Supporting Information

Visible-Light-Induced Electron-Donor-Acceptor (EDA) complex-Initiated Synthesis of Non-Anomeric S-Aryl Glycosides

Jin-Yu Hou,‡ Le Zhang,‡ Shi-Yun He, Mei-Ling Ye, Jian Chen, Tian-Le Huang, Guang-Hui Lv, Li Hai, Zhong-Zhen Yang* and Yong Wu*

Key Laboratory of Drug-Targeting and Drug Delivery System of the Education Ministry and Department of Medicinal Chemistry, Sichuan Engineering Laboratory for Plant-Sourced Drug and Sichuan Research Center for Drug Precision Industrial Technology, West China School of Pharmacy, Sichuan University, No. 17 Southern Renmin Road, Chengdu, Sichuan 610041, People's Republic of China.
E-mail: zhongzhenyang1991@163.com; wyong@scu.edu.cn

Table of contents

1.General Information

Unless otherwise specified, materials were purchased from commercial suppliers and used without further purification. All manipulations were performed in a dried sealed tube equipped with a magnetic stir bar under an argon atmosphere. Except for the specially mentioned dry solvent, all the solvents were treated according to general methods. All the reactions were monitored by TLC and were visualized using UV light. The product purification was done using silica gel column chromatography. TLC characterization was performed with precoated silica gel GF254 (0.2 mm), while column chromatography characterization was performed with silica gel (100−200 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS, δ = 0.00 ppm) as the internal standard. ^{1}H NMR spectra were recorded at 400 or 600 MHz (Varian), and ^{13}C NMR spectra were recorded at 100 or 150 MHz (Varian). ^{19}F NMR spectra were recorded at 376 MHz. Chemical shifts are reported in ppm downfield from $CDCl_3$ (δ = 7.26 ppm) for ^{1}H NMR, and chemical shifts for ^{13}C NMR spectra are reported in ppm relative to the central $CDCl_3$ (δ = 77.0 ppm) or DMSO-d6 (δ = 39.6 ppm). Coupling constants were given in Hz. The following notations were used: br-broad, s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet, dd-doublet of doublet, dt-doublet of triplet, td-triplet of doublet, and ddd-doublet of doublet of doublet. Melting points

were measured with a YRT-3 melting point apparatus (Shantou Keyi Instrument & Equipment Co., Ltd., Shantou, China). The blue light source (455nm) was provided by Shanghai 3S Technology Co., Ltd SSSTECH-LAL1CV 1.0 parallel reactor (Figure S1). The volume of the reaction tube is 10 ml.

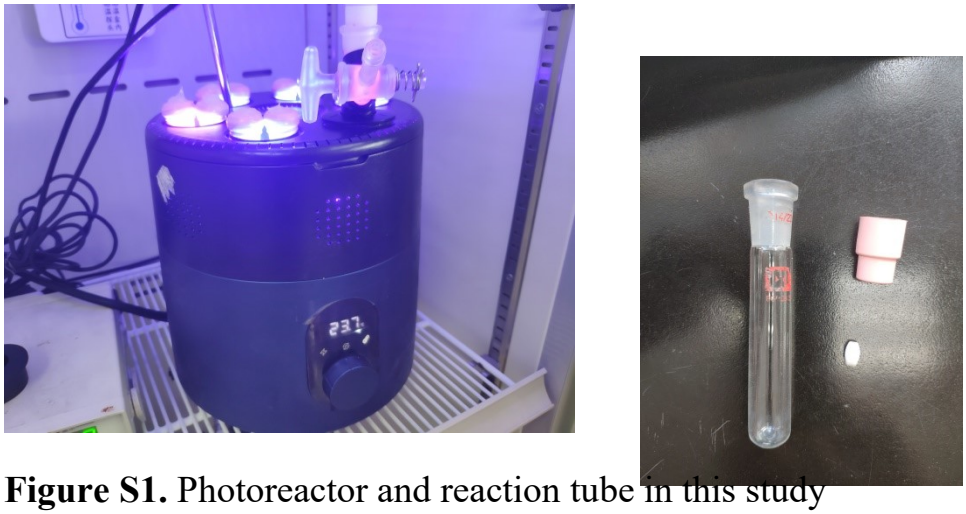
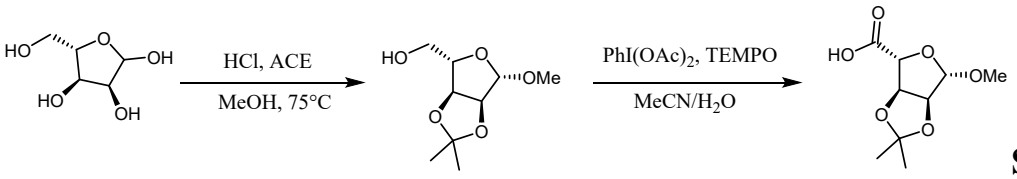


Figure S1. Photoreactor and reaction tube in this study

2.Substrates synthesis

2.1 General procedure for the synthesis of carboxylic acid

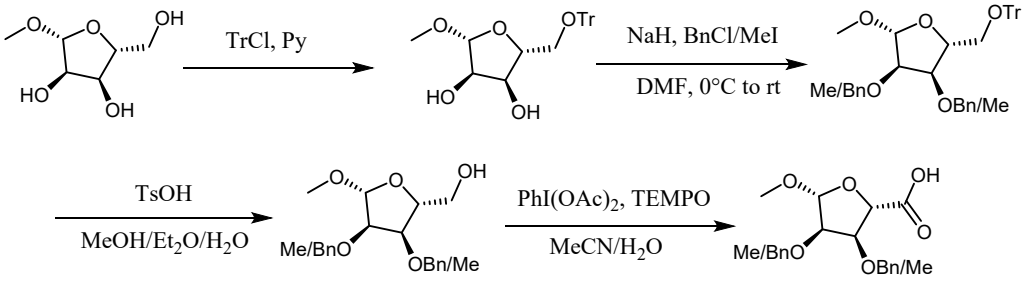


Scheme S1. General procedure for the synthesis of ribose-derived carboxylic acid.

Step 1[1]**:** To a 250 mL round bottom flask was added D-ribose (10.0 g, 66.1 mmol, 1 equiv.), methanol (40 mL), and acetone (40 mL). Next, concentrated HCl (1 mL) was added at room temperature, the flask was

heated to 75 °C for 4 h. The solution was cooled to room temperature and filtered to remove the solid then sat. Na_2CO_3 was added to adjust pH above 7. The solution was extracted by ethyl acetate, washed by brine, dried by Na_2SO_4, combined the organic phase and concentrated with reduced pressure. The desired crude product was obtained as a faint yellow oil (10.8 g, 80%)

Step 2[2]**:** The acid was prepared according to the reported paper. TEMPO (0.2 equiv.) and $PhI(OAc)_2$ (3 equiv.) were added to a solution of alcohol obtained from above step (1.0 equiv.) in $MeCN/H_2O$ (1:1, v/v, 0.2 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluant to afford carboxylic acid in more than 89% yield.



Scheme S2. General procedure for the synthesis of Bn-protected ribose-derived carboxylic acid.

Step 1[3]**:** To a solution of methyl beta D-ribofuranoside (1.0 equiv) in

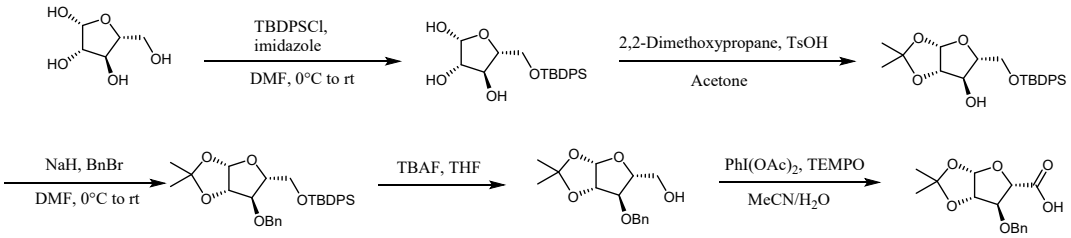
pyridine (0.5 M) was added trityl chloride (1.1 equiv) and the reaction mixture was stirred at room temperature overnight. The solvent was removed in vacuo and the residue was coevaporated with toluene, dissolve in EtOAc and washed with 1 M aqueous $CuSO_4$ solution, brine dried over Na_2SO_4, filtered, and concentrated to afford desired product. Purification by flash column chromatography (cyclohexane/EtOAc) yielded product as a white foam (86% yield).

Step 2[4]**:** The obtained compound from above step was dissolved in DMF (0.2 M) and cooled to 0 °C. Sodium hydride (60% in mineral oil, 4.0 equiv) was added portion-wise. Then, BnCl/MeI (3.0 equiv) was added dropwise. The mixture was stirred overnight and allowed to warm to room temperature. The reaction was quenched with MeOH and thiourea, and stirred for another 2 h at room temperature. The solvents were evaporated in vacuo and the residue was dissolved in EtOAc, and then washed with water. The aqueous phase was extracted with EtOAc, the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo to obtain crude product Purification by flash column chromatography (cyclohexane/CH_2Cl_2/EtOAc) yielded product as a white foam (about 80% yield).

Step 3[2]**:** The obtained compound from above step was dissolved in MeOH/Et_2O/H_2O (10:1:0.1, v/v/v ,0.2 M) followed by addition of TsOH (0.5 equiv). After being stirred for 20 min at room temperature, the

resultant mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluent to get the alcohol.

Step 4[2]**:** The acid was prepared according to the reported paper. TEMPO (0.2 equiv.) and $PhI(OAc)_2$ (3 equiv.) were added to a solution of alcohol obtained from above step (1.0 equiv.) in MeCN/H_2O (1:1, v/v, 0.2 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluant to afford carboxylic acid more than 78% yield.



Scheme S3. General procedure for the synthesis of arabinose-derived carboxylic acid.

Step 1[5]**:** To a solution of methyl beta D-arabinose (1.0 equiv) in DMF(0.1 M) was added imidazole (1.5 equiv) and cooled to 0 °C.Then TBDPSCl (1.5 equiv) was added dropwise. The mixture was stirred

overnight and allowed to warm to room temperature. The solvents were evaporated in vacuo and the residue was dissolved in EtOAc, and then washed with water. The aqueous phase was extracted with EtOAc, the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo to obtain crude product Purification by flash column chromatography (cyclohexane/ EtOAc) yielded product as a colorless oil (83% yield).

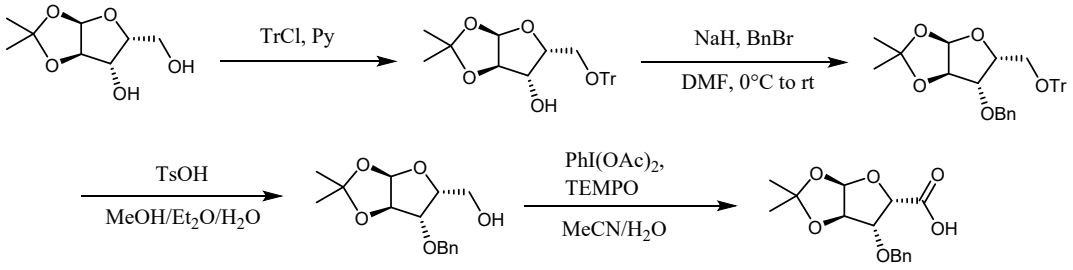
Step 2[6]**:** The obtained compound from above step was dissolved in acetone and 2, 2-dimethoxypropane (10 mL) and *p*-toluenesulfonic acid was added. The reaction was neutralized by triethylamine and concentrated after stired 30 min at room temperature. The solvents were evaporated in vacuo, purification by flash column chromatography (cyclohexane / EtOAc). yielded product as a colorless oil (84% yield).

Step 3[4]**:** The obtained compound from above step was dissolved in DMF (0.1 M) and cooled to 0 °C. Sodium hydride (60% in mineral oil, 2.0 equiv) was added portion wise. Then, BnCl (2.0 equiv) was added dropwise. The mixture was stirred overnight and allowed to warm to room temperature. The reaction was quenched with MeOH and thiourea, and stirred for another 2 h at room temperature. The solvents were evaporated in vacuo and the residue was dissolved in EtOAc, and then washed with water. The aqueous phase was extracted with EtOAc, the combined organic phases were washed with water, dried over Na_2SO_4,

filtered, and concentrated in vacuo to obtain crude product as an oil. Purification by flash column chromatography (cyclohexane / EtOAc). yielded product as a white solid (87% yield).

Step 4[5]**:** The obtained compound from above step was dissolved in anhydrous THF (0.5 M) , was reacted with TBAF (1 M in THF, 1.2 equiv). The solution was stirred at room temperature for 2 h. The solvents were evaporated in vacuo, purification by flash column chromatography (cyclohexane / EtOAc). yielded product as a white solid (79% yield).

Step 5[2]**:** The acid was prepared according to the reported paper. TEMPO (0.2 equiv.) and $PhI(OAc)_2$ (3 equiv.) were added to a solution of alcohol obtained from above step (1.0 equiv.) in $MeCN/H_2O$ (1:1, v/v, 0.2 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluant to afford carboxylic acid 78% yield.



Scheme S4. General procedure for the synthesis of xylose-derived

carboxylic acid.

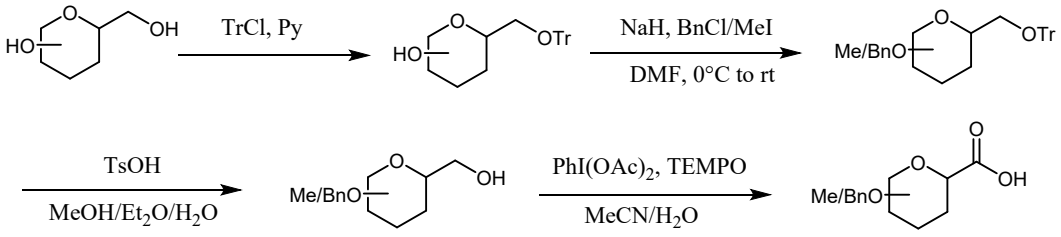
Step 1[3]**:** To a solution of 1,2-O-Isopropylidene-alpha-D-xylofuranose (1.0 equiv) in pyridine (0.5 M) was added trityl chloride (1.1 equiv) and the reaction mixture was stirred at room temperature overnight. The solvent was removed in vacuo and the residue was coevaporated with toluene, dissolve in EtOAc and washed with 1 M aqueous $CuSO_4$ solution, brine dried over Na_2SO_4, filtered, and concentrated to afford desired product. Purification by flash column chromatography (cyclohexane/EtOAc) yielded product as a white foam (83% yield).

Step 2[4]**:** The obtained compound from above step was dissolved in DMF (0.2 M) and cooled to 0 °C. Sodium hydride (60% in mineral oil, 2.0 equiv) was added portion-wise. Then, BnCl (1.5 equiv) was added dropwise. The mixture was stirred overnight and allowed to warm to room temperature. The reaction was quenched with MeOH and thiourea, and stirred for another 2 h at room temperature. The solvents were evaporated in vacuo and the residue was dissolved in EtOAc, and then washed with water. The aqueous phase was extracted with EtOAc, the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo to obtain crude product Purification by flash column chromatography (cyclohexane/CH_2Cl_2/EtOAc) yielded product as a white foam (81% yield).

Step 3[2]**:** The obtained compound from above step was dissolved in

MeOH/Et_2O/H_2O (10:1:0.1, v/v/v ,0.2 M) followed by addition of TsOH (0.5 equiv). After being stirred for 20 min at room temperature, the resultant mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluent to get the alcohol.

Step 4[2]**:** The acid was prepared according to the reported paper. TEMPO (0.2 equiv.) and $PhI(OAc)_2$ (3 equiv.) were added to a solution of alcohol obtained from above step (1.0 equiv.) in MeCN/H_2O (1:1, v/v, 0.2 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluant to afford carboxylic acid 78% yield.



Scheme S5. General procedure for the synthesis of Bn/Me-protected hexose-derived carboxylic acid.

Step 1[3]**:**To a solution of methyl-α-D-glucopyranoside (arbutin) (1.0

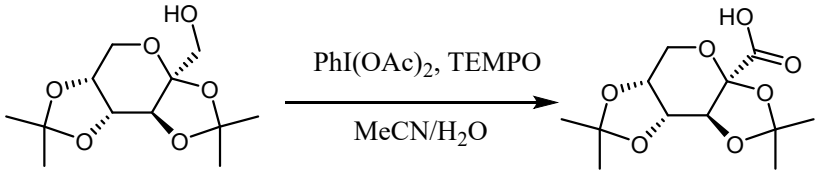
equiv) in pyridine (0.5 M) was added trityl chloride (1.1 equiv) and the reaction mixture was stirred at room temperature overnight. The solvent was removed in vacuo and the residue was coevaporated with toluene, dissolve in EtOAc and washed with 1 M aqueous $CuSO_4$ solution, brine dried over Na_2SO_4, filtered, and concentrated to afford desired product. Purification by flash column chromatography (cyclohexane/EtOAc) yielded product as a white foam (80% yield).

Step.2[1,4]**:** The obtained compound from above step was dissolved in DMF (0.2 M) and cooled to 0 °C. Sodium hydride (60% in mineral oil, 6.0 equiv) was added portion-wise. Then, BnCl/MeI (4.5 equiv) was added dropwise. The mixture was stirred overnight and allowed to warm to room temperature. The reaction was quenched with MeOH and thiourea, and stirred for another 2 h at room temperature. The solvents were evaporated in vacuo and the residue was dissolved in EtOAc, and then washed with water. The aqueous phase was extracted with EtOAc, the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo to obtain crude product Purification by flash column chromatography (cyclohexane/CH_2Cl_2/EtOAc) yielded product as a white foam (about 78% yield).

Step.3[2]**:** The obtained compound from above step was dissolved in MeOH/Et_2O/H_2O (10:1:0.1, v/v/v ,0.2 M) followed by addition of TsOH (0.5 equiv). After being stirred for 20 min at room temperature, the

resultant mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluent to get the alcohol.

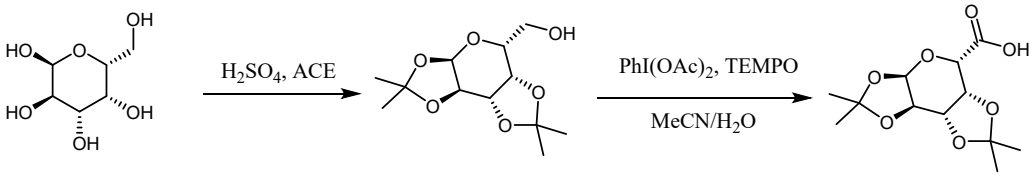
Step.4[2]**:** The acid was prepared according to the reported paper. TEMPO (0.2 equiv.) and $PhI(OAc)_2$ (3 equiv.) were added to a solution of alcohol obtained from above step (1.0 equiv.) in $MeCN/H_2O$ (1:1, v/v, 0.2 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluant to afford carboxylic acid more than 80% yield.



Scheme S6. General procedure for the synthesis of fructose-derived carboxylic acid.

(3aR,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-carboxylic acid[2]**:** To a 50 mL flask, the diacetonefructose (3 g, 11.5 mmol, 1.0 equiv) was treated with TEMPO (360 mg, 2.3 mmol, 0.2 equiv.) and $PhI(OAc)_2$ (11.1g,

34.5mmol, 3 equiv.) in MeCN/H_2O (60 ml, 1:1, v/v) at room temperature for 9 h, and then saturated aqueous $Na_2S_2O_3$ (5 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluant to afford carboxylic acid(2.6 g, 83%).



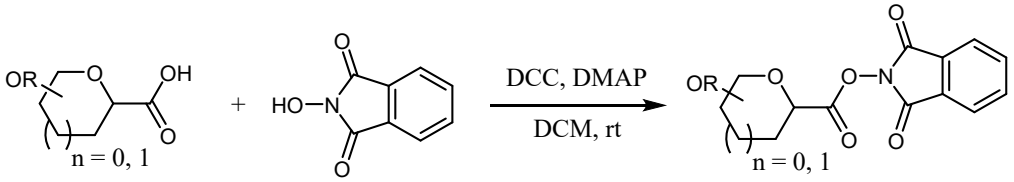
Scheme S7. General procedure for the synthesis of galactose-derived carboxylic acid.

((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methanol[7]**:**To a 250 mL round bottom flask was added D-galactose (7.0 g, 38.8 mmol, 1 equiv.), acetone (250 mL). Next, concentrated H_2SO_4 (7.7 mL) was added at 0 °C. The reaction mixtures were stirred at room temperature for 3-5 h and then neutralized by the addition of sat. Na_2CO_3 until pH = 7. The precipitate was removed by filtration and the filtrates were combined and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluent to get the product as a colorless oil.(8.5 g, 84%).

(3aR,5S,5aR,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-

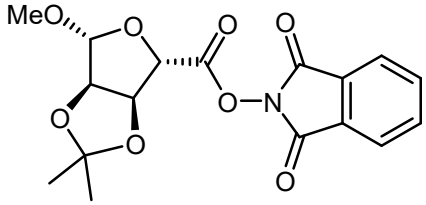
bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-carboxylic acid[2]**:** The acid was prepared according to the reported paper. TEMPO (0.2 equiv.) and $PhI(OAc)_2$ (3 equiv.) were added to a solution of alcohol obtained from above step (1.0 equiv.) in $MeCN/H_2O$ (1:1, v/v, 0.2 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluant to afford carboxylic acid 87% yield.

2.2 Synthetic procedure of N-hydroxyphthalimide esters

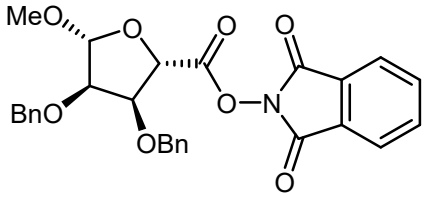


A round-bottom flask or culture tube was charged with carboxylic acid derived from sugar (1.0 equiv), N-hydroxyphthalimide (1.1 equiv) and 4-dimethylaminopyridine (0.05 equiv). Dichloromethane was added (0.1- 0.2 M), and the mixture was stirred vigorously. Dicyclohexylcarbodiimide (DCC, 1.1 equiv) was added, and then the mixture was allowed to stir until the acid was consumed (determined by TLC). Typical reaction times were between 0.5 h to 12 h. The mixture was filtered through a thin pad of Celite and rinsed with additional

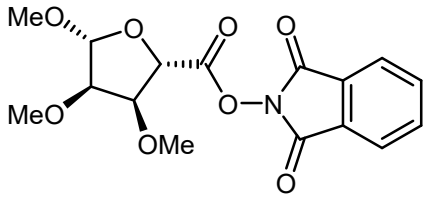
CH_2Cl_2. The solvent was removed under reduced pressure, and purification of the crude mixture by column chromatography (DCM/hexane/ethyl acetate as eluent) afforded the desired N-hydroxyphthalimide esters.



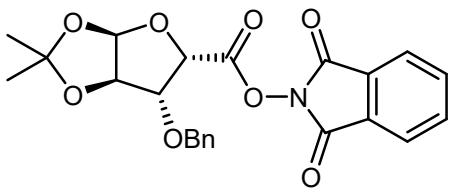
1,3-dioxoisoindolin-2-yl (3aS,4S,6R,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole-4-carboxylate (1a): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.36 (d, *J* = 5.8 Hz, 1H), 5.14 (s, 1H), 5.00 (s, 1H), 4.66 (d, *J* = 5.8 Hz, 1H), 3.50 (s, 3H), 1.52 (s, 3H), 1.35 (s, 3H). The compound was identified by spectral comparison with literature data.[4]



1,3-dioxoisoindolin-2-yl (2S,3S,4R,5R)-3,4-bis(benzyloxy)-5-methoxytetrahydrofuran-2-carboxylate (1b): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.42 – 7.28 (m, 10H), 5.00 (d, *J* = 6.6 Hz, 2H), 4.79 (d, *J* = 11.7 Hz, 1H), 4.71 – 4.60 (m, 4H), 3.87 (d, *J* = 4.5 Hz, 1H), 3.42 (s, 3H). The compound was identified by spectral comparison with literature data.[4]

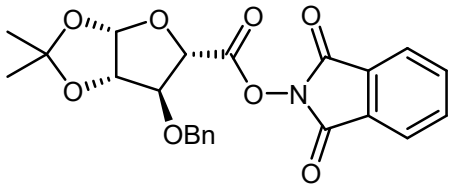


1,3-dioxoisoindolin-2-yl (2S,3S,4R,5R)-3,4,5-trimethoxytetrahydrofuran-2-carboxylate (1c): ^{1}H-NMR (600 MHz, Chloroform-*d*) δ 7.93 – 7.85 (m, 2H), 7.85 – 7.76 (m, 2H), 5.05 (s, 1H), 4.85 (d, *J* = 4.5 Hz, 1H), 4.47 (s, 1H), 3.83 (s, 1H), 3.57 (s, 3H), 3.53 (s, 3H), 3.46 (s, 3H). The compound was identified by spectral comparison with literature data.[4]

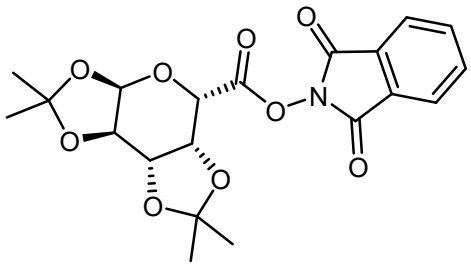


1,3-dioxoisoindolin-2-yl (3aR,5S,6R,6aR)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-

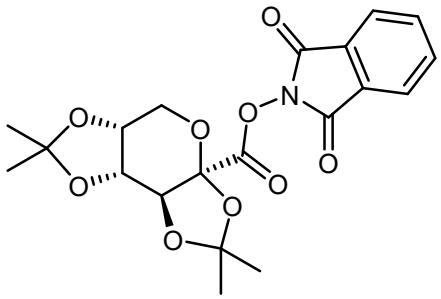
d][1,3]dioxole-5-carboxylate (1d): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.46 – 7.27 (m, 5H), 6.11 (d, *J* = 3.4 Hz, 1H), 5.20 (d, *J* = 3.5 Hz, 1H), 4.92 (d, *J* = 11.9 Hz, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.56 (d, *J* = 3.4 Hz, 1H), 4.46 (d, *J* = 3.5 Hz, 1H), 1.51 (s, 3H), 1.32 (s, 3H). The compound was identified by spectral comparison with literature data.[4]



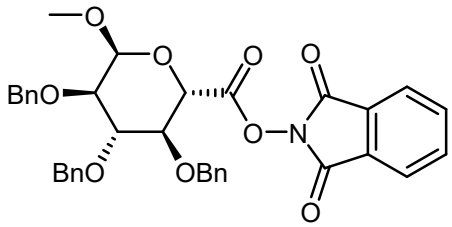
1,3-dioxoisoindolin-2-yl (3aS,5S,6S,6aS)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole-5-carboxylate (1e): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.39 – 7.28 (m, 5H), 6.07 (d, *J* = 3.4 Hz, 1H), 5.07 (d, *J* = 0.8 Hz, 1H), 4.78 – 4.72 (m, 2H), 4.71 – 4.65 (m, 2H), 1.50 (s, 3H), 1.33 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 166.3, 161.4, 136.5, 134.9, 128.8, 128.7, 128.3, 128.0, 124.1, 113.8, 107.0, 84.4, 82.9, 80.7, 72.5, 25.9, 25.7. HRMS (ESI) m/z $[M + Na]^+$ calculated for 462.1159, found 462.1161.



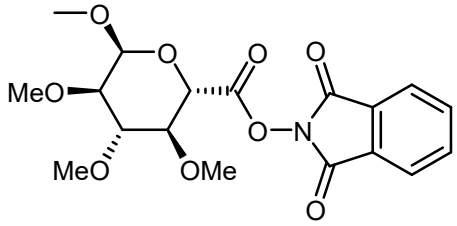
1,3-dioxoisoindolin-2-yl (3aR,5S,5aR,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-carboxylate (1f): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.70 (d, *J* = 5.0 Hz, 1H), 4.84 (d, *J* = 2.2 Hz, 1H), 4.74 (qd, *J* = 7.5, 2.4 Hz, 2H), 4.46 (dd, *J* = 5.0, 2.6 Hz, 1H), 1.61 (s, 3H), 1.54 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H). The compound was identified by spectral comparison with literature data.[4]



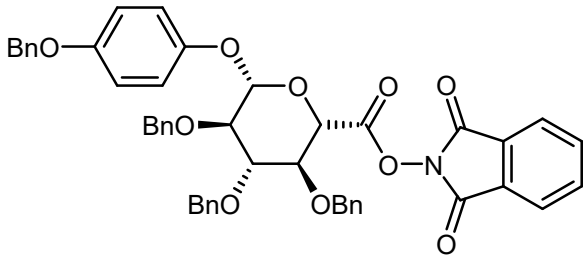
1,3-dioxoisoindolin-2-yl (3aR,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-carboxylate (1g): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.88 (d, *J* = 2.5 Hz, 1H), 4.69 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.31 (d, *J* = 7.9 Hz, 1H), 3.96 (s, 2H), 1.62 (s, 3H), 1.57 (s, 3H), 1.51 (s, 3H), 1.37 (s, 3H). The compound was identified by spectral comparison with literature data.[4]



1,3-dioxoisoindolin-2-yl (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-carboxylate (1h): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.43 – 7.26 (m, 15H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.93 (d, *J* = 10.1 Hz, 1H), 4.86 (d, *J* = 11.0 Hz, 2H), 4.82 (d, *J* = 2.4 Hz, 1H), 4.71 (d, *J* = 3.4 Hz, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 10.0 Hz, 1H), 4.07 (t, *J* = 9.2 Hz, 1H), 3.96 – 3.90 (m, 1H), 3.63 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.49 (s, 3H). The compound was identified by spectral comparison with literature data.[4]

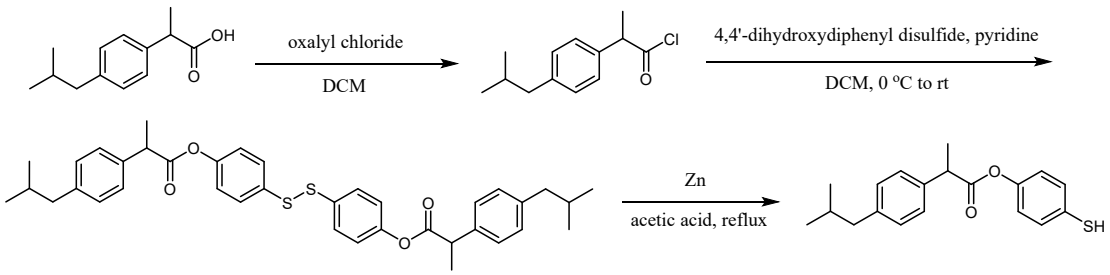


1,3-dioxoisoindolin-2-yl (2S,3S,4S,5R,6S)-3,4,5,6-tetramethoxytetrahydro-2H-pyran-2-carboxylate (1i): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.95 (d, *J* = 3.5 Hz, 1H), 4.42 (d, *J* = 9.9 Hz, 1H), 3.65 (d, *J* = 1.7 Hz, 6H), 3.57 (d, *J* = 9.6 Hz, 1H), 3.54 (s, 3H), 3.52 (s, 3H), 3.50 (d, *J* = 2.9 Hz, 1H), 3.30 (dd, *J* = 9.5, 3.5 Hz, 1H). The compound was identified by spectral comparison with literature data.[4]



1,3-dioxoisoindolin-2-yl (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-(4-(benzyloxy)phenoxy)tetrahydro-2H-pyran-2-carboxylate (1j): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.48 – 7.27 (m, 20H), 7.13 – 7.06 (m, 2H), 6.98 – 6.92 (m, 2H), 5.08 – 5.02 (m, 3H), 5.00 – 4.93 (m, 3H), 4.85 (dd, *J* = 10.7, 7.2 Hz, 3H), 4.38 (d, *J* = 9.8 Hz, 1H), 4.12 – 4.05 (m, 1H), 3.85 – 3.76 (m, 2H). The compound was identified by spectral comparison with literature data.[4]

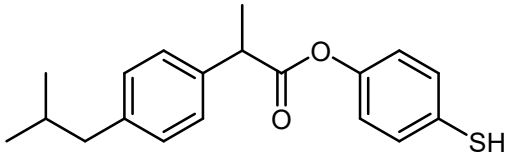
2.3 Synthetic procedure of ibuprofen derivant



Sept 1: To a solution of ibuprofen (1.0 equiv) in DCM (0.5 M) w as added oxalyl chloride (3.0 equiv) and the reaction mixture was s tirred at room temperature for 6 h. The solvent was removed in va cuo to get the crude product.

Sept 2: To a solution of 4,4'-dithiodiphenol (1.0 equiv) in DCM (0.2 M) was added pyridine (2.0 equiv) and cooled to 0 °C.Then the obtained compound from above step dissolved in DCM (0.2 M) was added dropwise. The mixture was stirred 6 h and allowed to warm to room temperature. The solvents were evaporated in vacuo and the residue was purified by flash column chromatography (cyclohexane/ EtOAc) to afford the product more than 95% yield.

Sept 3: The obtained compound from above step was dissolved in acetic acid (0.2 M) followed by addition of Zn powder (8.5 equiv). After refluxed for 4 h, the resultant mixture was filtered and the filtrate was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluent to get the product. (93% yield).



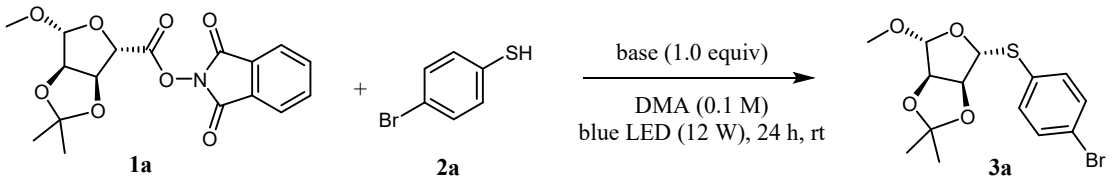
4-mercaptophenyl 2-(4-isobutylphenyl)propanoate (2z): Pale oil **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.93 – 6.82 (m, 2H), 3.91 (q, *J* = 7.1 Hz, 1H), 3.43 (s, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.86 (dp, *J* = 13.6, 6.8 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 6H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 173.2, 149.2, 140.9, 137.1, 130.8, 129.5, 127.5, 127.2 122.2, 45.2, 45.1, 30.2, 22.4, 18.5. HRMS (ESI) m/z $[M + Na]^+$ calculated for 649.2417, found 649.2419.

3. General Procedures and Optimization of Reaction Conditions

3.1 General procedure (standard condition): To an oven-dried 10 mL glass tube equipped with a stir bar, was added glycosyl NHP ester **1** (0.15 mmol), thiophenol **2** (0.1 mmol), *i*Pr_2NEt (0.1 mmol). The tube was evacuated and back-filled with N_2 (three times), then sealed with rubber stopper and parafilm. Then, anhydrous DMSO (1 mL) was added using a syringe. The solution was then stirred at room temperature under the irradiation of 12 W Blue LEDs for 24 h using electronic fan to cool the tube (reaction setup shown in Figure). After completion of the reaction, 5 mL water was added and extracted by ethyl acetate (3 × 5 mL). The combined organic layer was washed with brine (5 mL) and then dried over anhydrous Na_2SO_4 and evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel eluting with hexane/ethyl acetate or hexane/dichloromethane.

3.2 Optimization of Reaction Conditions

Table S1. Base screening.

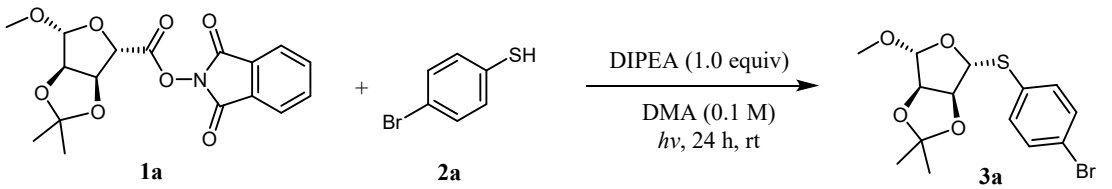


1a 2a 3a

entry [a]	base	yield [b](%)	d.r.
1	DIPEA	85	>20:1
2	TMEDA	73	>20:1
3	DABCO	trace	--
4	Et_3N	62	>20:1
5	DMAP	75	>20:1
6	Cs_2CO_3	trace	--
7	Na_2CO_3	52	>20:1
8	CsF	39	>20:1

[a] Reaction conditions: A mixture of 1a (0.15 mmol), 2a (0.10 mmol), Base (0.10 mmol) in DMA (1.0 mL) was irradiated with 12 W blue LEDs at room temperature under N_2 for 24 h; [b] Isolated yields.

Table S2. Light source screening.



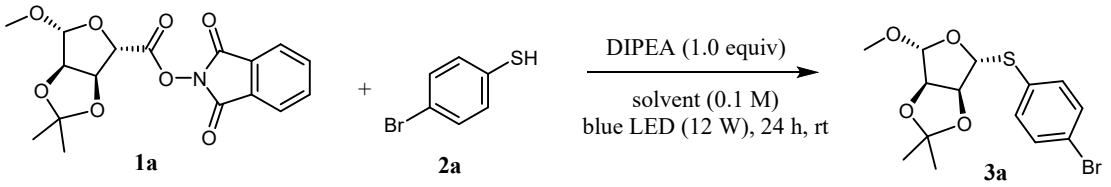
1a 2a 3a

entry [a]	light	yield [b] (%)	d.r.
1	390 nm	trace	>20:1
2	425 nm	37	>20:1

3	Blue LED	85	>20:1
4	Green LED	77	>20:1
5	White LED	67	>20:1

[a] Reaction conditions: A mixture of 1a (0.15 mmol), 2a (0.10 mmol), DIPEA (0.10 mmol) in DMA (1.0 mL) was irradiated with 12 W LEDs at room temperature under N_2 for 24 h; [b] Isolated yields.

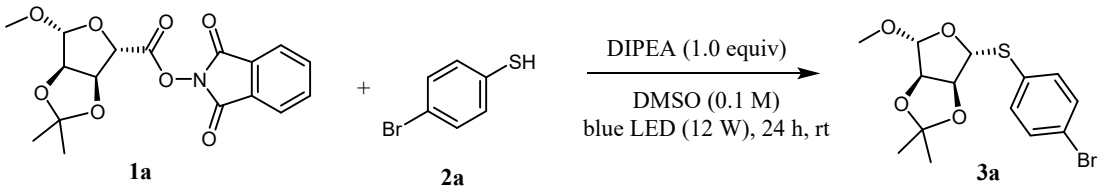
Table S3. Solvent screening.



entry [a]	solvent	yield [b] (%)	d.r.
1	1,4-Dioxane	N.R. [c]	--
2	DMA	85	>20:1
3	CH_3CN	N.R.	--
4	THF	trace	--
5	DMF	76	>20:1
6	DMSO	91	>20:1
7	N-Methyl-2-pyrrolidone	83	>20:1
8	Cyclohexanol	N.R.	--

[a] Reaction conditions: A mixture of 1a (0.15 mmol), 2a (0.10 mmol), DIPEA (0.10 mmol) in solvent (1.0 mL) was irradiated with 12 W blue LEDs at room temperature under N_2 for 24 h; [b] Isolated yields; [c] N.R. = No reaction.

Table S4. Control experiments under standard reaction condition.

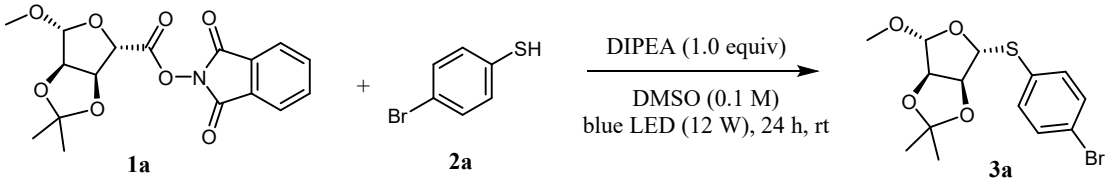


1a **2a** **3a**

entry [a]	change from the standard condition	yield [b] (%)	d.r.
1	standard condition	91	>20:1
2	without *hv*	N.R. [c]	--
3	without DIPEA	N.R.	--
4	air condition	42	>20:1

[a] Reaction conditions: A mixture of 1a (0.15 mmol), 2a (0.10 mmol), DIPEA (0.10 mmol) in DMSO (1.0 mL) was irradiated with 12 W blue LEDs at room temperature under N_2 for 24 h; [b] Isolated yields; [c] N.R. = No reaction.

4. Scale-up reaction:



1a **2a** **3a**

To a 100 mL round bottom flask with magnetic stirrer, glycosyl NHP ester **1a** (1.09 g, 3 mmol), thiophenol **2a** (378.1 mg, 2 mmol), *i*Pr_2NEt (348 ml, 2 mmol), and DMSO (30ml) were added. Then, the bottle was evacuated and back-filled with N_2 (three times). The solution was then stirred at room temperature under the irradiation of Blue LEDs for 24 h using electronic fan to cool the flask. (Figure S2). After completion of the reaction, 50 mL water was added and extracted by ethyl acetate (3 × 50 mL). The combined organic layer was washed with

brine (100 mL) and then dried over anhydrous Na_2SO_4 and evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel eluting with hexane/ethyl acetate to afford the desired product **3a** in 90% yield. It should be noted that two Kessil PR160L-456 nm lamps were used in the gram-scale reaction to provide the blue light source.

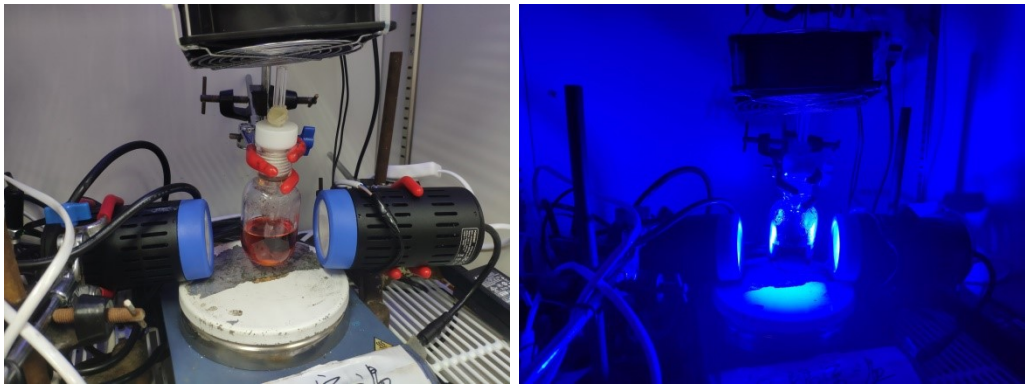
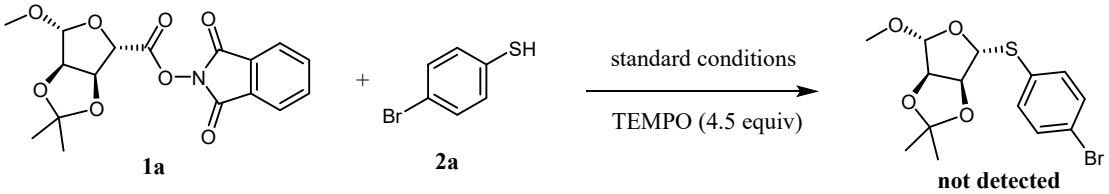


Figure S2 The photoreactor of gram-scale reaction

5.The mechanistic studies

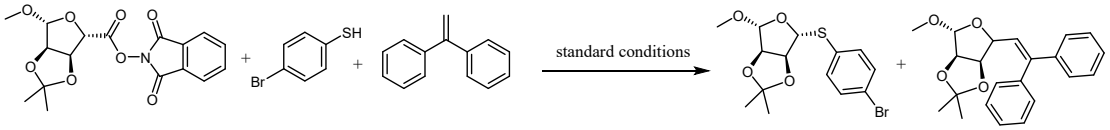
5.1 Radical trapping experiment



1a **2a** **not detected**

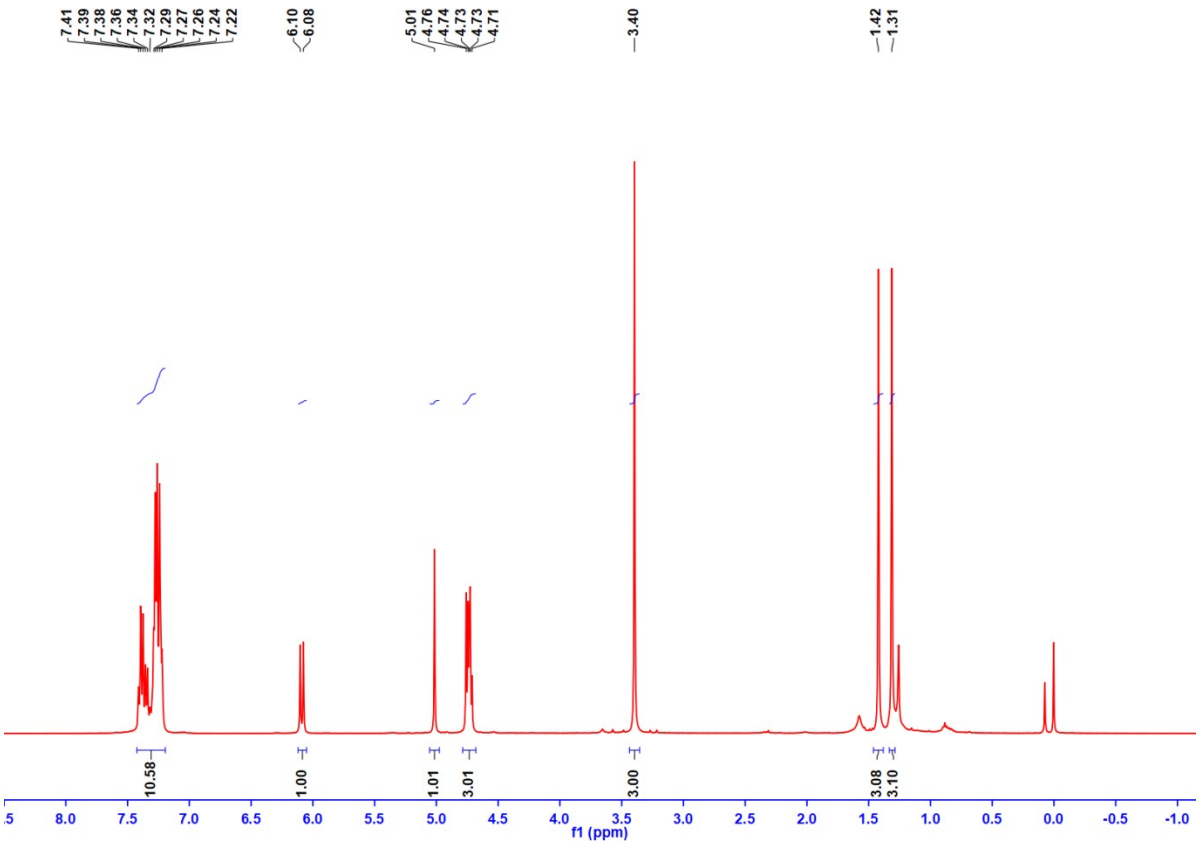
To an oven-dried 10 mL glass tube equipped with a stir bar, was added glycosyl NHP ester **1a** (0.15 mmol), thiophenol **2a** (0.1 mmol), *i*Pr_2NEt (0.1 mmol) ,TEMPO (0.45 mmol),. The tube was evacuated and back-filled with N_2 (three times), then sealed with rubber stopper and

parafilm. Then, anhydrous DMSO (1 mL) was added using a syringe. The solution was then stirred at room temperature under the irradiation of 12 W Blue LEDs for 24 h using electronic fan to cool the tube. After 24 h, no corresponding product **3a** was formed by TLC analysis, suggesting that the in-situ formed glycosyl radical might act as a key intermediate during this transformation.



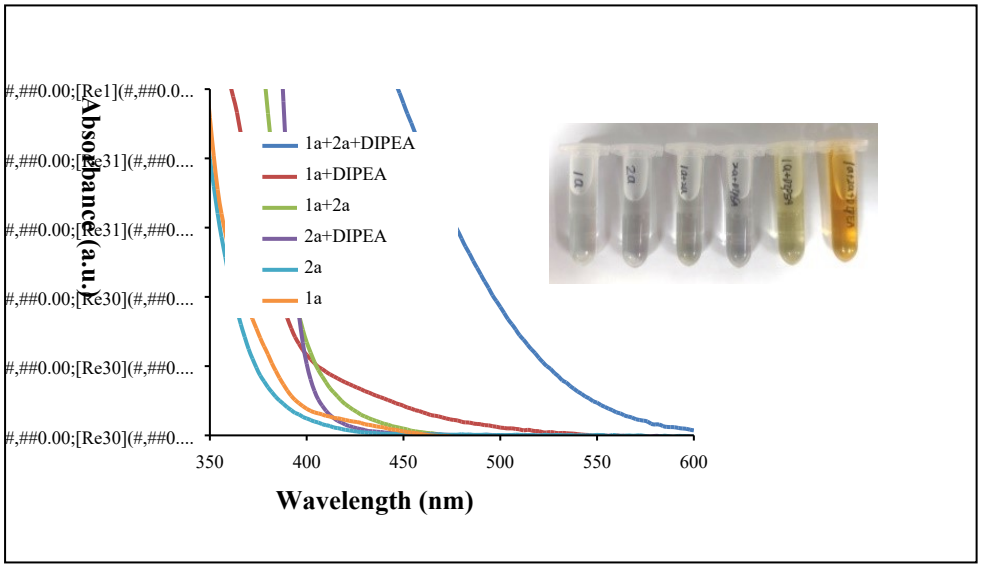
1a **2a** **3a trace** **4 67%**

To an oven-dried 10 mL glass tube equipped with a stir bar, was added glycosyl NHP ester **1a** (0.15 mmol), thiophenol **2a** (0.1 mmol), *i*Pr_2NEt (0.1 mmol) , 1,1-diphenylethylene (0.45 mmol),. The tube was evacuated and back-filled with N_2 (three times), then sealed with rubber stopper and parafilm. Then, anhydrous DMSO (1 mL) was added using a syringe. The solution was then stirred at room temperature under the irradiation of 12 W Blue LEDs for 24 h using electronic fan to cool the tube. After completion of the reaction, corresponding product **3a** was trace and the heck-type product **4** was isolated in 67% yield, indicating that this photo-induced thioglycosidation protocol may proceed through a radical-based mechanism. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.47 – 7.23 (m, 10H), 6.09 (d, *J* = 10.5 Hz, 1H), 5.01 (s, 1H), 4.79 – 4.68 (m, 3H), 3.40 (s, 3H), 1.42 (s, 3H), 1.31 (s, 3H).



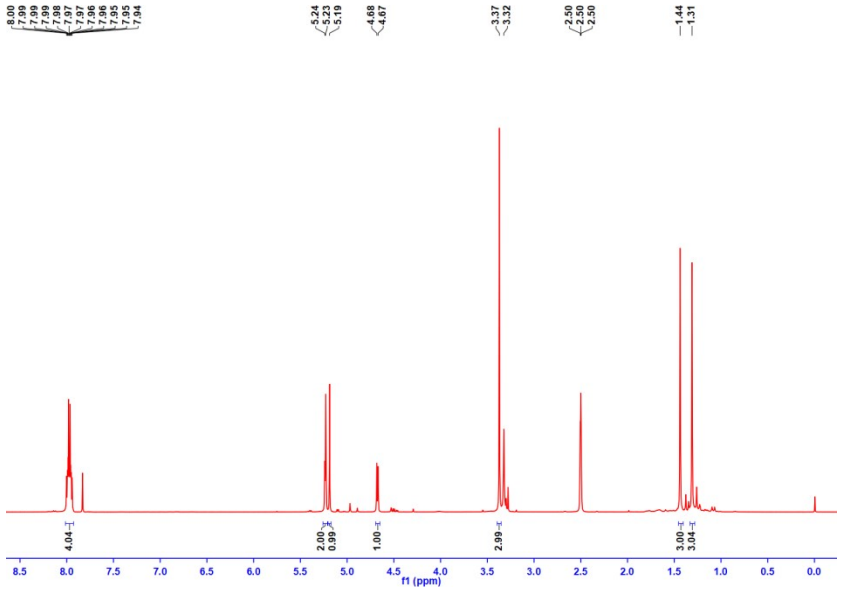
5.2 UV-vis absorption spectra

The UV-vis absorption spectra of glycosyl NHP ester (0.15 M), thiophenol (0.1 M), *i*Pr_2NEt (0.1 M) in DMSO were recored in 1 cm path quartz cuvettes by using a GENESYS UV-Visible spectrophotometer (thermo scientific).

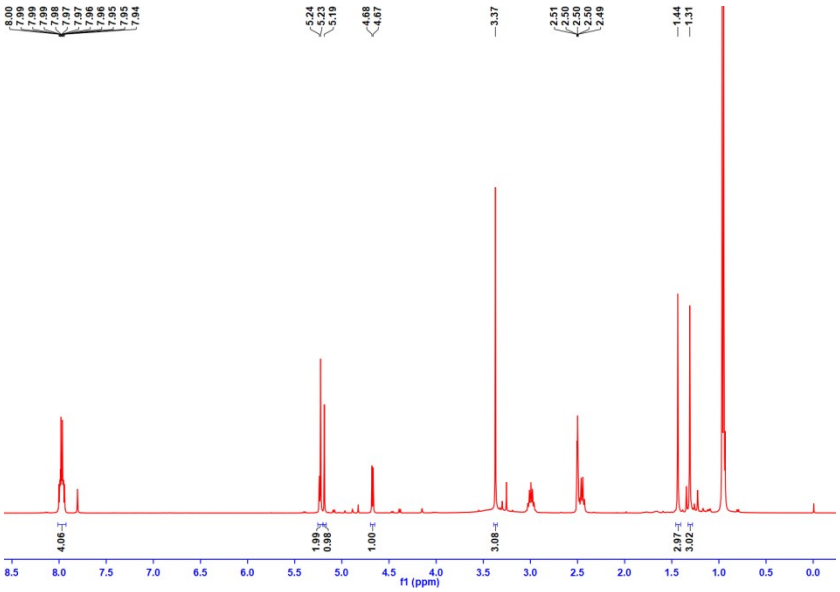


5.3 ^{1}H NMR spectra of 1a and 2a with or without DIPEA

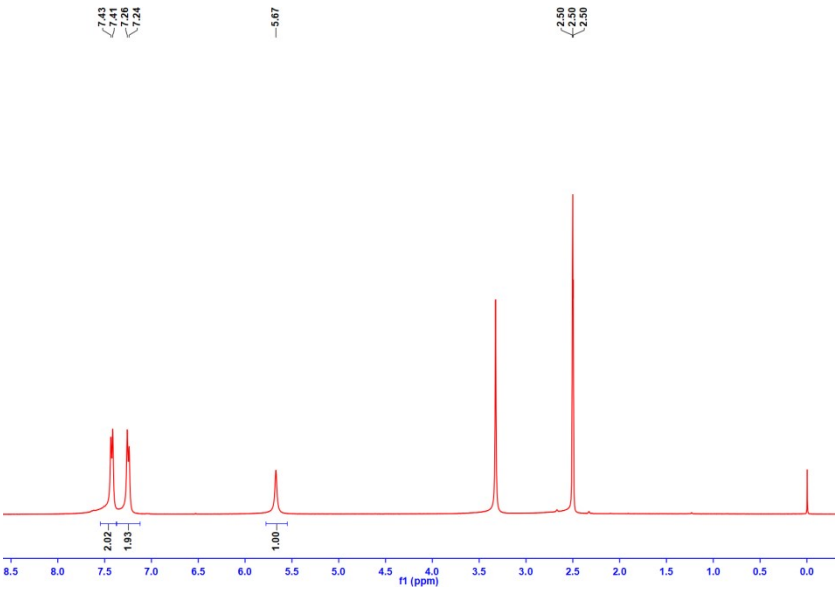
The ^{1}H NMR spectra (400 MHz) of **1a** (0.06 mmol in 0.8 ml d_6-DMSO)



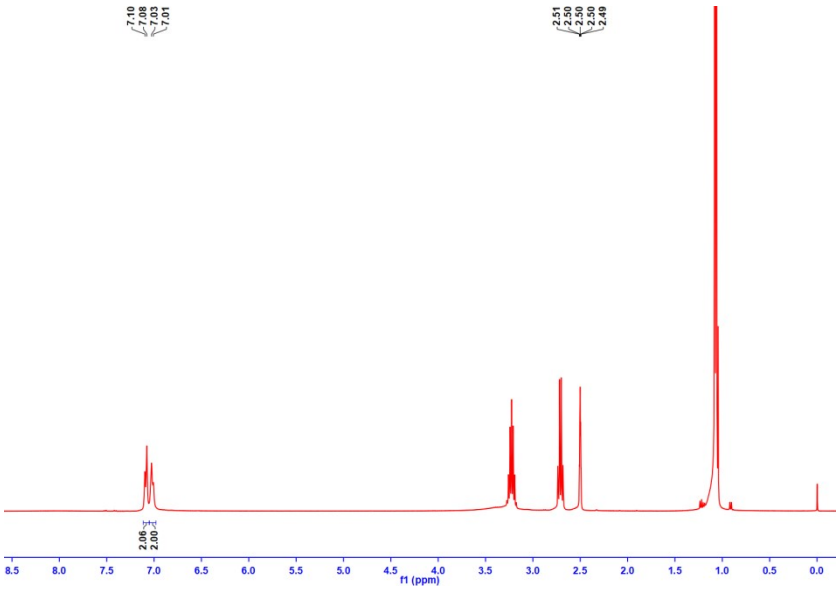
The ^{1}H NMR spectra (400 MHz) of **1a** (0.06 mmol in 0.8 ml d_6-DMSO) + DIPEA (0.04 mmol)



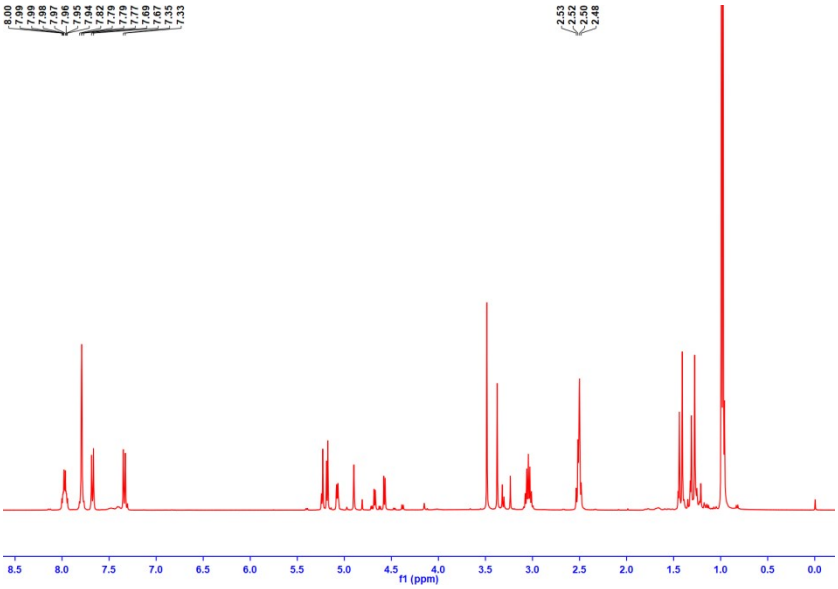
The ^{1}H NMR spectra (400 MHz) of **2a** (0.04 mmol in 0.8 ml d_6-DMSO)



The ^{1}H NMR spectra (400 MHz) of **2a** (0.04 mmol in 0.8 ml d_6-DMSO) + DIPEA (0.04 mmol)

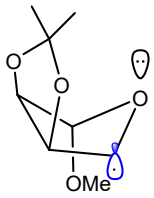


The ^{1}H NMR spectra (400 MHz) of **1a** (0.06 mmol in 0.8 ml d_6-DMSO) + **2a** (0.04 mmol) + DIPEA (0.04 mmol)

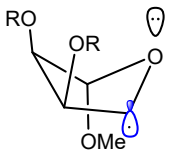


6. Configuration determination

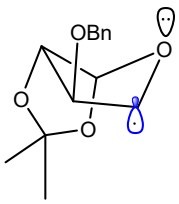
6.1 Plausible conformation of glycosyl radical



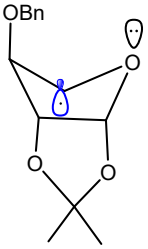
Ribose



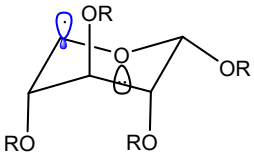
Ribose
R= Me, Bn



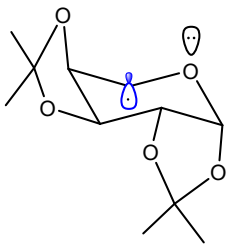
Arabinose



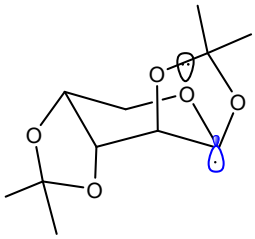
Xylose



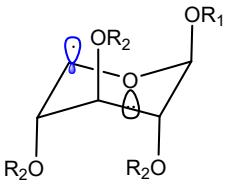
Glucose
R=Me, Bn



Galactose



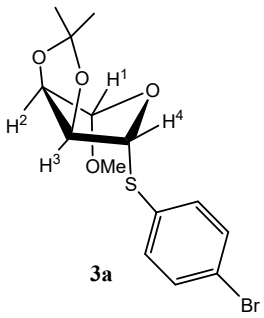
Fructose



Arbutin

The stereochemical outcome of glycosyl radical could be explained by a consequence of a combination of stereoelectronic and steric factors.

