

Supporting Information

TsOH-Catalyzed Acyl Migration Reaction of Bz-group: Innovative Assembly of Various Building Blocks for the Synthesis of Saccharides

Xing-Yong Liang*^a; An-Lin Liu^a; Hua-Jun Shawn Fan^a; Lei Wang^a; Zhi-Ning Xu^a;
Xin-Gang Ding^a; Bo-Shun Huang*^b.

^aSchool of Chemistry Engineering, Sichuan University of Science & Engineering,
Zigong 643000, China

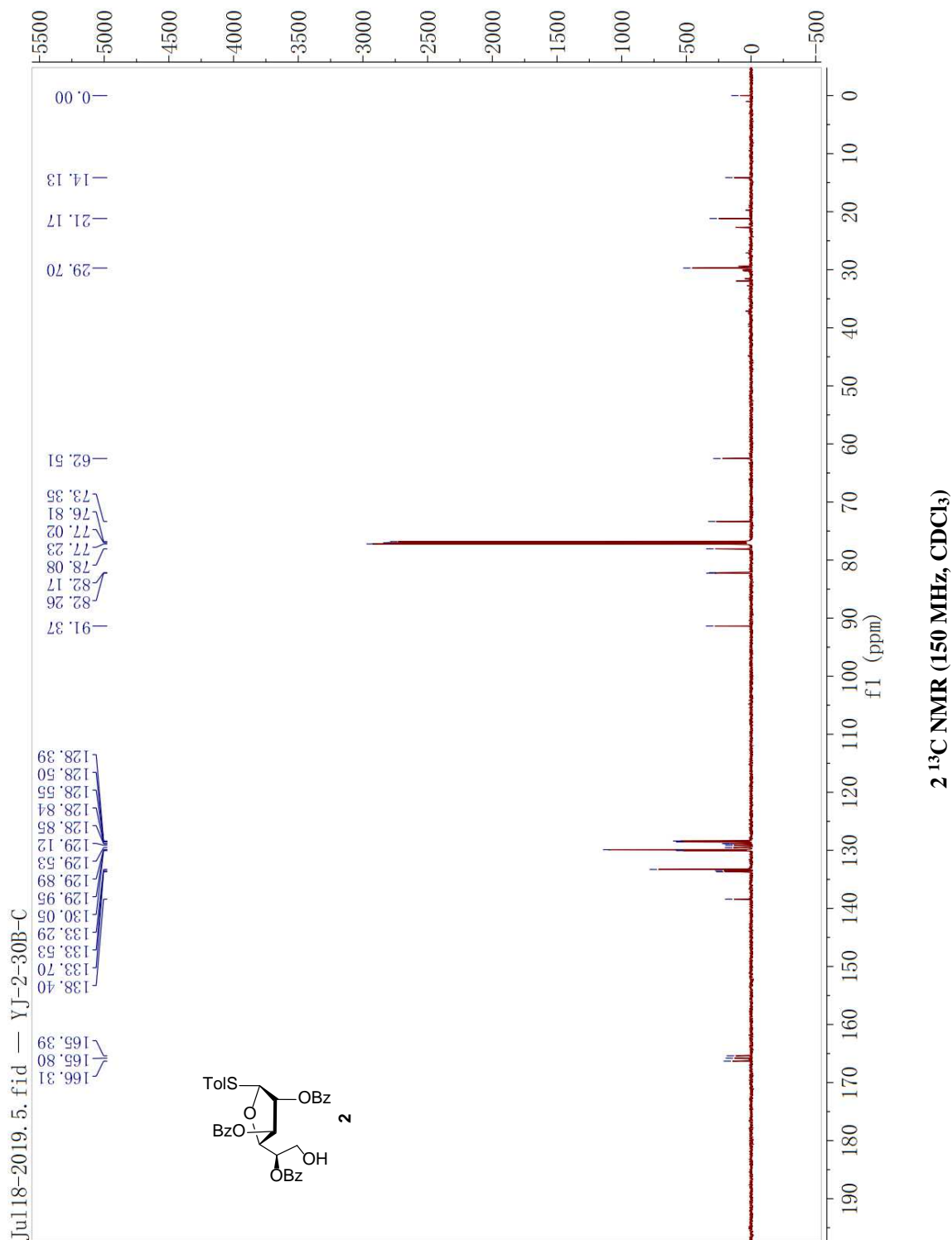
^bDivision of Chemistry and Chemical Engineering, California Institute of Technology
and Howard Hughes Medical Institute, 1200 East California Boulevard, Pasadena,
California 91125, United States

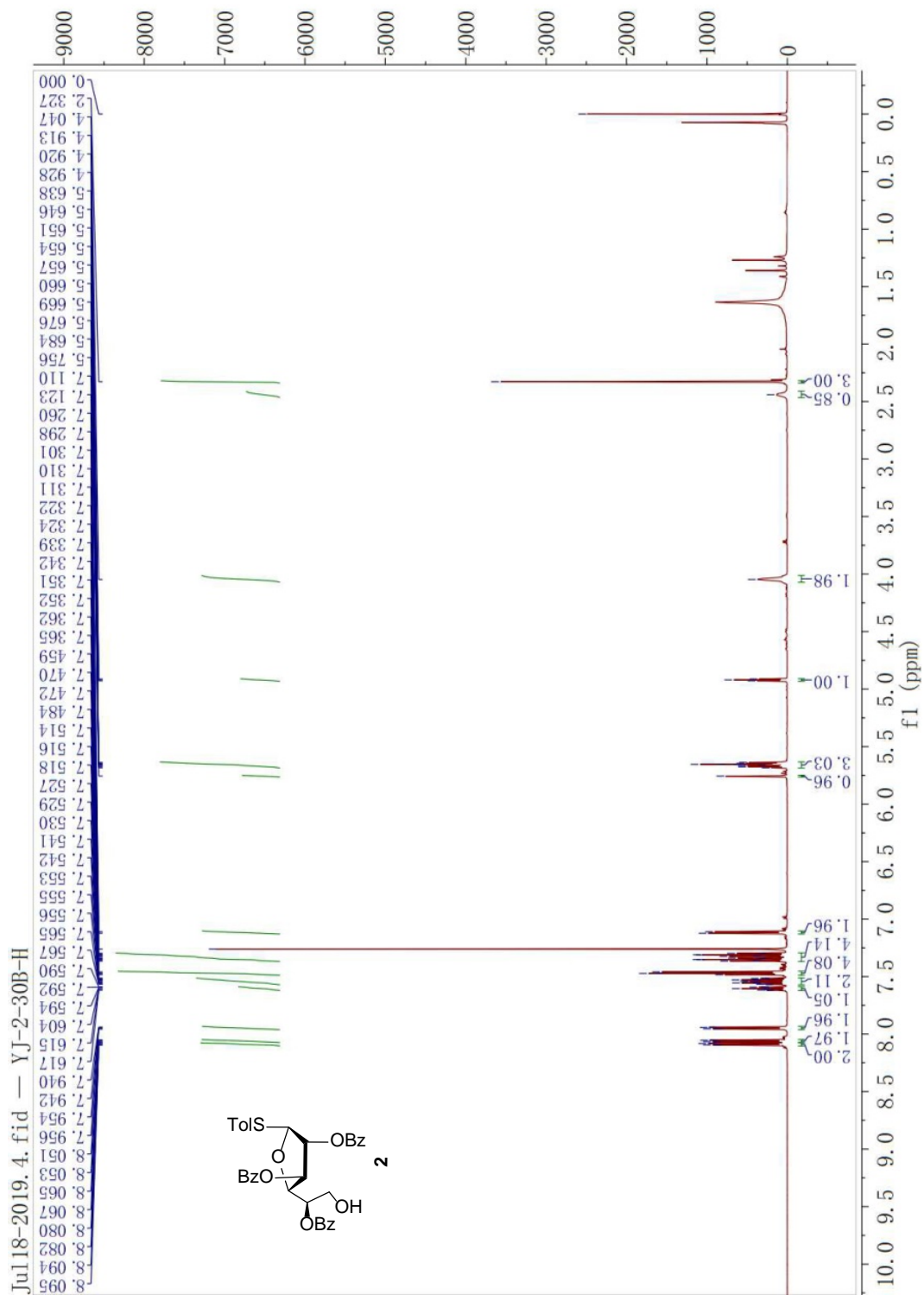
NMR spectra of products

Tolyl 2,3,6- <i>tri-O</i> -benzoyl-1-thio- β -D-galactofuranoside (2) and Tolyl 2,3,5- <i>tri-O</i> -benzoyl-1-thio- β -D-galactofuranoside (3).....	3
Tolyl 6- <i>O</i> -trityl-5- <i>O</i> -acetyl-2,3- <i>di-O</i> -benzoyl-1- <i>thio</i> - β -D-galactofuranoside (5a)	7
Tolyl 6- <i>O</i> -trityl-5- <i>O</i> -pivaloyl-2,3- <i>di-O</i> -benzoyl-1- <i>thio</i> - β -D-galactofuranoside (5b)	9
Tolyl 6- <i>O</i> -trityl-5- <i>O</i> - <i>p</i> -nitrobenzoyl-2,3- <i>di-O</i> -benzoyl-1- <i>thio</i> - β -D-galactofuranoside (5c) ...	11
Tolyl 6- <i>O</i> -trityl-5- <i>O</i> - <i>p</i> -methoxybenzoyl-2,3- <i>di-O</i> -benzoyl-1- <i>thio</i> - β -D-galactofuranoside (5d)	13
Tolyl 2,3- <i>di-O</i> -benzoyl-6- <i>O</i> -acetyl-1- <i>thio</i> - β -D-galactofuranoside (7a).....	15
Tolyl 6- <i>O</i> -pivaloyl-2,3- <i>di-O</i> -benzoyl-1- <i>thio</i> - β -D-galactofuranoside (7b).....	17
Tolyl 6- <i>O</i> - <i>p</i> -nitrobenzoyl-2,3- <i>di-O</i> -benzoyl-1- <i>thio</i> - β -D-galactofuranoside (7c).....	19
Tolyl 6- <i>O</i> - <i>p</i> -methoxybenzoyl-2,3- <i>di-O</i> -benzoyl-1- <i>thio</i> - β -D-galactofuranoside (7d)	21
2-Hydroxy-2-phenylethyl benzoate (10a)	23
2-Hydroxy-3-phenoxypropyl benzoate (10b).....	25
Methyl 2,3,6- <i>tri-O</i> -benzoyl- β -D-galactofuranoside (10c)	27
1,2- <i>O</i> -Isopropylidene-6- <i>O</i> -benzoyl-3- <i>O</i> -benzyl- α -D-glucofuranose (10d).....	29

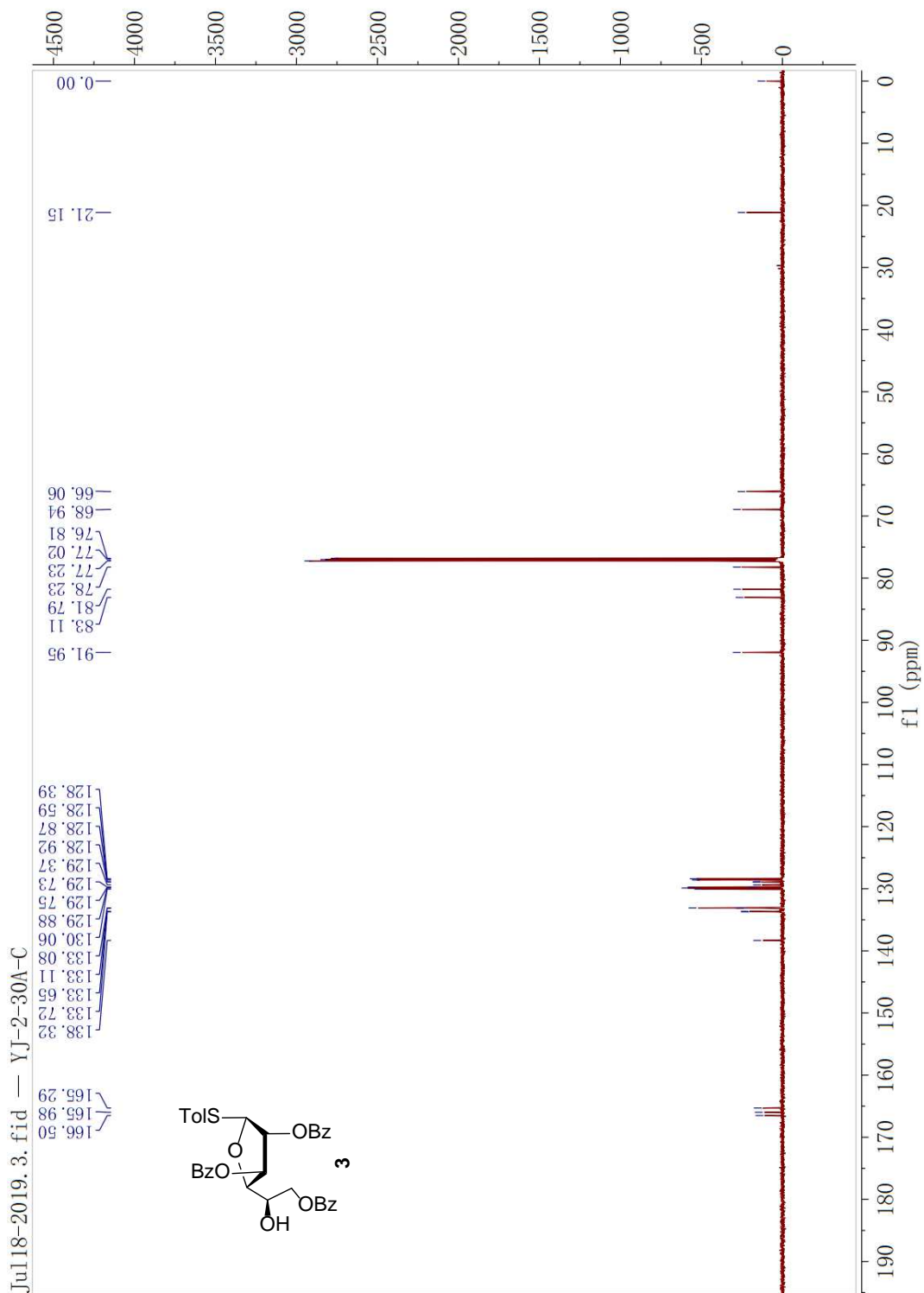
Tolyl 2,3,4- <i>tri-O</i> -benzoyl-1- <i>thio-β</i> -D-galactopyranoside (9e), Tolyl 2,3,6- <i>tri-O</i> -benzoyl-1- <i>thio-β</i> -D-galactopyranoside (10e) and Tolyl 2,4,6- <i>tri-O</i> -benzoyl-1- <i>thio-β</i> -D-galactopyranoside (10e')	31
Methyl 2,3,6- <i>tri-O</i> -benzoyl- α -D-galactopyranoside (10f)	37
1,2- <i>O,O</i> -Isopropylidene-5- <i>O</i> -benzoyl- α -D-xylofuranose (10g)	39
Methyl 2,3,6- <i>tri-O</i> -benzoyl- α -D-mannopyranoside (10h)	41
methyl 2,3,4- <i>tri-O</i> -benzoyl- α -D-glucopyranoside (9i) and Methyl 2,3,6- <i>tri-O</i> -benzoyl- α -D-glucopyranoside (10i)	43
(\pm)-[(3 <i>aRS</i> ,4 <i>SR</i> ,5 <i>RS</i> ,6 <i>aSR</i>)-5-Hydroxy-2-oxohexahydro-2 <i>H</i> -cyclopenta[<i>b</i>]furan-4-yl] methyl benzoate (10j)	45
Methyl 2,3- <i>di-O</i> -benzoyl- α -L-arabinofuranoside (9k)	47
Tolyl 6- <i>O-tert</i> -butyldiphenylsilyl-2,3- <i>di-O</i> -benzoyl-1- <i>thio-β</i> -D-galactopyranoside (10l)	48
Methyl 2,4- <i>di-O</i> -benzoyl- α -L-rhamnopyranoside (10m)	50
6- <i>O-tert</i> -Butyldiphenylsilyl-2,3,5- <i>tri-O</i> -benzoyl-1- <i>thio-β</i> -D-galactofuranoside (11)	52
Octyl 6- <i>O-tert</i> -butyldiphenylsilyl-2,3,5- <i>tri-O</i> -benzoyl- β -D-galactopyranosyl-(1 \rightarrow 6)-2,3,5- <i>tri-O</i> -benzoyl- β -D-galactofuranoside (14)	54
Octyl 2,3,5- <i>tri-O</i> -benzoyl- β -D-galactopyranosyl-(1 \rightarrow 6)-2,3,5- <i>tri-O</i> -benzoyl- β -D-galactofuranoside (15)	56
Octyl 2,3,6- <i>tri-O</i> -benzoyl- β -D-galactopyranosyl-(1 \rightarrow 6)-2,3,5- <i>tri-O</i> -benzoyl- β -D-galactofuranoside (16)	58
Octyl 2,3,5,6- <i>tetra-O</i> -benzoyl- β -D-galactopyranosyl-(1 \rightarrow 6)-2,3,5- <i>tri-O</i> -benzoyl- β -D-galactofuranosyl-(1 \rightarrow 5)-2,3,6- <i>tri-O</i> -benzoyl- β -D-galactopyranosyl-(1 \rightarrow 6)-2,3,5- <i>tri-O</i> -benzoyl- β -D-galactofuranoside (18)	60

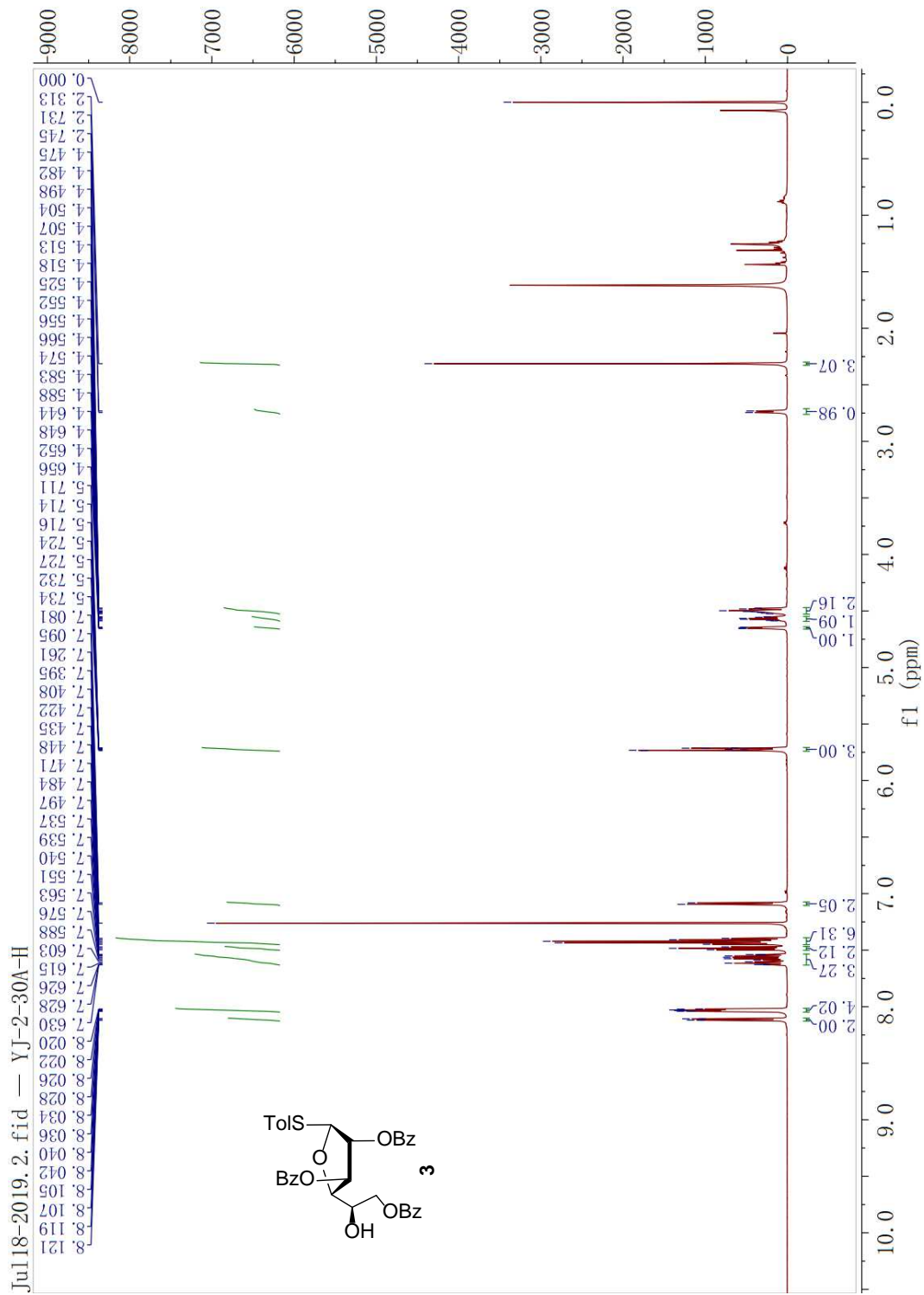
Tolyl 2,3,6-tri-O-benzoyl-1-thio-β-D-galactofuranoside (2) and Tolyl 2,3,5-tri-O-benzoyl-1-thio-β-D-galactofuranoside (3)



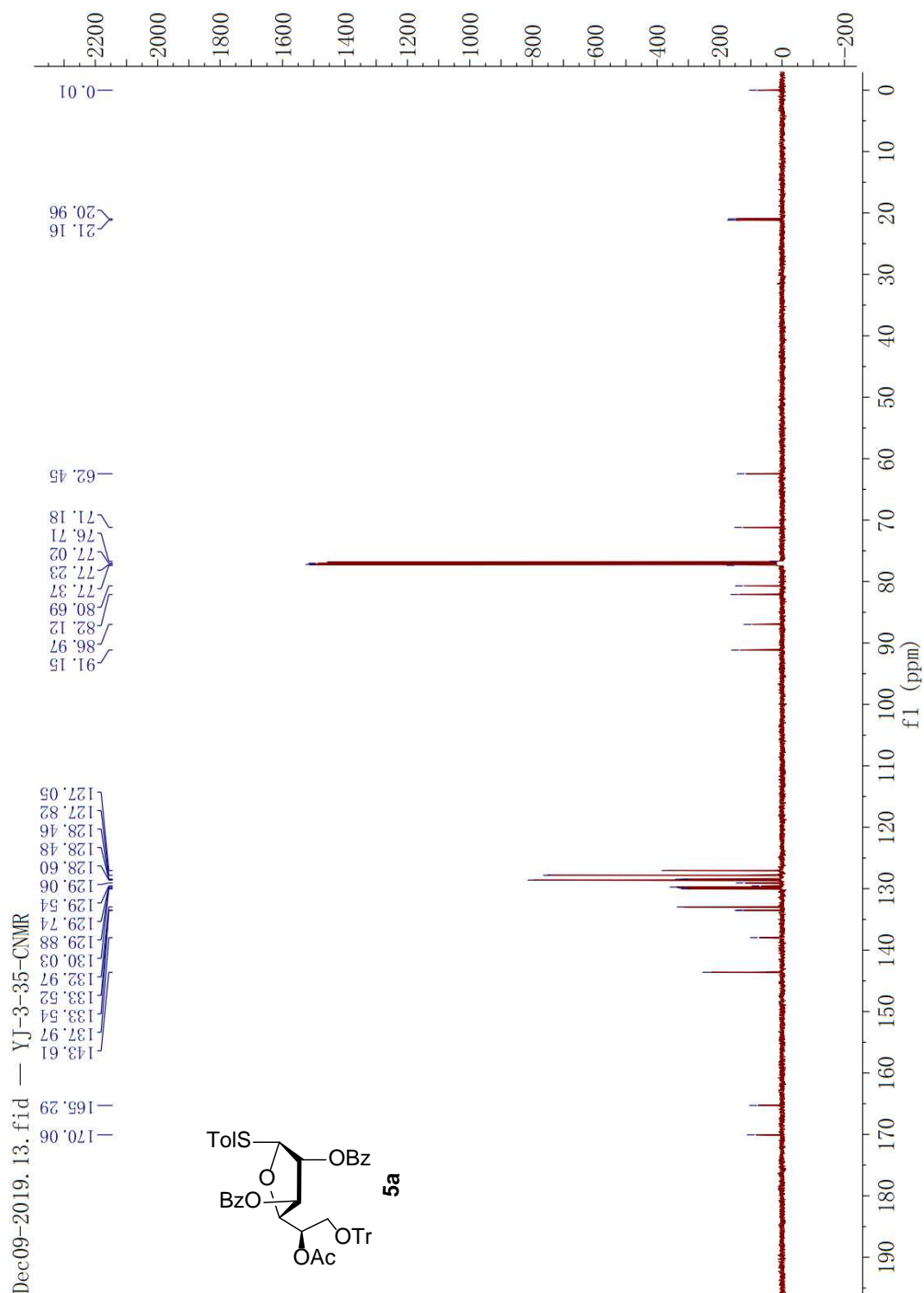


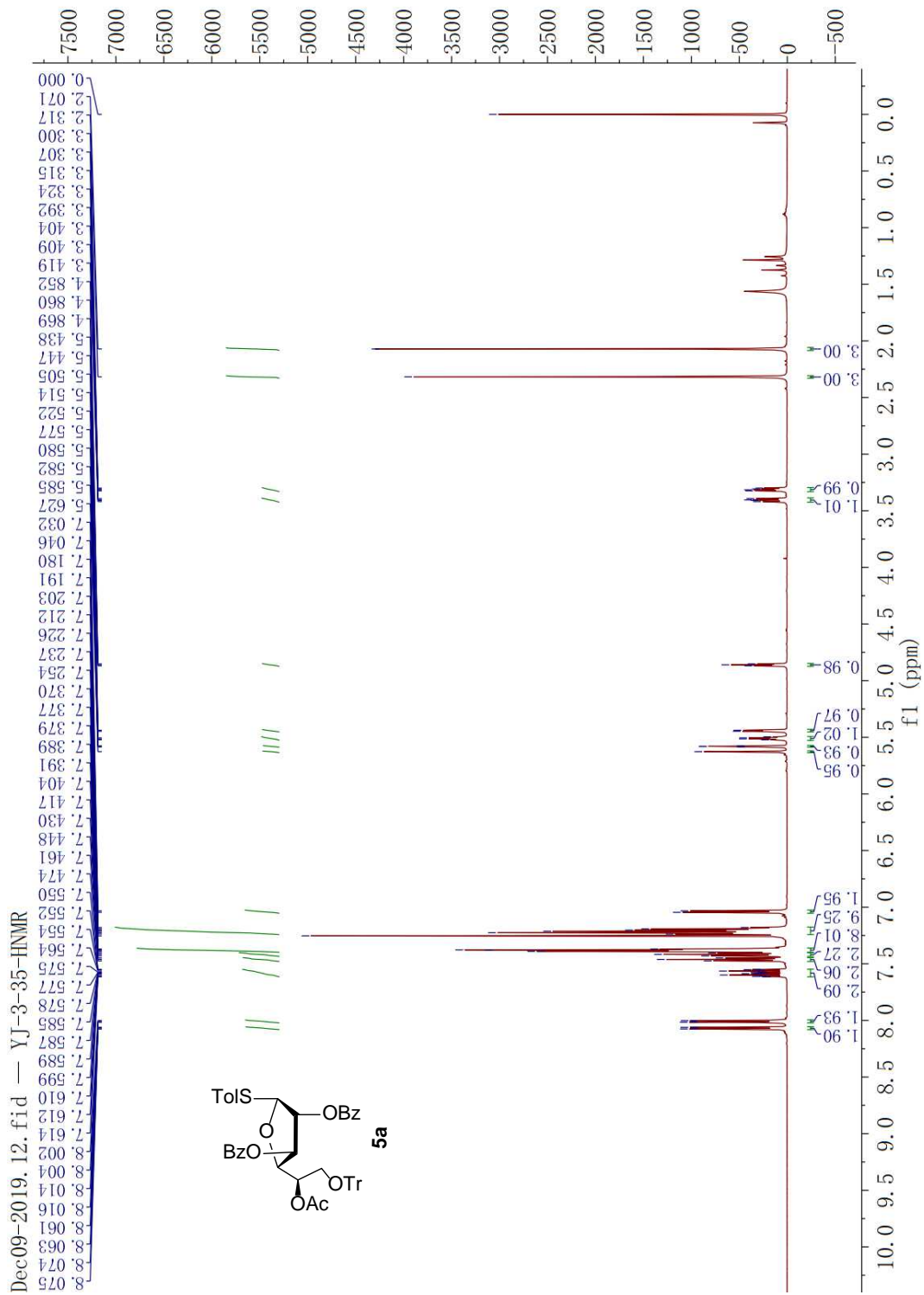
2 ¹H NMR (600 MHz, CDCl₃)





