Supporting Information

Visible Light Photoredox-Catalyzed *O*-Sialylation Using Thiosialoside Donors

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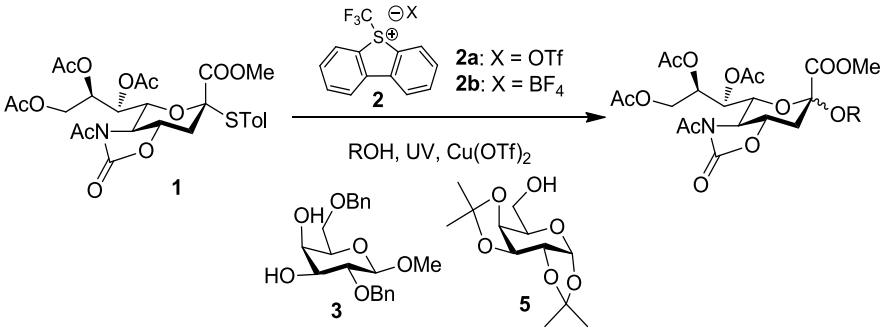
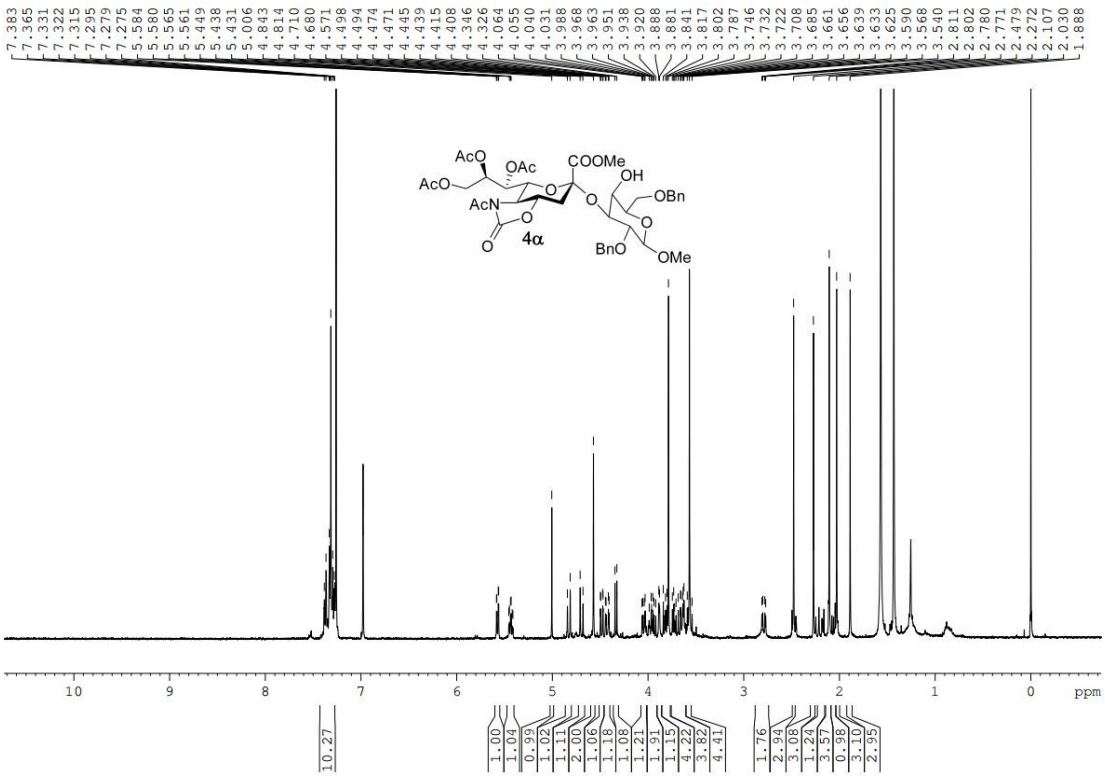
Contents

Table S1. Optimization of the reaction conditions under UV[a]



Entry	Acceptor	Light source	Activator (equiv)	Additive (equiv)	Solvent	T (^{o}C)	α:β[d]	Yield (%)
1	**3**	UV	**2a** (1.5)	$Cu(OTf)_2$ (1.3)	MeCN/DCM (2/1)	-40	α	85[b]
