Supporting Information

Preparing glycosyl benzothiazoles from 2-Isocyanoaryl Thioethers and Glycosyl Radicals under thermal conditions

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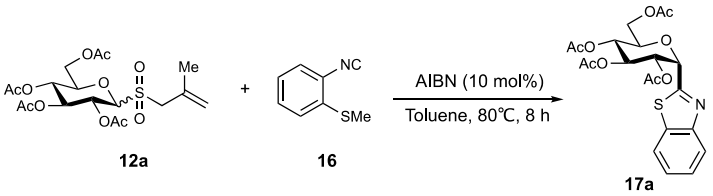
Contents

1. General Information

Flash column chromatography was performed using silica gel (300-400 mesh) purchased from Qindao Haiyang. Reaction solvents and deuterated solvents were purchased from Energy Chemicals and used as received. 2,2'-azobis(2-methylpropionitrile) (AIBN), heterocyclic compounds and glycosyl substrates were purchased from Adamas or Energy Chemicals and used as received. NMR yields were determined using 1,3,5-trimethoxybenzene as an internal standard. Unless otherwise noted, all reported yields are isolated yields of purified products. All new compounds were characterized by NMR spectroscopy, IR spectroscopy, high-resolution mass spectroscopy (HR-MS), and melting point (if solids). NMR spectra were recorded on a Bruker AMX 400 spectrometer and were calibrated using TMS (0.00 ppm) or residual deuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR; DMSO-d_6: 2.50 ppm for ^1H NMR and 39.50 ppm for ^{13}C NMR; CD_3OD: 3.31 ppm for ^1H NMR and 49.50 ppm for ^{13}C NMR), and the tabulated data were reported in ppm. All IR spectra were taken on Thermo Scientific Nicolet iS5 spectrometer (iD5 ATR, diamond). HR-MS spectra were recorded on a Waters Q-TOF Premier. Melting points (m. p.) were recorded on an INESA SGW X-4 melting point apparatus. Optical rotations were measured on a Hanon P850 polarimeter with $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{T}}$ values reported in degrees; concentration (c) is in g/100 mL.

2. Condition Optiomization

Table S1. Other Representative Conditions Not Listed in Table 1

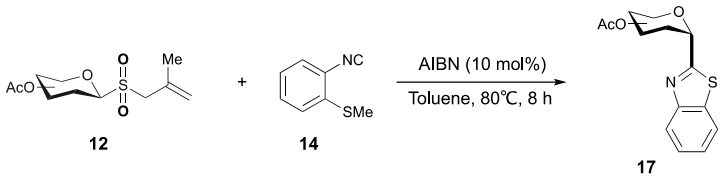


12a **16** **17a**

Entry	Variation from standard conditions	Yield of **12a**
1	MeCN instead of Tolunene	76%
2	THF instead of Tolunene	65%
3	DMF instead of Tolunene	47%
4	60 ℃ Instead of 80 ℃	trace
5	with 20% AIBN	92%
6	**16** (1.5 equiv.)	81%
7	DTBP instead of AIBN	46%
8	TBPB instead of AIBN	45%
9	DCE instead of Toluene	79%

[a]Reaction condition: **12a** (0.1 mmol, 1 equiv.), **16** (0.2 mmol, 2 equiv.), AIBN (10 mol%), Solvent (1 mL). The yield was determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard.

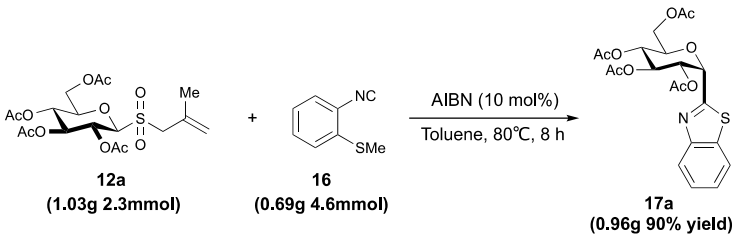
3. General Procedures for the Synthesis of Glycosyl Benzothiazoles



12 **14** **17**

Allyl glycosyl sulfone (1.0 equiv.), Isocyanide (2.0 equiv.), 2,2'-azobis(2-methylpropionitrile) (AIBN) (10 mmol%) were weighted into a screw-capped vial containing a magnetic stir bar. The vial was loosely capped and transferred into a nitrogen-filled glovebox. To the vial was added Toluene (0.4 M). The vial was tightly sealed with a Teflon-lined cap and stirred at 80 ℃ the indicated period of time. The reaction mixture was monitored by TLC using as the mobile phase. After disappearance of starting material, the solvent of reaction was concentrated under reduced pressure. The residue was subjected to silica gel chromatography to give the glycoside product.

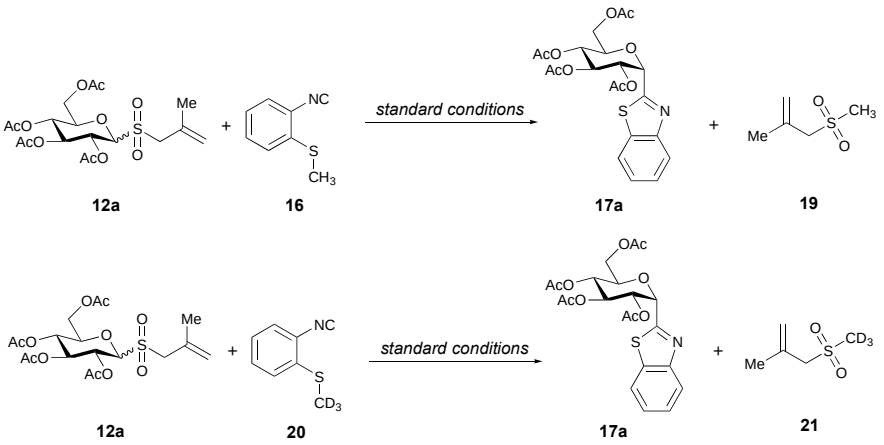
4. General Procedure of Gram-Scale Synthesis



12a (1.03g 2.3mmol) + **16** (0.69g 4.6mmol) → **17a** (0.96g 90% yield)

The glucose allyl glycosyl sulfone **12a** (2.3 mmol, 1.03 g), Isocyanide **16** (4.6 mmol, 0.69g), 2,2'-azobis(2-methylpropionitrile) (AIBN) (0.23 mmol, 0.038g) were weighted into a screw-capped vial containing a magnetic stir bar. The vial was loosely capped and transferred into a nitrogen-filled glovebox. To the vial was added Toluene (10 mL). The vial was tightly sealed with a Teflon-lined cap and stirred at 80 ℃ for 12 h. The reaction mixture was monitored by TLC using as the mobile phase. After disappearance of starting material, the solvent of reaction was concentrated under reduced pressure. The residue was subjected to silica gel chromatography to give the glycoside product. The residue was subjected to silica gel chromatography to give the glycoside product **17a** (90%, 0.96 g). (The reaction phenomenon: The reaction liquid was light yellow at first, and the color of the reaction liquid gradually deepened as the reaction progressed, and finally turned brown.)

5. Procedure of Mechanism Experiment



12a + **16** → **17a** + **19**

12a + **20** → **17a** + **21**

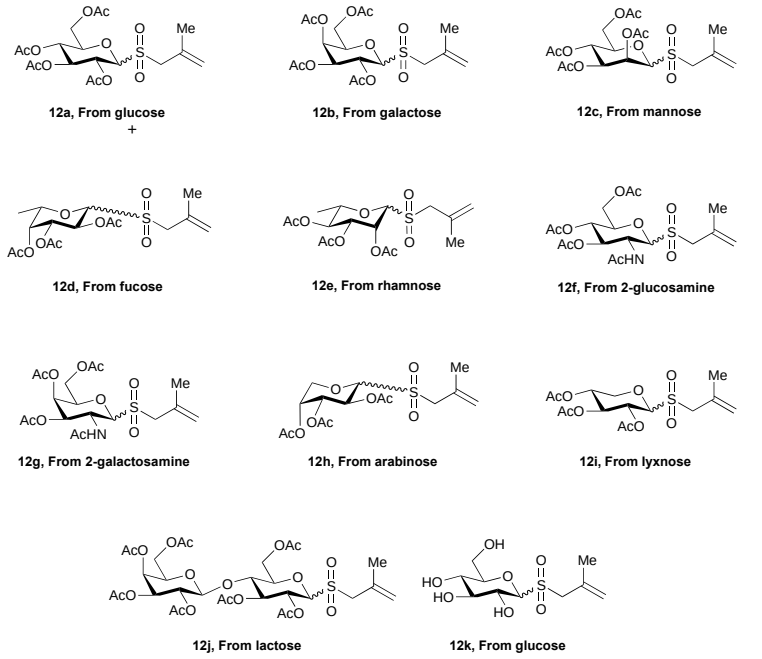
Allyl glycosyl sulfone **12a** (1.0 equiv.), Isocyanide **16** or **20** (2.0 equiv.), 2,2'-azobis(2-methylpropionitrile) (AIBN) (10 mmol%) were weighted into a screw-capped vial containing a magnetic stir bar. The vial was loosely capped and transferred into a nitrogen-filled glovebox. To the vial was added Toluene (0.4 M). The vial was tightly sealed with a Teflon-lined cap and stirred at 80 ℃ the indicated period of time. The reaction mixture was monitored by TLC using as the mobile phase. After disappearance of starting material, the solvent of reaction was

concentrated under reduced pressure. The residue was subjected to silica gel chromatography to give the corresponding byproduct **19** or **21**.

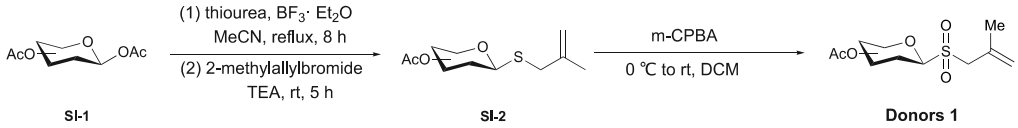
6. General Procedures for the Synthesis of Glycosyl Radical Donors

12a, **12b**, **12c**, **12d**, **12e**, **12h**, **12i** and **12j** were prepared according to general procedure A. **12f** and **12g** were prepared according to general procedure B. **12k** was prepared from the deprotection of **12a** according to general procedure C. All of characterization data had been reported in our previous work[1-2].

Substrate scope of the glycosyl donors:



General Procedure A:

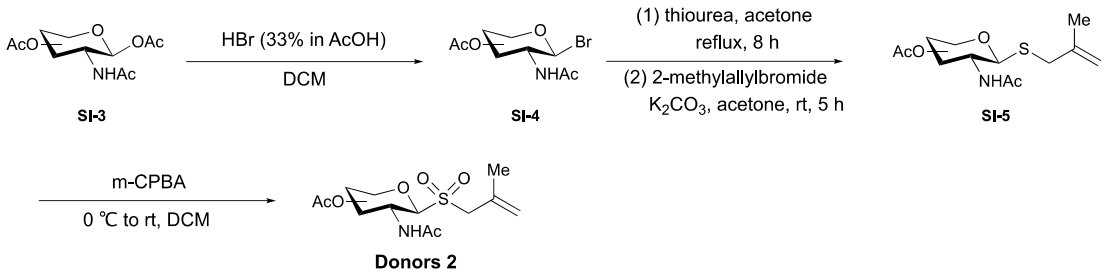


Step I: To a solution of **SI-1** (1.0 equiv.) and thiourea (1.5 equiv.) in MeCN was added $BF_3{\cdot}Et_2O$ (1.5 equiv.) dropwise at room temperature. The resulting mixture was heated reflux about 8 hours, stirred until **SI-1** was consumed completely by TLC analysis. Without further operation, TEA (1.5 equiv.) and 2-methylallylbromide (1.5 equiv.) were added to the resulting mixture. The resulting mixture was stirred at room temperature about 5 hours and then diluted by addition of EA. The organic phase was separated and washed by sat. aq. $NaHCO_3$ ($\times$2), brine ($\times$1), dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo, and purified by flash chromatography (SiO_2) to afford **SI-2**.

Step II: To a stirred solution of **SI-2** (1.0 equiv.) in DCM was added m-CPBA (2.5 equiv.) at 0℃. The resulting mixture was then stirred at the same temperature until **SI-2** was fully consumed as monitored by TLC (ca. 2~3 h). The reaction was quenched by addition of sat. aq.

$NaHCO_3$ at 0℃. The resulting mixture was allowed to warm up to ambient temperature. The organic phase was separated and washed by sat. aq. $NaHCO_3$ (×3), brine (×1), dried over anhydrous Na_2SO4, filtered, concentrated in vacuo, and purified by flash chromatography (SiO_2) to afford glycosyl radical **Donors 1**.

General Procedure B:

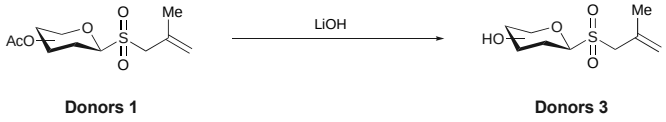


Step I: **SI-3** (1.0 equiv.) was dissolved in DCM, then Hydrogen bromide (33 wt.% in Acetic acid, Energy Seal) was added slowly into the reaction at 0℃. The reaction mixture was stirred at 0℃ overnight. The reaction was quenched with ice-water and extracted with DCM (×3). The organic phase was separated and washed by sat. aq. $NaHCO_3$ (×3), brine (×1), dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo, and purified by flash chromatography (SiO_2) to afford **SI-4**.

Step II: **SI-4** (1.0 equiv.) was dissolved in acetone, then thiourea (1.5 equiv.) was added. The resulting mixture was refluxed about 8 hours, stirred until **SI-4** was consumed completely by TLC analysis. Without further operation, H_2O (acetone/ H_2O = 1/1), K_2CO_3 (3.0 equiv.) and 2-methylallylbromide (1.5 equiv.) were added to the resulting mixture. The resulting mixture was stirred at room temperature about 5 hours and then diluted by addition of EA. The organic phase was separated and washed by sat. aq. $NaHCO_3$ (×2), brine (×1), dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo, and purified by flash chromatography (SiO_2) to afford **SI-5**.

Step III: To a stirred solution of **SI-5** (1.0 equiv.) in DCM was added m-CPBA (2.5 equiv.) at 0℃. The resulting mixture was then stirred at the same temperature until **SI-5** was fully consumed as monitored by TLC (ca. 2~3 h). The reaction was quenched by addition of sat. aq. $NaHCO_3$ at 0℃. The resulting mixture was allowed to warm up to ambient temperature. The organic phase was separated and washed by sat. aq. $NaHCO_3$ (×3), brine (×1), dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo, and purified by flash chromatography (SiO_2) to afford glycosyl radical **Donors 2**.

General Procedure C:

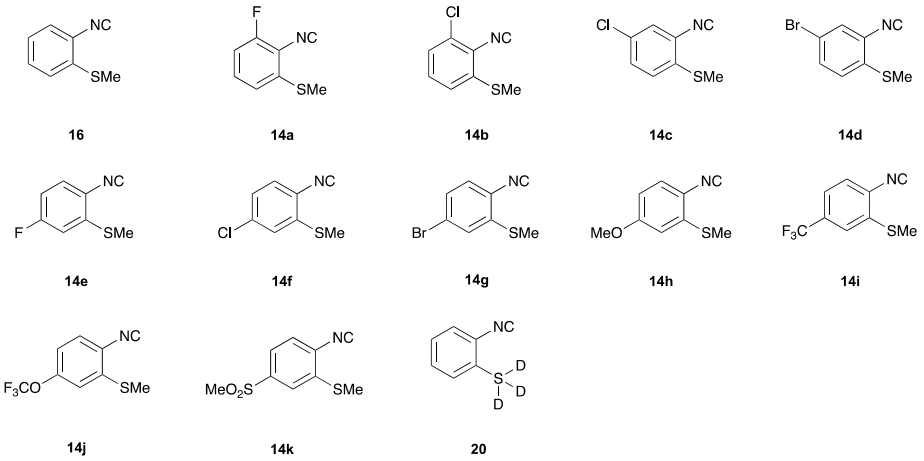


Donors 1 was dissolved in 20 mL MeOH at 0 °C, to which LiOH (0.5 equiv.) was added. The reaction was allowed to stir at 0 °C for 2 h. Silica gel was added to the mixture, which is then concentrated in vacuo. The resulting mixture was dry-loaded onto silica gel column, and eluted to give the corresponding polyols **Donors 3**.

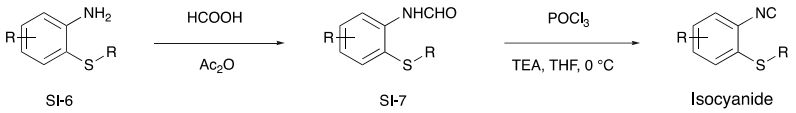
7. General Procedures for the Synthesis of 2-Isocyanoaryl Thioethers

16, **14a**, **14b**, **14c**, **14d**, **14e**, **14f**, **14g**, **14h**, **14i**, **14j**, **14k** and **20** were prepared according to general procedure D. All of characterization data had been reported[3-4].

Substrate scope of the Isocyanides:



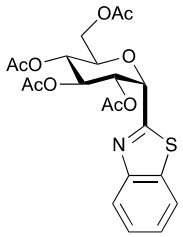
General Procedure D:



Step1: Acetic formic anhydride (0.89 mL) was added dropwise to a stirred solution of **SI-6** (4.30 mmol) at 0℃ in DCM (8 mL). The mixture was stirred for 2 h at room temperature. Then, the mixture was quenched with saturated aqueous solution of Na_2CO_3 and extracted with DCM for three times. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to give the formamide **SI-7** as pale-yellow oil. This compound was used for the subsequent dehydration without further purification.

Step 2: THF (8 mL) and TEA (4.3 mL) were added to a flask containing **SI-7** obtained above under nitrogen atmosphere. $POCl_3$ (0.7 mL) in 2 mL of THF was added slowly via syringe for a period of 1 h at 0 °C, and the mixture was stirred for another 2 h at 0°C. After then, the reaction mixture was diluted with 15 mL EA at 0℃ and slowly quenched with saturated aqueous solution of Na_2CO_3 with stirring for 30 min. The crude compound was purified by column chromatography (petroleum ether/ EA) to give corresponding isocyanides.

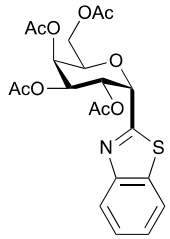
8. Characterization Data for Glycosyl Benzothiazoles:



(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(benzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (17a)

Following **General Procedure**, product **17a** was prepared from **12a** (0.20 mmol, 90 mg), **16** (0.40 mmol, 59.8 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (86.5 mg, 0.186 mmol, 93%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.84 (d, *J* = 5.0 Hz, 1H), 7.68 (s, 1H), 7.53 (d, *J* = 5.0 Hz, 1H), 5.78 (t, *J* = 6.4 Hz, 1H), 5.38 (t, *J* = 5.1 Hz, 1H), 5.33 (d, *J* = 4.7 Hz, 1H), 5.08 (t, *J* = 6.7 Hz, 1H), 4.49 – 4.35 (m, 2H), 4.18 – 4.05 (m, 1H), 2.11 (s, 3H), 2.09 (s, 6H), 1.85 (s, 3H). **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 170.7 , 169.6 , 169.5 , 169.5 , 158.4 , 150.0 , 124.9 , 124.6 , 121.3 , 116.3 , 73.0 , 71.9 , 69.6 , 69.3 , 67.8 , 61.5 , 20.8 , 20.8 , 20.8 , 20.5 . **IR (thin film, cm^{-1}):** 2921, 1745, 1597, 1552, 1369, 1222, 1099, 1044, 911 and 602 cm^{-1}. $[\alpha]_D^{22}$= +73.6 (c = 0.30, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{20}H_{22}N_2NaO_9$ 488.0986, found 488.0985.

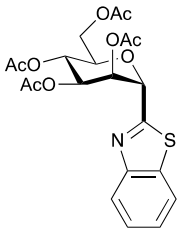


(2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(benzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (17b)

Following **General Procedure**, product **17b** was prepared from **12b** (0.20 mmol, 90 mg), **16** (0.40 mmol, 59.8 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (88.3 mg, 0.192 mmol, 95%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 5.94 (dd, *J* = 9.2, 1.6 Hz, 1H), 5.66 (d, *J* = 5.6 Hz, 1H), 5.63 – 5.54 (m, 2H), 4.73 (t, *J* = 5.6 Hz, 1H), 4.27 – 4.09 (m, 2H), 2.17 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.94 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.6, 170.2, 170.2, 169.9, 164.9, 153.2, 135.0, 126.5, 125.9, 124.1, 121.7, 71.7, 70.7, 68.2, 68.0, 67.8, 61.3, 20.9, 20.9, 20.8, 20.8. **IR** (thin film, cm-1): 2972, 1741, 1435, 1369, 1211, 1047, 919, 763 and 732.

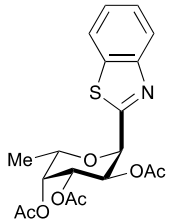
$[\alpha]_D^{28}$ = +88.7 (c = 0.39, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{21}H_{23}NO_9SNa$ 488.0986, found: 488.0985.



(2*R*,3*R*,4*S*,5*S*,6*S*)-2-(acetoxymethyl)-6-(benzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (17c)

Following **General Procedure**, product 1**7c** was prepared from **12c** (0.20 mmol, 90 mg), **16** (0.40 mmol, 59.8 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (89.3 mg, 0.19 mmol, 96%).

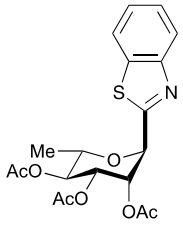
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 6.8 Hz, 1H), 6.17 (s, 1H), 5.57 (d, *J* = 8.0 Hz, 1H), 5.42 – 5.29 (m, 2H), 4.33 (dd, *J* = 11.6, 4.8 Hz, 1H), 4.12 (d, *J* = 11.9 Hz, 1H), 3.92 (br, 1H), 2.19 (s, 3H), 2.11 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.6, 170.1, 169.8, 169.7, 166.0, 152.9, 135.6, 126.4, 126.0, 124.1, 121.8, 76.2, 72.5, 69.7, 69.1, 66.6, 62.4, 21.0, 20.8, 20.7, 20.7. **IR** (thin film, cm-1): 2989, 1741, 1435, 1369, 1211, 1048, 919 and 764 cm^{-1}. $[\alpha]_D^{28}$= +75.1 (c = 0.36, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{21}H_{23}NO_9SNa^+$ 488.0986, found: 488.0985. The ^{1}H NMR spectra coincide with the previously reported data[6].



(2*S*,3*S*,4*R*,5*R*,6*S*)-2-(benzo[*d*]thiazol-2-yl)-6-methyltetrahydro-2*H*-pyran-3,4,5-triyl triacetate (17d)

Following **General Procedure**, product **17d** was prepared from **12d** (0.20 mmol, 78.5 mg), **16** (0.40 mmol, 59.8 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 11:1) afforded the title product as a colorless oil (65.1 mg, 0.16 mmol, 80%).

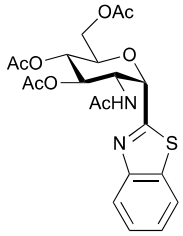
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.4 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 5.97 (dd, *J* = 9.6, 3.6 Hz, 1H), 5.64 – 5.50 (m, 2H), 5.44 (dd, *J* = 3.2, 2.0 Hz, 1H), 4.64 – 4.57 (m, 1H), 2.19 (s, 3H), 2.03 (s, 3H), 1.94 (s, 3H), 1.19 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.7, 170.4, 170.1, 165.3, 153.3, 135.1, 126.4, 125.8, 124.1, 121.7, 71.9, 70.8, 68.7, 68.2, 20.9, 20.8, 16.1. **IR** (thin film, cm^{-1}): 3005, 2989, 1744, 1435, 1370, 1275, 1260, 1219, 1054, 911, 764 and 750. $[\alpha]_D^{28}$= -90.8 (c = 0.30, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{19}H_{21}NO_7SNa$ 430.0931, found: 430.0928.



(2*S*,3*R*,4*R*,5*S*,6*S*)-2-(benzo[*d*]thiazol-2-yl)-6-methyltetrahydro-2*H*-pyran-3,4,5-triyl triacetate (17e)

Following **General Procedure**, product **17e** was prepared from **12e** (0.20 mmol, 90 mg), **16** (0.40 mmol, 59.8 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (78.9 mg, 0.19 mmol, 97%).

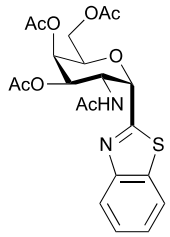
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 6.18 (s, 1H), 5.52 (dd, *J* = 9.6, 2.4 Hz, 1H), 5.31 (s, 1H), 5.17 (t, *J* = 9.6 Hz, 1H), 3.85 – 3.74 (m, 1H), 2.21 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H), 1.28 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.3, 170.0, 169.9, 167.1, 153.0, 135.6, 126.4, 125.9, 124.1, 121.8, 76.1, 71.4, 70.7, 70.1, 69.3, 21.1, 20.8, 17.6. **IR** (thin film, cm^{-1}): 3005, 2989, 1742, 1434, 1369, 1275, 1260, 1216, 1053, 911, 764 and 750. $[\alpha]_D^8$ = -87.5 (c = 0.49, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{19}H_{21}NO_7SNa$ 430.0931, found: 430.0930.



(2*R*,3*S*,4*R*,5*S*,6*S*)-5-acetamido-2-(acetoxymethyl)-6-(benzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (17f)

Following **General Procedure**, product **17f** was prepared from **12f** (0.20 mmol, 89 mg), **16** (0.40 mmol, 59.8 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 1:3) afforded the title product as a colorless oil (91 mg, 0.196 mmol, 98%).

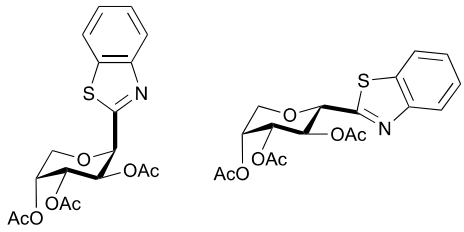
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 9.6 Hz, 1H), 5.72 (t, *J* = 9.6 Hz, 1H), 5.42 (d, *J* = 6.0 Hz, 1H), 5.17 (t, *J* = 9.6 Hz, 1H), 4.91 – 4.81 (m, 1H), 4.19 (dd, *J* = 12.0, 4.4 Hz, 1H), 4.04 (t, *J* = 12.0, 1.6 Hz, 1H), 3.74 – 3.67 (m, 1H), 2.08 (s, 3H), 2.04 (s, 3H), 1.95 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.2, 170.6, 170.1, 169.3, 168.4, 152.2, 135.2, 126.6, 126.3, 123.9, 121.9, 73.9, 71.6, 71.4, 68.7, 62.0, 50.9, 23.4, 20.8, 20.7, 20.6. **IR** (thin film, cm-1): 3006, 2989, 1740, 1677, 1510, 1433, 1366, 1275, 1260, 1220, 1037, 912, 764 and 750. $[\alpha]_D^8$ = +92.6 (c = 0.57, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{21}H_{24}N_2O_8SNa$ 487.1146, found: 487.1143.



(2*R*,3*R*,4*R*,5*R*,6*S*)-5-acetamido-2-(acetoxymethyl)-6-(benzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (17g)

Following **General Procedure**, product **17g** was prepared from **12g** (0.20 mmol, 89 mg), **16** (0.40 mmol, 59.8 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (87.2 mg, 0.188 mmol, 94%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 9.6 Hz, 1H), 5.62 (dd, *J* = 11.2, 2.8 Hz, 1H), 5.47 (d, *J* = 6.0 Hz, 1H), 5.38 (d, *J* = 2.0 Hz, 1H), 5.18 – 5.09 (m, 1H), 4.10 (d, *J* = 6.4 Hz, 2H), 3.93 (t, *J* = 6.4 Hz, 1H), 2.19 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.9, 170.5, 170.4, 170.3, 169.2, 152.2, 135.2, 126.6, 126.3, 123.8, 122.0, 74.4, 70.5, 68.8, 67.4, 61.9, 46.9, 23.6, 20.9, 20.9, 20.7. **IR** (thin film, cm-1): 3006, 2989, 1744, 1670, 1513, 1434, 1370, 1275, 1260, 1228, 1084, 1056, 917, 764 and 750. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{8}}$ **=** +96.7 (c = 0.16, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{21}H_{24}N_2O_8SNa$ 487.1146, found: 487.1144.

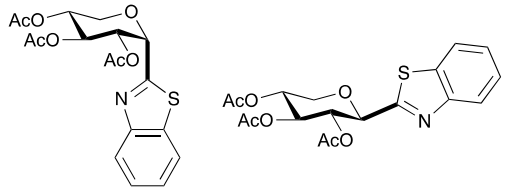


(3*S*,4*R*,5*R*)-2-(benzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (17h)

Following **General Procedure**, product **17h** was prepared from **12h** (0.20 mmol, 75.6 mg), **16** (0.40 mmol, 59.8 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (72.3 mg, 0.184 mmol, 92%, **α: β= 2.4: 1**).

^{1}H NMR (400 MHz, Chloroform-*d*) (**β isomer**) δ: 7.98 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.47 (dt, *J* = 7.2, 1.2 Hz, 1H), 7.39 (dt, *J* = 7.2, 1.2 Hz, 1H), 5.53 (t, *J* = 9.6 Hz, 1H), 5.44 (brs, 1H), 5.24 (dd, *J* = 10.0, 3.2 Hz, 1H), 4.81 (d, *J* = 9.2 Hz, 1H), 4.24 (dd, *J* = 13.2, 2.0 Hz, 1H), 3.91 (dd, *J* = 13.2, 1.2 Hz, 1H), 2.20 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H). (**α isomer**) δ: 7.99 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 5.56-5.47 (m, 2H), 5.40-5.31 (m, 2H), 4.13 (dd, *J* = 13.2, 2.0 Hz, 1H), 3.90 (t, *J* = 10.8 Hz, 1H), 2.19 (s, 3H), 2.04 (s, 3H), 1.92 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) (**β isomer**) δ: 170.5, 170.3, 169.7, 167.3, 152.8, 135.0, 126.3, 125.6, 123.4, 122.0, 78.6, 71.3, 69.1, 68.5, 68.5, 21.1, 20.8, 20.8. **(α isomer) δ**: 169.8, 169.2, 169.0, 167.5, 152.8, 134.9, 126.3, 125.4, 123.4, 121.8, 75.0,

70.0, 66.4, 65.1, 64.3, 20.9, 20.8, 20.7. **IR** (thin film, cm^{-1}): 3006, 2989, 1743, 1437, 1370, 1275, 1260, 1214, 1045, 931, 764 and 750. $[\alpha]_D^8$ = -62.1 (c = 0.34, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{18}H_{19}NO_7SNa$ 416.0774, found: 416.0772. **Structural Assignment:** The anomeric signal of **β isomer** is δ 4.81 (d, *J* = 9.2 Hz, 1H)，supporting the assigned **β-configuration.**

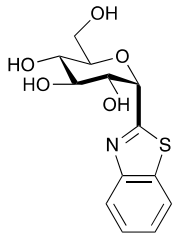


(3*R*,4*S*,5*R*)-2-(benzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (17i)

Following **General Procedure**, product **17i** was prepared from **12i** (0.20 mmol, 75.6 mg), **16** (0.40 mmol, 59.8 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (75.4 mg, 0.192 mmol, 96%, **α: β= 2: 1**).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (**β isomer**) δ: 7.98 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 6.8 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 5.41 (t, *J* = 9.6 Hz, 1H), 5.26 (t, *J* = 9.6 Hz, 1H), 5.16 (dt, *J* = 10.0, 5.6 Hz, 1H), 4.83 (d, *J* = 9.6 Hz, 1H), 4.35 (dd, *J* = 11.6, 6.0 Hz, 1H), 3.56 (t, *J* = 10.8 Hz, 1H), 2.07 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H). (**α isomer**) δ: 8.00 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 5.33 (s, 1H), 5.28 (s, 2H), 4.81 (s, 1H), 4.25 (d, *J* = 13.2 Hz, 1H), 4.09 (d, *J* = 13.2 Hz, 1H), 2.16 (s, 3H), 2.12 (s, 3H), 1.92 (s, 3H).