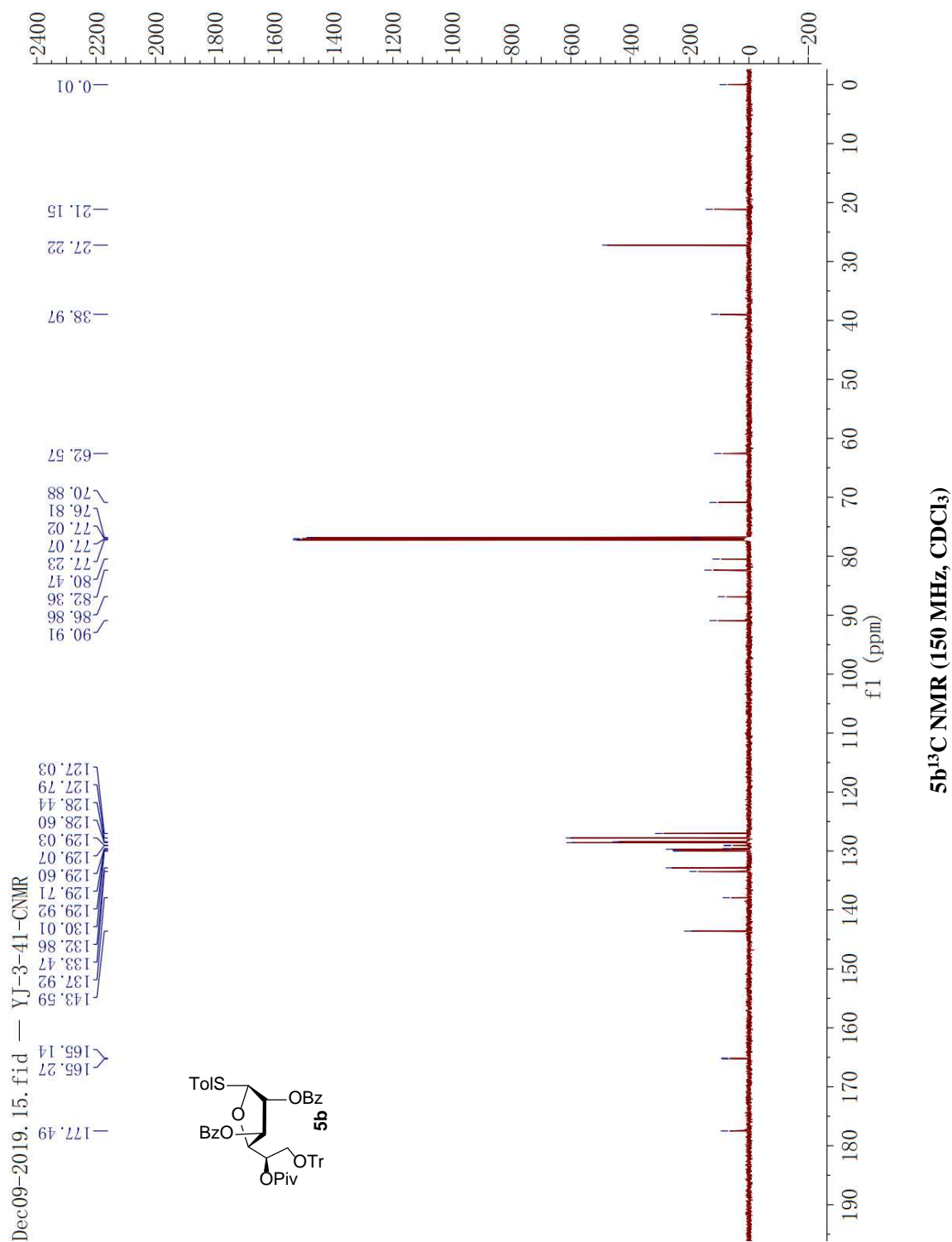
Tolyl 6-O-trityl-5-O-acetyl-2,3-di-O-benzoyl-1-thio-β-D-galactofuranoside (5a)

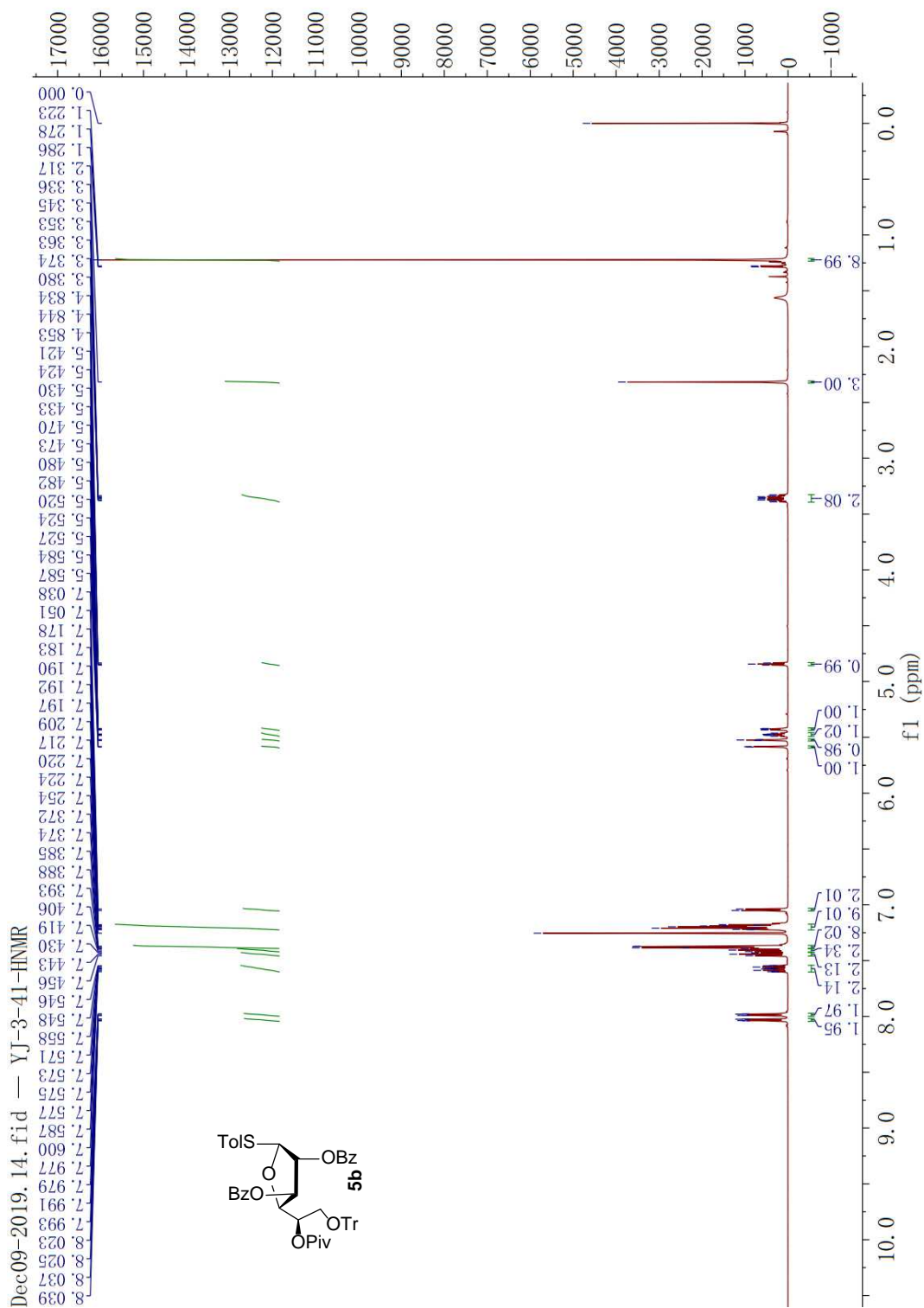




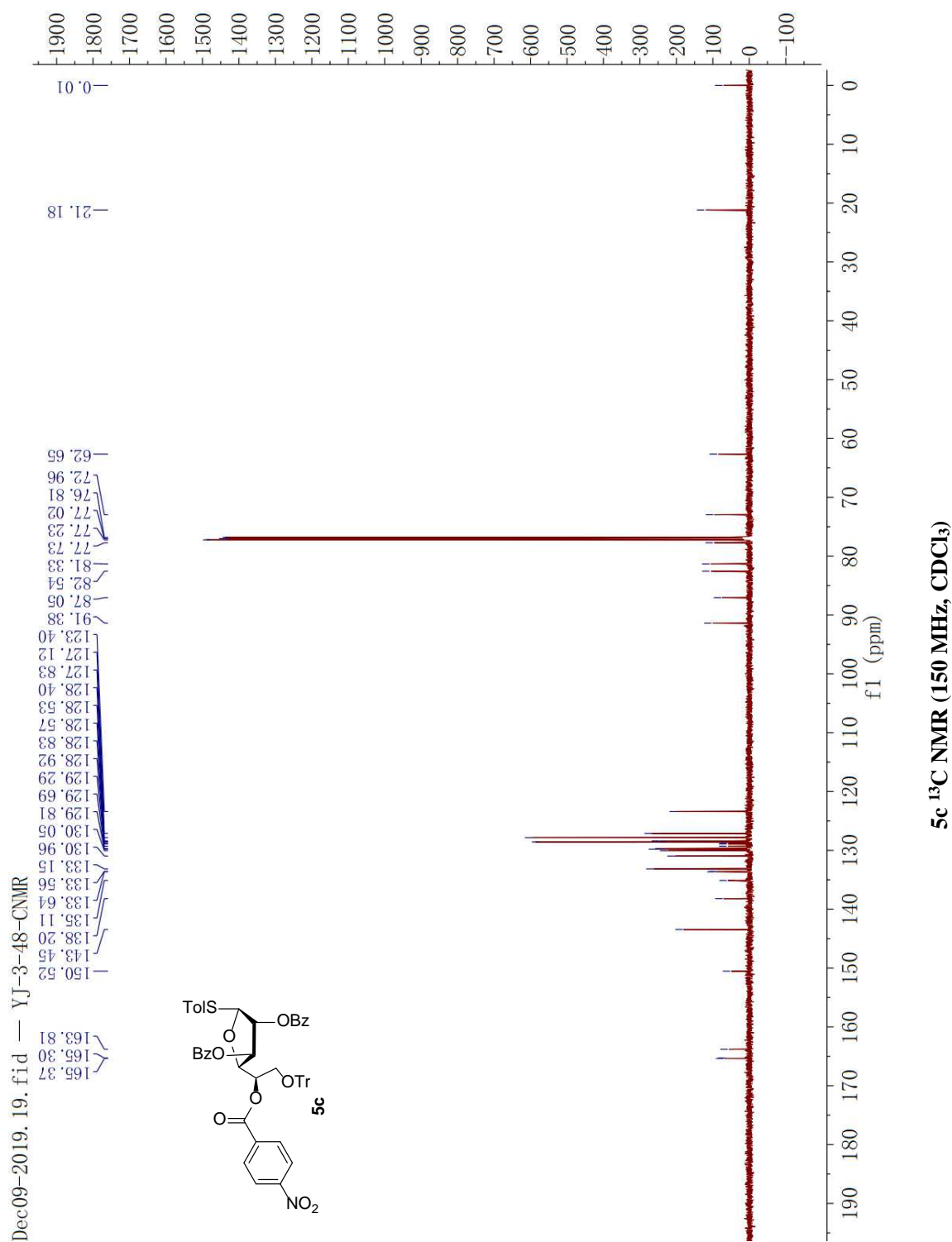
5a ¹H NMR (600 MHz, CDCl₃)

Tolyl 6-O-trityl-5-O-pivaloyl-2,3-di-O-benzoyl-1-thio- β -D-galactofuranoside (5b)

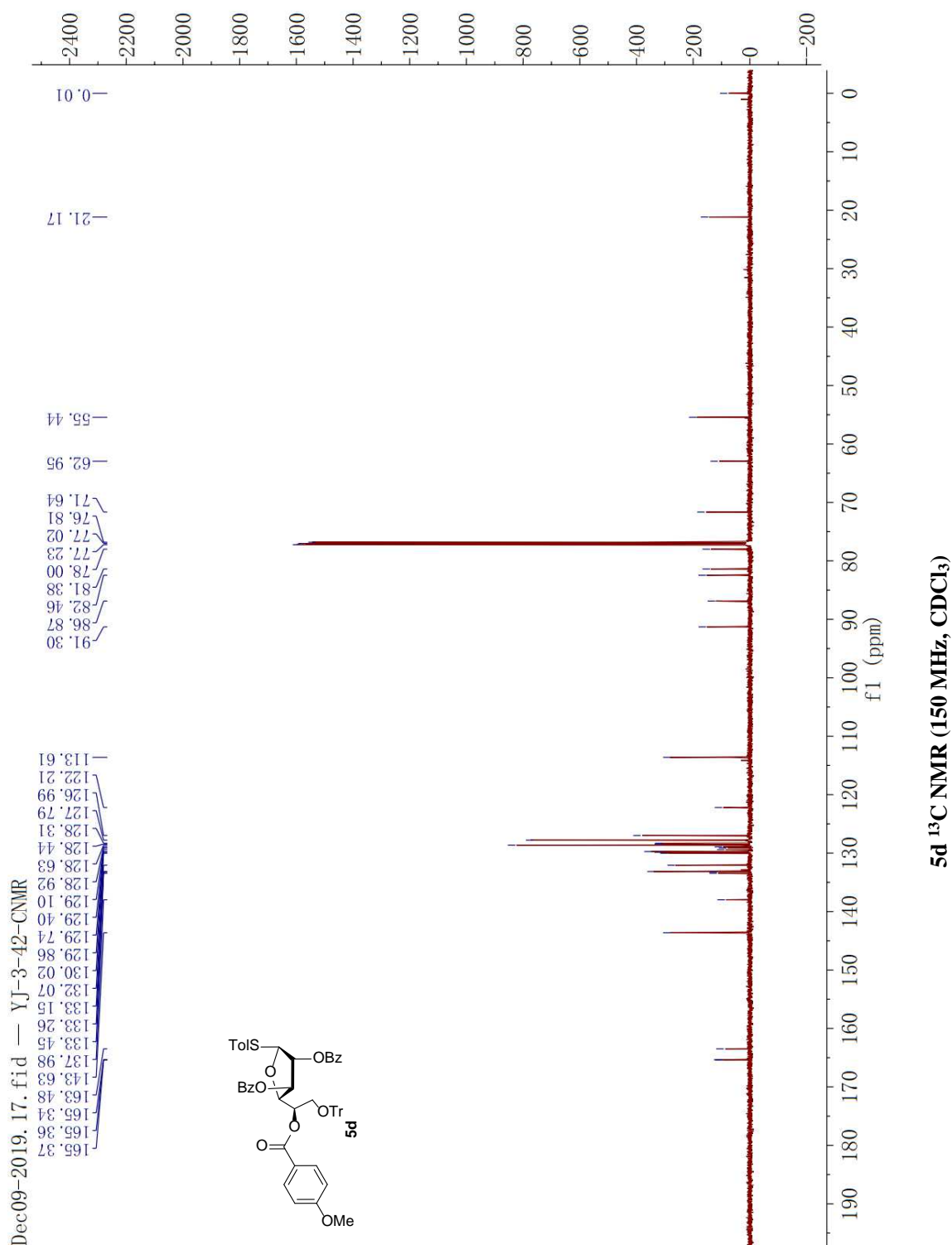


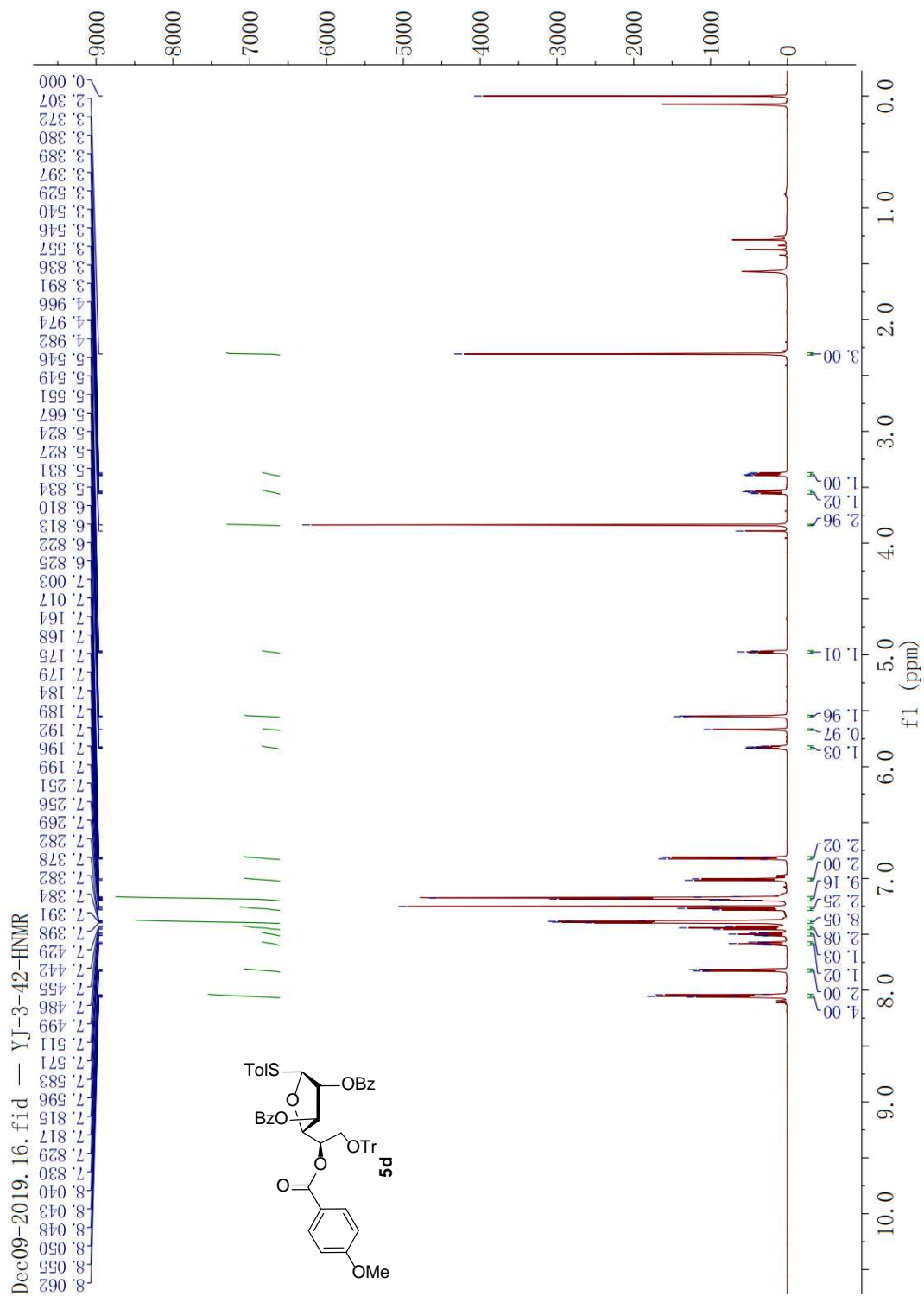


Tolyl 6-O-trityl-5-O-p-nitrobenzoyl-2,3-di-O-benzoyl-1-thio-β-D-galactofuranoside (5c)



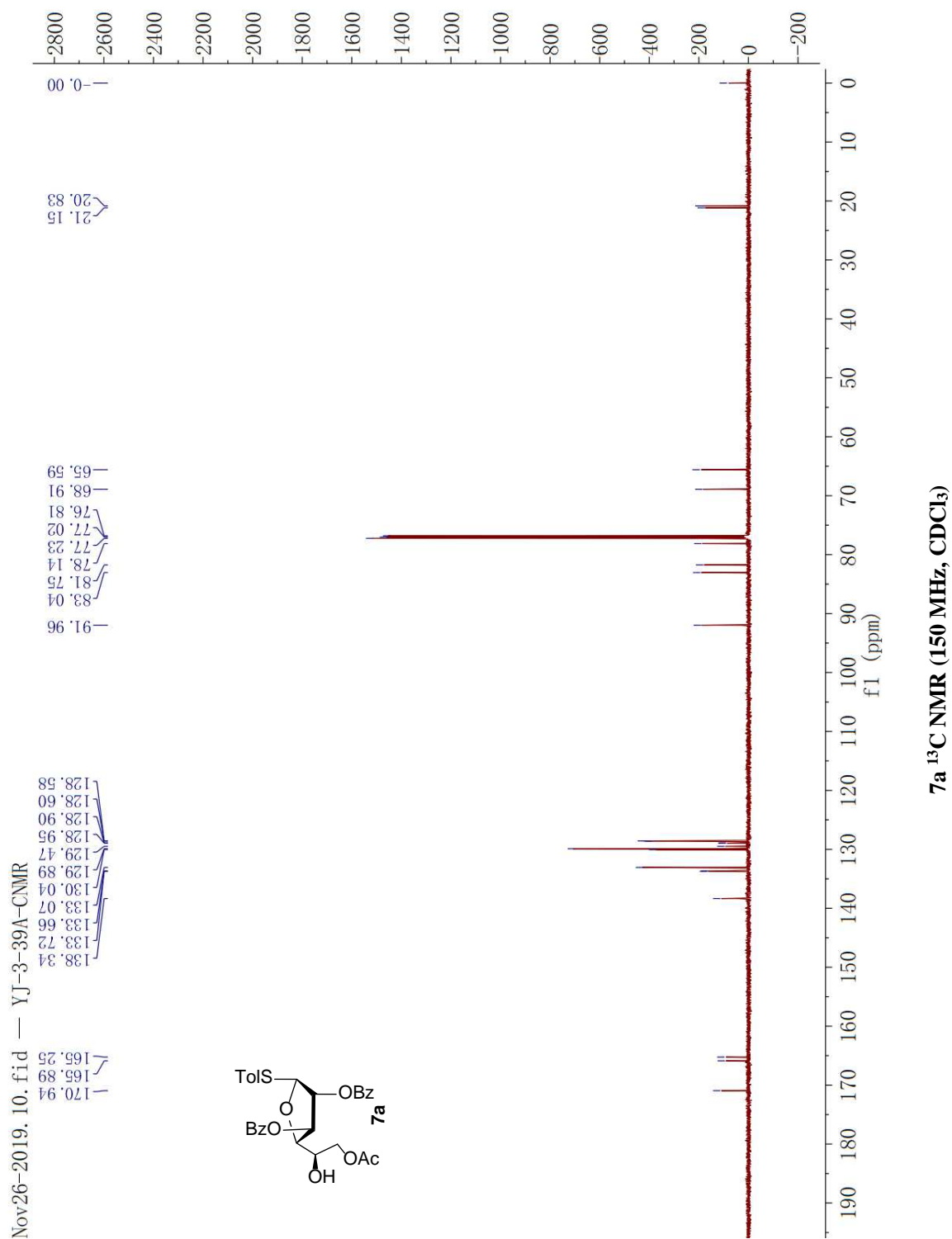
Tolyl **6-O-trityl-5-O-p-methoxybenzoyl-2,3-di-O-benzoyl-1-thio-β-D-galactofuranoside (5d)**



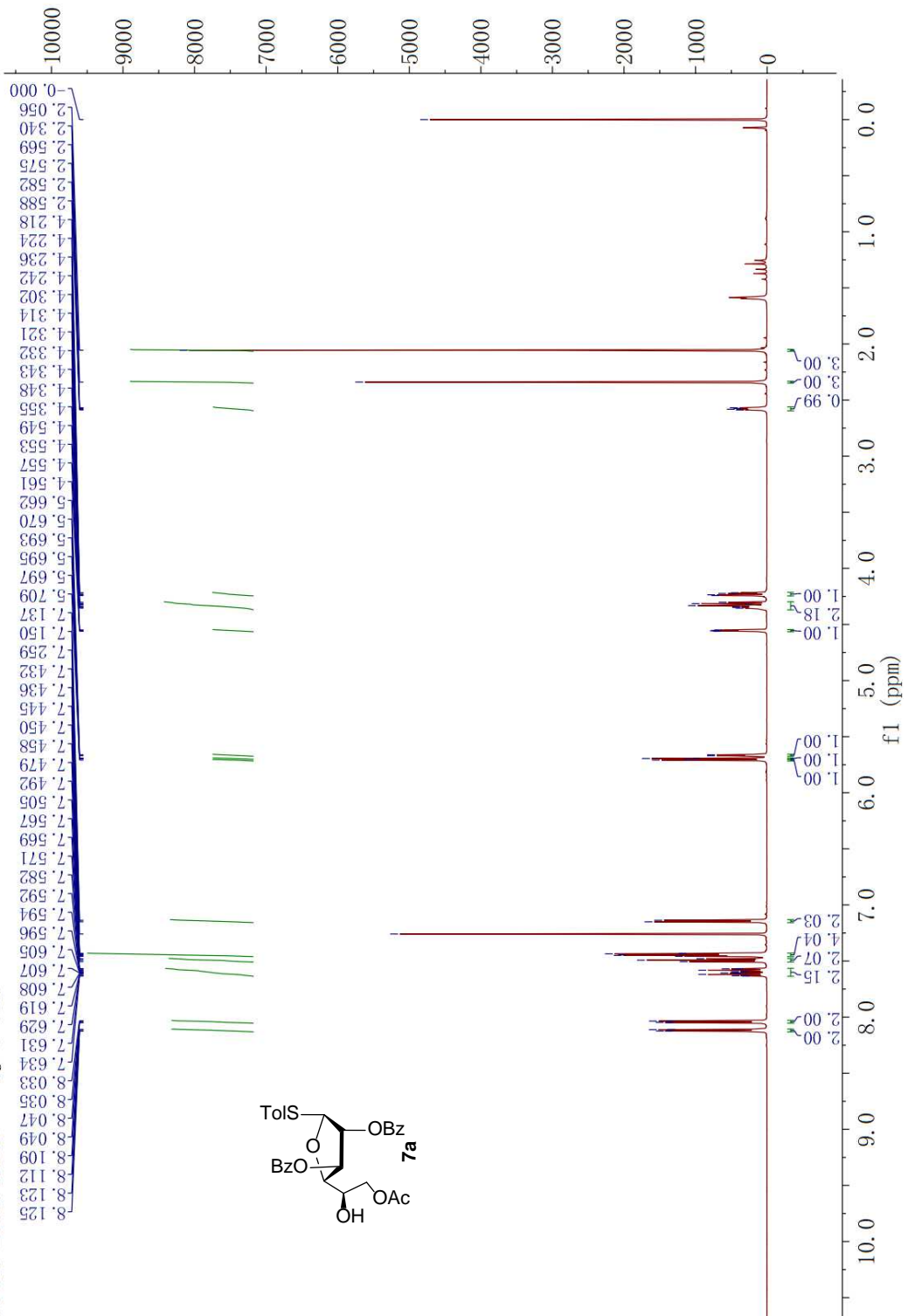


5d ¹H NMR (600 MHz, CDCl₃)

