Supporting Information

Nickel-Mediated Synthesis of Non-Anomeric *C*-Acyl Glycosides through Electron Donor-Acceptor Complex Photoactivation

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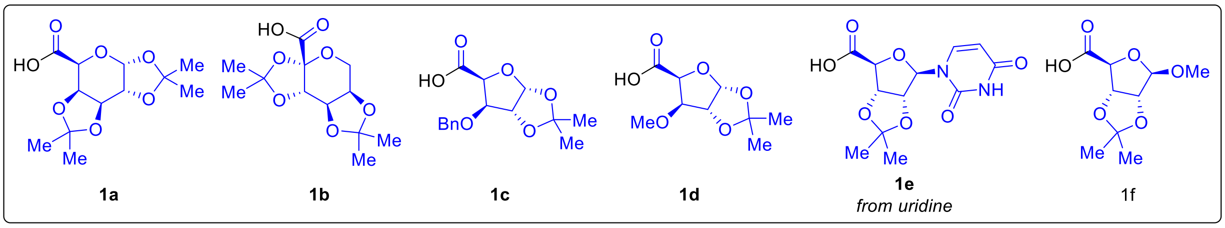
TABLE OF CONTENT

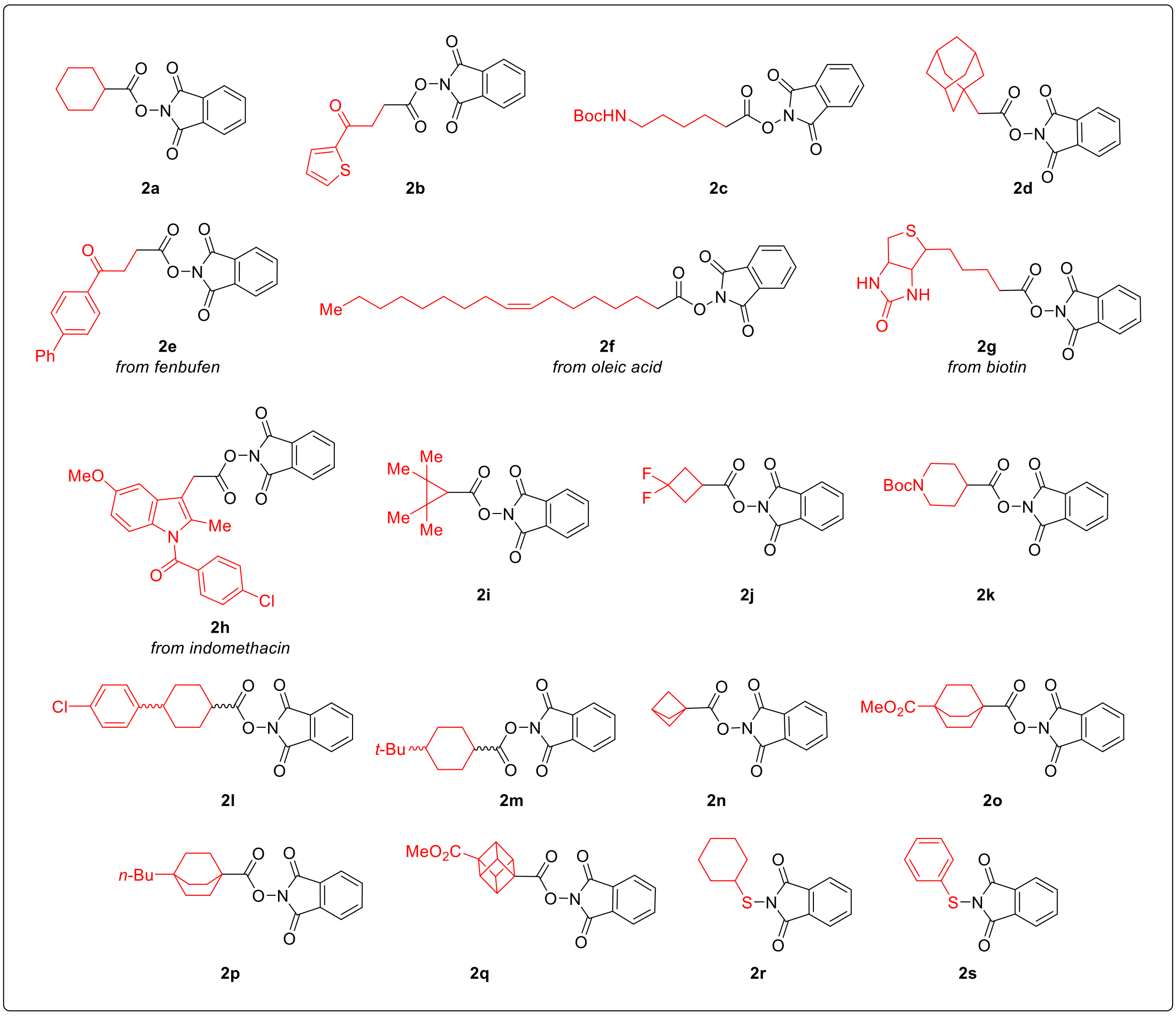
1. List of Sugar Acids

The sugar acid motifs **1a-f** were synthesized from the corresponding commercially available compounds, according to the literature procedure.[1,2]



2. List of Redox-Active Esters

Redox-active esters **2a-q** were synthesized from the corresponding commercially carboxylic acids following a reported literature procedure.[3,4] Redox-active thiols **2r-s** are commercially available.



3. Reaction Workflow

All photoredox reactions were performed with two Kessil PR160-purple LED lamps (30 W High Luminous DEX 2100 LED, 390 nm). The lamps were placed 1.5 inches away from the reaction vials within a ventilated fume hood. A typical reaction setup is shown below.

Figure S1. *Reaction setup for the decarboxylative arylation.*

Figure S2. Gram scale synthesis reaction setup of **3f**.

4. Mechanistic Investigations

A. UV/vis studies:

UV/vis absorption spectra were measured in a 1 cm quartz cuvette using a Genesys 150 UV/vis spectrophotometer from Thermo Scientific. Absorption spectra of individual reaction components and mixtures thereof were recorded. A bathochromic shift was observed for a mixture of alkyl RAE and HE in DMA (0.2 M), which was visibly yellow in color (*Figure S3*). This indicates the formation of an electron donor-acceptor (EDA) complex (*Figure S4*, orange band).

Figure S3. Visual appearance of reaction components and mixtures thereof.

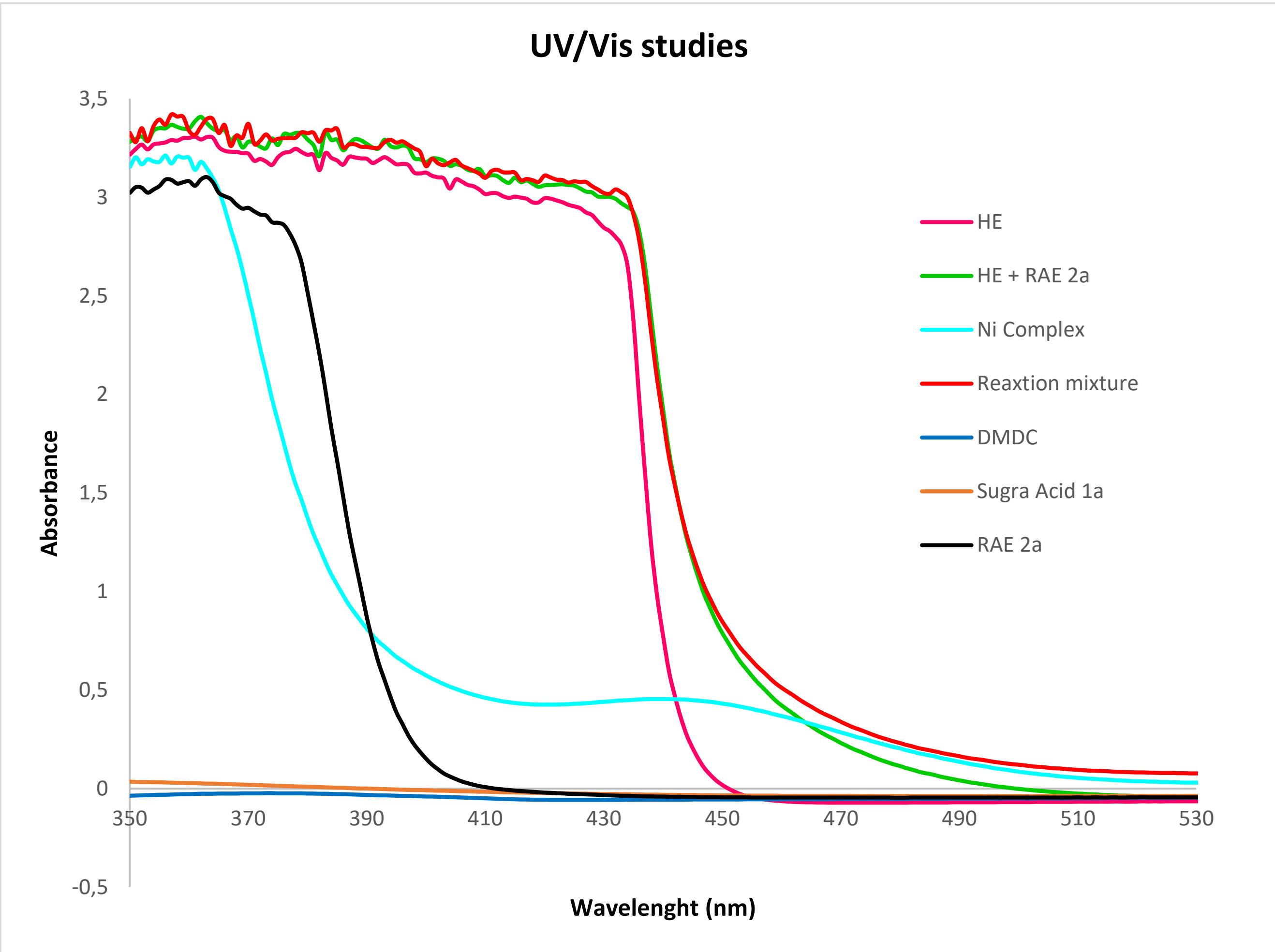
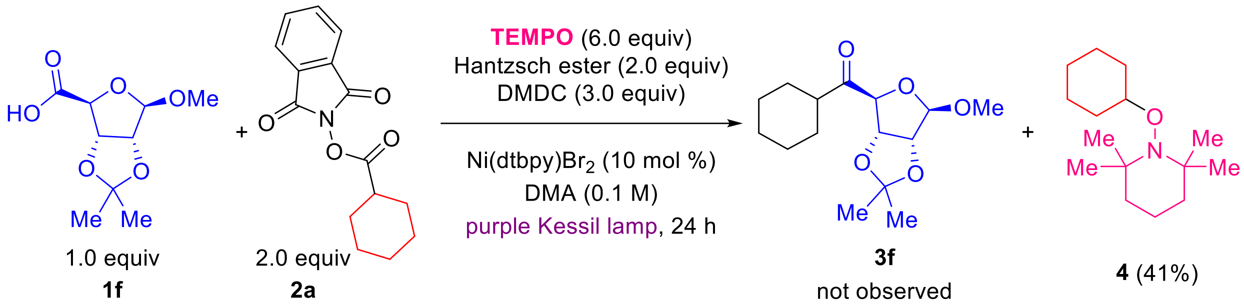


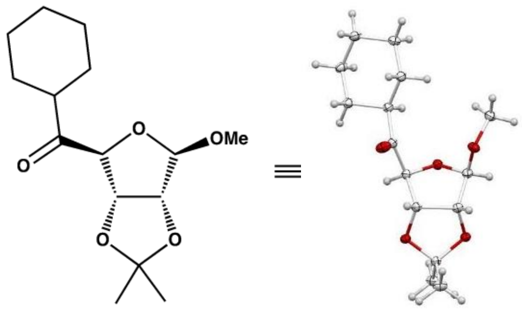
Figure S4. UV/vis absorption spectra of individual reaction components and a combination thereof. All spectra were measured in DMA and with a concentration of 0.1 M sugar acid **1a** (Acid), 0.2 M redox-active ester **2a** (RAE), 0.2 M Hantzsch ester (HE), 0.3M dimethyl dicarbonate (DMDC) and 0.01 M [$NiBr_2$(dtbpy)] (Ni complex). The stoichiometry and concentration of sample "mixture" reflects the reaction conditions.

B. TEMPO trapping experiment:



To probe the intermediacy of radical species, a trapping experiment was performed using TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] as a radical scavenger. The reaction was performed according to the *General Procedure* using sugar acid **1f** (109 mg, 1.0 equiv, 0.50 mmol) and redox-active ester **2a** (273 mg, 2.0 equiv, 1.0 mmol), in the presence of TEMPO (3 mmol, 6.0 equiv). After chromatographic purification (in hexanes), the corresponding TEMPO adduct **4** was isolated as a colorless oil (49 mg, 0.2 mmol, 41%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 3.62 – 3.55 (m, 1H), 2.06 – 2.02 (m, 2H), 1.77 – 1.70 (m, 2H), 1.57 – 1.43 (m, 6H), 1.25 – 1.04 (m, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 81.9, 59.7 (2C), 40.4 (2C), 33.0 (2C), 26.1 (3C), 25.2 (4C), 17.5. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{v}$ = 2970, 2928, 2855, 1467, 1452, 1374, 1359, 1257, 1243, 1182, 1132, 1094, 1074, 1058, 1033, 1020. **HRMS (EI)** calcd for $C_{15}H_{29}NO$ $[M]^+$: 239.2249, found 239.2252. The spectroscopic data were in agreement with those previously reported.[5]

5. X-ray Structure Determination of Compound 3f



Compound **3f**, $C_{15}H_{24}O_5$, crystallizes in the orthorhombic space group $P2_12_12_1$ (systematic absences h00: h=odd, 0k0: k=odd, and 00l: l=odd) with a=6.12528(3)Å, b=13.55731(6)Å, c=17.57670(8)Å, V=1459.610(12)$Å^3$, Z=4, and d_{calc}=1.294 g/cm^3 . X-ray intensity data were collected on a Rigaku XtaLAB Synergy-S diffractometer[6] equipped with an HPC area detector (HyPix-6000HE) and employing confocal multilayer optic-monochromated Cu-Kα radiation (λ=1.54184 Å) at a temperature of 100K. Preliminary indexing was performed from a series of sixty 0.5° rotation frames with exposures of 0.25 sec. for θ = +47.20° and 1 sec. for θ = 107.75°. A total of 12878 frames (131 runs) were collected employing ω scans with a crystal to detector distance of 34.0 mm, rotation widths of 0.5° and exposures of 0.10 sec. for θ = ±47.29°, +50.00°, +54.00°, +62.00°, +66.00, and +70.00 and 0.30 sec. for θ = -74.00, -78.00°, -82.00, -86.25°, +98.00°, and 107.75°.

Rotation frames were integrated using CrysAlisPro[6], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 59009 reflections were measured over the ranges $8.236 \leq 2\theta \leq 148.976°$, $-7 \leq h \leq 7$, $-16 \leq k \leq 16$, $-21 \leq l \leq 21$ yielding 2993 unique reflections (R_{int} = 0.0385). The intensity data were corrected for Lorentz and polarization effects and for absorption using SCALE3 ABSPACK[7] (minimum and maximum transmission 0.6988, 1.0000). The structure was solved by direct methods - ShelXT (Sheldrick, 2015)[8]. Refinement was by full-matrix least squares based on F^2 using SHELXL-2018[9]. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2) + (0.0368P)^2 + 0.2883P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0249 and wR2=0.0647 for 2981 observed reflections for which $F > 4\sigma(F)$ and R1=0.0249 and wR2=0.0648 and GOF =1.056 for all 2993 unique, non-zero reflections and 185 variables. The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +0.25 and -0.13 e/Å^3. The Hooft absolute structure parameter y[10] was calculated using PLATON[11] The resulting value was y = -0.04(3), indicating that the absolute structure has been assigned correctly. The Flack parameter[12] refined to a similar value of -0.03(3). If these parameters are equal to 0 (within 3 standard deviations) then the absolute structure has been assigned correctly; if they are 1, the opposite enantiomer has been modeled.

Table S1 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in *Tables S2* and *S3* Anisotropic thermal parameters are in *Table S4*. *Tables S5* and *S6* list bond distances and bond angles. *Figure S5* is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

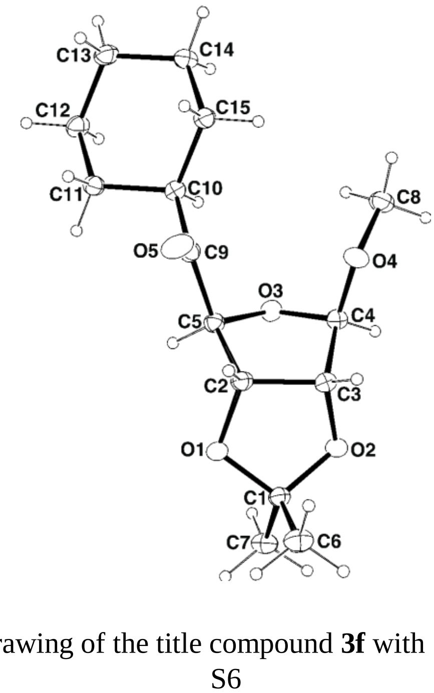


Figure S5. ORTEP drawing of the title compound **3f** with 50% thermal ellipsoids.

Table S1. Summary of Structure Determination of Compound **3f**

Empirical formula	$C_{15}H_{24}O_5$
Formula weight	284.34
Diffractometer	Rigaku XtaLAB Synergy-S
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a	6.12528(3)Å
b	13.55731(6)Å
c	17.57670(8)Å
Volume	1459.610(12)Å^3
Z	4
d_{calc}	1.294 g/cm^3
μ	0.790 mm^{-1}
F(000)	616.0
Crystal size, mm	0.22 × 0.19 × 0.18
2θ range for data collection	8.236 - 148.976°
Index ranges	-7 ≤ h ≤ 7, -16 ≤ k ≤ 16, -21 ≤ l ≤ 21
Reflections collected	59009
Independent reflections	2993[R(int) = 0.0385]
Data/restraints/parameters	2993/0/185
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0249, wR_2 = 0.0647
Final R indexes [all data]	R_1 = 0.0249, wR_2 = 0.0648
Largest diff. peak/hole	0.25/-0.13 eÅ^{-3}
Flack absolute structure parameter	-0.03(3)
Hooft absolute structure parameter	-0.04(3)

Table S2. Refined Positional Parameters for Compound **3f**

Atom	***x***	***y***	***z***	**U(eq)**
C1	0.6015(2)	0.84207(10)	0.61421(8)	0.0170(3)
C2	0.6728(2)	0.68117(10)	0.57750(8)	0.0163(3)
C3	0.8455(2)	0.71632(10)	0.63547(8)	0.0175(3)
C4	0.8519(2)	0.63400(10)	0.69468(8)	0.0174(3)
C5	0.5773(2)	0.58775(10)	0.61295(7)	0.0150(3)
C6	0.7220(3)	0.90747(11)	0.55791(9)	0.0229(3)
C7	0.4190(3)	0.89379(11)	0.65546(8)	0.0207(3)
C8	1.0702(3)	0.49959(11)	0.73301(8)	0.0224(3)
C9	0.6487(2)	0.49205(10)	0.57347(8)	0.0156(3)
C10	0.5922(2)	0.39640(10)	0.61339(8)	0.0152(3)
C11	0.3888(2)	0.35270(10)	0.57407(8)	0.0170(3)
C12	0.3252(2)	0.25487(10)	0.61117(9)	0.0199(3)
C13	0.5131(3)	0.18090(10)	0.61003(9)	0.0206(3)
C14	0.7181(2)	0.22399(10)	0.64635(8)	0.0203(3)
C15	0.7808(2)	0.32253(10)	0.61014(8)	0.0181(3)
O1	0.51184(17)	0.75780(7)	0.57653(6)	0.0195(2)
O2	0.75001(18)	0.80172(7)	0.66909(6)	0.0197(2)
O3	0.64279(16)	0.58887(7)	0.69178(5)	0.0166(2)
O4	1.01923(17)	0.56842(7)	0.67382(6)	0.0198(2)
O5	0.7304(2)	0.49289(8)	0.51069(6)	0.0238(2)

Table S3. Positional Parameters for Hydrogens in Compound **3f**

Atom	***x***	***y***	***z***	**U(eq)**
H2	0.736713	0.668823	0.52602	0.02
H3	0.991091	0.72959	0.611823	0.021
H4	0.880036	0.661758	0.746473	0.021
H5	0.41445	0.592133	0.61063	0.018
H6a	0.786031	0.963736	0.584887	0.034
H6b	0.61959	0.931439	0.519275	0.034
H6c	0.838213	0.869403	0.533264	0.034
H7a	0.344501	0.846898	0.68902	0.031
H7b	0.314722	0.920147	0.61838	0.031
H7c	0.479006	0.948011	0.685835	0.031
H8a	1.17938	0.452468	0.714571	0.034
H8b	0.937561	0.464044	0.747864	0.034
H8c	1.12851	0.535143	0.777093	0.034
H10	0.556575	0.410692	0.667813	0.018
H11a	0.265813	0.399777	0.57806	0.02
H11b	0.420088	0.341933	0.519434	0.02
H12a	0.280695	0.267033	0.664494	0.024
H12b	0.198558	0.226532	0.583857	0.024
H13a	0.469374	0.120634	0.637941	0.025
H13b	0.545153	0.162031	0.556775	0.025
H14a	0.840332	0.176817	0.640387	0.024
H14b	0.692689	0.233686	0.701466	0.024
H15a	0.822869	0.311542	0.55643	0.022
H15b	0.908618	0.35027	0.637156	0.022