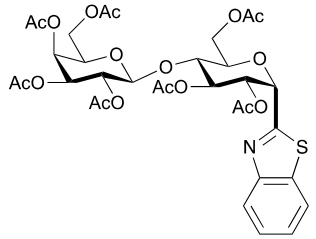
^{13}C NMR (101 MHz, Chloroform-*d*) δ (**β isomer**) δ: 170.4, 170.0, 169.5, 166.9, 152.8, 135.0, 126.4, 125.7, 123.5, 122.1, 78.3, 73.1, 71.7, 69.1, 67.3, 29.8, 20.9, 20.7. (**α isomer**) δ: 169.9, 169.5, 168.5, 167.9, 152.8, 134.9, 126.2, 125.3, 123.4, 121.8, 75.2, 68.2, 66.9, 66.5, 65.9, 21.1, 20.9, 20.7. **IR** (thin film, cm^{-1}): 3006, 2989, 1744, 1437, 1371, 1275, 1260, 1216, 1046, 931, 764 and 750. $[\alpha]_D^8$ = -55.3 (c = 0.37, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{18}H_{19}NO_7SNa$ 416.0774, found: 416.0773. The ^{1}H NMR spectra coincide with the previously reported data[7].



(2*S*,3*R*,4*S*,5*S*,6*R*)-2-(benzo[*d*]thiazol-2-yl)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3,4,5-triol (17k)

Following **General Procedure**, product **17k** was prepared from **12k** (0.20 mmol, 56 mg), **16** (0.40 mmol, 59.8 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, DCM: MeOH = 1:0 to 10:1) afforded the title product as a white solid. (53.5 mg, 0.18 mmol, 90%).

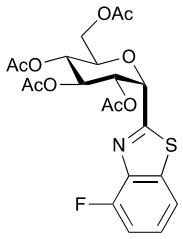
Mp: 128 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 5.44 (d, *J* = 4.4 Hz, 1H), 4.00 – 3.93 (m, 2H), 3.88 – 3.70 (m, 3H), 3.52 – 3.45 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.7, 153.5, 136.3, 127.3, 126.7, 123.8, 122.9, 78.2, 76.0, 75.0, 73.7, 71.6, 62.6. **IR** (thin film, cm^{-1}): 3309, 2988, 1450, 1276, 1261, 1021, 764 and 750. $[\alpha]_D^8$ = +71.1 (c = 0.63, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{13}H_{15}NO_5SNa$ 320.0563, found: 320.0565.



(2*R*,3*S*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-(benzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (17j)

Following **General Procedure**, product **17j** was prepared from **12j** (0.20 mmol, 147.6 mg), **16** (0.40 mmol, 59.8 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 1:1) afforded the title product as a colorless oil (105.4 mg, 0.14 mmol, 70%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 5.88 (t, *J* = 6.4 Hz, 1H), 5.53 (d, *J* = 4.8 Hz, 1H), 5.40 – 5.32 (m, 2H), 5.15 (dd, *J* = 10.0, 8.0 Hz, 1H), 4.99 (dd, *J* = 10.4, 3.2 Hz, 1H), 4.63 (d, *J* = 8.0 Hz, 1H), 4.42 – 4.33 (m, 2H), 4.26 (dd, *J* = 12.4, 6.4 Hz, 1H), 4.09 (d, *J* = 6.4 Hz, 2H), 3.93 (t, *J* = 6.4 Hz, 1H), 3.82 (t, *J* = 6.4 Hz, 1H), 2.13 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.6, 170.5, 170.2, 170.2, 170.0, 169.3, 169.3, 166.2, 153.2, 135.0, 126.4, 125.7, 124.0, 121.7, 101.3, 76.3, 72.7, 71.6, 71.2, 71.0, 69.7, 69.1, 69.0, 66.9, 62.1, 61.1, 21.0, 21.0, 20.8, 20.7, 20.7, 20.6. **IR** (thin film, cm^{-1}): 2988, 1742, 1434, 1369, 1259, 1213, 1050, 917 and 750. $[\alpha]_D^8$ = +56.3 (c = 0.61, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{33}H_{39}NO_{17}SNa$ 776.1831, found: 776.1830.

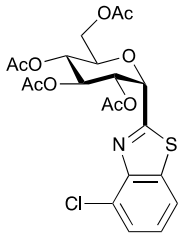


(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(4-fluorobenzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (18m)

Following **General Procedure**, product **18m** was prepared from **12a** (0.20 mmol, 90 mg), **14a** (0.40 mmol, 67 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash

chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (87.9 mg, 0.182 mmol, 91%).

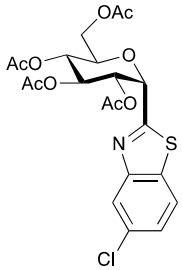
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.40 (m, 1H), 7.27 (dd, *J* = 18.0, 10.0 Hz, 1H), 5.86 (t, *J* = 8.0 Hz, 1H), 5.68 (d, *J* = 5.2 Hz, 1H), 5.43 (dd, *J* = 8.0, 6.0 Hz, 1H), 5.18 (t, *J* = 8.4 Hz, 1H), 4.61 – 4.52 (m, 1H), 4.41 (dd, *J* = 12.4, 5.2 Hz, 1H), 4.19 (d, *J* = 11.6 Hz, 1H), 2.14 (s, 3H), 2.11 (s, 6H), 2.02 (s, 3H). **^{113}C NMR** (101 MHz, Chloroform-*d*) δ 170.8, 169.9, 169.8, 169.7, 165.8, 156.21 (d, *J* = 258.2 Hz), 142.1 (d, J = 13.9 Hz), 137.7 (d, J = 3.4 Hz), 126.8 (d, J = 7.0 Hz), 117.4 (d, *J* = 4.4 Hz), 112.2 (d, *J* = 18.0 Hz), 72.0, 71.6, 70.0, 69.9, 68.2, 61.7, 20.8, 20.8, 20.8. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -120.5. **IR** (thin film, cm-1): 3006, 2989, 1747, 1476, 1369, 1275, 1261, 1222, 1038, 918, 764 and 750. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{8}}$ **=** +69.9 (c = 0.30, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{21}H_{22}FNO_9SNa$ 506.0892, found: 506.0897.



(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(4-chlorobenzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (18n)

Following **General Procedure**, product **18n** was prepared from **12a** (0.20 mmol, 90 mg), **14b** (0.40 mmol, 73.2 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (92.8 mg, 0.186 mmol, 93%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 5.85 (t, *J* = 8.0 Hz, 1H), 5.64 (d, *J* = 5.2 Hz, 1H), 5.39 (dd, *J* = 7.6, 6.0 Hz, 1H), 5.14 (t, *J* = 8.0 Hz, 1H), 4.58 – 4.47 (m, 1H), 4.36 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.15 (d, *J* = 12.4 Hz, 1H), 2.10 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.8, 169.9, 169.8, 169.7, 166.1, 150.2, 136.5, 129.0, 126.8, 126.4, 120.2, 72.0, 71.6, 69.9, 69.8, 68.2, 61.8, 20.9, 20.8, 20.8. **IR** (thin film, cm-1): 3006, 2990, 1743, 1457, 1368, 1275, 1260, 1217, 1037, 914, 764 and 750. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{8}}$ **=** +71.1 (c = 0.52, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{21}H_{22}ClNO_9SNa$ 522.0596, found: 522.0597.

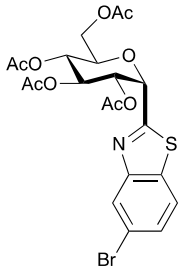


(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(5-chlorobenzo[*d*]thiazol-2-yl)tetrahydro-2*H*-

pyran-3,4,5-triyl triacetate (18o)

Following **General Procedure**, product **18o** was prepared from **12a** (0.20 mmol, 90 mg), **14c** (0.40 mmol, 73.2 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (89.8 mg, 0.18 mmol, 90%).

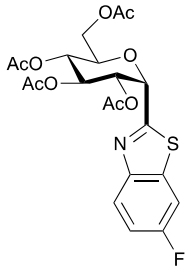
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 5.96 (t, *J* = 8.0 Hz, 1H), 5.58 (d, *J* = 5.2 Hz, 1H), 5.36 (t, *J* = 6.4 Hz, 1H), 5.15 (t, *J* = 8.4 Hz, 1H), 4.47 – 4.40 (m, 1H), 4.32 (dd, *J* = 12.0, 3.2 Hz, 1H), 4.08 (d, *J* = 12 Hz, 1H), 2.07 (s, 3H), 2.05 (s, 6H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.7, 169.9, 169.9, 169.7, 166.7, 154.0, 133.3, 132.7, 126.5, 124.0, 122.4, 71.6, 71.6, 70.1, 70.1, 68.4, 61.8, 20.8, 20.8, 20.7. **IR** (thin film, cm-1): 3006, 2989, 1741, 1437, 1367, 1275, 1260, 1211, 1033, 921, 764 and 750. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{8}}$ = +97.3 (c = 0.64, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{21}H_{22}ClNO_9SNa$ 522.0596, found: 522.0598.



(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(5-bromobenzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (18p)

Following **General Procedure**, product **18p** was prepared from **12a** (0.20 mmol, 90 mg), **14d** (0.40 mmol, 91 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (97.7 mg, 0.18 mmol, 90%).

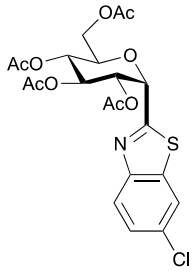
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 5.96 (t, *J* = 8.8 Hz, 1H), 5.58 (d, *J* = 6.0 Hz, 1H), 5.36 (dd, *J* = 9.2, 6.0 Hz, 1H), 5.15 (m, *J* = 8.8 Hz, 1H), 4.47 – 4.40 (m, 1H), 4.31 (dd, *J* = 12.4, 4.4 Hz, 1H), 4.07 (dd, *J* = 12.4, 1.6 Hz, 1H), 2.07 (s, 3H), 2.05 (s, 6H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.7, 169.9, 169.9, 169.7, 166.4, 154.3, 133.8, 129.1, 127.1, 122.8, 120.2, 71.6, 70.1, 70.0, 68.4, 61.8, 20.8, 20.8, 20.7. **IR** (thin film, cm-1): 3006, 2989, 1741, 1457, 1367, 1275, 1260, 1212, 1034, 913, 764 and 750. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{8}}$ = +67.4 (c = 0.41, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{21}H_{22}BrNO_9SNa$ 566.0091, found: 566.0090.



(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(6-fluorobenzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (18q)

Following **General Procedure**, product **18q** was prepared from **12a** (0.20 mmol, 90 mg), **14e** (0.40 mmol,67 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (82.1 mg, 0.17 mmol, 85%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (dd, *J* = 8.8, 4.8 Hz, 1H), 7.59 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.32 – 7.24 (m, 1H), 5.99 (t, *J* = 8.8 Hz, 1H), 5.59 (d, *J* = 5.6 Hz, 1H), 5.38 (dd, *J* = 9.2, 6.0 Hz, 1H), 5.17 (t, *J* = 8.8 Hz, 1H), 4.47 – 4.41 (m, 1H), 4.34 (dd, *J* = 12.4, 4.4 Hz, 1H), 4.08 (dd, *J* = 12.4, 1.6 Hz, 1H), 2.10 (s, 3H), 2.07 (s, 6H), 1.96 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.8, 170.0, 169.8, 164.3 (d, *J* = 3.2 Hz), 161.0 (d, *J* = 247.1 Hz) 149.9 (d, *J* = 1.3 Hz), 136.2 (d, *J* = 11.3 Hz), 125.3 (d, *J* = 9.5 Hz), 115.5 (d, *J* = 25.0 Hz), 107.9 (d, *J* = 26.8 Hz), 71.7, 71.5, 70.3, 70.1, 68.5, 61.8, 20.9, 20.9, 20.8, 20.8. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -114.7. **IR** (thin film, cm-1): 3006, 2989, 1742, 1456, 1367, 1275, 1260, 1212, 1033, 912, 764 and 750. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{8}}$ **= +74.3** (c = 0.41, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{21}H_{22}FNO_9SNa$ 506.0892, found: 506.0892.

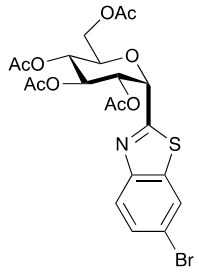


(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(6-chlorobenzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (18r)

Following **General Procedure**, product **18r** was prepared from **12a** (0.20 mmol, 90 mg), **14f** (0.40 mmol, 73.2 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (72.8 mg, 0.146 mmol, 73%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 1.6 Hz, 1H), 7.50 (dd, *J* = 8.8, 2.0 Hz, 1H), 5.95 (t, *J* = 8.8 Hz, 1H), 5.59 (d, *J* = 5.6 Hz, 1H), 5.37 (dd, *J* = 9.2, 6.0 Hz, 1H), 5.16 (t, *J* = 8.8 Hz, 1H), 4.47 – 4.40 (m, 1H), 4.33 (dd, *J* = 12.4, 4.8 Hz, 1H), 4.09 (dd, *J* = 12.4, 2.4 Hz, 1H), 2.09 (s, 3H), 2.06 (s, 6H), 1.95 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.8, 170.0, 170.0, 169.8, 151.8, 136.3, 132.1, 127.4, 125.0, 121.4, 71.6, 70.2, 70.1, 68.5, 61.8, 20.9, 20.8, 20.8. **IR** (thin film,

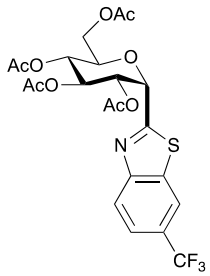
cm-1): 3006, 2989, 1742, 1436, 1367, 1275, 1260, 1213, 1035, 914, 764 and 750. $[\alpha]_D^8$ = +71.3 (c = 0.49, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{21}H_{22}ClNO_9SNa$ 522.0596, found: 522.0598.



(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(6-bromobenzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (18s)

Following **General Procedure**, product **18s** was prepared from **12a** (0.20 mmol, 90 mg), **14g** (0.40 mmol, 91 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (102.1 mg, 0.188 mmol, 94%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 5.94 (t, *J* = 8.8 Hz, 1H), 5.58 (d, *J* = 6.0 Hz, 1H), 5.37 (dd, *J* = 8.4, 6.0 Hz, 1H), 5.15 (t, *J* = 8.4 Hz, 1H), 4.46 – 4.40 (m, 1H), 4.33 (dd, *J* = 12.4, 4.8 Hz, 1H), 4.08 (d, *J* = 12.4 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 6H), 1.94 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.8, 170.0, 169.9, 169.7, 165.3, 152.1, 136.7, 130.1, 125.3, 124.3, 119.8, 71.6, 71.6, 70.2, 70.0, 68.4, 61.8, 20.9, 20.9, 20.8, 20.8. **IR** (thin film, cm-1): 3006, 2989, 1741, 1434, 1367, 1275, 1260, 1211, 1033, 914, 764 and 750. $[\alpha]_D^8$ = +69.3 (c = 0.52, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{21}H_{22}BrNO_9SNa$ 566.0091, found: 566.0090.

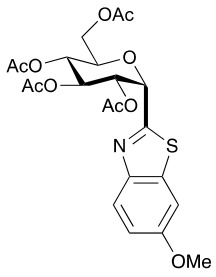


(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(6-(trifluoromethyl)benzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (18t)

Following **General Procedure**, product **18t** was prepared from **12a** (0.20 mmol, 90 mg), **14i** (0.40 mmol, 86.9 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (98.1 mg, 0.184 mmol, 92%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 5.91 (t, *J* = 8.4 Hz, 1H), 5.63 (d, *J* = 5.6 Hz, 1H), 5.39 (dd, *J* = 8.4, 6.0 Hz, 1H), 5.15 (t, *J* = 8.4 Hz, 1H), 4.49 – 4.42 (m, 1H), 4.35 (dd, *J* = 12.4, 5.2 Hz, 1H), 4.09 (dd, *J* = 12.0, 1.6 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 1.94 (s, 3H). **^{13}C NMR** (101 MHz,

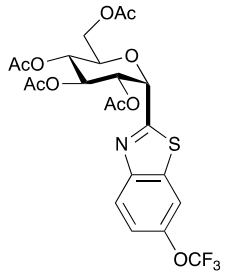
Chloroform-*d*) δ 170.7, 169.9, 169.8, 169.7, 168.4, 155.1, 135.2, 128.14 (q, *J* = 32.7 Hz), 124.6, 124.1 (q, *J* = 273 Hz), 123.5 (q, *J* = 3.2 Hz), 119.5 (q, *J* = 4.3 Hz), 71.9, 71.6, 70.0, 69.9, 68.3, 61.7, 20.8, 20.8, 20.8, 20.7. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -61.5. **IR** (thin film, cm-1): 3006, 2989, 1747, 1369, 1321, 1276, 1261, 1221, 1124, 1038, 897, 764 and 750. $[\alpha]_D^8$ = +79.3 (c = 0.31, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{22}H_{22}F_3NO_9SNa$ 556.0860, found: 556.0861.



(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(6-methoxybenzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (18u)

Following **General Procedure**, product **18u** was prepared from **12a** (0.20 mmol, 90 mg), **14h** (0.40 mmol, 72 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (93.1 mg, 0.188 mmol, 94%).

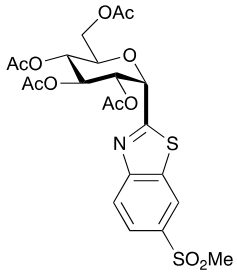
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 9.2 Hz, 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.11 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.04 (t, *J* = 8.8 Hz, 1H), 5.55 (d, *J* = 6.0 Hz, 1H), 5.34 (dd, *J* = 9.2, 6.0 Hz, 1H), 5.16 (t, *J* = 9.2 Hz, 1H), 4.47 – 4.40 (m, 1H), 4.30 (dd, *J* = 12.4, 4.4 Hz, 1H), 4.06 (dd, *J* = 12.4, 2.0 Hz, 1H), 3.87 (s, 3H), 2.07 (s, 3H), 2.04 (s, 6H), 1.94 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.8, 170.1, 170.0, 169.8, 161.4, 158.3, 147.8, 136.6, 124.7, 116.1, 103.8, 71.6, 71.2, 70.4, 70.2, 68.7, 61.9, 55.9, 55.9, 20.8, 20.8, 20.8, 20.8. **IR** (thin film, cm-1): 3006, 2989, 1746, 1367, 1275, 1262, 1222, 1034, 910, 764 and 750. $[\alpha]_D^8$ = +72.1 (c = 0.36, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{22}H_{25}NO_{10}SNa$ 518.1091, found: 518.1091.



(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(6-(trifluoromethoxy)benzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (18v)

Following **General Procedure**, product **18v** was prepared from **12a** (0.20 mmol, 90 mg), **14j** (0.40 mmol, 93.3mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (97.7 mg, 0.178 mmol, 89%).

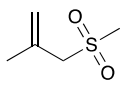
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.8 Hz, 1H), 7.77 (s, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 5.94 (t, *J* = 8.4 Hz, 1H), 5.59 (d, *J* = 6.0 Hz, 1H), 5.37 (dd, *J* = 9.2, 6.0 Hz, 1H), 5.14 (t, *J* = 8.8 Hz, 1H), 4.46 – 4.39 (m, 1H), 4.34 (dd, *J* = 12.4, 4.8 Hz, 1H), 4.07 (dd, *J* = 12.4, 2.4 Hz, 1H), 2.07 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.94 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.7, 169.9, 169.9, 169.7, 166.1, 151.6, 147.0, 135.9, 125.1, 120.6 (q, *J* = 259.6 Hz), 120.5, 114.2, 71.7, 71.6, 70.1, 70.0, 68.4, 61.7, 20.8, 20.7, 20.7. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -58.0. **IR** (thin film, cm-1): 3006, 2989, 1744, 1453, 1368, 1275, 1260, 1214, 1167, 1036, 914, 764 and 750. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{8}}$ **=** +74.2 (c = 0.30, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{22}H_{22}F_3NO_{10}SNa$ 572.0809, found: 572.0809.



(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(6-(methylsulfonyl)benzo[*d*]thiazol-2-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (18w)

Following **General Procedure**, product **18w** was prepared from **12a** (0.20 mmol, 90 mg), **14k** (0.40 mmol, 91 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 4:1) afforded the title product as a colorless oil (95.3 mg, 0.154 mmol, 77%).

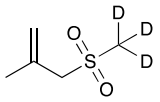
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 1.2 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.05 (dd, *J* = 8.8, 1.6, 1H), 5.83 (t, *J* = 8.0 Hz, 1H), 5.64 (d, *J* = 5.2 Hz, 1H), 5.39 (dd, *J* = 8.4, 5.6 Hz, 1H), 5.13 (t, *J* = 8.0 Hz, 1H), 4.48 – 4.41 (m, 1H), 4.37 (dd, *J* = 12.4, 5.6 Hz, 1H), 4.10 (dd, *J* = 12.4, 2.4 Hz, 1H), 3.11 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.7, 170.5, 169.8, 169.8, 169.6, 156.1, 137.9, 135.6, 125.1, 125.0, 122.4, 72.1, 71.6, 69.7, 68.1, 61.5, 44.9, 20.8, 20.8, 20.7. **IR** (thin film, cm-1): 3006, 2989, 1745, 1369, 1275, 1262, 1219, 1036, 912, 764 and 750. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{8}}$ **=** +81.7 (c = 0.50, $CHCl_3$). **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_{28}H_{29}NO_{11}S_2Na$ 642.1074, found: 642.1074.



2-methyl-3-(methylsulfonyl)prop-1-ene (19)

Following **Procedure of Mechanism Experiment**, product **19** was prepared from **12a** (0.20 mmol, 90 mg), **16** (0.40 mmol, 59.8 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.24 (s, 1H), 5.10 (s, 1H), 3.70 (s, 2H), 2.04 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 134.68, 120.64, 63.25, 22.67. **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_5H_{10}O_2SNa$ 157.0294, found: 157.0295.



2-methyl-3-((methyl-*d*$_3$)sulfonyl)prop-1-ene (21)

Following **Procedure of Mechanism Experiment**, product **21** was prepared from **12a** (0.20 mmol, 90 mg), **20** (0.40 mmol, 61 mg), **AIBN** (0.02 mmol, 3.2 mg, 10 mol%). Purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.24 (s, 1H), 5.10 (s, 1H), 3.69 (s, 2H), 2.00 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 134.55, 120.51, 63.12, 22.54. **HRMS (ESI) m/z: [M+Na]$^+$ Calcd for** $C_5H_7D_3O_2SNa$ 160.0482, found: 160.0484.

9. Reference

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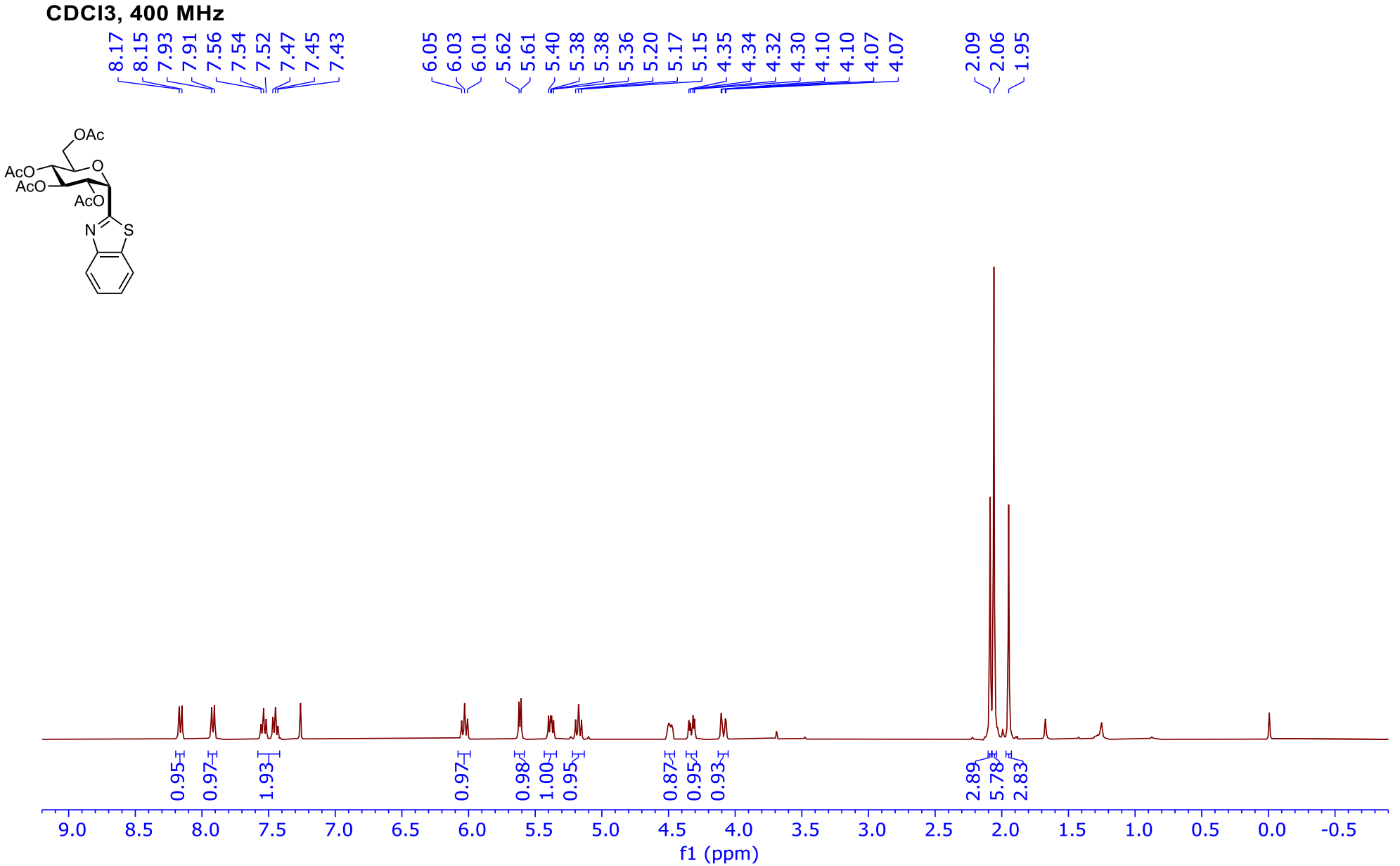
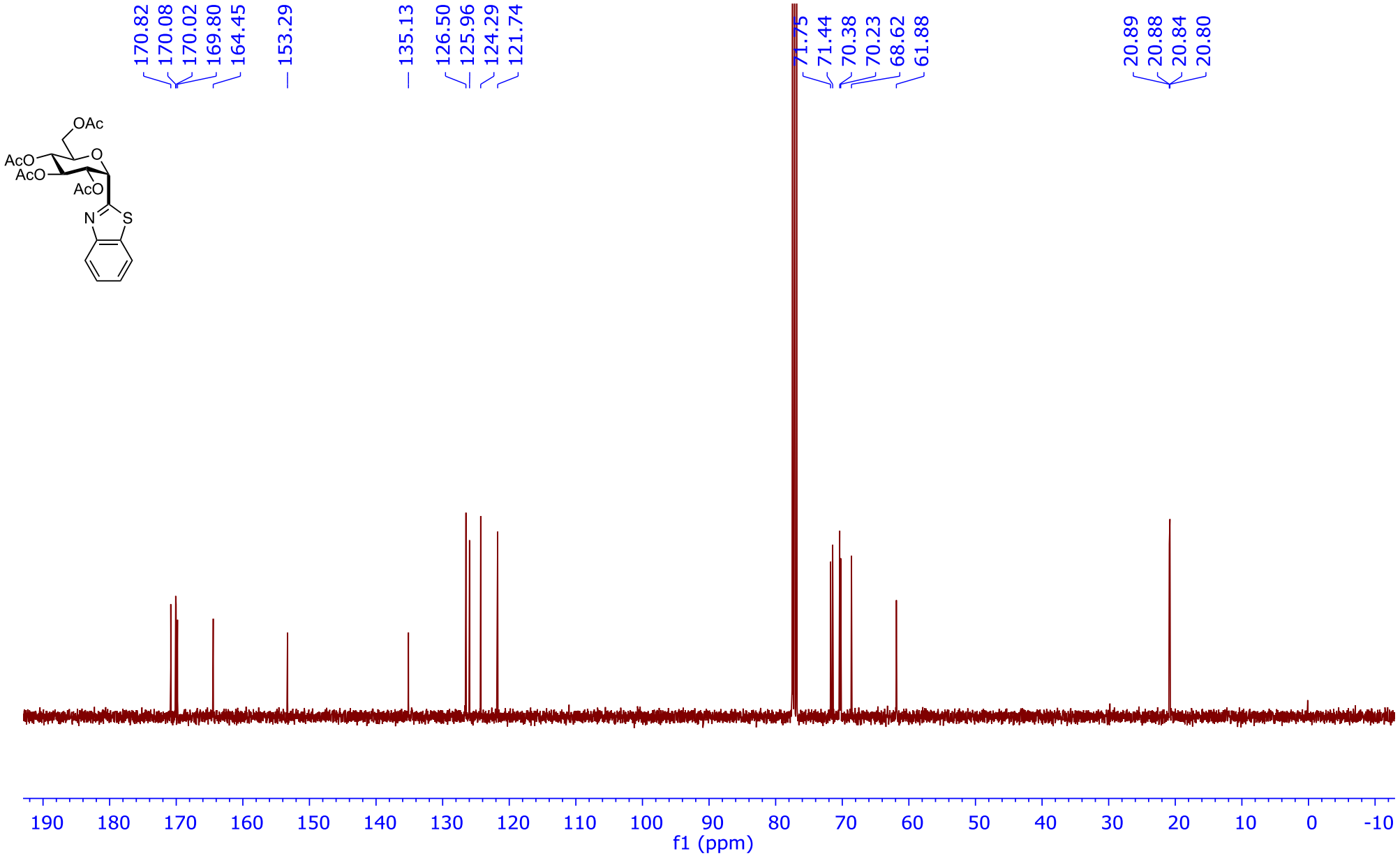
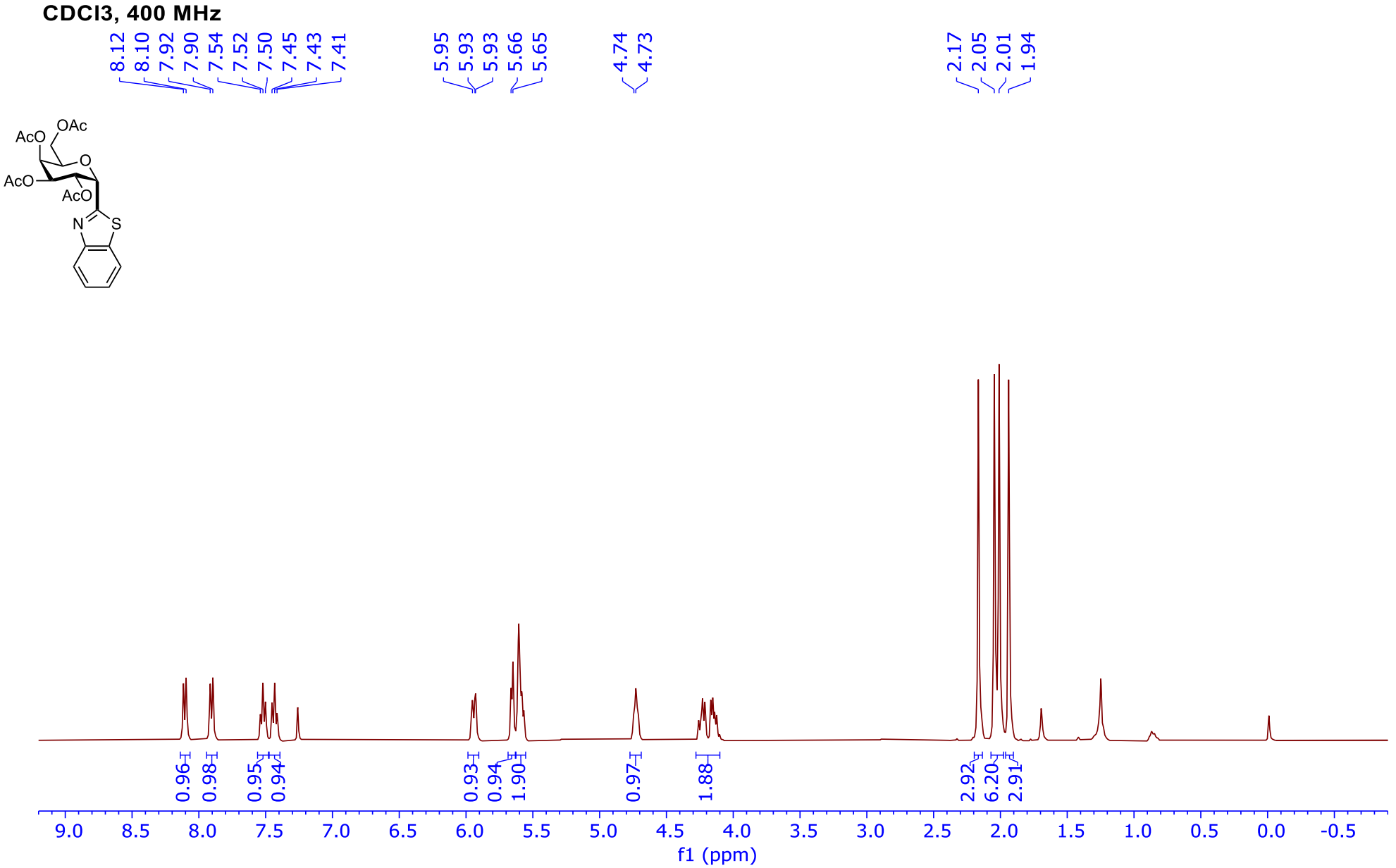
10. NMR Spectra



