SUPPORTING INFORMATION

Carbohydrate based chiral iodoarene catalysts: A survey through the development of an improved catalyst design

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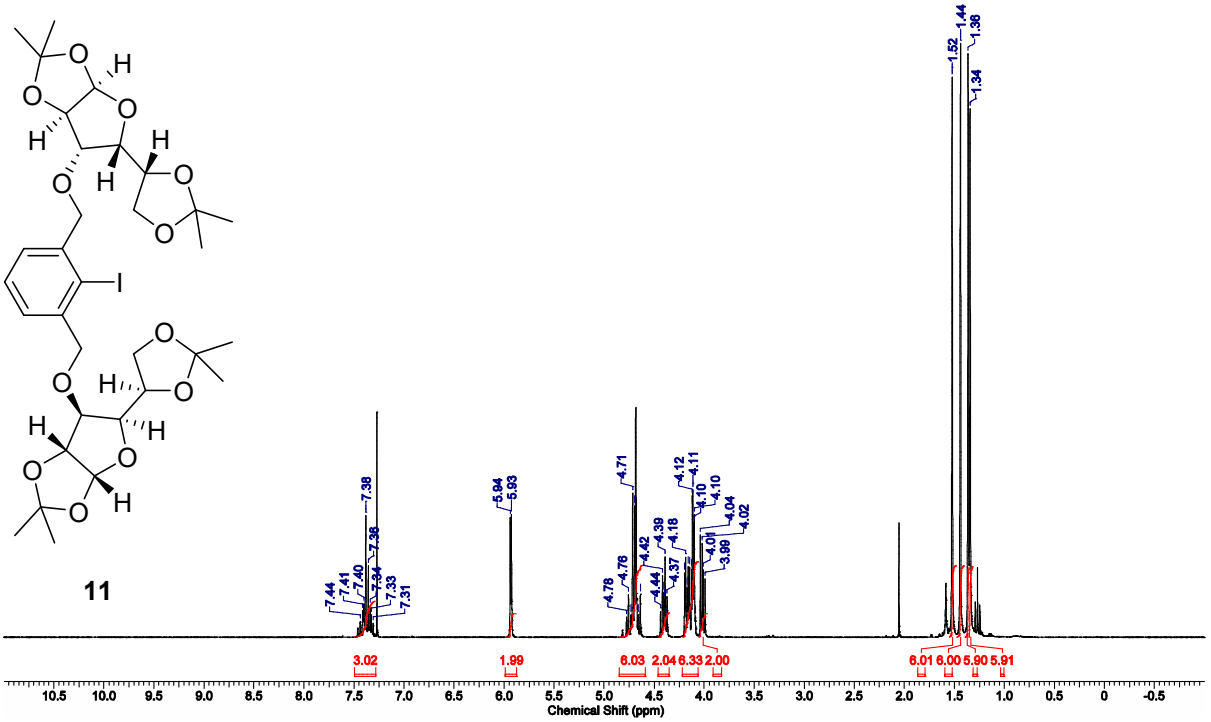
NMR Spectra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4.01
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6.00
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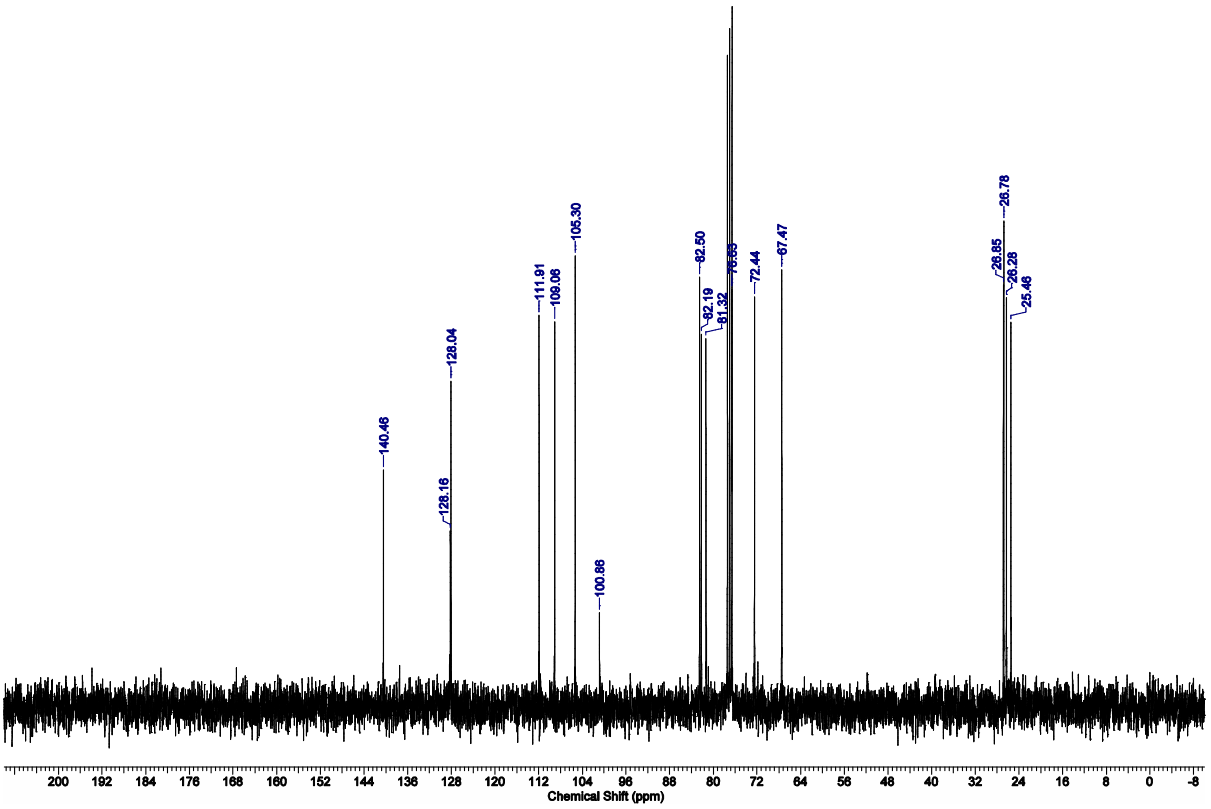
5.91
Chemical Shift (ppm)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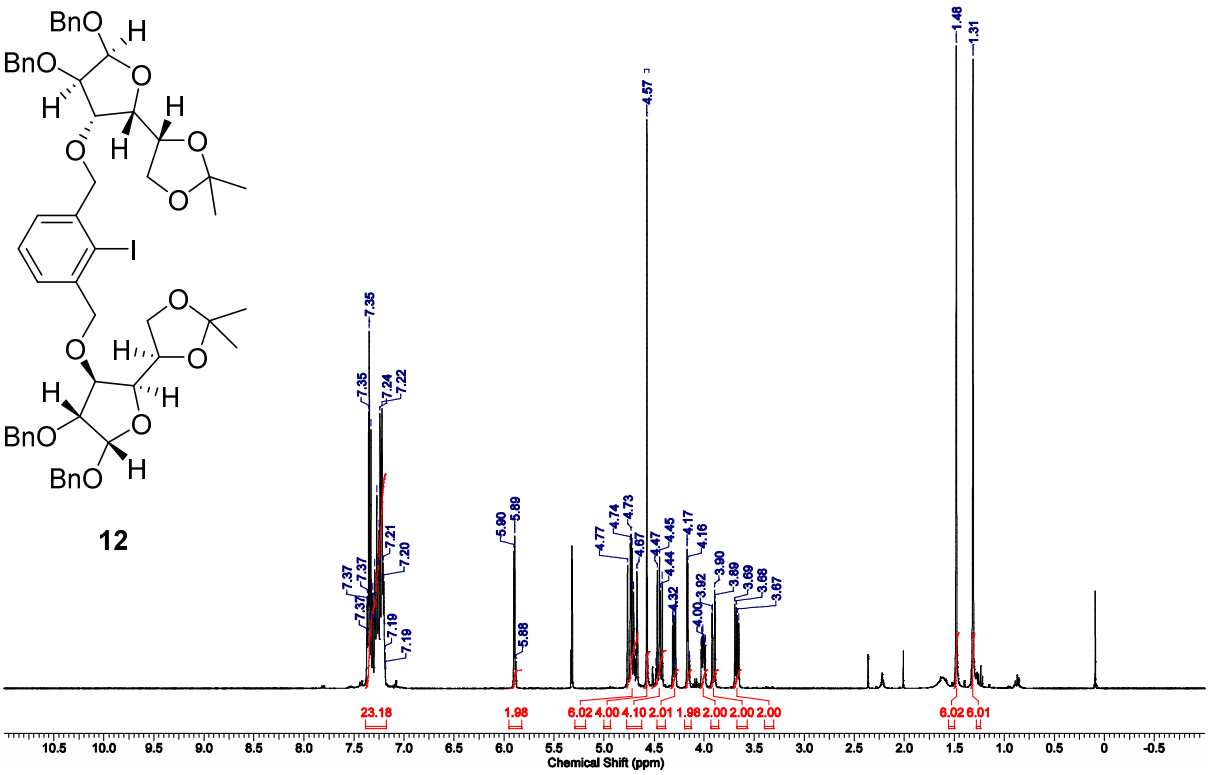
Chemical Shift (ppm)

