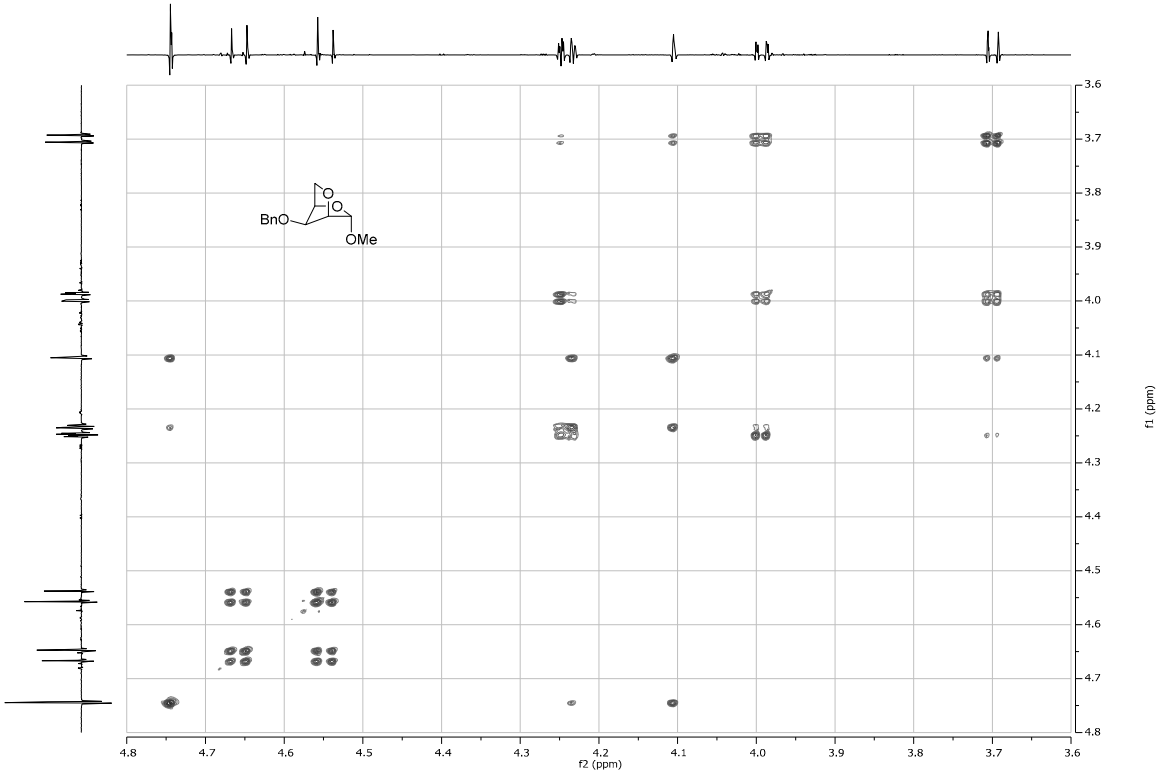
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **55**



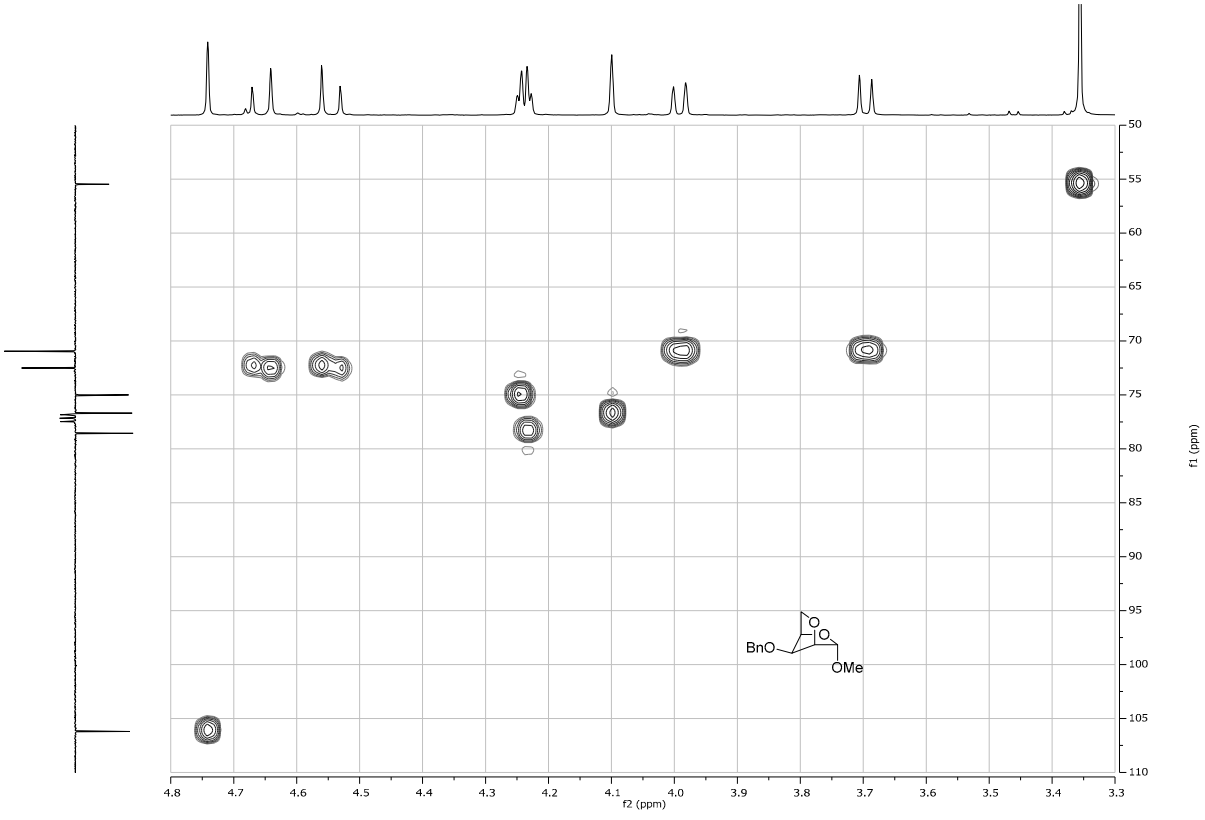
^{1}H-^{1}H COSY of compound **55**



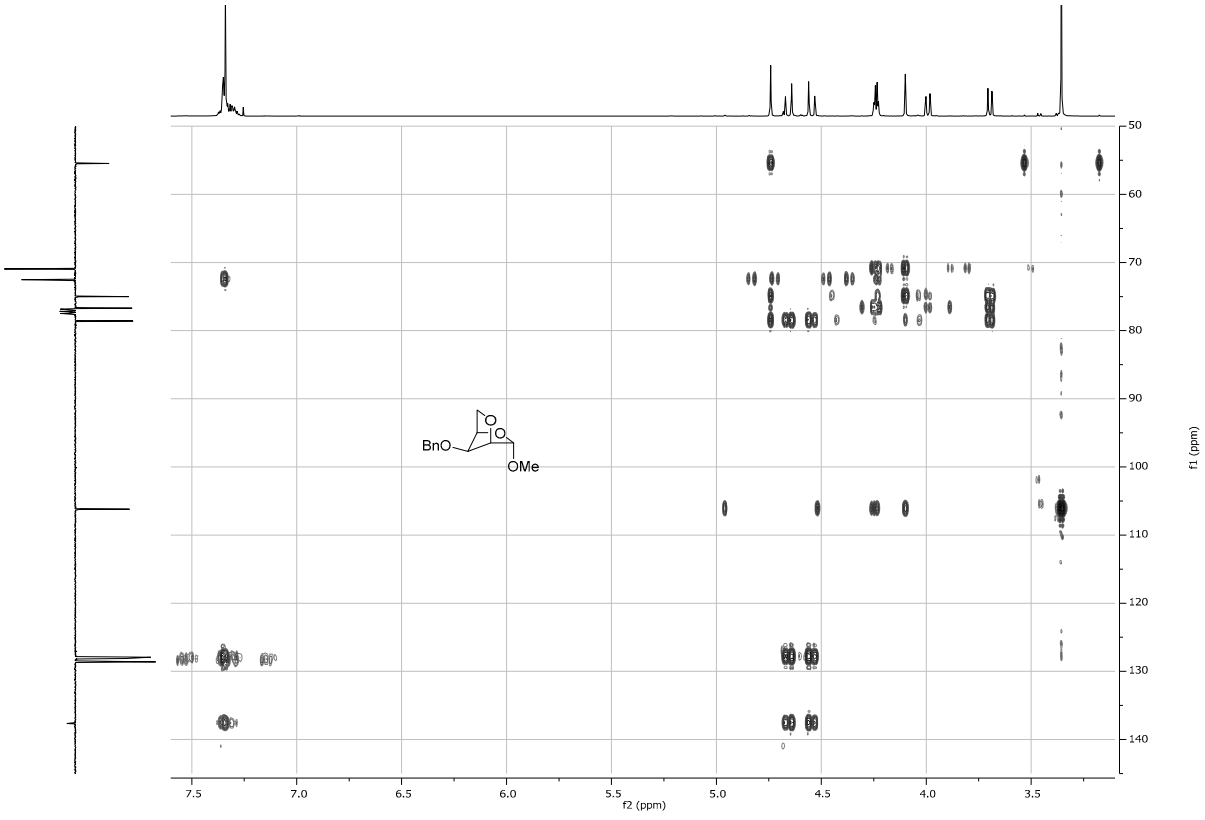
^{1}H-^{1}H COSY, optimized for long-range coupling constants (600 MHz) of compound **55**



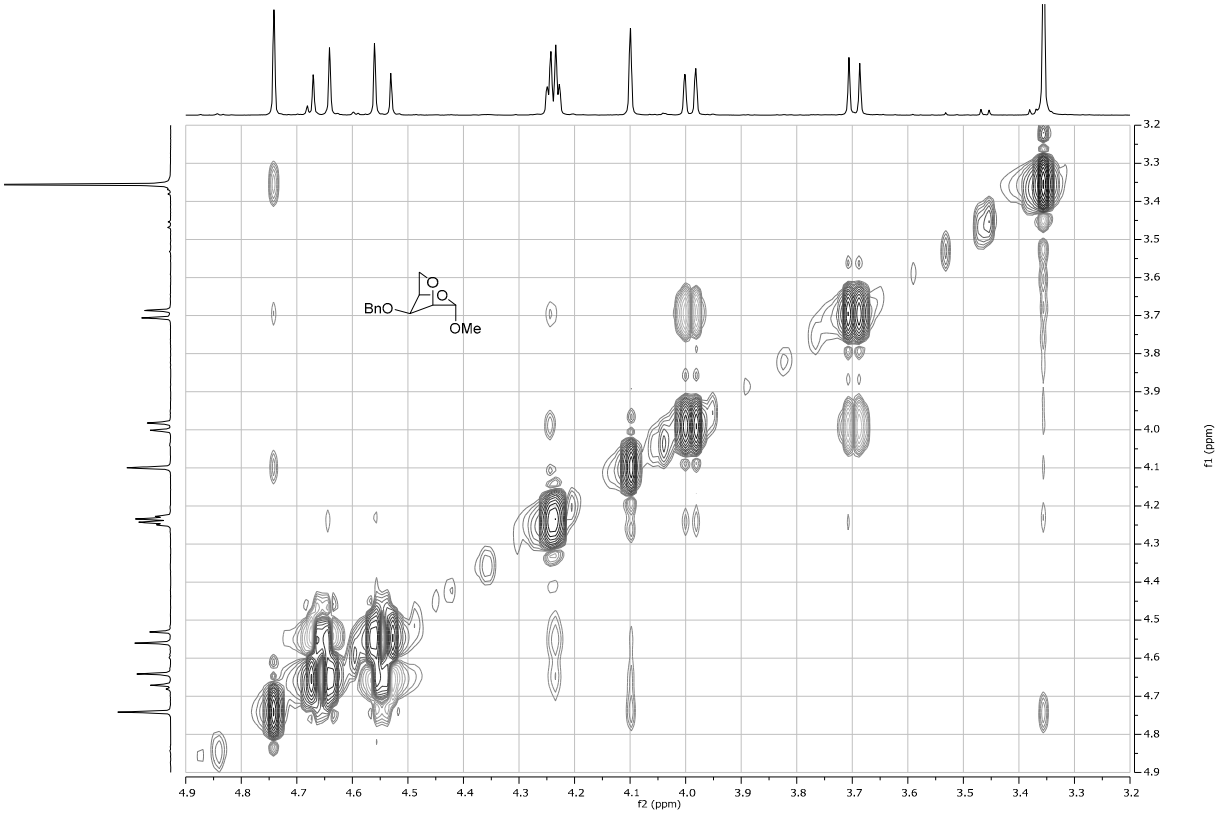
^{1}H-^{13}C HSQC of compound **55**



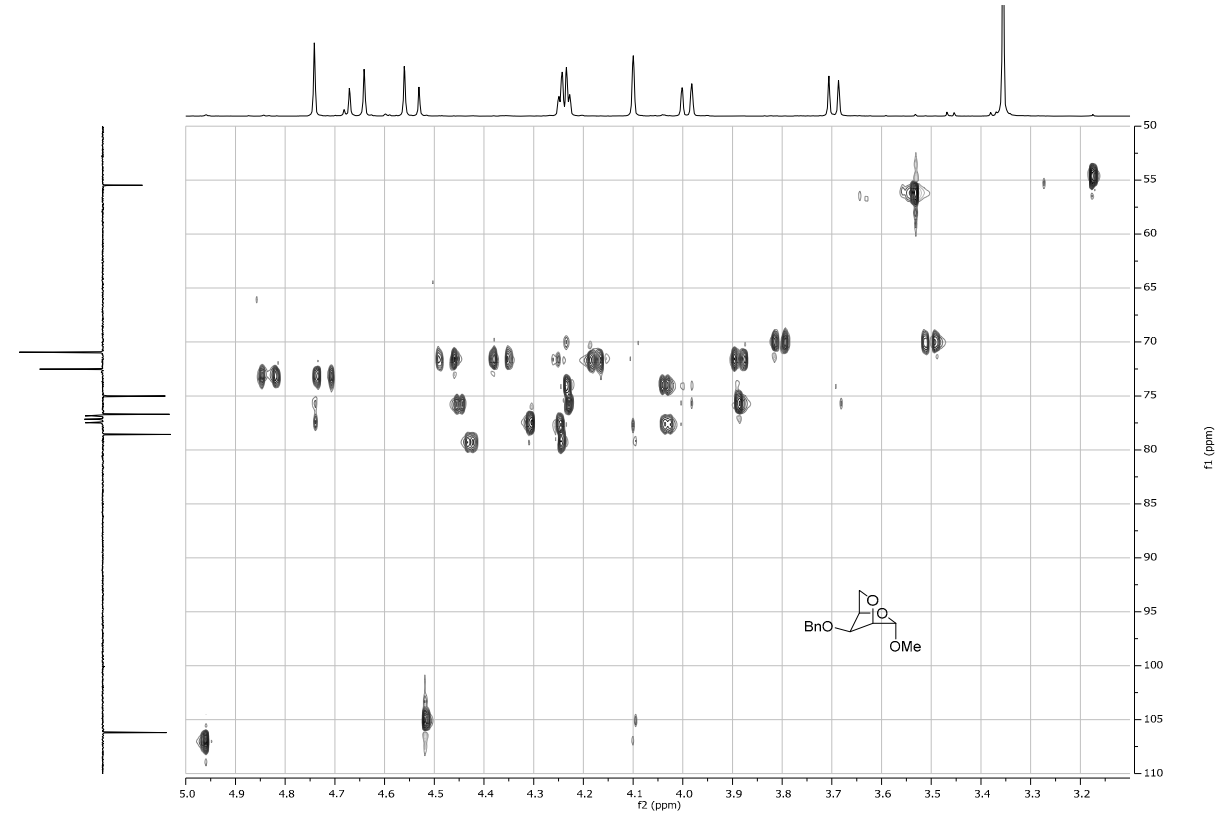
^{1}H-^{13}C HMBC of compound **55**



^{1}H-^{1}H NOESY of compound **55**

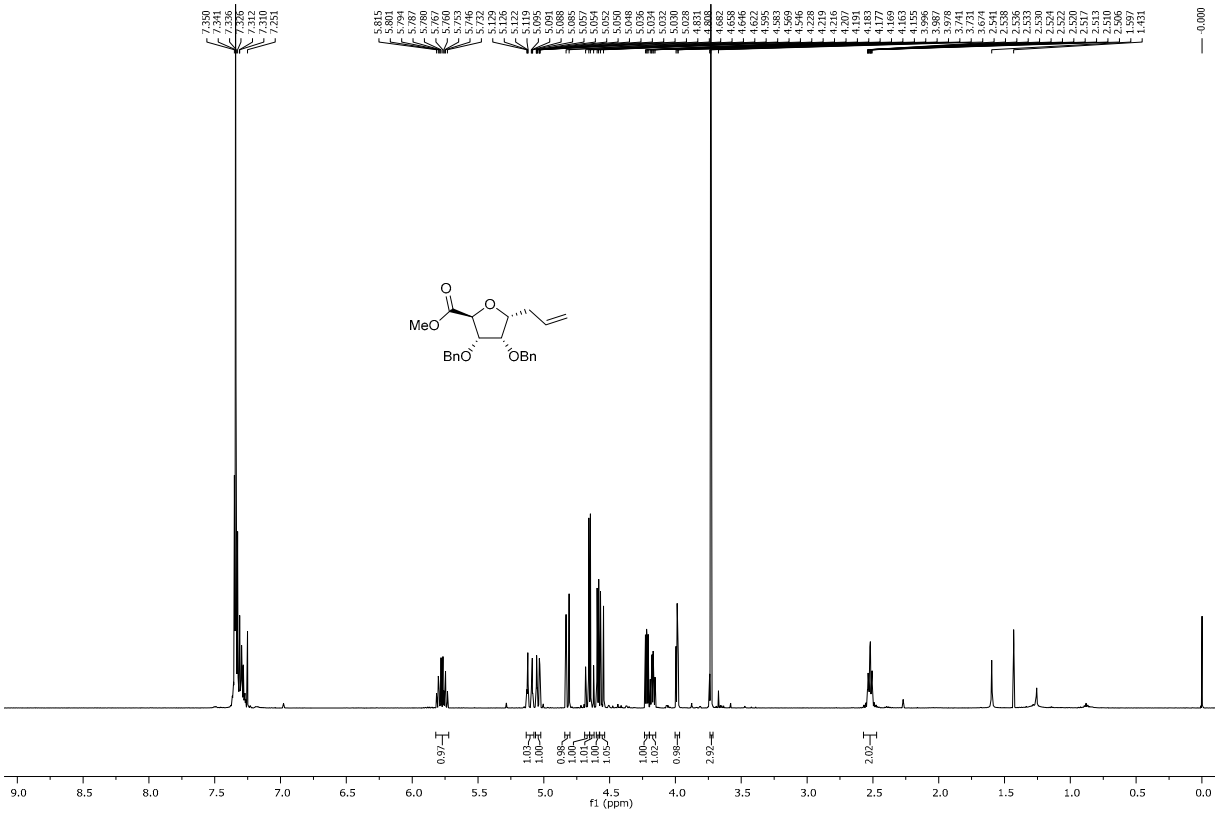


^{1}H-^{13}C HSQC-HECADE of compound **55**

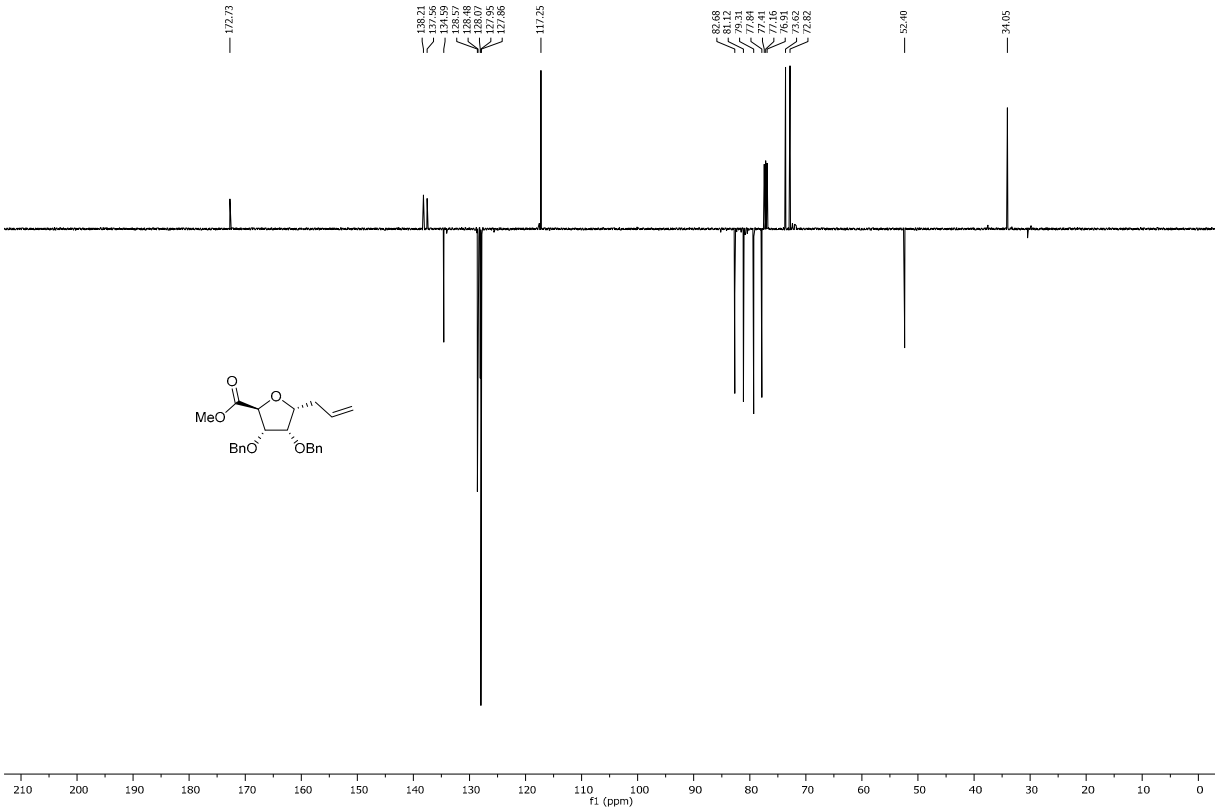


Methyl (1-allyl-2,3-di-*O*-benzyl-1-deoxy-α-D-ribofuranosyl uronate) (65)

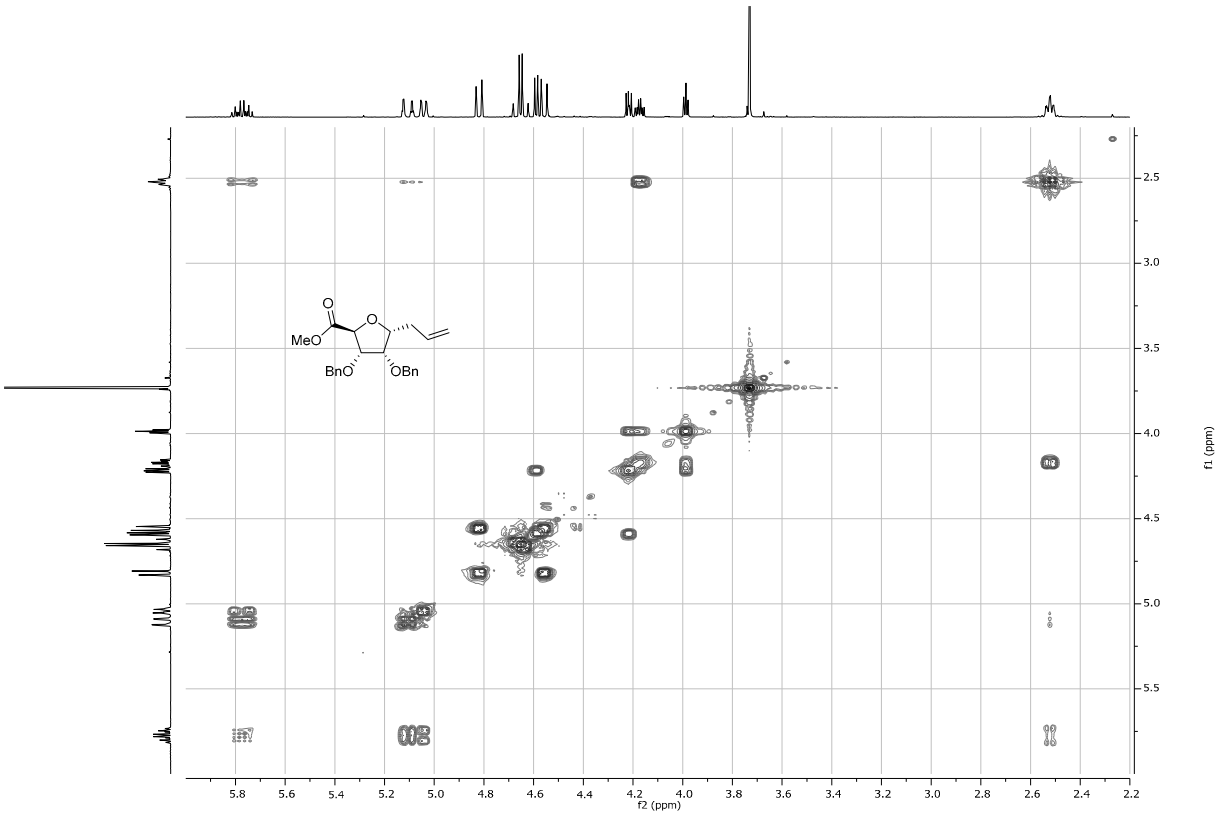
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **65**



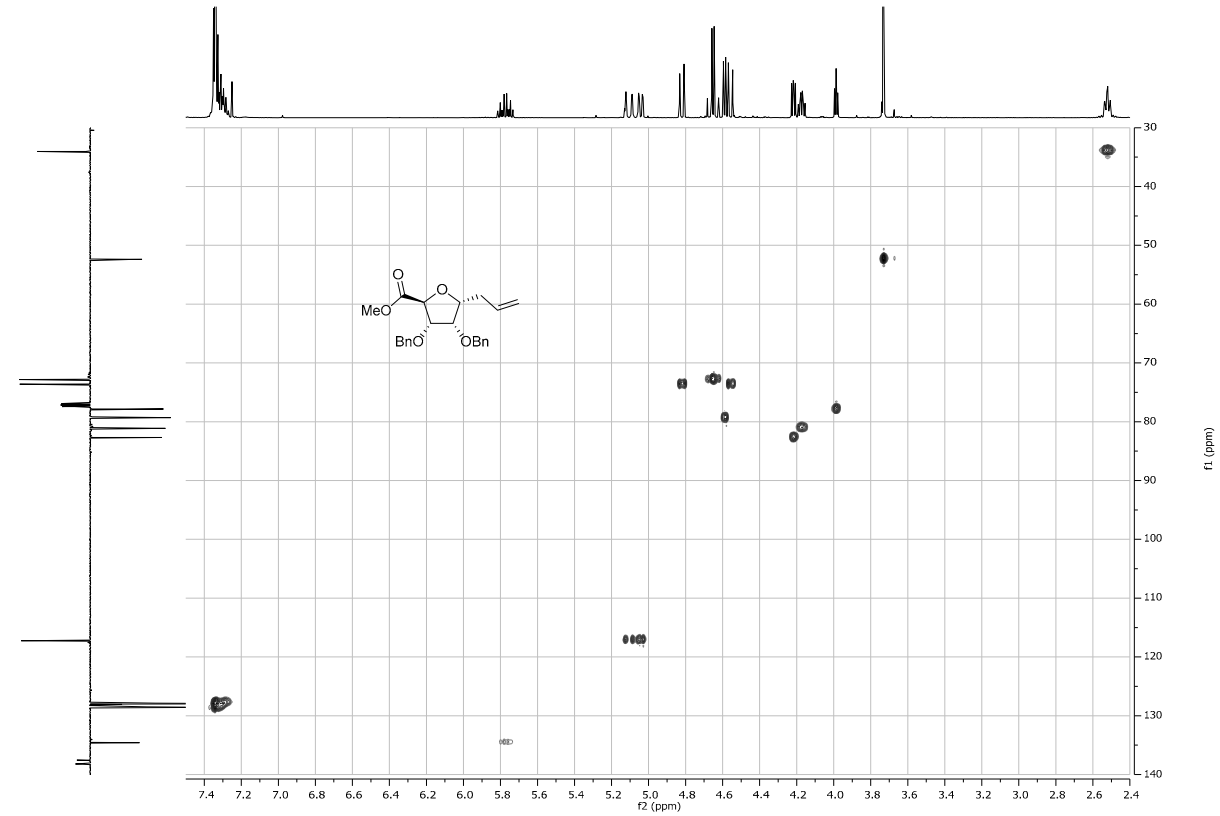
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **65**



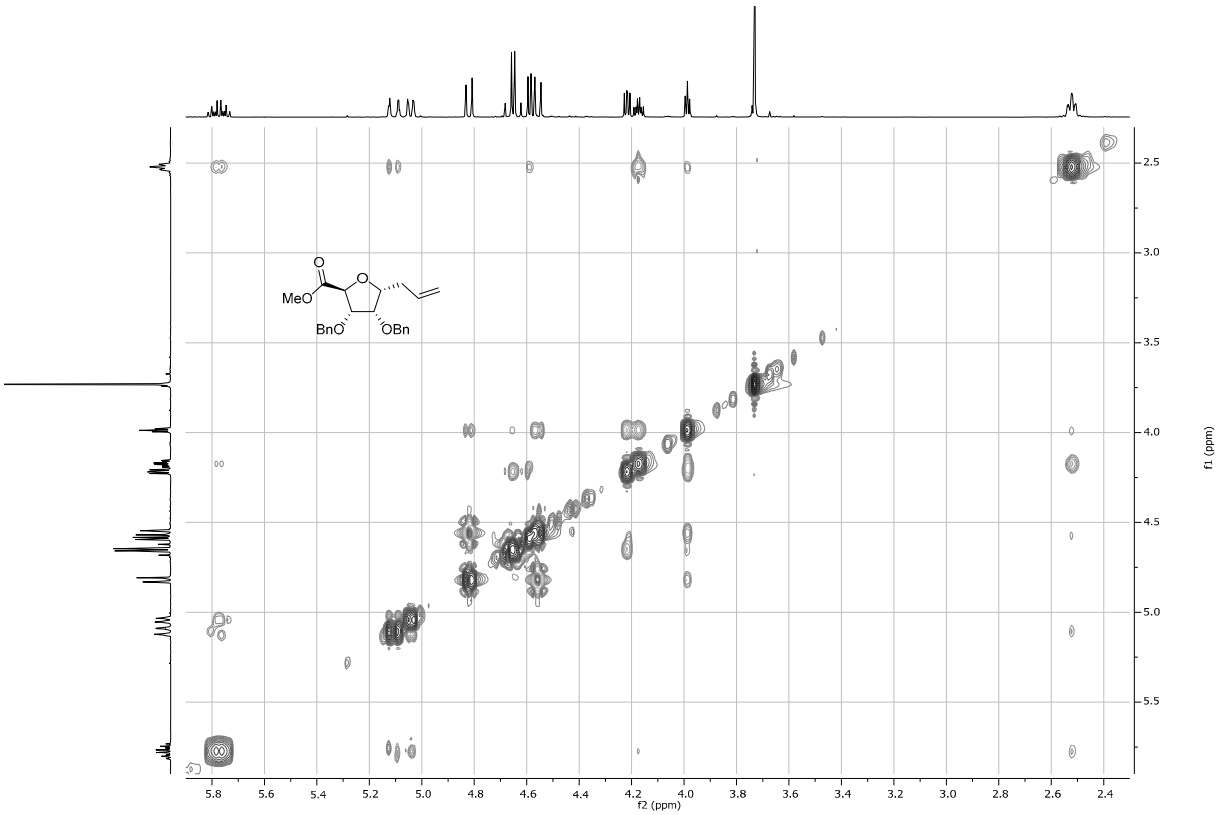
^{1}H-^{1}H COSY of compound **65**



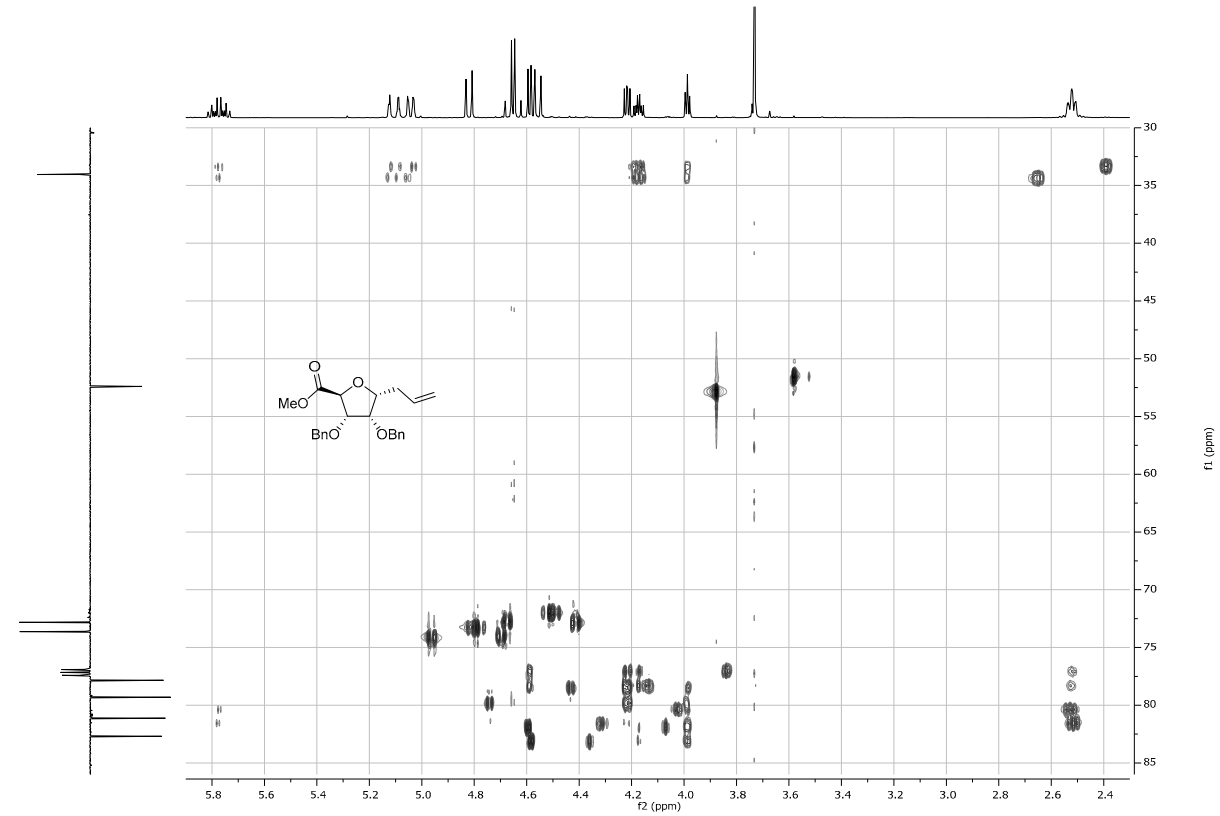
^{1}H-^{13}C HSQC of compound **65**



^{1}H-^{1}H NOESY of compound **65**

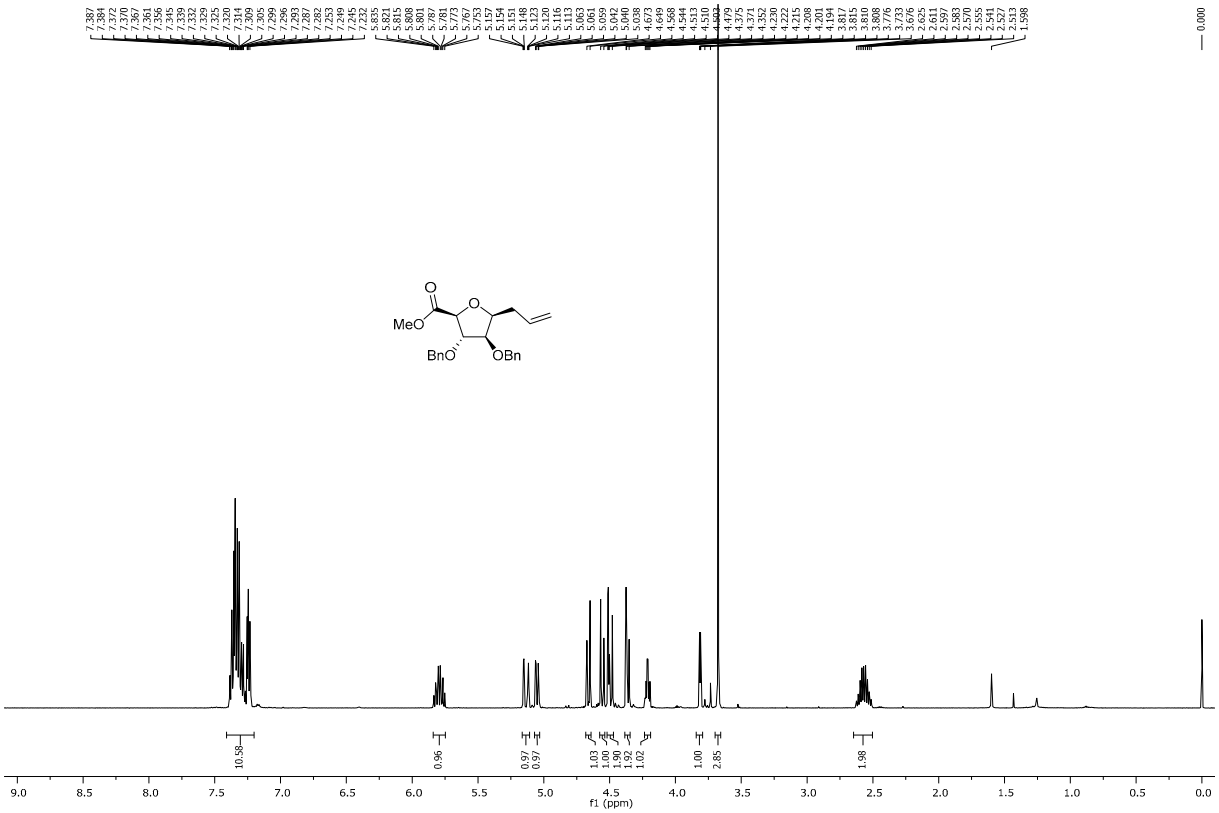


^{1}H-^{13}C HSQC-HECADE of compound **65**

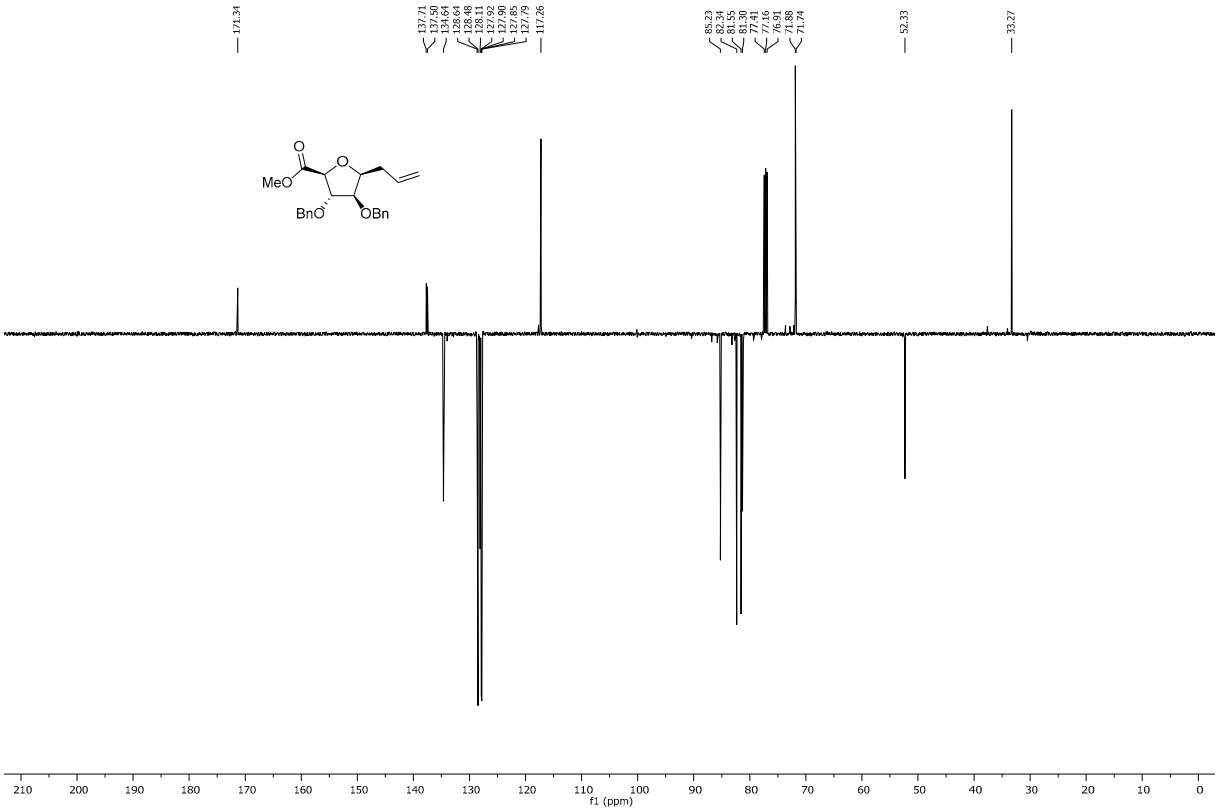


Methyl (1-allyl-2,3-di-*O*-benzyl-1-deoxy-β-D-arabinofuranosyl uronate) (66)

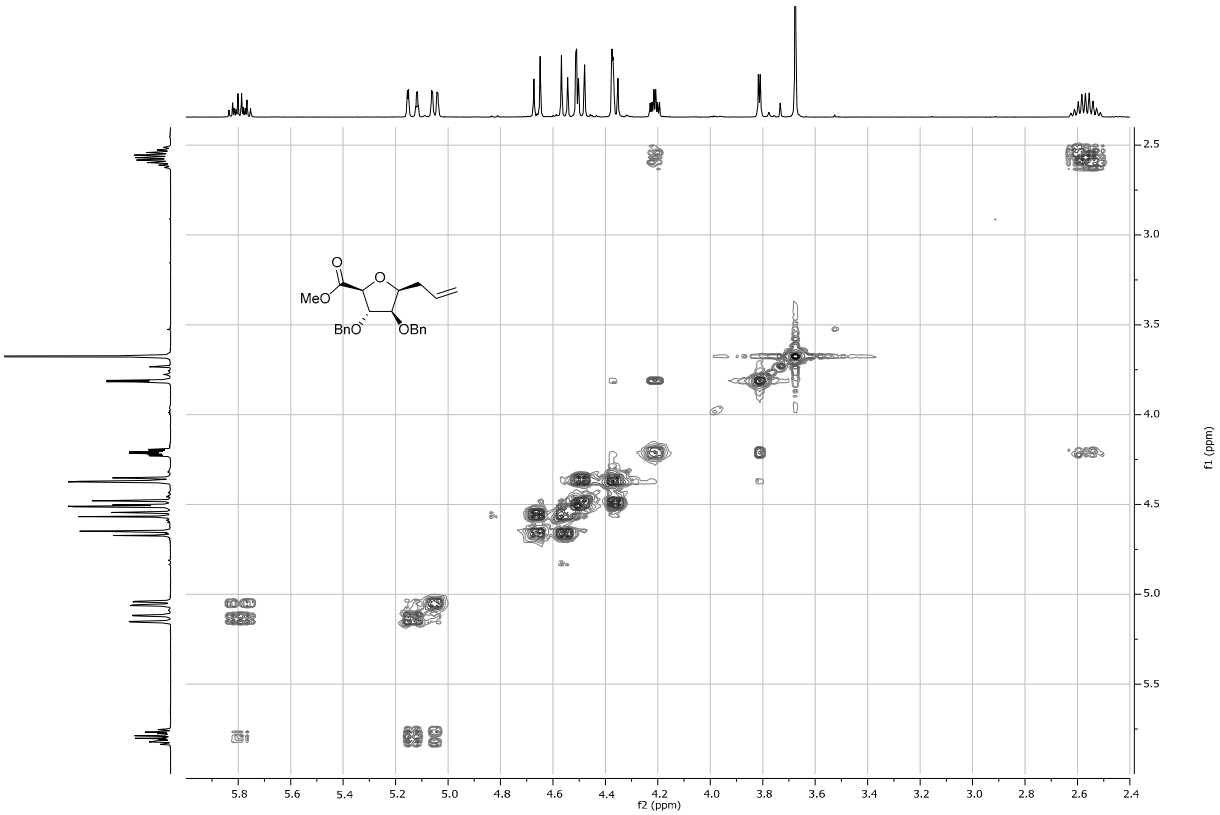
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **66**



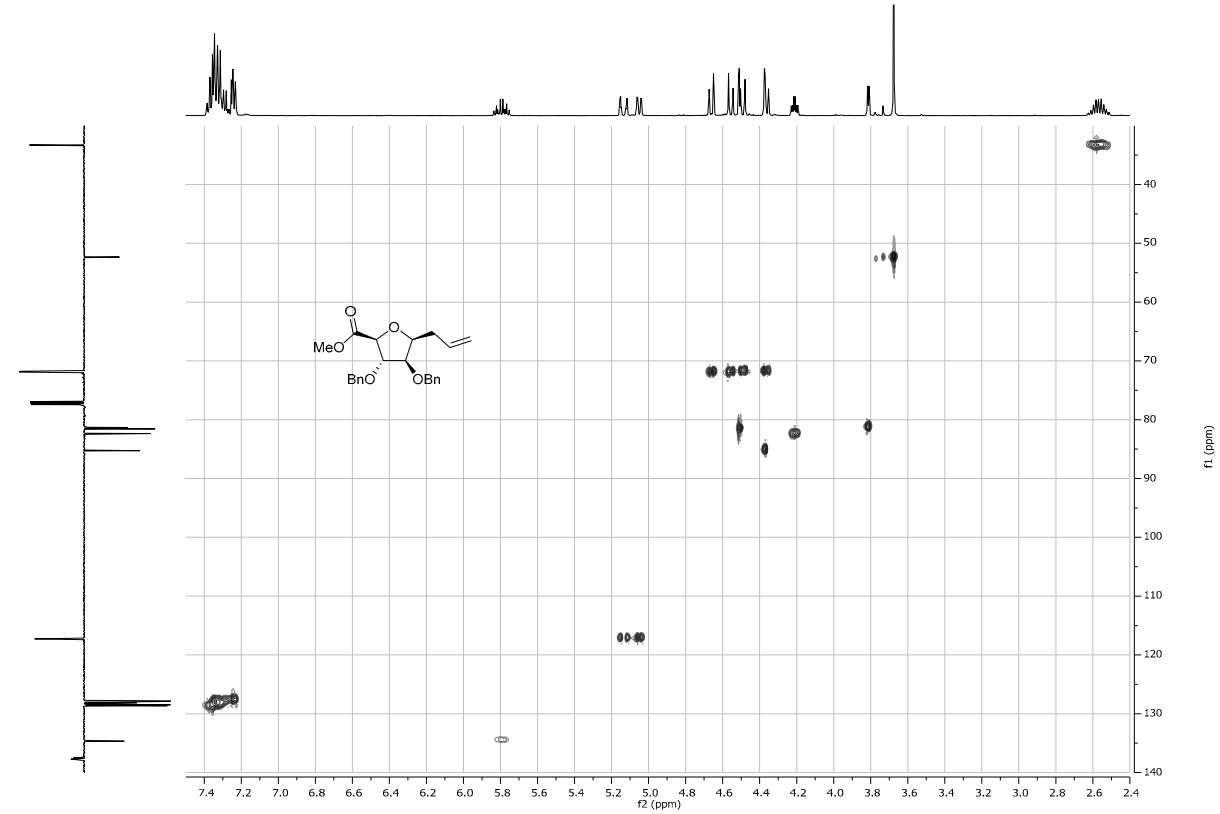
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **66**