2	**3**	UV	**2b** (1.5)	$Cu(OTf)_2$ (1.3)	MeCN/DCM (2/1)	-40	/	0[c]
3	**5**	UV	**2a** (1.5)	$Cu(OTf)_2$ (1.3)	MeCN/DCM (2/1)	-40	1:2	32[b]
4	**5**	UV	**2a** (1.5)	$Cu(OTf)_2$ (1.3)	THF	-40	/	0[c]
5	**5**	UV	**2a** (1.5)	$Cu(OTf)_2$ (1.3)	DCM	-40	/	0[c]
6	**5**	UV	**2a** (1.5)	$Cu(OTf)_2$ (1.3)	Et_2O	-40	/	0[c]
7	**5**	UV	**2a** (1.5)	$Cu(OTf)_2$ (1.3)	MeCN/DCM (2/1)	-20	1:1.7	16[b]
8	**5**	UV	**2a** (1.5)	$Cu(OTf)_2$ (1.3)	MeCN/DCM (2/1)	-72	/	0[c]
9	**5**	UV	**2a** (1.5)	$Cu(OTf)_2$ (1.3)	MeCN/DCM (2/1)	r.t.	/	0[c]

[a]General conditions: the reaction was conducted in anhydrous conditions with activated 3Å MS and $Cu(OTf)_2$ under the irradiation of UV light. [b]Isolated yield. [c]Determined by ^{1}H NMR analysis. [d]Ratio was determined by ^{1}H NMR analysis.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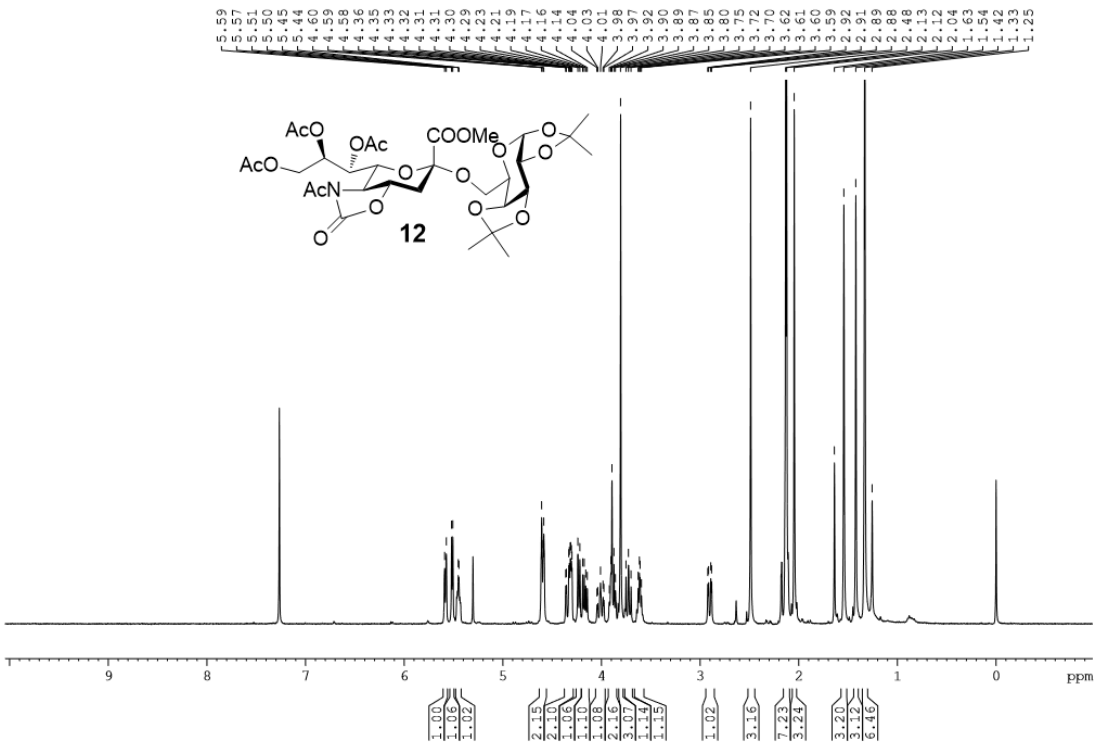
OBn
AcO
AcN
O
O
4α
BnO
OMe
ppm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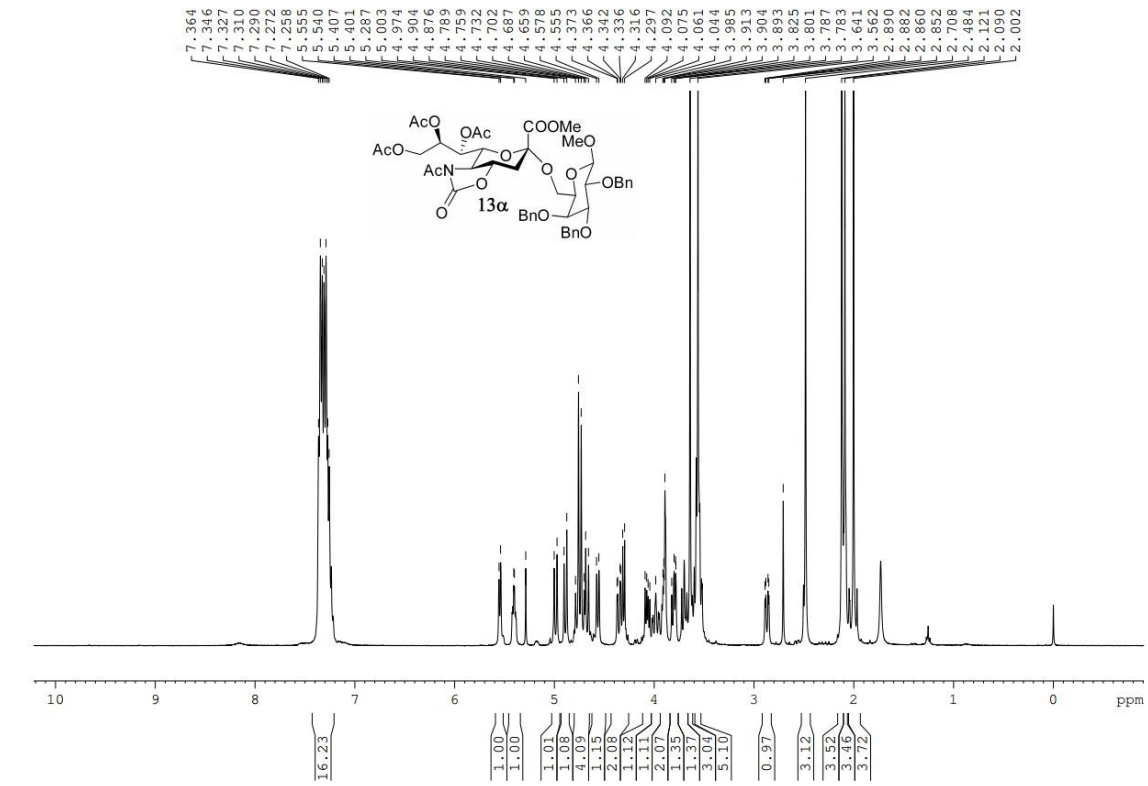
COOMe
AcO
AcN
O
O
12