12



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5.89
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4.73
4.67
4.57
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4.45
4.44
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4.17
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3.89
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3.68
3.67
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1.98
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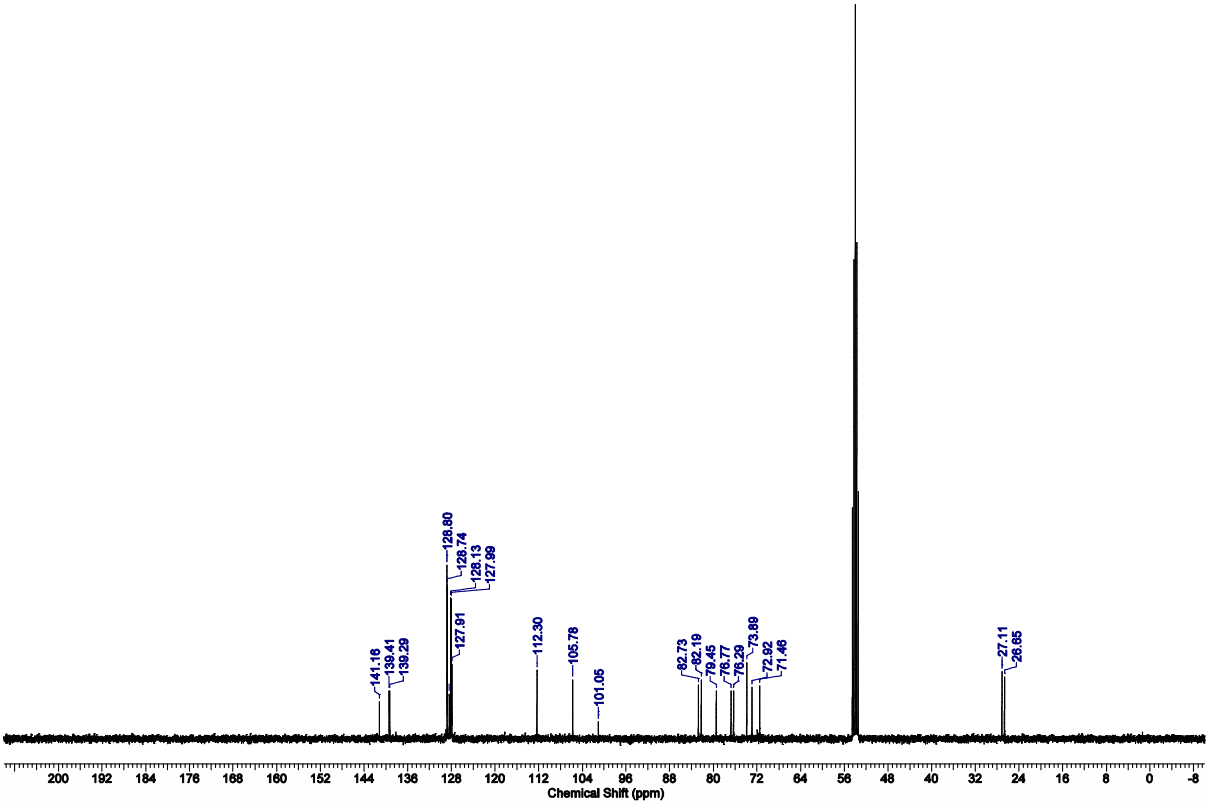
Chemical Shift (ppm)