Table S4. Refined Thermal Parameters (U's) for Compound **3f**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0213(7)	0.0128(6)	0.0169(6)	0.0006(5)	-0.0034(6)	0.0000(5)
C2	0.0194(6)	0.0126(6)	0.0171(6)	0.0005(5)	-0.0012(5)	0.0005(5)
C3	0.0192(7)	0.0132(6)	0.0202(6)	-0.0005(5)	-0.0020(6)	0.0001(5)
C4	0.0181(7)	0.0155(6)	0.0187(6)	-0.0014(5)	-0.0023(5)	0.0016(5)
C5	0.0165(6)	0.0142(6)	0.0143(6)	0.0002(5)	-0.0004(5)	0.0004(5)
C6	0.0260(7)	0.0181(7)	0.0247(7)	0.0031(6)	0.0041(6)	0.0010(6)
C7	0.0259(7)	0.0166(7)	0.0194(7)	0.0014(5)	0.0011(6)	0.0037(6)
C8	0.0269(8)	0.0186(7)	0.0217(7)	0.0004(6)	-0.0056(6)	0.0052(6)
C9	0.0151(6)	0.0147(6)	0.0169(6)	-0.0008(5)	0.0001(5)	-0.0004(5)
C10	0.0164(6)	0.0138(6)	0.0154(6)	-0.0006(5)	0.0003(5)	-0.0004(5)
C11	0.0151(6)	0.0150(6)	0.0208(6)	0.0008(5)	-0.0003(5)	0.0007(5)
C12	0.0167(6)	0.0158(6)	0.0273(7)	0.0003(6)	0.0023(5)	-0.0028(5)
C13	0.0231(7)	0.0131(6)	0.0256(7)	0.0009(5)	0.0009(6)	-0.0011(6)
C14	0.0224(7)	0.0157(6)	0.0228(7)	0.0015(5)	-0.0024(6)	0.0037(6)
C15	0.0158(6)	0.0148(6)	0.0237(7)	-0.0010(5)	-0.0007(6)	0.0000(5)
O1	0.0226(5)	0.0125(5)	0.0235(5)	-0.0017(4)	-0.0067(4)	0.0018(4)
O2	0.0244(5)	0.0137(5)	0.0210(5)	-0.0020(4)	-0.0069(4)	0.0033(4)
O3	0.0197(5)	0.0166(5)	0.0134(4)	-0.0001(4)	0.0000(4)	-0.0004(4)
O4	0.0202(5)	0.0175(5)	0.0215(5)	0.0018(4)	-0.0007(4)	0.0045(4)
O5	0.0350(6)	0.0165(5)	0.0200(5)	-0.0006(4)	0.0088(5)	-0.0013(5)

Table S5. Bond Distances in Compound **3f**, Å

C1-C6	1.520(2)	C1-C7	1.505(2)	C1-O1	1.4300(16)
C1-O2	1.4345(17)	C2-C3	1.544(2)	C2-C5	1.5279(18)
C2-O1	1.4323(17)	C3-C4	1.5264(18)	C3-O2	1.4255(17)
C4-O3	1.4205(17)	C4-O4	1.4054(17)	C5-C9	1.5350(18)
C5-O3	1.4426(16)	C8-O4	1.4320(17)	C9-C10	1.5145(18)
C9-O5	1.2118(17)	C10-C11	1.5426(19)	C10-C15	1.5300(18)
C11-C12	1.5285(19)	C12-C13	1.527(2)	C13-C14	1.525(2)
C14-C15	1.5287(19)				

Table S6. Bond Angles in Compound **3f**, °

C7-C1-C6	113.73(12)	O1-C1-C6	110.55(11)	O1-C1-C7	108.08(12)
O1-C1-O2	104.49(10)	O2-C1-C6	110.61(12)	O2-C1-C7	108.95(11)
C5-C2-C3	104.41(11)	O1-C2-C3	104.81(10)	O1-C2-C5	110.04(11)
C4-C3-C2	103.99(11)	O2-C3-C2	104.05(11)	O2-C3-C4	108.77(11)
O3-C4-C3	105.51(11)	O4-C4-C3	107.66(11)	O4-C4-O3	112.07(11)
C2-C5-C9	114.03(11)	O3-C5-C2	106.06(10)	O3-C5-C9	111.33(11)
C10-C9-C5	116.69(11)	O5-C9-C5	121.43(12)	O5-C9-C10	121.63(12)
C9-C10-C11	107.81(11)	C9-C10-C15	111.74(11)	C15-C10-C11	109.97(11)
C12-C11-C10	110.36(12)	C13-C12-C11	111.85(12)	C14-C13-C12	111.33(11)
C13-C14-C15	111.54(12)	C14-C15-C10	111.53(11)	C1-O1-C2	108.05(10)
C3-O2-C1	106.94(10)	C4-O3-C5	106.84(10)	C4-O4-C8	112.44(11)

This report has been created with Olex2[11], compiled on 2018.05.29 svn.r3508 for OlexSys

6. References

1. Sugar acids **1a-d**, and **1f** were synthesized following the reported procedure: Ji, P.; Zhang, Y.; Wei, Y.; Huang, H.; Hu, W.; Mariano, P. A.; Wang, W. Visible-Light-Mediated, Chemo- and Stereoselective Radical Process for the Synthesis of C-Glycoamino Acids. *Org. Lett.* **2019**, *21*, 3086-3092.
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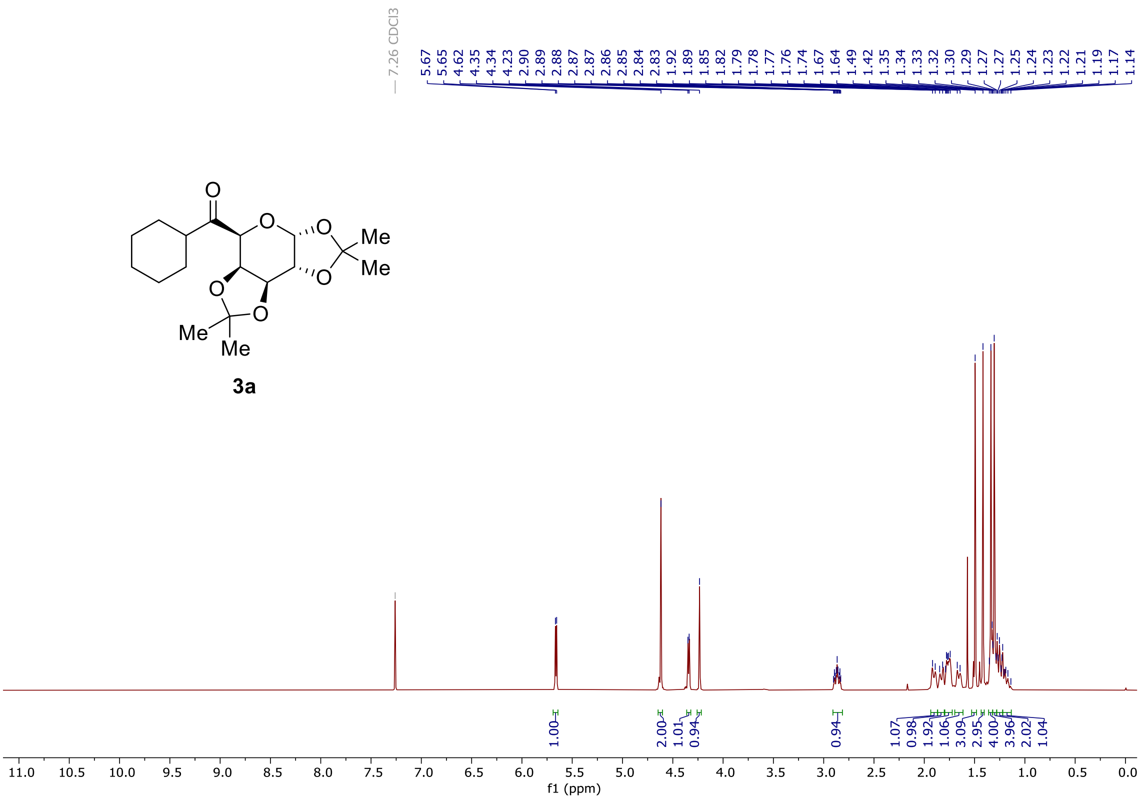
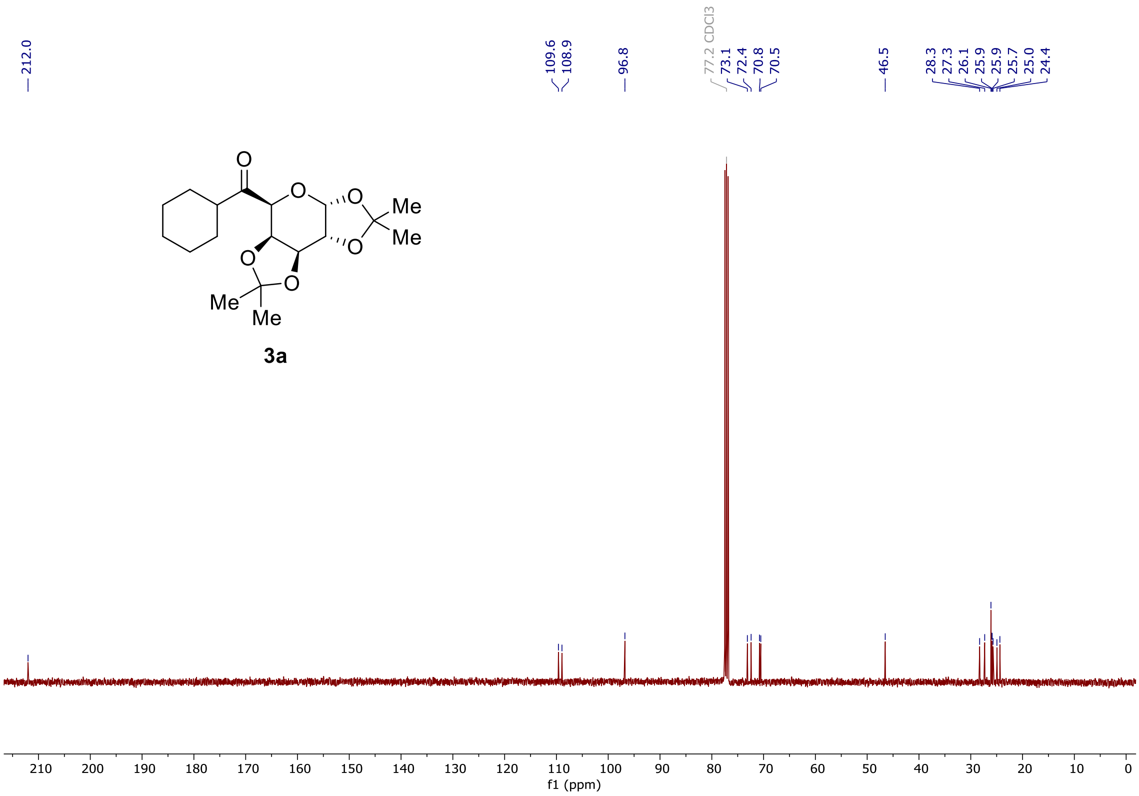
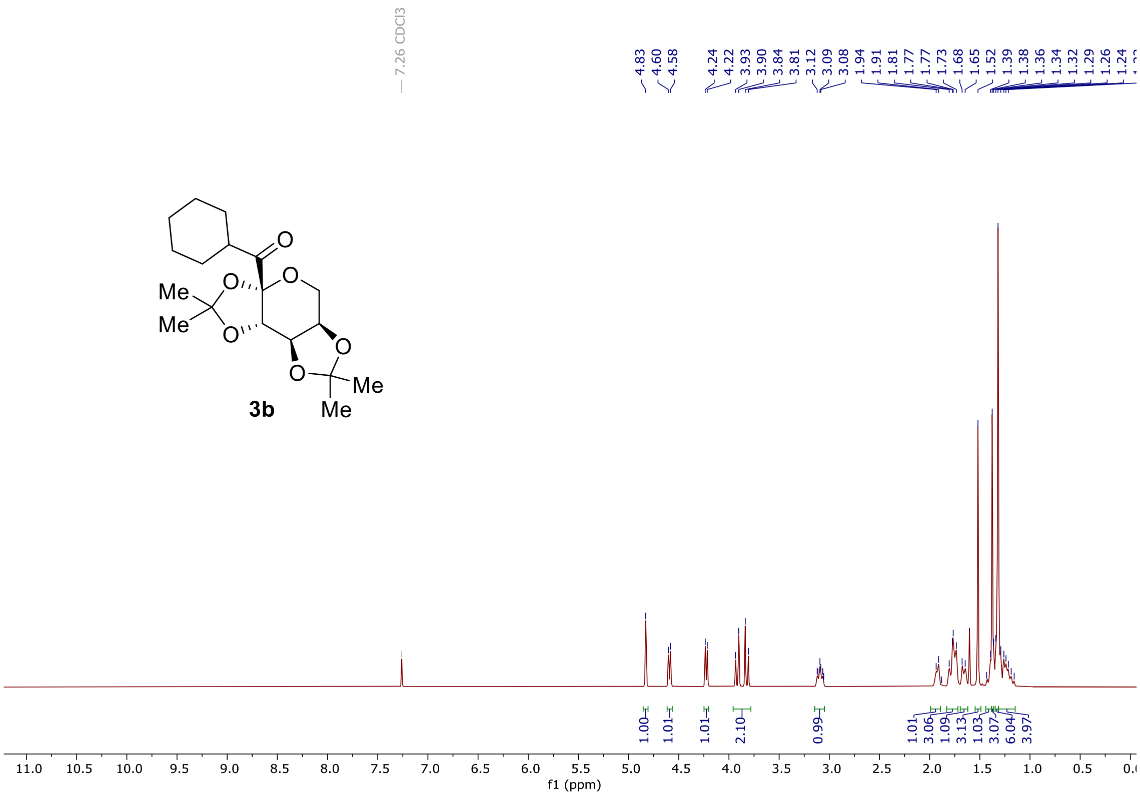
7. NMR spectra



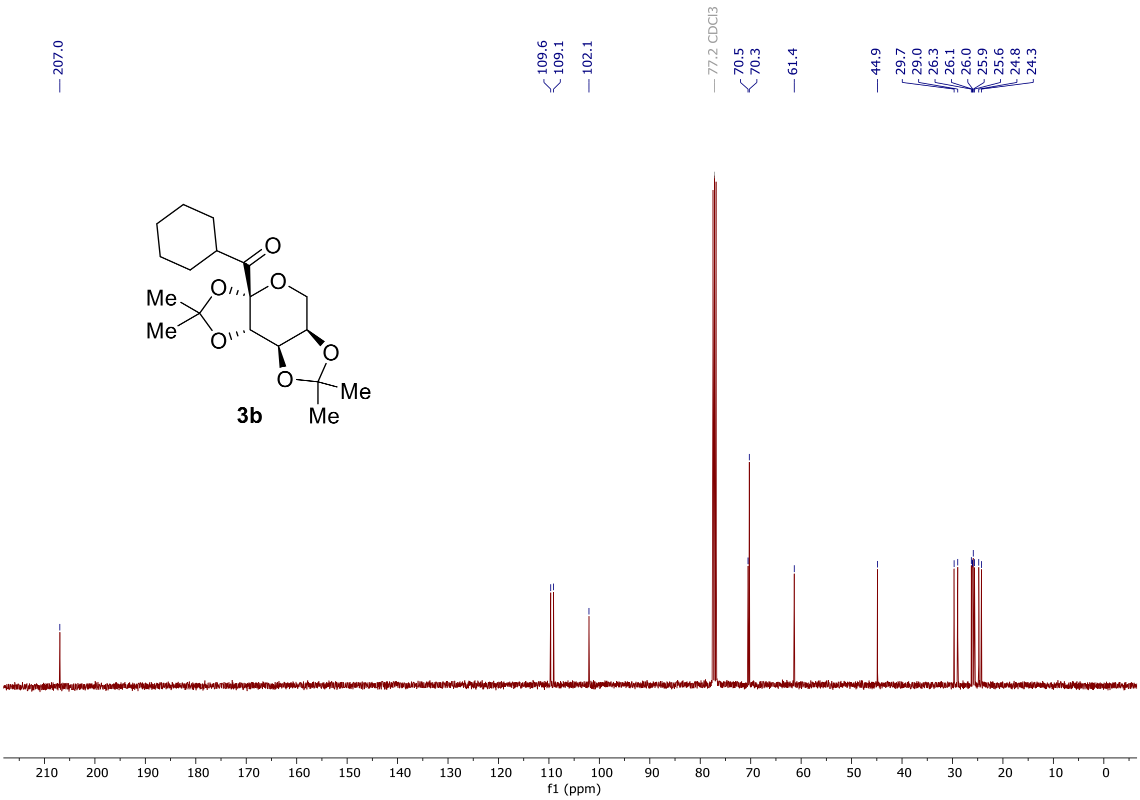
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**.



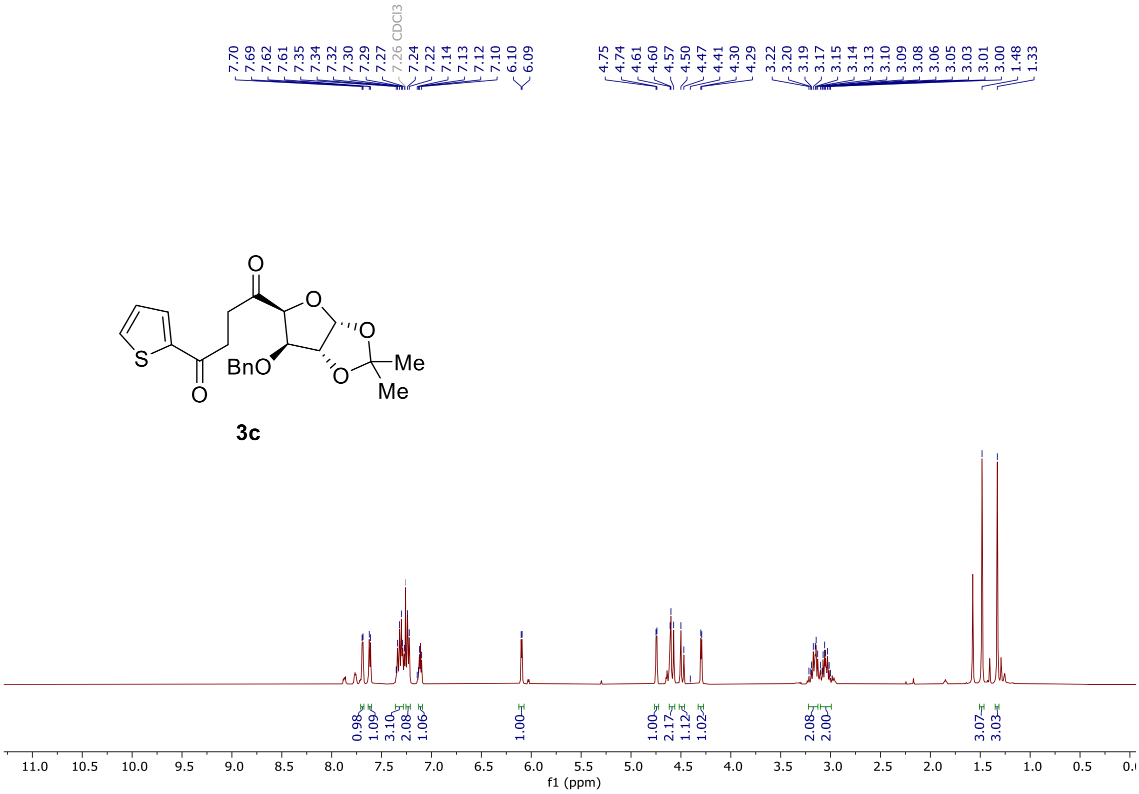
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of compound **3a**.



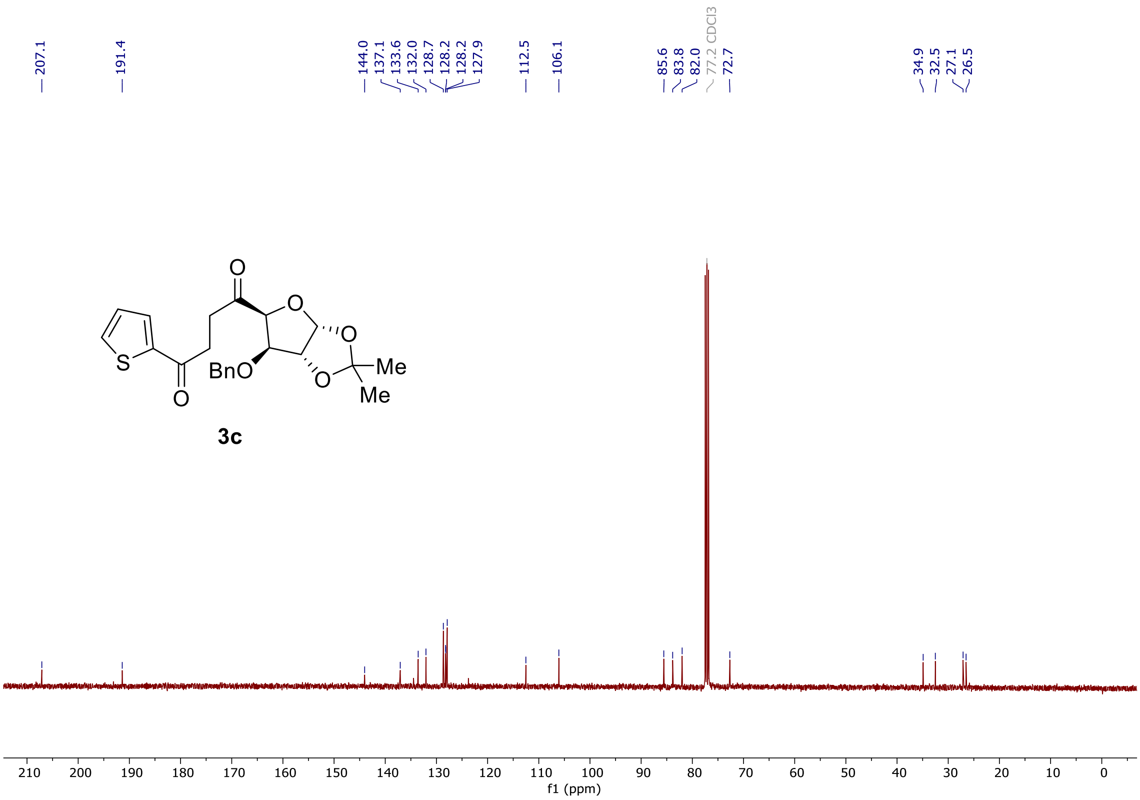
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**.



