Supporting Information

Visible-Light-Mediated Synthesis of Non-Anomeric S-Aryl Glycosides *via* Photoactive Electron-Donor-Acceptor Complex

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1.General Information

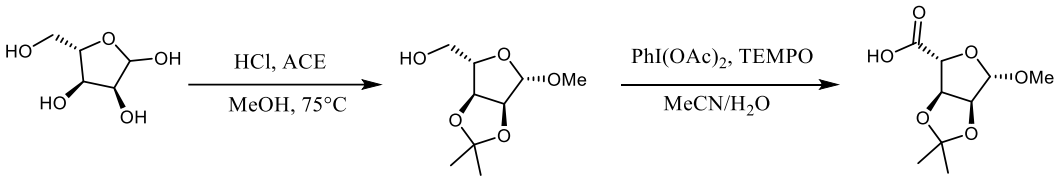
Unless otherwise specified, materials were purchased from commercial suppliers and used without further purification. All manipulations were performed in a dried sealed tube equipped with a magnetic stir bar under an argon atmosphere. Except for the specially mentioned dry solvent, all the solvents were 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 Examples of general procedures for the synthesis of carboxylic acid

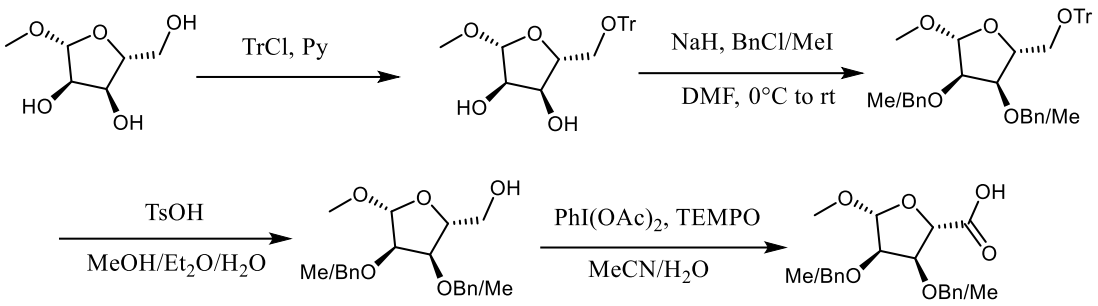


Scheme S1. Procedure for the synthesis of ribose-derived carboxylic acid.

Step 1[1]**:** To a 250 mL round bottom flask was added D-ribose (10 g, 66

mmol, 1.0 equiv.), methanol (40 mL), and acetone (40 mL). Next, concentrated HCl (1.0 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 (50 mL×2), washed by brine (50 mL×2) , 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 g, 80% yield).

Step 2[2]**:** The acid was prepared according to the reported paper. TEMPO (0.63 g, 4.0 mmol, 0.20 equiv.) and $PhI(OAc)_2$ (19 g, 60 mmol, 3.0 equiv.) were added to a solution of alcohol obtained from above step (4.1 g, 20 mmol, 1.0 equiv.) in MeCN/H_2O (50 mL/50 mL, 0.20 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5.0 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2 (30 mL×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 (3.8 g, 89% yield).



Scheme S2. Procedure for the synthesis of Bn/Me-protected ribose-derived carboxylic acid.

Step 1[3]**:** To a solution of methyl beta D-ribofuranoside (5.0 g, 30 mmol, 1.0 equiv) in pyridine (60 mL, 0.50 M) was added trityl chloride (9.2 g, 33 mmol, 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 (90 mL) and washed with 1.0 M aqueous $CuSO_4$ solution (50 mL×3), brine (50 mL×2), 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 (12g, 86% yield).

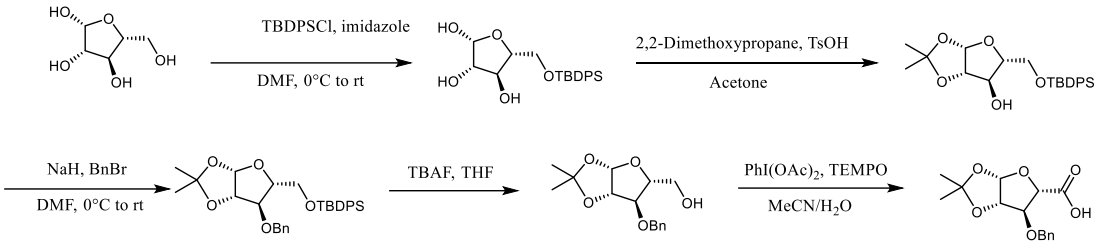
Step 2[4]**:** The obtained compound (5.0 g, 12 mmol, 1.0 equiv) from above step was dissolved in DMF (60 mL, 0.20 M) and cooled to 0 °C. Sodium hydride (60% in mineral oil, 1.9 g, 48 mmol, 4.0 equiv) was added portion-wise. Then, BnCl/MeI (4.3 mL/2.3 mL, 36mmol, 3.0 equiv) was added dropwise. The mixture 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 (50 mL) and then washed with water (50 mL × 2). The aqueous phase was extracted with EtOAc (30 mL), the combined organic phases were washed with brine (50 mL), 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 (5.6 g, 80% yield).

Step 3[2]**:** The obtained compound (take the Bn-protected as an example, 5.0 g, 8.5 mmol, 1.0 equiv) from above step was dissolved in MeOH/Et_2O/H_2O (42 mL/4.2 mL/0.42 mL, 0.20 M) followed by addition of TsOH (0.73 g, 4.3 mmol, 0.50 equiv). After being stirred for 20 min at room temperature, the resultant mixture was extracted with EtOAc (30 mL × 3). 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 (2.3 g, 80% yield).

Step 4[2]**:** The acid was prepared according to the reported paper. TEMPO (0.18 g， 1.2 mmol, 0.20 equiv.) and $PhI(OAc)_2$ (5.6 g, 17 mmol, 3.0 equiv.) were added to a solution of alcohol obtained from above step (take the Bn-protected as an example, 2.0 g， 5.8 mmol， 1.0 equiv.) in MeCN/H_2O (15 mL/15 mL, 0.20 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated

aqueous $Na_2S_2O_3$ (5.0 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2 (30 mL×3). 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 (1.6 g, 78% yield).



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

Step 1[5]**:** To a solution of methyl beta D-arabinose (8.0 g, 53 mmol, 1.0 equiv) in DMF(0.27 L, 0.20 M) was added imidazole (5.4 g, 80 mmol, 1.5 equiv) and cooled to 0 °C.Then TBDPSCl (21 mL,80 mmol, 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 (90 mL), and then washed with water (50 mL×2). The aqueous phase was extracted with EtOAc (30 mL), the combined organic phases were washed with brine (50 mL), 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 (17 g, 83% yield).

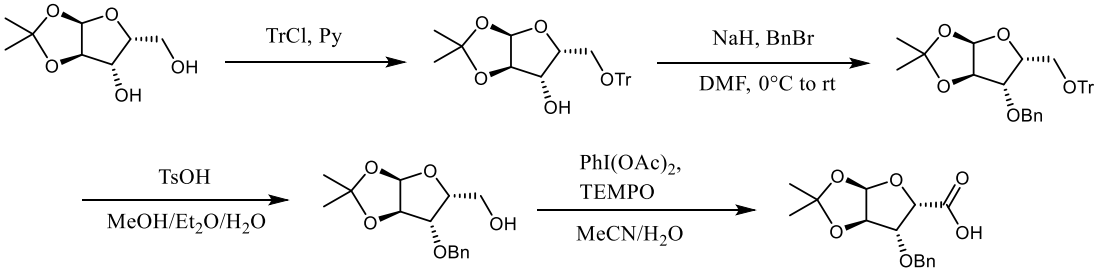
Step 2[6]**:** The obtained compound (11 g, 28 mmol, 1.0 equiv) from above step was dissolved in acetone (30 mL) and 2, 2-dimethoxypropane (10 mL) and *p*-toluenesulfonic acid (0.20 g) was added. The reaction was neutralized by triethylamine and concentrated after stired 30 min at room temperature. The solvents were evaporated in vacuo, purification by flash column chromatography (cyclohexane / EtOAc). yielded product as a colorless oil (10 g, 84% yield).

Step 3[4]**:** The obtained compound (10 g, 23 mmol, 1.0 equiv) from above step was dissolved in DMF (0.12 L, 0.20 M) and cooled to 0 °C. Sodium hydride (60% in mineral oil, 1.8 g, 46 mmol, 2.0 equiv) was added portion wise. Then, BnCl (4.1 mL, 35 mmol, 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 (90 mL), and then washed with water (50 mL × 2). The aqueous phase was extracted with EtOAc (30 mL), 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 (10 g, 87% yield).

Step 4[5]**:** The obtained compound (10 g, 19 mmol, 1.0 equiv) from above

step was dissolved in anhydrous THF (40 mL, 0.50 M), was reacted with TBAF (1.0 M in THF, 23 mL,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 (4.2 g, 79% yield).

Step 5[2]**:** The acid was prepared according to the reported paper. TEMPO (0.17 g, 0.20 equiv.) and $PhI(OAc)_2$ (5.2 g, 3.0 equiv.) were added to a solution of alcohol (1.5 g, 5.4 mmol, 1.0 equiv.) obtained from above step (1.0 equiv.) in MeCN/H_2O (15 mL/15 mL, 0.20 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5.0 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2 (30 mL × 3). 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 (white solid, 1.2 g).



Scheme S4. Procedure for the synthesis of xylose-derived carboxylic acid.

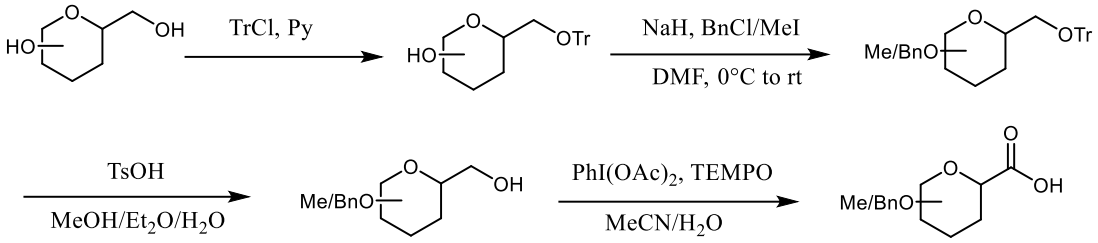
Step 1[3]**:** To a solution of 1,2-O-Isopropylidene-alpha-D-xylofuranose (5.0 g, 26 mmol, 1.0 equiv) in pyridine (52 mL,0.50 M) was added trityl chloride (8.0 g, 29 mmol, 1.1 equiv) and the reaction mixture was stirred at room temperature overnight. The solvent was removed in vacuo and the residue was coevaporated with toluene, dissolve in EtOAc (90 mL) and washed with 1 M aqueous $CuSO_4$ solution (50 mL×3), brine (50 mL ×2), 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 (8.7 g, 83% yield).

Step 2[4]**:** The obtained compound (6.0 g, 14 mmol, 1.0 equiv) from above step was dissolved in DMF (70 mL, 0.2 M) and cooled to 0 °C. Sodium hydride (60% in mineral oil, 1.1 g, 28 mmol, 2.0 equiv) was added portion-wise. Then, BnCl (2.5 mL, 21 mmol, 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 (90 mL), and then washed with water (50 mL×2). The aqueous phase was extracted with EtOAc (30 mL), the combined organic phases were washed with brine (50 mL), 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 (5.9 g, 81% yield).

Step 3[2]**:** The obtained compound (5.4 g, 10 mmol, 1.0 equiv) from above step was dissolved in MeOH/Et_2O/H_2O (50 mL/5.0 mL/0.50 mL,0.20 M) followed by addition of TsOH (0.86 g, 5.0 mmol, 0.50 equiv). After being stirred for 20 min at room temperature, the resultant mixture was extracted with EtOAc (30 mL×3). 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 (2.3g. 85%).

Step 4[2]**:** The acid was prepared according to the reported paper. TEMPO (0.17 g, 1.1 mmol, 0.20 equiv.) and $PhI(OAc)_2$ (5.2 g, 16 mmol, 3.0 equiv.) were added to a solution of alcohol (1.5 g, 5.4 mmol, 1.0 equiv.)obtained from above step in MeCN/H_2O (15 mL/15 mL, 0.20 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5.0 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2 (30 mL×3). 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 (1.2 g).



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

Step 1[3]**:**To a solution of methyl-α-D-glucopyranoside (10 g, 51 mmol, 1.0 equiv) in pyridine (0.10 L, 0.50 M) was added trityl chloride (16 g, 56 mmol, 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 (90 mL) and washed with 1 M aqueous $CuSO_4$ solution (50 mL×3), brine (50 mL×2), 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 (17 g, 80% yield).

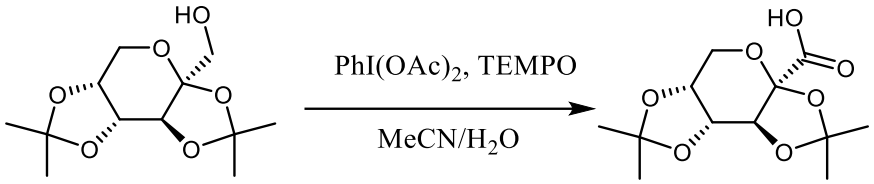
Step.2[1,4]**:** The obtained compound (8.0 g, 18 mmol, 1.0 equiv.) from above step was dissolved in DMF (90 mL, 0.20 M) and cooled to 0 °C. Sodium hydride (60% in mineral oil, 4.3 g, 0.11 mol 6.0 equiv) was added portion-wise. Then, BnCl (9.6 mL, 81 mmol, 4.5 equiv) /MeI was added dropwise. The mixture 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 (90

mL), and then washed with water (50 mL×2). The aqueous phase was extracted with EtOAc (30mL), the combined organic phases were washed with brine (50mL), 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 (9.9 g, 78% yield).

Step.3[2]**:** The obtained compound (8.0 g, 11 mmol, 1.0 equiv.) from above step was dissolved in MeOH/Et_2O/H_2O (50 mL/5.0 mL/0.50 mL, 0.20 M) followed by addition of TsOH (0.95 g, 5.5 mmol, 0.50 equiv). After being stirred for 20 min at room temperature, the resultant mixture was extracted with EtOAc (30 mL×3). 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 (4.2 g, 82% yield).

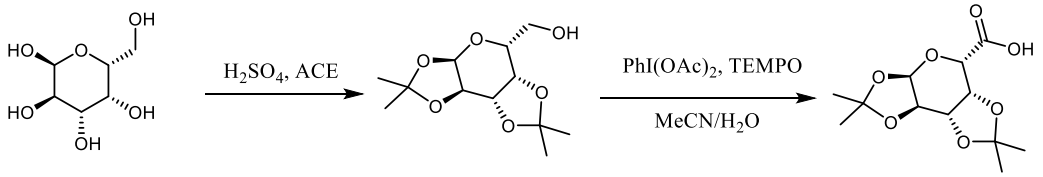
Step.4[2]**:** The acid was prepared according to the reported paper. TEMPO (0.20 g, 1.3 mmol, 0.20 equiv.) and $PhI(OAc)_2$ (6.3 g, 20 mmol, 3.0 equiv.) were added to a solution of alcohol (3.0g 6.5 mmol, 1.0 equiv.) obtained from above step in MeCN/H_2O (16 mL/16 mL, 0.20 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5.0 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2 (30 mL×3). 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 (2.4 g, 80% yield).



Scheme S6. 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 (3.0 g, 12 mmol, 1.0 equiv) was treated with TEMPO (0.36 g, 2.3 mmol, 0.20 equiv.) and $PhI(OAc)_2$ (11 g, 35 mmol, 3.0 equiv.) in $MeCN/H_2O$ (30 mL/30 mL, 0.20 M) at room temperature for 9 h, and then saturated aqueous $Na_2S_2O_3$ (5.0 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2 (30 mL × 3). 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. Procedure for the synthesis of galactose-derived carboxylic

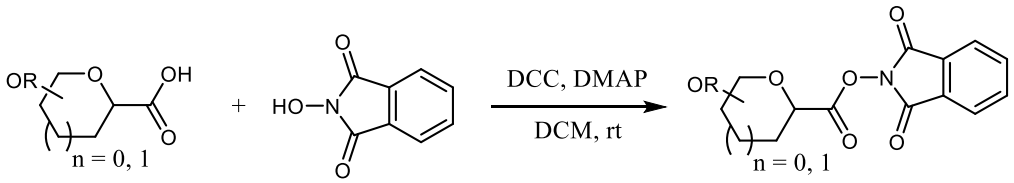
acid.

((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 round bottom flask was added D-galactose (7.0 g, 39 mmol, 1.0 equiv.), acetone (0.25 L). Next, concentrated H_2SO_4 (7.7 mL) was added at 0 °C. The reaction mixtures were stirred at room temperature for 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%).

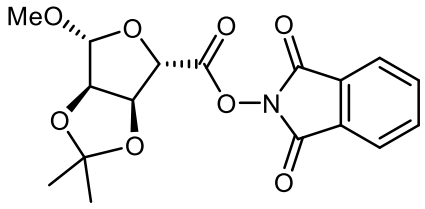
(3aR,5S,5aR,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-carboxylic acid[2]**:** The acid was prepared according to the reported paper. TEMPO (0.84 g, 5.4 mmol, 0.20 equiv.) and $PhI(OAc)_2$ (26 g, 81 mmol, 3.0 equiv.) were added to a solution of alcohol (7.0 g, 27 mmol, 1.0 equiv.) obtained from above step in $MeCN/H_2O$ (67 mL/67 mL, 0.20 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5.0 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2 (30 mL×3). 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 (5.1 g, 87% yield).

2.2 Synthetic procedure of N-hydroxyphthalimide esters

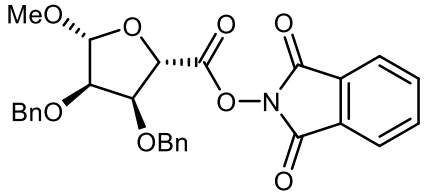


A round-bottom flask or culture tube was charged with carboxylic acid derived from sugar (1.0 equiv), N-hydroxyphthalimide (1.1 equiv) and 4-dimethylaminopyridine (0.050 equiv). Dichloromethane was added (0.10- 0.20 M), and the mixture was stirred vigorously. Dicyclohexylcarbodiimide (DCC, 1.1 equiv) 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.

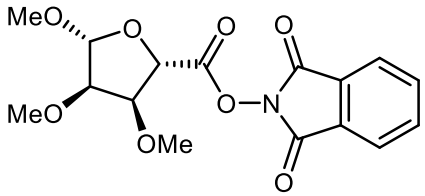


1,3-dioxoisoindolin-2-yl (3aS,4S,6R,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole-4-carboxylate (1a): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* =

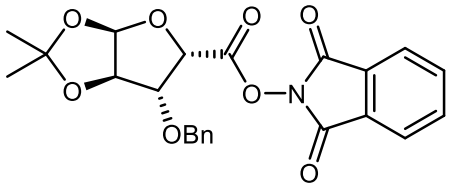
5.5, 3.1 Hz, 2H), 5.36 (d, *J* = 5.8 Hz, 1H), 5.14 (s, 1H), 5.00 (s, 1H), 4.66 (d, *J* = 5.8 Hz, 1H), 3.50 (s, 3H), 1.52 (s, 3H), 1.35 (s, 3H). The compound was identified by spectral comparison with literature data.[4]



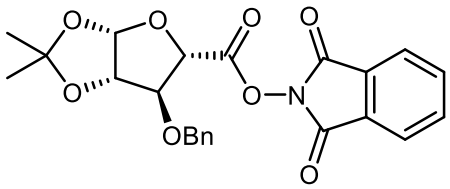
1,3-dioxoisoindolin-2-yl (2S,3S,4R,5R)-3,4-bis(benzyloxy)-5-methoxytetrahydrofuran-2-carboxylate (1b): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.42 – 7.28 (m, 10H), 5.00 (d, *J* = 6.6 Hz, 2H), 4.79 (d, *J* = 11.7 Hz, 1H), 4.71 – 4.60 (m, 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]

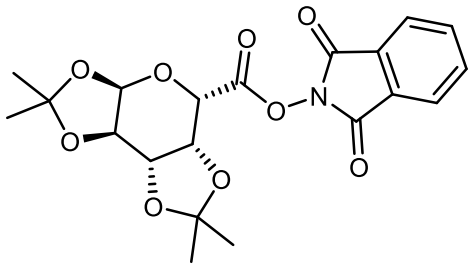


1,3-dioxoisoindolin-2-yl (3aR,5S,6R,6aR)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole-5-carboxylate (1d): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.46 – 7.27 (m, 5H), 6.11 (d, *J* = 3.4 Hz, 1H), 5.20 (d, *J* = 3.5 Hz, 1H), 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]

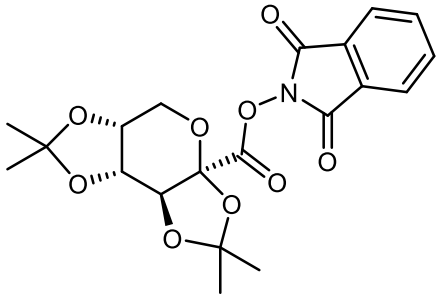


1,3-dioxoisoindolin-2-yl (3aS,5S,6S,6aS)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole-5-carboxylate (1e): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.39 – 7.28 (m, 5H), 6.07 (d, *J* = 3.4 Hz, 1H), 5.07 (d, *J* = 0.8 Hz, 1H), 4.78

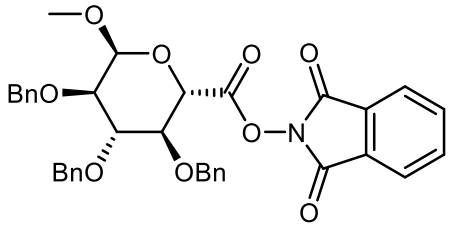
– 4.72 (m, 2H), 4.71 – 4.65 (m, 2H), 1.50 (s, 3H), 1.33 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 166.3, 161.4, 136.5, 134.9, 128.8, 128.7, 128.3, 128.0, 124.1, 113.8, 107.0, 84.4, 82.9, 80.7, 72.5, 25.9, 25.7. HRMS (ESI) m/z $[M + Na]^+$ calculated for 462.1159, found 462.1161.



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]

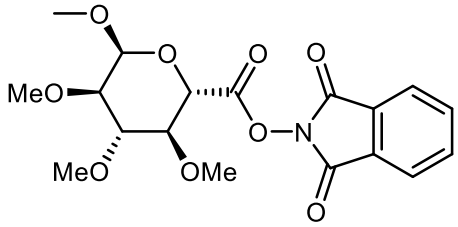


1,3-dioxoisoindolin-2-yl (3aR,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]py ran-3a-carboxylate (1g): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.88 (d, *J* = 2.5 Hz, 1H), 4.69 (dd, *J* = 7.9, 2.5 Hz, 1H), 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]

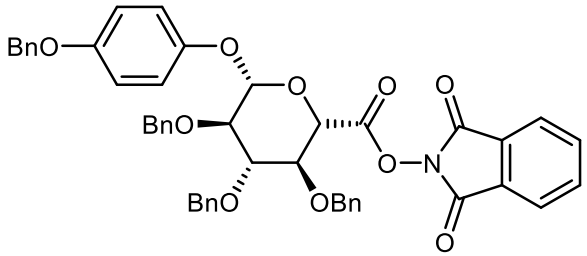


1,3-dioxoisoindolin-2-yl (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-carboxylate (1h): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.43 – 7.26 (m, 15H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.93 (d, *J* = 10.1 Hz, 1H), 4.86 (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]



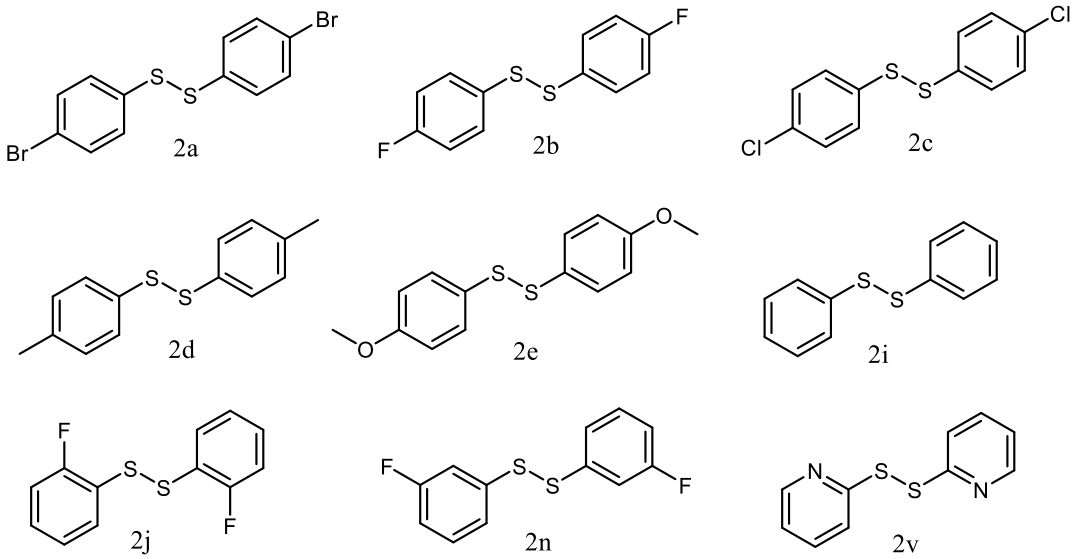
1,3-dioxoisoindolin-2-yl (2S,3S,4S,5R,6S)-3,4,5,6-tetramethoxytetrahydro-2H-pyran-2-carboxylate (1i): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.95 (d, *J* = 3.5 Hz, 1H), 4.42 (d, *J* = 9.9 Hz, 1H), 3.65 (d, *J* = 1.7 Hz, 6H), 3.57 (d, *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]



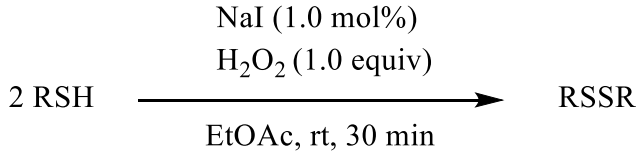
1,3-dioxoisoindolin-2-yl (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-(4-(benzyloxy)phenoxy)tetrahydro-2H-pyran-2-carboxylate (1j): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.48 – 7.27 (m, 20H), 7.13 – 7.06 (m, 2H), 6.98 – 6.92 (m, 2H), 5.08 – 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 disulfide

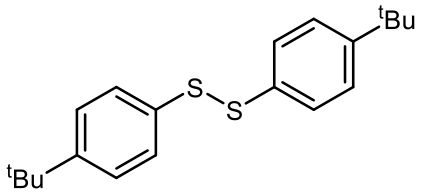
Disulfides 2a, 2b, 2c, 2d, 2e, 2i, 2j, 2n and 2v were purchased from commercial sources.



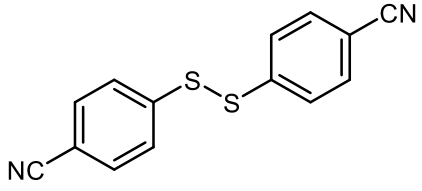
The rest of the diaryl disulfides were synthesized following the procedure reported by M. Kirihara and co-workers[8].



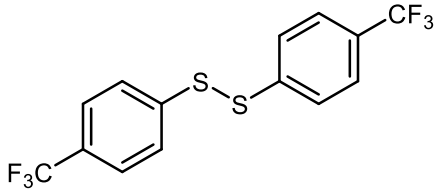
To a stirred solution of a thiol (2.0 mmol) in EtOAc (6.0 mL) were added NaI (3.0 mg, 0.020 mmol, 0.010 equiv) and 30% aqueous H_2O_2 solution (0.23 mL, 2.0 mmol, 1.0 equiv), and the mixture was stirred at room temperature for 30 min. Saturated aqueous $Na_2S_2O_3$ solution (15 mL) was added, and the resulting mixture was extracted with EtOAc (3 × 15 mL). The combined organic phase was washed with brine (15 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo. The crude mixture was purified by silica gel flash column chromatography (Hexane) to acquire the desired disulfide .



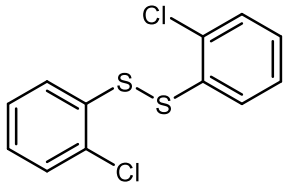
1,2-bis(4-(tert-butyl)phenyl)disulfane (2f): Yellow solid; 0.31 g; 95%. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.47– 7. 42 (m, 4H), 7.36 – 7.31 (m, 4H), 1.30 (s, 18H). The compound was identified by spectral comparison with literature data.[9]



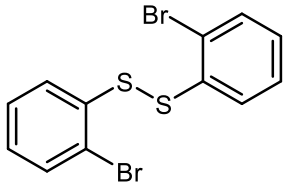
4,4'-disulfanediyldibenzonitrile (2g): White solid**;** 024 g; 90%. **^{1}H-NMR (600 MHz, Chloroform-*d*)** δ 7.60 (d, *J* = 6.8 Hz, 4H), 7.55 (d, *J* = 6.5 Hz, 4H). The compound was identified by spectral comparison with literature data.[9]



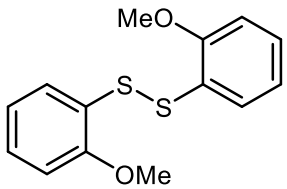
1,2-bis(4-(trifluoromethyl)phenyl)disulfane (2h): White solid; 0.32 g; 91%. **^{1}H-NMR (600 MHz, Chloroform-*d*)** δ 7.60 - 7.55 (m, 8H). The compound was identified by spectral comparison with literature data.[10]



1,2-bis(2-chlorophenyl)disulfane (2k): White solid; 0.27 g; 94%. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.56 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.37 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.23 (td, *J* = 7.7, 1.5 Hz, 2H), 7.16 (td, *J* = 7.6, 1.6 Hz, 2H). The compound was identified by spectral comparison with literature data.[11]

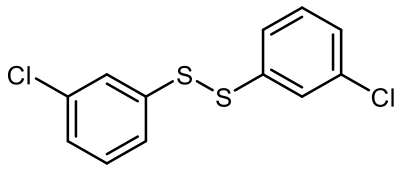


1,2-bis(2-bromophenyl)disulfane (2l): White solid; 0.33 g; 88%. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.54 (dd, *J* = 3.1, 1.3 Hz, 2H), 7.52 (dd, *J* = 3.2, 1.3 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.08 (td, *J* = 7.7, 1.4 Hz, 2H). The compound was identified by spectral comparison with literature data.[11]

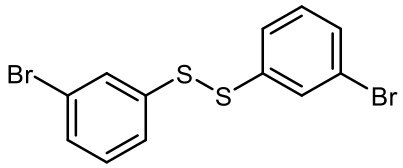


1,2-bis(2-methoxyphenyl)disulfane (2m): Pale yellow solid; 0.25 g; 90%. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.53 (d, *J* = 8.7 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 2H), 6.97 – 6.80 (m, 4H), 3.90 (s, 6H).. The compound was identified by spectral comparison with

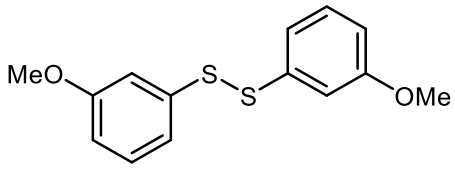
literature data.[11]



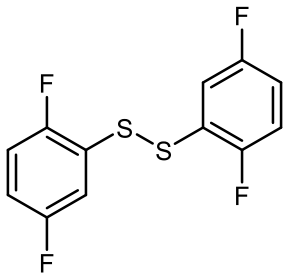
1,2-bis(3-chlorophenyl)disulfane (2o): Pale yellow oil; 0.27 g; 95%. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.48 – 7.47 (m, 2H), 7.35 (dt, *J* = 7.4, 1.7 Hz, 2H), 7.27 – 7.18 (m, 4H). The compound was identified by spectral comparison with literature data.[12]



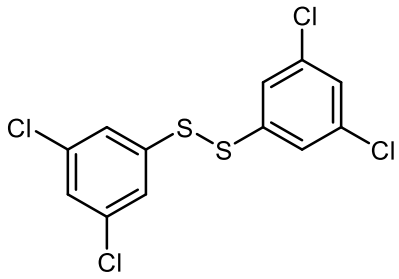
1,2-bis(3-bromophenyl)disulfane (2p): Pale yellow oil; 0.34 g; 93%. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.63 (t, *J* = 1.8 Hz, 2H), 7.41 – 7.36 (m, 4H), 7.18 (t, *J* = 7.9 Hz, 2H). The compound was identified by spectral comparison with literature data.[11]



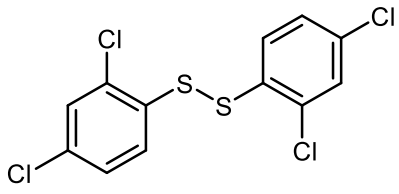
1,2-bis(3-methoxyphenyl)disulfane (2q): Yellow oil**;** 0.25 g; 92%. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.21 (t, *J* = 8.1 Hz, 2H), 7.11 – 7.05 (m, 4H), 6.78 – 6.75 (m, 2H), 3.77 (s, 6H). The compound was identified by spectral comparison with literature data.[12]



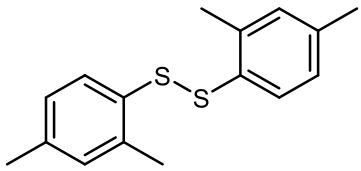
1,2-bis(2,5-difluorophenyl)disulfane (2r): Pale yellow oil; 0.25 g; 86%. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.31 (ddd, *J* = 8.4, 5.8, 3.1 Hz, 2H), 7.04 (td, *J* = 8.8, 4.5 Hz, 2H), 6.94 (dddd, *J* = 9.0, 7.1, 3.9, 3.1 Hz, 2H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 158.9 (dd, *J* = 245.0, 4.0 Hz), 156.3 (dd, *J* = 242.0, 4.0 Hz), 124.8 (dd, *J* = 19.0, 8.0 Hz), 116.8 (dd, *J* = 24.0, 9.0 Hz), 116.5 (dd, *J* = 27.0, 4.0 Hz), 116.1 (dd, *J* = 24.0, 8.0 Hz). **^{19}F-NMR (376 MHz, Chloroform-*d*)** δ -116.78 (dtd, *J* = 15.8, 7.7, 4.4 Hz), -116.89 – -117.01 (m). HRMS (EI) m/z $[M + Na]^+$ calculated for 312.9739, found 312.9737



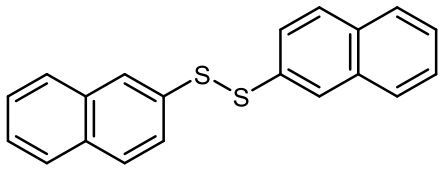
1,2-bis(3,5-dichlorophenyl)disulfane (2s): Pale yellow solid; 0.33 g; 95%. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.34 (d, *J* = 1.8 Hz, 4H), 7.24 (t, *J* = 1.8 Hz, 2H). The compound was identified by spectral comparison with literature data.[13]



1,2-bis(2,4-dichlorophenyl)disulfane (2t): White solid; 0.33 g; 93%. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.46 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 2.1 Hz, 2H), 7.21 (dd, *J* = 8.6, 2.2 Hz, 2H).. The compound was identified by spectral comparison with literature data.[14]

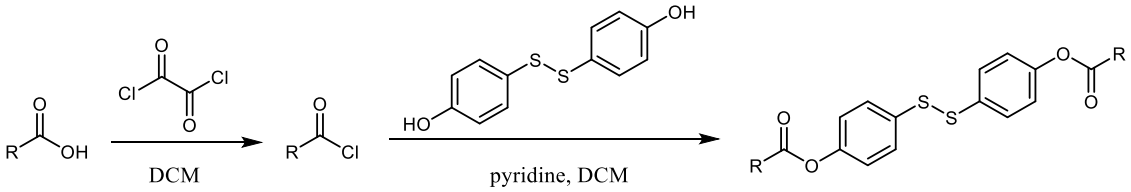


1,2-bis(2,4-dimethylphenyl)disulfane (2u): Pale yellow oil; 0.24 g; 0.88%. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.38 (d, *J* = 7.9 Hz, 2H), 6.99 (s, 2H), 6.93 (d, *J* = 7.9 Hz, 2H), 2.37 (s, 6H), 2.29 (s, 6H). The compound was identified by spectral comparison with literature data.[15]



1,2-di(naphthalen-2-yl)disulfane (2w): Yellow solid**;** 0.29g; 93%. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.99 (d, *J* = 1.6 Hz, 2H), 7.79 (dd, *J* = 9.0, 2.7 Hz, 4H), 7.76 – 7.71 (m, 2H), 7.63 (dd, *J* = 8.7, 1.9 Hz, 2H), 7.50 – 7.42 (m, 4H). The compound was identified by spectral comparison with literature data.[9]

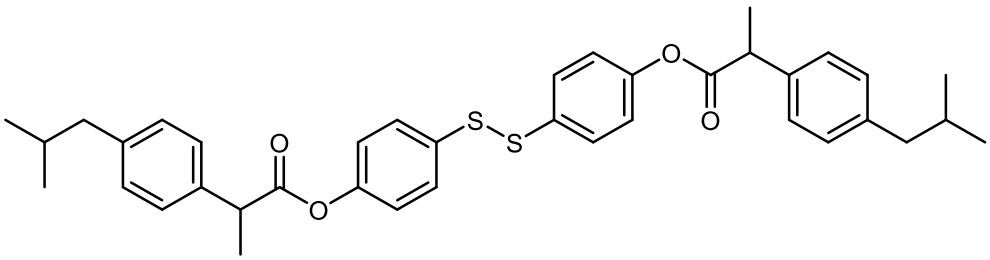
The disulfides 2x, 2y, 2z were synthesized following the procedure shown in the following figure.



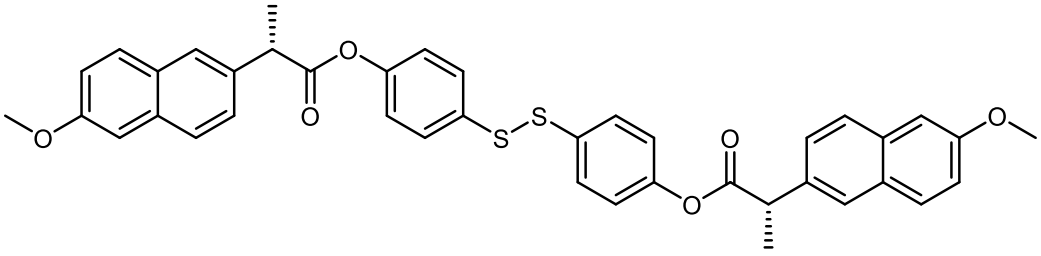
Sept 1: To a solution of ibuprofen (dehydrocholic acid, naproxen)

(1.0 equiv) in DCM (0.50 M) was added oxalyl chloride (3.0 equiv) and the reaction mixture was stirred at room temperature for 6 h. The solvent was removed in vacuo to get the crude product.

Sept 2: To a solution of 4,4'-dithiodiphenol (1.0 equiv) in DCM (0.20M) was added pyridine (2.0 equiv) and cooled to 0 °C.Then the obtained compound from above step dissolved in DCM (0.20 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 90% yield.

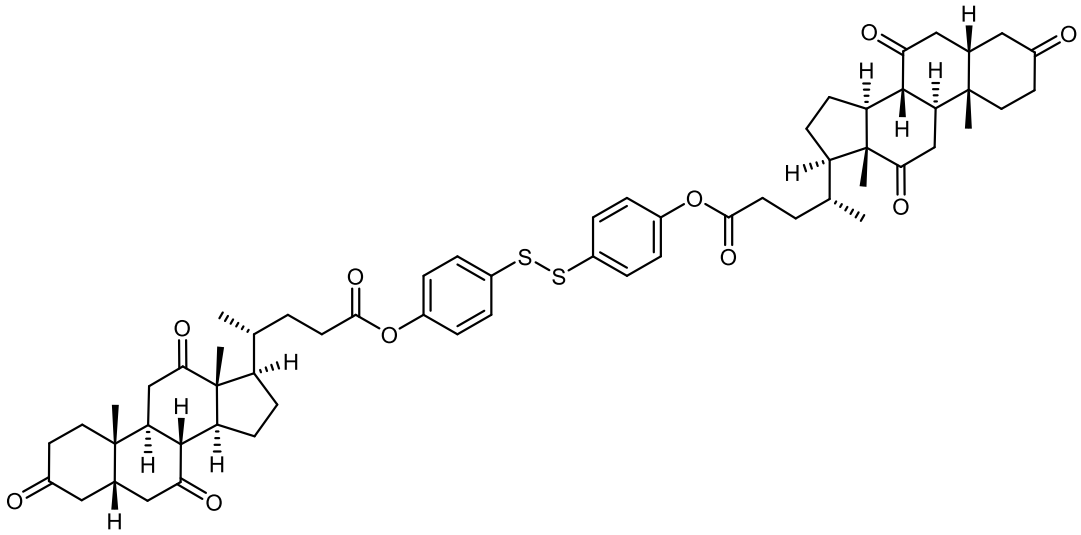


disulfanediylbis(4,1-phenylene) bis(2-(4-isobutylphenyl)propanoate) (2x): Pale yellow oil **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.45 – 7.40 (m, 4H), 7.28 (d, *J* = 8.1 Hz, 4H), 7.14 (d, *J* = 8.1 Hz, 4H), 6.97 – 6.92 (m, 4H), 3.92 (q, *J* = 7.1 Hz, 2H), 2.48 (d, *J* = 7.2 Hz, 4H), 1.87 (dp, *J* = 13.6, 6.8 Hz, 2H), 1.61 (s, 3H), 1.59 (s, 3H), 0.93 (s, 6H), 0.91 (s, 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, 18.51. HRMS (EI) m/z $[M + Na]^+$ calculated for 649.2417, found 649.2419



disulfanediylbis(4,1-phenylene) (2S,2'S)-bis(2-(6-methoxynaphthalen-2-yl)propanoate) (2y): white solid M.p. 131-132 °C **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.82 – 7.69 (m, 6H), 7.48 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.44 – 7.36 (m, 4H), 7.23 – 7.11 (m, 4H), 6.99 – 6.87 (m,

4H), 4.08 (q, *J* = 7.0 Hz, 2H), 3.93 (s, 6H), 1.69 (d, *J* = 7.1 Hz, 6H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 173.0, 157.8, 150.4, 135.0, 134.0, 133.9, 129.5, 129.3, 129.0, 127.5, 126.2, 126.1, 122.2, 119.2, 105.7, 55.4, 45.6, 18.5. HRMS (EI) m/z [M + Na]$^+$ calculated for 674.1797, found 674.1798



disulfanediylbis(4,1-phenylene) (4R,4'R)-bis(4-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate) (2z): white solid M.p. >300 ℃ **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.47 (dd, *J* = 9.1, 2.3 Hz, 4H), 7.02 (dd, *J* = 9.1, 2.3 Hz, 4H), 2.95 – 2.80 (m, 6H), 2.68 – 2.58 (m, 2H), 2.50 (dt, *J* = 16.0, 8.0 Hz, 2H), 2.39 – 1.90 (m, 30H), 1.90 – 1.80 (m, 3H), 1.66 – 1.44 (m, 5H), 1.39 (s, 6H), 1.08 (s, 6H), 0.90 (d, *J* = 6.6 Hz, 6H). **^{13}C-NMR (10 MHz, Chloroform-*d*)** δ 211.9, 209.1, 208.7, 172.3, 150.3, 134.0, 129.4, 122.4, 56.9, 51.8, 49.0, 46.8, 45.6, 45.5, 45.0, 42.8, 38.6, 36.5, 36.0, 35.5, 35.3, 31.5, 30.3, 27.7, 25.1, 21.9, 18.7, 11.9. HRMS (EI) m/z [M + Na]$^+$ calculated for 1041.4615, found 1041.4614

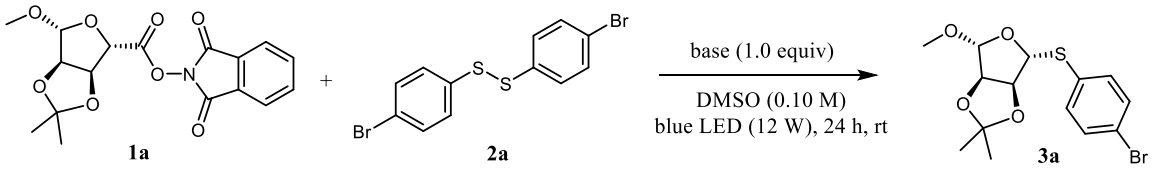
3. General Procedures and Optimization of Reaction Conditions

3.1 General procedure (standard condition): To an oven-dried 10 mL glass tube equipped with a stir bar, was added glycosyl NHP ester (0.15 mmol), disulfide (0.10 mmol), *i*Pr$_2$NEt (0.10 mmol). The tube was evacuated and back-filled with N_2 (three times), then sealed with rubber stopper and parafilm. Then, anhydrous DMSO (1.0 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 (Figure S1). After completion of the reaction, 5.0 mL water was added and extracted by ethyl acetate (3 × 5.0 mL). The combined organic layer was washed with brine (5.0 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

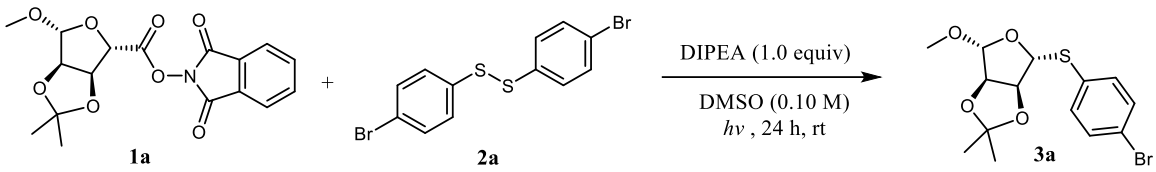
Table S1. Base screening.



entry [a]	base	yield [b](%)	d.r.
1	TMEDA	43	>20:1
2	DABCO	71	>20:1
3	Et_3N	68	>20:1
4	DIPEA	95	>20:1
5	DMAP	89	>20:1

[a] Reaction conditions: A mixture of 1a (0.15 mmol), 2a (0.10 mmol), Base (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.

Table S2. Light source screening.

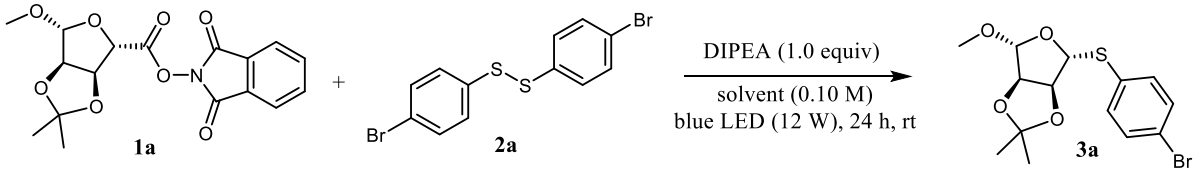


1a 2a 3a

entry [a]	light	yield [b] (%)	d.r.
1	425 nm	43	>20:1
2	Blue LED	95	>20:1
3	Green LED	91	>20:1
4	White LED	77	>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 LEDs at room temperature under N_2 for 24 h; [b] Isolated yields.

Table S3. Solvent screening.



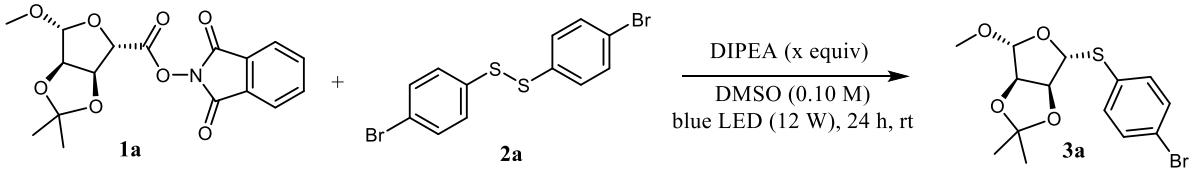
1a 2a 3a

entry [a]	solvent	yield [b] (%)	d.r.
1	1,4-Dioxane	Trace	--
2	1,2-Dichloroethane	30	>20:1
3	MeCN	N.R. [c]	--
4	THF	35	>20:1
5	DMA	90	>20:1
6	DMSO	95	>20:1

7	N-Methyl-2-pyrrolidone	88	>20:1

[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.

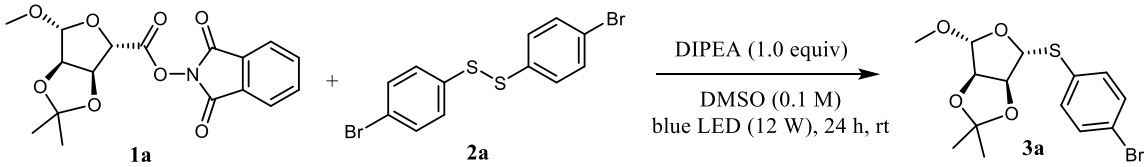
Table S4. DIPEA loading screening.



entry [a]	X	yield [b] (%)	d.r.
1	0.5	70	>20:1
2	1.0	95	>20:1
3	1.5	95	>20:1
4	2.0	92	>20:1

[a] Reaction conditions: A mixture of 1a (0.15 mmol), 2a (0.10 mmol), DIPEA (x 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.

Table S5. Control experiments under standard reaction condition.

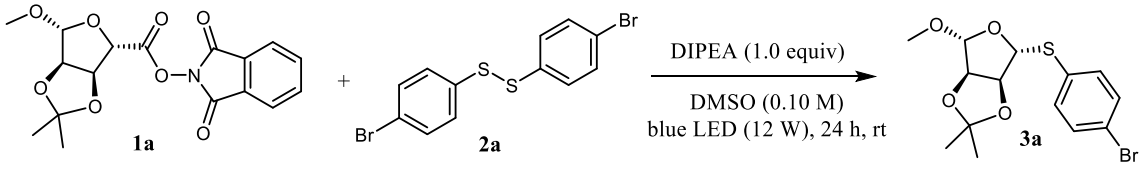


[a] entry	change from the standard condition	yield [b] (%)	d.r.
1	standard condition	95	>20:1
2	without *hv*	N.R. [c]	--
3	without DIPEA	N.R.	--

4	air condition	55	>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. Gram-scale reaction:



To a flame-dried 50 ml thick-walled pressure bottle equipped with magnetic stirrer, glycosyl NHP ester **1a** (1.6 g, 4.5 mmol), disulfide **2a** (1.1 g, 3.0 mmol), *i*Pr_2NEt (0.52 mL, 3.0 mmol), and anhydrous DMSO (30 mL) 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 (0.10 L) 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.

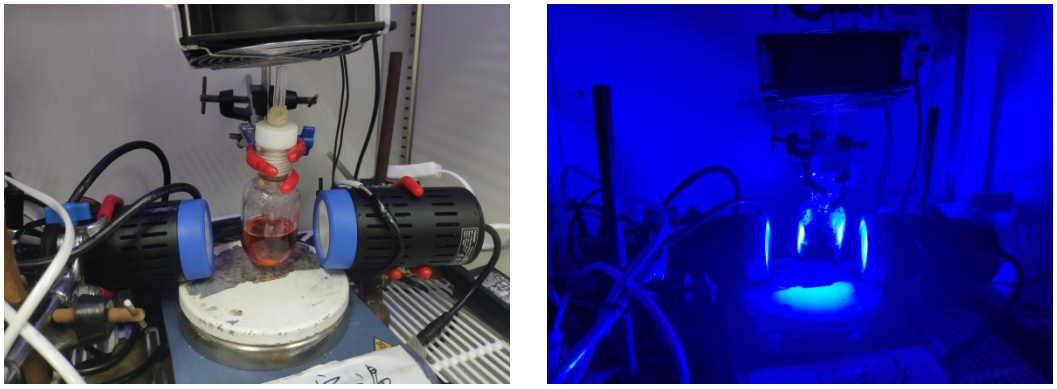
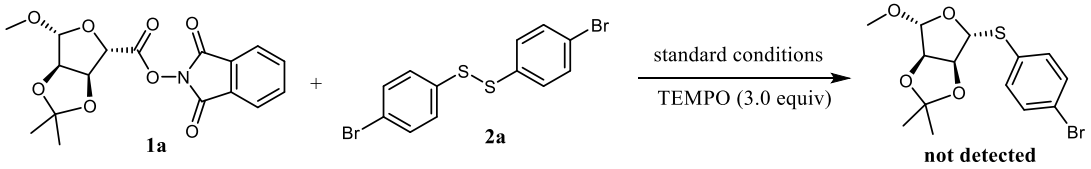


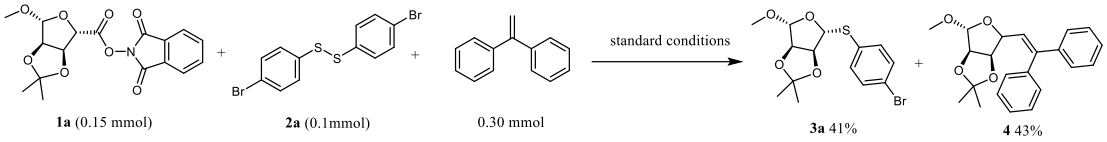
Figure S2 The photoreactor of gram-scale reaction

5.The mechanistic studies

5.1 Radical trapping experiment

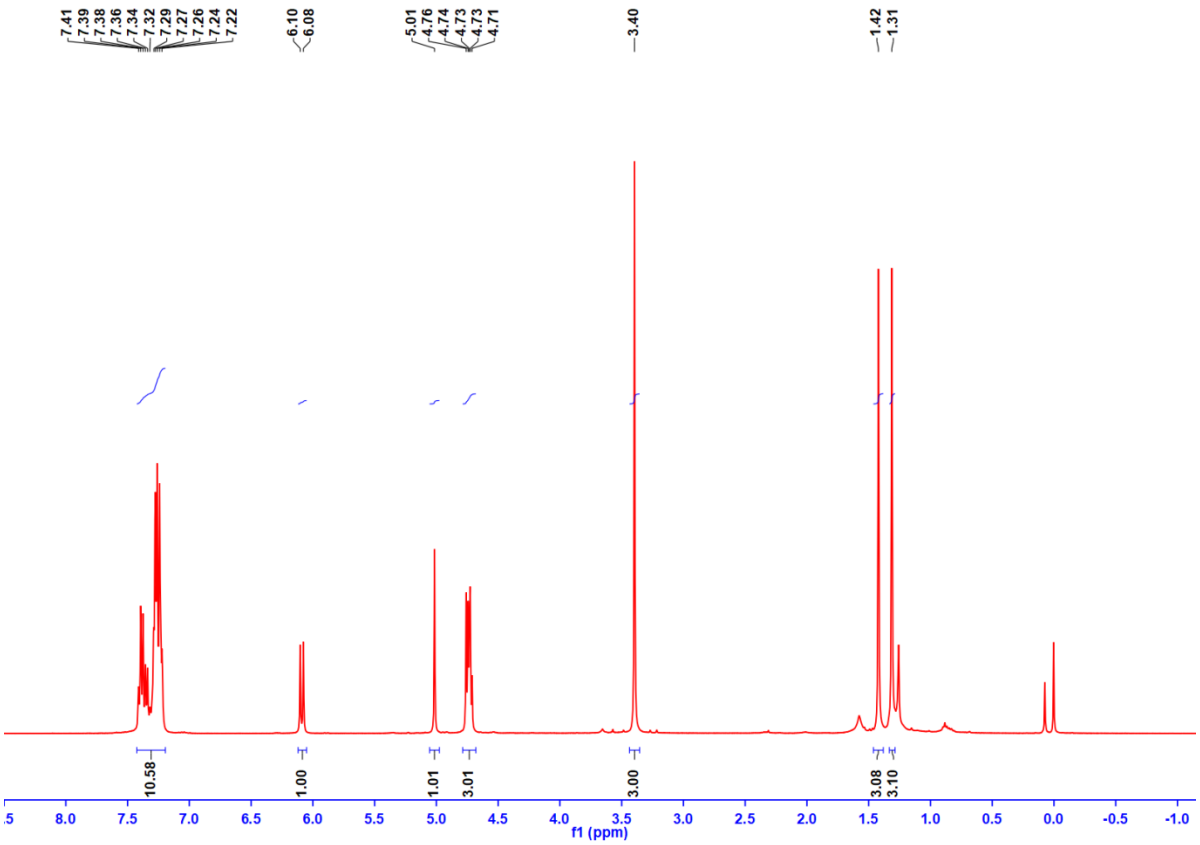


To an oven-dried 10 mL glass tube equipped with a stir bar, was added glycosyl NHP ester (0.15 mmol), disulfide (0.10 mmol), *i*Pr$_2$NEt (0.10 mmol) ,TEMPO (0.45 mmol),. The tube was evacuated and back-filled with N_2 (three times), then sealed with rubber stopper and parafilm. Then, anhydrous DMSO (1.0 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.



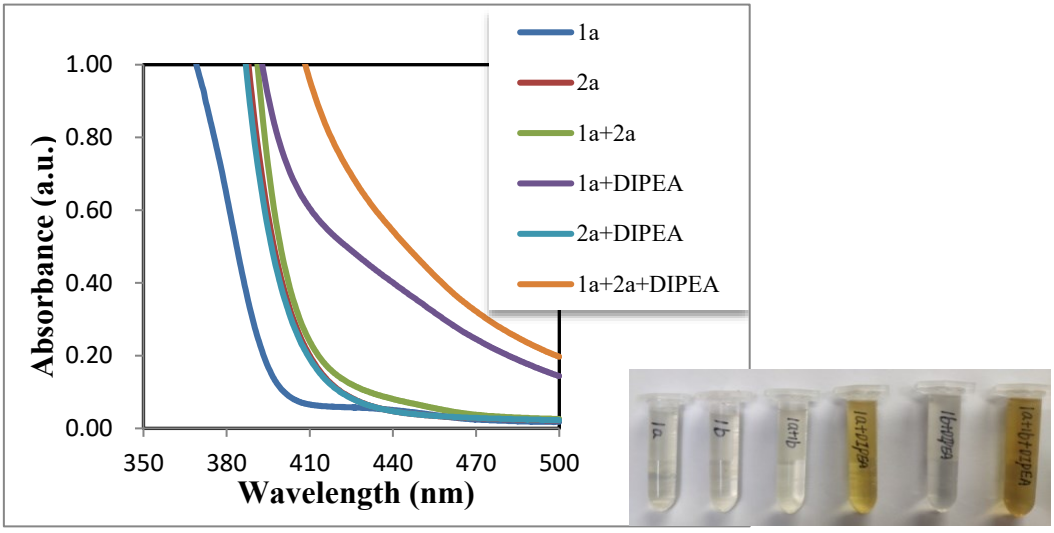
To an oven-dried 10 mL glass tube equipped with a stir bar, was added glycosyl NHP ester (0.15 mmol), disulfide (0.10 mmol), *i*Pr$_2$NEt (0.10 mmol) , 1,1-diphenylethylene (0.30 mmol),. The tube was evacuated and back-filled with N_2 (three times), then sealed with rubber stopper and parafilm. Then, anhydrous DMSO (1.0 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 isolated in 41% yield and the heck-type product **4** was isolated in 43% yield, indicating that this photo-induced thioglycosidation protocol may proceed through a radical-based mechanism. **^{1}H-NMR (400 MHz, Chloroform-*d*)**

δ 7.42 – 7.19 (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).

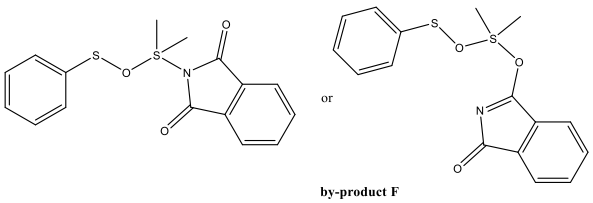


5.2 UV-vis absorption spectra

The UV-vis absorption spectra of glycosyl NHP ester **1a** (0.15 M), disulfide **2a** (0.10 M), *i*Pr$_2$NEt (0.10 M) in DMSO were recored in 1 cm path quartz cuvettes by using a GENESYS UV-Visible spectrophotometer (thermo scientific)



5.3 LC-MS report



LC-MS (ESI) m/z $[M + Na]^+$ calculated for 356.0, found 356.3.

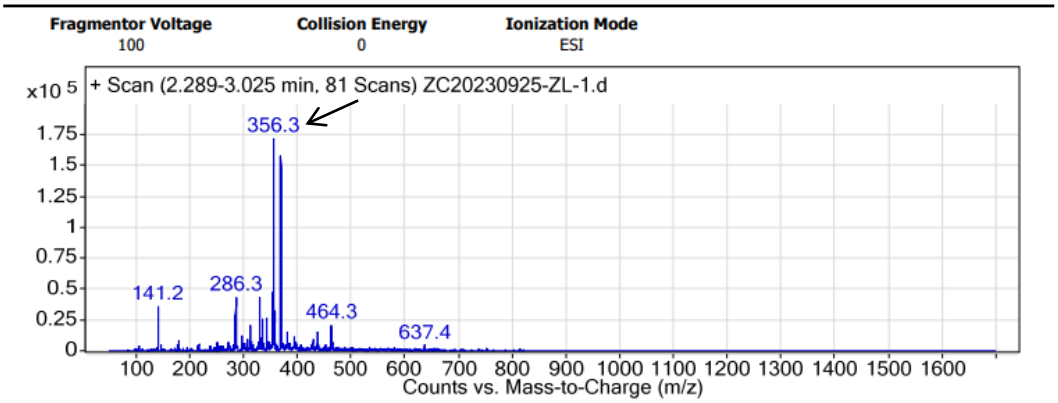
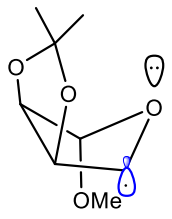


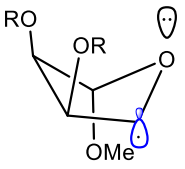
Figure S3 LC-MS detection report of by-product **F**

6. Configuration determination

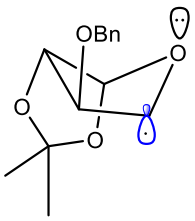
6.1 Plausible conformation of glycosyl radical



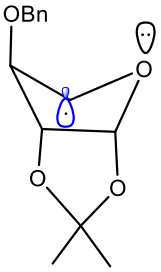
Ribose



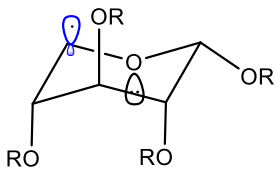
Ribose
R= Me, Bn



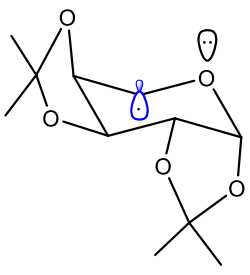
Arabinose



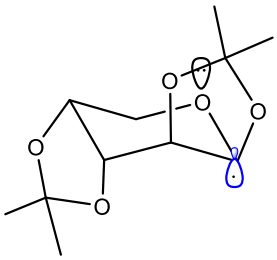
Xylose



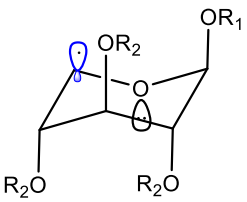
Glucose
R=Me, Bn



Galactose



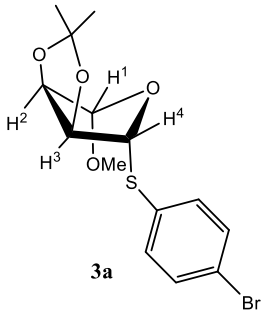
Fructose



Arbutin

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

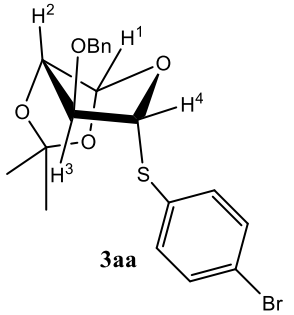
6.2 H-H coupling constant analysis



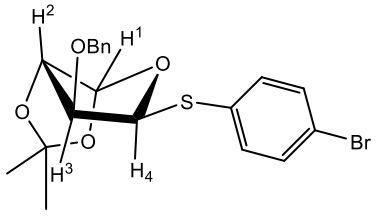
3a

(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* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), **5.57 (s, 1H), 5.11 (s, 1H), 4.90 (d, *J* = 5.7 Hz, 1H), 4.71 (d, *J* = 5.8 Hz, 1H)**, 3.39 (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), 4.90 (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.



3aa

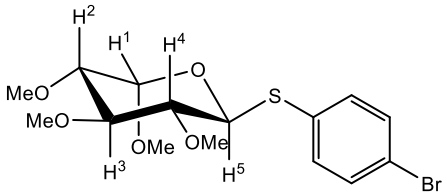


3aa'

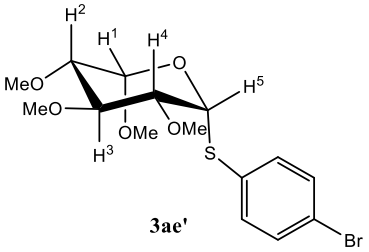
(3aR,5R,6S,6aS)-6-(benzyloxy)-5-((4-bromophenyl)thio)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole (3aa): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.28 (m, 9H), **6.02 (d, *J* = 3.8 Hz, H^1), 5.48 (s, H^4), 4.68 (d, *J* = 3.8 Hz, H^2),** 4.60 (s, 2H), **4.233 (s, H^3)**, 1.67 (s, 3H), 1.34 (s, 3H).

(3aR,5S,6S,6aS)-6-(benzyloxy)-5-((4-bromophenyl)thio)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole (3aa'): ^{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.