ppm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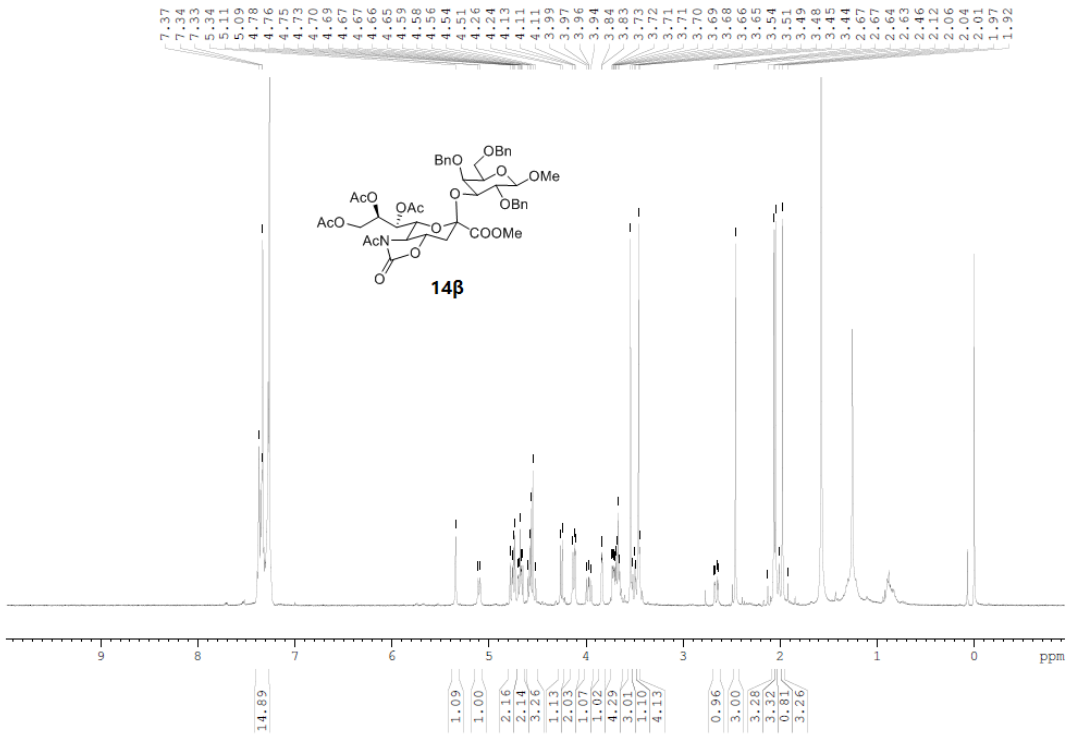
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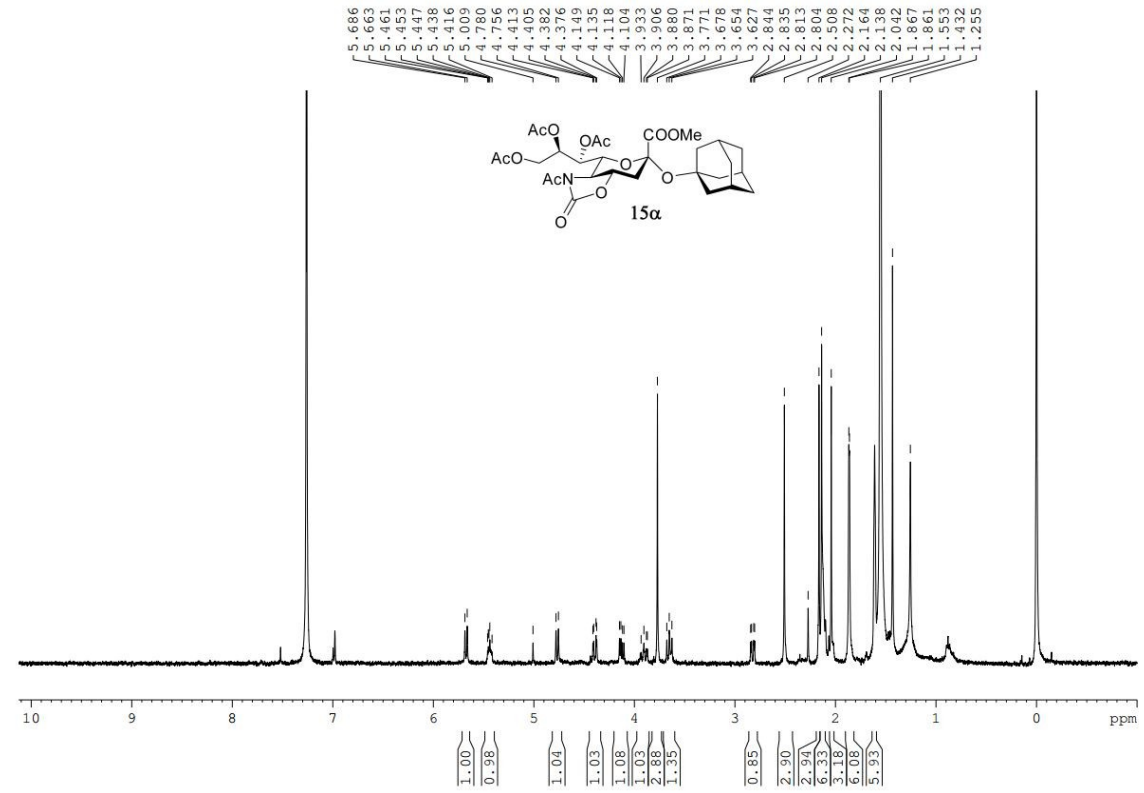
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5.461
5.453
5.447
5.438
5.416
5.009
4.780
4.756
4.413
4.405
4.382
4.376
4.149
4.135
4.118
4.104
3.933
3.906
3.880
3.871
3.771
3.678
3.654
3.627
2.844
2.835
2.813
2.804
2.508
2.272
2.164
2.138
2.042
1.867
1.861
1.553
1.432
1.255
AcO
OAc
COOMe
AcO
AcN
O
O
15α
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.98