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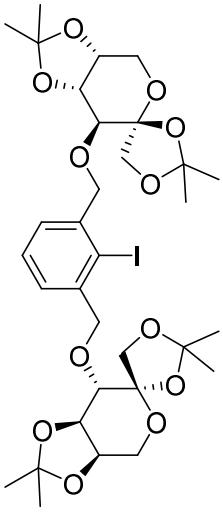
71.46
27.11
26.65
Chemical Shift (ppm)



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7.46
5.04
4.73
4.44
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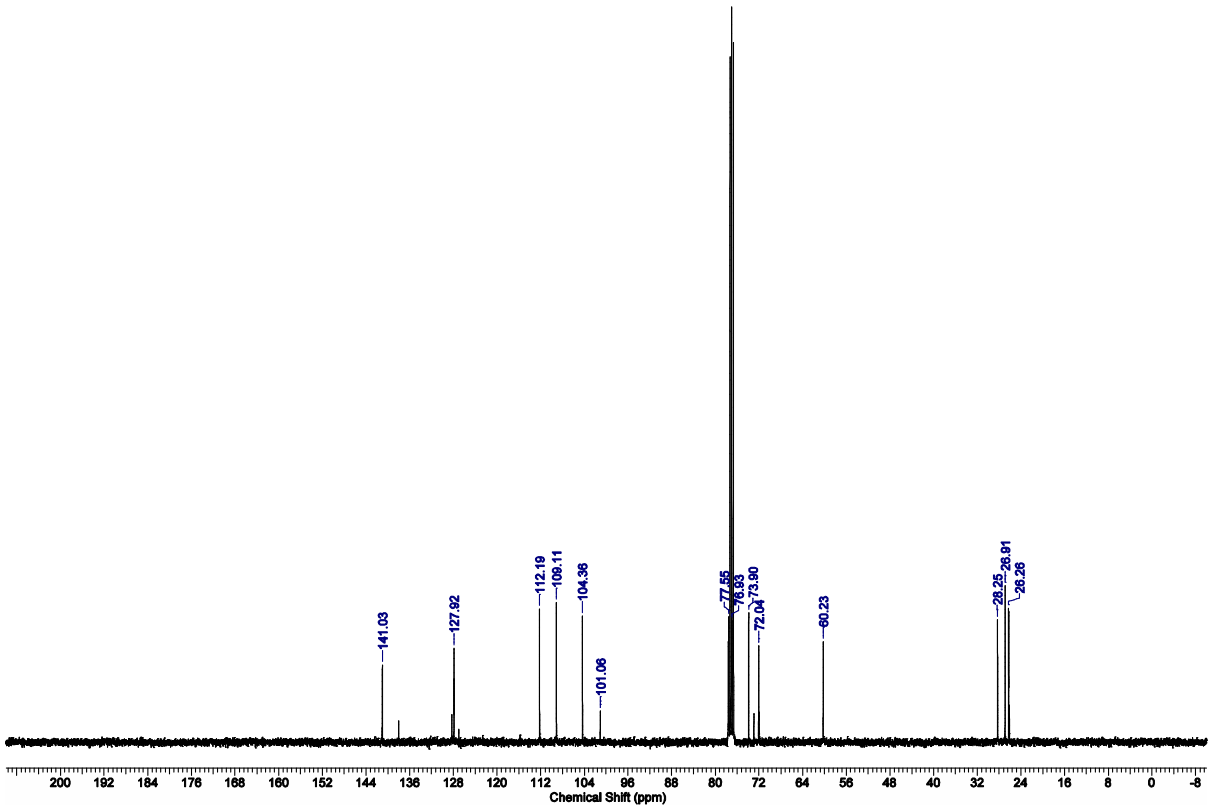
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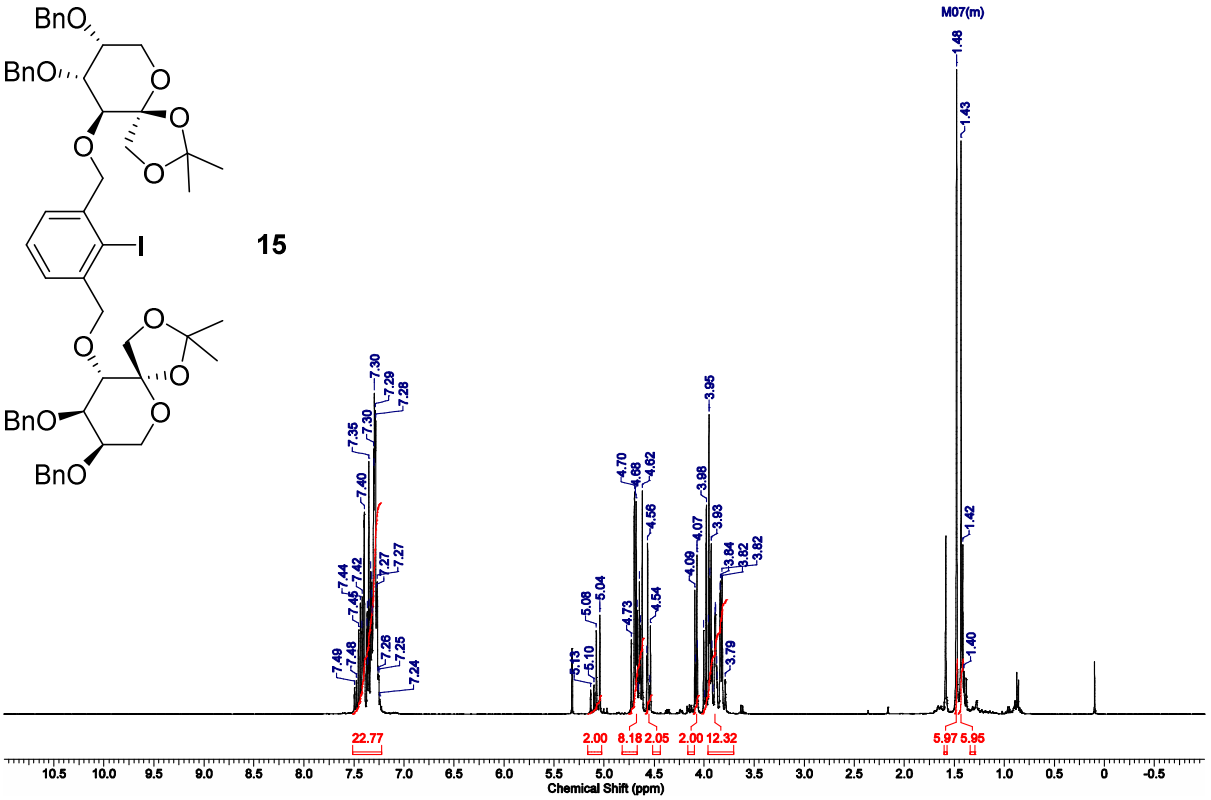
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BnO
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O
O
O
I
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M07(m)
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1.43
1.42
1.40
7.30
7.29
7.28
7.35
7.30
7.40
7.44
7.42
7.27
7.27
7.49
7.48
7.45
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7.25
7.24
6.13
6.10
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3.93
3.84
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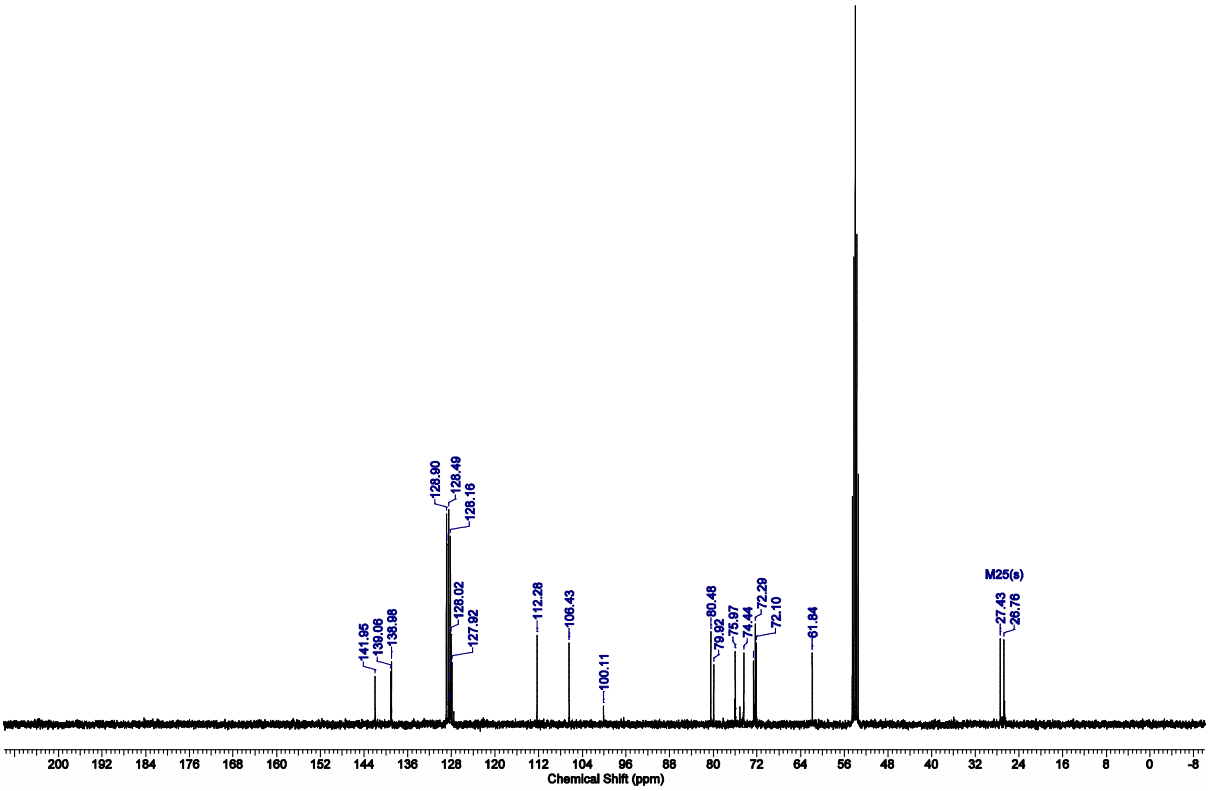
Chemical Shift (ppm)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61.84
M25(s)
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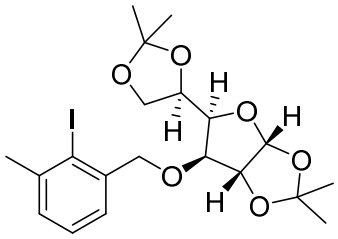
Chemical Shift (ppm)



