Supporting Information

A Convenient and Efficient Synthesis of Glycals by Zinc Nanoparticles

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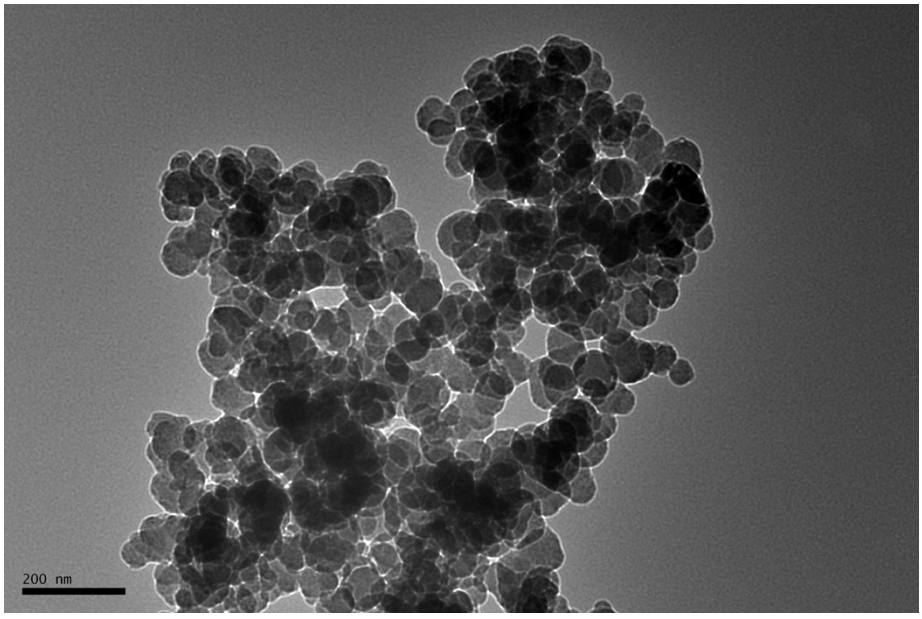
1. General experimental methods

Glycopyranosyl bromides were synthesized in our group[1, 2]. Zinc Nanoparticles were purchased from commercially sources (BEIJNG DK NANO TECHNOLOGY CO.LTD) and were used without further purification. All solvents were available commercially dried or freshly dried and distilled prior to use. Reactions were monitored by Thin Layer Chromatography (TLC) using silica gel GF254 plates. Column chromatography was conducted by silica gel (200-300 mesh) with ethyl acetate and petroleum ether (60–90°C) or dichloromethane and methanol as eluent. ^{1}HNMR and ^{13}CNMR were recorded with Bruker AV 400 spectrometer at 400 MHz (^{1}HNMR), 101 MHz (^{13}CNMR) using $CDCl_3$ as solvents. Chemical shifts were reported in δ (ppm) from TMS internal standard (0.00 ppm).

The TEM analysis of Zinc Nanoparticles



2. General procedure for glycals synthesis

The glycopyranosyl bromide (1.0 mmol) was dissolved in tetrahydrofuran (4 mL), and the solution was stirred at 0°C, followed by addition of sodium acetate trihydrate (6.0 mmol) or triethylamine hydrochloride (6.0 mmol), acetic acid (0.4 ml) and zinc nanoparticles (2.0 mmol). After the addition, the mixture was stirred at room

temperature until the reaction was completed (detected by TLC). The mixture was extracted with EtOAc. The organic phase was washed with satd. $NaHCO_3$, followed by water and brine, and then was dried over Na_2SO_4. The mixture was evaporated under reduced pressure, and the resultant residue was purified by column chromatography to yield pure product.

3. The optimization of reaction conditions for the synthesis of 14.

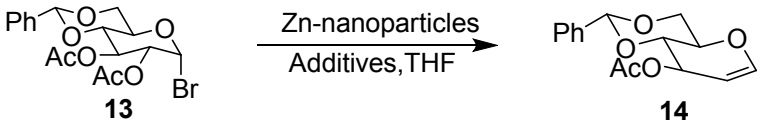


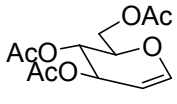
Table 2. Optimization of reaction conditions for synthesis of **14**.

Entry	Conditions	Yield[b] (%)	Time(h)
1[a]	AcOH / AcONa / THF	47	2
2[b]	AcOH / THF	33	2
3[c]	$Et_3N{\cdot}HCl$ / THF	trace	2
4[d]	AcOH / $Et_3N{\cdot}HCl$ / THF	68	2

[a] Reaction conditions: 1.0 mmol glycopyranosyl bromides, 2.0 mmol zinc nanoparticles, 6.0 mmol $Et_3N{\cdot}HCl$ and 0.4 mL AcOH, in 4 mL THF at r.t for 2 h .
[b] Isolated yield

Reaction conditions:
[a] **13** (1.0 mmol), Zn nanoparticles (2.0 mmol), AcOH (0.4 ml), AcONa (6.0 mmol), THF (4 mL), rt, 2 h;
[b] **13** (1.0 mmol), Zn nanoparticles (2.0 mmol), AcOH, THF (4 mL), rt, 2 h (0.4ml);
[c] **13** (1.0 mmol), Zn nanoparticles (2.0 mmol), $Et_3N{\cdot}HCl$ (6.0 mmol), THF (4 mL), rt, 2 h (0.4ml);
[d] **13** (1.0 mmol), Zn nanoparticles (2.0 mmol), AcOH (0.4 ml), $Et_3N{\cdot}HCl$ (6.0 mmol), THF (4 mL), rt, 2 h.

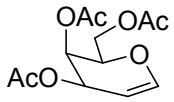
4. The characterization of the compounds



2

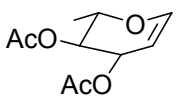
3,4,6-Tri-*O*-acetyl-D-glucal (2) $[\alpha]_D^{25}$ -26 (c 4.1, $CHCl_3$) [α]D25 -20 (c 1.1,

$CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 (dd, J = 6.1, 1.0 Hz, 1H, H1), 5.38 – 5.29 (m, 1H, H3), 5.22 (dd, J = 7.6, 5.8 Hz, 1H, H4), 4.85 (dd, J = 6.1, 3.2 Hz, 1H, H2), 4.41 (dd, J = 12.1, 5.7 Hz, 1H, H6a), 4.30 – 4.23 (m, 1H, H5), 4.20 (dd, J = 12.1, 3.1 Hz, 1H, H6b), 2.09 (s, 3H, CH3), 2.08 (s, 3H, CH3), 2.05 (s, 3H, CH3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.39, 170.22, 169.41, 145.56, 98.92, 73.87, 67.33, 67.10, 61.26, 20.84, 20.65, 20.57.MS (ESI+): m/z = 295.28 $[M + Na]^+$. The datum of **2** matched that reported. [3]



4

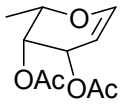
3,4,6-Tri-*O*-acetyl-D-galactal (4) $[\alpha]_D^{25}$ -11.6 (c 0.1, EtOAc). $[\alpha]_D^{23}$ -22.3 (c 1.1, $CHCl_3$).^{1}HNMR (400 MHz, $CDCl_3$) δ 6.47 (dd, J = 6.3, 1.5 Hz, 1H, H1), 5.56 (d, J = 1.8 Hz, 1H, H3), 5.43 (d, J = 4.5 Hz, 1H, H4), 4.78 – 4.69 (m, 1H, H2), 4.32 (dd, J = 11.3, 5.3 Hz, 1H, H6a), 4.26 (m, 1H, H5), 4.22 (dd, J = 11.3, 5.2 Hz, 1H, H6b), 2.13 (s, 3H, CH3), 2.09 (s, 3H, CH3), 2.03 (s, 3H, CH3); ^{13}CNMR (101 MHz, CDCl3) δ 170.53, 170.25, 170.11, 145.41, 98.85, 72.81, 63.89, 63.76, 61.91 20.79, 20.73, 20.63. MS (ESI+): m/z = 295.12 $[M + Na]^+$. MS (ESI+): m/z = 295.28 $[M + Na]^+$. The datum of **4** matched that reported. [3b,4]



