Supporting Information

Synthesis of Non-anomeric *C*-Glycosyl Pyrazolidinones Derivatives via Visible-Light Photoredox Catalysis

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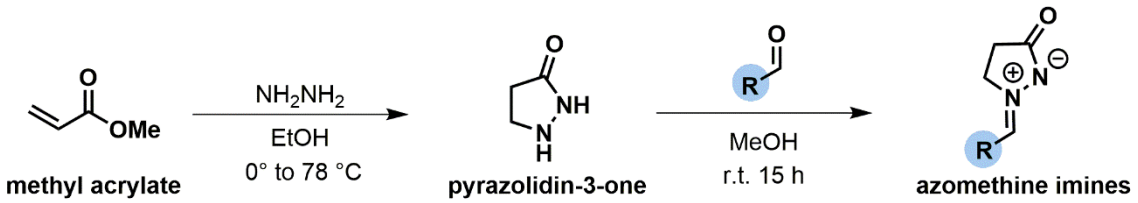
1. General Considerations

All reactions were prepared using standard Schlenk techniques and performed under a nitrogen atmosphere. HPLC-grade solvents were used in the photocatalyzed reactions. THF was distilled under argon from the sodium anion of benzophenone. Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. All sensitive to air or moisture reactions were carried out in flame-dried glassware under an argon atmosphere. Photocatalysts were purchased or synthesized unless otherwise noted. A 34 W Kessil H150 blue LED (λ_{max} = 456 nm) was used as the visible light source. Reactions were monitored by layer chromatography using Merck 60 F254 silica gel aluminum sheets, hexane/EtOAc or DCM/MeOH as mobile phase and visualized by UV lamp, permanganate or thymol spots. Flash column chromatography was performed using silica gel 60 (230-400 mesh) and hexane/EtOAc or DCM/MeOH as eluent systems. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on Brucker NMR spectrometers (400 for ^{1}H, 100 for ^{13}C and 376 MHz for ^{19}F). Chemical shifts (δ) for the ^{1}H and ^{13}C spectra given in ppm, residual solvent signals were used as a reference for the ^{1}H and ^{13}C NMR spectra, non-deuterated chloroform ($CDCl_3$): δ H = 7.26 ppm, δ C = 77.16 ppm). The values of the coupling constant(s) *J* are given in Hertz. The multiplicities are described as: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, m = multiplet. High-resolution mass spectra (HRMS) were recorded at Waters Technologies do Brasil using a Xevo G2-XS QTOF spectrometer (ESI-QTOF).

2. Synthesis of Starting Materials

2.1 Synthesis of Azomethine Imine[1]



Scheme S1. Preparation of azomethine imines.

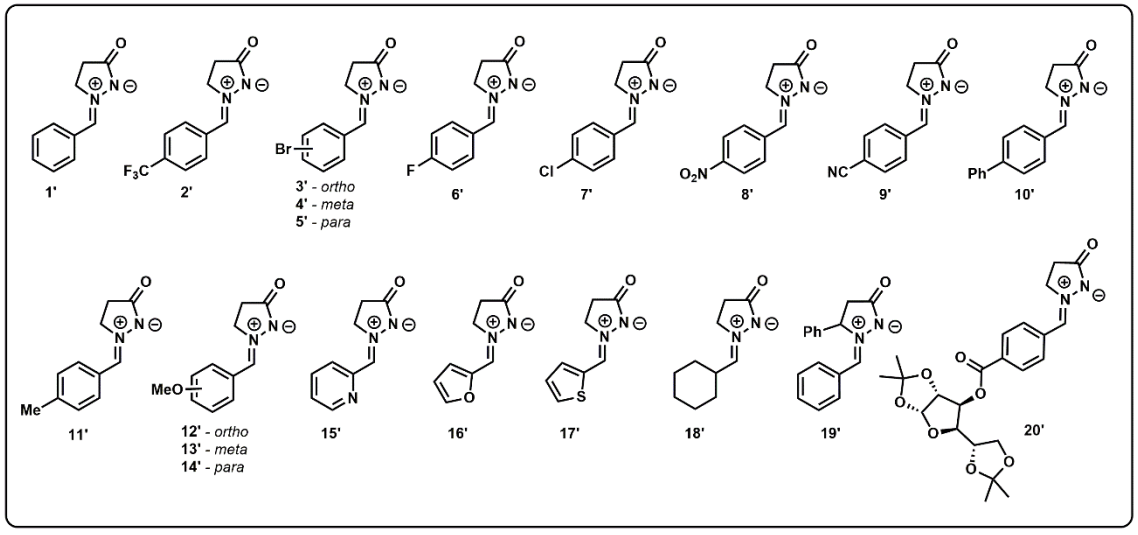
Pyrazolidin-3-one: In a round bottom flask, a solution of hydrazine monohydrate 78 % (1.0 equiv) in absolute ethanol (4 M) was cooled to 0 °C using an ice bath. Methyl acrylate

[1] S. E. Winterton and J. M. Ready, *Org. Lett.*, 2016, **18**, 2608–2611.

(1.0 equiv) was slowly added, and the solution was stirred at 0 °C for 30 min and then was heated to reflux using an oil bath until the reaction was completed judging by TLC analysis. The solution was concentrated under a vacuum to yield the crude pyrazolidin-3-one as a clear or yellow oil. The pyrazolidin-3-one was used immediately in the next step without purification.

Azomethine Imine: The crude pyrazolidinone (1.0 equiv) obtained in the previous step and the corresponding aldehydes (1.2 equiv) were dissolved in anhydrous MeOH (1 M). The mixture was stirred at room temperature overnight and then concentrated in a vacuum to remove the solvent. EtOAc was added to precipitate the product. The resulting solid was collected by filtration, washed with EtOAc, and dried to yield the final product. For substrates that do not precipitate, column chromatography purified reaction crudes using DCM/MeOH (20:1) as eluent.

Azomethine imines were used as starting materials for the scope evaluation (Scheme 2). The reported compounds (1' – 19') were prepared and characterized according to the literature.[2, 3] Compound 20' were prepared using the same experimental procedure, and their spectroscopic data was reported in the appropriate session in the SI.



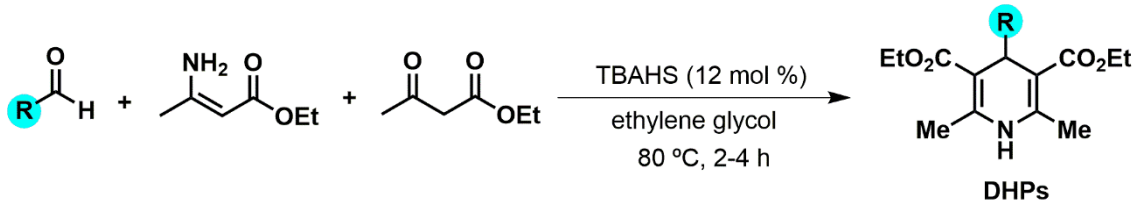
Scheme S2. Azomethines imines are used in this work.

Spectroscopic data of *C,N*-cyclic azomethine imines:

1', 2', 5', 7', 8', 14', 19', 15' [1], 4', 6', 9', 13', 11', 16' [2], 3', 12', 10', 17', 18' [3].

[2] Q. Du, J.-M. Neudörfl and H.-G. Schmalz, *Chem. Eur. J.*, 2018, **24**, 2379-2383.
[3] C. Li, C. -S. Wang, T.-Z. Li, G.-J. Mei and F. Shi, *Org. Lett.*, 2019, **21**, 598–602.

2.2 Synthesis of 1,4-Dihydropyridines Derivatives



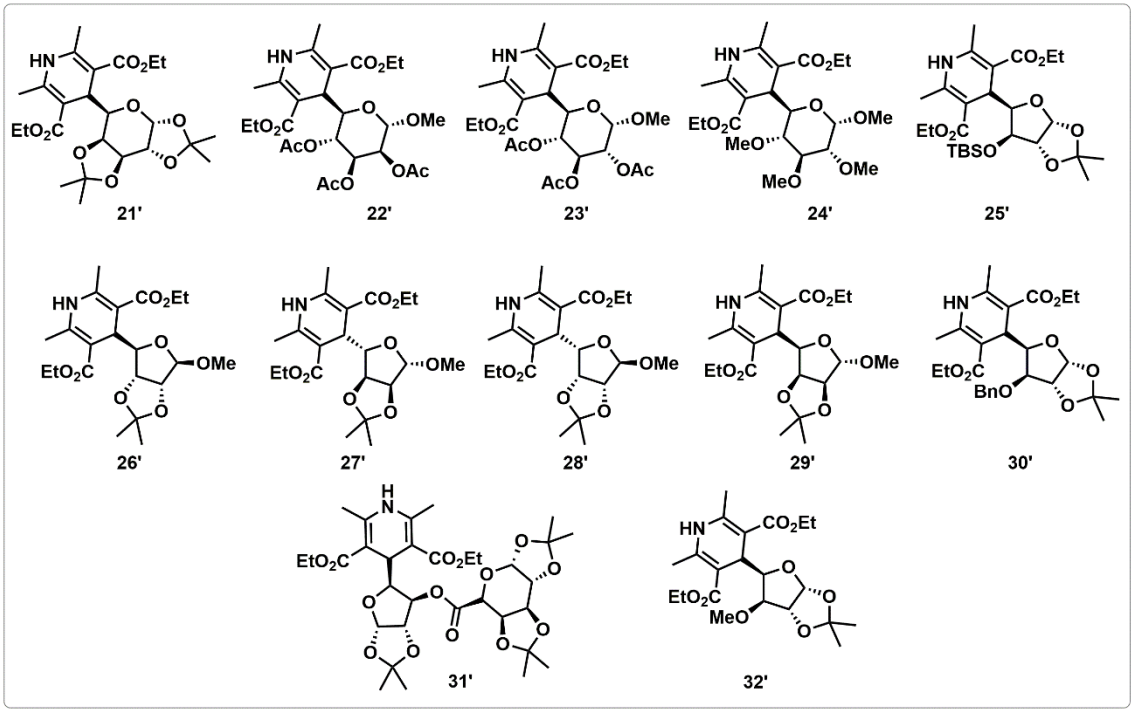
TBAHS = tetrabutylammonium hydrogen sulfate

Scheme S3. Synthesis of 1,4-DHP derivatives.

General procedure for DHPs synthesis:[4] In a round bottom flask, 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 tetrabutylammonium hydrogen sulfate (Bu_4NHSO_4) (12 mol %) in one part. The aldehydes used are very viscous, so they were dissolved in CH_2Cl_2 and added to the reaction mixture with no noticeable effect. The flask was sealed and heated at 80°C for 2-4 h. After completely consuming the aldehyde, the reaction was cooled to room temperature 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 brought to dryness. The crude reaction mixture was purified using silica gel chromatography using hexanes/EtOAc as eluent.

The following 4-glycosyl-1,4-dihydropyridines (Scheme S4) were used as starting materials for the scope evaluation. The reported compounds were prepared and characterized according to the literature.[4] The new compounds were prepared using the same experimental procedure and their spectroscopic data are reported in the appropriate session in the SI (compounds 22', 23', 27', 28', 29' and 31').

[4] A. Dumoulin, J. K. Matsui, Á. Gutiérrez-Bonet and G. A. Molander, *Angew. Chem. Int. Ed.*, 2018, **130**, 6724–6728.

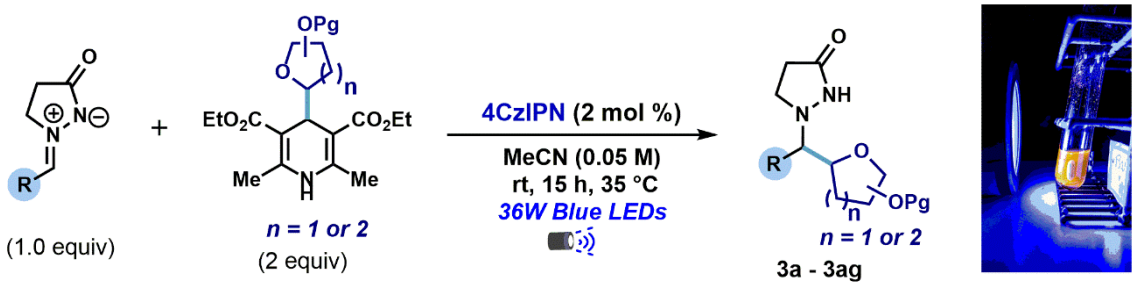


Scheme S4. 4-glycosyl-1,4-dihydropyridines are used in this work.

Spectroscopic data of 4-glycosyl-1,4-dihydropyridines:

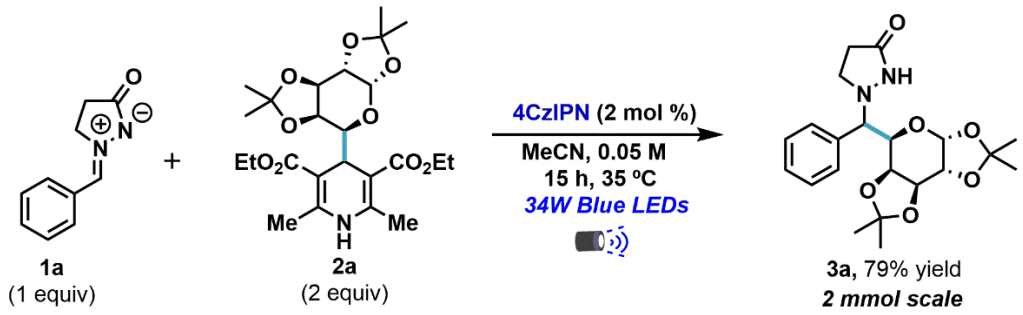
21', 24', 25', 26', 30', 32' [4].

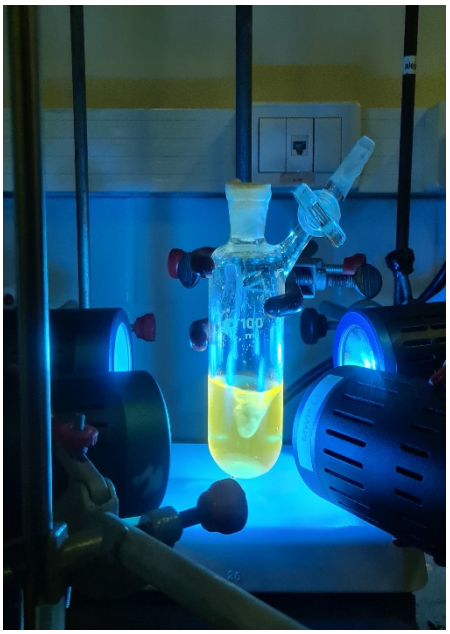
3. General Procedure for *C*-Glycosylation of Azomethine Imines



A dry borosilicate glass Schlenk tube equipped with a stir bar was charged with the azomethine imine (0.15 mmol, 1.0 equiv), the 4-glycoside-1,4-dihydropyridine (2 equiv, 0.3 mmol) and the photocatalyst 4CzIPN (2 mol %). Acetonitrile (3 mL) was added and the Schlenk tube was sealed with PTFE/silicon septum and connected to a vacuum line. The solution was degassed 3 times using a freeze-pump-thaw and stirred under irradiation by a 34 W Kessil H150 blue LED (with emission: 456 nm) with temperature controlled by a fan (~ 35 °C). After completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography using hexane/AcOEt (7:3) as a solvent mixture to provide the title compounds.

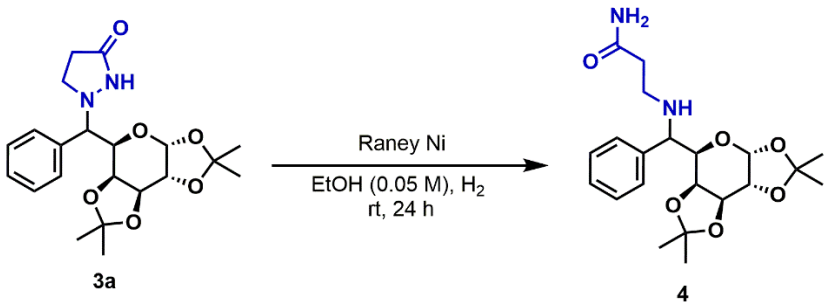
4. Scale-up Experiment





A dry 100 mL Schlenk borosilicate glass tube equipped with a stir bar was charged with the azomethine imine **1a** (349 mg, 2.00 mmol), 4-glycosyl-1,4-dihydropyridines **2a** (1.93 g, 2.0 equiv), and photocatalyst (32 mg, 2 mol %). Acetonitrile (40 mL) was added, and the Schlenk tube was sealed with a PTFE/silicon septum and connected to a vacuum line. The solution was degassed 3 times using a freeze-pump-thaw procedure and stirred under irradiation for 15 h by four 34 W Kessil H150 blue LEDs (emission: 380 – 525 nm) with the temperature controlled by two fans (distance between the Schlenk tube and the lamp was ~ 4 cm and the reaction temperature reached was 35 °C). Then, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography using hexane/EtOAc (3:7) as a mixture of solvents to provide compound **3a** as a white solid (639 mg, 79%).

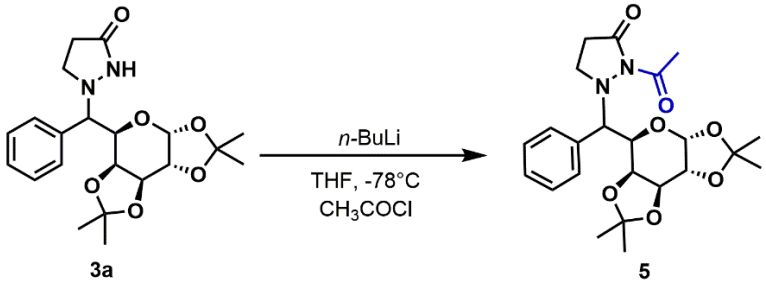
5. General Procedure for the Pyrazolidinone Reductive Cleavage[5]



[5] K. Woydowski and J. Liebscher, *J. prakt. Chem*. 1998, **340**, 567-571.

700 mg of Raney®-Nickel 2800 (slurry in H_2O) was added to a small vial and the catalyst was washed 3 times with EtOH. Then, a solution of **3a** (0.2 mmol) in EtOH (4 mL) was added to the vial containing the activated catalyst, which was sealed with a septum. The reaction mixture was placed under H_2 atmosphere using balloons containing H_2 and kept under vigorous agitation for 24 h at room temperature. The reaction crude was filtered through celite, concentrated under reduced pressure, and purified by column chromatography (EtOAc/MeOH 9:1) to furnish the corresponding **4**.

6. General Procedure for *N*(2)-Acylation of Pyrazolidinone[6]

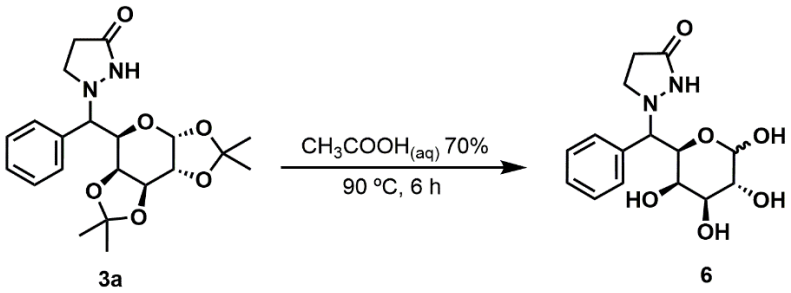


A stirred solution of the *C*-glycosyl pyrazolidinones in dry THF (0.3 M) at –78 °C was added 1.0 equivalent of *n*-BuLi. After 30 minutes, 1.1 equivalents of the appropriate acyl chloride were added. The mixture was stirred at –78 °C for 3 hours until the reaction was complete (TLC). The reaction was quenched with saturated aqueous ammonium chloride and THF was removed under reduced pressure. The residue was redissolved in CH_2Cl_2 and washed with saturated aqueous sodium bicarbonate. The organic layer was washed with brine, dried over $NaSO_4$, filtered, and concentrated under reduced pressure. Crude products were purified by column chromatography (EtOAc/MeOH 9:1) to furnish the corresponding **5**.

7. General Procedure for Unprotected Glycoside[7]

[6] M. P. Sibi, L. M. Stanley, X. Nie, L. Venkatraman, M. Liu, C. P. Jasperse, *J. Am. Chem. Soc.* 2007, **129**, 395–405.

[7] D. Gupta and A. Surolia, *J. Carbohydr. Chem.*, 1992, **11**, 171-182.

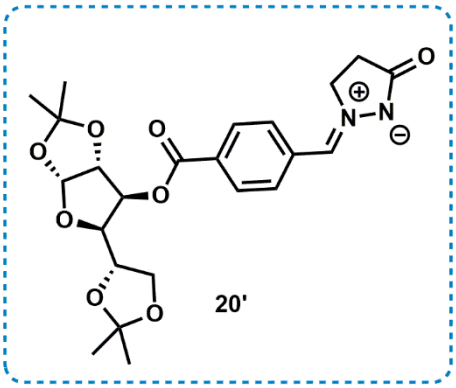


Compound **3a** (40.0 mg, 100 µmol) was heated for 6 hours at 90°C in refluxing 70% aqueous acetic acid (10 mL). The solution was evaporated under reduced pressure and purified by column chromatography (DCM/MeOH 8:2) to give the corresponding **6**.

8. Compound Characterization Data

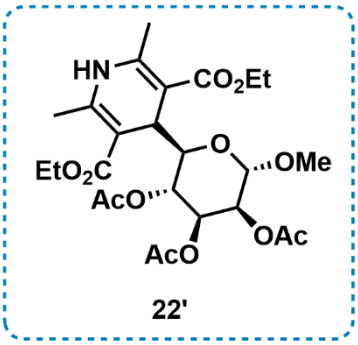
8.1 Starting Materials

2-((*E*)-4-((((3a*R*,5*R*,6*S*,6a*R*)-5-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)carbonyl)benzylidene)-5-oxopyrazolidin-2-ium-1-ide (20'):



The product **20'** was prepared according to the procedure described above as a yellow solid (325 mg, 50%). **^{1}H NMR (400 MHz, MeOD)** δ 8.32 (d, J = 8.5 Hz, 2H), 8.00 (d, J = 8.5 Hz, 2H), 7.64 (s, 1H), 5.90 (d, J = 3.7 Hz, 1H), 5.32 (d, J = 3.0 Hz, 1H), 4.64 – 4.56 (m, 3H), 4.29 (ddd, J = 7.9, 6.0, 5.0 Hz, 1H), 4.19 (dd, J = 8.0, 3.0 Hz, 1H), 4.03 (dd, J = 8.5, 6.1 Hz, 1H), 3.92 (dd, J = 8.6, 4.9 Hz, 1H), 3.21 (dt, J = 3.2, 1.6 Hz, 1H), 2.77 – 2.66 (m, 2H), 1.42 (s, 3H), 1.29 (s, 3H), 1.23 (s, 3H), 1.14 (s, 3H) ppm. **^{13}C NMR (101 MHz, MeOD)** δ 187.5, 164.2, 134.6, 133.6, 131.5, 131.5, 129.3, 112.0, 109.2, 105.3, 83.2, 79.8, 76.9, 72.6, 66.8, 58.0, 28.9, 25.6, 25.5, 24.9, 23.9 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{23}H_{29}N_2O_8$ 461.1918, found: 461.1925.

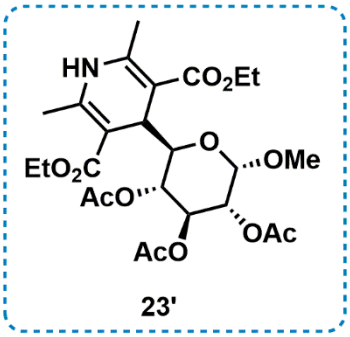
Diethyl 2,6-dimethyl-4-((2*R*,3*R*,4*S*,5*S*,6*S*)-3,4,5-triacetoxy-6-methoxytetrahydro-2*H*-pyran-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (22'):



22'

Following the general procedure using (2*S*,3*S*,4*S*,5*S*,6*S*)-2-formyl-6-methoxytetrahydro-2*H*-pyran-3,4,5-triyl triacetate[8,9] (2.1 g, 6.6 mmol, 1.0 equiv). The product was isolated as a yellow solid (1.6 g, 46% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.69 (s, 1H), 5.21 (dd, J = 9.2, 3.3 Hz, 1H), 5.10 (t, J = 9.6 Hz, 1H), 5.03 – 4.96 (m, 1H), 4.54 (d, J = 1.6 Hz, 1H), 4.47 (d, J = 3.9 Hz, 1H), 4.25 – 4.11 (m, 4H), 3.69 (dd, J = 9.9, 3.9 Hz, 1H), 3.26 (s, 3H), 2.28 (s, 3H), 2.27 (s, 3H), 2.13 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H), 1.29 (q, 6H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.3, 170.3, 169.8, 168.0, 167.8, 145.5, 145.3, 99.1, 98.3, 97.4, 72.6, 70.3, 70.1, 67.8, 59.9, 59.7, 54.4, 35.8, 21.0, 20.9, 20.8, 19.70, 19.05, 14.4, 14.3 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{25}H_{36}NO_{12}$ 542.2232, found: 542.2226.

Diethyl 2,6-dimethyl-4-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-triacetoxy-6-methoxytetrahydro-2*H*-pyran-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (23'):



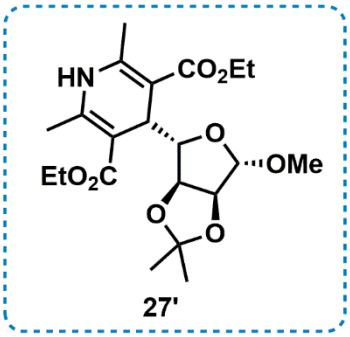
23'

Following the general procedure using (2*S*,3*S*,4*S*,5*R*,6*S*)-2-formyl-6-methoxytetrahydro-2*H*-pyran-3,4,5-triyl triacetate[8,9] (600 mg, 1.89 mmol, 1.0 equiv). The product was isolated as a white solid (398 mg, 39% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.85 (s, 1H), 5.29 (t, J = 9.2 Hz, 1H), 4.87 – 4.72 (m, 3H), 4.41 (d, J = 3.6 Hz, 1H), 4.28 – 4.04 (m, 4H), 3.68 (dd, J = 10.3, 3.6 Hz, 1H), 3.22 (s, 3H), 2.28 (s, 3H), 2.27 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H), 1.95 (s, 3H), 1.33 – 1.24 (m, 6H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.5, 170.3, 169.9, 168.0, 167.5, 146.3, 145.6, 98.6, 97.8, 95.8, 71.6, 71.5, 70.7, 69.6, 60.1, 59.8, 54.4, 34.7, 21.0, 20.8, 20.7, 19.9, 19.2, 14.3, 14.3 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{25}H_{36}NO_{12}$ 542.2216, found: 542.2232 .

Diethyl 4-((3a*S*,4*S*,6*S*,6a*S*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (27'):

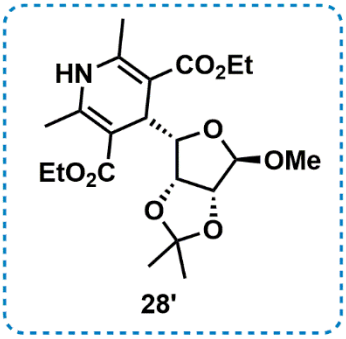
[8] P. Ji, Y. Zhang, Y. Wei, H. Huang, W. Hu, P. A. Mariano, W. Wang, *Org. Lett.* 2019, **21**, 9, 3086–3092.

[9] L. Luca, G. Giacomelli and A. Porcheddu, *Org. Lett.* 2001, **3**, 19, 3041–3043.



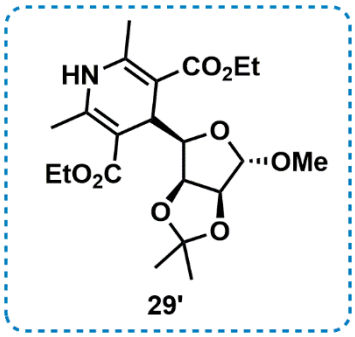
Following the general procedure using (3a*S*,4*R*,6*S*,6a*S*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole-4-carbaldehyde[8,9] (867 mg, 4.33 mmol, 1.0 equiv). The product was isolated as a white solid (1.12 g, 60% yield) mp = 149-154 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.80 (s, 1H), 4.73 (s, 1H), 4.63 (d, J = 8.2 Hz, 1H), 4.48 (dd, J = 5.8, 3.0 Hz, 1H), 4.41 (d, J = 5.8 Hz, 1H), 4.28 – 4.02 (m, 4H), 3.59 (dd, J = 8.2, 3.0 Hz, 1H), 3.16 (s, 3H), 2.31 (s, 3H), 2.24 (s, 3H), 1.43 (s, 3H), 1.38 – 1.21 (m, 9H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.5, 168.2, 144.5, 144.3, 112.4, 106.5, 100.8, 99.7, 85.3, 81.7, 79.6, 59.8, 59.4, 53.9, 33.5, 26.3, 25.8, 19.1, 18.5, 14.3, 14.2 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{21}H_{32}NO_8$ 426.2122, found: 426.2118.

Diethyl 4-((3a*R*,4*S*,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 (28'):



Following the general procedure using (3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole-4-carbaldehyde[8,9] (600 mg, 2.97 mmol, 1.0 equiv). The product was isolated as a white solid (610 mg, 48% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.81 (s, 1H), 4.72 (s, 1H), 4.63 (d, J = 8.2 Hz, 1H), 4.48 (dd, J = 5.8, 3.0 Hz, 1H), 4.41 (d, J = 5.8 Hz, 1H), 4.25 – 4.09 (m, 5H), 3.59 (dd, J = 8.2, 2.7 Hz, 1H), 3.16 (s, 3H), 2.31 (s, 3H), 2.24 (s, 3H), 1.43 (s, 3H), 1.33 – 1.21 (m, 9H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.5, 168.1, 144.5, 144.3, 112.4, 106.5, 100.8, 99.8, 85.3, 81.8, 79.6, 59.8, 59.4, 53.9, 33.5, 26.3, 25.8, 19.1, 18.5, 14.3, 14.2 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{21}H_{32}NO_8$ 426.2122, found: 426.2115.

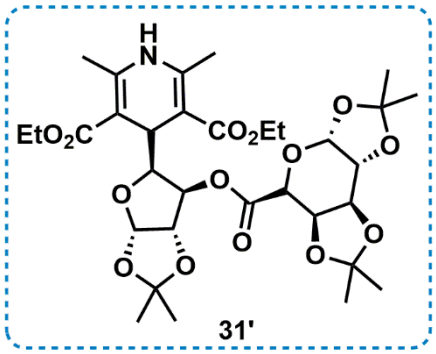
Diethyl 4-((3a*S*,4*R*,6*S*,6a*S*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (29'):



29'

Following the general procedure using (3a*S*,4*S*,6*S*,6a*S*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole-4-carbaldehyde[8,9] (400 mg, 1.98 mmol, 1.0 equiv). The product was isolated as a slightly yellow solid (400 mg, 47% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.77 (s, 1H), 4.73 (s, 1H), 4.63 (d, J = 8.2 Hz, 1H), 4.48 (dd, J = 5.8, 3.0 Hz, 1H), 4.41 (d, J = 5.8 Hz, 1H), 4.29 – 4.04 (m, 4H), 3.65 – 3.56 (m, 1H), 3.16 (s, 3H), 2.31 (s, 3H), 2.25 (s, 3H), 1.43 (s, 3H), 1.32 – 1.18 (m, 9H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.5, 168.1, 144.5, 144.2, 112.4, 106.5, 100.8, 99.8, 85.3, 81.8, 79.6, 59.8, 59.4, 53.9, 33.6, 26.3, 25.8, 19.1, 18.5, 14.3, 14.2 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{21}H_{32}NO_8$ 426.2122, found: 426.2114.

Diethyl 4-((3a*S*,5*S*,6*R*,6a*S*)-2,2-dimethyl-6-(((3a*R*,5*R*,5a*R*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-carbonyl)oxy) tetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (31'):

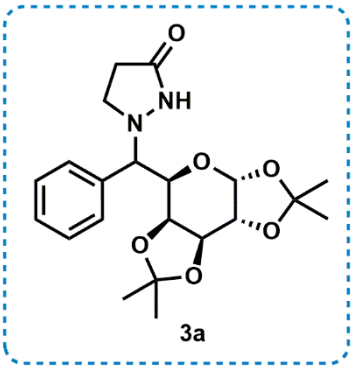


31'

Following the general procedure using (3a*S*,5*R*,6*R*,6a*S*)-5-formyl-2,2-dimethyl tetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl (3a*R*,5*R*,5a*R*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-carboxylate[8,9] (800 mg, 1.80 mmol, 1.0 equiv). The product was isolated as a white solid (479 mg, 40% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.76 (d, J = 3.8 Hz, 2H), 5.66 (d, J = 5.0 Hz, 1H), 5.11 (d, J = 2.4 Hz, 1H), 4.69 (d, J = 2.4 Hz, 1H), 4.66 (dd, J = 7.6, 2.7 Hz, 1H), 4.60 – 4.54 (m, 2H), 4.42 (d, J = 3.8 Hz, 1H), 4.38 (dd, J = 5.0, 2.7 Hz, 1H), 4.29 – 4.06 (m, 4H), 4.00 (dd, J = 8.5, 2.4 Hz, 1H), 2.33 (s, 3H), 2.27 (s, 3H), 1.63 (s, 3H), 1.43 (s, 6H), 1.34 (s, 3H), 1.31 (s, 3H), 1.29 – 1.20 (m, 9H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.7, 167.5, 167.3, 145.5, 145.1, 111.8, 110.0, 109.3, 104.5, 100.6, 99.6, 96.6, 82.7, 80.5, 76.0, 71.1, 70.5, 68.7, 60.3, 59.7, 32.8, 26.8, 26.3, 26.1, 25.8, 25.1, 25.0, 19.7, 19.4, 14.5, ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{32}H_{46}NO_{14}$ 668.2913, found: 668.2909.

8.2 Scope for the 4-Glycosyl-1,4-Dihydropyridines

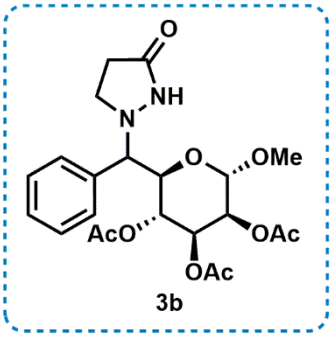
1-(phenyl((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-*d*]pyran-5-yl)methyl)pyrazolidin-3-one (3a):



3a

The product **3a** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a white solid (50 mg, 82% yield). dr = 2:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, CDCl$_3$ major diastereomer)** δ 7.45 – 7.30 (m, 5H), 5.63 (d, J = 5.0 Hz, 1H), 4.41 (dd, J = 7.9, 2.3 Hz, 1H), 4.31 (dd, J = 5.0, 2.4 Hz, 1H), 4.20 (d, J = 9.1 Hz, 1H), 3.98 (d, J = 9.7 Hz, 1H), 3.56 (d, J = 8.1 Hz, 1H), 3.19 – 3.10 (m, 1H), 3.00 (s, 1H), 2.28 – 2.14 (m, 2H), 1.65 (s, 3H), 1.47 (s, 3H), 1.34 (s, 3H), 1.17 (s, 3H) ppm. **^{1}H NMR (400 MHz, CDCl$_3$ minor diastereomer)** δ 7.45 – 7.29 (m, 5H), 5.47 (d, J = 5.1 Hz, 1H), 4.61 (dd, J = 7.9, 2.0 Hz, 1H), 4.54 (d, J = 8.0 Hz, 1H), 4.28 (dd, J = 5.1, 2.1 Hz, 1H), 4.13 (d, J = 8.1 Hz, 1H), 4.09 (d, J = 8.0 Hz, 1H), 3.42 – 3.26 (m, 1H), 1.95 – 1.68 (m, 1H), 1.57 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.30 (s, 3H) ppm. **^{13}C NMR (101 MHz, CDCl$_3$ CDCl$_3$ major diastereomer)** δ 175.2, 134.9, 129.3, 128.9, 128.5, 109.4, 109.2, 96.7, 70.6, 70.5, 70.4, 67.6, 51.5, 30.1, 26.1, 26.0, 24.9, 24.3 ppm. **^{13}C NMR (101 MHz, CDCl$_3$ minor diastereomer)** δ 173.2, 135.0, 129.5, 128.9, 128.3, 109.2, 108.5, 96.8, 71.2, 71.0, 70.5, 70.5, 50.7, 29.8, 26.1, 25.8, 24.7, 24.3 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{21}H_{29}N_2O_6$ 405.2020, found: 405.2014.

(2*S*,3*S*,4*S*,5*R*,6*R*)-2-methoxy-6-((3-oxopyrazolidin-1-yl)(phenyl)methyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3b):

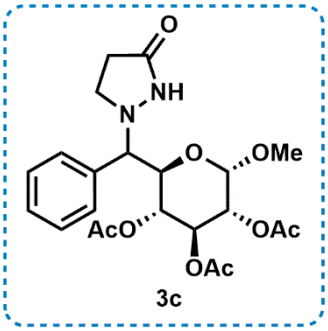


3b

The product **3b** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow viscous liquid (20 mg, 35% yield). dr = 1.1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, CDCl$_3$ major diastereomer)** δ 7.41 – 7.35 (m, 5H), 5.63 (t, J = 9.7 Hz, 1H), 5.36 – 5.26 (m, 1H), 5.24 – 5.22 (m, 1H), 4.79 (d, J = 11.3 Hz, 1H), 4.14

(dd, J = 9.7, 3.5 Hz, 1H), 3.66 (d, J = 3.6 Hz, 1H), 3.62 (s, 1H), 3.36 (s, 3H), 3.36 – 3.34 (m, 2H), 3.12 – 3.03 (m, 1H), 2.16 (s, 3H), 1.97 (s, 3H), 1.84 (s, 3H) ppm. **^{1}H NMR (400 MHz, $CDCl_3$ minor diastereomer)** δ 7.47 – 7.40 (m, 5H), 5.36 – 5.27 (m, 2H), 5.15 – 5.11 (m, 1H), 4.95 (t, J = 9.7 Hz, 1H), 4.79 (d, J = 11.3 Hz, 1H), 4.46 (d, J = 8.4 Hz, 1H), 3.99 – 3.88 (m, 2H), 3.48 (s, 3H), 2.15 – 2.04 (m, 2H), 2.03 (s, 3H), 2.01 (s, 3H), 1.92 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 174.0, 170.0, 169.9, 169.7, 135.2, 129.9, 128.7, 128.5, 98.6, 73.5, 69.3, 69.1, 69.1, 67.5, 56.0, 51.1, 29.8, 20.9, 20.7, 20.6 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 174.0, 170.0, 169.9, 169.8, 135.2, 131.0, 129.3, 128.8, 98.4, 71.6, 70.4, 69.4, 69.0, 67.5, 56.1, 51.0, 29.6, 20.8, 20.7, 20.6 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{22}H_{29}N_2O_9$ 465.1868, found: 465.1863.

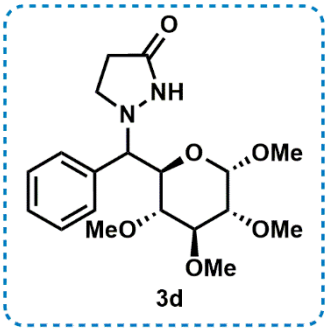
(2*S*,3*R*,4*S*,5*R*,6*R*)-2-methoxy-6-((3-oxopyrazolidin-1-yl)(phenyl)methyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3c)



3c

The product **3c** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 80/20%) to afford a slightly yellow viscous liquid (19 mg, 28% yield). dr = 2:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 7.43 (s, 1H), 7.36 – 7.27 (m, 5H), 5.43 – 5.30 (m, 1H), 4.99 (d, J = 3.6 Hz, 1H), 4.79 (dd, J = 9.3, 3.6 Hz, 1H), 4.10 (dd, J = 9.3, 3.6 Hz, 1H), 3.60 – 3.57 (m, 3H), 3.55 (d, J = 3.6 Hz, 1H), 3.32 (s, 3H), 3.17 – 3.06 (m, 1H), 3.03 – 2.94 (m, 1H), 2.01 (s, 3H), 1.99 (s, 3H), 1.93 (s, 3H) ppm. **^{1}H NMR (400 MHz, $CDCl_3$ minor diastereomer)** δ 7.43 (s, 1H), 7.36 – 7.27 (m, 3H), 7.26 – 7.22 (m, 2H), 4.91 (d, J = 3.7 Hz, 1H), 4.66 (dd, J = 10.3, 3.7 Hz, 1H), 4.57 (dd, J = 10.1, 9.2 Hz, 1H), 4.34 (dd, J = 10.3, 4.0 Hz, 1H), 3.66 (d, J = 4.0 Hz, 1H), 3.62 – 3.57 (m, 1H), 3.53 – 3.47 (m, 2H), 3.41 (s, 3H), 3.28 – 3.19 (m, 2H), 1.97 (s, 3H), 1.86 (s, 3H), 1.78 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 170.1, 170.1, 170.1, 169.6, 134.8, 130.5, 130.1, 128.6, 96.9, 72.3, 70.5, 70.1, 69.8, 56.2, 51.2, 29.7, 20.7, 20.6, 20.6, 14.1 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 170.1, 170.1, 169.1, 169.0, 134.8, 129.1, 128.8, 128.7, 96.9, 70.7, 70.4, 70.3, 70.2, 56.1, 51.2, 31.9, 29.3, 22.6, 20.8, 20.6 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{22}H_{29}N_2O_9$ 465.1868, found: 465.1867.

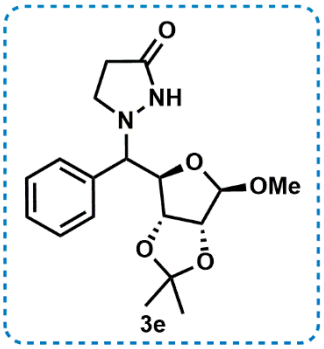
1-(phenyl((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5,6-tetramethoxytetrahydro-2*H*-pyran-2-yl)methyl)pyrazolidin-3-one (3d):



3d

The product **3d** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 80/20%) to afford a slightly yellow viscous liquid (24 mg, 42% yield). dr = 3:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, CDCl$_3$ major diastereomer)** δ 7.40 (s, 1H), 7.31 – 7.25 (m, 5H), 4.80 (d, J = 3.5 Hz, 1H), 3.89 (d, J = 1.8 Hz, 1H), 3.70 (dd, J = 9.6, 1.8 Hz, 1H), 3.56 (s, 3H), 3.55 (s, 3H), 3.49 (d, J = 3.6 Hz, 1H), 3.46 (s, 3H), 3.18 (s, 3H), 3.13 (dd, J = 9.4, 3.6 Hz, 1H), 3.06 (ddd, J = 10.8, 9.2, 6.9 Hz, 1H), 2.10 – 2.00 (m, 2H), 1.75 – 1.64 (m, 2H) ppm. **^{13}C NMR (101 MHz, CDCl$_3$ major diastereomer)** δ 173.9, 135.5, 131.1, 130.5, 128.3, 97.8, 83.5, 81.6, 79.7, 74.5, 66.8, 60.9, 60.6, 59.1, 55.9, 50.6, 30.0 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{19}H_{29}N_2O_6$ 381.2020, found: 381.2011.

1-(((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)(phenyl)methyl)pyrazolidin-3-one (3e):

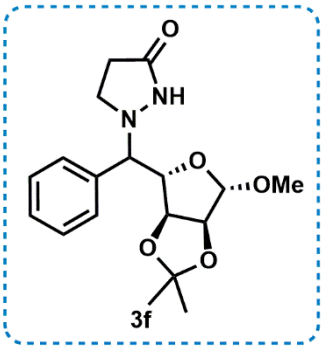


3e

The product **3e** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow viscous liquid (44 mg, 85% yield). dr = 2:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, CDCl$_3$ major diastereomer)** δ 8.18 (s, 1H), 7.38 – 7.22 (m, 5H), 5.01 (s, 1H), 4.52 (dd, J = 10.0, 1.4 Hz, 1H), 4.42 (d, J = 6.0 Hz, 1H), 4.22 (dd, J = 6.0, 1.3 Hz, 1H), 3.52 (d, J = 10.0 Hz, 1H), 3.44 (s, 3H), 3.09 – 2.99 (m, 1H), 2.92 (s, 1H), 2.22 – 2.04 (m, 2H), 1.37 (s, 3H), 1.09 (s, 3H) ppm. **^{1}H NMR (400 MHz, CDCl$_3$ minor diastereomer)** δ 8.13 (s, 1H), 7.40 – 7.22 (m, 5H), 5.08 (d, J = 6.0 Hz, 1H), 4.77 (s, 1H), 4.56 (d, J = 6.0 Hz, 1H), 4.47 (d, J = 11.3 Hz, 1H), 3.69 (d, J = 11.4 Hz, 1H), 3.55 – 3.42 (m, 1H), 3.33 – 3.23 (m, 1H), 2.83 (s, 3H), 1.61 – 1.52 (m, 1H), 1.44 (s, 3H), 1.47 – 1.37 (m, 1H), 1.29 (s, 3H) ppm. **^{13}C NMR (101 MHz, CDCl$_3$ major diastereomer)** δ 176.9, 135.6, 129.2, 128.9, 128.4, 112.5, 110.4, 85.5, 84.3, 82.0, 74.2, 56.3, 51.5, 30.1, 25.0 ppm. **^{13}C NMR (101 MHz, CDCl$_3$ minor diastereomer)** δ 173.7, 134.6, 129.9, 128.9,

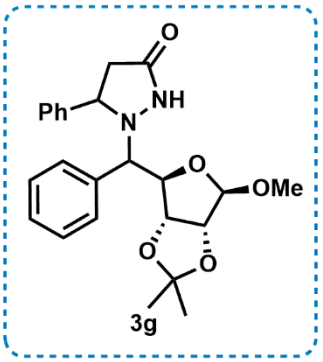
128.3, 112.6, 109.6, 90.8, 85.1, 82.9, 72.6, 55.6, 50.3, 29.8, 26.5 ppm. **HRMS** (ESI) [M + H]$^+$ *m/z*: calculated for $C_{18}H_{25}N_2O_5$ 349.1758, found: 349.1752.

1-(((3a*S*,4*S*,6*S*,6a*S*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)(phenyl)methyl)pyrazolidin-3-one (3f):



The product **3e** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 60/40%) to afford a yellow viscous liquid (42 mg, 81% yield). dr = 2:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 7.97 (s, 1H), 7.39 – 7.21 (m, 5H), 5.01 (s, 1H), 4.52 (dd, *J* = 9.8, 1.7 Hz, 1H), 4.42 (d, *J* = 6.0 Hz, 1H), 4.23 (dd, *J* = 6.0, 1.7 Hz, 1H), 3.51 (d, *J* = 9.9 Hz, 1H), 3.44 (s, 1H), 3.08 – 2.99 (m, 1H), 2.88 (s, 1H), 2.19 – 2.05 (m, 2H), 1.37 (s, 3H), 1.09 (s, 3H) ppm. **^{1}H NMR (400 MHz, $CDCl_3$ minor diastereomer)** 7.72 (s, 1H), 7.37 – 7.21 (m, 5H), 5.07 (dd, *J* = 6.0, 1.1 Hz, 1H), 4.78 (s, 1H), 4.55 (d, *J* = 6.0 Hz, 1H), 4.46 – 4.41 (m, 1H), 3.67 (d, *J* = 11.1 Hz, 1H), 3.32 – 3.21 (m, 2H), 2.86 (s, 3H), 1.64 – 1.51 (m, 2H), 1.44 (s, 3H), 1.29 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 173.6, 135.7, 129.2, 128.9, 128.5, 112.5, 110.5, 85.1, 84.3, 82.0, 74.3, 56.3, 51.6, 30.1, 26.5, 25.0 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 176.9, 134.7, 129.8, 128.9, 128.3, 112.7, 109.5, 91.0, 85.8, 85.1, 82.8, 72.6, 64.3, 55.6, 29.7, 26.5 ppm. **HRMS** (ESI) [M + H]$^+$ *m/z*: calculated for $C_{18}H_{25}N_2O_5$ 349.1758, found: 349.1758.

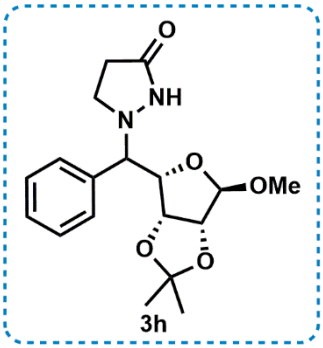
1-(((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)(phenyl)methyl)-5-phenylpyrazolidin-3-one (3g):



The product **3g** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow viscous liquid (22 mg, 50% yield). dr = 1.5:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 8.27 (s, 1H), 7.31 (s, 2H), 7.14 – 7.05 (m, 6H), 7.01 – 6.98 (m, 2H), 5.01 (s, 1H), 4.59 (dd, *J* = 9.5, 1.7 Hz, 1H), 4.39 (d, *J* = 5.9 Hz, 1H), 4.23 (dd, *J* = 6.0, 1.5 Hz, 1H), 4.16 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.83 (d, *J* = 9.6 Hz, 1H), 3.45 (s, 3H), 2.84 (dd, *J* = 17.0, 9.2 Hz, 1H), 2.01 – 1.97 (m, 2H), 1.34 (s, 3H),

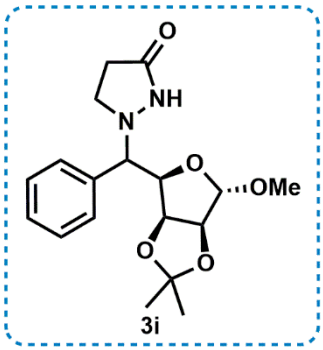
1.07 (s, 3H) ppm. **^{1}H NMR (400 MHz, $CDCl_3$ minor diastereomer)** δ 8.18 (s, 1H), 7.31 (s, 2H), 7.27 – 7.21 (m, 4H), 7.20 – 7.15 (m, 4H), 5.06 (d, J = 5.9 Hz, 1H), 4.76 (s, 1H), 4.52 (d, J = 5.9 Hz, 1H), 4.43 (d, J = 10.5 Hz, 1H), 4.39 (d, J = 5.9 Hz, 1H), 4.05 (q, J = 7.2 Hz, 1H), 3.97 (d, J = 10.6 Hz, 1H), 2.28 (dd, J = 16.9, 4.6 Hz, 2H), 1.37 (s, 3H), 1.23 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 172.0, 141.2, 135.1, 129.2, 129.1, 128.7, 128.6, 128.4, 126.5, 112.6, 110.6, 85.1, 84.3, 82.1, 74.5, 63.8, 56.7, 36.9, 26.7 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 174.7, 141.5, 135.6, 129.0, 128.6, 128.4, 127.6, 127.2, 112.7, 109.5, 91.7, 85.4, 83.2, 72.3, 60.7, 55.6, 37.3, 25.2 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{24}H_{29}N_2O_5$ 425.2071, found: 425.2075.

1-(((3a*R*,4*S*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)(phenyl)methyl)pyrazolidin-3-one (3h):



The product **3h** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow iol (41 mg, 79% yield). dr = 2:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 8 7.86 (s, 1H), 7.41 – 7.23 (m, 5H), 5.01 (s, 1H), 4.51 (dd, J = 9.8, 1.8 Hz, 1H), 4.42 (d, J = 6.0 Hz, 1H), 4.23 (dd, J = 6.0, 1.7 Hz, 1H), 3.50 (d, J = 9.8 Hz, 1H), 3.44 (s, 3H), 3.07 – 2.96 (m, 1H), 2.86 (s, 1H), 2.25 – 2.03 (m, 2H), 1.37 (s, 4H), 1.10 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 173.4, 135.7, 129.3, 128.9, 128.9, 112.5, 110.5, 84.3, 81.9, 74.4, 56.4, 51.7, 30.1, 26.6, 25.0 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{18}H_{25}N_2O_5$ 349.1758, found: 349.1751.

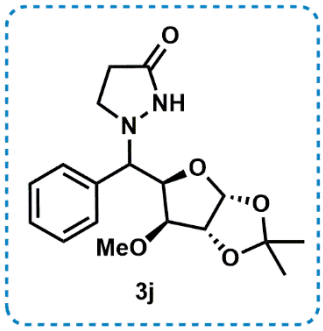
1-(((3a*S*,4*R*,6*S*,6a*S*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)(phenyl)methyl)pyrazolidin-3-one (3i):



3i

The product **3i** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow viscous liquid (35 mg, 67% yield). dr = 1:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 7.59 (s, 1H), 7.38 – 7.22 (m, 5H), 5.07 (dd, J = 6.0, 1.0 Hz, 1H), 4.78 (s, 1H), 4.55 (d, J = 6.0 Hz, 1H), 4.46 – 4.40 (m, 1H), 3.67 (d, J = 11.2 Hz, 1H), 3.27 (ddd, J = 11.8, 9.0, 5.2 Hz, 1H), 2.86 (s, 3H), 2.26 – 2.03 (m, 2H), 1.60 (ddd, J = 16.3, 8.7, 5.2 Hz, 1H), 1.44 (s, 3H), 1.29 (s, 3H) ppm. **^{1}H NMR (400 MHz, $CDCl_3$ minor diastereomer)** δ 7.94 (s, 1H), 7.36 – 7.21 (m, 5H), 5.01 (s, 1H), 4.54 – 4.49 (m, 1H), 4.45 – 4.40 (m, 1H), 4.23 (dd, J = 6.0, 1.7 Hz, 1H), 3.51 (d, J = 9.8 Hz, 1H), 3.44 (s, 3H), 3.08 – 2.98 (m, 1H), 1.95 – 1.71 (m, 2H), 1.43 – 1.34 (m, 4H), 1.09 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 176.8, 134.7, 129.8, 129.2, 128.5, 110.5, 109.5, 85.1, 84.3, 82.7, 72.7, 55.6, 51.6, 26., 25.0 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 173.5, 135.7, 129.8, 128.9, 128.4, 112.7, 112.5, 85.8, 84.3, 82.0, 74.3, 72.7, 56.3, 30.1, 29.7 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{18}H_{25}N_2O_5$ 349.1758, found: 349.1757.

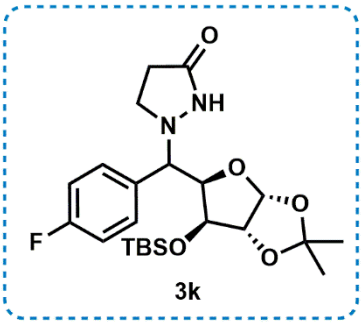
1-(((3a*R*,5*R*,6*S*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)(phenyl)methyl)pyrazolidin-3-one (3j):



3j

The product **3j** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 60/40%) to afford a yellow viscous liquid (44 mg, 85% yield). dr = >20:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 8.09 (s, 1H), 7.43 – 7.29 (m, 5H), 5.92 (d, J = 3.7 Hz, 1H), 4.46 (d, J = 3.8 Hz, 1H), 4.35 (dd, J = 9.5, 2.1 Hz, 1H), 3.82 (d, J = 9.5 Hz, 1H), 3.44 (d, J = 2.0 Hz, 1H), 3.19 – 3.10 (m, 1H), 2.88 (s, 3H), 2.84 (s, 1H), 2.35 – 2.26 (m, 2H), 1.60 (s, 3H), 1.32 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 172.6, 135.9, 129.1, 129.0, 128.8, 113.2, 106.3, 89.1, 85.0, 83.8, 73.4, 57.0, 52.1, 30.3, 26.8, 26.0 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{18}H_{25}N_2O_5$ 349.1758, found: 349.1769.

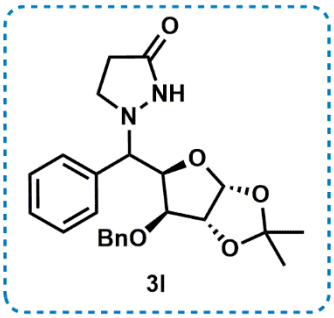
1-(((3a*R*,5*R*,6*S*,6a*R*)-6-((*tert*-butyldimethylsilyl)oxy)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)(4-fluorophenyl)methyl)pyrazolidin-3-one (3k):



3k

The product **3k** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 40/60%) to afford a yellow viscous liquid (53 mg, 83% yield). dr = >20:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 7.32 (dd, J = 8.4, 5.4 Hz, 2H), 7.08 (t, J = 8.6 Hz, 2H), 5.98 (d, J = 3.6 Hz, 1H), 4.30 (d, J = 3.6 Hz, 1H), 4.26 (d, J = 9.9 Hz, 1H), 3.90 (s, 1H), 3.86 (d, J = 9.9 Hz, 1H), 3.13 – 3.03 (m, 1H), 2.78 – 2.66 (m, 1H), 2.31 – 2.25 (m, 2H), 1.63 (s, 3H), 1.31 (s, 3H), 0.72 (s, 9H), -0.25 (s, 3H), -0.38 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 172.4, 164.0, 161.6 (d, J = 248.6 Hz), 132.1(d, J = 4 Hz), 130.9, 130.8 (d, J = 7.5 Hz), 116.3, 116.1 (d, J = 21.4 Hz), 112.9, 106.7, 93.4, 86.1, 76.4, 72.0, 52.0, 30.2, 26.5, 25.84, 25.70, 25.4, 17.6, -5.3, -5.6 ppm. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -112.37 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{23}H_{36}FN_2O_5Si$ 467.2372, found: 467.2360.

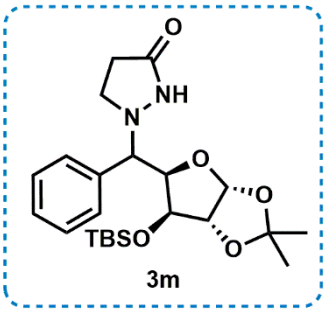
1-(((3a*R*,5*R*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)(phenyl)methyl)pyrazolidin-3-one (3l):



3l

The product **3l** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 50/50%) to afford a yellow viscous liquid (43 mg, 68% yield). dr = >20:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 8.09 (s, 1H), 7.32 – 7.23 (m, 6H), 7.16 – 7.11 (m, 2H), 6.83 (dd, J = 6.5, 2.8 Hz, 2H), 5.90 (d, J = 3.7 Hz, 1H), 4.46 (d, J = 3.8 Hz, 1H), 4.39 (dd, J = 9.6, 2.1 Hz, 1H), 3.96 (q, J = 11.7 Hz, 1H), 3.75 (d, J = 9.6 Hz, 1H), 3.62 (d, J = 2.1 Hz, 1H), 3.10 – 3.00 (m, 1H), 2.72 (s, 1H), 2.28 – 2.18 (m, 2H), 1.54 (s, 3H), 1.25 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 172.6, 136.6, 136.0, 129.1, 129.1, 128.8, 128.3, 127.8, 127.7, 113.2, 106.4, 89.5, 84.1, 82.5, 73.4, 71.3, 52.0, 30.3, 26.8, 26.1 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{24}H_{29}N_2O_5$ 425.2071, found: 425.2080.