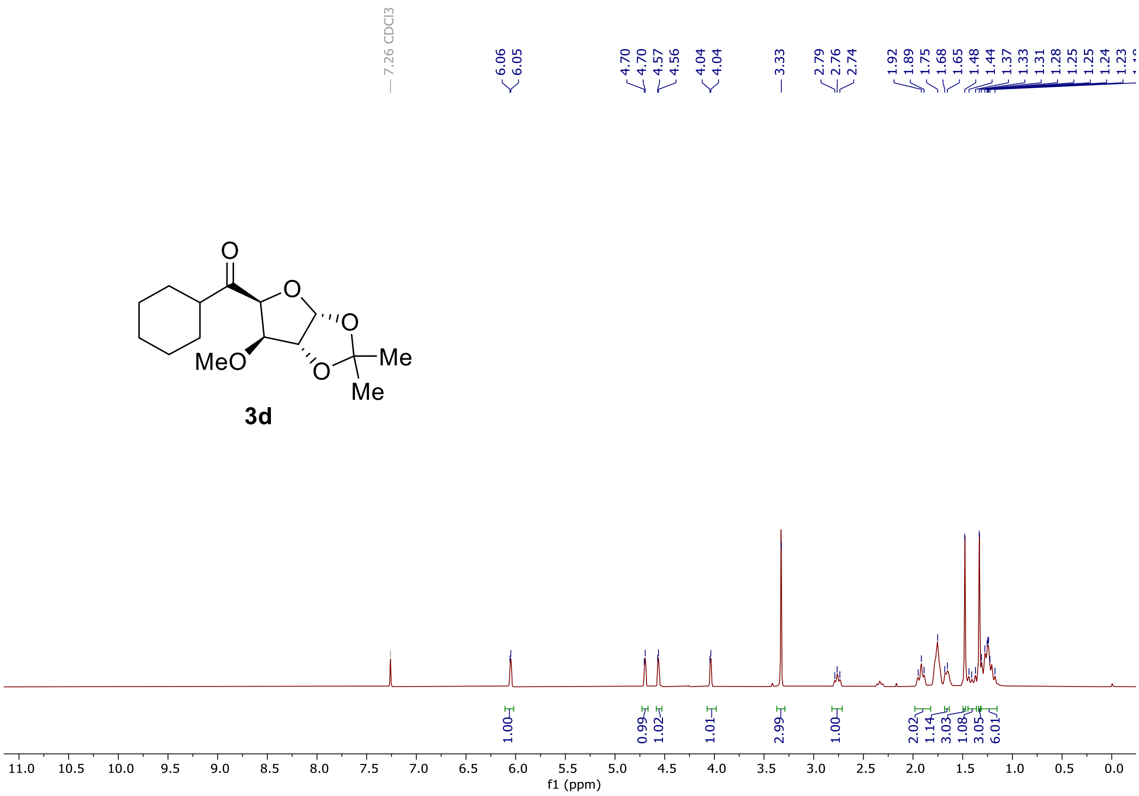
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of compound **3b**.



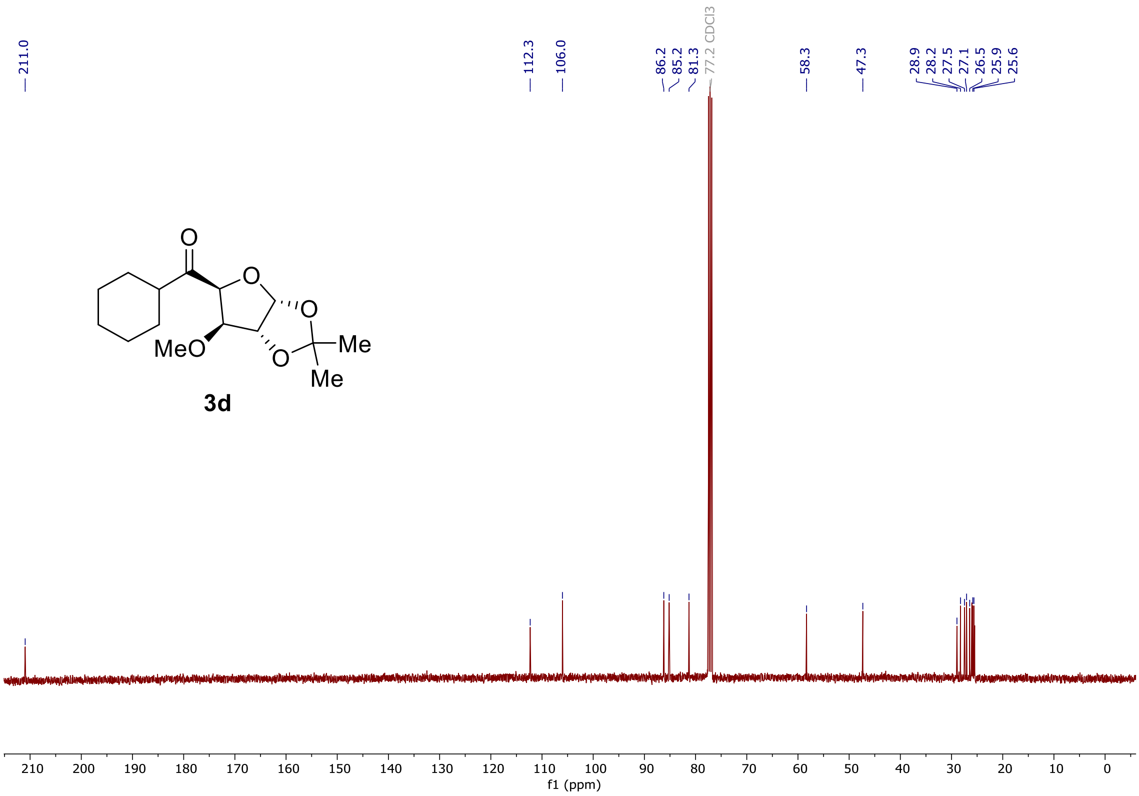
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3c**.



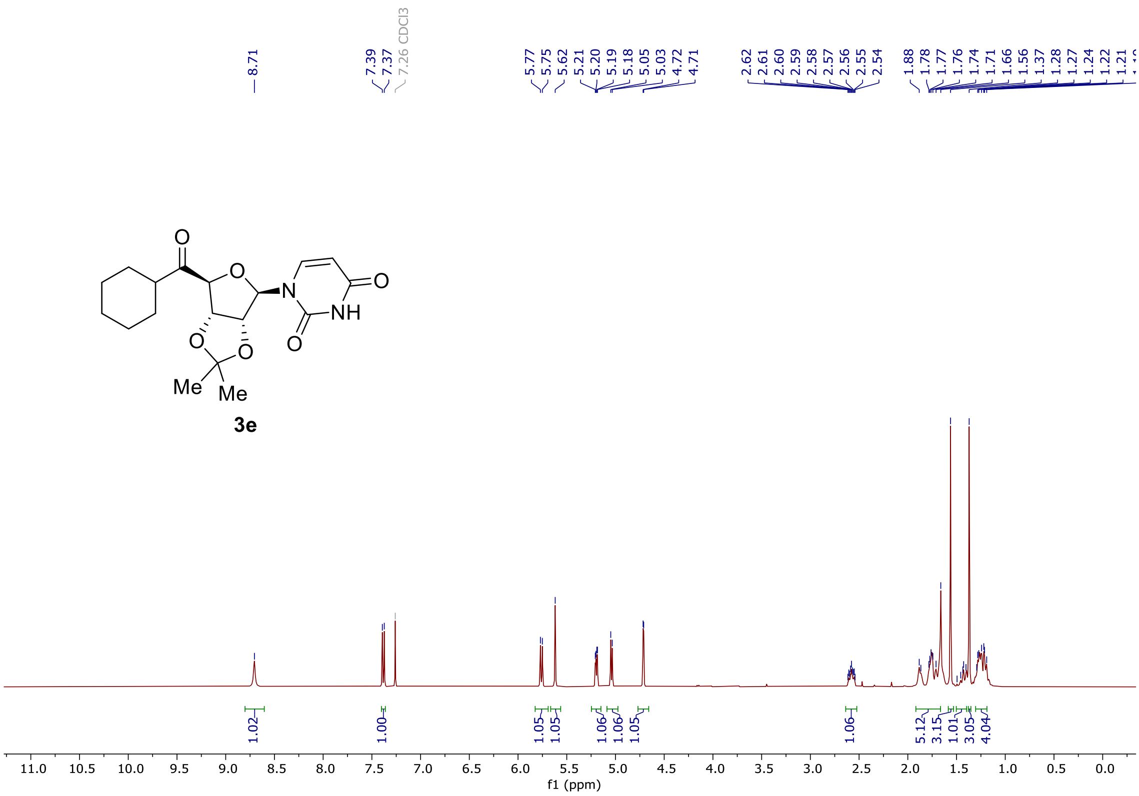
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) of compound **3c**.



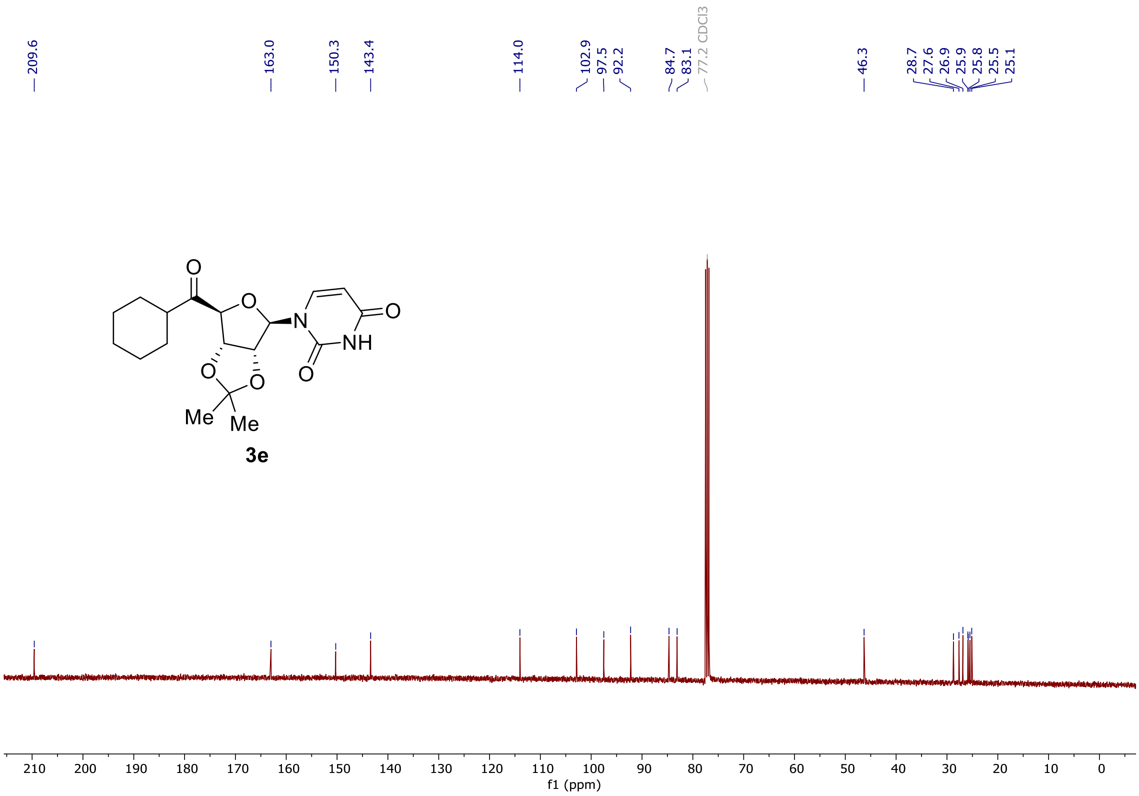
^1H NMR (400 MHz, $CDCl_3$) of compound **3d**.



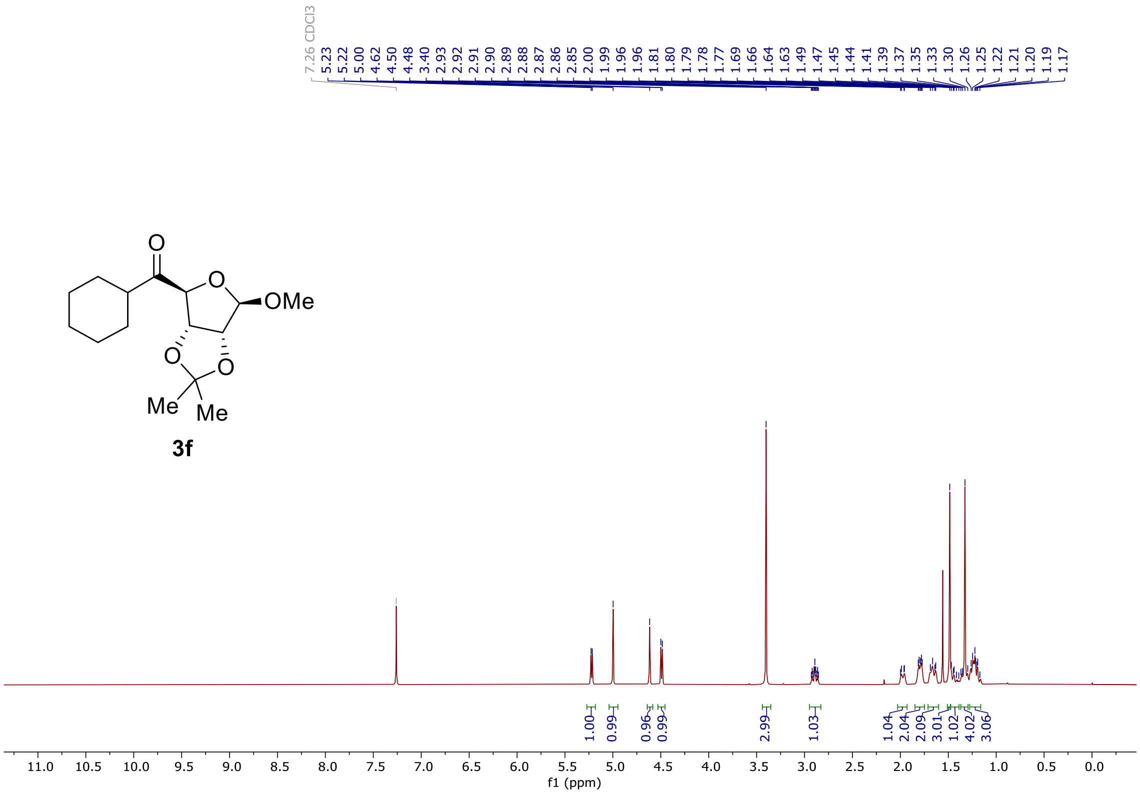
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of compound **3d**.



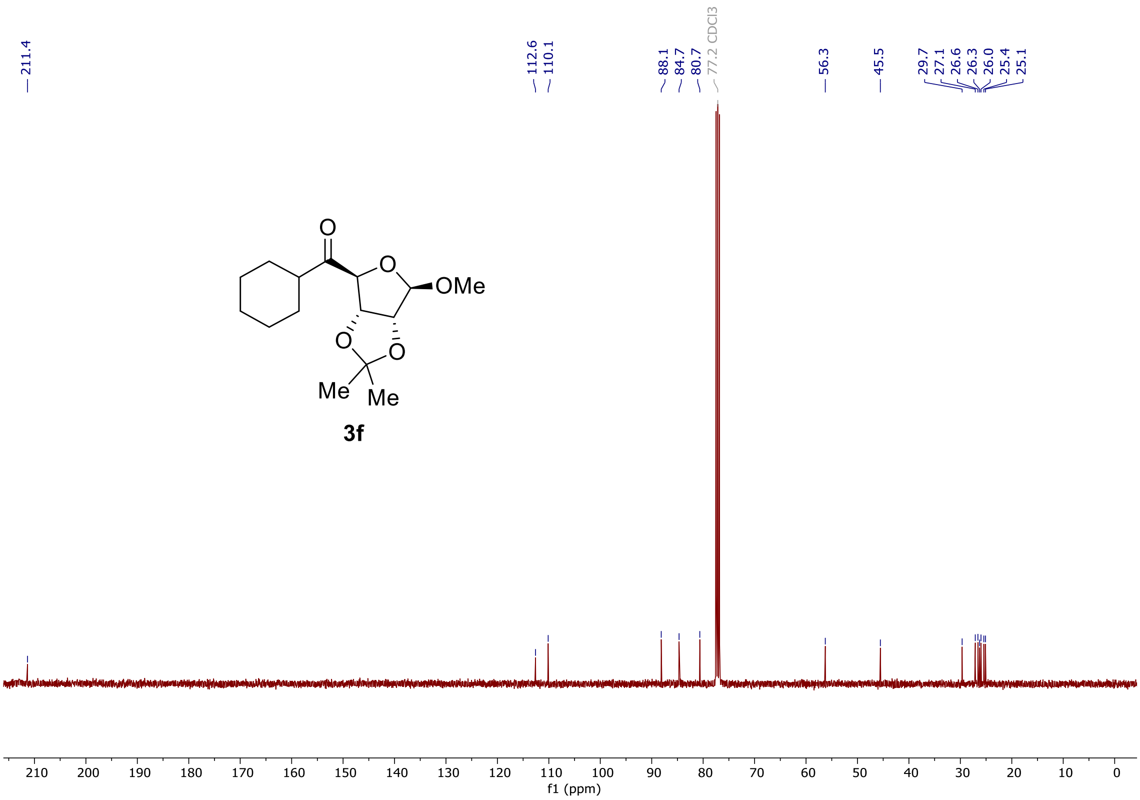
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3e**.



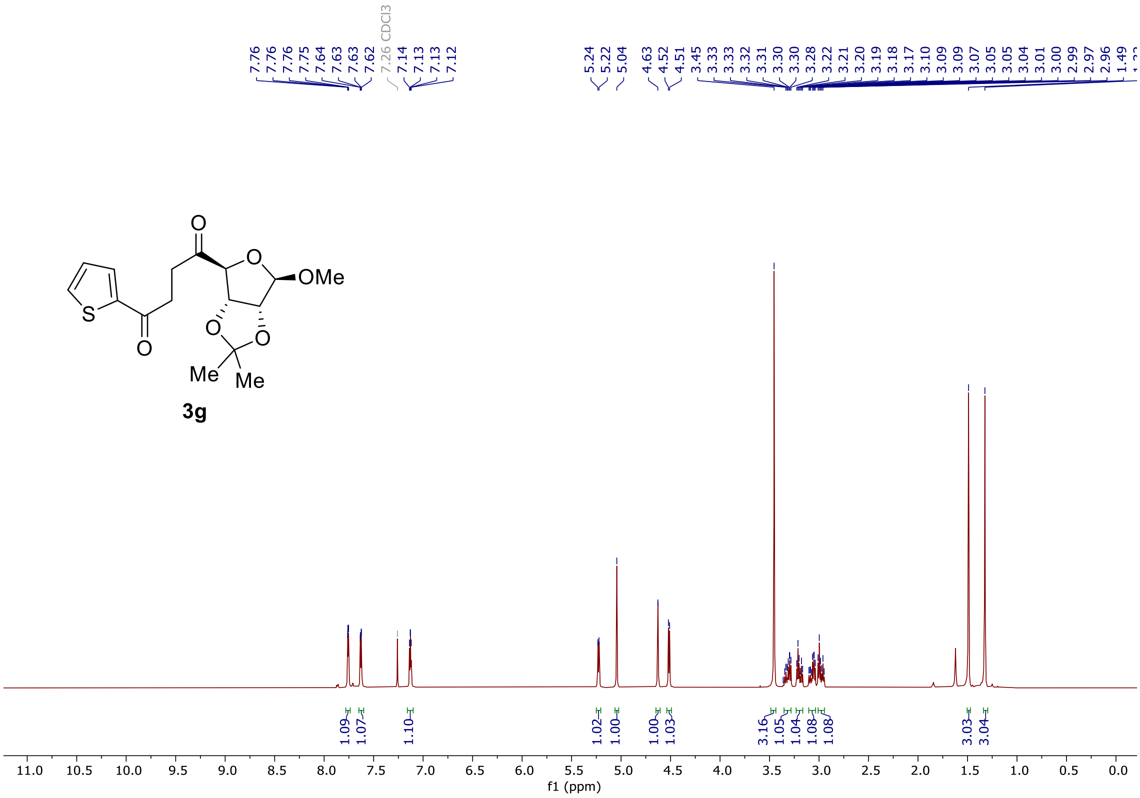
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) of compound **3e**.



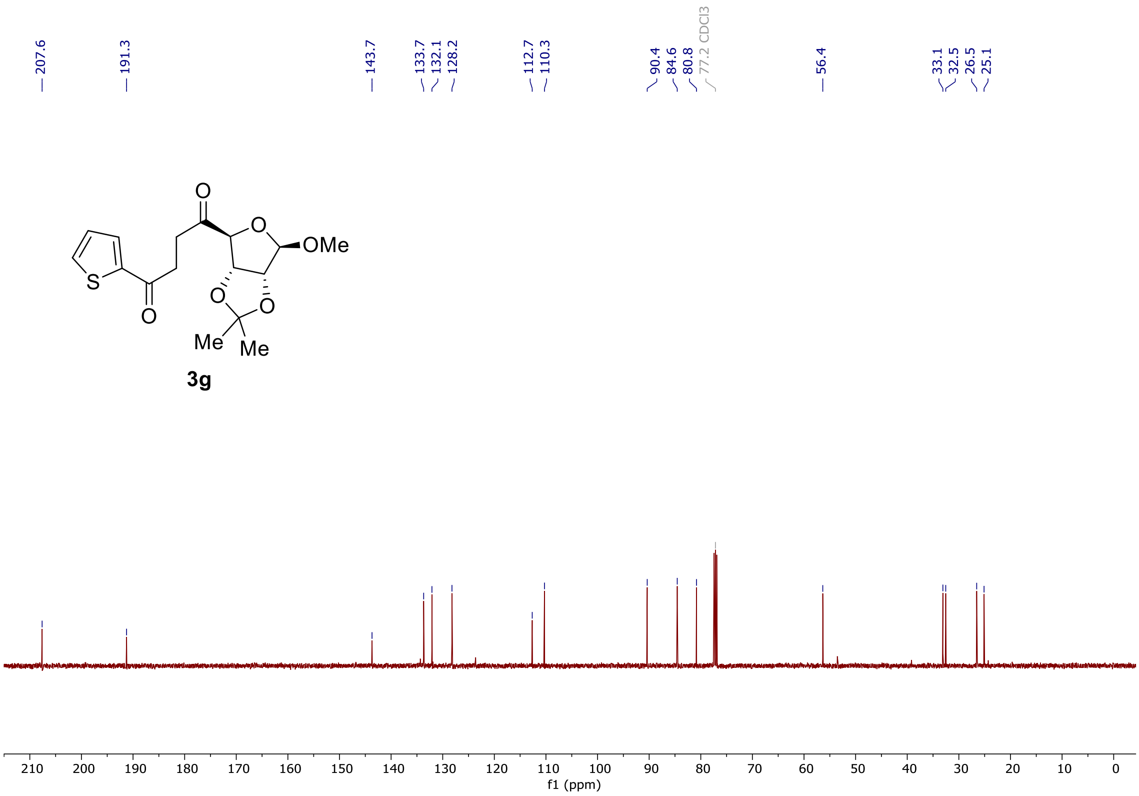
^1H NMR (400 MHz, $CDCl_3$) of compound **3f**.