6

3,4-Di-*O*-acetyl-L-rhamnal (6) $[\alpha]_D^{25}$ +70 (c 1.1, $CHCl_3$), $[\alpha]_D^{25}$ +58 (c 1.0,$CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 (dd, *J* = 6.1, 1.0 Hz, 1H, H1), 5.41 – 5.27 (m, 1H, H3), 5.03 (dd, *J* = 8.1, 6.2 Hz, 1H,H4), 4.78 (dd, *J* = 6.1, 3.0 Hz, 1H,H2), 4.17 – 4.02

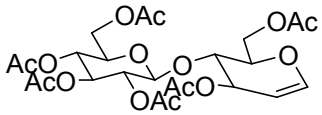
(m, 1H, H5), 2.09 (s, 3H, CH3), 2.04 (s, 3H, CH3), 1.31 (d, *J* = 6.5 Hz, 3H,H6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.62, 169.88, 145.97, 98.77, 72.51, 71.83, 68.29, 21.05, 20.87, 16.54.MS (ESI+): m/z = 214.01 $[M]^+$. MS (ESI+): m/z = 214.06 $[M]^+$. The data is consistent with that reported previously for **6**.[5]



8

3,4-Di-*O*-acetyl-L-fucal (8) $[\alpha]_D^{25}$ +51 (c 0.4, $CHCl_3$), $[\alpha]_D^{25}$ +12 (c 0.1,$CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 (dd, *J* = 6.3, 1.8 Hz, 1H,H1), 5.60 – 5.55 (m, 1H,H3), 5.29 (d, *J* = 4.6 Hz, 1H,H4), 4.64 (m, *J* = 6.3, 1.9 Hz, 1H,H2), 4.22 (q, *J* = 6.6 Hz, 1H,H5), 2.16 (s, 3H, CH3), 2.02 (s, 3H, CH3), 1.28 (d, *J* = 6.6 Hz, 3H,H6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.68, 170.38, 146.10, 98.26, 71.52, 66.28, 65.04, 20.84, 20.68, 16.50. MS (ESI+): m/z = 214.09 $[M]^+$. The data is consistent with that reported previously for **8**.[6]

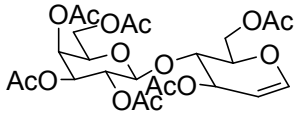


10

Per-*O*-acetyl-D-cellobial (10) $[\alpha]_D^{26}$ –18 (c 1.0, $CHCl_3$) , $[\alpha]_D^{18}$ –25 (c 1.2, $CHCl_3$)].

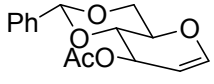
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 (d, J = 6.1 Hz, 1H, H1), 5.48 – 5.43 (m, 1H，H1′), 5.22 (t, J = 9.4 Hz, 1H，H3), 5.12 (dd, J = 10.0, 9.4 Hz, 1H，H3′), 5.01 (dd, J = 9.4, 8.0 Hz, 1H, H4′), 4.86 (dd, J = 5.8, 3.3 Hz, 1H, H2), 4.72 (d, J = 7.9 Hz, 1H, H2′), 4.51 – 4.44 (m, 1H, H6a), 4.34 (dd, J = 12.3, 4.3 Hz, 1H, H4), 4.20 (m, 2H, H6b, H6a′), 4.10 (d, J = 12.2 Hz, 1H，H6b′), 4.02 (t, J = 7.5, 5.7 Hz, 1H, H5), 3.75 – 3.68

(m, 1H, H5′), 2.15 (s, 3H), 2.12 (s, 3H, CH3), 2.08 (s, 6H, 2CH3), 2.05 (s, 3H, CH3), 2.03 (s, 3H, CH3); ^{13}C NMR (101 MHz, $CDCl_3$) δ170.60, 170.37, 170.22, 169.91, 169.29, 169.16, 145.43, 100.54, 99.09, 74.66, 74.36, 72.75, 72.01, 71.38, 68.61, 68.09, 61.79, 20.97, 20.81, 20.65, 20.55, 20.53. MS (ESI+): m/z = 583.09 $[M + Na]^+$.The collected data is consistent with that a previously.reported sample of **10**.[7]



12

Per-*O*-acetyl-D-lactal (12) $[\alpha]_D^{30}$ –15.8 (c 0.8, $CHCl_3$) $[\alpha]_D^{23}$ –20 (c 0.8, $CHCl_3$)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.41 (d, *J* = 5.9 Hz, 1H, H1), 5.39 (m, 1H, H1′), 5.37 (m, 1H, H2′),5.20 (dd, *J* = 10.4, 8.0 Hz, 1H, H3), 5.00 (d, *J* = 10.5 Hz, 1H, H4), 4.84 (d, *J* = 3.6 Hz, 1H, H3′), 4.66 (d, *J* = 8.0 Hz, 1H, H4′), 4.44 (d, *J* = 11.4 Hz, 1H, H2), 4.23 – 4.00 (m, 4H，H6′, H′ - 6′, H - 6, H′ - 6), 4.01 (d, *J* = 4.3 Hz, 1H，H5), 3.91 (dd, *J* = 7.1, 6.4 Hz, 1H，H5′), 2.16 (s, 3H，CH3), 2.12 (s, 3H，CH3), 2.09 (s, 3H，CH3), 2.06 (s, 3H，CH3), 2.06 (s, 3H，CH3), 1.98 (s, 3H，CH3); ^{13}C NMR (101 MHz, CDCl3) δ 170.27, 170.07, 169.93, 169.83, 169.15, 145.33, 100.85, 98.92, 74.51, 74.08, 70.70, 70.56, 68.83, 68.78, 66.69, 61.73, 60.94, 20.92, 20.69, 20.47, 20.39. MS (ESI+): m/z = 583.69 $[M + Na]^+$. The collected data is consistent with that a previously reported sample of **12**.[7]



14

3-*O*-acetyl-4,6-*O*-benzylidene-D-glucal (14) $[\alpha]_D^{27}$ -85 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (m, *J* = 6.2, 3.6 Hz, 5H, Ph), 6.13 (d, *J* = 3.6 Hz, 1H,H1), 5.95 (s,

1H,acetal), 5.13 (m, *J* = 7.5, 4.3 Hz, 1H, H5), 5.00 (t, *J* = 3.9 Hz, 1H,H3), 4.80 (d, *J* = 3.6 Hz, 1H,H2), 4.65 (d, *J* = 3.6 Hz, 1H,H4), 4.08 (dd, *J* = 8.4, 7.3 Hz, 1H,H6a), 3.74 (t, *J* = 8.4 Hz, 1H,H6b), 2.15 (s, 3H,CH3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.37, 135.84, 129.84, 128.47, 126.57, 106.70, 104.33, 85.19, 84.82, 82.22, 73.65, 68.18, 20.68. MS (ESI+): m/z = 276.09 $[M]^+$.The datum of **14** accorded with that reported.[8]