3ae

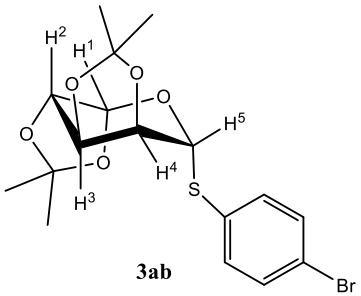


3ae'

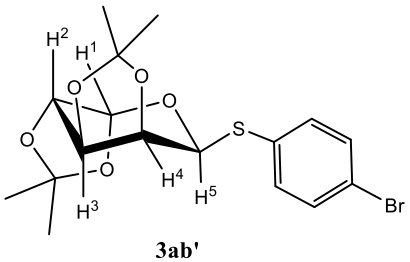
(2R,3S,4R,5R,6S)-2-((4-bromophenyl)thio)-3,4,5,6-tetramethoxytetrahydro-2H-pyran (3ae): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.37 (m, 4H), **4.79 (d, *J* = 3.5 Hz, H^1), 4.71 (d, *J* = 10.0 Hz, H^5),** 3.60 (s, 3H), 3.58 (s, 3H), 3.49 (s, 3H,1H), 3.27 (s, 3H), **3.17 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.02 – 2.94 (m, 1H).**

(2S,3S,4R,5R,6S)-2-((4-bromophenyl)thio)-3,4,5,6-tetramethoxytetrahydro-2H-pyran (3ae'): ^{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* = 3.4 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 – 3.44 (m, 1H),** 3.39 (s, 3H), **3.23 (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.[16] 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 3ae was α -isomer.



3ab



3ab'

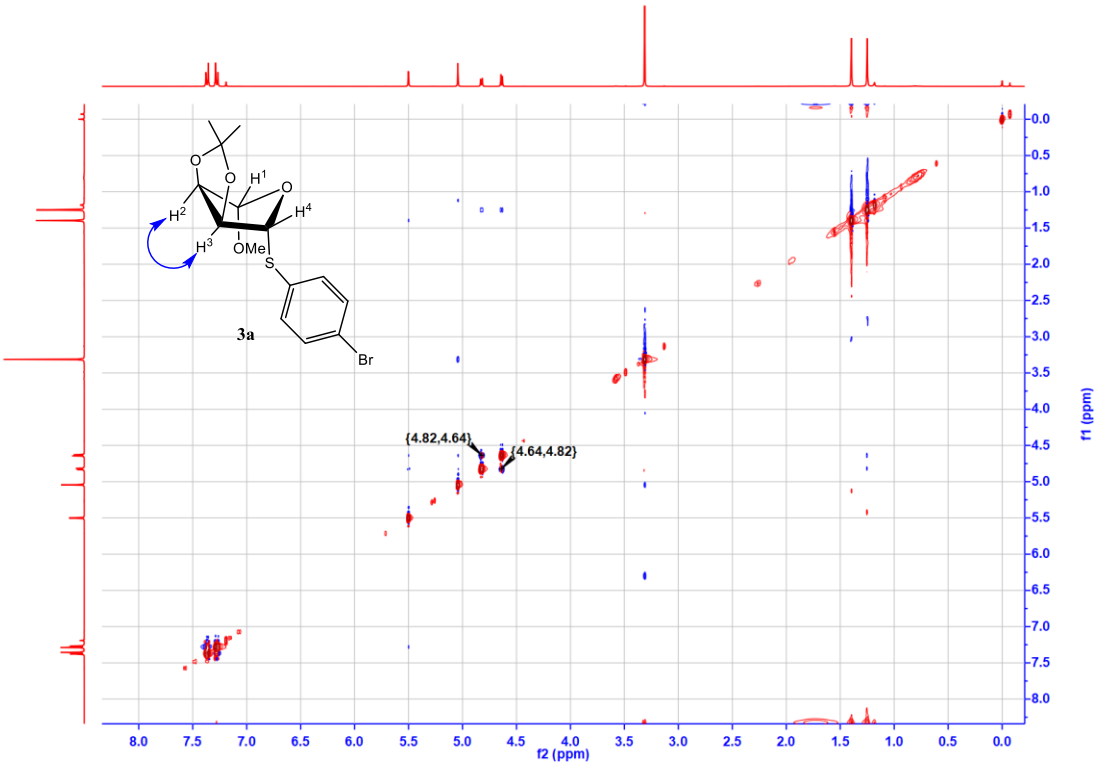
(3aS,5S,5aR,8aR,8bR)-5-((4-bromophenyl)thio)-2,2,7,7-tetramethyltetrahydro-5H-bis([1

,3]dioxolo)[4,5-b:4',5'-d]pyran (3ab): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.38 (m, 4H), **5.31 (d, *J* = 2.2 Hz, H^1), 4.54 (d, *J* = 5.3 Hz, H^5), 4.43 (d, *J* = 9.6 Hz, 1H), 4.26 – 4.22 (m, 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).

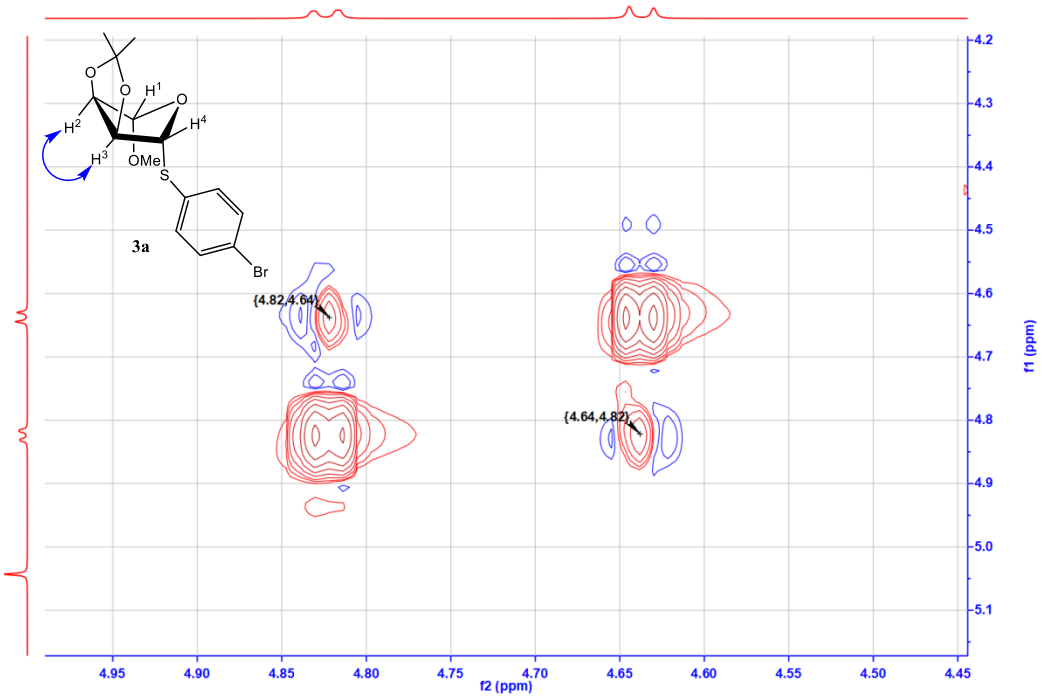
(3aS,5R,5aR,8aR,8bR)-5-((4-bromophenyl)thio)-2,2,7,7-tetramethyltetrahydro-5H-bis([1 ,3]dioxolo)[4,5-b:4',5'-d]pyran (3ab'): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.39 (s, 4H), **5.67 (d, *J* = 4.9 Hz, H^5), 5.19 (d, *J* = 1.5 Hz, H^1), 4.67 (dd, *J* = 7.5, 2.6 Hz, H^3), 4.47 (dd, *J* = 7.5, 1.7 Hz, H^2), 4.38 (dd, *J* = 4.9, 2.7 Hz, H^4),** 1.54 (s, 3H), 1.45 (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 3ae/3ae'. 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 3ab' are clear and easy to assign. **5.67 (d, *J* = 4.9 Hz, H^5), 5.19 (d, *J* = 1.5 Hz, H^1), 4.67 (dd, *J* = 7.5, 2.6 Hz, H^3), 4.47 (dd, *J* = 7.5, 1.7 Hz, H^2), 4.38 (dd, *J* = 4.9, 2.7 Hz, H^4).**

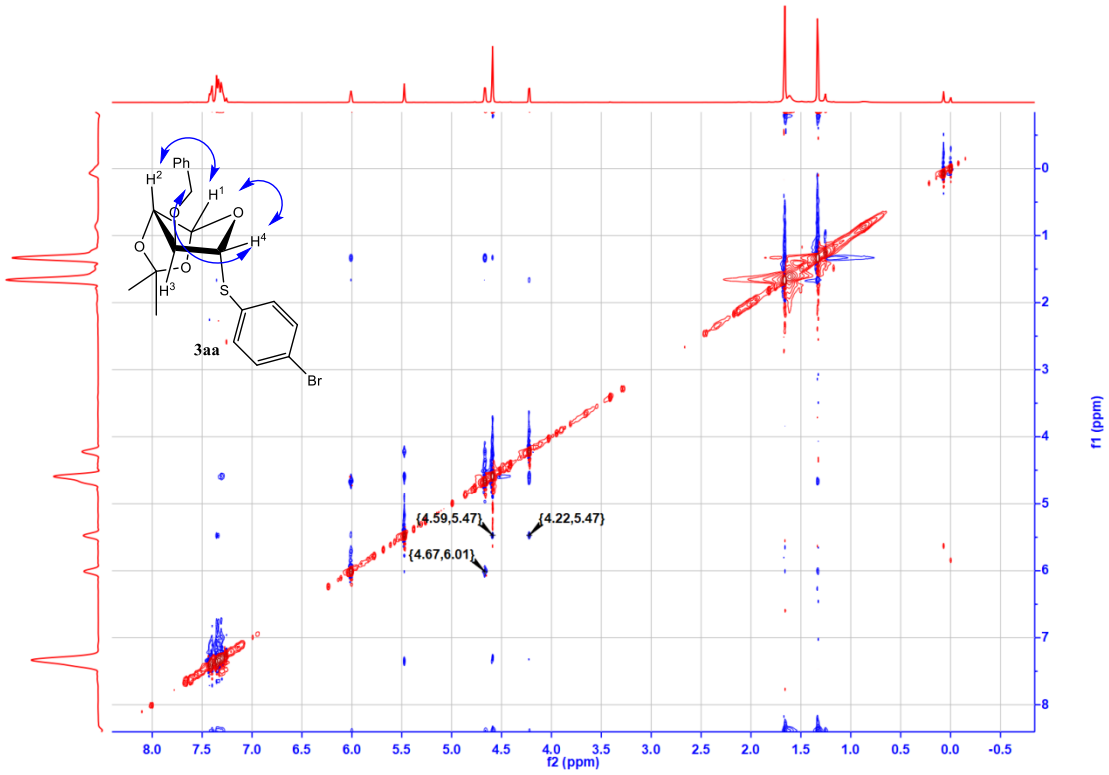
6.3 NOE experiments



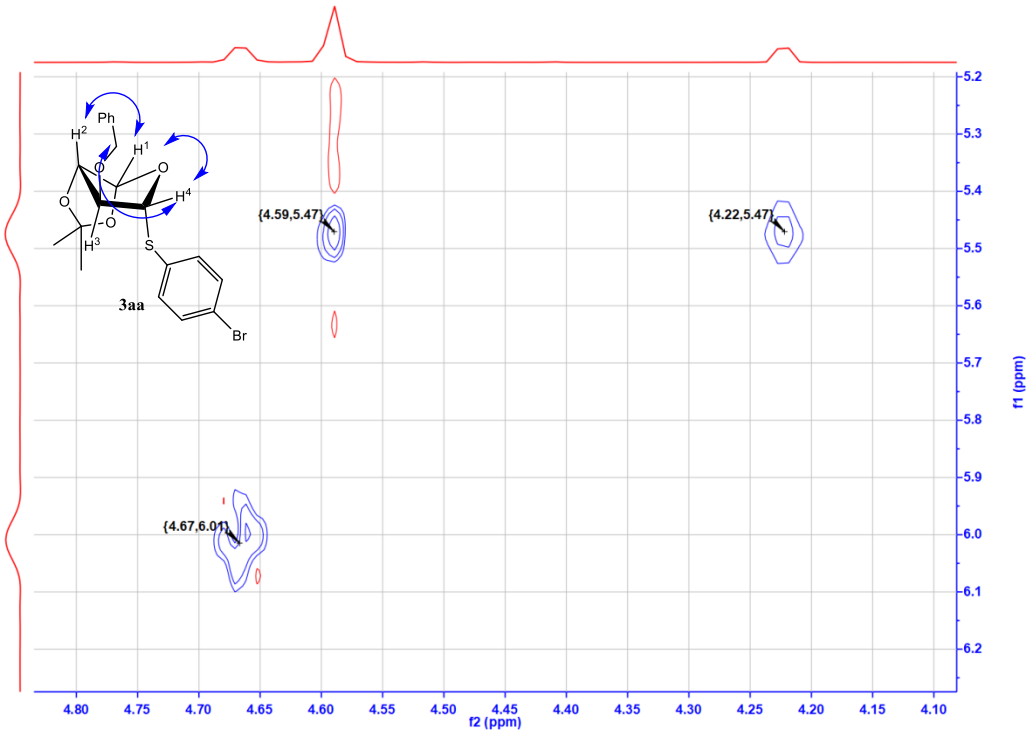
NOESY spectrum of compound **3a**



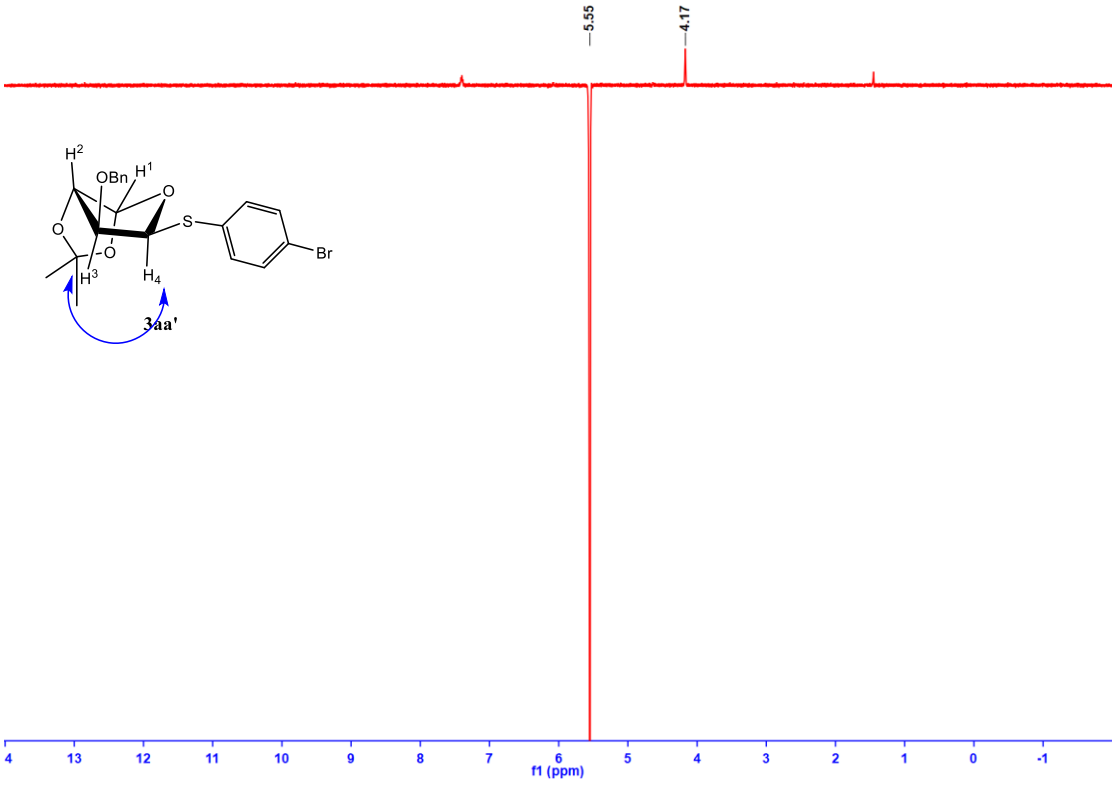
NOESY spectrum of compound **3a**



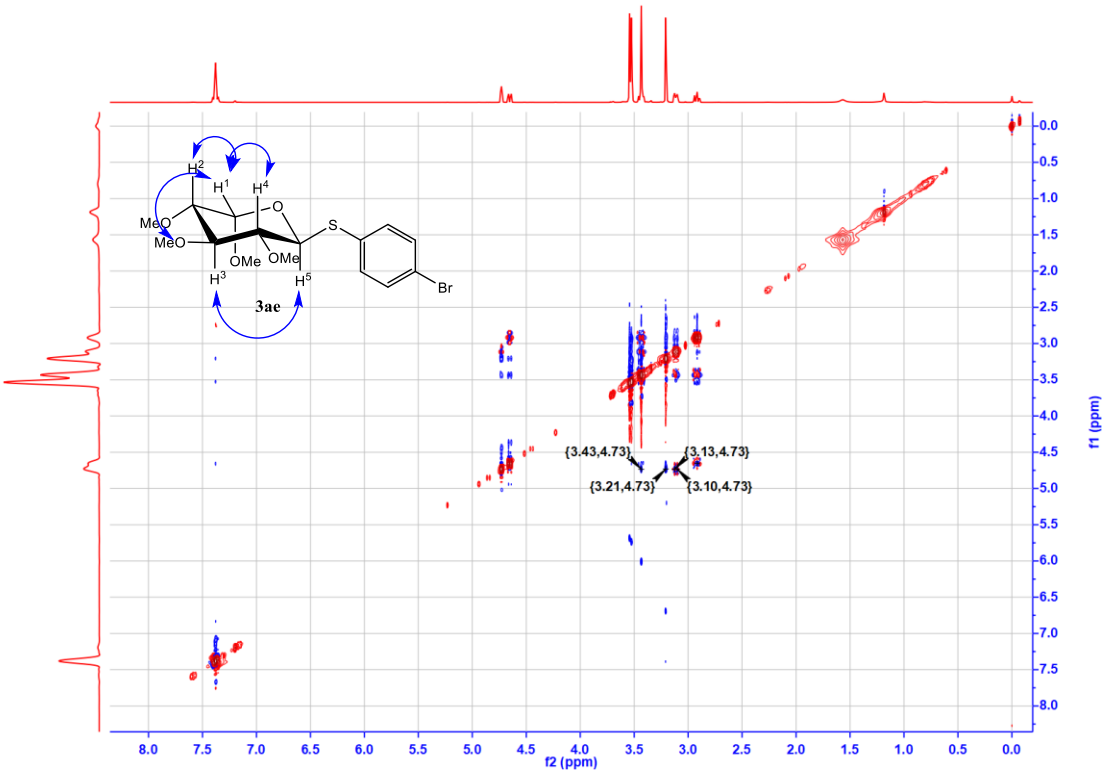
NOESY spectrum of compound **3aa**



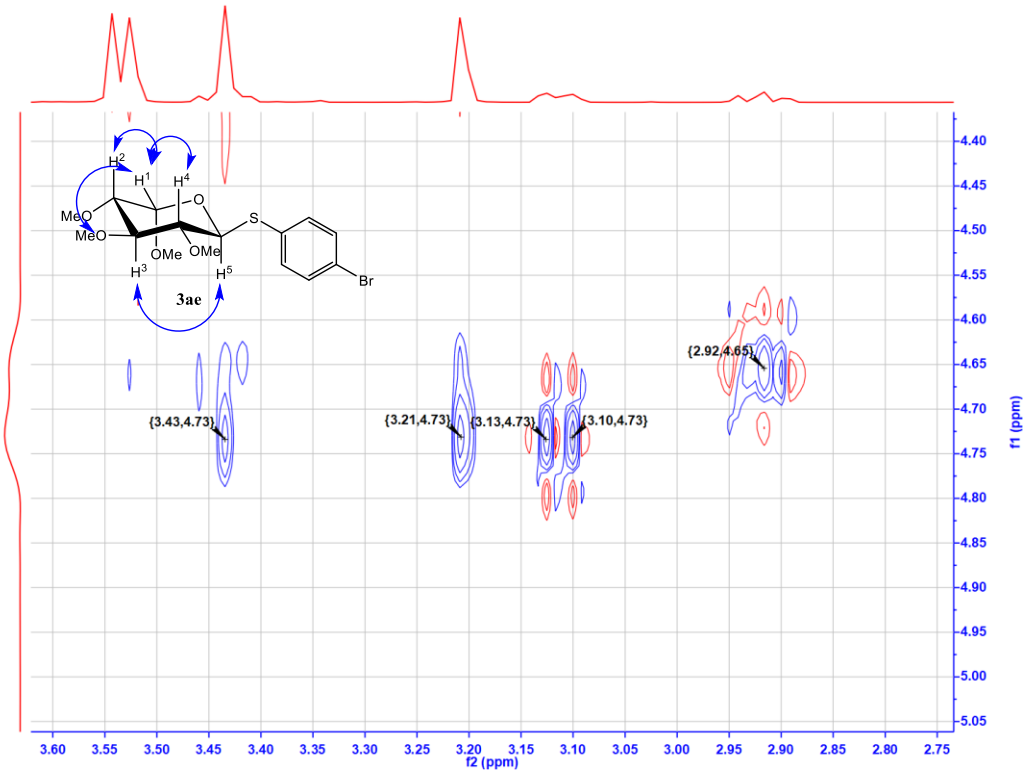
NOESY spectrum of compound **3aa**



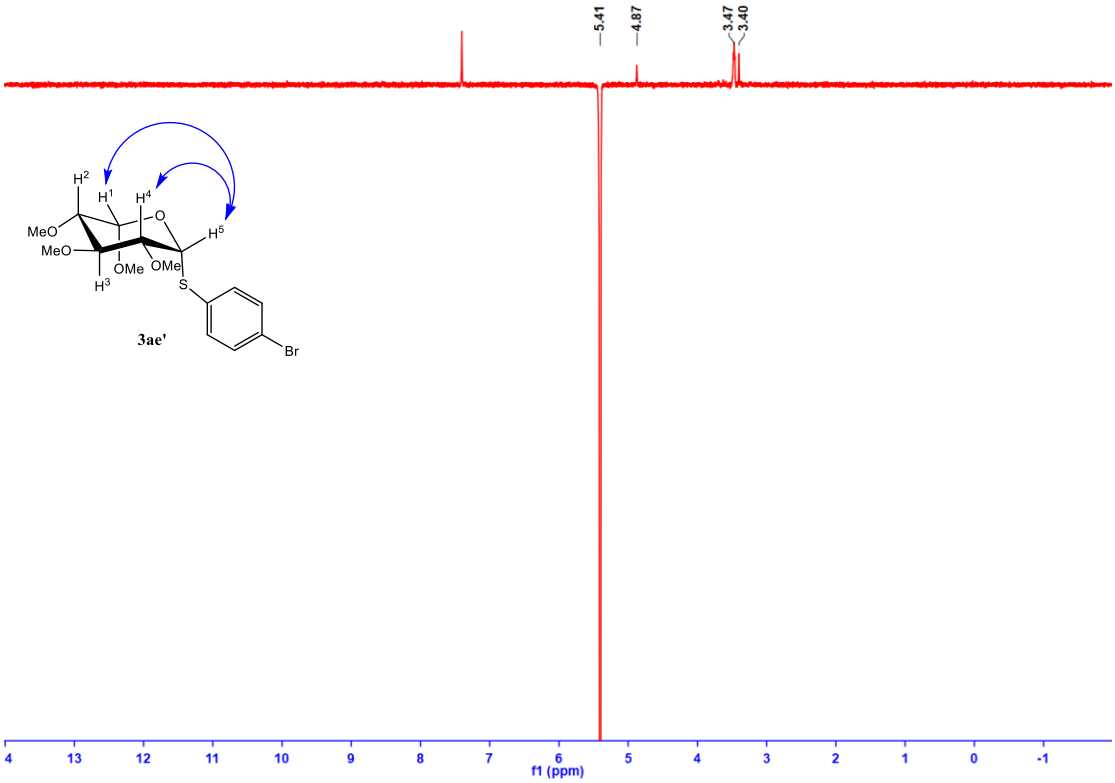
1D-NOE spectrum of compound **3aa'**



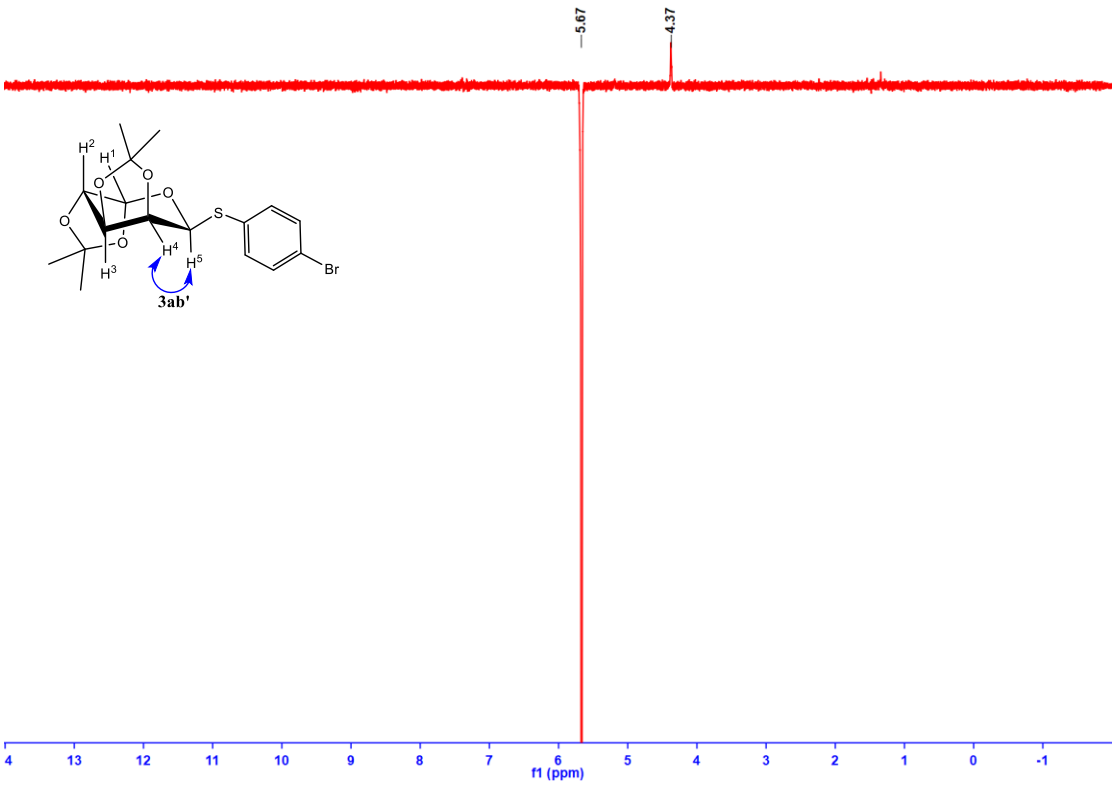
NOESY spectrum of compound **3ae**



NOESY spectrum of compound **3ae**



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



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

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

7. References

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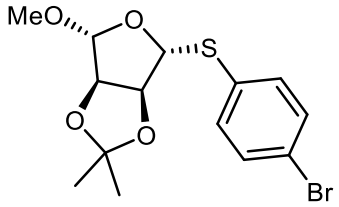
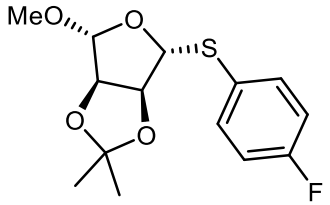
16 Feng, G.; Luo, T.; Guo, Y.; Liu, C.; Dong, H. *J Org Chem* **2022,** *87* (5), 3638-3646

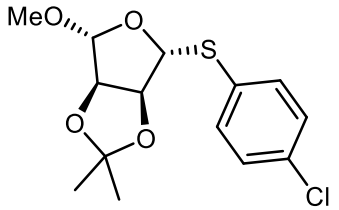
8. Characterization of products



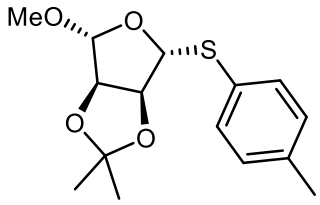
(3aS,4R,6R,6aR)-4-((4-bromophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3a): White solid; 34.2 mg; 95% yield; >20:1 d.r.; M.p. 79–80 ℃. **^{1}H-NMR (400 MHz, Chloroform-d)** δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 5.57 (s, 1H), 5.11 (s, 1H), 4.90 (d, *J* = 5.7 Hz, 1H), 4.71 (d, *J* = 5.8 Hz, 1H), 3.39 (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 (EI) m/z $[M + Na]^+$ calculated for 382.9923, found 382.9925.



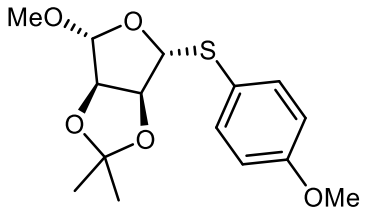
(3aS,4R,6R,6aR)-4-((4-fluorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3b): White solid; 28.9 mg; 96% yield; >20:1 d.r.; M.p. 56-57 ℃. **^{1}H-NMR (400 MHz, Chloroform-d)** δ 7.49 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 5.50 (s, 1H), 5.10 (s, 1H), 4.90 (d, *J* = 5.7 Hz, 1H), 4.71 (d, *J* = 5.8 Hz, 1H), 3.42 (s, 3H), 1.45 (s, 3H), 1.32 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-d)** δ 162.4 (d, *J* = 248.5 Hz), 133.7 (d, *J* = 8.1 Hz), 130.1 (d, *J* = 3.0 Hz), 116.3 (d, *J* = 22.2 Hz), 113.0, 110.5, 94.1 85.8, 84.7, 55.2, 26.4, 25.1. **^{19}F-NMR (376 MHz, Chloroform-d)** δ -114.10 (tt, *J* = 8.6, 5.2 Hz). HRMS (EI) m/z $[M + Na]^+$ calculated for 323.0724, found 323.0723.



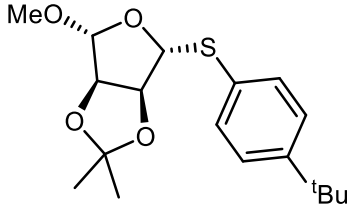
(3aS,4R,6R,6aR)-4-((4-chlorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3c): White solid; 28.3 mg; 89% yield; >20:1 d.r.; M.p. 64- 65℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 5.56 (s, 1H), 5.11 (s, 1H), 4.90 (d, *J* = 5.7 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 132.8, 132.2, 131.0, 128.2, 112.1, 109.4, 92.2, 84.7, 83.6, 54.2, 25.4, 24.1. HRMS (EI) m/z $[M + Na]^+$ calculated for 339.0428, found 339.0431.



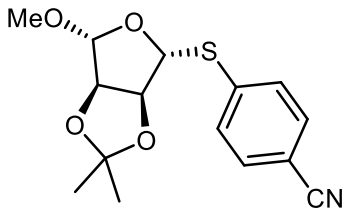
(3aR,4R,6R,6aS)-4-methoxy-2,2-dimethyl-6-(p-tolylthio)tetrahydrofuro[3,4-d][1,3]dioxol e (3d): White solid; 25.0 mg; 84% yield; >20:1 d.r.; M.p. 75-76 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 5.54 (s, 1H), 5.10 (s, 1H), 4.92 (d, *J* = 5.7 Hz, 1H), 4.72 (d, *J* = 5.8 Hz, 1H), 3.42 (s, 3H), 2.33 (s, 3H), 1.46 (s, 3H), 1.32 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 136.4, 130.5, 130.3, 128.9, 111.9, 109.4, 92.8, 84.8, 83.7, 54.2, 25.4, 24.1, 20.1. HRMS (EI) m/z [M + Na]$^+$ calculated for 319.0974, found 319.0977.



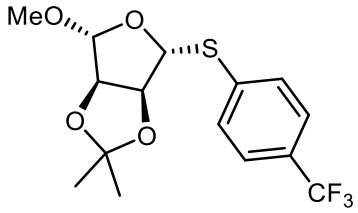
(3aR,4R,6R,6aS)-4-methoxy-6-((4-methoxyphenyl)thio)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3e): White solid; 26.5 mg; 84% yield; >20:1 d.r.; M.p. 85-86 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.46 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.44 (s, 1H), 5.09 (s, 1H), 4.91 (d, *J* = 5.7 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 (EI) m/z [M + Na]$^+$ calculated for 335.0923, found 335.0921.



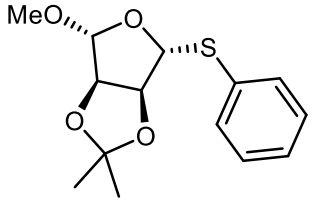
(3aS,4R,6R,6aR)-4-((4-(tert-butyl)phenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3 ,4-d][1,3]dioxole (3f): Pale oil; 31.1 mg; 91% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.46 – 7.42 (m, 2H), 7.37 – 7.33 (m, 2H), 5.57 (s, 1H), 5.11 (s, 1H), 4.94 (d, *J* = 5.8 Hz, 1H), 4.73 (d, *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 150.5, 131.6, 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 (EI) m/z [M + Na]$^+$ calculated for 361.1444, found 361.1442.



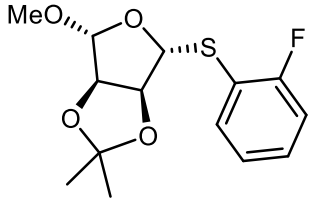
4-(((3aS,4R,6R,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)thio)benzonitrile (3g): White solid; 22.4 mg; 72% yield; >20:1 d.r.; M.p. 61-62 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.58 – 7.54 (m, 2H), 7.51 – 7.48 (m, 2H), 5.72 (s, 1H), 5.14 (s, 1H), 4.89 (d, *J* = 6.6 Hz, 1H), 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, 132.4, 128.3, 118.7, 113.4, 110.5, 109.5, 91.4, 85.6, 84.5, 55.2, 26.4, 25.1. HRMS (EI) m/z [M + Na]$^+$ calculated for 330.0770, found 330.0773.



(3aR,4R,6R,6aS)-4-methoxy-2,2-dimethyl-6-((4-(trifluoromethyl)phenyl)thio)tetrahydrofuro[3,4-d][1,3]dioxole (3h): White solid; 34.0 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), 5.14 (s, 1H), 4.91 (d, *J* = 6.4 Hz, 1H), 4.72 (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 140.0 (d, *J* = 1.0 Hz), 128.0, 127.5 (q, *J* = 32.3 Hz), 124.8 (q, *J* = 4.1 Hz), 123.0 (q, *J* = 272.7 Hz), 112.2, 109.4, 91.1, 84.7, 83.5, 54.2, 25.4, 24.1. **^{19}F-NMR (376 MHz, Chloroform-*d*)** δ -62.55. HRMS (EI) m/z [M + Na]$^+$ calculated for 373.0692, found 373.0691.

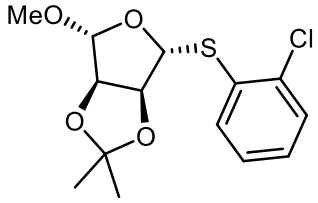


(3aR,4R,6R,6aS)-4-methoxy-2,2-dimethyl-6-(phenylthio)tetrahydrofuro[3,4-d][1,3]dioxole (3i): Pale oil; 26.1 mg; 92% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.45 – 7.39 (m, 2H), 7.25 – 7.14 (m, 3H), 5.54 (s, 1H), 5.04 (s, 1H), 4.85 (d, *J* = 5.7 Hz, 1H), 4.64 (d, *J* = 5.8 Hz, 1H), 3.33 (s, 3H), 1.39 (s, 3H), 1.25 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 134.3, 129.8, 128.1, 126.1, 112.0, 109.4, 92.3, 84.9, 83.7, 54.2, 25.4, 24.1. HRMS (EI) m/z [M + Na]$^+$ calculated for 305.0818, found 305.0820.

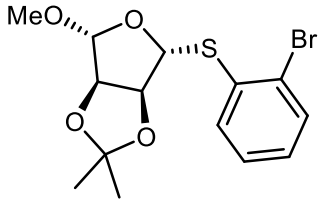


(3aS,4R,6R,6aR)-4-((2-fluorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3j): Pale oil; 24.9 mg; 83% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.51 (td, *J* = 7.4, 1.5 Hz, 1H), 7.23 (td, *J* = 5.8, 1.7 Hz, 1H), 7.11 – 7.02 (m, 2H), 5.57 (s, 1H), 5.06 (s, 1H), 4.93 (d, *J* = 5.7 Hz, 1H), 4.70 (d, *J* = 5.8 Hz, 1H), 3.35 (s, 3H), 1.42 (s, 3H), 1.28 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 161.5 (d, *J* = 247.4 Hz), 133.6 (d, *J* = 2.0 Hz), 129.5 (d, *J* = 8.1 Hz), 124.7 (d, *J* = 4.0 Hz), 121.9 (d, *J* = 18.2 Hz), 115.9 (d, *J* = 22.2 Hz), 113.0, 110.6, 92.3, 86.1, 84.6, 55.3, 26.4, 25.1. **^{19}F-NMR (376 MHz,**

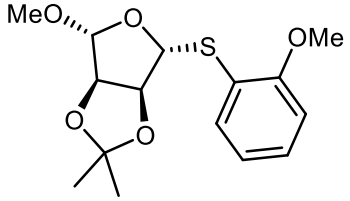
Chloroform-*d*) δ -108.10 (ddd, *J* = 9.3, 7.4, 5.2 Hz). HRMS (EI) m/z [M + Na]$^+$ calculated for 323.0724, found 323.0723.



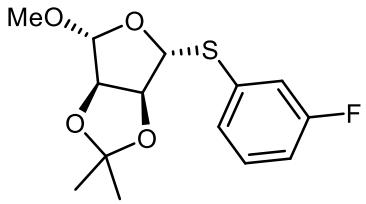
(3aS,4R,6R,6aR)-4-((2-chlorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3k): Pale oil; 29.5 mg; 93% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.60 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.39 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.19 – 7.15 (m, 1H), 5.68 (s, 1H), 5.13 (s, 1H), 4.96 (d, *J* = 5.7 Hz, 1H), 4.74 (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 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 (EI) 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; 31.0 mg; 85% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.58 (ddd, *J* = 12.0, 7.9, 1.3 Hz, 2H), 7.30 (td, *J* = 7.8, 1.3 Hz, 1H), 7.08 (td, *J* = 7.9, 1.5 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), 3.36 (s, 3H), 1.49 (s, 3H), 1.33 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 136.1, 132.1, 129.1, 127.0, 126.6, 123.4, 112.1, 109.4, 90.8, 84.7, 83.6, 54.2, 25.4, 24.1. HRMS (EI) m/z [M + Na]$^+$ calculated for 382.9923, found 382.9921.

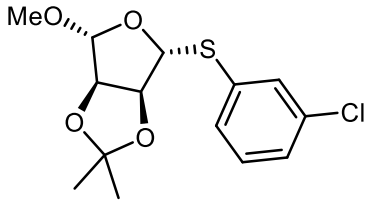


(3aR,4R,6R,6aS)-4-methoxy-6-((2-methoxyphenyl)thio)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3m): Pale oil; 24.0 mg; 71% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.50 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.29 – 7.23 (m, 1H), 6.93 (td, *J* = 7.6, 1.1 Hz, 1H), 6.90 – 6.86 (m, 1H), 5.69 (s, 1H), 5.08 (s, 1H), 4.95 (d, *J* = 5.8 Hz, 1H), 4.74 (d, *J* = 5.8 Hz, 1H), 3.89 (s, 3H), 3.37 (s, 3H), 1.46 (s, 3H), 1.31 (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 (EI) m/z [M + Na]$^+$ calculated for 335.0923, found 335.0926.

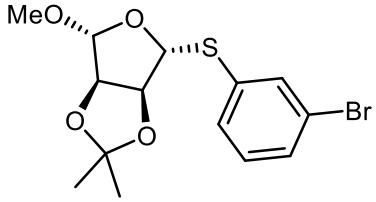


(3aS,4R,6R,6aR)-4-((3-fluorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][

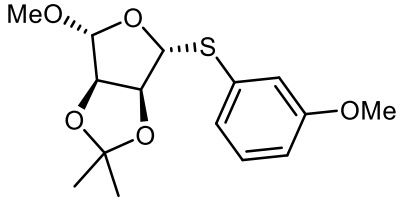
1,3]dioxole (3n): Pale oil; 29.1 mg; 97% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.25 – 7.16 (m, 3H), 6.91 (t, *J* = 8.3 Hz, 1H), 5.61 (s, 1H), 5.11 (s, 1H), 4.88 (d, *J* = 5.7 Hz, 1H), 4.69 (d, *J* = 5.8 Hz, 1H), 3.36 (s, 3H), 1.46 (s, 3H), 1.30 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 161.7 (d, *J* = 249.5 Hz), 136.8 (d, *J* = 8.1 Hz), 129.3 (d, *J* = 8.1 Hz), 124.6 (d, *J* = 3.0 Hz), 115.9 (d, *J* = 22.2 Hz), 112.8 (d, *J* = 21.2 Hz), 112.1, 109.4, 91.8, 84.7, 83.6, 54.2, 25.4, 24.1. **^{19}F-NMR (376 MHz, Chloroform-*d*)** δ -111.82 (td, *J* = 8.8, 5.9 Hz). HRMS (EI) m/z $[M + Na]^+$ calculated for 323.0724, found 323.0729.



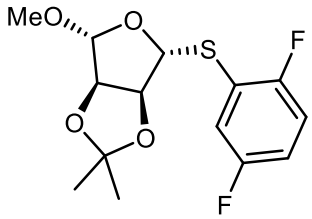
(3aS,4R,6R,6aR)-4-((3-chlorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3o): White solid; 30.0 mg; 94% yield; >20:1 d.r.; M.p. 57-58 °C. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.49 (d, *J* = 1.8 Hz, 1H), 7.35 (dt, *J* = 7.2, 1.7 Hz, 1H), 7.25 – 7.18 (m, 2H), 5.62 (s, 1H), 5.13 (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 137.5, 134.8, 130.1, 130.0, 128.3, 127.1, 113.1, 110.4, 92.9, 85.7, 84.6, 55.2, 26.5, 25.1. HRMS (EI) m/z $[M + Na]^+$ calculated for 339.0428, found 339.0427.



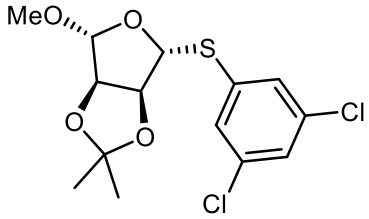
(3aS,4R,6R,6aR)-4-((3-bromophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3p): White solid; 34.9 mg; 96% yield; >20:1 d.r.; M.p. 58-59 °C. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.64 (t, *J* = 1.7 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.18 (t, *J* = 7.9 Hz, 1H), 5.61 (s, 1H), 5.12 (s, 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 136.8, 131.8, 129.3, 129.0, 127.8, 121.8, 112.1, 109.4, 91.9, 84.7, 83.6, 54.2, 25.4, 24.1. HRMS (EI) m/z $[M + Na]^+$ calculated for 382.9923, found 382.9927.



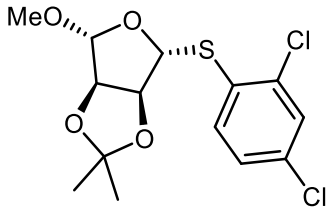
(3aR,4R,6R,6aS)-4-methoxy-6-((3-methoxyphenyl)thio)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3q): Pale oil; 26.9 mg; 86% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.23 (t, *J* = 8.0 Hz, 1H), 7.09 – 7.03 (m, 2H), 6.79 (dd, *J* = 8.3, 2.4 Hz, 1H), 5.63 (s, 1H), 5.12 (s, 1H), 4.92 (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 (EI) m/z $[M + Na]^+$ calculated for 335.0923, found 335.0924.



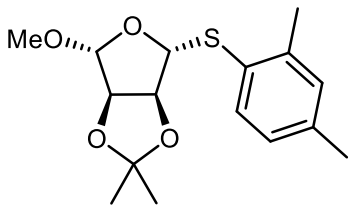
(3aS,4R,6R,6aR)-4-((2,5-difluorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3r): faint yellow oil; 28.9 mg; 90% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.28 (td, *J* = 5.6, 2.8 Hz, 1H), 7.04 (td, *J* = 8.8, 4.6 Hz, 1H), 6.93 (ddd, *J* = 8.8, 6.5, 3.8 Hz, 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), 1.32 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 159.1 (dd, *J* = 140.4 Hz, 3.0 Hz),156.6 (dd, *J* = 137.4 Hz, 3.0 Hz),124.0 (dd, *J* = 20.2 Hz, 8.1 Hz), 118.8 (dd, *J* = 25.2 Hz, 2.0 Hz), 116.5 (dd, *J* = 26.3 Hz, 9.1 Hz), 115.3 (dd, *J* = 24.2 Hz, 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 -115.01 (dddd, *J* = 16.4, 9.1, 5.6, 3.9 Hz), -117.77 (dtd, *J* = 16.1, 7.9, 4.6 Hz). HRMS (EI) m/z $[M + Na]^+$ calculated for 341.0629, found 341.0630.



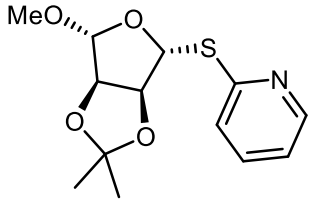
(3aS,4R,6R,6aR)-4-((3,5-dichlorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3s): White solid; 33.7 mg; 96% yield; >20:1 d.r.; M.p. 46-47 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.35 (d, *J* = 1.8 Hz, 2H), 7.22 (t, *J* = 1.8 Hz, 1H), 5.62 (s, 1H), 5.14 (s, 1H), 4.88 (d, *J* = 5.8 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, 85.5, 84.5, 55.3, 26.4, 25.1. HRMS (EI) m/z $[M + Na]^+$ calculated for 373.0038, found 373.0036.



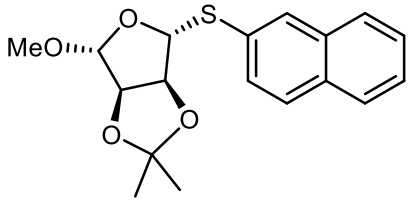
(3aS,4R,6R,6aR)-4-((2,4-dichlorophenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3t): faint yellow oil; 33.4 mg; 95% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.53 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 2.2 Hz, 1H), 7.23 (dd, *J* = 8.5, 2.2 Hz, 1H), 5.63 (s, 1H), 5.12 (s, 1H), 4.93 (d, *J* = 5.7 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 (EI) m/z $[M + Na]^+$ calculated for 373.0038, found 373.0039.



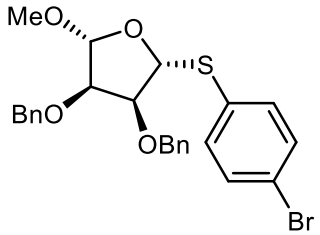
(3aS,4R,6R,6aR)-4-((2,4-dimethylphenyl)thio)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (3u): Pale oil; 25.1 mg; 81% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.44 (d, *J* = 7.9 Hz, 1H), 7.03 (s, 1H), 7.02 – 6.97 (m, 1H), 5.48 (s, 1H), 5.10 (s, 1H), 4.95 (d, *J* = 5.8 Hz, 1H), 4.73 (d, *J* = 5.8 Hz, 1H), 3.42 (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 (EI) m/z [M + Na]$^{+}$ calculated for 333.1131, found 333.1132.



2-(((3aS,4R,6R,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)thio)pyridine (3v): Pale oil; 27.0 mg; 95% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 8.49 (d, *J* = 4.1 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.04 – 6.99 (m, 1H), 6.43 (s, 1H), 5.11 (s, 1H), 4.99 (d, *J* = 5.7 Hz, 1H), 4.71 (d, *J* = 5.7 Hz, 1H), 3.37 (s, 3H), 1.52 (s, 3H), 1.33 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 158.1, 149.7, 136.3, 122.5, 120.0, 113.0, 110.4, 88.8, 86.5, 84.5, 55.2, 26.5, 25.2. HRMS (EI) m/z [M + Na]$^{+}$ calculated for 306.0770, found 306.0771.

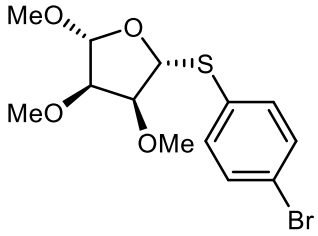


(3aR,4R,6R,6aS)-4-methoxy-2,2-dimethyl-6-(naphthalen-2-ylthio)tetrahydrofuro[3,4-d][1,3]dioxole (3w): White solid; 31.3 mg; 94% yield; >20:1 d.r.; M.p.70-71 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 8.00 – 7.96 (m, 1H), 7.80 (t, *J* = 7.1 Hz, 3H), 7.56 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.52 – 7.44 (m, 2H), 5.76 (s, 1H), 5.16 (s, 1H), 4.99 (d, *J* = 5.7 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, 113.1, 110.5, 93.1, 85.9, 84.7, 55.3, 26.5, 25.2. HRMS (EI) m/z [M + Na]$^{+}$ calculated for 355.0974, found 355.0977.

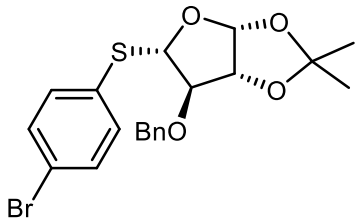


(2R,3S,4R,5R)-3,4-bis(benzyloxy)-2-((4-bromophenyl)thio)-5-methoxytetrahydrofuran

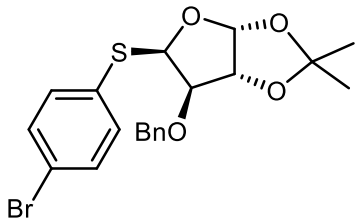
(3x): White solid; 46.3 mg; 92% yield; >20:1 d.r.; M.p. 47-48 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.43 – 7.31 (m, 14H), 5.51 (d, *J* = 6.3 Hz, 1H), 4.98 (s, 1H), 4.63 (d, *J* = 10.2 Hz, 4H), 4.17 – 4.11 (m, 1H), 3.89 (d, *J* = 4.3 Hz, 1H), 3.37 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 137.5, 137.4, 133.9, 132.8, 132.0, 128.4, 128.1, 128.0, 127.9, 121.4, 107.4, 88.9, 81.8, 79.4, 72.9, 72.7, 55.4. HRMS (EI) m/z $[M + Na]^+$ calculated for 523.0549, found 523.0550.



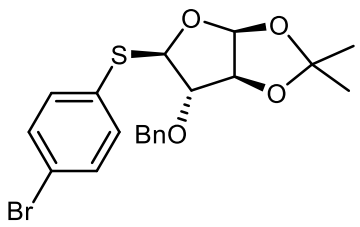
(2R,3S,4R,5R)-2-((4-bromophenyl)thio)-3,4,5-trimethoxytetrahydrofuran (3y): Pale oil; 33.7 mg; 96% yield; >20:1 d.r.. **^{1}H-NMR (600 MHz, Chloroform-*d*)** δ 7.44 – 7.35 (m, 4H), 5.40 (d, *J* = 6.1 Hz, 1H), 4.99 (s, 1H), 4.02 – 3.97 (m, 1H), 3.80 – 3.77 (m, 1H), 3.51 – 3.47 (m, 6H), 3.43 – 3.40 (m, 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 (EI) m/z $[M + Na]^+$ calculated for 370.9923, found 370.9925.



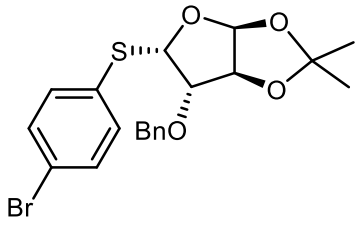
(3aS,5S,6R,6aR)-6-(benzyloxy)-5-((4-bromophenyl)thio)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole (3z): Pale oil; 35.5 mg; 81% yield. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.45 – 7.27 (m, 9H), 6.01 (d, *J* = 3.7 Hz, 1H), 5.48 (s, 1H), 4.67 (d, *J* = 3.7 Hz, 1H), 4.59 (s, 2H), 4.23 (s, 1H), 1.67 (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, 127.9, 121.5, 113.6, 107.1, 91.4, 86.5, 83.4, 72.2, 26.3, 26.1. HRMS (EI) m/z $[M + Na]^+$ calculated for 459.0236, found 459.0238.



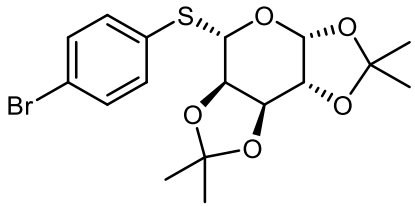
(3aS,5R,6R,6aR)-6-(benzyloxy)-5-((4-bromophenyl)thio)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole (3z'): Pale oil; 6.0 mg; 14% yield. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.46 – 7.27 (m, 9H), 6.08 (d, *J* = 3.8 Hz, 1H), 5.55 (d, *J* = 3.4 Hz, 1H), 4.78 – 4.66 (m, 2H), 4.64 (d, *J* = 3.7 Hz, 1H), 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 (EI) m/z $[M + Na]^+$ calculated for 459.0236, found 459.0237.



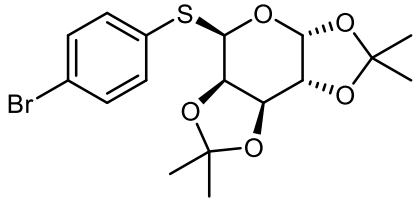
(3aR,5R,6S,6aS)-6-(benzyloxy)-5-((4-bromophenyl)thio)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole (3aa): Pale oil; 35.2 mg; 81% yield. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.44 – 7.28 (m, 9H), 6.02 (d, *J* = 3.8 Hz, 1H), 5.48 (s, 1H), 4.68 (d, *J* = 3.8 Hz, 1H), 4.60 (s, 2H), 4.23 (s, 1H), 1.67 (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, 127.9, 121.5, 113.6, 107.1, 91.4, 86.5, 83.5, 72.2, 26.4, 26.2. HRMS (EI) 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 (3aa'): Pale oil; 5.8 mg; 14% yield. **^{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 (EI) m/z $[M + Na]^+$ calculated for 459.0236, found 459.0237.

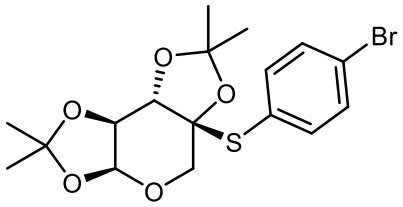


(3aS,5S,5aR,8aR,8bR)-5-((4-bromophenyl)thio)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (3ab): Pale oil; 26.5 mg; 63% yield. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.49 – 7.38 (m, 4H), 5.31 (d, *J* = 2.2 Hz, 1H), 4.54 (d, *J* = 5.3 Hz, 1H), 4.43 (d, *J* = 9.6 Hz, 1H), 4.26 – 4.22 (m, 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 (EI) m/z $[M + Na]^+$ calculated for 439.0185, found 439.0183.

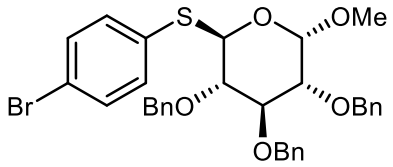


(3aS,5R,5aR,8aR,8bR)-5-((4-bromophenyl)thio)-2,2,7,7-tetramethyltetrahydro-5H-bis([1

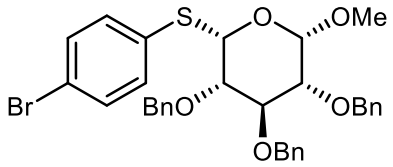
,3]dioxolo)[4,5-b:4',5'-d]pyran (3ab'): Yellow solid; 11 mg; 26% yield. M.p. 87-88 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.39 (s, 4H), 5.67 (d, *J* = 4.9 Hz, 1H), 5.19 (d, *J* = 1.5 Hz, 1H), 4.67 (dd, *J* = 7.5, 2.6 Hz, 1H), 4.47 (dd, *J* = 7.5, 1.7 Hz, 1H), 4.38 (dd, *J* = 4.9, 2.7 Hz, 1H), 1.54 (s, 3H), 1.45 (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 (EI) m/z $[M + Na]^+$ calculated for 439.0185, found 439.0184.



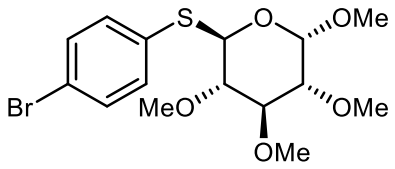
(3aS,5aS,8aS,8bS)-5a-((4-bromophenyl)thio)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (3ac): Pale oil; 34.4 mg; 82% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.55 – 7.41 (m, 4H), 4.55 (dd, *J* = 7.7, 2.0 Hz, 1H), 4.33 (d, *J* = 2.0 Hz, 1H), 4.22 (d, *J* = 7.7 Hz, 1H), 3.81 (d, *J* = 1.7 Hz, 2H), 1.48 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.22 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 138.1, 131.8, 129.2, 123.8, 110.1, 109.4, 109.4, 75.2, 71.0, 69.8, 62.9, 26.4, 26.0, 24.4, 24.2. HRMS (EI) m/z $[M + Na]^+$ calculated for 439.0185, found 439.0184.



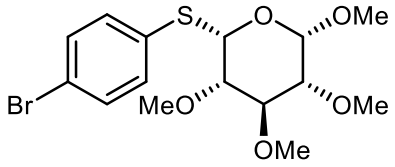
(2R,3S,4R,5R,6S)-3,4,5-tris(benzyloxy)-2-((4-bromophenyl)thio)-6-methoxytetrahydro-2H-pyran (3ad): White solid; 24.2 mg; 39% yield. M.p. 87-88 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.52 – 7.27 (m, 19H), 4.90 (dd, *J* = 17.3, 10.4 Hz, 2H), 4.85 – 4.74 (m, 4H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.57 (d, *J* = 3.5 Hz, 1H), 3.98 (t, *J* = 9.2 Hz, 1H), 3.52 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.43 – 3.34 (m, 1H), 3.24 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 138.5, 138.1, 138.0, 134.7, 132.1, 132.03, 128.6, 128.5, 128.4, 128.2, 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 (EI) m/z $[M + Na]^+$ calculated for 643.1124, found 643.1122.



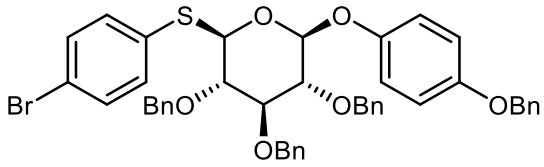
(2S,3S,4R,5R,6S)-3,4,5-tris(benzyloxy)-2-((4-bromophenyl)thio)-6-methoxytetrahydro-2H-pyran (3ad'): White solid; 24.4 mg; 39% yield. M.p. 86-87 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.52 – 7.28 (m, 19H), 5.36 (d, *J* = 4.9 Hz, 1H), 4.91 (s, 2H), 4.87 (d, *J* = 12.3 Hz, 1H), 4.78 – 4.67 (m, 3H), 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 (EI) m/z $[M + Na]^+$ calculated for 643.1124, found 643.1123.



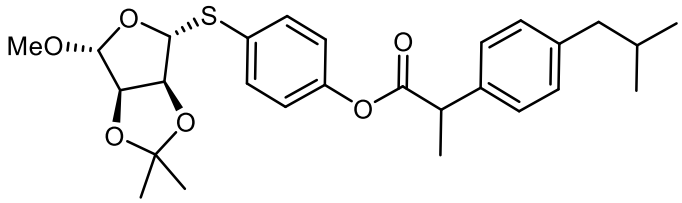
(2R,3S,4R,5R,6S)-2-((4-bromophenyl)thio)-3,4,5,6-tetramethoxytetrahydro-2H-pyran (3ae): Pale oil; 18.3 mg; 47% yield.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.50 – 7.37 (m, 4H), 4.79 (d, *J* = 3.5 Hz, 1H), 4.71 (d, *J* = 10.0 Hz, 1H), 3.60 (s, 3H), 3.58 (s, 3H), 3.49 (s, 4H), 3.27 (s, 3H), 3.17 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.02 – 2.94 (m, 1H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 135.0, 132.0, 131.9, 122.5, 98.2, 83.2, 82.3, 81.2, 80.5, 61.1, 60.8, 59.2, 55.7. HRMS (EI) 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 (3ae'): White solid; 18.9 mg; 47% yield. 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* = 3.4 Hz, 1H), 3.70 (t, *J* = 8.5 Hz, 1H), 3.62 (s, 3H), 3.53 (s, 3H), 3.49 (s, 3H), 3.47 – 3.44 (m, 1H), 3.39 (s, 3H), 3.23 (dd, *J* = 8.5, 3.5 Hz, 1H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 136.9, 132.1, 131.9, 120.64, 100.3, 85.3, 81.2, 80.3, 78.2, 60.6, 59.3, 59.0, 57.1. HRMS (EI) m/z [M + Na]$^+$ calculated for 415.0185, found 415.0184.

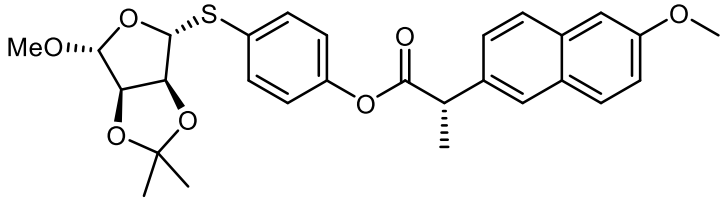


(2R,3R,4R,5S,6R)-3,4,5-tris(benzyloxy)-2-(4-(benzyloxy)phenoxy)-6-((4-bromophenyl)thio)tetrahydro-2H-pyran (3af): White solid; 66.4 mg; 84% yield; >20:1 d.r.; M.p. 148-149 ℃. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.46 – 7.28 (m, 22H), 7.18 – 7.13 (m, 2H), 6.78 – 6.71 (m, 4H), 5.61 (d, *J* = 3.3 Hz, 1H), 5.59 (s, 1H), 5.03 (s, 2H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.93 – 4.84 (m, 2H), 4.81 (d, *J* = 10.9 Hz, 1H), 4.78 – 4.71 (m, 2H), 3.99 – 3.90 (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 (EI) m/z [M + Na]$^+$ calculated for 811.1699, found 811.1700

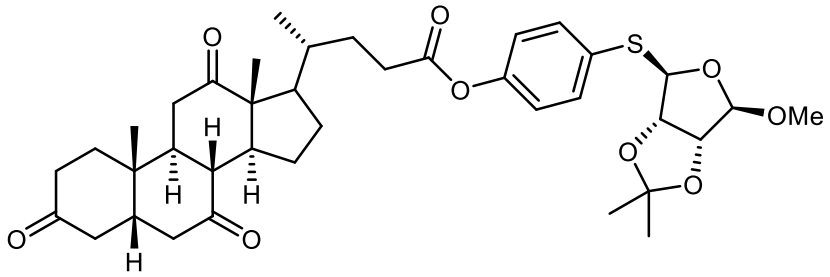


4-(((3aS,4R,6R,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)thio)phenyl 2-(4-isobutylphenyl)propanoate (3ag): Pale oil; 28.0 mg; 57% yield; >20:1 d.r..

^{1}H-NMR (600 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 6.9 Hz, 2H), 7.28 (d, *J* = 6.6 Hz, 2H), 7.14 (d, *J* = 6.6 Hz, 2H), 6.96 (d, *J* = 6.9 Hz, 2H), 5.54 (s, 1H), 5.10 (s, 1H), 4.90 (d, *J* = 4.8 Hz, 1H), 4.70 (d, *J* = 5.1 Hz, 1H), 3.93 (d, *J* = 6.7 Hz, 1H), 3.39 (s, 3H), 2.47 (d, *J* = 6.3 Hz, 2H), 1.91 – 1.83 (m, 1H), 1.60 (d, *J* = 6.4 Hz, 3H), 1.45 (s, 3H), 1.31 (s, 3H), 0.92 (s, 3H), 0.91 (s, 3H). **^{13}C-NMR (150 MHz, Chloroform-*d*)** δ 173.0, 150.2, 140.9, 137.1, 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 (EI) m/z $[M + Na]^+$ calculated for 509.1968, found 509.1970.