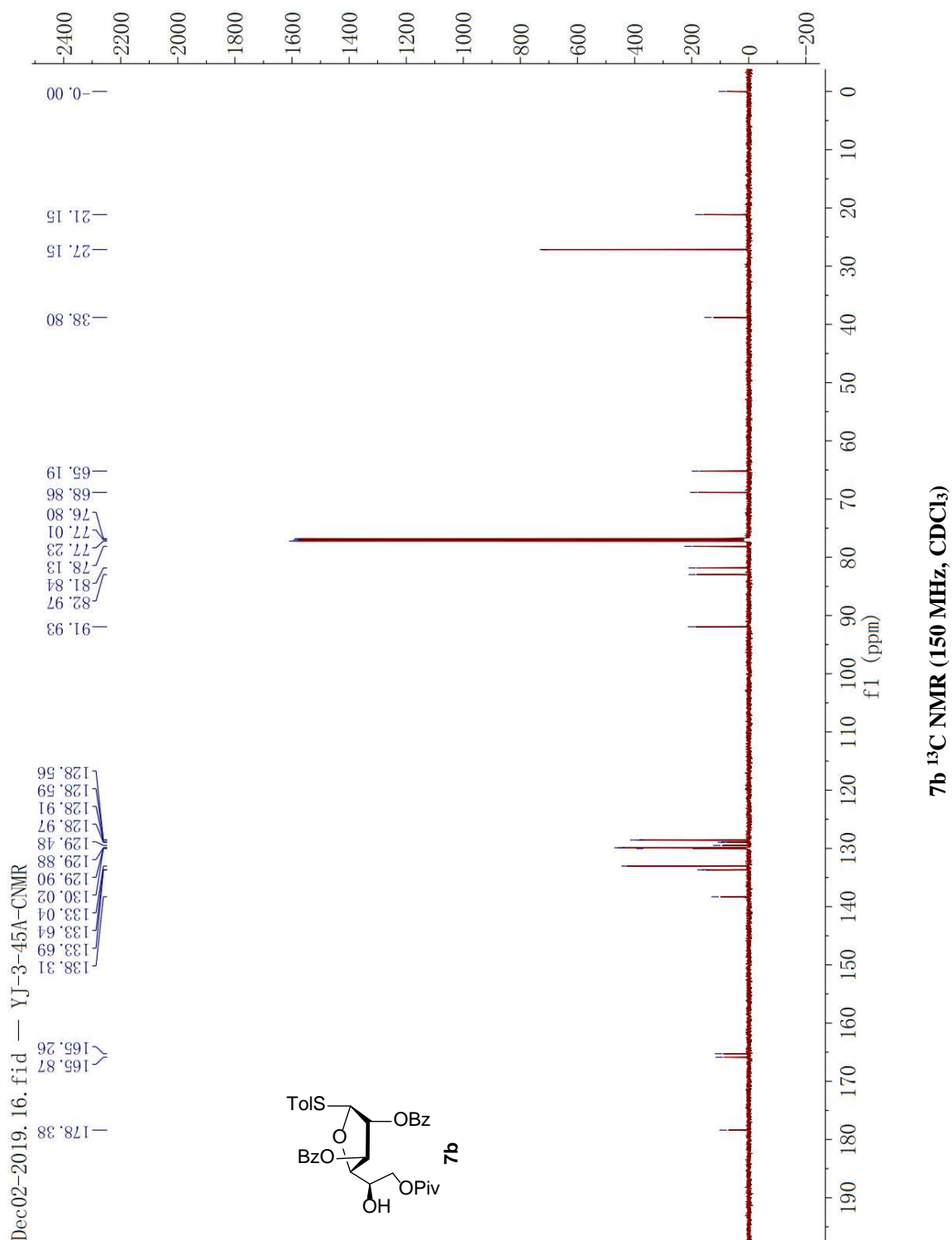
Tolyl 2,3-di-O-benzoyl-6-O-acetyl-1-thio-β-D-galactofuranoside (7a)



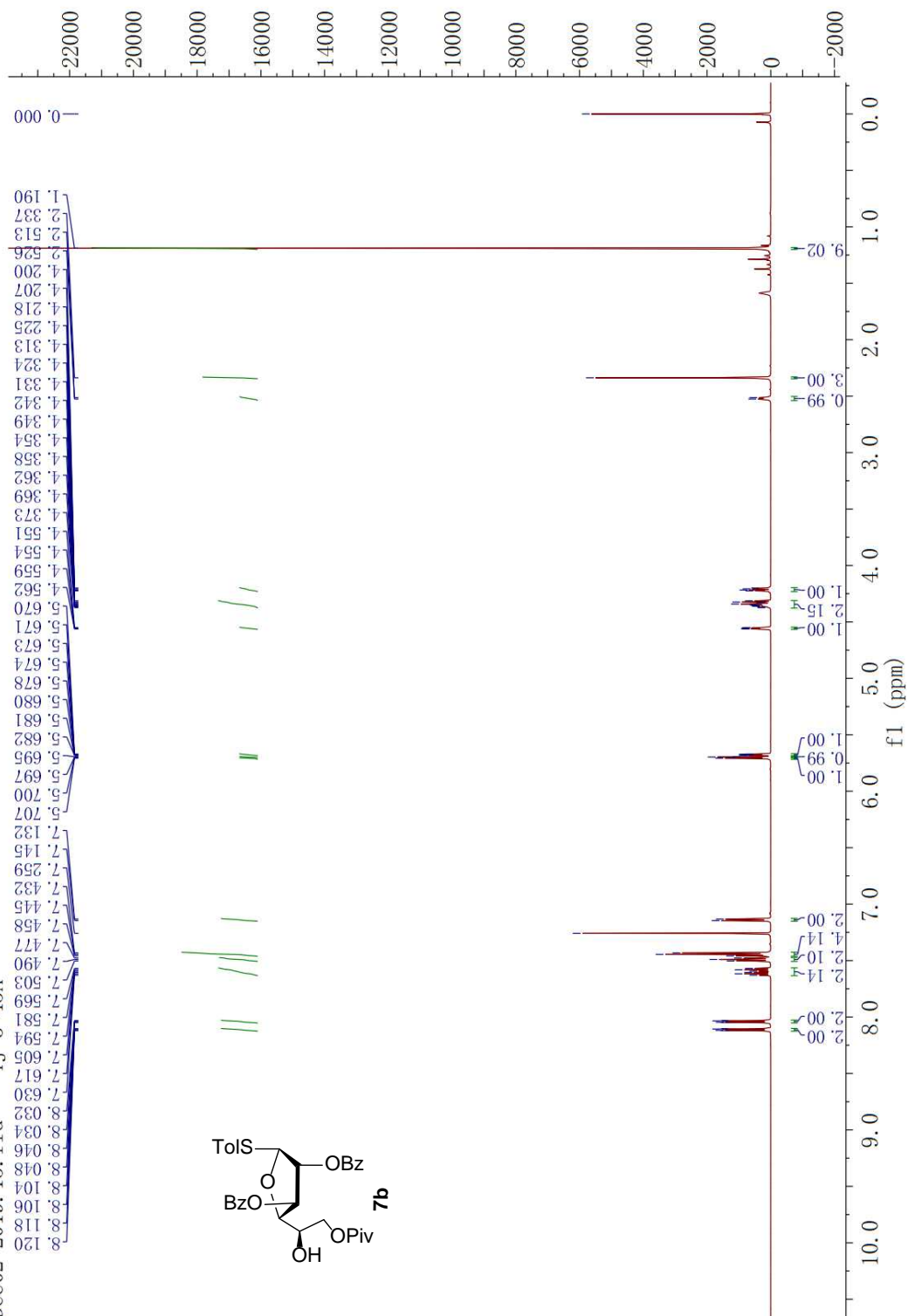
Nov26-2019.9.fid — YJ-3-39A



Tolyl 6-O-pivaloyl-2,3-di-O-benzoyl-1-thio-β-D-galactofuranoside (7b)

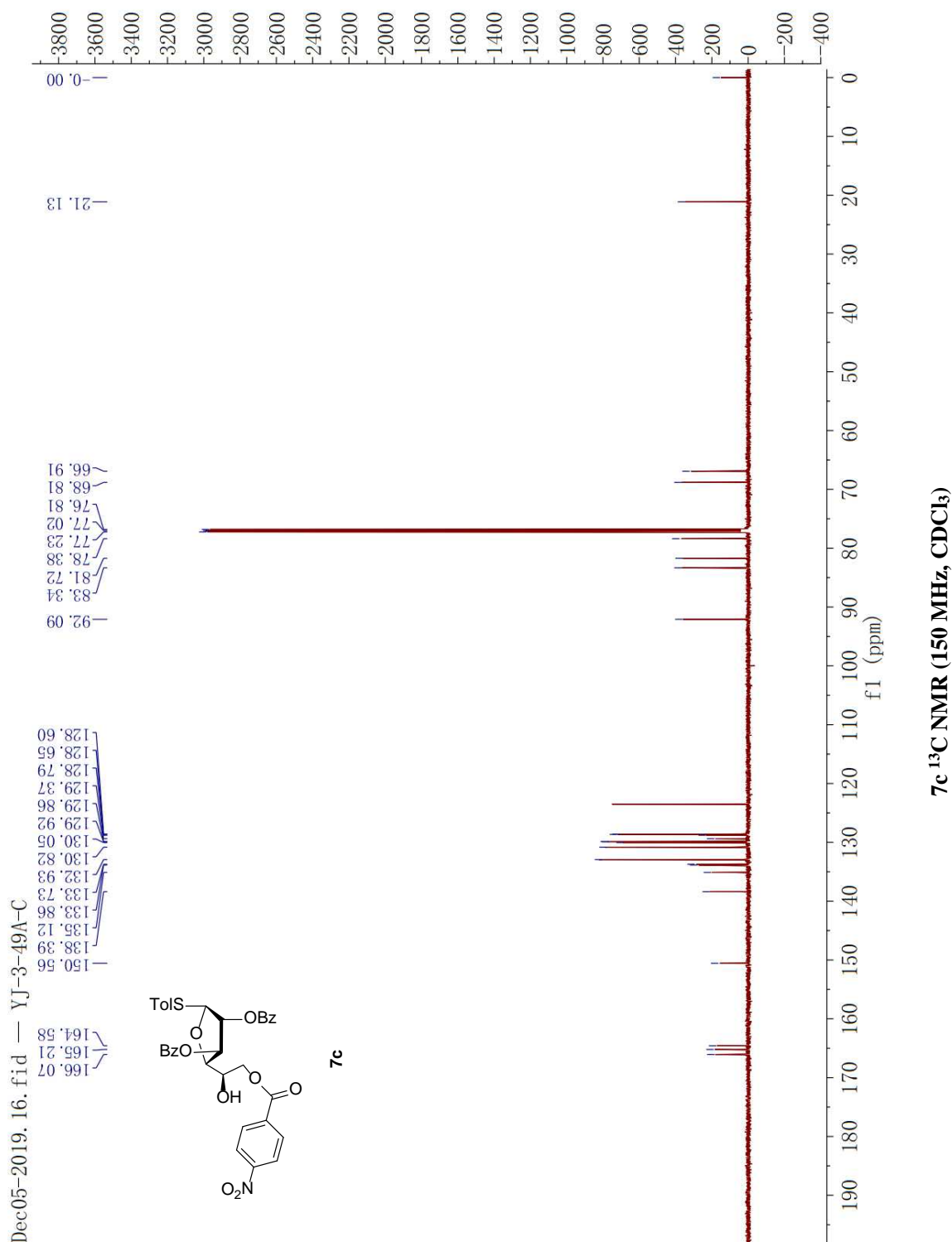


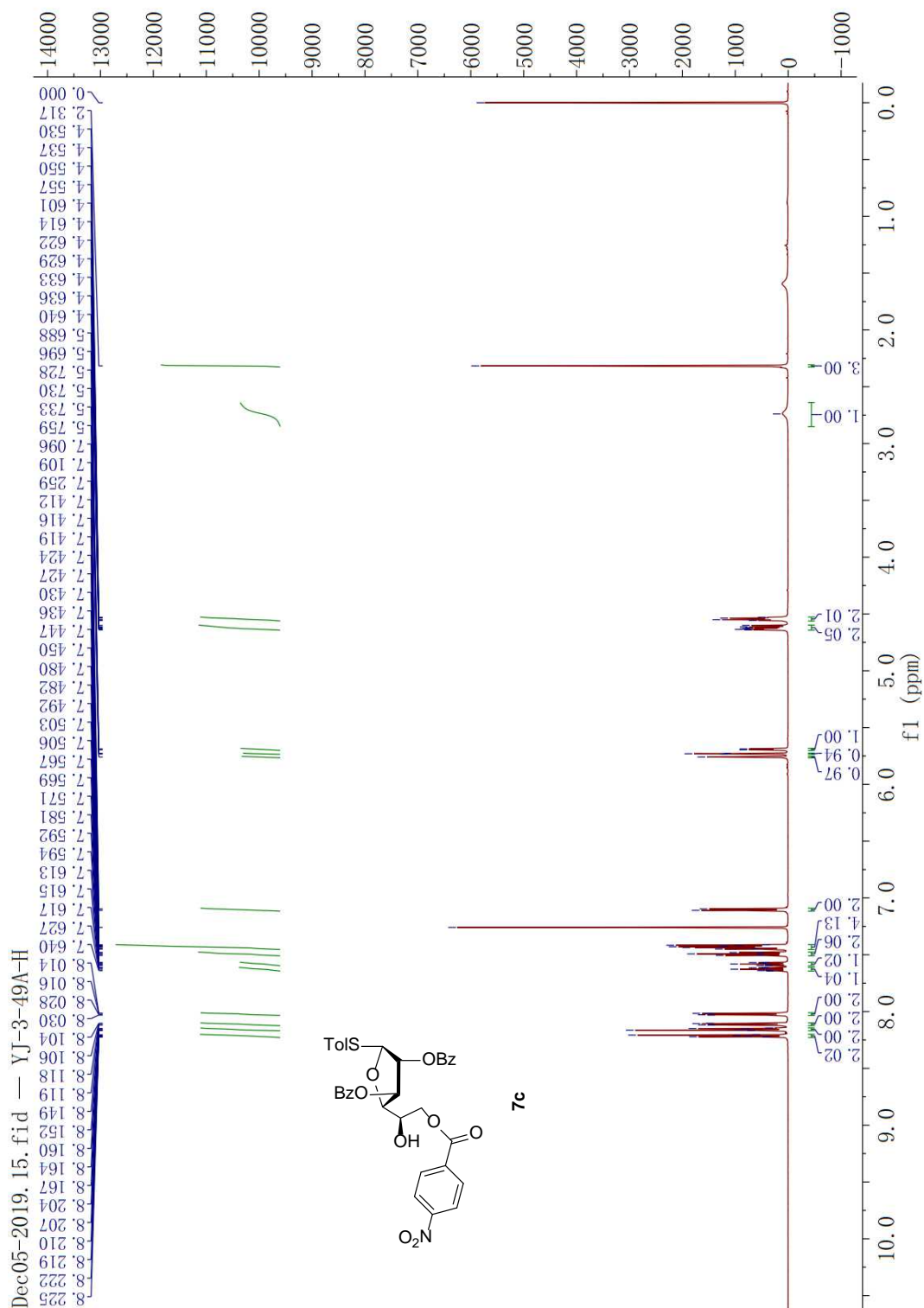
Dec02-2019.15.fid — YJ-3-45A



7b ¹H NMR (600 MHz, CDCl₃)

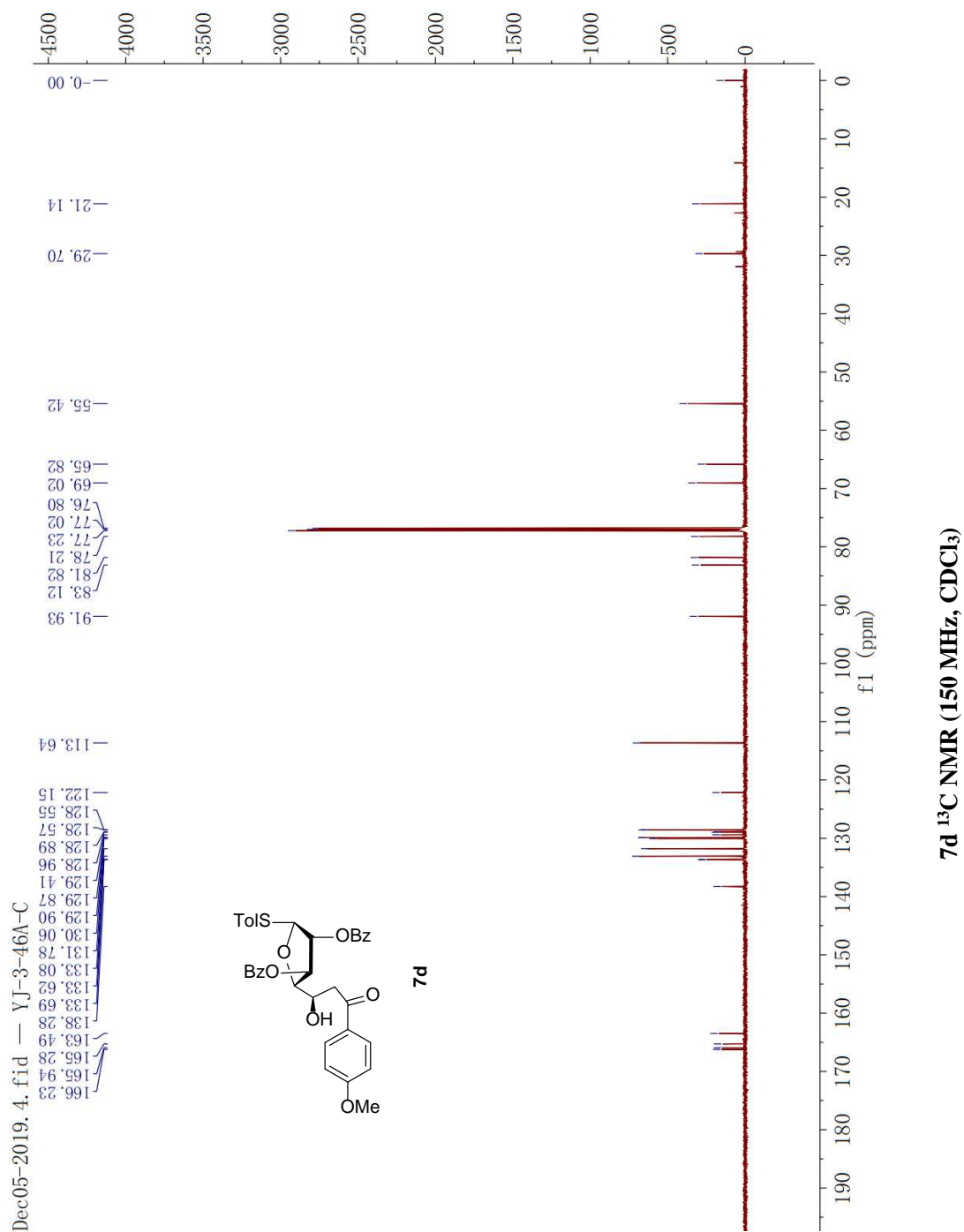
Tolyl 6-O-p-nitrobenzoyl-2,3-di-O-benzoyl-1-thio-β-D-galactofuranoside (7c)

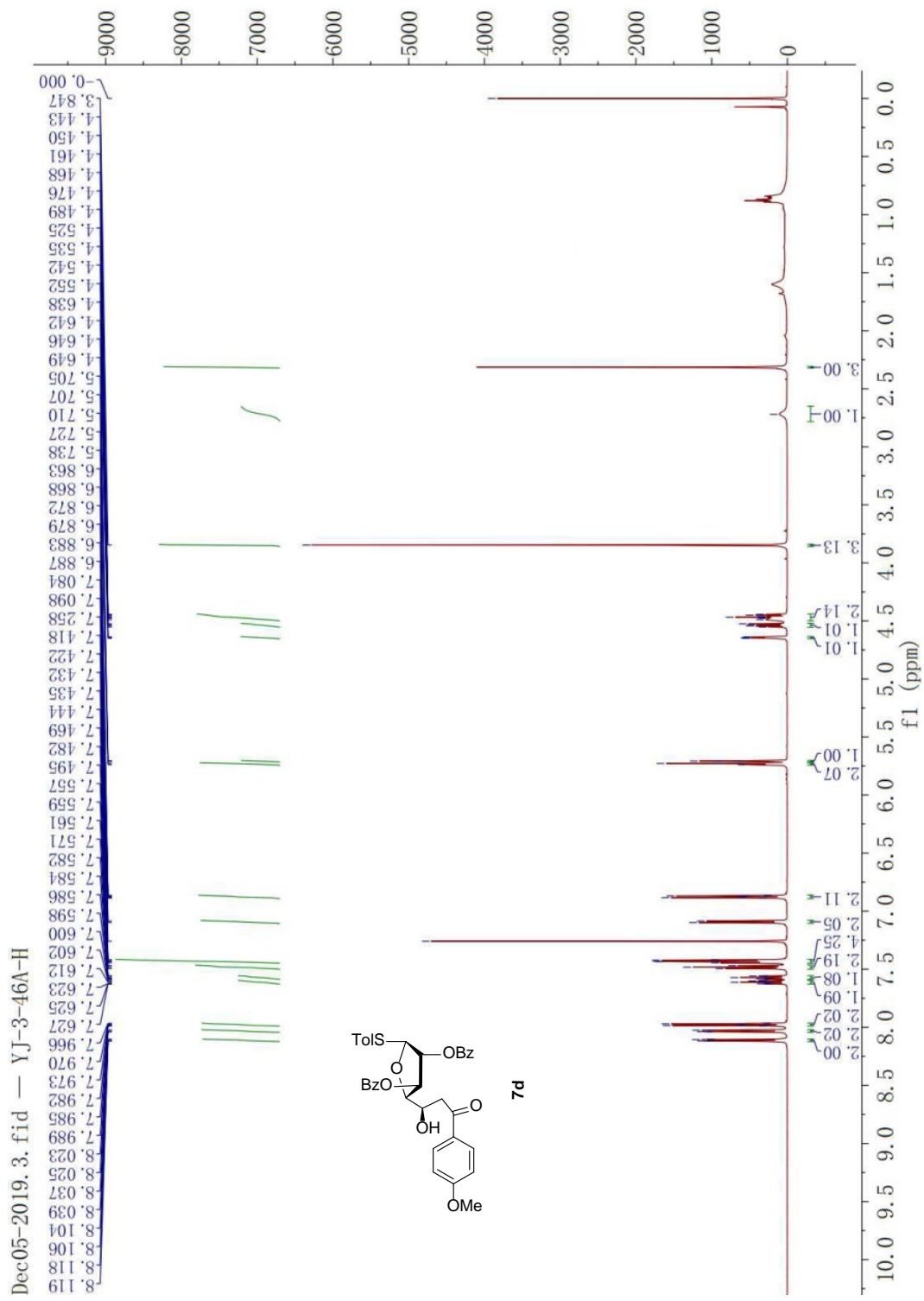




7c ¹H NMR (600 MHz, CDCl₃)

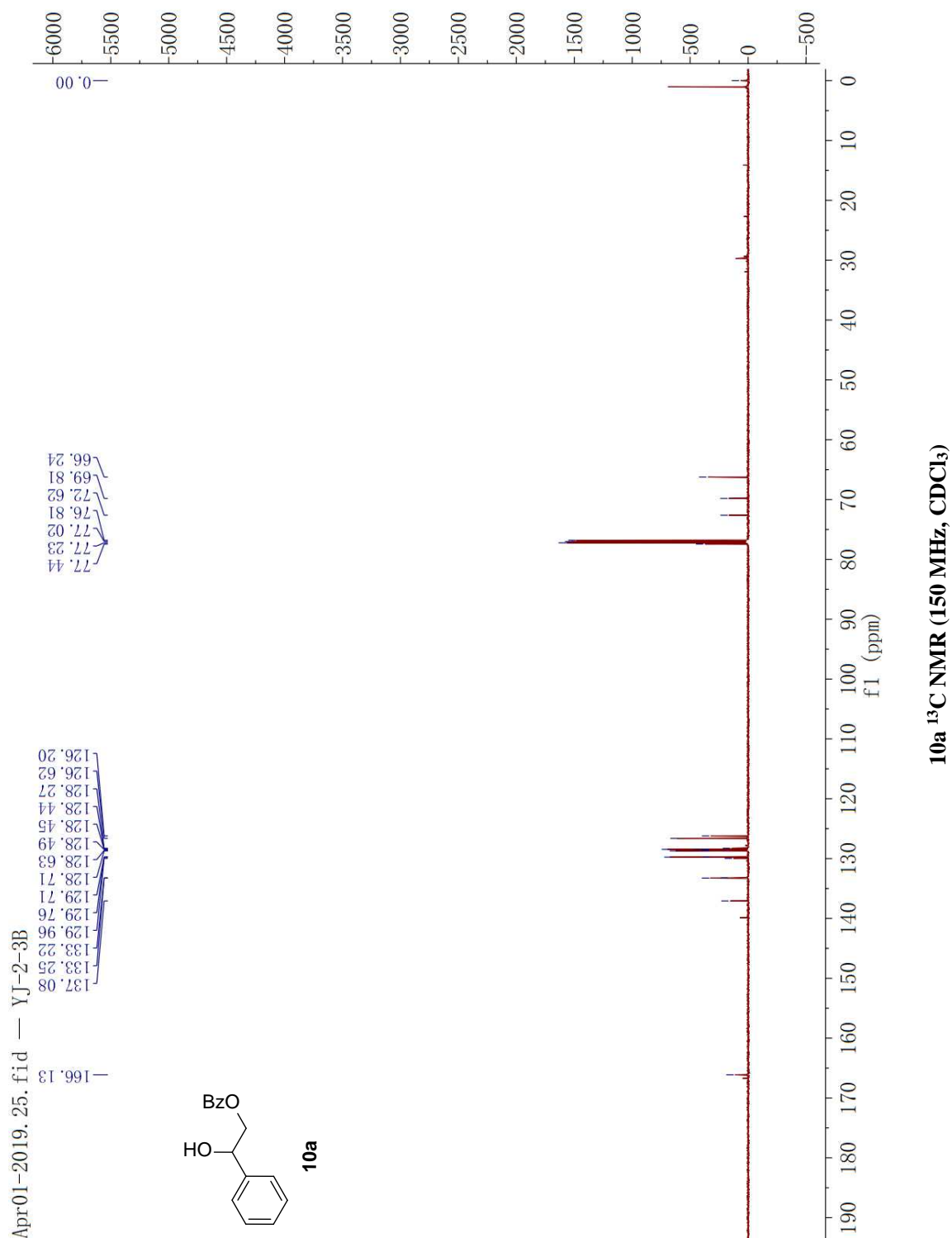
Tolyl 6-*O*-*p*-methoxybenzoyl-2,3-*di-O*-benzoyl-1-*thio*- β -D-galactofuranoside (7d)

