Synthesis of Non-Classical, Arylated *C*-Saccharides *via* Photoredox/Nickel Dual Catalysis

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Supporting Information

1. General considerations

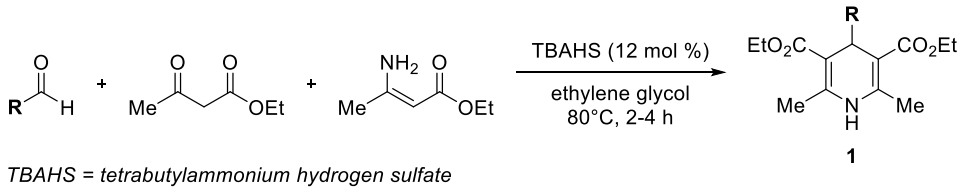
1.1 Reagents

All reactions were carried out under an inert atmosphere of argon unless otherwise noted. Standard Schlenk techniques were used for the manipulation of solvents and reagents. Reactions were monitored by GC/MS, HPLC, ^{1}H NMR, and/or by TLC on silica gel plates (60 Å porosity, 250 µm thickness). TLC analysis was performed using hexanes/EtOAc as the eluent and visualized using *p*-anisaldehyde stain and/or UV light. Flash chromatography was accomplished using an automated system (visualizing at 254 nm and 280 nm) with silica cartridges (60 Å porosity, 20-40 µm). All chemicals were used as received unless otherwise noted. Solvents were purified by use of drying cartridges through a solvent delivery system.

1.2 Analytical Methods

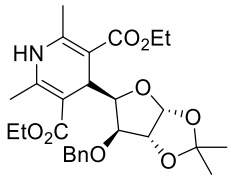
Melting points (°C) are uncorrected. NMR Spectra (^{1}H, ^{13}C {1H}) were recorded on a 500 MHz or 300 MHz spectrometer at 298 K. All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for $CHCl_3$ (7.26 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.2 ppm) and were obtained with ^{1}H decoupling. Coupling constants, *J*, are reported in Hertz (Hz). In the case of diastereomeric mixtures, crude NMR was recorded to determine the ratio. HRMS was obtained by either ESI or CI with a TOF spectrometer in CH_3CN or CH_2Cl_2. IR spectra were obtained on neat samples.

2. Synthesis of 1,4-Dihydropyridine derivatives



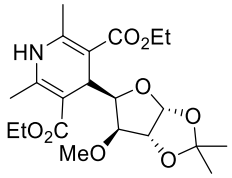
Scheme S1. Synthesis of 1,4-DHP derivatives.

General Procedure for DHPs Synthesis: 1,4-Dihydropyridines were prepared following a modified literature protocol.[1] Into a solution of ethyl 3-aminocrotonate (1.0 equiv), ethyl acetoacetate (1.0 equiv) and the corresponding aldehyde (1.0 equiv) in ethylene glycol (2.5 M) was added Bu_4NHSO_4 (12 mol %) in one portion. If the aldehyde was too viscous it could be dissolved in CH_2Cl_2 and added to the reaction mixture with no noticeable effect. The vial was sealed and heated at 80 ºC for 2-4 h. After complete consumption of the aldehyde, the reaction was cooled to rt and diluted with EtOAc. The solution was poured into a separatory funnel containing brine and extracted three times with EtOAc. The organic layer was dried ($MgSO_4$), filtered, and taken to dryness. The crude reaction mixture was purified using an automated system (visualizing at 254 nm, monitoring at 280 nm) with silica cartridges (60 Å porosity, 20-40 µm) using hexanes/EtOAc (0 to 40%) as eluent.



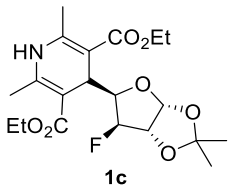
1a

Diethyl 4-((3a*R*,5*R*,6*S*,6a*R*)-6-(Benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1a): Following the General Procedure using (3a*R*,5*S*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole-5-carbaldehyde[2] (2.88 g, 10.3 mmol, 1.0 equiv). The product was isolated as a white solid (2.98 g, 58% yield). mp = 53-55 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.15 (m, 5H), 5.82 (d, *J* = 3.9 Hz, 1H), 5.58 (s, 1H), 4.73 (d, *J* = 7.9 Hz, 1H), 4.58 (d, AB syst, *J* = 11.9 Hz, 1H), 4.46 (d, AB syst, *J* = 11.9 Hz, 1H), 4.22 – 4.03 (m, 4H), 3.99 (dd, *J* = 7.9, 3.1 Hz, 1H), 3.90 – 3.80 (m, 1H), 3.78 (d, *J* = 3.1 Hz, 1H), 2.29 (s, 3H), 2.18 (s, 3H), 1.42 (s, 3H), 1.25 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 168.3/168.0 (rot.1/rot.2), 145.2, 145.1, 138.2, 127.9 (2C), 127.1, 126.6 (2C), 110.8, 104.4, 99.9, 99.5, 82.0, 82.0, 81.4, 70.8, 60.1, 59.5/59.3 (rot.1/rot.2), 32.7, 26.5, 26.0, 18.9, 18.3, 14.1, 14.0 ppm. The spectroscopic data were in agreement with those previously reported.[1]



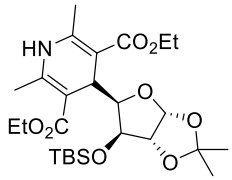
1b

Diethyl 4-((3a*R*,5*R*,6*S*,6a*R*)-6-Methoxy-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1b): Following the General Procedure using (3a*R*,5*S*,6*S*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole-5-carbaldehyde[3] (2.41 g, 10.9 mmol, 1.0 equiv). The product was isolated as a white solid (2.68 g, 53% yield). mp = 76-78 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (d, *J* = 4.0 Hz, 1H), 5.74 (s, 1H), 4.55 (d, *J* = 7.6 Hz, 1H), 4.46 (d, *J* = 4.0 Hz, 1H), 4.30 – 4.02 (m, 4H), 3.87 (dd, *J* = 7.6, 3.1 Hz, 1H), 3.49 (d, *J* = 3.2 Hz, 1H), 3.27 (s, 3H), 2.31 (s, 3H), 2.25 (s, 3H), 1.40 (s, 3H), 1.33 – 1.15 (m, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 168.1, 145.2, 145.2, 110.7, 104.5, 100.0, 99.0, 83.7, 82.0, 80.6, 60.3, 59.6, 56.7, 33.1, 26.5, 26.0, 19.0, 18.2, 14.3, 14.2 ppm. The spectroscopic data were in agreement with those previously reported.[1]



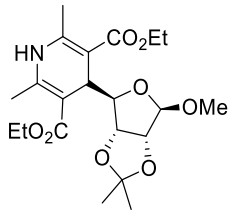
1c

Diethyl 4-((3a*R*,5*R*,6*S*,6a*S*)-6-Fluoro-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1c): Following the General Procedure using the corresponding aldehyde[4] (1.99 g of crude material, 10.5 mmol, 1.0 equiv). The product was isolated (CombiFlash, silica gel, hexanes/EtOAc 0 to 30%) as a yellow solid (1.33 g, 31% yield). mp = 106-109 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (d, *J* = 3.9 Hz, 1H), 5.70 (s, 1H), 4.73 (dd, *J* = 49.6, 1.5 Hz, 1H), 4.64 (d, *J* = 7.6 Hz, 1H), 4.56 (dd, *J* = 11.5, 3.9 Hz, 1H), 4.31 – 4.07 (m, 4H), 3.89 (ddd, *J* = 31.5, 7.5, 1.7 Hz, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 1.42 (s, 3H), 1.33 – 1.25 (m, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9 (2C), 146.3, 145.1, 111.6, 104.4, 100.2, 99.3, 93.6 (d, *J* = 185.4 Hz), 82.6 (d, *J* = 34.0 Hz), 81.8 (d, *J* = 18.8 Hz), 60.0, 59.8, 32.7 (d, *J* = 4.6 Hz), 26.7, 26.3, 19.6, 19.5, 14.5, 14.4 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -205.02 ppm. IR (neat, cm^{-1}): 3323, 1695, 1651, 1260, 1230, 1209, 1077. HRMS (ES+) *calcd for* $C_{20}H_{29}FNO_7$ $[M+H]^+$ 414.1928, *found* 414.1948.



1h

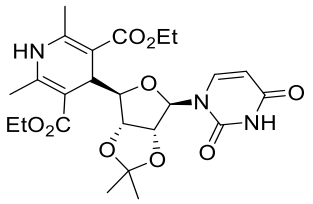
Diethyl 4-((3a*R*,5*R*,6*S*,6a*S*)-6-((*tert*-Butyldimethylsilyl)oxy)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1d): Following the General Procedure using the corresponding aldehyde[5] (3.02 g of crude material, 10.0 mmol, 1.0 equiv). The product was isolated (CombiFlash, silica gel, hexanes/EtOAc 0 to 20%) as a white solid (2.04 g, 39% yield). mp = 59-64 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 (d, *J* = 3.8 Hz, 1H), 5.62 (s, 1H), 4.57 (d, *J* = 8.2 Hz, 1H), 4.40 (d, *J* = 3.8 Hz, 1H), 4.27 – 4.11 (m, 4H), 4.09 – 4.06 (m, 1H), 3.82 (dd, *J* = 8.3, 2.8 Hz, 1H), 2.31 (s, 3H), 2.25 (s, 3H), 1.40 (s, 3H), 1.31 – 1.23 (m, 9H), 0.15 (s, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 167.6, 144.5, 144.1, 111.4, 104.1, 101.4, 100.8, 85.5, 83.2, 75.7, 59.9, 59.6, 32.3, 27.2, 26.8, 26.2, 20.0, 19.4, 18.5, 14.6, 14.6, -4.0, -4.3 ppm. IR (neat, cm^{-1}): 3384, 2932, 1693, 1483, 1370, 1077, 1012. HRMS (EI+) calcd for C 26 H 28 NO 8 Si [M] + 525.2758, found 525.2773.



1e

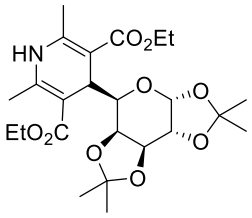
Diethyl 4-((3a*R*,4*R*,6*R*,6a*R*)-6-Methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1f): Following the General Procedure using the corresponding aldehyde[6] (1.68 g, 8.3 mmol, 1.0 equiv). The product was isolated (CombiFlash, silica gel, hexanes/EtOAc 0 to 20%) as a yellowish solid (1.46 g, 41% yield). mp = 112-116 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (s, 1H), 4.87 (s, 1H), 4.71 (dd, *J* = 6.0, 1.5 Hz, 1H), 4.45 (d, *J* = 6.0 Hz, 1H), 4.33 – 4.07 (m, 5H), 3.94 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.31 (s, 3H), 2.36 (s, 3H), 2.32 (s, 3H), 1.42 (s, 3H), 1.33 – 1.28 (m, 6H),

1.27 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 167.5, 147.0, 144.6, 112.1, 110.9, 101.4, 99.0, 89.5, 85.4, 81.6, 60.0, 60.0, 56.3, 37.3, 27.1, 25.5, 19.9, 19.5, 14.6, 14.5 ppm. IR (neat, cm^{-1}): 3335, 2978, 1687, 1661, 1483, 1210, 1093, 1050. HRMS (EI+) *calcd for* $C_{21}H_{31}NO_8$ $[M]^+$ 425.2050, *found* 425.2025.



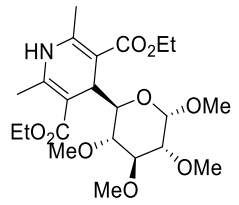
1d

Diethyl 4-((3a*R*,4*R*,6*R*,6a*R*)-6-(2,4-Dioxo-3,4-dihydropyrimidin-1(2H)-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1g): Following the General Procedure using the corresponding aldehyde[7] (1.25 g, 4.43 mmol, 1.0 equiv). The product was isolated (CombiFlash, silica gel, CH_2Cl_2/MeOH 0 to 10%) as a slightly yellow solid (1.05 g, 48% yield). mp = 92-94 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.14 (s, 1H), 5.87 (d, *J* = 3.2 Hz, 1H), 5.74 (d, *J* = 8.1 Hz, 1H), 4.78 – 4.70 (m, 1H), 4.56 (dd, *J* = 6.5, 3.3 Hz, 1H), 4.42 (d, *J* = 6.4 Hz, 1H), 4.25 – 4.12 (m, 4H), 3.94 – 3.82 (m, 1H), 2.32 (s, 3H), 2.32 (s, 3H), 1.31 – 1.27 (m, 6H), 1.21 (s, 3H), 1.20 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 167.9, 163.7, 150.2, 147.5, 147.0, 140.8, 114.5, 102.4, 98.2, 97.9, 88.7, 87.2, 83.7, 80.2, 64.1, 59.9, 35.8, 27.2, 25.1, 19.2, 19.1, 14.3 (2C) ppm. IR (neat, cm^{-1}): 3325, 2964, 1704, 1349, 1203, 1079. HRMS (ES+) *calcd for* $C_{24}H_{31}N_3O_9Na$ $[M+Na]^+$ 528.1958, *found* 528.1970.



1f

Diethyl 2,6-Dimethyl-4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1h): Following the General Procedure using (3a*R*,5*S*,5a*R*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-carbaldehyde[8] (1.24 g, 4.94 mmol, 1.0 equiv). The product was isolated as a white solid (1.27 g, 53% yield). mp = 154-159 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.40 (d, *J* = 4.9 Hz, 1H), 4.49 (d, *J* = 7.3 Hz, 1H), 4.46 (d, *J* = 7.9 Hz, 1H), 4.26 – 4.08 (m, 6H), 3.46 (d, *J* = 7.5 Hz, 1H), 2.31 (s, 3H), 2.29 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H), 1.33 – 1.23 (m, 12H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 168.3, 145.7, 144.0, 109.2, 108.2, 101.1, 99.4, 96.8, 71.7, 71.3, 70.1, 59.9, 59.5, 35.0, 26.1, 26.0, 25.2, 24.9, 19.2, 14.4, 14.4 ppm. The spectroscopic data were in agreement with those previously reported.[1]



1g

Diethyl 2,6-Dimethyl-4-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5,6-tetramethoxytetrahydro-2H-pyran-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1i): Following the General Procedure using the corresponding aldehyde (1.0 g, 4.2 mmol, 1.0 equiv). The product was isolated (CombiFlash, silica gel, hexanes/EtOAc 0 to 70%) as a slightly yellow foam (630 mg, 28% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.40 (s, 1H), 4.63 (d, *J* = 3.1 Hz, 1H), 4.46 (d, *J* = 4.2 Hz, 1H), 4.28 – 4.08 (m, 4H), 3.57 (s, 3H), 3.49 (s, 3H), 3.47 (s, 3H), 3.31 (dd, *J* = 9.8, 4.3 Hz, 1H), 3.25 (s, 3H), 3.13 – 3.05 (m, 2H), 2.29 (s, 6H), 1.30 (t, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 167.9, 145.1, 145.0, 99.7, 98.8, 96.3, 84.0, 81.8, 79.7, 72.8, 60.2, 59.6, 59.5, 58.7, 58.6, 54.1, 35.5, 19.3, 19.0, 14.3, 14.3 ppm. IR (neat, cm^{-1}): 3342, 2979, 2933, 1677, 1487, 1304, 1209, 1154, 1092, 1047. HRMS (EI+) calcd for C22H35NO9 [M]+ 458.2390, found 458.2379.

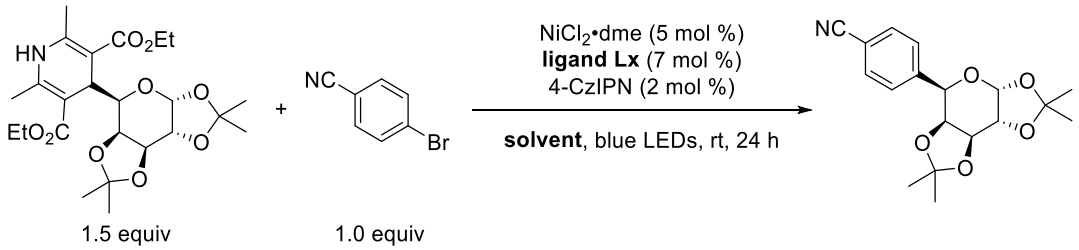
3. High-throughput Experimentation (HTE) Information

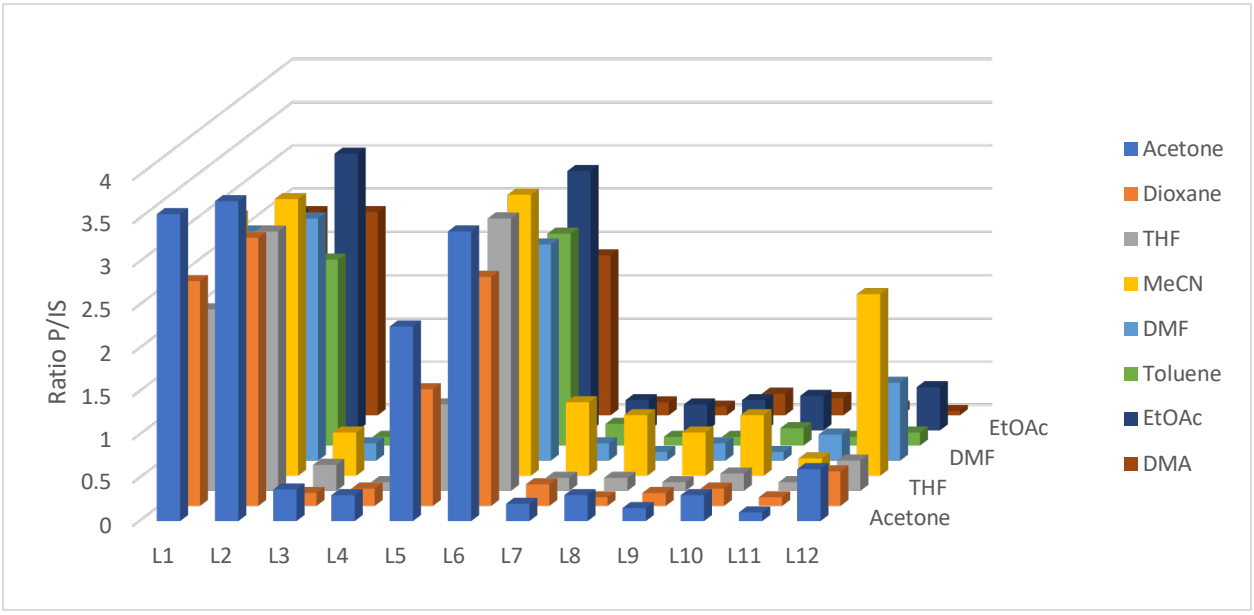
High Throughput Experimentation was performed at the Penn/Merck Center for High Throughput Experimentation at the University of Pennsylvania. The screens were run on a 0.01 mmol scale (relative to ArBr) and analyzed by UPLC with addition of 4,4′-di-*tert*-butylbiphenyl as internal standard (IS). The areas for the internal standard (IS) and the product (P) from each of the screens are shown in the tables below. The ratios calculated are pertinent only to that specific screen; the ratios from one screen should not be quantitatively compared to those from a different screen.

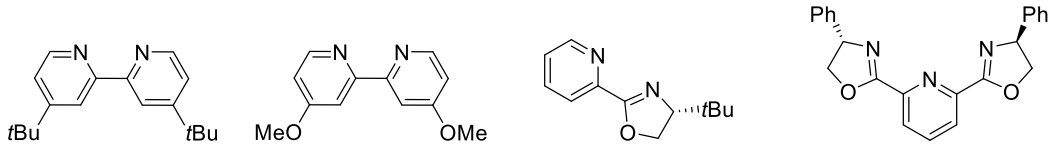
4. Screens using HTE Screening Center

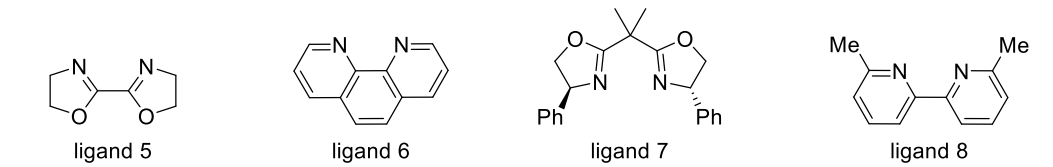
General Procedure for Screens: Reactions were run in glass vials in 24 or 96 well plate reactor blocks having hollowed bottoms, and the vials were equipped with Teflon-coated magnetic stir bars. The plate was placed in a glovebox, then the various compounds (DHP, ArBr, ligands, nickel complexes, photoredox catalysts) were added as solutions using micropipettes. If needed, dispensing solvents were removed using a centrifugal evaporator. The plate was sealed, removed from the glovebox, and stirred (500 rpm) over blue LED lights while a fan was blown across the reaction setup. After 24 h, the plate was unsealed, and reaction mixtures were diluted with MeCN (500 μL) and stirred for a further 5 min. Aliquots (25 μL) were taken and introduced into a 96-well UPLC block, diluted with MeCN (700 μL), and then analyzed by UPLC.

Screen 1. Variation of solvents and ligands.









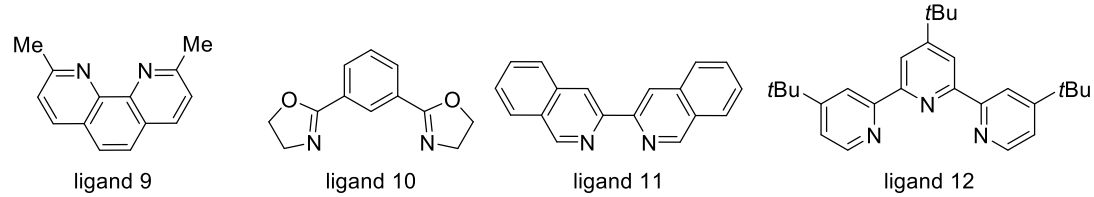
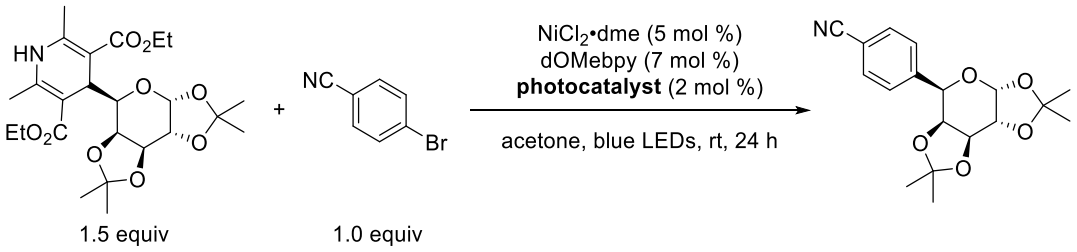


Figure S1. Optimization of solvents and ligands.

Screen 2. Variation of photocatalysts.



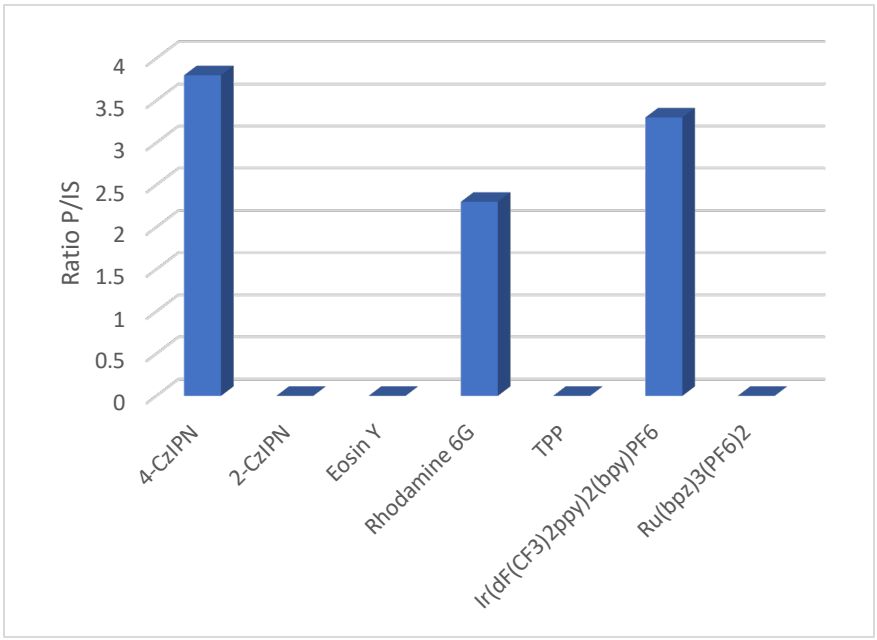
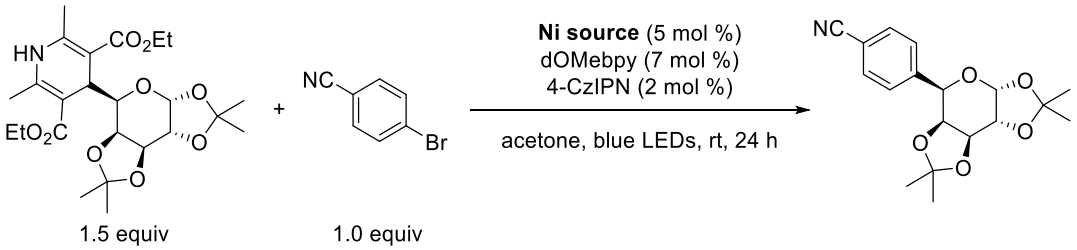


Figure S2. Ratio P/IS for the optimization of photocatalysts.

Screen 3. Variation of nickel sources.



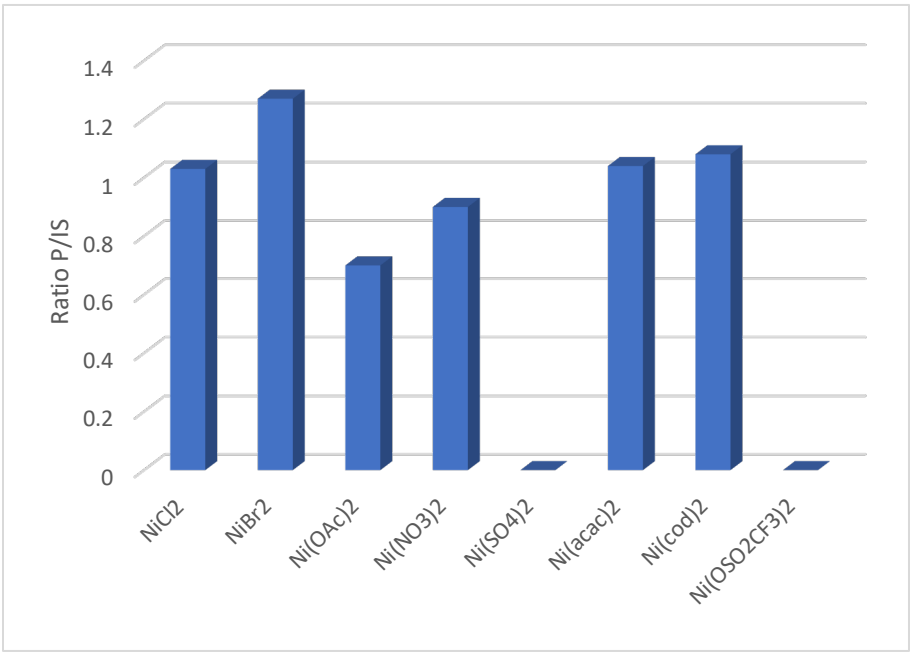
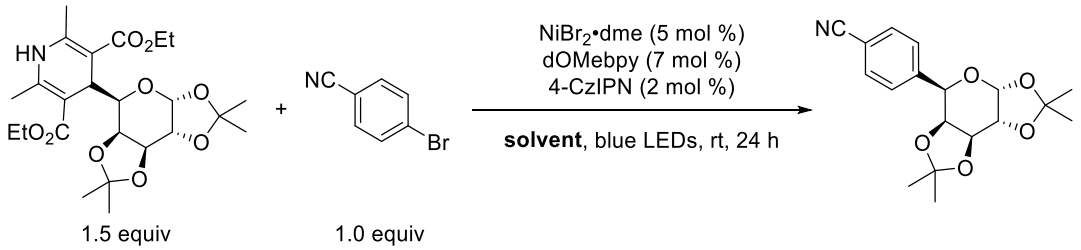


Figure S3. Ratio P/IS for the optimization of nickel sources.

Screen 4. Further variation of solvents.



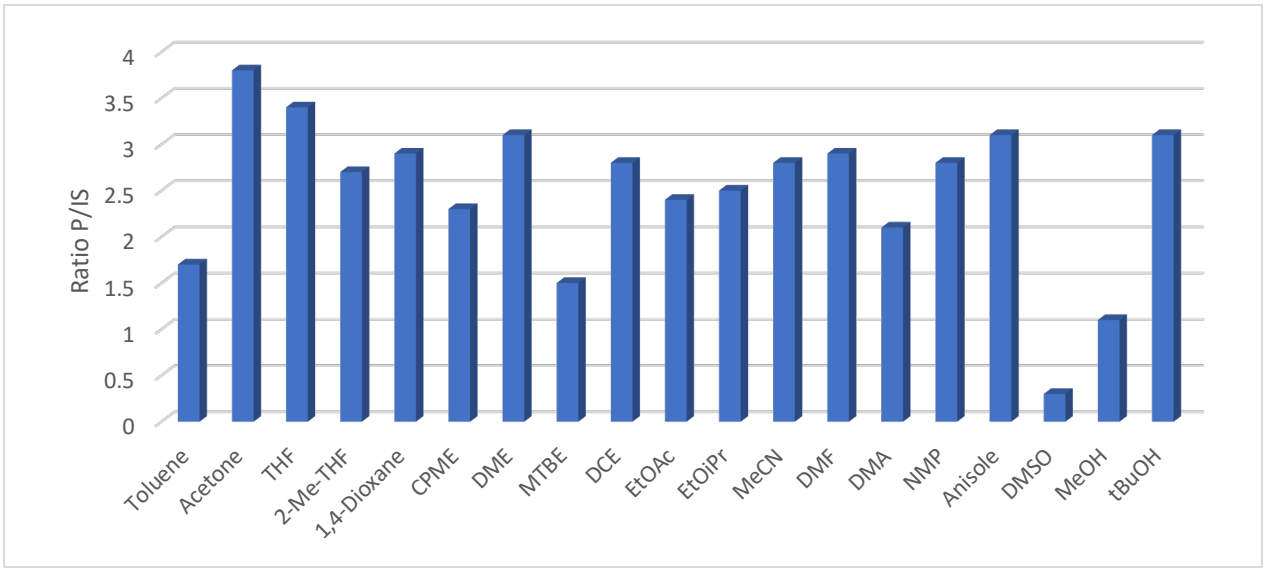
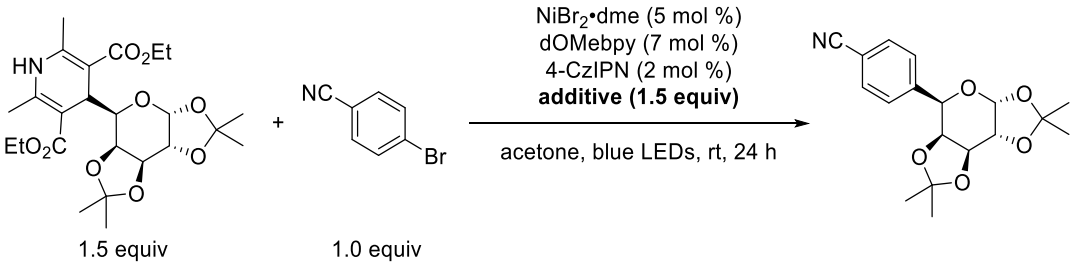


Figure S4. Ratio P/IS for further optimization of solvents.

Screen 5. Influence of various additives and different loadings.



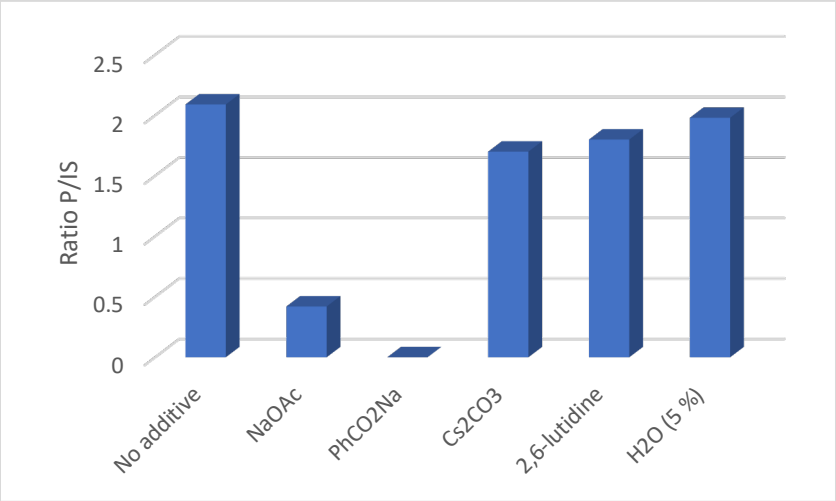


Figure S5. Ratio P/IS for additives screening.

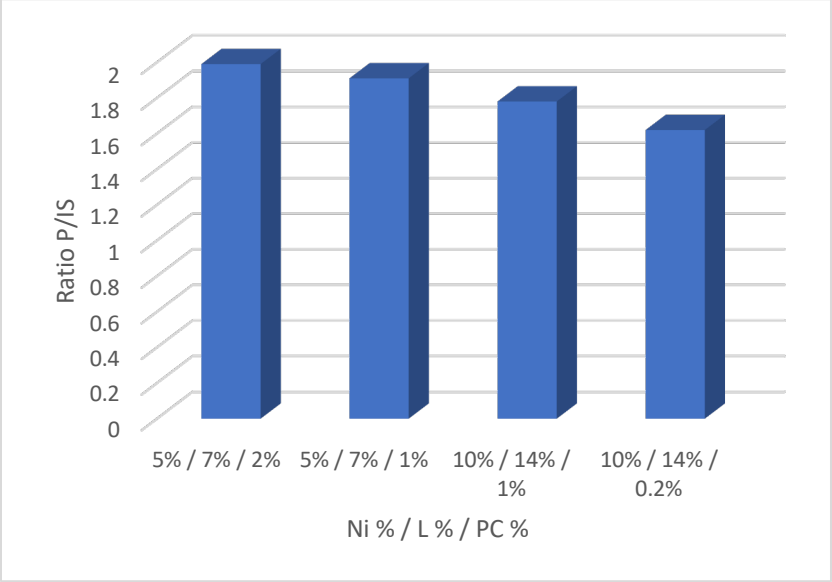


Figure S6. Evaluation of the loading for Nickel source / Ligand / Photocatalyst.

Table S1. Control Experiments.

entry	Conditions[a]	Yield (%)[b]
1	no 4-CzIPN	0
2	no $NiBr_2$•dme	0
3	no light	< 5

[a] Reactions were carried out on 0.1 mmol scale. [b] NMR yields using 1,3,6-trimethoxybenzene as internal standard.

5. General Procedure for Cross-Coupling Reactions

General Procedure I: A 10.0 mL sealable screw cap vial was charged with **1** (0.45 mmol, 1.5 equiv) and **2** (if solids, 0.3 mmol, 1.0 equiv) followed by addition of $NiBr_2$•dme (4.6 mg, 0.015 mmol, 5 mol %), dMeObpy (4.5 mg, 0.021 mmol, 7 mol %) and 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %). The vial was sealed and subsequently purged with argon and evacuated three times. Dry and degassed acetone was then added (6.0 mL, 0.05 M). If the (hetero)aryl bromide **2** or **1** were oils, they were added at this point as a solution in acetone or directly via microsyringe. The reaction was placed under blue LED irradiation and stirred for 24 h while a fan was blown across the reaction setup to maintain an ambient temperature of 24 °C. After completion, the reaction was taken to dryness and purified on an automated liquid chromatographic system to obtain the pure product.

General Procedure II: A 10.0 mL sealable screw cap vial was charged with **1** (0.45 mmol, 1.5 equiv) and **2** (if solids, 0.3 mmol, 1.0 equiv) followed by addition of $NiBr_2$•dme (9.2 mg, 0.030 mmol, 10 mol %), dMeObpy (9.1 mg, 0.042 mmol, 14 mol %) and 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %). The vial was sealed and subsequently purged with argon and evacuated three times. Dry and degassed acetone was then added (6.0 mL, 0.05 M). If the (hetero)aryl bromide **2** or **1** were oils, they were added at this point as a solution in acetone or directly via microsyringe. The reaction was placed under blue LED irradiation and stirred for 24 h while a fan was blown across the reaction setup to maintain an ambient temperature of 24 °C. After completion, the reaction was taken to dryness and purified on an automated liquid chromatographic system to obtain the pure product.

Note: In rare cases, the product was isolated as a mixture with the pyridine by-product. In such cases, the mixture obtained was dissolved in Et_2O and washed with HCl (1 M) several times to completely remove the pyridine.

6. Cyclic Voltammetry Measurements

Voltammetric measurements were recorded on a CH Instrument: Model 600E Series Electrochemical Analyzer using a standard three electrodes setup in dry, degassed MeCN (10.0 mL), with ferrocene as internal reference ($E^{0}_{1/2}$ = + 0.41 V vs SCE) and Bu_4NPF_6 as electrolyte (0.1 mmol). Cyclic voltammograms were recorded with a step potential of 0.002 V at a scan rate of 0.1 V/s. Voltammetric measurements were repeated at different scan rates to ensure the accuracy of the measurement.

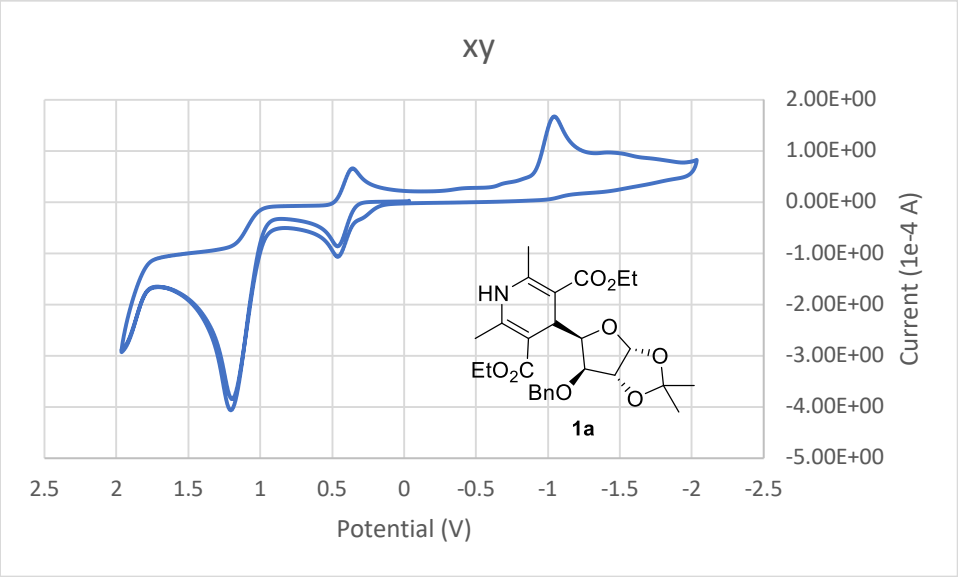
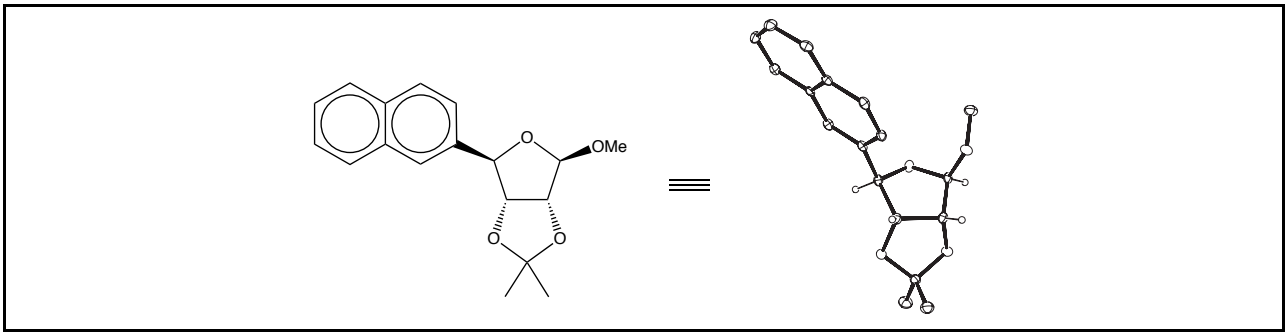


Figure S7. Cyclic Voltammetry Measurements for **1a-DHP**.

7. X-ray Structure Determination of Compound 2e



Compound **2e**, $C_{18}H_{20}O_4$, crystallizes in the orthorhombic space group $P2_12_12_1$ (systematic absences h00: h=odd, 0k0: k=odd, and 00l: l=odd) with a=5.8690(6)Å, b=8.4253(8)Å, c=29.710(3)Å, V=1469.1(3)Å^3, Z=4, and d_{calc}=1.358 g/cm$_3$. X-ray intensity data were collected on a Bruker D8QUEST [1] CMOS area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073Å) at a temperature of 100K. Preliminary indexing was performed from a series of twenty-four 0.5° rotation frames with exposures of 10 seconds. A total of 1719 frames were collected with a crystal to detector distance of 41.0 mm, rotation widths of 0.5° and exposures of 30 seconds:

scan type	2θ	ω	φ	χ	Frames
ω	0.09	186.59	144.00	54.72	333
ω	0.09	186.59	72.00	54.72	333
ω	0.09	186.59	0.00	54.72	333
ϕ	0.09	186.41	0.00	54.72	720

Rotation frames were integrated using SAINT [2], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 43158 reflections were measured over the ranges $6.35 \leq 2\theta \leq 50.842°$, $-7 \leq h \leq 7$, $-10 \leq k \leq 9$, $-35 \leq l \leq 35$ yielding 2699 unique reflections (R_{int} = 0.0511). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS [3] (minimum and maximum transmission 0.6626, 0.7452). The structure was solved by direct methods - SHELXT [4]. Refinement was by full-matrix least squares based on F^2 using SHELXL-2014 [5]. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0412P)^2 + 0.4144P]$ 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=0.0304 and wR2=0.0746 for 2607 observed reflections for which $F > 4\sigma(F)$ and R1=0.0320 and wR2=0.0756 and GOF =1.118 for all 2699 unique, non-zero reflections and 202 variables. The maximum Δ/σ in the final cycle of least squares was 0.000 and the two most prominent peaks in the final difference Fourier were +0.17 and -0.34 e/Å^3.

Table 1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables 2. and 3. Anisotropic thermal parameters are in Table 4. Tables 5. and 6. list bond distances and bond angles. Figure S8 is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

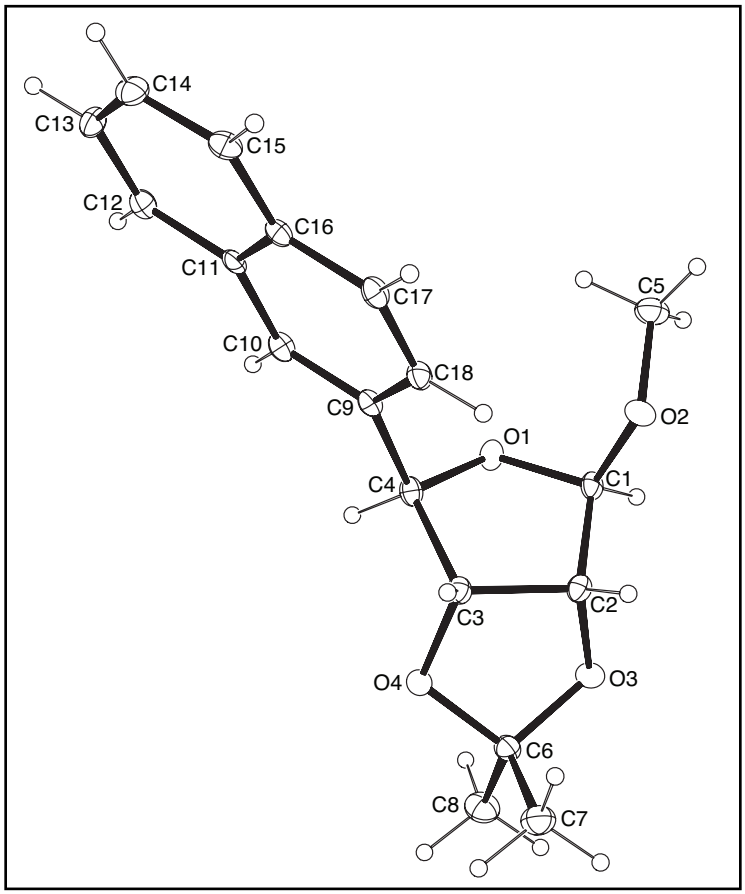


Figure S8. ORTEP drawing of the title compound with 50% thermal ellipsoids.