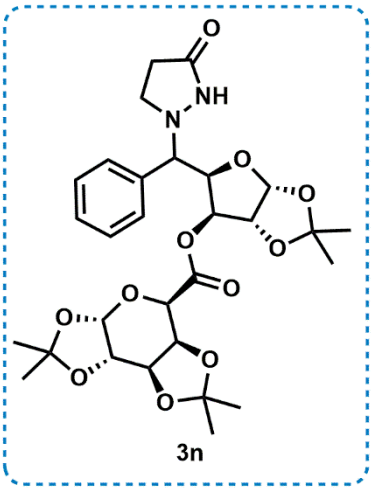
1-(((3a*R*,5*R*,6*S*,6a*R*)-6-((tert-butyldimethylsilyl)oxy)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)(phenyl)methyl)pyrazolidin-3-one (3m):



3m

The product **3m** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 50/50%) to afford a yellow viscous liquid (46 mg, 72% yield). dr = 9:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 7.42 – 7.29 (m, 5H), 5.99 (d, J = 3.6 Hz, 1H), 4.34 – 4.28 (m, 2H), 3.92 (s, 1H), 3.85 (d, J = 10.1 Hz, 1H), 3.10 (s, 1H), 2.73 (s, 1H), 2.32 – 2.24 (m, 2H), 1.65 (s, 3H), 1.31 (s, 3H), 0.70 (s, 9H), -0.31 (s, 3H), -0.43 (s, 3H) ppm. **^{1}H NMR (400 MHz, $CDCl_3$ minor diastereomer)** δ 7.40 – 7.29 (m, 5H), 5.73 (d, J = 4.1 Hz, 1H), 4.37 (dd, J = 4.1, 1.8 Hz, 1H), 4.11 (d, J = 6.1 Hz, 1H), 4.04 (dd, J = 5.6, 1.5 Hz, 1H), 3.79 (d, J = 6.3 Hz, 1H), 3.29 – 3.18 (m, 1H), 2.04 – 1.90 (m, 1H), 1.82 – 1.69 (m, 1H), 1.22 (s, 6H), 0.90 (s, 9H), 0.11 (s, 3H), 0.07 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 172.4, 136.2, 130.1, 129.2, 112.8, 106.8, 93.7, 86.1, 76.4, 72.9, 52.1, 30.3, 26.4, 25.8, 25.4, 17.6, -5.4, -5.6 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 175.1, 134.0, 130.1, 128.8, 128.6, 128.5, 113.8, 104.4, 87.7, 84.6, 77.7, 71.5, 50.7, 29.9, 29.7, 27.2, 26.9, 25.7, 24.8, 17.6, -4.5, -5.0 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{23}H_{37}N_2O_5Si$ 449.2466, found: 449.2463.

(3a*R*,5*R*,6*S*,6a*R*)-2,2-dimethyl-5-((3-oxopyrazolidin-1-yl)(phenyl)methyl)tetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl (3a*S*,5*R*,5a*S*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-*d*]pyran-5-carboxylate (3n):



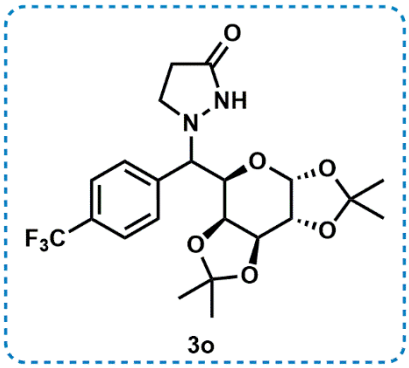
3n

The product **3n** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 60/40%) to afford a yellow viscous liquid (46 mg, 52% yield). dr = >20:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 8.01 (s, 1H), 7.33 – 7.22 (m, 5H), 5.89 (d, J = 3.7 Hz, 1H), 5.52 (d, J = 5.0 Hz, 1H), 4.89 (d, J = 1.6 Hz, 1H), 4.55 (dd, J = 7.5, 2.7 Hz, 1H), 4.50 (d, J = 3.6 Hz, 1H), 4.41 (dd, J = 9.3, 1.9 Hz, 1H), 4.35 (dd, J = 7.6, 2.4

Hz, 1H), 4.28 (dd, *J* = 5.0, 2.8 Hz, 1H), 4.17 (d, *J* = 2.3 Hz, 1H), 3.89 (d, *J* = 9.3 Hz, 1H), 3.08 (dt, *J* = 10.4, 6.8 Hz, 1H), 2.80 (s, 1H), 2.25 – 2.18 (m, 2H), 1.58 (s, 3H), 1.43 (s, 3H), 1.31 (s, 3H), 1.27 – 1.23 (m, 9H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 172.9, 166.4, 135.1, 129.1, 129.0, 113.6, 110.1, 109.0, 106.2, 96.3, 88.6, 83.4, 77.8, 72.7, 72.1, 70.6, 69.9, 68.3, 52.0, 30.2, 26.5, 25.9, 25.9, 24.9, 24.7 ppm. **^{19}F NMR (376 MHz, $CDCl_3$ major diastereomer)** δ -113.61 ppm. **^{19}F NMR (376 MHz, $CDCl_3$ minor diastereomer)** δ -112.43 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{29}H_{39}N_2O_{11}$ 591.2548, found: 591.2546.

8.3 Scope for the Glycosylation of Azomethine Imines

1-(((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)(4-(trifluoromethyl)phenyl)methyl)pyrazolidin-3-one (3o):

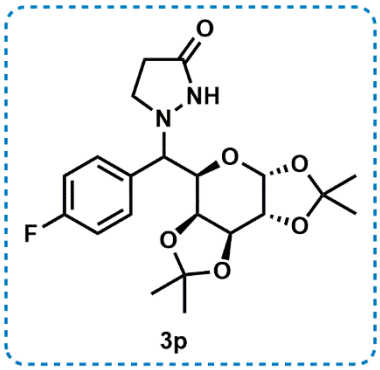


3o

The product **3o** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a white solid (60 mg, 94% yield). dr = 2:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 5.62 (d, *J* = 5.0 Hz, 1H), 4.41 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.31 (dd, *J* = 5.1, 2.4 Hz, 1H), 4.11 (dd, *J* = 16.2, 9.4 Hz, 2H), 3.98 (d, *J* = 9.5 Hz, 1H), 3.47 (d, *J* = 8.0 Hz, 1H), 3.12 – 3.02 (m, 1H), 2.88 (s, 1H), 2.31 – 2.14 (m, 2H), 1.62 (s, 3H), 1.46 (s, 3H), 1.33 (s, 3H), 1.18 (s, 3H) ppm. **^{1}H NMR (400 MHz, $CDCl_3$ minor diastereomer)** δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 1H), 5.44 (d, *J* = 5.1 Hz, 1H), 4.63 (dd, *J* = 7.9, 2.1 Hz, 1H), 4.52 (d, *J* = 8.0 Hz, 1H), 4.29 (dd, *J* = 6.3, 2.2 Hz, 1H), 4.19 – 4.06 (m, 2H), 3.42 – 3.28 (m, 2H), 1.92 – 1.80 (m, 1H), 1.74 – 1.65 (m, 1H), 1.58 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H), 1.30 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 175.7, 166.0, 141.9, 139.7, 131.4, 131.1, 130.7, 130.5, 129.6, 127.9, 125.7, 123.9 (q, *J* = 271.3 Hz), 122.4, 122.4 (q, *J* = 3.8 Hz), 119.7, 109.5, 109.2, 96.6, 70.7, 70.5, 70.2, 69.5, 51.7, 26.1, 26.0, 24.8, 24.3 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 173.1, 139.2, 131.3, 131.1, 130.8, 130.5, 130.4, 130.1, 127.9, 124.1 (q, *J* = 266.2 Hz), 112.8, 122.7 (q, *J* = 5.6 Hz), 109.4, 108.6, 96.8, 71.7, 70.9, 70.5, 70.5, 67.1, 50.4, 29.9, 25.9, 25.8, 24.6, 24.4 ppm. **^{19}F NMR (376 MHz, $CDCl_3$ major diastereomer)** δ -62.68 ppm. **^{19}F NMR (376 MHz, $CDCl_3$ minor**

diastereomer) δ -62.55 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{22}H_{28}F_3N_2O_6$ 473.1894, found: 473.1886.

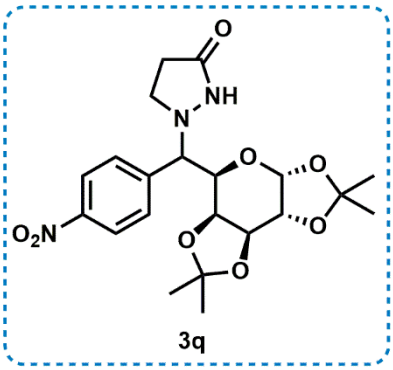
1-((4-fluorophenyl)((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)pyrazolidin-3-one (3p):



3p

The product **3p** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow solid (47 mg, 74% yield). dr = 2:1.4 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 7.31 (m, 2H), 7.01 (m, 2H), 5.56 (d, *J* = 5.0 Hz, 1H), 4.35 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.25 (dd, *J* = 4.9, 2.3 Hz, 1H), 4.08 – 3.99 (m, 1H), 3.86 (d, *J* = 9.4 Hz, 1H), 3.47 (dd, *J* = 7.9, 1.4 Hz, 1H), 3.08 – 2.99 (m, 1H), 2.87 (s, 1H), 2.21 – 2.11 (m, 2H), 1.57 (s, *J* = 12.7 Hz, 3H), 1.40 (s, 3H), 1.28 (s, 3H), 1.12 (s, 3H) ppm. **^{1}H NMR (400 MHz, $CDCl_3$ minor diastereomer)** δ 7.31 (m, 2H), 7.01 (m, 2H), 5.39 (d, *J* = 5.1 Hz, 1H), 4.57 (dd, *J* = 7.9, 2.3 Hz, 1H), 4.47 (dd, *J* = 7.9, 1.1 Hz, 1H), 4.23 (dd, *J* = 5.1, 2.2 Hz, 1H), 4.07 – 4.00 (m, 2H), 3.35 – 3.21 (m, 2H), 1.86 – 1.73 (m, 1H), 1.70 – 1.59 (m, 1H), 1.51 (s, 3H), 1.35 (s, 3H), 1.30 (s, 3H), 1.24 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 175.7, 164.0, 161.6 (d, *J* = 248.1 Hz), 131.3, 131.2 (d, *J* = 8.0 Hz), 116.0, 115.8 (d, *J* = 21.3 Hz), 109.4, 109.1, 96.7, 70.5, 70.3, 70.1, 69.2, 50.4, 30.2, 26.0, 24.8, 24.3 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 173.2, 163.9, 161.4 (d, *J* = 247.5 Hz), 130.9, 130.8 (d, *J* = 6.5 Hz), 115.5, 115.3 (d, *J* = 21.2 Hz), 109.3, 108.5, 96.8, 71.5, 70.9, 70.7, 70.5, 67.2, 51.5, 29.9, 26.1, 25.8, 24.6, 24.4 ppm. **^{19}F NMR (376 MHz, $CDCl_3$ major diastereomer)** δ -112.43 ppm. **^{19}F NMR (376 MHz, $CDCl_3$ minor diastereomer)** δ -113.61 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{21}H_{28}FN_2O_6$ 423.1926, found: 423.1920.

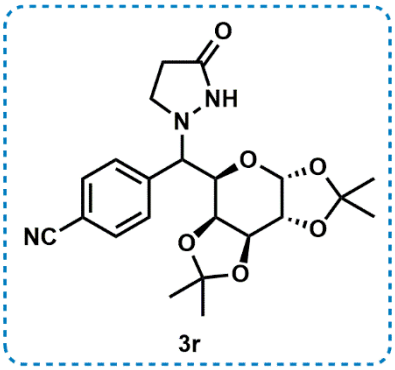
1-((4-nitrophenyl)((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)pyrazolidin-3-one (3q):



3q

The product **3q** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow solid (32 mg, 51% yield). dr = 2:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, CDCl$_3$ major diastereomer)** δ 8.18 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.3 Hz, 2H), 5.56 (d, J = 5.0 Hz, 1H), 4.35 (dd, J = 7.9, 2.3 Hz, 1H), 4.26 (dd, J = 5.0, 2.5 Hz, 1H), 4.07 (d, J = 9.4 Hz, 1H), 3.97 (d, J = 9.3 Hz, 1H), 3.39 (d, J = 7.9 Hz, 1H), 3.08 – 2.99 (m, 1H), 2.82 (s, 1H), 2.31 – 2.12 (m, 3H), 1.56 (s, 2H), 1.41 (s, 3H), 1.28 (s, 3H), 1.11 (s, 3H) ppm. **^{1}H NMR (400 MHz, CDCl$_3$ minor diastereomer)** δ 8.16 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 5.38 (d, J = 5.2 Hz, 1H), 4.57 (dd, J = 7.9, 2.1 Hz, 1H), 4.44 (d, J = 8.0 Hz, 1H), 4.25 (dd, J = 5.3, 2.1 Hz, 1H), 4.11 (s, 2H), 3.35 – 3.27 (m, 2H), 1.96 – 1.84 (m, 1H), 1.77 – 1.65 (m, 1H), 1.55 (s, 3H), 1.27 (s, 3H), 1.25 (s, 6H) ppm. **^{13}C NMR (101 MHz, CDCl$_3$ major diastereomer)** δ 175.6, 148.1, 143.0, 130.2, 123.9, 109.6, 109.3, 96.6, 70.5, 70.4, 70.2, 69.3, 51.8, 30.1, 26.1, 25.9, 24.8, 24.3 ppm. **^{13}C NMR (101 MHz, CDCl$_3$ minor diastereomer)** δ 173.0, 147.7, 143.0, 130.8, 123.2, 109.5, 108.7, 96.8, 71.7, 70.9, 70.8, 70.5, 67.2, 50.4, 29.8, 25.9, 25.7, 24.6, 24.4 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{21}H_{28}N_3O_8$ 450.1871, found: 450.1865.

4-((3-oxopyrazolidin-1-yl)((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)benzonitrile (3r):

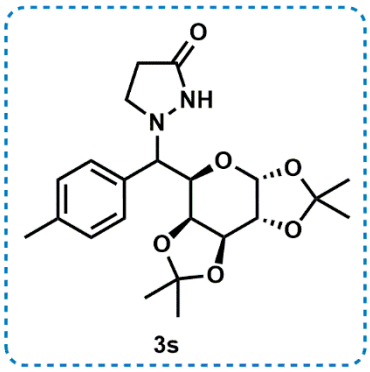


3r

The product **3r** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a white solid (57 mg, 88% yield). dr = 2:1.2 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, CDCl$_3$ major diastereomer)** δ 7.62 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 5.55 (d, J = 5.0 Hz, 1H), 4.35 (dd, J = 7.9, 2.4 Hz, 1H), 4.06 (dd, J = 12.7, 6.7 Hz, 1H), 3.90 (d, J = 9.3 Hz, 1H), 3.38 (dd, J = 8.0, 1.1 Hz, 1H), 3.05 – 2.99 (m, 1H), 2.82 (s, 1H), 2.25 – 2.15 (m, 2H), 1.55 (s, 3H), 1.40 (s, 3H), 1.28 (s, 3H), 1.11 (s, 3H) ppm. **^{1}H NMR (400 MHz, CDCl$_3$ minor diastereomer)** δ 7.60 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 5.36 (d, J = 5.2 Hz, 1H), 4.57 (dd, J = 7.9, 2.2 Hz, 1H), 4.45 (d, J = 8.7 Hz, 1H), 4.25 – 4.22 (m, 2H), 4.06

(dd, *J* = 12.7, 6.7 Hz, 1H), 3.33 – 3.23 (m, 2H), 1.92 – 1.78 (m, 1H), 1.71 – 1.59 (m, 1H), 1.53 (s, 3H), 1.28 (s, 6H), 1.25 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ $CDCl_3$ major diastereomer)** δ 175.7, 141.0, 132.5, 130.0, 118.2, 112.7, 109.6, 109.2, 96.6, 70.5, 70.4, 70.2, 69.4, 51.8, 30.1, 26.1, 25.9, 24.8, 24.3 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 173.1, 140.8, 131.8, 130.7, 118.5, 112.0, 109.4, 108.6, 96.8, 71.6, 70.9, 70.8, 70.5, 66.9, 50.4, 29.9, 25.9, 25.7, 24.6, 24.4. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{22}H_{28}N_3O_6$ 430.1973, found: 430.1966.

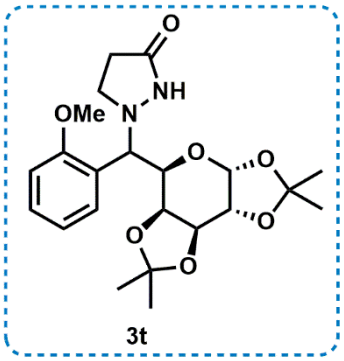
1-(((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)(p-tolyl)methyl)pyrazolidin-3-one (3s):



3s

The product **3s** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a slightly yellowish solid (36 mg, 56% yield). dr = 2:1.2 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 7.25 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 5.62 (d, *J* = 5.0 Hz, 1H), 4.39 (dd, *J* = 7.9, 2.3 Hz, 1H), 4.29 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.15 – 4.01 (m, 1H), 3.88 (d, *J* = 9.7 Hz, 1H), 3.57 (d, *J* = 8.1 Hz, 1H), 3.11 – 3.05 (m, 1H), 2.91 (m, 1H), 2.35 (s, 3H), 2.19 – 1.99 (m, 2H), 1.63 (s, 3H), 1.45 (s, 3H), 1.33 (s, 3H), 1.17 (m, 3H) ppm. **^{1}H NMR (400 MHz, $CDCl_3$ minor diastereomer)** δ 7.25 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 5.45 (d, *J* = 5.1 Hz, 1H), 4.61 (dd, *J* = 8.0, 2.1 Hz, 1H), 4.54 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.27 (dd, *J* = 5.1, 2.2 Hz, 1H), 4.15 – 4.00 (m, 2H), 3.33 (t, *J* = 7.9 Hz, 2H), 2.32 (s, 3H), 1.86 – 1.76 (m, 1H), 1.74 – 1.65 (m, 1H), 1.55 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H), 1.29 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 175.6, 138.5, 131.8, 129.5, 129.2, 109.3, 109.0, 96.7, 70.6, 70.4, 70.0, 50.6, 30.2, 26.1, 26.0, 24.9, 24.3, 21.2 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 173.6, 138.0, 132.2, 129.3, 129.1, 109.3, 108.4, 96.8, 71.3, 71.0, 70.6, 67.5, 51.3, 30.0, 26.0, 25.9, 24.7, 24.4, 21.2 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{22}H_{31}N_2O_6$ 419.2177, found: 419.2170.

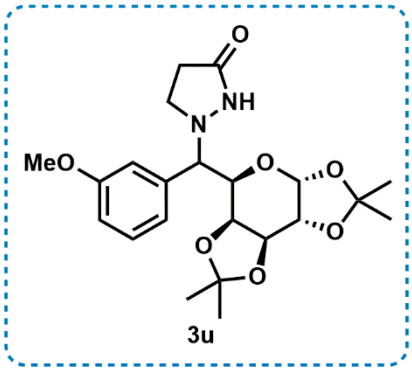
1-((2-methoxyphenyl)((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)pyrazolidin-3-one (3t):



3t

The product **3t** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow viscous liquid (36 mg, 57% yield). dr = 2:1.2 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, CDCl$_3$ major diastereomer)** δ 7.33 – 7.26 (m, 1H), 7.00 – 6.86 (m, 3H), 5.64 (d, J = 5.0 Hz, 1H), 4.42 (dd, J = 8.0, 2.4 Hz, 1H), 4.31 (dd, J = 5.2, 2.4 Hz, 1H), 4.18 – 4.05 (m, 1H), 3.90 (d, J = 9.6 Hz, 1H), 3.82 (s, 3H), 3.60 (d, J = 8.0 Hz, 1H), 3.18 – 3.12 (m, 1H), 2.97 (s, 1H), 2.27 – 2.24 (m, 2H), 1.65 (s, 3H), 1.48 (s, 3H), 1.35 (s, 3H), 1.20 (s, 3H) ppm. **^{1}H NMR (400 MHz, CDCl$_3$ minor diastereomer)** δ 7.32 – 7.26 (m, 1H), 7.01 – 6.86 (m, 3H), 5.49 (d, J = 5.1 Hz, 1H), 4.63 (dd, J = 8.0, 2.2 Hz, 1H), 4.56 (dd, J = 8.0, 1.3 Hz, 1H), 4.30 (dd, J = 6.0, 2.3 Hz, 1H), 4.18 – 4.05 (m, 2H), 3.81 (s, 3H), 3.44 – 3.26 (m, 2H), 1.93 – 1.74 (m, 2H), 1.59 (s, 3H), 1.48 (s, 3H), 1.40 (s, 3H), 1.32 (s, 3H) ppm. **^{13}C NMR (101 MHz, CDCl$_3$ major diastereomer)** δ 175.5, 159.7, 136.6, 129.8, 121.9, 114.0, 109.3, 109.0, 96.7, 70.6, 70.4, 70.2, 55.2, 51.4, 30.3, 26.1, 26.0, 24.9, 24.3 ppm. **^{13}C NMR (101 MHz, CDCl$_3$ minor diastereomer)** δ 173.5, 159.5, 137.0, 129.4, 121.4, 114.8, 109.0, 108.4, 96.9, 71.5, 71.0, 70.6, 67.6, 55.2, 51.4, 30.0, 26.0, 25.9, 24.7, 24.4. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{22}H_{31}N_2O_7$ 435.2126, found: 435.2121.

1-((3-methoxyphenyl)((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)pyrazolidin-3-one (3u):

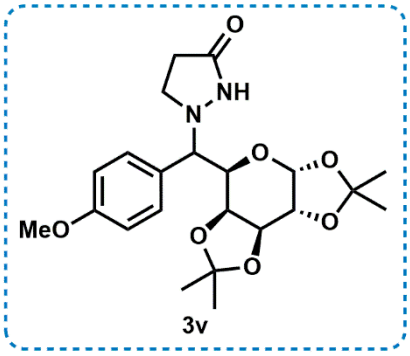


3u

The product **3u** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow viscous liquid (40 mg, 63% yield). dr = 2:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, CDCl$_3$ major diastereomer)** δ 7.32 – 7.24 (m, 1H), 6.98 – 6.84 (m, 3H), 5.61 (d, J = 5.0 Hz, 1H), 4.40 (dd, J = 8.0, 2.4 Hz, 1H), 4.29 (dd, J = 5.2, 2.4 Hz, 1H), 4.14 – 4.01 (m, 1H), 3.87 (d, J = 9.4 Hz, 1H), 3.80 (s, 3H), 3.58 (dd, J = 8.0, 1.0, 1H), 3.17 – 3.08 (m, 1H), 2.95 (s, 1H), 2.28 – 2.13 (m, 2H), 1.62 (s, 3H), 1.45 (s, 3H), 1.33 (s, 3H), 1.18 (s, 3H) ppm. **^{1}H NMR (400 MHz, CDCl$_3$ minor diastereomer)** δ 7.30 – 7.21 (m, 1H), 6.99 – 6.82 (m, 3H), 5.47 (d, J = 5.1 Hz, 1H), 4.61 (dd, J = 8.0, 2.2 Hz, 1H), 4.53 (dd, J = 8.0, 1.2 Hz, 1H), 4.28 (dd, J

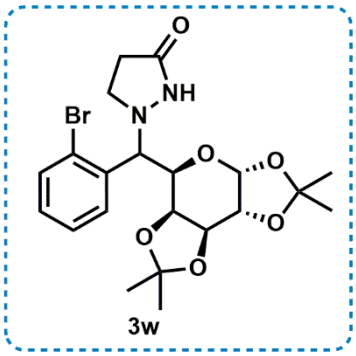
= 5.4, 2.3 Hz, 1H), 4.13 – 4.01 (m, 2H), 3.78 (s, 3H), 3.38 – 3.28 (m, 2H), 1.90 – 1.73 (m, 2H), 1.56 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H), 1.30 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 175.4, 159.7, 137.1, 129.8, 121.9, 114.8, 113.9, 109.3, 109.0, 96.7, 70.6, 70.4, 70.3, 55.2, 51.4, 30.3, 26.1, 26.0, 24.9, 24.3. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 173.4, 159.5, 136.6, 129.5, 121.4, 114.0, 109.0, 108.4, 96.9, 71.6, 71.0, 70.6, 67.6, 55.2, 50.6, 29.9, 26.1, 25.9, 24.7, 24.3. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{22}H_{31}N_2O_7$ 435.2126, found: 435.2120.

1-((4-methoxyphenyl)((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)pyrazolidin-3-one (3v):



The product **3v** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30 %) to afford a yellow viscous liquid (49 mg, 77 % yield). dr = 2:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 7.29 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.63 (d, *J* = 5.0 Hz, 1H), 4.42 (dd, *J* = 7.9, 2.3 Hz, 1H), 4.31 (dd, *J* = 5.1, 2.5 Hz, 1H), 4.12 – 4.04 (m, 1H), 3.88 (d, *J* = 9.8 Hz, 1H), 3.82 (s, 3H), 3.60 (d, *J* = 8.0 Hz, 1H), 3.14 – 3.04 (m, 1H), 2.94 (s, 1H), 2.25 – 2.04 (m, 2H), 1.64 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.19 (s, 3H) ppm. **^{1}H NMR (400 MHz, $CDCl_3$ minor diastereomer)** δ 7.29 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 5.47 (d, *J* = 5.1 Hz, 1H), 4.63 (dd, *J* = 7.9, 2.2 Hz, 1H), 4.57 (dd, *J* = 8.0, 1.3 Hz, 1H), 4.29 (dd, *J* = 5.3, 2.3 Hz, 1H), 4.12 – 4.04 (m, 2H), 3.80 (s, 3H), 3.38 – 3.32 (m, 2H), 1.84 – 1.74 (m, 1H), 1.74 – 1.66 (m, 1H), 1.58 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H), 1.31 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 175.8, 159.7, 130.6, 127.3, 114.1, 109.3, 109.0, 96.7, 70.6, 70.4, 69.8, 69.4, 55.2, 51.3, 30.3, 26.1, 26.0, 24.9, 24.3 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 173.6, 159.5, 130.2, 126.7, 113.9, 109.2, 108.4, 96.8, 70.9, 70.7, 70.6, 67.3, 55.1, 50.4, 30.0, 26.0, 25.9, 24.7, 24.4 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{22}H_{31}N_2O_7$ 435.2126, found: 435.2121.

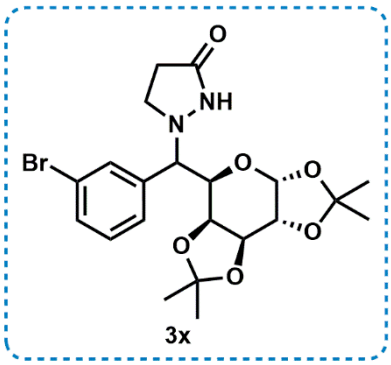
1-((2-bromophenyl)((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)pyrazolidin-3-one (3w):



3w

The product **3w** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow viscous liquid (37 mg, 59% yield). dr = 1:5 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, CDCl$_3$ major diastereomer)** δ 7.83 (s, 1H), 7.58 (d, J = 8.1 Hz, 2H), 7.32 (t, J = 7.6 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 5.49 (d, J = 5.1 Hz, 1H), 4.79 (d, J = 6.3 Hz, 1H), 4.57 (dd, J = 7.9, 2.0 Hz, 1H), 4.42 (d, J = 7.8 Hz, 1H), 4.27 (dd, J = 5.1, 2.1 Hz, 1H), 4.04 (d, J = 6.1 Hz, 1H), 3.48 – 3.41 (m, 1H), 3.22– 3.14 (m, 1H), 2.36 – 2.20 (m, 1H), 2.02 – 1.91 (m, 1H), 1.56 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H), 1.29 (s, 3H) ppm. **^{1}H NMR (400 MHz, CDCl$_3$ minor diastereomer)** δ 7.83 (s, 1H), 7.65 (s, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 1H), 5.65 (d, J = 5.0 Hz, 1H), 4.68 (d, J = 9.4 Hz, 1H), 4.45 (d, J = 2.4 Hz, 1H), 4.33 (dd, J = 4.9, 2.7 Hz, 1H), 4.19 (d, J = 8.9 Hz, 1H), 4.11 (q, J = 7.1 Hz, 1H), 3.62 (d, J = 8.0 Hz, 1H), 3.24 – 3.11 (m, 2H), 3.22– 3.14 (m, 1H), 2.04 (s, 3H), 1.64 (s, 3H), 1.48 (s, 3H), 1.18 (s, 3H) ppm. **^{13}C NMR (101 MHz, CDCl$_3$ major diastereomer)** δ 175.0, 135.5, 133.0, 130.7, 129.5, 127.3, 125.9, 109.4, 108.6, 96.8, 71.2, 70.6, 70.5, 68.3, 68.0, 51.2, 29.9, 25.9, 25.8, 24.6, 24.3 ppm. **^{13}C NMR (101 MHz, CDCl$_3$ minor diastereomer)** δ 175.0, 135.1, 133.8, 129.9, 129.4, 127.8, 126.6, 109.7, 109.1, 96.8, 70.8, 70.7, 70.3, 68.0, 60.4, 50.2, 30.3, 26.2, 26.0, 24.8, 24.6 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{21}H_{28}BrN_2O_6$ 483.1125, found: 483.1113.

1-((3-bromophenyl)((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)pyrazolidin-3-one (3x):

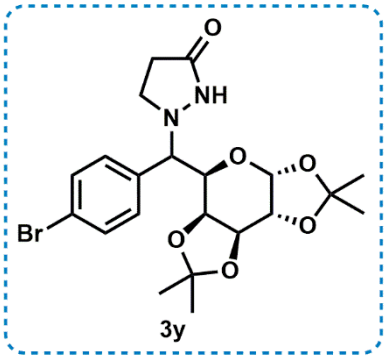


3x

The product **3x** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow viscous liquid (44 mg, 69% yield). dr = 2:1.2 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, CDCl$_3$ major diastereomer)** δ 7.50 – 7.43 (m, 2H), 7.26 – 7.21 (m, 2H), 5.60 (d, J = 5.0 Hz, 1H), 4.41 (dd, J = 7.9, 2.2 Hz, 1H), 4.29 (dd, J = 5.1, 2.3 Hz, 1H), 4.10 – 4.06 (m, 1H), 3.84 (d, J = 9.4 Hz, 1H), 3.53 (d, J = 8.1 Hz, 1H), 3.11 – 3.06 (m, 1H), 2.87 (s, 1H), 2.33 – 2.11 (m, 2H), 1.61 (s, 3H), 1.45 (s, 3H), 1.33 (s, 3H), 1.18 (s, 3H) ppm. **^{1}H NMR (400 MHz, CDCl$_3$**

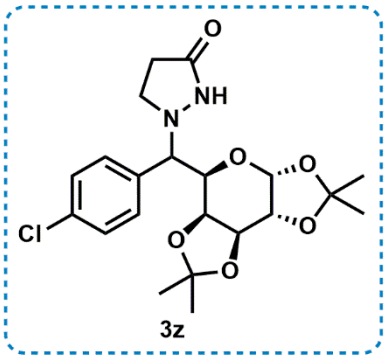
minor diastereomer) δ 7.50 – 7.43 (m, 2H), 7.33– 7.29 (m, 2H), 5.44 (d, J = 5.1 Hz, 1H), 4.62 (dd, J = 7.9, 2.0 Hz, 1H), 4.51 (d, J = 8.3 Hz, 1H), 4.28 (dd, J = 5.3, 2.2 Hz, 1H), 4.10 – 4.06 (m, 1H), 4.01 (d, J = 8.6 Hz, 1H), 3.37 – 3.29 (m, 2H), 1.96 – 1.85 (m, 1H), 1.83 – 1.71 (m, 1H), 1.58 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H), 1.30 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 175.6, 138.0, 132.8, 131.8, 130.3, 128.2, 122.8, 109.4, 109.1, 96.6, 70.5, 70.5, 70.3, 69.5, 51.6, 30.2, 26.1, 25.9, 24.8, 24.2 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 173.2, 137.6, 132.2, 131.2, 129.8, 127.7, 122.4, 109.4, 108.6, 96.8, 71.6, 70.9, 70.7, 70.5, 67.2, 50.5, 30.0, 25.9, 25.8, 24.7, 24.4 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{21}H_{28}BrN_2O_6$ 483.1125, found: 483.1119.

1-((4-bromophenyl)((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)pyrazolidin-3-one (3y):



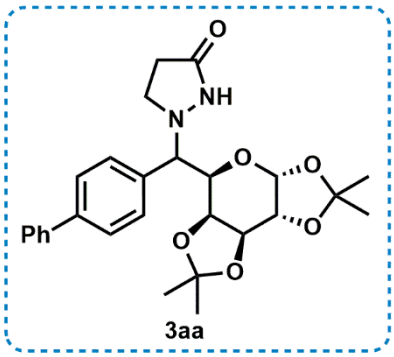
The product **3y** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow solid (51 mg, 81% yield). dr = 2:1.2 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 7.58 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 5.56 (d, J = 5.0 Hz, 1H), 4.35 (dd, J = 7.9, 2.5 Hz, 1H), 4.25 (dd, J = 5.0, 2.5 Hz, 1H), 4.06 (dd, J = 9.5, 1.4 Hz, 1H), 3.92 (d, J = 9.5 Hz, 1H), 3.42 (dd, J = 7.9, 1.5 Hz, 1H), 3.09 – 2.96 (m, 1H), 2.81 (s, 1H), 2.26 – 2.08 (m, 2H), 1.56 (s, 3H), 1.41 (s, 3H), 1.28 (s, 3H), 1.12 (s, 3H) ppm. **^{1}H NMR (400 MHz, $CDCl_3$ minor diastereomer)** δ 7.56 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 5.38 (d, J = 5.2 Hz, 1H), 4.57 (dd, J = 7.9, 2.3 Hz, 1H), 4.47 (d, J = 8.0 Hz, 1H), 4.24 (dd, J = 5.2, 2.3 Hz, 1H), 4.09 (s, 2H), 3.35 – 3.21 (m, 2H), 1.83 – 1.78 (m, 1H), 1.69 – 1.58 (m, 1H), 1.52 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H), 1.24 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 175.8, 139.7, 130.1, 129.6, 125.7, 125.2, 109.5, 109.2, 96.6, 70.5, 70.5, 70.2, 69.4, 51.7, 30.2, 26.1, 26.0, 24.8, 24.3 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 173.2, 139.2, 130.1, 129.6, 125.79, 125.2, 109.4, 108.6, 96.8, 71.7, 70.9, 70.7, 70.5, 67.0, 50.3, 29.9, 25.9, 25.8, 24.6, 24.4 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{21}H_{28}BrN_2O_6$ 483.1125, found: 483.1115.

1-((4-chlorophenyl)((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)pyrazolidin-3-one (3z):



The product **3z** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a slightly yellowish solid (59 mg, 93% yield). dr = 2:1.6 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 7.36 – 7.39 (m, 4H), 5.61 (d, J = 5.0 Hz, 1H), 4.40 (dd, J = 7.9, 2.3 Hz, 1H), 4.30 (dd, J = 5.0, 2.3 Hz, 1H), 4.12 – 4.02 (m, 1H), 3.88 (d, J = 9.6 Hz, 1H), 3.52 (d, J = 7.9 Hz, 1H), 3.10 – 3.04 (m, 1H), 2.87 (s, 1H), 2.32 – 2.12 (m, 3H), 1.61 (s, 3H), 1.45 (s, 2H), 1.33 (s, 3H), 1.17 (s, 3H) ppm. **^{1}H NMR (400 MHz, $CDCl_3$ minor diastereomer)** δ 7.36 – 7.39 (m, 4H), 5.43 (d, J = 5.1 Hz, 1H), 4.62 (dd, J = 7.9, 2.0 Hz, 1H), 4.52 (d, J = 8.1 Hz, 1H), 4.28 (dd, J = 5.2, 1.9 Hz, 1H), 4.12 – 4.02 (m, 2H), 3.43 – 3.27 (m, 2H), 1.94 – 1.83 (m, 1H), 1.77 – 1.66 (m, 1H), 1.55 (s, 3H), 1.41 (s, 3H), 1.36 (s, 3H), 1.29 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 175.8, 134.2, 133.6, 130.9, 129.1, 109.4, 109.1, 96.7, 70.5, 70.3, 70.1, 69.3, 50.5, 30.2, 26.1, 26.0, 24.8, 24.3 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 173.3, 134.6, 134.1, 130.5, 128.6, 109.3, 108.5, 96.8, 71.6, 70.9, 70.7, 70.5, 67.2, 51.5, 29.9, 25.9, 25.9, 24.6, 24.4 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{21}H_{28}ClN_2O_6$ 439.1630, found: 439.1628.

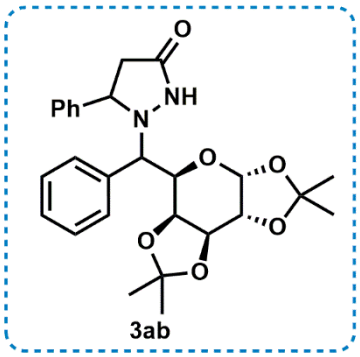
1-([1,1'-biphenyl]-4-yl((3aR,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)pyrazolidin-3-one (3aa)



The product **3aa** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow viscous liquid (38 mg, 60% yield). dr = 2:1.2 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 7.63 – 7.59 (m, 4H), 7.49 – 7.31 (m, 5H), 5.65 (d, J = 5.1 Hz, 1H), 4.43 (dd, J = 7.9, 2.2 Hz, 1H), 4.32 (dd, J = 5.3, 2.5 Hz, 1H), 4.22 – 4.12 (m, 1H), 3.97 (d, J = 9.5 Hz, 1H), 3.64 (d, J = 8.0 Hz, 1H), 3.21 – 3.11 (m, 1H), 2.99 (s, 1H), 2.32 – 2.13 (m, 2H), 1.66 (s, 3H), 1.48 (s, 3H), 1.35 (s, 3H), 1.20 (s, 3H) ppm. **^{1}H NMR (400 MHz, $CDCl_3$ minor diastereomer)** δ 7.63 – 7.59 (m, 4H), 7.49 – 7.31 (m, 5H), 5.49 (d, J = 5.1 Hz, 1H), 4.64 (dd, J = 7.9, 1.9 Hz, 1H), 4.57 (d, J = 8.0 Hz, 1H), 4.30 (dd, J = 5.7, 2.4 Hz, 1H), 4.20 – 4.09 (m, 2H), 3.44 – 3.32 (m, 2H), 1.93 – 1.71 (m, 2H), 1.57 (s, 3H), 1.46 (s,

3H), 1.39 (s, 3H), 1.29 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 175.6, 141.5, 140.2, 134.0, 129.9, 128.9, 127.4, 127.0, 127.0, 109.4, 109.1, 96.8, 70.6, 70.4, 50.6, 30.3, 26.2, 26.0, 24.9, 24.4 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 173.4, 141.0, 140.4, 134.4, 129.6, 128.7, 127.6, 127.1, 127.0, 109.3, 108.5, 96.9, 71.0, 70.6, 69.9, 67.5, 51.5, 30.0, 26.0, 25.9, 24.7, 24.4 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{27}H_{33}N_2O_6$ 481.2333, found: 481.2325.

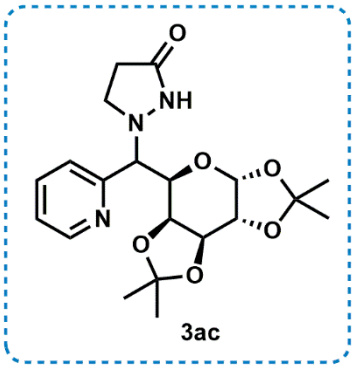
5-phenyl-1-(phenyl((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)pyrazolidin-3-one (3ab):



3ab

The product **3ab** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow viscous liquid (43 mg, 60% yield). dr = 1.6:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 7.20 – 7.11 (m, 8H), 7.06 – 7.03 (m, 2H), 5.62 (d, J = 5.0 Hz, 1H), 4.37 – 4.34 (m, 1H), 4.29 – 4.24 (m, 2H), 4.20 (dd, J = 9.2, 5.2 Hz, 1H), 4.13 (d, J = 9.2 Hz, 1H), 3.47 (d, J = 8.1 Hz, 1H), 3.01 (dd, J = 16.9, 9.3 Hz, 1H), 2.31 (dd, J = 16.9, 5.2 Hz, 1H), 1.63 (s, 3H), 1.46 (s, 3H), 1.35 (s, 3H), 1.14 (s, 3H) ppm. **^{1}H NMR (400 MHz, $CDCl_3$ minor diastereomer)** δ 7.35 (dd, J = 9.7, 3.5 Hz, 4H), 7.29 (d, J = 7.2 Hz, 3H), 7.24 – 7.20 (m, 3H), 5.48 (d, J = 5.2 Hz, 1H), 4.55 (dd, J = 7.9, 2.2 Hz, 1H), 4.47 (dd, J = 7.9, 1.3 Hz, 1H), 4.39 – 4.34 (m, 1H), 4.29 – 4.23 (m, 2H), 4.08 (d, J = 9.1 Hz, 1H), 2.13 (dd, J = 17.4, 9.8 Hz, 1H), 1.99 (dd, J = 16.8, 3.9 Hz, 1H), 1.50 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.30 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 171.4, 142.5, 135.8, 129.2, 128.5, 128.4, 128.1, 126.7, 126.3, 109.2, 109.1, 96.5, 71.0, 70.7, 70.5, 68.9, 64.1, 38.1, 26.1, 26.0, 25.0, 24.2 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 173.2, 141.8, 134.4, 129.7, 128.7, 128.5, 128.4, 128.3, 127.4, 126.3, 109.3, 108.4, 97.0, 72.9, 71.5, 70.5, 66.5, 61.3, 38.2, 26.0, 25.9, 24.7, 24.6 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{27}H_{33}N_2O_6$ 481.2333, found: 481.2328.

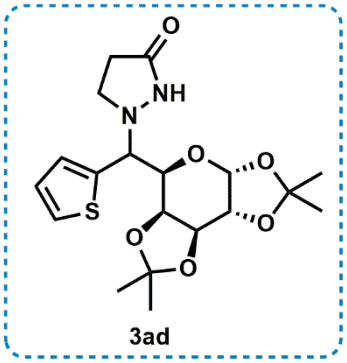
1-(pyridin-2-yl((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)pyrazolidin-3-one (3ac):



3ac

The product **3ac** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow viscous liquid (41 mg, 68% yield). dr = >20:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, CDCl$_3$ major diastereomer)** δ 8.54 (d, J = 4.9 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.47 (dd, J = 14.7, 8.1 Hz, 1H), 7.29 (d, J = 5.7 Hz, 1H), 5.37 (d, J = 5.0 Hz, 1H), 4.57 (dd, J = 8.0, 2.2 Hz, 1H), 4.48 (d, J = 8.1 Hz, 1H), 4.35 (s, 1H), 4.22 (dd, J = 5.0, 2.3 Hz, 1H), 3.43 (t, 2H), 2.08 – 1.91 (m, 1H), 1.82 – 1.67 (m, 1H), 1.56 (s, 3H), 1.25 – 1.22 (m, 9H) ppm. **^{13}C NMR (101 MHz, CDCl$_3$ major diastereomer)** δ 175.2, 155.5, 149.1, 126.0, 123.4, 109.3, 108.9, 96.6, 77.3, 77.0, 76.7, 71.0, 70.8, 70.6, 67.8, 50.3, 29.9, 25.8, 25.7, 24.9, 24.3 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{20}H_{28}N_3O_6$ 406.1973, found: 406.1973.

1-(((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)(thiophen-2-yl)methyl)pyrazolidin-3-one (3ad):

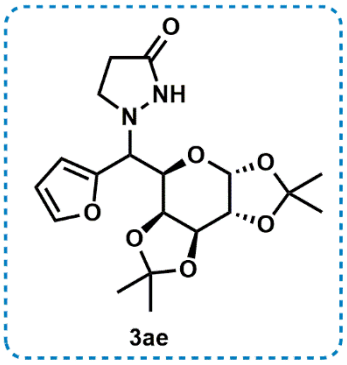


3ad

The product **3ad** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow viscous liquid (32 mg, 52% yield). dr = 2:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, CDCl$_3$ major diastereomer)** δ 7.36 (d, J = 5.1 Hz, 1H), 7.12 (d, J = 3.4 Hz, 1H), 7.08 – 7.00 (m, 1H), 5.64 (d, J = 5.1 Hz, 1H), 4.48 (dd, J = 7.9, 2.4 Hz, 1H), 4.38 (d, J = 9.8 Hz, 1H), 4.33 (dd, J = 5.1, 2.5 Hz, 1H), 4.03 (d, J = 9.3 Hz, 1H), 3.77 (d, J = 7.7 Hz, 1H), 3.56 – 3.46 (m, 1H), 3.26 – 3.17 (m, 1H), 2.13 – 2.01 (m, 2H), 1.65 (s, 3H), 1.46 (s, 3H), 1.34 (s, 3H), 1.22 (s, 3H) ppm. **^{1}H NMR (400 MHz, CDCl$_3$ minor diastereomer)** δ 7.34 (d, J = 5.1 Hz, 1H), 7.09 – 7.00 (m, 2H), 5.47 (d, J = 5.1 Hz, 1H), 4.64 (dd, J = 7.9, 2.3 Hz, 1H), 4.55 (dd, J = 7.9, 1.5 Hz, 1H), 4.34 (dd, J = 5.2, 2.7 Hz, 1H), 4.07 – 4.03 (m, 2H), 3.42 – 3.31 (m, 2H), 1.87 – 1.68 (m, 2H), 1.58 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H), 1.30 (s, 3H) ppm. **^{13}C NMR (101 MHz, CDCl$_3$ major diastereomer)** δ 176.5, 136.4, 128.5, 126.9, 126.6, 109.6, 109.2, 97.1, 70.8, 70.5, 70.4, 68.5, 50.3, 30.3, 26.0, 25.9, 24.9, 24.4 ppm. **^{13}C NMR (101 MHz, CDCl$_3$ minor diastereomer)** δ 175.5, 136.2, 128.4, 126.8, 126.6, 109.3, 108.7, 96.8, 70.8, 70.5, 65.4,

64.7, 50.2, 30.0, 26.0, 25.9, 24.8, 24.5 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{19}H_{27}N_2O_6S$ 411.1584, found: 411.1581.

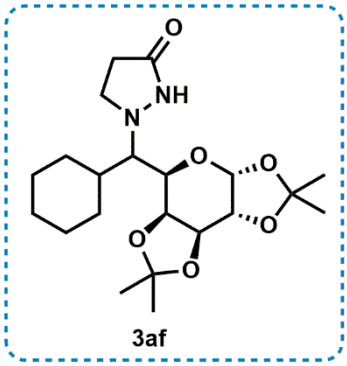
1-(furan-2-yl((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)pyrazolidin-3-one (3ae):



3ae

The product **3ae** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow viscous liquid (31 mg, 48% yield). dr = 6:4 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 7.44 (d, J = 1.6 Hz, 1H), 6.38 – 6.33 (m, 2H), 5.60 (d, J = 5.1 Hz, 1H), 4.49 (dd, J = 7.9, 2.4 Hz, 1H), 4.31 (dd, J = 5.1, 2.5 Hz, 1H), 4.21 (d, J = 10.7 Hz, 1H), 4.14 (d, J = 10.1 Hz, 1H), 3.78 (d, J = 8.1 Hz, 1H), 3.56 – 3.41 (m, 1H), 3.24 (ddd, J = 11.8, 9.0, 3.0 Hz, 1H), 2.02 – 1.90 (m, 2H), 1.60 (s, 3H), 1.40 (s, 3H), 1.29 (s, 3H), 1.18 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 175.2, 148.5, 143.4, 111.1, 111.0, 109.8, 109.2, 97.1, 70.9, 70.7, 70.4, 67.1, 50.2, 29.7, 25.9, 25.8, 24.9, 24.4 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{19}H_{27}N_2O_7$ 395.1813, found: 395.1809.

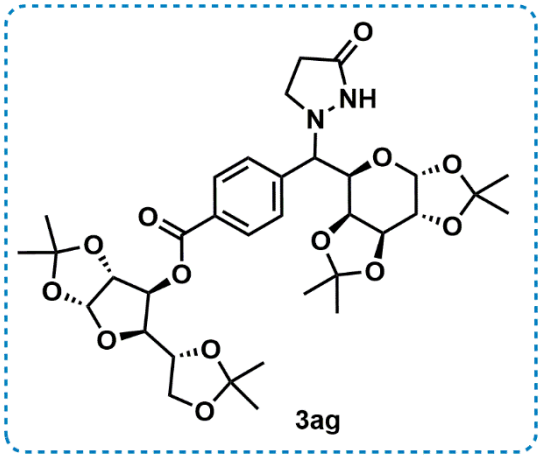
1-(cyclohexyl((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)pyrazolidin-3-one (3af):



3af

The product **3af** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow viscous liquid (35 mg, 57% yield). dr = > 20:1 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 5.52 (d, J = 5.0 Hz, 1H), 4.62 (dd, J = 7.6, 2.4 Hz, 1H), 4.31 (dd, J = 5.0, 2.5 Hz, 1H), 4.19 (d, J = 8.2 Hz, 2H), 3.94 – 3.81 (m, 1H), 3.51 – 3.42 (m, 1H), 2.97 – 2.81 (m, 2H), 2.41 (d, J = 4.1 Hz, 1H), 1.82 – 1.54 (m, 8H), 1.53 (s, 3H), 1.46 (s, 3H), 1.34 (s, 3H), 1.30 (s, 3H), 1.26 – 1.14 (m, 2H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ major diastereomer)** δ 175.9, 109.4, 109.1, 96.3, 77.3, 77.0, 76.7, 71.9, 70.9, 70.2, 65.5, 54.3, 39.2, 30.6, 29.3, 26.8, 26.6, 26.3, 26.0, 25.6, 24.9, 24.4 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{21}H_{35}N_2O_6$ 411.2490, found: 411.2485.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-((3-oxopyrazolidin-1-yl)((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)benzoate (3ag):

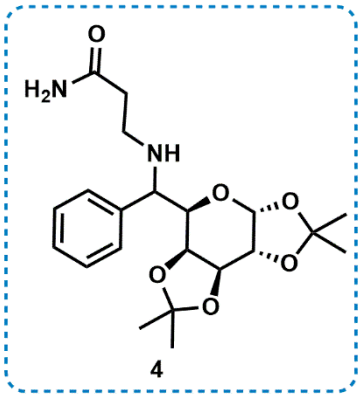


3ag

The product **3ag** was prepared according to general process and was purified by flash chromatography on silica gel (EtOAc/hexane 70/30%) to afford a yellow viscous liquid (32 mg, 31% yield). dr = 2:1.2 based on ^{1}H NMR of the isolated mixture. **^{1}H NMR (400 MHz, CDCl$_3$ major diastereomer)** δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 5.89 – 5.86 (m, 1H), 5.43 (dd, J = 9.1, 2.7 Hz, 2H), 4.57 (dd, J = 11.4, 3.6 Hz, 2H), 4.30 (dd, J = 9.2, 4.0 Hz, 2H), 4.27 – 4.21 (m, 2H), 4.12 (s, 2H), 4.09 – 3.97 (m, 3H), 3.39 – 3.27 (m, 2H), 2.22 (s, 2H), 1.49 (s, 6H), 1.35 (s, 6H), 1.25 (s, 6H), 1.25 (s, 3H), 1.22 (s, 3H) ppm. **^{1}H NMR (400 MHz, CDCl$_3$ minor diastereomer)** δ 7.98 (d, J = 7.9 Hz, 2H), 7.49 (d, J = 7.9 Hz, 2H), 5.90 – 5.82 (m, 1H), 5.56 (d, J = 5.1 Hz, 1H), 5.38 (d, J = 5.1 Hz, 1H), 4.57 (dd, J = 11.4, 3.6 Hz, 2H), 4.47 (d, J = 8.0 Hz, 1H), 4.35 (dd, J = 8.0, 2.3 Hz, 1H), 4.32 (d, J = 2.8 Hz, 1H), 4.28 – 4.20 (m, 2H), 4.10 – 3.95 (m, 3H), 3.42 (d, J = 8.3 Hz, 1H), 3.15 – 3.05 (m, 1H), 2.92 (s, 1H), 1.89 – 1.78 (m, 1H), 1.74 – 1.61 (m, 1H), 1.58 (s, 3H), 1.53 (s, 3H), 1.41 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H), 1.28 (s, 3H), 1.25 (s, 3H), 1.11 (s, 3H) ppm. **^{13}C NMR (101 MHz, CDCl$_3$ major diastereomer)** δ 175.5, 164.8, 140.8, 130.2, 130.1, 129.6, 112.3, 109.4, 105.1, 96.7, 83.3, 79.9, 72.4, 70.9, 70.7, 70.5, 69.7, 67.2, 50.6, 26.9, 26.7, 26.1, 26.0, 25.8, 25.2, 24.6 ppm. **^{13}C NMR (101 MHz, CDCl$_3$ minor diastereomer)** δ 175.5, 164.6, 140.8, 130.1, 129.6, 129.4, 112.4, 109.6, 109.3, 108.6, 105.0, 96.6, 79.8, 72.5, 70.9, 70.7, 70.5, 70.26, 69.7, 67.3, 51.7, 29.9, 29.8, 26.0, 25.8, 24.8, 24.6, 24.4, 24.3 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{34}H_{47}N_2O_{13}$ 691.3073, found: 691.3073.

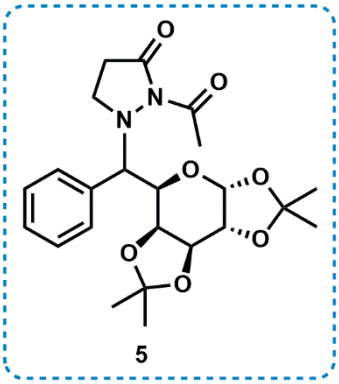
8.4 Derivatization

3-((phenyl((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)amino)propanamide (4)



The product **4** was obtained as a colorless viscous liquid (73 mg, 89 % yield) following the general procedure 6. The crude material was purified by flash column chromatography (DCM/MeOH 80/20 %). **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 7.50 (s, 1H), 7.42 – 7.26 (m, 5H), 5.77 (s, 1H), 5.58 (d, J = 4.9 Hz, 1H), 4.40 (dd, J = 8.0, 2.2 Hz, 1H), 4.29 – 4.25 (m, 1H), 3.91 – 3.89 (m, 1H), 3.81 (dd, J = 9.6, 0.9 Hz, 1H), 3.64 (dd, J = 8.0, 1.3 Hz, 1H), 2.47 (s, 1H), 2.41 – 2.15 (m, 4H), 1.56 (s, 3H), 1.49 (s, 3H), 1.33 (s, 3H), 1.22 (s, 3H) ppm. **^{1}H NMR (400 MHz, $CDCl_3$ minor diastereomer)** δ 7.78 (s, 1H), 7.42 – 7.23 (m, 5H), 5.77 (s, 1H), 5.44 (d, J = 5.1 Hz, 1H), 4.59 (dd, J = 8.0, 2.3 Hz, 1H), 4.43 (d, J = 8.0 Hz, 1H), 4.28 – 4.25 (m, 1H), 3.91 – 3.89 (m, 2H), 2.80 – 2.72 (m, 2H), 2.67 – 2.54 (m, 2H), 2.47 (s, 1H), 1.49 (s, 6H), 1.35 (s, 3H), 1.27 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ $CDCl_3$ major diastereomer)** δ 175.4, 139.0, 128.5, 128.4, 127.6, 109.0, 108.6, 96.5, 71.6, 70.9, 70.6, 70.1, 62.9, 43.4, 36.0, 26.1, 26.0, 24.9, 24.1 ppm. **^{13}C NMR (101 MHz, $CDCl_3$ minor diastereomer)** δ 175.8, 140.1, 128.5, 127.9, 127.5, 109.3, 108.4, 96.5, 71.0, 70.8, 70.5, 69.9, 62.7, 43.1, 35.6, 26.0, 25.9, 24.8, 24.4 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{21}H_{31}N_2O_6$ 407.2177, found: 407.2179.

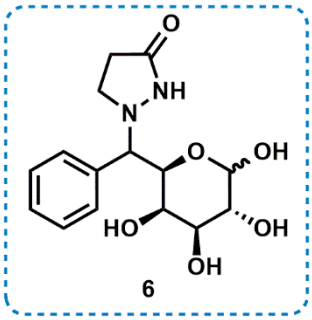
2-acetyl-1-(phenyl((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)pyrazolidin-3-one (5):



The product **5** was obtained as a colorless oil (20 mg, 30% yield) following the general procedure 7. The crude material was purified by flash column chromatography (EtOAc/hexane 40/60%). **^{1}H NMR (400 MHz, $CDCl_3$ major diastereomer)** δ 7.38 – 7.31 (m, 3H), 7.29 – 7.24 (m, 2H), 5.44 (d, J = 5.1 Hz, 1H), 4.94 (d, J = 7.6 Hz, 1H), 4.71 (dd, J = 8.0, 2.3 Hz, 1H), 4.49 (d, J = 10.5 Hz, 1H), 4.36 (d,

J = 10.4 Hz, 1H), 4.31 (dd, J = 5.1, 2.3 Hz, 1H), 3.62 – 3.43 (m, 2H), 2.42 (s, 3H), 2.18 – 2.06 (m, 1H), 1.67 (s, 3H), 1.45 (s, 3H), 1.42 (s, 3H), 1.33 (s, 3H), 1.26 (td, J = 6.8, 4.2 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$ $CDCl_3$ major diastereomer)** δ 175.0, 167.9, 134.5, 130.0, 128.6, 109.0, 108.3, 97.0, 71.1, 71.0, 70.8, 65.9, 32.3, 26.0, 24.8, 24.5, 24.5 ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{23}H_{31}N_2O_7$ 447.2126, found: 447.2127.