5. Reference

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2. Osman, H.; Larsenet, D. S.; Simpson, J. T*etrahedron* 2009, **65,** 4092.
3. (a) Grugel, H.; Minuth, T.; Boysen, M. M. K. *Synthesis* 2010, **19**, 3248; (b) Zhao, J. Z.; Wei, S. Q.; Ma, X. F.; Shao, H. W., *Green Chem* 2009, **11** (8), 1124; (c) Raina, S.; Prasad, B. A. B.; Singh, V. K. *Arkivoc* 2003, 16; (d)Pollon, J. H. P.; Llewellyn, G.; Williams, J. M. *Synthesis* 1989, 758.
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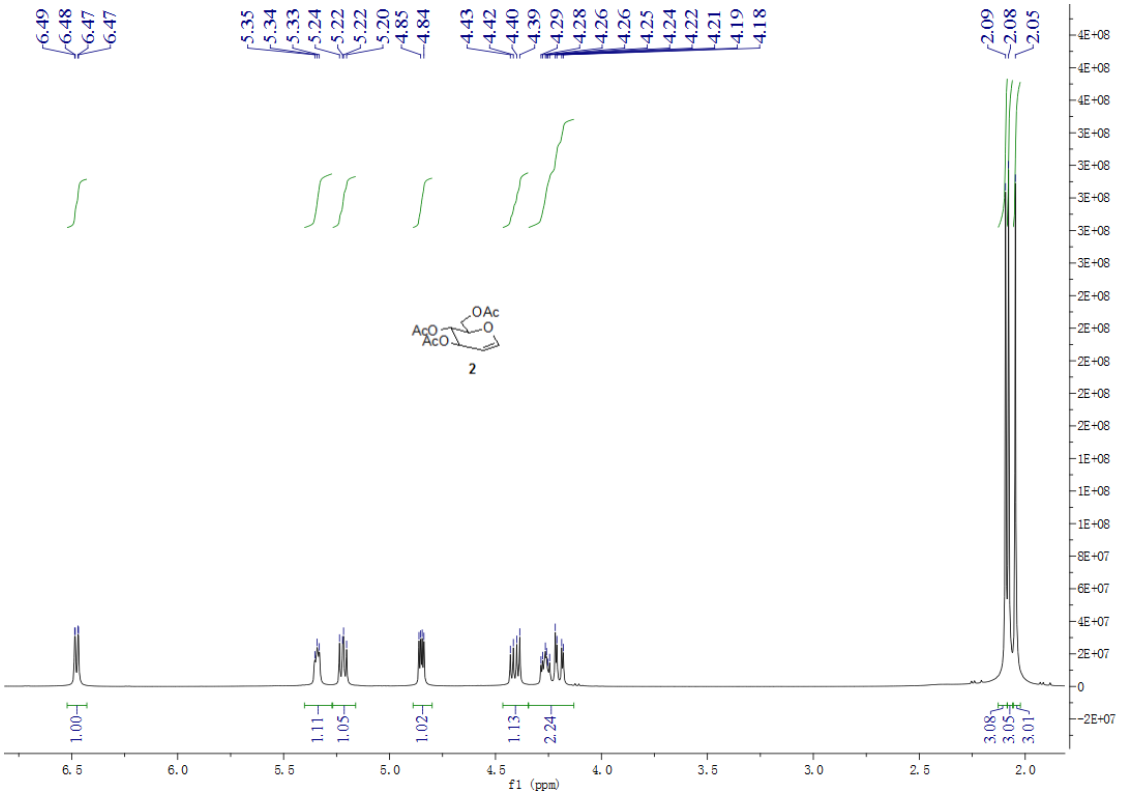
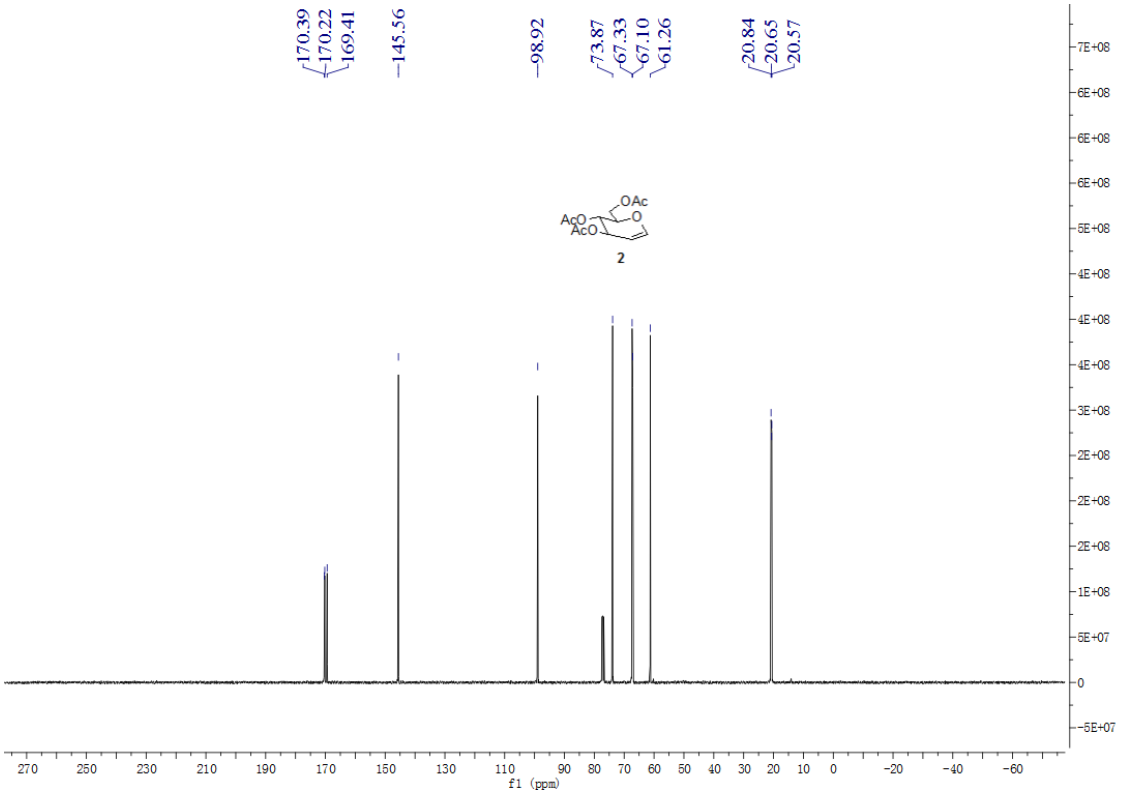
6. (a)Ding, F. Q.; William, R.; Wang, F.; Ma, J. M.; Ji, L.; Liu, X. W. *Org Lett* 2011, **13** (4), 652; (b) Xu, X.; Tan, Q.; Hayashi, M., *Synthesis* 2008, **2008** (05), 770.
7. Xu, X. Y.; Tan, Q. T.; Hayashi, M., *Synthesis* 2008, **5**, 770.
8. Sharma, M.; Brown, R. K. *Can J Chem* 1966, **44**, 2825.