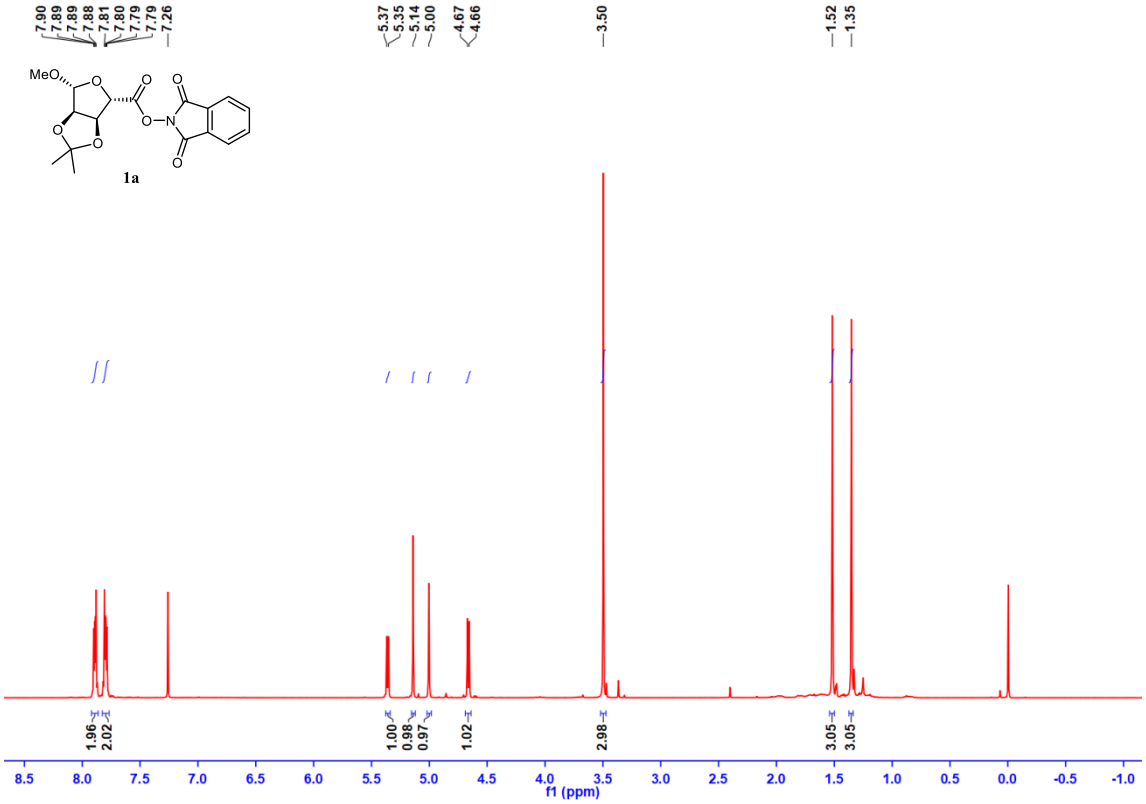


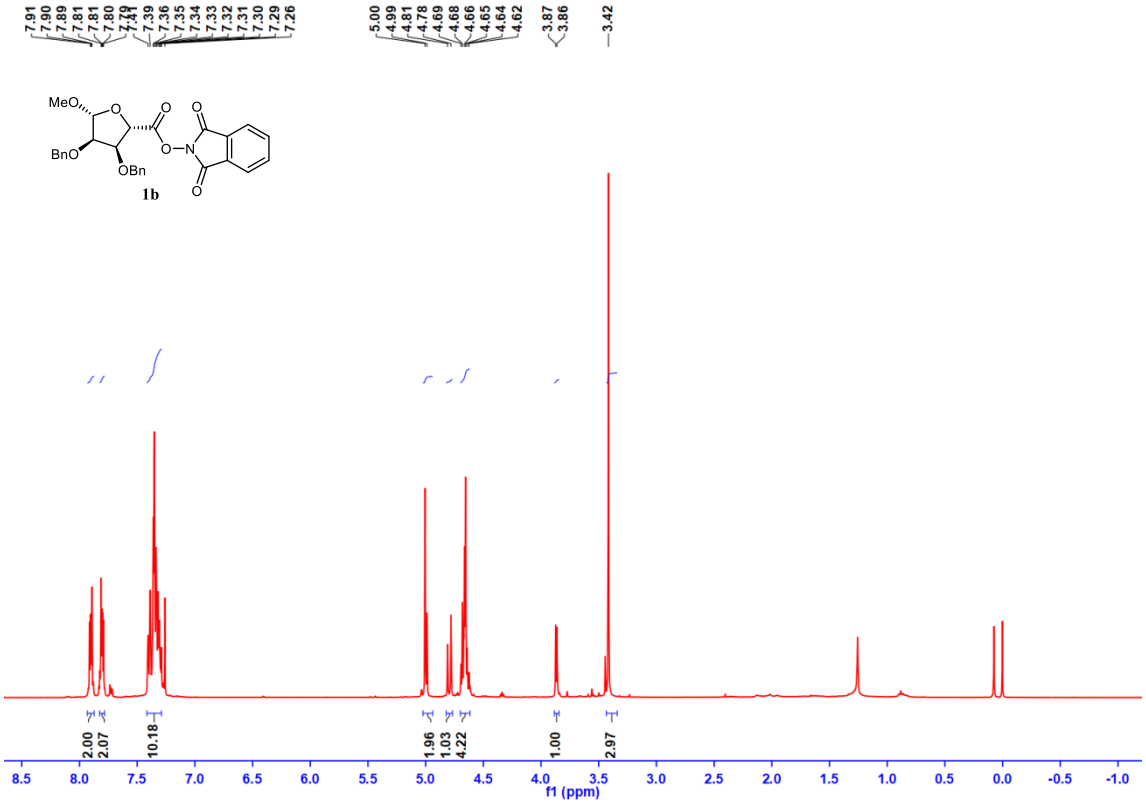
4-(((3aS,4R,6R,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)thio)phenyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (3ah): Pale oil; 22.1 mg; 43% yield; >20:1 d.r.. **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.81 – 7.69 (m, 3H), 7.47 (dd, *J* = 14.9, 8.8 Hz, 3H), 7.21 – 7.10 (m, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 5.53 (s, 1H), 5.09 (s, 1H), 4.89 (d, *J* = 5.6 Hz, 1H), 4.70 (d, *J* = 5.7 Hz, 1H), 4.09 (q, *J* = 7.0 Hz, 1H), 3.93 (s, 3H), 3.38 (s, 3H), 1.69 (d, *J* = 7.1 Hz, 3H), 1.45 (s, 3H), 1.31 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 172.0, 156.8, 149.1, 133.9, 132.8, 131.3, 131.1, 128.3, 128.0, 126.4, 125.1, 125.0, 121.1, 118.1, 112.0, 109.4, 104.6, 92.5, 84.8, 83.6, 54.3, 54.2, 44.5, 25.4, 24.1, 17.4. HRMS (EI) m/z $[M + Na]^+$ calculated for 510.1712, found 510.1711.

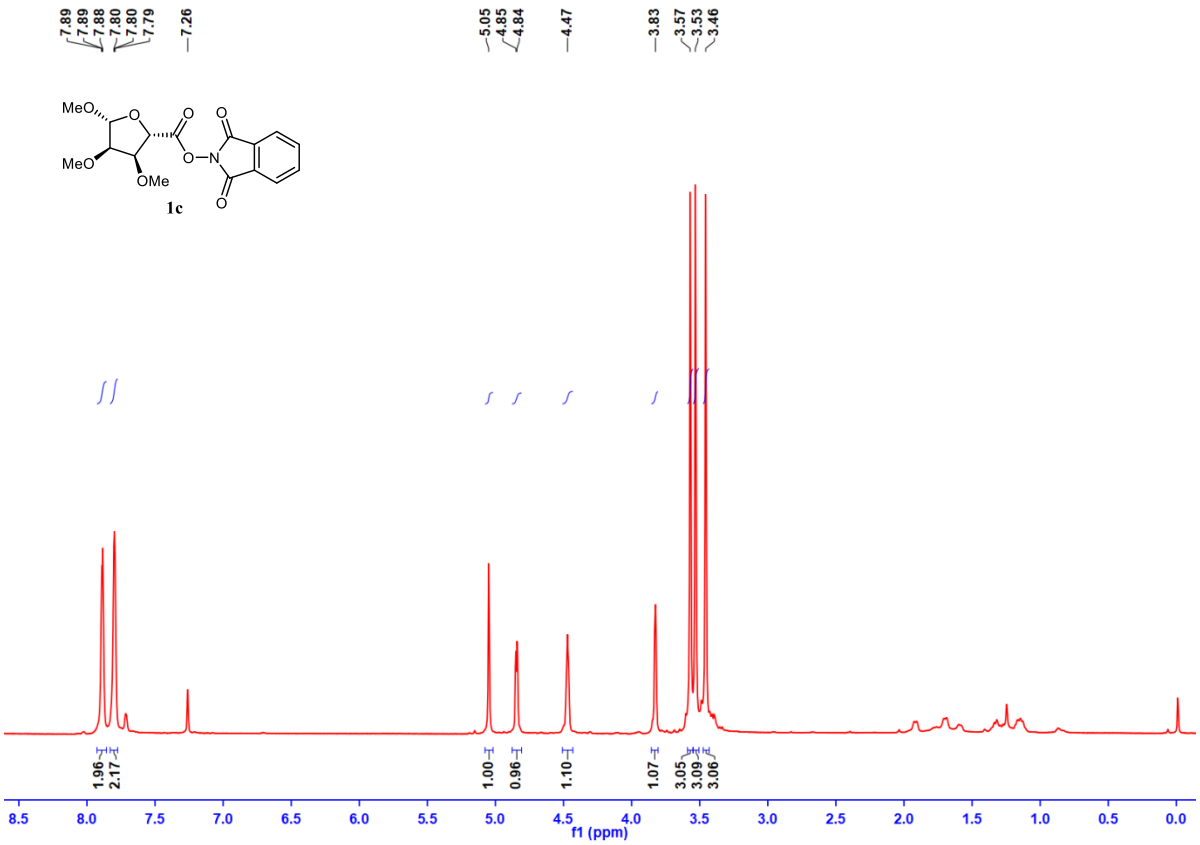


4-(((3aS,4R,6R,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)thio)phenyl
(4R)-4-((5S,8R,9S,10S,13R,14S)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (3ai): White solid; 43.0 mg; 63% yield; >20:1 d.r.; M.p. 204-205 °C **^{1}H-NMR (400 MHz, Chloroform-*d*)** δ 7.49 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 5.55 (s, 1H), 5.09 (s, 1H), 4.90 (d, *J* = 5.7 Hz, 1H), 4.70 (d, *J* = 5.8 Hz, 1H), 3.39 (s, 3H), 2.89 (ddd, *J* = 17.7, 13.1, 6.3 Hz, 3H), 2.63 (ddd, *J* = 14.6, 9.0, 5.3 Hz, 1H), 2.50 (dt, *J* = 16.0, 8.0 Hz, 1H), 2.33 (ddt, *J* = 13.8, 10.1, 5.3 Hz, 4H), 2.26 – 2.09 (m, 5H), 2.08 – 1.80 (m, 7H), 1.73 – 1.47 (m, 3H), 1.45 (s, 3H), 1.39 (s, 3H), 1.30 (s, 3H), 1.08 (s, 3H), 0.90 (d, *J* = 6.6 Hz, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 210.9, 208.0, 207.6, 171.3, 149.0, 131.3, 131.2, 121.3, 112.0, 109.4, 92.6, 84.8, 83.6, 55.9, 54.2, 50.7, 48.0, 45.8, 44.6, 44.5, 44.0, 41.8, 37.6, 35.5, 35.0, 34.5, 34.3, 30.5, 29.3, 26.6, 25.4, 24.1, 20.9, 17.7, 10.9. HRMS (EI) m/z $[M + Na]^+$ calculated for 705.3068, found 705.3066.

9. NMR spectra



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3.53
3.46
MeO
MeO
OMe
1c
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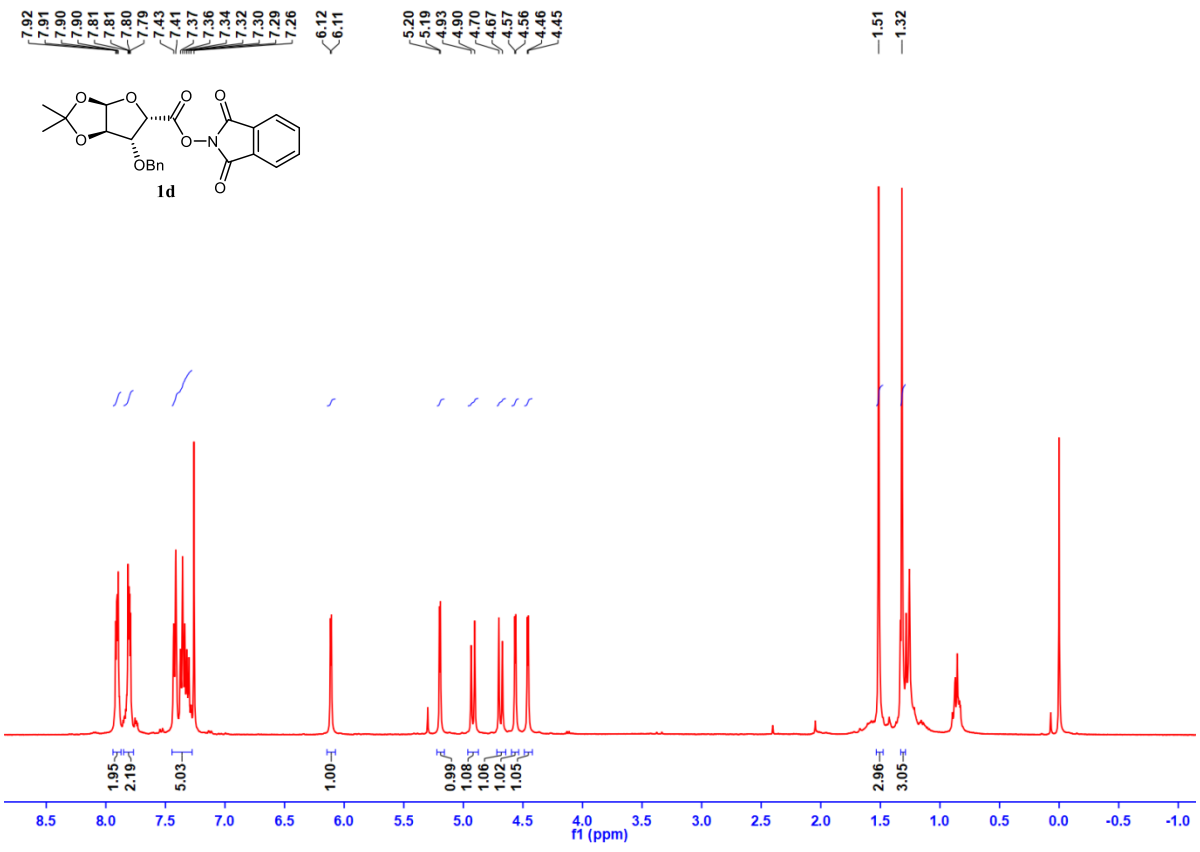
3.06
f1 (ppm)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7.26
6.12
6.11
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5.19
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4.90
4.70
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4.57
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1.51
1.32
OBn
1d
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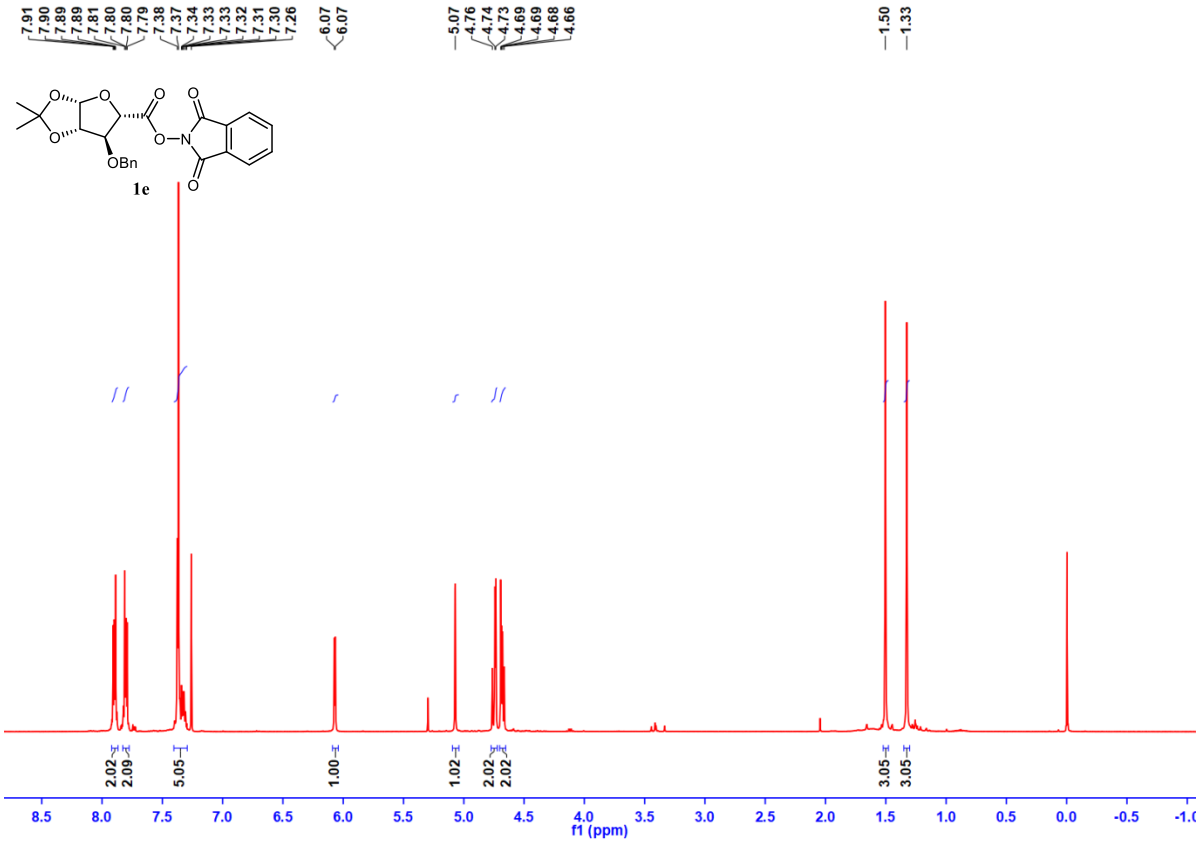
f1 (ppm)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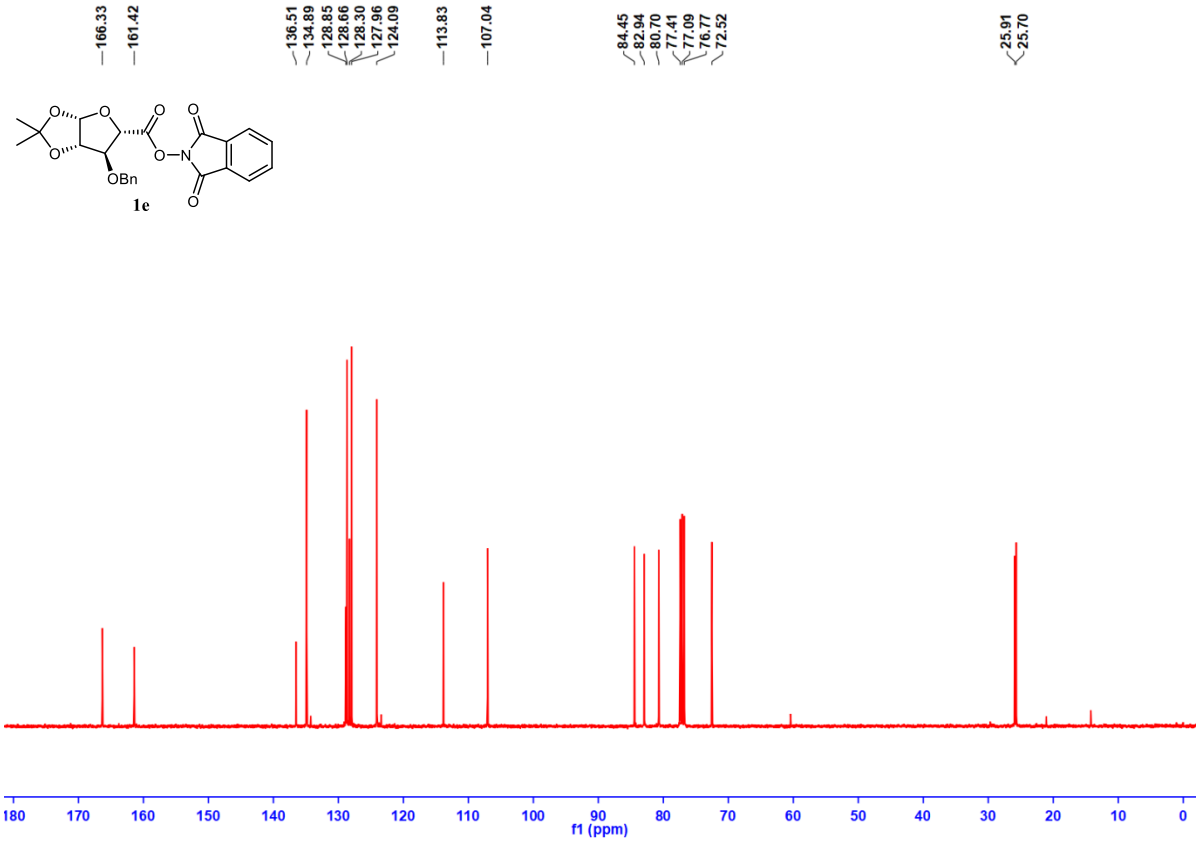
f1 (ppm)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76.77
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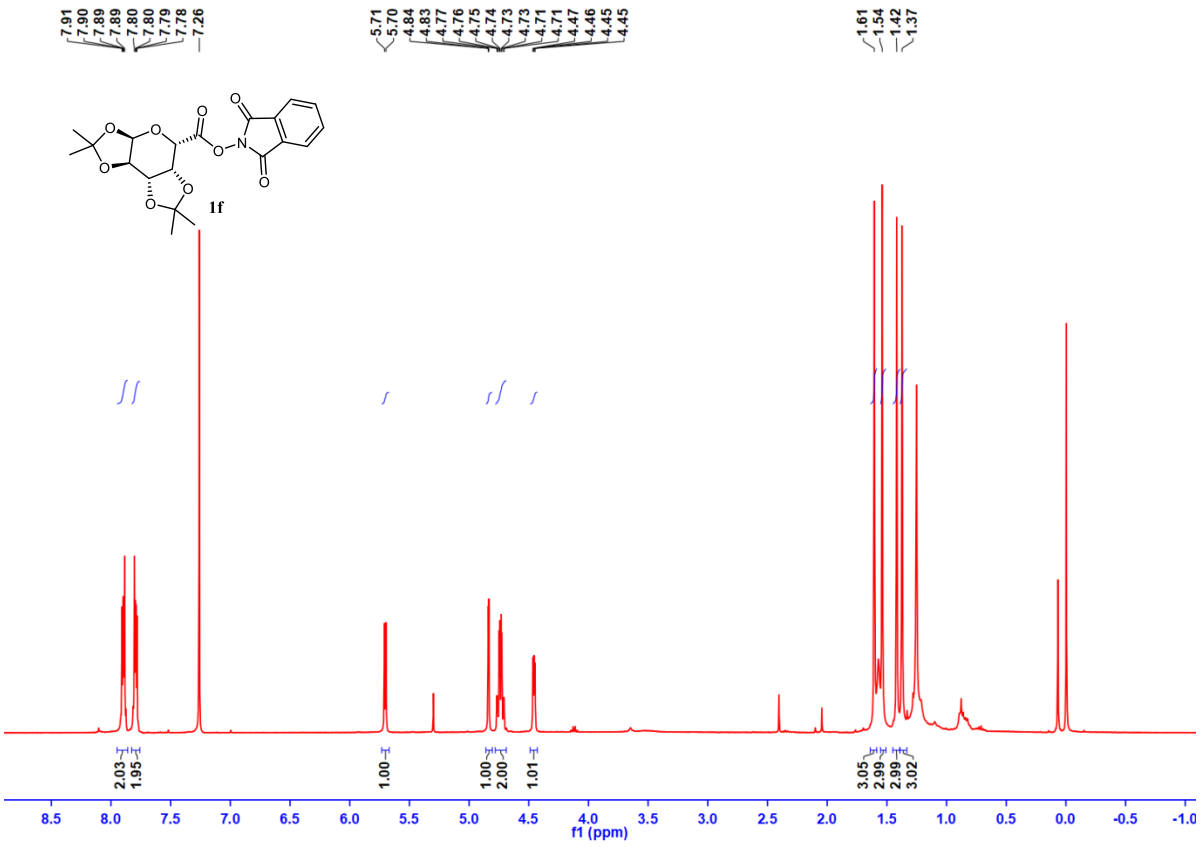
25.91
25.70
OBn
1e
f1 (ppm)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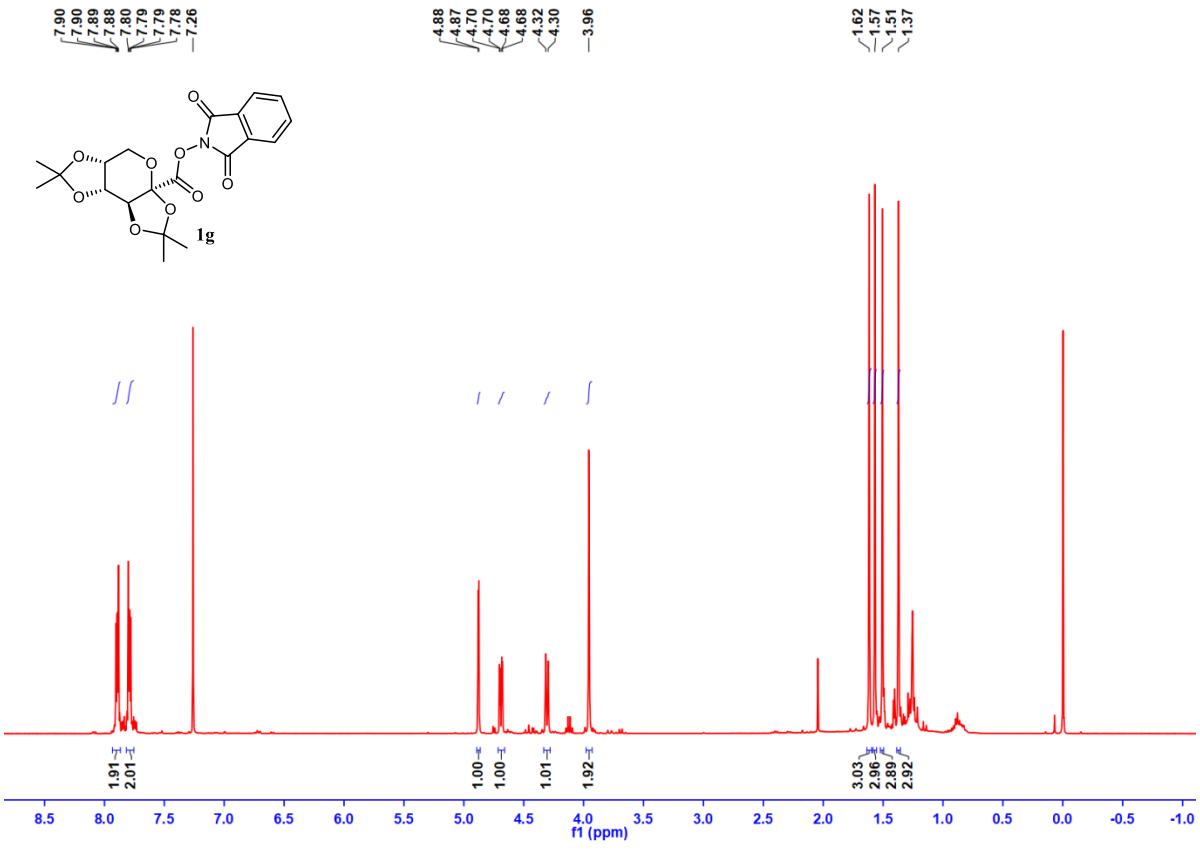
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4.30
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1.57
1.51
1.37
1g
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1.00
1.00
1.01
1.92
3.03
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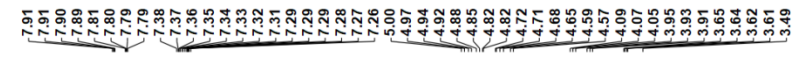
f1 (ppm)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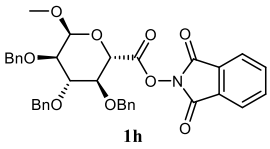
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OBn
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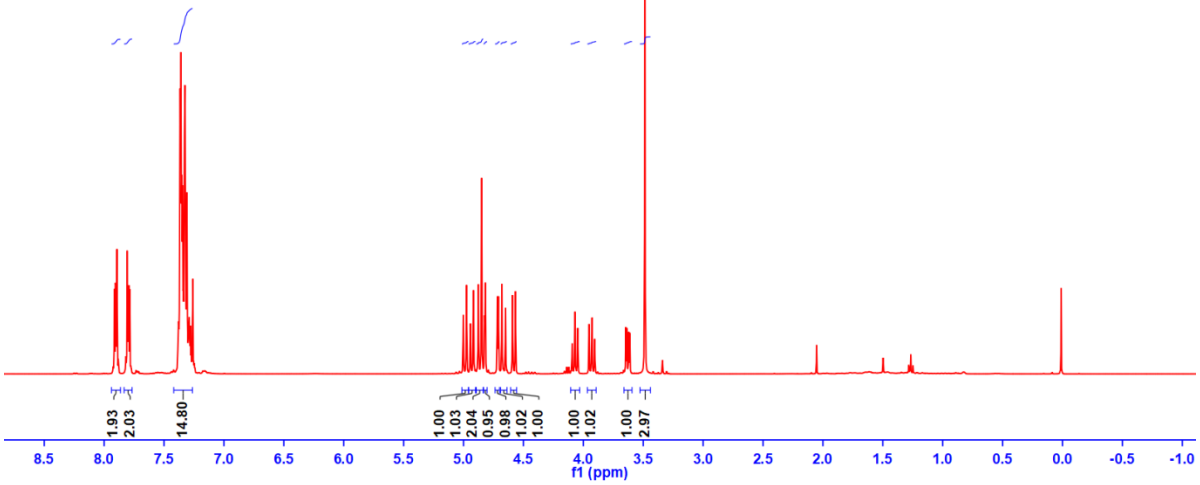
O
O
N

1h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7.0
6.5
6.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


7.91
7.91
7.90
7.89
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7.81
7.80
7.79
7.26
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4.94
4.43
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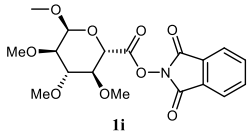
3.28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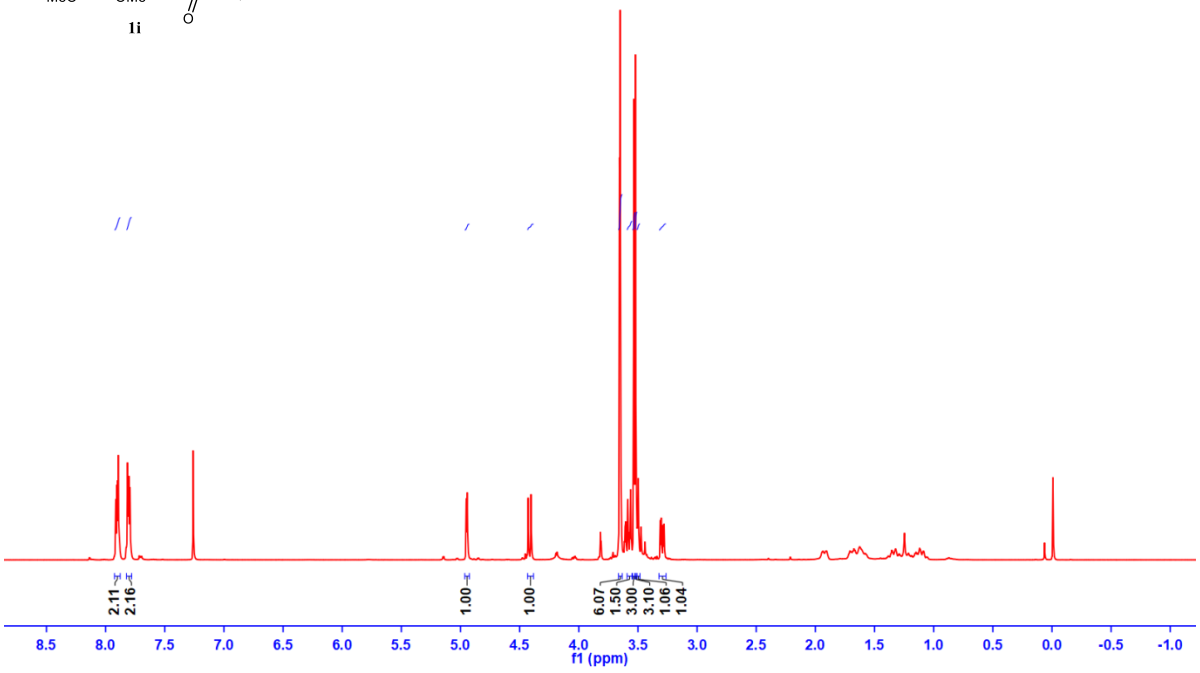
O
N

1i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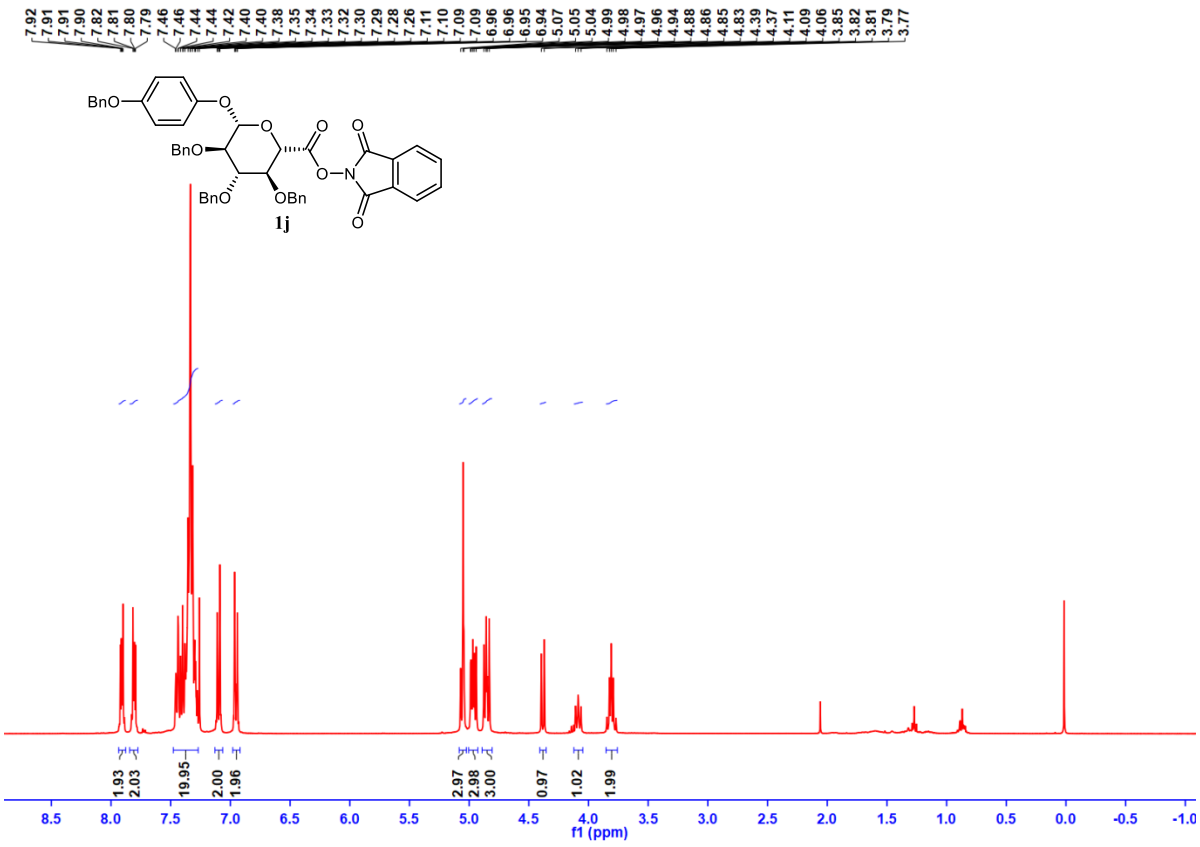
f1 (ppm)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BnO
BnO
BnO
OBn
1j
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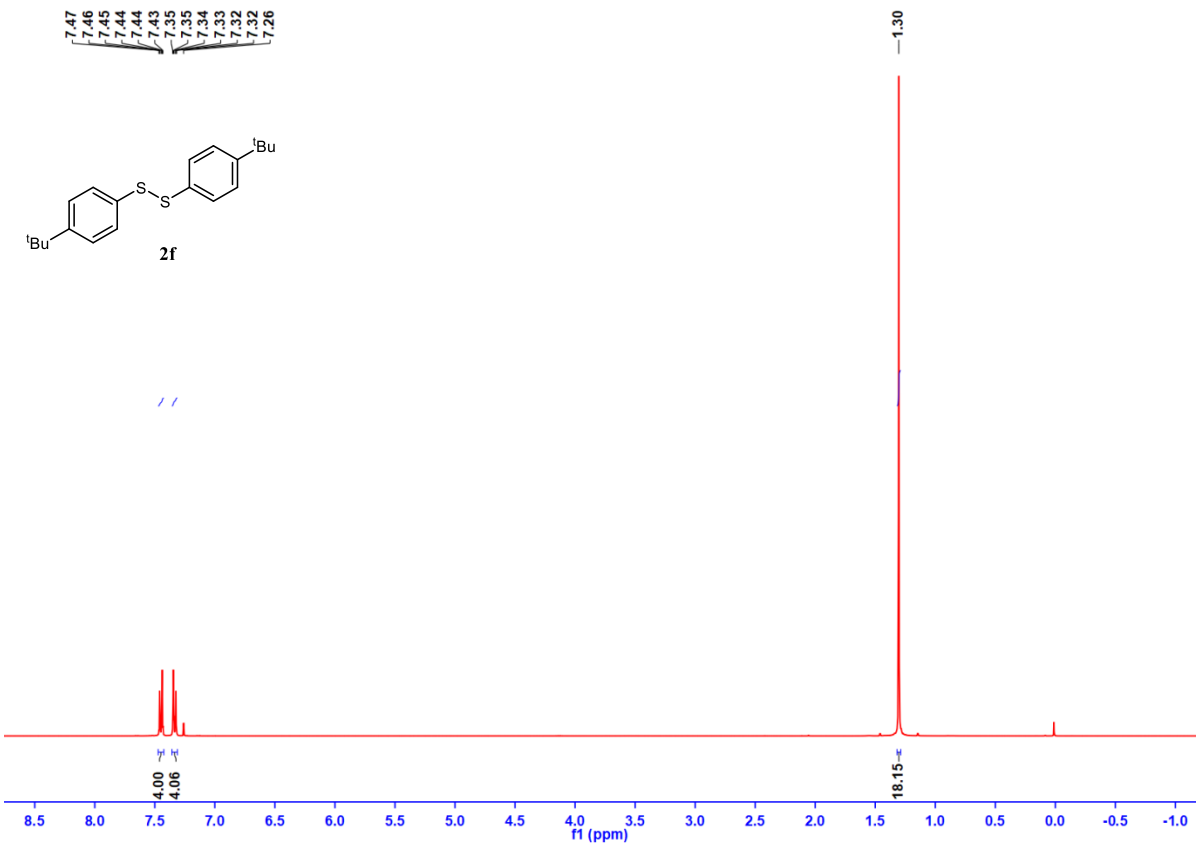
f1 (ppm)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tBu
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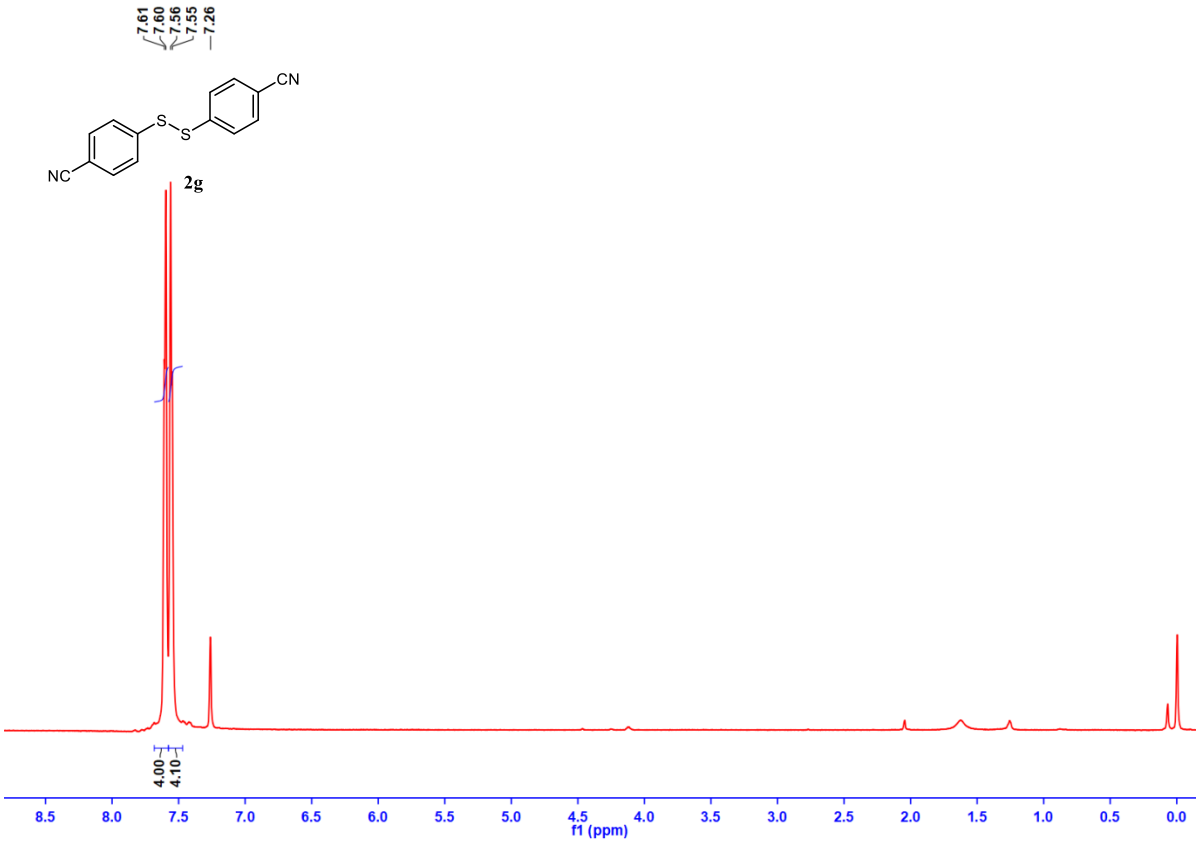
f1 (ppm)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7.0
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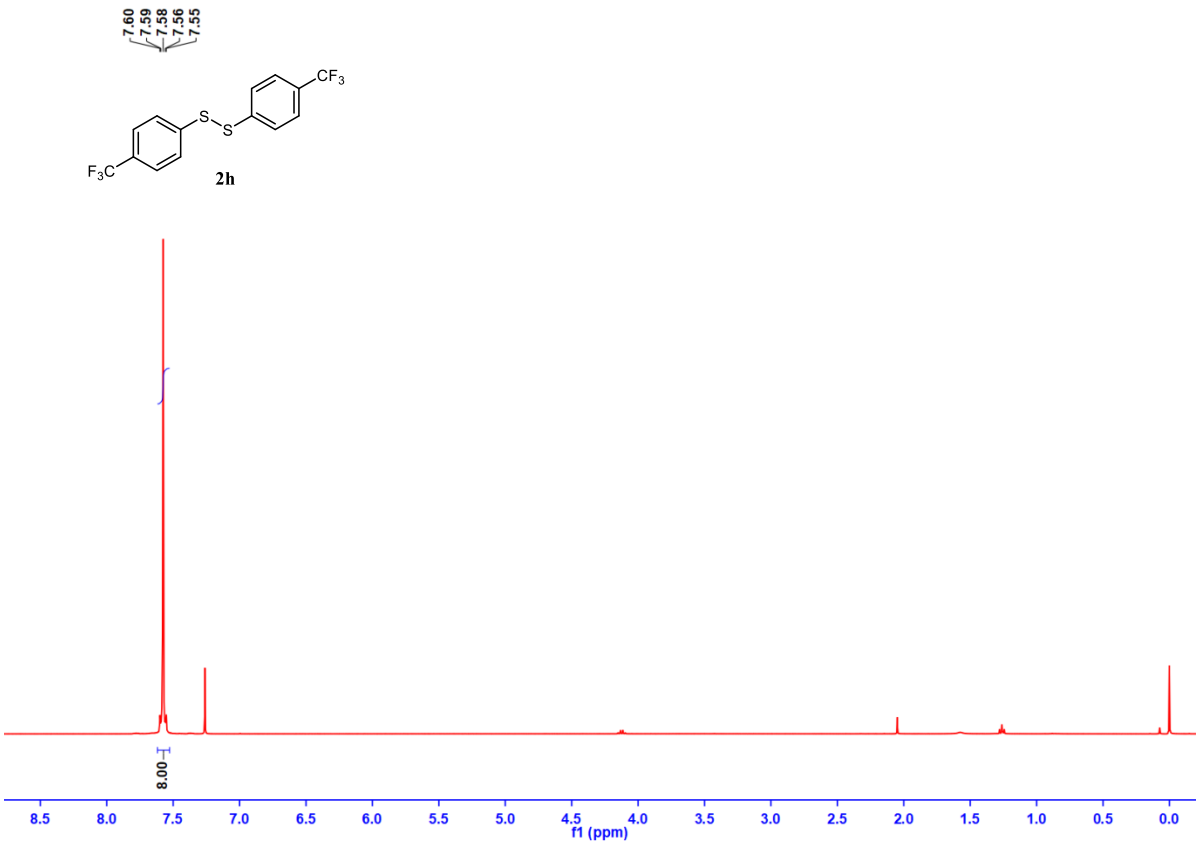
f1 (ppm)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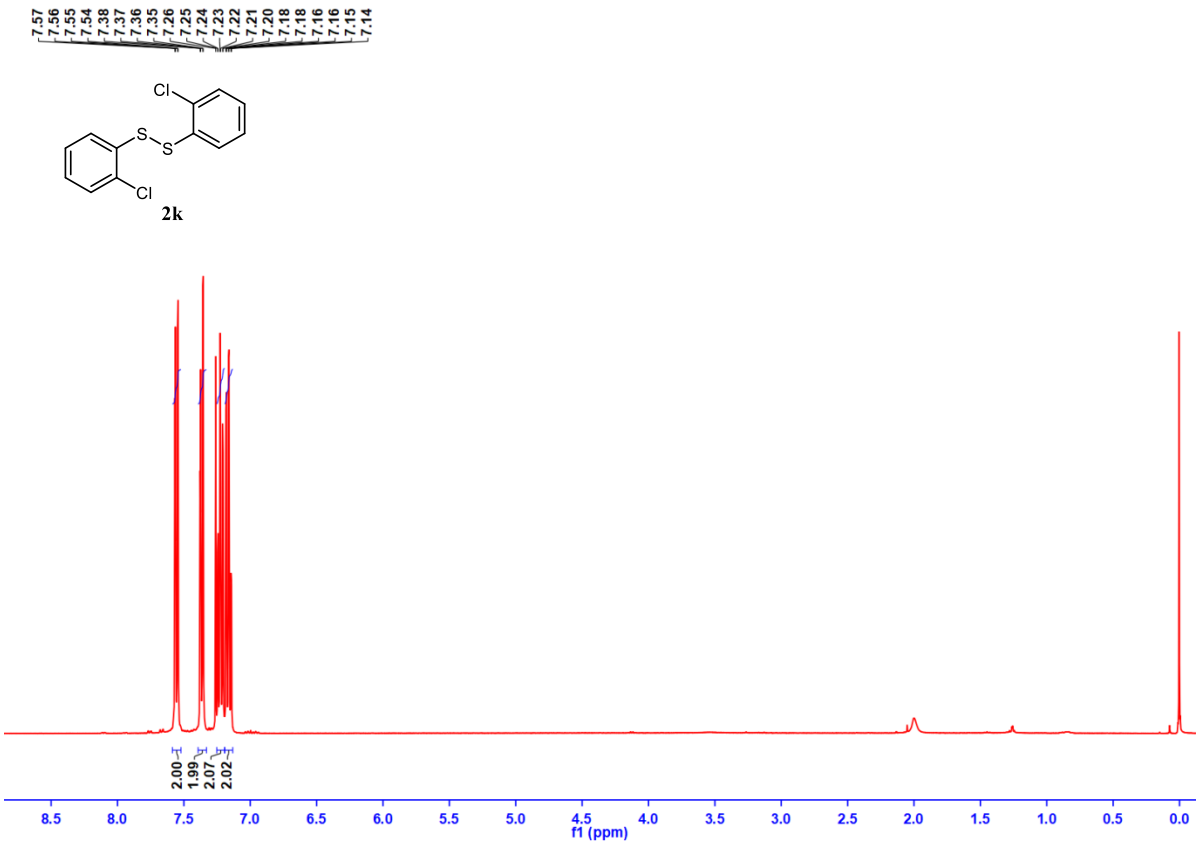
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7.18
7.18
7.16
7.16
7.15
7.14
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S
S
Cl
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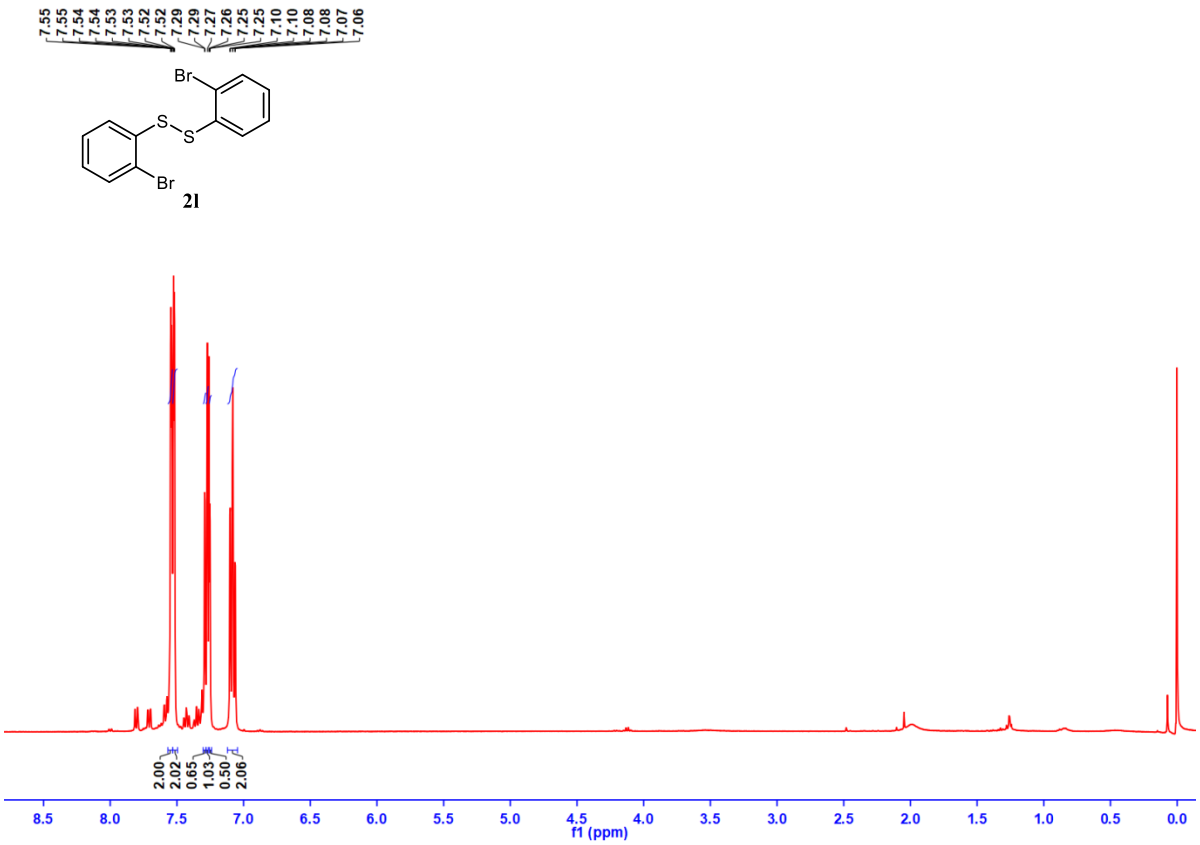
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7.25
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7.10
7.08
7.08
7.07
7.06
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S
S
Br
2l
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2.02
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0.50
2.06
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7.5
7.0
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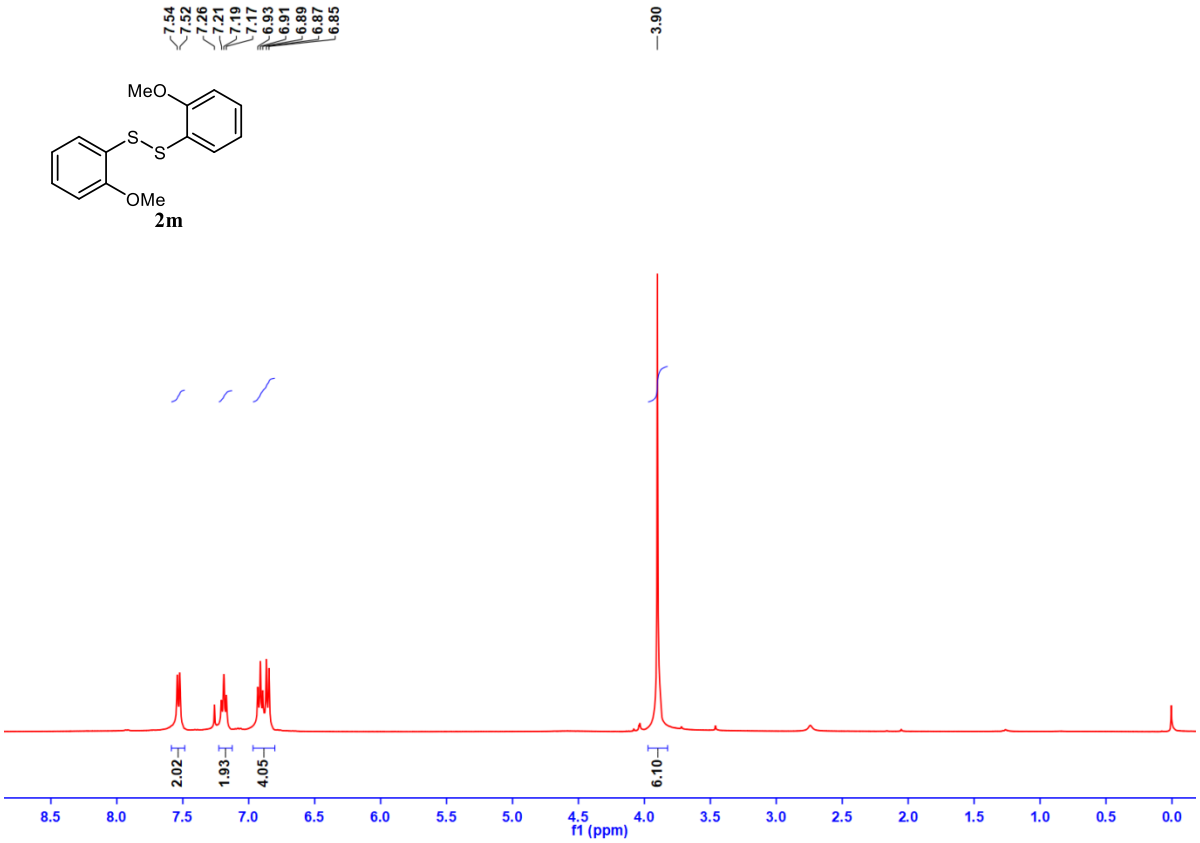
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S
S
OMe
2m
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4.05
6.10
8.5
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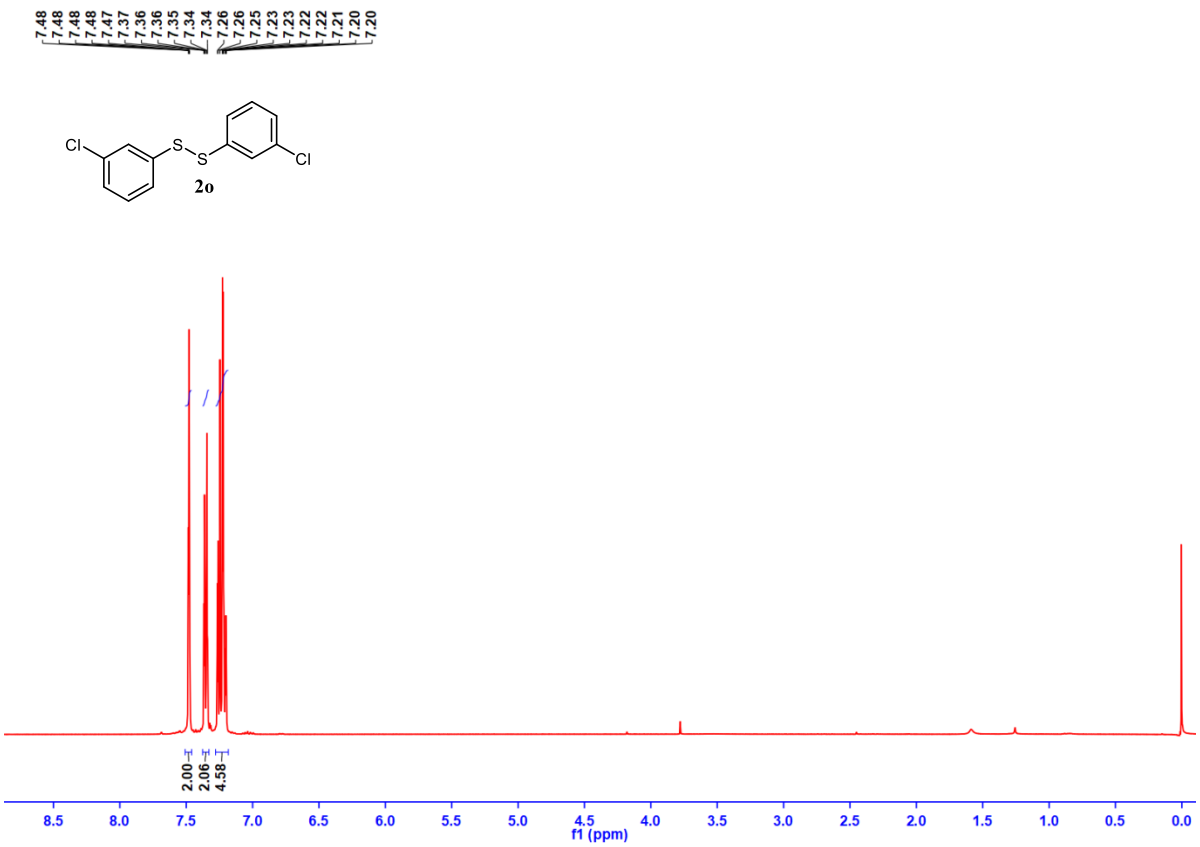
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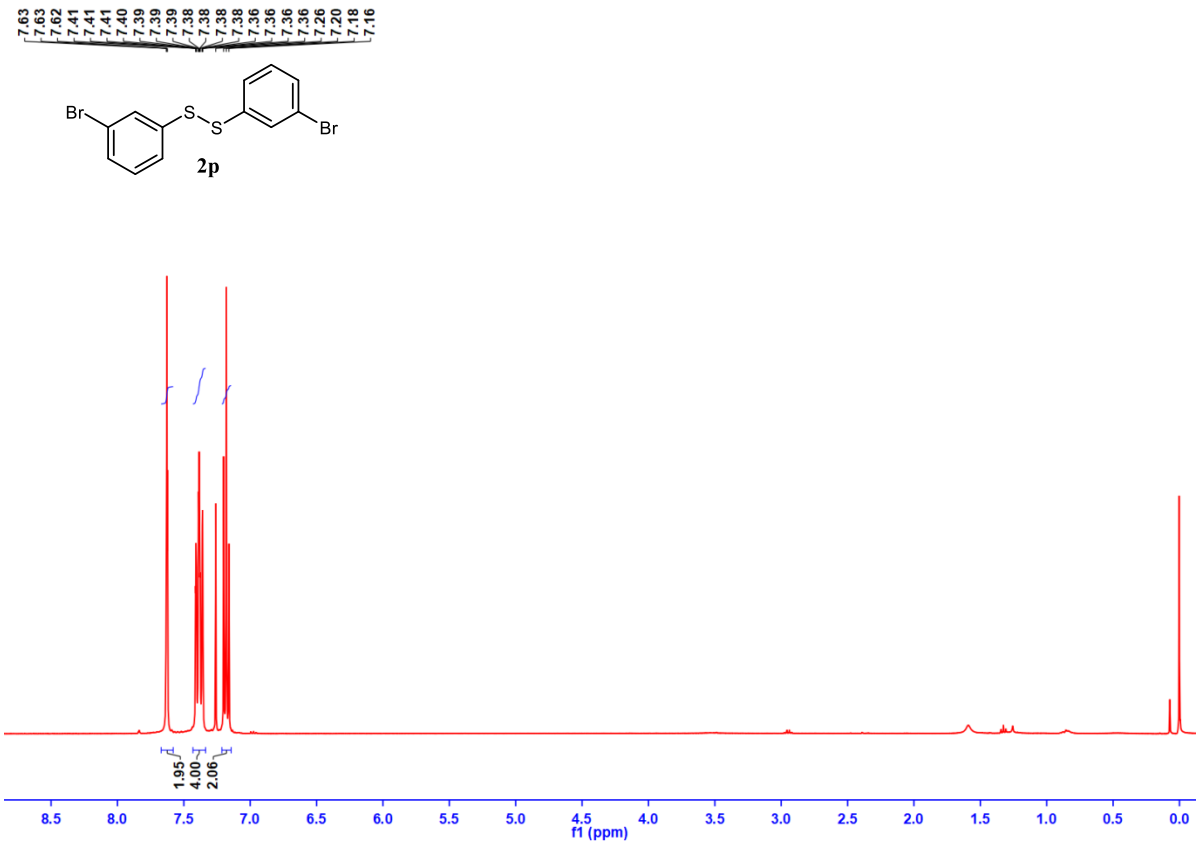
f1 (ppm)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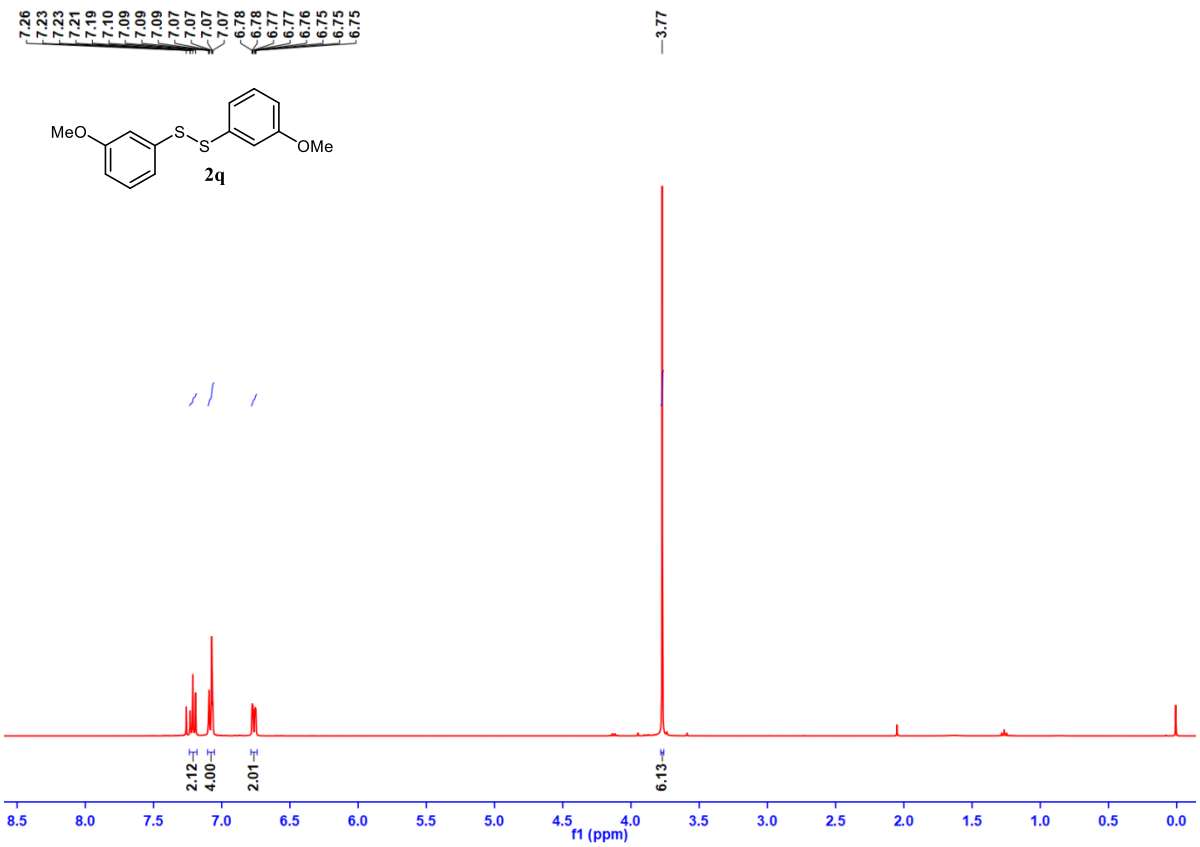
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S
OMe
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6.0
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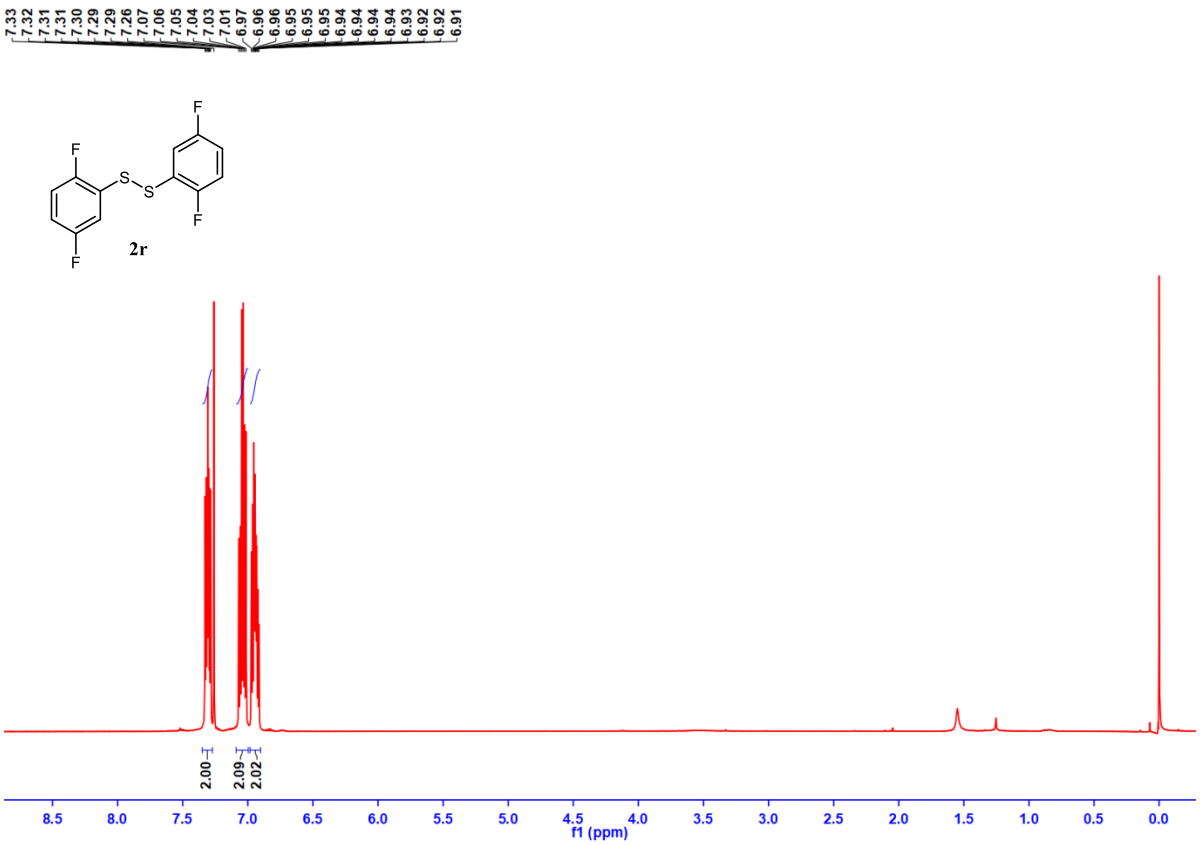
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6.91
F
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S
F
F
2r
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2.09
2.02
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
1.5
1.0
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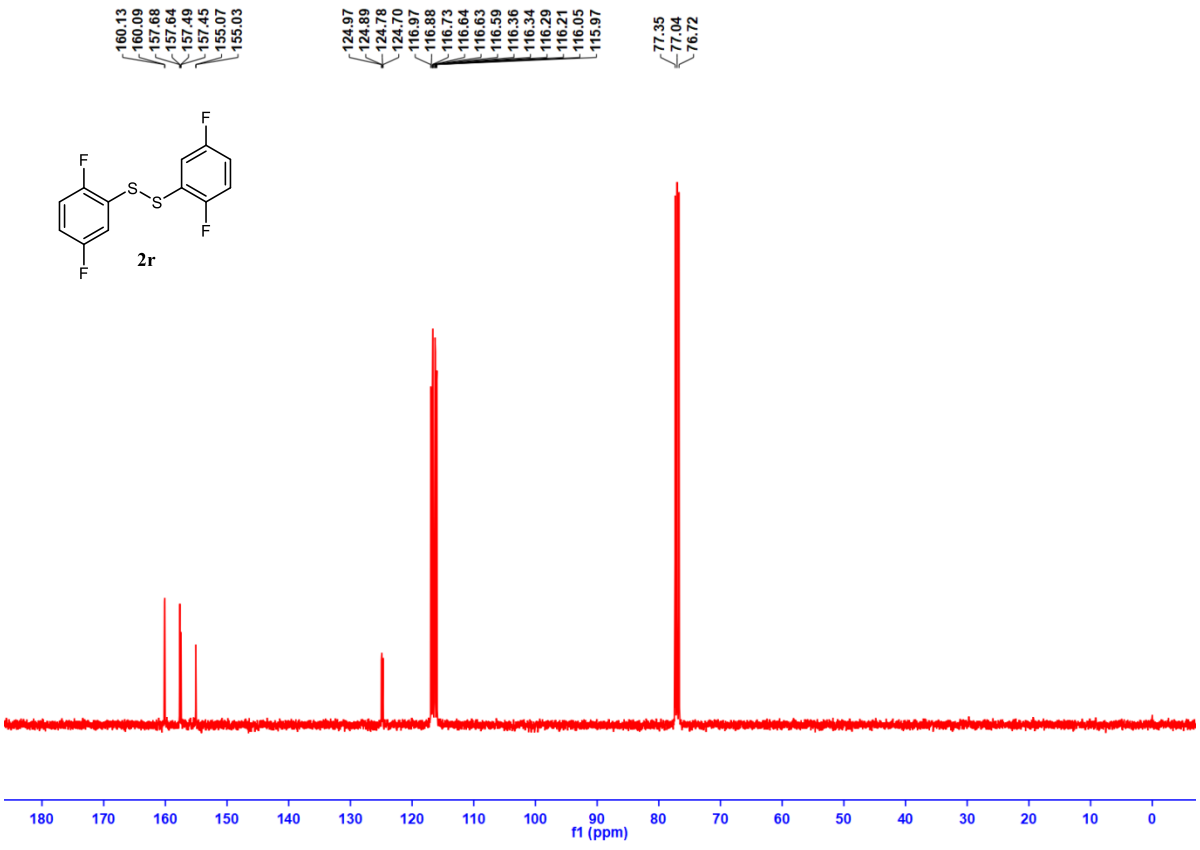
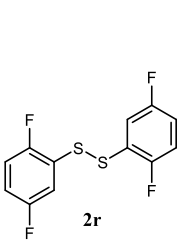
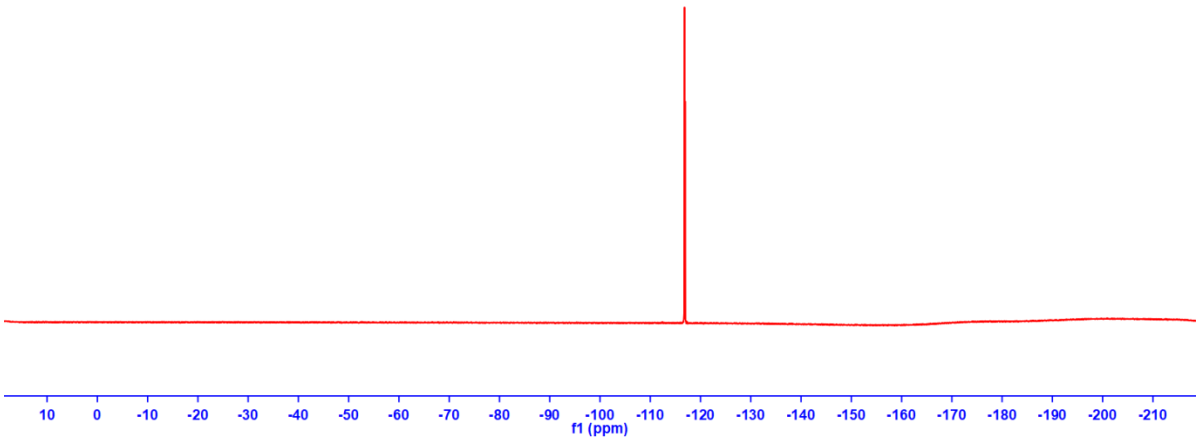
0.0
f1 (ppm)