1-(phenyl((2*R*,3*R*,4*S*,5*R*)-3,4,5,6-tetrahydroxytetrahydro-2*H*-pyran-2-yl)methyl)pyrazolidin-3-one (6):



6

The product **6** was obtained as a colorless oil (21 mg, 65 % yield) following the general procedure 8. The crude material was purified by flash column chromatography (DCM/MeOH 70/30 %).**^{1}H NMR (400 MHz, CD_3OD)** δ 5.24 (d, J = 3.9 Hz, 1H$_\alpha$), 4.91 (d, J = 3.8 Hz, 1H$_\alpha$), 4.53 (d, J = 7.8 Hz, 1H$_\beta$), 4.33 (d, J = 7.6 Hz, 1H$_\beta$) ppm. **^{13}C NMR (101 MHz, MeOD)** δ 97.7 (C$_\beta$), 97.4 (C$_\beta$), 93.0 (C$_\alpha$), 92.7(C$_\alpha$) ppm. **HRMS** (ESI) $[M + H]^+$ *m/z*: calculated for $C_{22}H_{29}N_2O_9$ 325.1394, found: 325.1396.

9. Cyclic Voltammetry Measurements

The electrochemical measurement by cyclic voltammetry was performed in a potentiostat/galvanostat model Autolab PGSTAT-204 (EcoChemie, Netherlands) controlled by the NOVA 2.1.2 software. A conventional three-electrode system was used, with a platinum plate as the auxiliary electrode; the reference electrode was Ag/AgCl/KCl (3.0 mol.L^{-1}) and the glassy carbon electrode (GCE) as the working electrode. A solution of Bu_4NPF_6 (0.10 mol.L^{-1}) in degassed MeCN was used with electrolyte, with ferrocene as internal reference ($E^0_{1/2}$ = + 0.40 V) and **21'** (0.1 mmol.L^{-1}). A potential sweep was performed from − 2.0 to + 2.0 V, with a sweep speed of 50 mV.s^{-1}, three cycles were obtained during the potential sweep to ensure measurement accuracy.

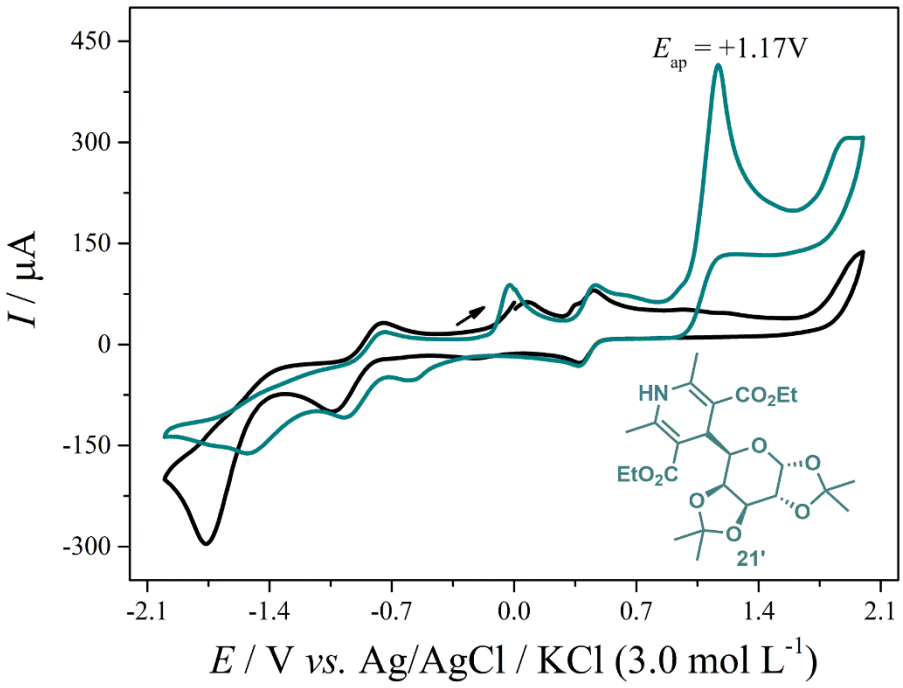


Figure S1. Cyclic voltammetry measurements for 21'.

10. Stern-Volmer Quenching Experiments

Fluorescence measurements were acquired at room temperature using an RF-5301 PC Fluorescence Spectrophotometer with excitation slits open at 1.5 nm and emission slit open at 3 nm. All prepared solutions were degassed. The 4CzIPN (1.67 mM) was dissolved in different concentrations of DHP-**21'** indicated using acetonitrile as solvent, the emission spectra are shown below. The excitation wavelength is 545 nm.

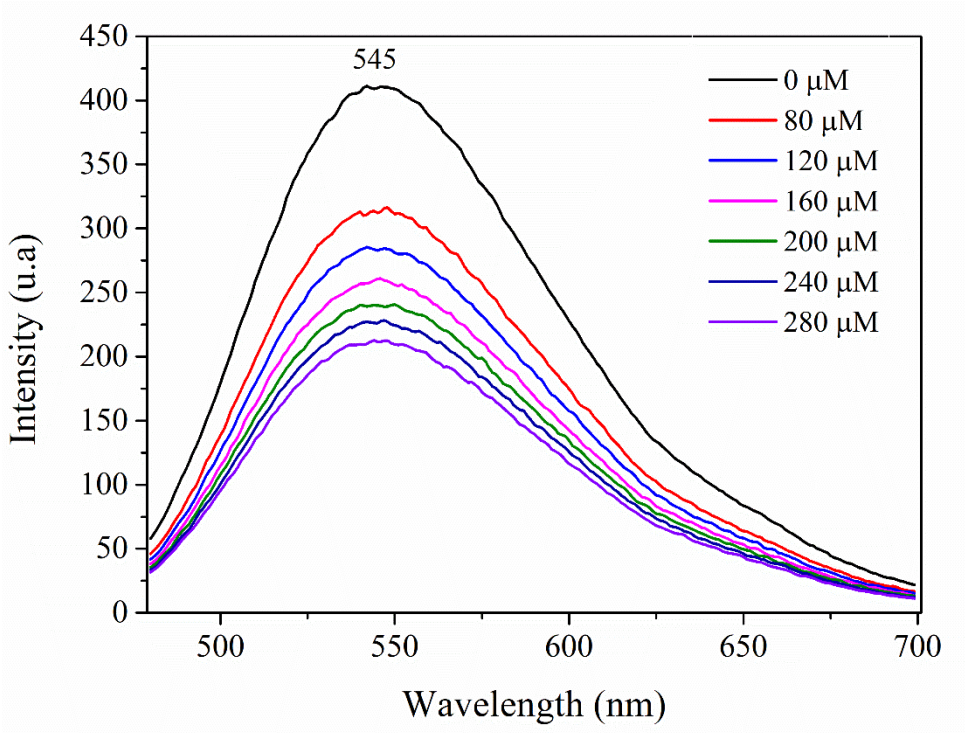


Figure S2. Emission of 4CzIPN (black line) at different DHP-21' concentrations, using acetonitrile as the solvent, and the emission spectrum is shown above. The excitation wavelength is 450 nm.

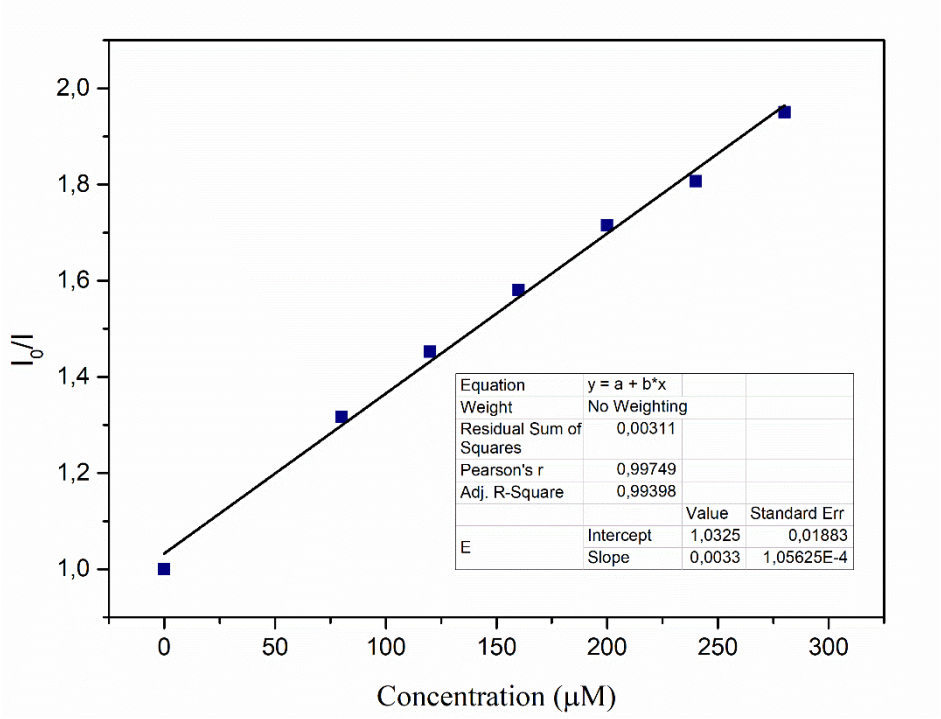
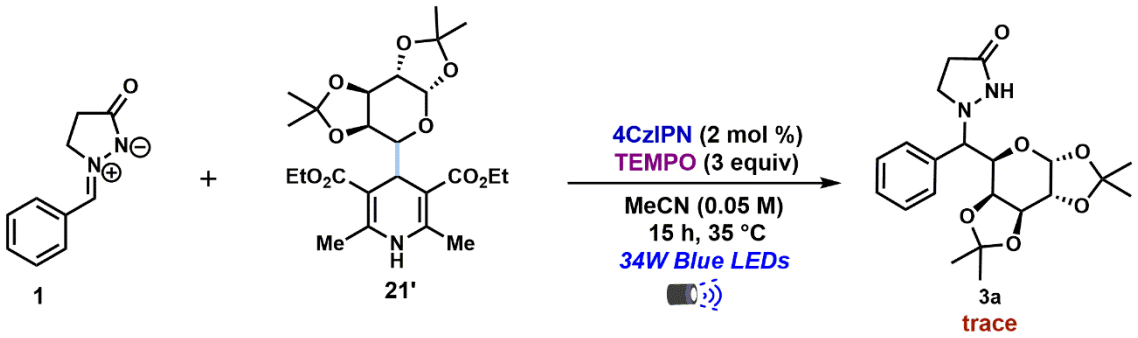


Figure S3. Stern-Volmer plot analysis derived from the data extracted from **Figure S2**.

11. Trapping experiment

The radical-trapping experiment was carried out using TEMPO (2,2,6,6- Tetramethyl-1-piperidinyloxy) as radical scavenger. The starting material **1** (0.15 mmol, 1.0 equiv), **21'** (0.30 mmol, 2 equiv), the photocatalyst 4CzIPN (2 mol %) and TEMPO (3.0 equiv) were dissolved in 3.0 mL of MeCN in a dried Schlenk tube equipped with a stir bar. The Schlenk tube was sealed with PTFE/silicon septum and connected to a vacuum line and the solution was degassed 3 times via a freeze-pump-thaw procedure. The resulting solution was stirred for 15 h ~ 4 cm from the irradiation source (a 34 W Kessil H150 blue LED lamp).



Results: After the reaction time, the product **3a** could not be noticed on the TLC plate. An aliquot was removed from the crude reaction and a sample was prepared in 1 % HCOOH/MeOH and analyzed by mass spectrometry using an ACQUITY UPC2-MS apparatus through direct infusion.

The MS full scan experiment indicated the presence of the hydrogenated radical scavenger as shown in Figure S4. Furthermore, the peak at *m/z* 386.2498 is associated with coupling of the radical scavenger with the glycoside radical. The peak at *m/z* 405.1819 is evidence of product **3a** formed, but only traces.

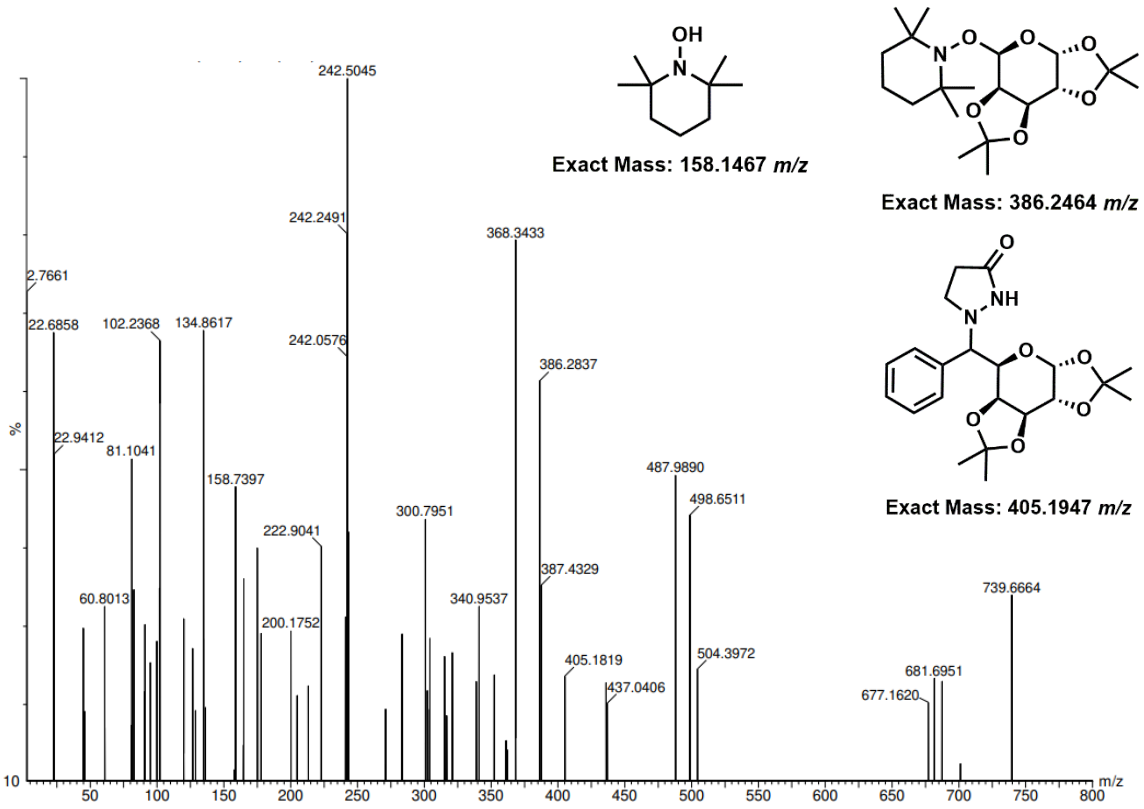


Figure S4. MS full scan experiment via direct infusion of the reaction crude. The exact mass of compounds are reported as the $[M+H]^+$ adduct.

12. Experiment of Nuclear Overhauser Effect (NOE)

1D NOE spectrum of the major compound, applied with an initial selective pulse at 3.53 ppm creates a peak at 4.38 ppm, and a same phase peak at 4.12 ppm due to dipolar coupling (see Figure S5). It was also applied with an initial selective pulse at 4.54 ppm creating a peak at 4.63 ppm, and a peak of the same phase at 4.10 ppm referring to the minor diasteoisomer (see Figure S6). In contrast, normal NOE enhancements appear in the opposite phase of the selective pulse peak. This proves that both hydrogens are in the same spatial region, as the special position of H_4 is defined, so H_5 is in the same spatial region, consequently we can assume that this hydrogen is *syn* in relation to hydrogen H_4 in both molecules.

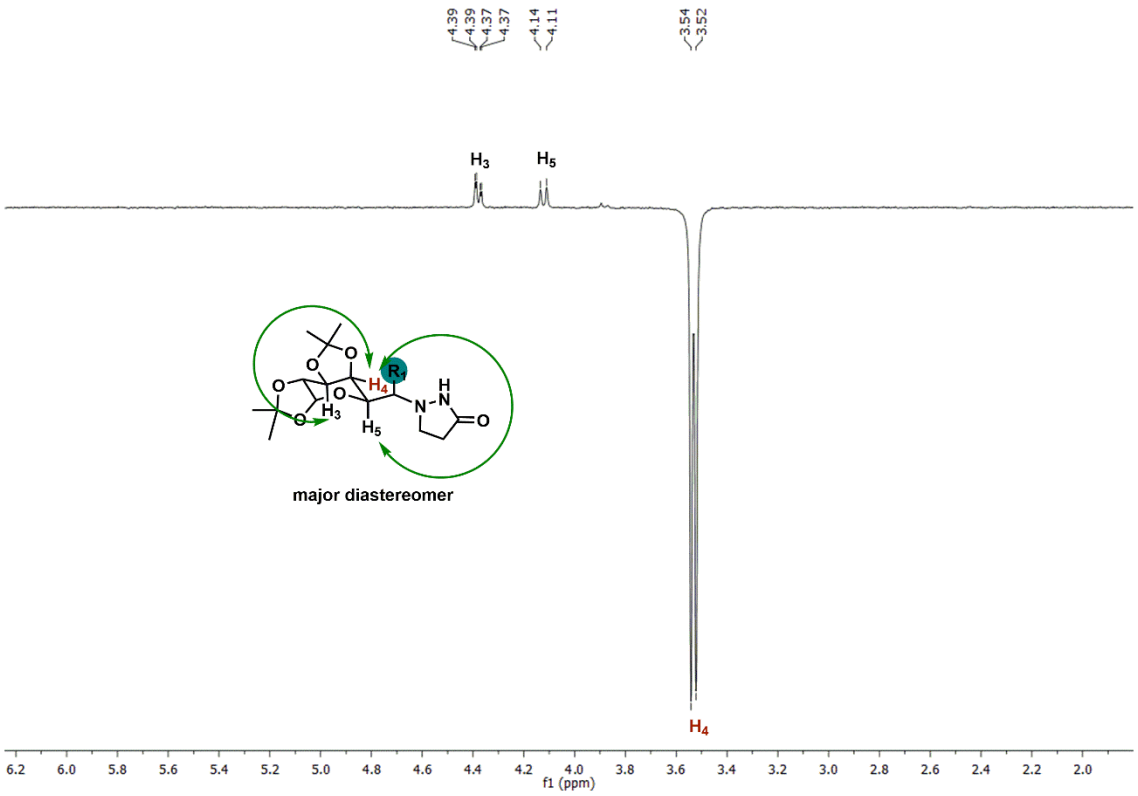


Figure S5. Selective irradiation of peak at 3.53 ppm in a 1D NOE experiment.

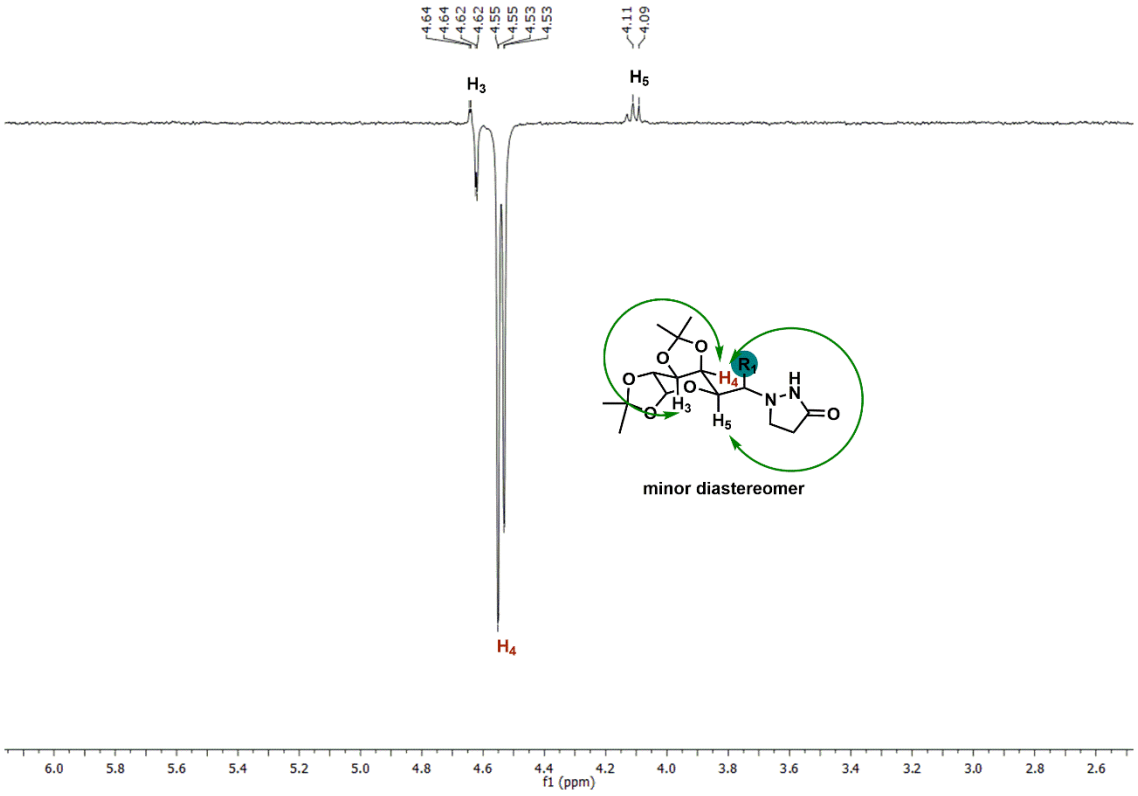


Figure S6. Selective irradiation of peak at 4.54 ppm in a 1D NOE experimen

13. ^{1}H and ^{13}C NMR spectra

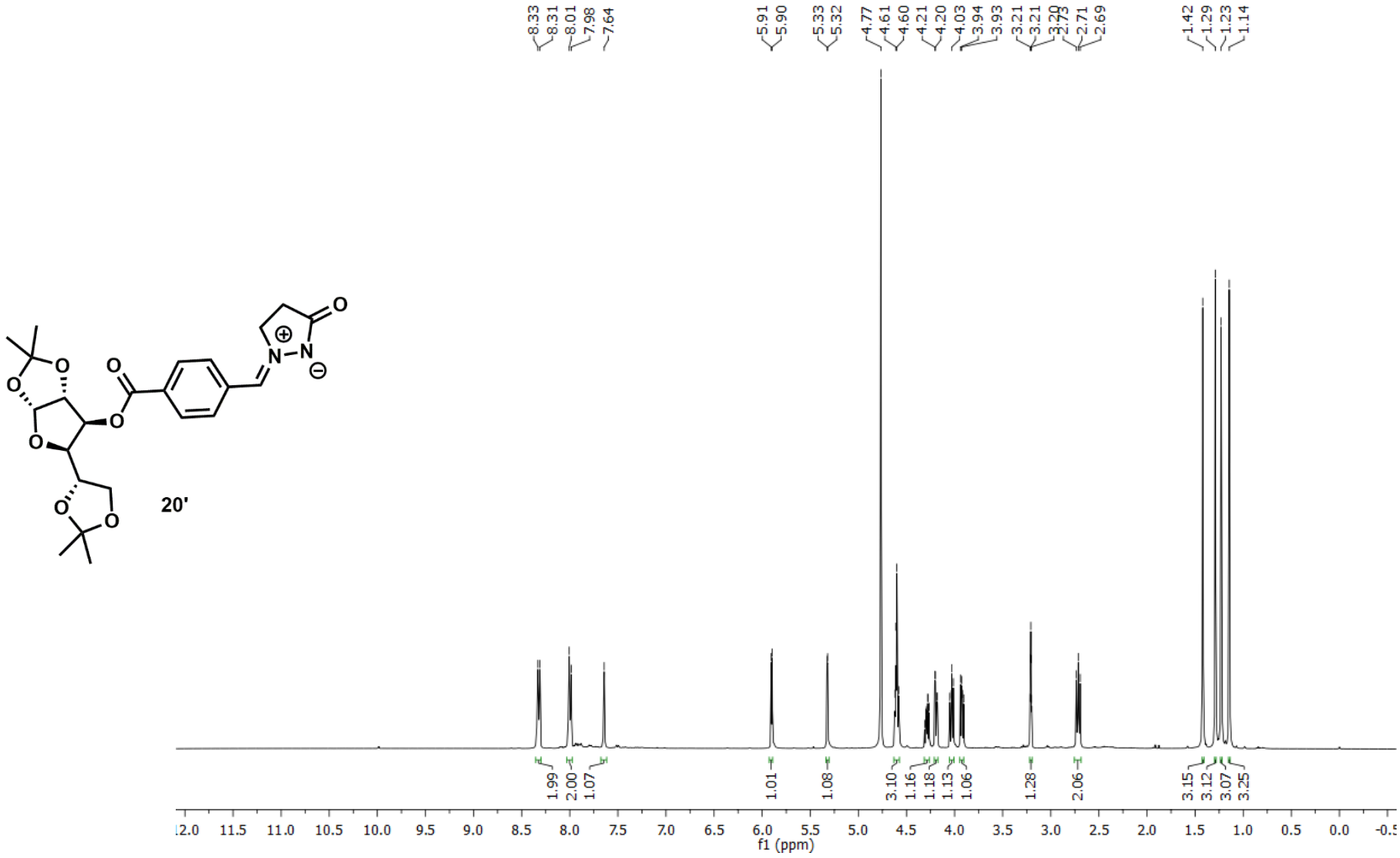


Figure S7. ^{1}H NMR spectrum of **20'** (400 MHz, MeOD)

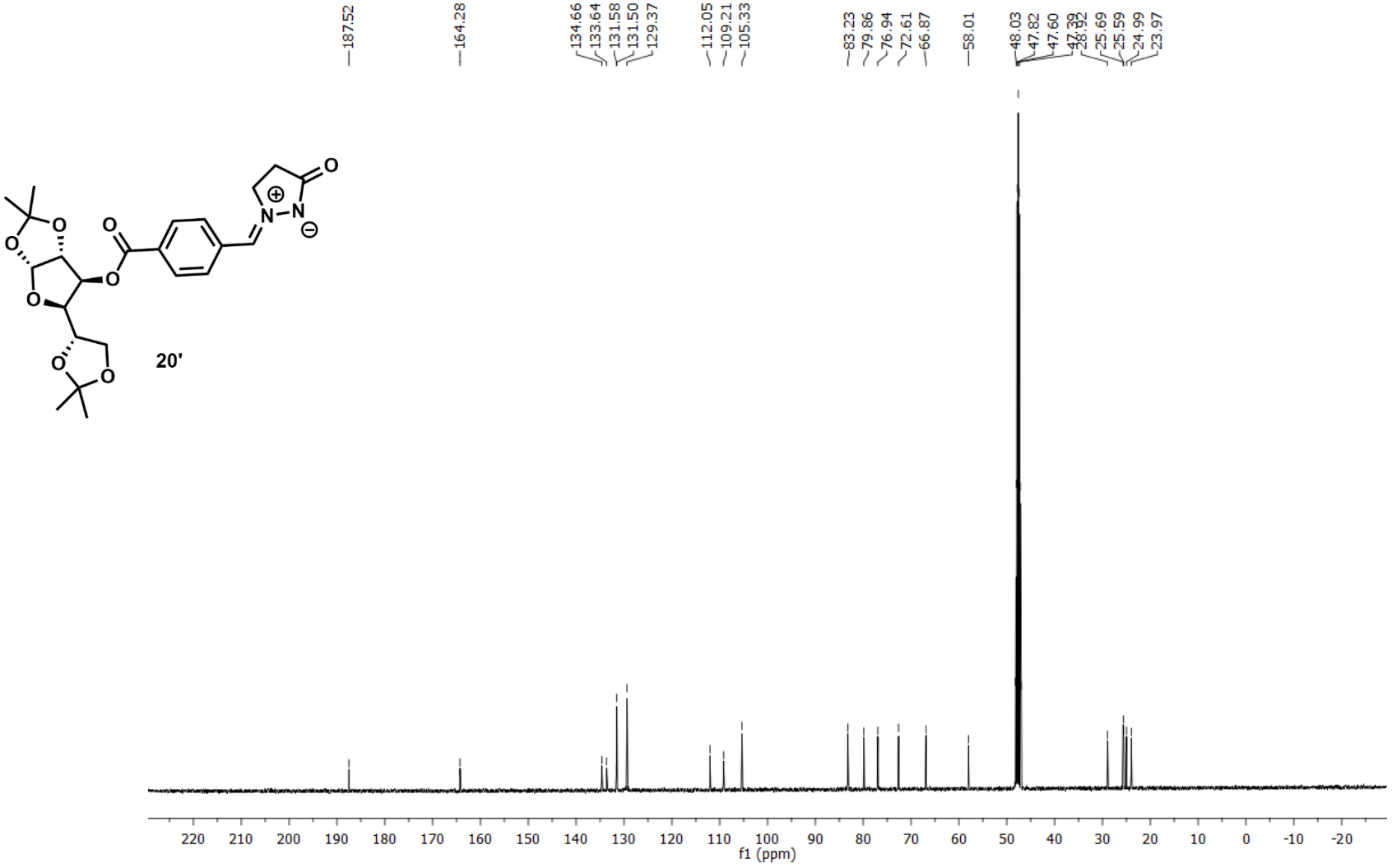


Figure S8. ^{13}C NMR spectrum of **20'** (101 MHz, MeOD)

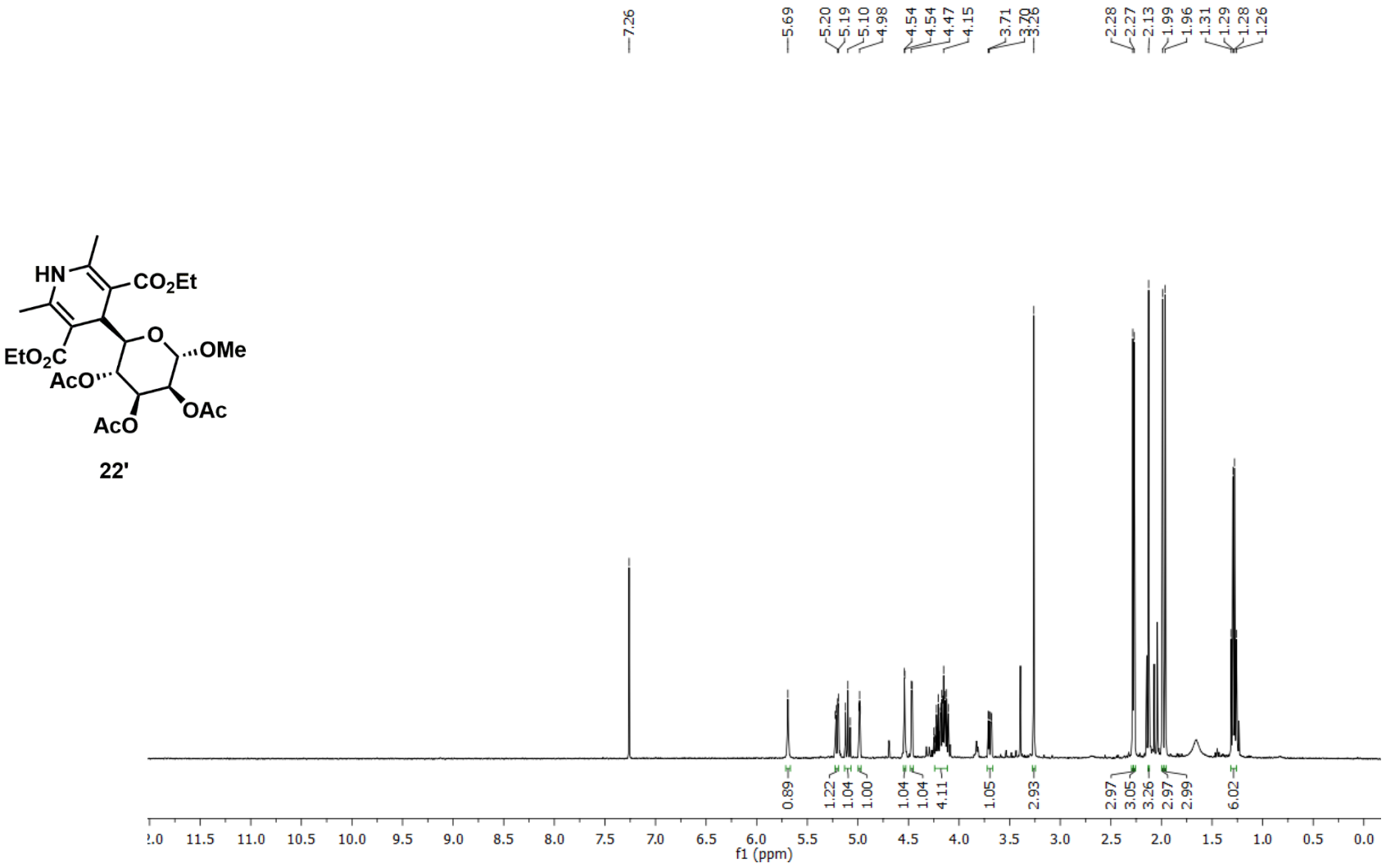


Figure S9. ^{1}H NMR spectrum of **22'** (400 MHz, $CDCl_3$)

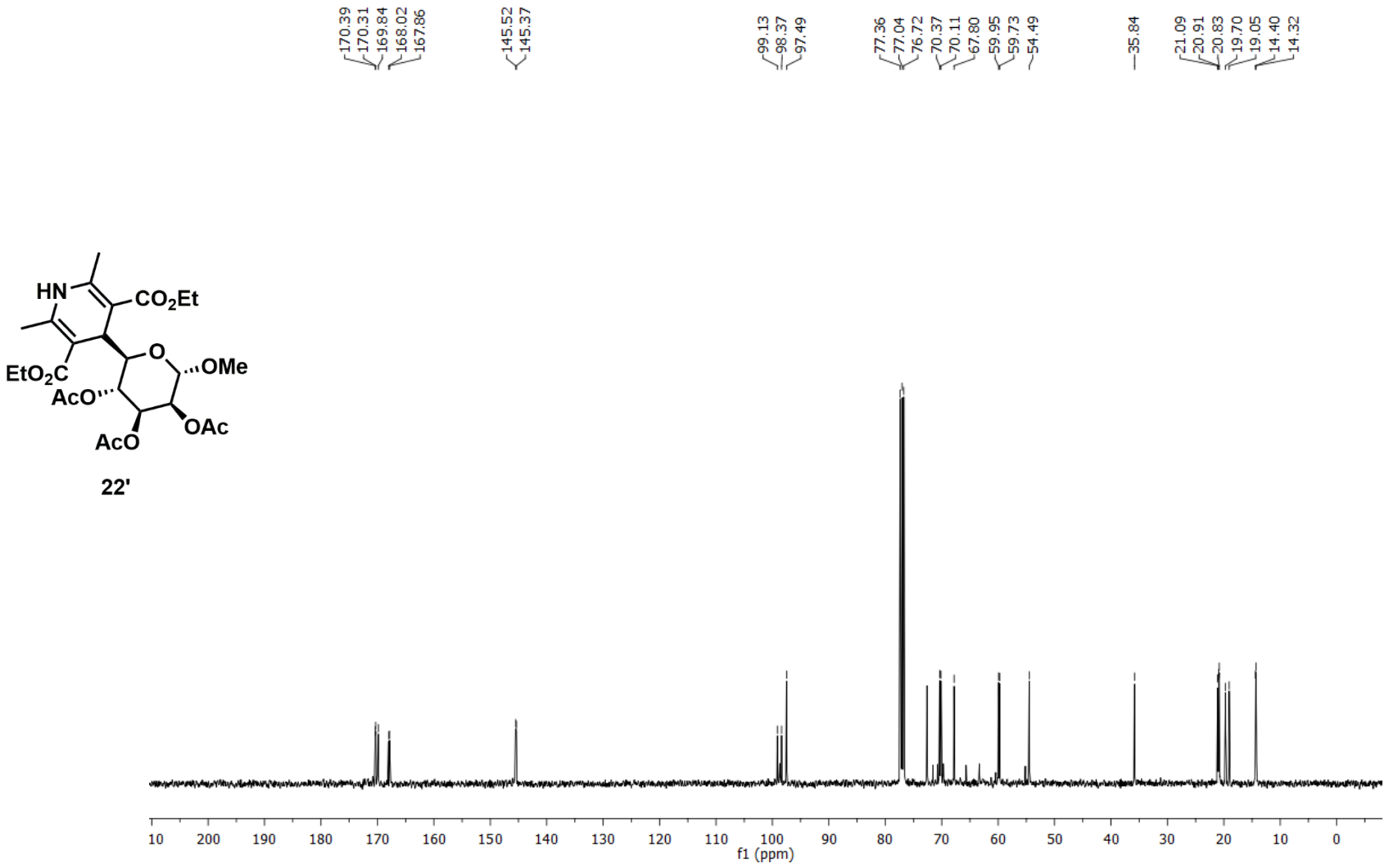


Figure S10. ^{13}C NMR spectrum of **22'** (101 MHz, $CDCl_3$)

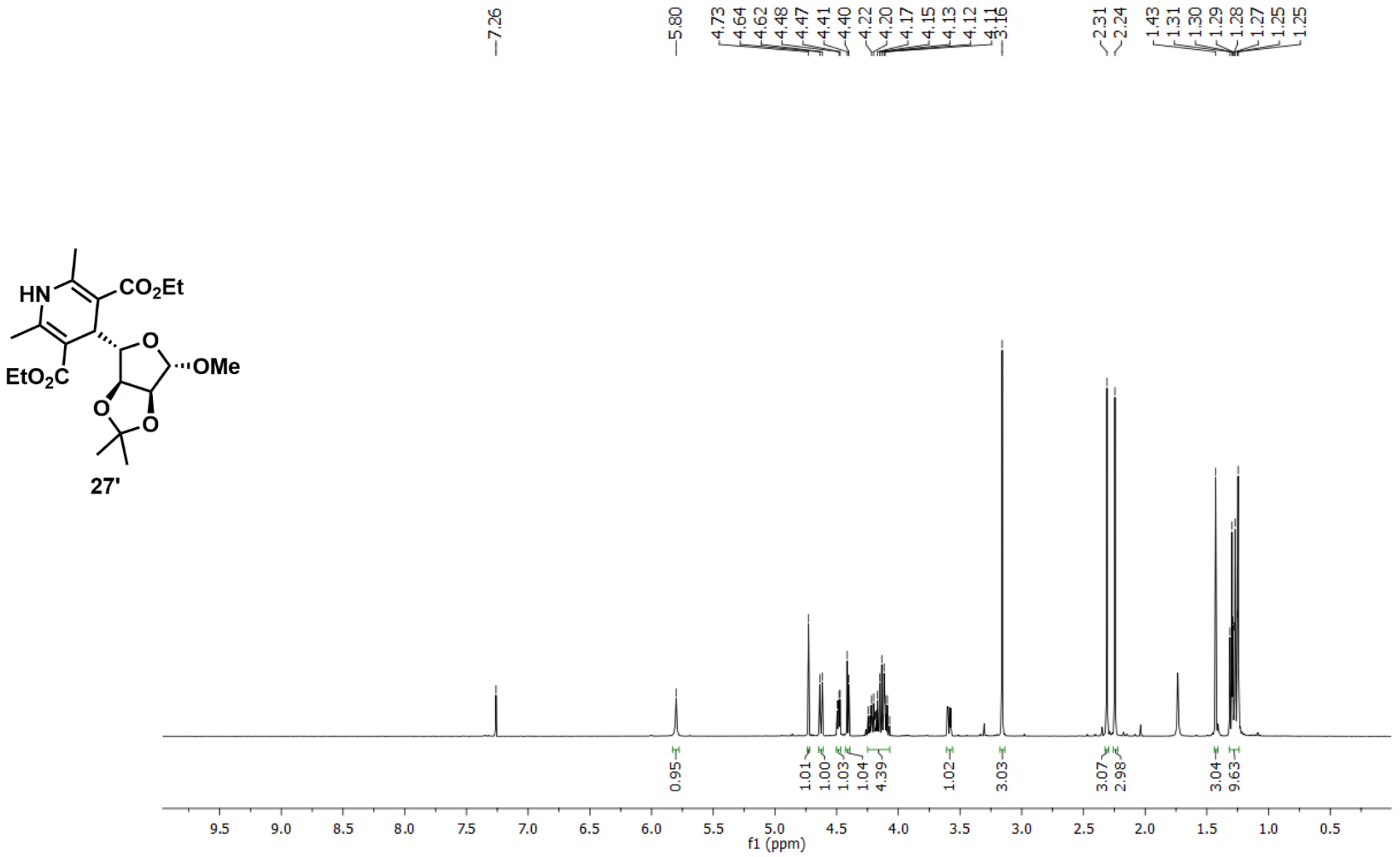


Figure S11. ^{1}H NMR spectrum of **27'** (400 MHz, $CDCl_3$)

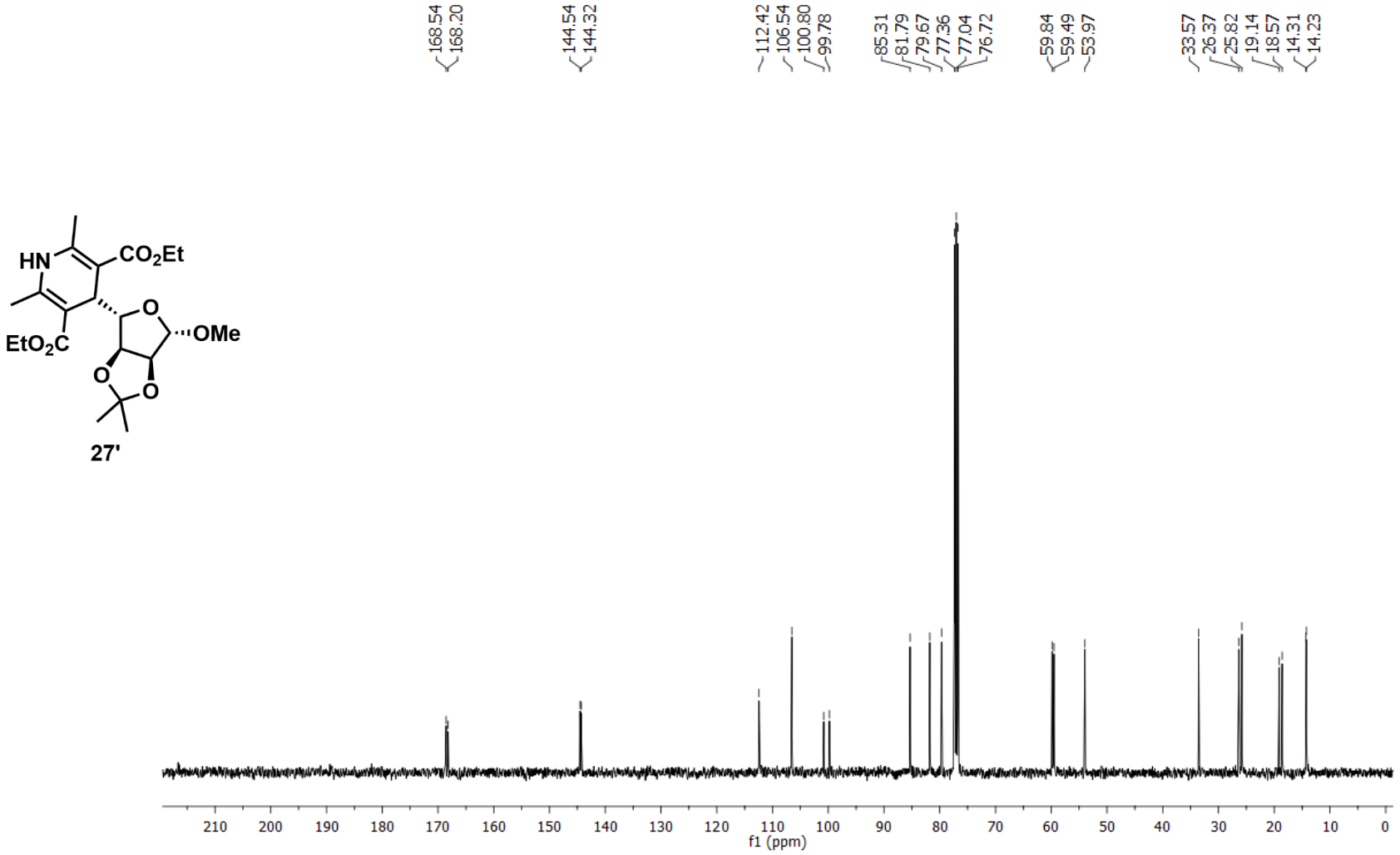


Figure S12. ^{13}C NMR spectrum of **27'** (101 MHz, $CDCl_3$)

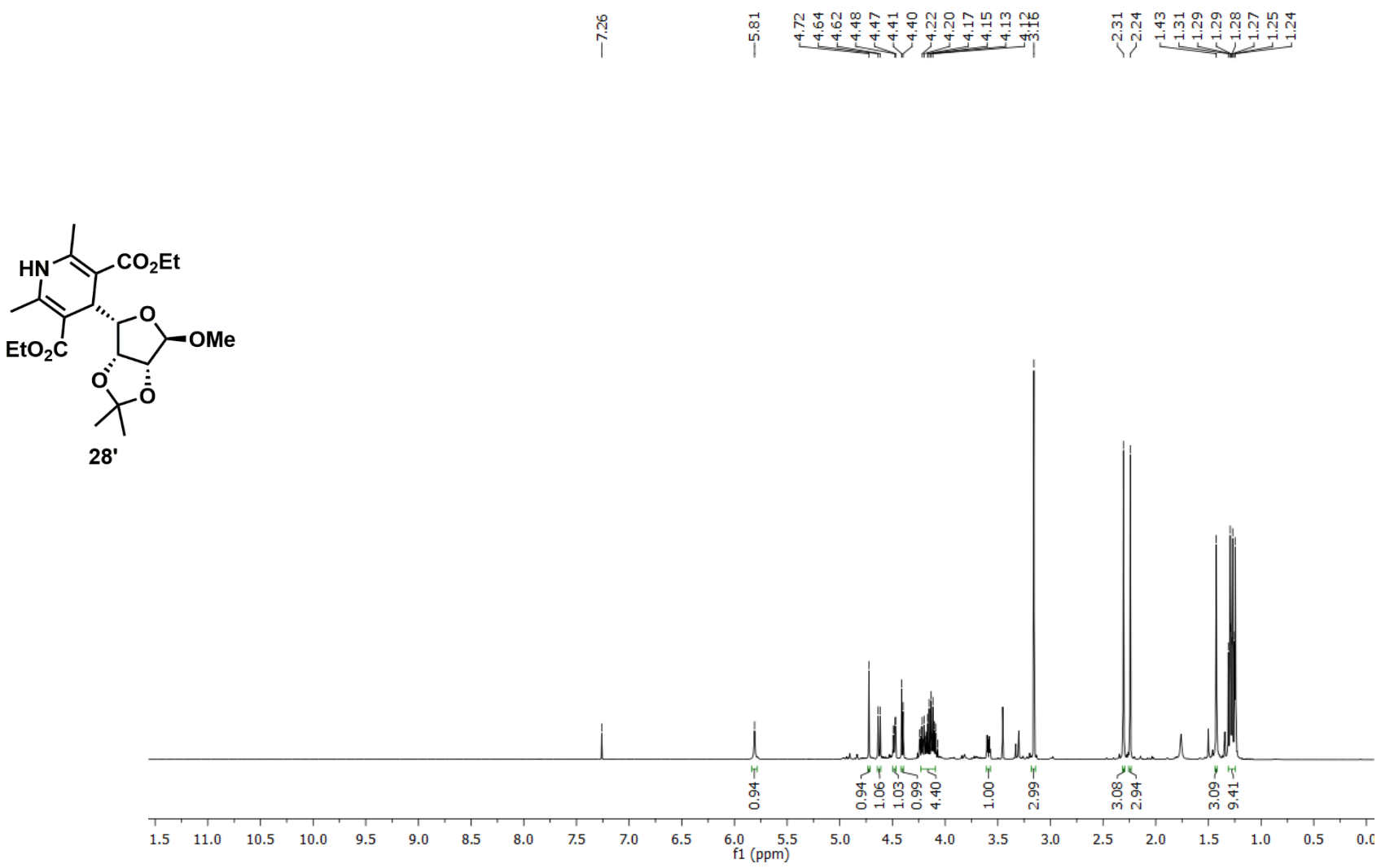


Figure S13. ^{1}H NMR spectrum of **28'** (400 MHz, $CDCl_3$)

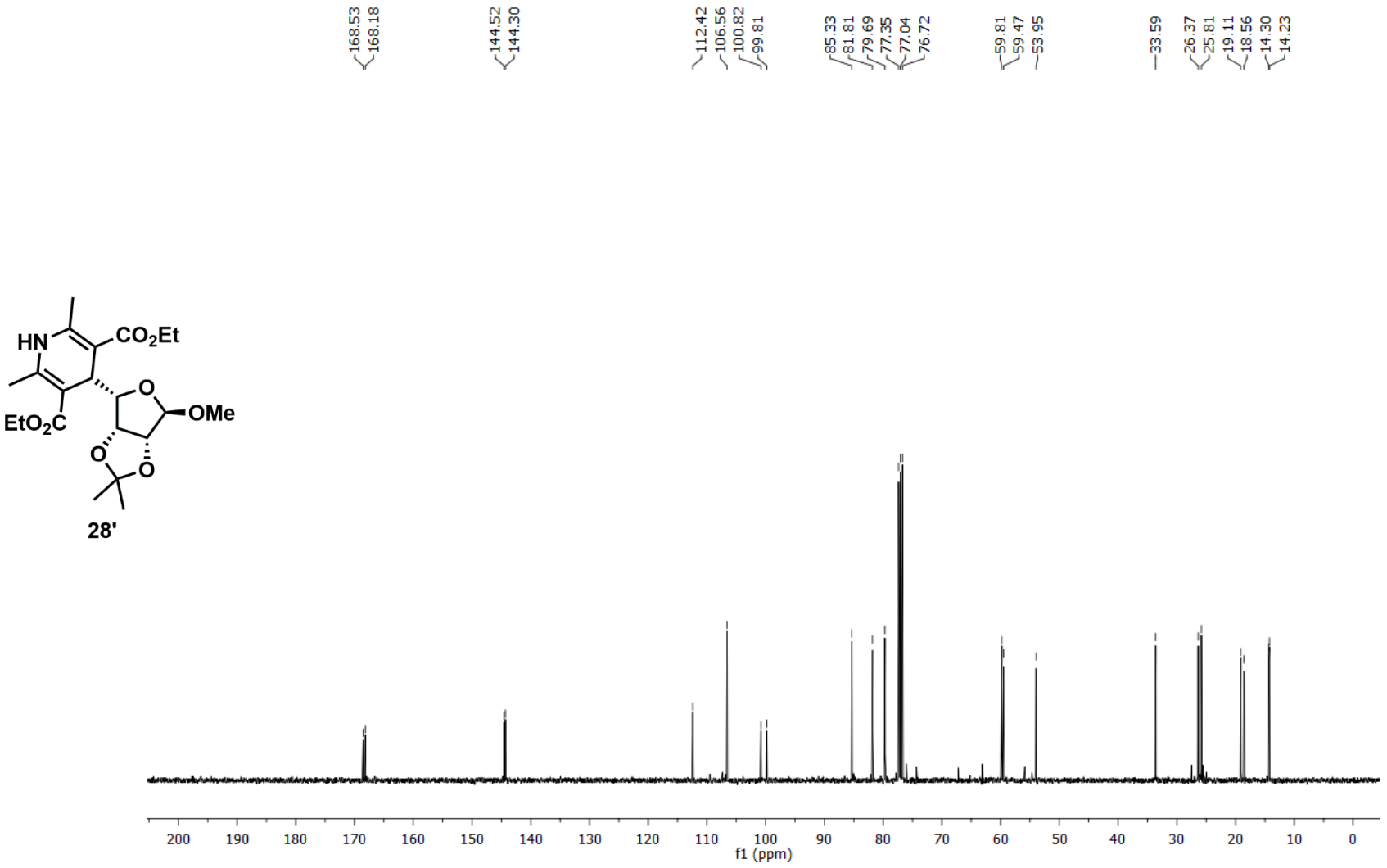


Figure S14. ^{13}C NMR spectrum of **28'** (101 MHz, $CDCl_3$)

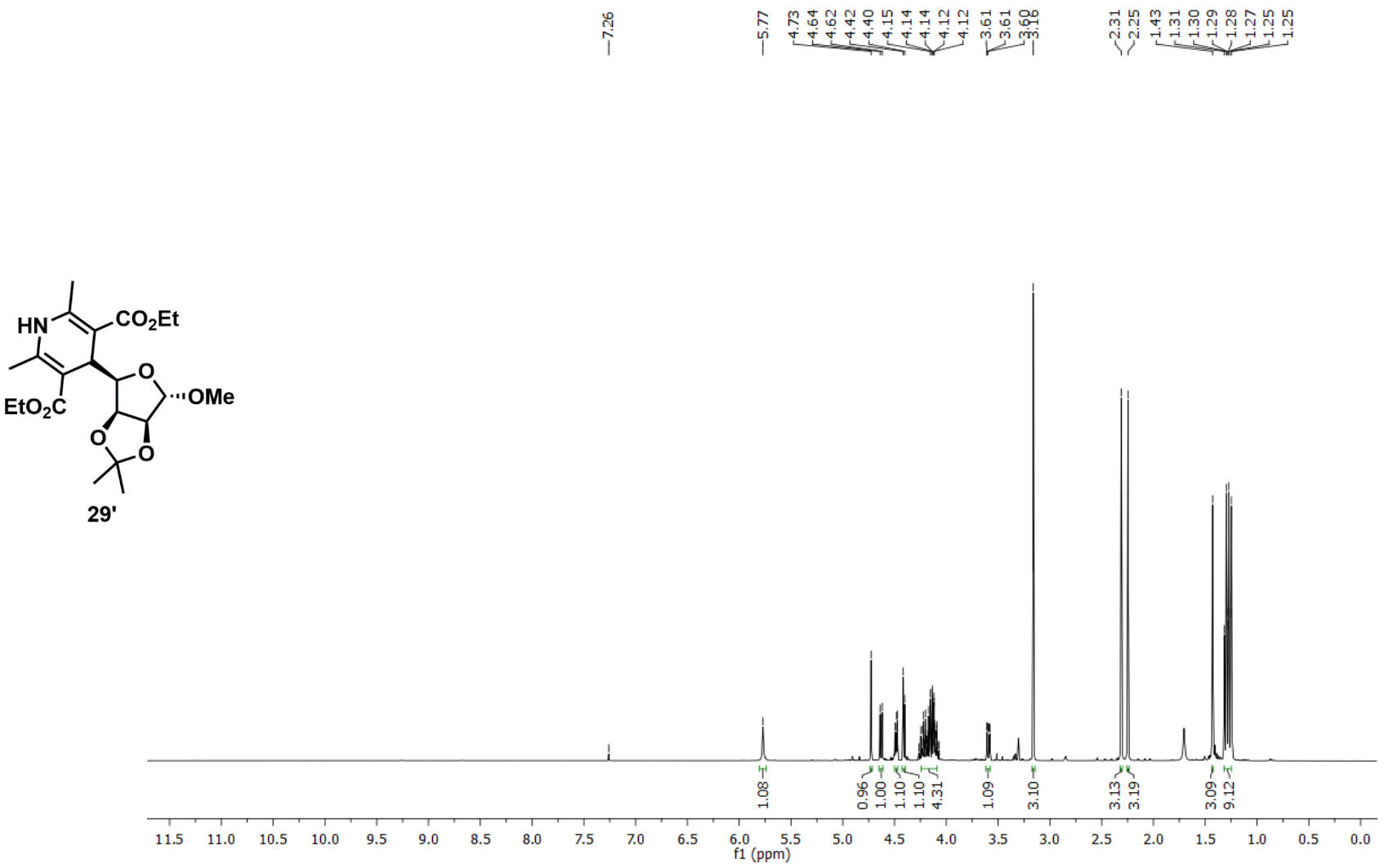


Figure S15. ^{1}H NMR spectrum of **29'** (400 MHz, $CDCl_3$)

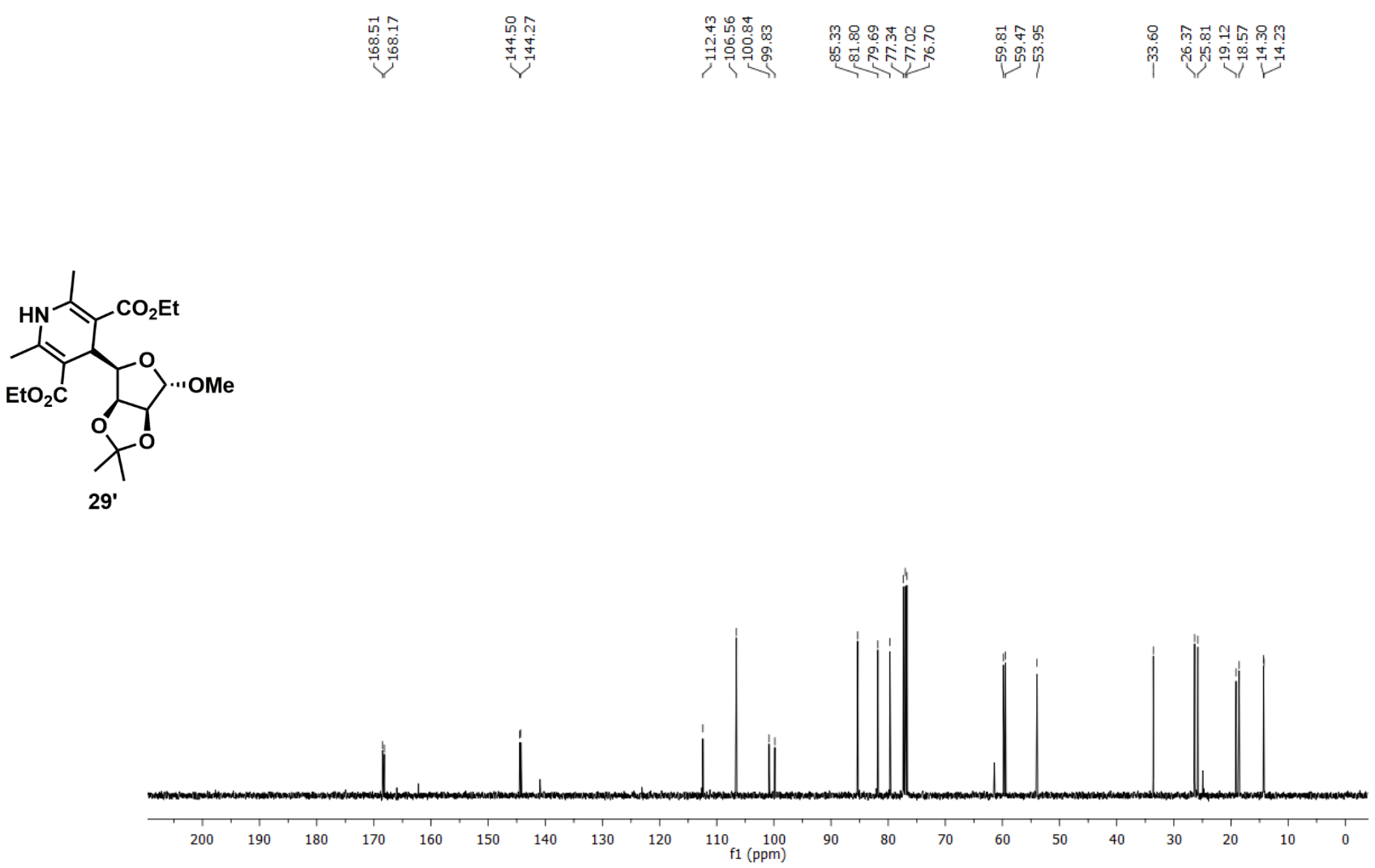


Figure S16. ^{13}C NMR spectrum of **29'** (101 MHz, $CDCl_3$)