Table S2. Summary of Structure Determination of Compound 2e

Empirical formula	$C_{18}H_{20}O_4$
Formula weight	300.34
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a	5.8690(6)Å
b	8.4253(8)Å
c	29.710(3)Å
Volume	1469.1(3)$Å^3$
Z	4
d_{calc}	1.358 g/cm^3
μ	0.095 mm^{-1}
F(000)	640.0
Crystal size, mm	0.25 × 0.12 × 0.07
2θ range for data collection	6.35 - 50.842°
Index ranges	$-7 \leq h \leq 7$, $-10 \leq k \leq 9$, $-35 \leq l \leq 35$
Reflections collected	43158
Independent reflections	2699[R(int) = 0.0511]
Data/restraints/parameters	2699/0/202
Goodness-of-fit on F^2	1.118
Final R indexes [I>=2σ (I)]	R_1 = 0.0304, wR_2 = 0.0746
Final R indexes [all data]	R_1 = 0.0320, wR_2 = 0.0756
Largest diff. peak/hole	0.17/-0.34 e$Å^{-3}$

Flack parameter -0.1(3)

Table S3. Refined Positional Parameters for Compound 2e

Atom	*x*	*y*	*z*	U(eq)
O1	0.2632(2)	0.91891(16)	0.33767(4)	0.0120(3)
O2	0.6636(2)	0.89583(15)	0.33905(5)	0.0130(3)
O3	0.3317(2)	0.60915(16)	0.28199(4)	0.0137(3)
O4	0.0872(2)	0.56092(16)	0.33901(5)	0.0138(3)
C1	0.4592(3)	0.8545(2)	0.31689(6)	0.0108(4)
C2	0.4412(3)	0.6752(2)	0.32065(6)	0.0110(4)
C3	0.2693(3)	0.6475(2)	0.35942(6)	0.0114(4)
C4	0.1848(3)	0.8131(2)	0.37316(6)	0.0110(4)
C5	0.7007(4)	1.0630(2)	0.34080(7)	0.0166(4)
C6	0.1738(3)	0.4927(2)	0.29857(6)	0.0128(4)
C7	0.2968(4)	0.3379(2)	0.30875(7)	0.0175(4)
C8	-0.0190(4)	0.4746(3)	0.26536(7)	0.0186(4)
C9	0.2528(3)	0.8707(2)	0.41944(6)	0.0107(4)
C10	0.1020(3)	0.9629(2)	0.44339(6)	0.0116(4)
C11	0.1515(3)	1.0171(2)	0.48743(6)	0.0103(4)
C12	-0.0030(3)	1.1122(2)	0.51245(7)	0.0128(4)
C13	0.0457(4)	1.1563(2)	0.55583(7)	0.0145(4)
C14	0.2523(4)	1.1079(2)	0.57619(6)	0.0150(4)
C15	0.4063(3)	1.0188(2)	0.55258(7)	0.0132(4)
C16	0.3615(3)	0.9717(2)	0.50765(6)	0.0112(4)

C17	0.5160(3)	0.8781(2)	0.48230(7)	0.0121(4)
C18	0.4648(3)	0.8299(2)	0.43961(7)	0.0120(4)

Table S4. Positional Parameters for Hydrogens in Compound 2e

Atom	*x*	*y*	*z*	U(eq)
H1	0.4658	0.8864	0.2852	0.013
H2	0.589	0.6254	0.3266	0.013
H3	0.3375	0.5899	0.3847	0.014
H4	0.0179	0.8114	0.372	0.013
H5a	0.6811	1.1074	0.3113	0.025
H5b	0.8527	1.0837	0.3512	0.025
H5c	0.5932	1.1103	0.3611	0.025
H7a	0.3597	0.2955	0.2815	0.026
H7b	0.191	0.2631	0.3213	0.026
H7c	0.4172	0.3573	0.3299	0.026
H8a	-0.0887	0.576	0.2602	0.028
H8b	-0.1302	0.4023	0.2773	0.028
H8c	0.0393	0.4338	0.2375	0.028
H10	-0.0363	0.9905	0.4303	0.014
H12	-0.1389	1.1449	0.4993	0.015
H13	-0.0572	1.2182	0.5719	0.017
H14	0.2836	1.1368	0.6058	0.018

H15	0.5423	0.9887	0.5662	0.016
H17	0.6548	0.849	0.495	0.015
H18	0.5696	0.7697	0.4235	0.014

Table S5. Refined Thermal Parameters (U's) for Compound 2e

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
O1	0.0101(6)	0.0129(6)	0.0128(6)	0.0022(5)	0.0016(5)	0.0038(5)
O2	0.0107(7)	0.0109(7)	0.0173(7)	0.0005(5)	-0.0031(6)	-0.0005(5)
O3	0.0168(7)	0.0145(7)	0.0097(6)	-0.0016(5)	-0.0001(5)	-0.0041(6)
O4	0.0113(7)	0.0161(7)	0.0140(7)	-0.0043(6)	0.0013(5)	-0.0037(6)
C1	0.0064(9)	0.0151(10)	0.0108(8)	-0.0006(7)	-0.0005(7)	0.0009(8)
C2	0.0100(9)	0.0132(9)	0.0098(8)	-0.0004(7)	-0.0003(7)	0.0014(8)
C3	0.0094(9)	0.0135(9)	0.0112(9)	-0.0003(7)	-0.0001(7)	-0.0003(8)
C4	0.0078(9)	0.0138(9)	0.0114(9)	0.0020(7)	0.0000(7)	0.0009(8)
C5	0.0166(10)	0.0116(9)	0.0217(10)	-0.0012(8)	-0.0021(9)	-0.0006(8)
C6	0.0142(10)	0.0131(9)	0.0112(9)	-0.0004(7)	0.0012(7)	-0.0032(8)
C7	0.0202(11)	0.0137(10)	0.0186(10)	-0.0011(8)	0.0001(9)	-0.0002(9)
C8	0.0184(11)	0.0204(10)	0.017(1)	-0.0013(8)	-0.0045(8)	-0.0032(9)
C9	0.0098(9)	0.0103(8)	0.0121(9)	0.0020(7)	0.0006(7)	-0.0015(7)
C10	0.0091(9)	0.0129(9)	0.0128(9)	0.0033(7)	-0.0014(7)	-0.0005(8)
C11	0.0094(9)	0.0078(8)	0.0136(9)	0.0015(7)	0.0013(7)	-0.0028(8)
C12	0.0101(10)	0.0131(10)	0.0152(9)	0.0013(8)	0.0005(8)	-0.0007(8)
C13	0.0147(9)	0.0138(10)	0.0150(9)	-0.0025(8)	0.0044(8)	0.0015(8)

C14	0.0189(11)	0.0159(10)	0.0102(9)	-0.0011(7)	-0.0015(8)	-0.0023(8)
C15	0.0117(10)	0.0132(9)	0.0145(9)	0.0010(8)	-0.0042(8)	-0.0016(8)
C16	0.0117(9)	0.0096(9)	0.0124(9)	0.0029(7)	0.0004(7)	-0.0028(8)
C17	0.0079(9)	0.0132(9)	0.0152(9)	0.0027(8)	-0.0010(7)	0.0005(8)
C18	0.0086(9)	0.0125(9)	0.0149(9)	-0.0003(7)	0.0013(8)	-0.0002(8)

Table S6. Bond Distances in Compound 2e, Å

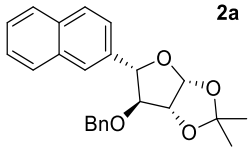
O1-C1	1.414(2)	O1-C4	1.455(2)	O2-C1	1.412(2)
O2-C5	1.426(2)	O3-C2	1.429(2)	O3-C6	1.436(2)
O4-C3	1.429(2)	O4-C6	1.426(2)	C1-C2	1.519(3)
C2-C3	1.549(3)	C3-C4	1.536(3)	C4-C9	1.512(3)
C6-C7	1.521(3)	C6-C8	1.509(3)	C9-C10	1.376(3)
C9-C18	1.423(3)	C10-C11	1.416(3)	C11-C12	1.420(3)
C11-C16	1.424(3)	C12-C13	1.372(3)	C13-C14	1.415(3)
C14-C15	1.368(3)	C15-C16	1.417(3)	C16-C17	1.418(3)
C17-C18	1.365(3)				

Table S7. Bond Angles in Compound 2e, °

C1-O1-C4	109.79(14)	C1-O2-C5	112.96(15)	C2-O3-C6	106.29(14)
C6-O4-C3	107.25(14)	O1-C1-C2	107.04(15)	O2-C1-O1	113.12(15)
O2-C1-C2	105.67(15)	O3-C2-C1	111.07(16)	O3-C2-C3	104.26(15)
C1-C2-C3	104.47(15)	O4-C3-C2	104.38(14)	O4-C3-C4	109.57(15)
C4-C3-C2	105.71(15)	O1-C4-C3	105.19(14)	O1-C4-C9	112.26(15)
C9-C4-C3	116.61(16)	O3-C6-C7	110.35(16)	O3-C6-C8	109.20(16)
O4-C6-O3	104.11(14)	O4-C6-C7	110.31(15)	O4-C6-C8	108.94(16)
C8-C6-C7	113.50(17)	C10-C9-C4	118.81(17)	C10-C9-C18	118.75(17)
C18-C9-C4	122.42(17)	C9-C10-C11	121.87(17)	C10-C11-C12	122.31(18)
C10-C11-C16	118.75(17)	C12-C11-C16	118.92(17)	C13-C12-C11	120.76(18)
C12-C13-C14	120.16(18)	C15-C14-C13	120.32(18)	C14-C15-C16	120.92(18)
C15-C16-C11	118.88(18)	C15-C16-C17	122.49(18)	C17-C16-C11	118.62(17)
C18-C17-C16	121.18(18)	C17-C18-C9	120.80(18)		

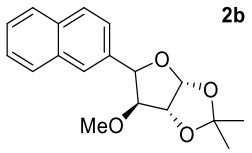
This report has been created with Olex2 [6], compiled on 2016.09.09 svn.r3337 for OlexSys.

8. Compound Characterization Data

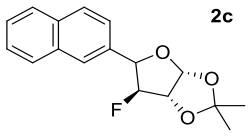


(3a*R*,5*S*,6*S*,6a*R*)-6-(Benzyloxy)-2,2-dimethyl-5-(naphthalen-2-yl)tetrahydrofuro[2,3-d] [1,3]dioxole (2a): Following General Procedure I using corresponding DHP (375.9 mg, 0.75 mmol, 1.5 equiv), 2-bromonaphthalene (103.0 mg, 0.5 mmol, 1.0 equiv), 4-CzIPN (7.8 mg, 0.01 mmol, 2 mol %), $NiBr_2 \cdot dme$ (7.7 mg, 0.025 mmol, 5 mol %), and dMeObpy (7.5 mg, 0.035 mmol, 7 mol %) in anhydrous acetone (5.0 mL, 0.1 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 10%, 10 to 30%) to afford a semi solid (154.2 mg, 82% yield). dr > 20:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.81 (d, J = 7.7 Hz, 3H), 7.48 (dd, J = 17.7, 7.8 Hz, 3H), 7.33 (d, J = 19.5

Hz, 5H), 6.06 (s, 1H), 5.19 (s, 1H), 4.84 – 4.68 (m, 2H), 4.61 (d, *J* = 11.7 Hz, 1H), 4.19 (s, 1H), 1.40 (s, 3H), 1.38 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 137.0, 133.2, 133.0, 128.7, 128.2, 128.2, 128.2, 128.0, 127.8, 126.3, 126.0, 124.8, 123.9, 114.0, 105.5, 88.3, 86.0, 84.8, 72.4, 27.3, 27.0 ppm. IR (neat, cm^{-1}): 3060, 2936, 1455, 1382, 1074, 860. HRMS (EI+) *calcd for* $C_{24}H_{24}O_4$ $[M]^+$ 376.1675, *found* 376.1670.

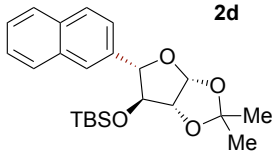


(3a*R*,5*R*,6*S*,6a*R*)-6-Methoxy-2,2-dimethyl-5-(naphthalen-2-yl)tetrahydrofuro[2,3-d] [1,3]dioxole (2b): Following General Procedure II using corresponding DHP (300.9 mg, 0.6 mmol, 2.0 equiv), 2-bromonaphthalene (62.1 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (9.2 mg, 0.03 mmol, 10 mol %), and dMeObpy (9.1 mg, 0.042 mmol, 14 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 15%) to afford a white solid (40.0 mg, 44% yield). dr = 2:1 based on ^{1}H NMR of the crude reaction mixture. mp = 68-70 °C. ^{1}H NMR (500 MHz, $CDCl_3$, major diastereomer) δ 7.95 (s, 1H), 7.87 – 7.81 (m, 3H), 7.59 – 7.44 (m, 3H), 6.04 (d, *J* = 4.0 Hz, 1H), 5.10 (d, *J* = 5.0 Hz, 1H), 4.71 (dd, *J* = 4.0, 1.5 Hz, 1H), 3.97 (dd, *J* = 4.5, 1.0 Hz, 1H), 3.50 (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H) ppm. ^{1}H NMR (500 MHz, $CDCl_3$, minor diastereomer) δ 7.92 (s, 1H), 7.87 – 7.81 (m, 3H), 7.59 – 7.44 (m, 3H), 6.16 (d, *J* = 3.5 Hz, 1H), 5.44 (d, *J* = 3.0 Hz, 1H), 4.73 (d, *J* = 3.5 Hz, 1H), 3.91 (d, *J* = 3.0 Hz, 1H), 3.05 (s, 3H), 1.61 (s, 3H), 1.41 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, major diastereomer) δ 137.1, 133.3, 133.1, 128.2, 128.2, 127.8, 126.3, 126.0, 124.9, 123.9, 113.9, 105.4, 90.6, 85.5, 84.8, 58.1, 27.4, 27.0 ppm. ^{13}C NMR (126 MHz, $CDCl_3$, minor diastereomer) δ 137.1, 133.3, 133.2, 128.3, 128.2, 127.7, 126.1, 125.9, 125.1, 123.9, 111.8, 105.0, 86.3, 82.9, 81.9, 58.6, 27.0, 26.4 ppm. IR (neat, cm^{-1}): 2987, 2934, 1373, 1382, 1315, 1193, 958. HRMS (EI+) *calcd for* $C_{18}H_{20}O_4$ $[M]^+$ 300.1362, *found* 300.1350.



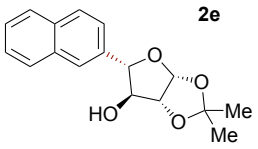
(3a*R*,6*S*,6a*S*)-6-Fluoro-2,2-dimethyl-5-(naphthalen-2-yl)tetrahydrofuro[2,3-*d*][1,3]dioxole (2c): Following General Procedure II using corresponding DHP (248.1 mg, 0.6 mmol, 2.0 equiv), 2-bromonaphthalene (62.1 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (9.3 mg, 0.03 mmol, 10 mol %), and dMeObpy (9.1 mg, 0.042 mmol, 14 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The two diastereomers were independently isolated by flash chromatography on silica gel (hexanes/EtOAc 0 to 5%) as crystalline white solids (25.1 mg, 29% yield, dr = 6.7:1 for the major diastereomer, 12.9 mg, 15% yield, dr > 20:1 for the minor diastereomer. 44% combined yield). mp (minor) = 81-84 ºC, mp (major) = 90-94 ºC. dr = 1.5:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$, minor diastereomer) δ 7.97 (s, 1H), 7.90 – 7.80 (m, 3H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.51 – 7.44 (m, 2H), 6.17 (d, *J* = 3.9 Hz, 1H), 5.49 (d, *J* = 24.1 Hz, 1H), 5.29 (d, *J* = 50.1 Hz, 1H), 4.87 (dd, *J* = 14.7, 4.0 Hz, 1H), 1.31

(s, 3H), 1.18 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, minor diastereomer) δ 133.1, 133.0, 128.3, 128.2, 127.8, 126.5, 126.2 (2C), 125.0, 123.7, 113.7, 106.0, 99.2 (d, J = 182.5 Hz), 86.1 (d, J = 26.8 Hz), 84.7 (d, J = 32.0 Hz), 26.5, 26.3 ppm. ^{1}H NMR (500 MHz, $CDCl_3$, major diastereomer) δ 7.92 (s, 1H), 7.89 – 7.81 (m, 3H), 7.57 – 7.44 (m, 3H), 6.23 (d, J = 3.7 Hz, 1H), 5.45 (d, J = 29.4 Hz, 1H), 5.06 (dd, J = 49.7, 1.8 Hz, 1H), 4.86 (dd, J = 10.1, 3.8 Hz, 1H), 1.61 (s, 3H), 1.41 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, major diastereomer) δ 133.4, 133.3, 131.3 (d, J = 3.7 Hz), 128.2, 128.0, 127.9, 126.5, 126.3, 126.3, 124.9, 112.4, 105.0, 95.2 (d, J = 187.2 Hz), 83.0 (d, J = 32.8 Hz), 81.6 (d, J = 19.2 Hz), 26.9, 26.4 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -183.14, -203.98 ppm. IR (neat, cm^{-1}): 2960, 2924, 2850, 1374, 1119, 1053, 1001 (minor diastereomer), 2992, 2938, 1386, 1374, 1217, 1163, 1079, 1020 (major diastereomer). HRMS (EI+) *calcd for* $C_{18}H_{20}O_4$ $[M]^+$ 288.1156, *found* 288.1177.



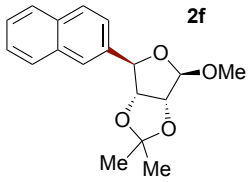
***tert*-Butyl(((3a*R*,6*S*,6a*R*)-2,2-dimethyl-5-(naphthalen-2-yl)tetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)dimethylsilane (2d):** Following General Procedure I using corresponding DHP (262.9 mg, 0.5 mmol, 2.0 equiv), 2-bromonaphthalene (51.8 mg, 0.25 mmol, 1.0 equiv), 4-CzIPN (3.9 mg, 0.005 mmol, 2 mol %), $NiBr_2$·dme (3.9 mg, 0.00125 mmol, 5 mol %), and dMeObpy (3.8 mg, 0.0175 mmol, 7 mol %) in anhydrous acetone (5.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 10%) to afford a yellow, viscous oil (40.9 mg, 41% yield). dr = 9:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.88 – 7.76 (m, 3H), 7.53 (d, J = 8.5 Hz, 1H), 7.49 – 7.42 (m, 2H), 6.02 (d, J = 4.0 Hz, 1H), 4.97 (d, J = 4.9 Hz, 1H), 4.58 (d, J = 4.0 Hz, 1H), 4.32 (d, J = 4.9 Hz, 1H), 1.43 (s, 3H), 1.37 (s, 3H), 0.90 (s, 9H), 0.05 (s, 3H), -0.03 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.8, 133.2, 133.1, 128.2, 128.1, 127.8, 126.2, 125.9, 125.1, 124.0, 113.8, 105.1, 88.6, 87.1, 82.6, 27.5, 27.2, 25.8, 18.1, -4.6, -4.8 ppm. IR (neat, cm^{-1}): 2953, 2930, 2858, 1472, 1382, 1257, 1119, 1079, 1017. HRMS (EI+) *calcd for* $C_{23}H_{32}O_4Si$ $[M]^+$ 400.2070, *found* 400.2080.

For the conformation elucidation of product **2d**, a combination of DEPT 45, COSY, HMBC and HSQC experiments were taken to unequivocally assigned each proton and carbon signals. Next, coupled ^{13}C NMR experiment allowed us to detect a $^2J_{C3,H4}$ constant of 5.5 Hz. When compared this value with previous literature, a relative *trans configuration* between the OTBS and the naphthyl groups was established.[9]

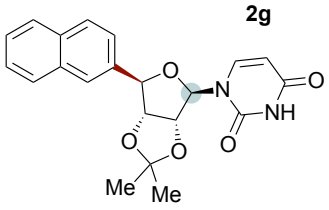


(3a*R*,6*S*,6a*R*)-2,2-Dimethyl-5-(naphthalen-2-yl)tetrahydrofuro[2,3-d][1,3]dioxol-6-ol (2e): Following General Procedure II using corresponding DHP (262.9 mg, 0.5 mmol, 2.0 equiv), 2-bromonaphthalene (51.8 mg, 0.25 mmol, 1.0 equiv), 4-CzIPN (3.9 mg, 0.005 mmol, 2 mol %), $NiBr_2$·dme (7.8 mg, 0.0025 mmol, 10 mol %), and dMeObpy (7.6 mg, 0.035 mmol, 14 mol %) in anhydrous acetone (4.0 mL, 0.05 M). After 24 h,

a solution of TBAF (1.5 mL, 1.0 M in THF, 6.0 equiv) was added dropwise at 0 °C. The reaction was allowed to stir for 5 h at rt, then quenched by addition of a saturated aq solution of $NaHCO_3$ (15 mL). The aqueous layer was extracted with EtOAc (3 x 15 mL), the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The crude was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 40%) to afford a crystalline solid (48.4 mg, 67% yield). dr > 20:1 based on ^{1}H NMR of the crude reaction mixture. mp = 105-107 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.87 – 7.70 (m, 3H), 7.55 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.50 – 7.36 (m, 2H), 6.04 (d, *J* = 4.1 Hz, 1H), 5.07 (d, *J* = 4.5 Hz, 1H), 4.66 (dd, *J* = 4.1, 1.5 Hz, 1H), 4.46 (s, 1H), 2.67 (d, *J* = 4.0 Hz, 1H), 1.34 (s, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.5, 133.2, 133.1, 128.3, 128.2, 127.8, 126.3, 126.1, 124.9, 123.9, 113.8, 105.3, 88.0, 87.0, 81.3, 27.0, 26.9 ppm. IR (neat, cm^{-1}): 3437, 2986, 2937, 1374, 1316, 1212, 1070, 1014. HRMS (EI+) *calcd for* $C_{17}H_{18}O_4$ $[M]^+$ 286.1205, *found* 286.1201.

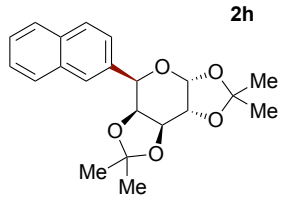


(3a*R*,4*R*,6*R*,6a*R*)-4-Methoxy-2,2-dimethyl-6-(naphthalen-2-yl)tetrahydrofuro[3,4-*d*][1,3]dioxole (2f): Following General Procedure II using corresponding DHP (191.5 mg, 0.45 mmol, 1.5 equiv), 2-bromonaphthalene (62.1 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (9.3 mg, 0.03 mmol, 10 mol %), and dMeObpy (9.1 mg, 0.042 mmol, 14 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 10%) to afford a crystalline white solid (52.0 mg, 58% yield). mp = 104-106 ºC. dr > 20:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 4H), 7.53 (d, *J* = 8.9 Hz, 1H), 7.50 – 7.45 (m, 2H), 5.41 (s, 1H), 5.19 (s, 1H), 4.97 (dd, *J* = 5.9, 1.6 Hz, 1H), 4.72 (d, *J* = 6.0 Hz, 1H), 3.41 (s, 3H), 1.62 (s, 3H), 1.38 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.0, 133.3, 133.0, 128.3, 128.2, 127.7, 126.3, 126.1, 125.3, 124.4, 113.1, 110.2, 89.4, 86.0, 85.9, 55.6, 27.0, 25.4 ppm. IR (neat, cm^{-1}): 2949, 2927, 2854, 1456, 1370, 1199, 1082, 825. HRMS (EI+) *calcd for* $C_{18}H_{20}O_4$ $[M]^+$ 300.1362, *found* 300.1369.

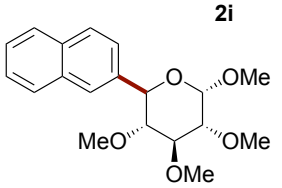


1-((3a*R*,6*R*,6a*R*)-2,2-Dimethyl-6-(naphthalen-2-yl)tetrahydrofuro[3,4-d][1,3]dioxol-4-yl) pyrimidine-2,4(1H,3H)-dione (2g): Following General Procedure II using corresponding DHP (151.4 mg, 0.3 mmol, 1.0 equiv), 2-bromonaphthalene (124.2 mg, 0.6 mmol, 2.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (9.3 mg, 0.03 mmol, 10 mol %), and dMeObpy (9.1 mg, 0.042 mmol, 14 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (CH_2Cl_2/MeOH 0

to 10%) to afford a white solid (27,4 mg, 24% yield). mp = 137-139 ºC. dr > 20:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.13 (br s, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.85 – 7.80 (m, 3H), 7.52 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.27 (d, *J* = 5.2 Hz, 1H), 5.86 (d, *J* = 2.2 Hz, 1H), 5.75 (d, *J* = 8.0 Hz, 1H), 5.18 (d, *J* = 5.3 Hz, 1H), 5.11 (dd, *J* = 6.5, 2.2 Hz, 1H), 4.98 (t, *J* = 5.0 Hz, 1H), 1.70 (s, 3H), 1.40 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.4, 150.0, 142.3, 135.5, 133.4, 133.2, 128.9, 128.2, 127.9, 126.5, 126.4, 125.1, 123.5, 115.5, 102.9, 93.4, 87.6, 85.4, 84.4, 27.5, 25.6 ppm. IR (neat, cm^{-1}): 3214, 3085, 2981, 2919, 1697, 1387, 1293, 1072. HRMS (ES+) *calcd for* $C_{21}H_{21}N_2O_5$ $[M+H]^+$ 381.1450, *found* 381.1474.

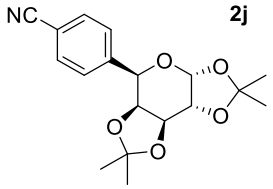


(3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyl-5-(naphthalen-2-yl)tetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (2h): Following General Procedure I using corresponding DHP (216.7 mg, 0.45 mmol, 1.5 equiv), 2-bromonaphthalene (62.1 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (4.6 mg, 0.015 mmol, 5 mol %), and dMeObpy (4.5 mg, 0.021 mmol, 7 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 10%) to afford a white solid (95.1 mg, 89% yield). mp = 122-124 ºC. dr = 9:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.86 – 7.79 (m, 3H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.49 – 7.42 (m, 2H), 5.80 (d, *J* = 5.0 Hz, 1H), 5.09 (s, 1H), 4.78 (dd, *J* = 7.8, 2.2 Hz, 1H), 4.57 (dd, *J* = 7.8, 1.9 Hz, 1H), 4.48 – 4.44 (m, 1H), 1.63 (s, 3H), 1.50 (s, 3H), 1.42 (s, 3H), 1.32 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.3, 133.3, 133.1, 128.2, 127.8, 127.7, 126.0, 125.8 (2C), 125.0, 109.4, 108.8, 97.1, 74.0, 71.3, 70.9, 69.7, 26.4, 26.1, 25.1, 24.4 ppm. IR (neat, cm^{-1}): 2988, 1381, 1372, 1253, 1142, 1102, 963. HRMS (ES+) *calcd for* $C_{21}H_{24}O_5Na$ $[M+Na]^+$ 379.1516, *found* 379.1520.

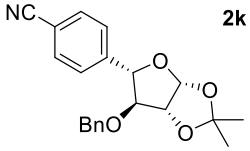


(2*S*,3*R*,4*S*,5*R*)-2,3,4,5-Tetramethoxy-6-(naphthalen-2-yl)tetrahydro-2H-pyran (2i): Following General Procedure II using corresponding DHP (171.6 mg, 0.375 mmol, 1.5 equiv), 2-bromonaphthalene (51.8 mg, 0.25 mmol, 1.0 equiv), 4-CzIPN (3.9 mg, 0.005 mmol, 2 mol %), $NiBr_2$·dme (7.8 mg, 0.025 mmol, 10 mol %), dMeObpy (7.8 mg, 0.036 mmol, 14 mol %) in anhydrous acetone (5.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 30%) to afford a colorless oil (56.8 mg, 68% yield). dr = 4:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.77 (m, 4H), 7.61 – 7.45 (m, 3H), 4.96 (d, *J* = 3.6 Hz, 1H), 4.62 (d, *J* = 9.7 Hz, 1H), 3.66 (s, 3H), 3.65 (s, 1H), 3.60 (s, 3H), 3.46 (s, 3H), 3.41 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.20 (t, *J* = 9.3 Hz, 1H), 3.00 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.4, 133.5, 133.3, 128.3, 128.2, 127.8, 127.2, 126.3, 126.2, 125.2, 98.1, 85.9, 83.4,

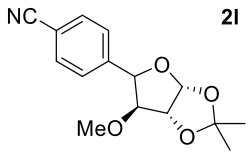
82.0, 73.1, 61.2, 60.6, 59.3, 55.5 ppm. (*Only the signals corresponding to the major stereoisomer are reported*). IR (neat, cm^{-1}): 2930, 2831, 1444, 1158, 1126, 1094, 1067, 1048, 1030. HRMS (ES+) *calcd for* $C_{19}H_{24}O_5Na$ $[M+Na]^+$ 355.1521, *found* 355.1526.



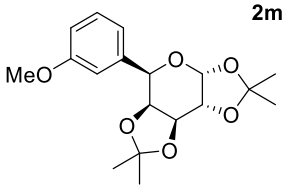
4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d] pyran-5-yl)benzonitrile (2j): Following General Procedure I using corresponding DHP (216.7 mg, 0.45 mmol, 1.5 equiv), 4-bromobenzonitrile (54.6 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (4.6 mg, 0.015 mmol, 5 mol %), and dMeObpy (4.5 mg, 0.021 mmol, 7 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 10%) to afford a white solid (69.6 mg, 70% yield). mp = 89-91 ºC. dr > 20:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 5.70 (d, *J* = 5.0 Hz, 1H), 4.92 (d, *J* = 1.3 Hz, 1H), 4.73 (dd, *J* = 7.8, 2.4 Hz, 1H), 4.45 – 4.40 (m, 2H), 1.56 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H), 1.28 (s, 3H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$) δ 143.3, 131.9 (2C), 127.7 (2C), 119.0, 111.4 (2C), 109.7, 109.0, 96.9, 73.5, 71.1, 70.7, 69.1, 26.3, 26.0, 25.0, 24.3 ppm. IR (neat, cm^{-1}): 2988, 2227, 1382, 1254, 1142, 1042, 974. HRMS (EI+) *calcd for* $C_{17}H_{18}NO_5$ $[M-CH_3]$ 316.1185, *found* 316.1195.



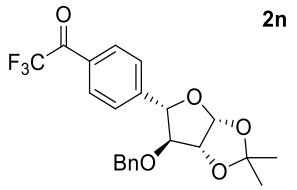
4-((3a*R*,5*R*,6*S*,6a*R*)-6-(Benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl) benzonitrile (2k): Following General Procedure I using corresponding DHP (225.7 mg, 0.45 mmol, 1.5 equiv), 4-bromobenzonitrile (54.6 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (4.6 mg, 0.015 mmol, 5 mol %), and dMeObpy (4.5 mg, 0.021 mmol, 7 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 10%) to afford a colorless oil (56.9 mg, 54% yield). dr = 9:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.43 – 7.28 (m, 5H), 6.03 (d, *J* = 4.1 Hz, 1H), 5.06 (d, *J* = 4.4 Hz, 1H), 4.75 (d, AB syst, *J* = 11.5 Hz, 1H), 4.74 (dd, *J* = 4.0, 0.7 Hz, 1H), 4.59 (d, AB syst, *J* = 11.8 Hz, 1H), 4.05 (d, *J* = 4.4 Hz, 1H), 1.35 (s, 3H), 1.31 (s, 3H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$) δ 145.2, 137.0, 132.2 (2C), 128.7 (2C), 128.3, 128.0 (2C), 126.4 (2C), 118.9, 113.9, 111.5, 105.7, 88.0, 85.4, 84.0, 72.4, 27.1, 26.8 ppm. IR (neat, cm^{-1}): 2988, 2937, 2228, 1609, 1455, 1383, 1308, 888. HRMS (ES+) *calcd for* $C_{21}H_{21}NO_4Na$ $[M+Na]^+$ 374.1363, *found* 374.1385.



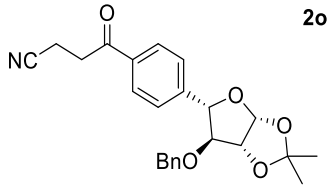
4-((3a*R*,5*R*,6*S*,6a*R*)-6-Methoxy-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl) benzonitrile (2l): Following General Procedure I using corresponding DHP (191.5 mg, 0.45 mmol, 1.5 equiv), 4-bromobenzonitrile (54.6 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (4.6 mg, 0.015 mmol, 5 mol %), and dMeObpy (4.5 mg, 0.021 mmol, 7 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 15%) to afford a colorless oil (49.5 mg, 60% yield). dr = 2:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (360 MHz, $CDCl_3$, major diastereomer) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 5.99 (d, *J* = 4.1 Hz, 1H), 4.97 (d, *J* = 4.4 Hz, 1H), 4.66 (dd, *J* = 4.1, 1.2 Hz, 1H), 3.85–3.82 (m, 1H), 3.48 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H) ppm. ^{1}H NMR (360 MHz, $CDCl_3$, minor diastereomer) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 6.07 (d, *J* = 3.7 Hz, 1H), 5.28 (d, *J* = 3.1 Hz, 1H), 4.69 (d, *J* = 3.7 Hz, 1H), 3.84 (d, *J* = 3.2 Hz, 1H), 3.10 (s, 3H), 1.56 (s, 3H), 1.38 (s, 3H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$, major diastereomer) δ 141.4, 131.8 (2C), 127.7 (2C), 118.9, 111.9, 111.5, 105.0, 85.9, 82.3, 81.0, 58.3, 26.8, 26.2 ppm. IR (neat, cm^{-1}): 2989, 2229, 1733, 1406, 1375, 1164 (major diastereomer), 2936, 2228, 1458, 1376, 1286, 1223. HRMS (EI+) *calcd for* $C_{14}H_{14}NO_4$ $[M\text{-}CH_3]^+$ 260.0923, *found* 260.0911.



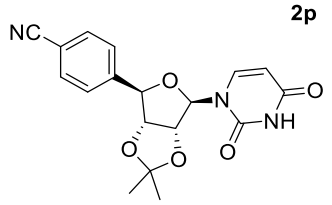
(3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-5-(3-Methoxyphenyl)-2,2,7,7-tetramethyltetrahydro-5H-bis ([1,3]dioxolo) [4,5-b:4',5'-d]pyran (2m): Following General Procedure I using corresponding DHP (216.7 mg, 0.45 mmol, 1.5 equiv), 3-bromoanisole (44.3 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (4.6 mg, 0.015 mmol, 5 mol %), and dMeObpy (4.5 mg, 0.021 mmol, 7 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 20%) to afford a colorless oil (74.5 mg, 74% yield). dr = 9:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.9 Hz, 1H), 7.03 – 6.94 (m, 2H), 6.82 (dd, *J* = 8.0, 2.3 Hz, 1H), 5.71 (d, *J* = 5.0 Hz, 1H), 4.88 (d, *J* = 0.8 Hz, 1H), 4.72 (dd, *J* = 7.8, 2.3 Hz, 1H), 4.44 (dd, *J* = 7.8, 1.9 Hz, 1H), 4.40 (dd, *J* = 5.0, 2.3 Hz, 1H), 3.81 (s, 3H), 1.57 (s, 3H), 1.47 (s, 3H), 1.38 (s, 3H), 1.31 (s, 3H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$) δ 159.5, 139.4, 129.1, 119.2, 113.3, 112.8, 109.4, 108.8, 97.1, 74.0, 71.3, 70.9, 69.4, 55.3, 26.3, 26.1, 25.1, 24.4 ppm. IR (neat, cm^{-1}): 2989, 1684, 1491, 1455, 1381, 1287, 1252, 1102. HRMS (ES+) *calcd for* $C_{18}H_{24}O_6Na$ $[M+Na]^+$ 359.1471, *found* 359.1476.



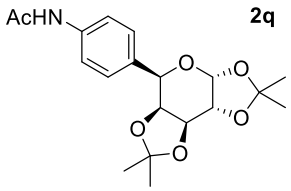
1-(4-((3a*R*,5*S*,6*S*,6a*R*)-6-(Benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)phenyl)-2,2,2-trifluoroethan-1-one (2n): Following General Procedure I using corresponding DHP (375.9 mg, 0.75 mmol, 1.5 equiv), 1-bromo-2-(trifluoromethyl)benzene (112.0 mg, 0.5 mmol, 1.0 equiv), 4-CzIPN (7.8 mg, 0.01 mmol, 2 mol %), $NiBr_2$·dme (7.7 mg, 0.025 mmol, 5 mol %), and dMeObpy (7.5 mg, 0.035 mmol, 7 mol %) in anhydrous acetone (5.0 mL, 0.1 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 10%, 10 to 25%) to afford a semi solid (100.5 mg, 49% yield). dr > 20:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.29 (m, 5H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.00 (d, *J* = 4.1 Hz, 1H), 5.00 (d, *J* = 4.8 Hz, 1H), 4.77 – 4.69 (m, 2H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.06 (d, *J* = 4.8 Hz, 1H), 1.36 (s, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 138.4, 137.2, 128.7, 128.2, 127.9, 127.4, 120.9, 114.0, 105.4, 100.1, 88.2, 85.8, 83.8, 72.3, 27.2, 27.0 ppm. IR (neat, cm^{-1}): 2990, 1939, 1725, 1260, 1222, 1164. HRMS (EI+) *calcd for* $C_{21}H_{21}F_3O_5$ $[M]^+$ 410.1341, *found* 410.1367.



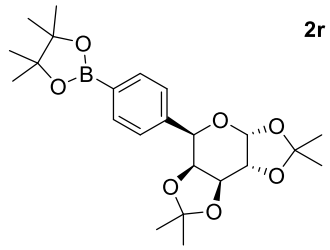
4-(4-((3a*R*,5*S*,6*S*,6a*R*)-6-(Benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)phenyl)-4-oxobutanenitrile (2o): Following General Procedure I using corresponding DHP (225.6 mg, 0.45 mmol, 1.5 equiv), 2-bromo-1,4-dimethylbenzene (71.1 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (4.6 mg, 0.015 mmol, 5 mol %), and dMeObpy (4.5 mg, 0.021 mmol, 7 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 20%) to afford a clear oil (83.0 mg, 68% yield). dr > 20:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.28 (m, 5H), 6.03 (s, 1H), 5.08 (s, 1H), 4.74 (d, *J* = 11.8 Hz, 2H), 4.60 (d, *J* = 11.7 Hz, 1H), 4.09 (d, *J* = 15.6 Hz, 1H), 3.36 (t, *J* = 7.3 Hz, 2H), 2.77 (t, *J* = 7.2 Hz, 2H), 1.35 (s, 3H), 1.33 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.0, 146.1, 137.1, 134.9, 128.7, 128.3, 128.2, 128.0, 126.2, 119.3, 113.9, 105.7, 88.1, 85.5, 84.2, 72.3, 60.5, 53.9, 34.4, 29.4, 27.1, 26.8, 21.2, 14.3, 11.9 ppm. IR (neat, cm^{-1}): 2937, 1685, 1608, 1374, 1212, 1073. HRMS (EI+) *calcd for* $C_{24}H_{25}NO_5$ $[M]^+$ 407.1733, *found* 407.1714.



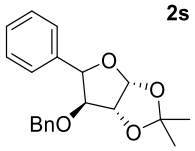
4-((3a*R*,4*R*,6*R*,6a*R*)-6-(2,4-Dioxo-3,4-dihydropyrimidin-1(2H)-yl)-2,2-dimethyltetrahydrofuro [3,4-d][1,3]dioxol-4-yl)benzonitrile (2p): Following General Procedure II using corresponding DHP (151.6 mg, 0.3 mmol, 1.0 equiv), 4-bromobenzonitrile (109.8 mg, 0.6 mmol, 2.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (9.3 mg, 0.03 mmol, 10 mol %), and dMeObpy (9.1 mg, 0.042 mmol, 14 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (CH_2Cl_2/EtOAc 0 to 30%) to afford a white solid (50.1 mg, 47% yield). mp = 131-133 ºC. dr > 20:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (360 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.24 (s, 1H), 5.77 (d, *J* = 6.8 Hz, 1H), 5.67 (d, *J* = 1.4 Hz, 1H), 5.16 (dd, *J* = 6.4, 1.4 Hz, 1H), 5.00 (d, *J* = 5.5 Hz, 1H), 4.89 (t, *J* = 5.9 Hz, 1H), 1.64 (s, 3H), 1.37 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.5, 150.0, 143.9, 143.2, 132.5 (2C), 126.5 (2C), 118.8, 115.6, 112.1, 103.1, 95.0, 87.4, 85.7, 84.2, 27.5, 25.6 ppm. IR (neat, cm^{-1}): 2989, 2228, 1632, 1612, 1421, 1156, 1018. HRMS (EI+) *calcd for* $C_{17}H_{14}N_3O_5$ $[M\text{-}CH_3]^+$ 340.0933, *found* 340.0936.



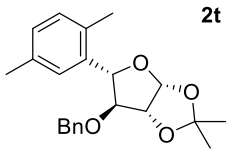
***N*-(4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)phenyl)acetamide (2q):** Following General Procedure I using corresponding DHP (216.7 mg, 0.45 mmol, 1.5 equiv), *N*-acetyl-4-bromoaniline **2c** (64.2 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (4.6 mg, 0.015 mmol, 5 mol %), and dMeObpy (4.5 mg, 0.021 mmol, 7 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 50%) to afford a white solid (44.6 mg, 41% yield). mp = 204-206 ºC. dr = 9:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.41 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 5.69 (d, *J* = 5.0 Hz, 1H), 4.85 (s, 1H), 4.70 (dd, *J* = 7.8, 2.2 Hz, 1H), 4.43–4.34 (m, 2H), 2.12 (s, 3H), 1.56 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H), 1.29 (s, 3H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$) δ 168.4, 137.4, 133.7, 127.7 (2C), 119.6 (2C), 109.4, 108.7, 97.0, 73.9, 71.2, 70.8, 69.2, 26.3, 26.1, 25.1, 24.7, 24.3 ppm. IR (neat, cm^{-1}): 1667, 1604, 1535, 1411, 1381, 1142, 1040, 962. HRMS (ES+) *calcd for* $C_{19}H_{25}NO_6Na$ $[M+Na]^+$ 386.1580, *found* 386.1583.



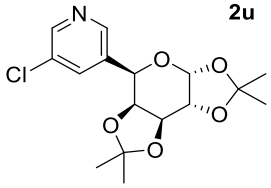
4,4,5,5-Tetramethyl-2-(4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)phenyl)-1,3,2-dioxaborolane (2r): Following General Procedure I using corresponding DHP (288.9 mg, 0.6 mmol, 2.0 equiv), (4-bromophenyl)-pinacolborane (84.9 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (4.6 mg, 0.015 mmol, 5 mol %), and dMeObpy (4.5 mg, 0.021 mmol, 7 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 3%) to afford a white crystalline solid (75.4 mg, 58% yield). mp = 135-137 °C. dr = 9:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 2H), 5.72 (d, *J* = 4.9 Hz, 1H), 4.91 (s, 1H), 4.71 (dd, *J* = 7.7, 1.9 Hz, 1H), 4.44 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.39 (d, *J* = 2.4 Hz, 1H), 1.56 (s, 3H), 1.44 (s, 3H), 1.37 (s, 3H), 1.33 (s, 12H), 1.27 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.0, 134.6 (2C), 126.1 (2C), 111.2, 109.4, 108.7, 97.0, 83.8 (2C), 74.0, 71.2, 70.8, 69.6, 26.3, 26.0, 25.1, 25.0 (4C), 24.4 ppm. ^{11}B NMR (128.38 MHz, $CDCl_3$) δ 30.7 (br,s). IR (neat, cm^{-1}): 2980, 1399, 1358, 1210, 1165, 1142, 1088, 1066. HRMS (ES+) *calcd for* ($C_{23}H_{33}BO_7Na$, $[M+Na]^+$) 454.2253, *found* 454.2278.



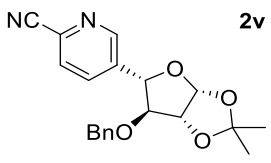
(3a*R*,6*S*,6a*R*)-6-(Benzyloxy)-2,2-dimethyl-5-phenyltetrahydrofuro[2,3-*d*][1,3]dioxole (2s): Following General Procedure II using corresponding DHP (225.7 mg, 0.45 mmol, 1.5 equiv), 2-bromobenzene (47.1 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (4.6 mg, 0.015 mmol, 5 mol %), and dMeObpy (4.5 mg, 0.021 mmol, 7 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 10%) to afford a colorless oil (29.7 mg, 30% yield). dr = 2.6:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$, major diastereomer) δ 7.42 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.27 (m, 8H), 6.00 (d, *J* = 4.1 Hz, 1H), 5.02 (d, *J* = 4.9 Hz, 1H), 4.74 (d, *J* = 3.6 Hz, 1H), 4.70 (d, *J* = 11.6 Hz, 1H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.10 (d, *J* = 4.7 Hz, 1H), 1.40 (s, 3H), 1.37 (s, 3H) ppm. ^{1}H NMR (500 MHz, $CDCl_3$, minor diastereoisomer) δ 7.44 – 7.31 (m, 6H), 7.23 – 7.20 (m, 2H), 6.94 – 6.87 (m, 2H), 6.12 (d, *J* = 3.9 Hz, 1H), 5.28 (d, *J* = 3.0 Hz, 1H), 4.71 (d, *J* = 3.7 Hz, 1H), 4.25 (d, *J* = 11.9 Hz, 1H), 4.08 (d, *J* = 12.0 Hz, 1H), 3.98 (d, *J* = 3.1 Hz, 1H), 1.56 (s, 3H), 1.37 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, major diastereomer) δ 139.6, 137.4, 128.6 (2C), 128.4 (2C), 128.1, 127.9 (2C), 127.7, 126.0 (2C), 113.9, 105.3, 88.4, 86.0, 84.4, 72.3, 27.3, 27.1 ppm. ^{13}C NMR (126 MHz, $CDCl_3$, minor diastereomer) δ 137.43, 135.75, 128.4 (2C), 128.1 (2C), 127.8, 127.8, 127.7 (2C), 127.3 (2C), 111.7, 105.1, 83.6 (2C), 81.9, 72.4, 27.0, 26.4 ppm. IR (neat, cm^{-1}): 2930, 1724, 1498, 1455, 1374, 1071, 1020 (major diastereomer), 2981, 2923, 2854, 1724, 1454, 1075 (minor diastereomer). HRMS (EI+) *calcd for* $C_{19}H_{19}O_4$ [M-CH_3] 311.1283, *found* 311.1305.



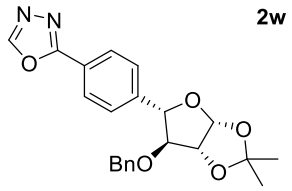
(3a*R*,5*S*,6*S*,6a*R*)-6-(Benzyloxy)-5-(2,5-dimethylphenyl)-2,2-dimethyltetrahydrofuro[2,3-d] [1,3] dioxole (2t): Following General Procedure I using corresponding DHP (225.6 mg, 0.45 mmol, 1.5 equiv), 2-bromo-1,4-dimethylbenzene (54.6 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (4.6 mg, 0.015 mmol, 5 mol %), and dMeObpy (4.5 mg, 0.021 mmol, 7 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 20%) to afford a clear oil (46.8 mg, 44% yield). dr = 7.3:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.32 (dt, *J* = 14.2, 7.3 Hz, 5H), 7.01 (t, *J* = 8.3 Hz, 2H), 6.00 (d, *J* = 4.2 Hz, 1H), 5.20 (d, *J* = 4.9 Hz, 1H), 4.74 (d, *J* = 4.1 Hz, 1H), 4.68 (d, *J* = 11.6 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.08 (d, *J* = 4.9 Hz, 1H), 2.30 (s, 3H), 2.26 (s, 3H), 1.57 (s, 3H), 1.40 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 137.2, 135.4, 132.4, 130.4, 128.6, 128.4, 128.1, 127.9, 126.9, 113.9, 105.5, 88.2, 85.6, 83.4, 72.3, 27.3, 27.0, 21.3, 19.1 ppm. IR (neat, cm^{-1}): 3581, 2941, 1455, 1214, 1074, 864. HRMS (EI+) *calcd for* $C_{22}H_{26}O_4$ $[M]^+$ 354.1831, *found* 354.1856.



3-Chloro-5-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)pyridine (2u): Following General Procedure I using corresponding DHP (216.7 mg, 0.45 mmol, 1.5 equiv), 3-bromo-5-chloropyridine (57.7 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (4.6 mg, 0.015 mmol, 5 mol %), and dMeObpy (4.5 mg, 0.021 mmol, 7 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 30%) to afford a colorless foam (45.1 mg, 44% yield). dr > 20:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.47 (d, *J* = 7.0 Hz, 2H), 7.75 (t, *J* = 1.7 Hz, 1H), 5.68 (d, *J* = 5.0 Hz, 1H), 4.90 (d, *J* = 1.3 Hz, 1H), 4.73 (dd, *J* = 7.8, 2.4 Hz, 1H), 4.43–4.36 (m, 2H), 1.57 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H), 1.29 (s, 3H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$) δ 147.9, 146.2, 135.1, 135.0, 129.8, 109.8, 109.1, 96.9, 73.3, 71.1, 70.7, 67.4, 26.3, 26.0, 25.0, 24.3 ppm. IR (neat, cm^{-1}): 2980, 2929, 1424, 1382, 1372, 1142, 1024, 1000. HRMS (ES+) *calcd for* $C_{16}H_{21}ClNO_5$ $[M+H]^+$ 342.1108, *found* 342.1093.

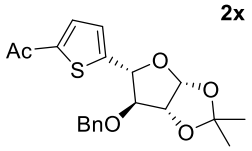


5-((3a*R*,5*S*,6*S*,6a*R*)-6-(Benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl) picolinonitrile (2v): Following General Procedure I using corresponding DHP (225.6 mg, 0.45 mmol, 1.5 equiv), 5-bromopicolinonitrile (54.6 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (4.6 mg, 0.015 mmol, 5 mol %), and dMeObpy (4.5 mg, 0.021 mmol, 7 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 20%) to afford a clear oil (73.9 mg, 70% yield). dr > 20:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 – 8.68 (m, 1H), 7.84 (ddd, J = 8.1, 2.2, 1.0 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.36 (q, J = 7.3, 6.6 Hz, 5H), 6.04 (d, J = 4.1 Hz, 1H), 5.10 (d, J = 4.2 Hz, 1H), 4.78 – 4.74 (m, 2H), 4.59 (d, J = 11.8 Hz, 1H), 4.07 (dd, J = 4.3, 1.3 Hz, 1H), 1.34 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.9, 139.5, 136.7, 134.3, 133.0, 128.9, 128.5, 128.1, 128.0, 117.3, 114.0, 106.6, 105.9, 87.5, 85.2, 82.3, 72.5, 61.6, 27.5, 27.0, 26.6, 25.0, 14.4 ppm. IR (neat, cm^{-1}): 2987, 2938, 1720, 1455, 1374, 1212, 1075. HRMS (EI+) *calcd for* $C_{20}H_{20}N_2O_4$ $[M]^+$ 352.1423, *found* 352.1450.



2w

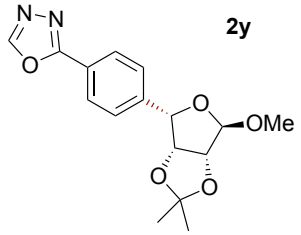
2-(4-((3aR,5S,6S,6aR)-6-(Benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)phenyl) -1,3,4-oxadiazole (2w): Following General Procedure II using the corresponding DHP (225.7 mg, 0.45 mmol, 1.5 equiv), aryl bromide **2e** (66.9 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (4.6 mg, 0.015 mmol, 5 mol %), and dMeObpy (4.5 mg, 0.021 mmol, 7 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 10%) to afford a colorless oil (29.7 mg, 30% yield). dr = 2.6:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$, major diastereomer) δ 7.42 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.27 (m, 8H), 6.00 (d, *J* = 4.1 Hz, 1H), 5.02 (d, *J* = 4.9 Hz, 1H), 4.74 (d, *J* = 3.6 Hz, 1H), 4.70 (d, *J* = 11.6 Hz, 1H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.10 (d, *J* = 4.7 Hz, 1H), 1.40 (s, 3H), 1.37 (s, 3H) ppm. ^{1}H NMR (500 MHz, $CDCl_3$, minor diastereoisomer) δ 7.44 – 7.31 (m, 6H), 7.23 – 7.20 (m, 2H), 6.94 – 6.87 (m, 2H), 6.12 (d, *J* = 3.9 Hz, 1H), 5.28 (d, *J* = 3.0 Hz, 1H), 4.71 (d, *J* = 3.7 Hz, 1H), 4.25 (d, *J* = 11.9 Hz, 1H), 4.08 (d, *J* = 12.0 Hz, 1H), 3.98 (d, *J* = 3.1 Hz, 1H).