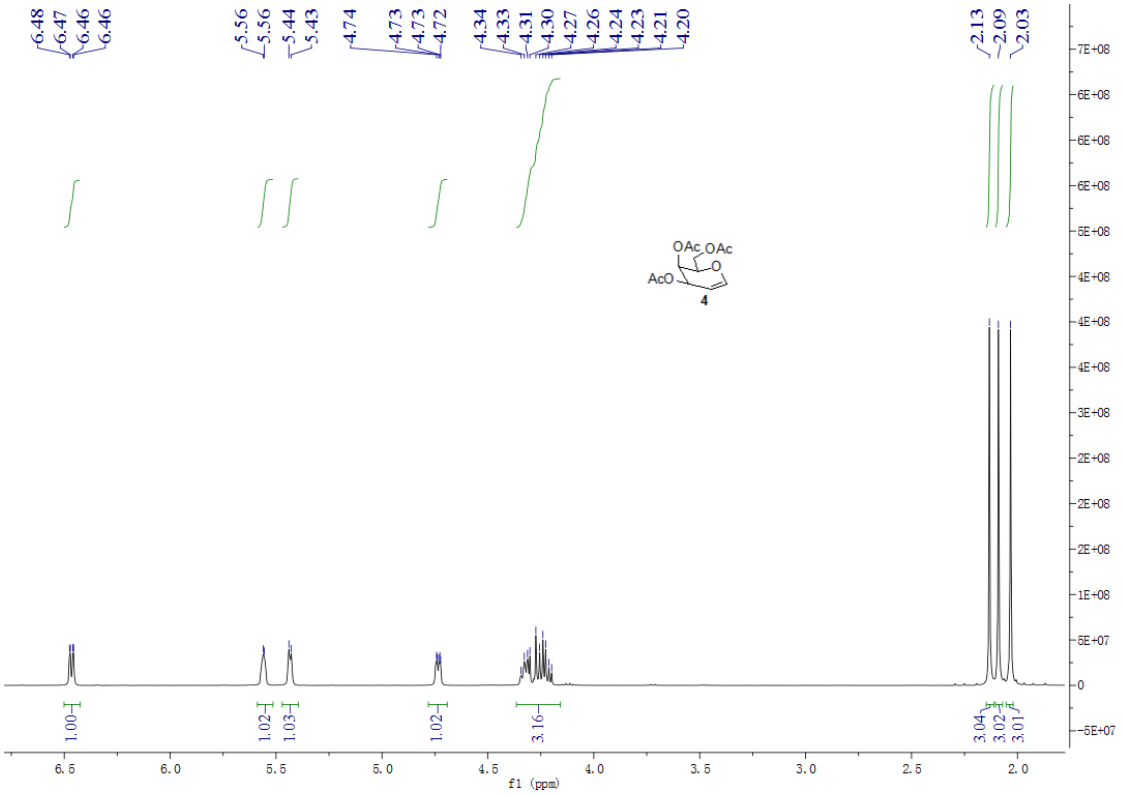
6. NMR spectra of compounds

Compound 2





Compound 4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4.30
4.27
4.26
4.24
4.23
4.21
4.20
2.13
2.09
2.03
OAc
OAc
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AcO
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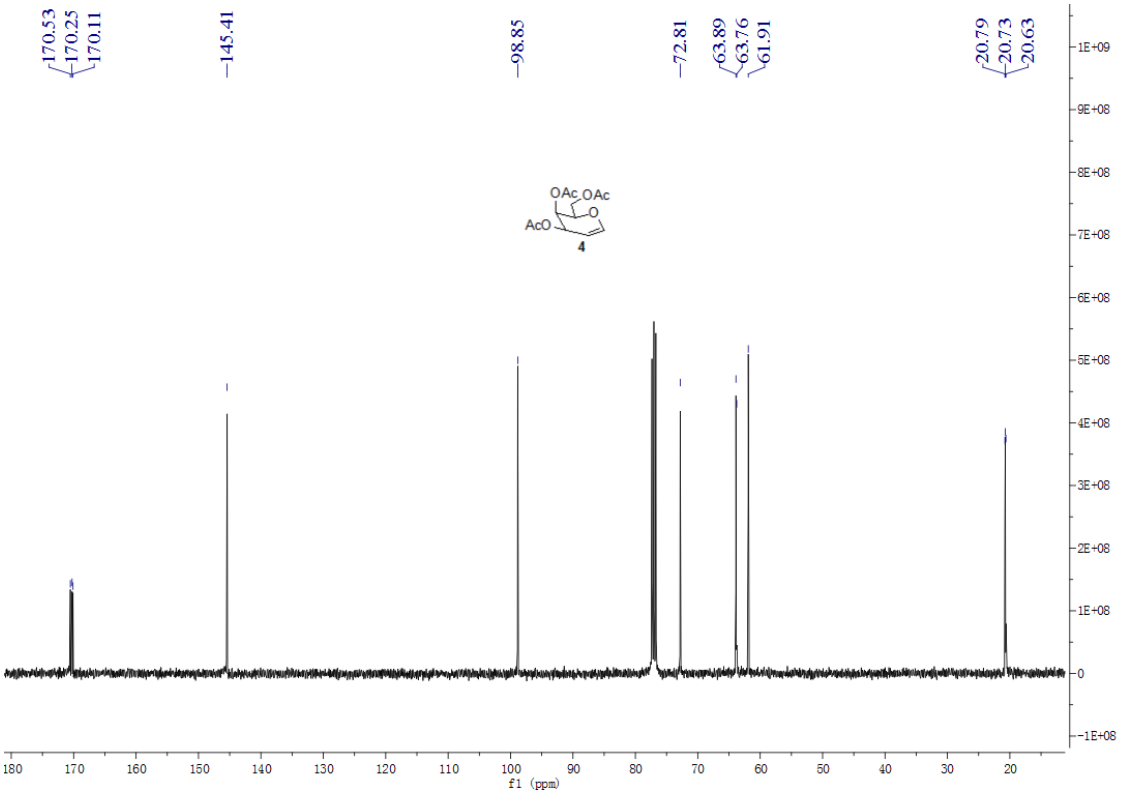
1.03
1.02
3.16
3.04
3.02
3.01
f1 (ppm)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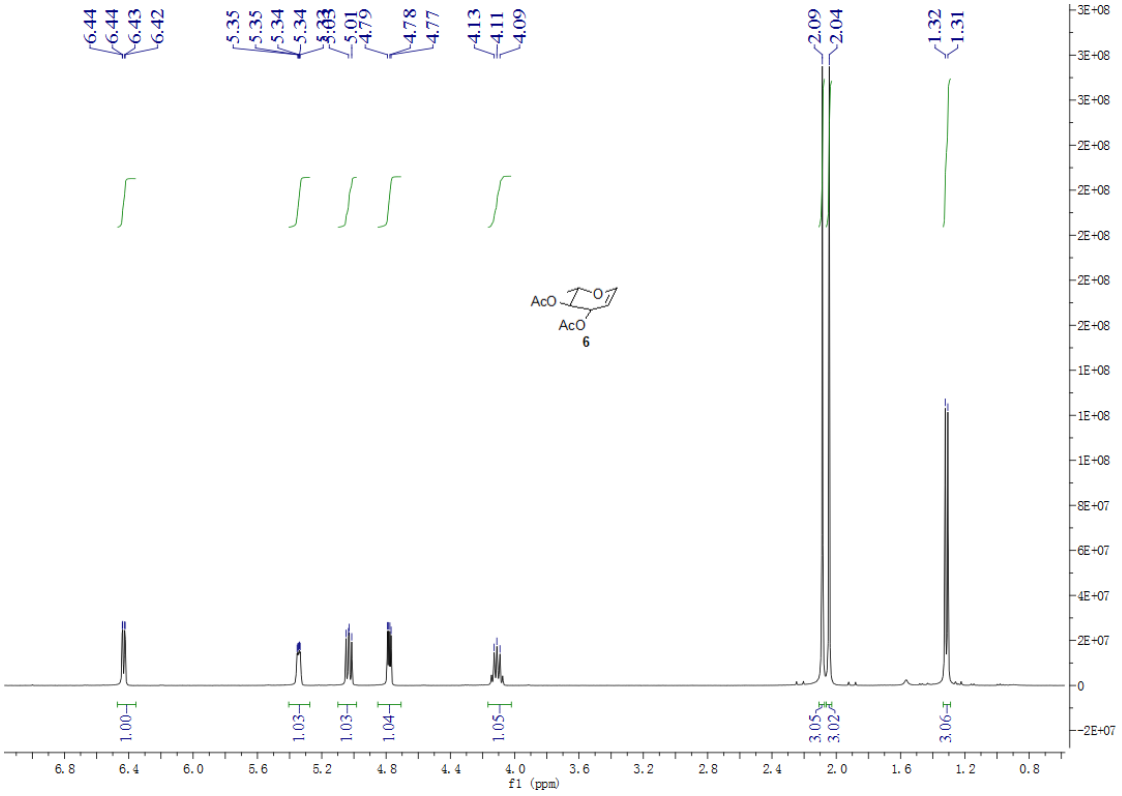
OAc
O
AcO
4
f1 (ppm)