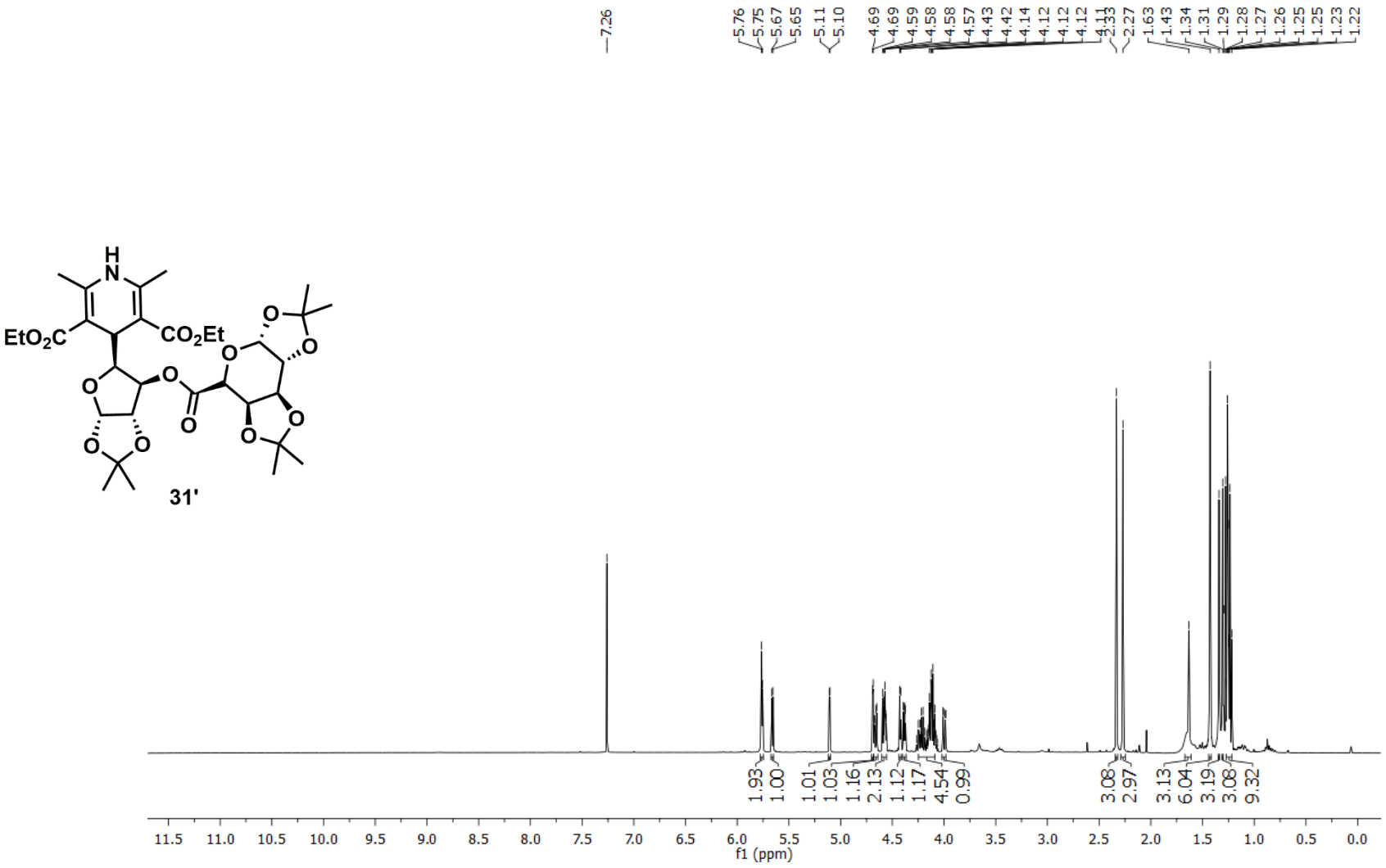


Figure S17. ^{1}H NMR spectrum of **31'** (400 MHz, $CDCl_3$)

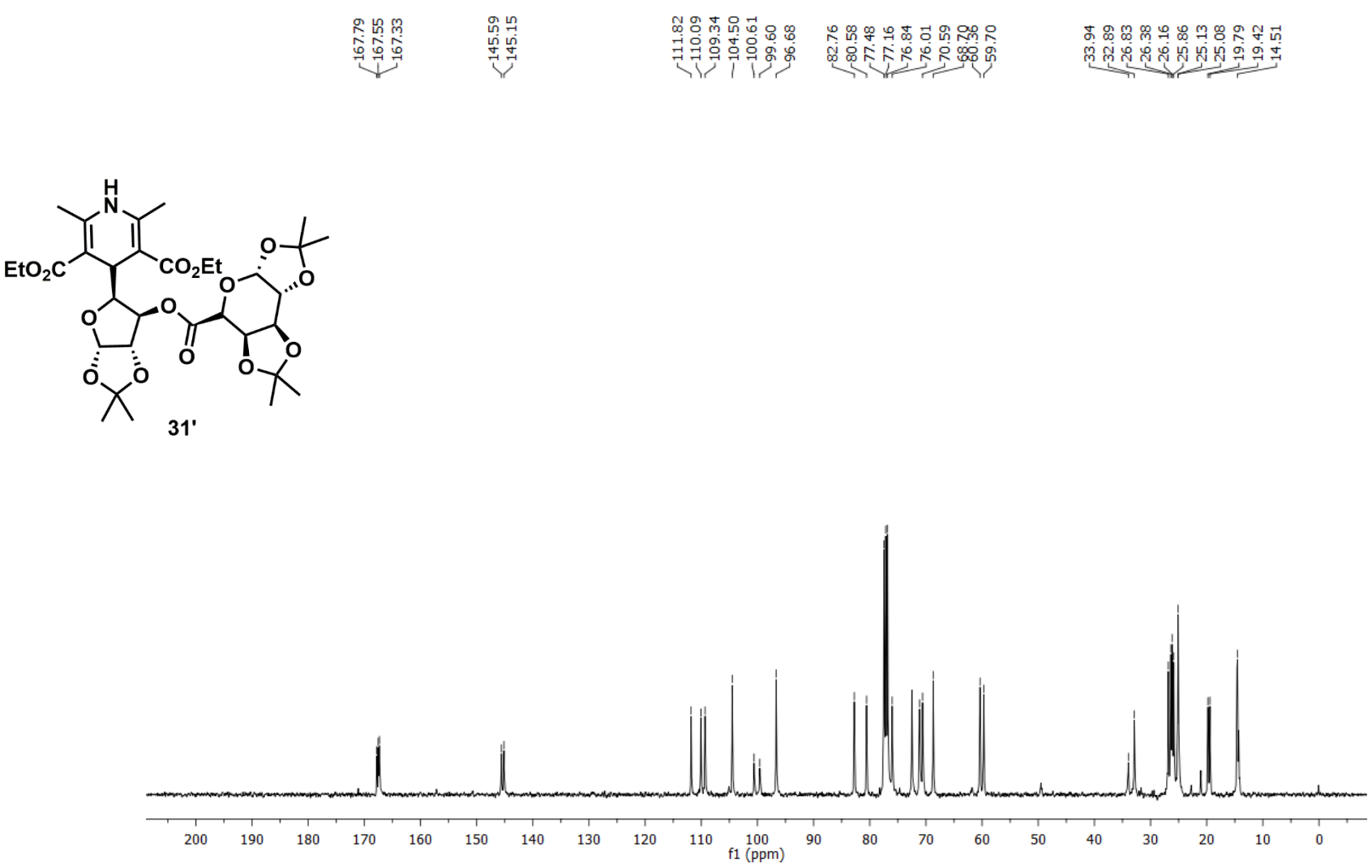


Figure S18. ^{13}C NMR spectrum of **31'** (101 MHz, $CDCl_3$

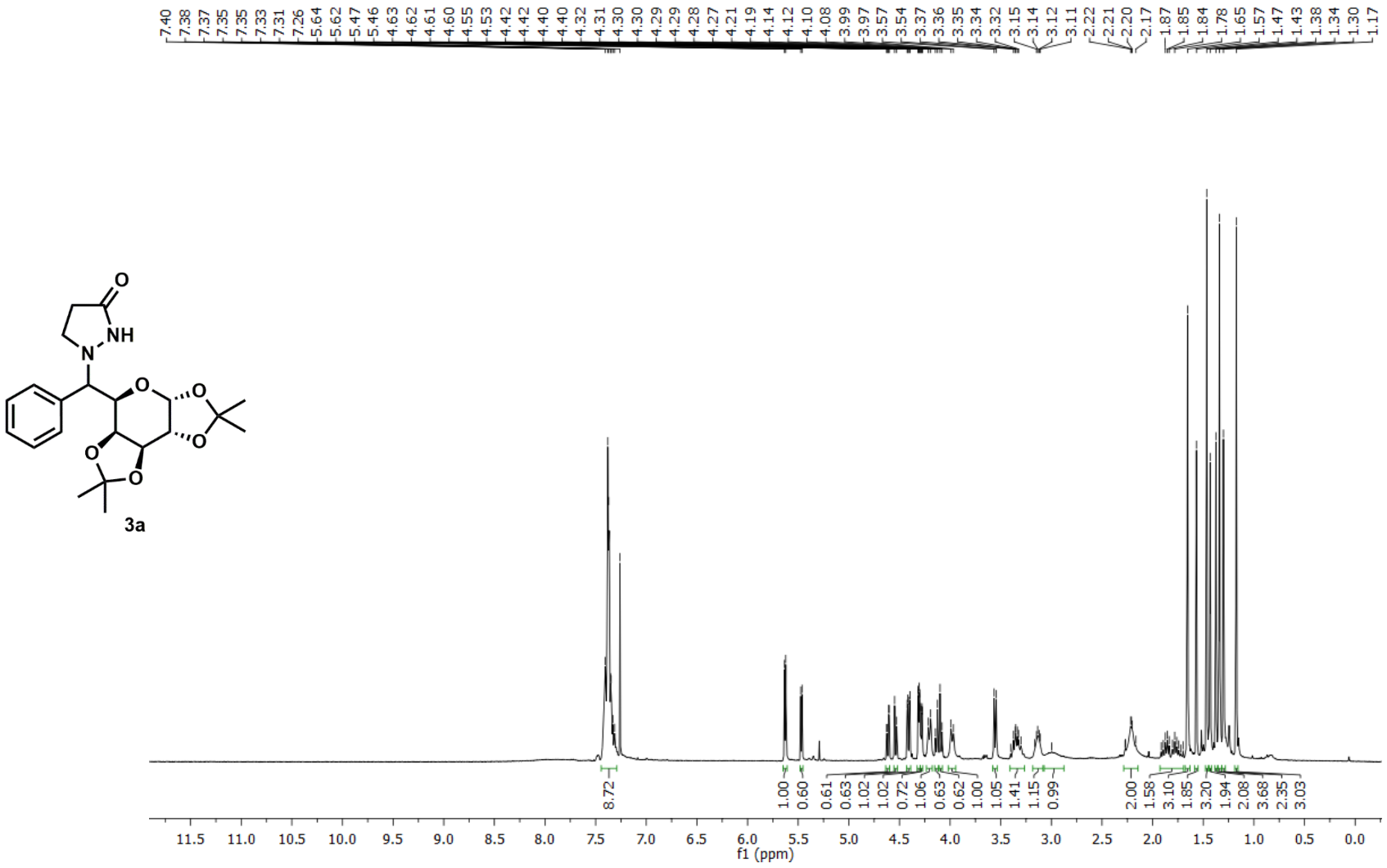


Figure S19. ^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)

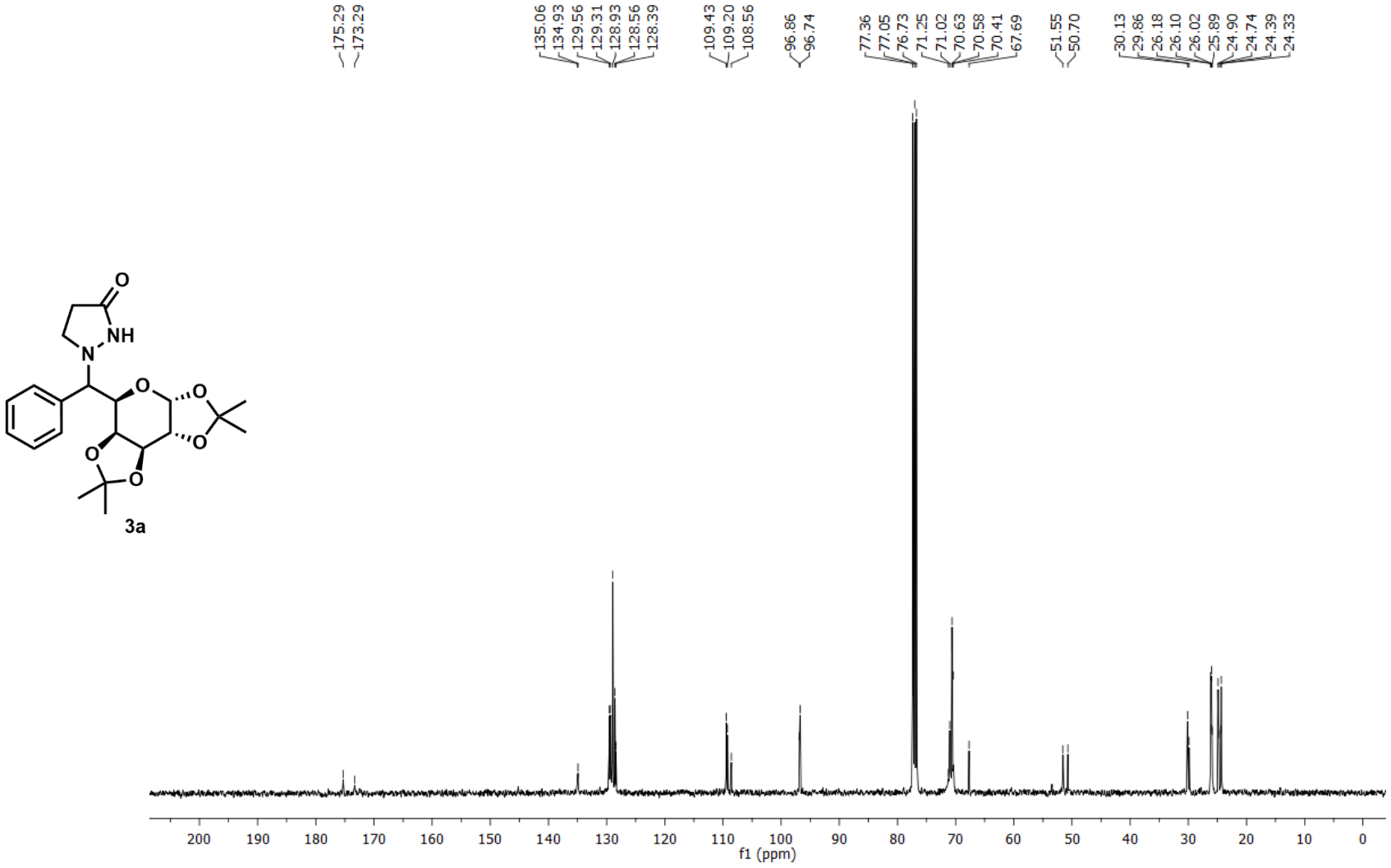


Figure S20. ^{13}C NMR spectrum of **3a** (101 MHz, $CDCl_3$)

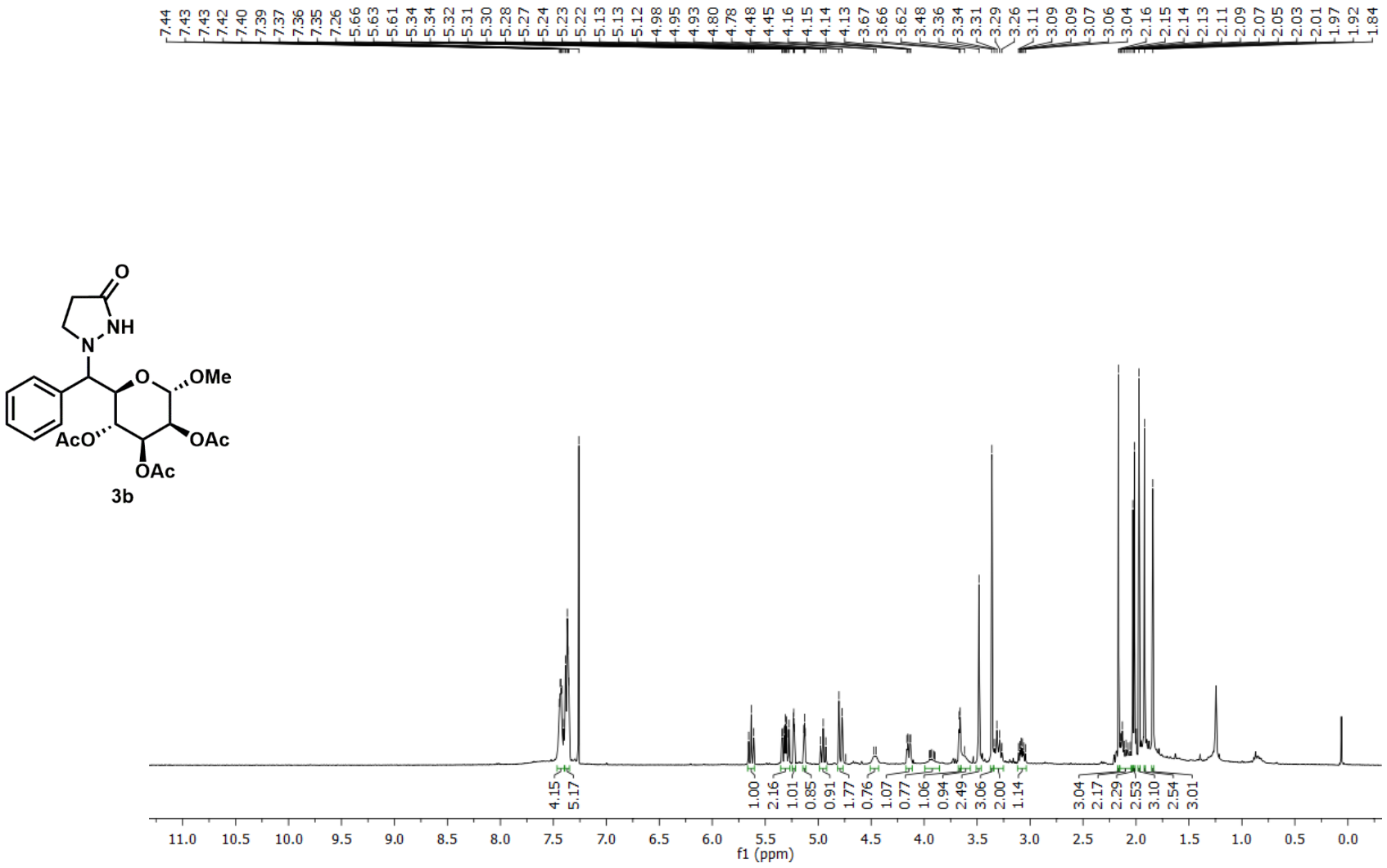


Figure S21. ^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$)

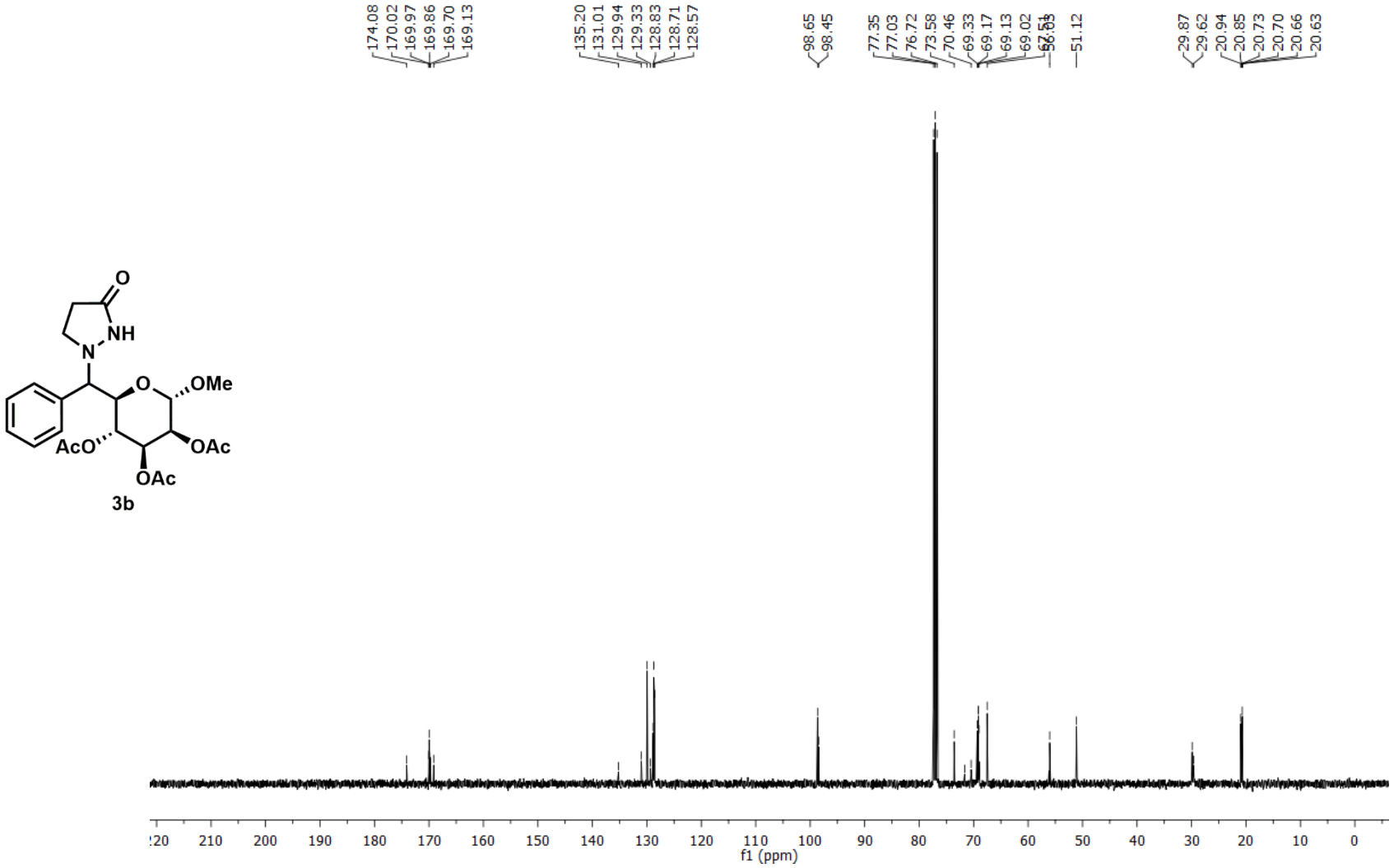


Figure S22. ^{13}C NMR spectrum of **3b** (101 MHz, $CDCl_3$)

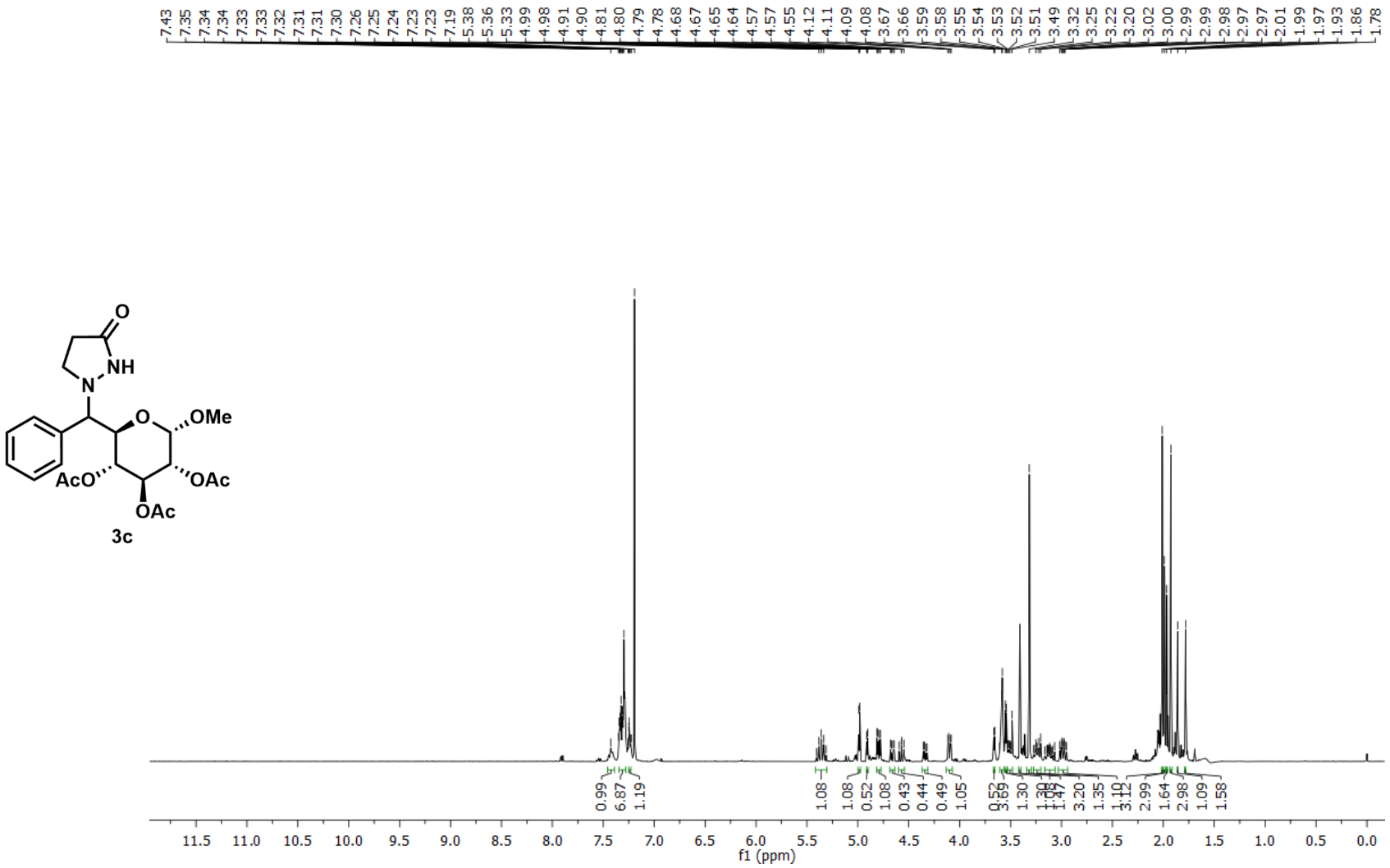


Figure S23. ^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$)

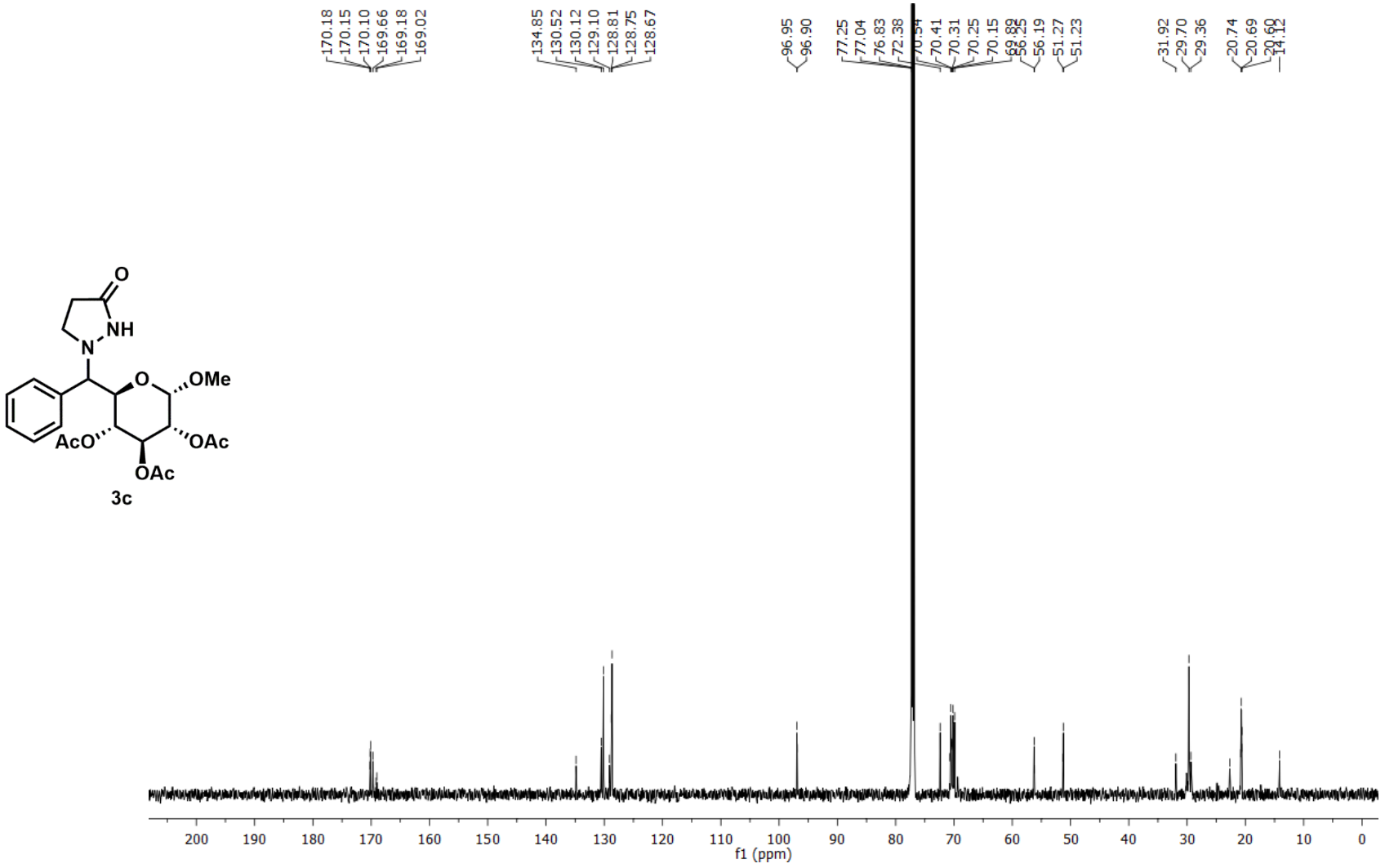


Figure S24. ^{13}C NMR spectrum of **3c** (101 MHz, $CDCl_3$)

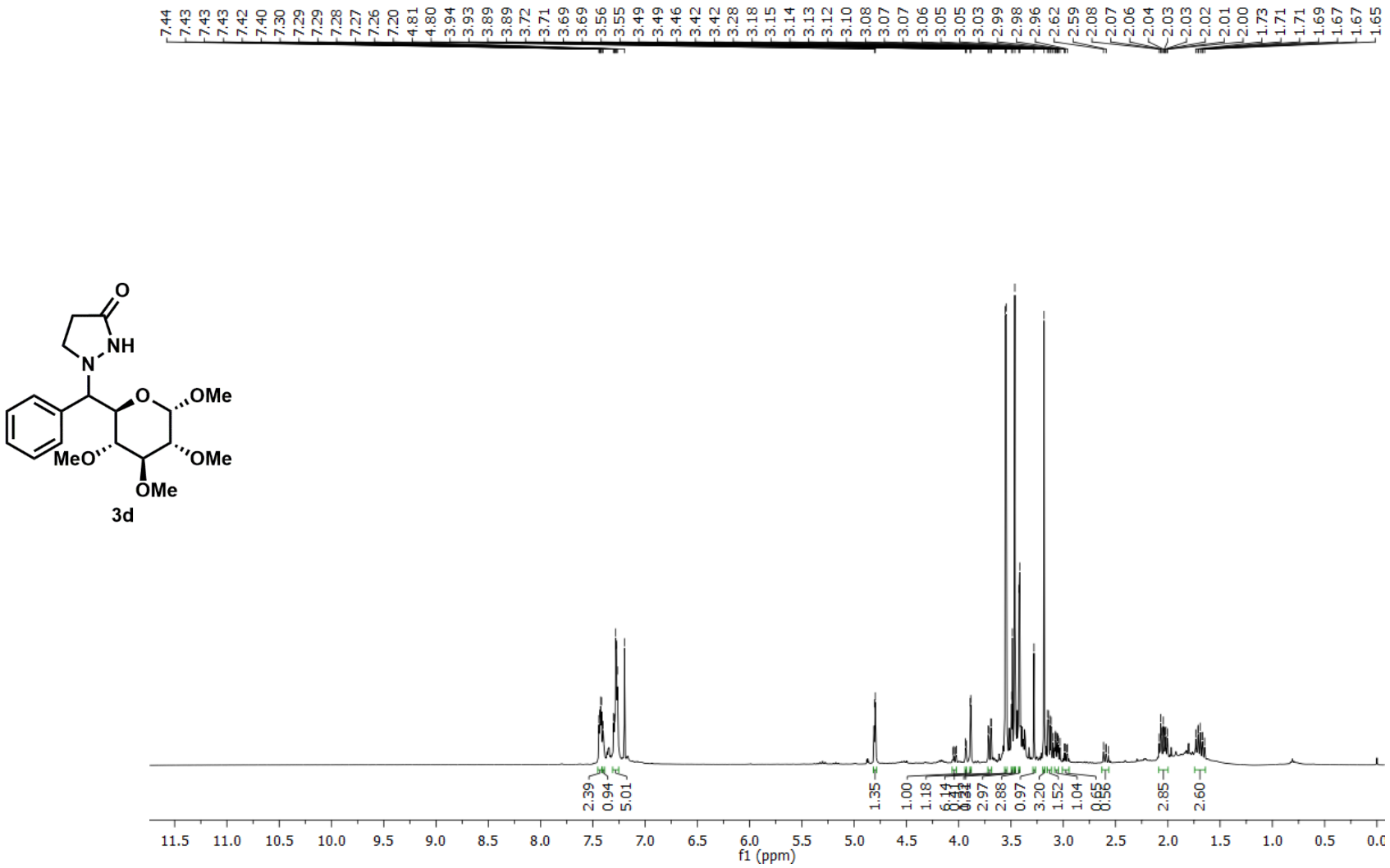


Figure S25. ^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$)

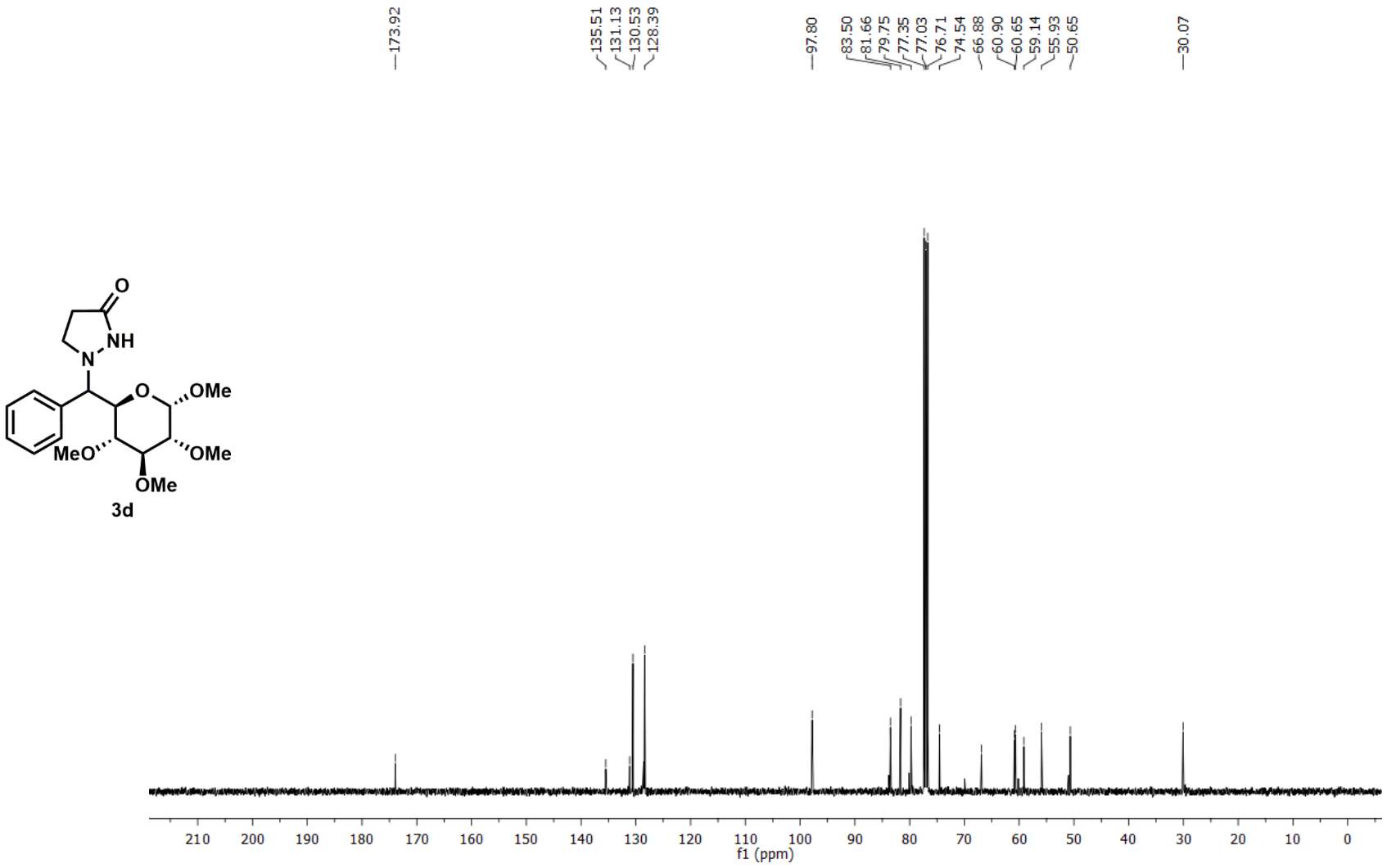


Figure S26. ^{13}C NMR spectrum of **3d** (101 MHz, $CDCl_3$)

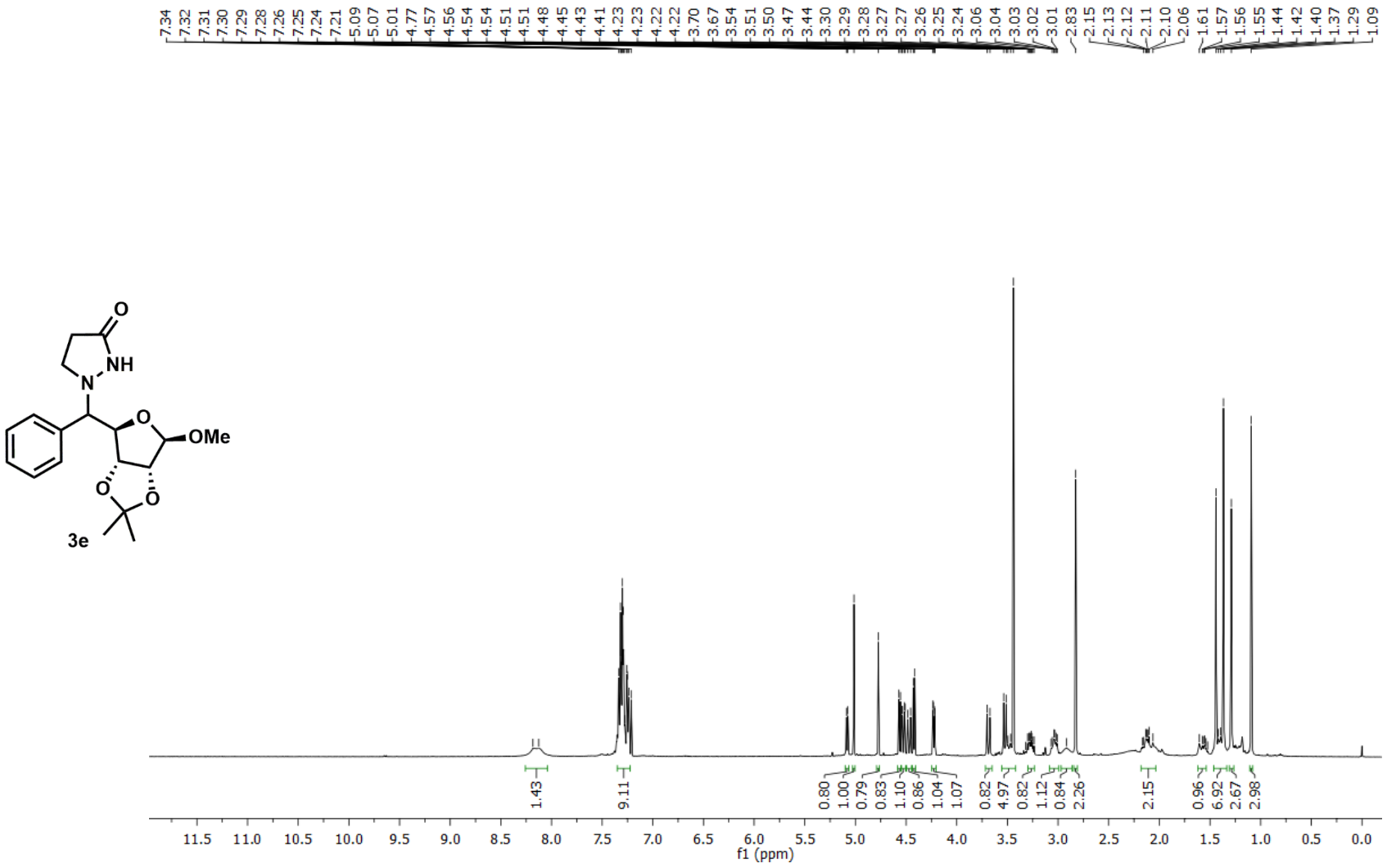


Figure S27. ^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$)

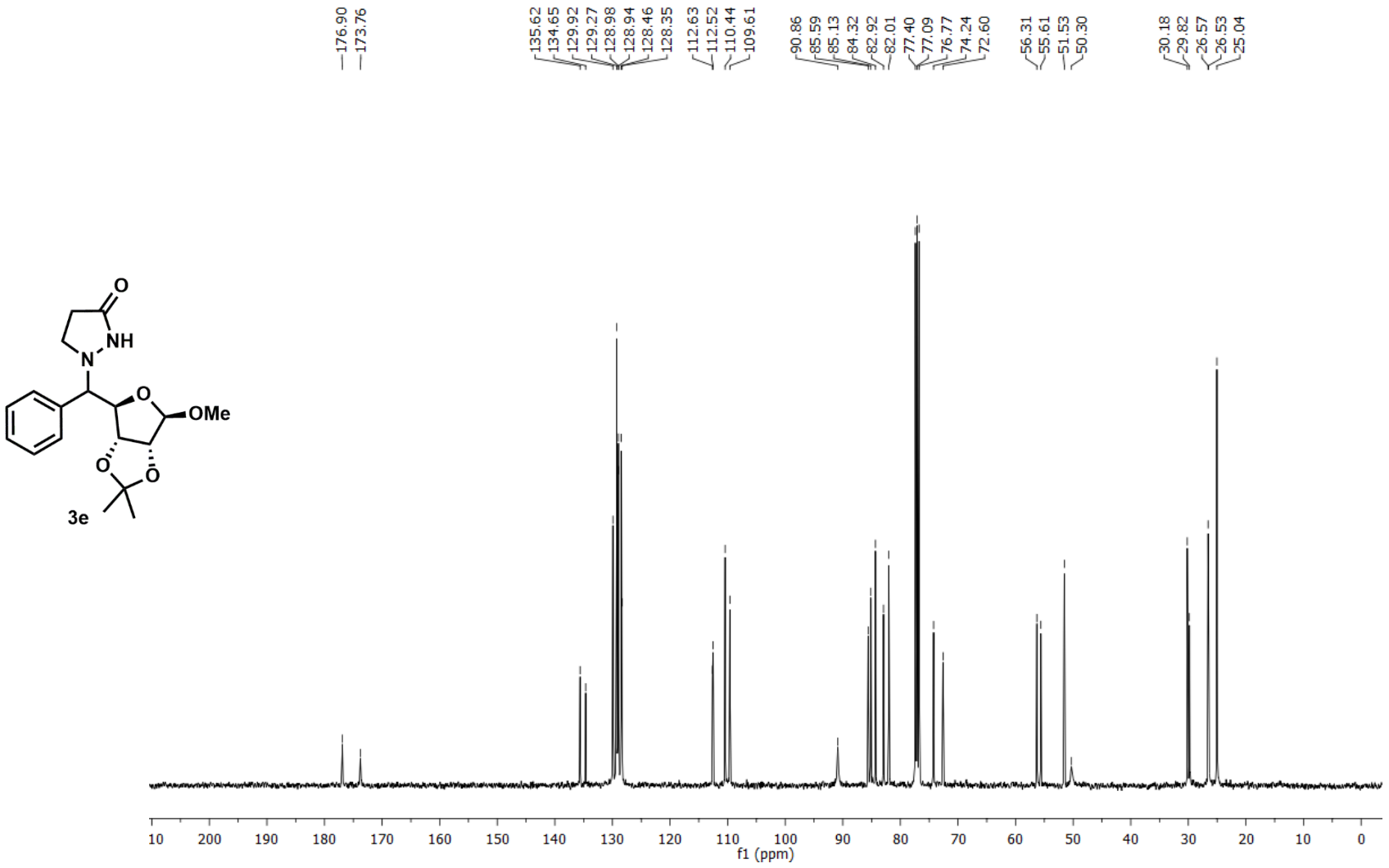


Figure S28. ^{13}C NMR spectrum of **3e** (101 MHz, $CDCl_3$)

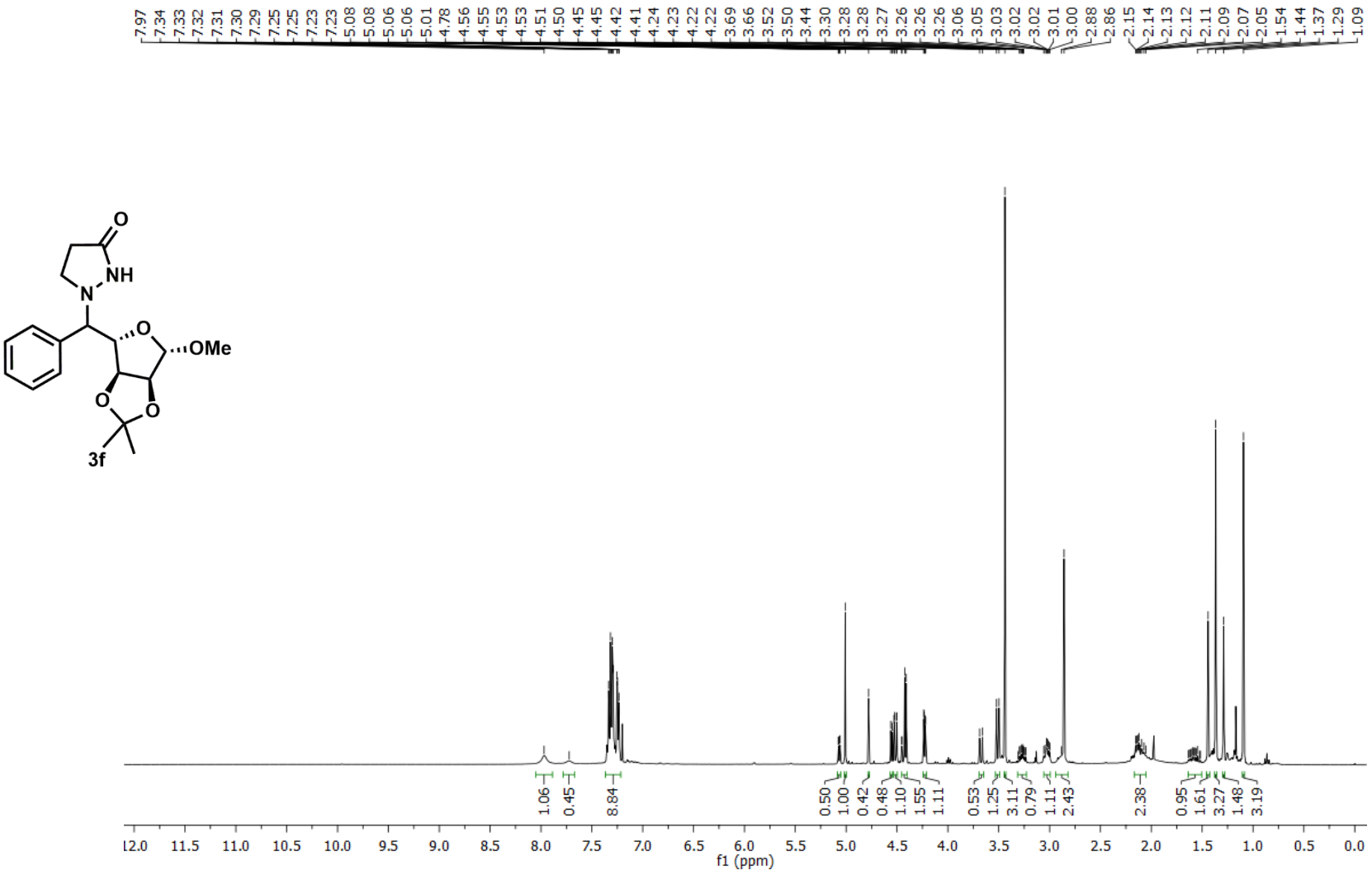


Figure S29. ^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$)

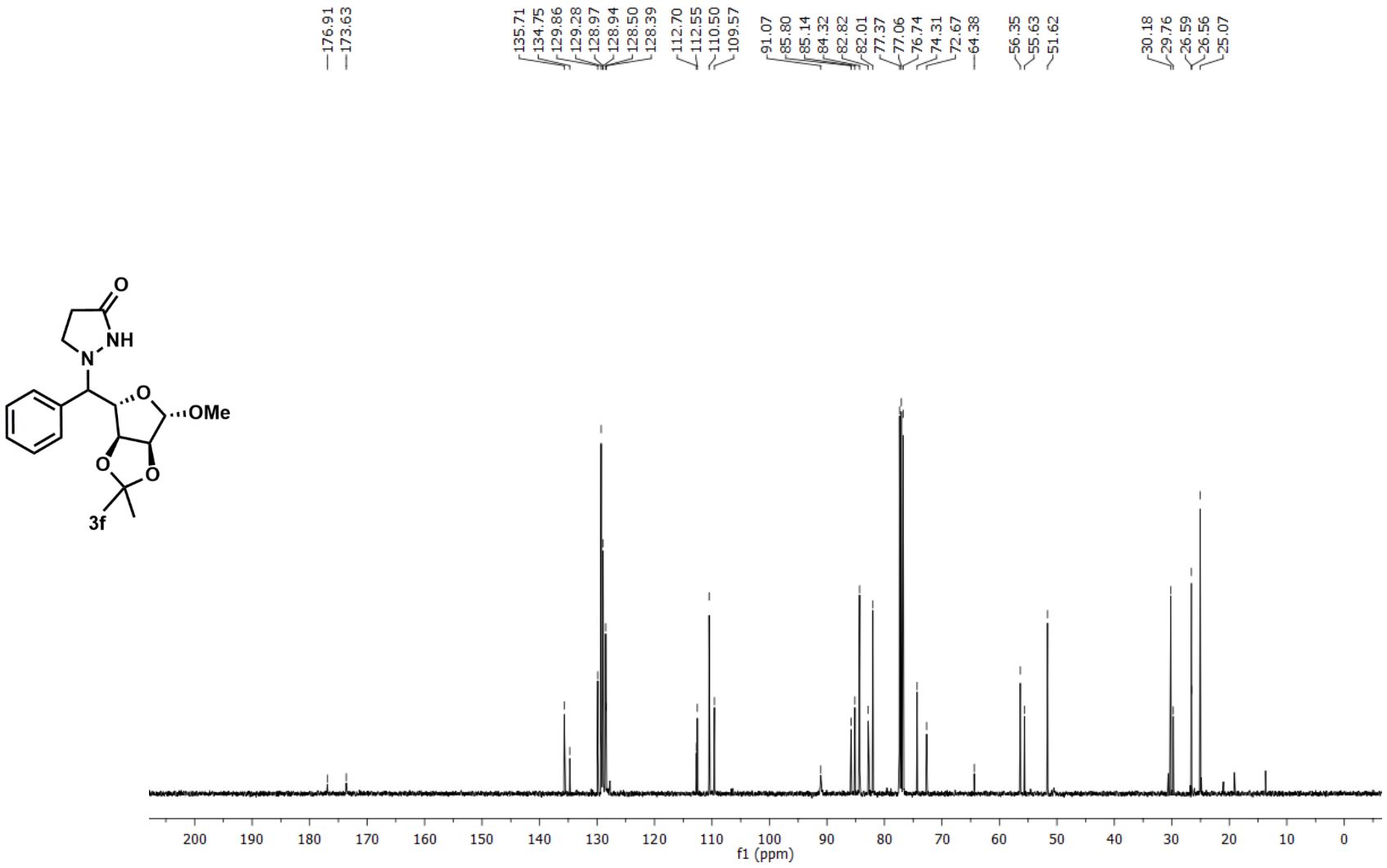


Figure S30. ^{13}C NMR spectrum of **3f** (101 MHz, $CDCl_3$)

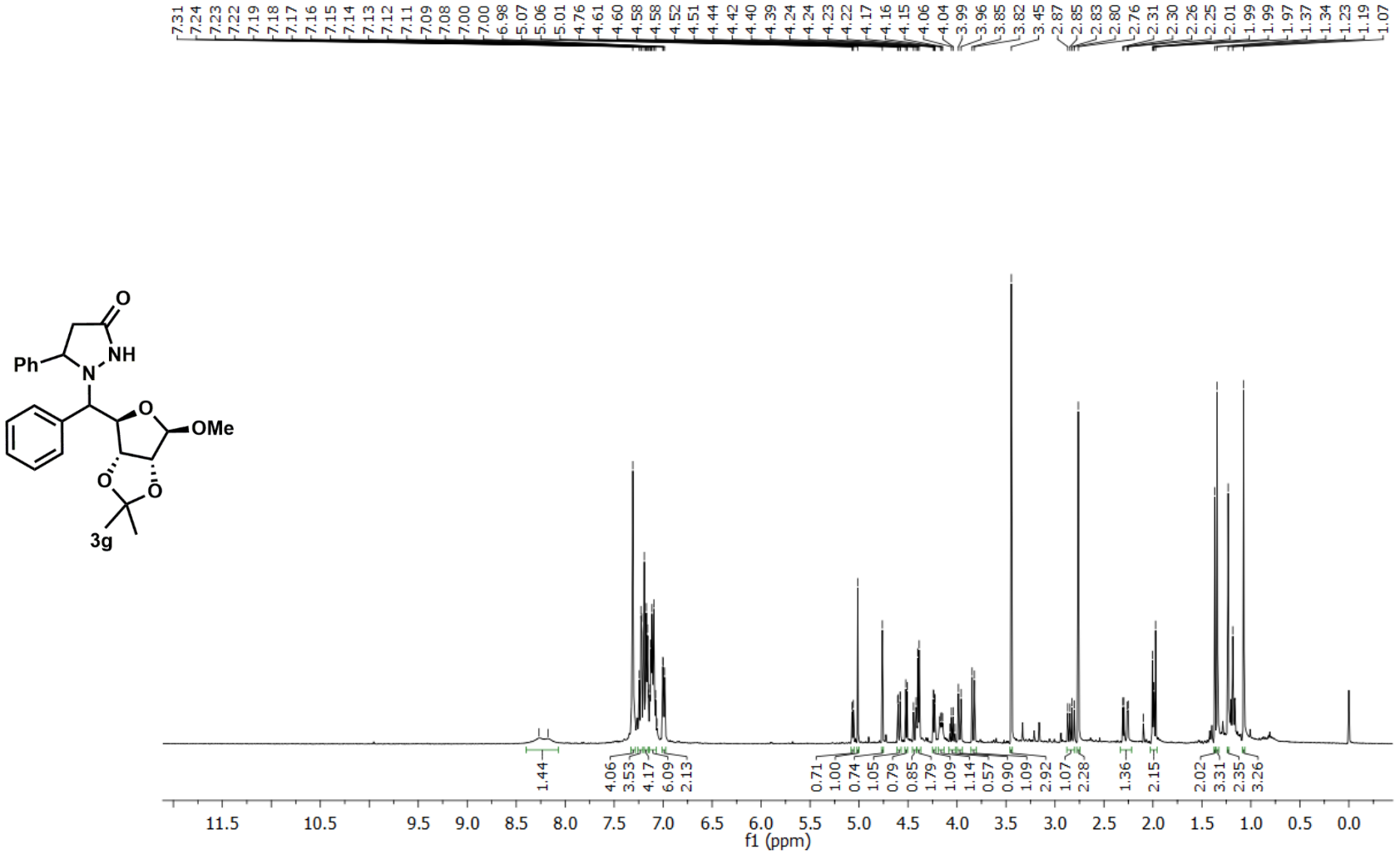


Figure S31. ^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$)