2x

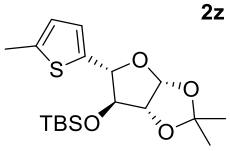
1-(5-((3a*R*,5*R*,6*R*,6a*R*)-6-(Benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl) thiophen-2-yl)ethan-1-one (2x): Following General Procedure I using corresponding DHP (225.6 mg, 0.45 mmol, 1.5 equiv), 1-(5-bromothiophen-2-yl)ethan-1-one (61.1 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (4.6 mg, 0.015 mmol, 5 mol %), and dMeObpy (4.5 mg, 0.021 mmol, 7 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel

(hexanes/EtOAc 0 to 20%) to afford a yellow oil (87.5 mg, 78% yield). dr > 20:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 3.8 Hz, 1H), 7.34 (m, 5H), 7.03 (d, *J* = 3.8 Hz, 1H), 5.99 (d, *J* = 4.0 Hz, 1H), 5.19 (d, *J* = 4.1 Hz, 1H), 4.75 – 4.68 (m, 2H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.18 (d, *J* = 4.1 Hz, 1H), 2.53 (s, 3H), 1.35 (s, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.8, 152.2, 143.6, 136.9, 132.4, 128.8, 128.3, 128.0, 125.6, 114.2, 106.6, 105.8, 88.2, 85.6, 81.5, 72.6, 29.9, 27.1, 26.9, 26.9 ppm. IR (neat, cm^{-1}): 2987, 2937, 1722, 1663, 1251, 1214, 1073, 855. HRMS (EI+) *calcd for* $C_{20}H_{22}O_5S$ $[M]^+$ 374.1188, *found* 374.1203.



2y

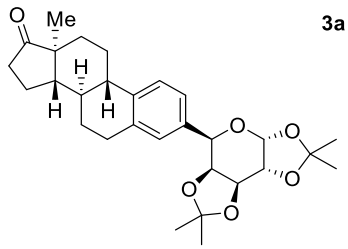
(3a*R*,5*S*,5a*R*,8a*S*,8b*R*)-5-(Benzo[b]thiophen-2-yl)-2,2,7,7-tetramethyltetrahydro-5H-bis ([1,3]dioxolo)[4,5-b:4',5'-d]pyran (2y): Following General Procedure II using corresponding DHP (216.7 mg, 0.45 mmol, 1.5 equiv), aryl bromide **2e** (66.9 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (9.2 mg, 0.03 mmol, 10 mol %), and dMeObpy (9.1 mg, 0.042 mmol, 14 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 20%) to afford a clear oil (76.1 mg, 70% yield). dr > 20:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.15 – 8.02 (m, 2H), 7.57 (d, J = 8.3 Hz, 2H), 5.29 (d, *J* = 2.3 Hz, 1H), 5.16 (s, 1H), 4.87 (dd, *J* = 6.0, 2.2 Hz, 1H), 4.68 (d, *J* = 5.9 Hz, 1H), 3.40 (s, 3H), 1.59 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.8, 152.8, 145.1, 127.4, 127.2, 123.0, 113.4, 110.4, 88.8, 86.0, 85.9, 55.9, 27.1, 25.5. IR (neat, cm^{-1}): 2988, 2937, 1719, 1617, 1558, 1516, 1498, 1458, 1374, 1211, 1104. HRMS (EI+) *calcd for* $C_{15}H_{15}N_2O_5$ $[M\text{-}CH_3]^+$ 303.0981, *found* 303.0957.



2z

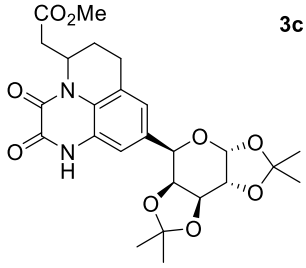
***tert*-Butyl(((3a*R*,5*R*,6*R*,6a*R*)-2,2-dimethyl-5-(5-methylthiophen-2-yl)tetrahydrofuro[2,3-d][1,3] dioxol-6-yl)oxy)dimethylsilane (2z):** Following General Procedure I using using corresponding DHP (262.9 mg, 0.5 mmol, 2.0 equiv), 2-bromo-5-methylthiophene (44.3 mg 0.25 mmol, 1.0 equiv), 4-CzIPN (3.9 mg, 0.005 mmol, 2 mol %), $NiBr_2$·dme (3.9 mg, 0.00125 mmol, 5 mol %), and dMeObpy (3.8 mg, 0.0175 mmol, 7 mol %) in anhydrous acetone (5.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 10%) to afford a colorless foam (42.8 mg, 46% yield). dr = 1.8:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80 (d, *J* = 3.3 Hz, 1H), 6.63 – 6.52 (m, 1H), 5.91 (d, *J* = 4.0 Hz, 1H), 4.91 (d, *J* = 4.4 Hz, 1H), 4.51 (dd, *J* = 4.1, 1.5 Hz, 1H), 4.34 (dd, *J* = 4.4, 1.4 Hz, 1H), 2.45 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H), 0.88 (s, 9H), 0.06 (s, 3H), 0.01 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 140.0, 125.3, 124.6, 113.8, 105.1, 88.4, 84.1, 82.5, 27.3, 27.2, 25.8 (3C), 18.1, 15.5, 0.1, -4.8 ppm. (*Only the signals corresponding to the major stereoisomer are reported*). IR (neat, cm^{-1}): 2929, 2857, 1471,

1382, 1373, 1254, 1213, 1119, 1017, 837. HRMS (ES+) *calcd for* $C_{12}H_{16}O_4S$ $[M\text{-}TBS]^+$ 256.0769, *found* 256.0764.



3a

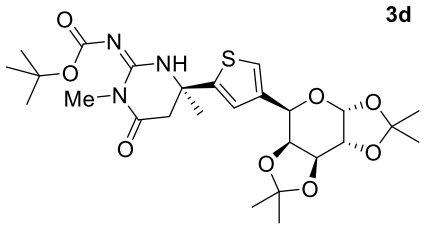
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis ([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta [a]phenanthren-17-one (3a): Following General Procedure II using corresponding DHP (216.7 mg, 0.45 mmol, 1.5 equiv), estrone derivative[10] (57.7 mg, 0.3 mmol, 1.0 equiv), 4-CzIPN (4.7 mg, 0.006 mmol, 2 mol %), $NiBr_2$·dme (4.6 mg, 0.015 mmol, 5 mol %), and dMeObpy (4.5 mg, 0.021 mmol, 7 mol %) in anhydrous acetone (6.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 20%) to afford a slightly yellow solid (60.8 mg, 42% yield). mp = 70-72 ºC. dr = 8:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.2 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.12 (s, 1H), 5.70 (d, *J* = 5.0 Hz, 1H), 4.84 (s, 1H), 4.71 (dd, *J* = 7.9, 2.3 Hz, 1H), 4.44 (dd, *J* = 7.9, 1.8 Hz, 1H), 4.39 (dd, *J* = 5.0, 2.3 Hz, 1H), 2.93 (dd, *J* = 8.7, 3.9 Hz, 2H), 2.56 – 2.37 (m, 2H), 2.34 – 2.24 (m, 1H), 2.19 – 1.92 (m, 4H), 1.68 – 1.58 (m, 2H), 1.57 – 1.41 (m, 10H), 1.37 (s, 3H), 1.31 (s, 3H), 0.90 (s, 3H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$) δ 190.9, 139.0, 136.2, 135.3, 127.5, 125.2, 124.4, 109.4, 108.7, 97.1, 72.9, 71.3, 70.9, 69.3, 50.7, 48.1, 44.5, 38.2, 36.0, 31.8, 29.6, 26.7, 26.3, 26.1, 25.8, 25.1, 24.4, 21.7, 14.0 ppm. IR (neat, cm^{-1}): 2987, 2931, 1736, 1380, 1372, 1209, 1100, 1066, 997. HRMS (EI+) *calcd for* $C_{29}H_{38}O_6$ $[M]^+$ 482.2668, *found* 482.2667.



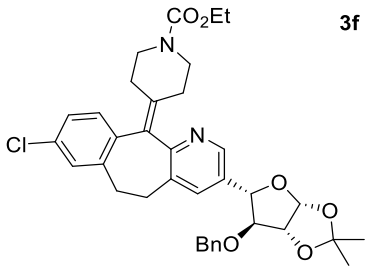
3c

Methyl 2-(2,3-Dioxo-9-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis ([1,3] dioxolo)[4,5-b:4',5'-d]pyran-5-yl)-2,3,6,7-tetrahydro-1H,5H-pyrido[1,2,3-de]quinoxalin-5-yl) acetate (3b): Following General Procedure II using corresponding DHP (72.2 mg, 0.15 mmol, 1.5 equiv), the heteroaryl bromide (35.3 mg, 0.1 mmol, 1.0 equiv), 4-CzIPN (1.5 mg, 0.002 mmol, 2 mol %), $NiBr_2$·dme (3.1 mg, 0.01 mmol, 10 mol %), and dMeObpy (3.0 mg, 0.014 mmol, 14 mol %) in anhydrous acetone (2.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexane/EtOAc/MeOH 6/3/1) to afford a white solid (26.7 mg,

53% yield). mp = 93-95 ºC. dr = 9:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (360 MHz, $CDCl_3$) mixture of rotamers: δ 11.50 (br s, 1H), 7.18 – 7.07 (m, 2H), 5.69 (dd, *J* = 4.8, 3.3 Hz, 1H), 5.44 – 5.31 (m, 1H), 4.92 (s, 1H), 4.74 (td, *J* = 7.6, 2.2 Hz, 1H), 4.57 (dd, *J* = 7.9, 1.7 Hz, 0.5H, rot.1), 4.48 (dd, *J* = 7.9, 1.7 Hz, 0.5H, rot.2), 4.41 – 4.35 (m, 1H), 3.70 (br s, 3H), 3.06 – 2.90 (m, 1H), 2.89 – 2.69 (m, 2H), 2.58 – 2.47 (m, 1H), 2.28 (br s, 1H), 2.04 – 1.83 (m, 1H), 1.57 (s, 1.5H, rot.1), 1.56 (s, 1.5H, rot.2), 1.50 (s, 1.5H, rot.1), 1.46 (s, 1.5H, rot.2), 1.36 (s, 3H), 1.32 (s, 1.5H, rot.1), 1.29 (s, 1.5H, rot.2) ppm. ^{13}C NMR (91 MHz, $CDCl_3$) mixture of rotamers: δ 170.6, 155.5/155.0 (rot.1/rot.2), 154.2, 134.4, 124.6/124.5 (rot.1/rot.2), 124.4, 123.4/123.2 (rot.1/rot.2), 122.1/121.9 (rot.1/rot.2), 112.9/112.8 (rot.1/rot.2), 109.6/109.5 (rot.1/rot.2), 109.0, 96.9, 73.9, 71.1, 70.8, 68.6/68.5 (rot.1/rot.2), 52.1, 48.0/47.9 (rot.1/rot.2), 35.3, 26.4, 26.1, 25.0, 24.3, 23.3, 22.0/21.8 (rot.1/rot.2) ppm. IR (neat, cm^{-1}): 2980, 2901, 1696, 1674, 1326, 1256, 1165, 1101, 1064. HRMS (ES+) *calcd for* $C_{25}H_{31}N_2O_9$ $[M+H]^+$ 503.2030, *found* 503.2046.



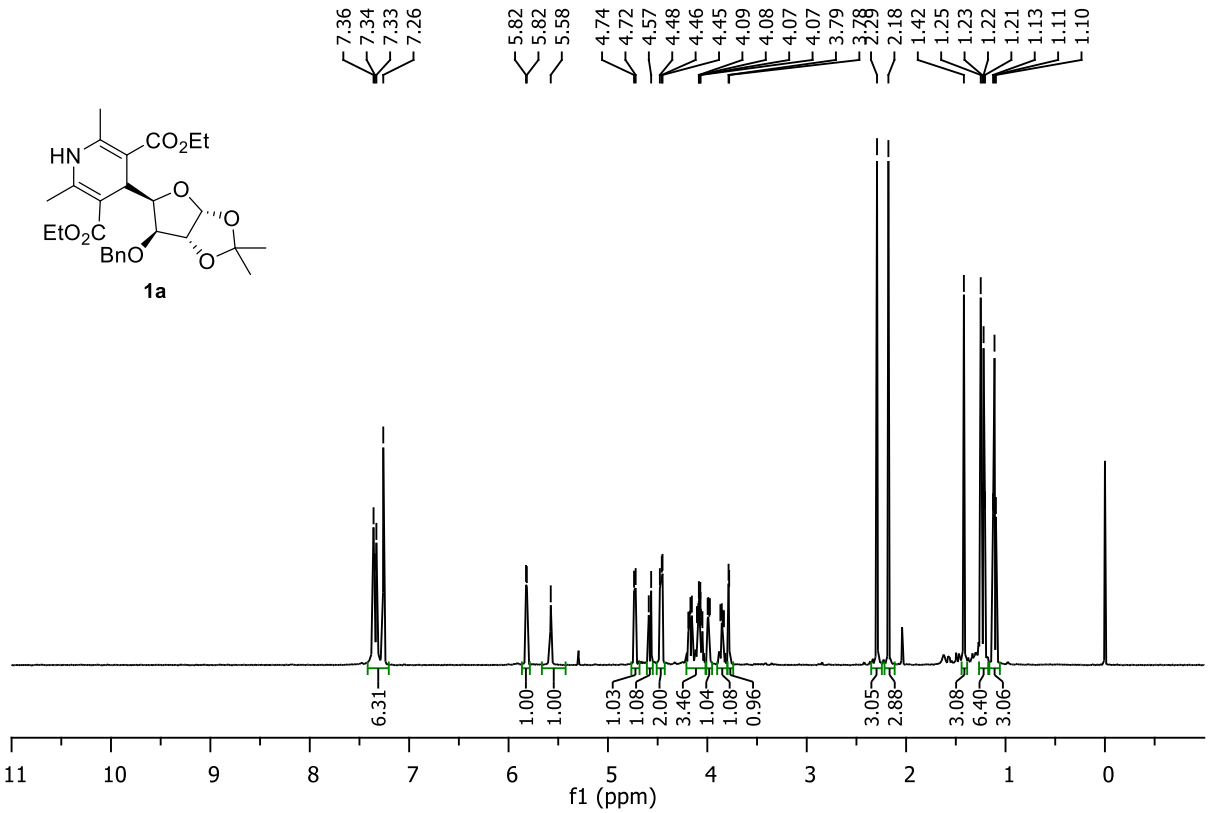
***tert*-Butyl ((*R*,*Z*)-1,4-Dimethyl-6-oxo-4-(4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyl tetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)thiophen-2-yl) tetrahydro pyrimidin-2(1H)-ylidene)carbamate (3c):** Following General Procedure II using corresponding DHP (72.2 mg, 0.15 mmol, 1.5 equiv), the heteroaryl bromide (35.3 mg, 0.1 mmol, 1.0 equiv), 4-CzIPN (1.5 mg, 0.002 mmol, 2 mol %), $NiBr_2$·dme (3.1 mg, 0.01 mmol, 10 mol %), and dMeObpy (3.0 mg, 0.014 mmol, 14 mol %) in anhydrous acetone (2.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexane/EtOAc/acetone 85:10:5) to afford a yellow oil (51.8 mg, 94% yield). dr = 4:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.28 (br s, 1H), 7.20 (s, 1H), 6.97 (d, *J* = 1.2 Hz, 1H), 5.61 (d, *J* = 5.0 Hz, 1H), 4.82 (s, 1H), 4.66 (dd, *J* = 7.8, 2.3 Hz, 1H), 4.36 – 4.30 (m, 2H), 3.25 (s, 3H), 3.12 (d, *J* = 16.2 Hz, 1H), 2.88 (d, *J* = 16.2 Hz, 1H), 1.74 (s, 3H), 1.55 (s, 3H), 1.51 (s, 9H), 1.47 (s, 3H), 1.35 (s, 3H), 1.31 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 163.9, 157.6, 147.4, 138.6, 124.3, 122.7, 109.5, 108.8, 96.9, 80.0, 73.3, 71.1, 70.7, 66.7, 53.3, 45.9, 30.0, 28.6, 28.3 (3C), 26.4, 26.1, 25.0, 24.5 ppm. IR (neat, cm^{-1}): 2989, 1713, 1640, 1597, 1269, 1251, 1157, 1066, 997. HRMS (ES+) *calcd for* $C_{26}H_{38}N_3O_8S$ $[M+H]^+$ 552.2380, *found* 552.239



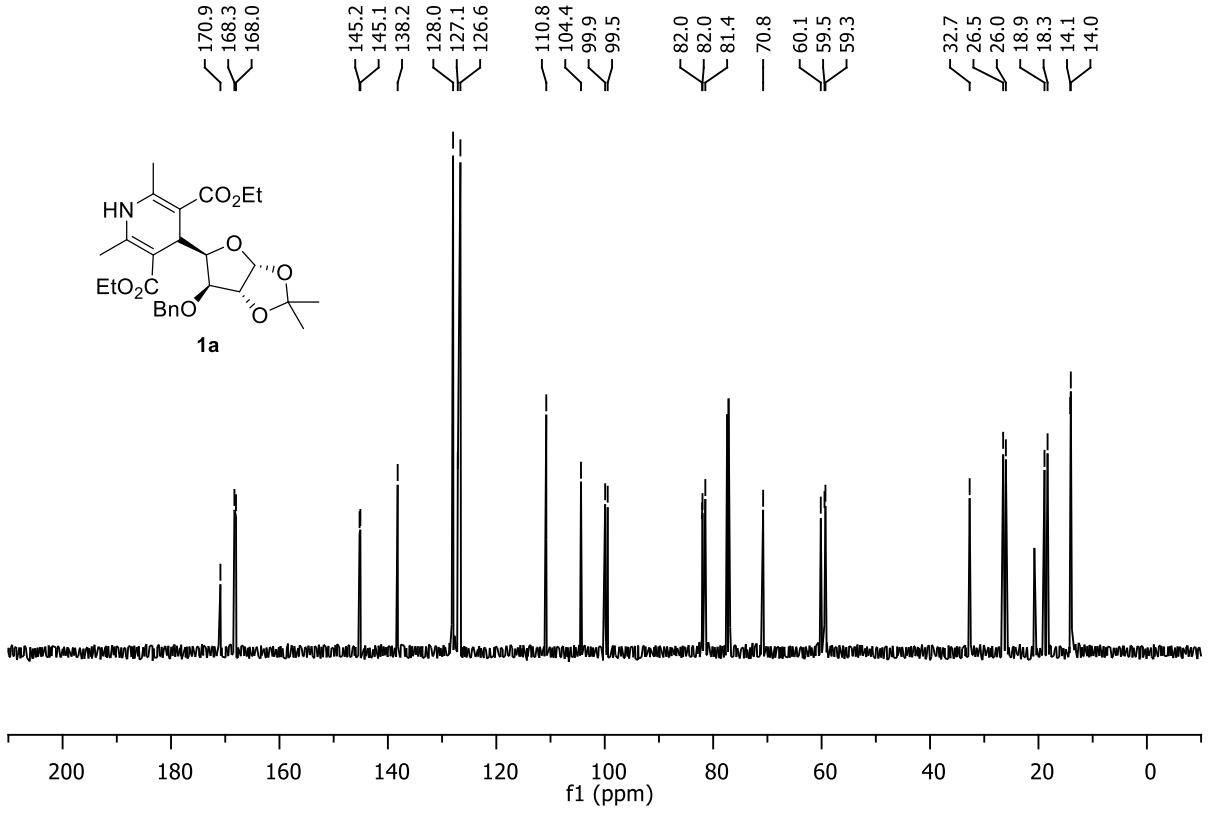
Ethyl 4-(3-((3a*R*,5*S*,6*S*,6a*R*)-6-(Benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (3d): Following General Procedure I using corresponding DHP (225.6 mg, 0.45 mmol, 3.0 equiv), ethyl 4-(3-bromo-8-chloro-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (69.0 mg, 0.15 mmol, 1.0 equiv), 4-CzIPN (2.3 mg, 0.006 mmol, 2 mol %), $NiBr_2 \cdot dme$ (2.3 mg, 0.015 mmol, 5 mol %), and dMeObpy (2.3 mg, 0.021 mmol, 7 mol %) in anhydrous acetone (3.0 mL, 0.05 M). The product was purified by flash chromatography on silica gel (hexanes/EtOAc 0 to 60%) to afford a light yellow oil (78.5 mg, 83% yield). dr > 20:1 based on ^{1}H NMR of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$, major diastereomer) δ 8.42 (s, 1H), 7.52 – 7.41 (m, 1H), 7.32 – 7.27 (m, 5H), 7.19 – 7.10 (m, 3H), 5.98 (d, *J* = 4.1 Hz, 1H), 4.96 (dd, *J* = 9.4, 4.7 Hz, 1H), 4.75 – 4.67 (m, 2H), 4.58 – 4.53 (m, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 4.04 (dd, *J* = 17.3, 4.8 Hz, 1H), 3.79 (d, *J* = 14.9 Hz, 2H), 3.41 – 3.28 (m, 2H), 3.12 (ddt, *J* = 14.3, 10.0, 5.2 Hz, 2H), 2.79 (dddd, *J* = 15.1, 11.1, 8.2, 3.9 Hz, 2H), 2.48 (t, *J* = 13.1 Hz, 1H), 2.40 – 2.25 (m, 3H), 1.35 (s, 6H), 1.26 (d, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers) δ 155.6, 139.6, 138.9, 138.7, 137.8, 137.7, 137.0 (2C), 133.2, 130.7, 130.6, 129.1 (2C), 128.8 (2C), 128.7 (2C), 128.6 (2C), 128.4, (2C), 128.3 (2C), 128.2 (2C), 128.1, 128.1, 128.0, 127.7 (2C), 127.6, 126.4, 114.1, 114.0, 111.9, 105.5, 105.3, 87.7, 87.5, 85.7, 85.6, 82.4 (2C), 82.0 (2C), 75.7, 73.6, 72.9, 72.4 (2C), 72.2, 71.5, 61.6, 61.5, 44.9, 44.8, 31.7 (3C), 30.9, 30.7, 29.9, 27.3 (2C), 26.9, 26.5, 14.8, 14.4, 14.3, 0.2. IR (neat, cm^{-1}): 2931, 1696, 1445, 1383, 1229, 1074, 769, 699. HRMS (ES+) *calcd for* $C_{36}H_{40}ClN_2O_6$ $[M+H]^+$ 631.2575, *found* 631.2589.

9. Spectral Data

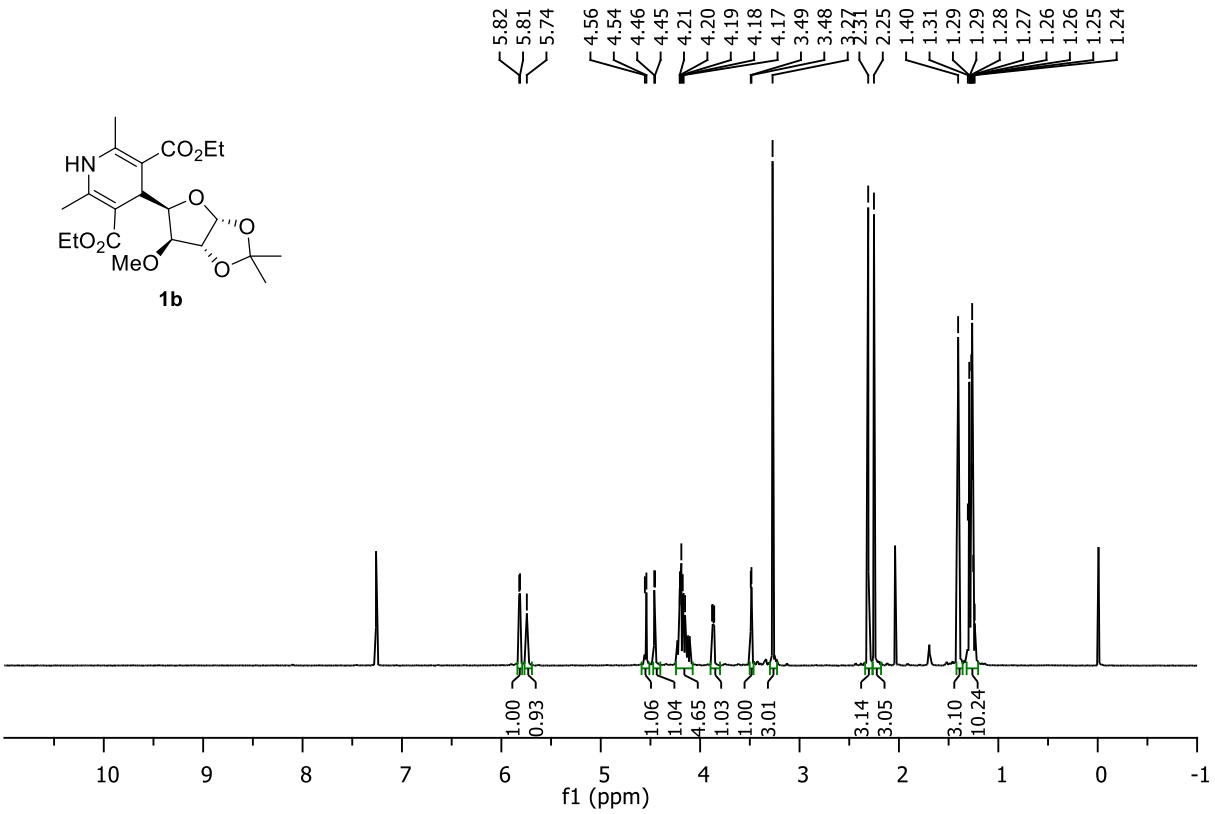
^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 4-((3a*R*,5*R*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1a**)



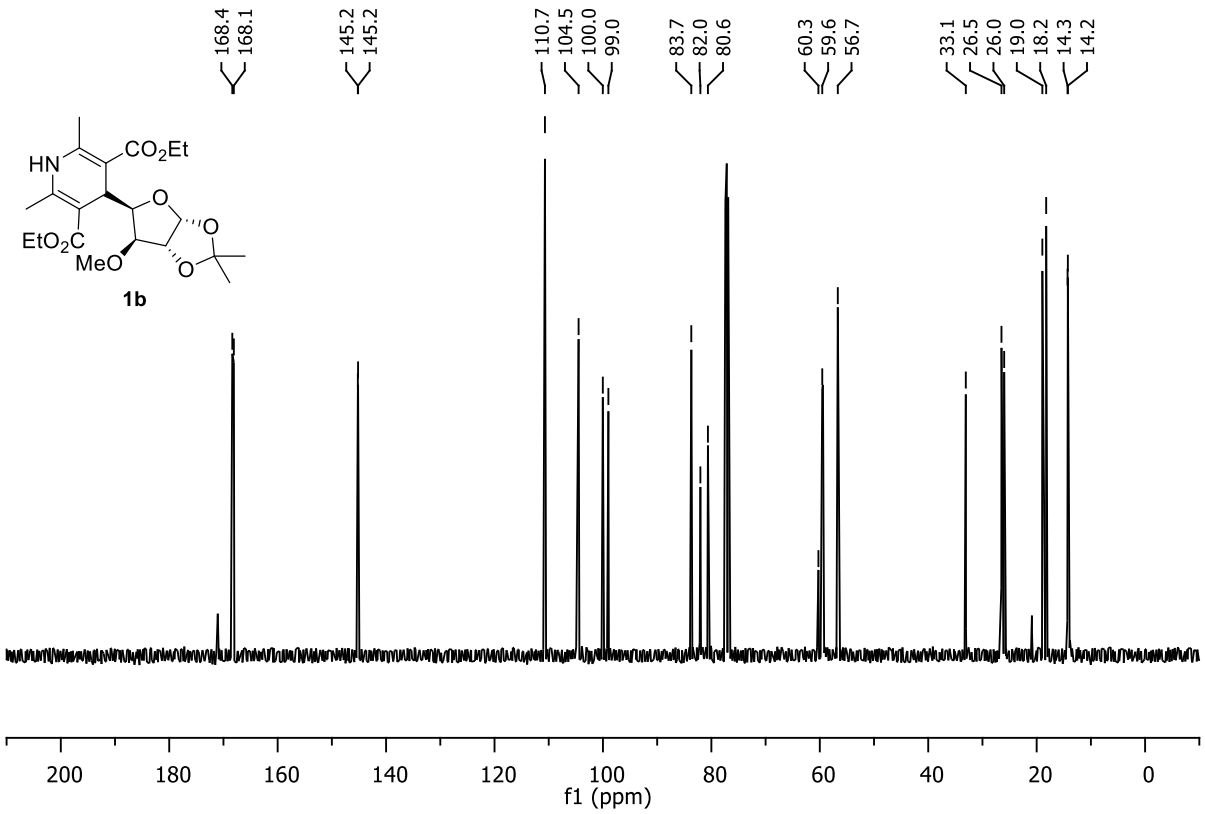
^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 4-((3a*R*,5*R*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1a**)



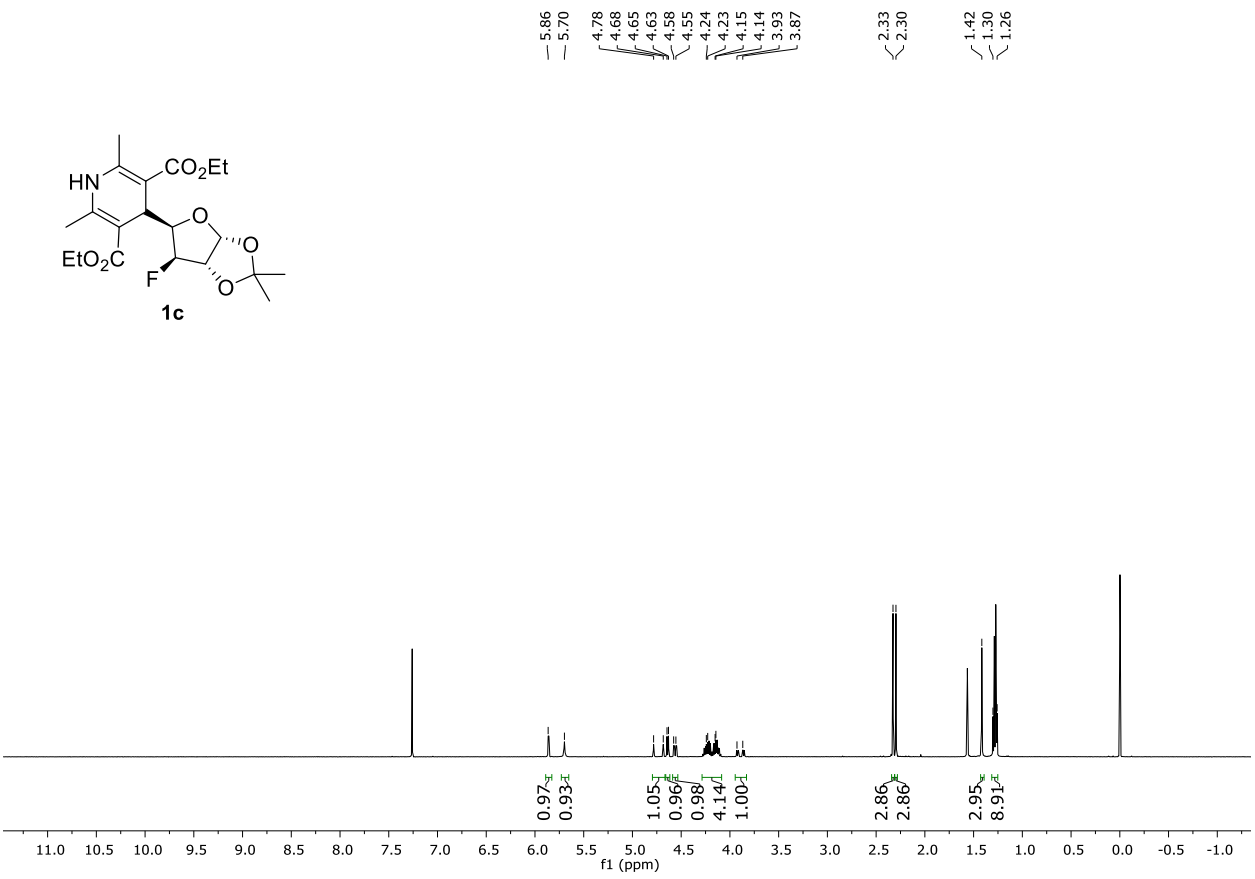
^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 4-((3a*R*,5*R*,6*S*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1b**)



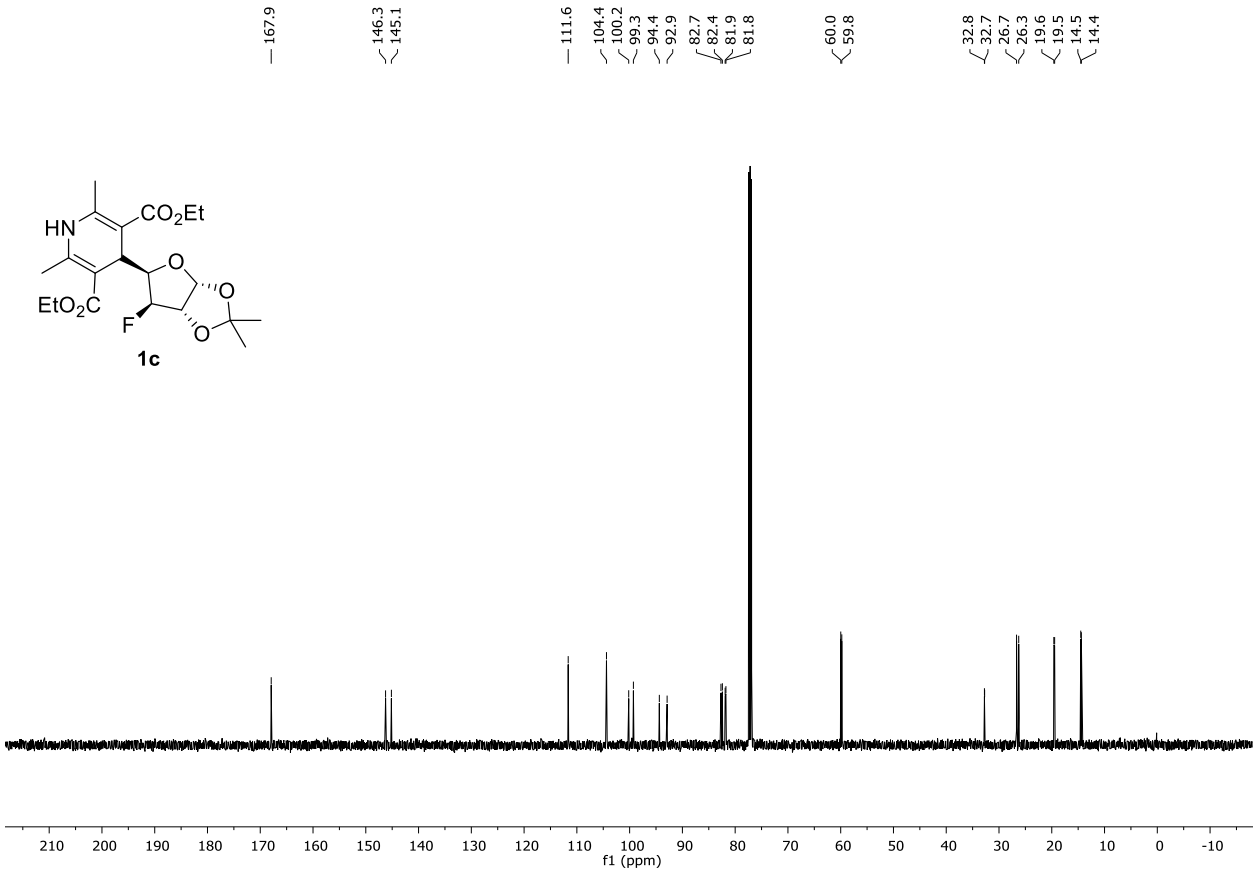
^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 4-((3a*R*,5*R*,6*S*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1b**)



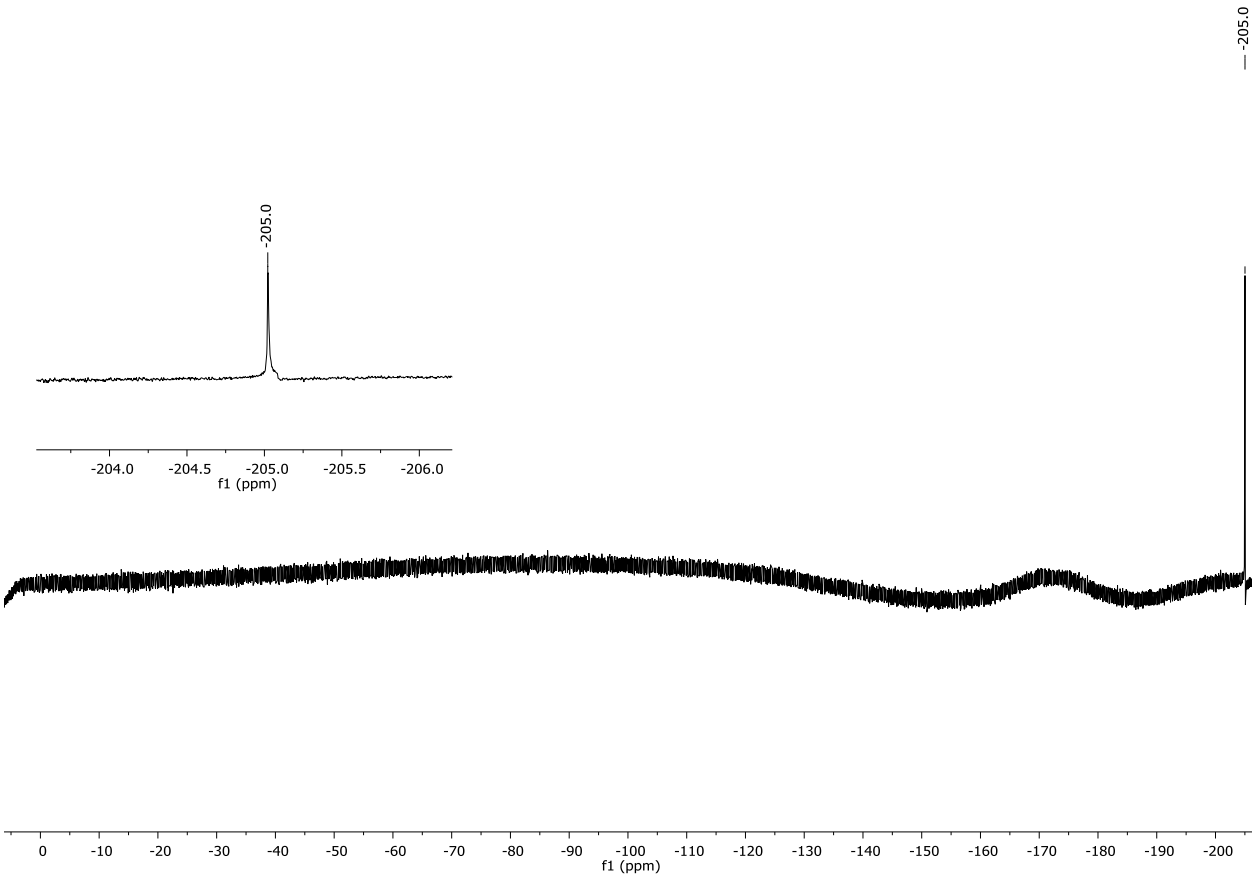
^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 4-((3a*R*,5*R*,6*S*,6a*S*)-6-Fluoro-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1c**)



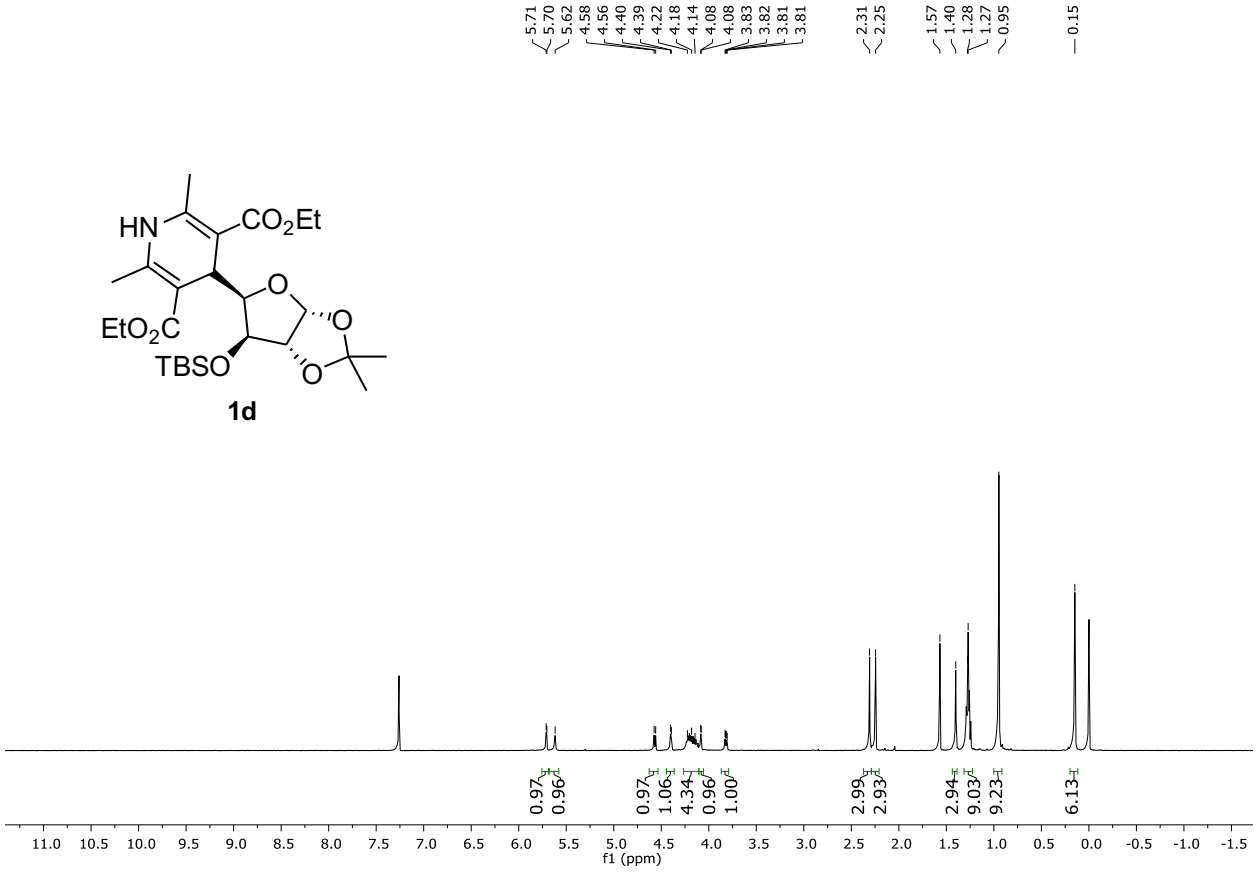
^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 4-((3a*R*,5*R*,6*S*,6a*S*)-6-Fluoro-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1c**)



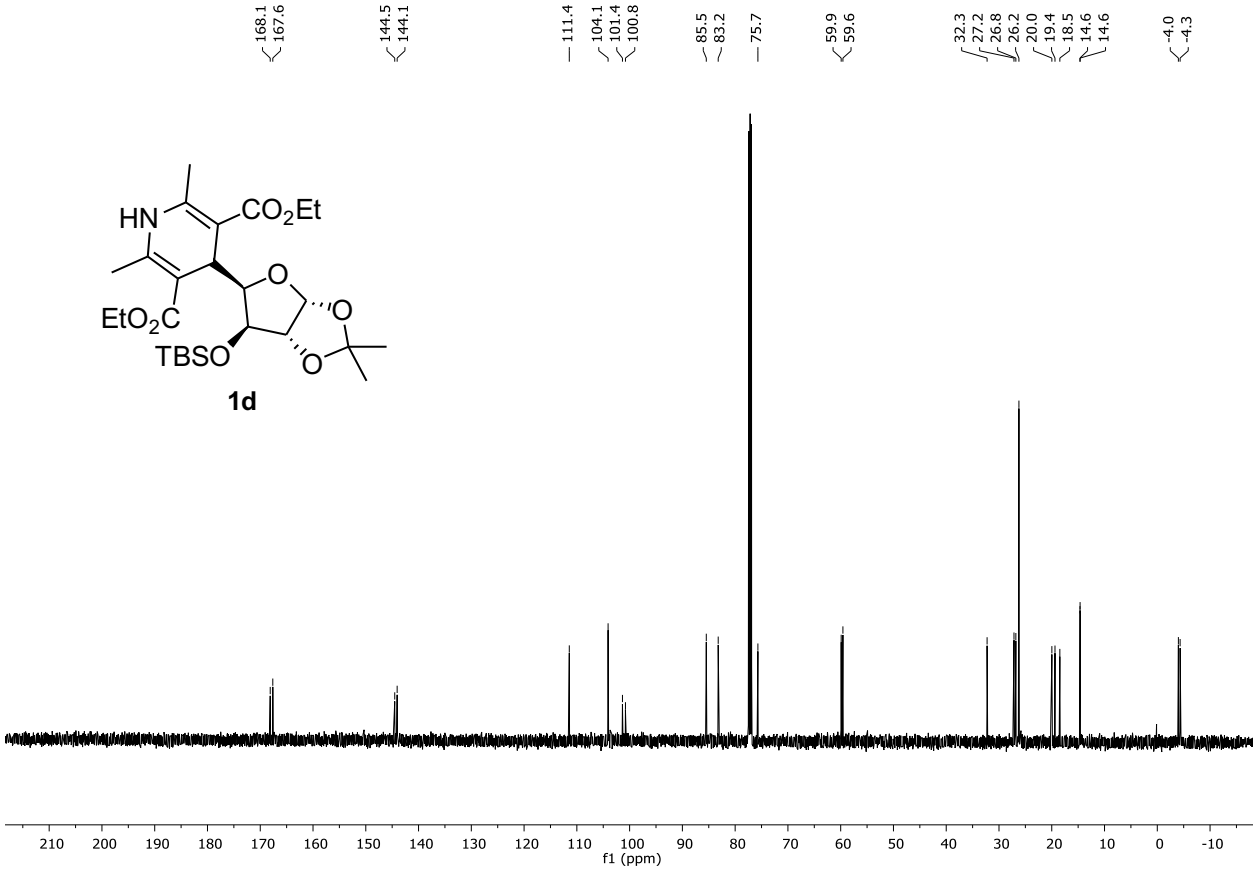
^{19}F NMR ($CDCl_3$, 471 MHz) of diethyl 4-((3a*R*,5*R*,6*S*,6a*S*)-6-Fluoro-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1c**)



