Supporting Information (SI)

Photoinitiated Thiol-ene Mediated Functionalization of 4,5-Enoses

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Supporting Information II

NMR spectra and X-ray crystallographic data

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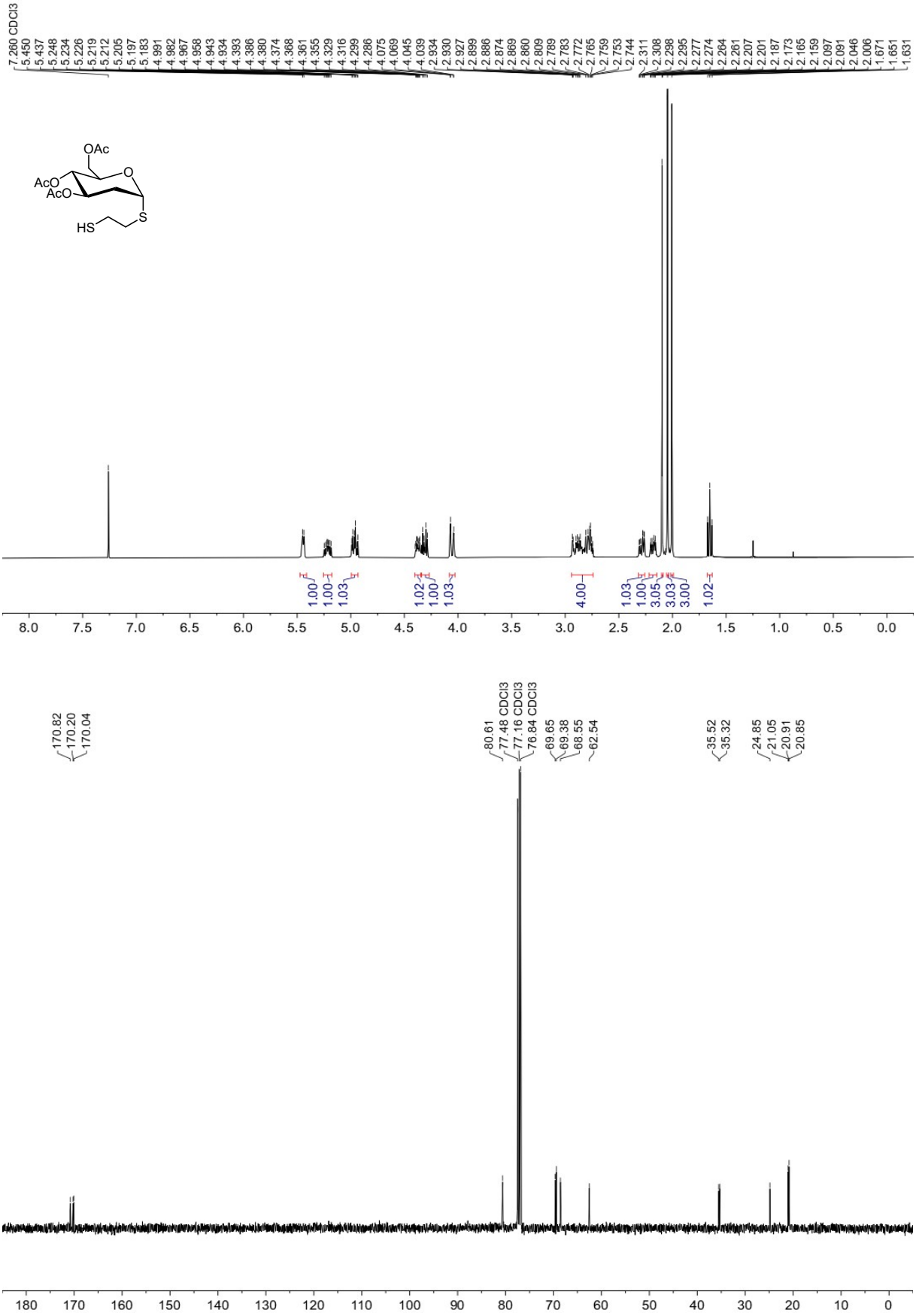
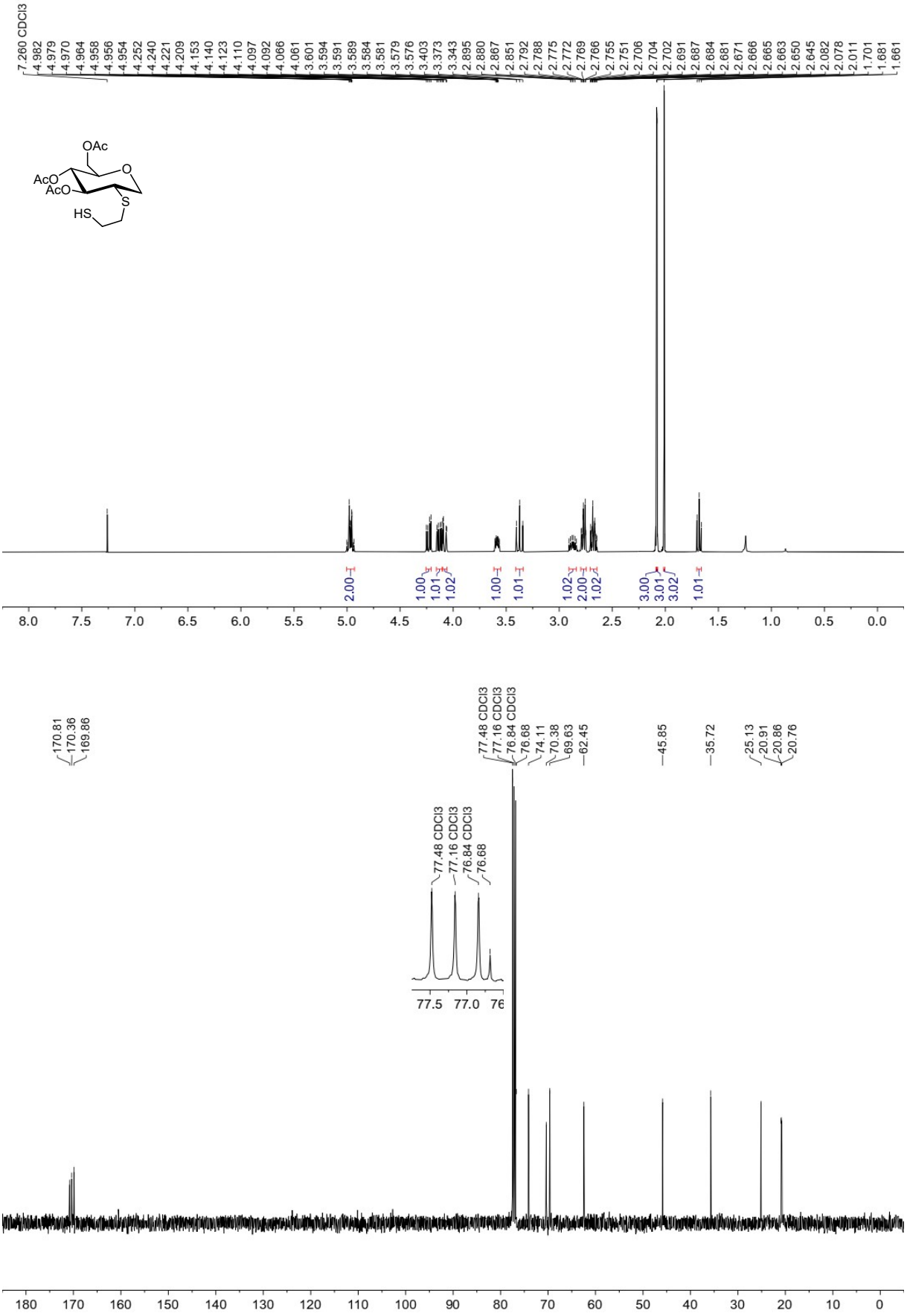
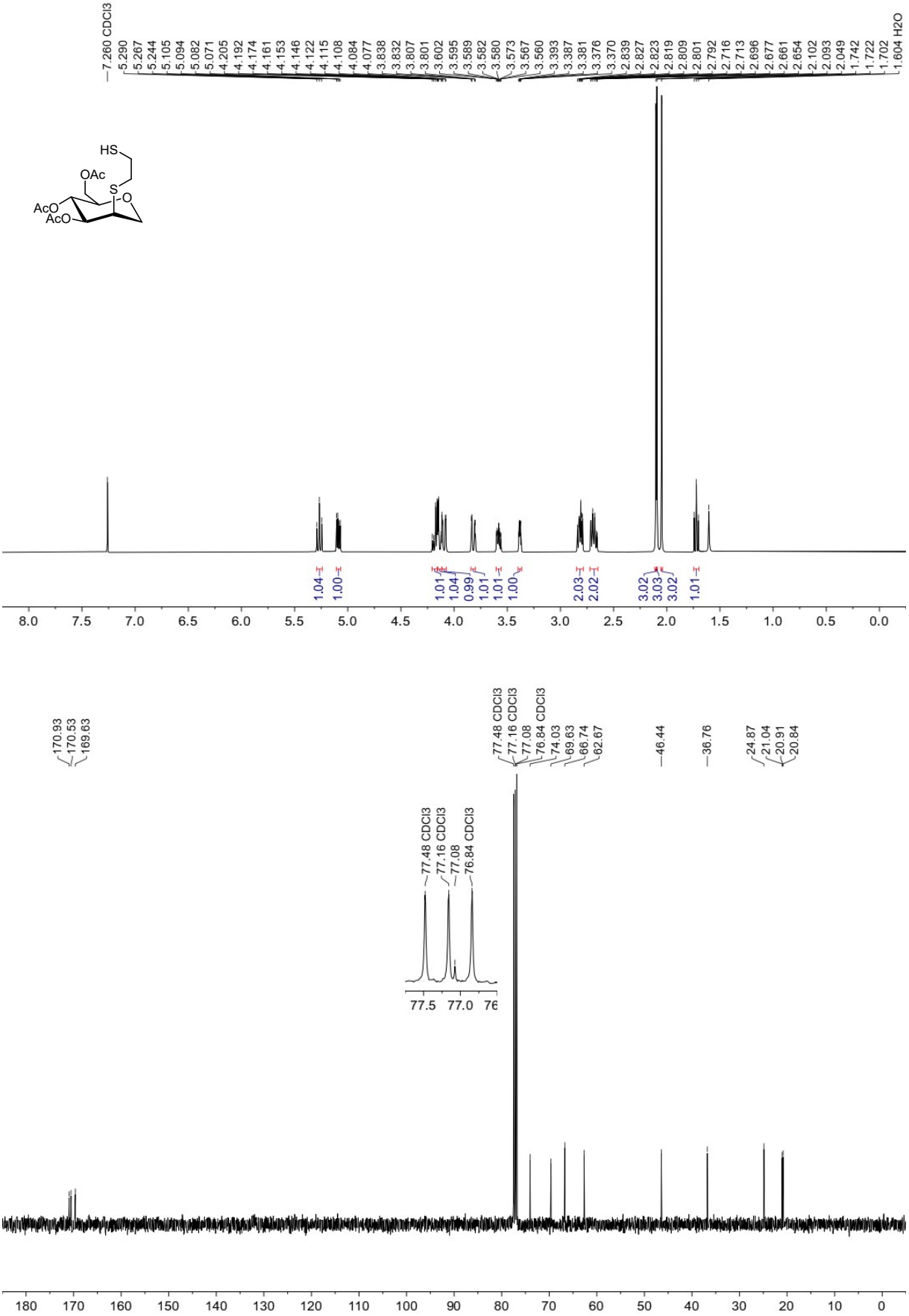
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **S3a**



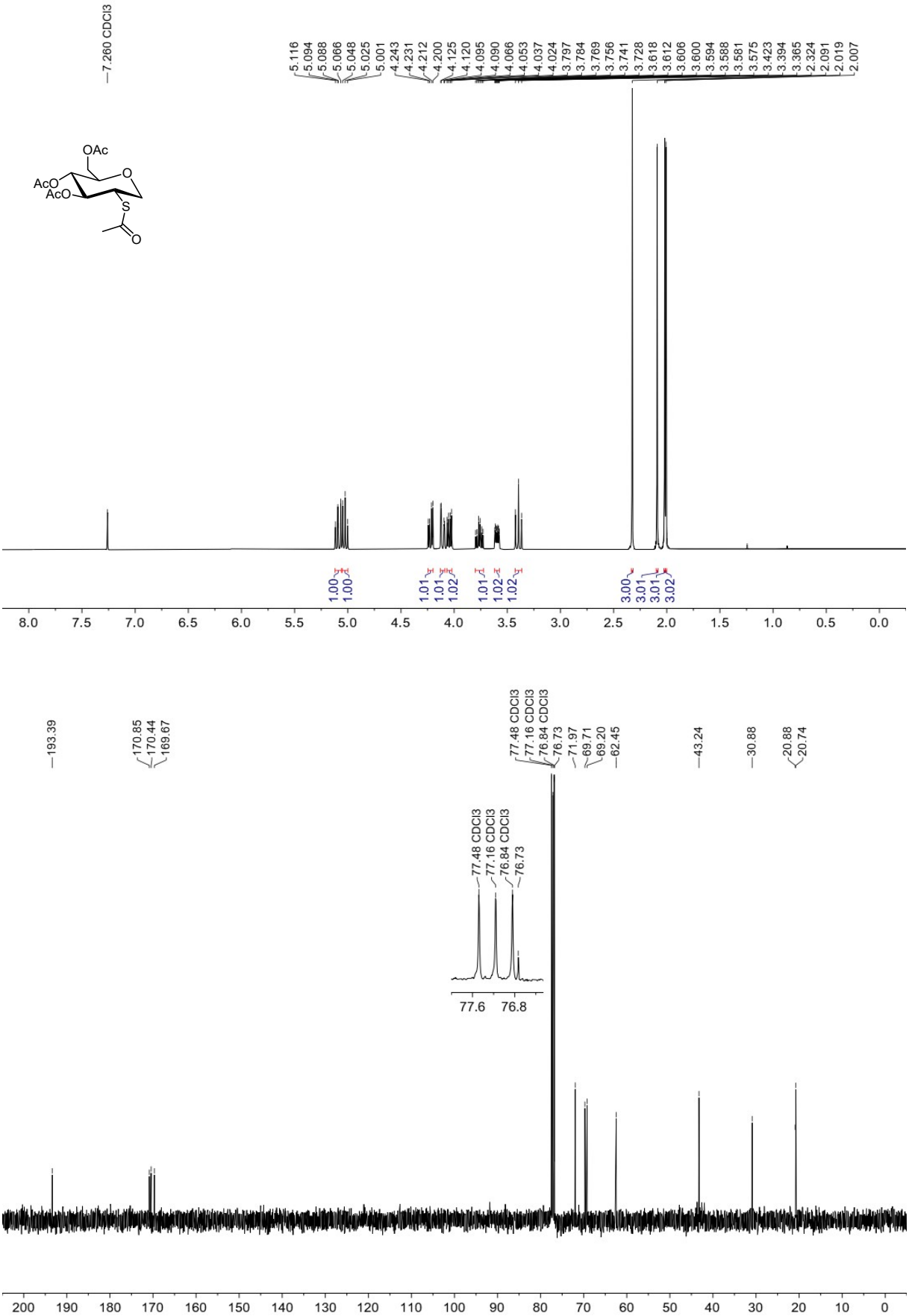
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **S3b**



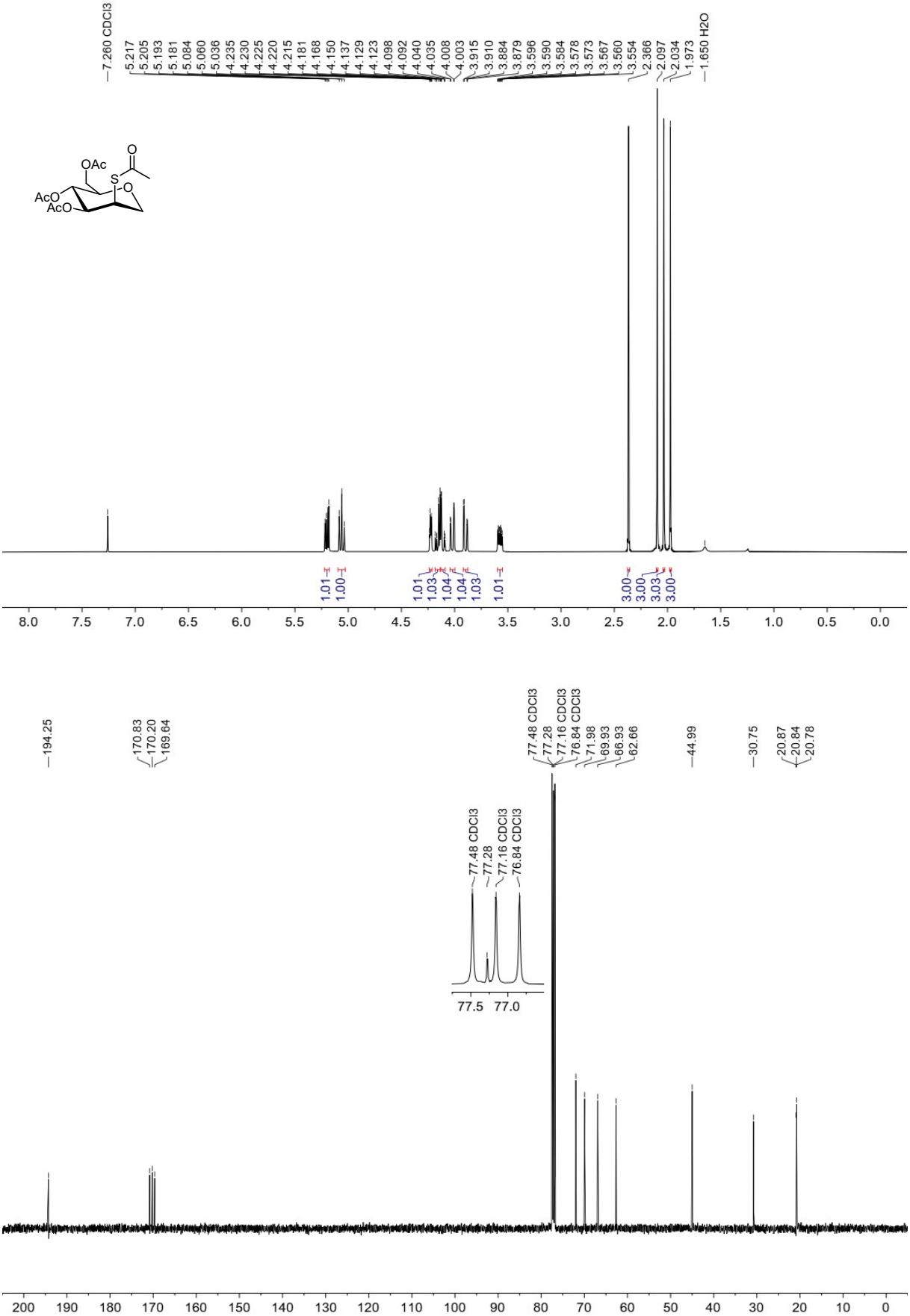
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **S3c**



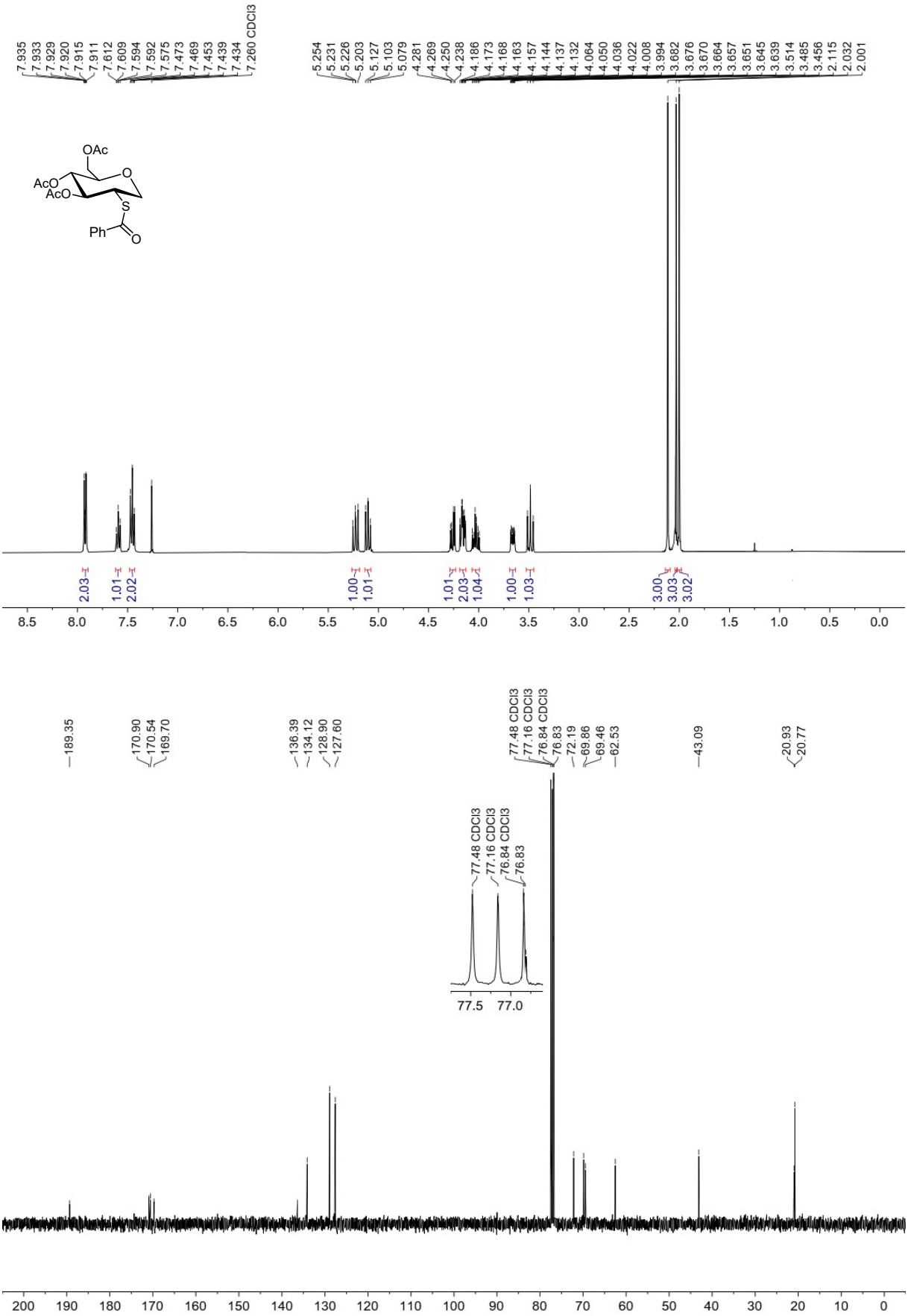
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **S4a**



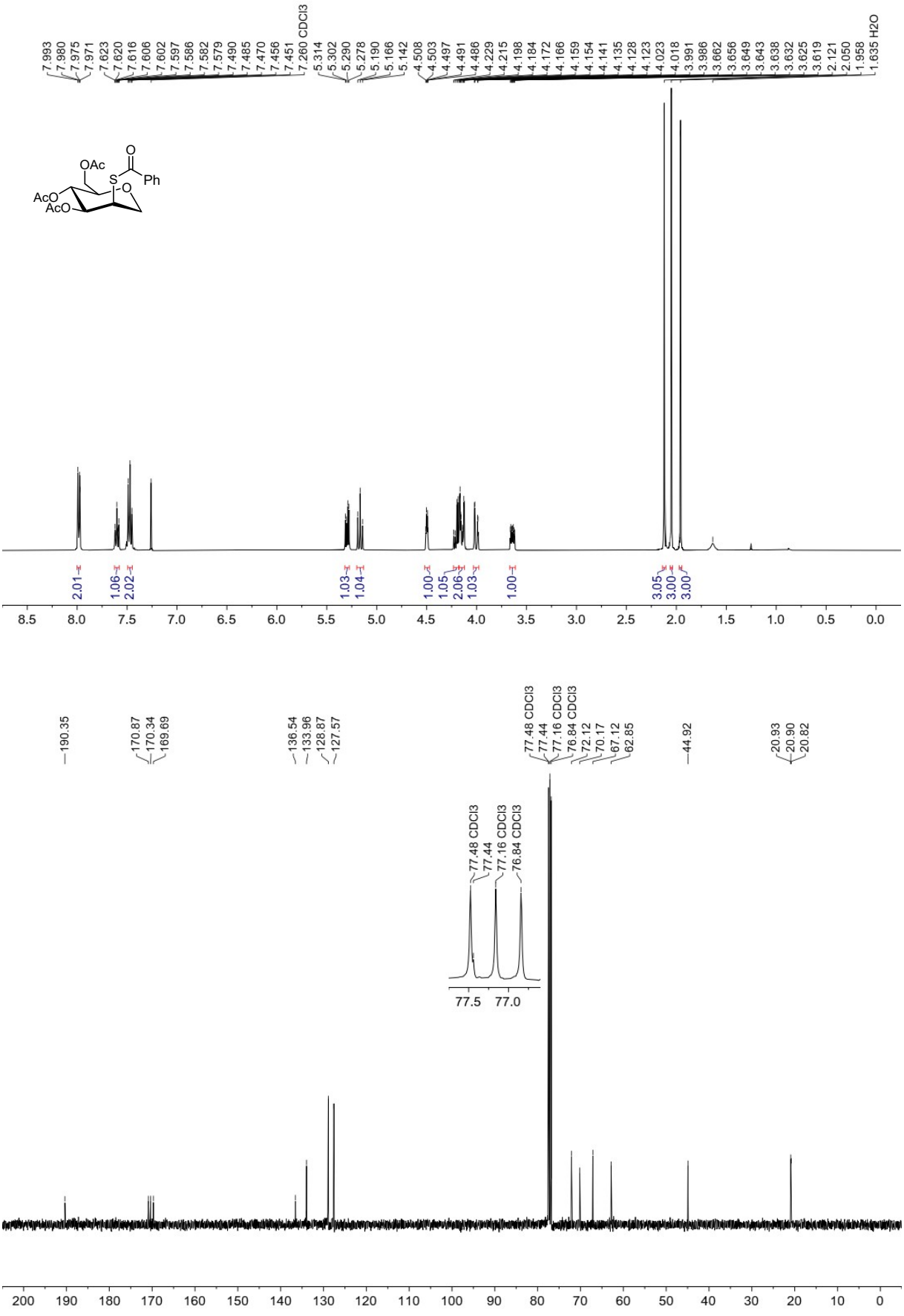
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **S4b**