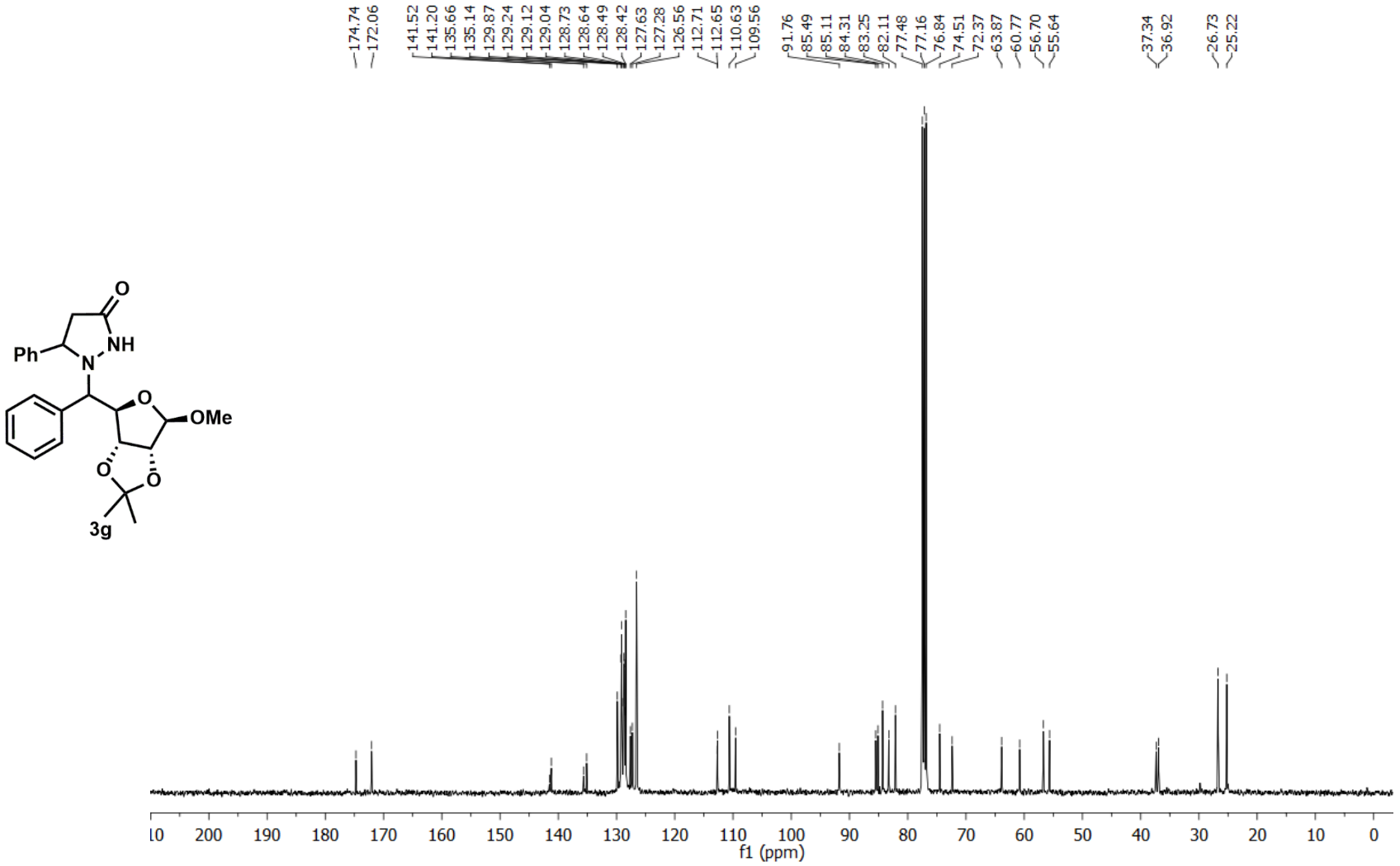


Figure S32. ^{13}C NMR spectrum of **3g** (101 MHz, $CDCl_3$)

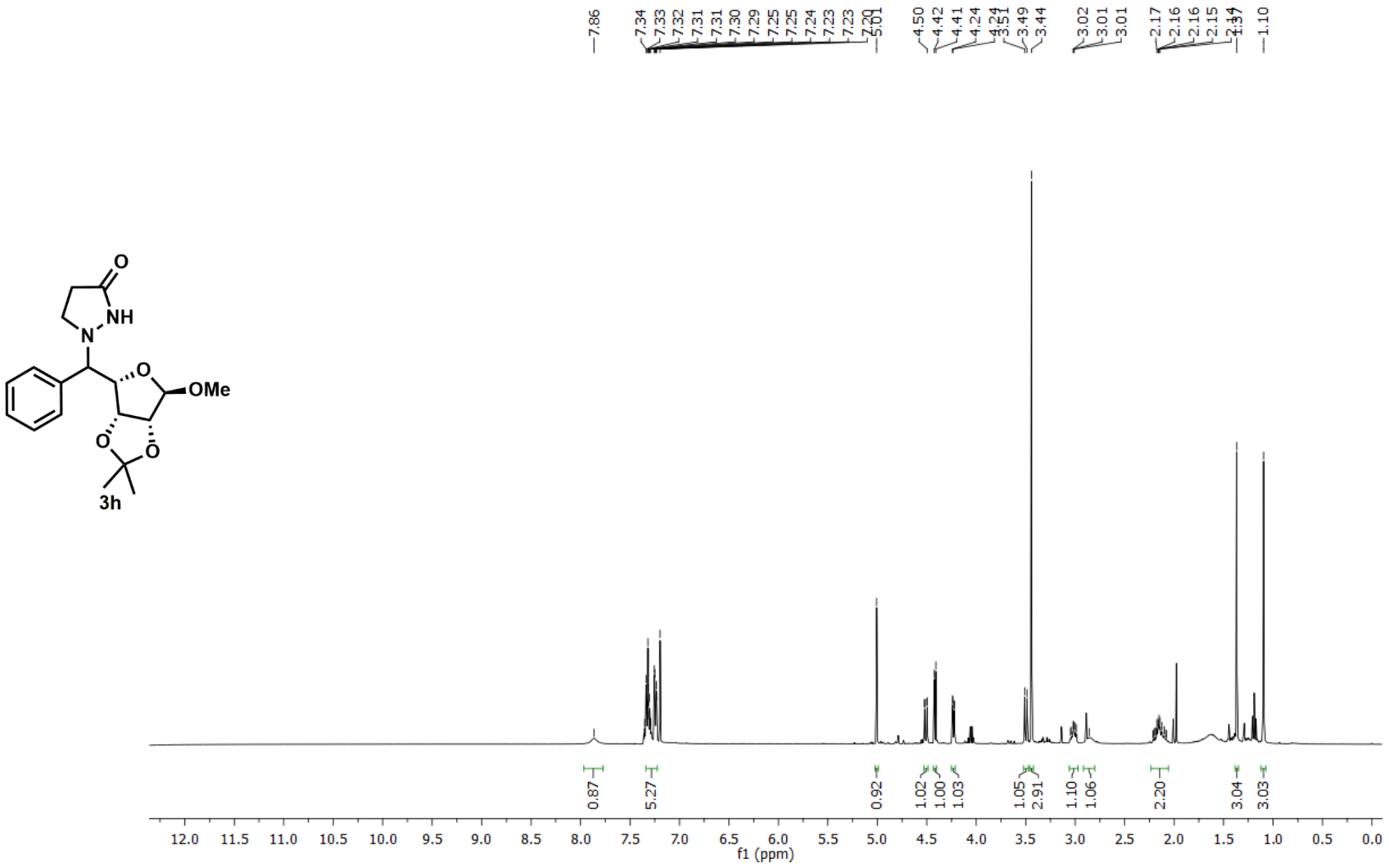


Figure S33. ^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$)

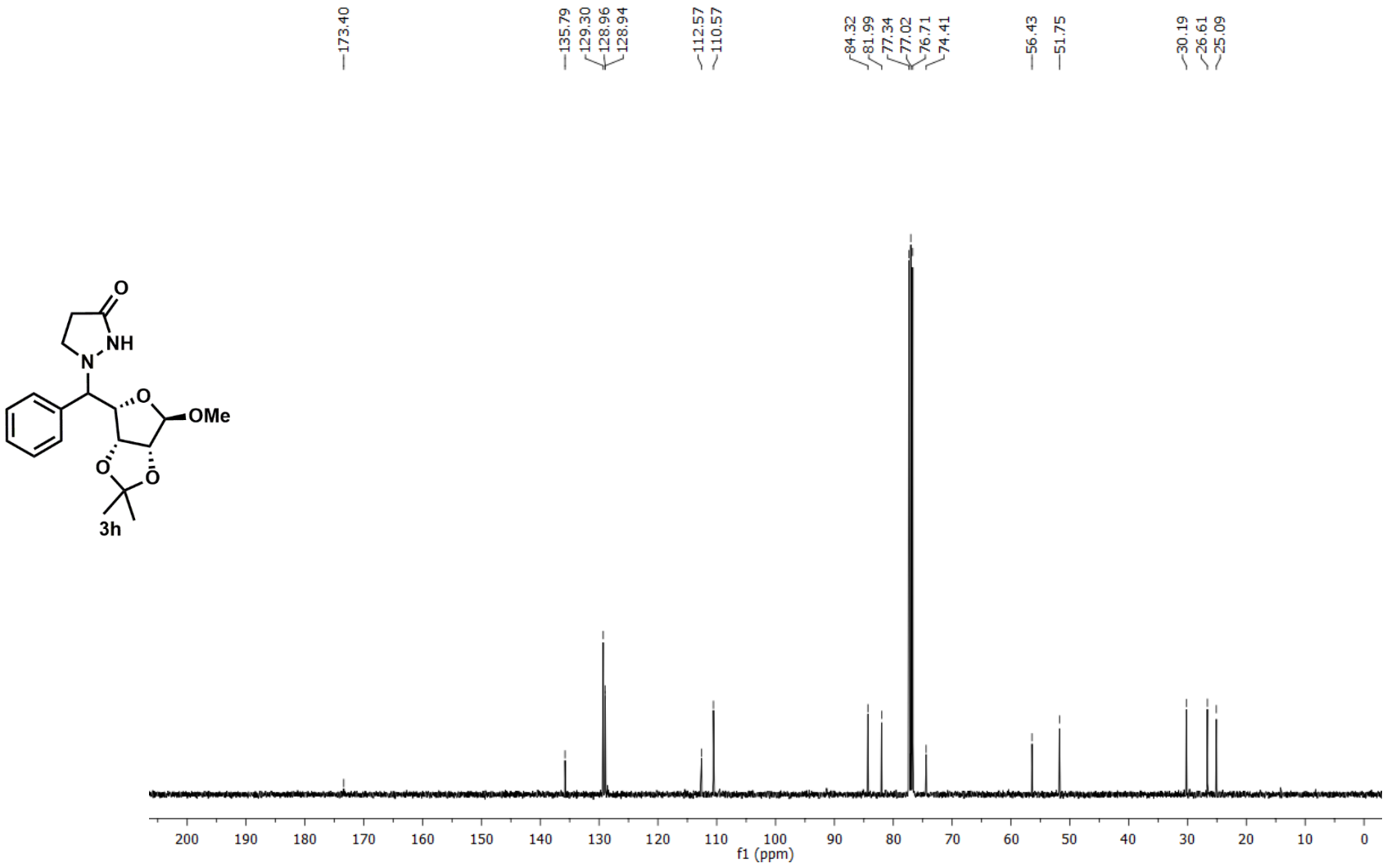


Figure S34. ^{13}C NMR spectrum of **3h** (101 MHz, $CDCl_3$)

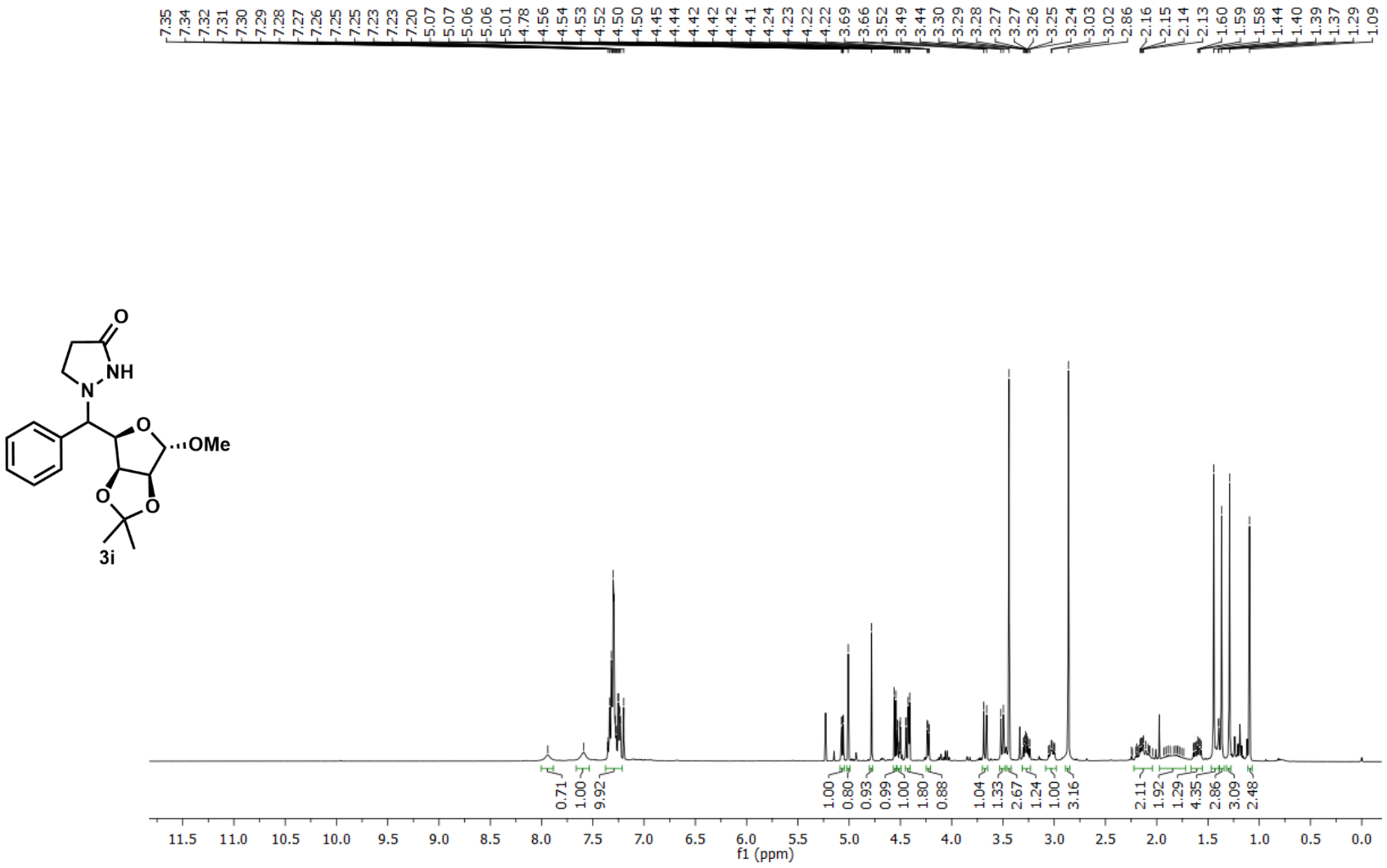


Figure S35. ^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$)

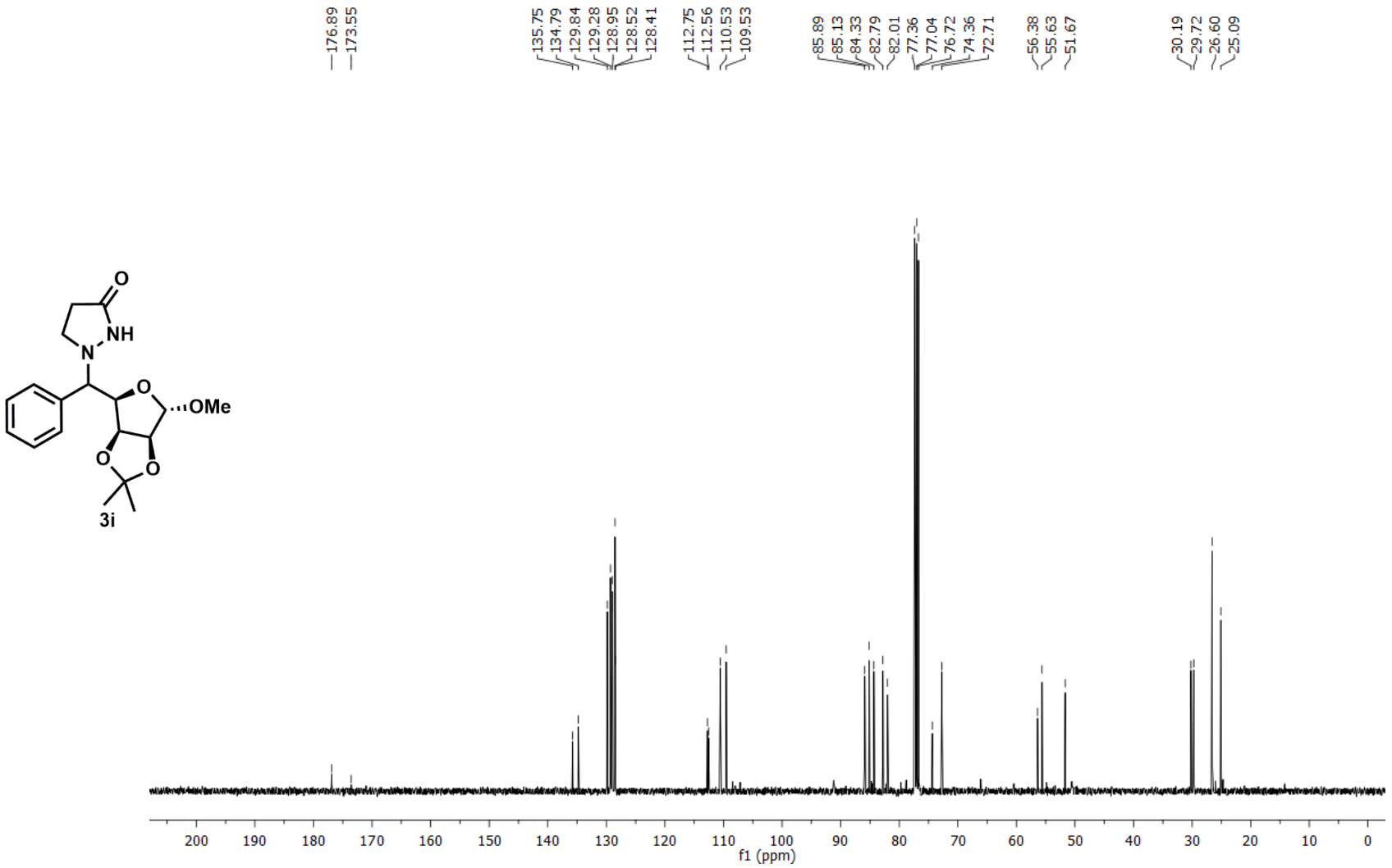


Figure S36. ^{13}C NMR spectrum of **3i** (101 MHz, $CDCl_3$)

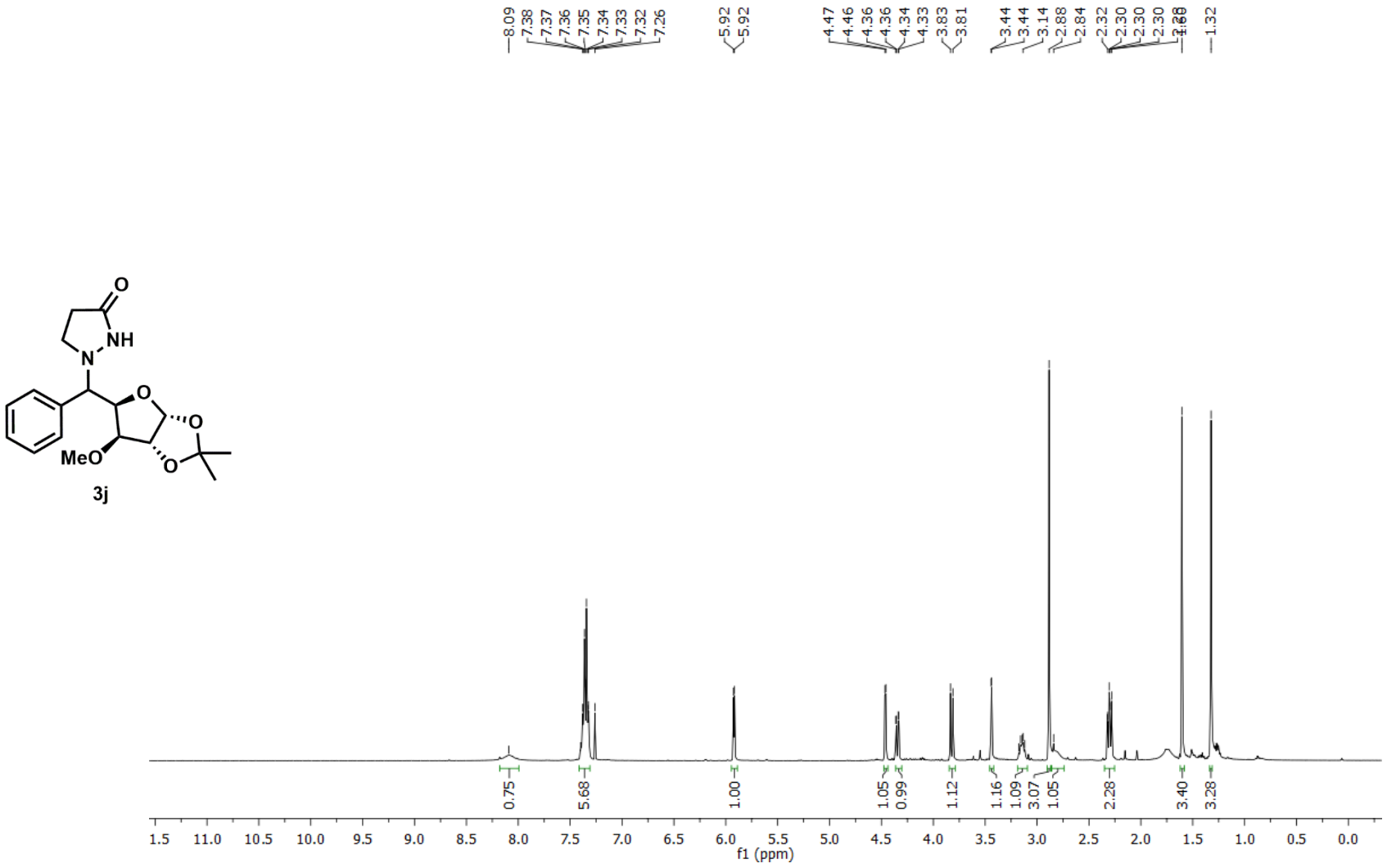


Figure S37. ^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$)

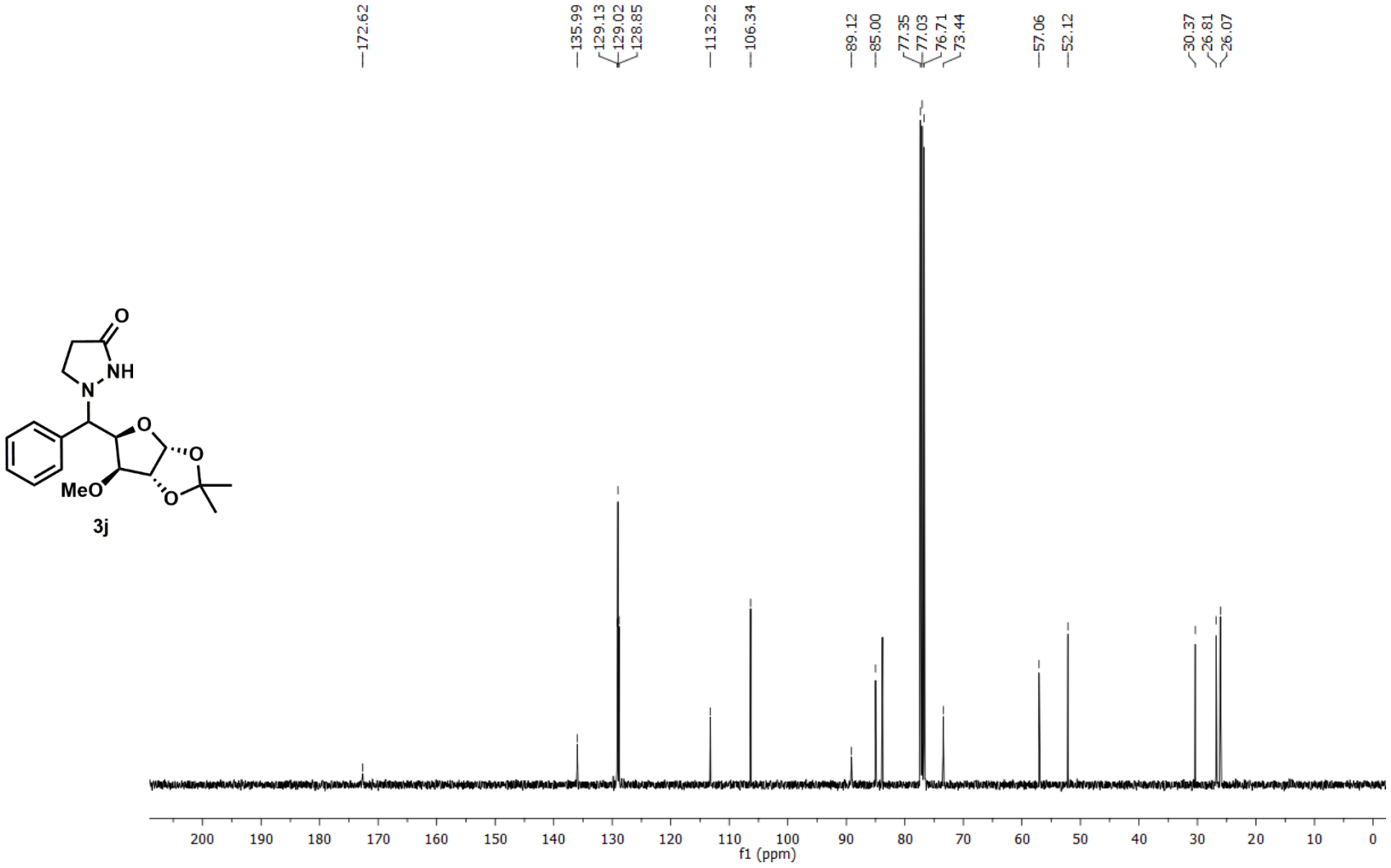


Figure S38. ^{13}C NMR spectrum of **3j** (101 MHz, $CDCl_3$)

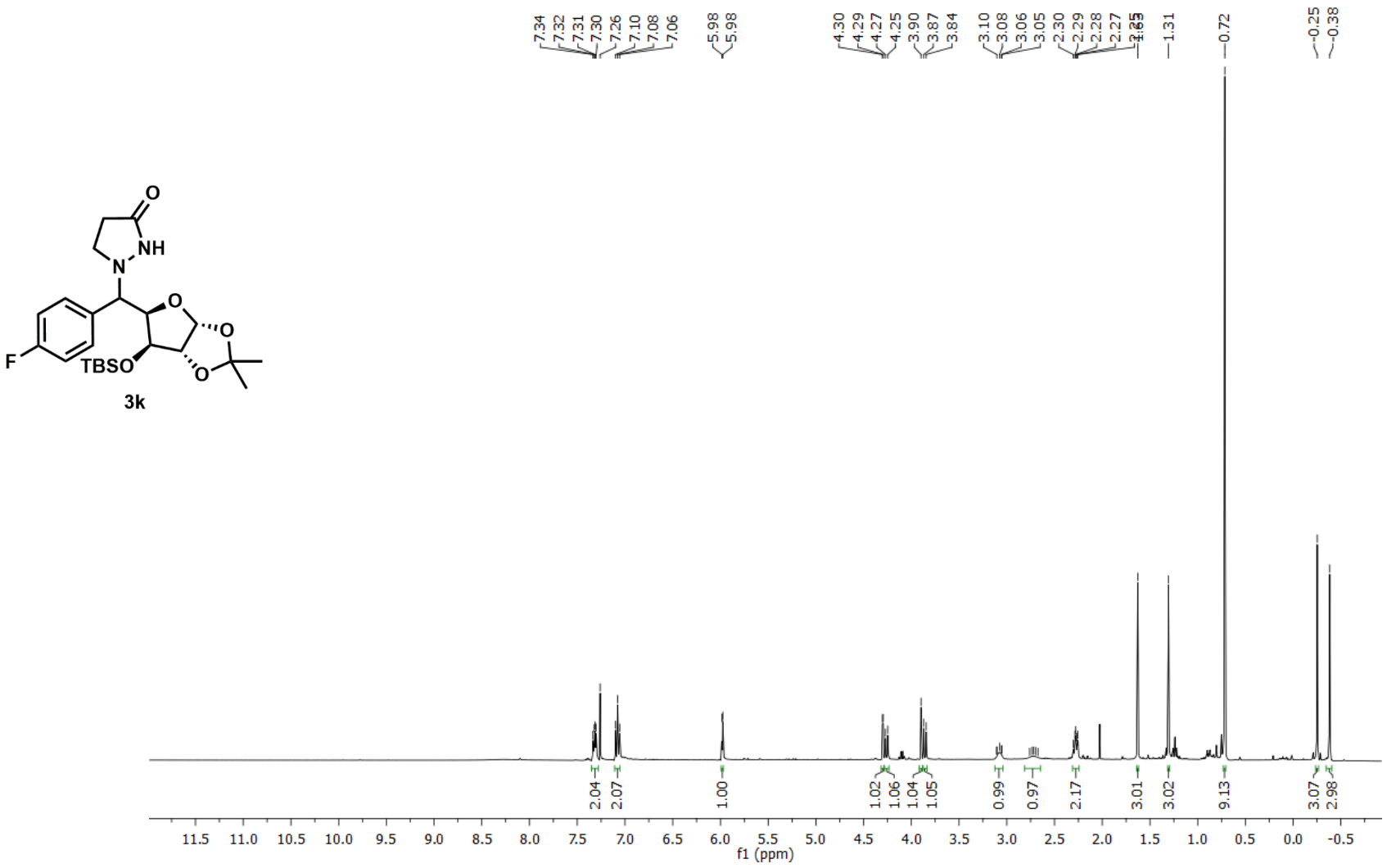


Figure S39. ^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$)

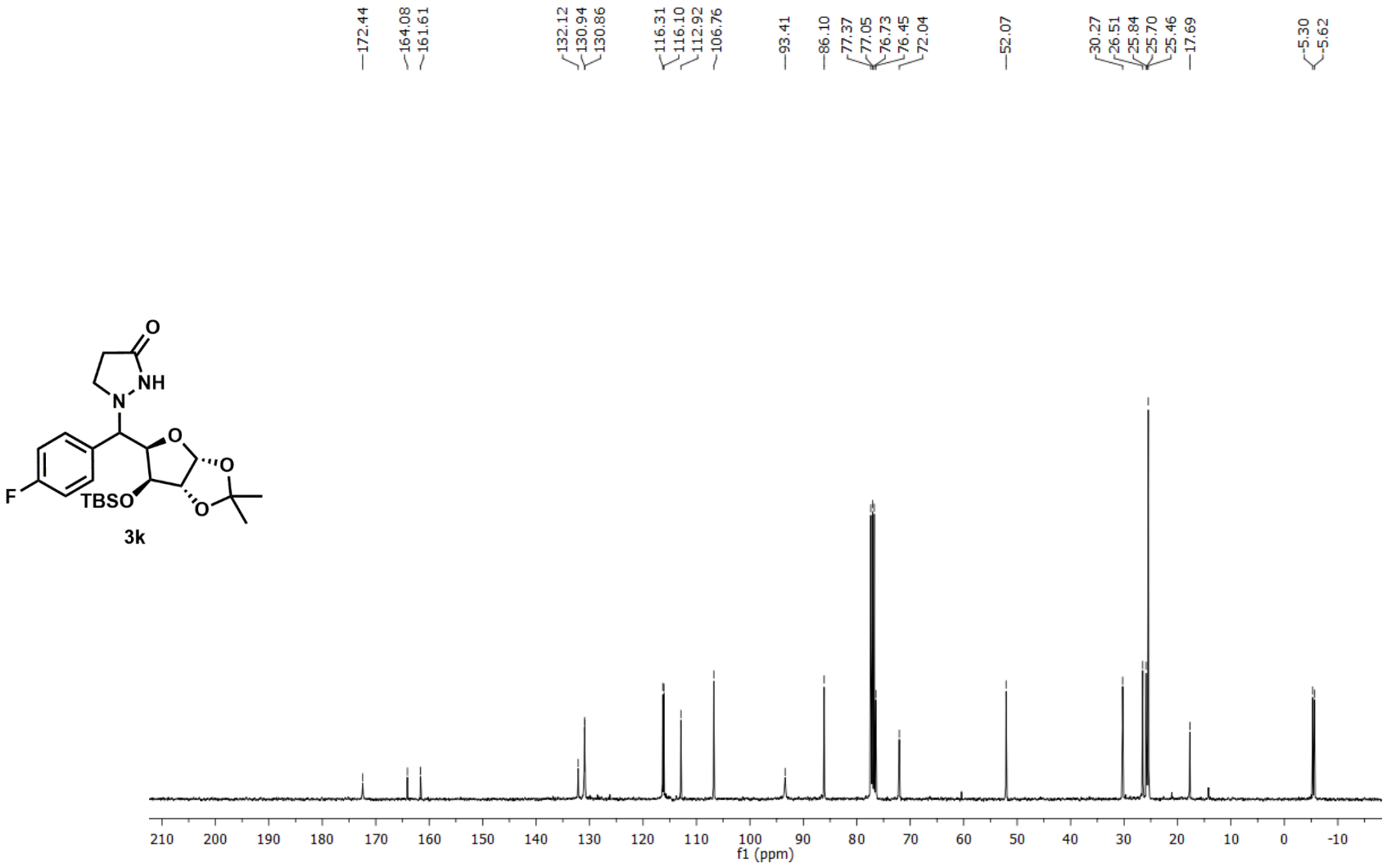


Figure S40. ^{13}C NMR spectrum of **3k** (101 MHz, $CDCl_3$)

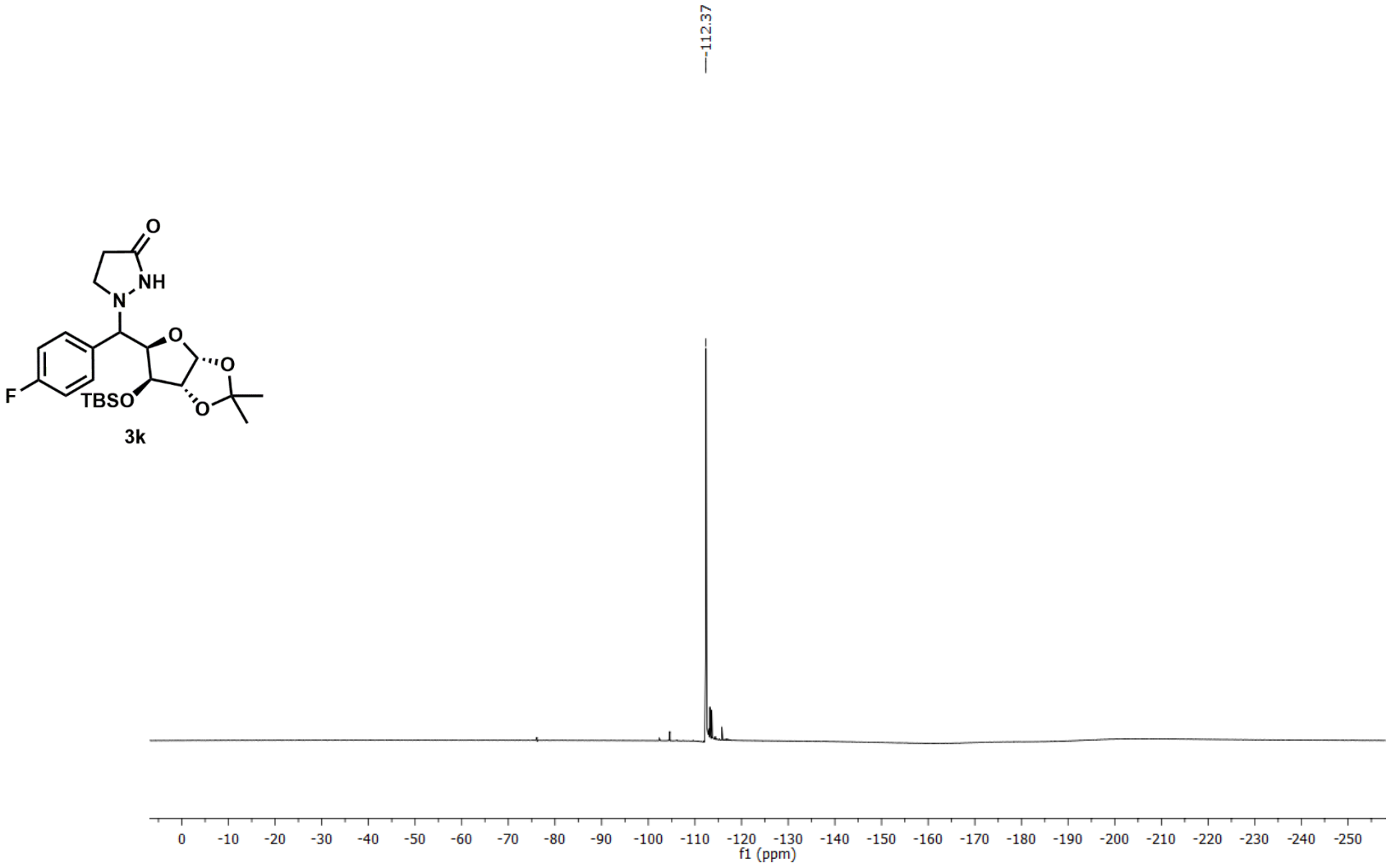


Figure S41. ^{19}F NMR spectrum of **3k** (376 MHz, $CDCl_3$)

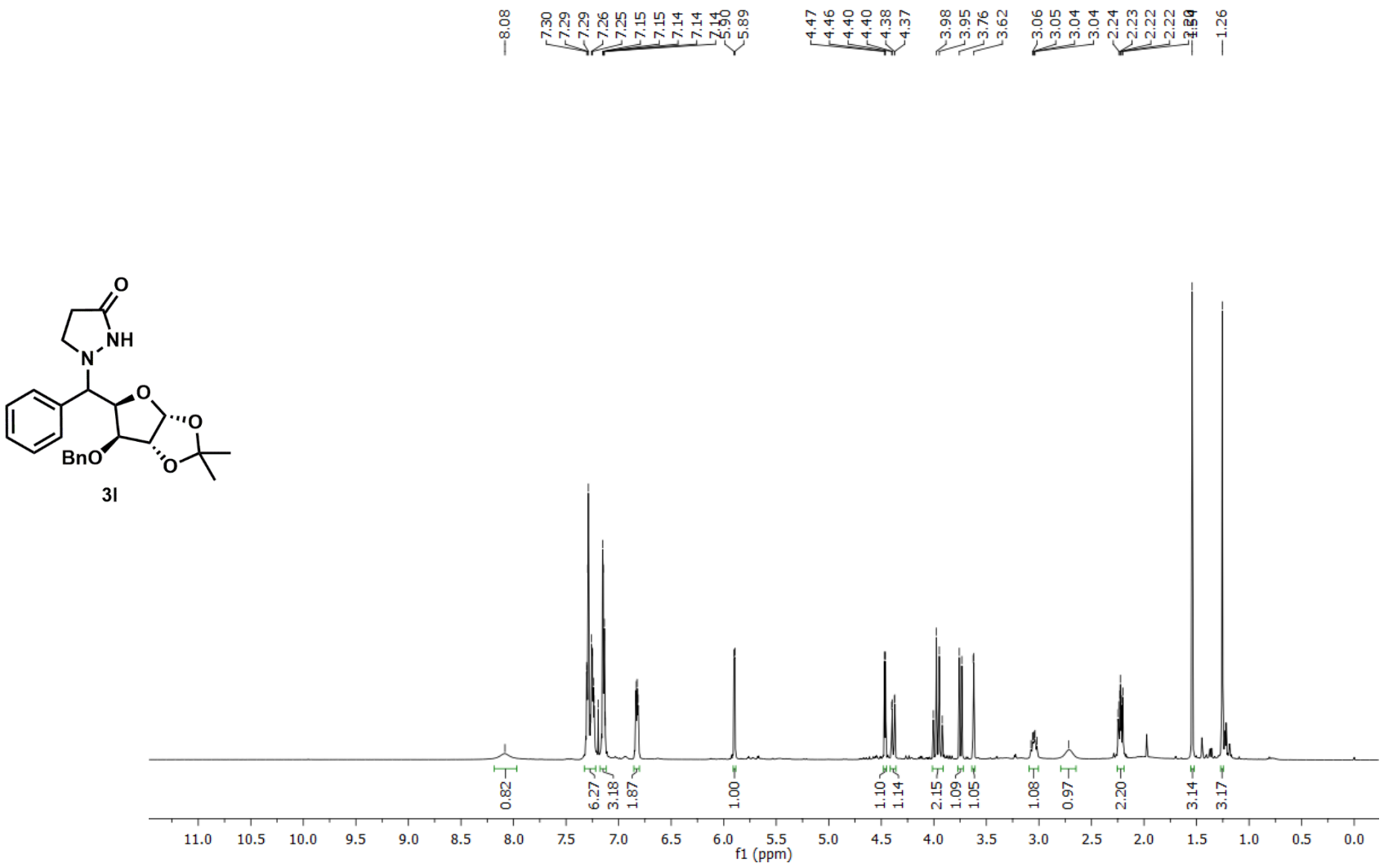


Figure S42. ^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$)

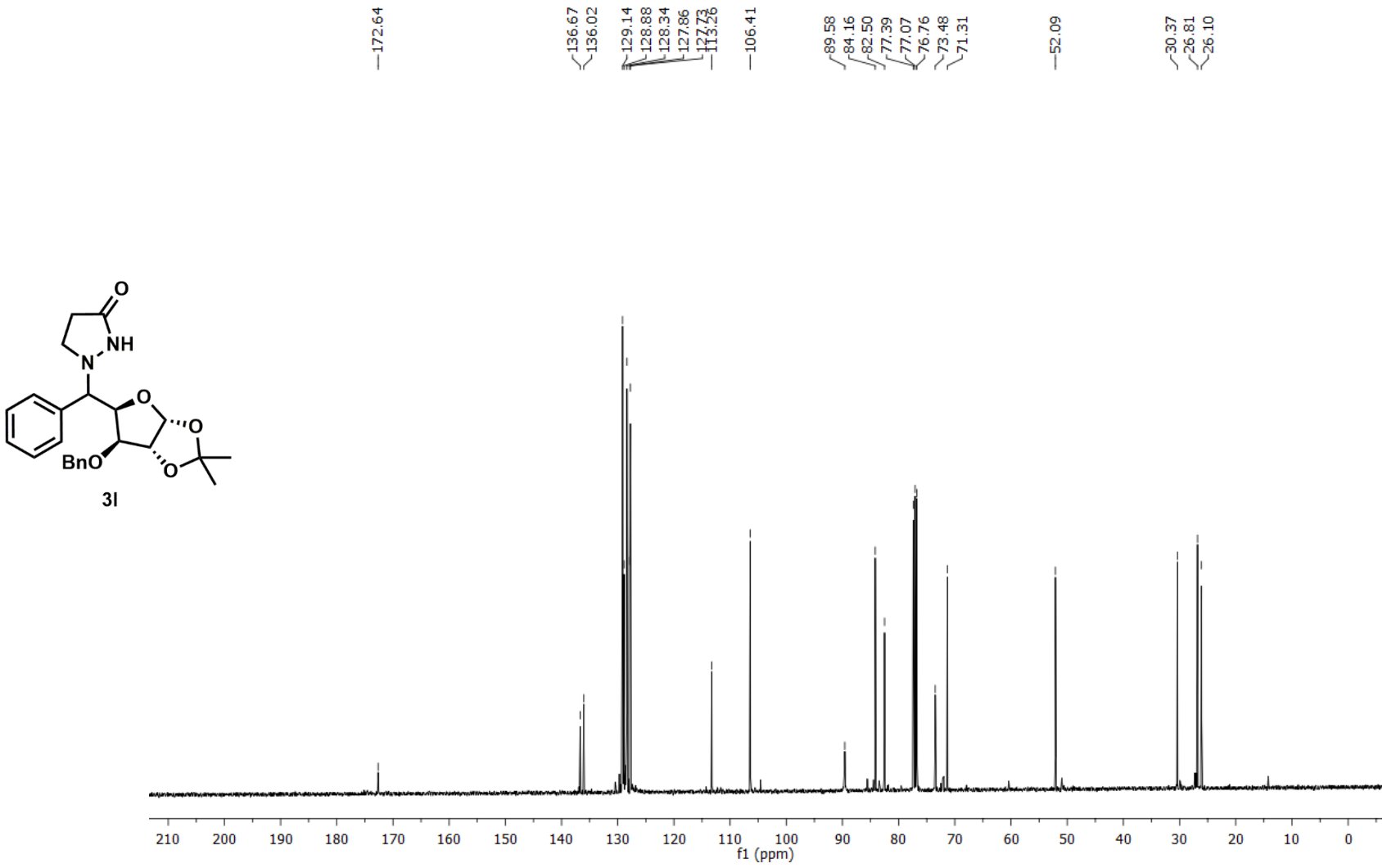


Figure S43. ^{13}C NMR spectrum of **3l** (101 MHz, $CDCl_3$)

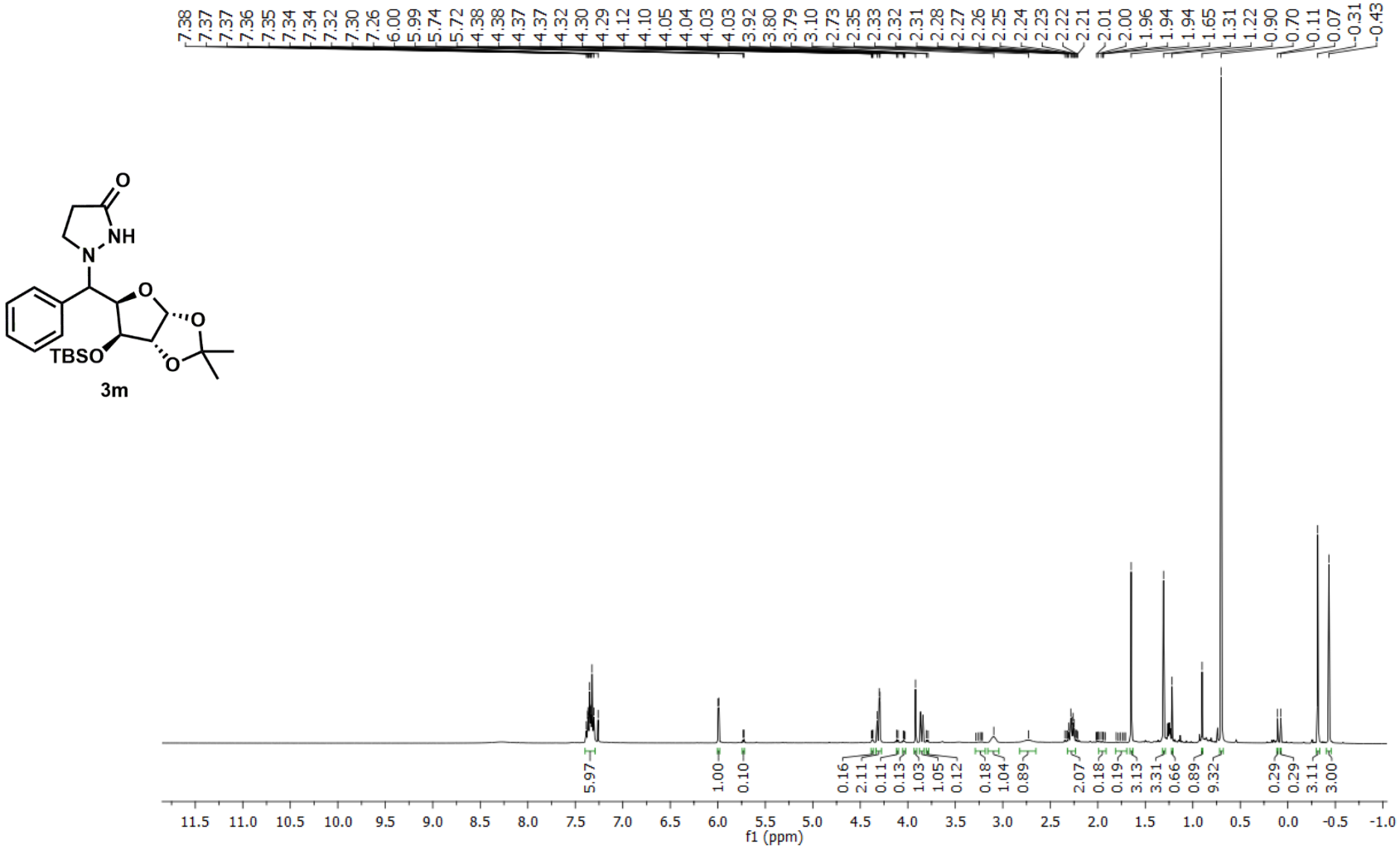


Figure S44. ^{1}H NMR spectrum of **3m** (400 MHz, $CDCl_3$)

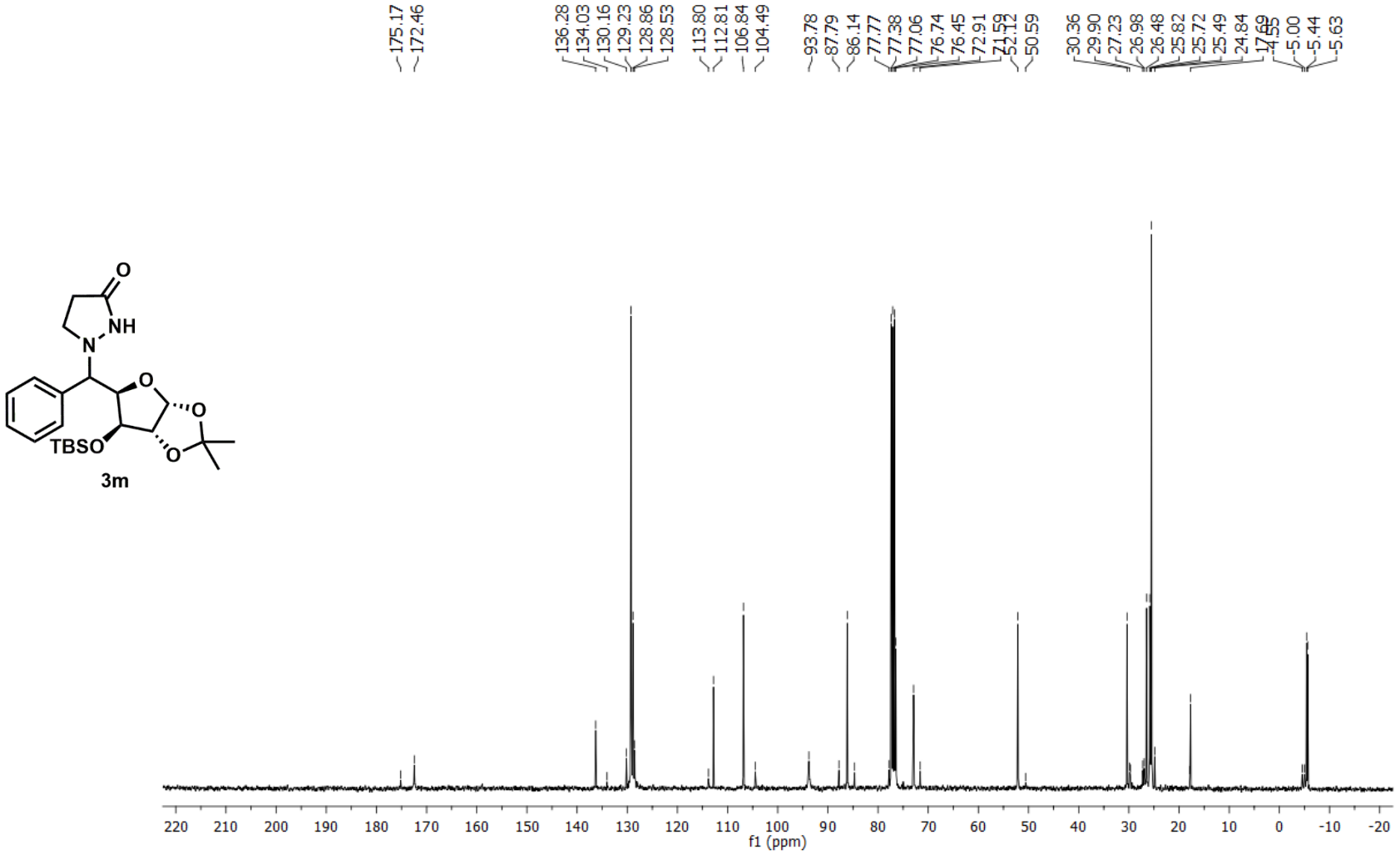


Figure S45. ^{13}C NMR spectrum of **3m** (101 MHz, $CDCl_3$)

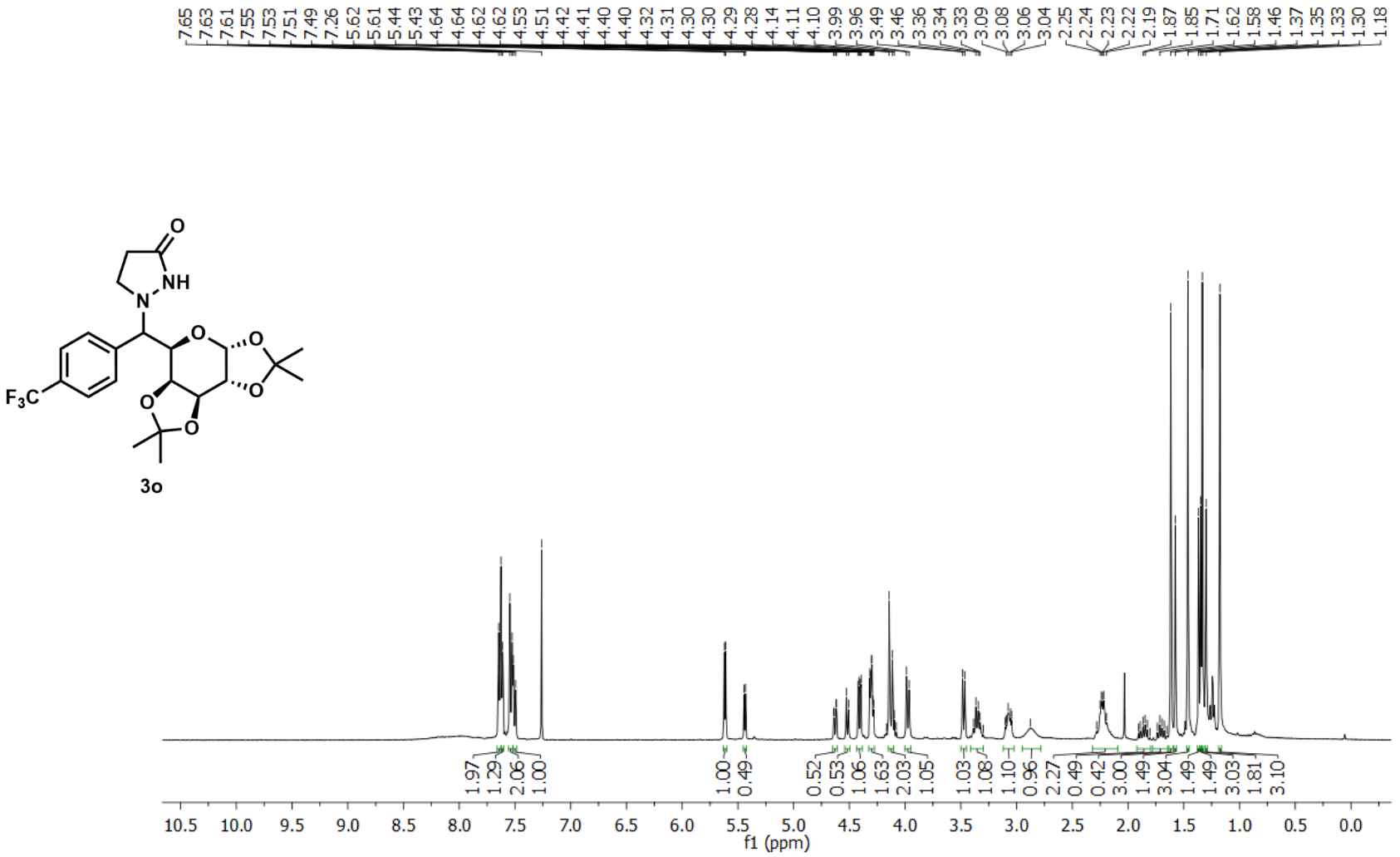


Figure S46. ^{1}H NMR spectrum of **3o** (400 MHz, $CDCl_3$)