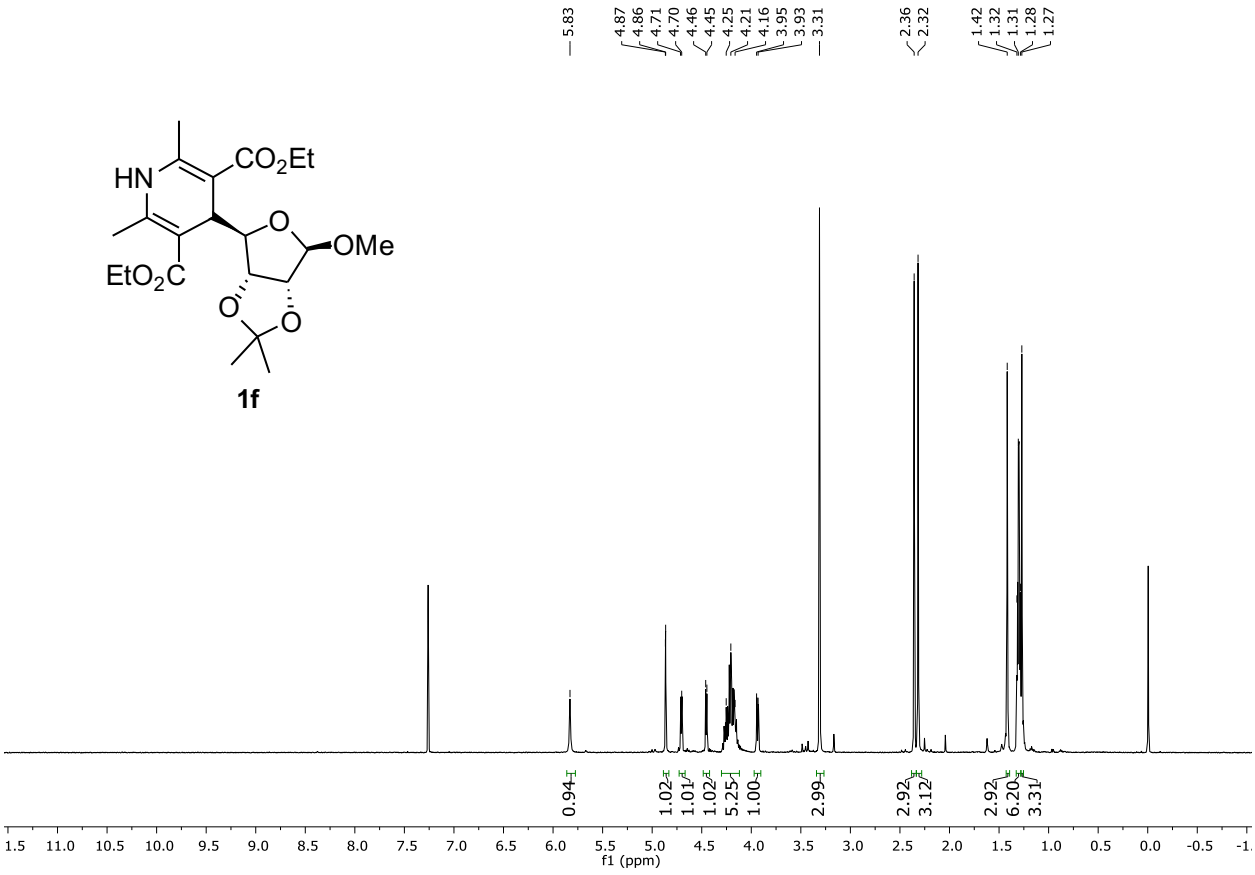
^{1}H NMR ($CDCl_3$, 500 MHz) of 4-((3a*R*,5*R*,6*S*,6a*S*)-6-((*tert*-Butyldimethylsilyl)oxy)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1d**)



^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 4-((3a*R*,5*R*,6*S*,6a*S*)-6-((*tert*-Butyldimethylsilyl)oxy)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1d**)

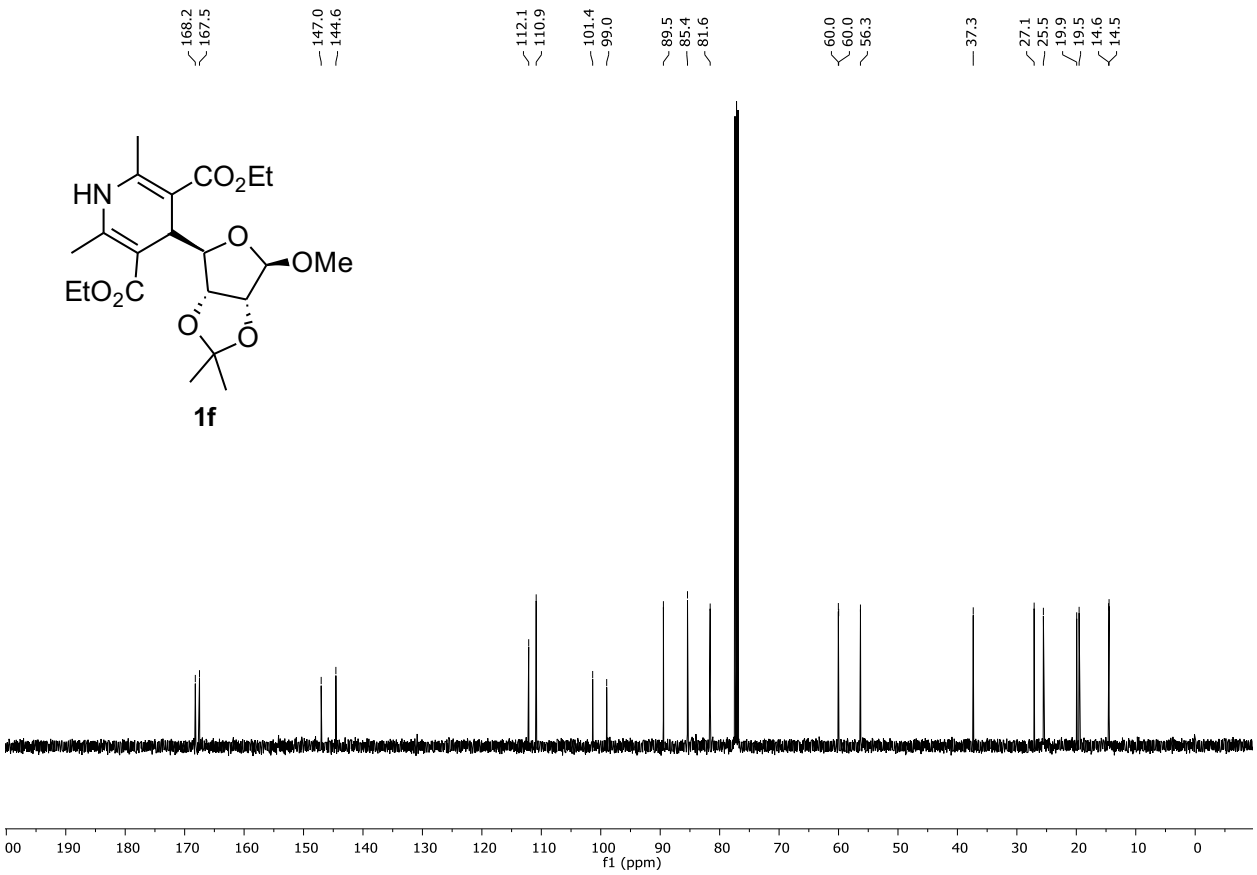


^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl ^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 4-((3a*R*,4*R*,6*R*,6a*R*)-6-Methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1f**)

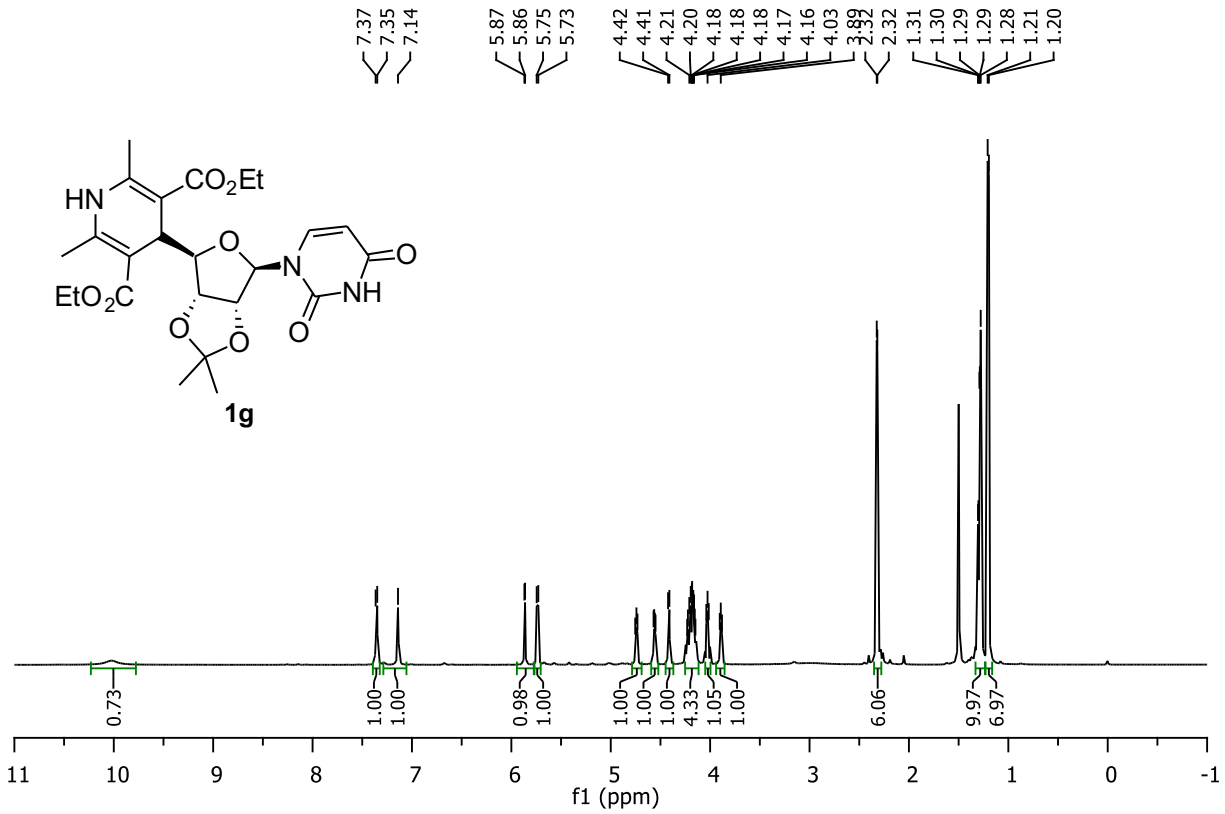


1f

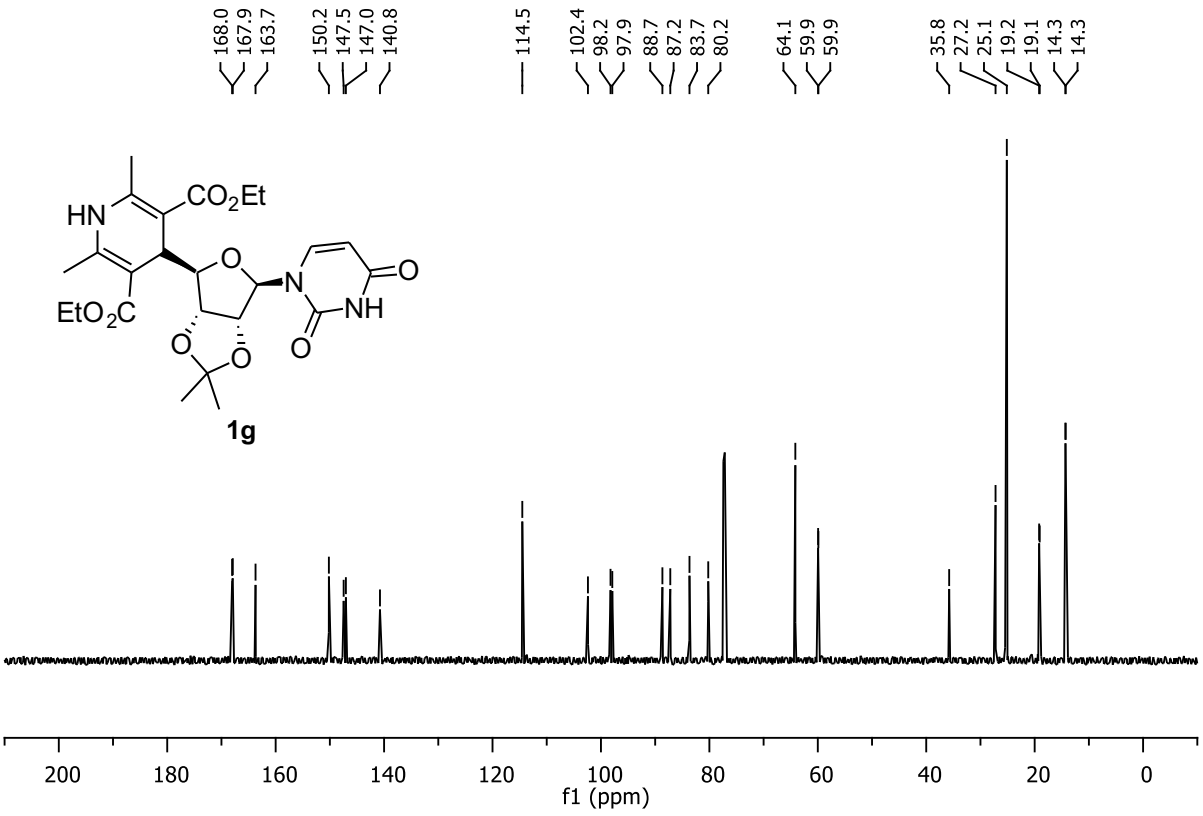
^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 4-((3a*R*,4*R*,6*R*,6a*R*)-6-Methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1f**)



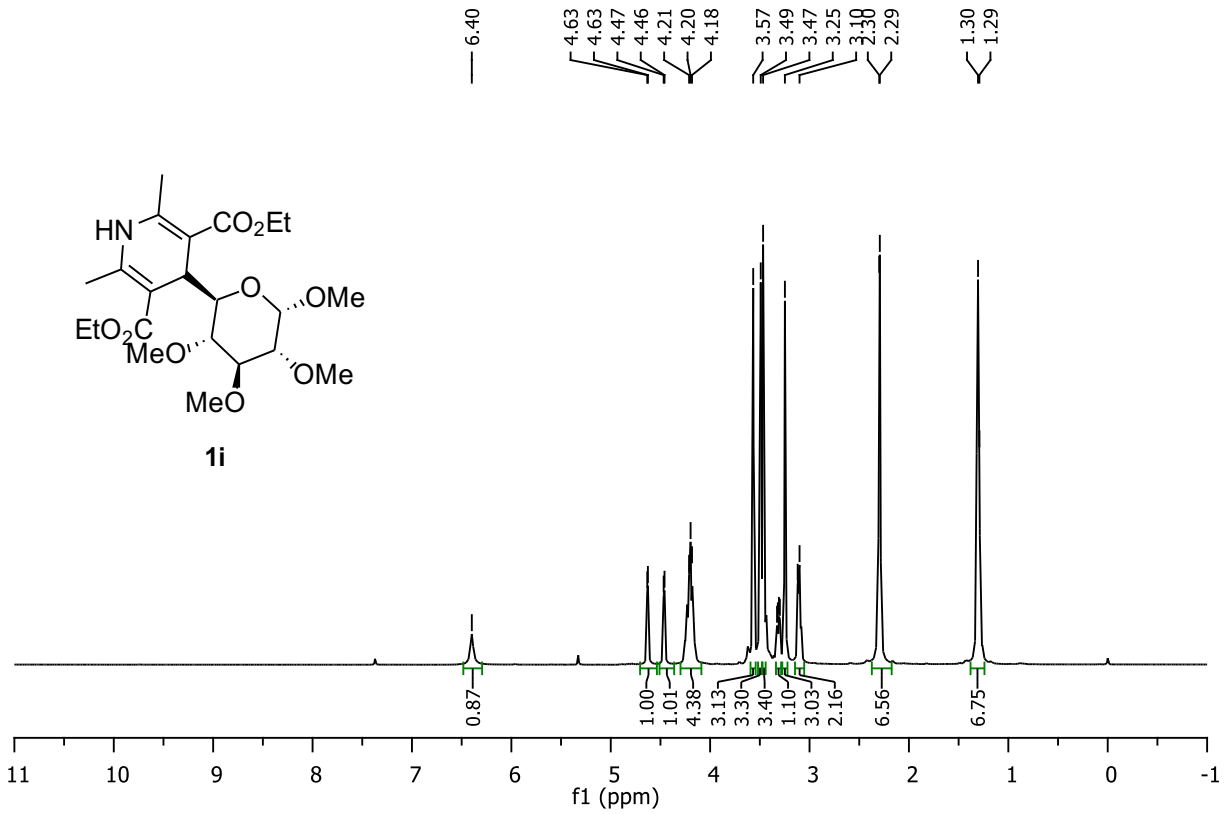
^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 4-((3a*R*,4*R*,6*R*,6a*R*)-6-(2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1g**)



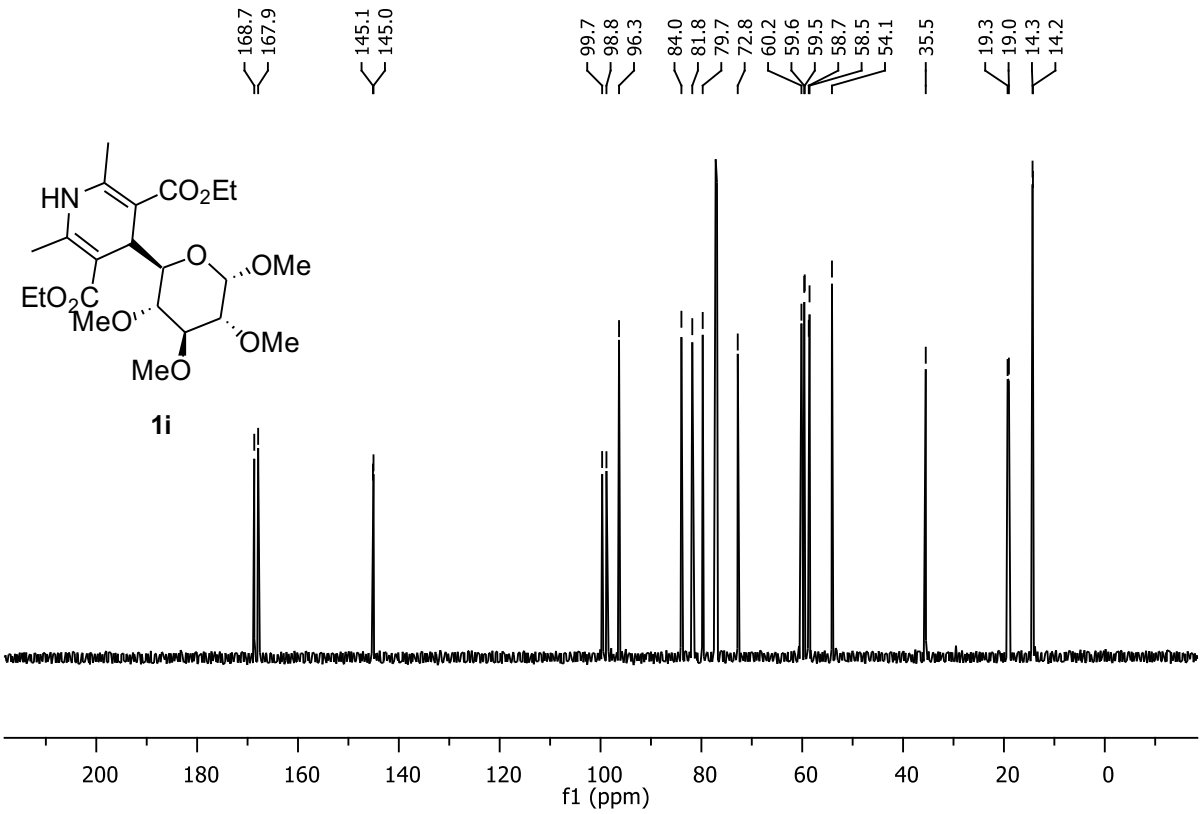
^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 4-((3a*R*,4*R*,6*R*,6a*R*)-6-(2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1g**)



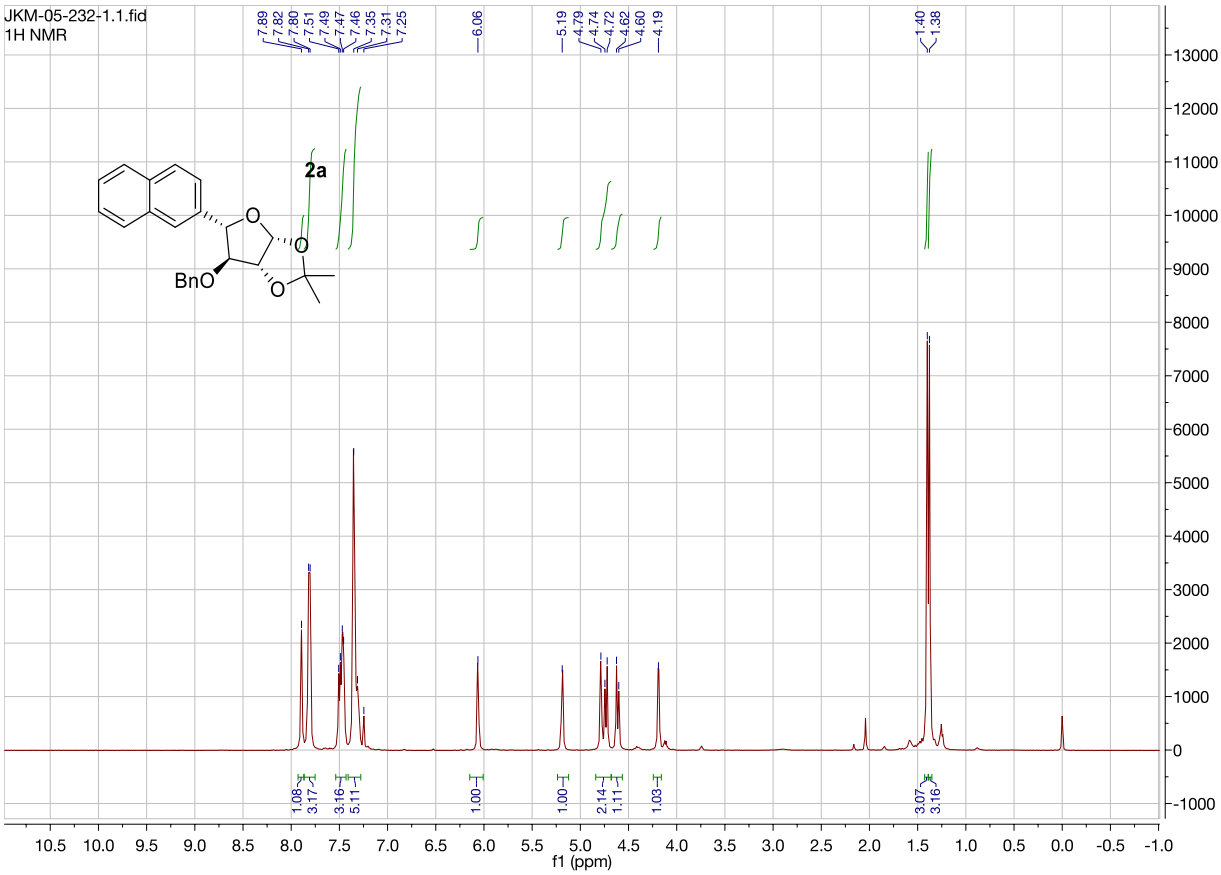
^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 2,6-dimethyl-4-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5,6-tetramethoxytetrahydro-2H-pyran-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (**1i**)



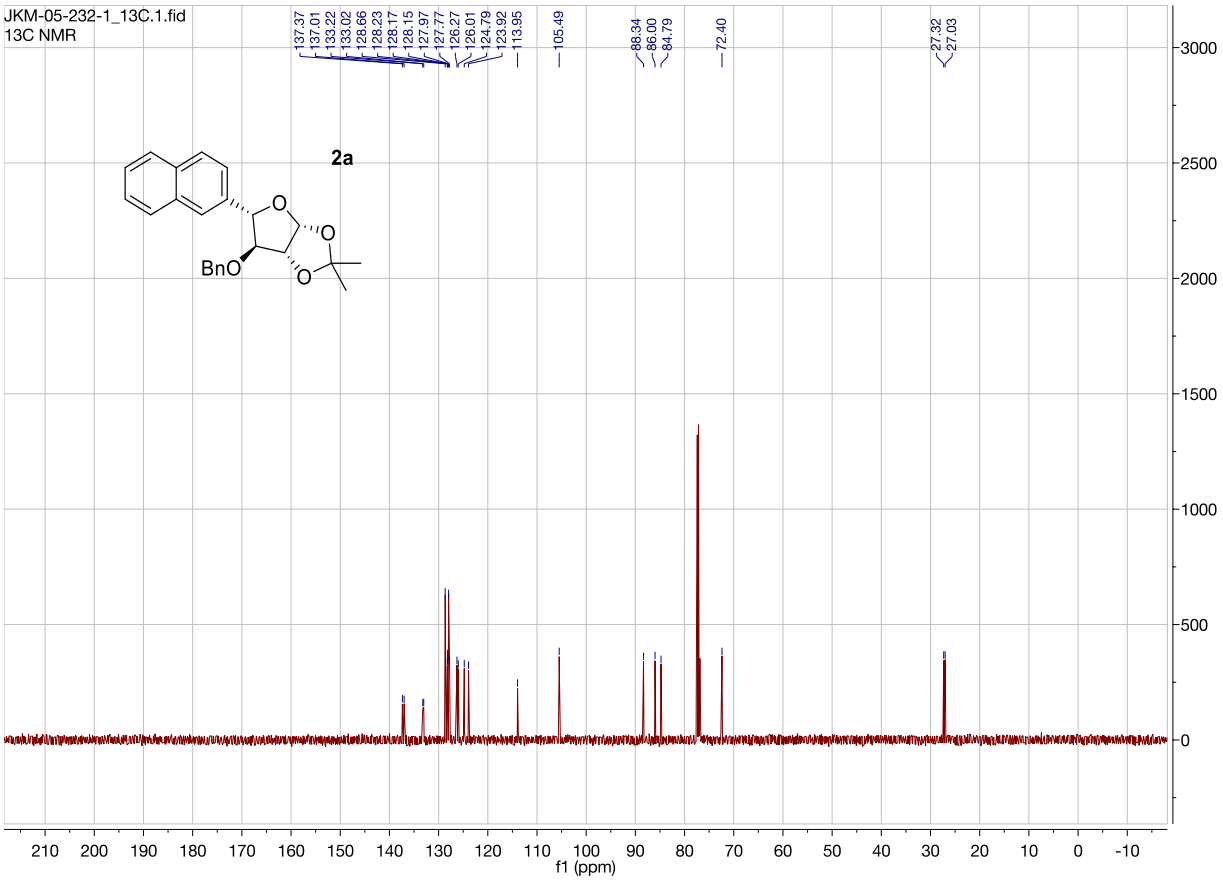
^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 2,6-dimethyl-4-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5,6-tetramethoxytetrahydro-2H-pyran-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (**1i**)



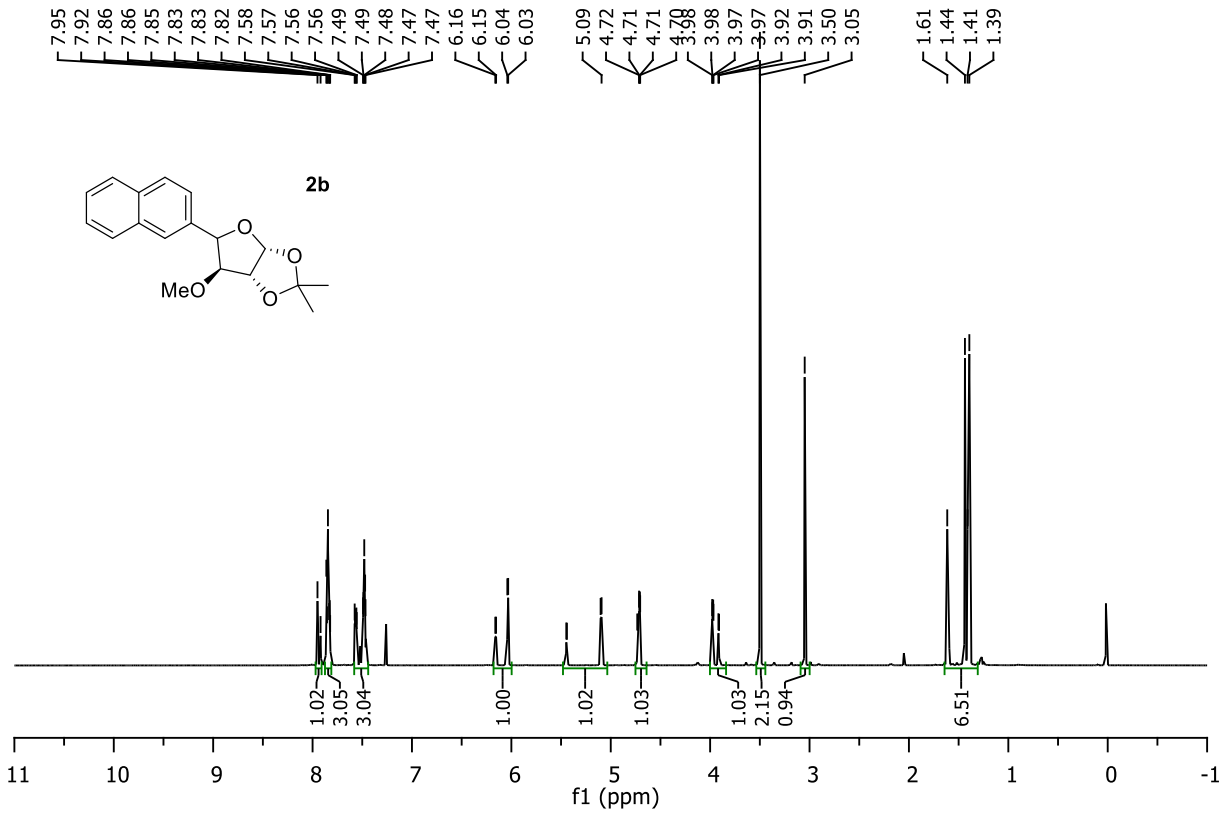
^{1}H NMR ($CDCl_3$, 500 MHz) of (3a*R*,5*S*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyl-5-(naphthalen-2-yl)tetrahydrofuro[2,3-d] [1,3]dioxole (**2a**)



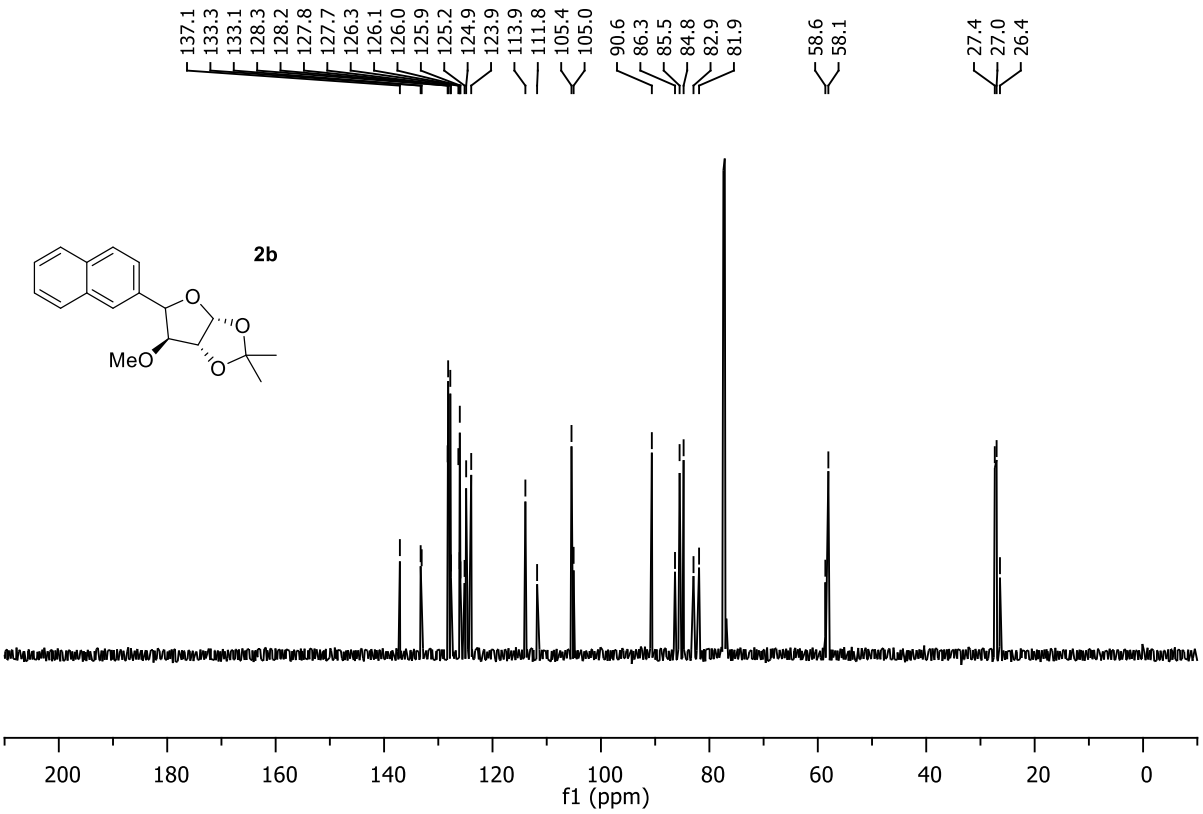
^{13}C NMR (126 MHz, $CDCl_3$) of (3a*R*,5*S*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyl-5-(naphthalen-2-yl)tetrahydrofuro[2,3-d] [1,3]dioxole (**2a**)



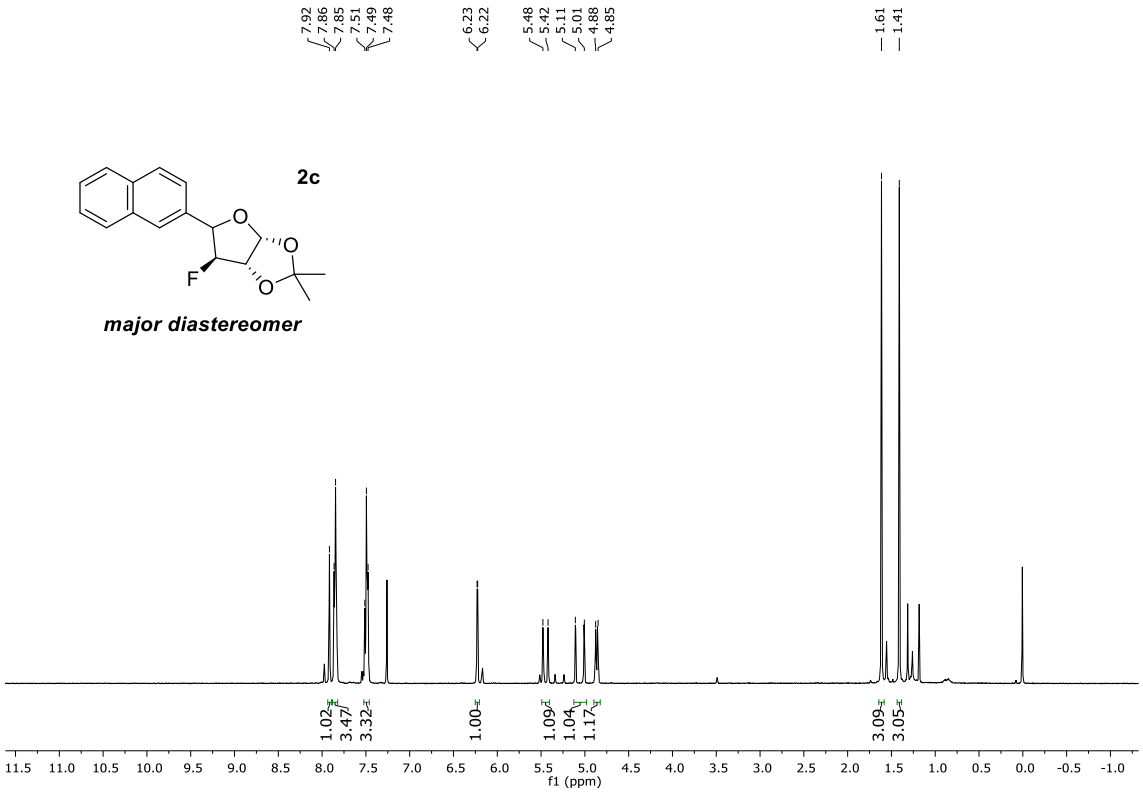
^{1}H NMR ($CDCl_3$, 500 MHz) of (3a*R*,5*R*,6*S*,6a*R*)-6-methoxy-2,2-dimethyl-5-(naphthalen-2-yl)tetrahydrofuro[2,3-d] [1,3]dioxole (**2b**)

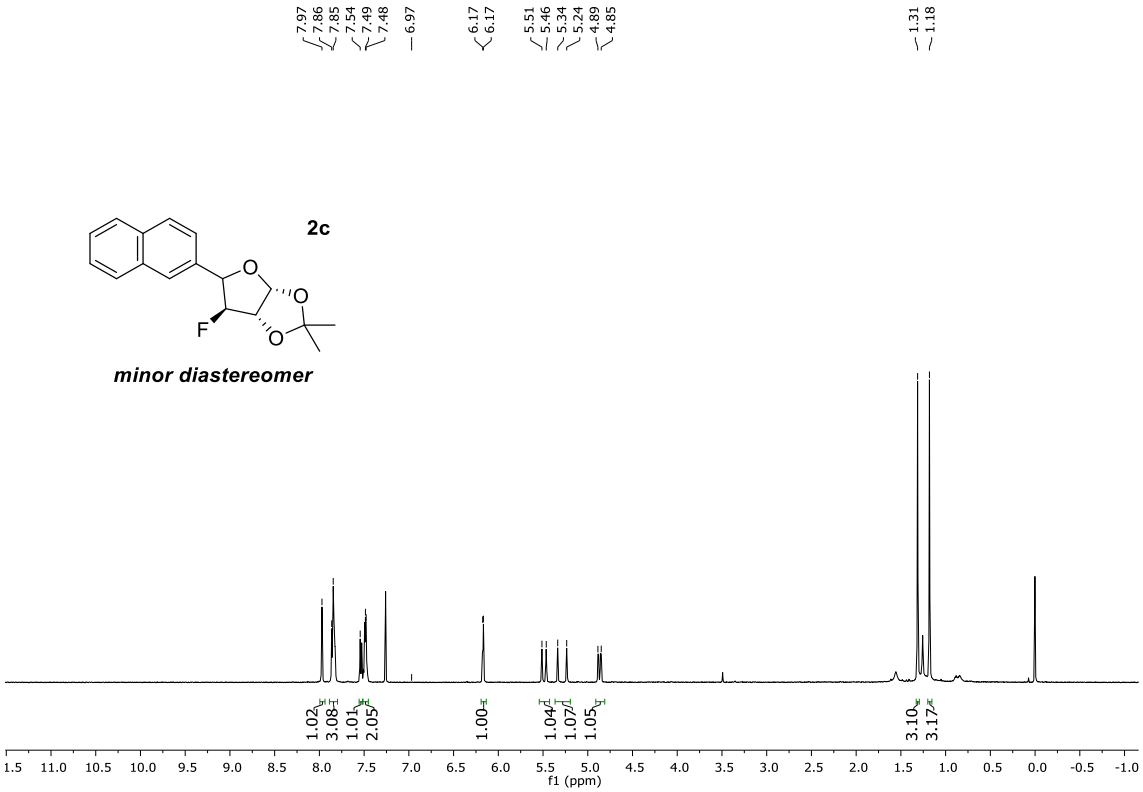


^{13}C NMR (126 MHz, $CDCl_3$) of (3a*R*,5*R*,6*S*,6a*R*)-6-methoxy-2,2-dimethyl-5-(naphthalen-2-yl)tetrahydrofuro[2,3-d] [1,3]dioxole (**2b**)

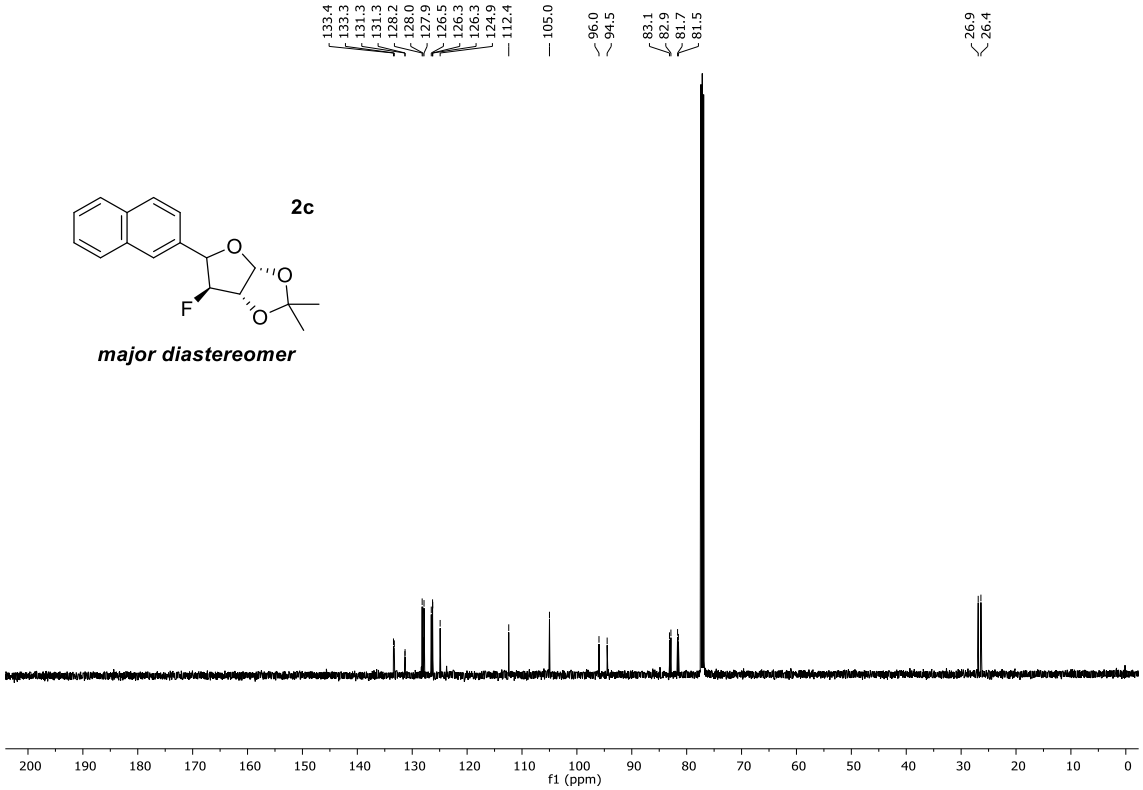


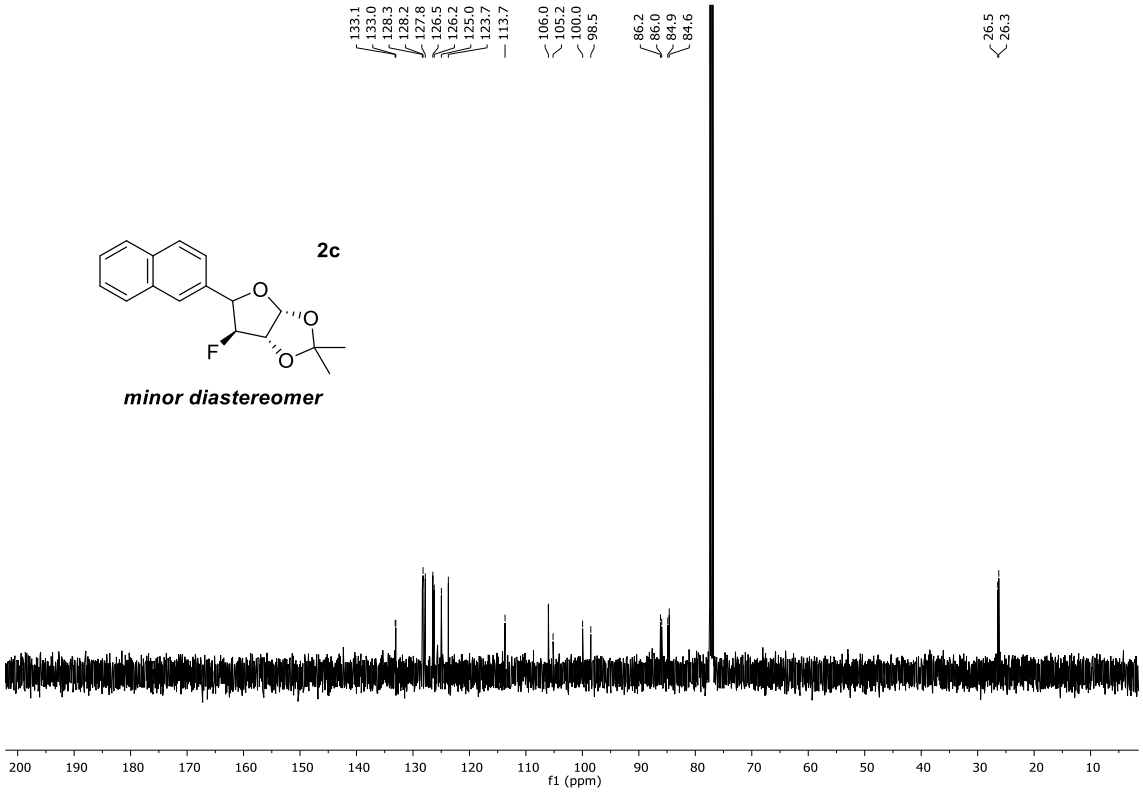
^{1}H NMR ($CDCl_3$, 500 MHz) of (3a*R*,6*S*,6a*S*)-6-Fluoro-2,2-dimethyl-5-(naphthalen-2-yl) tetrahydrofuro[2,3-*d*][1,3]dioxole (**2c**)



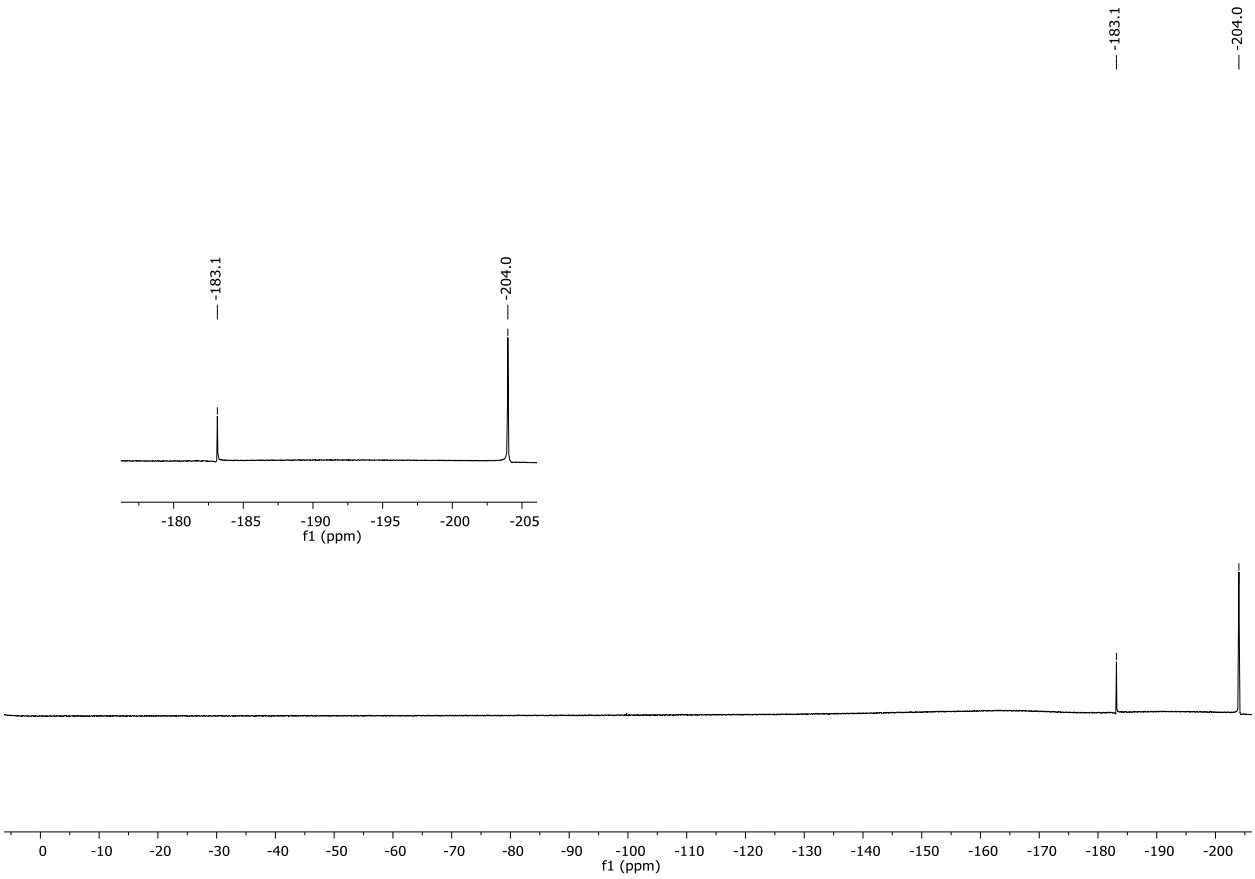


^{13}C NMR (126 MHz, $CDCl_3$) of (3a*R*,6*S*,6a*S*)-6-Fluoro-2,2-dimethyl-5-(naphthalen-2-yl) tetrahydrofuro[2,3-*d*][1,3]dioxole (**2c**)