1.04
1.03
1.08
1.03
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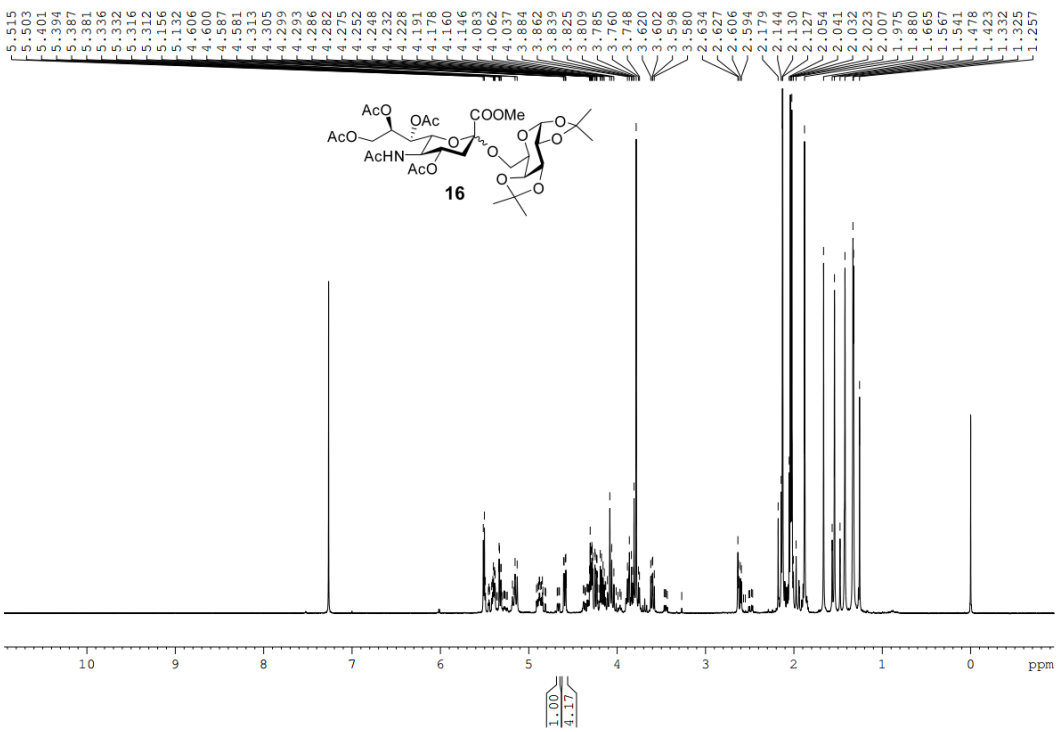
1.35
0.85
2.90
2.94
6.33
3.18
6.08
5.93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4.299
4.293
4.286
4.282
4.275
4.252
4.248
4.232
4.228
4.191
4.178
4.160
4.146
4.083
4.062
4.037
3.884
3.862
3.839
3.825
3.809
3.785
3.760
3.748
3.620
3.602
3.598
3.580
2.634
2.627
2.606
2.594
2.179
2.144
2.130
2.127
2.054
2.041
2.032
2.023
2.007
1.975
1.880
1.665
1.567
1.541
1.478