^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **S5a**

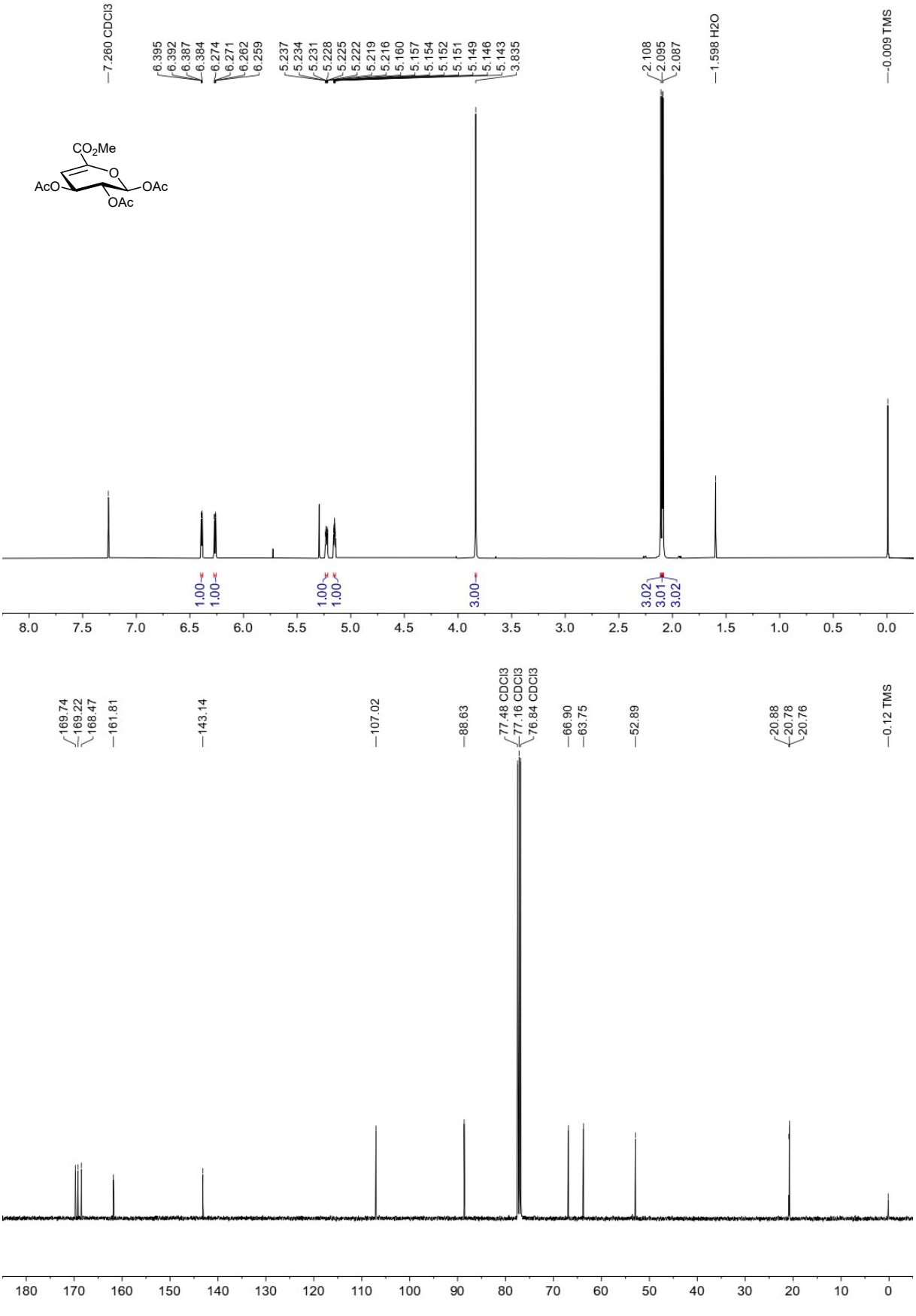


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **S5b**



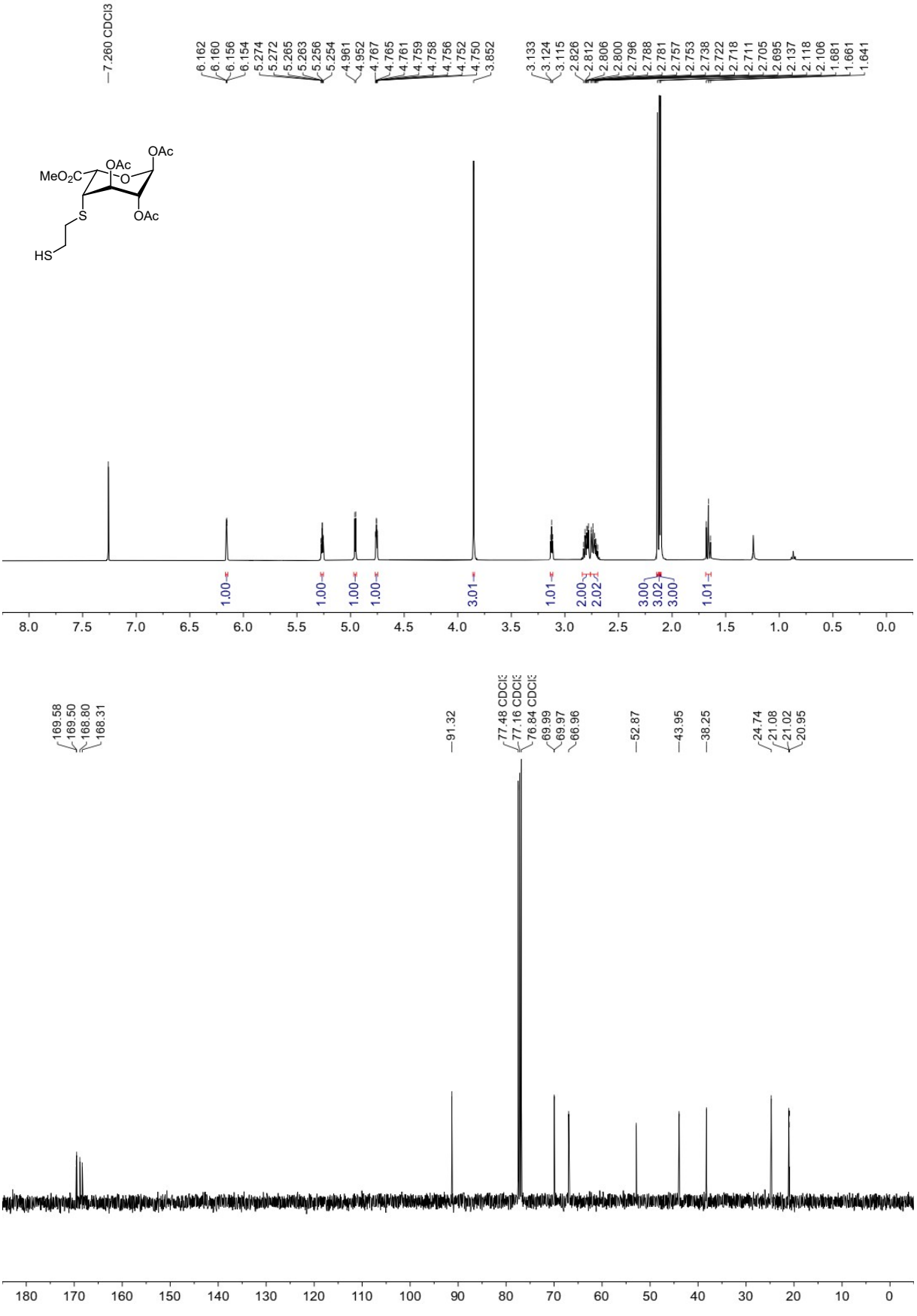
2. Synthesis of 4,5-glycal 1

^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **1**

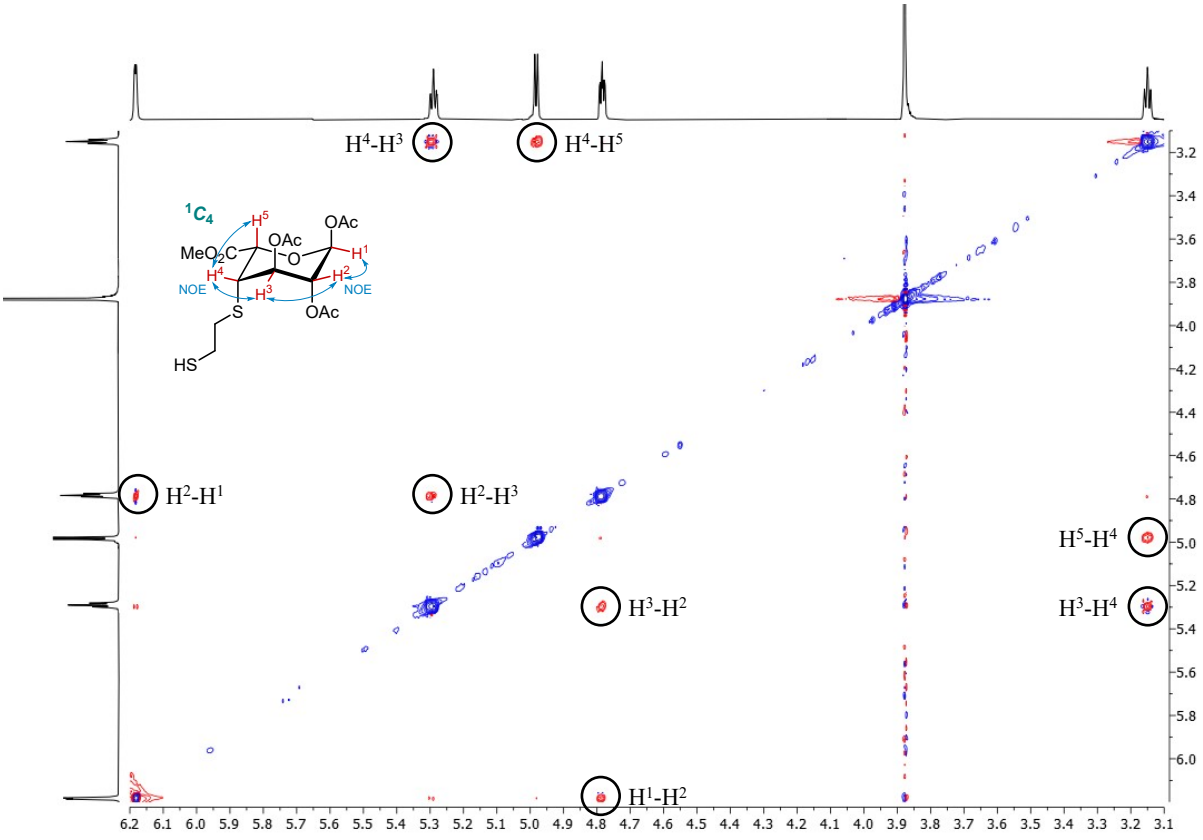


3. Thiol-ene reactions on 4,5-glycal 1

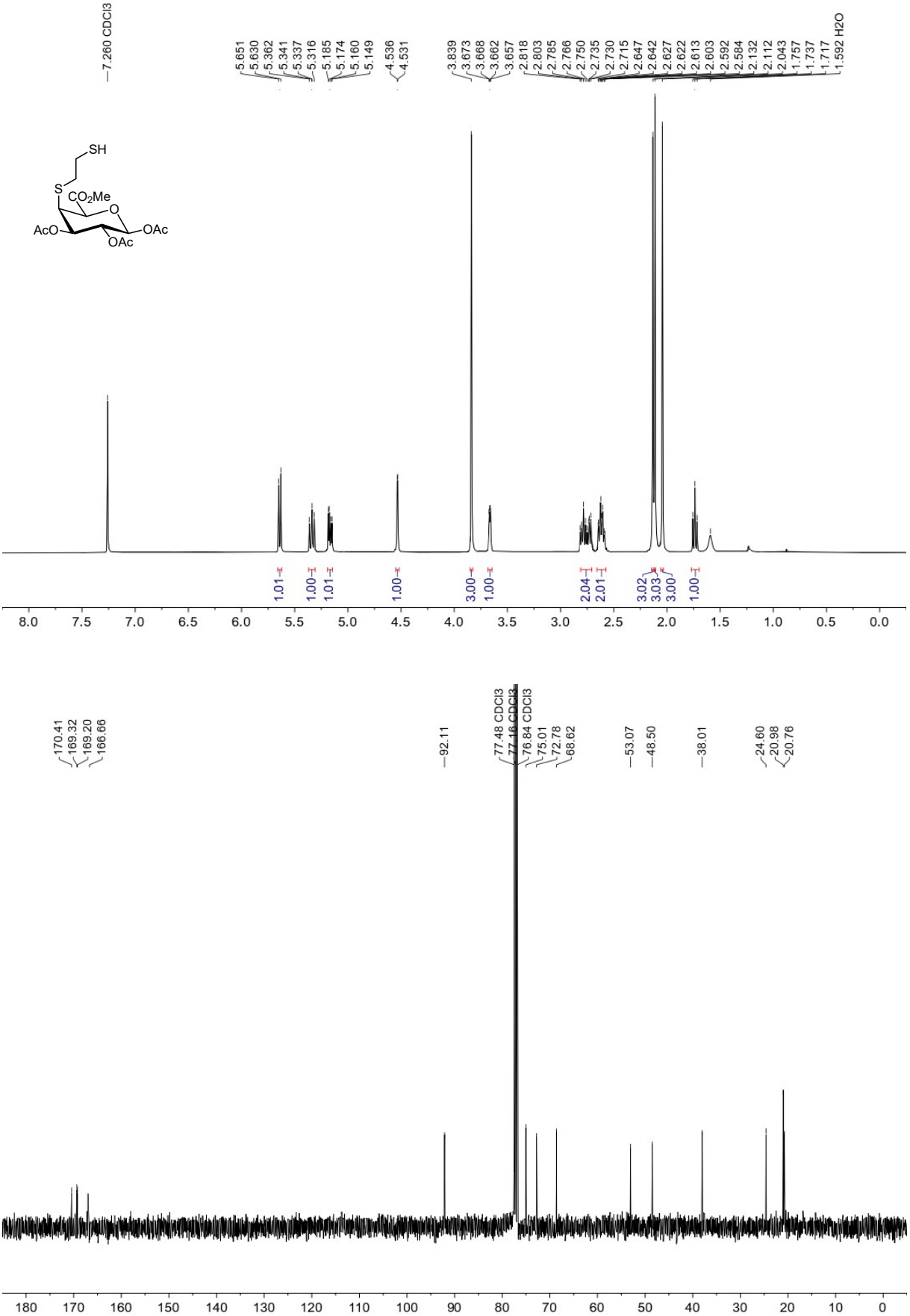
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **5a**



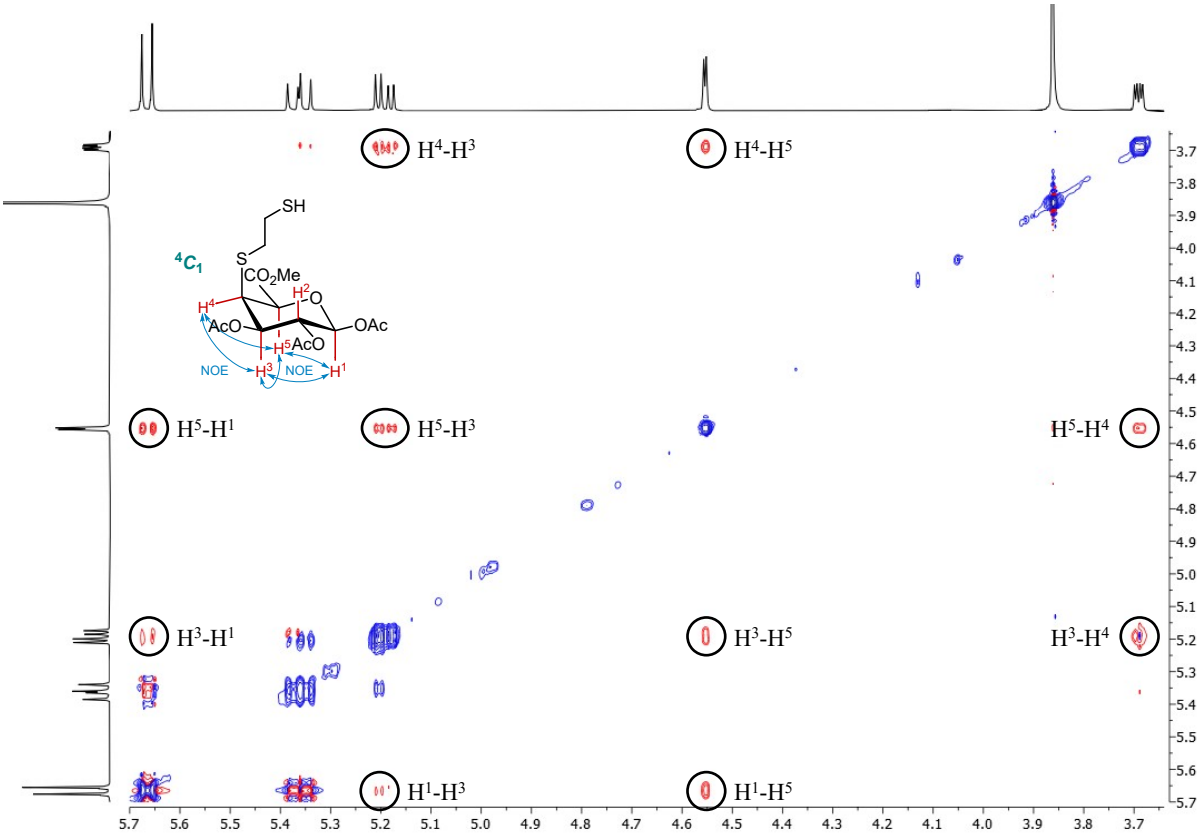
2D ^{1}H,^{1}H-NOESY (400 MHz, $CDCl_3$) spectra of **5a**



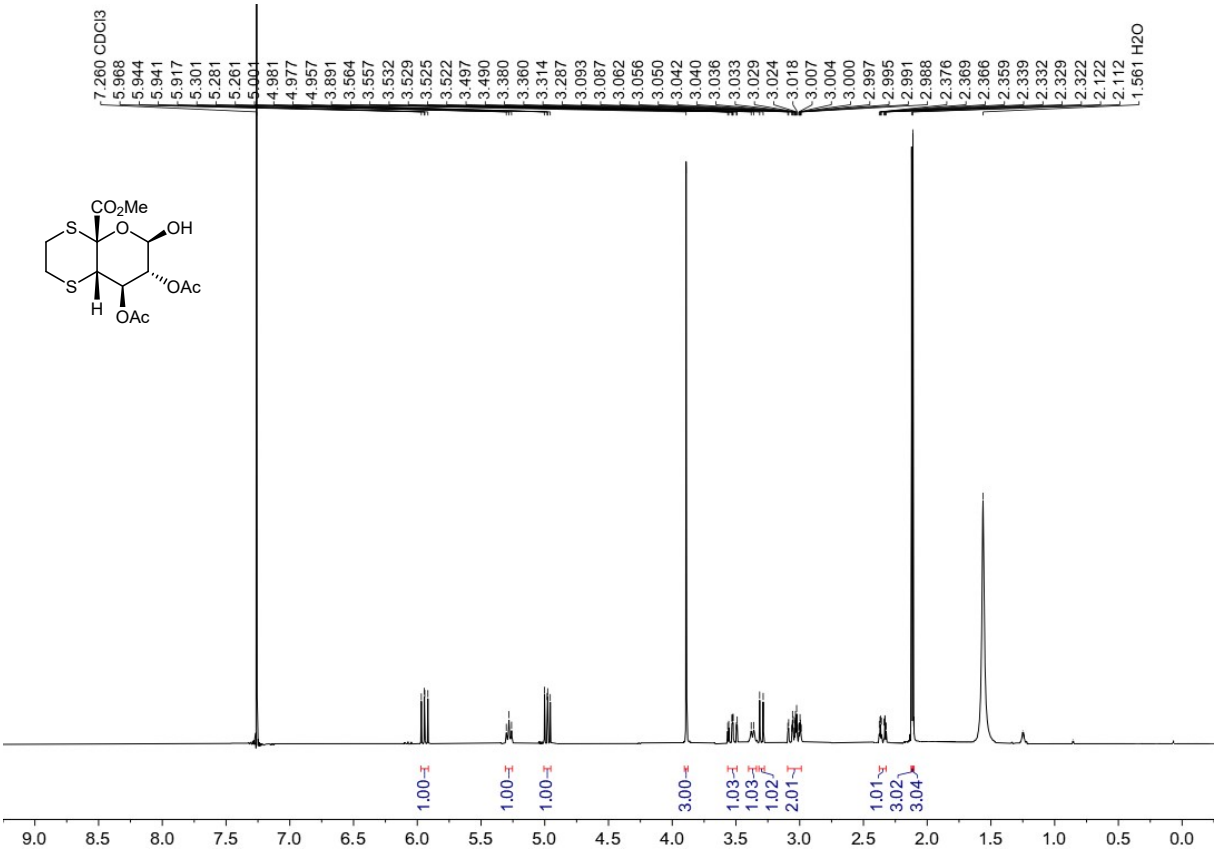
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **6a**

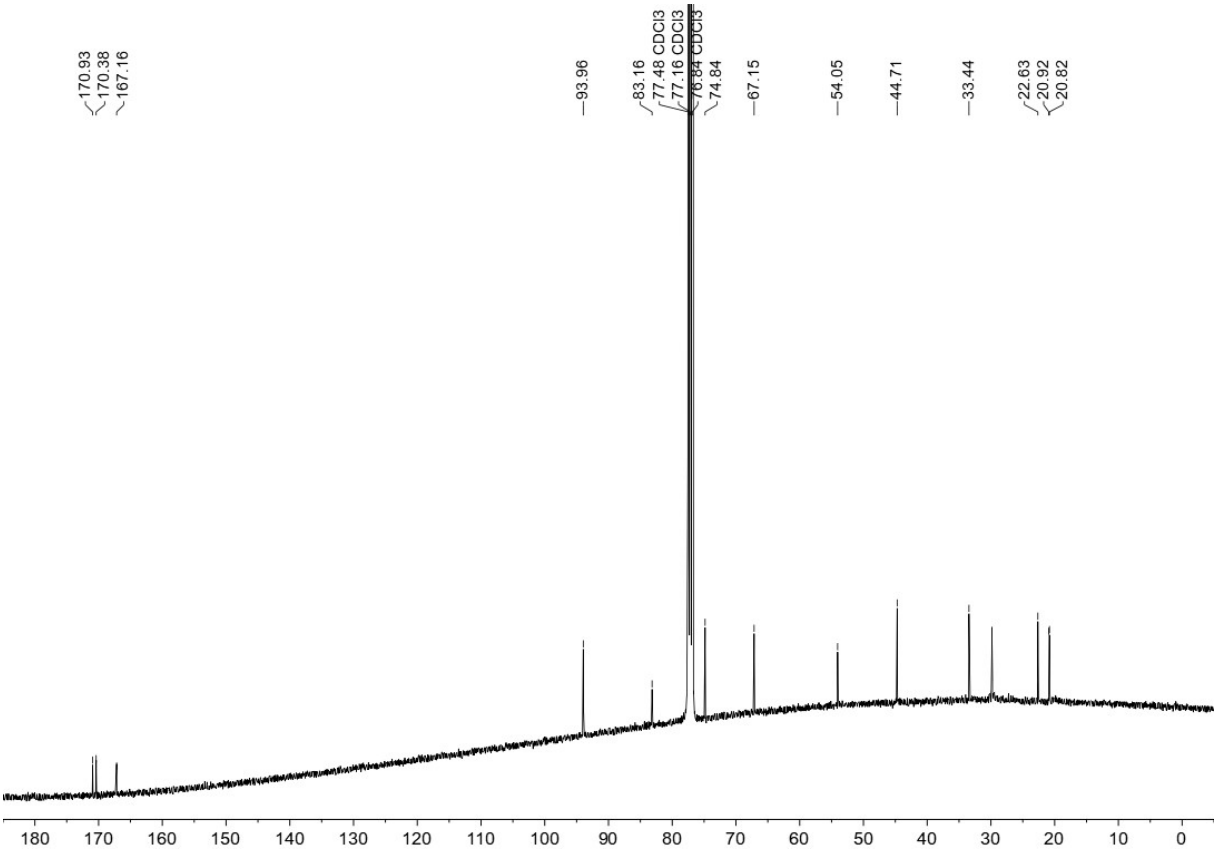


2D $^{1}H,^{1}H$-NOESY (400 MHz, $CDCl_3$) spectra of **6a**

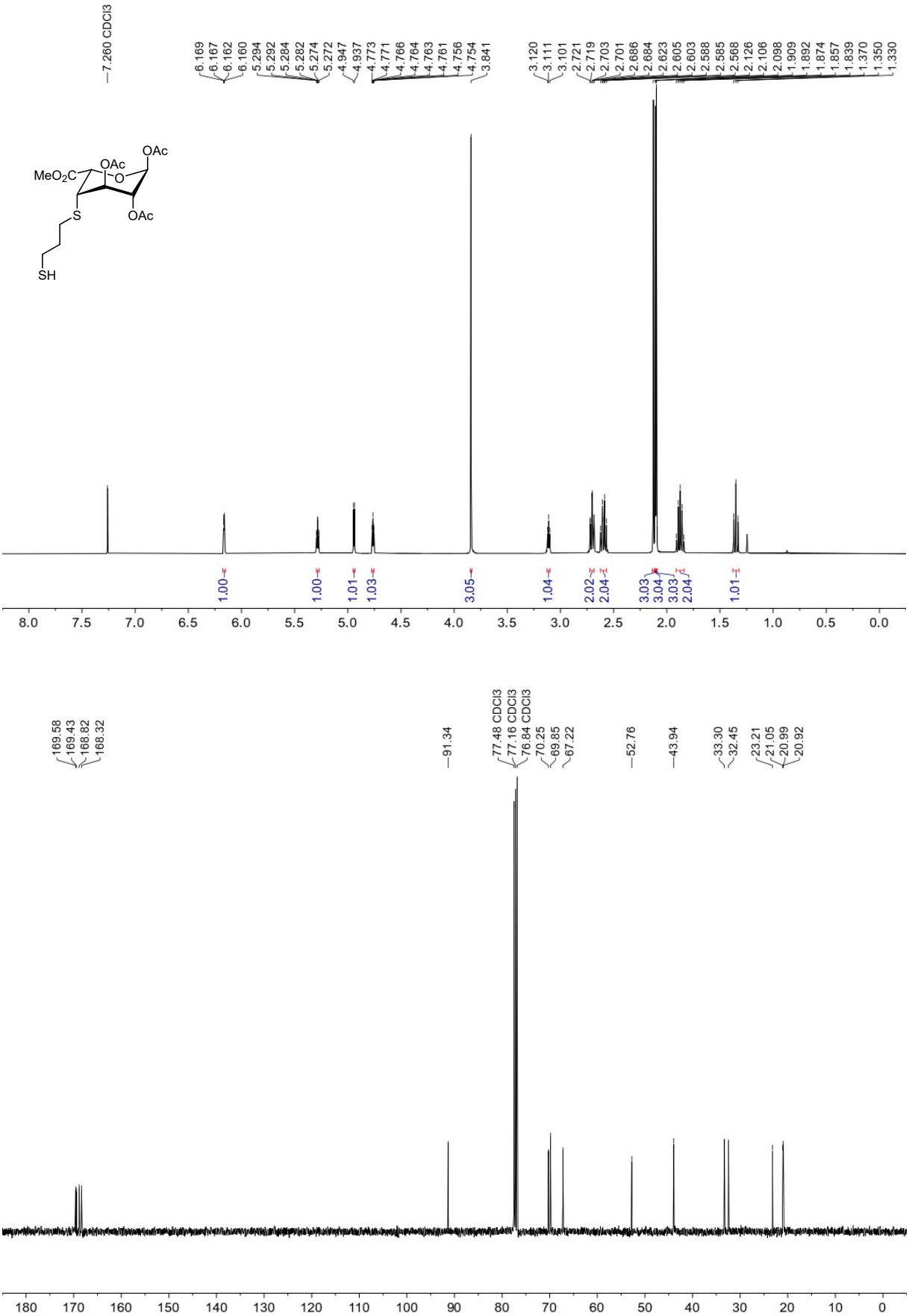


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **6a'**

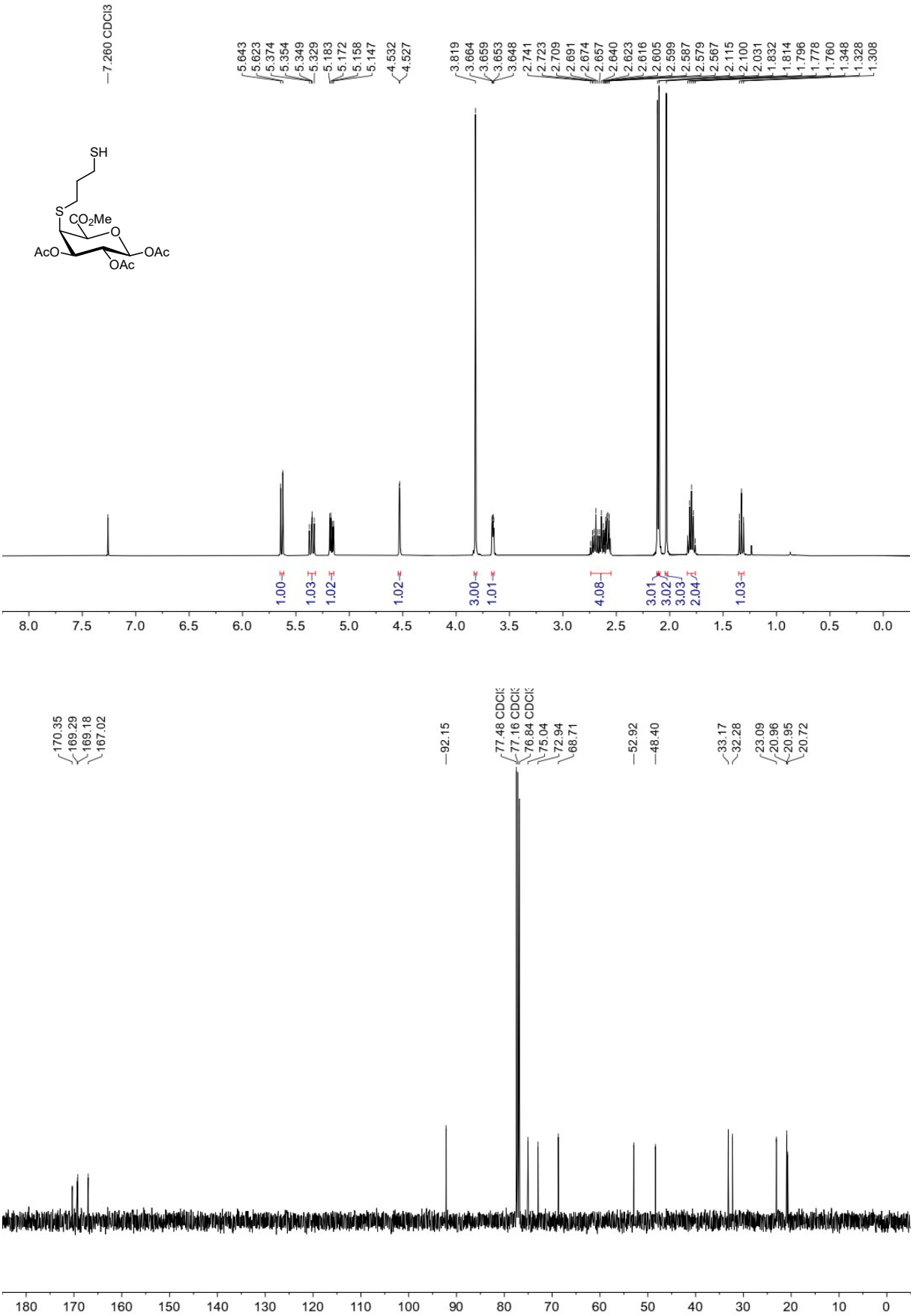




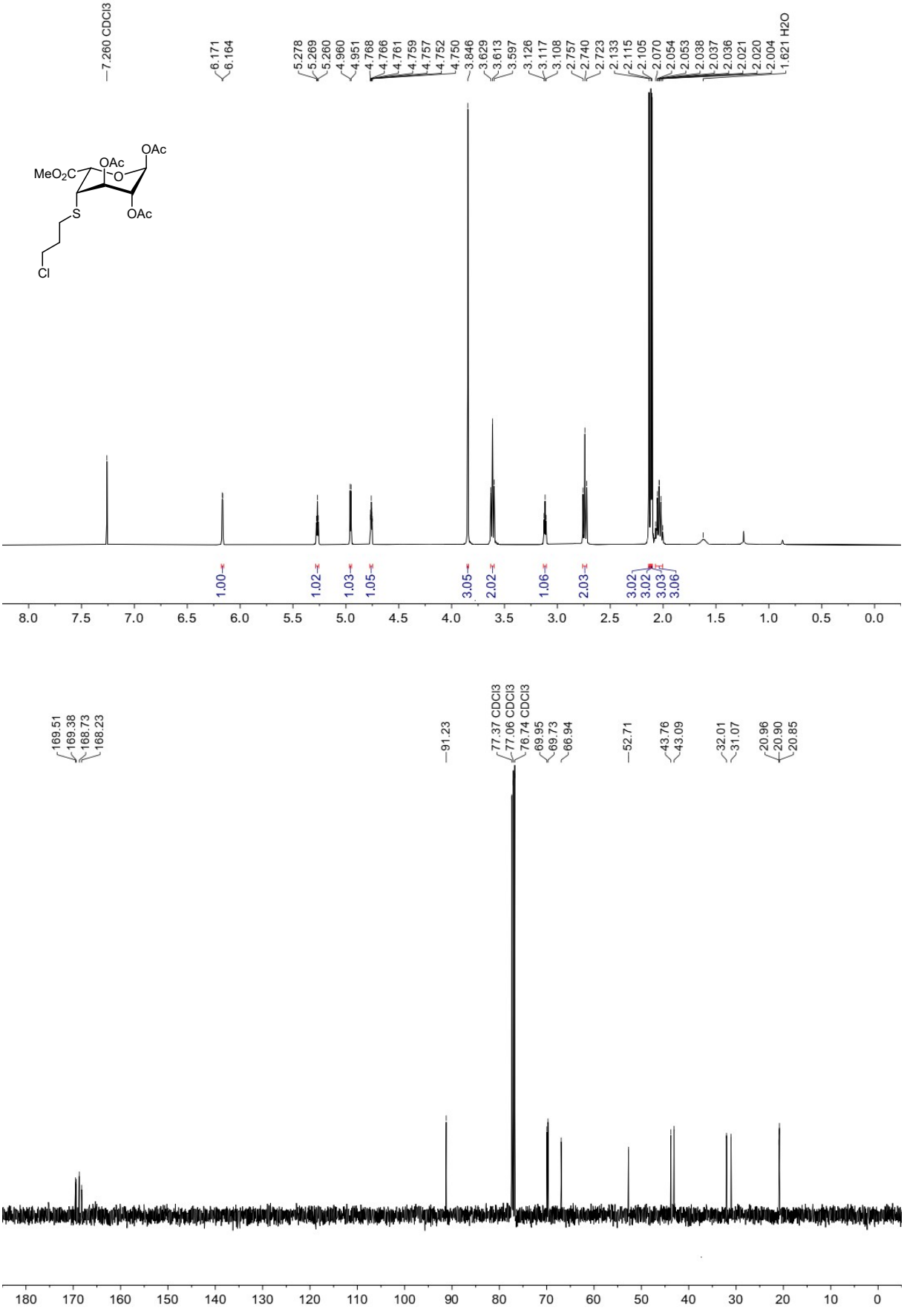
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **5b**