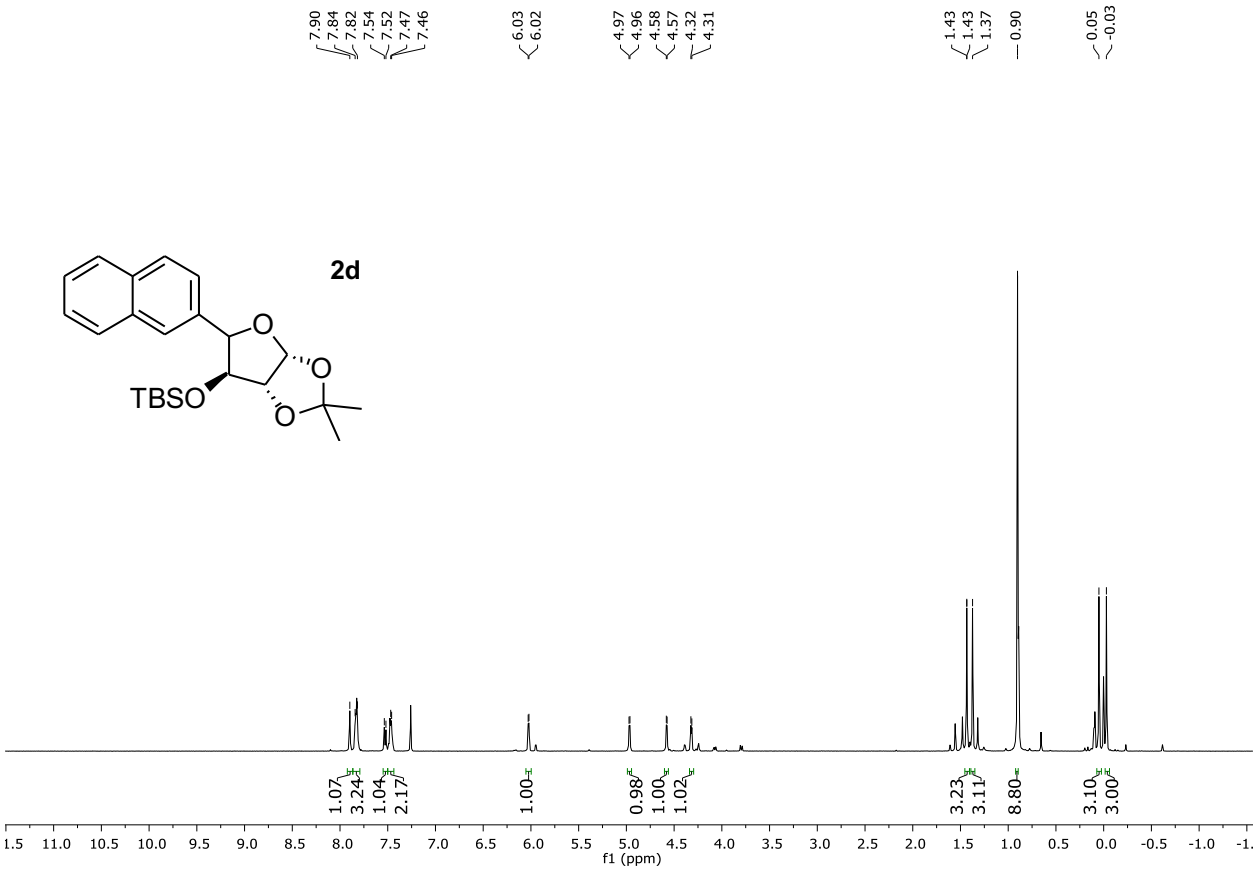




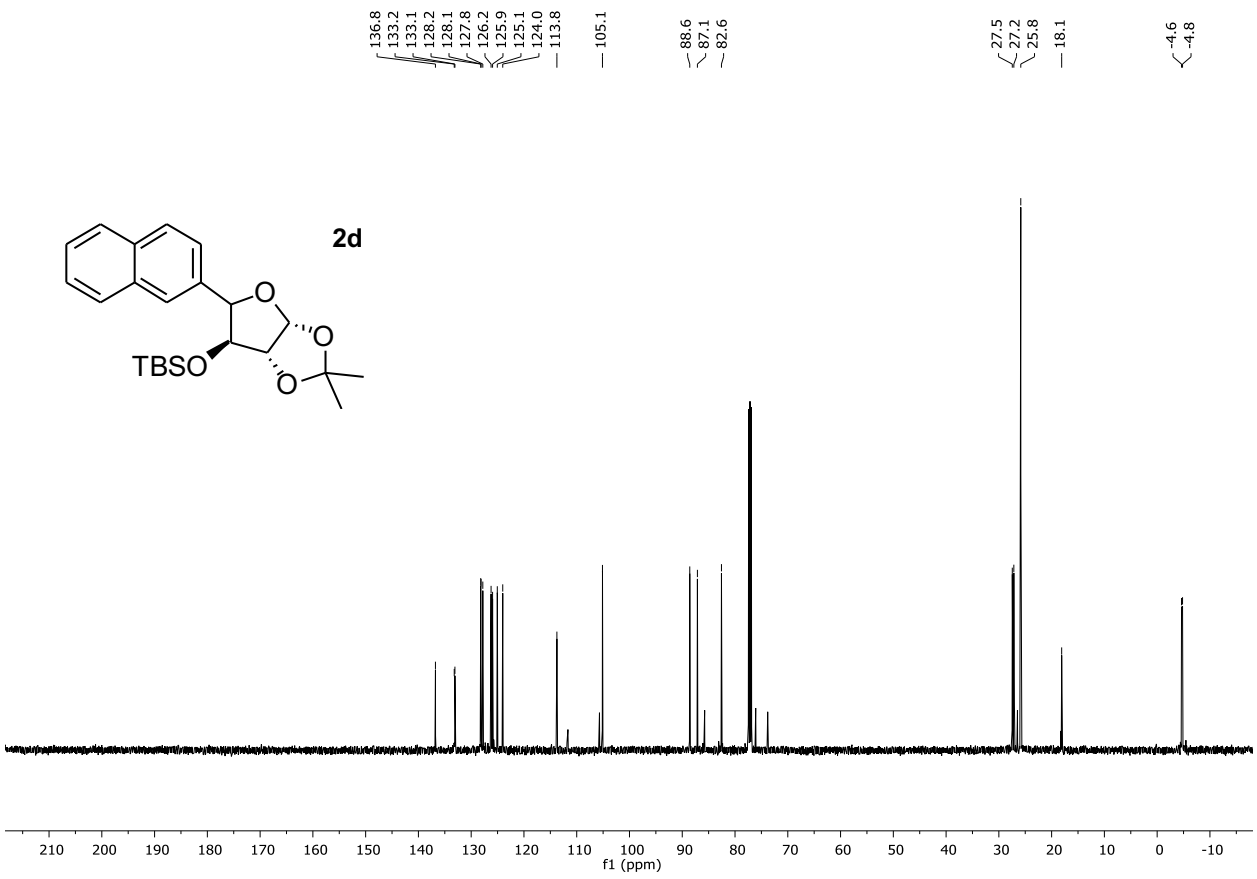
^{19}F NMR (471 MHz, $CDCl_3$) of (3a*R*,6*S*,6a*S*)-6-Fluoro-2,2-dimethyl-5-(naphthalen-2-yl) tetrahydrofuro[2,3-*d*][1,3]dioxole (**2c**)



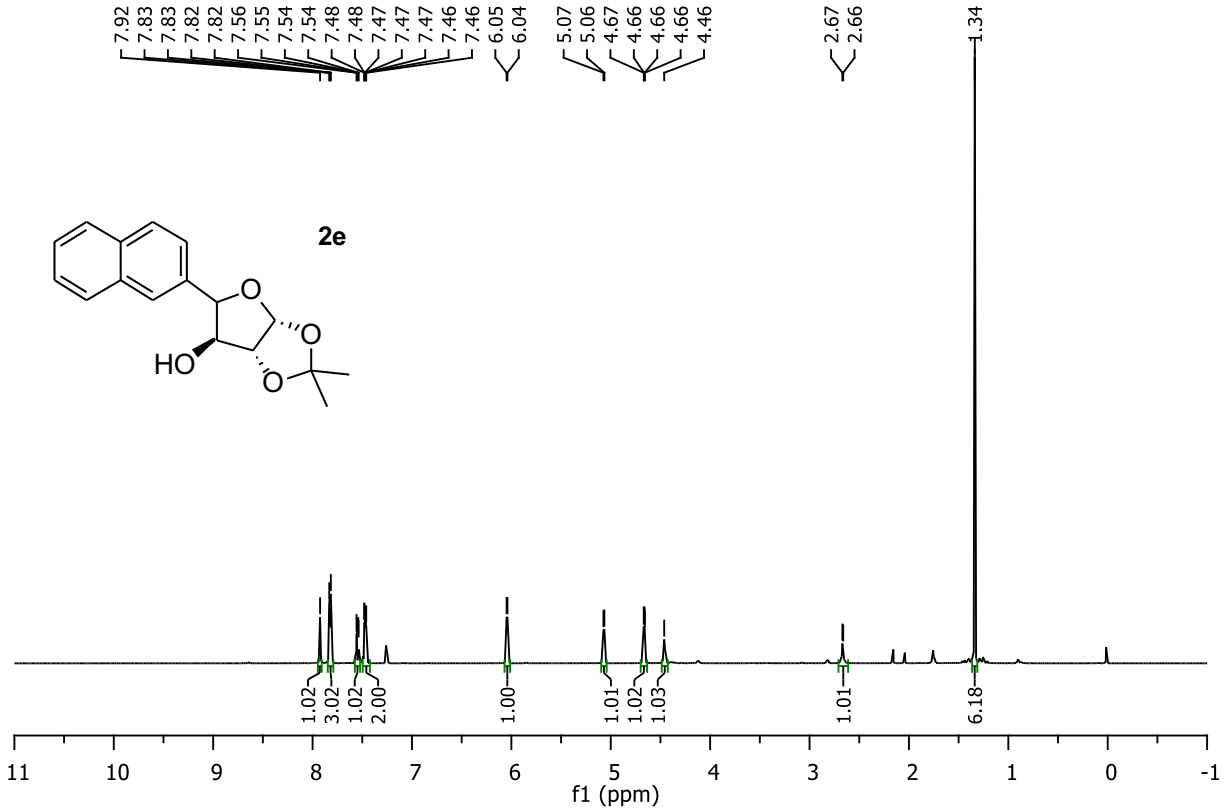
^{1}H NMR ($CDCl_3$, 500 MHz) of *tert*-Butyl(((3a*R*,6*S*,6a*R*)-2,2-dimethyl-5-(naphthalen-2-yl)tetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)dimethylsilane (**2d**)



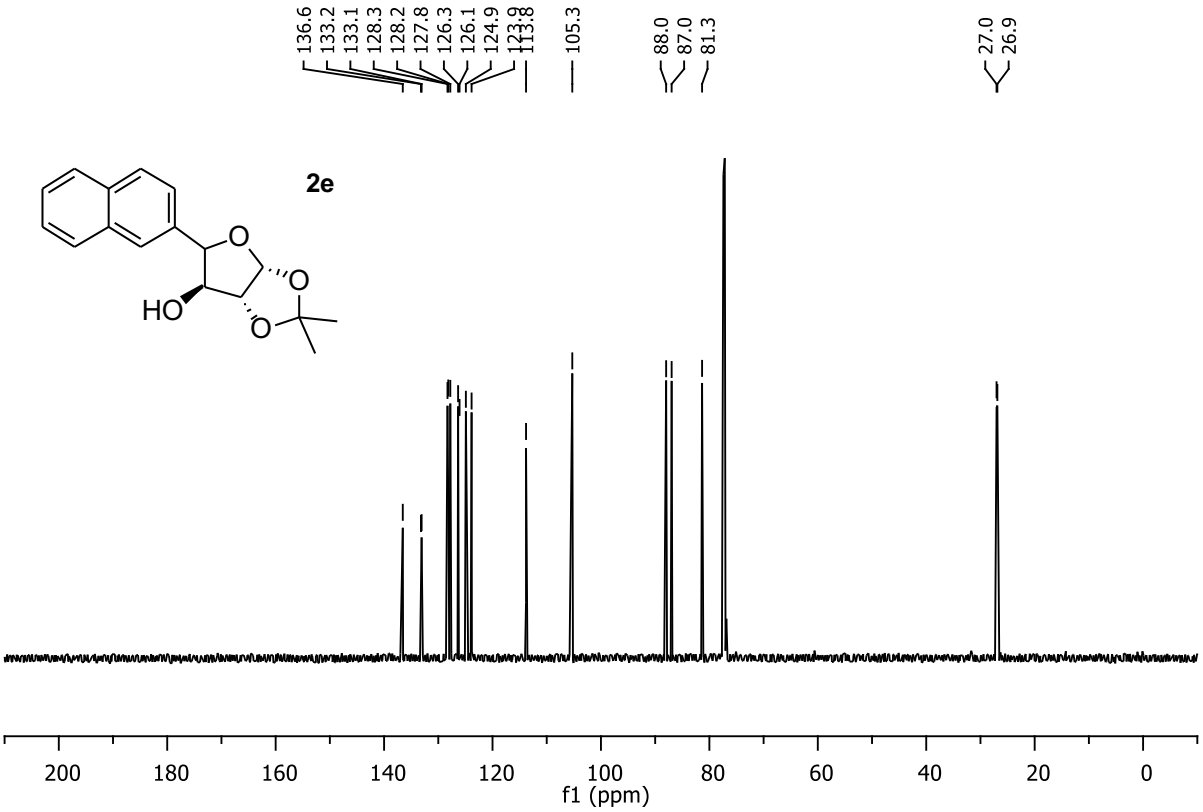
^{13}C NMR (126 MHz, $CDCl_3$) of *tert*-Butyl(((3a*R*,6*S*,6a*R*)-2,2-dimethyl-5-(naphthalen-2-yl)tetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)dimethylsilane (**2d**)



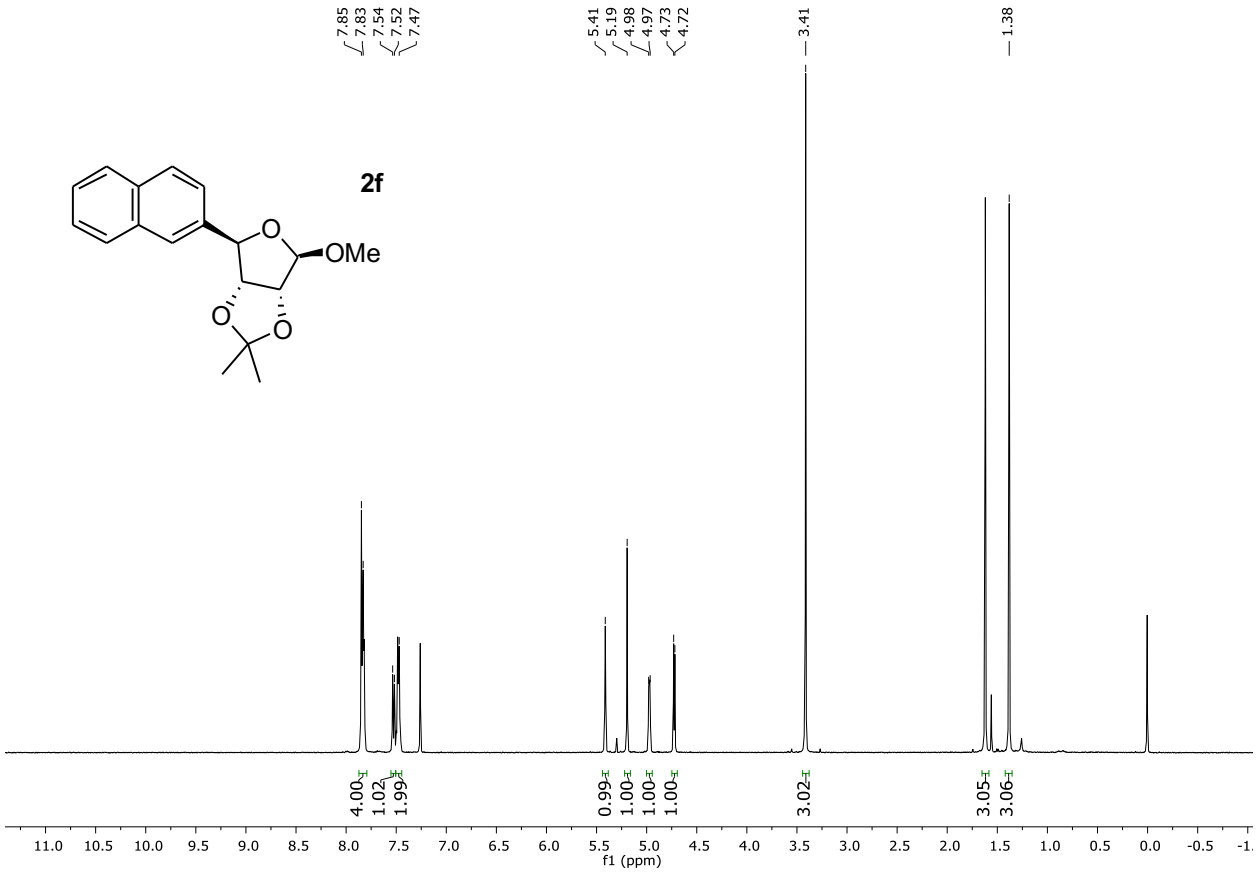
^{1}H NMR ($CDCl_3$, 500 MHz) of (3a*R*,6*S*,6a*R*)-2,2-dimethyl-5-(naphthalen-2-yl)tetrahydrofuro[2,3-d][1,3]dioxol-6-ol (**2e**)



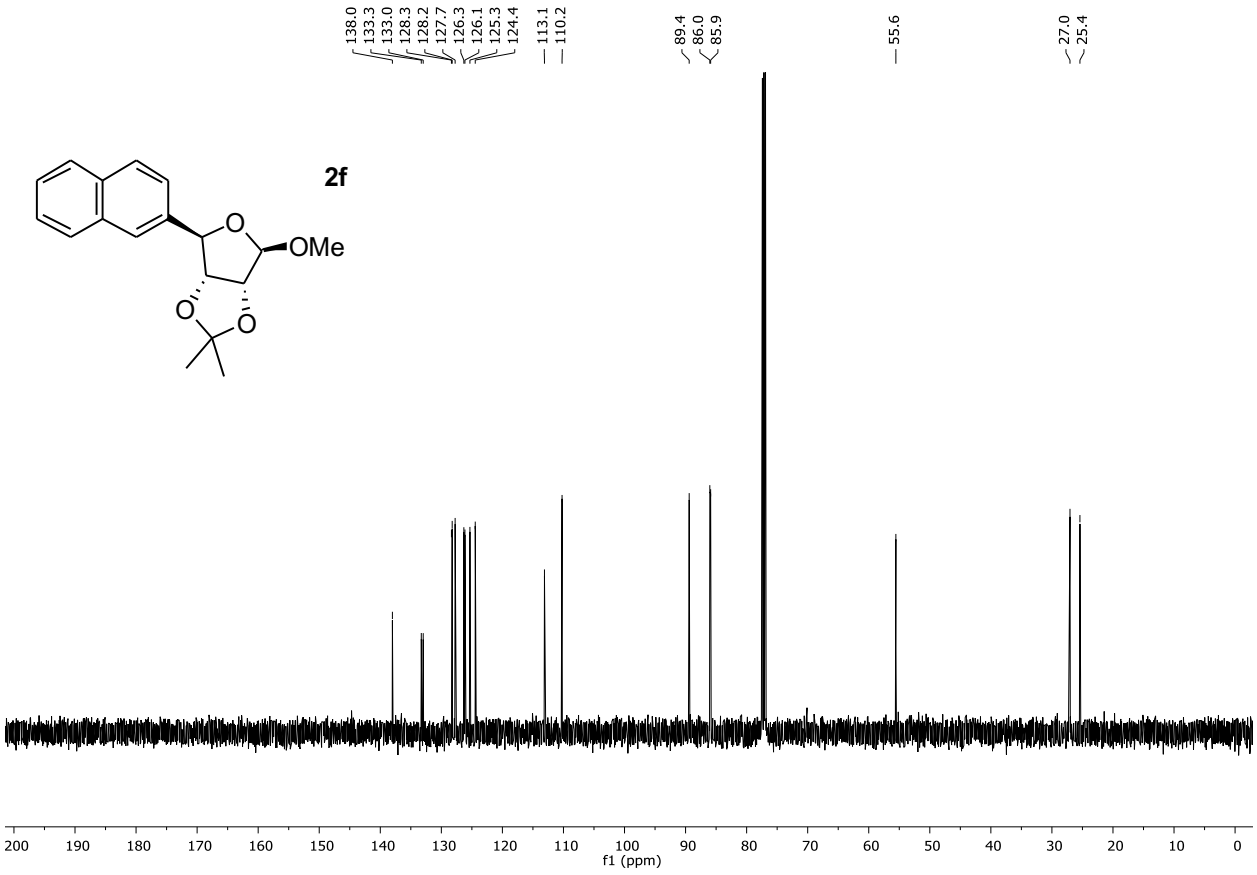
^{13}C NMR ($CDCl_3$, 126 MHz) of (3a*R*,6*S*,6a*R*)-2,2-dimethyl-5-(naphthalen-2-yl)tetrahydrofuro[2,3-d][1,3]dioxol-6-ol (**2e**)



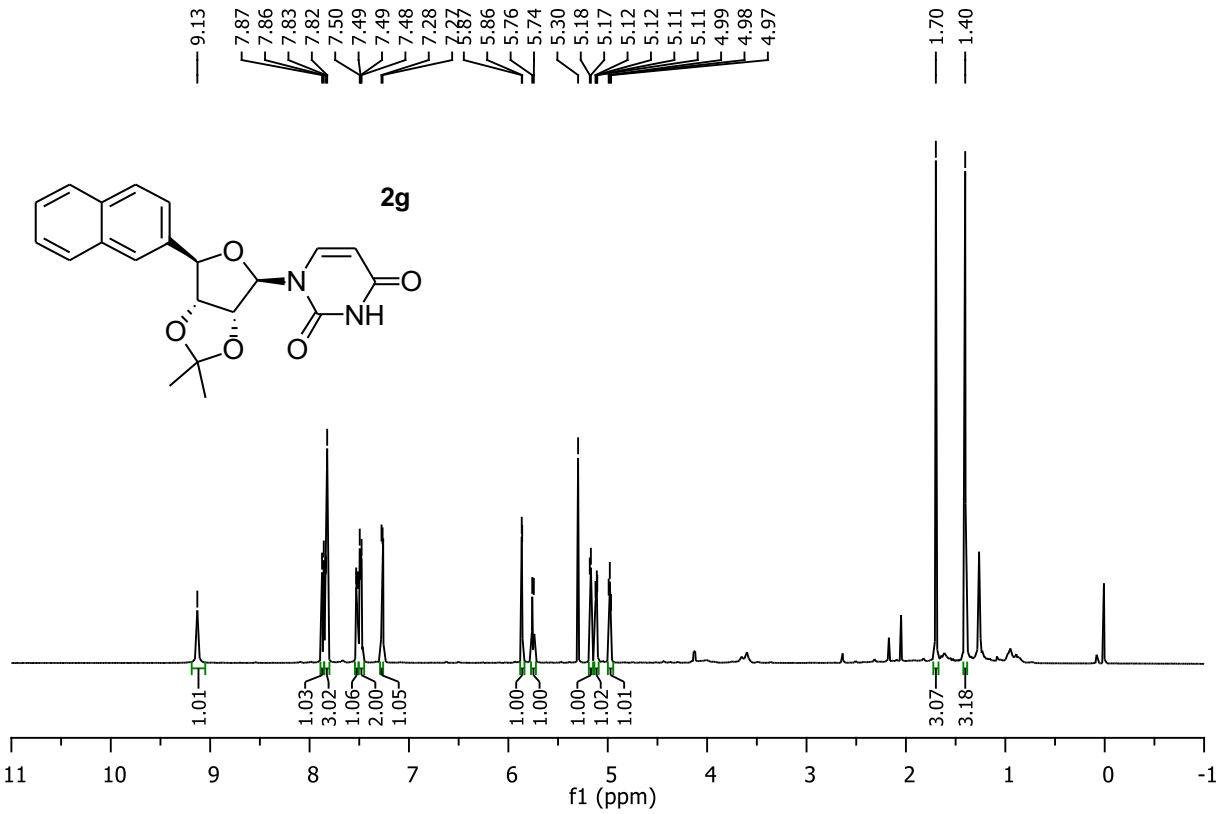
^{1}H NMR ($CDCl_3$, 500 MHz) of (3a*R*,4*R*,6*R*,6a*R*)-4-Methoxy-2,2-dimethyl-6-(naphthalen-2-yl)tetrahydrofuro[3,4-*d*][1,3]dioxole (**2f**)



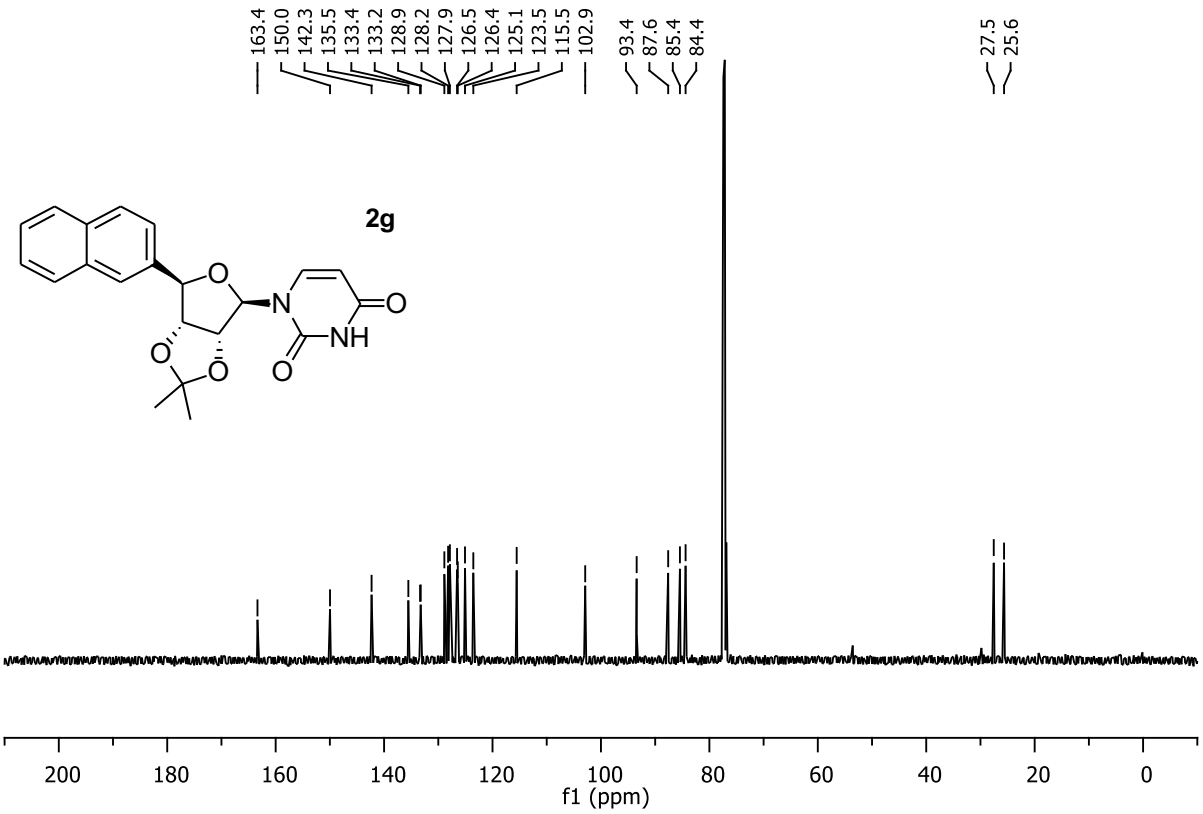
^{13}C NMR (126 MHz, $CDCl_3$) of (3a*R*,4*R*,6*R*,6a*R*)-4-Methoxy-2,2-dimethyl-6-(naphthalen-2-yl)tetrahydrofuro[3,4-*d*][1,3]dioxole (**2f**)



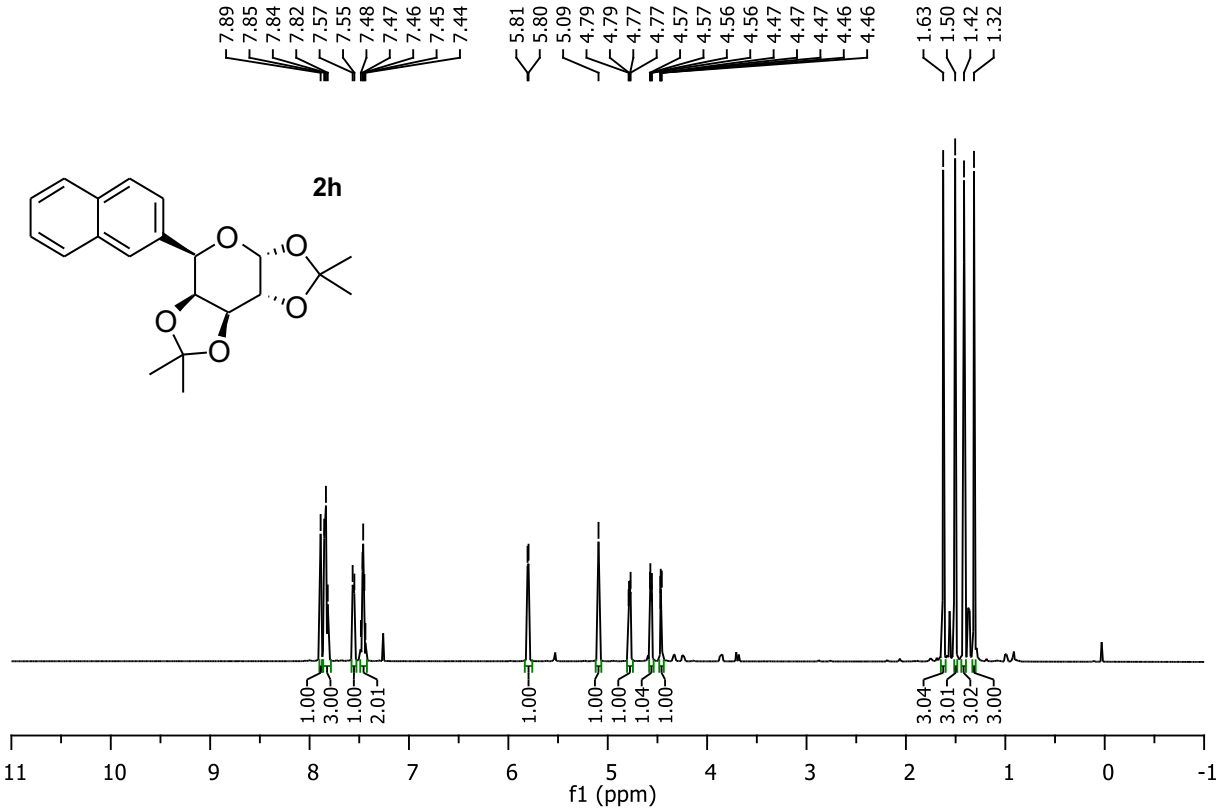
^{1}H NMR ($CDCl_3$, 500 MHz) of 1-((3a*R*,4*R*,6*R*,6a*R*)-2,2-dimethyl-6-(naphthalen-2-yl) tetrahydrofuro[3,4-d][1,3]dioxol-4-yl) pyrimidine-2,4(1H,3H)-dione (**2g**)



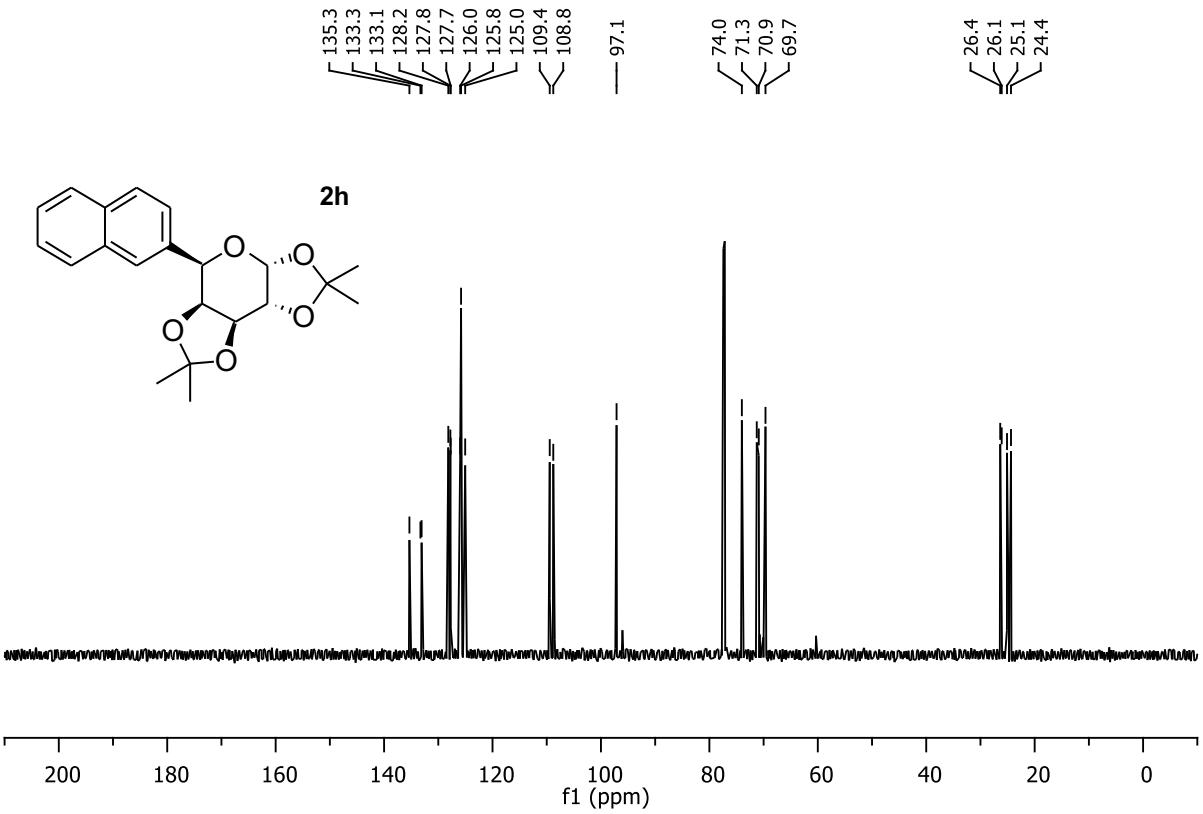
^{13}C NMR (126 MHz, $CDCl_3$) of 1-((3a*R*,4*R*,6*R*,6a*R*)-2,2-dimethyl-6-(naphthalen-2-yl) tetrahydrofuro[3,4-d][1,3]dioxol-4-yl) pyrimidine-2,4(1H,3H)-dione (**2g**)



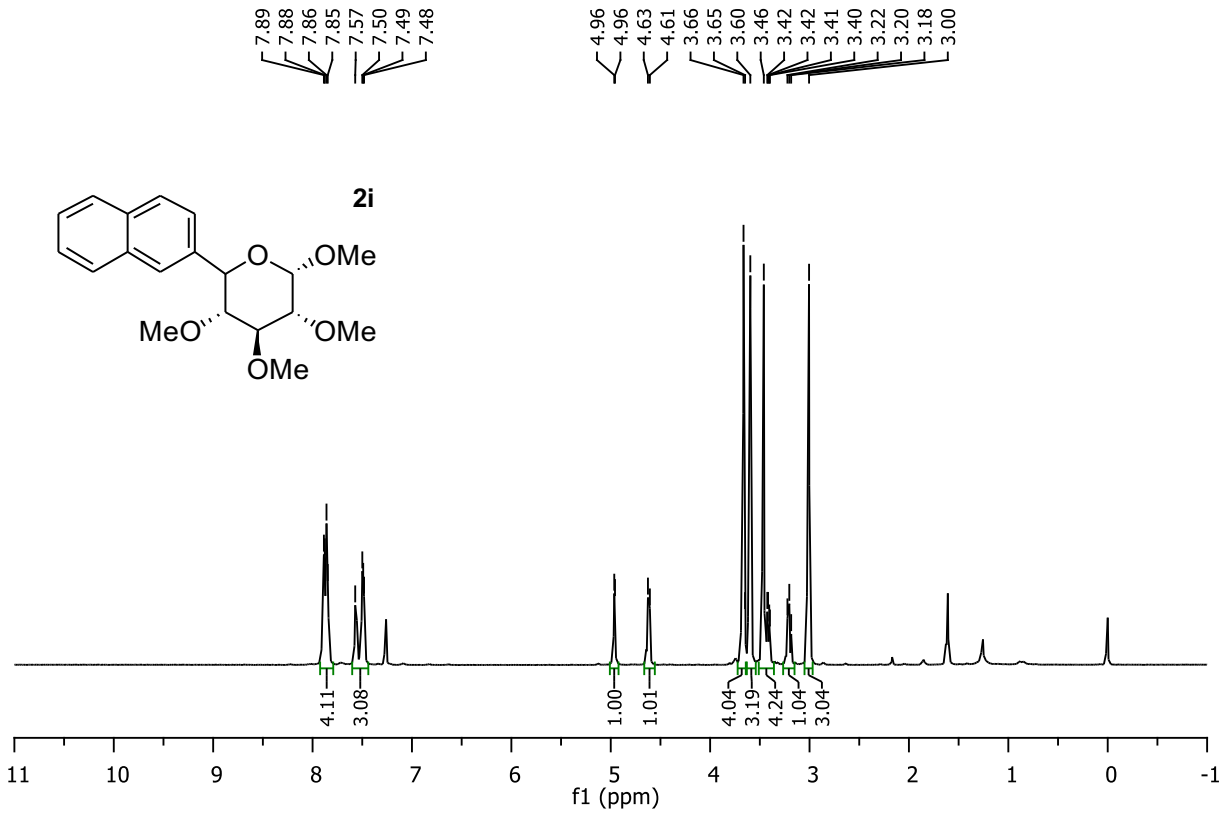
^{1}H NMR ($CDCl_3$, 500 MHz) of (3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyl-5-(naphthalen-2-yl)tetrahydro-5H-bis ([1,3]dioxolo)[4,5-b:4',5'-d]pyran (**2h**)



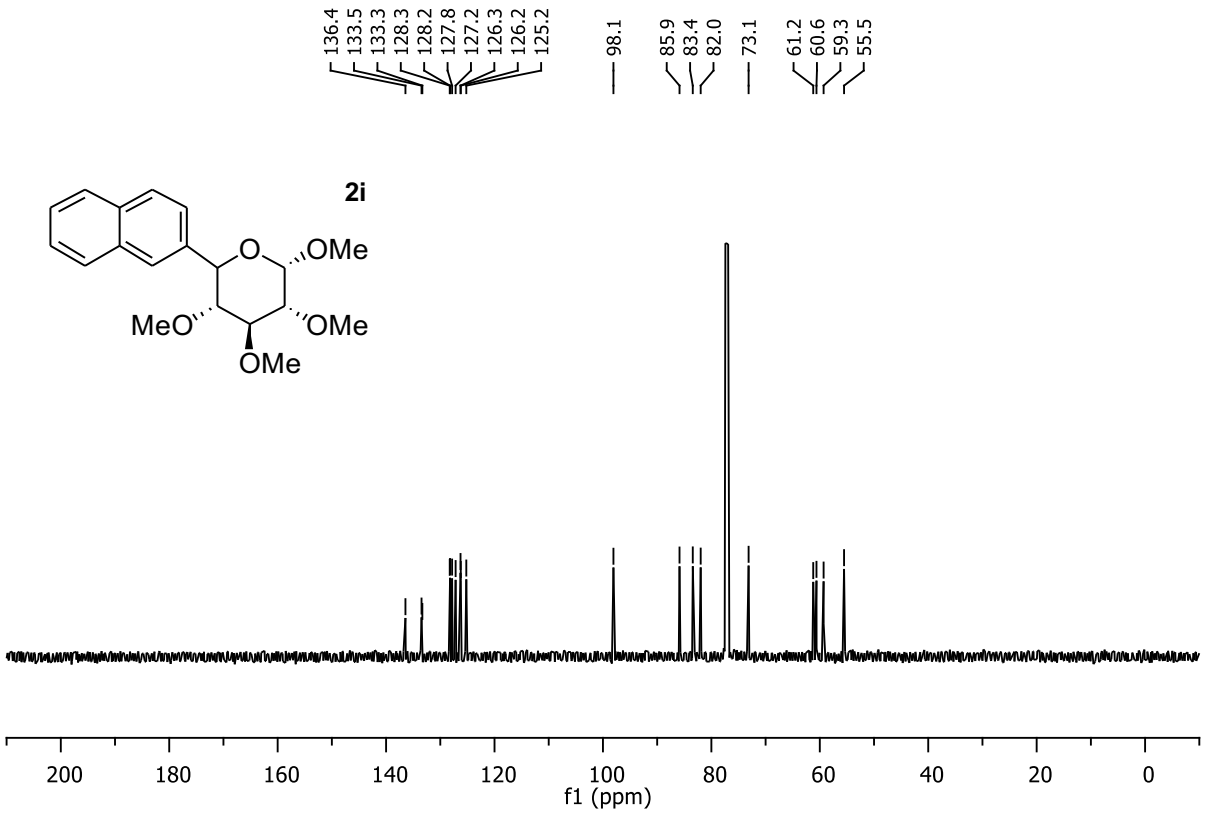
^{13}C NMR (126 MHz, $CDCl_3$) of (3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyl-5-(naphthalen-2-yl)tetrahydro-5H-bis ([1,3]dioxolo)[4,5-b:4',5'-d]pyran **(2h)**



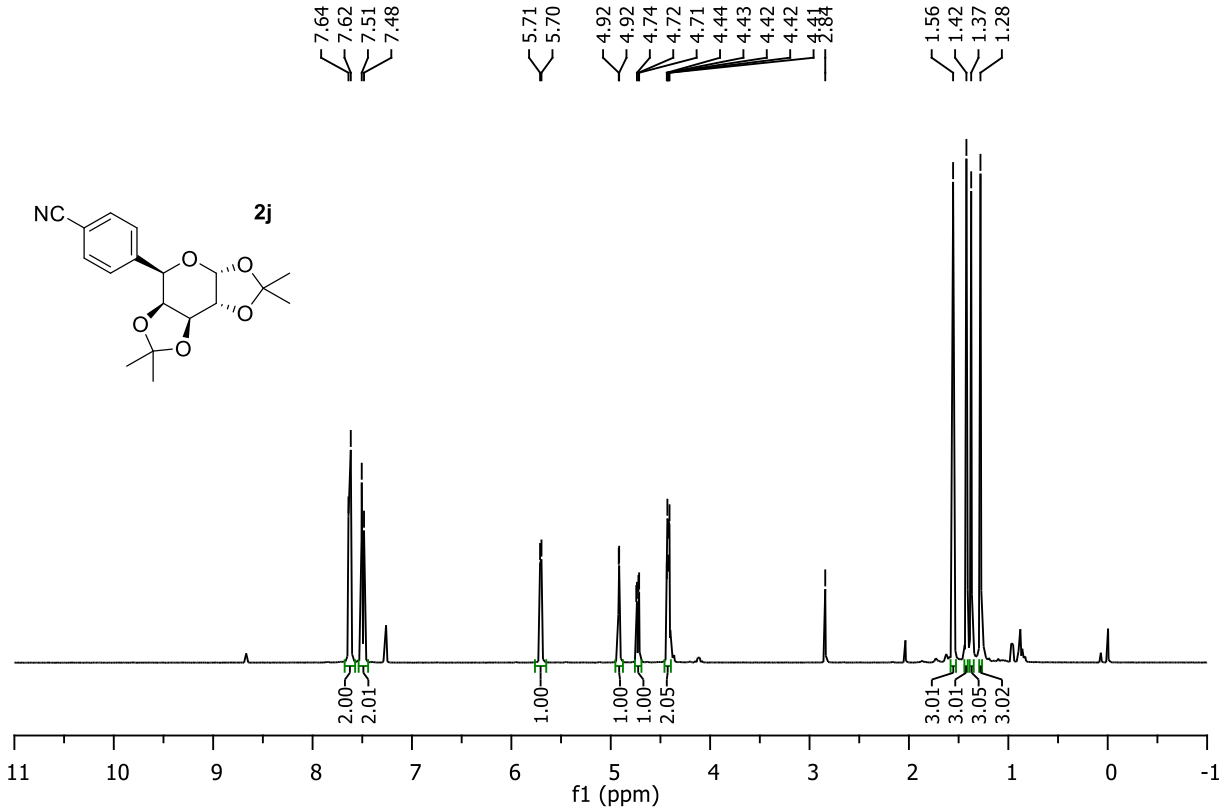
^{1}H NMR ($CDCl_3$, 500 MHz) of (2*S*,3*R*,4*S*,5*R*)-2,3,4,5-tetramethoxy-6-(naphthalen-2-yl)tetrahydro-2H-pyran (**2i**)



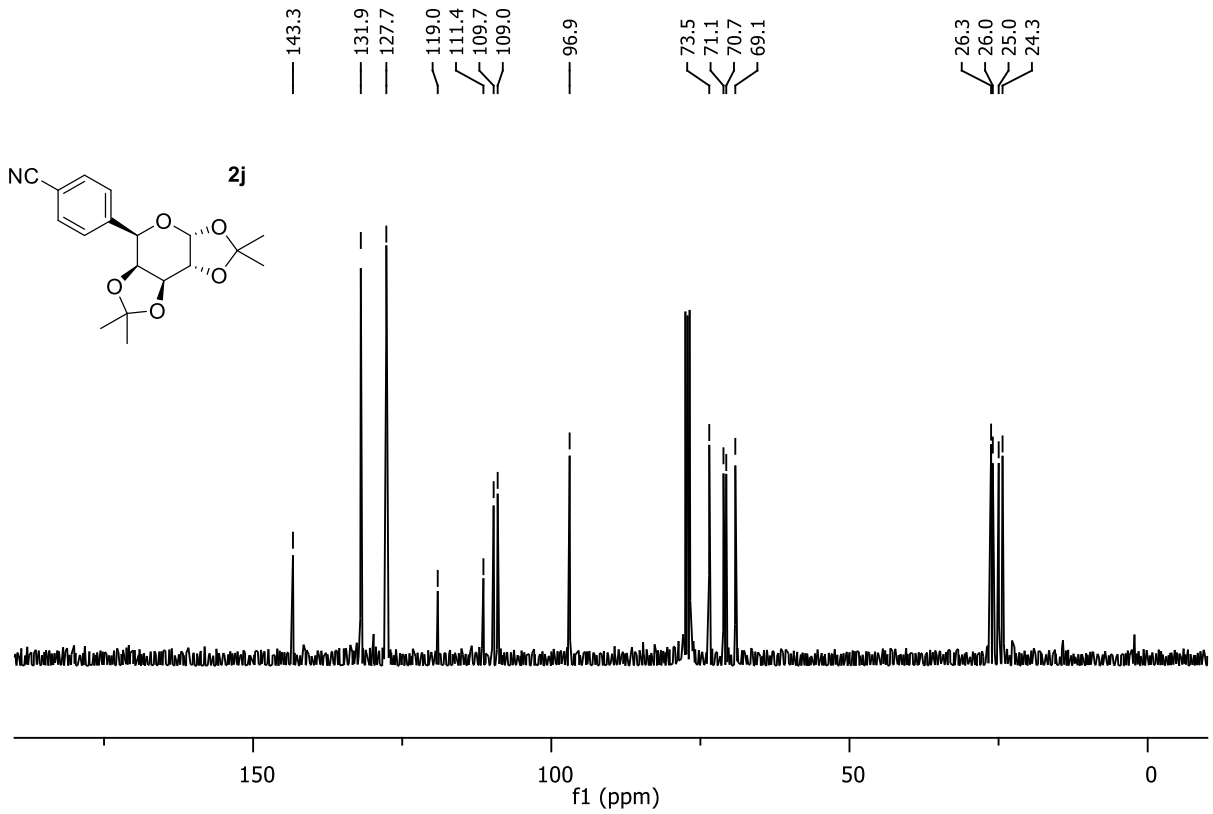
^{13}C NMR ($CDCl_3$, 126 MHz) of (2*S*,3*R*,4*S*,5*R*)-2,3,4,5-tetramethoxy-6-(naphthalen-2-yl)tetrahydro-2H-pyran (**2i**)