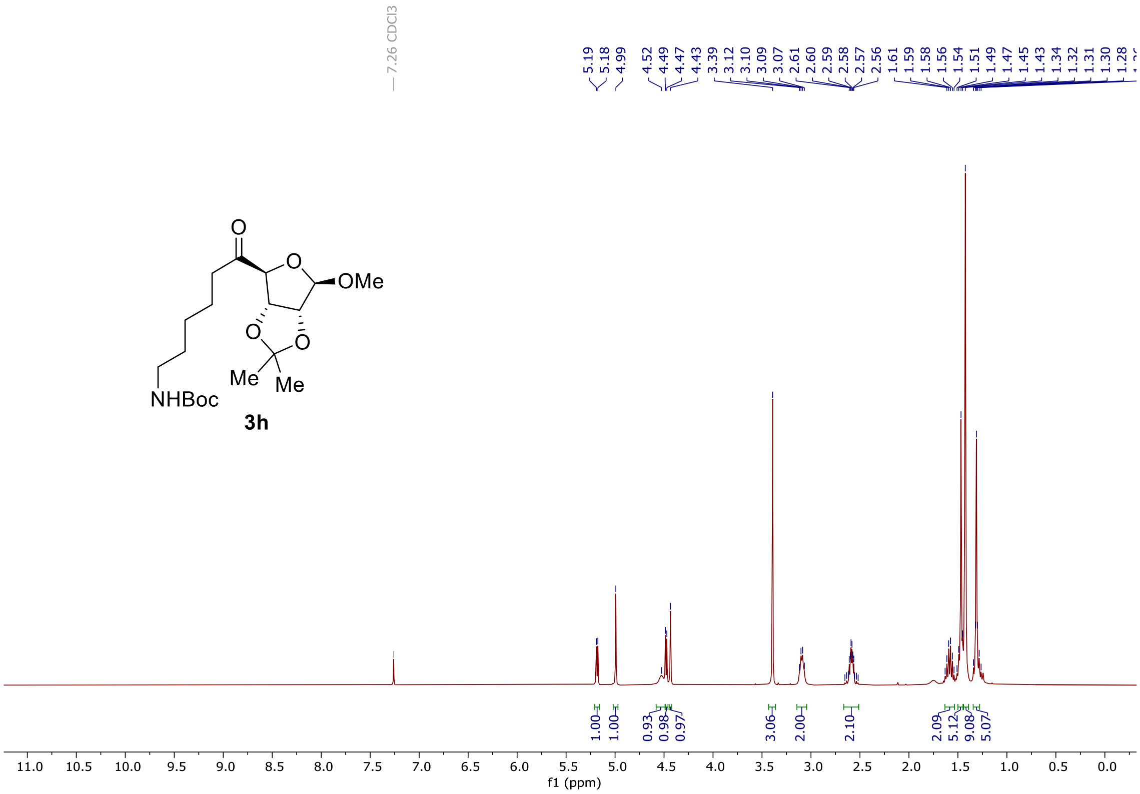
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of compound **3f**.



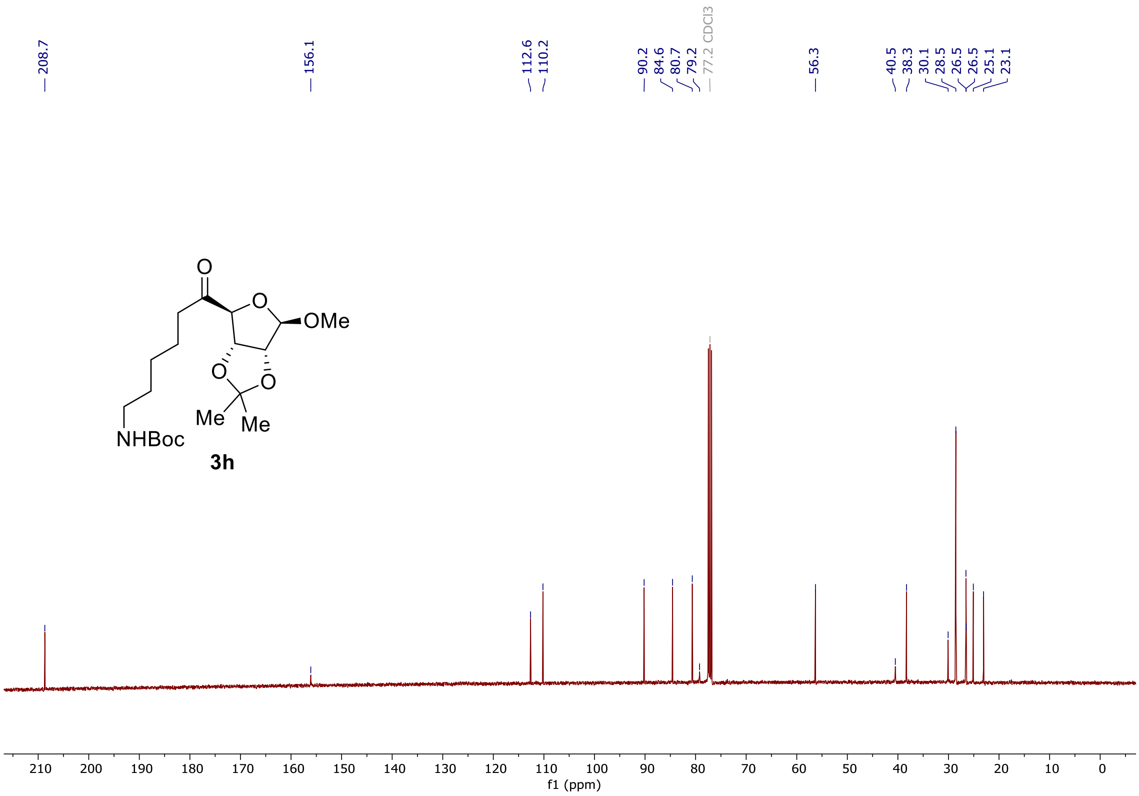
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g**.



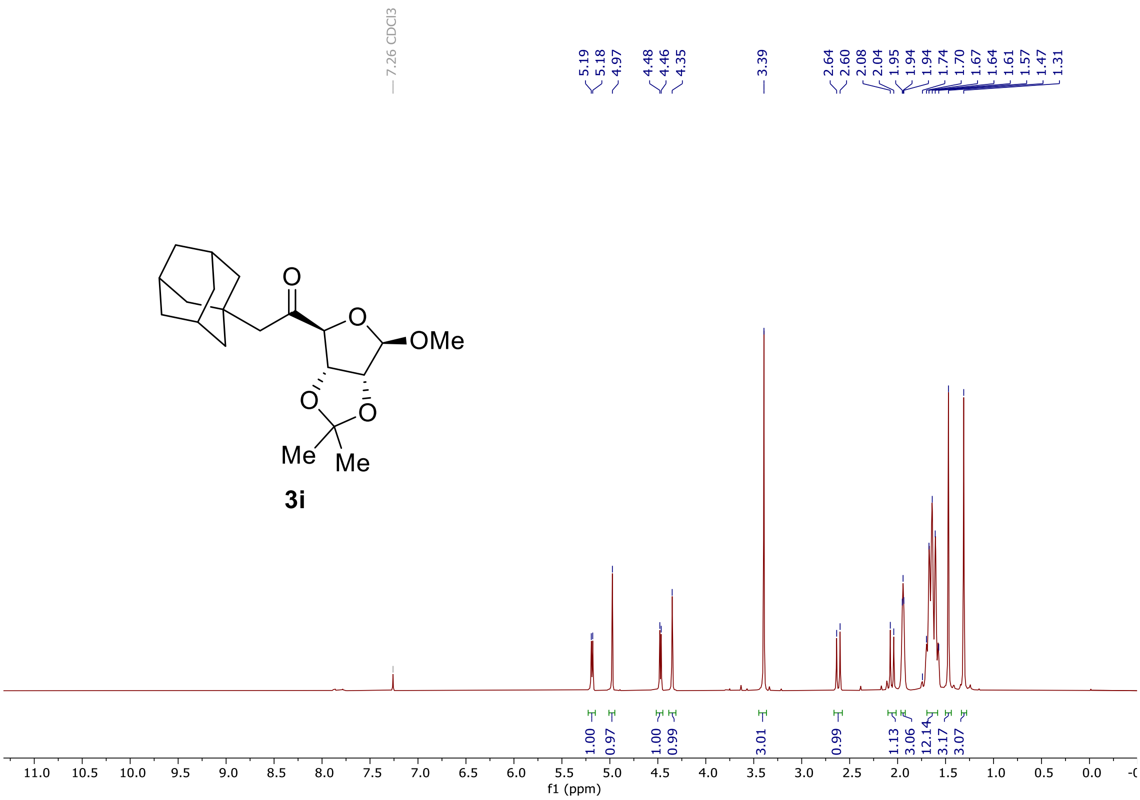
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) of compound **3g**.



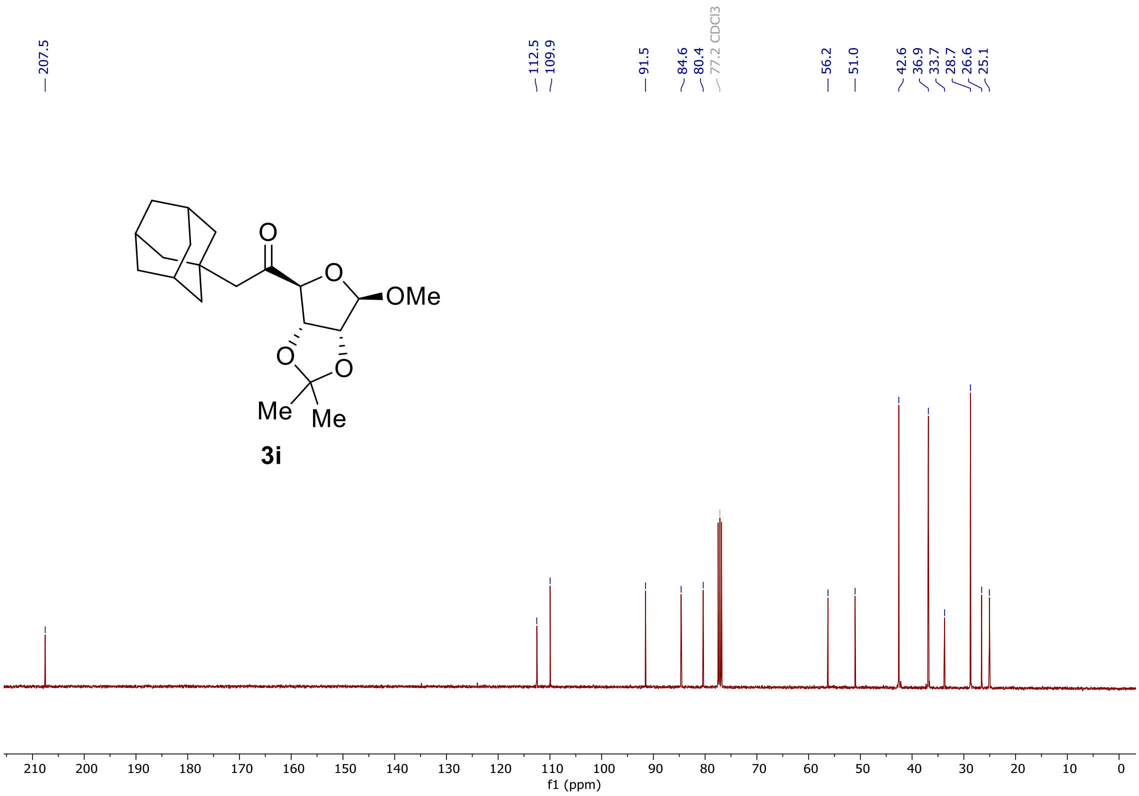
^1H NMR (400 MHz, $CDCl_3$) of compound **3h**.



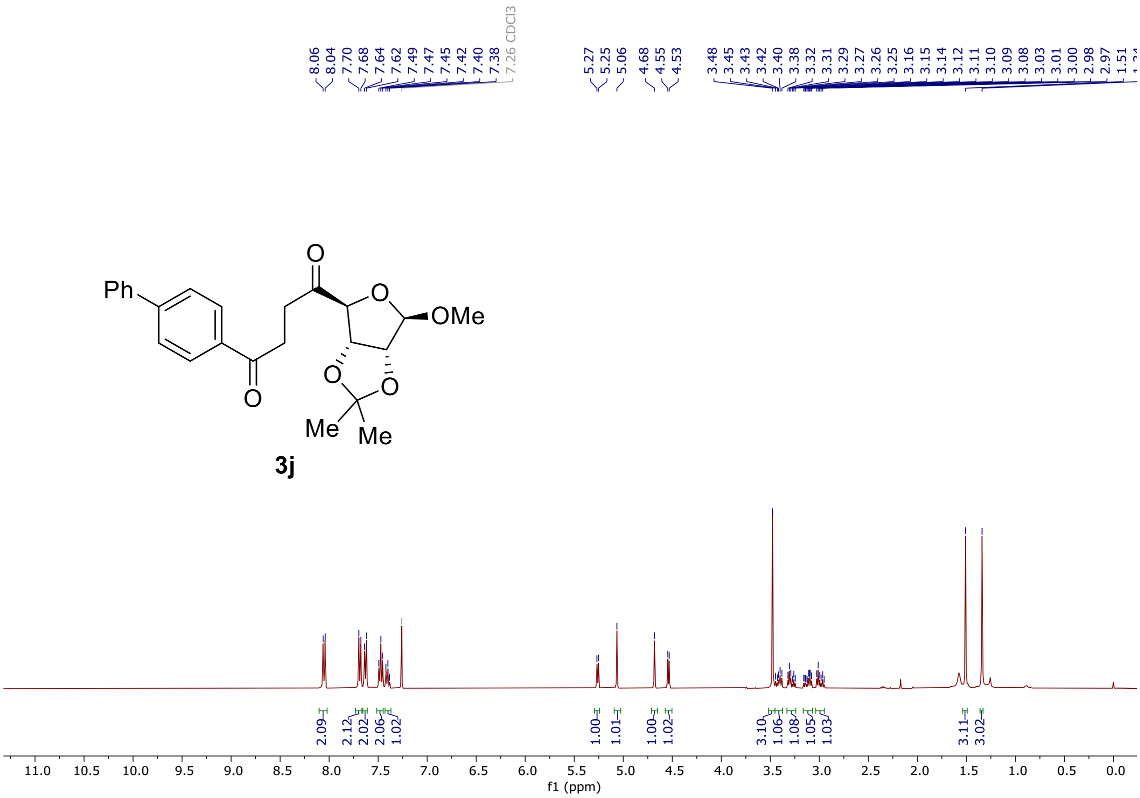
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of compound **3h**.



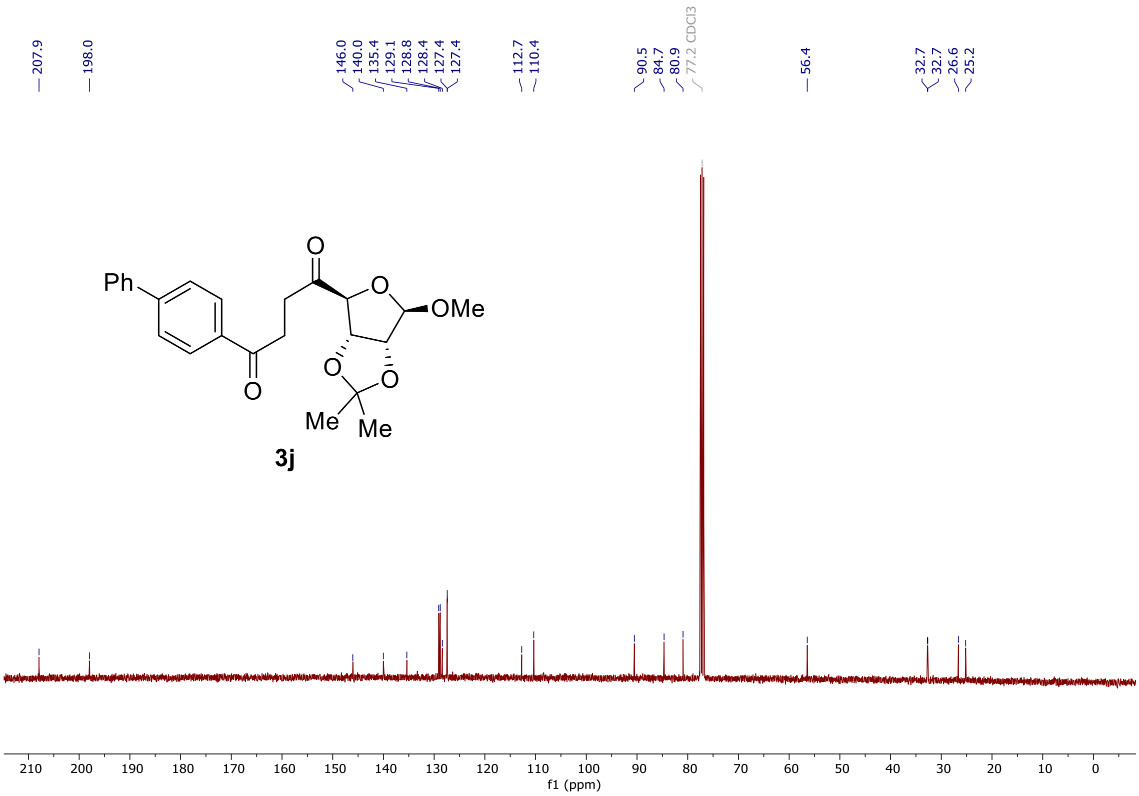
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i**.



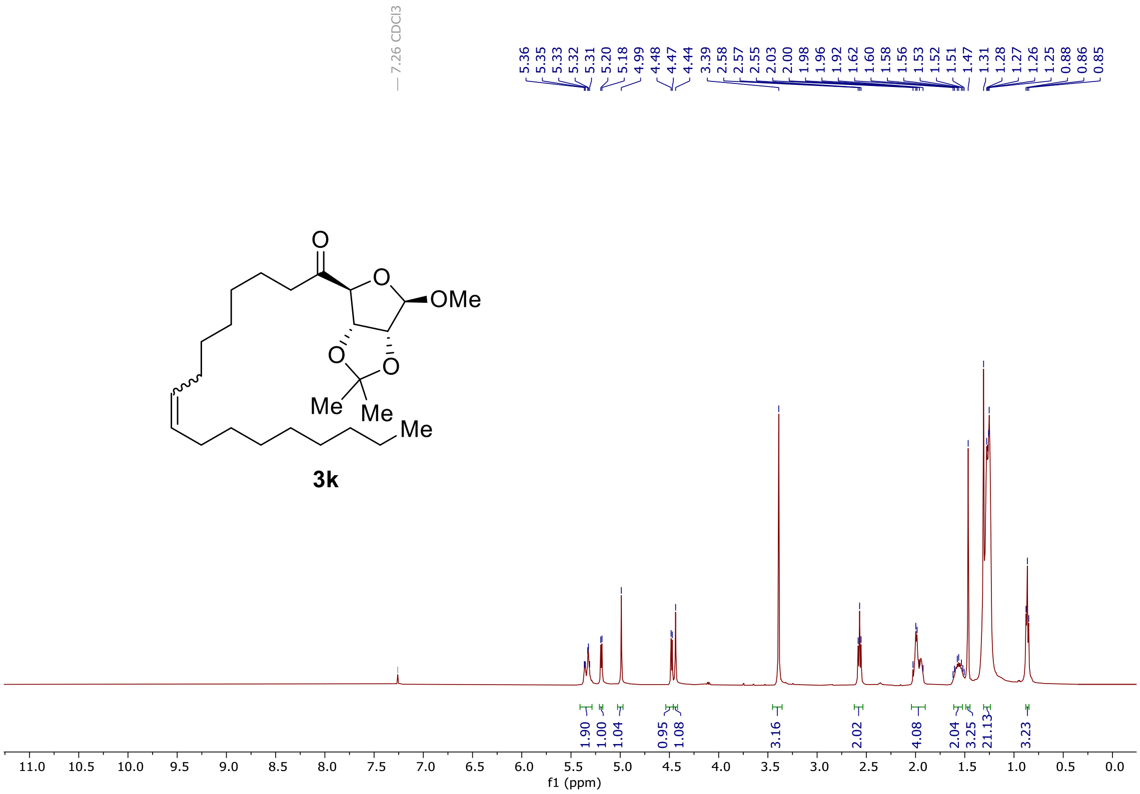
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of compound **3i.**



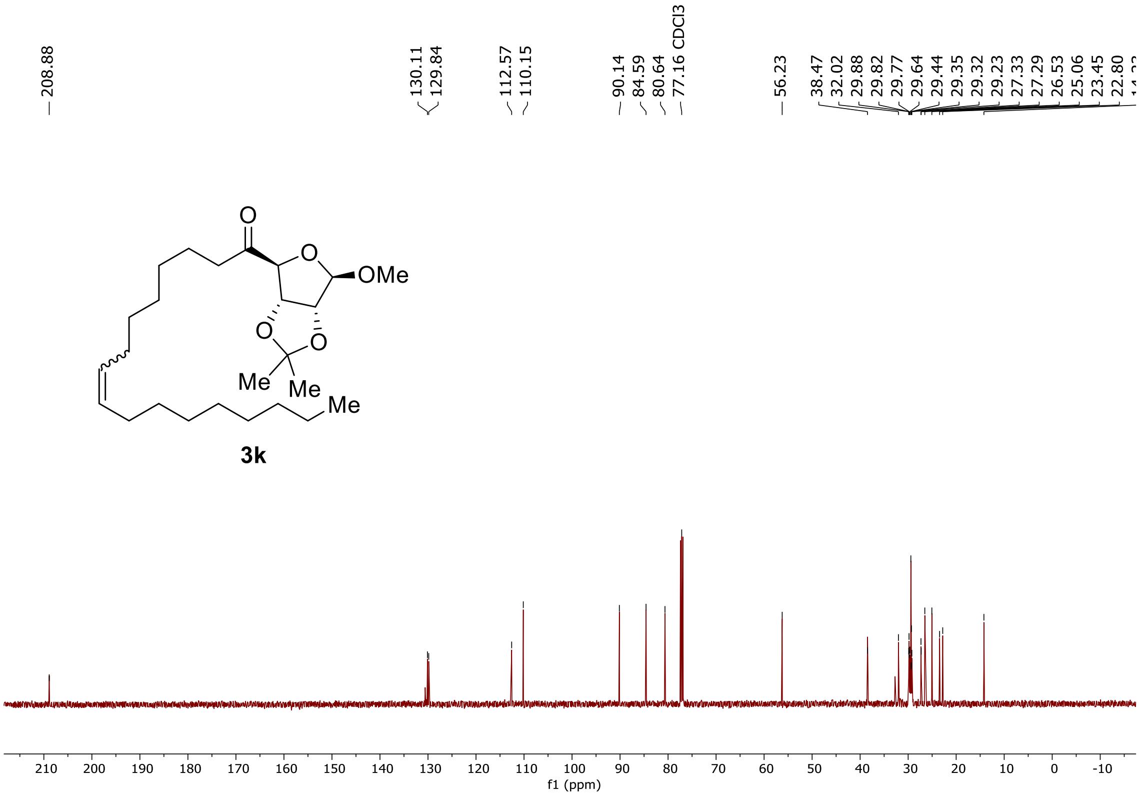
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3j**.