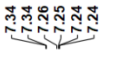

160.13
160.09
157.68
157.64
157.49
157.45
155.07
155.03
124.97
124.89
124.78
124.70
116.97
116.88
116.73
116.64
116.63
116.59
116.36
116.34
116.29
116.21
116.05
115.97
77.35
77.04
76.72
F
F
S
S
F
F
2r
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

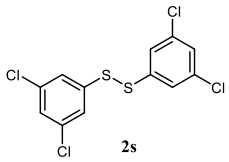

F
F
S
S
F
F

2r

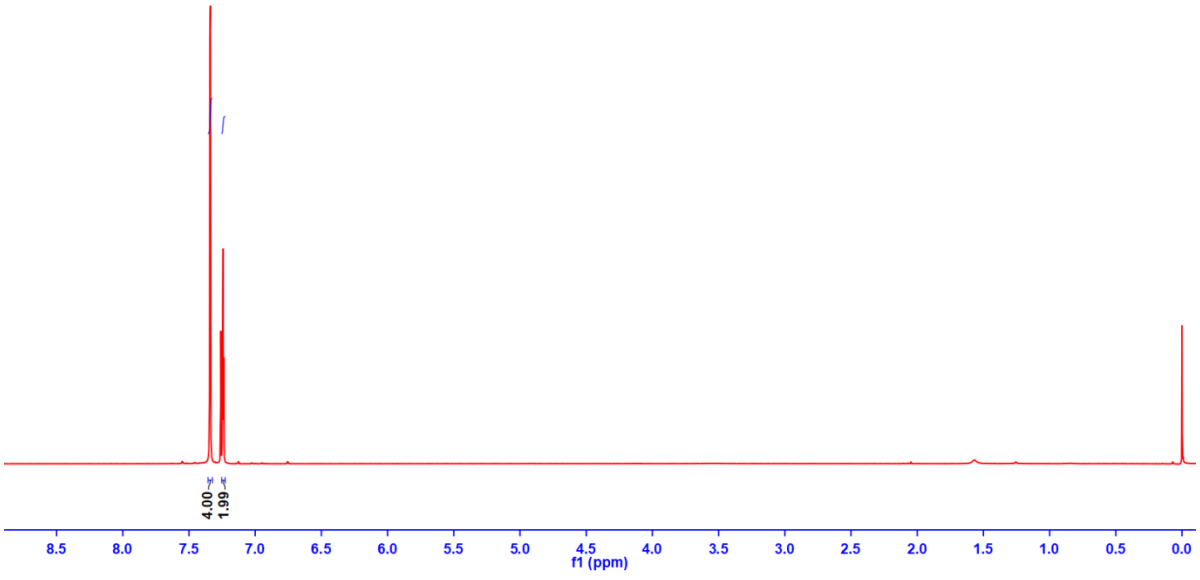

-116.73
-116.75
-116.75
-116.77
-116.78
-116.79
-116.80
-116.81
-116.82
-116.83
-116.90
-116.91
-116.92
-116.93
-116.93
-116.94
-116.94
-116.95
-116.95
-116.96
-116.96
-116.97
-116.98
-116.99
-117.00

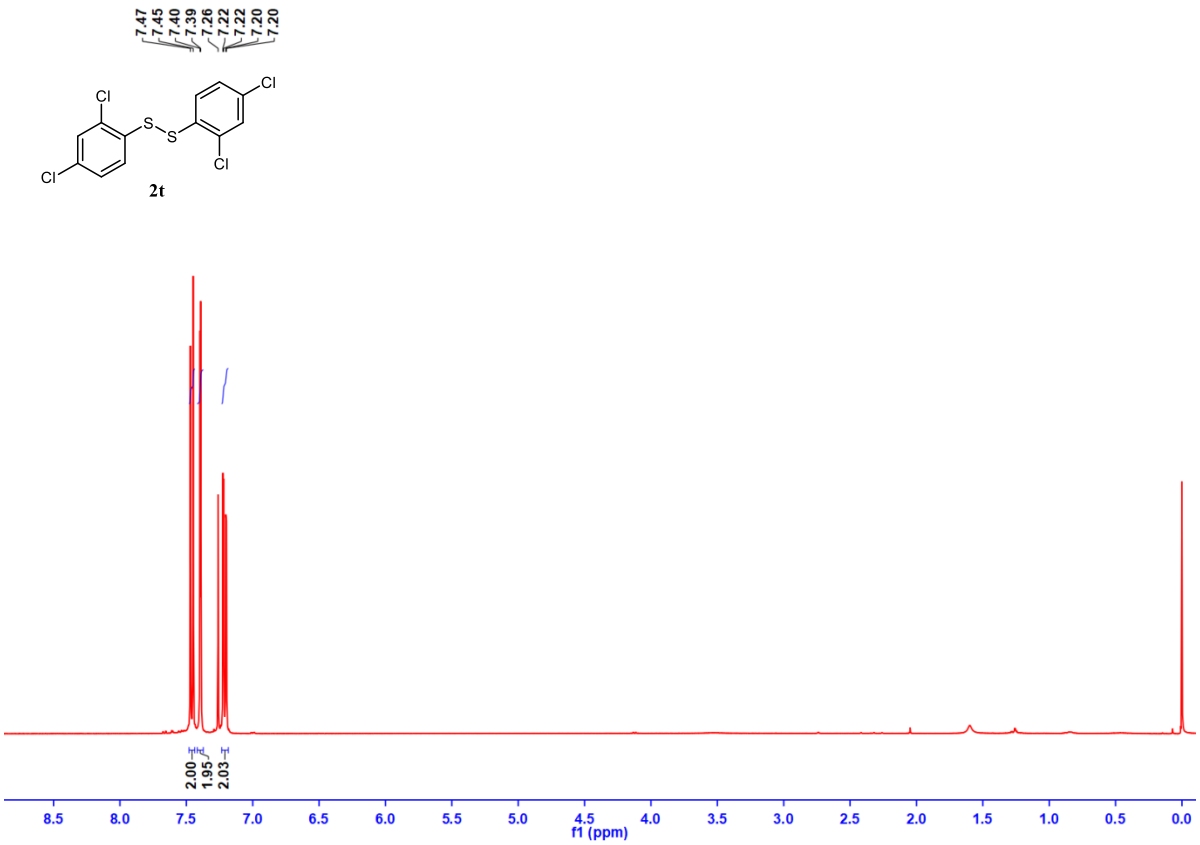

10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

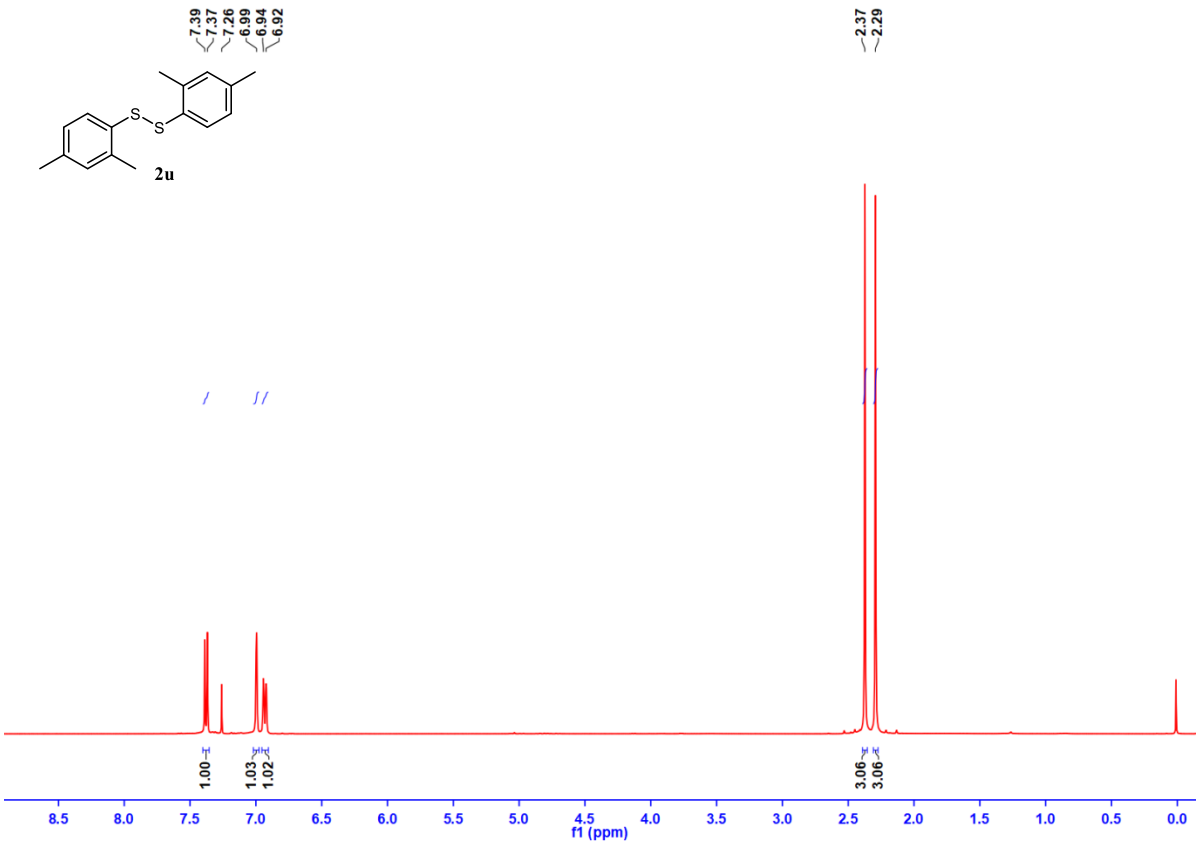

7.34
7.34
7.26
7.25
7.24
7.24

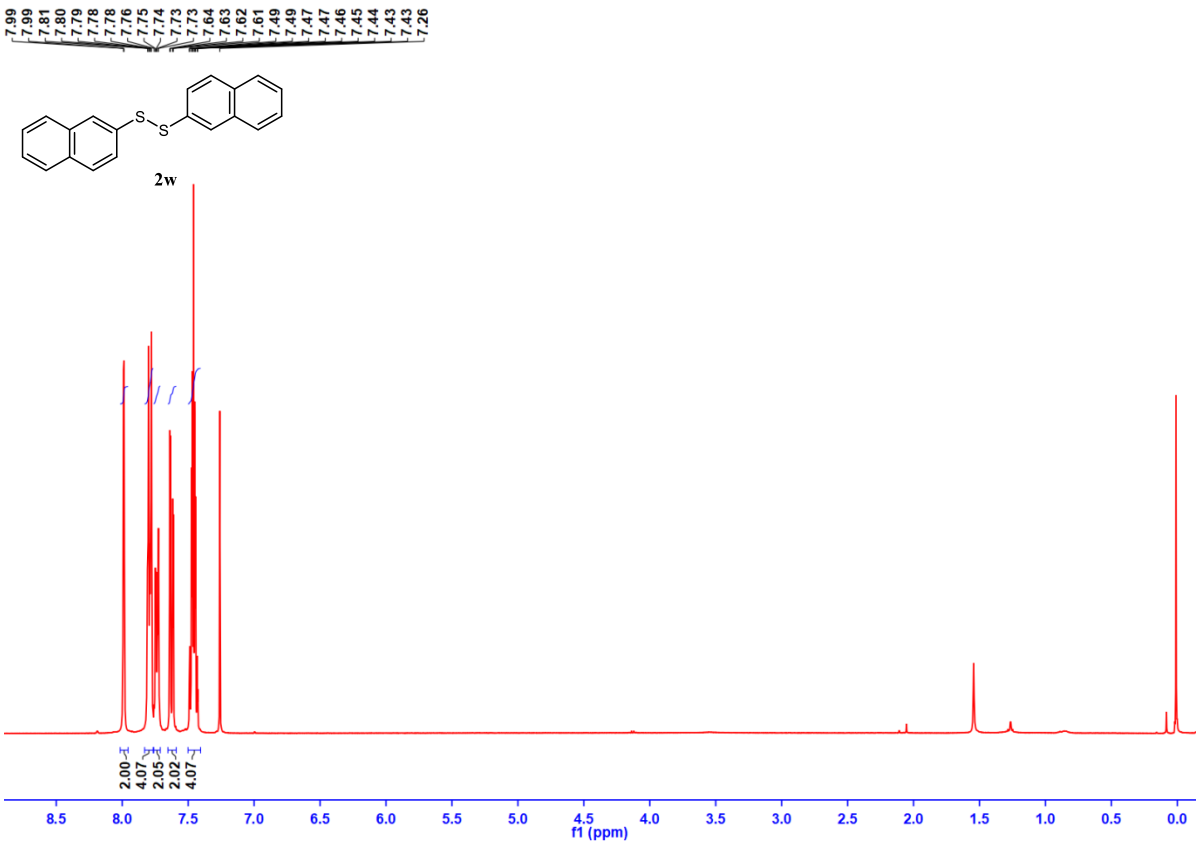

Cl
Cl
S
S
Cl
Cl

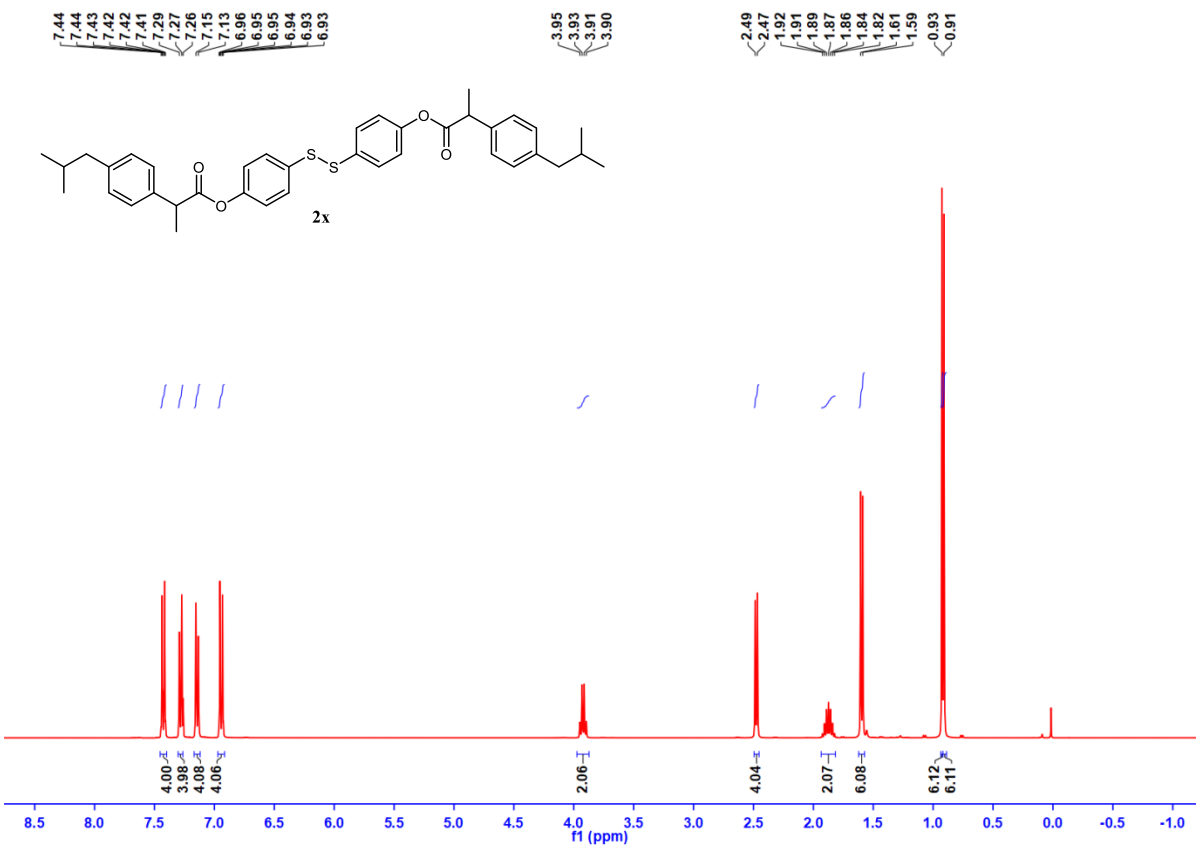
2s

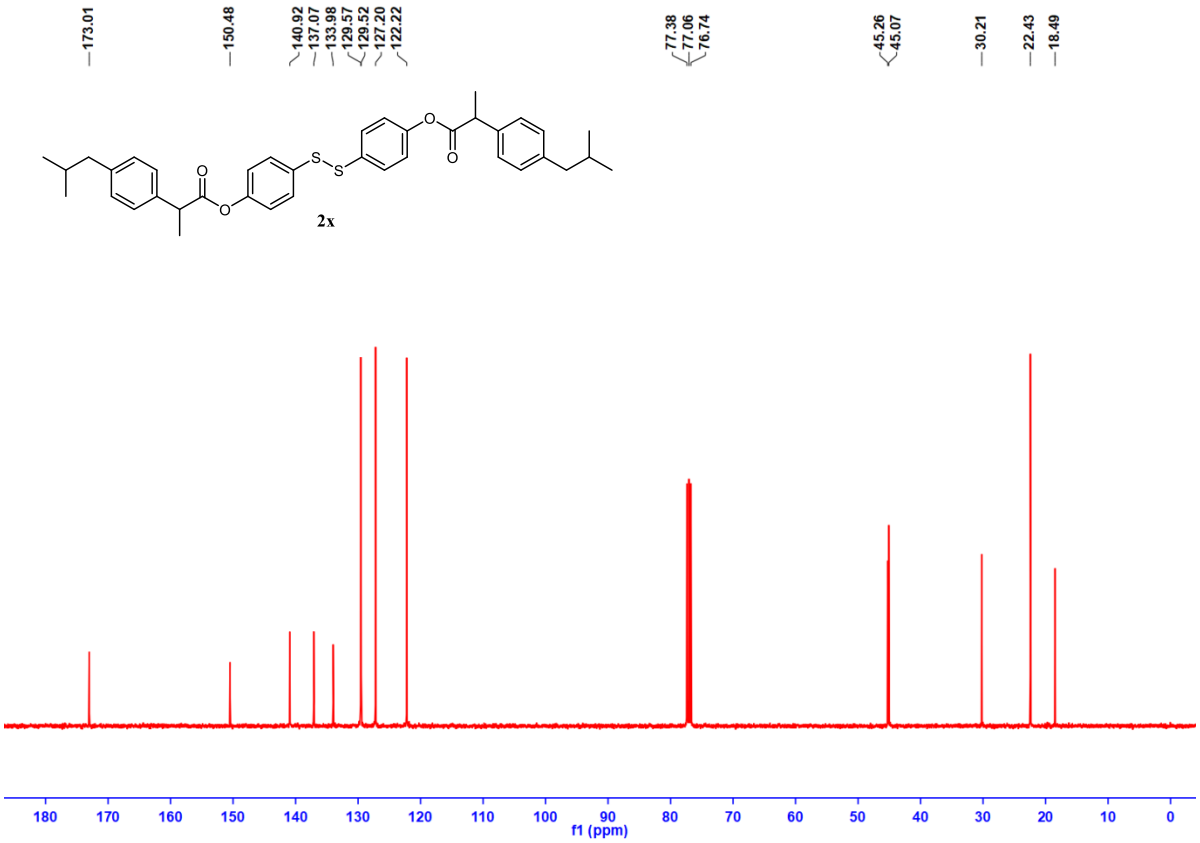

4.00
1.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

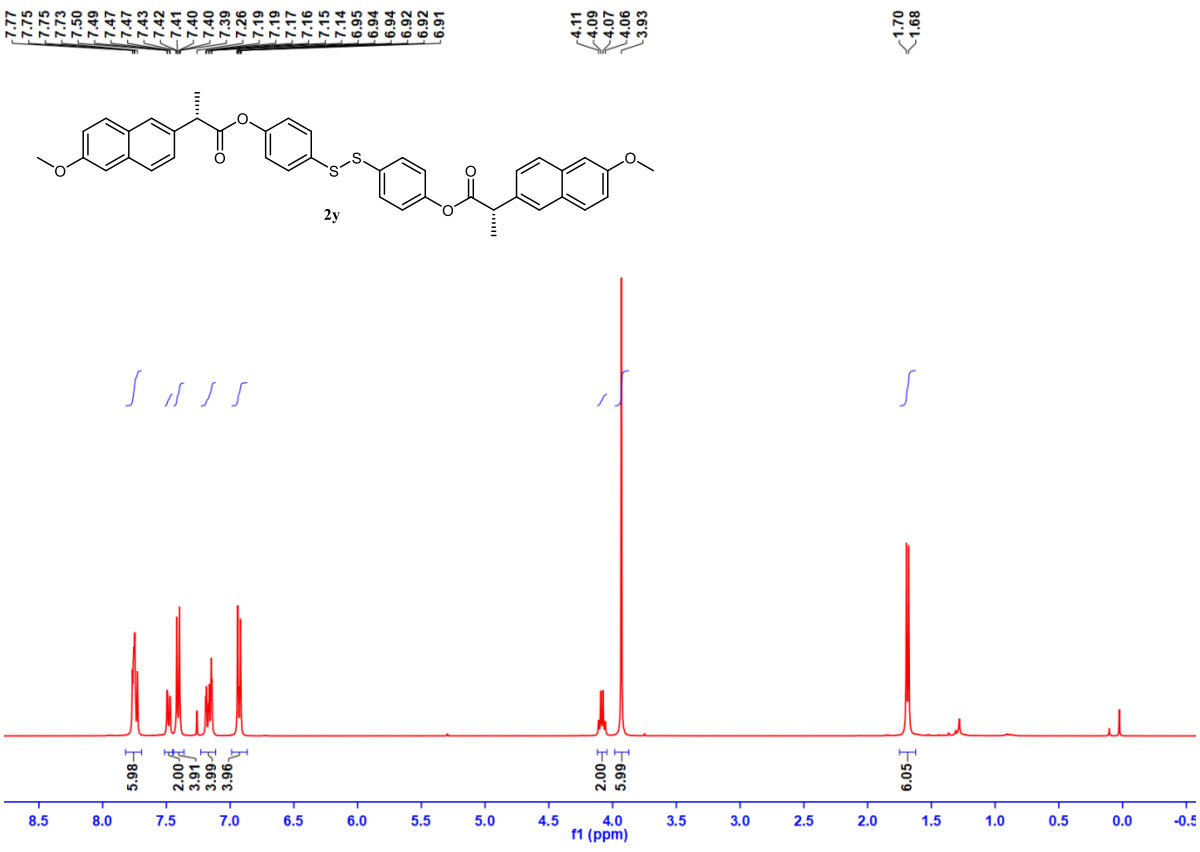

7.47
7.45
7.40
7.39
7.26
7.22
7.22
7.20
7.20
Cl
Cl
S
S
Cl
Cl
2t
2.00
1.95
2.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


7.39
7.37
7.26
6.99
6.94
6.92
2.37
2.29
S
S
2u
1.00
1.03
1.02
3.06
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)


7.99
7.99
7.81
7.80
7.79
7.78
7.78
7.76
7.75
7.74
7.73
7.73
7.64
7.63
7.62
7.61
7.49
7.49
7.47
7.47
7.46
7.45
7.44
7.43
7.43
7.26
S
S
2w
2.00
4.07
2.05
2.02
4.07
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
f1 (ppm)


7.44
7.44
7.43
7.42
7.42
7.41
7.29
7.27
7.26
7.15
7.13
6.96
6.95
6.95
6.94
6.93
6.93
3.95
3.93
3.91
3.90
2.49
2.47
1.92
1.91
1.89
1.87
1.86
1.84
1.82
1.61
1.59
0.93
0.91
O
O
O
O
S
S
2x
4.00
3.98
4.08
4.06
2.06
4.04
2.07
6.08
6.12
6.11
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)


173.01
150.48
140.92
137.07
133.98
129.57
129.52
127.20
122.22
77.38
77.06
76.74
45.26
45.07
30.21
22.43
18.49
2x
f1 (ppm)


7.77
7.75
7.75
7.73
7.50
7.49
7.47
7.47
7.43
7.42
7.41
7.40
7.40
7.39
7.26
7.19
7.19
7.17
7.16
7.15
7.14
6.95
6.94
6.94
6.92
6.92
6.91
4.11
4.09
4.07
4.06
3.93
1.70
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5.98
2.00
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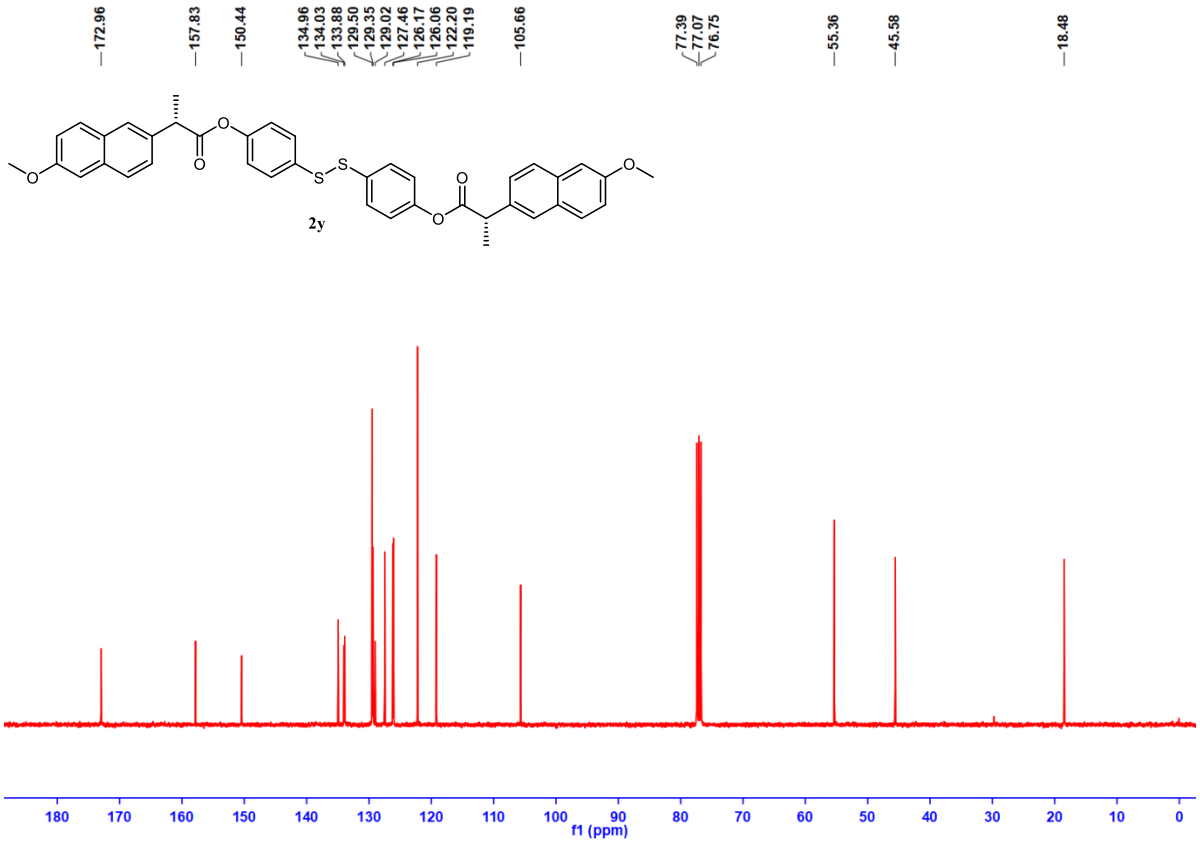
3.99
3.96
2.00
5.99
6.05
f1 (ppm)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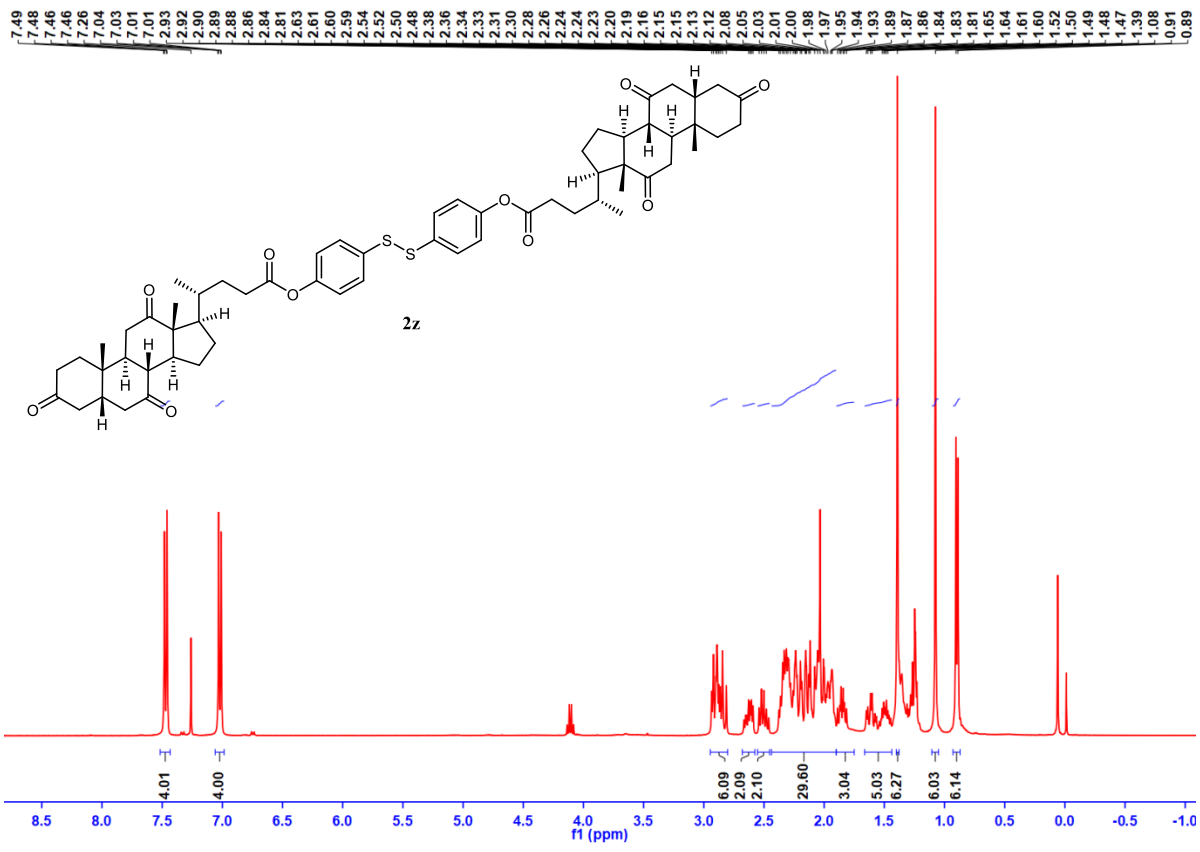
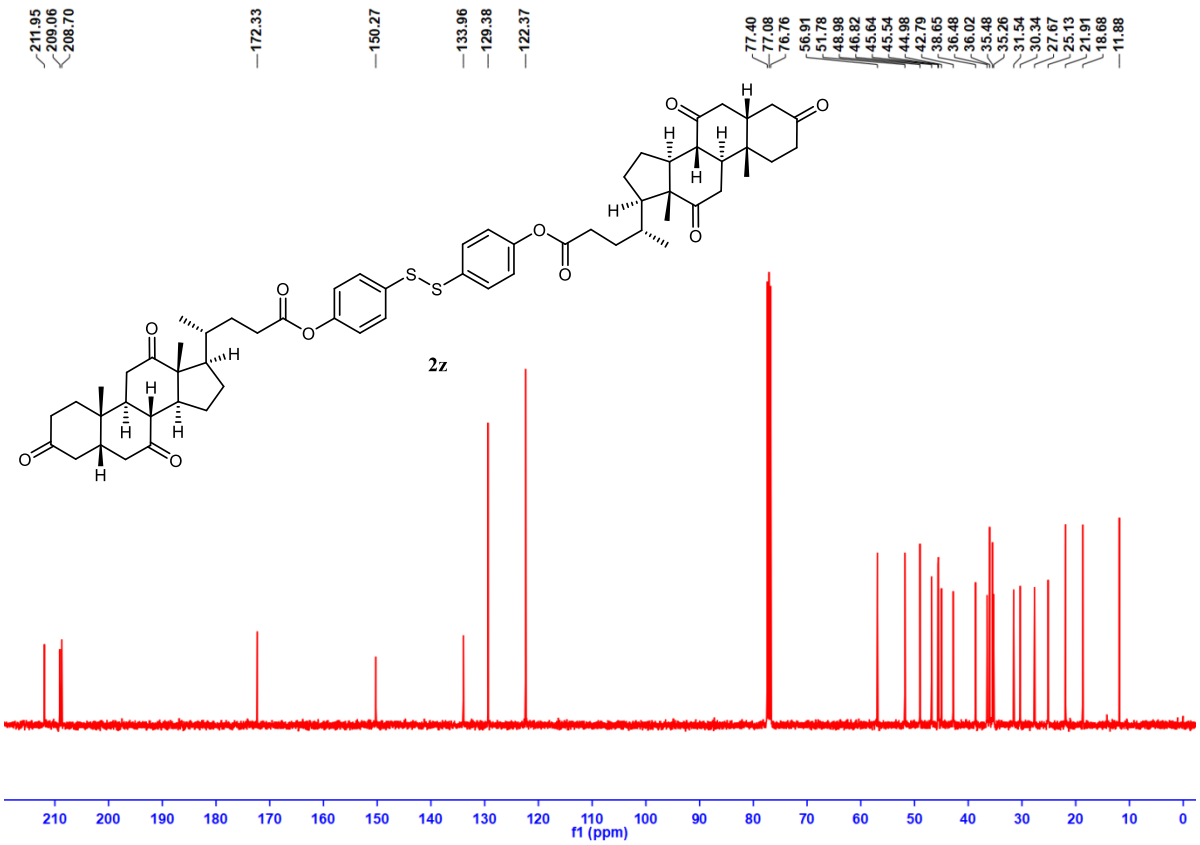
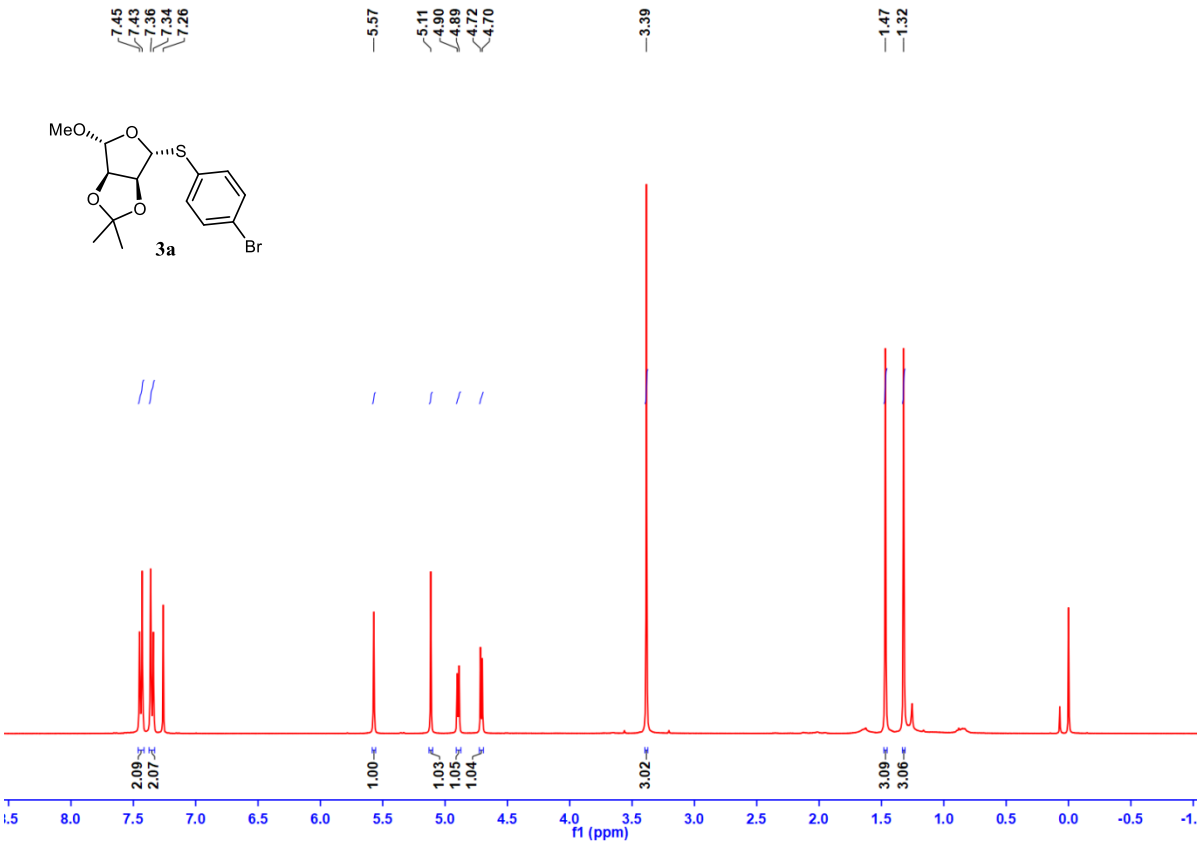
157.83
150.44
134.96
134.03
133.88
129.50
129.35
129.02
127.46
126.17
126.06
122.20
119.19
105.66
77.39
77.07
76.75
55.36
45.58
18.48
2y
f1 (ppm)


2z
4.01
4.00
6.09
2.09
2.10
29.60
3.04
5.03
6.27
6.03
6.14
f1 (ppm)


211.95
209.06
208.70
172.33
150.27
133.96
129.38
122.37
77.40
77.08
76.76
56.91
51.78
48.98
46.82
45.64
45.54
44.98
42.79
38.65
36.48
36.02
35.48
35.26
31.54
30.34
27.67
25.13
21.91
18.68
11.88
2z
f1 (ppm)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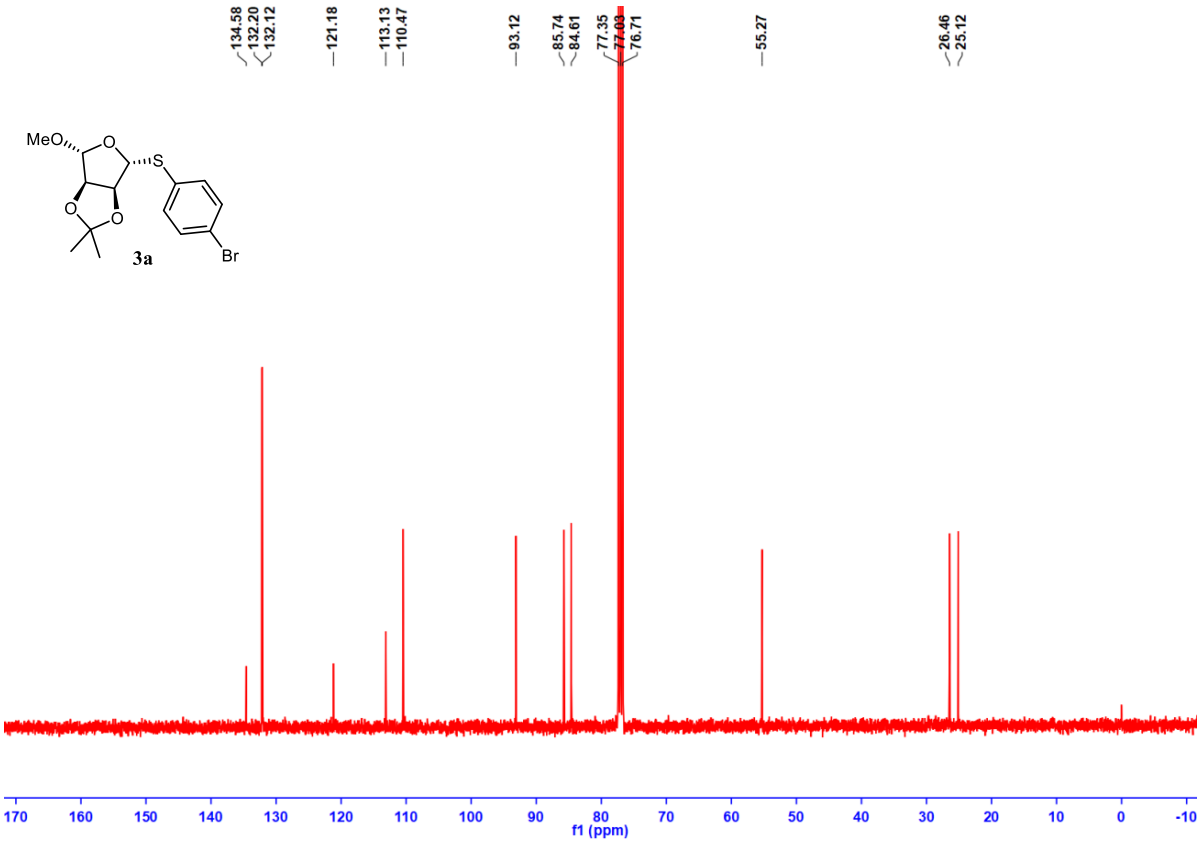
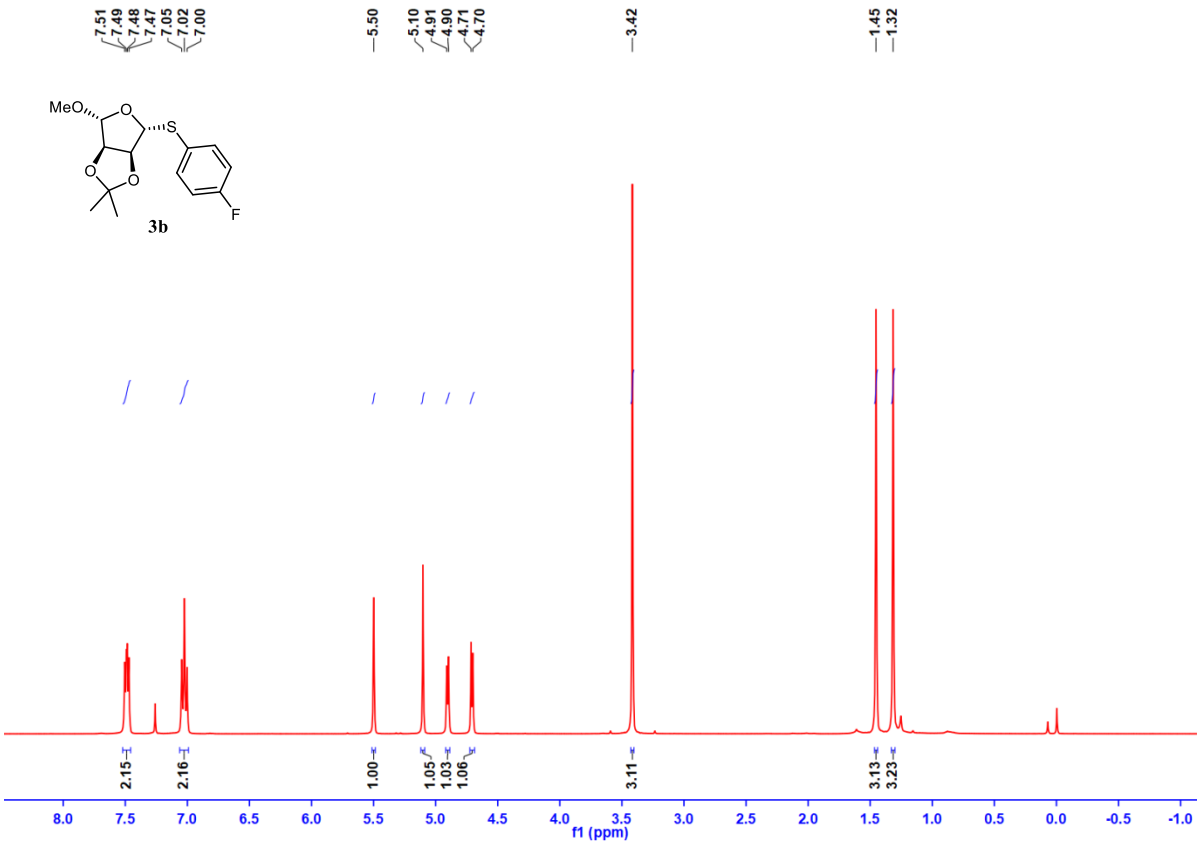
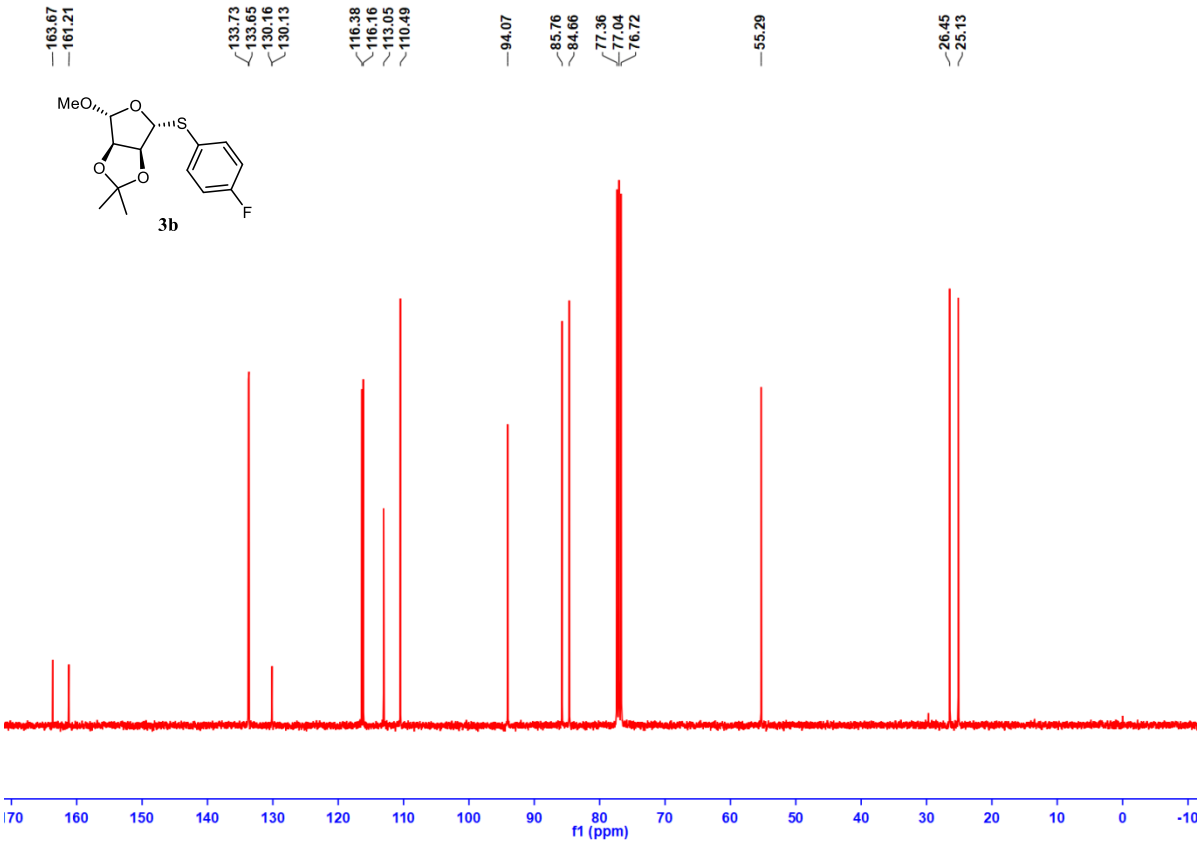
7.43
7.36
7.34
7.26
5.57
5.11
4.90
4.89
4.72
4.70
3.39
1.47
1.32
MeO
Br
3a
2.09
2.07
1.00
1.03
1.05
1.04
3.02
3.09
3.06
f1 (ppm)


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)


7.51
7.49
7.48
7.47
7.05
7.02
7.00
5.50
5.10
4.91
4.90
4.71
4.70
3.42
1.45
1.32
MeO
O
S
O
O
F
3b
2.15
2.16
1.00
1.05
1.03
1.06
3.11
3.13
3.23
f1 (ppm)


163.67
161.21
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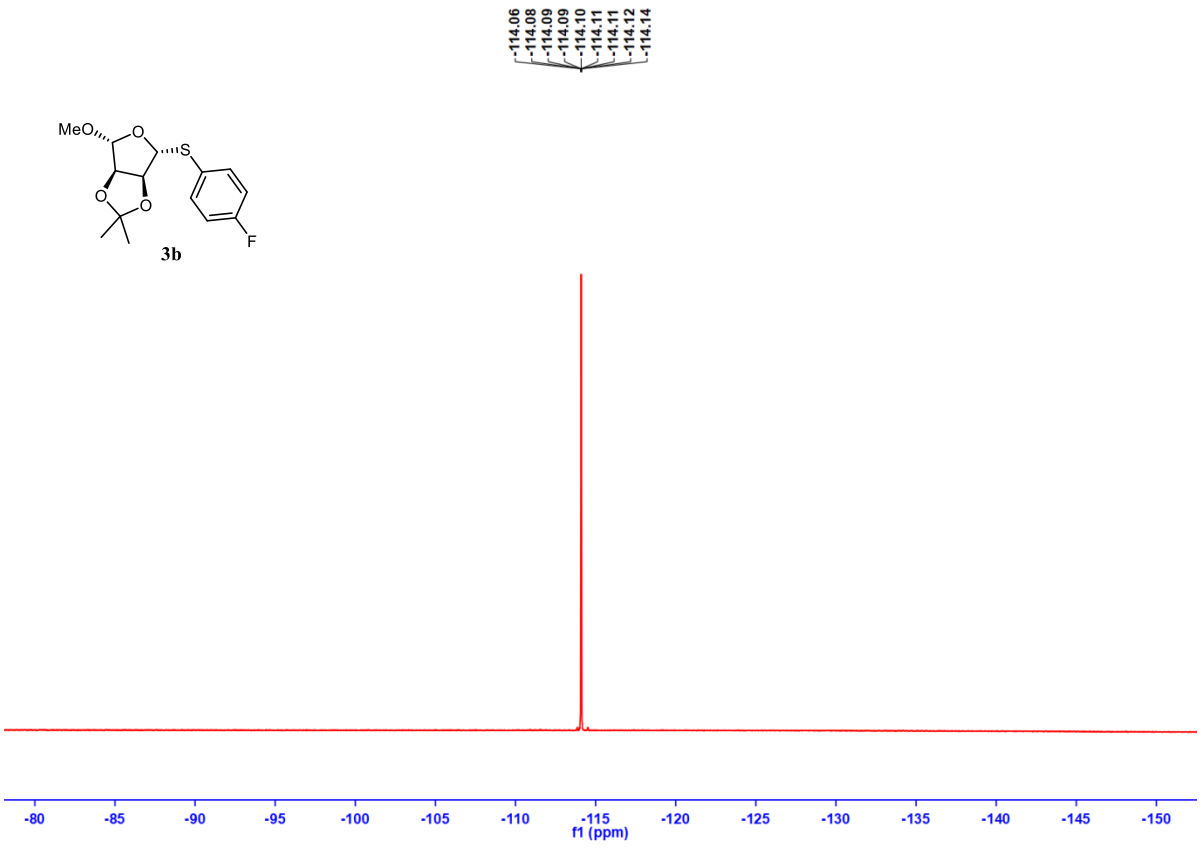
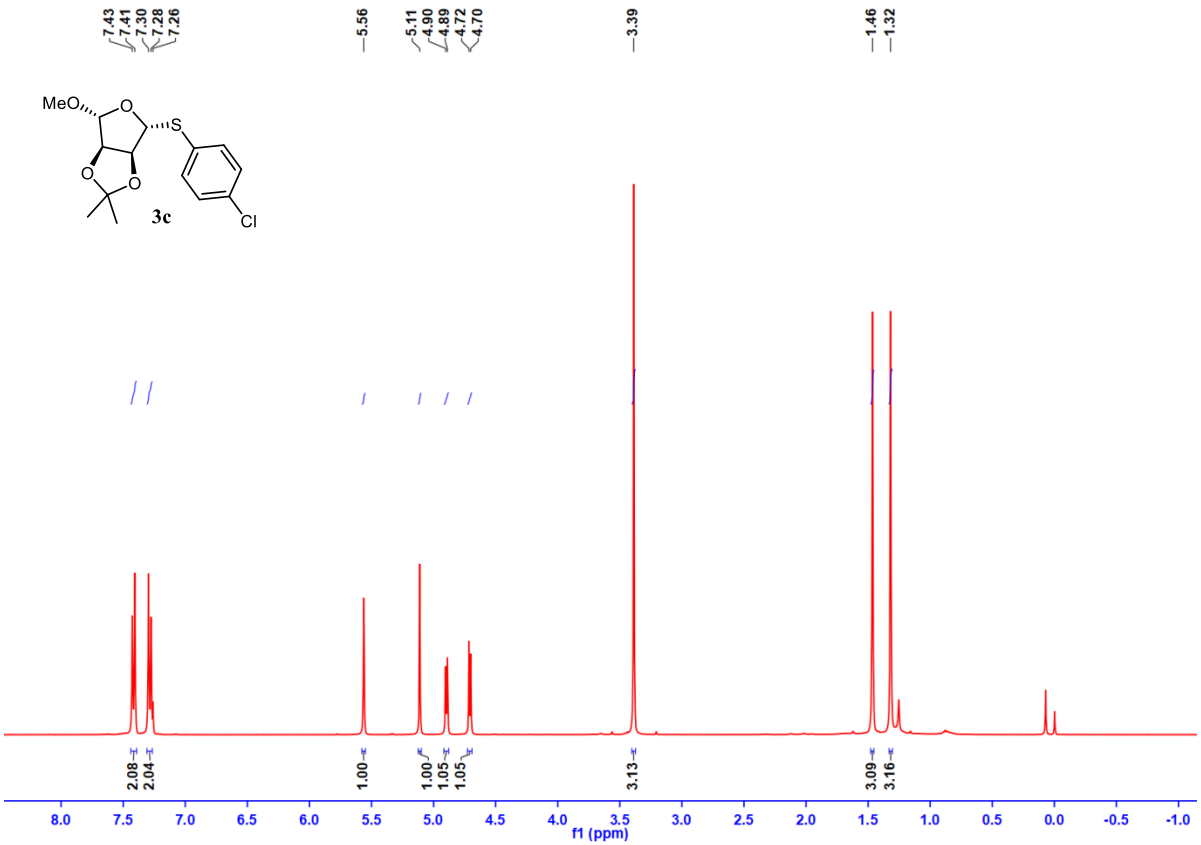
133.65
130.16
130.13
116.38
116.16
113.05
110.49
94.07
85.76
84.66
77.36
77.04
76.72
55.29
26.45
25.13
MeO
O
S
O
O
F
3b
f1 (ppm)


-114.06
-114.08
-114.09
-114.09
-114.10
-114.11
-114.11
-114.12
-114.14
MeO
O
S
O
O
F
3b
f1 (ppm)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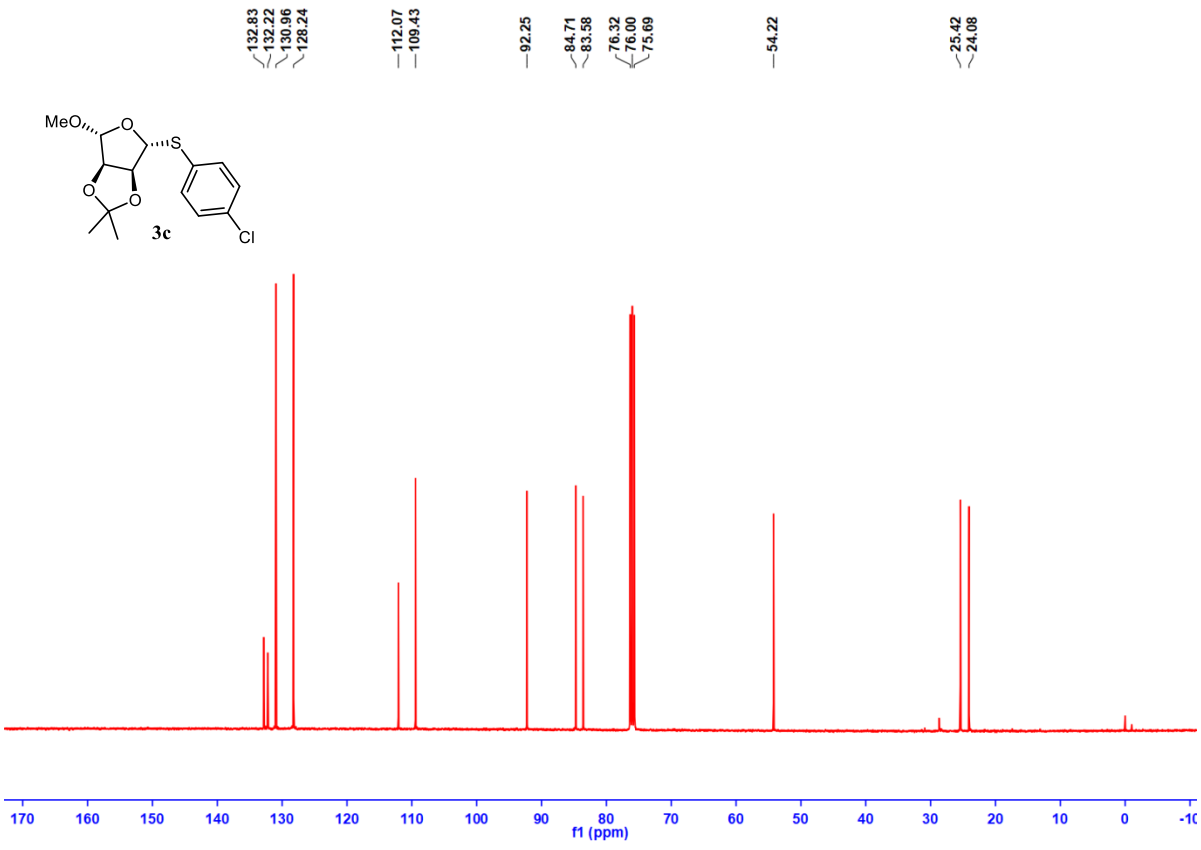
7.41
7.30
7.28
7.26
5.56
5.11
4.90
4.89
4.72
4.70
3.39
1.46
1.32
MeO
O
S
O
O
Cl
3c
2.08
2.04
1.00
1.00
1.05
1.05
3.13
3.09
3.16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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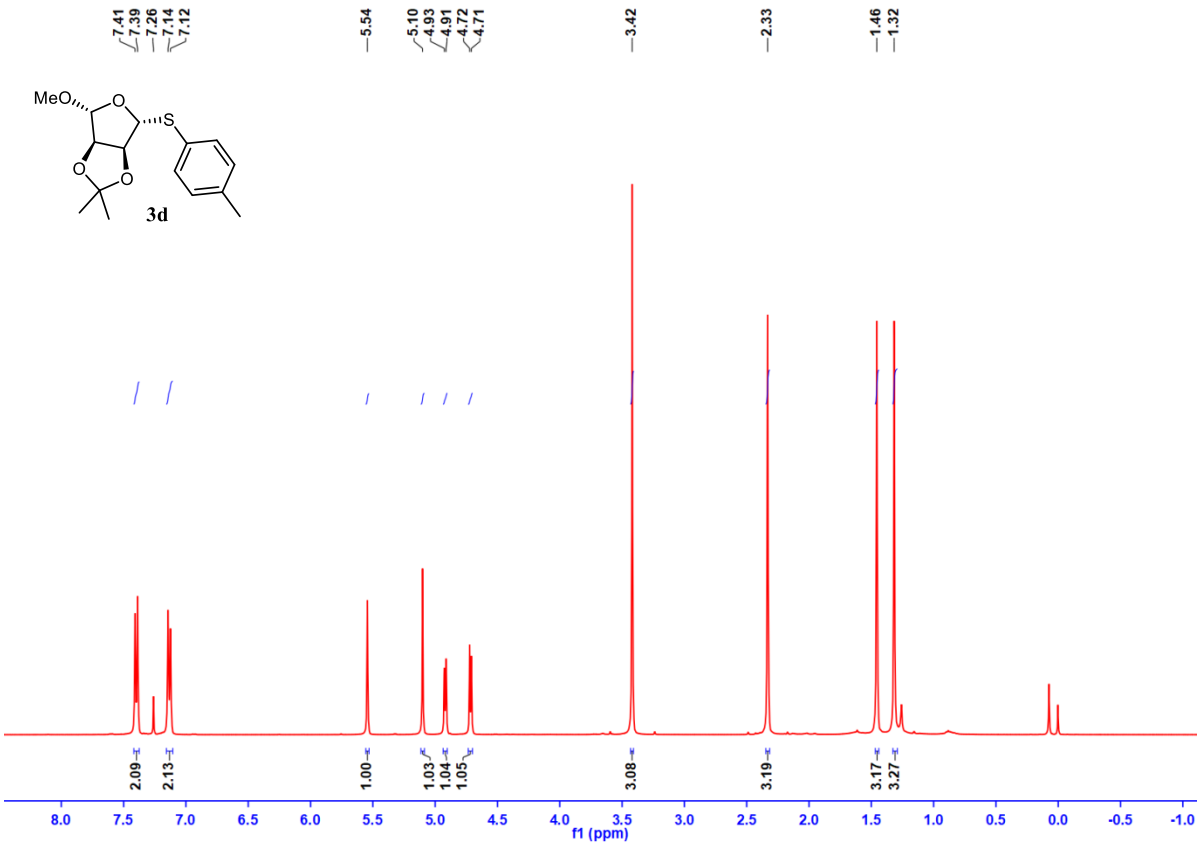
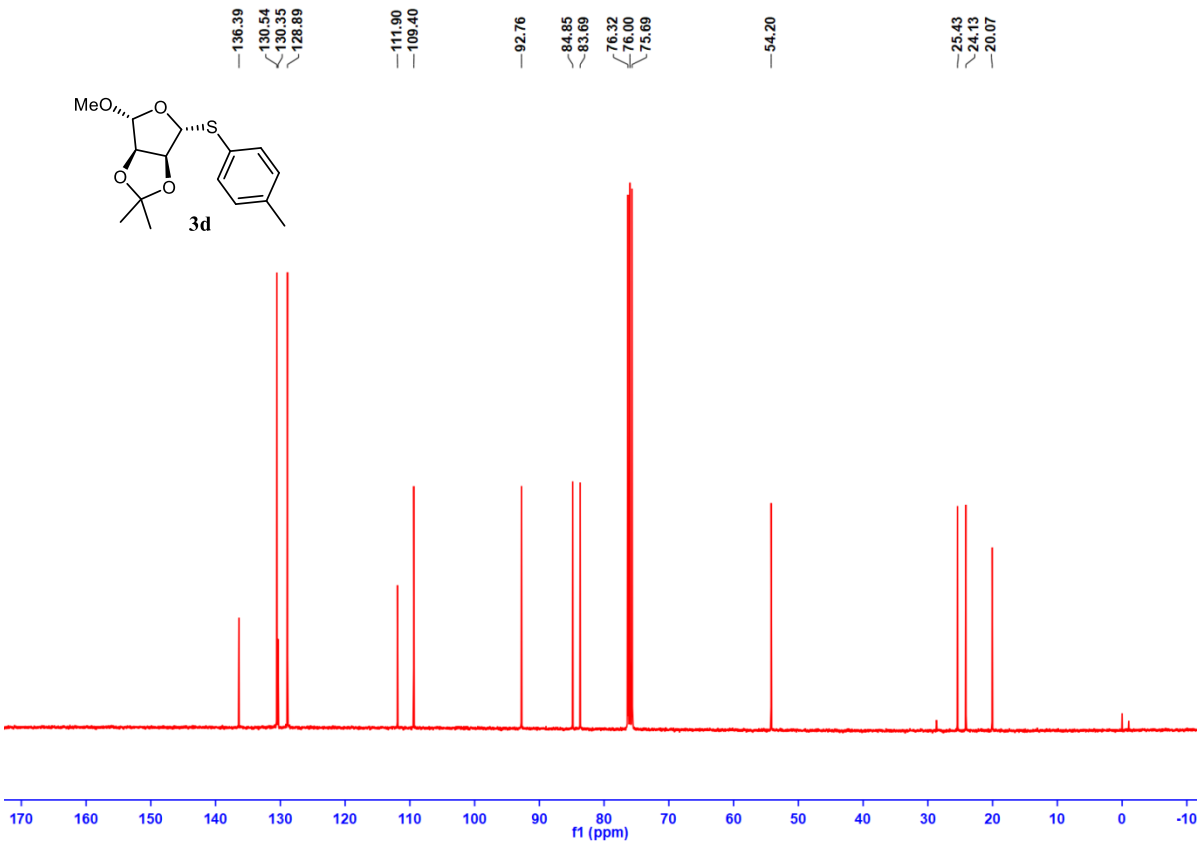
128.24
112.07
109.43
92.25
84.71
83.58
76.32
76.00
75.69
54.22
25.42
24.08
MeO
O
S
O
O
Cl
3c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