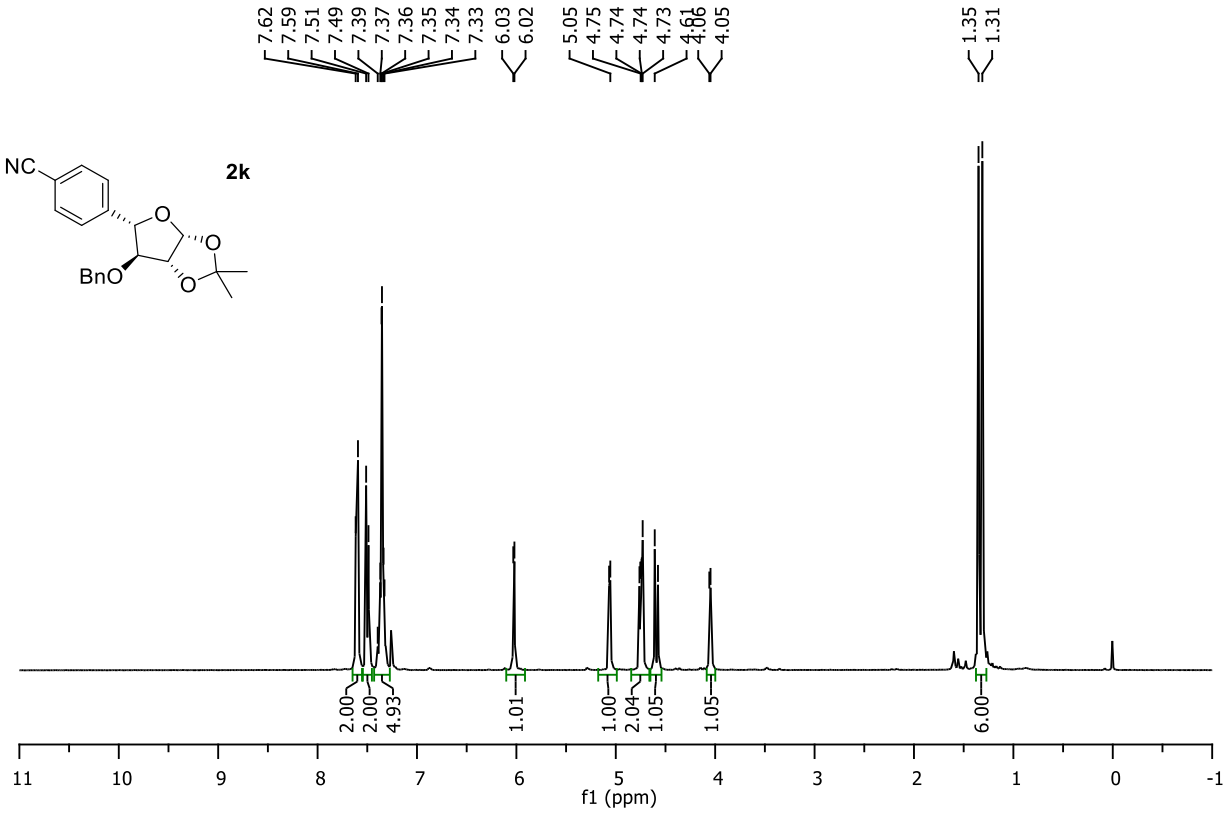
^{1}H NMR ($CDCl_3$, 360 MHz) of 4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d] pyran-5-yl)benzonitrile (**2j**)



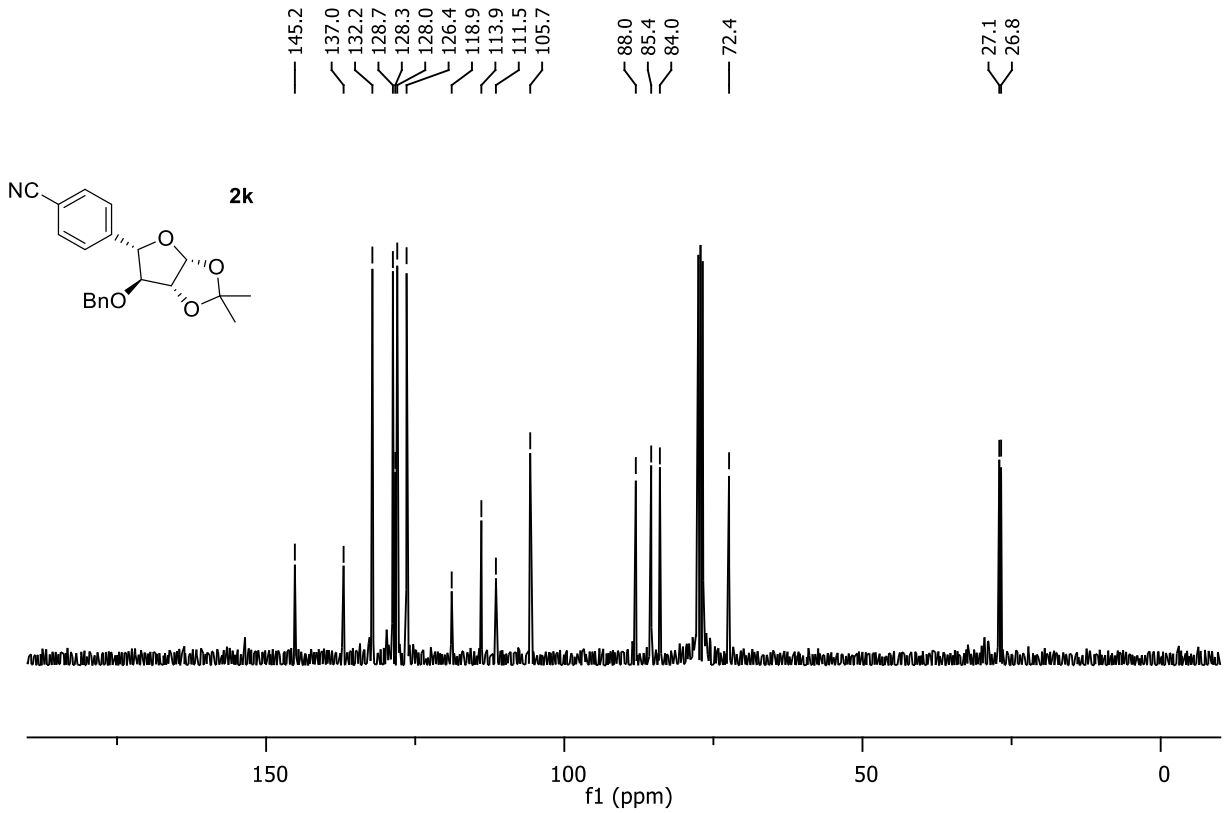
^{13}C NMR ($CDCl_3$, 91 MHz) of of 4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d] pyran-5-yl)benzonitrile (**2j**)



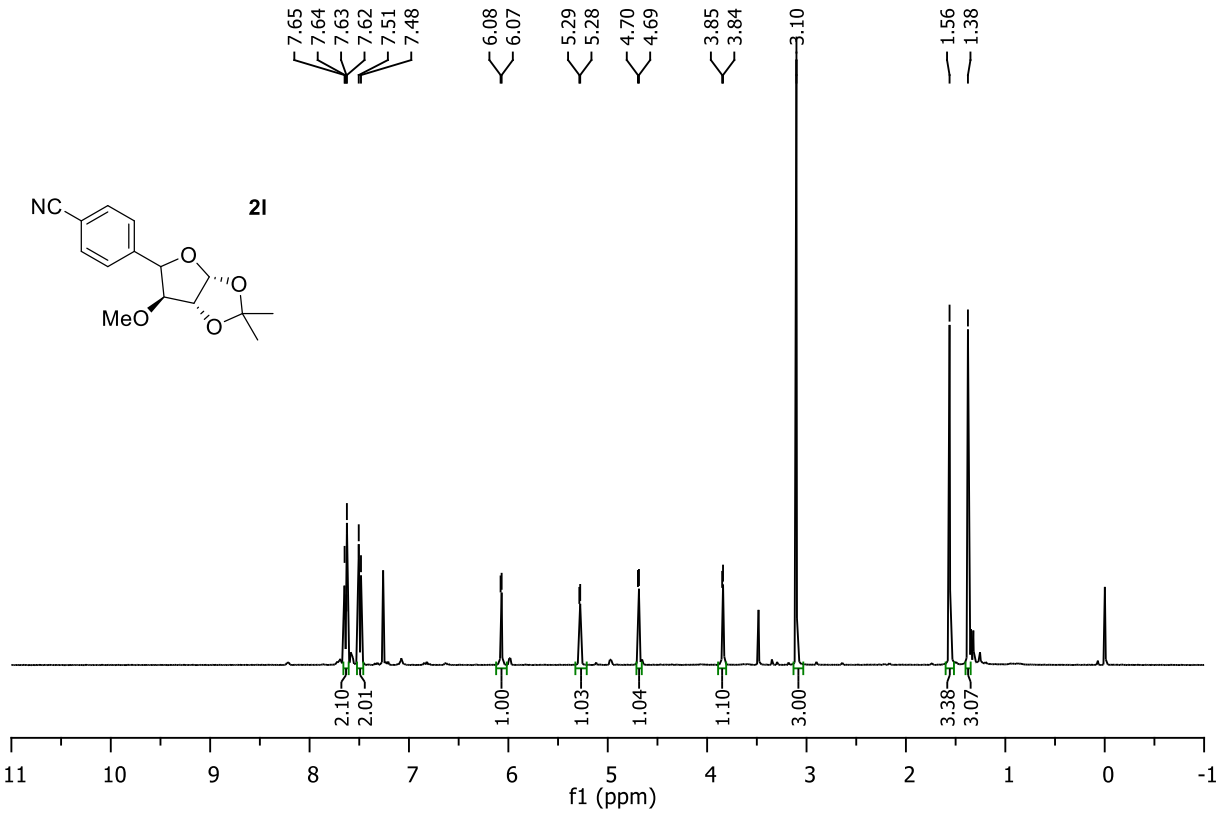
^{1}H NMR ($CDCl_3$, 360 MHz) of 4-((3a*R*,5*R*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro [2,3-d] [1,3]dioxol-5-yl)benzonitrile (**2k**)



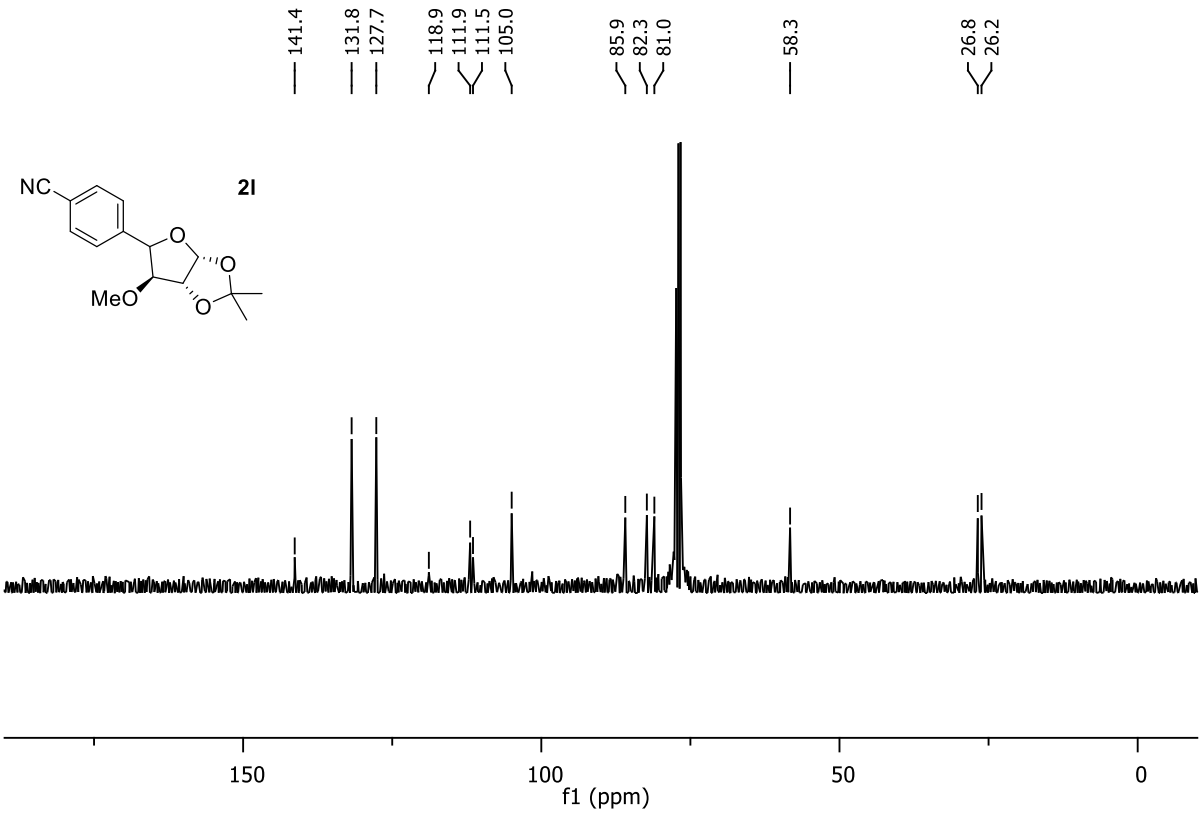
^{13}C NMR ($CDCl_3$, 91 MHz) of 4-((3a*R*,5*R*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro [2,3-d] [1,3]dioxol-5-yl)benzonitrile (**2k**)



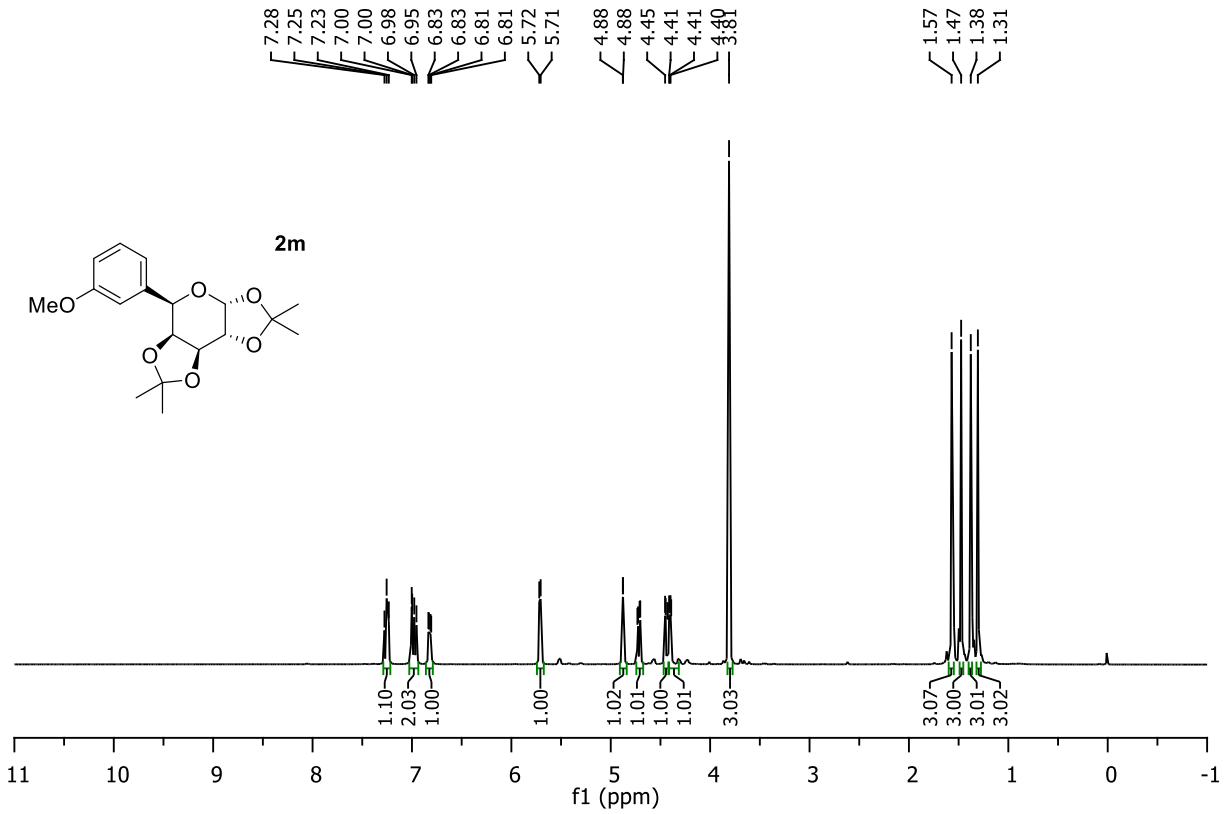
^{1}H NMR ($CDCl_3$, 360 MHz) of 4-((3a*R*,5*R*,6*S*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl) benzonitrile (**2l**)



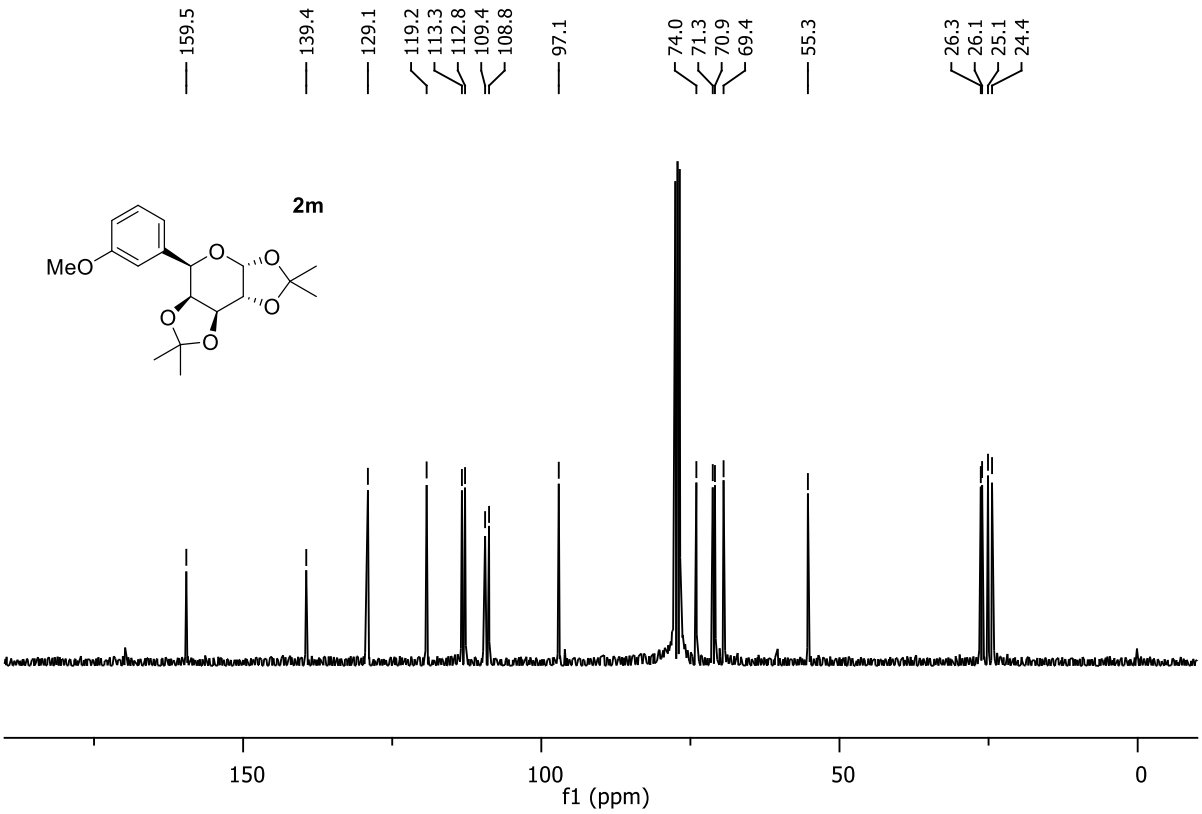
^{13}C NMR ($CDCl_3$, 91 MHz) of 4-((3a*R*,5*R*,6*S*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl) benzonitrile (**2l**)



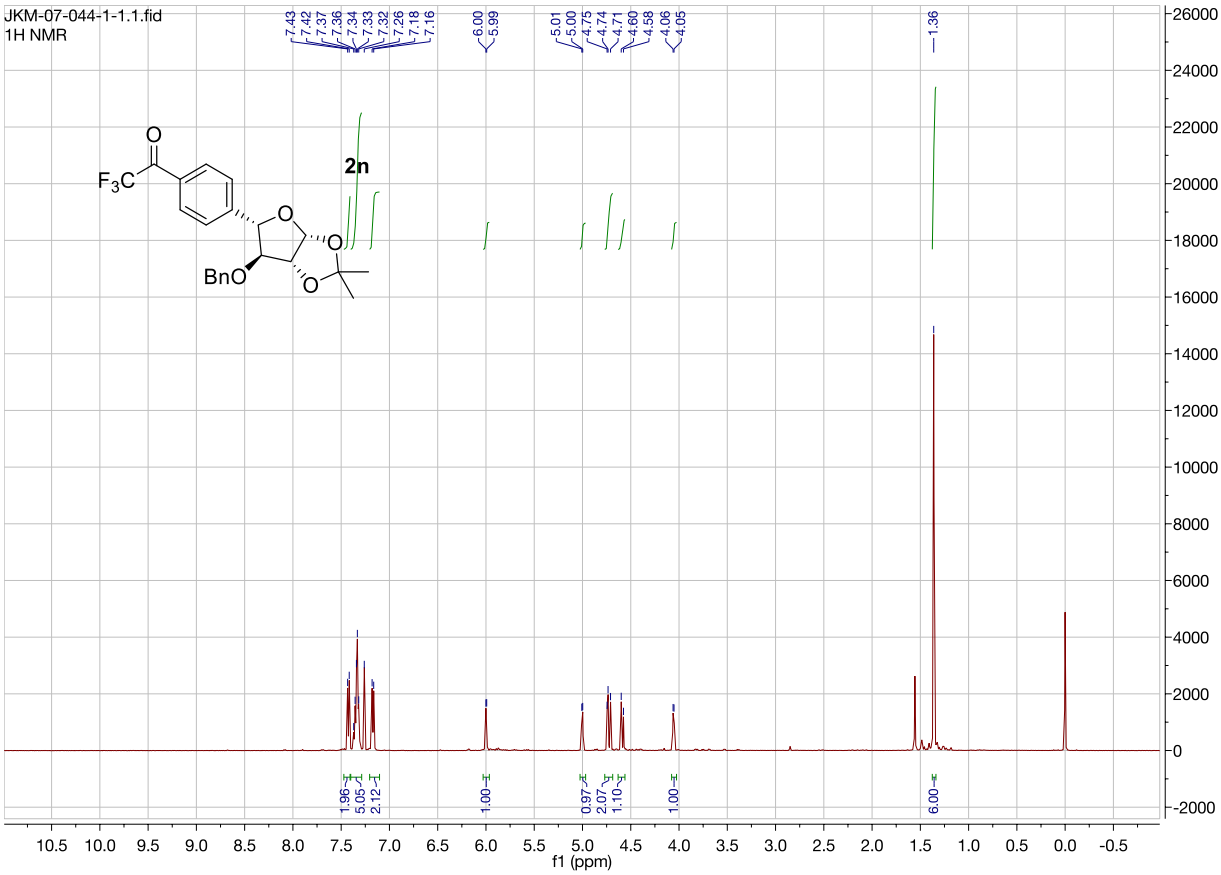
^{1}H NMR ($CDCl_3$, 360 MHz) of (3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-5-(3-methoxyphenyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (**2m**)



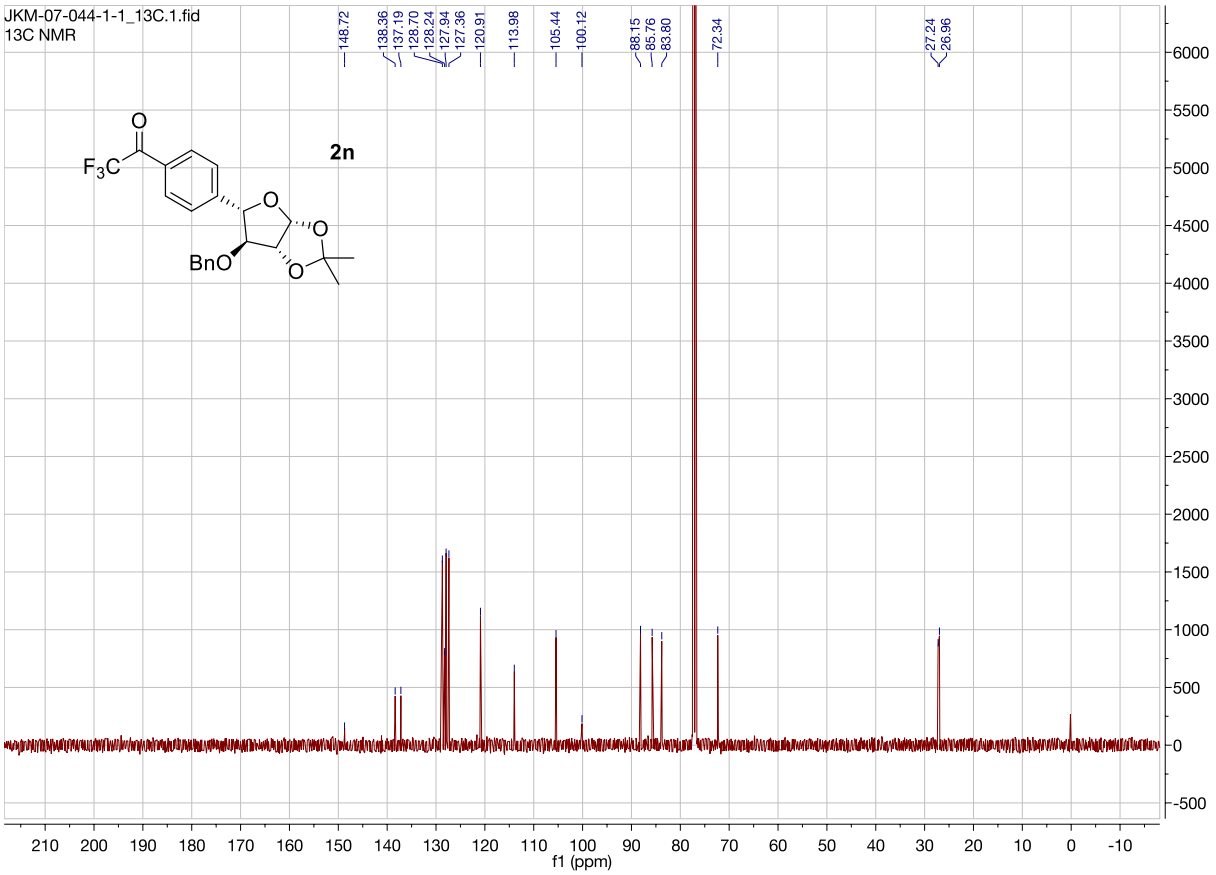
^{13}C NMR ($CDCl_3$, 91 MHz) of (3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-5-(3-methoxyphenyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (**2m**)



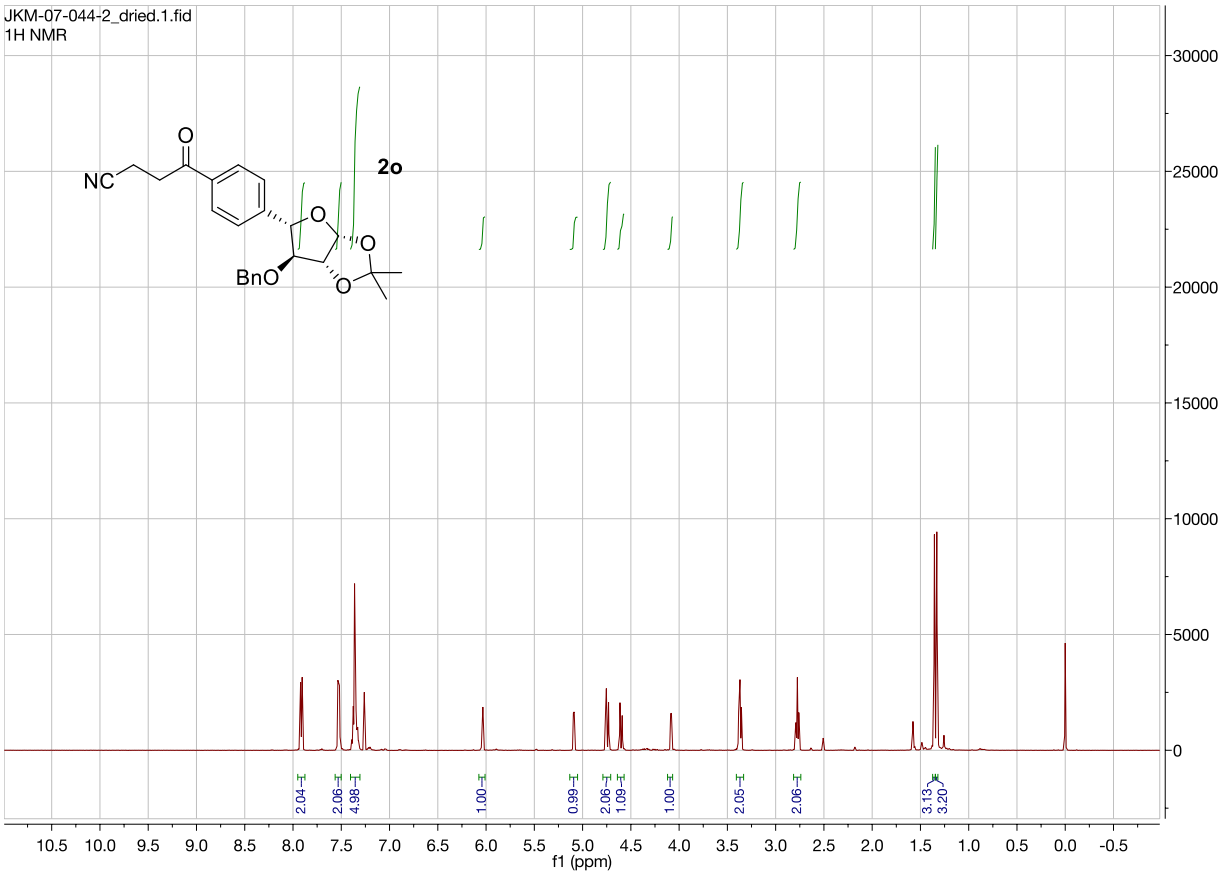
^{1}H NMR ($CDCl_3$, 500 MHz) of 1-(4-((3a*R*,5*S*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro [2,3-d][1,3]dioxol-5-yl)phenyl)-2,2,2-trifluoroethan-1-one (**2n**)



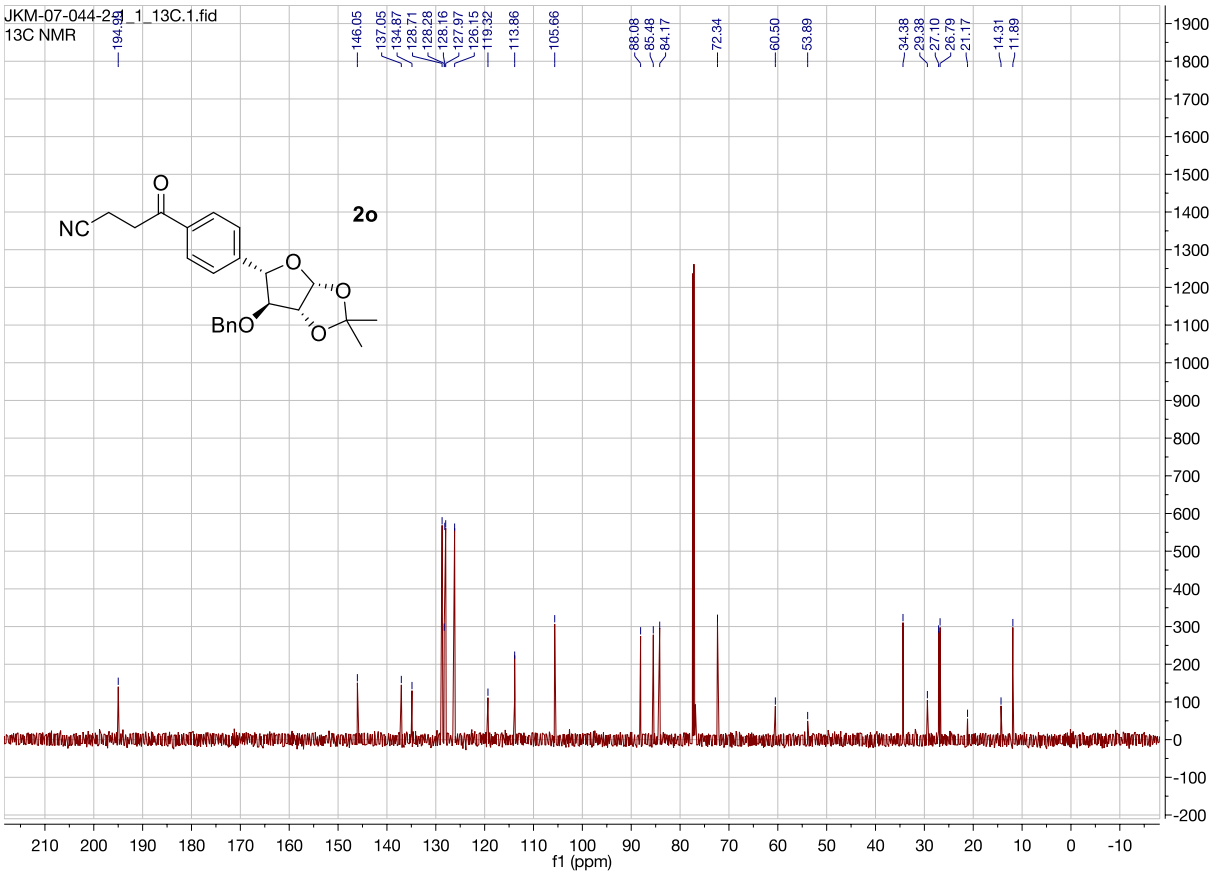
^{13}C NMR ($CDCl_3$, 126 MHz) of 1-(4-((3a*R*,5*S*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro [2,3-d][1,3]dioxol-5-yl)phenyl)-2,2,2-trifluoroethan-1-one (**2n**)



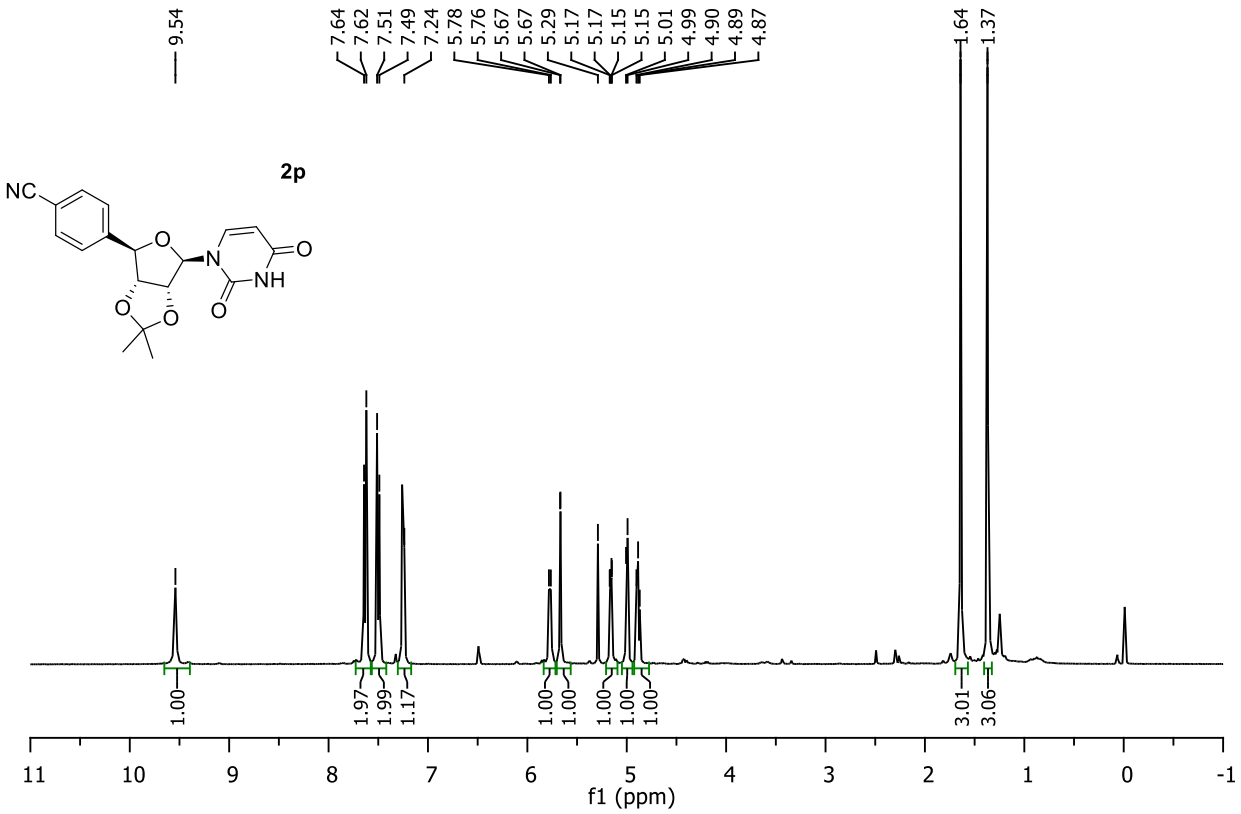
^{1}H NMR ($CDCl_3$, 500 MHz) of 4-(4-((3aR,5S,6S,6aR)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro [2,3-d][1,3]dioxol-5-yl)phenyl)-4-oxobutanenitrile (**2o**)



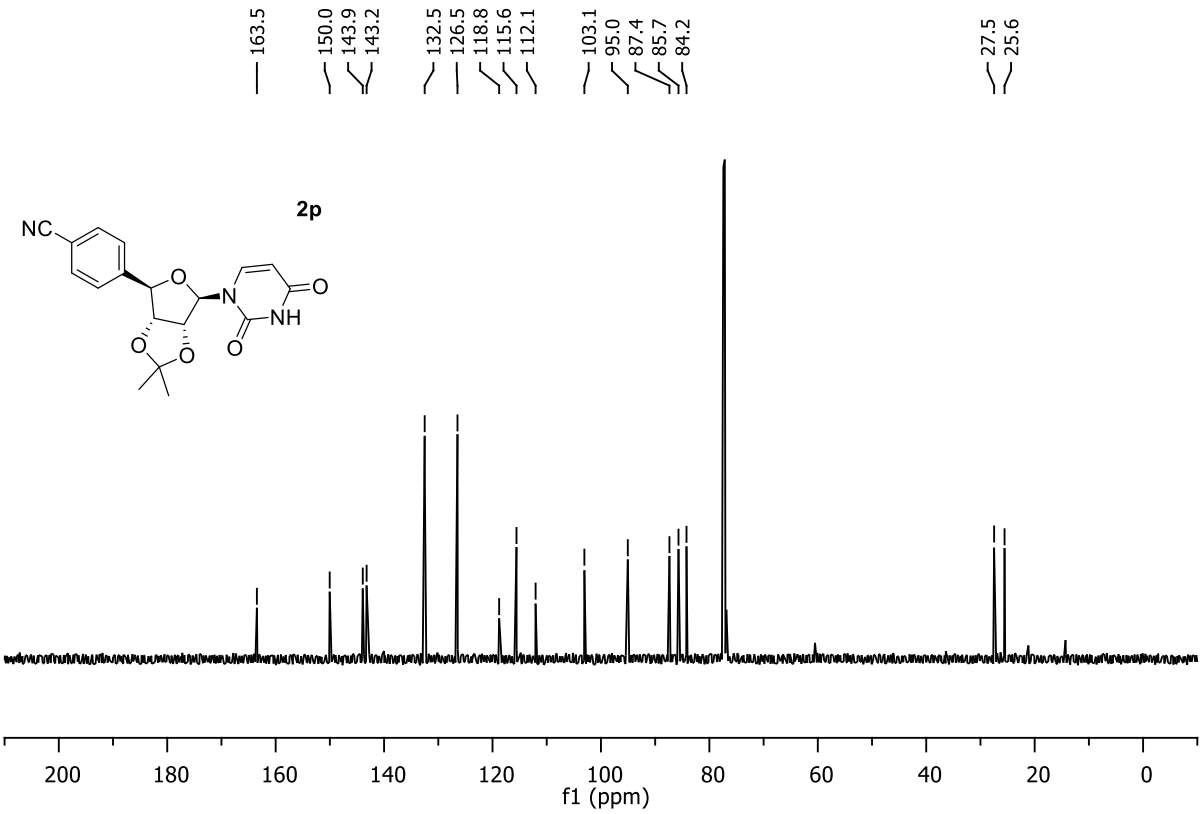
^{13}C NMR ($CDCl_3$, 126 MHz) of 4-(4-((3aR,5S,6S,6aR)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro [2,3-d][1,3]dioxol-5-yl)phenyl)-4-oxobutanenitrile (**2o**)



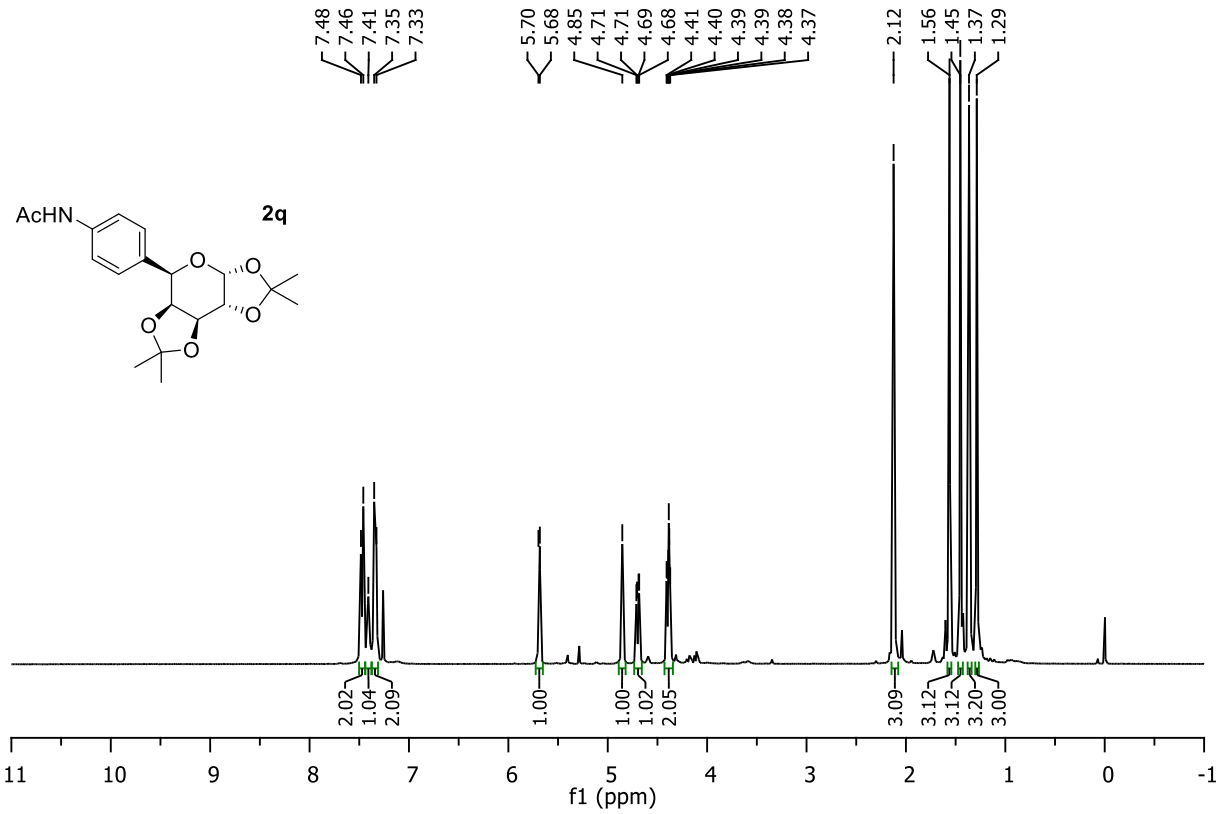
^{1}H NMR ($CDCl_3$, 360 MHz) of 4-((3a*R*,4*R*,6*R*,6a*R*)-6-(2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)benzonitrile (**2p**)



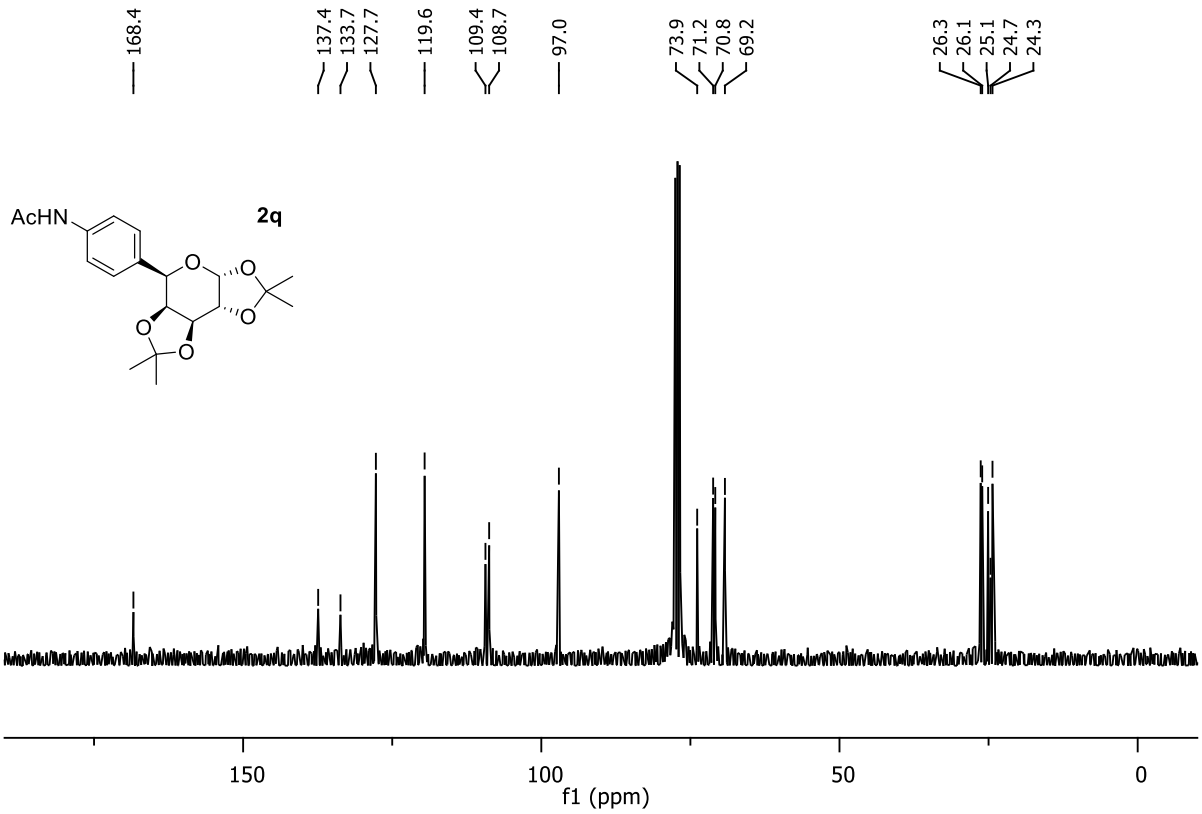
^{13}C NMR ($CDCl_3$, 126 MHz) of 4-((3a*R*,4*R*,6*R*,6a*R*)-6-(2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)benzonitrile (**2p**)