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4.48
4.46
4.45
4.25
4.20
4.18
4.17
4.08
4.07
4.05
2.54
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1.50
1.42
1.40
3.31
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0.99
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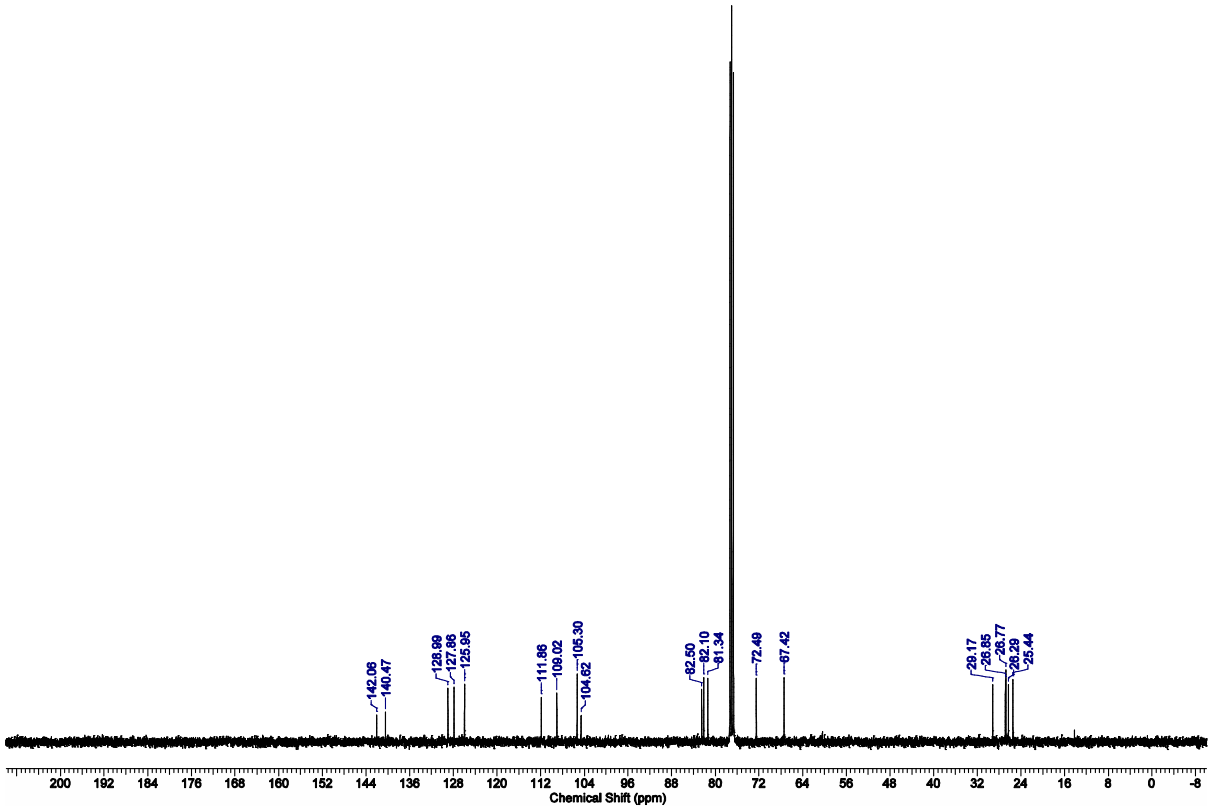
1.00
2.97
2.99
2.97
2.99
3.00
Chemical Shift (ppm)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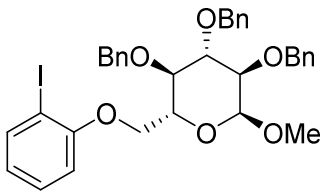
Chemical Shift (ppm)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BnO
OBn
I
O
O
OMe