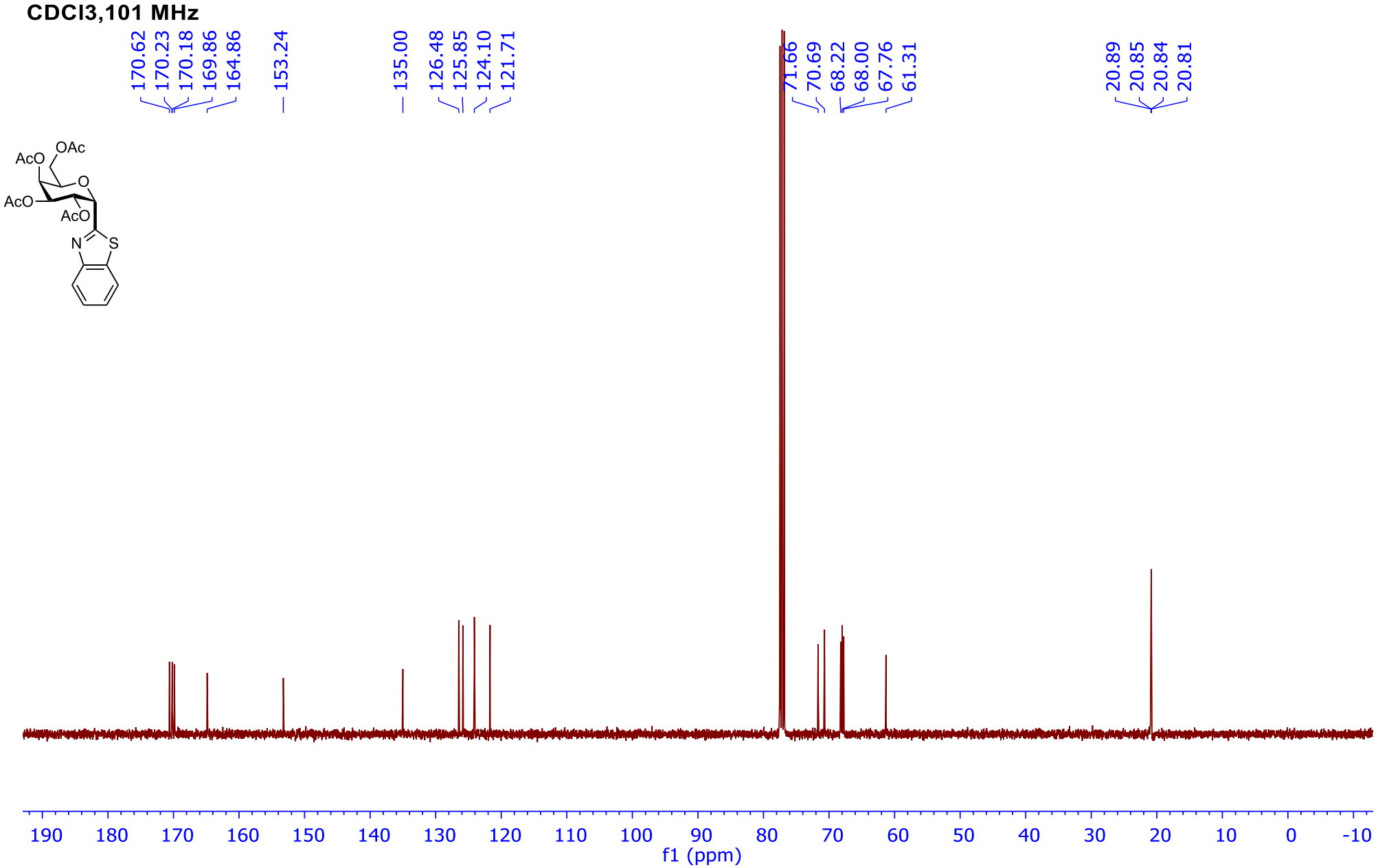
^{1}H NMR Spectrum of 17a



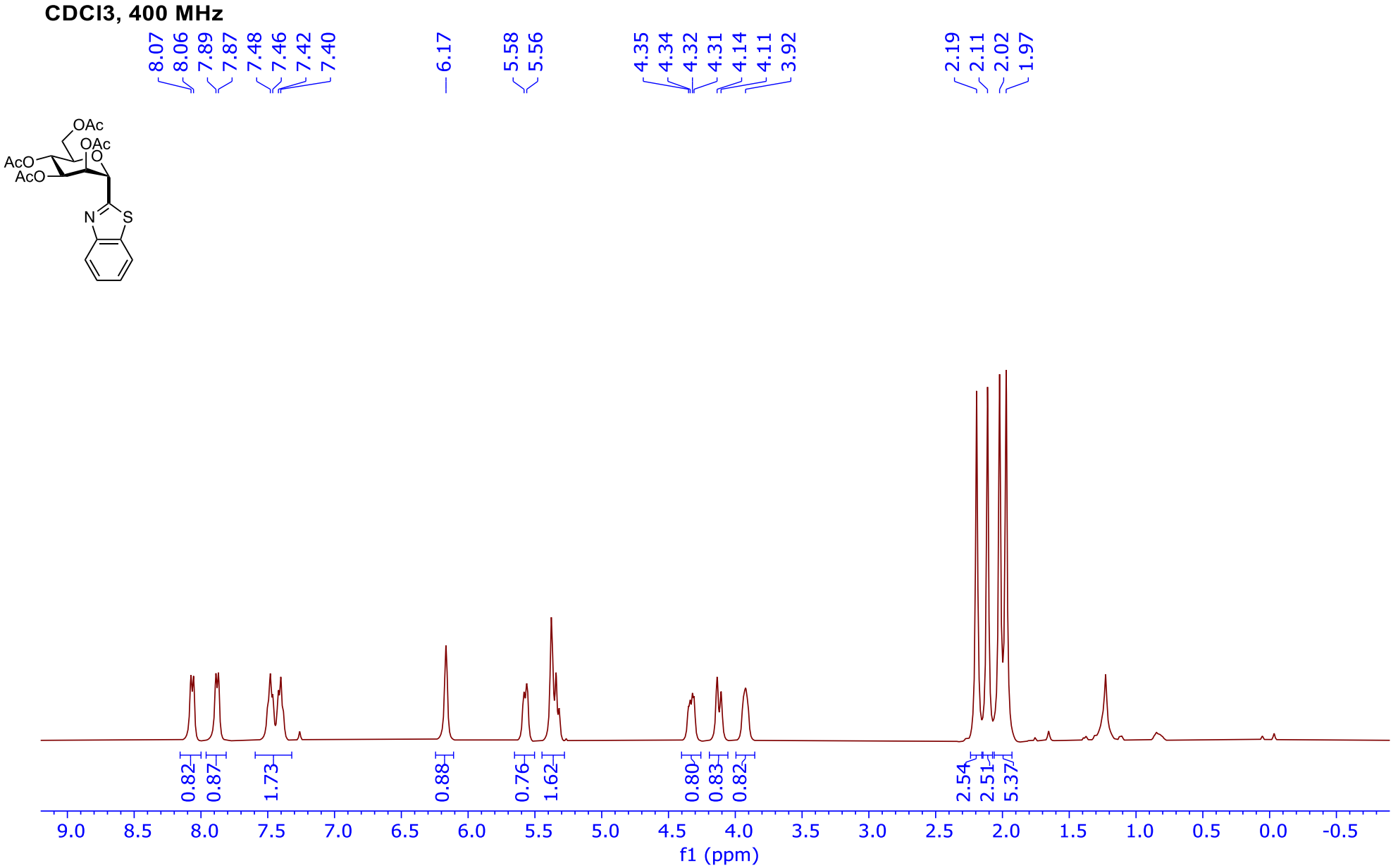
^{13}C NMR Spectrum of 17a



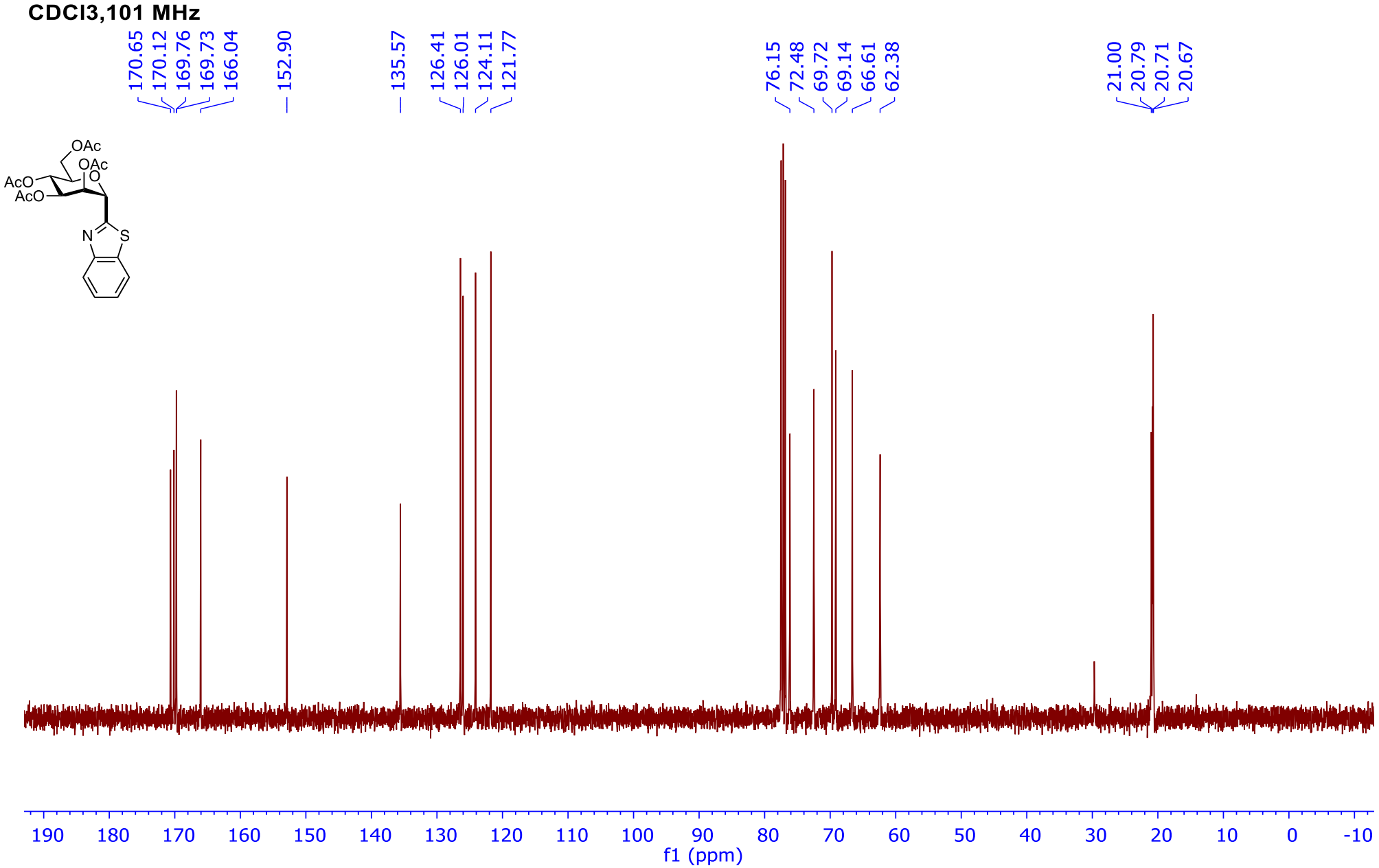
^{1}H NMR Spectrum of 17b



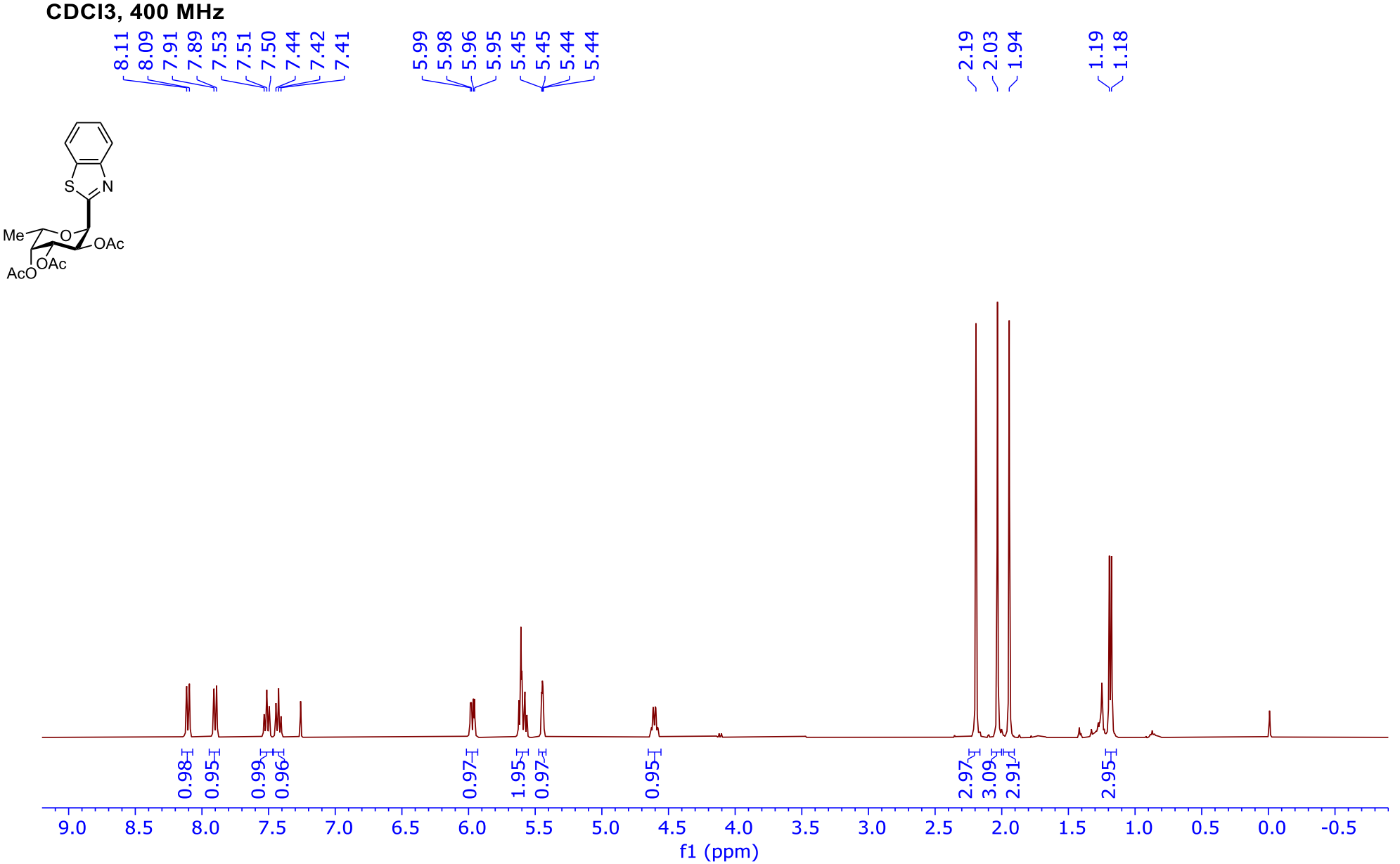
^{13}C NMR Spectrum of 17b



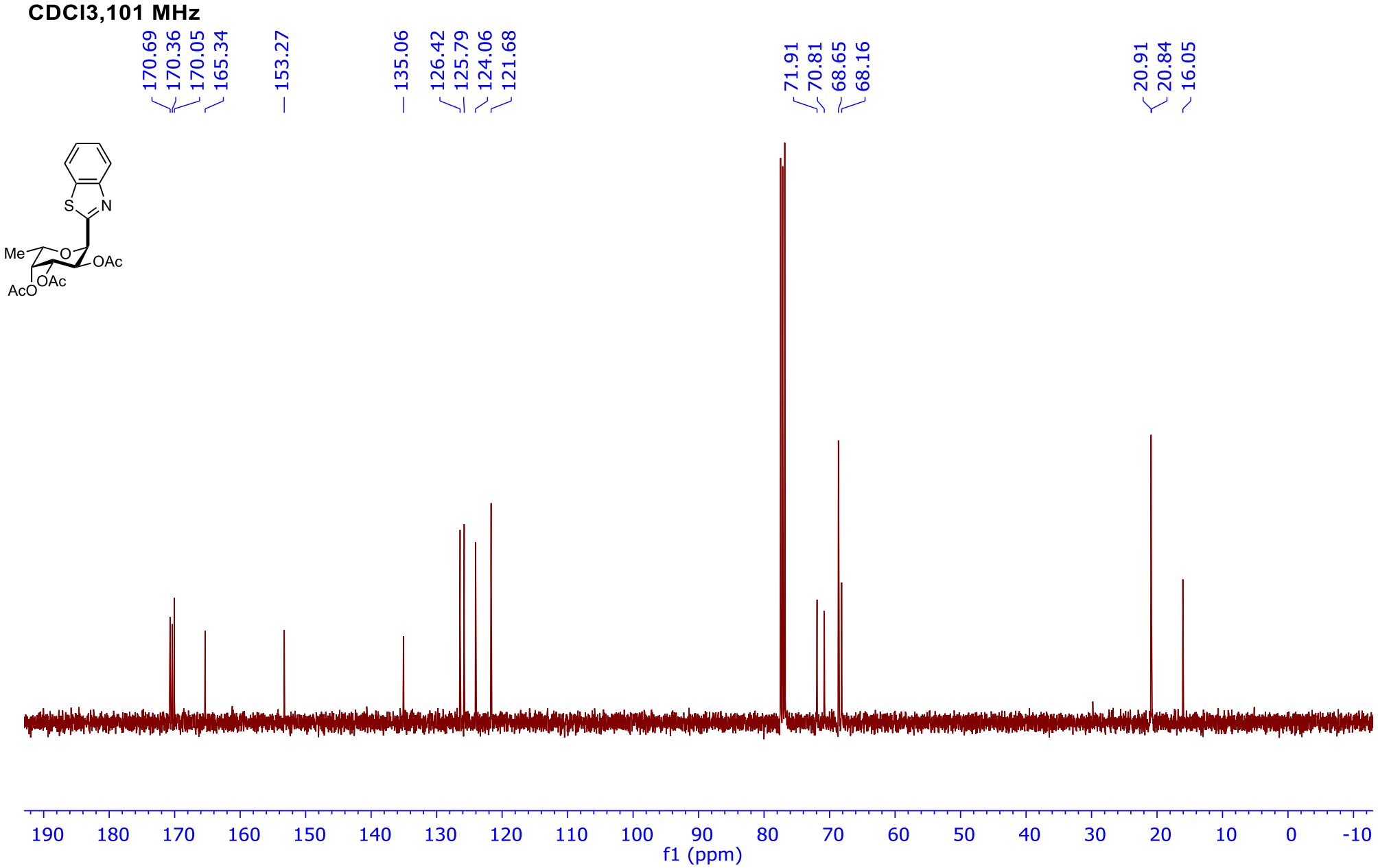
^{1}H NMR Spectrum of 17c



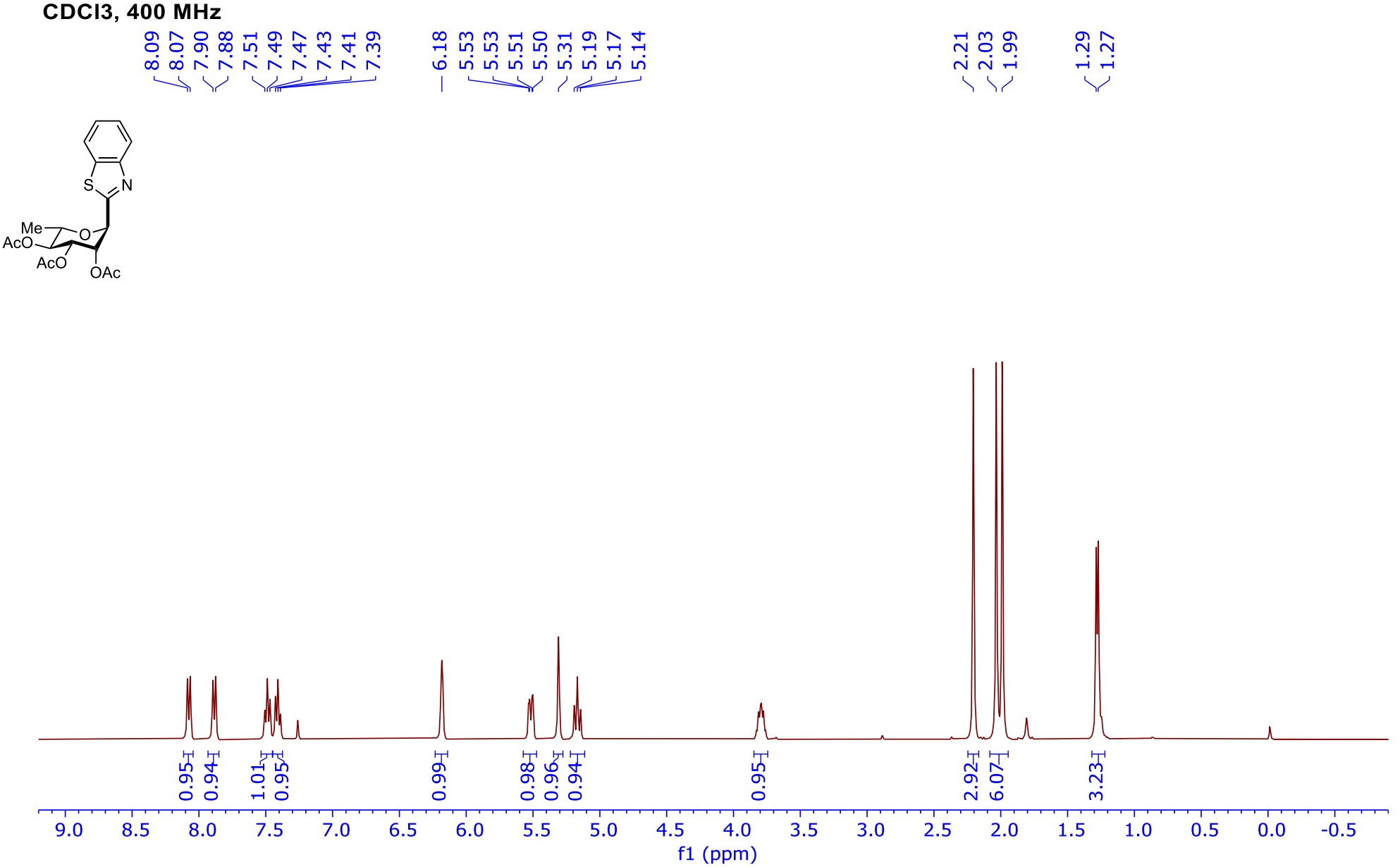
^{13}C NMR Spectrum of 17c



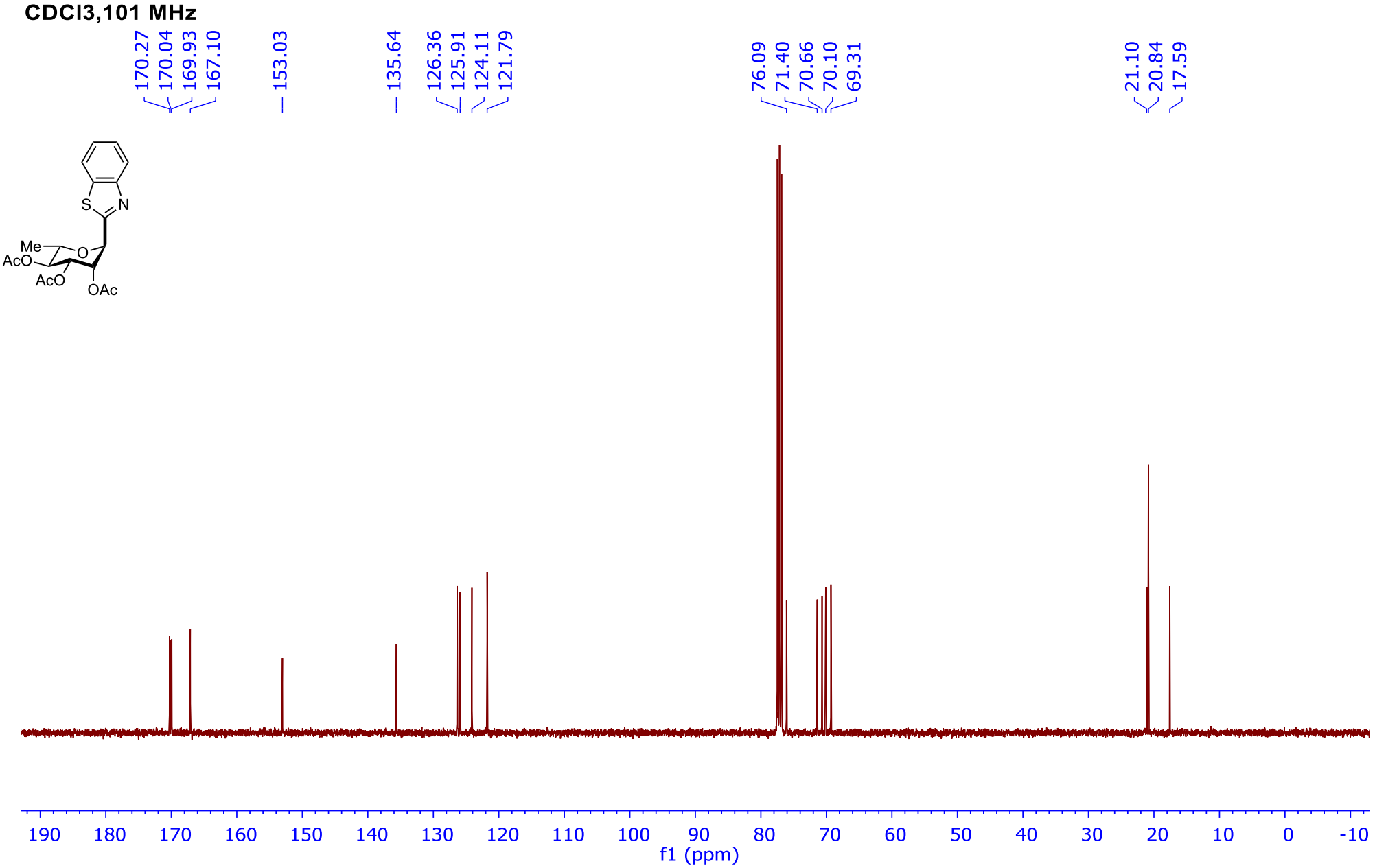
^{1}H NMR Spectrum of 17d



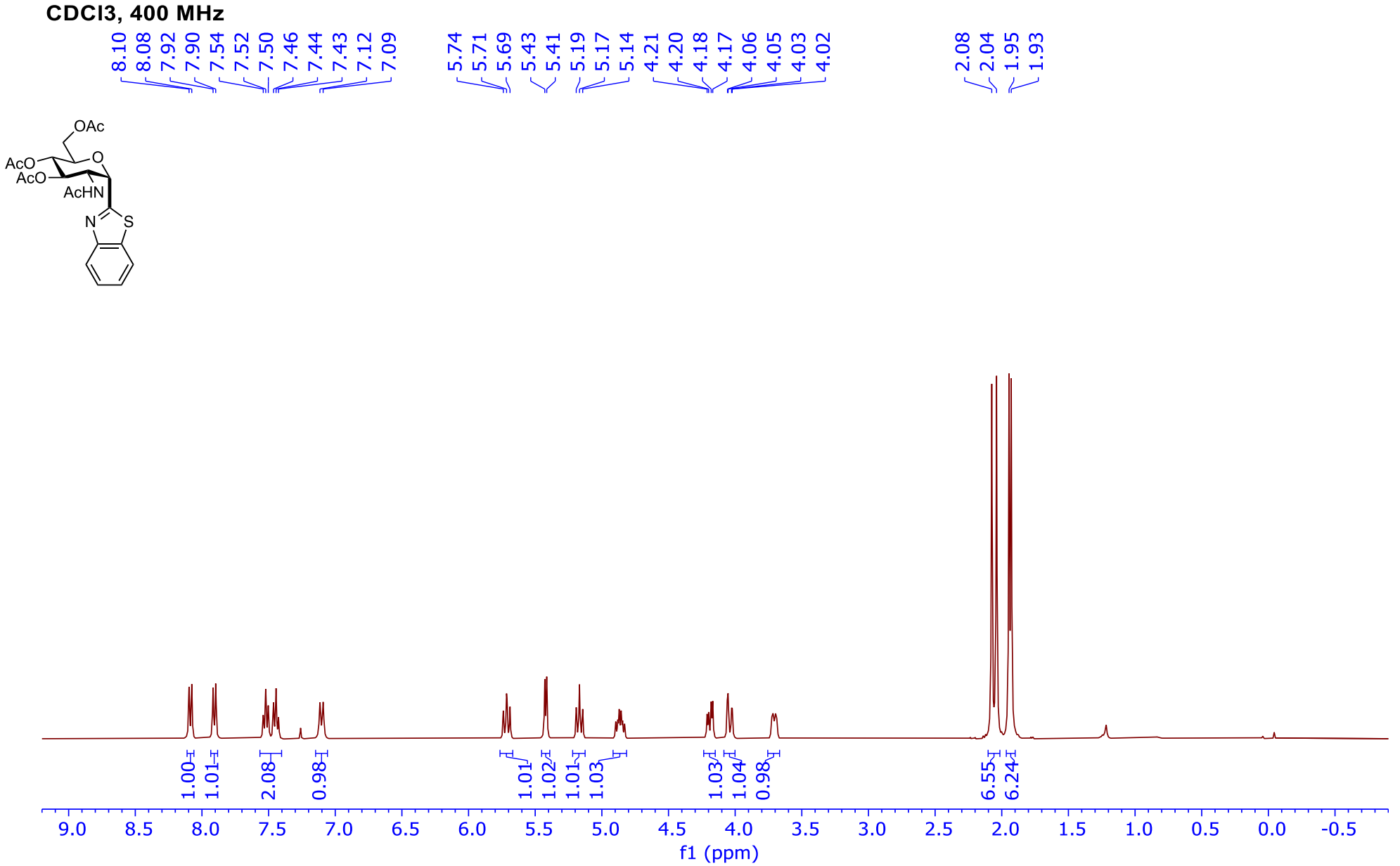
^{13}C NMR Spectrum of 17d



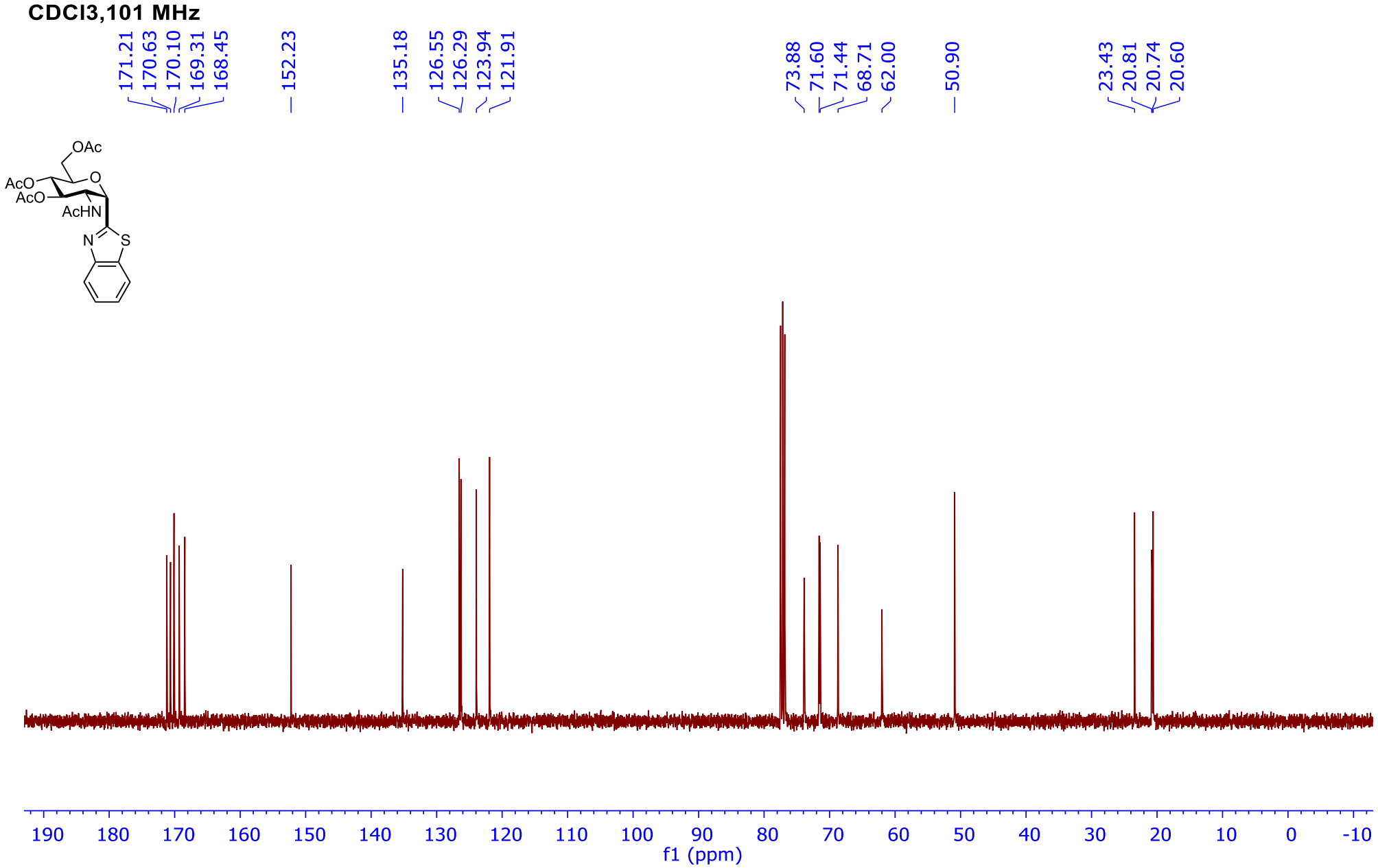
^{1}H NMR Spectrum of 17e



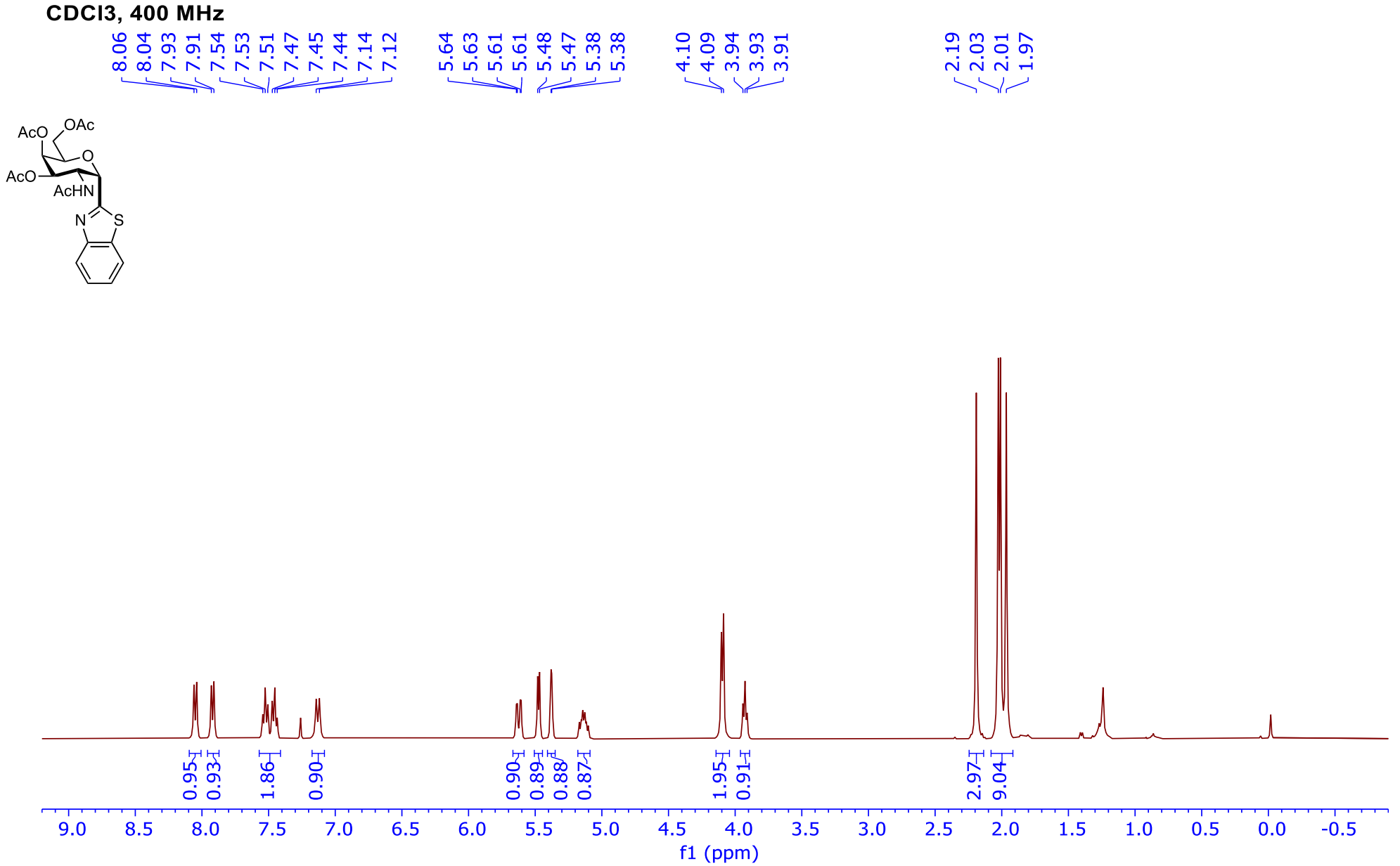