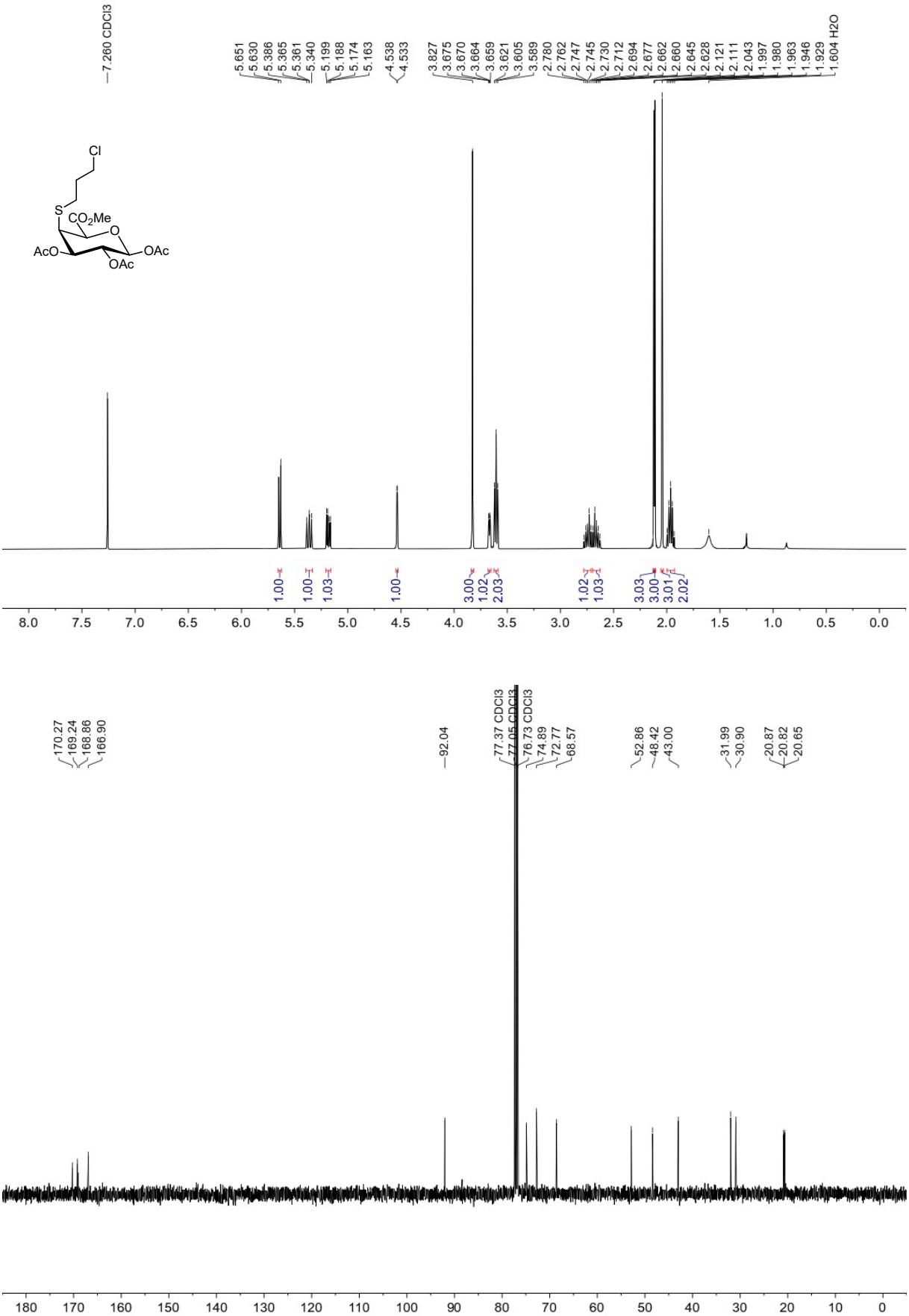
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **6b**



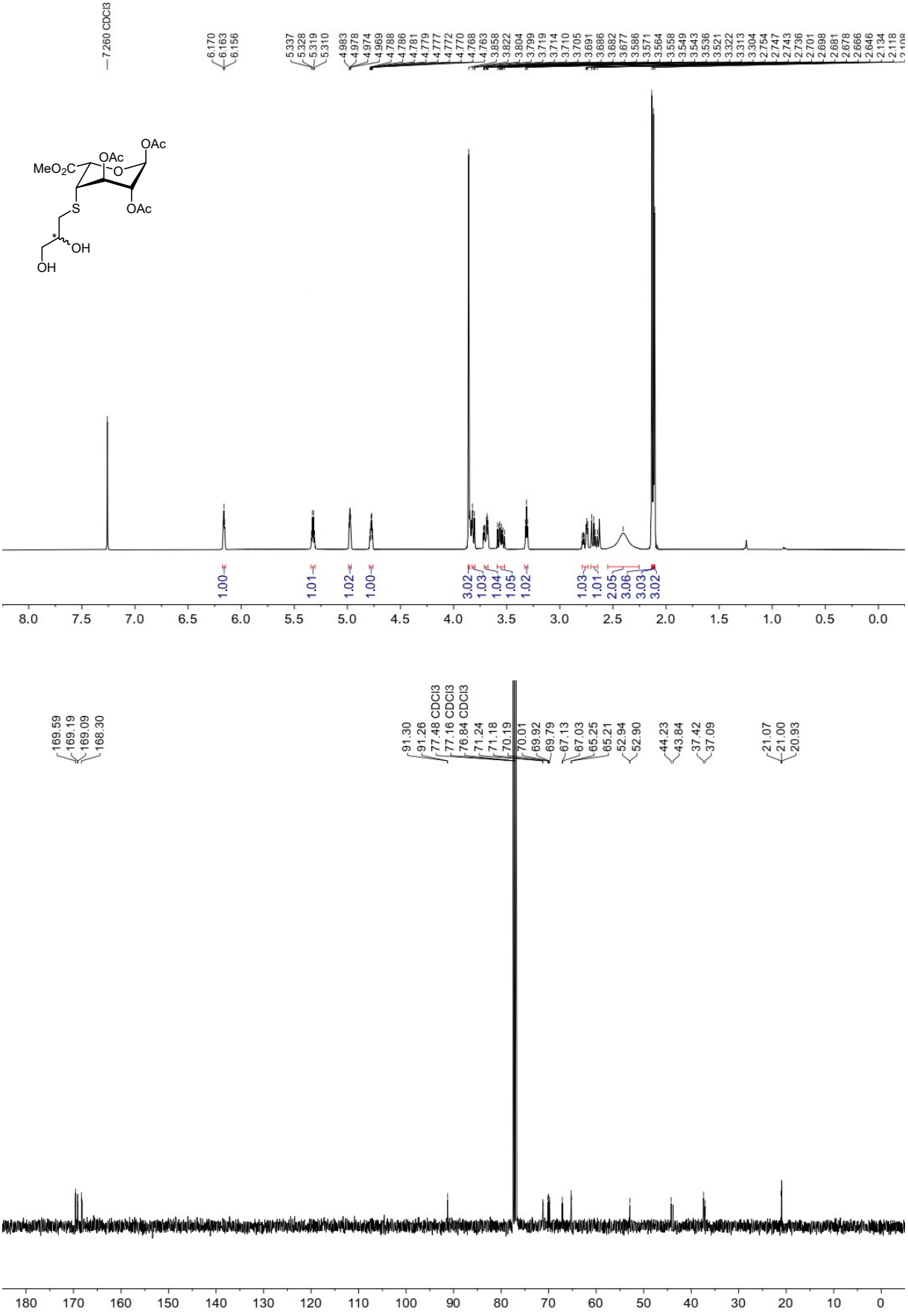
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **5c**



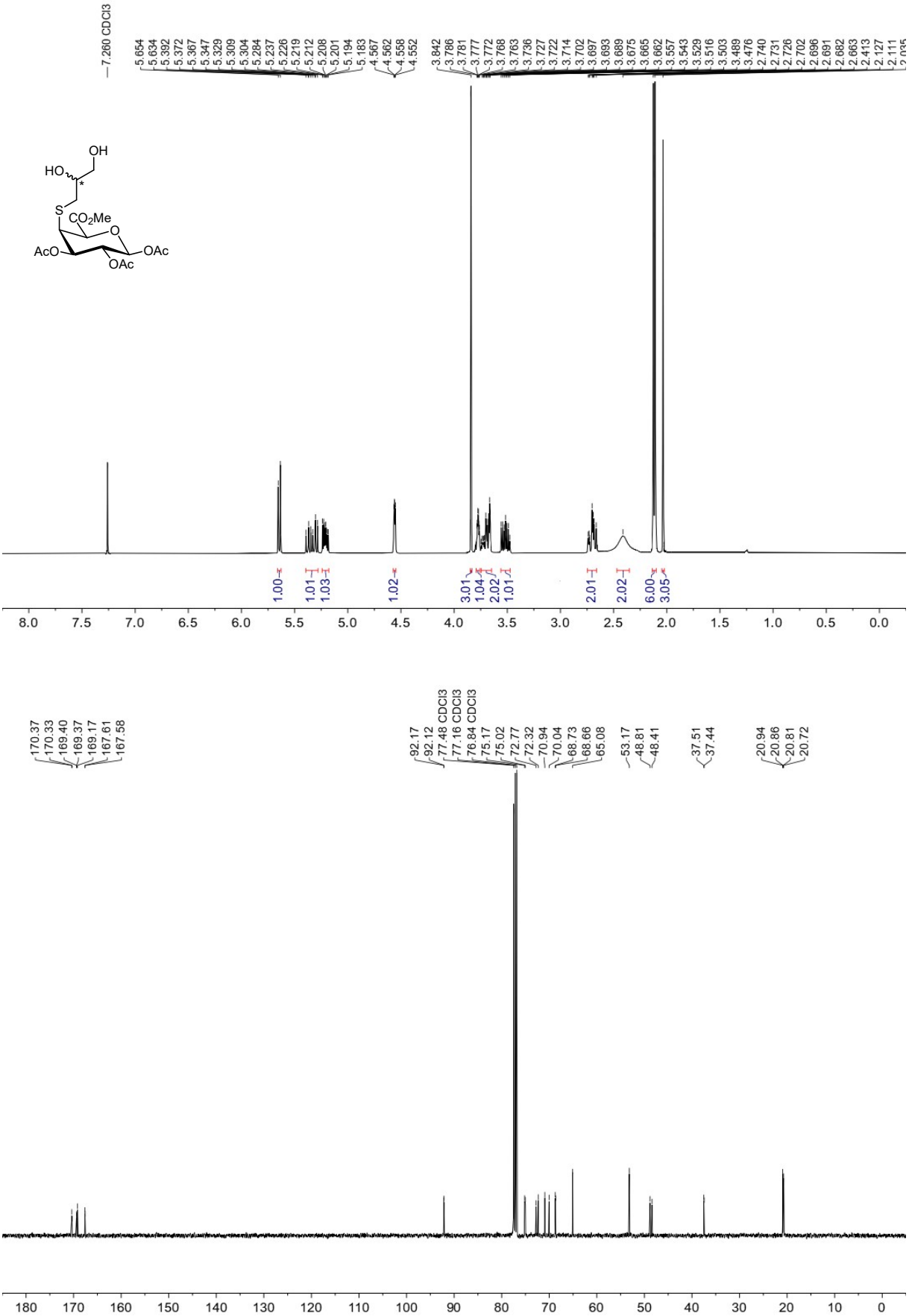
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **6c**



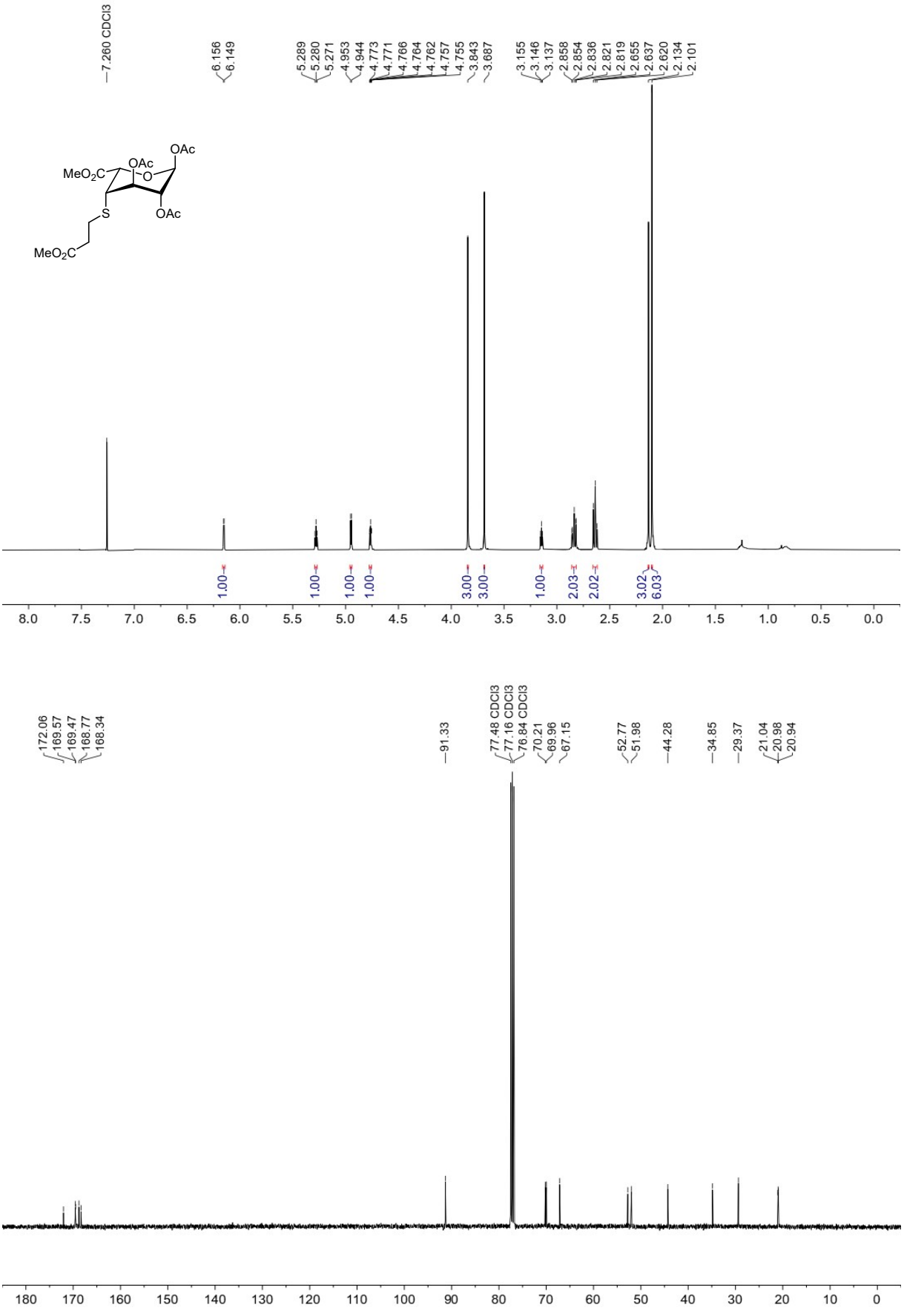
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **5d**



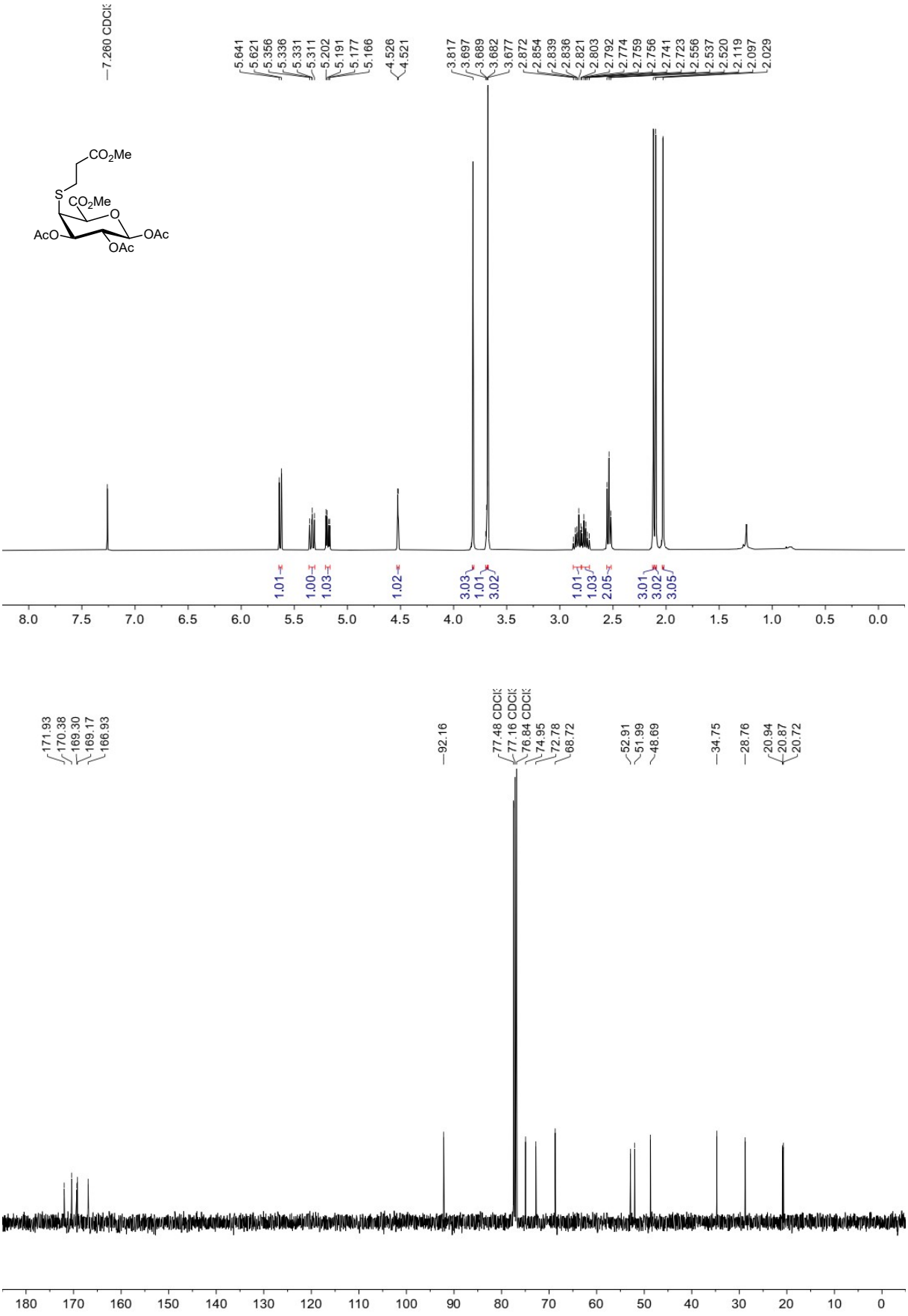
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **6d**



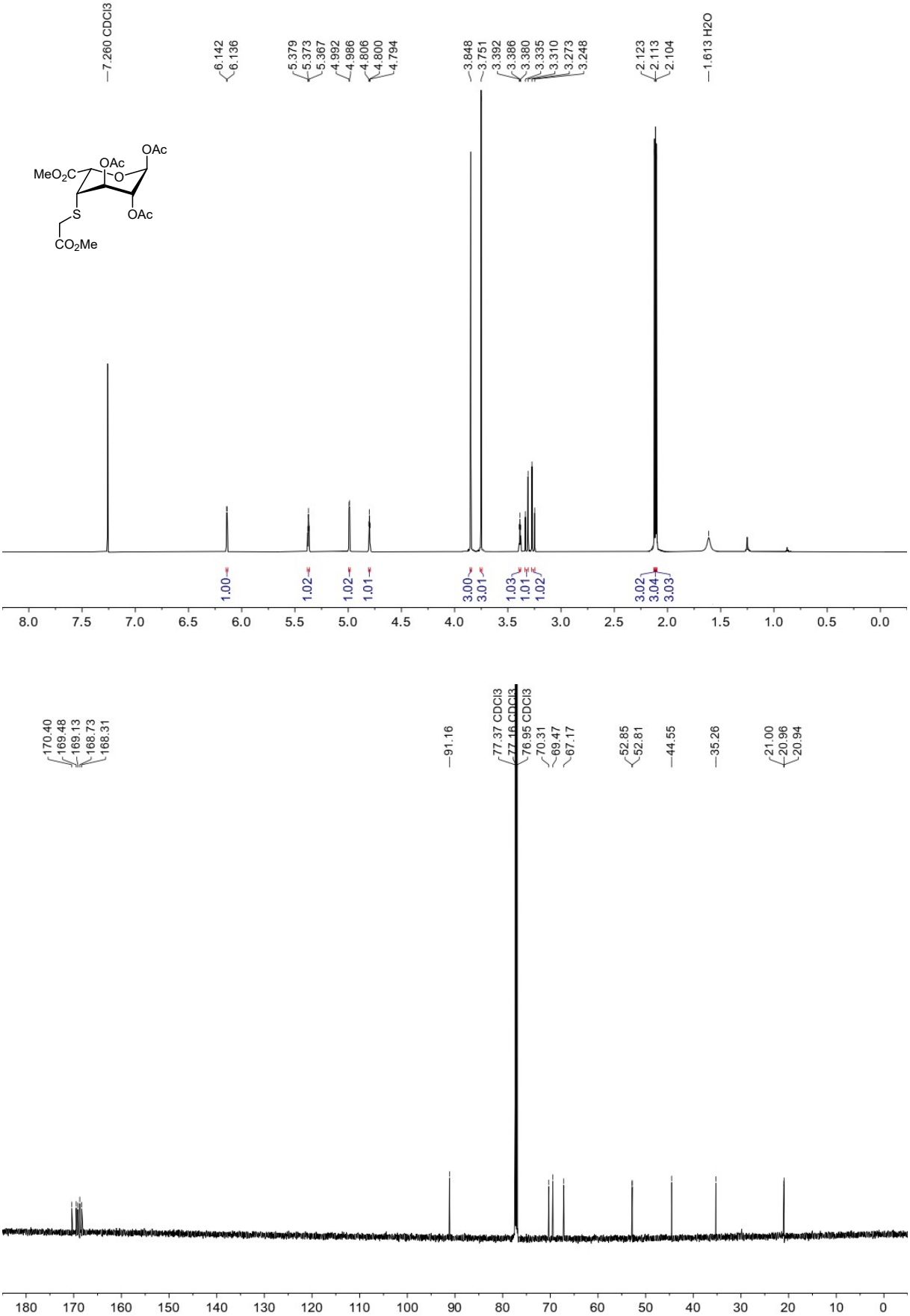
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **5e**



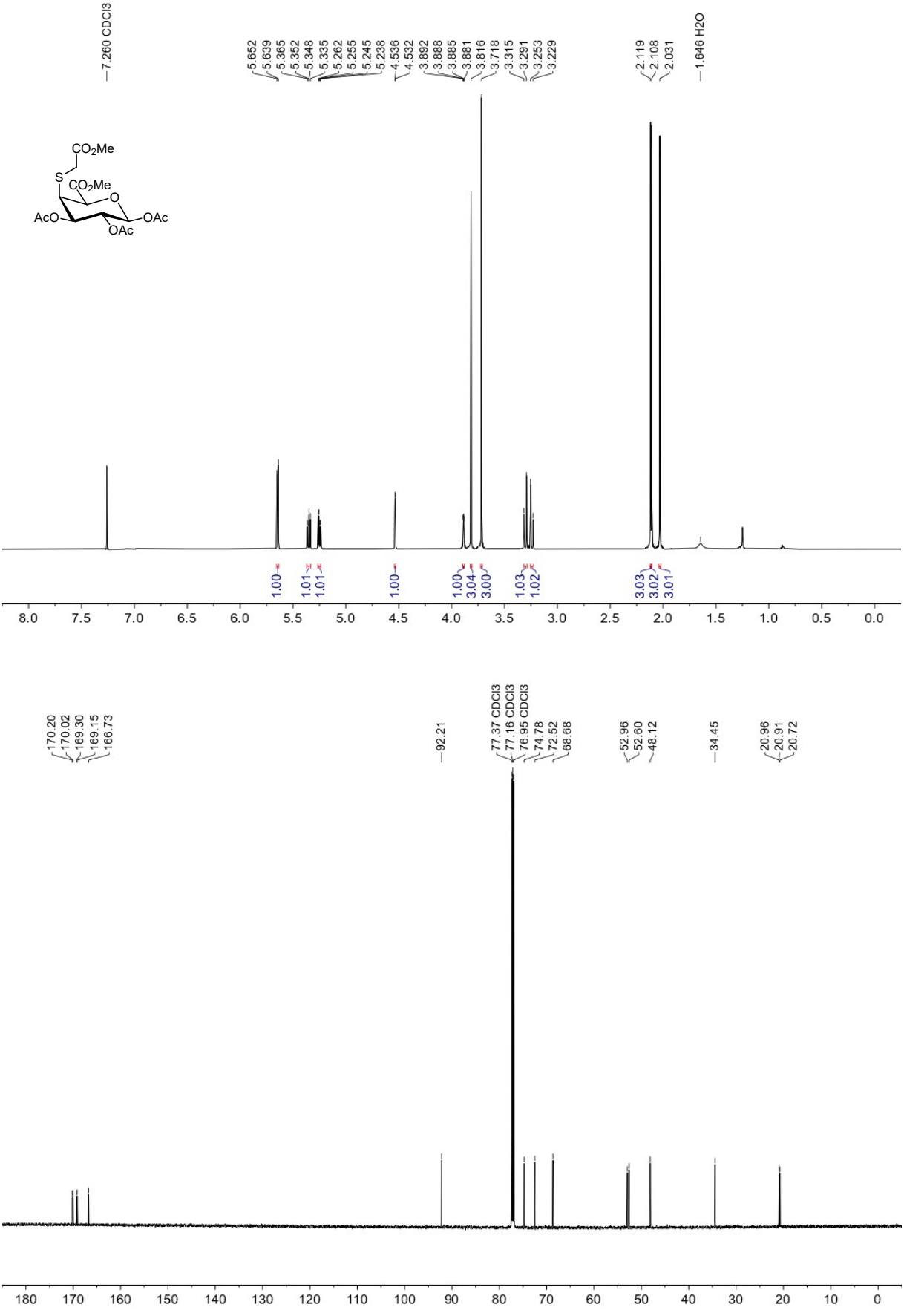
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **6e**



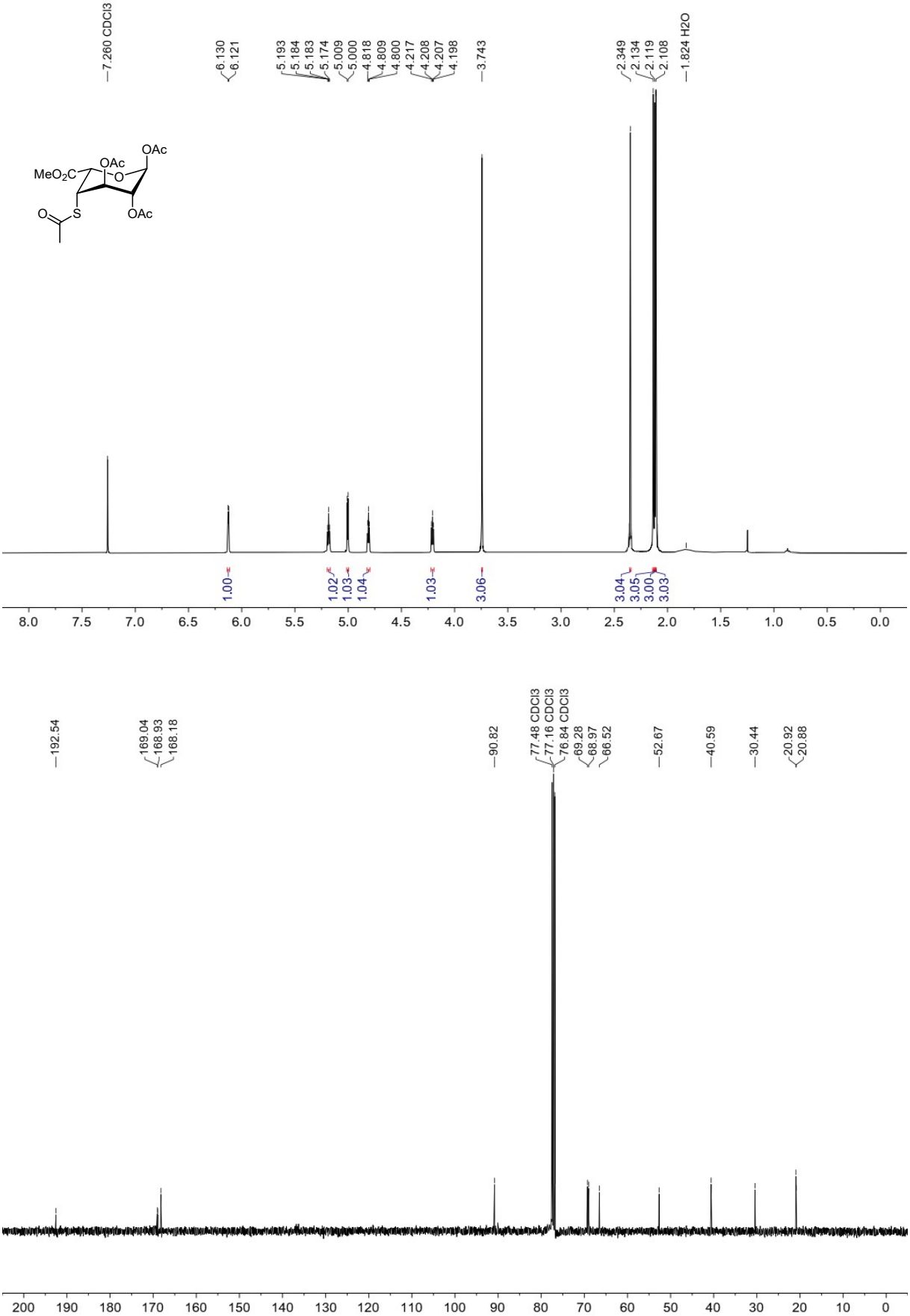
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectra of **5f**



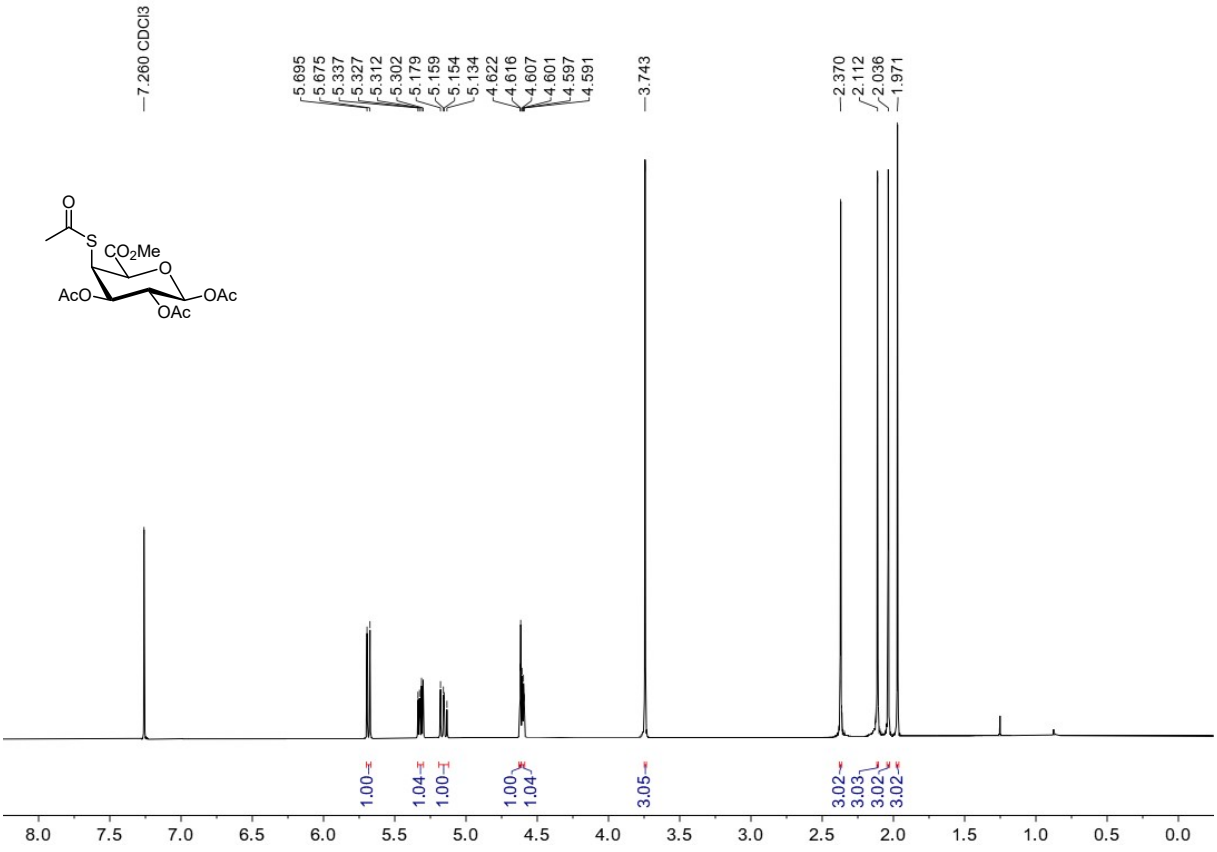
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectra of **6f**