20

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7.38
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4.00
4.02
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3.85
4.20
4.19
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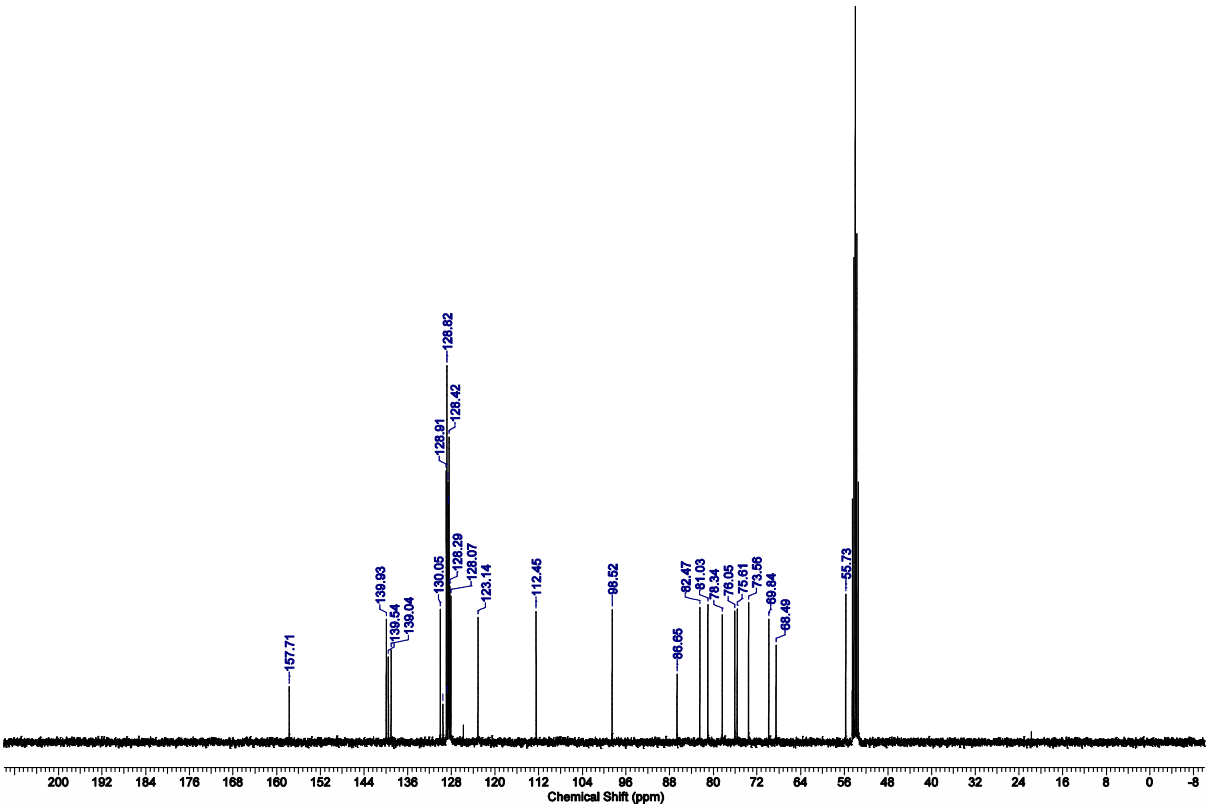
1.99
1.04 1.00 1.01 2.01 2.03 0.99 1.01 2.03 1.01 1.03 3.00
Chemical Shift (ppm)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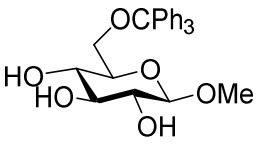
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HO
O
OMe
OH