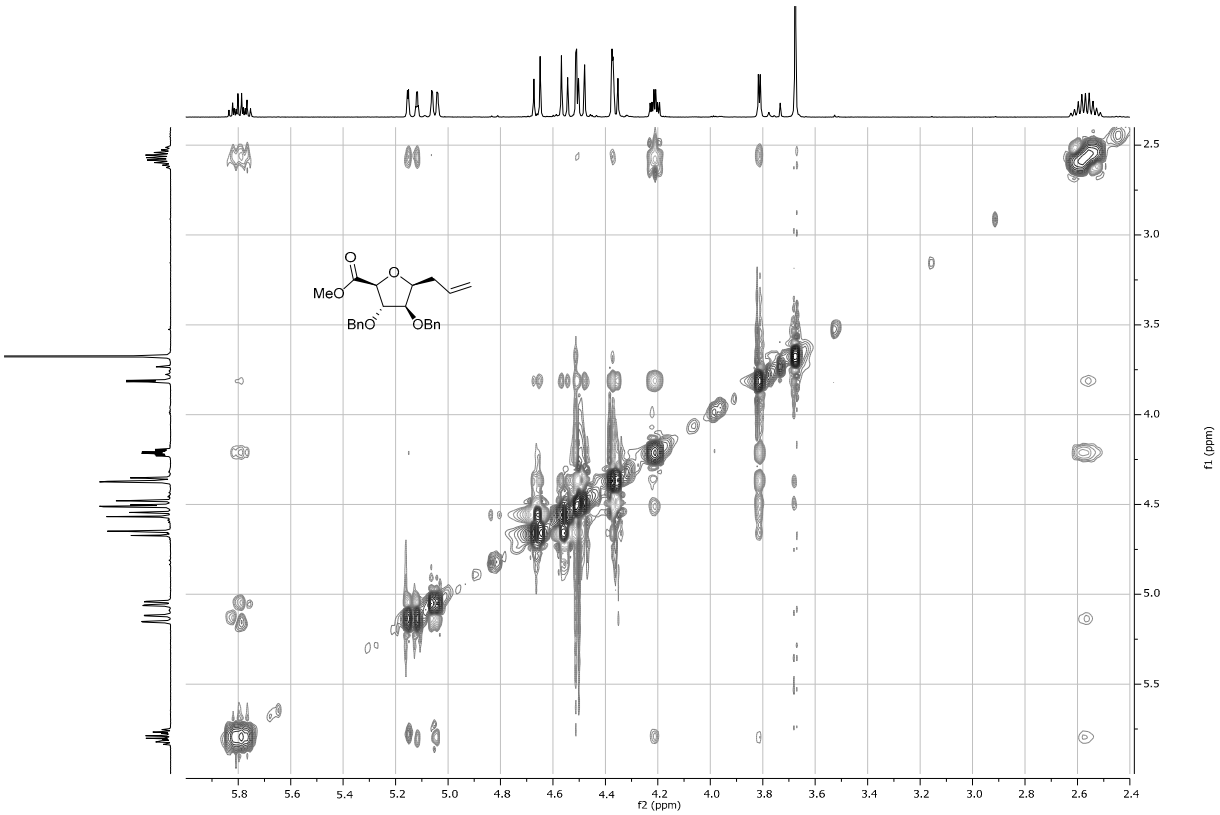
^{1}H-^{1}H COSY of compound **66**



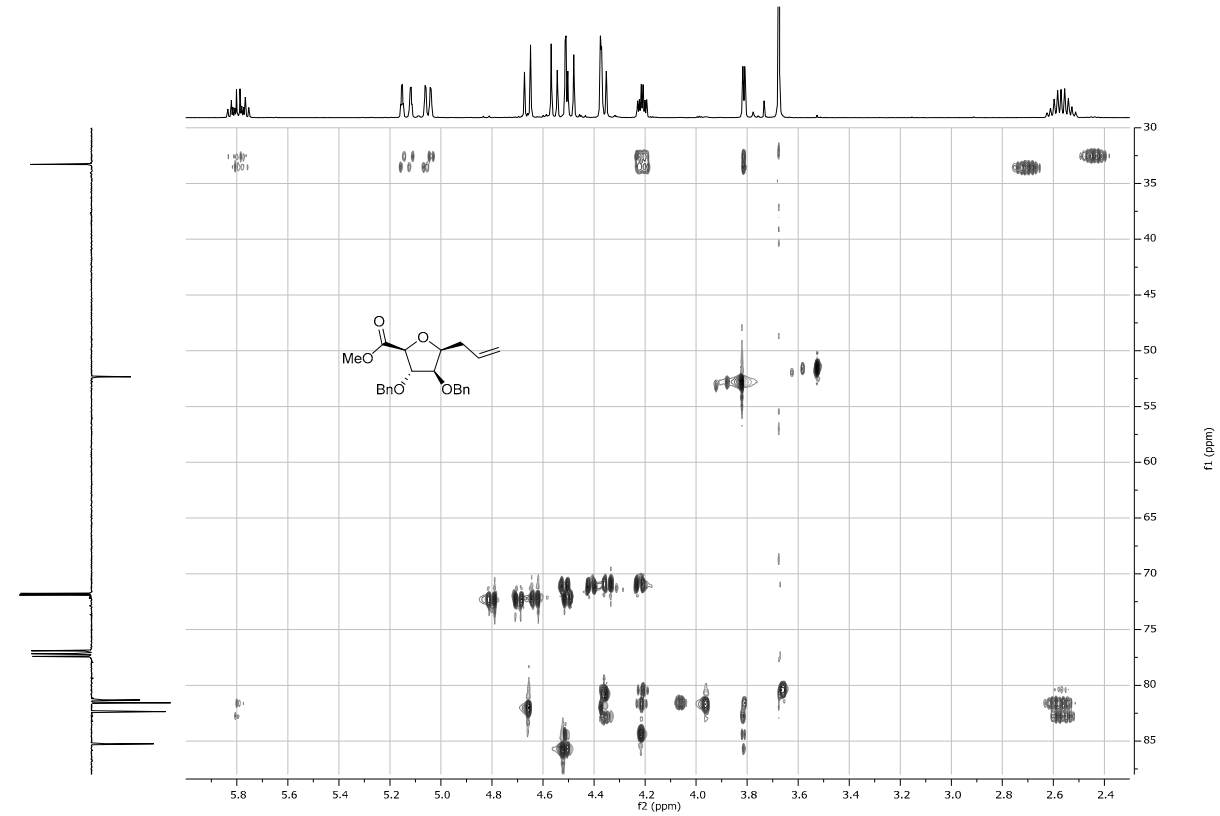
^{1}H-^{13}C HSQC of compound **66**



^{1}H-^{1}H NOESY of compound **66**

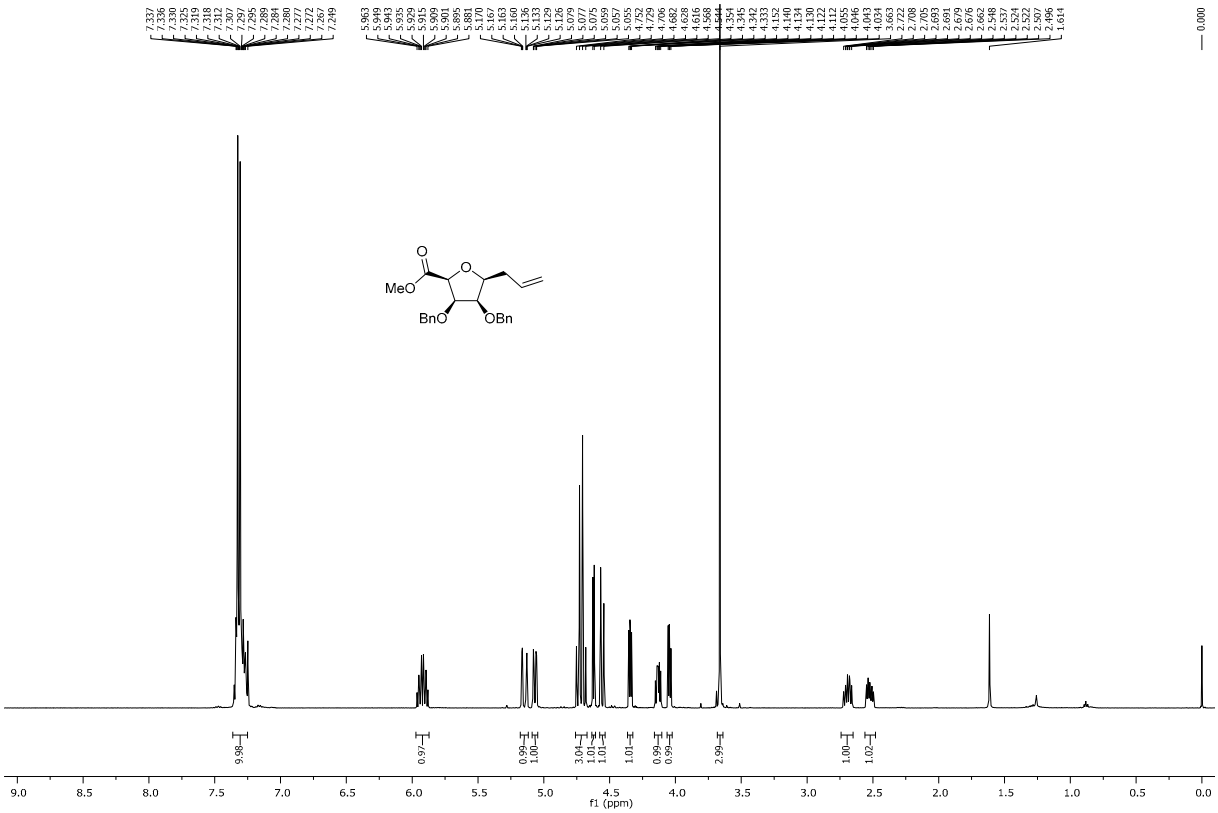


^{1}H-^{13}C HSQC-HECADE of compound **66**

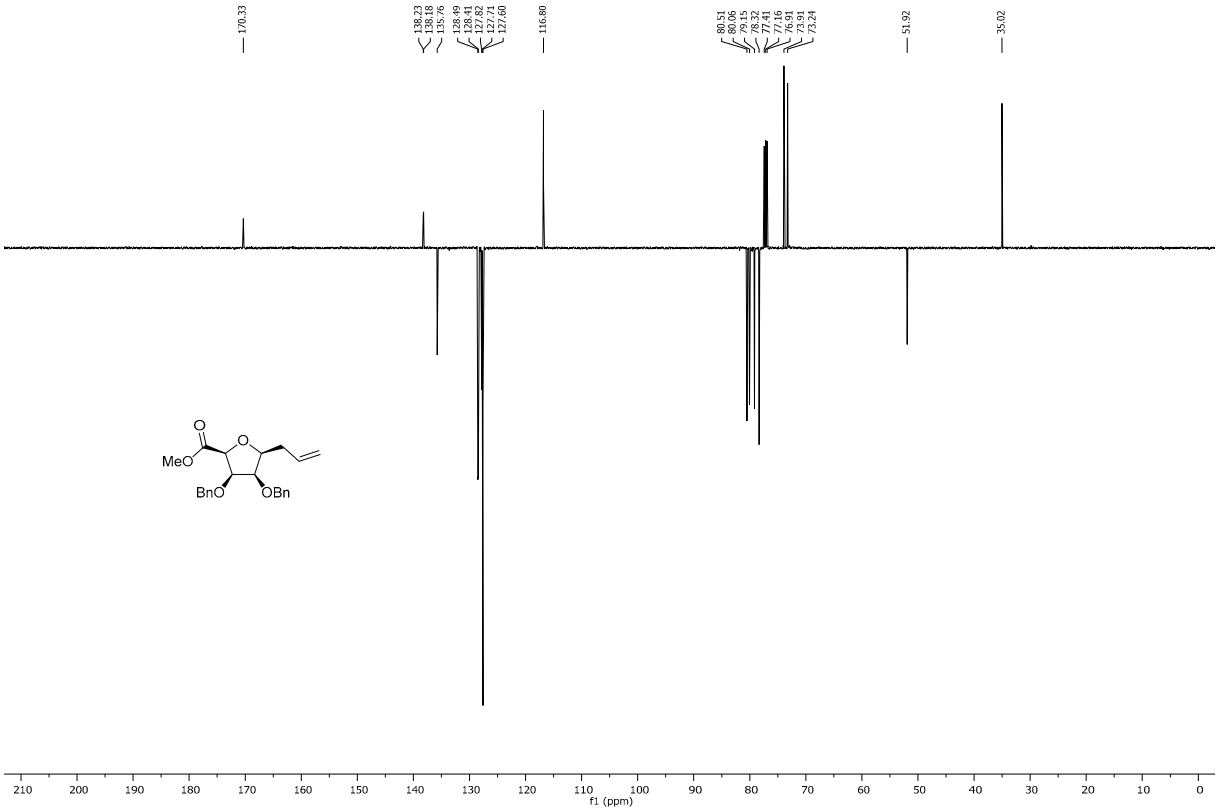


Methyl (1-allyl-2,3-di-*O*-benzyl-1-deoxy-β-D-lyxofuranosyl uronate) (67)

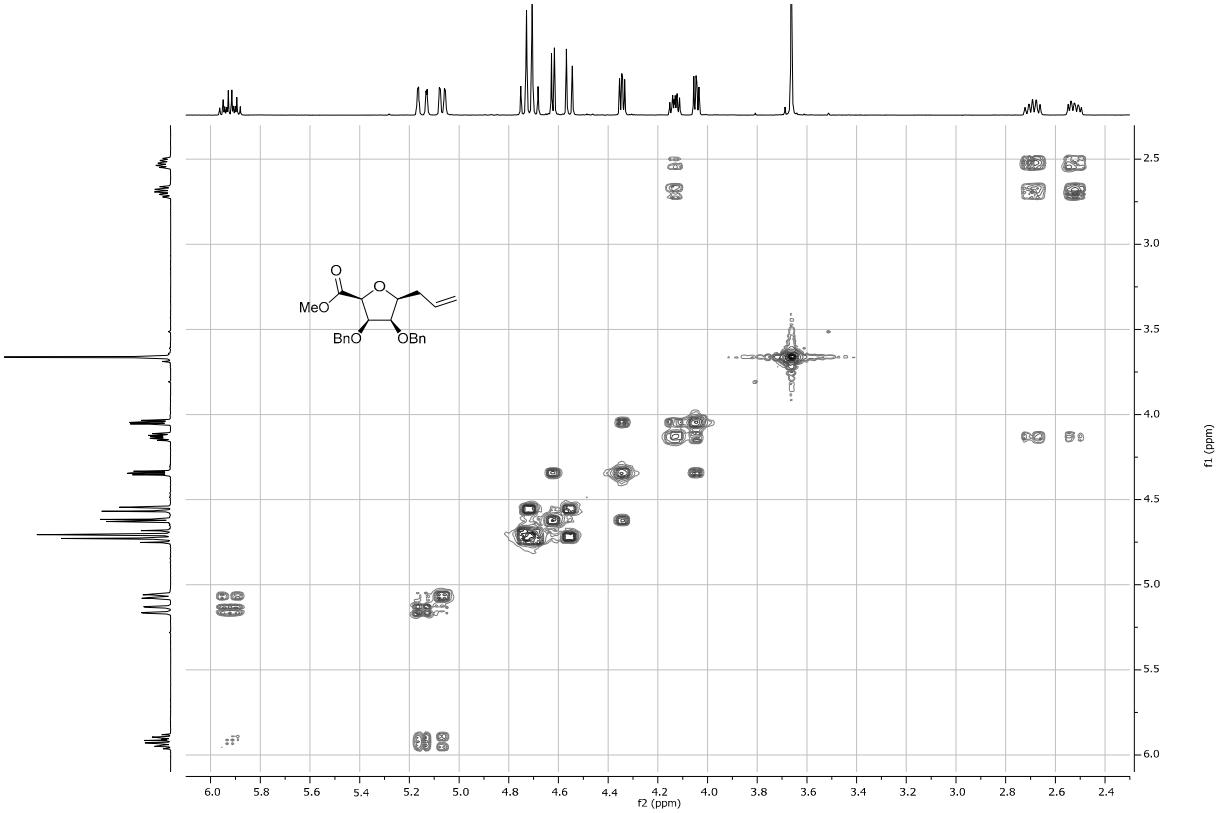
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **67**



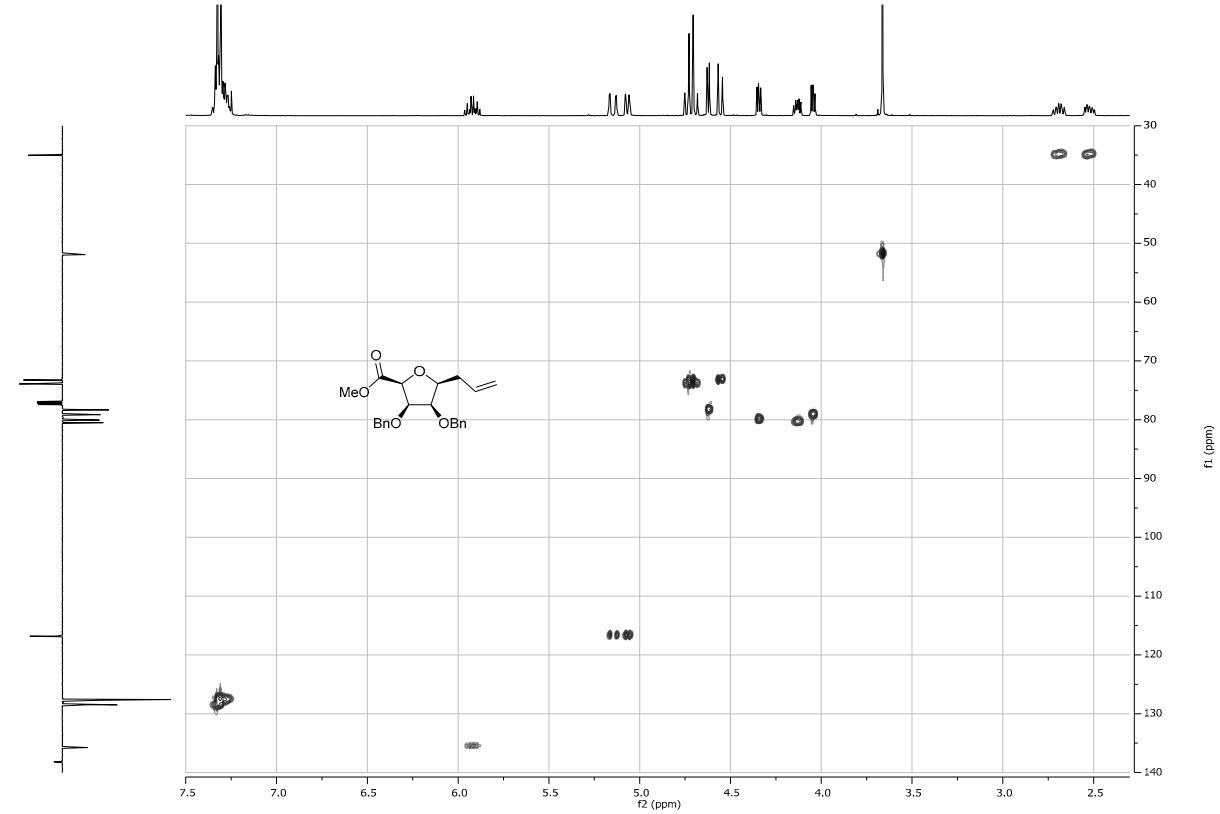
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **67**



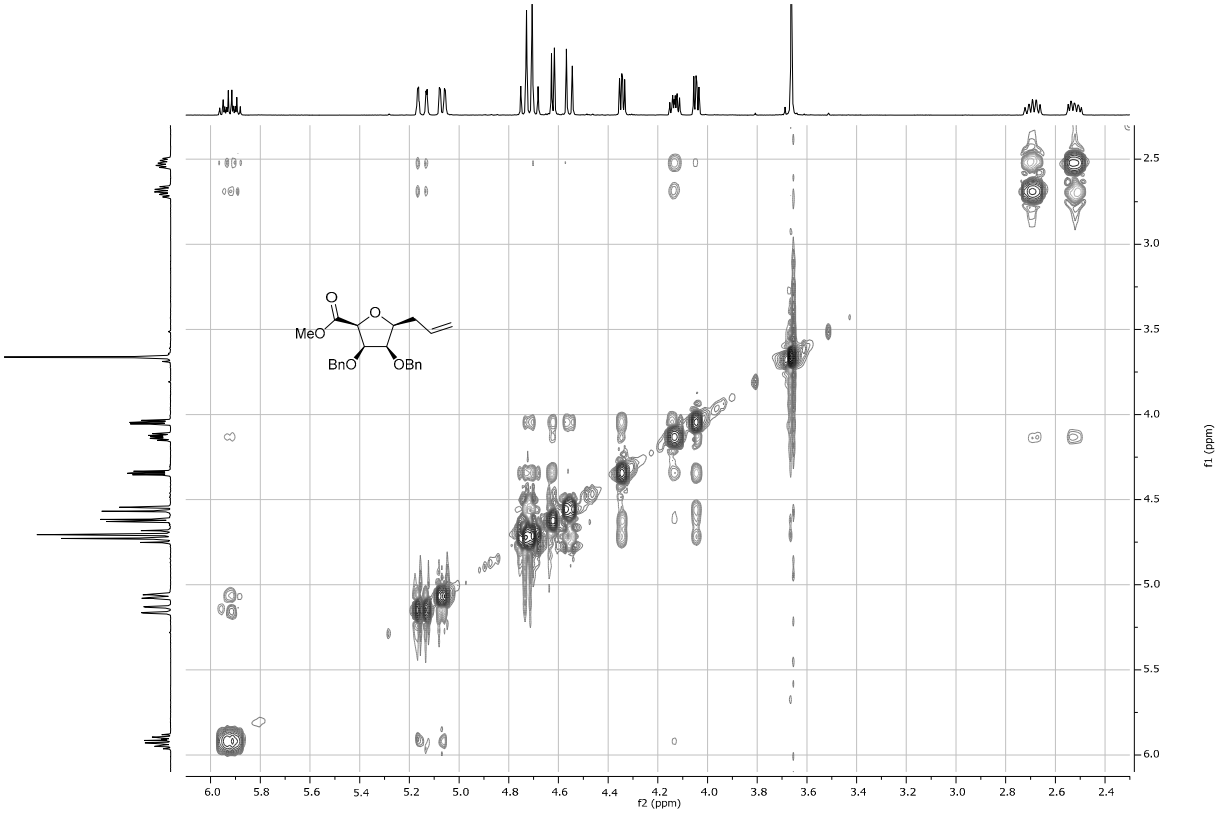
^{1}H-^{1}H COSY of compound **67**



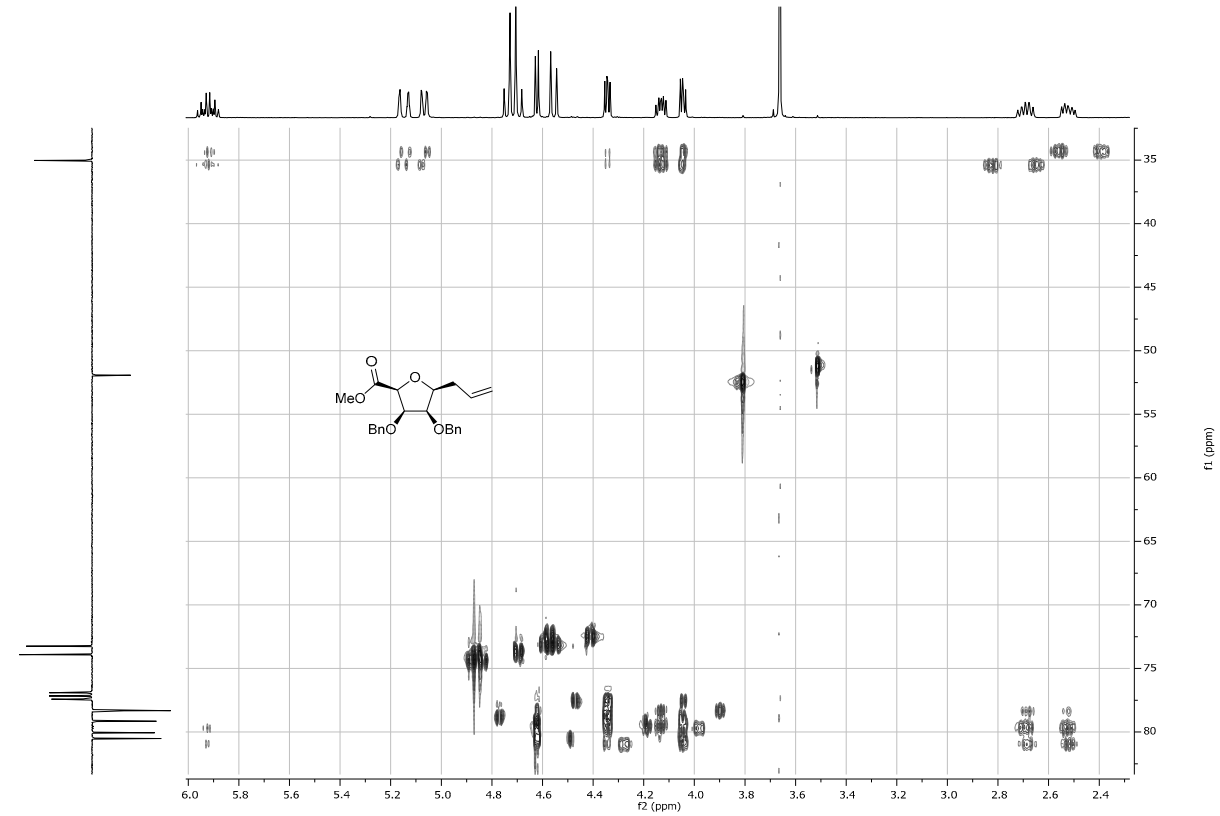
^{1}H-^{13}C HSQC of compound **67**



^{1}H-^{1}H NOESY of compound **67**

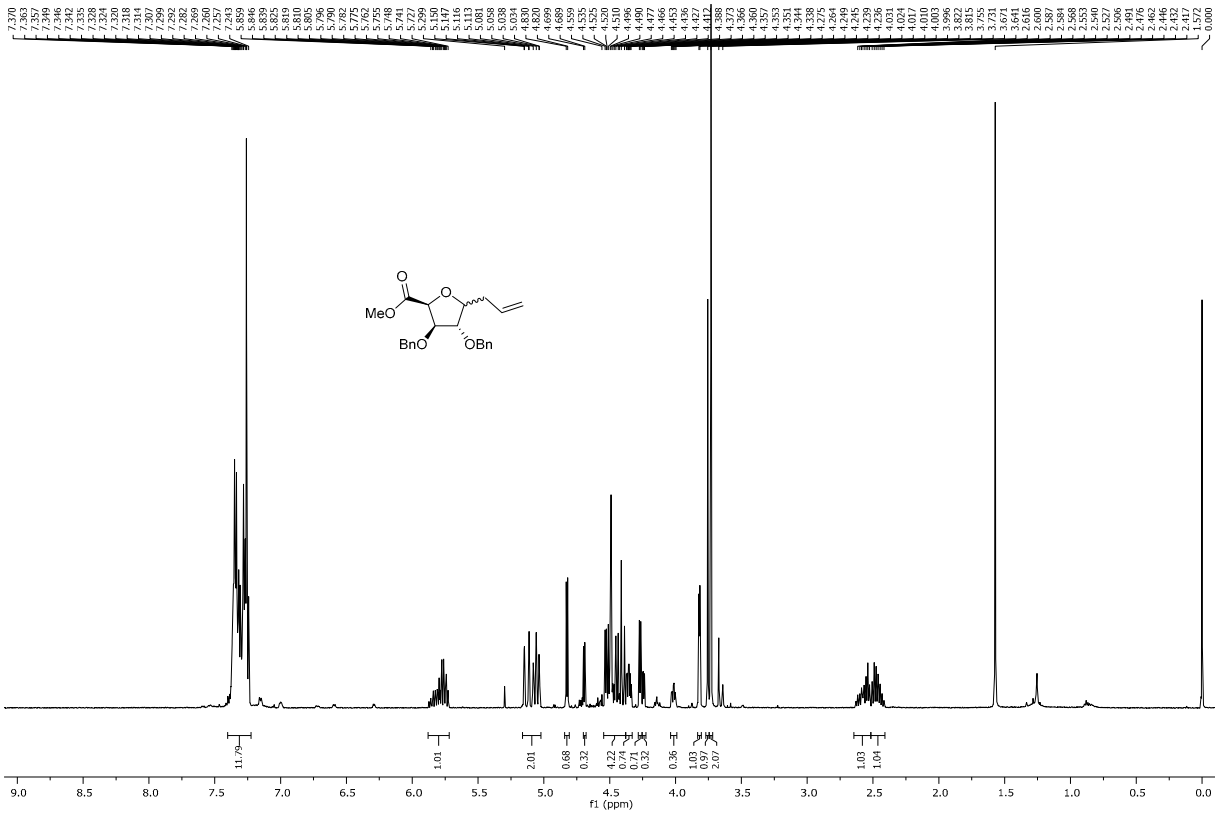


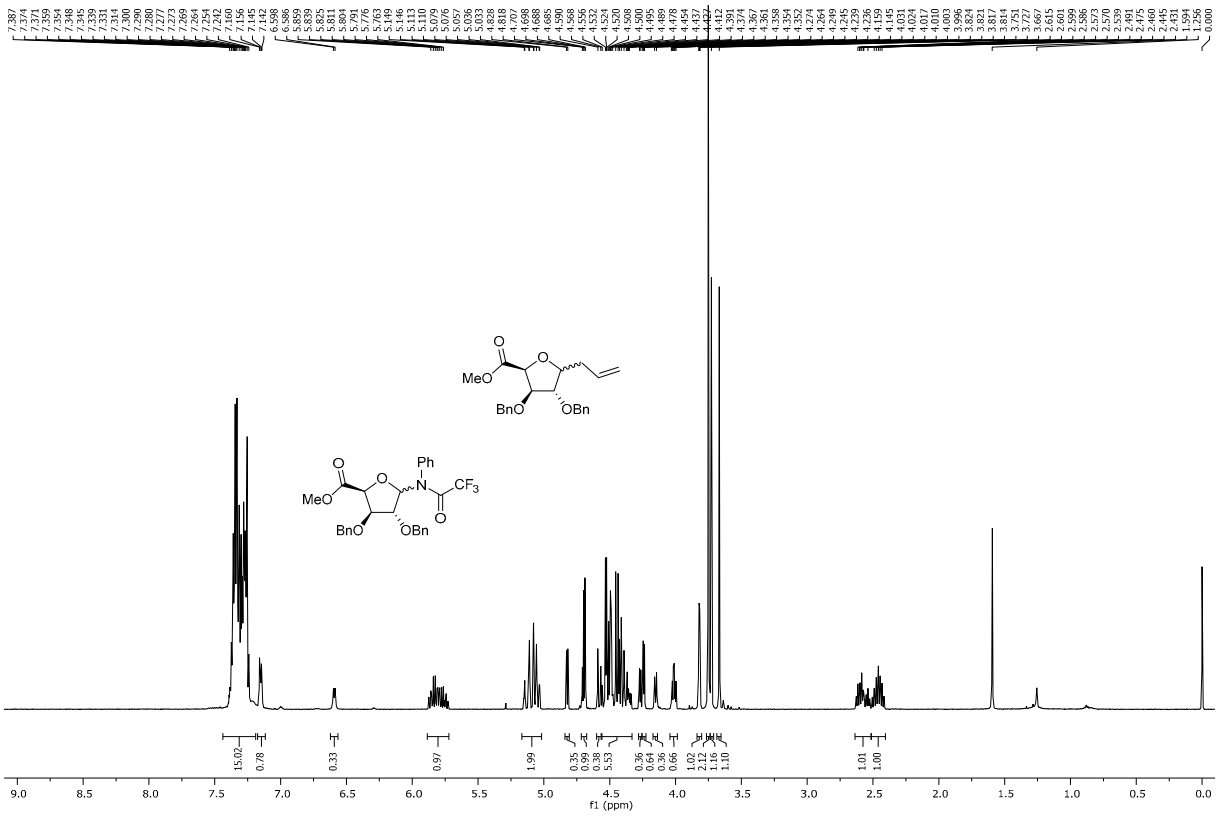
^{1}H-^{13}C HSQC-HECADE of compound **67**

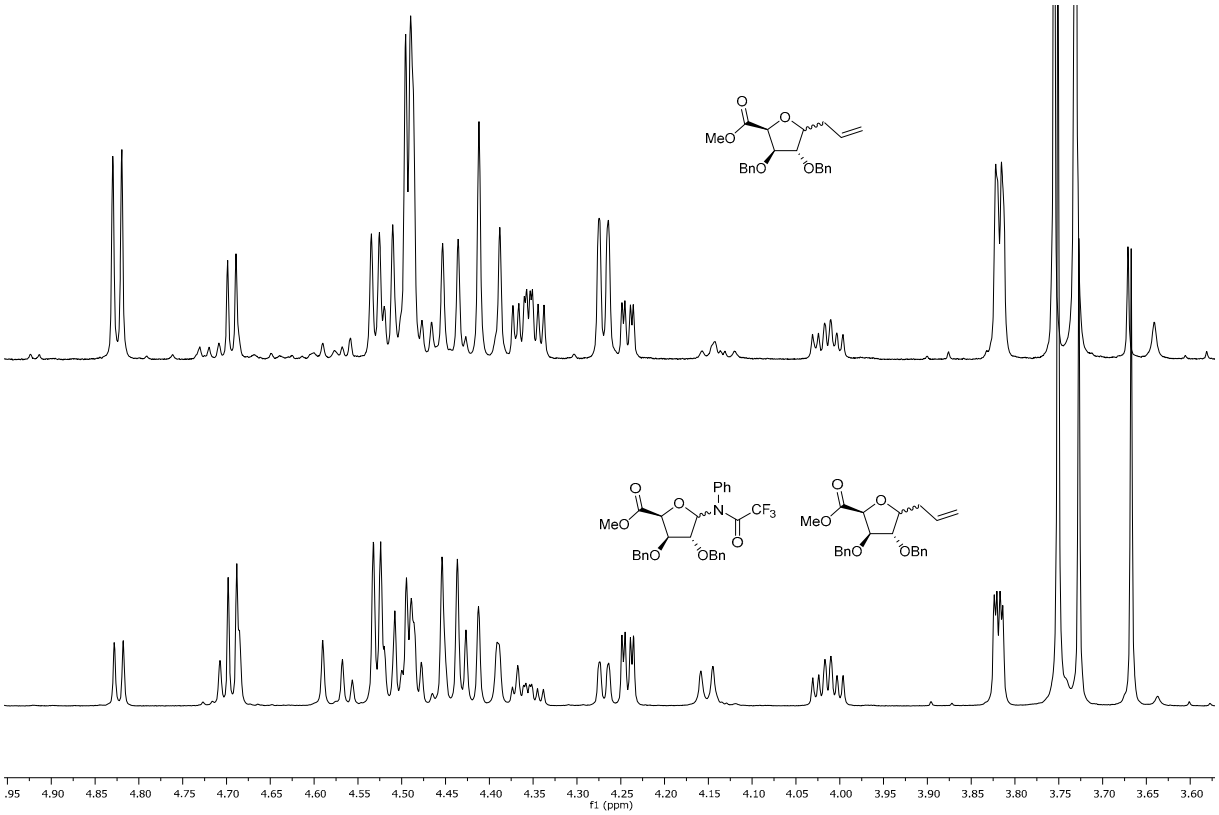


Methyl (1-allyl-2,3-di-*O*-benzyl-1-deoxy-α/β-D-xylofuranosyl uronate) (68)

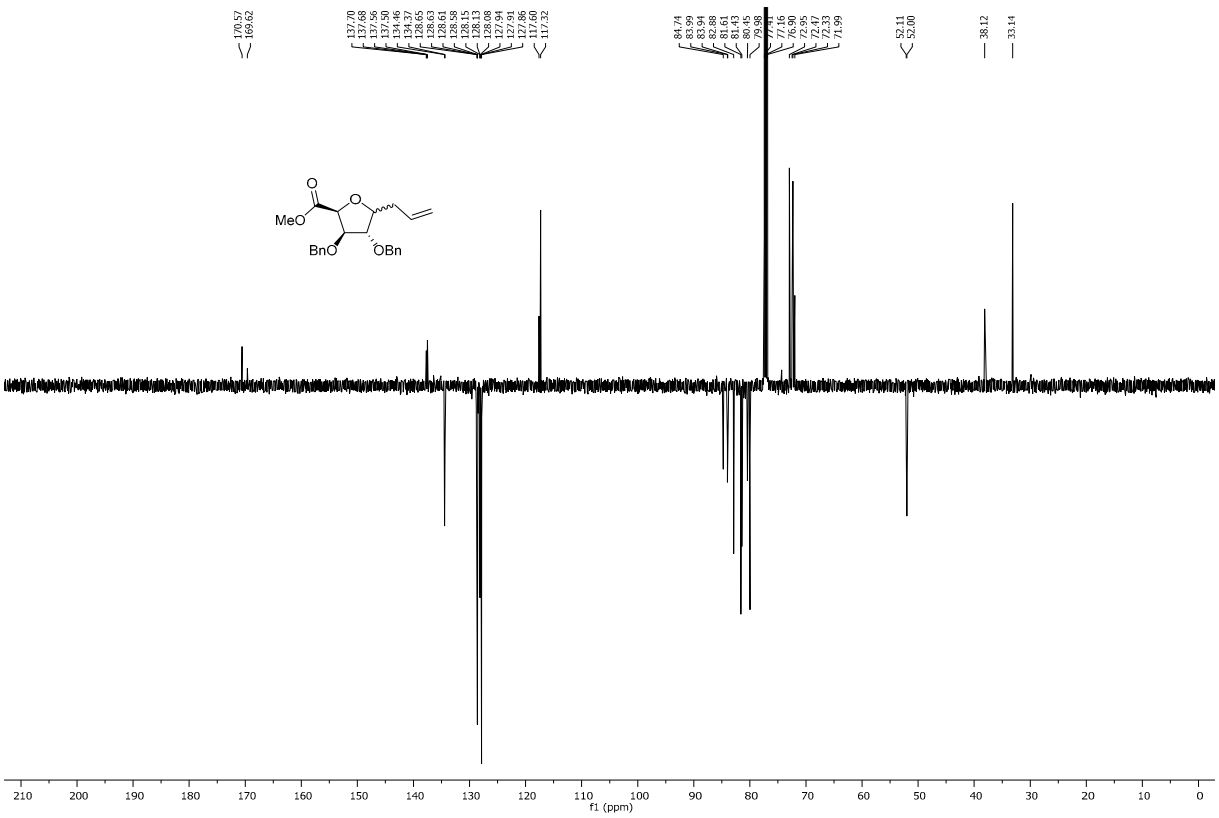
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **68**

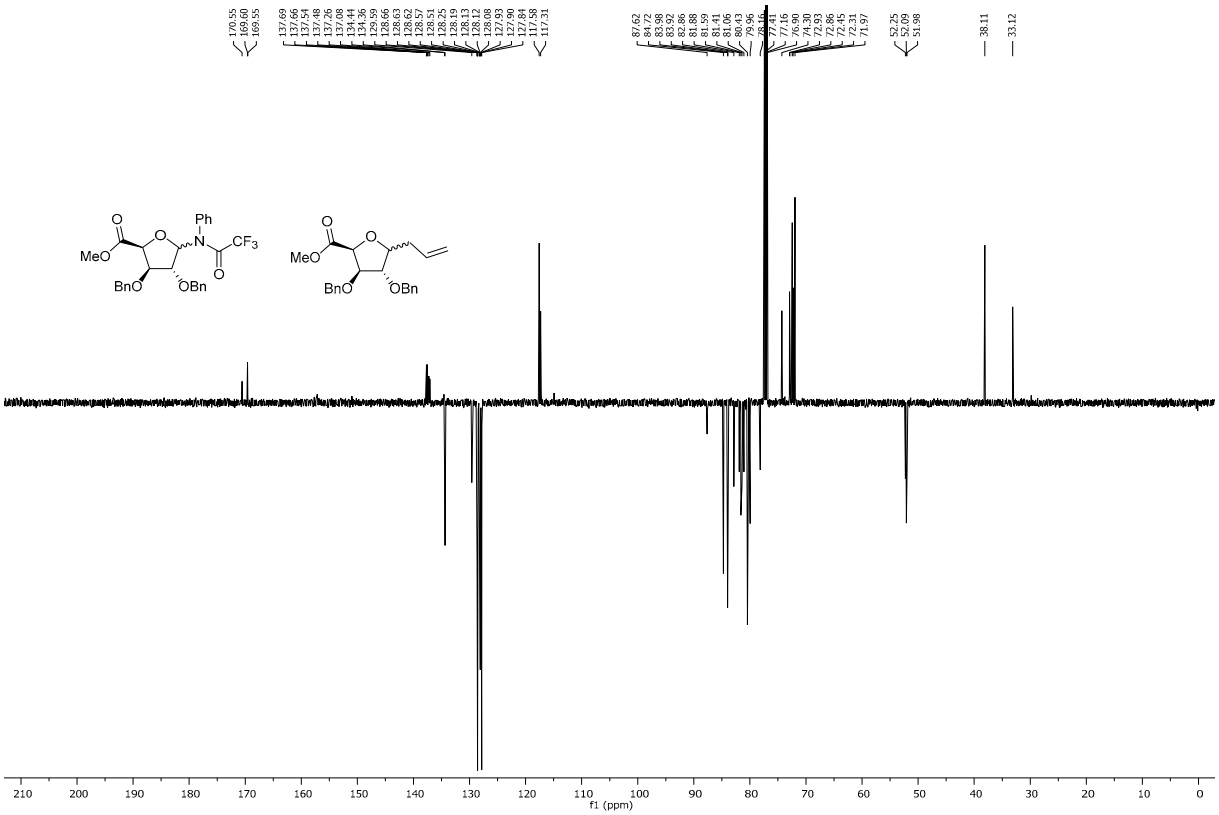






^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **68**




170.55
169.60
169.55
137.69
137.66
137.54
137.48
137.26
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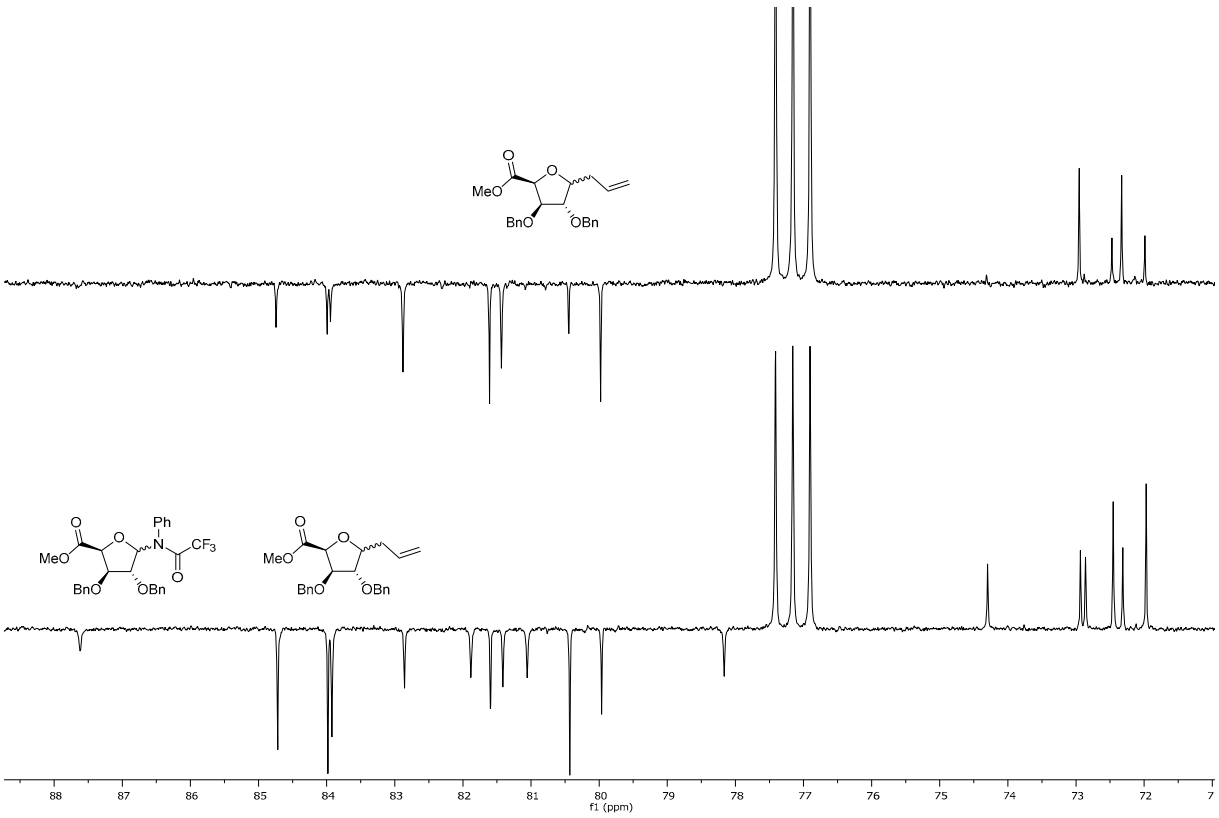
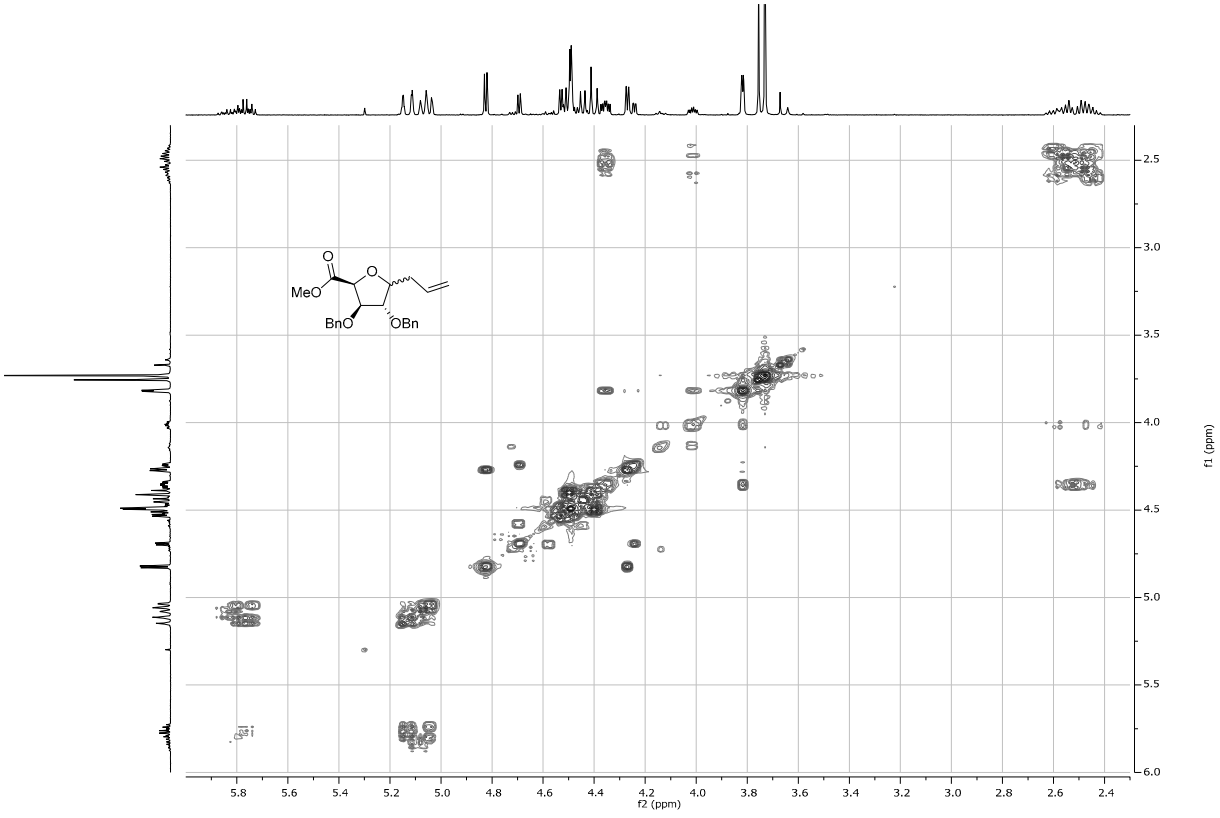
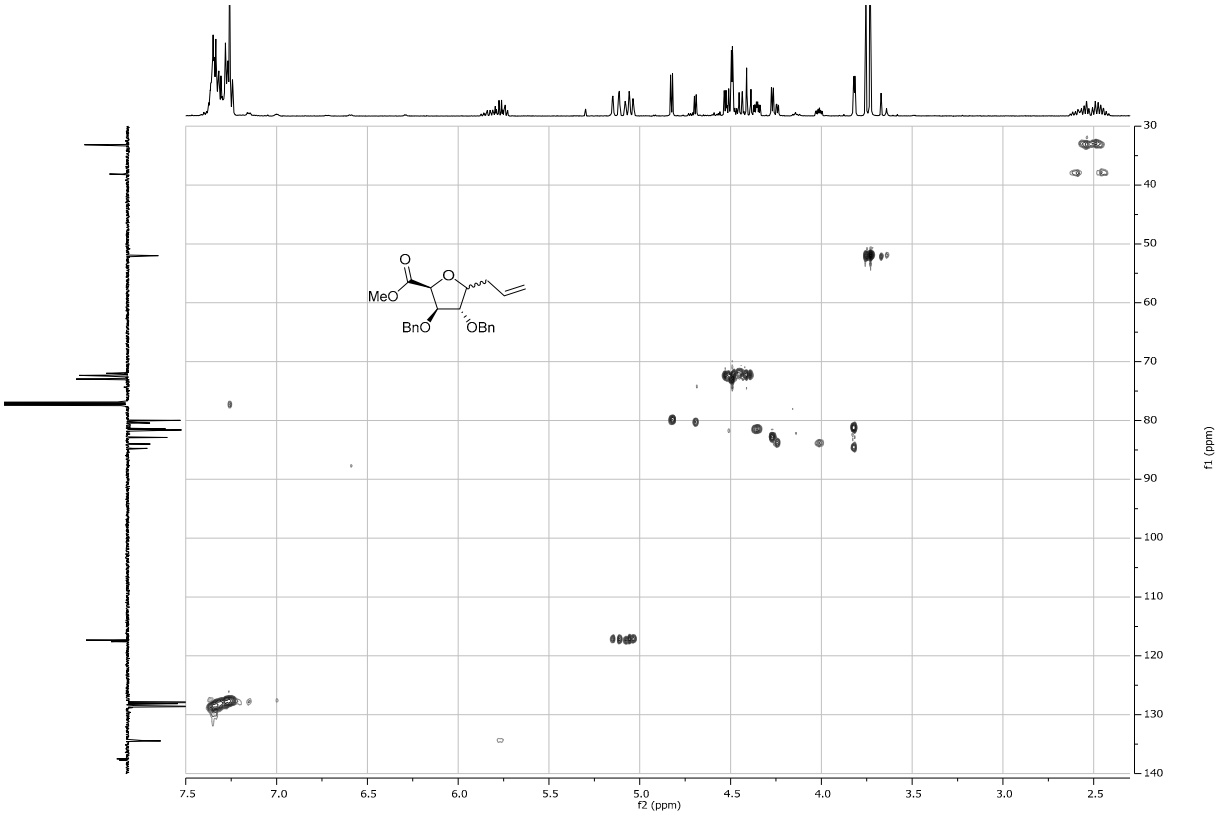
134.44
134.36
129.30
128.66
128.63
128.62
128.57
128.51
128.25
128.19
128.13
128.12
128.08
127.93
127.90
127.84
117.58
117.31
87.62
84.72
83.98
83.92
82.86
81.88
81.59
81.41
81.06
80.43
79.96
78.16
77.41
77.16
76.90
74.30
72.93
72.86
72.45
72.31
71.97
52.25
52.09
51.98
38.11
33.12
Ph
N
CF3
O
MeO
BnO
OBn
f1 (ppm)


MeO
BnO
OBn
Ph
N
CF3
f1 (ppm)