^{13}C NMR Spectrum of 17e



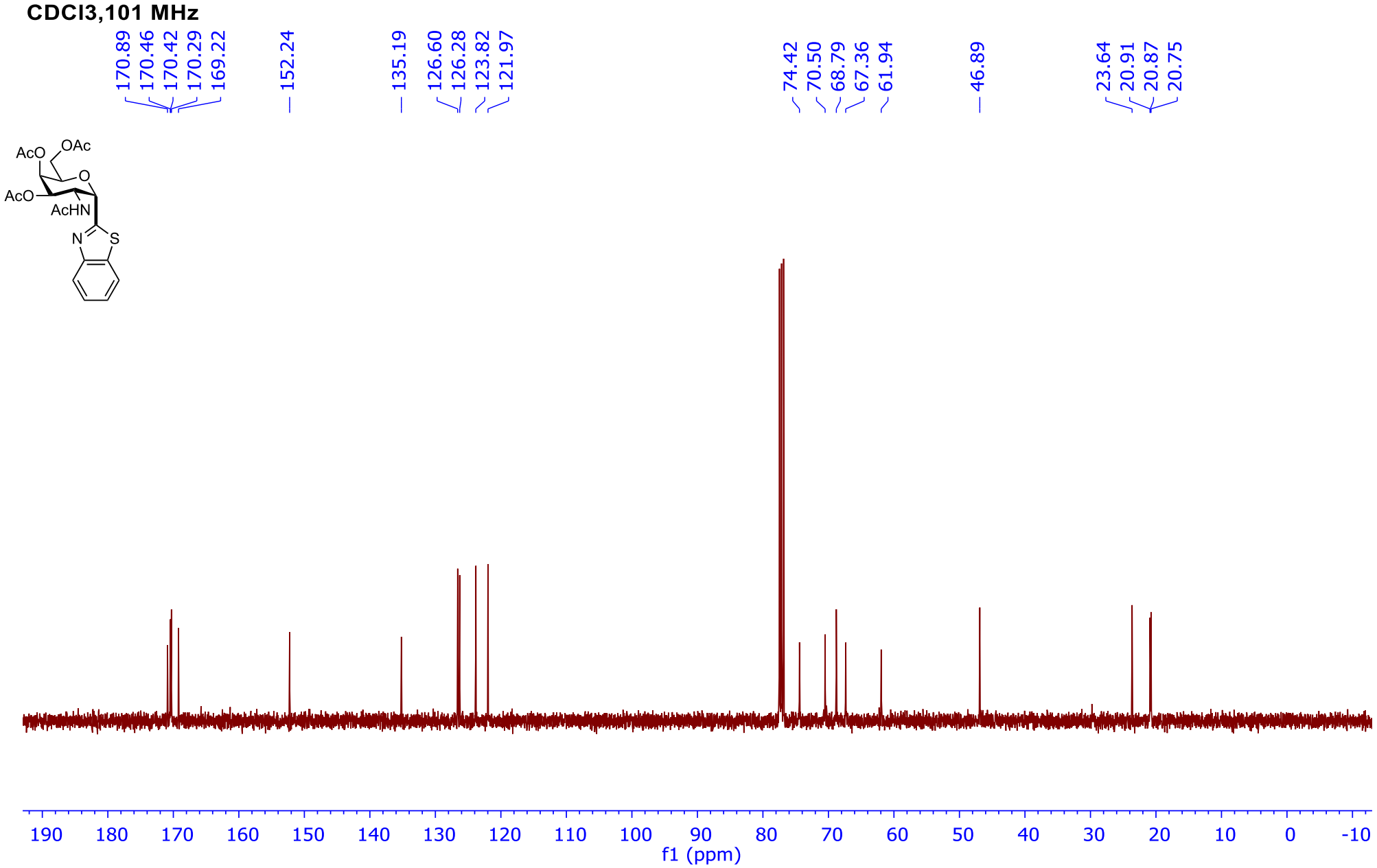
^{1}H NMR Spectrum of 17f



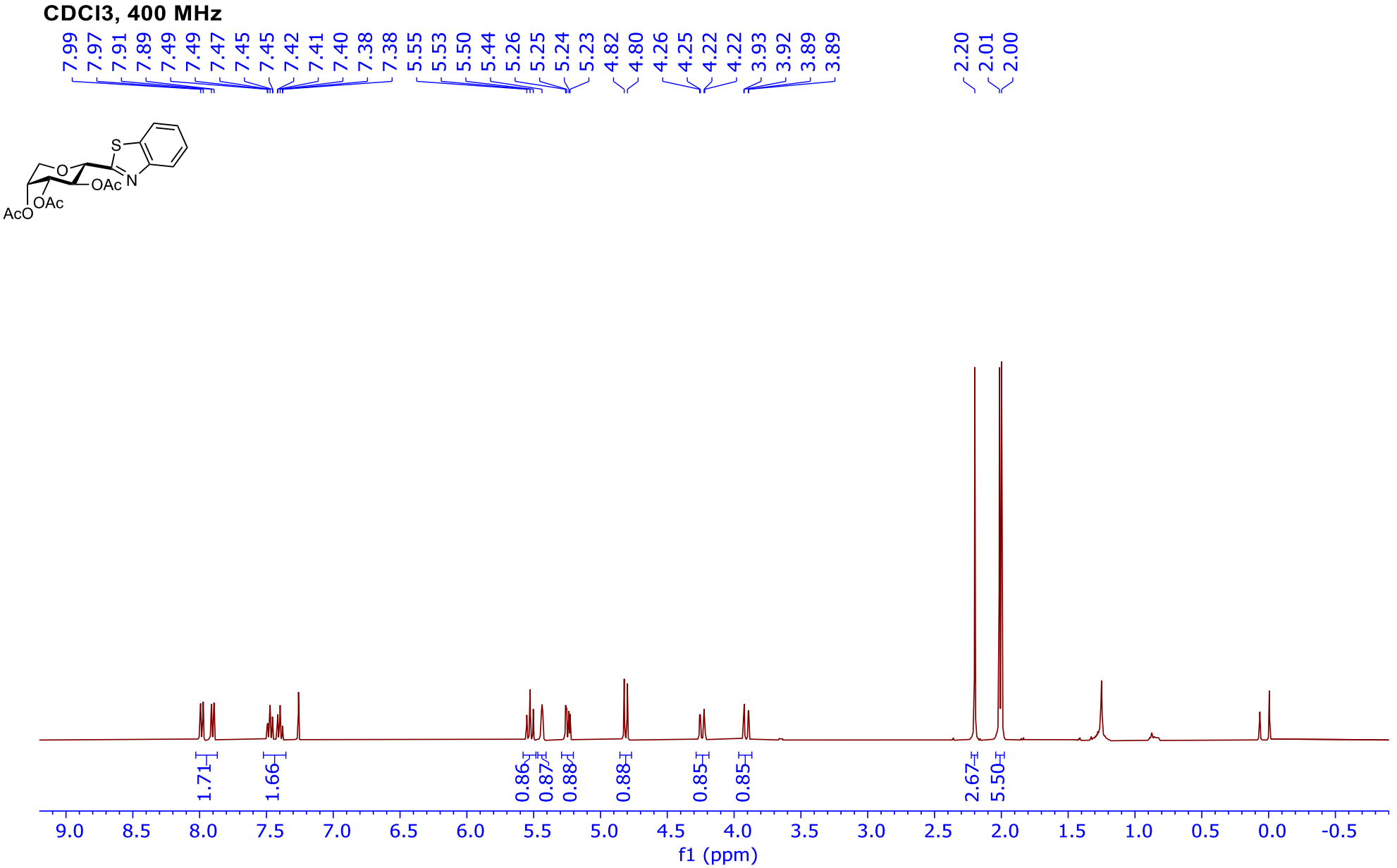
^{13}C NMR Spectrum of 17f



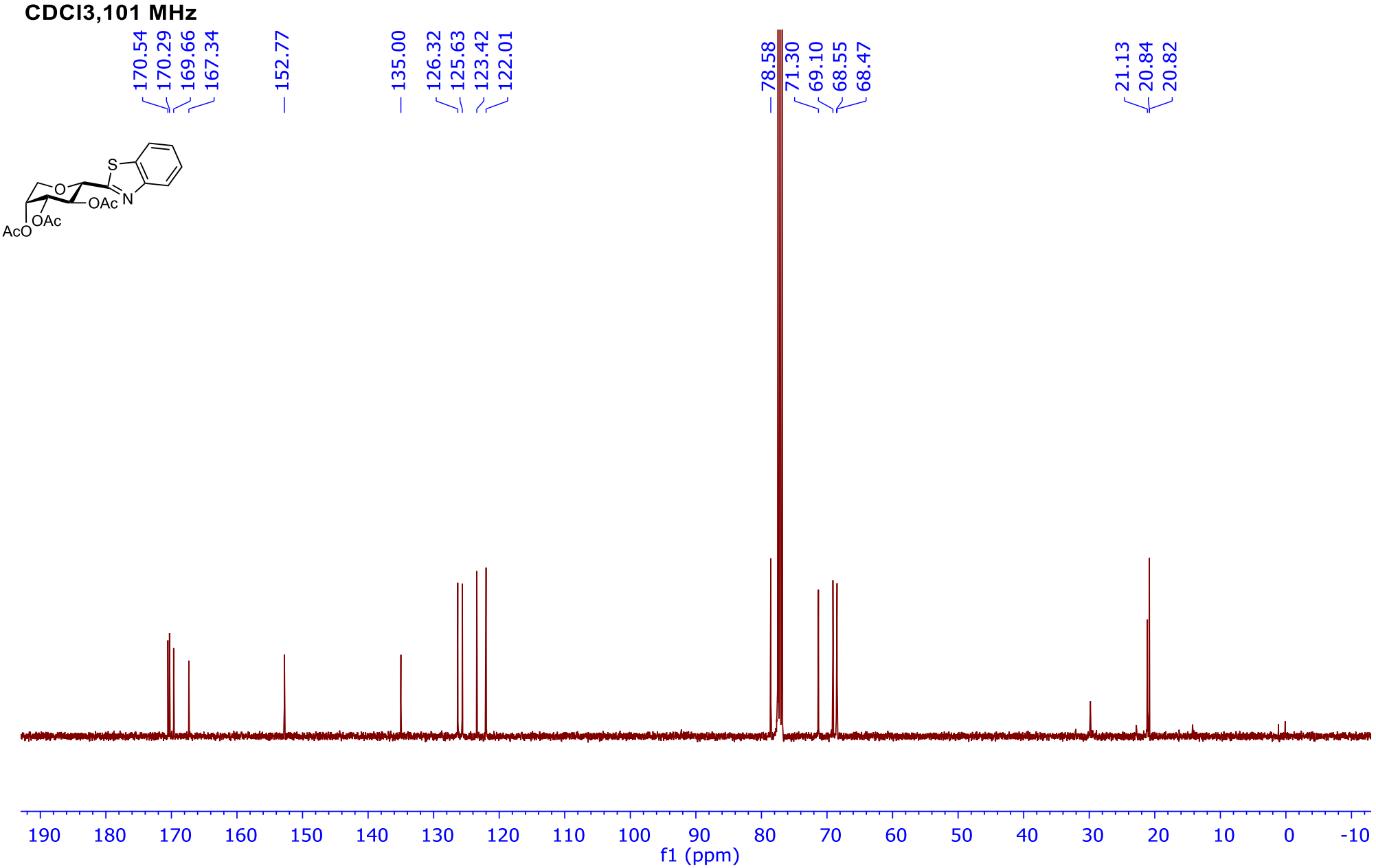
^{1}H NMR Spectrum of 17g



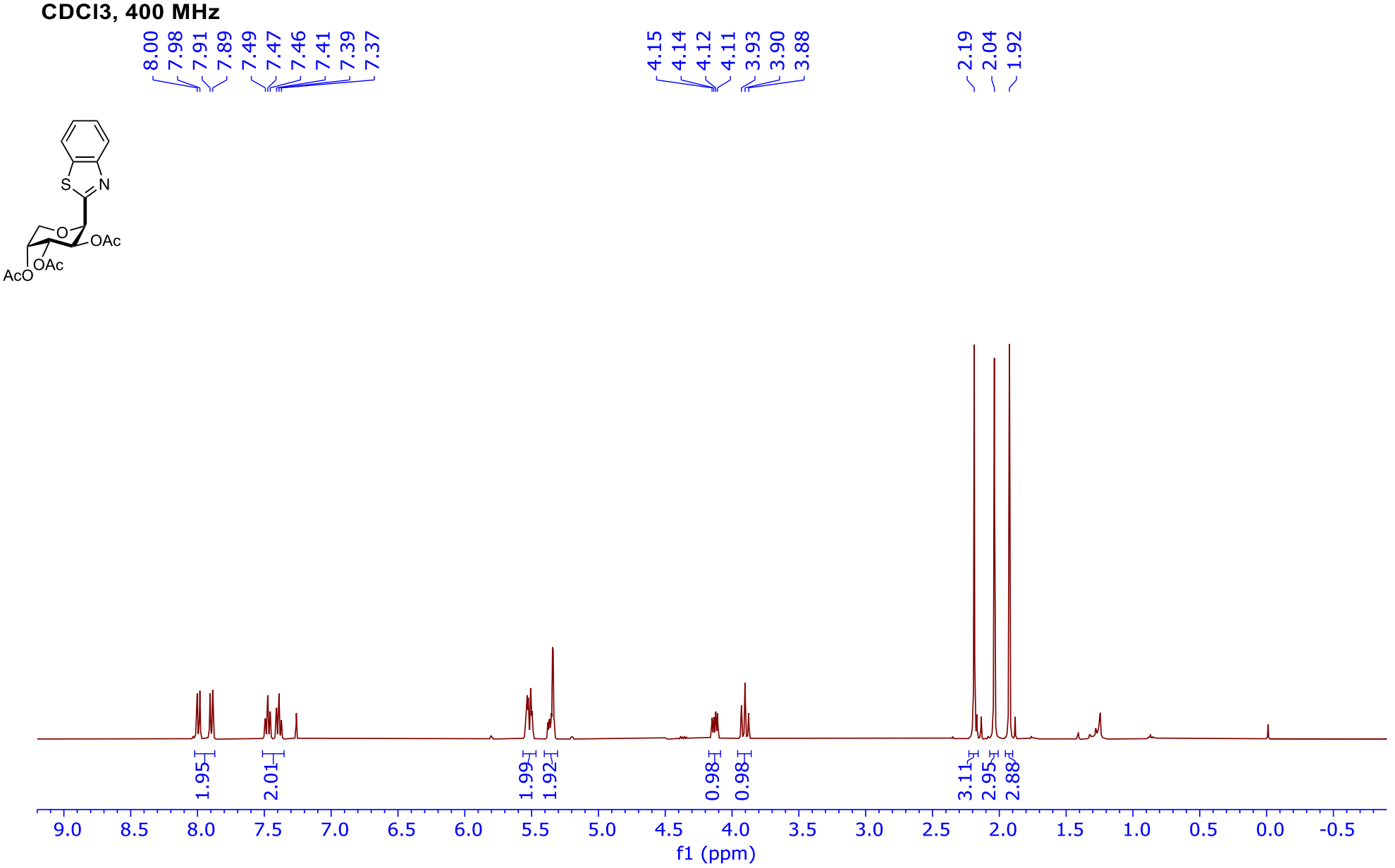
^{13}C NMR Spectrum of 17g



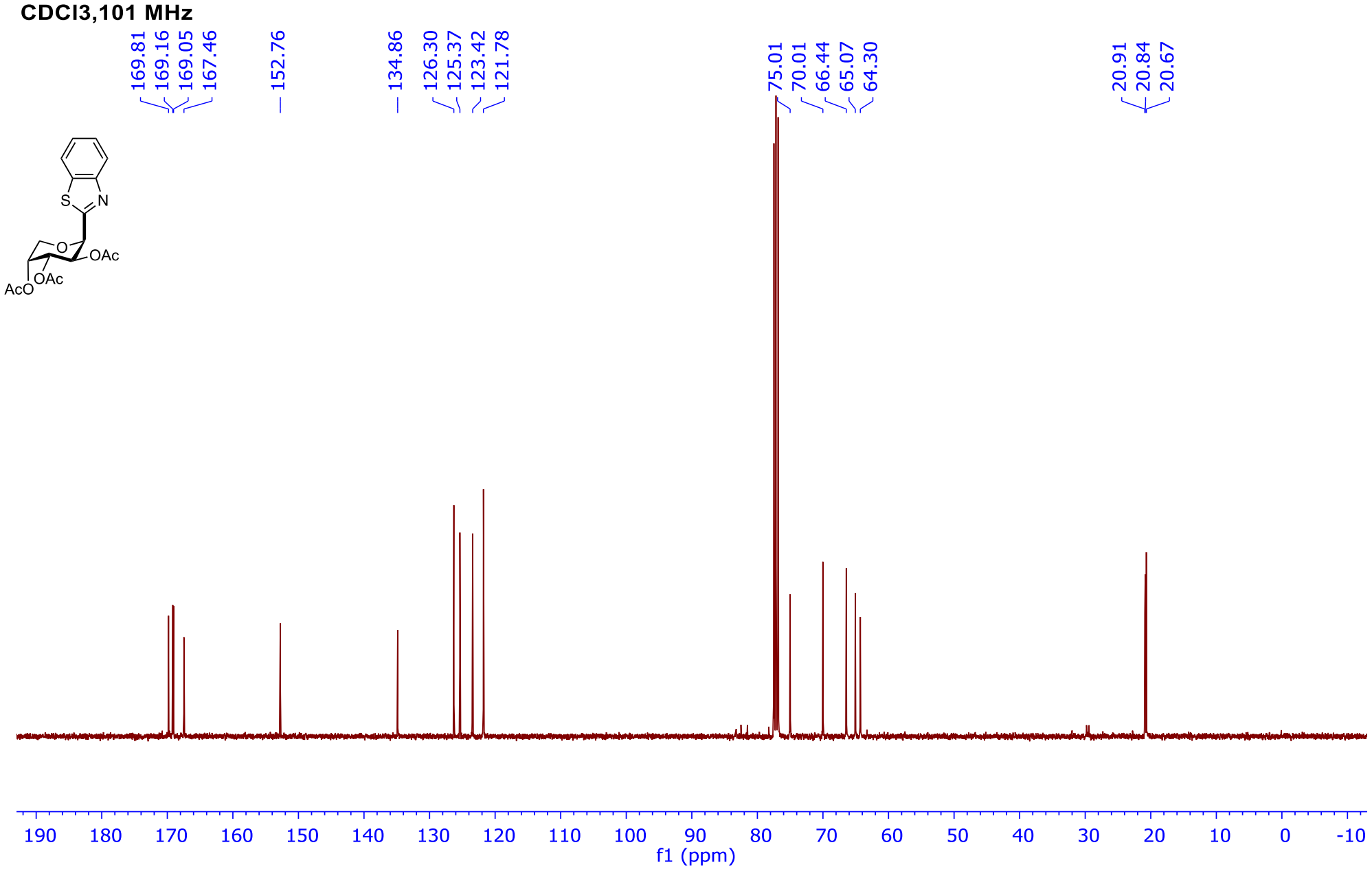
^{1}H NMR Spectrum of 17h



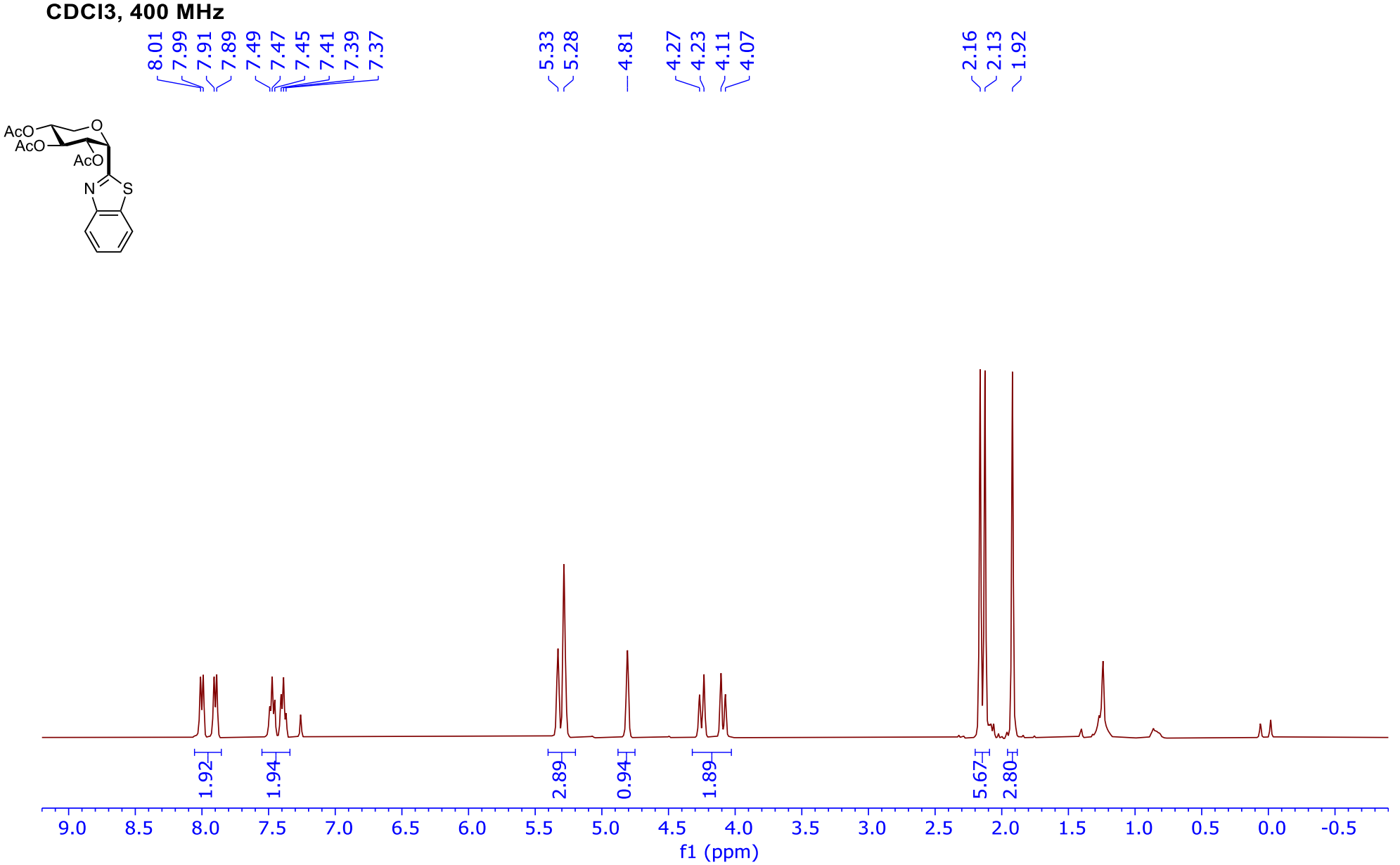
^{13}C NMR Spectrum of 17h



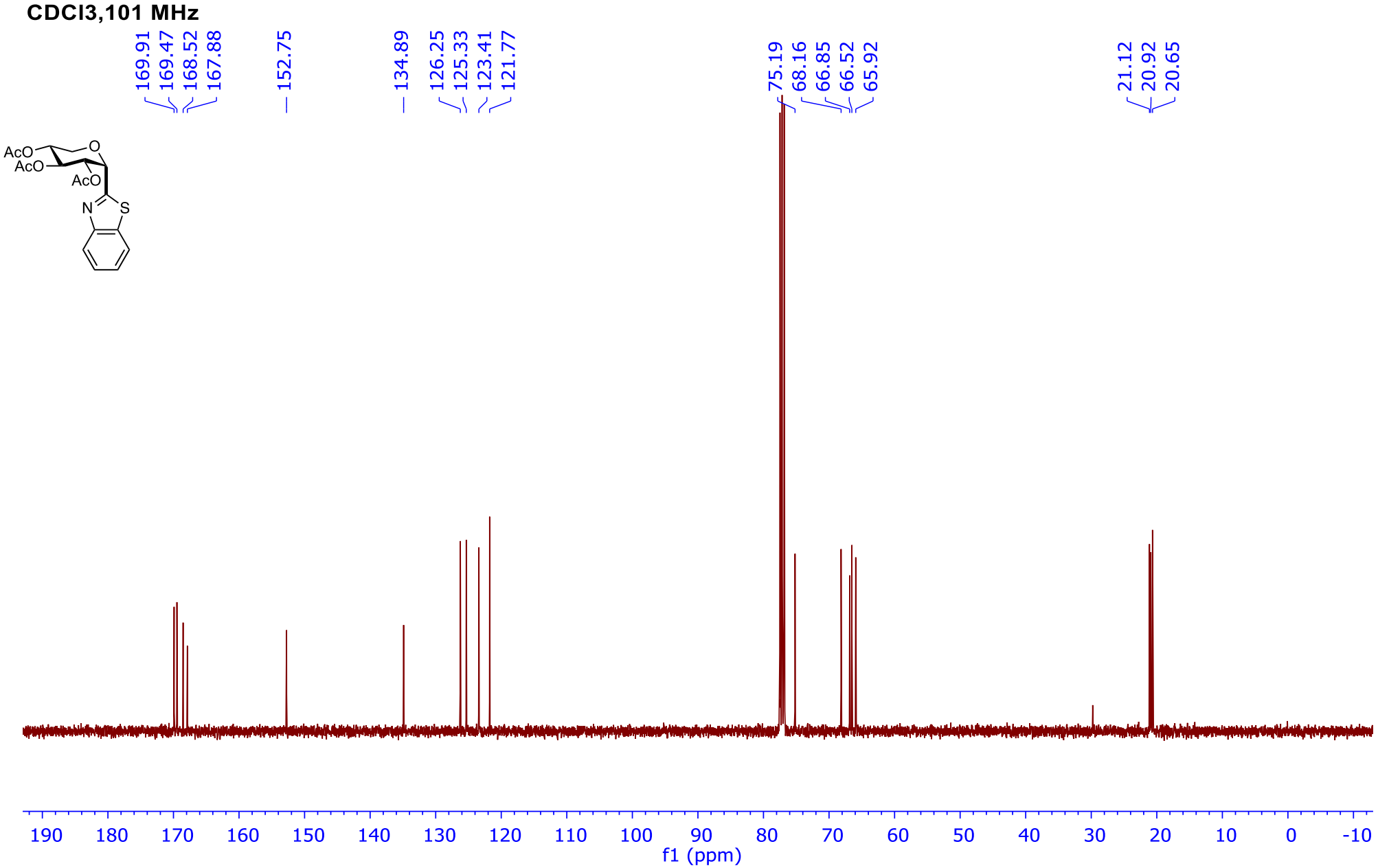
^{1}H NMR Spectrum of 17h



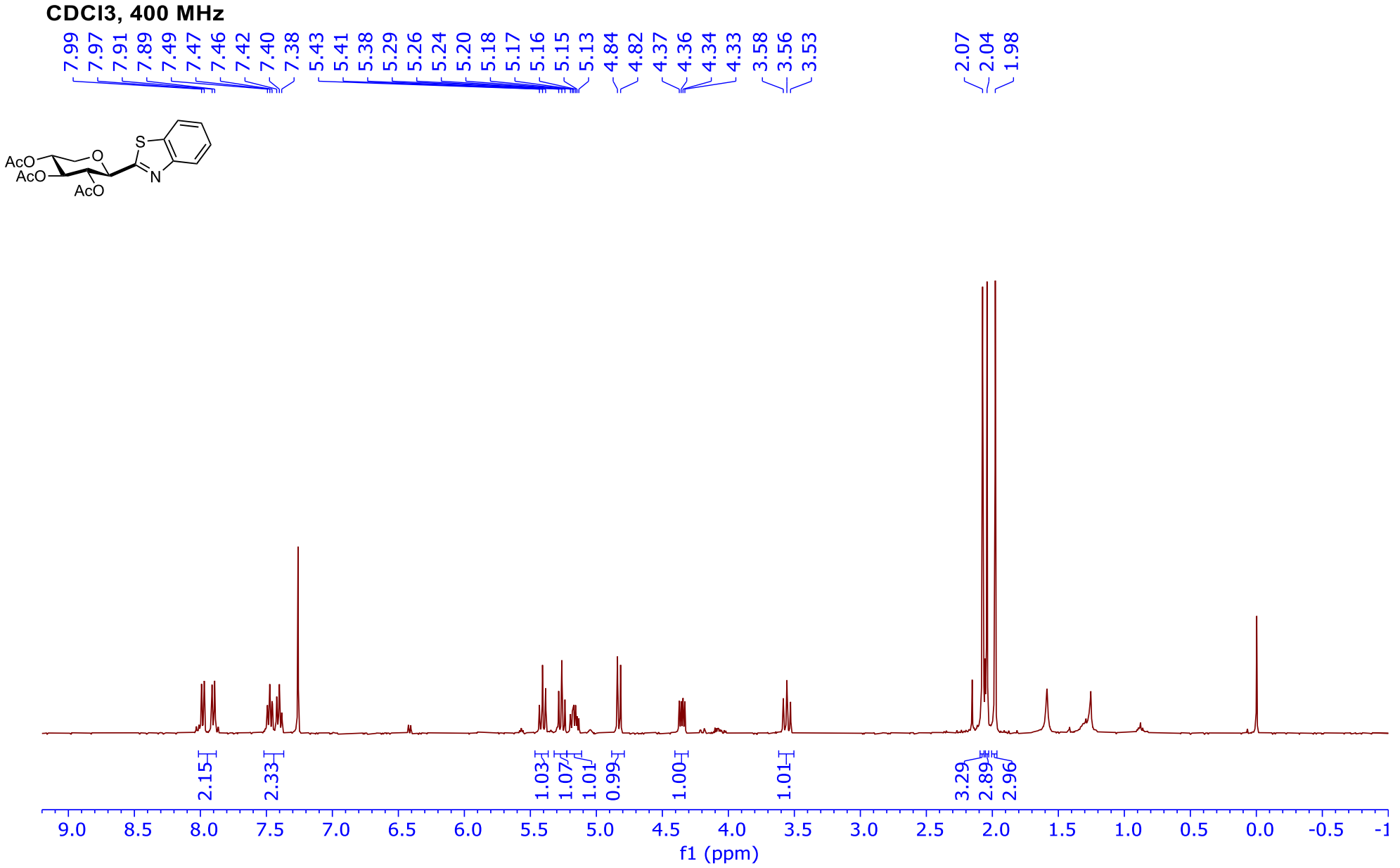
^{13}C NMR Spectrum of 17h



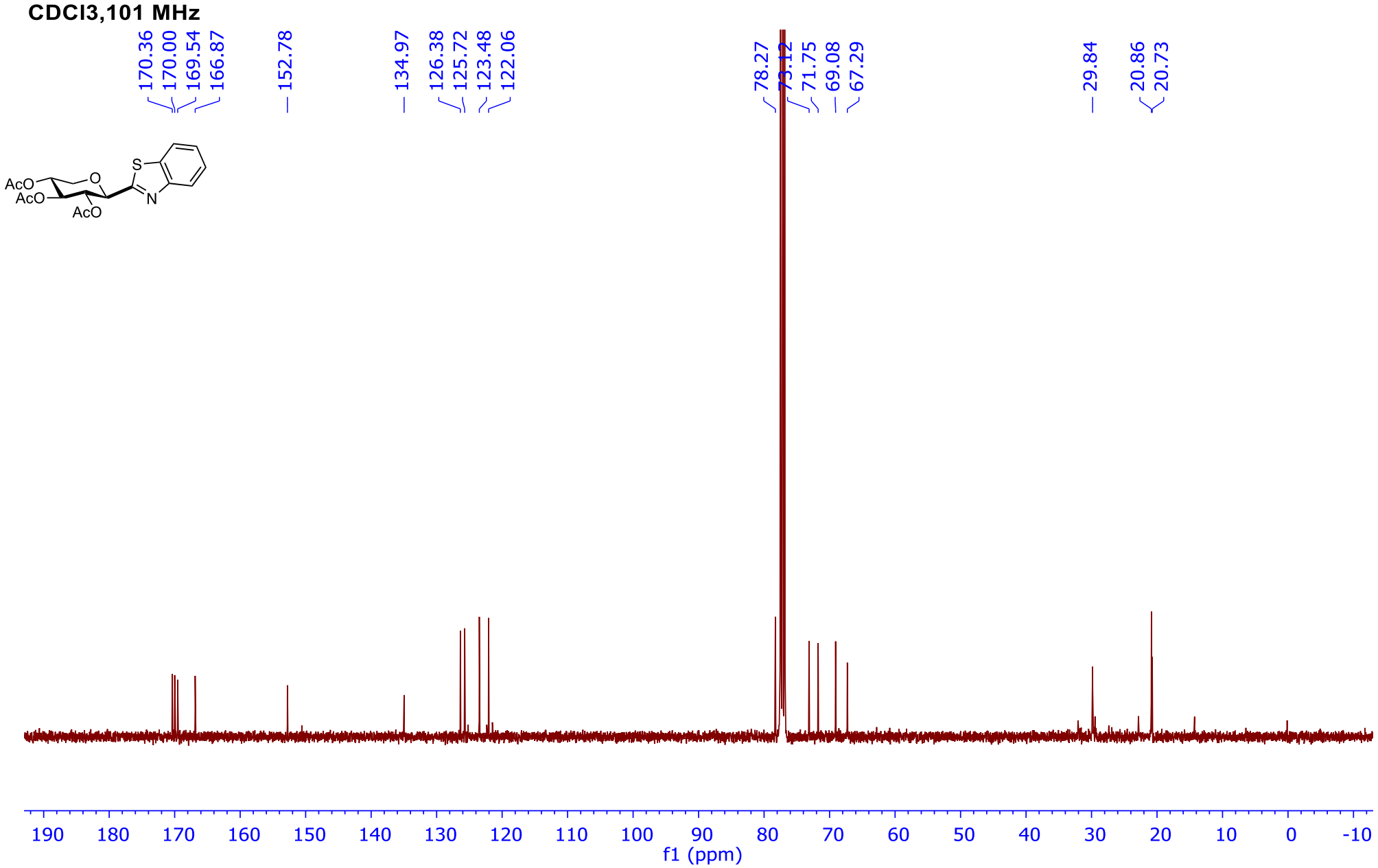
