Trivalent Dialkylaminopyridine-Catalyzed Site-Selective Mono-*O*-acylation of Partially-Protected Pyranosides

Kalyan Dey, Narayanaswamy Jayaraman*

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India

E-mail: jayaraman@iisc.ac.in

Supporting Information

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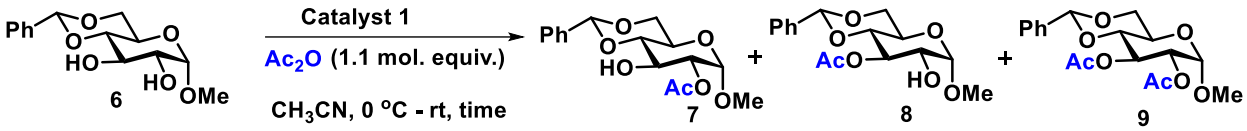
1. Reaction optimization:

The screening of the reactions was performed under kinetically controlled condition.[1] As given in the tables below, a catalyst loading of 1.5 mol% was optimized for all the acylations. With the increase in steric bulkiness of the anhydrides, reactions were conducted at different durations, in order to optimize the yield of the major product, with 1.5 mol% of the catalyst **1**.

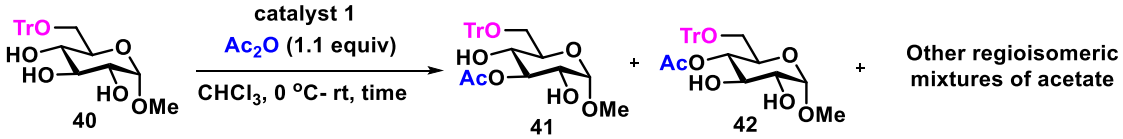
Table S1. Acetylation of **6** under varied reaction conditions.[a]



Entry	Catalyst (mol%)	Time (h)	7 (%)	8 (%)	9 (%)
1	10	2	41	3	56
2	5	2	42	6	52
3	3.3	2	48	8	34
4	1.1	3	53	8	21
5	**1.5**	**3**	**65**	**10**	**25**

[a]Reactions were conducted in 30 mg (0.106 mmol). Product ratios determined by HPLC analysis.

Table S2. Acetylation of **40** under varied reaction condition.[a]

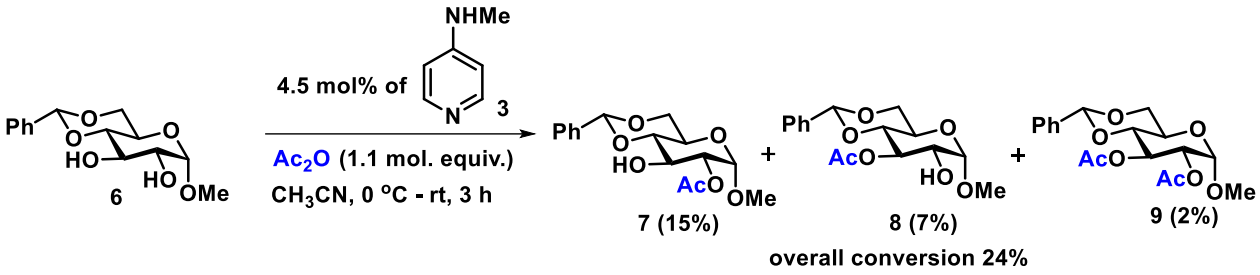


Entry	Catalyst (mol%)	Time (min)	41 (%)	42 (%)	Multiple acylated products	Conversion
1	10	30	32	ND	19% + 25% + 14% + 8%	Quantitative
2	5	30	41	ND	14% + 23% + 13% + 9%	Quantitative
3	3.3	30	54	9	4% + 8%	86

4	1.1	30	58	6	5% + 1% + 4%	77
5	1.5	30	64	9	6% + 2%	86
6	1.1	45	65	11	6% + 3%	85
7	**1.5**	**45**	**74**	**9**	**7% + 3%**	**94**

[a]Reactions were conducted in 30 mg (0.106 mmol). Product ratios determined by HPLC analysis.

2. 4-*N*-Methylamino pyridine (3)-mediated acylation:

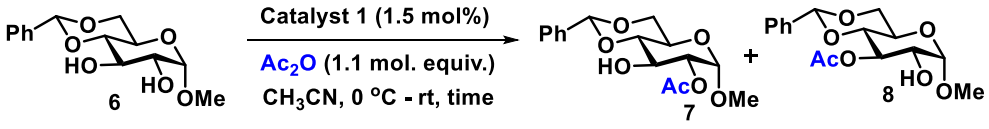


The product ratios determined by HPLC analysis. 4-*N*-methylamino pyridine **3** was not an active catalyst for site-selective acetylation of **6**.

3. Calculation of the regioisomeric ratio:

An aliquot of the reaction mixture was quenched with a few drops of MeOH. After 30 min, the solvent was evaporated, diluted in CH_2Cl_2 (1 mL) and analyzed by HPLC (analytical silica column, photodiode array detector and using hexane/EtOAc binary elution).

Table S3. Site-selectivity for the acetylation of **6** at different time intervals.[a]

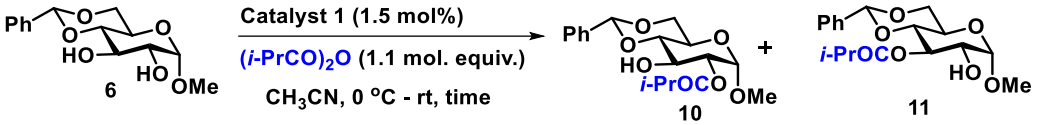


Time (min)	7 (%)	8 (%)	Ratio of 7/8
15	13	2	6.5
30	25	4	6.2
45	34	5	6.8

60	41	6	6.8
90	49	7	7.0
120	57	8	7.1
150	63	9	7.0
180	65	10	6.5

[a]Reactions were conducted in 30 mg (0.106 mmol). Product ratios determined by HPLC analysis.

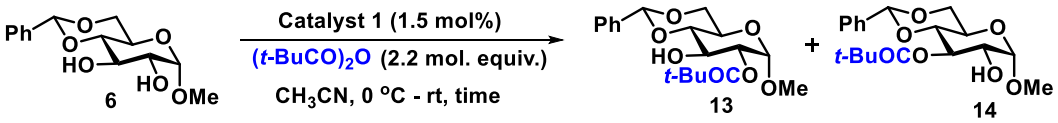
Table S4. Site-selectivity for the isobutyration of **6** at different time intervals.[a]



Time (min)	10 (%)	11 (%)	Ratio of 10/11
10	46	5.6	8.2
30	64	7.9	8.1
50	68	8.6	7.9
70	71	9.3	7.6
90	73	9.8	7.4
120	75	10	7.5

[a]Reactions were conducted in 30 mg (0.106 mmol). Product ratios determined by HPLC analysis.

Table S5. Site-selectivity for the pivaloylation of **6** at different time intervals.[a]

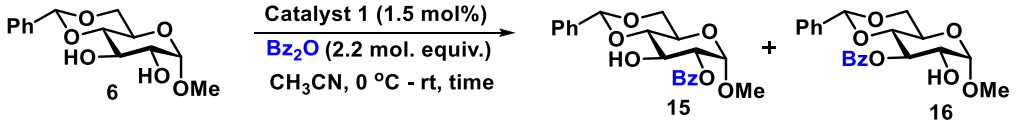


Time (h)	13 (%)	14 (%)	Ratio of 13/14
1	17	4	4.2
2	33	9	3.6
3	40	12	3.3
4	47	14	3.3
6	56	16	3.5
8	64	18	3.5

10	68	19	3.6
12	72	20	3.6
14	75	22	3.4
16	77	23	3.3

[a]Reactions were conducted in 30 mg (0.106 mmol). Product ratios determined by HPLC analysis.

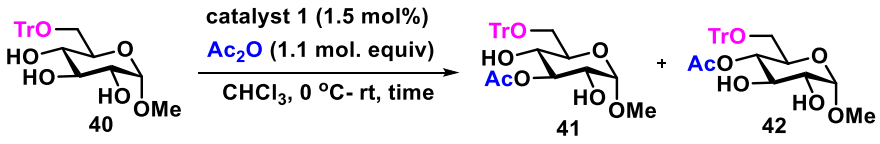
Table S6. Site-selectivity for the benzoylation of **6** at different time intervals.[a]



Time (h)	15 (%)	16 (%)	Ratio of 15/16
1	22	5	4.4
2	32	7	4.6
3	42	9	4.6
4	47	10	4.7
6	50	11	4.5
8	52	11.5	4.5
10	54	12	4.5

[a]Reactions were conducted in 30 mg (0.106 mmol). Product ratios determined by HPLC analysis.

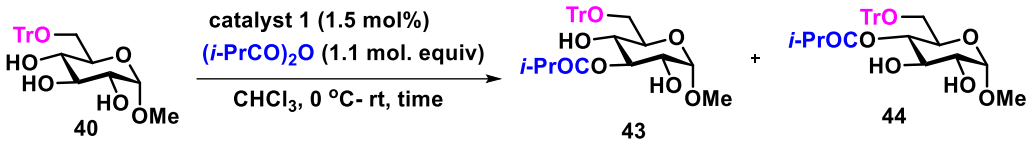
Table S7. Site-selectivity for the acetylation of **40** at different time intervals.[a]



Time (min)	41 (%)	42 (%)	Ratio of 41/42
5	20	3	6.6
10	34	6	5.6
15	43	7	6.1
25	57	8	7.1
35	68	8.5	8.0
45	74	9	8.2

[a]Reactions were conducted in 30 mg (0.106 mmol). Product ratios determined by HPLC analysis.

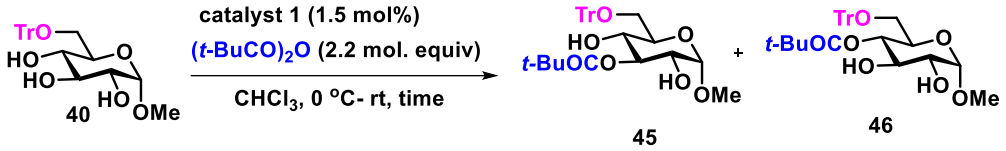
Table S8. Site-selectivity for the isobutyration of **40** at different time intervals.[a]



Time (min)	43 (%)	44 (%)	Ratio of 43/44
5	35	2.5	14
10	53	3.6	14.5
15	69	4.7	14.7
20	80	5.5	14.5
30	89	6	14.8

[a]Reactions were conducted in 30 mg (0.106 mmol). Product ratios determined by HPLC analysis.

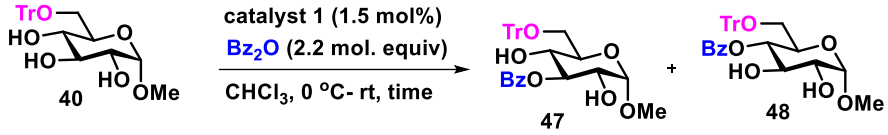
Table S9. Site-selectivity for the pivaloylation of **40** at different time intervals.[a]



Time (h)	45 (%)	46 (%)	Ratio of 45/46
1	19	3	6.1
2	35	5.5	6.3
3	45	7	6.4
4	53	9	5.8
5	59	10	5.9
7	66	11	6
9	73	12	6.0
11	78	12.5	6.2
13	82	13.5	6.0
16	84	14	6

[a]Reactions were conducted in 30 mg (0.106 mmol). Product ratios determined by HPLC analysis.

Table S10. Site-selectivity for the benzoylation of **40** at different time intervals.[a]



Time (h)	47 (%)	48 (%)	Ratio of 47/48
0.5	12	3	4
1	23	5	4.6
2	35	8	4.4
4	50	14	3.6
5	58	18	3.2
6	64	20	3.2
8	73	23	3.2

[a]Reactions were conducted in 30 mg (0.106 mmol). Product ratios determined by HPLC analysis.

No significant change in the regioisomeric ratios was observed at different time intervals for the acylations.

4. Turnover Frequency (TOF) for major regioisomeric product:

Catalyst **1** (1.5 mol%) was used in each case. Conversion to major site-selective product at different time intervals are given in Table 3-10. TOF = mole of product formed / (mole of catalyst used × time)[2]

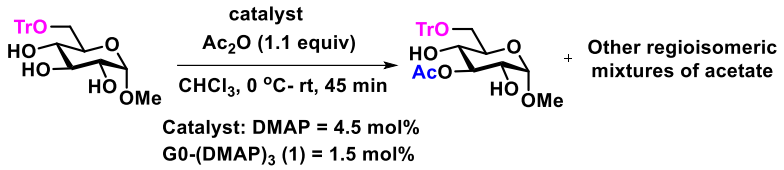
Table 11. Comparison of TOF for acylation of **6** with varied acylation agents.

Reaction type	TOF (h^{-1})	Reaction Type	TOF (h^{-1})
Acetylation of **6**	21.8	Acetylation of **40**	92.4
Isobutyration of **6**	54.6	Isobutyration of **40**	184
Pivaloylation of **6**	7.8	Pivaloylation of **40**	8.8
Benzoylation of **6**	9.3	Benzoylation of **40**	8.3

5. HPLC traces and determination of the product ratios and conversion.

(Note: Void volume appears between 0 and ~ 3.5 min. in all HPLC traces).

Acylation of methyl-6-*O*-trityl glucopyranoside (40)



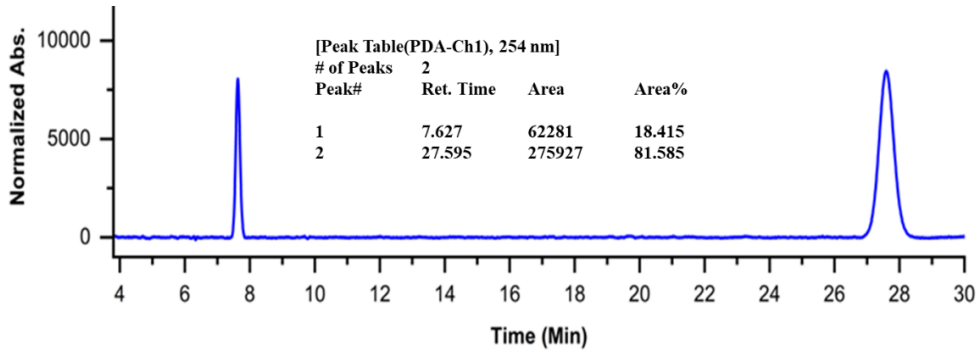


Figure S1. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 90:10) for acylation of **40** by DMAP. Retention times: 7.6 min. (major isomer **41**), 27.6 min. (starting material **40**).

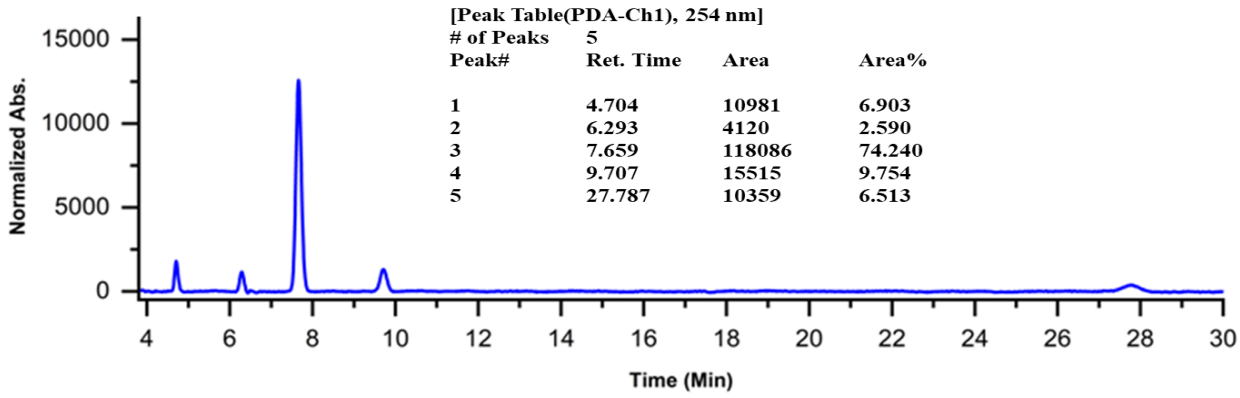


Figure S2. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 90:10) for acylation of **40** by **1**. Retention times: 7.7 min. (major isomer **41**), 27.8 min. (starting material **40**) and remaining peaks correspond to the minor isomers.

Isobutyration of methyl-6-*O*-trityl glucopyranoside (40)

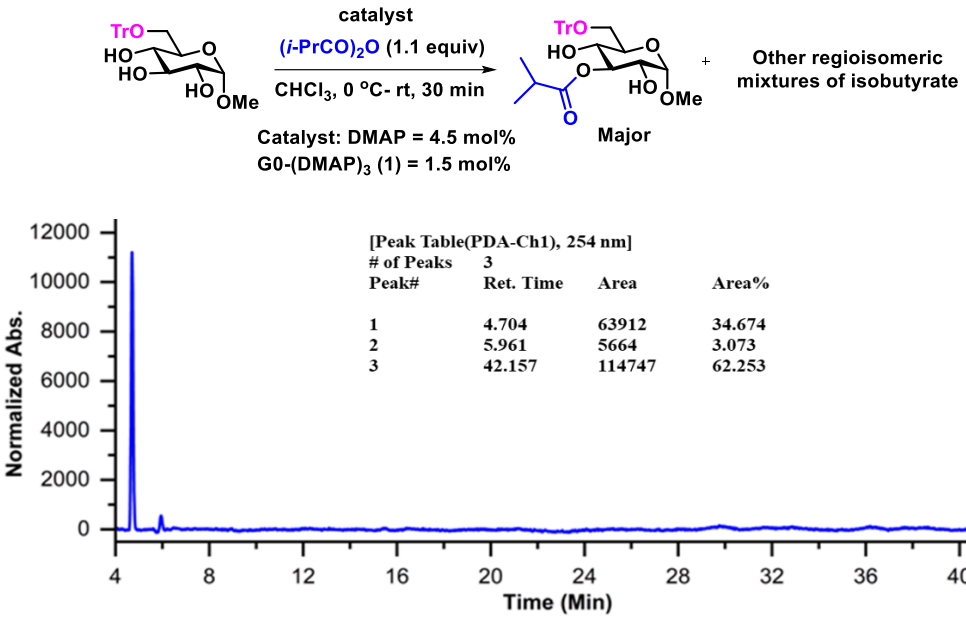


Figure S3. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of DMAP-catalyzed isobutyration of **40**. Retention times: 4.7 min. (major isomer **43**), 42.2 min. (starting material **40**) and remaining peaks correspond to the minor isomers.

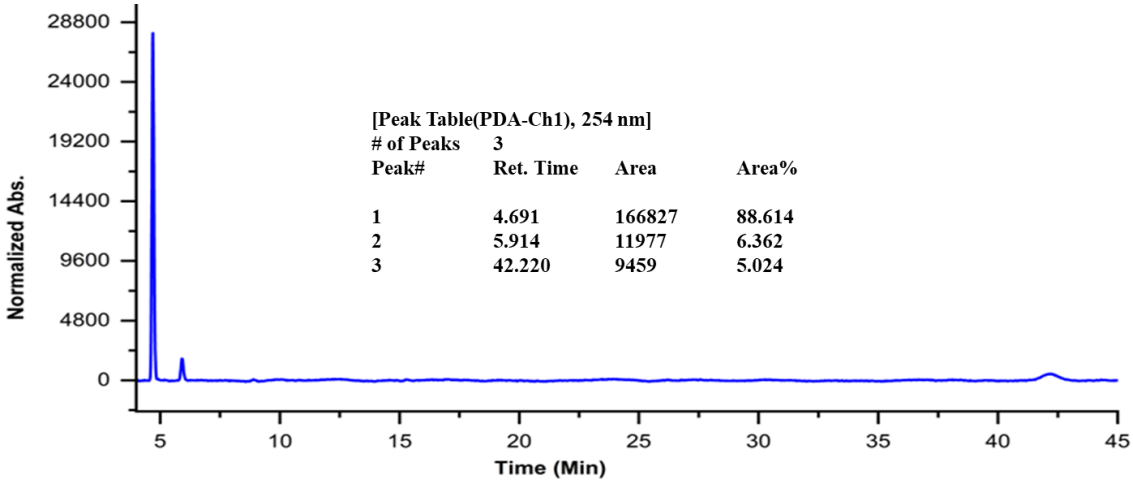


Figure S4. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of **1**-catalyzed isobutyration of **40**. Retention times: 4.7 min. (major isomer **43**), 42.2 min. (starting material **40**) and remaining peaks correspond to the minor isomers.

Pivaloylation of methyl-6-*O*-trityl glucopyranoside (40)

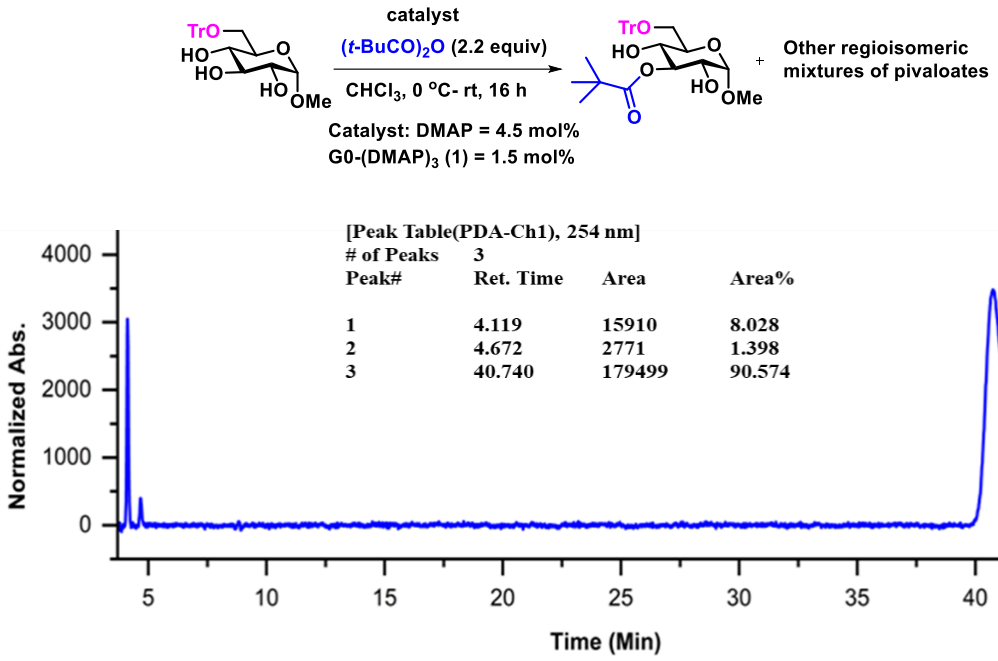


Figure S5. HPLC chromatogram (eluant: EtOAc-n-hexane = 60:40) of DMAP-catalyzed pivaloylation of **40**. Retention times: 4.1 min. (major isomer **45**), 40.7 min. (starting material **40**) and remaining peaks correspond to the minor isomers.

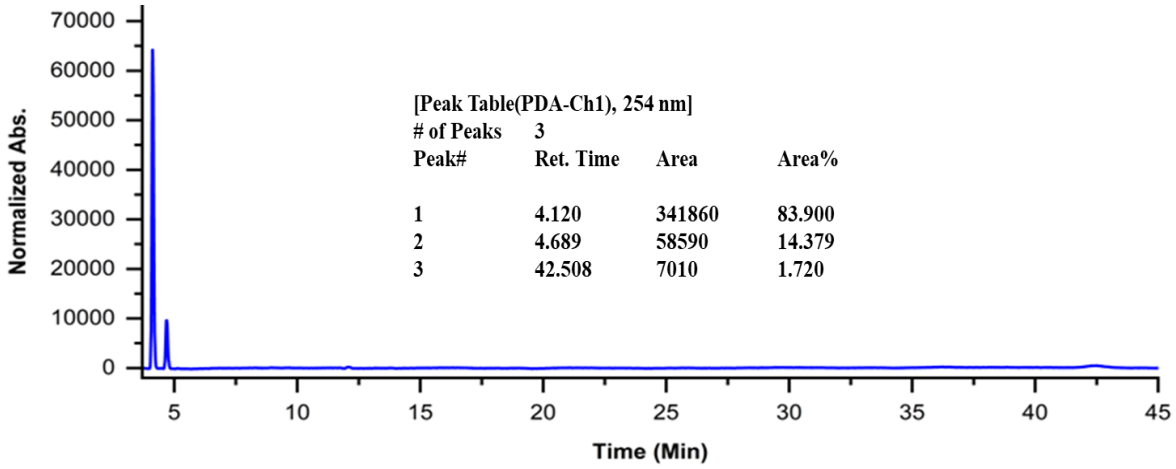
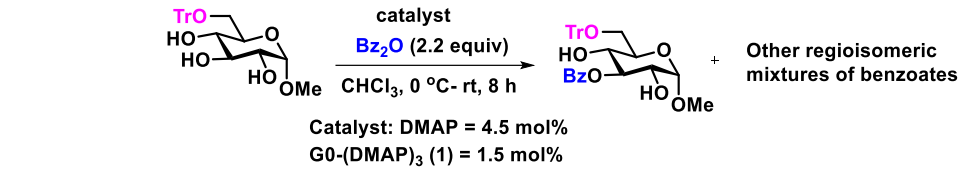


Figure S6. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of **1**-catalyzed pivaloylation of **40**. Retention times: 4.1 min. (major isomer **45**), 42.5 min. (starting material **40**) and remaining peaks correspond to the minor isomers.