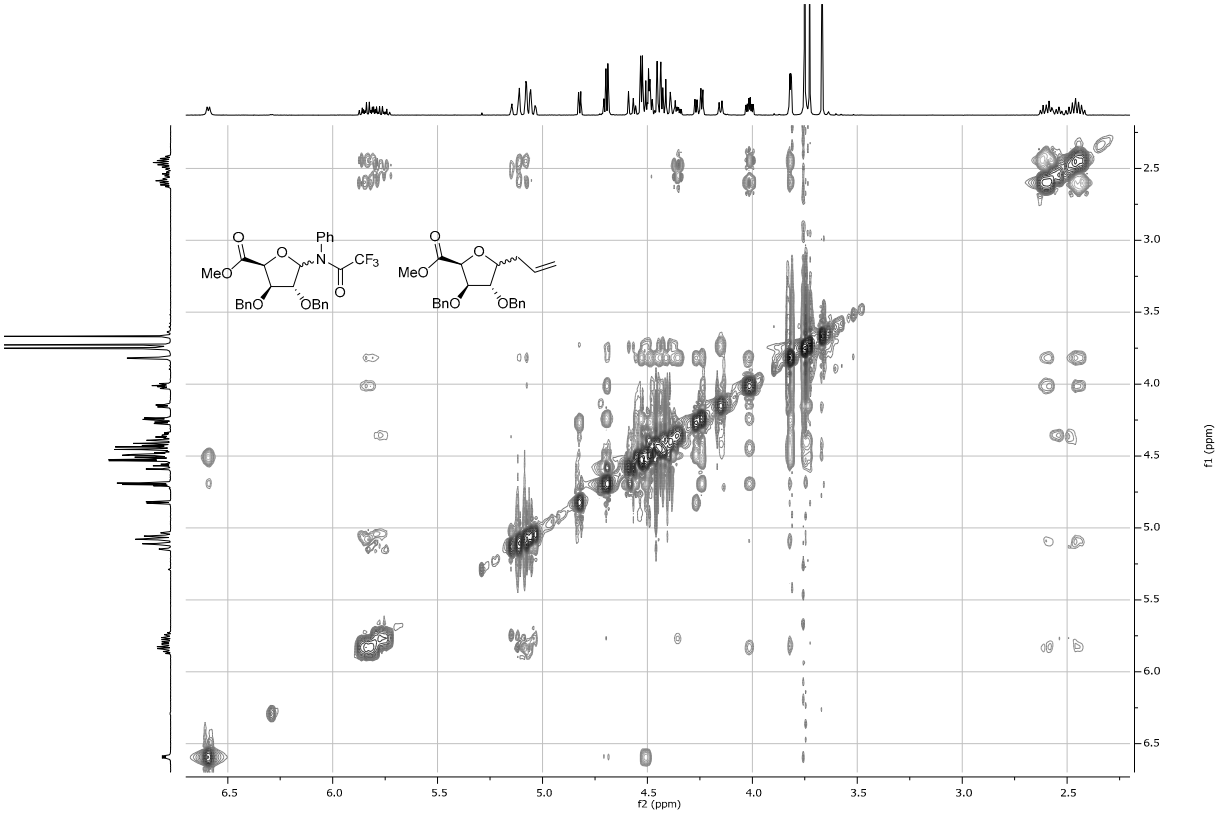
^{1}H-^{1}H COSY of compound **68**



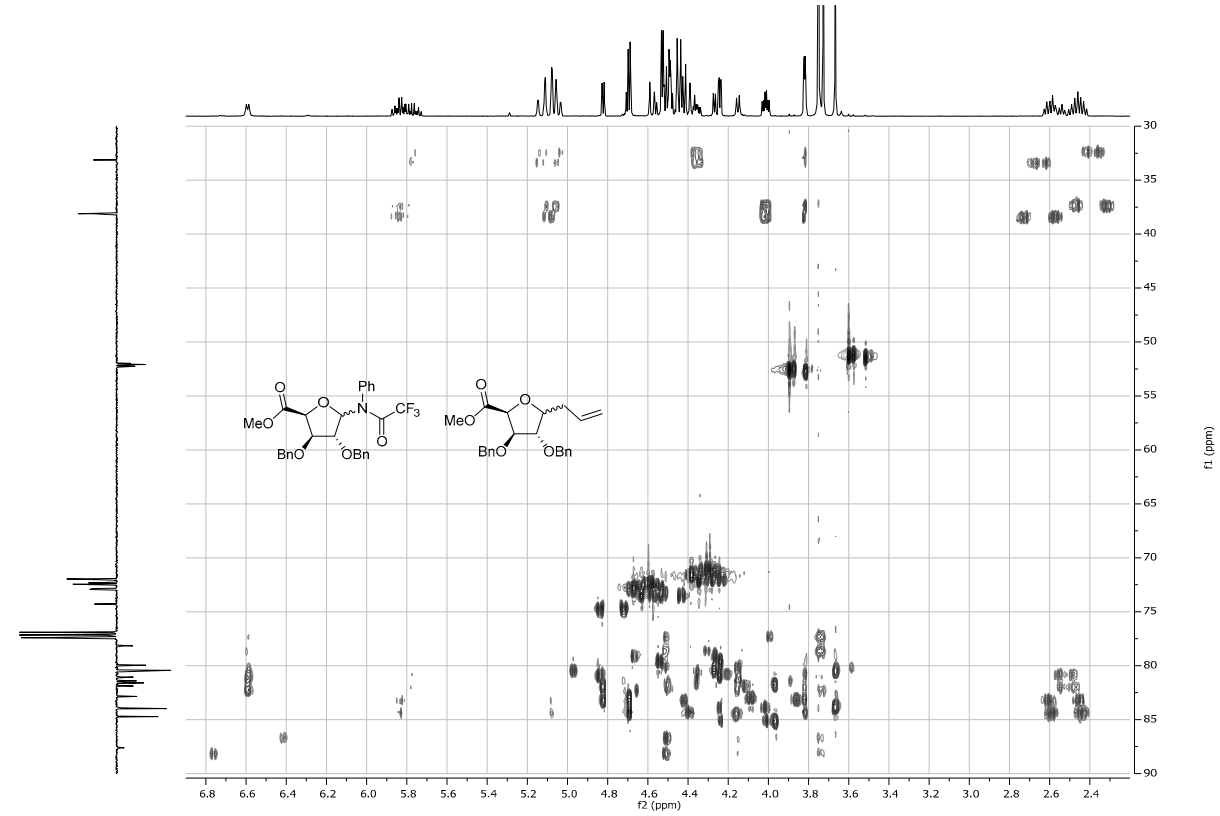
^{1}H-^{13}C HSQC of compound **68**



^{1}H-^{1}H NOESY of compound **68**

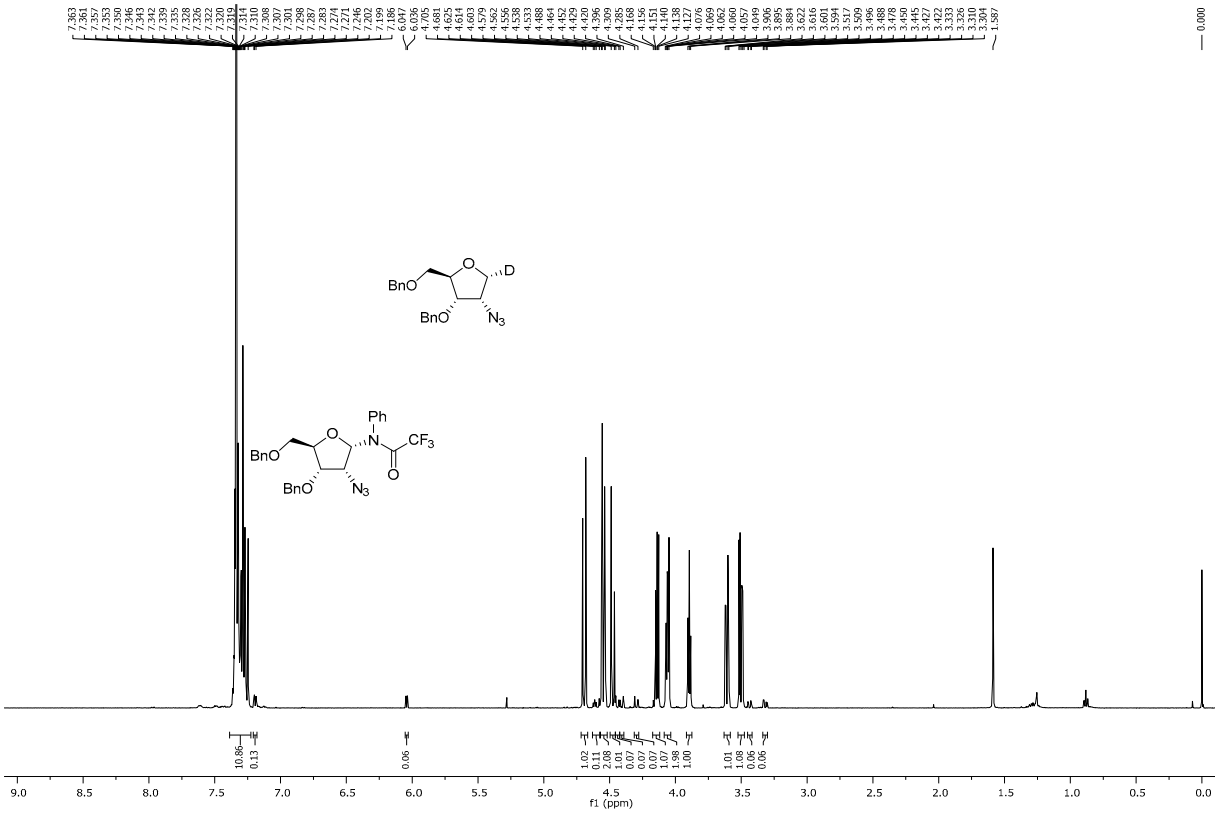


^{1}H-^{13}C HSQC-HECADE of compound **68**

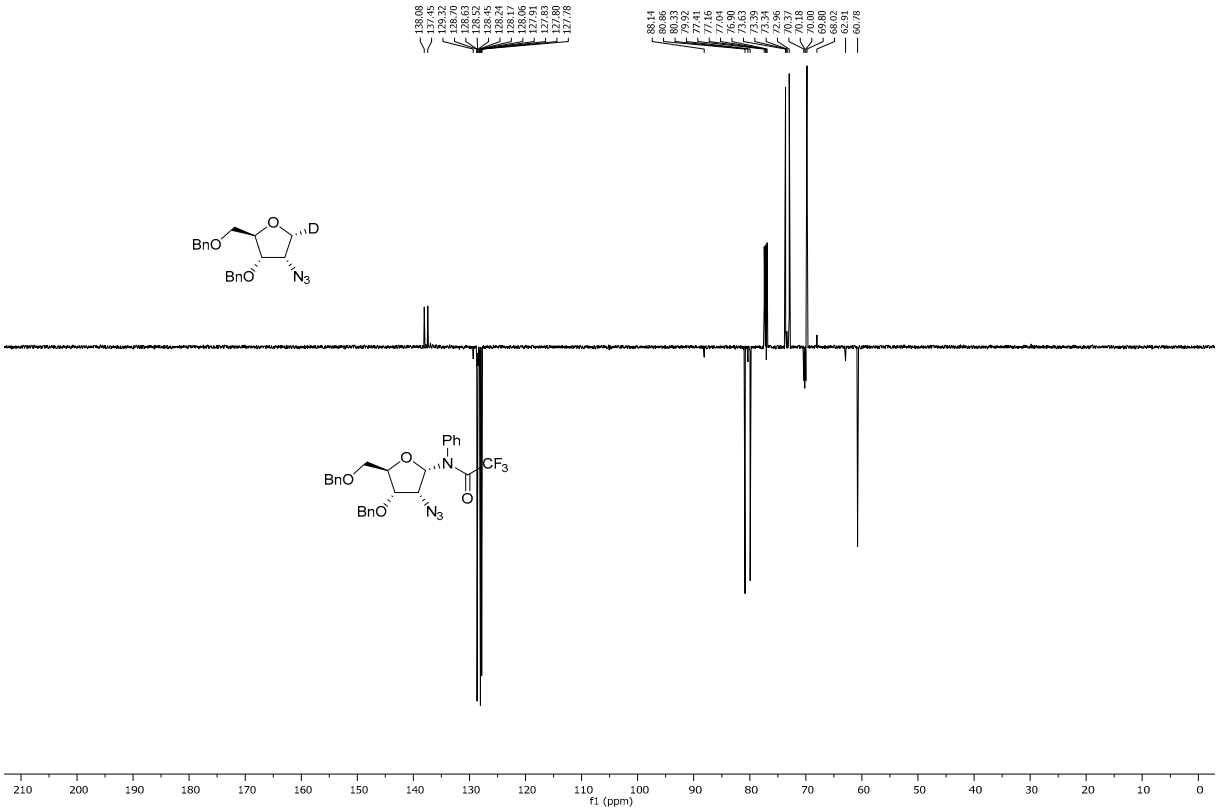


1-[^{2}H]-1,4-anhydro-2-azido-3,5-di-*O*-benzyl-2-deoxy-α-D-ribitol (69)

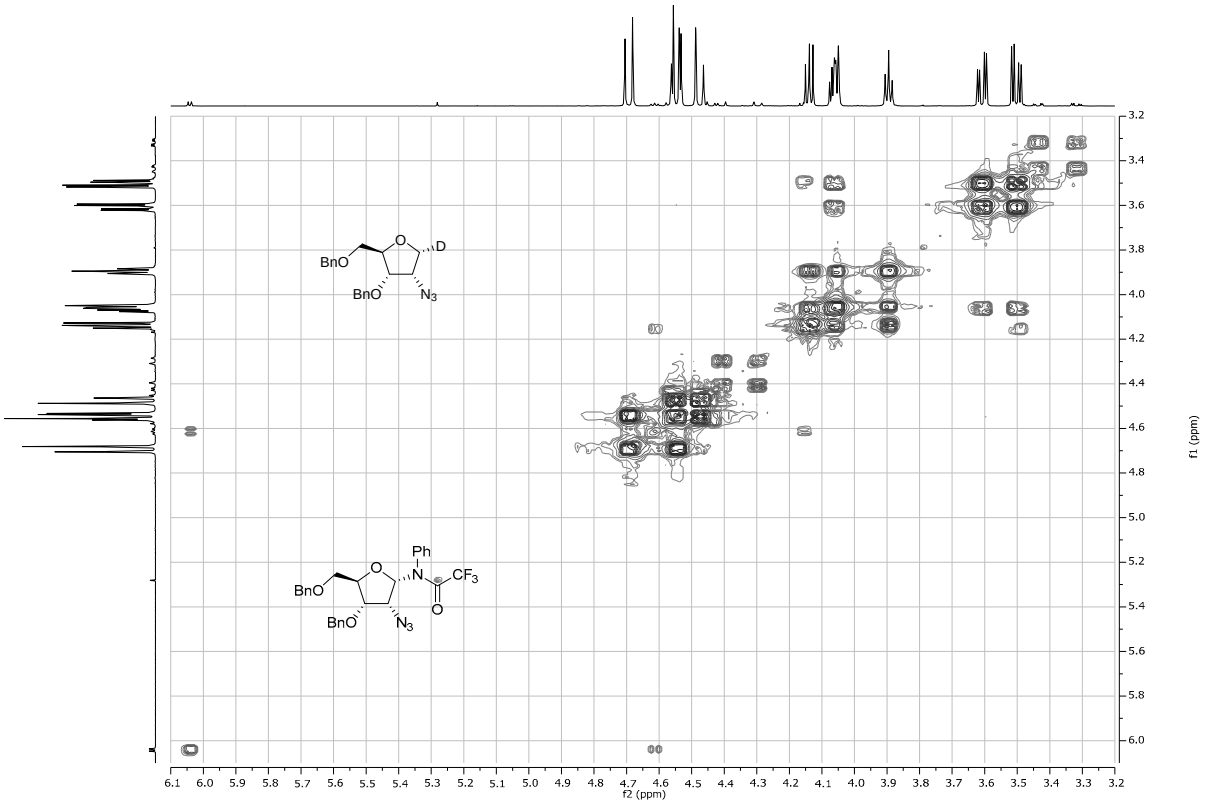
^{1}H NMR, 500 MHz, $CDCl_3$ of compounds **69** and **98**



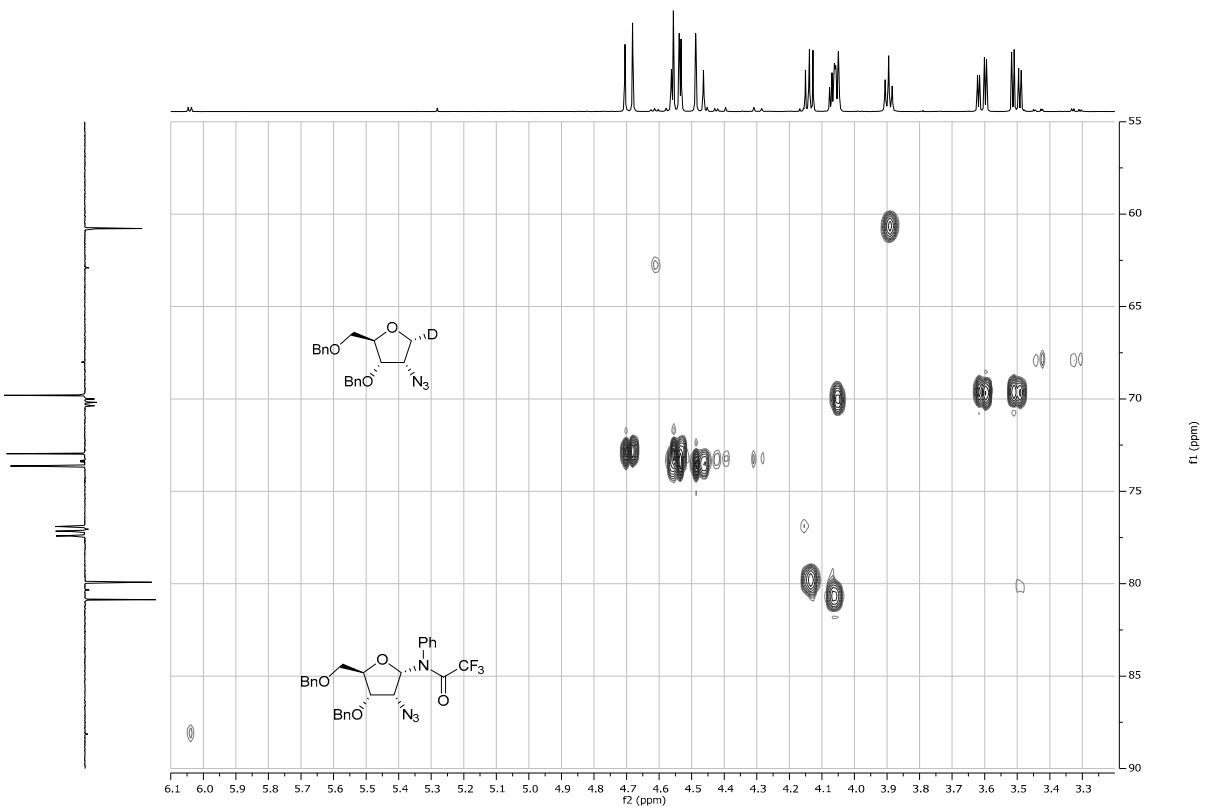
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compounds **69** and **98**



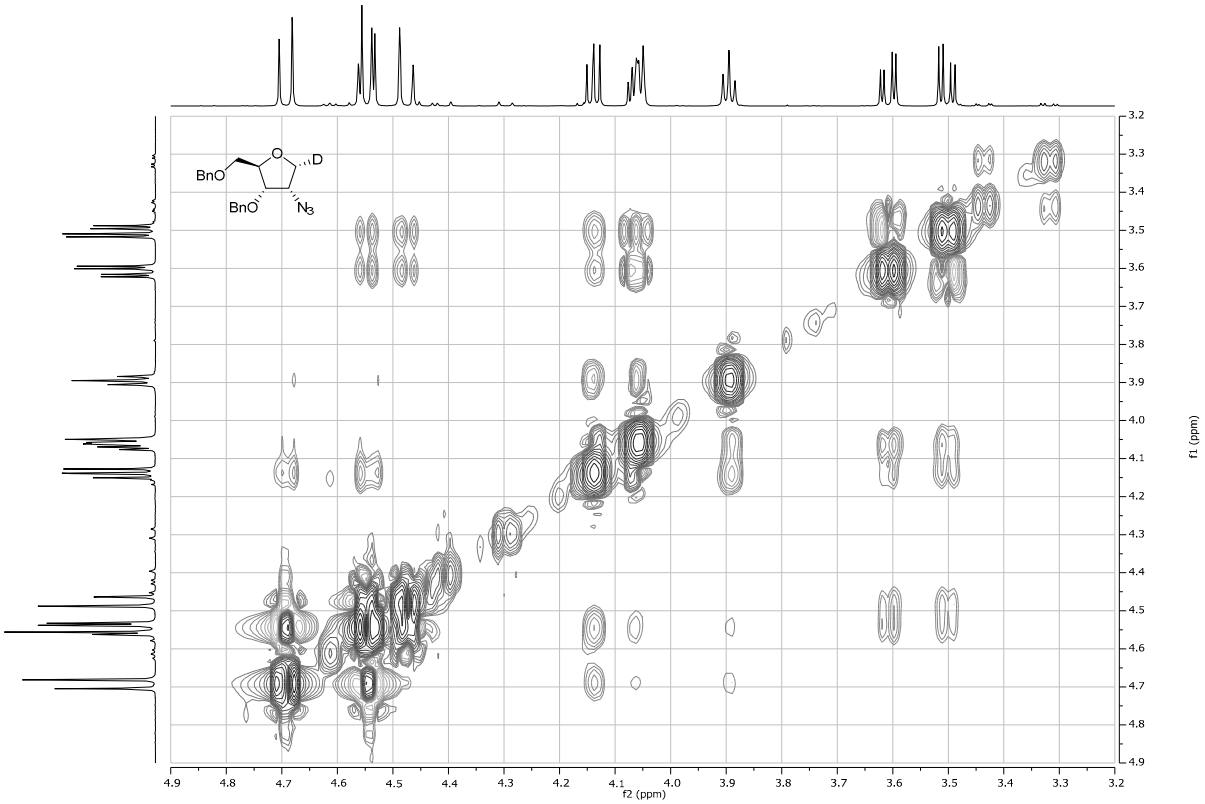
^{1}H-^{1}H COSY of compounds **69** and **98**



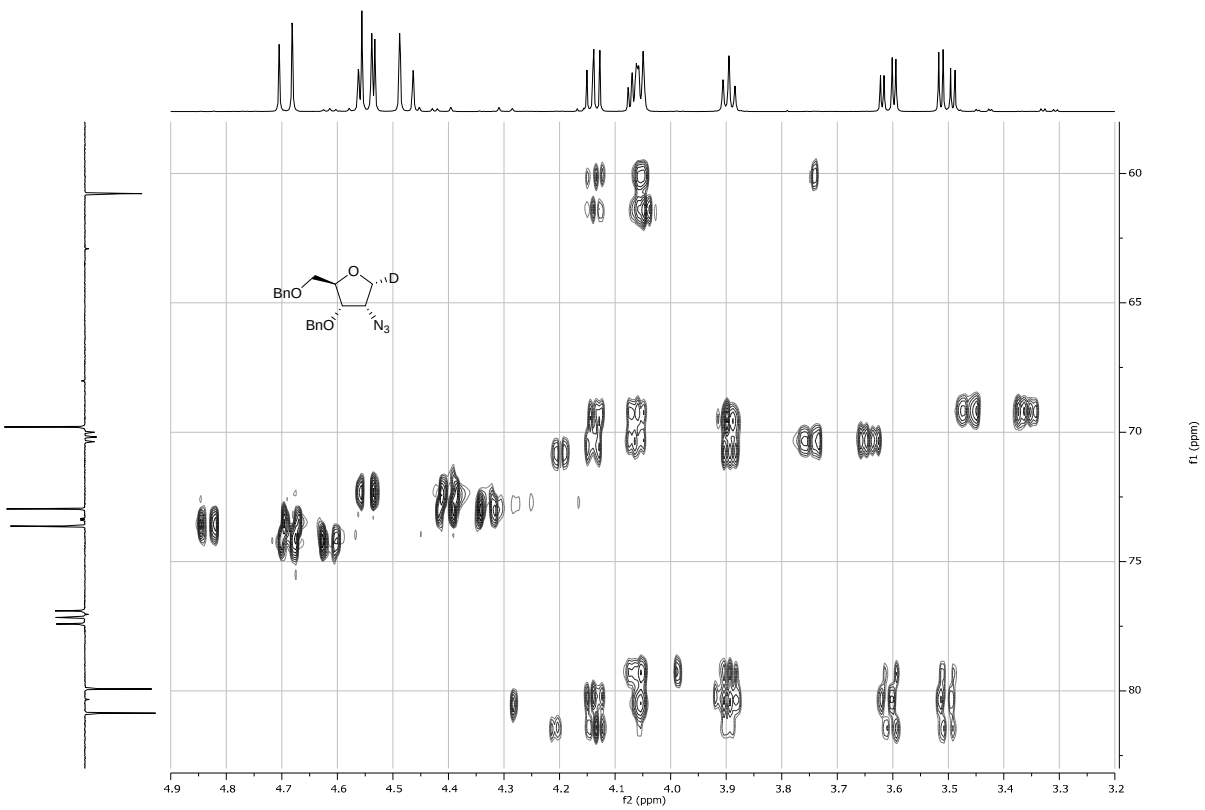
^{1}H-^{13}C HSQC of compounds **69** and **98**



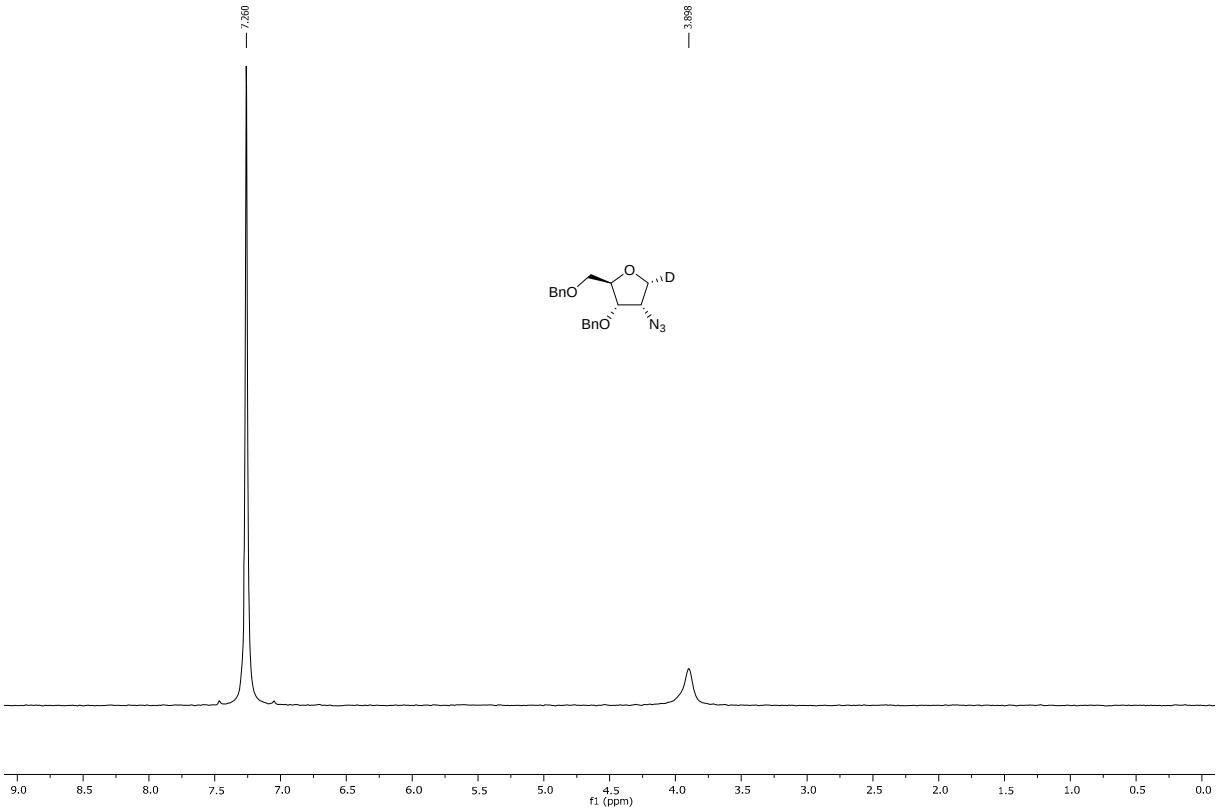
^{1}H-^{1}H NOESY of compounds **69** and **98**



^{1}H-^{13}C HSQC-HECADE of compounds **69** and **98**

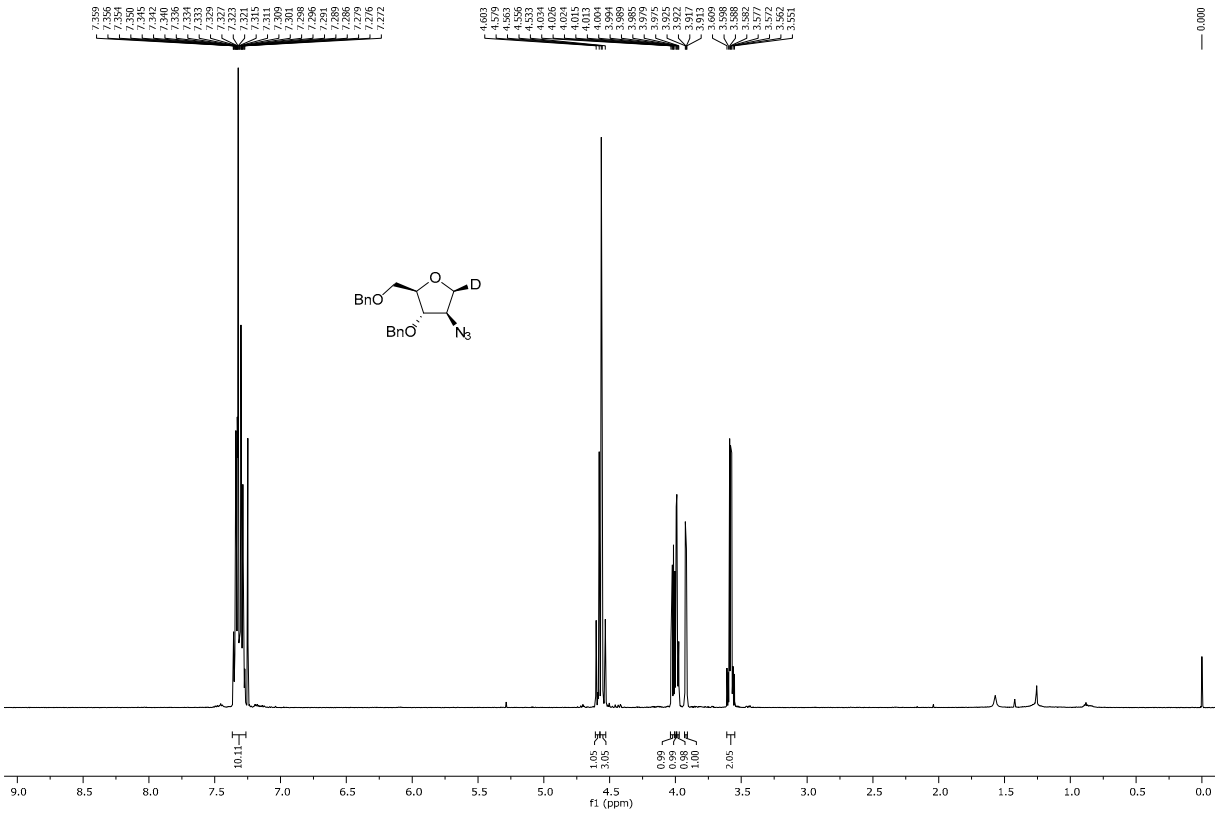


^{2}H NMR, 77 MHz, $CHCl_3$ of compound **69**

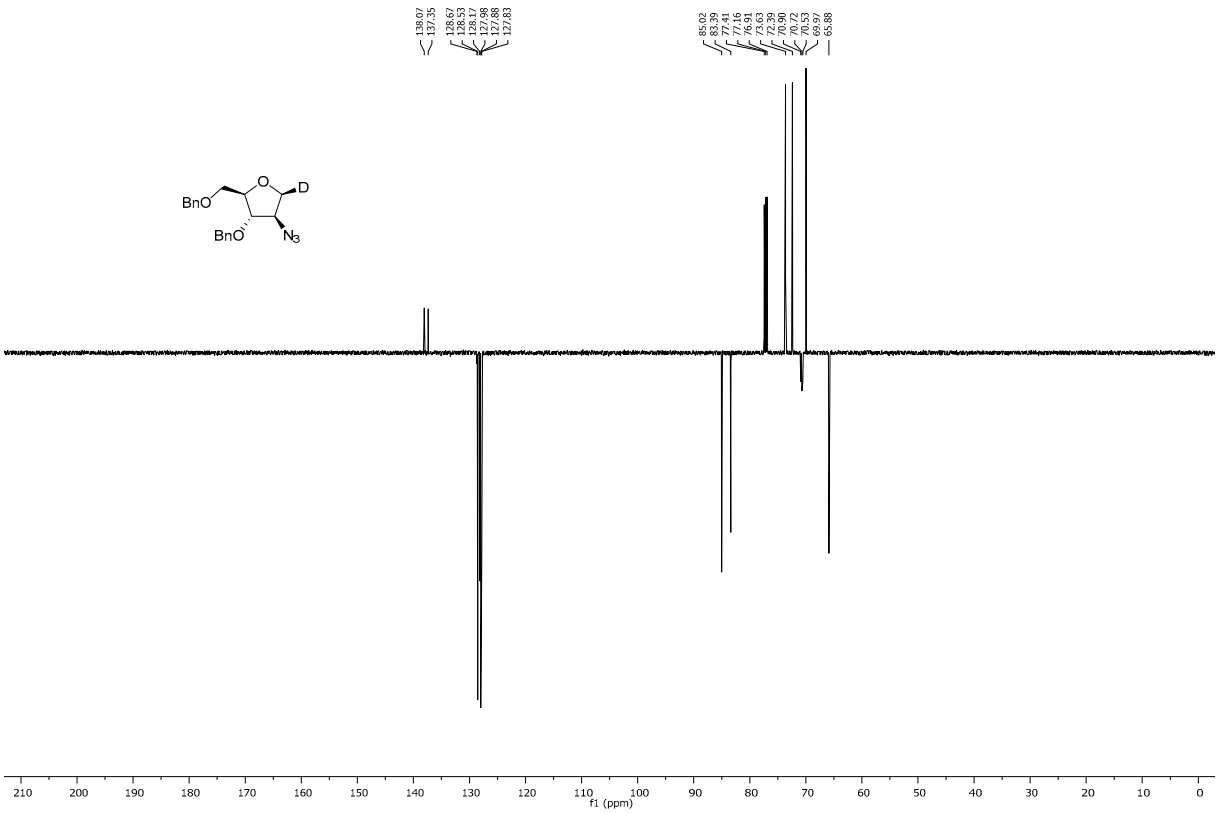


1-[^{2}H]-1,4-anhydro-2-azido-3,5-di-*O*-benzyl-2-deoxy-β-D-arabitol (70)

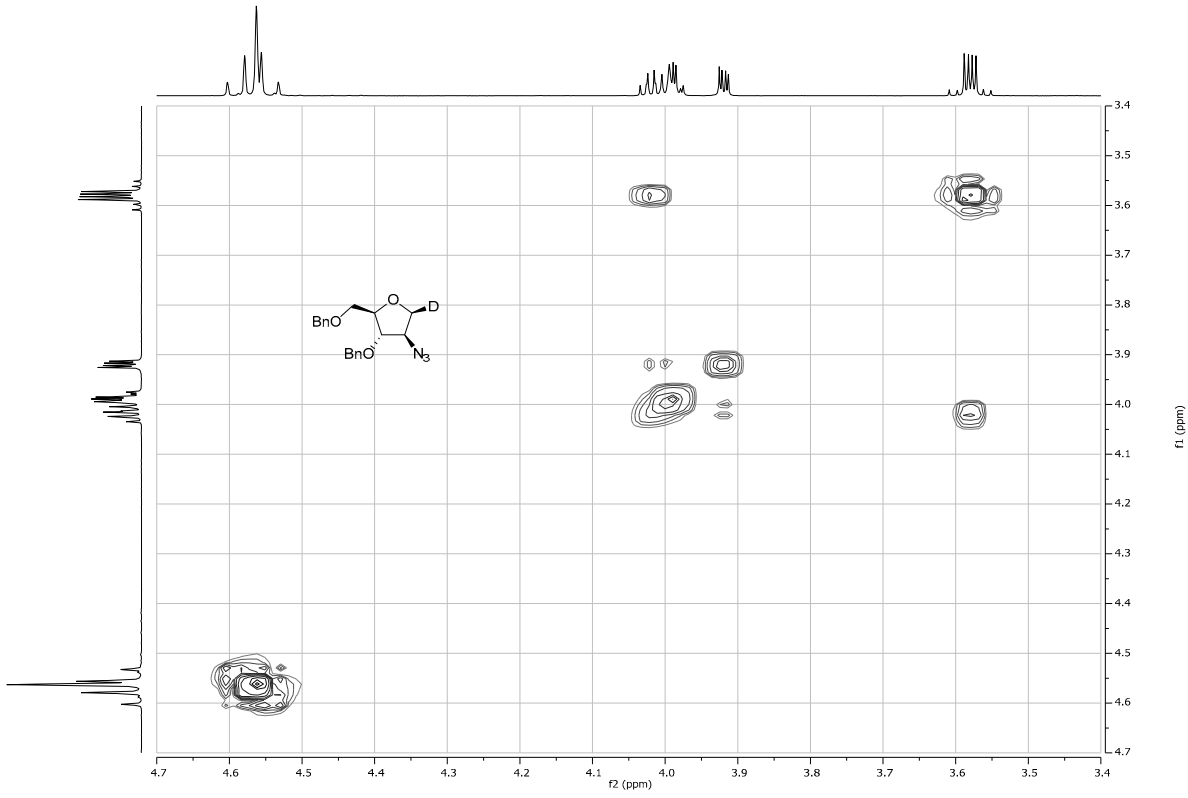
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **70**



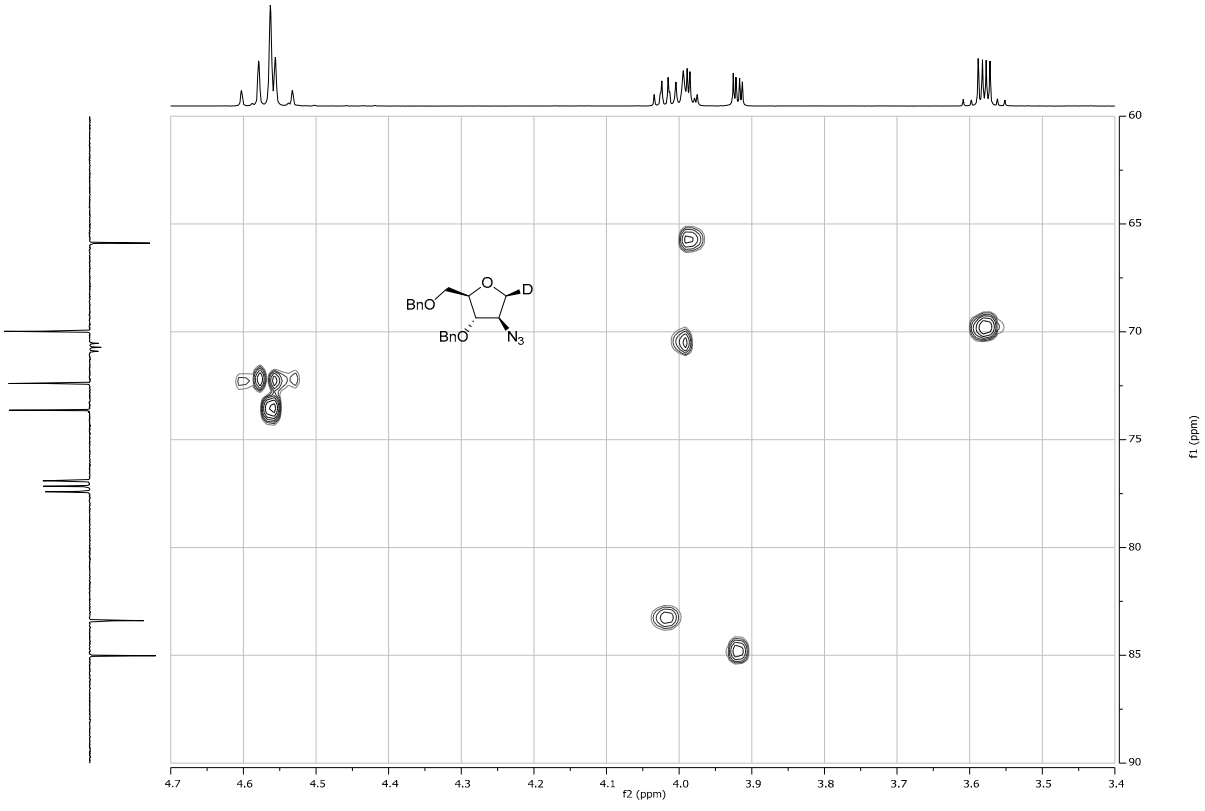
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **70**



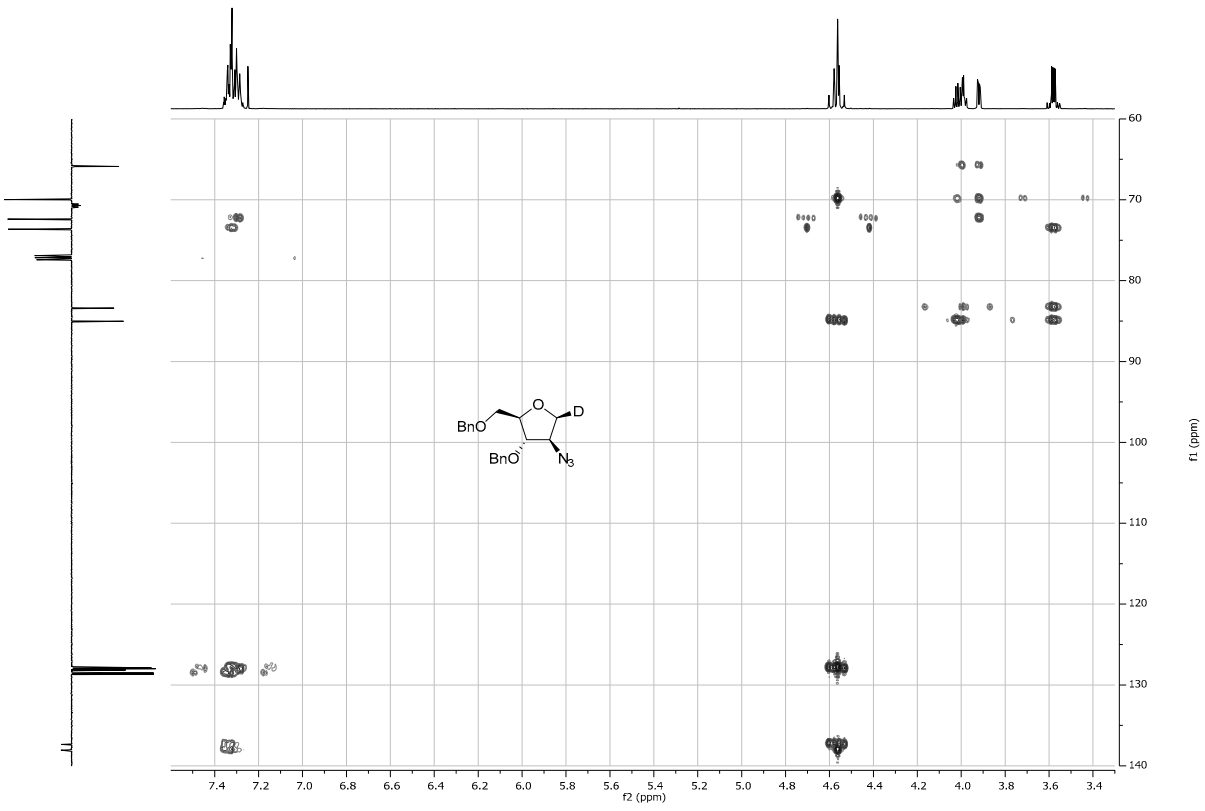
^{1}H-^{1}H COSY of compound **70**



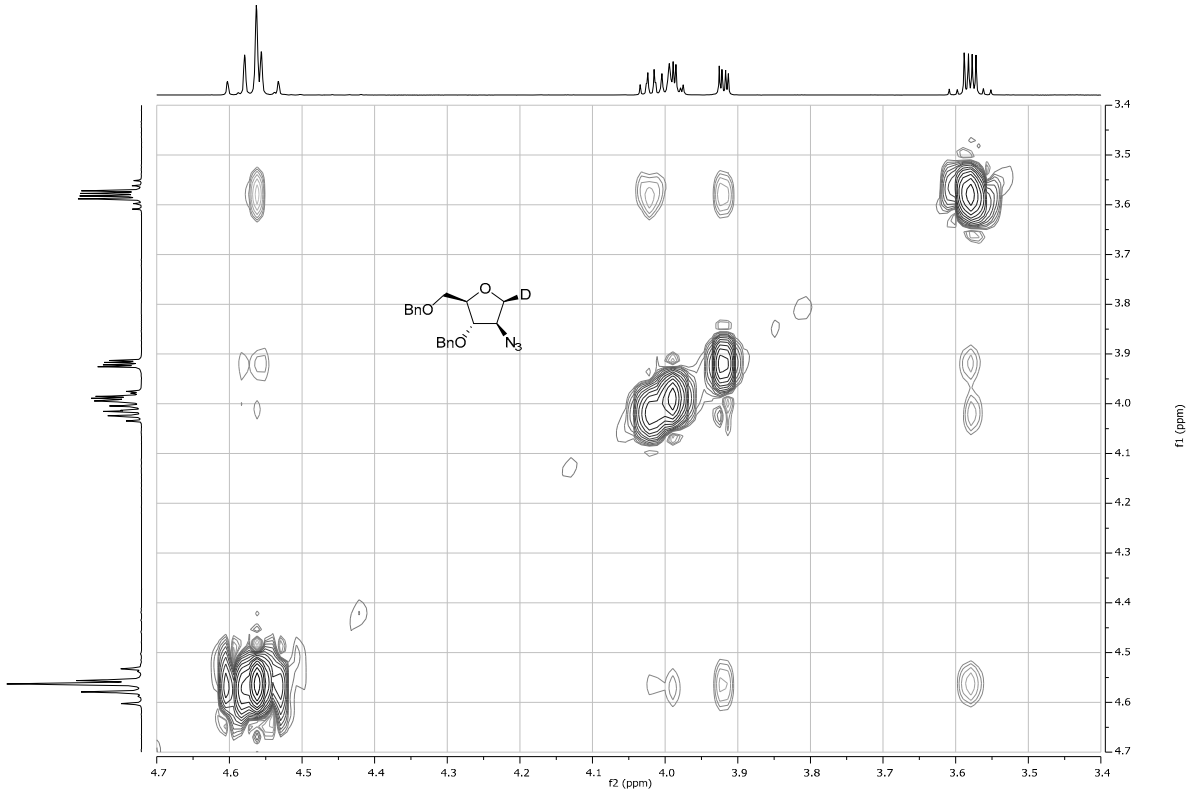
^{1}H-^{13}C HSQC of compound **70**



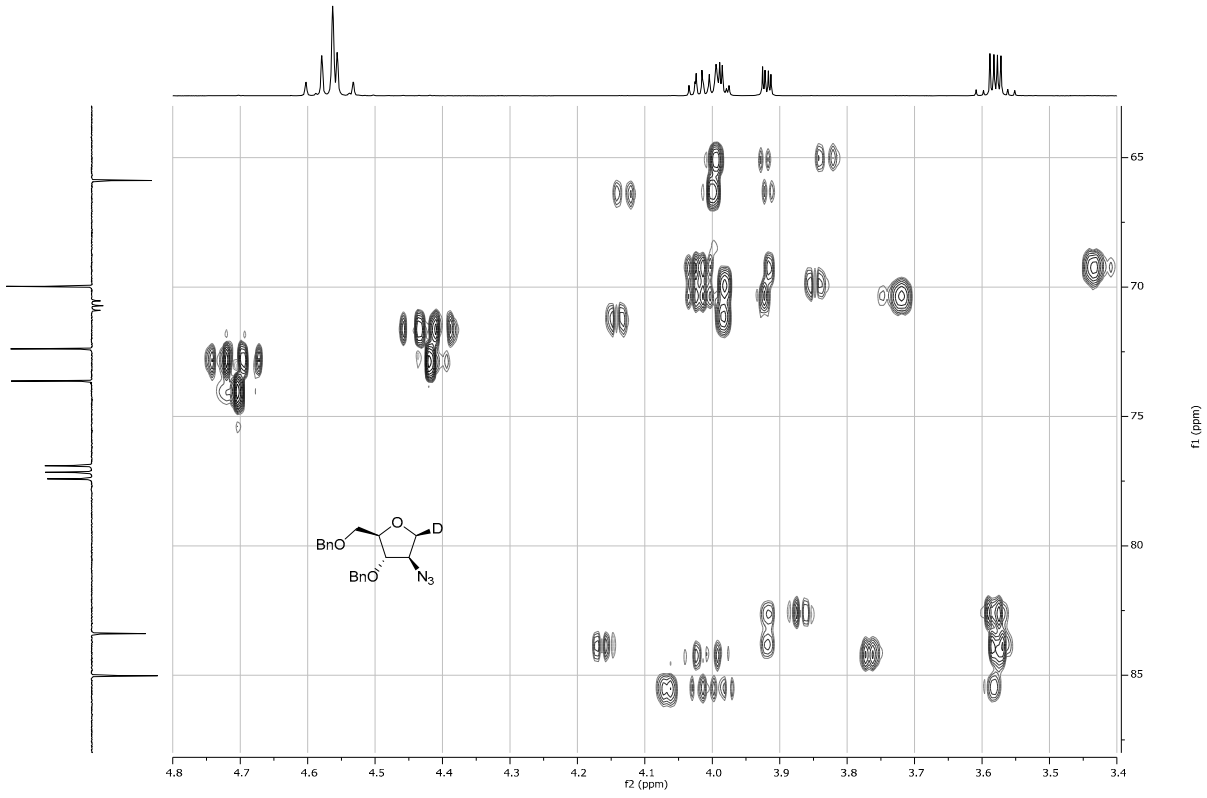
^{1}H-^{13}C HMBC of compound **70**



^{1}H-^{1}H NOESY of compound **70**

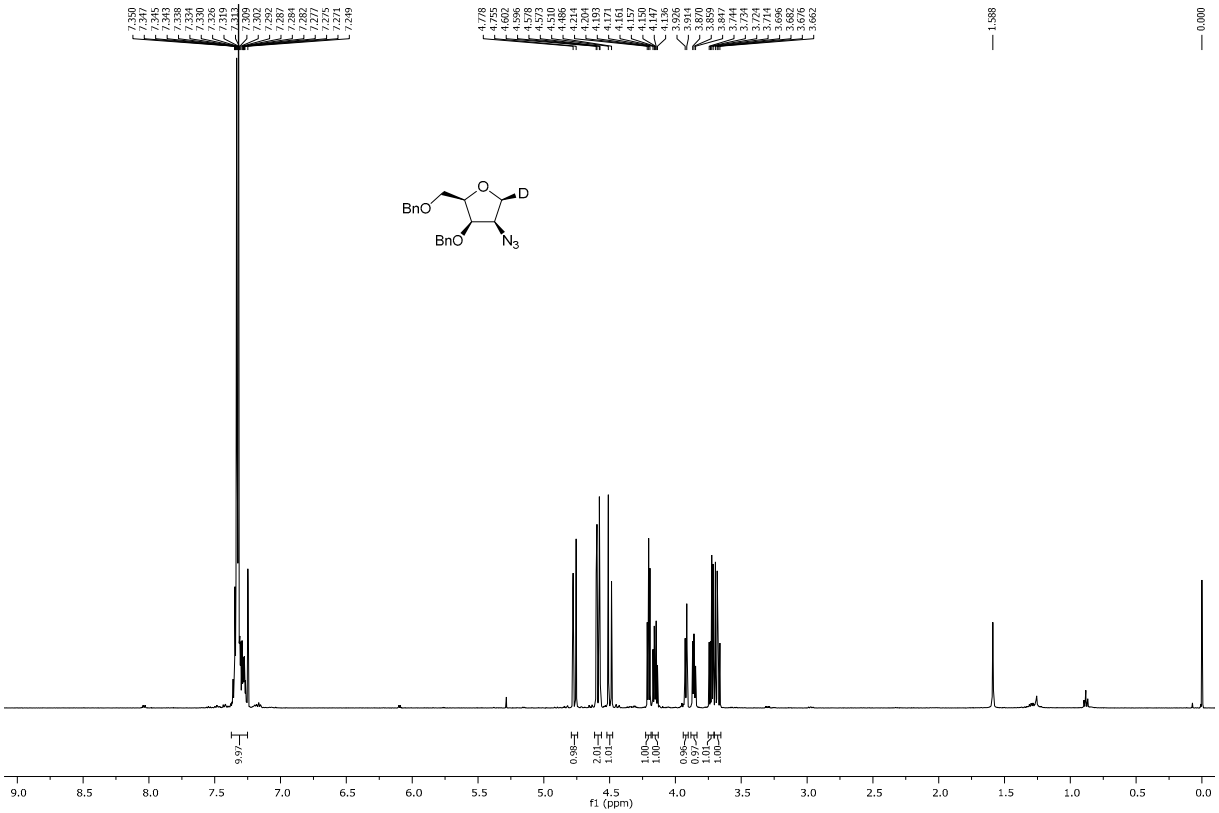


^{1}H-^{13}C HSQC-HECADE of compound **70**

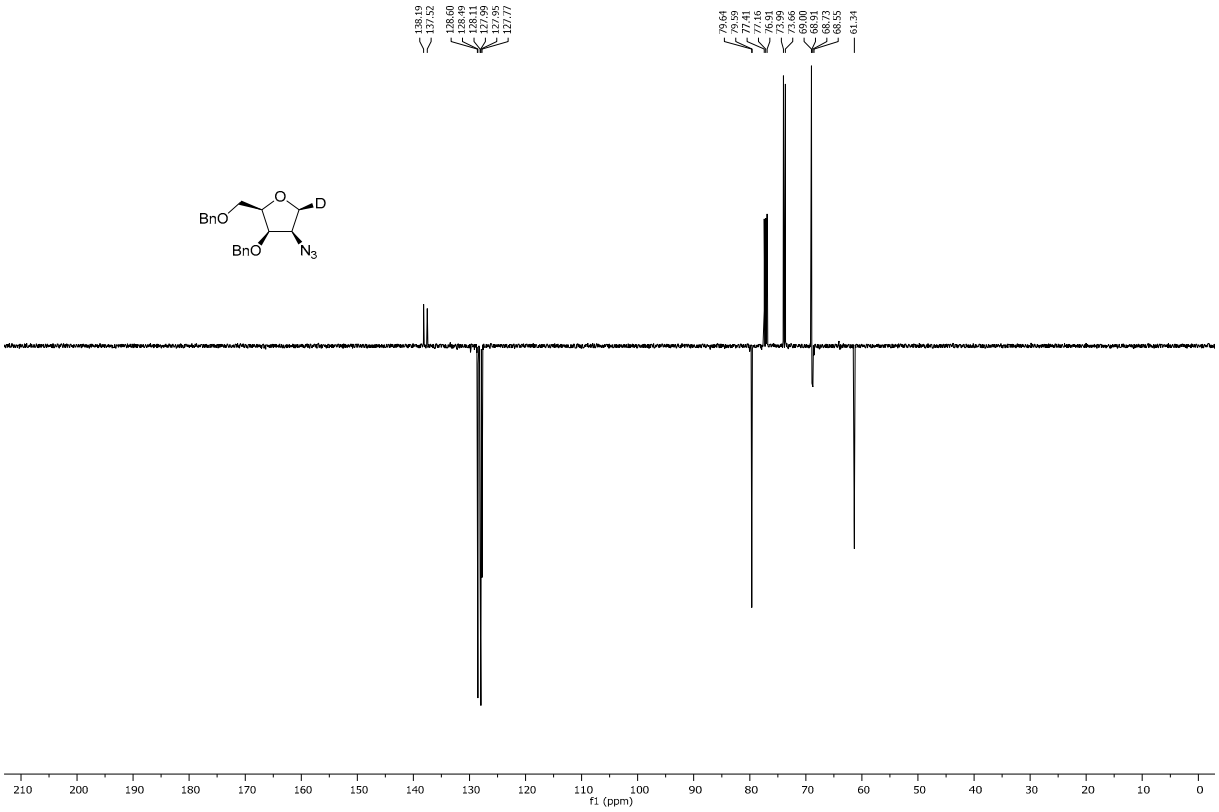


1-[^{2}H]-1,4-anhydro-2-azido-3,5-di-*O*-benzyl-2-deoxy-β-D-lyxitol (71)