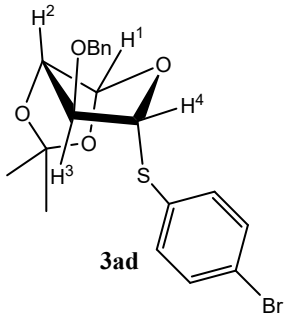
6.2 H-H coupling constant analysis



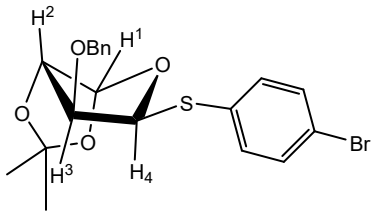
3a

(3aS,4R,6R,6aR)-4-((4-bromophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3a): ^{1}H-NMR (400 MHz, Chloroform-d) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), **5.57 (s, 1H), 5.11 (s, 1H), 4.89 (d, *J* = 5.7 Hz, 1H), 4.71 (d, *J* = 5.8 Hz, 1H),** 3.38 (s, 3H), 1.47 (s, 3H), 1.32 (s, 3H).

For furanose, the hydrogens on the same side of the sugar are coupled. It is easy to assign different hydrogens of the sugar ring based on the chemical shift value: **5.57 (s, H^1 or H^4), 5.11 (s, H^1 or H^4), 4.89 (d, *J* = 5.7 Hz, 1H), 4.71 (d, *J* = 5.8 Hz, 1H).** Therefore, we can conclude that H^1 and H^4 are on the same side of the sugar ring based on the H-H coupling constants.



3ad



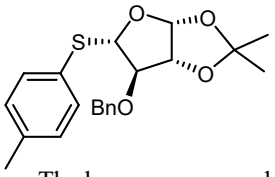
3ad'

(3aR,5R,6S,6aS)-6-(benzyloxy)-5-((4-bromophenyl)thio)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole (3ad): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.28 (m, 9H), **6.01 (d, *J* = 3.8 Hz, H^1), 5.48 (s, H^4), 4.67 (d, *J* = 3.8 Hz, H^2),** 4.60 (s, 2H), **4.23 (s, H^3),** 1.67 (s, 3H), 1.34 (s, 3H).

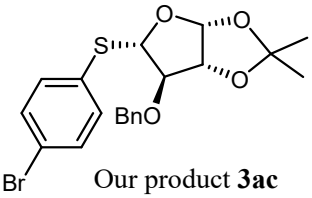
(3aR,5S,6S,6aS)-6-(benzyloxy)-5-((4-bromophenyl)thio)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole (3ad'): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.27 (m, 9H), **6.08 (d, *J* = 3.8 Hz, H^1), 5.55 (d, *J* = 3.4 Hz, H^4),** 4.79 – 4.66 (m, 2H), **4.64 (d, *J* = 3.8 Hz, H^2), 4.17 (d, *J* = 3.4 Hz, H^3)**, 1.45 (s, 3H), 1.33 (s, 3H).

By comparing the 1H-NMR data, we easily distinguish the configurations of the two isomers. It is the β -isomer when H^3 and H^4 are all singlet or the α -isomer when H^3 and H^4 are coupled to each other.

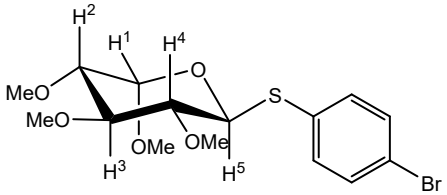
There is one compound [8] that has been reported that is very similar to our product 3ac. There is almost no difference between the chemical shift value and coupling constant of the hydrogen in the sugar ring between these two compounds. And they are all beta-isomer which proves our peak assignments and coupling constant analysis are correct.



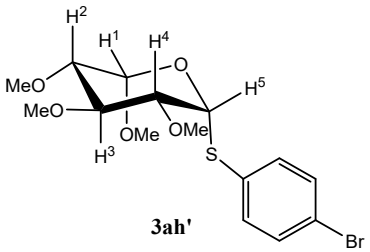
The known compound



Our product **3ac**



3ah



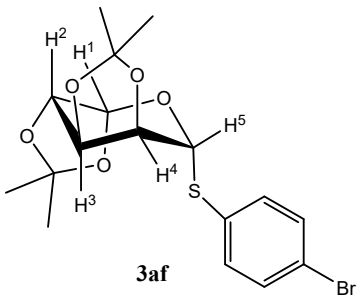
3ah'

(2R,3S,4R,5R,6S)-2-((4-bromophenyl)thio)-3,4,5,6-tetramethoxytetrahydro-2H-pyran (3ah): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.34 (m, 4H), **4.79 (d, *J* = 3.5 Hz, H^1), 4.72 (d, *J* = 10.0 Hz, H^5),** 3.60 (s, 3H), 3.59 (s, 3H), 3.50 (s, 3H,1H), 3.27 (s, 3H), **3.18 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.02 – 2.94 (m, 1H).**

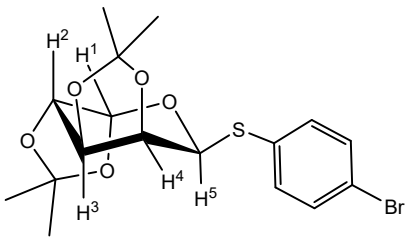
(2S,3S,4R,5R,6S)-2-((4-bromophenyl)thio)-3,4,5,6-tetramethoxytetrahydro-2H-pyran (3ah'): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.40 (s, 4H), **5.40 (d, *J* = 5.1 Hz, H^5), 4.87 (d, *J* = 3.5 Hz, H^1), 3.70 (t, *J* = 8.5 Hz, 1H)**, 3.62 (s, 3H), 3.53 (s, 3H), 3.49 (s, 3H), **3.47 (dd, *J* = 8.5, 5.2 Hz, 1H),** 3.40 (s, 3H), **3.24 (dd, *J* = 8.5, 3.5 Hz, 1H).**

We identified H^1 and H^5 through the chemical shift because they had the largest chemical shift among the hydrogens in the sugar ring at first. When H^4 and H^5 are on the same side, the chemical shift of H^5 will be redshifted obviously according to the previous work about thioglycoside.[9] What's more, it is when the dihedral angle of H^4 and H^5 is about 180 degrees that the coupling constant of these two hydrogens

could be 10.0 Hz. So we concluded that **3ah** was α -isomer.



3af



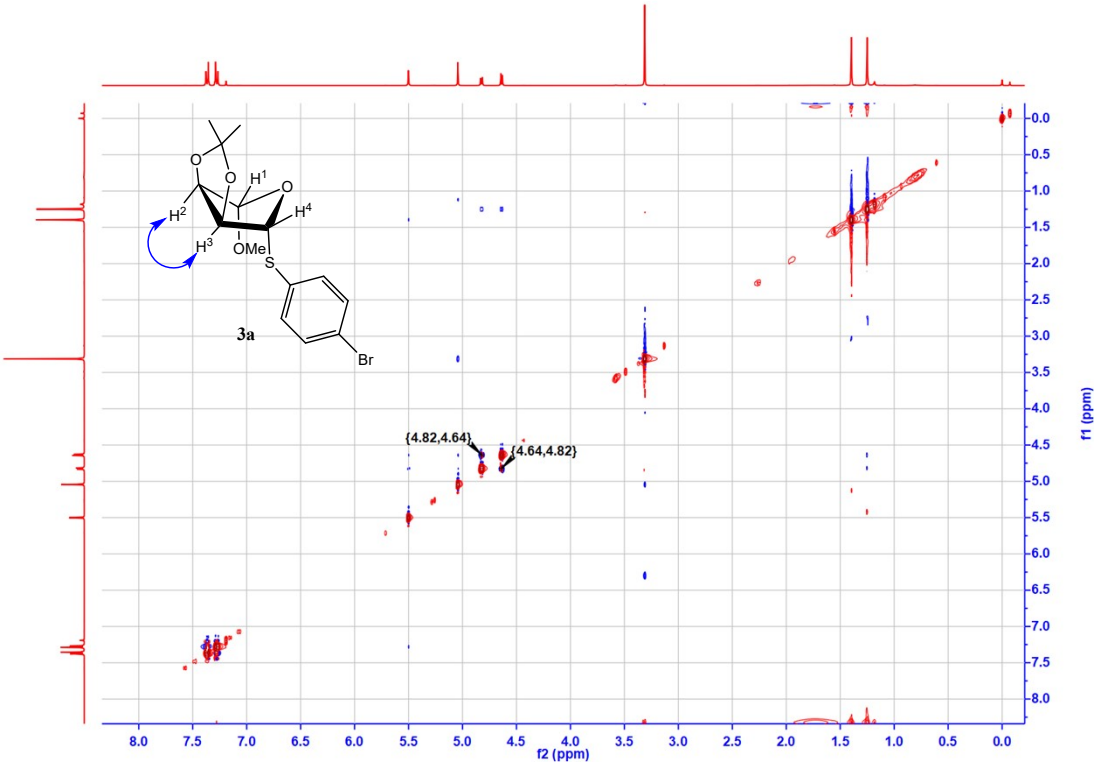
3af'

(3aS,5S,5aR,8aR,8bR)-5-((4-bromophenyl)thio)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (3af): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.38 (m, 4H), **5.31 (d, *J* = 2.4 Hz, H^1), 4.54 (d, *J* = 5.4 Hz, H^5), 4.43 (d, *J* = 9.7 Hz, 1H), 4.24 (d, *J* = 1.7 Hz, 1H), 4.00 (dd, *J* = 9.6, 5.4 Hz, 1H),** 1.52 (s, 3H), 1.47 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H).

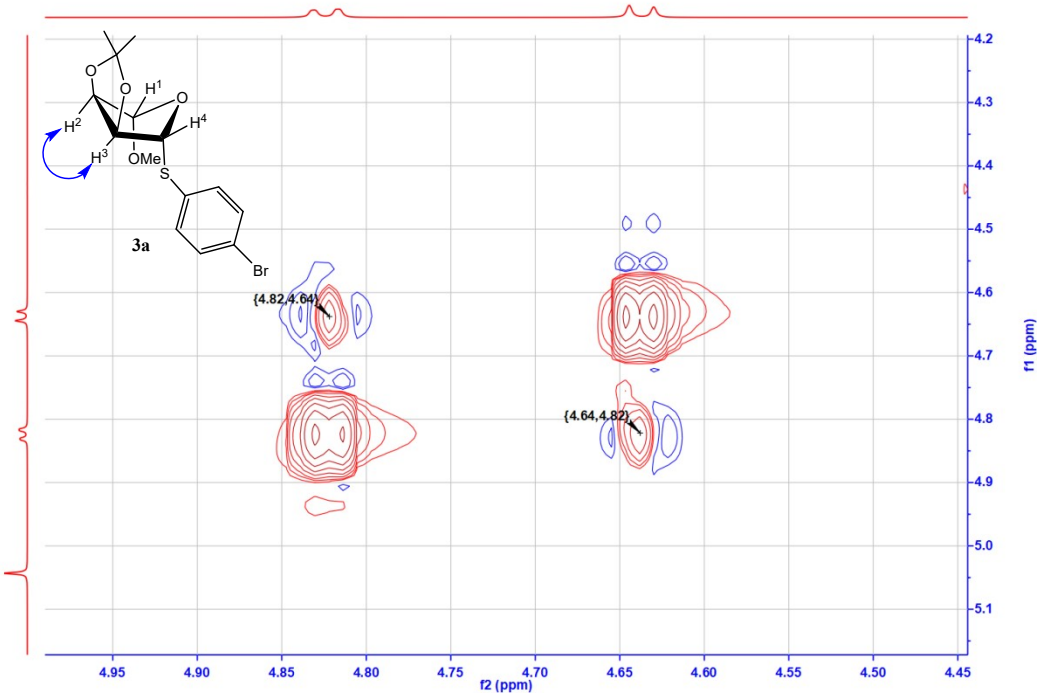
(3aS,5R,5aR,8aR,8bR)-5-((4-bromophenyl)thio)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (3af'): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.40 (s, 4H), **5.68 (d, *J* = 5.0 Hz, H^5), 5.20 (d, *J* = 1.8 Hz, H^1), 4.67 (dd, *J* = 7.6, 2.7 Hz, H^3), 4.48 (dd, *J* = 7.6, 1.9 Hz, H^2), 4.38 (dd, *J* = 5.0, 2.7 Hz, H^4),** 1.55 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H).

We determined the two isomers by judging the redshift which was similar to the compounds 3ah/3ah'. In this case, the coupling constants of H^5 of two isomers are basically the same because the H^4 is on the equatorial bond (e bond). The coupling constants of the hydrogens of the sugar ring of compound 3af' are clear and easy to assign. **5.68 (d, *J* = 5.0 Hz, H^5), 5.20 (d, *J* = 1.8 Hz, H^1), 4.67 (dd, *J* = 7.6, 2.7 Hz, H^3), 4.48 (dd, *J* = 7.6, 1.9 Hz, H^2), 4.38 (dd, *J* = 5.0, 2.7 Hz, H^4)**

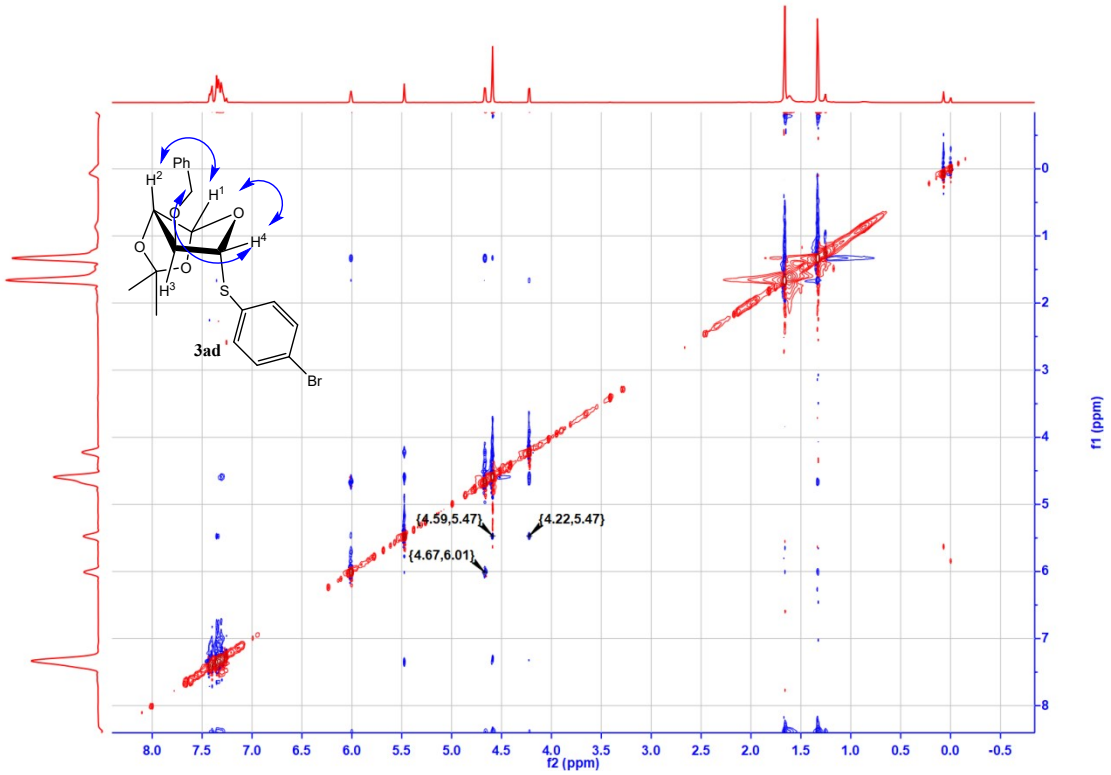
6.3 NOE experiments



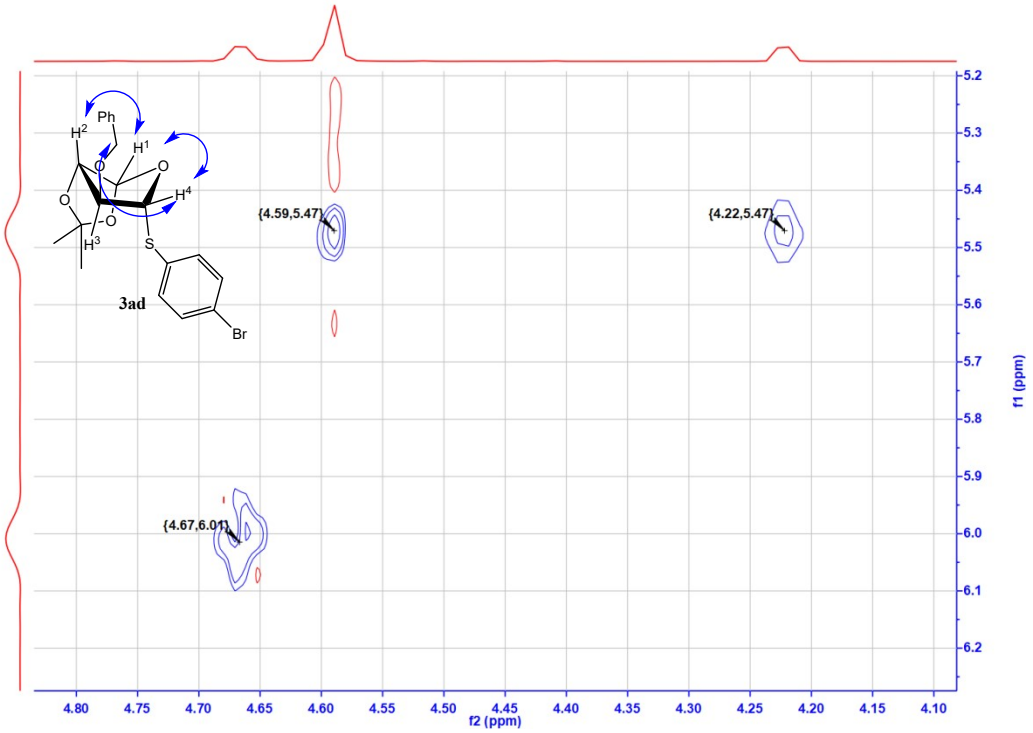
NOESY spectrum of compound **3a**



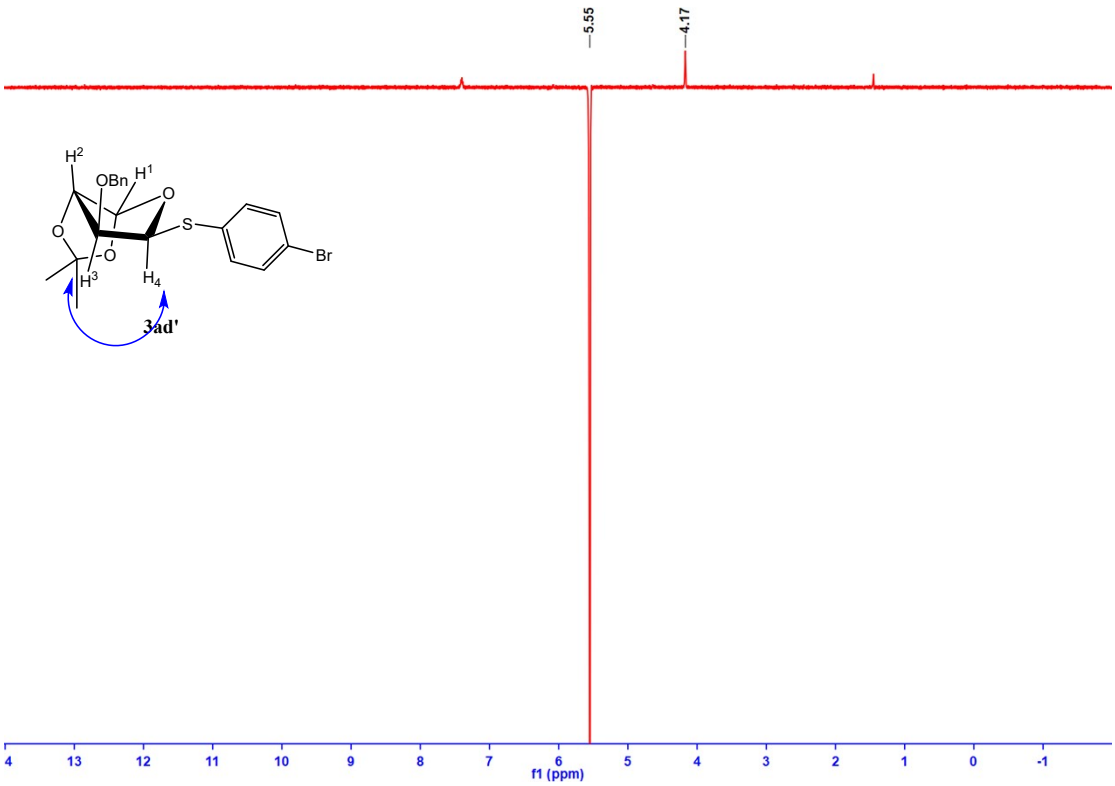
NOESY spectrum of compound **3a**



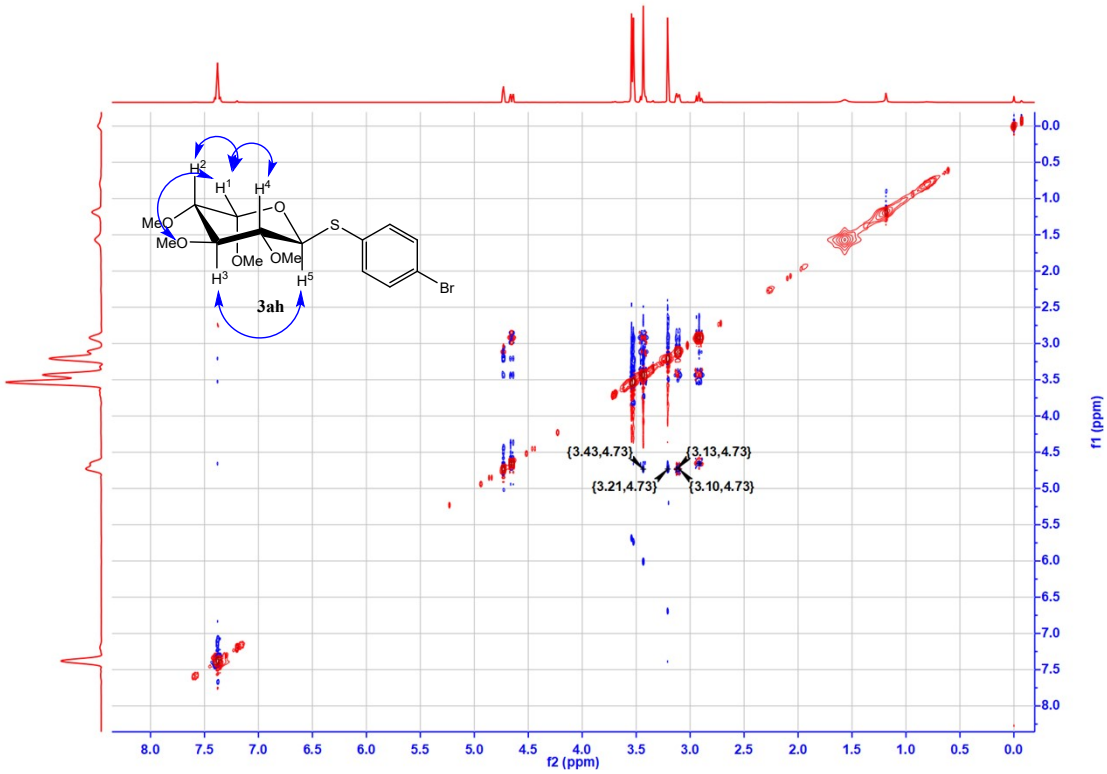
NOESY spectrum of compound **3ad**



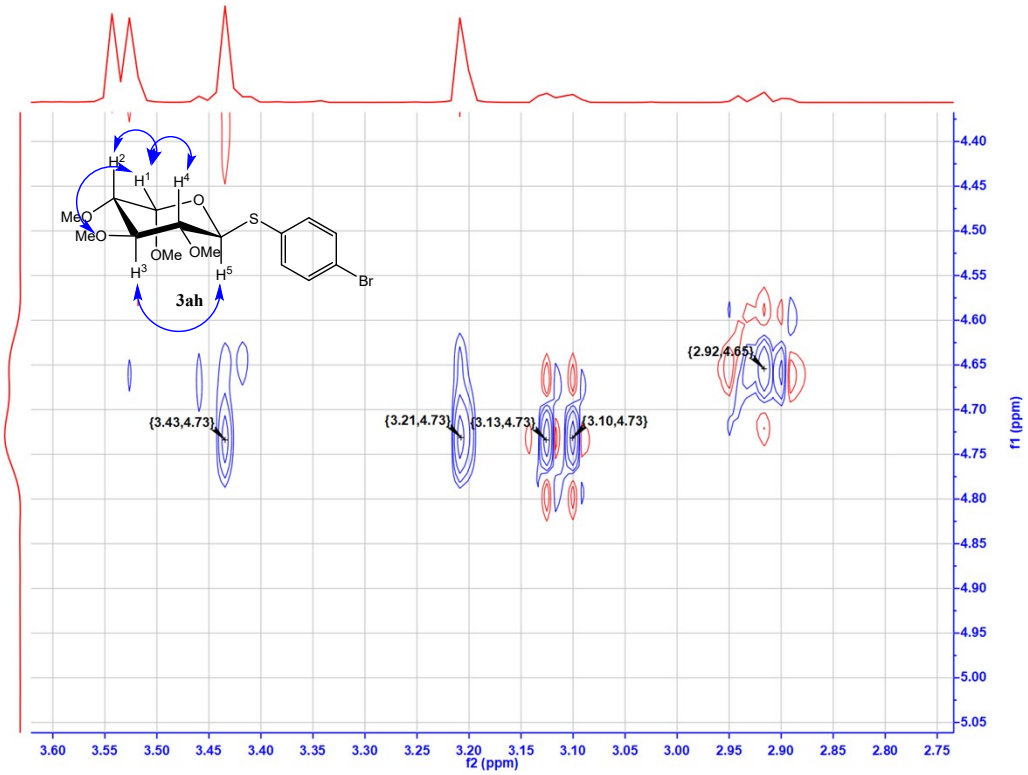
NOESY spectrum of compound **3ad**



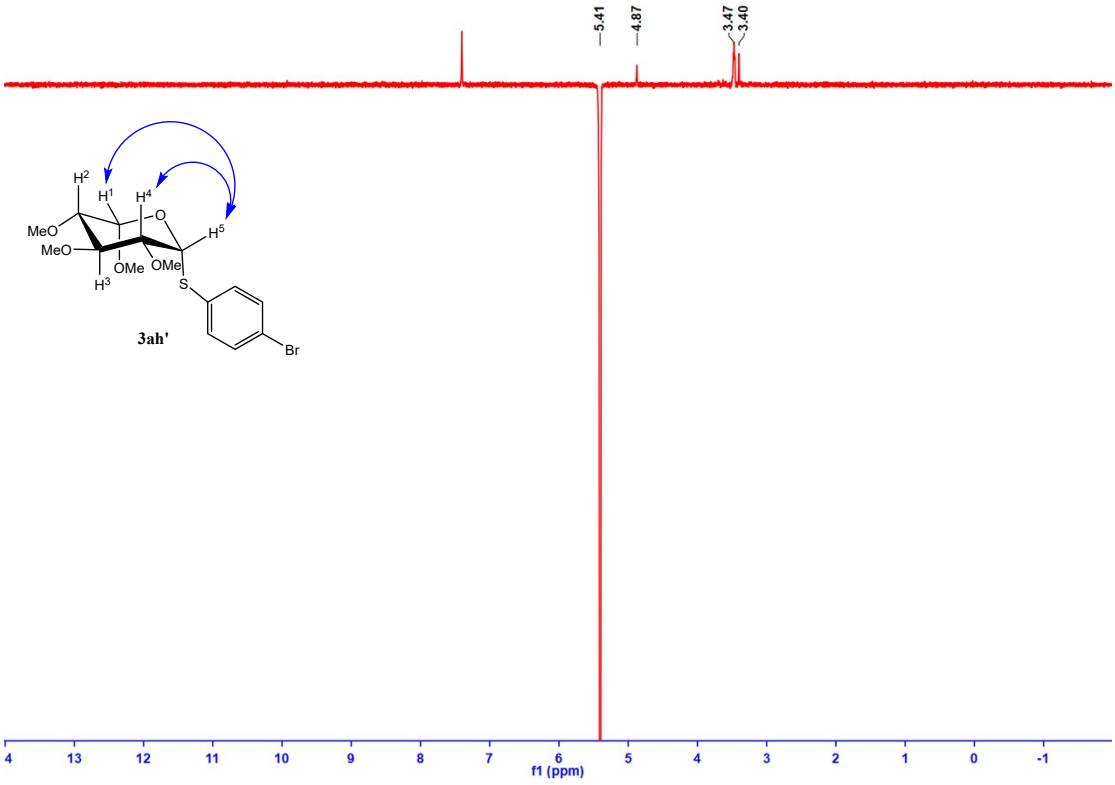
1D-NOE spectrum of compound **3ad'**



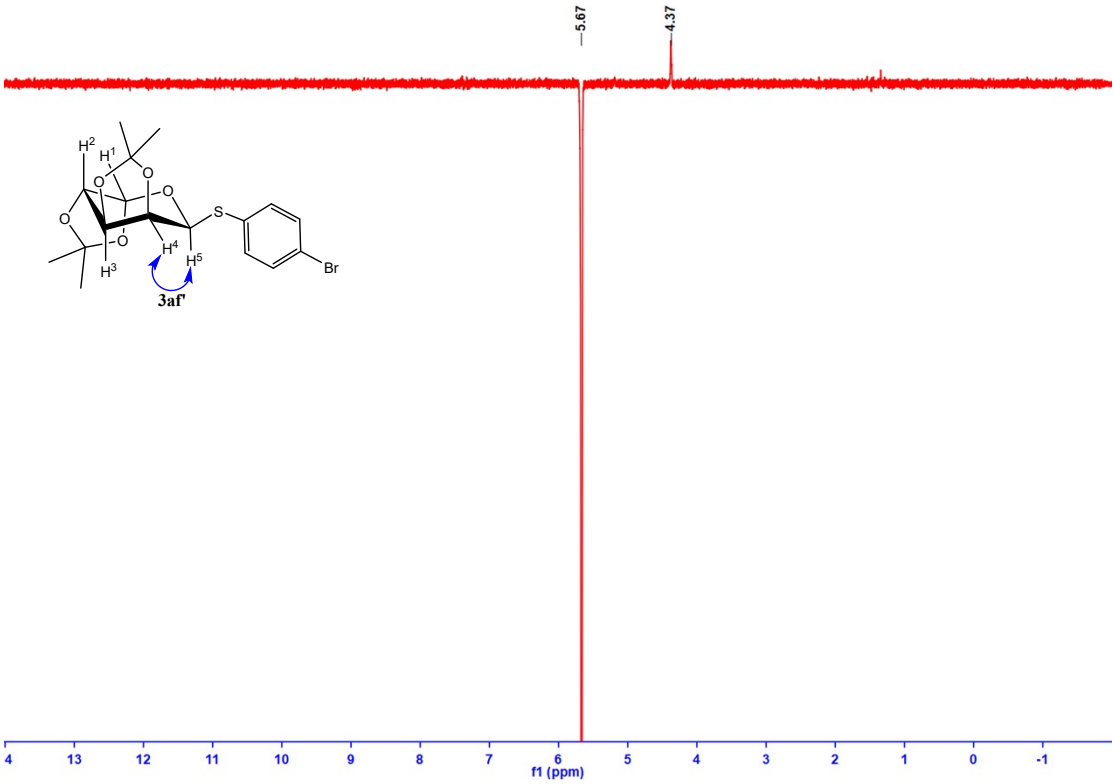
NOESY spectrum of compound **3ah**



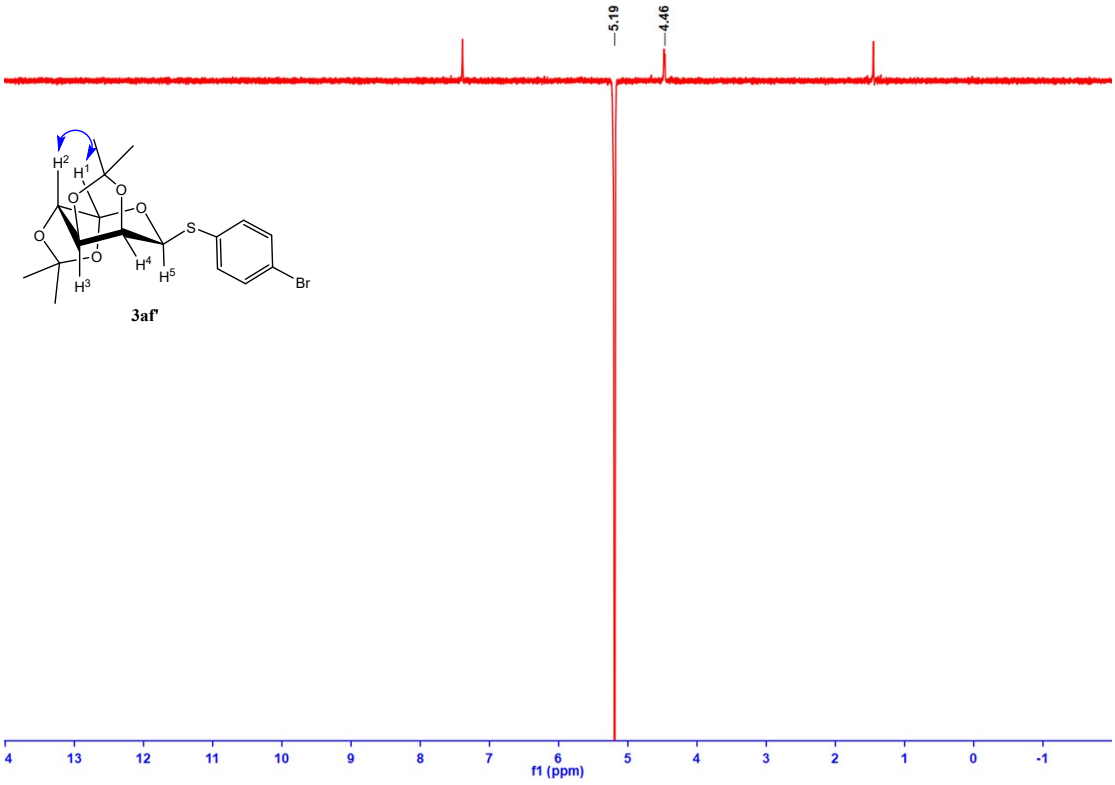
NOESY spectrum of compound **3ah**



1D-NOE spectrum of compound **3ah'**



1D-NOE spectrum of compound **3af'**

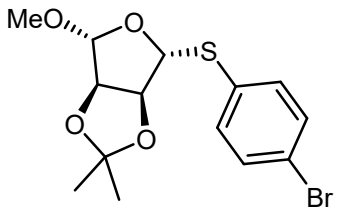


1D-NOE spectrum of compound **3af'**

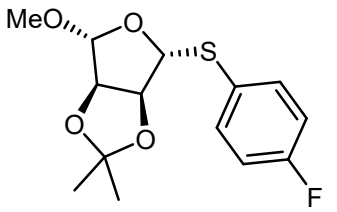
7. References

1. Ji, P.; Zhang, Y.; Wei, Y.; Huang, H.; Hu, W.; Mariano, P. A.; Wang, W., Visible-Light-Mediated, Chemo- and Stereoselective Radical Process for the Synthesis of C-Glycoamino Acids. *Org Lett* 2019, **21** (9), 3086-3092.
2. Masuda, K.; Nagatomo, M.; Inoue, M., Direct assembly of multiply oxygenated carbon chains by decarbonylative radical-radical coupling reactions. *Nat Chem* 2017**, 9** (3), 207-212.
3. Agnihotri, G.; Misra, A. K., Synthesis of a di- and a trisaccharide related to the O-antigen of Escherichia coli O83:K24:H31. *Carbohydr Res* 2006, **341** (14), 2420-5.
4. Qi, R.; ang, C.; Ma, Z.; Wang, H.; Chen, Q.; Liu, L.; Pan, D.; Ren, X.; Wang, R.; Xu, Z., Visible-Light-Promoted Stereoselective C(sp(3))-H Glycosylation for the Synthesis of C-Glycoamino Acids and C-Glycopeptides. *Angew Chem Int Ed Engl* 2022, **61** (24), e202200822.
5. Takashima, K.; Sakano, M.; Kinouchi, E.; Nakamura, S.; Marumoto, S.; Ishikawa, F.; Ninomiya, K.; Nakanishi, I.; Morikawa, T.; Tanabe, G., Elongation of the side chain by linear alkyl groups increases the potency of salacinol, a potent alpha-glucosidase inhibitor from the Ayurvedic traditional medicine "Salacia," against human intestinal maltase. *Bioorg Med Chem Lett* 2021, **33**, 127751.
6. Yamada, K.; Hayakawa, H.; Sakata, S.; Ashida, N.; Yoshimura, Y., Synthesis and antiviral evaluation of alpha-D-2',3'-didehydro-2',3'-dideoxy-3'-C-hydroxymethyl nucleosides. *Bioorg Med Chem Lett* 2010, **20** (20), 6013-6.
7. Annika, G., Martin, Hiersemann., (-)-Lytophilippine A: Synthesis of a C1-C18 Building Block. *Org Lett* 2010, **12** (22), 5258-5261.
8. Li, J.; Y, X.; Wang, S.; Zhang, L.; Zhou, X.; Wang, S.; Ji, S., Visible-Light-Promoted Cross-Coupling Reactions of 4-Alkyl-1,4- dihydropyridines with Thiosulfonate or Selenium Sulfonate: A Unified Approach to Sulfides, Selenides, and Sulfoxides. *Org Lett* 2020, **22** (12), 4908-4913.
9. Feng, G.; Luo, T.; Guo, Y.; Liu, C.; Dong, H., Concise Synthesis of 1-Thioalkyl Glycoside Donors by Reaction of Per-O-acetylated Sugars with Sodium Alkanethiolates under Solvent-Free Conditions. *J. Org. Chem.* 2022, **87** (5), 3638-3646.

8. Characterization of products

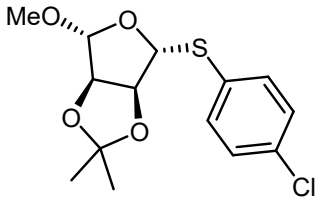


(3aS,4R,6R,6aR)-4-((4-bromophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3a): White solid; 32.8 mg; 91% yield; >20:1 d.r.; M.p. 79–80 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 5.57 (s, 1H), 5.11 (s, 1H), 4.89 (d, *J* = 5.7 Hz, 1H), 4.71 (d, *J* = 5.8 Hz, 1H), 3.38 (s, 3H), 1.47 (s, 3H), 1.32 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 134.6, 132.2, 132.1, 121.2, 113.1, 110.5, 93.1, 85.7, 84.6, 55.3, 26.5, 25.1. HRMS (ESI) m/z $[M + Na]^+$ calculated for 382.9923, found 382.9925.

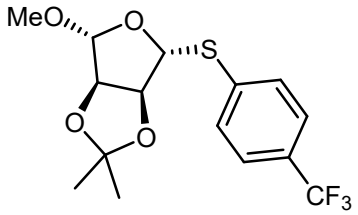


(3aS,4R,6R,6aR)-4-((4-fluorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3b): White solid; 25.3 mg; 84% yield; >20:1 d.r.; M.p. 56-57 ℃. **^{1}H-NMR**

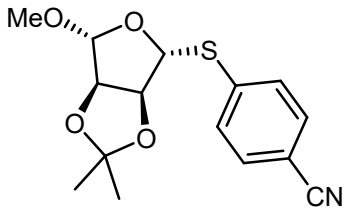
(400 MHz, Chloroform-*d*) δ 7.49 (ddt, *J* = 8.3, 5.3, 2.6 Hz, 2H), 7.06 – 7.00 (m, 2H), 5.50 (s, 1H), 5.11 (s, 1H), 4.91 (d, *J* = 6.3 Hz, 1H), 4.71 (d, *J* = 5.8 Hz, 1H), 3.42 (s, 3H), 1.46 (s, 3H), 1.32 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 162.4 (d, *J* = 248.4 Hz), 133.7 (d, *J* = 8.1 Hz), 130.1 (d, *J* = 3.0 Hz), 116.3 (d, *J* = 22.2 Hz), 113.0, 110.0, 94.1, 85.8, 84.7, 55.3, 26.4, 25.1. **^{19}F-NMR (376 MHz, Chloroform-*d*)** δ -114.11 (tt, *J* = 8.6, 5.3 Hz). HRMS (ESI) m/z [M + Na]$^+$ calculated for 323.0724, found 323.0723.



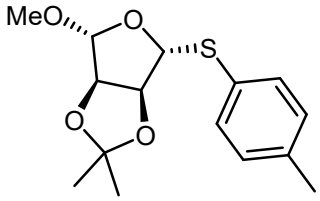
(3aS,4R,6R,6aR)-4-((4-chlorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3c): White solid; 27.2 mg; 85% yield; >20:1 d.r.; M.p. 64-65 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.44 – 7.39 (m, 2H), 7.31 – 7.27 (m, 2H), 5.56 (s, 1H), 5.11 (s, 1H), 4.90 (d, *J* = 6.3 Hz, 1H), 4.71 (d, *J* = 5.8 Hz, 1H), 3.39 (s, 3H), 1.46 (s, 3H), 1.32 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 133.9, 133.3, 132.0, 129.3, 113.1, 110.5, 93.3, 85.8, 84.6, 55.3, 26.5, 25.1. HRMS (ESI) m/z [M + Na]$^+$ calculated for 339.0428, found 339.0431.



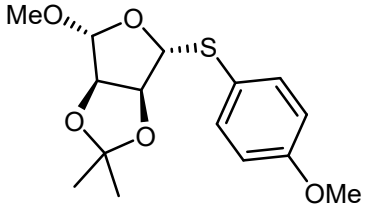
(3aR,4R,6R,6aS)-4-methoxy-2,2-dimethyl-6-((4-(trifluoromethyl)phenyl)thio)tetrahydrofuro[3,4-d][1,3]dioxole (3d): White solid; 34.1 mg; 97% yield; >20:1 d.r.; M.p.81-82 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.55 (s, 4H), 5.70 (s, 1H), 5.15 (s, 1H), 4.91 (d, *J* = 5.8 Hz, 1H), 4.73 (d, *J* = 5.8 Hz, 1H), 3.36 (s, 3H), 1.49 (s, 3H), 1.33 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 141.0 (d, *J* = 1.0 Hz), 129.0, 128.5 (q, *J* = 32.0 Hz), 125.9 (q, *J* = 4.0 Hz), 124.1 (q, *J* = 270.0 Hz), 113.25, 110.46, 92.07, 85.70, 84.56, 55.22, 26.45, 25.07. **^{19}F-NMR (376 MHz, Chloroform-*d*)** δ -62.55. HRMS (ESI) m/z [M + Na]$^+$ calculated for 373.0692, found 373.0691.



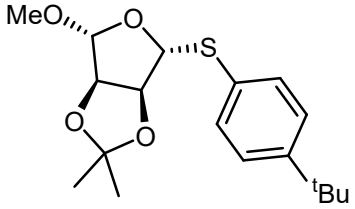
4-(((3aS,4R,6R,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)thio)benzonitrile (3e): White solid; 22.6 mg; 73% yield; >20:1 d.r.; M.p.61- 62℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.59 – 7.54 (m, 2H), 7.52 – 7.48 (m, 2H), 5.72 (s, 1H), 5.15 (s, 1H), 4.89 (d, *J* = 6.5 Hz, 1H), 4.71 (d, *J* = 5.8 Hz, 1H), 3.32 (s, 3H), 1.49 (s, 3H), 1.33 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 143.4, 132.5, 128.3, 118.7, 113.4, 110.5, 109.4, 91.4, 85.5, 84.5, 55.2, 26.4, 25.0. HRMS (ESI) m/z [M + Na]$^+$ calculated for 330.0770, found 330.0773.



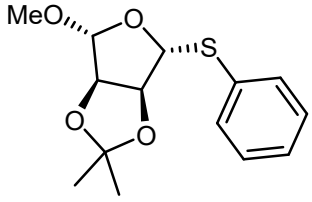
(3aR,4R,6R,6aS)-4-methoxy-2,2-dimethyl-6-(p-tolylthio)tetrahydrofuro[3,4-d][1,3]dioxole (3f): White solid; 14.0 mg; 47% yield; >20:1 d.r.; M.p. 75-76 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 5.54 (s, 1H), 5.10 (s, 1H), 4.92 (d, *J* = 5.8 Hz, 1H), 4.72 (d, *J* = 5.8 Hz, 1H), 3.42 (s, 3H), 2.33 (s, 3H), 1.45 (s, 3H), 1.32 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 137.4, 131.6, 131.4, 129.9, 112.9, 110.4, 93.8, 85.9, 84.7, 55.2, 26.5, 25.2, 21.1. HRMS (ESI) m/z $[M + Na]^+$ calculated for 319.0974, found 319.0977.



(3aR,4R,6R,6aS)-4-methoxy-6-((4-methoxyphenyl)thio)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3g): White solid; 24.5 mg; 78% yield; >20:1 d.r.; M.p. 85-86 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.46 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.44 (s, 1H), 5.09 (s, 1H), 4.91 (d, *J* = 5.8 Hz, 1H), 4.71 (d, *J* = 5.8 Hz, 1H), 3.80 (s, 3H), 3.44 (s, 3H), 1.44 (s, 3H), 1.31 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 159.6, 134.4, 125.2, 114.8, 112.9, 110.5, 94.6, 85.8, 84.7, 55.3, 55.3, 26.5, 25.2. HRMS (ESI) m/z $[M + Na]^+$ calculated for 335.0923, found 335.0921.

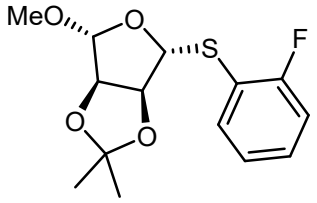


(3aS,4R,6R,6aR)-4-((4-(tert-butyl)phenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3h): Pale oil; 26.3 mg; 77% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.46 – 7.41 (m, 2H), 7.36 – 7.32 (m, 2H), 5.56 (s, 1H), 5.11 (s, 1H), 4.93 (d, *J* = 6.1 Hz, 1H), 4.72 (d, *J* = 5.8 Hz, 1H), 3.43 (s, 3H), 1.46 (s, 3H), 1.32 (s, 3H), 1.31 (s, 9H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 150.6, 131.5, 131.2, 126.2, 112.9, 110.4, 93.7, 86.0, 84.7, 55.2, 34.6, 31.3, 26.5, 25.2. HRMS (ESI) m/z $[M + Na]^+$ calculated for 361.1444, found 361.1442.

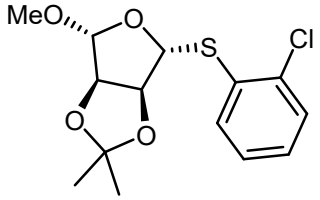


(3aR,4R,6R,6aS)-4-methoxy-2,2-dimethyl-6-(phenylthio)tetrahydrofuro[3,4-

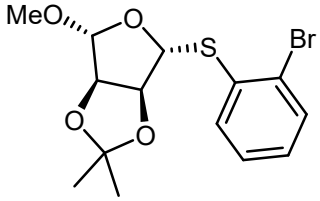
d][1,3]dioxole (3i): Pale oil; 17.9 mg; 63% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.52 – 7.48 (m, 2H), 7.35 – 7.30 (m, 2H), 7.28 – 7.26 (m, 1H), 5.63 (s, 1H), 5.13 (s, 1H), 4.94 (d, *J* = 6.3 Hz, 1H), 4.73 (d, *J* = 5.8 Hz, 1H), 3.42 (s, 3H), 1.48 (s, 3H), 1.33 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 135.3, 130.6, 129.1, 127.1, 113.0, 110.4, 93.3, 85.9, 84.7, 55.2, 26.7, 25.1. HRMS (ESI) m/z [M + Na]$^{+}$ calculated for 305.0818, found 305.0820.



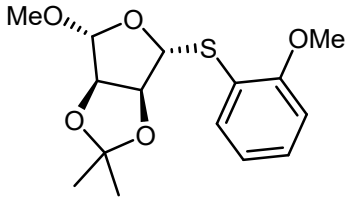
(3aS,4R,6R,6aR)-4-((2-fluorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3j): Pale oil; 25.3 mg; 84% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.54 (t, *J* = 7.1 Hz, 1H), 7.33 – 7.23 (m, 1H), 7.10 (q, *J* = 8.8, 8.4 Hz, 2H), 5.61 (s, 1H), 5.09 (s, 1H), 4.96 (d, *J* = 5.6 Hz, 1H), 4.73 (d, *J* = 5.6 Hz, 1H), 3.39 (s, 3H), 1.46 (s, 3H), 1.32 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 160.5 (d, *J* = 245.0 Hz), 132.6 (d, *J* = 1.0 Hz), 128.5 (d, *J* = 8.0 Hz), 123.7 (d, *J* = 4.0 Hz), 120.8 (d, *J* = 18 Hz), 114.9 (d, *J* = 22 Hz), 112.0, 109.6, 91.3 (d, *J* = 2 Hz), 85.1, 83.6, 54.3, 25.4, 24.1. **^{19}F-NMR (376 MHz, Chloroform-*d*)** δ -108.10 (ddd, *J* = 9.3, 7.4, 5.2 Hz). HRMS (ESI) m/z [M + Na]$^{+}$ calculated for 323.0724, found 323.0723.



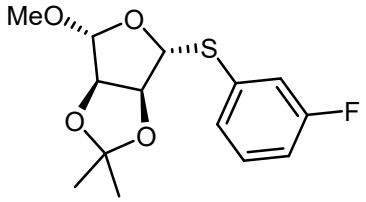
(3aS,4R,6R,6aR)-4-((2-chlorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3k): Pale oil; 25.6 mg; 81% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.60 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.39 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.25 (td, *J* = 7.6, 1.5 Hz, 1H), 7.17 (td, *J* = 7.7, 1.6 Hz, 1H), 5.68 (s, 1H), 5.13 (s, 1H), 4.97 (d, *J* = 5.8 Hz, 1H), 4.74 (d, *J* = 5.8 Hz, 1H), 3.37 (s, 3H), 1.49 (s, 3H), 1.33 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 134.9, 134.3, 130.6, 129.8, 127.7, 127.4, 113.1, 110.5, 91.6, 85.9, 84.6, 55.2, 26.5, 25.1. HRMS (ESI) m/z [M + Na]$^{+}$ calculated for 339.0428, found 339.0427.



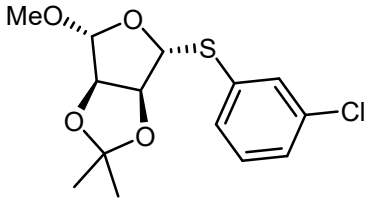
(3aS,4R,6R,6aR)-4-((2-bromophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3l): Pale oil; 28.1 mg; 77% yield; >20:1 d.r.. **^{1}H-NMR (600 MHz, Chloroform-*d*)** δ 7.59 (dd, *J* = 17.7, 7.8 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 5.68 (s, 1H), 5.14 (s, 1H), 4.97 (d, *J* = 5.4 Hz, 1H), 4.74 (d, *J* = 5.5 Hz, 1H), 3.37 (s, 3H), 1.49 (s, 3H), 1.34 (s, 3H). **^{13}C-NMR (150 MHz, Chloroform-*d*)** δ 137.1, 133.1, 130.1, 128.0, 127.6, 124.4, 113.1, 110.4, 91.8, 85.7, 84.6, 55.2, 26.4, 25.1. HRMS (ESI) m/z [M + Na]$^{+}$ calculated for 382.9923, found 382.9921.



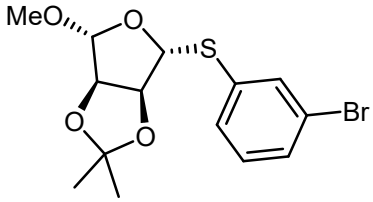
(3aR,4R,6R,6aS)-4-methoxy-6-((2-methoxyphenyl)thio)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3m): Pale oil; 19.4 mg; 62% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.50 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.29 – 7.22 (m, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 5.69 (s, 1H), 5.08 (s, 1H), 4.95 (d, *J* = 5.8 Hz, 1H), 4.74 (d, *J* = 5.8 Hz, 1H), 3.90 (s, 3H), 3.38 (s, 3H), 1.46 (s, 3H), 1.32 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 156.9, 131.3, 127.7, 121.8, 120.2, 111.8, 109.8, 109.6, 90.0, 85.1, 83.7, 54.8, 54.3, 25.4, 24.1. HRMS (ESI) m/z $[M + Na]^+$ calculated for 335.0923, found225.0926.



(3aS,4R,6R,6aR)-4-((3-fluorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3n): Pale oil; 26.3 mg; 87% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.30 – 7.21 (m, 3H), 6.98 – 6.91 (m, 1H), 5.64 (s, 1H), 5.14 (s, 1H), 4.91 (d, *J* = 5.7 Hz, 1H), 4.72 (d, *J* = 5.8 Hz, 1H), 3.39 (s, 3H), 1.49 (s, 3H), 1.34 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 162.8 (d, *J* = 247.0 Hz), 137.8 (d, *J* = 8.0 Hz), 130.0 (d, *J* = 8.0 Hz), 125.6 (d, *J* = 3 Hz), 116.9 (d, *J* = 23 Hz), 113.9 (d, *J* = 21 Hz), 113.15, 110.44, 92.81, 85.76, 84.60, 55.22, 26.46, 25.11. **^{19}F-NMR (376 MHz, Chloroform-*d*)** δ -111.78 – -111.88 (m). HRMS (ESI) m/z $[M + Na]^+$ calculated for 323.0724, found 323.0729.

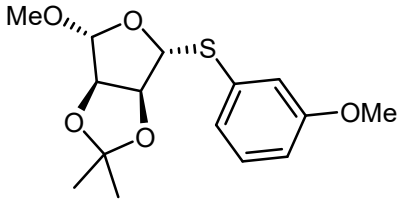


(3aS,4R,6R,6aR)-4-((3-chlorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3o): White solid; 26.8 mg; 84% yield; >20:1 d.r.; M.p.57-58 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.49 (t, *J* = 1.5 Hz, 1H), 7.35 (dt, *J* = 7.1, 1.8 Hz, 1H), 7.25 – 7.19 (m, 2H), 5.62 (s, 1H), 5.13 (s, 1H), 4.90 (d, *J* = 6.3 Hz, 1H), 4.71 (d, *J* = 5.8 Hz, 1H), 3.39 (s, 3H), 1.48 (s, 3H), 1.32 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 137.5, 134.8, 130.1, 130.0, 128.3, 127.1, 113.1, 110.5, 92.9, 85.7, 84.6, 55.2, 26.7, 25.1. HRMS (ESI) m/z $[M + Na]^+$ calculated for 339.0428, found 339.0427.