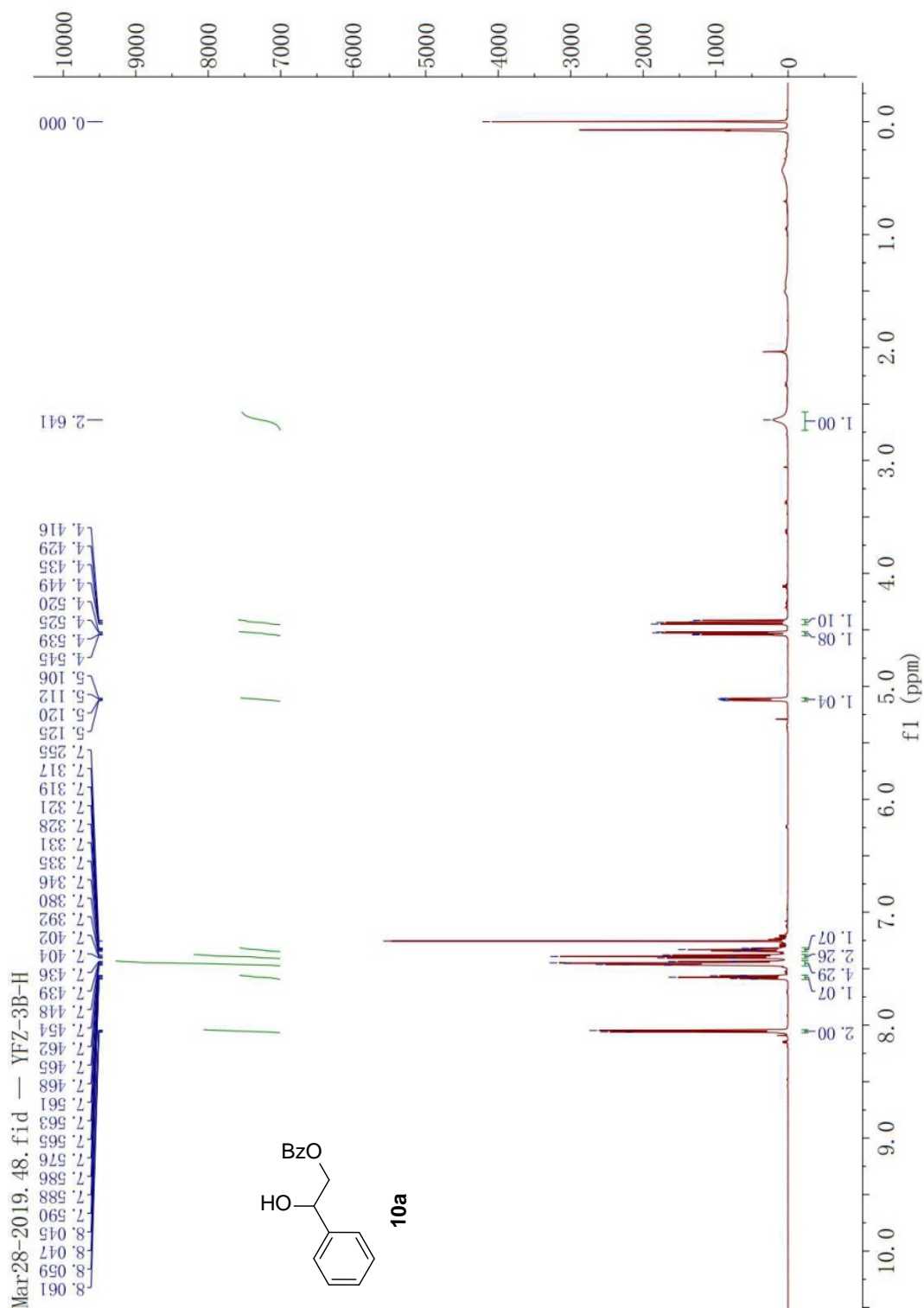




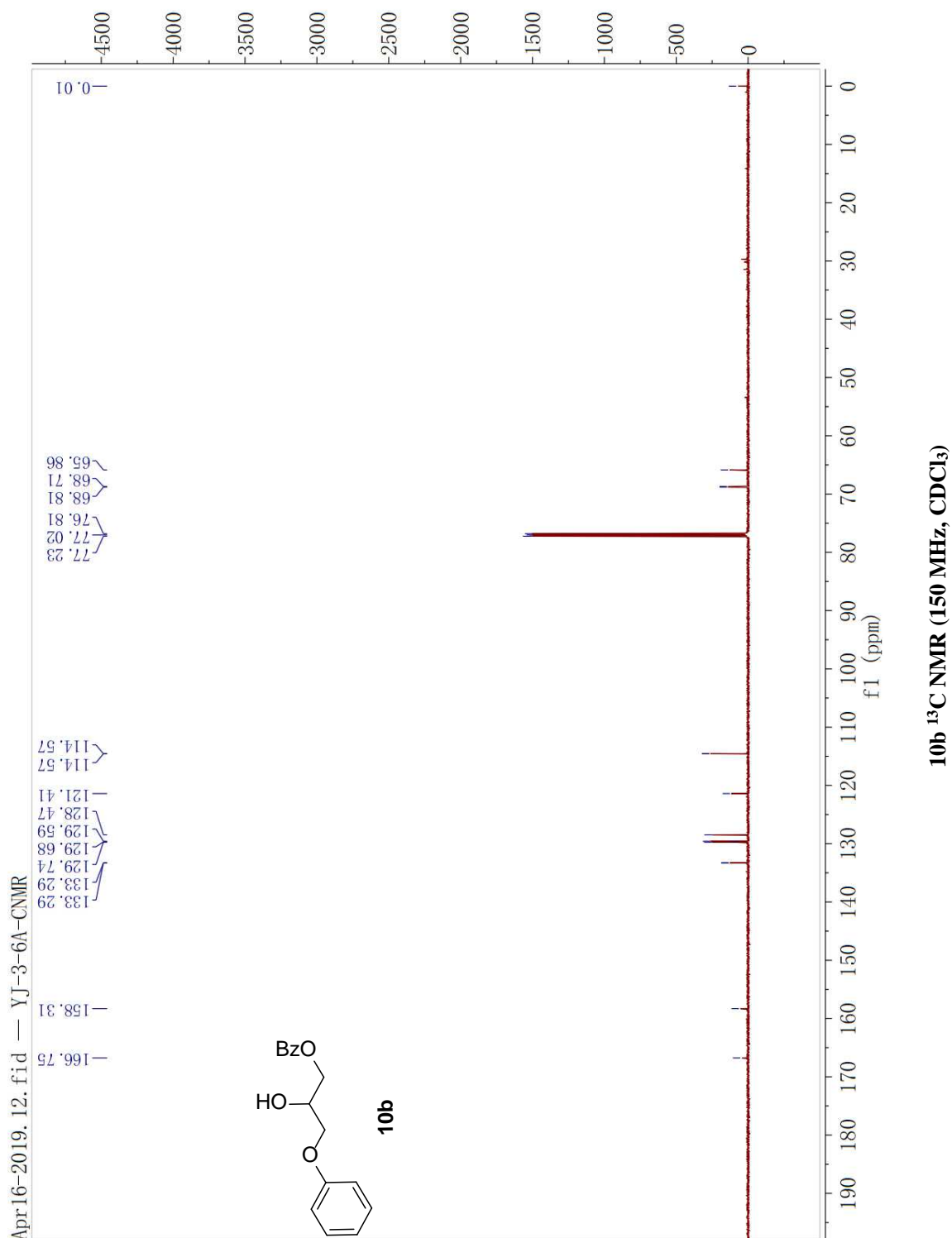
7d ¹H NMR (600 MHz, CDCl₃)

2-Hydroxy-2-phenylethyl benzoate (10a)

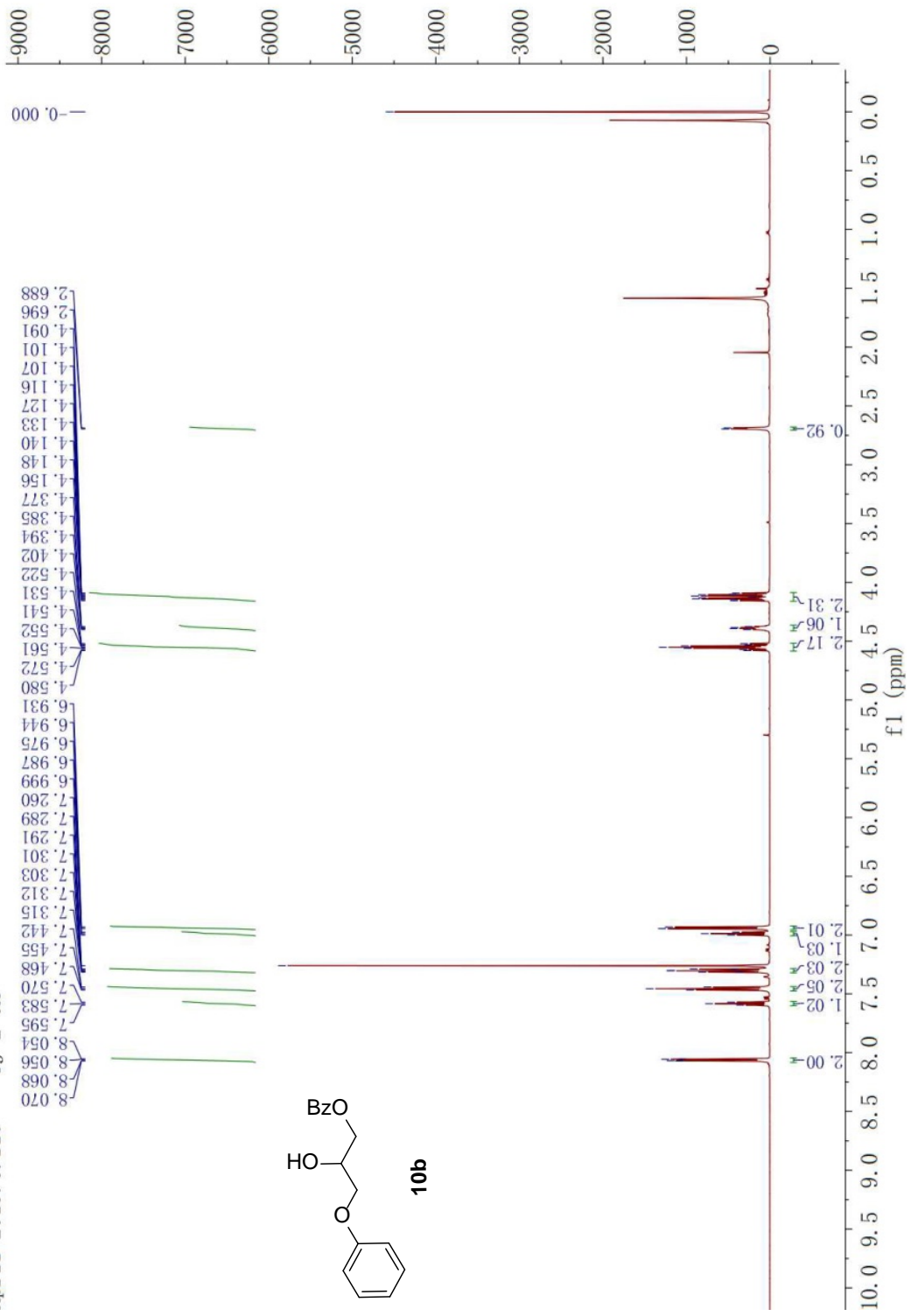




2-Hydroxy-3-phenoxypropyl benzoate (10b)

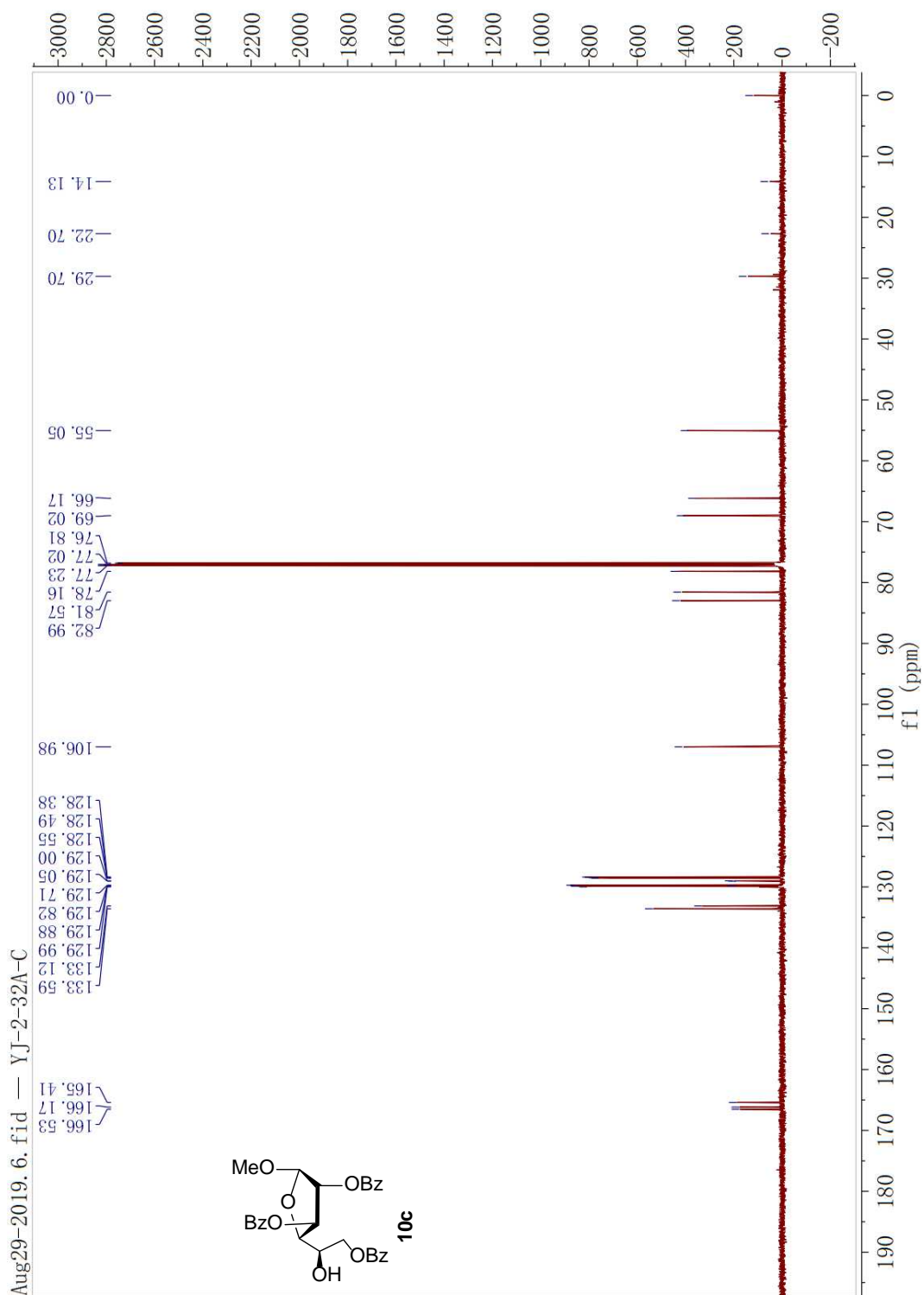


Apr 11-2019. 5. fid — YJ-2-6A



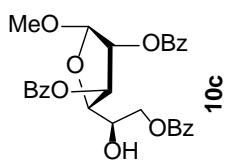
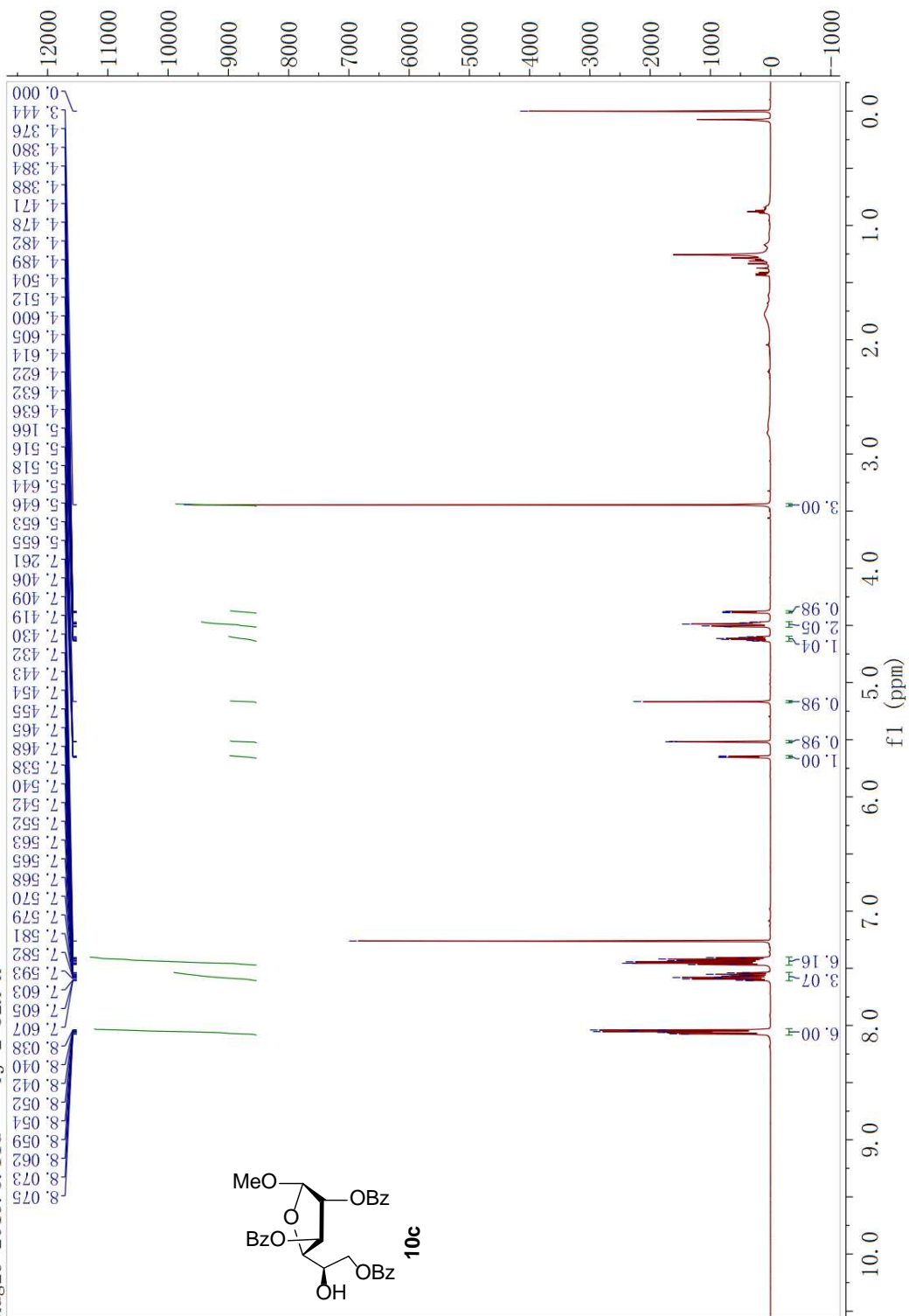
10b ¹H NMR (600 MHz, CDCl₃)

Methyl 2,3,6-tri-O-benzoyl-β-D-galactofuranoside (10c)



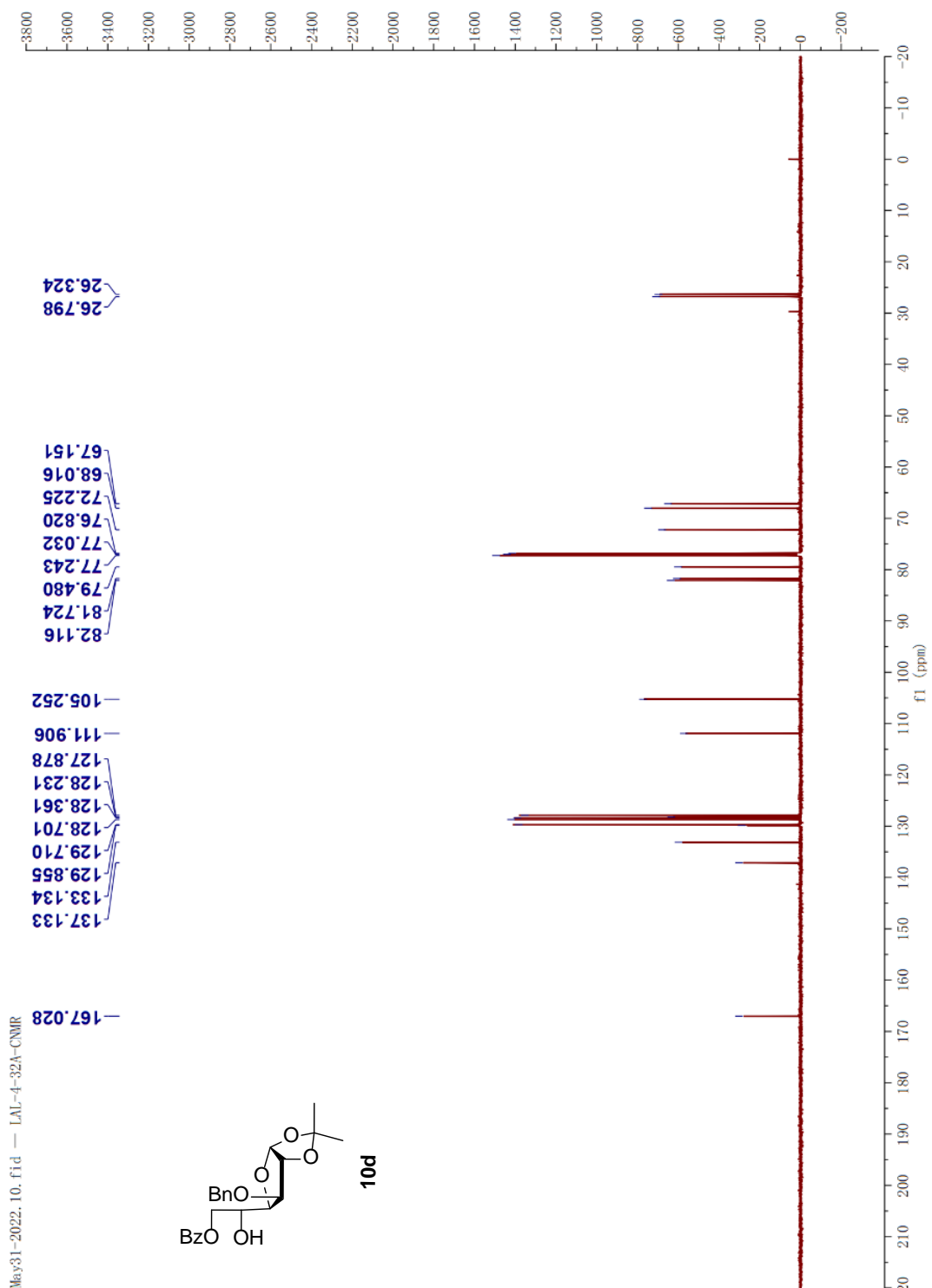
10c ¹³C NMR (150 MHz, CDCl₃)

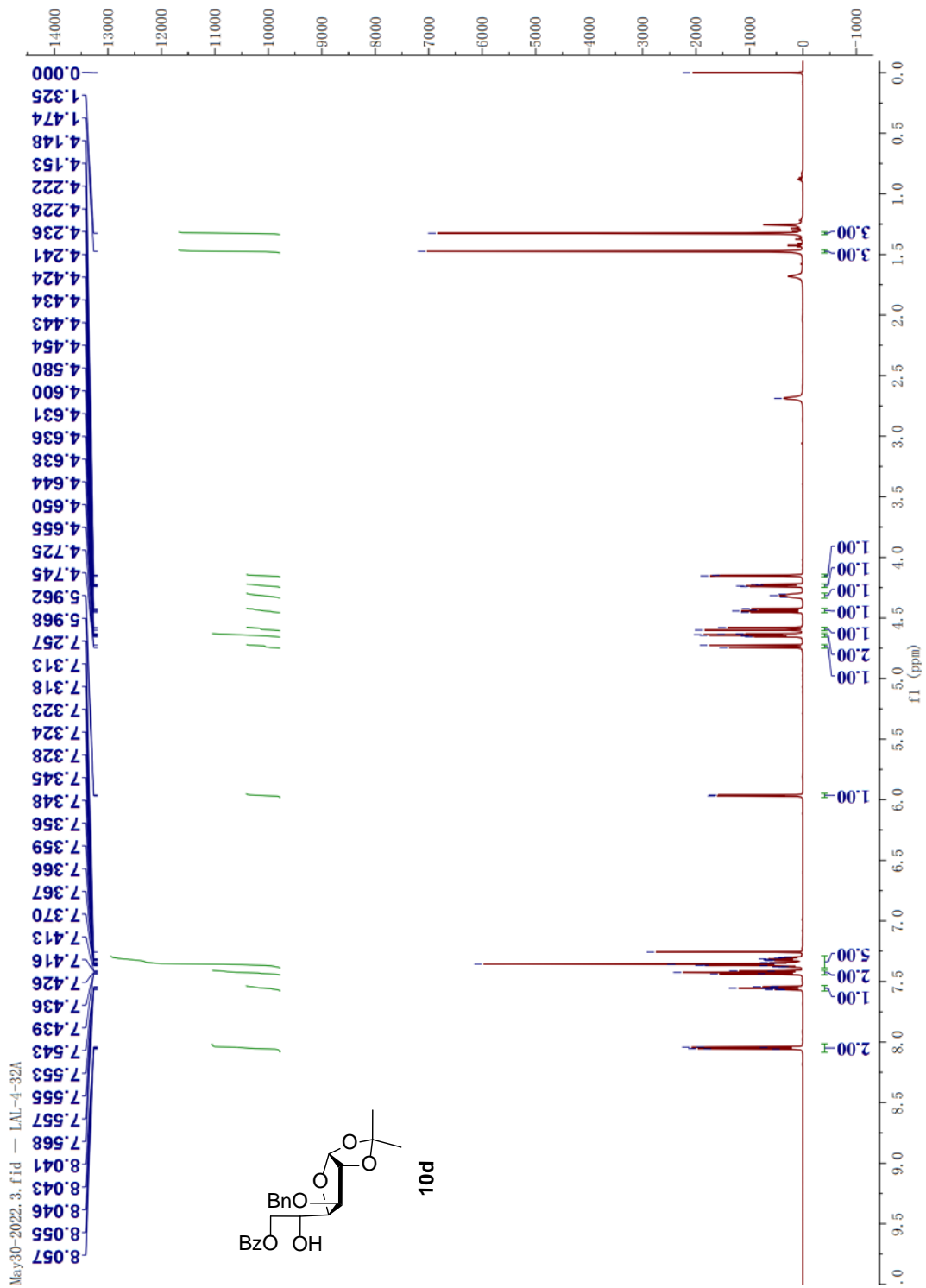
Aug29-2019, 5. fid — YJ-2-32A-H



10c ¹H NMR (600 MHz, CDCl₃)

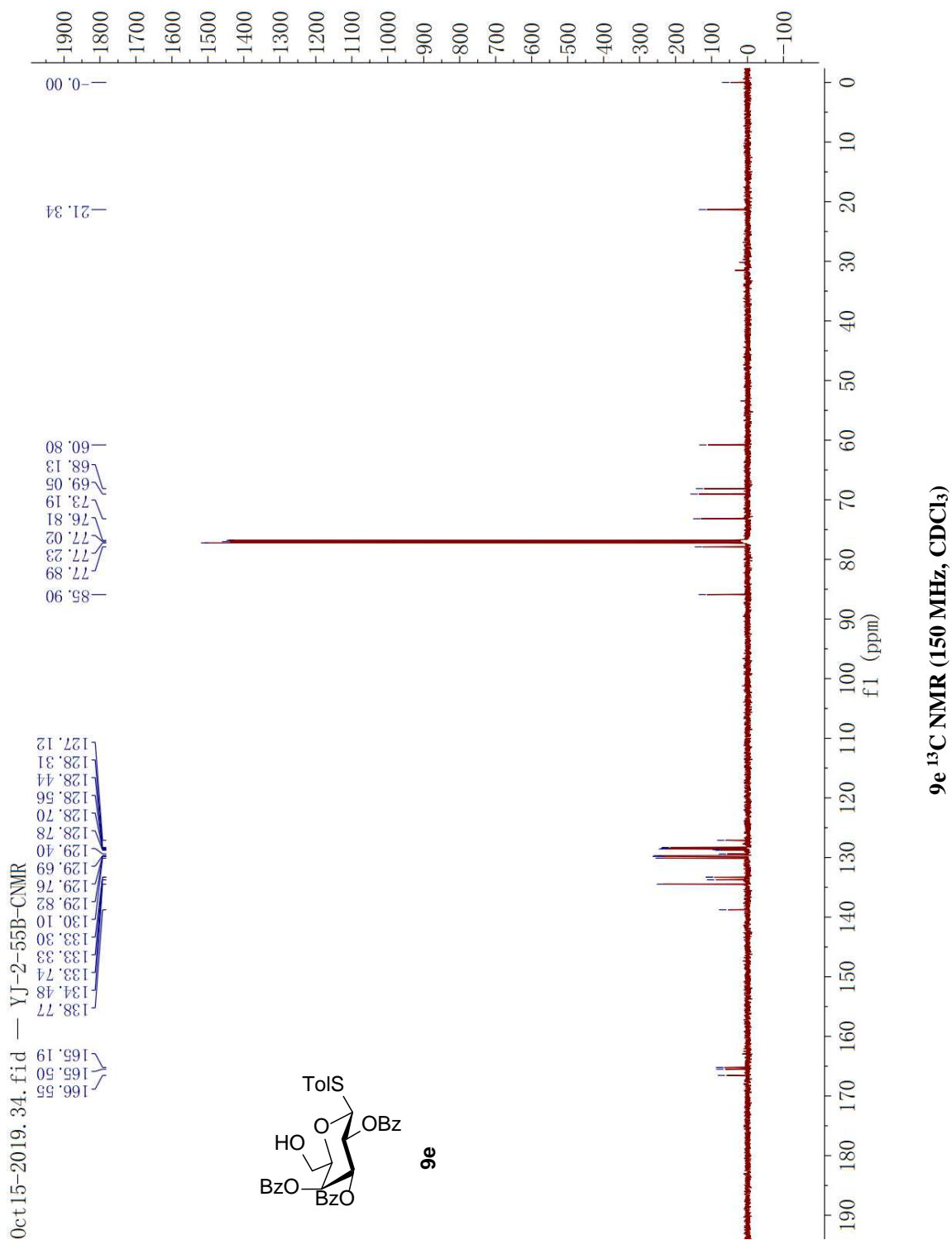
1,2-*O*-Isopropylidene-6-*O*-benzoyl-3-*O*-benzyl- α -D-glucofuranose (10d)