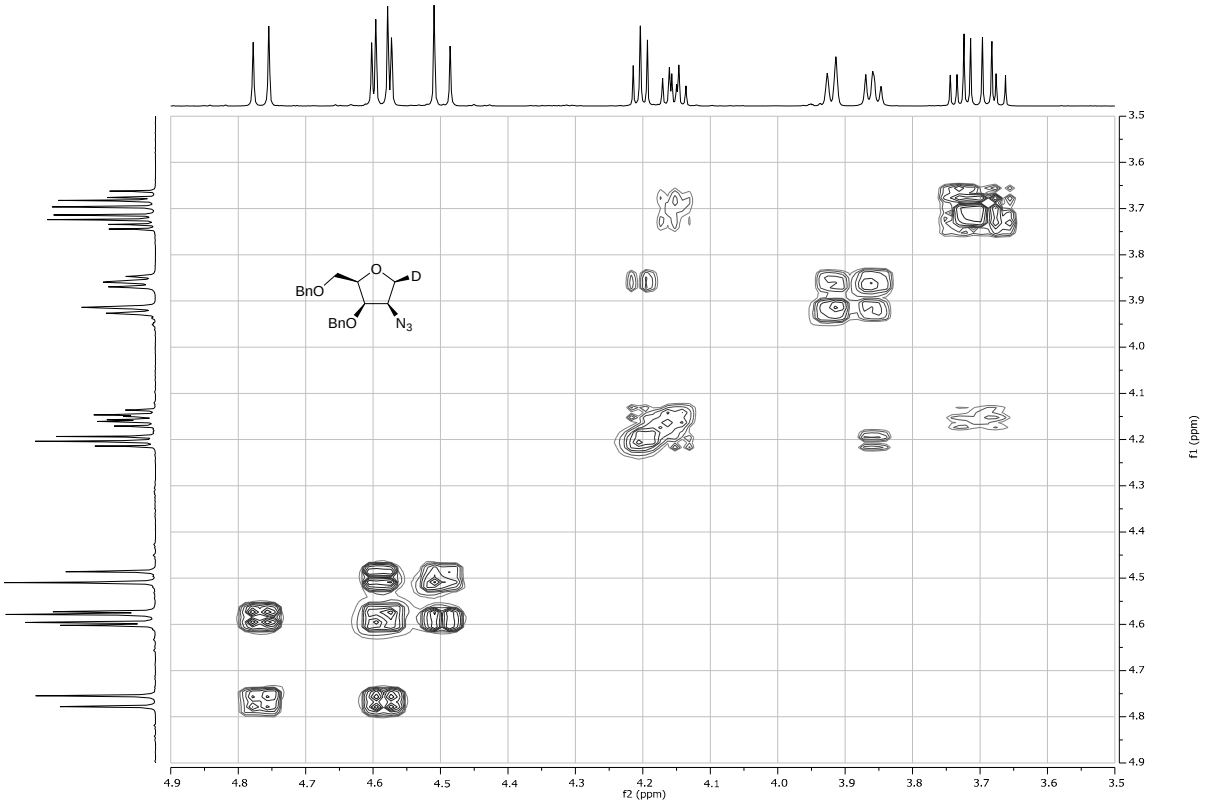
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **71**



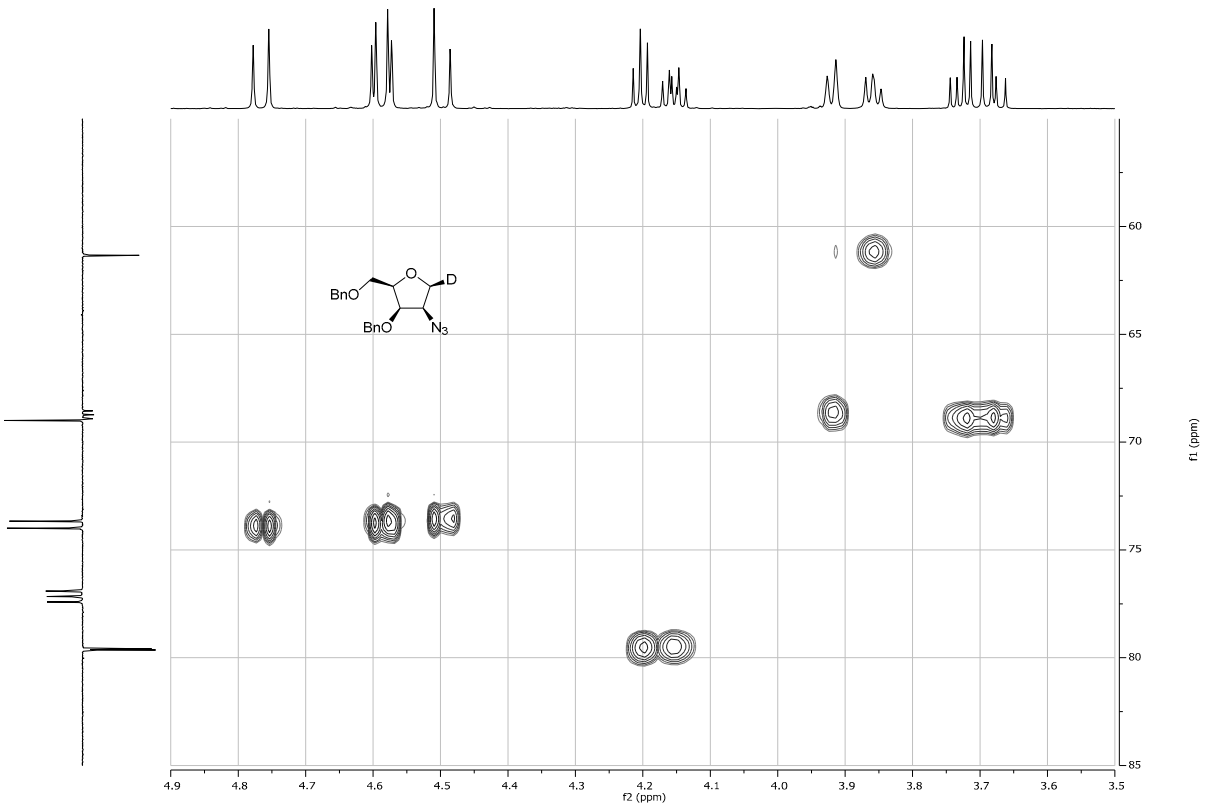
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **71**



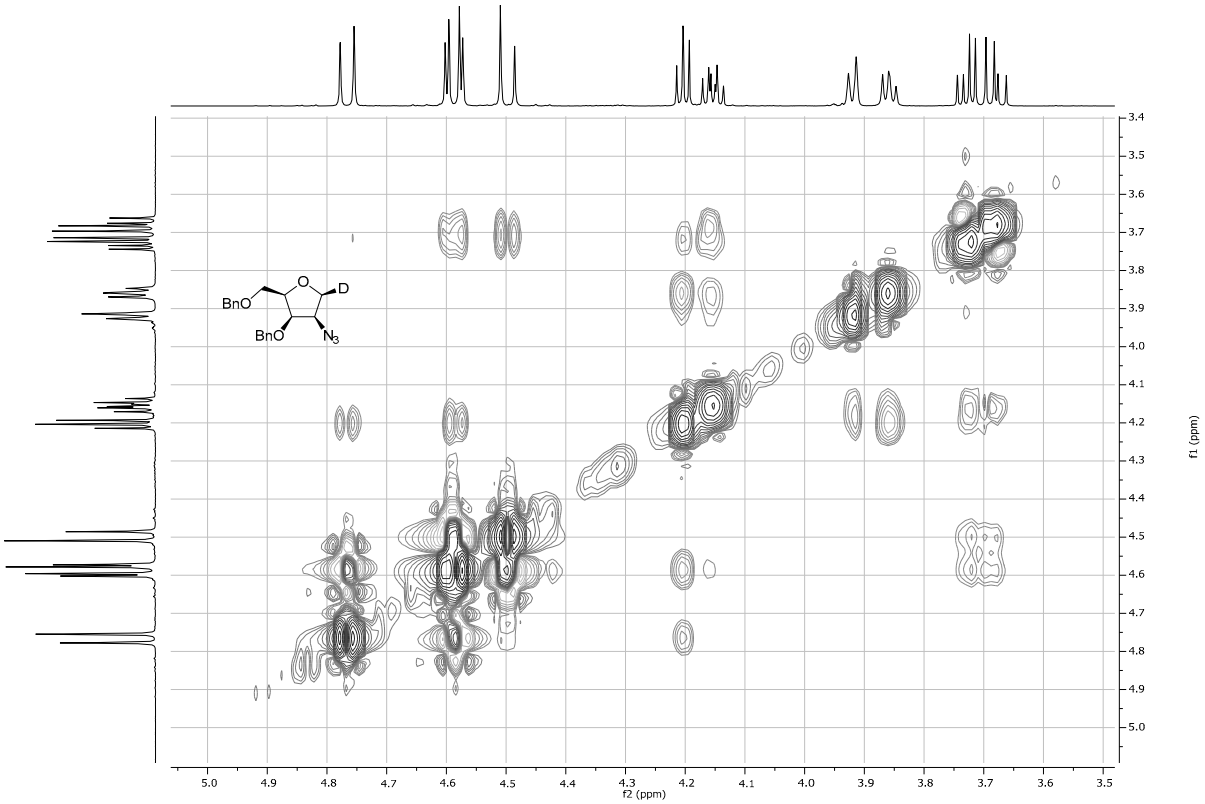
^{1}H-^{1}H COSY of compound **71**



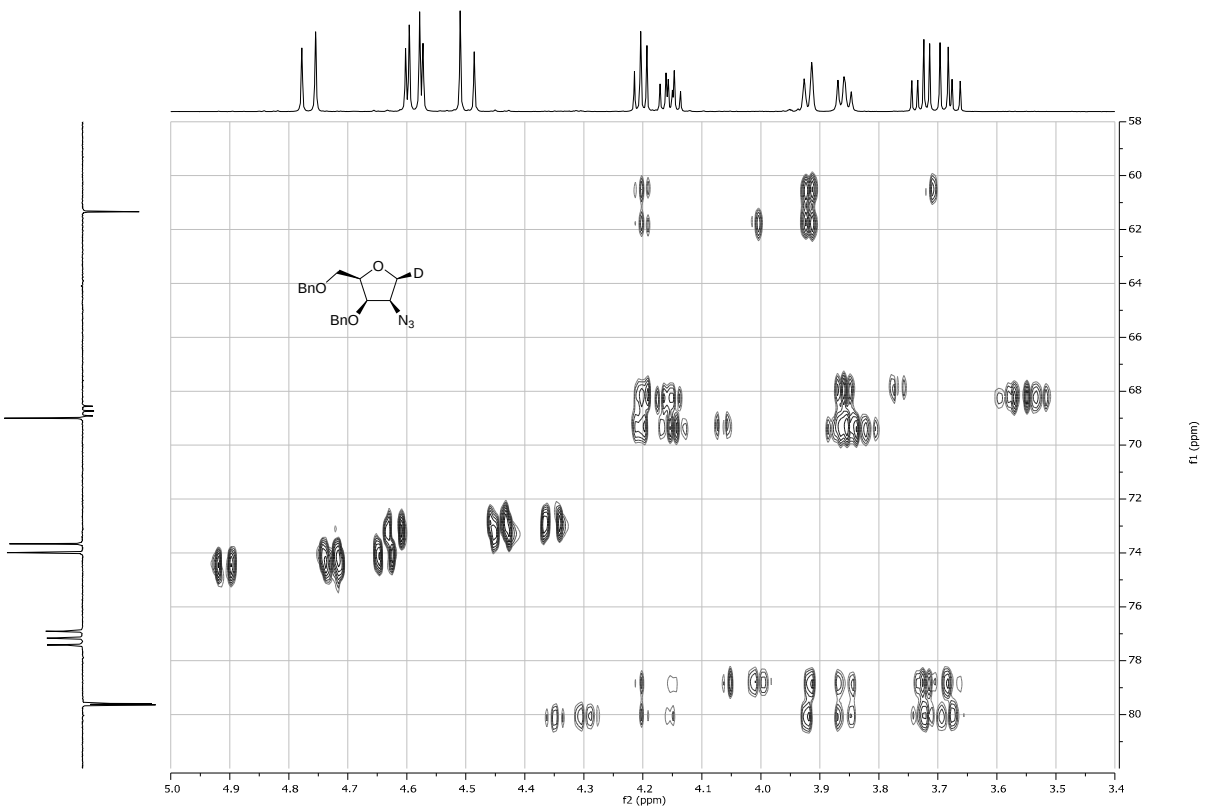
^{1}H-^{13}C HSQC of compound **71**



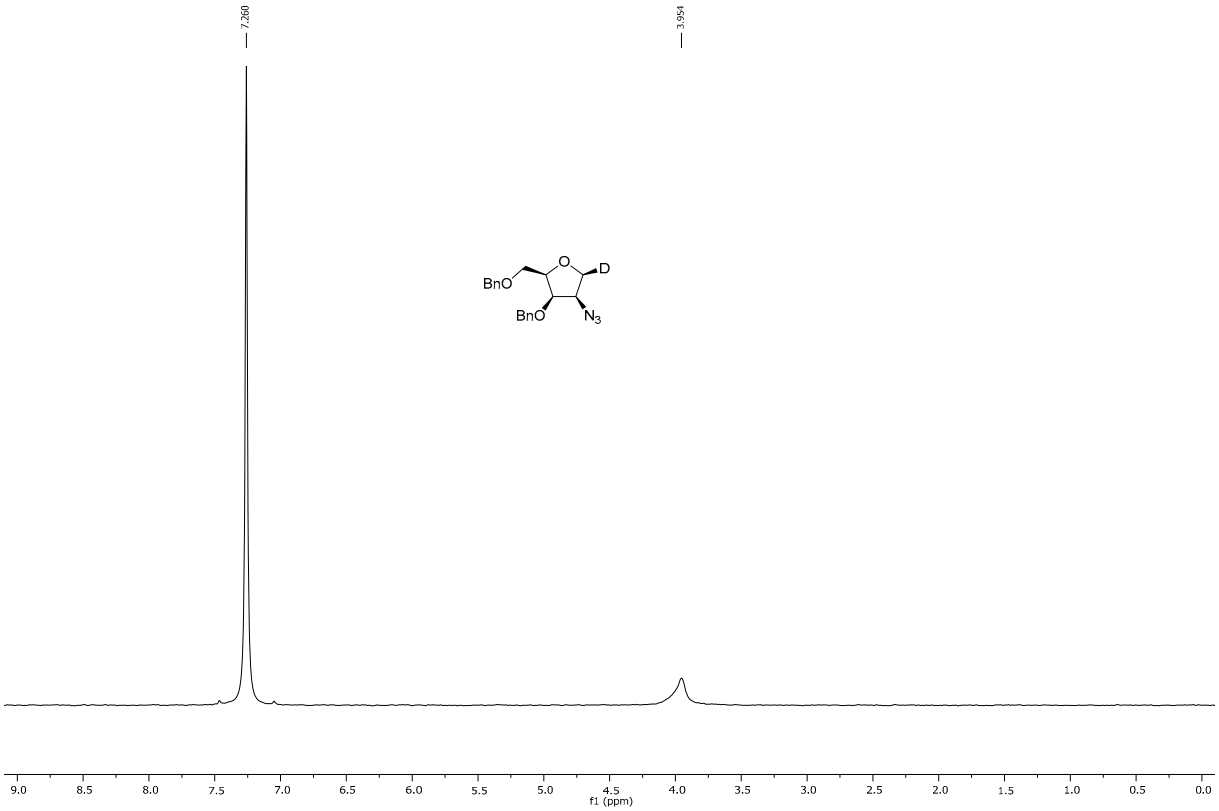
^{1}H-^{1}H NOESY of compound **71**



^{1}H-^{13}C HSQC-HECADE of compound **71**

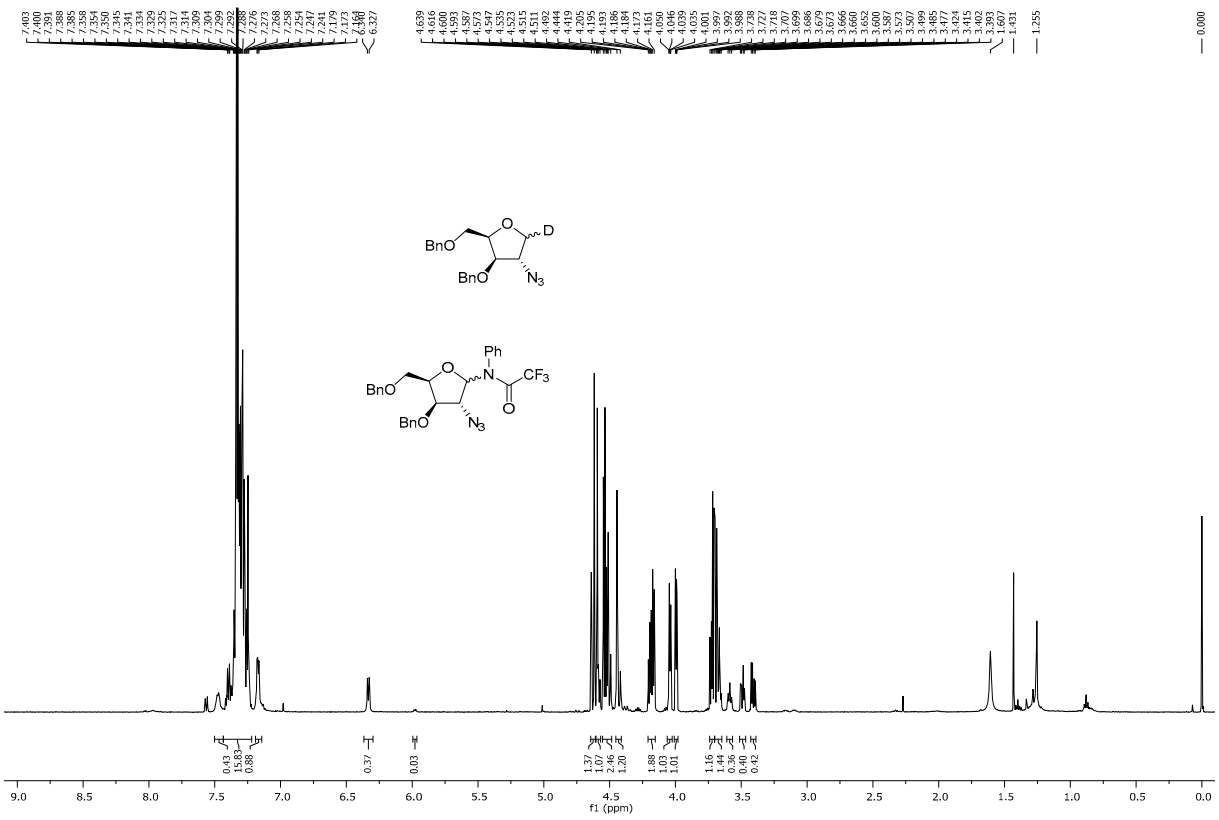


^{2}H NMR, 77 MHz, $CHCl_3$ of compound **71**

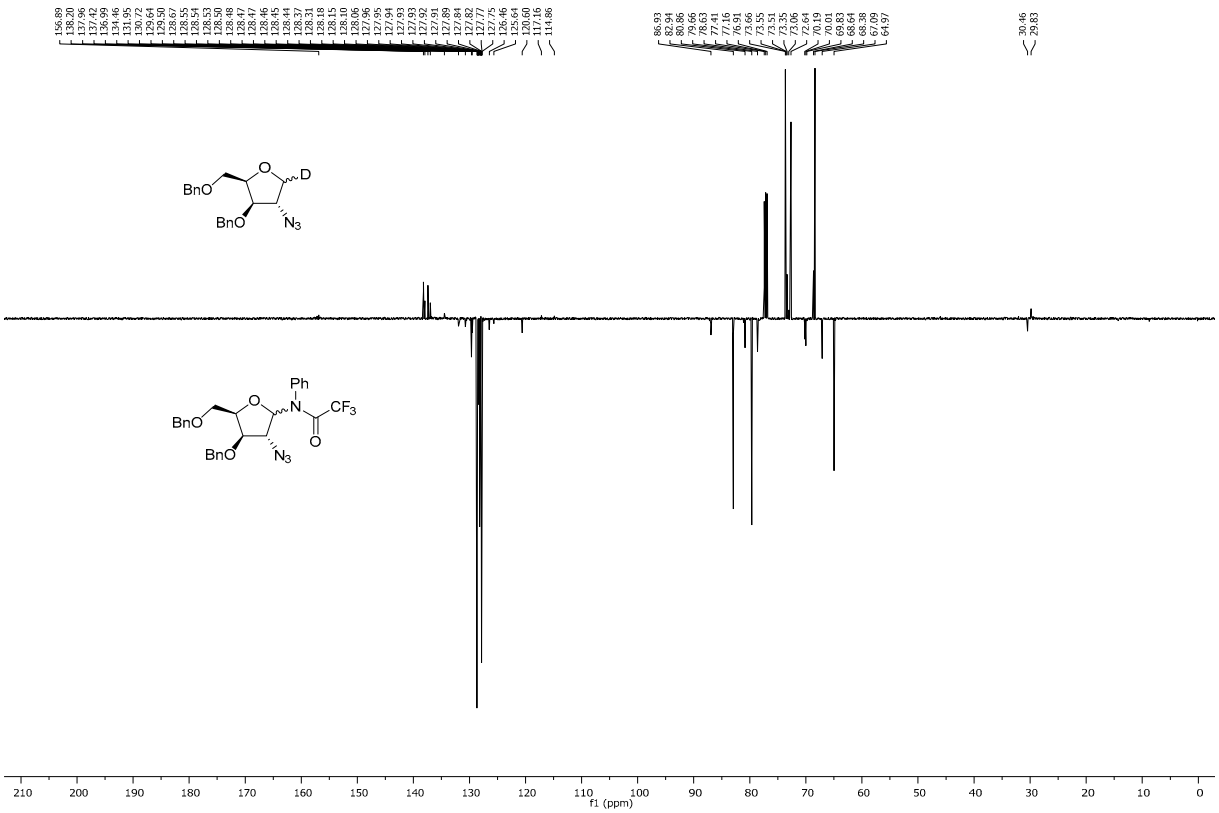


1-[^{2}H]-1,4-anhydro-2-azido-3,5-di-*O*-benzyl-2-deoxy-α/β-D-xylitol (72)

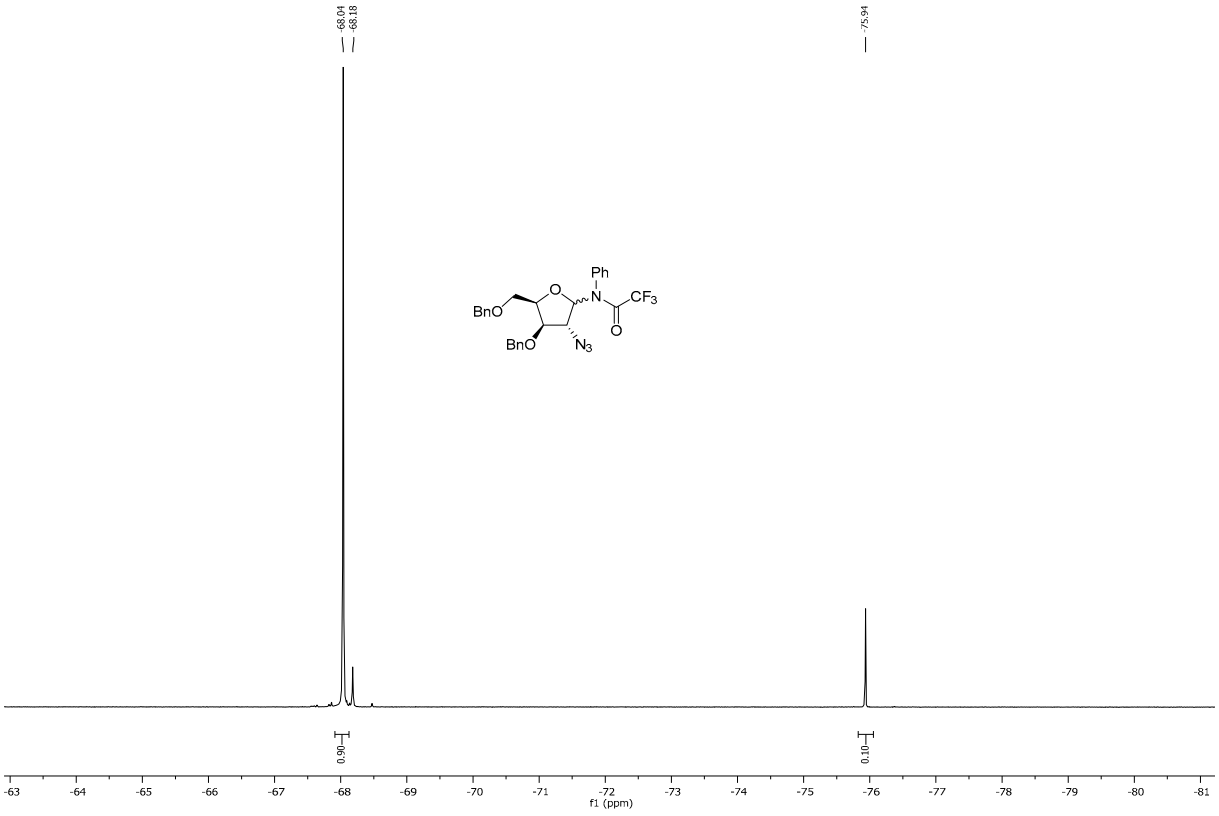
^{1}H NMR, 500 MHz, $CDCl_3$ of compounds **72** and **79**



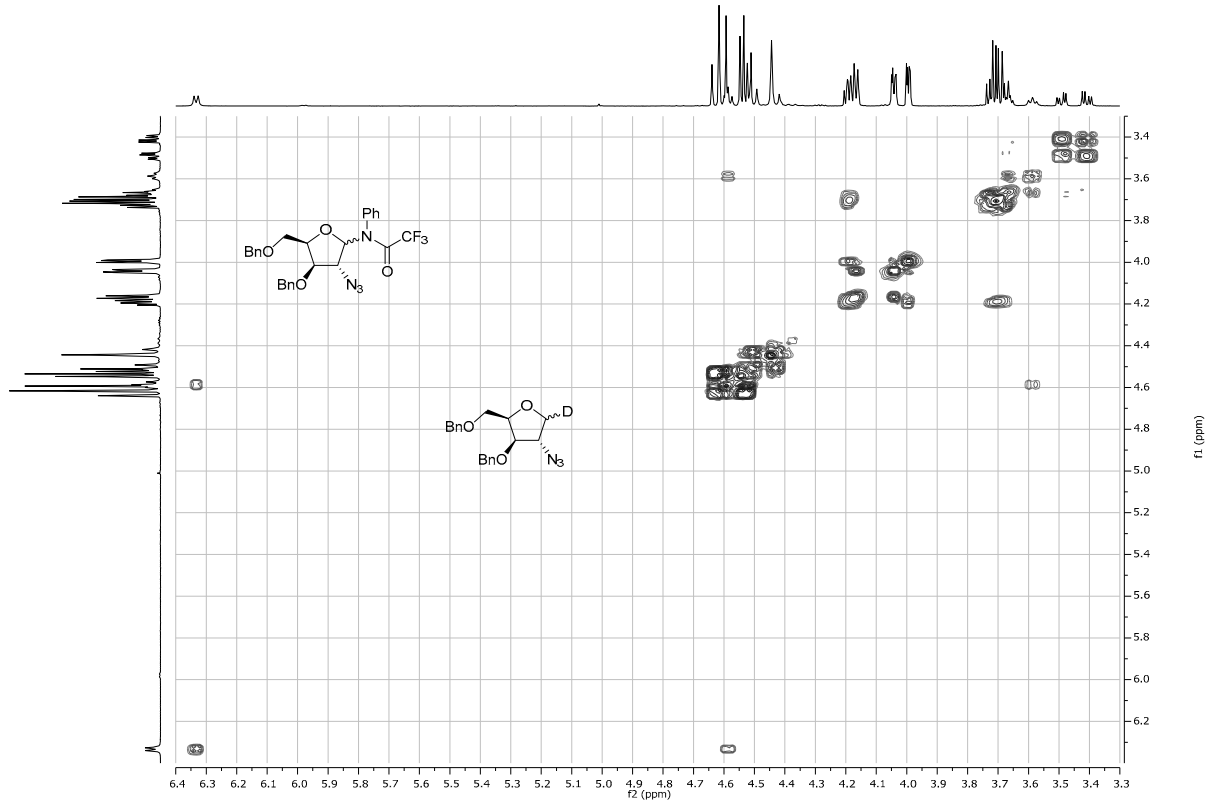
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compounds **72** and **79**



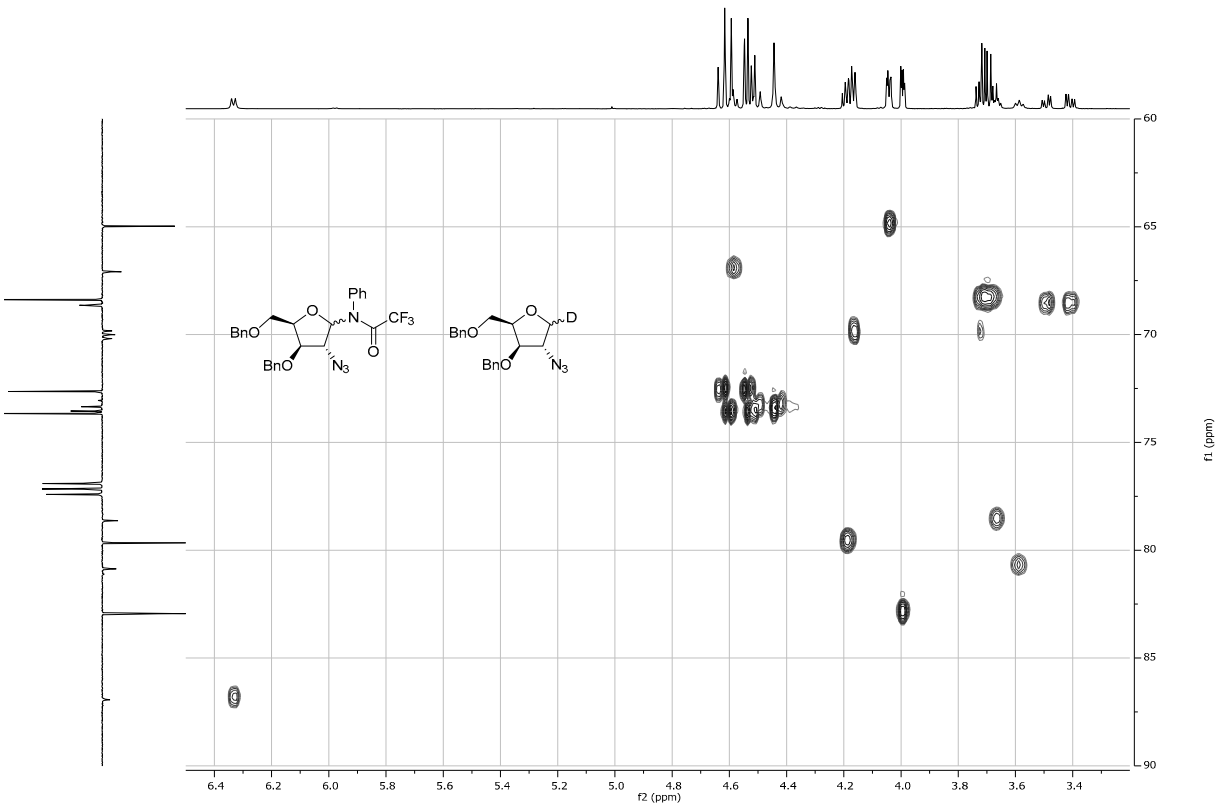
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **79**



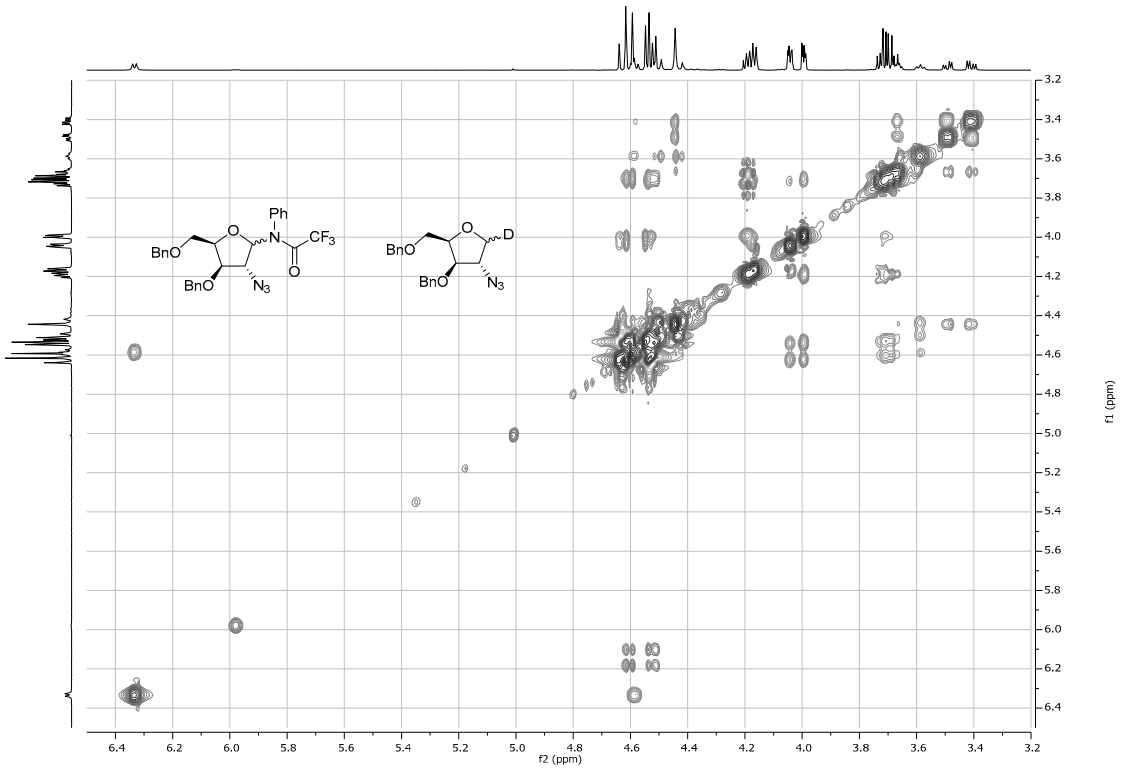
^{1}H-^{1}H COSY of compounds **72** and **79**



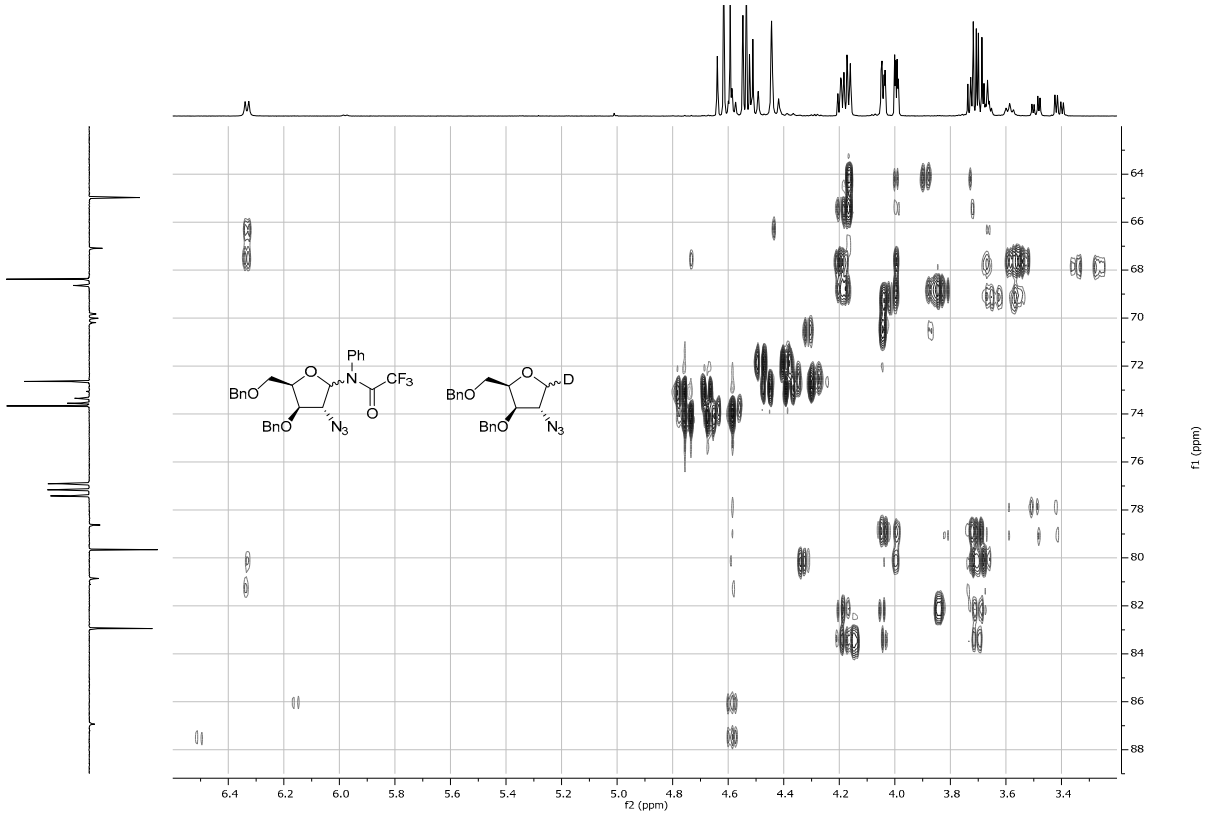
^{1}H-^{13}C HSQC of compounds **72** and **79**



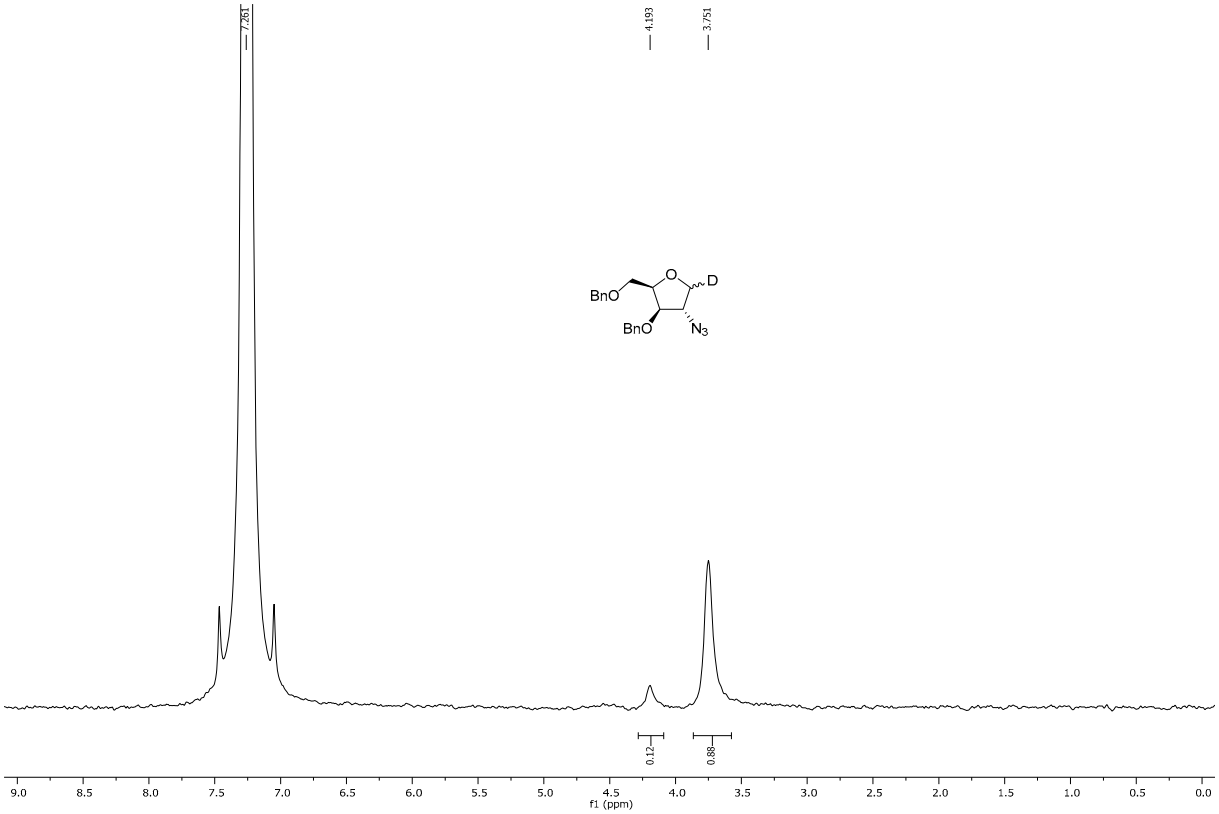
^{1}H-^{1}H NOESY of compounds **72** and **79**