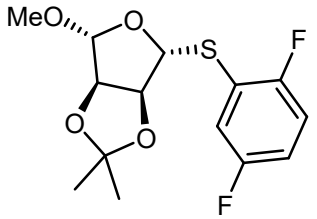


(3aS,4R,6R,6aR)-4-((3-bromophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3p): White solid; 33.7 mg; 93% yield; >20:1 d.r.; M.p.58-59 ℃. **^{1}H-NMR**

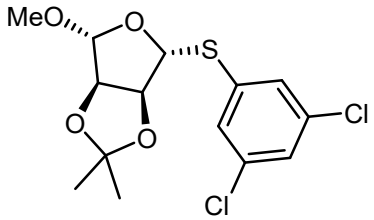
(400 MHz, Chloroform-*d*) δ 7.64 (t, *J* = 1.6 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.18 (t, *J* = 7.9 Hz, 1H), 5.61 (s, 1H), 5.12 (s, 1H), 4.90 (d, *J* = 5.7 Hz, 1H), 4.71 (d, *J* = 5.8 Hz, 1H), 3.39 (s, 3H), 1.48 (s, 3H), 1.32 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 137.8, 132.9, 130.4, 130.0, 128.8, 122.9, 113.1, 110.5, 93.0, 85.7, 84.6, 55.3, 26.5, 25.1. HRMS (ESI) m/z [M + Na]$^+$ calculated for 382.9923, found 382.9927.



(3aR,4R,6R,6aS)-4-methoxy-6-((3-methoxyphenyl)thio)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3q): Pale oil; 27.7 mg; 88% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.23 (t, *J* = 8.0 Hz, 1H), 7.10 – 7.03 (m, 2H), 6.82 – 6.77 (m, 1H), 5.63 (s, 1H), 5.11 (s, 1H), 4.92 (d, *J* = 5.8 Hz, 1H), 4.72 (d, *J* = 5.8 Hz, 1H), 3.80 (s, 3H), 3.40 (s, 3H), 1.47 (s, 3H), 1.32 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 159.9, 136.5, 129.9, 122.8, 116.0, 113.0, 112.9, 110.4, 93.1, 85.9, 84.7, 55.3, 55.2, 26.5, 25.1. HRMS (ESI) m/z [M + Na]$^+$ calculated for 335.0923, found 335.0924.

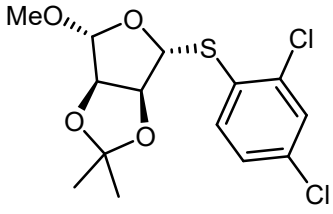


(3aS,4R,6R,6aR)-4-((2,5-difluorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3r): faint yellow oil; 26.8 mg; 84% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.31 – 7.26 (m, 1H), 7.04 (td, *J* = 8.8, 4.6 Hz, 1H), 6.97 – 6.90 (m, 1H), 5.62 (s, 1H), 5.11 (s, 1H), 4.94 (d, *J* = 5.8 Hz, 1H), 4.72 (d, *J* = 5.8 Hz, 1H), 3.37 (s, 3H), 1.47 (s, 3H), 1.33 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 159.1 (dd, *J* = 139.4 Hz, *J* = 2.0 Hz), 156.7 (dd, *J* = 133.3 Hz, *J* = 3.0 Hz), 124.0 (dd, *J* = 20.2 Hz, *J* = 8.1 Hz), 118.8 (dd, *J* = 25.2 Hz, *J* = 2.0 Hz), 116.5 (dd, *J* = 26.3 Hz, *J* = 9.1 Hz), 115.3 (dd, *J* = 24.2 Hz, *J* = 8.1 Hz), 113.2, 110.7, 91.9, 85.9, 84.5, 55.3, 26.4, 25.1. **^{19}F-NMR (376 MHz, Chloroform-*d*)** δ -114.95 – -115.07 (m), -117.78 (dtd, *J* = 16.2, 7.9, 4.7 Hz). HRMS (ESI) m/z [M + Na]$^+$ calculated for 341.0629, found 341.0630.

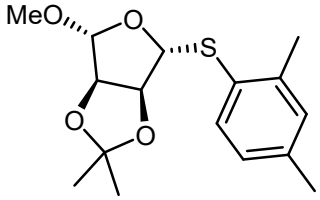


(3aS,4R,6R,6aR)-4-((3,5-dichlorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3s): White solid; 31.3 mg; 89% yield; >20:1 d.r.; M.p.46-47 °C. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.35 (d, *J* = 1.8 Hz, 2H), 7.22 (t, *J* = 1.8 Hz, 1H), 5.62 (s, 1H), 5.14 (s, 1H), 4.88 (d, *J* = 5.7 Hz, 1H), 4.70 (d, *J* = 5.8 Hz, 1H), 3.37 (s, 3H), 1.49 (s, 3H), 1.33 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 139.2, 135.3,

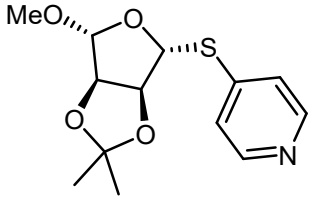
127.6, 126.9, 113.3, 110.5, 92.5, 85.6, 84.5, 55.3, 26.4, 25.1. HRMS (ESI) m/z [M + Na]$^+$ calculated for 373.0038, found 373.0036.



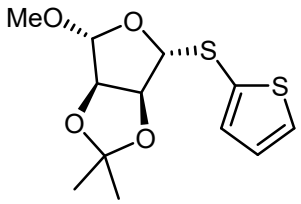
3aS,4R,6R,6aR)-4-((2,4-dichlorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3t): faint yellow oil; 33.0 mg; 94% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.54 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 2.2 Hz, 1H), 7.23 (dd, *J* = 8.5, 2.2 Hz, 1H), 5.63 (s, 1H), 5.12 (s, 1H), 4.94 (d, *J* = 5.8 Hz, 1H), 4.73 (d, *J* = 5.8 Hz, 1H), 3.35 (s, 3H), 1.48 (s, 3H), 1.33 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 135.0, 133.6, 133.0, 131.3, 129.6, 127.7, 113.2, 110.5, 91.6, 85.7, 84.5, 55.3, 26.4, 25.1. HRMS (ESI) m/z [M + Na]$^+$ calculated for 373.0038, found 373.0039.



(3aS,4R,6R,6aR)-4-((2,4-dimethylphenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3u): Pale oil; 13.4 mg; 47% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.44 (d, *J* = 7.9 Hz, 1H), 7.03 (s, 1H), 7.01 – 6.97 (m, 1H), 5.48 (s, 1H), 5.10 (s, 1H), 4.95 (d, *J* = 6.3 Hz, 1H), 4.73 (d, *J* = 5.8 Hz, 1H), 3.41 (s, 3H), 2.40 (s, 3H), 2.30 (s, 3H), 1.46 (s, 3H), 1.32 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 138.9, 137.3, 131.6, 131.3, 131.0, 127.5, 112.9, 110.4, 93.1, 86.2, 84.7, 55.3, 26.5, 25.2, 21.0, 20.7. HRMS (ESI) m/z [M + Na]$^+$ calculated for 333.1131, found 333.1132.

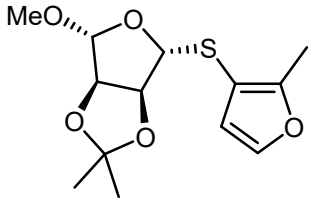


4-(((3aS,4R,6R,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)thio)pyridine (3v): White solid; 23.7 mg; 83% yield; >20:1 d.r.; M.p. 88-89 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 8.44 (d, *J* = 5.7 Hz, 2H), 7.29 (dd, *J* = 4.7, 1.5 Hz, 2H), 5.79 (s, 1H), 5.16 (s, 1H), 4.89 (d, *J* = 6.3 Hz, 1H), 4.72 (d, *J* = 5.8 Hz, 1H), 3.31 (s, 3H), 1.51 (s, 3H), 1.34 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 149.5, 148.0, 121.6, 113.4, 110.4, 90.0, 85.5, 84.5, 55.2, 26.4, 25.0. HRMS (ESI) m/z [M + Na]$^+$ calculated for 306.0770, found 306.0773.

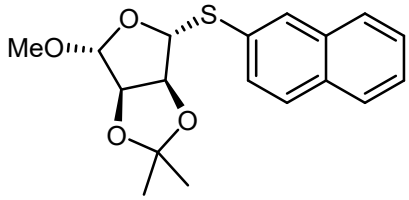


(3aR,4R,6R,6aS)-4-methoxy-2,2-dimethyl-6-(thiophen-2-ylthio)tetrahydrofuro[3,4-

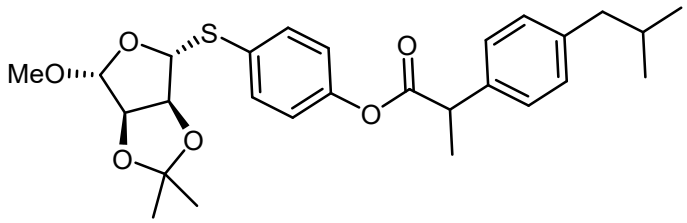
d][1,3]dioxole (3w): White solid; 18.7 mg; 65% yield; >20:1 d.r.; M.p. 69-70 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.43 – 7.37 (m, 1H), 7.23 – 7.19 (m, 1H), 7.01 (dd, *J* = 5.3, 3.6 Hz, 1H), 5.38 (s, 1H), 5.10 (s, 1H), 4.95 (d, *J* = 5.7 Hz, 1H), 4.71 (d, *J* = 5.8 Hz, 1H), 3.48 (s, 3H), 1.43 (s, 3H), 1.31 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 133.5, 131.1, 129.3, 126.8, 112.0, 109.6, 94.6, 84.5, 83.6, 54.4, 25.4, 24.1. HRMS (ESI) m/z [M + Na]$^+$ calculated for 311.0382, found 311.0381.



(3aR,4R,6R,6aS)-4-methoxy-2,2-dimethyl-6-((2-methylfuran-3-yl)thio)tetrahydrofuro[3,4-d][1,3]dioxole (3x): Pale oil; 20.3 mg; 71% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.29 (d, *J* = 1.8 Hz, 1H), 6.42 (d, *J* = 1.7 Hz, 1H), 5.24 (s, 1H), 5.06 (s, 1H), 4.87 (d, *J* = 5.8 Hz, 1H), 4.70 (d, *J* = 5.8 Hz, 1H), 3.45 (s, 3H), 2.36 (s, 3H), 1.43 (s, 3H), 1.31 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 155.1, 140.9, 114.8, 112.9, 110.5, 109.3, 93.8, 86.0, 84.7, 55.4, 26.4, 25.2, 11.9. HRMS (ESI) m/z [M + Na]$^+$ calculated for 309.0767, found 309.0769.

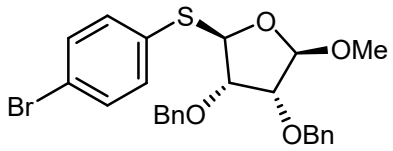


(3aR,4R,6R,6aS)-4-methoxy-2,2-dimethyl-6-(naphthalen-2-ylthio)tetrahydrofuro[3,4-d][1,3]dioxole (3y): White solid; 26.1 mg; 78% yield; >20:1 d.r.; M.p.70-71 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.97 (d, *J* = 1.4 Hz, 1H), 7.80 (t, *J* = 7.2 Hz, 3H), 7.56 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.52 – 7.44 (m, 2H), 5.75 (s, 1H), 5.16 (s, 1H), 4.99 (d, *J* = 5.8 Hz, 1H), 4.76 (d, *J* = 5.8 Hz, 1H), 3.43 (s, 3H), 1.49 (s, 3H), 1.34 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 133.8, 132.8, 132.2, 129.1, 128.7, 128.3, 127.7, 127.5, 126.6, 126.1, 113.0, 110.5, 93.1, 85.9, 84.7, 55.3, 26.5, 25.1. HRMS (ESI) m/z [M + Na]$^+$ calculated for 355.0974, found 355.0977.

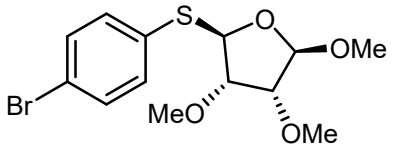


4-(((3aS,4R,6R,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)thio)phenyl 2-(4-isobutylphenyl)propanoate (3z): Pale oil; 26.3 mg; 54% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 5.54 (s, 1H), 5.10 (s, 1H), 4.89 (d, *J* = 5.7 Hz, 1H), 4.70 (d, *J* = 5.7 Hz, 1H), 3.92 (q, *J* = 7.0 Hz, 1H), 3.39 (s, 3H), 2.47 (d, *J* = 7.1 Hz, 2H), 1.86 (dp, *J* = 13.3, 6.7 Hz, 1H), 1.60 (d, *J* = 7.1 Hz, 4H), 1.45 (s, 3H), 1.31 (s, 3H), 0.92 (s, 3H), 0.90 (s, 3H). **^{13}C-NMR (150 MHz, Chloroform-*d*)** δ 173.0, 150.2, 140.9, 137.0,

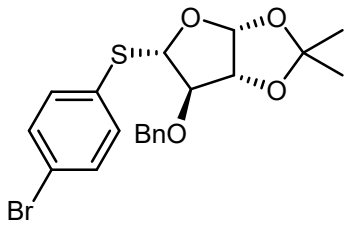
132.3, 132.1, 129.5, 127.2, 122.2, 113.0, 110.4, 93.5, 85.8, 84.6, 55.2, 45.2, 45.0, 30.2, 26.4, 25.1, 22.4, 18.4. HRMS (ESI) m/z [M + Na]$^+$ calculated for 509.1968, found 509.1970.



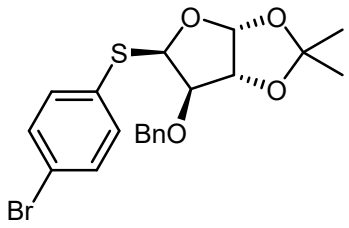
(2R,3S,4R,5R)-3,4-bis(benzyloxy)-2-((4-bromophenyl)thio)-5-methoxytetrahydrofuran (3aa): White solid; 43.5 mg; 86% yield; >20:1 d.r.; M.p.47-48 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.43 – 7.32 (m, 14H), 5.52 (d, *J* = 6.4 Hz, 1H), 4.99 (s, 1H), 4.65 (d, *J* = 1.2 Hz, 2H), 4.63 (s, 2H), 4.15 (dd, *J* = 6.3, 4.7 Hz, 1H), 3.92 – 3.88 (m, 1H), 3.37 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 137.5, 137.4, 133.9, 132.8, 132.0, 128.5, 128.05, 128.0, 127.9, 121.4, 107.4, 88.9, 81.8, 79.4, 72.9, 72.7, 55.4. HRMS (ESI) m/z [M + Na]$^+$ calculated for 523.0549, found 523.0550.



(2R,3S,4R,5R)-2-((4-bromophenyl)thio)-3,4,5-trimethoxytetrahydrofuran (3ab): Pale oil; 31.7 mg; 91% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.43 – 7.40 (m, 2H), 7.39 – 7.36 (m, 2H), 5.40 (d, *J* = 6.3 Hz, 1H), 4.99 (s, 1H), 3.99 (dd, *J* = 6.2, 4.7 Hz, 1H), 3.79 (d, *J* = 5.3 Hz, 1H), 3.49 (s, 6H), 3.41 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 134.0, 132.6, 132.0, 121.4, 106.5, 88.5, 84.1, 81.6, 58.9, 58.6, 55.5. HRMS (ESI) m/z [M + Na]$^+$ calculated for 370.9923, found 370.9925.

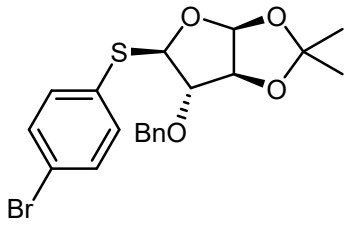


(3aS,5S,6R,6aR)-6-(benzyloxy)-5-((4-bromophenyl)thio)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole (3ac): Pale oil; 34.2 mg; 78% yield; d.r. = 6:1. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.46 – 7.28 (m, 9H), 6.02 (d, *J* = 3.8 Hz, 1H), 5.48 (s, 1H), 4.67 (d, *J* = 3.8 Hz, 1H), 4.59 (s, 2H), 4.23 (s, 1H), 1.67 (s, 3H), 1.34 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 136.7, 134.6, 132.9, 132.0, 128.6, 128.2, 127.95, 121.5, 113.6, 107.1, 91.4, 86.5, 83.4, 72.2, 26.4, 26.1. HRMS (ESI) m/z [M + Na]$^+$ calculated for 459.0236, found 459.0238.

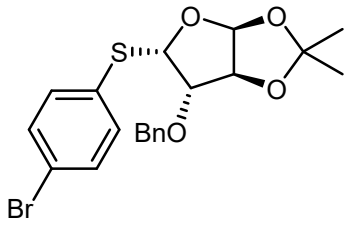


(3aS,5R,6R,6aR)-6-(benzyloxy)-5-((4-bromophenyl)thio)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole (3ac'): Pale oil; 5.7 mg; 13% yield; d.r. = 6:1.

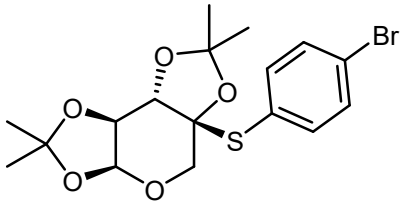
^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.27 (m, 9H), 6.08 (d, *J* = 3.8 Hz, 1H), 5.55 (d, *J* = 3.4 Hz, 1H), 4.78 – 4.66 (m, 2H), 4.64 (d, *J* = 3.7 Hz, 1H), 4.17 (d, *J* = 3.4 Hz, 1H), 1.45 (s, 3H), 1.33 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 136.9, 134.6, 132.2, 132.1, 128.5, 128.1, 127.9, 121.1, 112.6, 105.5, 89.8, 83.5, 82.0, 72.8, 27.1, 26.5. HRMS (ESI) m/z $[M + Na]^+$ calculated for 459.0236, found 459.0237.



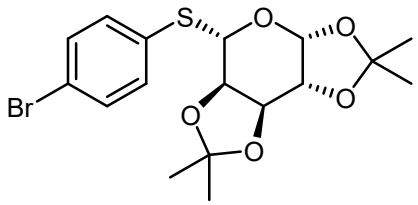
(3aR,5R,6S,6aS)-6-(benzyloxy)-5-((4-bromophenyl)thio)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole (3ad): Pale oil; 34.3 mg; 78% yield; d.r. = 6:1. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.44 – 7.28 (m, 9H), 6.01 (d, *J* = 3.8 Hz, 1H), 5.48 (s, 1H), 4.67 (d, *J* = 3.8 Hz, 1H), 4.60 (s, 2H), 4.23 (s, 1H), 1.67 (s, 3H), 1.34 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 136.7, 134.6, 132.9, 132.0, 128.6 128.2, 127.94, 121.5, 113.6, 107.1, 91.4, 86.5, 83.4, 72.2, 26.4, 26.1. HRMS (ESI) m/z $[M + Na]^+$ calculated for 459.0236, found 459.0239.



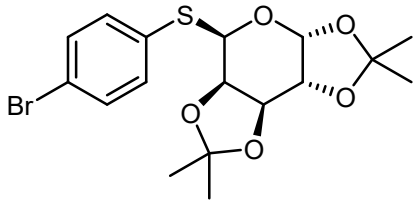
(3aR,5S,6S,6aS)-6-(benzyloxy)-5-((4-bromophenyl)thio)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole (3ad'): Pale oil; 5.8 mg; 13% yield; d.r. = 6:1. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.45 – 7.27 (m, 9H), 6.08 (d, *J* = 3.8 Hz, 1H), 5.55 (d, *J* = 3.4 Hz, 1H), 4.79 – 4.66 (m, 2H), 4.64 (d, *J* = 3.8 Hz, 1H), 4.17 (d, *J* = 3.4 Hz, 1H), 1.45 (s, 3H), 1.33 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 136.9, 134.6, 132.2, 132.1, 128.5, 128.1, 127.9, 121.1, 112.6, 105.5, 89.8, 83.5, 82.0, 72.8, 27.1, 26.5. HRMS (ESI) m/z $[M + Na]^+$ calculated for 459.0236, found 459.0237.



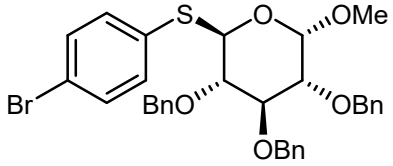
(3aS,5aS,8aS,8bS)-5a-((4-bromophenyl)thio)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (3ae): Pale oil; 28.7 mg; 68% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 4.55 (d, *J* = 7.5 Hz, 1H), 4.33 (s, 1H), 4.22 (d, *J* = 7.4 Hz, 1H), 3.81 (s, 2H), 1.48 (s, 3H), 1.47 (s, 3H), 1.34 (s, 3H), 1.22 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 137.1, 130.7, 128.2, 122.7, 109.0, 108.3, 108.3, 74.2, 70.0, 68.8, 61.8, 25.3, 24.9, 23.4, 23.1. HRMS (ESI) m/z $[M + Na]^+$ calculated for 439.0185, found 439.0184.



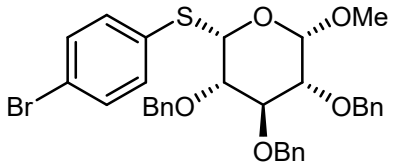
(3aS,5S,5aR,8aR,8bR)-5-((4-bromophenyl)thio)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (3af): Pale oil; 24.4 mg; 58% yield; d.r. = 3:1. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.48 – 7.38 (m, 4H), 5.31 (d, *J* = 2.4 Hz, 1H), 4.54 (d, *J* = 5.4 Hz, 1H), 4.43 (d, *J* = 9.7 Hz, 1H), 4.24 (d, *J* = 1.7 Hz, 1H), 4.00 (dd, *J* = 9.6, 5.4 Hz, 1H), 1.52 (s, 3H), 1.47 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 134.8, 132.0, 131.2, 122.5, 111.4, 109.3, 97.2, 81.5, 75.5, 74.4, 71.5, 28.0, 27.8, 25.8, 25.4. HRMS (ESI) m/z $[M + Na]^+$ calculated for 439.0185, found 439.0183.



(3aS,5R,5aR,8aR,8bR)-5-((4-bromophenyl)thio)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (3af'): Yellow solid; 9.7 mg; 23% yield; d.r. = 3:1. M.p.87-88℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.40 (s, 4H), 5.68 (d, *J* = 5.0 Hz, 1H), 5.20 (d, *J* = 1.8 Hz, 1H), 4.67 (dd, *J* = 7.6, 2.7 Hz, 1H), 4.48 (dd, *J* = 7.6, 1.9 Hz, 1H), 4.38 (dd, *J* = 5.0, 2.7 Hz, 1H), 1.55 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 135.3, 131.9, 130.3, 120.4, 110.5, 109.3, 97.5, 78.9, 73.6, 71.7, 70.0, 26.0, 25.8, 24.9, 24.7. HRMS (ESI) m/z $[M + Na]^+$ calculated for 439.0185, found 439.0184.

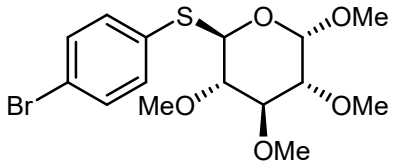


(2R,3S,4R,5R,6S)-3,4,5-tris(benzyloxy)-2-((4-bromophenyl)thio)-6-methoxytetrahydro-2H-pyran (3ag): White solid; 24.5 mg; 39% yield; d.r. = 1:1. M.p.87 -88 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.56 – 7.27 (m, 19H), 4.93 (d, *J* = 10.7 Hz, 1H), 4.88 (d, *J* = 10.0 Hz, 1H), 4.85 – 4.75 (m, 4H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.57 (d, *J* = 3.5 Hz, 1H), 4.03 – 3.94 (m, 1H), 3.52 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.39 (dd, *J* = 10.0, 8.9 Hz, 1H), 3.24 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 138.5, 138.0, 138.0, 134.7, 132.1, 132.0, 128.5, 128.4, 128.4, 128.1, 128.1, 128.0, 127.9, 127.7, 122.4, 98.9, 81.6, 81.0, 80.8, 79.3, 76.1, 75.6, 73.6, 55.7. HRMS (ESI) m/z $[M + Na]^+$ calculated for 643.1124, found 643.1122.

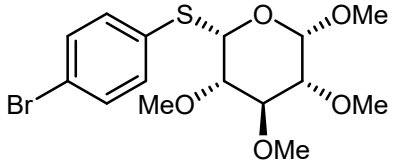


(2S,3S,4R,5R,6S)-3,4,5-tris(benzyloxy)-2-((4-bromophenyl)thio)-6-methoxytetrahydro-2H-pyran (3ag'): White solid; 24.1 mg; 39% yield; d.r. = 1:1. M.p. 86-87 ℃. **^{1}H-NMR (400**

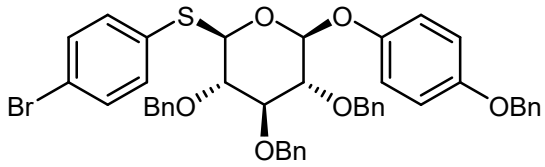
MHz, Chloroform-*d*) δ 7.52 – 7.28 (m, 19H), 5.36 (d, *J* = 4.9 Hz, 1H), 4.91 (s, 2H), 4.87 (d, *J* = 12.3 Hz, 1H), 4.78 – 4.67 (m, 3H), 4.56 (d, *J* = 11.6 Hz, 1H), 4.17 (t, *J* = 8.6 Hz, 1H), 3.80 (dd, *J* = 8.2, 5.2 Hz, 1H), 3.57 (d, *J* = 3.1 Hz, 1H), 3.54 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 138.5, 138.3, 137.6, 137.1, 132.4, 131.9, 128.4, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 120.6, 100.9, 86.0, 79.1, 78.3, 75.4, 73.7, 73.4, 57.2. HRMS (ESI) m/z $[M + Na]^+$ calculated for 643.1124, found 643.1123.



(2R,3S,4R,5R,6S)-2-((4-bromophenyl)thio)-3,4,5,6-tetramethoxytetrahydro-2H-pyran (3ah): Pale oil; 17.3 mg; 44% yield; d.r. = 1:1. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.56 – 7.34 (m, 4H), 4.79 (d, *J* = 3.5 Hz, 1H), 4.72 (d, *J* = 10.0 Hz, 1H), 3.60 (s, 3H), 3.59 (s, 3H), 3.50 (s, 4H), 3.27 (s, 3H), 3.18 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.03 – 2.94 (m, 1H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 133.9, 131.0, 130.8, 121.5, 97.2, 82.2, 81.3, 80.1, 79.5, 60.0, 59.8, 58.2, 54.7. HRMS (ESI) m/z $[M + Na]^+$ calculated for 415.0185, found 415.0183.

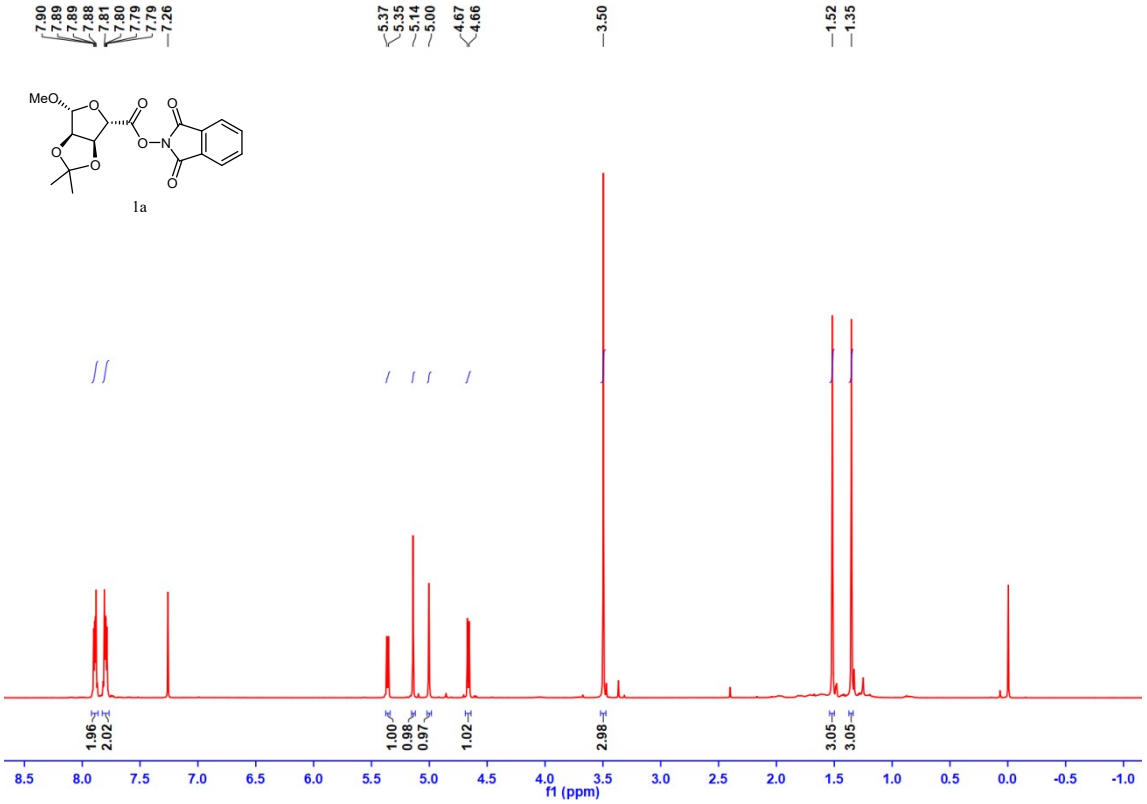


(2S,3S,4R,5R,6S)-2-((4-bromophenyl)thio)-3,4,5,6-tetramethoxytetrahydro-2H-pyran (3ah'): White solid; 16.9 mg; 43% yield; d.r. = 1:1. M.p. 122-123 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.40 (s, 4H), 5.40 (d, *J* = 5.1 Hz, 1H), 4.87 (d, *J* = 3.5 Hz, 1H), 3.70 (t, *J* = 8.5 Hz, 1H), 3.62 (s, 3H), 3.53 (s, 3H), 3.49 (s, 3H), 3.47 (dd, *J* = 8.5, 5.2 Hz, 1H), 3.40 (s, 3H), 3.24 (dd, *J* = 8.5, 3.5 Hz, 1H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 137.0, 132.1, 131.9, 120.6, 100.3, 85.3, 81.2, 80.3, 78.2, 60.7, 59.3, 59.0, 57.1. HRMS (ESI) m/z $[M + Na]^+$ calculated for 415.0185, found 415.0184.

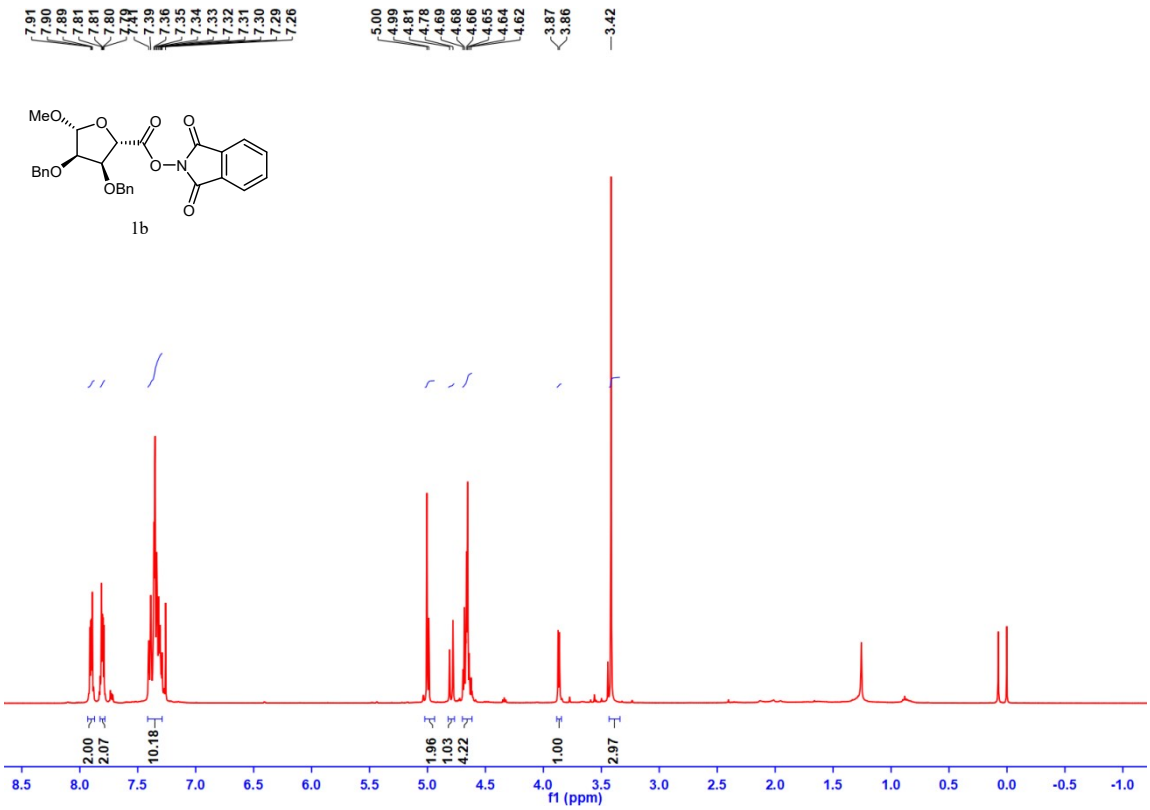


(2R,3R,4R,5S,6R)-3,4,5-tris(benzyloxy)-2-(4-(benzyloxy)phenoxy)-6-((4-bromophenyl)thio)tetrahydro-2H-pyran (3ai): White solid; 66.4 mg; 84% yield; >20:1 d.r.; M.p.148-149 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.53 – 7.27 (m, 22H), 7.18 – 7.12 (m, 2H), 6.79 – 6.70 (m, 4H), 5.61 (d, *J* = 3.3 Hz, 1H), 5.59 (s, 1H), 5.03 .s, 2H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.94 – 4.84 (m, 2H), 4.81 (d, *J* = 10.9 Hz, 1H), 4.78 – 4.70 (m, 2H), 3.99 – 3.89 (m, 2H), 3.68 (t, *J* = 8.1 Hz, 1H).**^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 154.6, 150.9, 138.3, 138.2, 137.5, 137.1, 133.0, 132.6, 132.1, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5,127.2, 118.6, 115.5, 98.7, 84.1, 81.4, 80.4, 79.0, 75.9, 75.2, 73.2, 70.5. HRMS (ESI) m/z $[M + Na]^+$ calculated for 811.1699, found 811.1700.

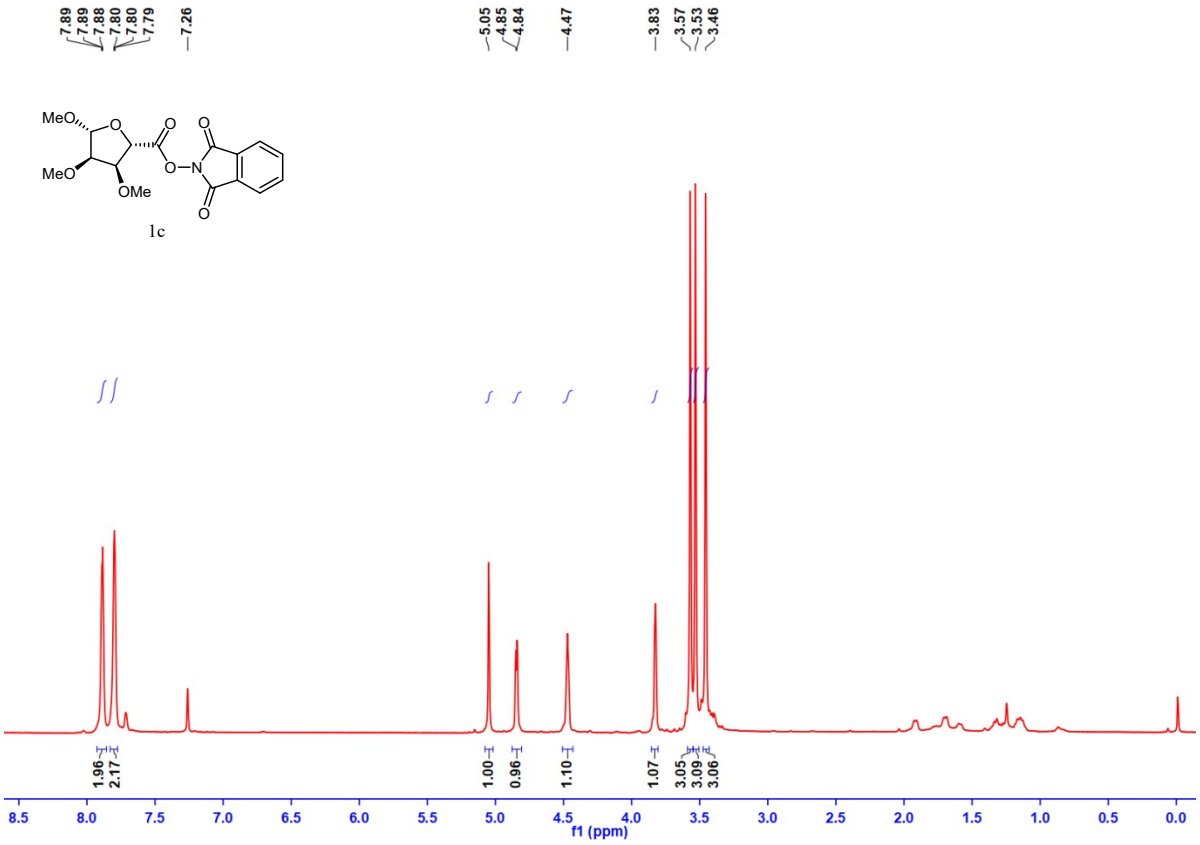
9. NMR spectra



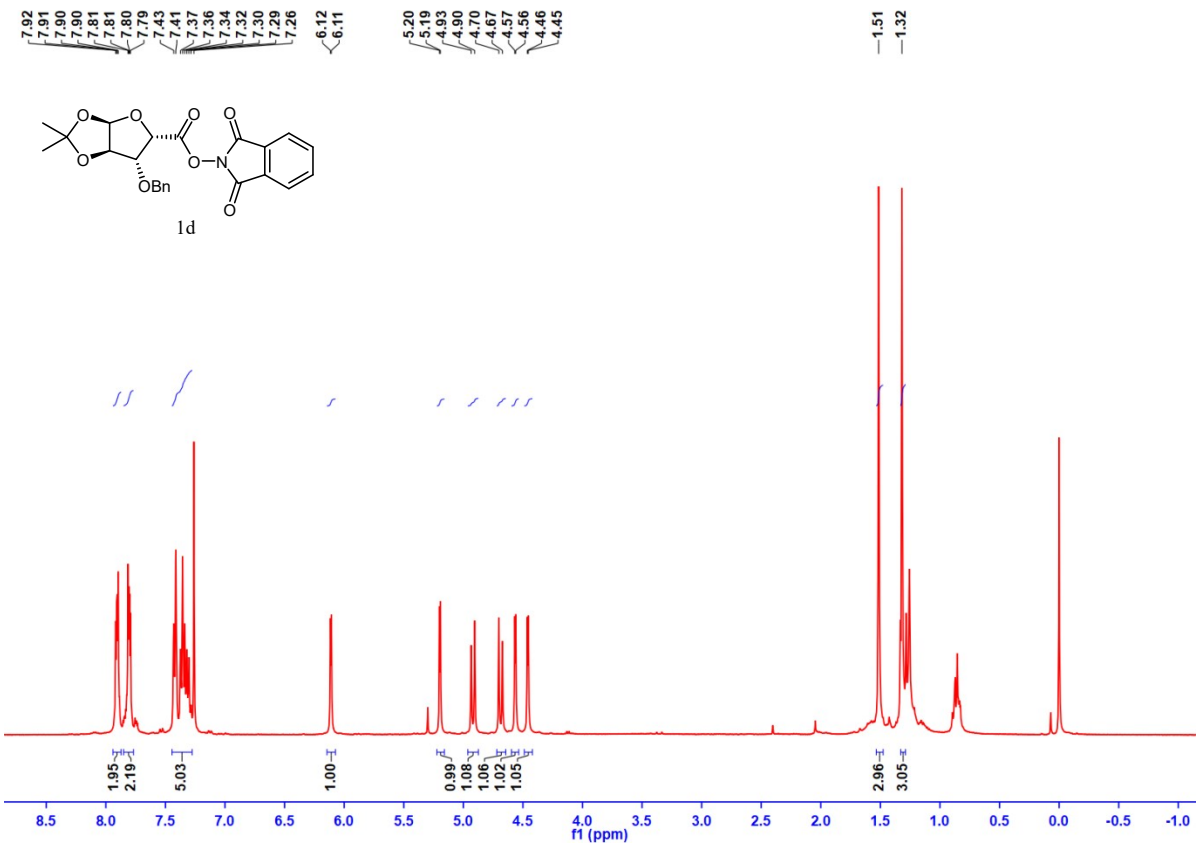
1a



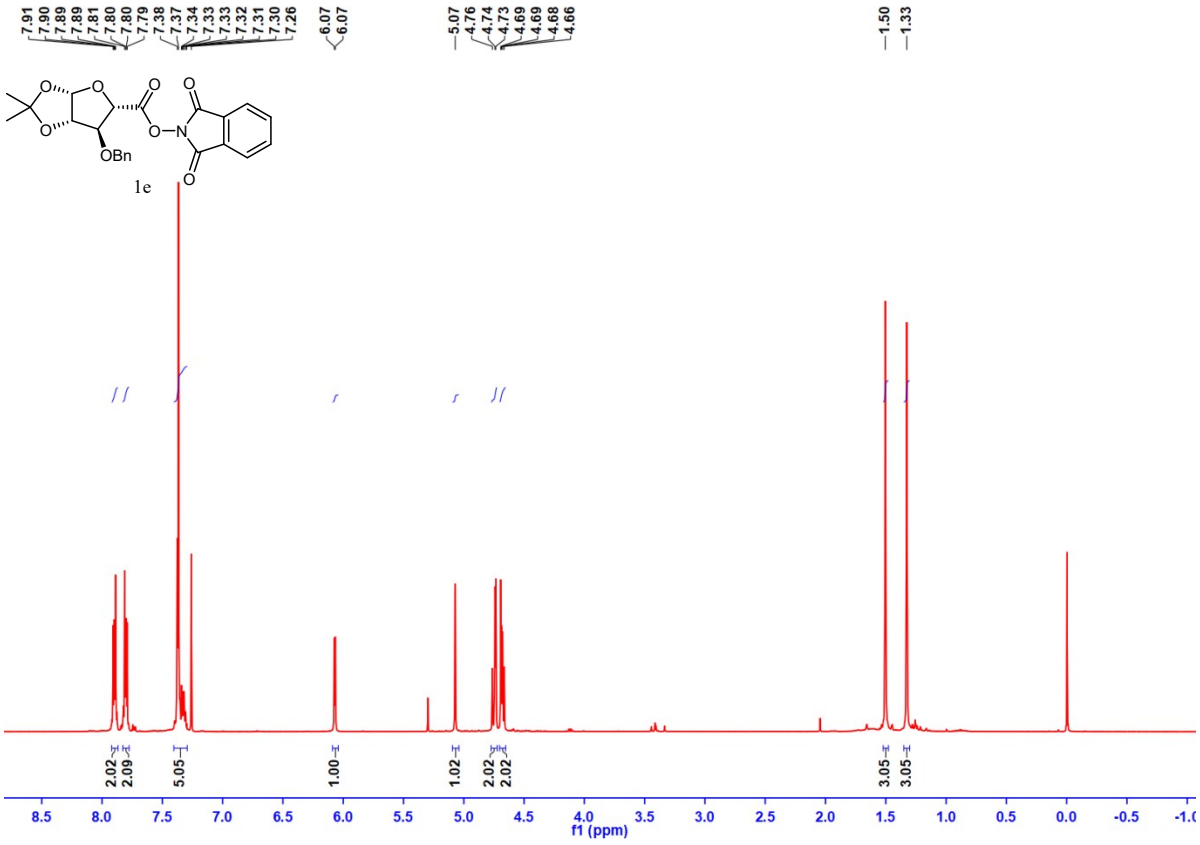
1b

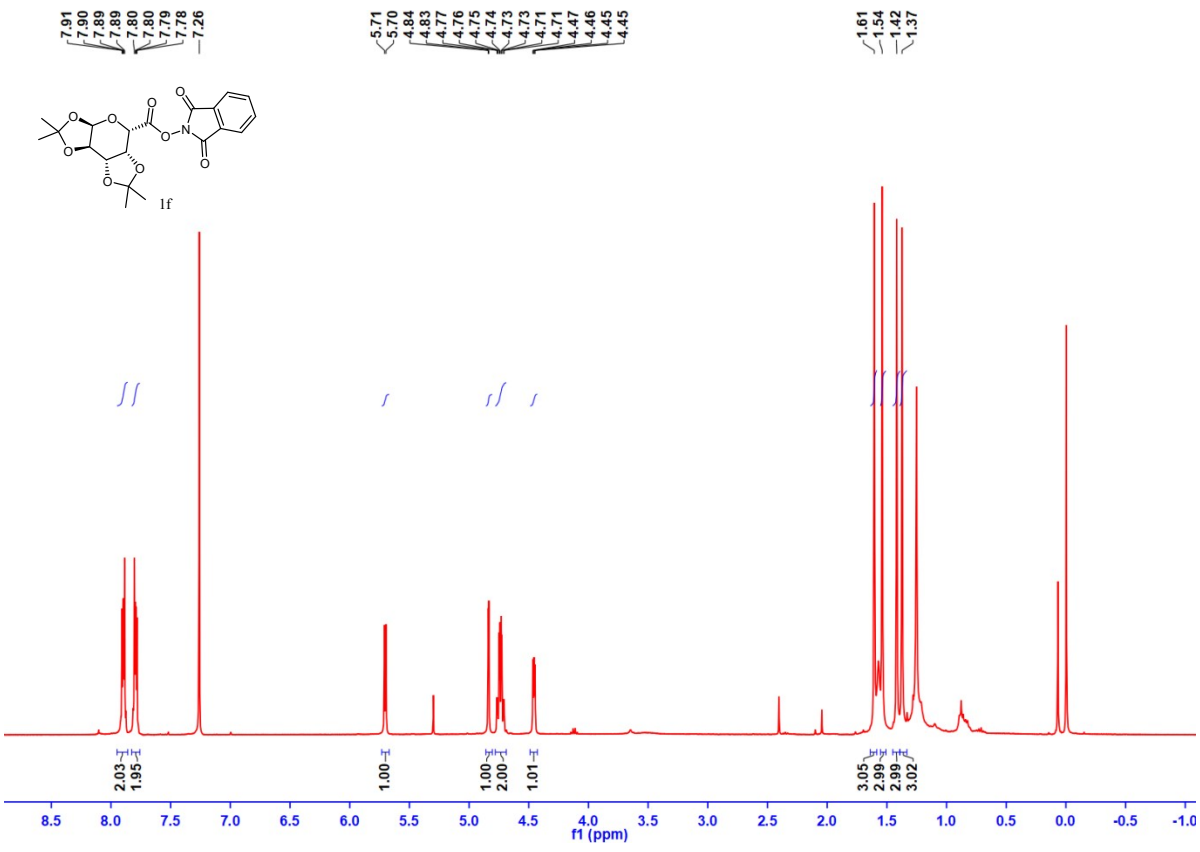

7.89
7.89
7.88
7.80
7.80
7.79
7.26
5.05
4.85
4.84
4.47
3.83
3.57
3.53
3.46
MeO
MeO
OMe
O
O
O
O
N
O
1.96
2.17
1.00
0.96
1.10
1.07
3.05
3.09
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

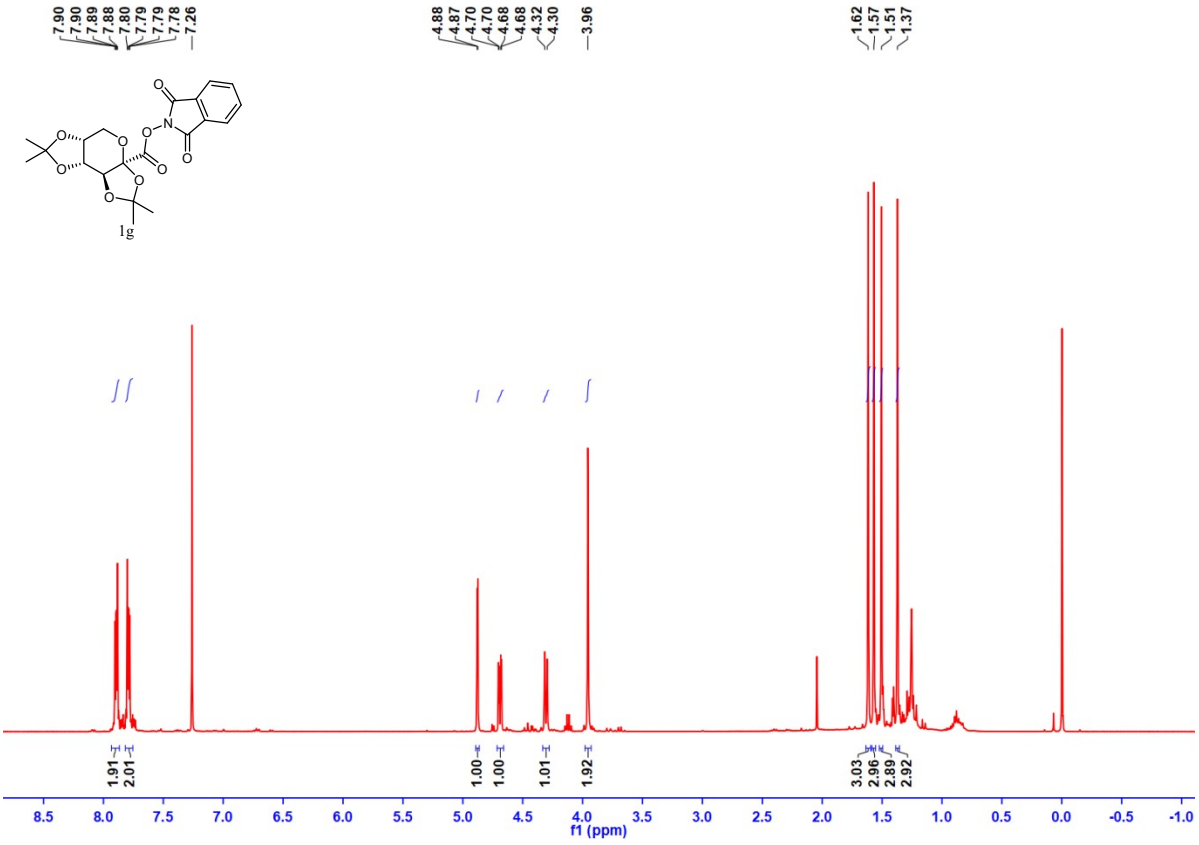
1c


7.92
7.91
7.90
7.90
7.81
7.81
7.80
7.79
7.43
7.41
7.37
7.36
7.34
7.32
7.30
7.29
7.26
6.12
6.11
5.20
5.19
4.93
4.90
4.70
4.67
4.57
4.56
4.46
4.45
1.51
1.32
O
O
O
O
O
N
O
OBn
1.95
2.19
5.03
1.00
0.99
1.08
1.06
1.02
1.05
2.96
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

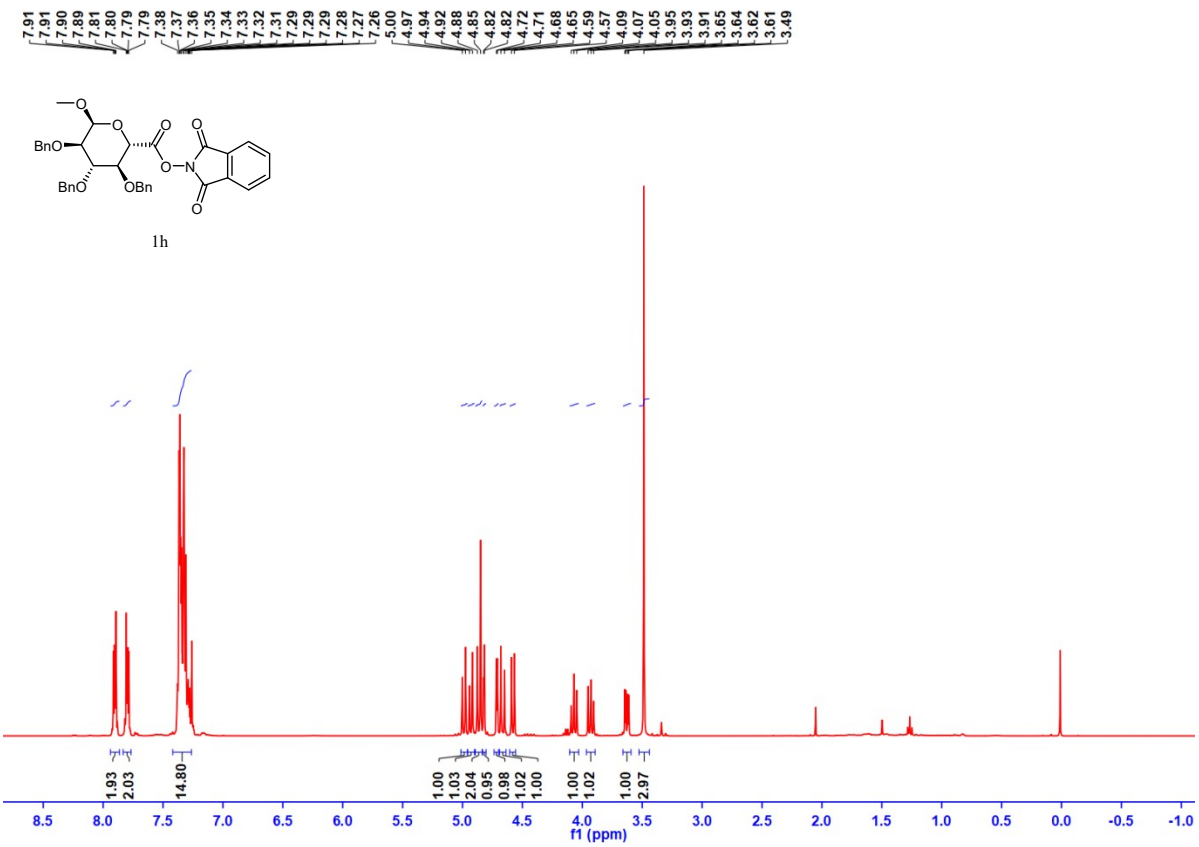
1d


7.91
7.90
7.89
7.89
7.81
7.80
7.80
7.79
7.38
7.37
7.34
7.33
7.33
7.32
7.31
7.30
7.26
6.07
6.07
5.07
4.76
4.74
4.73
4.69
4.69
4.68
4.66
1.50
1.33
O
O
O
O
O
O
N
O
OBn
1e
2.02
2.09
5.05
1.00
1.02
2.02
2.02
3.05
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

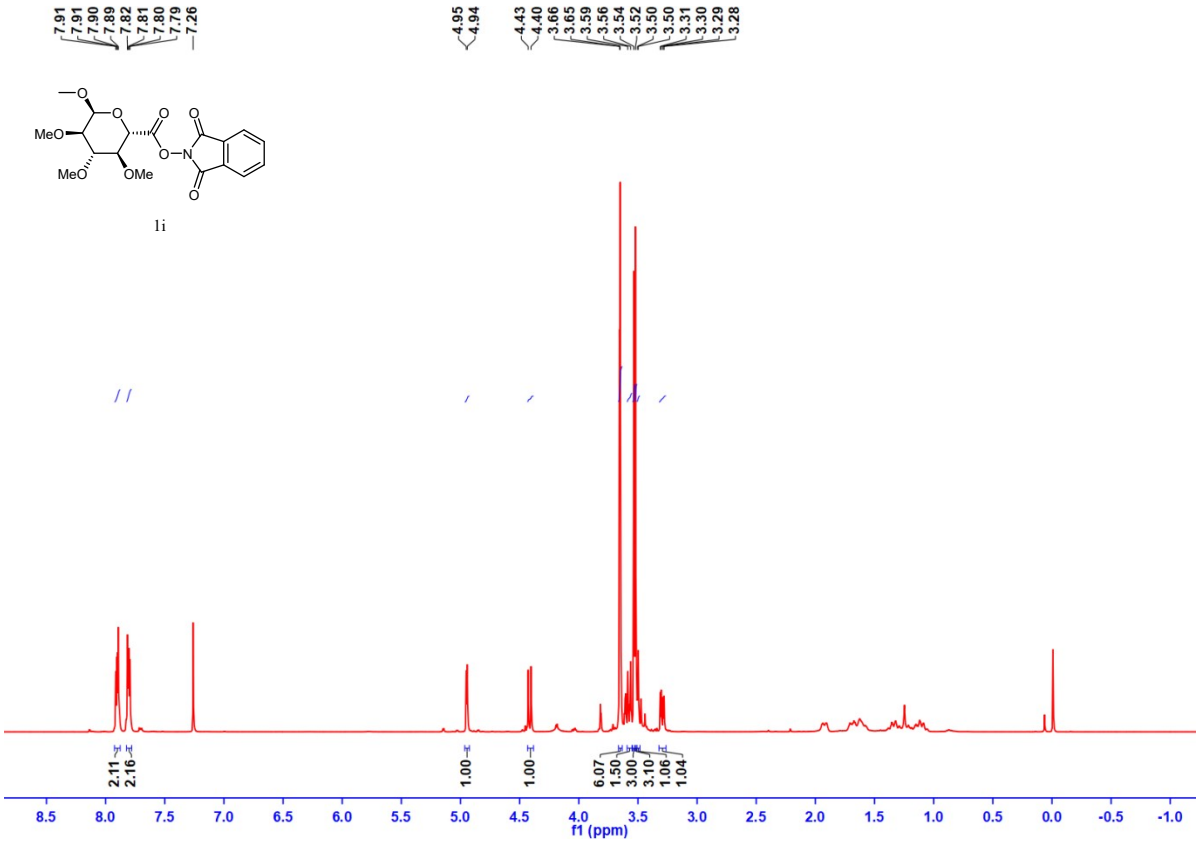

7.91
7.90
7.89
7.89
7.80
7.80
7.79
7.78
7.26
5.71
5.70
4.84
4.83
4.77
4.76
4.75
4.74
4.73
4.73
4.71
4.71
4.47
4.46
4.45
4.45
1.61
1.54
1.42
1.37
O
O
O
O
O
O
N
O
O
1f
2.03
1.95
1.00
1.00
2.00
1.01
3.05
2.99
2.99
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