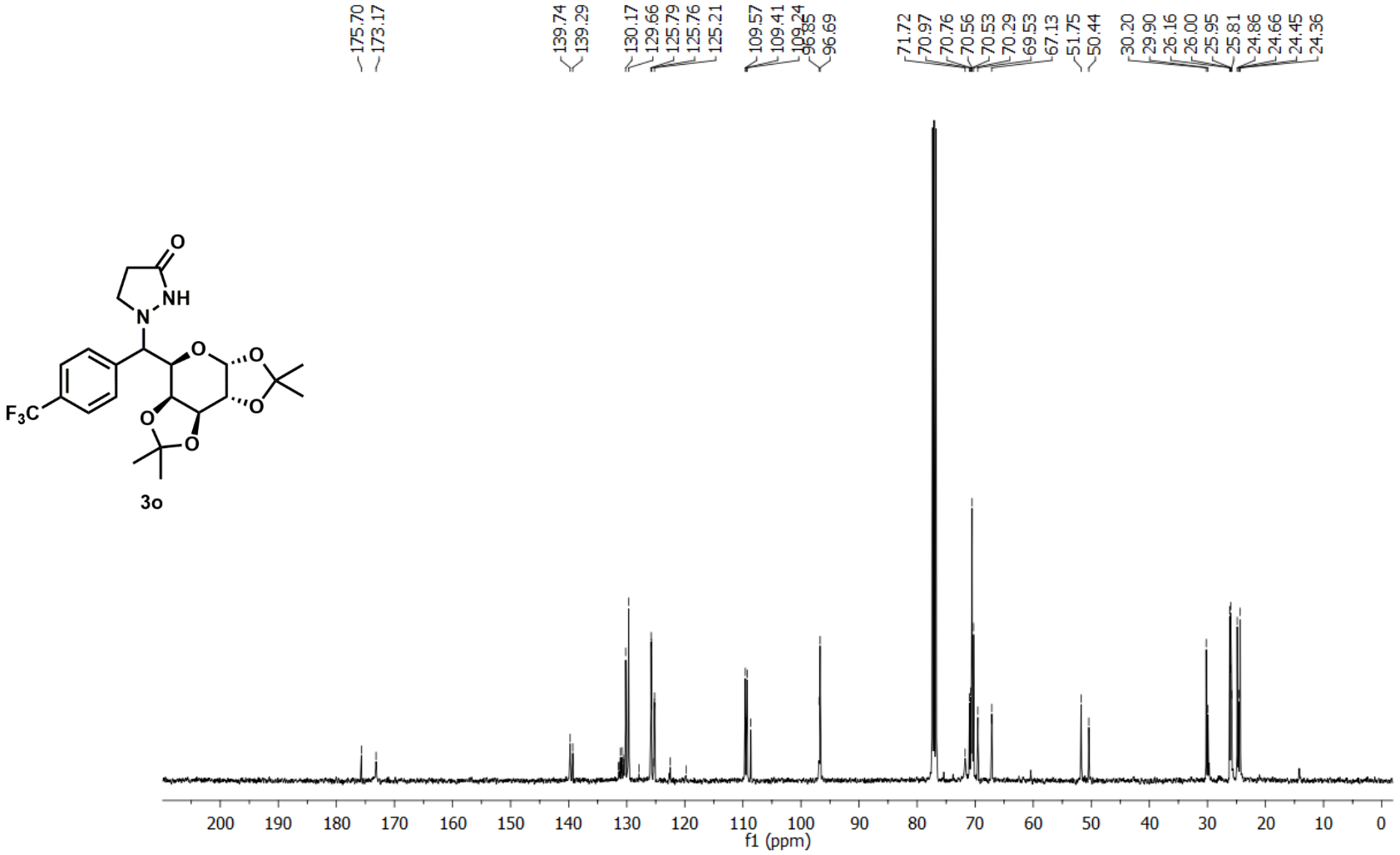


Figure S47. ^{13}C NMR spectrum of **3o** (101 MHz, $CDCl_3$)

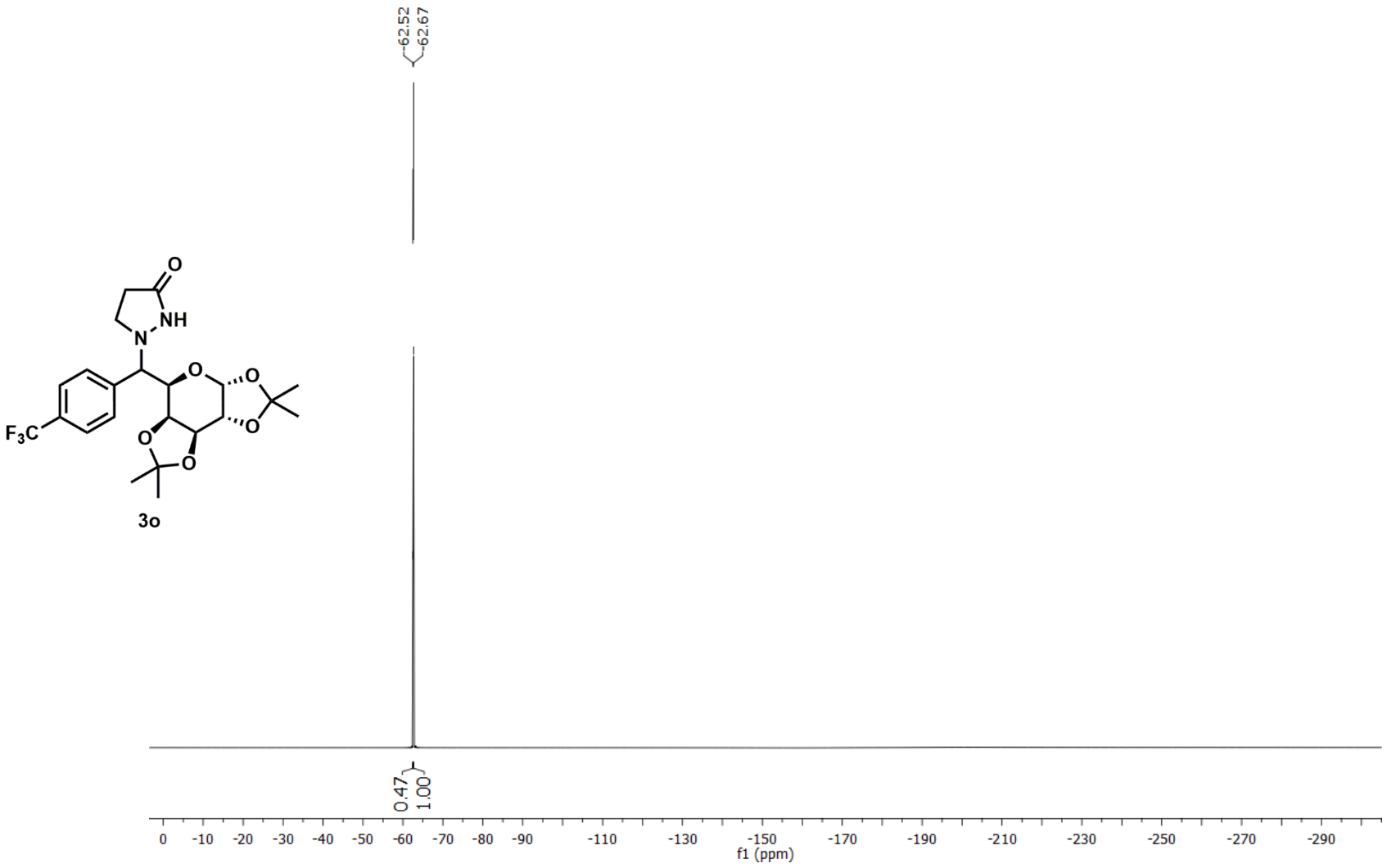


Figure S48. ^{19}F NMR spectrum of **3o** (376 MHz, $CDCl_3$)

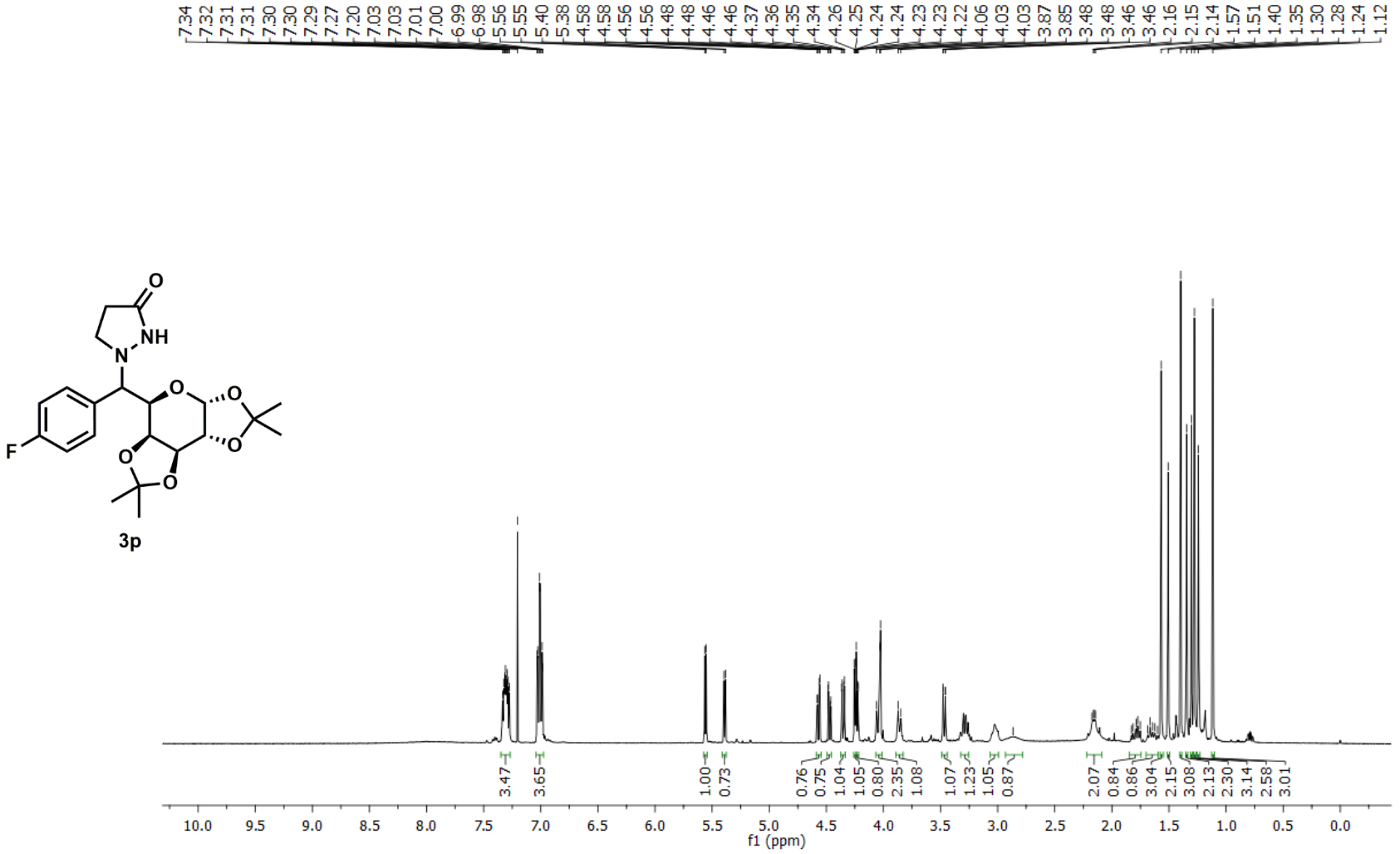


Figure S49. ^{1}H NMR spectrum of **3p** (400 MHz, $CDCl_3$)

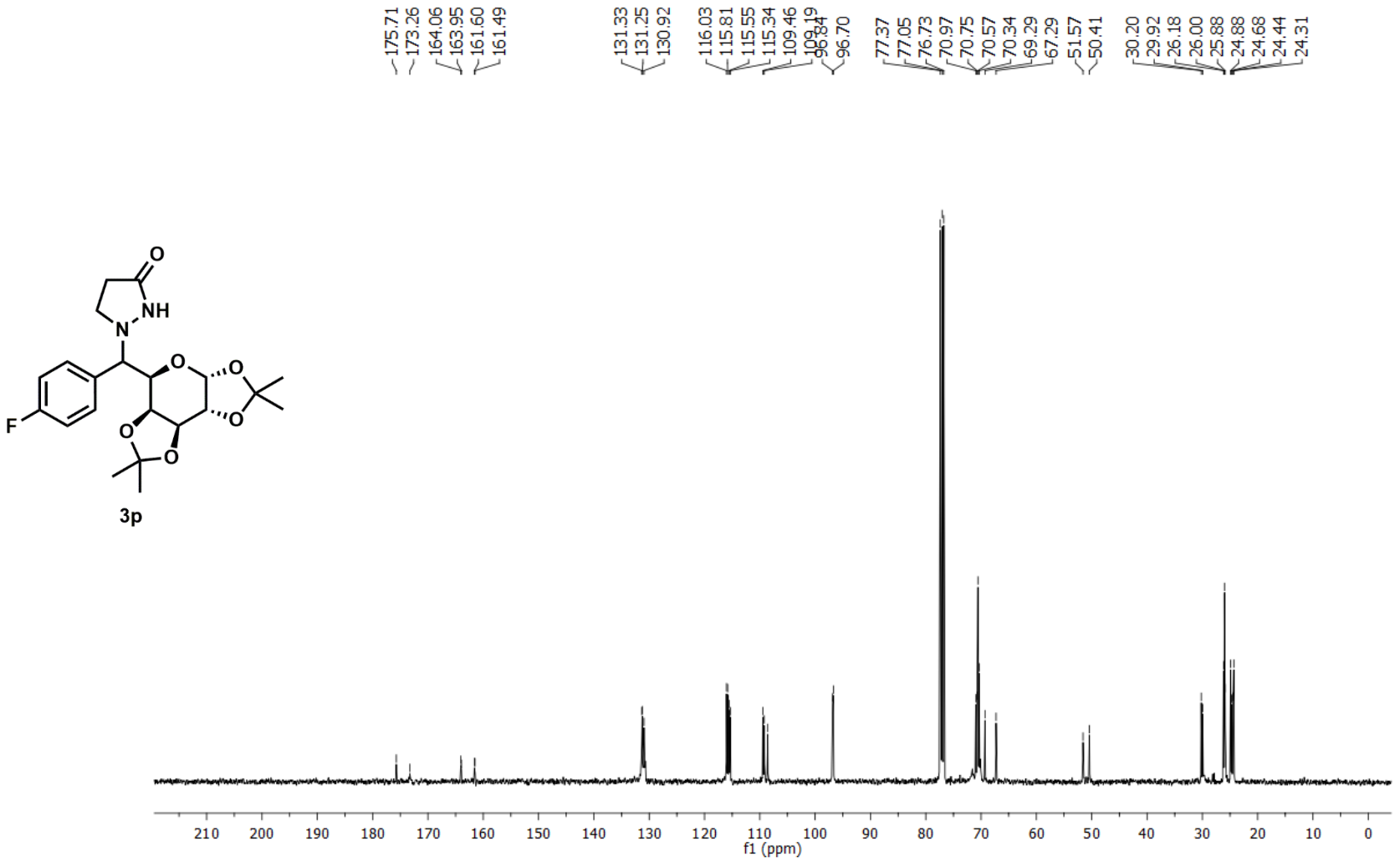


Figure S50. ^{13}C NMR spectrum of **3p** (101 MHz, $CDCl_3$)

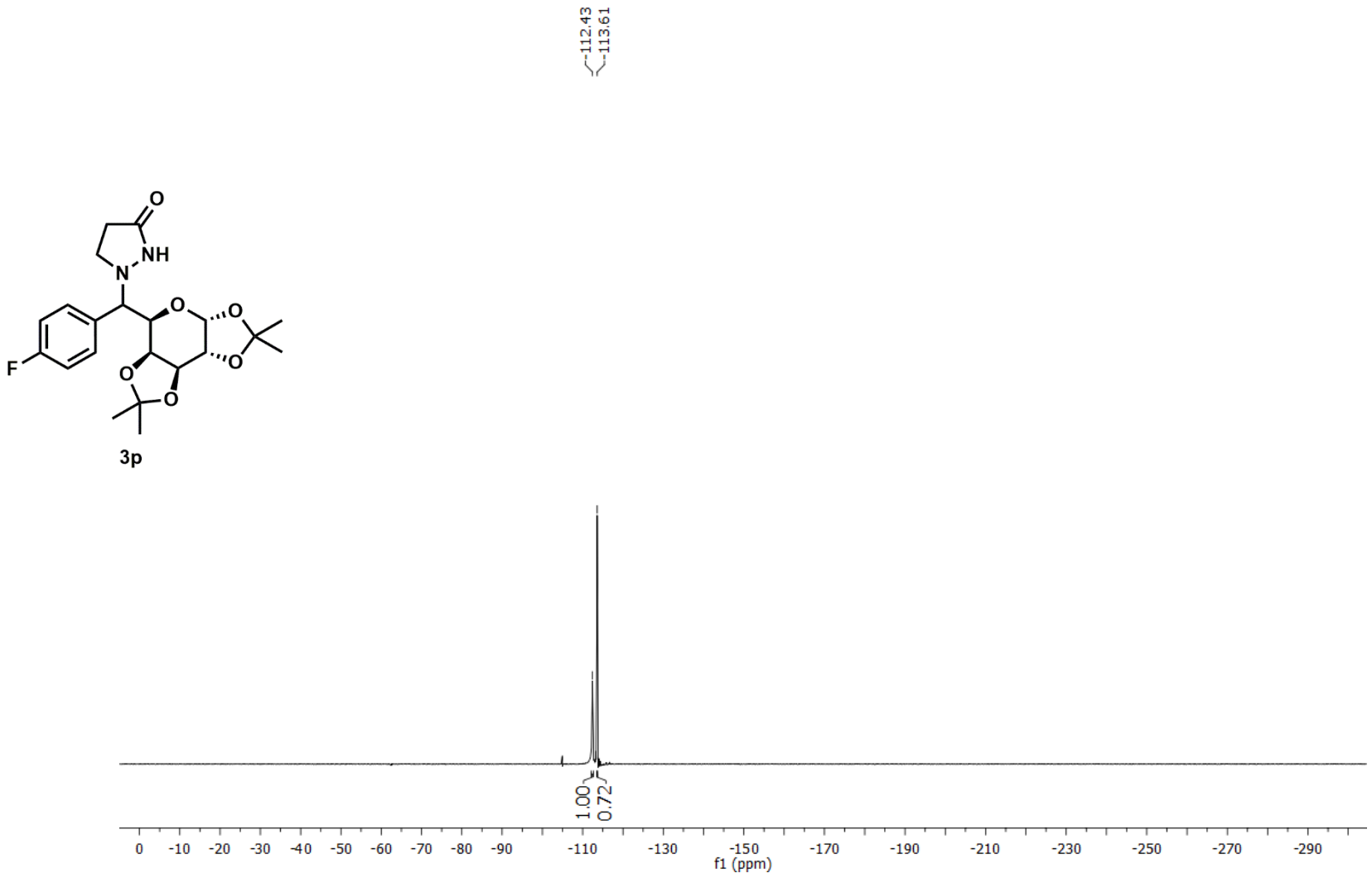


Figure S51. ^{19}F NMR spectrum of **3p** (376 MHz, $CDCl_3$)

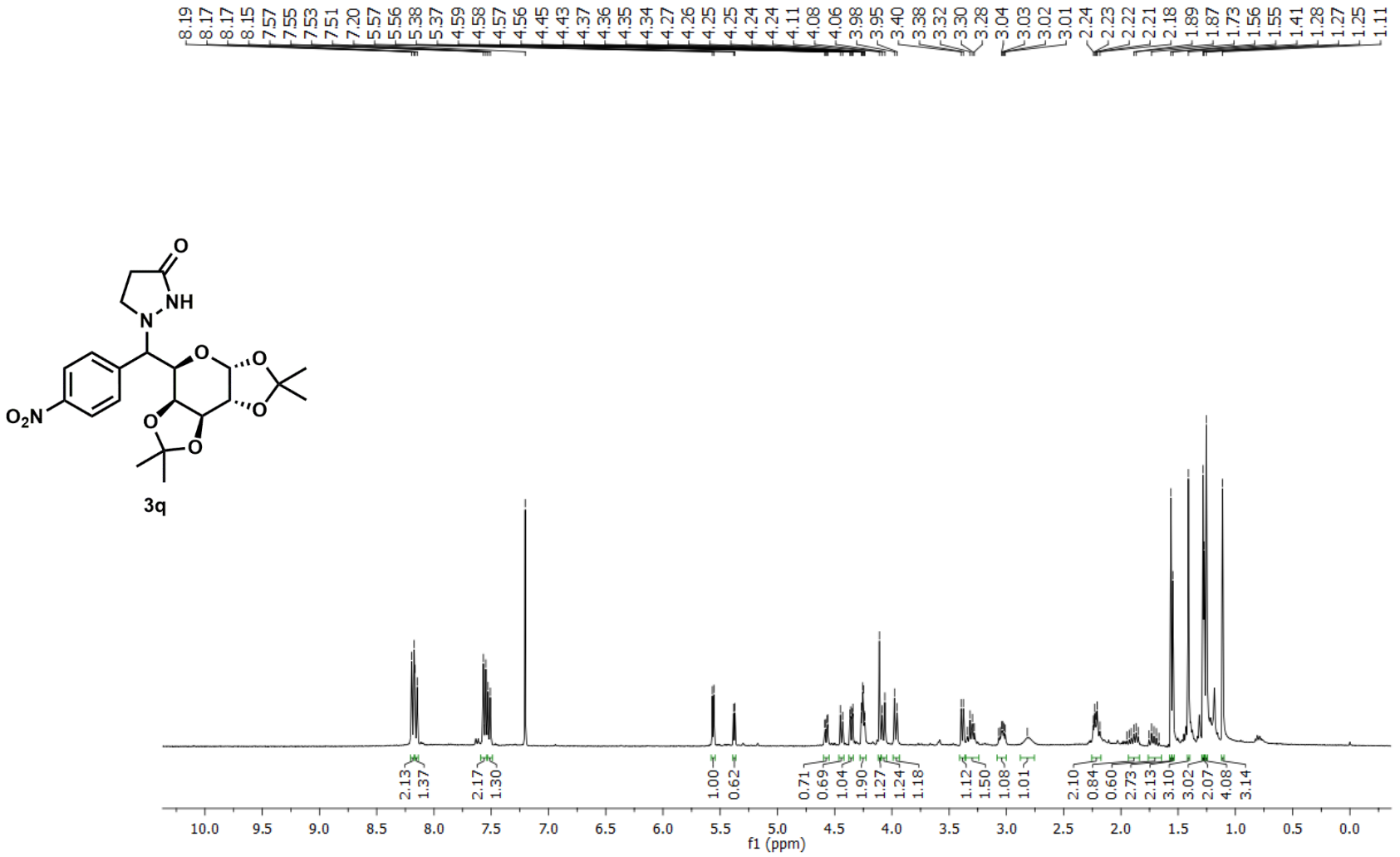


Figure S52. ^{1}H NMR spectrum of **3q** (400 MHz, $CDCl_3$)

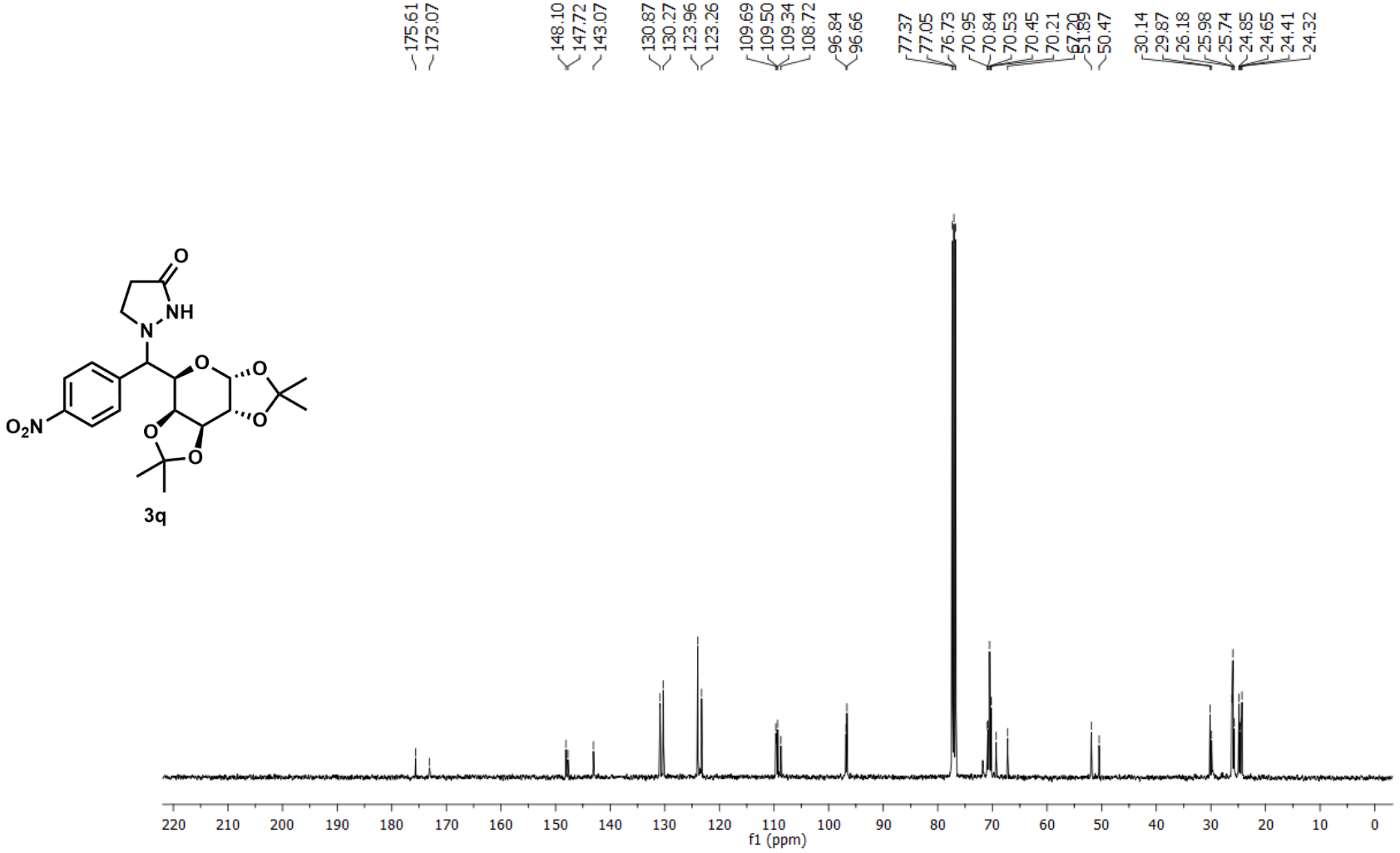


Figure S53. ^{13}C NMR spectrum of **3q** (101 MHz, $CDCl_3$)

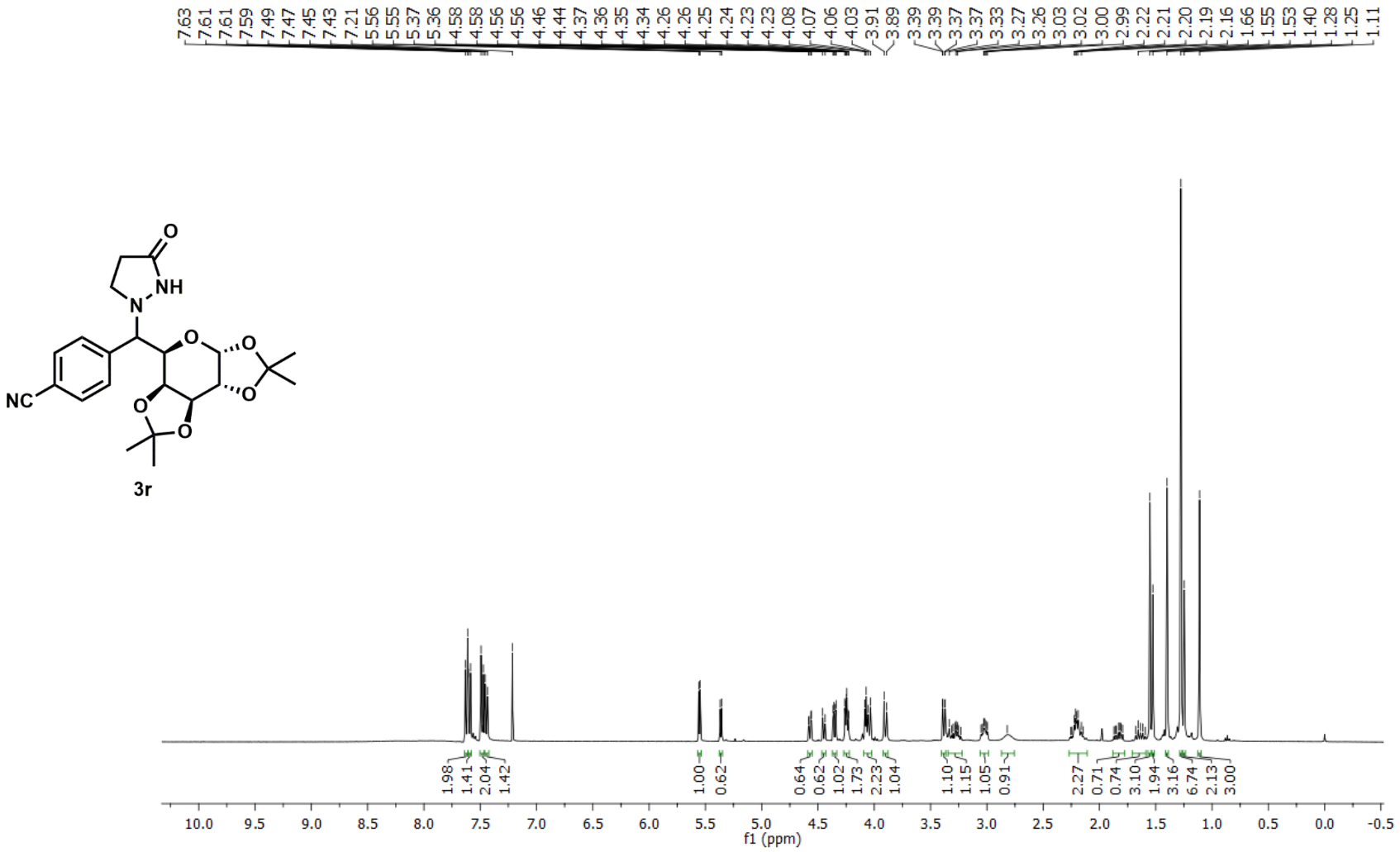


Figure S54. ^{1}H NMR spectrum of **3r** (400 MHz, $CDCl_3$)

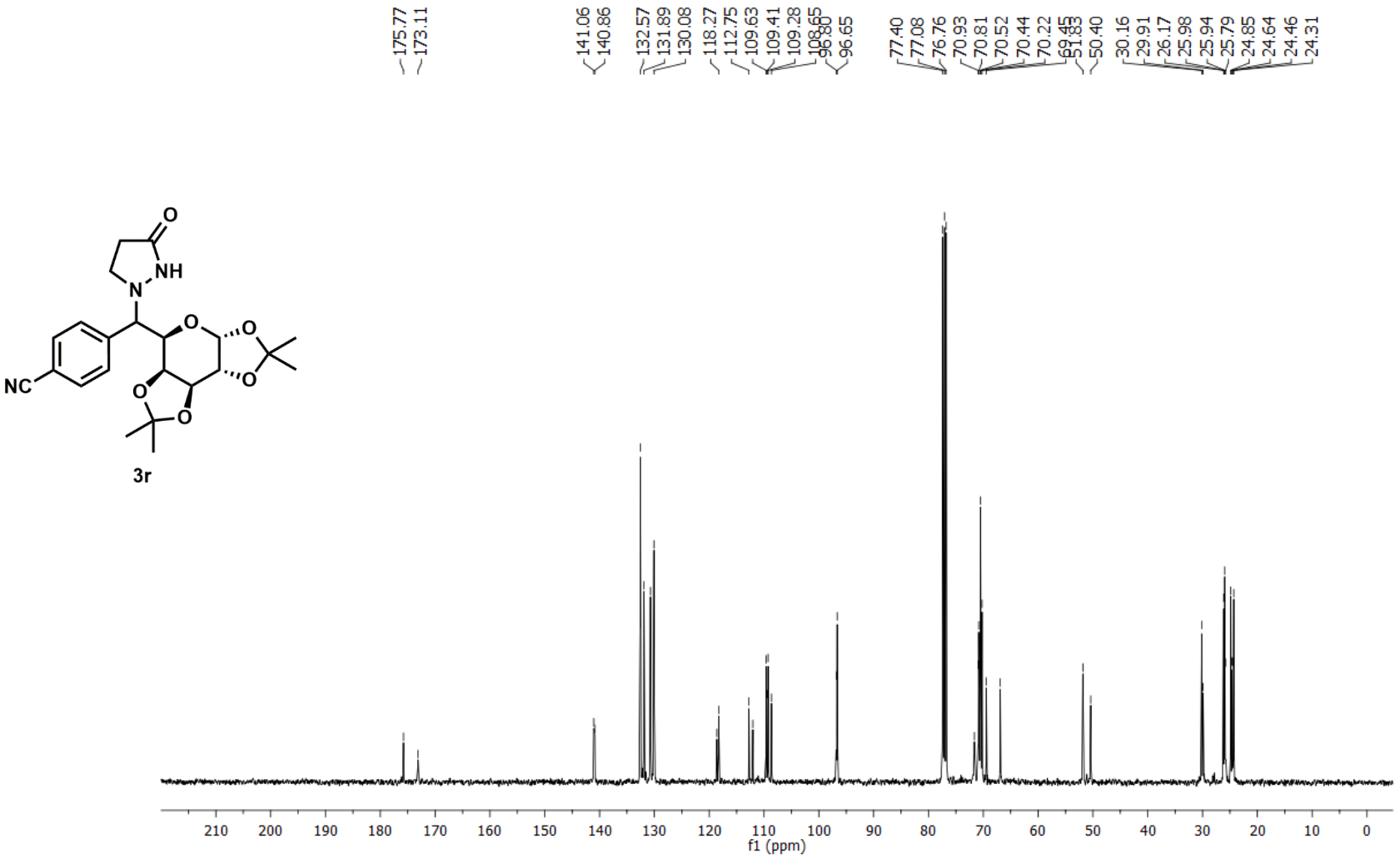


Figure S55. ^{13}C NMR spectrum of **3r** (101 MHz, $CDCl_3$)

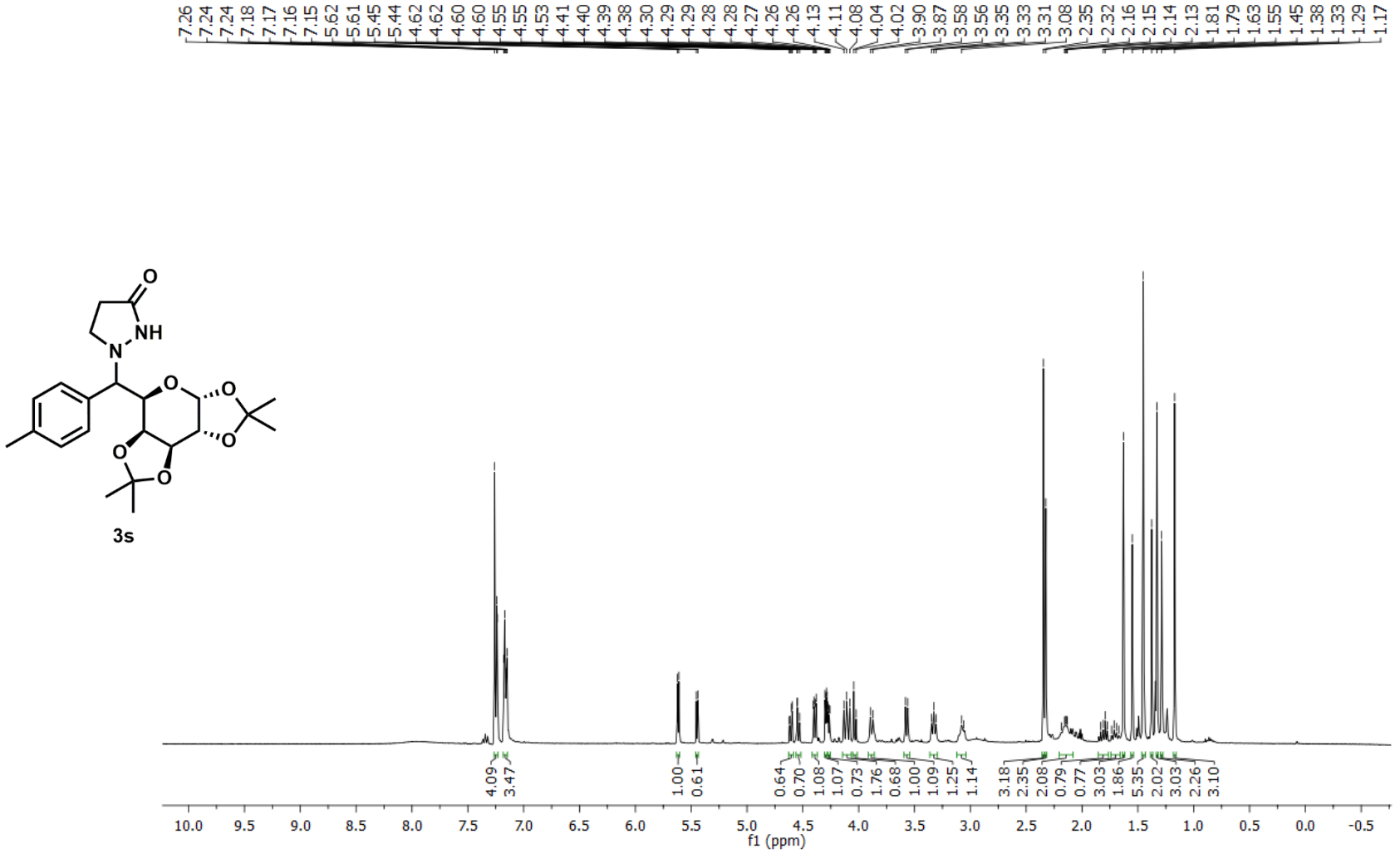


Figure S56. ^{1}H NMR spectrum of **3s** (400 MHz, $CDCl_3$)

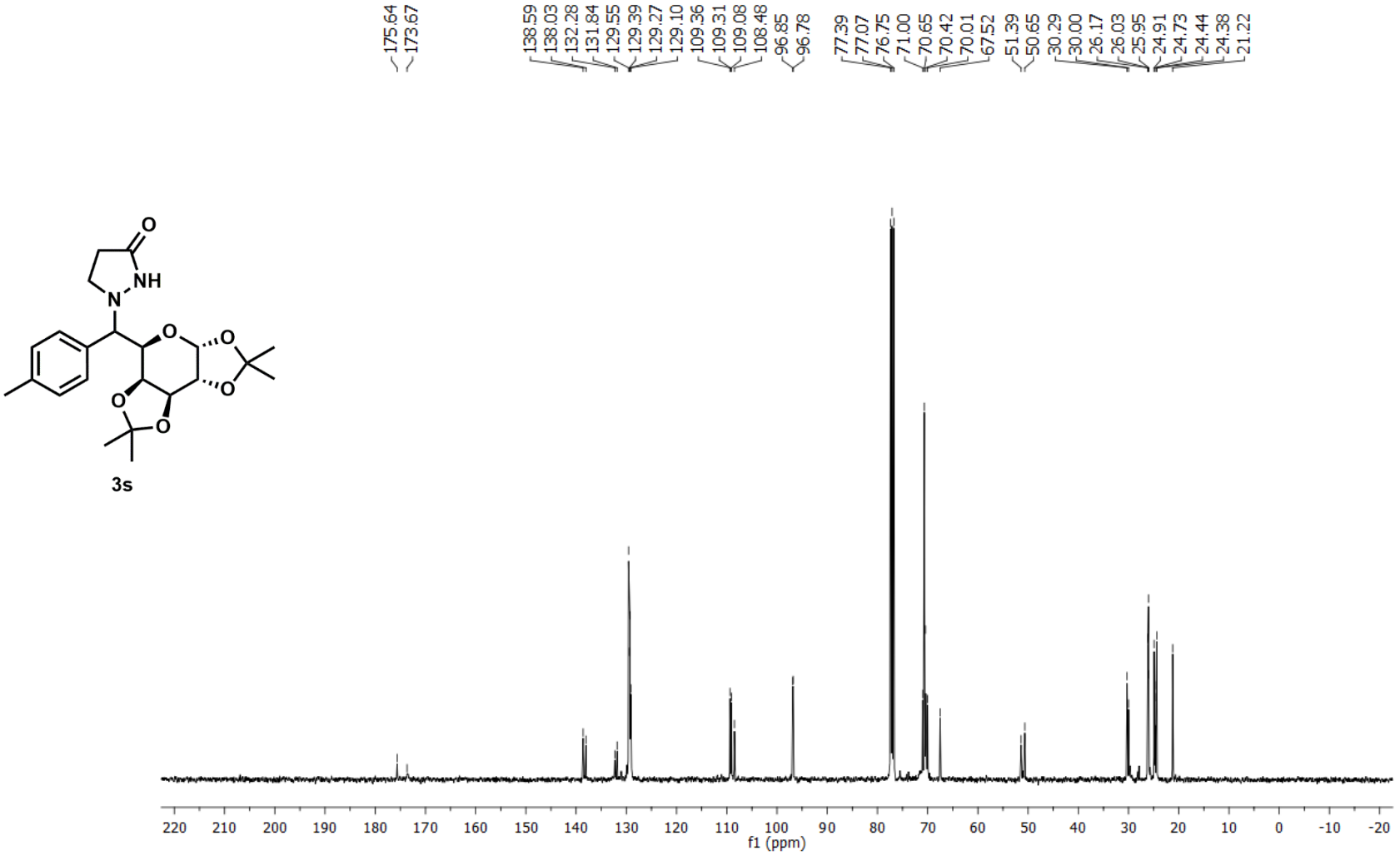


Figure S57. ^{13}C NMR spectrum of **3s** (101 MHz, $CDCl_3$)

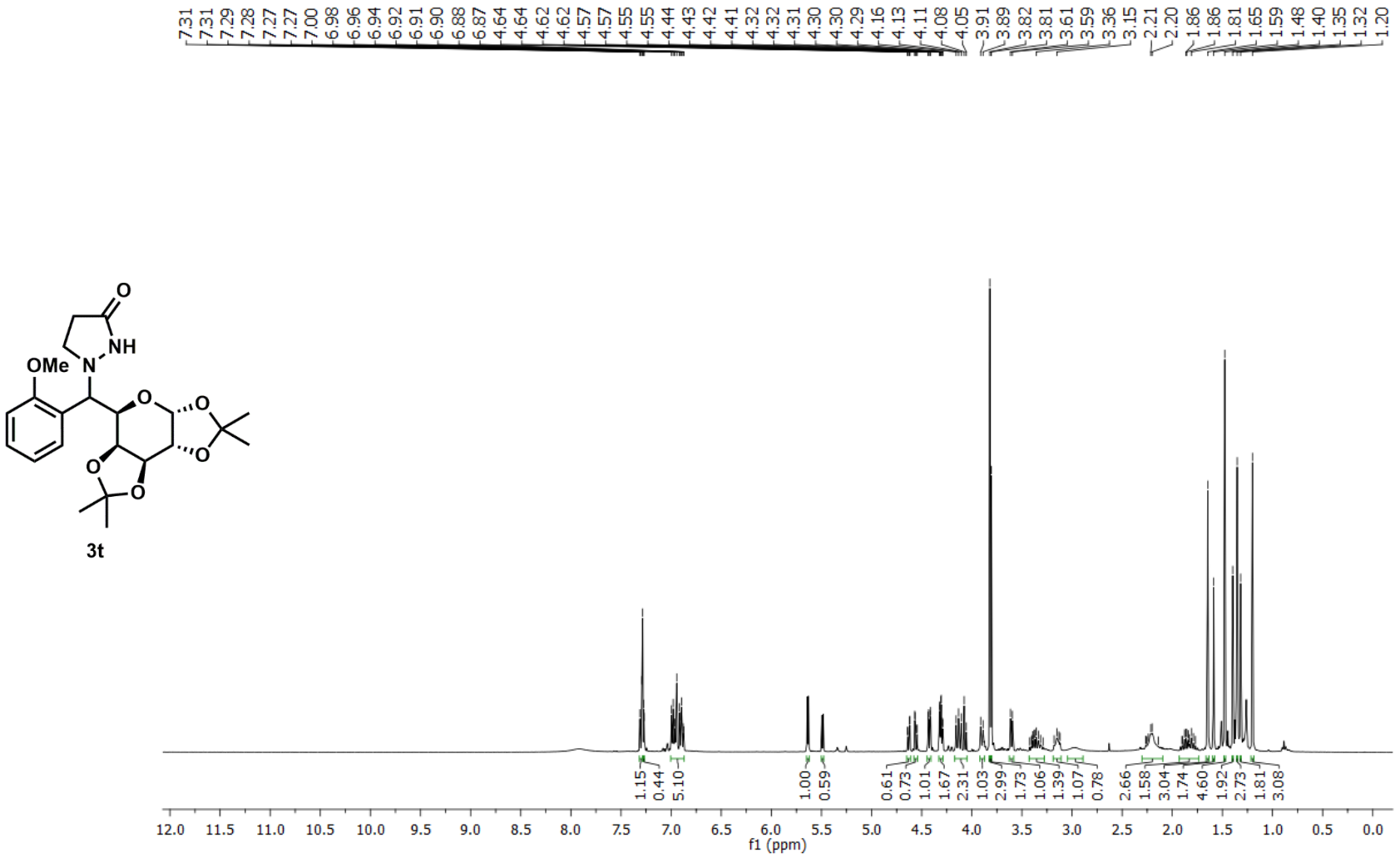


Figure S58. ^{1}H NMR spectrum of **3t** (400 MHz, $CDCl_3$)

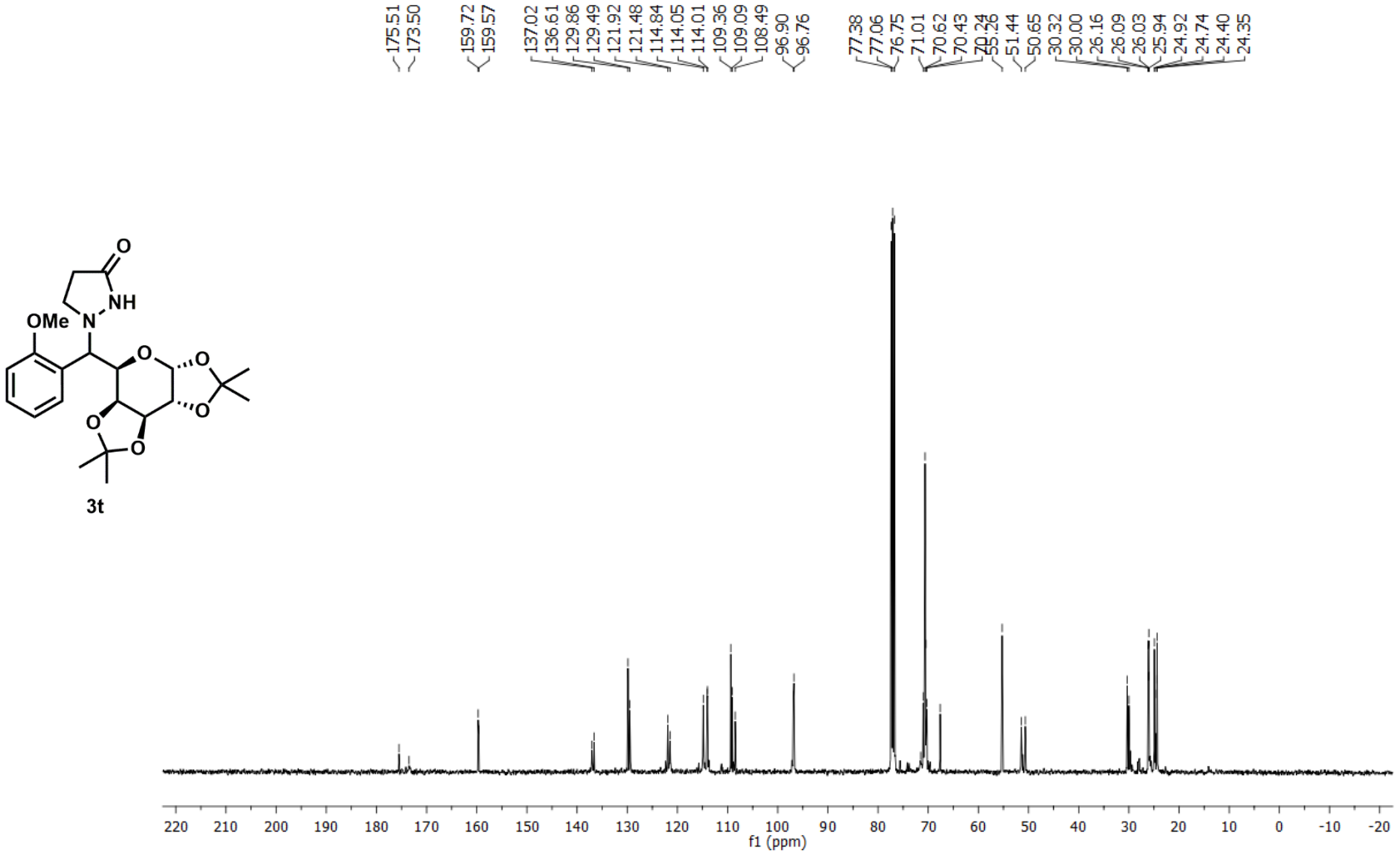


Figure S59. ^{13}C NMR spectrum of **3t** (101 MHz, $CDCl_3$)

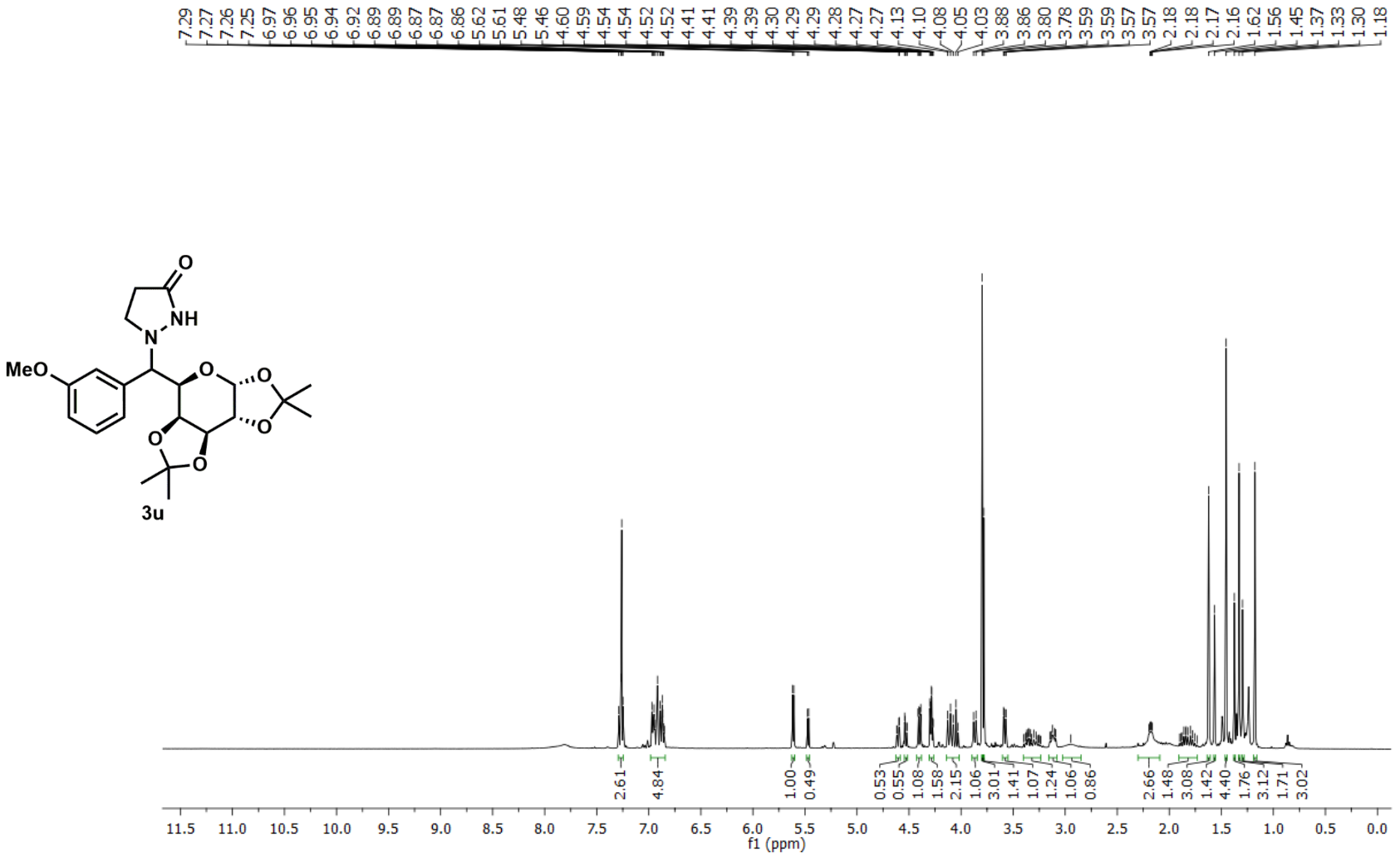


Figure S60. ^{1}H NMR spectrum of **3u** (400 MHz, $CDCl_3$)

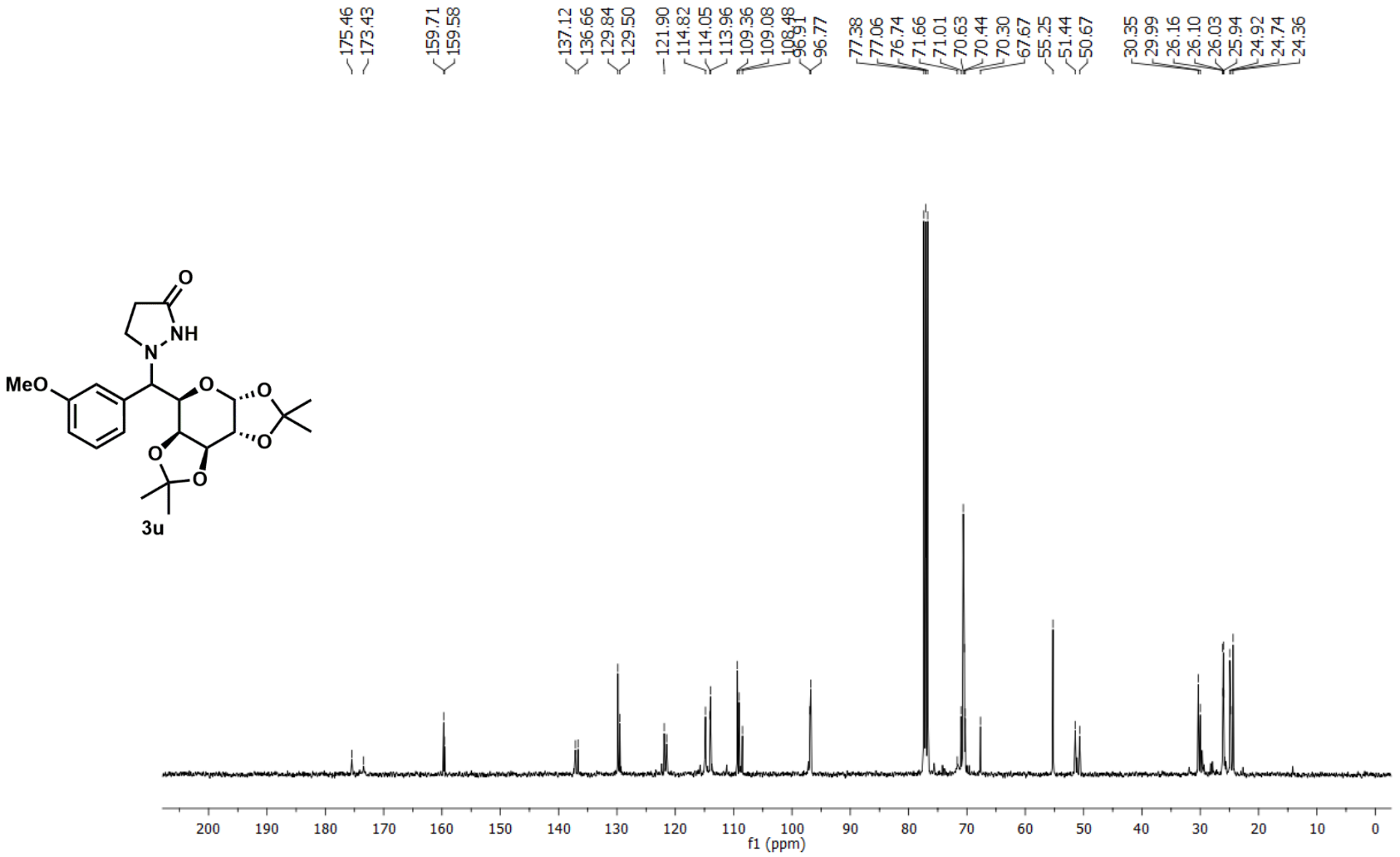


Figure S61. ^{13}C NMR spectrum of **3u** (101 MHz, $CDCl_3$)