^{1}H-^{13}C HSQC-HECADE of compounds **72** and **79**

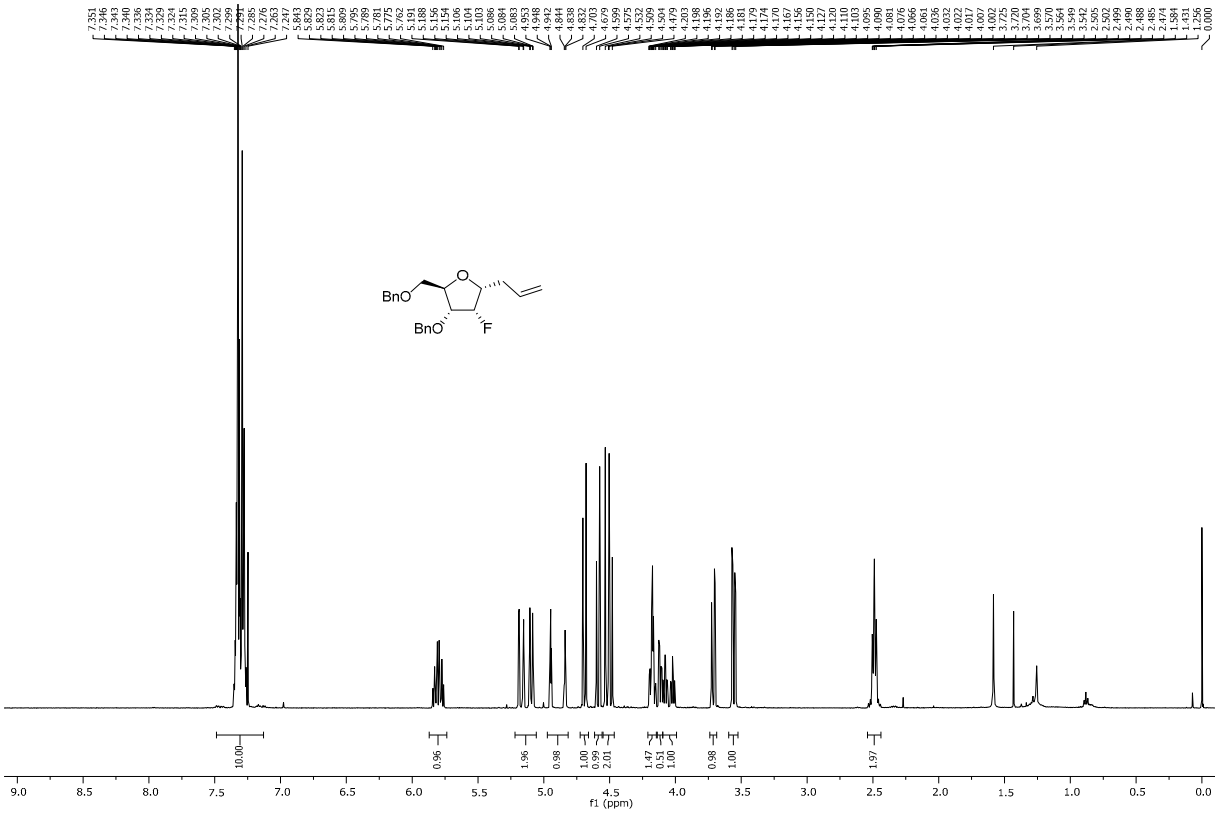


^{2}H NMR, 77 MHz, $CHCl_3$ of compound **72**

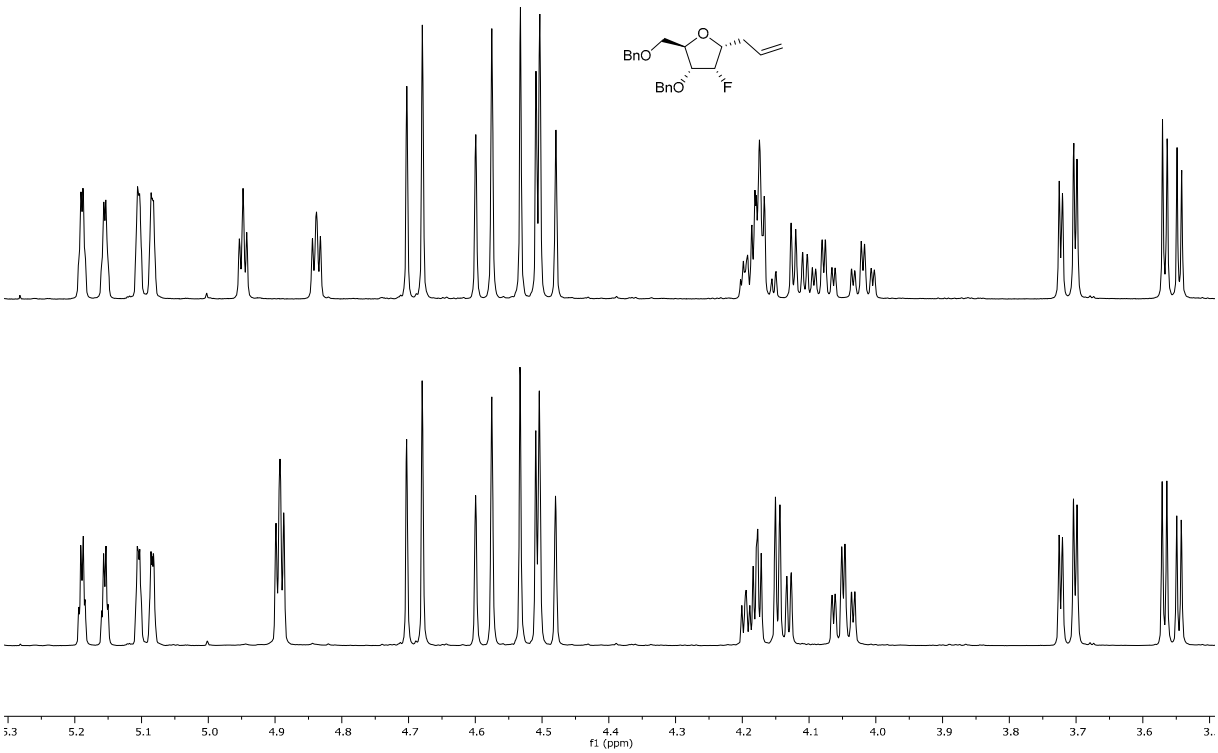


Allyl 3,5-di-*O*-benzyl-1,2-dideoxy-2-fluoro-α-D-ribofuranoside (73)

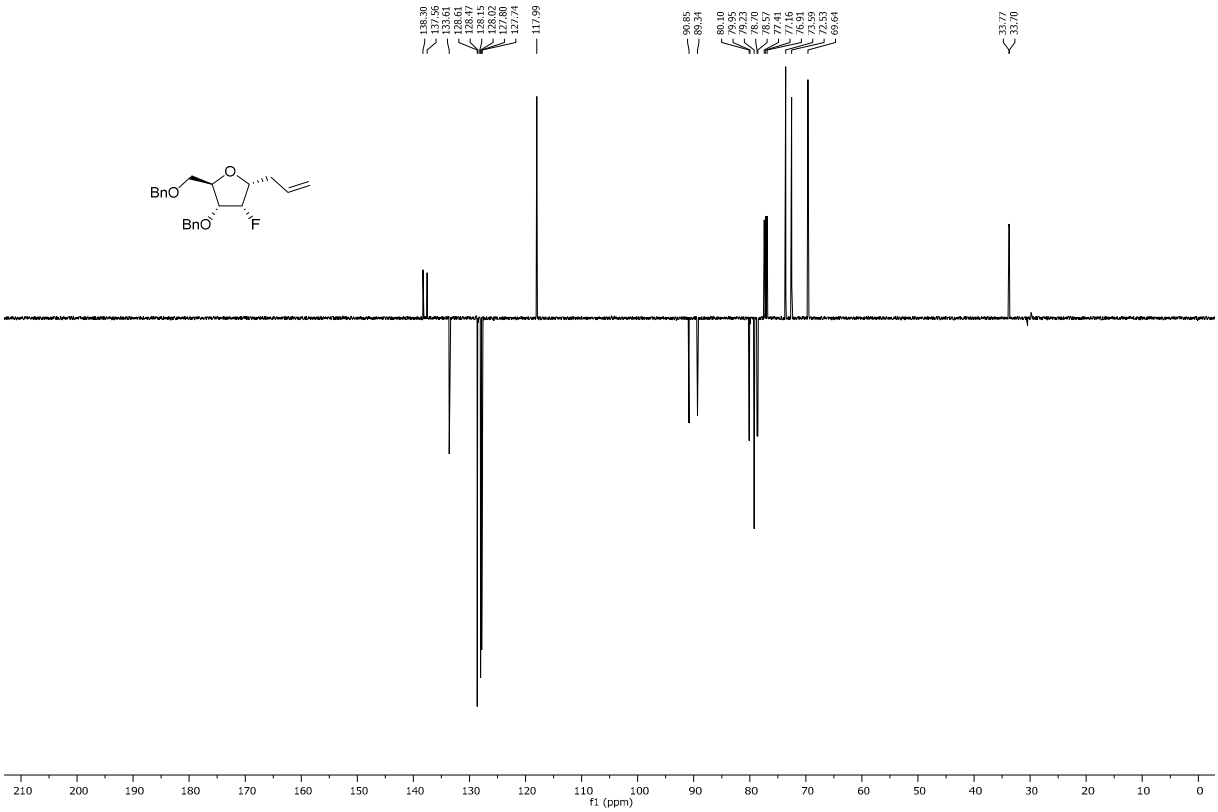
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **73**



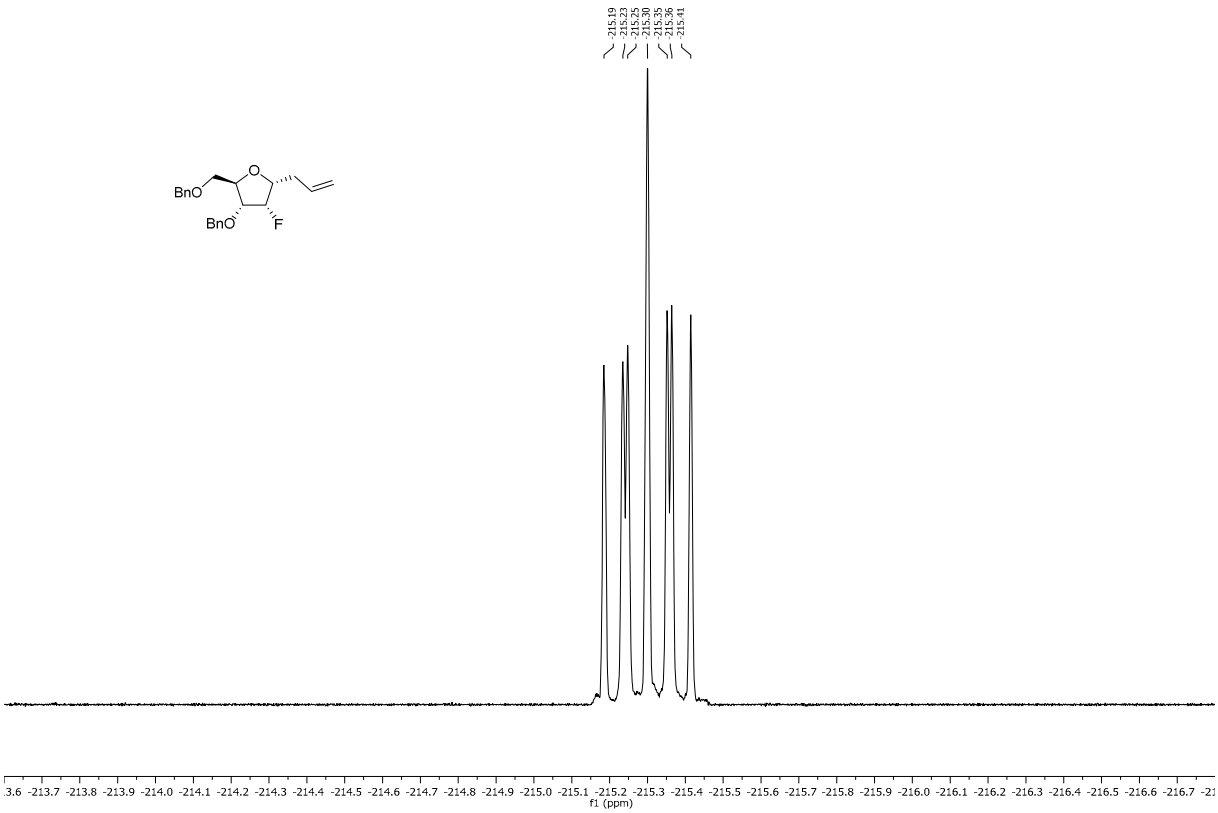
^{19}F-decoupled ^{1}H NMR, (-215 ppm)



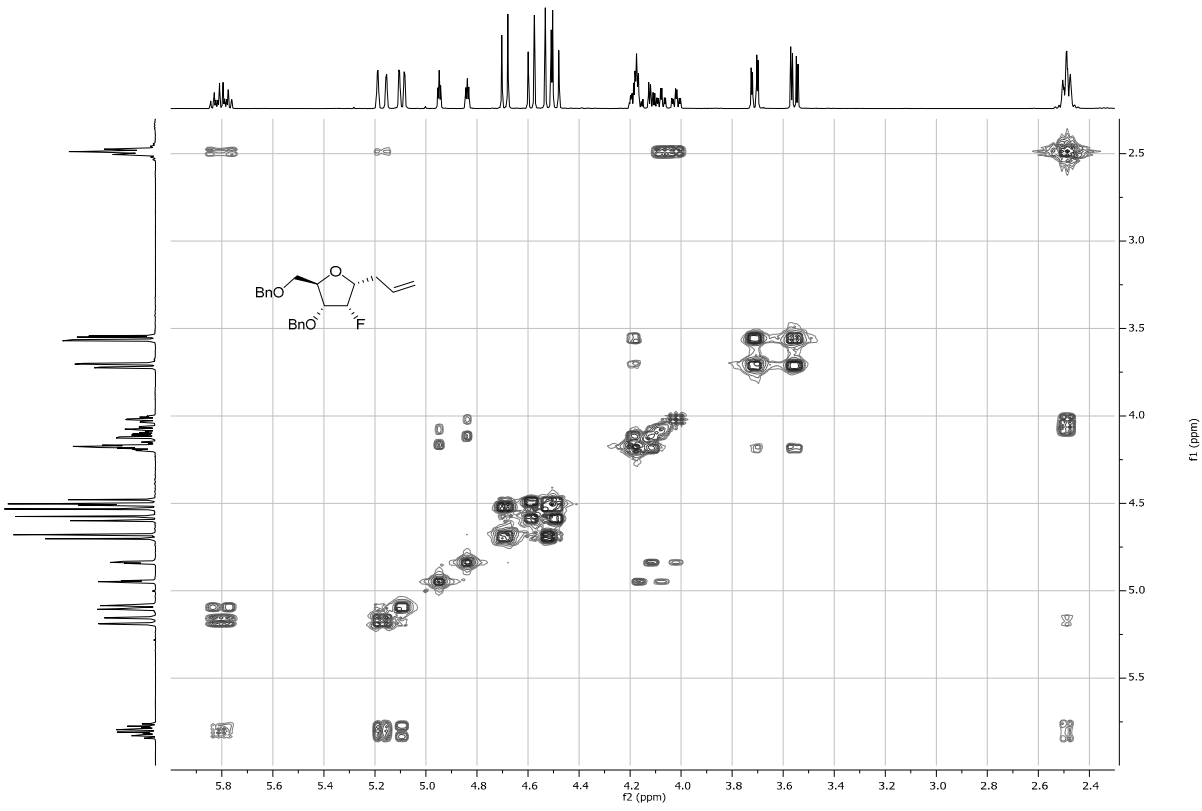
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **73**



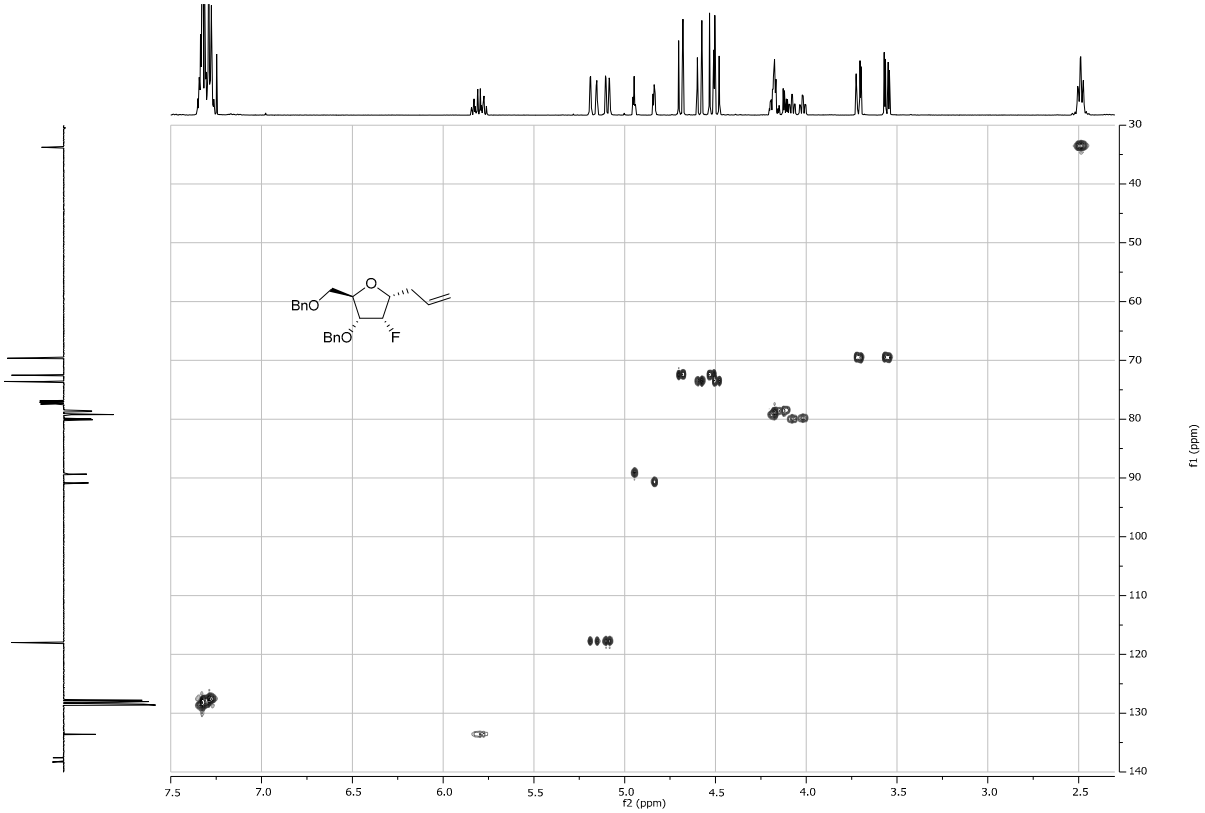
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **73**



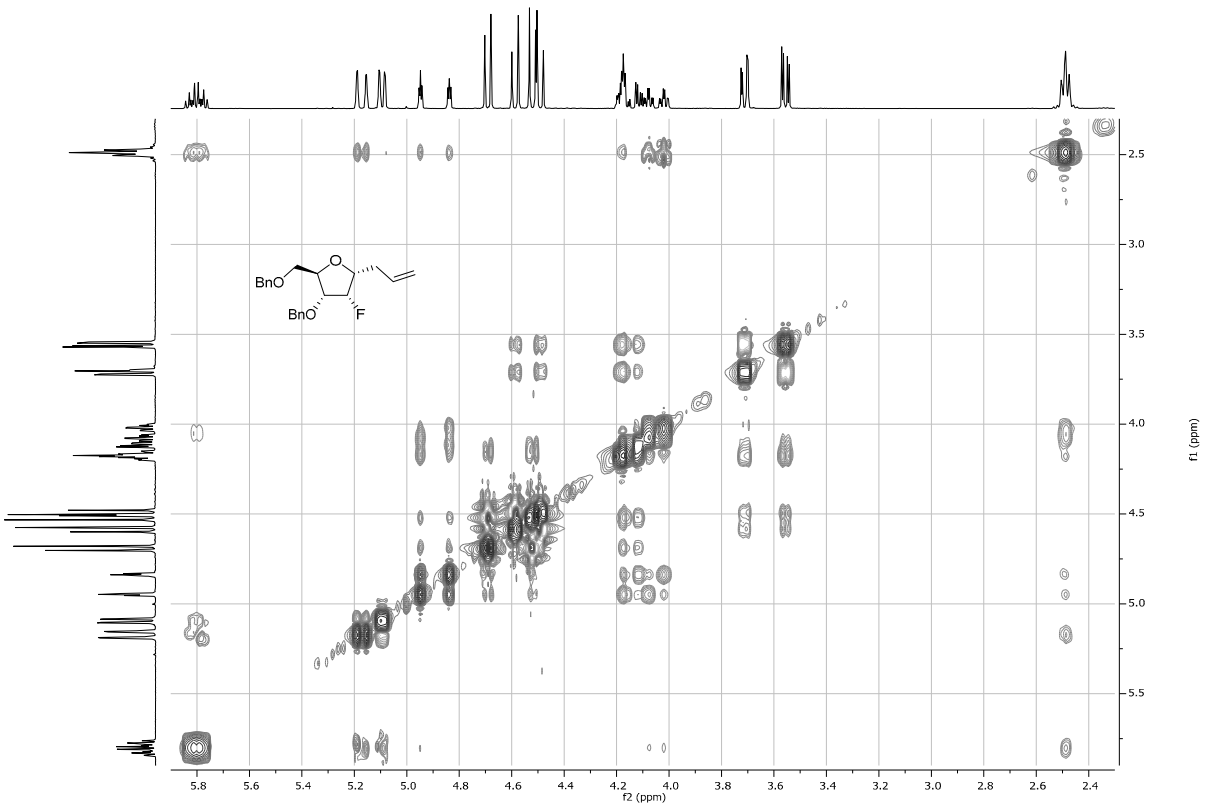
^{1}H-^{1}H COSY of compound **73**



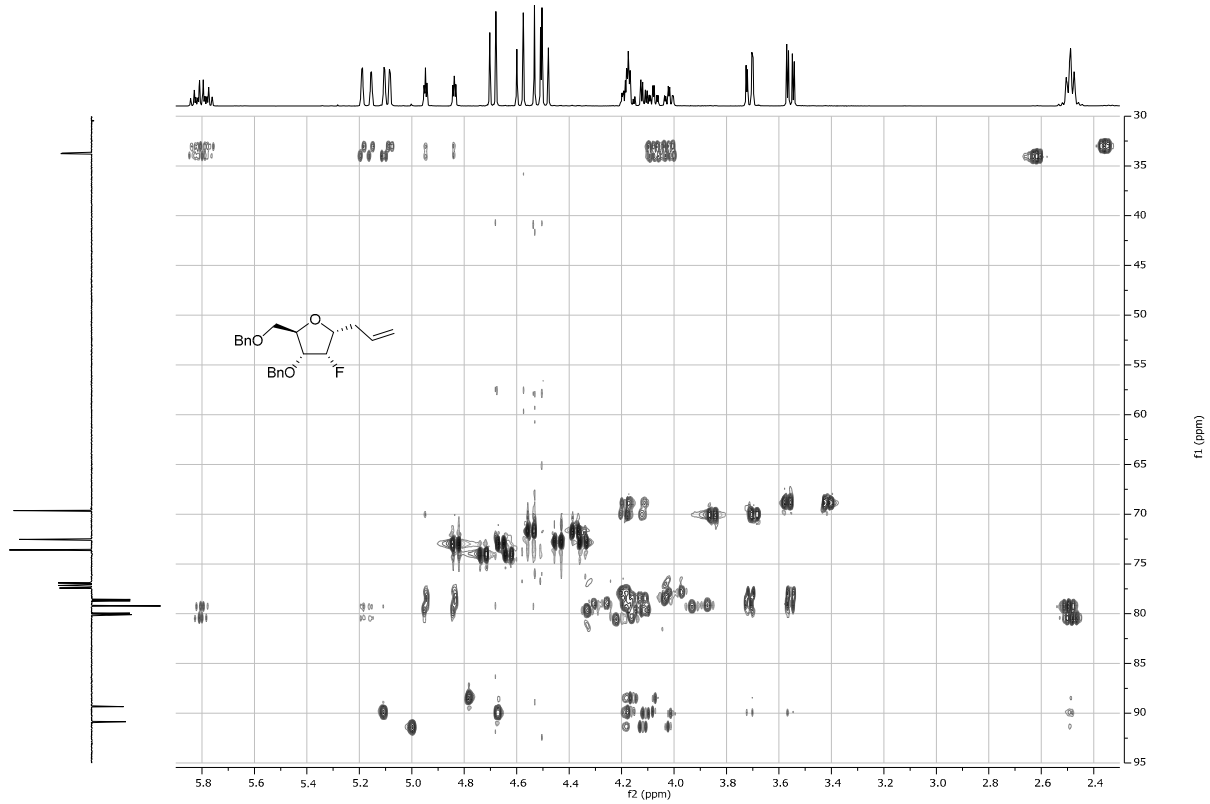
^{1}H-^{13}C HSQC of compound **73**



^{1}H-^{1}H NOESY of compound **73**

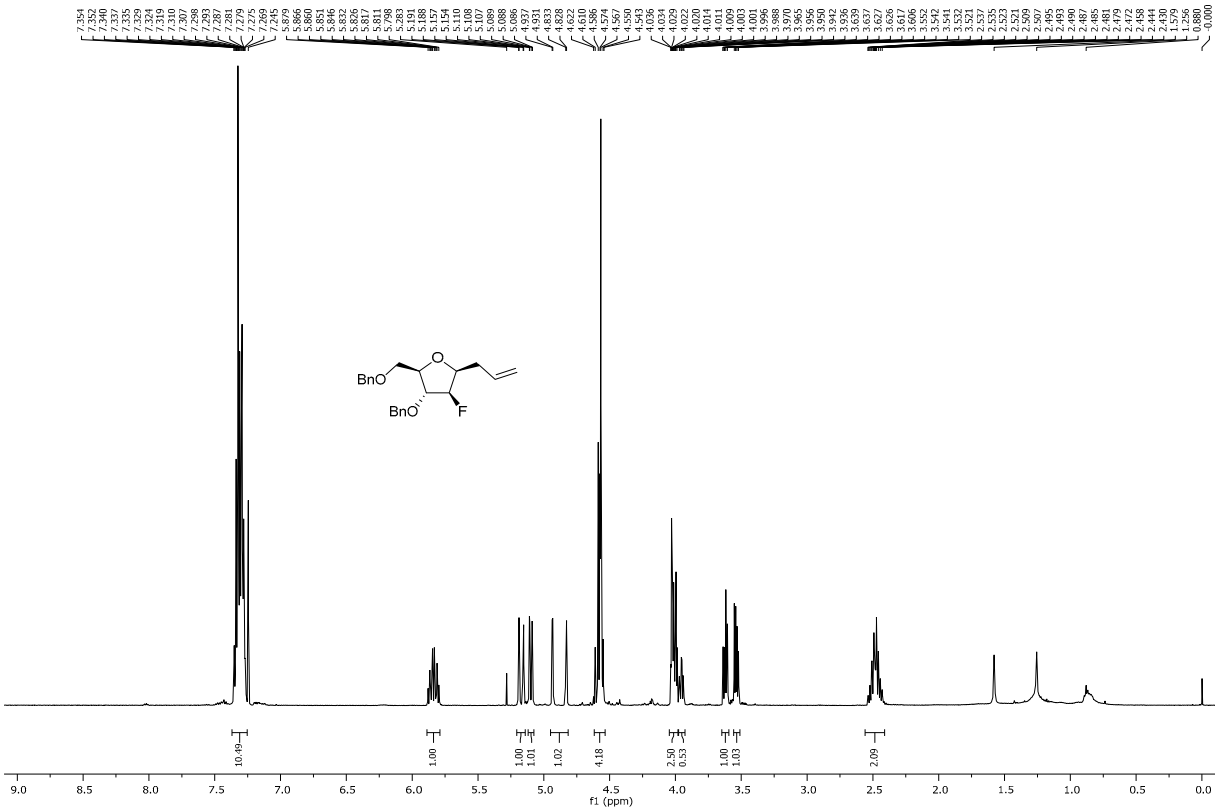


^{1}H-^{13}C HSQC-HECADE of compound **73**

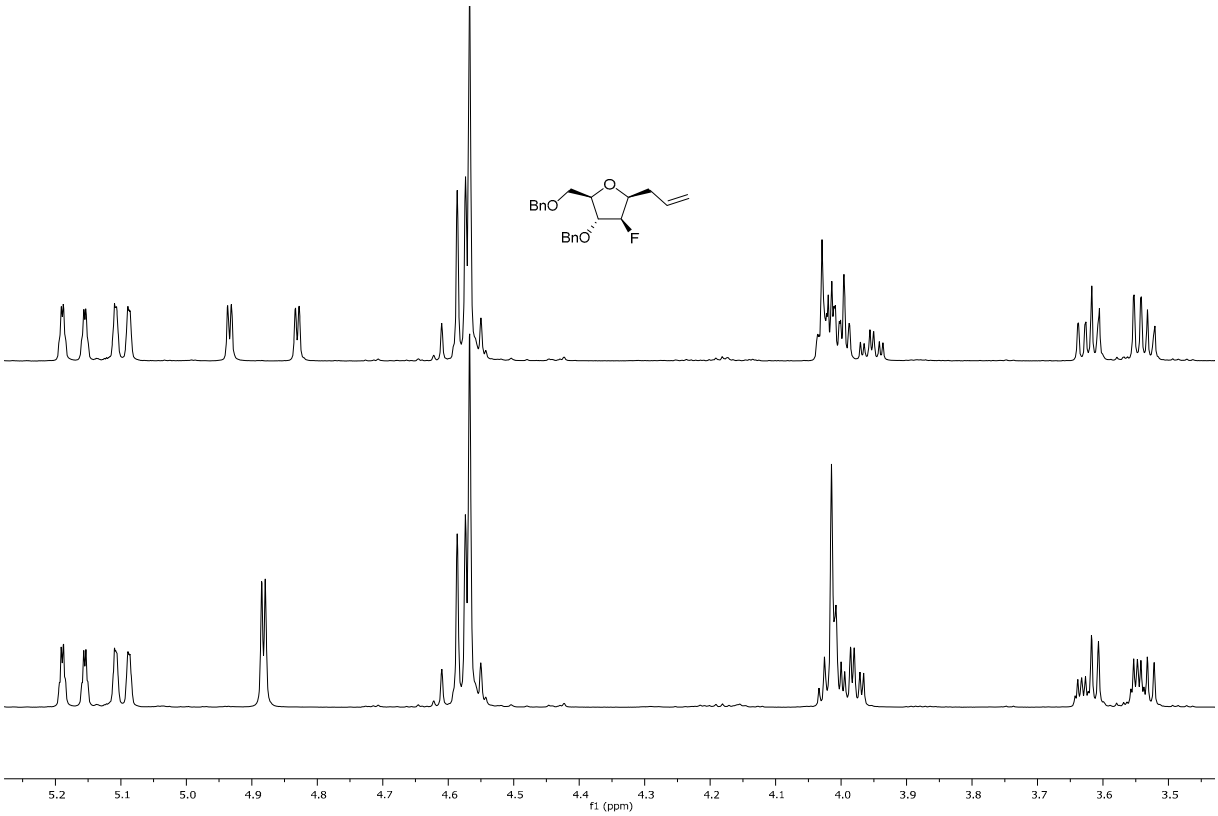


Allyl 3,5-di-*O*-benzyl-1,2-dideoxy-2-fluoro-β-D-arabinofuranoside (74)

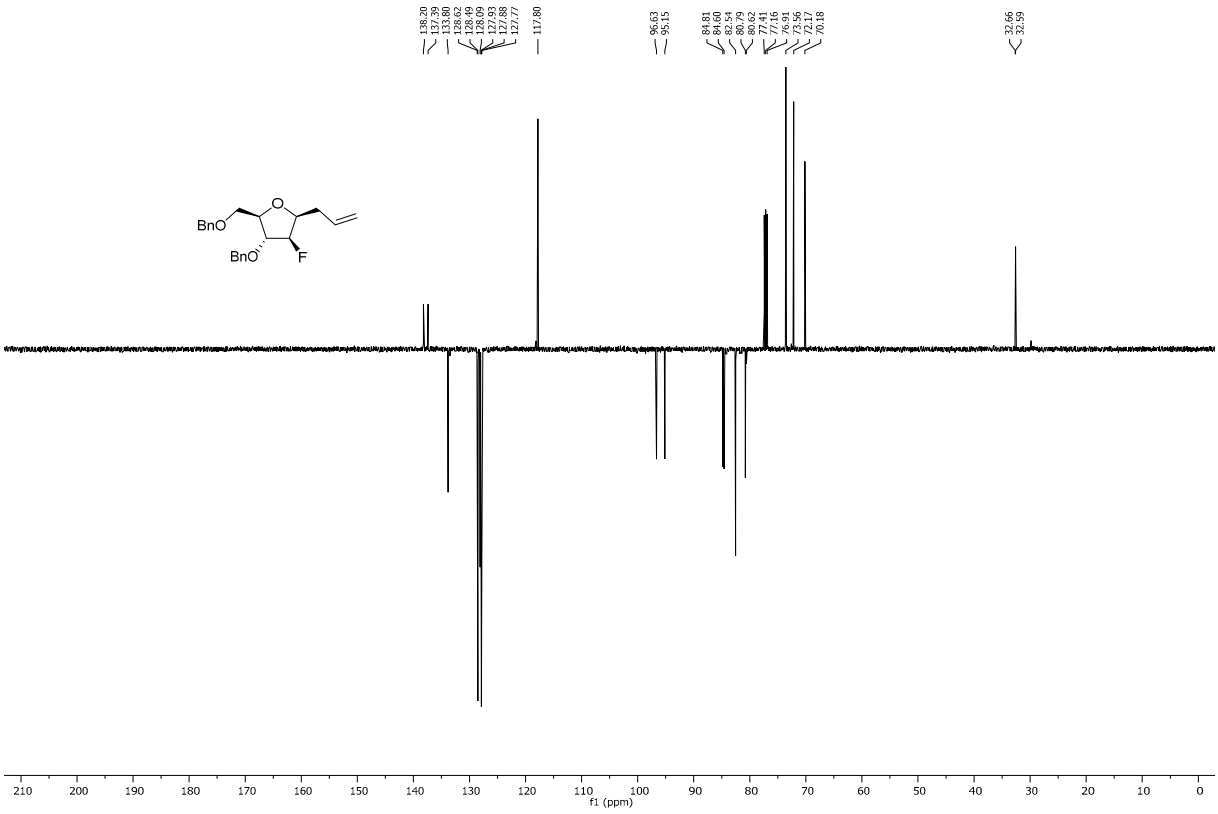
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **74**



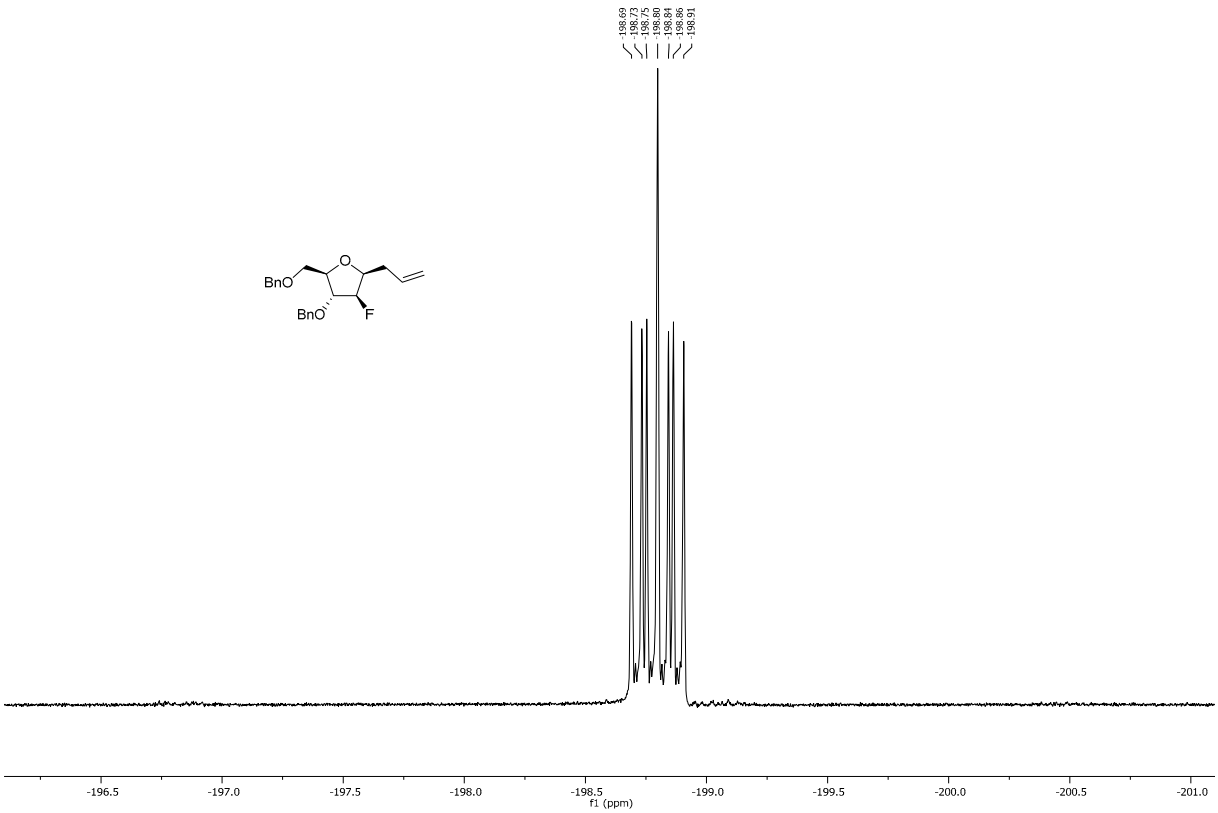
^{19}F-decoupled ^{1}H NMR, (-200 ppm)



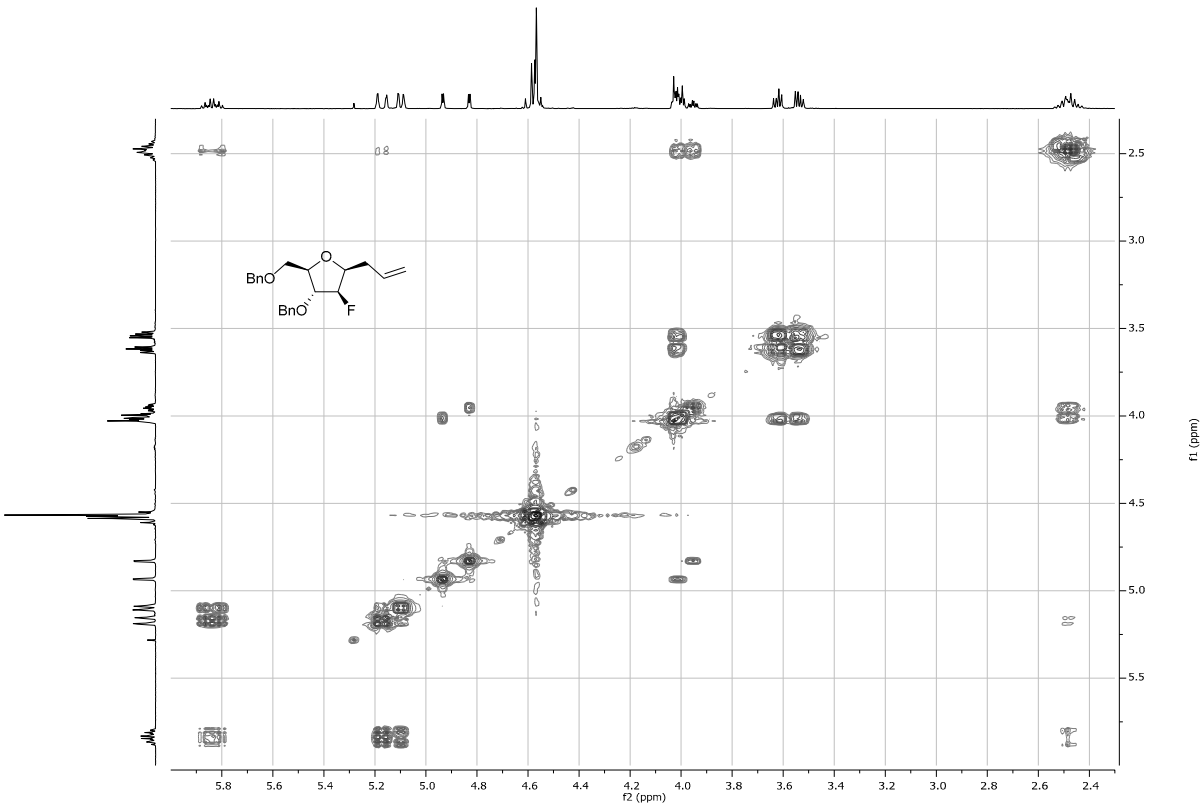
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **74**



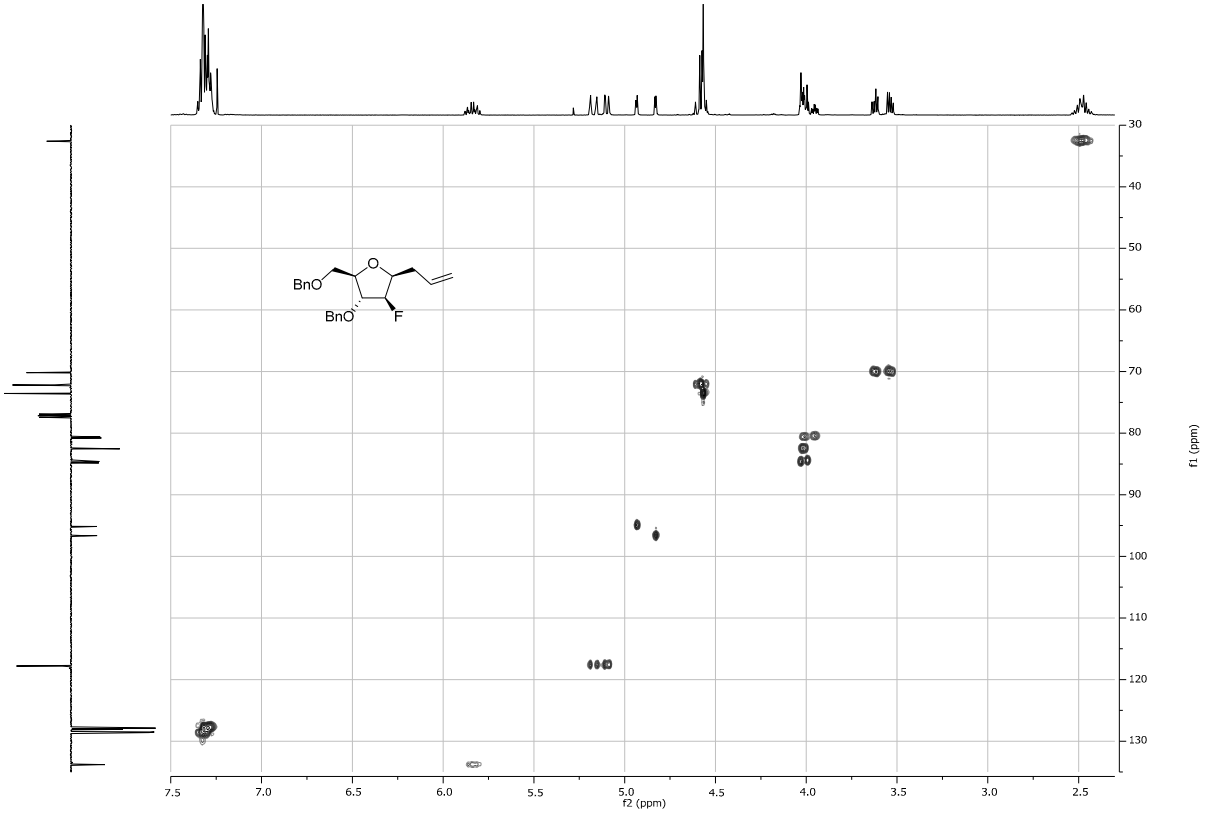
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **74**



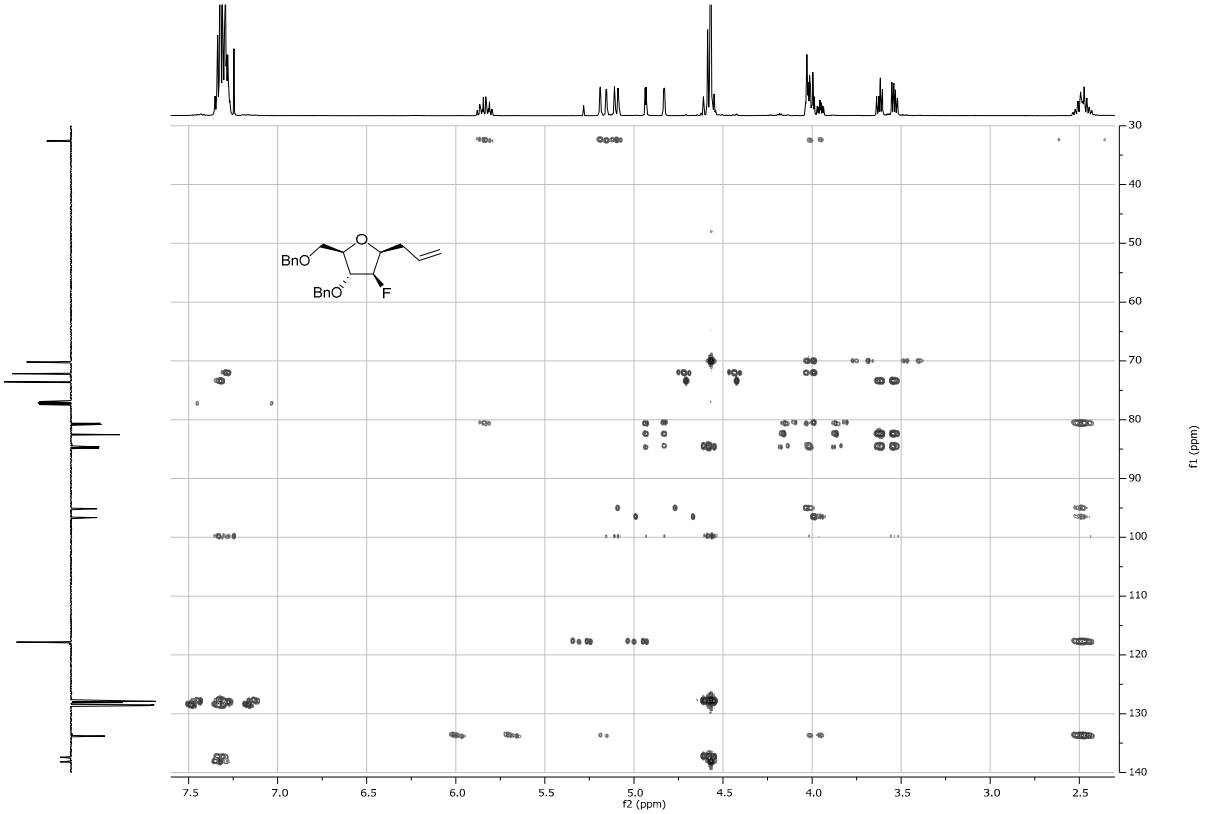
^{1}H-^{1}H COSY of compound **74**



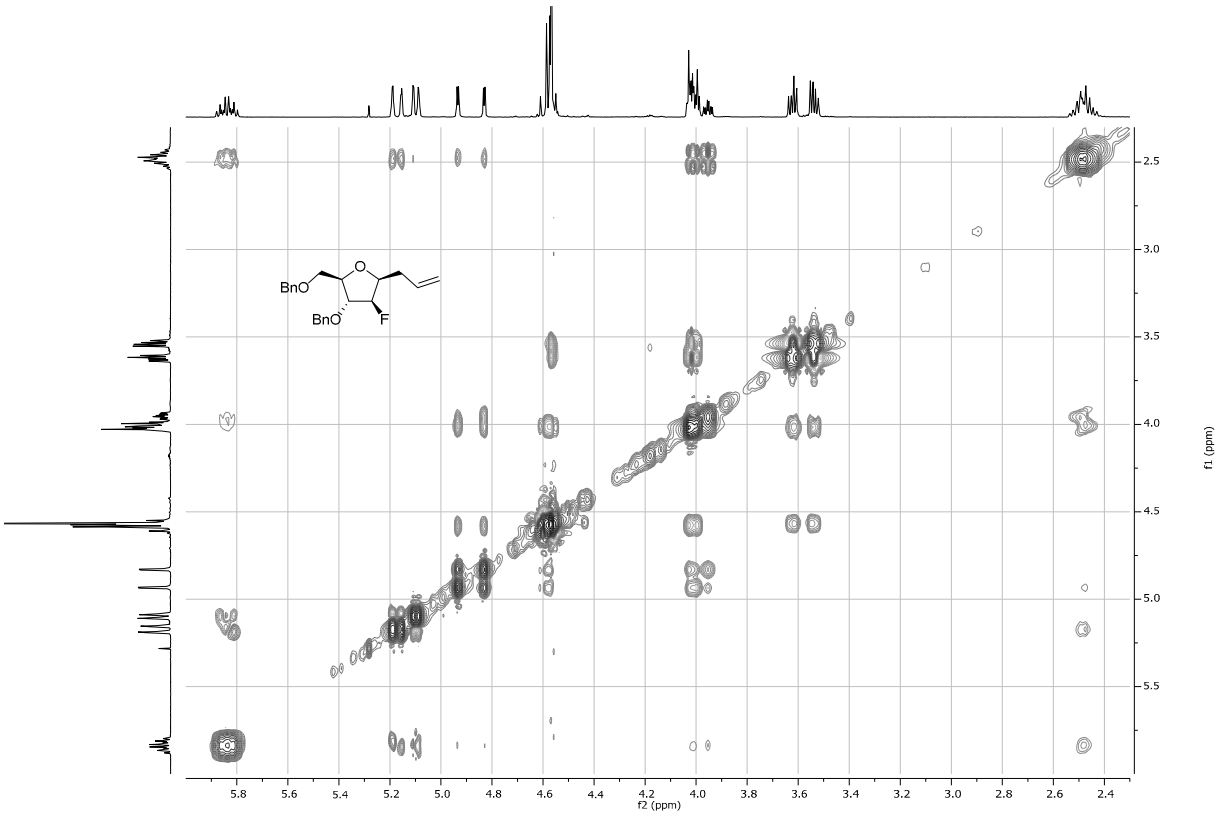
^{1}H-^{13}C HSQC of compound **74**



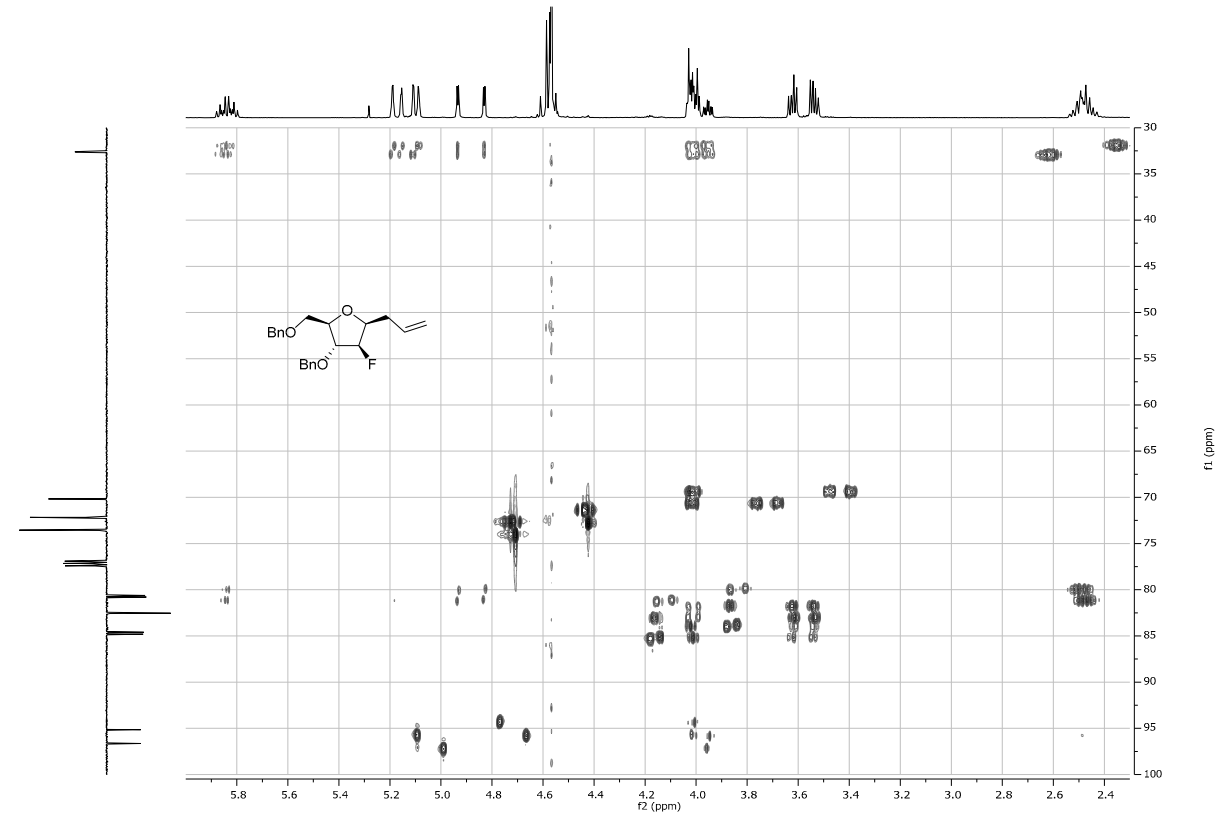
^{1}H-^{13}C HMBC of compound **74**



^{1}H-^{1}H NOESY of compound **74**

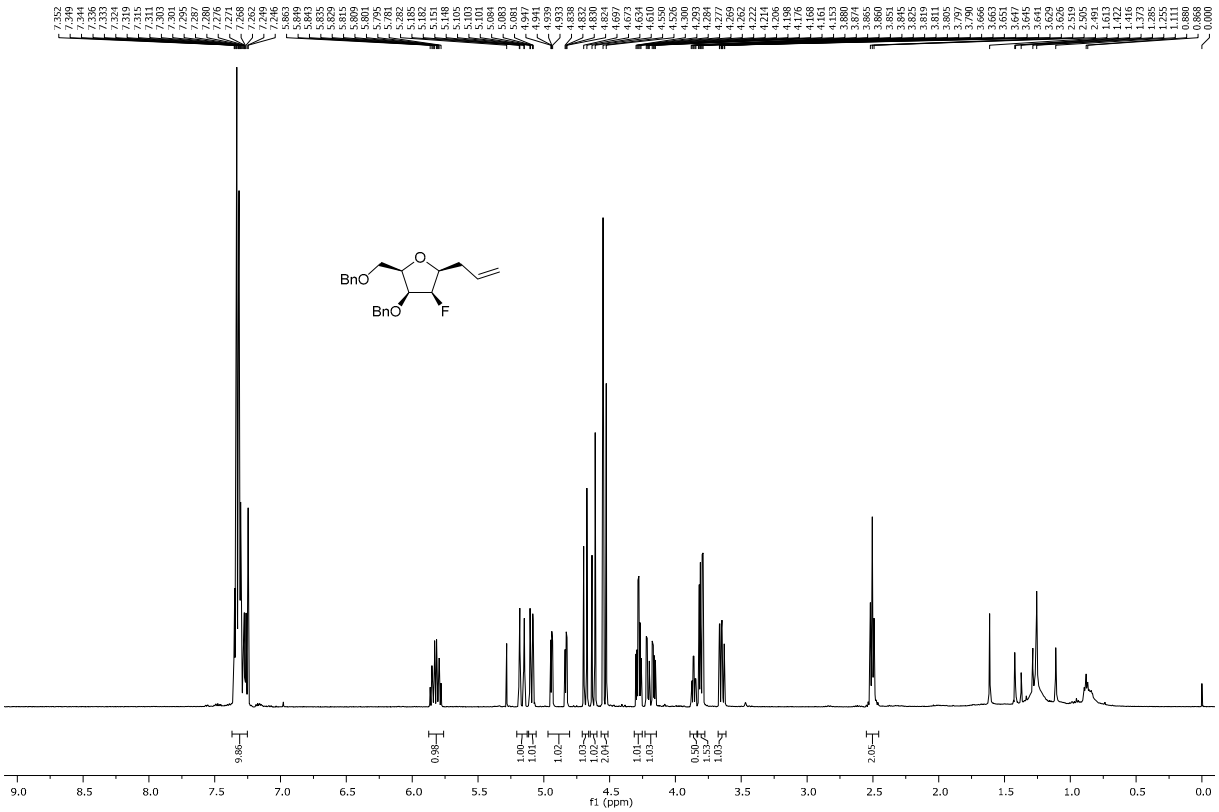


^{1}H-^{13}C HSQC-HECADE of compound **74**

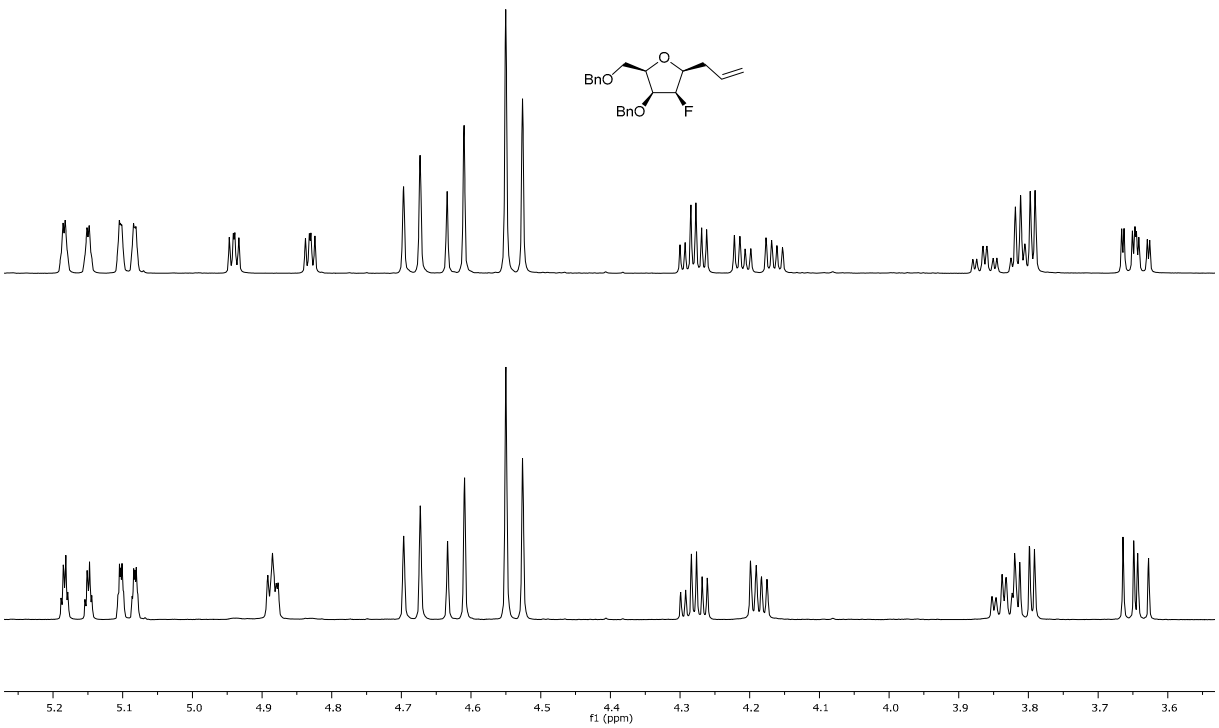


Allyl 3,5-di-*O*-benzyl-1,2-dideoxy-2-fluoro-β-D-lyxofuranoside (75)