Compound 6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4.13
4.11
4.09
2.09
2.04
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AcO
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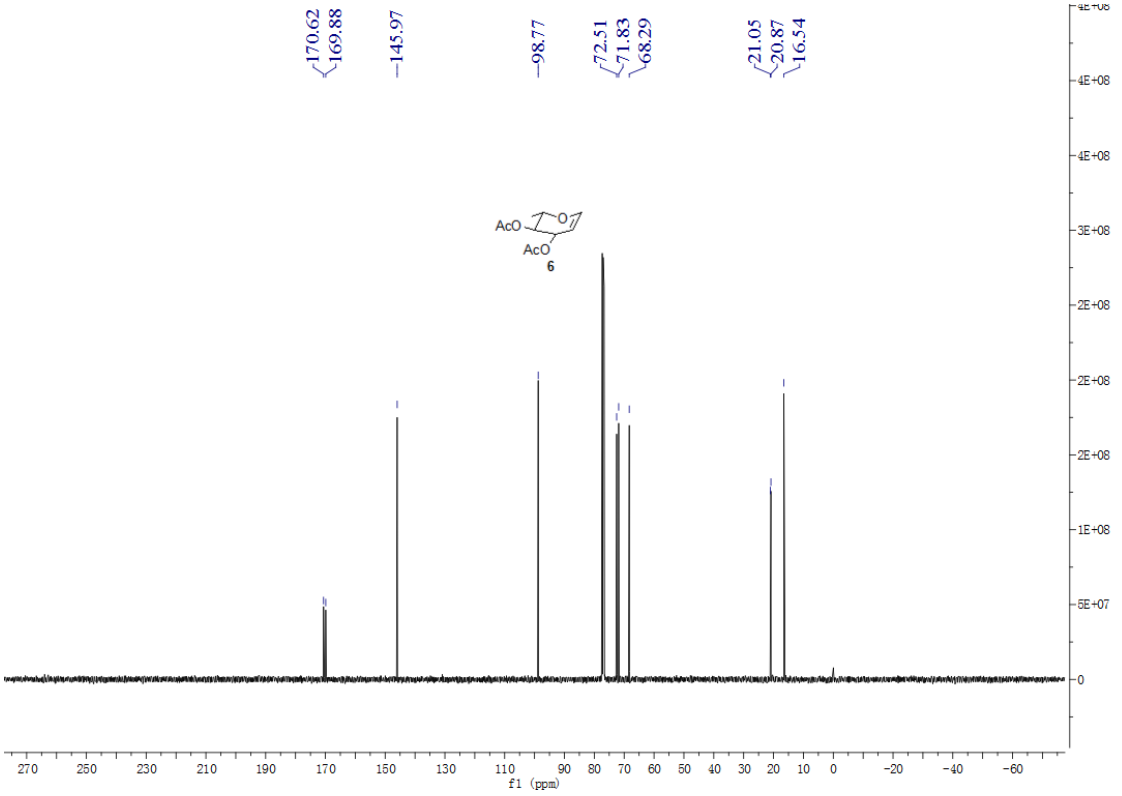
f1 (ppm)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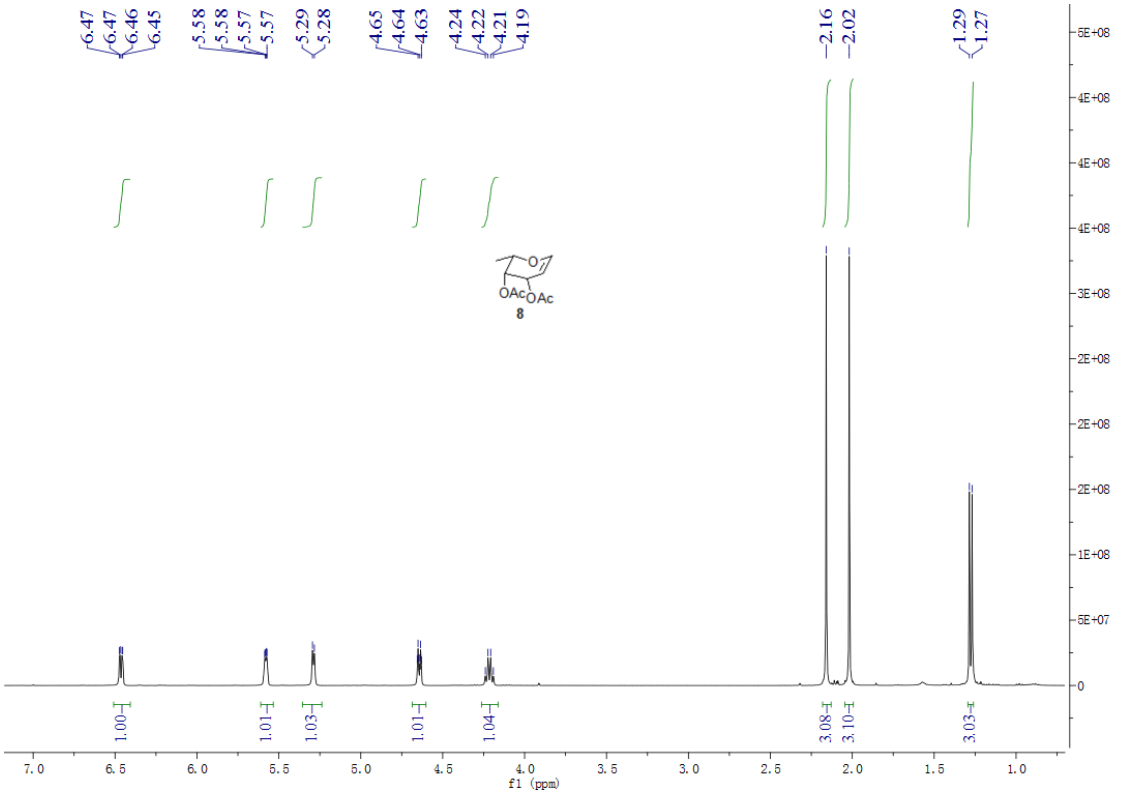
20.87
16.54
AcO
AcO
6
f1 (ppm)