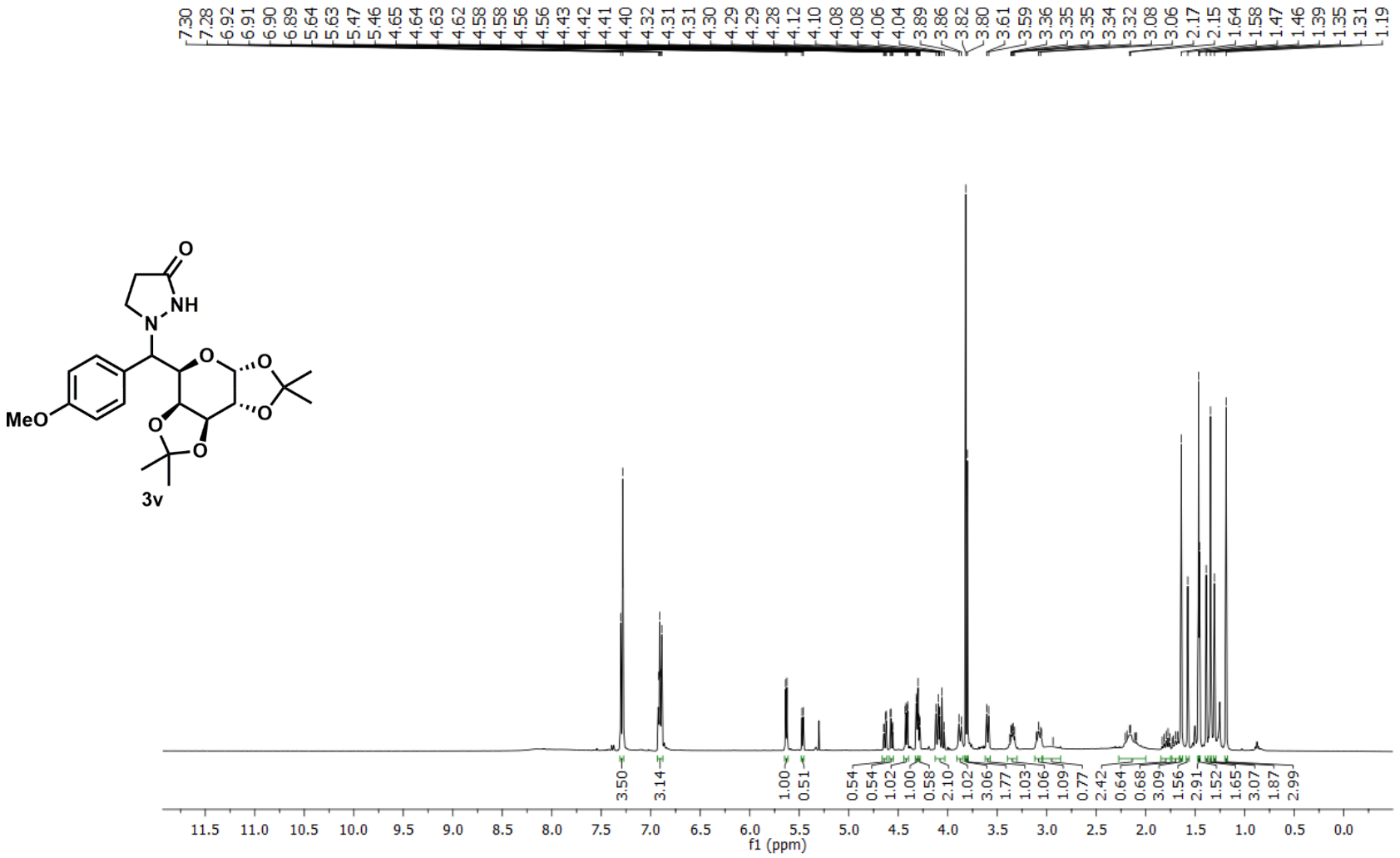


Figure S62. ^{1}H NMR spectrum of **3v** (400 MHz, $CDCl_3$)

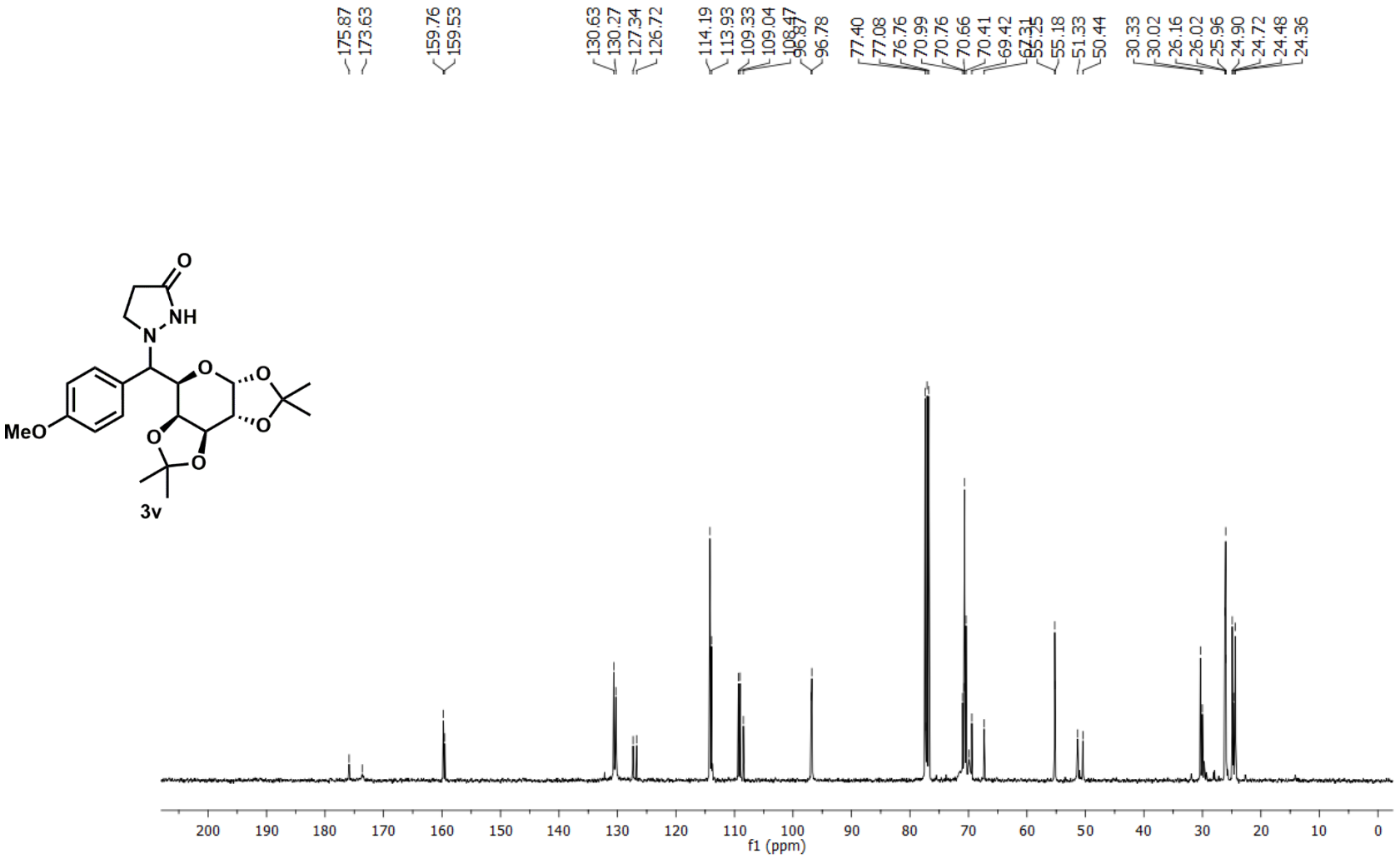


Figure S63. ^{13}C NMR spectrum of **3v** (101 MHz, $CDCl_3$)

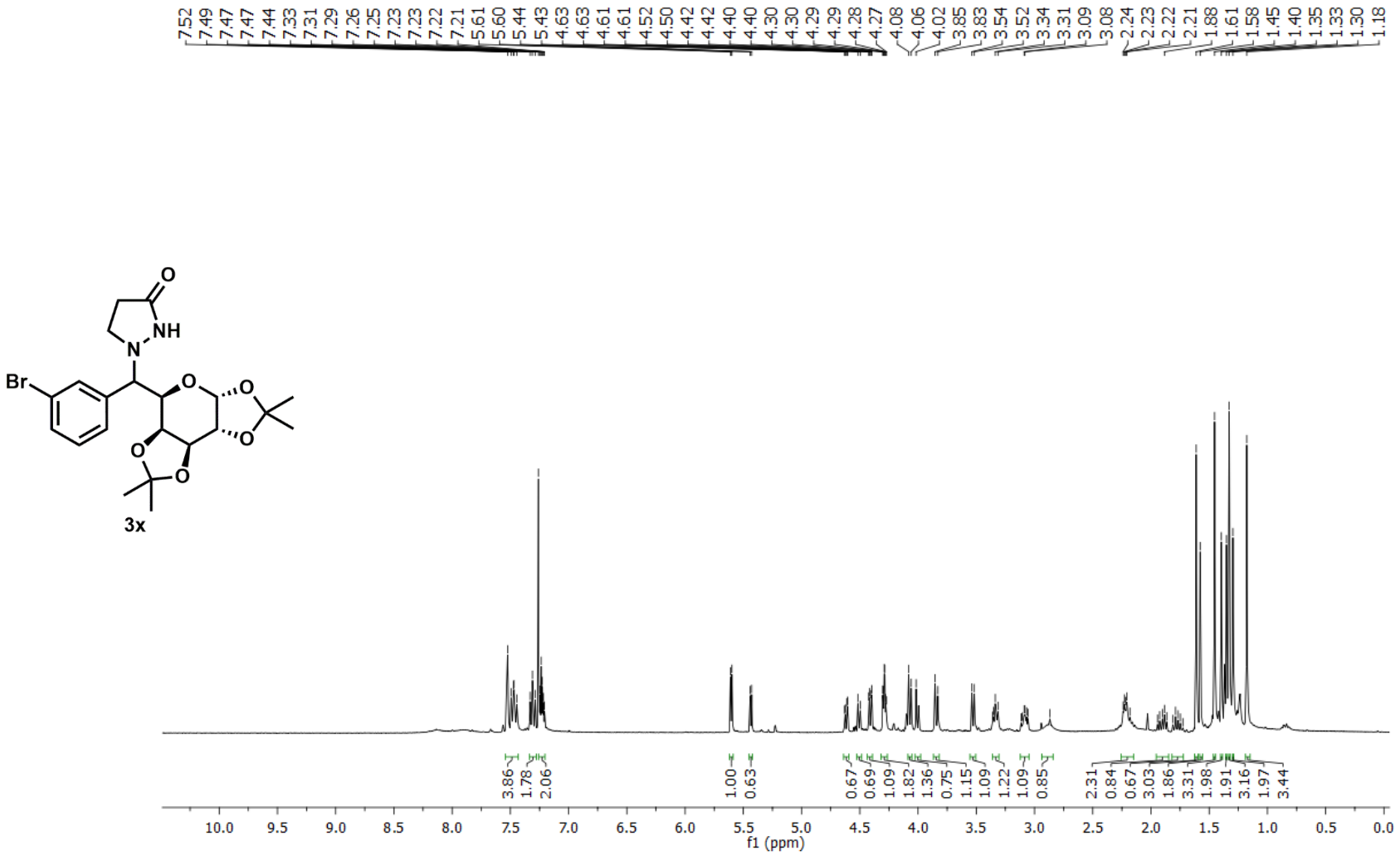


Figure S64. ^{1}H NMR spectrum of **3x** (400 MHz, $CDCl_3$)

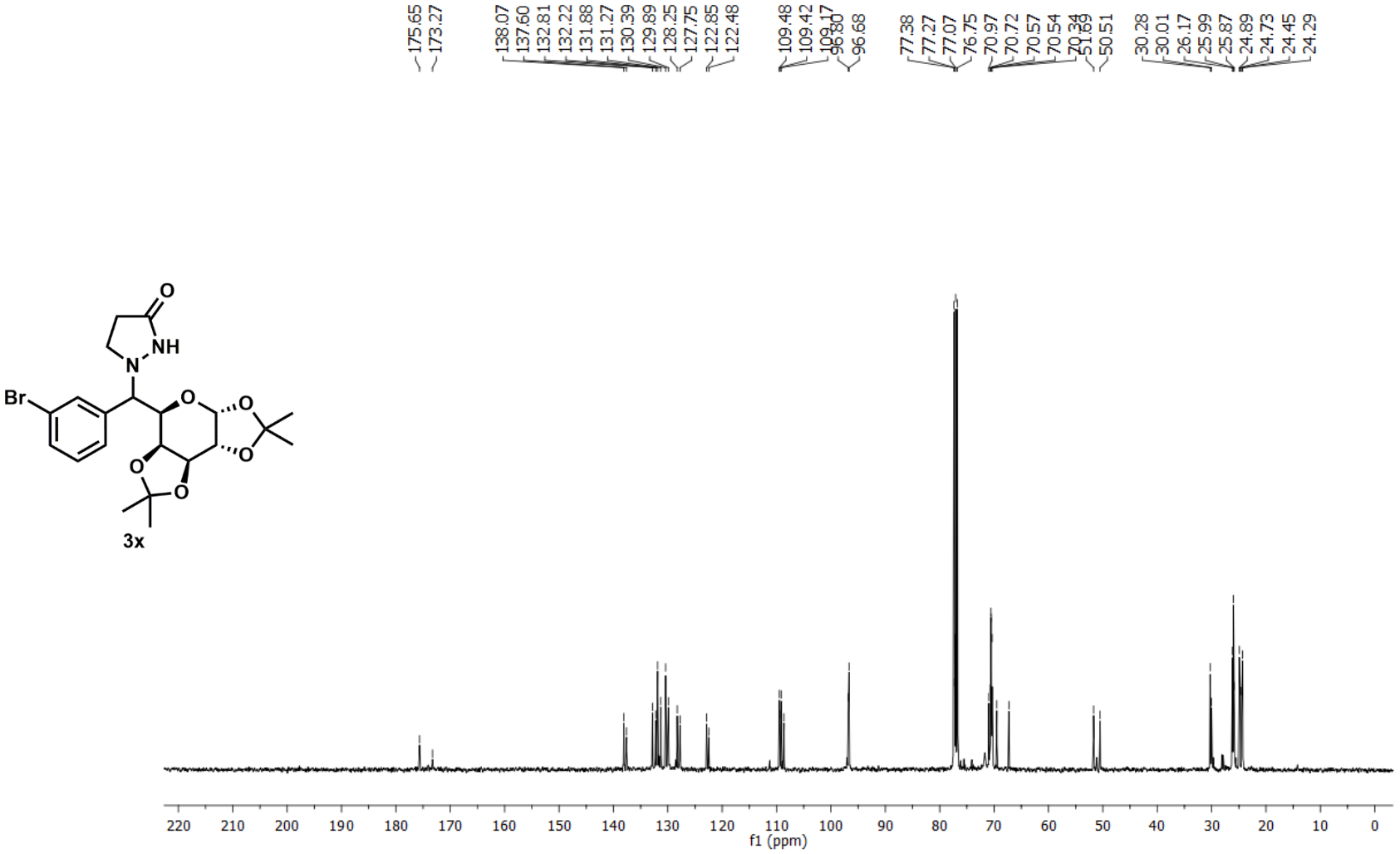


Figure S65. ^{13}C NMR spectrum of **3x** (101 MHz, $CDCl_3$)

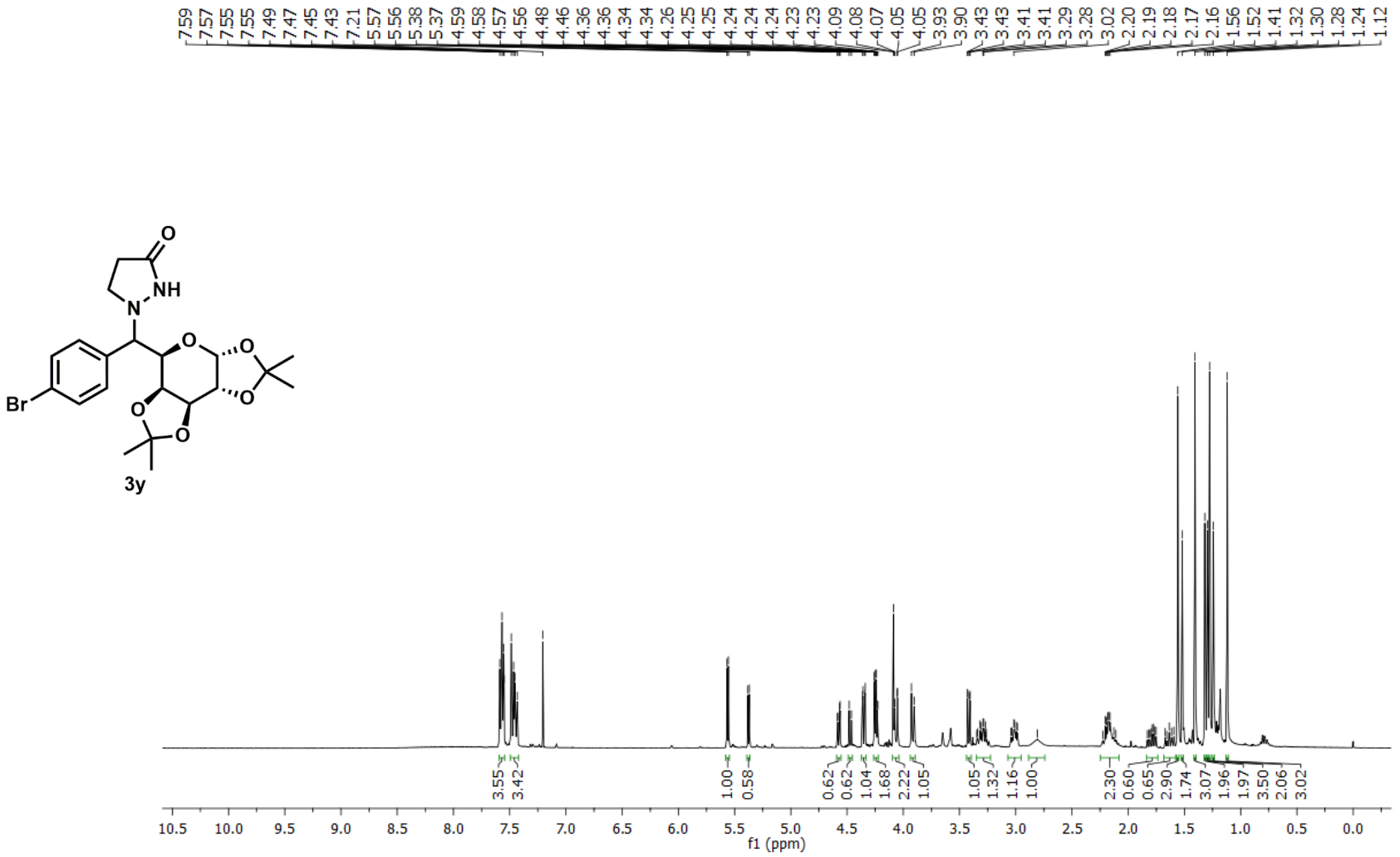


Figure S66. ^{1}H NMR spectrum of **3y** (400 MHz, $CDCl_3$)

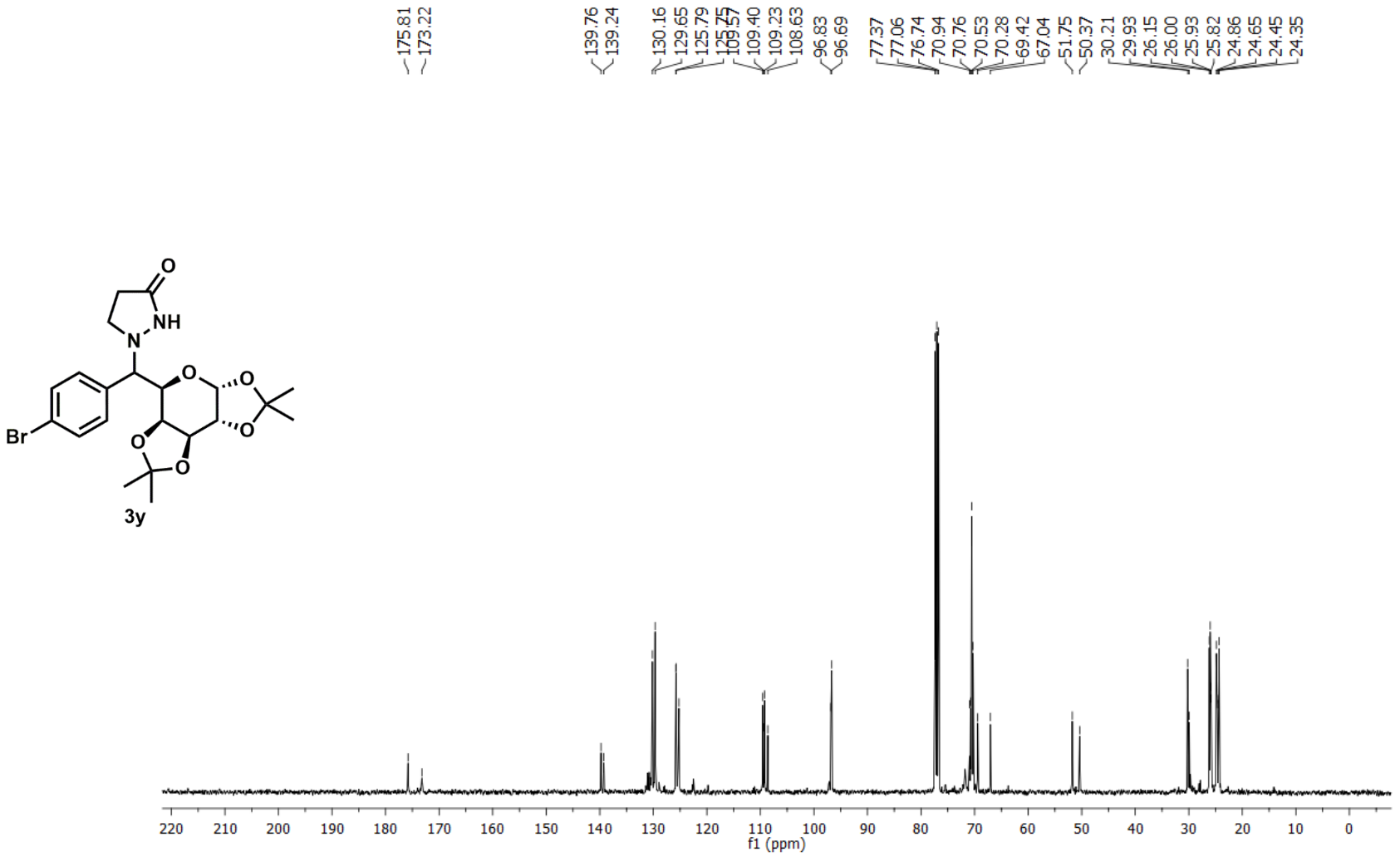


Figure S67. ^{13}C NMR spectrum of **3y** (101 MHz, $CDCl_3$)

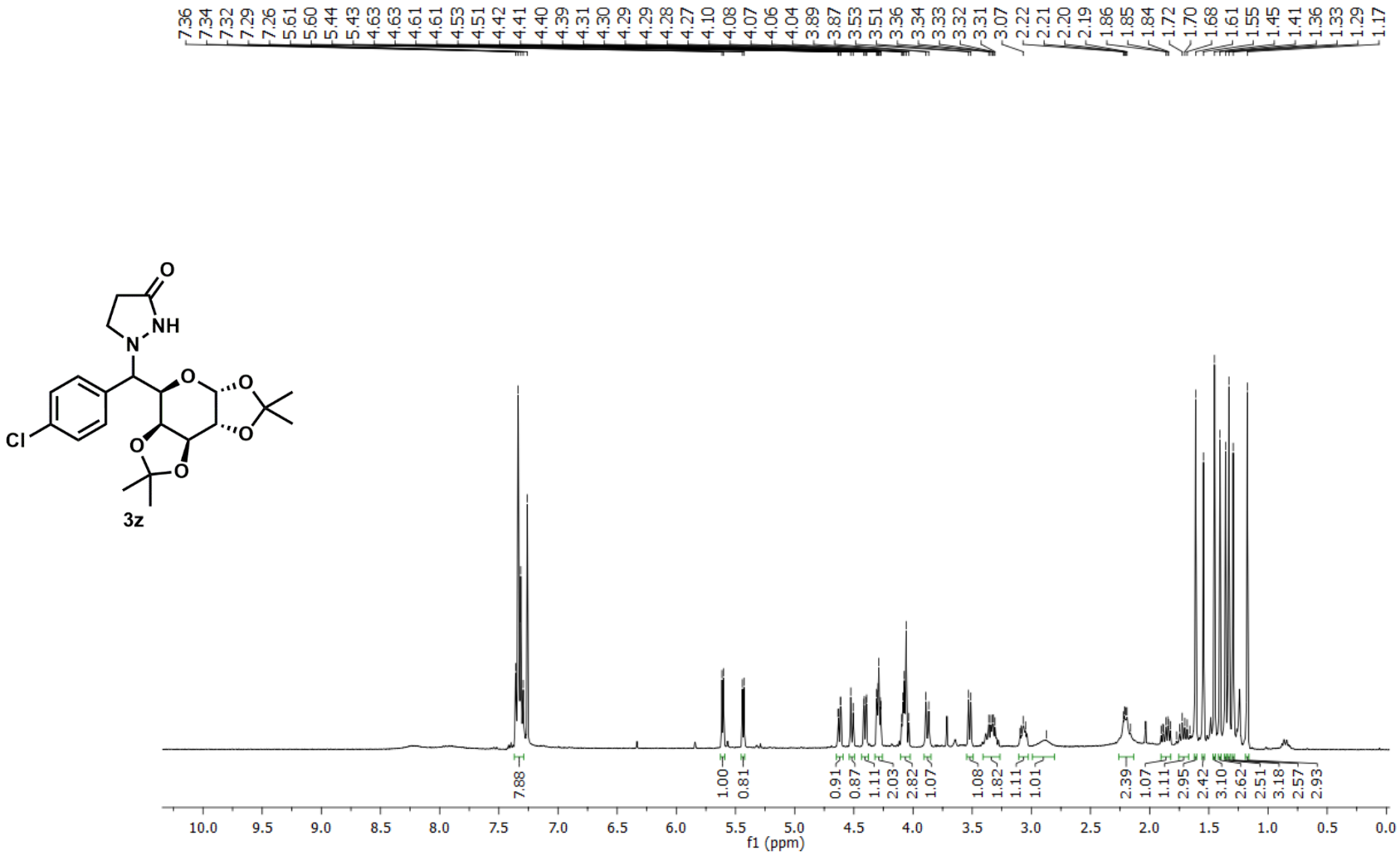


Figure S68. ^{1}H NMR spectrum of **3z** (400 MHz, $CDCl_3$)

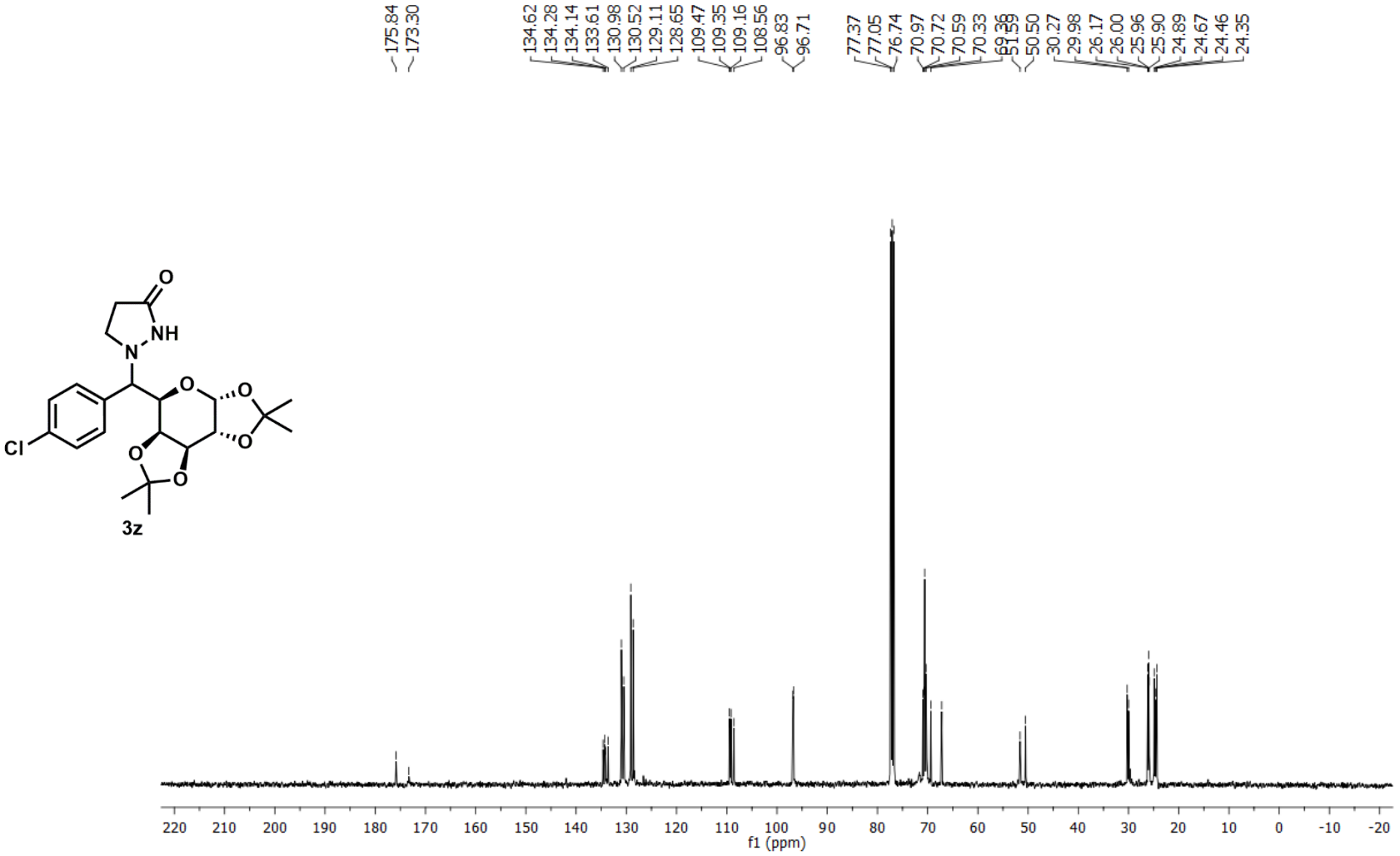


Figure S69. ^{13}C NMR spectrum of **3z** (101 MHz, $CDCl_3$)

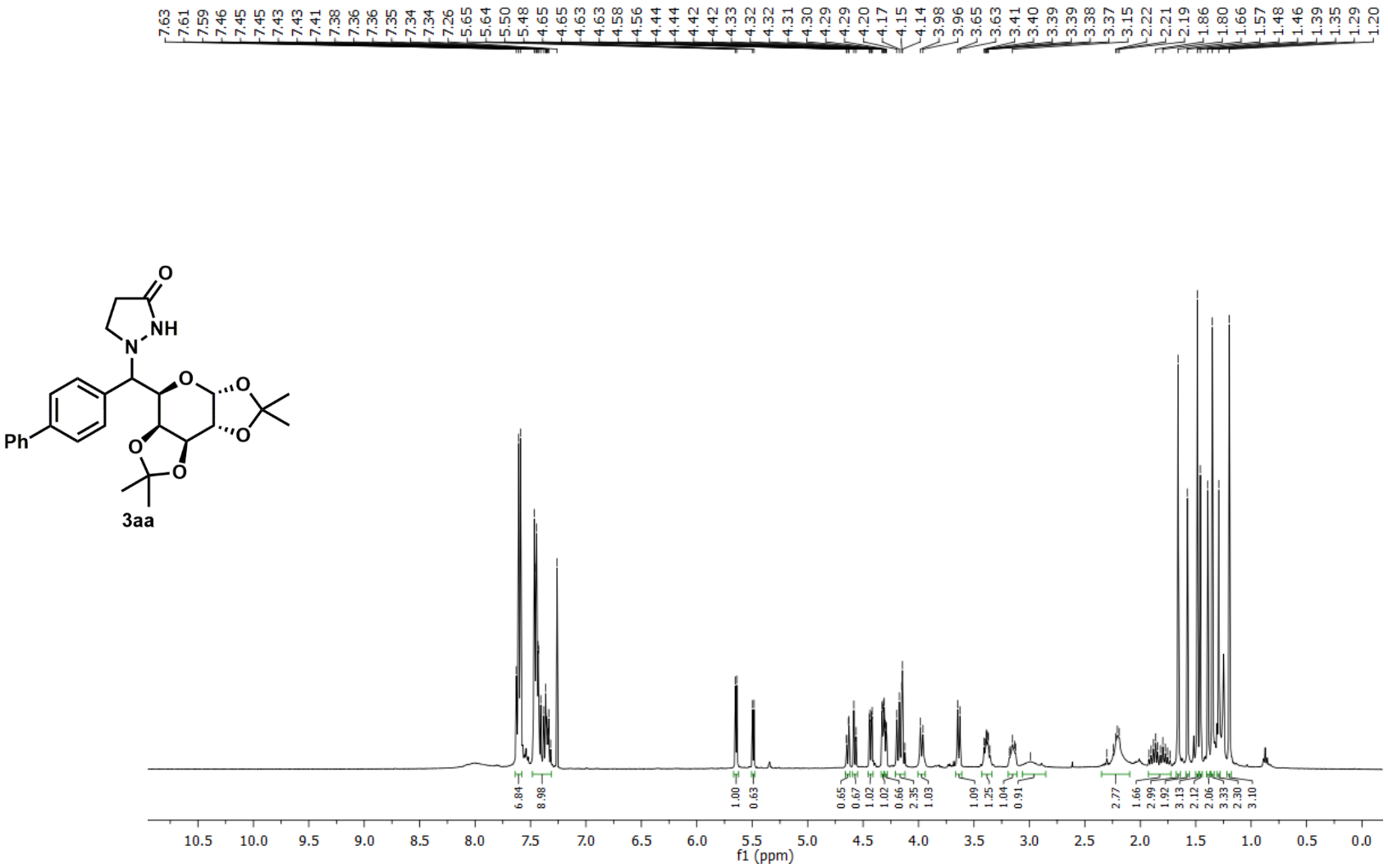


Figure S70. ^{1}H NMR spectrum of **3aa** (400 MHz, $CDCl_3$)

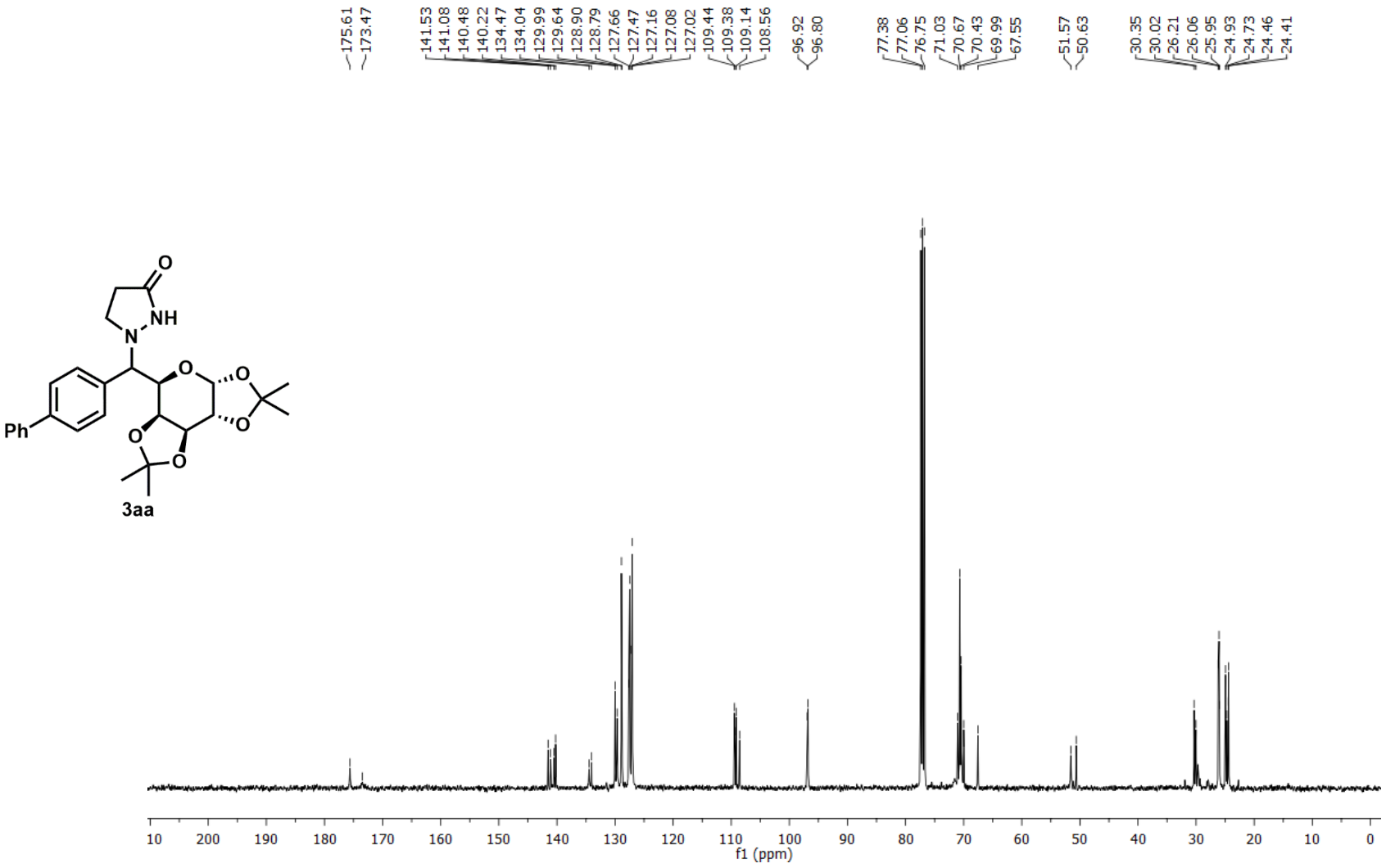


Figure S71. ^{13}C NMR spectrum of **3aa** (101 MHz, $CDCl_3$)

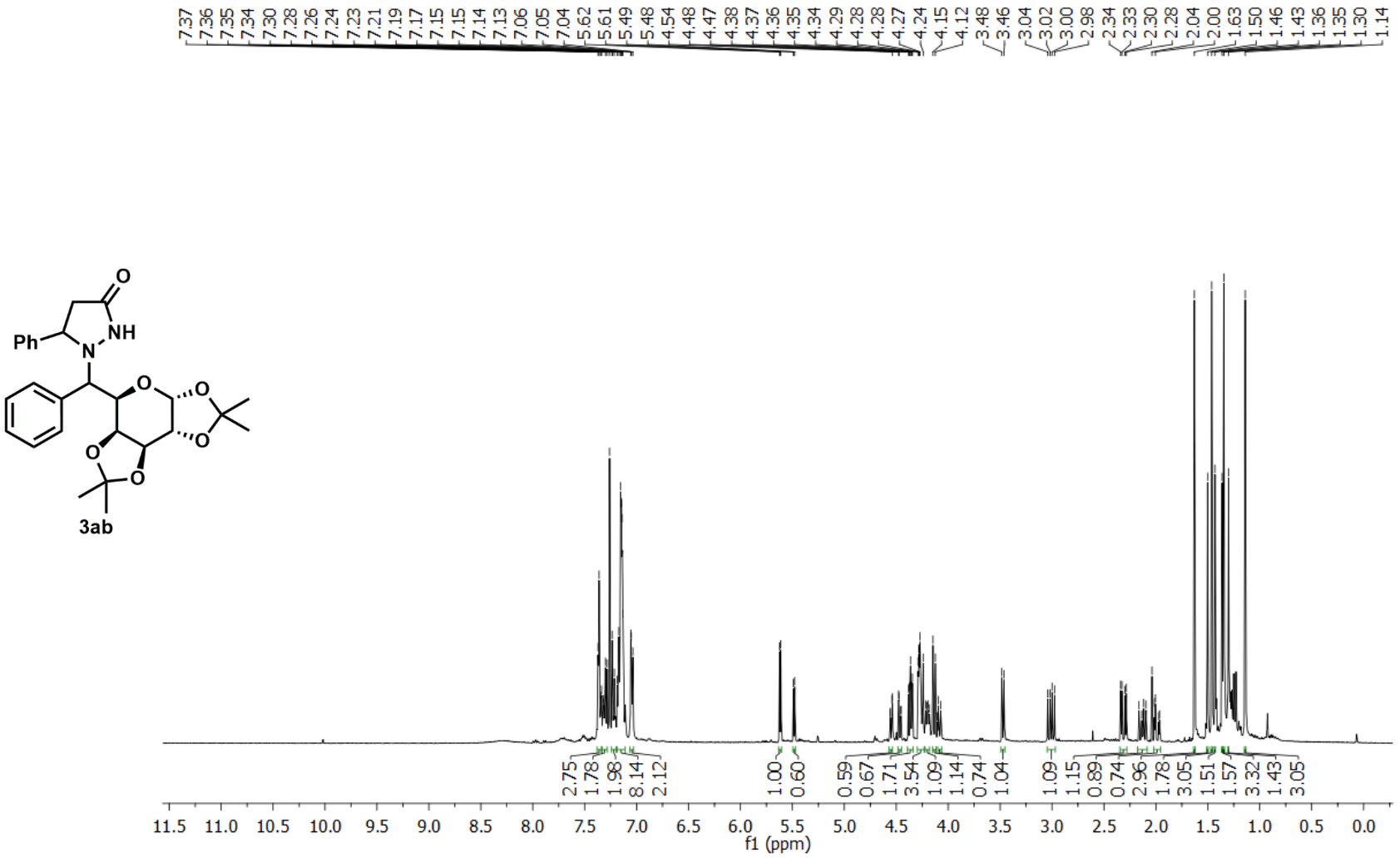


Figure S72. ^{1}H NMR spectrum of **3ab** (400 MHz, $CDCl_3$)

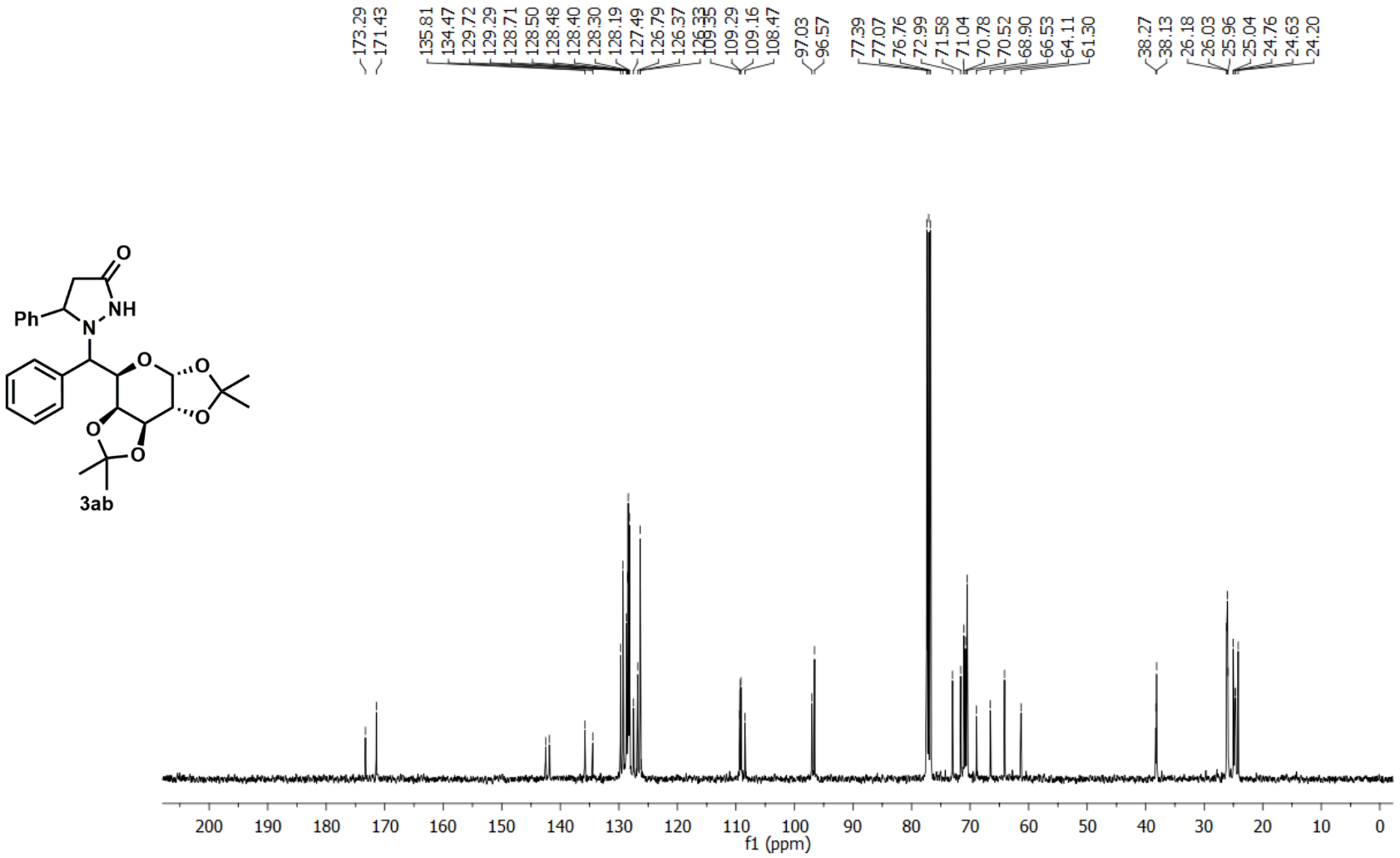


Figure S73. ^{13}C NMR spectrum of **3ab** (101 MHz, $CDCl_3$)

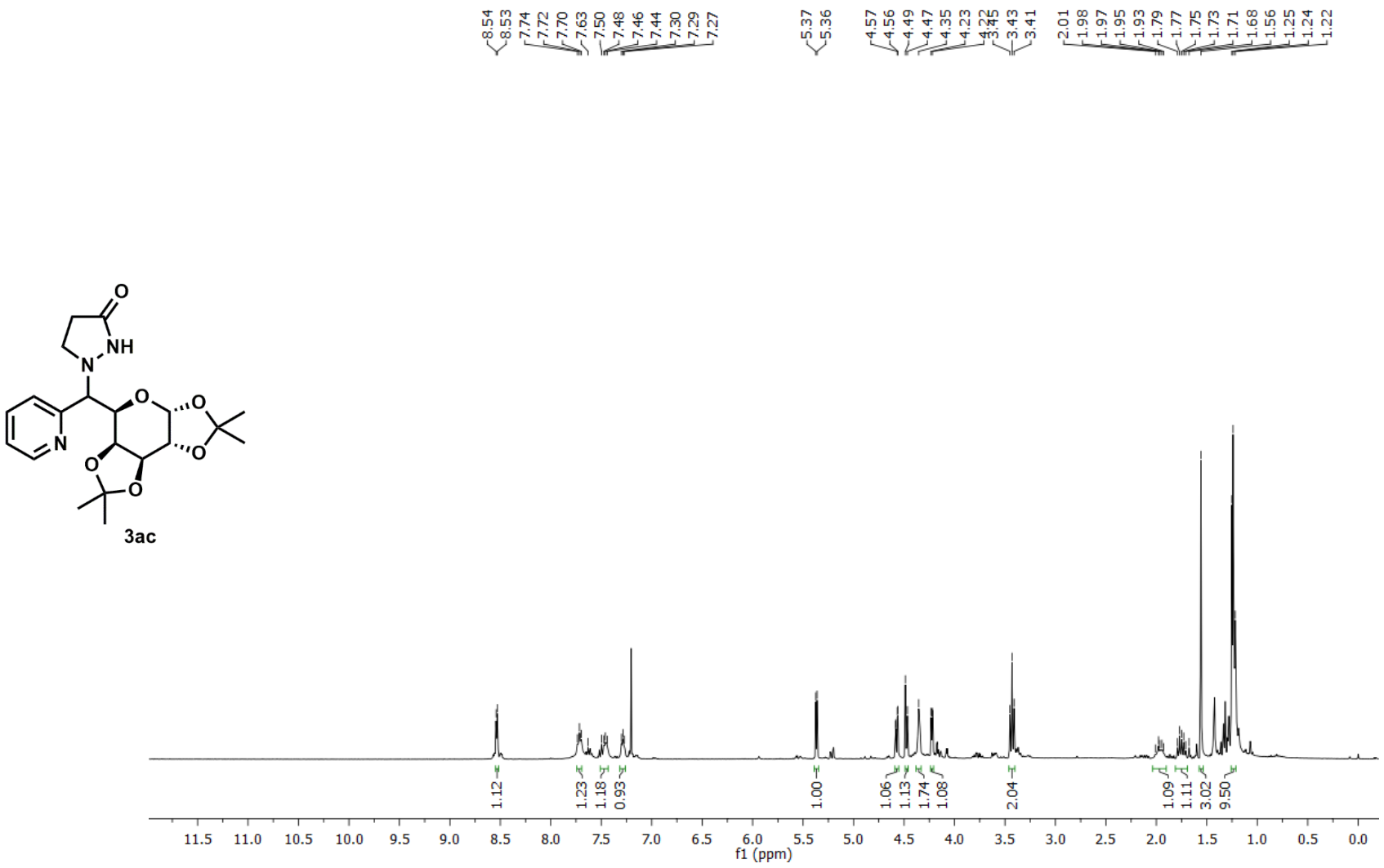


Figure S74. ^{1}H NMR spectrum of **3ac** (400 MHz, $CDCl_3$)

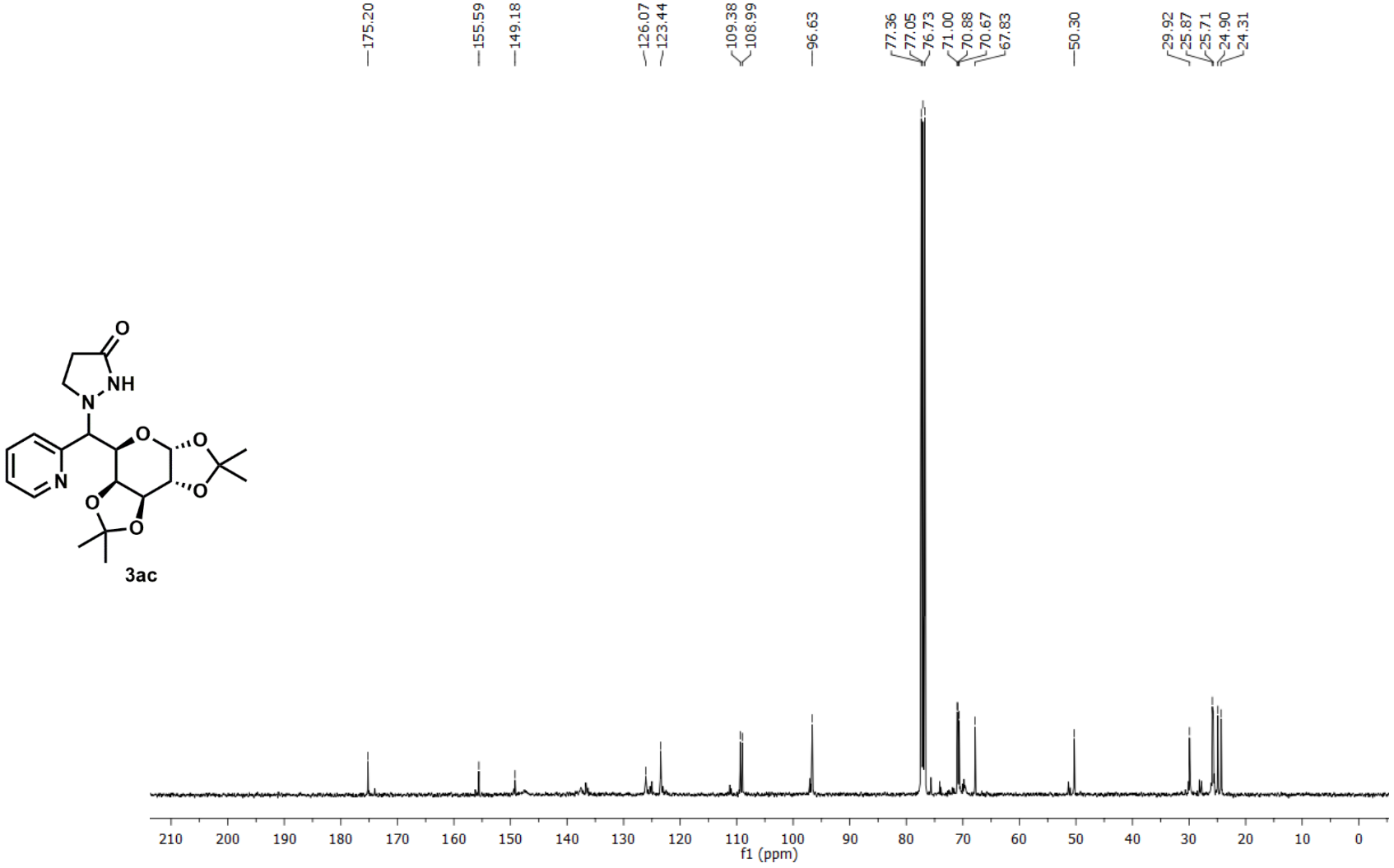


Figure S75. ^{13}C NMR spectrum of **3ac** (101 MHz, $CDCl_3$)

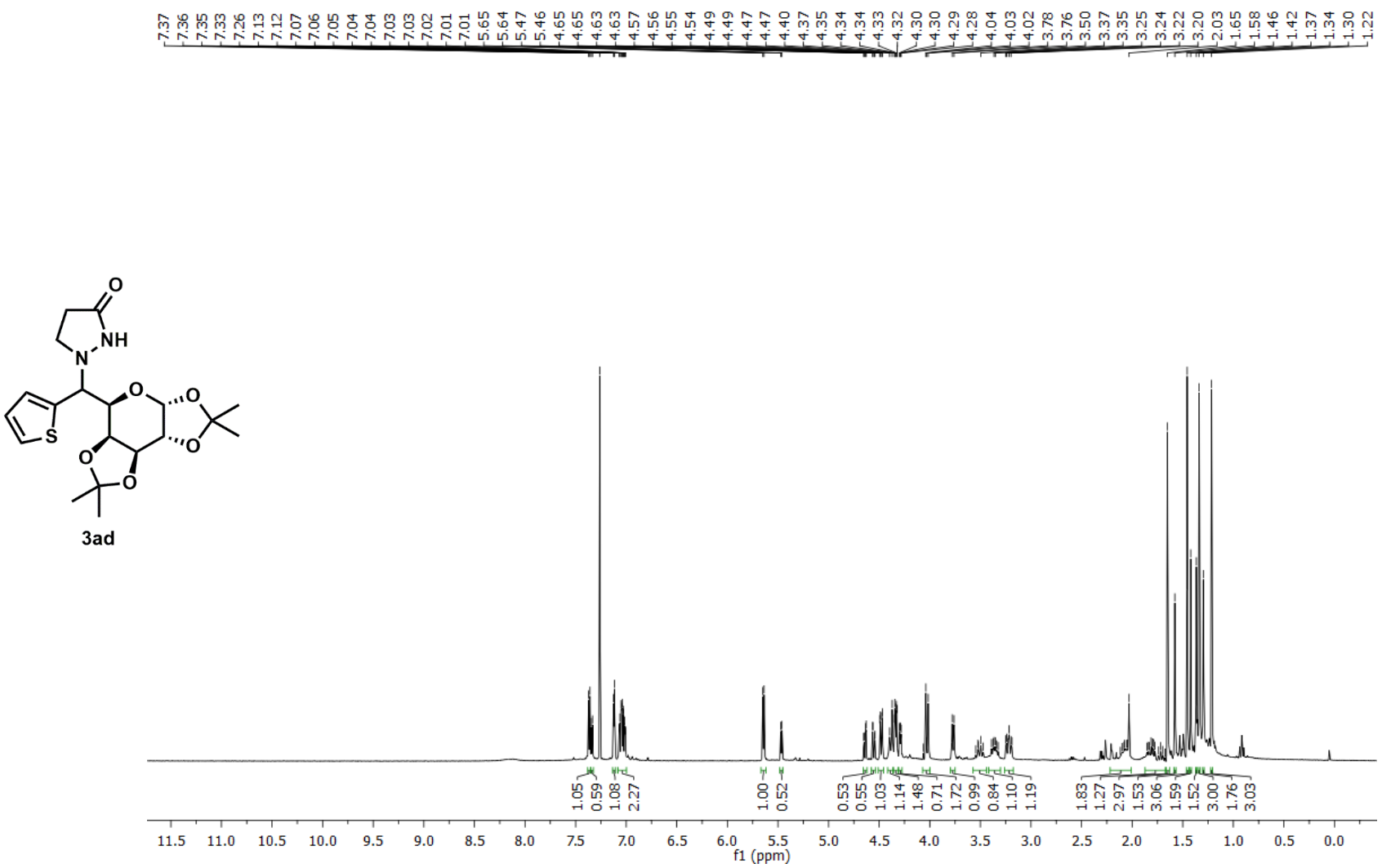


Figure S76. ^{1}H NMR spectrum of **3ad** (400 MHz, $CDCl_3$)

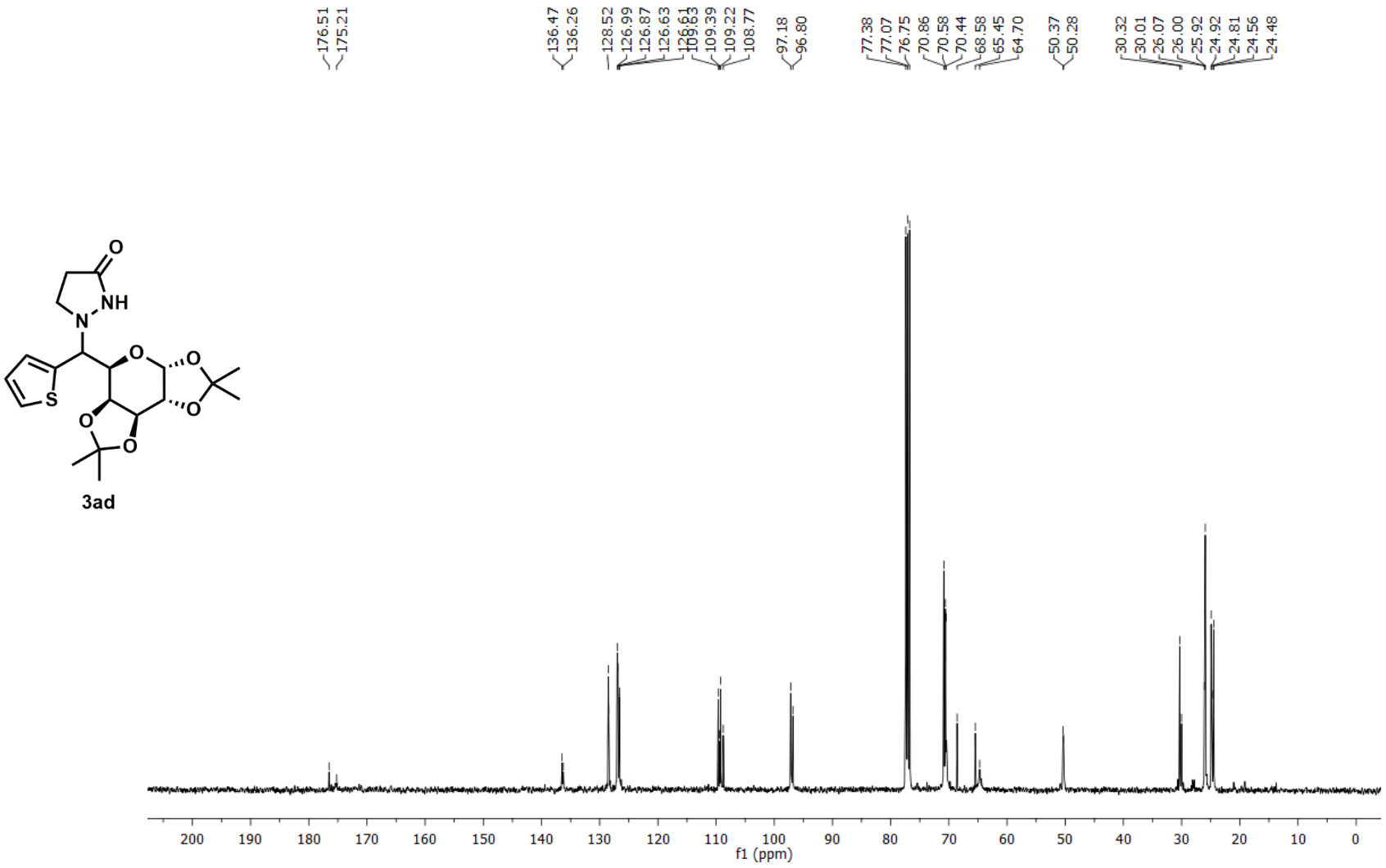


Figure S77. ^{13}C NMR spectrum of **3ad** (101 MHz, $CDCl_3$)