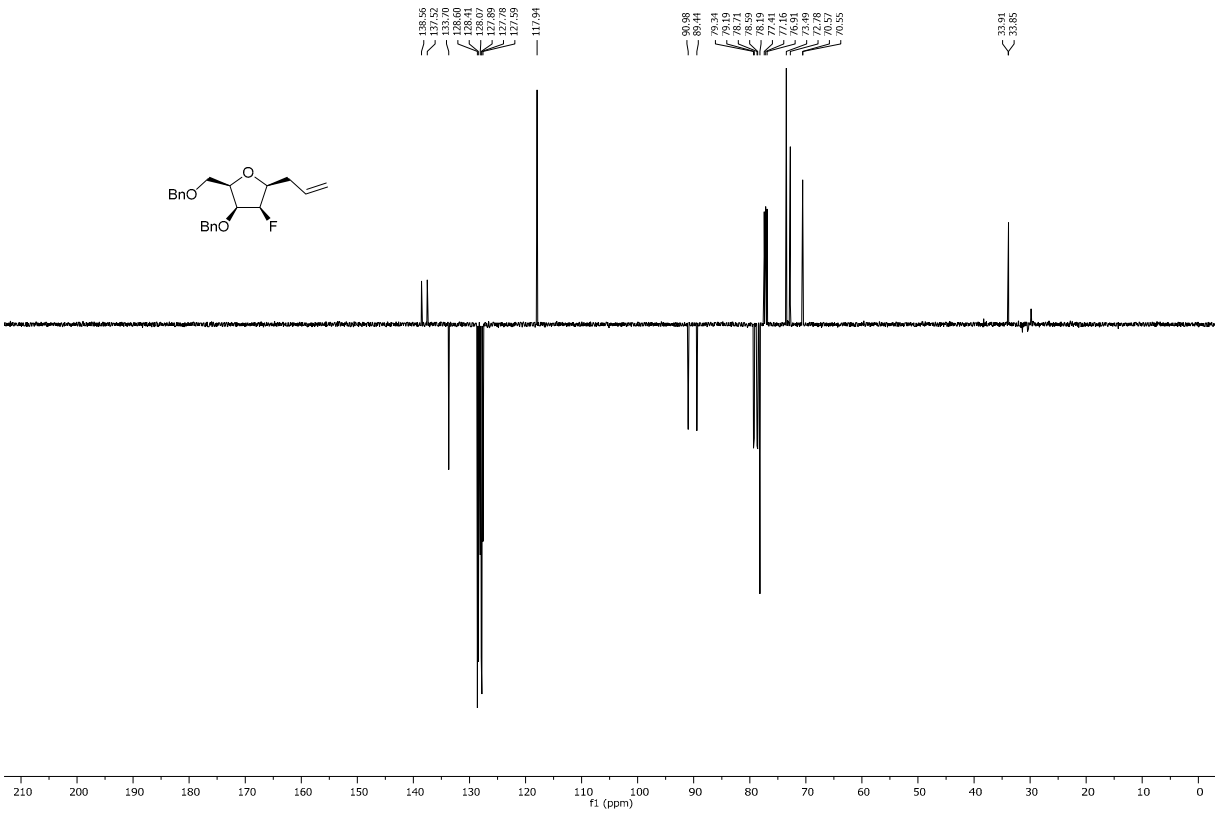
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **75**



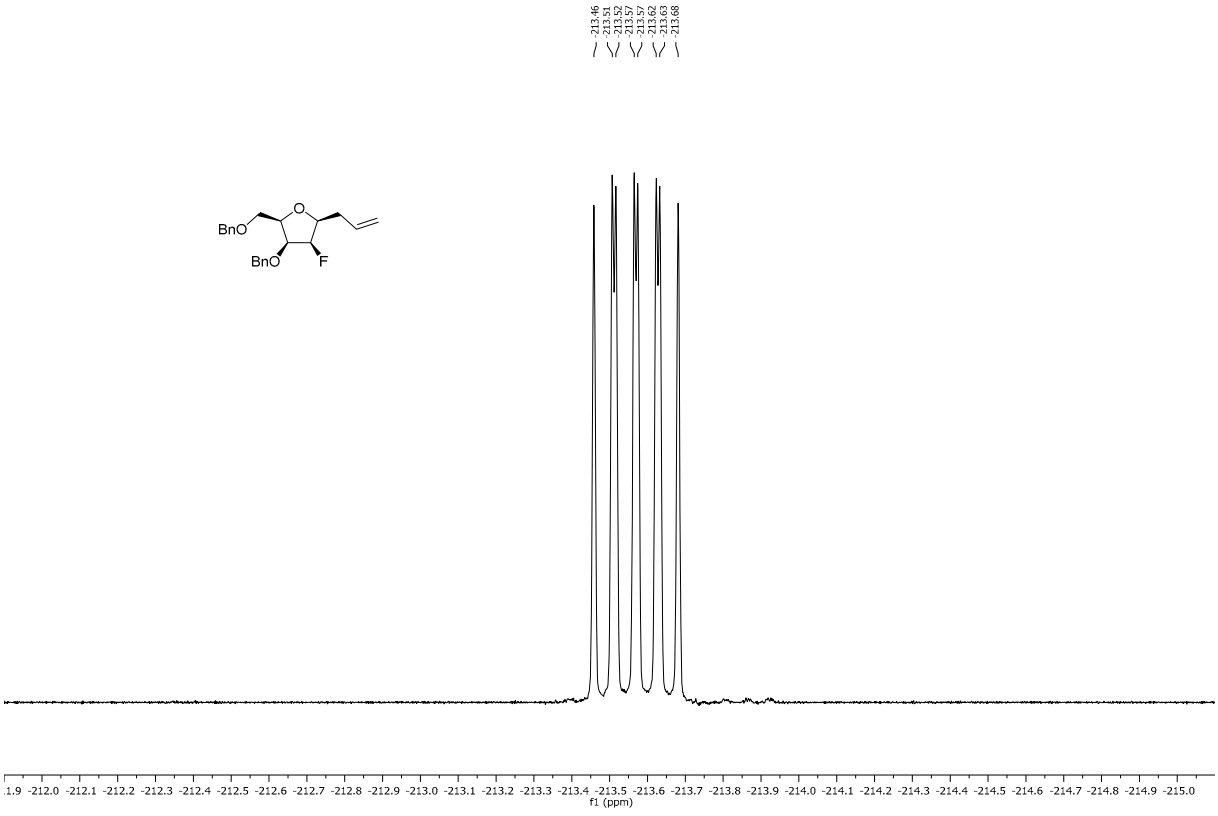
^{19}F-decoupled ^{1}H NMR (-200 ppm)



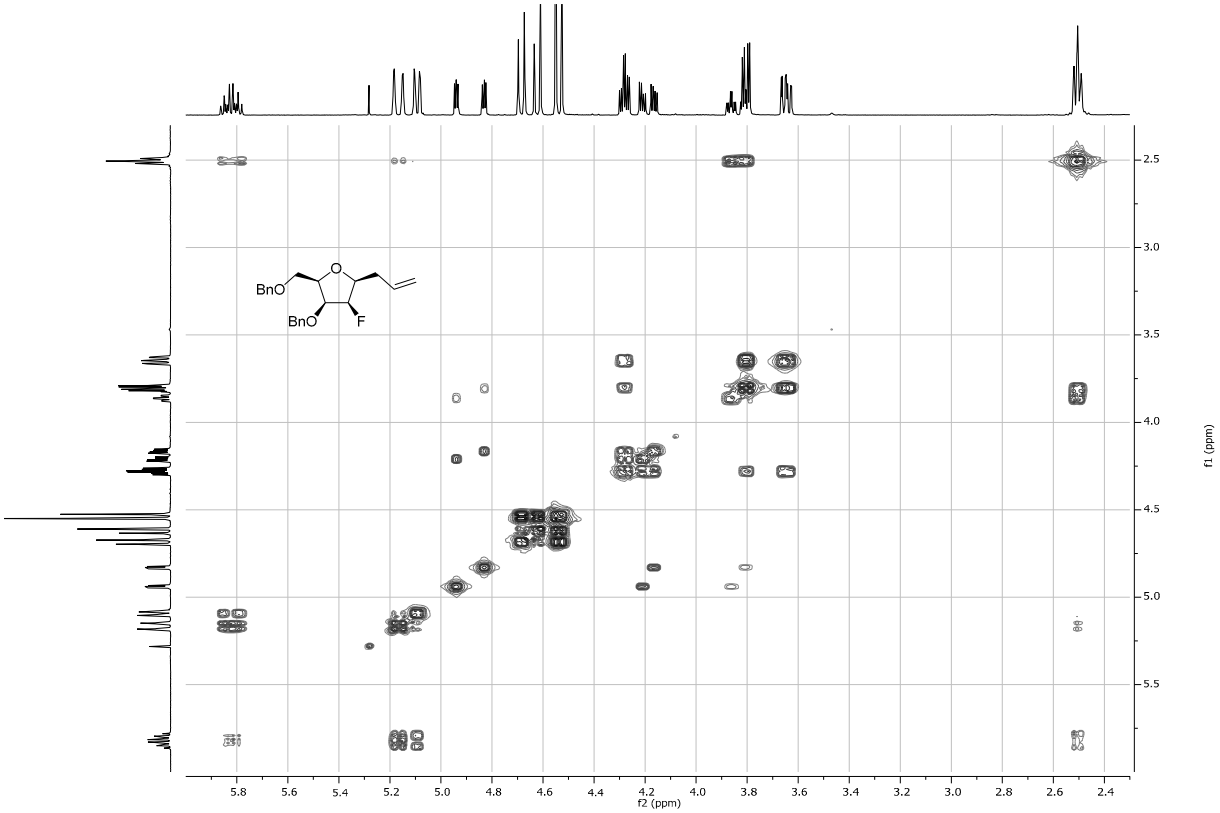
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **75**



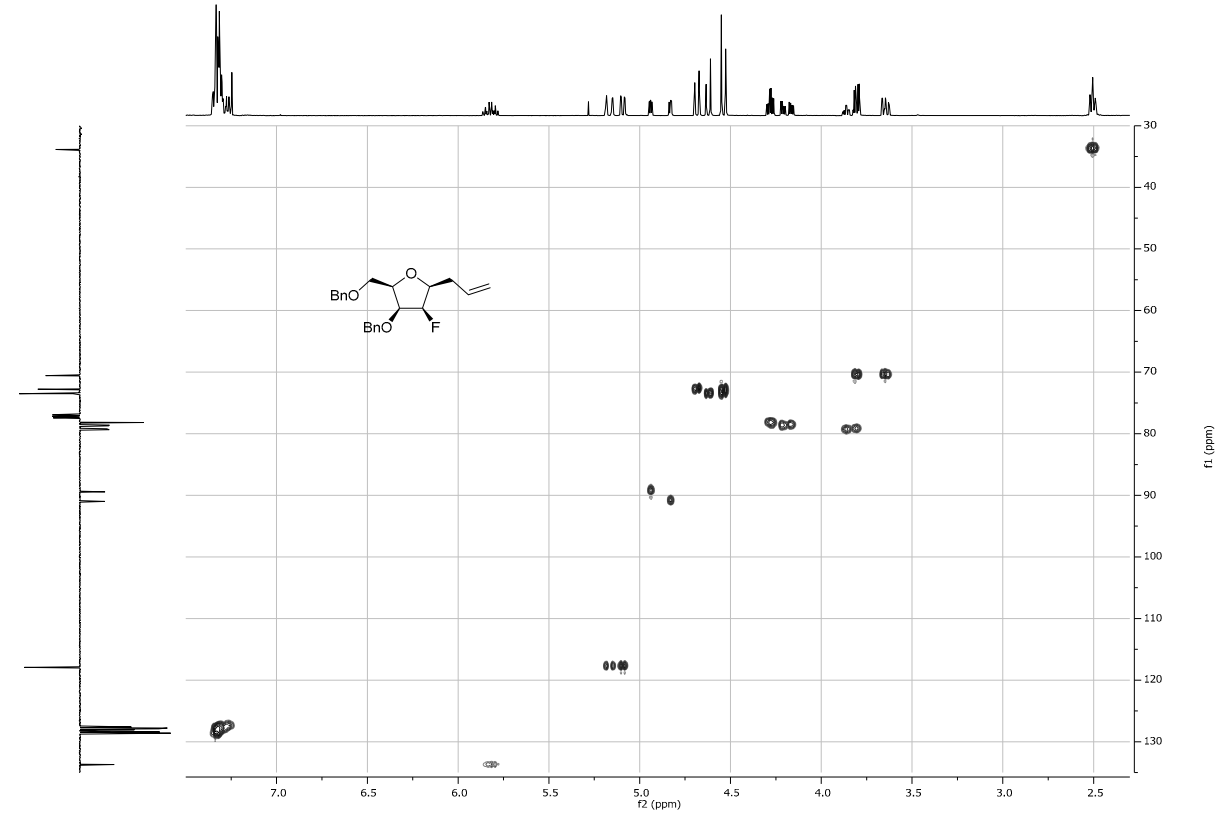
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **75**



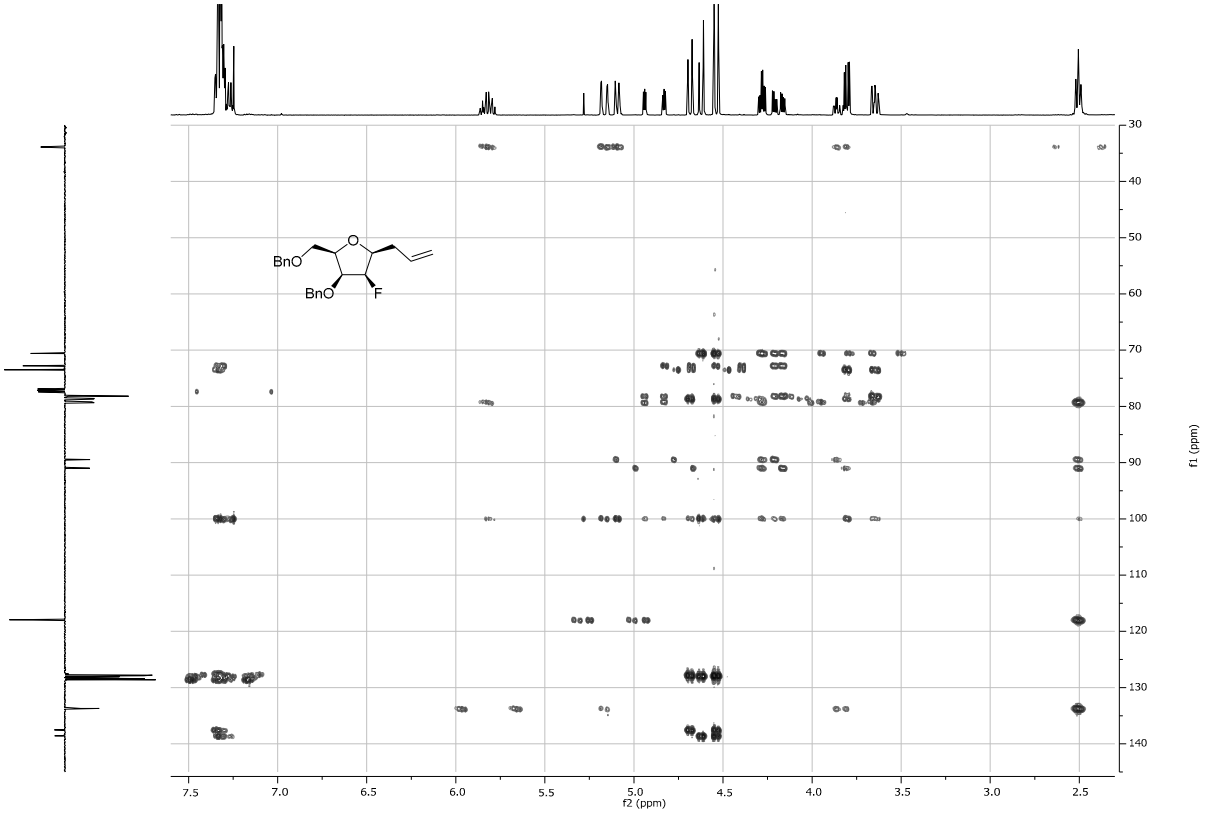
^{1}H-^{1}H COSY of compound **75**



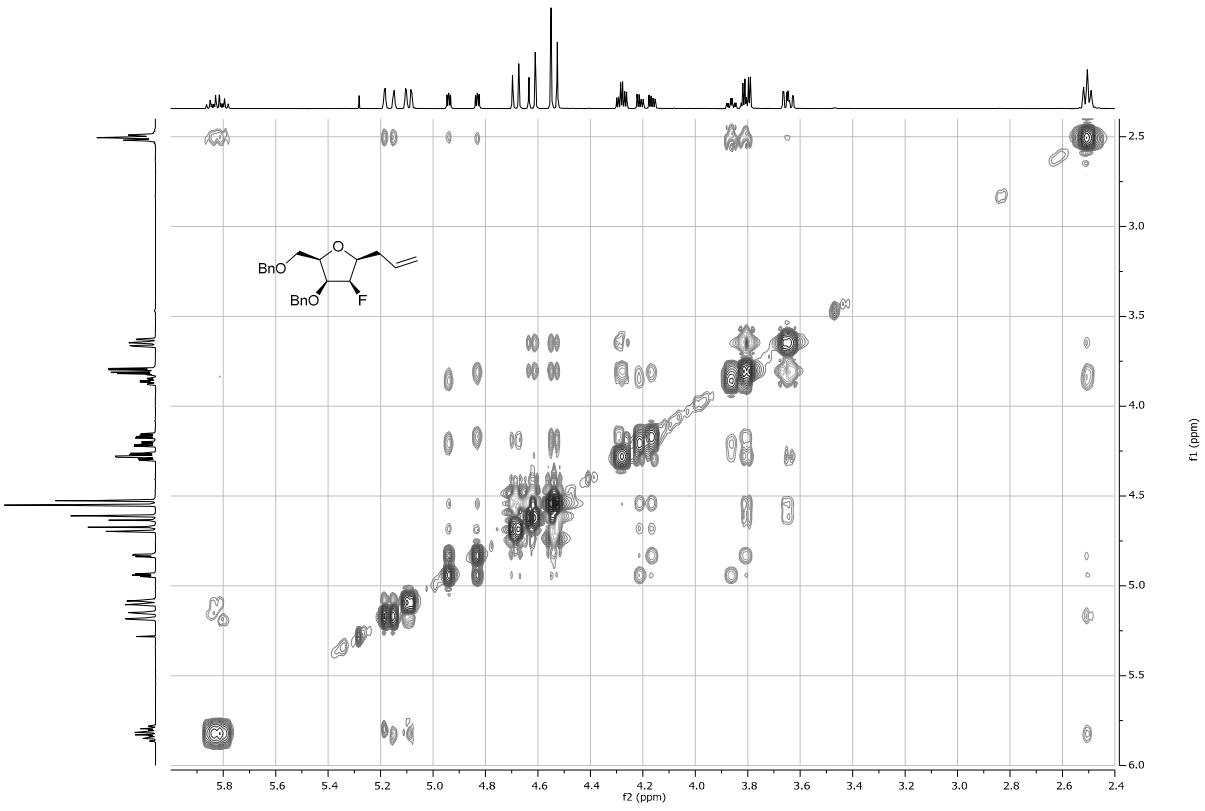
^{1}H-^{13}C HSQC of compound **75**



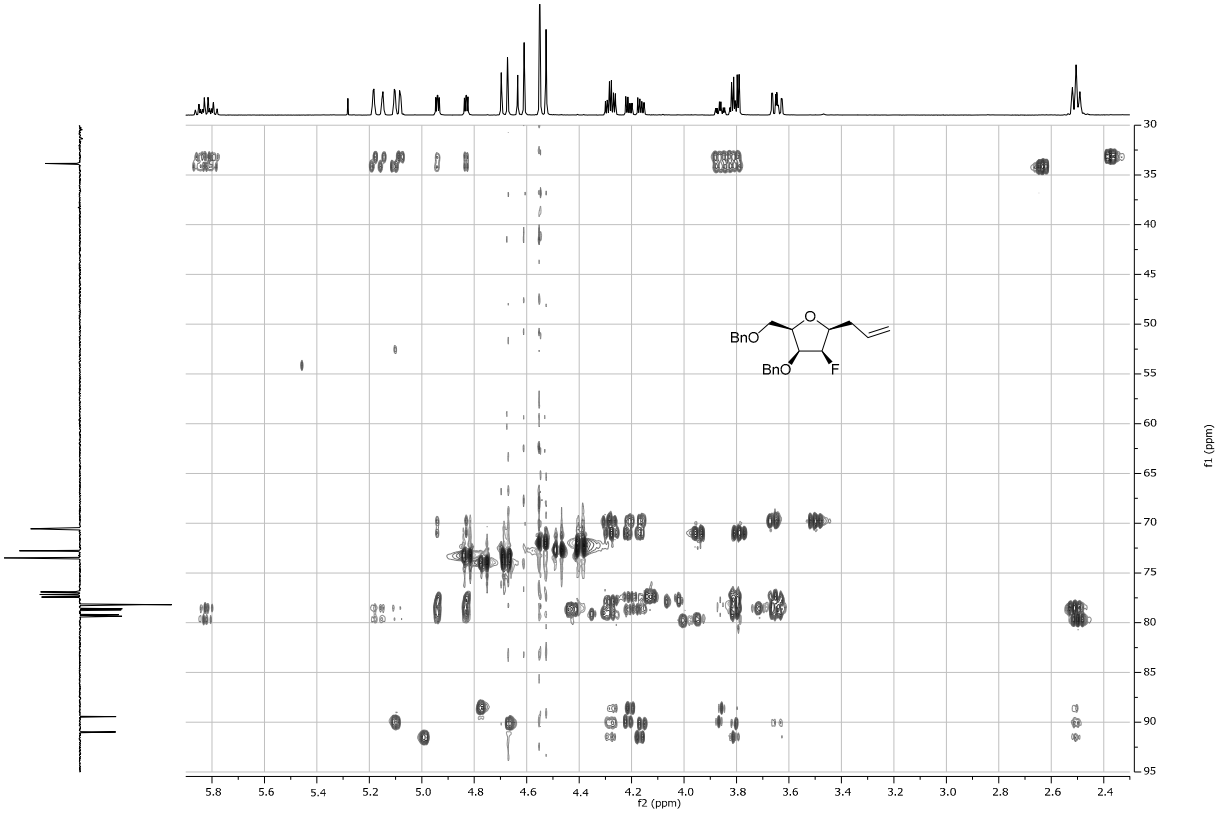
^{1}H-^{13}C HMBC of compound **75**



^{1}H-^{1}H NOESY of compound **75**

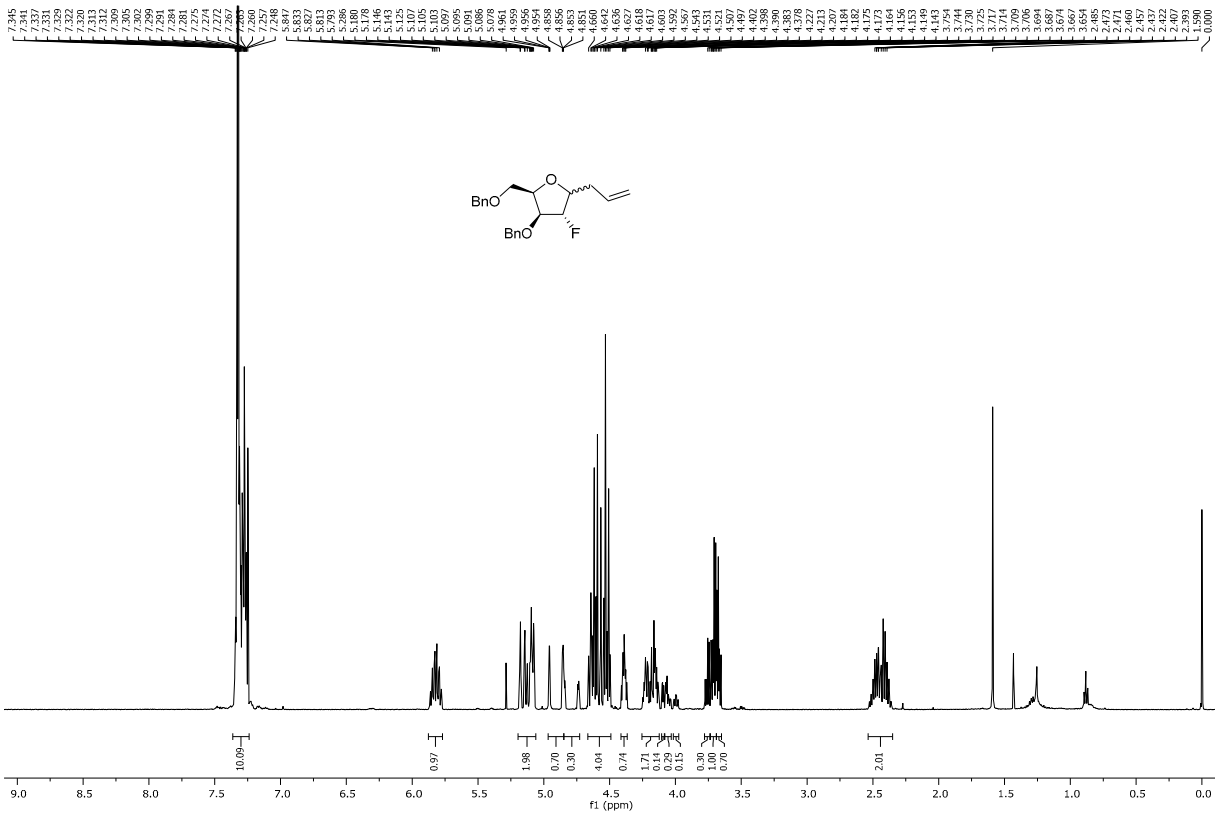


^{1}H-^{13}C HSQC-HECADE of compound **75**

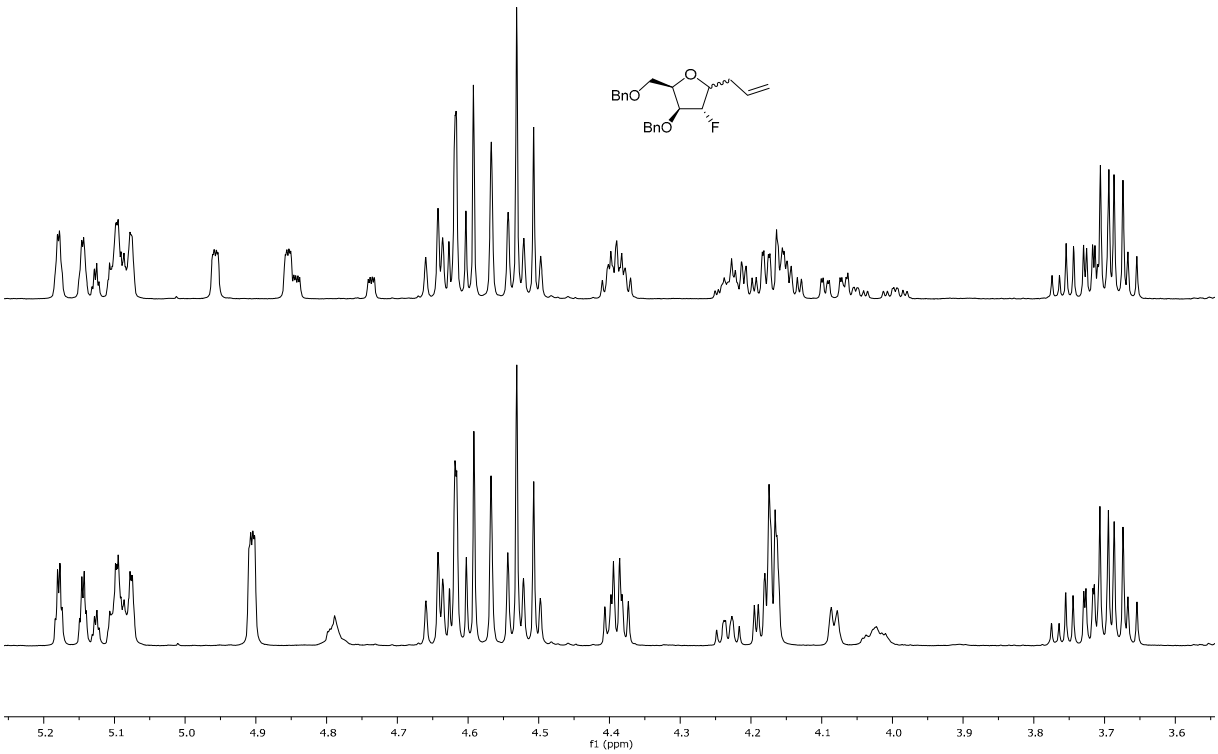


Allyl 3,5-di-*O*-benzyl-1,2-dideoxy-2-fluoro-α/β-D-xylofuranoside (76)

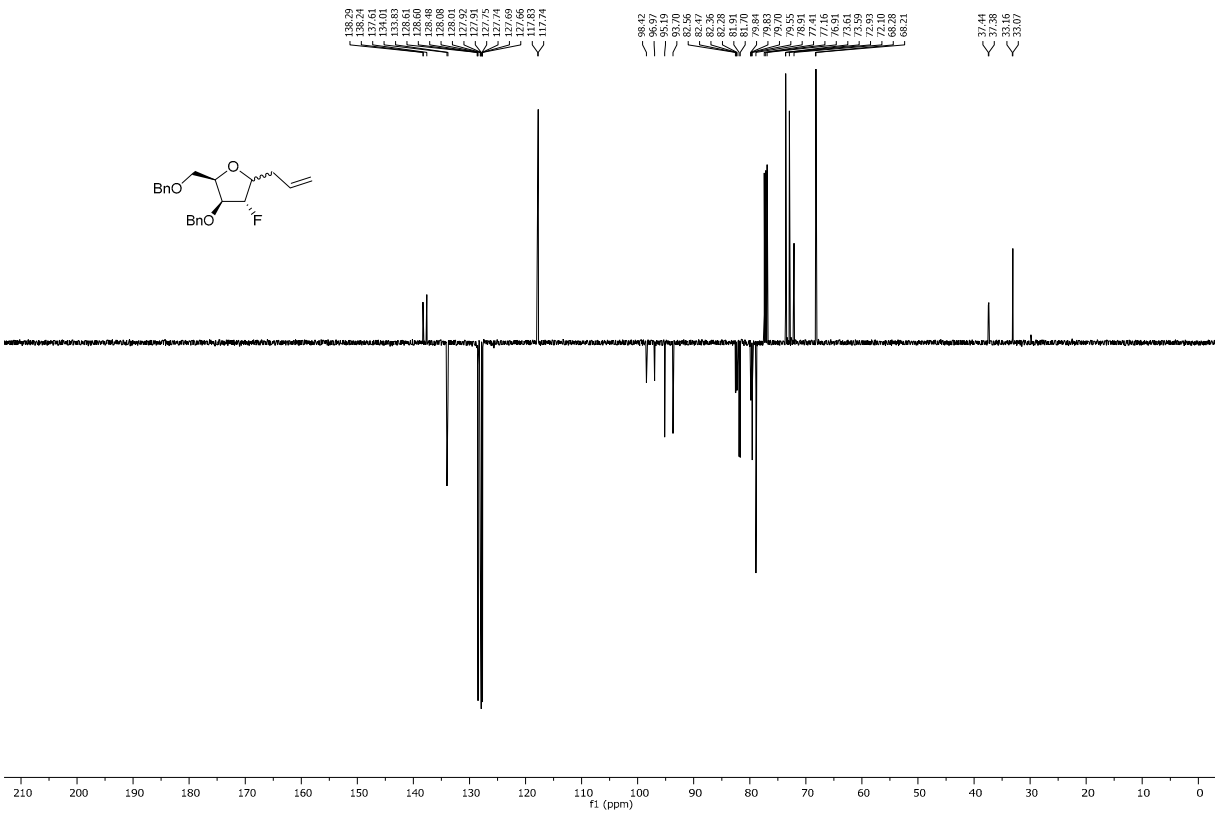
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **76**



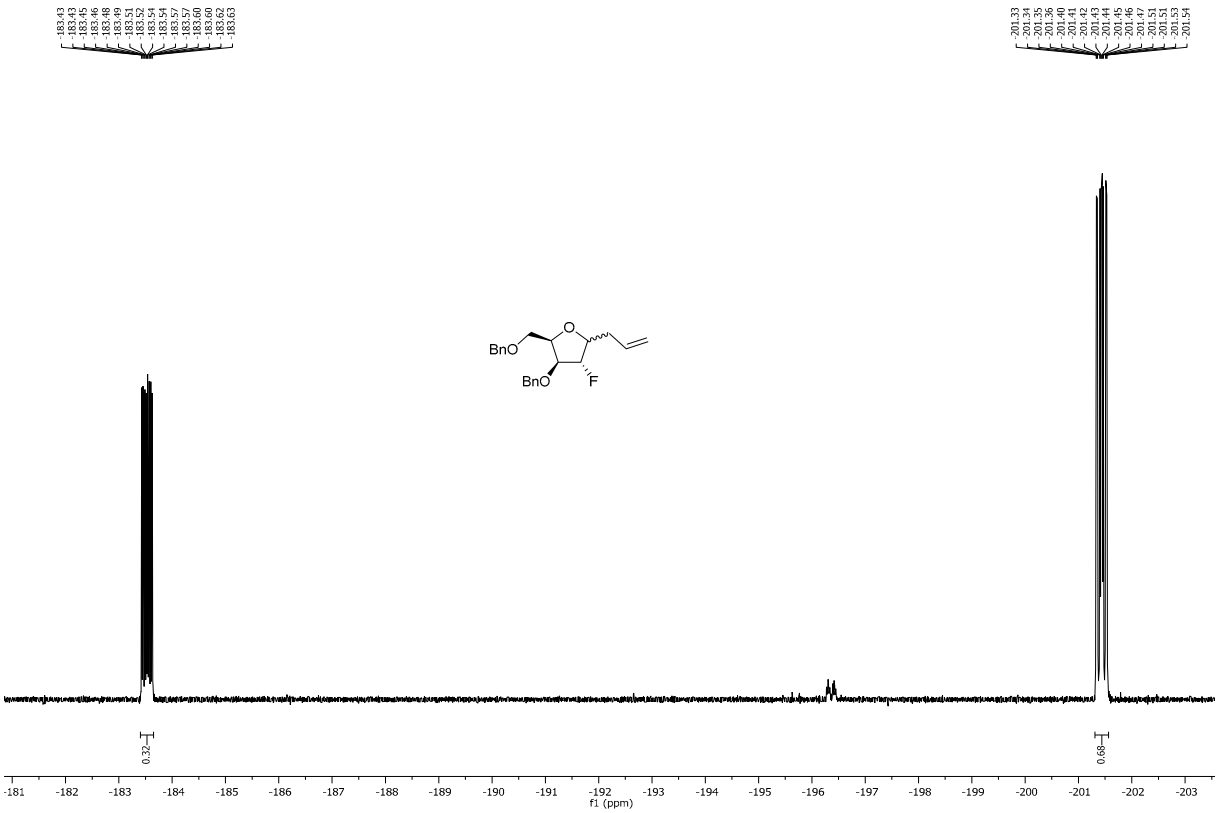
^{19}F-decoupled ^{1}H NMR, (-200 ppm)



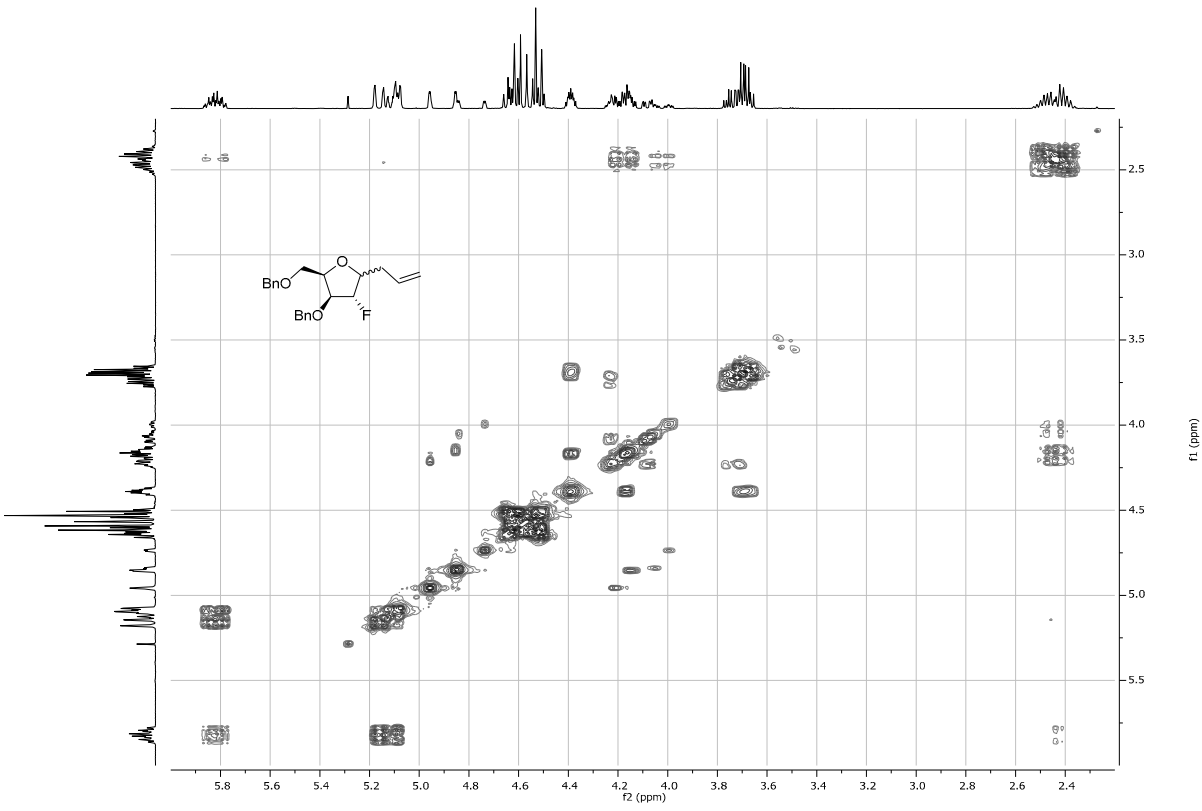
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **76**



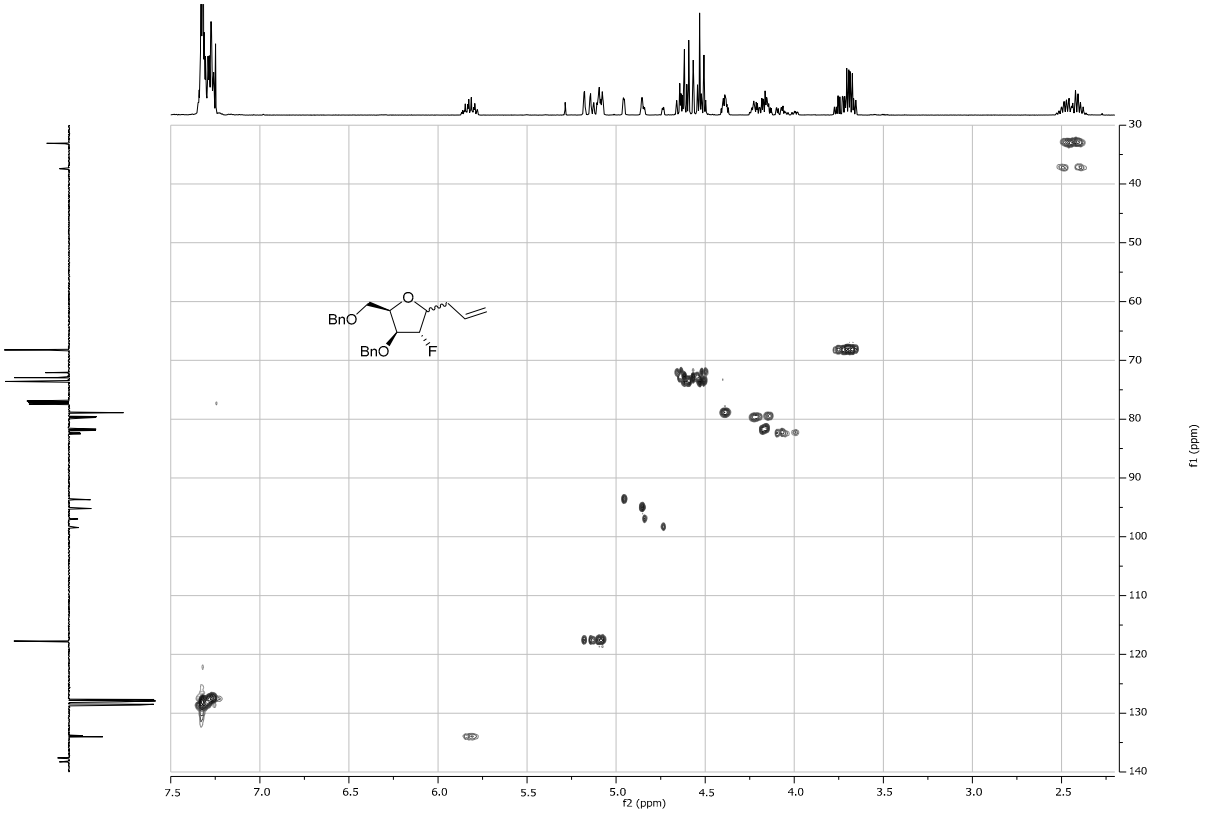
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **76**