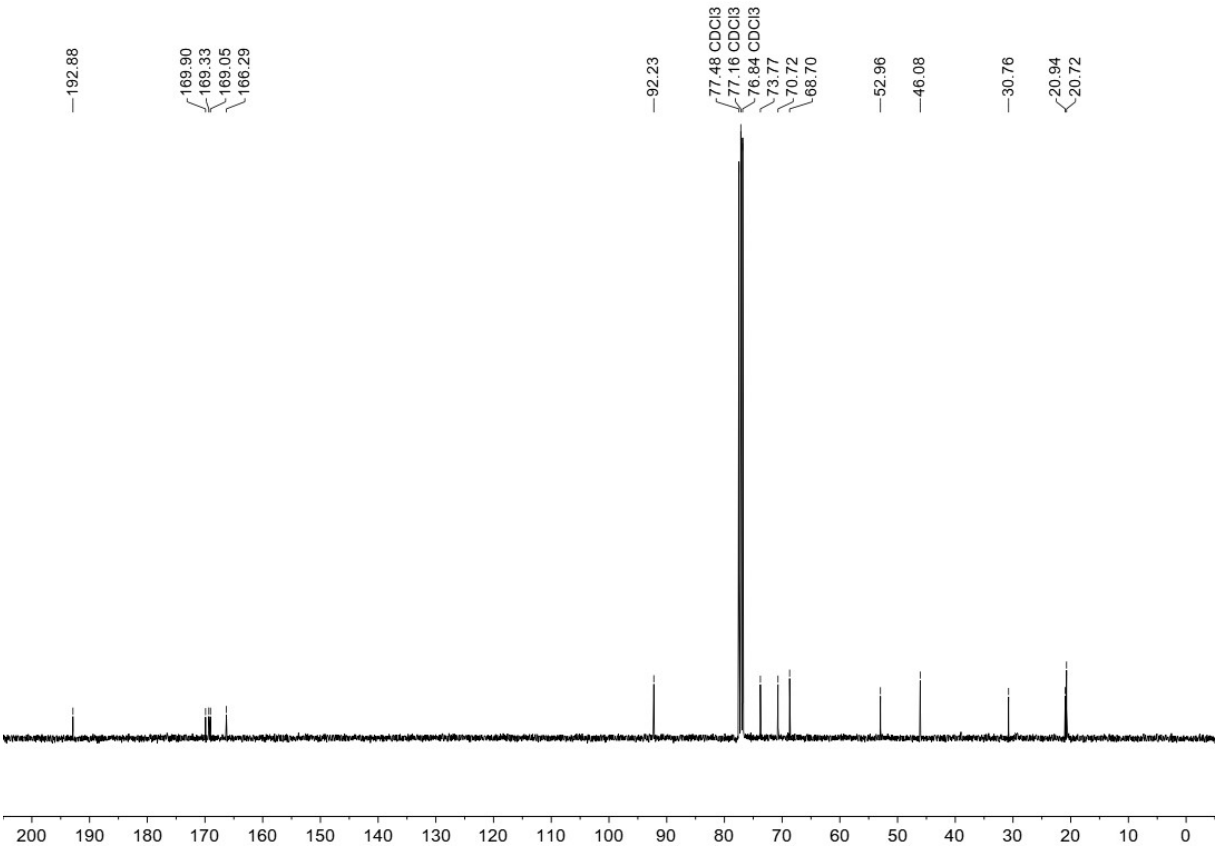


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **5g**

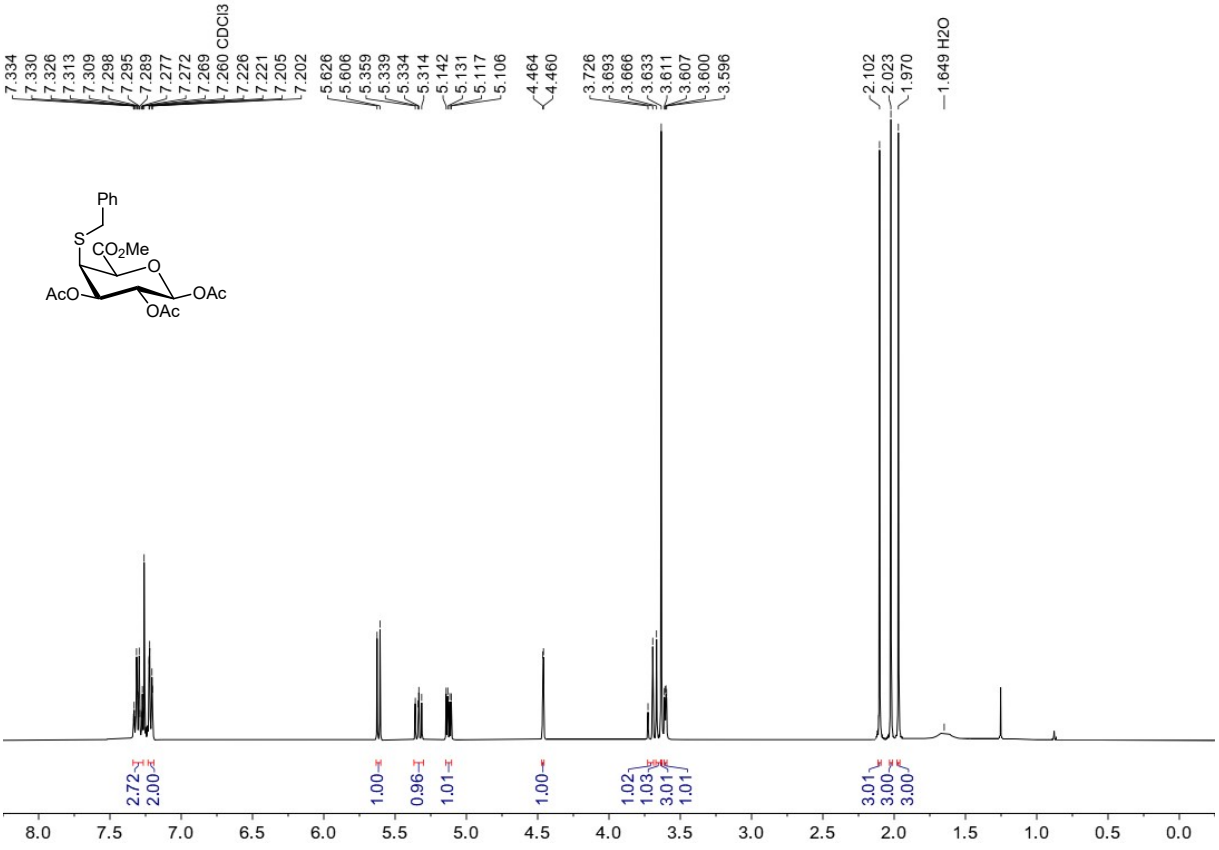


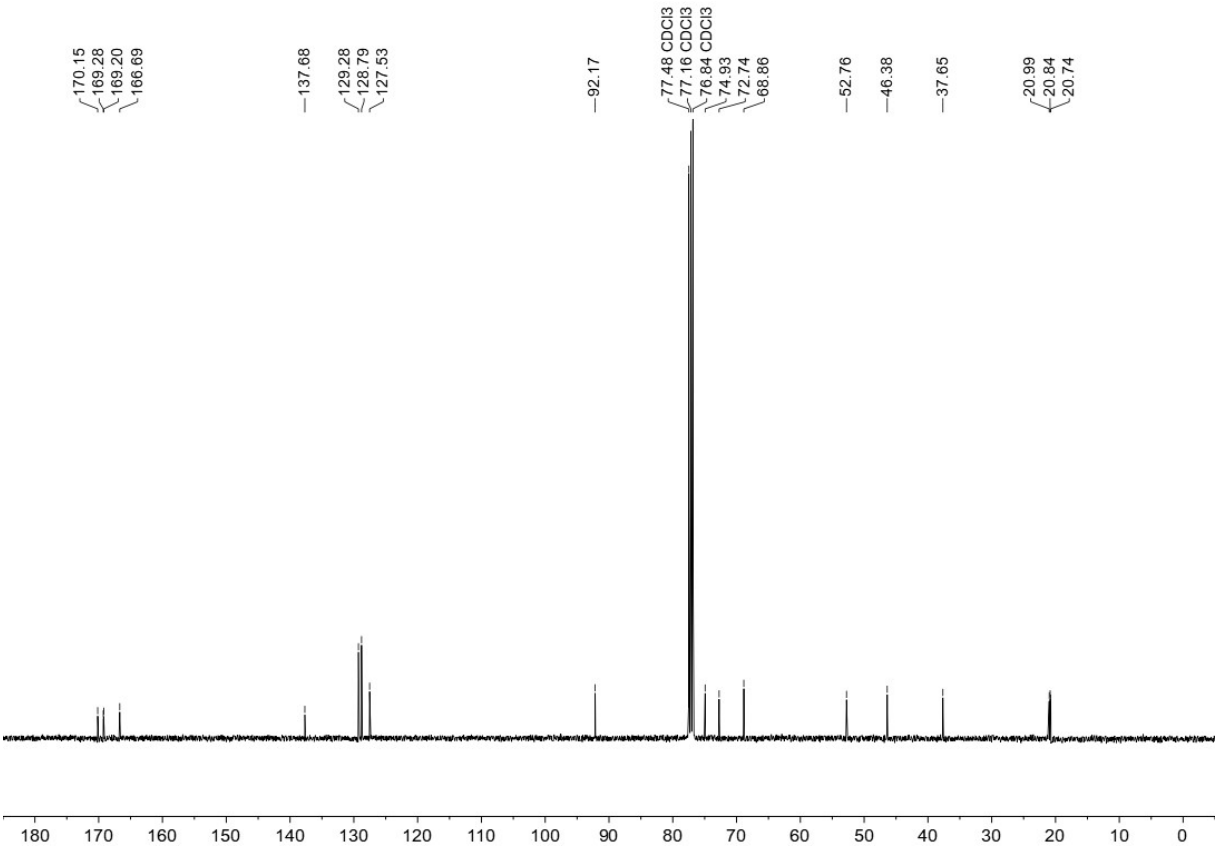
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **6g**





^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **6h**

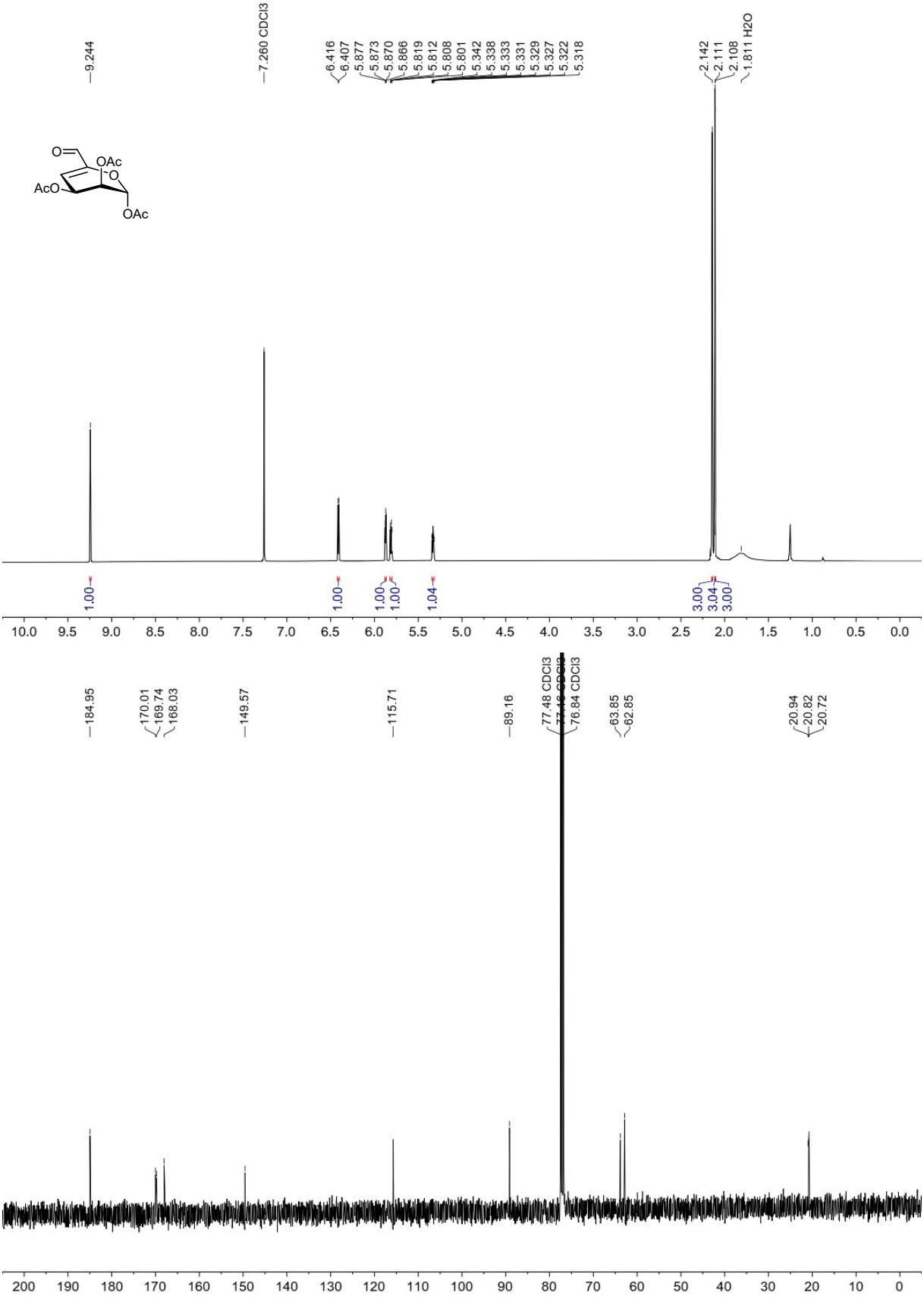




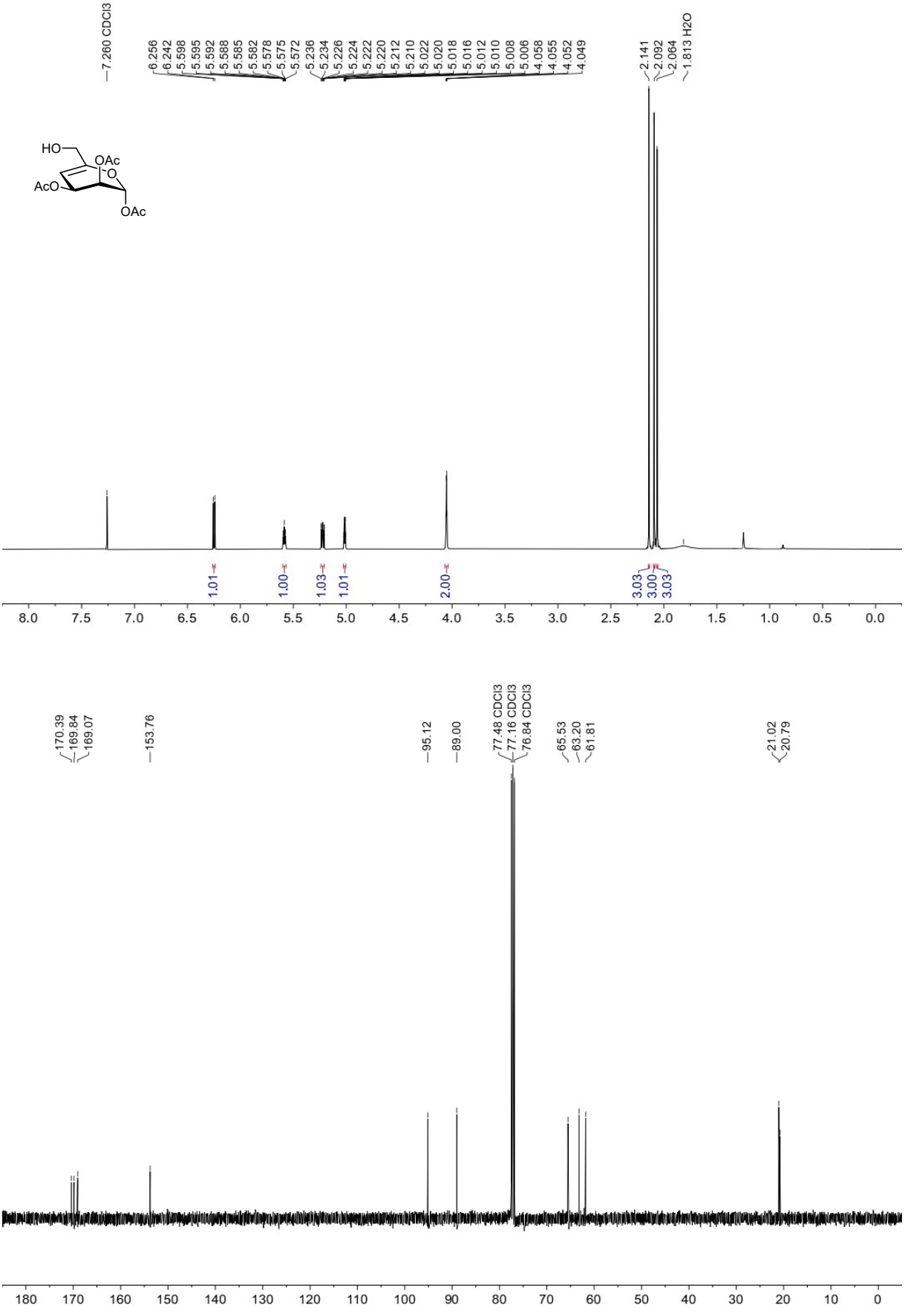
4. Synthesis of 4,5-glycals 7-10

4.1. Synthesis of 7

^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$NMR (101 MHz, $CDCl_3$) spectra of **12***α*

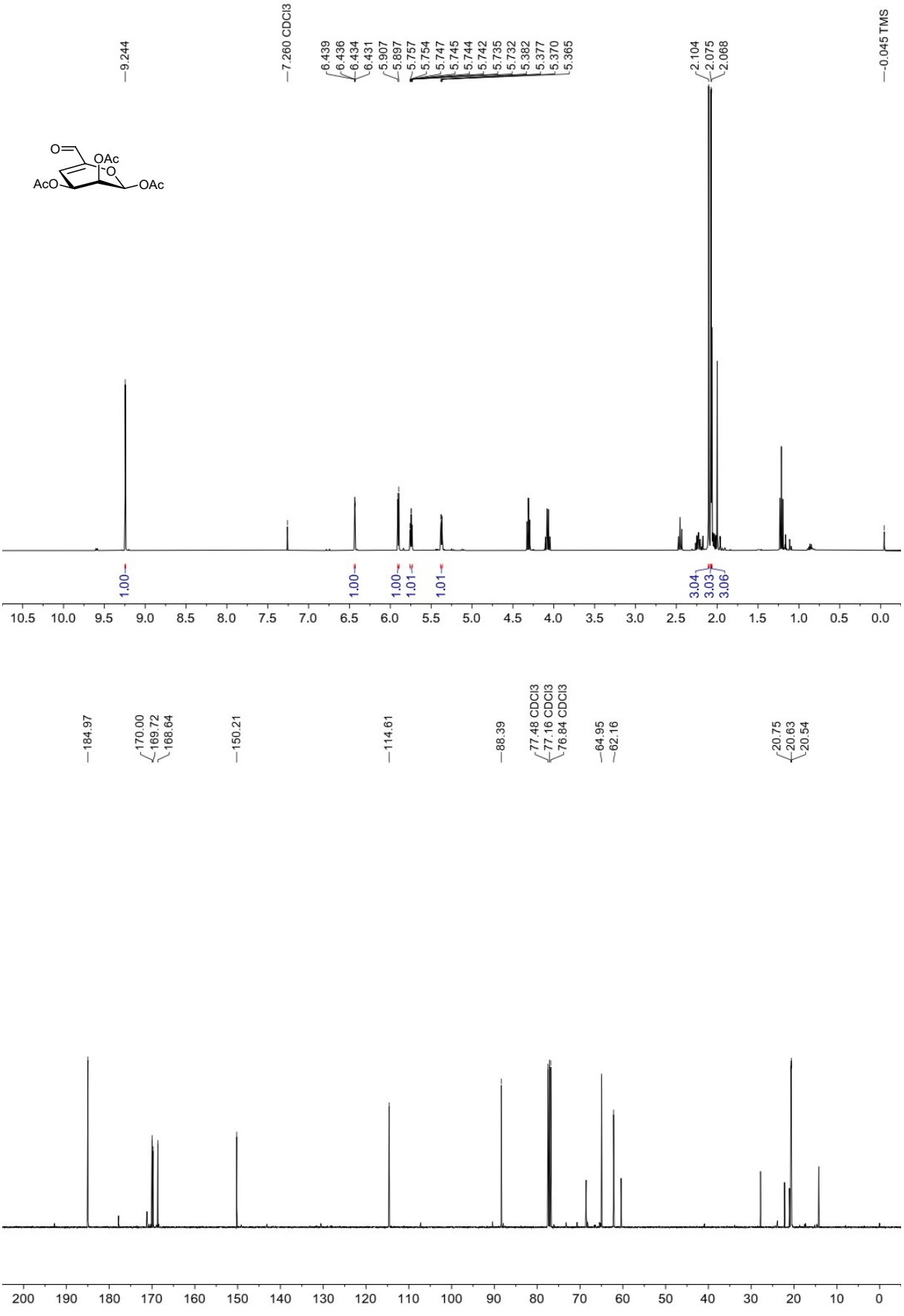


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **7**

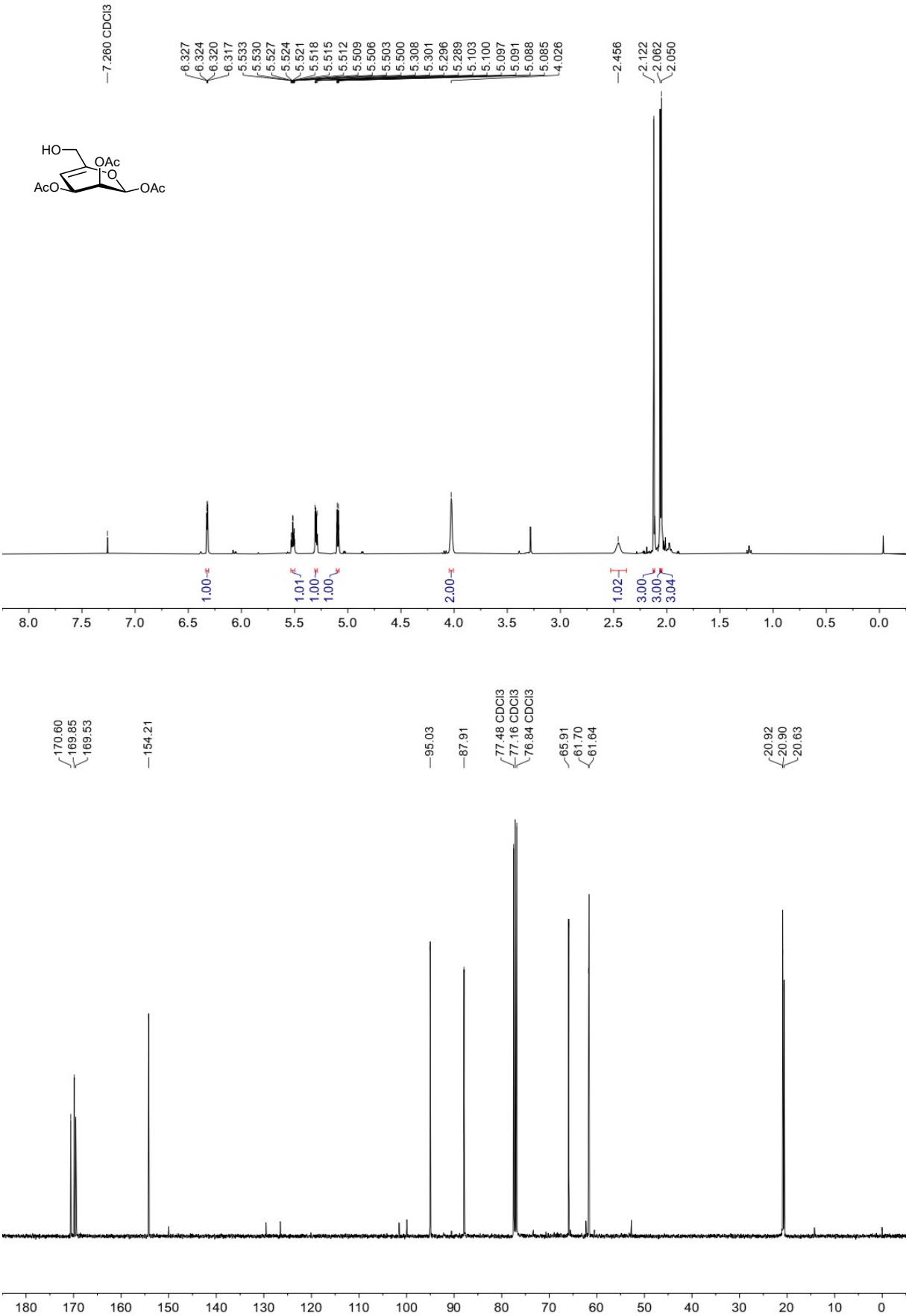


4.2. Synthesis of 8

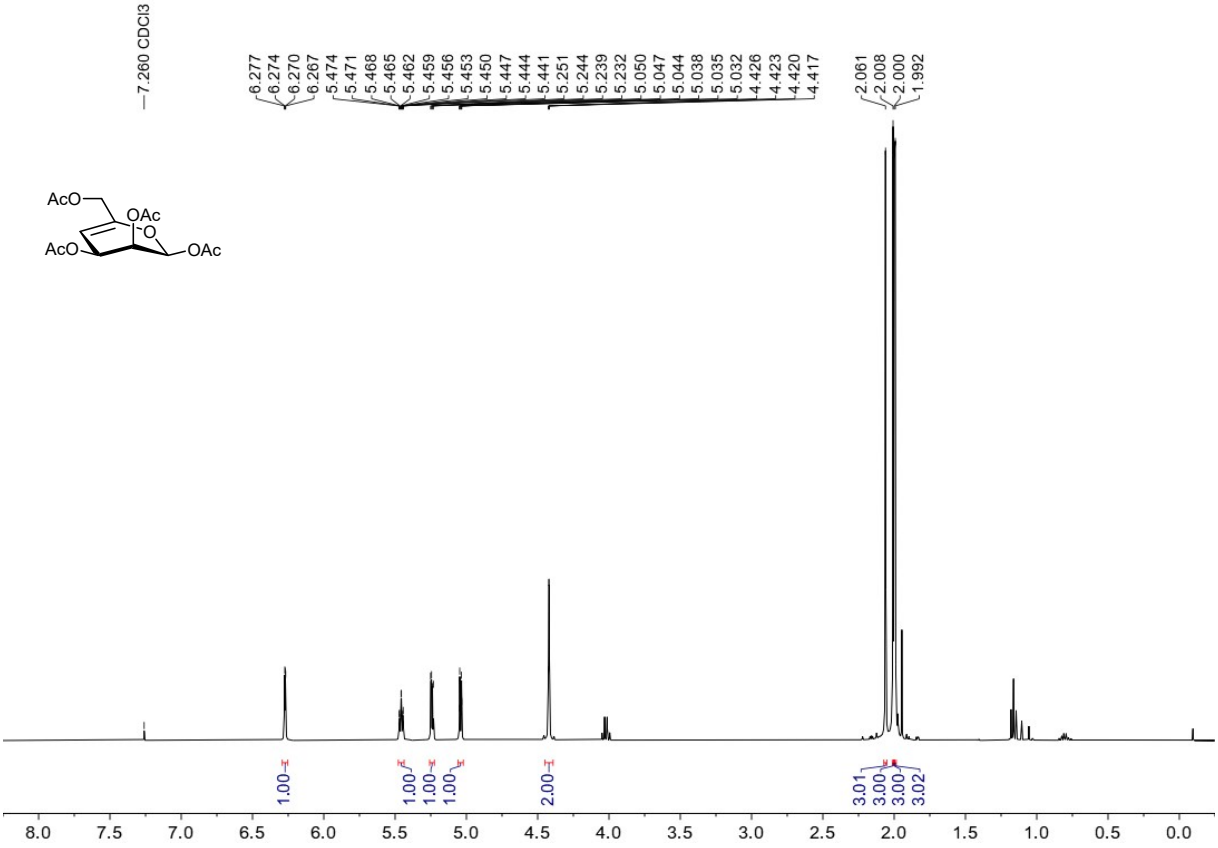
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$NMR (101 MHz, $CDCl_3$) spectra of **12***β*