7.90
7.90
7.89
7.88
7.80
7.79
7.79
7.78
7.26
4.88
4.87
4.70
4.70
4.68
4.68
4.32
4.30
3.96
1.62
1.57
1.51
1.37
1.91
2.01
1.00
1.00
1.01
1.92
3.03
2.96
2.89
2.92
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

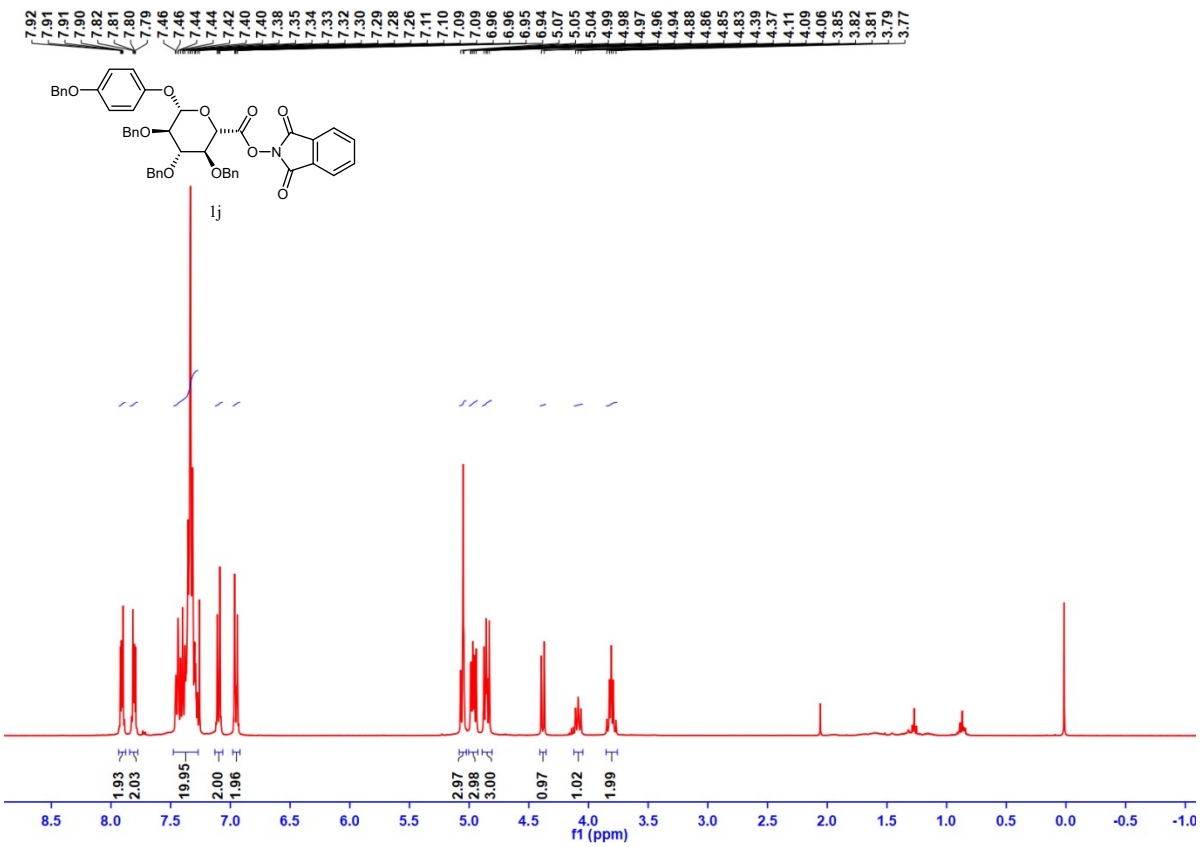
1g


7.91
7.91
7.90
7.89
7.81
7.80
7.79
7.79
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.29
7.29
7.29
7.28
7.27
7.26
5.00
4.97
4.94
4.92
4.88
4.85
4.82
4.82
4.72
4.71
4.68
4.65
4.59
4.57
4.09
4.07
4.05
3.95
3.93
3.91
3.65
3.64
3.62
3.61
3.49
1.93
2.03
14.80
1.00
1.03
2.04
0.95
0.98
1.02
1.00
1.00
1.02
1.00
2.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

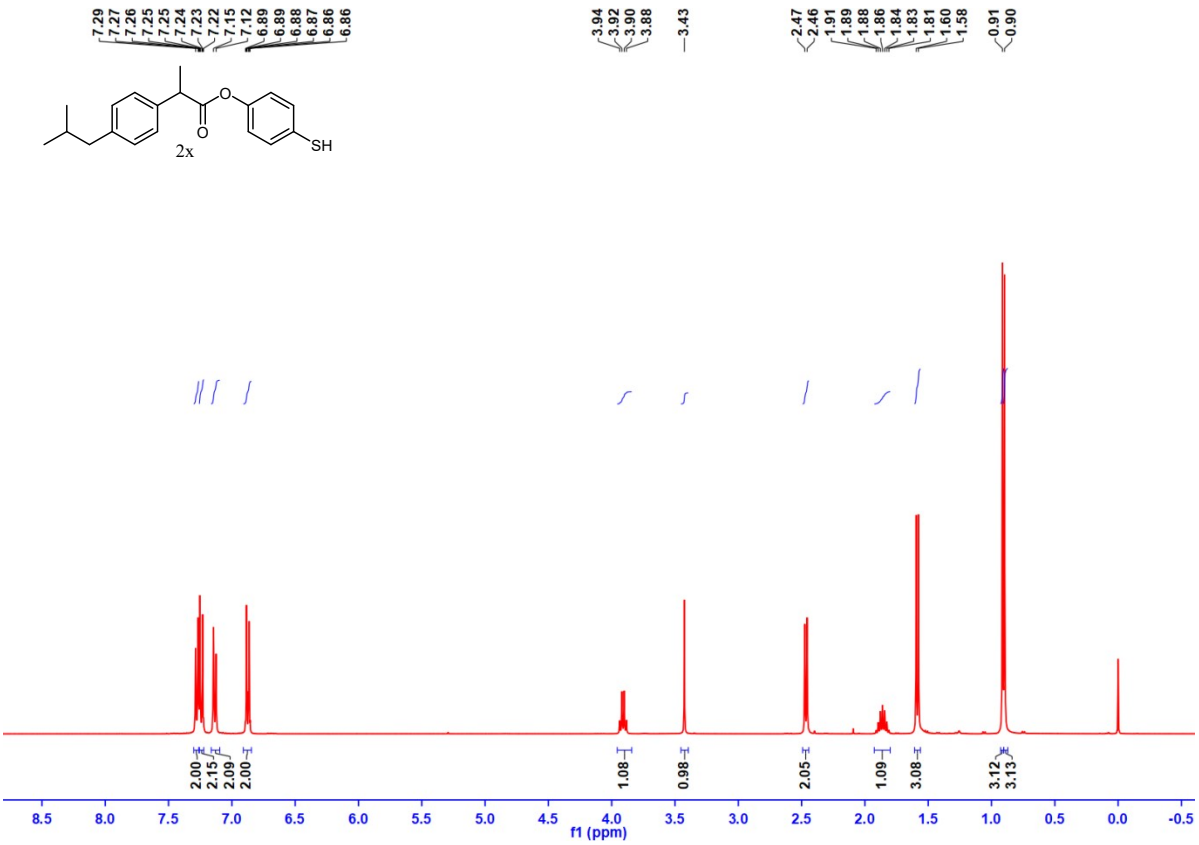
1h

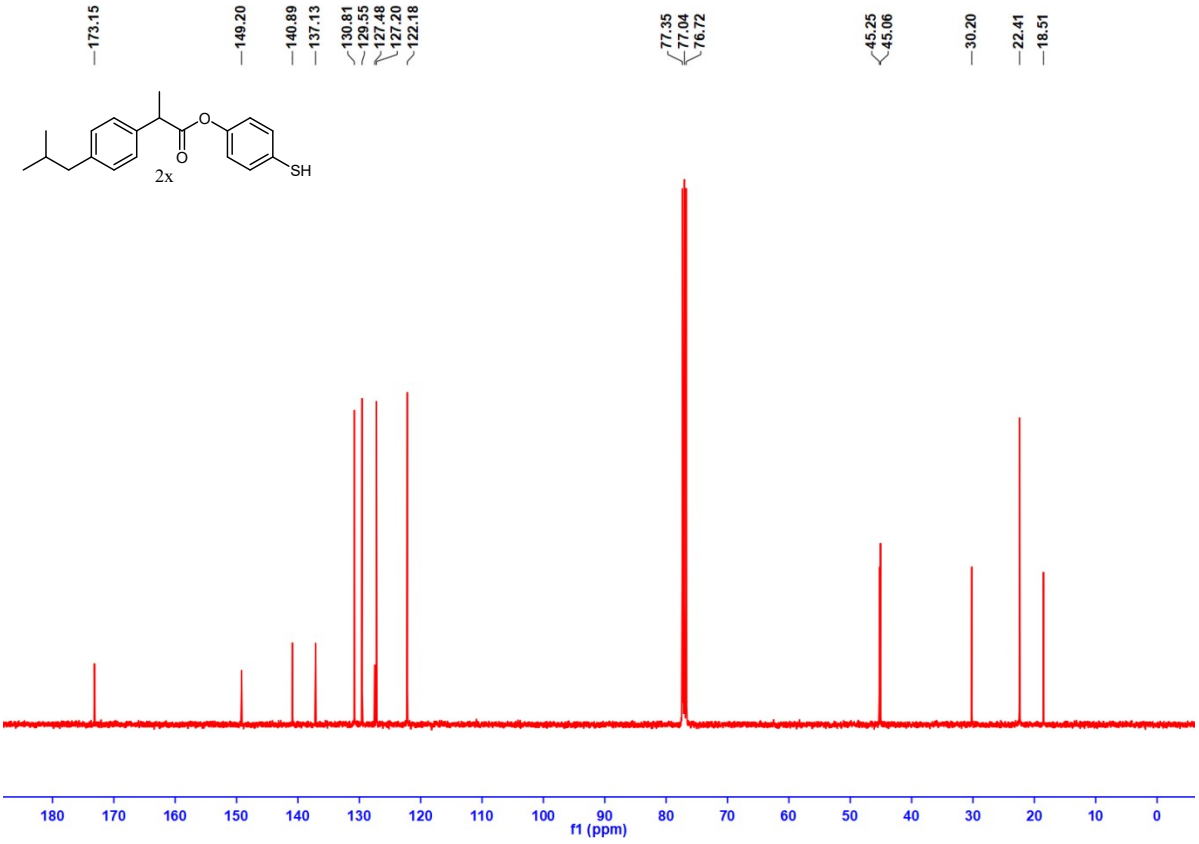

7.91
7.91
7.90
7.89
7.82
7.81
7.80
7.79
7.26
4.95
4.94
4.43
4.40
3.66
3.65
3.59
3.56
3.54
3.52
3.50
3.50
3.31
3.30
3.29
3.28
MeO
MeO
OMe
O
O
O
O
N
O
2.11
2.16
1.00
1.00
6.07
1.50
3.00
3.10
1.06
1.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

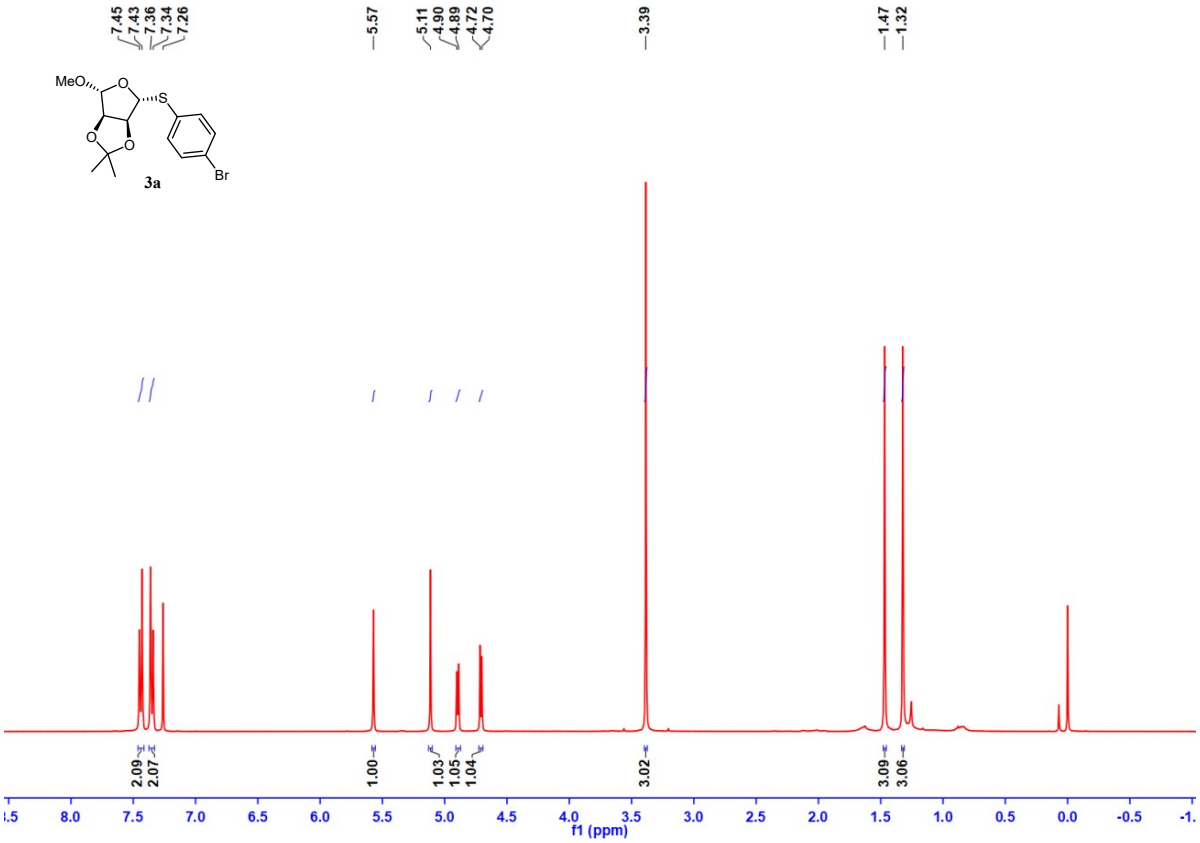
1i

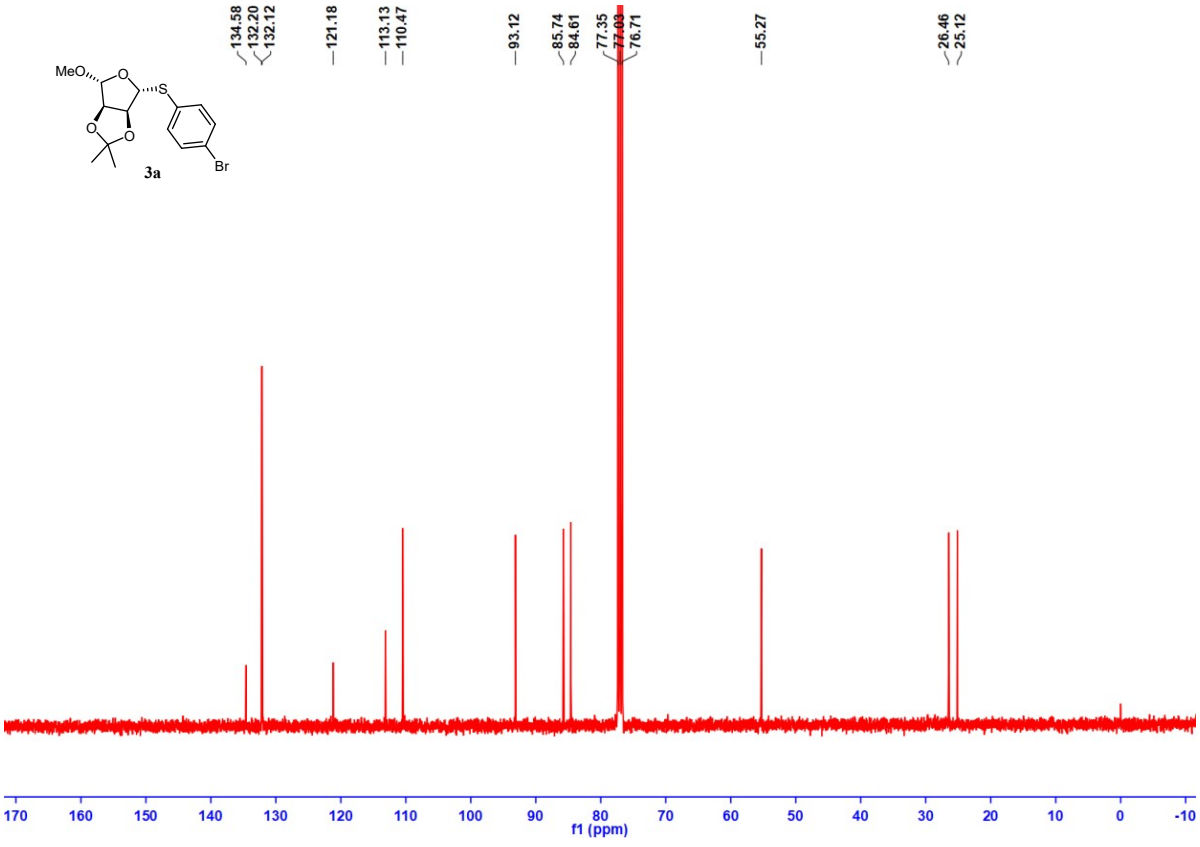

7.92
7.91
7.91
7.90
7.82
7.81
7.80
7.79
7.46
7.46
7.44
7.44
7.42
7.40
7.40
7.38
7.35
7.34
7.33
7.32
7.30
7.29
7.28
7.26
7.11
7.10
7.09
7.09
6.96
6.96
6.95
6.94
5.07
5.05
5.04
4.99
4.98
4.97
4.96
4.94
4.88
4.86
4.85
4.83
4.39
4.37
4.11
4.09
4.06
3.85
3.82
3.81
3.79
3.77
BnO
BnO
BnO
OBn
O
O
O
O
N
O
1.93
2.03
19.95
2.00
1.96
2.97
2.98
3.00
0.97
1.02
1.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

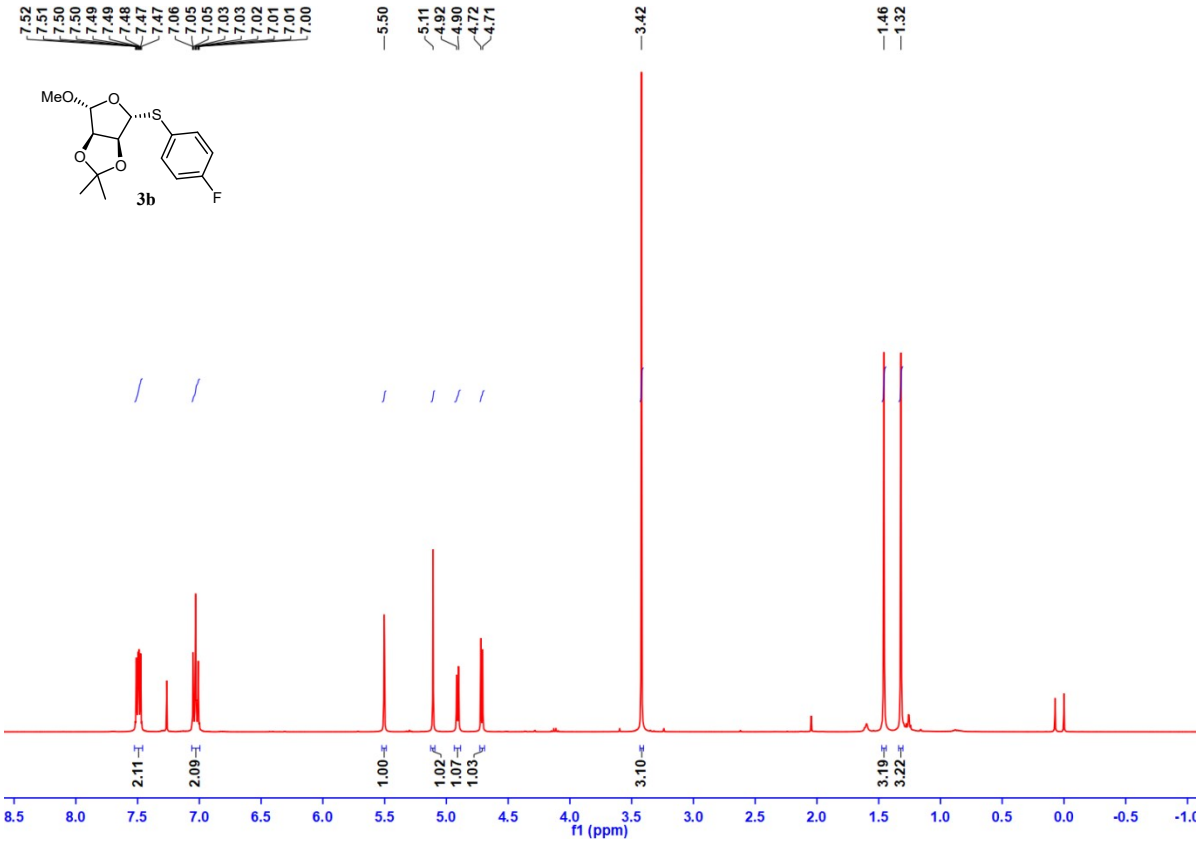
1j

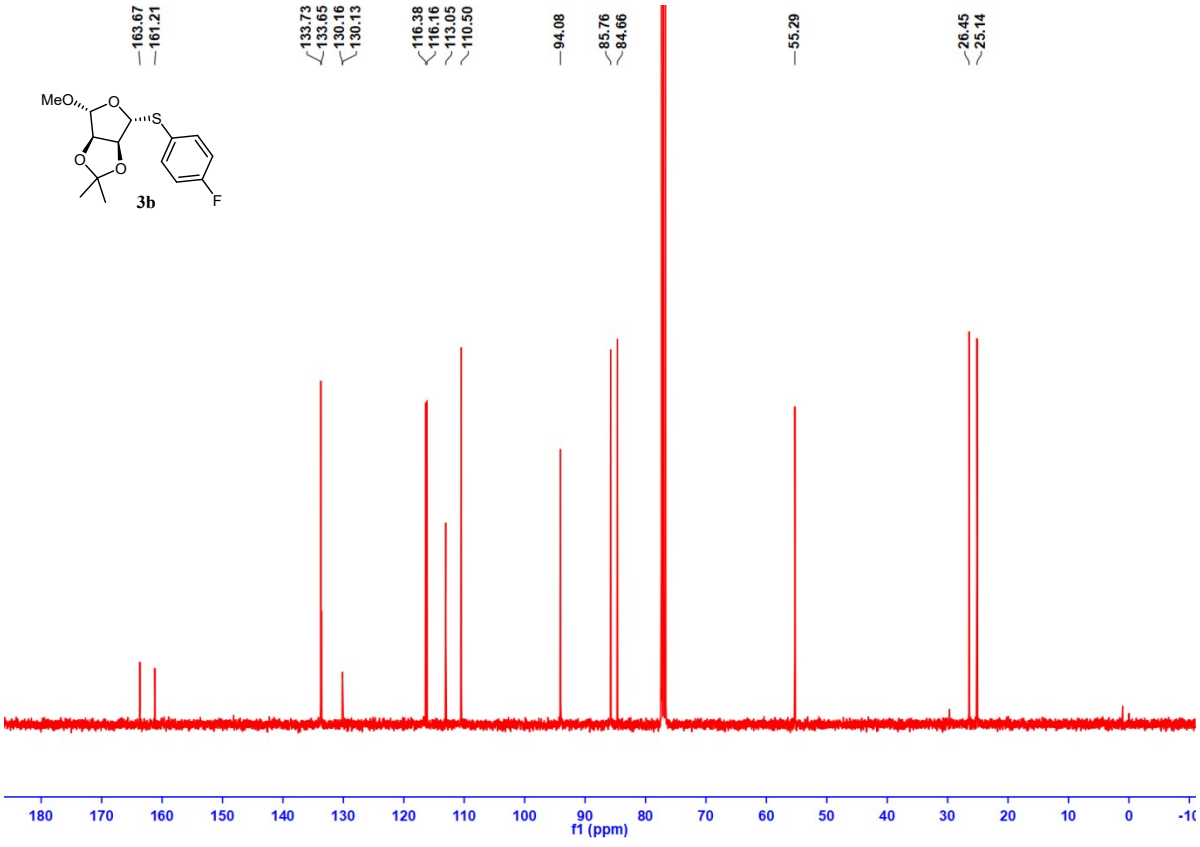

7.29
7.27
7.26
7.25
7.25
7.24
7.23
7.22
7.15
7.12
6.89
6.89
6.88
6.87
6.86
6.86
3.94
3.92
3.90
3.88
3.43
2.47
2.46
1.91
1.89
1.88
1.86
1.84
1.83
1.81
1.60
1.58
0.91
0.90
O
O
SH
2x
2.00
2.15
2.09
2.00
1.08
0.98
2.05
1.09
3.08
3.12
3.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

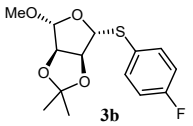

173.15
149.20
140.89
137.13
130.81
129.55
127.48
127.20
122.18
77.35
77.04
76.72
45.25
45.06
30.20
22.41
18.51
O
O
SH
2x
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.45
7.43
7.36
7.34
7.26
5.57
5.11
4.90
4.89
4.72
4.70
3.39
1.47
1.32
MeO
O
S
O
O
Br
3a
2.09
2.07
1.00
1.03
1.05
1.04
3.02
3.09
3.06
f1 (ppm)


134.58
132.20
132.12
121.18
113.13
110.47
93.12
85.74
84.61
77.35
77.03
76.71
55.27
26.46
25.12
MeO
O
S
O
O
Br
3a
f1 (ppm)

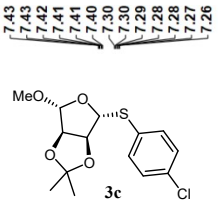

7.52
7.51
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.06
7.05
7.05
7.03
7.03
7.02
7.01
7.01
7.00
5.50
5.11
4.92
4.90
4.72
4.71
3.42
1.46
1.32
MeO
O
S
O
O
F
3b
2.11
2.09
1.00
1.02
1.07
1.03
3.10
3.19
3.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


163.67
161.21
133.73
133.65
130.16
130.13
116.38
116.16
113.05
110.50
94.08
85.76
84.66
55.29
26.45
25.14
MeO
O
S
O
O
F
3b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO
O
S
O
O
F

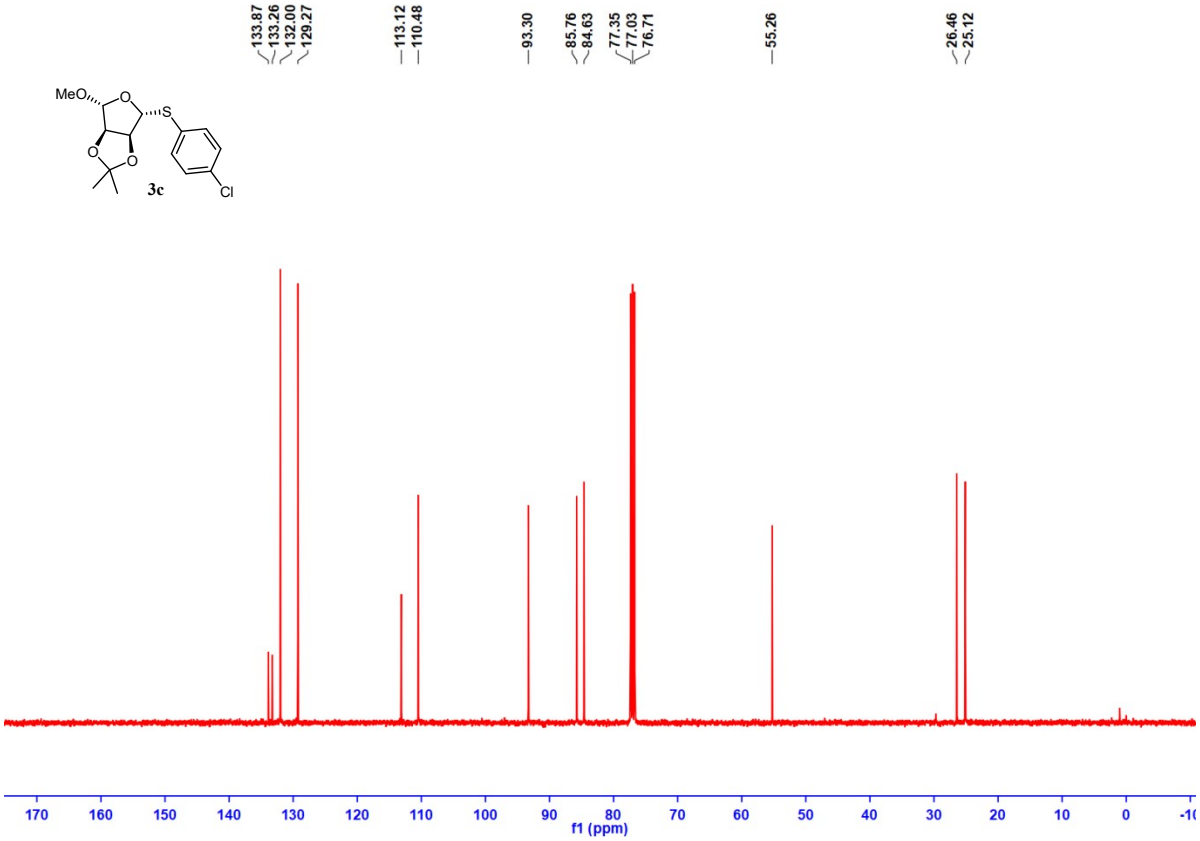
3b

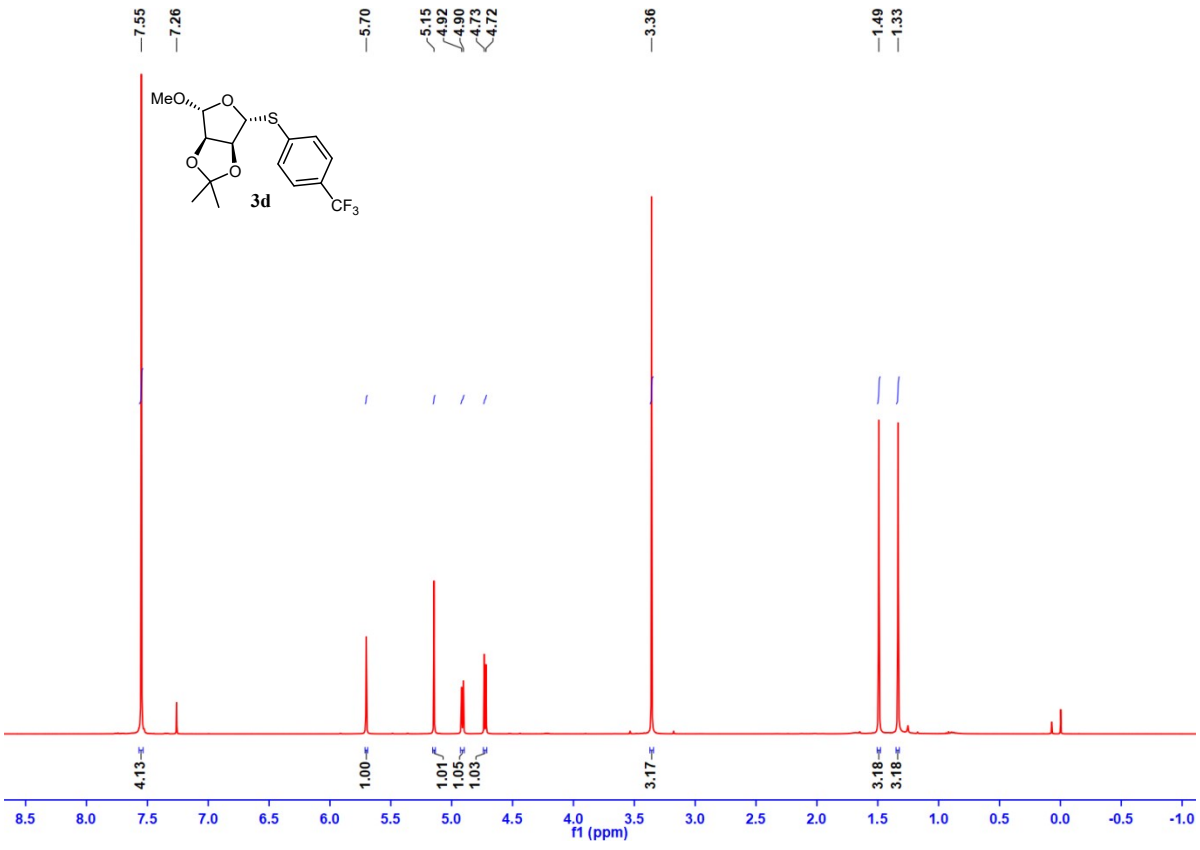
-114.07
-114.08
-114.09
-114.10
-114.11
-114.11
-114.12
-114.13
-114.14
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

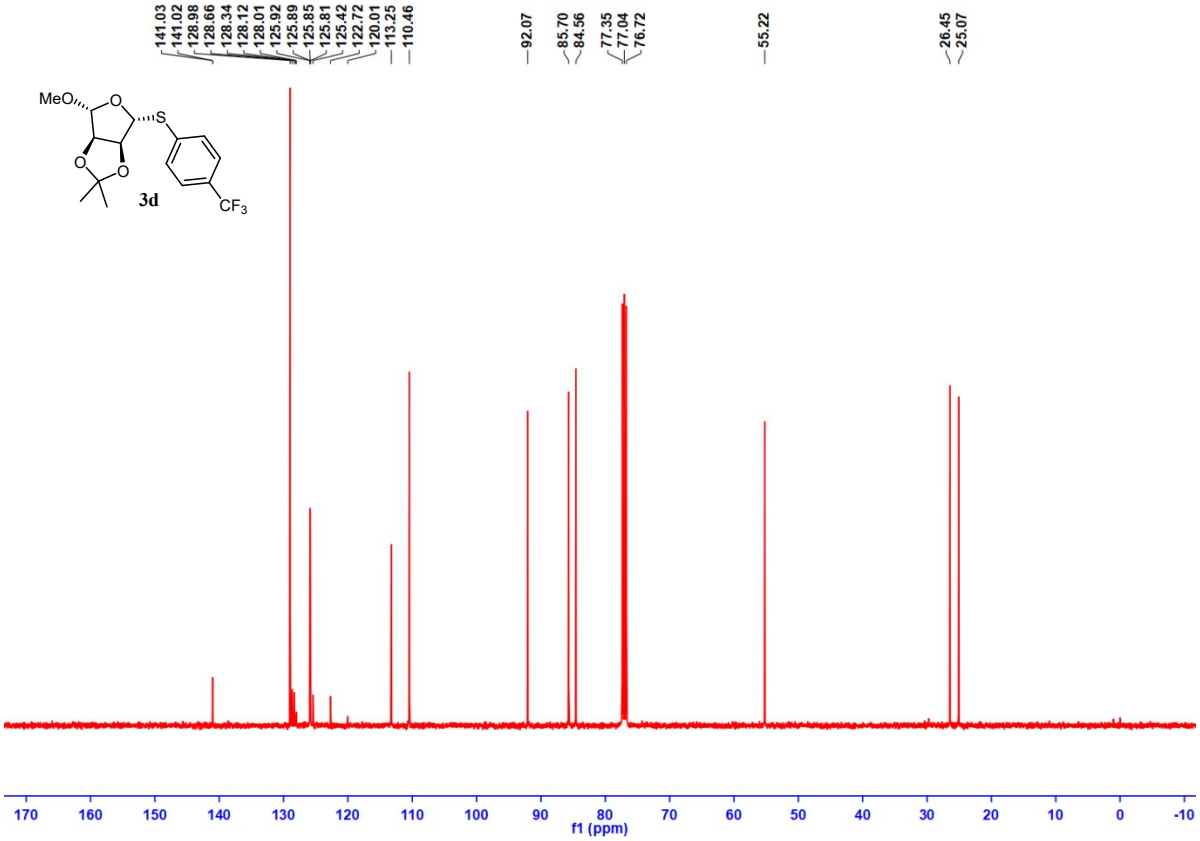

MeO
O
S
O
O
Cl

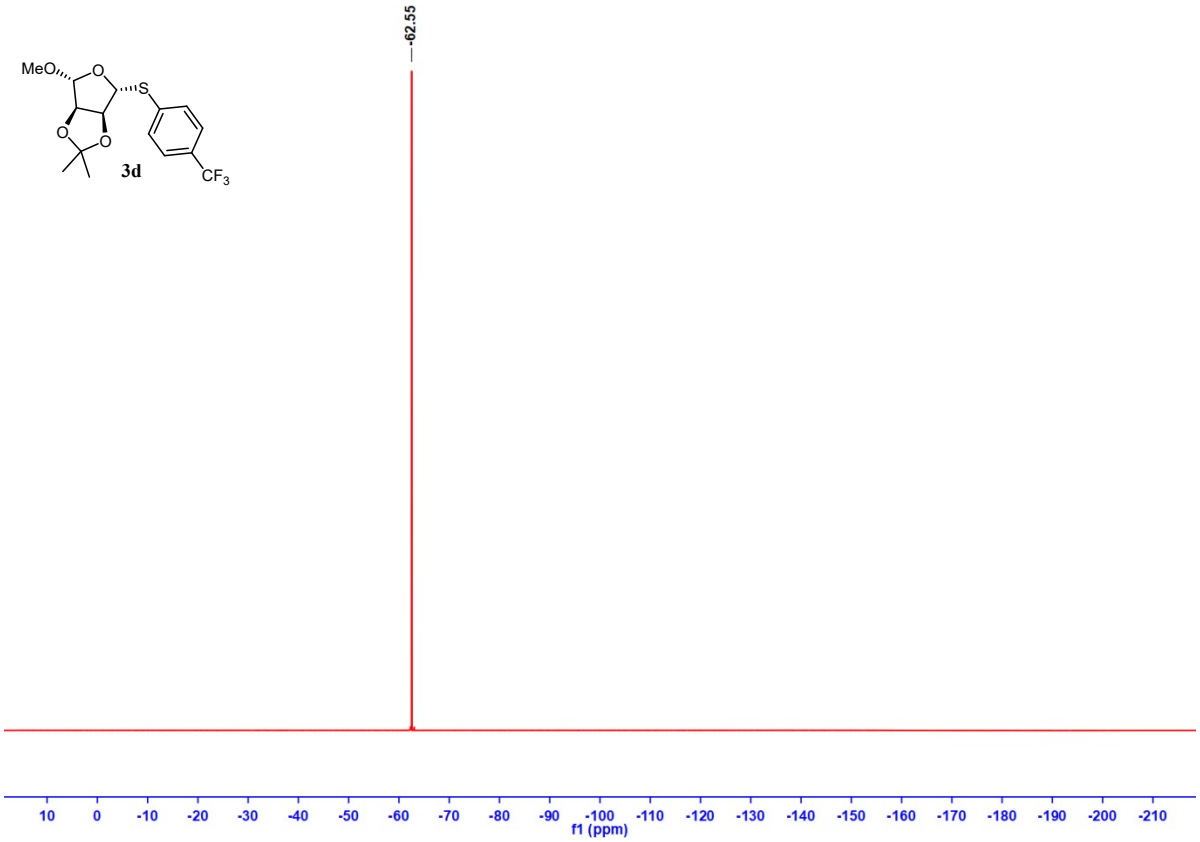
3c

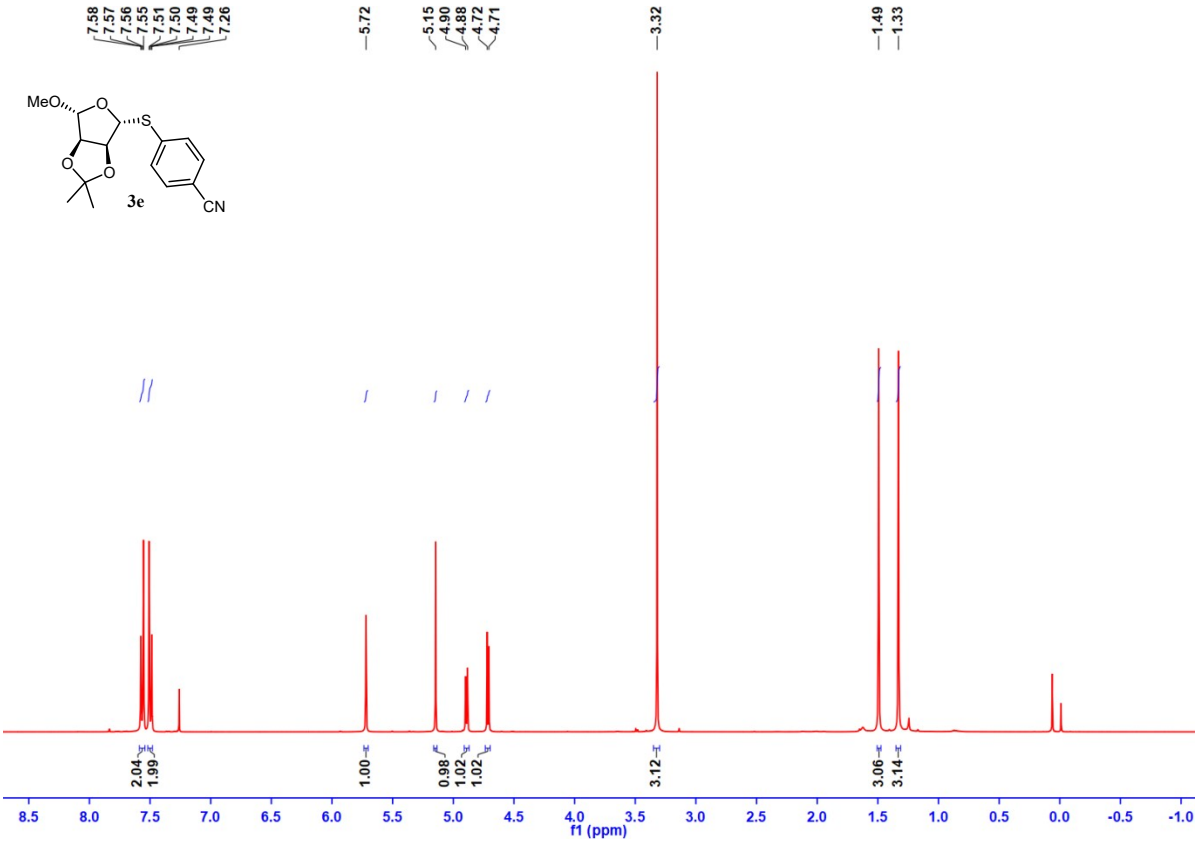
7.43
7.43
7.42
7.41
7.41
7.40
7.30
7.30
7.29
7.28
7.28
7.27
7.26
5.56
5.11
4.90
4.89
4.72
4.70
3.39
1.46
1.32
2.06
2.04
1.00
1.01
1.03
1.04
3.15
3.14
3.06
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

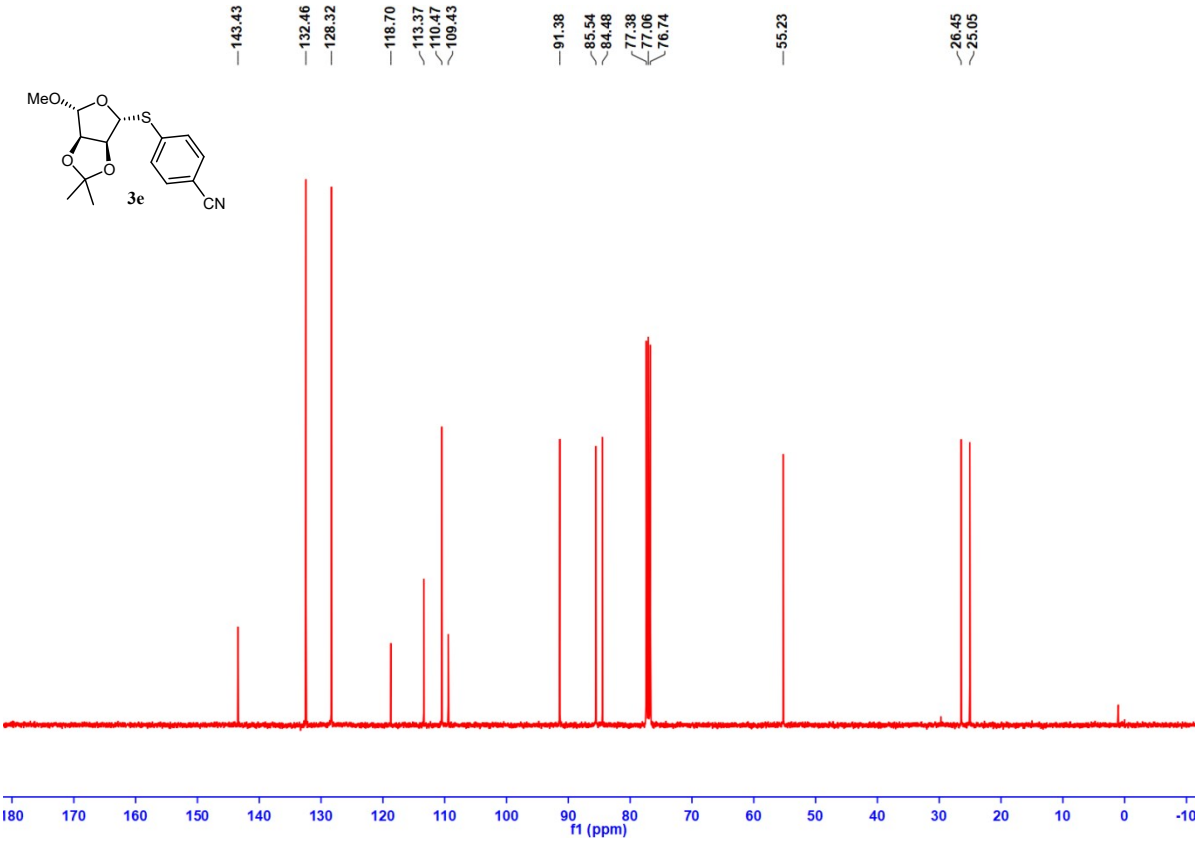

133.87
133.26
132.00
129.27
113.12
110.48
93.30
85.76
84.63
77.35
77.03
76.71
55.26
26.46
25.12
MeO
O
S
O
O
Cl
3c
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

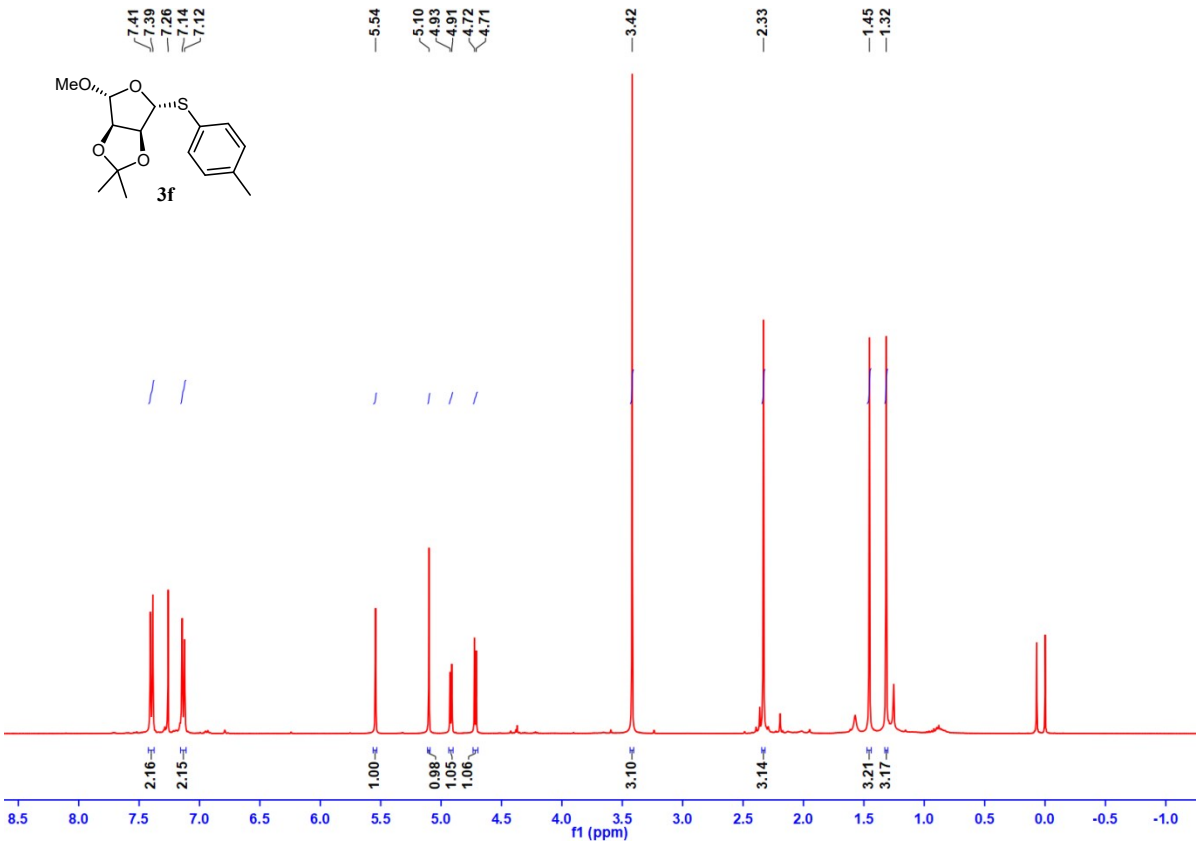

7.55
7.26
5.70
5.15
4.92
4.90
4.73
4.72
3.36
1.49
1.33
MeO
O
S
O
O
CF3
3d
4.13
1.00
1.01
1.05
1.03
3.17
3.18
3.18
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

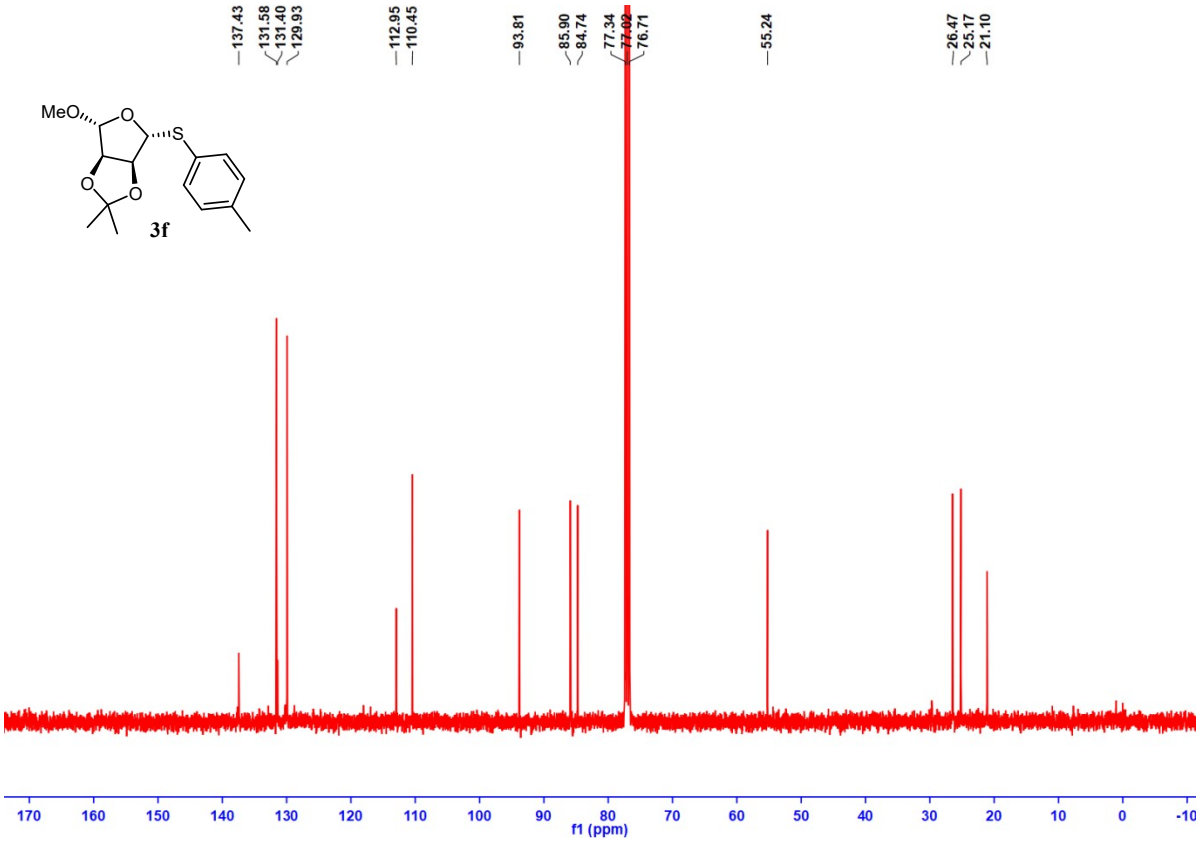

141.03
141.02
128.98
128.66
128.34
128.12
128.01
125.92
125.89
125.85
125.81
125.42
122.72
120.01
113.25
110.46
92.07
85.70
84.56
77.35
77.04
76.72
55.22
26.45
25.07
MeO
O
S
O
O
CF3
3d
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

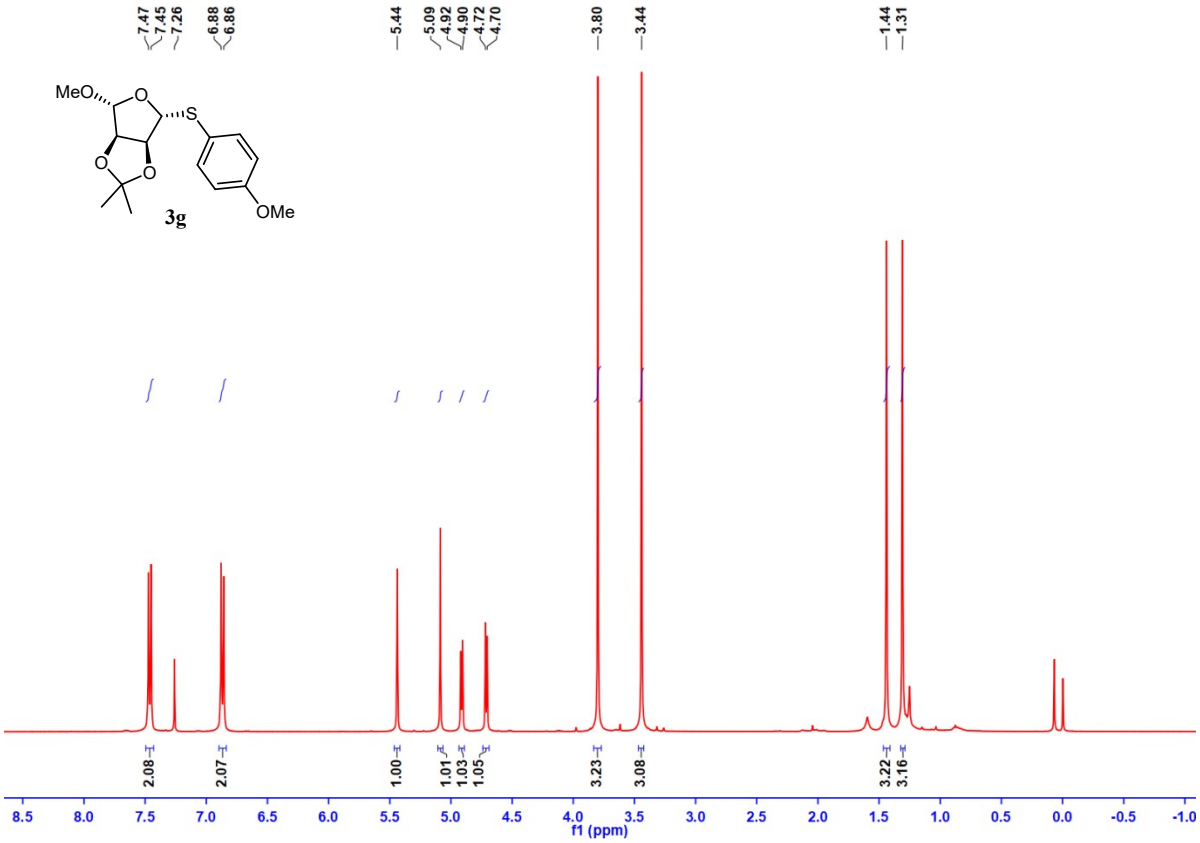

-62.55
MeO
O
S
O
O
CF3
3d
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

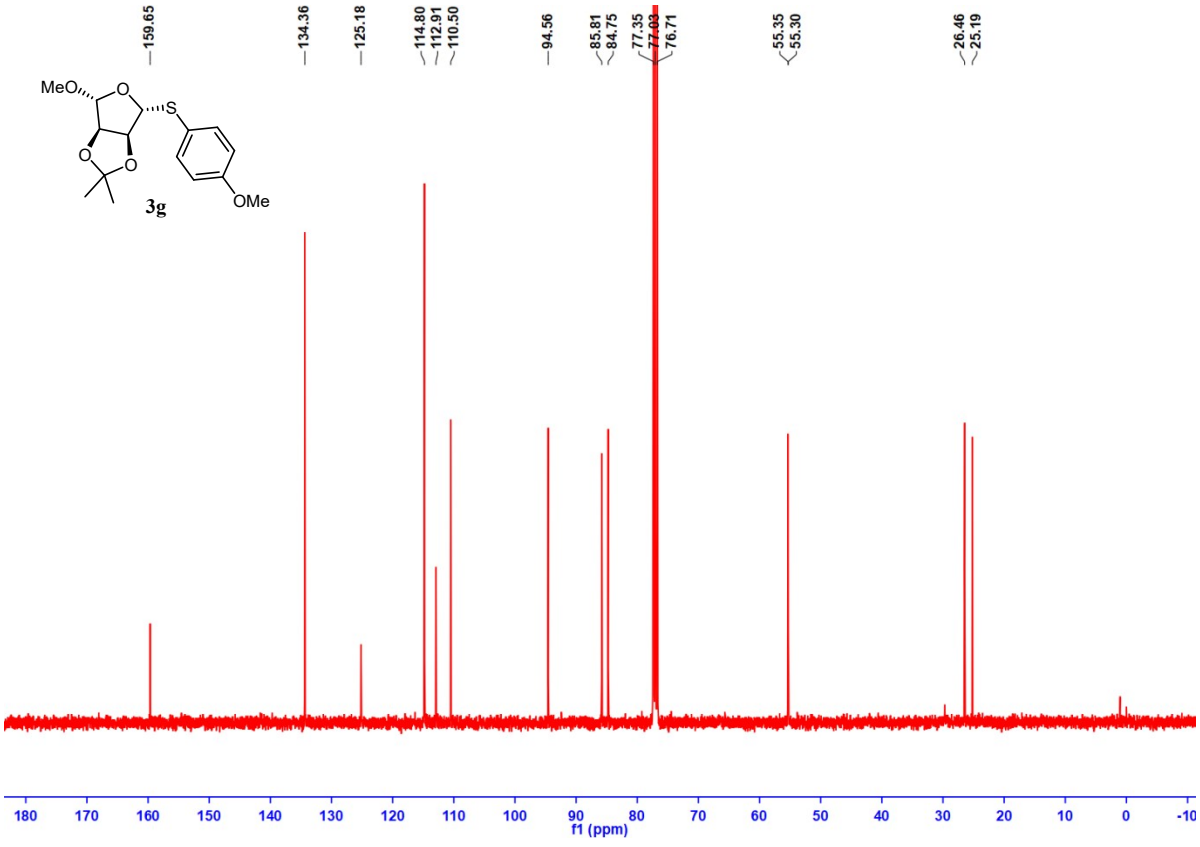

7.58
7.57
7.56
7.55
7.51
7.50
7.49
7.49
7.26
5.72
5.15
4.90
4.88
4.72
4.71
3.32
1.49
1.33
MeO
O
S
O
O
CN
3e
2.04
1.99
1.00
0.98
1.02
1.02
3.12
3.06
3.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