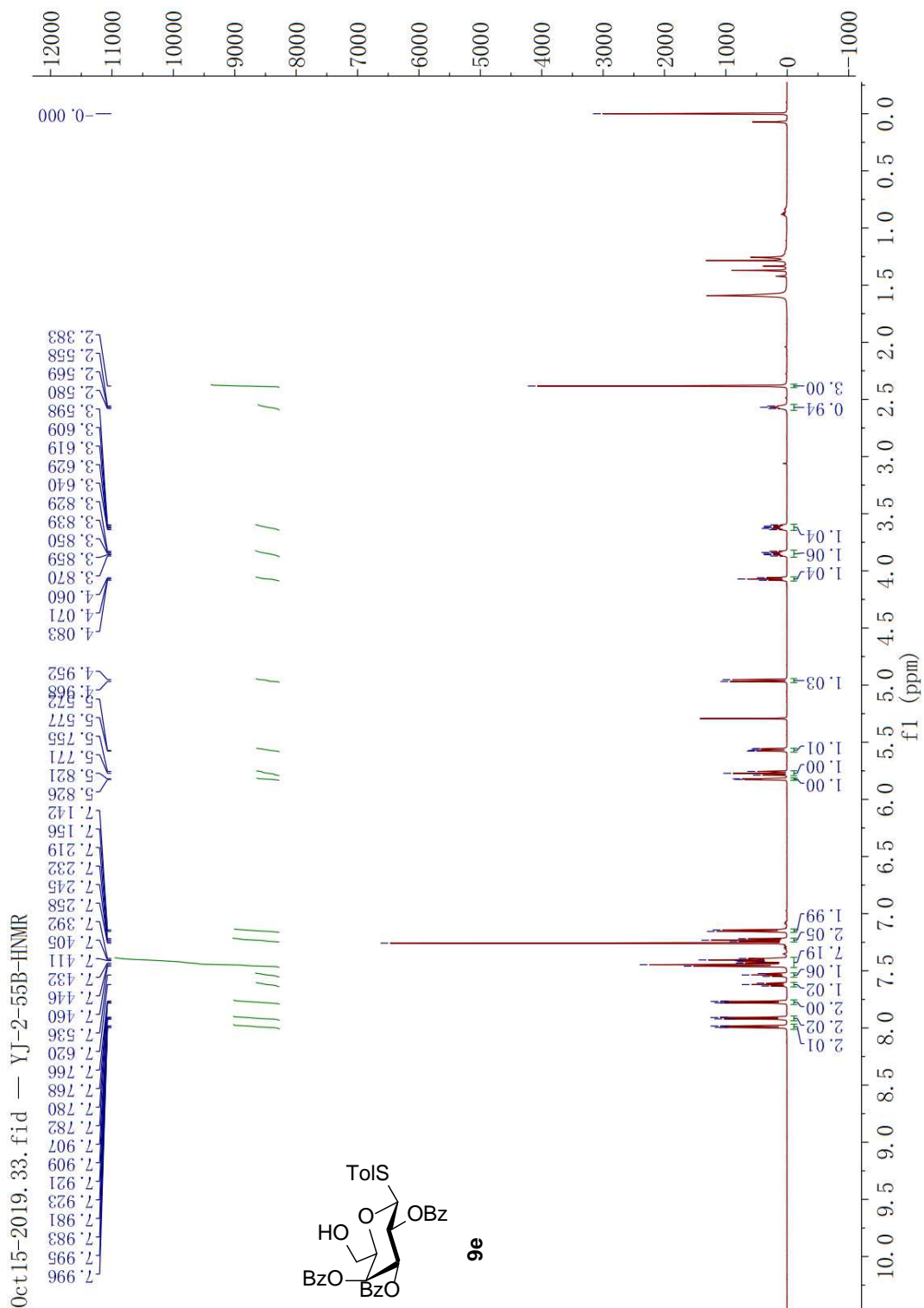




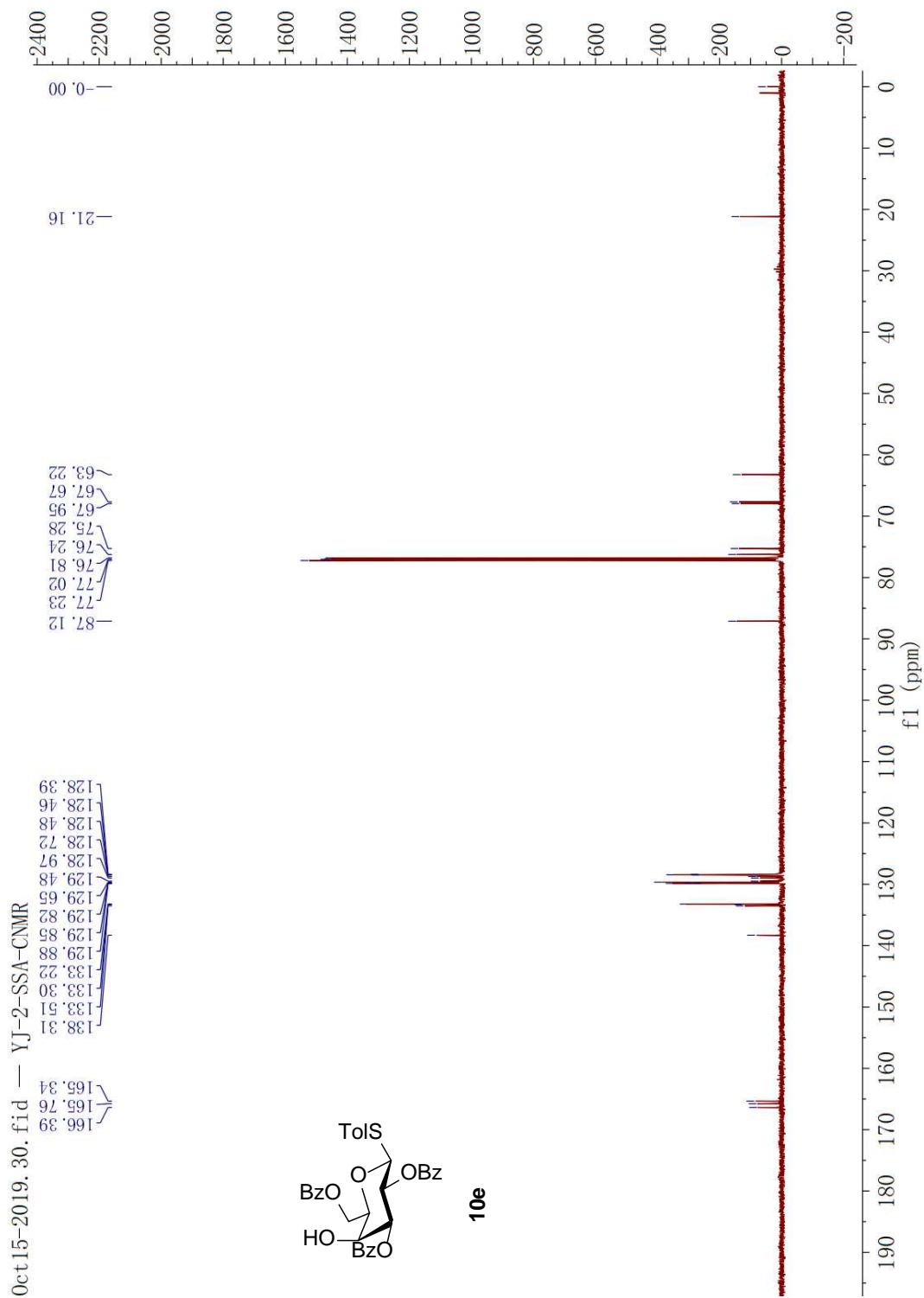
10d ¹H NMR (600 MHz, CDCl₃)

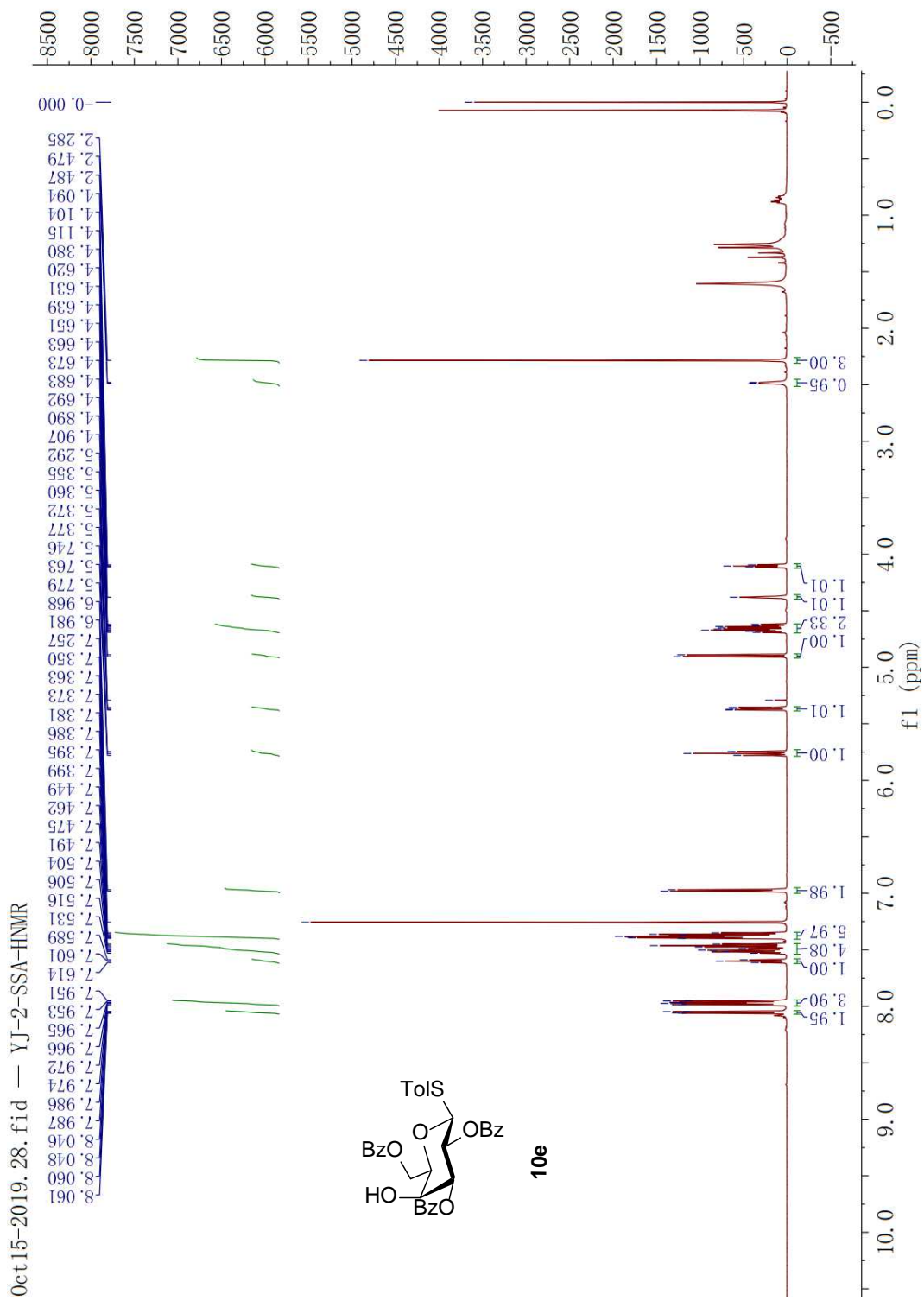
Tolyl 2,3,4-tri-O-benzoyl-1-thio- β -D-galactopyranoside (9e), Tolyl 2,3,6-tri-O-benzoyl-1-thio- β -D-galactopyranoside (10e) and Tolyl 2,4,6-tri-O-benzoyl-1-thio- β -D-galactopyranoside (10e')





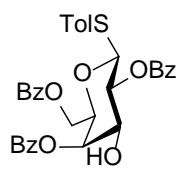
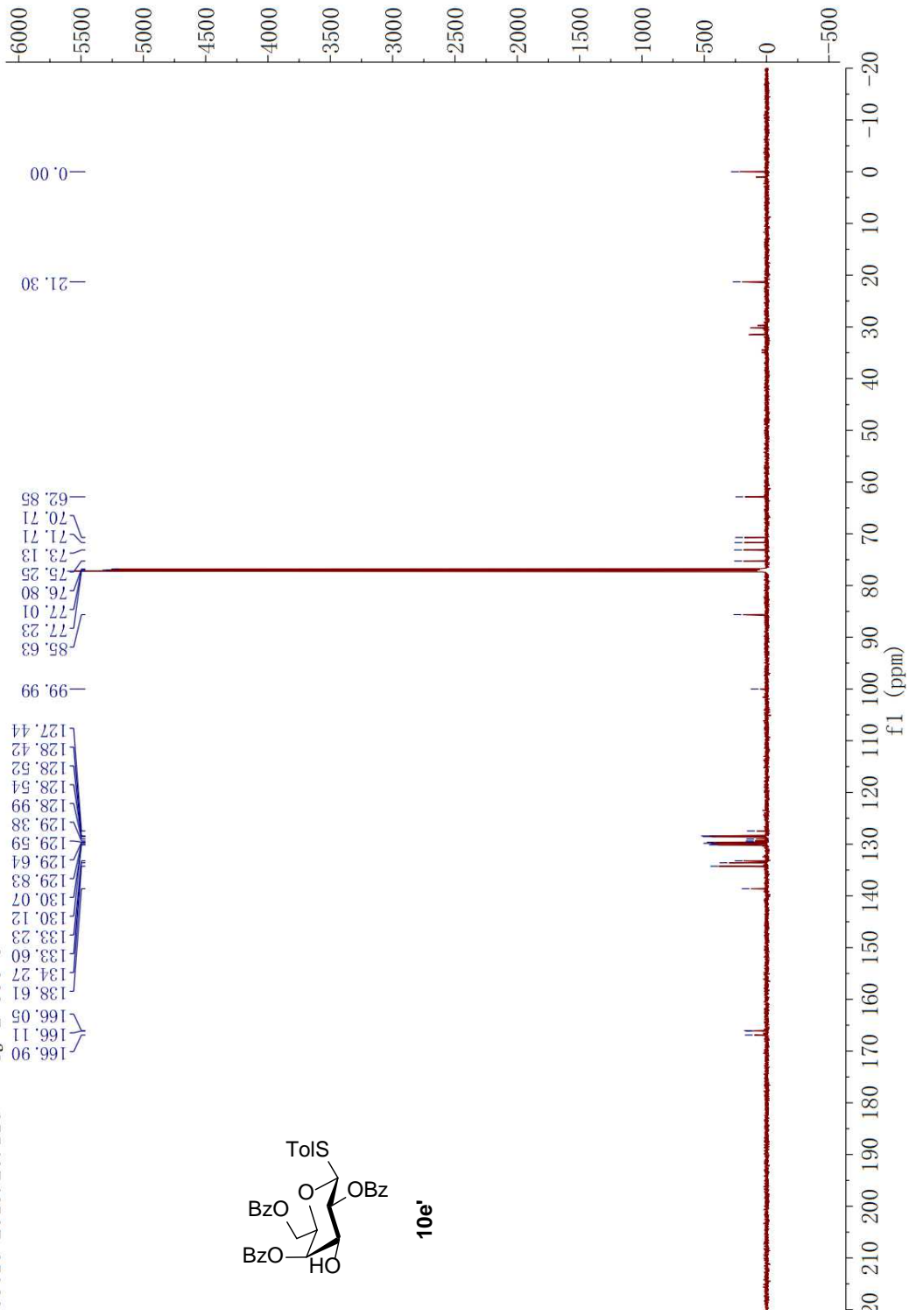
9e ¹H NMR (600 MHz, CDCl₃)





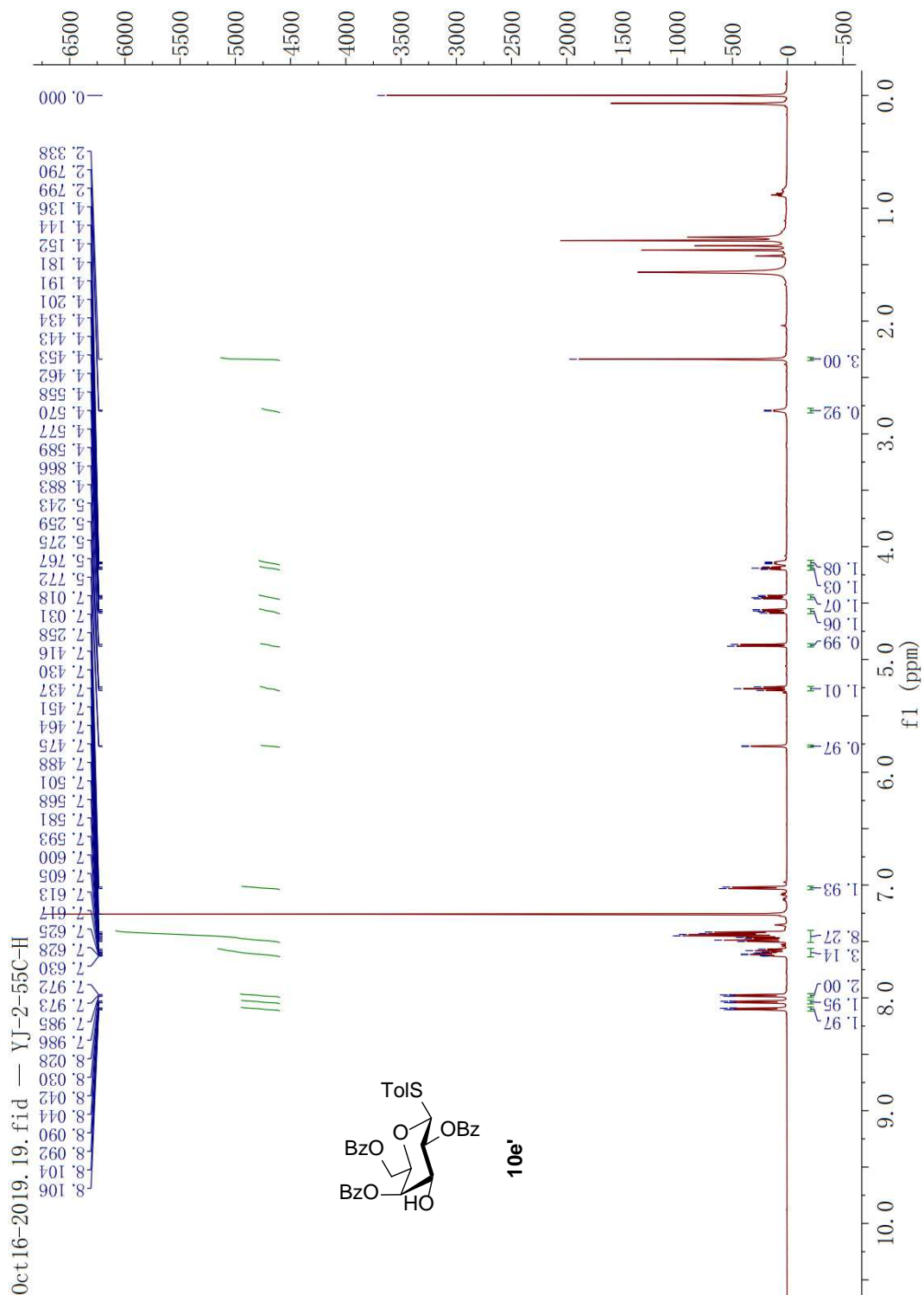
10e ¹H NMR (600 MHz, CDCl₃)

Oct16-2019. 20. fid — YJ-2-55C-C



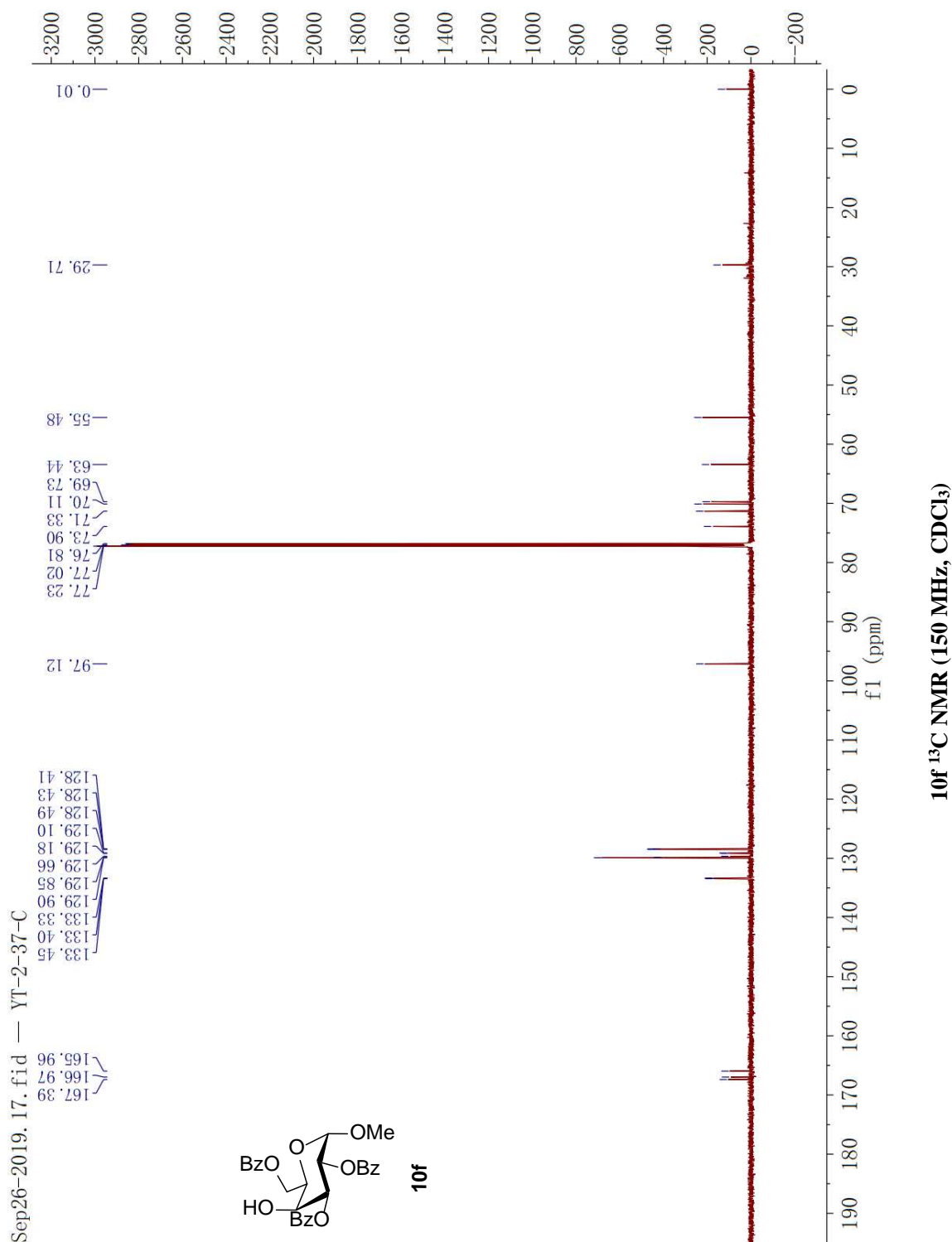
10e'

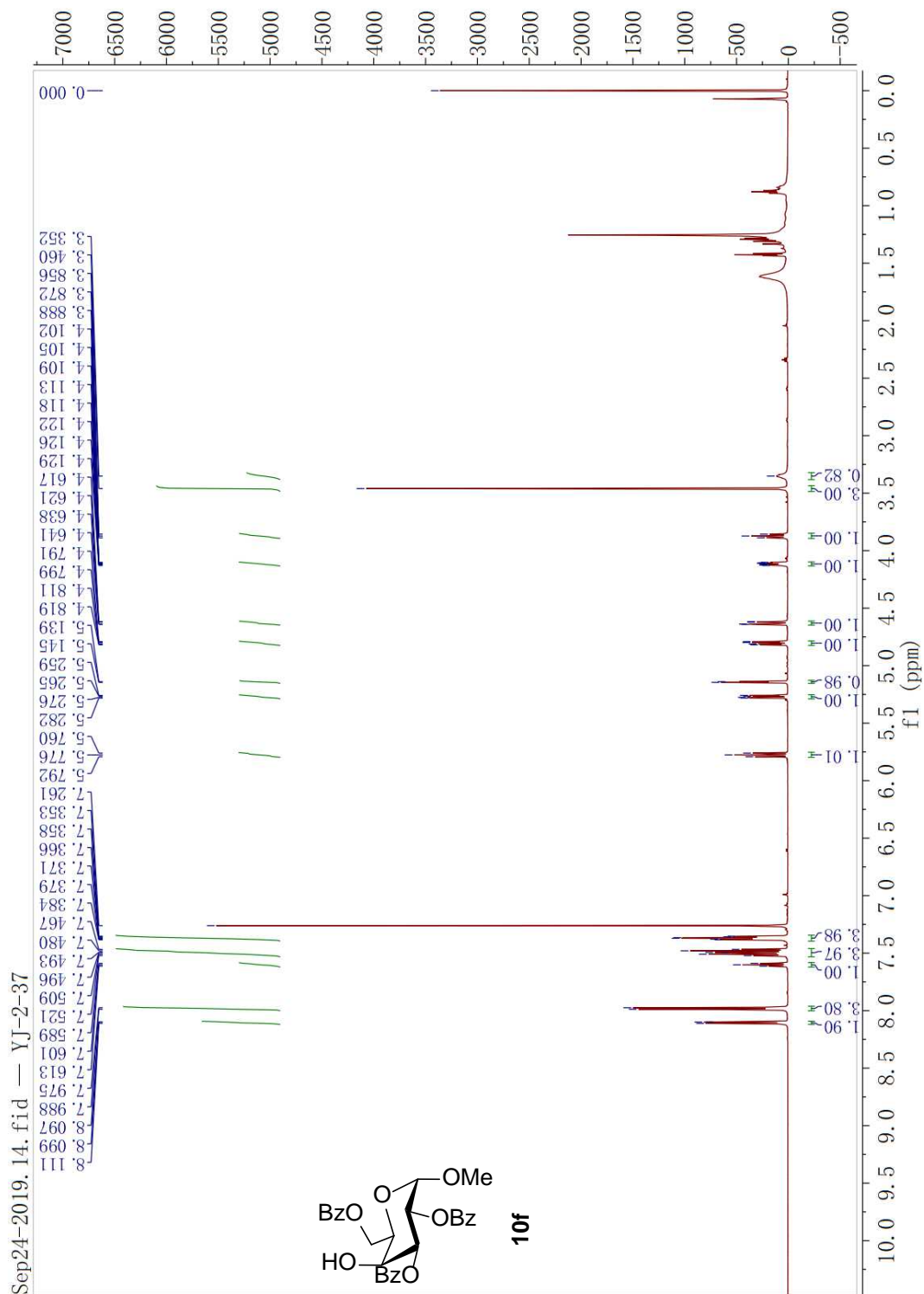
10e' ¹³C NMR (150 MHz, CDCl₃)



10e' ¹H NMR (600 MHz, CDCl₃)

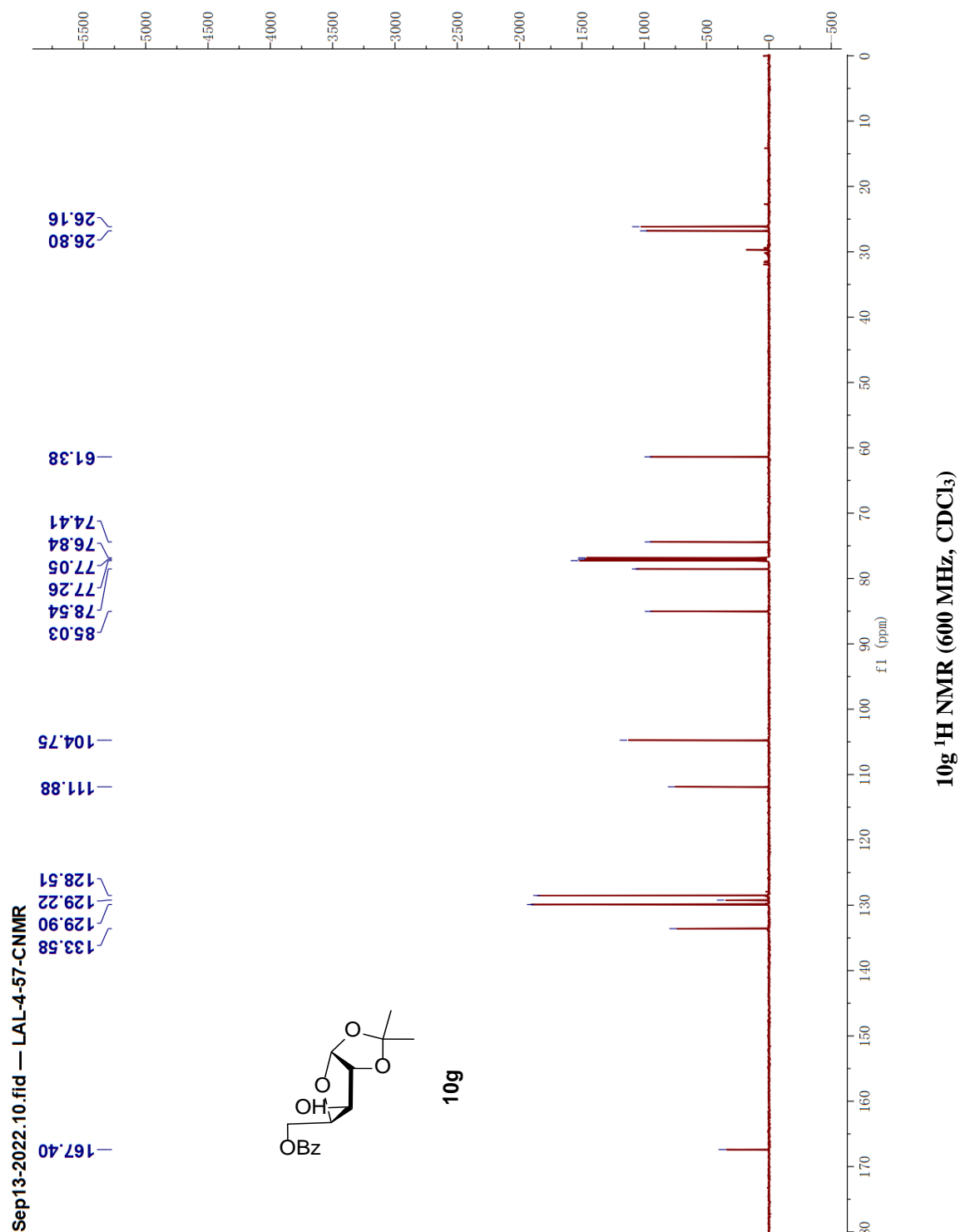
Methyl 2,3,6-tri-O-benzoyl- α -D-galactopyranoside (10f)