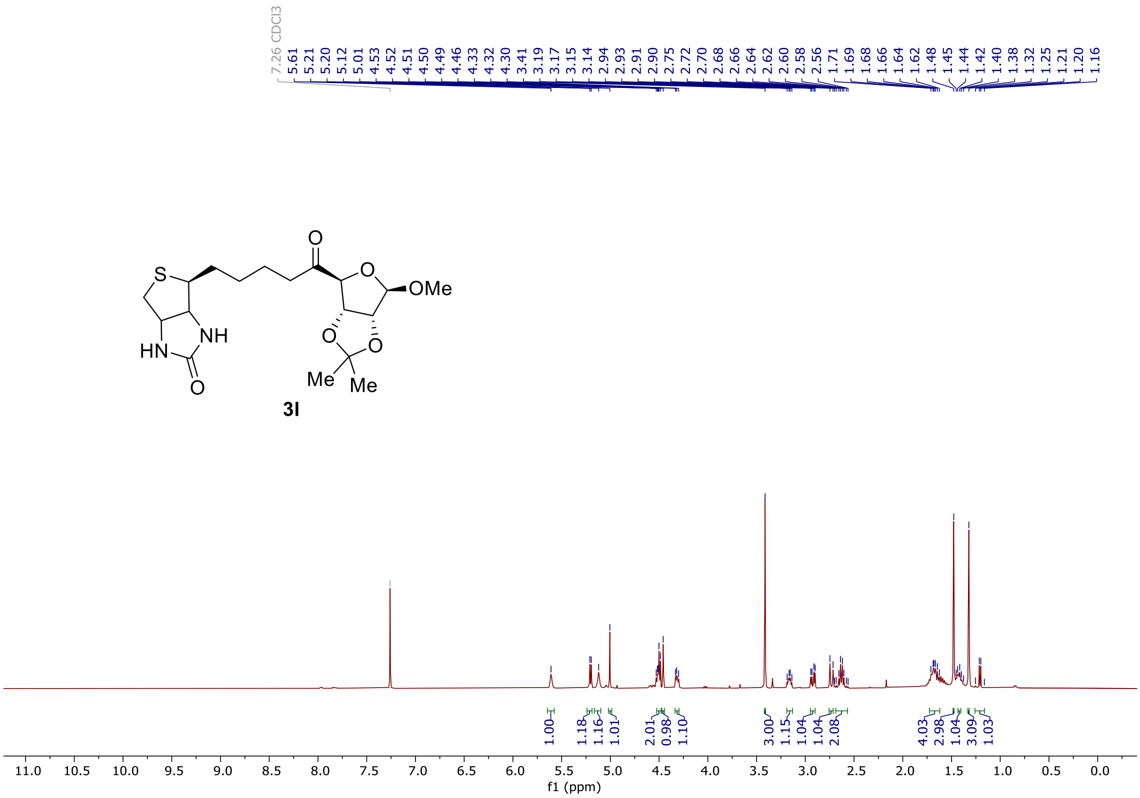
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of compound **3j**.



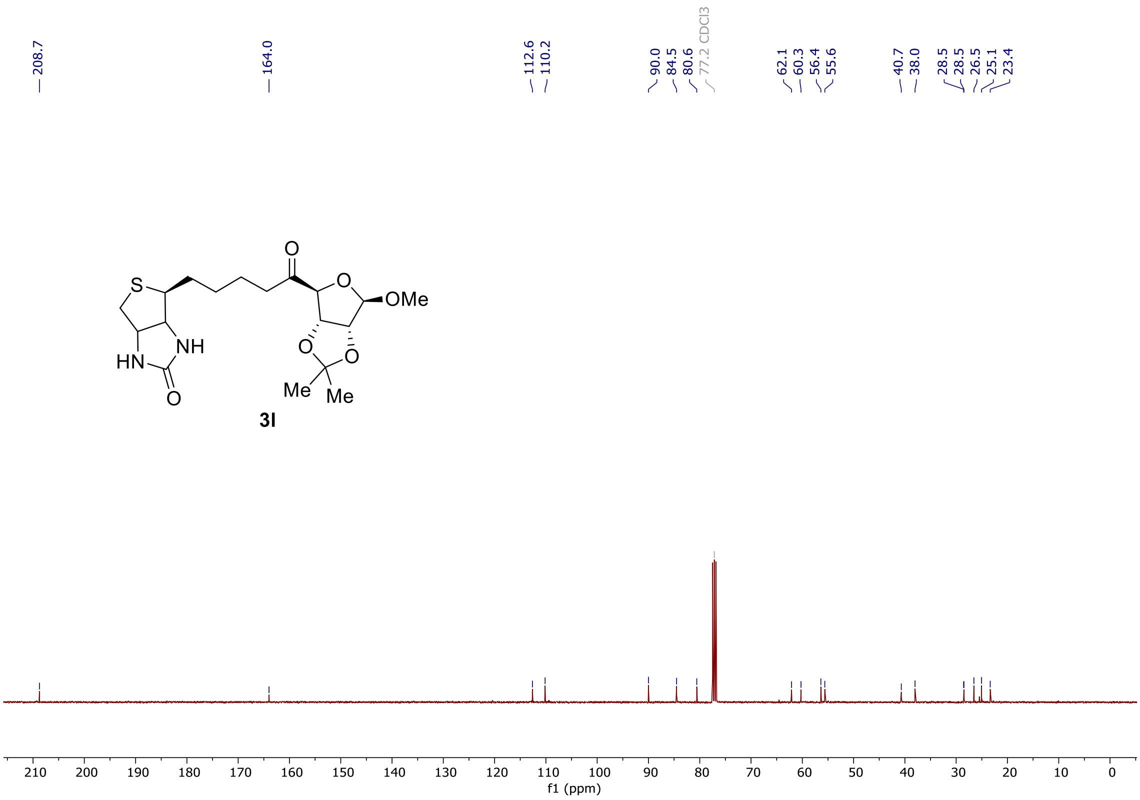
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3k**.



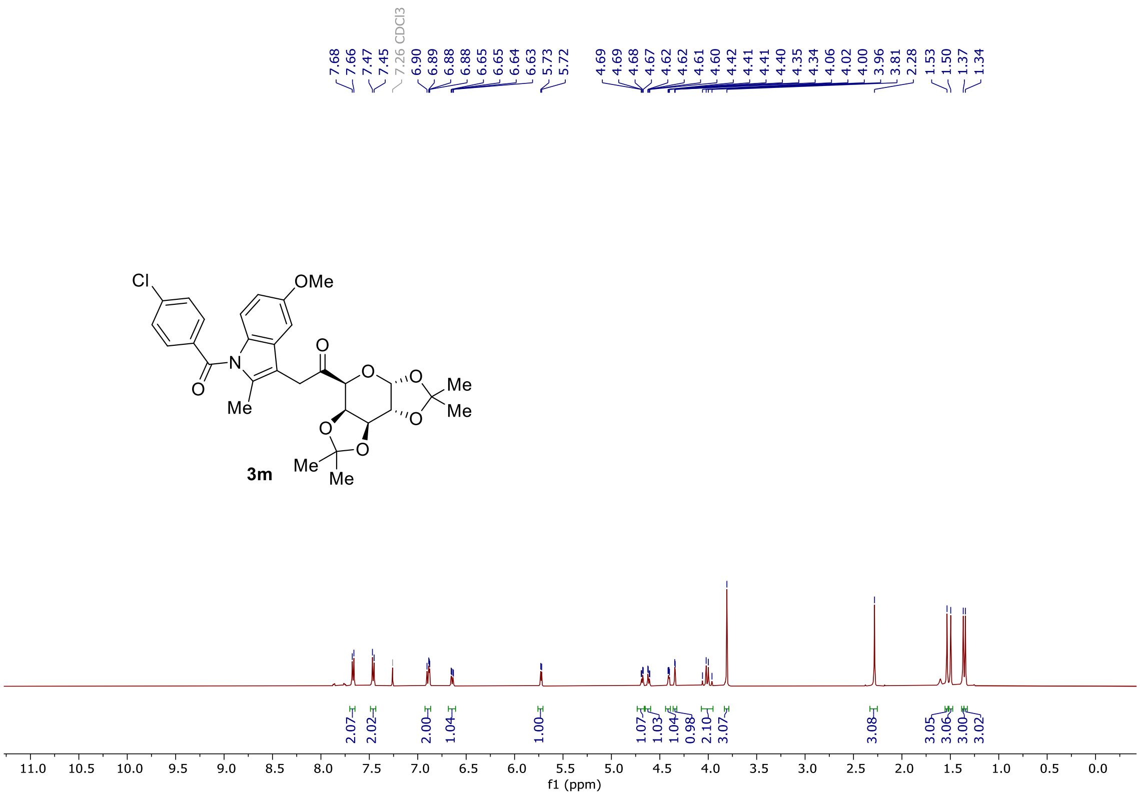
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **3k.**



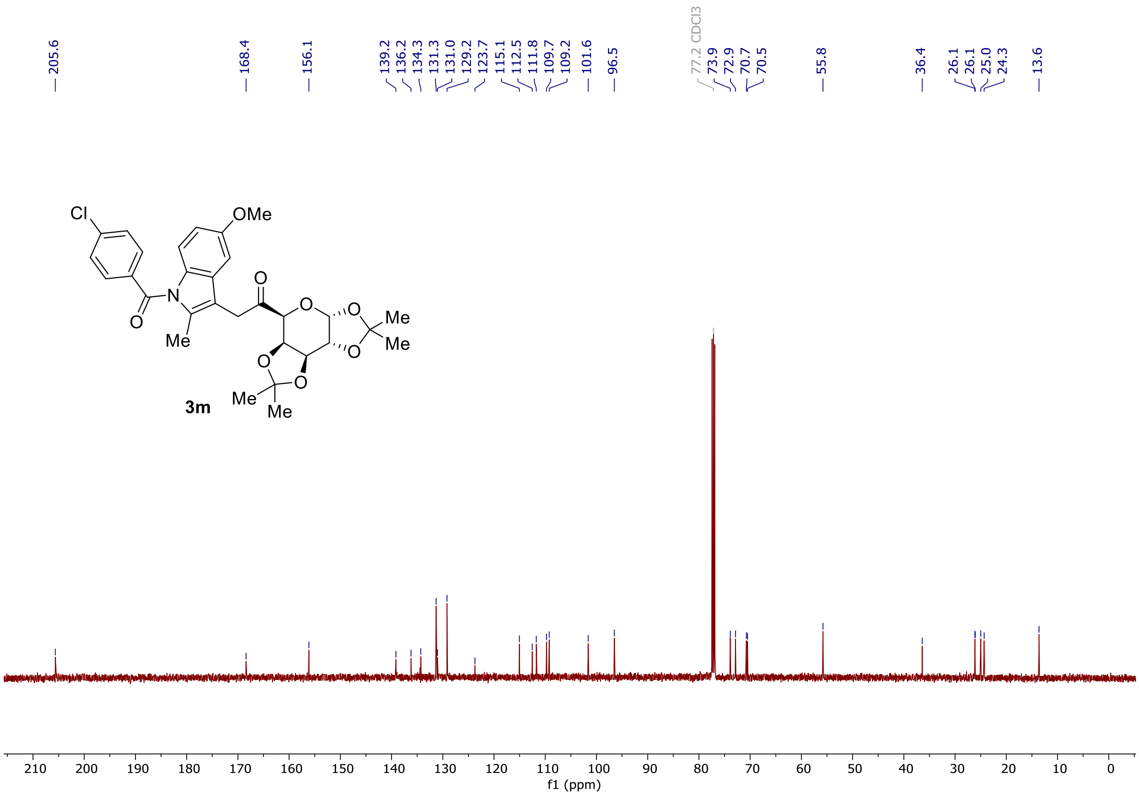
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3l**.



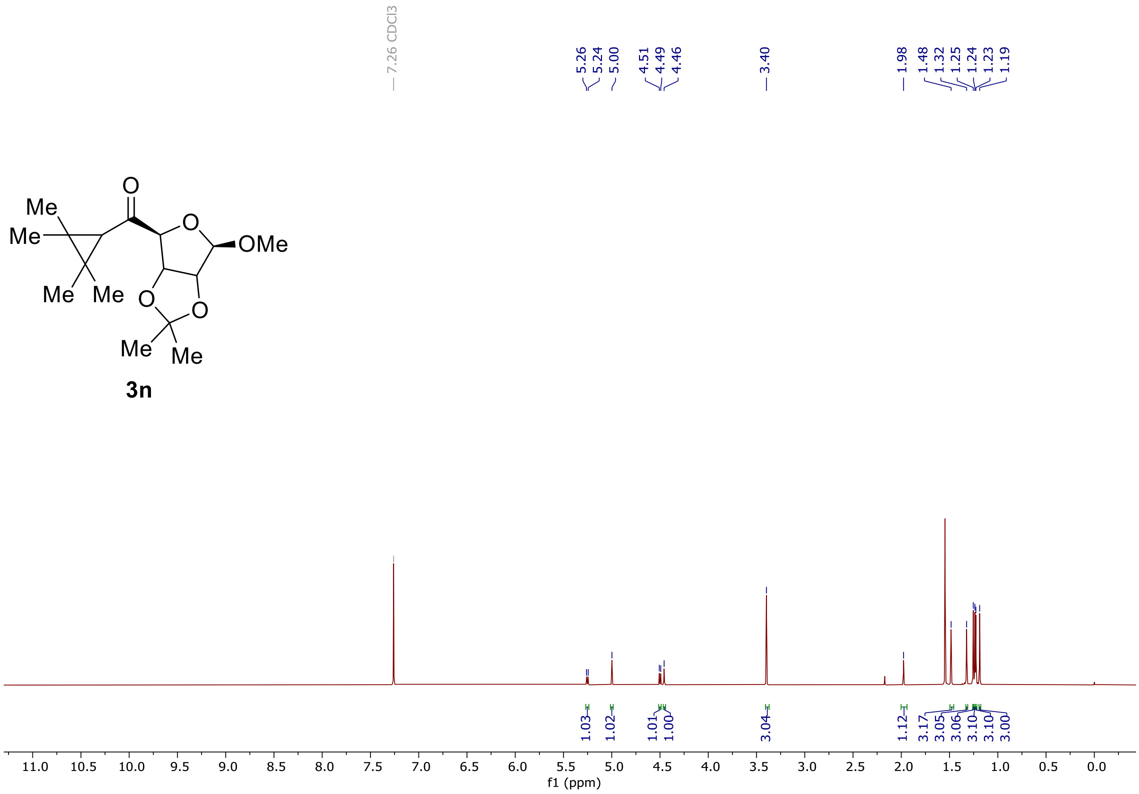
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of compound **3l.**



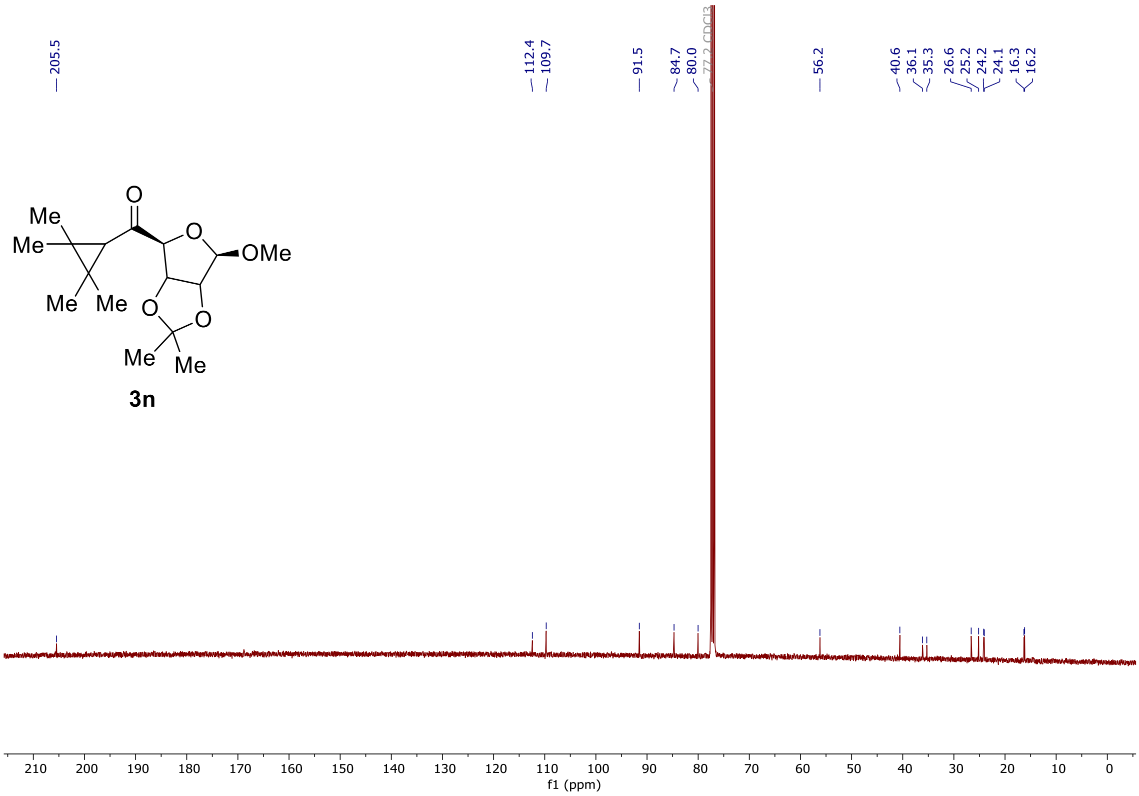
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3m**.



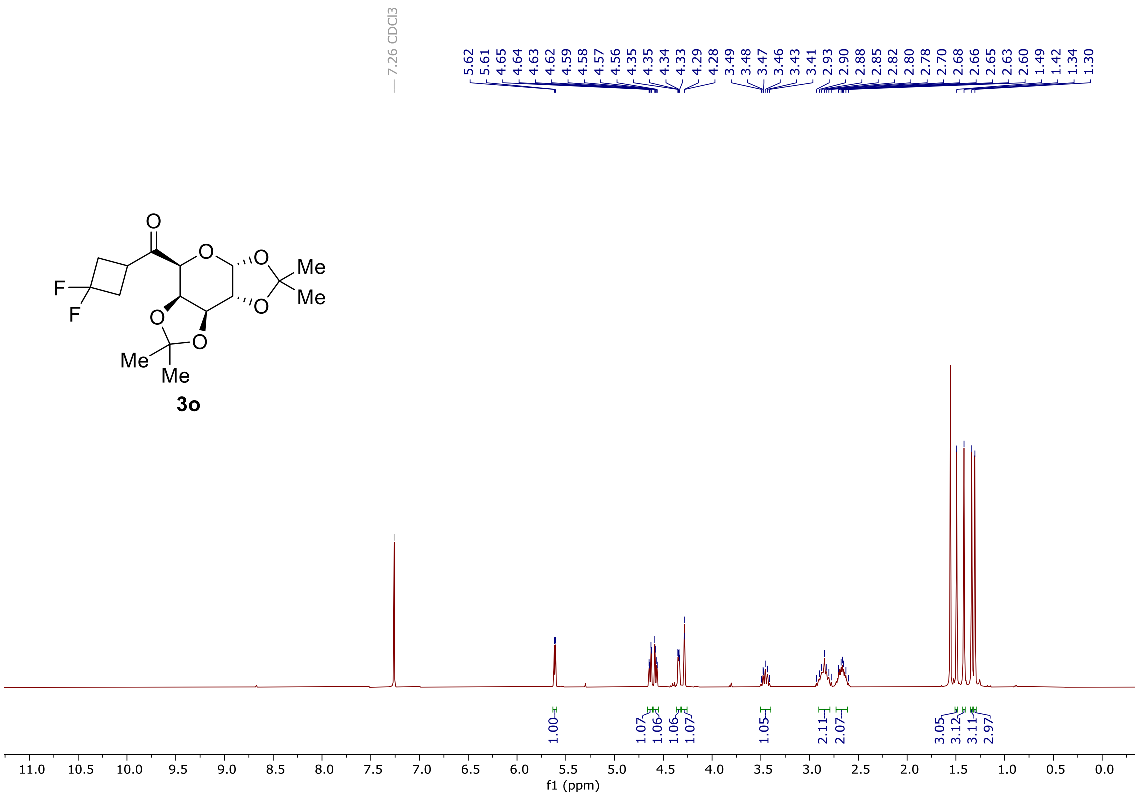
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **3m.**



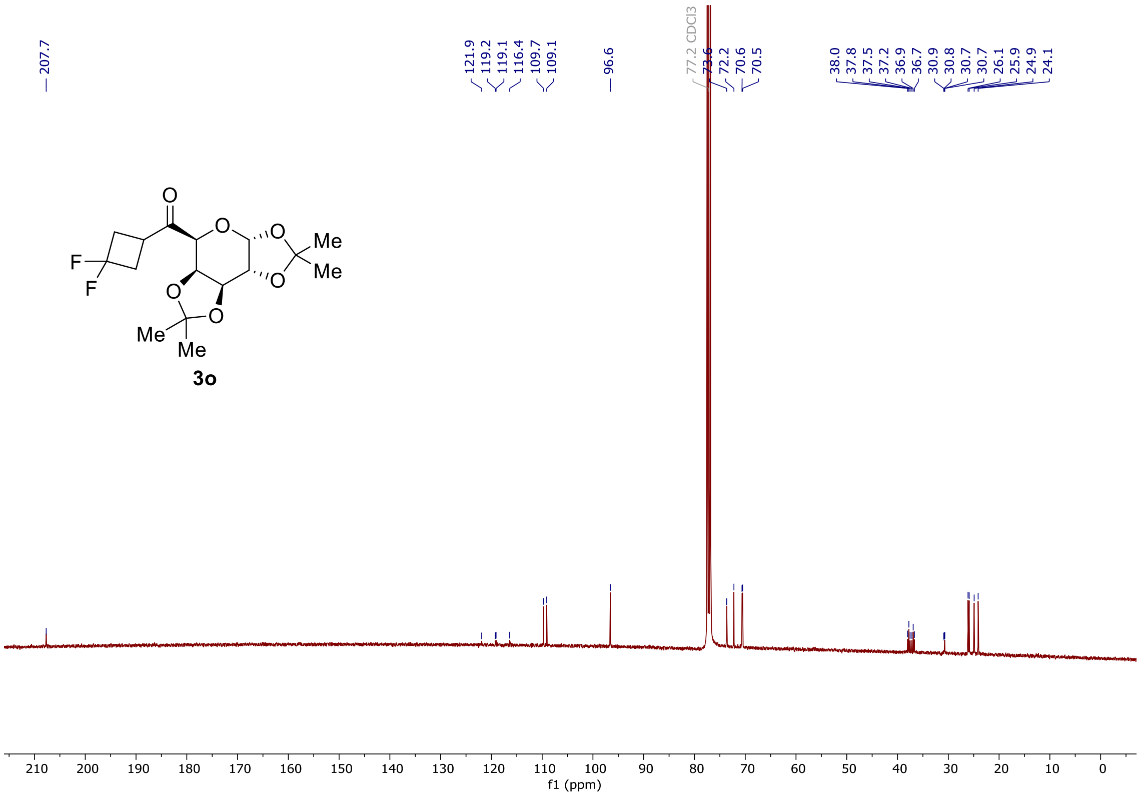
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3n**.