^{1}H NMR Spectrum of 17i



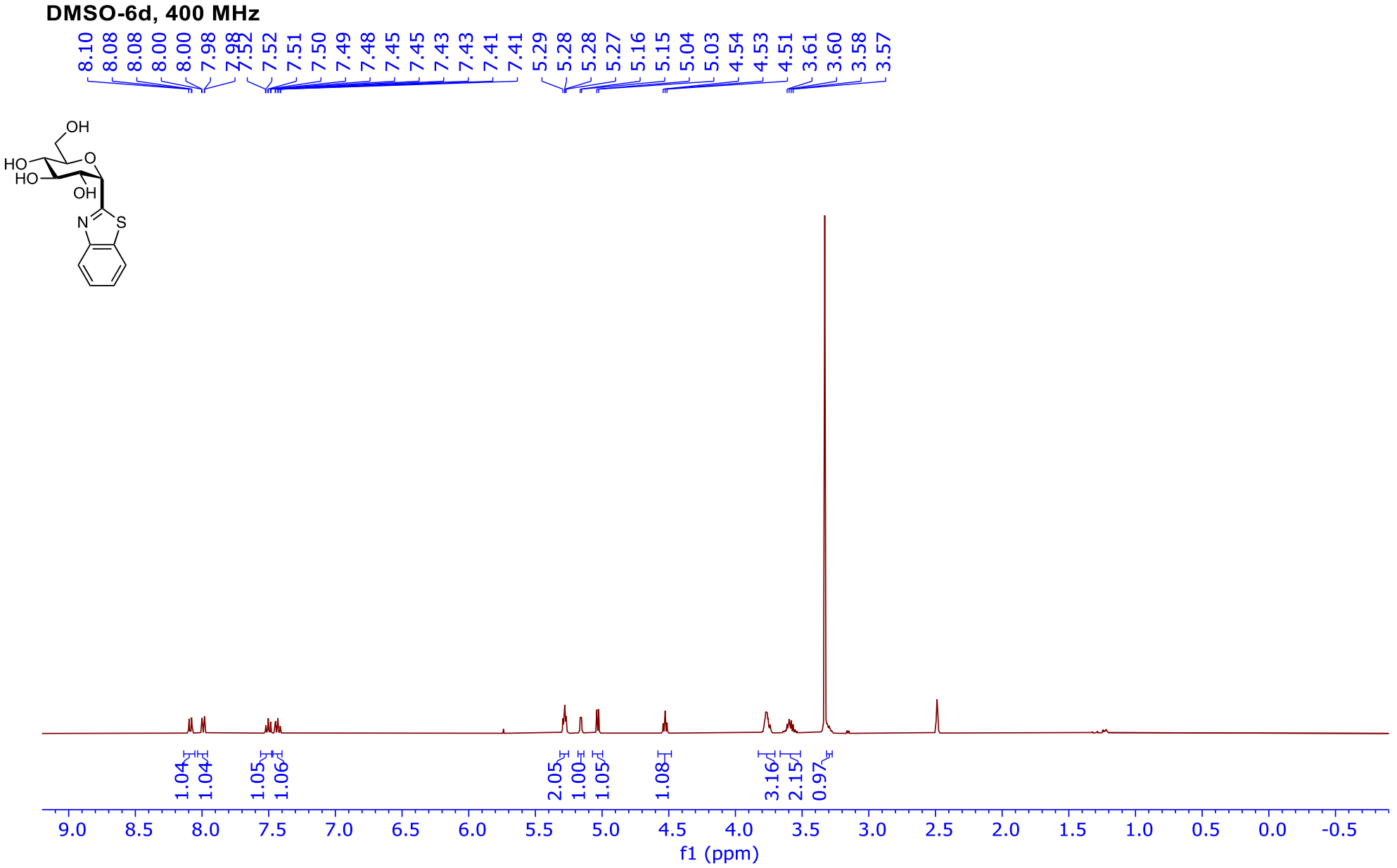
^{13}C NMR Spectrum of 17i



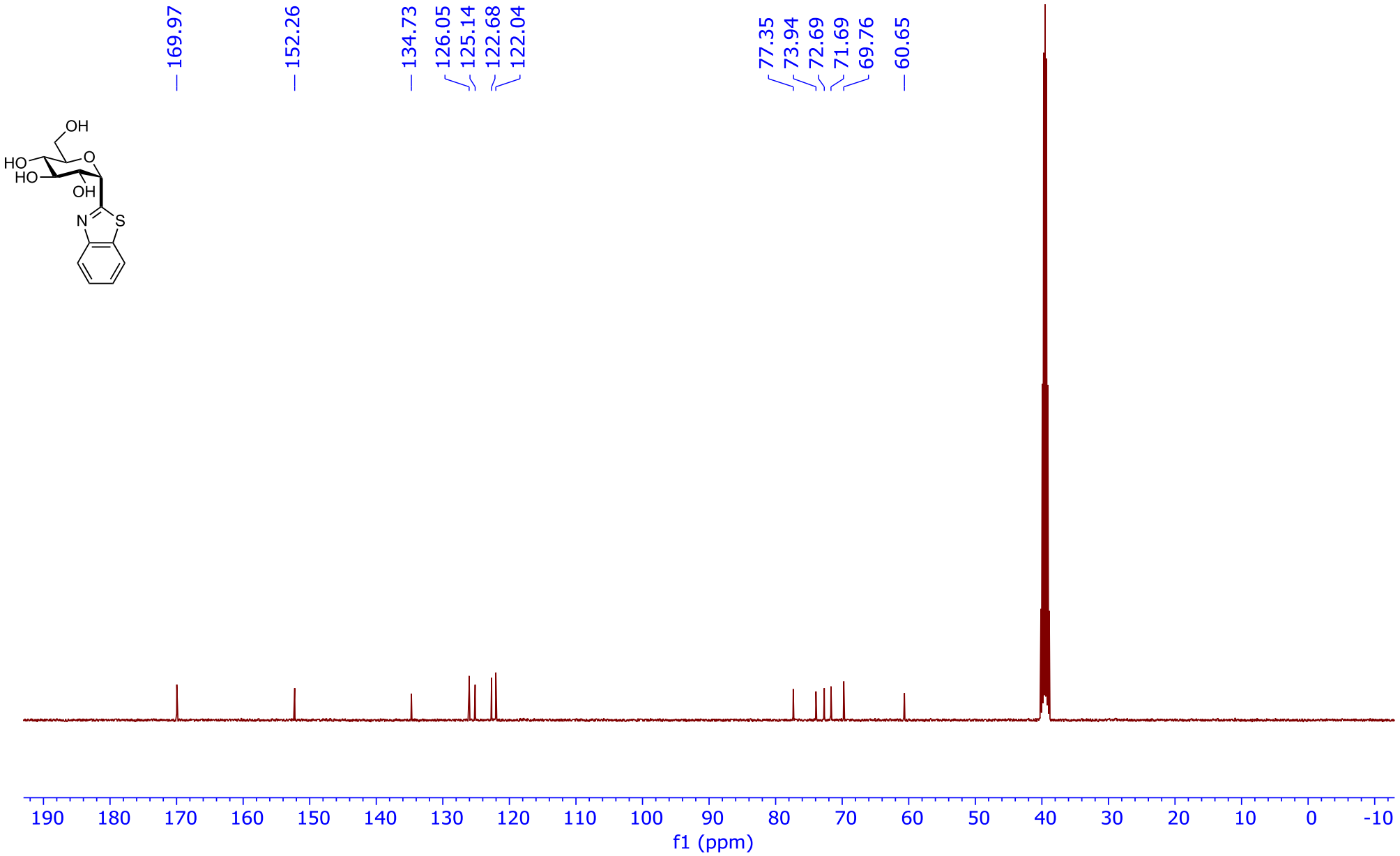
^{1}H NMR Spectrum of 17i



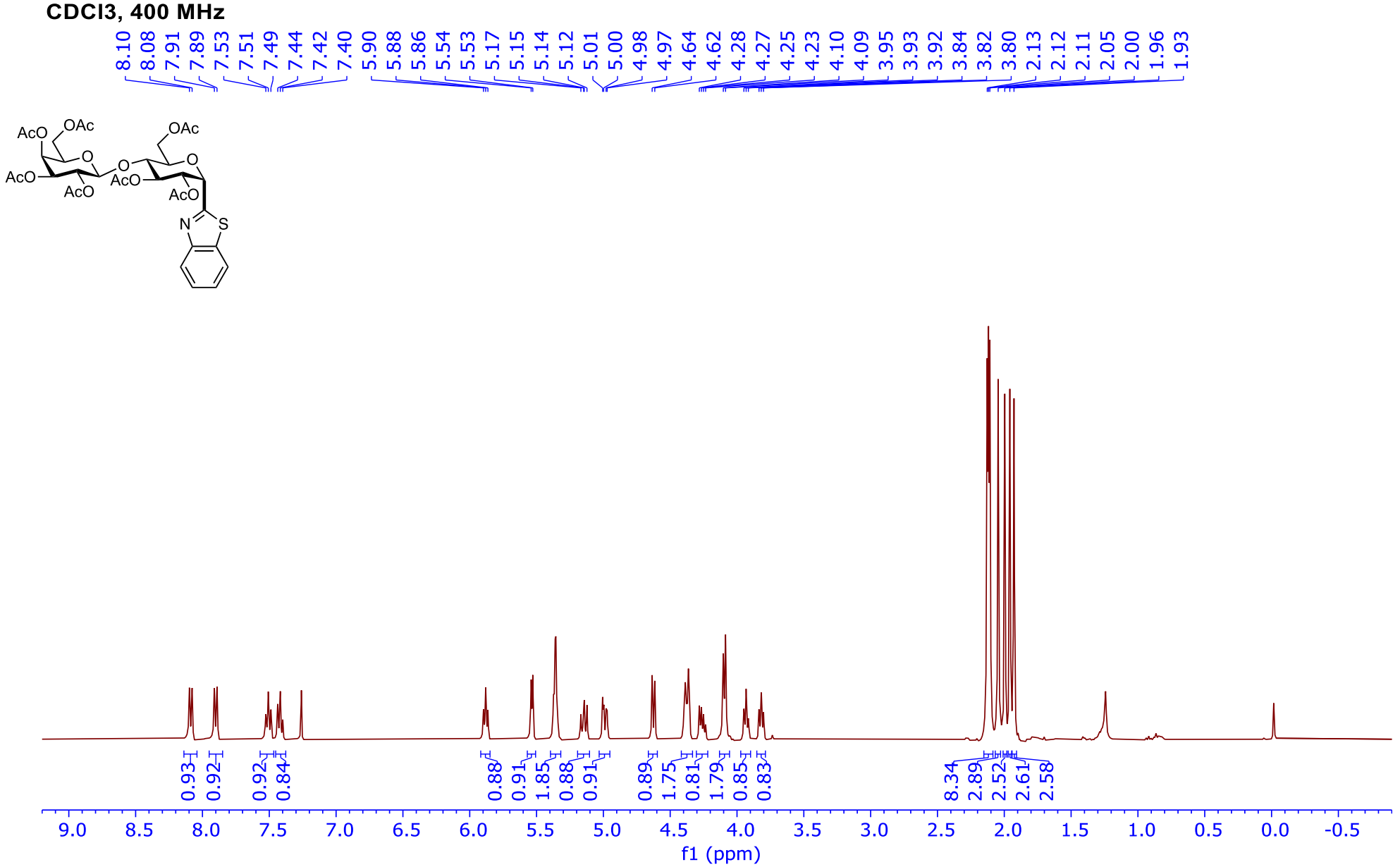
^{13}C NMR Spectrum of 17i



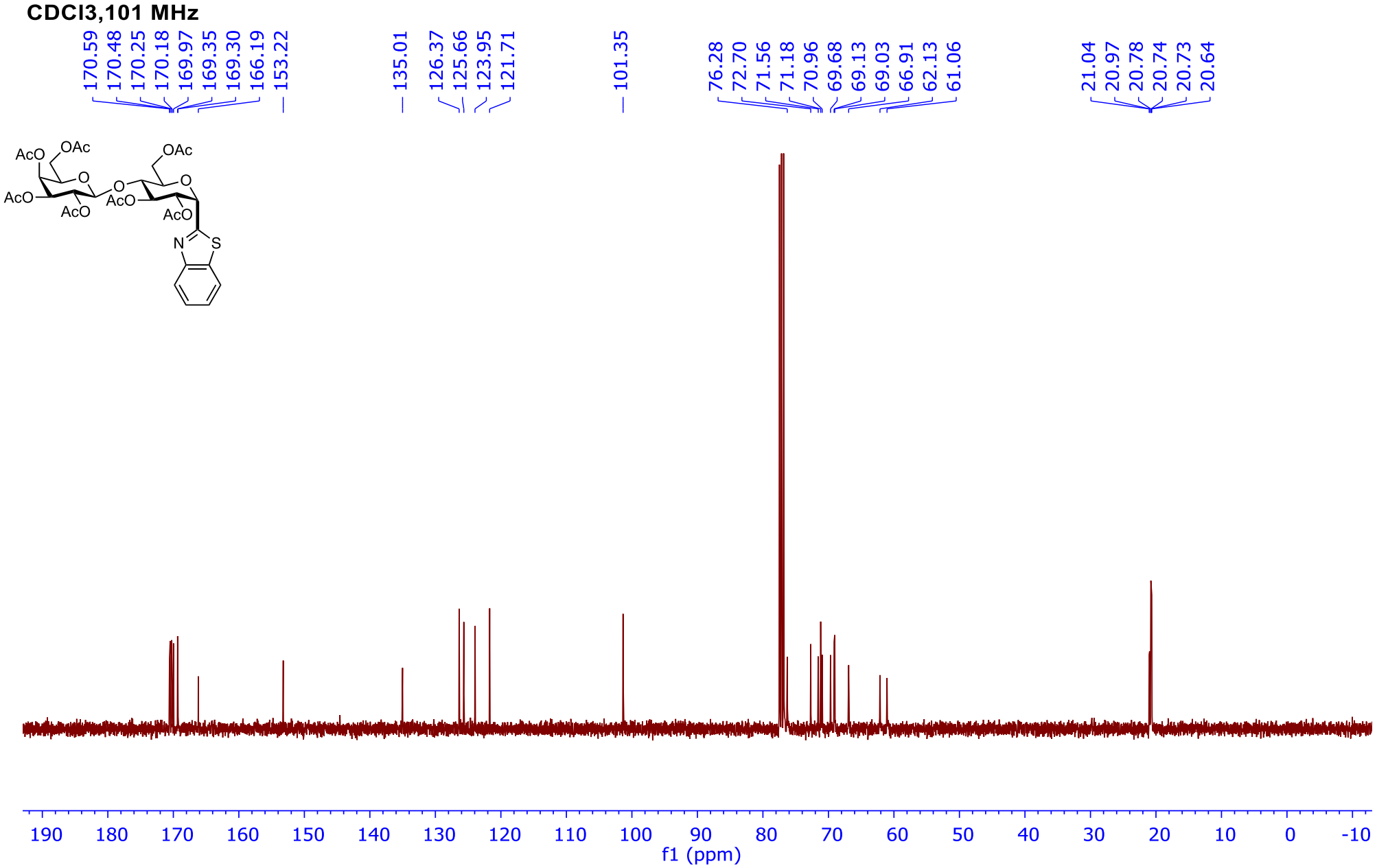
^{1}H NMR Spectrum of 17k



^{13}C NMR Spectrum of 17k

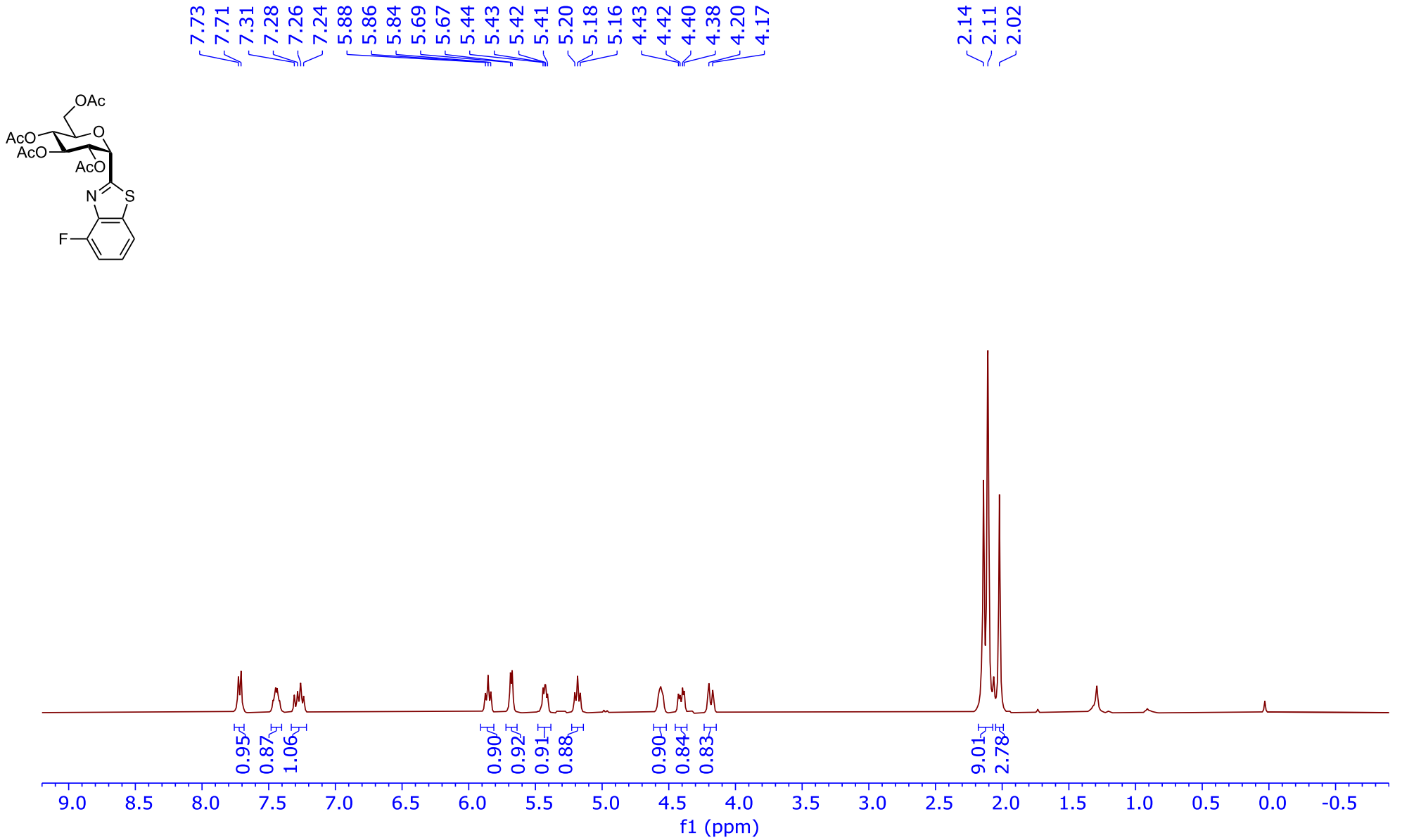


^{1}H NMR Spectrum of 17j

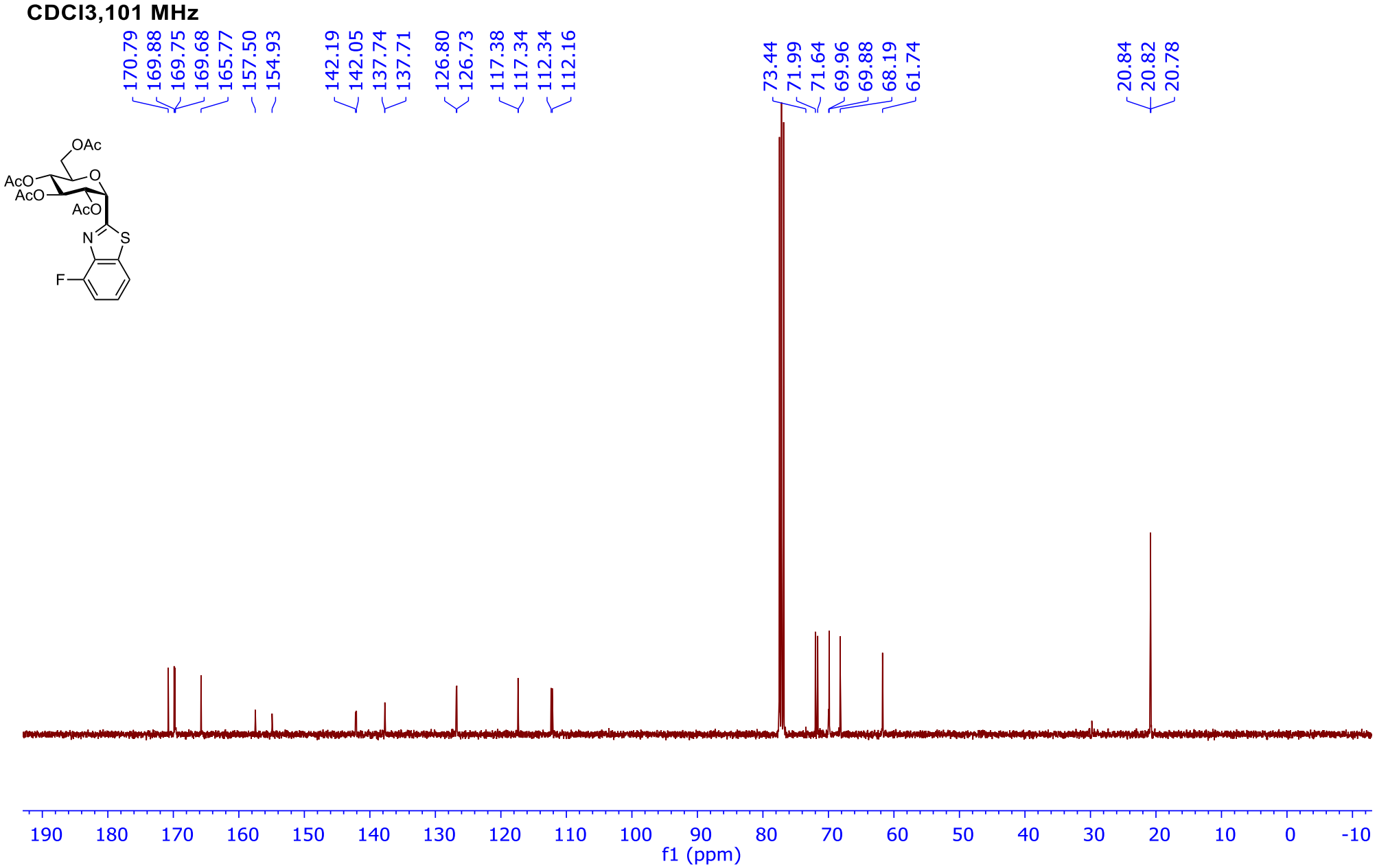


^{13}C NMR Spectrum of 17j

CDCl3, 400 MHz

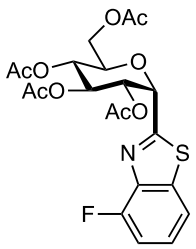


^{1}H NMR Spectrum of 18m



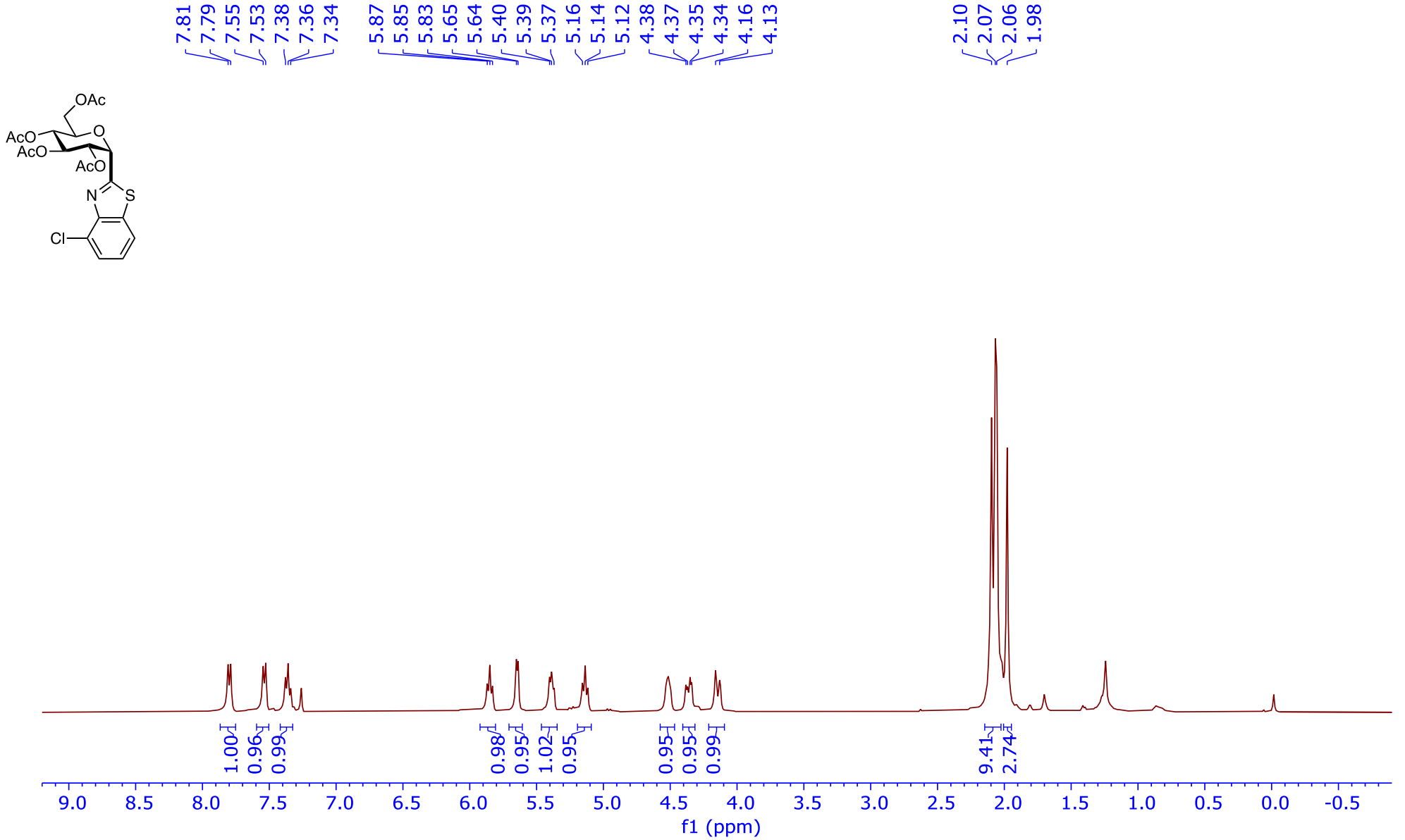
^{13}C NMR Spectrum of 18m

CDCl3,376 MHz