Benzoylation of methyl-6-*O*-trityl glucopyranoside (40)



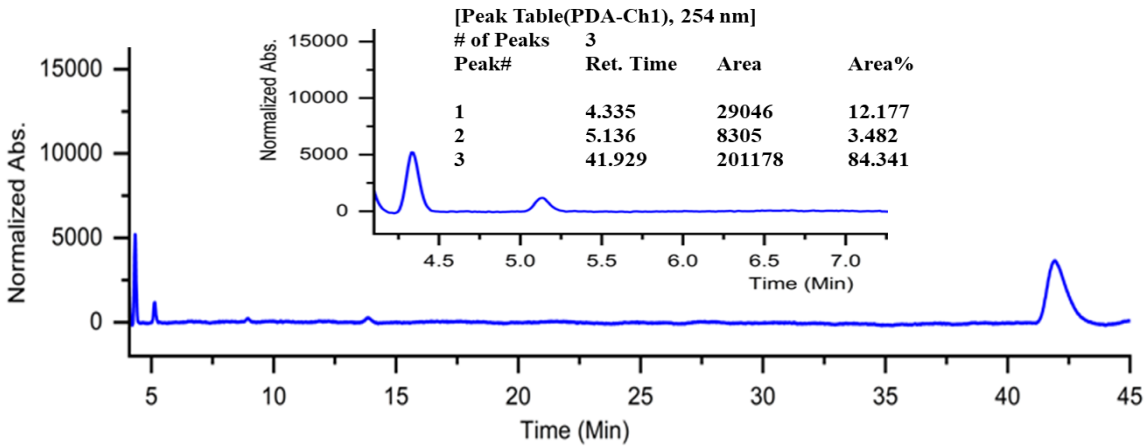


Figure S7. HPLC chromatogram (eluant: EtOAc-n-hexane = 60:40) of DMAP-catalyzed benzoylation of **40**. Retention times: 4.3 min. (major isomer **47**), 41.9 min. (starting material **40**) and remaining peaks correspond to the minor isomers.

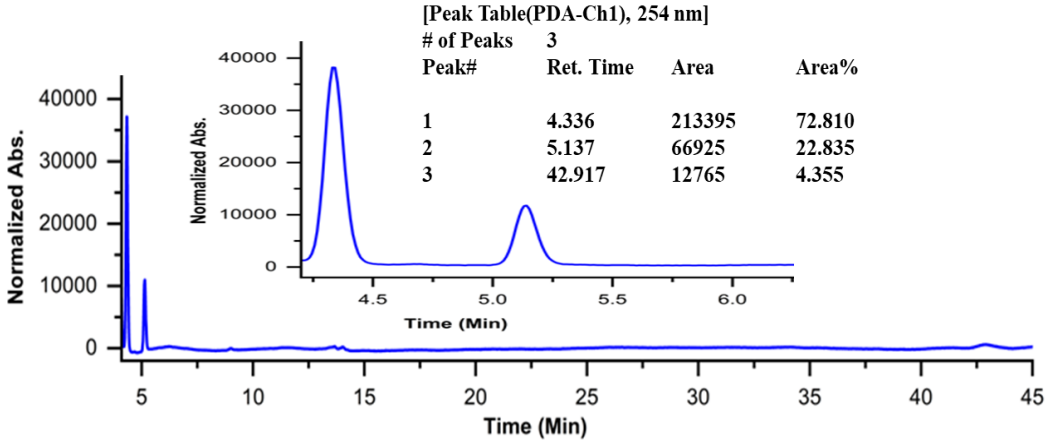
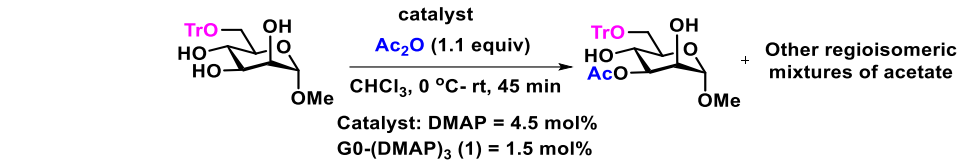


Figure S8. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of **1**-catalyzed benzoylation of **40**. Retention times: 4.3 min. (major isomer **47**), 42.9 min (starting material **40**) and remaining peaks correspond to the minor isomers.

Acylation of methyl 6-*O*-trityl-α-D-mannopyranoside (49)



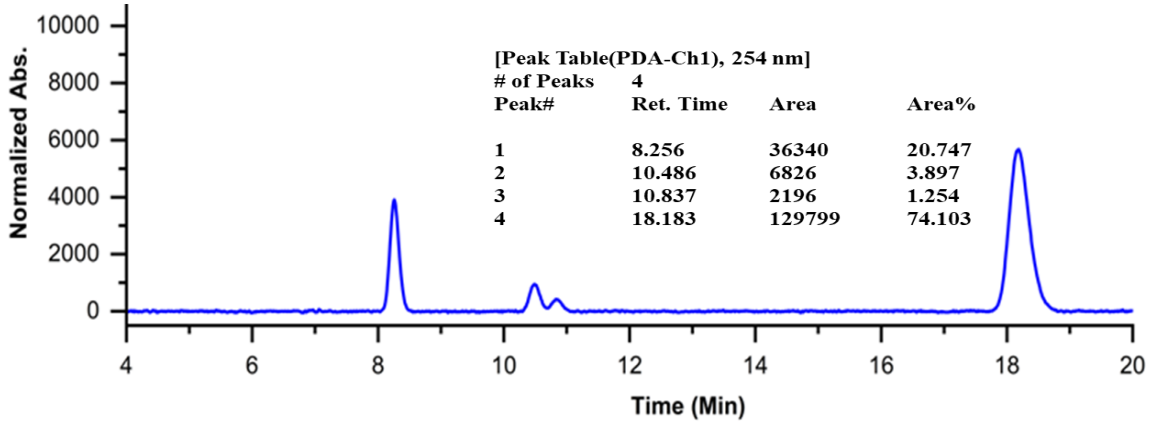


Figure S9. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of DMAP-catalyzed acylation of **49**. Retention times: 8.2 min. (major isomer **50**), 18.2 min. (starting material **49**) and remaining peaks correspond to the minor isomers.

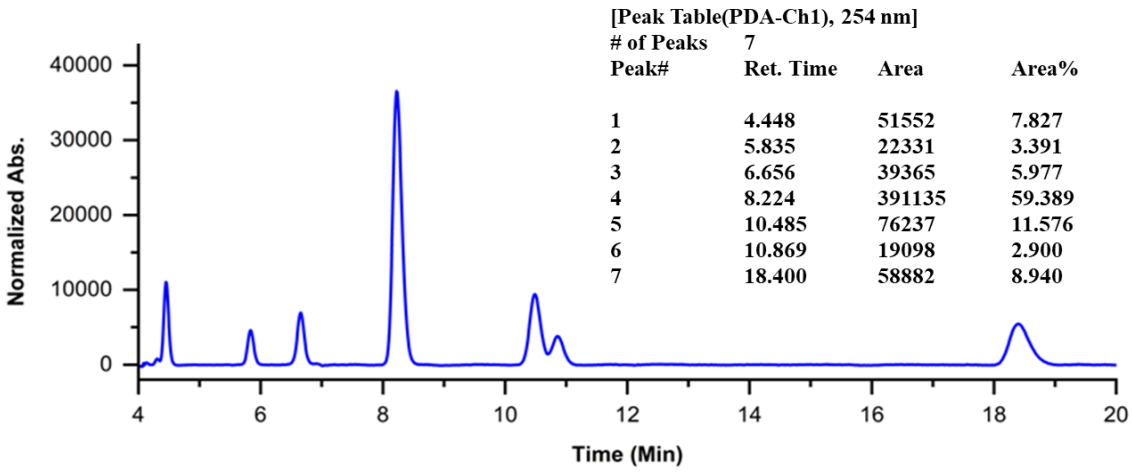
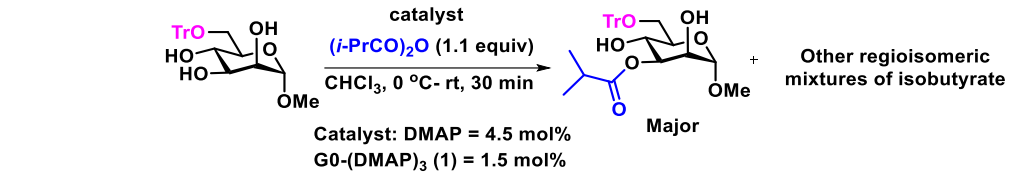


Figure S10. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of **1**-catalyzed acylation of **49**. Retention times: 8.2 min. (major isomer **50**), 18.4 min. (starting material **49**) and remaining peaks correspond to the minor isomers.

Isobutyration of methyl 6-*O*-trityl-α-D-mannopyranoside (49)



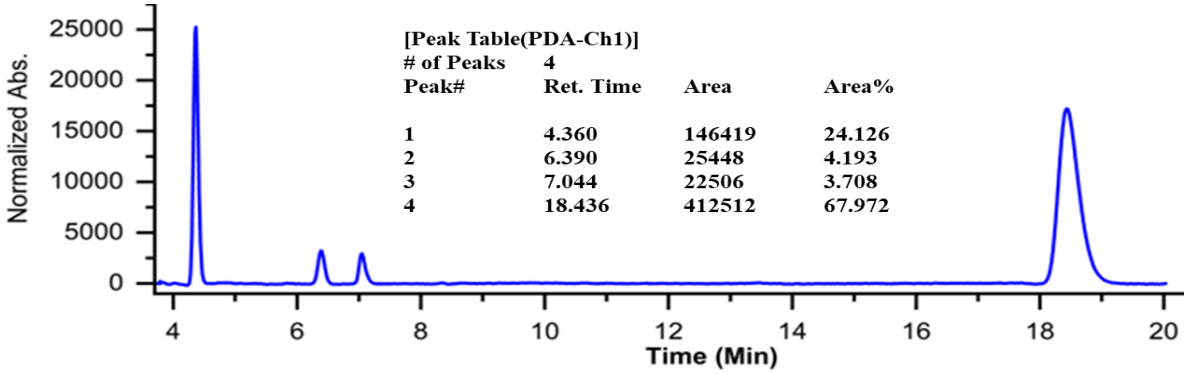


Figure S11. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of DMAP-catalyzed isobutyration of **49**. Retention times: 4.4 min. (major isomer **52**), 18.4 min. (starting material **49**) and remaining peaks correspond to the minor isomers.

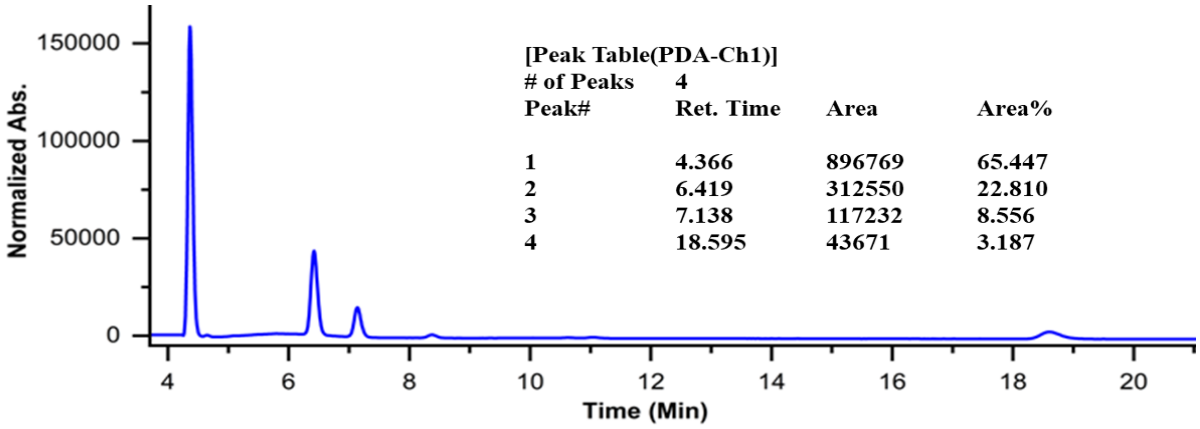
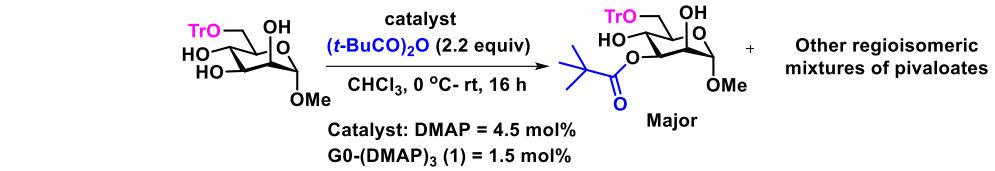


Figure S12. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of **1**-catalyzed isobutyration of **49**. Retention times: 4.4 min. (major isomer **52**), 18.6 min. (starting material **49**) and remaining peaks correspond to the minor isomers.

Pivaloylation of methyl 6-*O*-trityl-α-D-mannopyranoside (49)



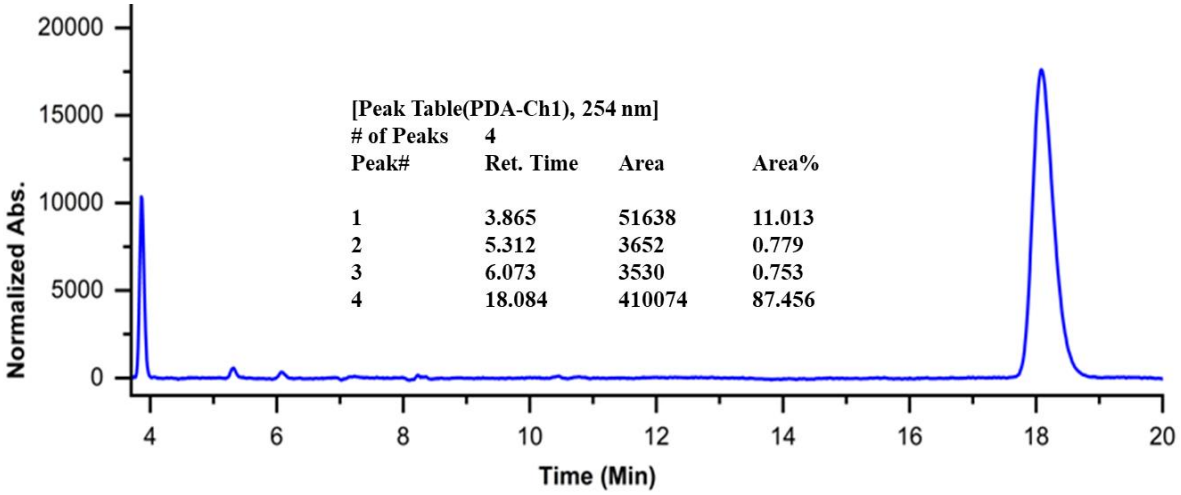


Figure S13. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of DMAP-catalyzed pivaloylation of **49**. Retention times: 3.9 min. (major isomer **54**), 18.1 min. (starting material **49**) and remaining peaks correspond to the minor isomers.

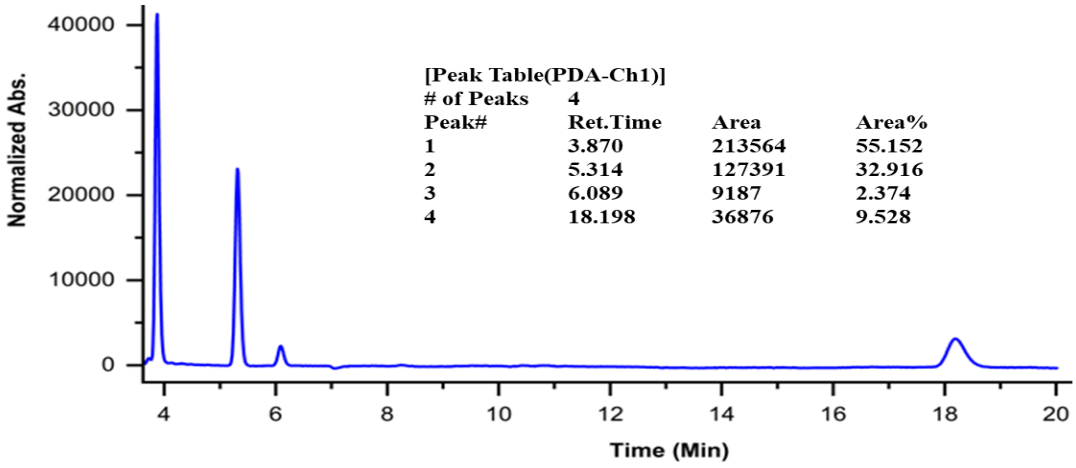
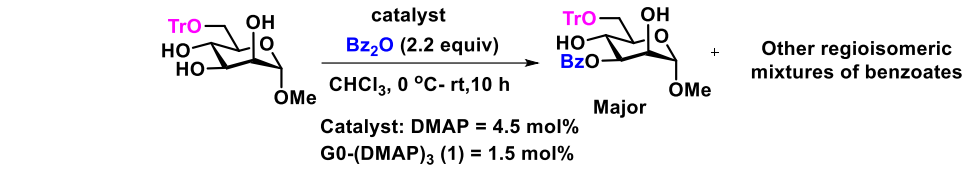


Figure S14. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of **1**-catalyzed pivaloylation of **49**. Retention times: 3.9 min. (major isomer **54**), 18.2 min. (starting material **49**) and remaining peaks correspond to the minor isomers.

Benzoylation of methyl 6-*O*-trityl-α-D-mannopyranoside (49)



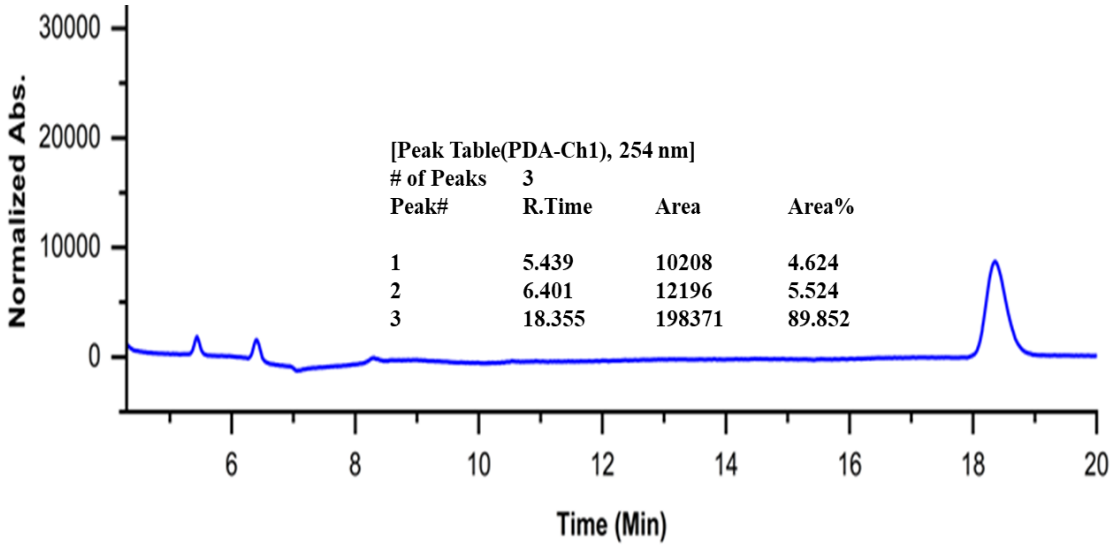


Figure S15. HPLC chromatogram (eluant: EtOAc-n-hexane = 60:40) of DMAP-catalyzed benzoylation of **49**. Retention times: 5.4 min. (major isomer **56**), 18.4 min. (starting material **49**) and remaining peaks correspond to the minor isomers.

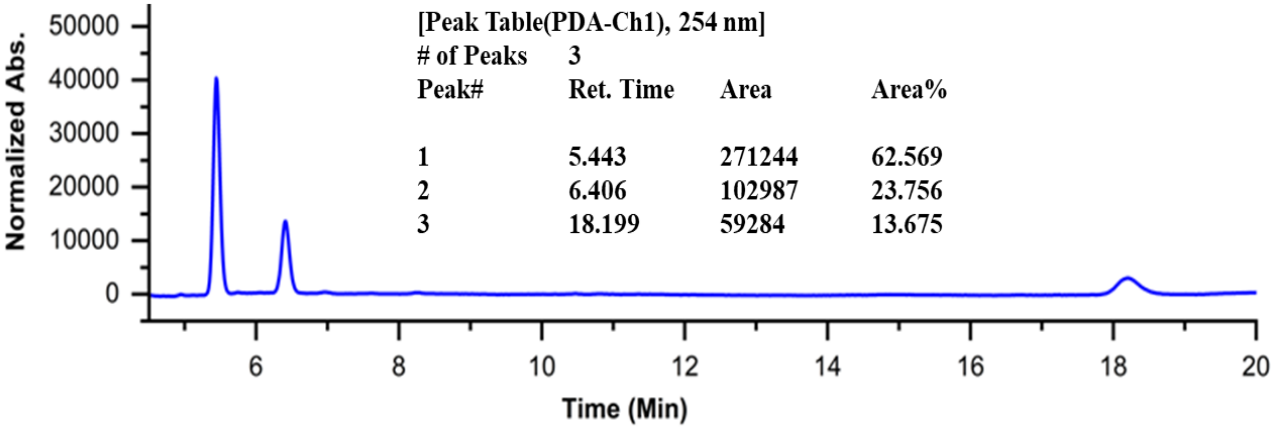
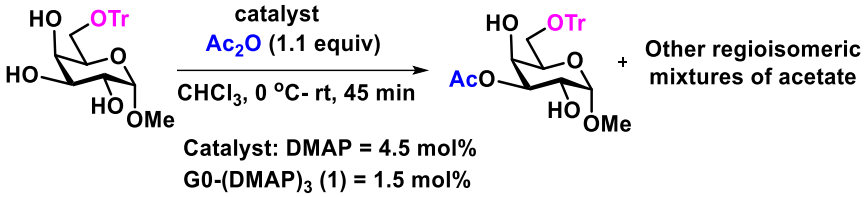


Figure S16. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of **1**-catalyzed benzoylation of **49**. Retention times: 5.4 min. (major isomer **56**), 18.2 min. (starting material **49**) and remaining peaks correspond to the minor isomers.

Acylation of methyl 6-*O*-trityl-α-D-galactopyranoside (58)



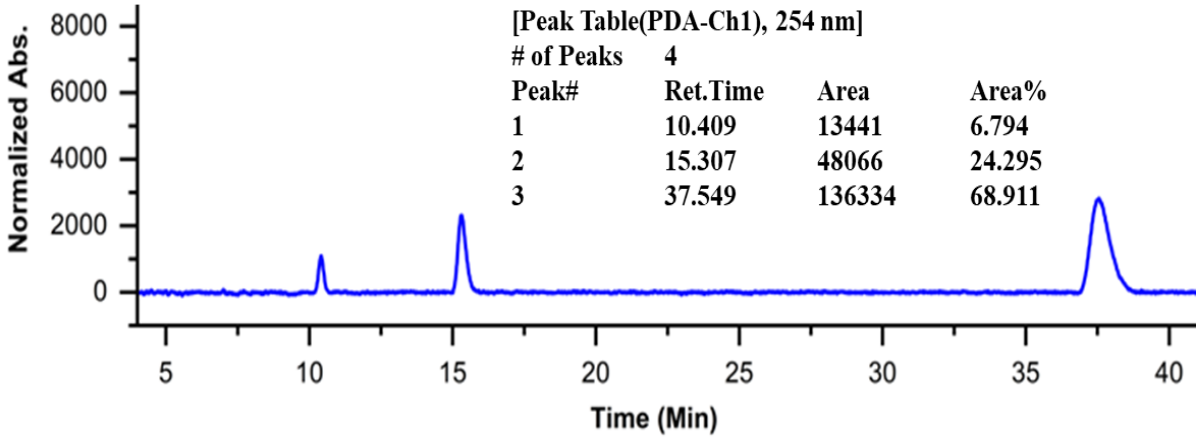


Figure S17. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of DMAP-catalyzed acylation of **58**. Retention times: 15.3 min. (major isomer **59**), 37.5 min. (starting material **58**) and remaining peaks correspond to the minor isomers.

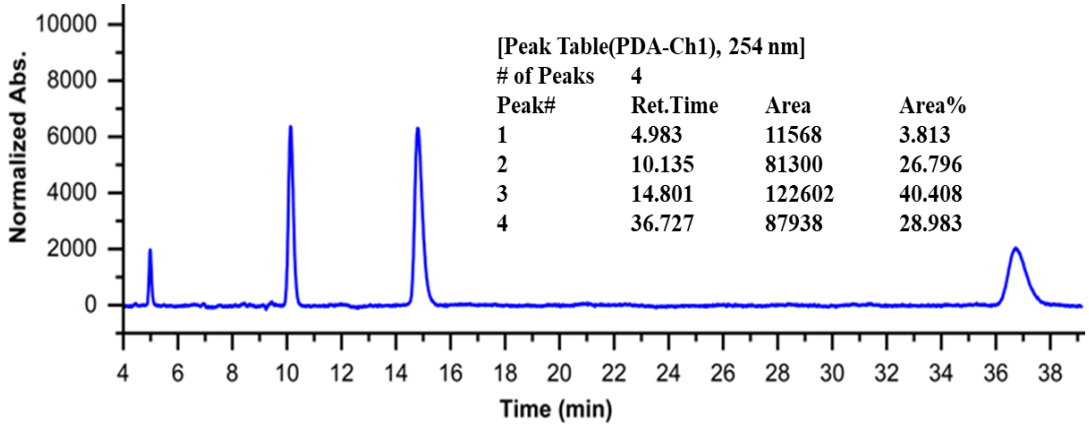


Figure S18. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of **1**-catalyzed acylation of **58**. Retention times: 14.9 min. (major isomer **59**), 36.7 min. (starting material **58**) and remaining peaks correspond to the minor isomers.

Isobutyration of methyl 6-*O*-trityl-α-D-galactopyranoside (58)

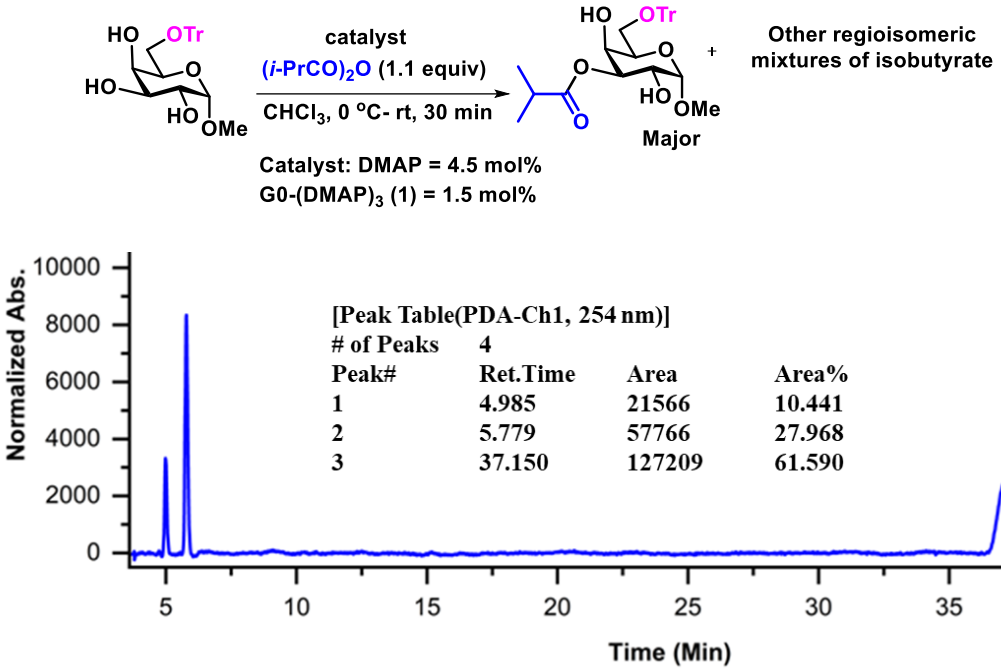


Figure S19. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of DMAP-catalyzed isobutyration of **58**. Retention times: 5.8 min. (major isomer **61**), 37.2 min. (starting material **58**) and remaining peaks correspond to the minor isomers.