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4.08
4.04
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3.44
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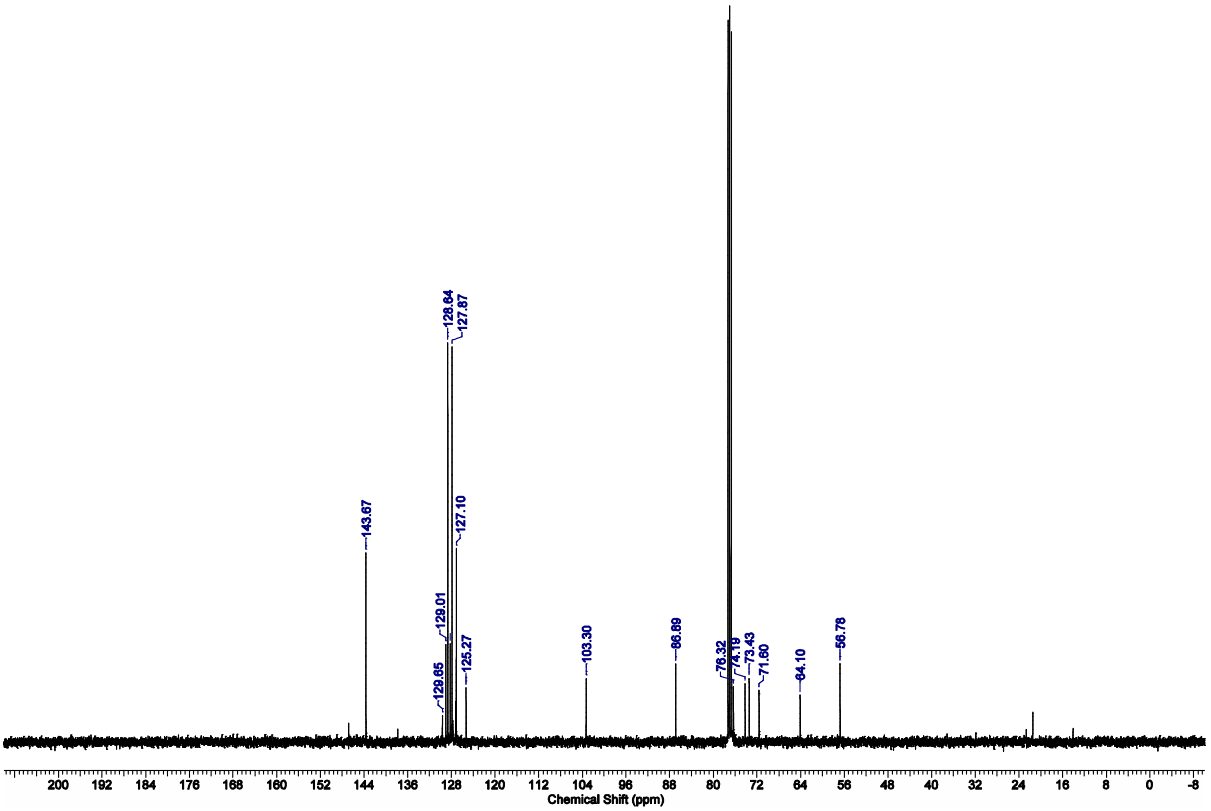
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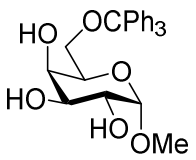
HO
OCPh3
O
HO
HO
OMe

26

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4.70
3.90
3.89
3.73
3.71
3.70
3.34
3.29
3.28
3.27
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1.05
4.00
1.16
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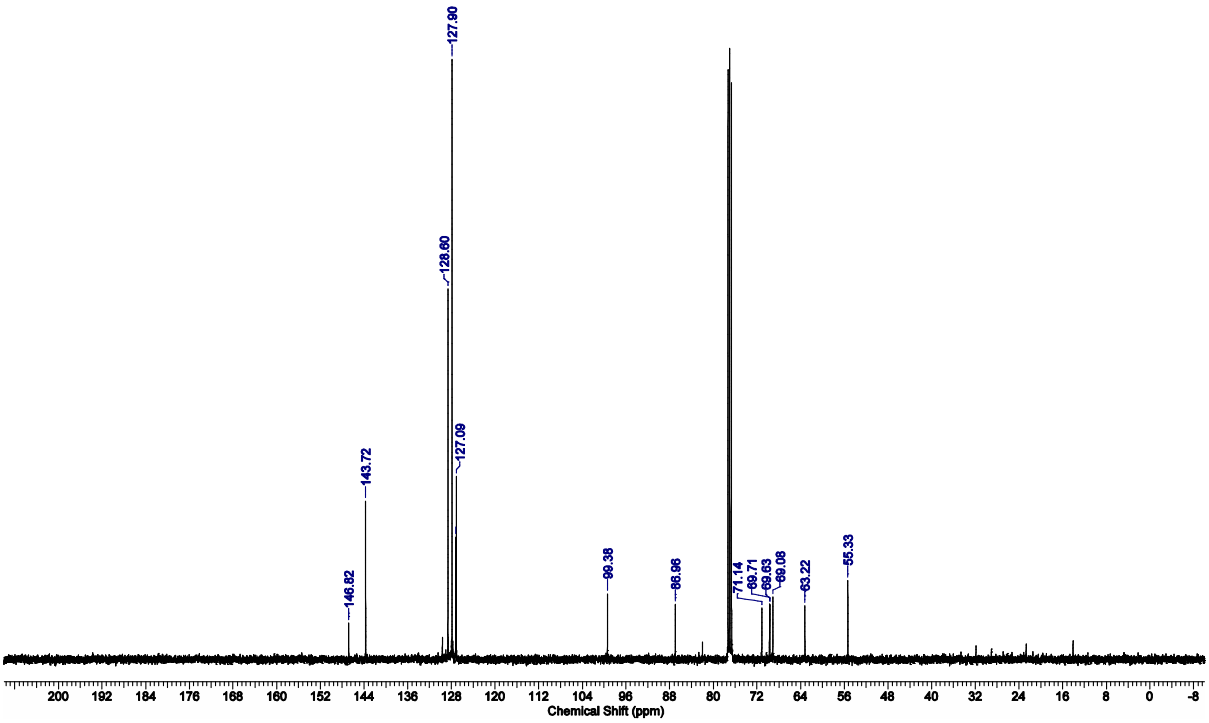
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69.08
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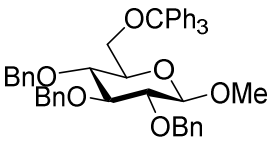
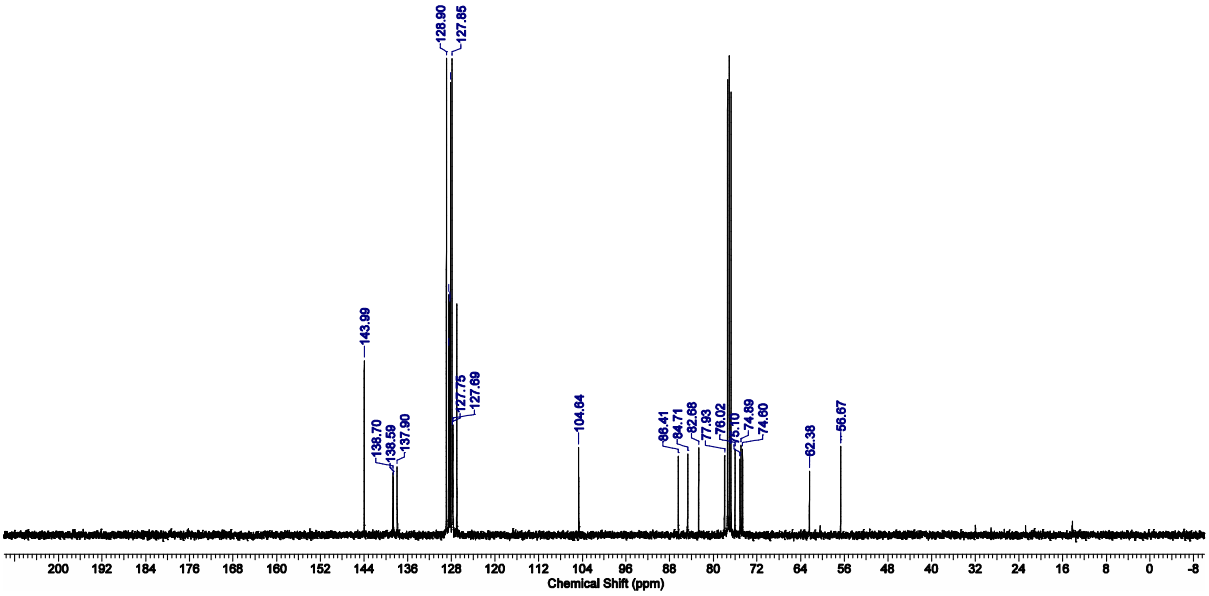
55.33
Chemical Shift (ppm)