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
1.46
1.32
MeO
O
S
O
O
3d
2.09
2.13
1.00
1.03
1.04
1.05
3.08
3.19
3.17
3.27
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)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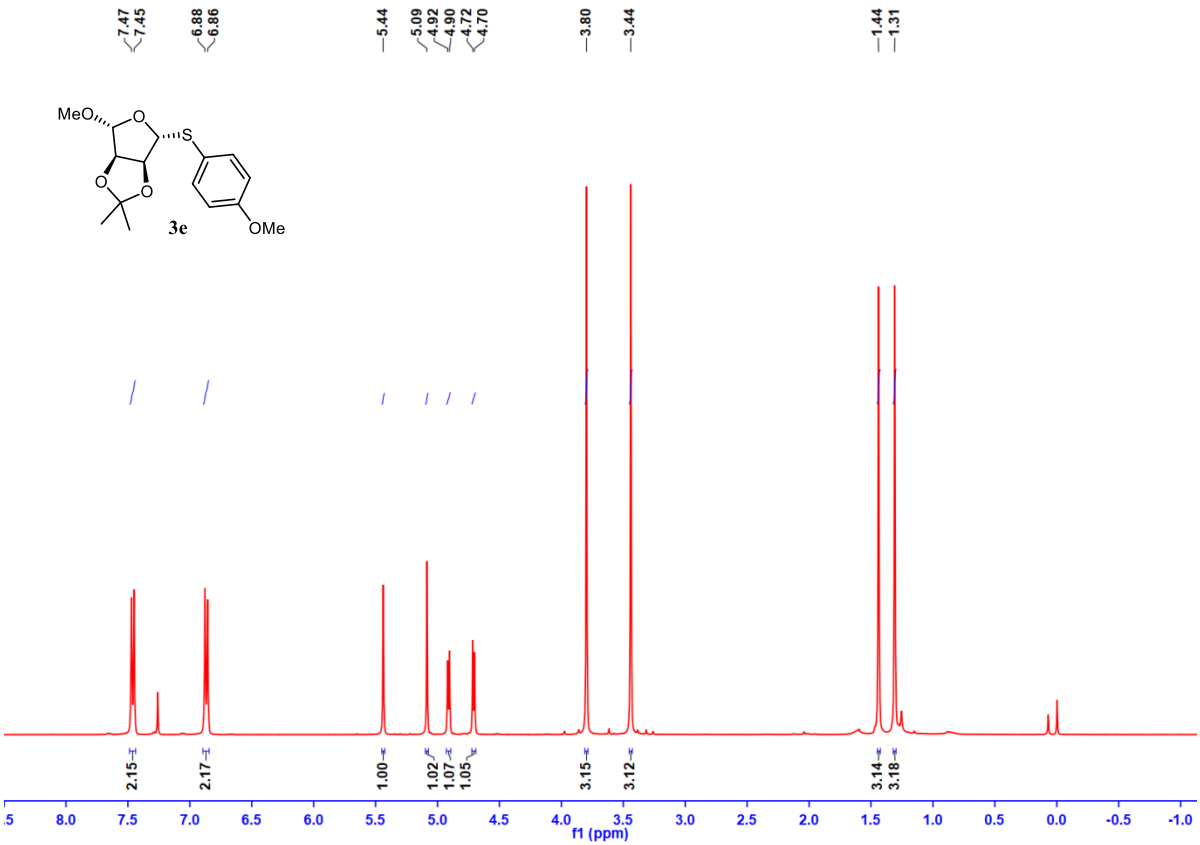
128.89
111.90
109.40
92.76
84.85
83.69
76.32
76.00
75.69
54.20
25.43
24.13
20.07
MeO
O
S
O
O
3d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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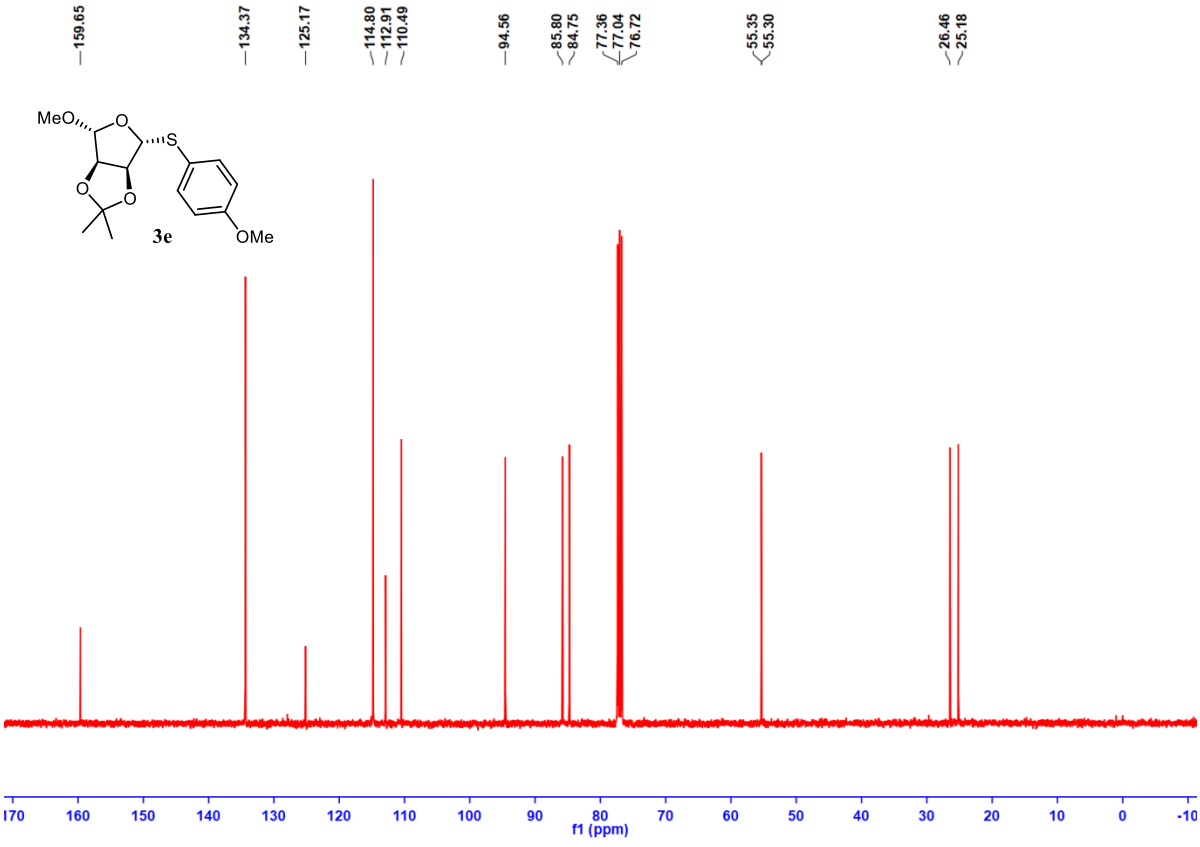
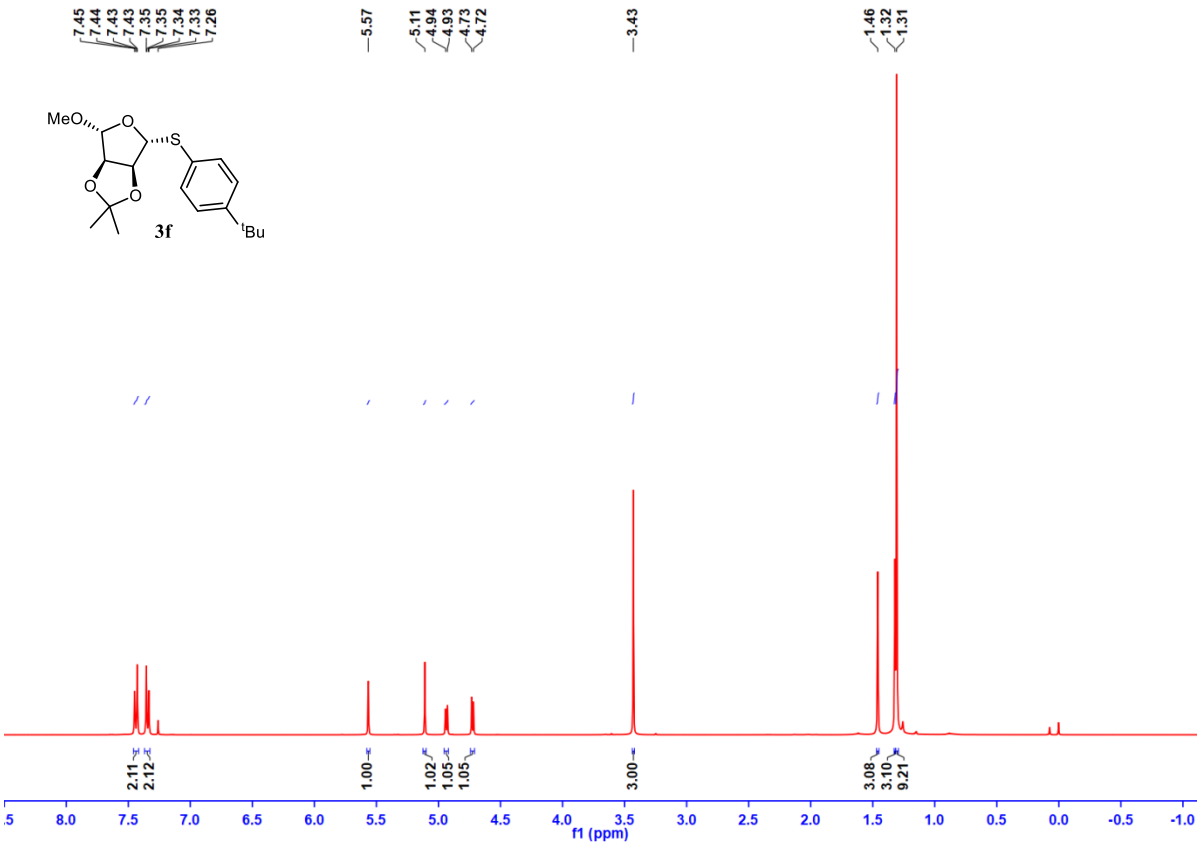
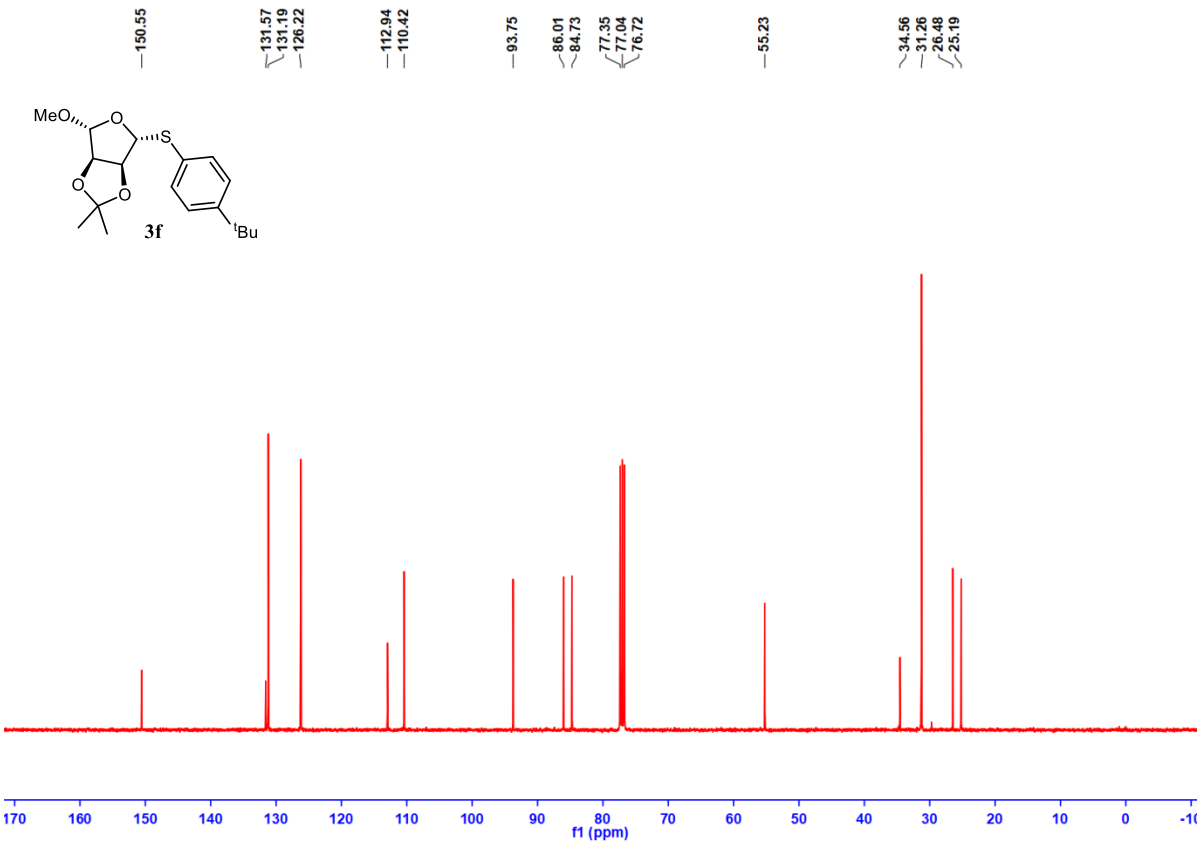
7.45
6.88
6.86
5.44
5.09
4.92
4.90
4.72
4.70
3.80
3.44
1.44
1.31
MeO
O
S
O
O
3e
OMe
2.15
2.17
1.00
1.02
1.07
1.05
3.15
3.12
3.14
3.18
f1 (ppm)


159.65
134.37
125.17
114.80
112.91
110.49
94.56
85.80
84.75
77.36
77.04
76.72
55.35
55.30
26.46
25.18
MeO
O
S
O
O
3e
OMe
f1 (ppm)


7.45
7.44
7.43
7.43
7.35
7.35
7.34
7.33
7.26
5.57
5.11
4.94
4.93
4.73
4.72
3.43
1.46
1.32
1.31
MeO
O
S
O
O
3f
tBu
2.11
2.12
1.00
1.02
1.05
1.05
3.00
3.08
3.10
9.21
f1 (ppm)