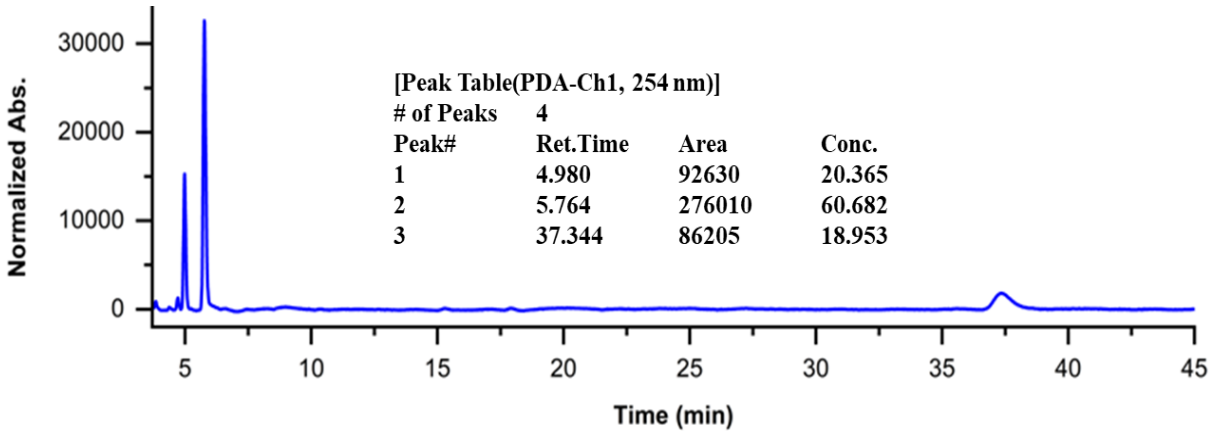


Figure S20. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of **1**-catalyzed isobutyration of **58**. Retention times: 5.8 min. (major isomer **61**), 37.3 min. (starting material **58**) and remaining peaks correspond to the minor isomers.

Pivaloylation of methyl 6-*O*-trityl-α-D-galactopyranoside (58)

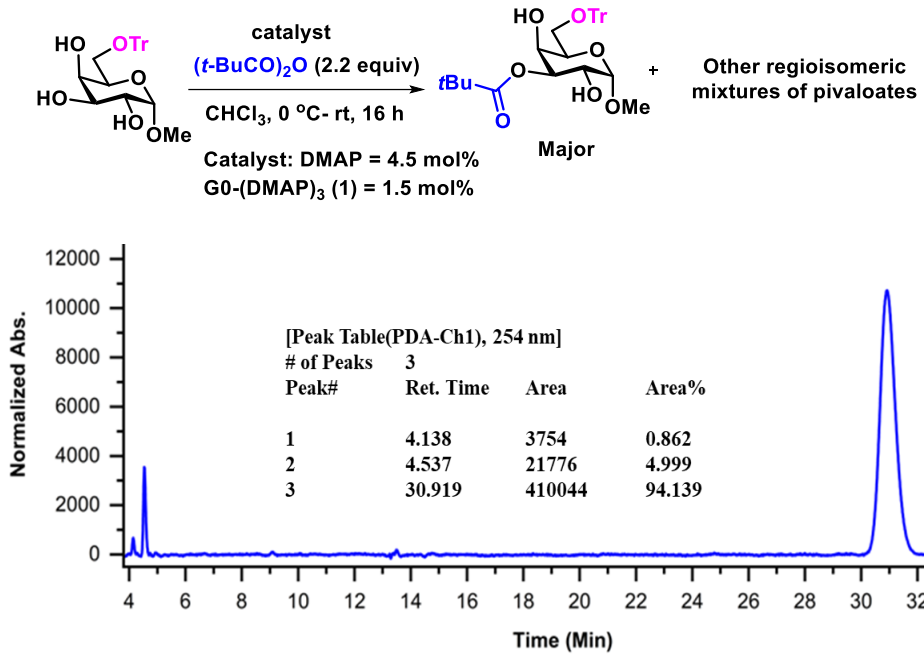


Figure S21. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 65:35) of DMAP-catalyzed pivaloylation of **58**. Retention times: 4.5 min. (major isomer **63**), 31 min. (starting material **58**) and remaining peaks correspond to the minor isomers.

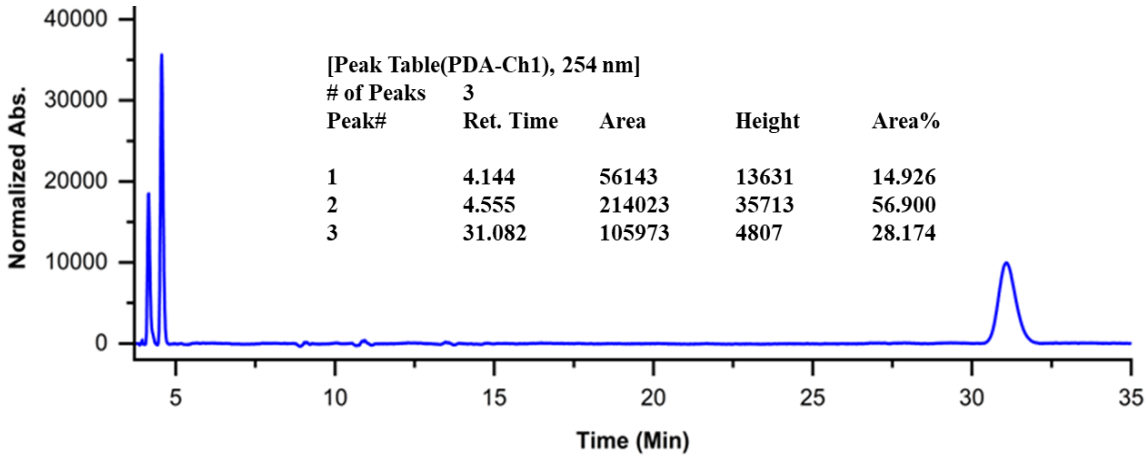


Figure S22. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 65:35) of **1**-catalyzed pivaloylation of **58**. Retention times: 4.6 min. (major isomer **63**), 31 min. (starting material **58**) and remaining peaks correspond to the minor isomers.

Benzoylation of methyl 6-*O*-trityl-α-D-galactopyranoside (58)

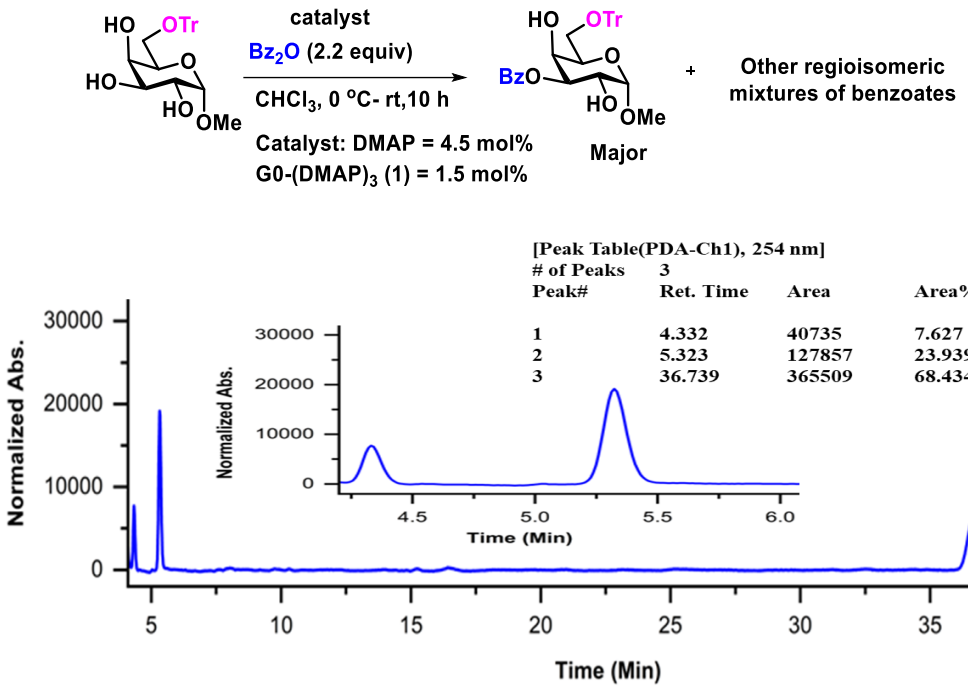


Figure S23. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of DMAP-catalyzed benzoylation of **58**. Retention times: 5.3 min. (major isomer **65**), 36.7 min. (starting material **58**) and remaining peaks correspond to the minor isomers.

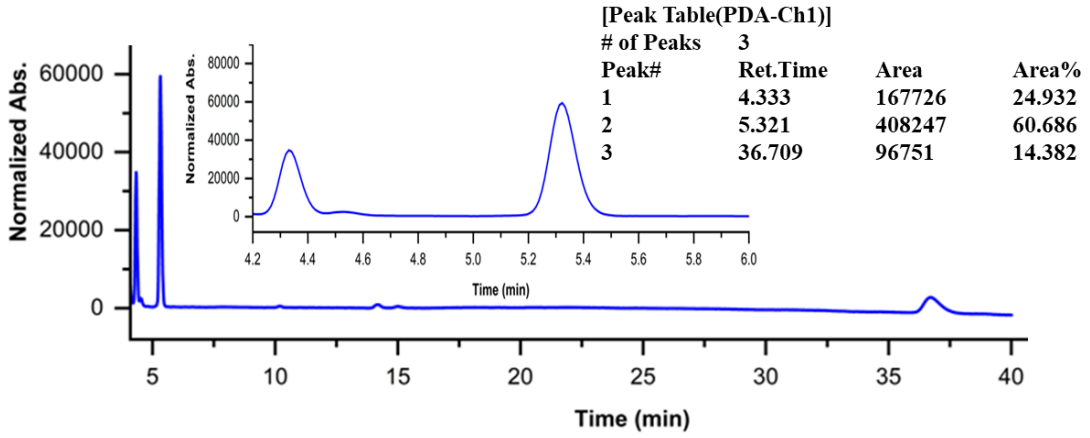


Figure S24. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 60:40) of **1**-catalyzed benzoylation of **58**. Retention times: 5.3 min. (major isomer **65**), 36.7 min. (starting material **58**) and remaining peaks correspond to the minor isomers.

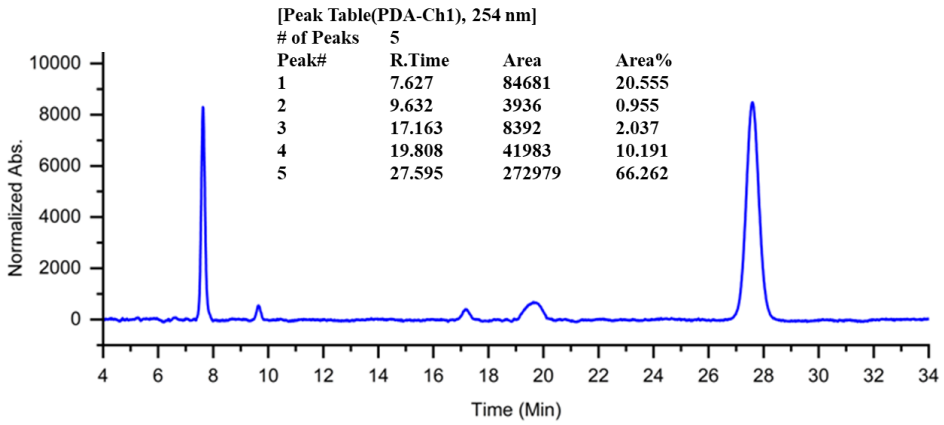


Figure S25. HPLC chromatogram (eluant: EtOAc-*n*-hexane = 90:10) for acylation of **40** by DMAP and Et_3N (1.1 mol. equiv.). Retention times: 7.6 min. (major isomer **41**), 27.6 min. (starting material **40**).

6. General characterization information of catalysts 1 and 5.

The DAAP catalysts **1** and **5** were characterized by NMR spectroscopies and mass spectrometry. Characteristics of ^{1}H NMR spectra were the changes of the chemical shifts of the C*H*$_2$- moieties at the peripheries, depending on the nature of the attached functional group. Thus, resonance of -C*H*$_2$Cl at ~ 3.60 ppm (t) is replaced by resonance at ~ 3.91 ppm (t) of -C*H*$_2$-DAAP. ^{13}C NMR chemical shifts also ascertained the peripheral –*C*H$_2$– moiety, that of ~ 43 ppm for - *C*H$_2$Cl and ~ 56 ppm for -*C*H$_2$-DAAP. Further, differences in the resonance values for -NCH$_3$- moiety of DAAP prior to (**3**) and after functionalization (**1** and **5**) were noted. Mass spectrometry ascertained the structural homogeneity of derivatives **1** and **5**.

7. References

1. P. G. Goekjian and S. Vidal, Regioselective Protection at the Secondary Positions of Carbohydrates with Acyclic Protecting Groups, in *Protecting Groups – Strategies and Applications in Carbohydrate Chemistry*, ed. S. Vidal, Wiley-VCH: Weinheim, 2019; ch. 4, pp. 109-144.
2. K. Price and D. T. McQuade, *Chem. Commun.*, 2005, 1714.

NMR Spectra

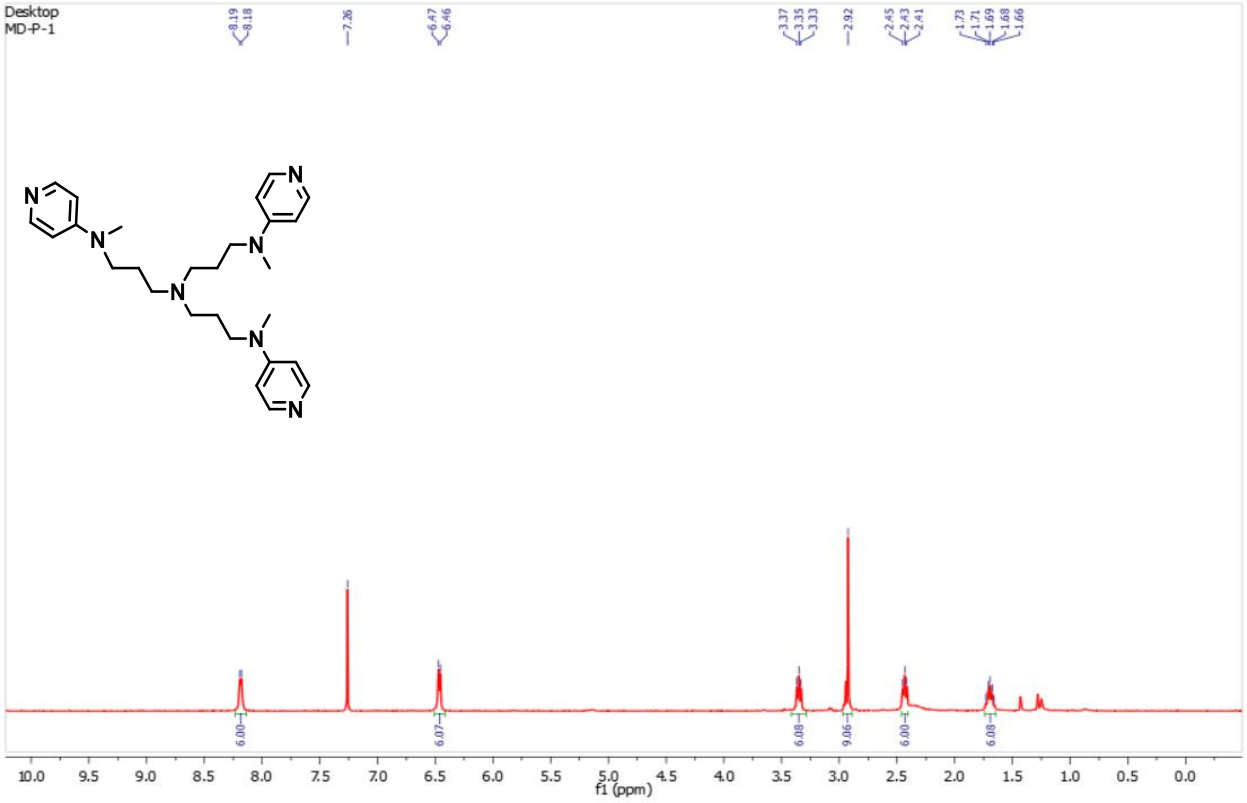


Figure S26. ^{1}H NMR spectrum of **1** ($CDCl_3$, 400 MHz).

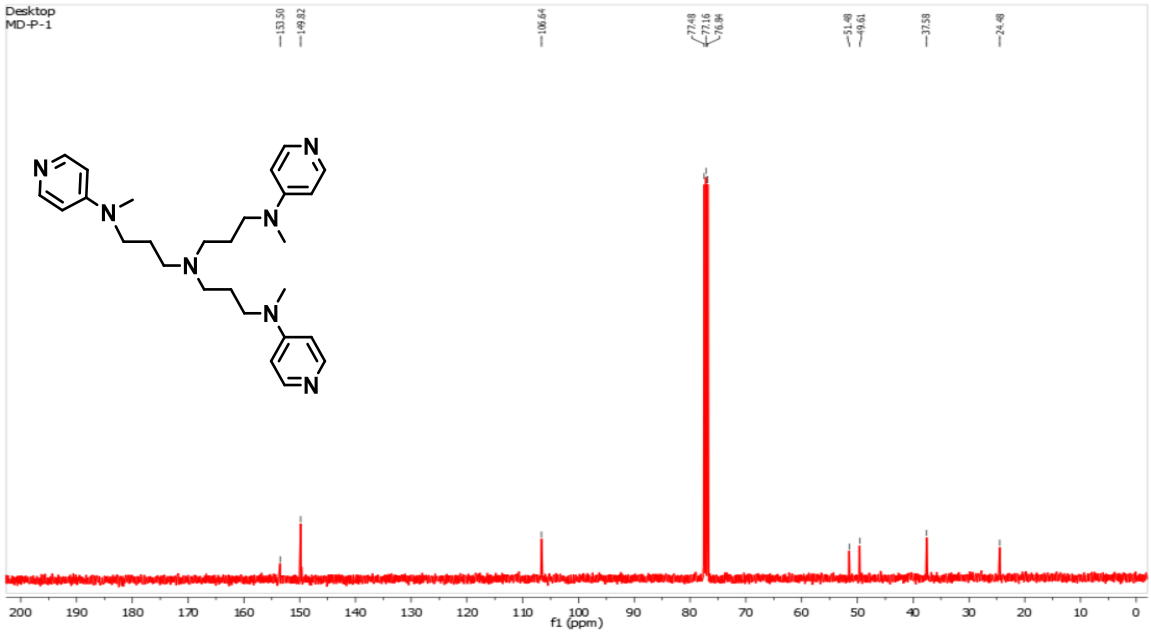


Figure S27. ^{13}C NMR spectrum **1** ($CDCl_3$, 100 MHz).

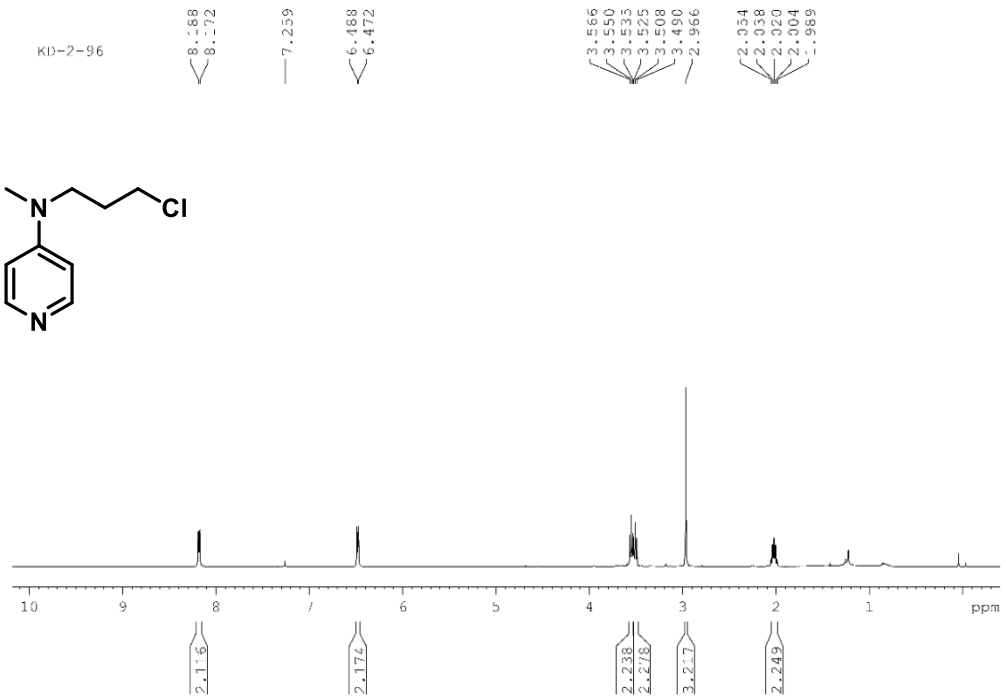


Figure S28. ^{1}H NMR spectrum of compound **4** ($CDCl_3$, 400 MHz).

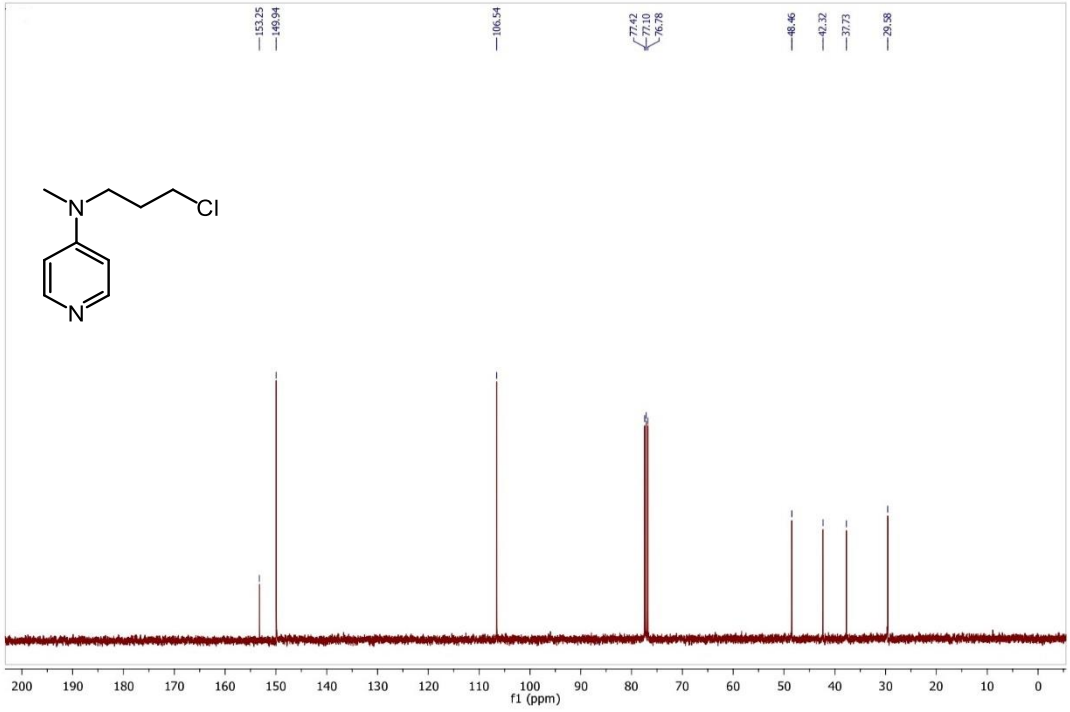


Figure S29. ^{13}C NMR spectrum of compound **4** ($CDCl_3$, 100 MHz).

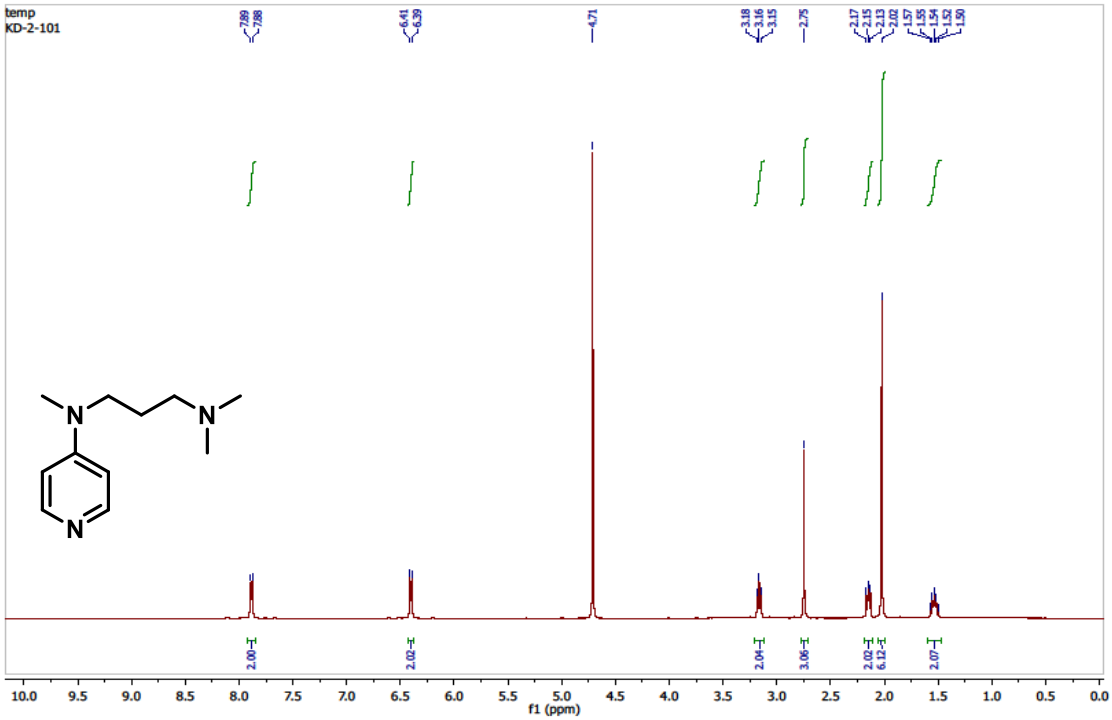


Figure S30. ^{1}H NMR spectrum of **5** (D_2O, 400 MHz).