OCPh3
BnO
BnO
O
OMe
OBn

27

Chemical Shift (ppm)


Chemical Shift (ppm)

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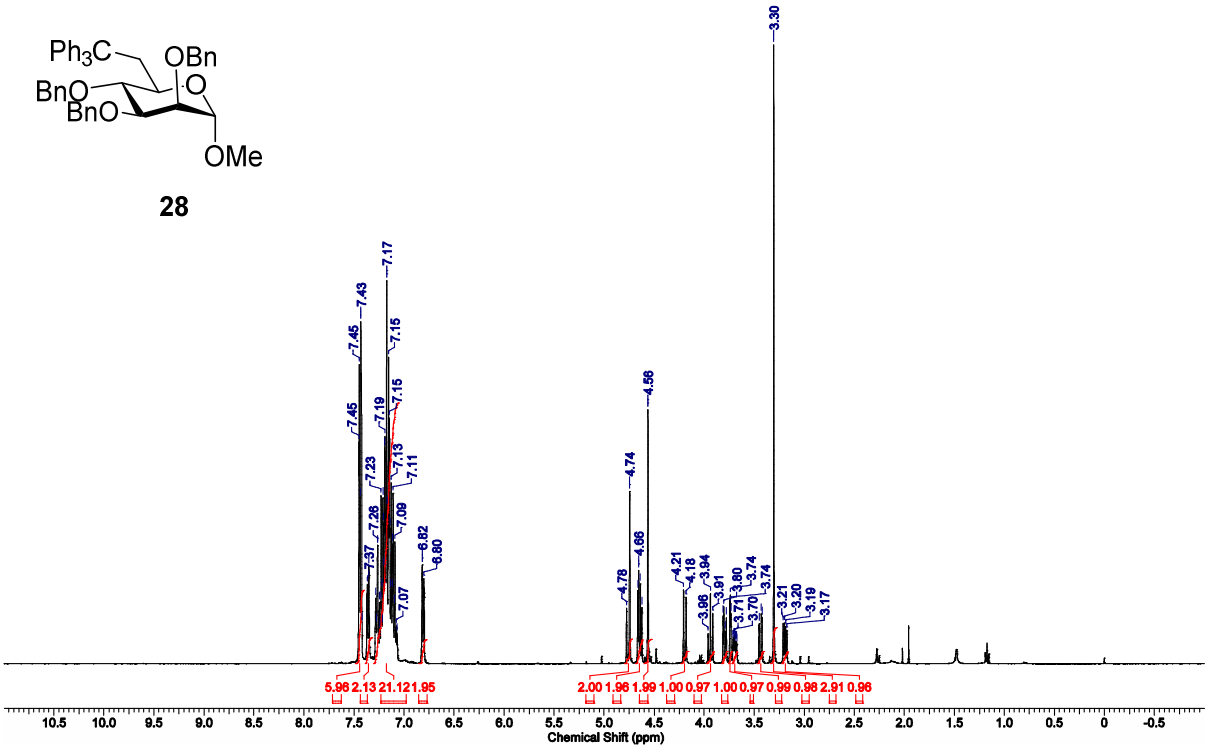
OBn
BnO
BnO
O
OMe