150.55
131.57
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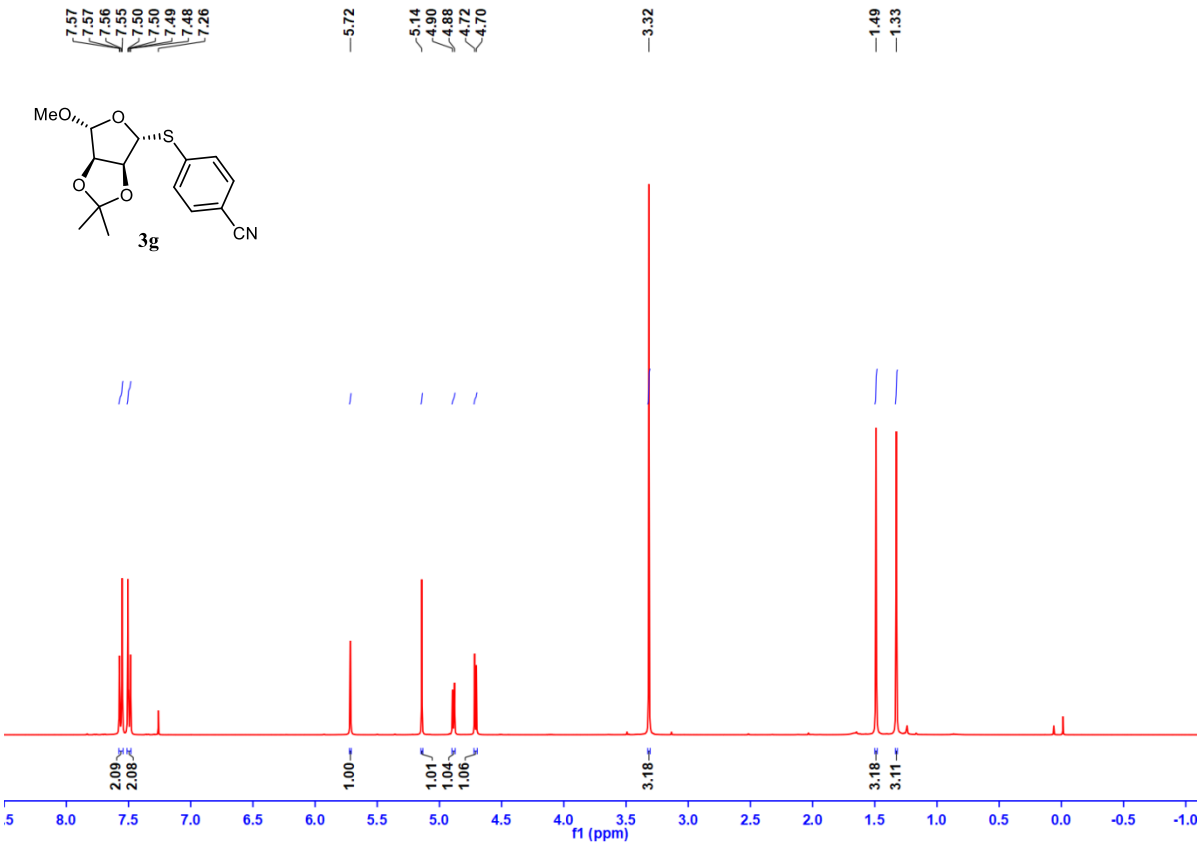
126.22
112.94
110.42
93.75
86.01
84.73
77.35
77.04
76.72
55.23
34.56
31.26
26.48
25.19
MeO
O
S
O
O
3f
tBu
f1 (ppm)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7.57
7.56
7.55
7.50
7.50
7.49
7.48
7.26
5.72
5.14
4.90
4.88
4.72
4.70
3.32
1.49
1.33
MeO
O
S
O
O
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2.08
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1.01
1.04
1.06
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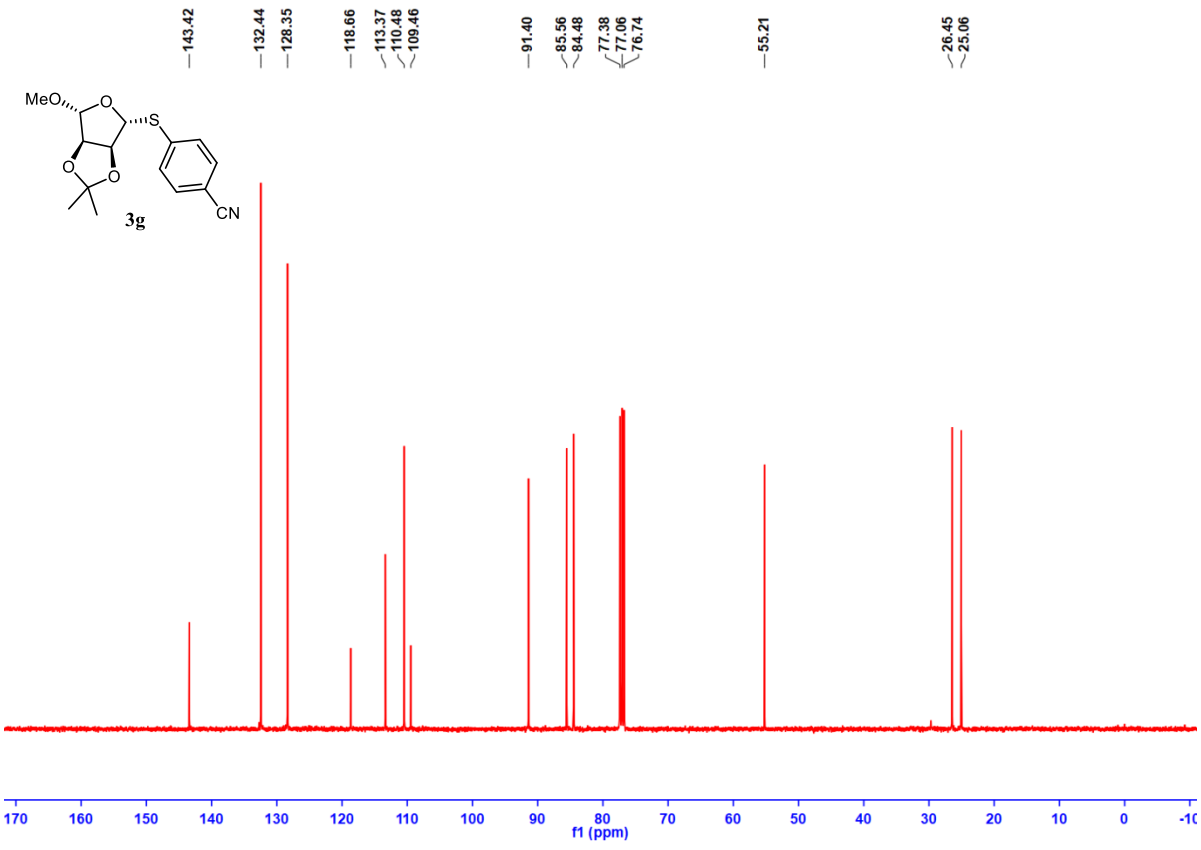
3.18
3.11
f1 (ppm)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84.48
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25.06
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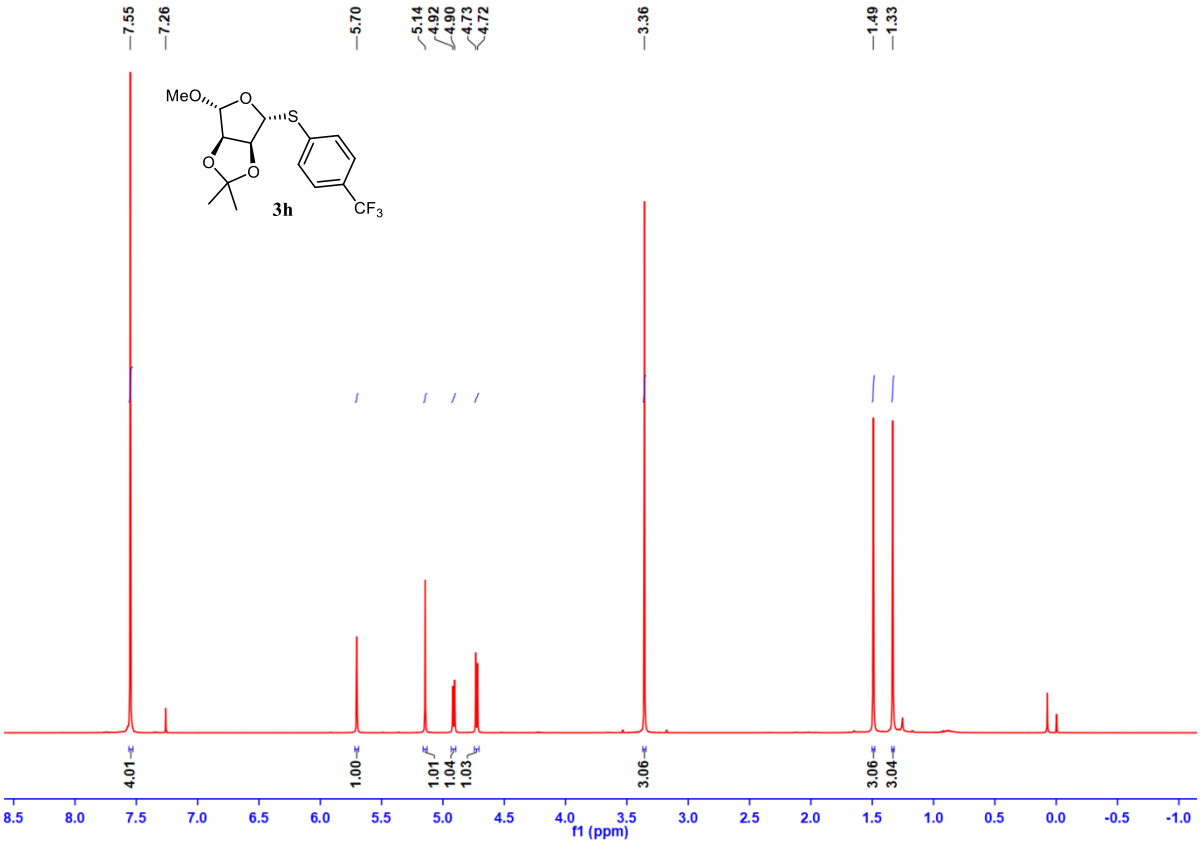
S
O
O
CN
3g
f1 (ppm)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4.72
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1.33
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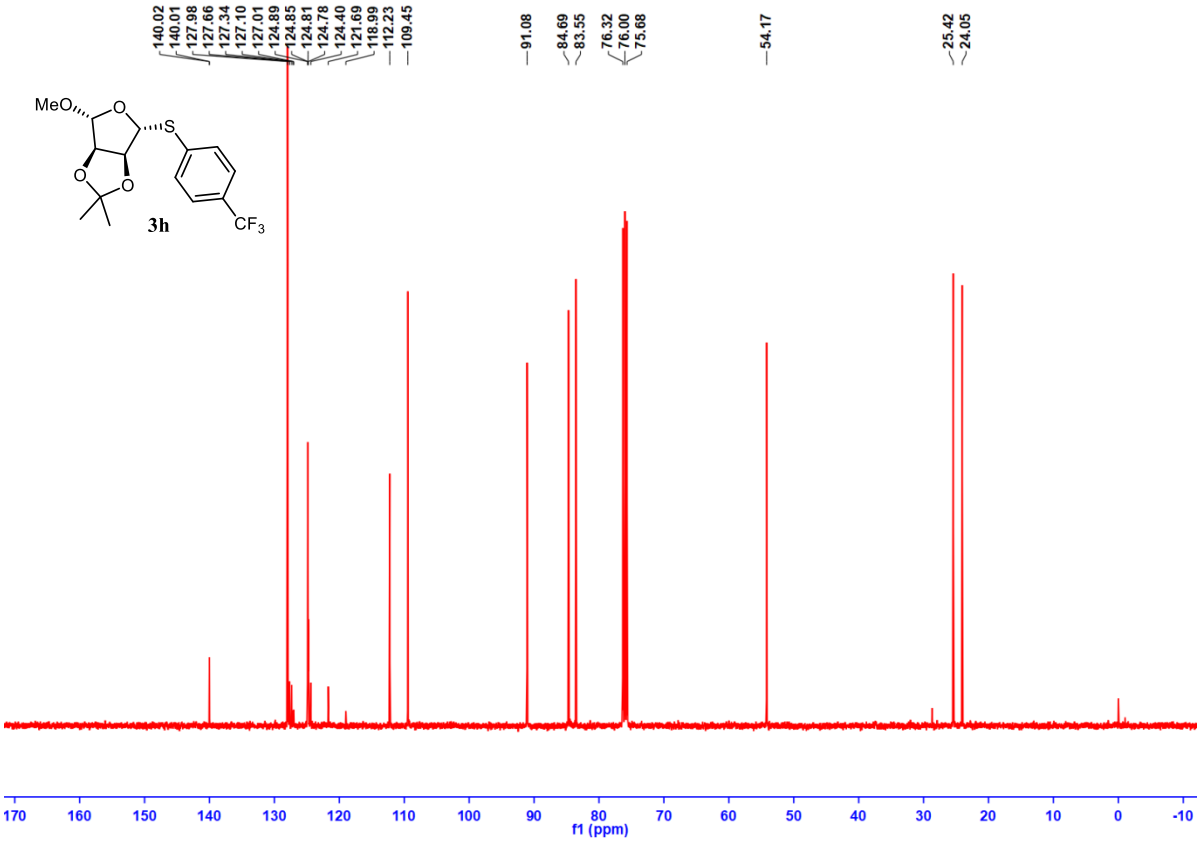
O
S
O
O
3h
CF3
4.01
1.00
1.01
1.04
1.03
3.06
3.06
3.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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121.69
118.99
112.23
109.45
91.08
84.69
83.55
76.32
76.00
75.68
54.17
25.42
24.05
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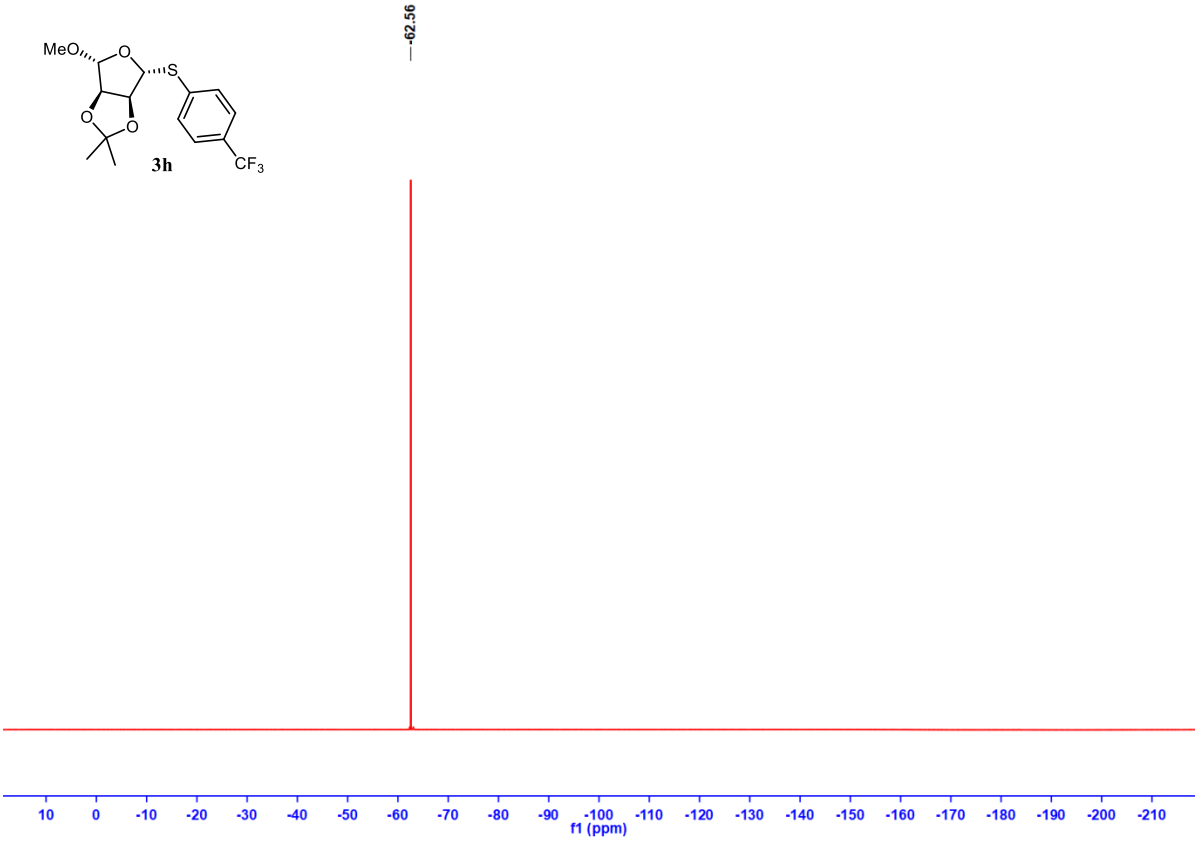
O
S
O
O
3h
CF3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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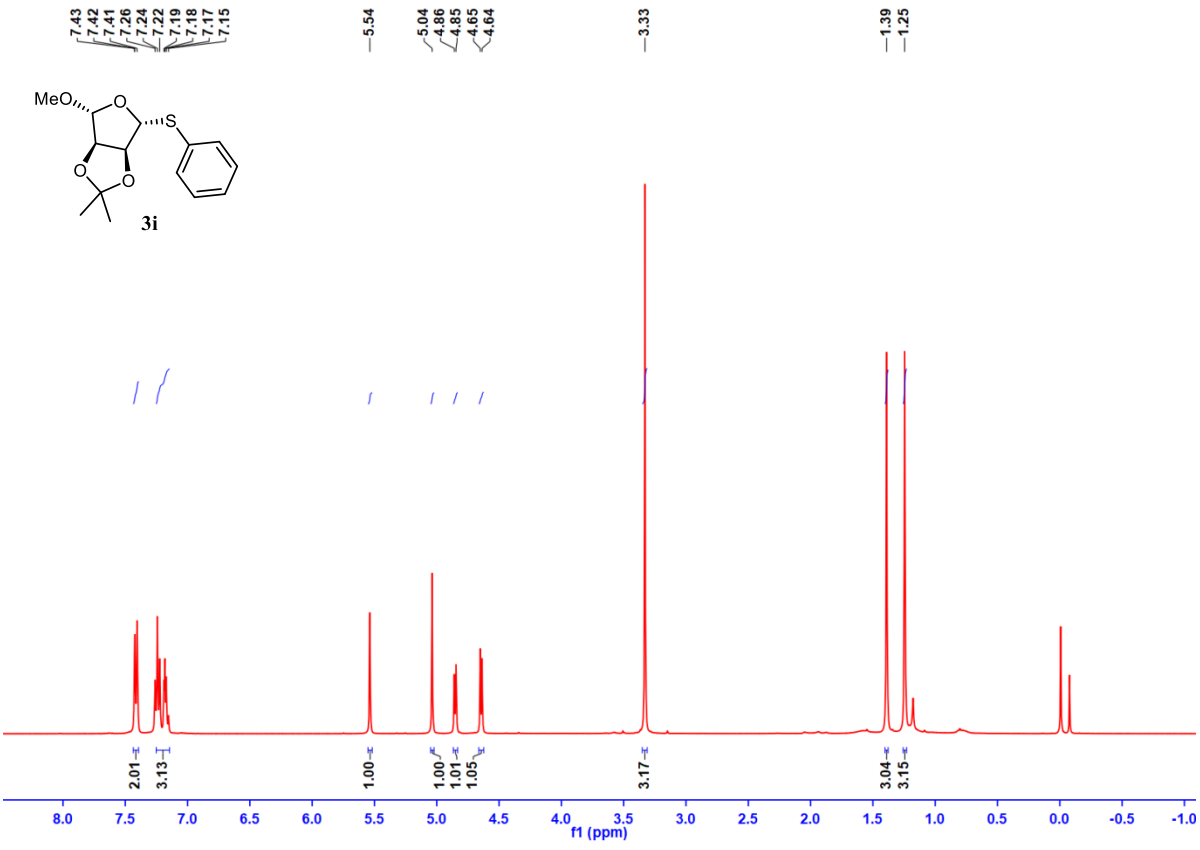
O
O
CF3
3h
-62.56
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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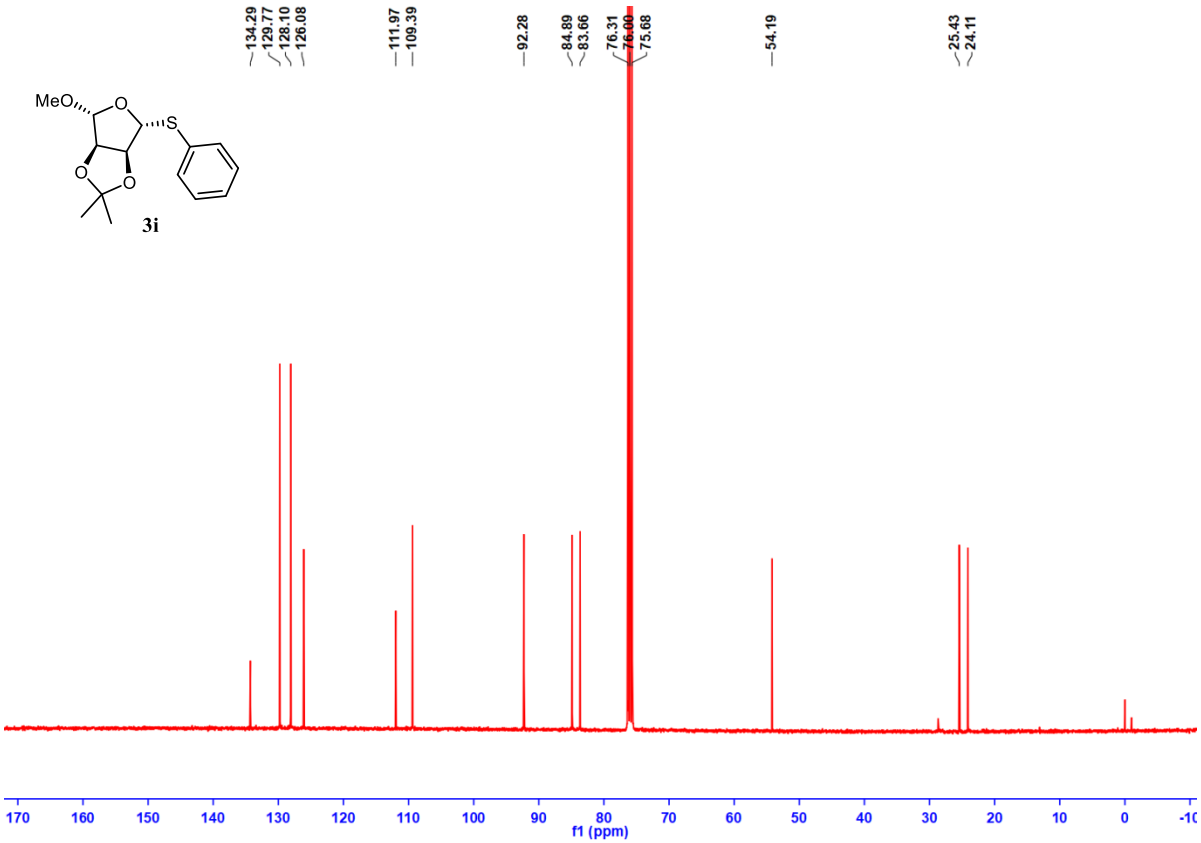
5.04
4.86
4.85
4.65
4.64
3.33
1.39
1.25
MeO
O
S
O
O
3i
2.01
3.13
1.00
1.00
1.01
1.05
3.17
3.04
3.15
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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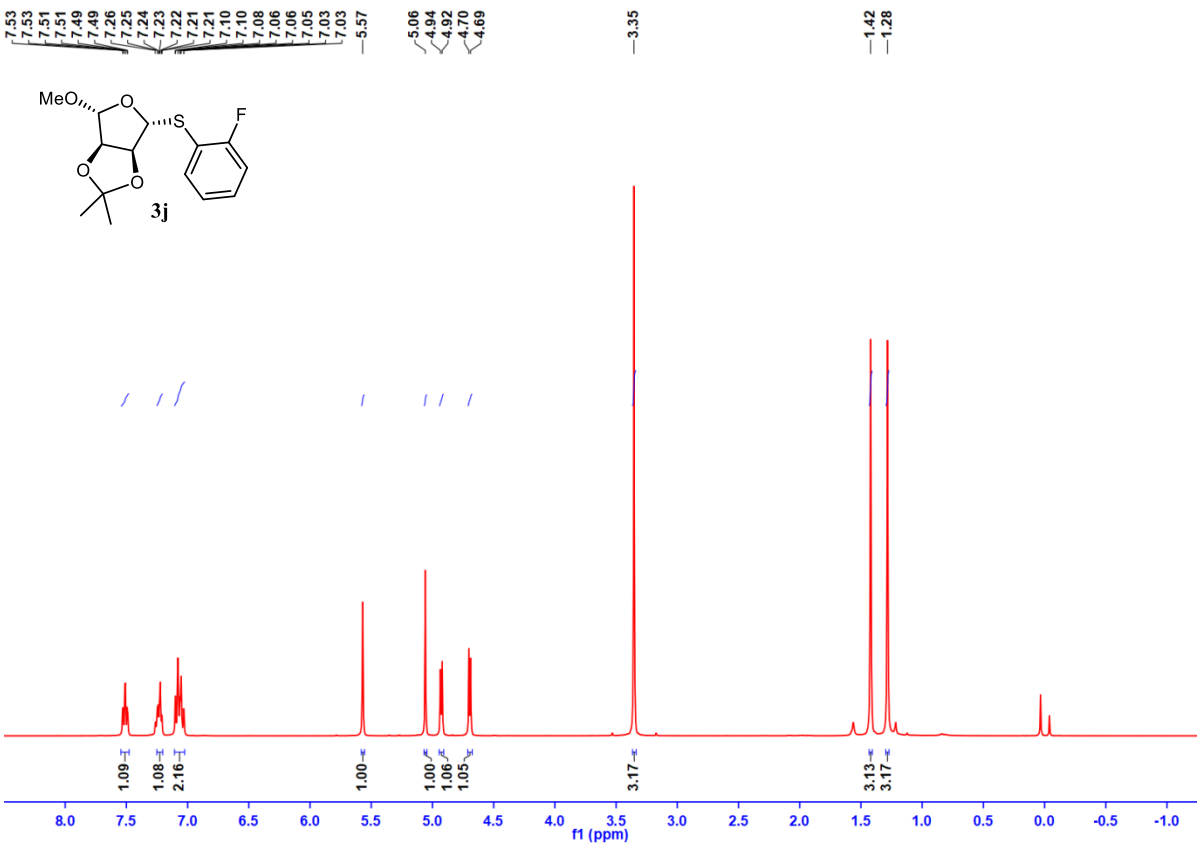
25.43
24.11
MeO
O
S
O
O
3i
f1 (ppm)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7.21
7.10
7.08
7.06
7.06
7.05
7.03
7.03
5.57
5.06
4.94
4.92
4.70
4.69
3.35
1.42
1.28
MeO
O
S
F
O
O
3j
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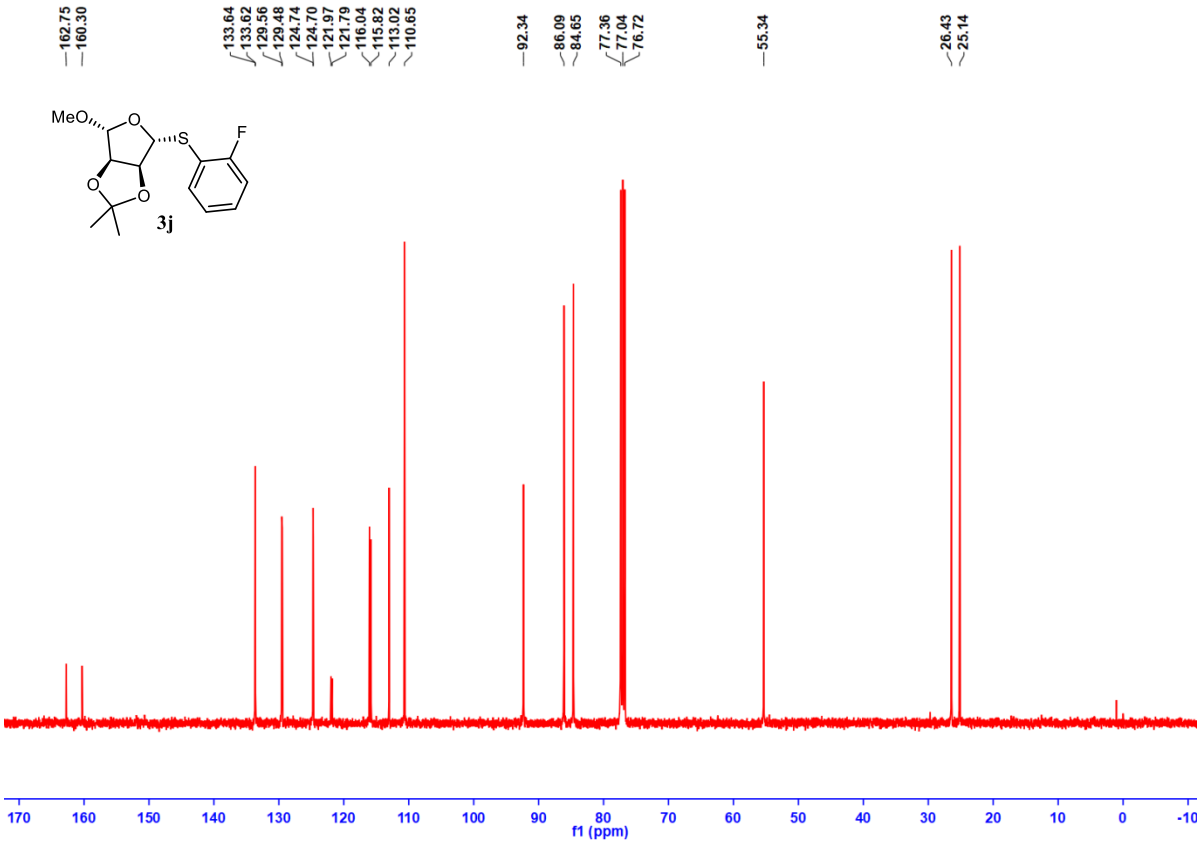
1.00
1.06
1.05
3.17
3.13
3.17
f1 (ppm)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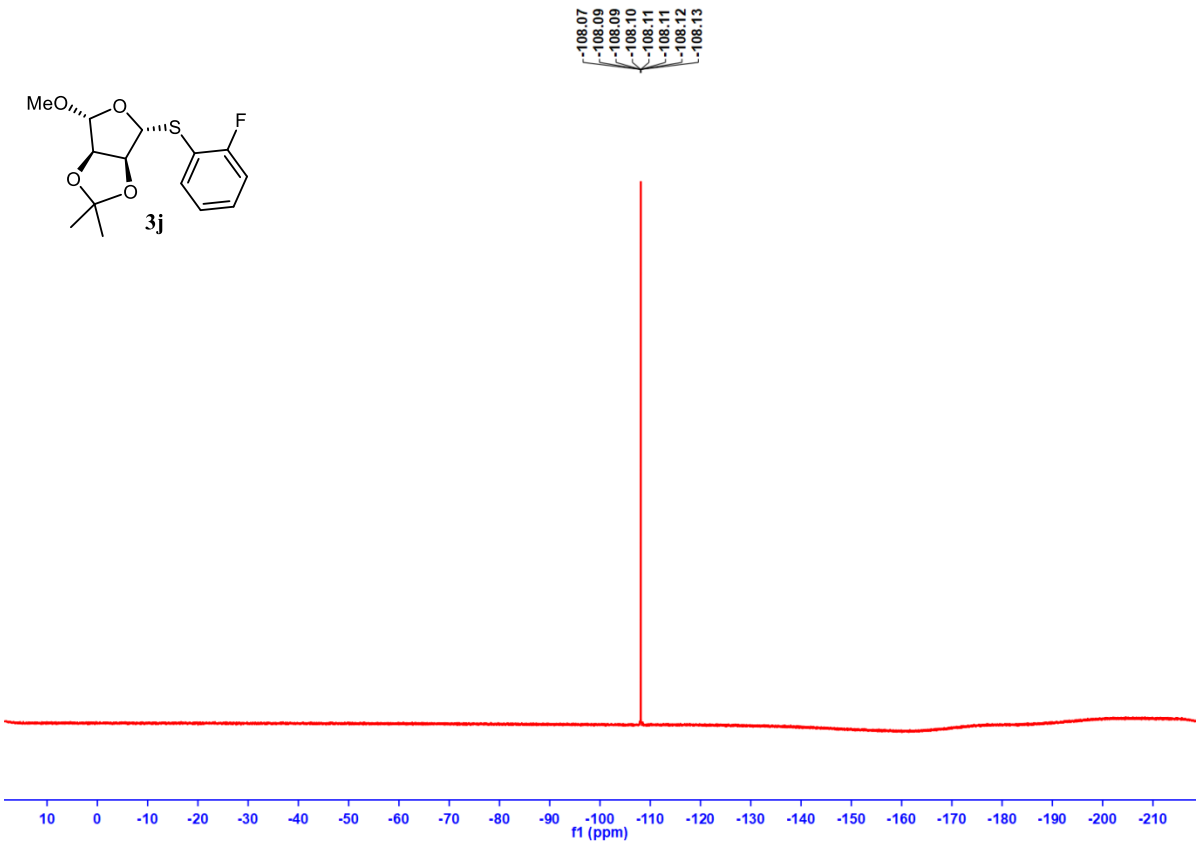
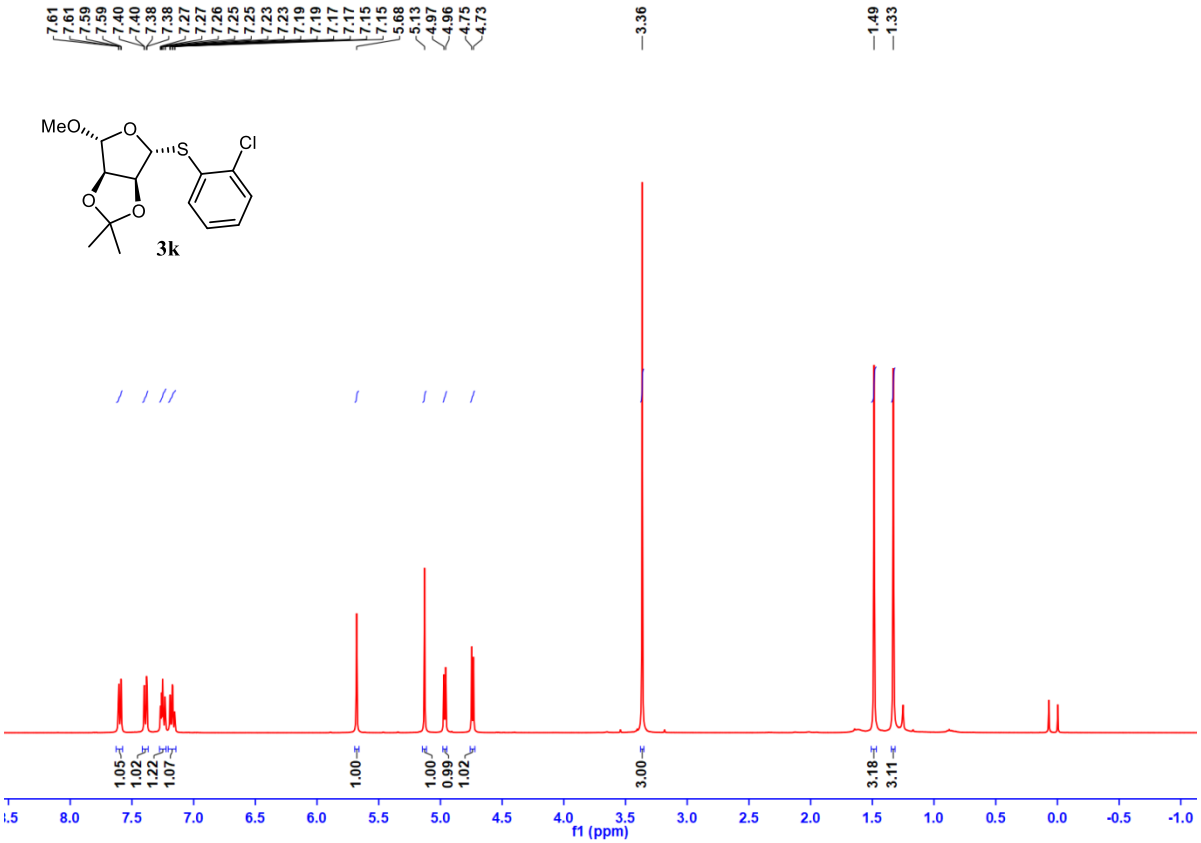
121.79
116.04
115.82
113.02
110.65
92.34
86.09
84.65
77.36
77.04
76.72
55.34
26.43
25.14
MeO
O
S
F
O
O
3j
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-108.07
-108.09
-108.09
-108.10
-108.11
-108.11
-108.12
-108.13
MeO
O
S
F
O
O
3j
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)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7.25
7.23
7.23
7.19
7.19
7.17
7.17
7.15
7.15
5.68
5.13
4.97
4.96
4.75
4.73
3.36
1.49
1.33
MeO
O
S
Cl
O
O
3k
1.05
1.02
1.22
1.07
1.00
1.00
0.99
1.02
3.00
3.18
3.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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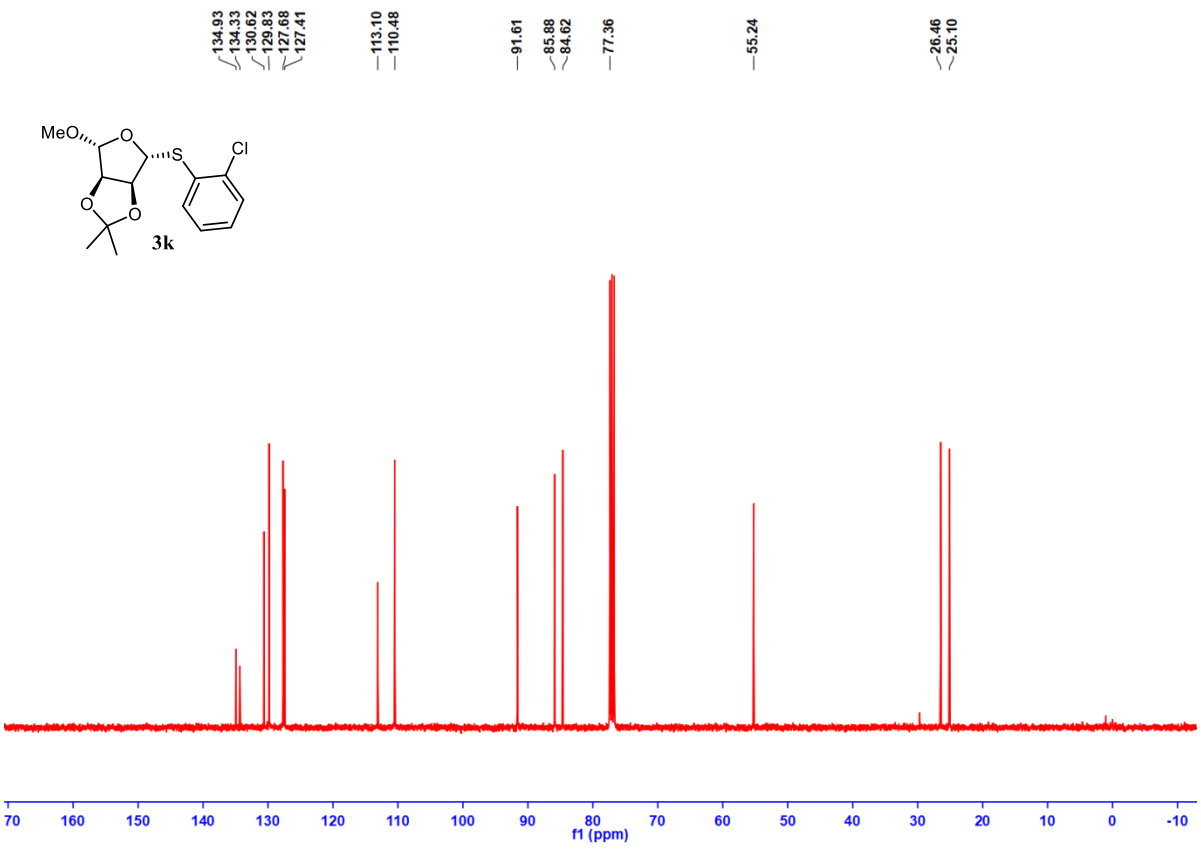
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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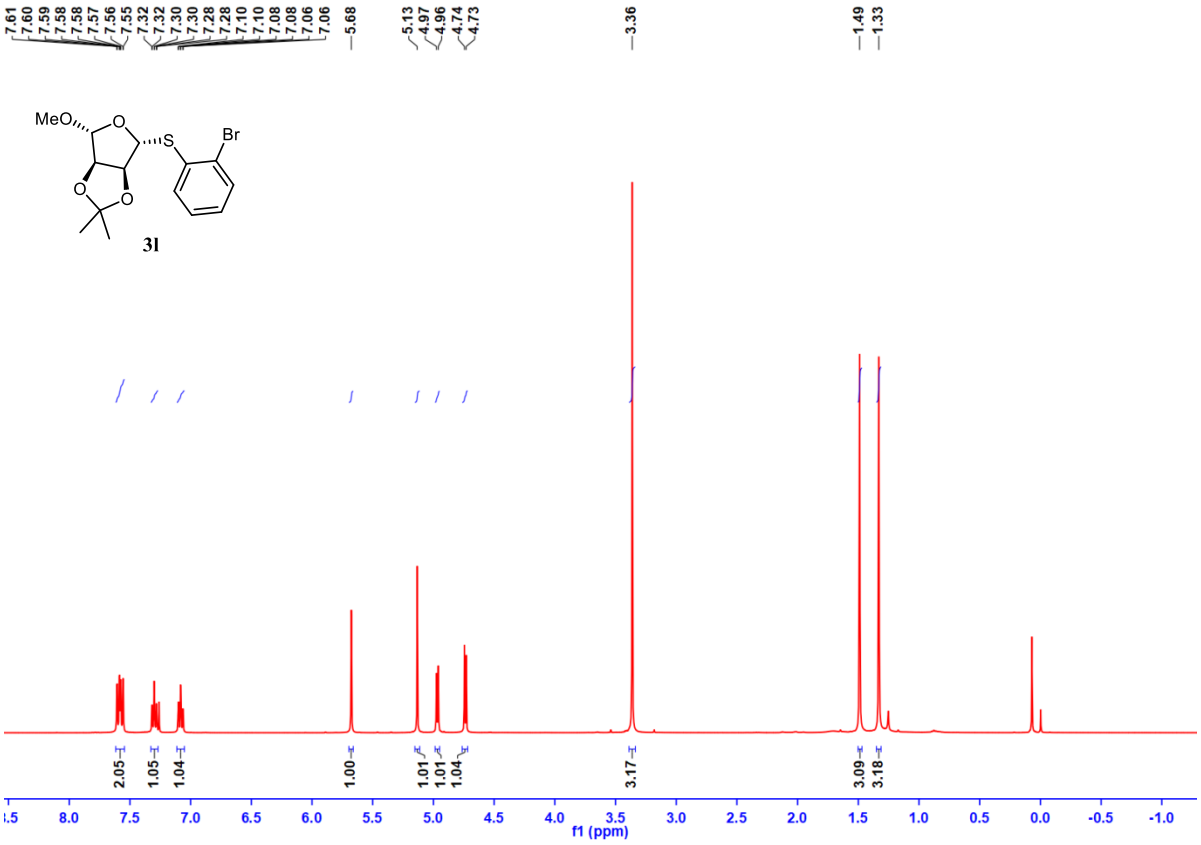
85.88
84.62
77.36
55.24
26.46
25.10
MeO
O
S
Cl
O
O
3k
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.10
7.08
7.08
7.06
7.06
5.68
5.13
4.97
4.96
4.74
4.73
3.36
1.49
1.33
MeO
O
S
Br
O
O
31
2.05
1.05
1.04
1.00
1.01
1.01
1.04
3.17
3.09
3.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
1.5
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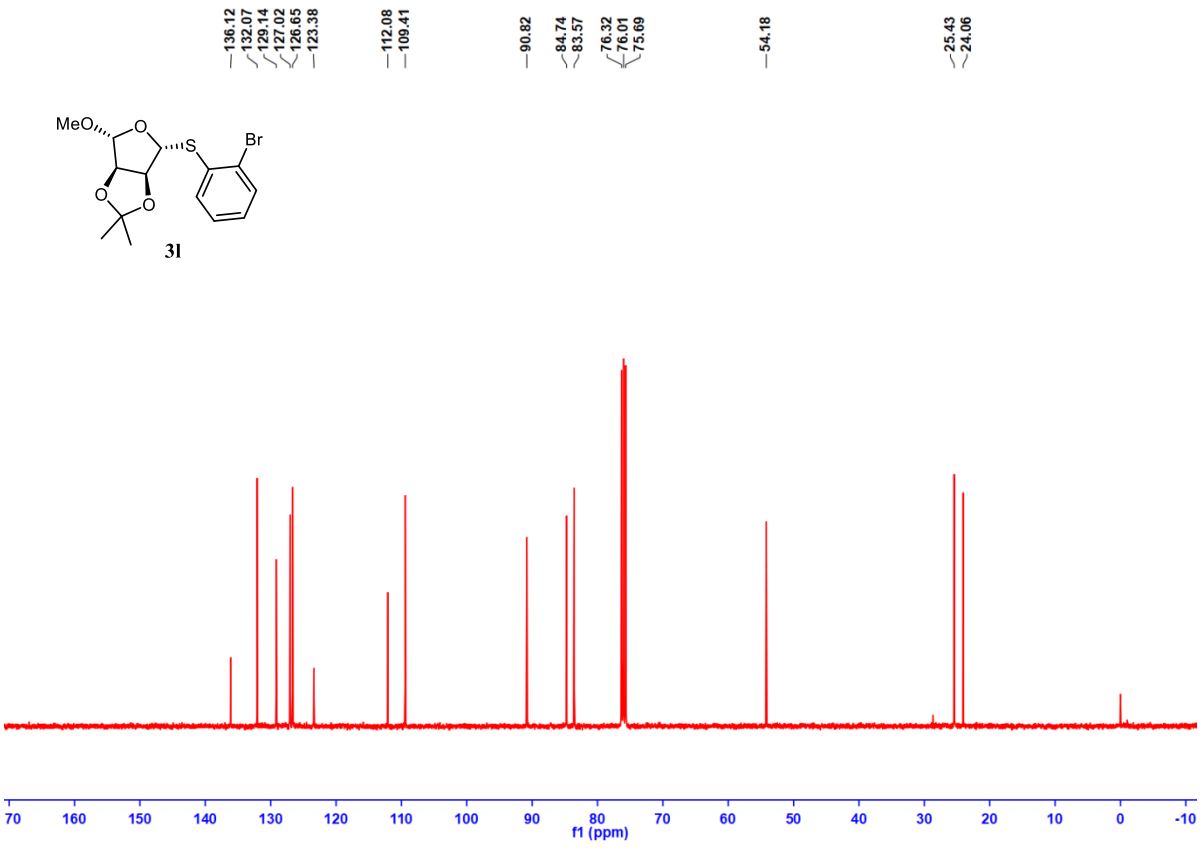
0.0
-0.5
-1.0
f1 (ppm)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83.57
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76.01
75.69
54.18
25.43
24.06
MeO
O
S
Br
O
O
31
160
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140
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120
110
100
90
80
70
60
50
40
30
20
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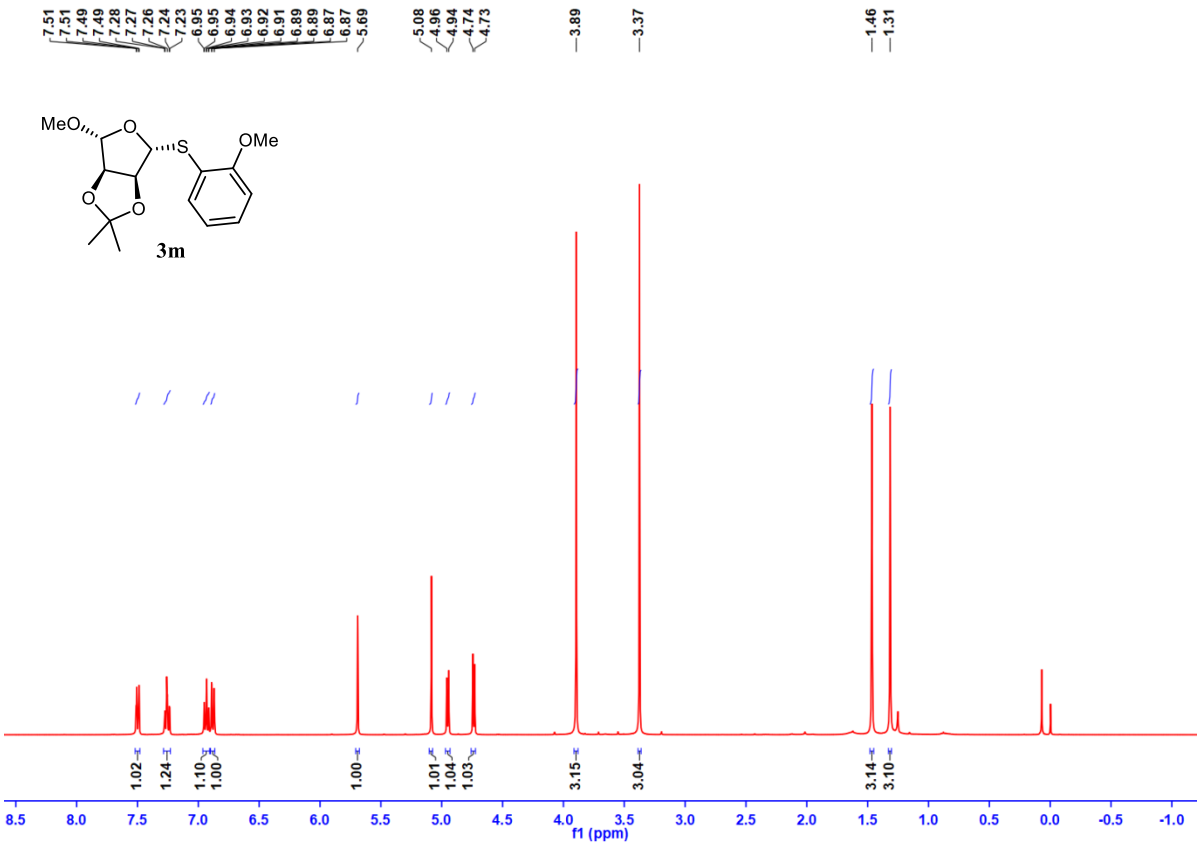
-10
f1 (ppm)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6.89
6.87
6.87
5.69
5.08
4.96
4.94
4.74
4.73
3.89
3.37
1.46
1.31
MeO
O
S
OMe
O
O
3m
1.02
1.24
1.10
1.00
1.00
1.01
1.04
1.03
3.15
3.04
3.14
3.10
8.5
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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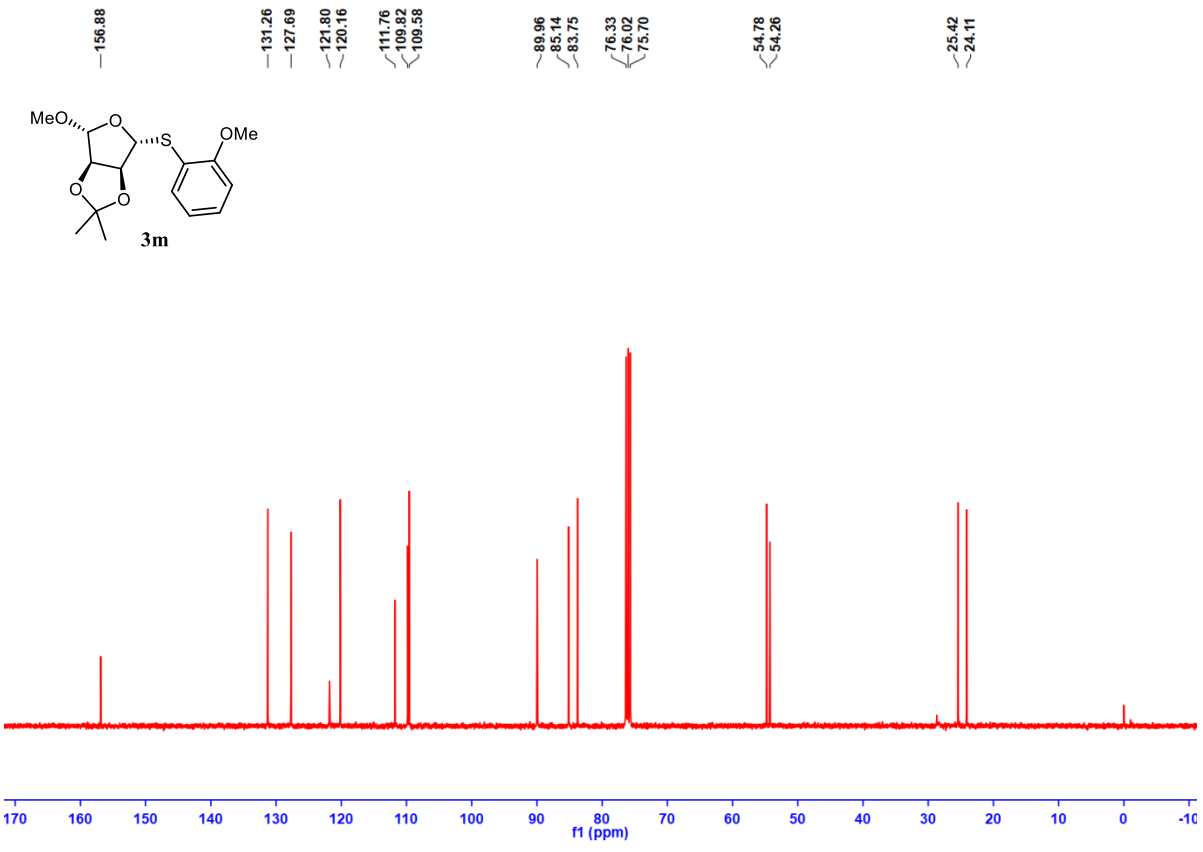
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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76.33
76.02
75.70
54.78
54.26
25.42
24.11
MeO
O
S
OMe
O
O
3m
170
160
150
140
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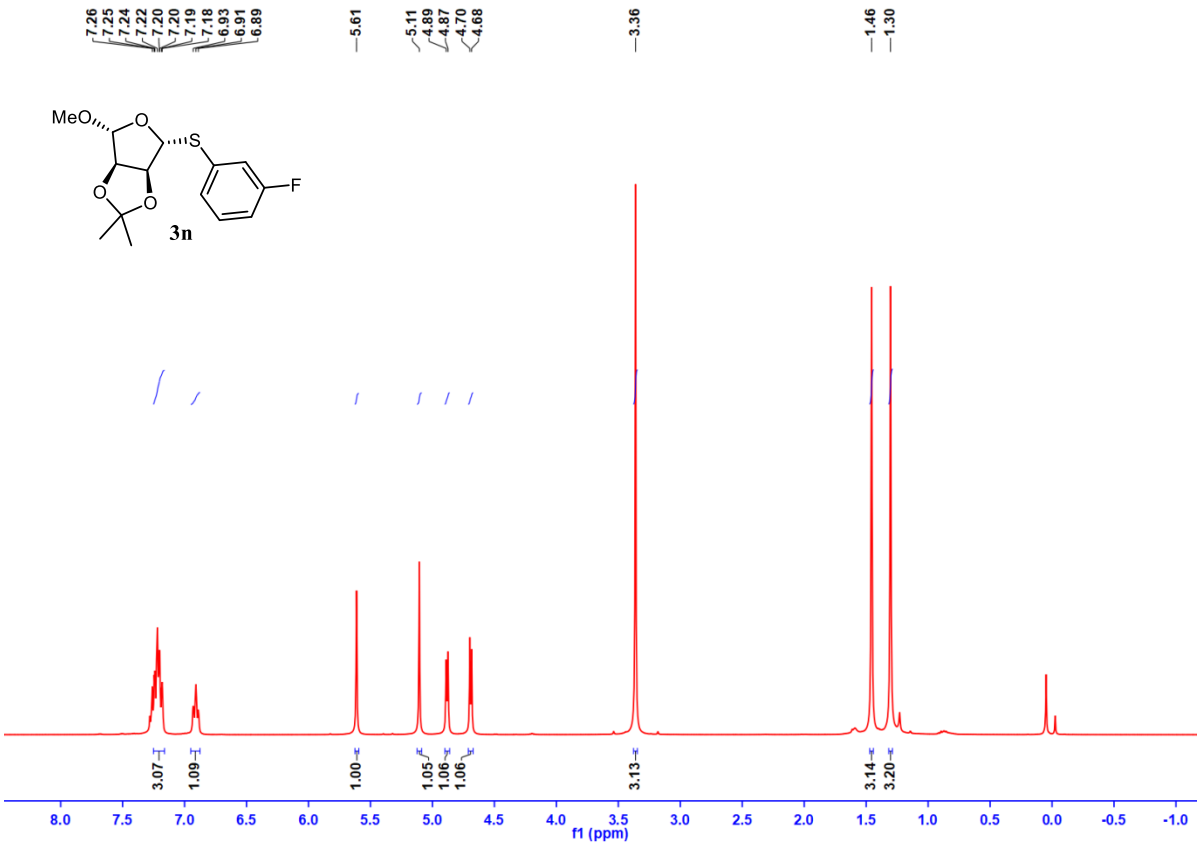
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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5.11
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4.87
4.70
4.68
3.36
1.46
1.30
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O
S
F
O
O
3n
3.07
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1.00
1.05
1.06
1.06
3.13
3.14
3.20
8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
1.5
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0.5
0.0
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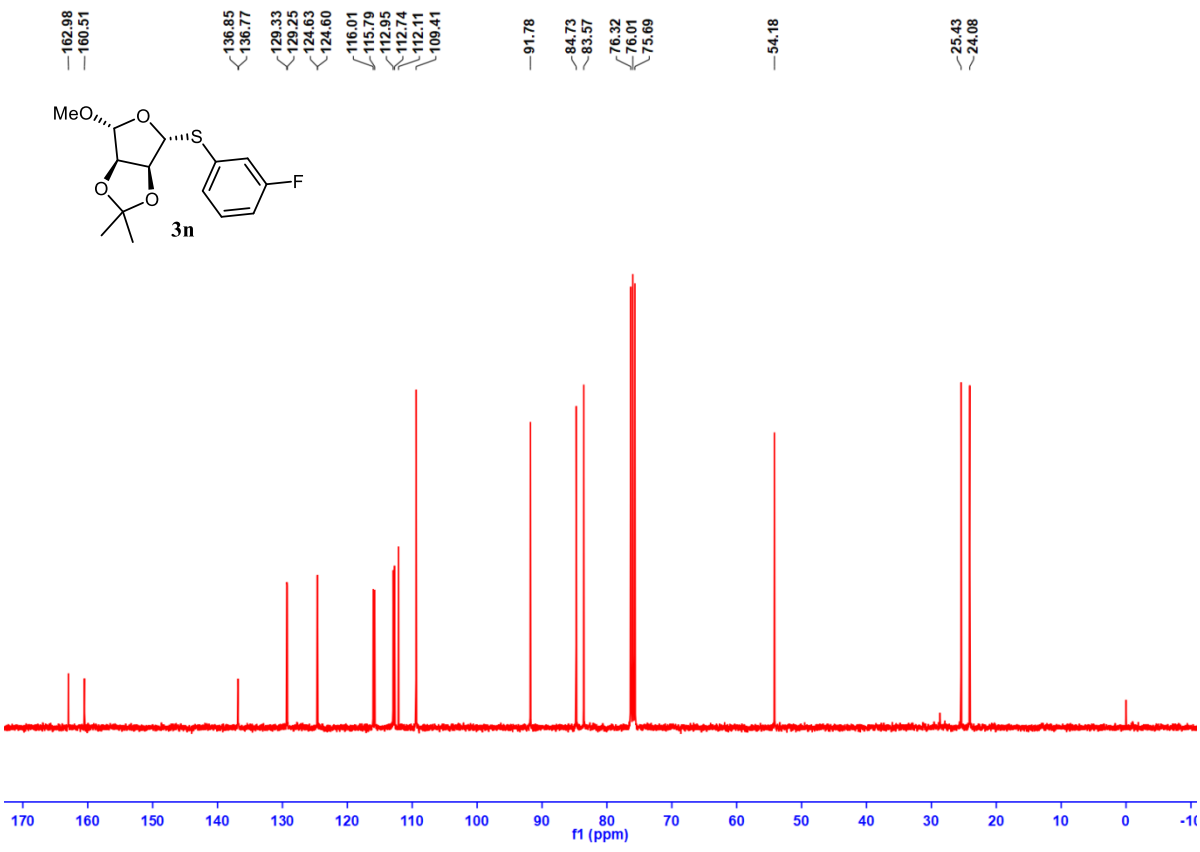
-1.0
f1 (ppm)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112.11
109.41
91.78
84.73
83.57
76.32
76.01
75.69
54.18
25.43
24.08
MeO
O
S
F
O
O
3n
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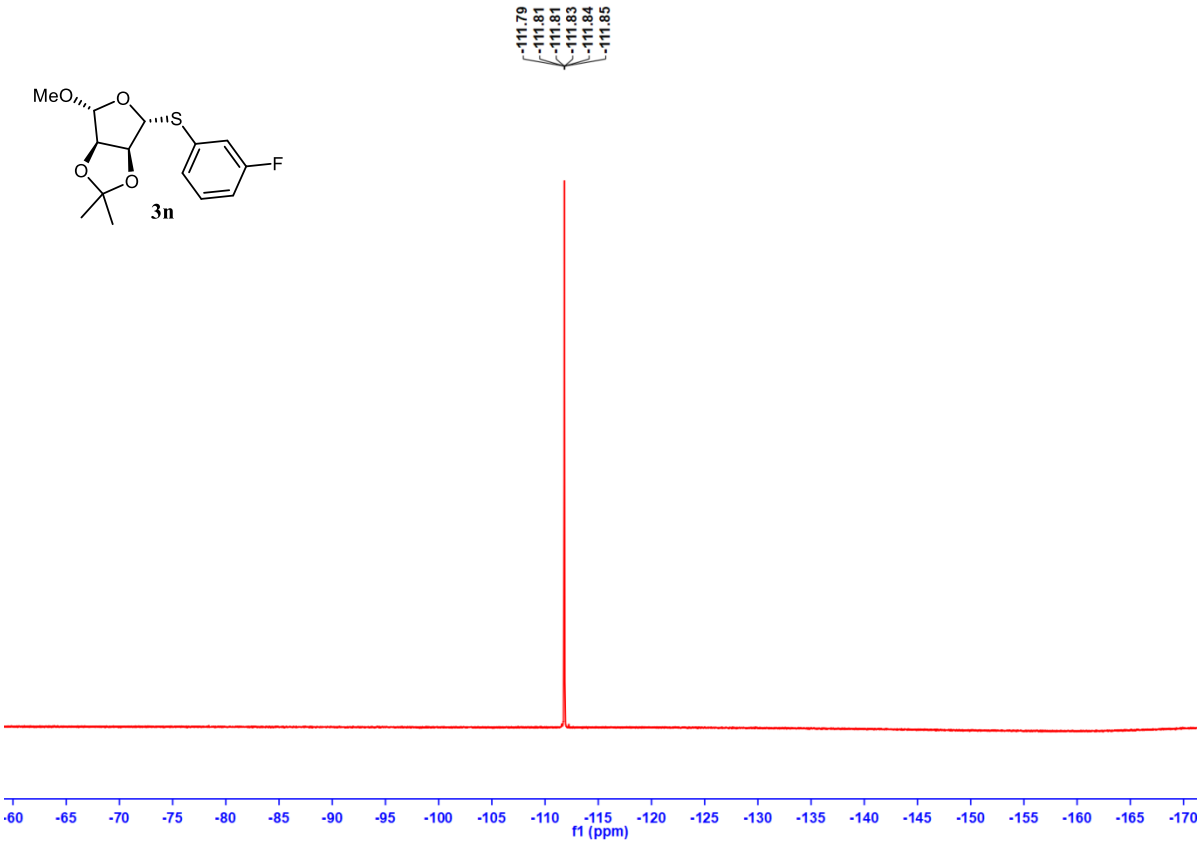
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-111.79
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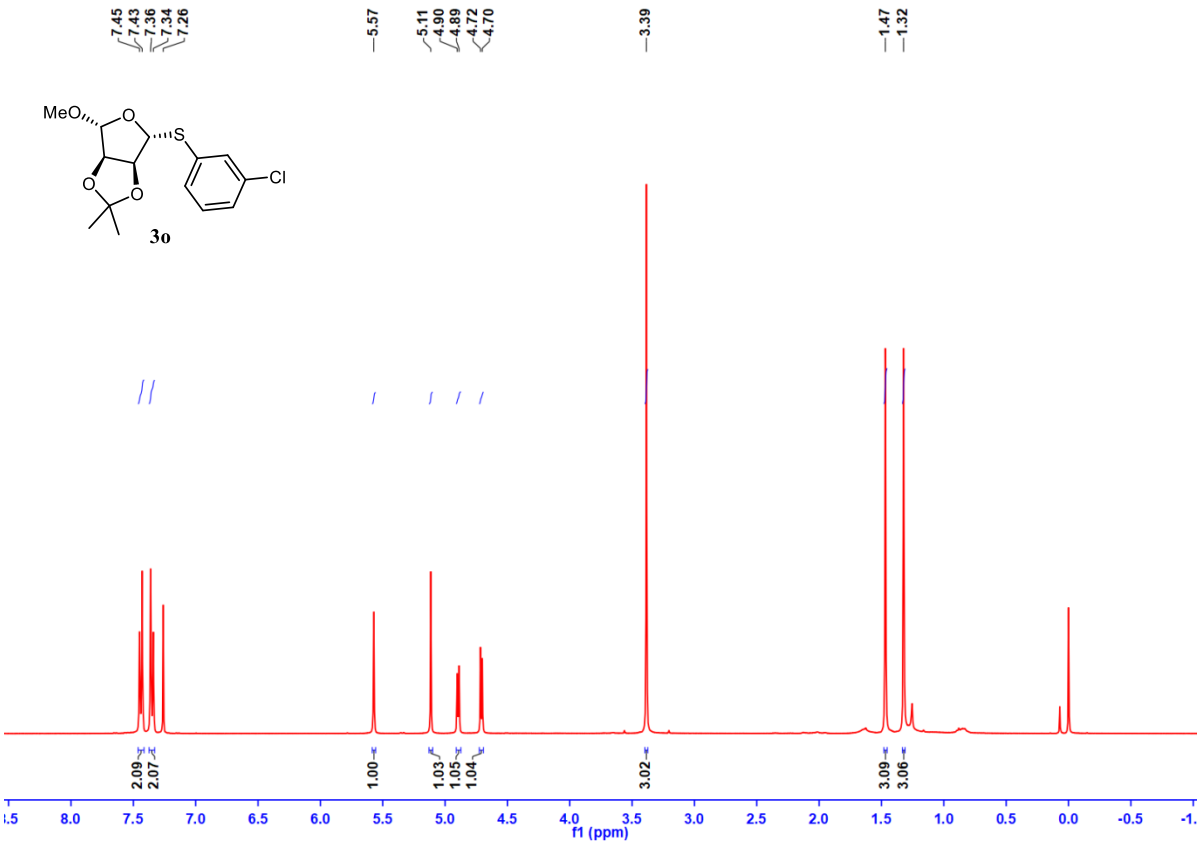
-111.81
-111.83
-111.84
-111.85
MeO
O
S
F
O
O
3n
f1 (ppm)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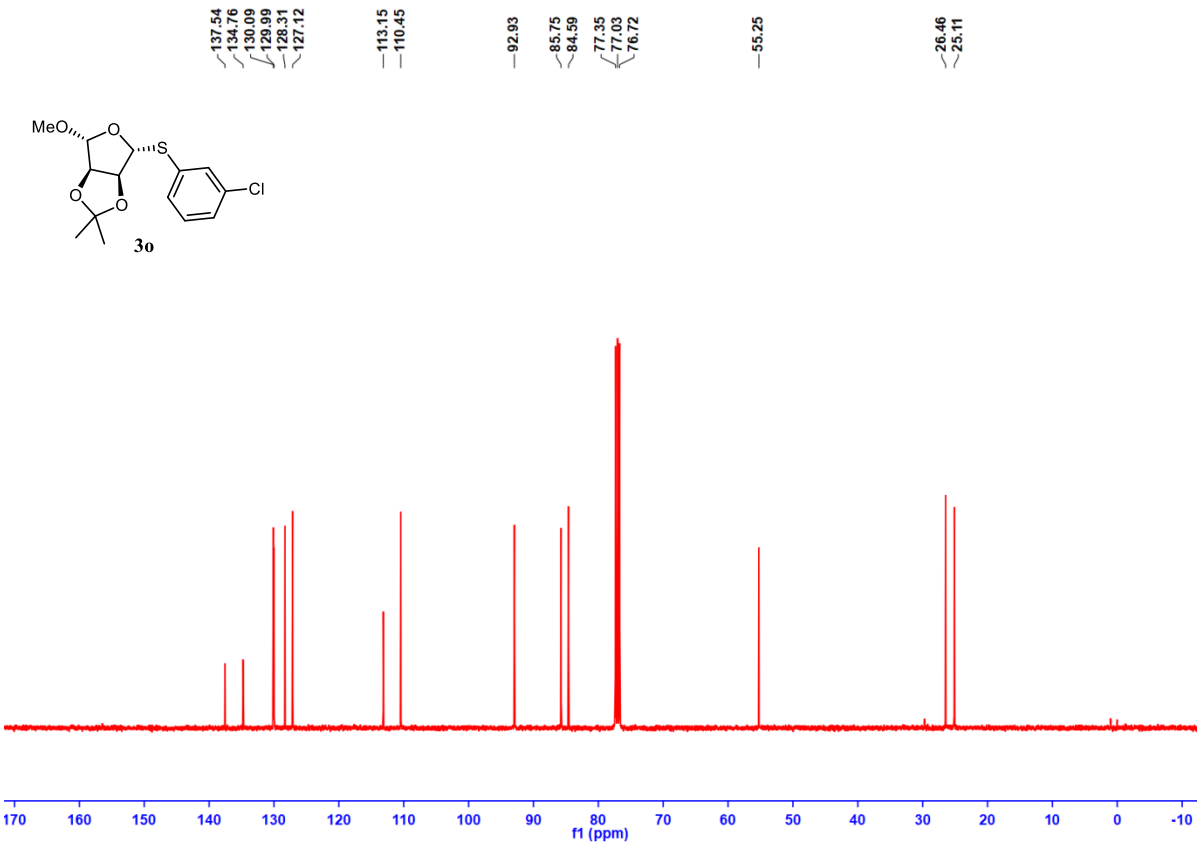
4.89
4.72
4.70
3.39
1.47
1.32
MeO
O
S
Cl
O
O
3o
2.09
2.07
1.00
1.03
1.05
1.04
3.02
3.09
3.06
f1 (ppm)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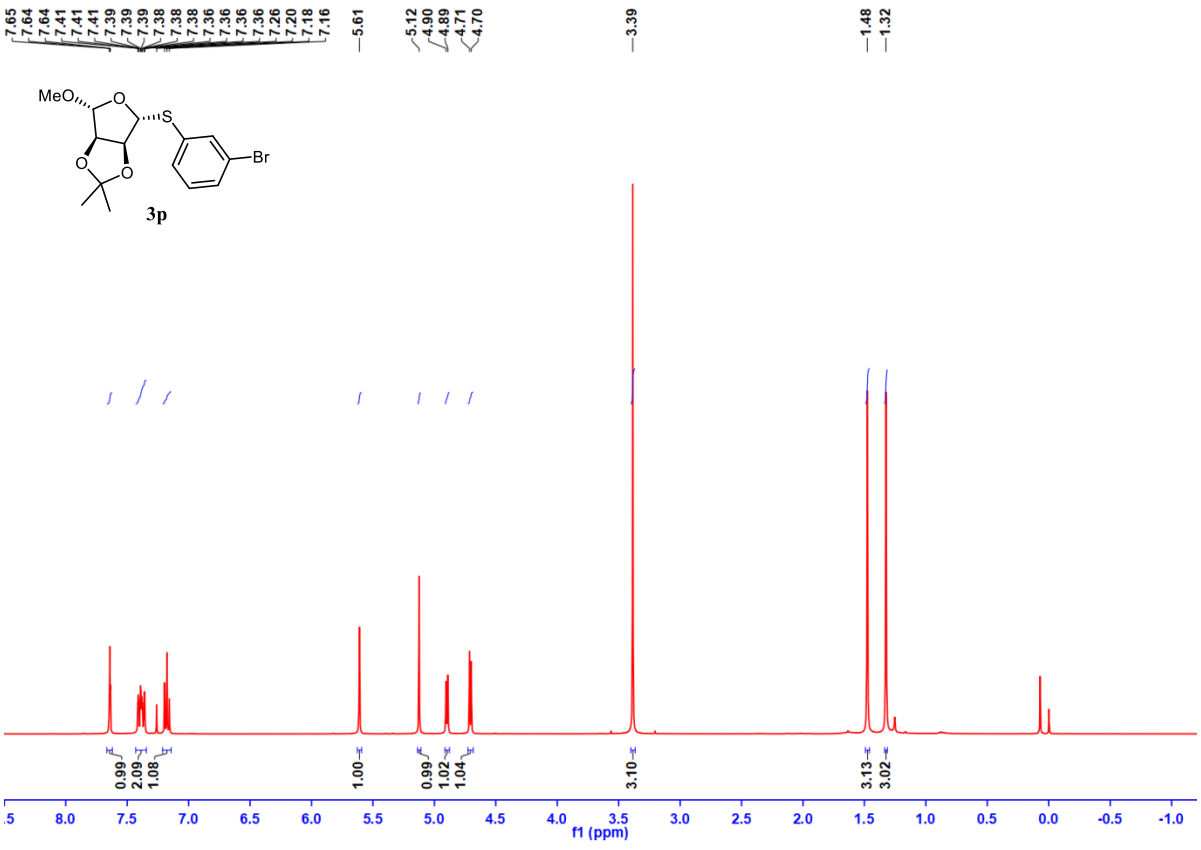
77.35
77.03
76.72
55.25
26.46
25.11
MeO
O
S
Cl
O
O
3o
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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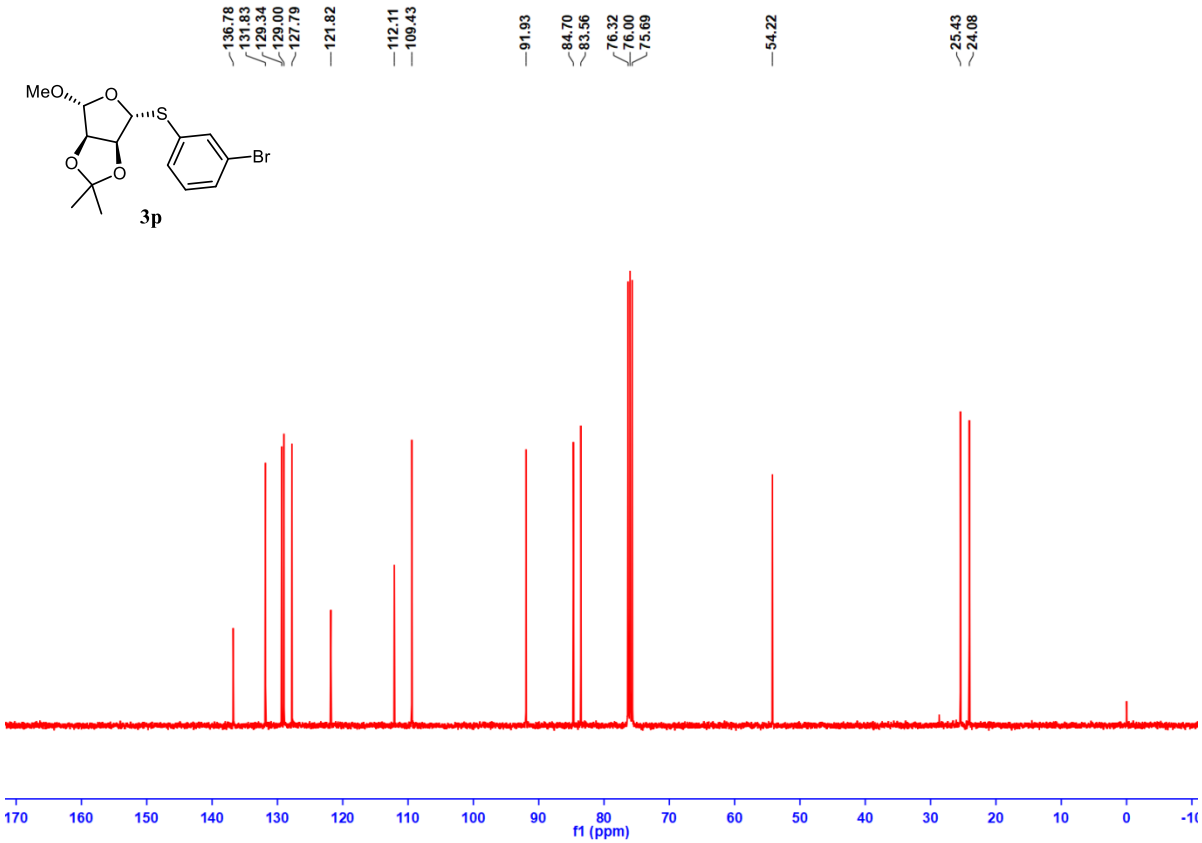
7.36
7.36
7.36
7.26
7.20
7.18
7.16
5.61
5.12
4.90
4.89
4.71
4.70
3.39
1.48
1.32
MeO
O
S
Br
O
O
3p
0.99
2.09
1.08
1.00
0.99
1.02
1.04
3.10
3.13
3.02
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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83.56
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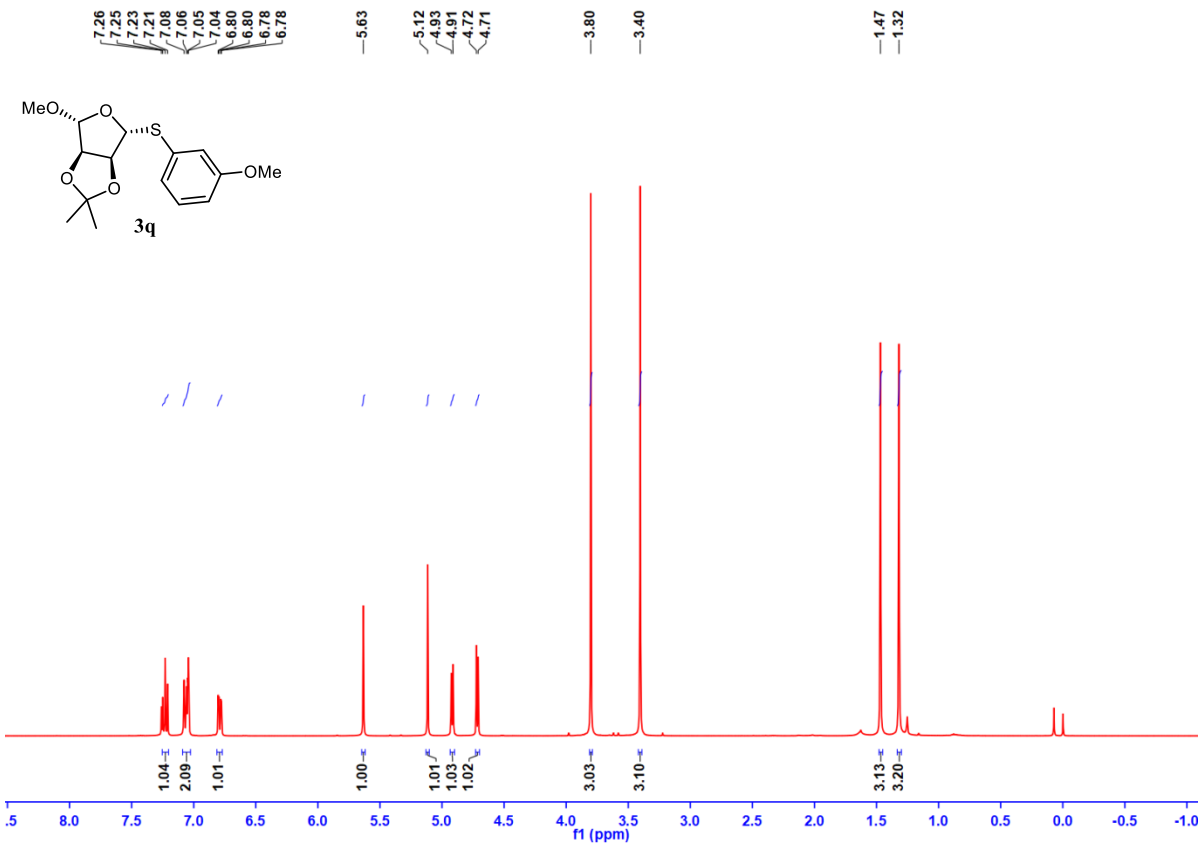
54.22
25.43
24.08
MeO
O
S
Br
O
O
3p
f1 (ppm)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7.04
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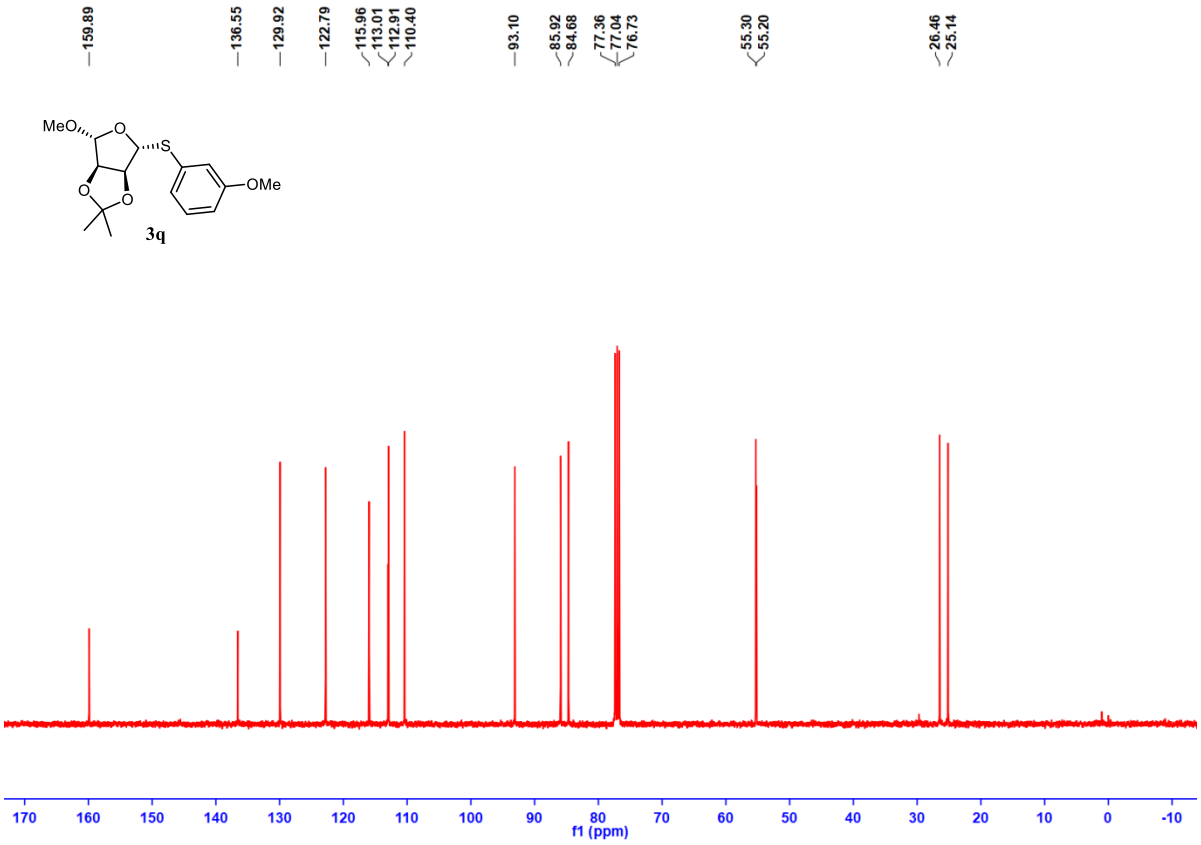
6.80
6.78
6.78
5.63
5.12
4.93
4.91
4.72
4.71
3.80
3.40
1.47
1.32
MeO
O
S
OMe
O
O
3q
1.04
2.09
1.01
1.00
1.01
1.03
1.02
3.03
3.10
3.13
3.20
f1 (ppm)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85.92
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77.36
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76.73
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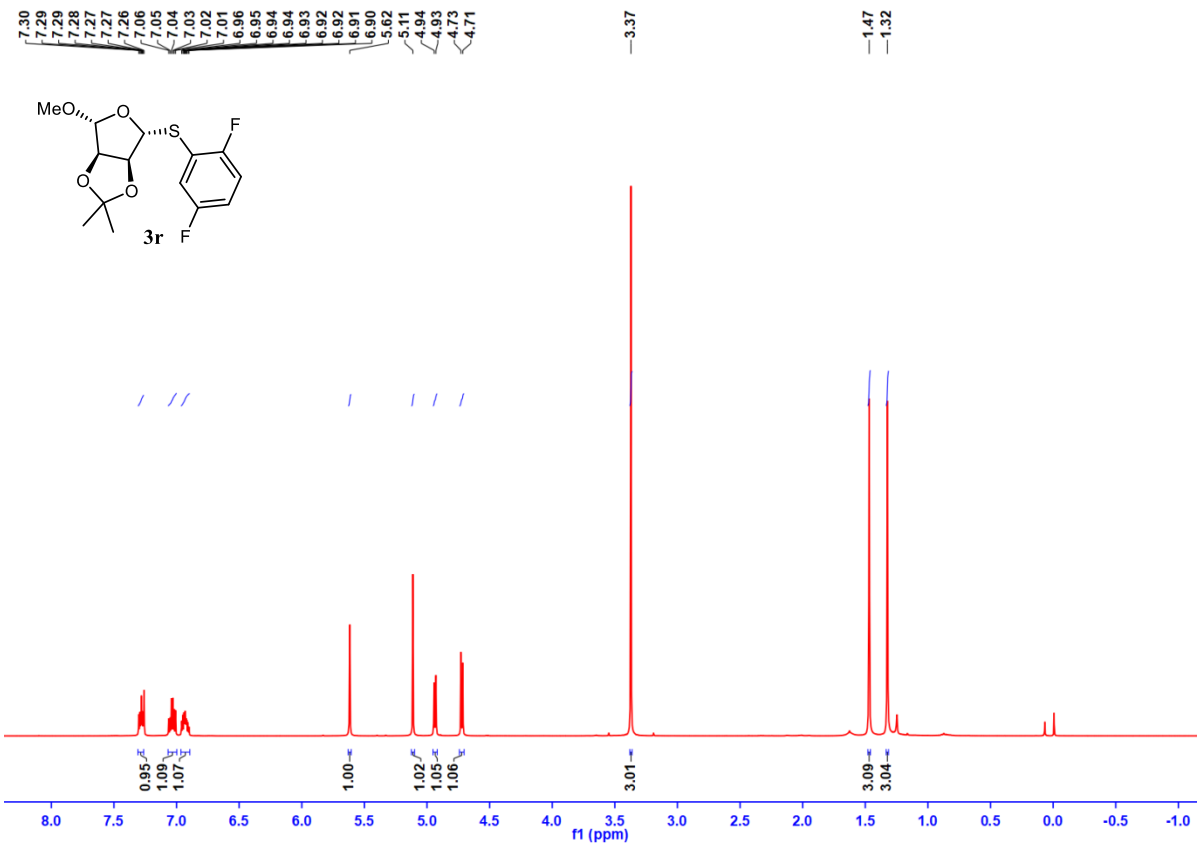
55.20
26.46
25.14
MeO
O
S
OMe
O
O
3q
f1 (ppm)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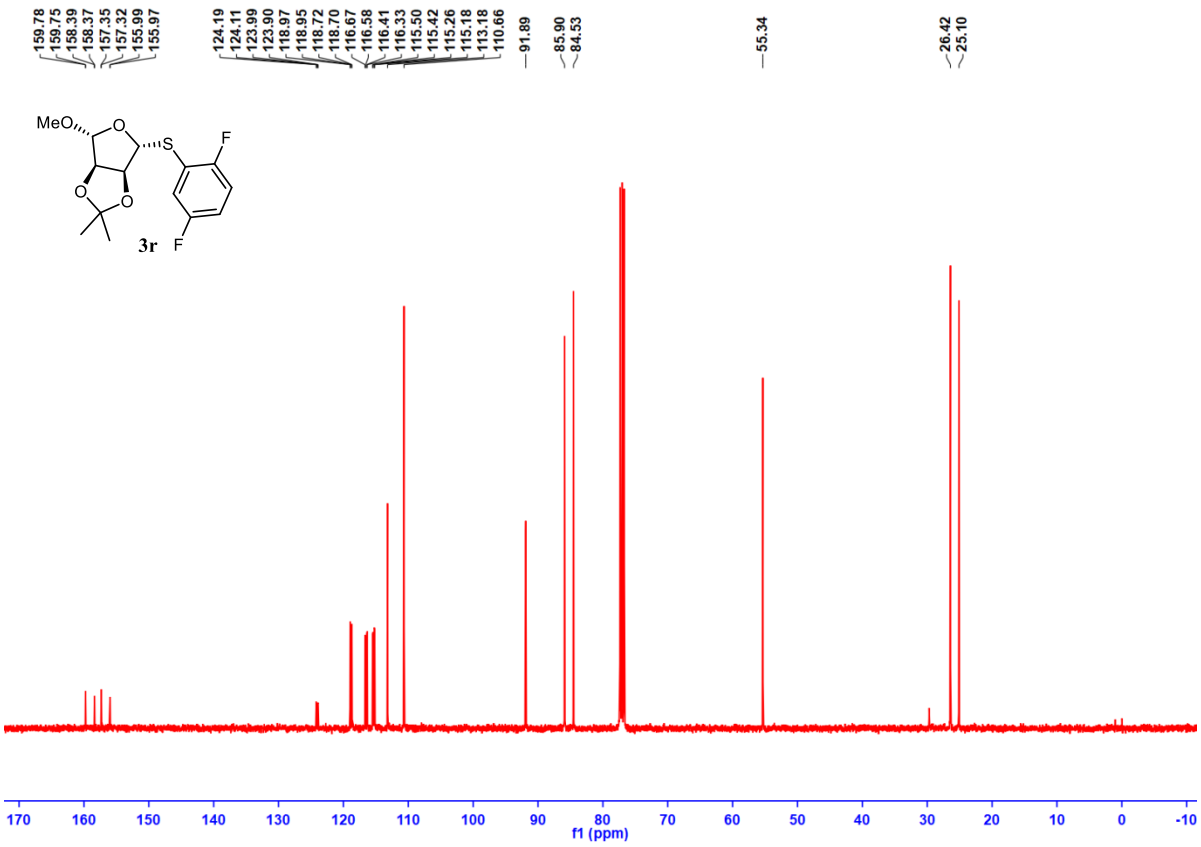
4.94
4.93
4.73
4.71
3.37
1.47
1.32
MeO
O
S
F
O
O
3r
F
0.95
1.09
1.07
1.00
1.02
1.05
1.06
3.01
3.09
3.04
f1 (ppm)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123.90
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118.95
118.72
118.70
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116.58
116.41
116.33
115.50
115.42
115.26
115.18
113.18
110.66
91.89
85.90
84.53
55.34
26.42
25.10
MeO
O
S
F
O
O
F
3r
170
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120
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100
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80
70
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40
30
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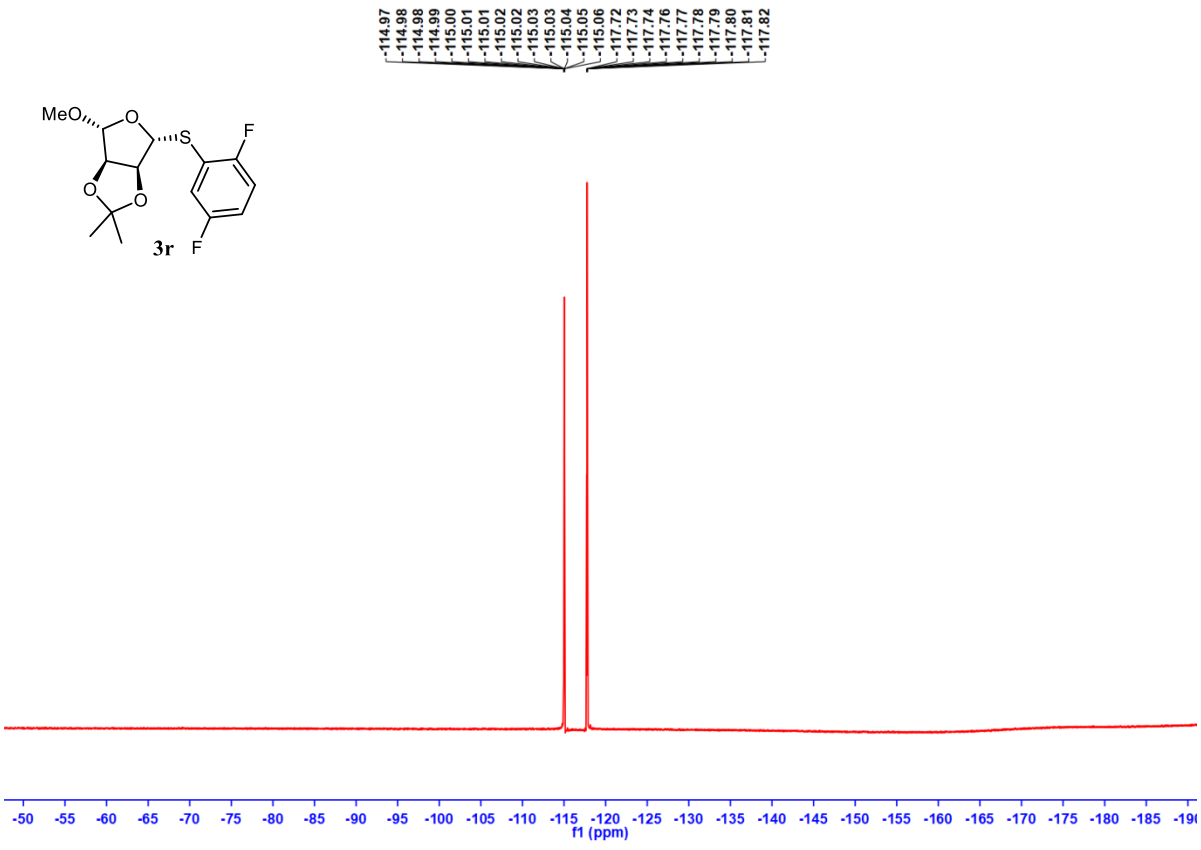
f1 (ppm)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-115.03
-115.04
-115.05
-115.06
-117.72
-117.73
-117.74
-117.76
-117.77
-117.78
-117.79
-117.80
-117.81
-117.82
MeO
O
S
F
O
O
F
3r
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
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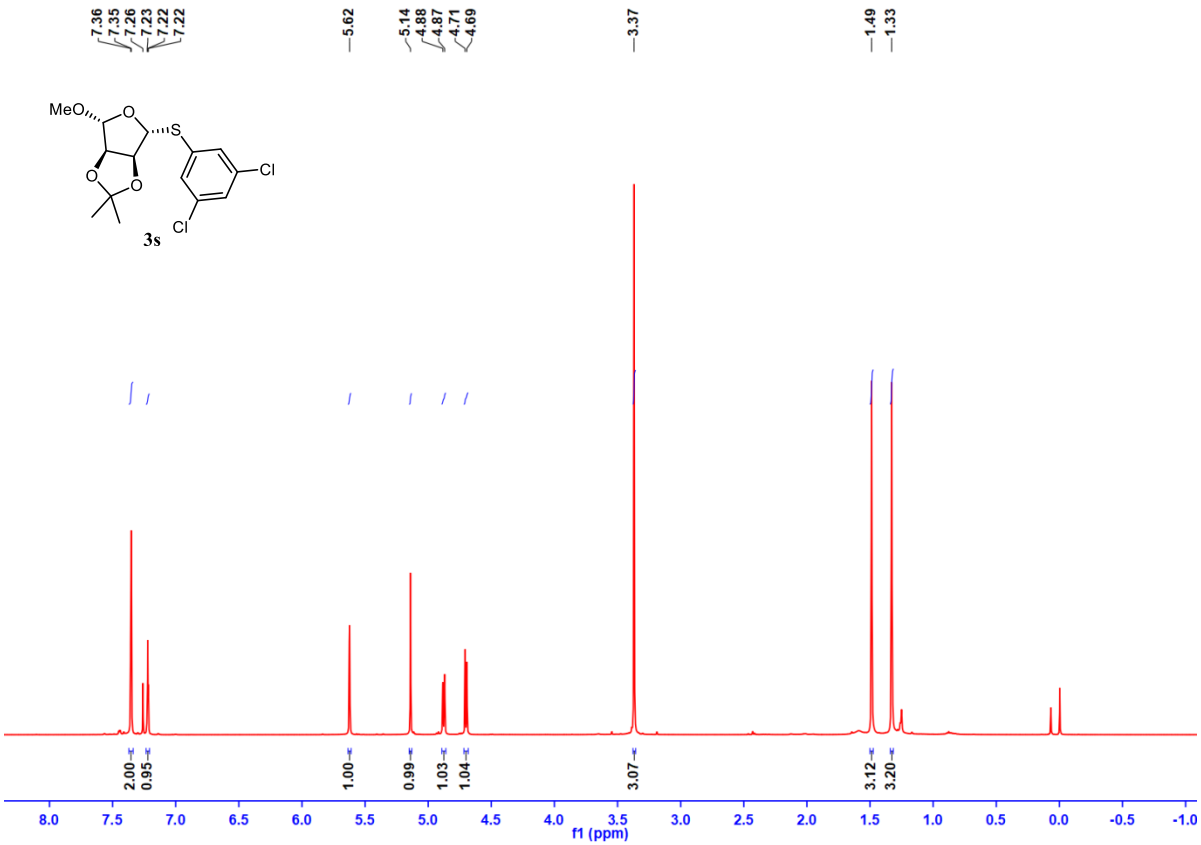
-165
-170
-175
-180
-185
f1 (ppm)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4.69
3.37
1.49
1.33
MeO
O
S
Cl
O
O
Cl
3s
2.00
0.95
1.00
0.99
1.03
1.04
3.07
3.12
3.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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0.0
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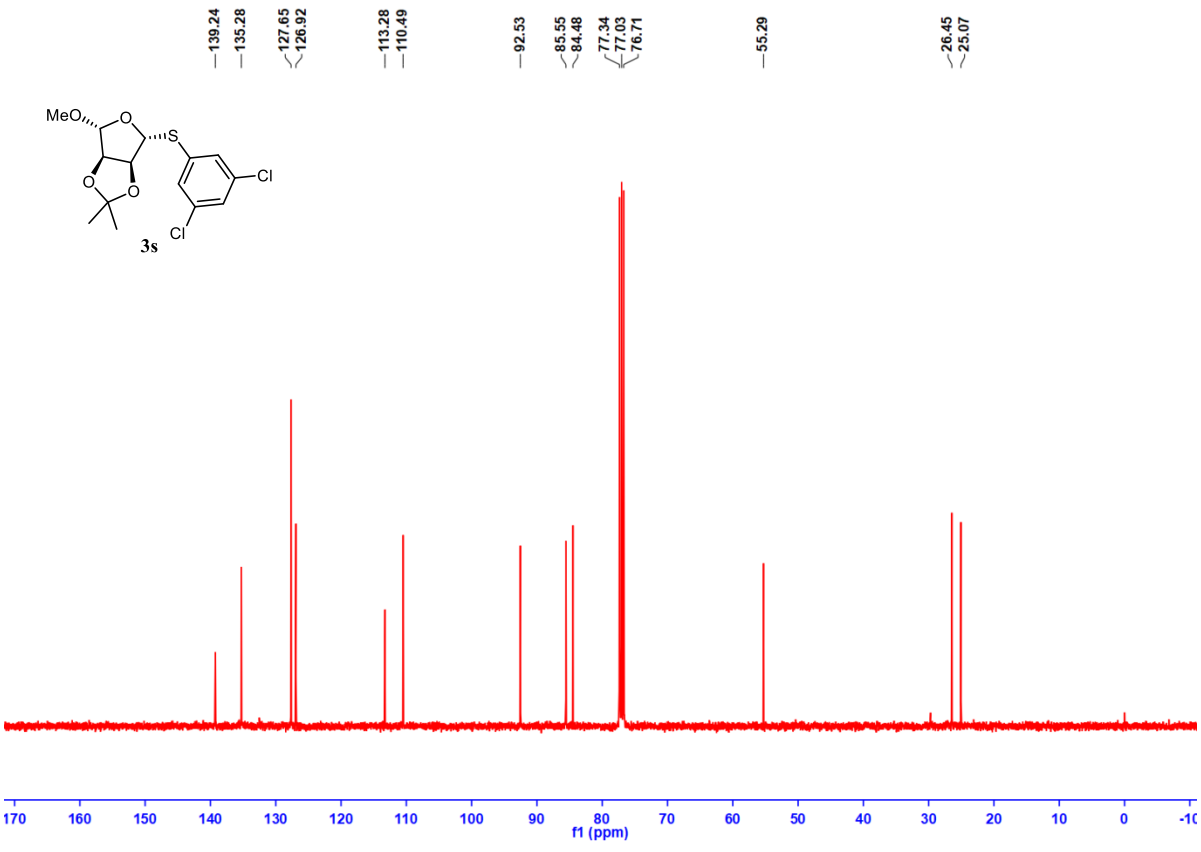
-1.0
f1 (ppm)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77.34
77.03
76.71
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26.45
25.07
MeO
O
S
Cl
O
O
Cl
3s
170
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100
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80
70
60
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40
30
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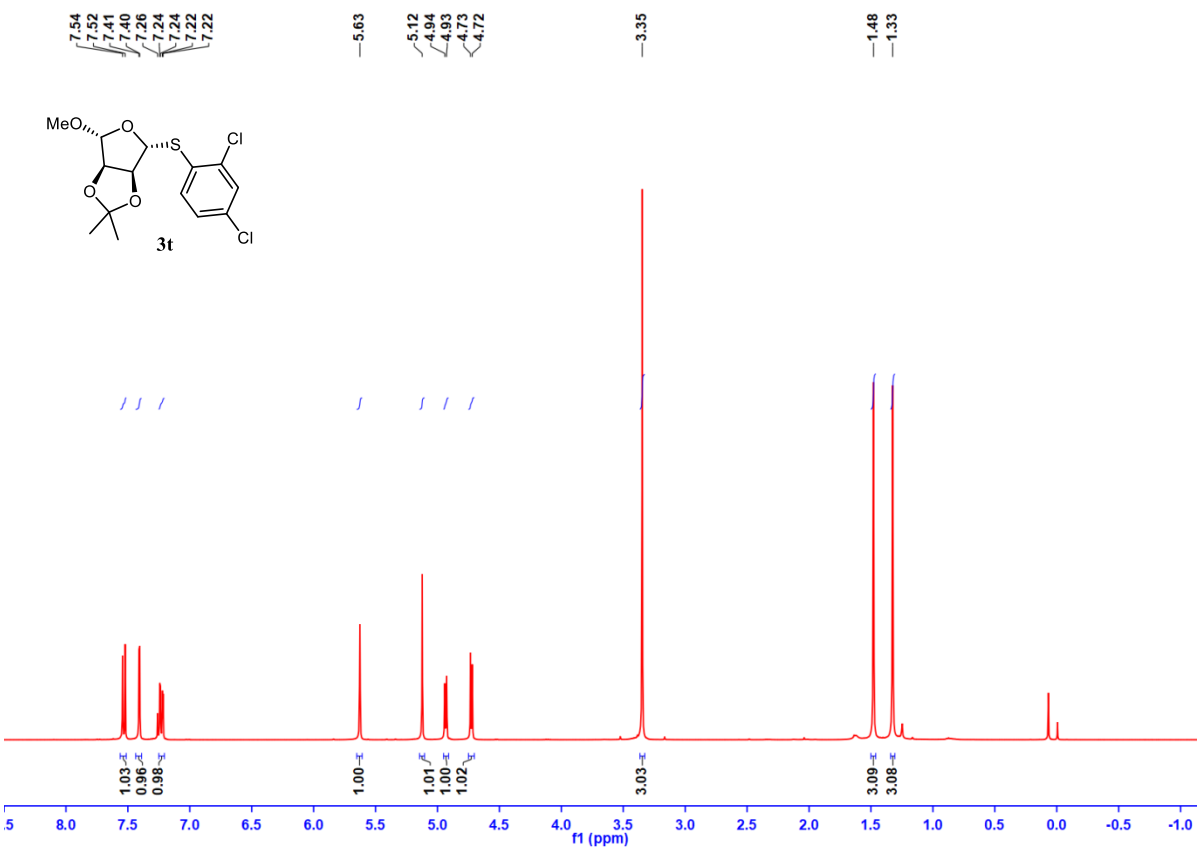
-10
f1 (ppm)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4.73
4.72
3.35
1.48
1.33
MeO
O
S
Cl
Cl
O
O
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0.98
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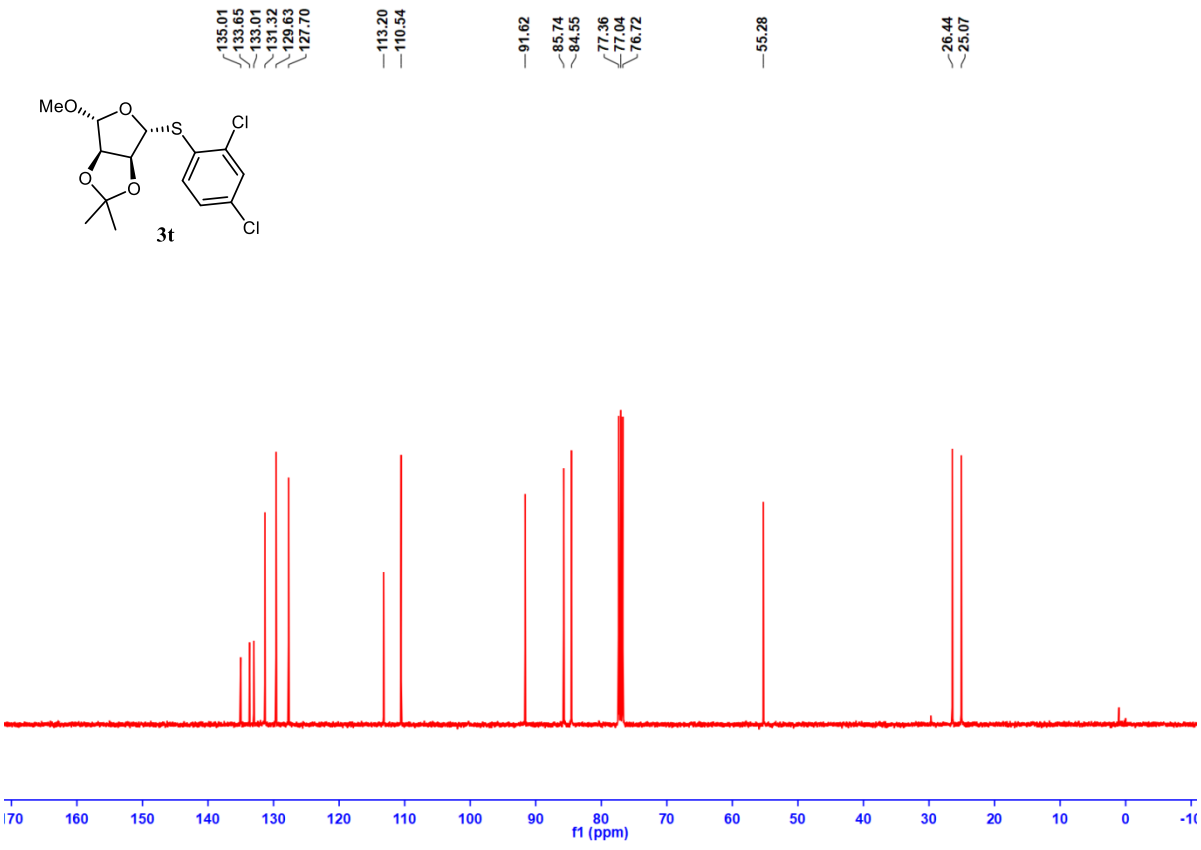
1.01
1.00
1.02
3.03
3.09
3.08
f1 (ppm)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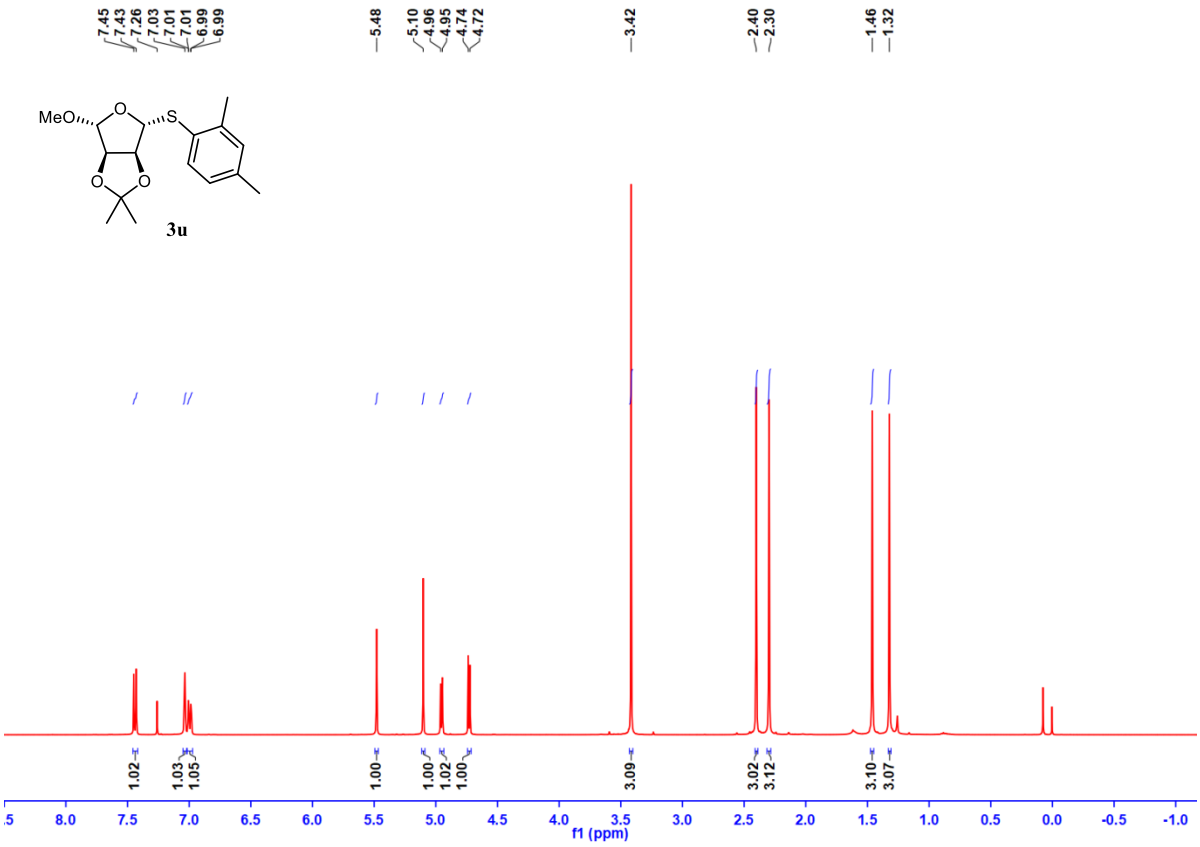
26.44
25.07
MeO
O
S
Cl
Cl
O
O
3t
f1 (ppm)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4.95
4.74
4.72
3.42
2.40
2.30
1.46
1.32
MeO
O
S
O
O
1.02
1.03
1.05
1.00
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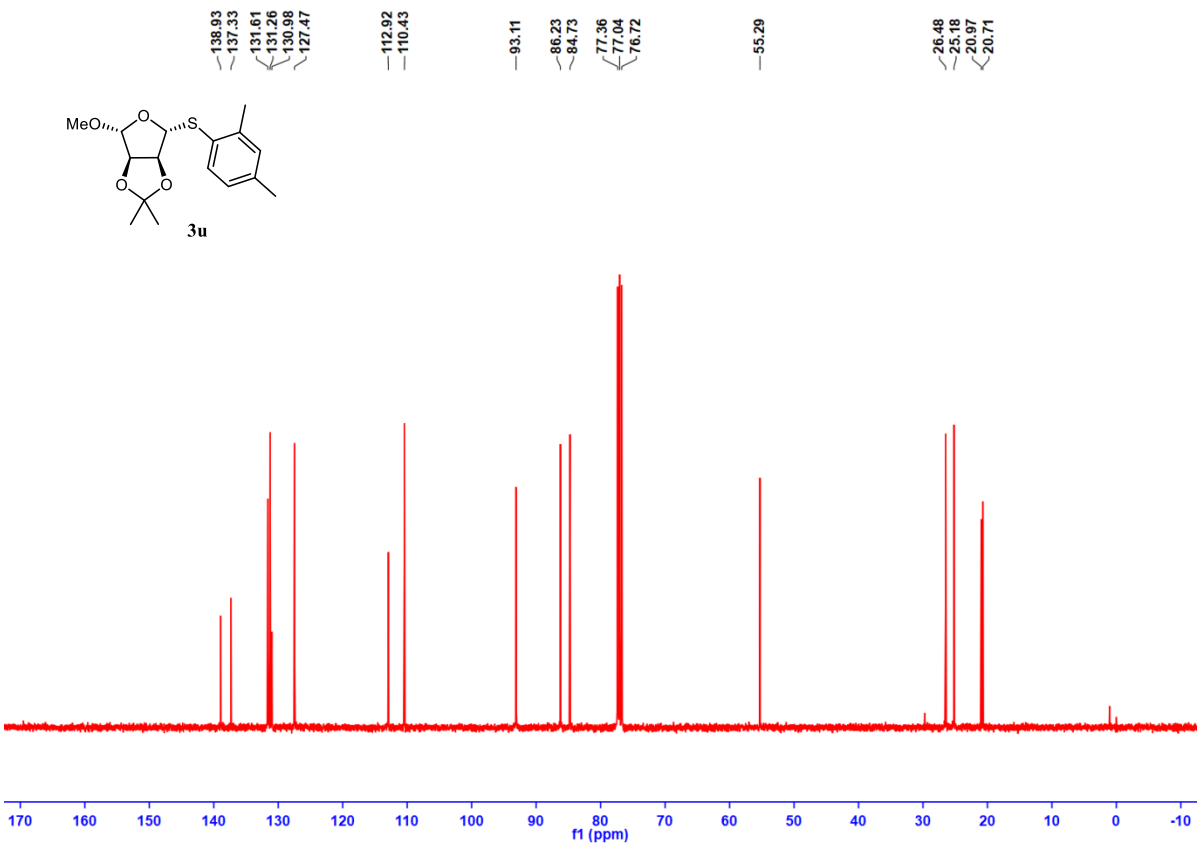
1.02
1.00
3.09
3.02
3.12
3.10
3.07
f1 (ppm)