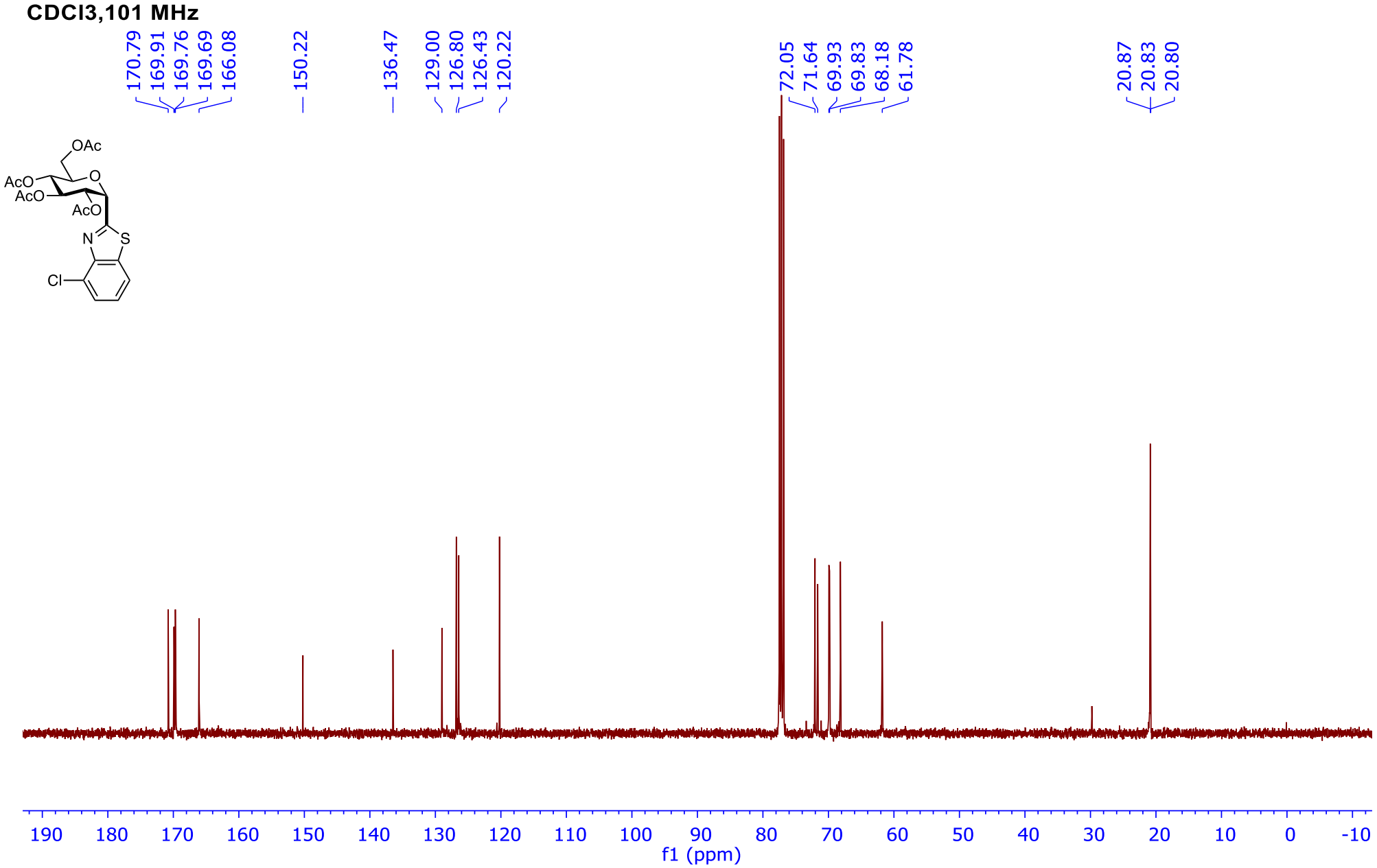


^{19}F NMR Spectrum of 18m

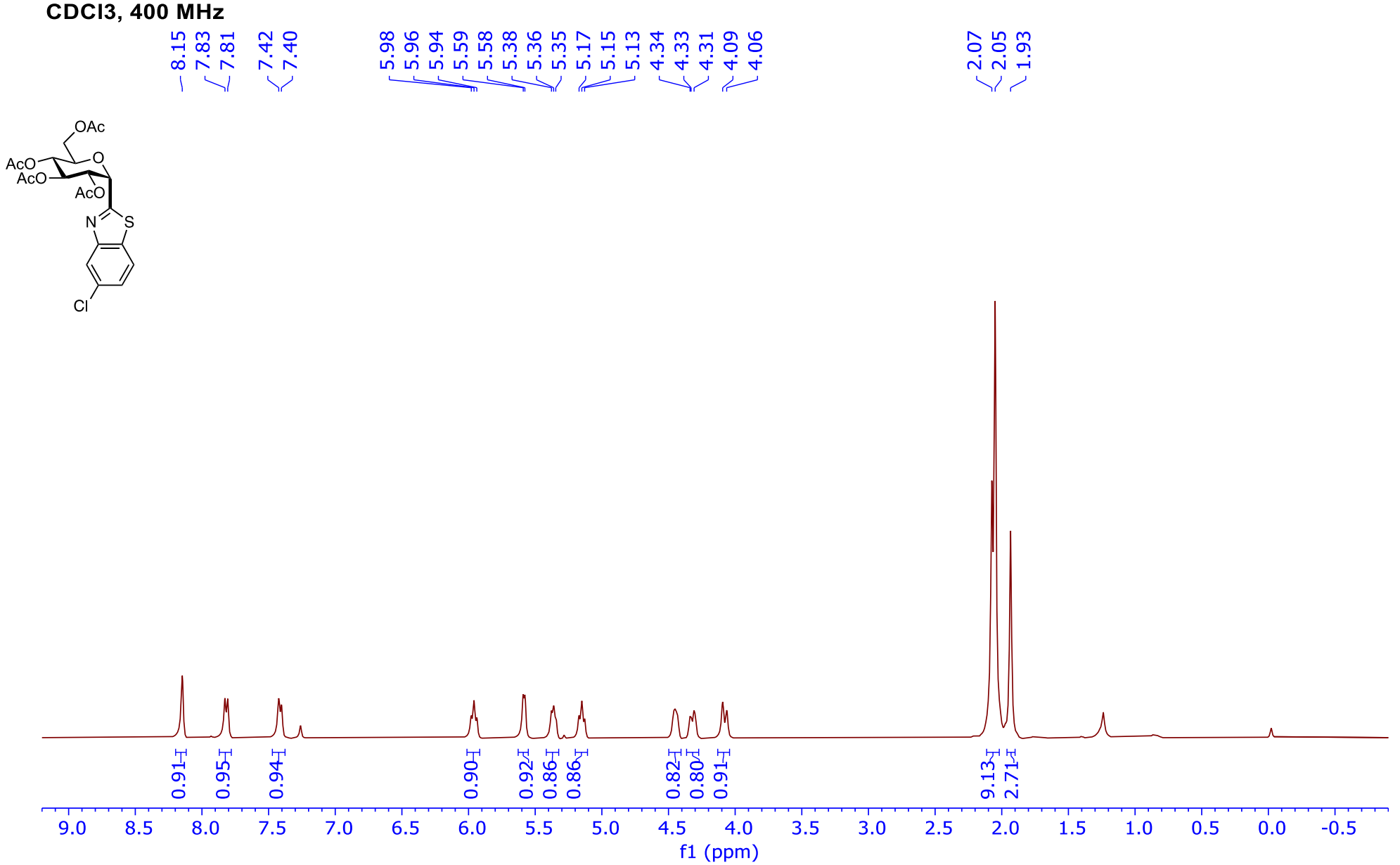
CDCl3, 400 MHz



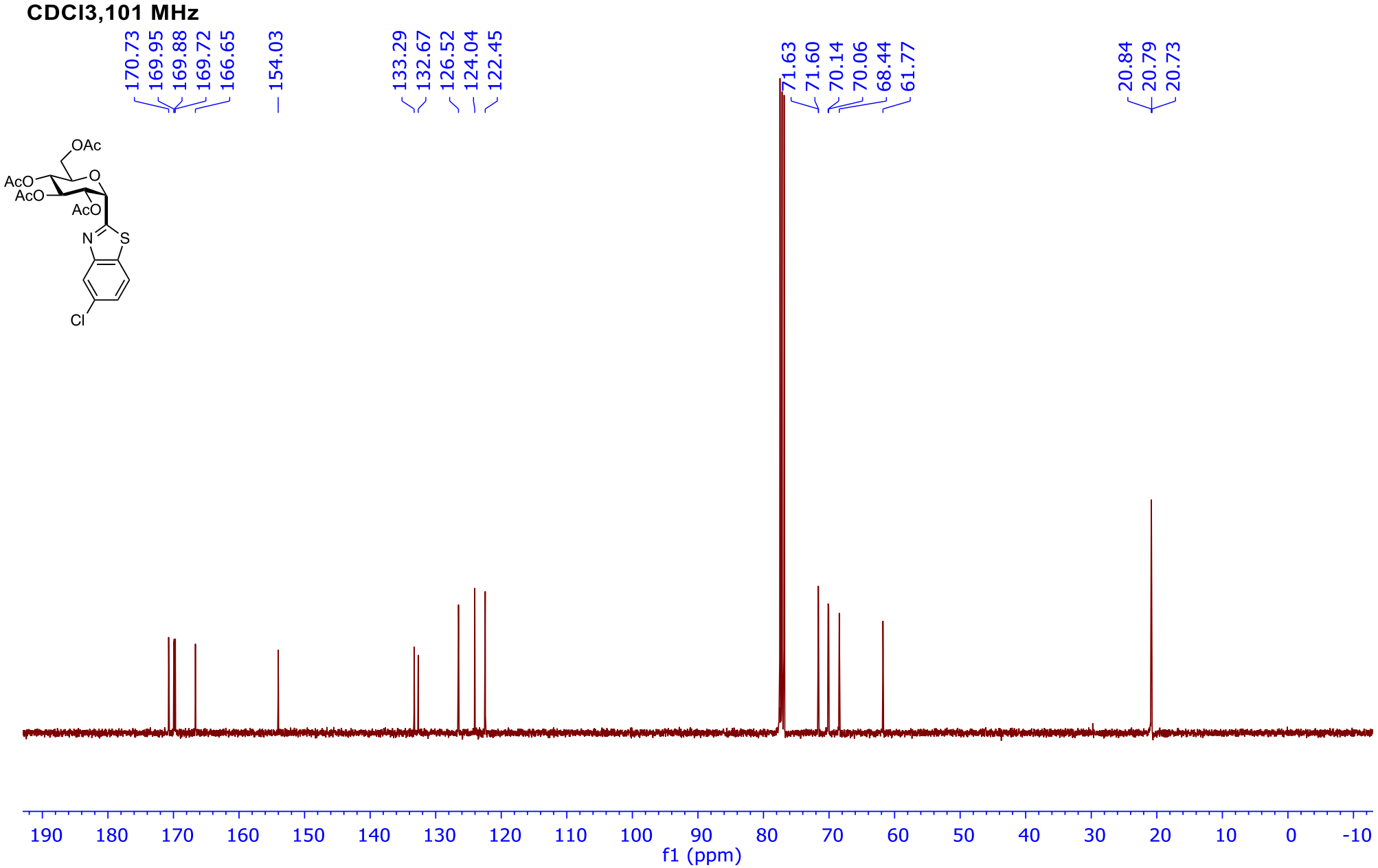
^{1}H NMR Spectrum of 18n



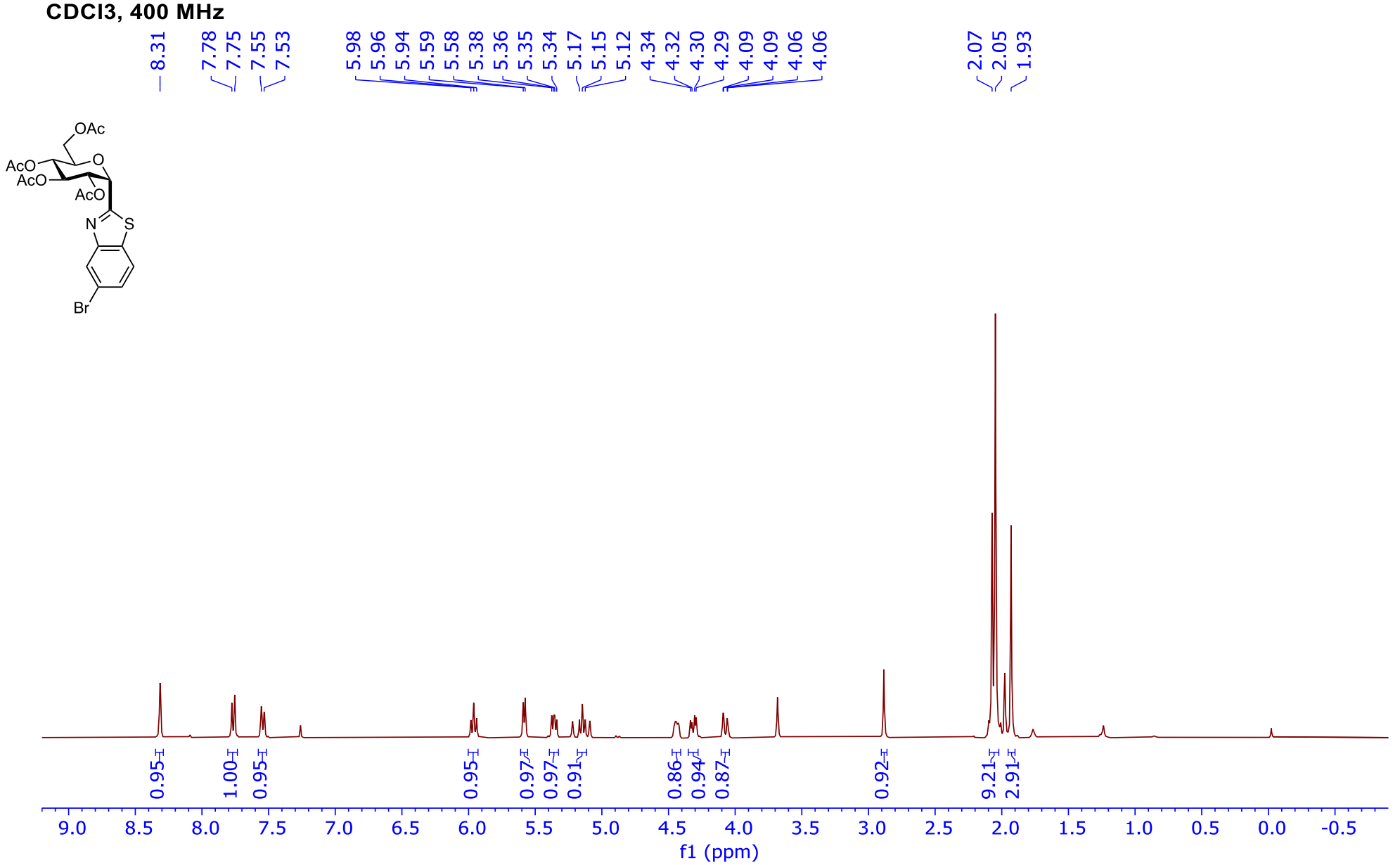
^{13}C NMR Spectrum of 18n



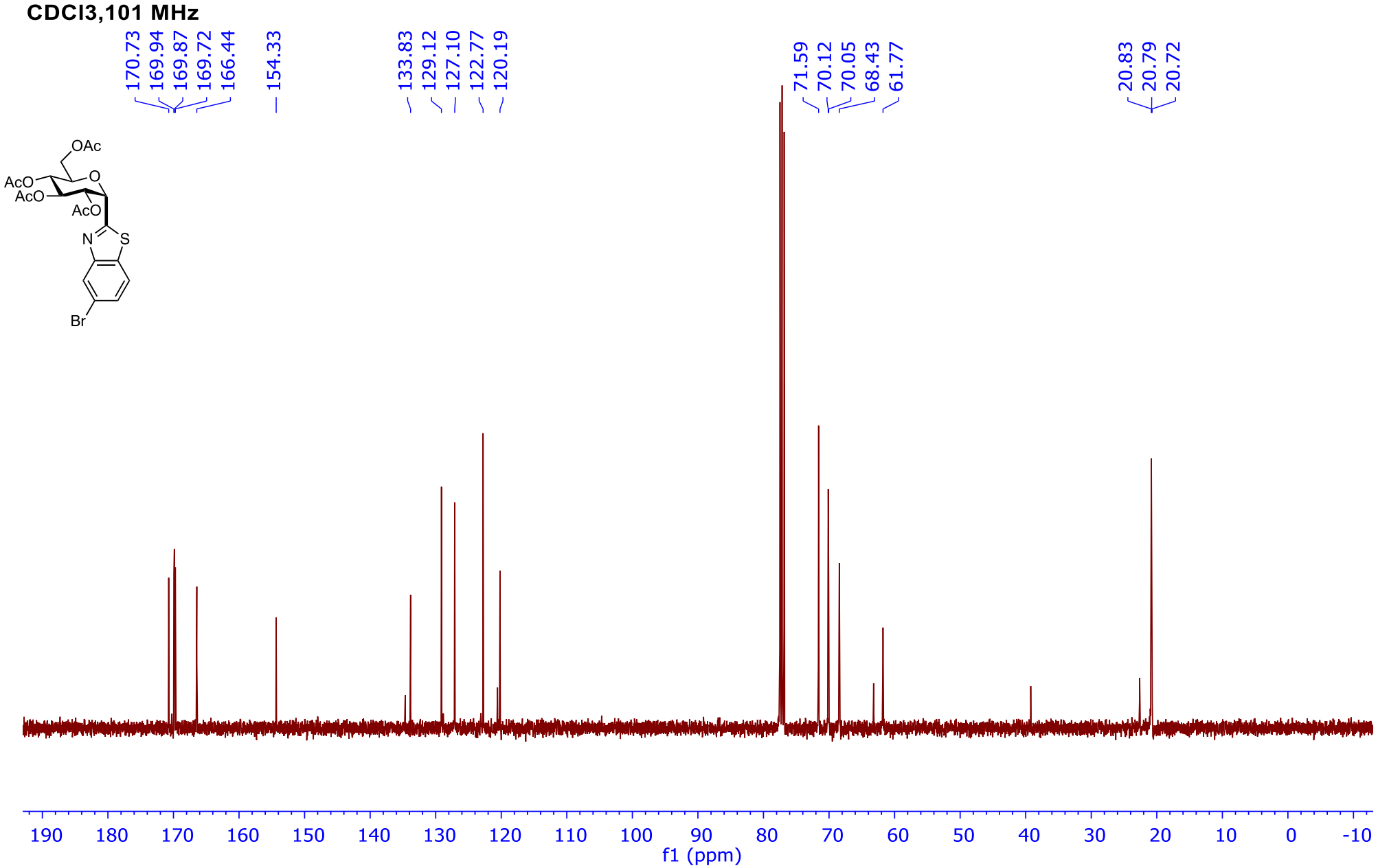
^{1}H NMR Spectrum of 18o



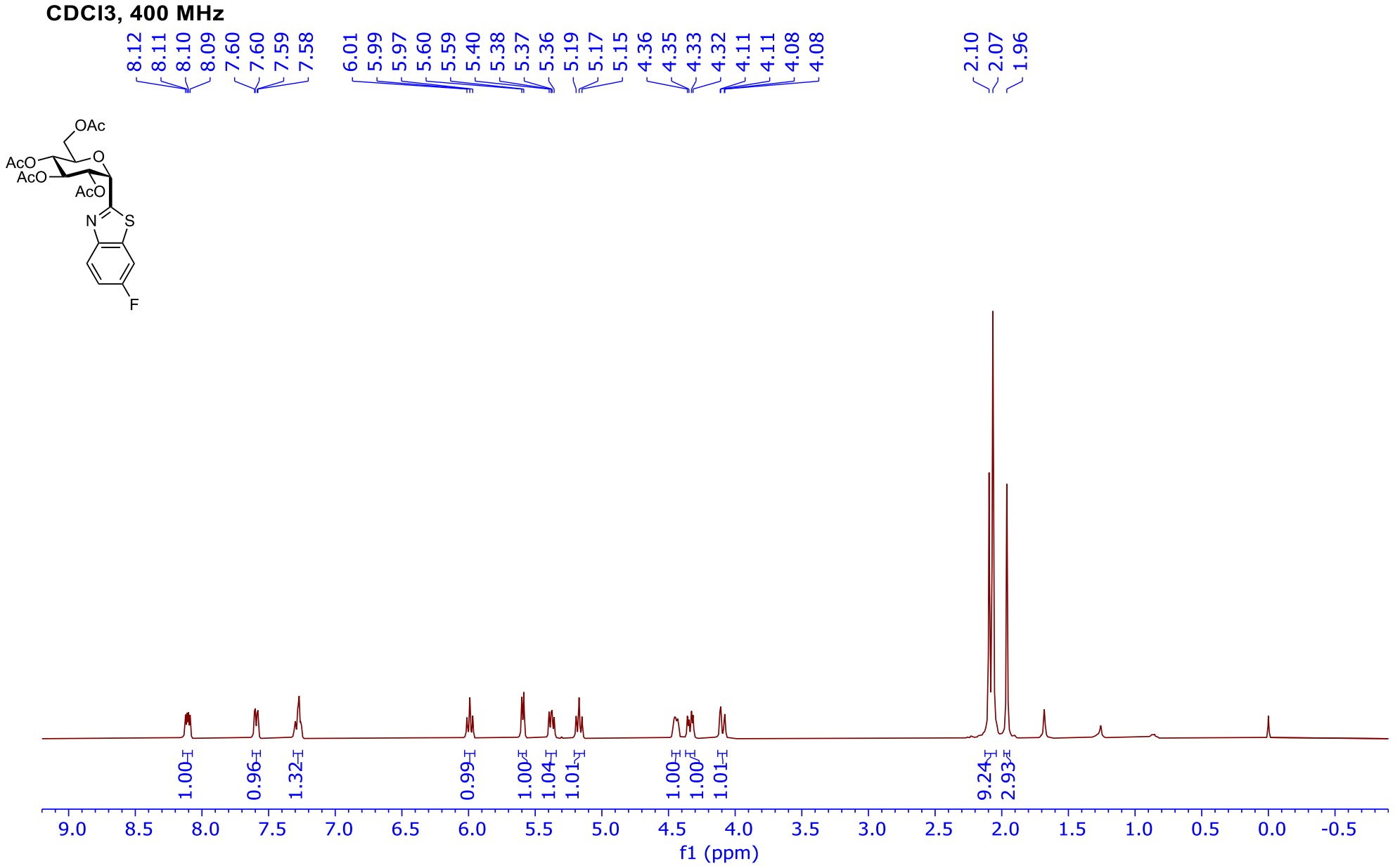
^{13}C NMR Spectrum of 18o



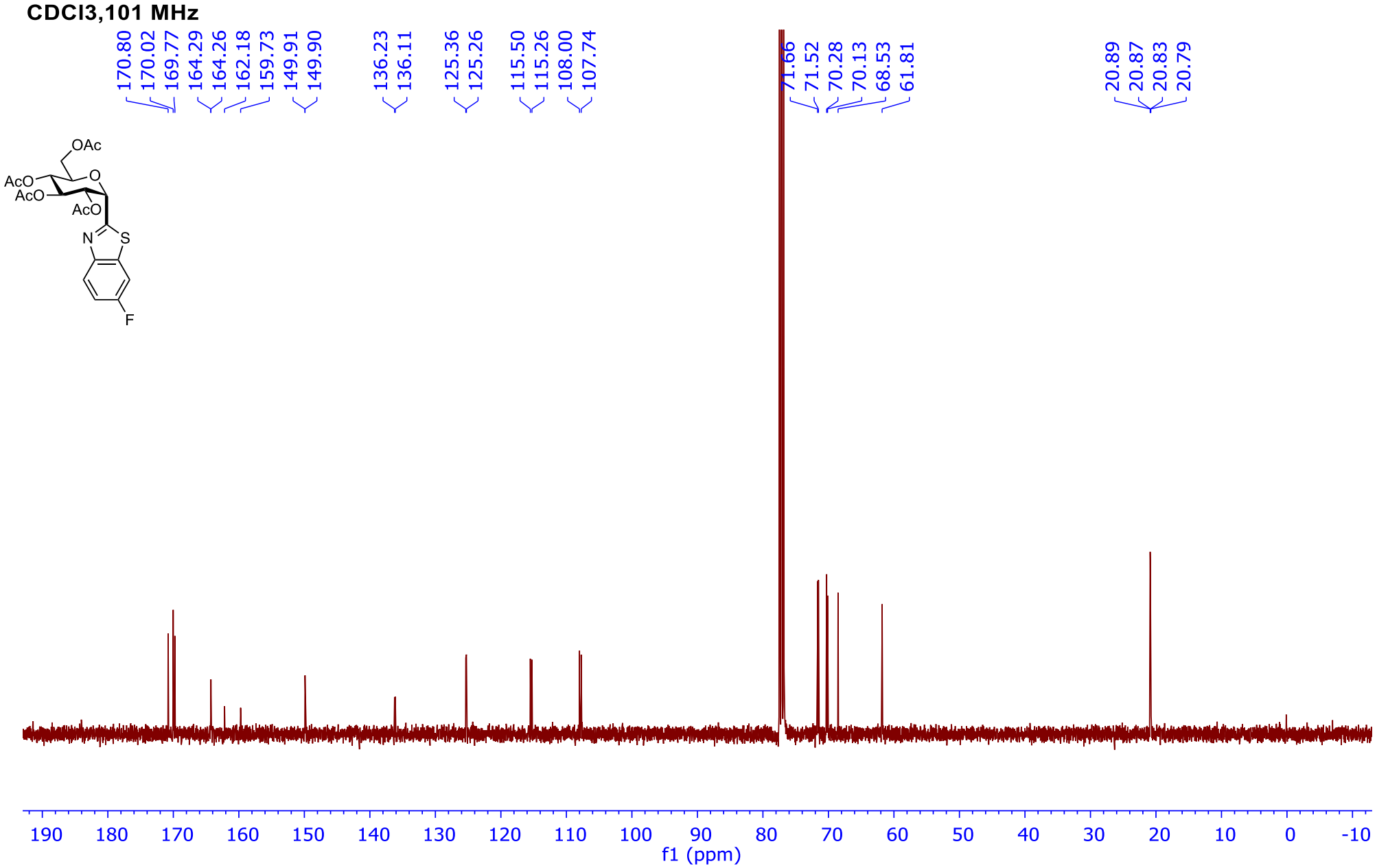
^{1}H NMR Spectrum of 18p



^{13}C NMR Spectrum of 18p

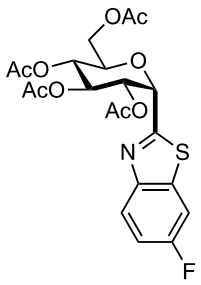


^{1}H NMR Spectrum of 18q

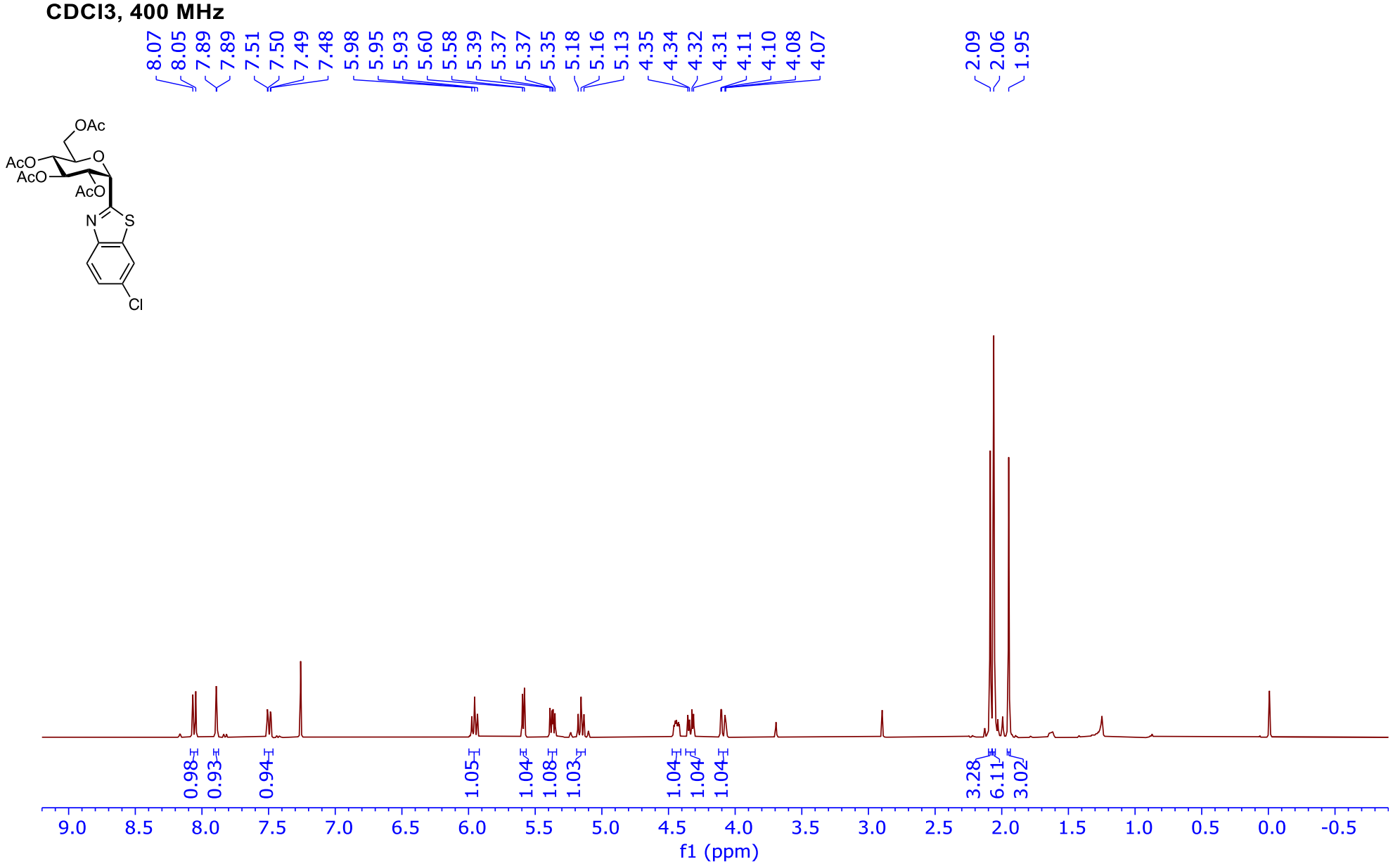


^{13}C NMR Spectrum of 18q