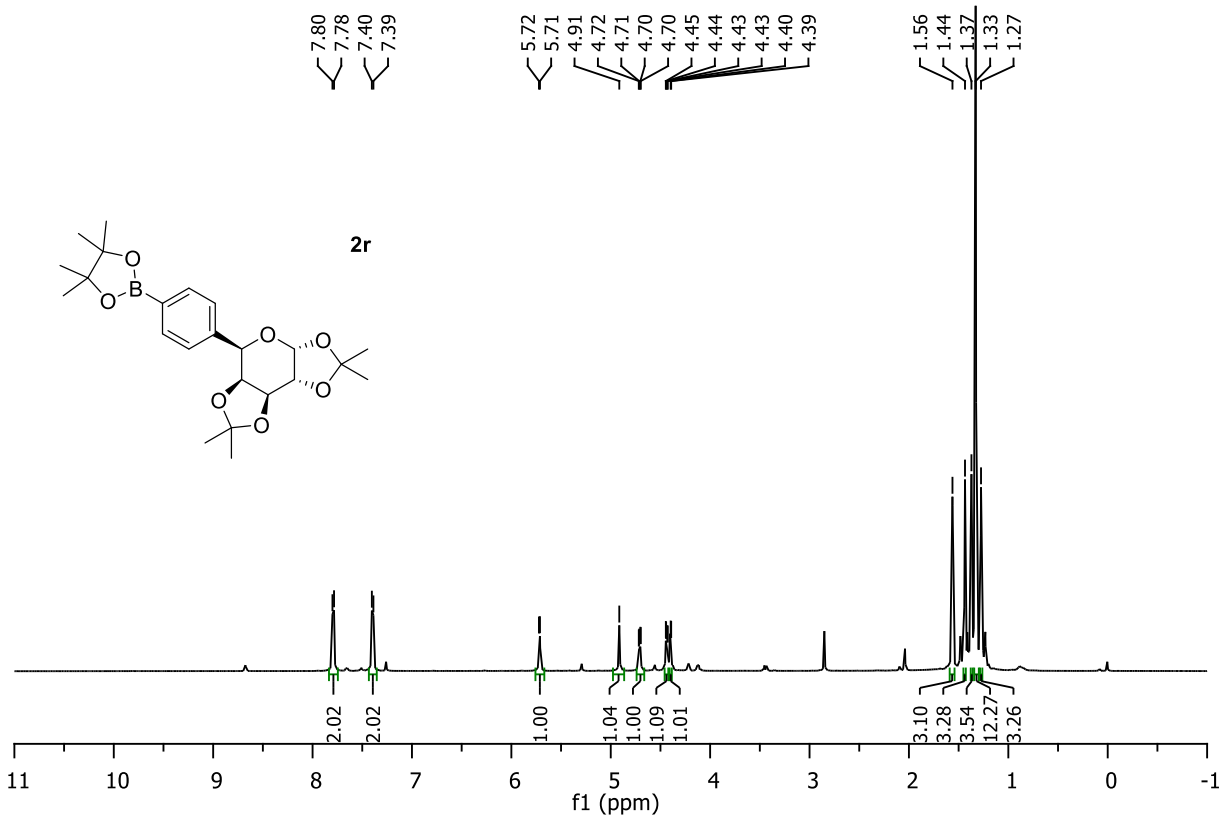
^{1}H NMR ($CDCl_3$, 360 MHz) of *N*-(4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)phenyl)acetamide (**2q**)



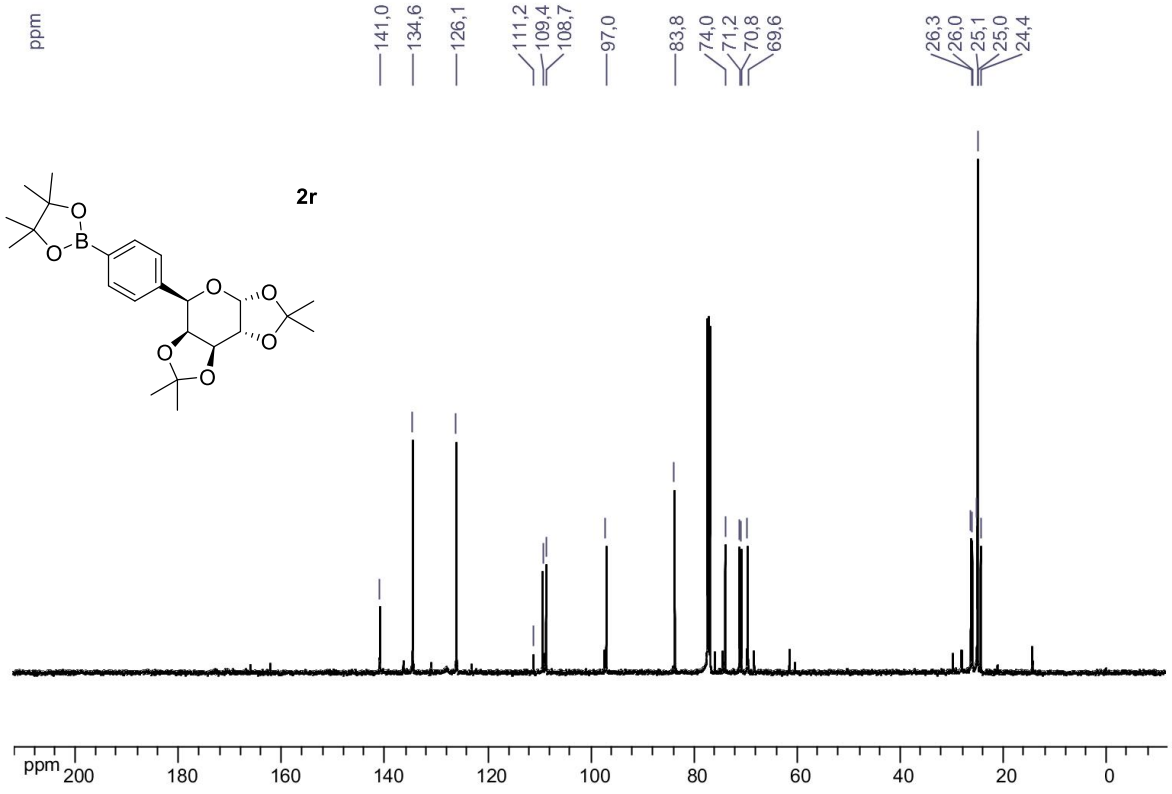
^{13}C NMR ($CDCl_3$, 91 MHz) of *N*-(4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)phenyl)acetamide (**2q**)



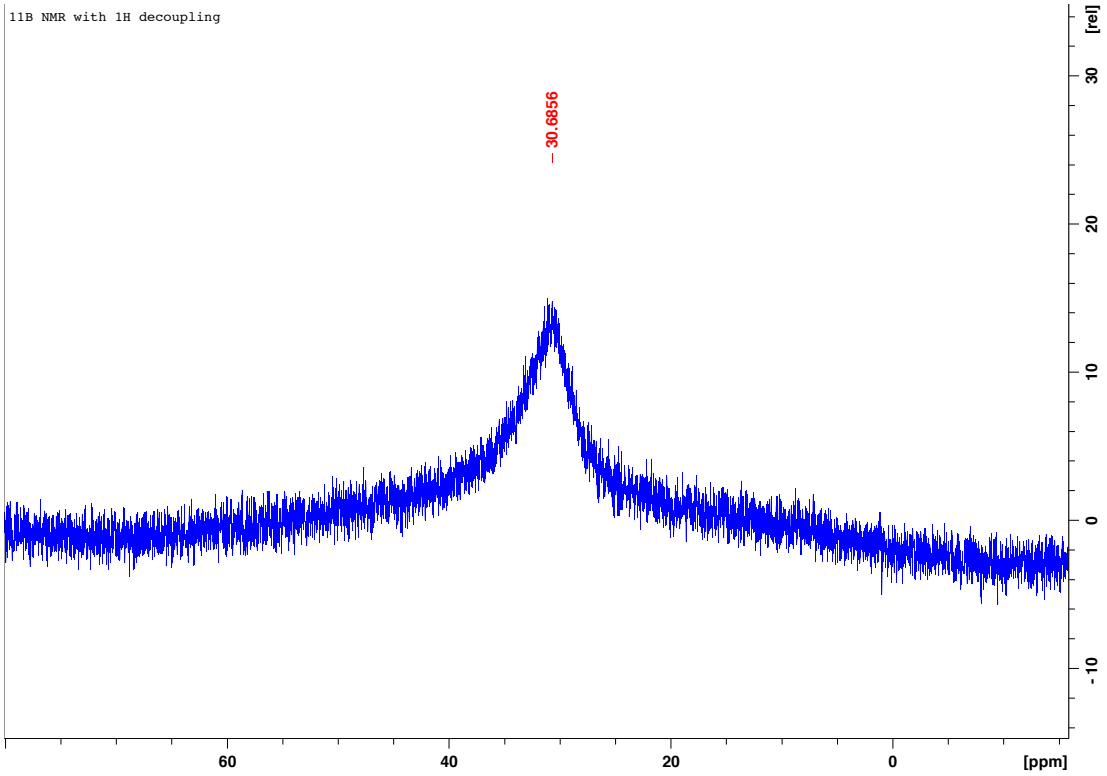
^{1}H NMR ($CDCl_3$, 360 MHz) of 4,4,5,5-tetramethyl-2-(4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis ([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)phenyl)-1,3,2-dioxaborolane (**2r**)



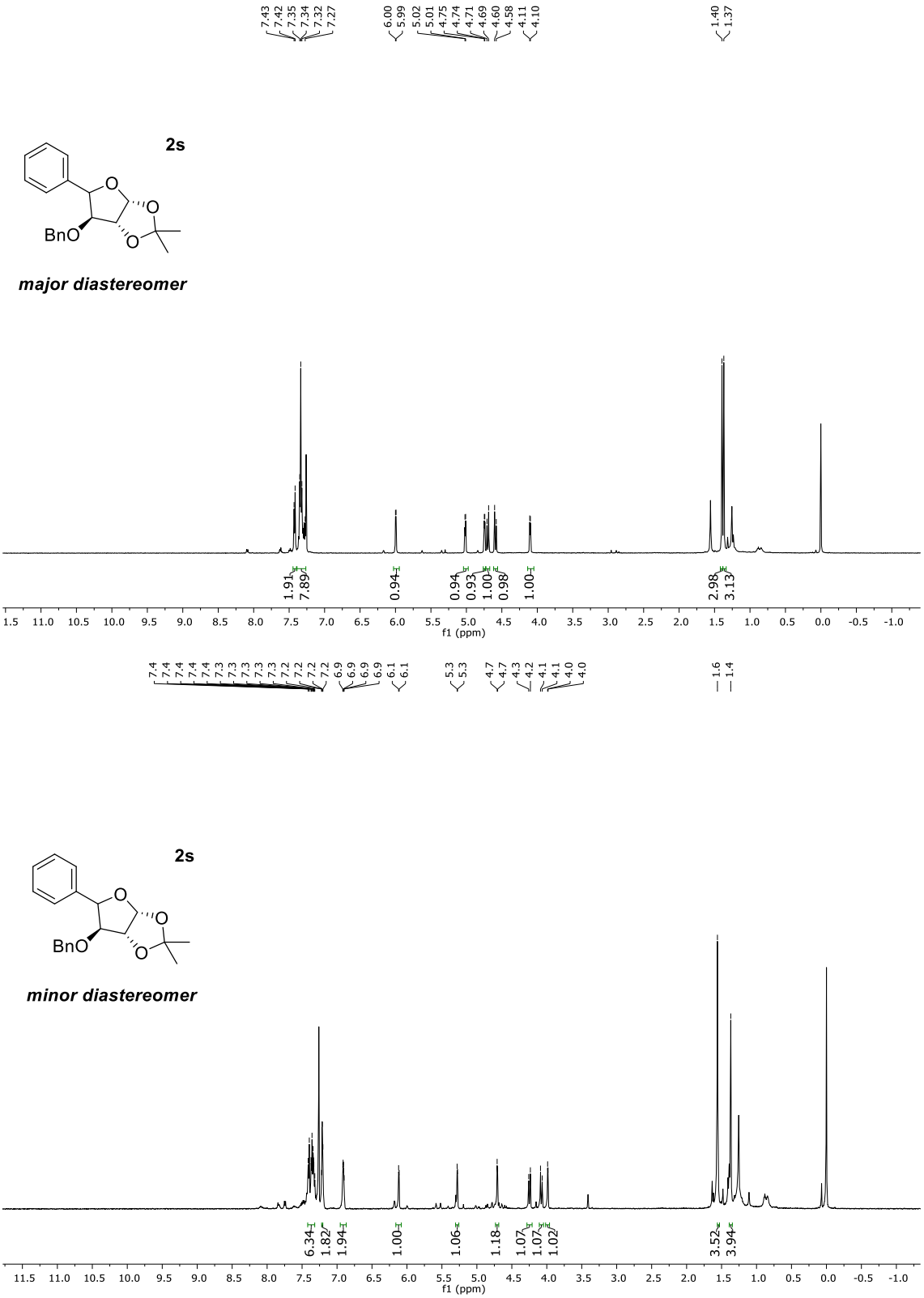
^{13}C NMR ($CDCl_3$, 91 MHz) of 4,4,5,5-tetramethyl-2-(4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis ([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)phenyl)-1,3,2-dioxaborolane (**2r**)



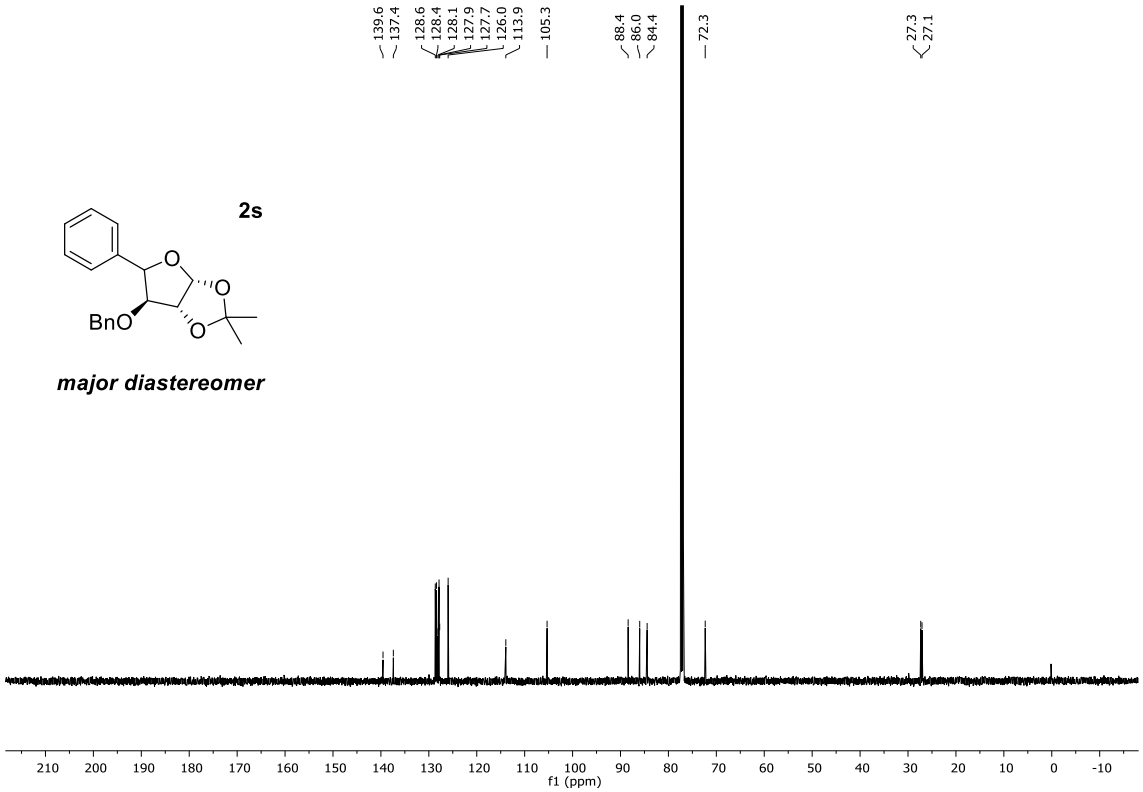
^{11}B NMR ($CDCl_3$, 128.38 MHz) of 4,4,5,5-tetramethyl-2-(4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis ([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)phenyl)-1,3,2-dioxaborolane (**2r**)

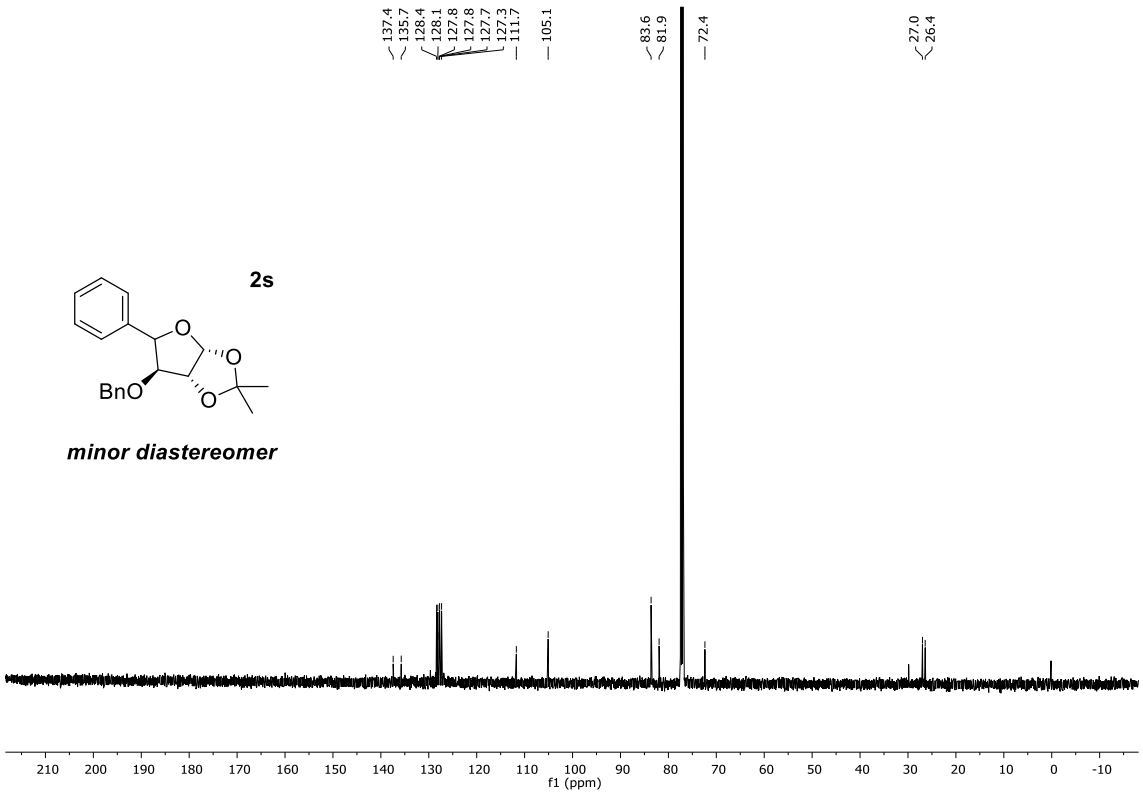


^{1}H NMR ($CDCl_3$, 500 MHz) of *tert*-b ^{1}H NMR ($CDCl_3$, 500 MHz) of (3a*R*,6*S*,6a*R*)-6-(Benzyloxy)-2,2-dimethyl-5-phenyltetrahydrofuro [2,3-*d*][1,3]dioxole (**2s**)

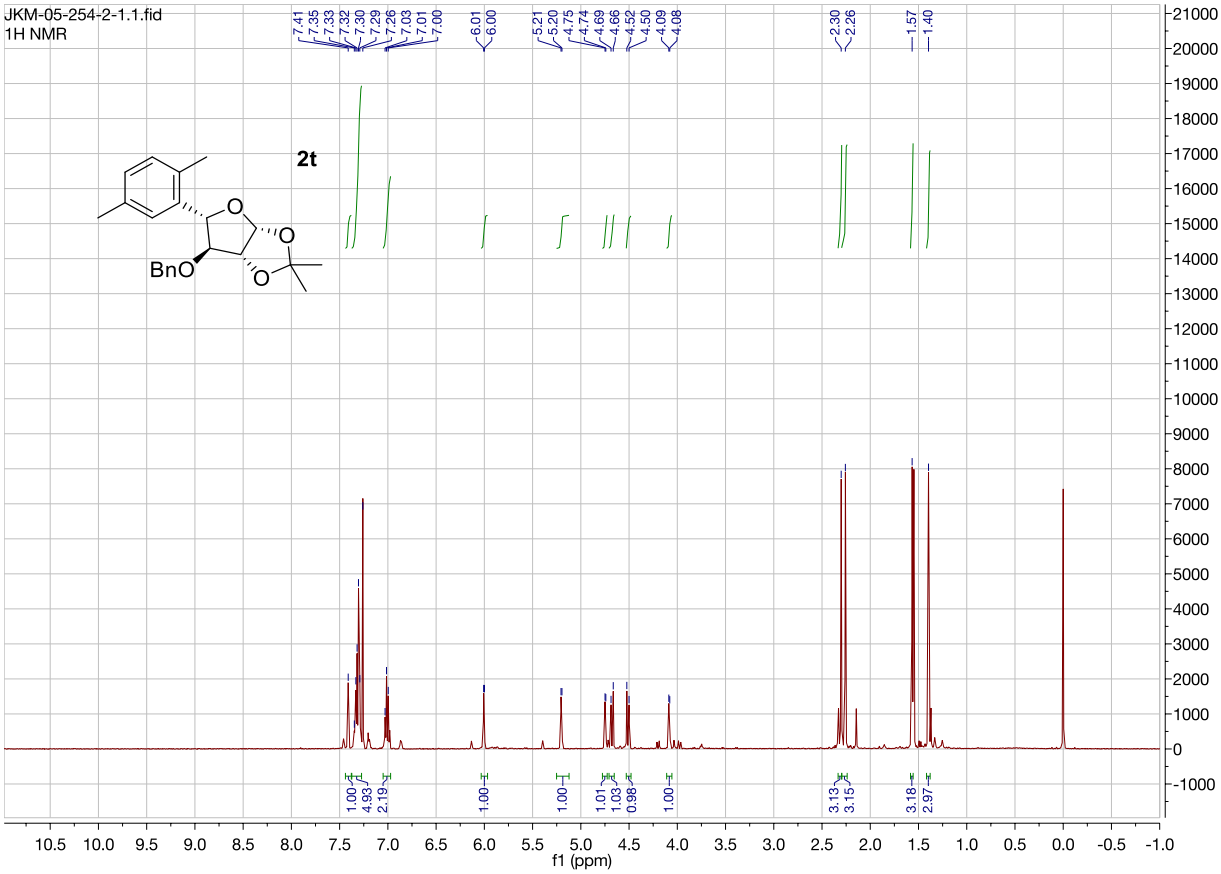


^{13}C NMR ($CDCl_3$, 126 MHz) of (3a*R*,6*S*,6a*R*)-6-(Benzyloxy)-2,2-dimethyl-5-phenyltetrahydrofuro [2,3-*d*][1,3]dioxole (**2s**)

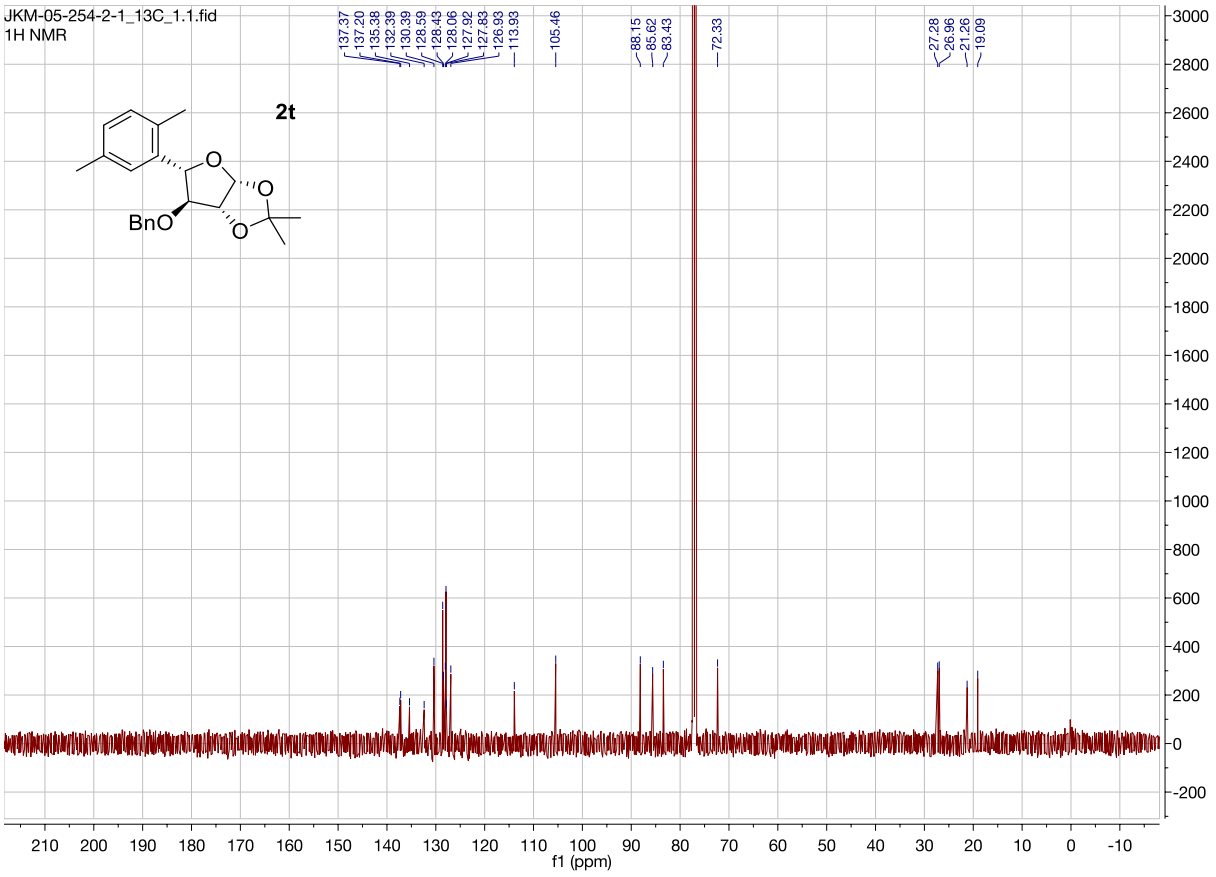




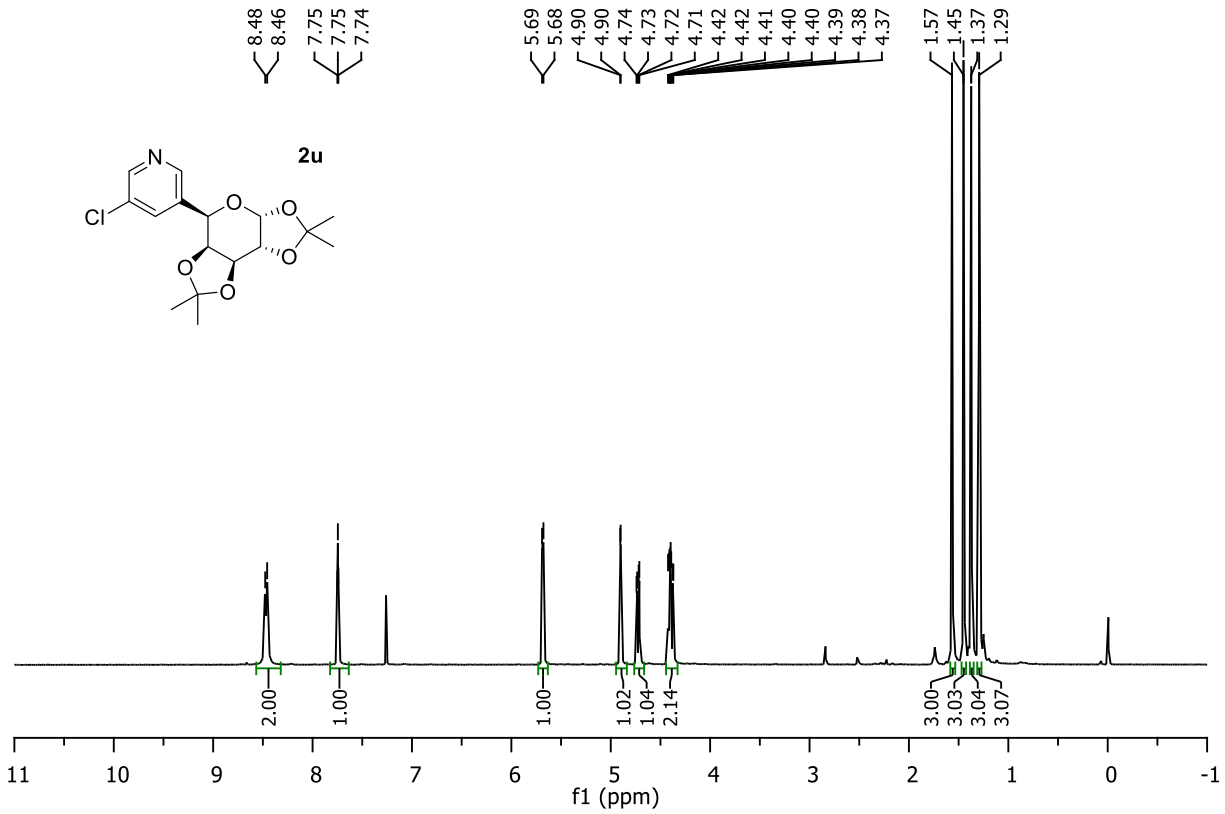
^{1}H NMR ($CDCl_3$, 500 MHz) of (3a*R*,5*S*,6*S*,6a*R*)-6-(benzyloxy)-5-(2,5-dimethylphenyl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole (**2t**)



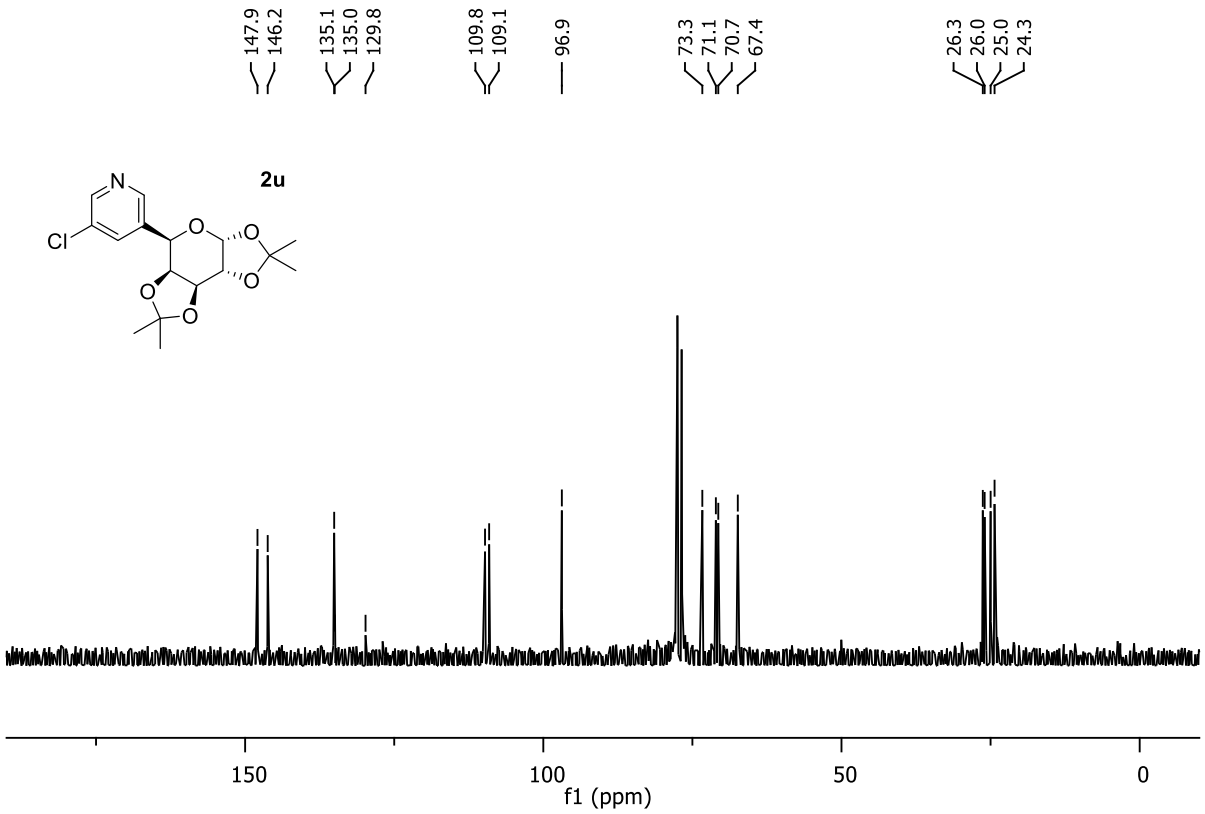
^{13}C NMR ($CDCl_3$, 126 MHz) of (3a*R*,5*S*,6*S*,6a*R*)-6-(benzyloxy)-5-(2,5-dimethylphenyl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole (**2t**)



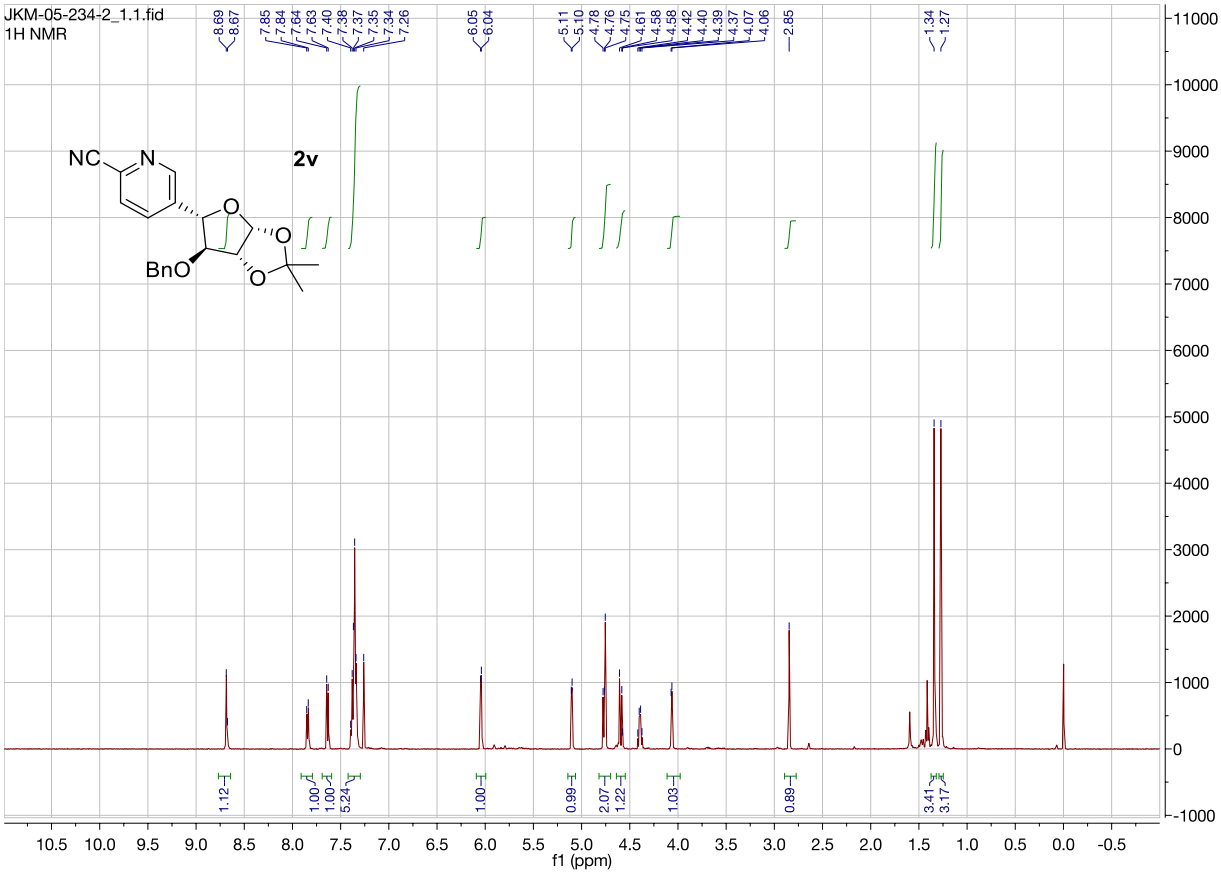
^{1}H NMR ($CDCl_3$, 360 MHz) of 3-chloro-5-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)pyridine (**2u**)



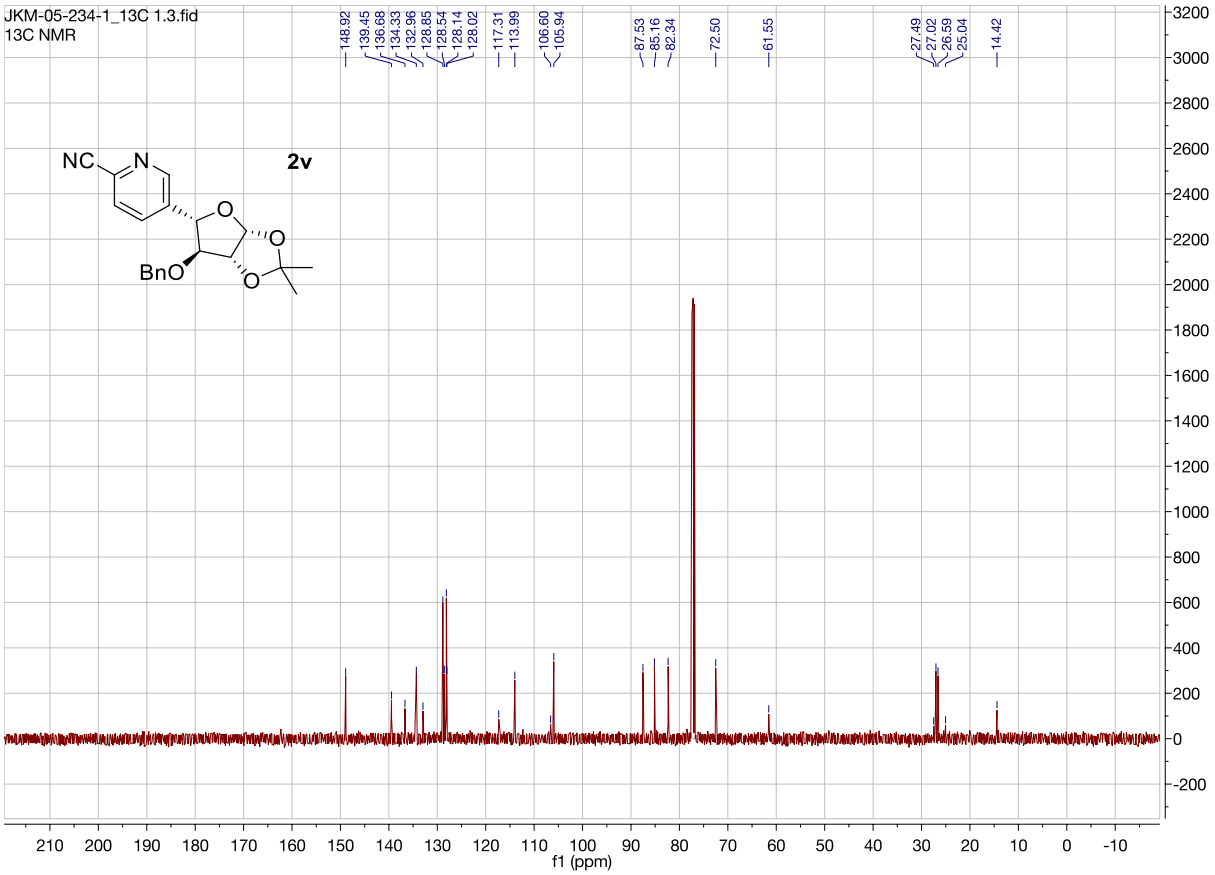
^{13}C NMR ($CDCl_3$, 91 MHz) of 3-chloro-5-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)pyridine (**2u**)



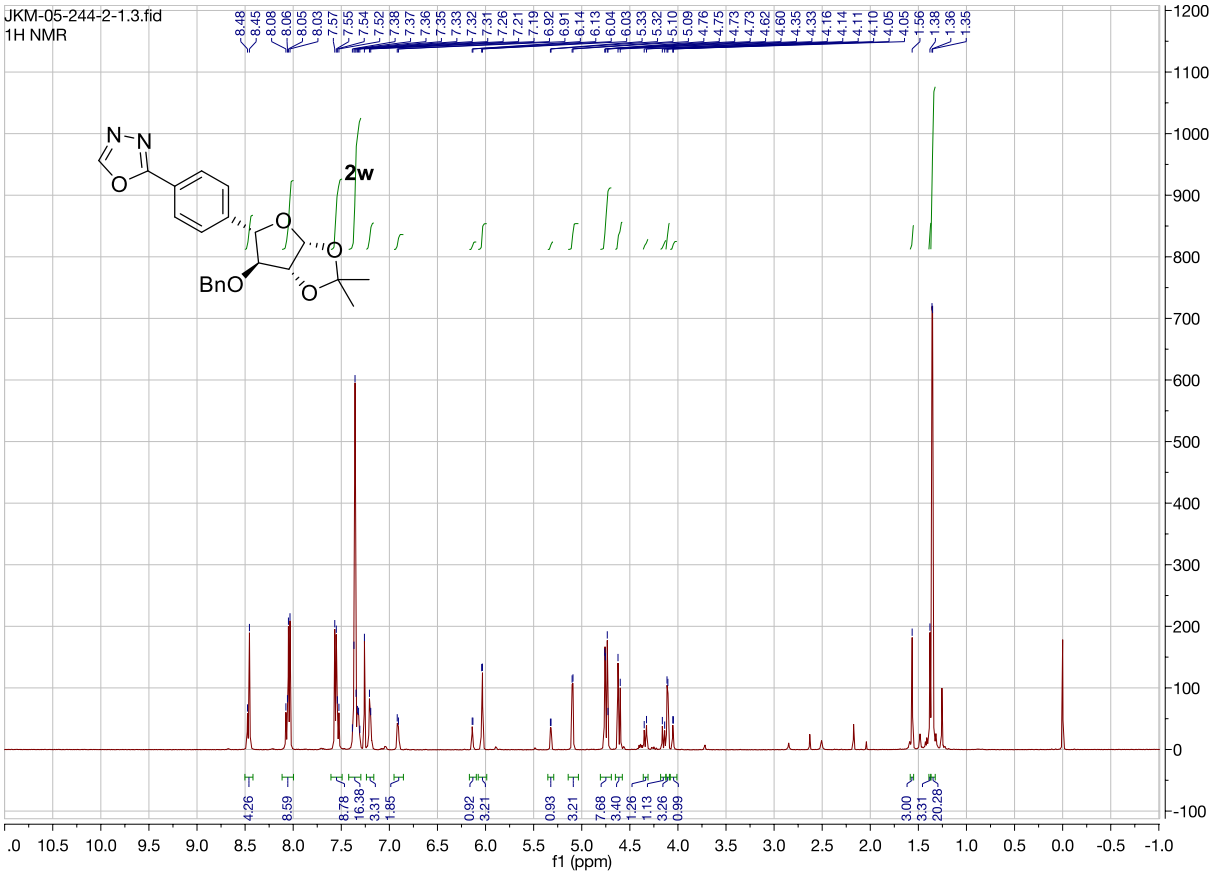
^{1}H NMR ($CDCl_3$, 500 MHz) of 5-((3a*R*,5*S*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl) picolinonitrile (**2v**)



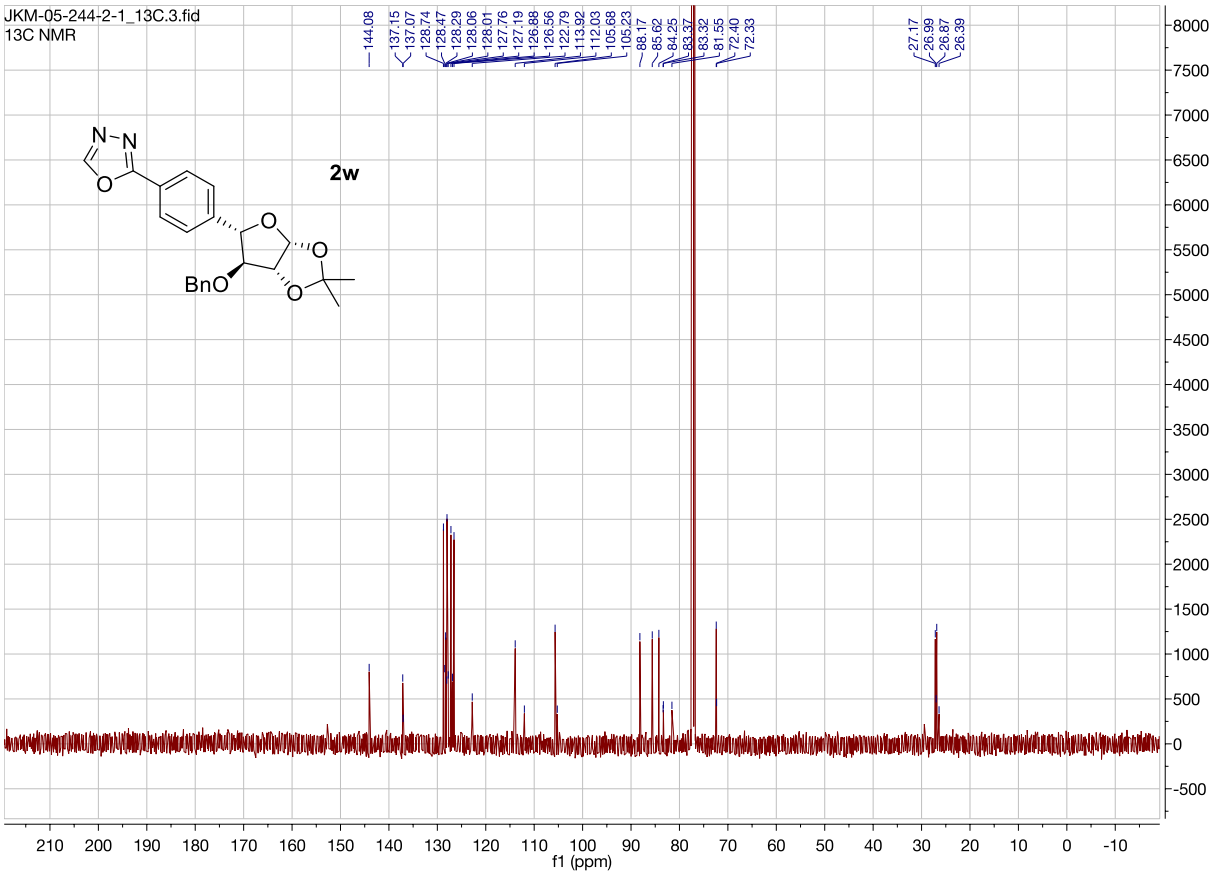
^{13}C NMR ($CDCl_3$, 126 MHz) of 5-((3a*R*,5*S*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl) picolinonitrile (**2v**)



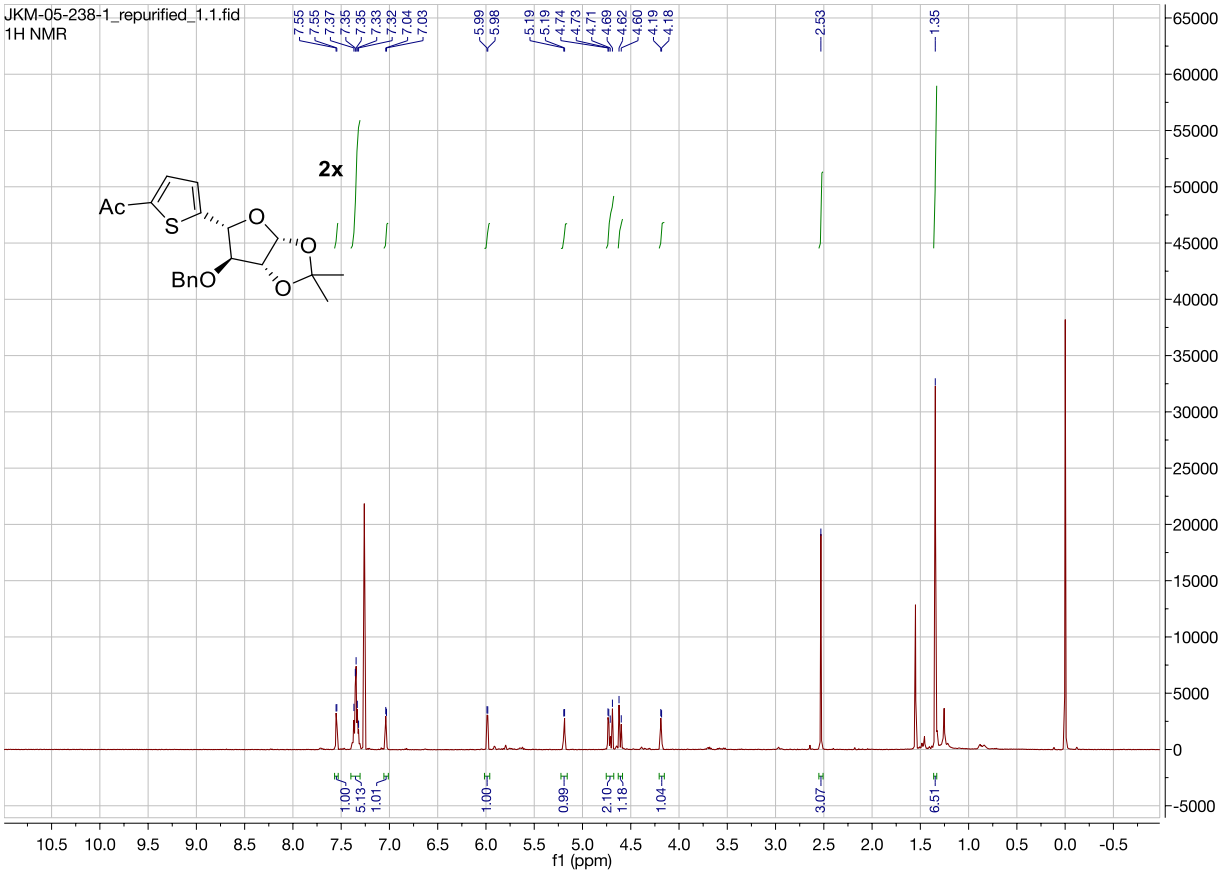
^{1}H NMR ($CDCl_3$, 500 MHz) of 2-(4-((3aR,5S,6S,6aR)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro [2,3-d][1,3]dioxol-5-yl)phenyl) -1,3,4-oxadiazole (**2w**)