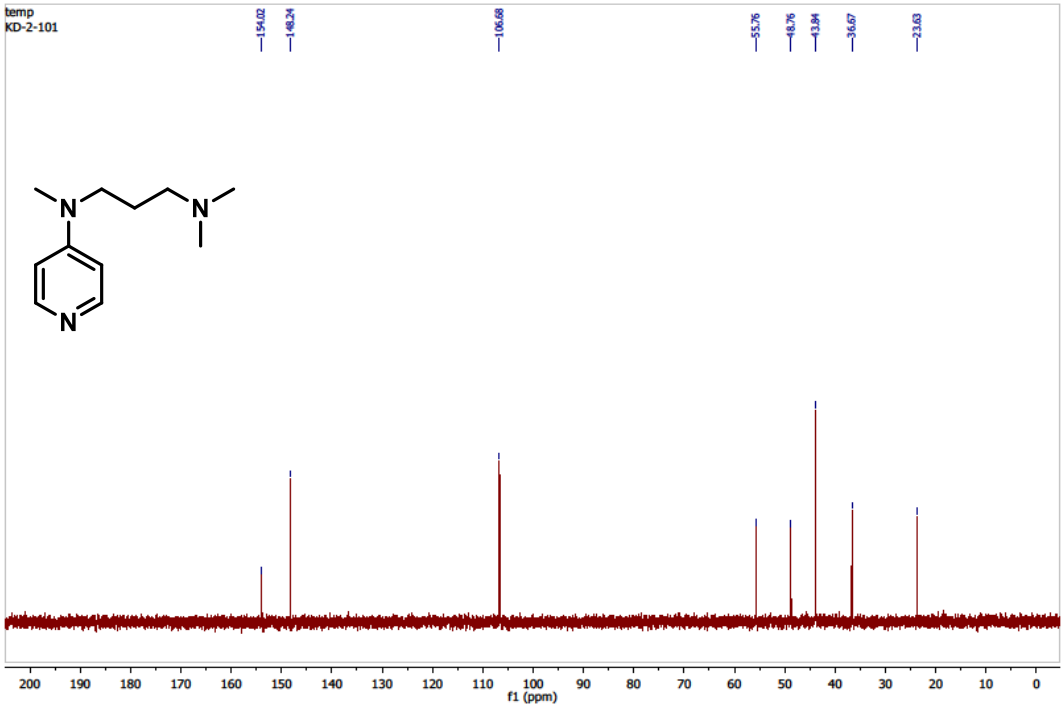


Figure S31. ^{13}C NMR spectrum of **5** (D_2O, 100 MHz).

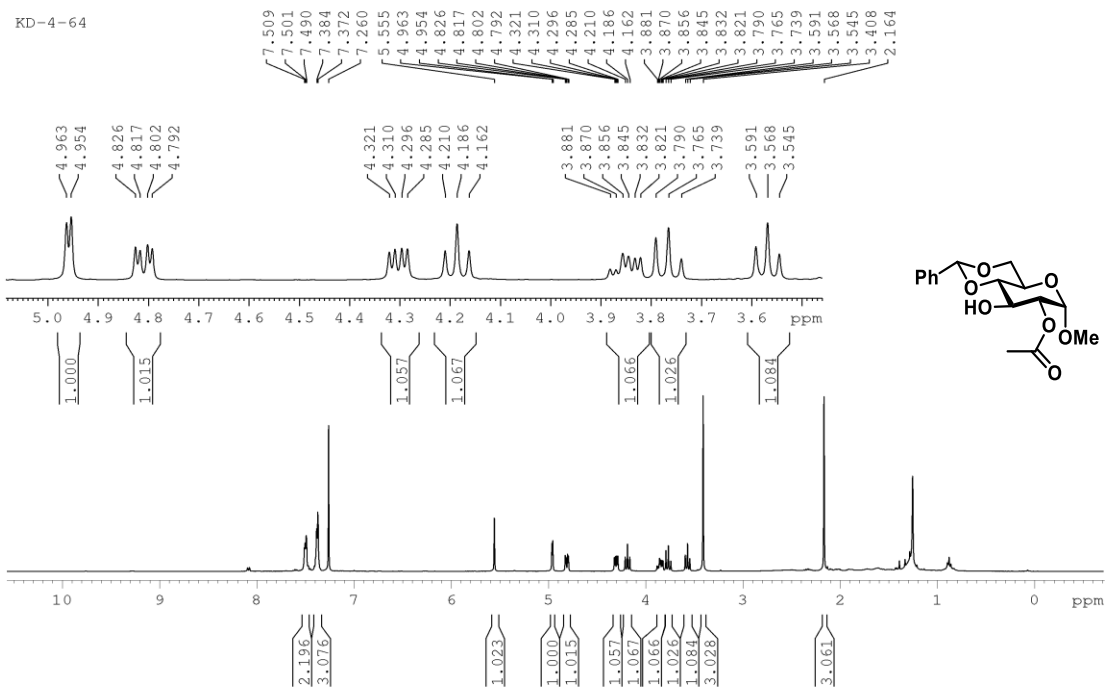


Figure S32. ^{1}H NMR spectrum of **7** ($CDCl_3$, 400 MHz).

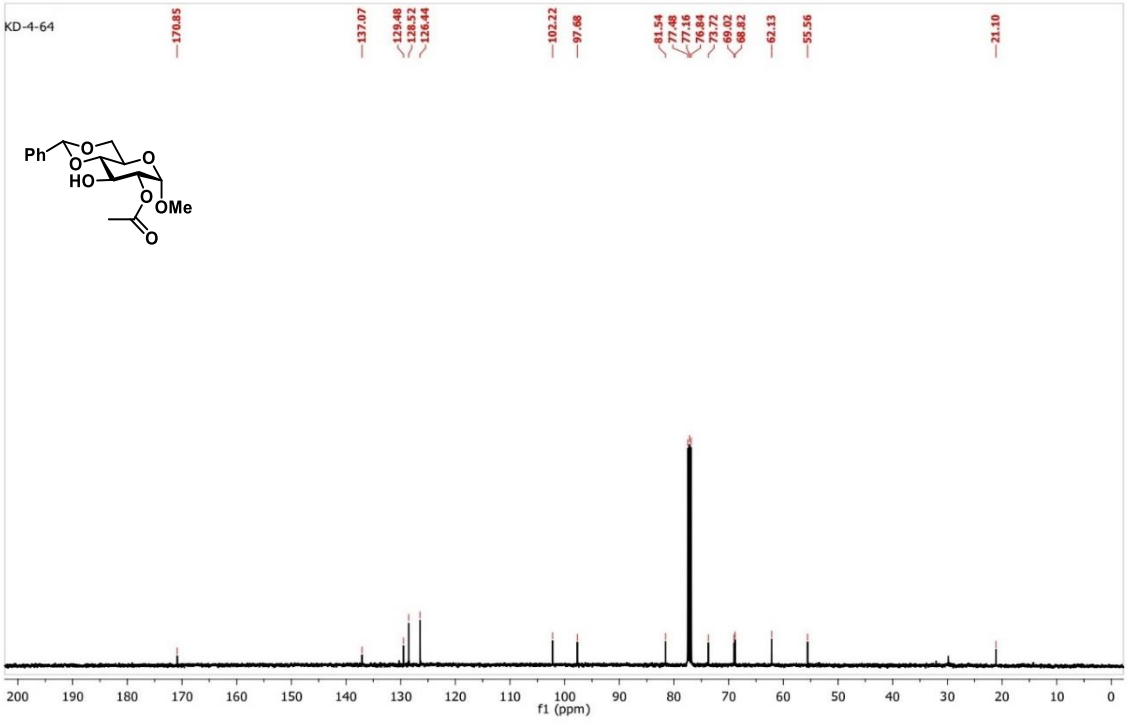


Figure S33. ^{13}C NMR spectrum of **7** ($CDCl_3$, 100 MHz).

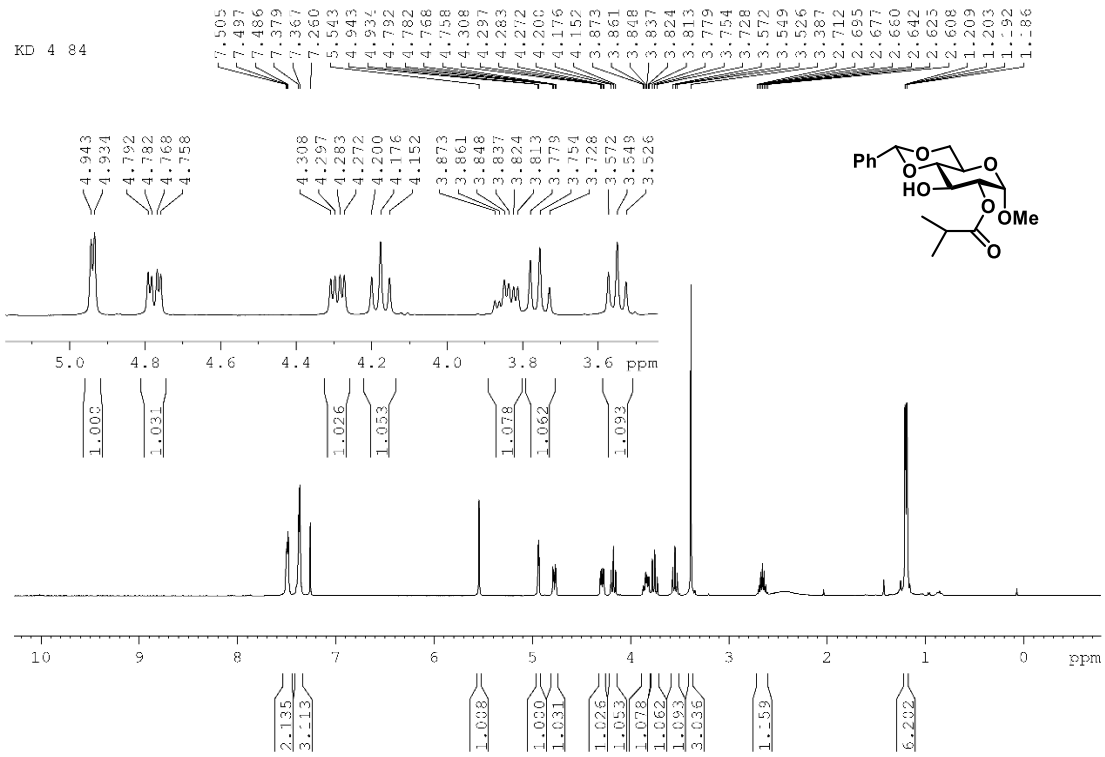


Figure S34. ^{1}H NMR spectrum of **10** ($CDCl_3$, 400 MHz).

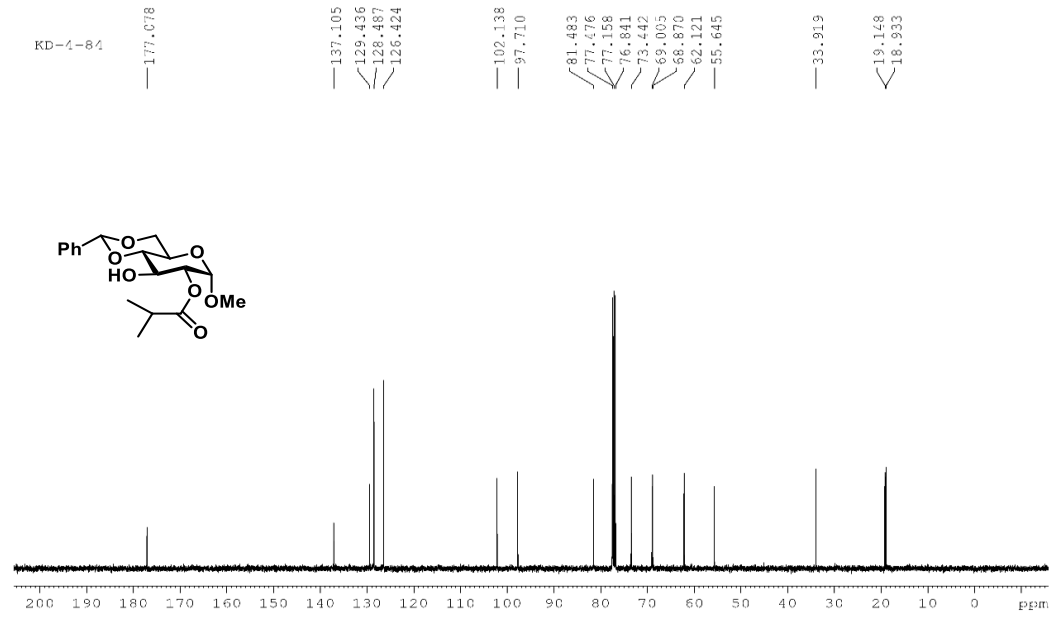


Figure S35. ^{13}C NMR spectrum of **10** ($CDCl_3$, 100 MHz).

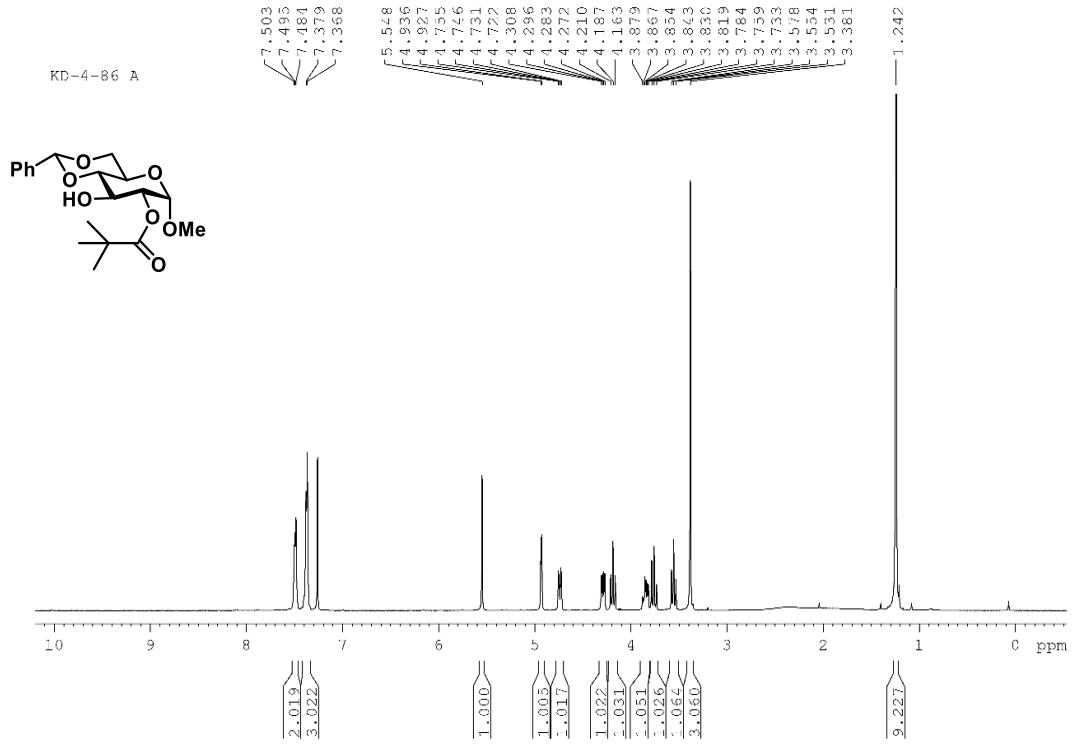


Figure S36. ^{1}H NMR spectrum of **13** ($CDCl_3$, 400 MHz).

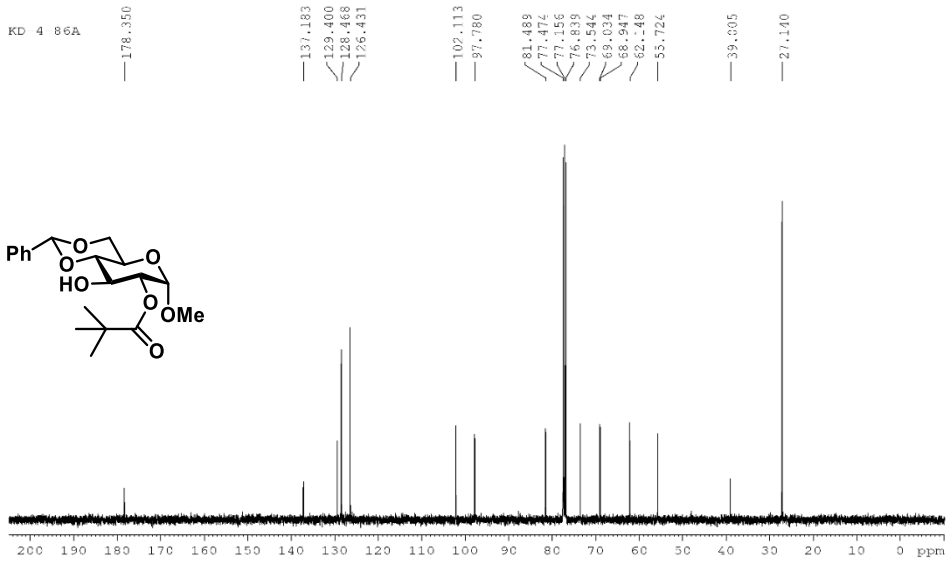


Figure S37. ^{13}C NMR spectrum of **13** ($CDCl_3$, 100 MHz).

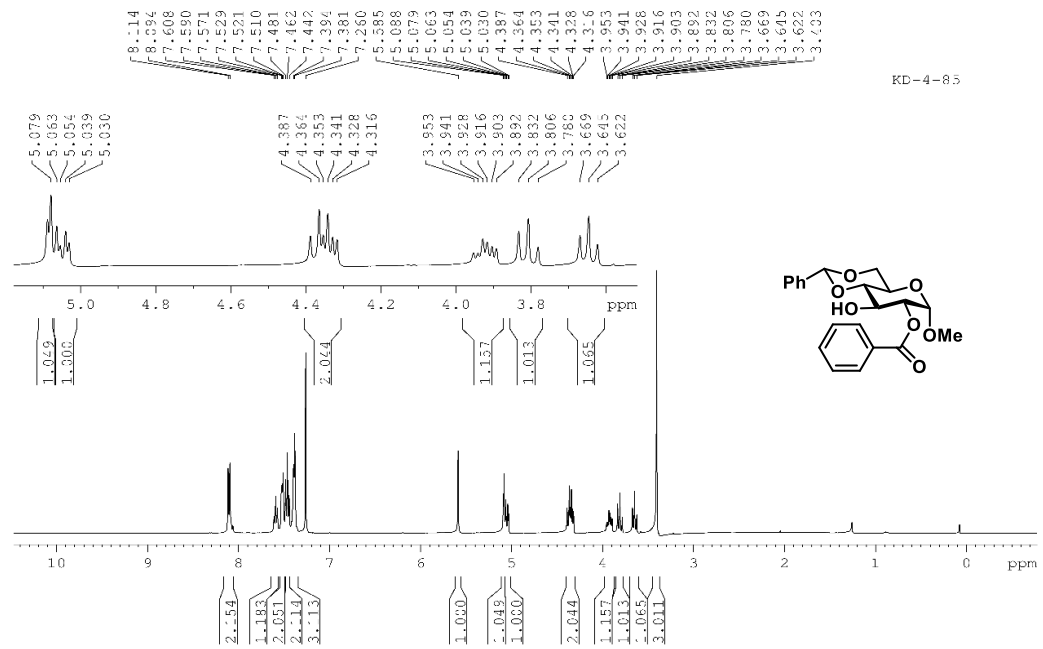


Figure S38. ^{1}H NMR spectrum of **15** ($CDCl_3$, 400 MHz).

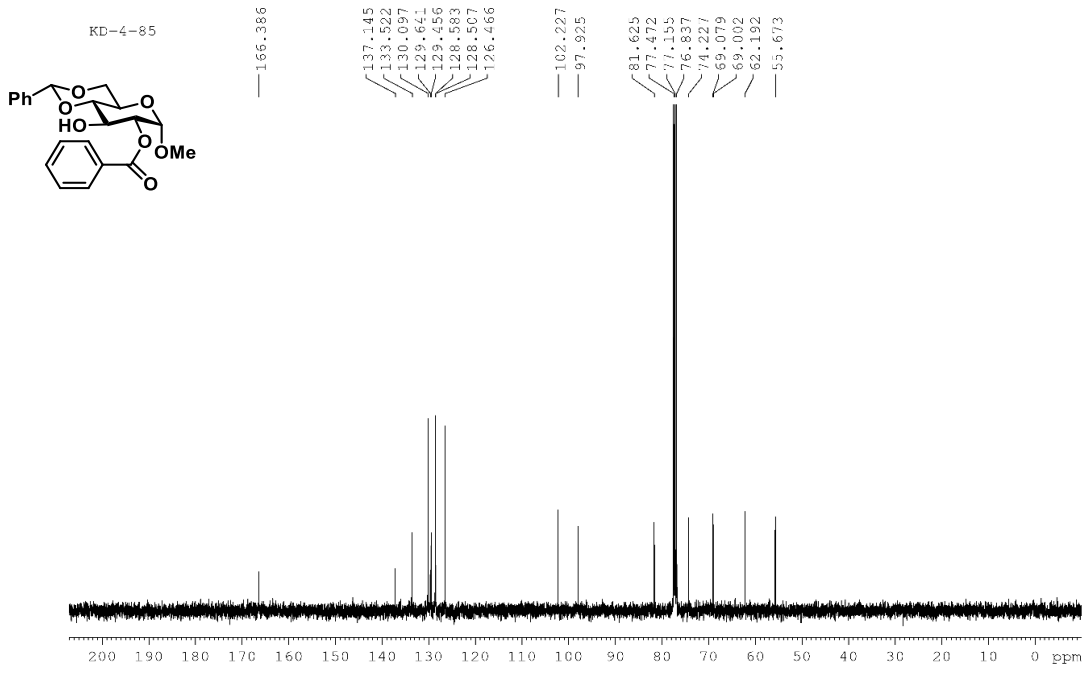


Figure S39. ^{13}C NMR spectrum of **15** ($CDCl_3$, 100 MHz).

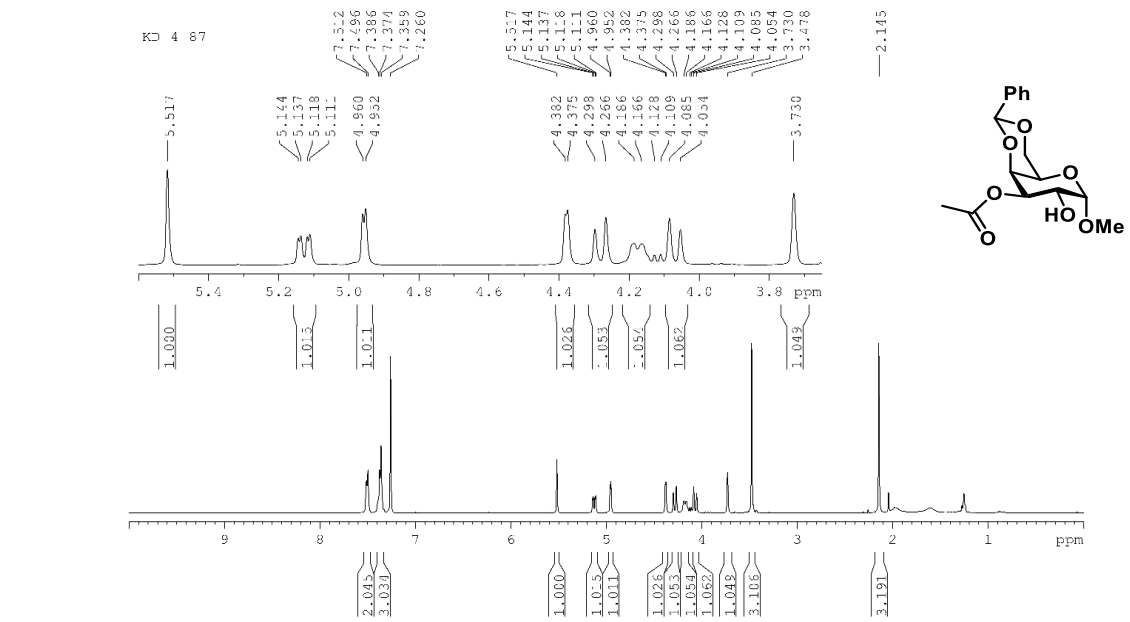


Figure S40. ^{1}H NMR spectrum of **20** ($CDCl_3$, 400 MHz).