3u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86.23
84.73
77.36
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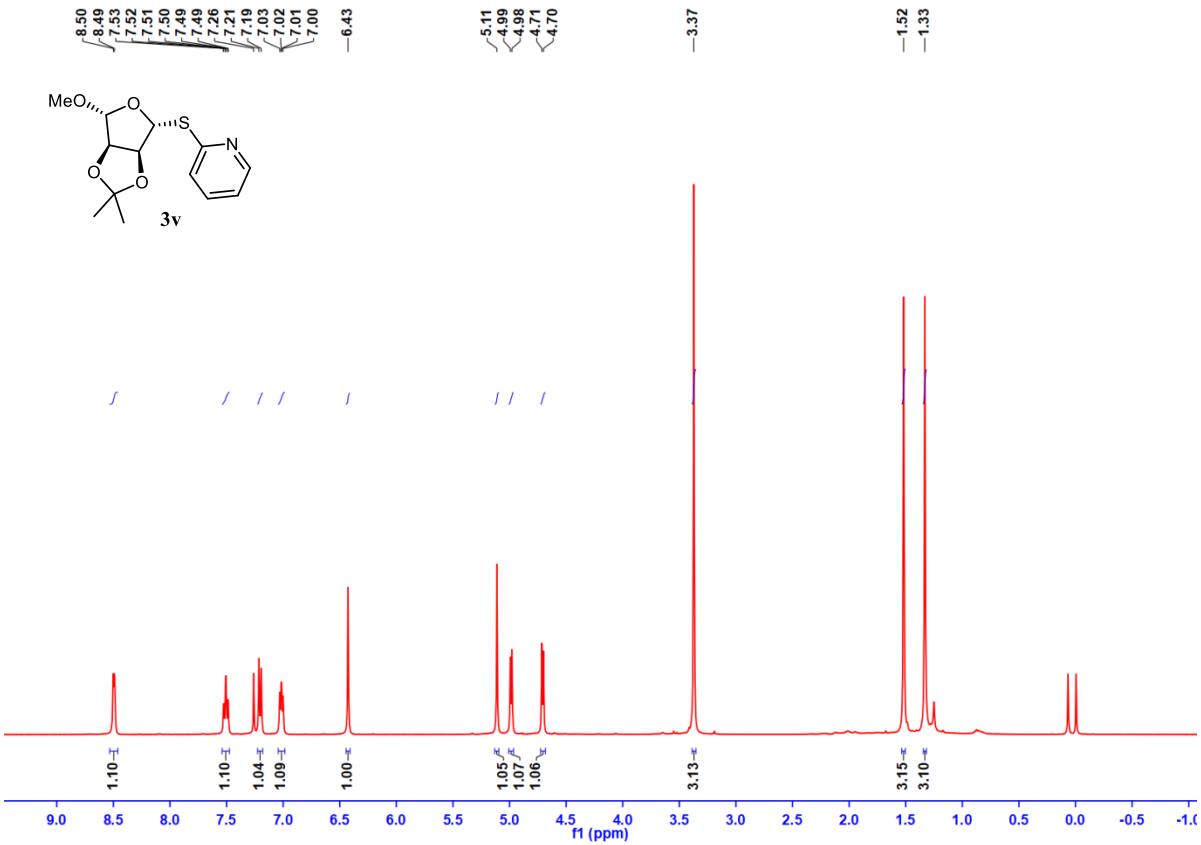
26.48
25.18
20.97
20.71
MeO
O
S
O
O
f1 (ppm)

3u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7.02
7.01
7.00
6.43
5.11
4.99
4.98
4.71
4.70
3.37
1.52
1.33
MeO
O
S
N
O
O
3v
1.10
1.10
1.04
1.09
1.00
1.05
1.07
1.06
3.13
3.15
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
2.5
2.0
1.5
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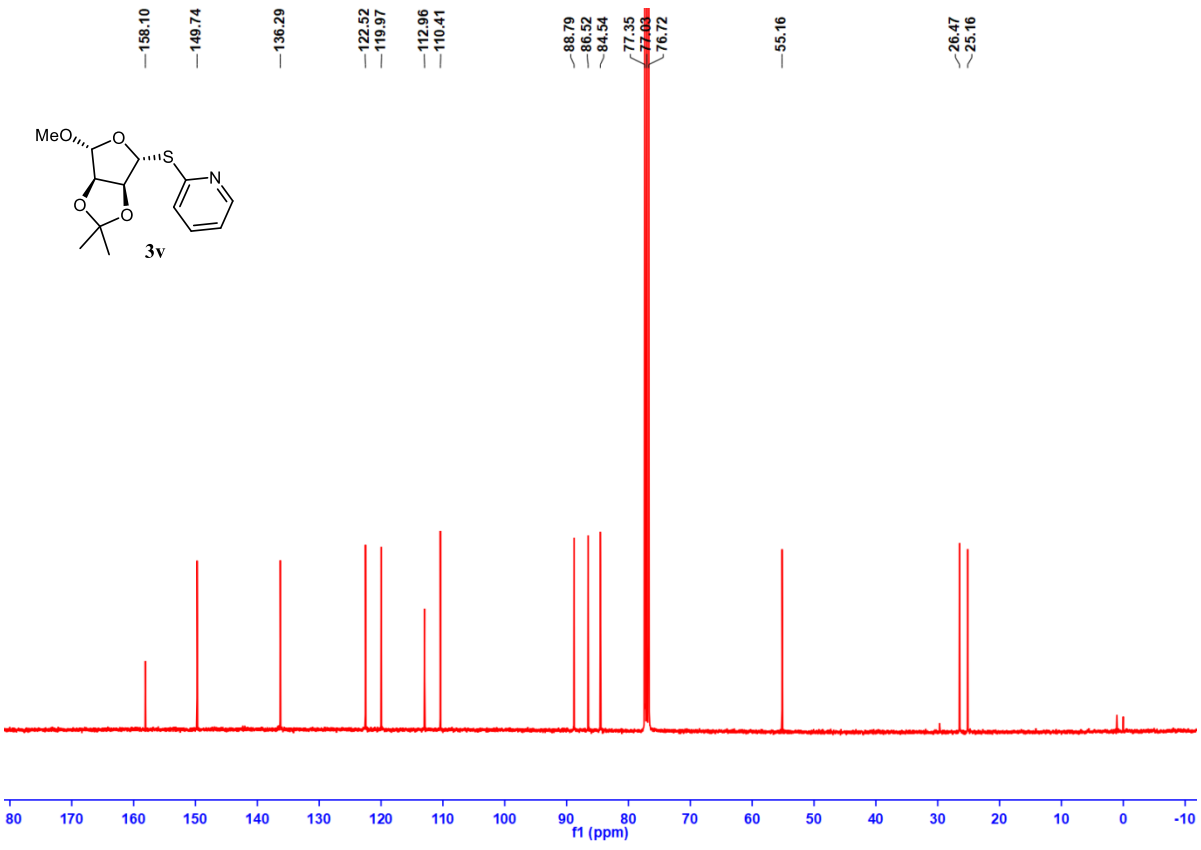
f1 (ppm)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84.54
77.35
77.03
76.72
55.16
26.47
25.16
MeO
O
S
N
O
O
3v
80
170
160
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140
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120
110
100
90
80
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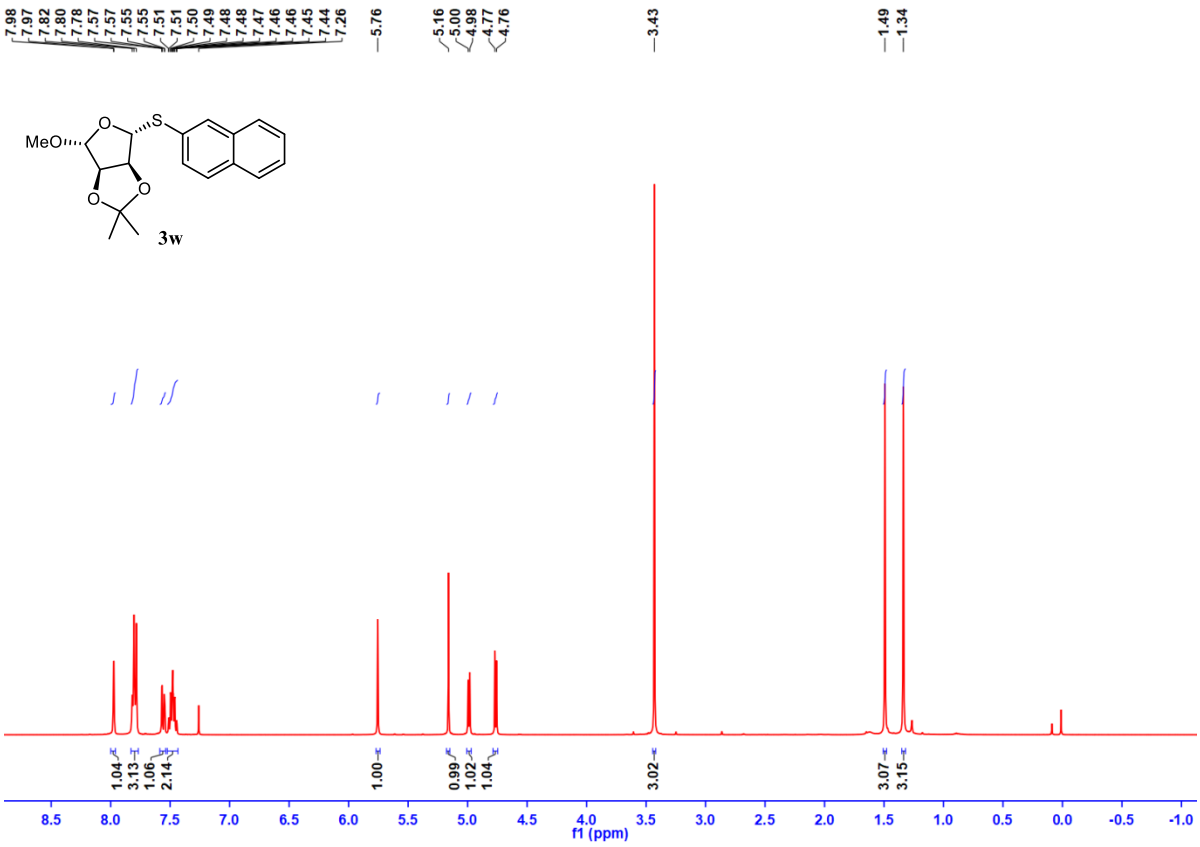
60
50
40
30
20
10
0
-10
f1 (ppm)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7.49
7.48
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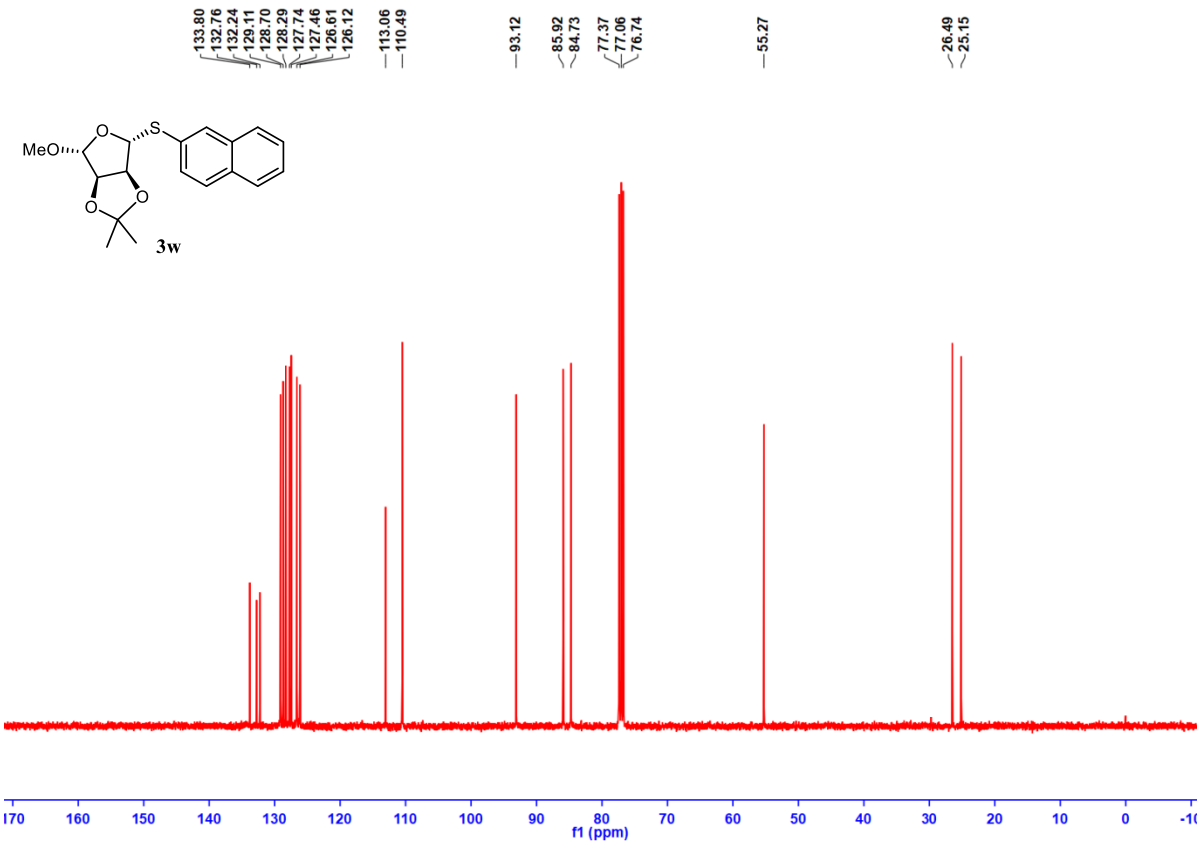
7.47
7.46
7.46
7.45
7.44
7.26
5.76
5.16
5.00
4.98
4.77
4.76
3.43
1.49
1.34
MeO
3w
1.04
3.13
1.06
2.14
1.00
0.99
1.02
1.04
3.02
3.07
3.15
f1 (ppm)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76.74
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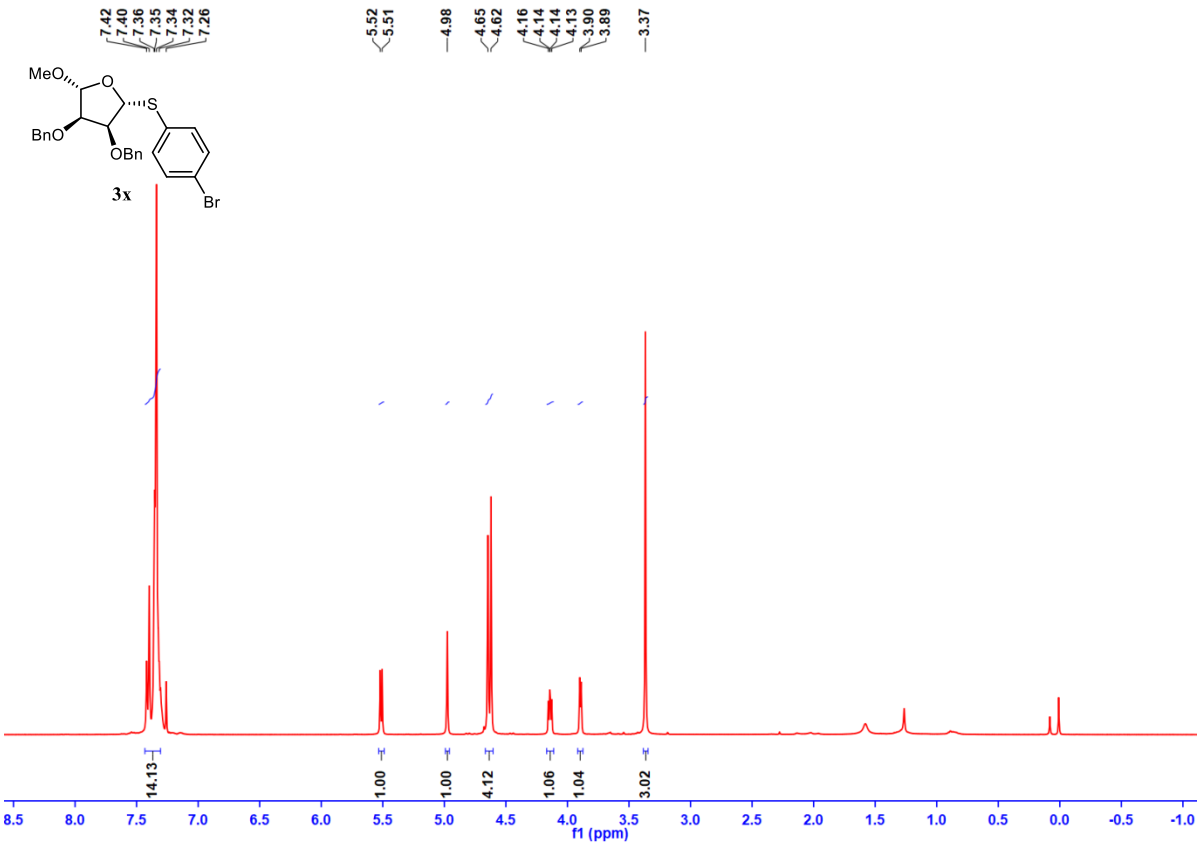
26.49
25.15
MeO
3w
f1 (ppm)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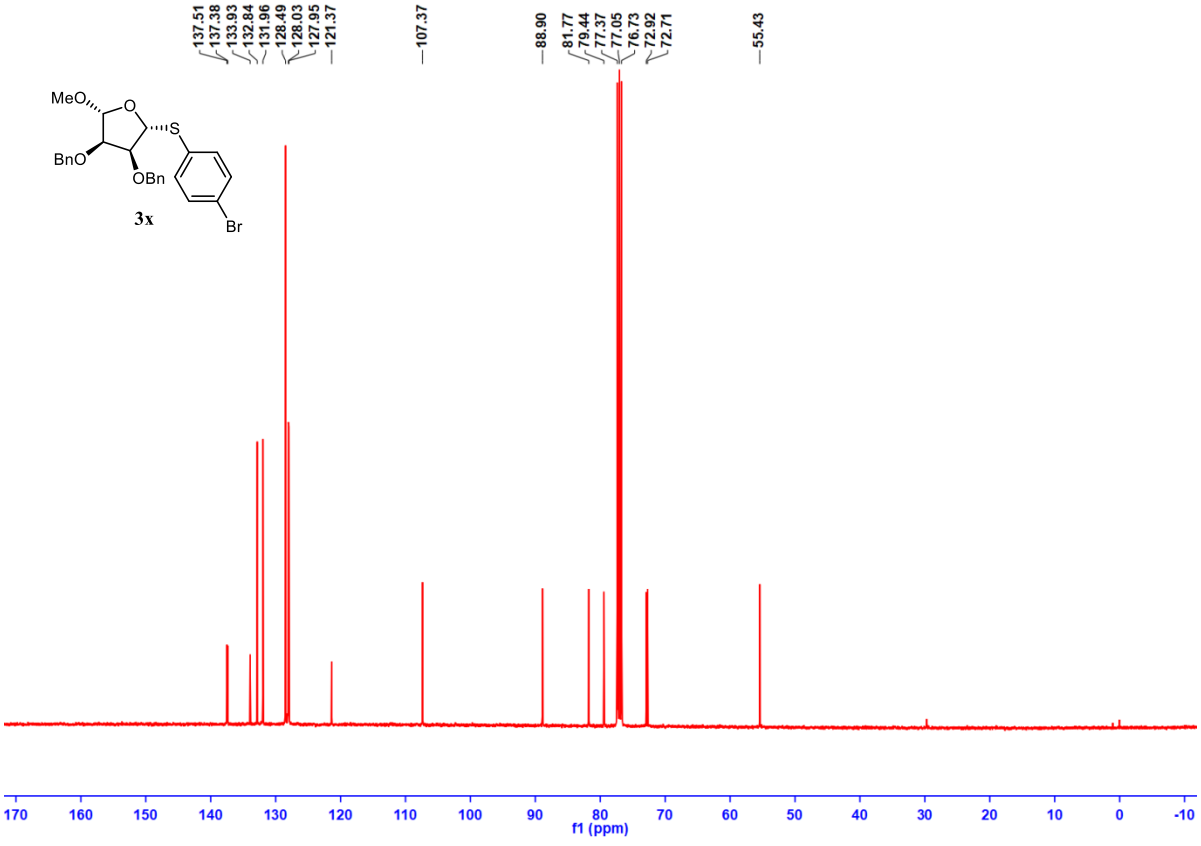
4.62
4.16
4.14
4.14
4.13
3.90
3.89
3.37
MeO
O
S
BnO
OBn
Br
3x
14.13
1.00
1.00
4.12
1.06
1.04
3.02
f1 (ppm)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79.44
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77.05
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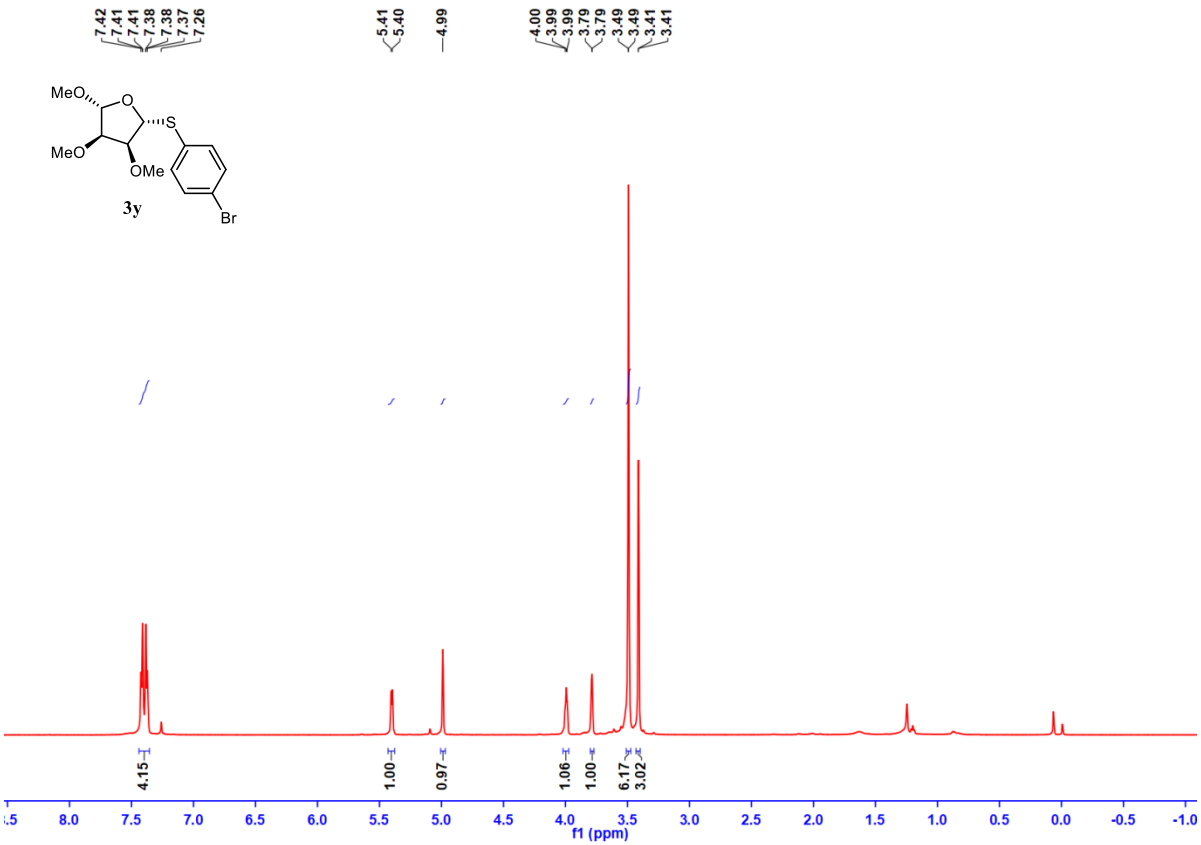
72.92
72.71
55.43
MeO
O
S
BnO
OBn
Br
3x
f1 (ppm)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3.79
3.49
3.49
3.41
3.41
MeO
MeO
OMe
O
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Br
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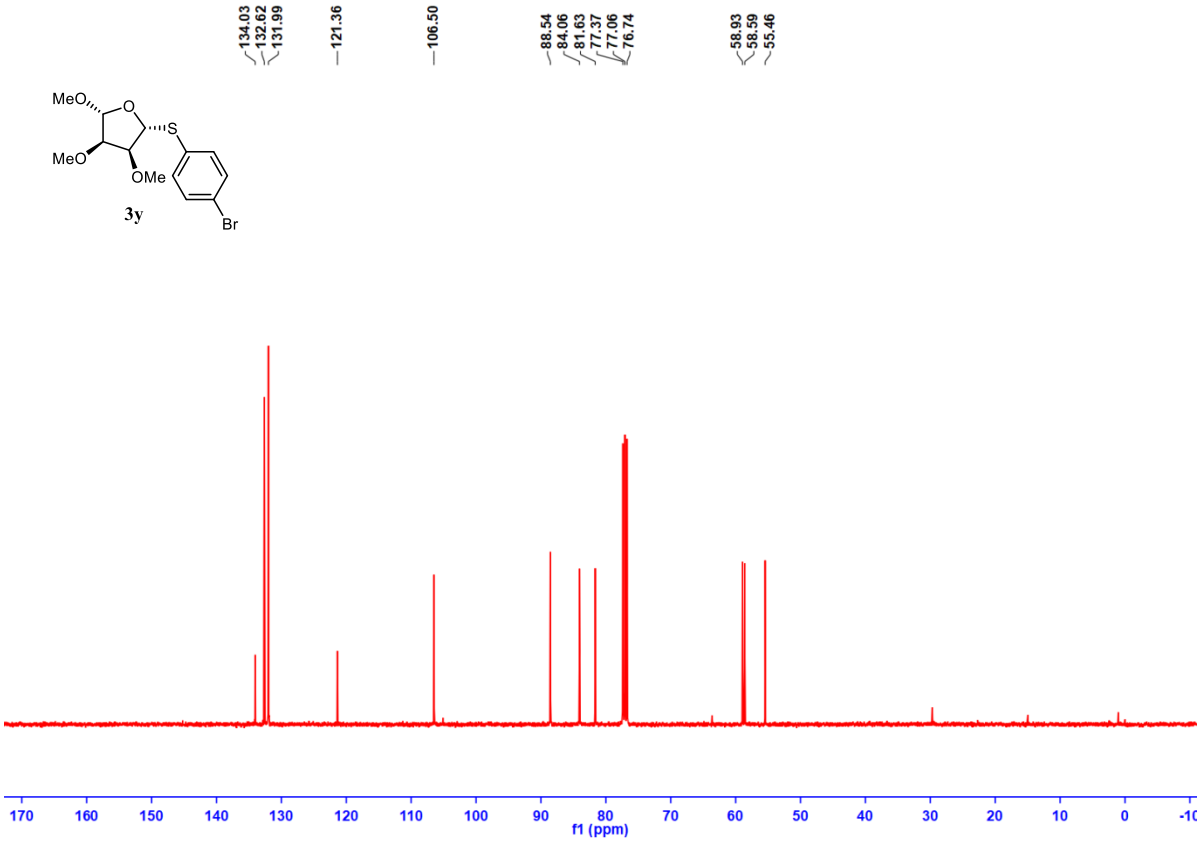
0.97
1.06
1.00
6.17
3.02
f1 (ppm)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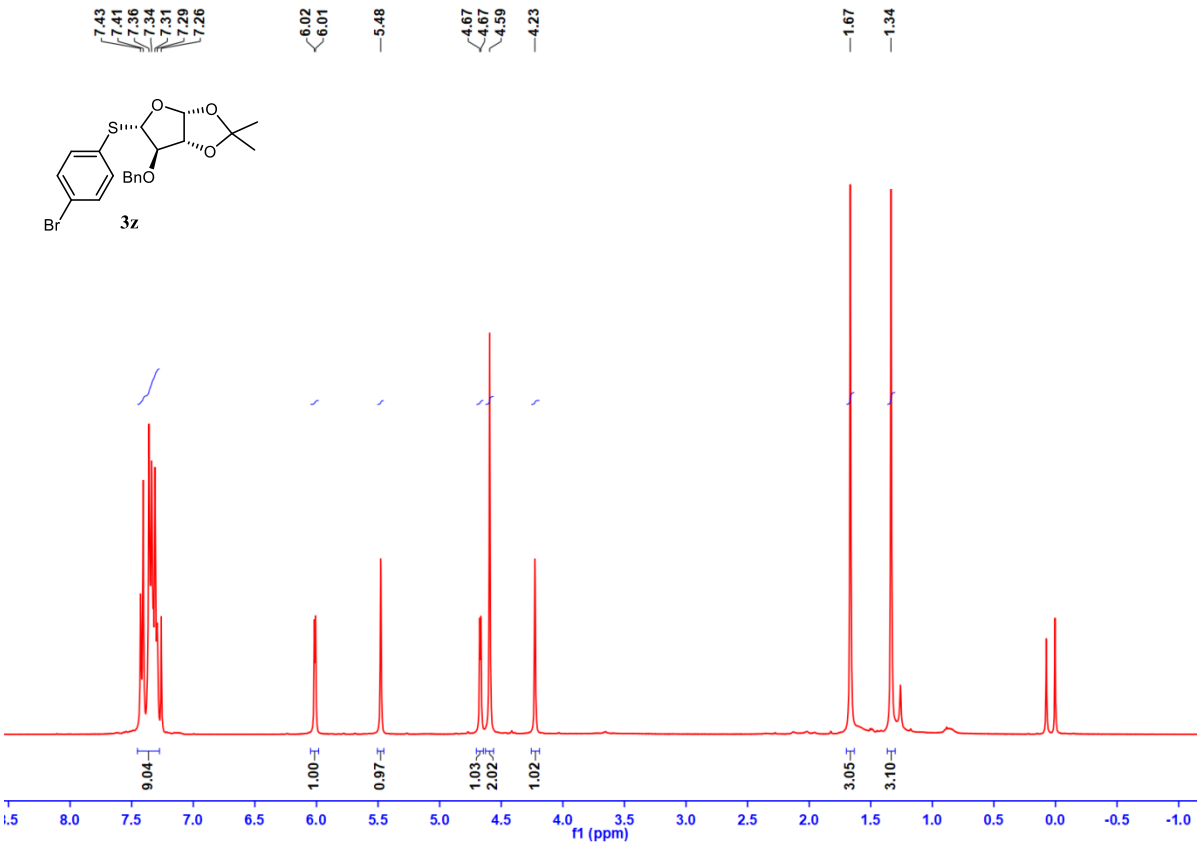
58.59
55.46
MeO
MeO
OMe
O
S
Br
3y
f1 (ppm)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4.59
4.23
1.67
1.34
BnO
Br
3z
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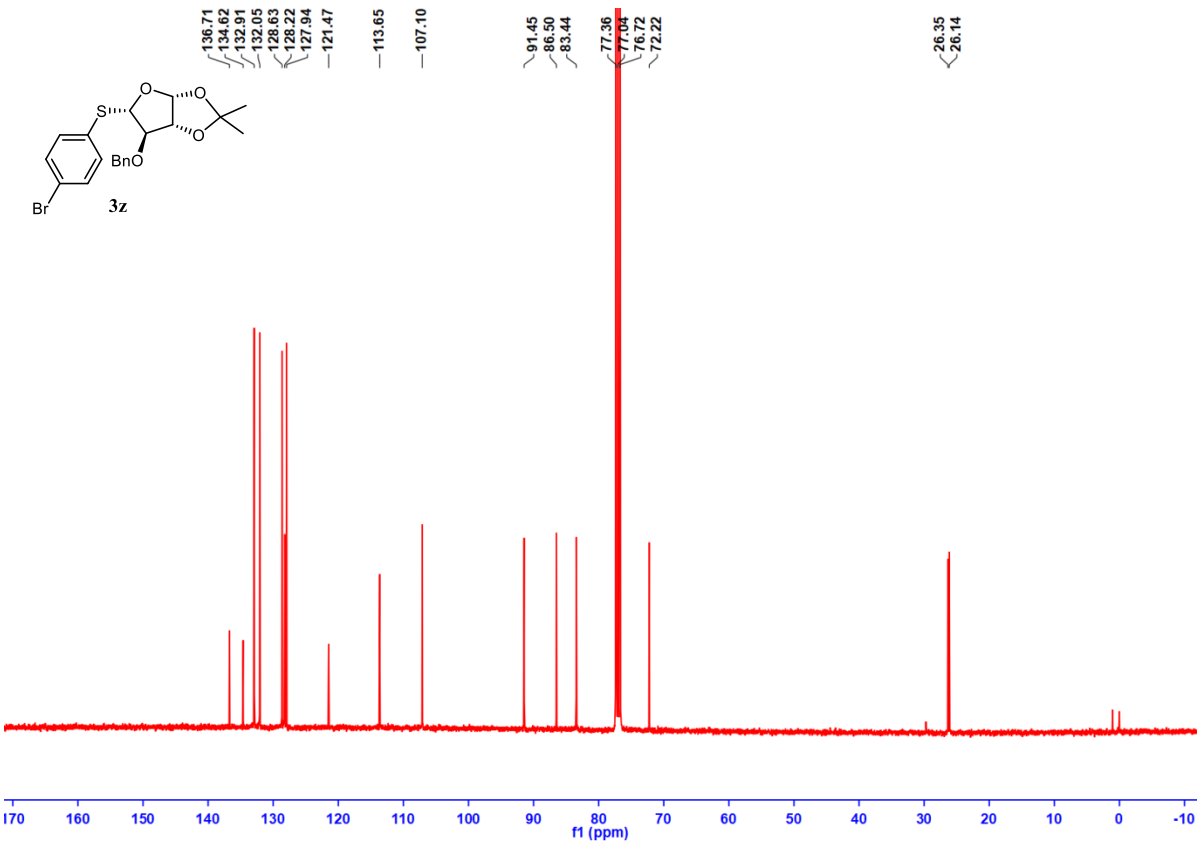
0.97
1.03
2.02
1.02
3.05
3.10
f1 (ppm)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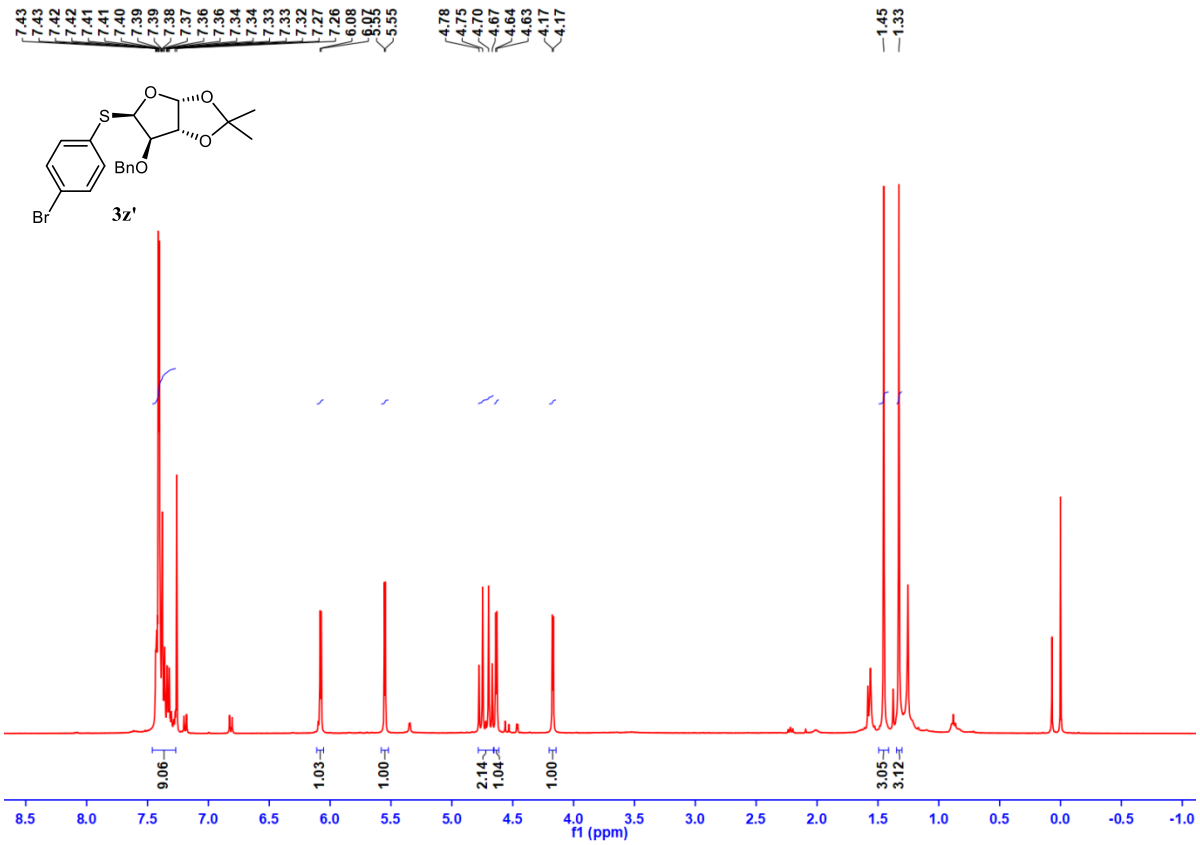
72.22
26.35
26.14
BnO
Br
3z
f1 (ppm)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7.32
7.27
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6.07
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4.70
4.67
4.64
4.63
4.17
4.17
1.45
1.33
S
O
O
O
BnO
Br
3z'
9.06
1.03
1.00
2.14
1.04
1.00
3.05
3.12
8.5
8.0
7.5
7.0
6.5
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4.0
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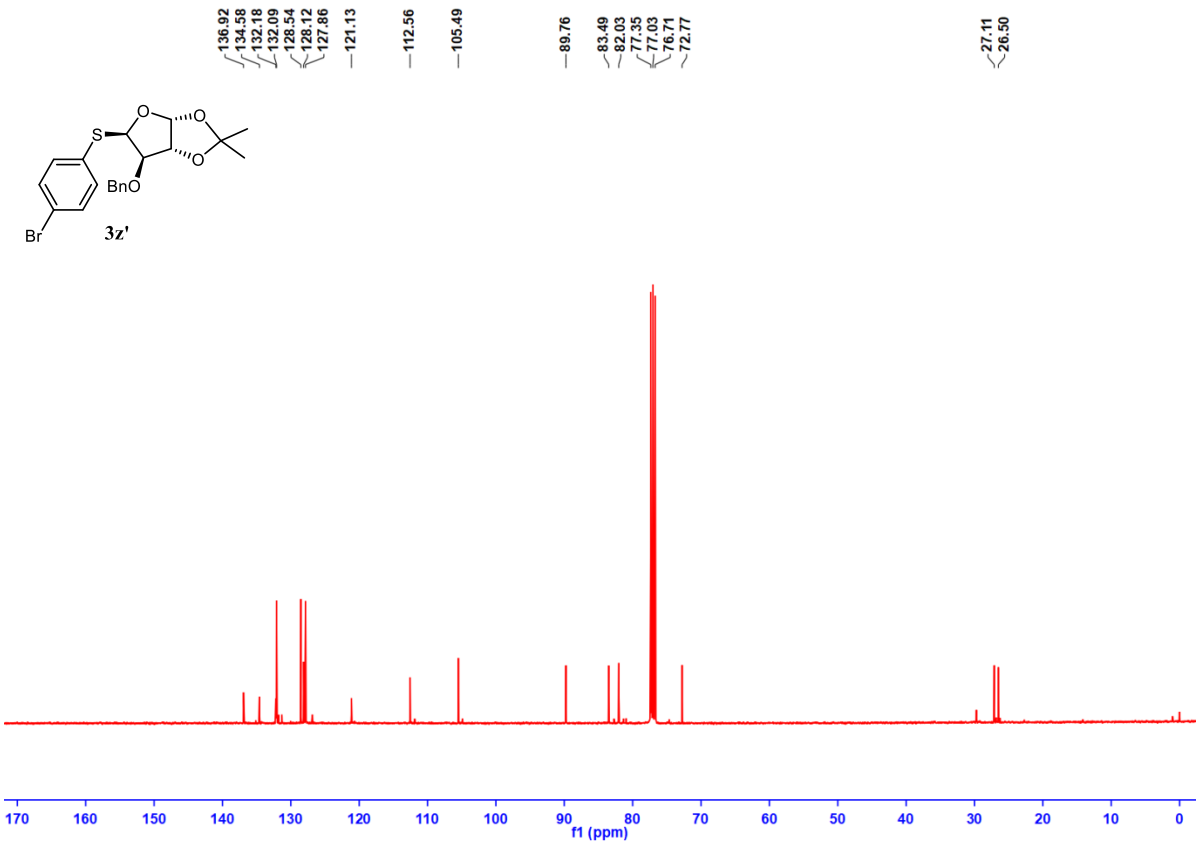
f1 (ppm)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82.03
77.35
77.03
76.71
72.77
27.11
26.50
S
O
O
O
BnO
Br
3z'
170
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140
130
120
110
100
90
80
70
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50
40
30
20
10
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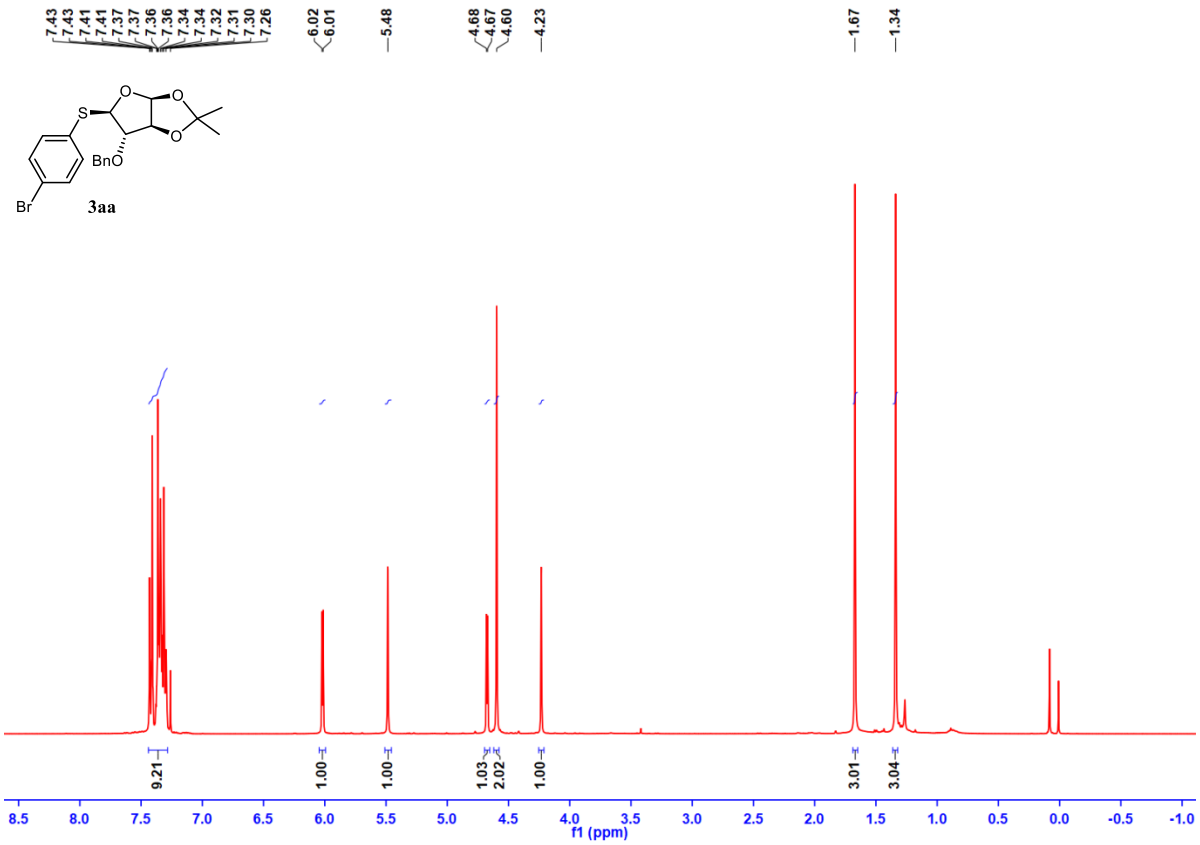
f1 (ppm)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7.26
6.02
6.01
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4.67
4.60
4.23
1.67
1.34
S
O
O
O
BnO
Br
3aa
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1.00
1.00
1.03
2.02
1.00
3.01
3.04
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
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0.0
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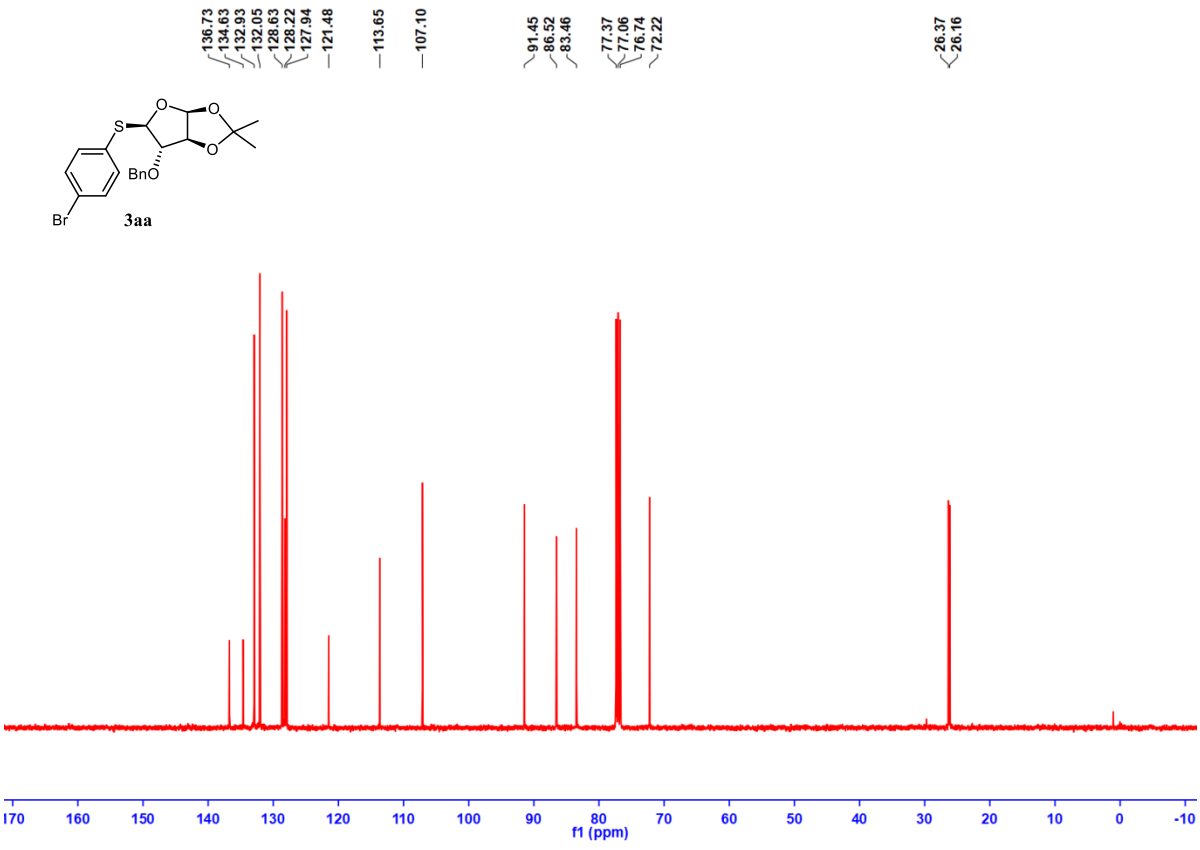
-1.0
f1 (ppm)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83.46
77.37
77.06
76.74
72.22
26.37
26.16
S
O
O
O
BnO
Br
3aa
170
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100
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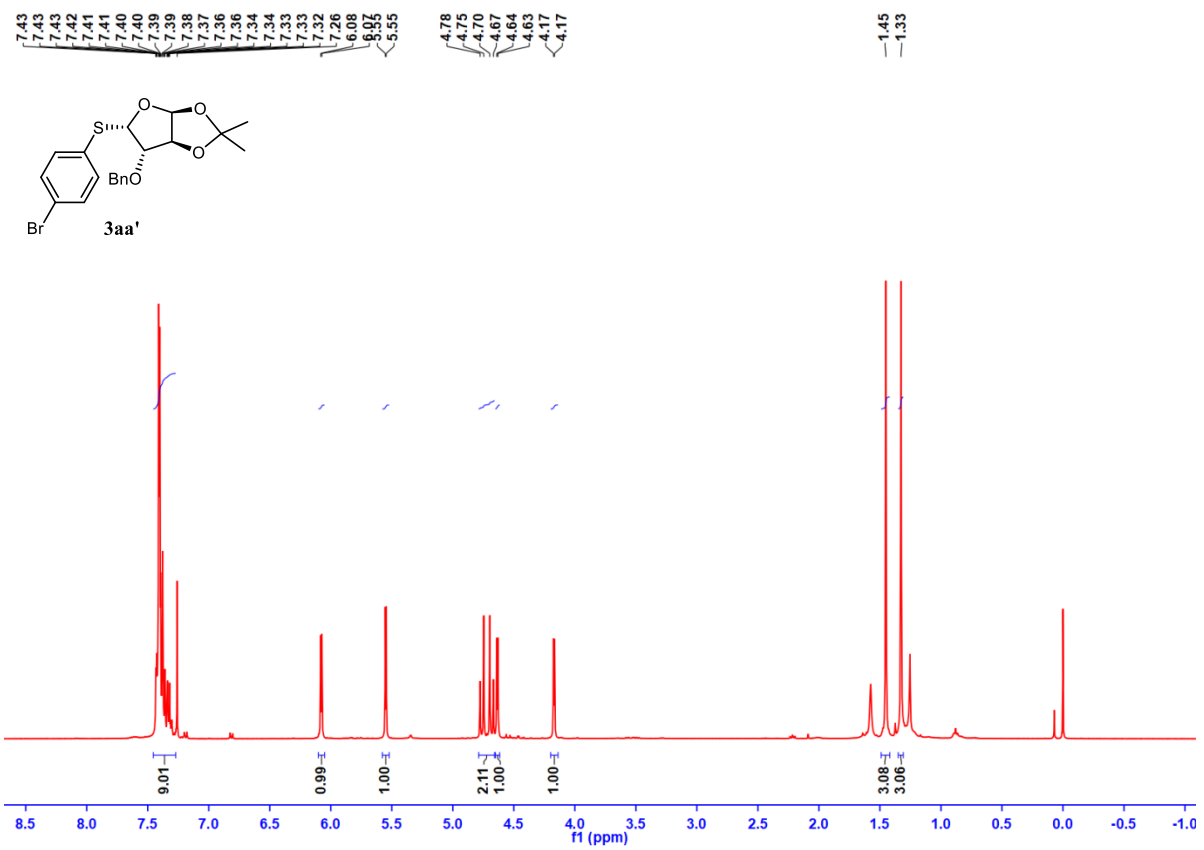
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.33
7.33
7.32
7.26
6.08
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5.55
4.78
4.75
4.70
4.67
4.64
4.63
4.17
4.17
1.45
1.33
BnO
Br
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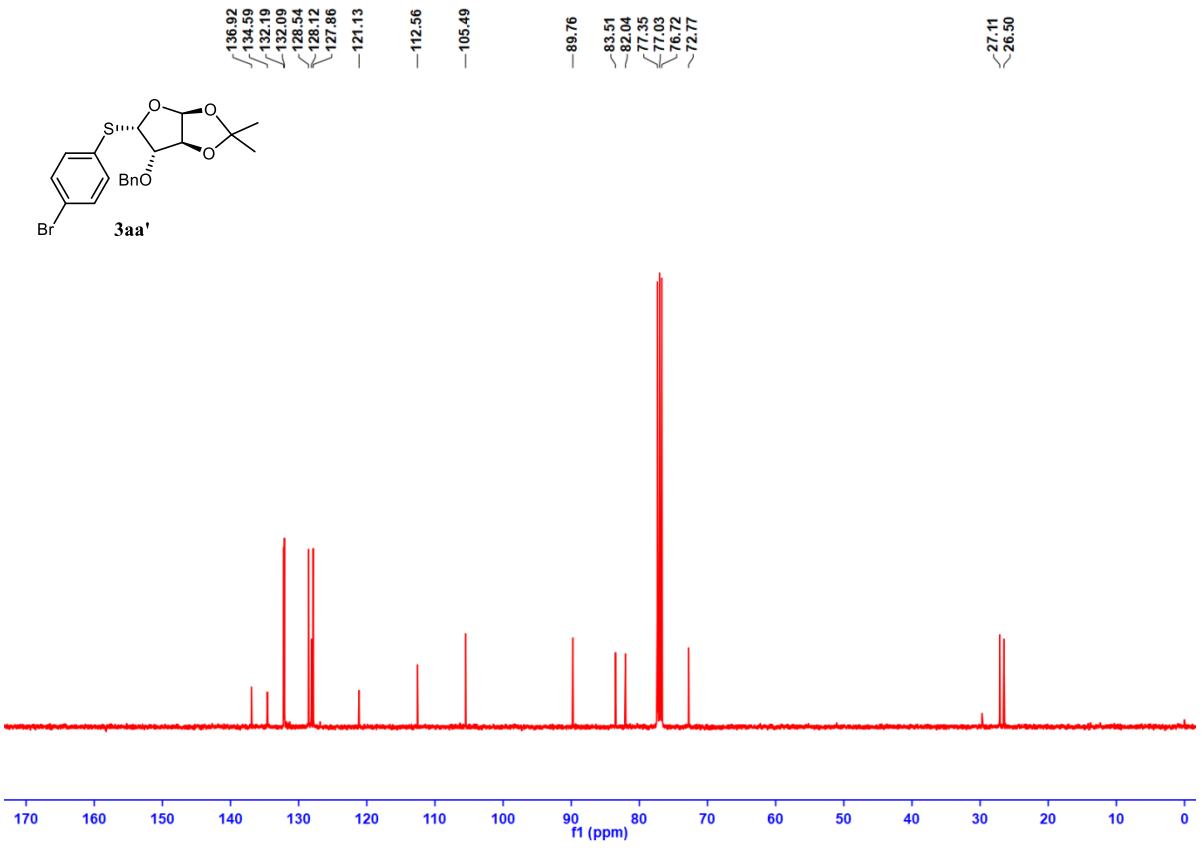
9.01
0.99
1.00
2.11
1.00
1.00
3.08
3.06
f1 (ppm)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89.76
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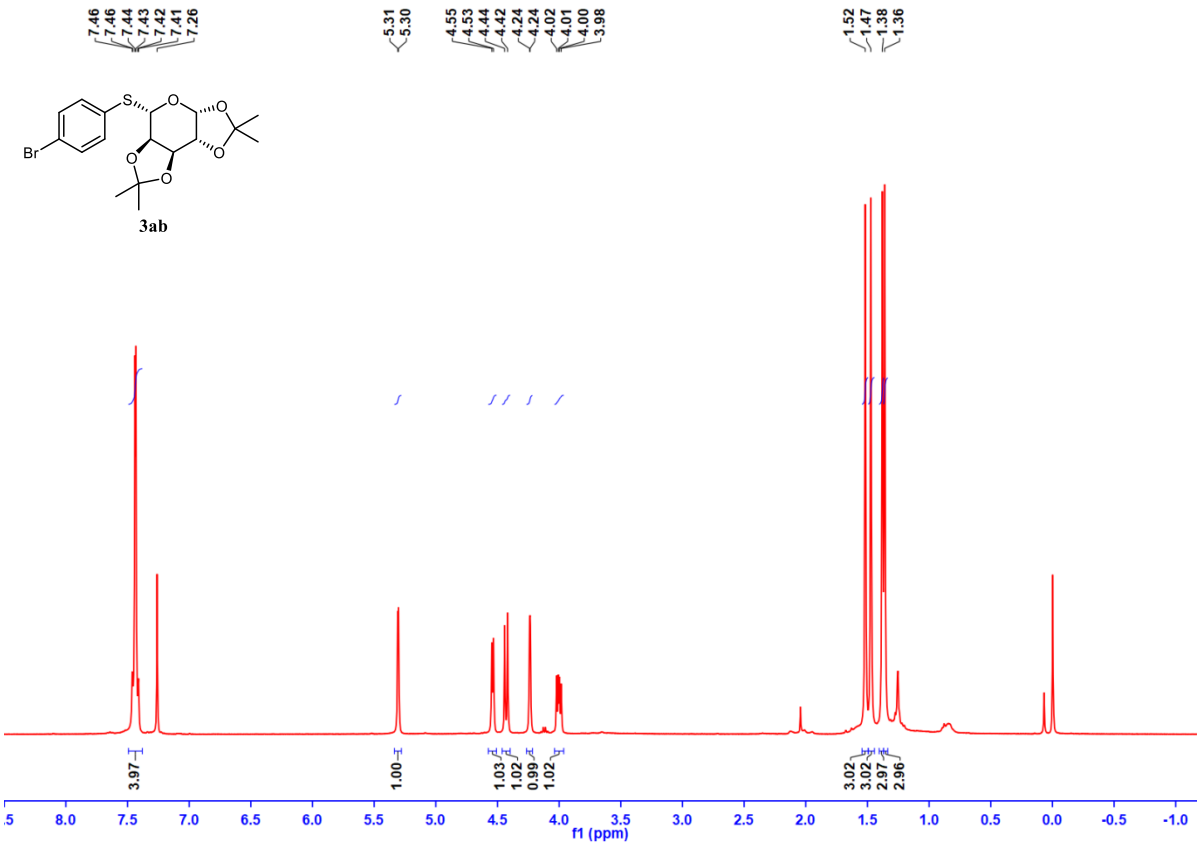
77.03
76.72
72.77
27.11
26.50
BnO
Br
3aa'
f1 (ppm)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4.01
4.00
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1.47
1.38
1.36
Br
3ab
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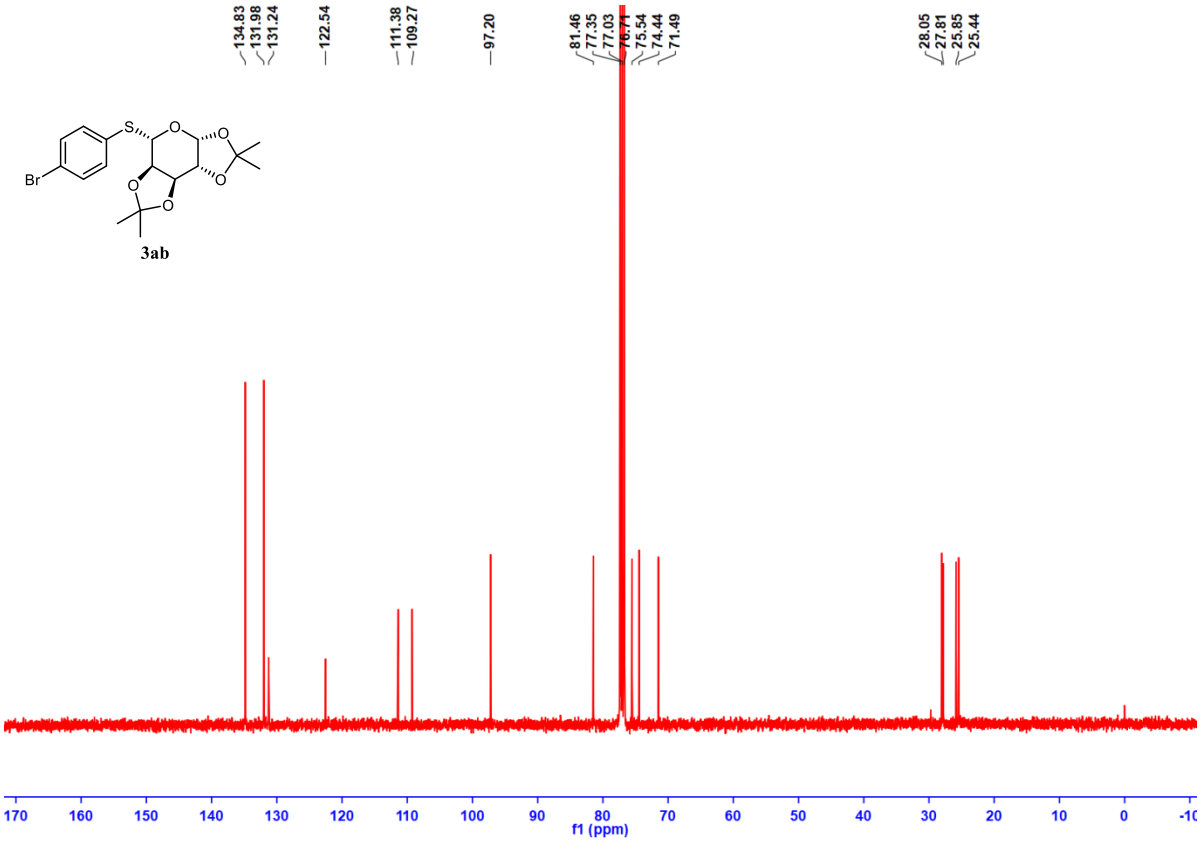
1.02
0.99
1.02
3.02
3.02
2.97
2.96
f1 (ppm)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77.35
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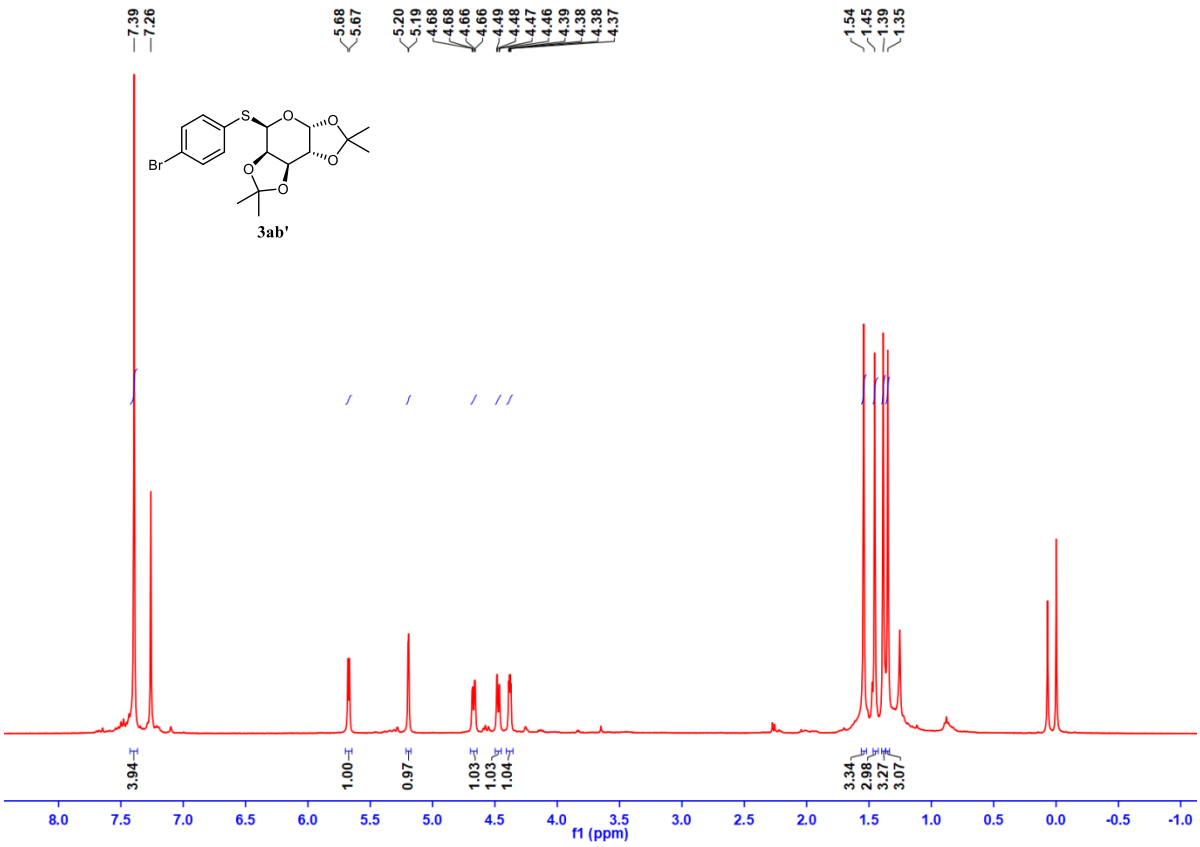
75.54
74.44
71.49
28.05
27.81
25.85
25.44
Br
3ab
f1 (ppm)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7.26
5.68
5.67
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5.19
4.68
4.68
4.66
4.66
4.49
4.48
4.47
4.46
4.39
4.38
4.38
4.37
1.54
1.45
1.39
1.35
Br
3ab'
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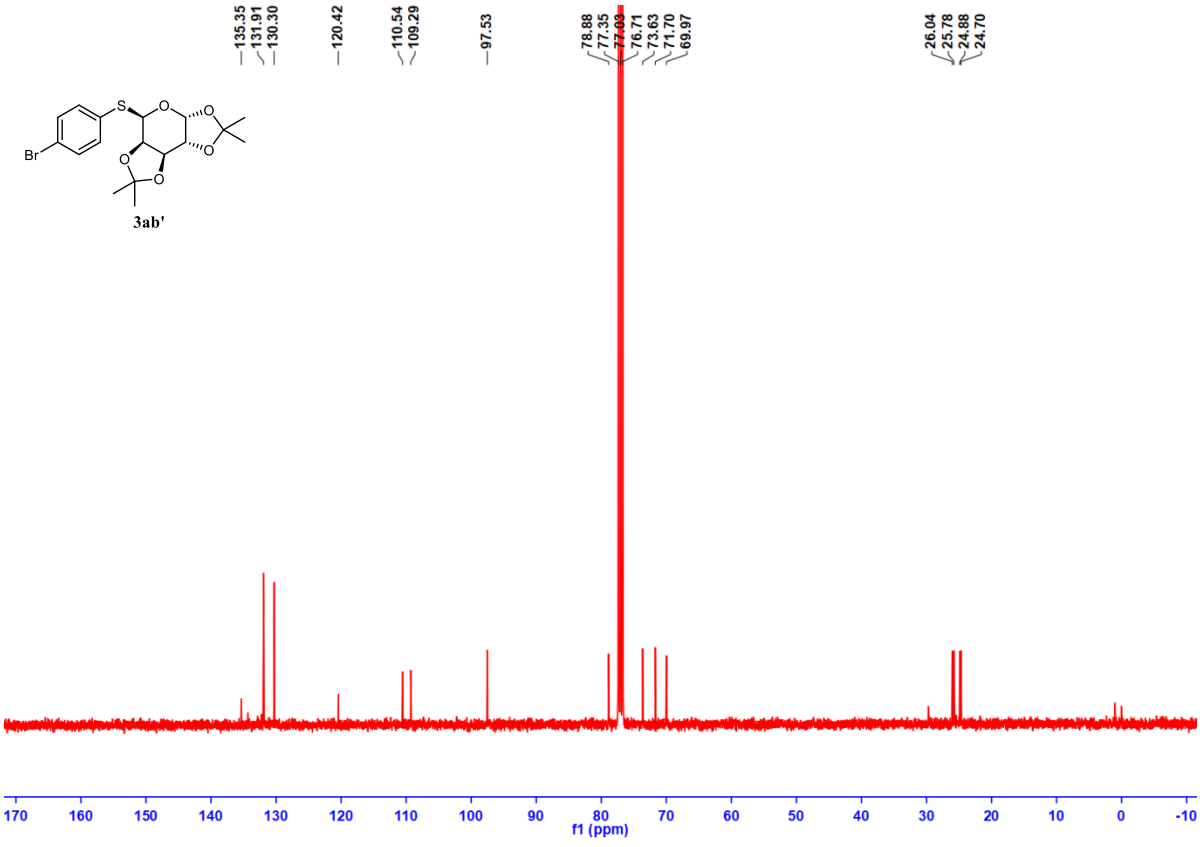
0.97
1.03
1.03
1.04
3.34
2.98
3.27
3.07
f1 (ppm)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110.54
109.29
97.53
78.88
77.35
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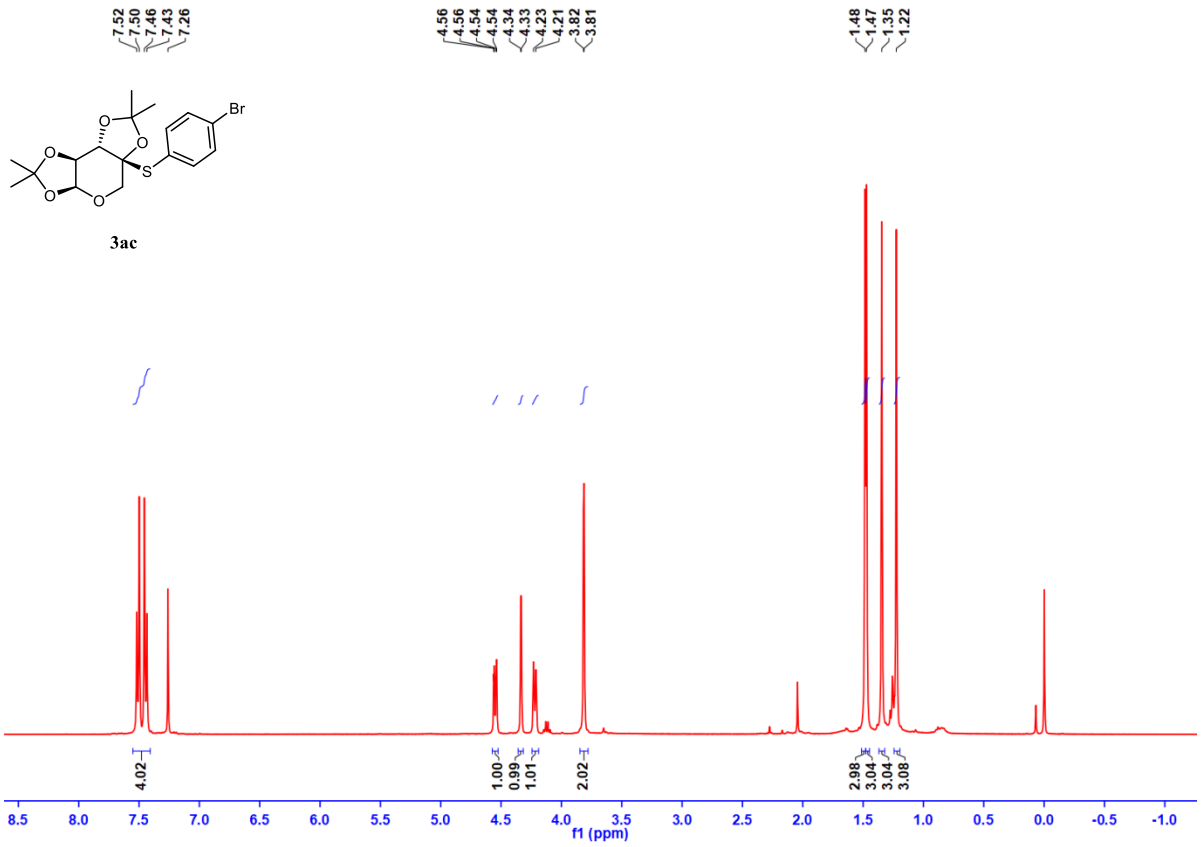
76.71
73.63
71.70
69.97
26.04
25.78
24.88
24.70
Br
3ab'
f1 (ppm)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7.50
7.46
7.43
7.26
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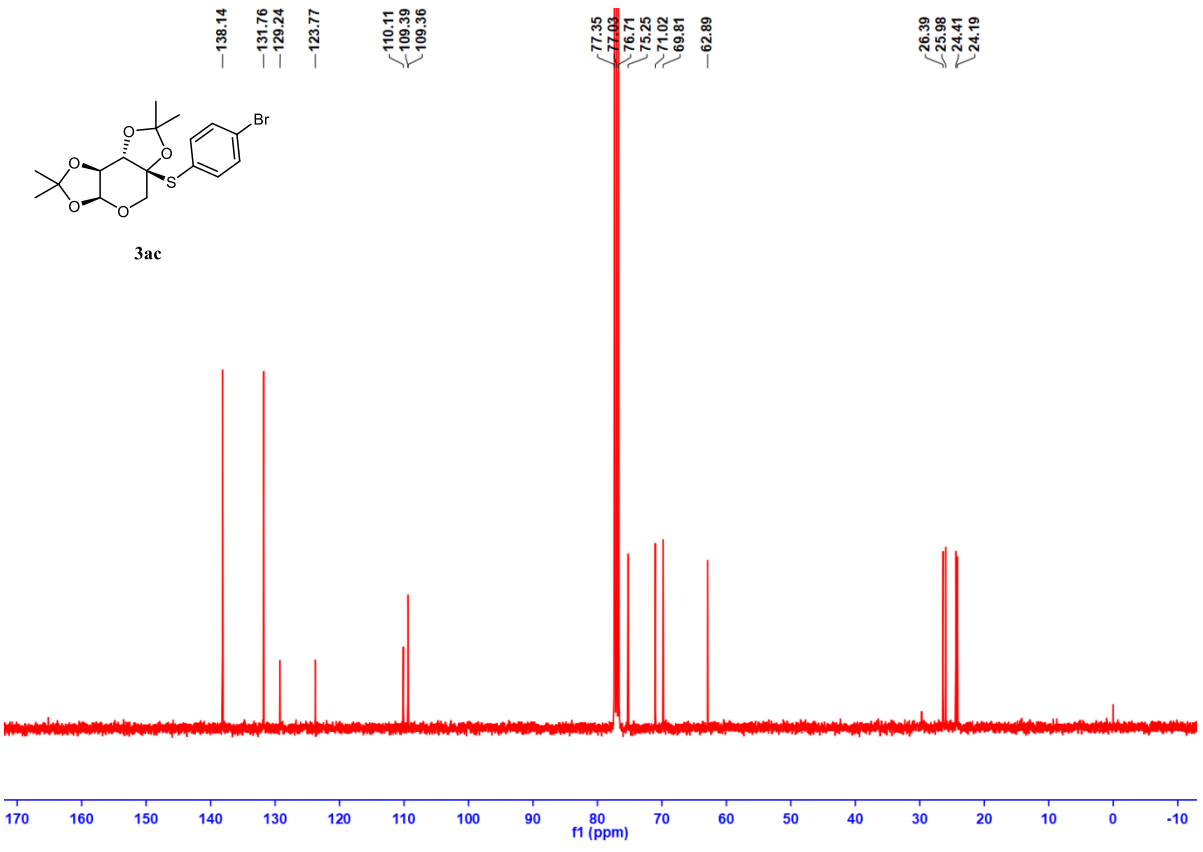
4.56
4.54
4.54
4.34
4.33
4.23
4.21
3.82
3.81
1.48
1.47
1.35
1.22
Br
O
O
O
O
O
S
4.02
1.00
0.99
1.01
2.02
2.98
3.04
3.04
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