1.423
1.332
1.325
1.257
AcO
OAc
COOMe
AcO
AcHN
AcO
O
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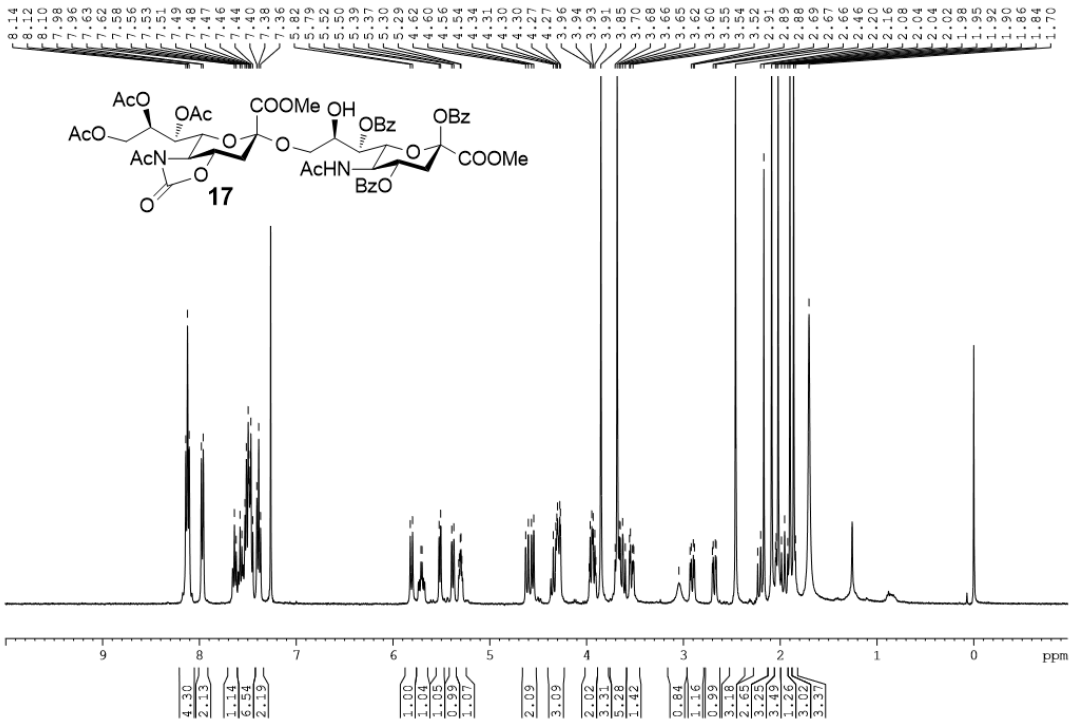
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
4.17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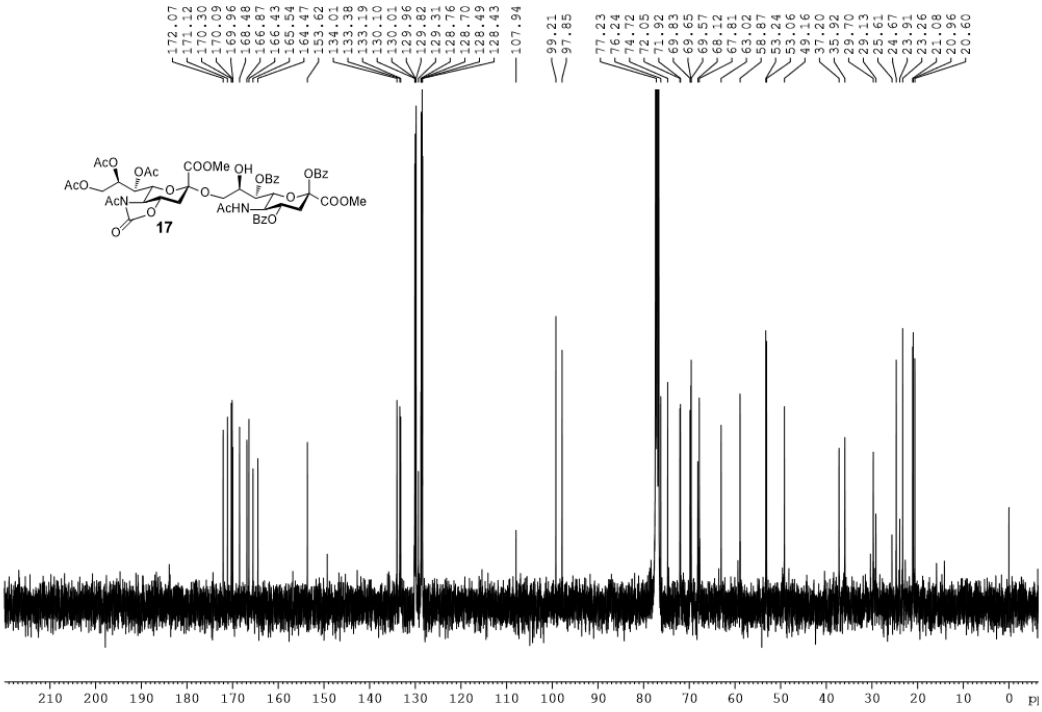
COOMe
OH
OBz
OBz
AcHN
BzO
COOMe
17
ppm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OAc
AcO
AcN
COOMe
OH
OBz
OBz
AcHN
BzO
COOMe
17
ppm

Selective-proton-decoupling ^{13}C NMR spectrum of compound **17**