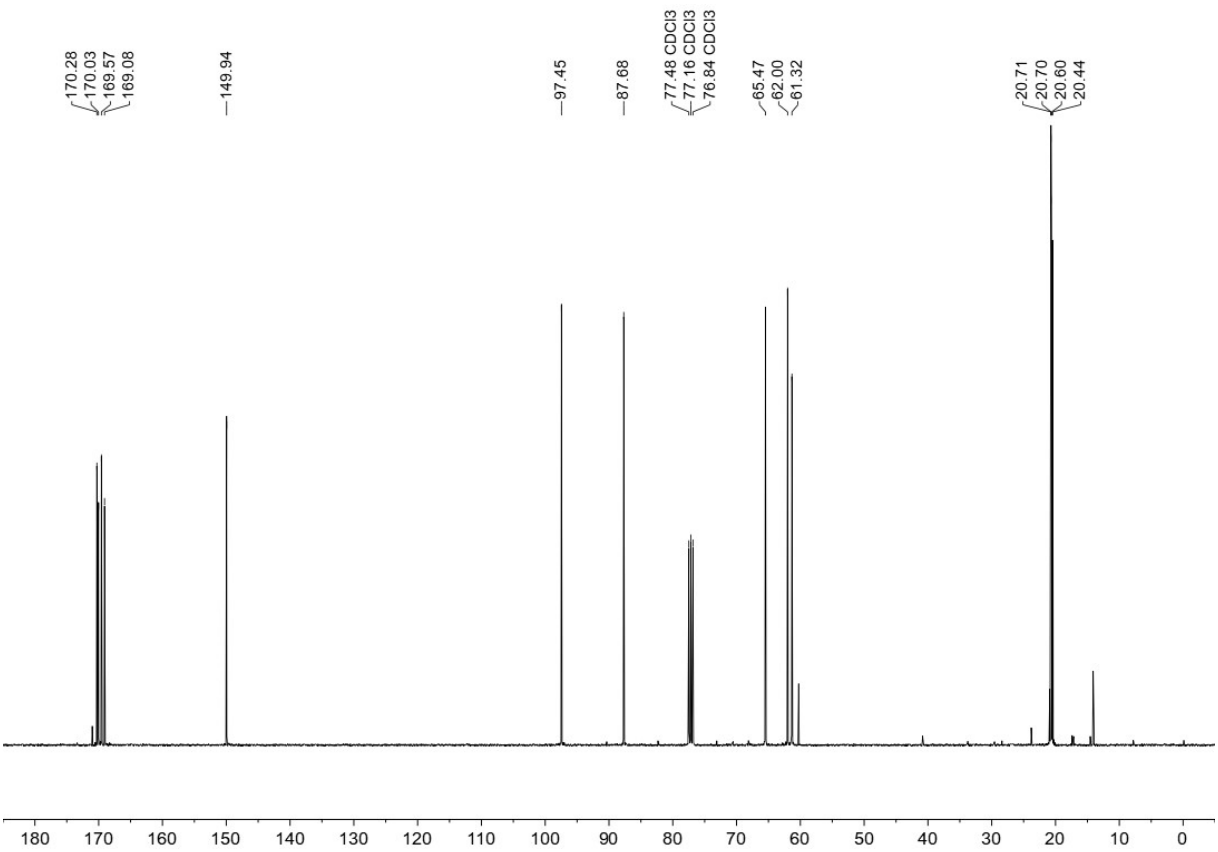


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$NMR (101 MHz, $CDCl_3$) spectra of **13**



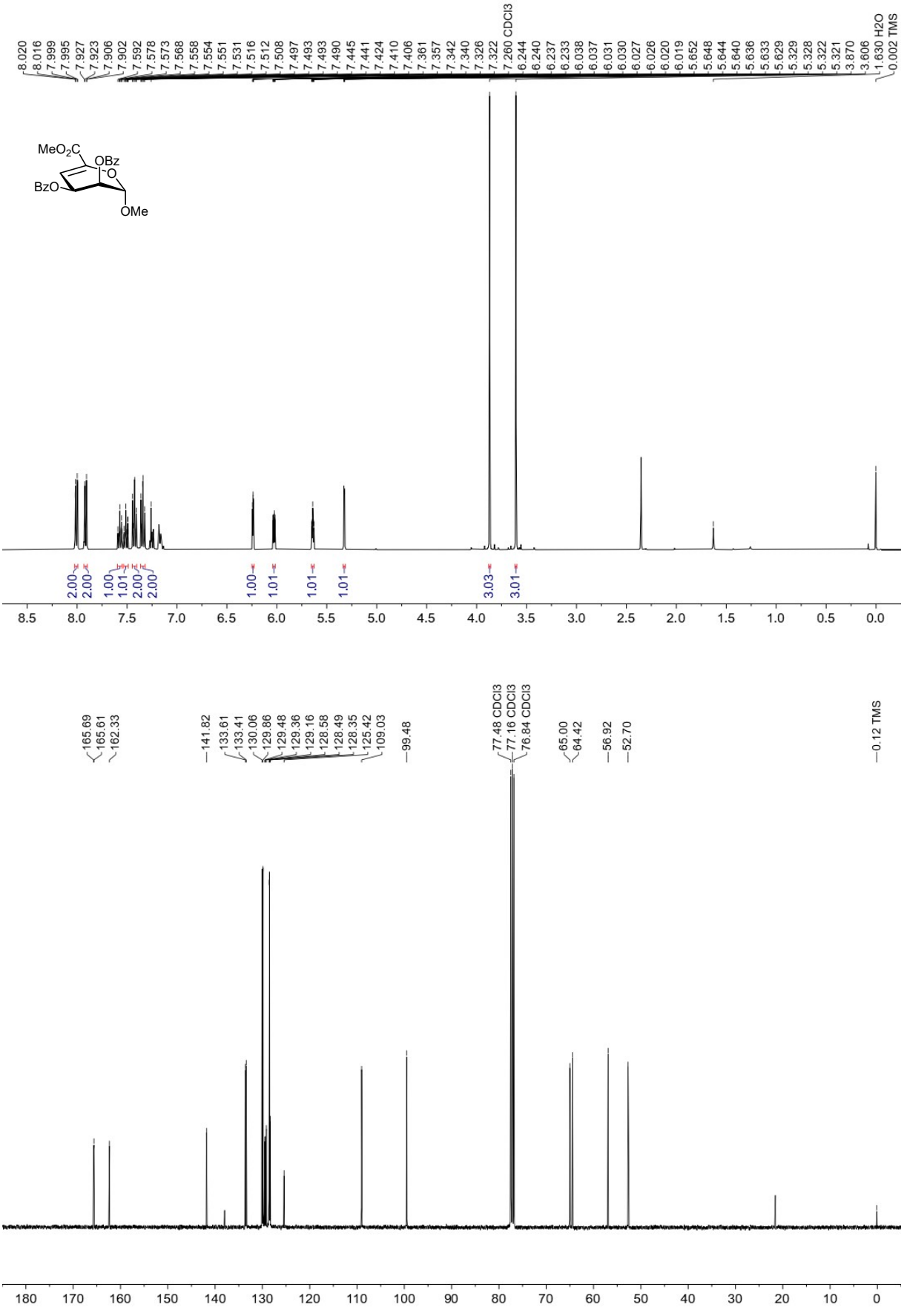
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$NMR (101 MHz, $CDCl_3$) spectra of **8**





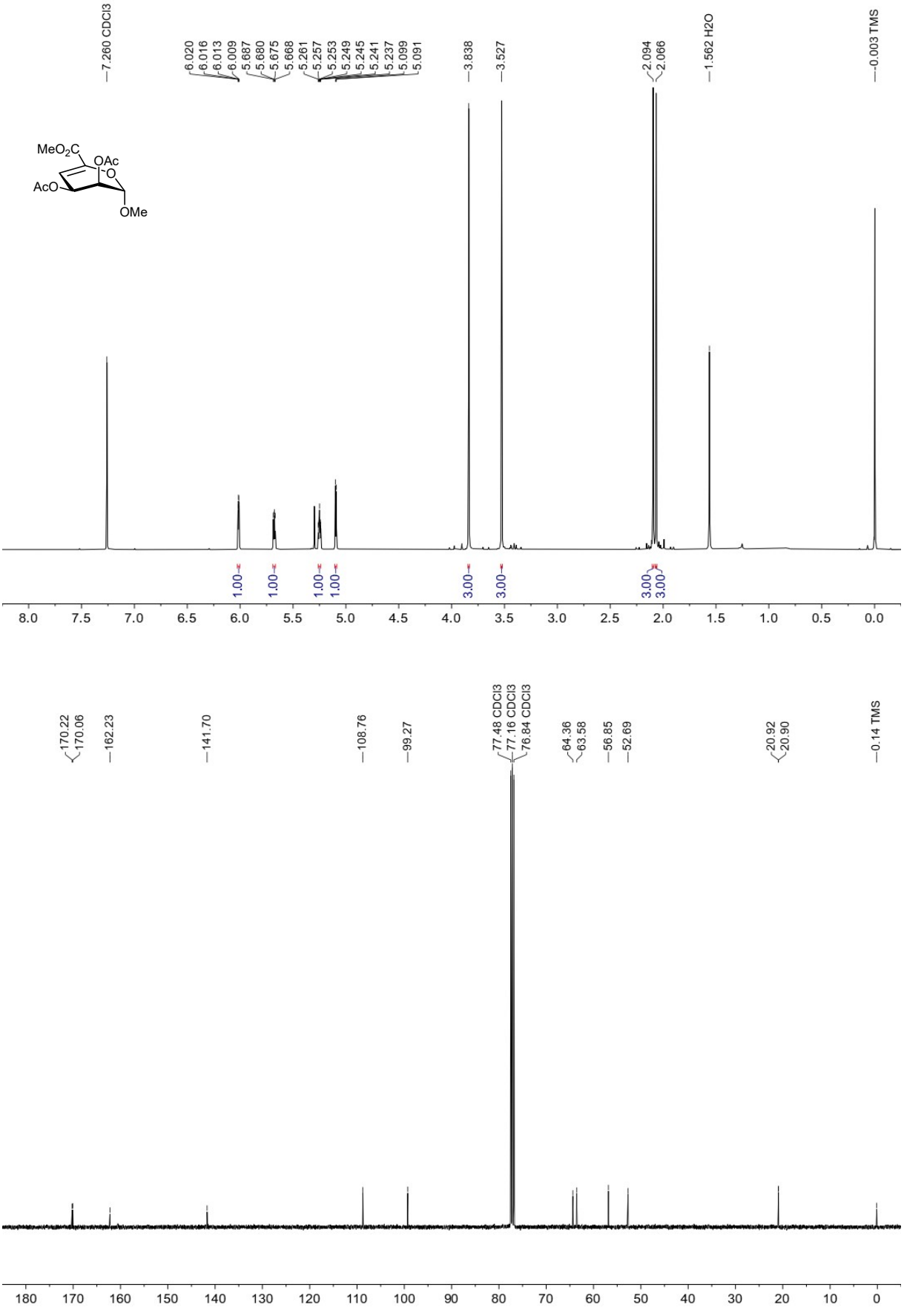
4.3. Synthesis of 9

^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$NMR (101 MHz, $CDCl_3$) spectra of **9**

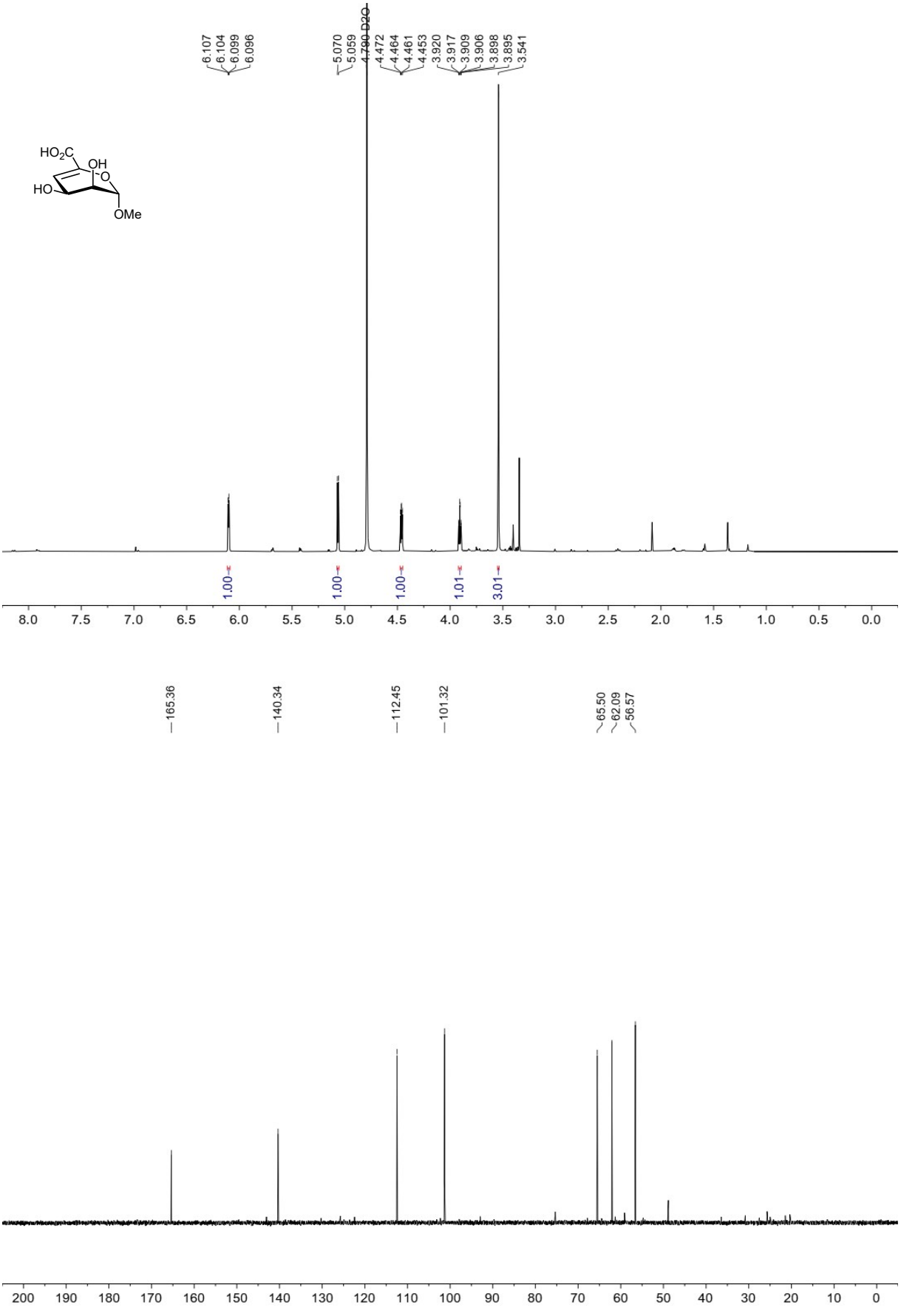


4.4. Synthesis of 10

^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$NMR (101 MHz, $CDCl_3$) spectra of **17**

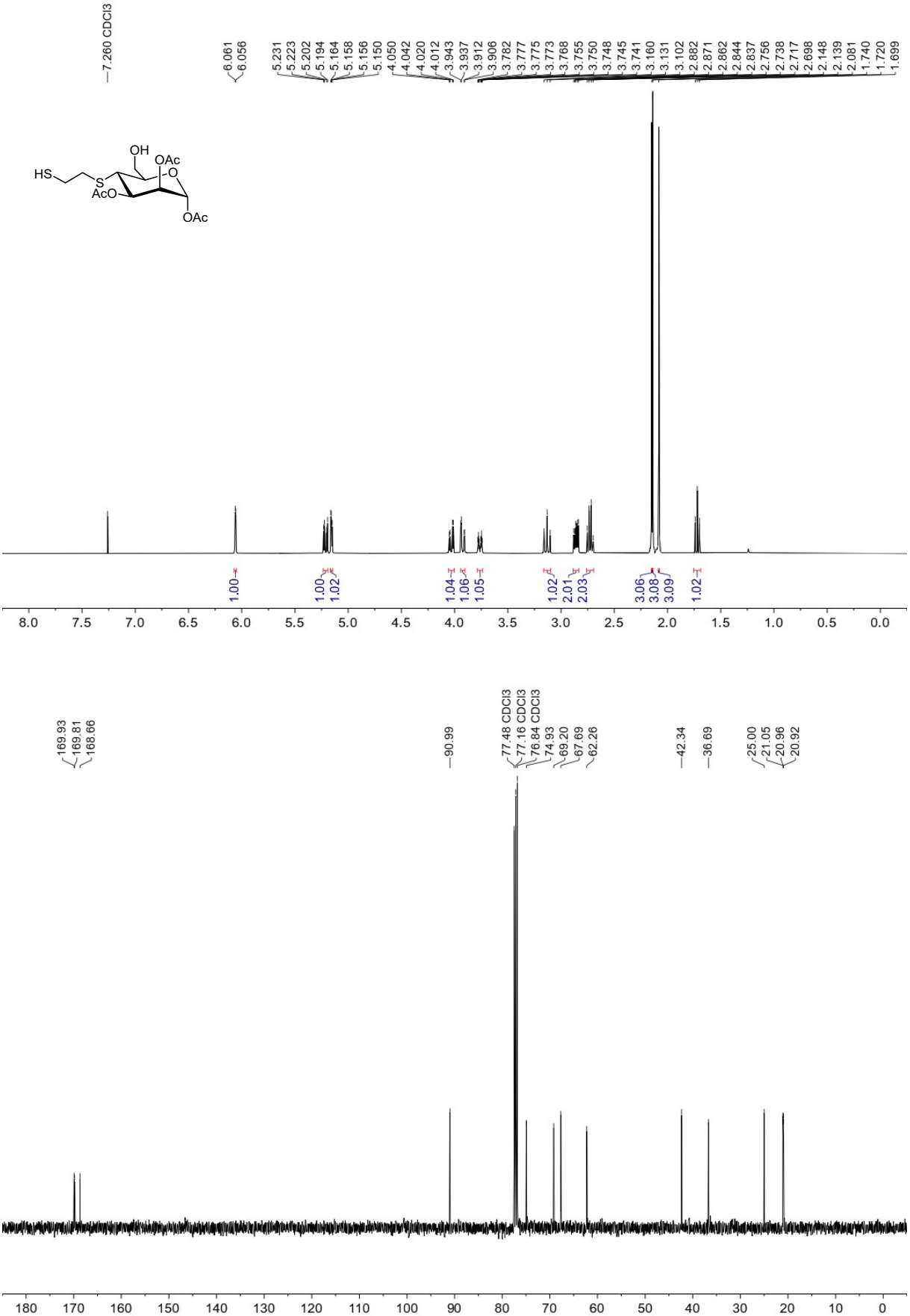


^{1}H NMR (400 MHz, D_2O) and $^{13}C\{^{1}H\}$NMR (101 MHz, D_2O) spectra of **10**

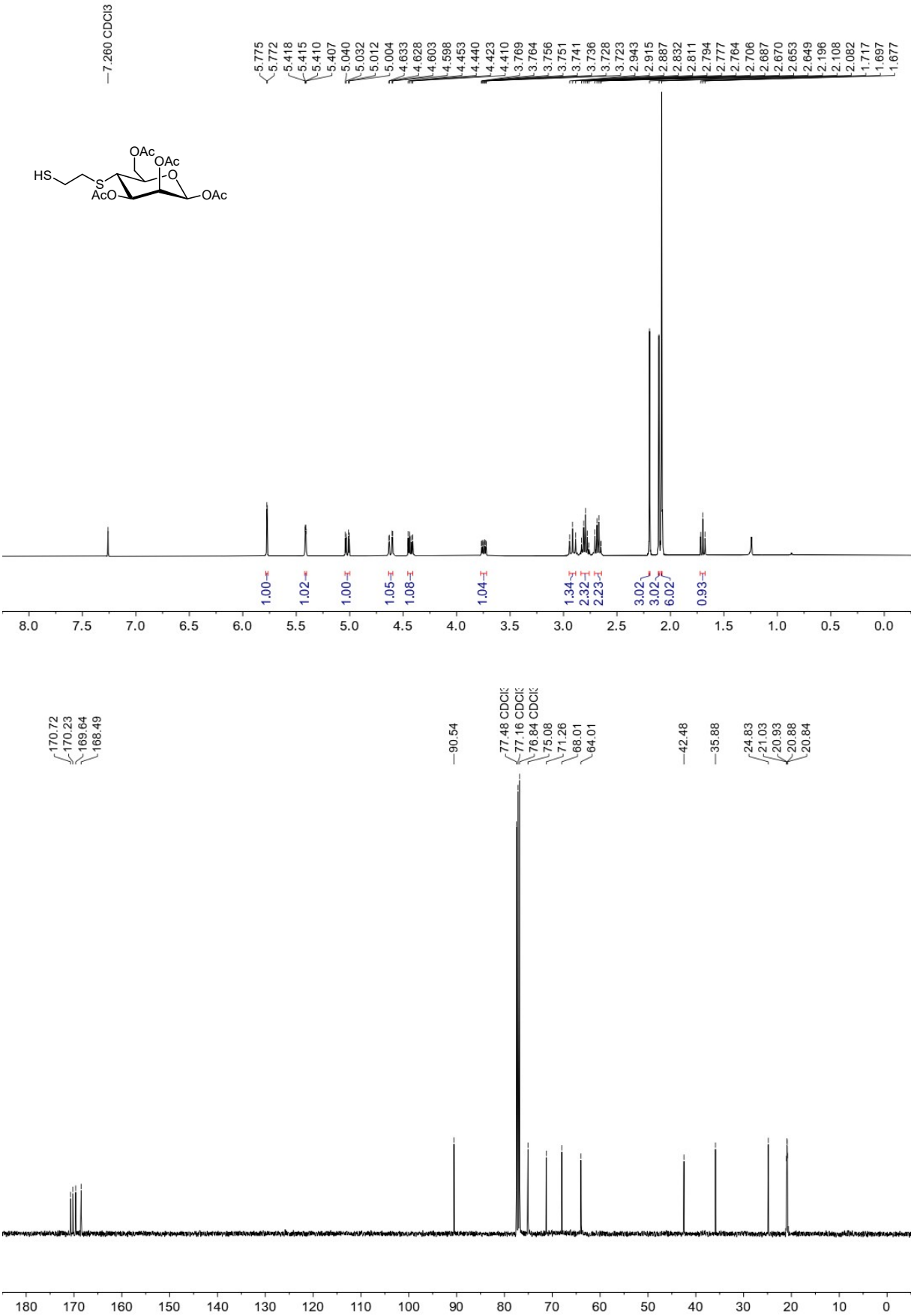


5. Thiol-ene reactions on 4,5-glycals 7-10

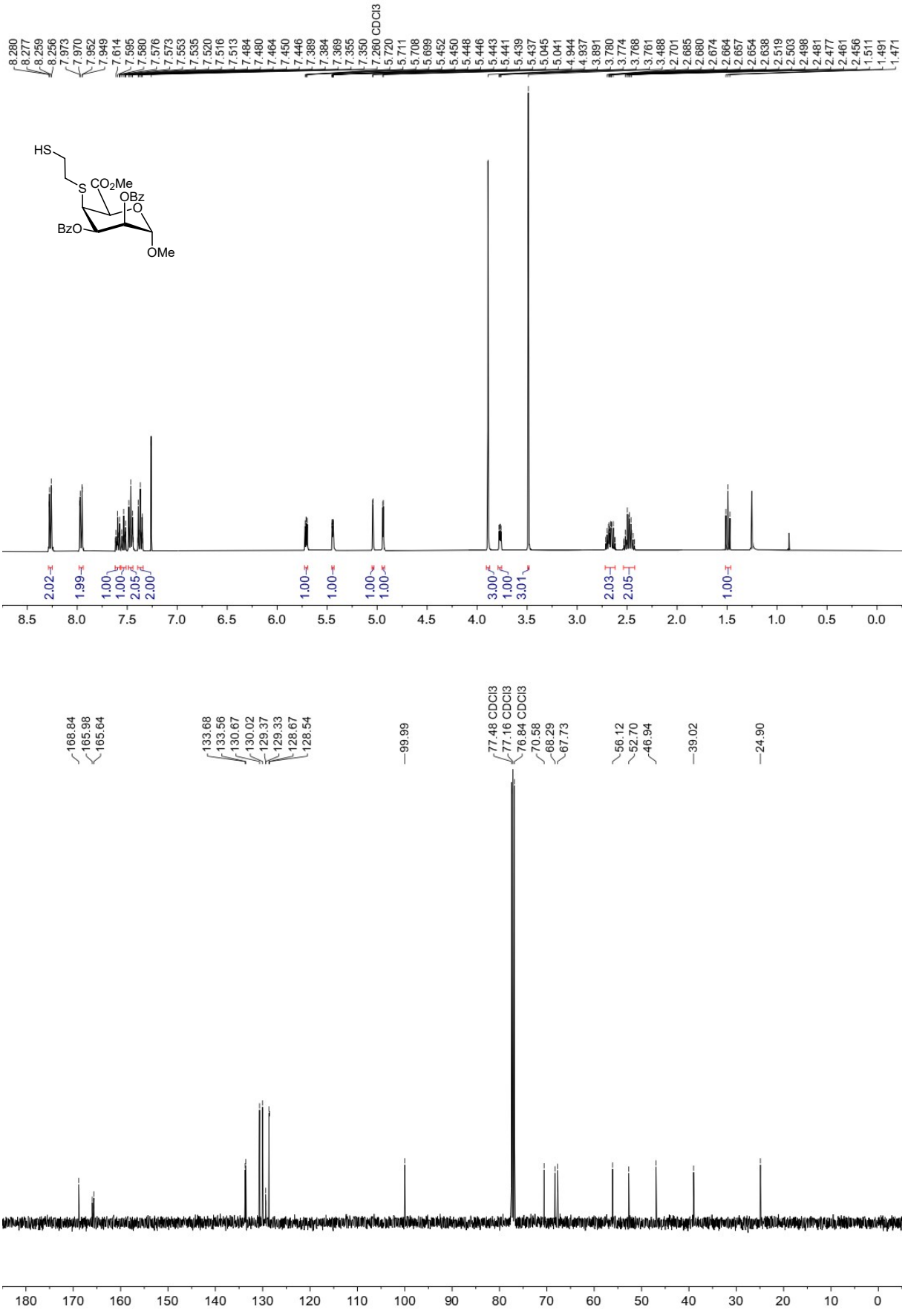
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **18**



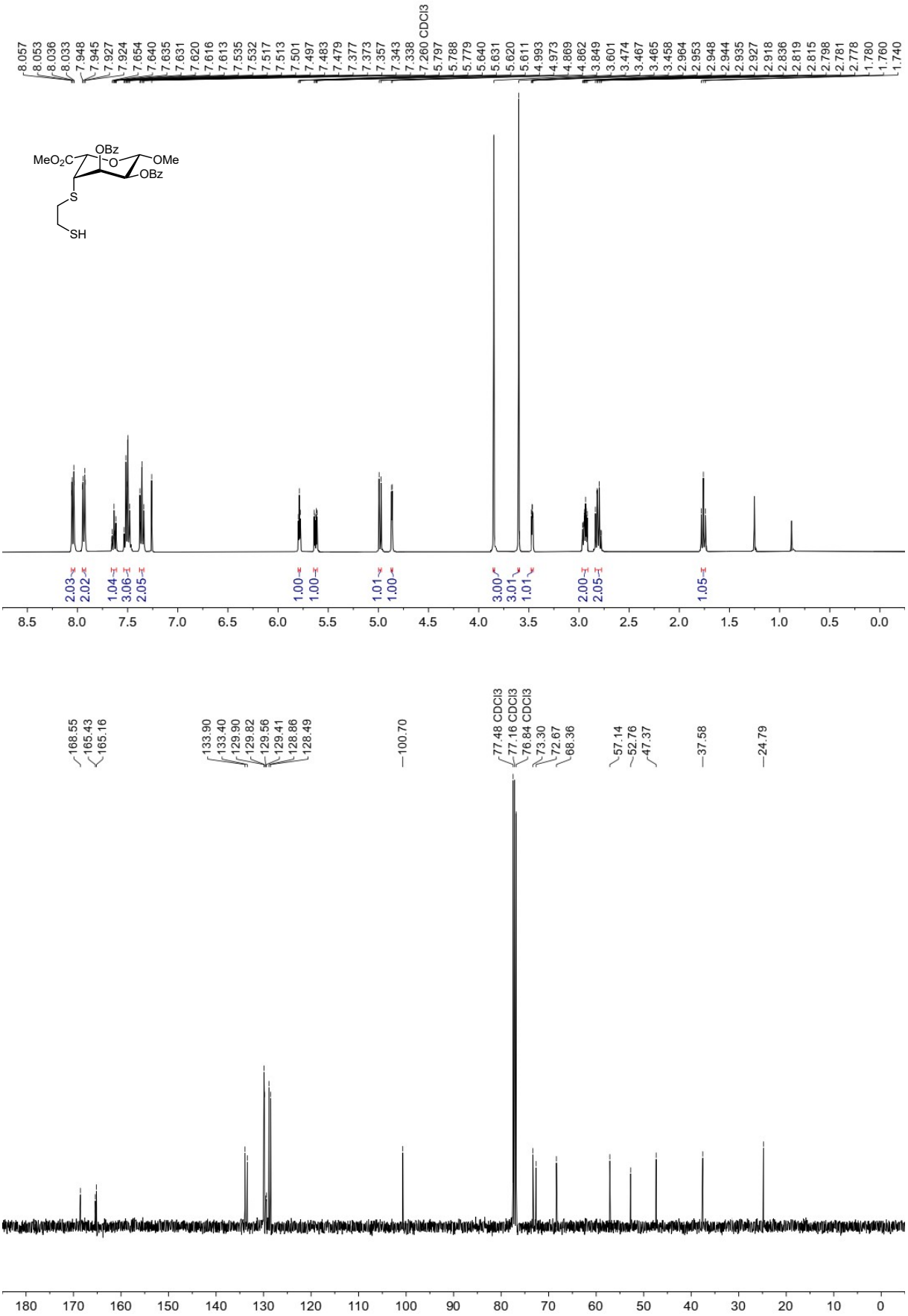
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **19**



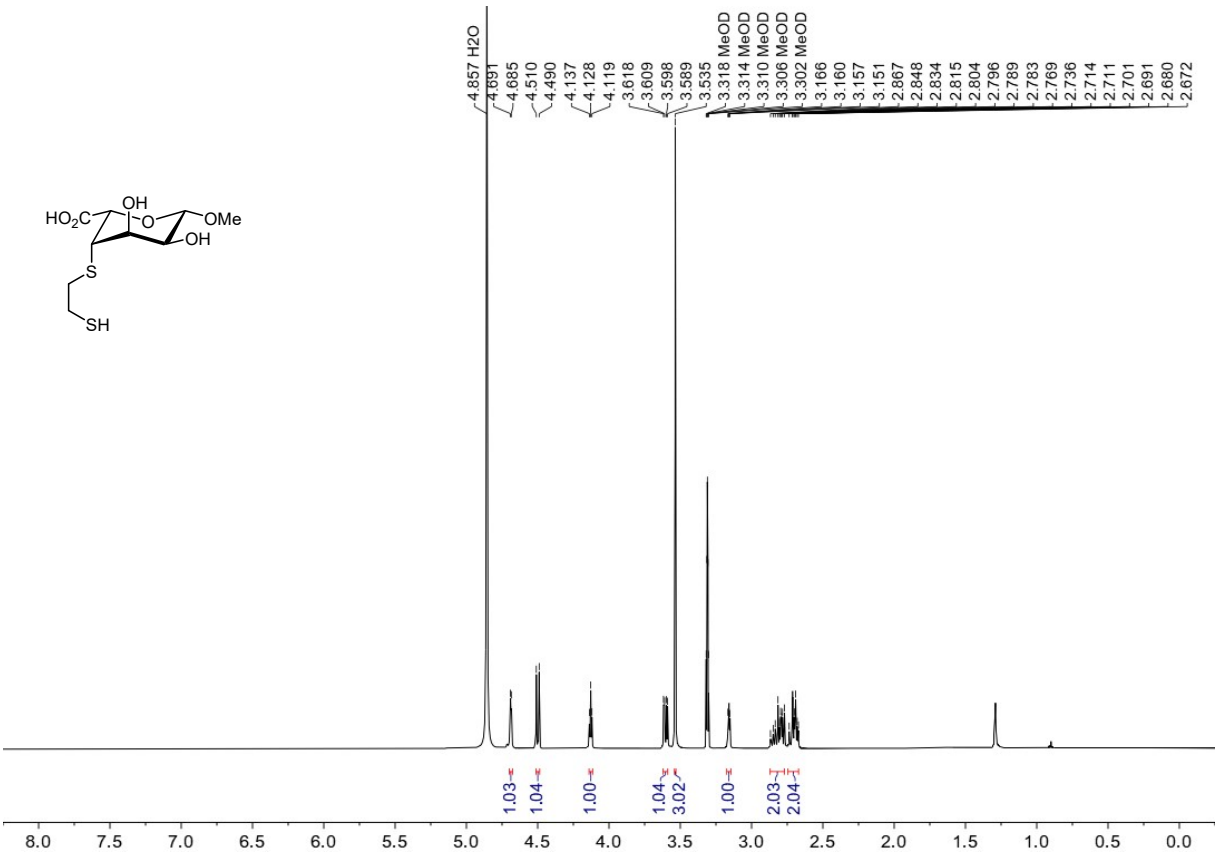
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **20a**