Compound 8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4.63
4.24
4.22
4.21
4.19
2.16
2.02
1.29
1.27
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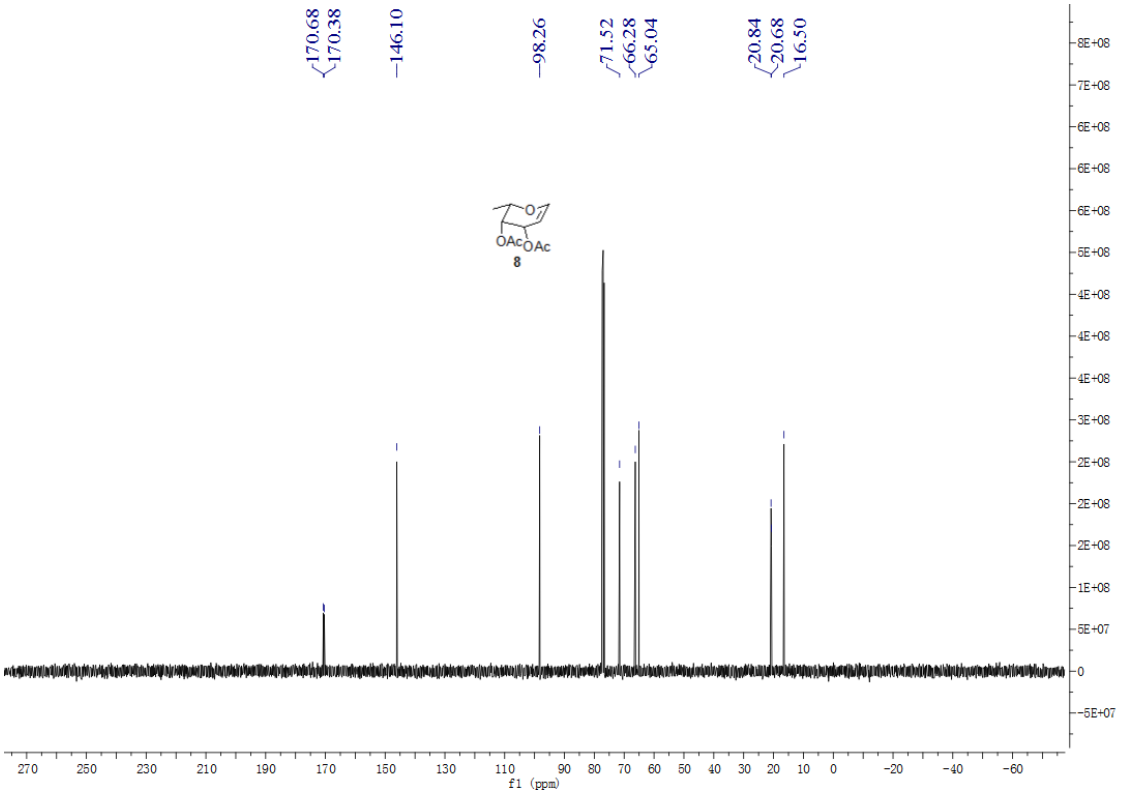
3.03
f1 (ppm)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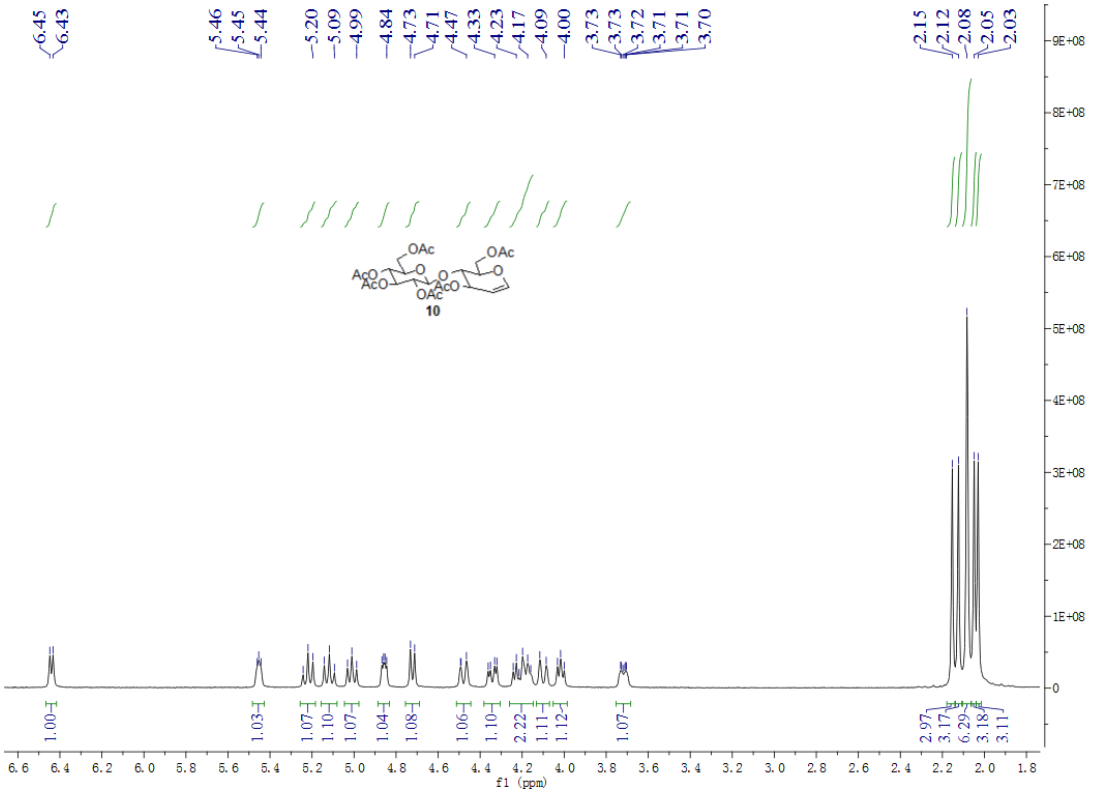
65.04
20.84
20.68
16.50
OAc
OAc
8
f1 (ppm)