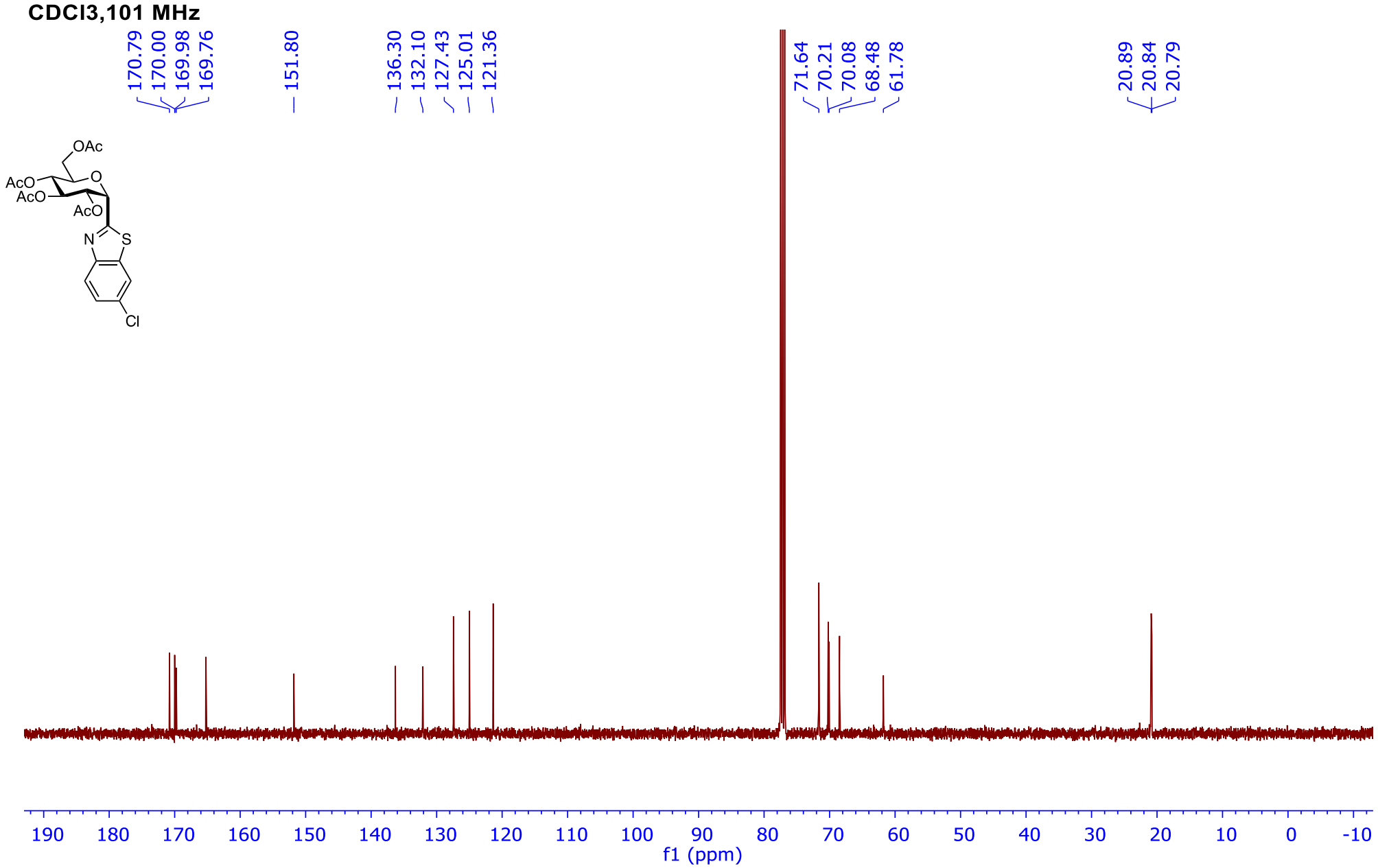
CDCl3,376 MHz



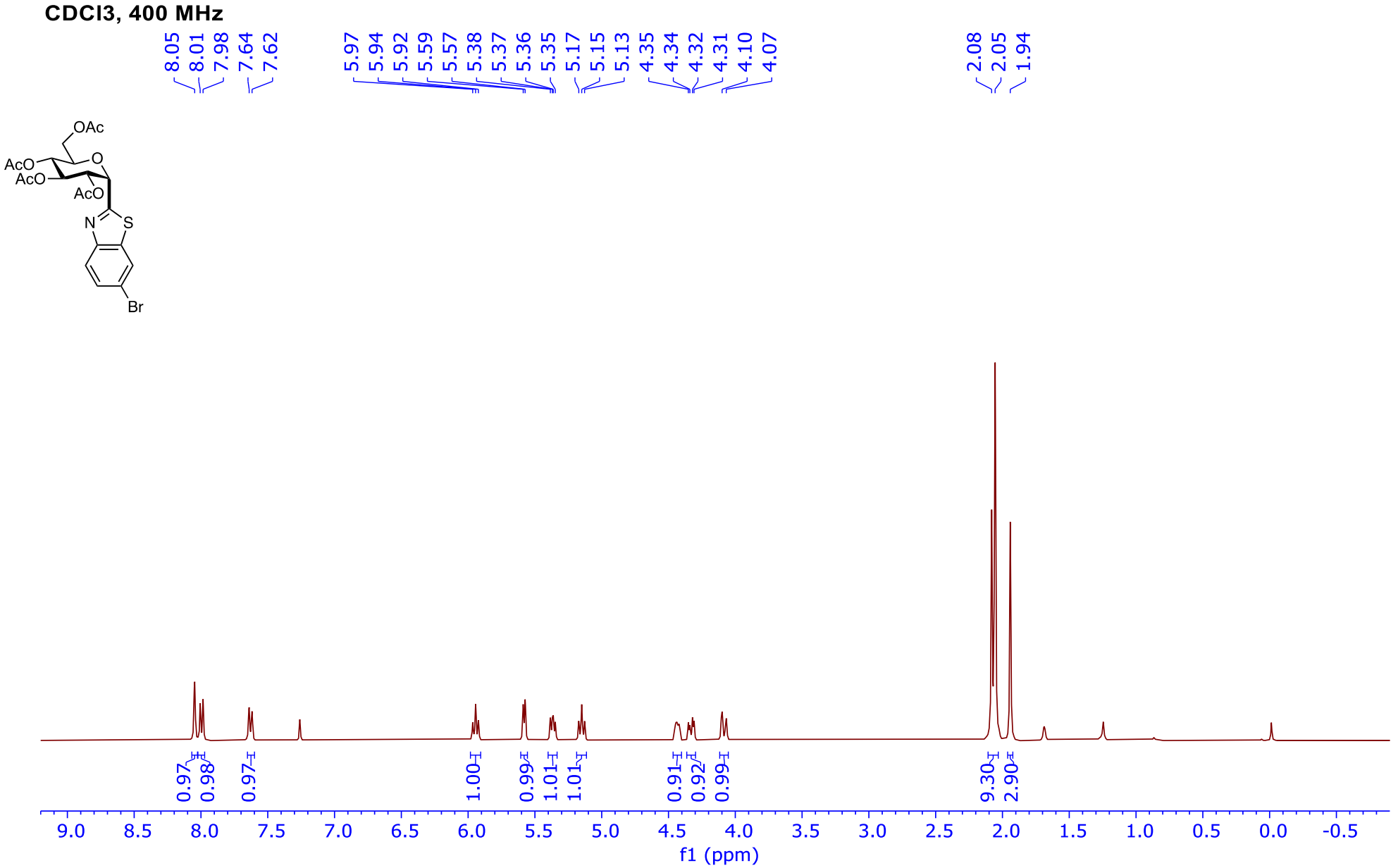
^{19}F NMR Spectrum of 18q



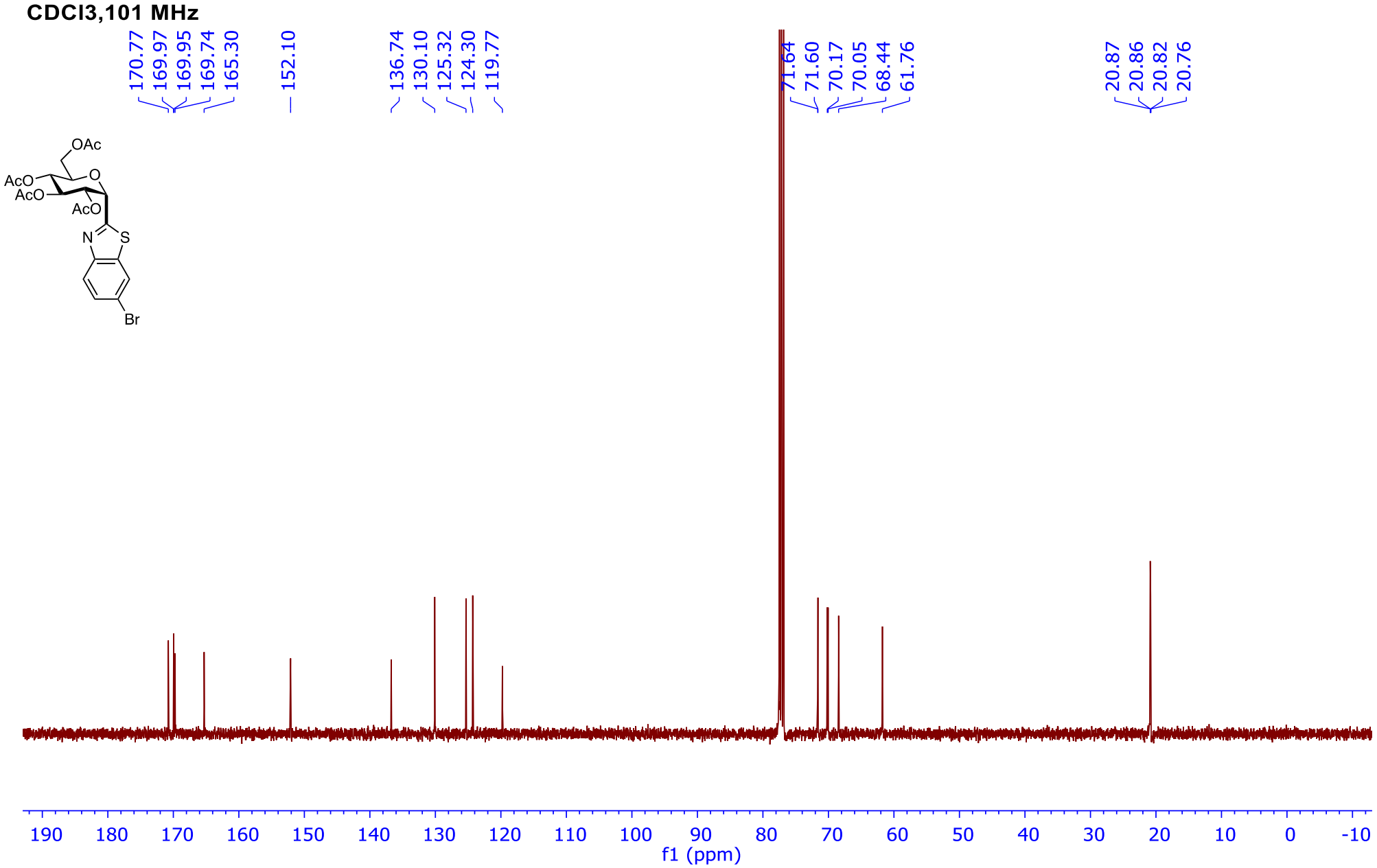
^{1}H NMR Spectrum of 18r



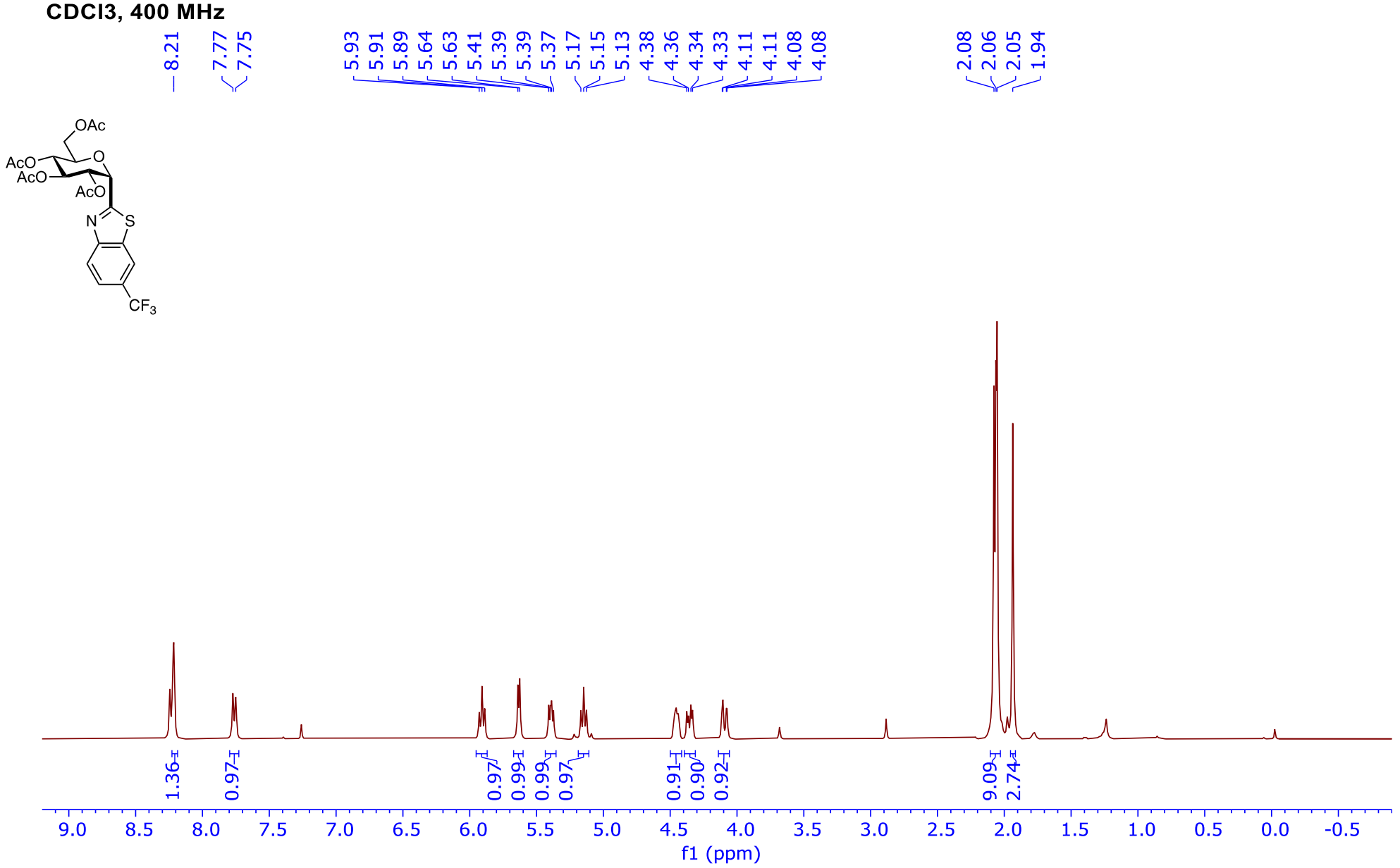
^{13}C NMR Spectrum of 18r



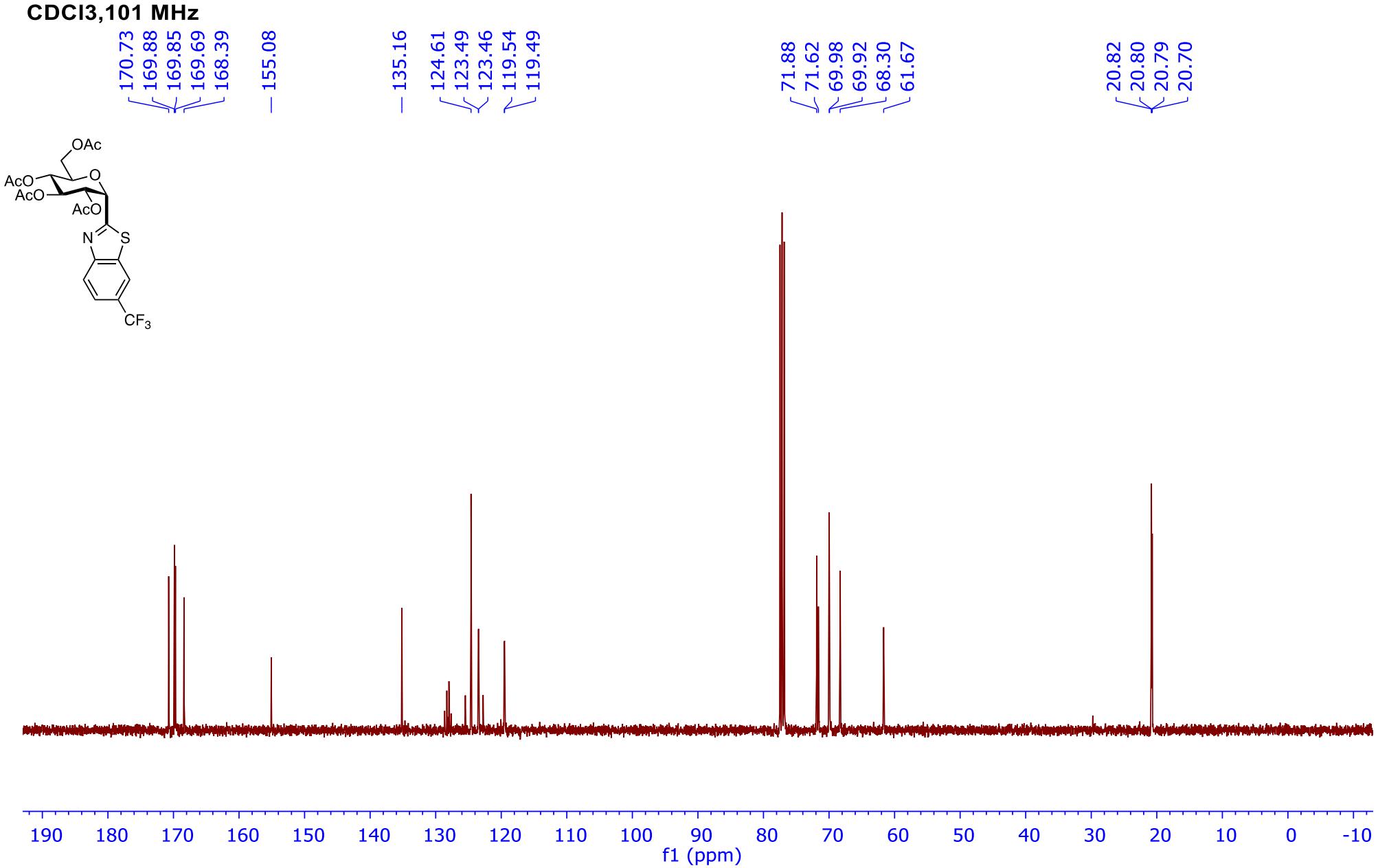
^{1}H NMR Spectrum of 18s



^{13}C NMR Spectrum of 18s

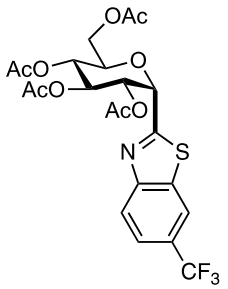


^{1}H NMR Spectrum of 18t

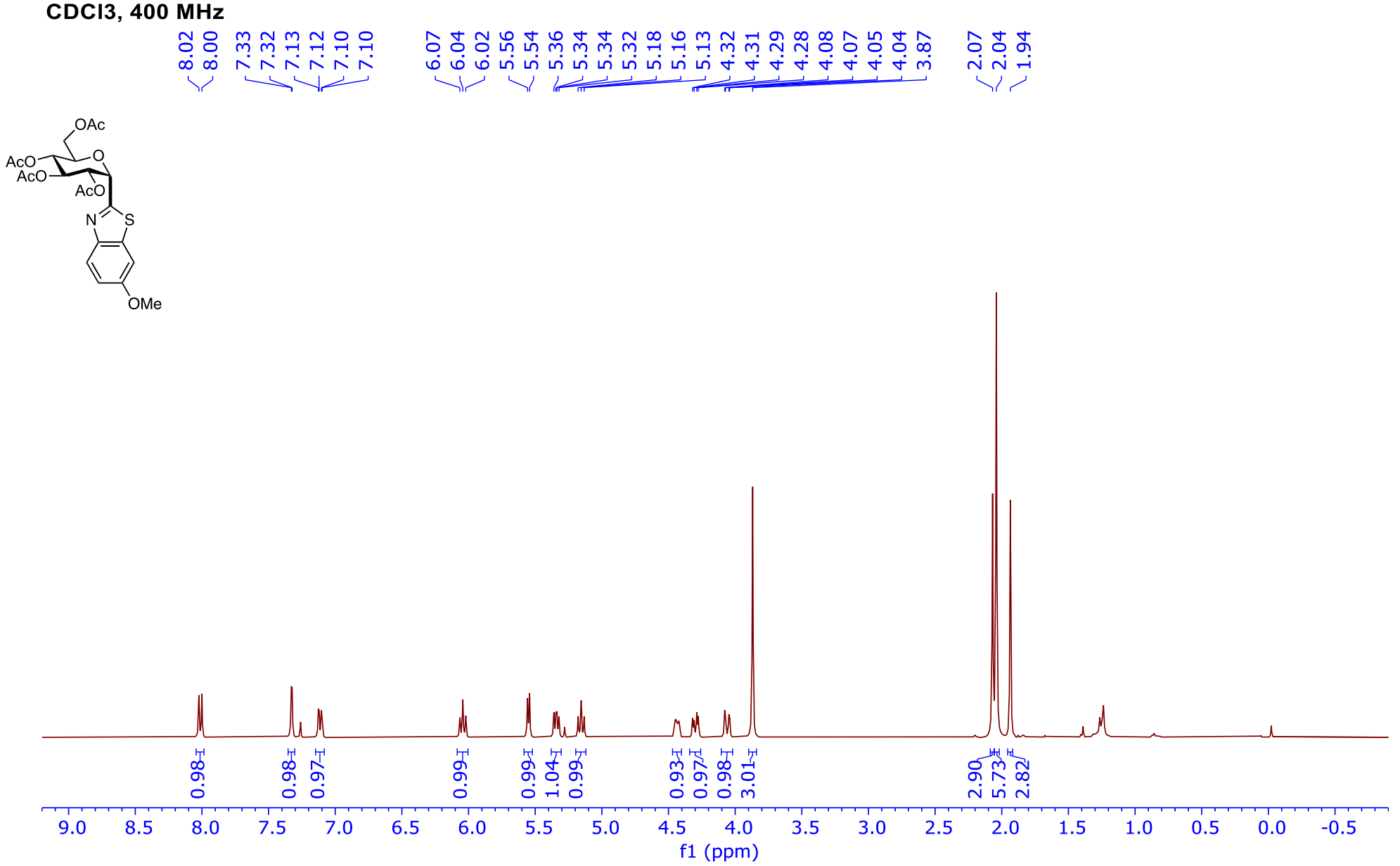


^{13}C NMR Spectrum of 18t

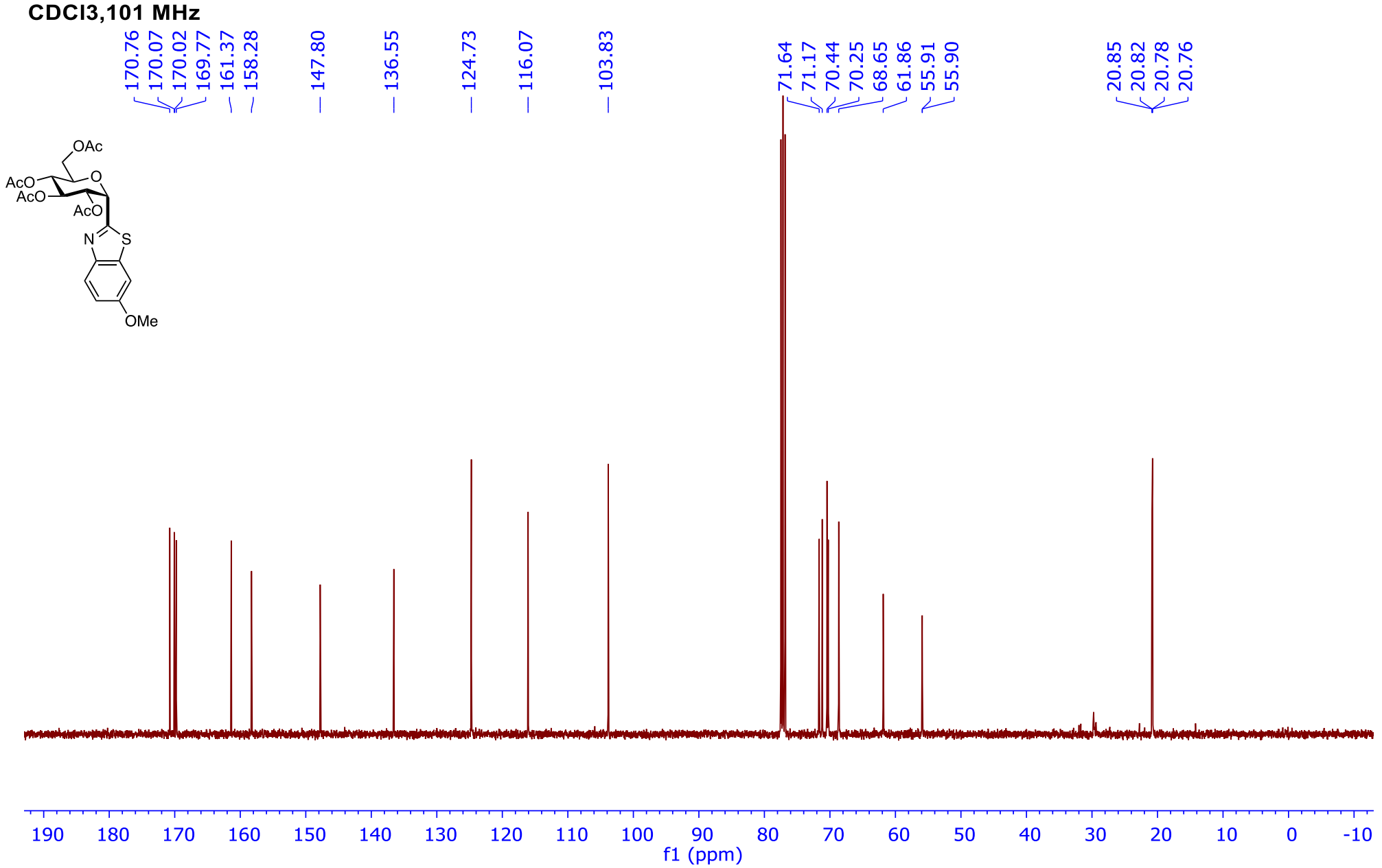
CDCl3,376 MHz



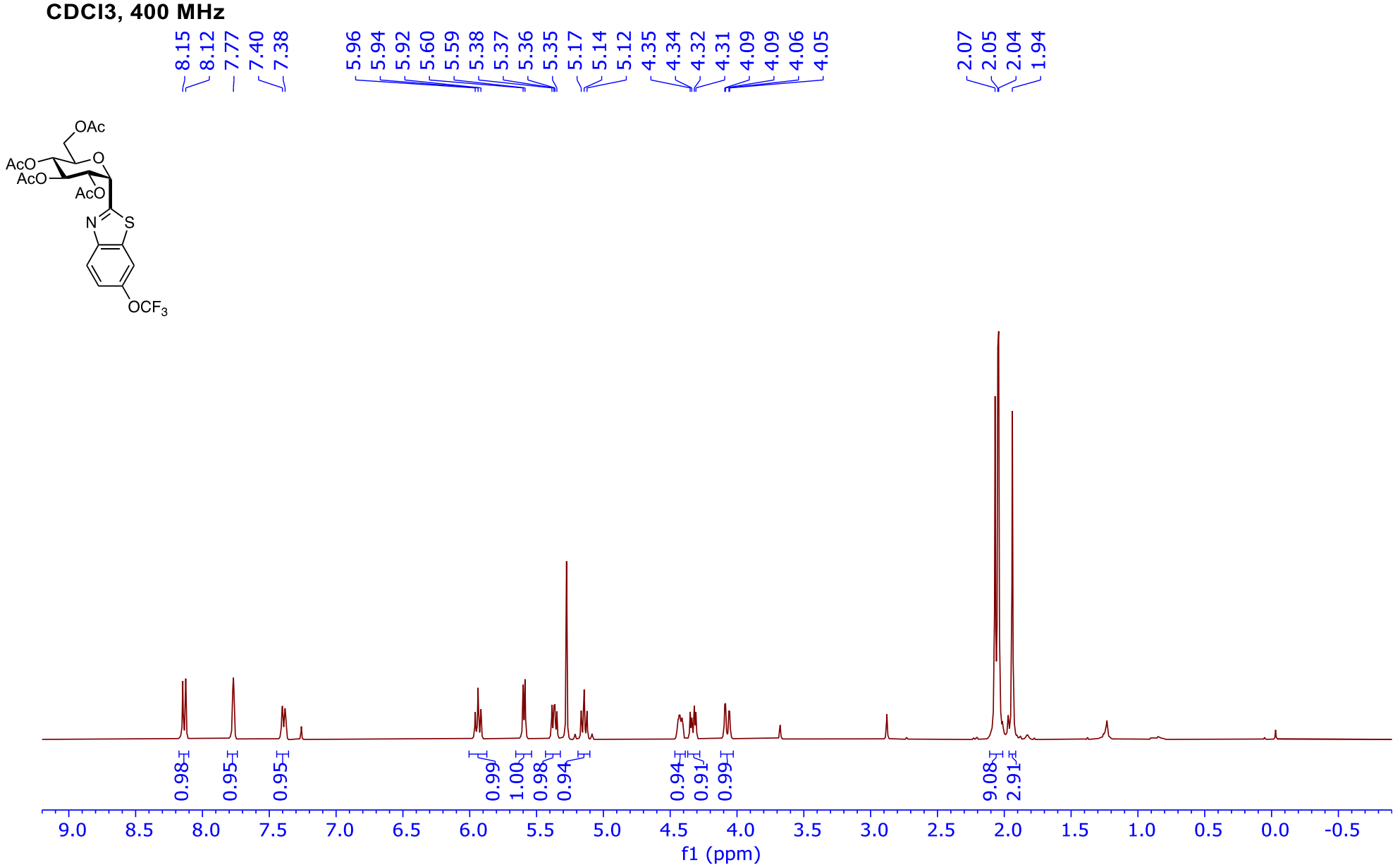
^{19}F NMR Spectrum of 18t



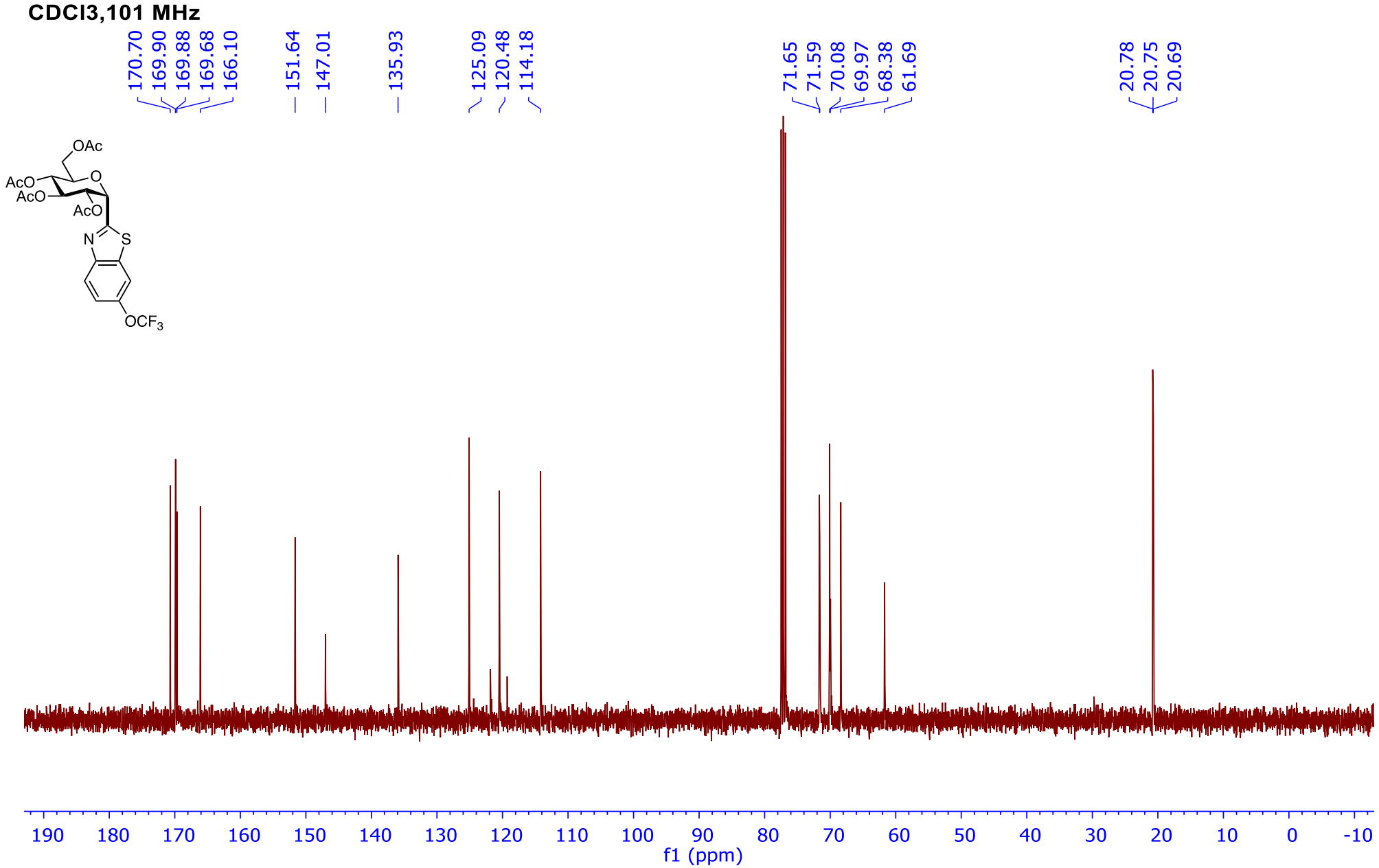