3ac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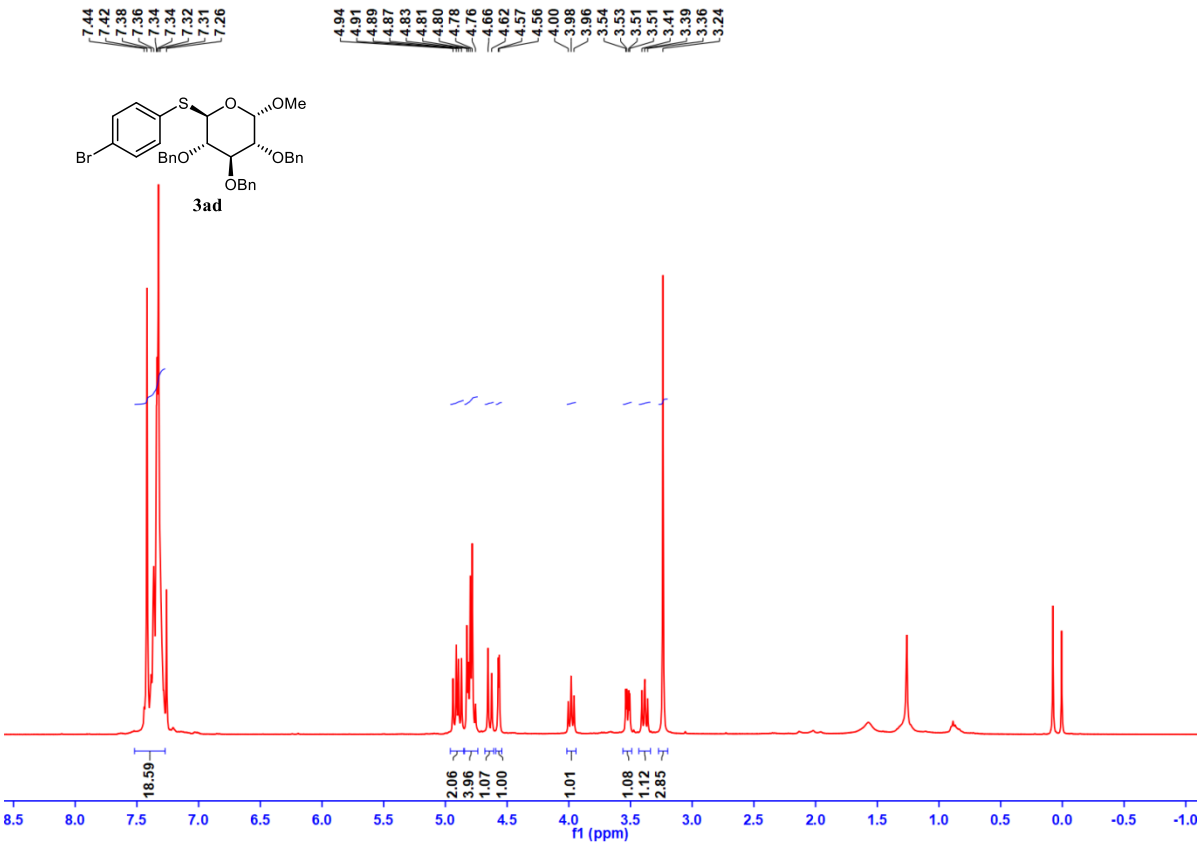
123.77
110.11
109.39
109.36
77.35
77.03
76.71
75.25
71.02
69.81
62.89
26.39
25.98
24.41
24.19
Br
O
O
O
O
O
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3ac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7.42
7.38
7.36
7.34
7.34
7.32
7.31
7.26
4.94
4.91
4.89
4.87
4.83
4.81
4.80
4.78
4.76
4.66
4.62
4.57
4.56
4.00
3.98
3.96
3.54
3.53
3.51
3.51
3.41
3.39
3.36
3.24
S
O
OMe
Br
BnO
OBn
OBn
3ad
18.59
2.06
3.96
1.07
1.00
1.01
1.08
1.12
2.85
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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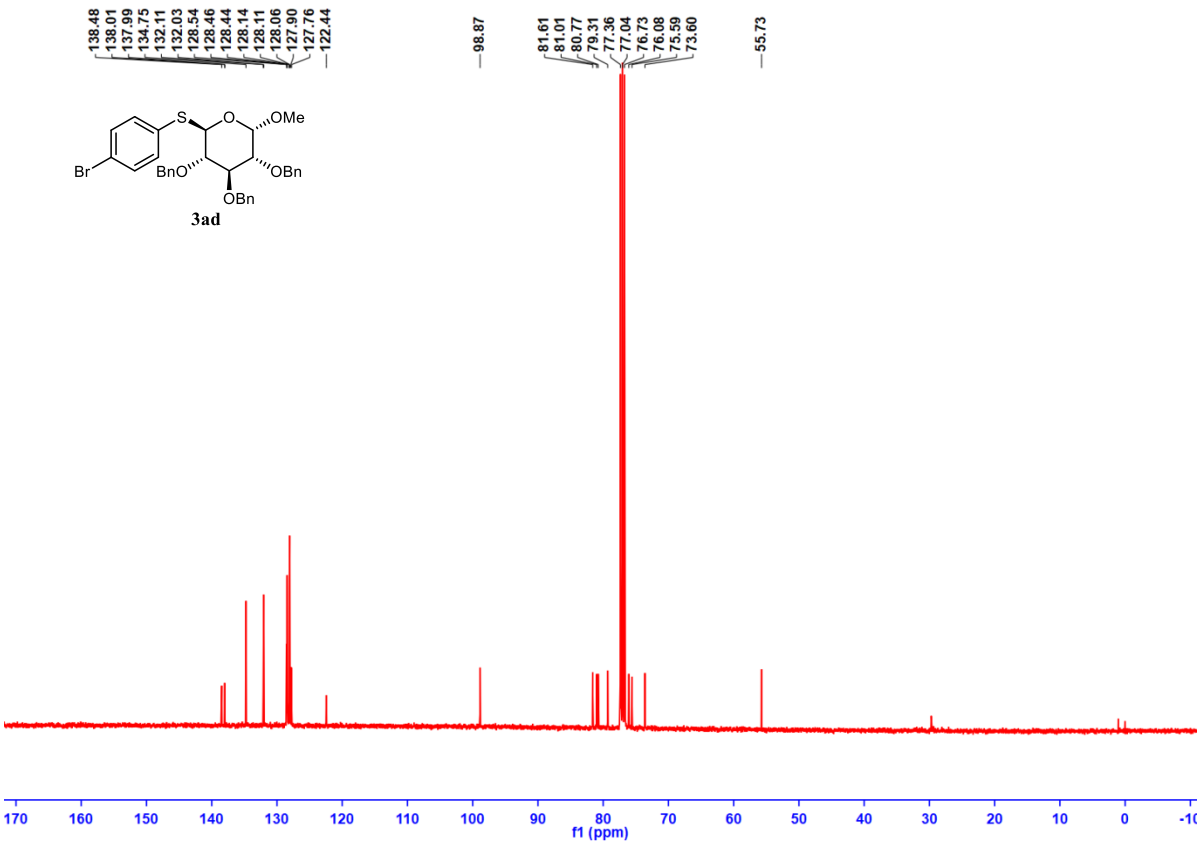
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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128.46
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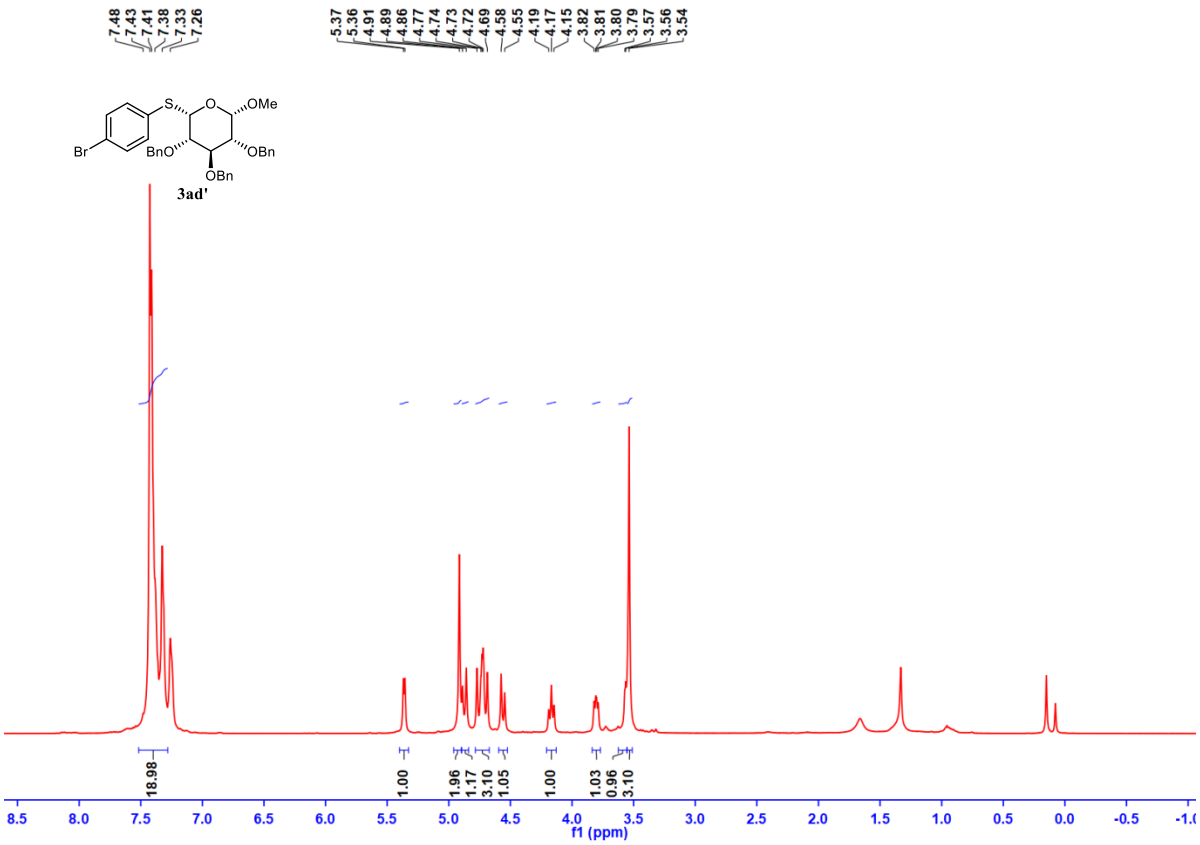
128.11
128.06
127.90
127.76
122.44
98.87
81.61
81.01
80.77
79.31
77.36
77.04
76.73
76.08
75.59
73.60
55.73
S
O
OMe
Br
BnO
OBn
OBn
3ad
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.43
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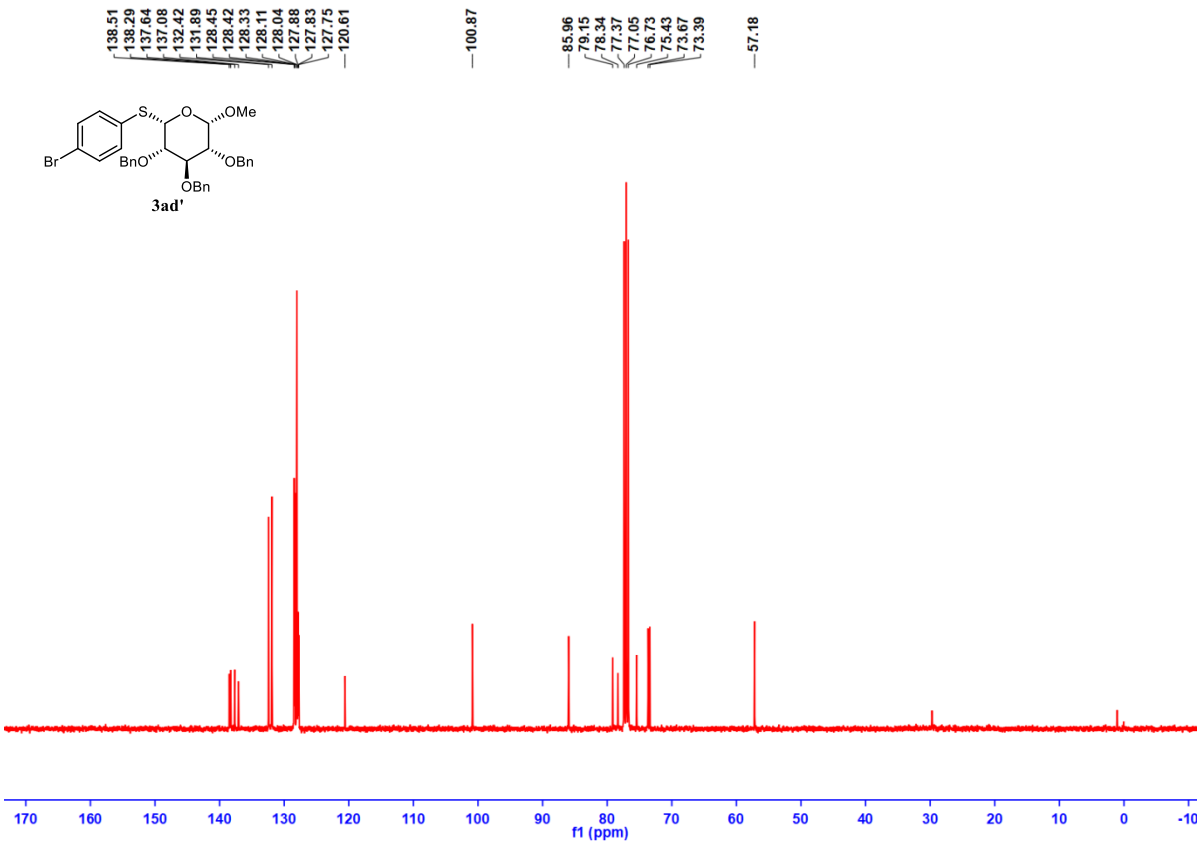
7.38
7.33
7.26
5.37
5.36
4.91
4.89
4.86
4.77
4.74
4.73
4.72
4.69
4.58
4.55
4.19
4.17
4.15
3.82
3.81
3.80
3.79
3.57
3.56
3.54
Br
BnO
OMe
OBn
OBn
3ad'
18.98
1.00
1.96
1.17
3.10
1.05
1.00
1.03
0.96
3.10
f1 (ppm)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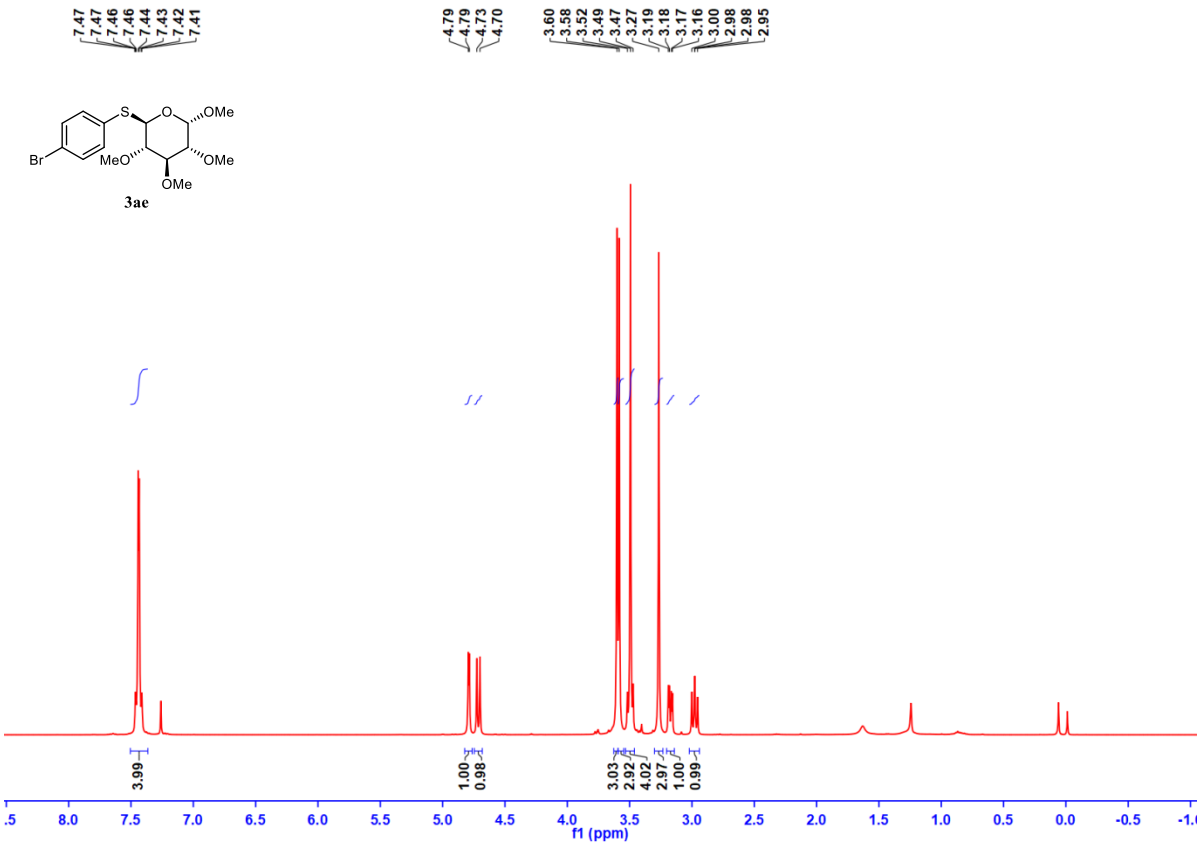
128.42
128.33
128.11
128.04
127.88
127.83
127.75
120.61
100.87
85.96
79.15
78.34
77.37
77.05
76.73
75.43
73.67
73.39
57.18
Br
BnO
OMe
OBn
OBn
3ad'
f1 (ppm)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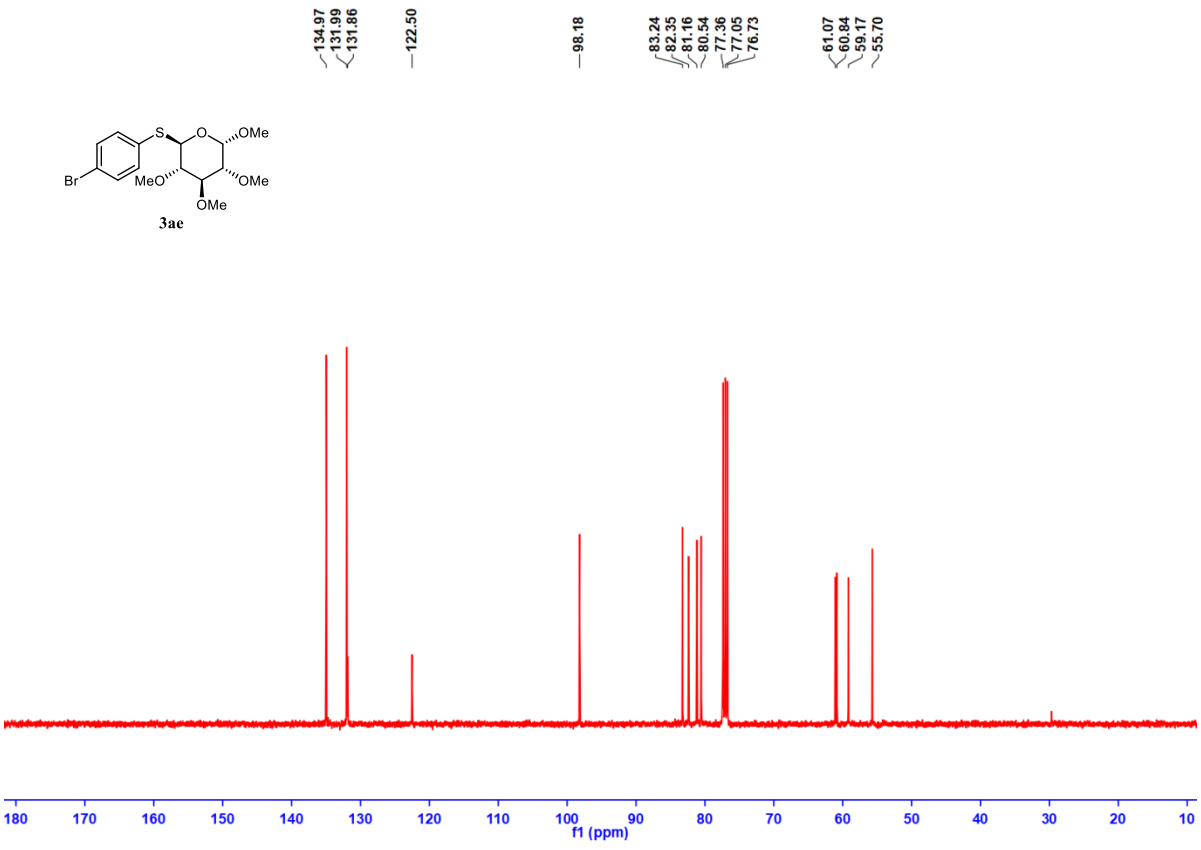
7.47
7.46
7.46
7.44
7.43
7.42
7.41
4.79
4.79
4.73
4.70
3.60
3.58
3.52
3.49
3.47
3.27
3.19
3.18
3.17
3.16
3.00
2.98
2.98
2.95
Br
MeO
OMe
OMe
OMe
S
O
3ae
3.99
1.00
0.98
3.03
2.92
4.02
2.97
1.00
0.99
f1 (ppm)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83.24
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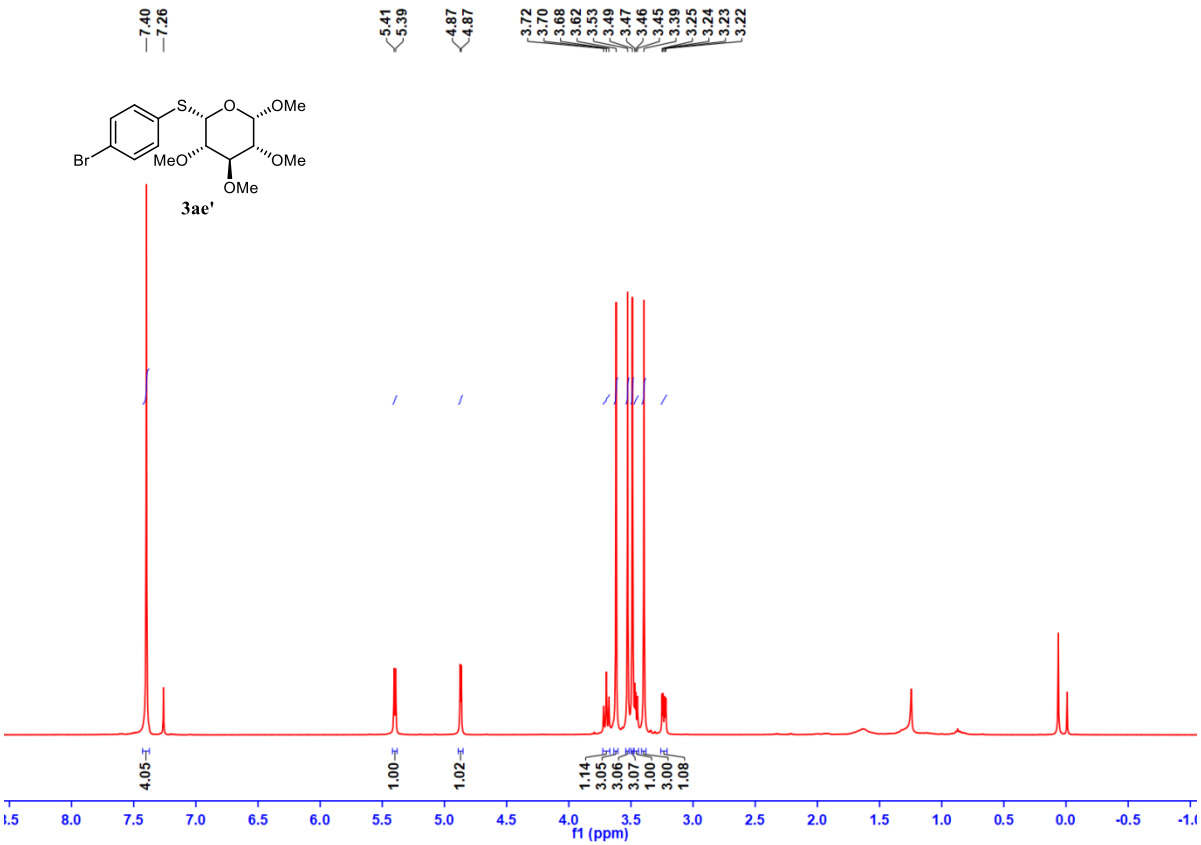
81.16
80.54
77.36
77.05
76.73
61.07
60.84
59.17
55.70
Br
MeO
OMe
OMe
OMe
S
O
3ae
f1 (ppm)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7.26
5.41
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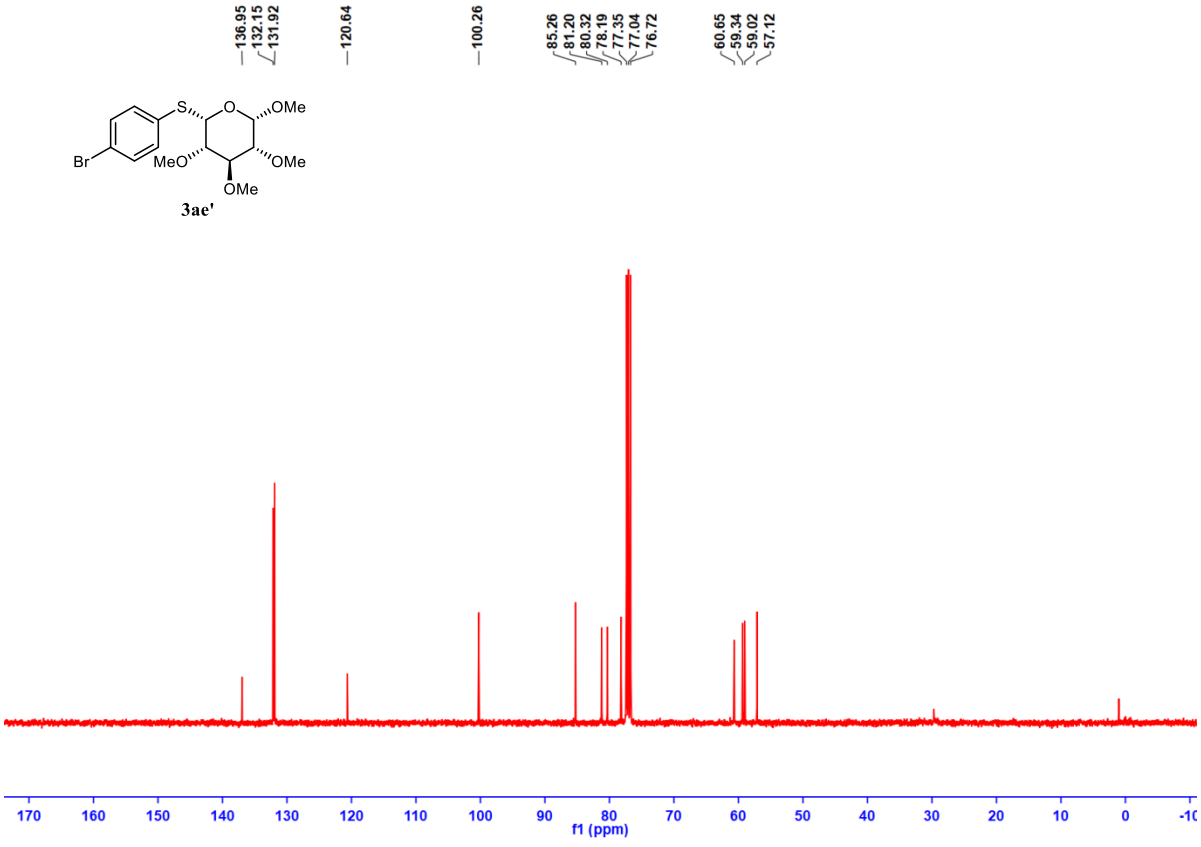
4.87
3.72
3.70
3.68
3.62
3.53
3.49
3.47
3.46
3.45
3.39
3.25
3.24
3.23
3.22
S
O
OMe
Br
MeO
OMe
OMe
3ae'
4.05
1.00
1.02
1.14
3.05
3.06
3.07
1.00
3.00
1.08
f1 (ppm)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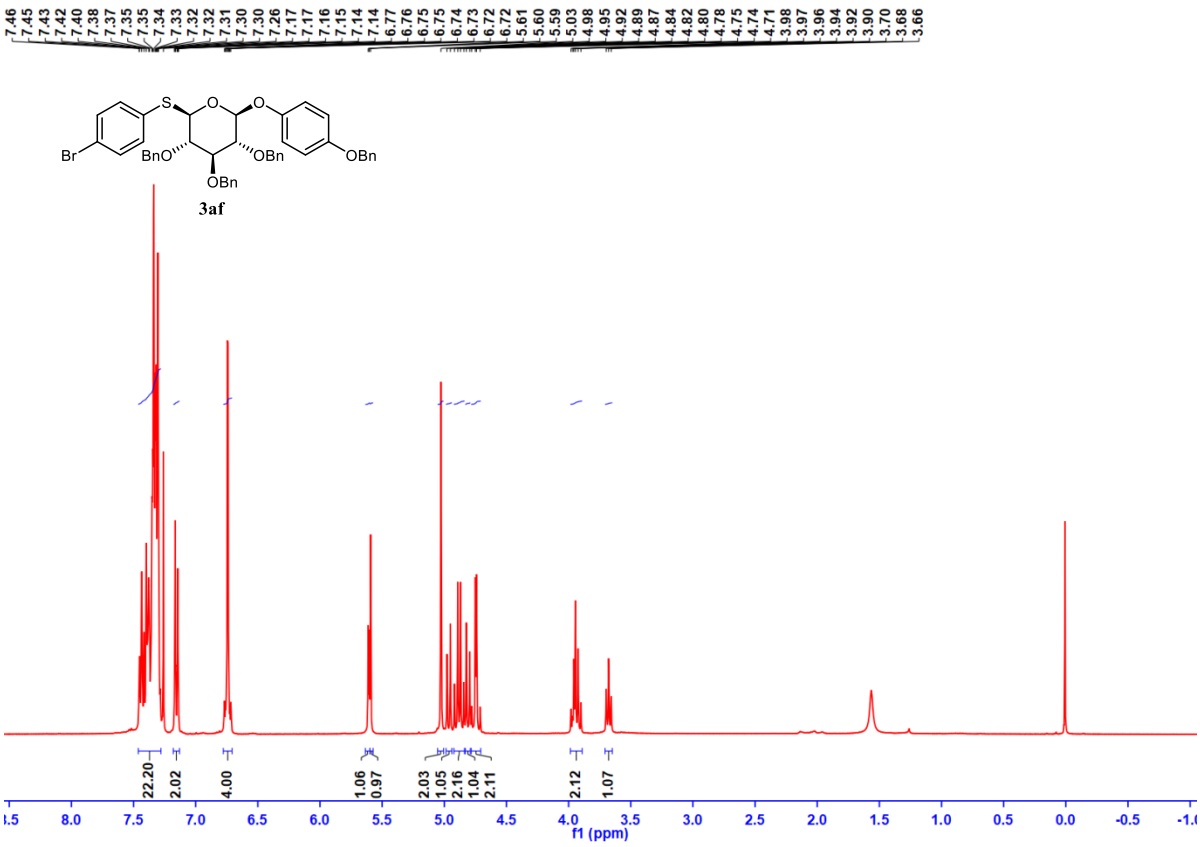
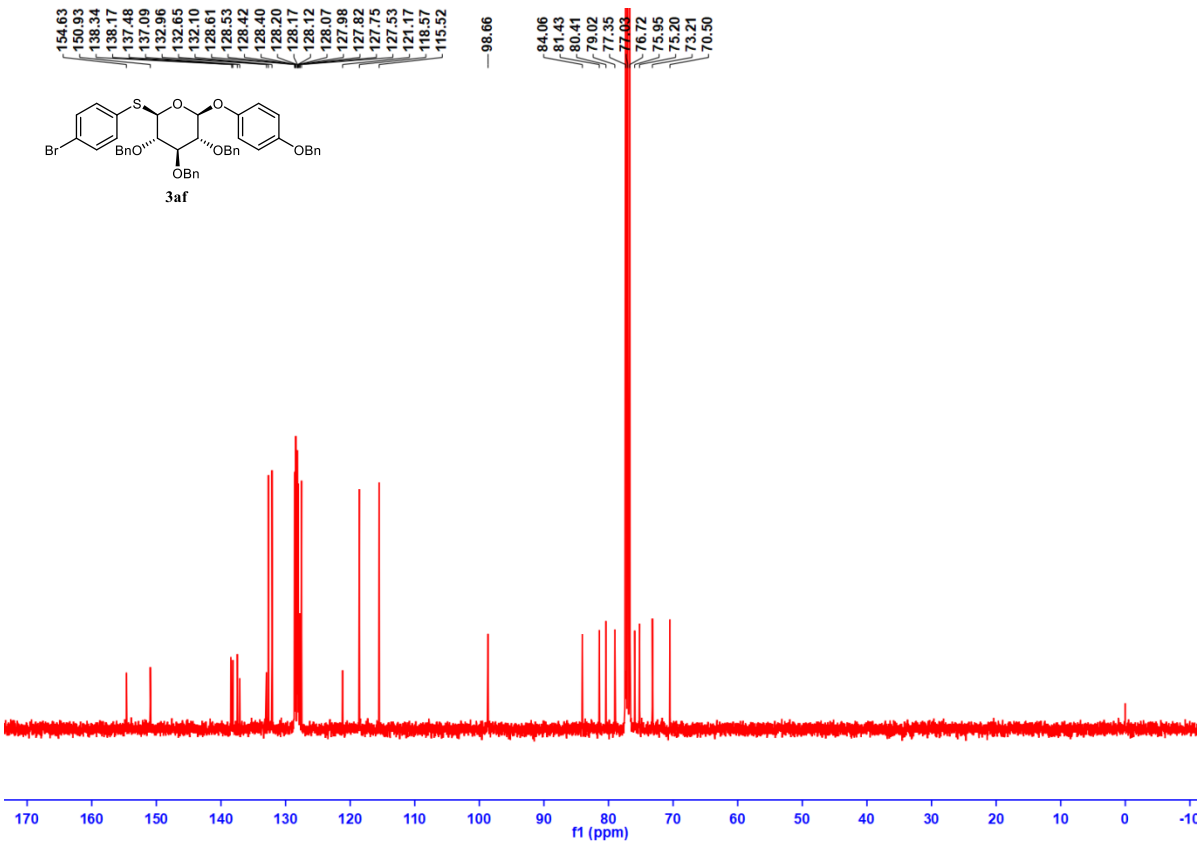
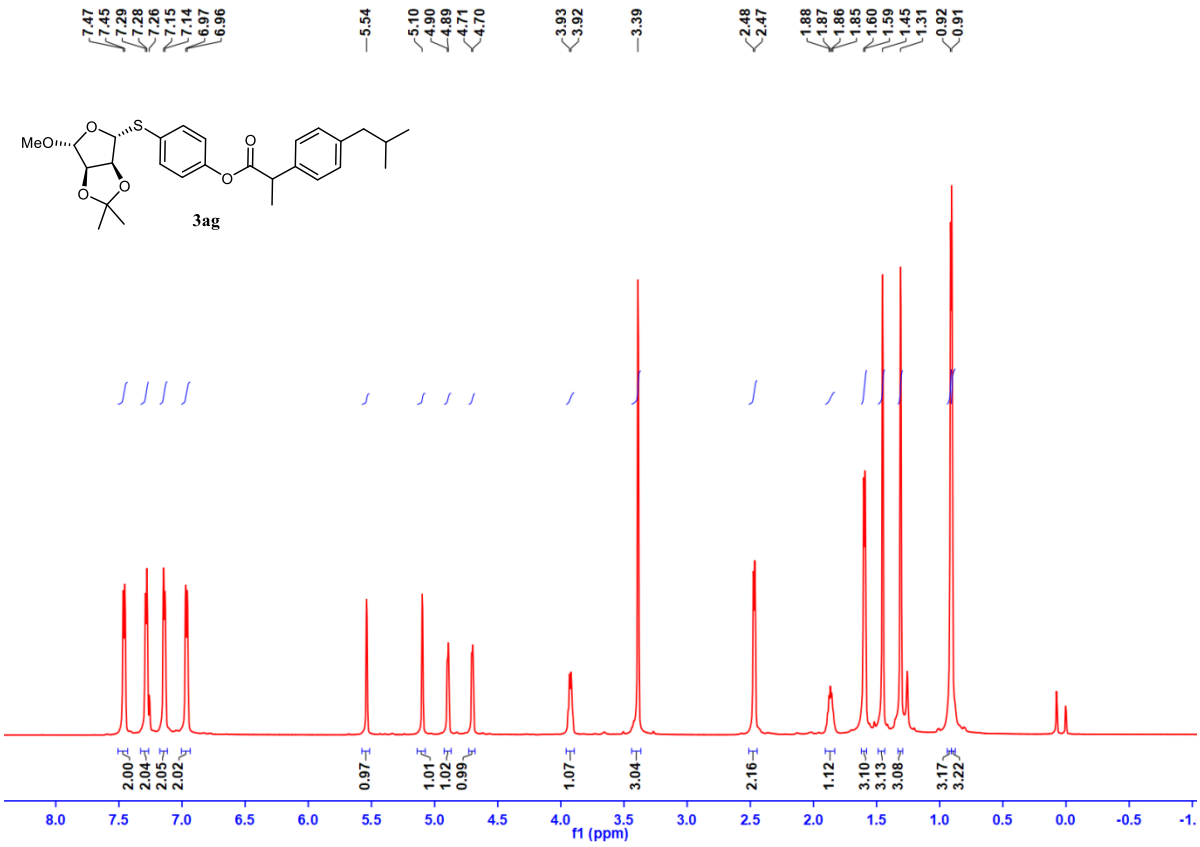
120.64
100.26
85.26
81.20
80.32
78.19
77.35
77.04
76.72
60.65
59.34
59.02
57.12
S
O
OMe
Br
MeO
OMe
OMe
3ae'
f1 (ppm)


7.46 7.45 7.43 7.42 7.40 7.38 7.37 7.35 7.35 7.34 7.33 7.32 7.32 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 3.97 3.96 3.94 3.92 3.90 3.70 3.68 3.66
Br
BnO
OBn
OBn
OBn
3af
22.20 2.02 4.00 1.06 0.97 2.03 1.05 2.16 1.04 2.11 2.12 1.07
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
Br
BnO
OBn
OBn
OBn
3af
f1 (ppm)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6.97
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5.10
4.90
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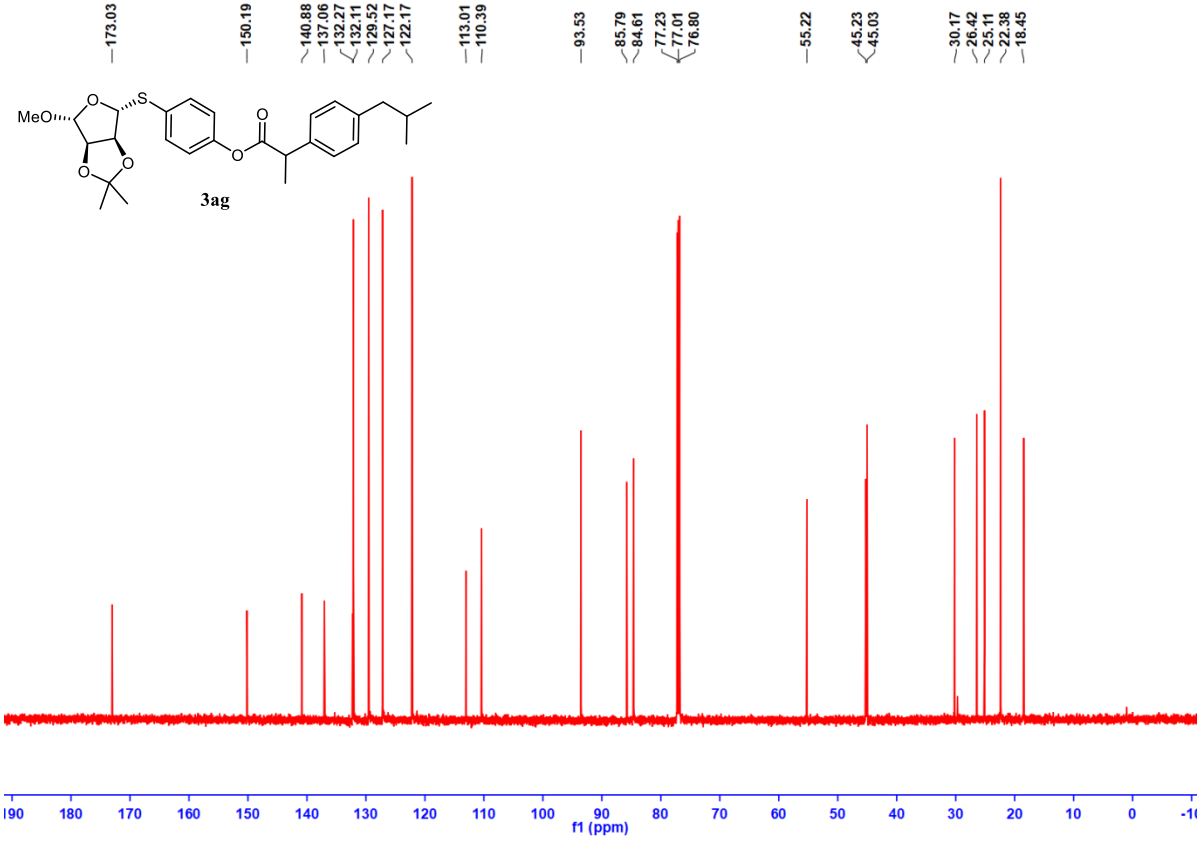
4.71
4.70
3.93
3.92
3.39
2.48
2.47
1.88
1.87
1.86
1.85
1.60
1.59
1.45
1.31
0.92
0.91
MeO
3ag
2.00
2.04
2.05
2.02
0.97
1.01
1.02
0.99
1.07
3.04
2.16
1.12
3.10
3.13
3.08
3.17
3.22
f1 (ppm)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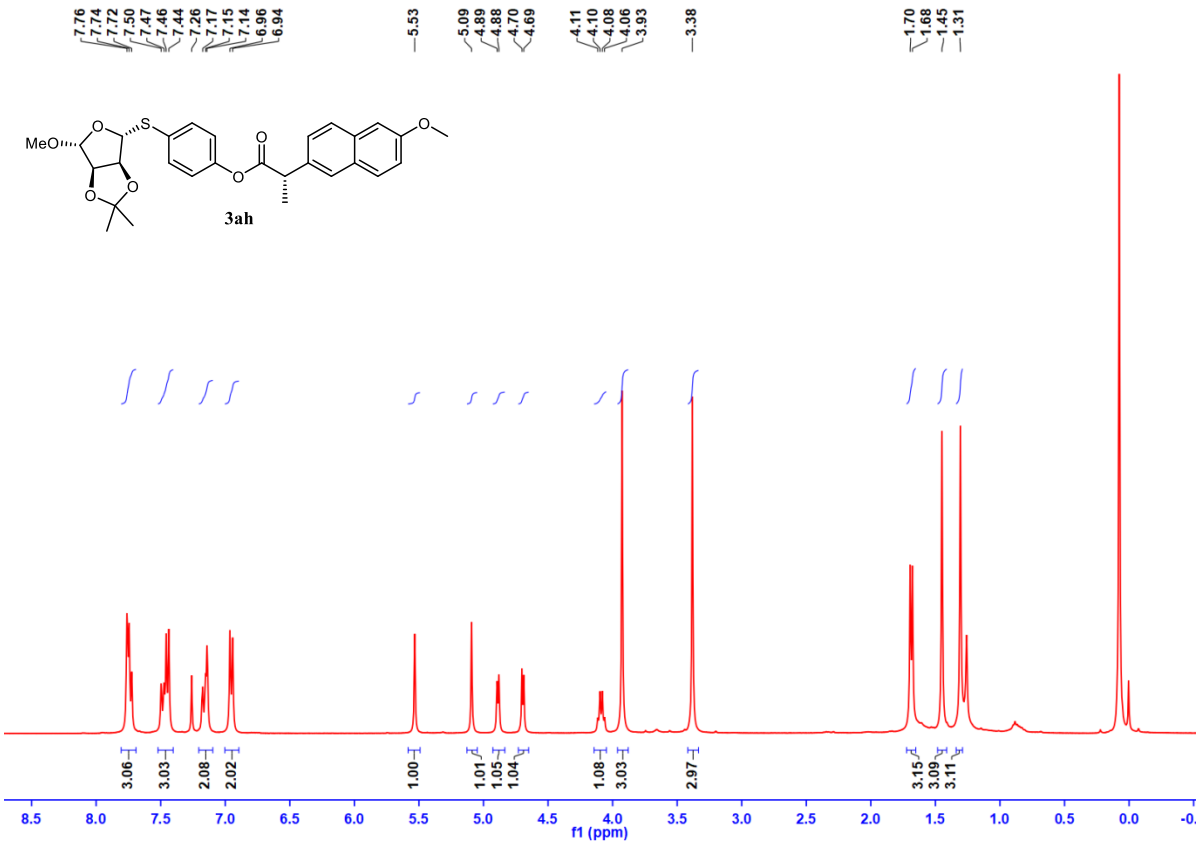
113.01
110.39
93.53
85.79
84.61
77.23
77.01
76.80
55.22
45.23
45.03
30.17
26.42
25.11
22.38
18.45
MeO
3ag
f1 (ppm)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7.26
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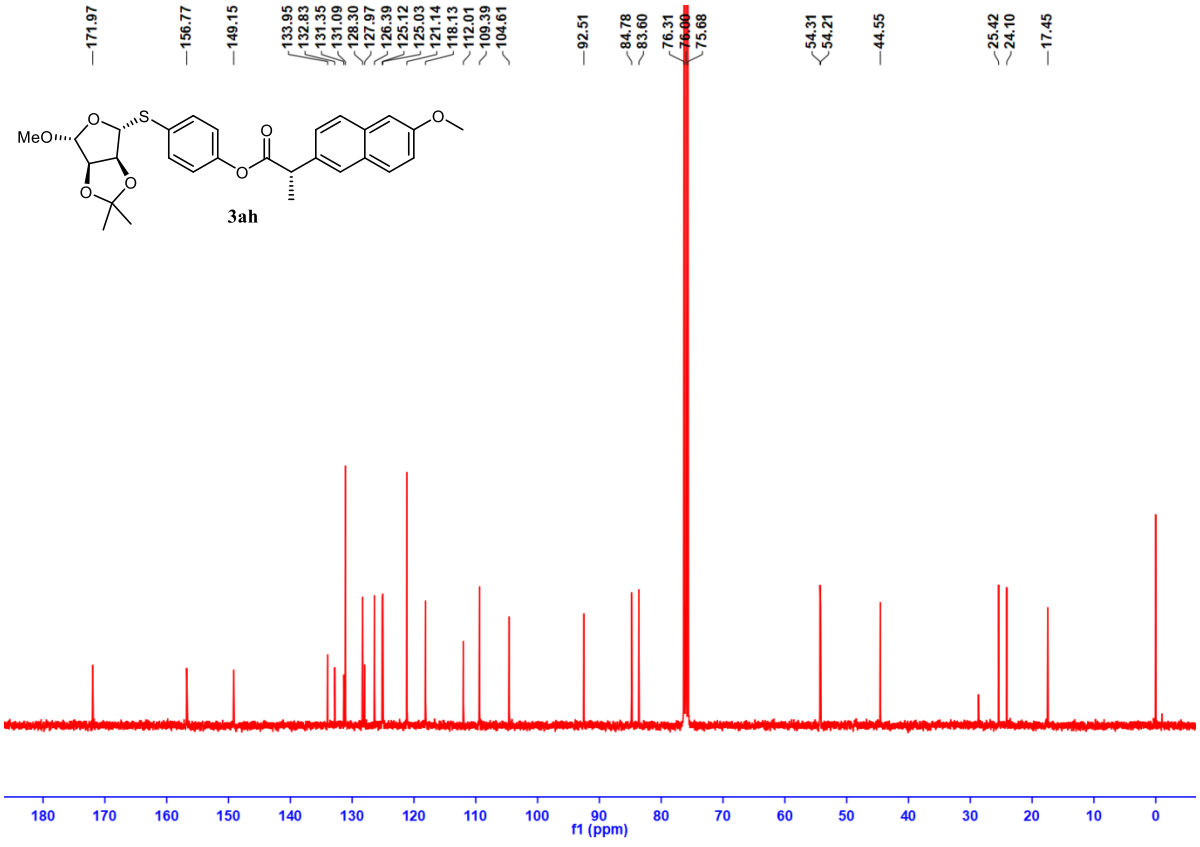
6.96
6.94
5.53
5.09
4.89
4.88
4.70
4.69
4.11
4.10
4.08
4.06
3.93
3.38
1.70
1.68
1.45
1.31
MeO
3ah
3.06
3.03
2.08
2.02
1.00
1.01
1.05
1.04
1.08
3.03
2.97
3.15
3.09
3.11
f1 (ppm)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131.35
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128.30
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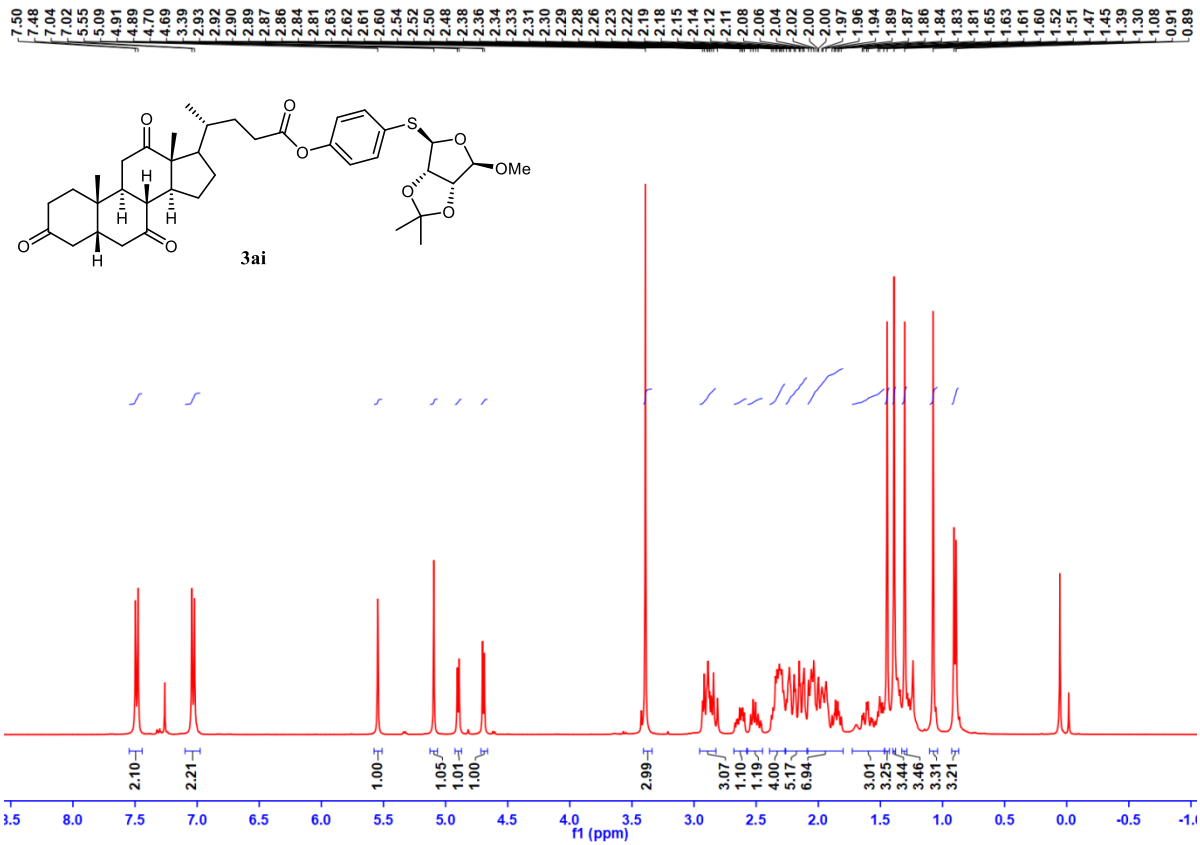
126.39
125.12
125.03
121.14
118.13
112.01
109.39
104.61
92.51
84.78
83.60
76.31
76.00
75.68
54.31
54.21
44.55
25.42
24.10
17.45
MeO
3ah
f1 (ppm)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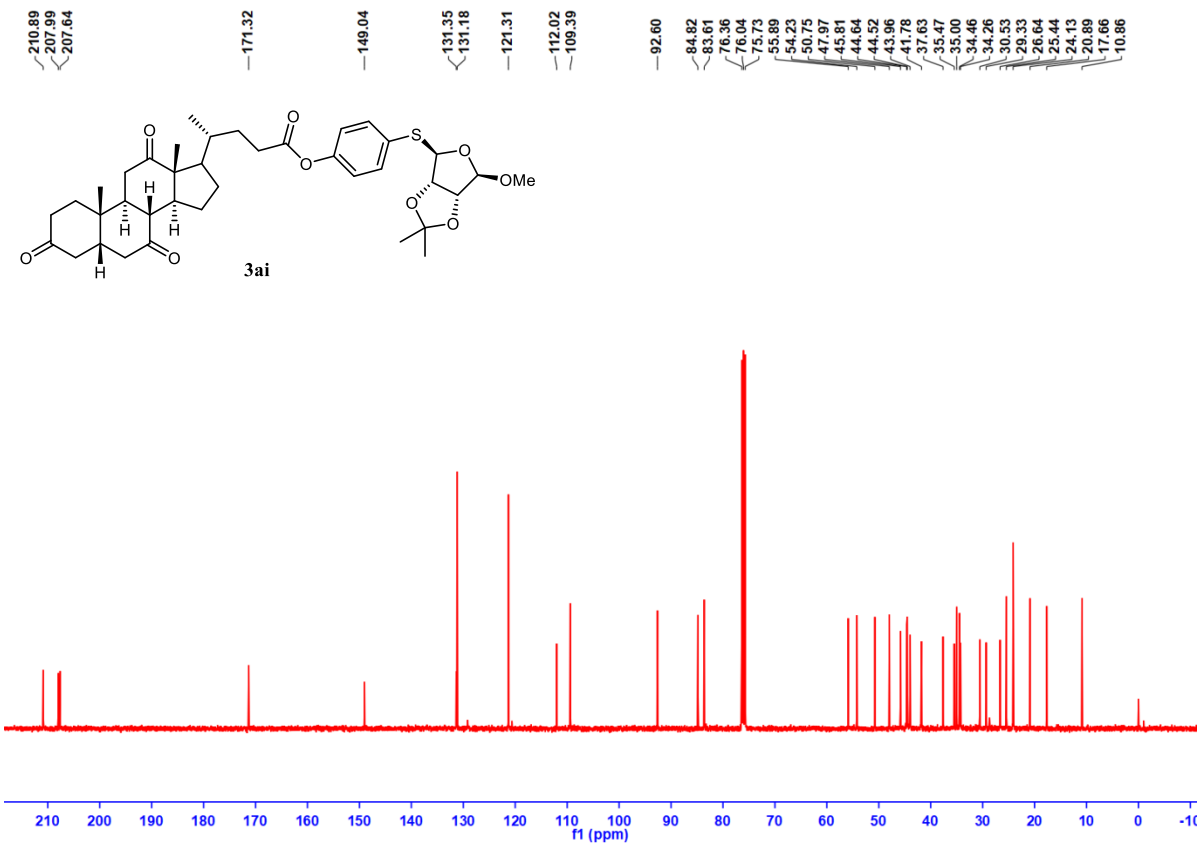
OMe
3ai
2.10 2.21 1.00 1.05 1.01 1.00 2.99 3.07 1.10 1.19 4.00 5.17 6.94 3.01 3.25 3.44 3.46 3.31 3.21
f1 (ppm)


210.89 207.99 207.64 171.32 149.04 131.35 131.18 121.31 112.02 109.39 92.60 84.82 83.61 76.36 76.04 75.73 55.89 54.23 50.75 47.97 45.81 44.64 44.52 43.96 41.78 37.63 35.47 35.00 34.46 34.26 30.53 29.33 26.64 25.44 24.13 20.89 17.66 10.86
OMe
3ai
f1 (ppm)