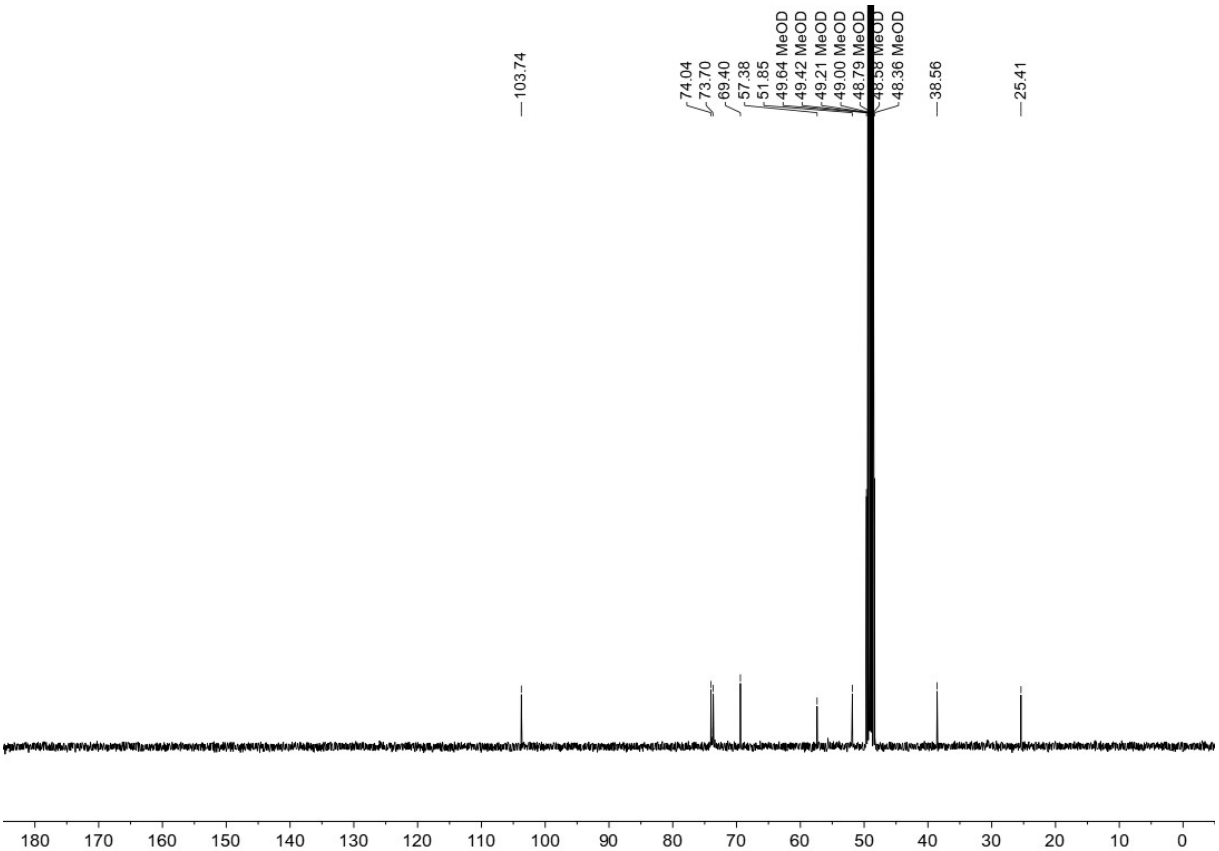


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **20b**



^{1}H NMR (400 MHz, CD_3OD) and $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) spectra of **21**

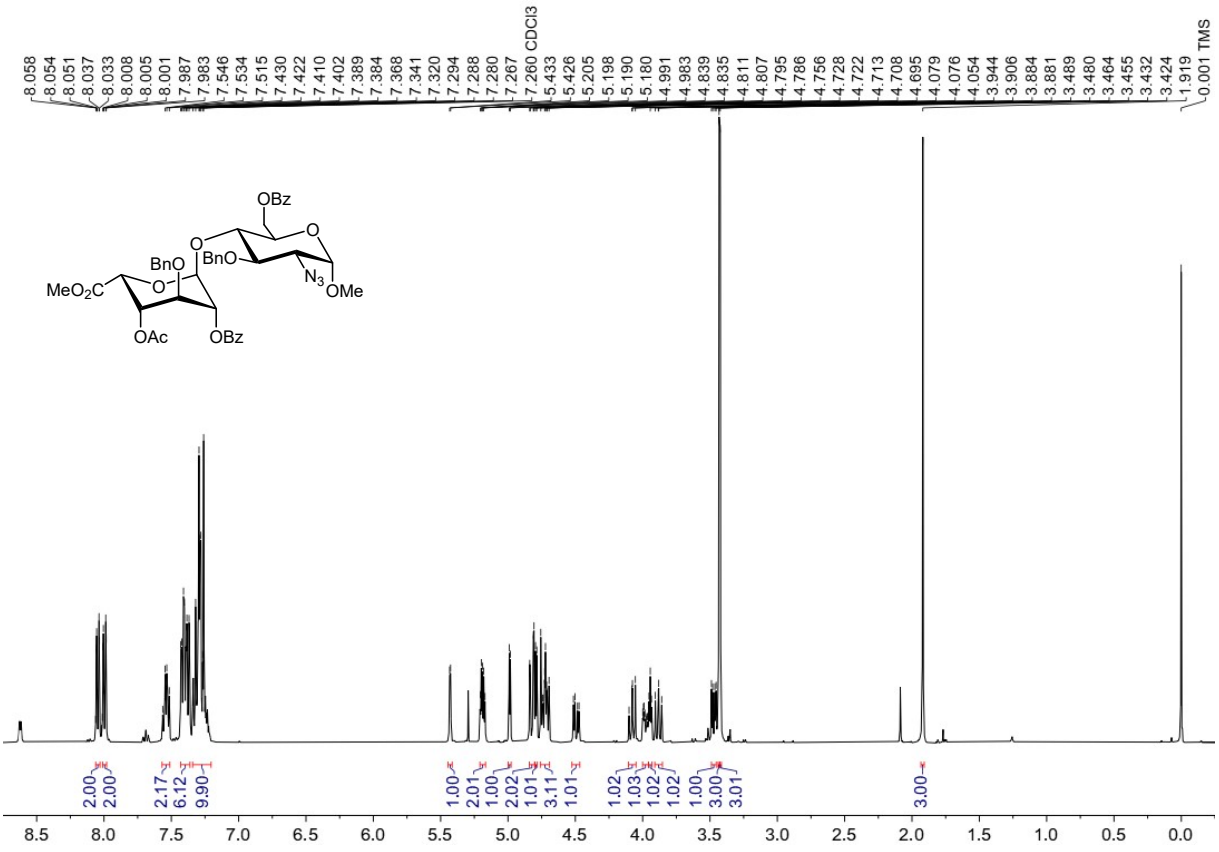


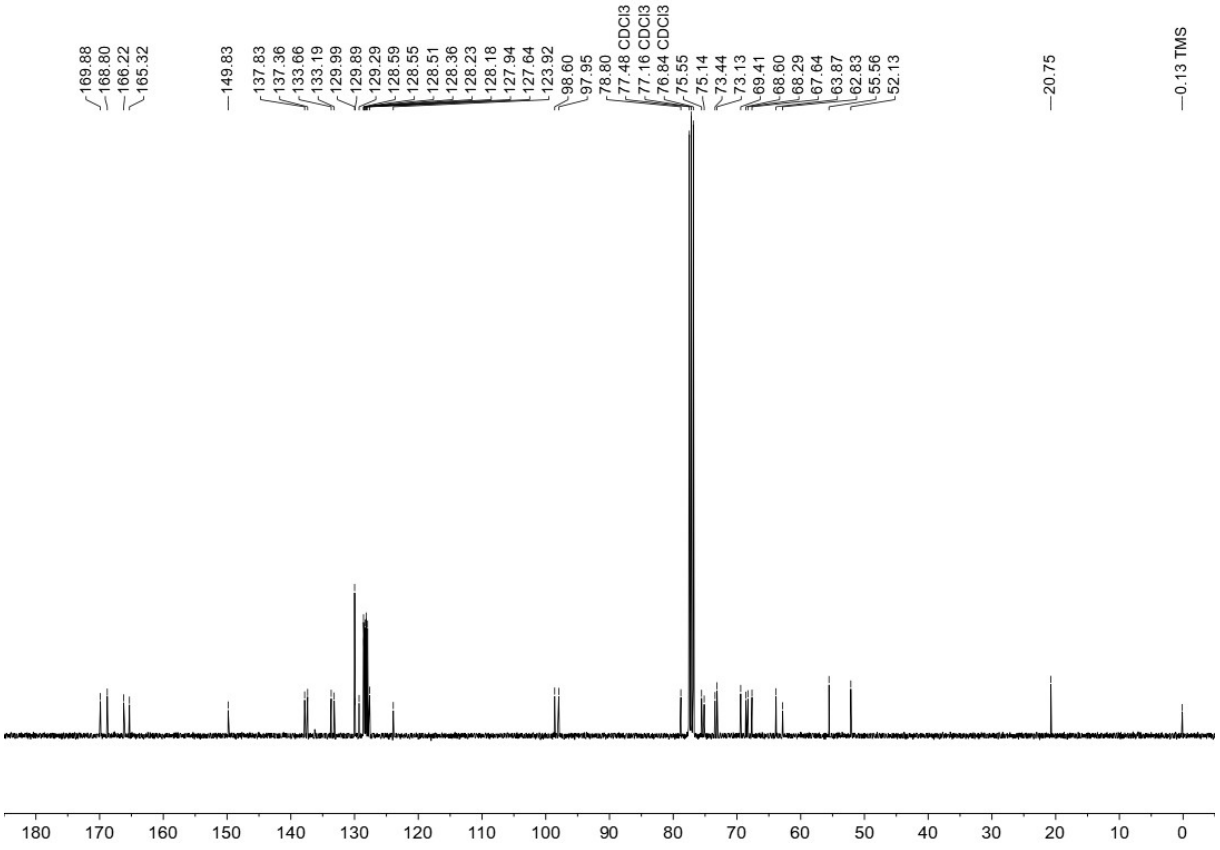


6. Synthesis of disaccharide 22 and thiol-ene reaction

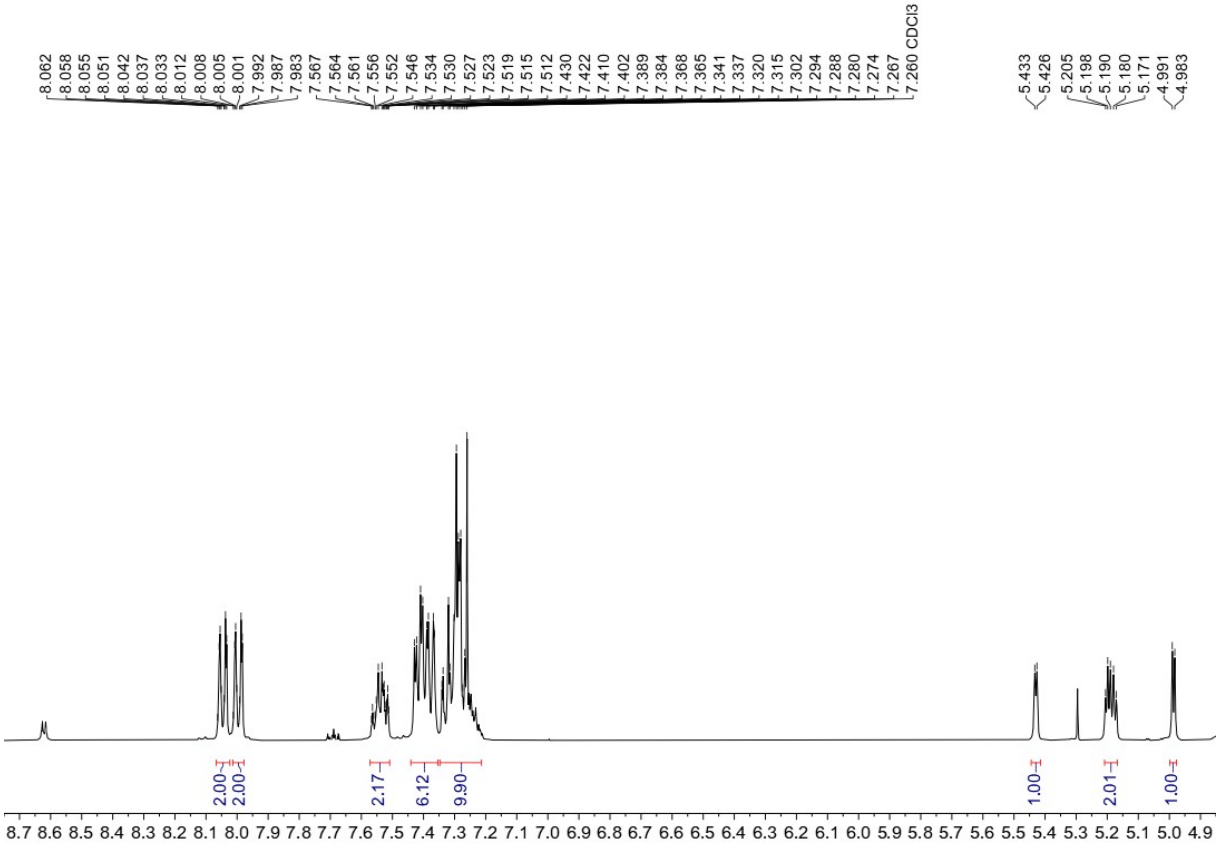
6.1. Synthesis of disaccharide 22

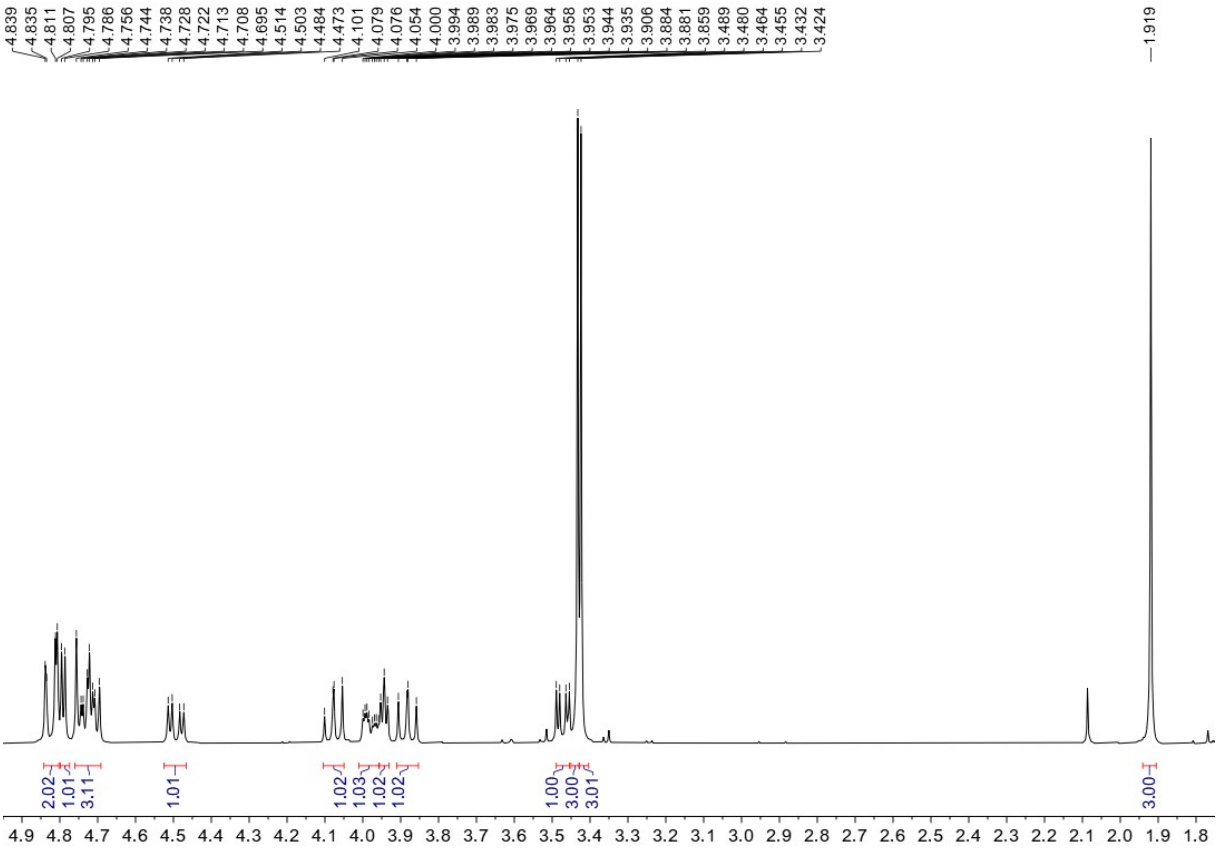
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **24**





^{1}H NMR (400 MHz, $CDCl_3$) magnified spectra of **24**

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4.795
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4.708
4.695
4.514
4.503
4.484
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3.489
3.480
3.464
3.455
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3.424
1.919
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1.01
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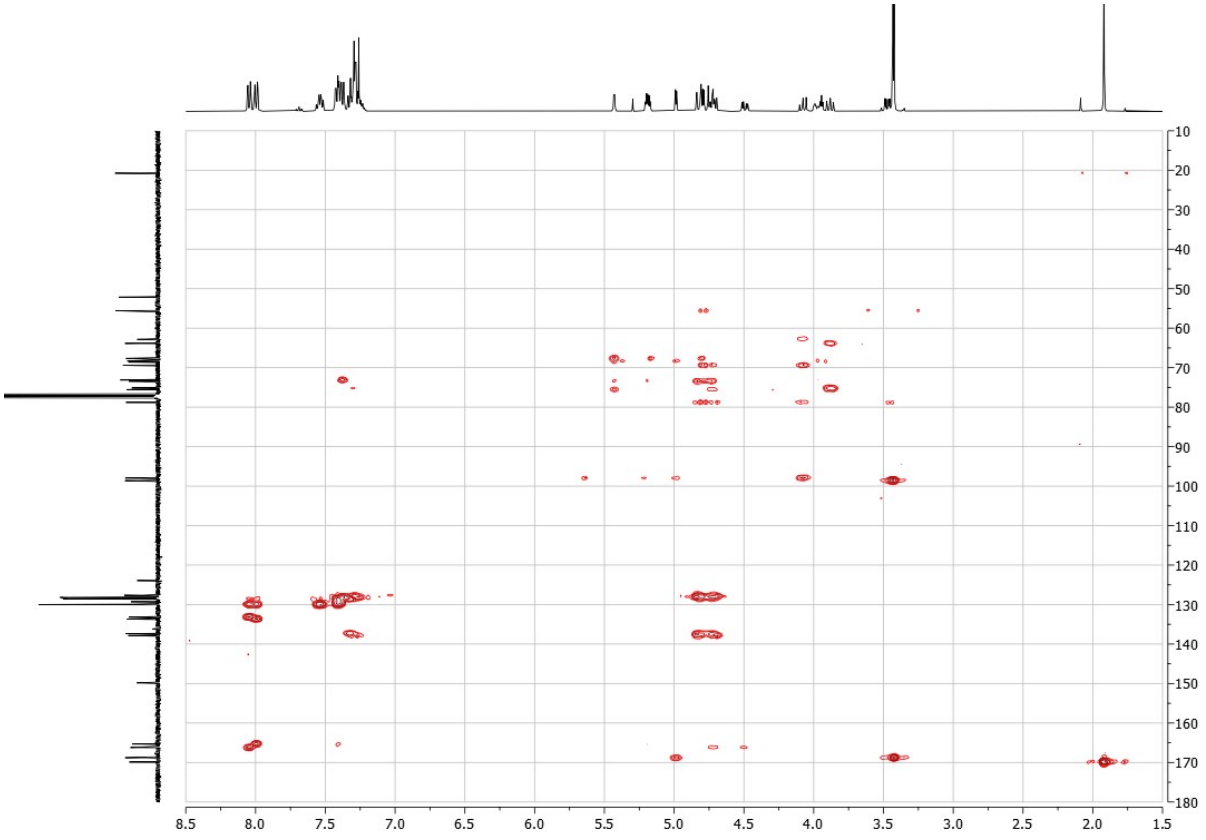
3.00
3.01
3.00
4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8

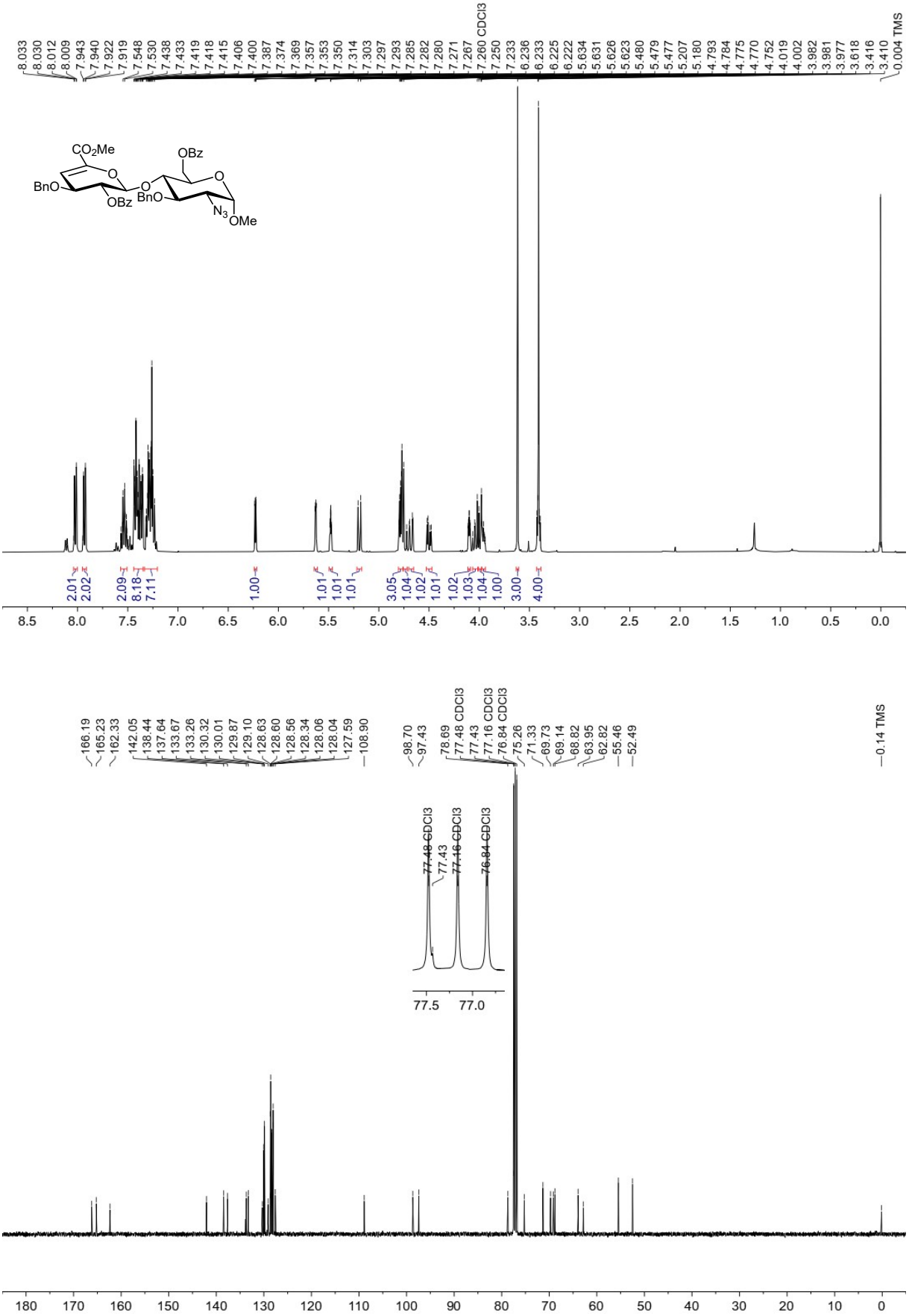
2D $^{1}H,^{1}H$-COSY (400 MHz, $CDCl_3$) spectra of **24**

2D $^{1}H,^{13}C$-HSQC (400 MHz x 101 MHz, $CDCl_3$) spectra of **24**

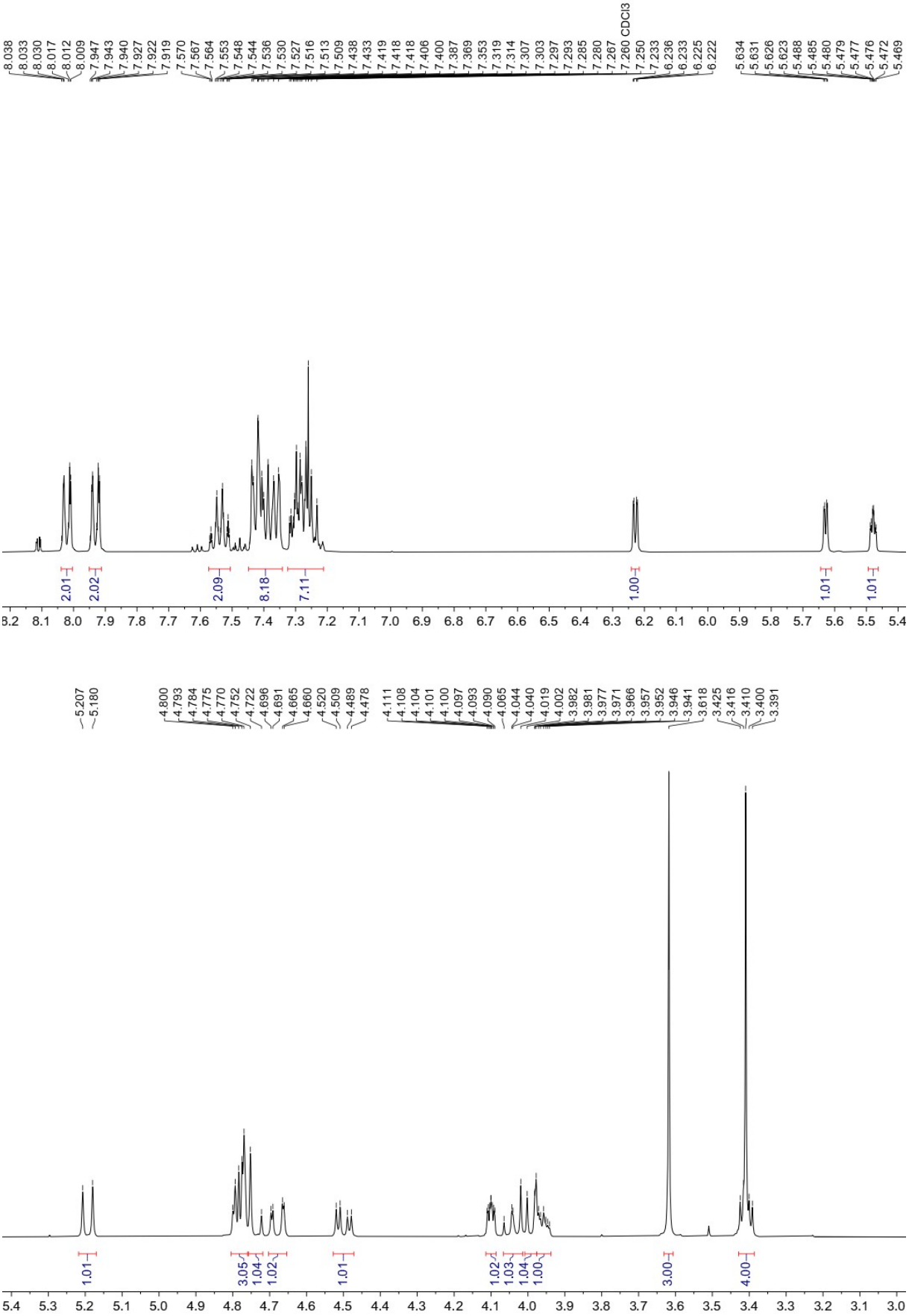
2D $^{1}H,^{13}C$-HMBC (400 MHz x 101 MHz, $CDCl_3$) spectra of **24**



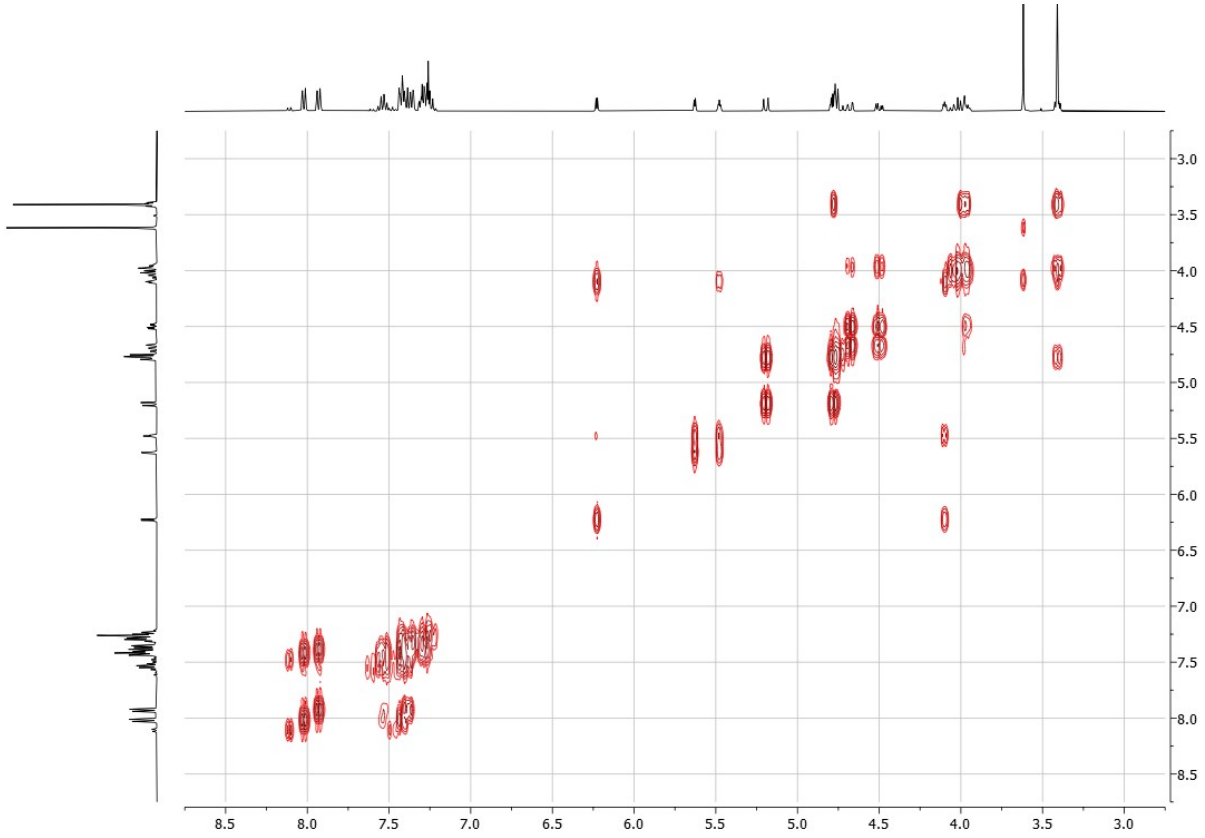
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$NMR (101 MHz, $CDCl_3$) spectra of **25**