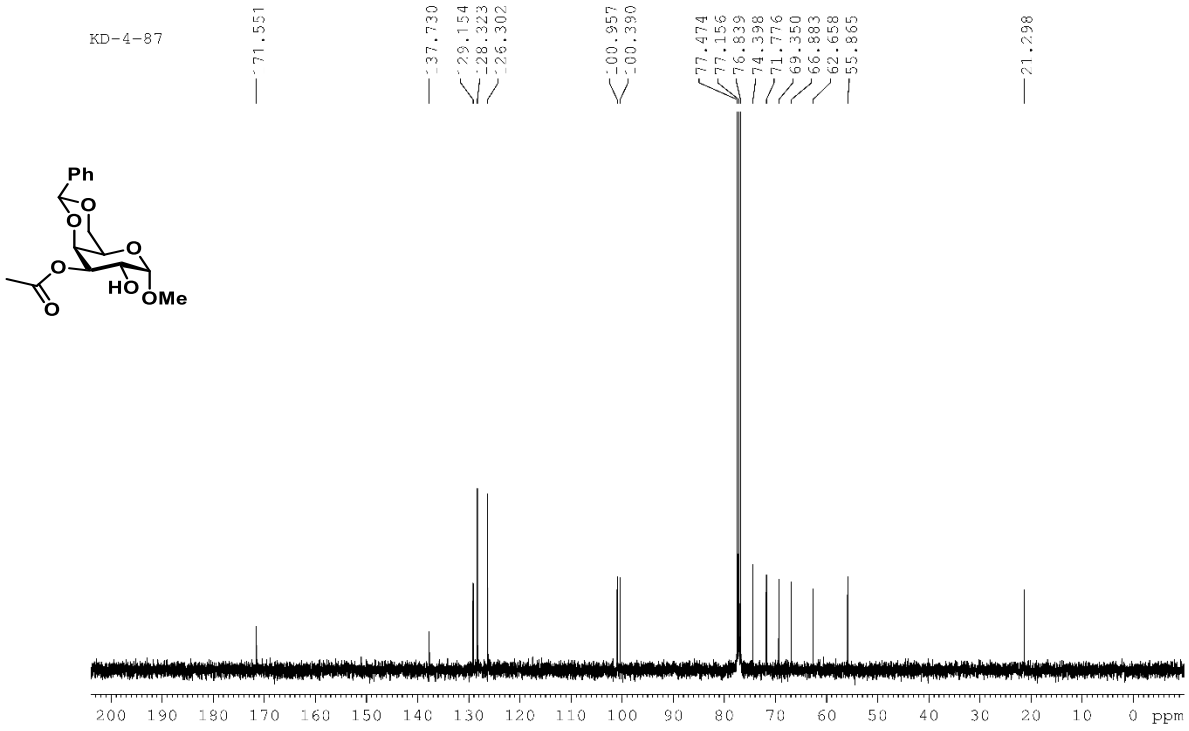


Figure S41. ^{13}C NMR spectrum of **20** ($CDCl_3$, 100 MHz).

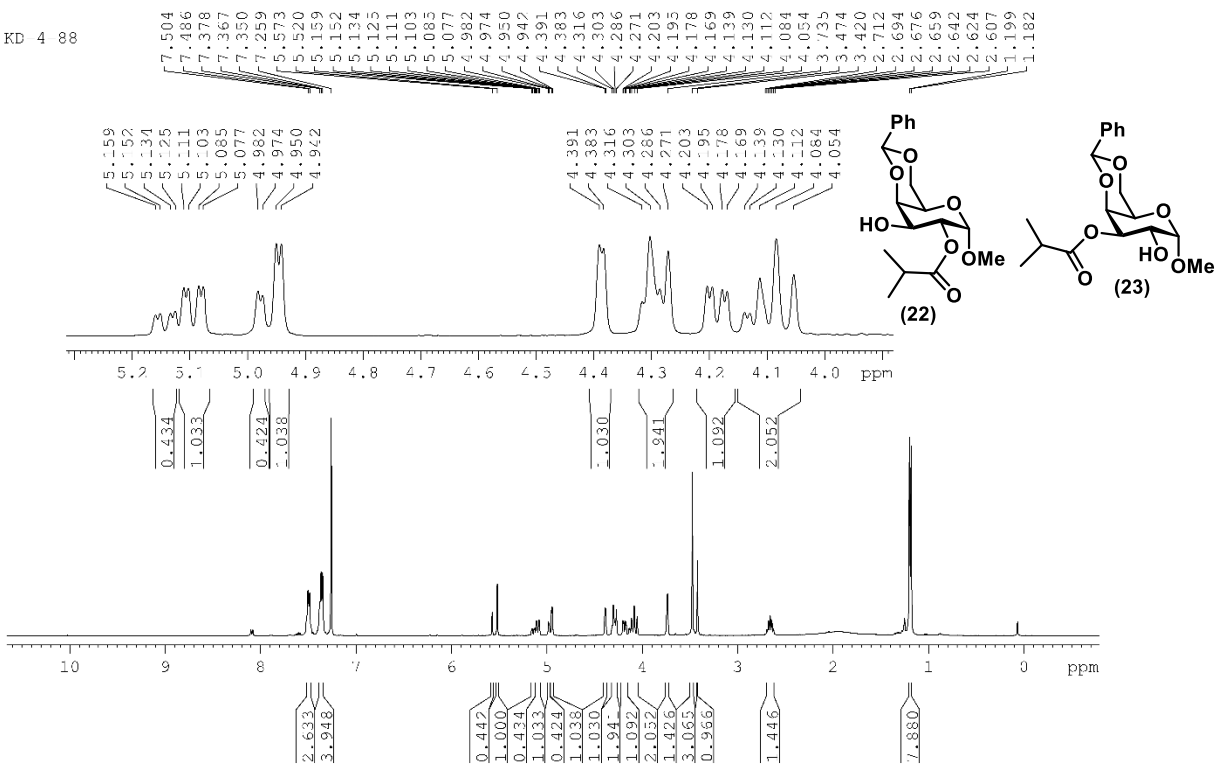


Figure S42. ^{1}H NMR spectrum of a mixture of **22** (30%) and **23** (70%) ($CDCl_3$, 400 MHz).

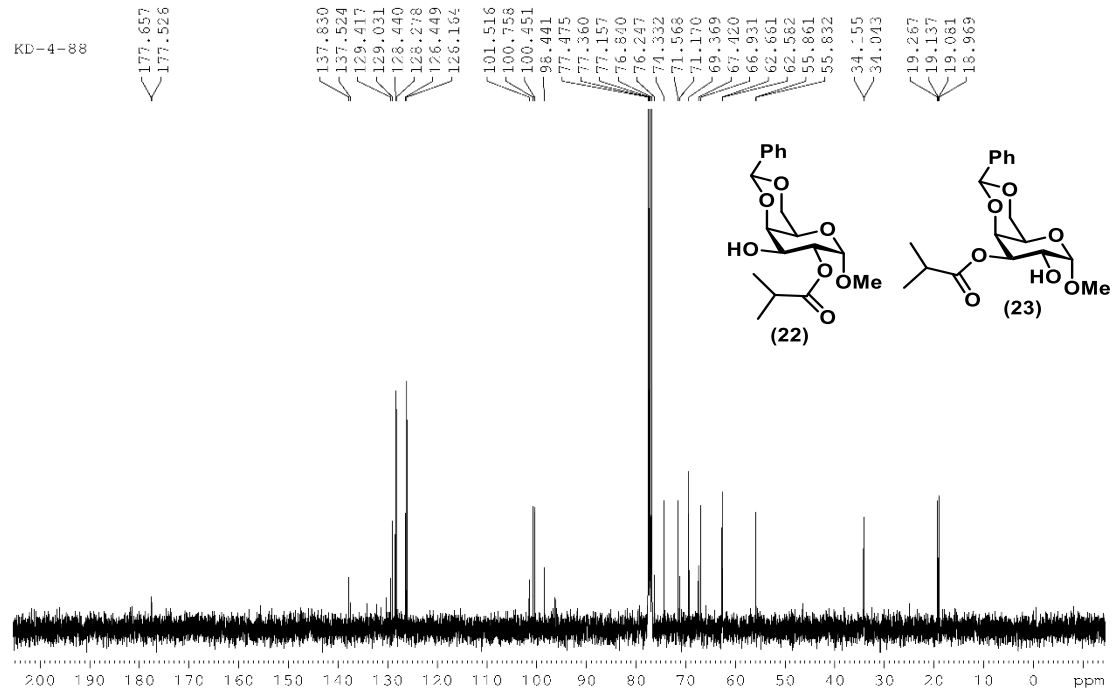


Figure S43. ^{13}C NMR spectrum of a mixture of **22** and **23** ($CDCl_3$, 100 MHz).

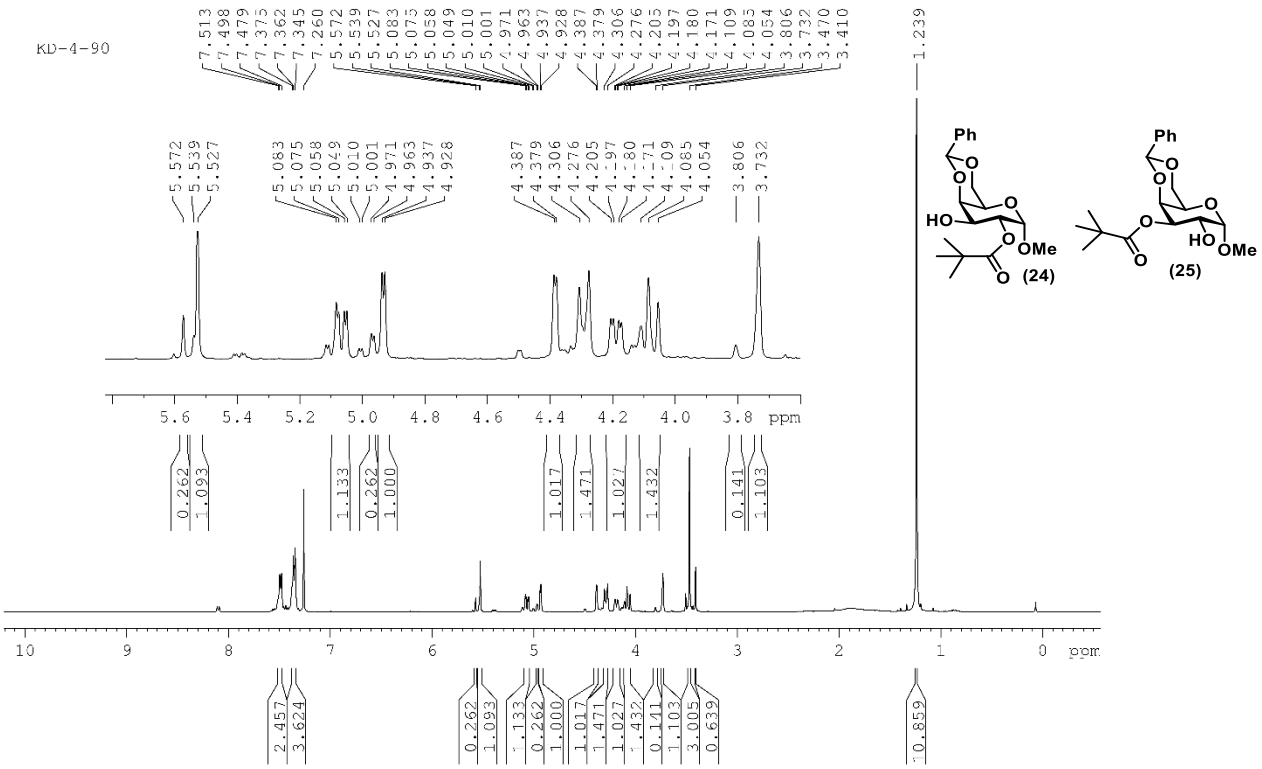


Figure S44. ^{1}H NMR spectrum of a mixture of **24** (21%) and **25** (79%) ($CDCl_3$, 400 MHz).

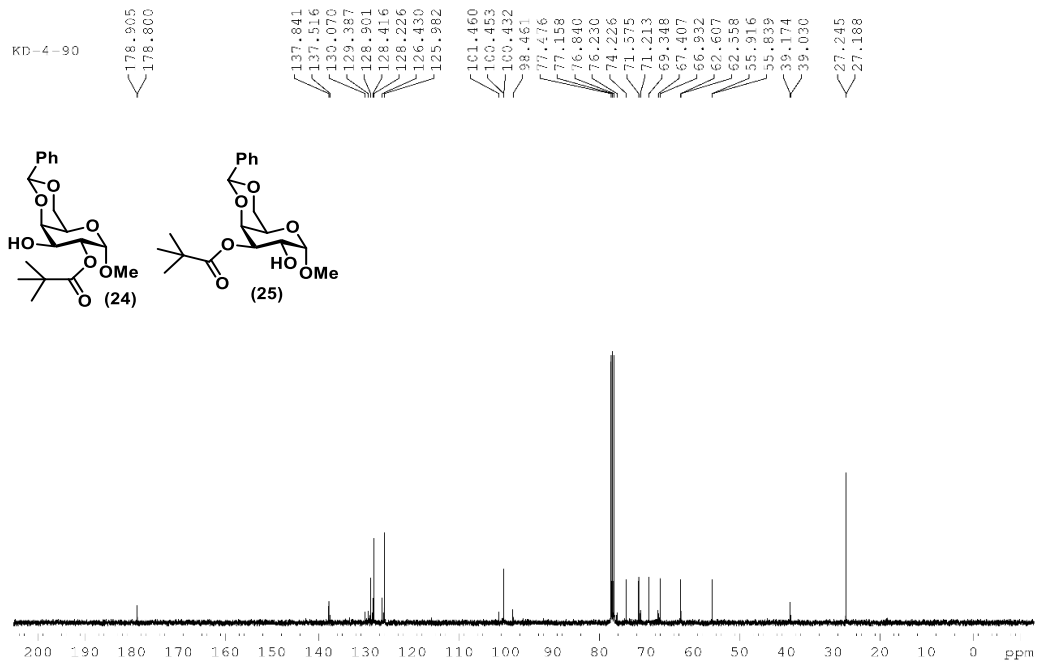


Figure S45. ^{13}C NMR spectrum of a mixture of **24** and **25** ($CDCl_3$, 100 MHz).

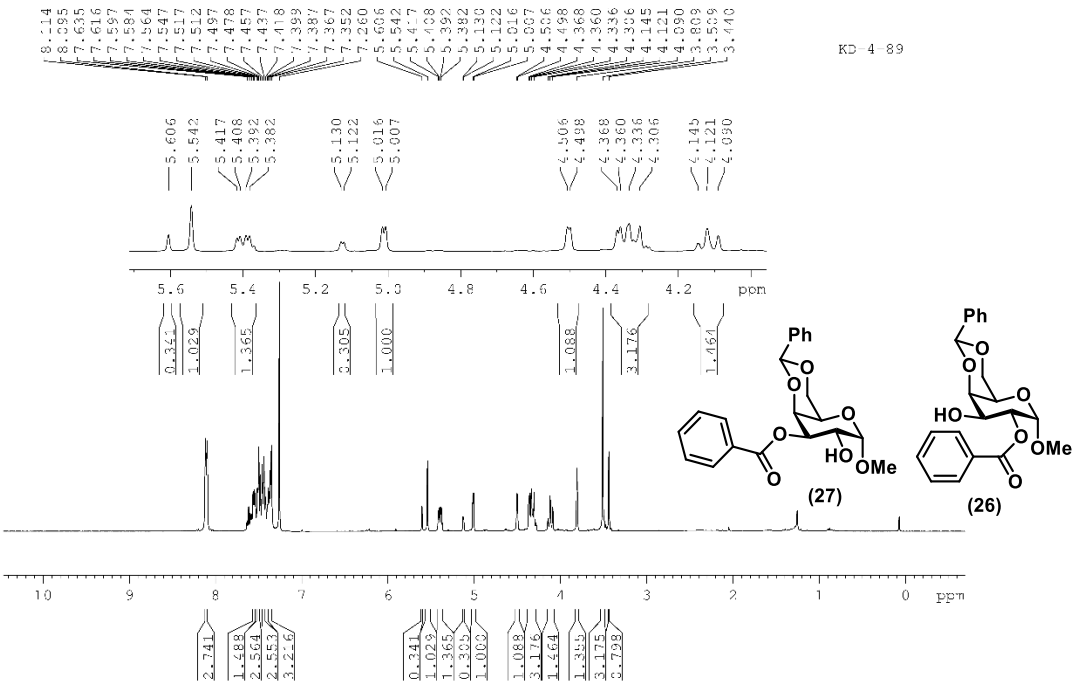


Figure S46. ^{1}H NMR spectrum of a mixture of **26** (23%) and **27** (77%) ($CDCl_3$, 400 MHz).

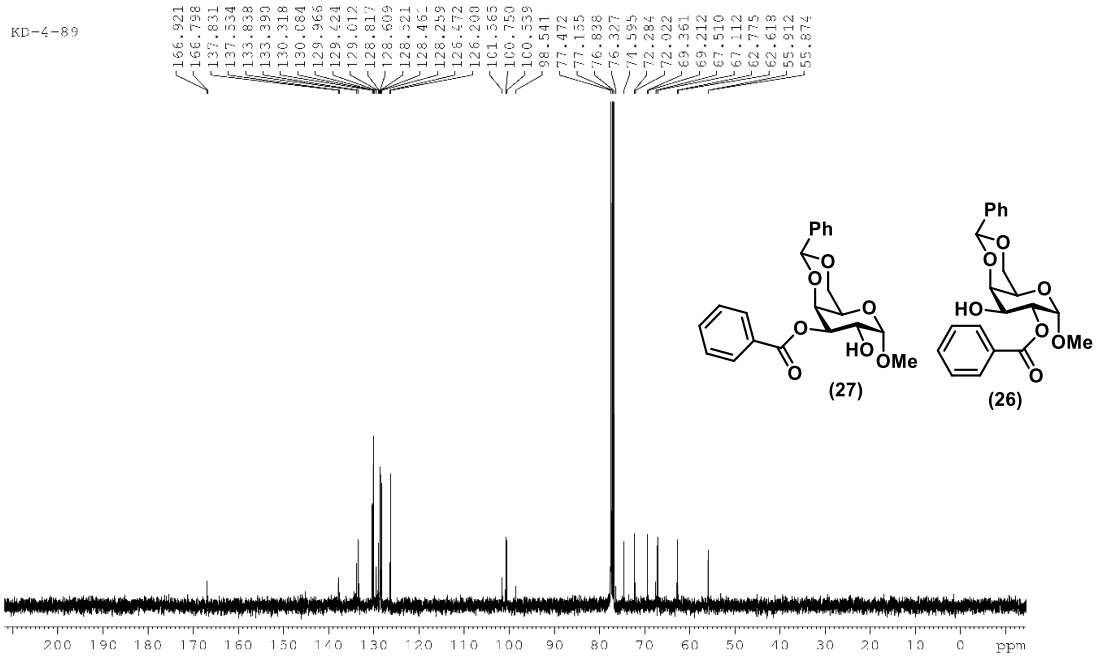


Figure S47. ^{13}C NMR spectrum of a mixture of **26** and **27** ($CDCl_3$, 100 MHz).

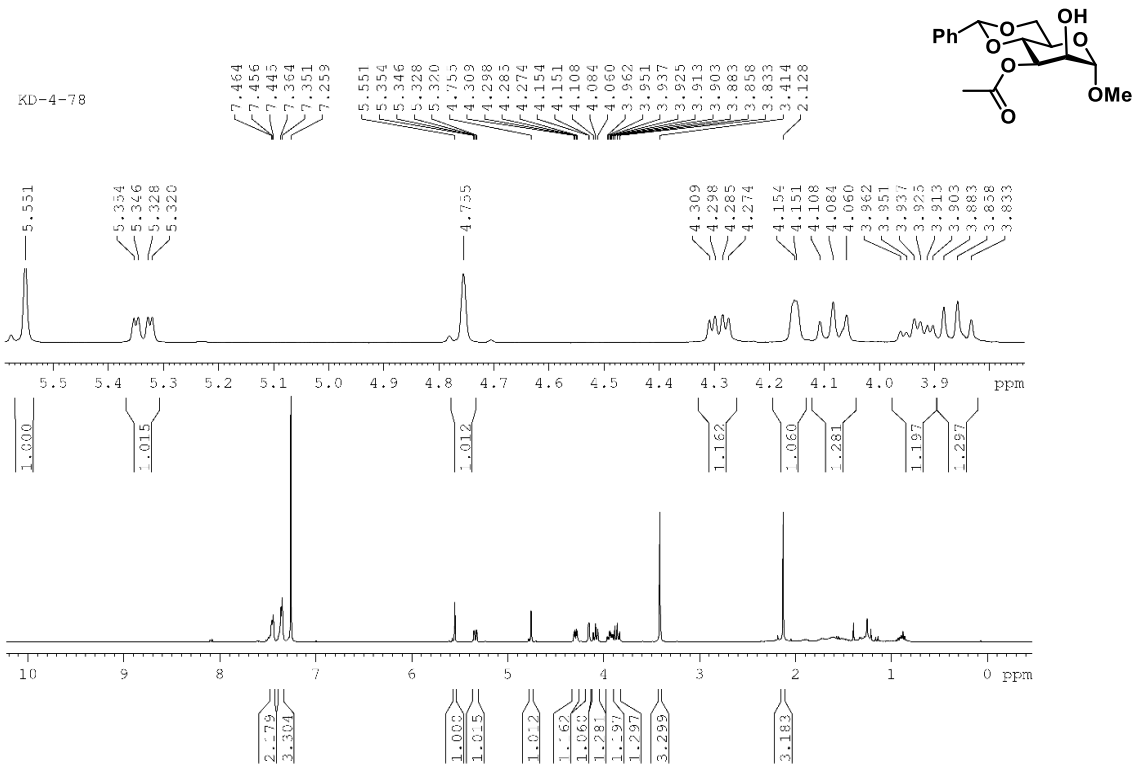


Figure S48. ^{1}H NMR spectrum of **31** ($CDCl_3$, 400 MHz).

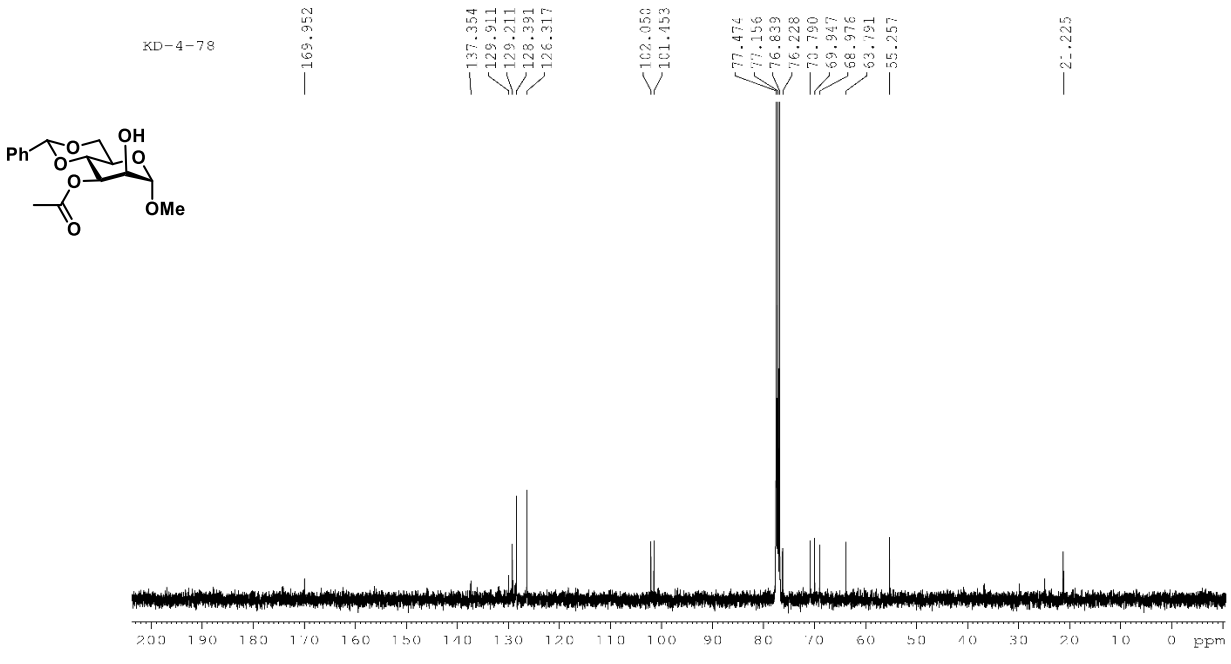


Figure S49. ^{13}C NMR spectrum of **31** ($CDCl_3$, 100 MHz).

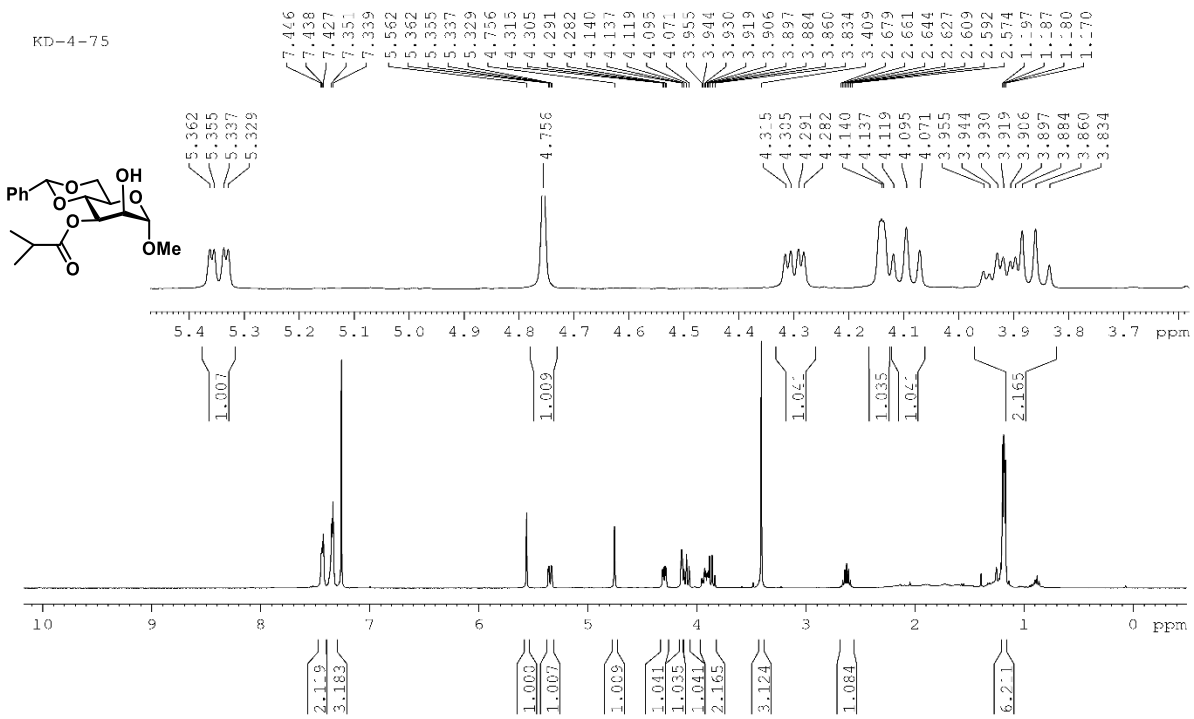


Figure S50. ^{1}H NMR spectrum of **34** ($CDCl_3$, 400 MHz).