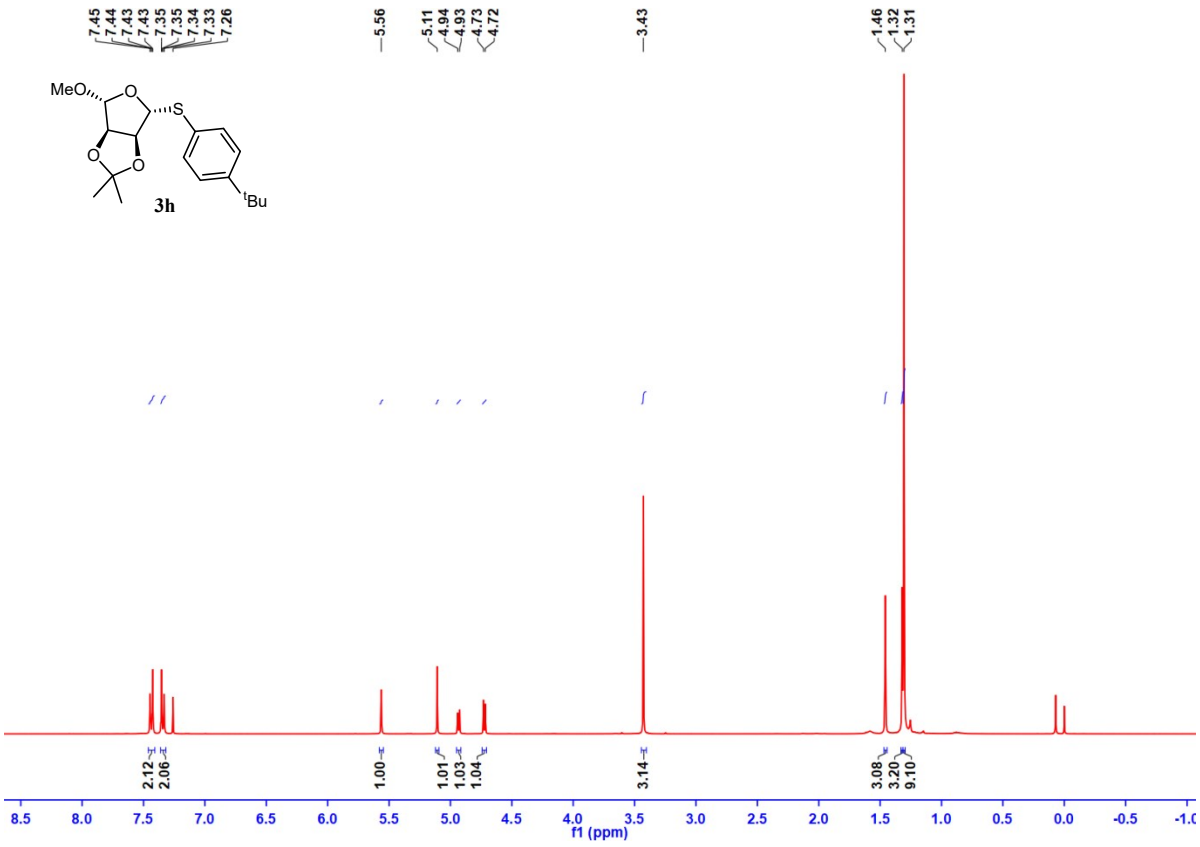

143.43
132.46
128.32
118.70
113.37
110.47
109.43
91.38
85.54
84.48
77.38
77.06
76.74
55.23
26.45
25.05
MeO
O
S
O
O
CN
3e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

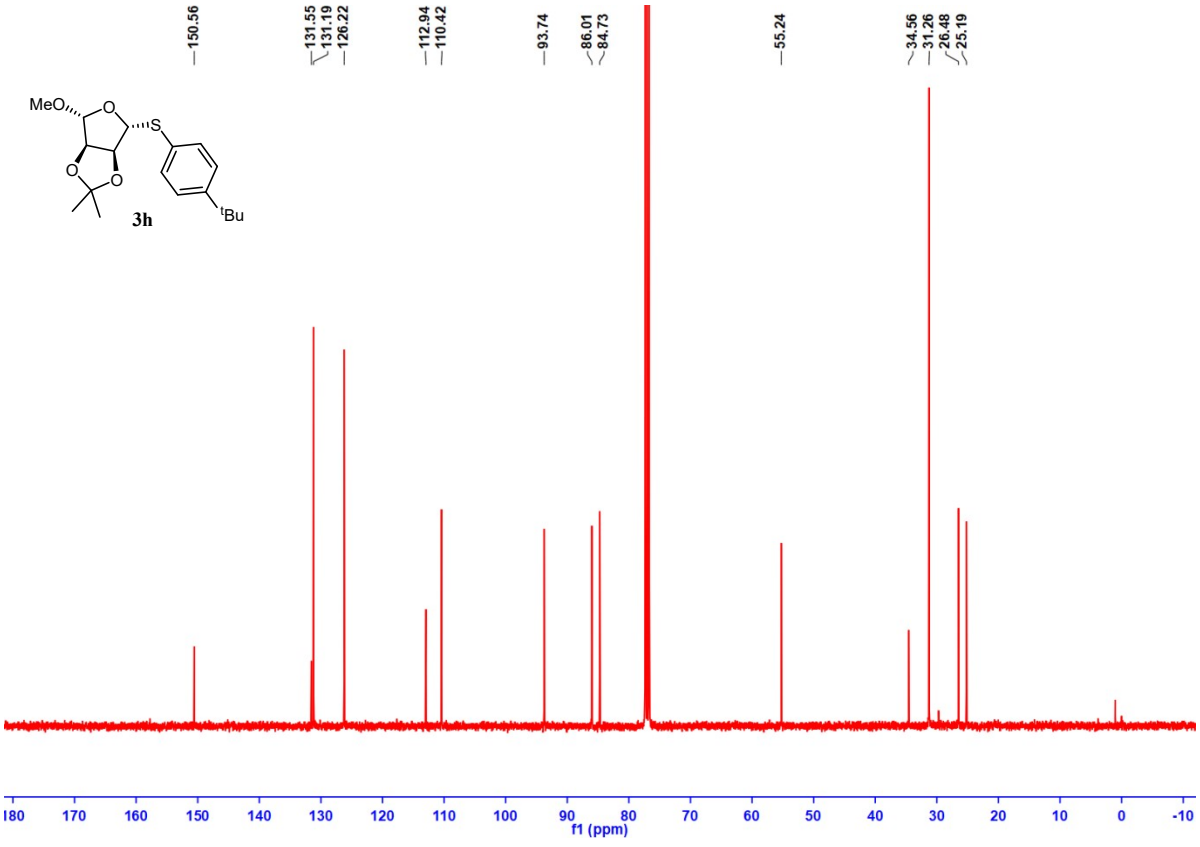

7.41
7.39
7.26
7.14
7.12
5.54
5.10
4.93
4.91
4.72
4.71
3.42
2.33
1.45
1.32
MeO
O
S
O
O
3f
2.16
2.15
1.00
0.98
1.05
1.06
3.10
3.14
3.21
3.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

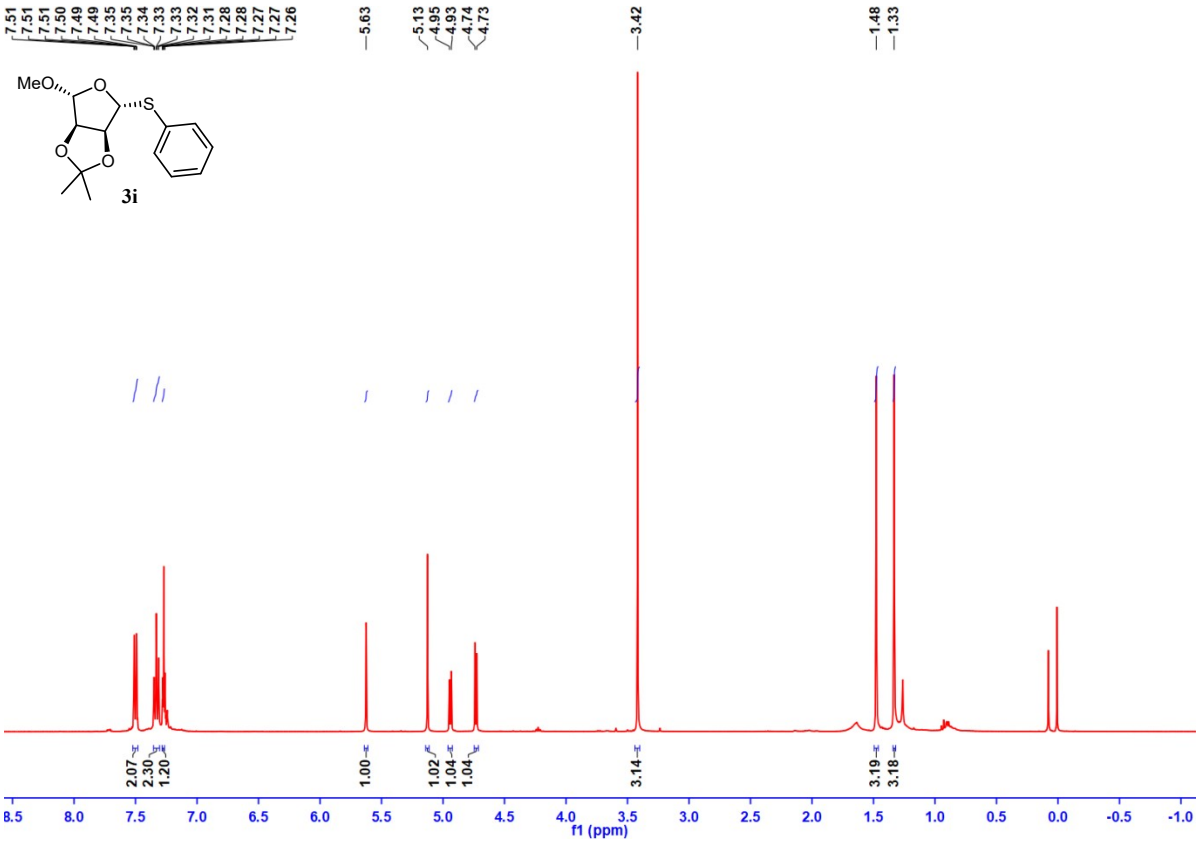

137.43
131.58
131.40
129.93
112.95
110.45
93.81
85.90
84.74
77.34
77.02
76.71
55.24
26.47
25.17
21.10
MeO
O
S
O
O
3f
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.47
7.45
7.26
6.88
6.86
5.44
5.09
4.92
4.90
4.72
4.70
3.80
3.44
1.44
1.31
MeO
O
S
O
O
OMe
3g
2.08
2.07
1.00
1.01
1.03
1.05
3.23
3.08
3.22
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

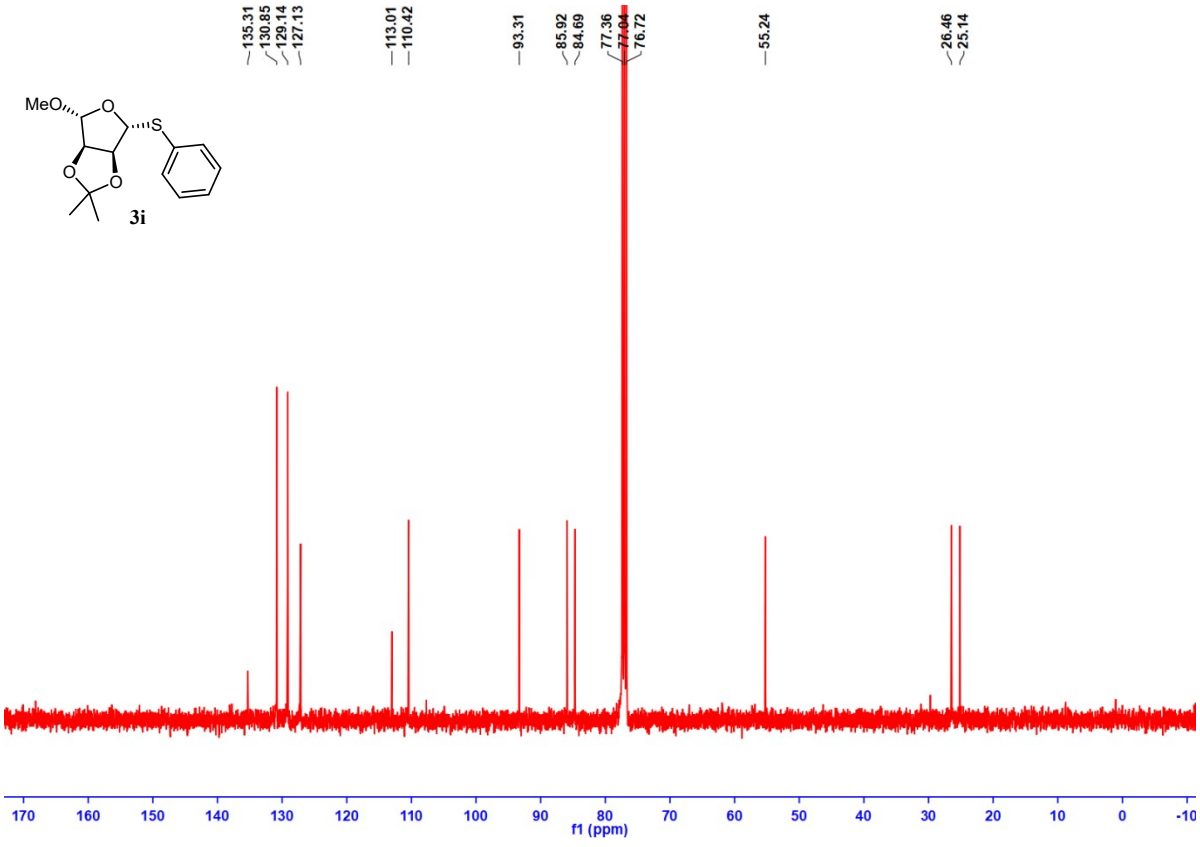

159.65
134.36
125.18
114.80
112.91
110.50
94.56
85.81
84.75
77.35
77.03
76.71
55.35
55.30
26.46
25.19
MeO
O
S
O
O
OMe
3g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.45
7.44
7.43
7.43
7.35
7.35
7.34
7.33
7.26
5.56
5.11
4.94
4.93
4.73
4.72
3.43
1.46
1.32
1.31
MeO
O
S
O
O
tBu
3h
2.12
2.06
1.00
1.01
1.03
1.04
3.14
3.08
3.20
9.10
f1 (ppm)

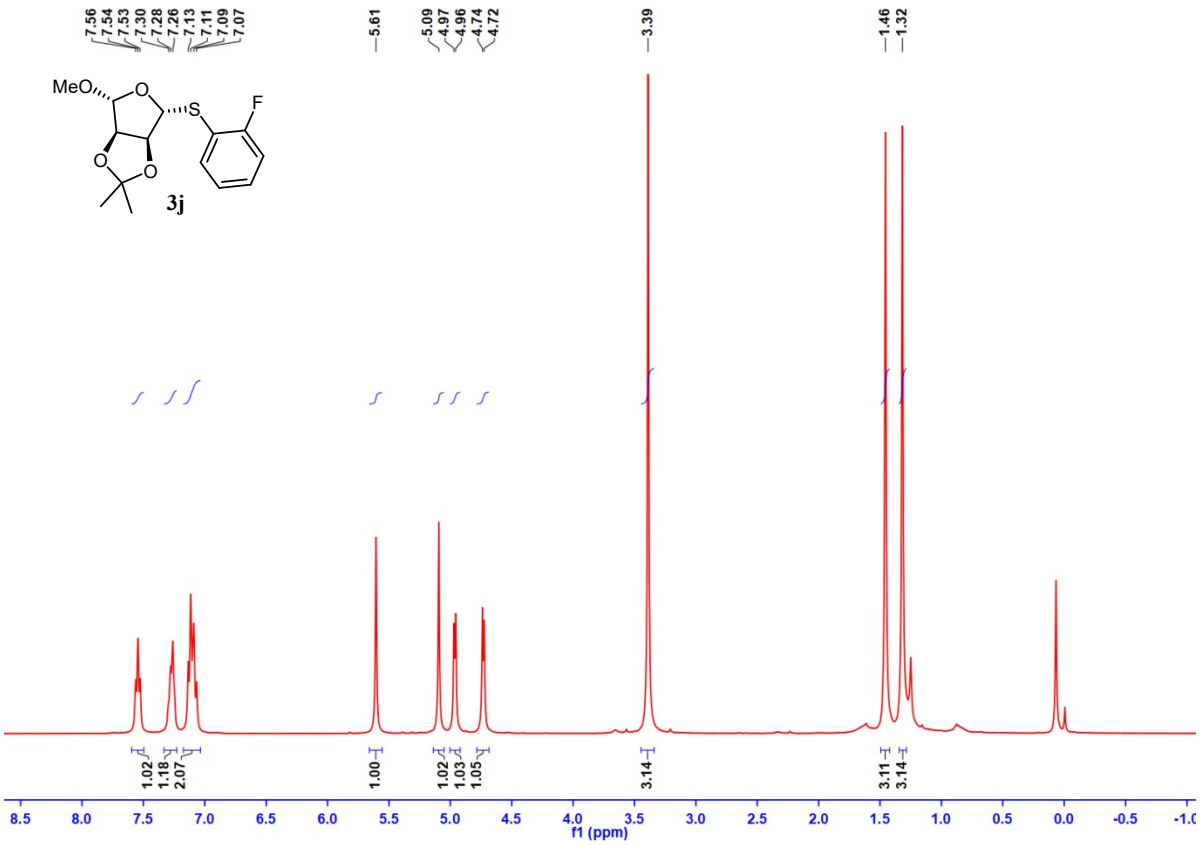

150.56
131.55
131.19
126.22
112.94
110.42
93.74
86.01
84.73
55.24
34.56
31.26
26.48
25.19
MeO
O
S
O
O
tBu
3h
f1 (ppm)

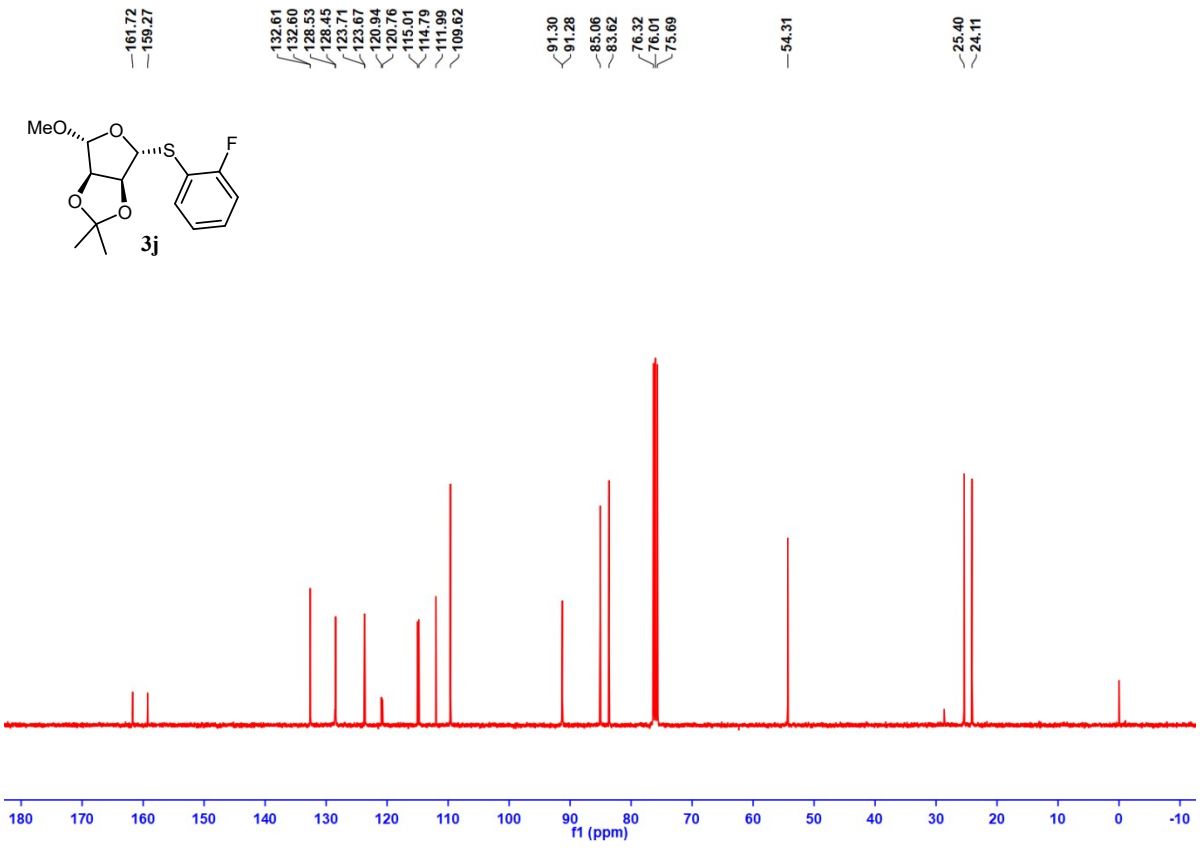

7.51
7.51
7.51
7.50
7.49
7.49
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.28
7.28
7.27
7.27
7.26
5.63
5.13
4.95
4.93
4.74
4.73
3.42
1.48
1.33
MeO
O
S
O
O
2.07
2.30
1.20
1.00
1.02
1.04
1.04
3.14
3.19
3.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

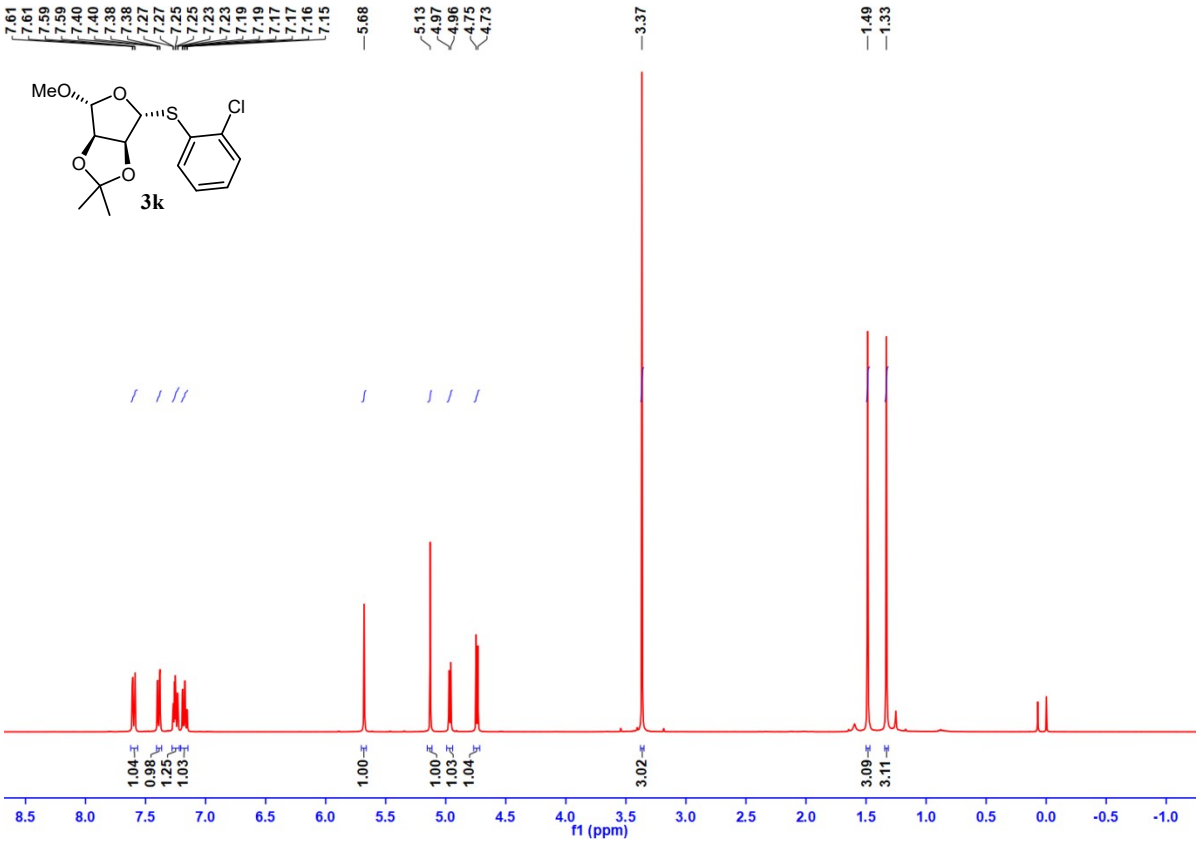
3i

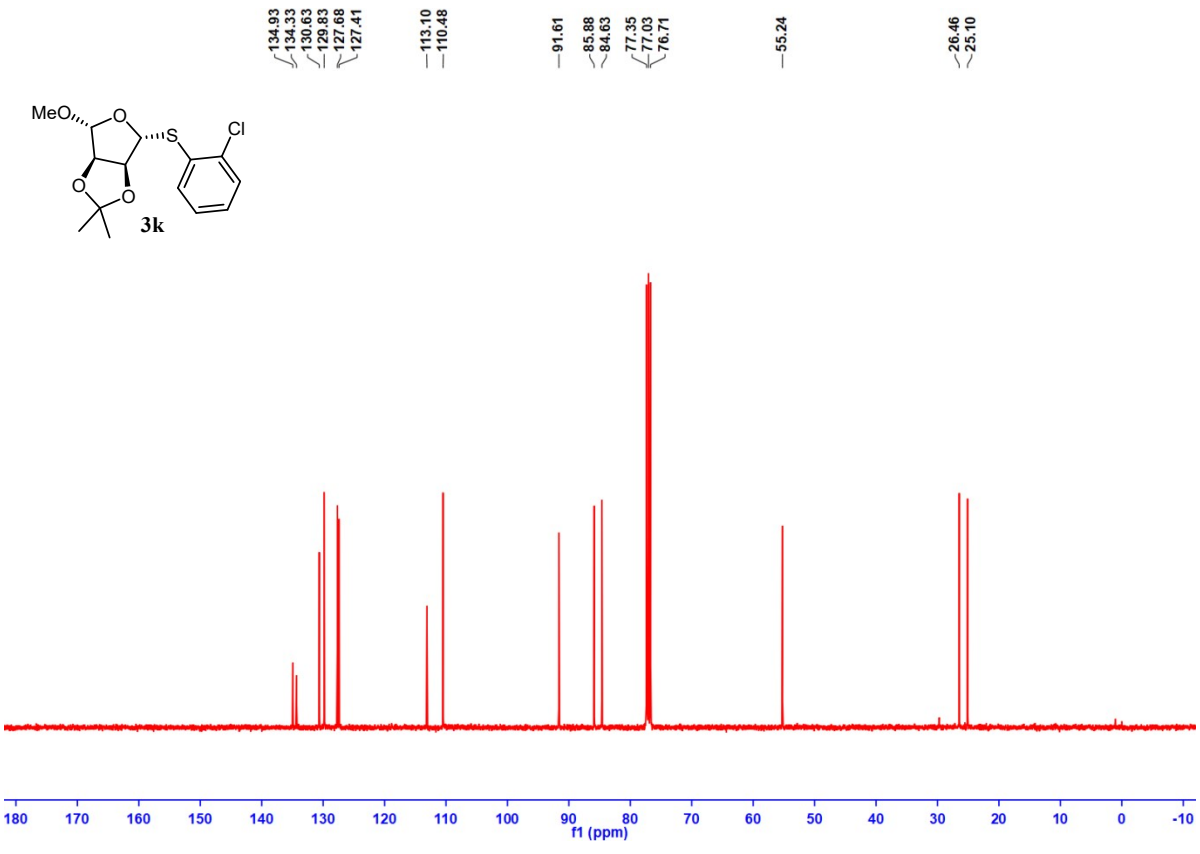

135.31
130.85
129.14
127.13
113.01
110.42
93.31
85.92
84.69
77.36
77.04
76.72
55.24
26.46
25.14
MeO
O
S
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

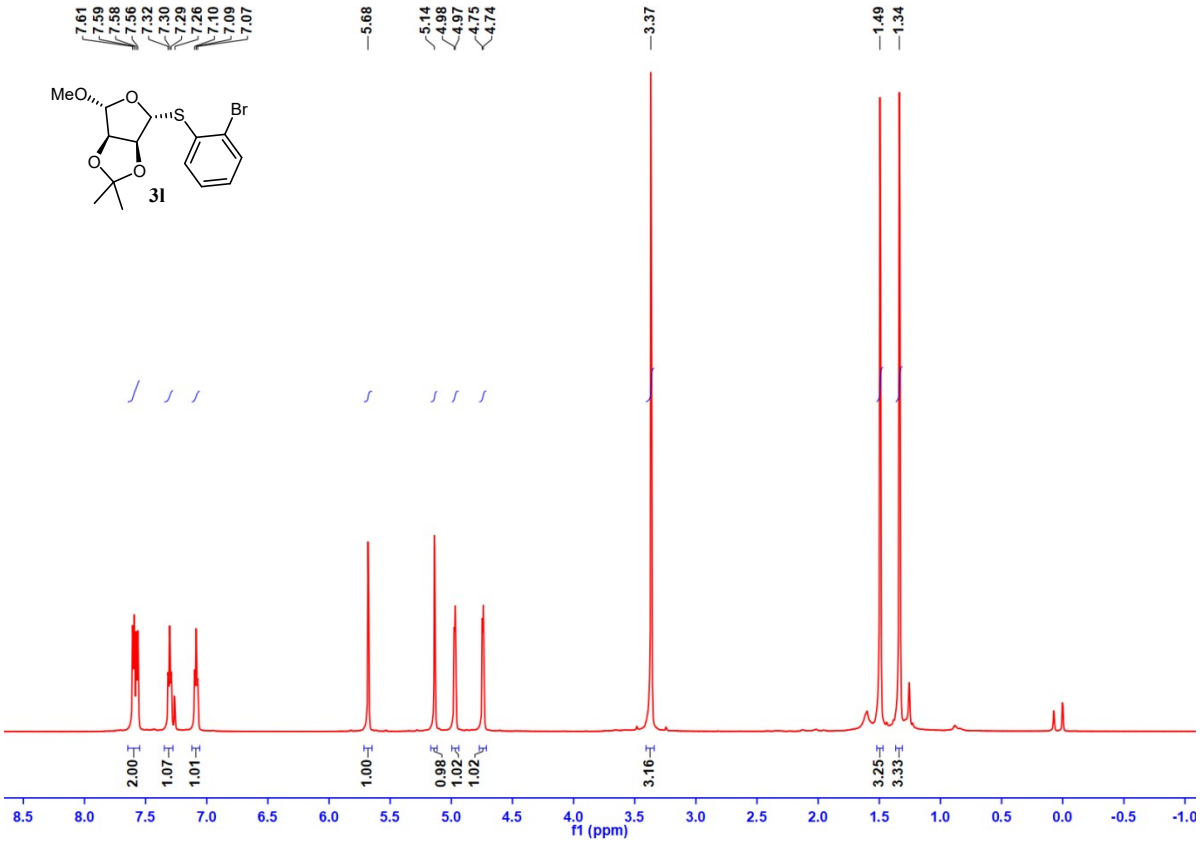
3i

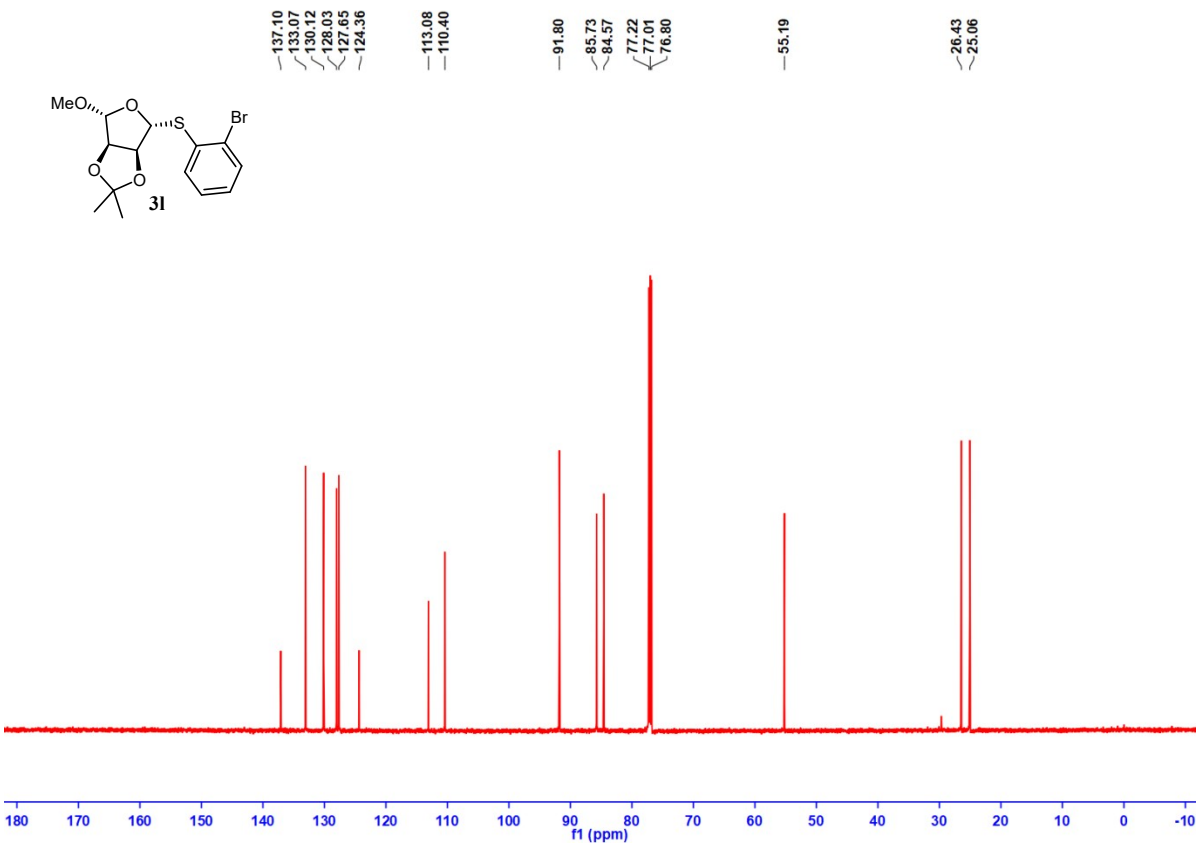

7.56
7.54
7.53
7.30
7.28
7.26
7.13
7.11
7.09
7.07
5.61
5.09
4.97
4.96
4.74
4.72
3.39
1.46
1.32
MeO
O
S
F
O
O
3j
1.02
1.18
2.07
1.00
1.02
1.03
1.05
3.14
3.11
3.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

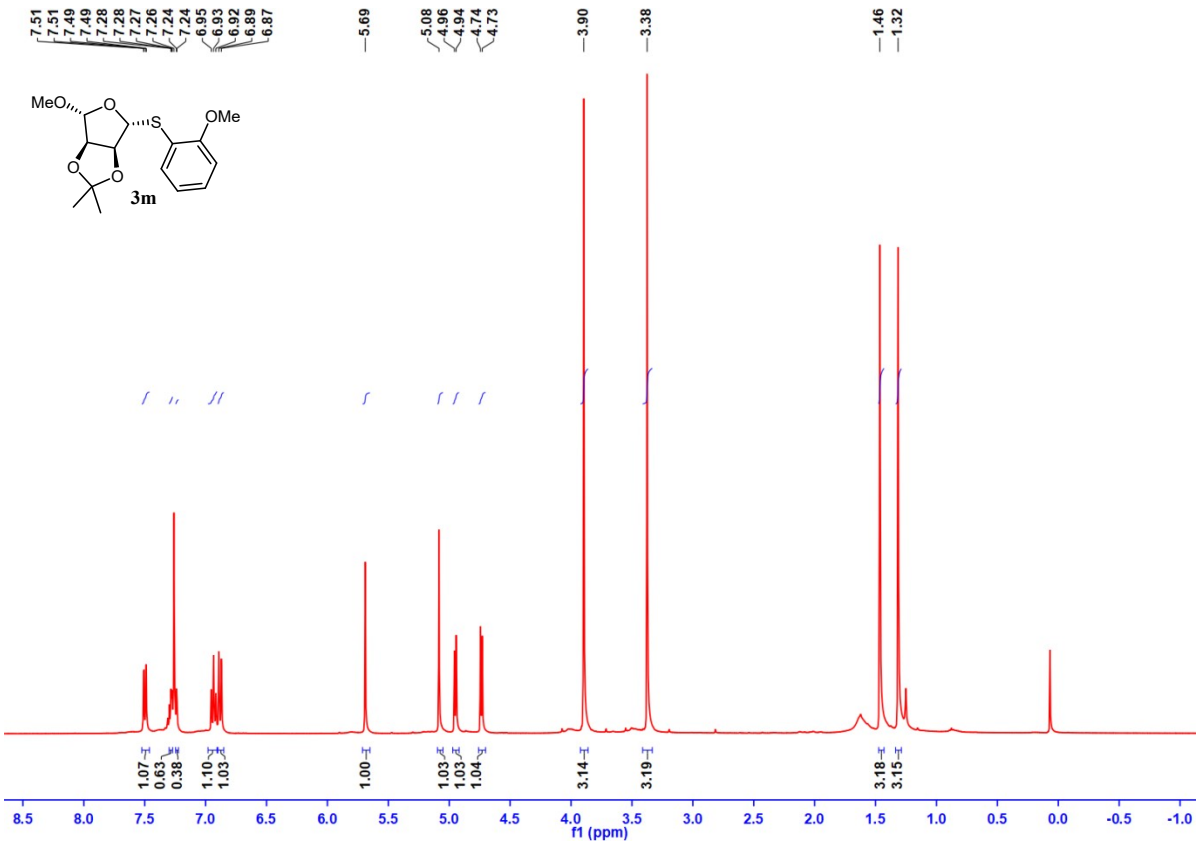

161.72
159.27
132.61
132.60
128.53
128.45
123.71
123.67
120.94
120.76
115.01
114.79
111.99
109.62
91.30
91.28
85.06
83.62
76.32
76.01
75.69
54.31
25.40
24.11
MeO
O
S
F
O
O
3j
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

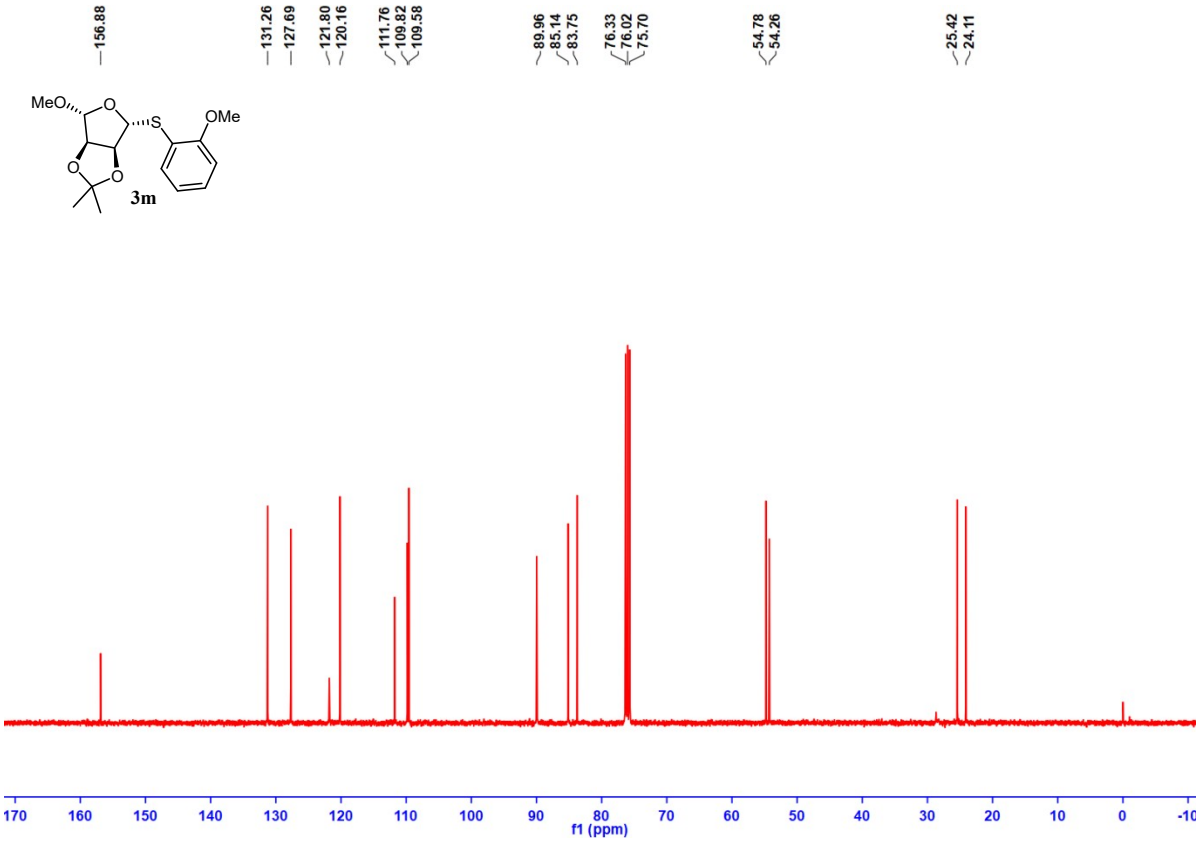

7.61
7.61
7.59
7.59
7.40
7.40
7.38
7.38
7.27
7.27
7.25
7.25
7.23
7.23
7.19
7.19
7.17
7.17
7.16
7.15
5.68
5.13
4.97
4.96
4.75
4.73
3.37
1.49
1.33
MeO
O
S
Cl
O
O
3k
1.04
0.98
1.25
1.03
1.00
1.00
1.03
1.04
3.02
3.09
3.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

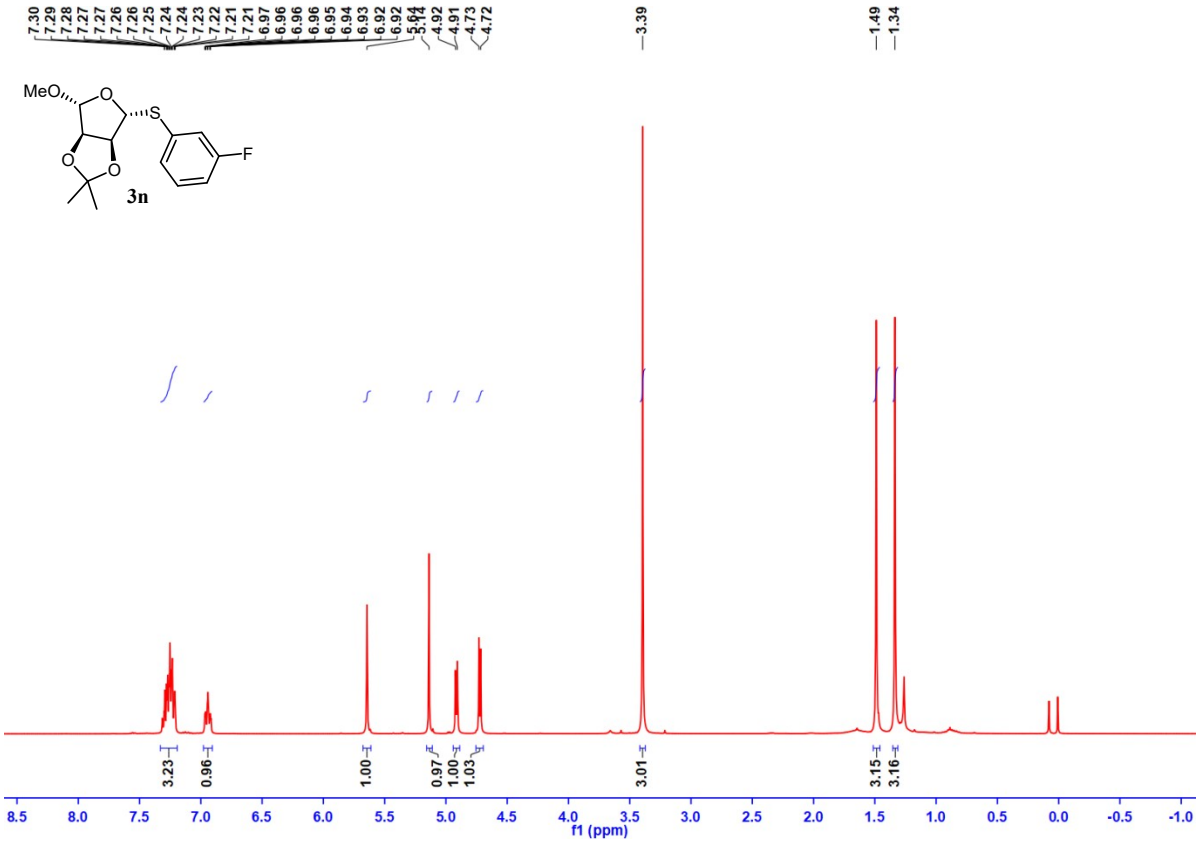

134.93
134.33
130.63
129.83
127.68
127.41
113.10
110.48
91.61
85.88
84.63
77.35
77.03
76.71
55.24
26.46
25.10
MeO
O
S
Cl
O
O
3k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

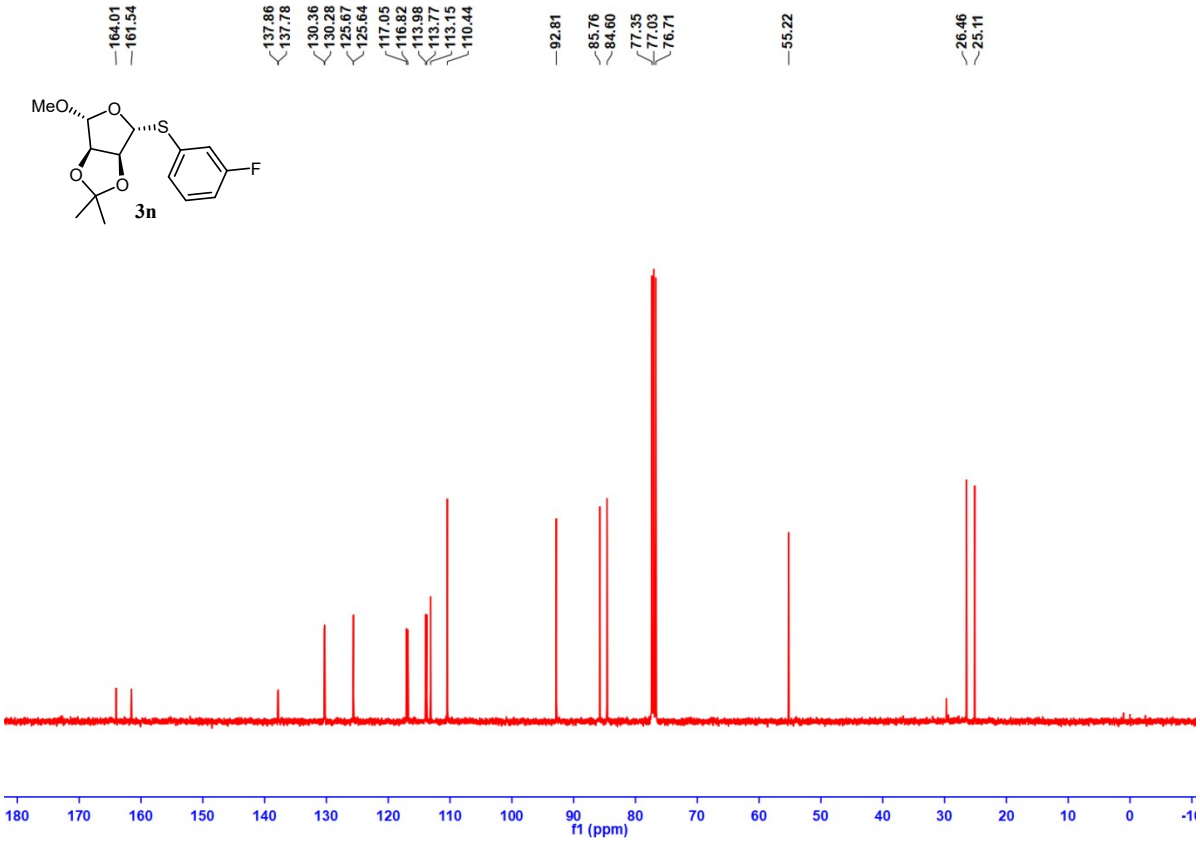

7.61
7.59
7.58
7.56
7.32
7.30
7.29
7.26
7.10
7.09
7.07
5.68
5.14
4.98
4.97
4.75
4.74
3.37
1.49
1.34
MeO
O
S
Br
O
O
3l
2.00
1.07
1.01
1.00
0.98
1.02
1.02
3.16
3.25
3.33
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

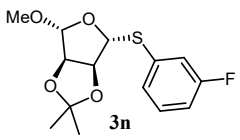

137.10
133.07
130.12
128.03
127.65
124.36
113.08
110.40
91.80
85.73
84.57
77.22
77.01
76.80
55.19
26.43
25.06
MeO
O
S
Br
O
O
3l
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.51
7.51
7.49
7.49
7.28
7.28
7.27
7.26
7.24
7.24
6.95
6.93
6.92
6.89
6.87
5.69
5.08
4.96
4.94
4.74
4.73
3.90
3.38
1.46
1.32
MeO
O
S
OMe
O
O
3m
1.07
0.63
0.38
1.10
1.03
1.00
1.03
1.03
1.04
3.14
3.19
3.18
3.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

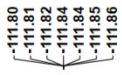

156.88
131.26
127.69
121.80
120.16
111.76
109.82
109.58
89.96
85.14
83.75
76.33
76.02
75.70
54.78
54.26
25.42
24.11
MeO
O
S
OMe
O
O
3m
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

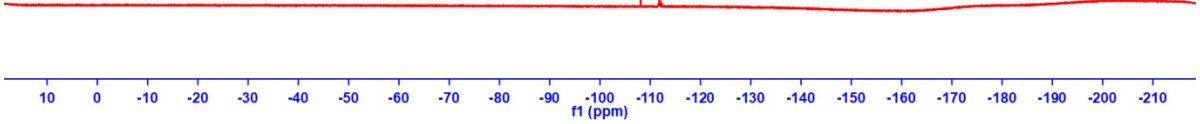

7.30
7.29
7.28
7.27
7.27
7.26
7.26
7.25
7.24
7.24
7.23
7.22
7.21
7.21
6.97
6.96
6.96
6.96
6.95
6.94
6.93
6.92
6.92
5.84
5.84
4.92
4.91
4.73
4.72
3.39
1.49
1.34
MeO
O
S
O
O
F
3n
3.23
0.96
1.00
0.97
1.00
1.03
3.01
3.15
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

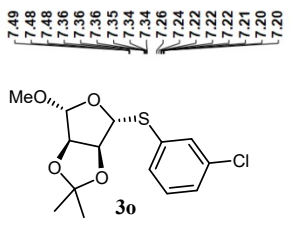

164.01
161.54
137.86
137.78
130.36
130.28
125.67
125.64
117.05
116.82
113.98
113.77
113.15
110.44
92.81
85.76
84.60
77.35
77.03
76.71
55.22
26.46
25.11
MeO
O
S
O
O
F
3n
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO
O
S
F
O
O