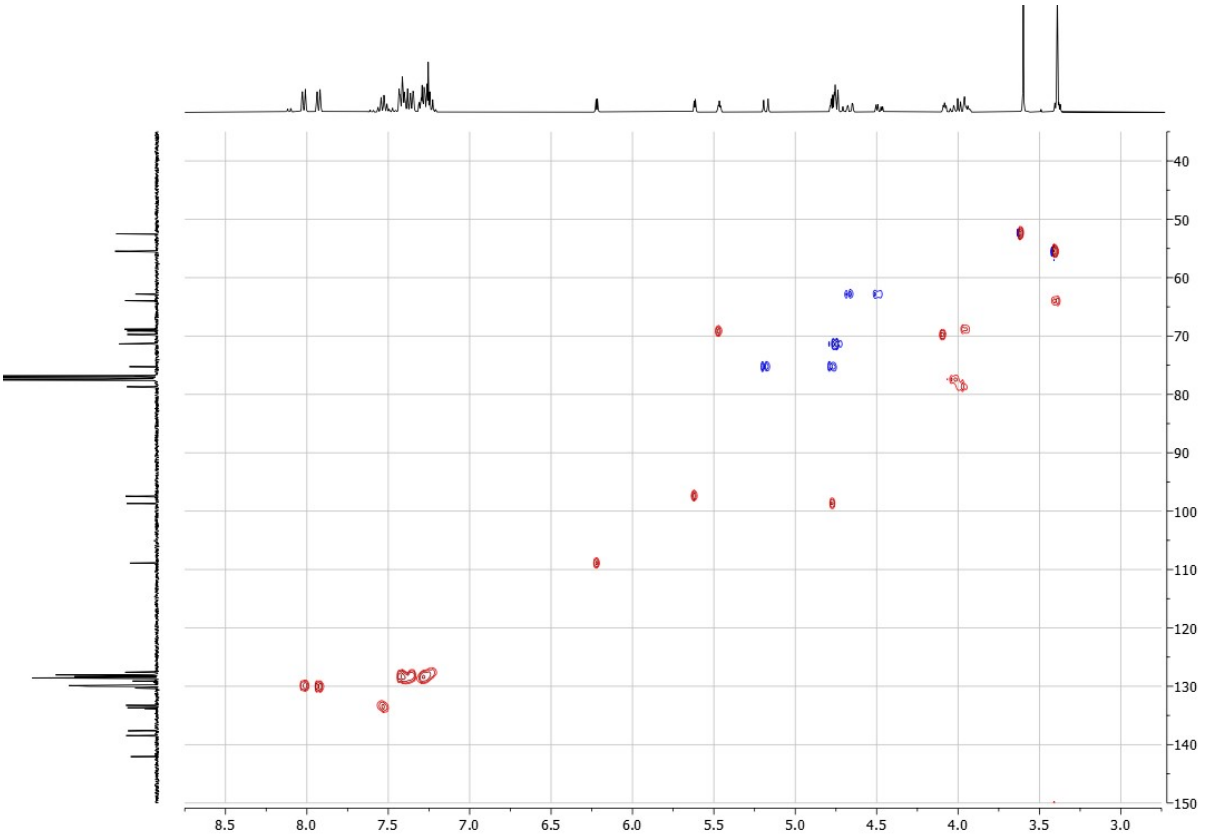
^{1}H NMR (400 MHz, $CDCl_3$) magnified spectra of **25**



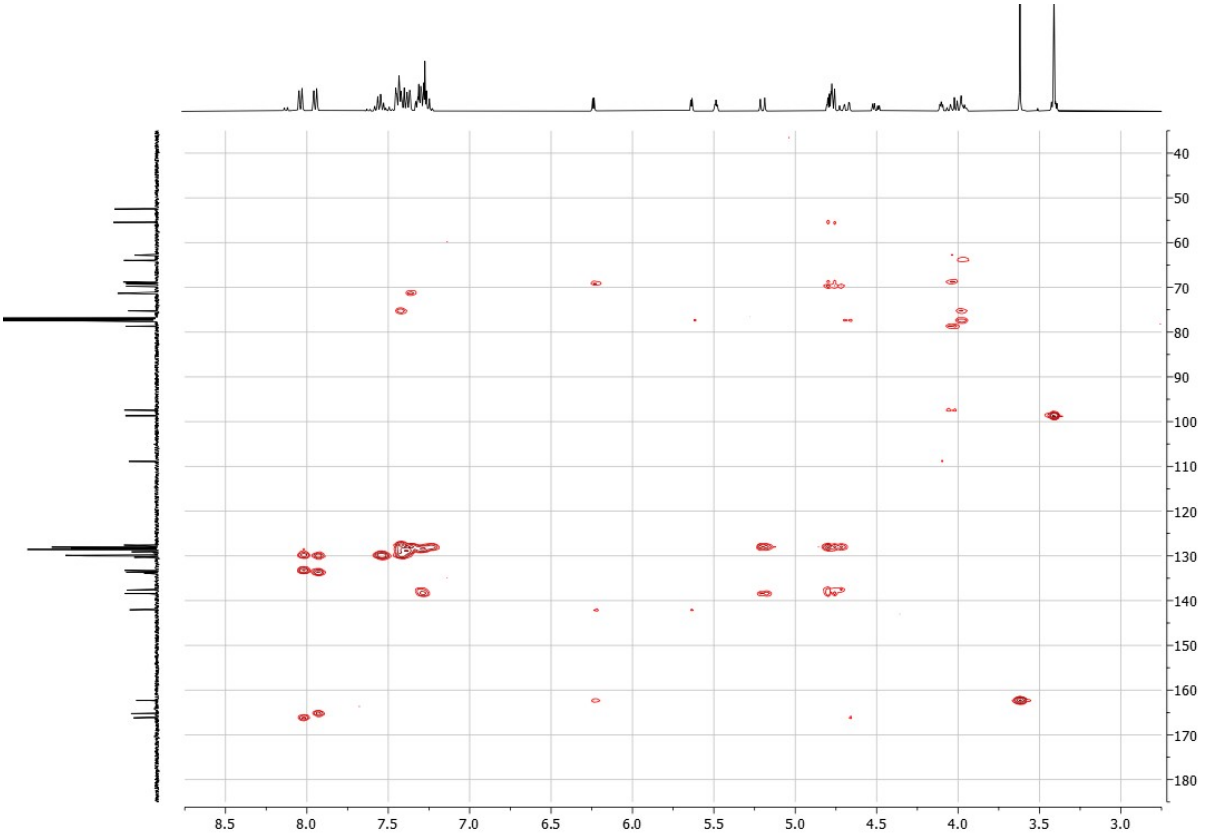
2D $^{1}H,^{1}H$-COSY (400 MHz, $CDCl_3$) spectra of **25**



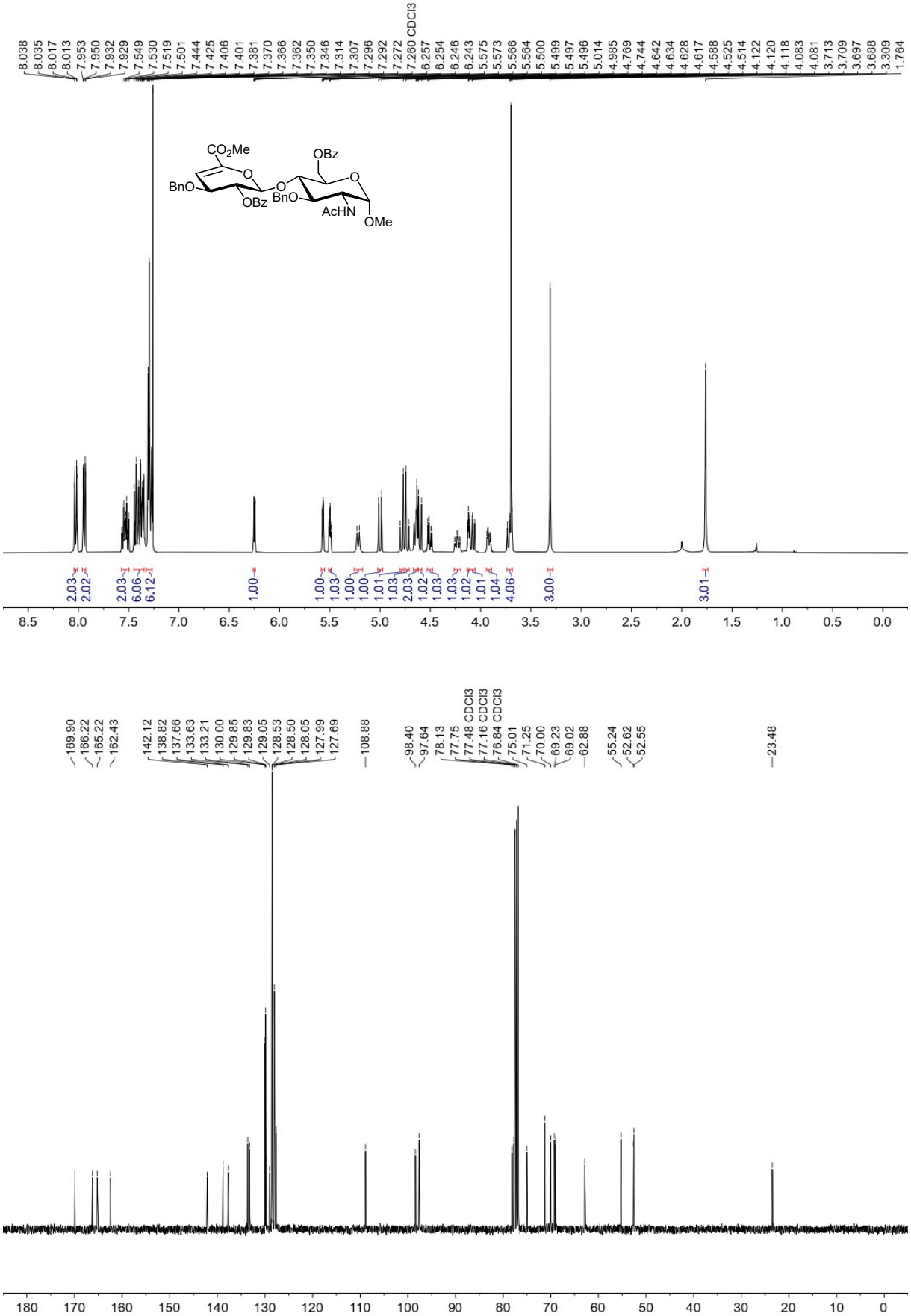
2D $^{1}H,^{13}C$-HSQC (400 MHz x 101 MHz, $CDCl_3$) spectra of **25**



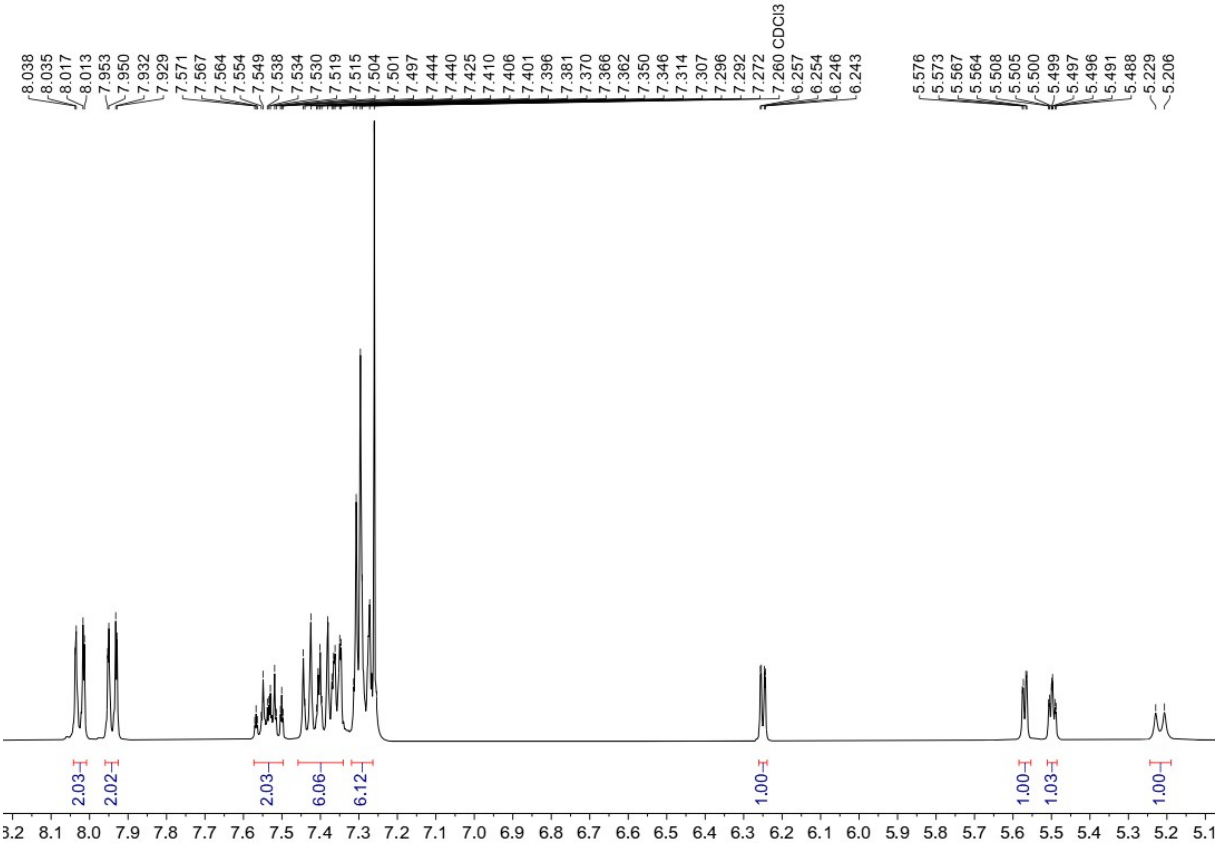
2D $^{1}H,^{13}C$-HMBC (400 MHz x 101 MHz, $CDCl_3$) spectra of **25**

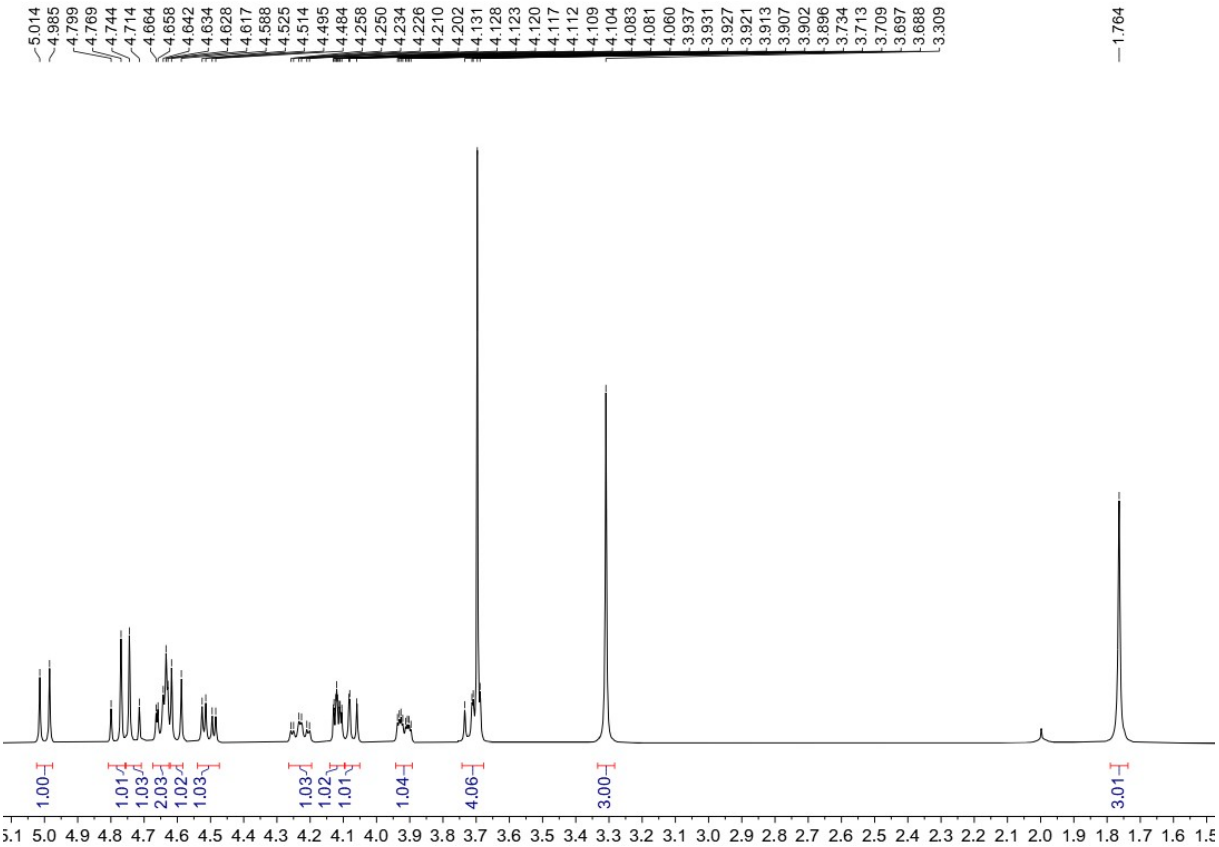


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **22**

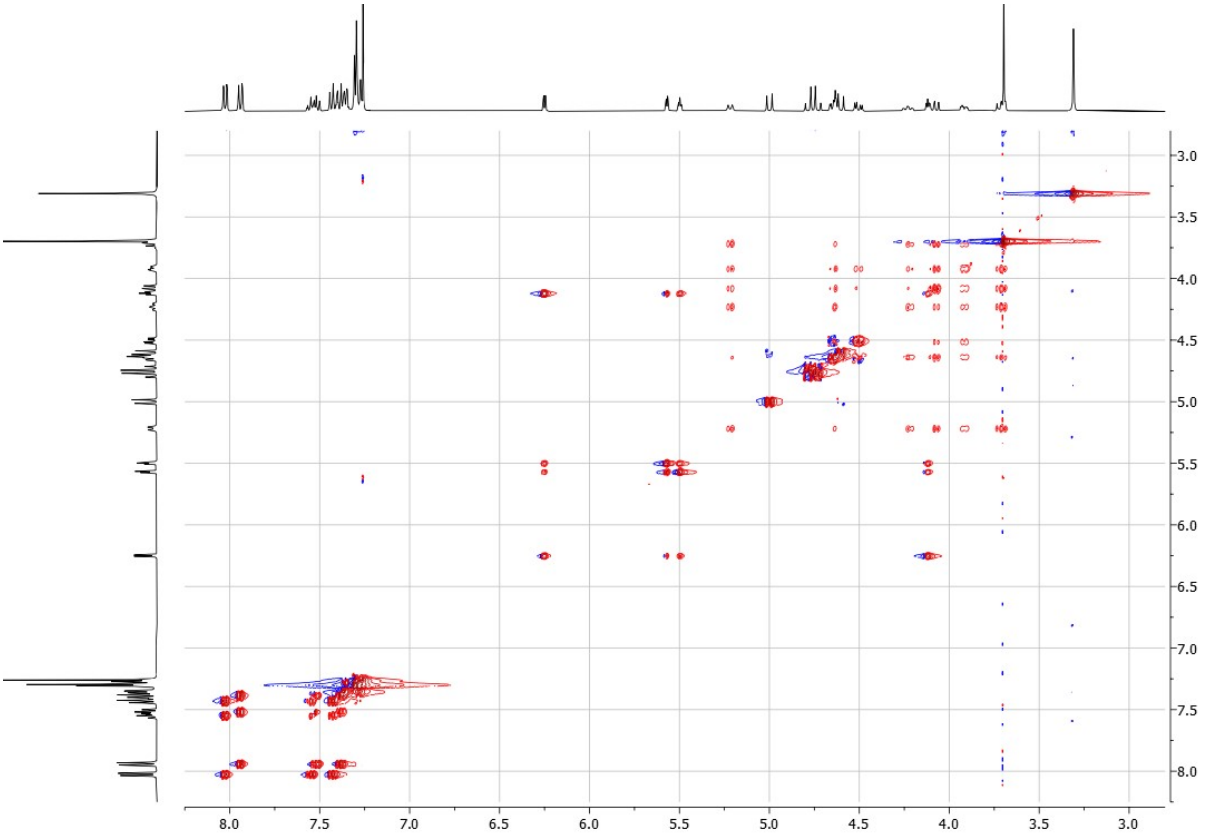


^{1}H NMR (400 MHz, $CDCl_3$) magnified spectra of **22**

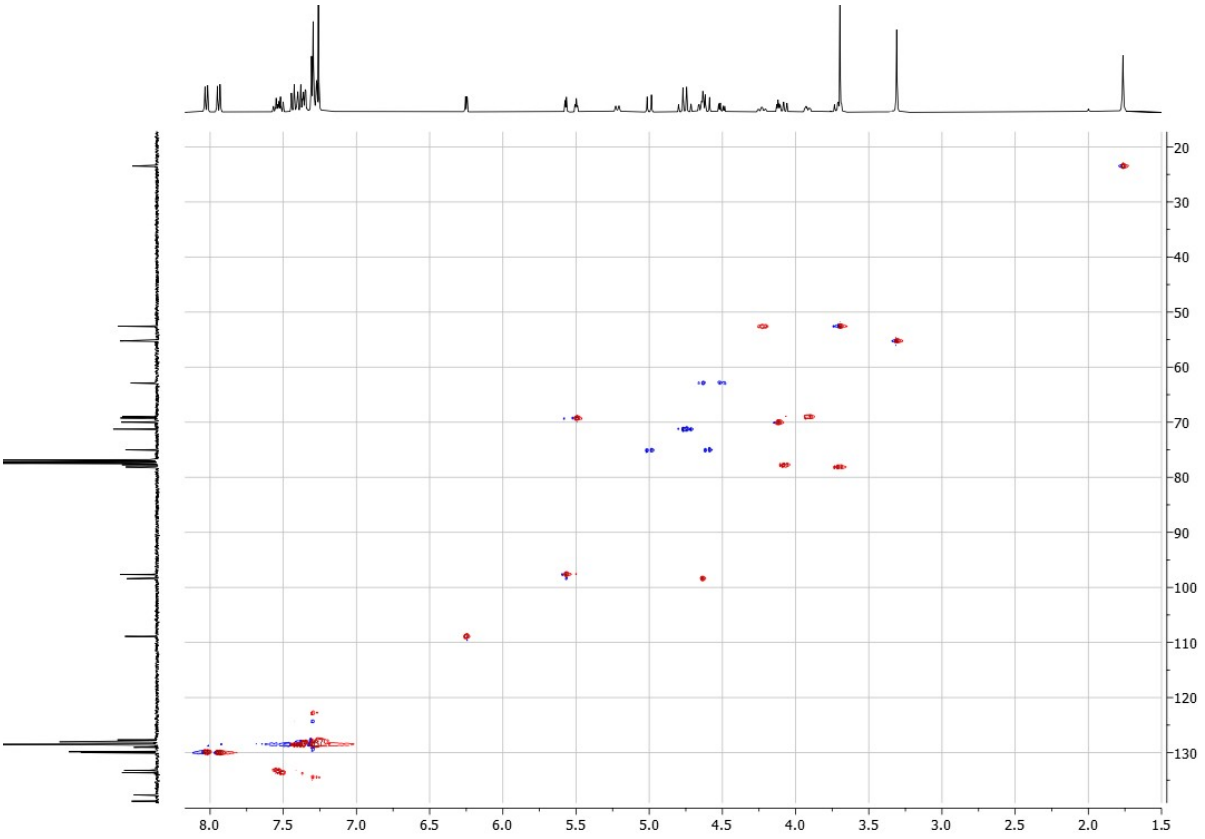




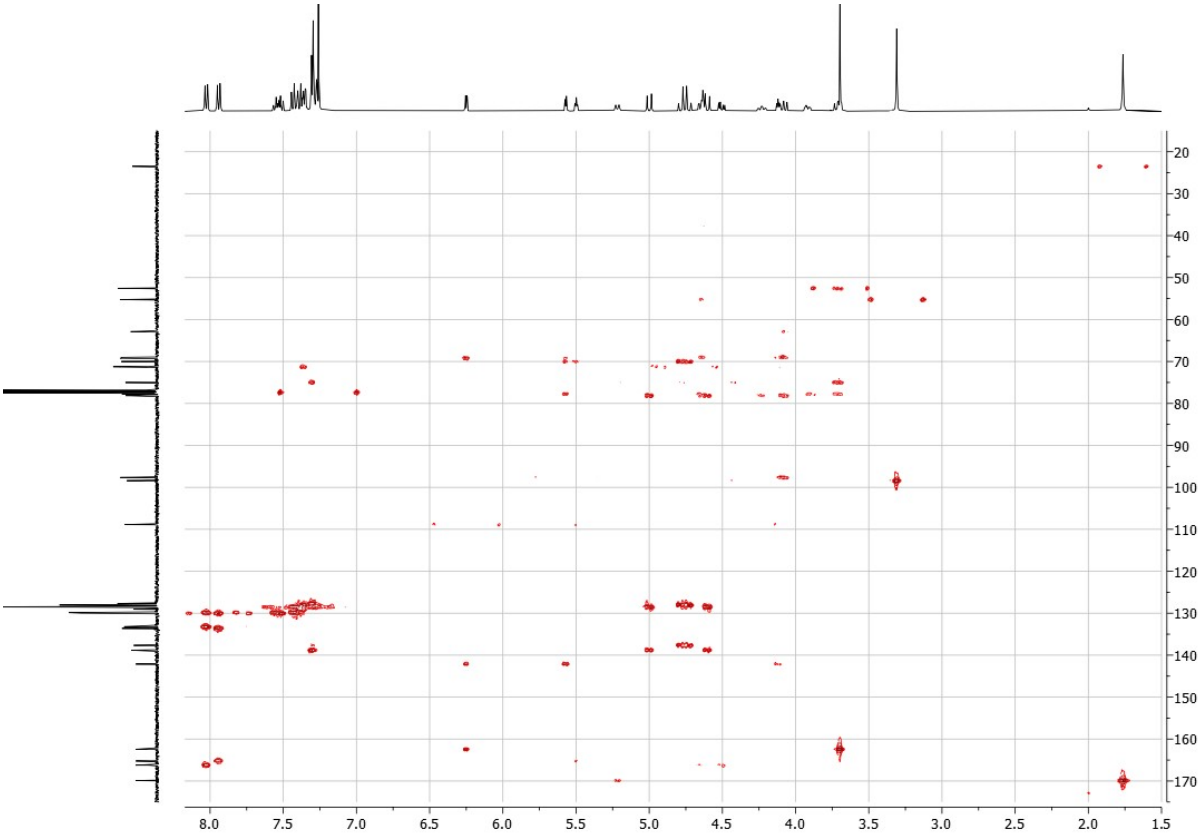
2D $^{1}H,^{1}H$-TOCSY (400 MHz, $CDCl_3$) spectra of **22**