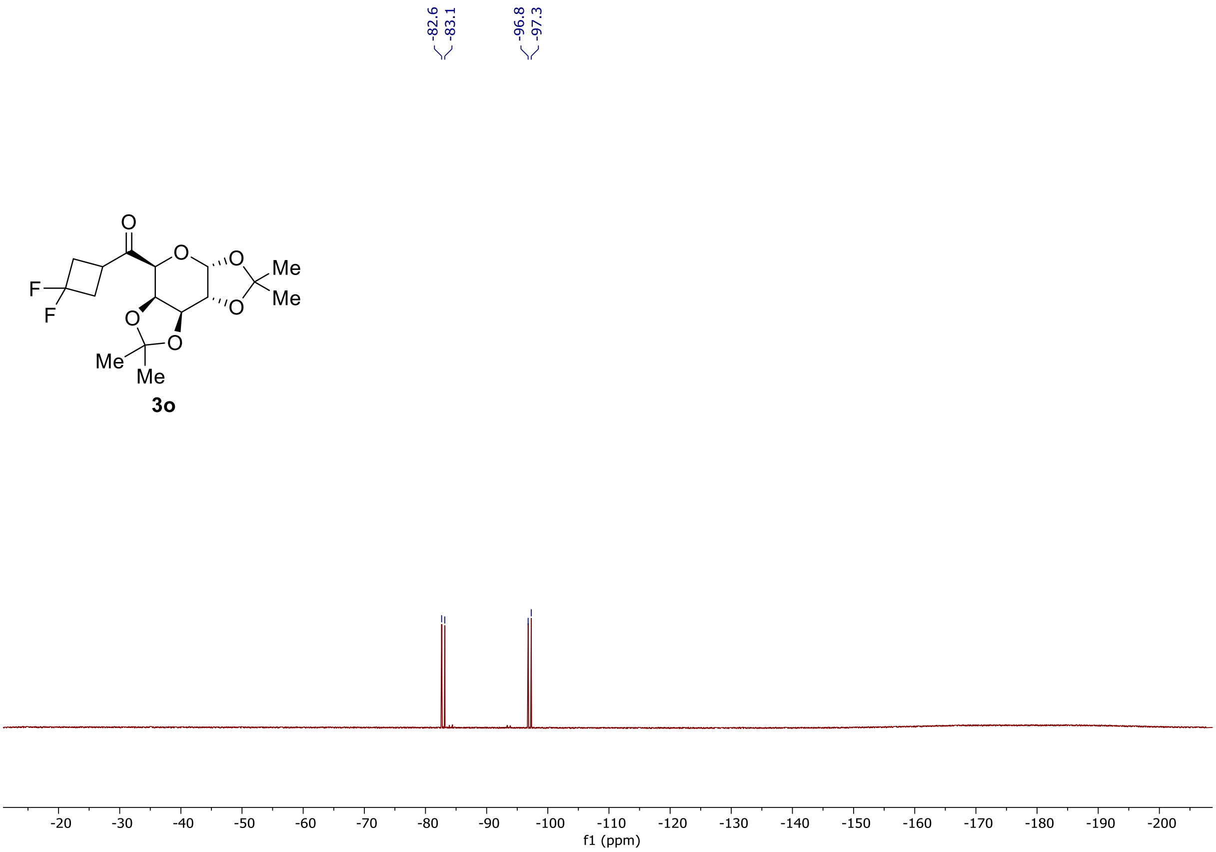
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) of compound **3n.**



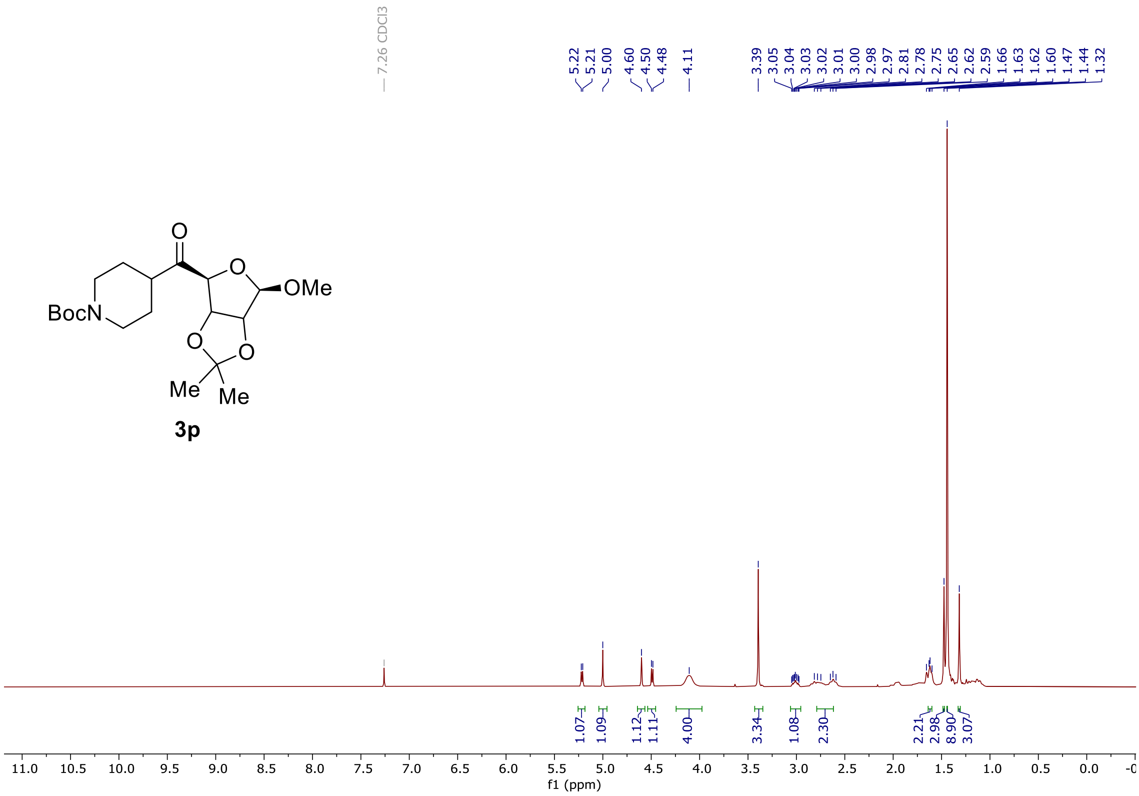
^1H NMR (400 MHz, $CDCl_3$) of compound **3o**.



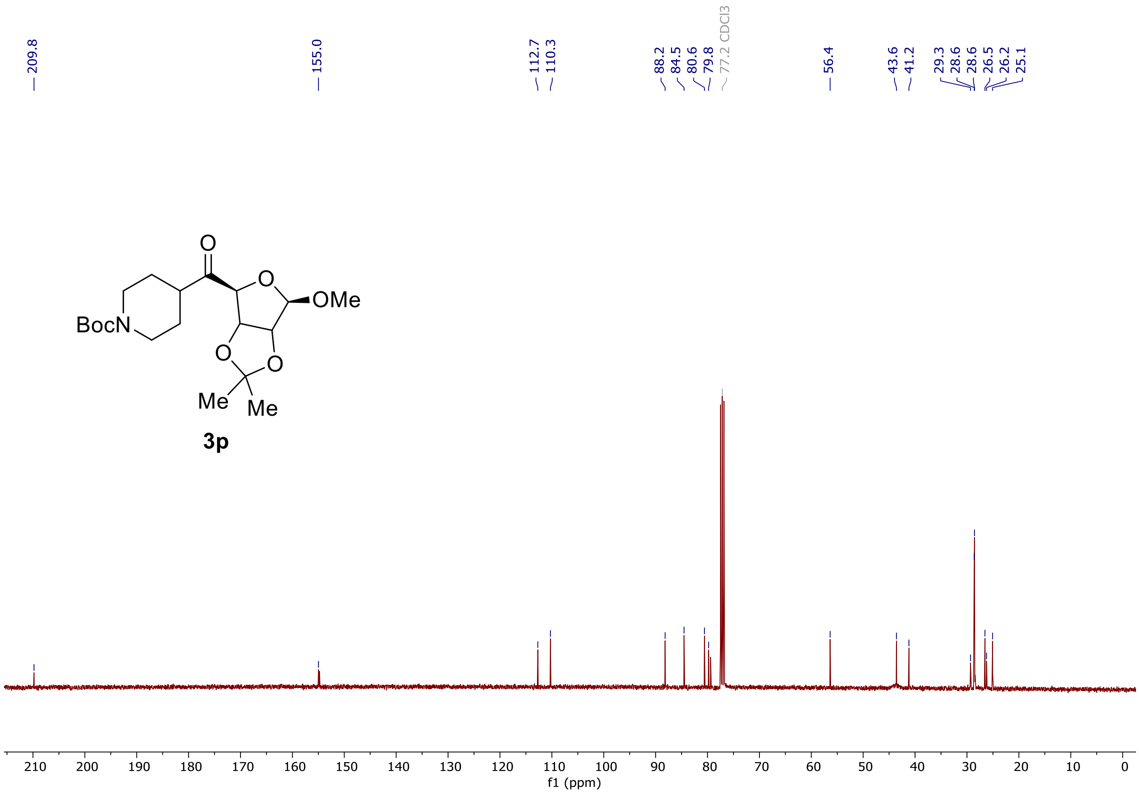
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of compound **3o.**



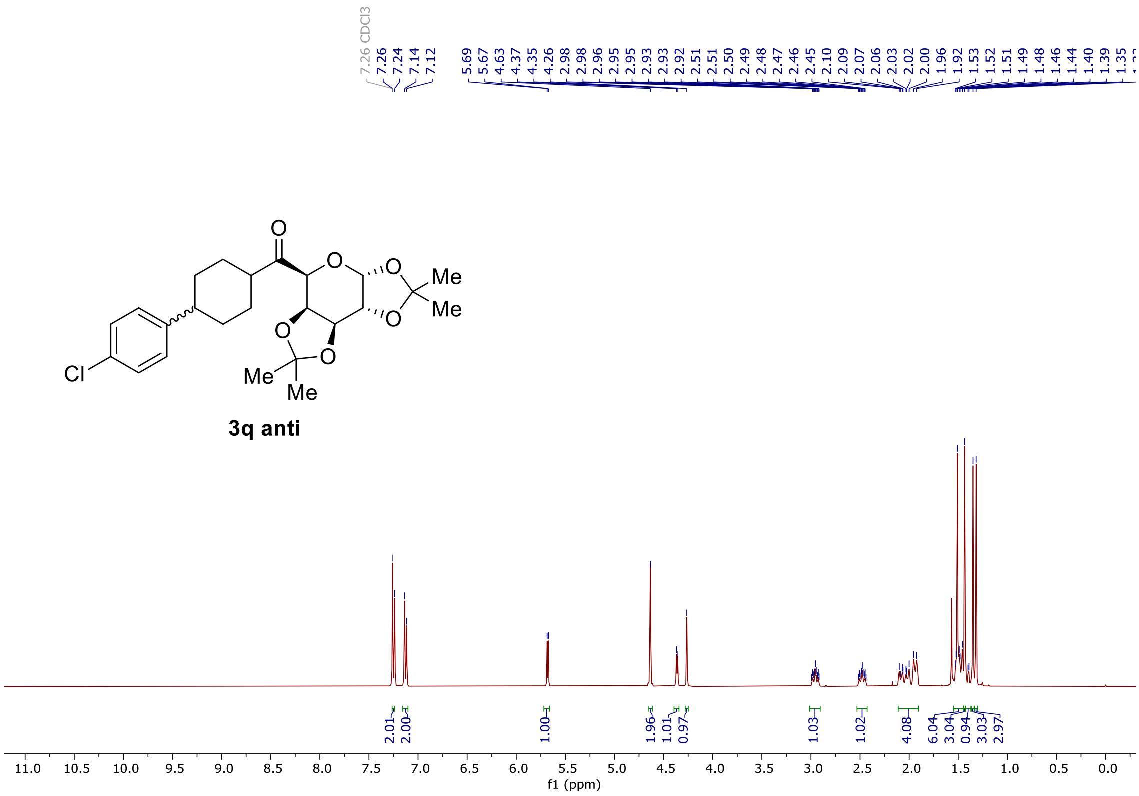
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of compound **3o**.



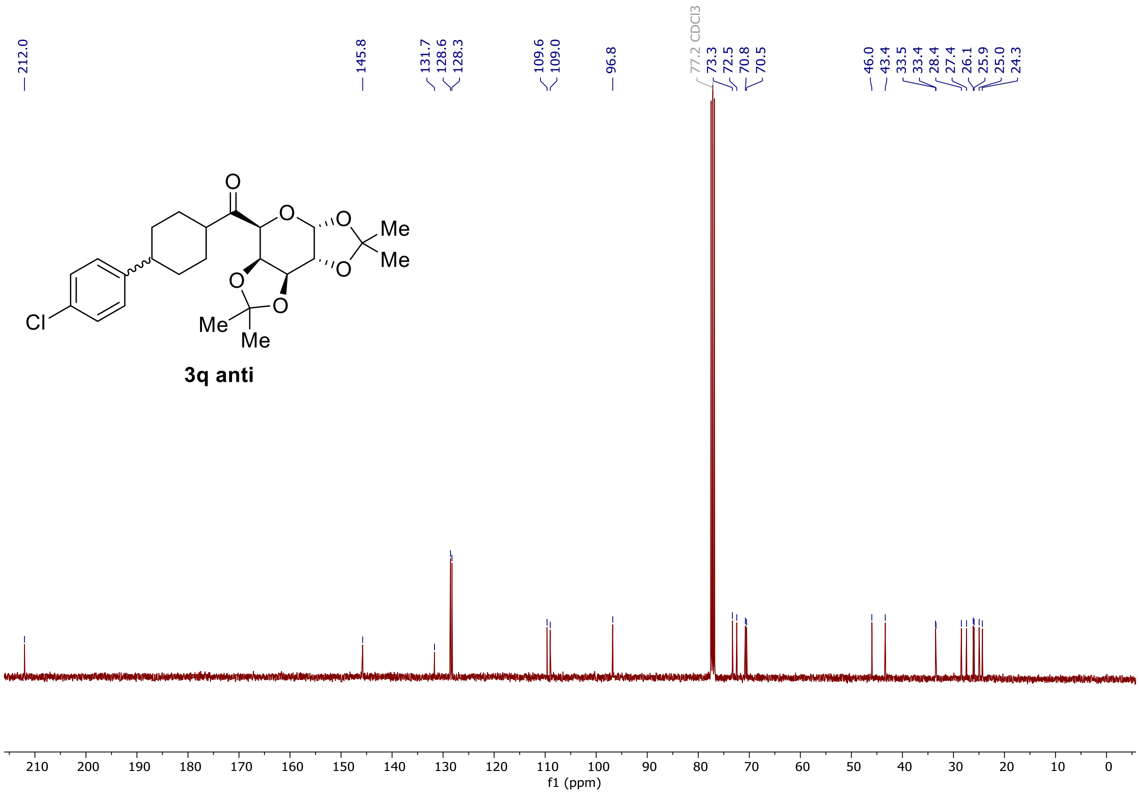
[1]H NMR (400 MHz, $CDCl_3$) of compound **3p**.



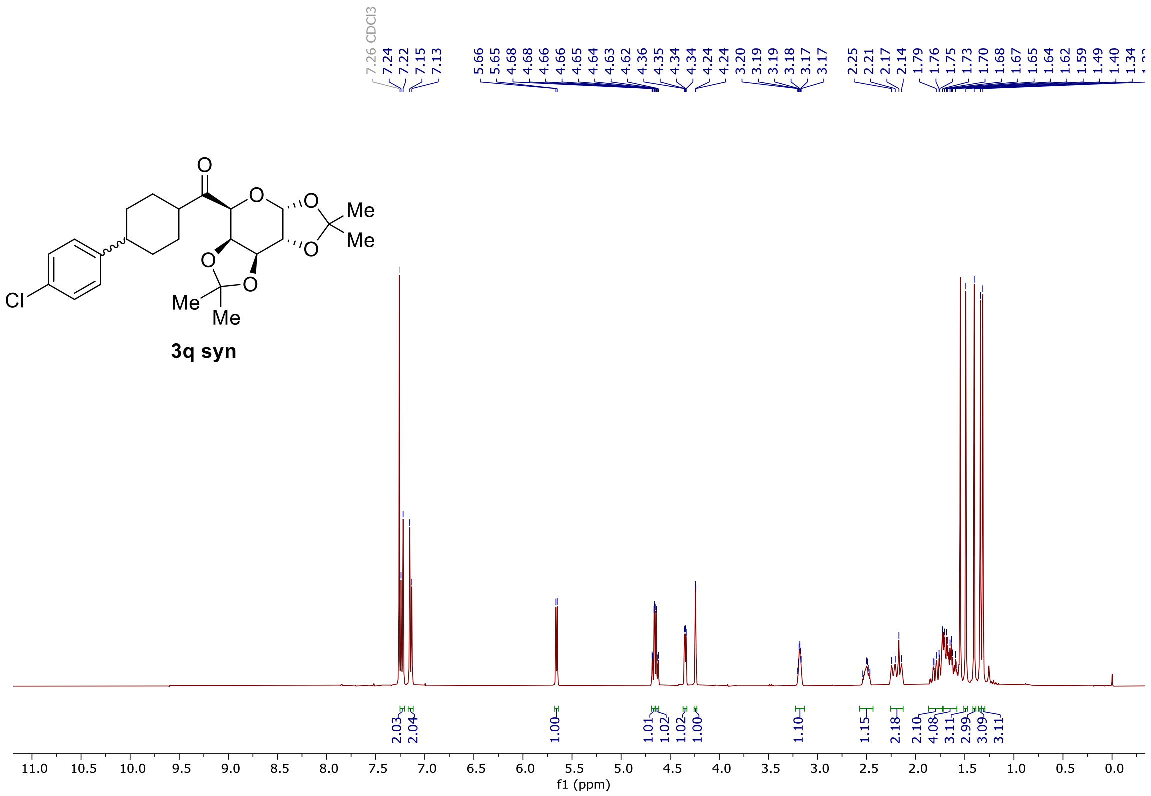
[13]C{[1]H} NMR (101 MHz, $CDCl_3$) of compound **3p.**



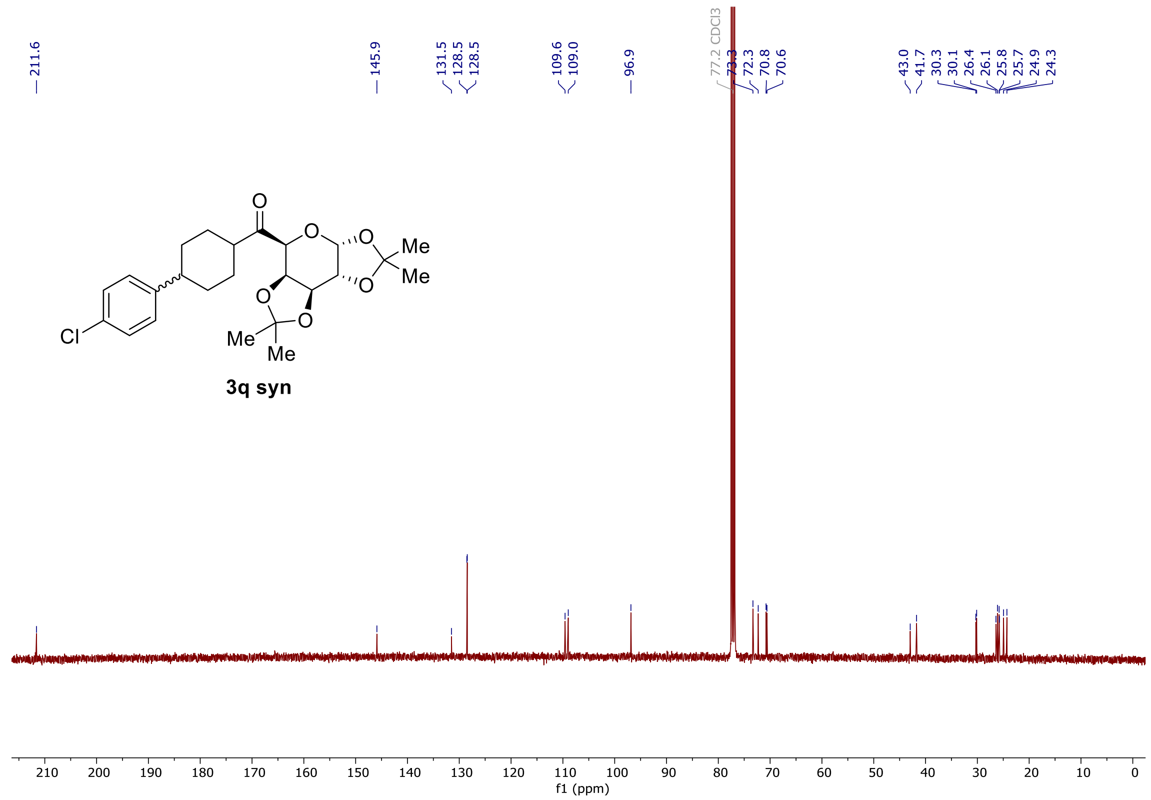
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3q anti**.