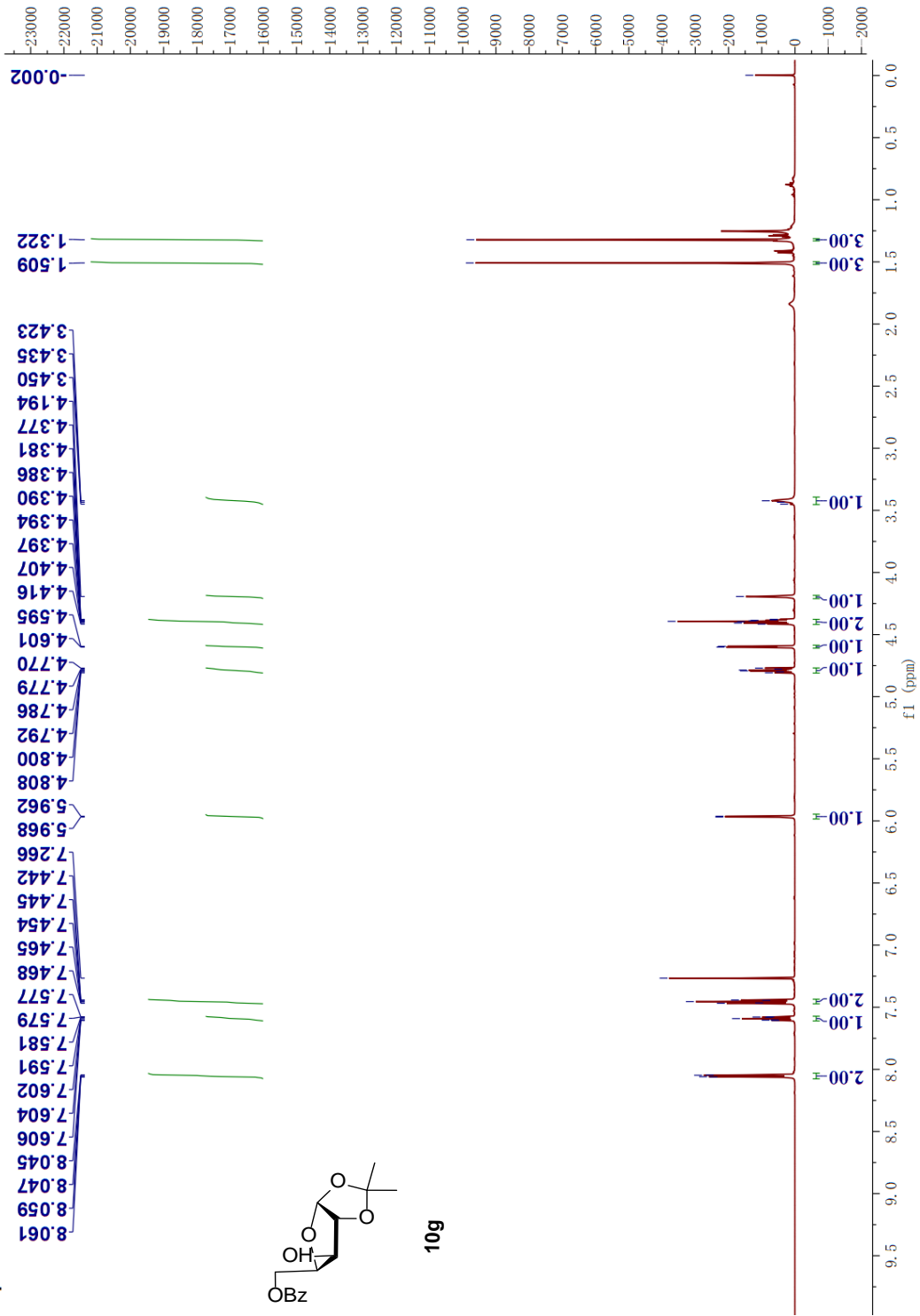


10f ¹H NMR (600 MHz, CDCl₃)

1,2-*O,O*-Isopropylidene-5-*O*-benzoyl- α -D-xylofuranose (10g)

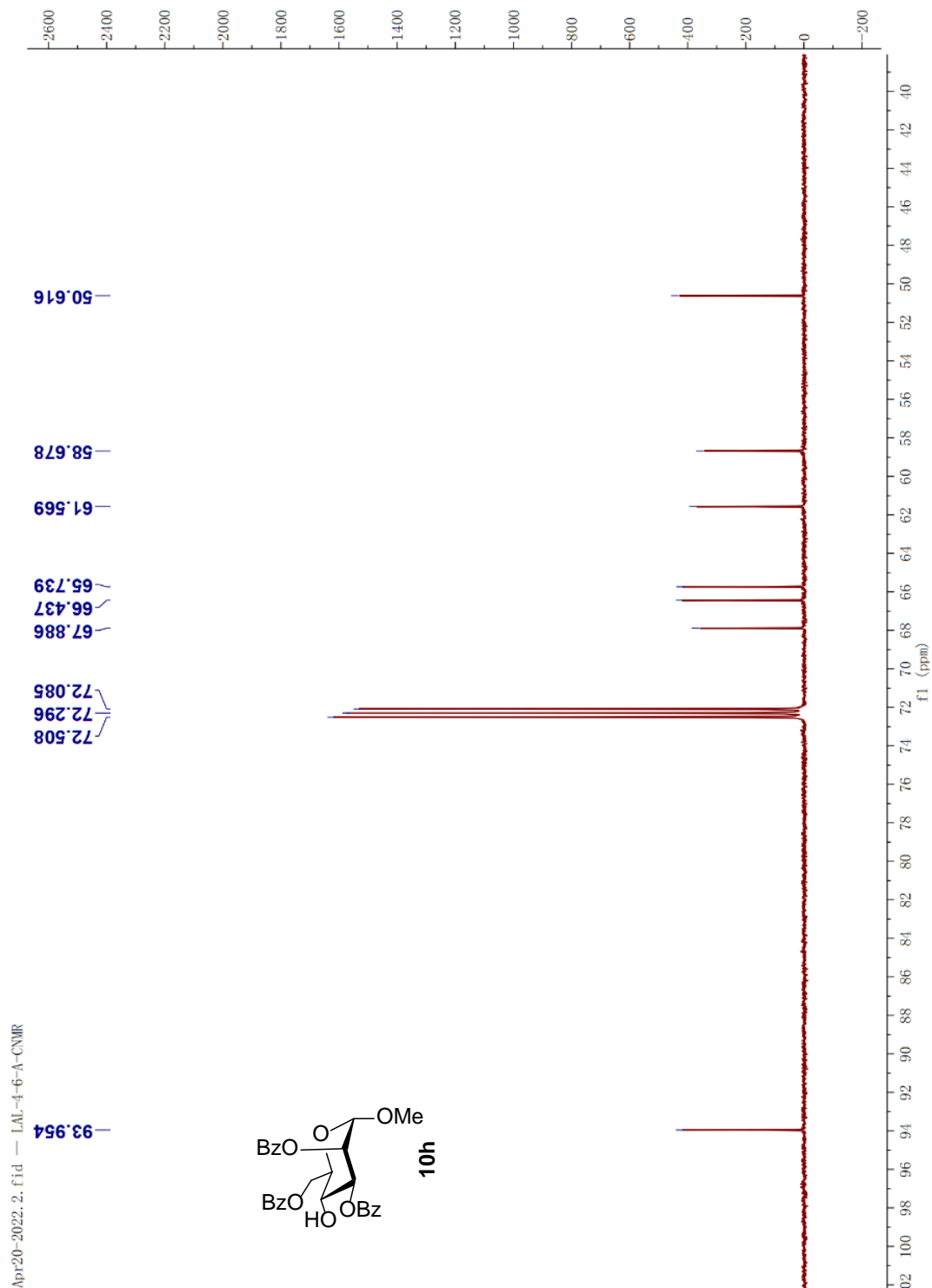


Sep13-2022.9.fid — LAL-4-57-HNMR



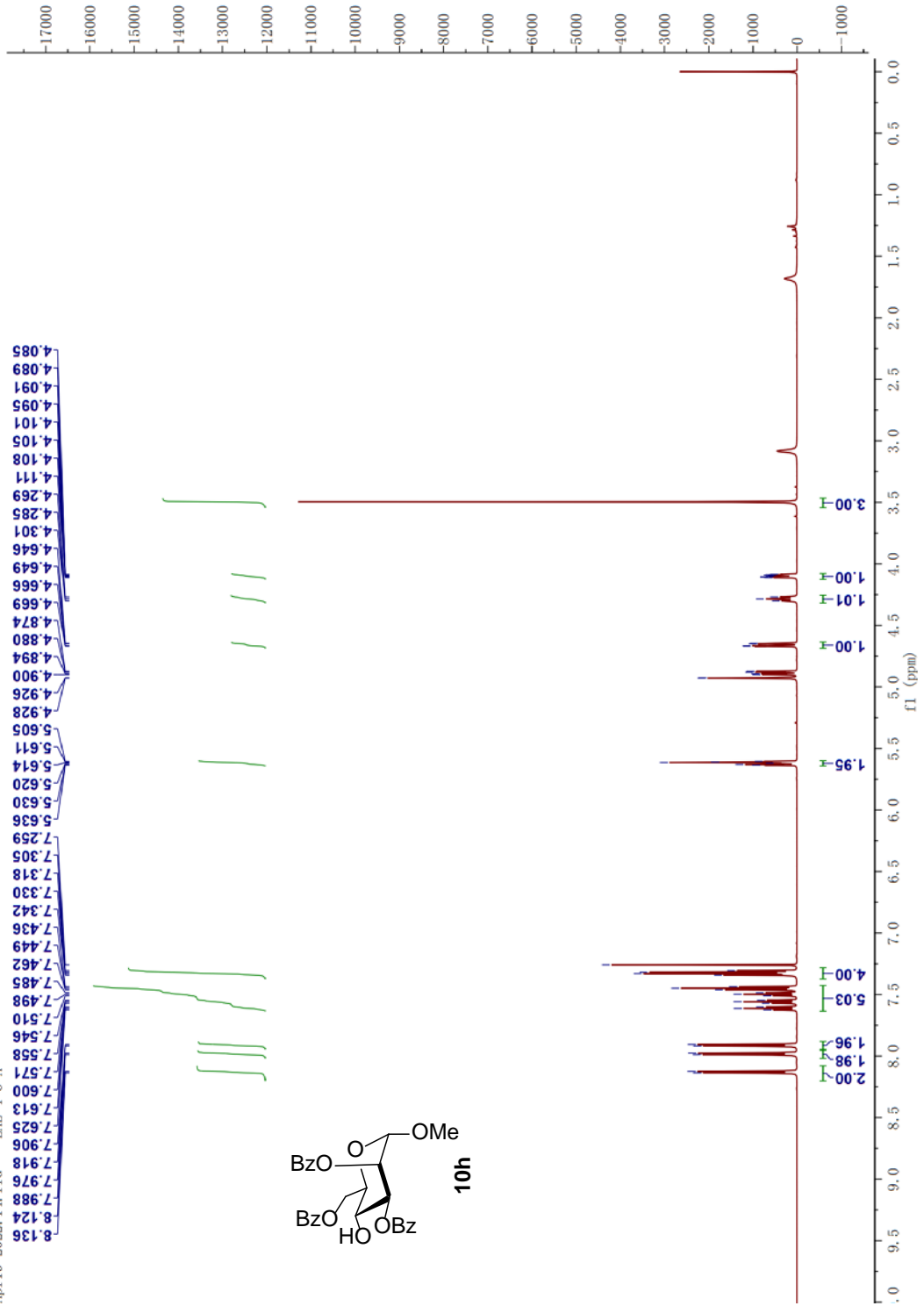
10g ¹H NMR (600 MHz, CDCl₃)

Methyl 2,3,6-tri-O-benzoyl- α -D-mannopyranoside (10h)



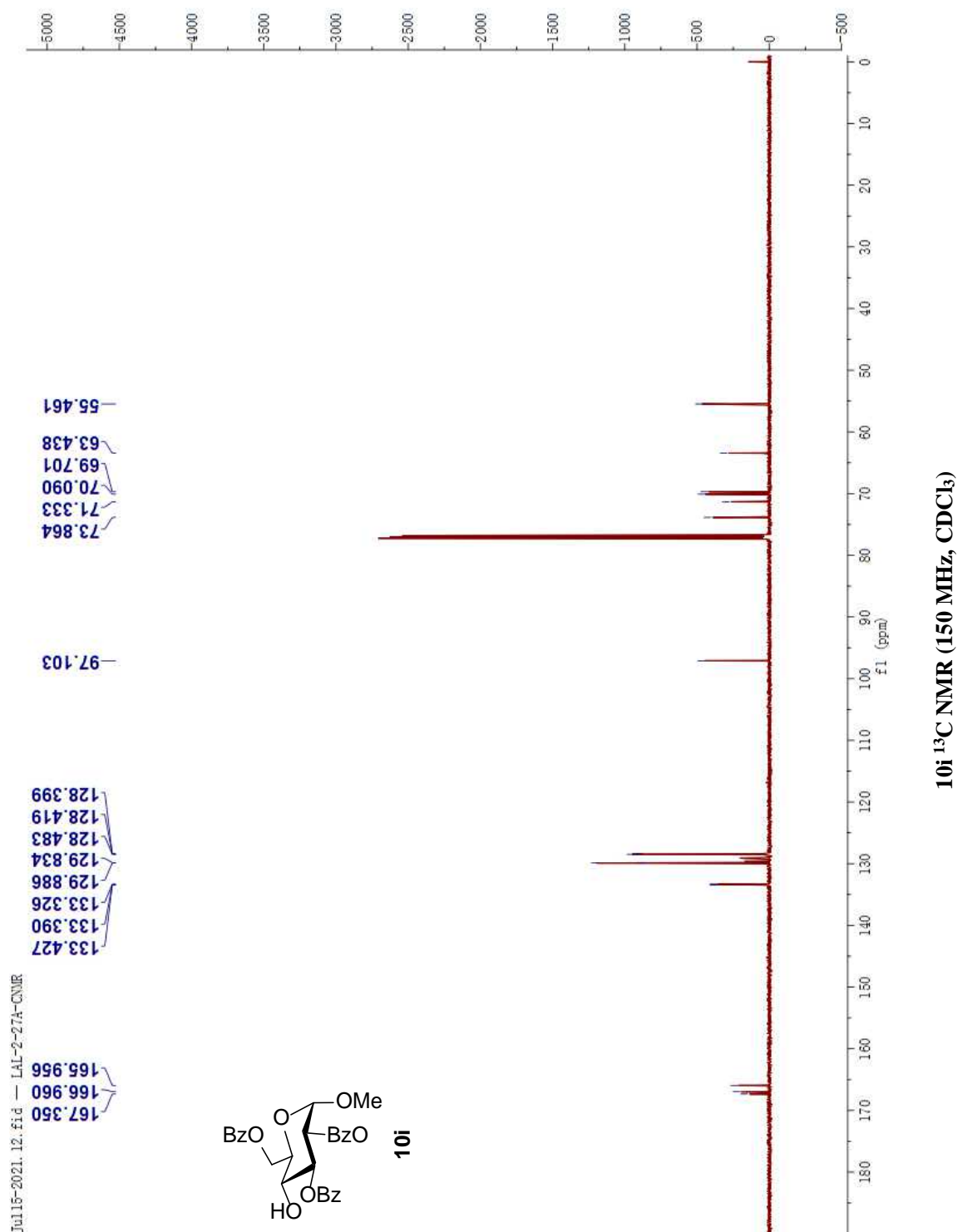
Apr20-2022. 2. fid - LAL-4-6-A-CNMR

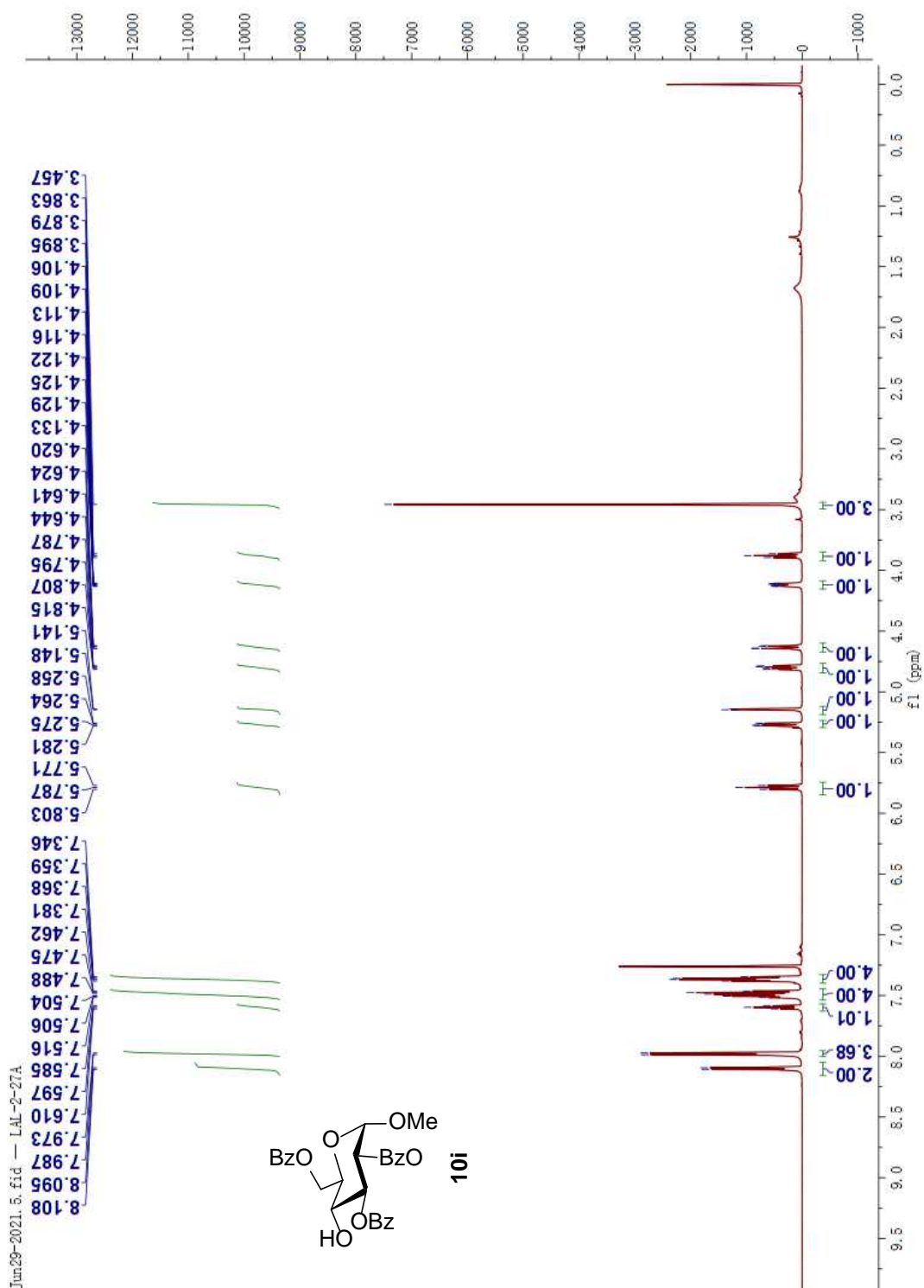
Apr19-2022, 14, f1d — LAL-4-6-A



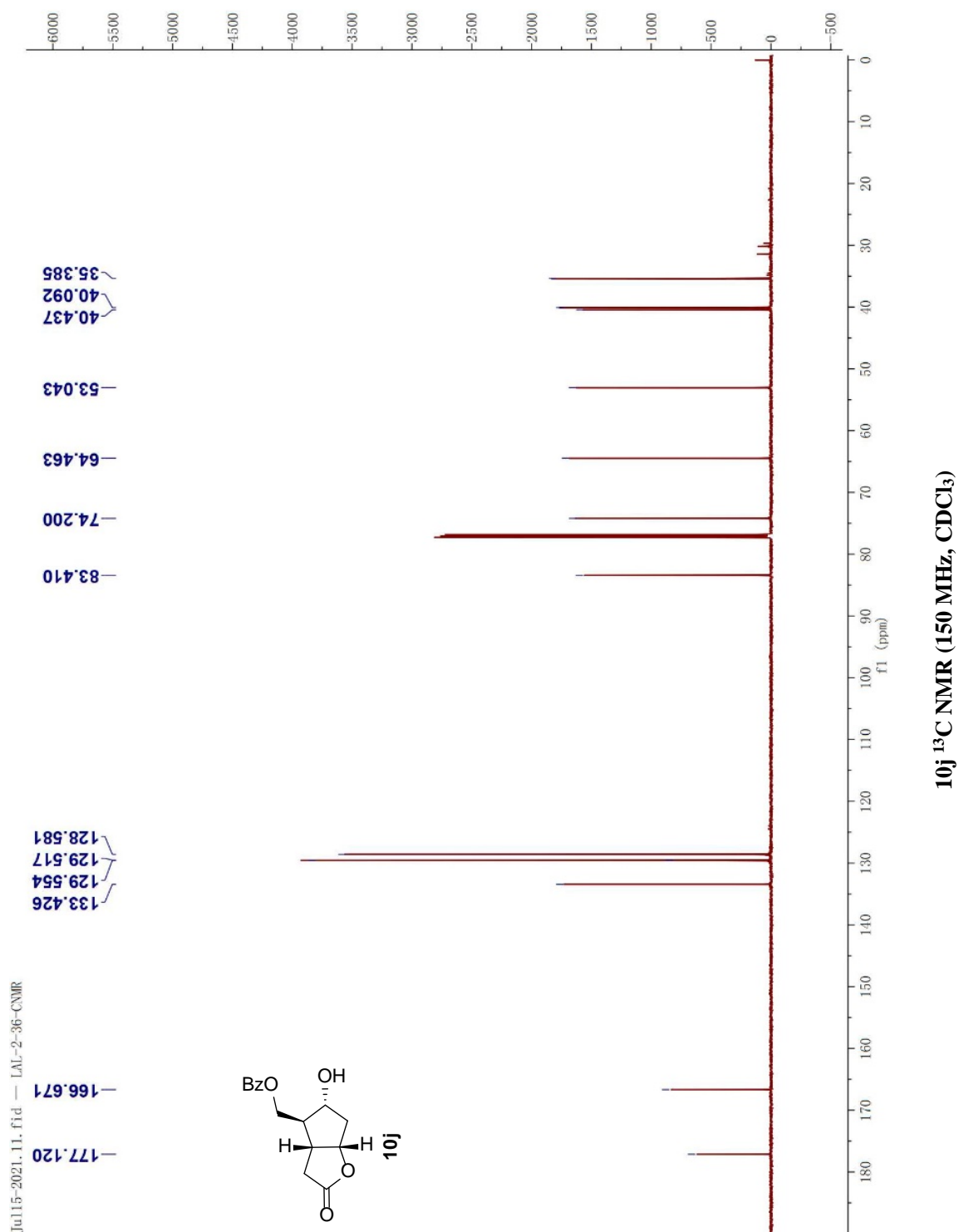
10h ¹H NMR (600 MHz, CDCl₃)

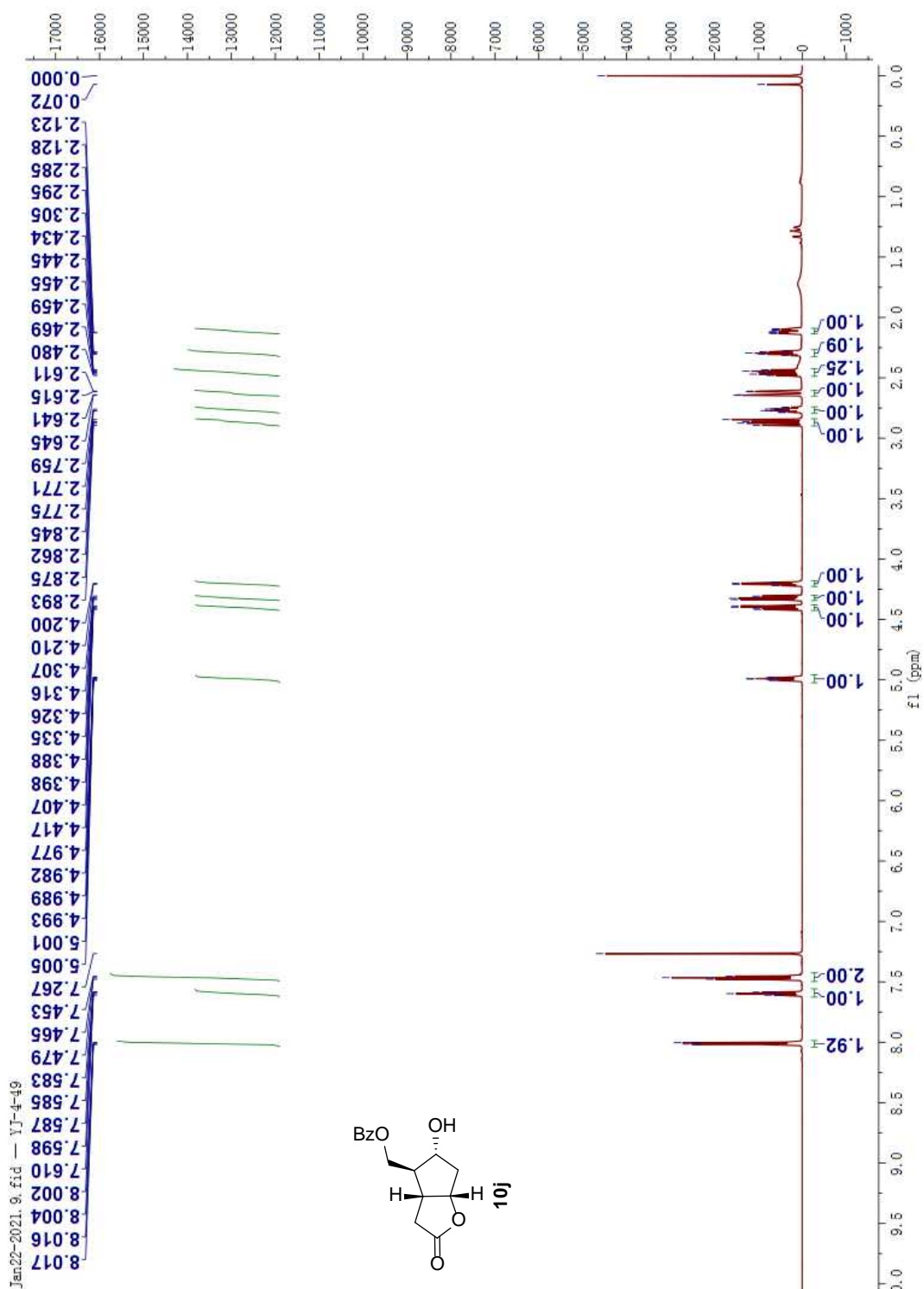
methyl 2,3,4-*tri-O*-benzoyl- α -D-glucopyranoside (9i) and Methyl 2,3,6-*tri-O*-benzoyl- α -D-glucopyranoside (10i)