Compound 10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3.73
3.72
3.71
3.71
3.70
2.15
2.12
2.08
2.05
2.03
OAc
AcO
AcO
OAc
OAc
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1.00
1.03
1.07
1.10
1.07
1.04
1.08
1.06
1.10
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1.11
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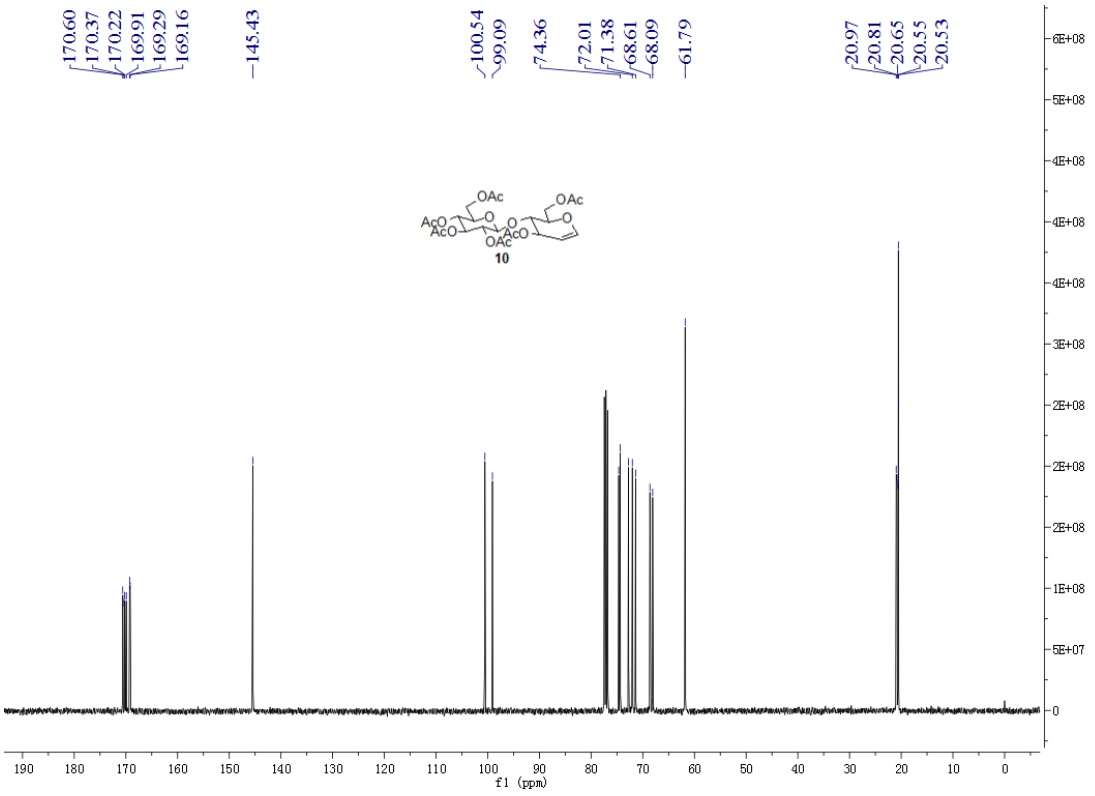
3.17
6.29
3.18
3.11
f1 (ppm)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68.09
61.79
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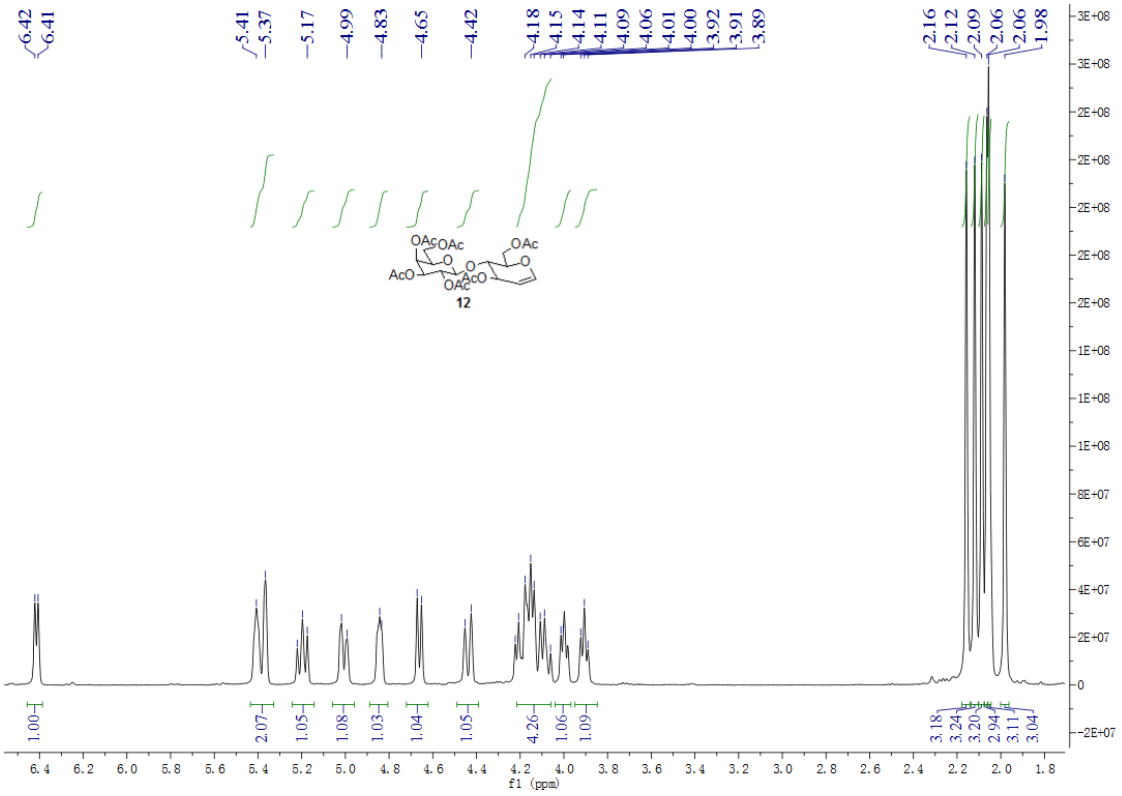
AcO
AcO
OAc
OAc
10
f1 (ppm)