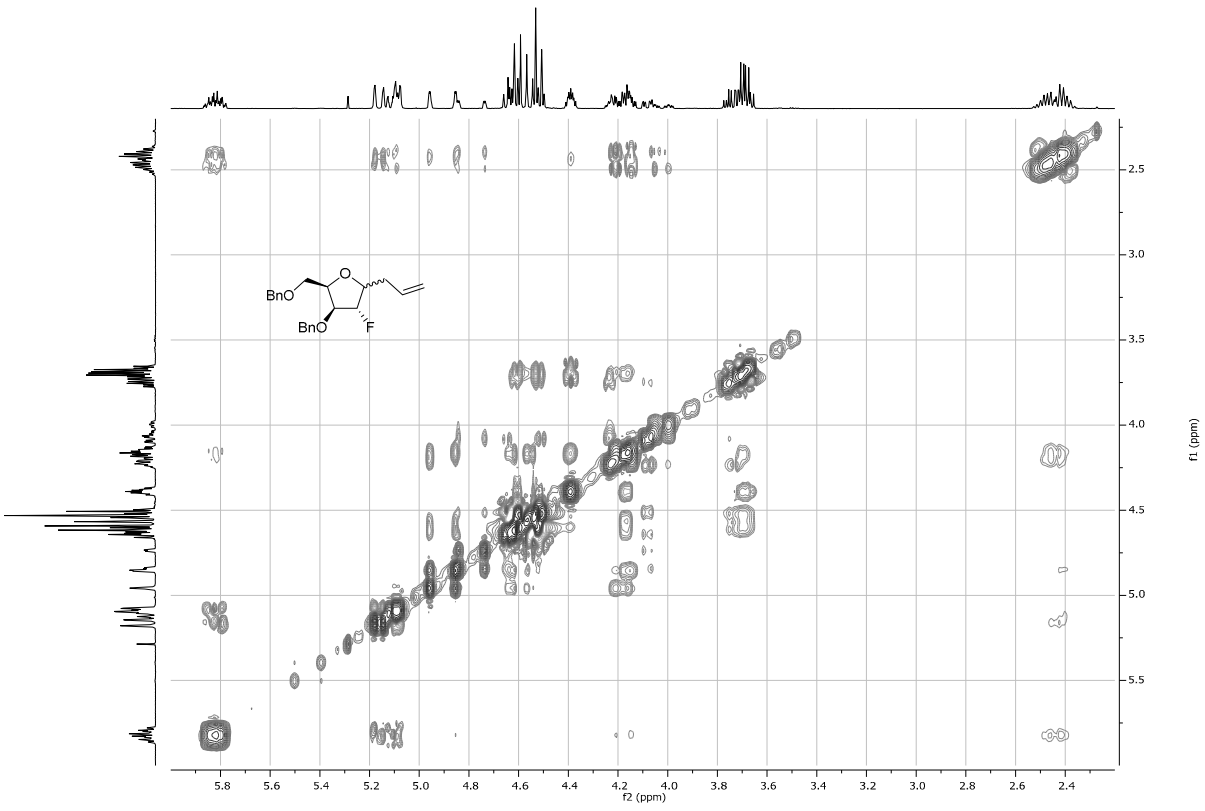
^{1}H-^{1}H COSY of compound **76**



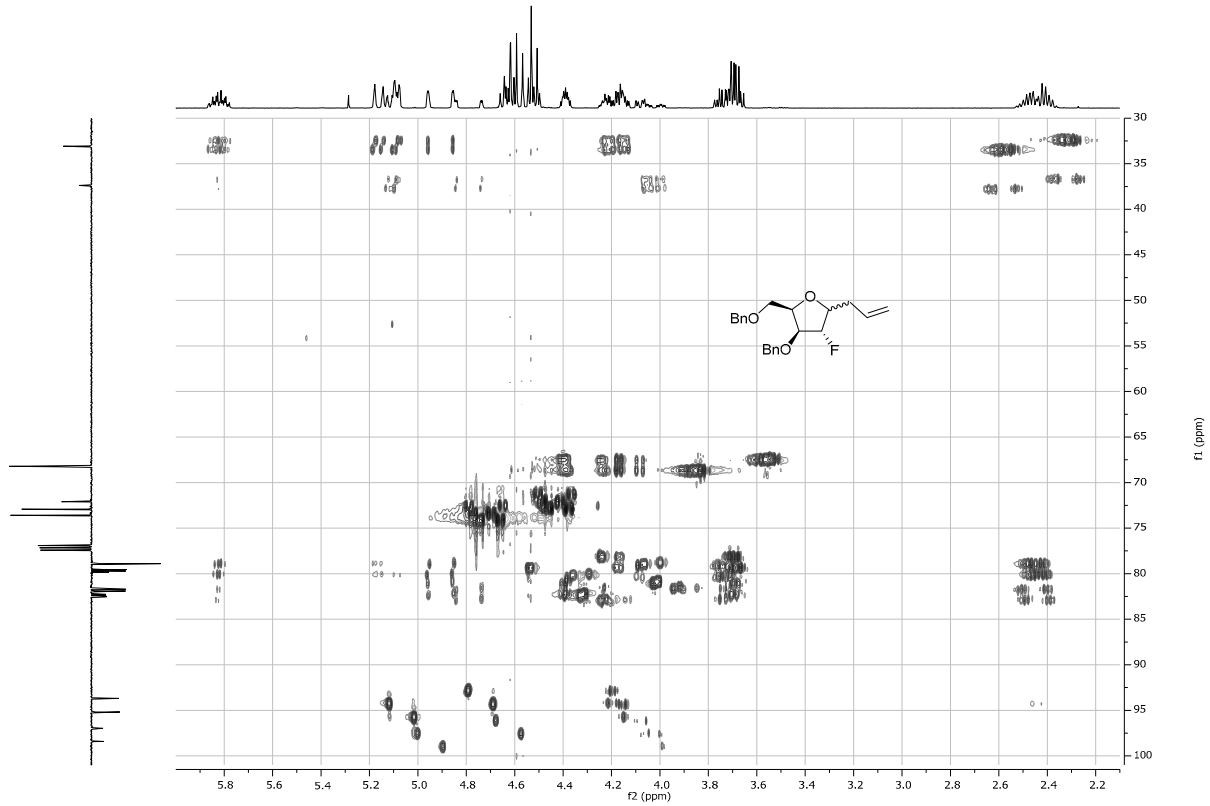
^{1}H-^{13}C HSQC of compound **76**



^{1}H-^{1}H NOESY of compound **76**

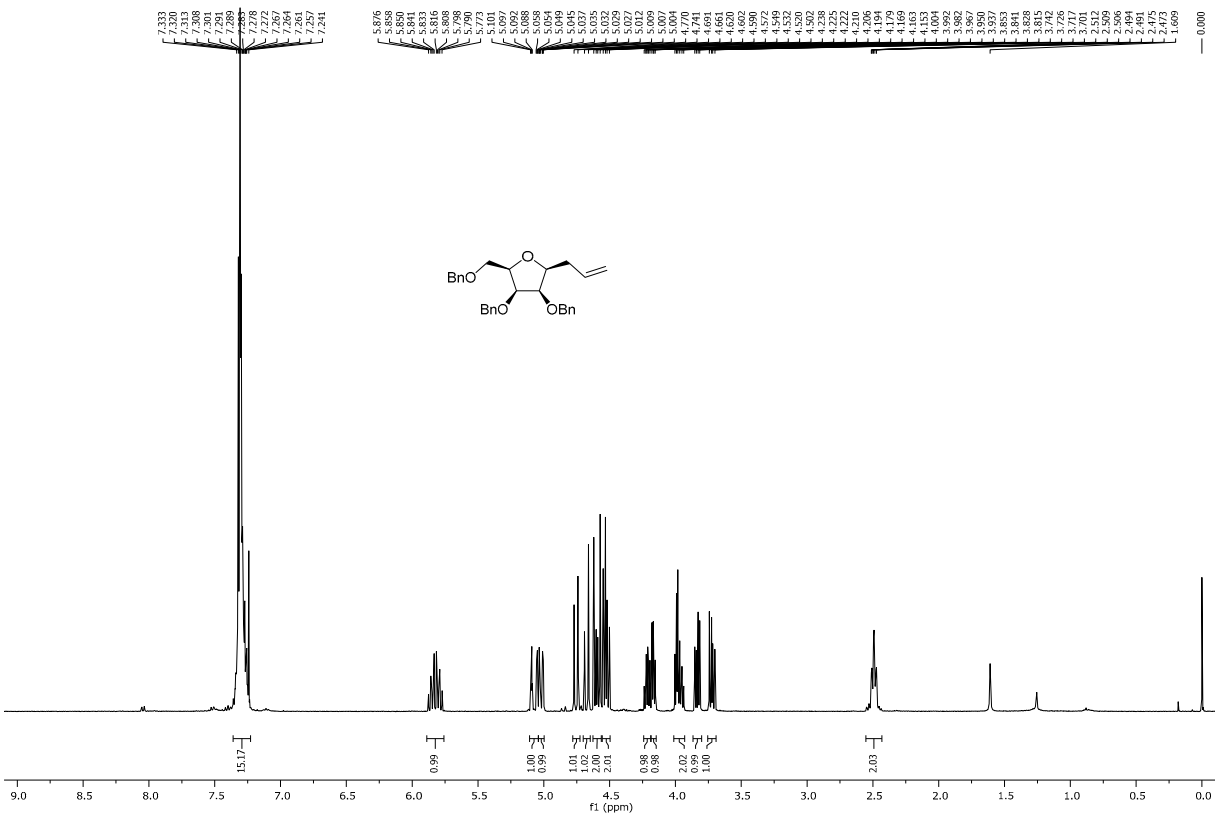


^{1}H-^{13}C HSQC-HECADE of compound **76**

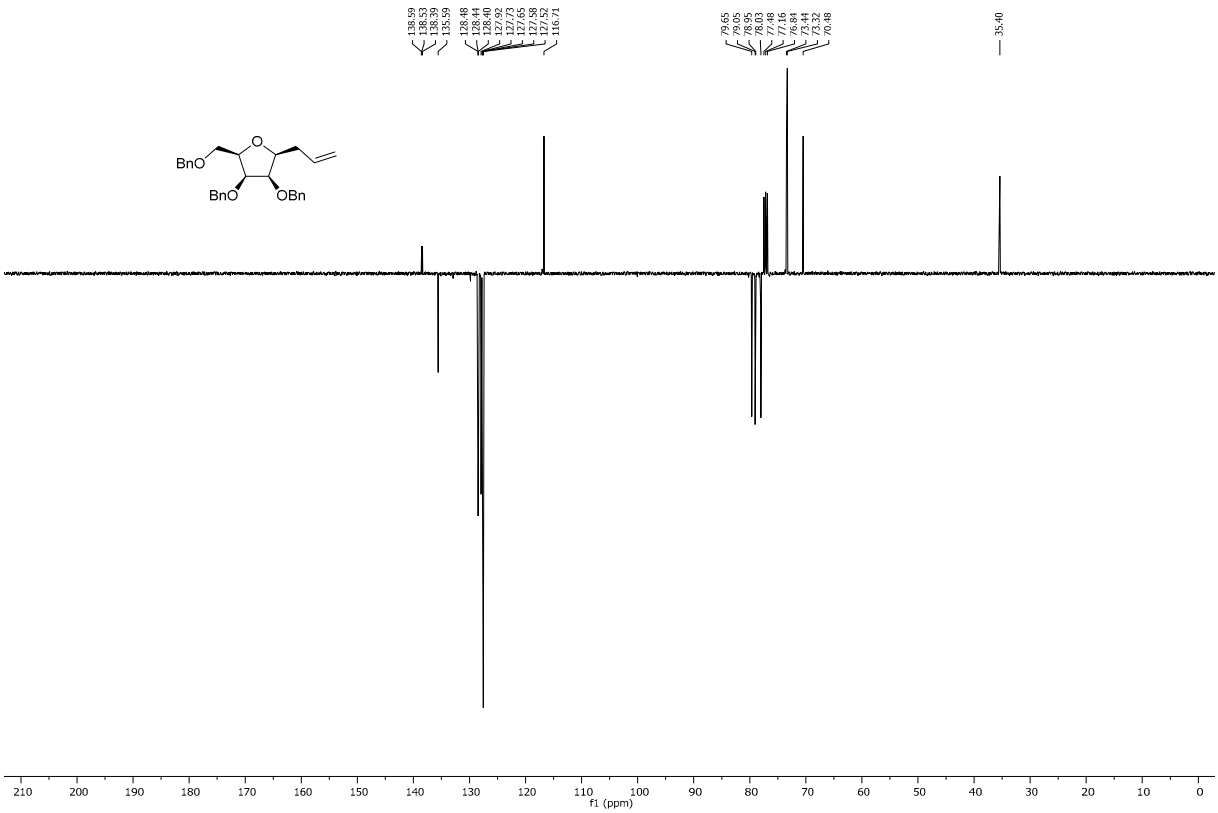


Allyl 2,3,5-tri-*O*-benzyl-1-deoxy-β-D-lyxofuranoside (77)

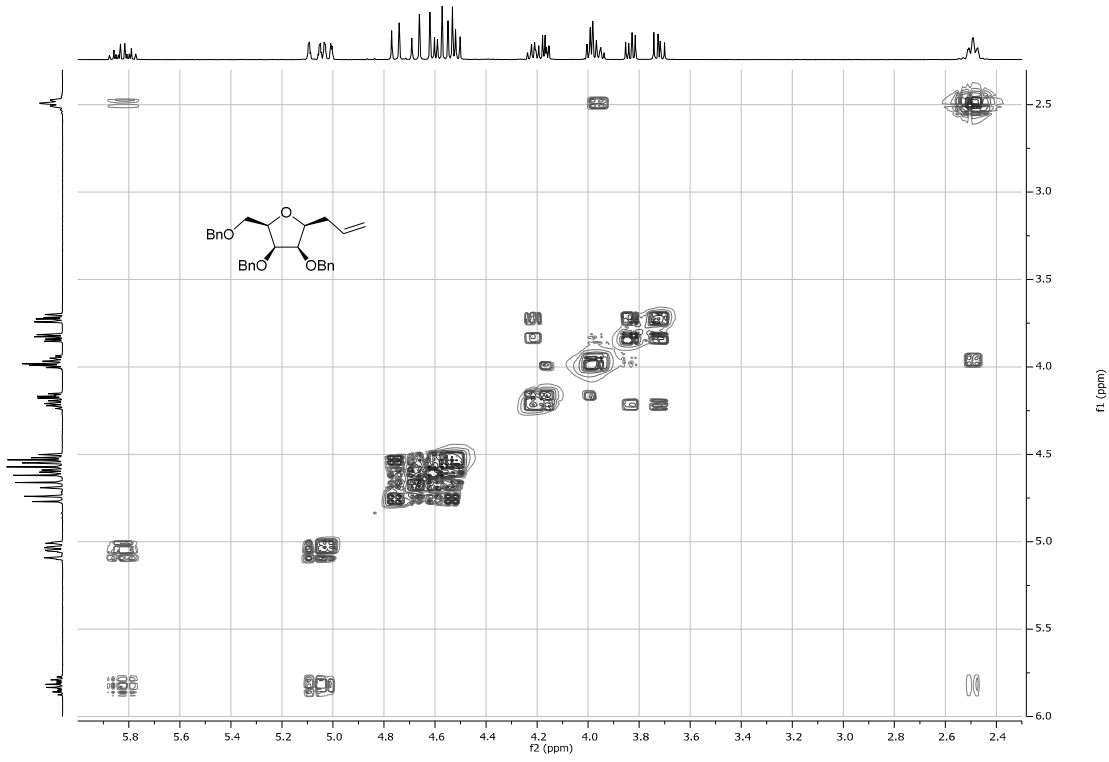
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **77**



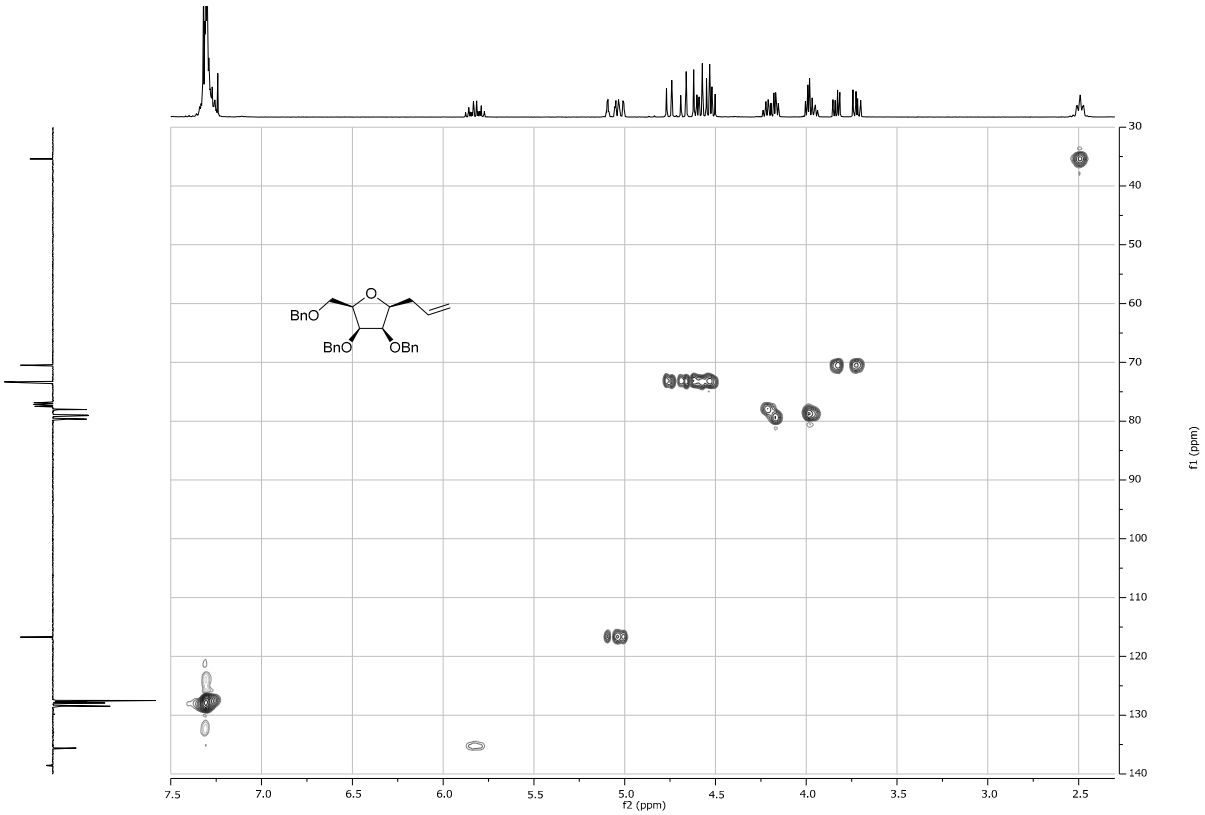
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **77**



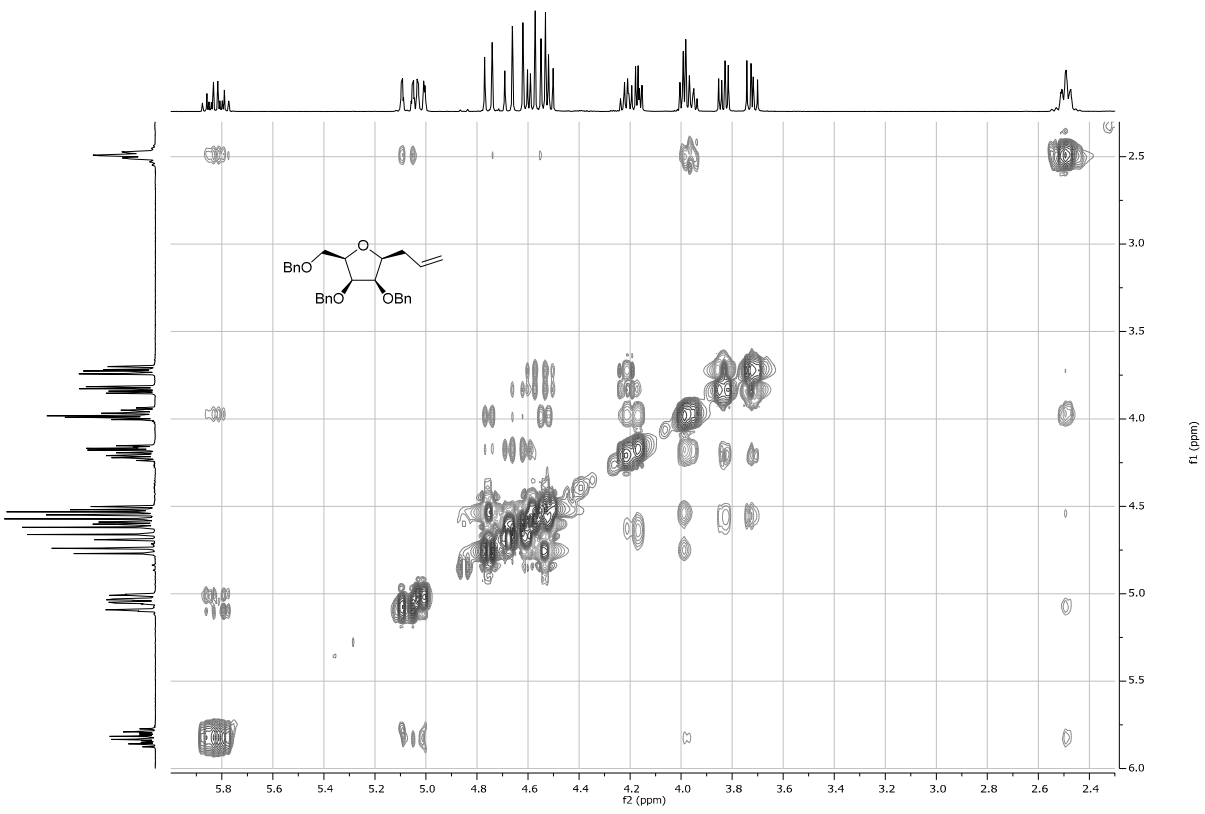
^{1}H-^{1}H COSY of compound **77**



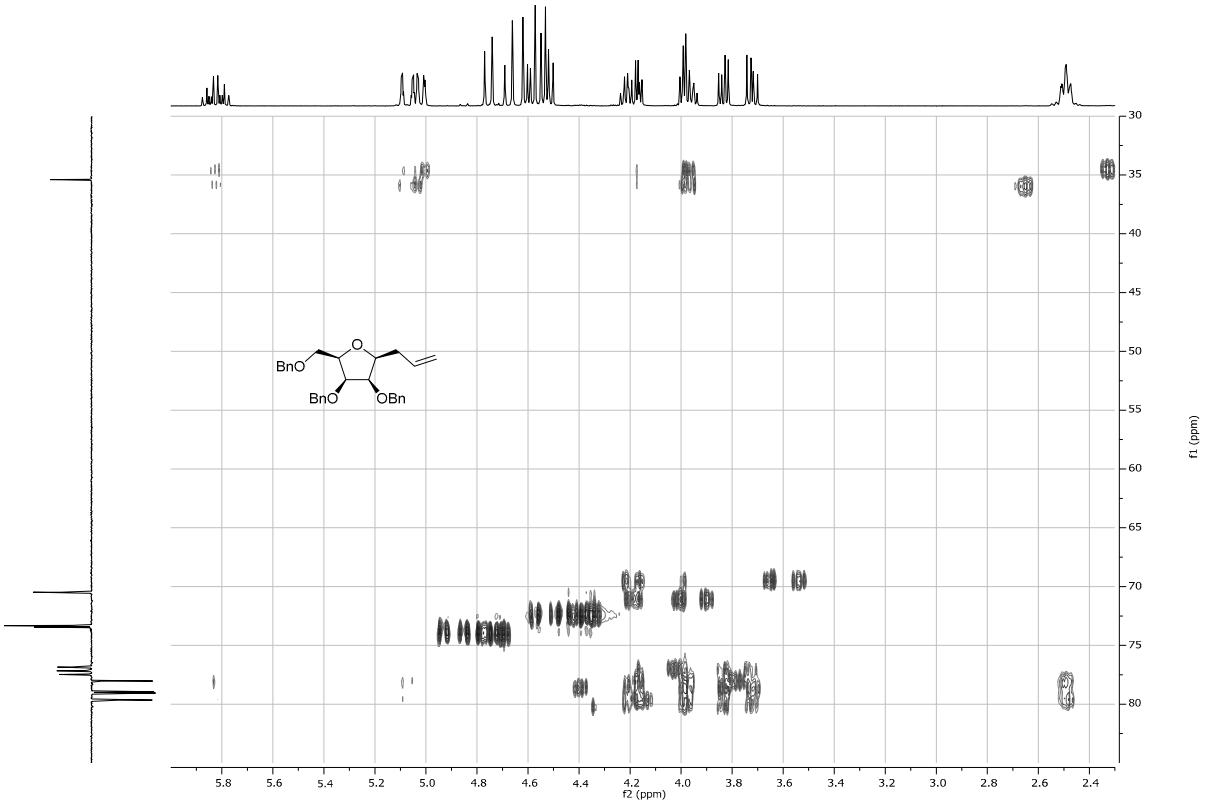
^{1}H-^{13}C HSQC of compound **77**



^{1}H-^{1}H NOESY of compound **77**

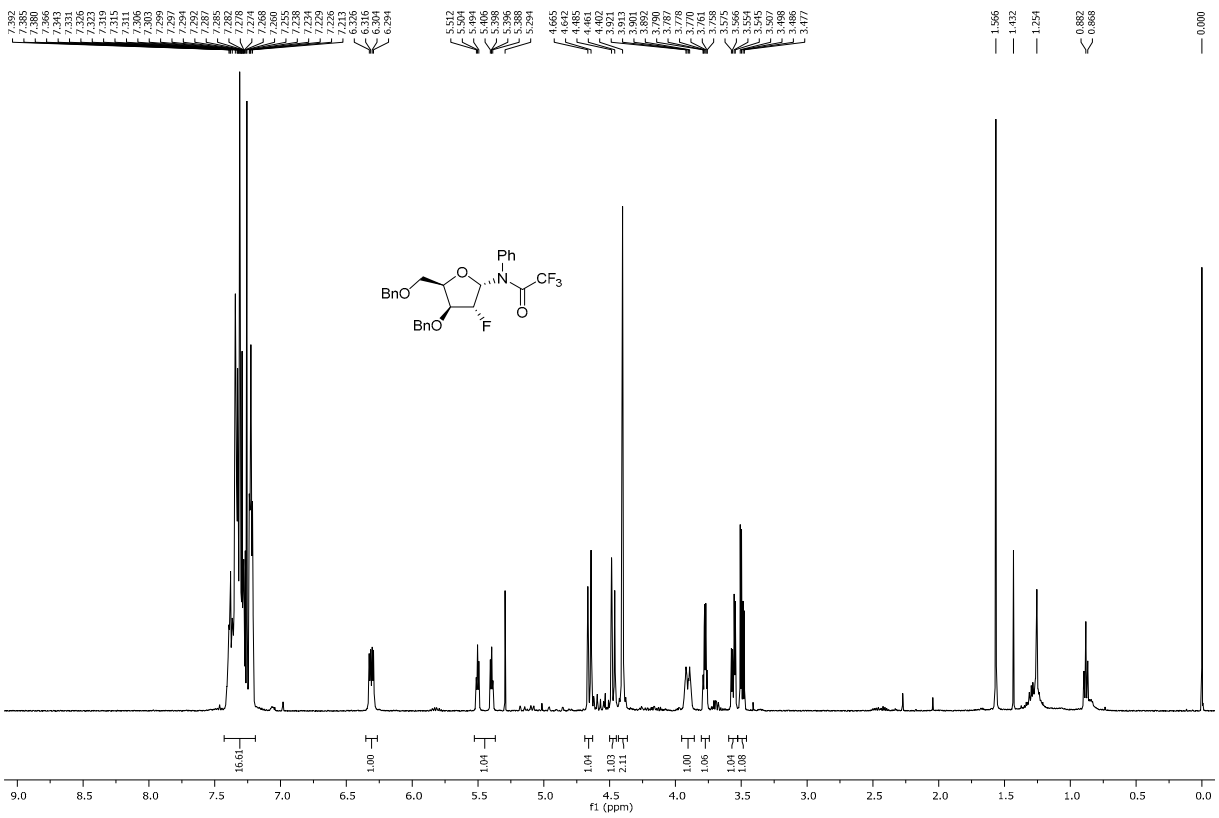


^{1}H-^{13}C HSQC-HECADE of compound **77**

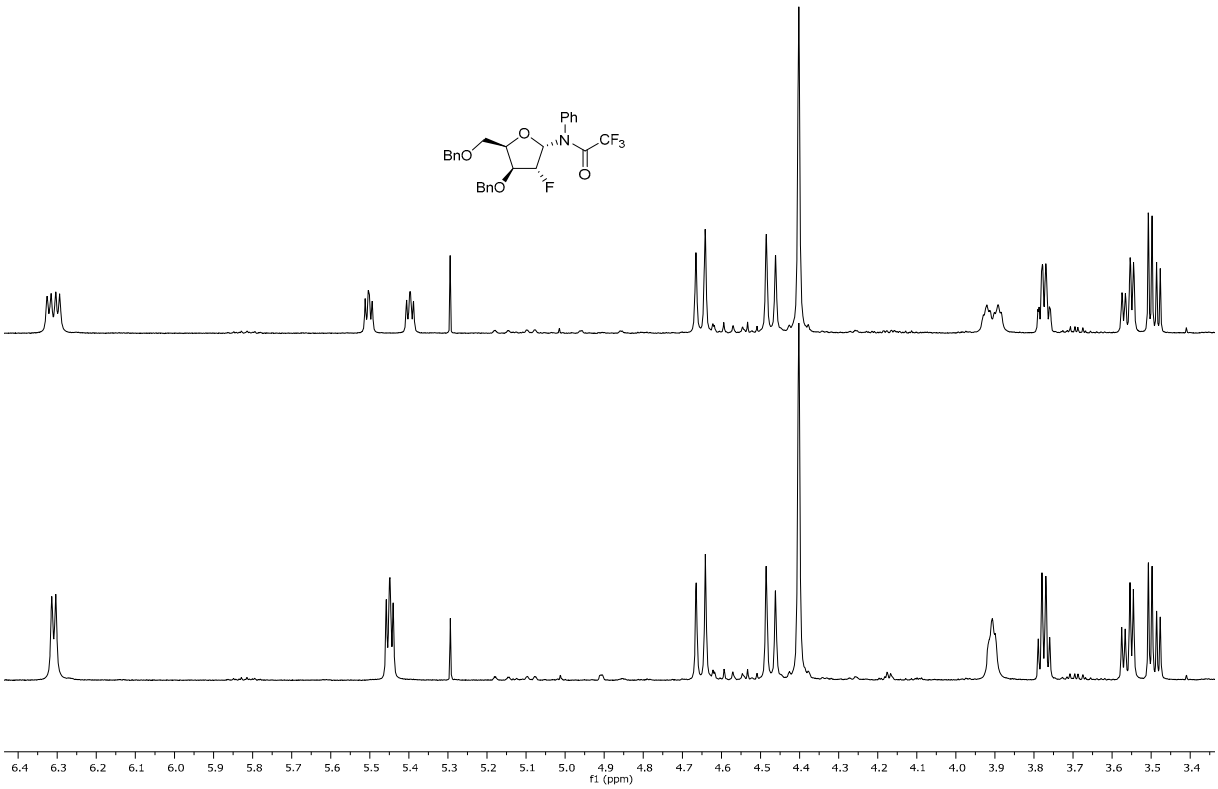


3,5-di-*O*-benzyl-1,2-dideoxy-2-fluoro-1-*N*-[phenyl]trifluoroacetyl-α/β-D-xylofuranoside (78)

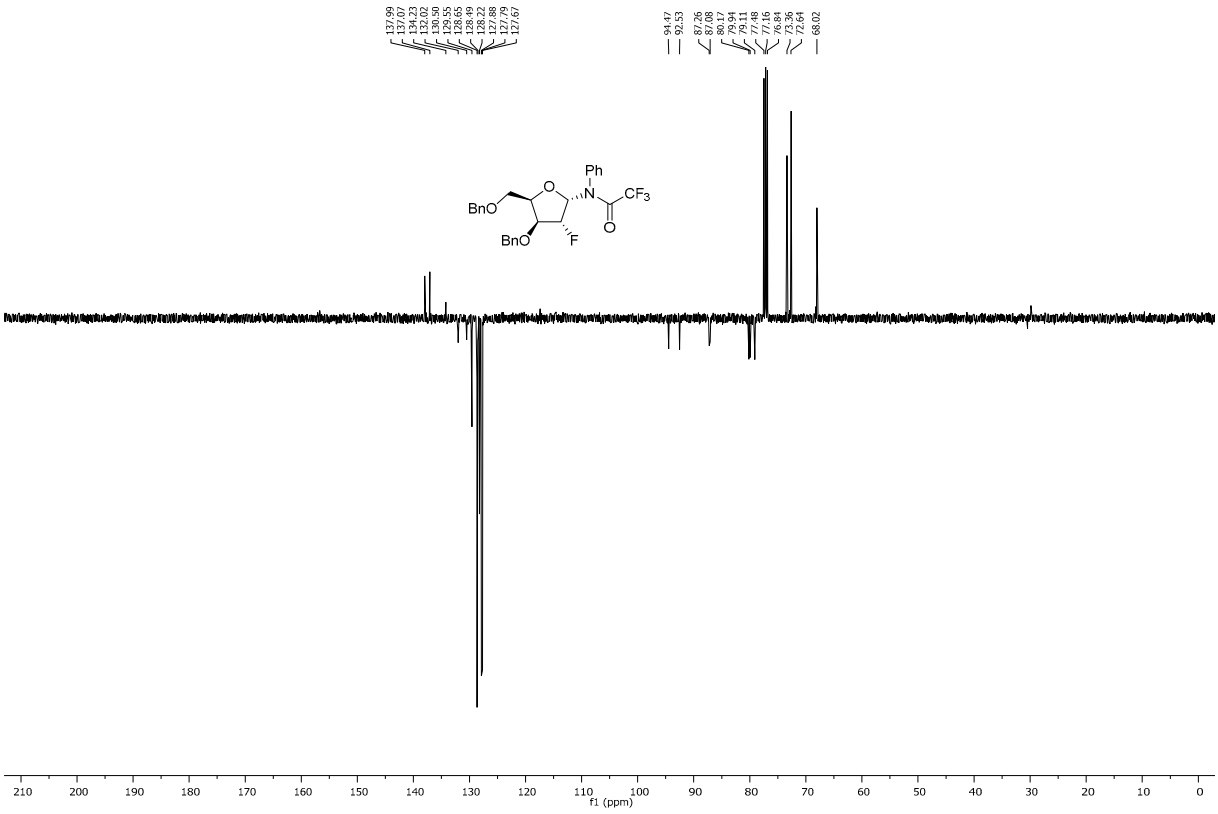
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **78**



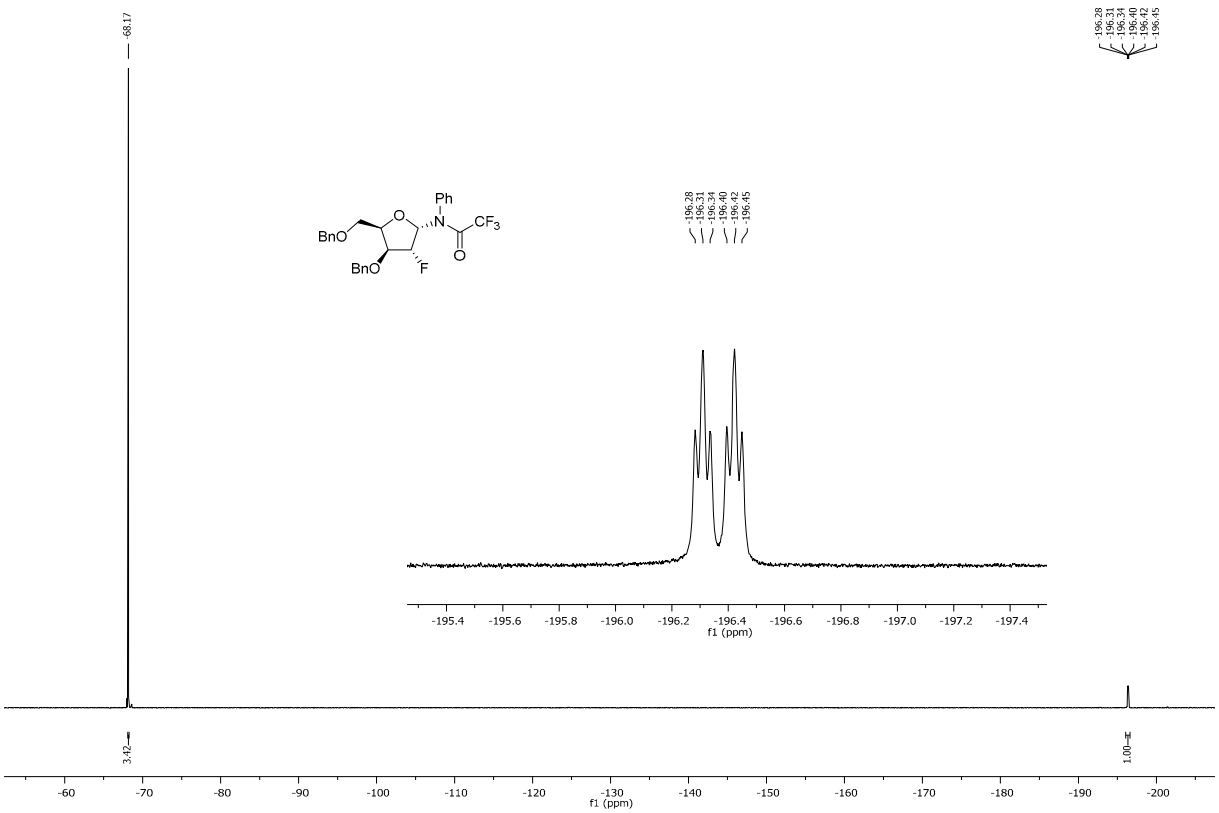
^{19}F-decoupled ^{1}H NMR, (-200 ppm)



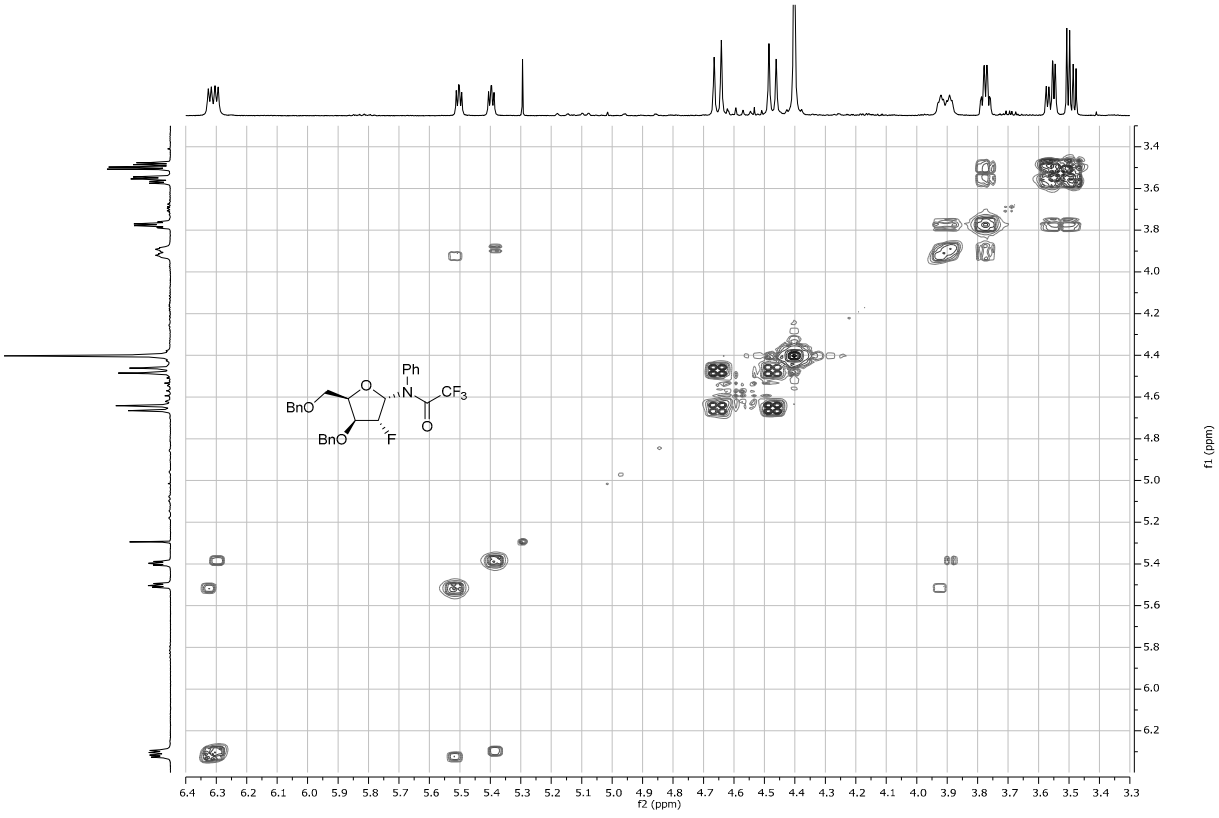
^{13}C-APT NMR, 101 MHz, $CDCl_3$ of compound **78**



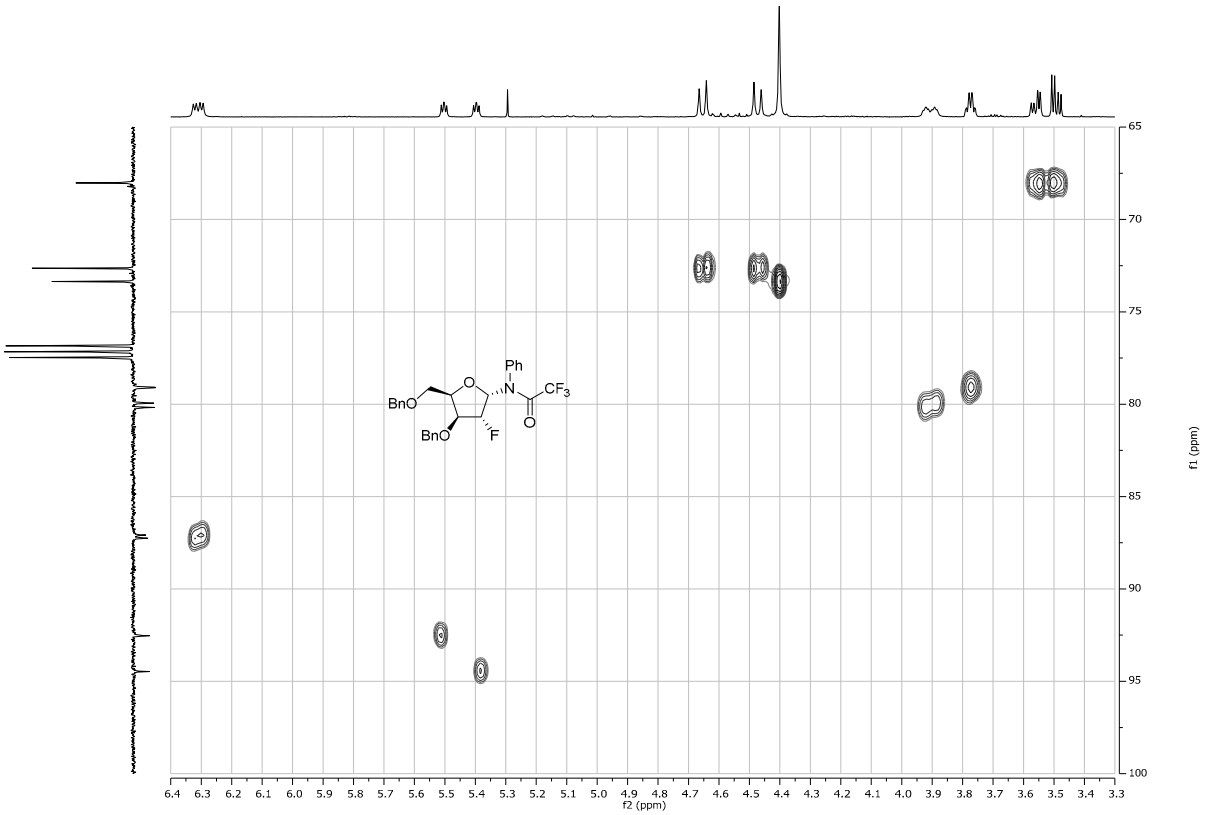
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **78**



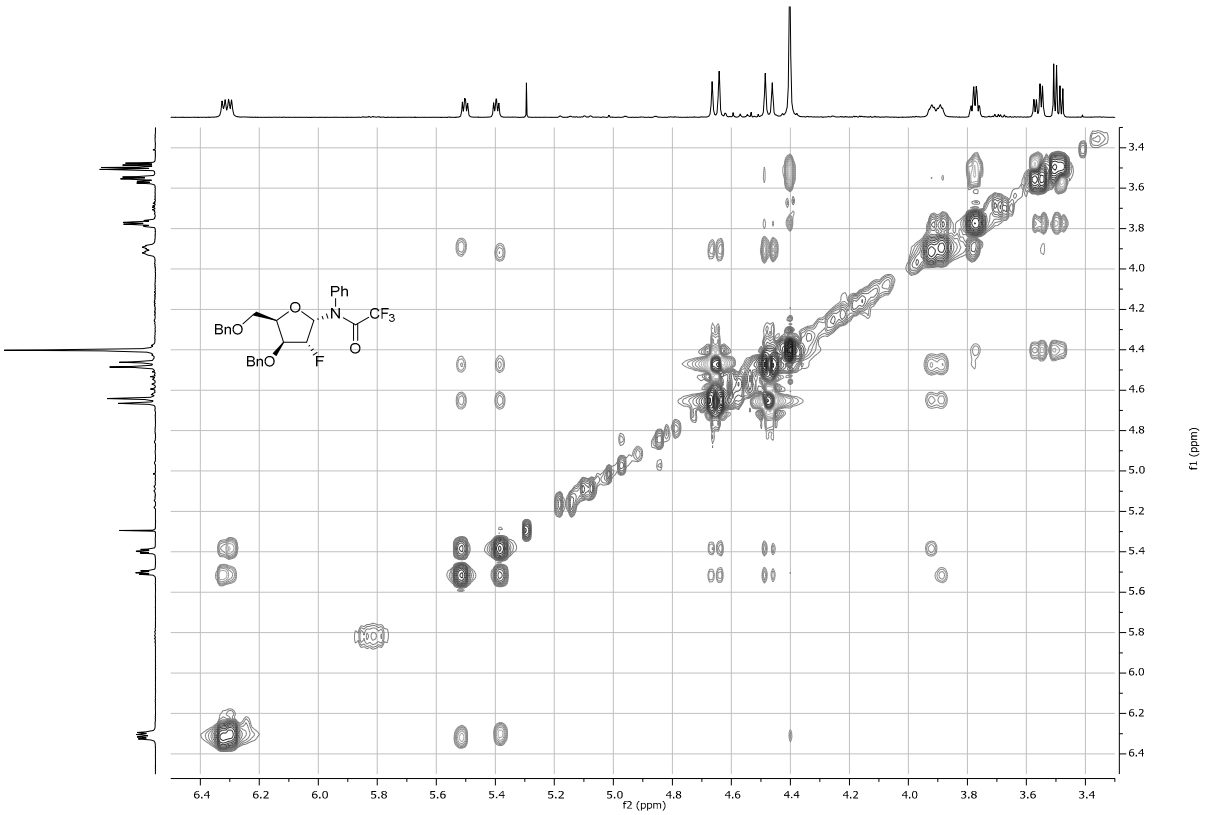
^{1}H-^{1}H COSY of compound **78**



^{1}H-^{13}C HSQC of compound **78**

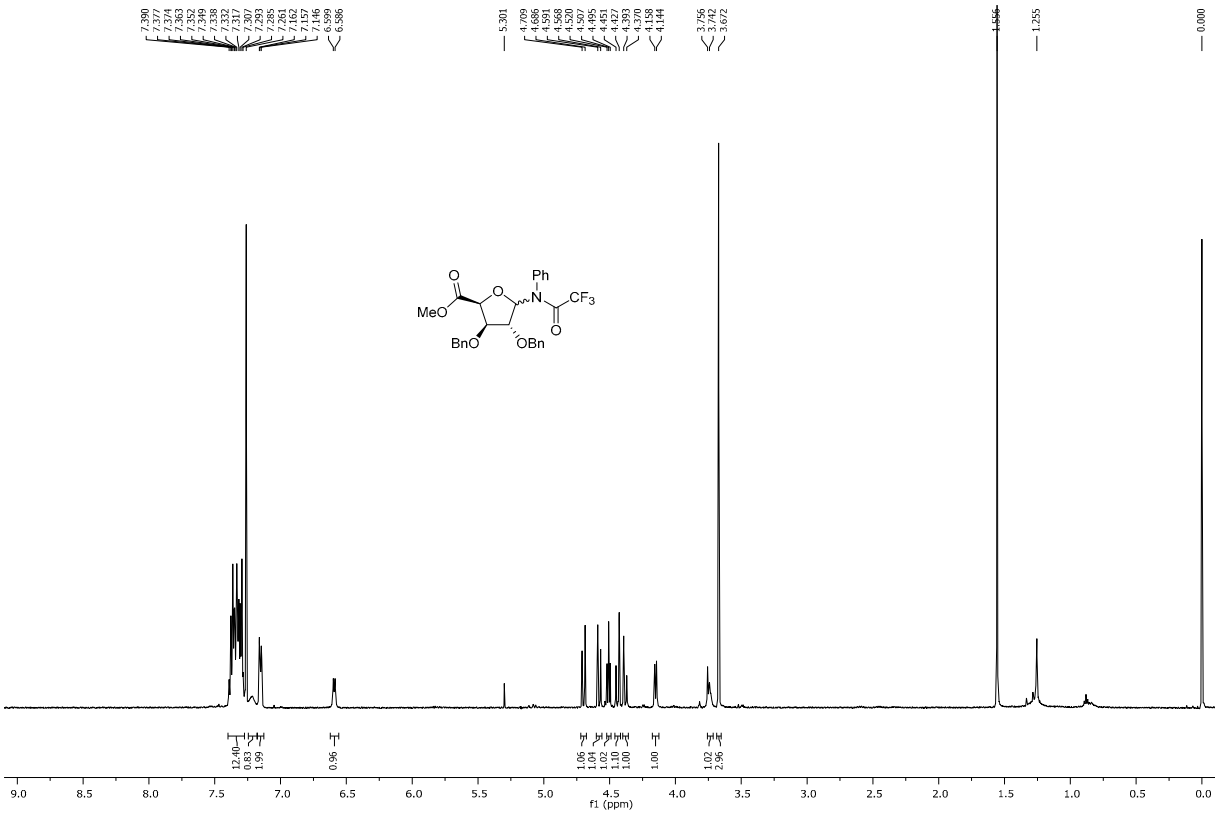


^{1}H-^{1}H NOESY of compound **78**



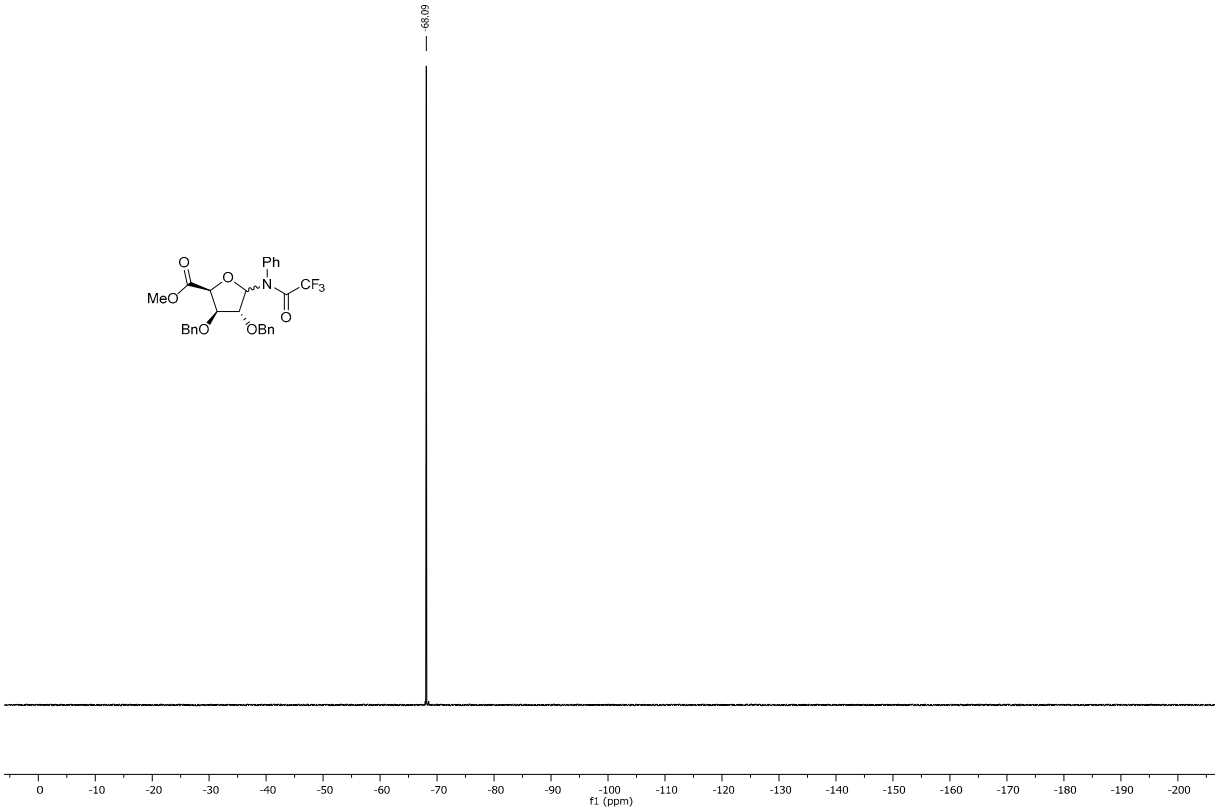
Methyl (2,3-di-*O*-benzyl-1-deoxy-1-*N*-[phenyl]trifluoroacetyl-α/β-D-xylofuranosyl uronate) (80).