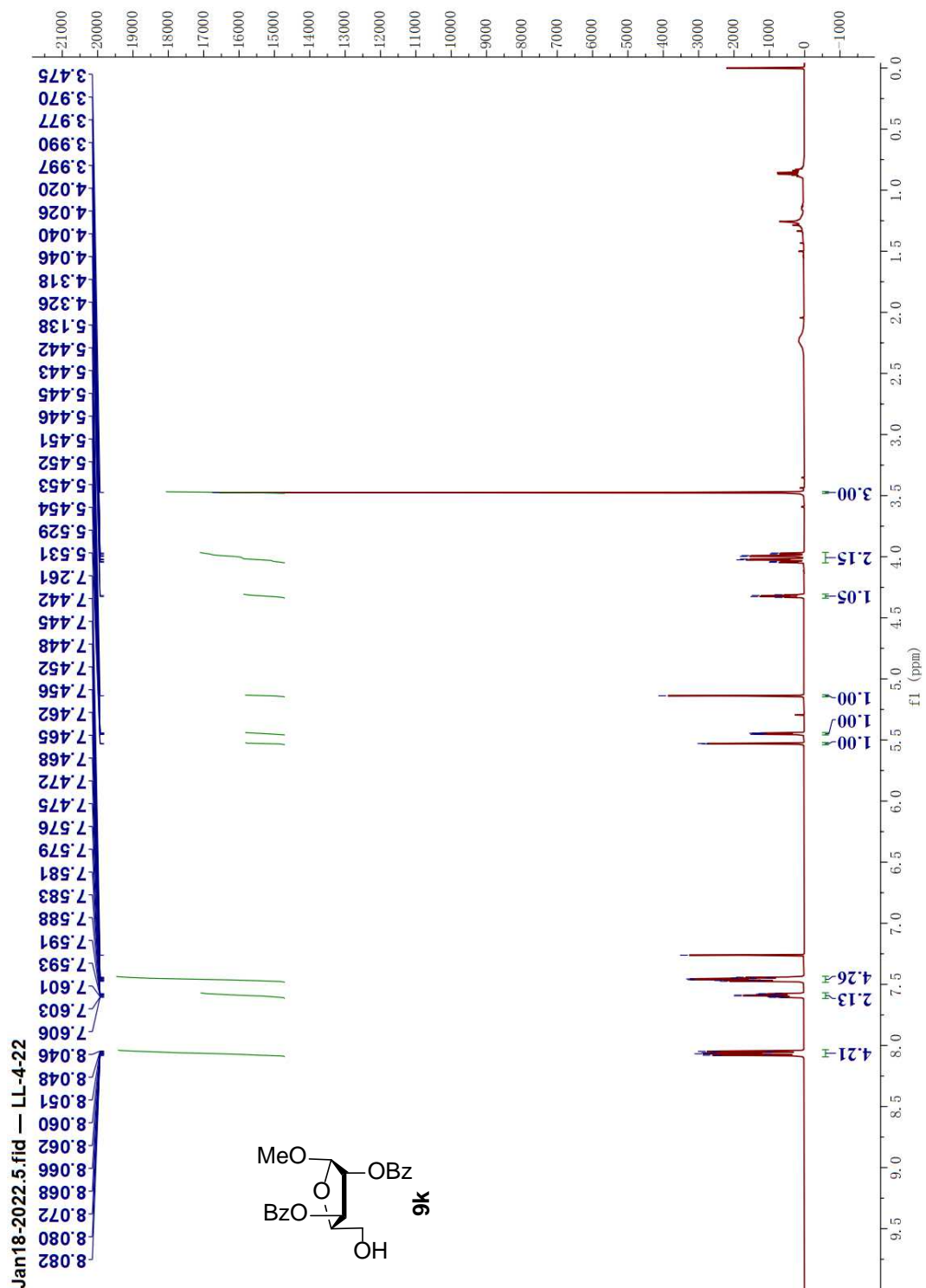
(±)-[(3*aRS*,4*SR*,5*RS*,6*aSR*)-5-Hydroxy-2-oxohexahydro-2*H*-cyclopenta[*b*]furan-4-yl] methyl benzoate (**10j**)





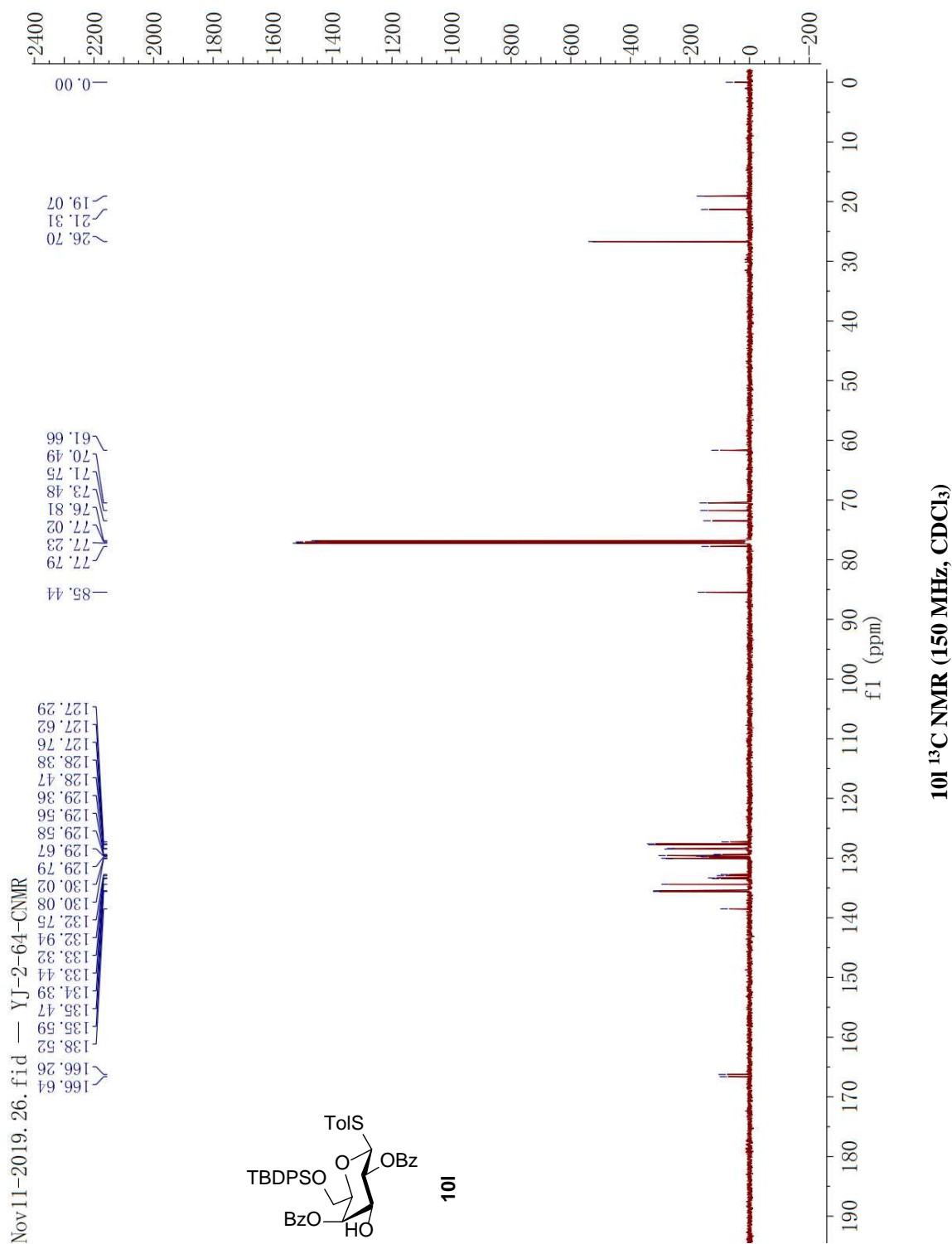
10j ¹H NMR (600 MHz, CDCl₃)

Methyl 2,3-di-O-benzoyl- α -L-arabinofuranoside (9k)

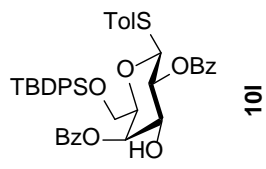
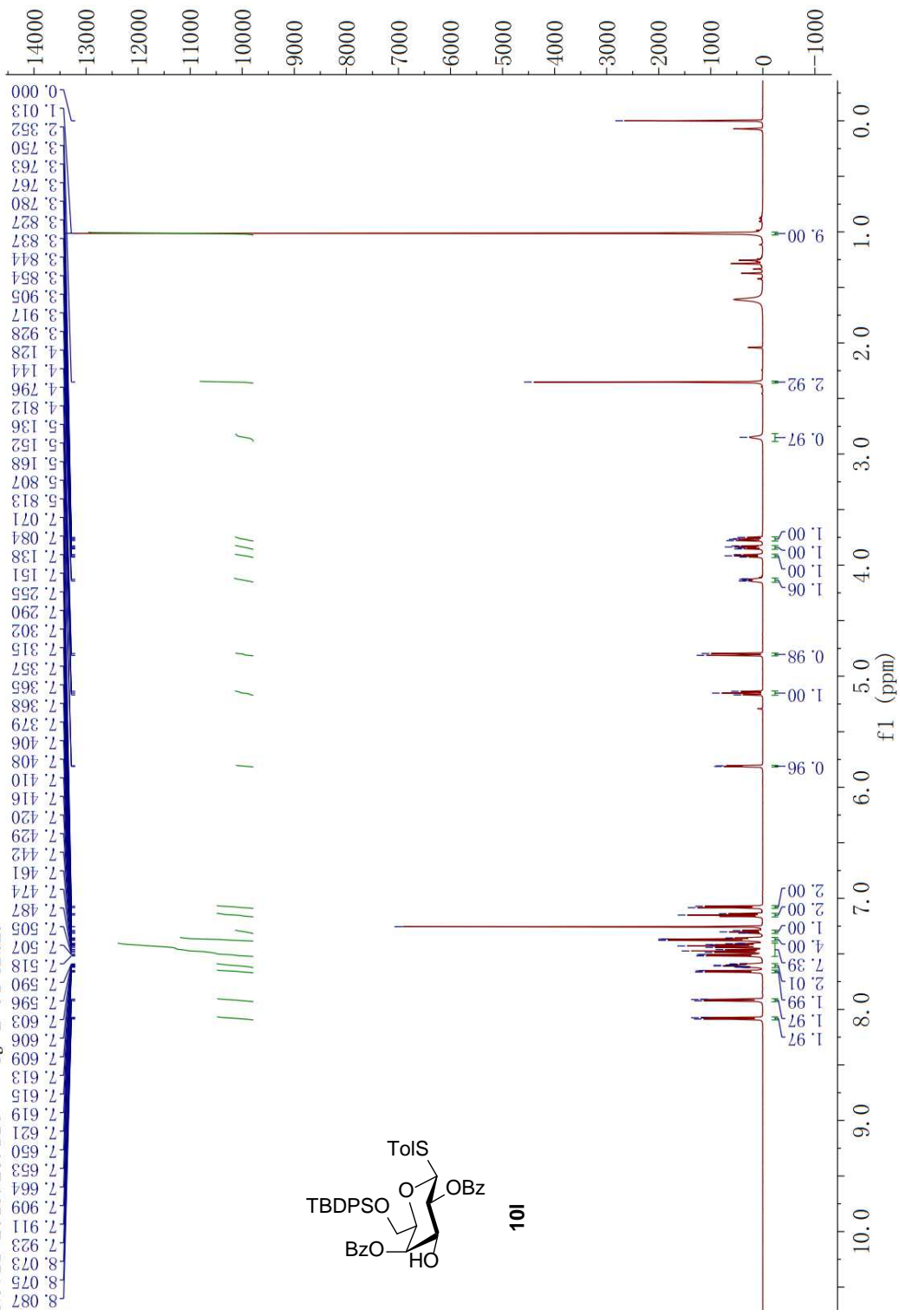


9k ^1H NMR (600 MHz, CDCl_3)

Tolyl 6-*O*-*t*-butyldiphenylsilyl-2,3-*di-O*-benzoyl-1-*thio*- β -D-galactopyranoside (101)

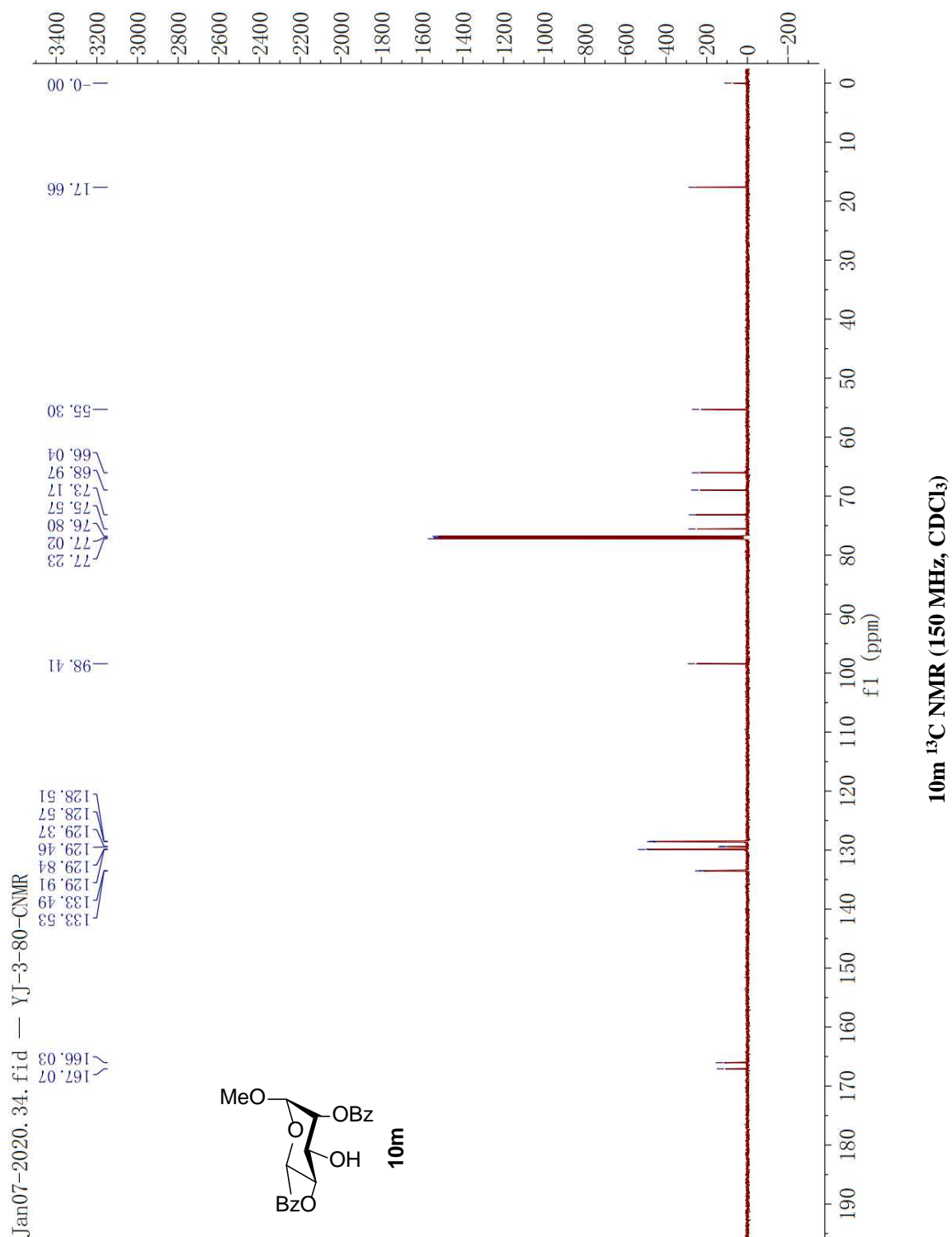


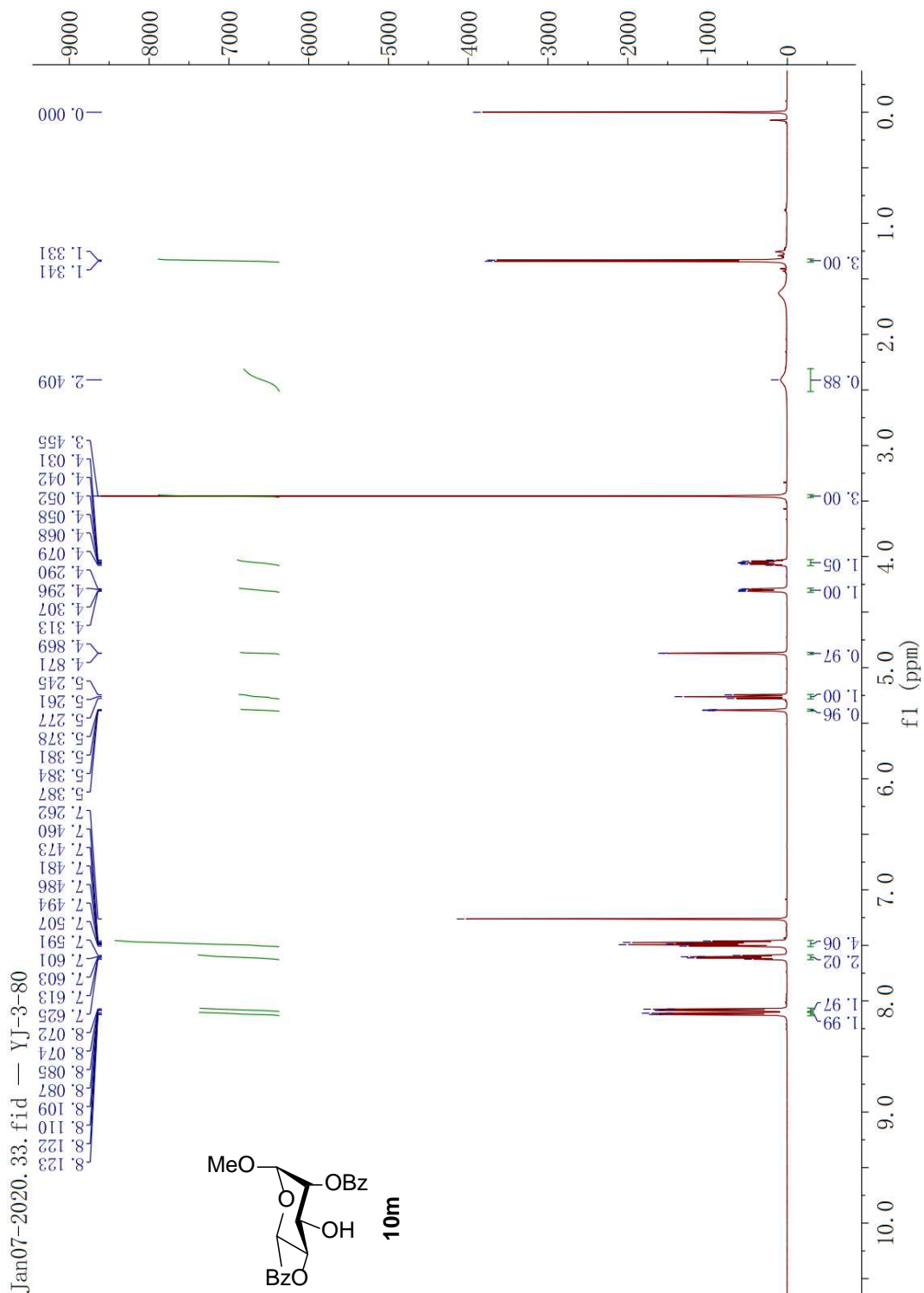
Nov 11-2019, 25. f1 d — YJ-2-64-HNMR



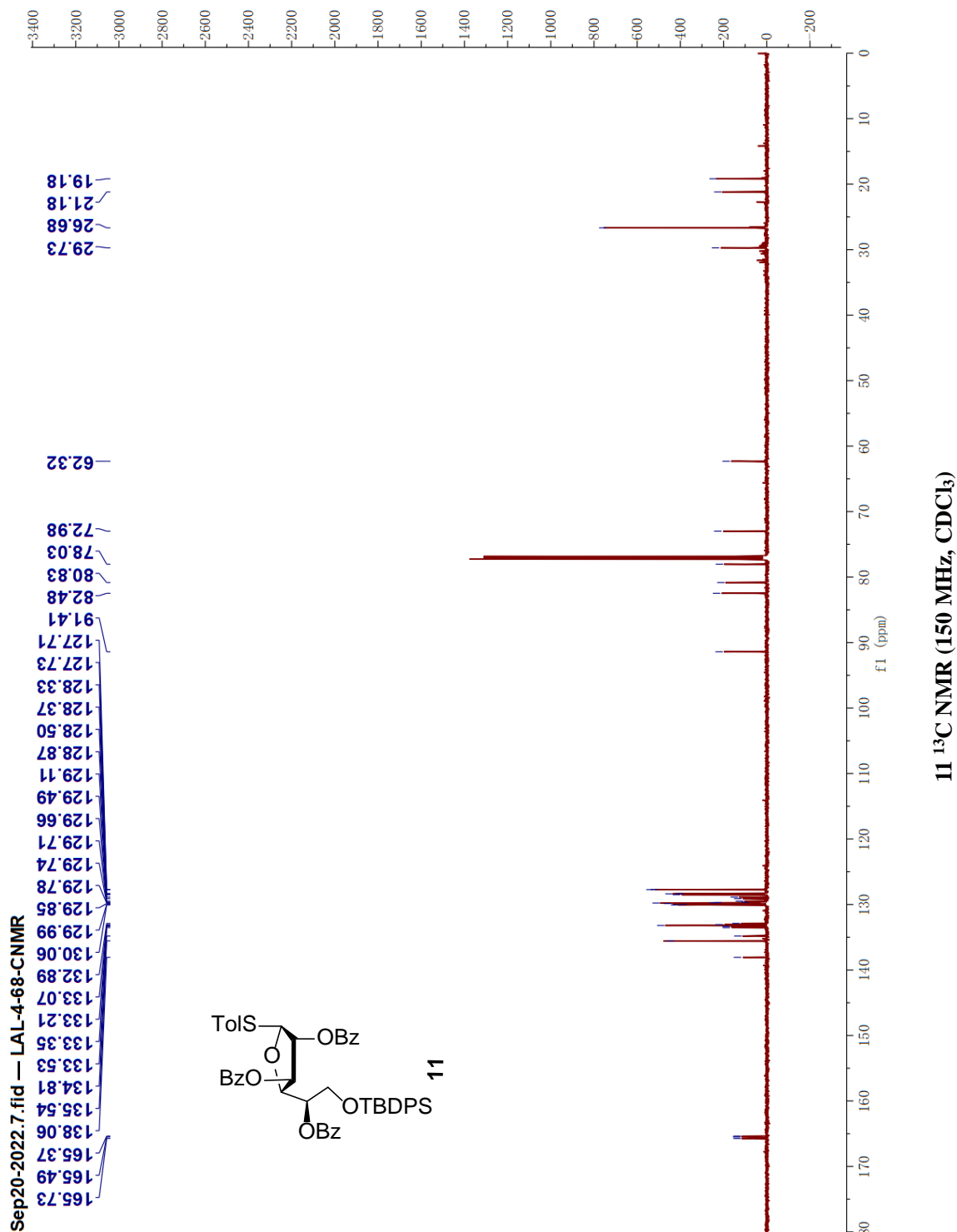
101 ¹H NMR (600 MHz, CDCl₃)

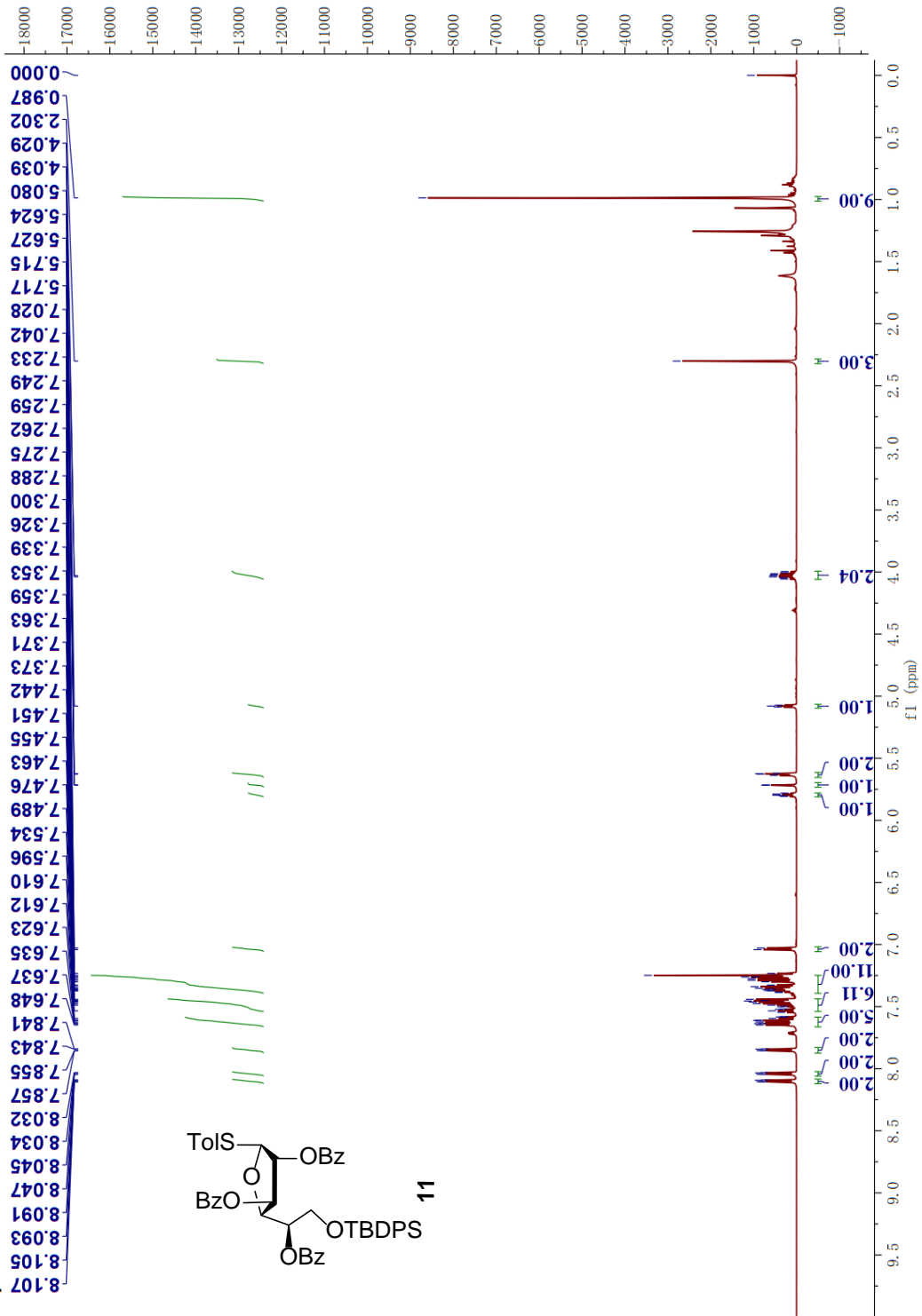
Methyl 2,4-di-O-benzoyl- α -L-rhamnopyranoside (10m)





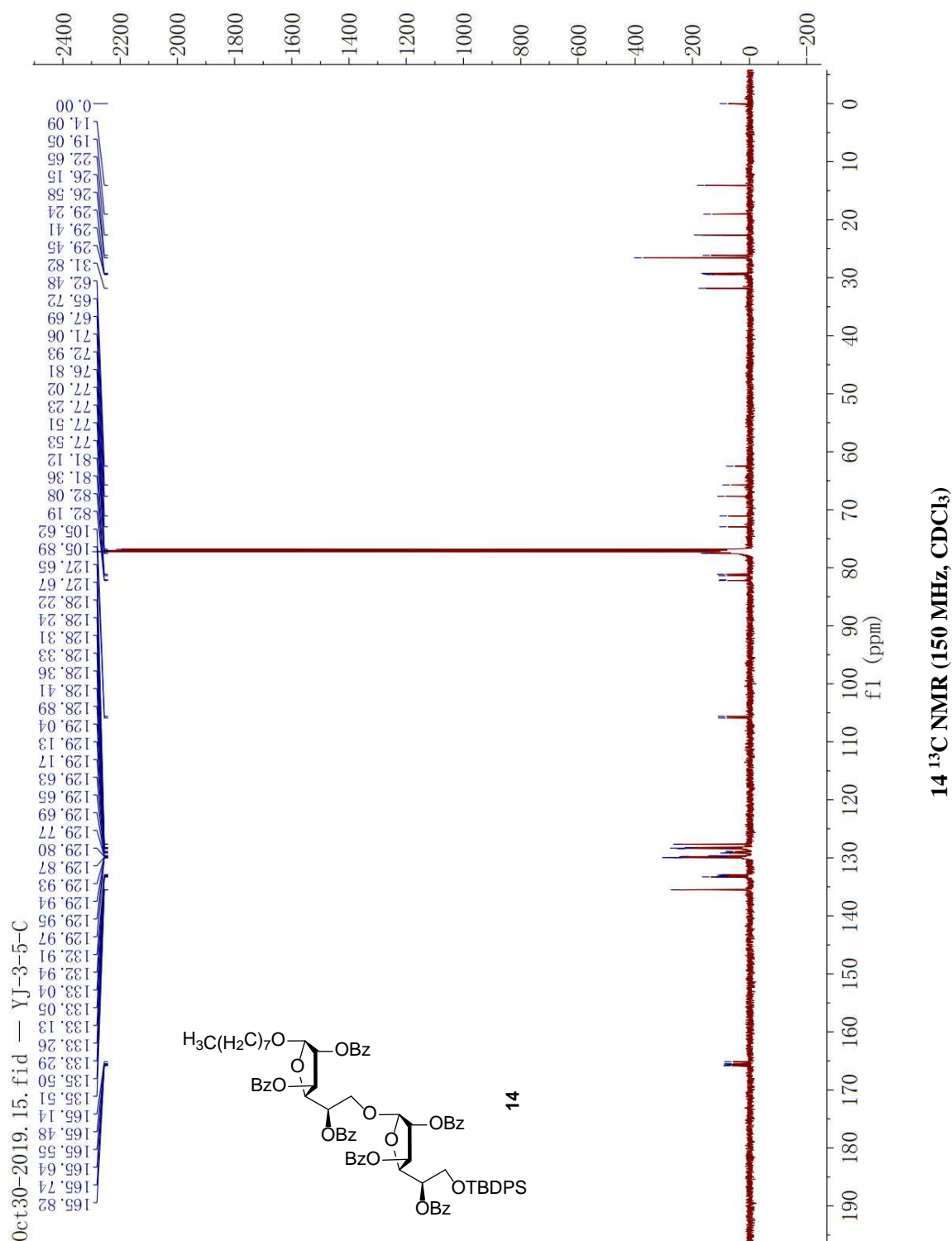
6-*O*-*tert*-Butyldiphenylsilyl-2,3,5-*tri-O*-benzoyl-1-*thio*- β -D-galactofuranoside (11)