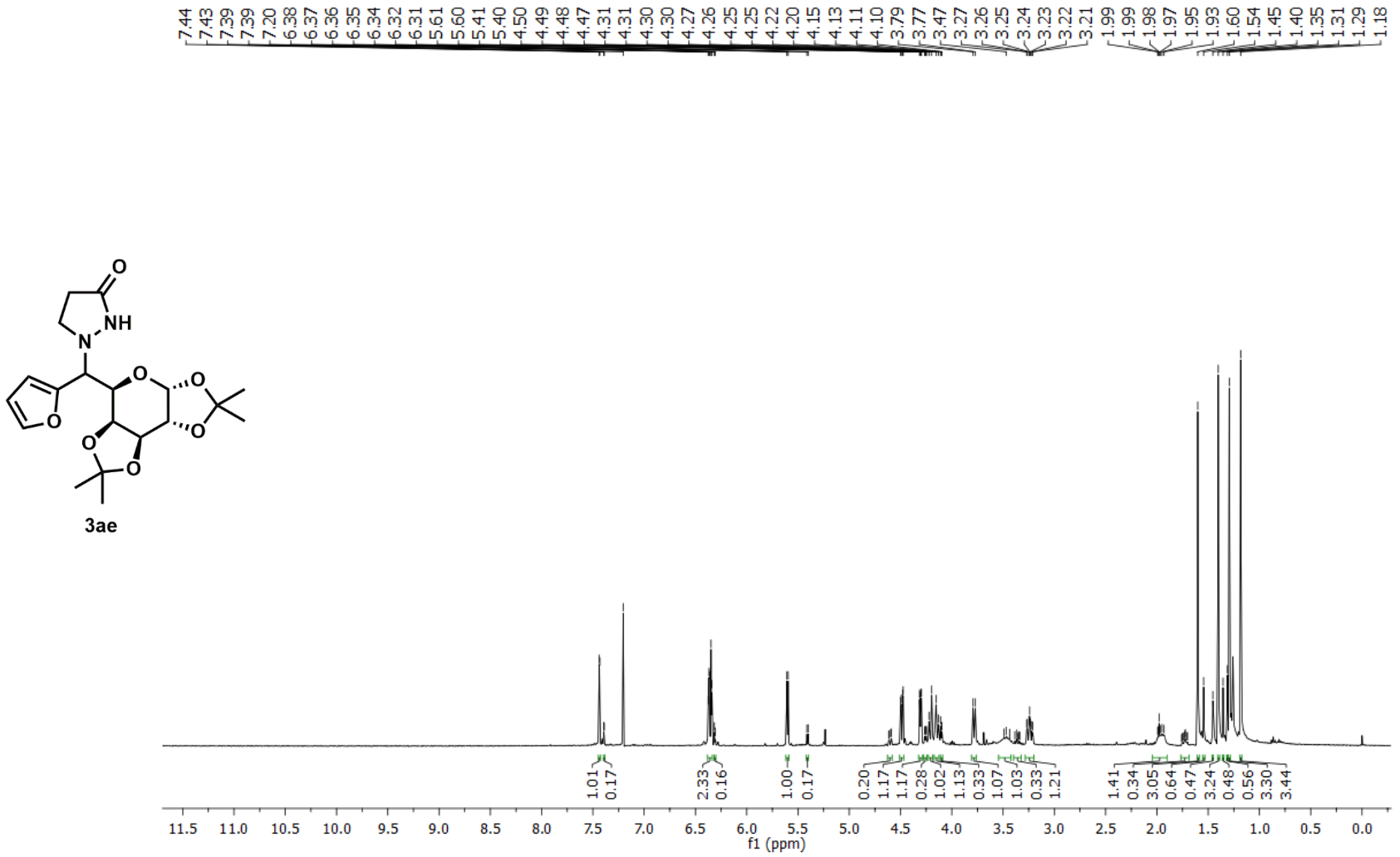


Figure S78. ^{1}H NMR spectrum of **3ae** (400 MHz, $CDCl_3$)

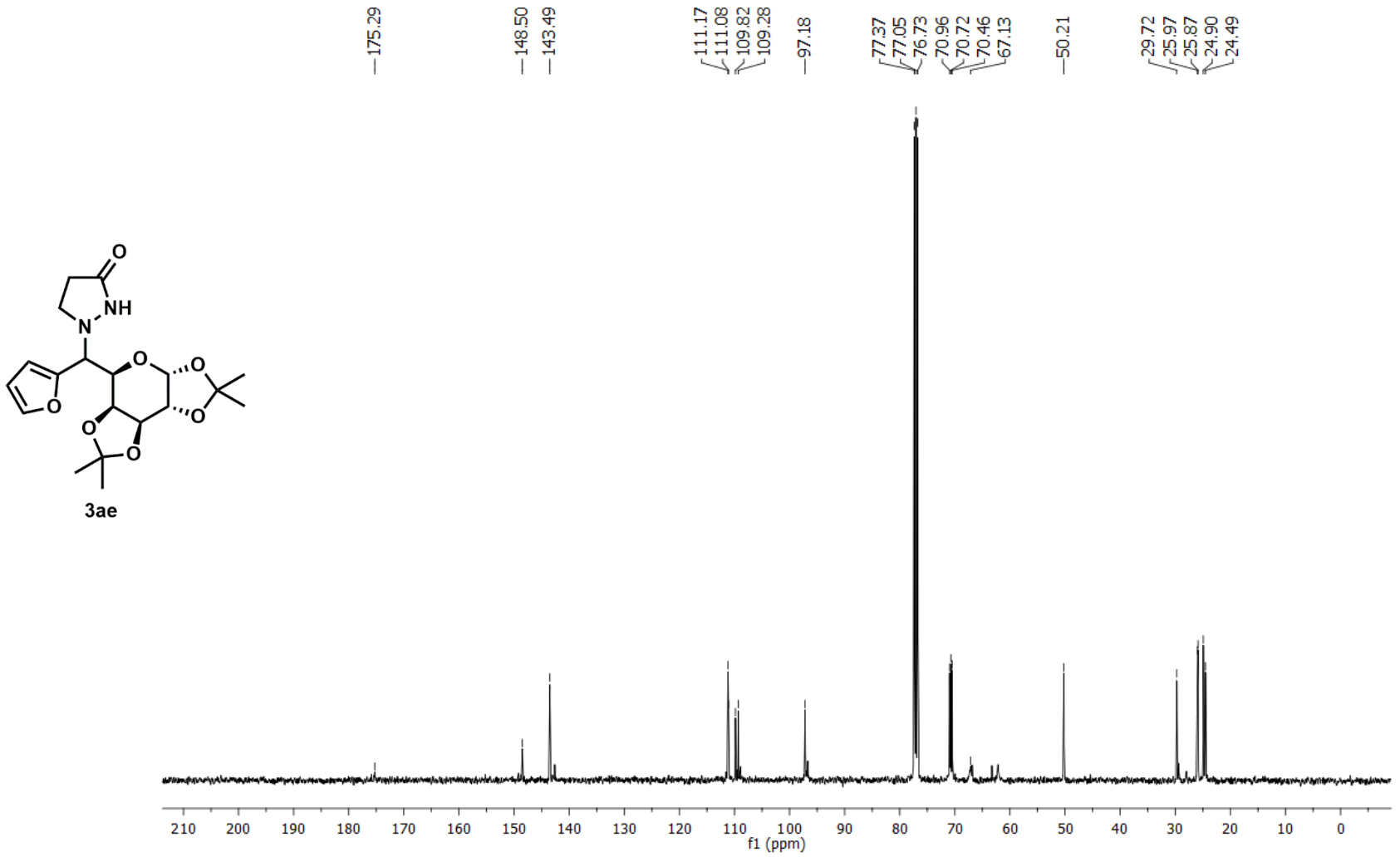


Figure S79. ^{13}C NMR spectrum of **3ae** (101 MHz, $CDCl_3$)

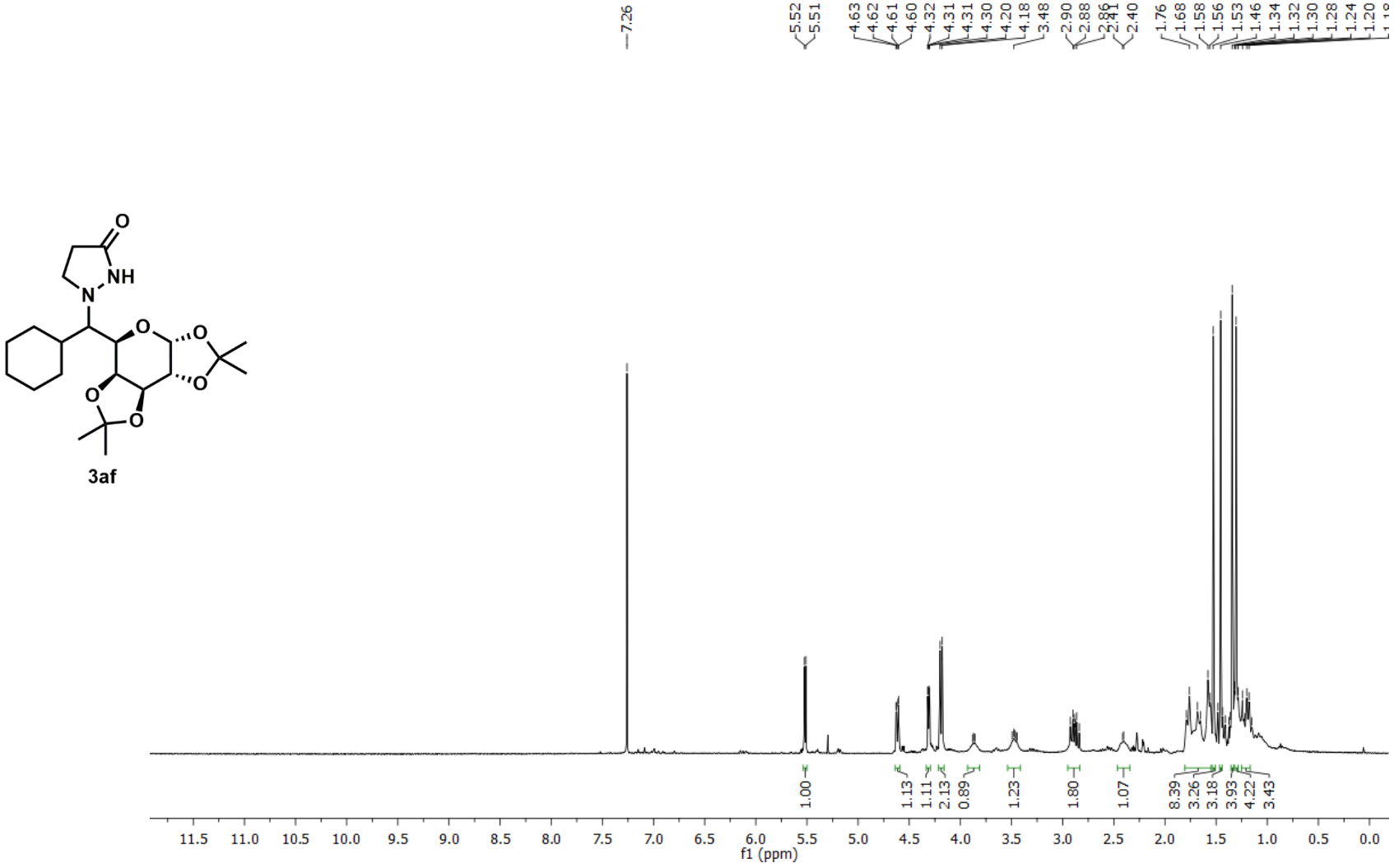


Figure S80. ^{1}H NMR spectrum of **3af** (400 MHz, $CDCl_3$)

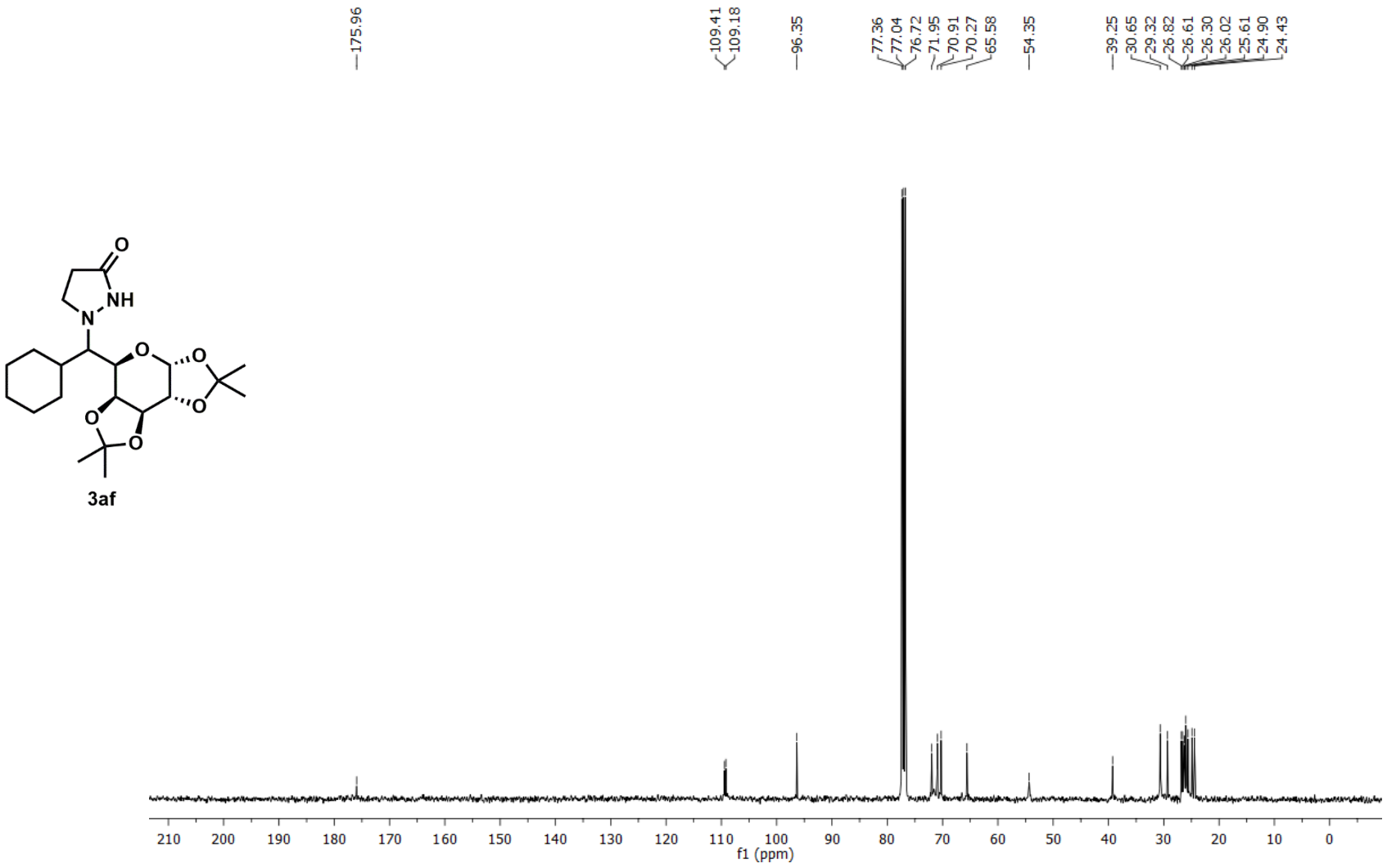


Figure S81. ^{13}C NMR spectrum of **3af** (101 MHz, $CDCl_3$)

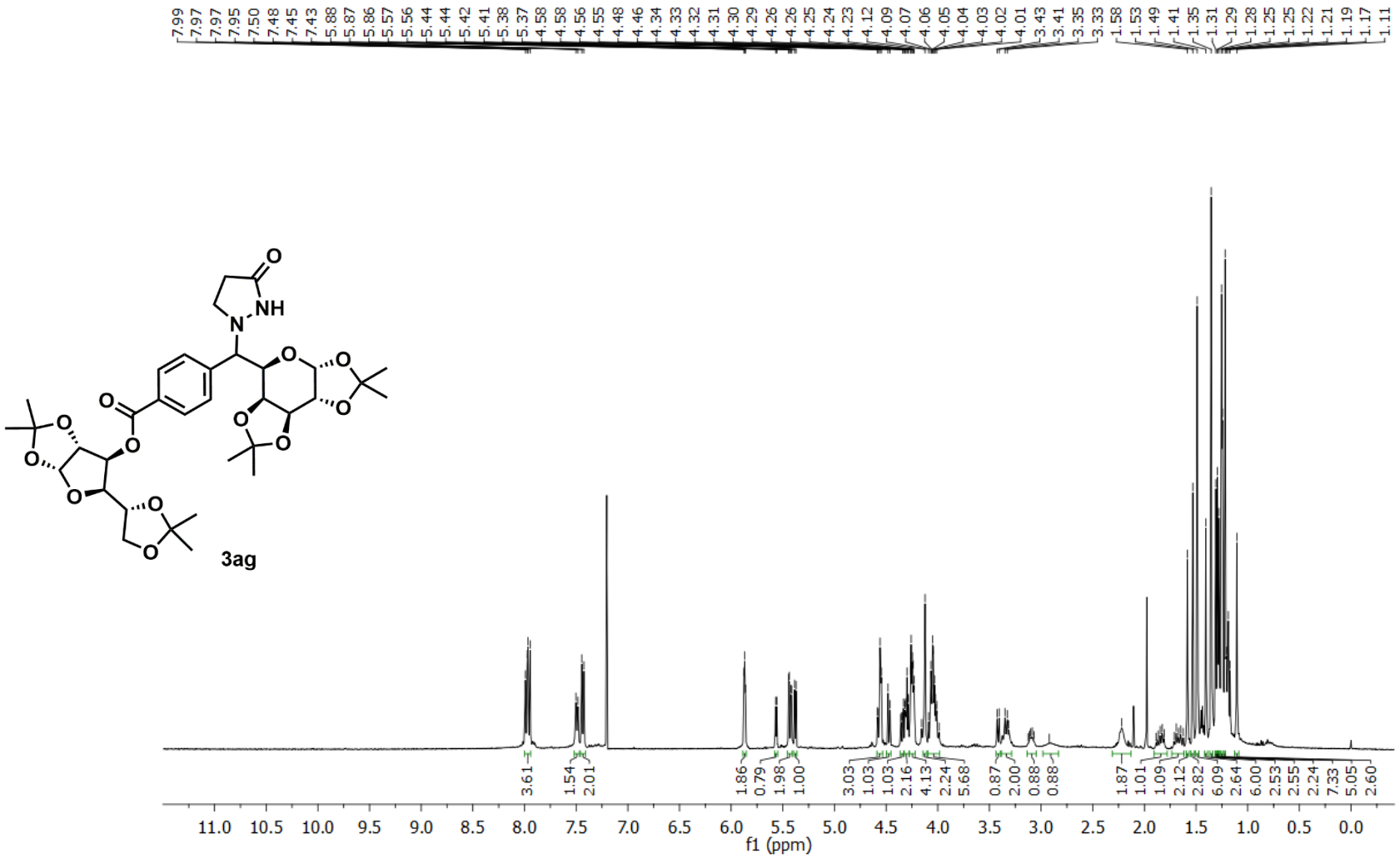


Figure S82. ^{1}H NMR spectrum of **3ag** (400 MHz, $CDCl_3$)

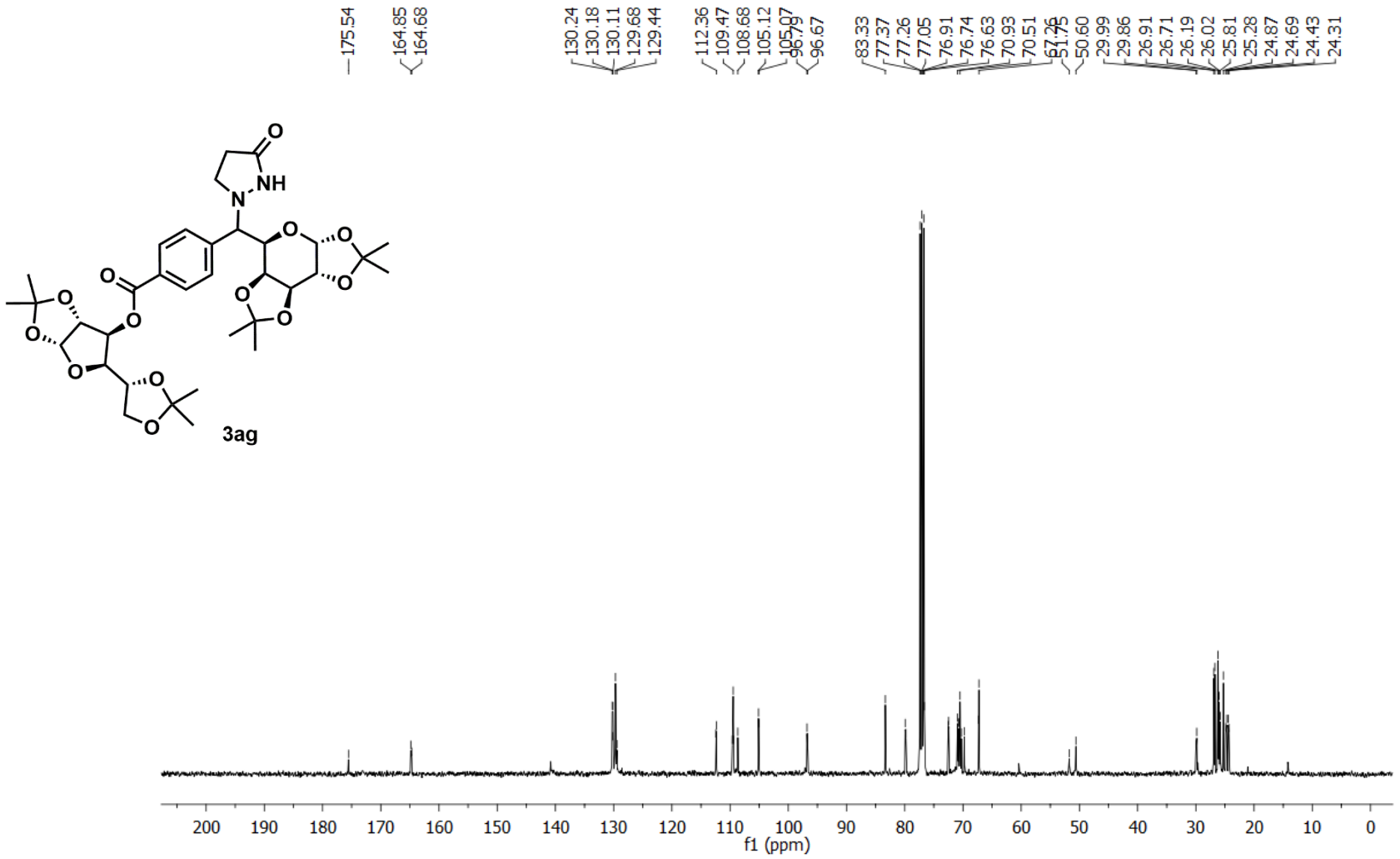


Figure S83. ^{13}C NMR spectrum of **3ag** (101 MHz, $CDCl_3$)

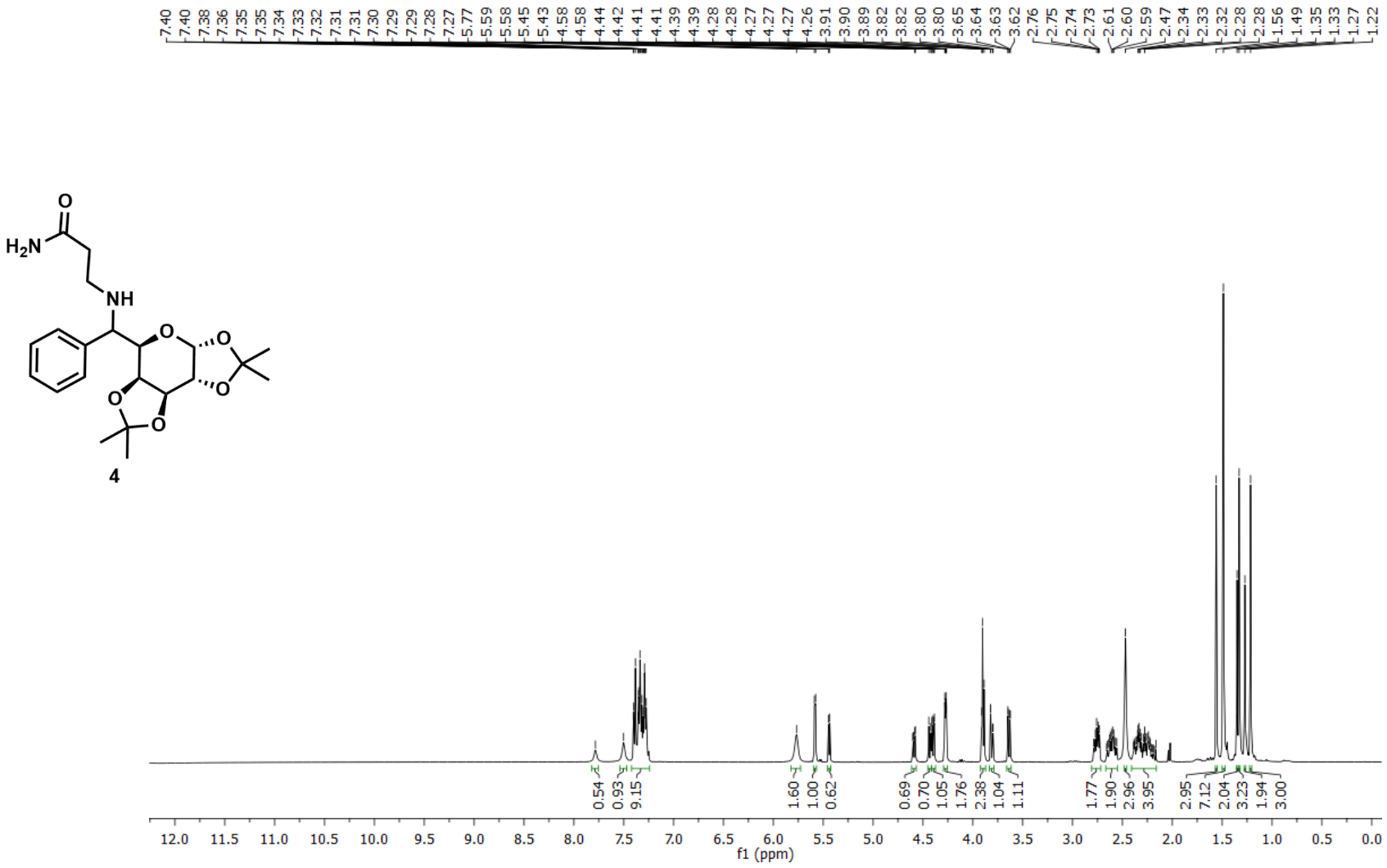


Figure S84. ^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$)

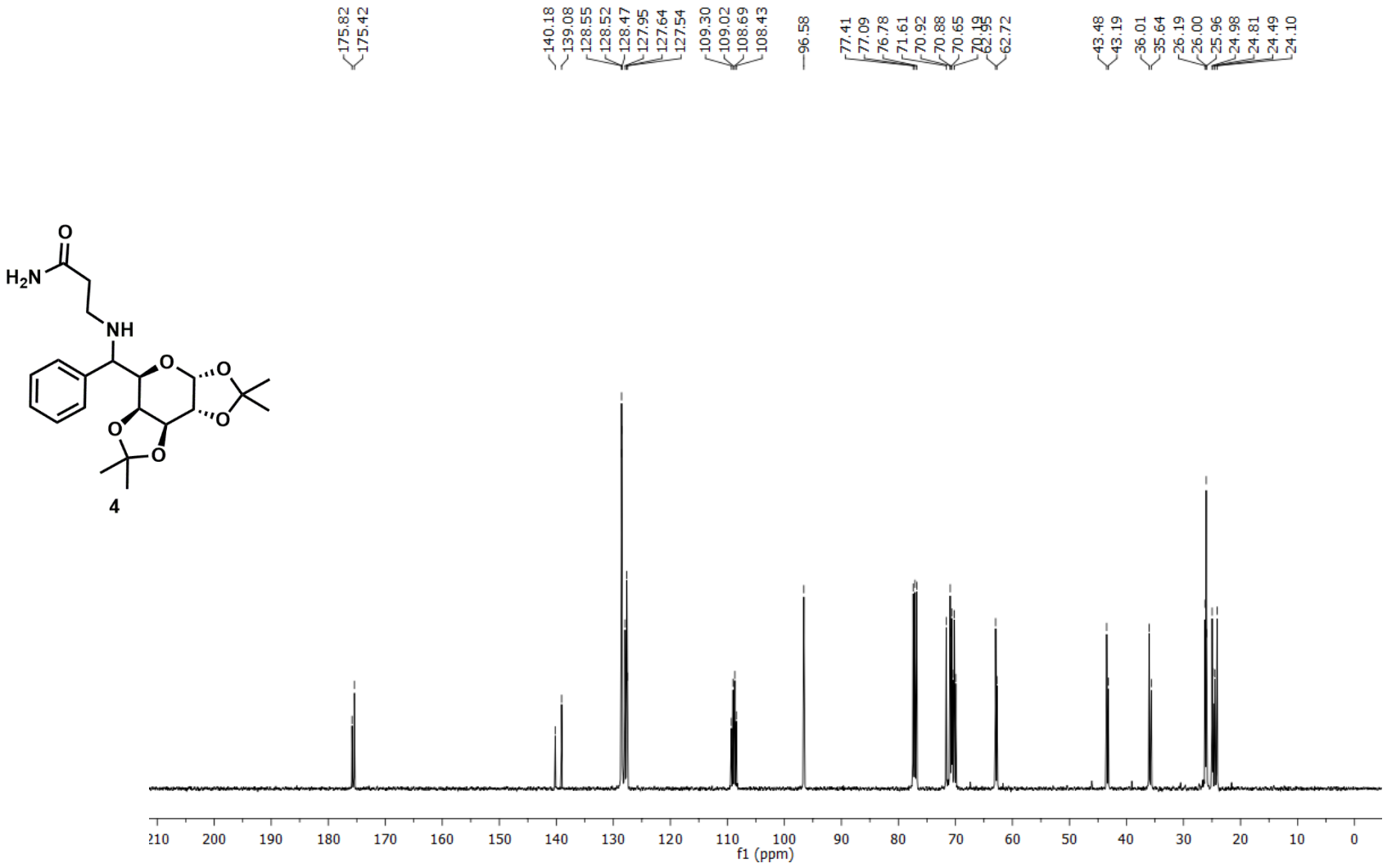


Figure S85. ^{13}C NMR spectrum of **4** (101 MHz, $CDCl_3$)

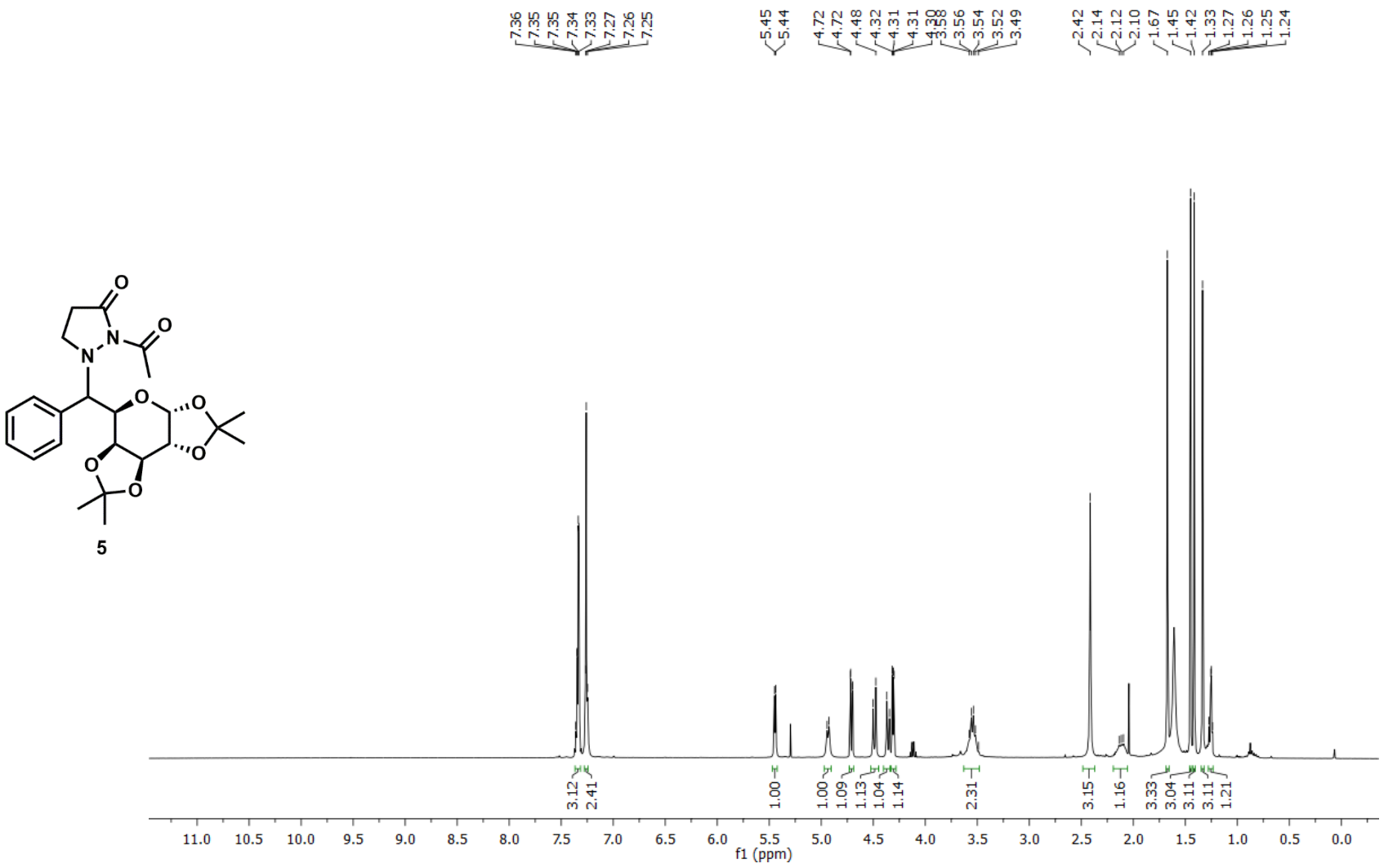


Figure S86. ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$)

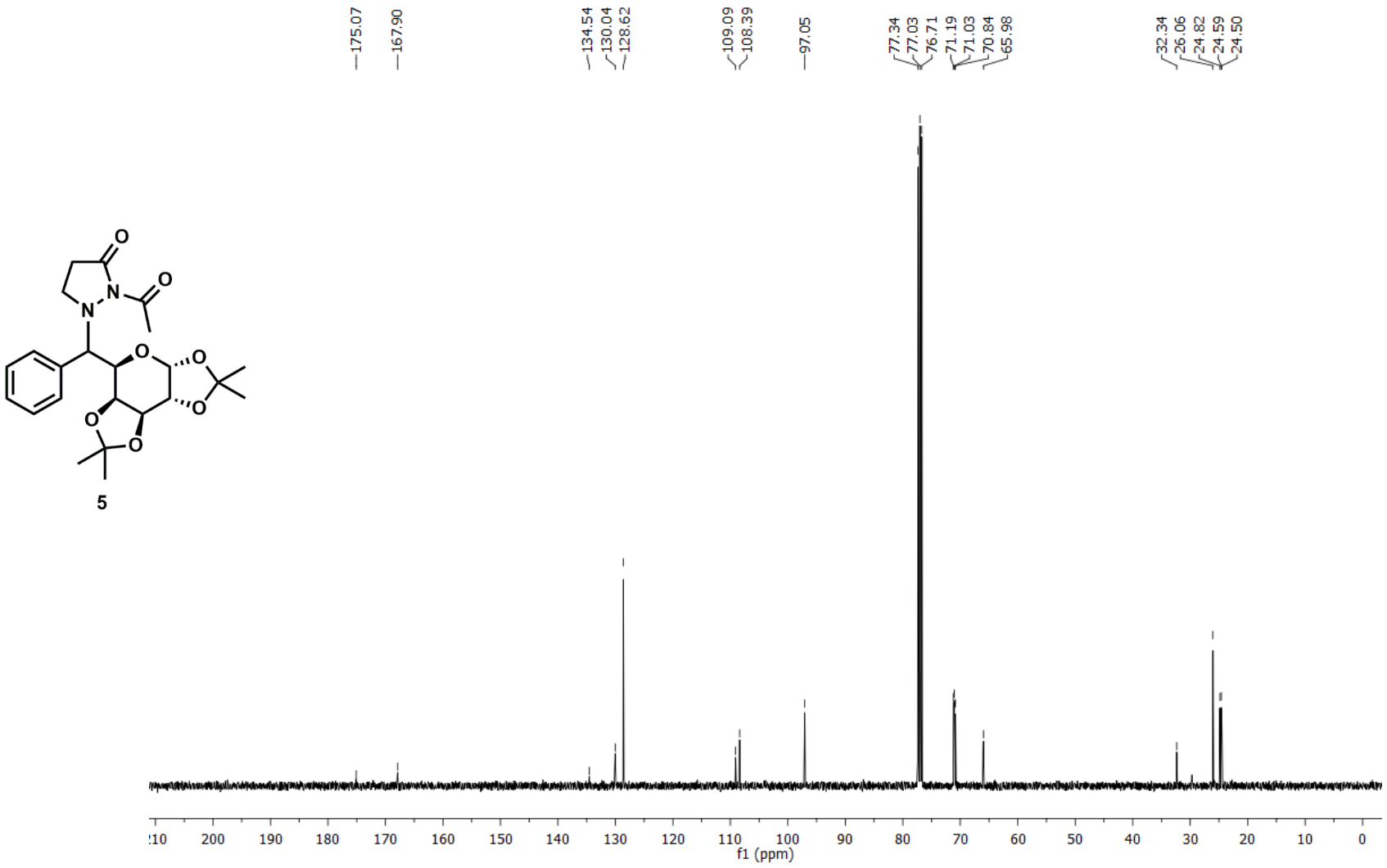


Figure S87. ^{13}C NMR spectrum of **5** (101 MHz, $CDCl_3$)

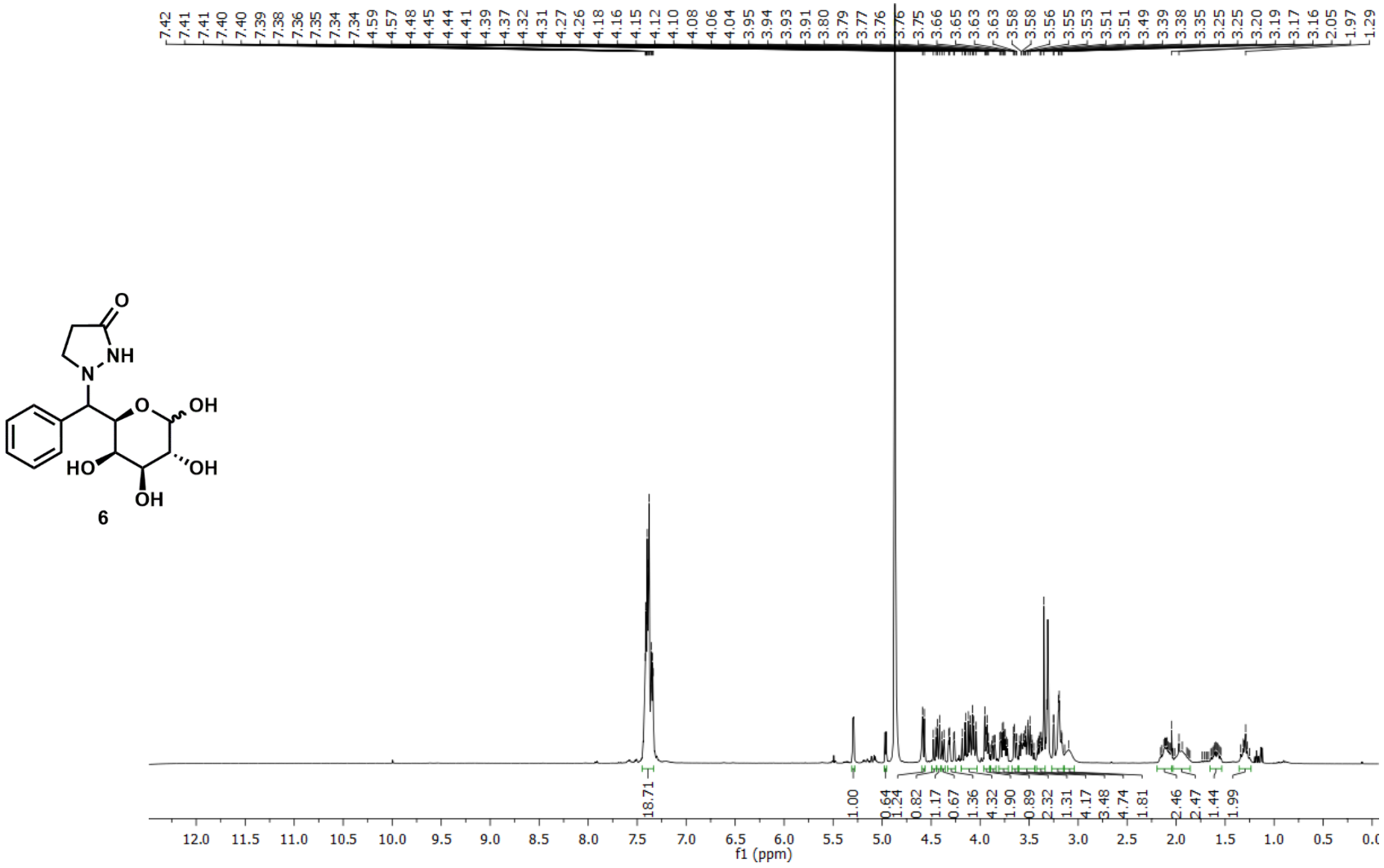


Figure S88. ^{1}H NMR spectrum of **6** (400 MHz, MeOD)

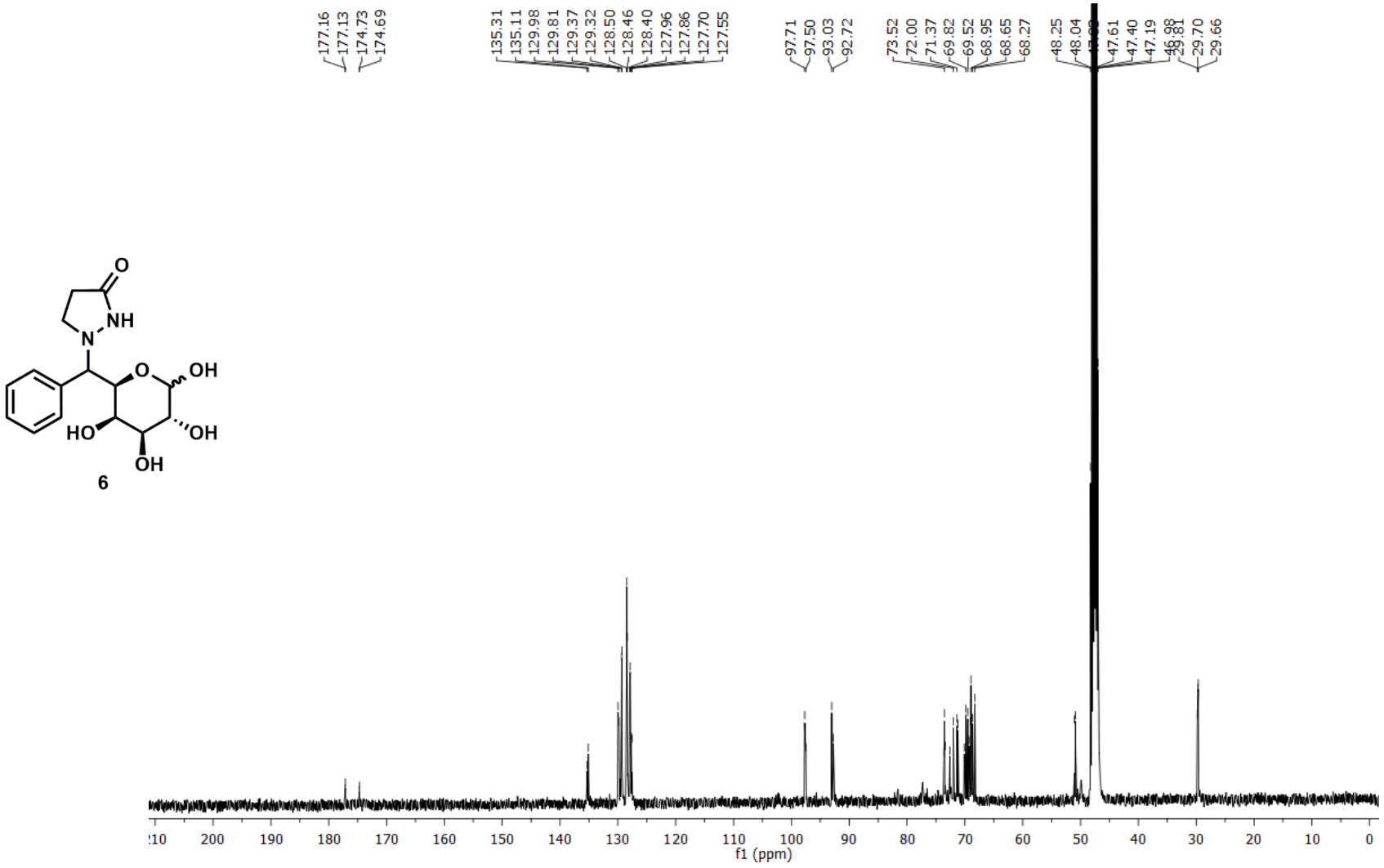


Figure S89. ^{13}C NMR spectrum of **6** (101 MHz, MeOD)

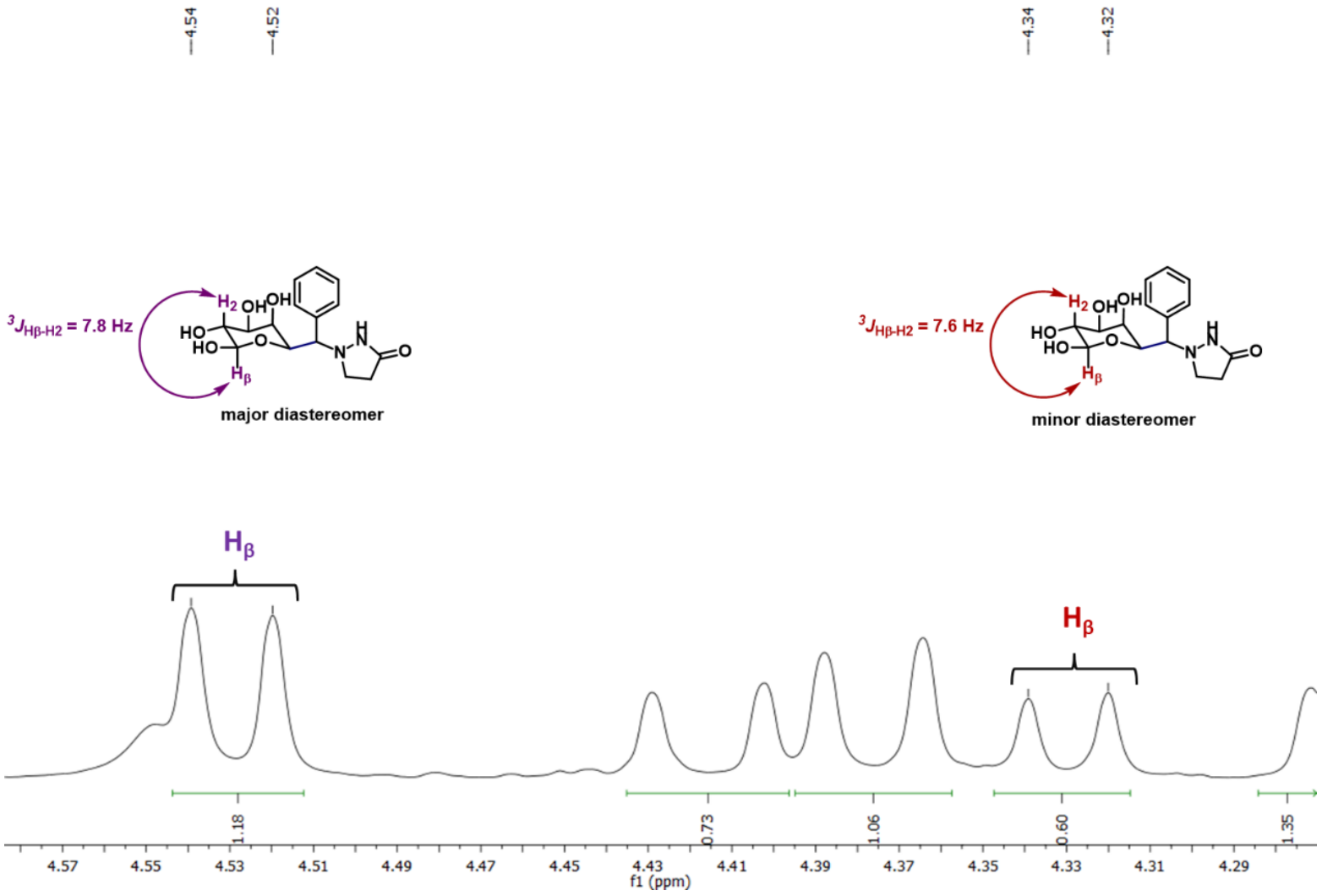


Figure S90. Partial ^{1}H NMR spectrum of **6** (400 MHz, MeOD)

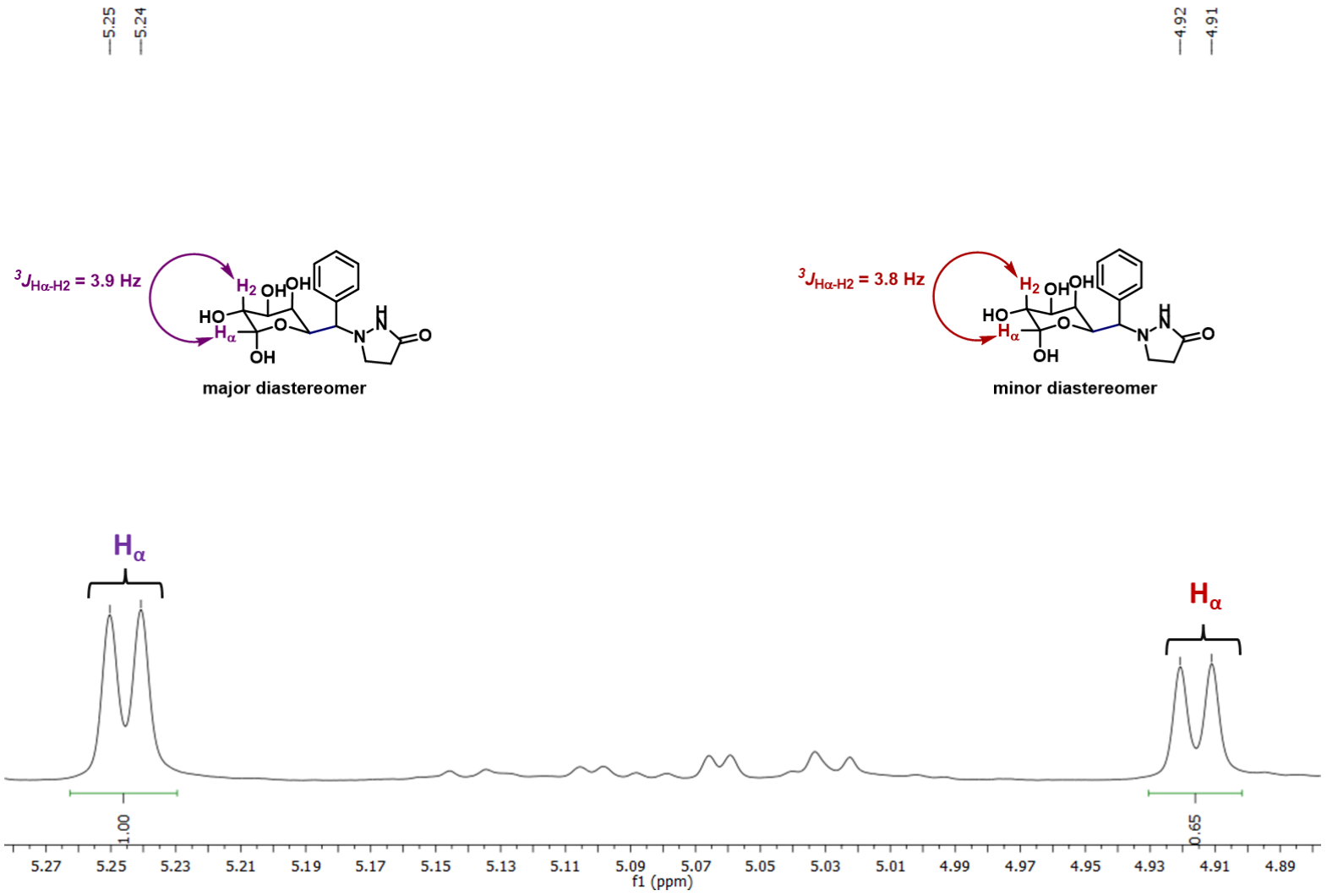


Figure S91. Partial ^{1}H NMR spectrum of **6** (400 MHz, MeOD)

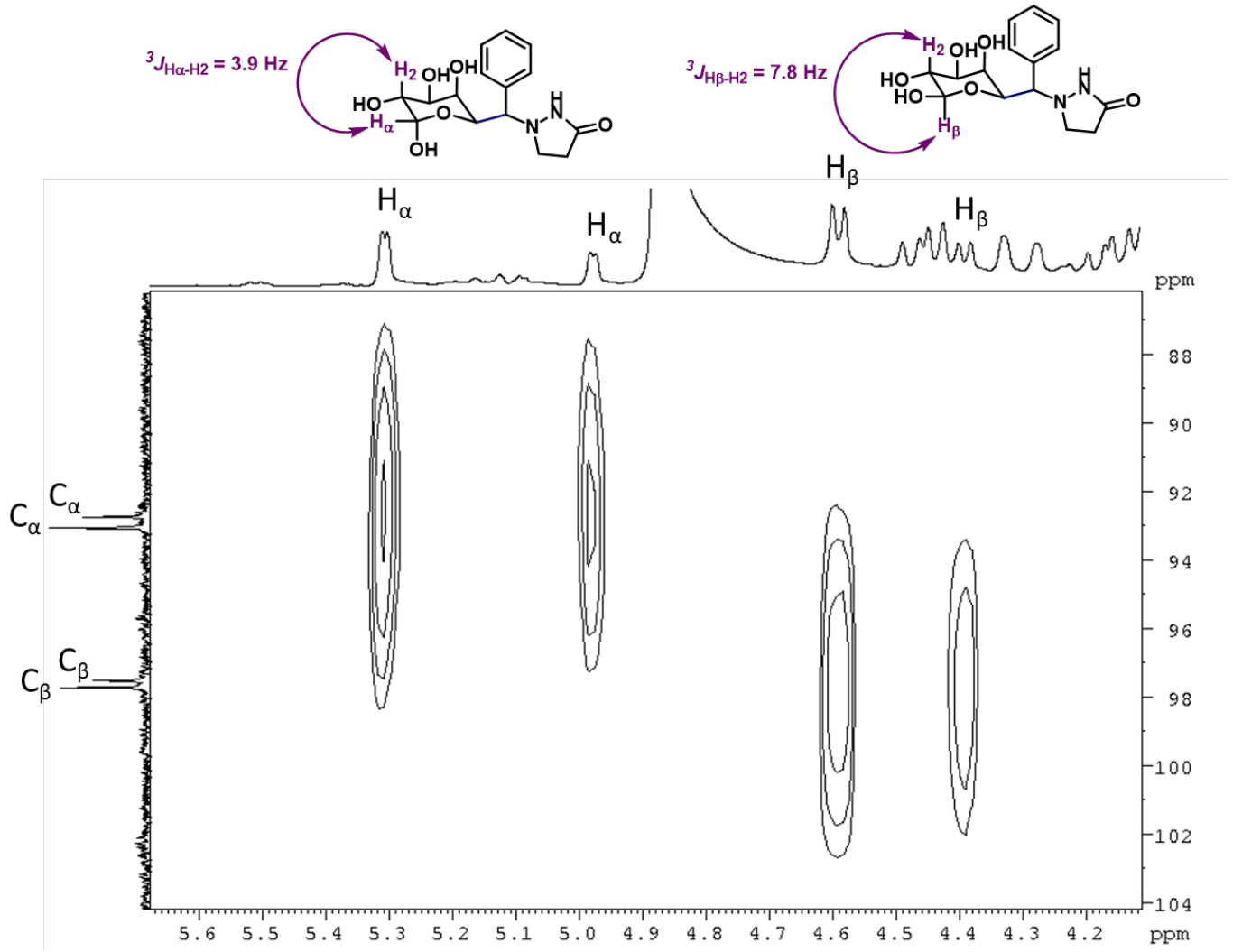


Figure S92. Partial HSQC spectrum of **6** (400 MHz, MeOD)