3n

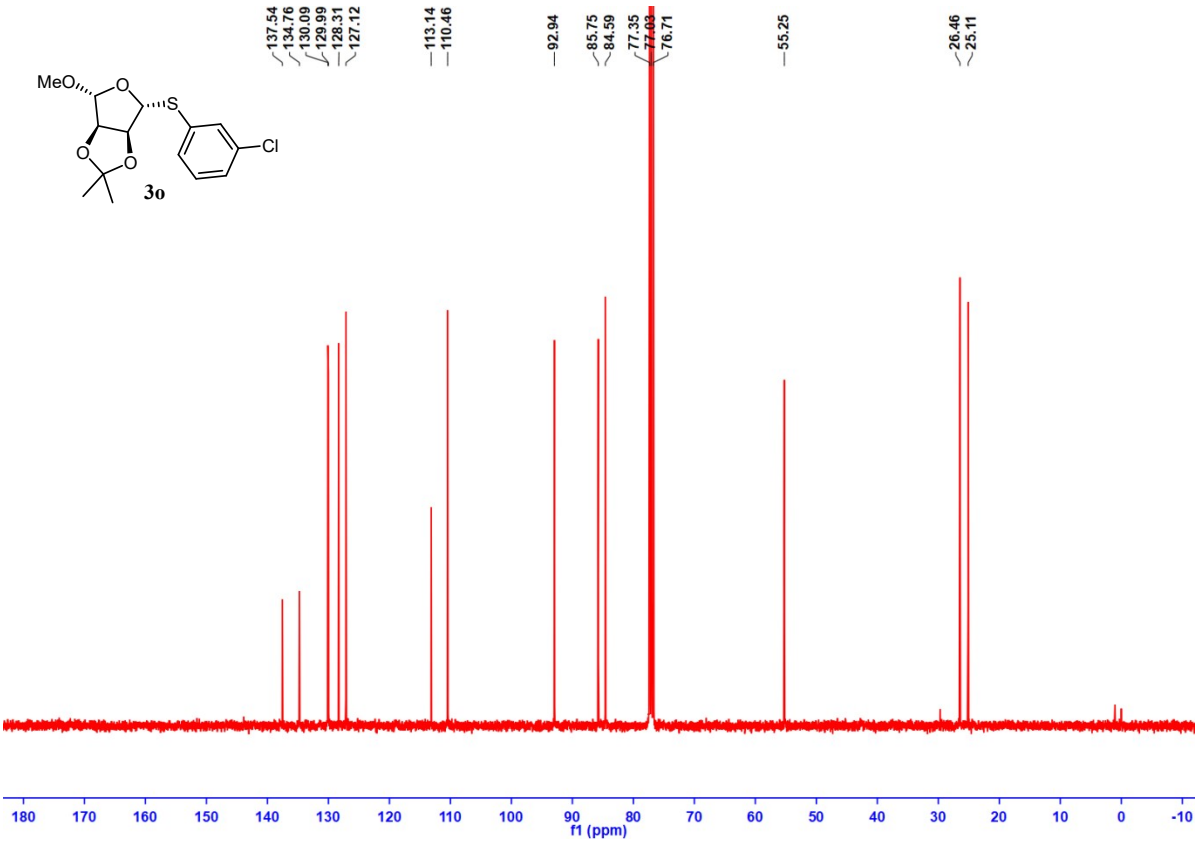

-111.80
-111.81
-111.82
-111.84
-111.84
-111.85
-111.86

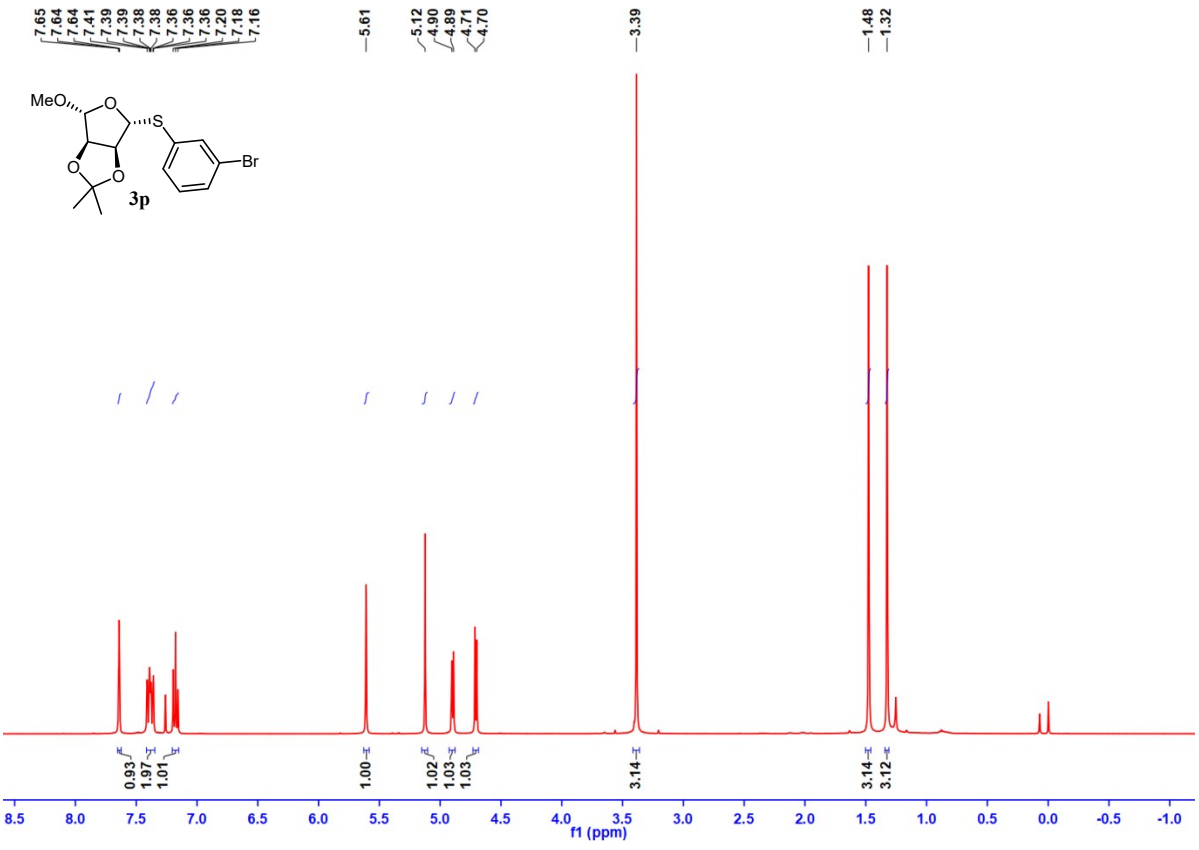

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

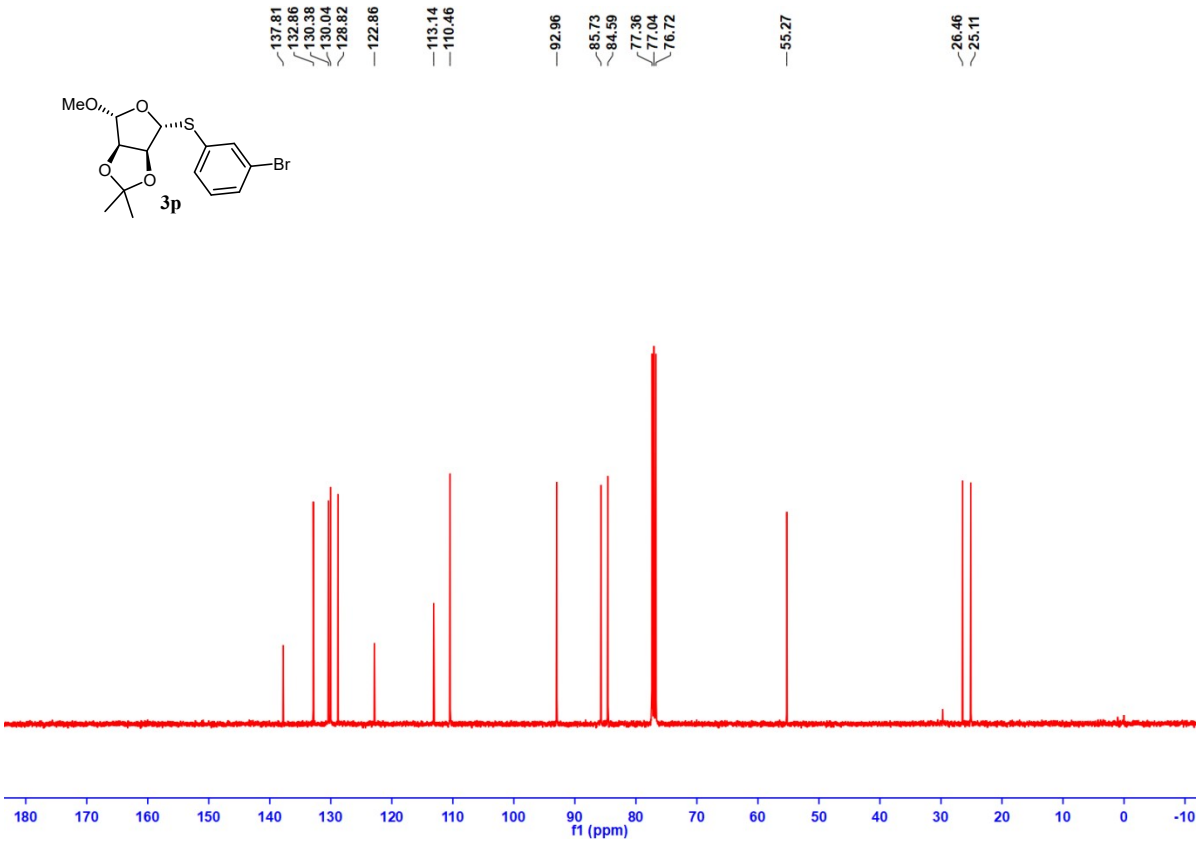

MeO
O
S
Cl
O
O

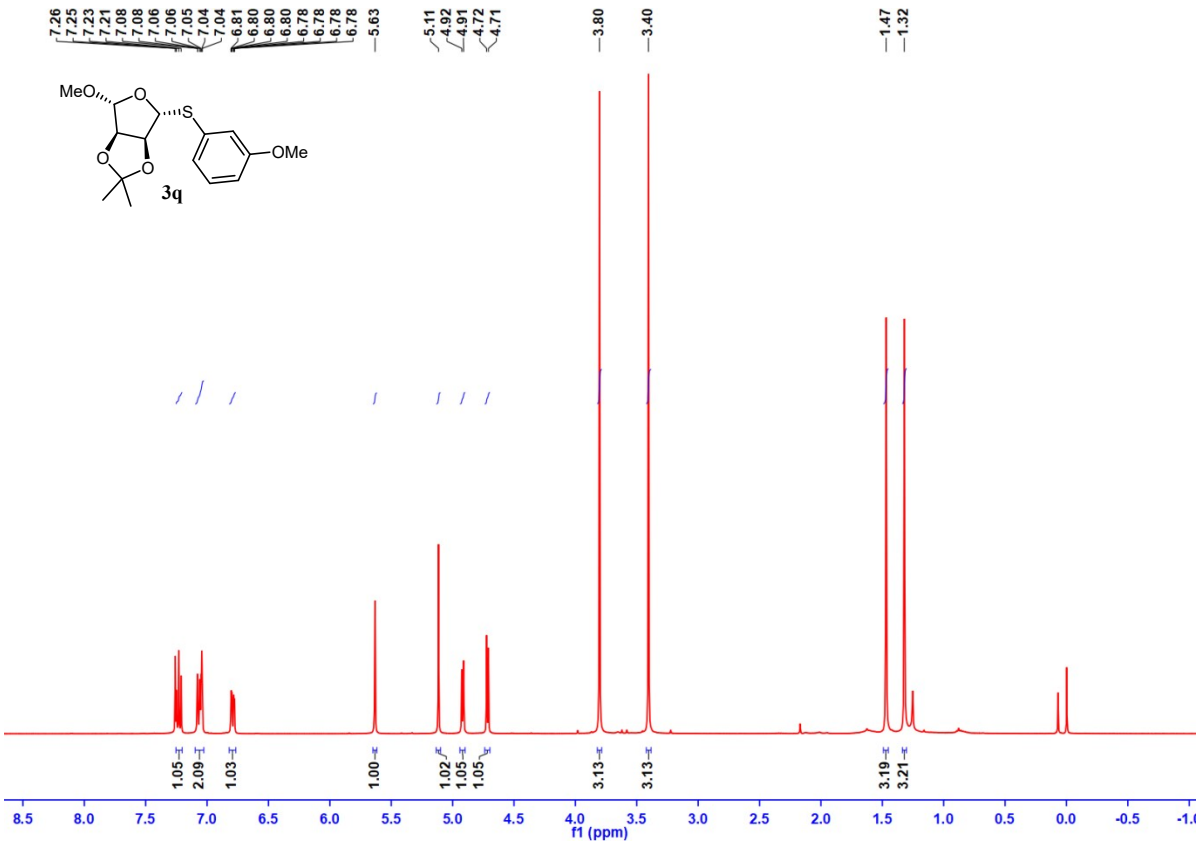
3o

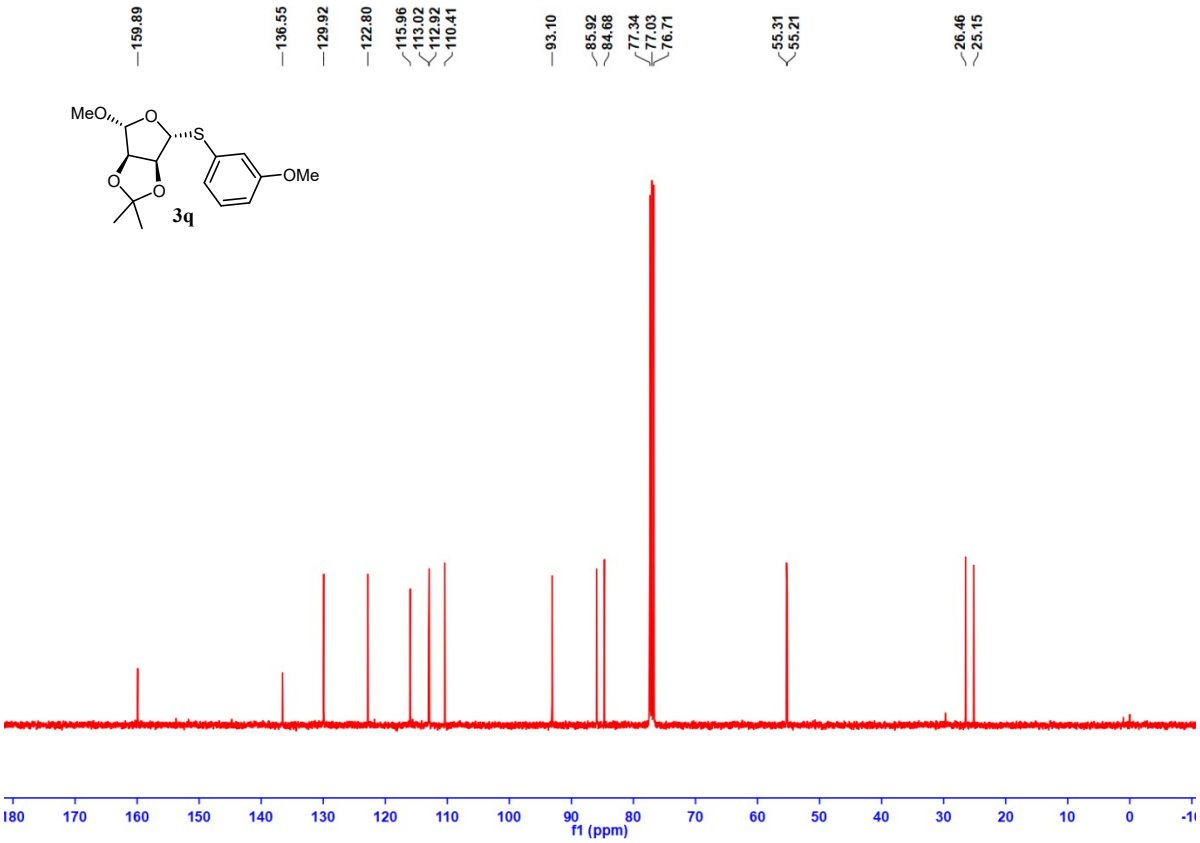
7.49
7.48
7.48
7.36
7.36
7.36
7.35
7.34
7.34
7.26
7.24
7.22
7.22
7.22
7.21
7.20
7.20
5.62
5.13
4.91
4.89
4.72
4.70
3.39
1.48
1.32
1.25
0.95
0.99
1.90
1.00
0.99
1.01
1.04
3.19
3.17
3.19
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

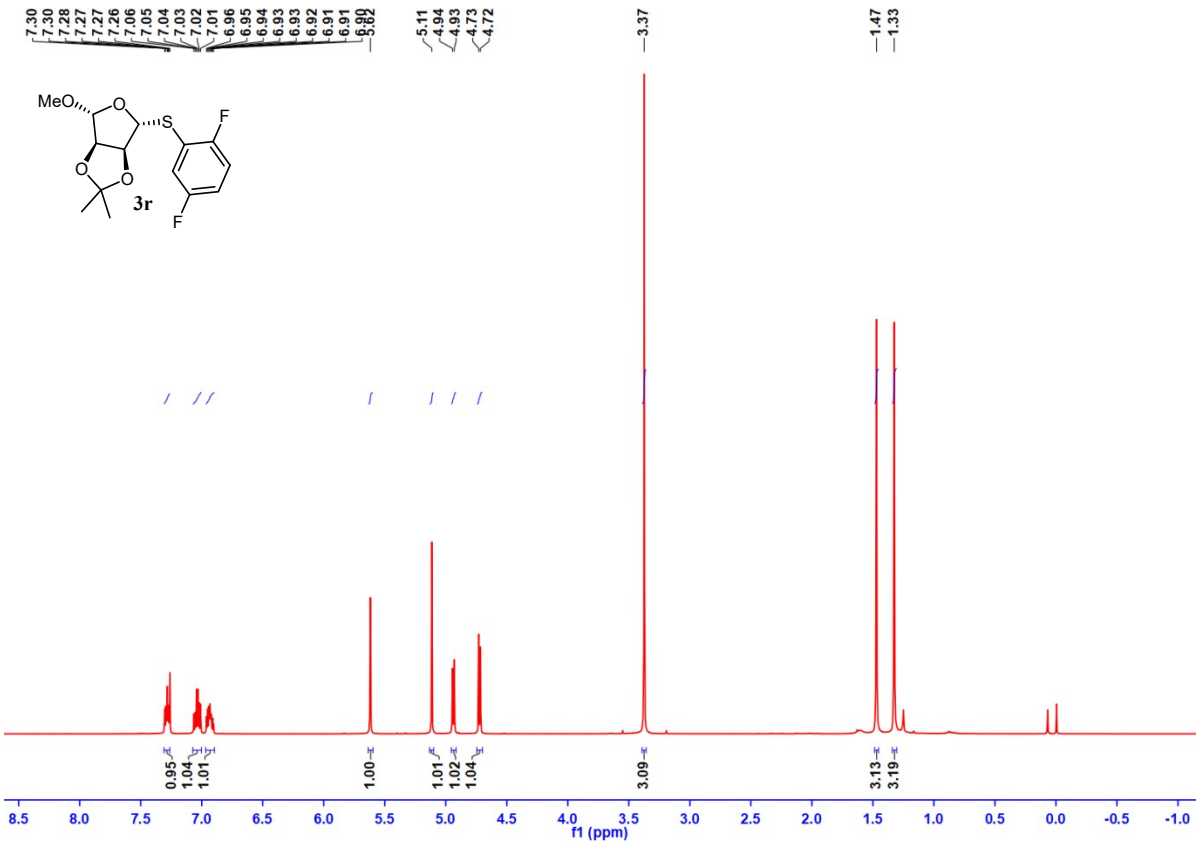

137.54
134.76
130.09
129.99
128.31
127.12
113.14
110.46
92.94
85.75
84.59
77.35
77.03
76.71
55.25
26.46
25.11
MeO
O
S
Cl
O
O
3o
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

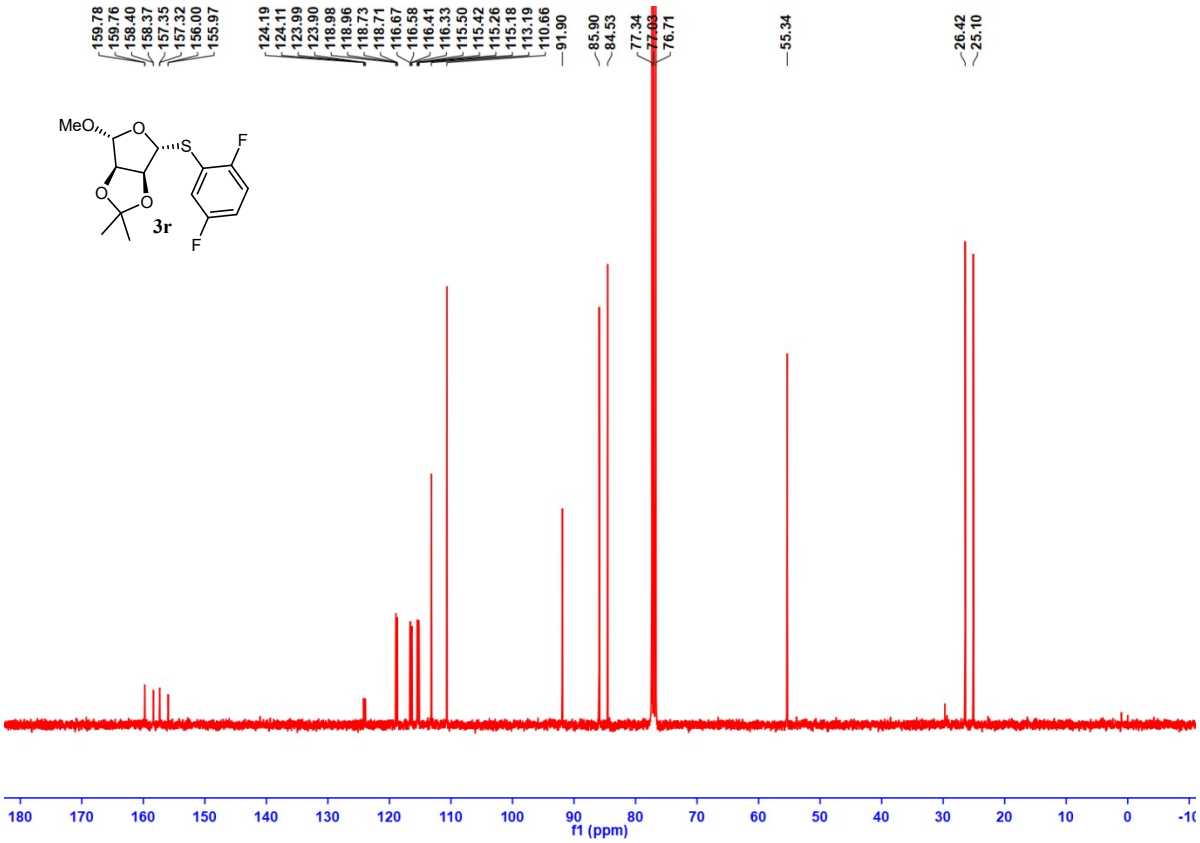

7.65
7.64
7.64
7.41
7.39
7.39
7.38
7.38
7.36
7.36
7.36
7.20
7.18
7.16
5.61
5.12
4.90
4.89
4.71
4.70
3.39
1.48
1.32
MeO
O
S
Br
O
O
3p
0.93
1.97
1.01
1.00
1.02
1.03
1.03
3.14
3.14
3.12
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

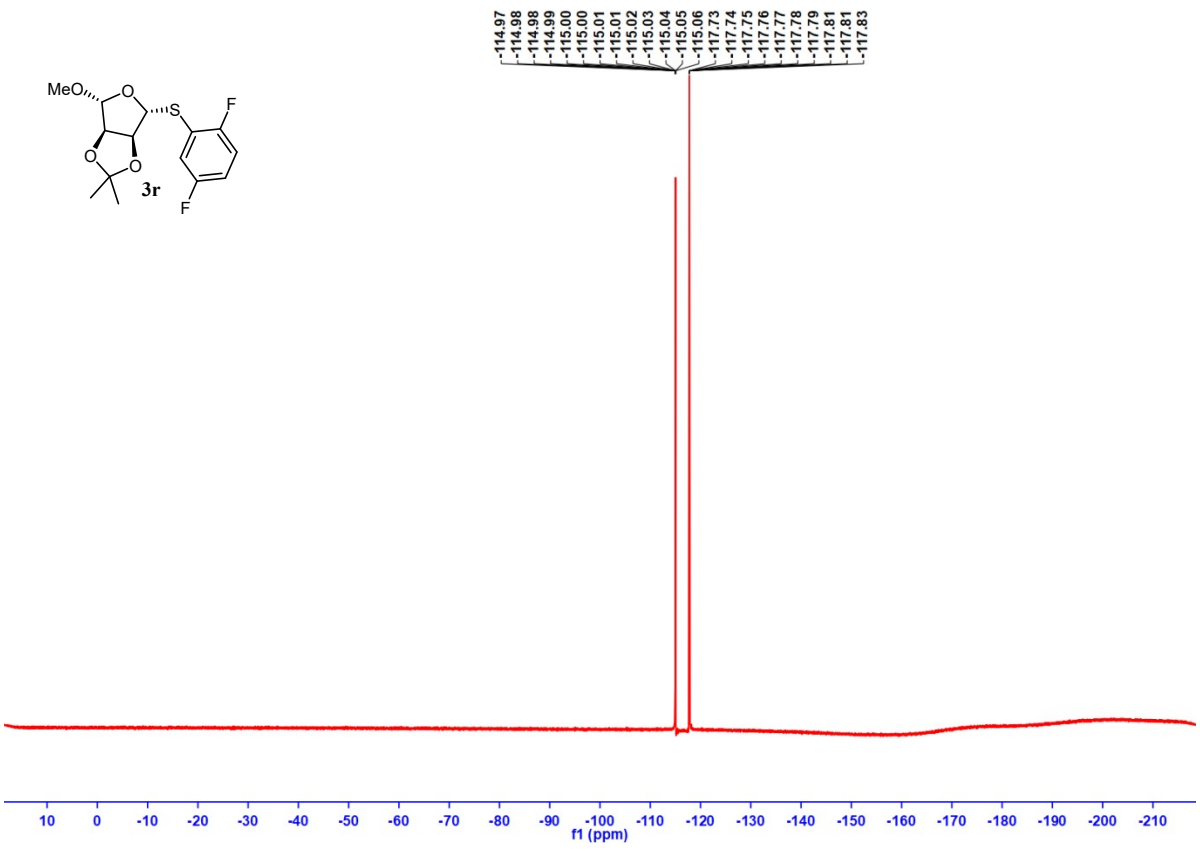

137.81
132.86
130.38
130.04
128.82
122.86
113.14
110.46
92.96
85.73
84.59
77.36
77.04
76.72
55.27
26.46
25.11
MeO
O
S
Br
O
O
3p
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

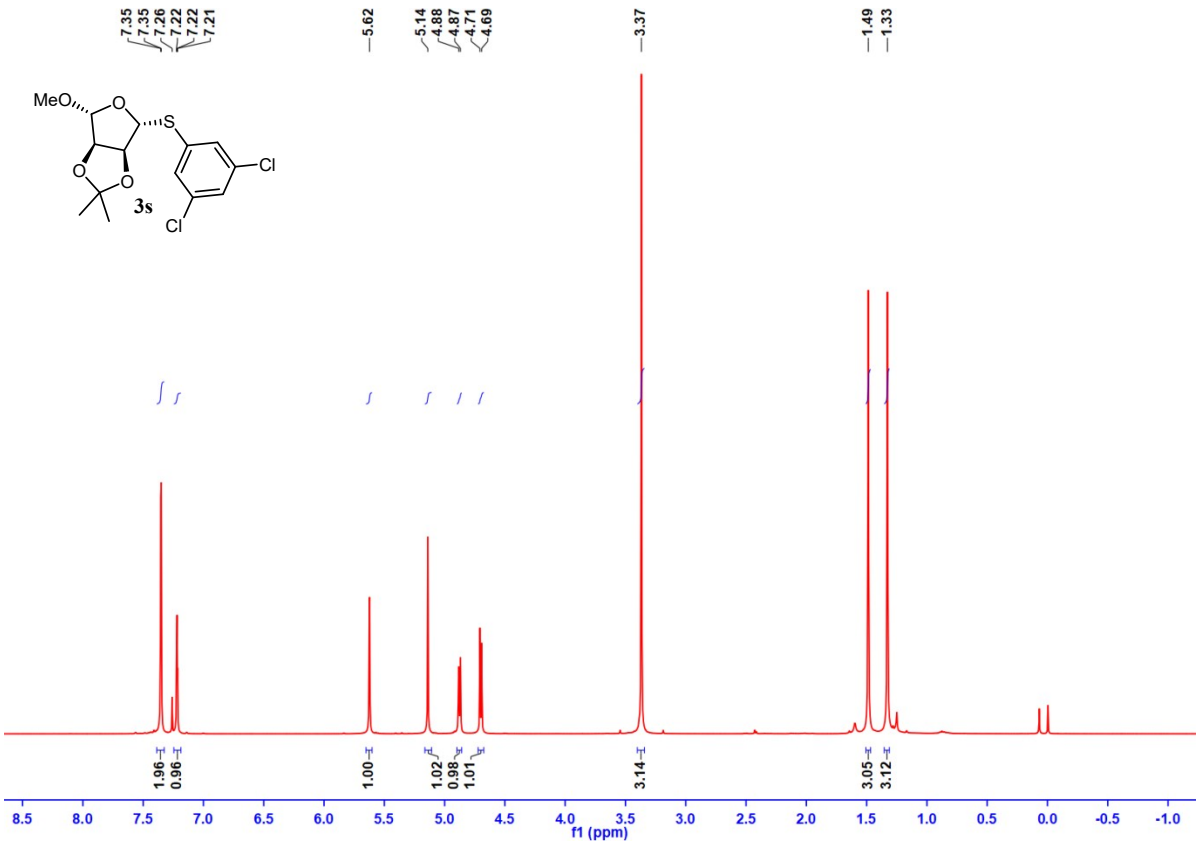

7.26
7.25
7.23
7.21
7.08
7.08
7.06
7.06
7.05
7.04
7.04
6.81
6.80
6.80
6.80
6.78
6.78
6.78
6.78
5.63
5.11
4.92
4.91
4.72
4.71
3.80
3.40
1.47
1.32
MeO
O
S
OMe
O
O
3q
1.05
2.09
1.03
1.00
1.02
1.05
1.05
3.13
3.13
3.19
3.21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

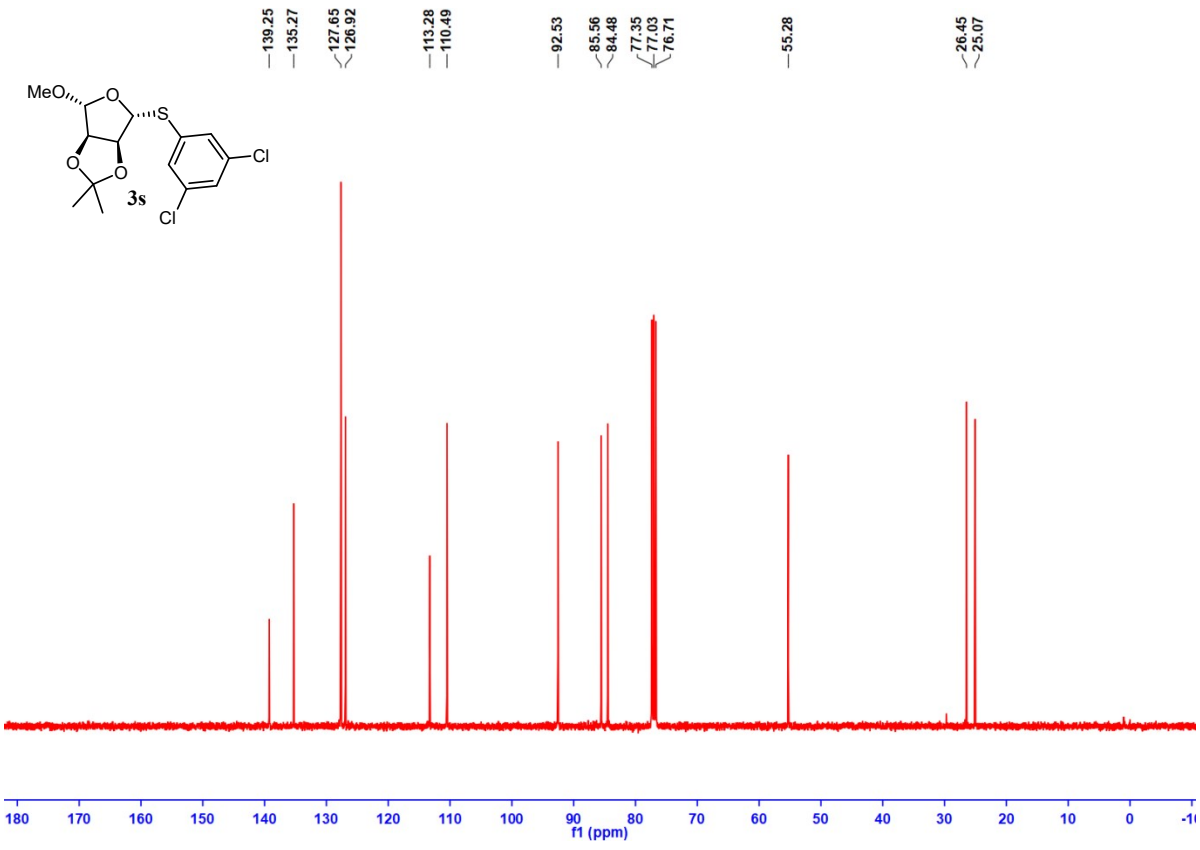

159.89
136.55
129.92
122.80
115.96
113.02
112.92
110.41
93.10
85.92
84.68
77.34
77.03
76.71
55.31
55.21
26.46
25.15
MeO
O
S
OMe
O
O
3q
f1 (ppm)

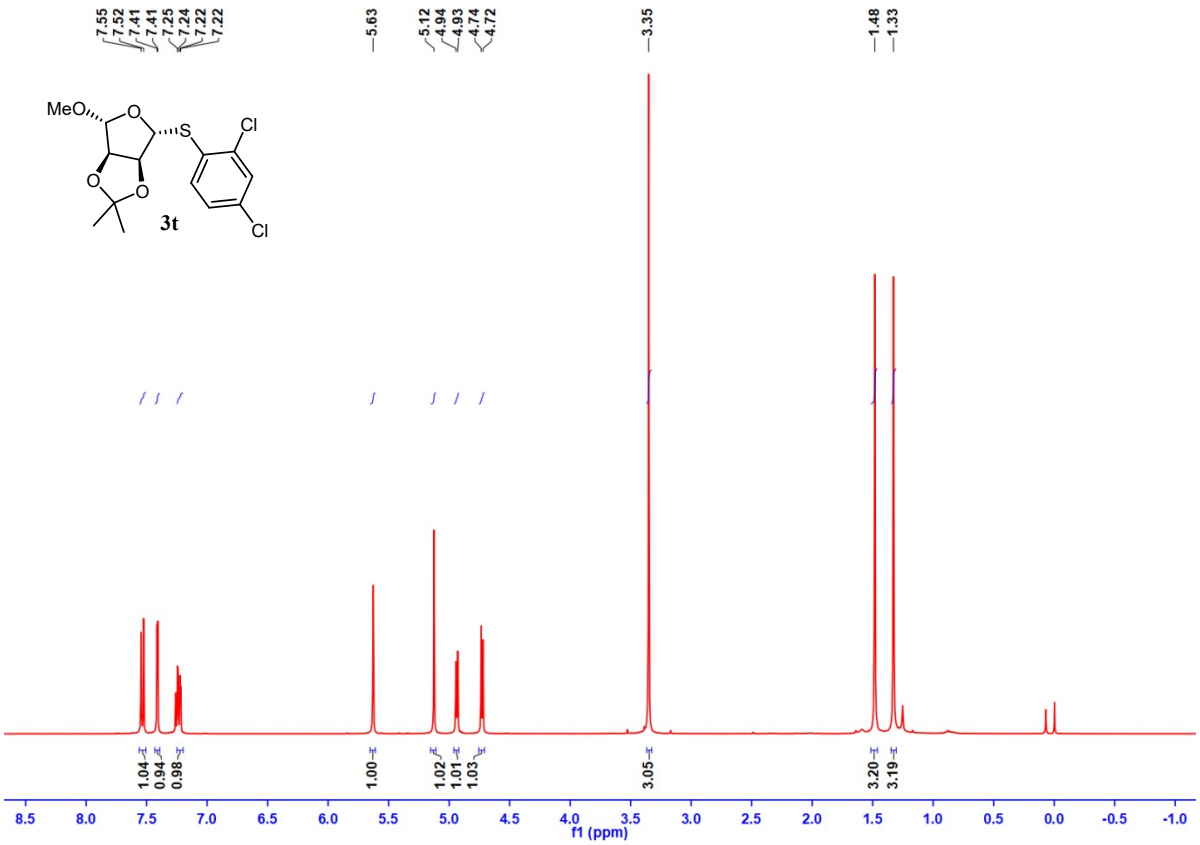

7.30
7.30
7.28
7.27
7.27
7.26
7.06
7.05
7.04
7.03
7.02
7.01
6.96
6.95
6.94
6.93
6.93
6.92
6.91
6.91
6.90
5.82
5.11
4.94
4.93
4.73
4.72
3.37
1.47
1.33
MeO
O
S
F
O
O
3r
F
0.95
1.04
1.01
1.00
1.01
1.02
1.04
3.09
3.13
3.19
f1 (ppm)

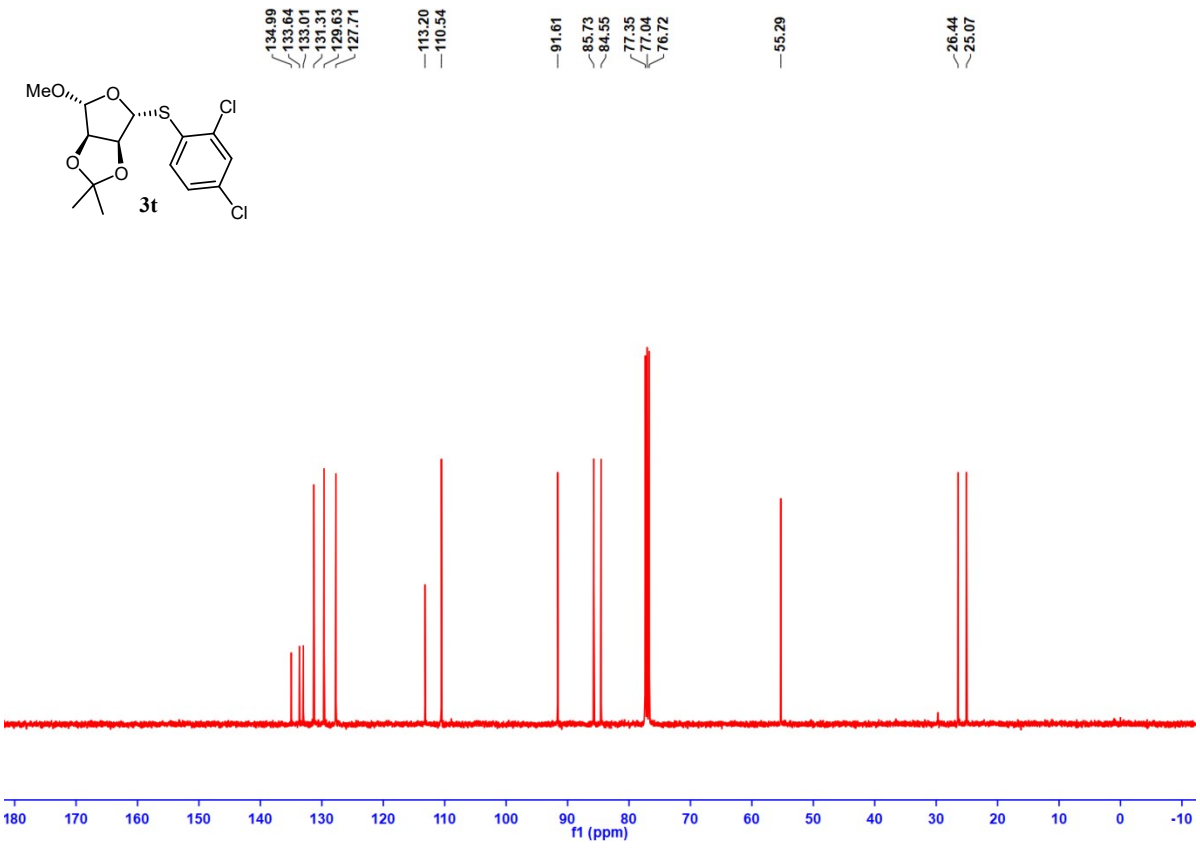

159.78
159.76
158.40
158.37
157.35
157.32
156.00
155.97
124.19
124.11
123.99
123.90
118.98
118.96
118.73
118.71
116.67
116.58
116.41
116.33
115.50
115.42
115.26
115.18
113.19
110.66
91.90
85.90
84.53
77.34
77.03
76.71
55.34
26.42
25.10
MeO
O
S
F
O
O
3r
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

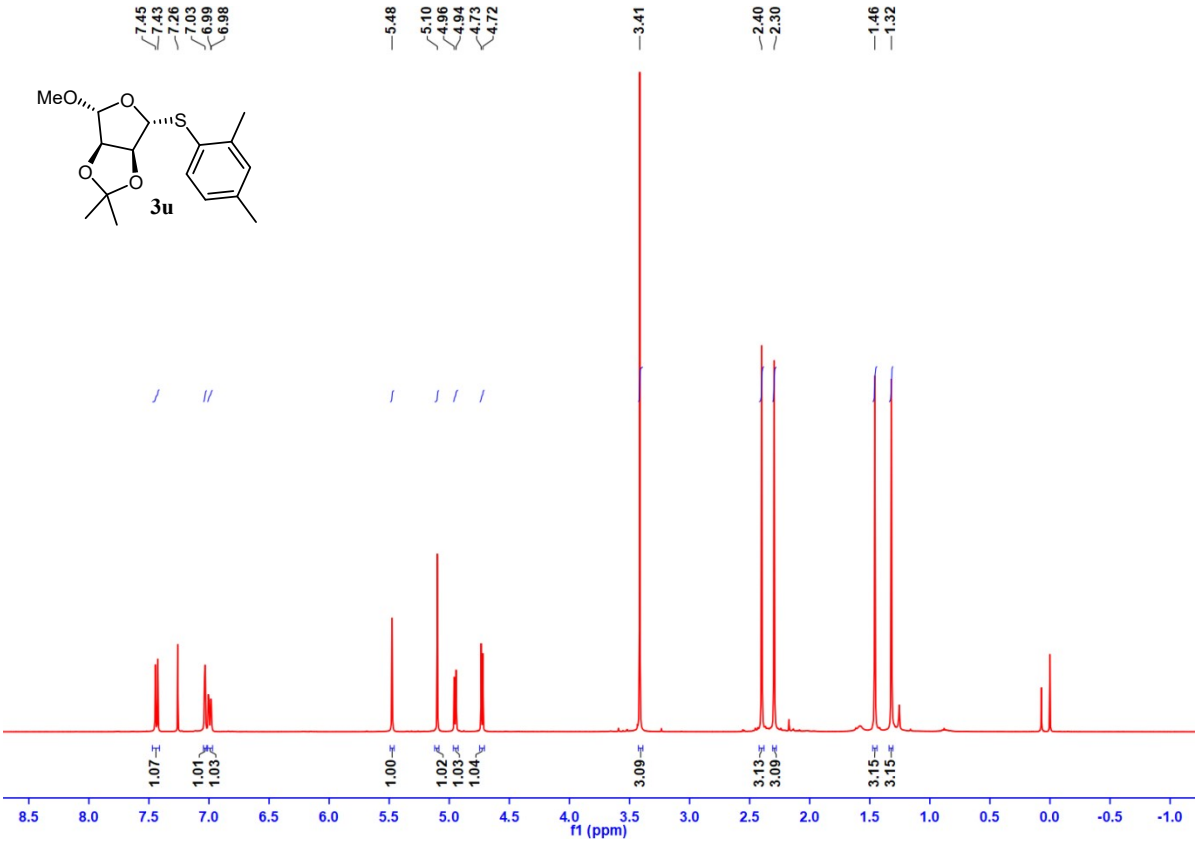

-114.97
-114.98
-114.98
-114.99
-115.00
-115.00
-115.01
-115.01
-115.02
-115.03
-115.04
-115.05
-115.06
-117.73
-117.74
-117.75
-117.76
-117.77
-117.78
-117.79
-117.81
-117.81
-117.83
MeO
O
S
F
O
O
3r
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

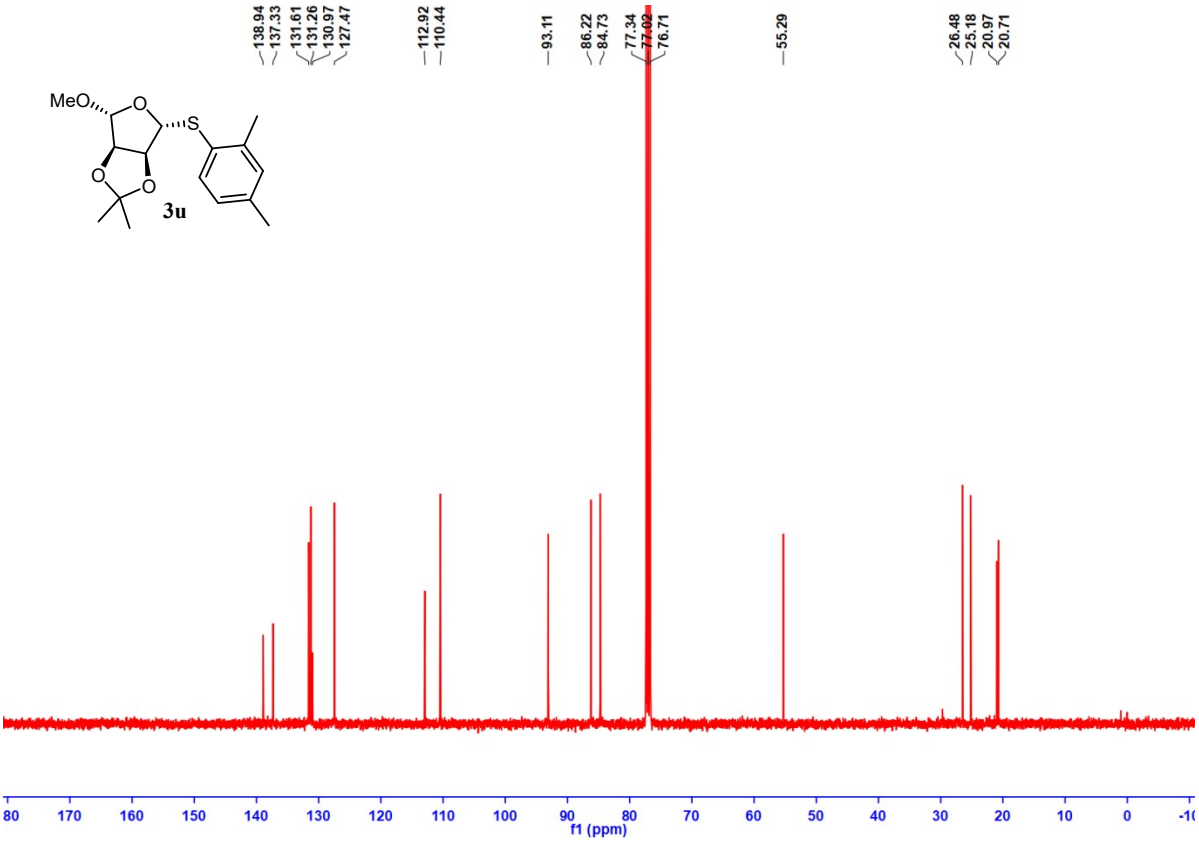

7.35
7.35
7.26
7.22
7.22
7.21
5.62
5.14
4.88
4.87
4.71
4.69
3.37
1.49
1.33
MeO
O
S
Cl
O
O
3s
Cl
1.96
0.96
1.00
1.02
0.98
1.01
3.14
3.05
3.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

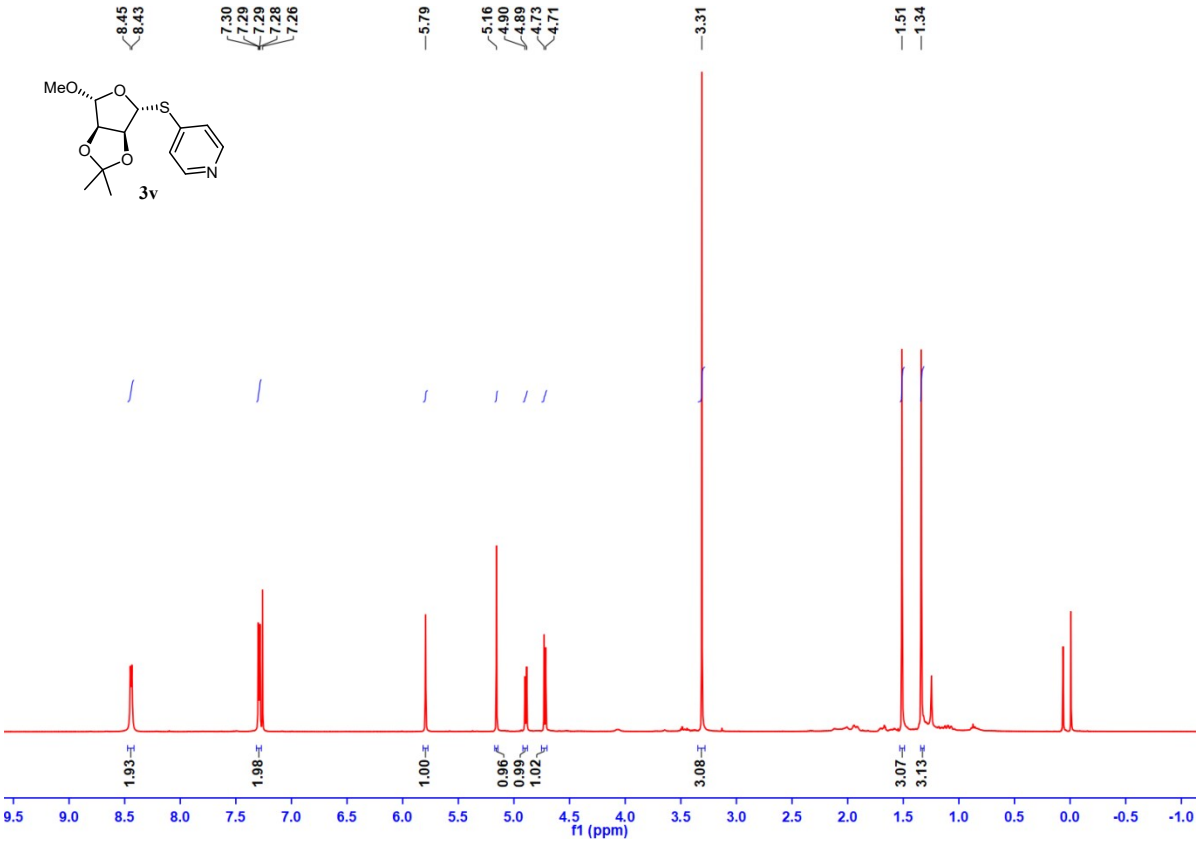

139.25
135.27
127.65
126.92
113.28
110.49
92.53
85.56
84.48
77.35
77.03
76.71
55.28
26.45
25.07
MeO
O
S
Cl
O
O
3s
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

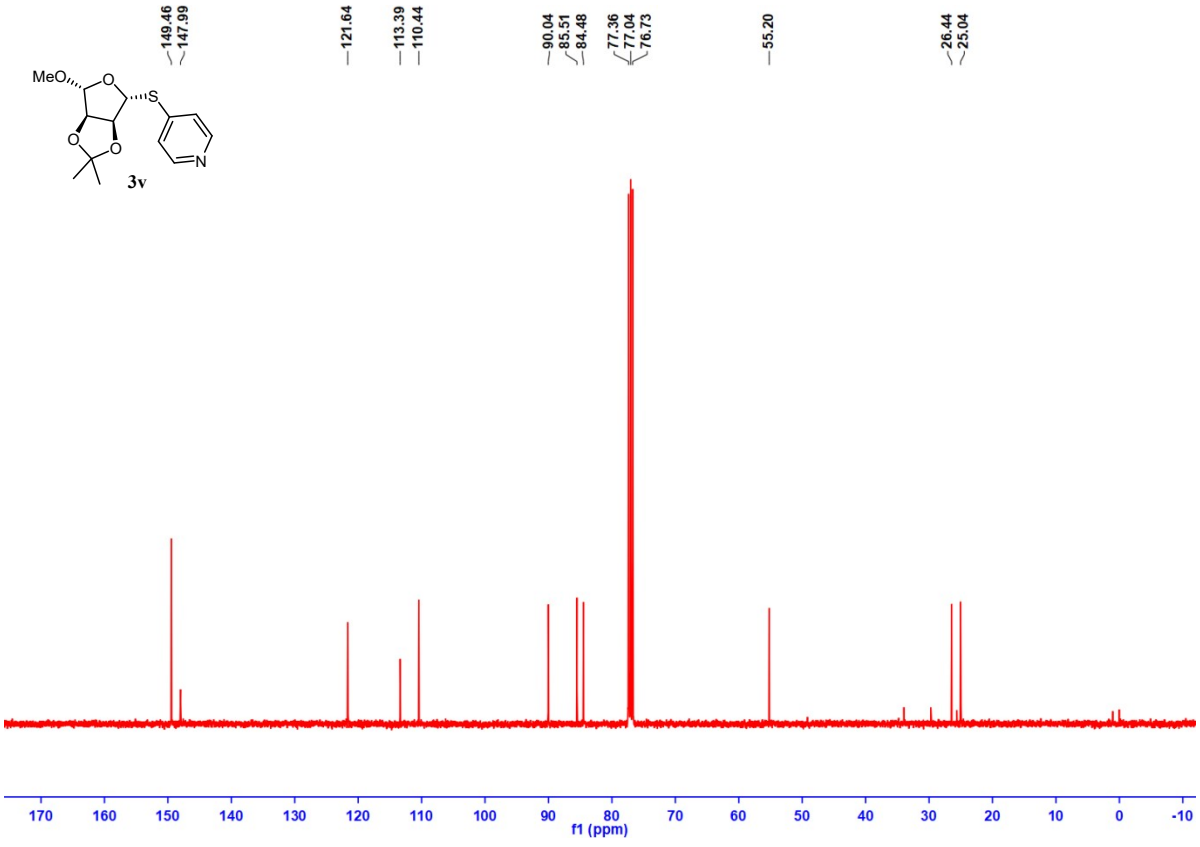

7.55
7.52
7.41
7.41
7.25
7.24
7.22
7.22
5.63
5.12
4.94
4.93
4.74
4.72
3.35
1.48
1.33
MeO
O
S
Cl
O
O
Cl
3t
1.04
0.94
0.98
1.00
1.02
1.01
1.03
3.05
3.20
3.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

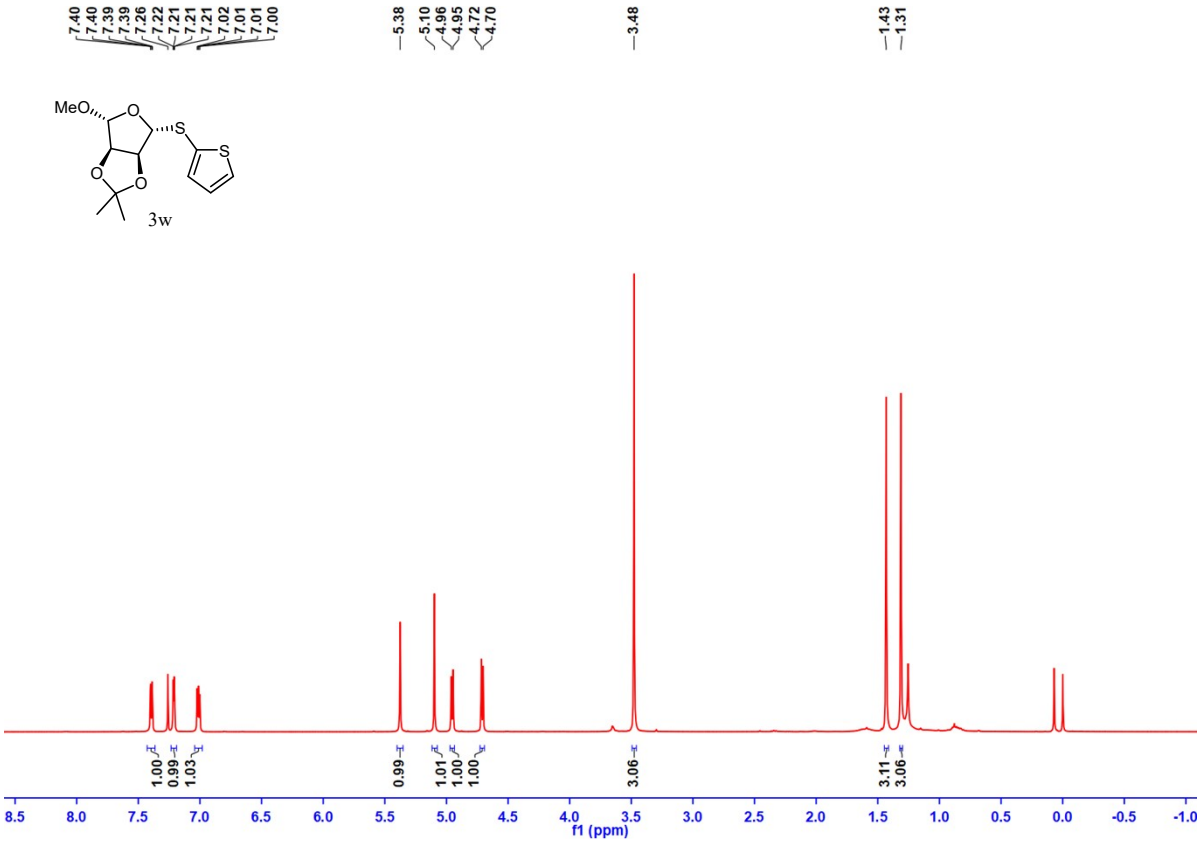

134.99
133.64
133.01
131.31
129.63
127.71
113.20
110.54
91.61
85.73
84.55
77.35
77.04
76.72
55.29
26.44
25.07
MeO
O
S
Cl
O
O
Cl
3t
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

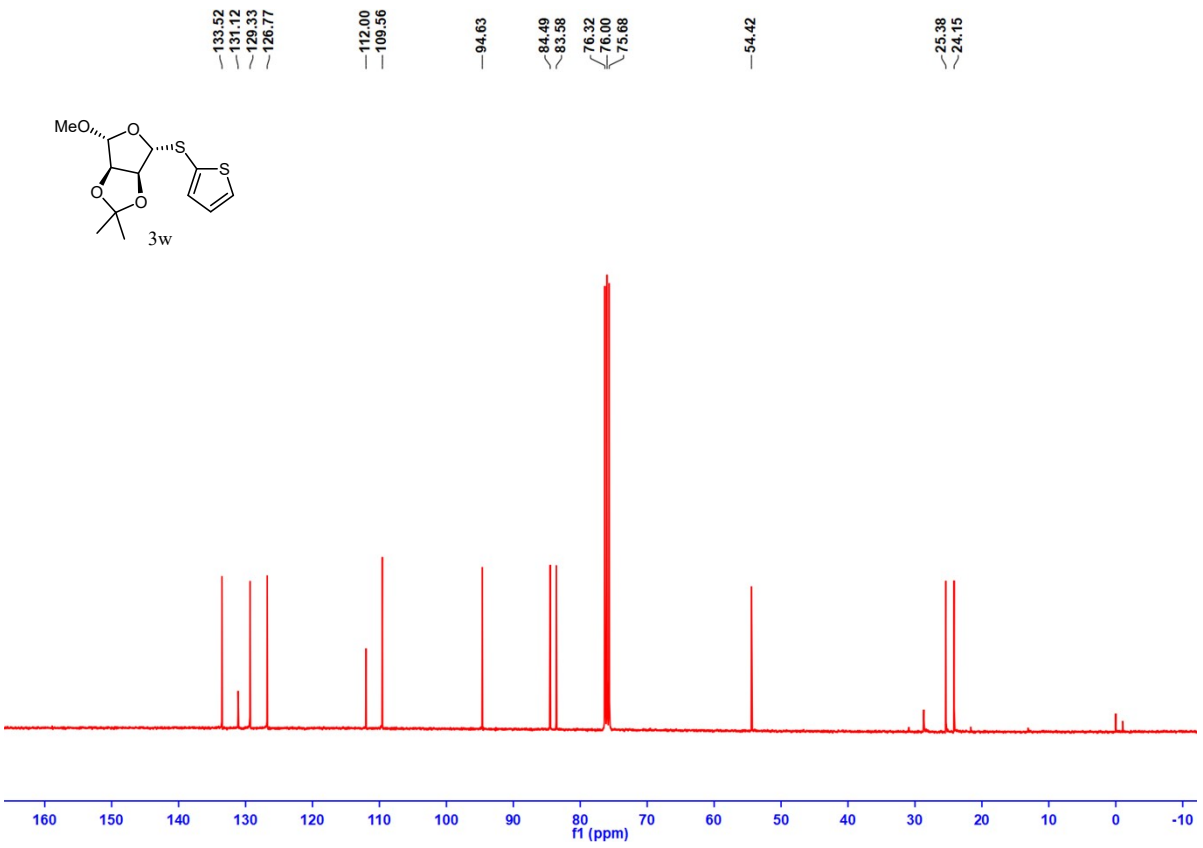

7.45
7.43
7.26
7.03
6.99
6.98
5.48
5.10
4.96
4.94
4.73
4.72
3.41
2.40
2.30
1.46
1.32
MeO
O
S
O
O
3u
1.07
1.01
1.03
1.00
1.02
1.03
1.04
3.09
3.13
3.09
3.15
3.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