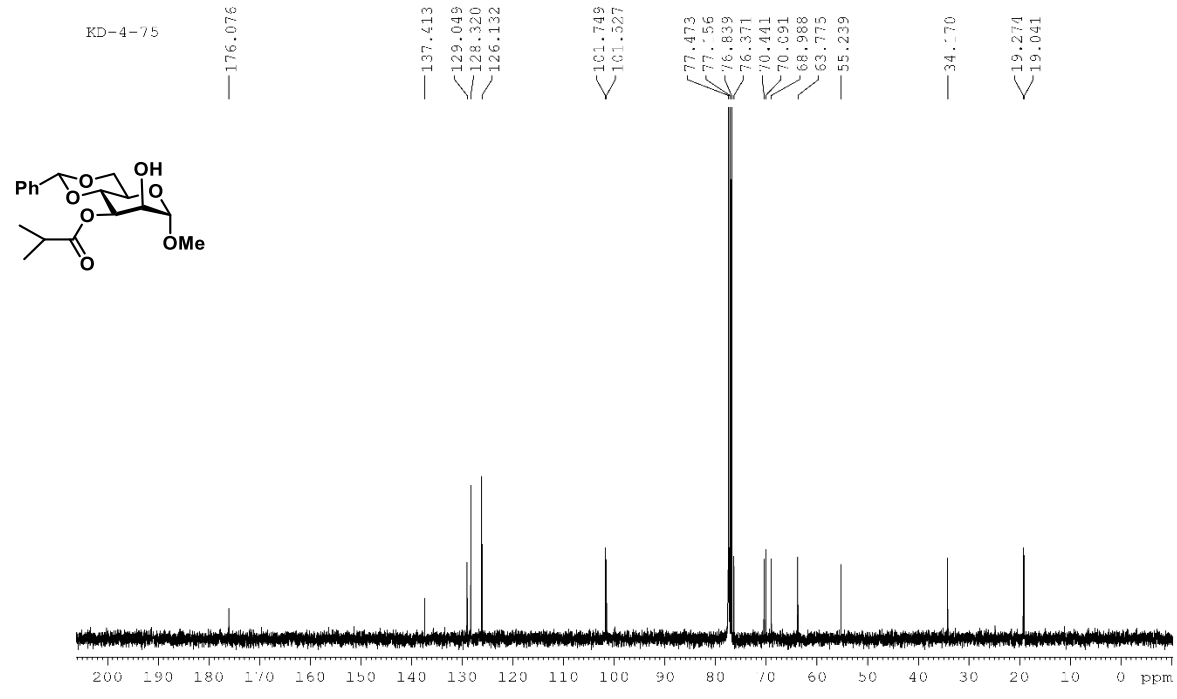


Figure S51. ^{13}C NMR spectrum of **34** ($CDCl_3$, 100 MHz).

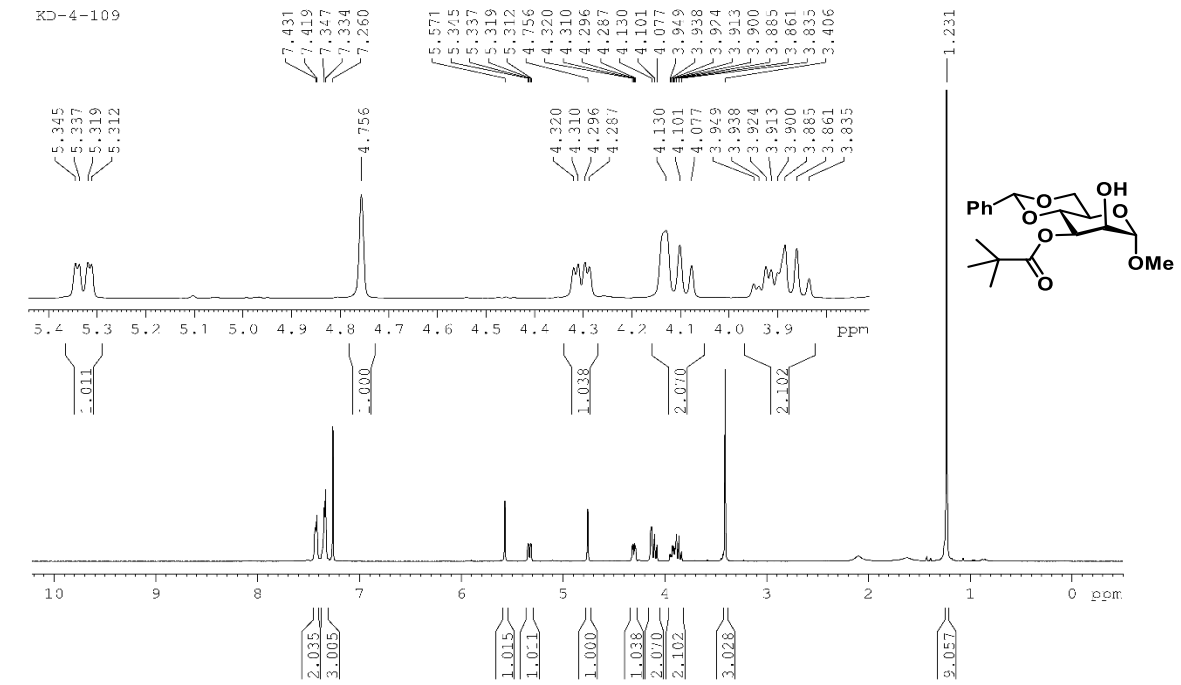


Figure S52. ^{1}H NMR spectrum of **36** ($CDCl_3$, 400 MHz).

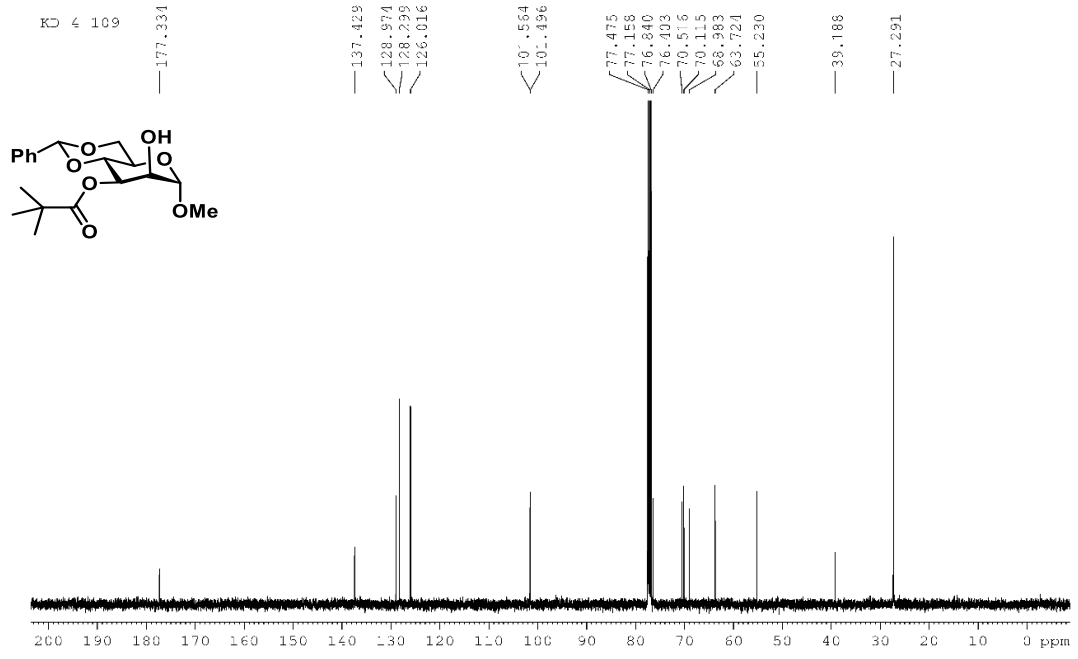


Figure S53. ^{13}C NMR spectrum of **36** ($CDCl_3$, 100 MHz).

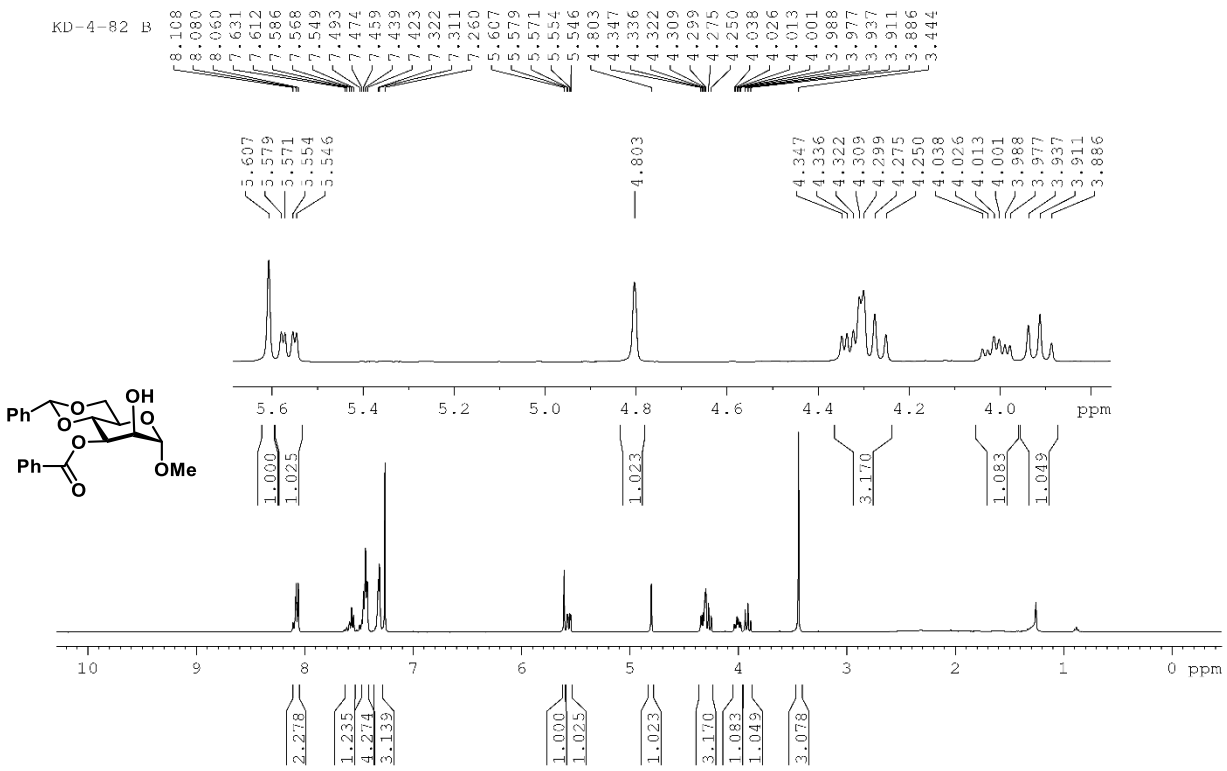


Figure S54. ^{1}H NMR spectrum of **38** ($CDCl_3$, 400 MHz).

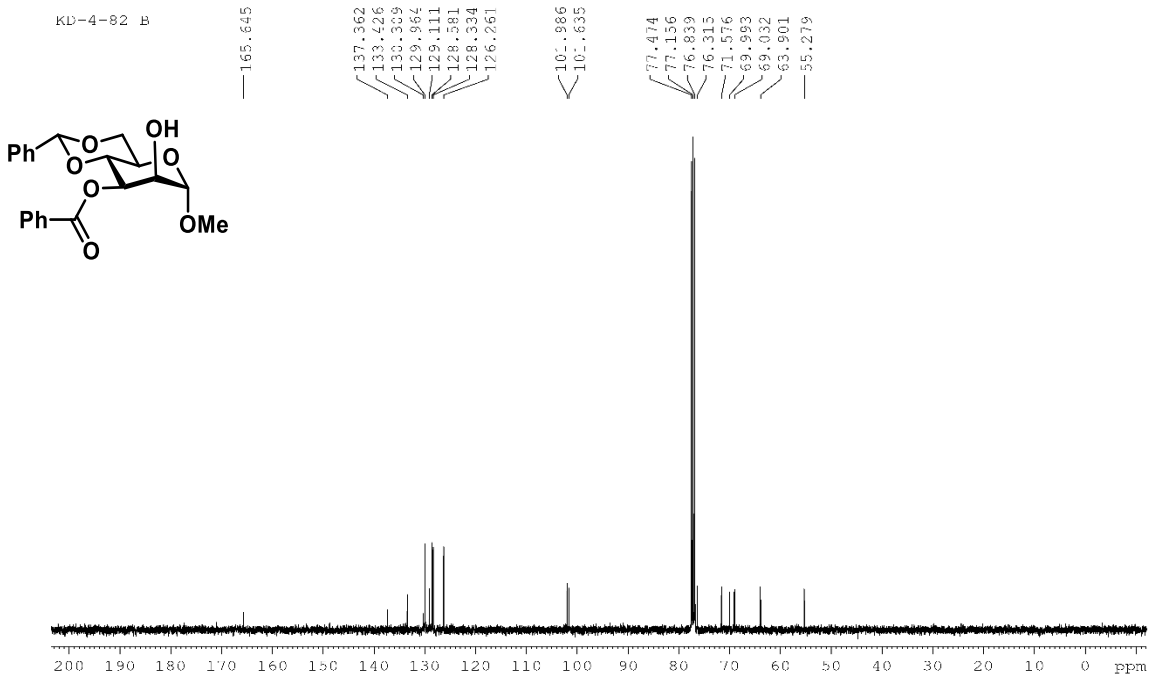


Figure S55. ^{13}C NMR spectrum of **38** ($CDCl_3$, 100 MHz).

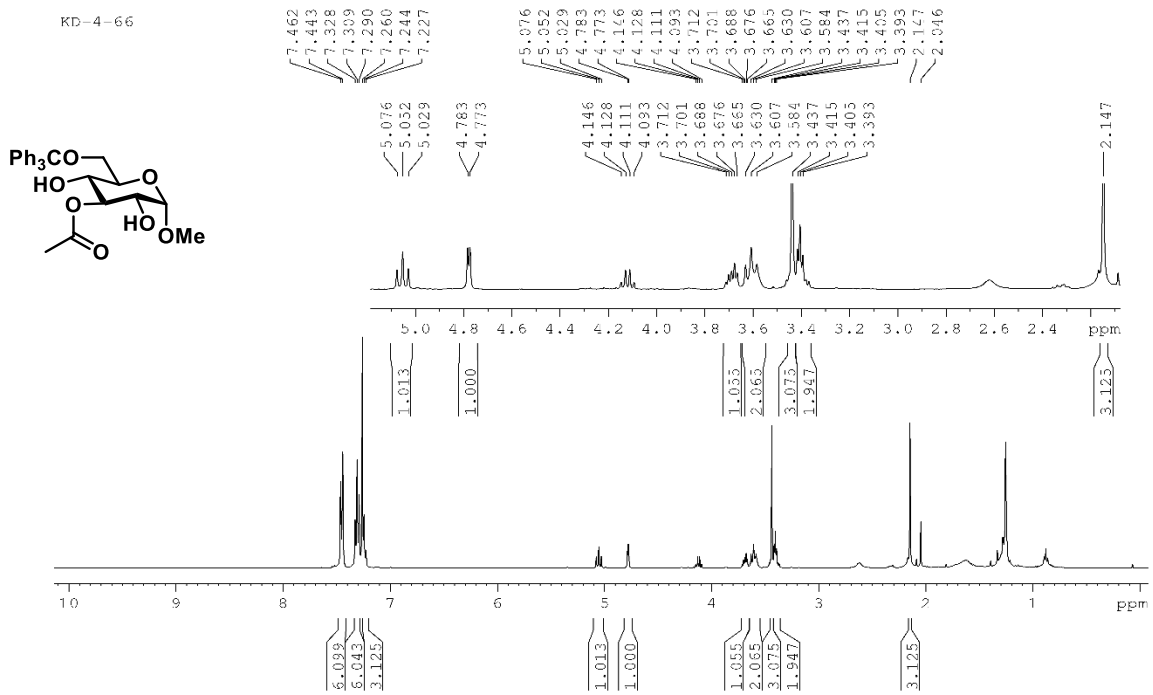


Figure S56. ^{1}H NMR spectrum of **41** ($CDCl_3$, 400 MHz).

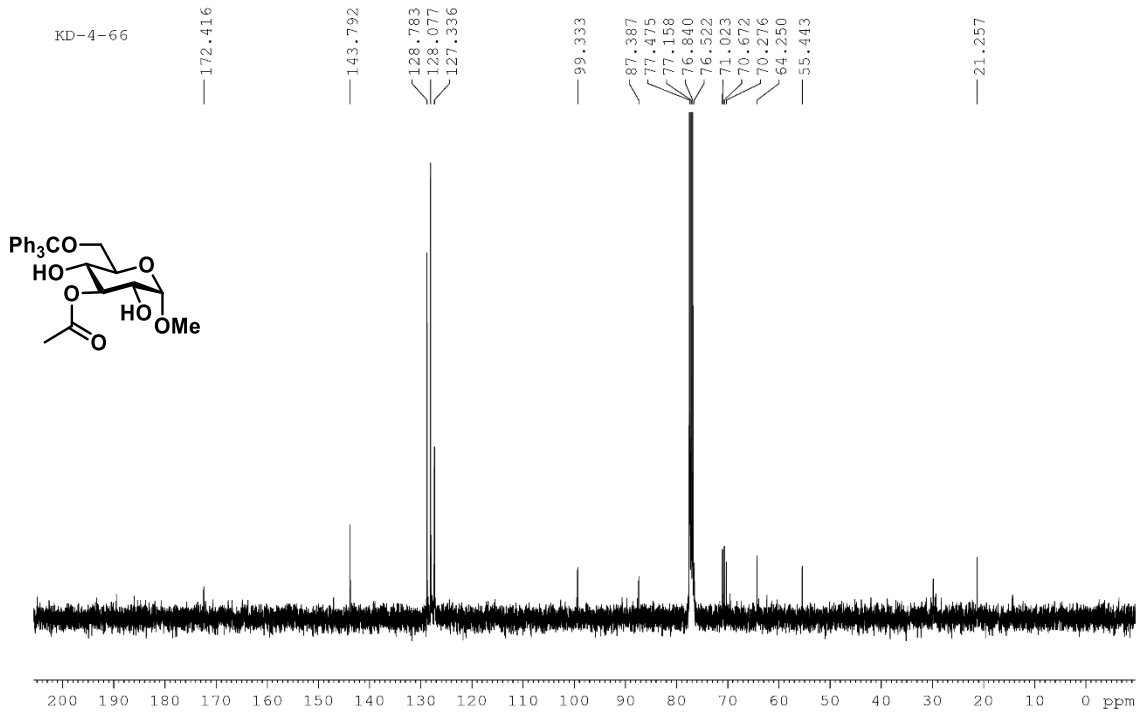


Figure S57. ^{13}C NMR spectrum of **41** ($CDCl_3$, 100 MHz).

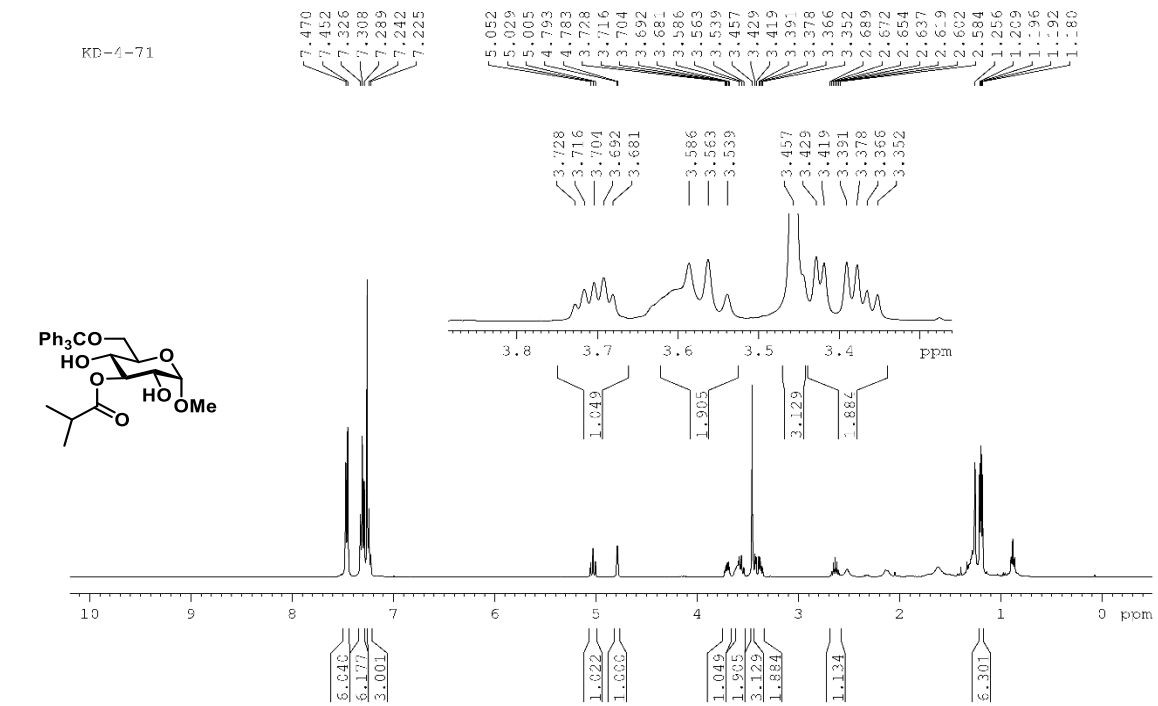


Figure S58. ^{1}H NMR spectrum of **43** ($CDCl_3$, 400 MHz).

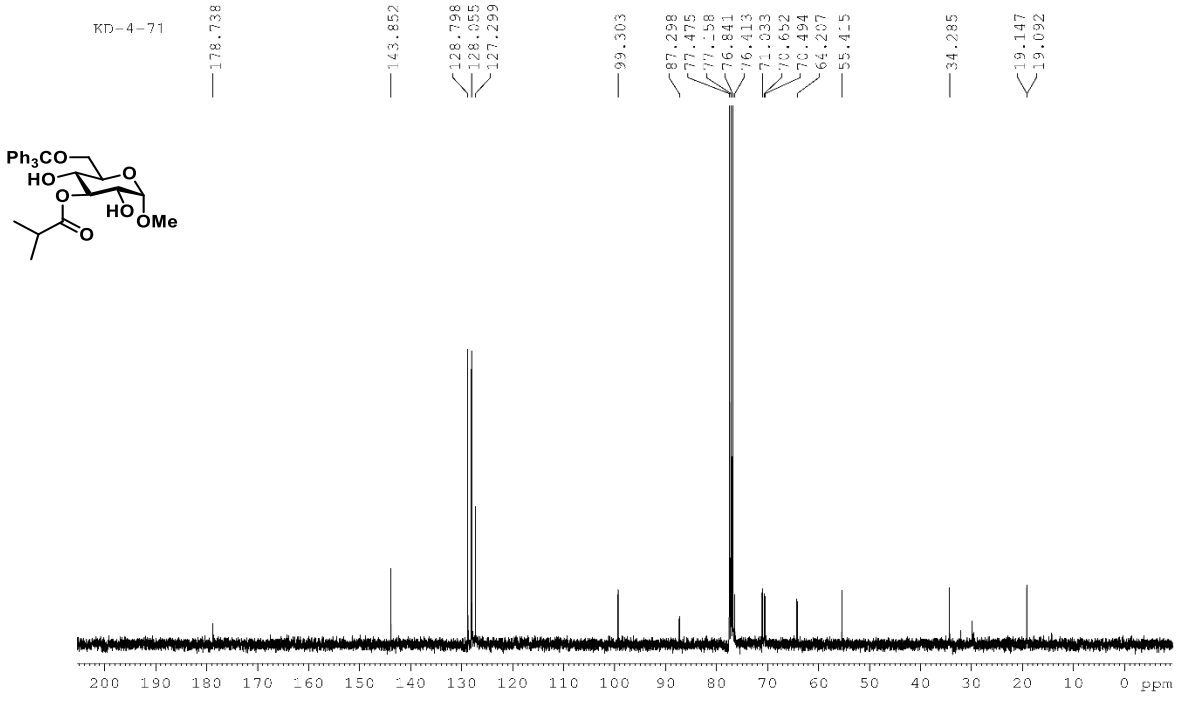


Figure S59. ^{13}C NMR spectrum of **43** ($CDCl_3$, 100 MHz).

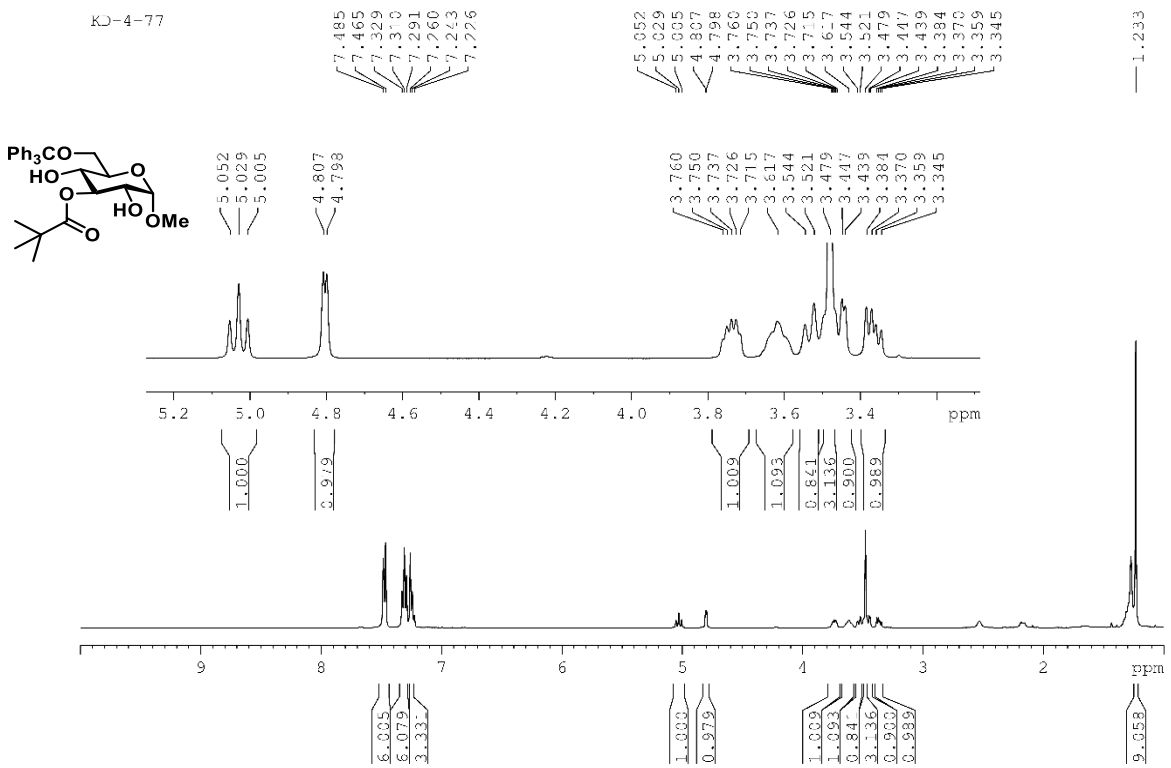


Figure S60. ^{1}H NMR spectrum of **45** ($CDCl_3$, 400 MHz).