^{1}H NMR, 500 MHz, $CDCl_3$ of compound **80**

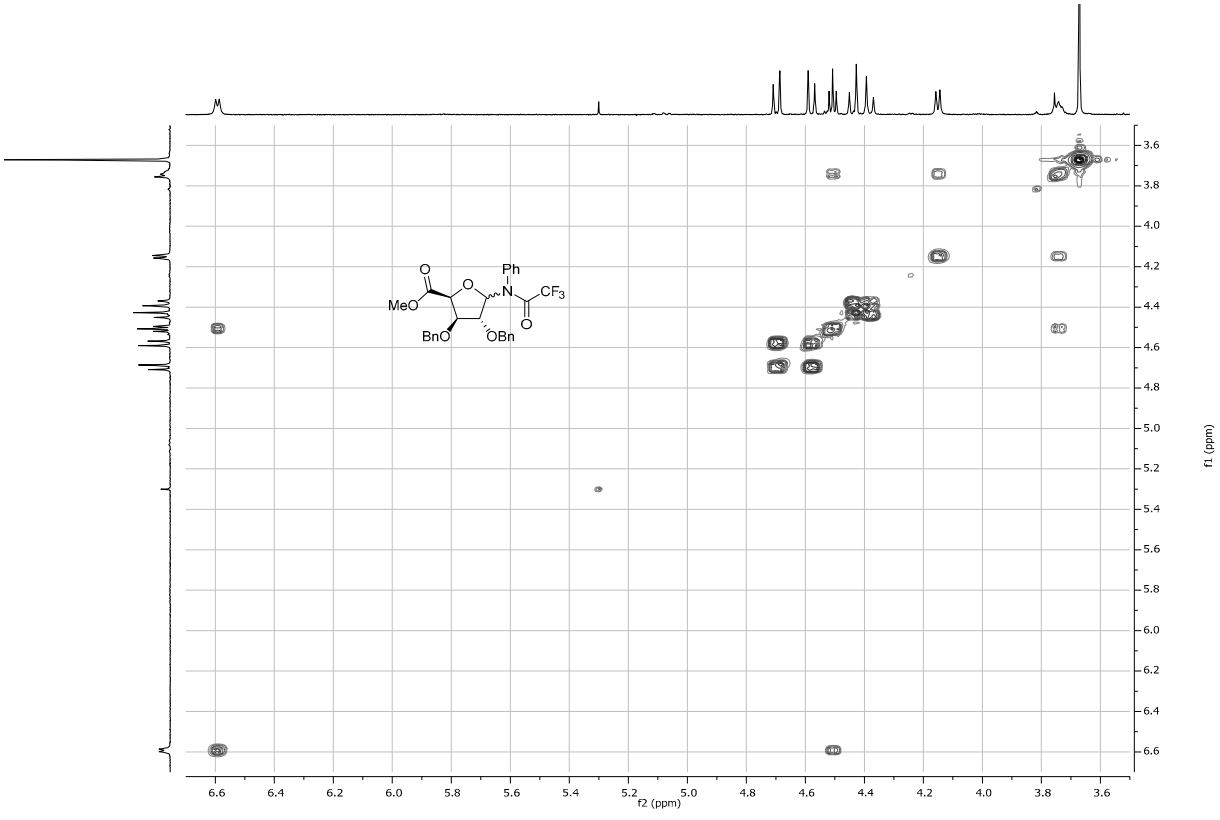


^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **80** is reported for the mixed fraction, see **68**

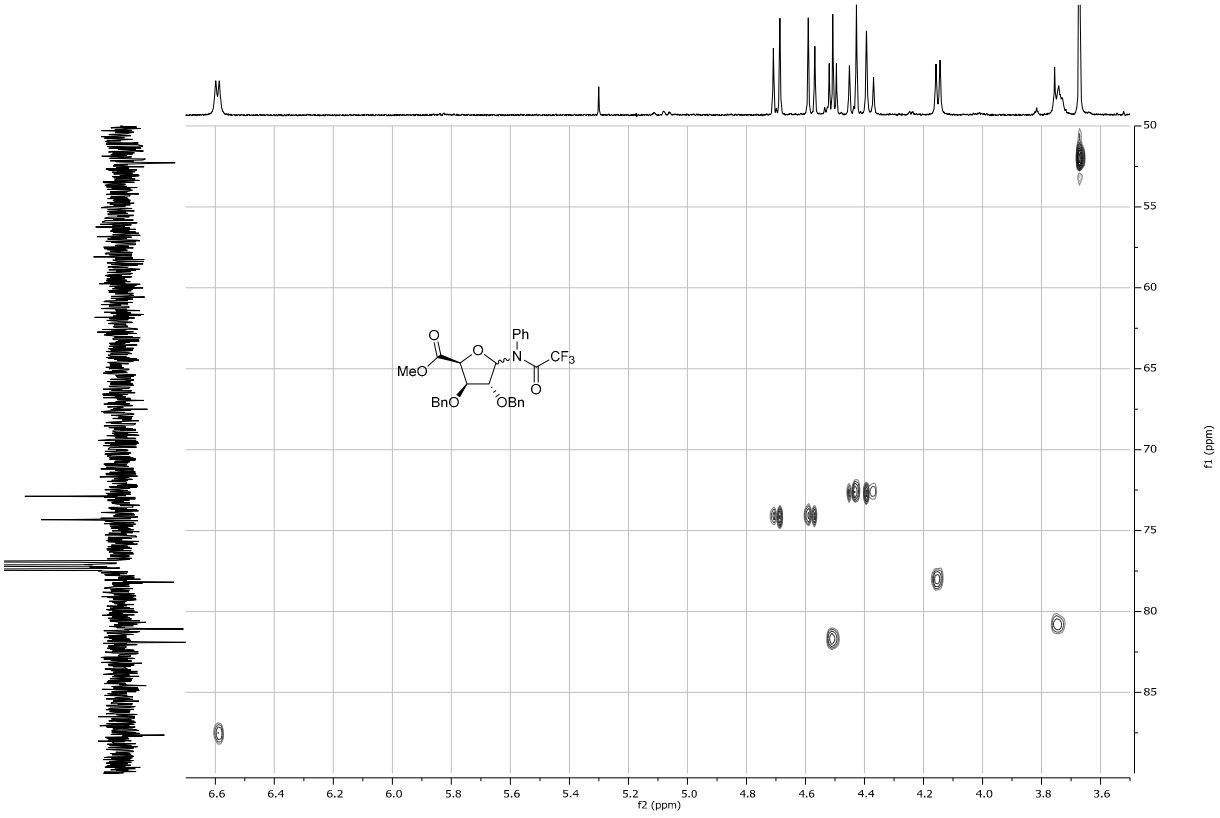
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **80**



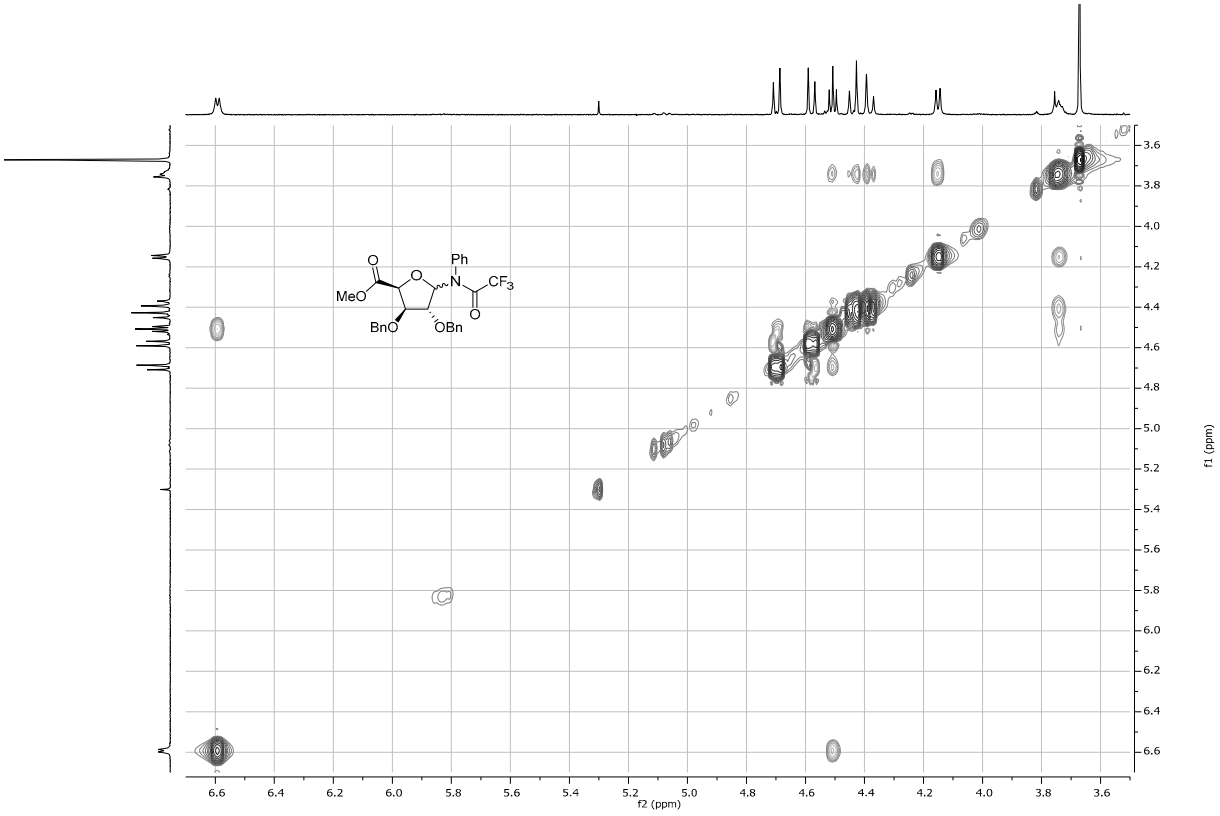
^{1}H-^{1}H COSY of compound **80**



^{1}H-^{13}C HSQC of compound **80**

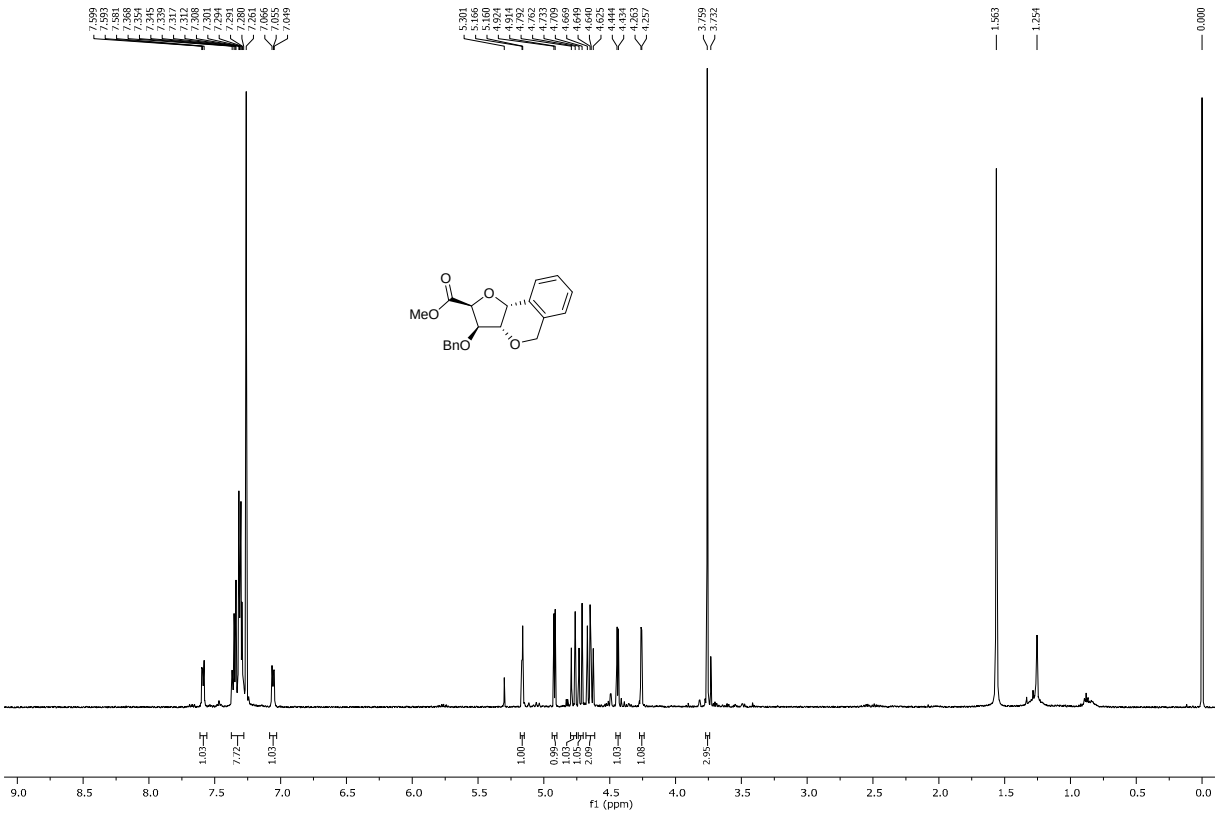


^{1}H-^{1}H NOESY of compound **80**

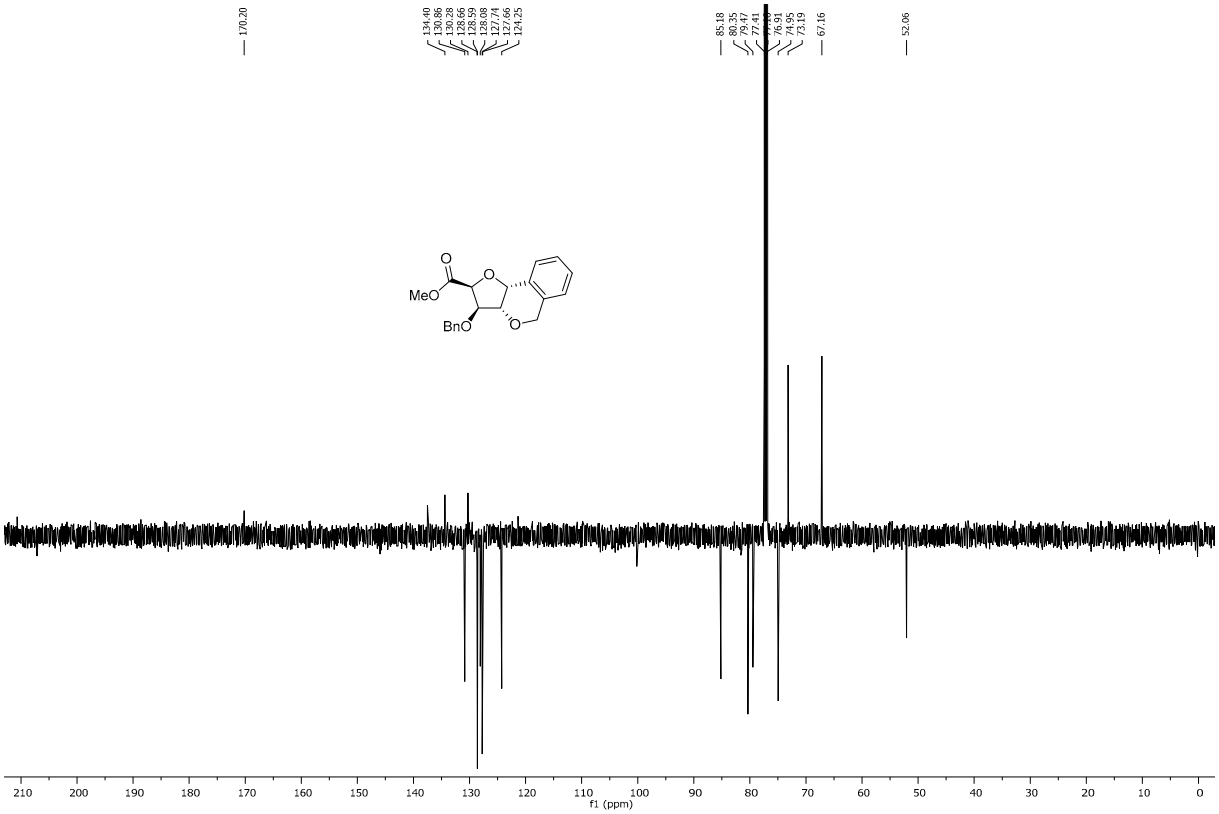


Methyl (2*S*,3*R*,3a*S*,9b*R*)-3-(benzyloxy)-3,3a,5,9b-tetrahydro-2*H*-furo[3,2-*c*]isochromene-2-carboxylate (81)

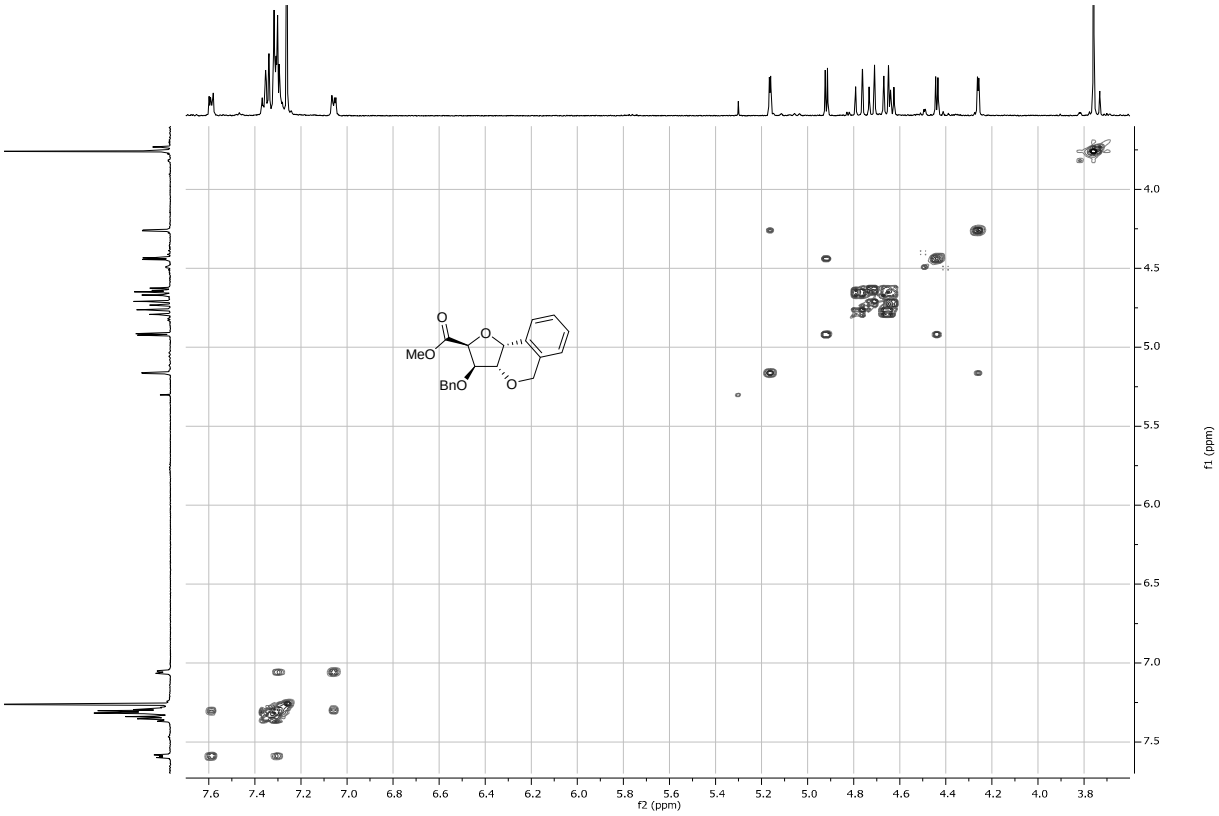
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **81**



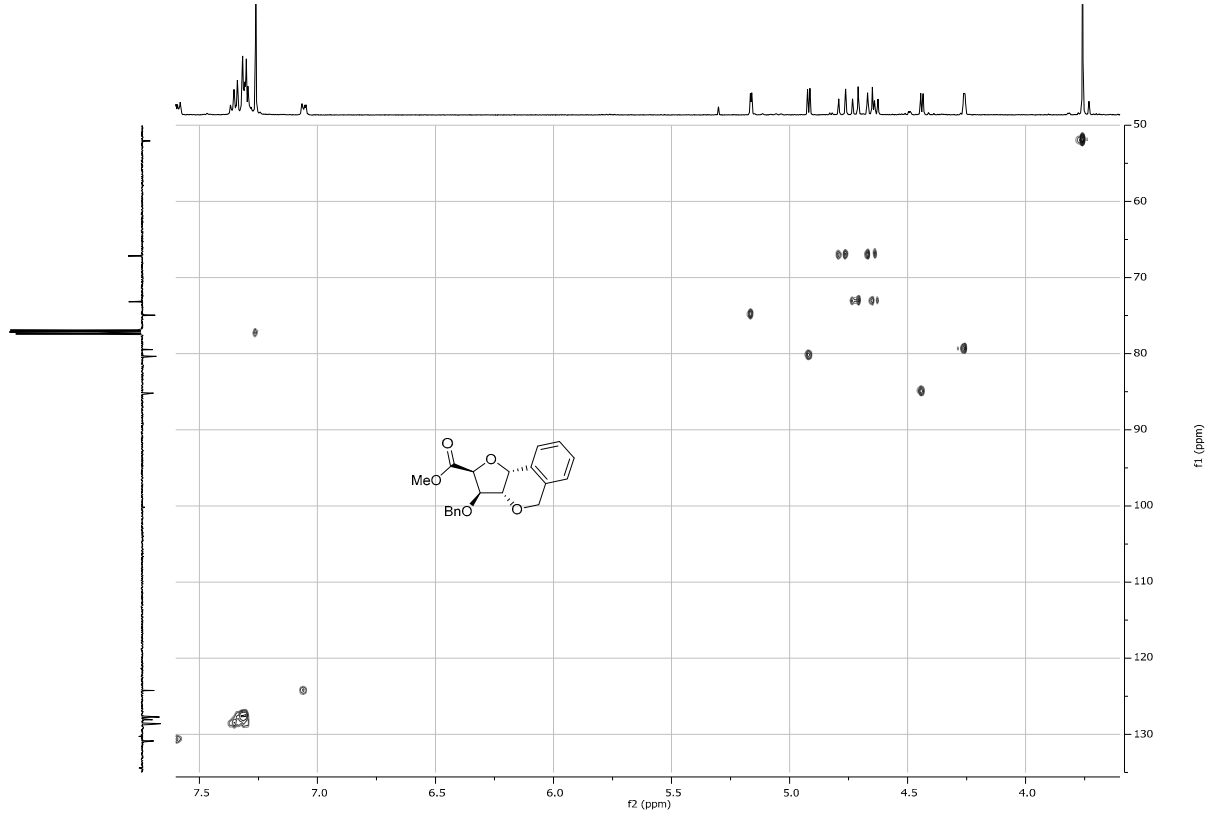
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **81**



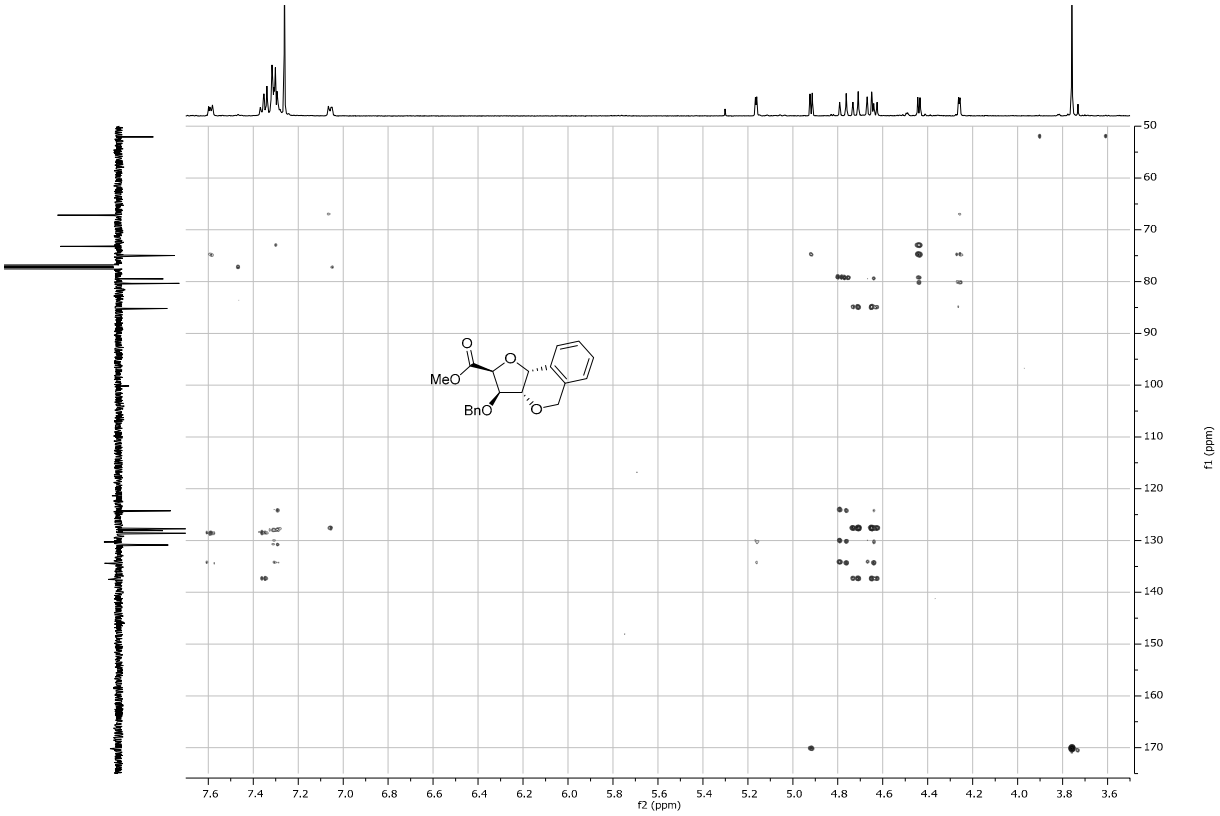
^{1}H-^{1}H COSY of compound **81**



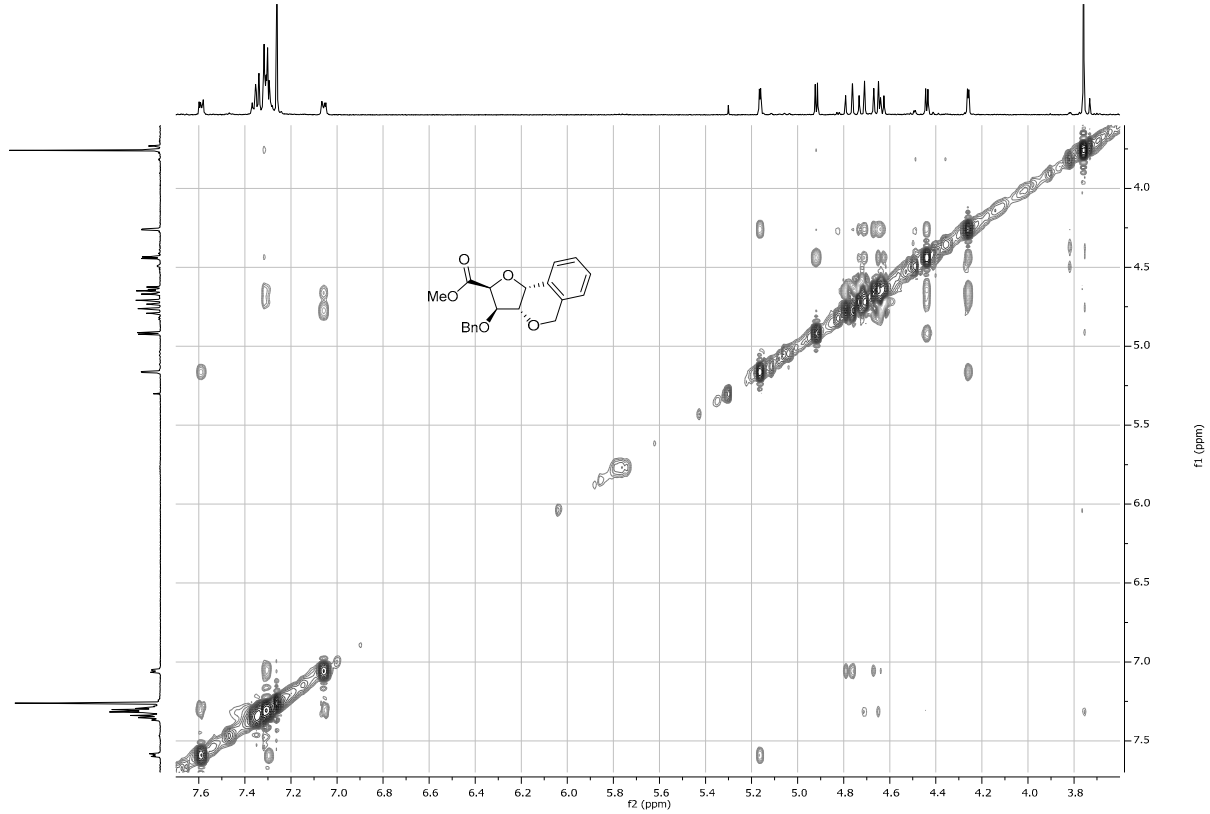
^{1}H-^{13}C HSQC of compound **81**



^{1}H-^{13}C HMBC of compound **81**

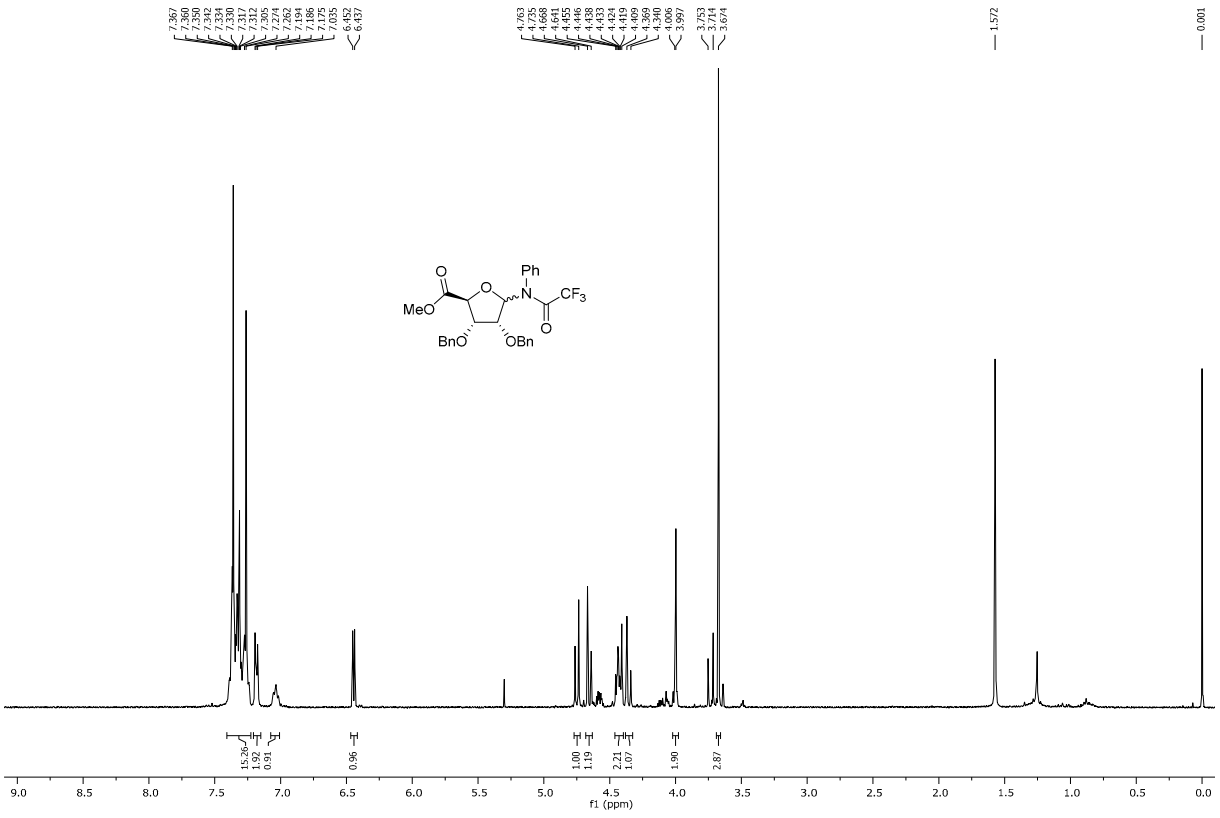


^{1}H-^{1}H NOESY of compound **81**

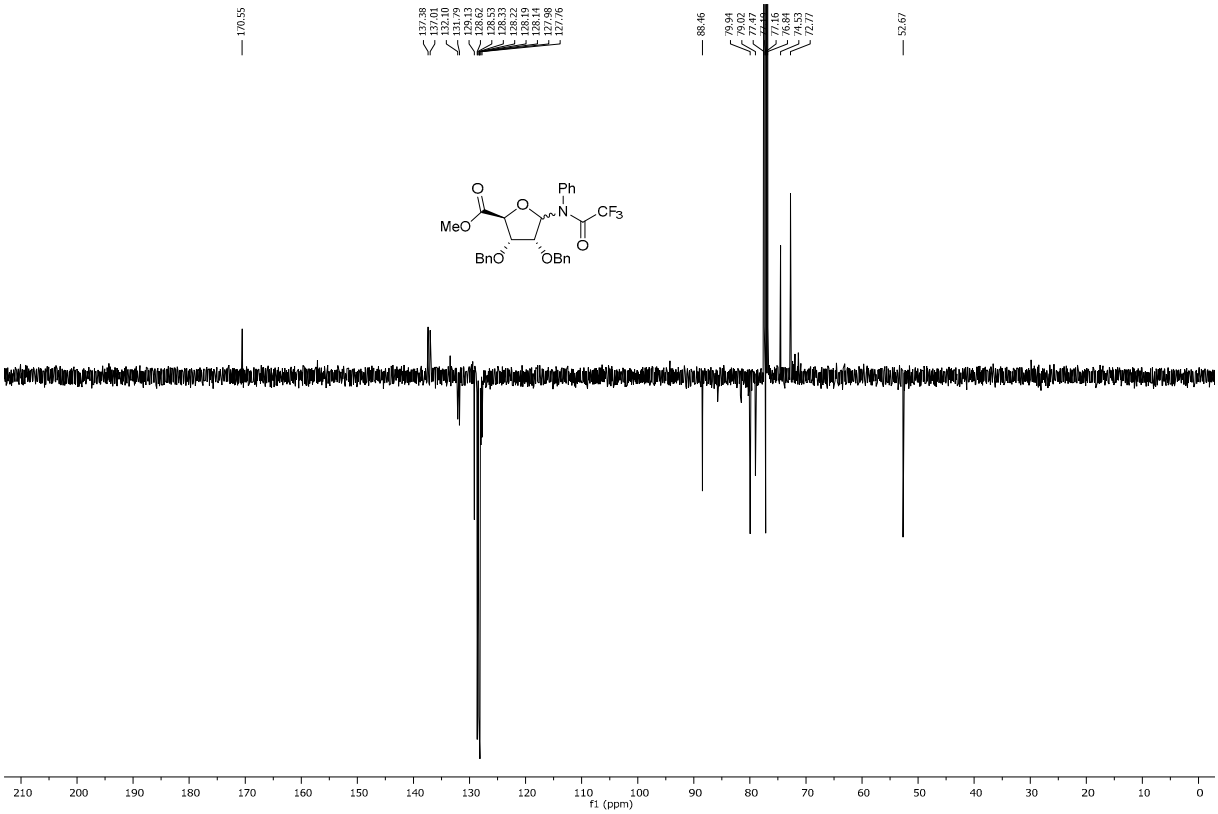


Methyl (2,3-di-*O*-benzyl-1-deoxy-1-*N*-[phenyl]trifluoroacetyl-α-D-ribofuranosyl uronate) (99)

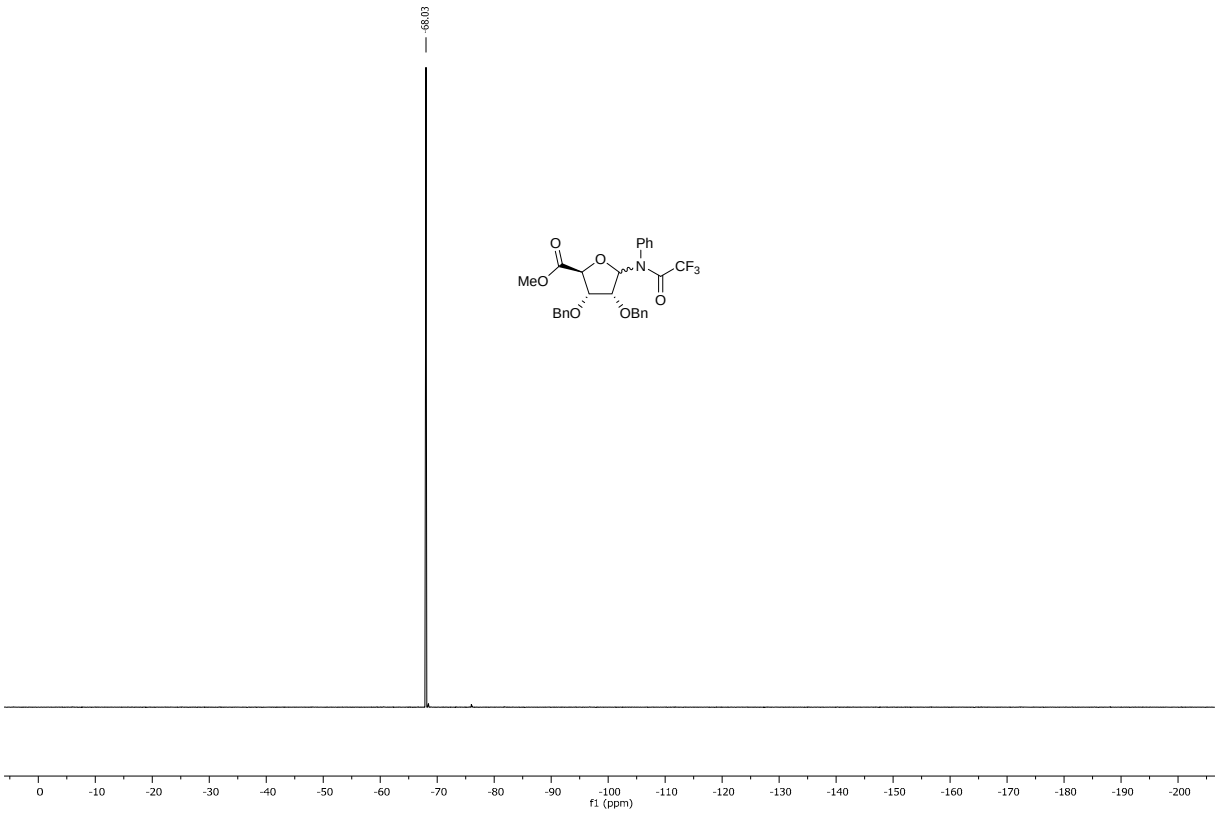
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **99**



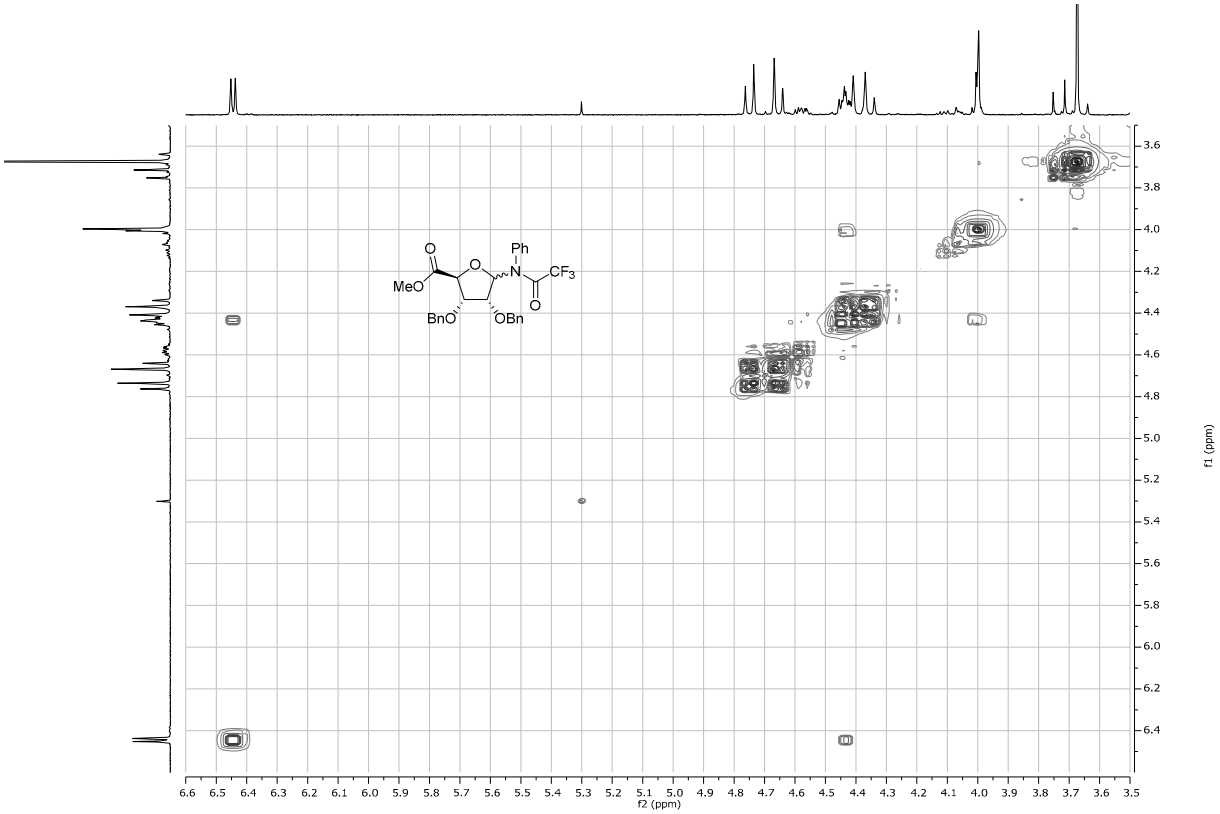
^{13}C-APT NMR, 126 MHz, $CDCl_3$ of compound **99**



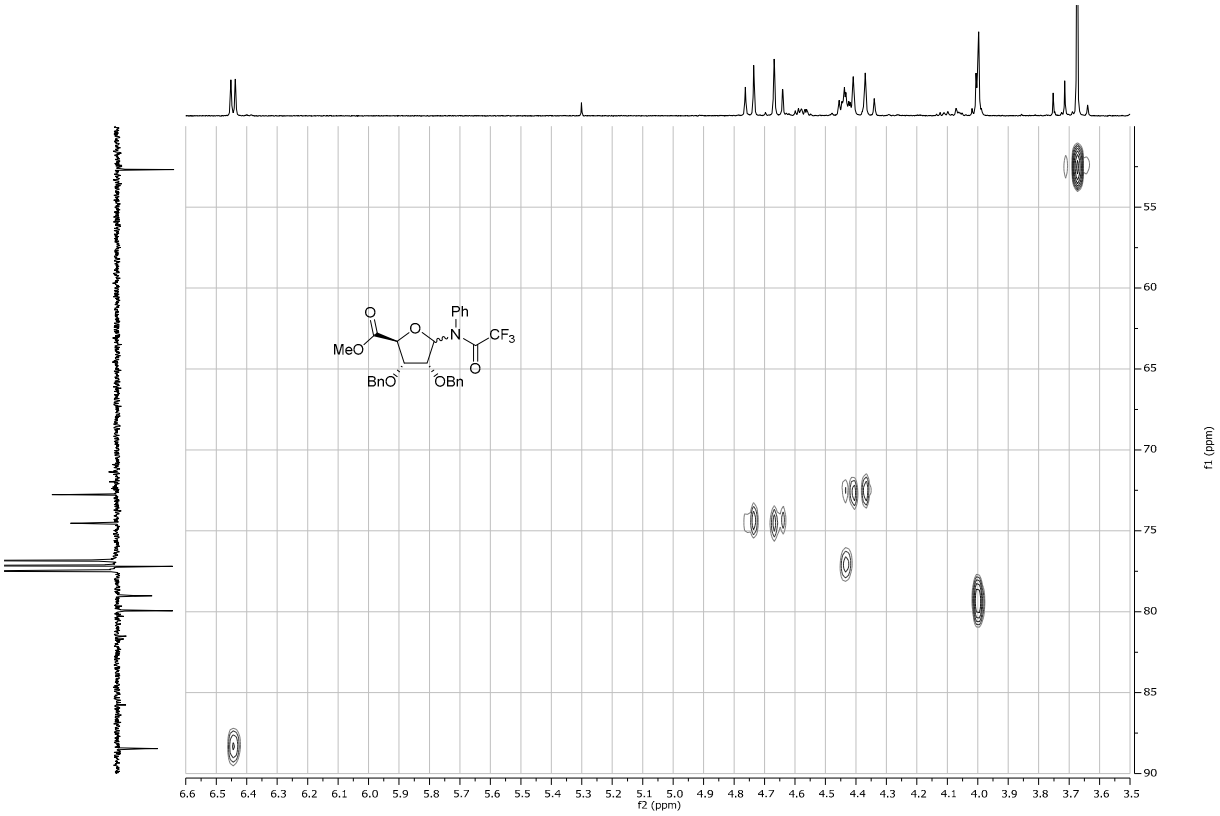
^{19}F NMR, 471 MHz, $CDCl_3$ of compound **99**



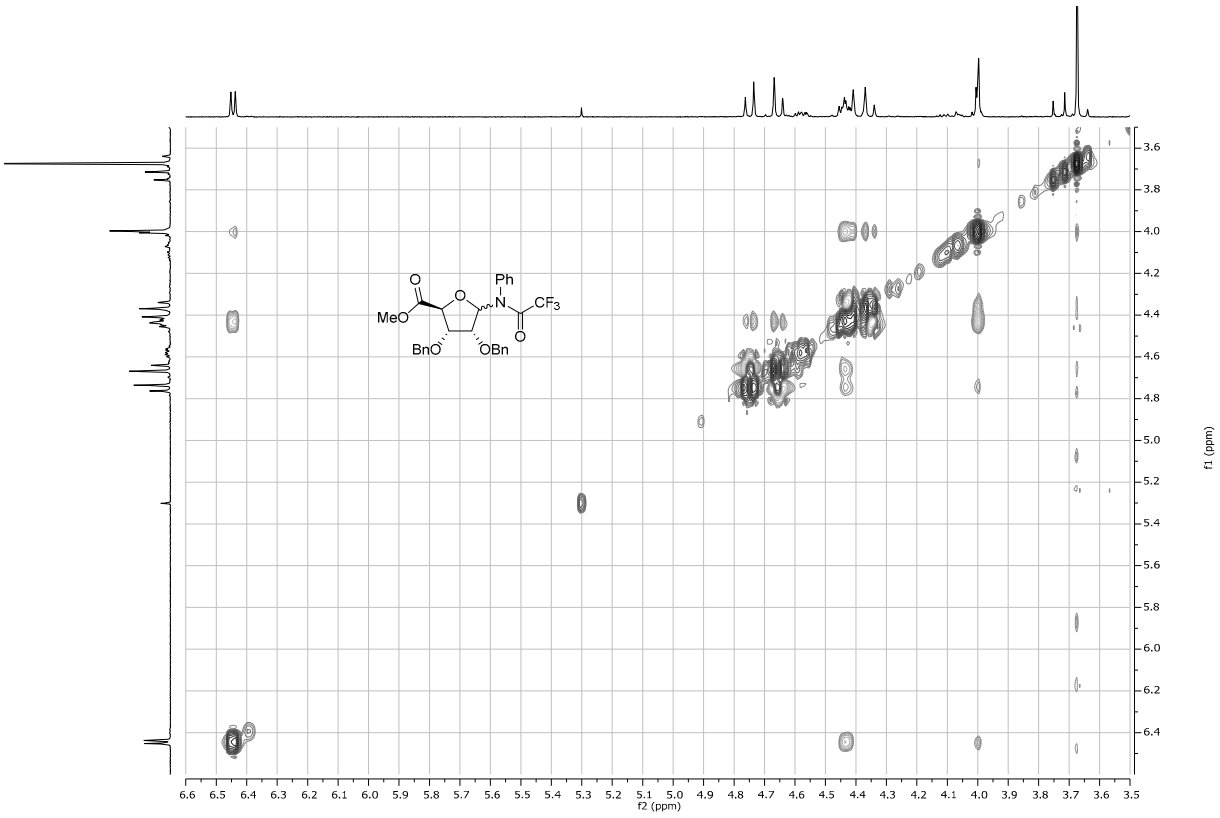
^{1}H-^{1}H COSY of compound **99**



^{1}H-^{13}C HSQC of compound **99**



^{1}H-^{1}H NOESY of compound **99**



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