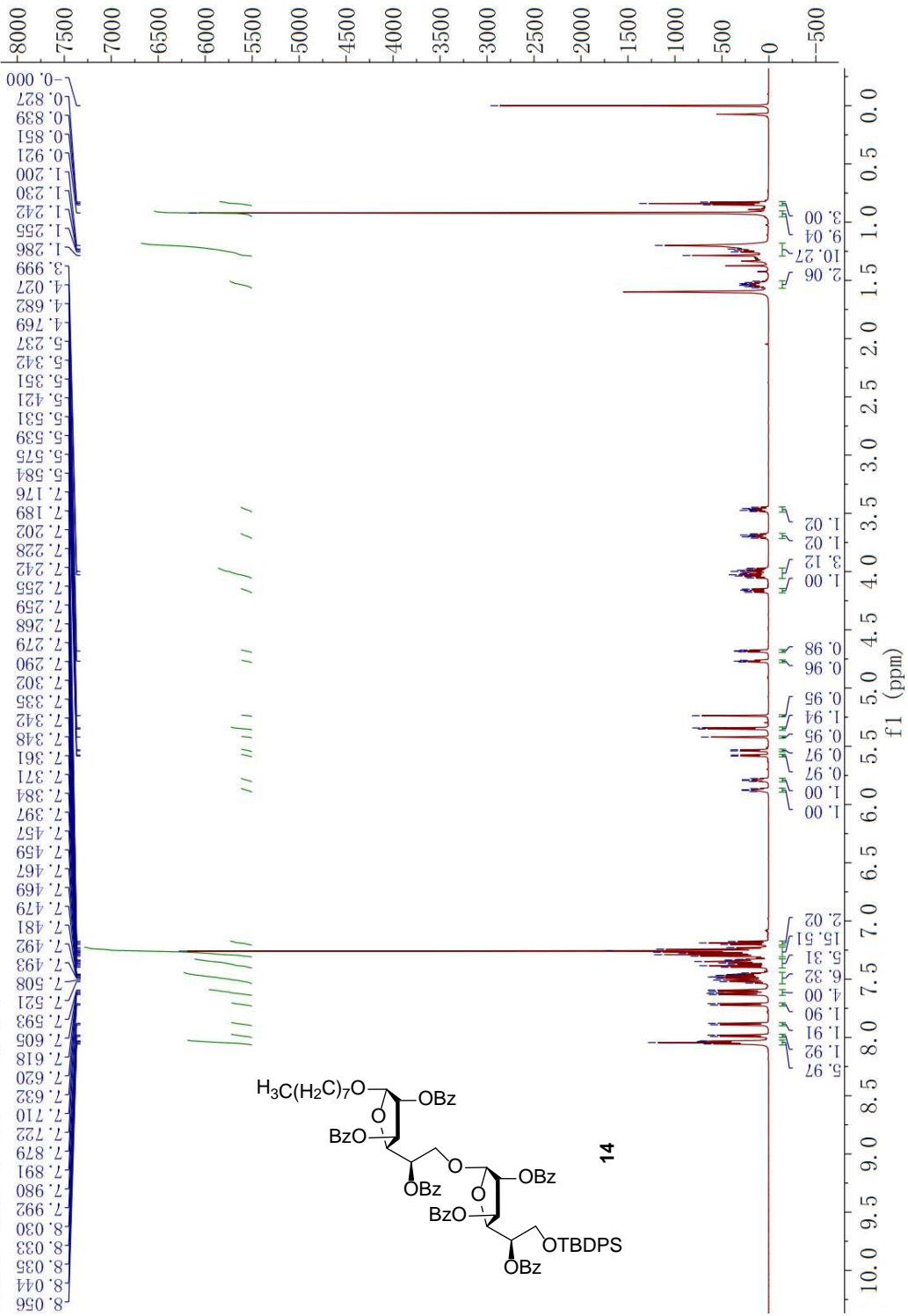


11 ¹H NMR (600 MHz, CDCl₃)

Octyl 6-*O*-*tert*-butyldiphenylsilyl-2,3,5-tri-*O*-benzoyl- β -D-galactopyranosyl-(1 \rightarrow 6)-2,3,5-tri-*O*-benzoyl- β -D-galactofuranoside (14)

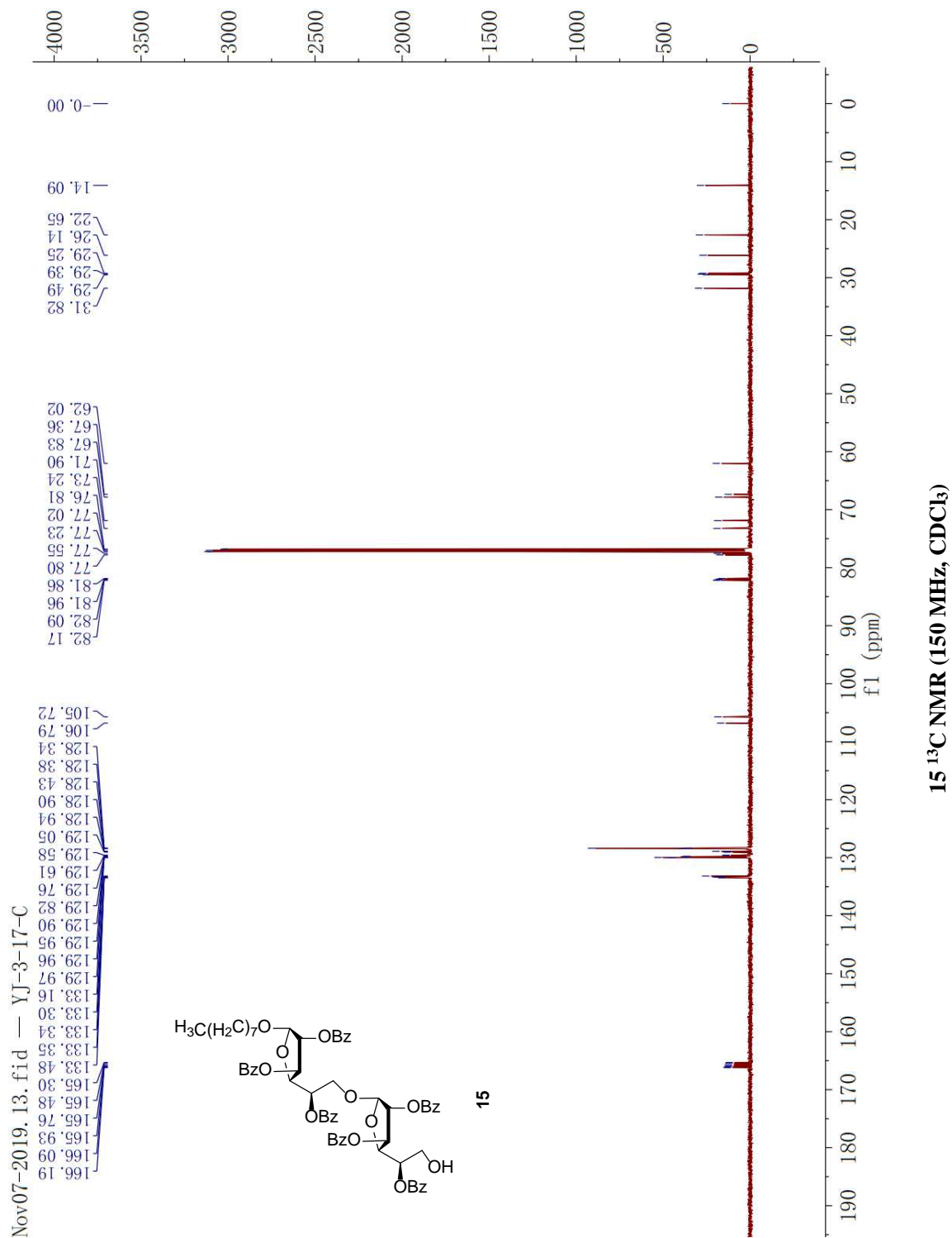


Oct28-2019, 23. fid — YJ-3-5

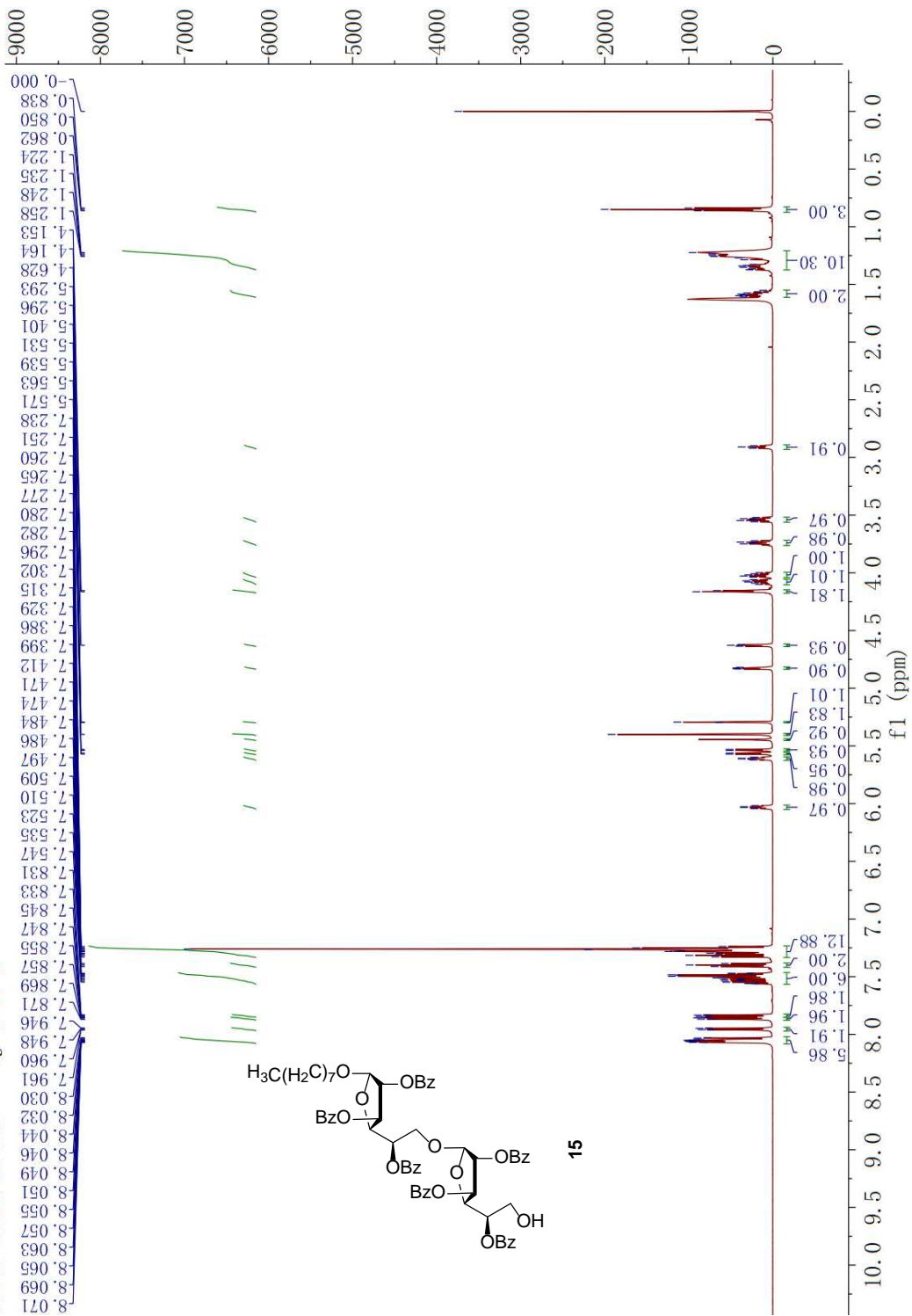


14 ¹H NMR (600 MHz, CDCl₃)

Octyl 2,3,5-tri-O-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranoside (15)

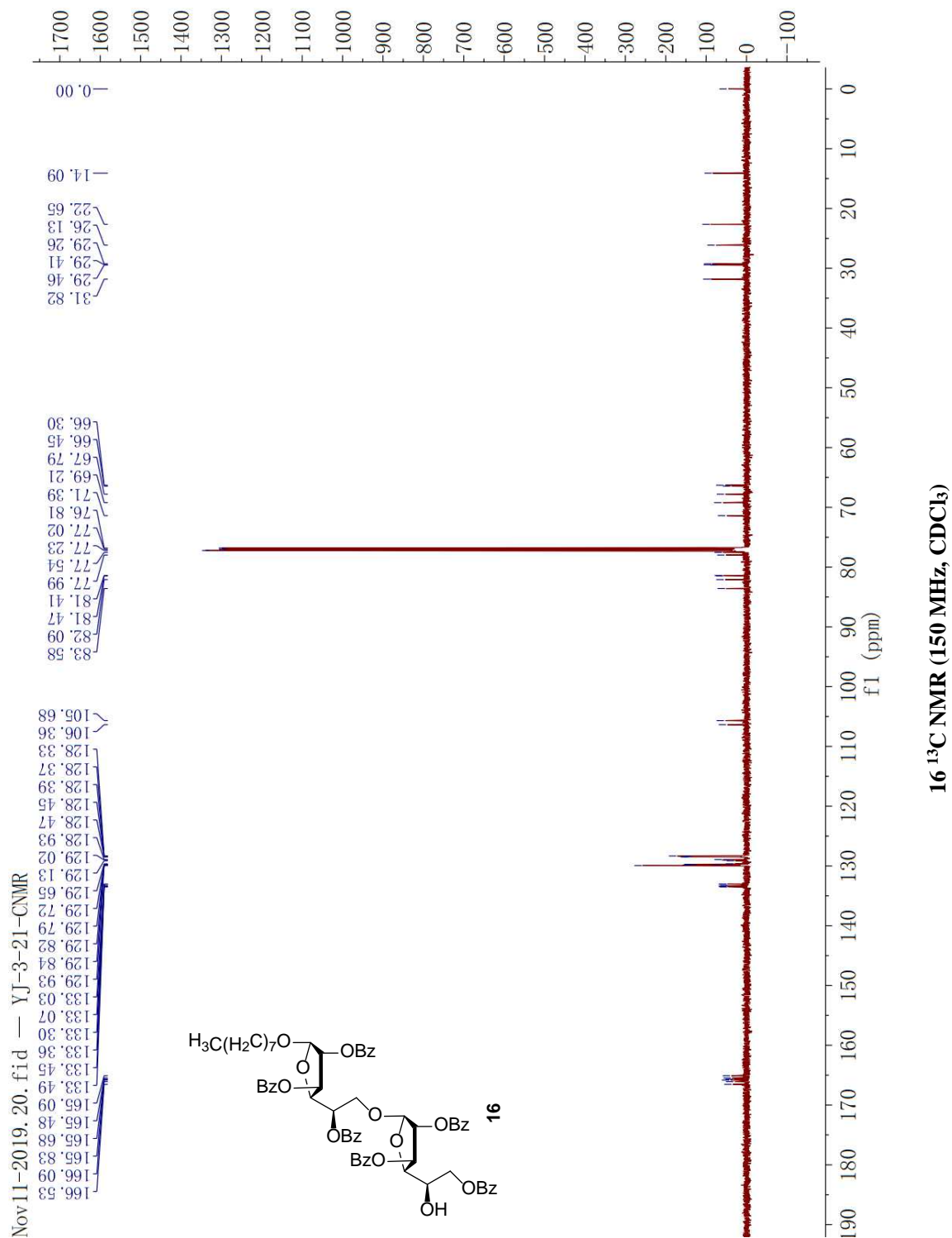


Nov07-2019. 12. fid — YJ-3-17-H

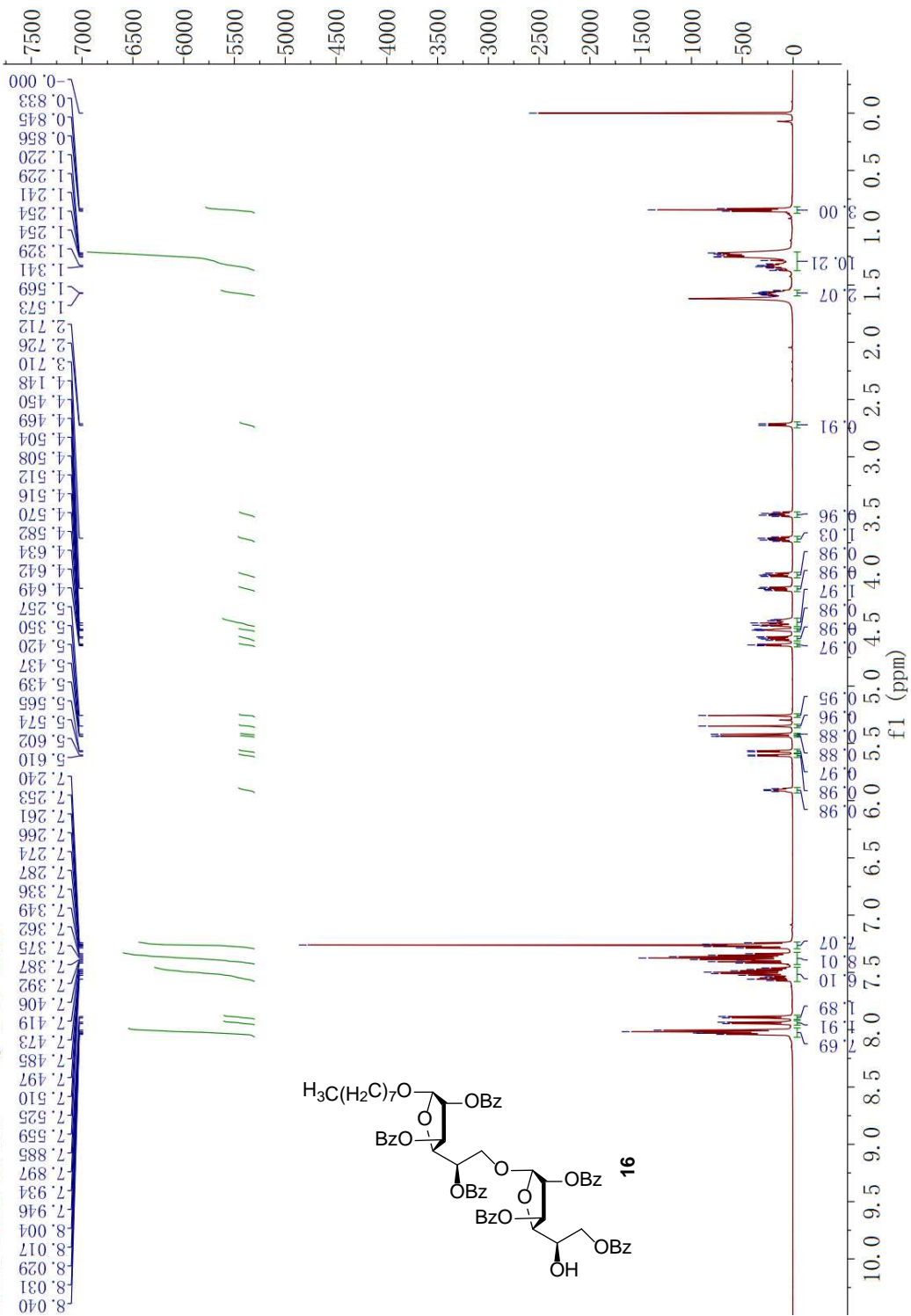


15 ¹H NMR (600 MHz, CDCl₃)

Octyl 2,3,6-tri-O-benzoyl- β -D-galactopyranosyl-(1 \rightarrow 6)-2,3,5-tri-O-benzoyl- β -D-galactofuranoside (16)

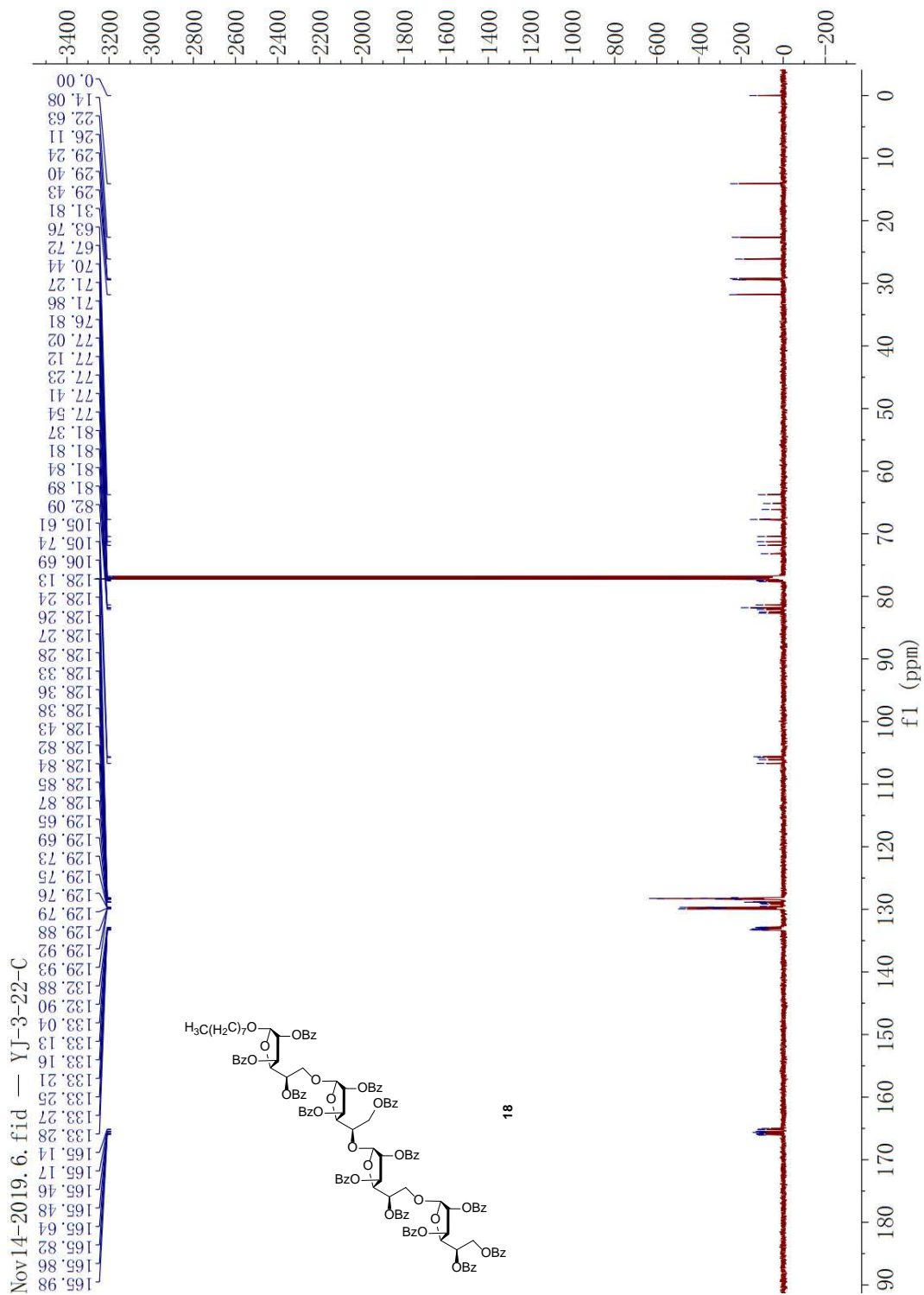


Nov11-2019. 19. fid — YJ-3-21-HNMR

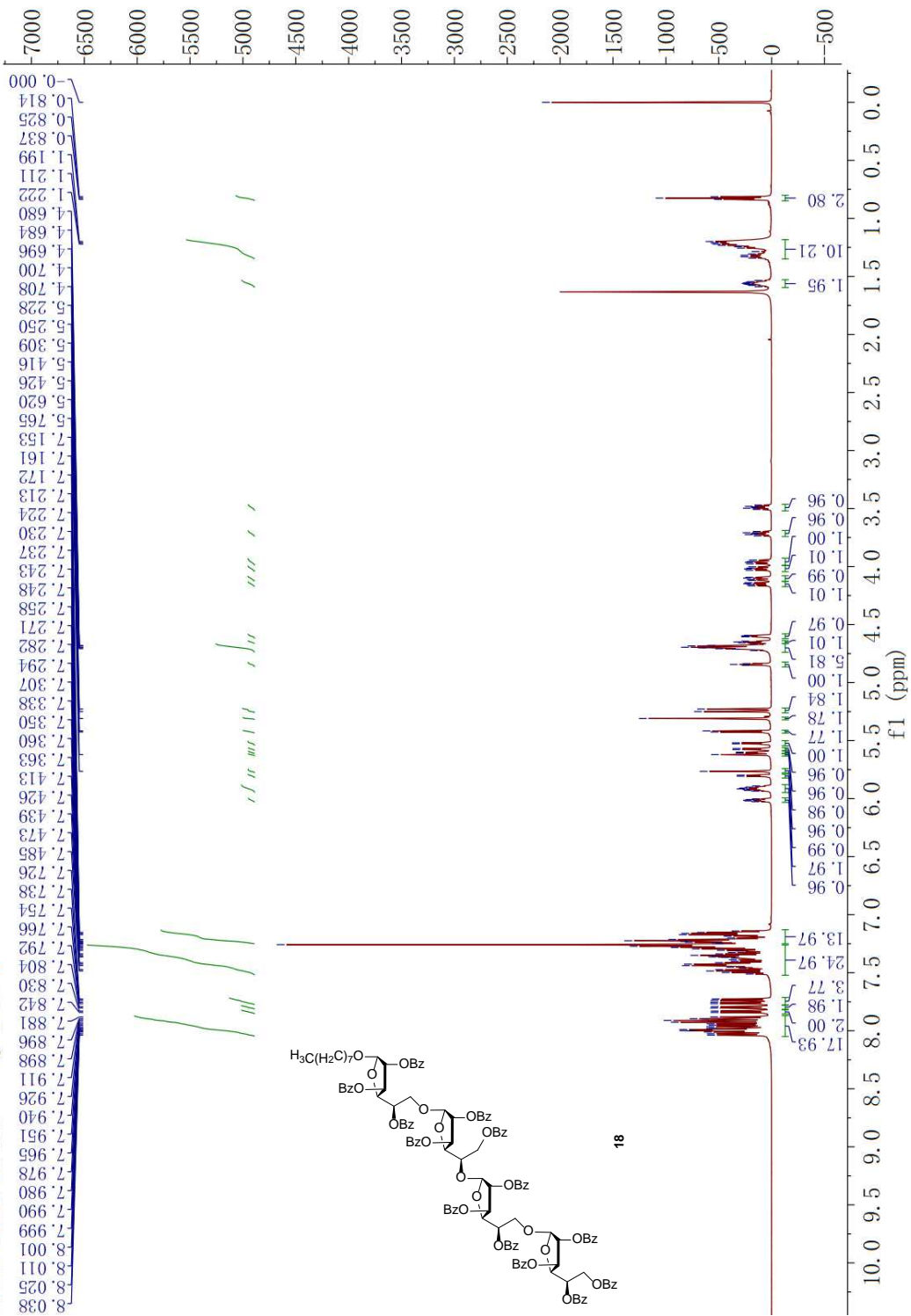


16 ¹H NMR (600 MHz, CDCl₃)

Octyl 2,3,5,6-tetra-O-benzoyl- β -D-galactopyranosyl-(1 \rightarrow 6)-2,3,5-tri-O-benzoyl- β -D-galactofuranosyl-(1 \rightarrow 5)-2,3,6-tri-O-benzoyl- β -D-galactopyranosyl-(1 \rightarrow 6)-2,3,5-tri-O-benzoyl- β -D-galactofuranoside (18)



Nov14-2019. 15. fid — YJ-3-22-H



18 ¹H NMR (600 MHz, CDCl₃)