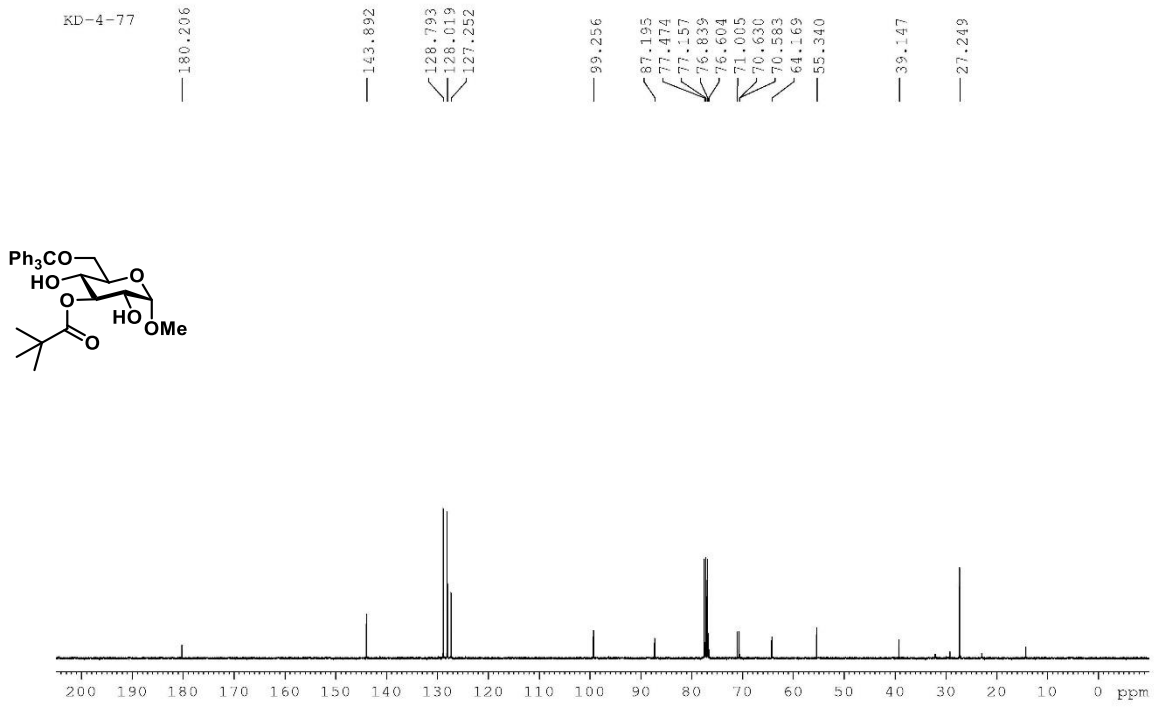


Figure S61. ^{13}C NMR spectrum of **45** ($CDCl_3$, 100 MHz).

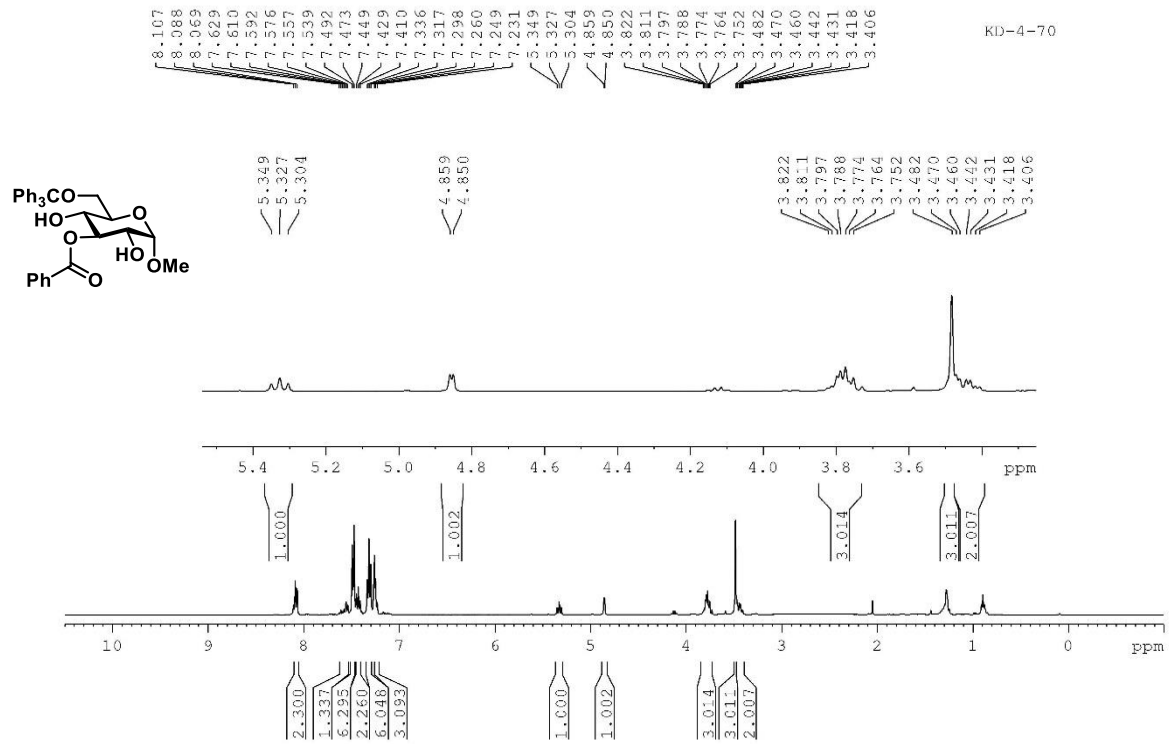


Figure S62. ^{1}H NMR spectrum of **47** ($CDCl_3$, 400 MHz).

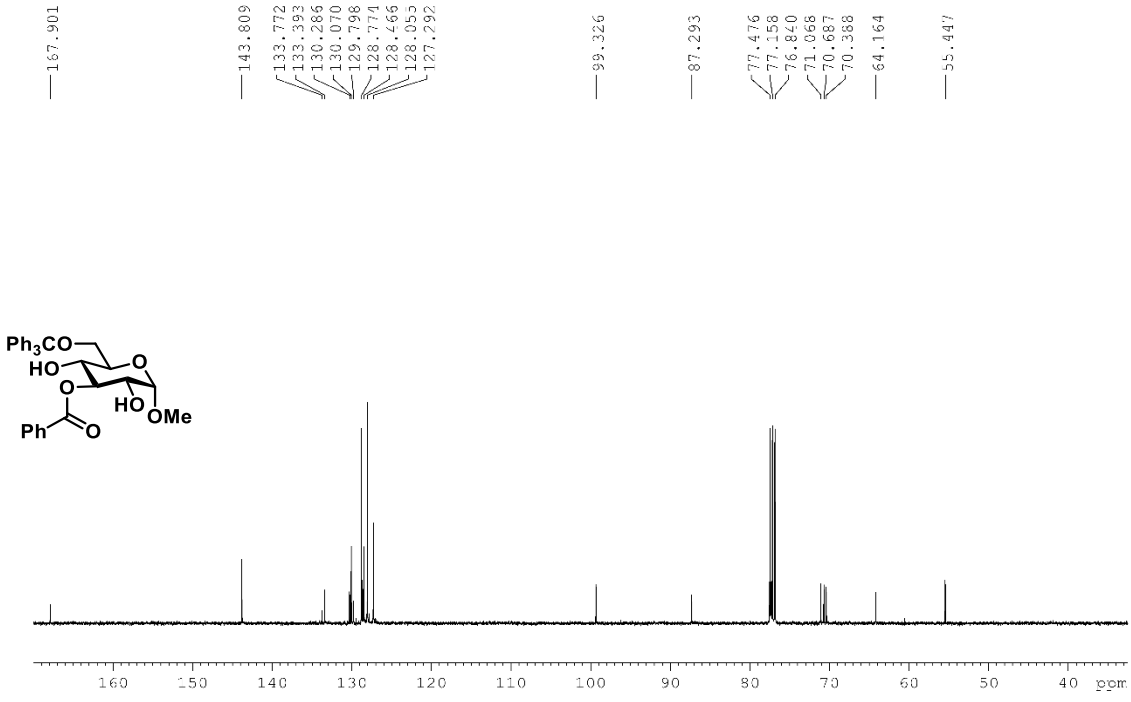


Figure S63. ^{13}C NMR spectrum of **47** ($CDCl_3$, 100 MHz).

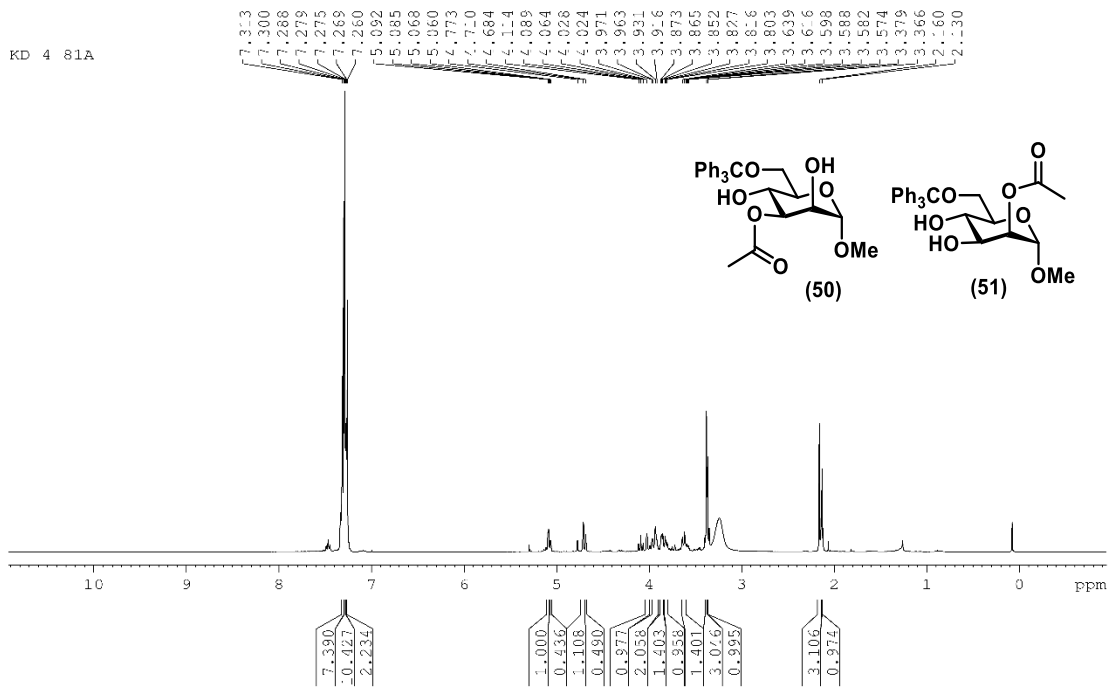


Figure S64. ^{1}H NMR spectrum of a mixture of **50** (70%) and **51** (30%) ($CDCl_3$, 400 MHz).

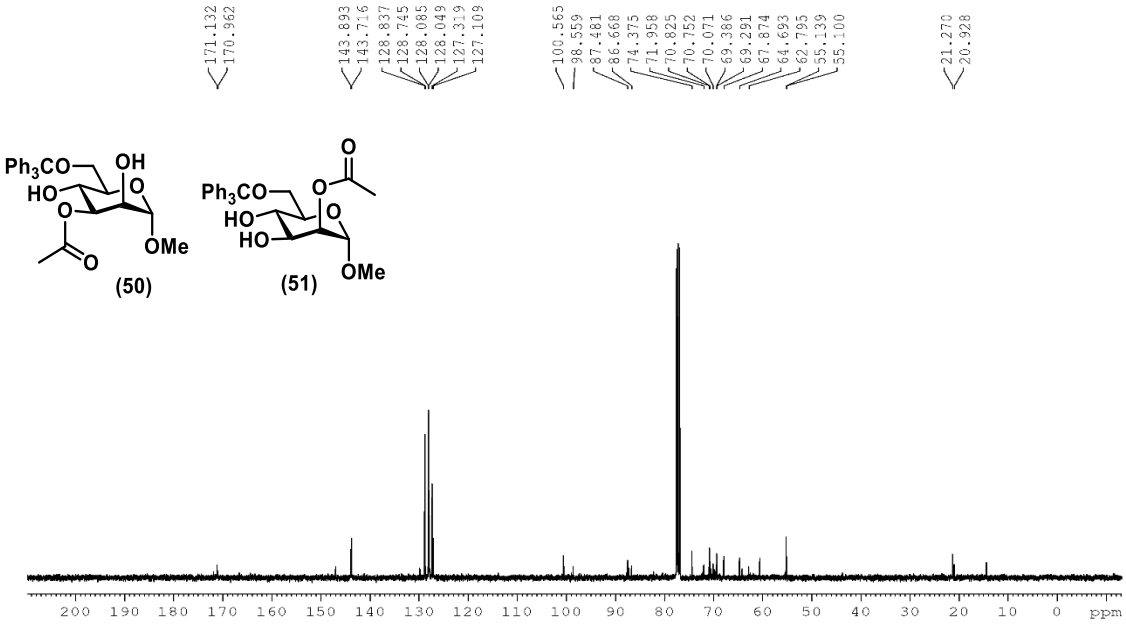


Figure S65. ^{13}C NMR spectrum of a mixture of **50** and **51** ($CDCl_3$, 100 MHz).

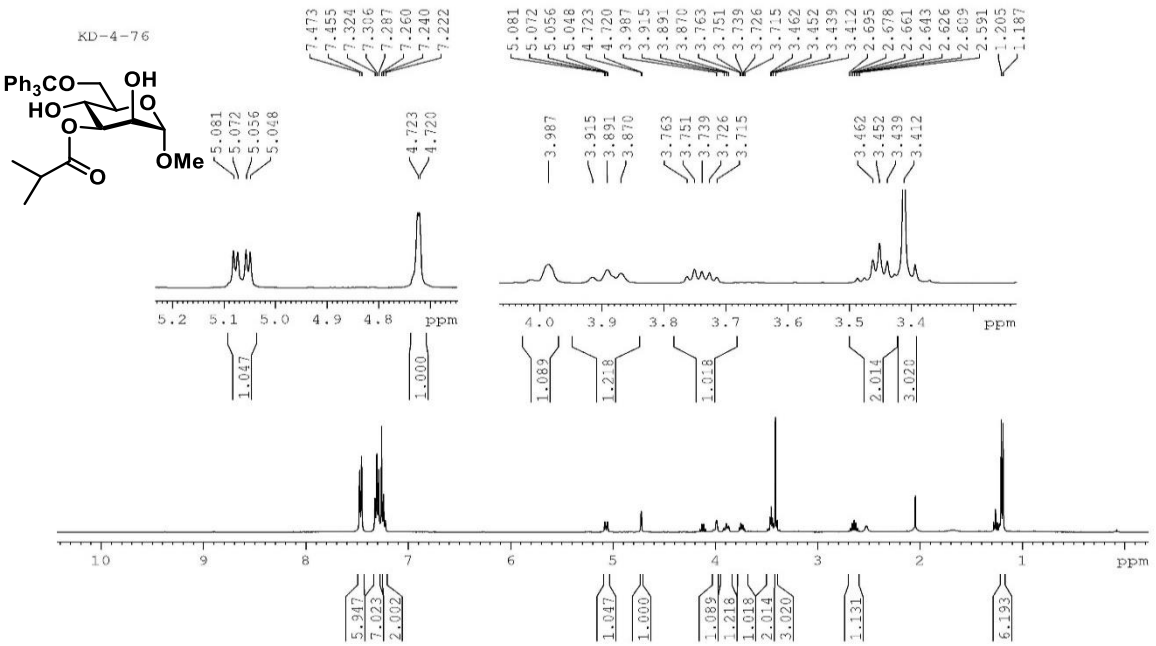


Figure S66. ^{1}H NMR spectrum of **52** ($CDCl_3$, 400 MHz).

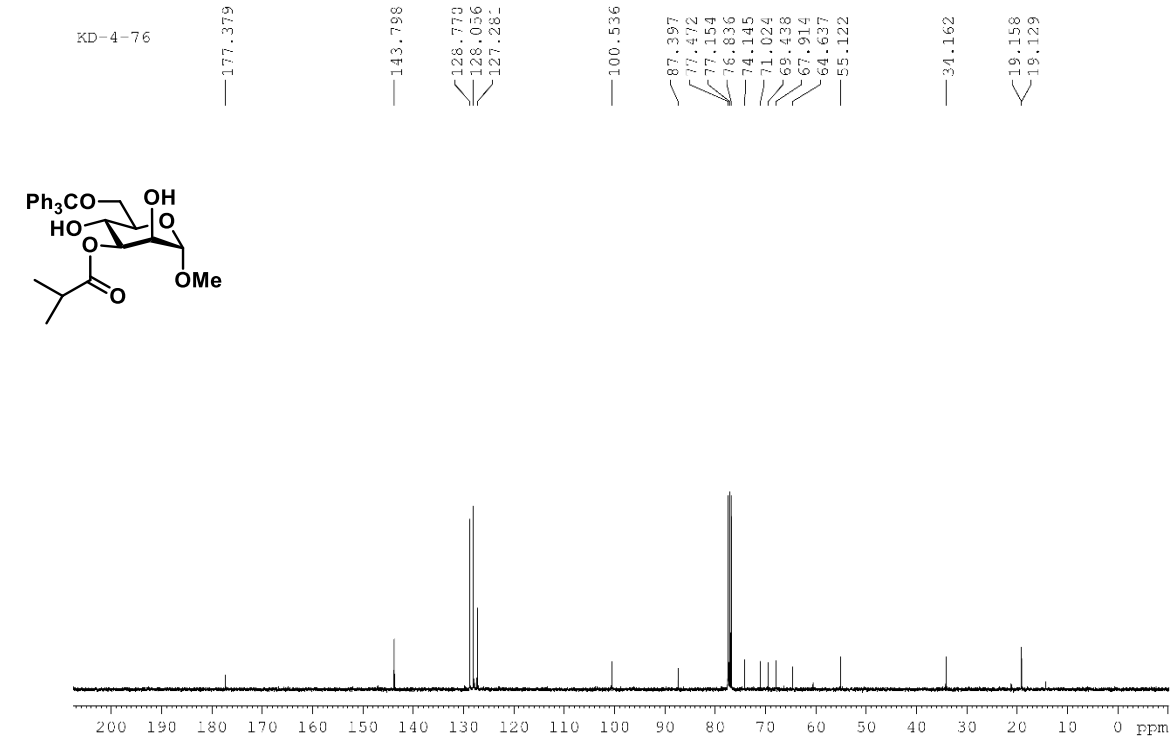


Figure S67. ^{13}C NMR spectrum of **52** ($CDCl_3$, 100 MHz).

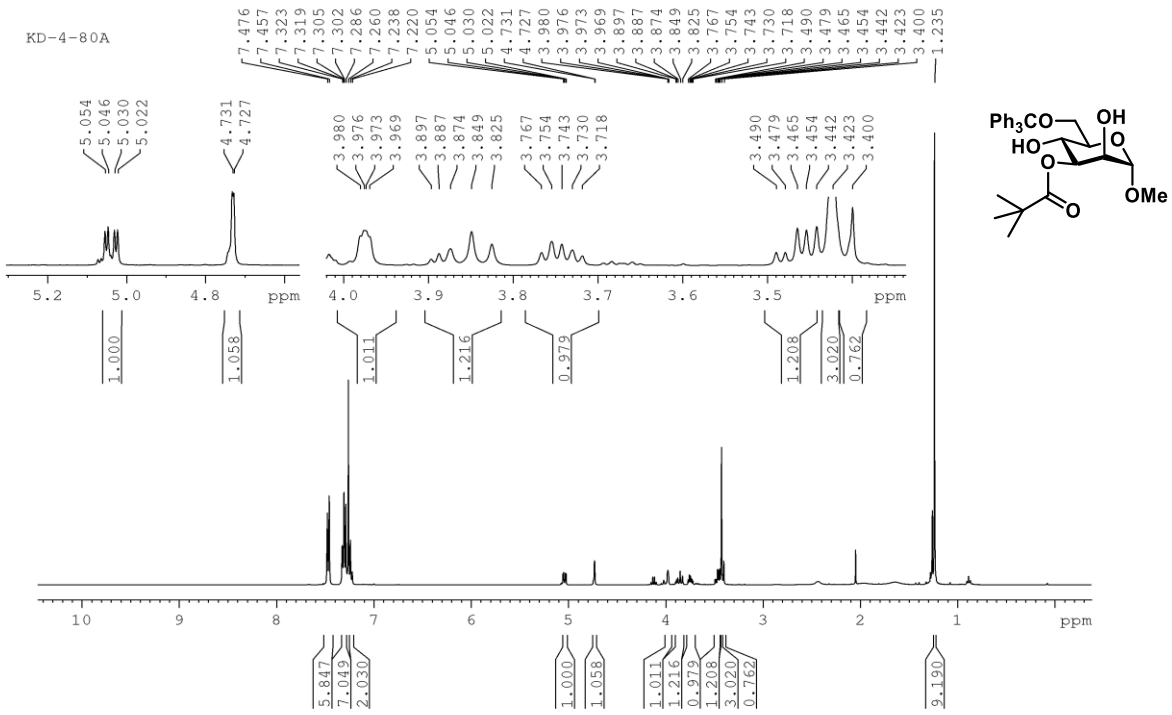


Figure S68. ^{1}H NMR spectrum of **54** ($CDCl_3$, 400 MHz).

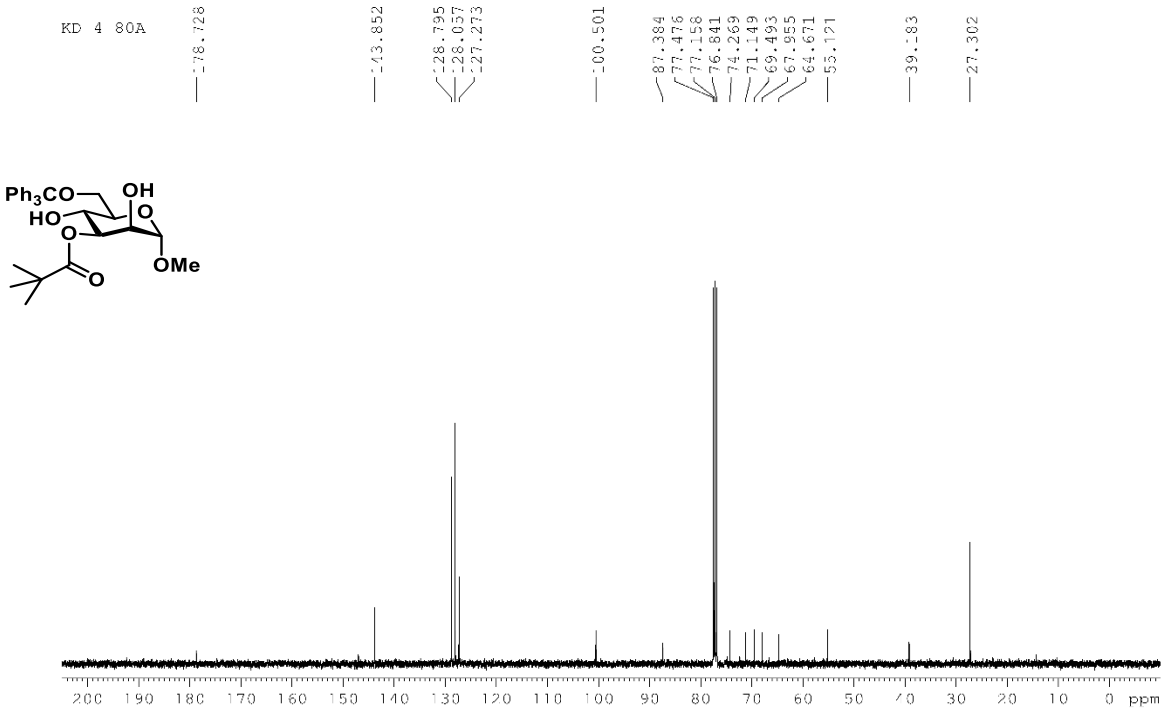


Figure S69. ^{13}C NMR spectrum of **54** ($CDCl_3$, 100 MHz).