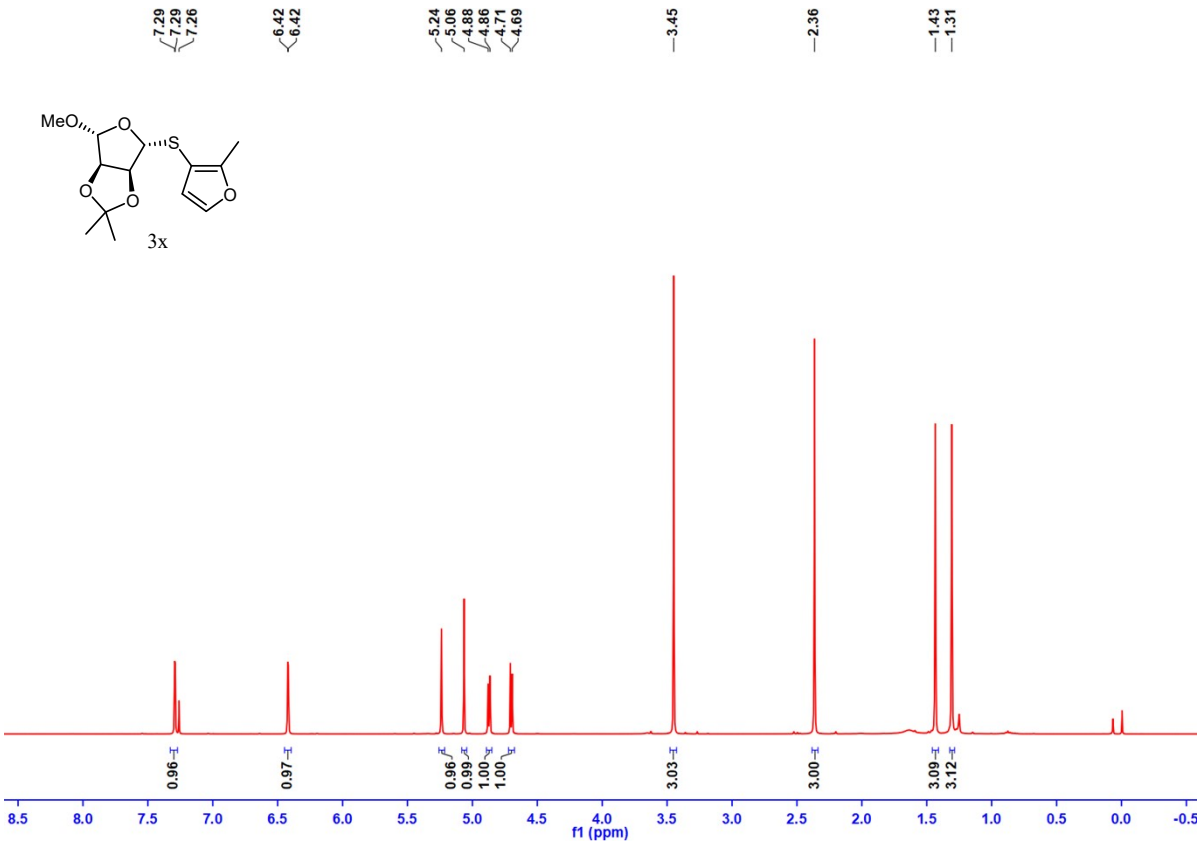

138.94
137.33
131.61
131.26
130.97
127.47
112.92
110.44
93.11
86.22
84.73
77.34
77.02
76.71
55.29
26.48
25.18
20.97
20.71
MeO
O
S
O
O
3u
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

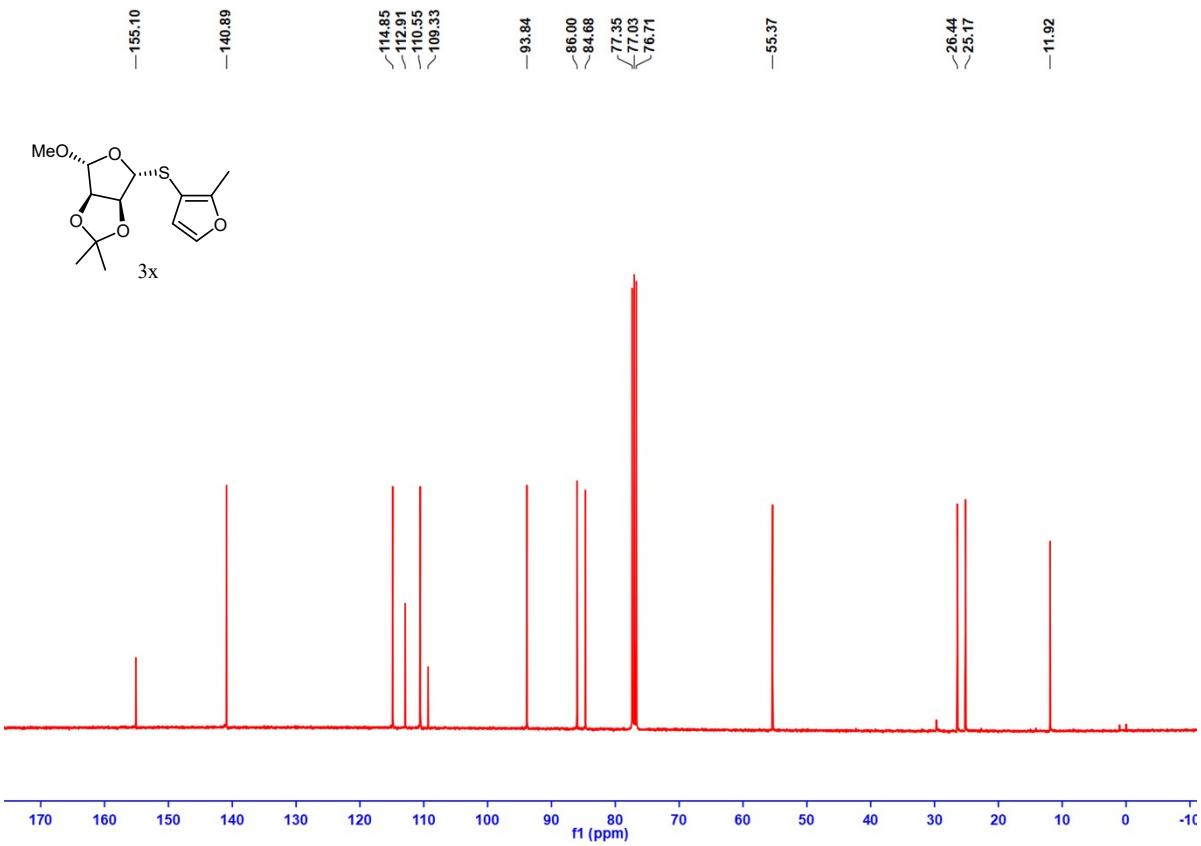

8.45
8.43
7.30
7.29
7.29
7.28
7.26
5.79
5.16
4.90
4.89
4.73
4.71
3.31
1.51
1.34
MeO
O
S
O
O
N
3v
1.93
1.98
1.00
0.96
0.99
1.02
3.08
3.07
3.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

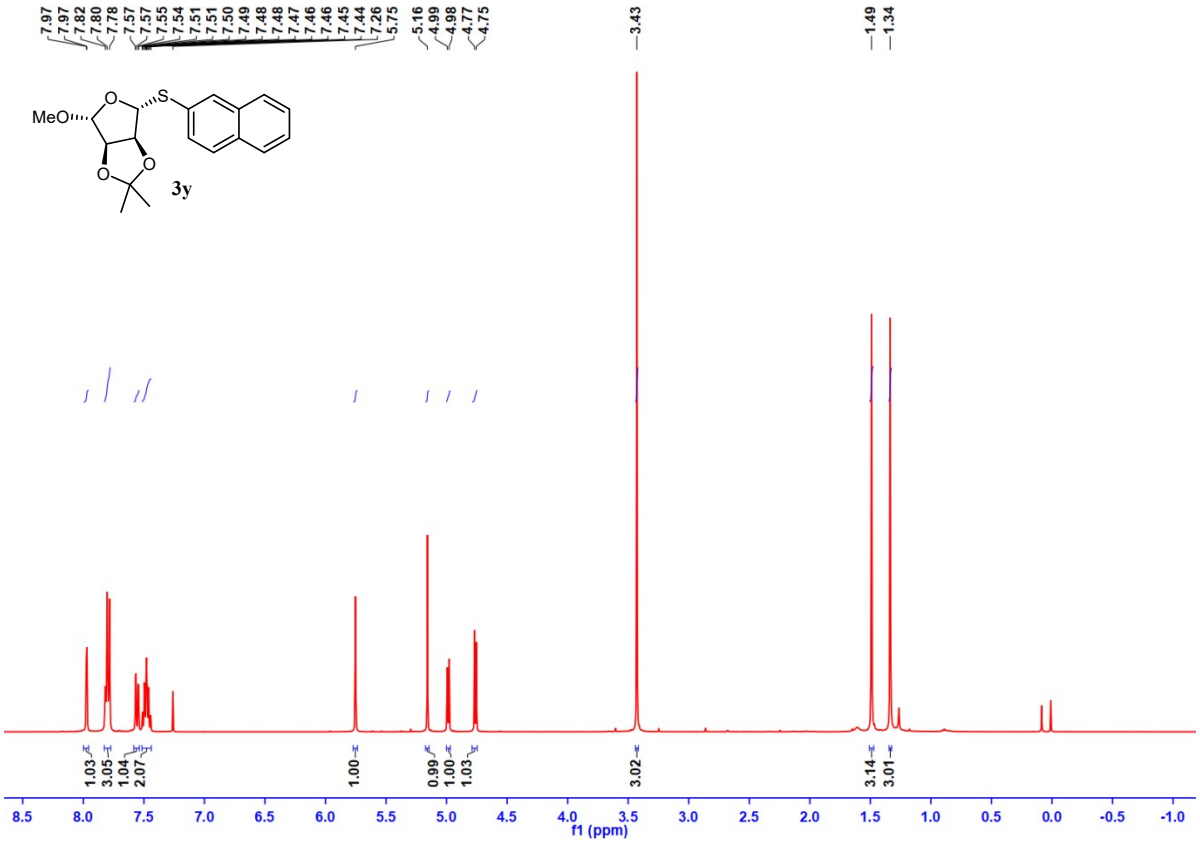

149.46
147.99
121.64
113.39
110.44
90.04
85.51
84.48
77.36
77.04
76.73
55.20
26.44
25.04
MeO
O
S
O
O
N
3v
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

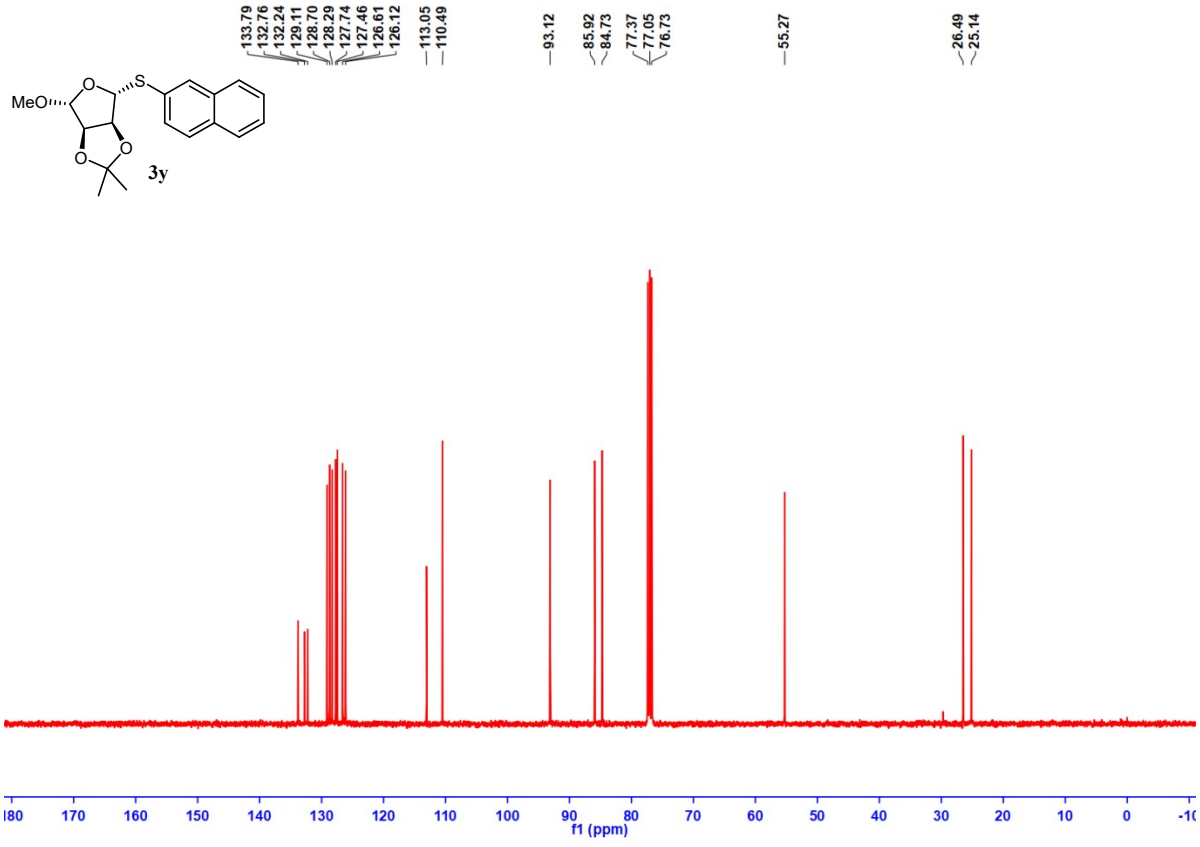

7.40
7.40
7.39
7.39
7.26
7.22
7.21
7.21
7.21
7.02
7.01
7.01
7.00
5.38
5.10
4.96
4.95
4.72
4.70
3.48
1.43
1.31
MeO
O
S
S
O
O
3w
1.00
0.99
1.03
0.99
1.01
1.00
1.00
3.06
3.11
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

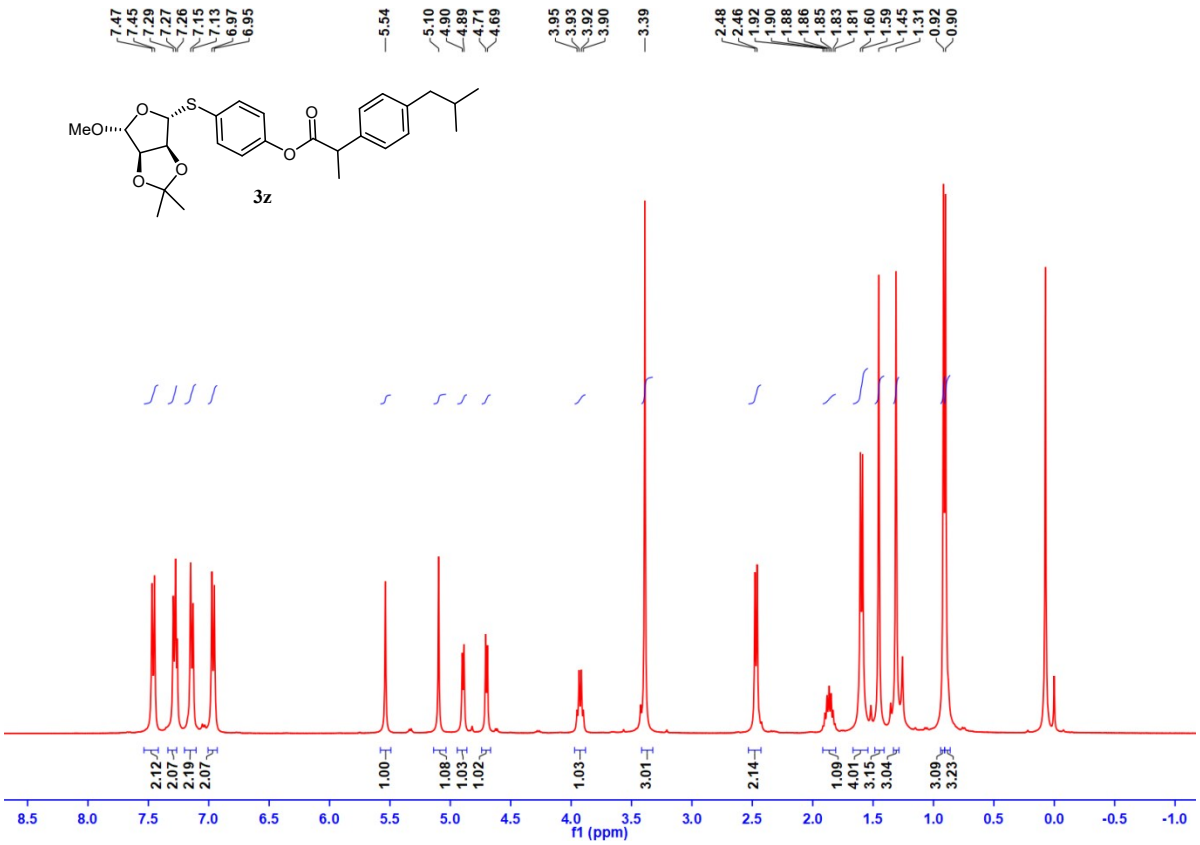

133.52
131.12
129.33
126.77
112.00
109.56
94.63
84.49
83.58
76.32
76.00
75.68
54.42
25.38
24.15
MeO
O
S
S
O
O
3w
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

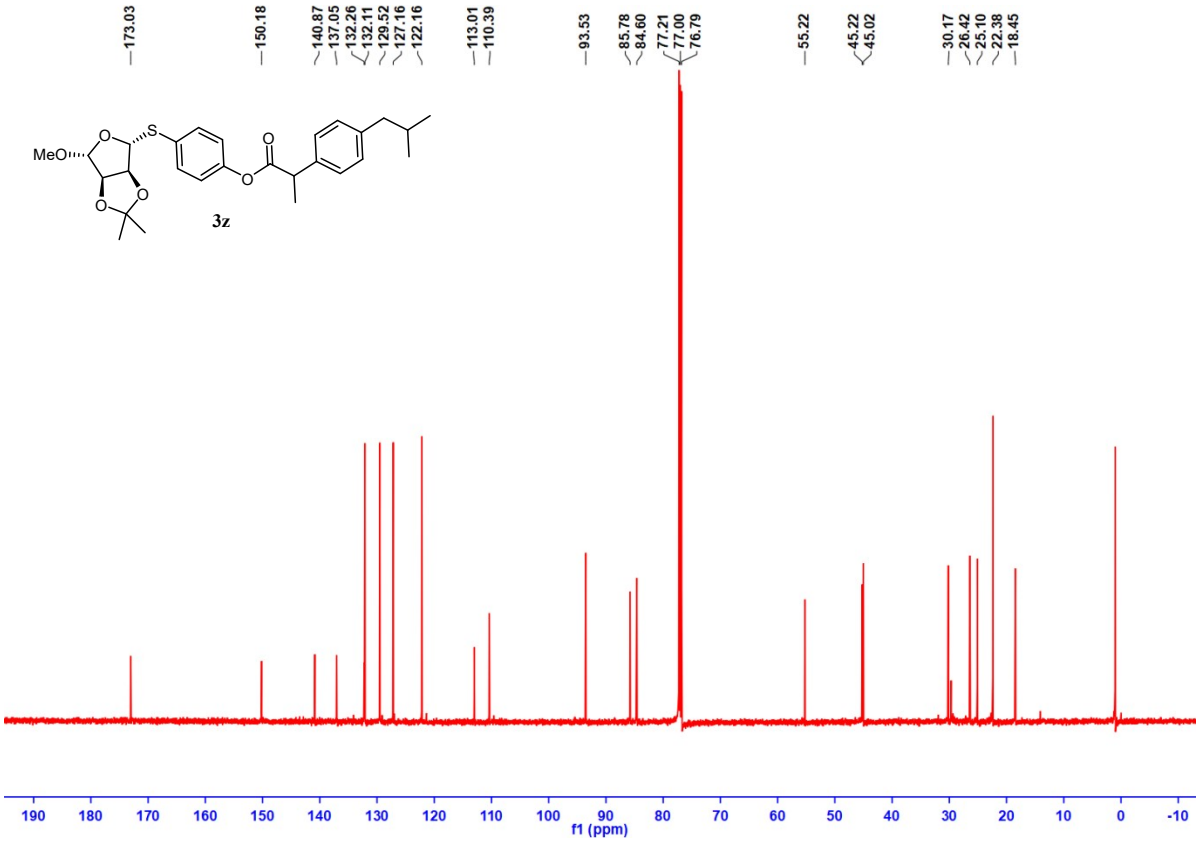

7.29
7.29
7.26
6.42
6.42
5.24
5.06
4.88
4.86
4.71
4.69
3.45
2.36
1.43
1.31
MeO
O
S
O
O
O
3x
0.96
0.97
0.96
0.99
1.00
1.00
3.03
3.00
3.09
3.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

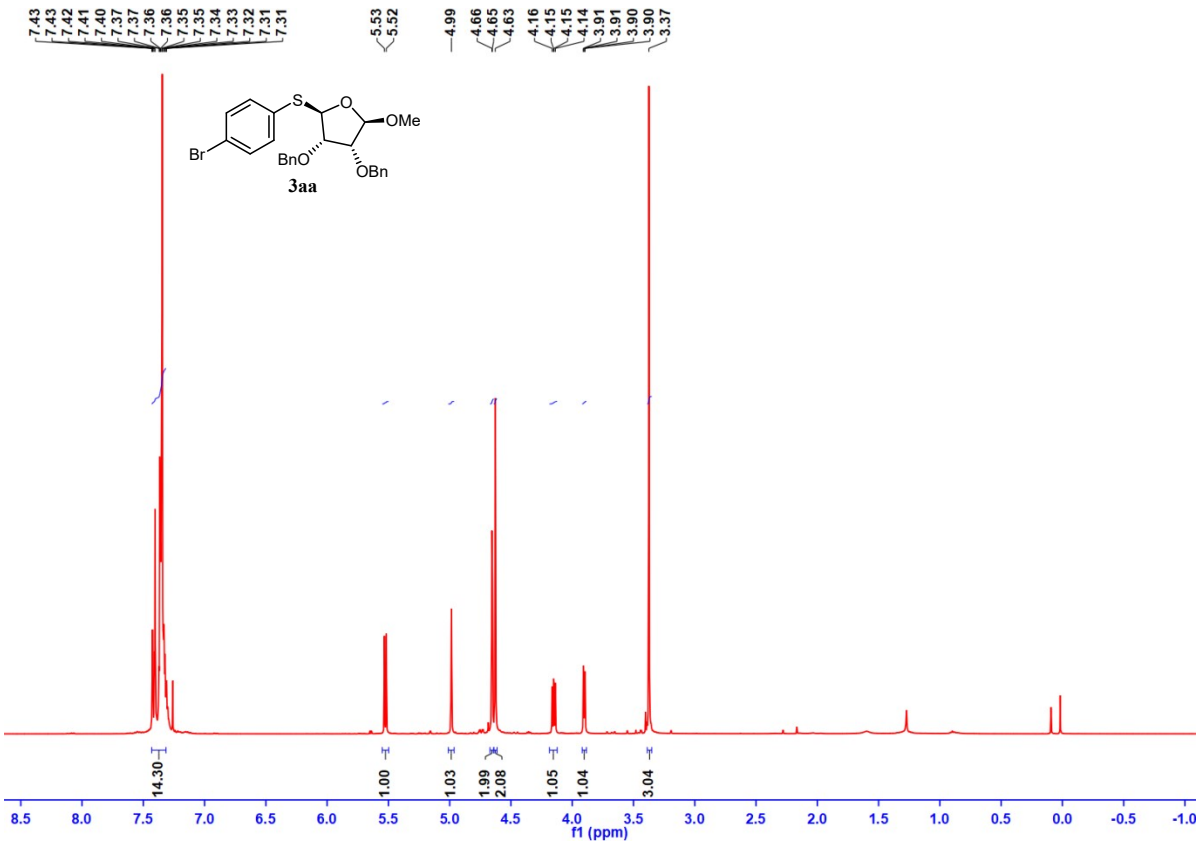

155.10
140.89
114.85
112.91
110.55
109.33
93.84
86.00
84.68
77.35
77.03
76.71
55.37
26.44
25.17
11.92
MeO
O
S
O
O
O
3x
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

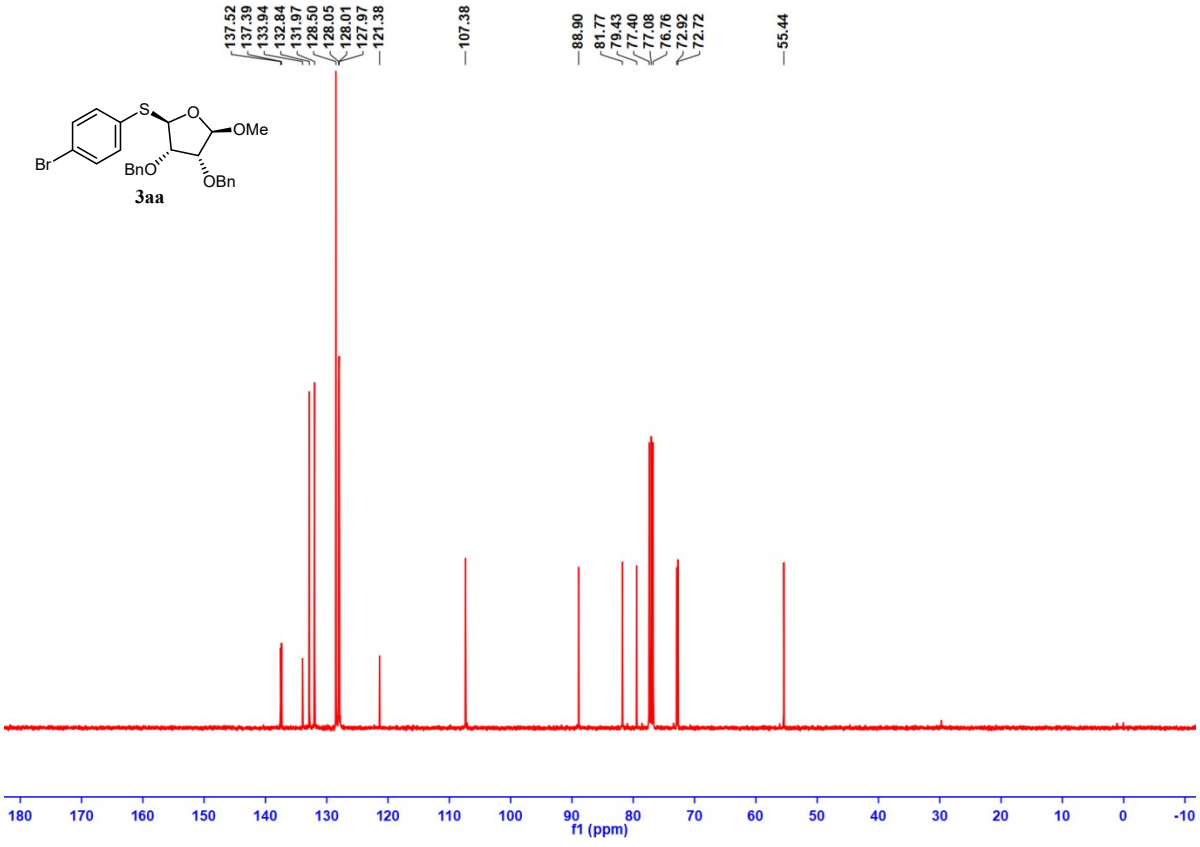

7.97
7.97
7.82
7.80
7.78
7.57
7.57
7.55
7.54
7.51
7.51
7.50
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.26
5.75
5.16
4.99
4.98
4.77
4.75
3.43
1.49
1.34
MeO
O
S
O
O
3y
1.03
3.05
1.04
2.07
1.00
0.99
1.00
1.03
3.02
3.14
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

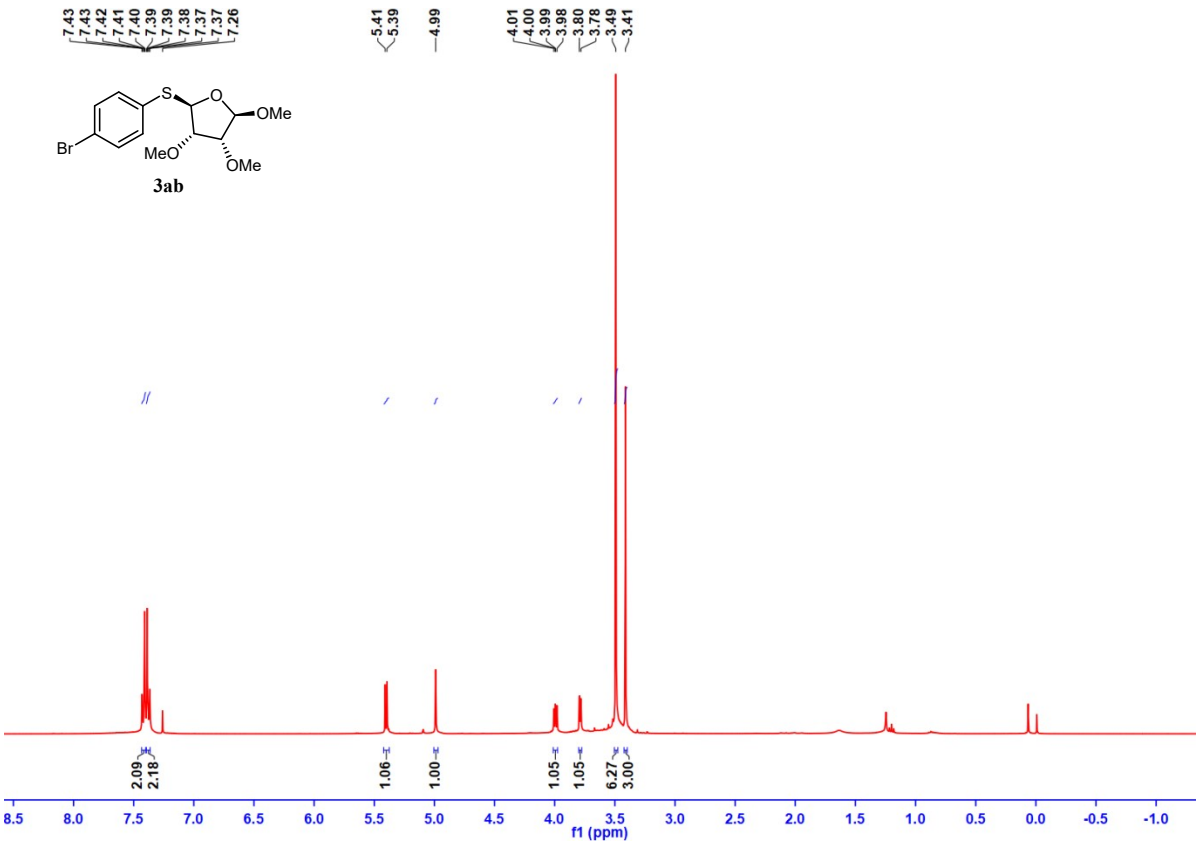

133.79
132.76
132.24
129.11
128.70
128.29
127.74
127.46
126.61
126.12
113.05
110.49
93.12
85.92
84.73
77.37
77.05
76.73
55.27
26.49
25.14
MeO
O
S
O
O
3y
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.47
7.45
7.29
7.27
7.26
7.15
7.13
6.97
6.95
5.54
5.10
4.90
4.89
4.71
4.69
3.95
3.93
3.92
3.90
3.39
2.48
2.46
1.92
1.90
1.88
1.86
1.85
1.83
1.81
1.60
1.59
1.45
1.31
0.92
0.90
MeO
O
S
O
O
O
O
3z
2.12
2.07
2.19
2.07
1.00
1.08
1.03
1.02
1.03
3.01
2.14
1.09
4.01
3.15
3.04
3.09
3.23
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

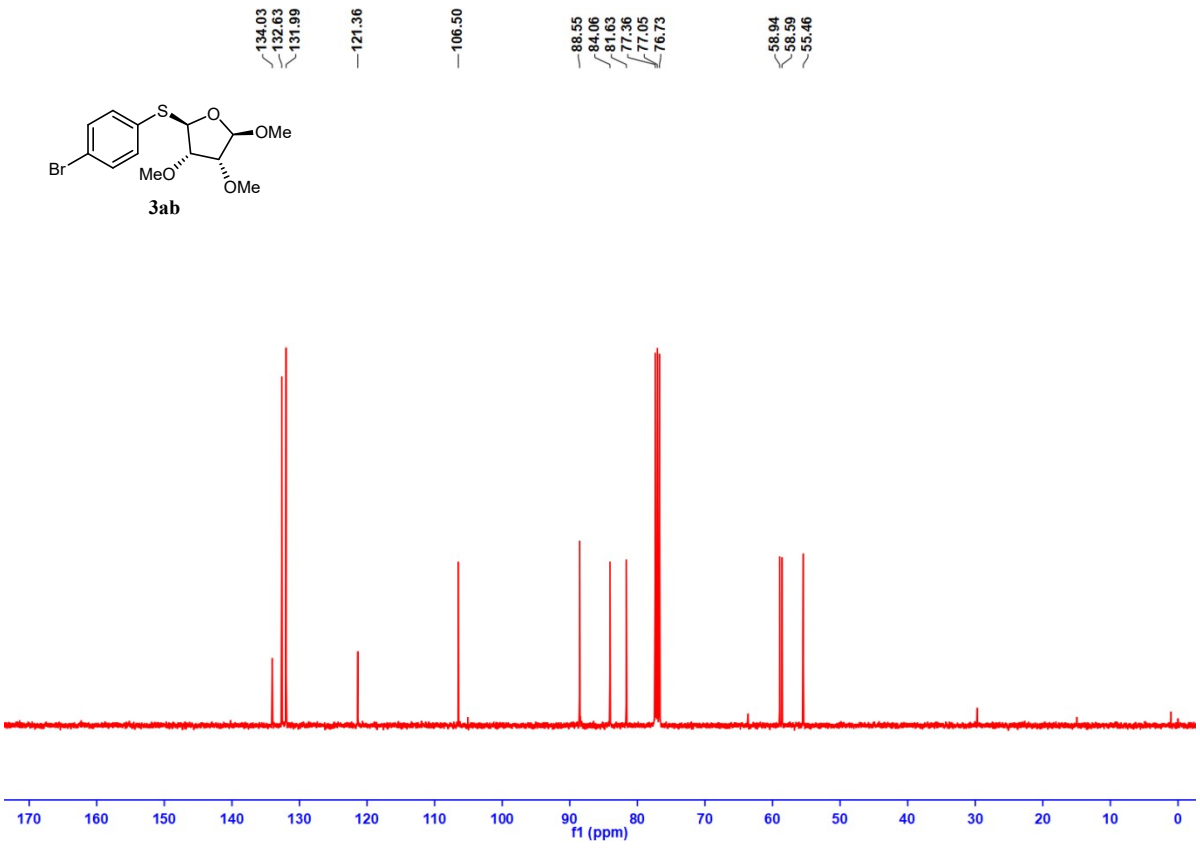

173.03
150.18
140.87
137.05
132.26
132.11
129.52
127.16
122.16
113.01
110.39
93.53
85.78
84.60
77.21
77.00
76.79
55.22
45.22
45.02
30.17
26.42
25.10
22.38
18.45
MeO
O
S
O
O
O
O
3z
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.43
7.43
7.42
7.41
7.40
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.32
7.31
7.31
5.53
5.52
4.99
4.66
4.65
4.63
4.16
4.15
4.15
4.14
3.91
3.91
3.90
3.90
3.37
S
O
OMe
Br
BnO
OBn
3aa
14.30
1.00
1.03
1.99
2.08
1.05
1.04
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

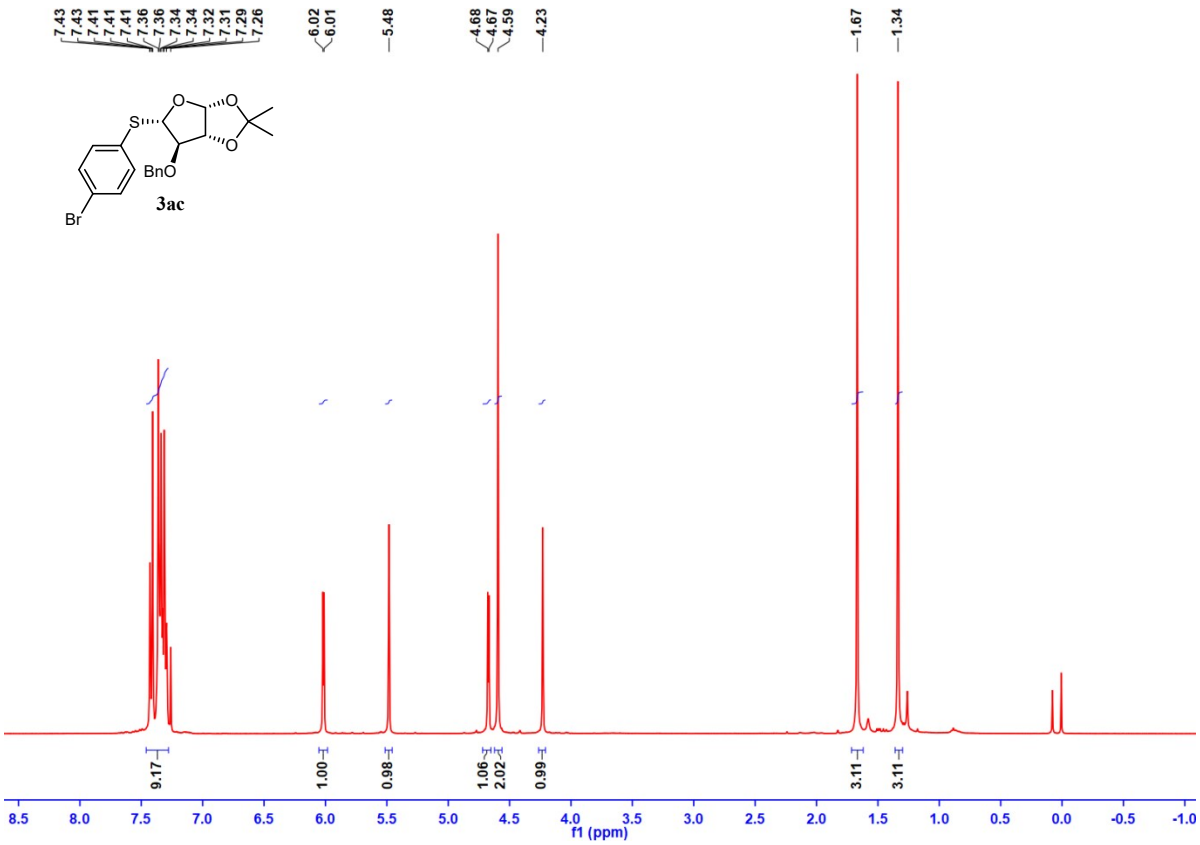

137.52
137.39
133.94
132.84
131.97
128.50
128.05
128.01
127.97
121.38
107.38
88.90
81.77
79.43
77.40
77.08
76.76
72.92
72.72
55.44
S
O
OMe
Br
BnO
OBn
3aa
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

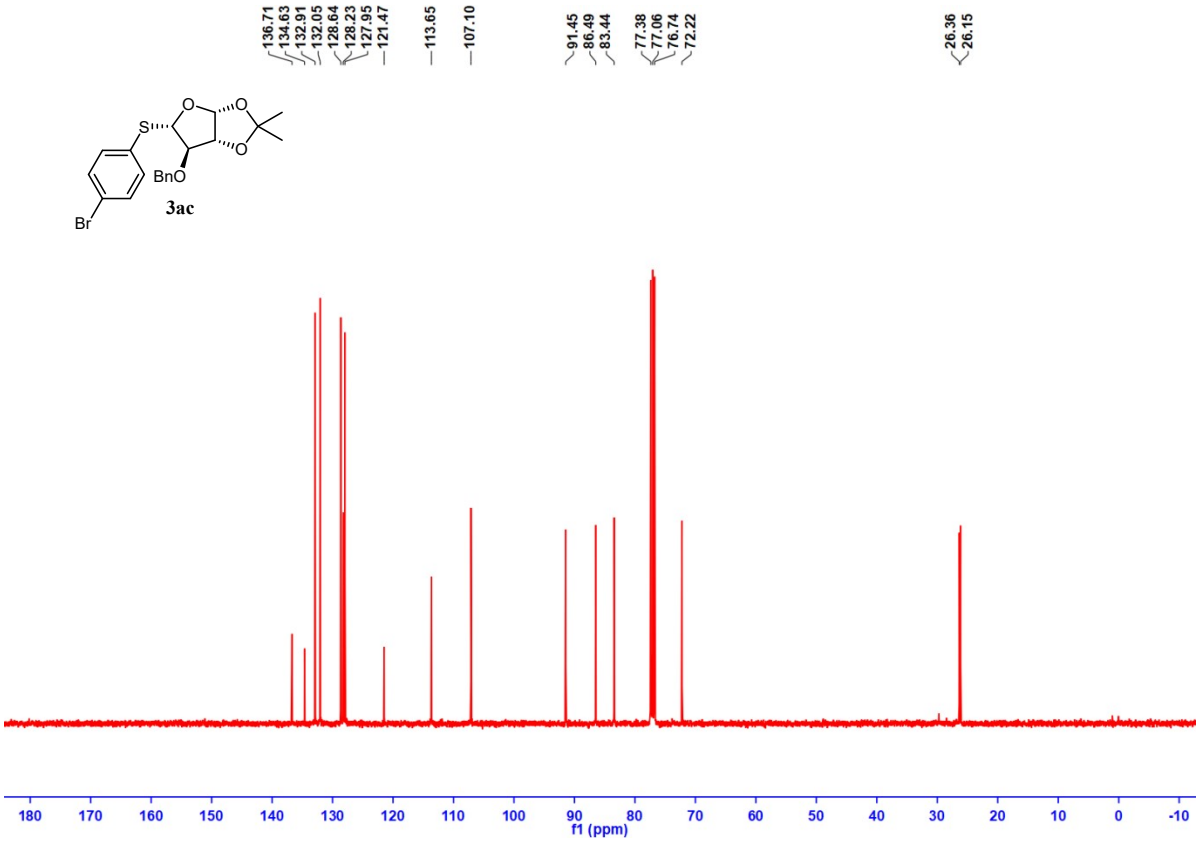

7.43
7.43
7.42
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.26
5.41
5.39
4.99
4.01
4.00
3.99
3.98
3.80
3.78
3.49
3.41
S
O
OMe
Br
MeO
OMe
2.09
2.18
1.06
1.00
1.05
1.05
6.27
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

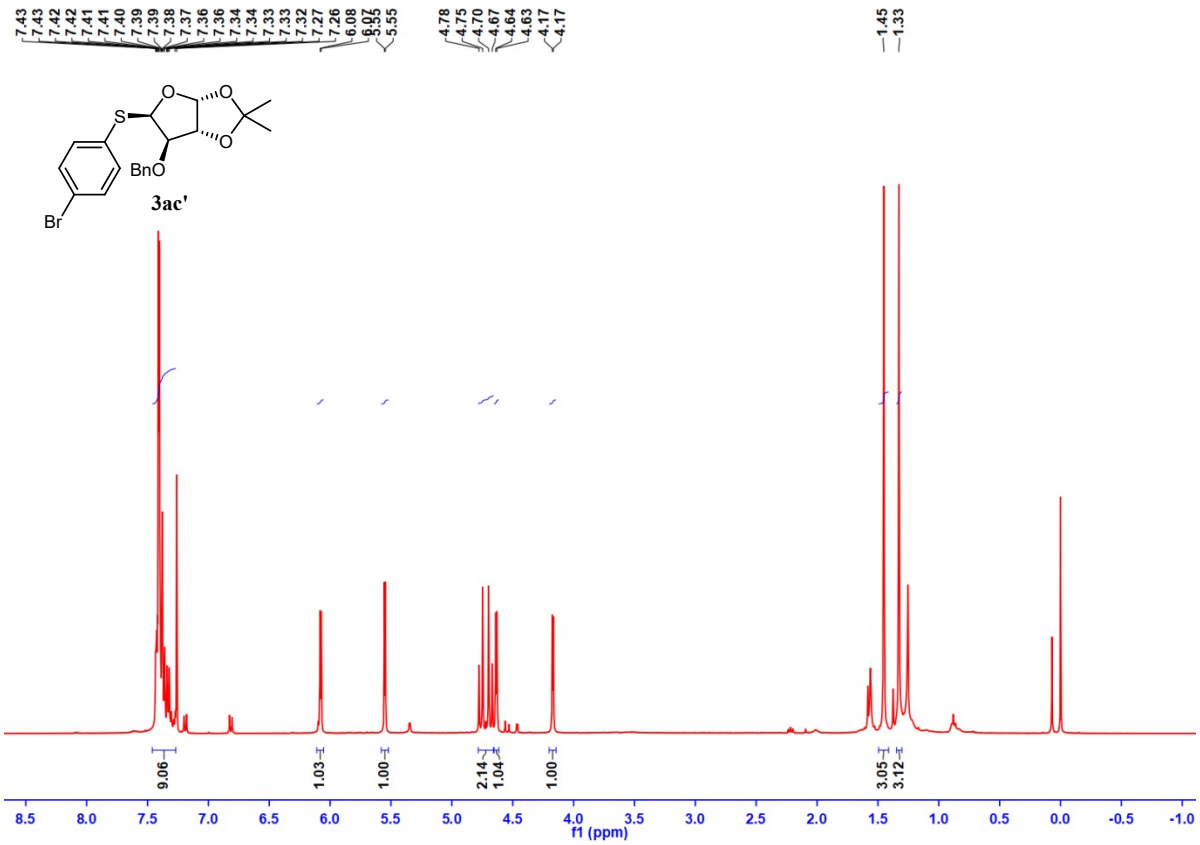
3ab

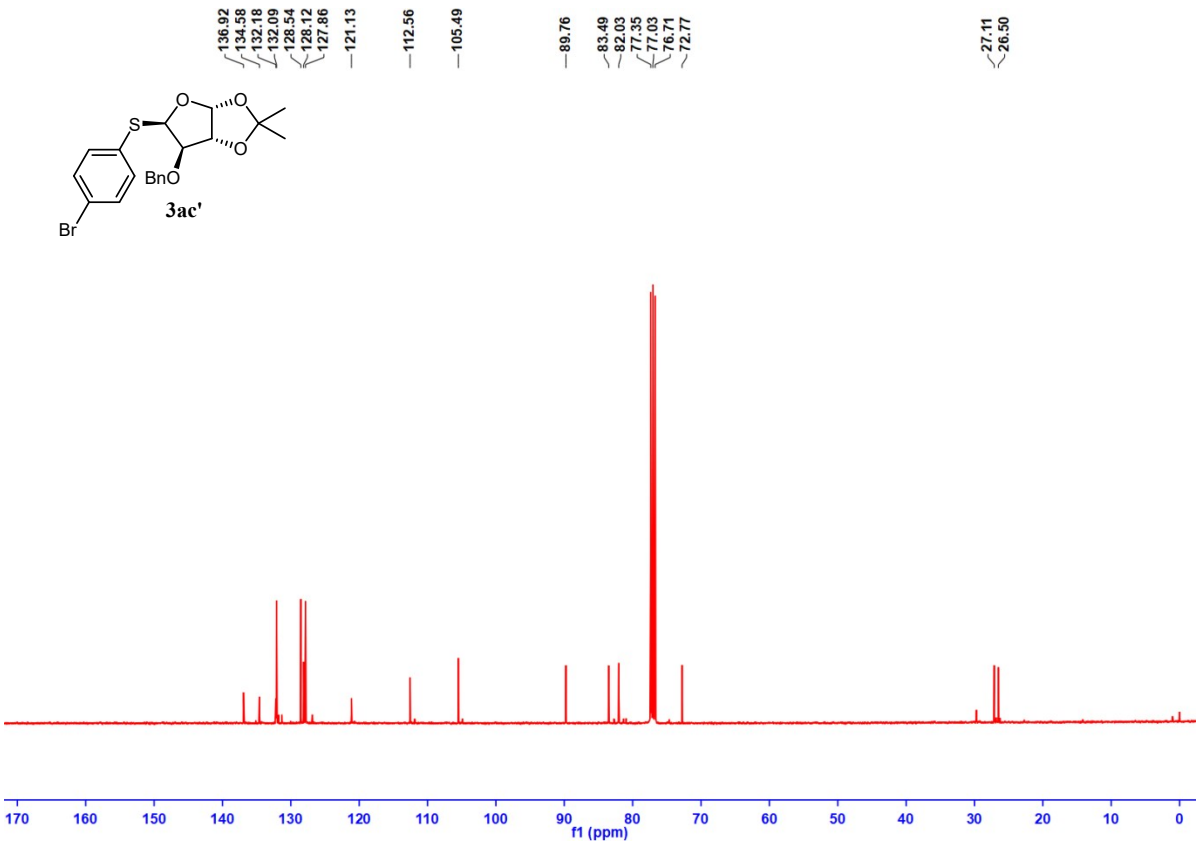

134.03
132.63
131.99
121.36
106.50
88.55
84.06
81.63
77.36
77.05
76.73
58.94
58.59
55.46
S
O
OMe
Br
MeO
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

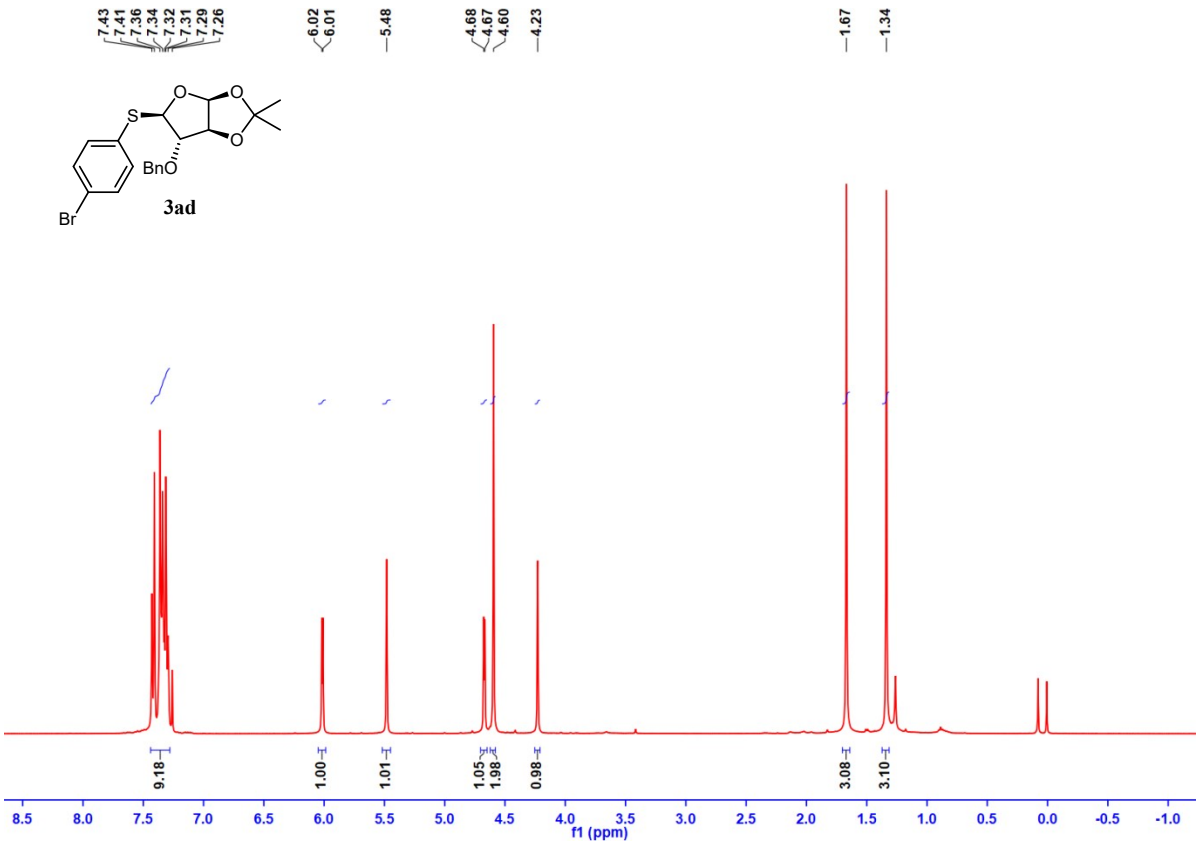
3ab

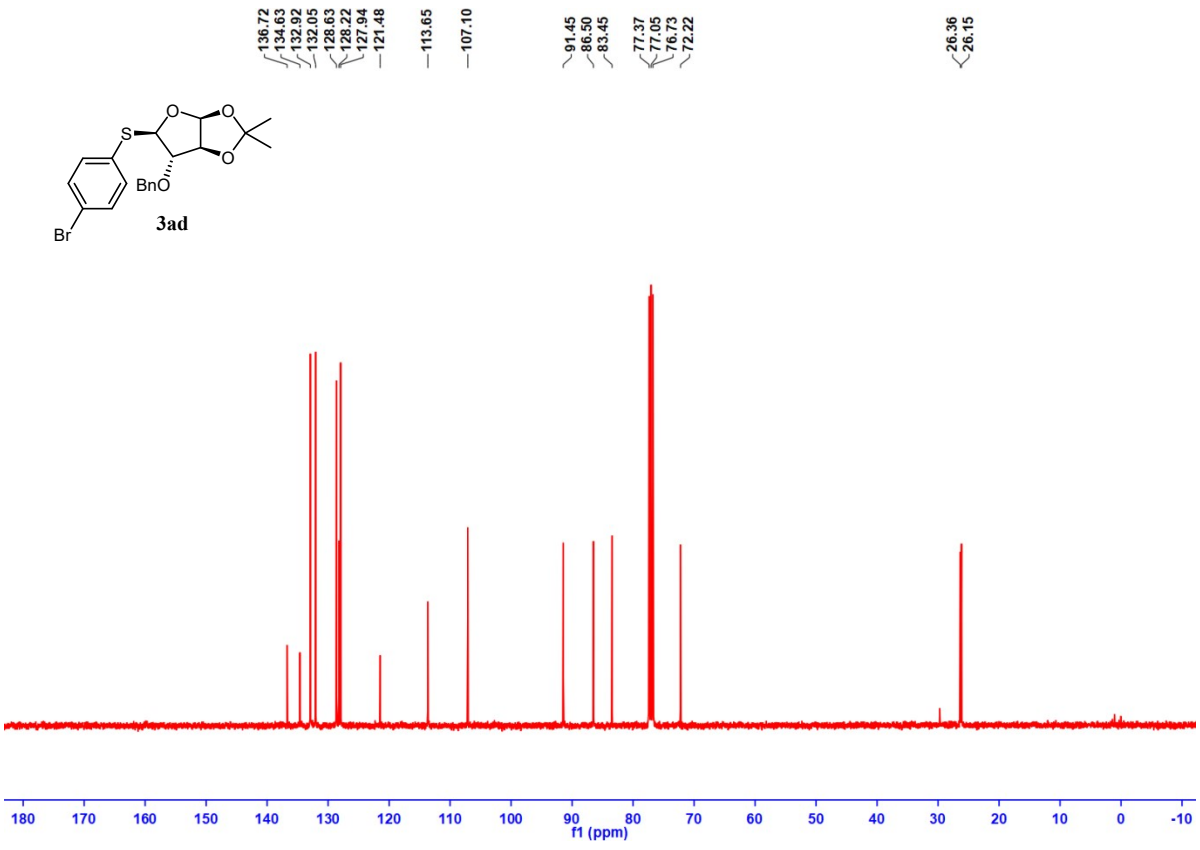

7.43
7.43
7.41
7.41
7.41
7.36
7.36
7.34
7.34
7.32
7.31
7.29
7.26
6.02
6.01
5.48
4.68
4.67
4.59
4.23
1.67
1.34
BnO
Br
3ac
9.17
1.00
0.98
1.06
2.02
0.99
3.11
3.11
f1 (ppm)

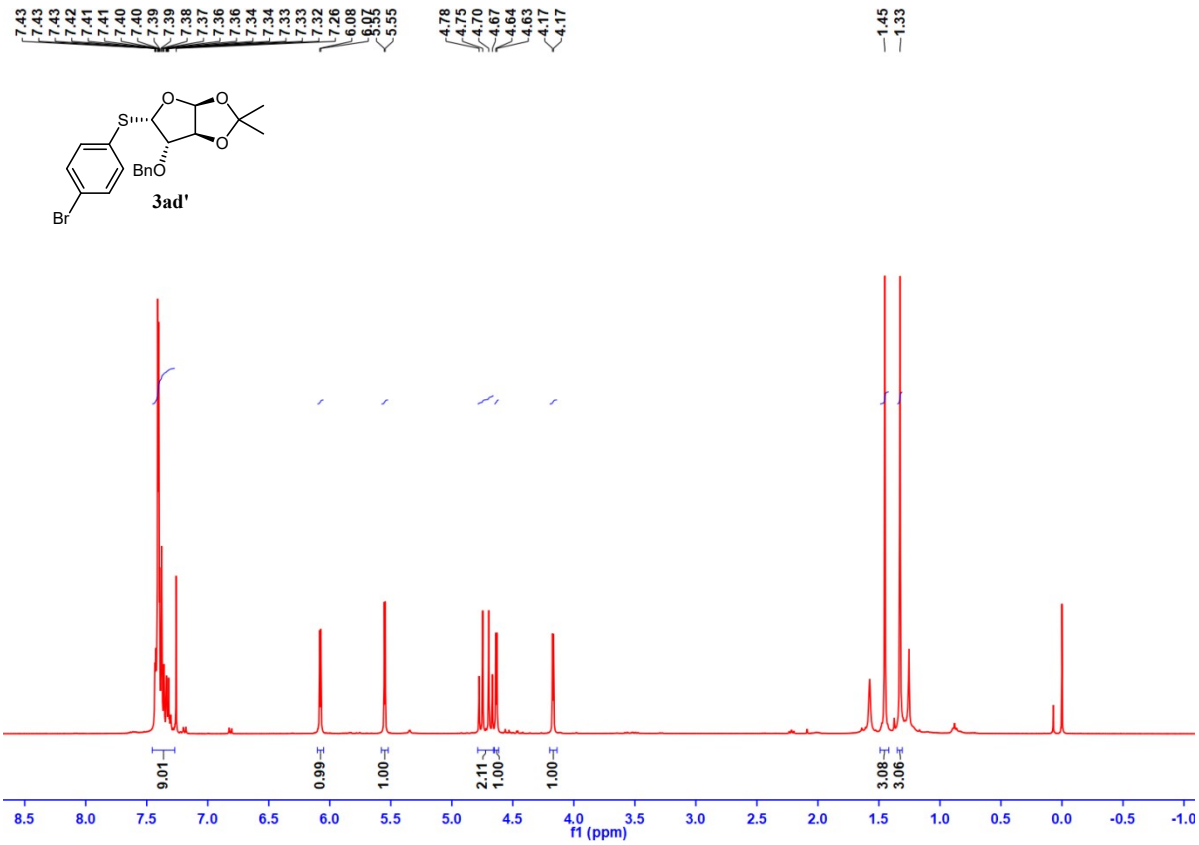

136.71
134.63
132.91
132.05
128.64
128.23
127.95
121.47
113.65
107.10
91.45
86.49
83.44
77.38
77.06
76.74
72.22
26.36
26.15
BnO
Br
3ac
f1 (ppm)