^{1}H NMR Spectrum of 18u



^{13}C NMR Spectrum of 18u

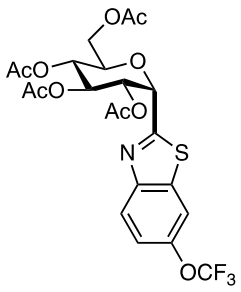


^{1}H NMR Spectrum of 18v

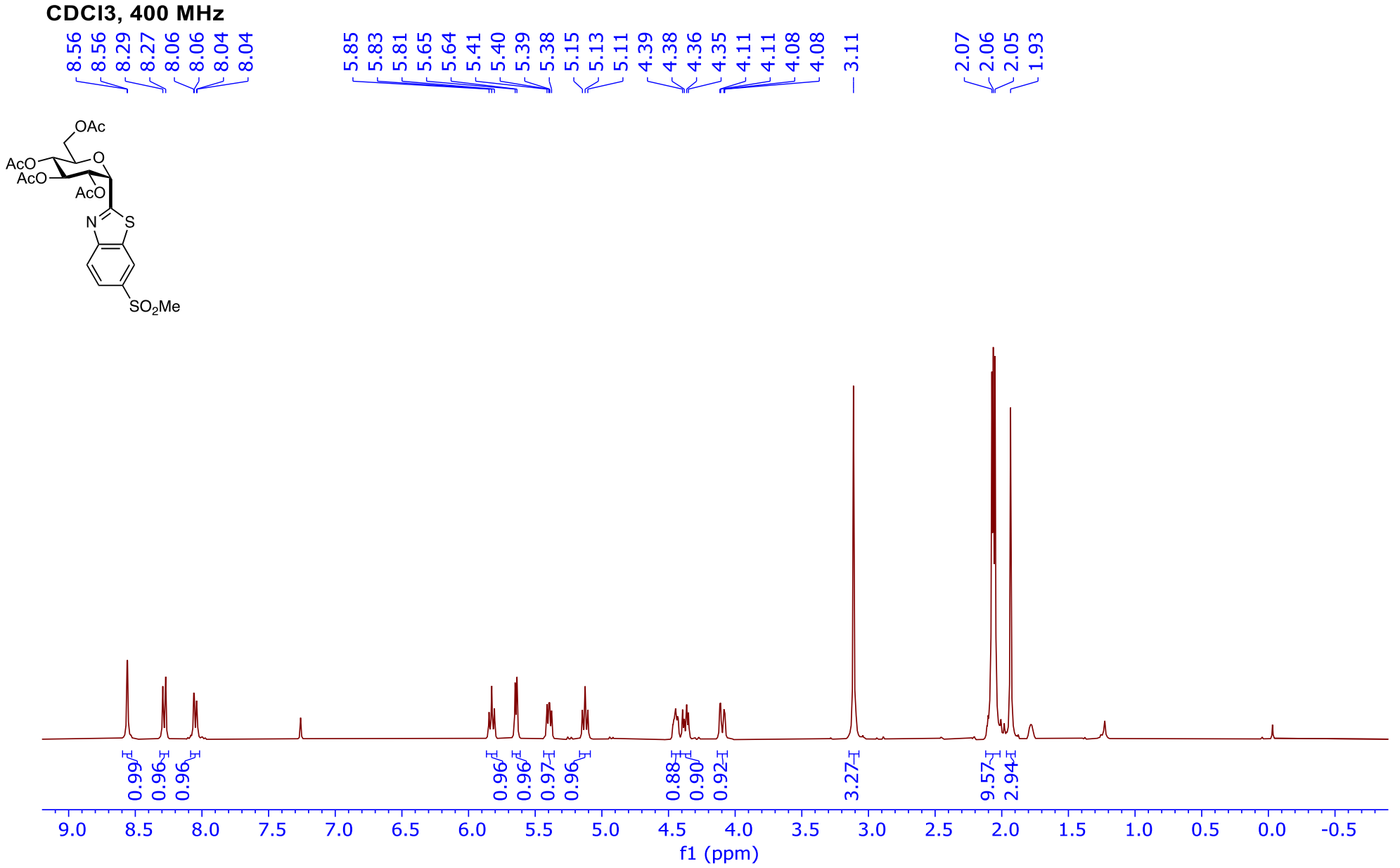


^{13}C NMR Spectrum of 18v

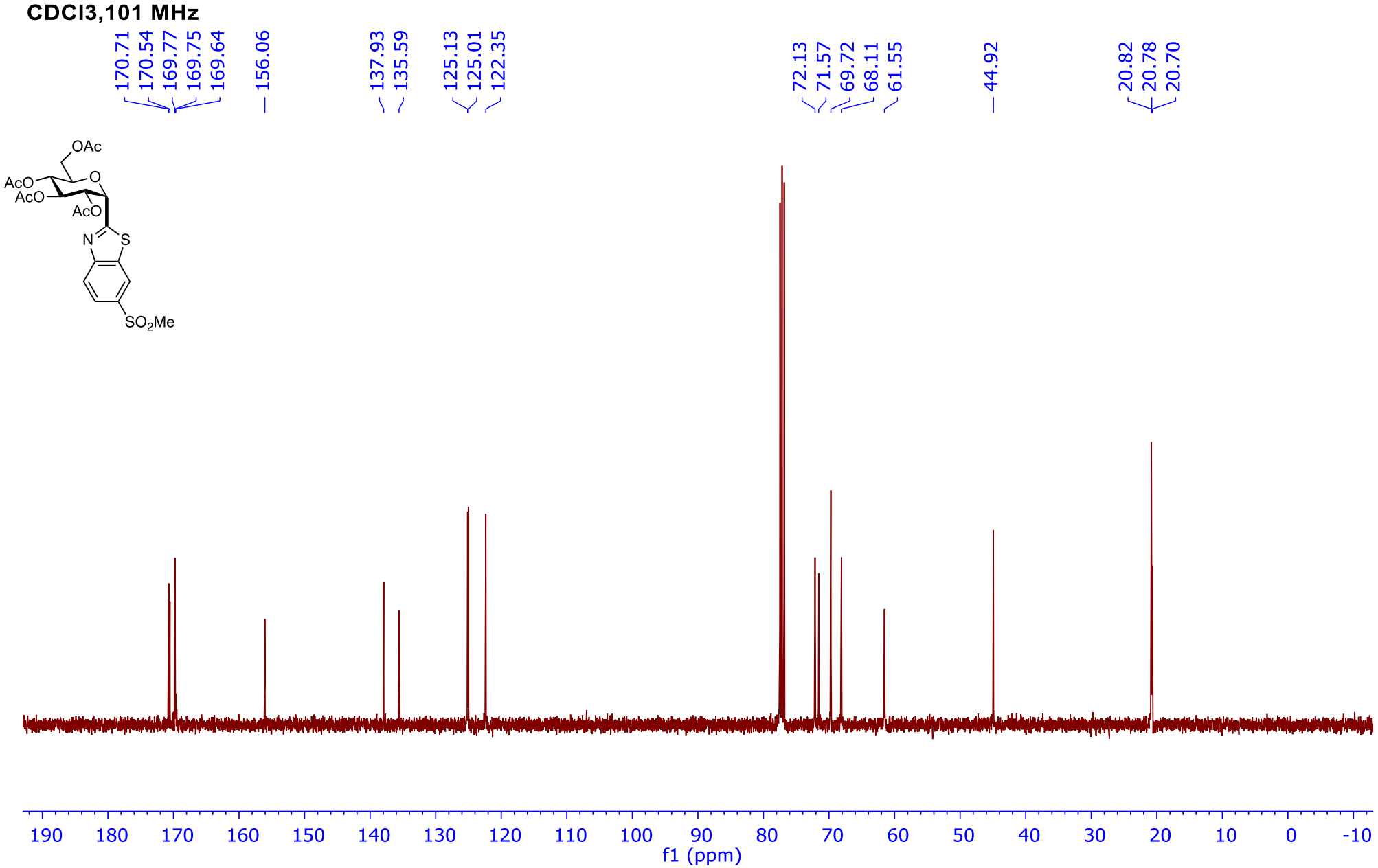
CDCl3,376 MHz



^{19}F NMR Spectrum of 18v

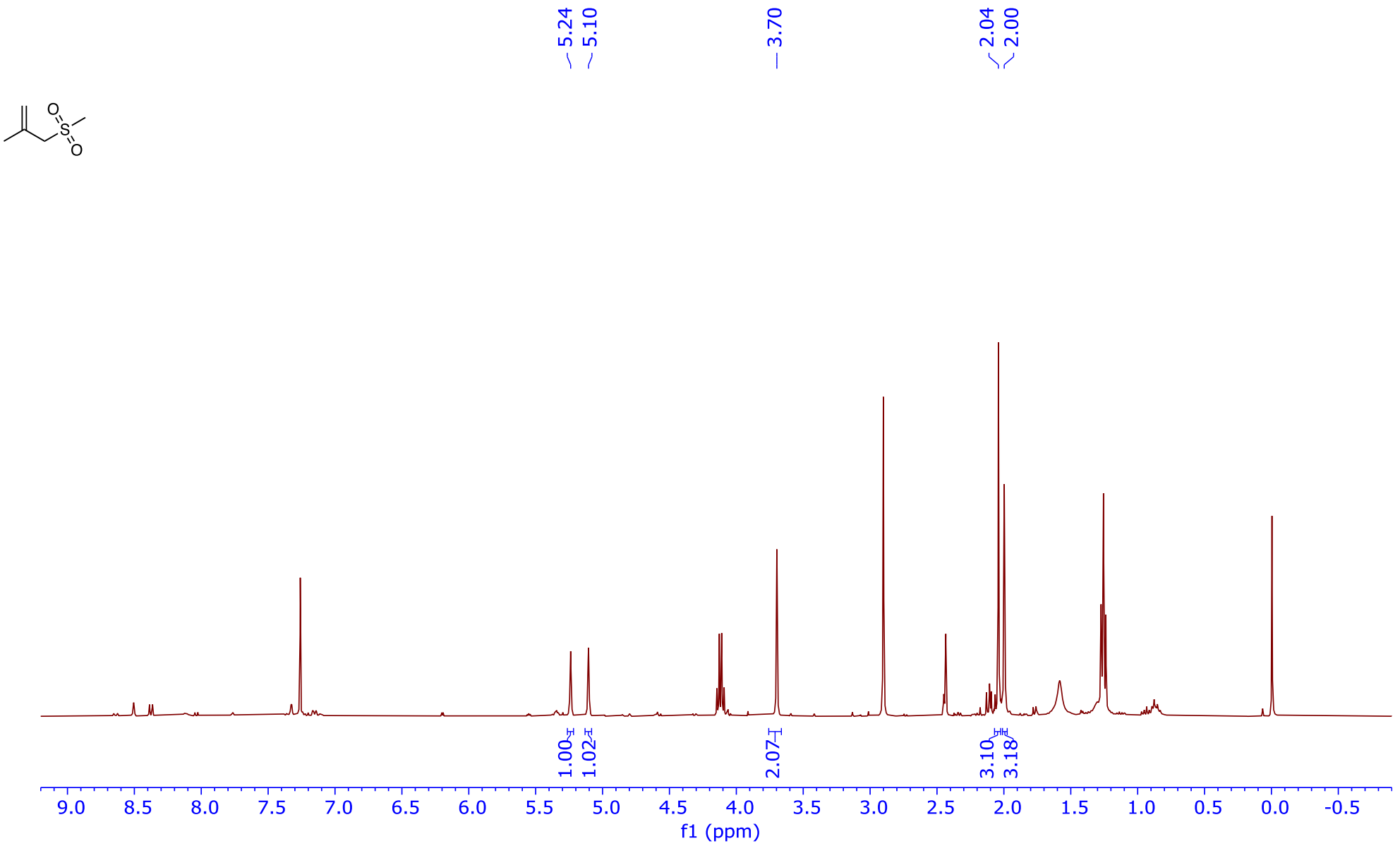


^{1}H NMR Spectrum of 18w

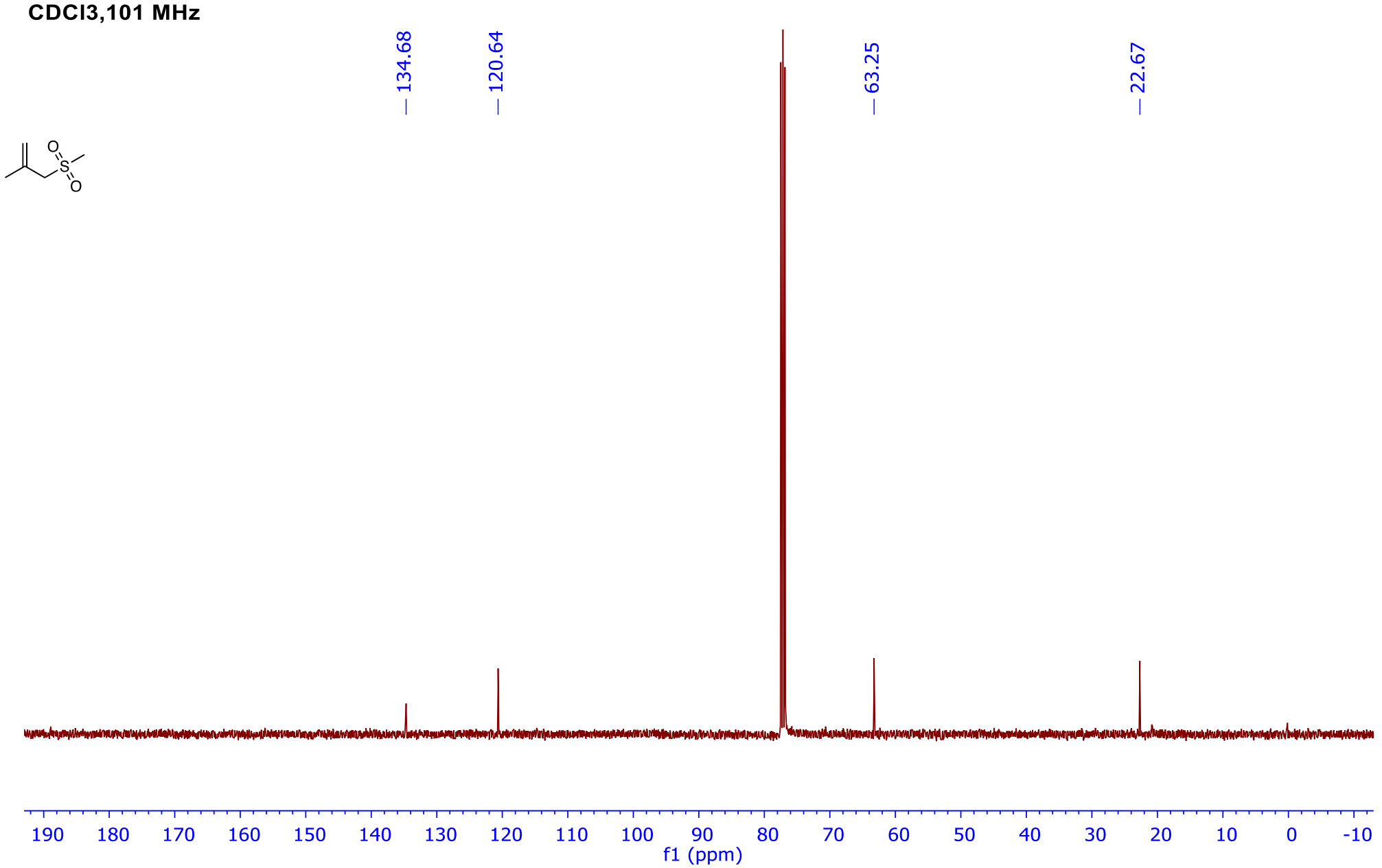


^{13}C NMR Spectrum of 18w

CDCl3, 400 MHz

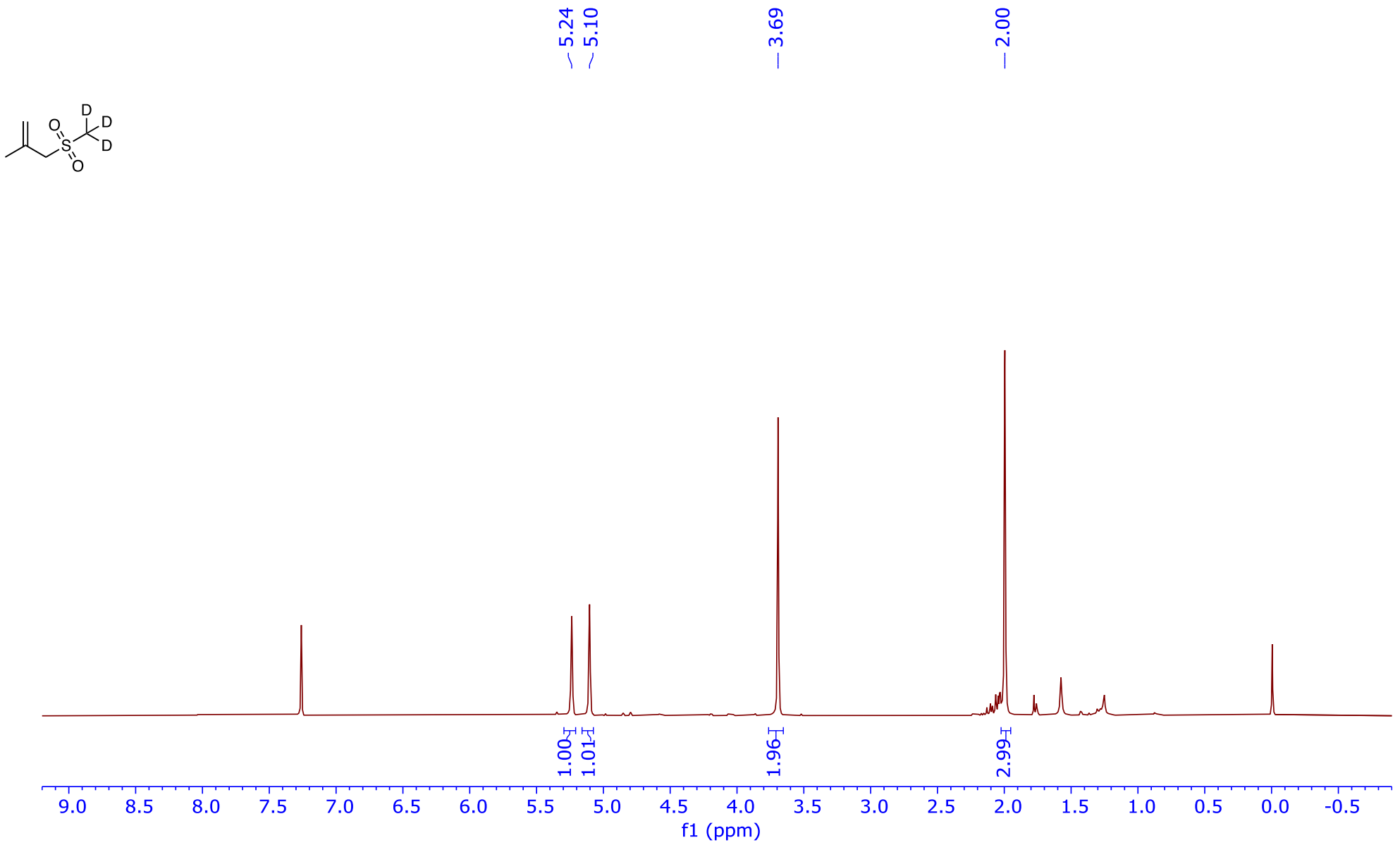


^{1}H NMR Spectrum of 19

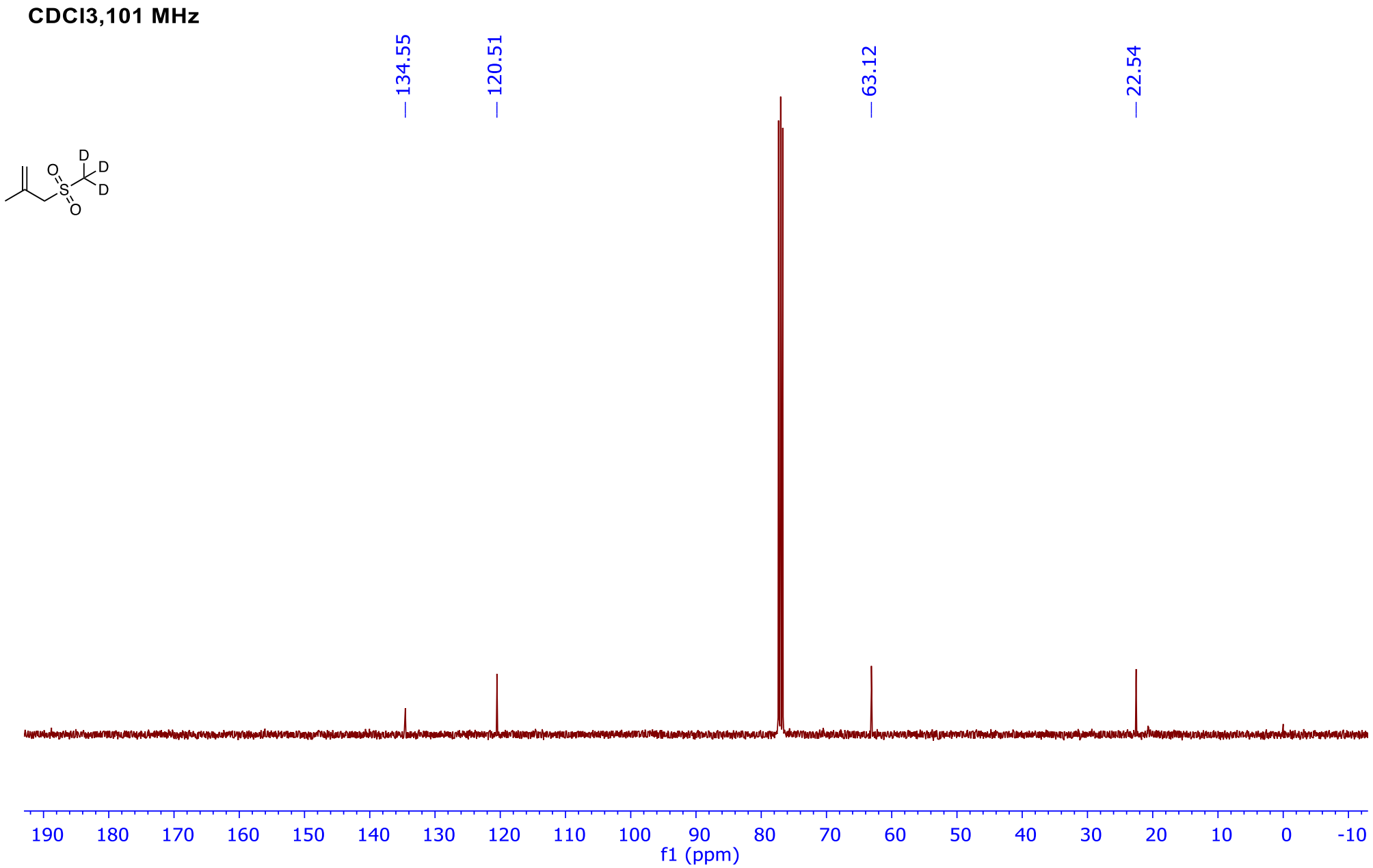


^{13}C NMR Spectrum of 19

CDCl3, 400 MHz



^{1}H NMR Spectrum of 21



^{13}C NMR Spectrum of 21