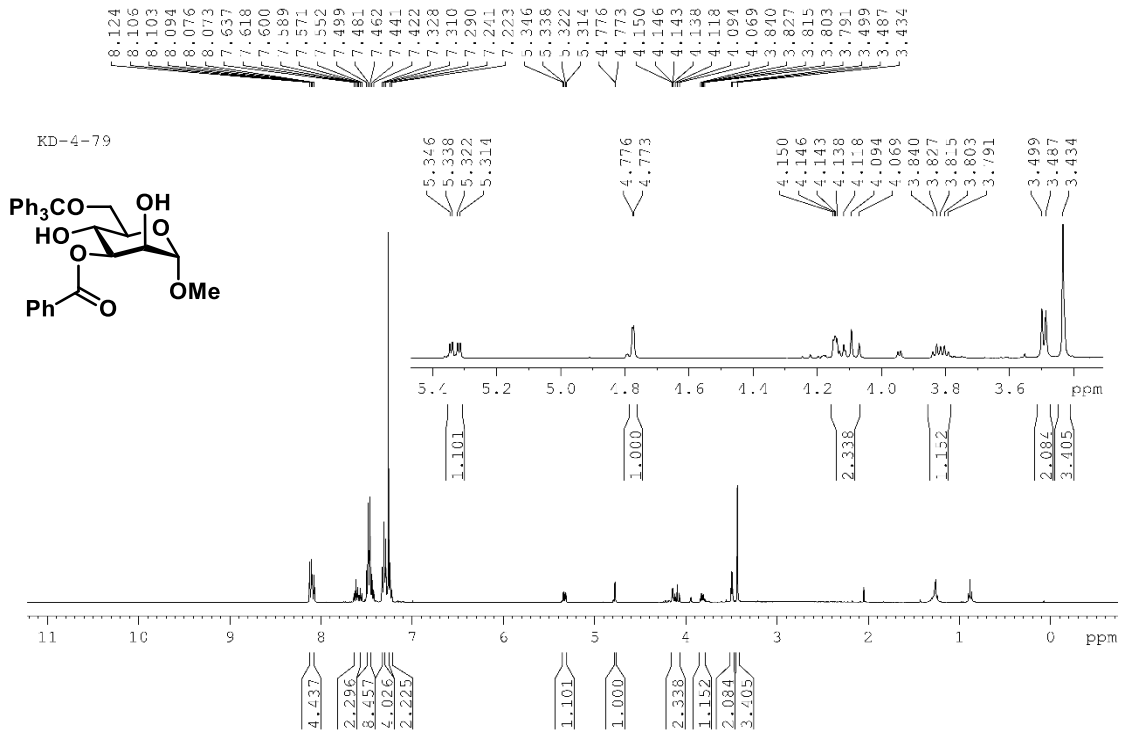


Figure S70. ^{1}H NMR spectrum of **56** ($CDCl_3$, 400 MHz).

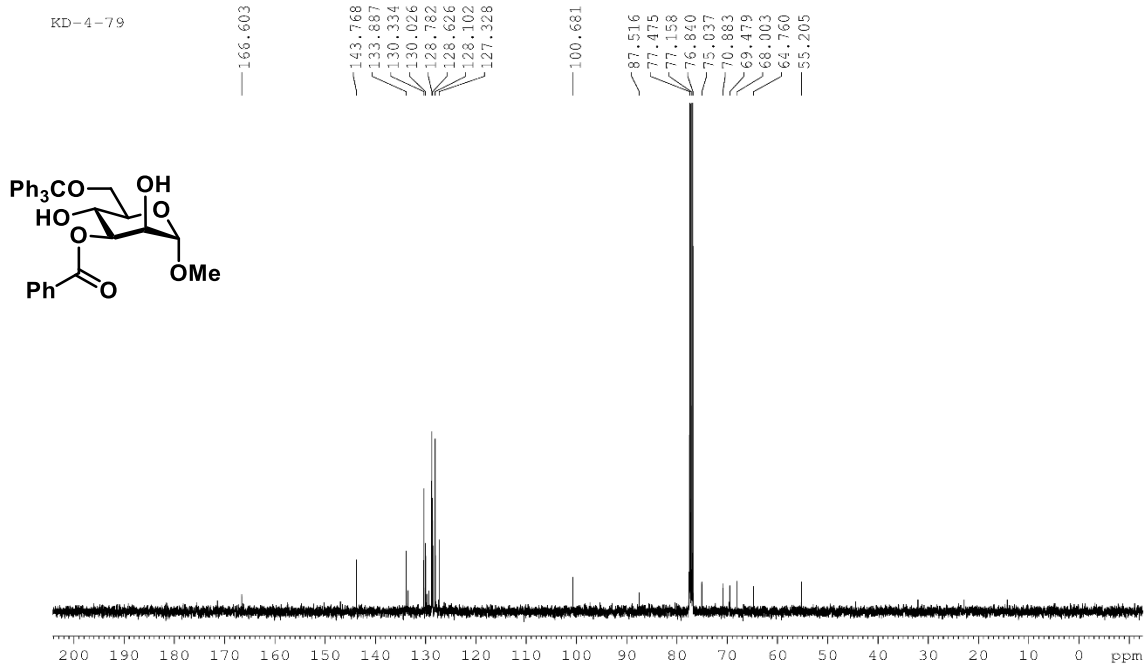


Figure S71. ^{13}C NMR spectrum of **56** ($CDCl_3$, 100 MHz).

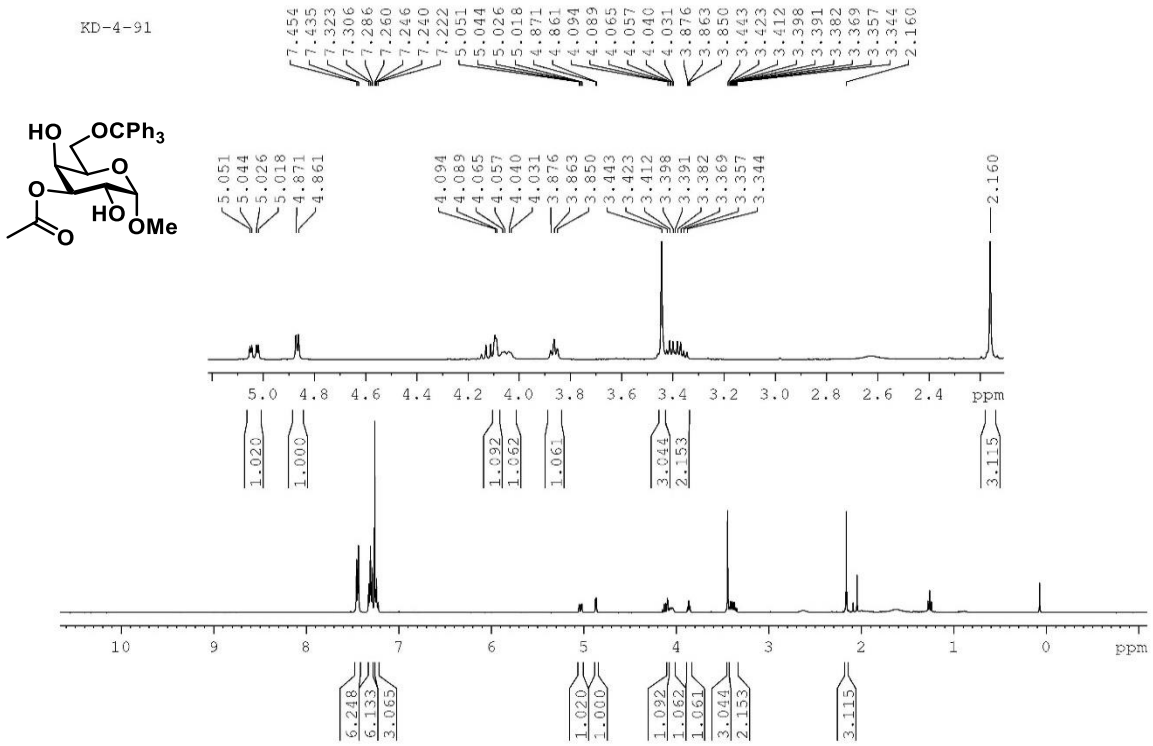


Figure S72. ^{1}H NMR spectrum of **59** ($CDCl_3$, 400 MHz).

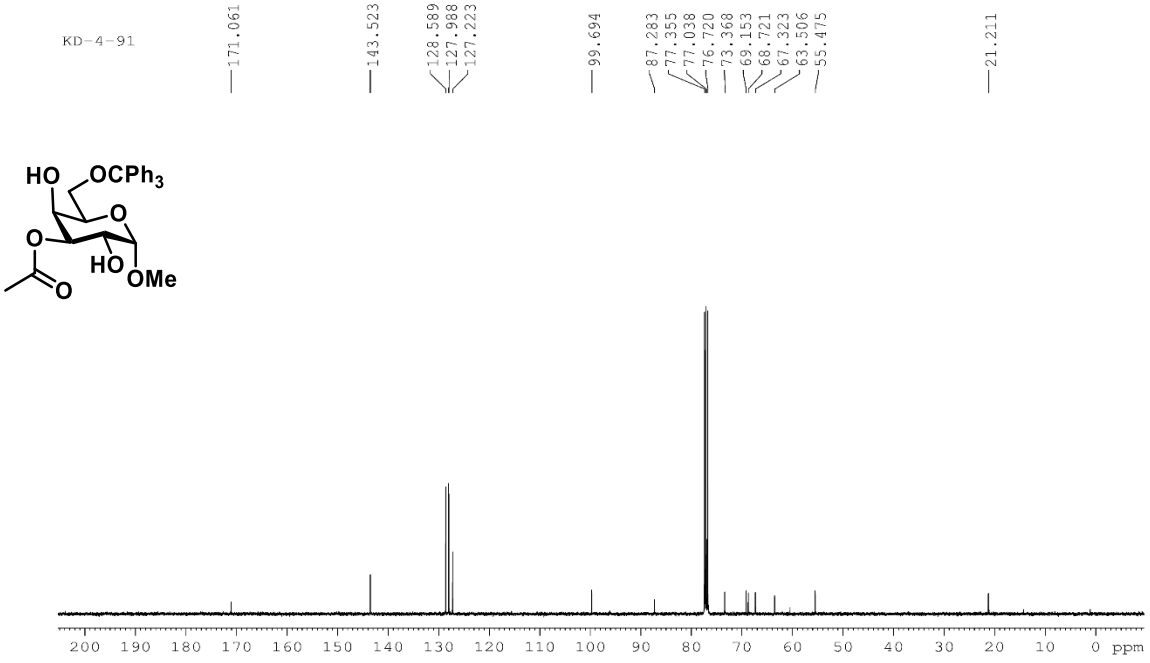


Figure S73. ^{13}C NMR spectrum of **59** ($CDCl_3$, 100 MHz).

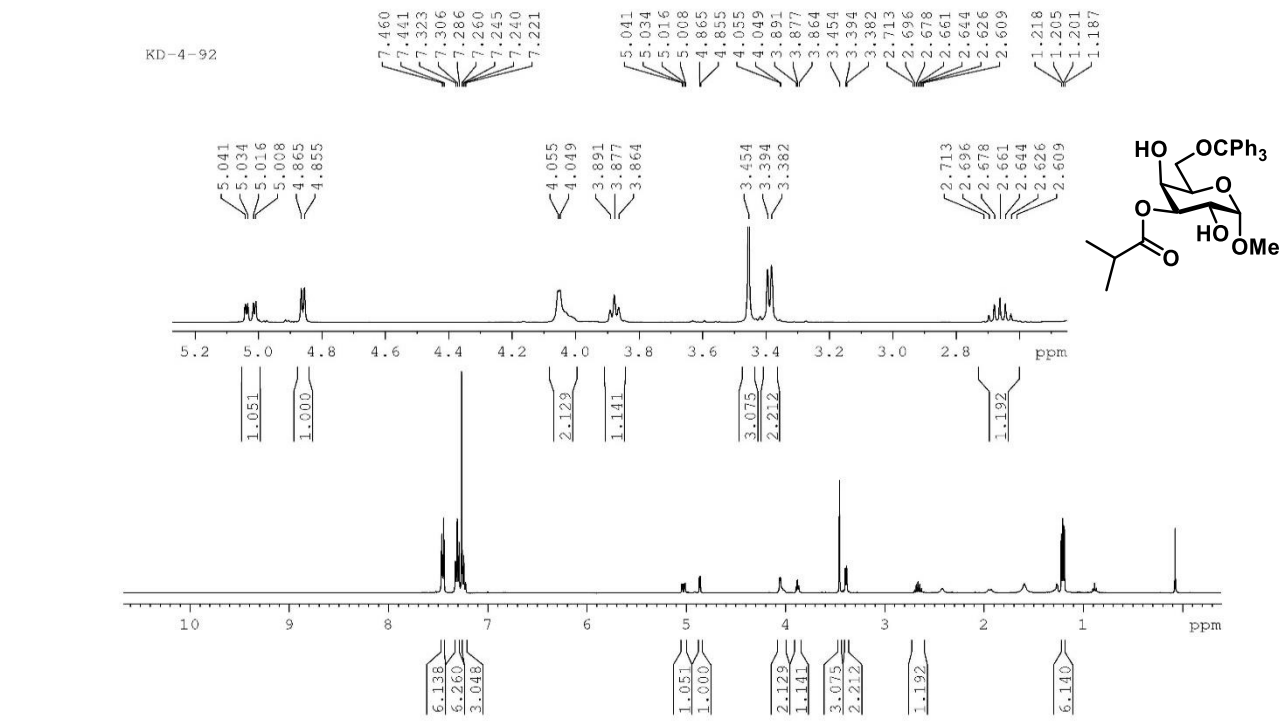


Figure S74. ^{1}H NMR spectrum of **61** ($CDCl_3$, 400 MHz).

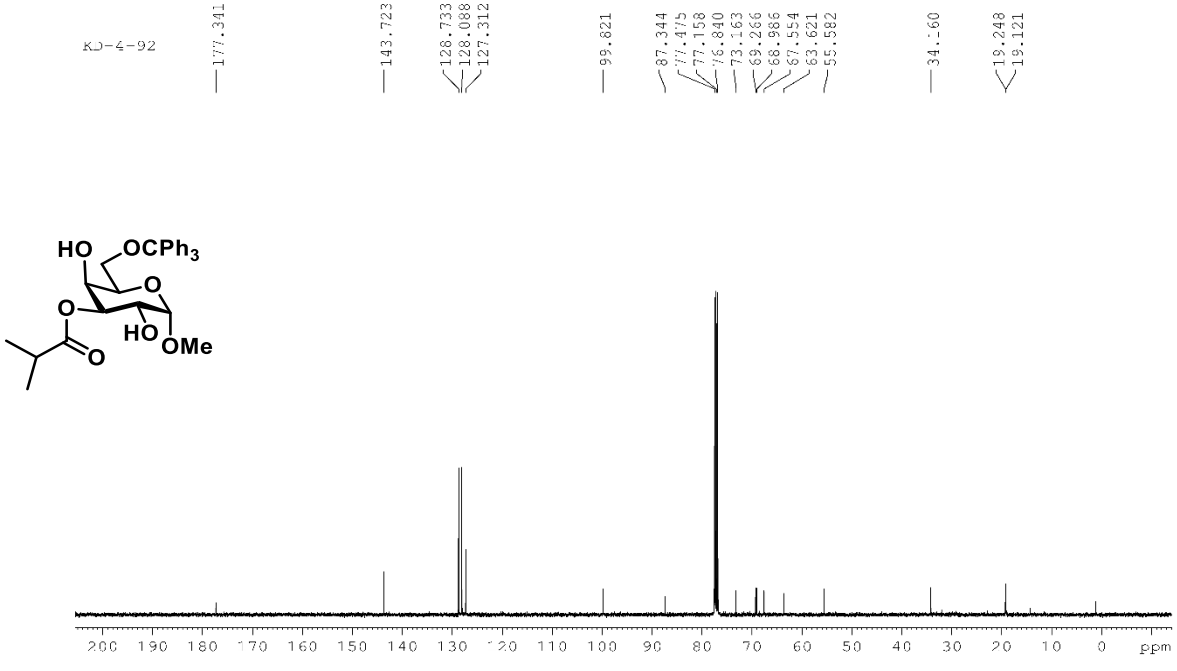


Figure S75. ^{13}C NMR spectrum of **61** ($CDCl_3$, 100 MHz).

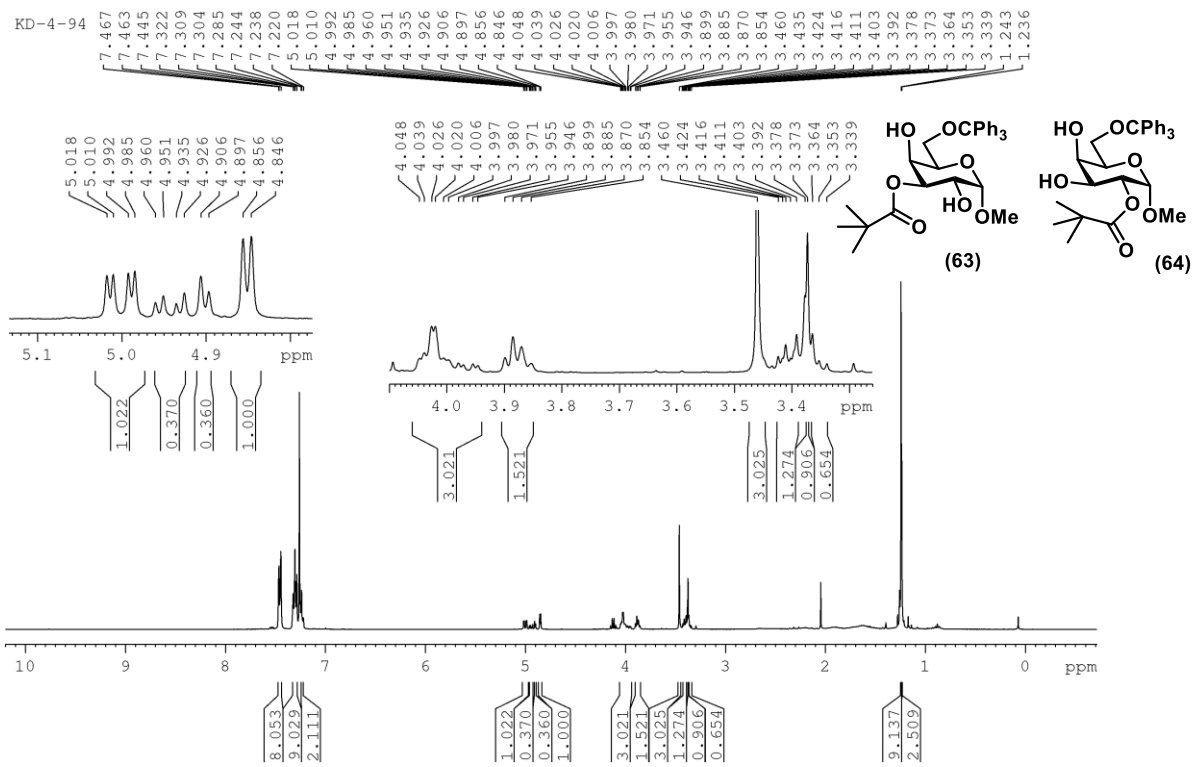


Figure S76. ^{1}H NMR spectrum of a mixture of **63** (77%) and **64** (23%) ($CDCl_3$, 400 MHz).

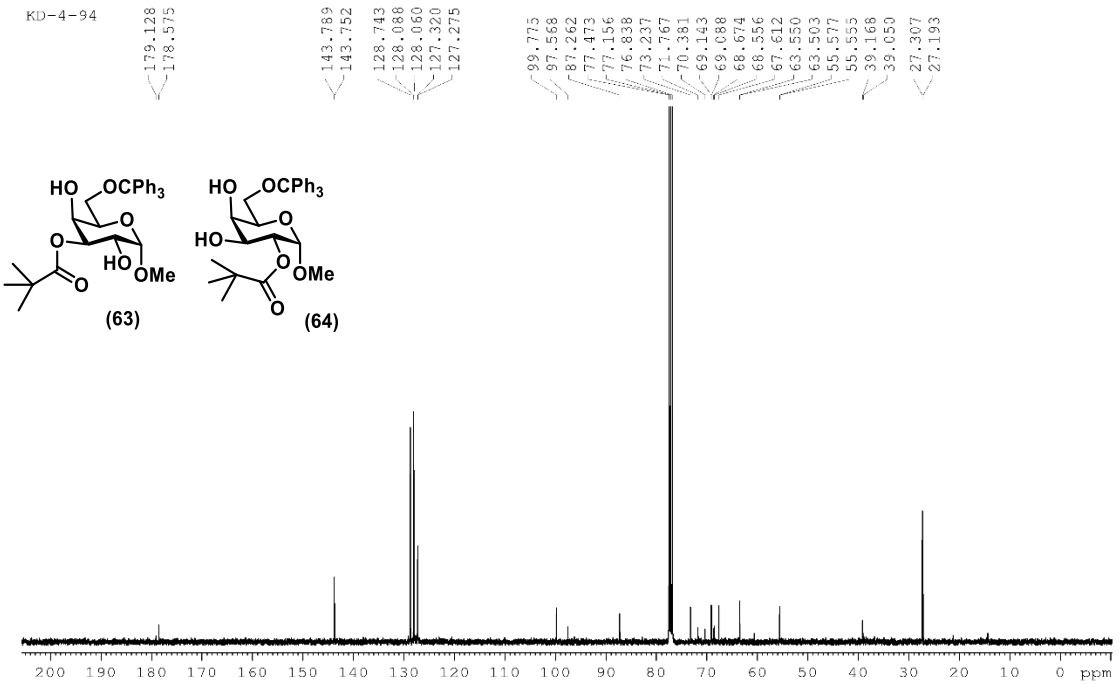


Figure S77. ^{13}C NMR spectrum of a mixture of **63** and **64** ($CDCl_3$, 100 MHz).

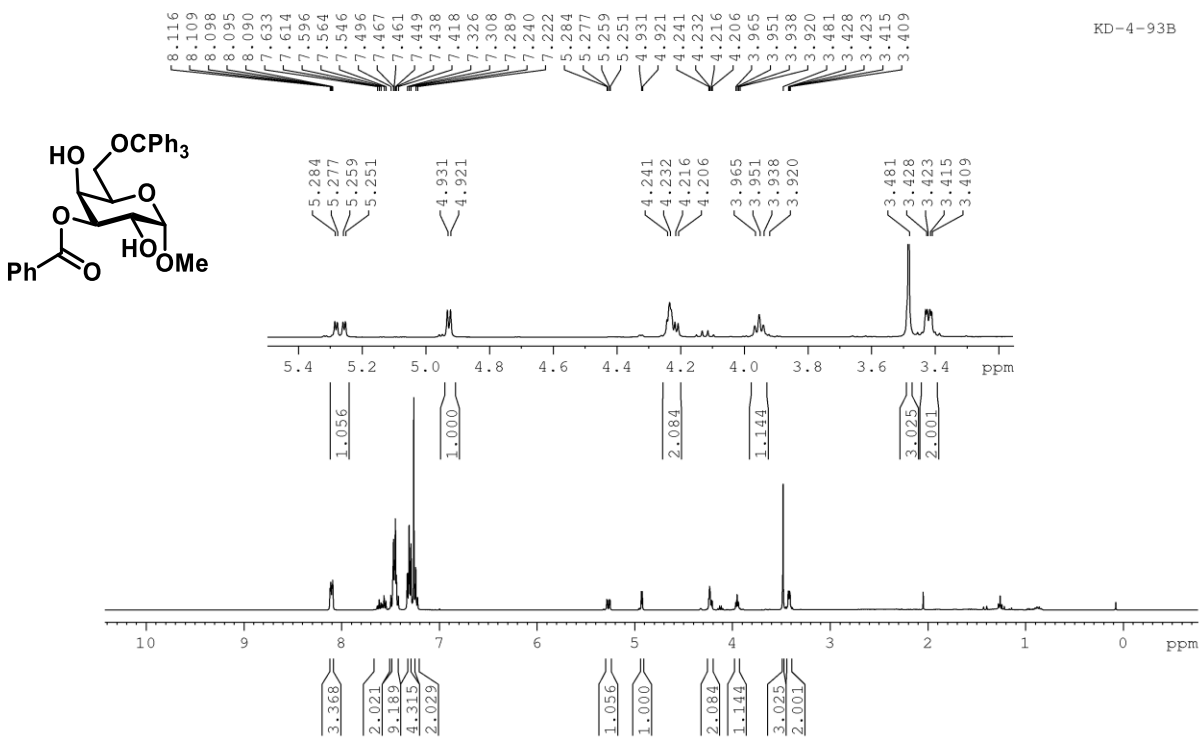


Figure S78. ^{1}H NMR spectrum of **65** ($CDCl_3$, 400 MHz).

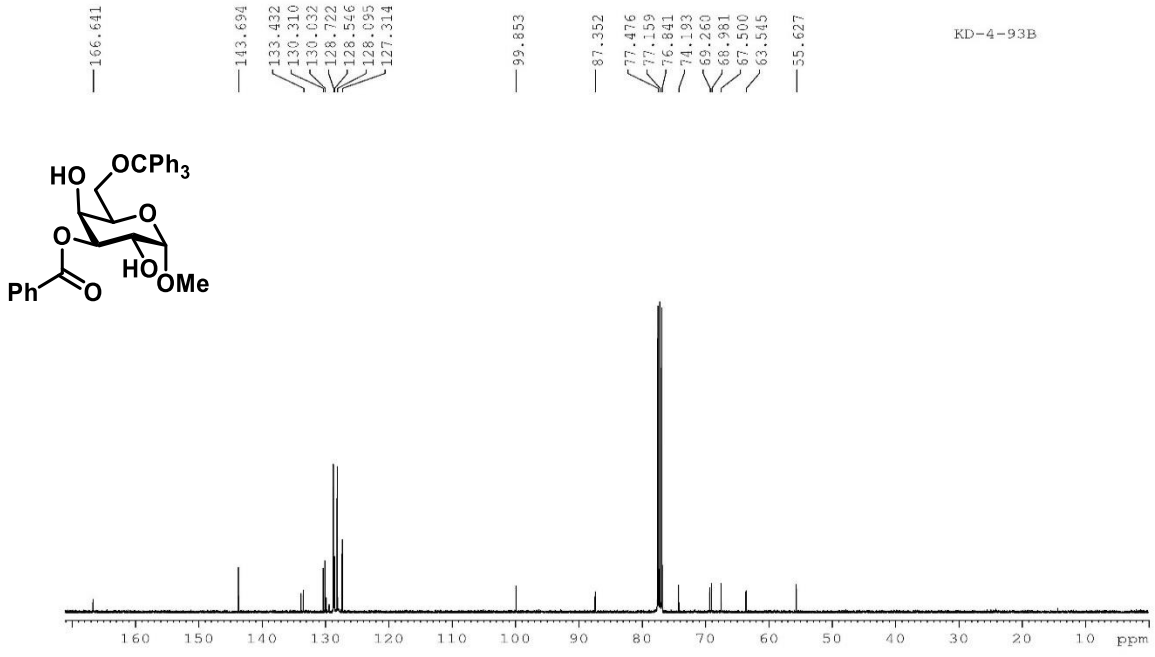


Figure S79. ^{13}C NMR spectrum of **65** ($CDCl_3$, 100 MHz).