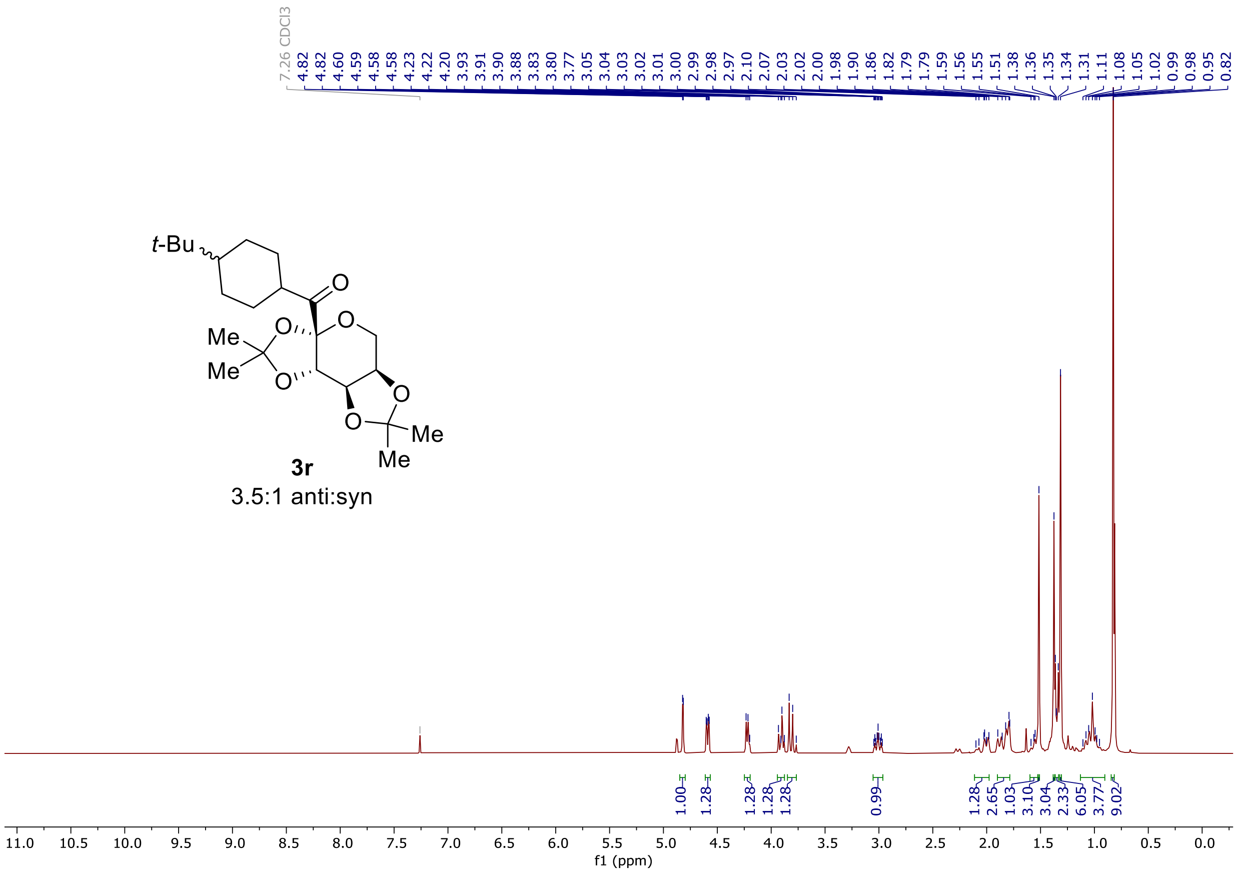
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of compound **3q anti.**



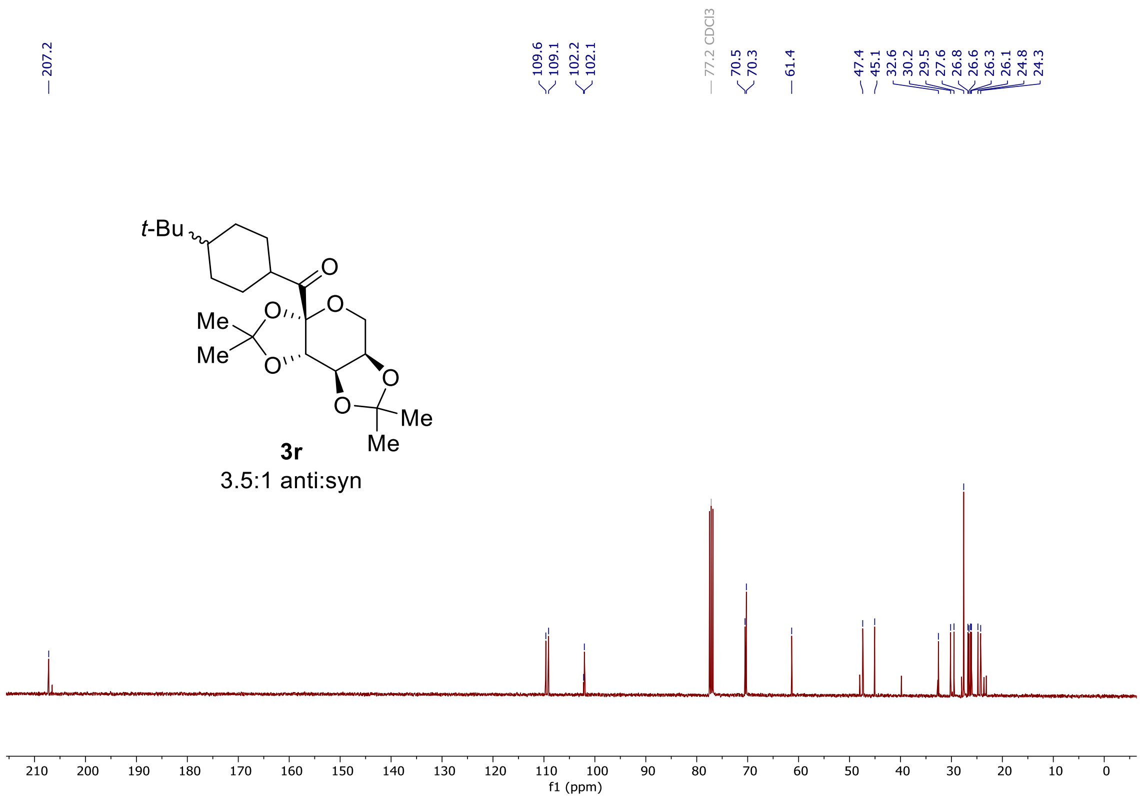
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3q syn**.



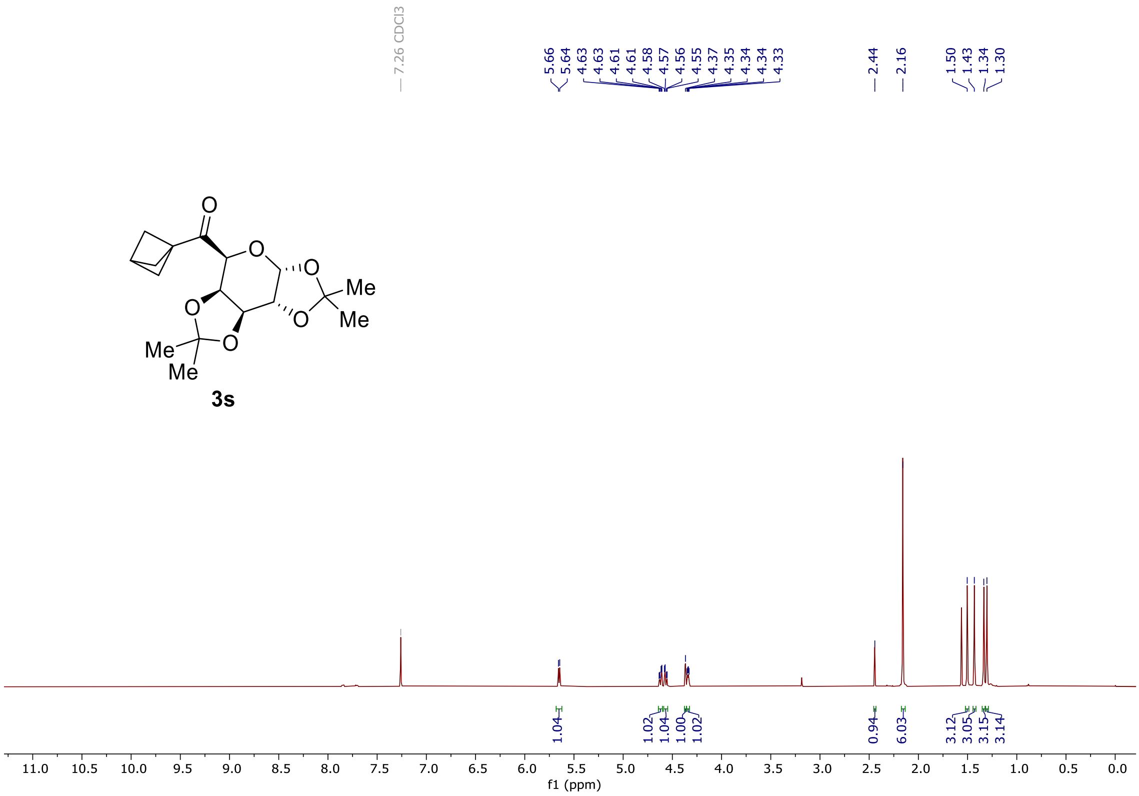
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) of compound **3q syn.**



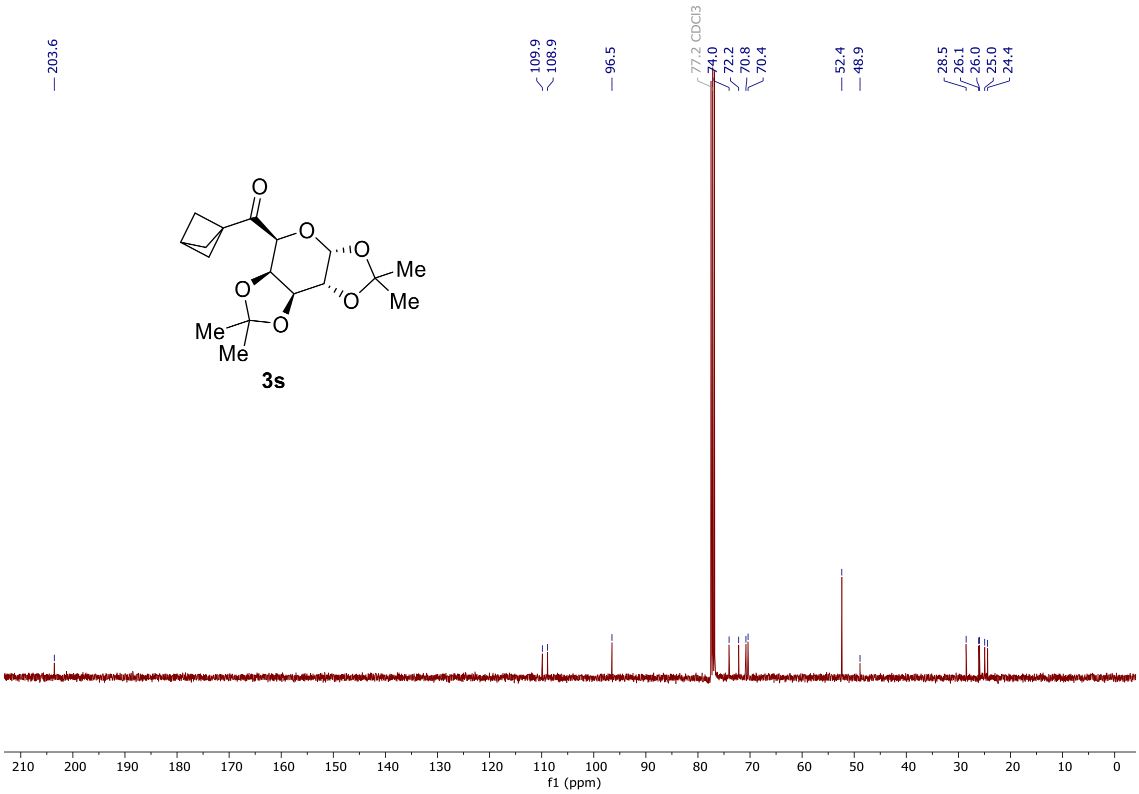
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3r**.



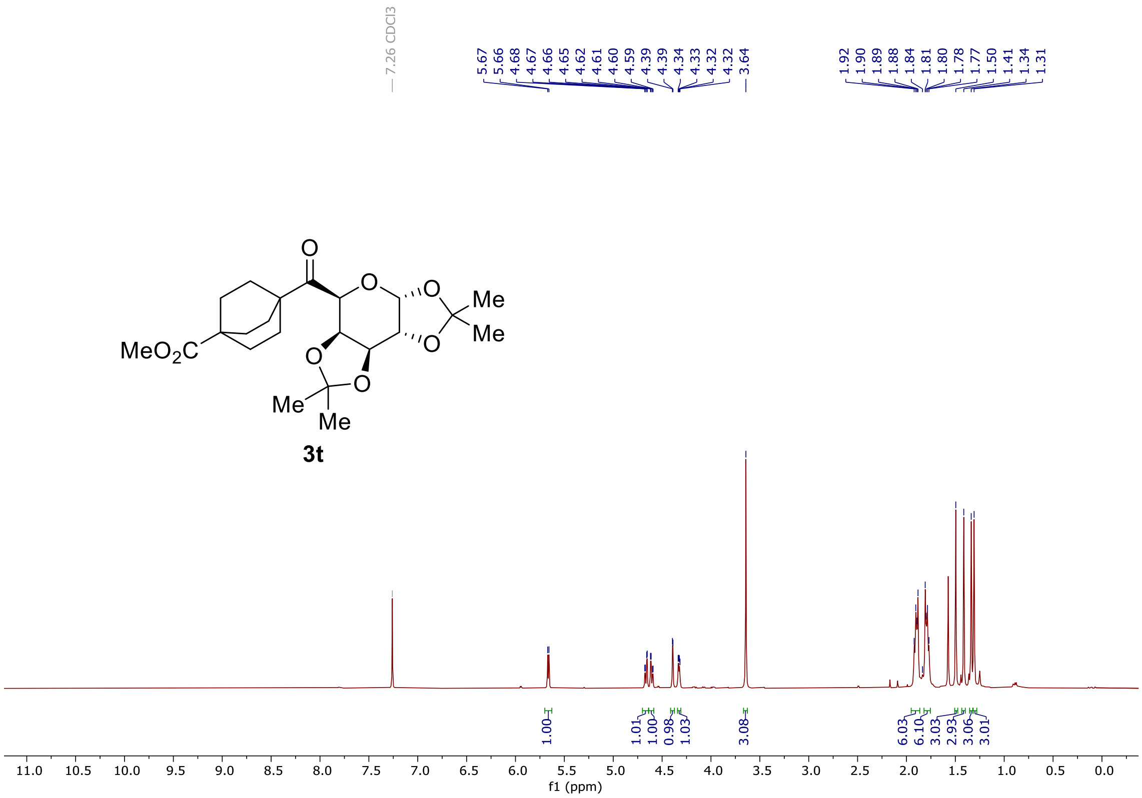
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of compound **3r.**



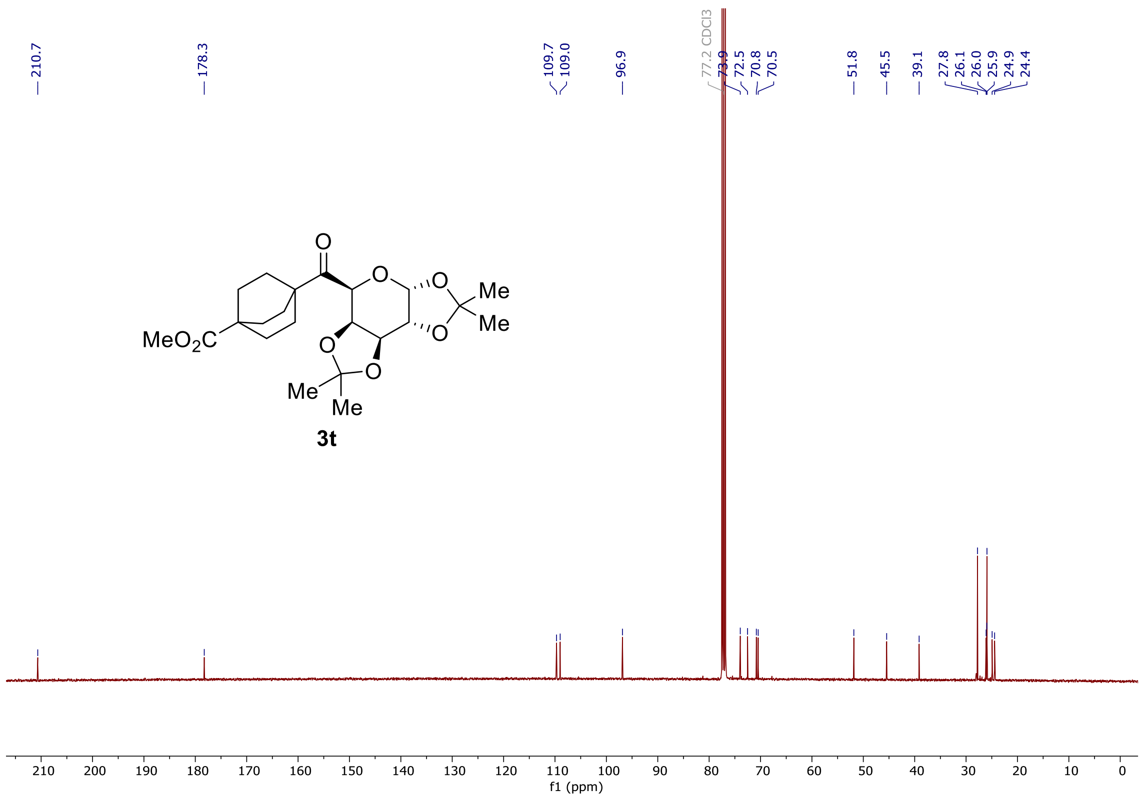
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3s**.



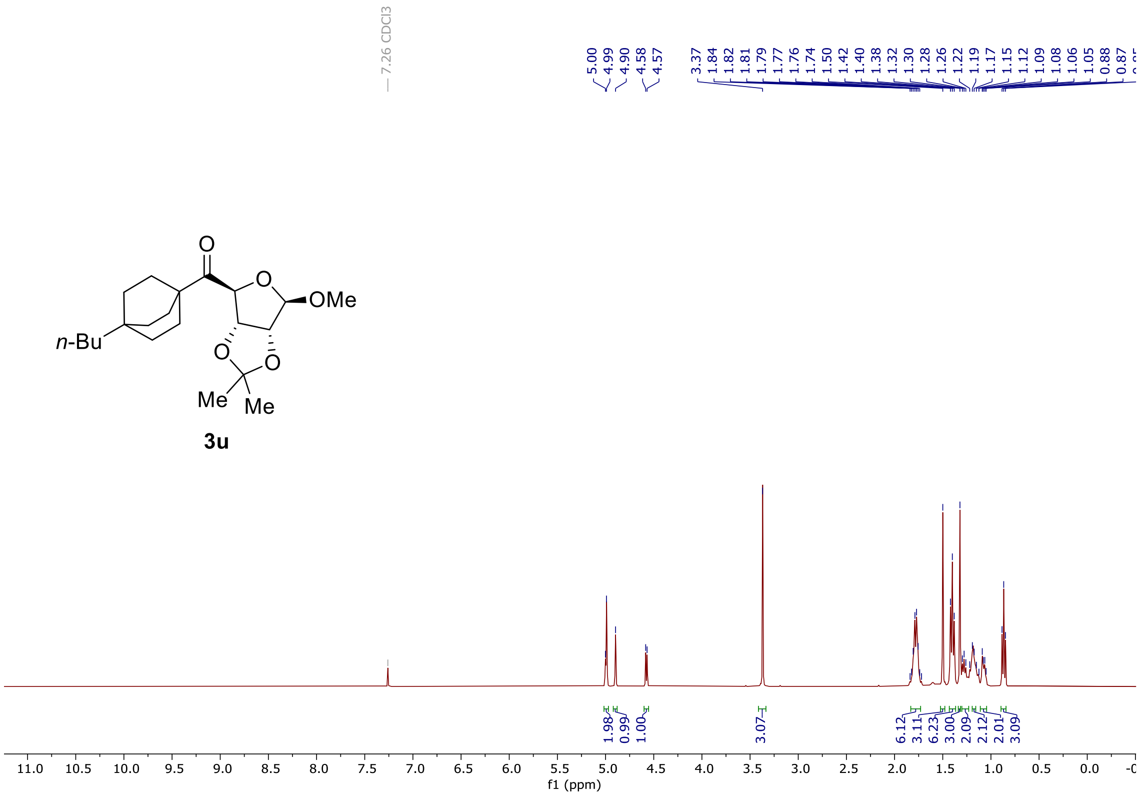
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of compound **3s.**



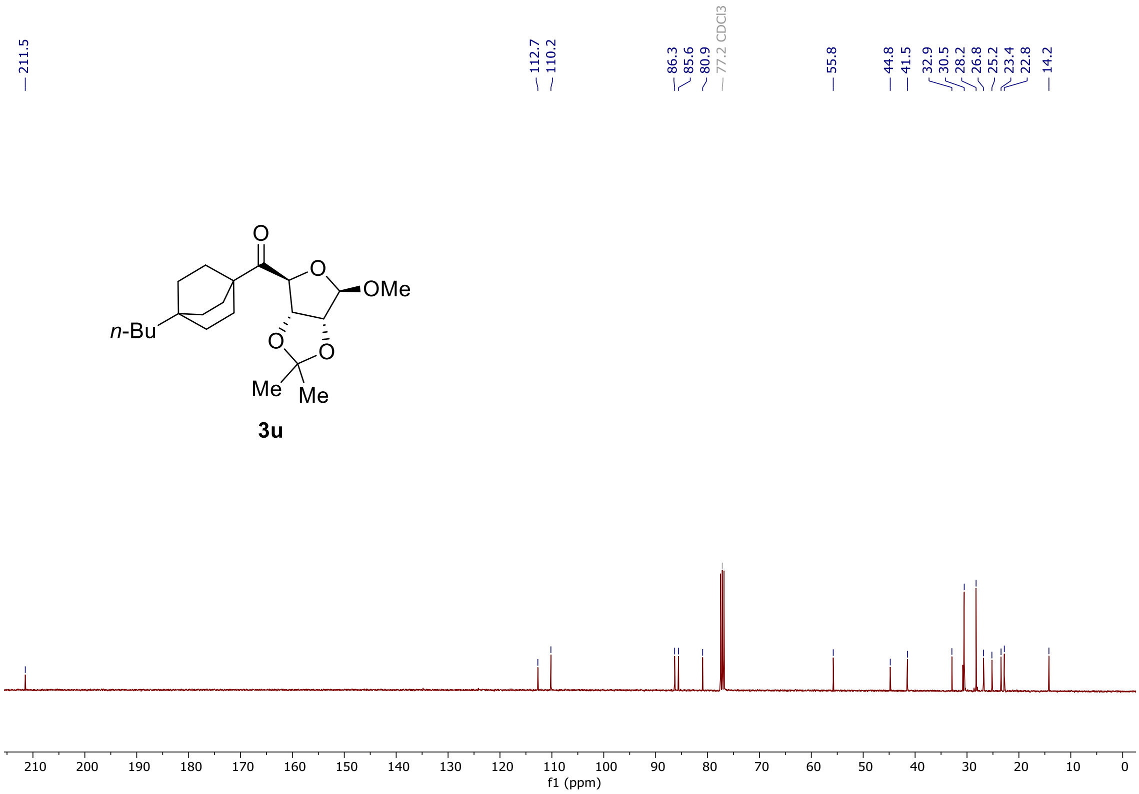
[1]H NMR (400 MHz, $CDCl_3$) of compound **3t**.