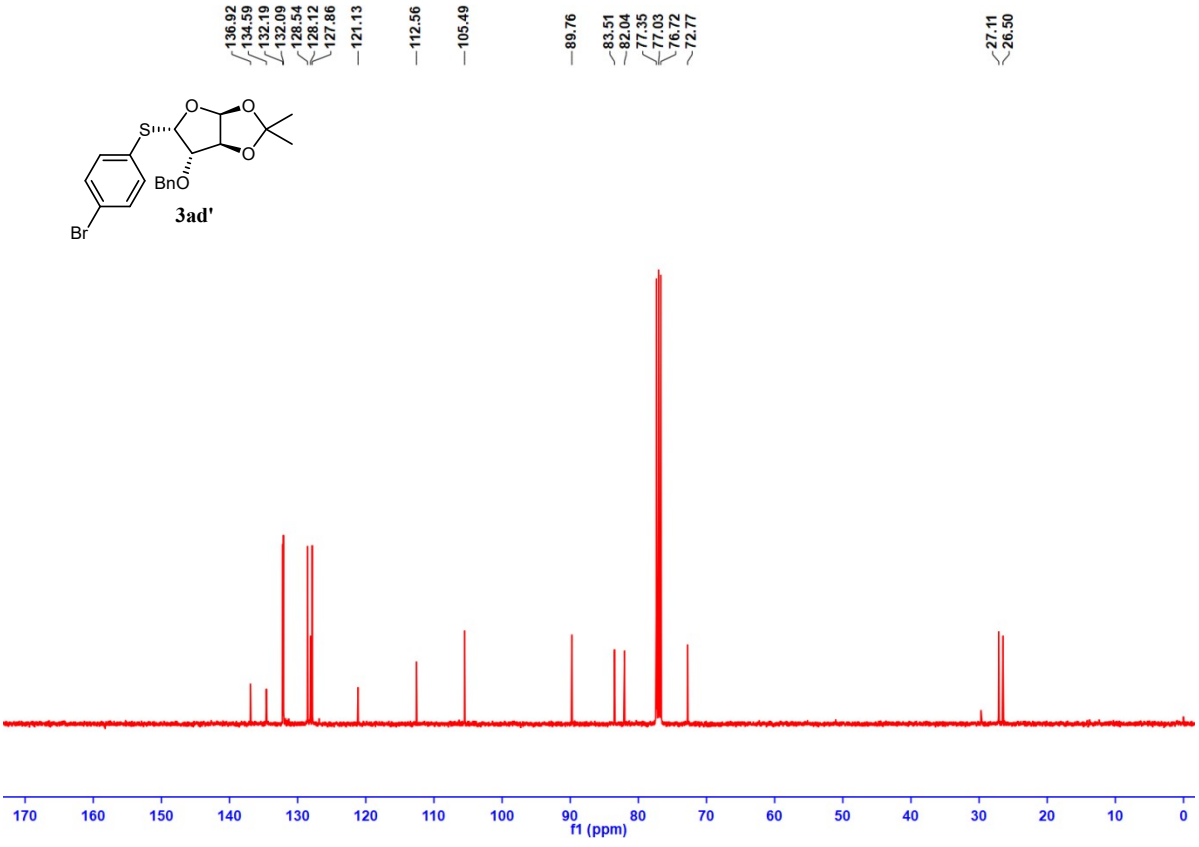

7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.37
7.36
7.36
7.34
7.34
7.33
7.33
7.32
7.27
7.26
6.08
6.07
5.55
4.78
4.75
4.70
4.67
4.64
4.63
4.17
4.17
1.45
1.33
S
O
O
O
BnO
Br
3ac'
9.06
1.03
1.00
2.14
1.04
1.00
3.05
3.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

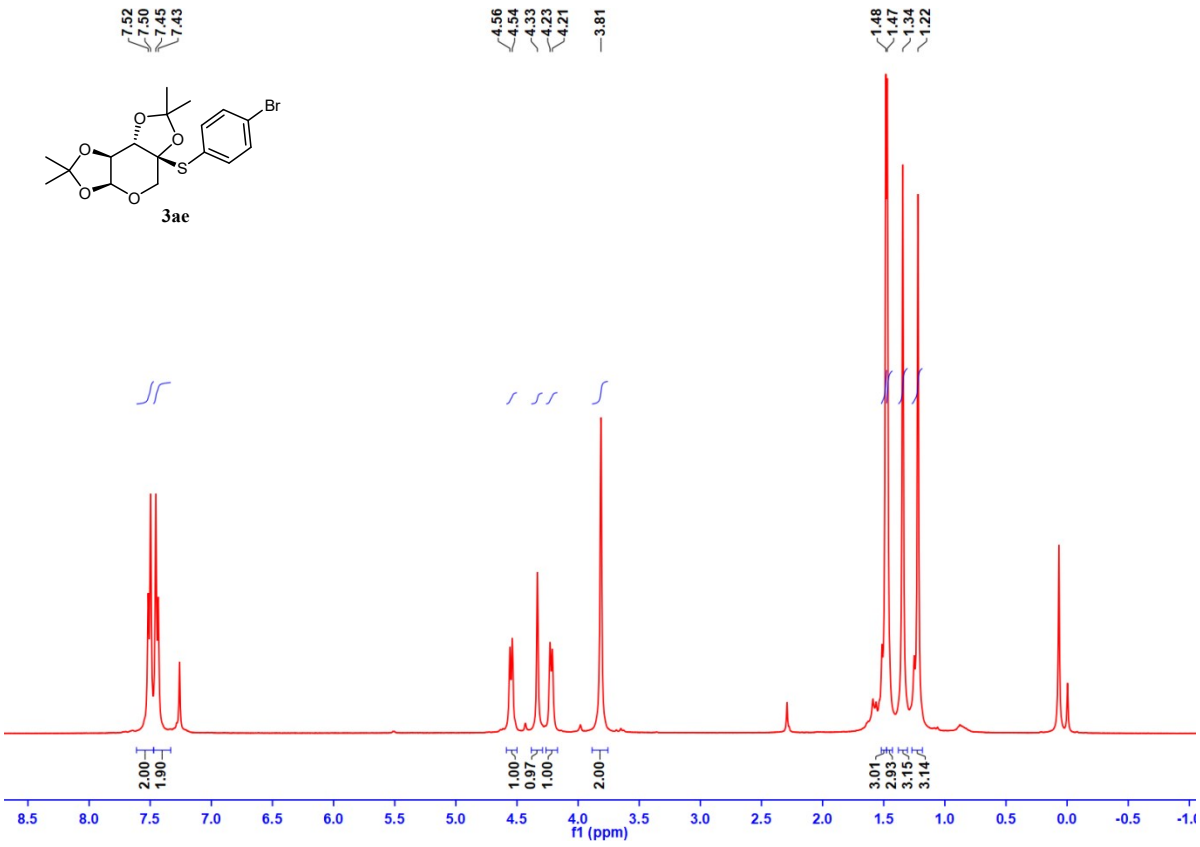

136.92
134.58
132.18
132.09
128.54
128.12
127.86
121.13
112.56
105.49
89.76
83.49
82.03
77.35
77.03
76.71
72.77
27.11
26.50
S
O
O
O
BnO
Br
3ac'
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.43
7.41
7.36
7.34
7.32
7.31
7.29
7.26
6.02
6.01
5.48
4.68
4.67
4.60
4.23
1.67
1.34
S
O
O
O
O
BnO
Br
3ad
9.18
1.00
1.01
1.05
1.98
0.98
3.08
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

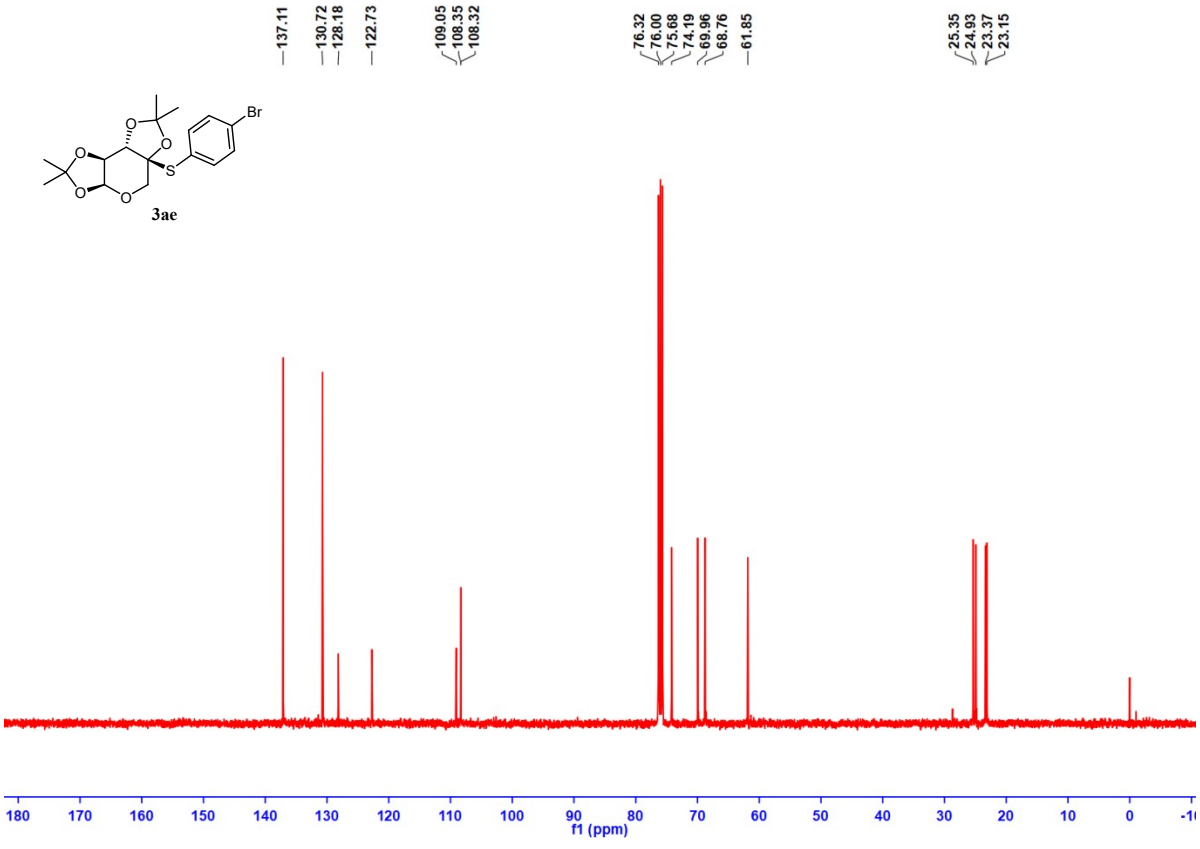

136.72
134.63
132.92
132.05
128.63
128.22
127.94
121.48
113.65
107.10
91.45
86.50
83.45
77.37
77.05
76.73
72.22
26.36
26.15
S
O
O
O
O
BnO
Br
3ad
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.43
7.43
7.43
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.36
7.36
7.34
7.34
7.33
7.33
7.32
7.26
6.08
5.57
5.55
4.78
4.75
4.70
4.67
4.64
4.63
4.17
4.17
1.45
1.33
S
O
O
O
BnO
Br
3ad'
9.01
0.99
1.00
2.11
1.00
1.00
3.08
3.06
f1 (ppm)

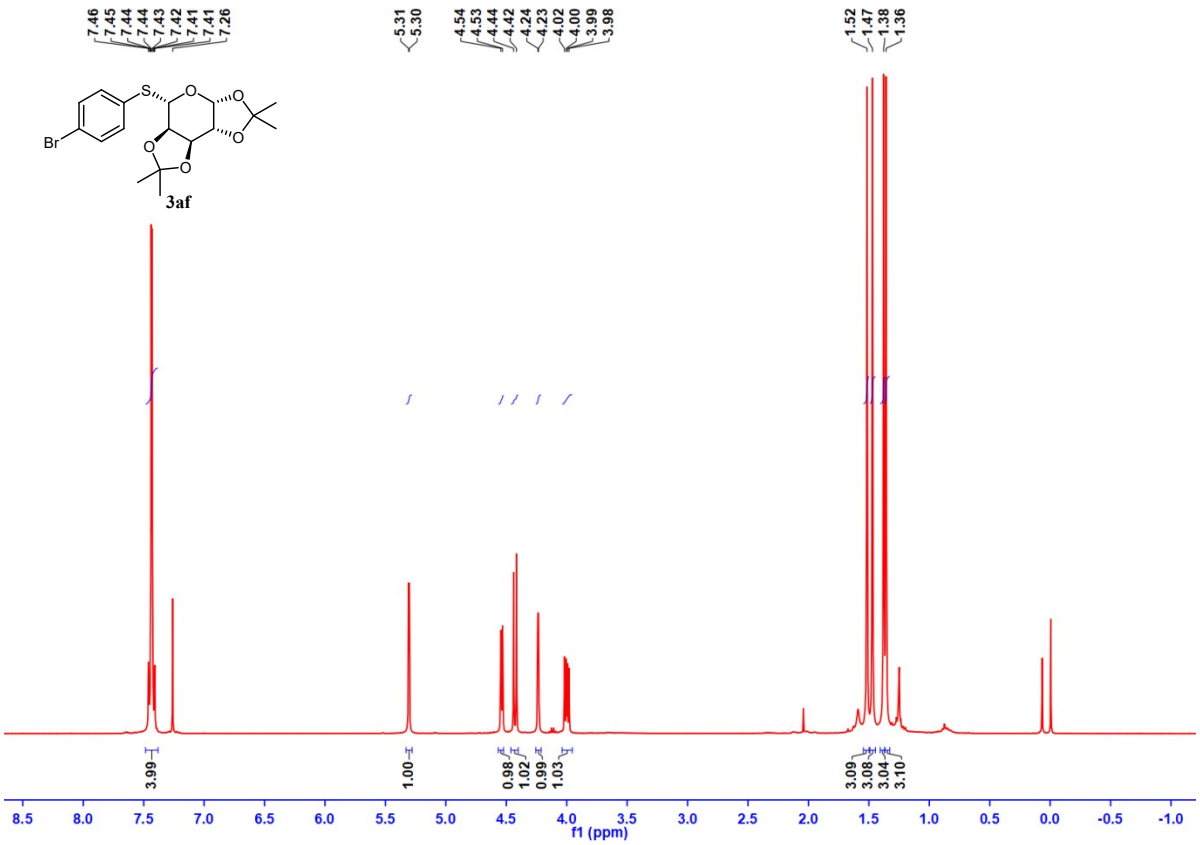

136.92
134.59
132.19
132.09
128.54
128.12
127.86
121.13
112.56
105.49
89.76
83.51
82.04
77.35
77.03
76.72
72.77
27.11
26.50
S
O
O
O
BnO
Br
3ad'
f1 (ppm)

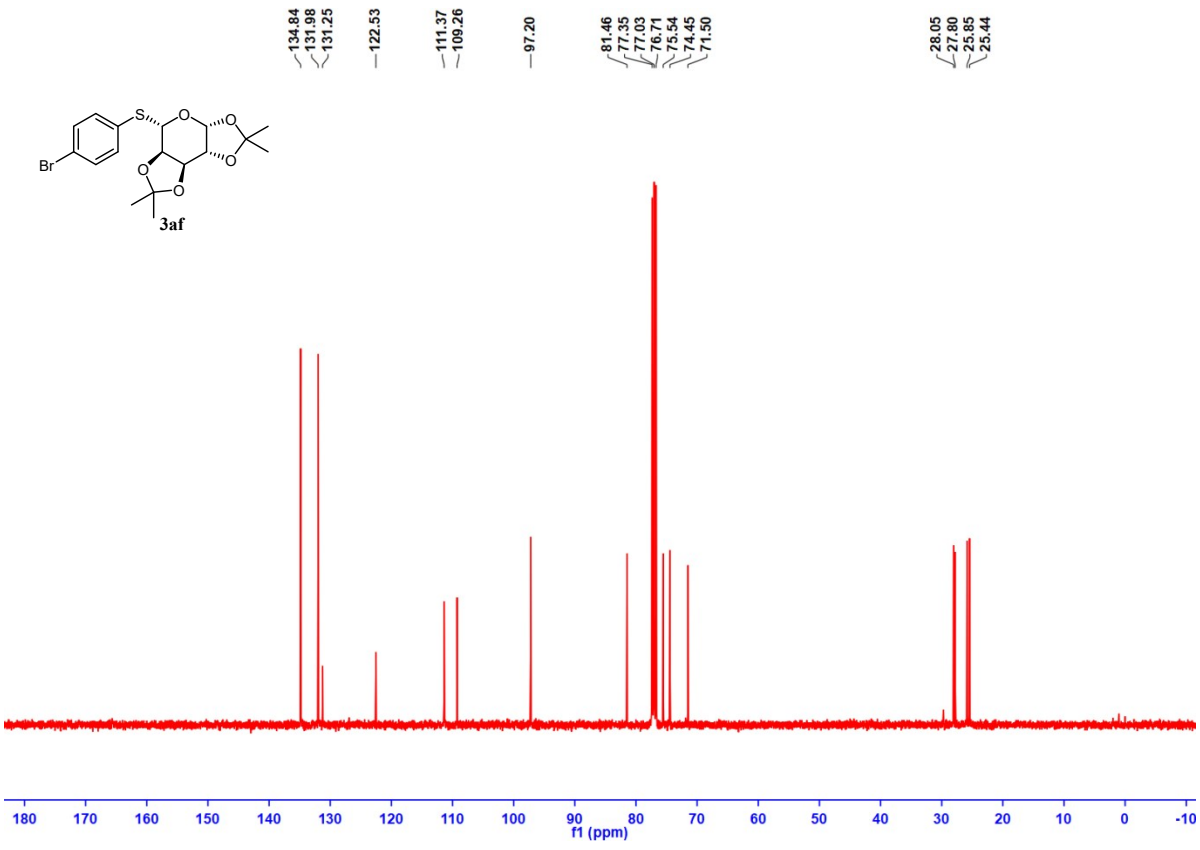

7.52
7.50
7.45
7.43
4.56
4.54
4.33
4.23
4.21
3.81
1.48
1.47
1.34
1.22
Br
O
O
O
O
O
S
2.00
1.90
1.00
0.97
1.00
2.00
3.01
2.93
3.15
3.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

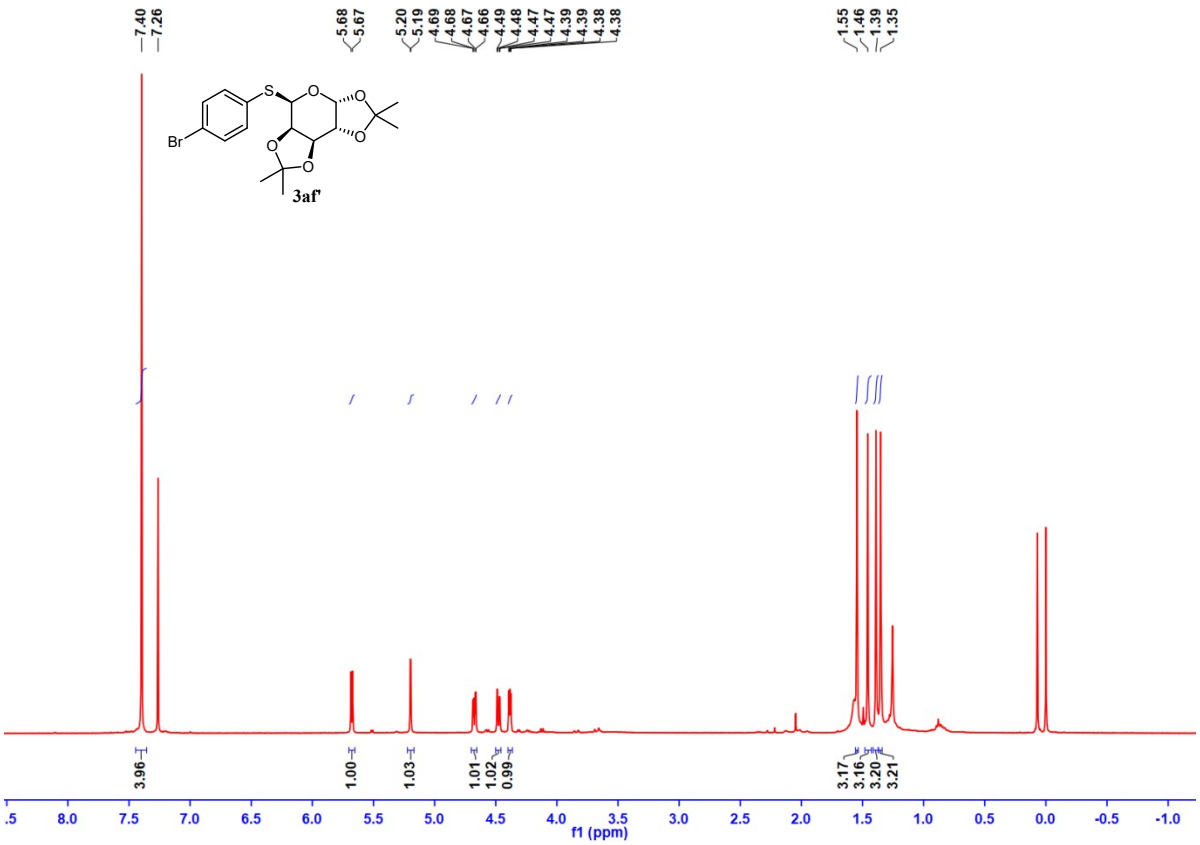
3ae

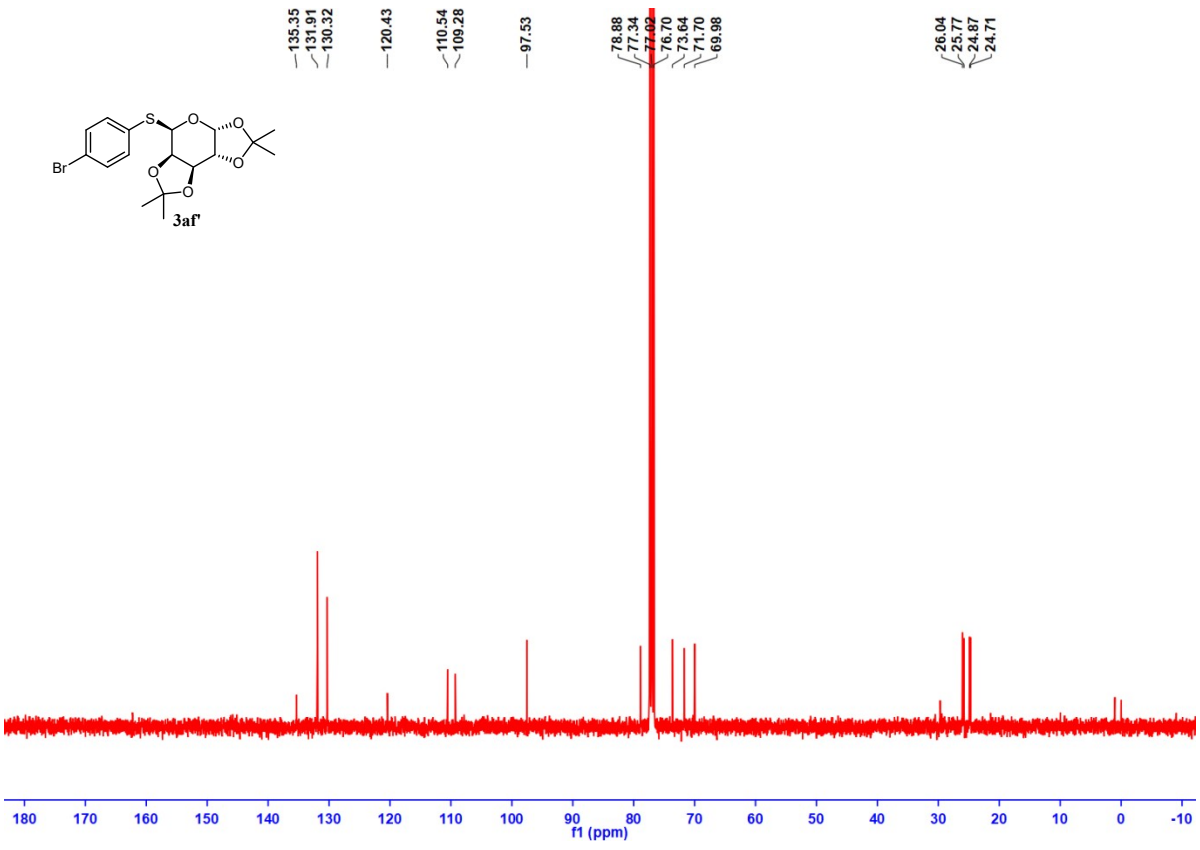

137.11
130.72
128.18
122.73
109.05
108.35
108.32
76.32
76.00
75.68
74.19
69.96
68.76
61.85
25.35
24.93
23.37
23.15
Br
O
O
O
O
O
S
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

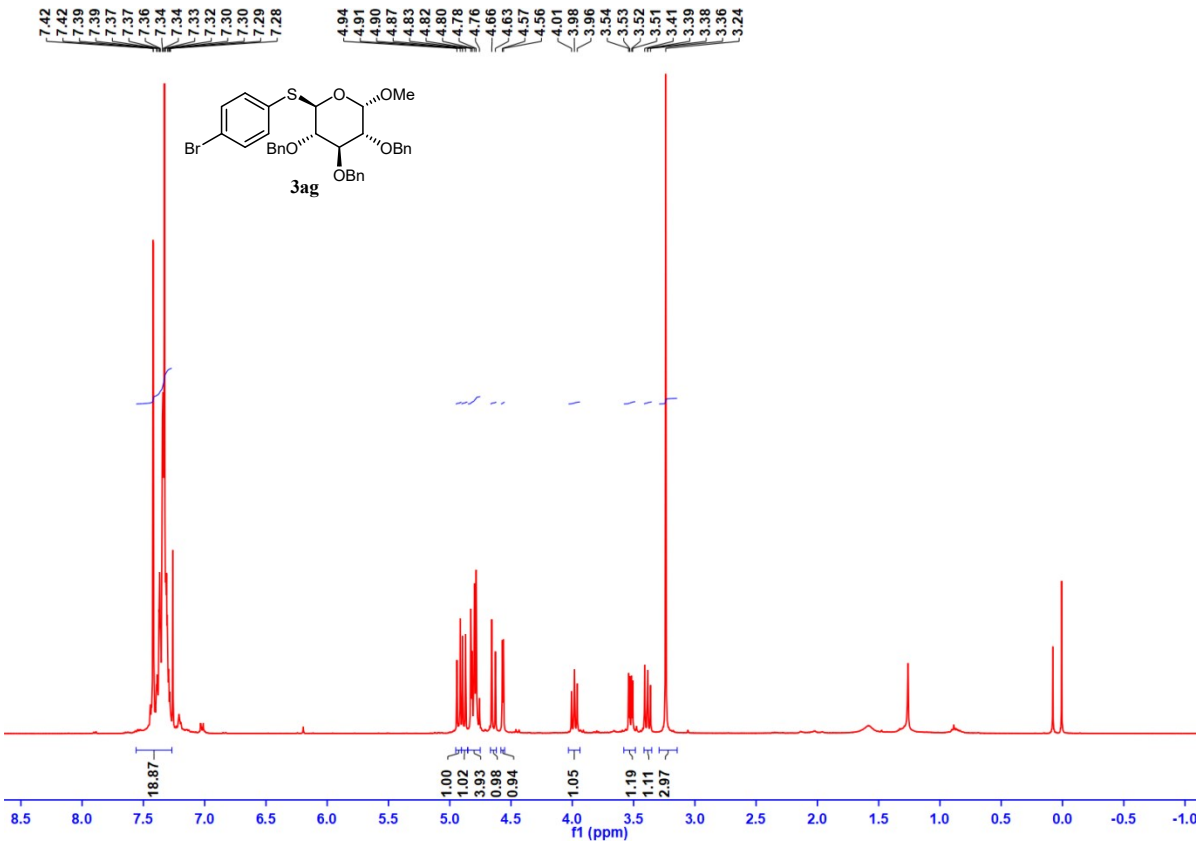
3ae

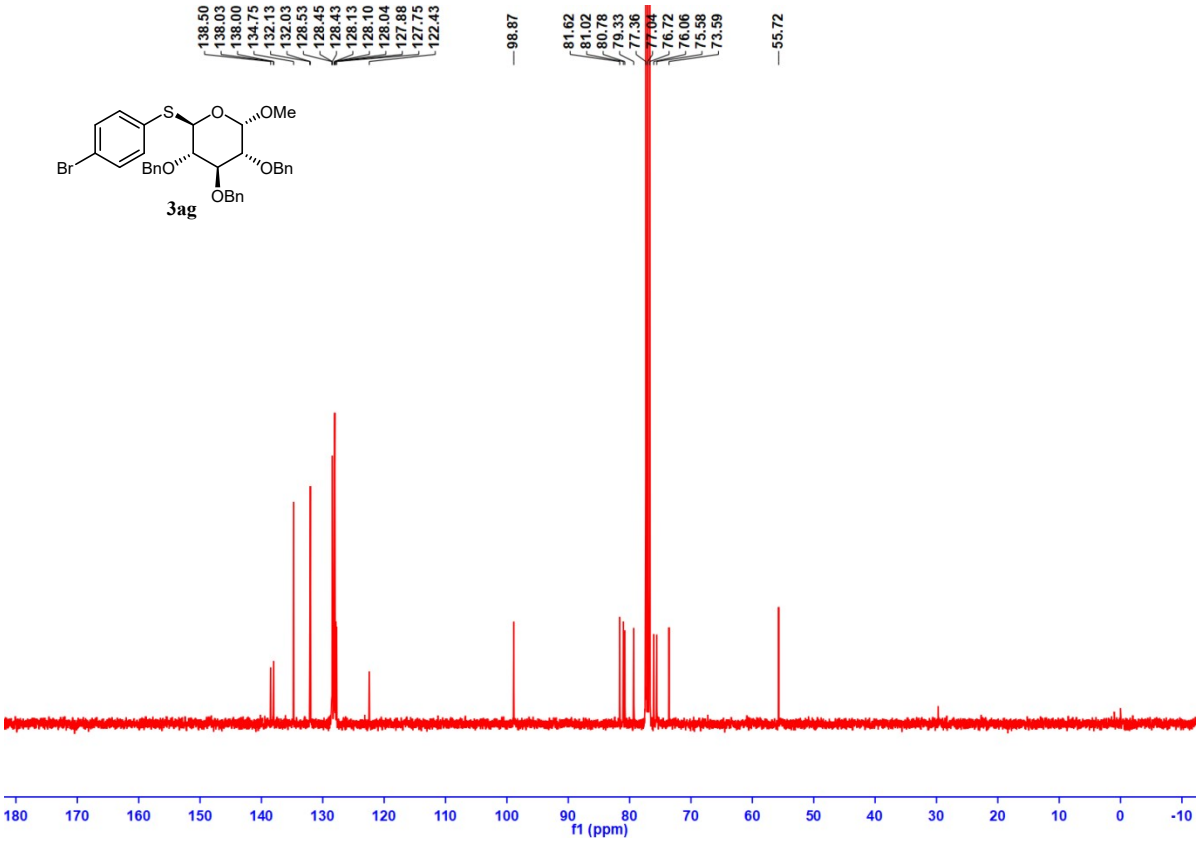

7.46
7.45
7.44
7.44
7.43
7.42
7.41
7.41
7.26
5.31
5.30
4.54
4.53
4.44
4.42
4.24
4.23
4.02
4.00
3.99
3.98
1.52
1.47
1.38
1.36
Br
S
O
3af
3.99
1.00
0.98
1.02
0.99
1.03
3.09
3.08
3.04
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

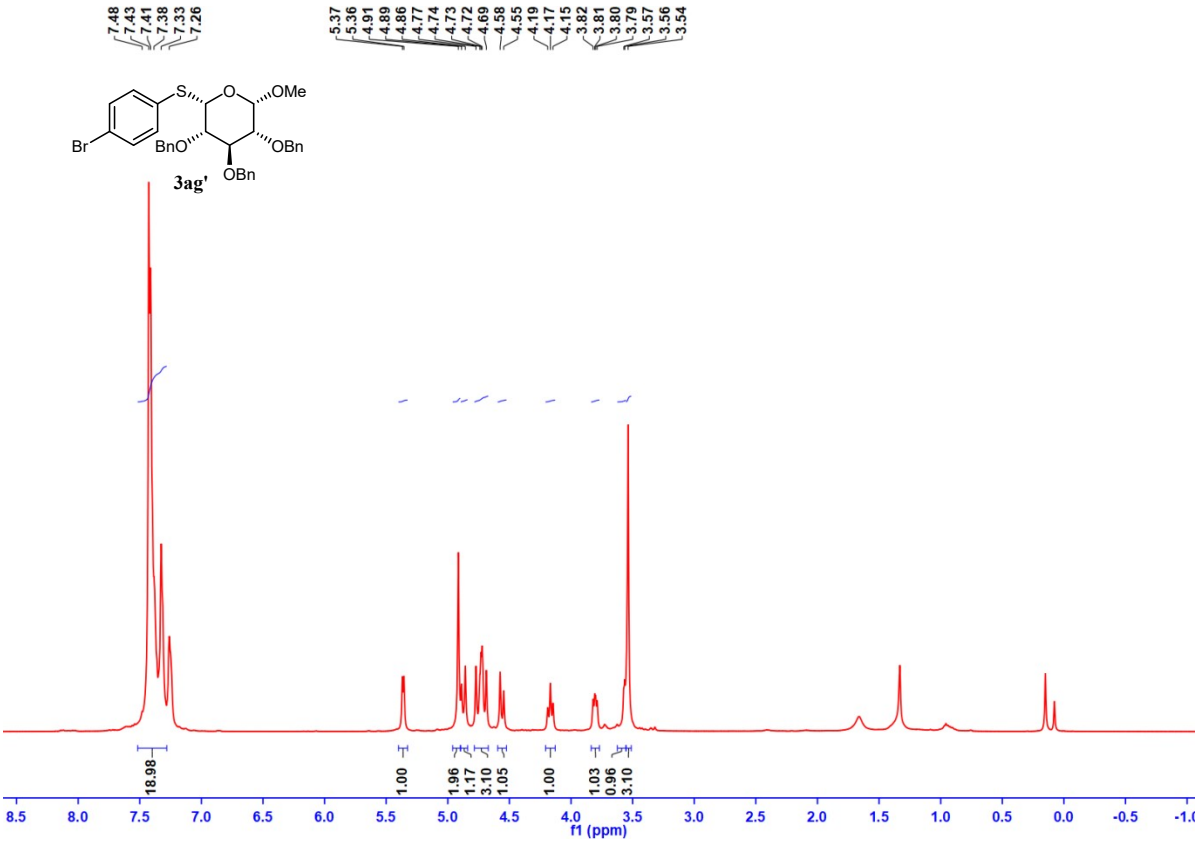

134.84
131.98
131.25
122.53
111.37
109.26
97.20
81.46
77.35
77.03
76.71
75.54
74.45
71.50
28.05
27.80
25.85
25.44
Br
S
O
3af
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

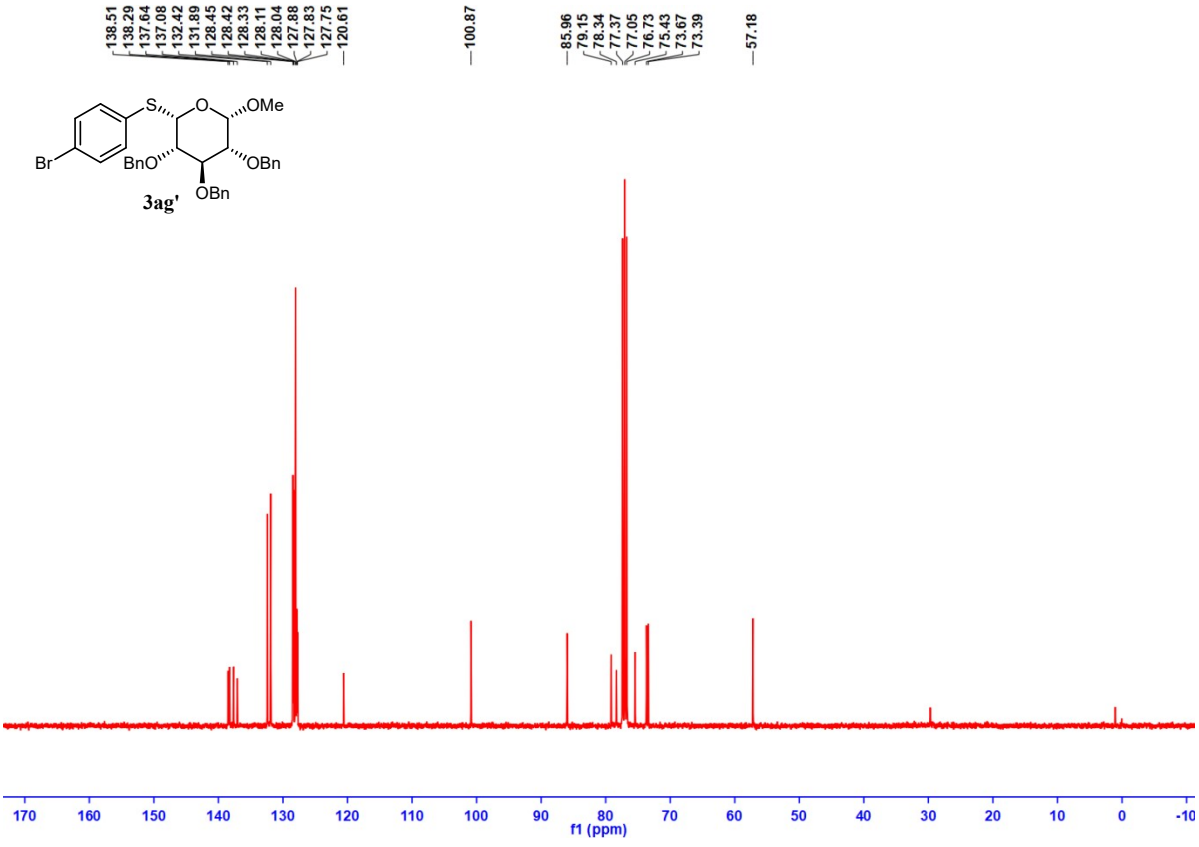

7.40
7.26
5.68
5.67
5.20
5.19
4.69
4.68
4.67
4.66
4.49
4.48
4.47
4.47
4.39
4.39
4.38
4.38
1.55
1.46
1.39
1.35
Br
S
O
3af'
3.96
1.00
1.03
1.01
1.02
0.99
3.17
3.16
3.20
3.21
f1 (ppm)

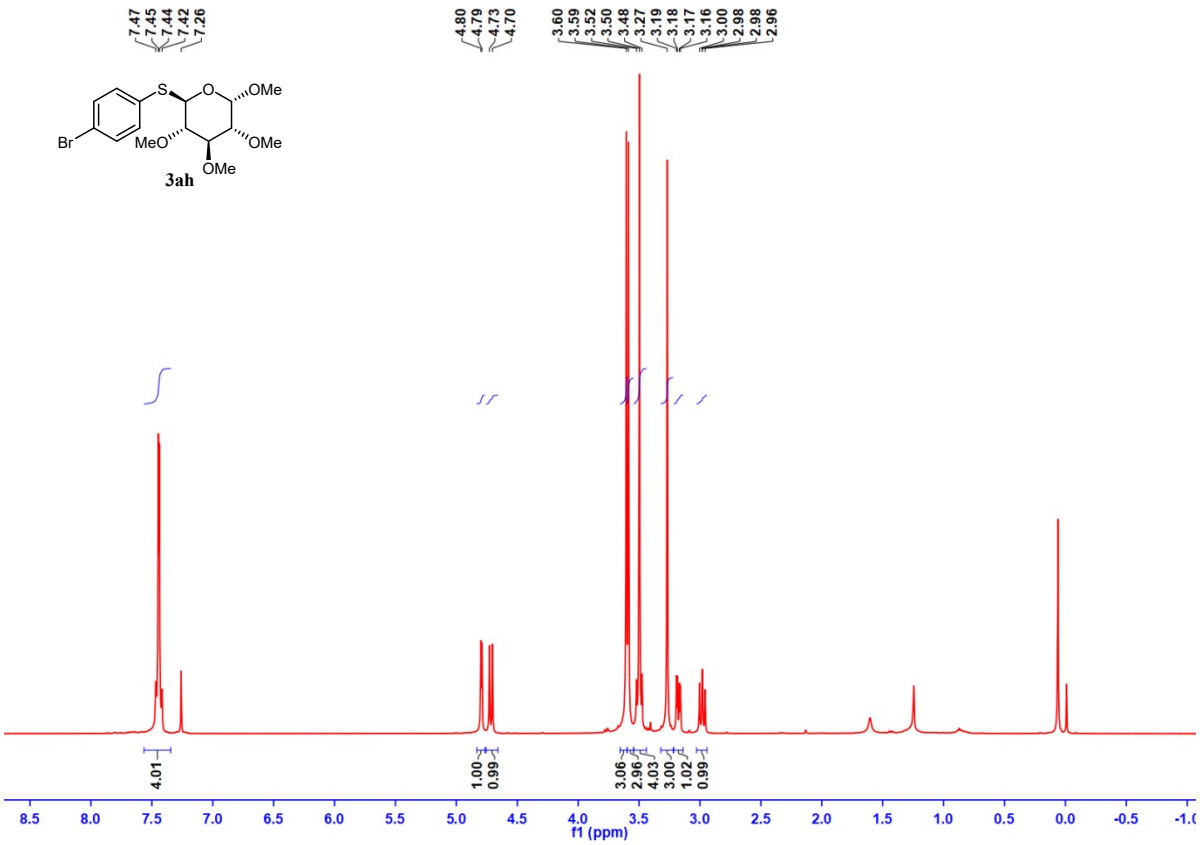

135.35
131.91
130.32
120.43
110.54
109.28
97.53
78.88
77.34
77.02
76.70
73.64
71.70
69.98
26.04
25.77
24.87
24.71
Br
S
O
3af'
f1 (ppm)


7.42
7.42
7.39
7.39
7.37
7.37
7.36
7.34
7.34
7.33
7.32
7.30
7.30
7.29
7.28
4.94
4.91
4.90
4.87
4.83
4.82
4.80
4.78
4.76
4.66
4.63
4.57
4.56
4.01
3.98
3.96
3.54
3.53
3.52
3.51
3.41
3.39
3.38
3.36
3.24
S
O
OMe
Br
BnO
OBn
OBn
3ag
18.87
1.00
1.02
3.93
0.98
0.94
1.05
1.19
1.11
2.97
f1 (ppm)

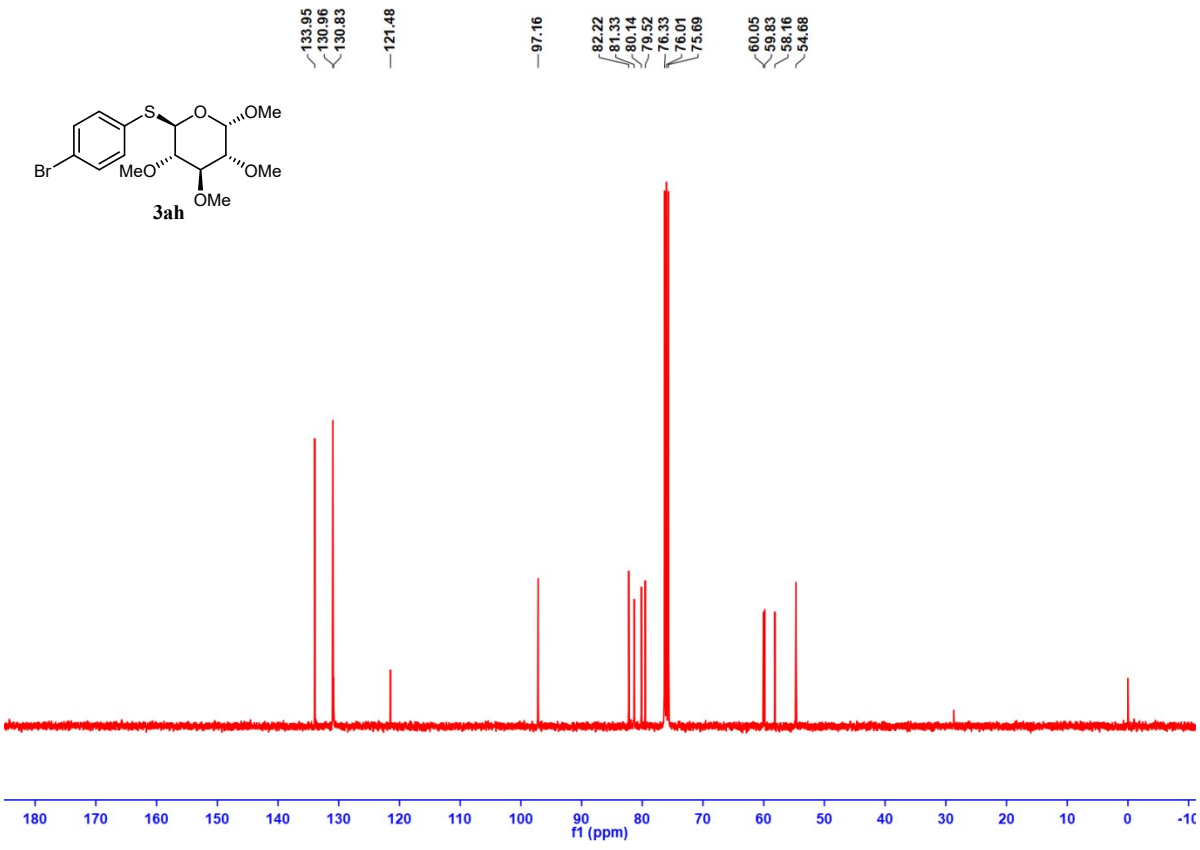

138.50
138.03
138.00
134.75
132.13
132.03
128.53
128.45
128.43
128.13
128.10
128.04
127.88
127.75
122.43
98.87
81.62
81.02
80.78
79.33
77.36
77.04
76.72
76.06
75.58
73.59
55.72
S
O
OMe
Br
BnO
OBn
OBn
3ag
f1 (ppm)


7.48
7.43
7.41
7.38
7.33
7.26
5.37
5.36
4.91
4.89
4.86
4.77
4.74
4.73
4.72
4.69
4.58
4.55
4.19
4.17
4.15
3.82
3.81
3.80
3.79
3.57
3.56
3.54
S
O
OMe
Br
BnO
OBn
OBn
3ag'
18.98
1.00
1.96
1.17
3.10
1.05
1.00
1.03
0.96
3.10
f1 (ppm)

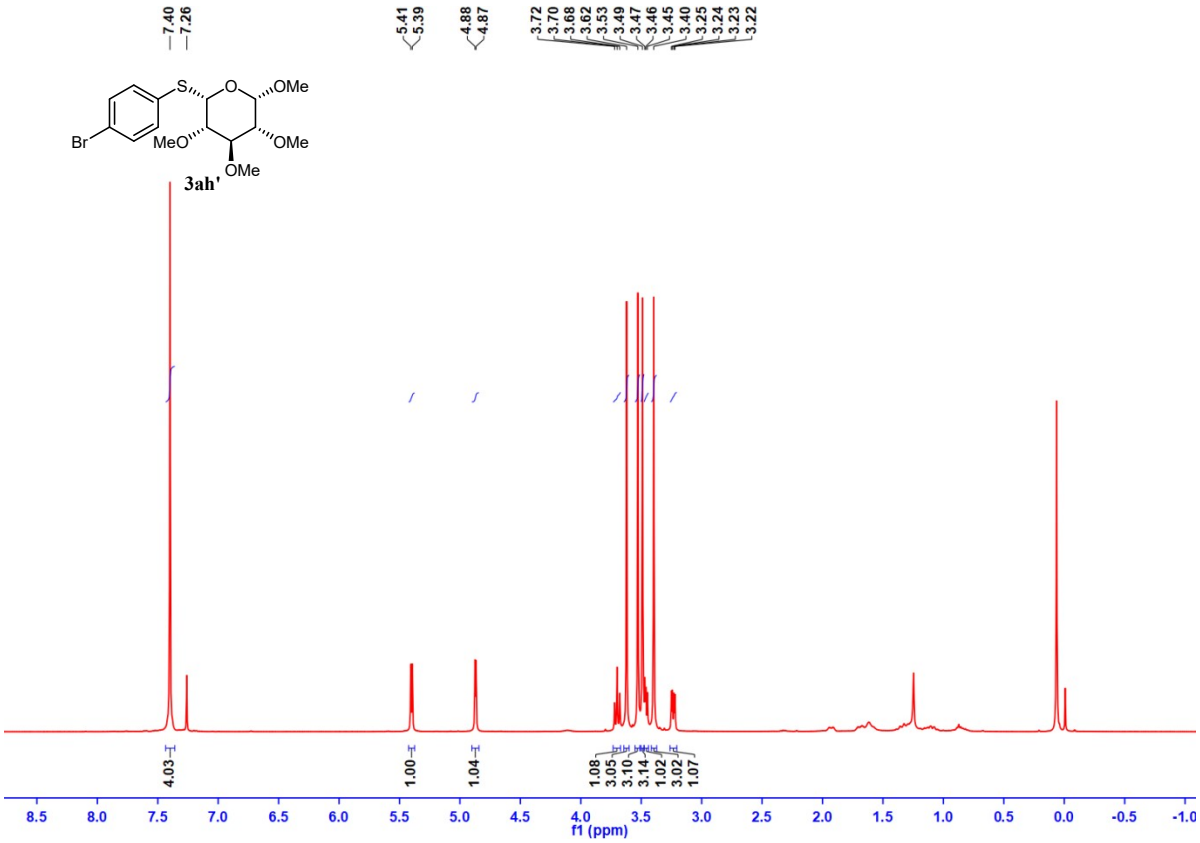

138.51
138.29
137.64
137.08
132.42
131.89
128.45
128.42
128.33
128.11
128.04
127.88
127.83
127.75
120.61
100.87
85.96
79.15
78.34
77.37
77.05
76.73
75.43
73.67
73.39
57.18
S
O
OMe
Br
BnO
OBn
OBn
3ag'
f1 (ppm)

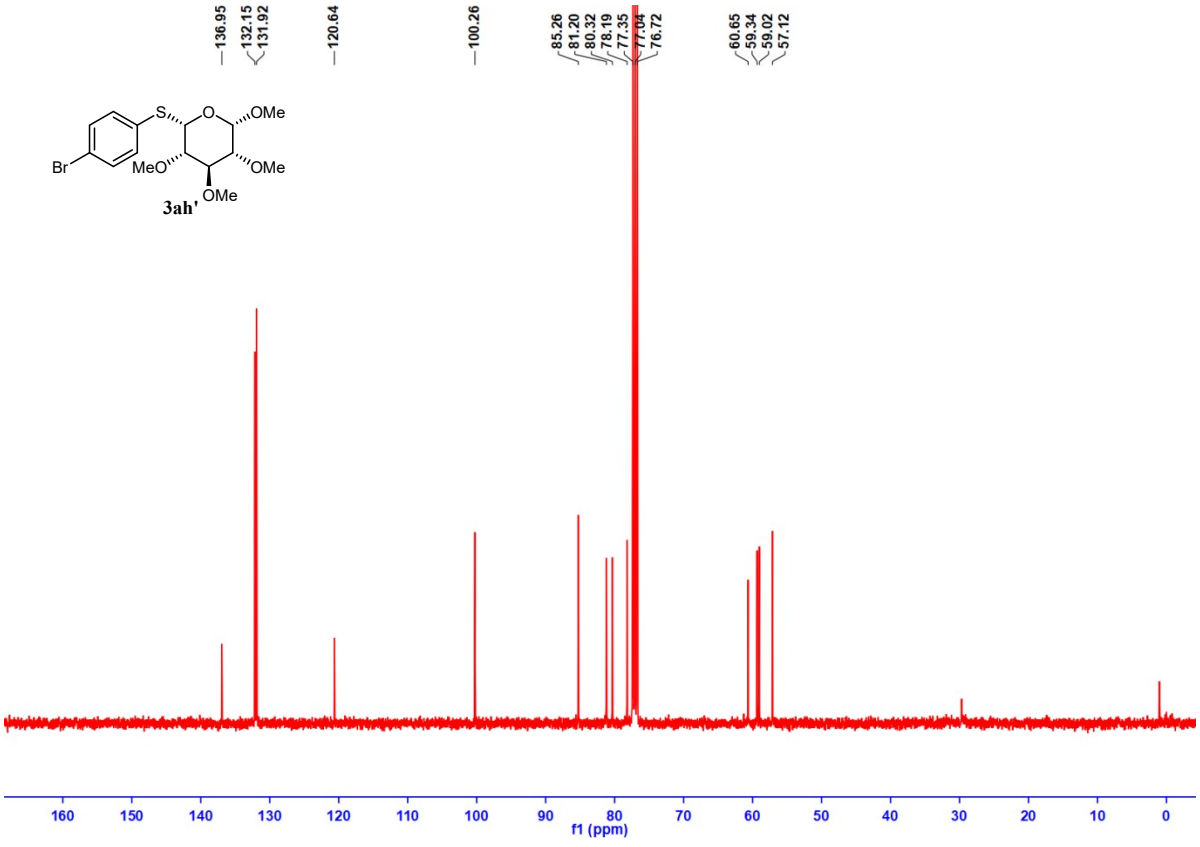

7.47
7.45
7.44
7.42
7.26
4.80
4.79
4.73
4.70
3.60
3.59
3.52
3.50
3.48
3.27
3.19
3.18
3.17
3.16
3.00
2.98
2.98
2.96
S
O
OMe
Br
MeO
OMe
OMe
4.01
1.00
0.99
3.06
2.96
4.03
3.00
1.02
0.99
f1 (ppm)

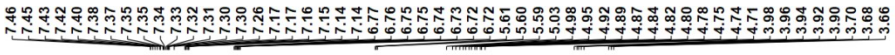
3ah

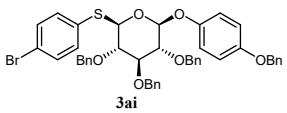

133.95
130.96
130.83
121.48
97.16
82.22
81.33
80.14
79.52
76.33
76.01
75.69
60.05
59.83
58.16
54.68
S
O
OMe
Br
MeO
OMe
OMe
f1 (ppm)

3ah

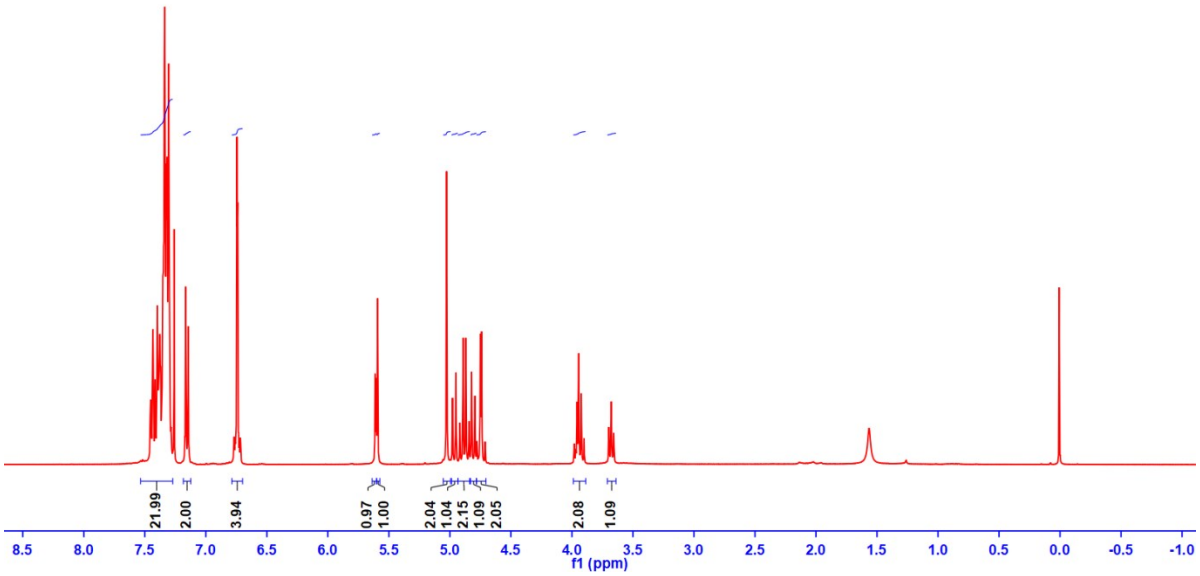

7.40
7.26
5.41
5.39
4.88
4.87
3.72
3.70
3.68
3.62
3.53
3.49
3.47
3.46
3.45
3.40
3.25
3.24
3.23
3.22
S
O
OMe
Br
MeO
OMe
OMe
3ah'
4.03
1.00
1.04
1.08
3.05
3.10
3.14
1.02
3.02
1.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

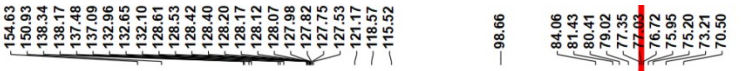

136.95
132.15
131.92
120.64
100.26
85.26
81.20
80.32
78.19
77.35
77.04
76.72
60.65
59.34
59.02
57.12
S
O
OMe
Br
MeO
OMe
OMe
3ah'
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

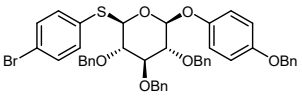

7.46
7.45
7.43
7.42
7.40
7.38
7.37
7.35
7.35
7.34
7.33
7.32
7.31
7.30
7.30
7.26
7.17
7.17
7.16
7.15
7.14
7.14
6.77
6.76
6.75
6.75
6.74
6.73
6.72
6.72
5.61
5.60
5.59
5.03
4.98
4.95
4.92
4.89
4.87
4.84
4.82
4.80
4.78
4.75
4.74
4.71
3.98
3.96
3.94
3.92
3.90
3.70
3.68
3.66


S
O
O
Br
BnO
OBn
OBn
OBn

3ai


21.99
2.00
3.94
0.97
1.00
2.04
1.04
2.15
1.09
2.05
2.08
1.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


154.63
150.93
138.34
138.17
137.48
137.09
132.96
132.65
132.10
128.61
128.53
128.42
128.40
128.20
128.17
128.12
128.07
127.98
127.82
127.75
127.53
121.17
118.57
115.52
98.66
84.06
81.43
80.41
79.02
77.35
77.03
76.72
75.95
75.20
73.21
70.50


S
O
O
Br
BnO
OBn
OBn
OBn

3ai

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)