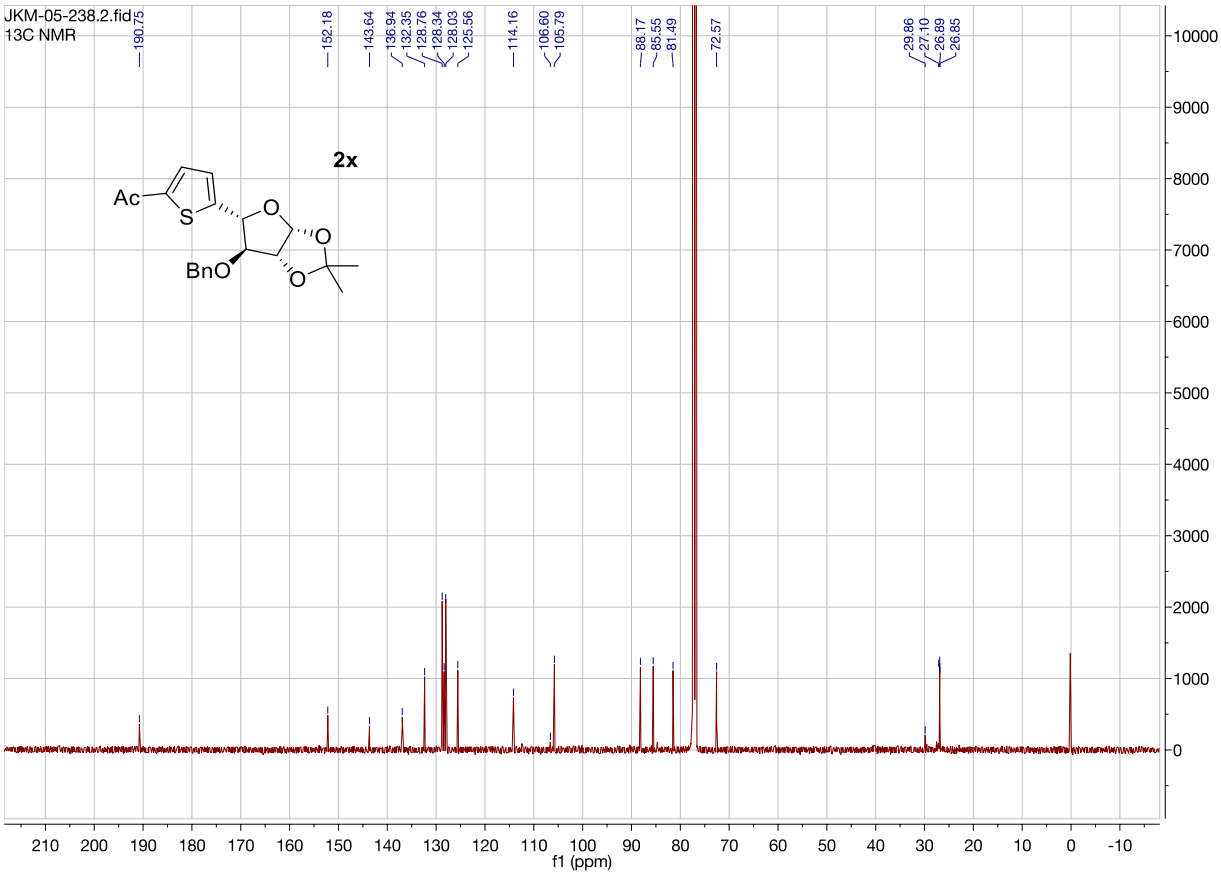
^{13}C NMR ($CDCl_3$, 126 MHz) of 2-(4-((3aR,5S,6S,6aR)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro [2,3-d][1,3]dioxol-5-yl)phenyl) -1,3,4-oxadiazole (**2w**)



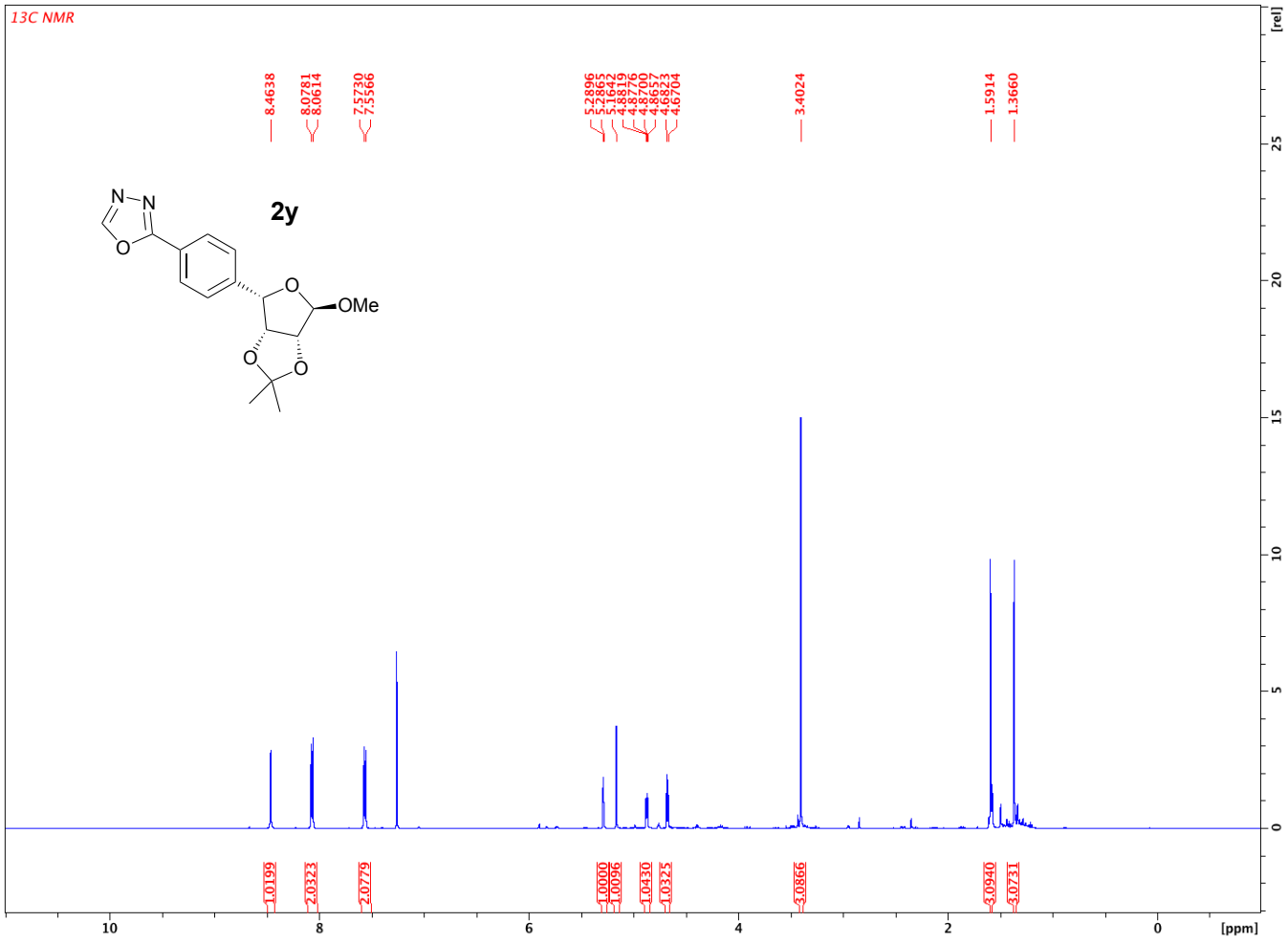
^{1}H NMR ($CDCl_3$, 500 MHz) of 1-(5-((3a*R*,5*R*,6*R*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro [2,3-d][1,3]dioxol-5-yl) thiophen-2-yl)ethan-1-one (**2x**)



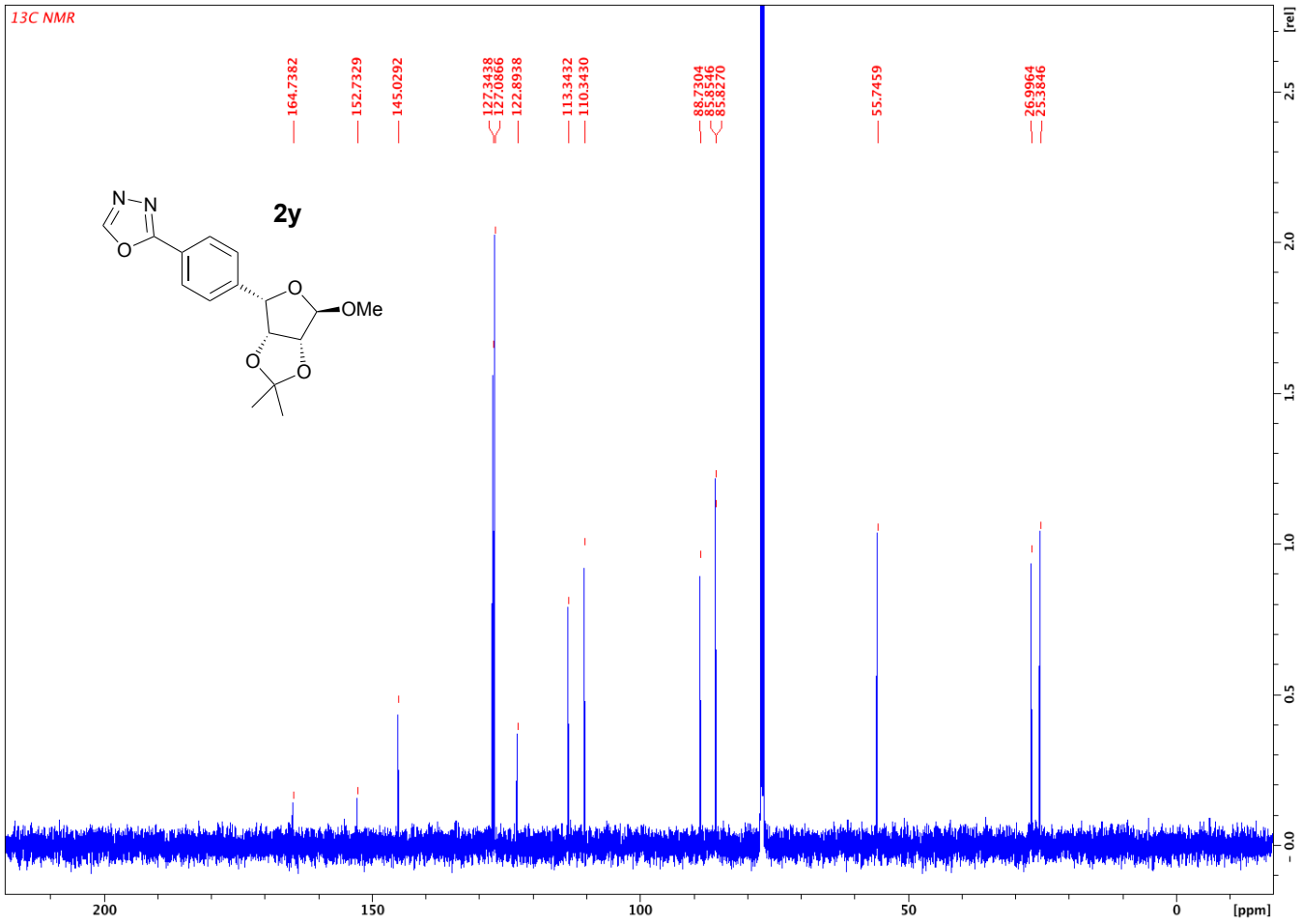
^{13}C NMR ($CDCl_3$, 126 MHz) of 1-(5-((3a*R*,5*R*,6*R*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro [2,3-d][1,3]dioxol-5-yl) thiophen-2-yl)ethan-1-one (**2x**)



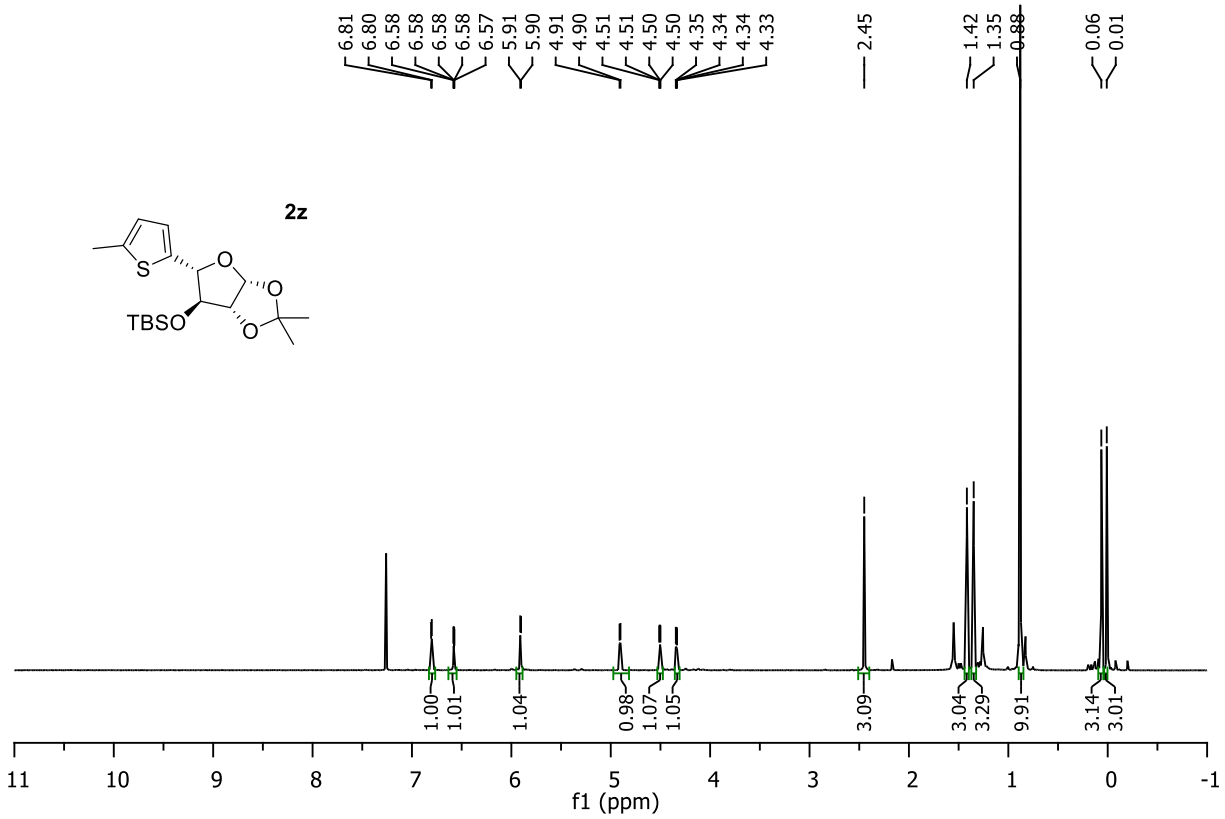
^{1}H NMR ($CDCl_3$, 500 MHz) of 2-(4-((3aR,4S,6R,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)phenyl)-1,3,4-oxadiazole (**2y**)



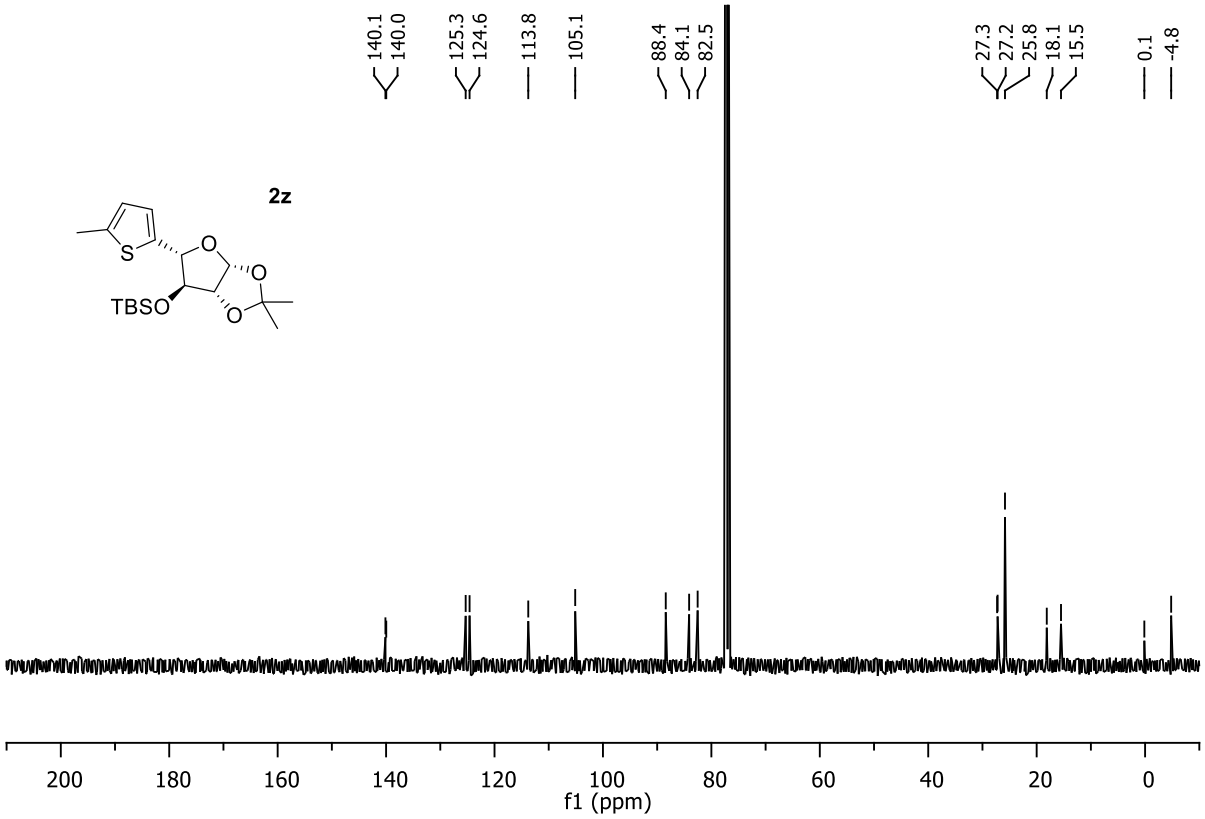
^{13}C NMR ($CDCl_3$, 126 MHz) of 2-(4-((3aR,4S,6R,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)phenyl)-1,3,4-oxadiazole (**2y**)



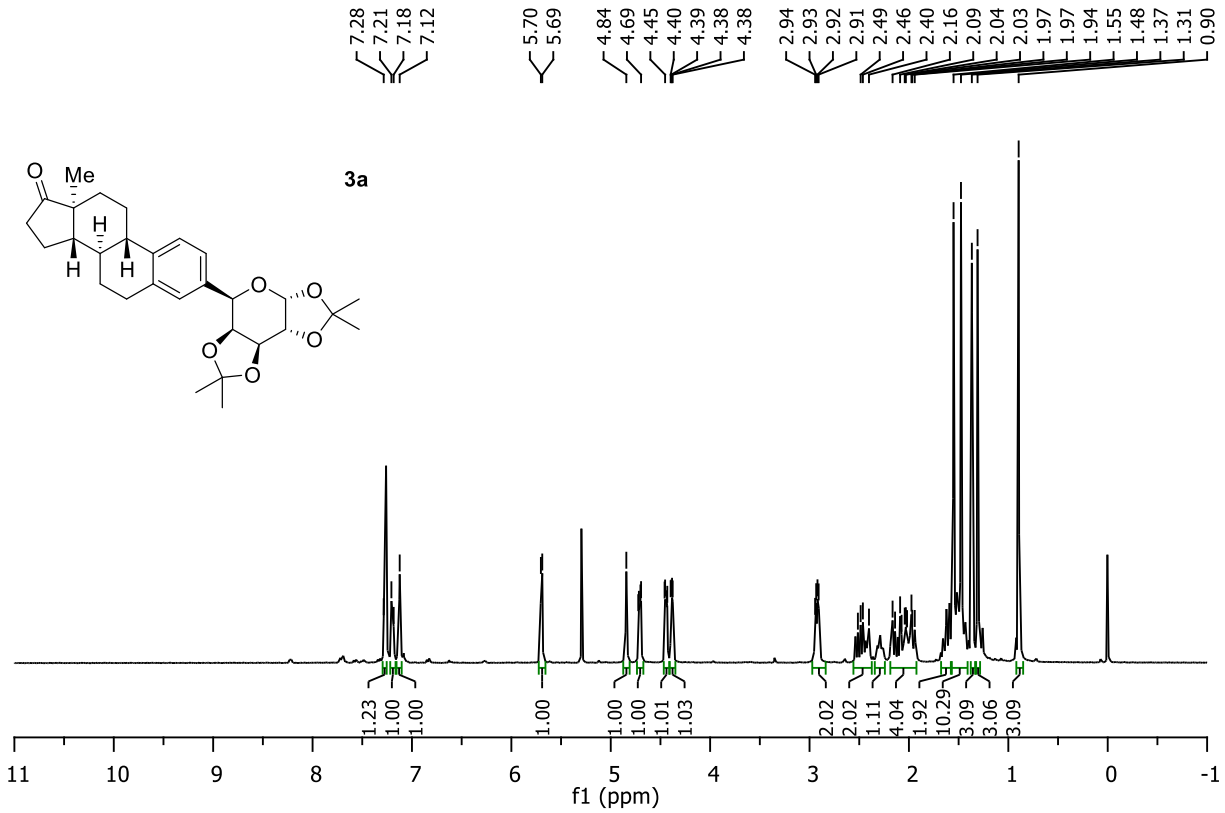
utyl(((3a*R*,5*R*,6*R*,6a*R*)-2,2-dimethyl-5-(5-methylthiophen-2-yl)tetrahydrofuro[2,3-d][1,3] dioxol-6-yl)oxy)dimethylsilane (**2z**)



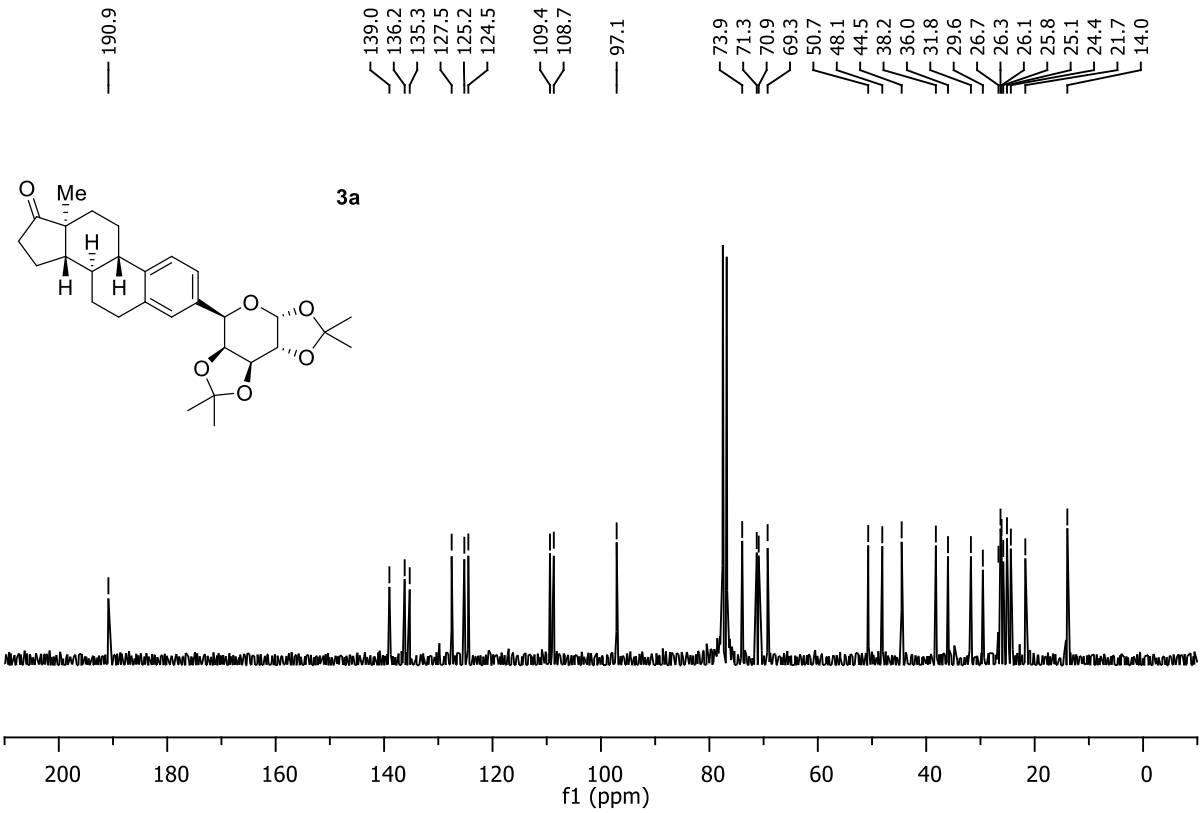
^{13}C NMR ($CDCl_3$, 126 MHz) of *tert*-butyl(((3a*R*,5*R*,6*R*,6a*R*)-2,2-dimethyl-5-(5-methylthiophen-2-yl)tetrahydrofuro[2,3-d][1,3] dioxol-6-yl)oxy)dimethylsilane (**2z**)



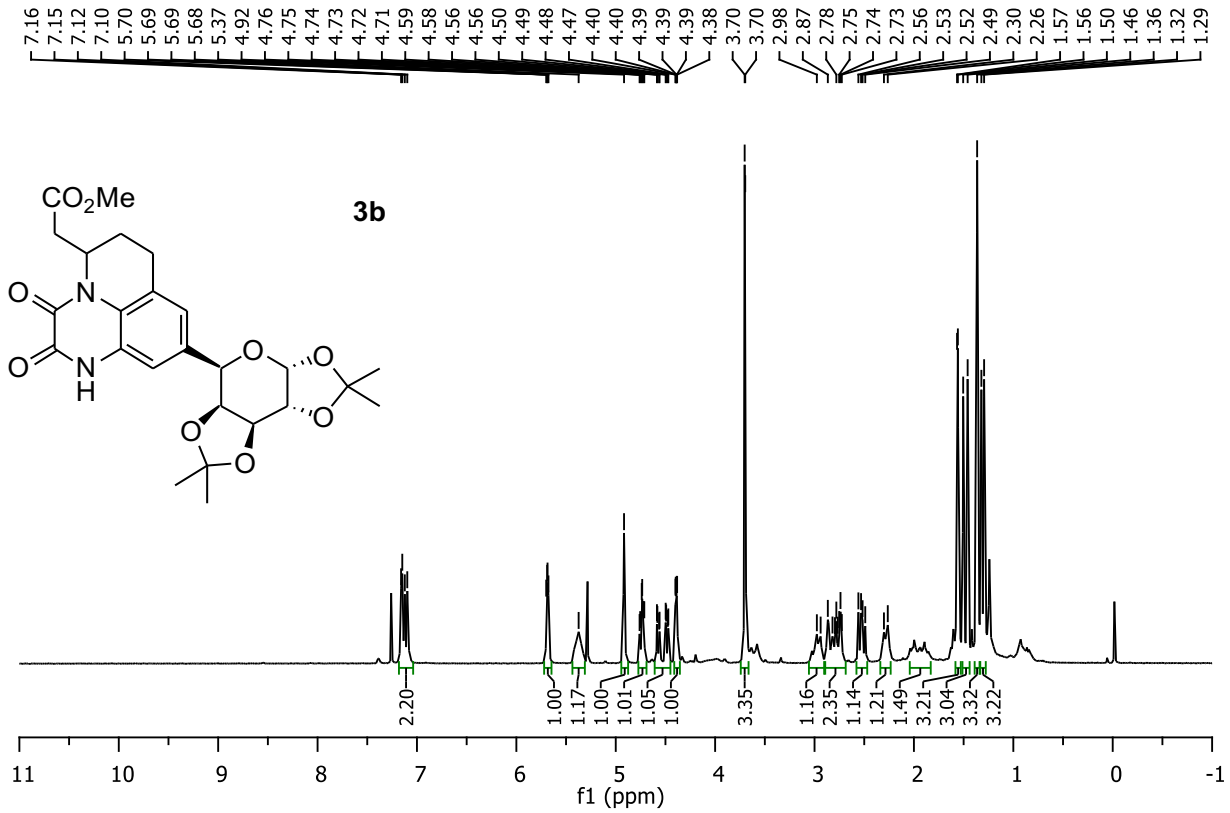
^{1}H NMR ($CDCl_3$, 360 MHz) of (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (**3a**)



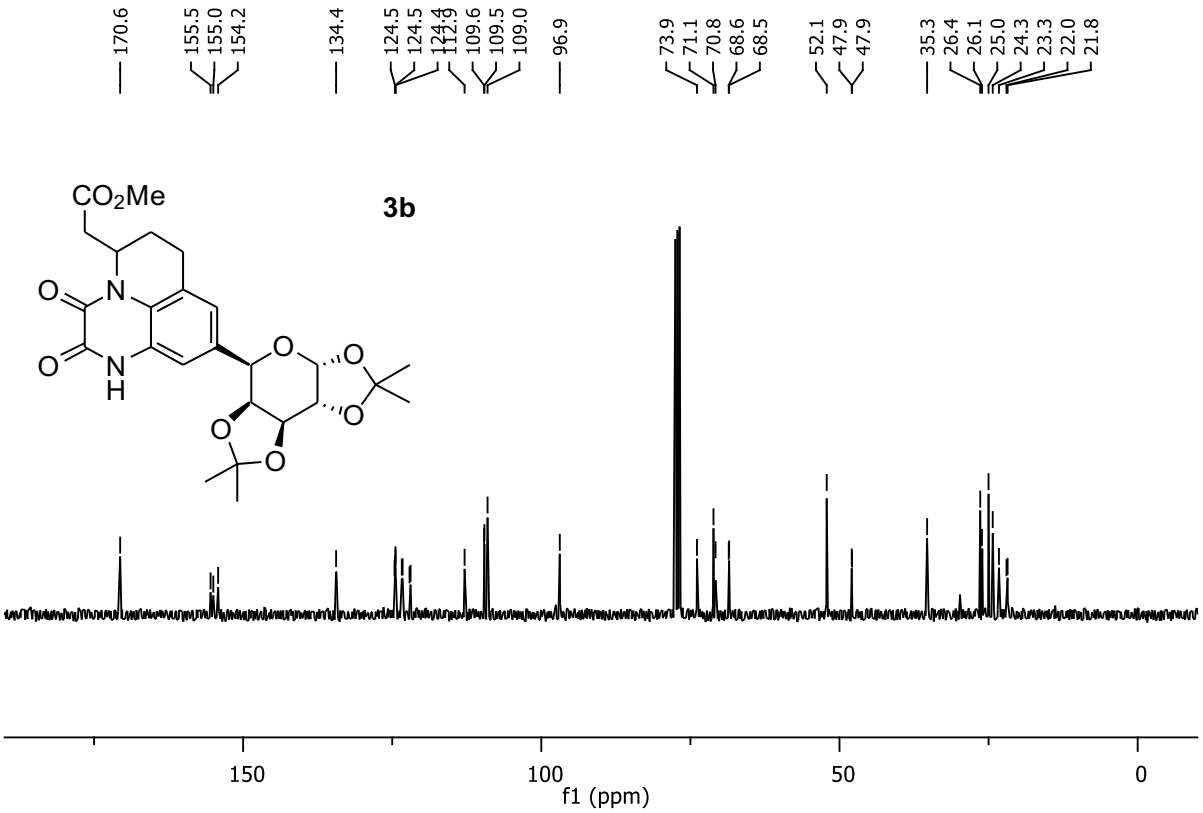
^{13}C NMR ($CDCl_3$, 91 MHz) of (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (**3a**)



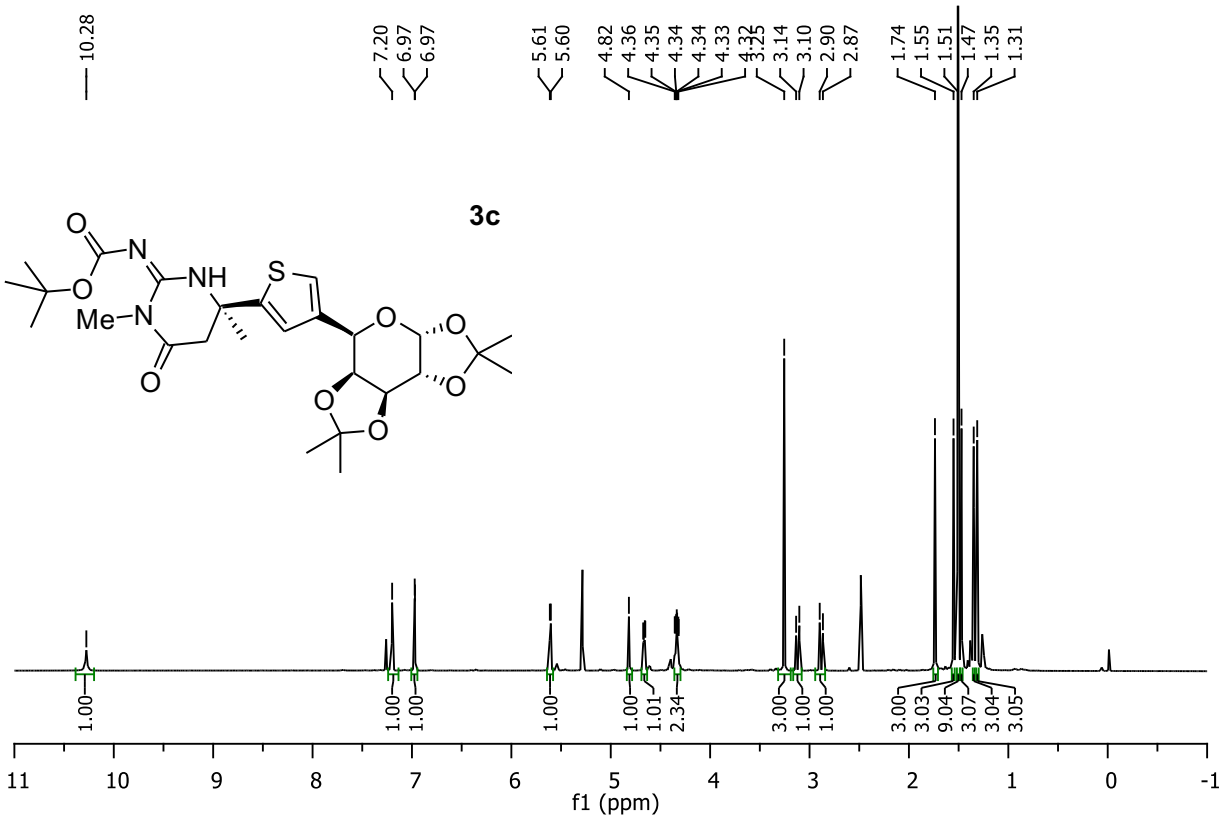
^{1}H NMR ($CDCl_3$, 360 MHz) of methyl 2-(2,3-dioxo-9-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis ([1,3] dioxolo)[4,5-b:4',5'-d]pyran-5-yl)-2,3,6,7-tetrahydro-1H,5H-pyrido[1,2,3-de]quinoxalin-5-yl) acetate (**3b**)



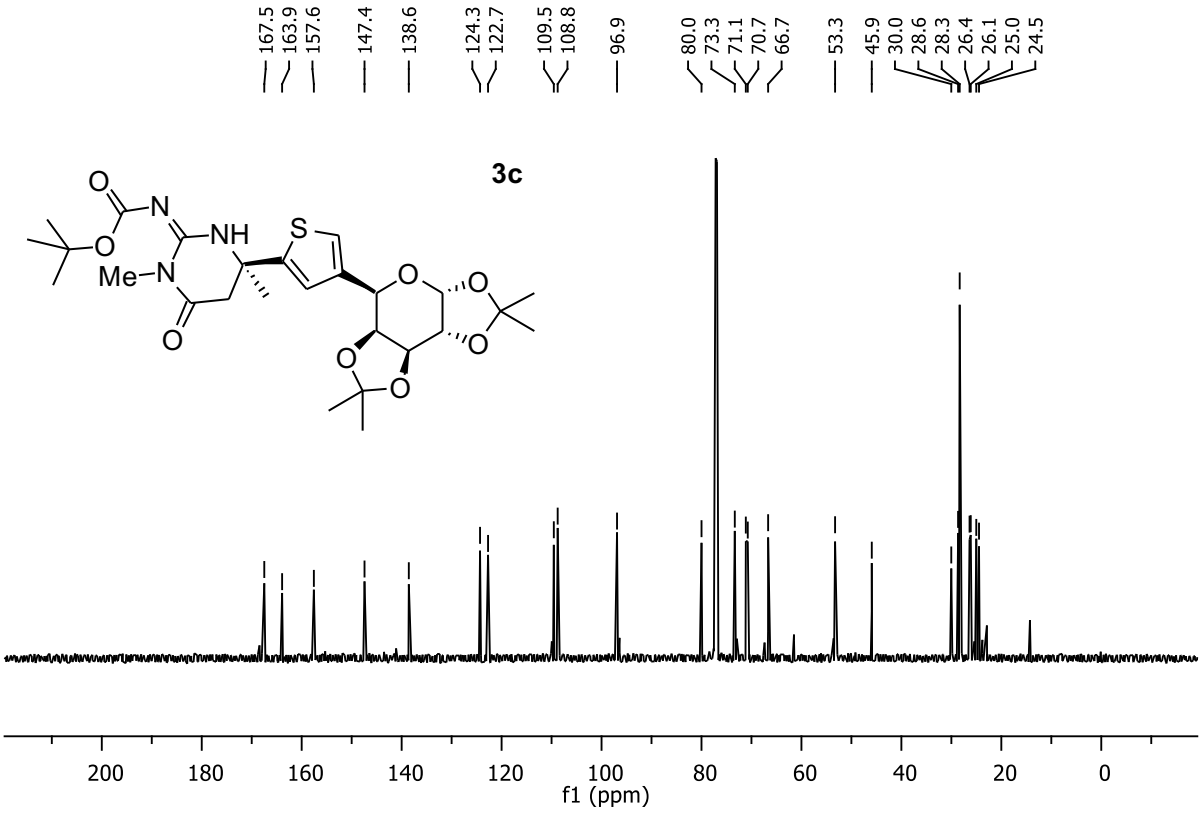
^{13}C NMR ($CDCl_3$, 91 MHz) of methyl 2-(2,3-dioxo-9-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis ([1,3] dioxolo)[4,5-b:4',5'-d]pyran-5-yl)-2,3,6,7-tetrahydro-1H,5H-pyrido[1,2,3-de]quinoxalin-5-yl) acetate (**3b**)



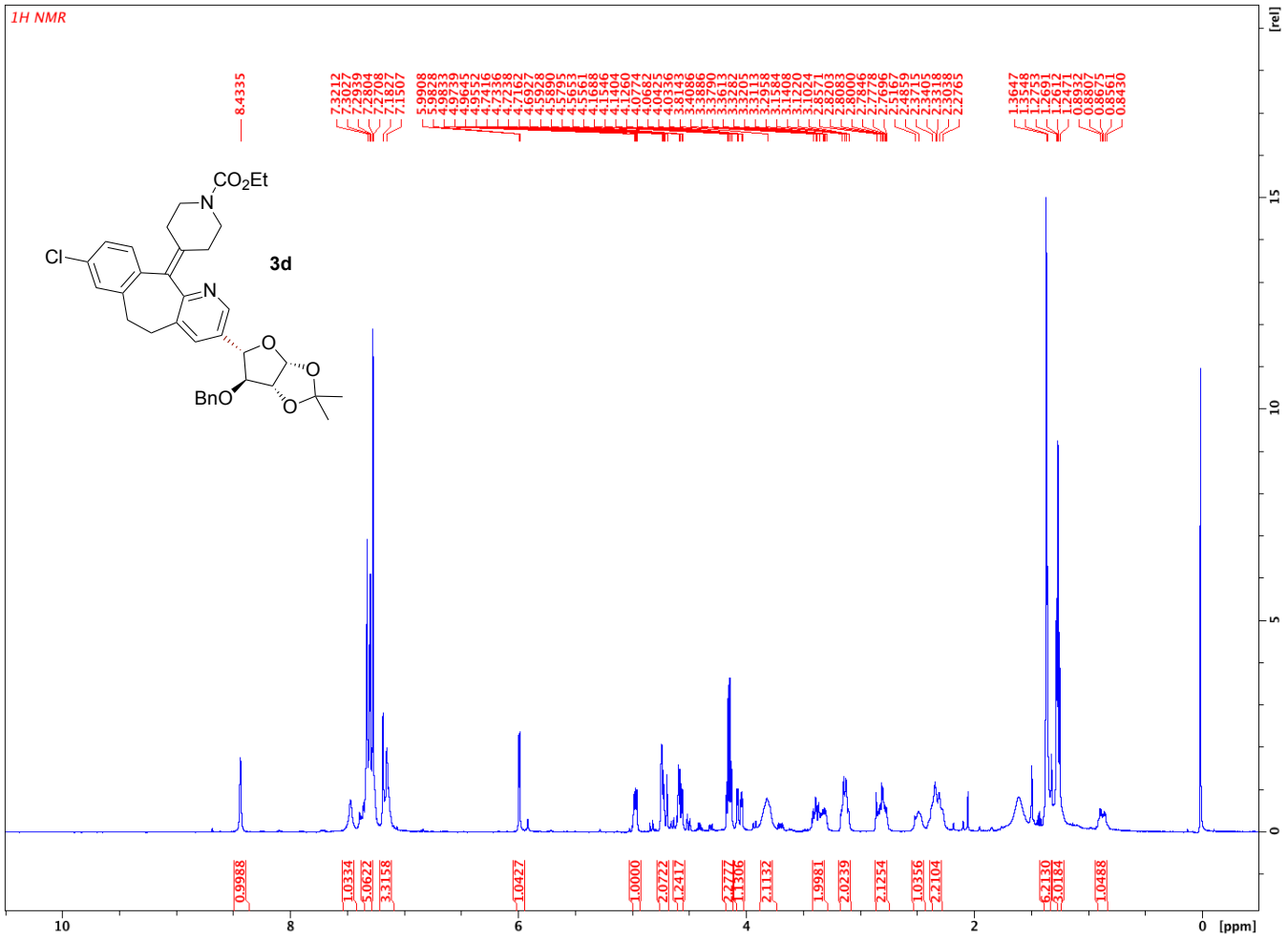
^{1}H NMR ($CDCl_3$, 500 MHz) of *tert*-butyl ((*R*,*Z*)-1,4-dimethyl-6-oxo-4-(4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*) -2,2,7,7-tetramethyl tetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)thiophen-2-yl) tetrahydro pyrimidin-2(1H)-ylidene)carbamate (**3c**)



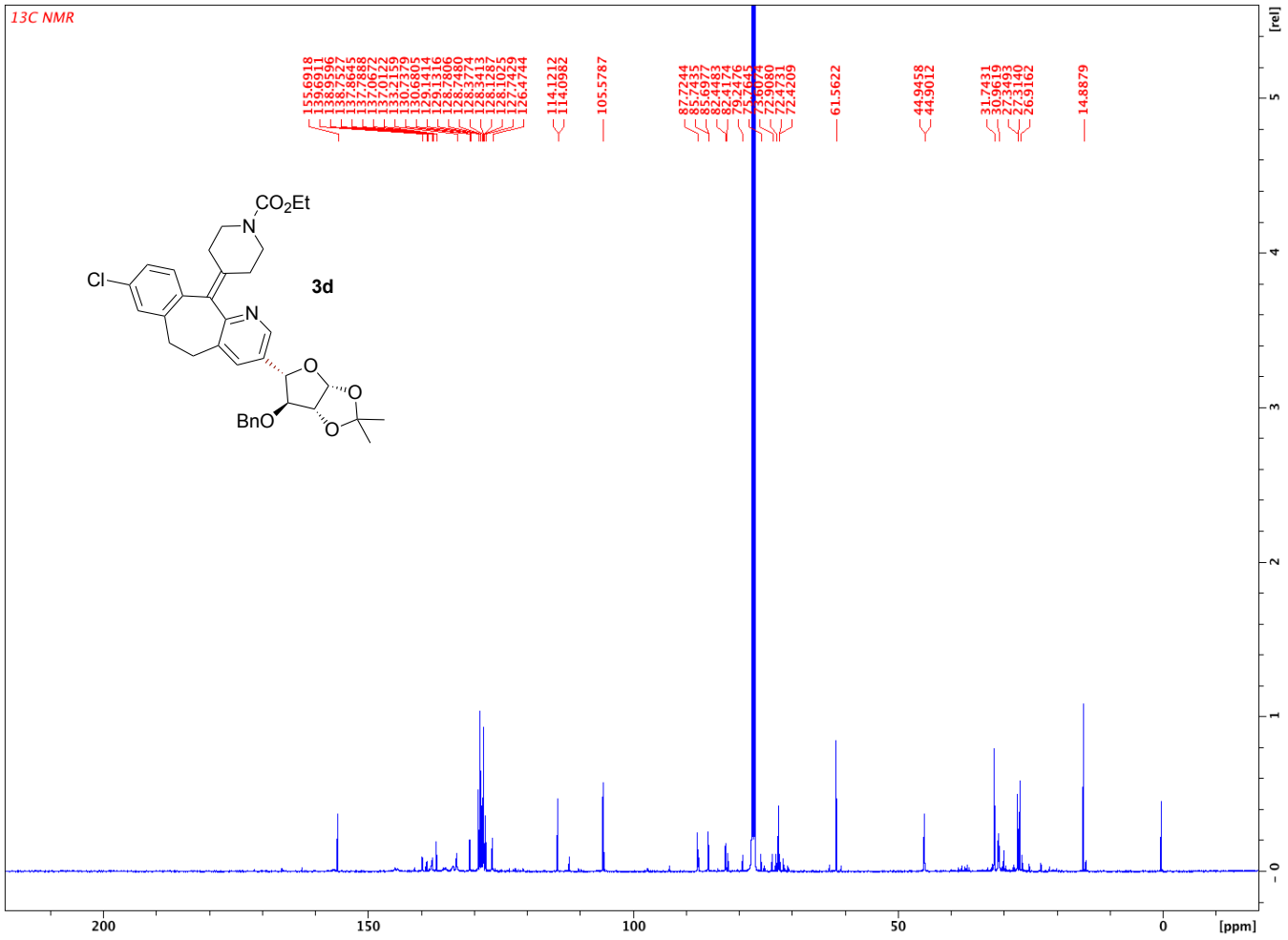
^{13}C NMR ($CDCl_3$, 126 MHz) of *tert*-butyl ((*R*,*Z*)-1,4-dimethyl-6-oxo-4-(4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*) -2,2,7,7-tetramethyl tetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)thiophen-2-yl) tetrahydro pyrimidin-2(1H)-ylidene)carbamate (**3c**)



^{1}H NMR ($CDCl_3$, 500 MHz) of ethyl 4-(3-((3a*R*,5*S*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (**3d**)



^{13}C NMR ($CDCl_3$, 126 MHz) of ethyl 4-(3-((3a*R*,5*S*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (**3d**) (mixture of rotamers)



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