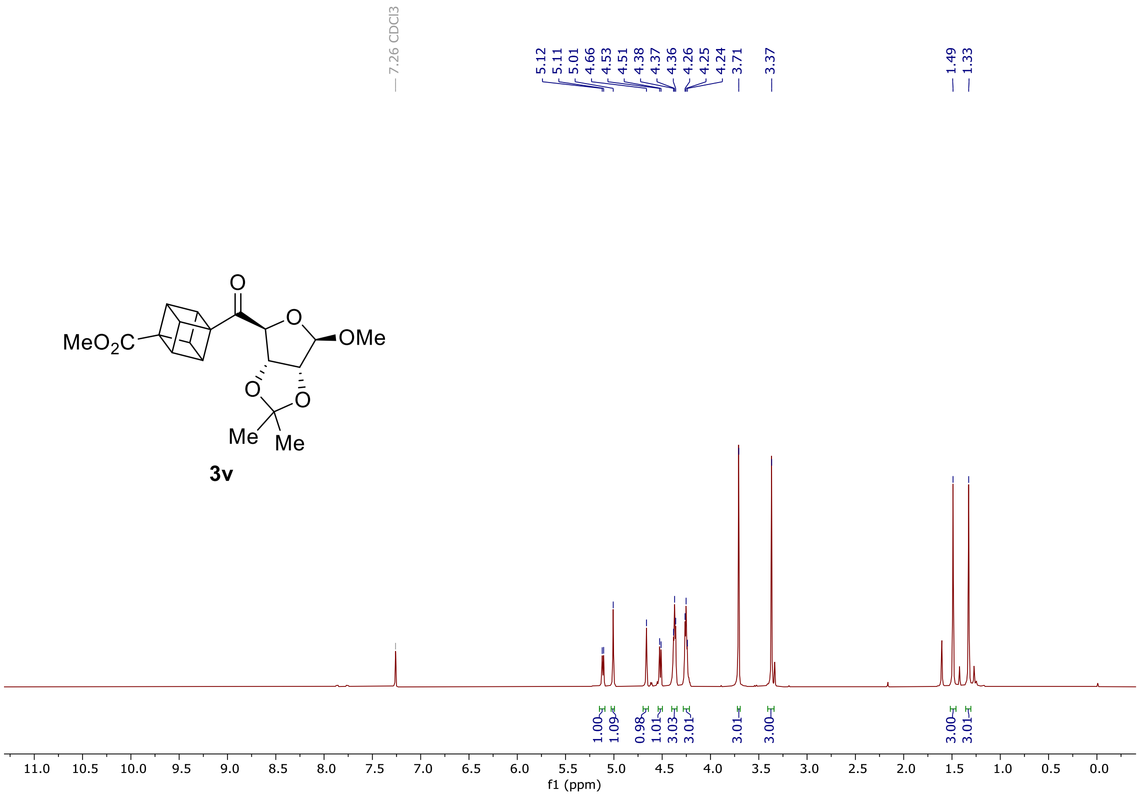
[13]C{[1]H} NMR (101 MHz, $CDCl_3$) of compound **3t.**



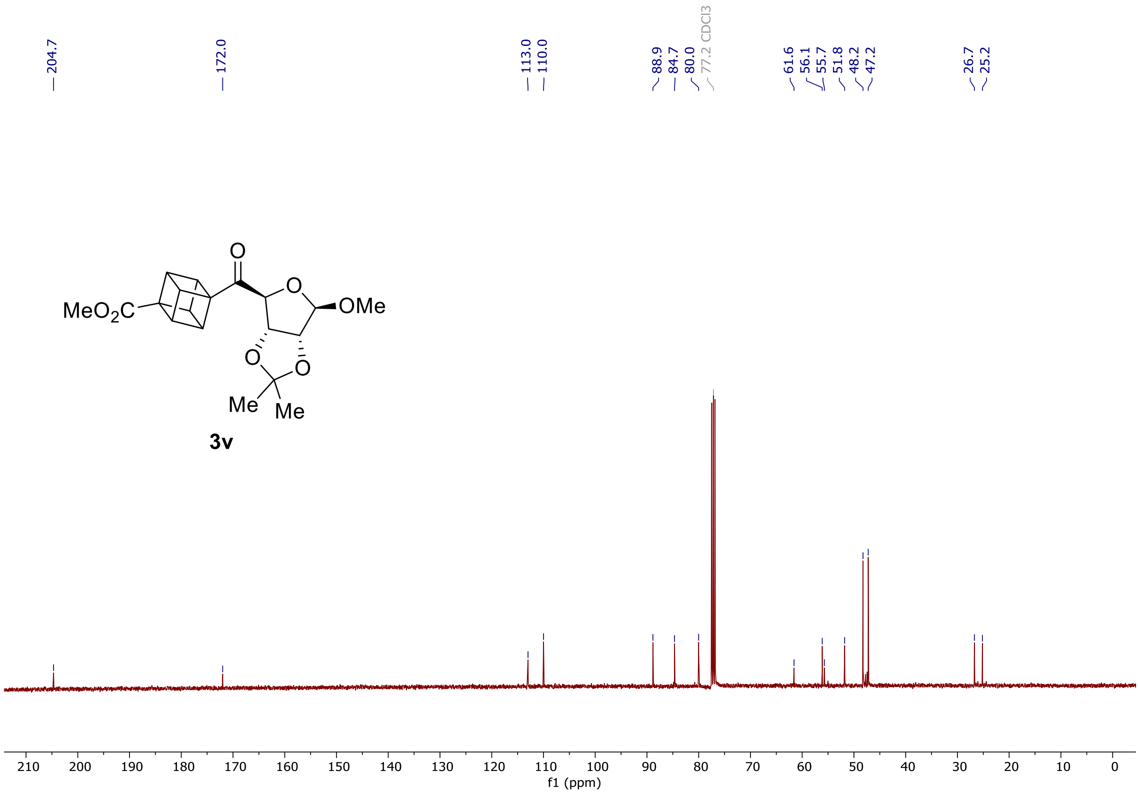
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3u**.



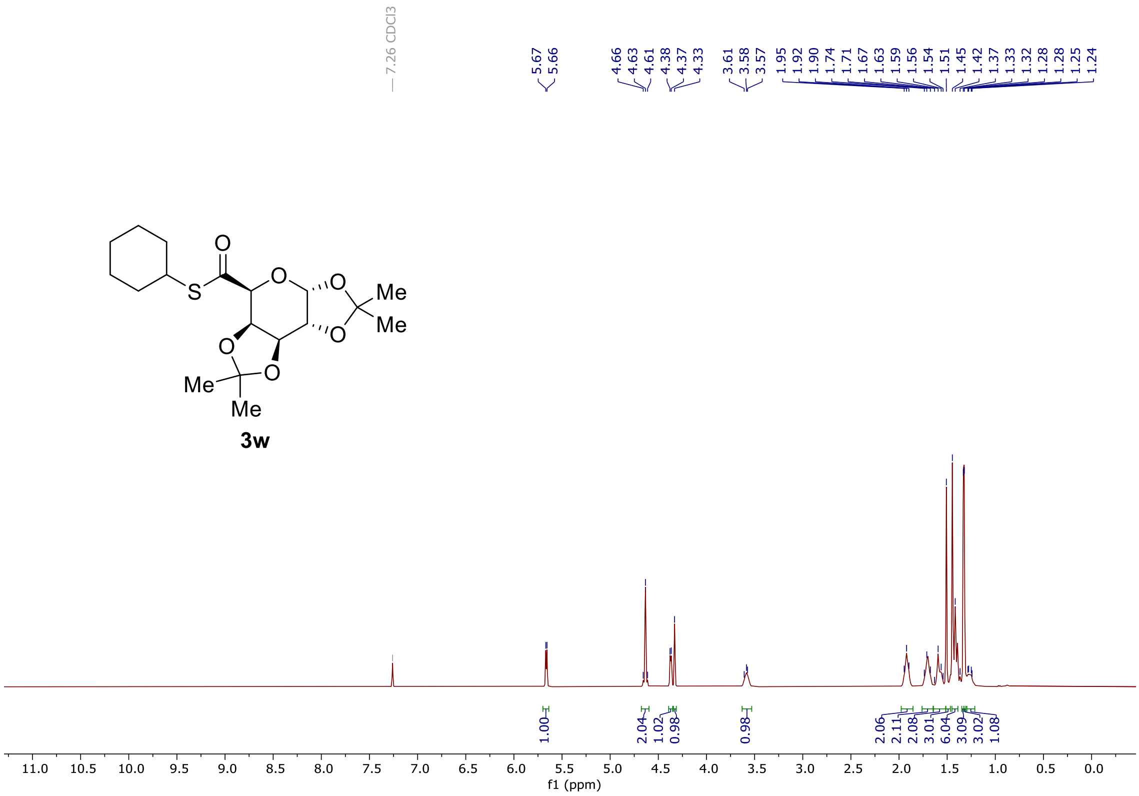
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of compound **3u.**



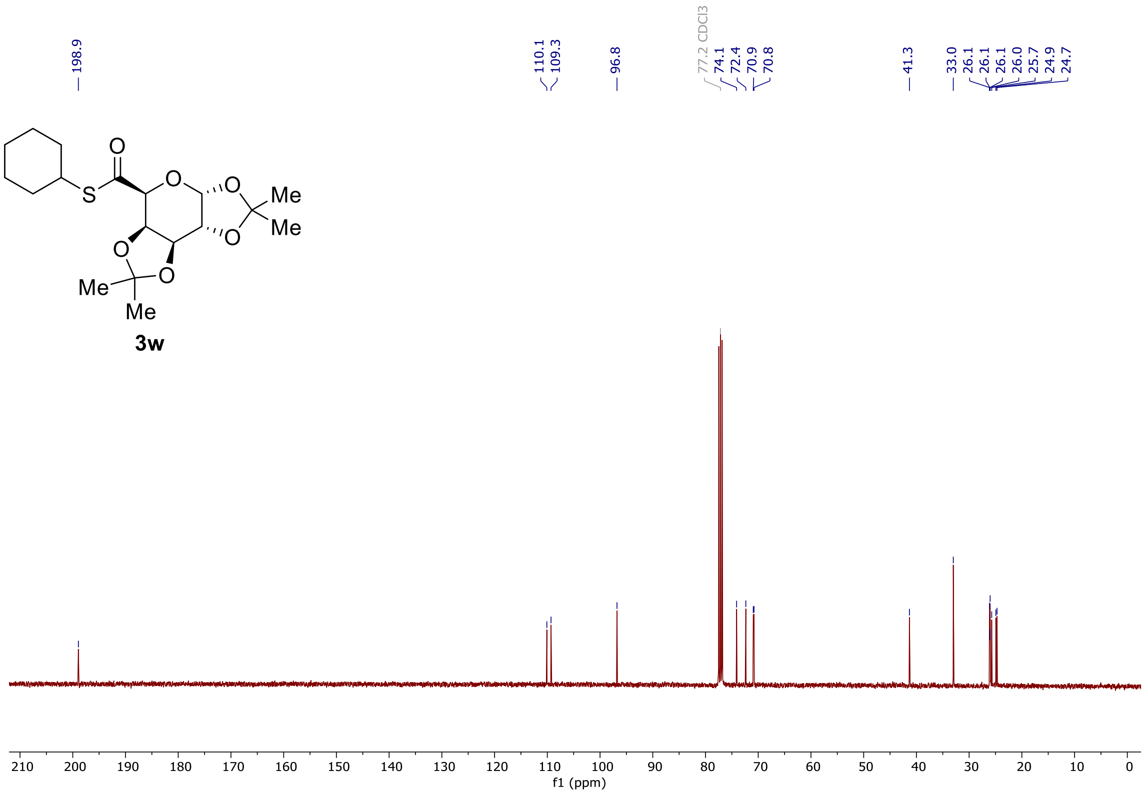
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3v**.



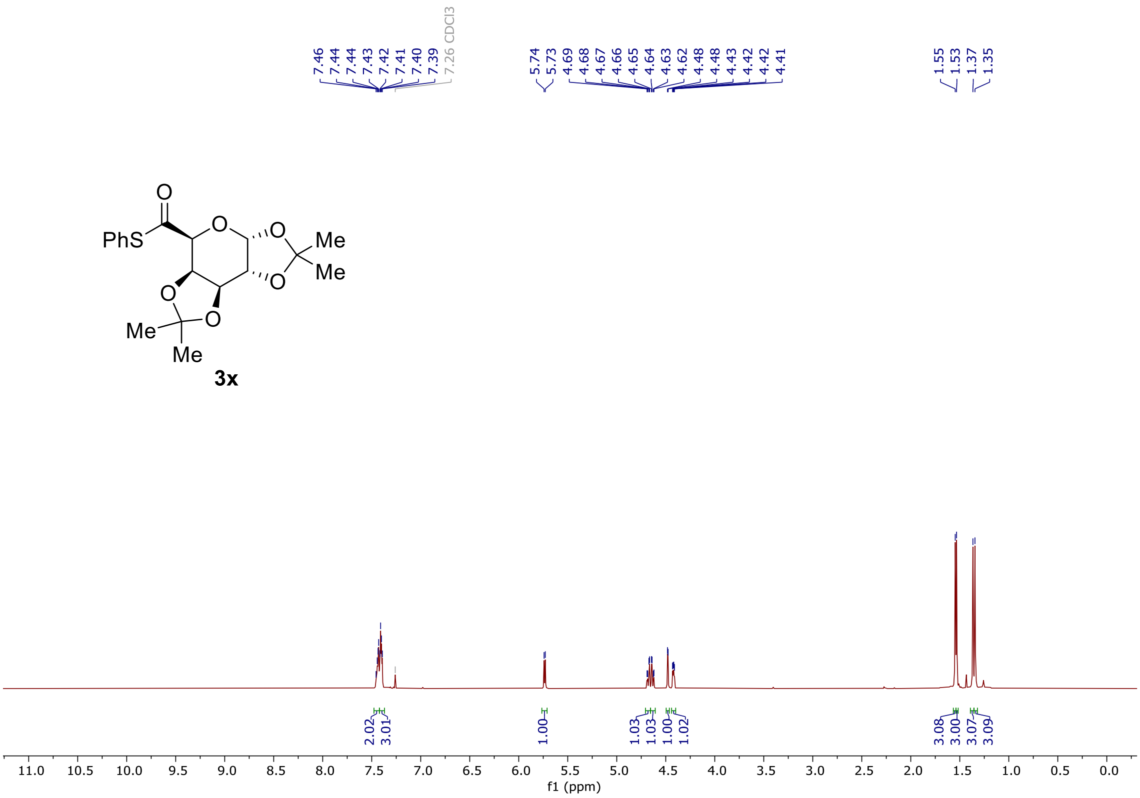
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of compound **3v.**



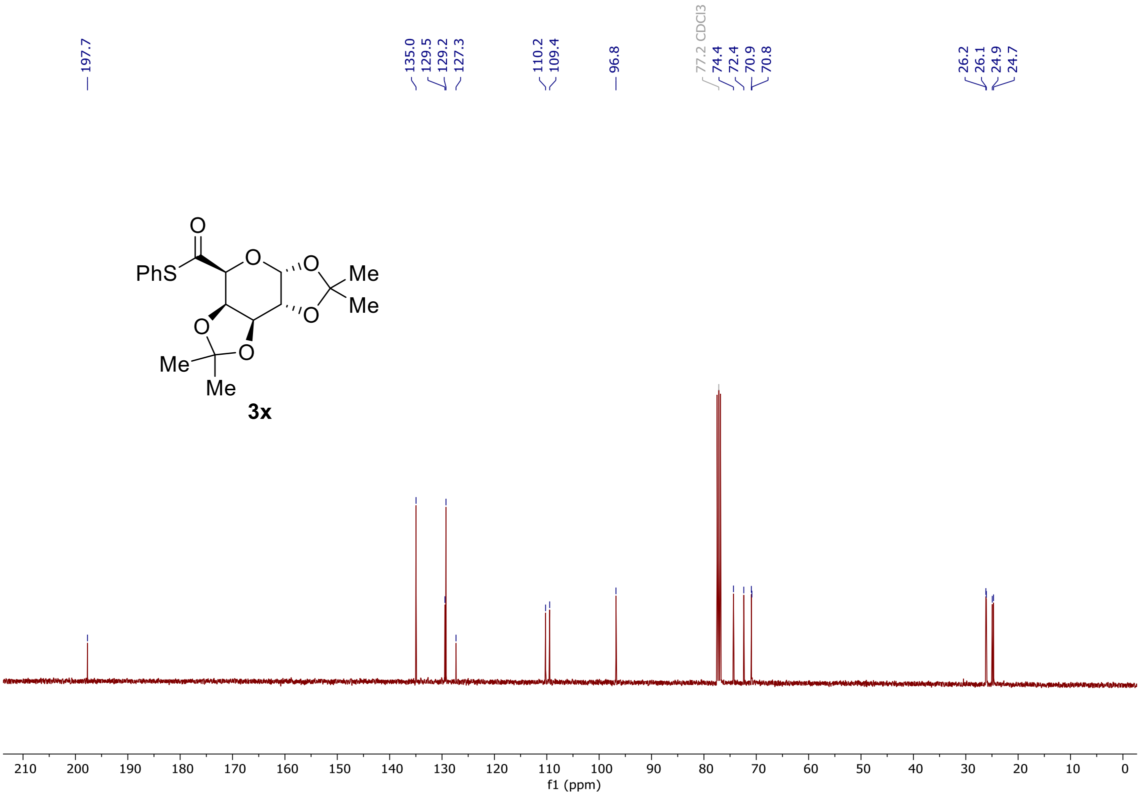
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3w**.



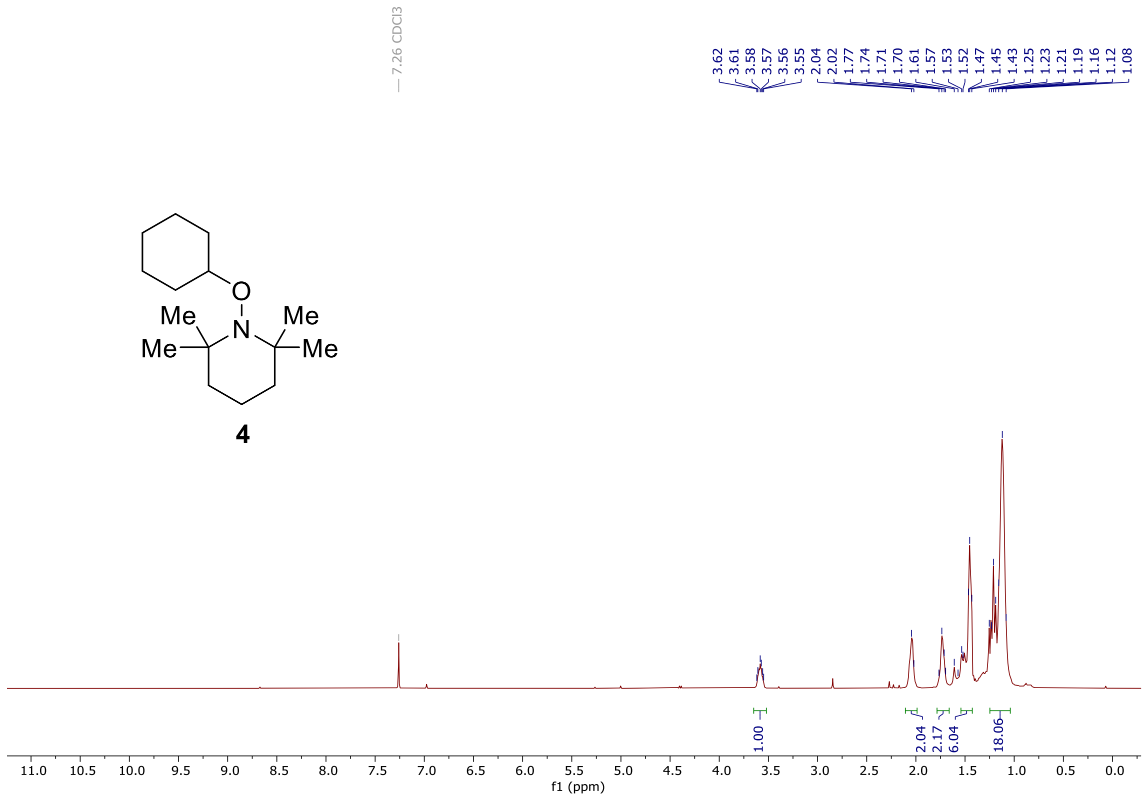
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of compound **3w.**



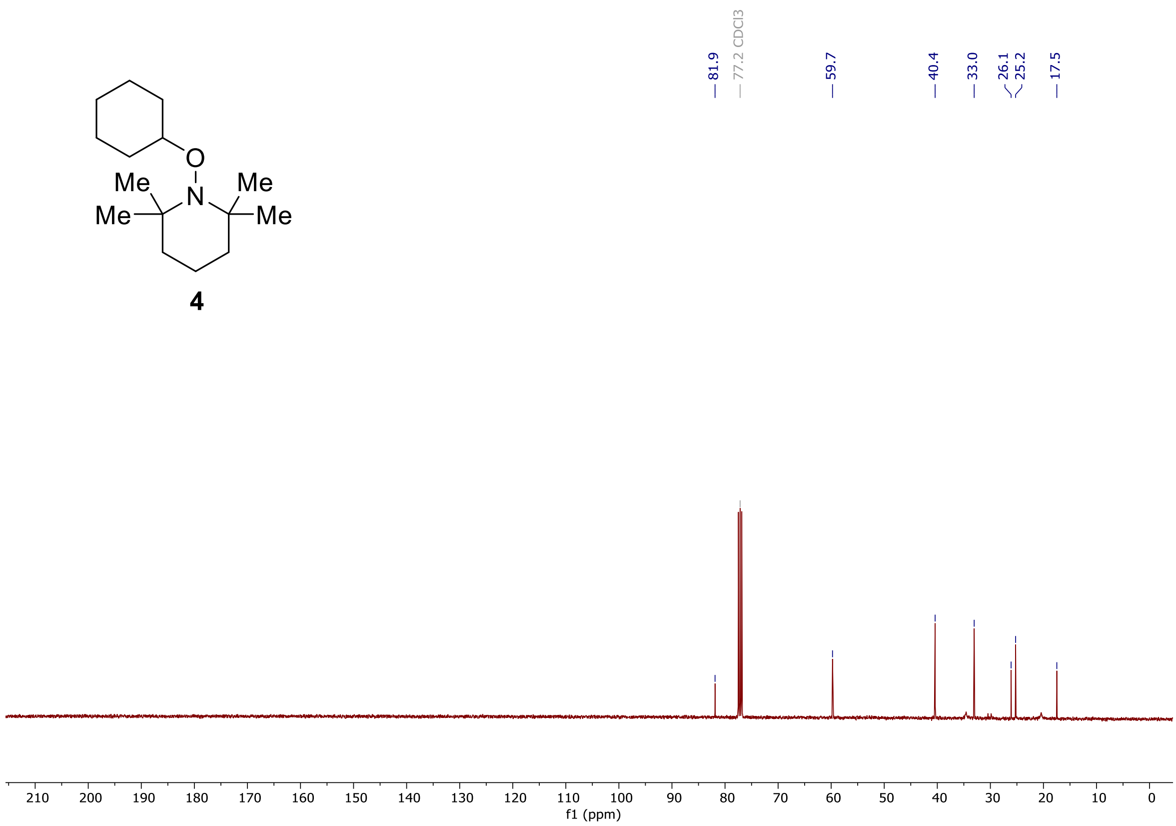
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3x**.



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of compound **3x.**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **4**.



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of compound **4.**