2D $^{1}H,^{13}C$-HSQC (400 MHz x 101 MHz, $CDCl_3$) spectra of **22**

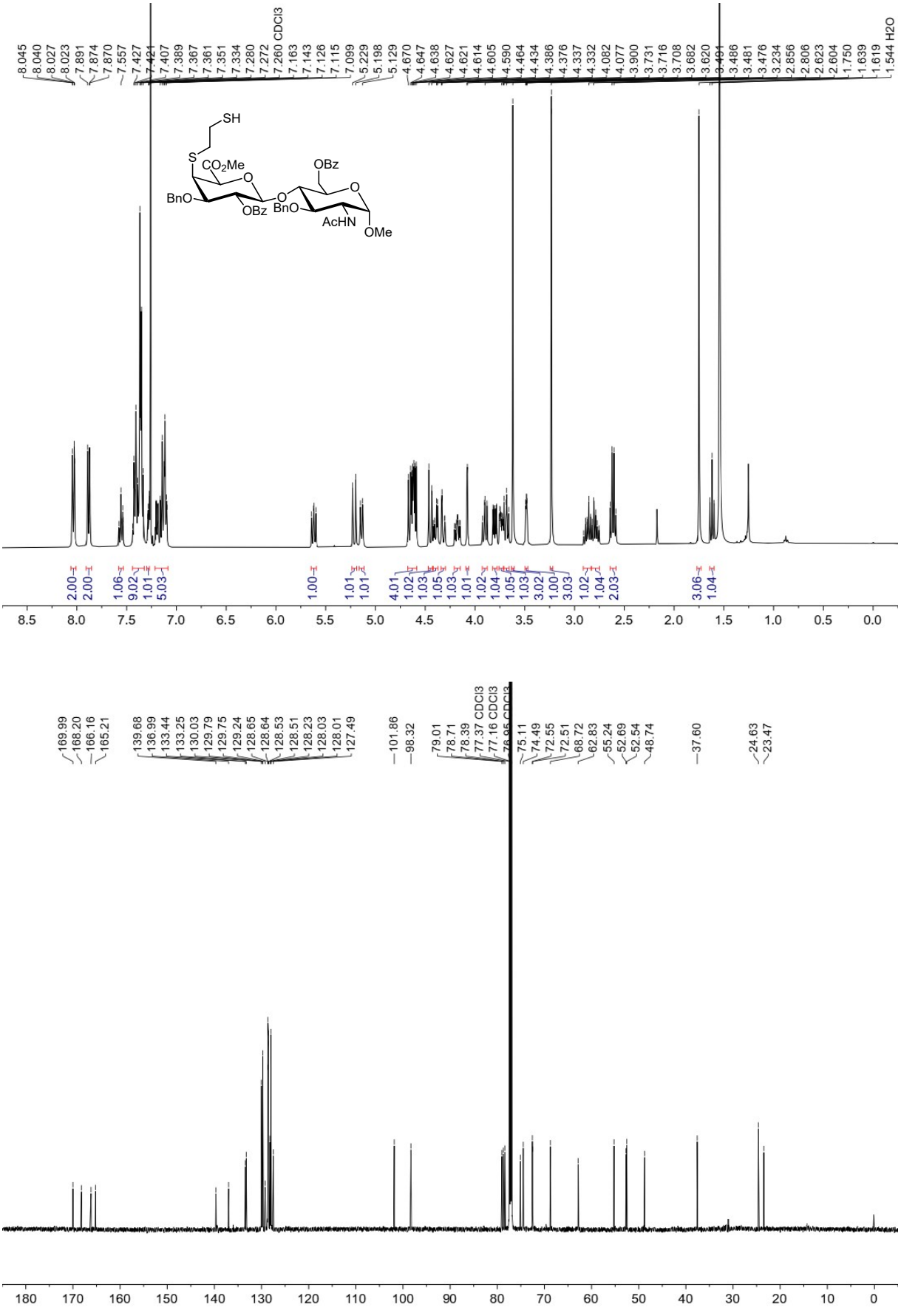


2D $^{1}H,^{13}C$-HMBC (400 MHz x 101 MHz, $CDCl_3$) spectra of **22**

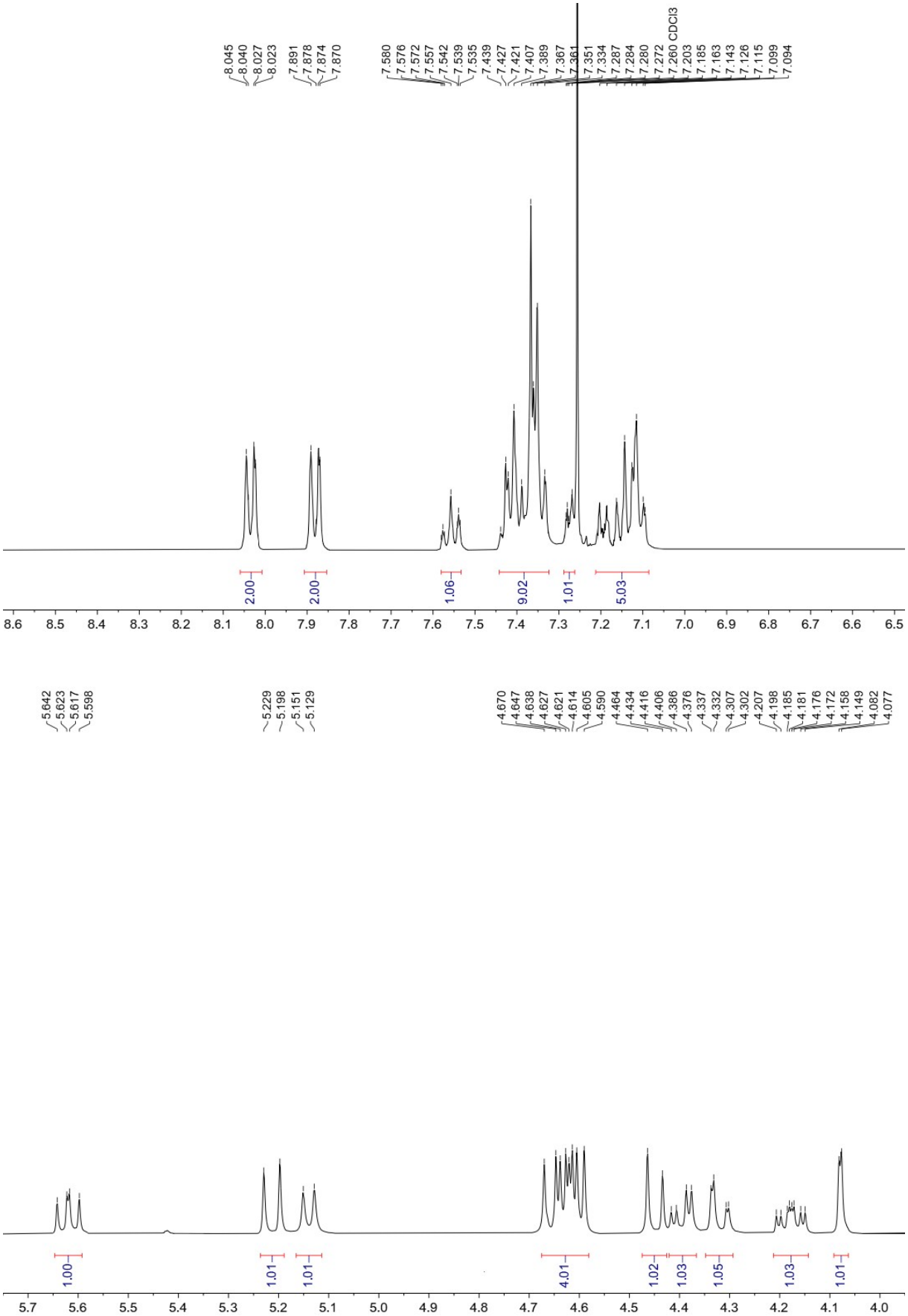


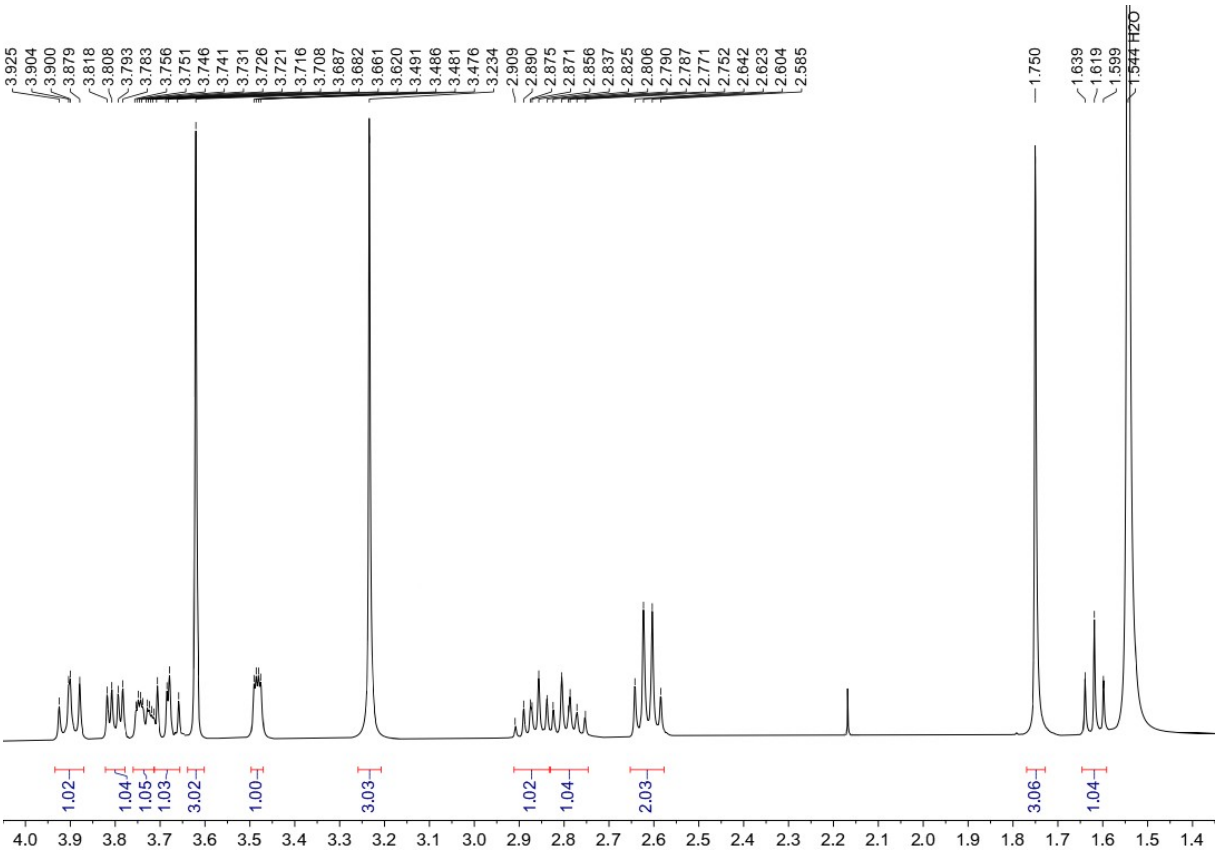
6.2. Thiol-ene reaction on disaccharide 22

^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **26**

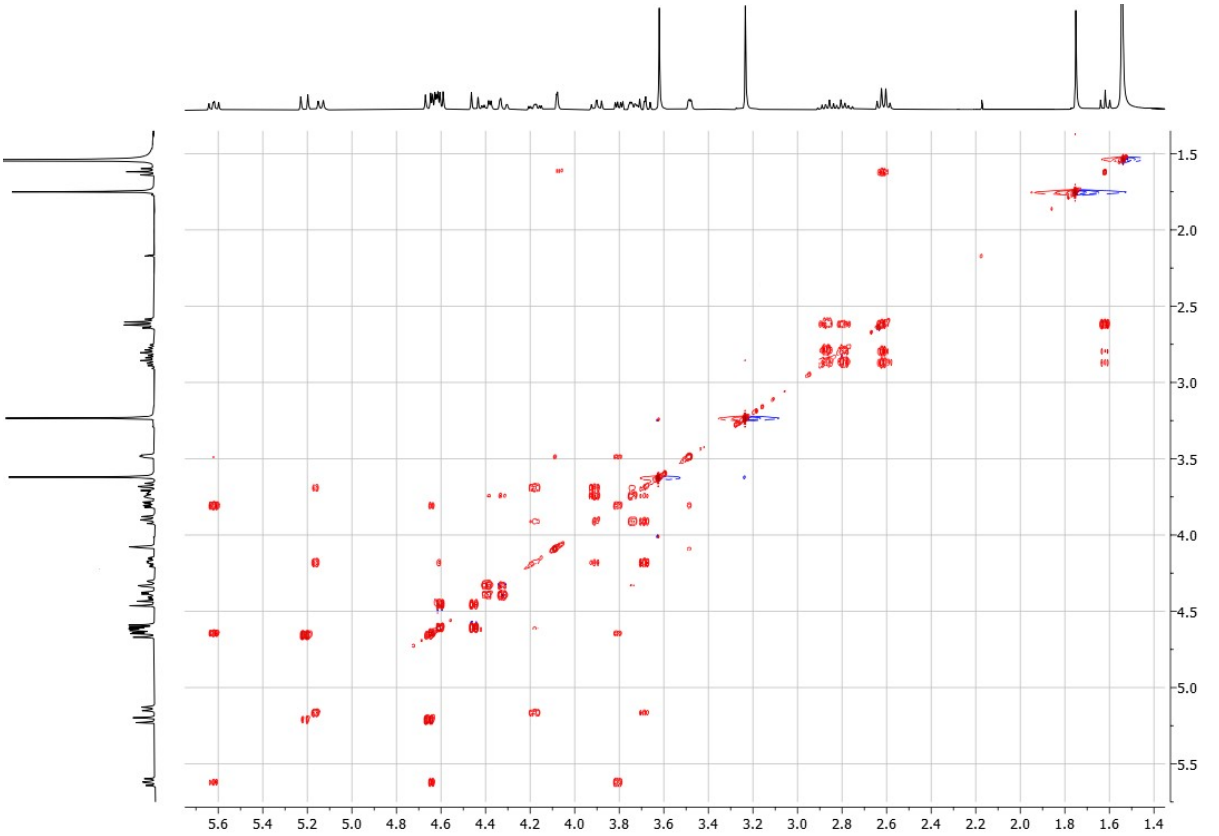


^{1}H NMR (400 MHz, $CDCl_3$) magnified spectra of **26**

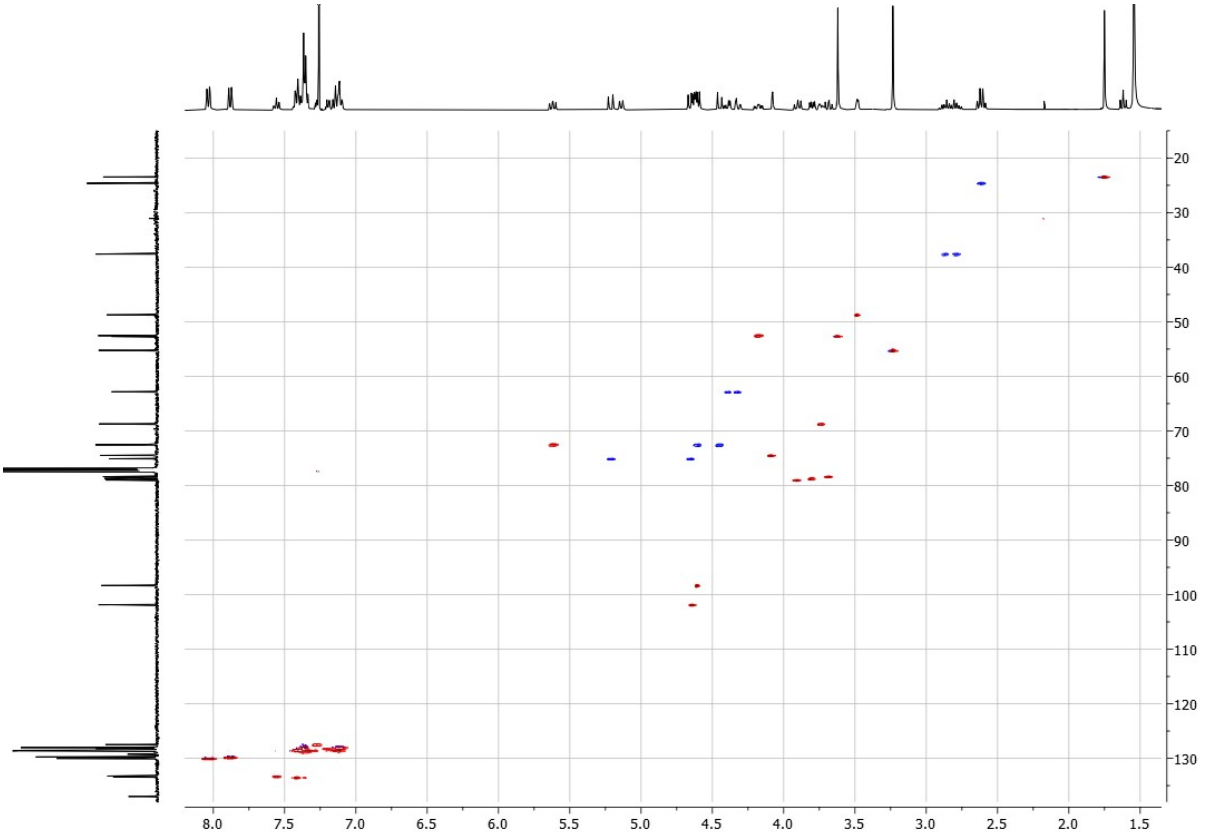




2D $^{1}H,^{1}H$-COSY (400 MHz, $CDCl_3$) spectra of **26**



2D $^{1}H,^{13}C$-HSQC (400 MHz x 101 MHz, $CDCl_3$) spectra of **26**



2D $^{1}H,^{13}C$-HMBC (400 MHz x 101 MHz, $CDCl_3$) spectra of **26**

7. X-ray crystal structure data

Colourless crystals of **5a**, **6a'**, **6b** and **26** were mounted on a MiTeGen micromount with NVH immersion oil. Data were collected from a shock-cooled single crystal at 100(2)º K for **5a** on a Bruker D8 Quest ECO PhotonIII C7 three-circle diffractometer with a sealed X-ray tube using a graphite monochromator and a Bruker PHOTON III C7 detector and for **6a'**, **6b** and **26** on a Bruker APEX2 Kappa Duo Kappa diffractometer with a microfocus sealed sealed X-ray tube using mirror optics as a monochromator and an APEX2 detector. The Bruker D8 Quest ECO was equipped was equipped with an Oxford Cryostream 800 low temperature device and used Mo K_α radiation (λ = 0.71073 Å) and the Bruker DUO was equipped with an Oxford Cobra low temperature device and used Cu K_α radiation (λ = 1.54178 Å).

All data were integrated with SAINT and a multi-scan absorption correction using SADABS was applied.[1,2] The structures were solved by by dual methods using XT and refined by full-matrix least-squares methods against F^2 by XL using Olex2.[3-5] All non-hydrogen atoms were refined with anisotropic displacement parameters. Some of their coordinates were refined freely and some on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints.

Refinement details:

In **5a** the thiol S-H hydrogen located on the difference map and refined with restraints (DFIX). One AcO group was disordered over two locations (70:30 %) and modelled with geometric and displacement restraints (SADI, RIGU, ISOR) and constraints (EADP, C26).

In **6a'** part of the sugar ring (O1-C1-C2), methyl ester group and the dithiol are disordered and modelled in two locations (61:31 %) using restraints (SADI, RIGU, SIMU). Donor O-H hydrogen located on the difference map and refined using restraints (DFIX).

In **26** there are four independent molecules in the asymmetric unit with two water molecules. One benzyl aromatic ring is disordered and modelled in two locations with 50% occupancy. Restraints (SIMU, DANG, RIGU, SADI) and constraints (EADP, C15B, C15E) were used in the model. Water hydrogen atoms were fixed in place in optimum positions for hydrogen bonding. Other donor hydrogens (N-H) were placed on geometrically calculated positions and then refined using a riding model. Thiol hydrogens were located on the difference map and refined semi-free using restraints (DFIX).

Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre.[6] CCDC 2389449 (**5a**), 2389448 (**6a'**), 2389447 (**6b**) and 2389446 (**26**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures.

Table S1. Crystal data and structure refinements for **5a**, **6a'**, **6b** and **26**.

Identification No.	**5a**	**6a'**	**6b**	**26**
CCDC number	2389449	2389448	2389447	2389446
Empirical formula	$C_{15}H_{22}O_9S_2$	$C_{13}H_{18}O_8S_2$	$C_{16}H_{24}O_9S_2$	$C_{92}H_{104}N_2O_{27}S_4$
Formula weight	410.44	366.39	424.47	1798.01
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic
Space group (number)	$P2_1$ (4)	$P2_1$ (4)	$P2_12_12_1$ (19)	$P1$ (1)
***a* (Å)**	11.1283(3)	9.1441(5)	8.5662(3)	10.8947(7)
***b* (Å)**	7.6491(2)	8.1239(4)	11.8991(4)	15.2408(9)
***c* (Å)**	11.5435(3)	11.0985(5)	19.6088(7)	27.3806(16)
α (º)	90	90	90	81.262(4)
β (º)	92.8088(14)	94.130(3)	90	85.221(4)
γ (º)	90	90	90	81.397(4)
Volume (Å^3)	981.42(4)	822.32(7)	1998.73(12)	4434.5(5)
Z	2	2	4	2
ρ_{calc} (gcm^{-3})	1.389	1.480	1.411	1.347
μ (mm^{-1})	0.314	3.296	2.828	1.658
***F*(000)**	432	384	896	1900
Crystal size (mm^3)	0.432x0.073x0.055	0.358x0.034x0.032	0.194x0.176x0.116	0.416x0.122x0.055
Crystal colour	colourless	colourless	colourless	colourless
Crystal shape	needle	plate	fragment	plate
Radiation	Mo K_α (λ = 0.71073 Å)	Cu K_α (λ = 1.54178 Å)	Cu K_α (λ = 1.54178 Å)	Cu K_α (λ = 1.54178 Å)
2θ range (º)	6.39 to 56.62 (0.75Å)	7.99 to 140.69 (0.82Å)	8.69 to 140.00 (0.82Å)	3.27 to 141.43 (0.82Å)
Index ranges	-14 ≤ h ≤ 14 -10 ≤ k ≤ 10 -15 ≤ l ≤ 15	-11 ≤ h ≤ 11 -9 ≤ k ≤ 9 -13 ≤ l ≤ 13	-10 ≤ h ≤ 10 -14 ≤ k ≤ 13 -23 ≤ l ≤ 23	-12 ≤ h ≤ 13 -18 ≤ k ≤ 18 -33 ≤ l ≤ 32
Reflections collected	27083	12870	29973	90545
Independent reflections	4871 R_{int} = 0.0611 R_{sigma} = 0.0531	3072 R_{int} = 0.0610 R_{sigma} = 0.0512	3770 R_{int} = 0.0429 R_{sigma} = 0.0212	31569 R_{int} = 0.0696 R_{sigma} = 0.0830
Completeness	99.8 %	99.9 %	100.0 %	99.7 %
Data / Restraints / Parameters	4871/59/266	3072/475/316	3770/1/252	31569/273/2299
Goodness-of-fit on F^2	1.080	1.079	1.036	1.046
Final *R* indexes	R_1 = 0.0440	R_1 = 0.0530	R_1 = 0.0326	R_1 = 0.0884
[$I \geq 2\sigma(I)$]	wR_2 = 0.0982	wR_2 = 0.1413	wR_2 = 0.0897	wR_2 = 0.2286
Final *R* indexes	R_1 = 0.0671	R_1 = 0.0602	R_1 = 0.0329	R_1 = 0.1098
[all data]	wR_2 = 0.1080	wR_2 = 0.1476	wR_2 = 0.0900	wR_2 = 0.2512
Largest diff. peak / hole (eÅ^{-3})	0.39/-0.30	0.28/-0.18	0.37/-0.25	0.65/-0.56
Flack X parameter	-0.02(4)	0.01(4)	-0.009(5)	0.01(2)

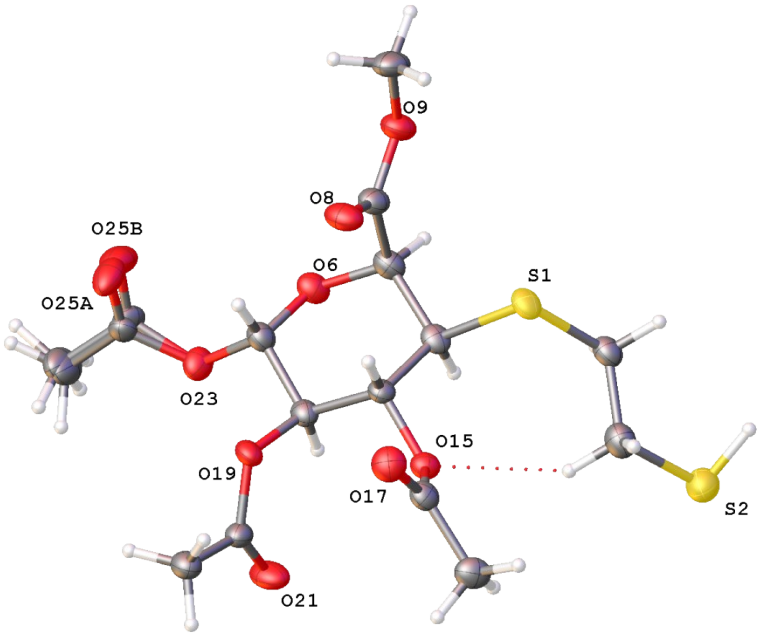


Fig. S1. Disordered molecular structure of **5a** with one AcO group disordered over two locations (70:30 %). Displacement parameters shown at 50% probability. Heteroatoms labelled only.

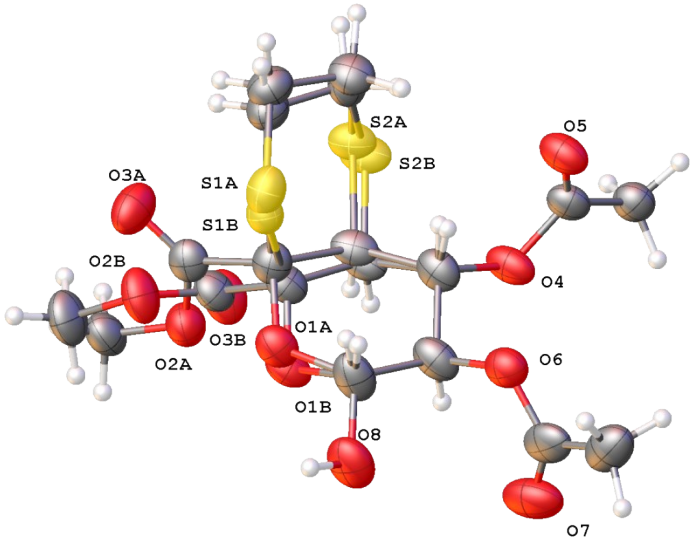


Fig. S2. Structure of **6a'** showing the disorder in the sugar ring, methyl ester and dithiol ring. Displacement parameters shown at 50% probability. Heteroatoms labelled only.

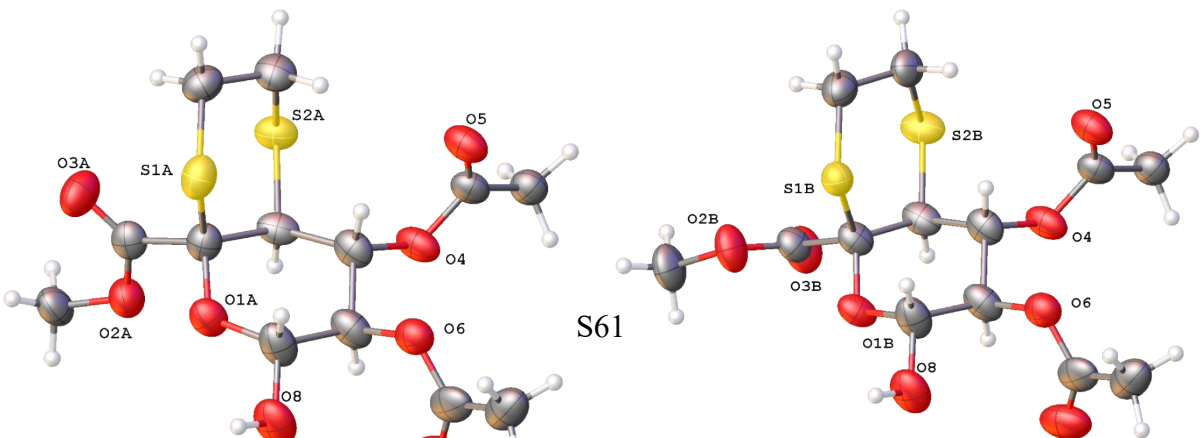


Fig. S3. Individual representation of each disordered moiety in **6a'** with (**A**) majority occupied with sugar ring O1a-C1a-C2a, methyl ester and dithiol ring 61% occupied and (**B**) minority moiety with sugar ring O1b-C1b-C2b, methyl ester and dithiol ring 39% occupied. Displacement parameters shown at 50% probability. Heteroatoms labelled only.

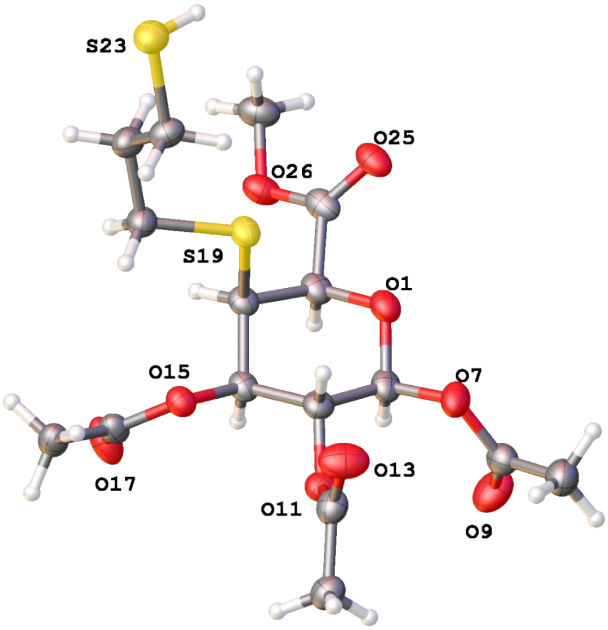


Fig. S4. Structure of **6b** with heteroatoms labelled. Atomic displacement shown at 50% probability.

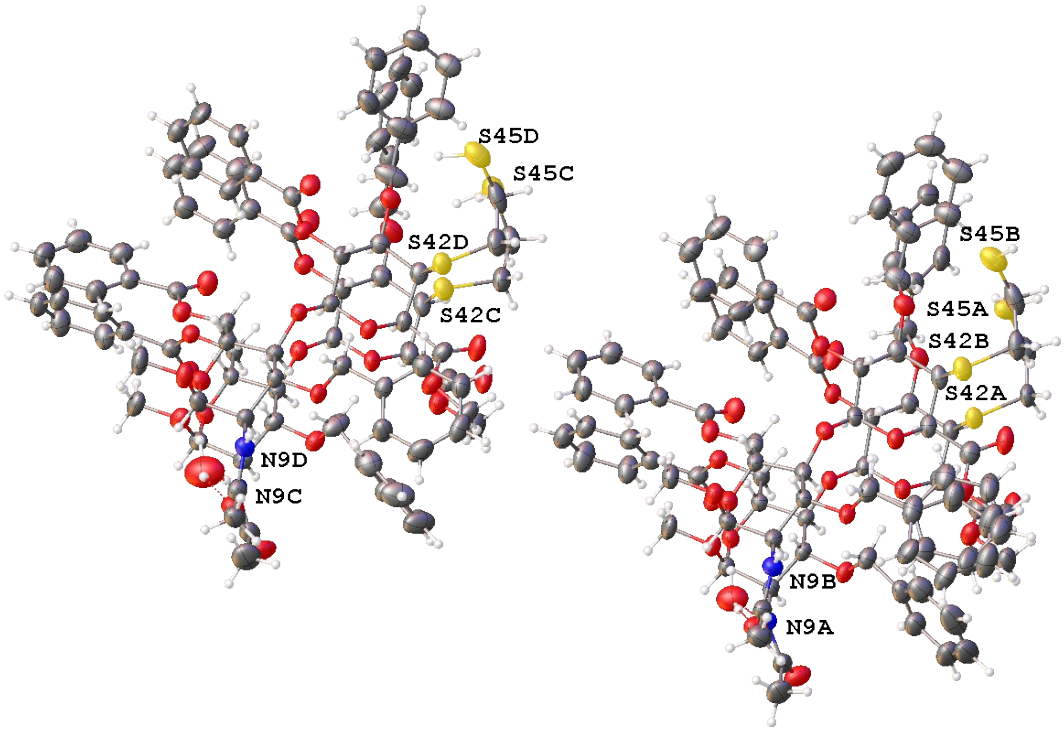


Fig. S5. Four independent molecules of **26** in the asymmetric unit with two water molecules. One benzyl ring is disordered over two locations at 50% occupancy. Only selected heteroatoms labelled.

Atomic displacement shown at 50% probability.

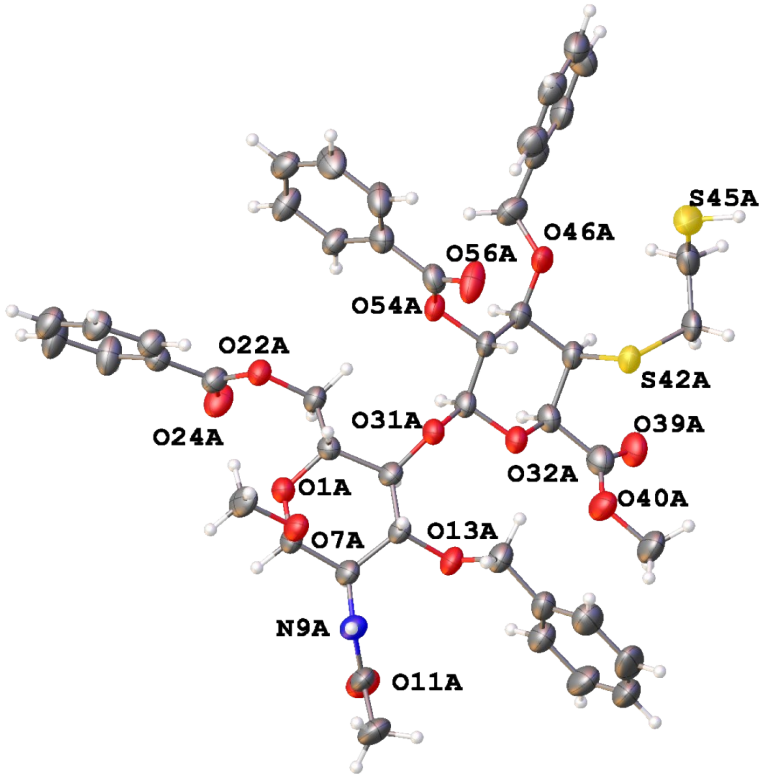


Fig. S6. A single molecule of **26** with full heteroatom labelling. Atomic displacement shown at 50% probability.

References for X-ray crystal structure data

(1) Bruker, *SAINT*, *v8.37A*, Bruker AXS Inc., Madison, Wisconsin, USA.

(2) Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. *J. Appl. Cryst*. **2015**, *48*, 3-10.

(3) Sheldrick, G. M. *Acta Cryst*. **2015**, *A71*, 3-8.

(4) Sheldrick, G. M. *Acta Cryst*. **2015**, *C71*, 3-8.

(5) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

(6) Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. *Acta Cryst*. **2016**, *B72*, 171-179.