Compound 12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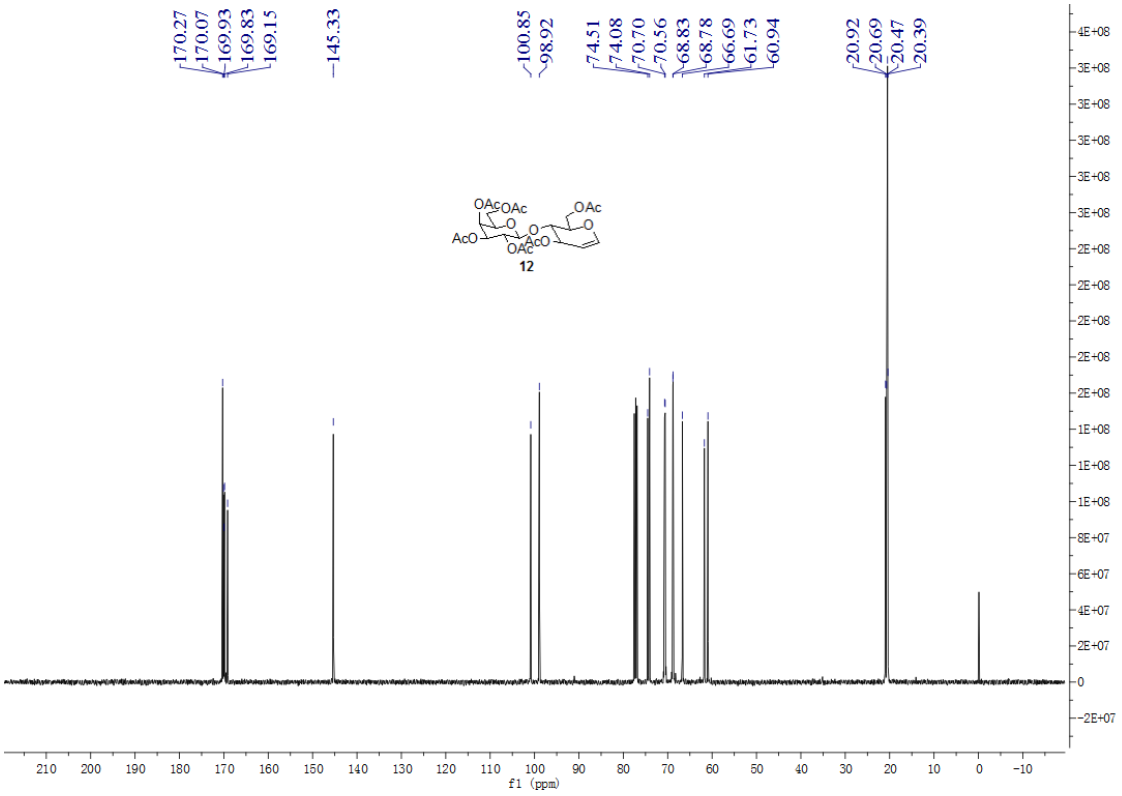
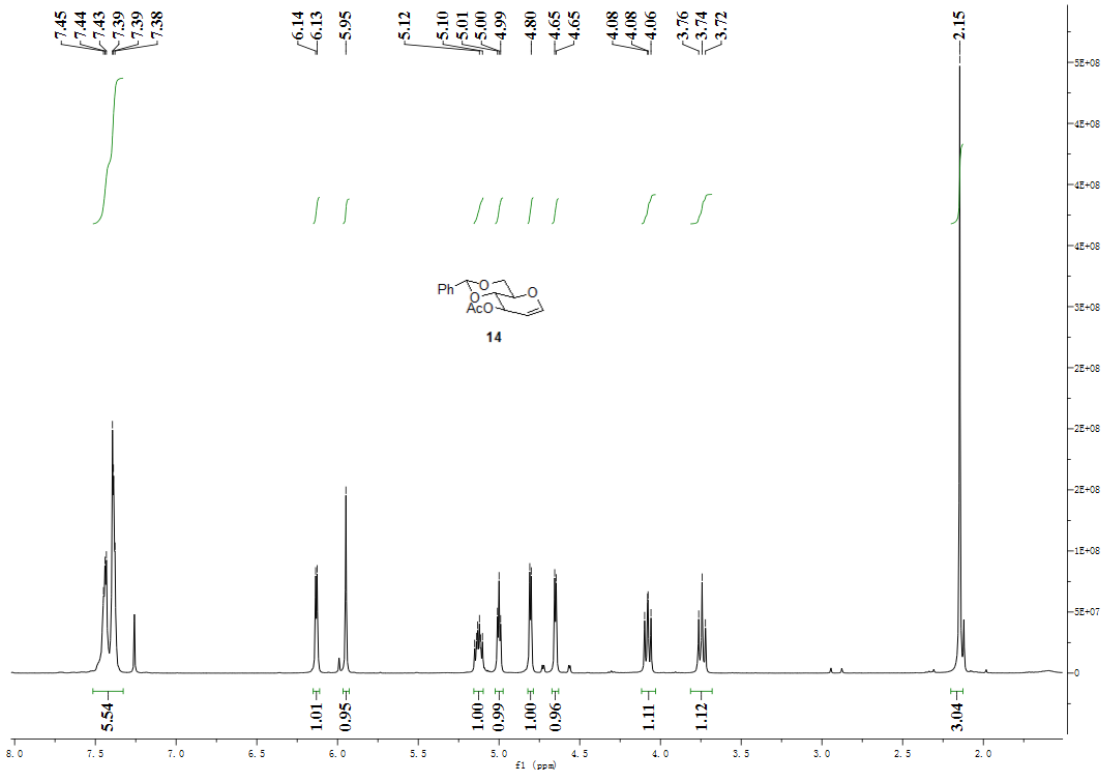
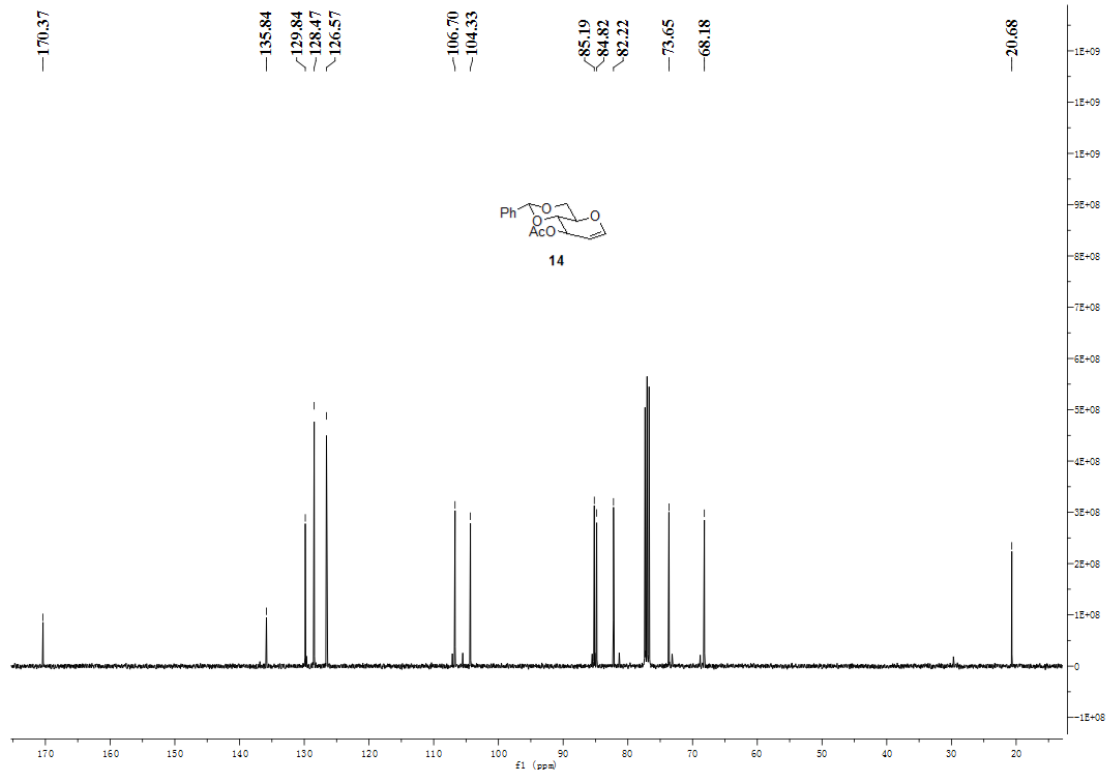
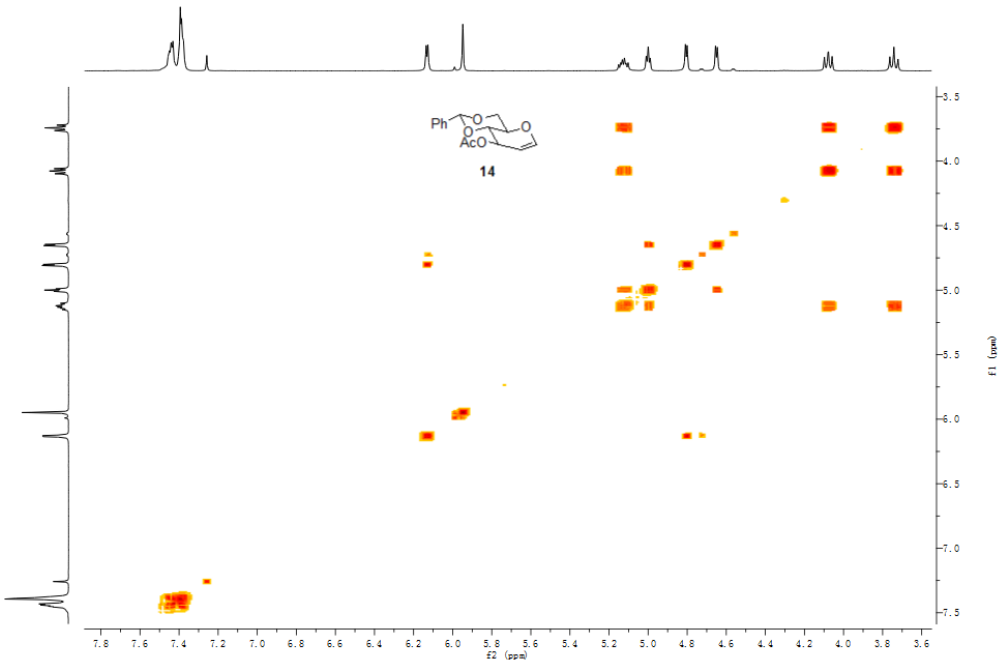
4.09
4.06
4.01
4.00
3.92
3.91
3.89
2.16
2.12
2.09
2.06
2.06
1.98
12
1.00
2.07
1.05
1.08
1.03
1.04
1.05
4.26
1.06
1.09
3.18
3.24
3.20
2.94
3.11
3.04
f1 (ppm)


170.27
170.07
169.93
169.83
169.15
145.33
100.85
98.92
74.51
74.08
70.70
70.56
68.83
68.78
66.69
61.73
60.94
20.92
20.69
20.47
20.39
12
f1 (ppm)

Compound 14


7.45
7.44
7.43
7.39
7.39
7.38
6.14
6.13
5.95
5.12
5.10
5.01
5.00
4.99
4.80
4.65
4.65
4.08
4.08
4.06
3.76
3.74
3.72
2.15
Ph
O
O
AcO
O
14
5.54
1.01
0.95
1.00
0.99
1.00
0.96
1.11
1.12
3.04
f1 (ppm)


170.37
135.84
129.84
128.47
126.57
106.70
104.33
85.19
84.82
82.22
73.65
68.18
20.68
Ph
O
O
AcO
O
14
f1 (ppm)


Ph
O
O
O
AcO
14
f2 (ppm)
f1 (ppm)