28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4.78
4.21
4.18
3.94
3.96
3.91
3.80
3.71
3.74
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3.74
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3.19
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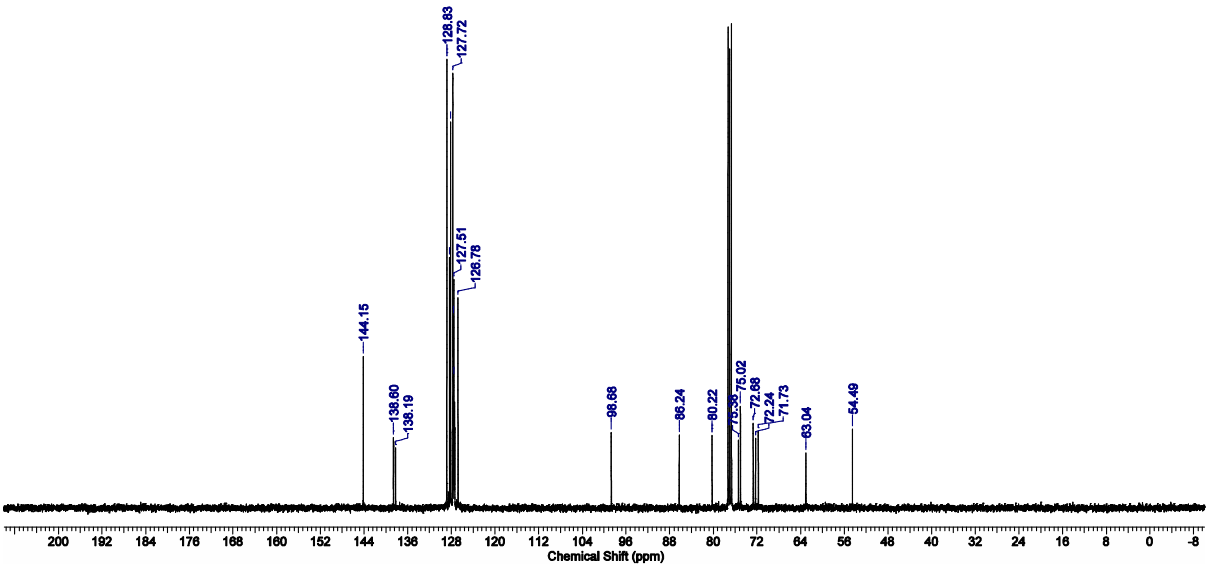
Chemical Shift (ppm)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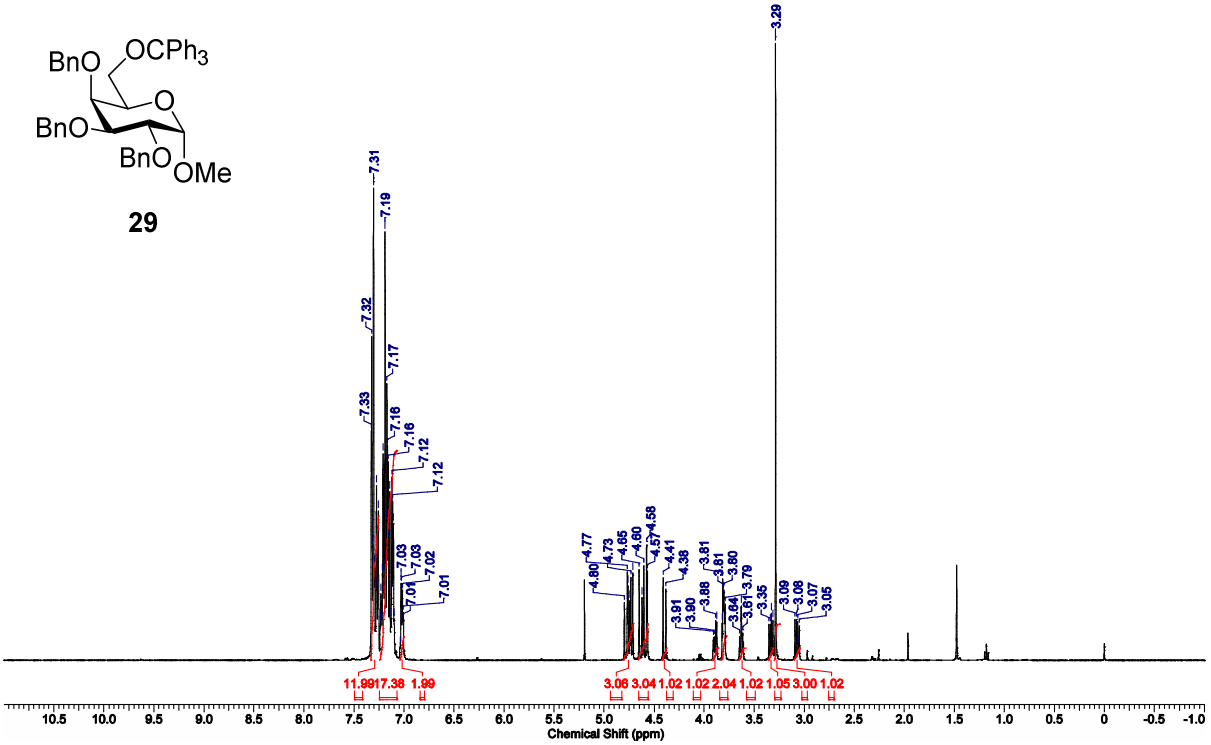
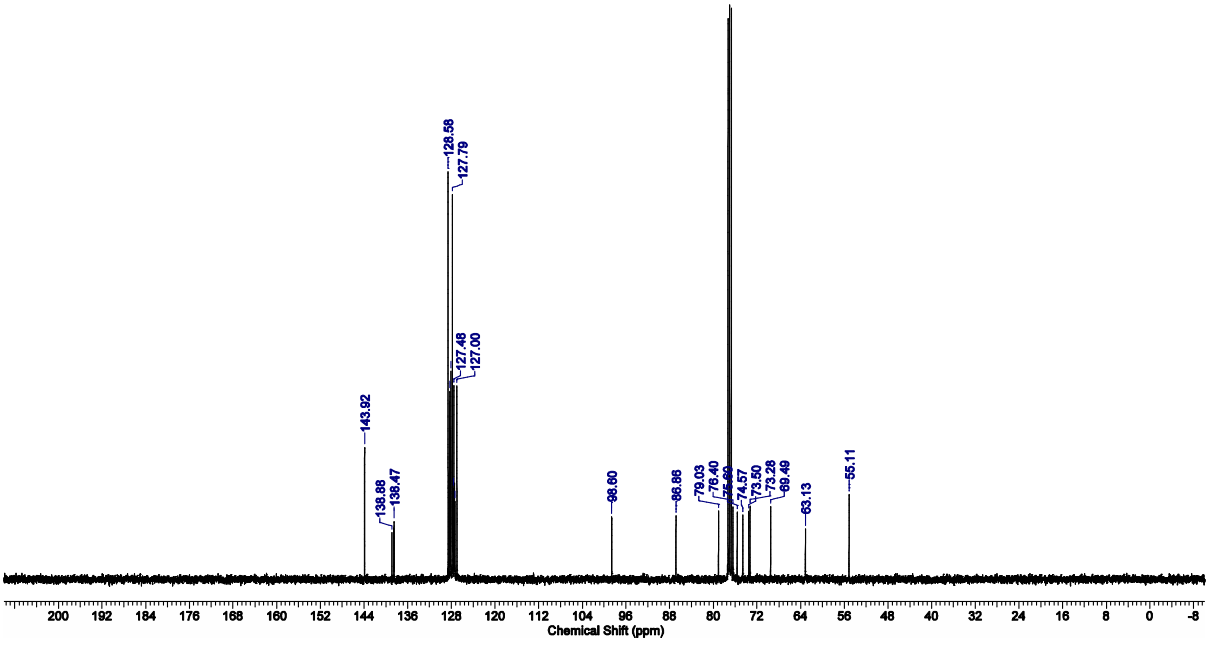
71.73
63.04
54.49
Chemical Shift (ppm)


BnO
OCPh3
O
BnO
BnO
OMe
29
Chemical Shift (ppm)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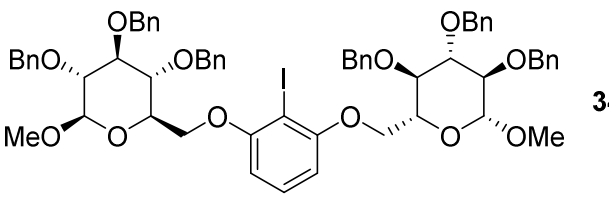
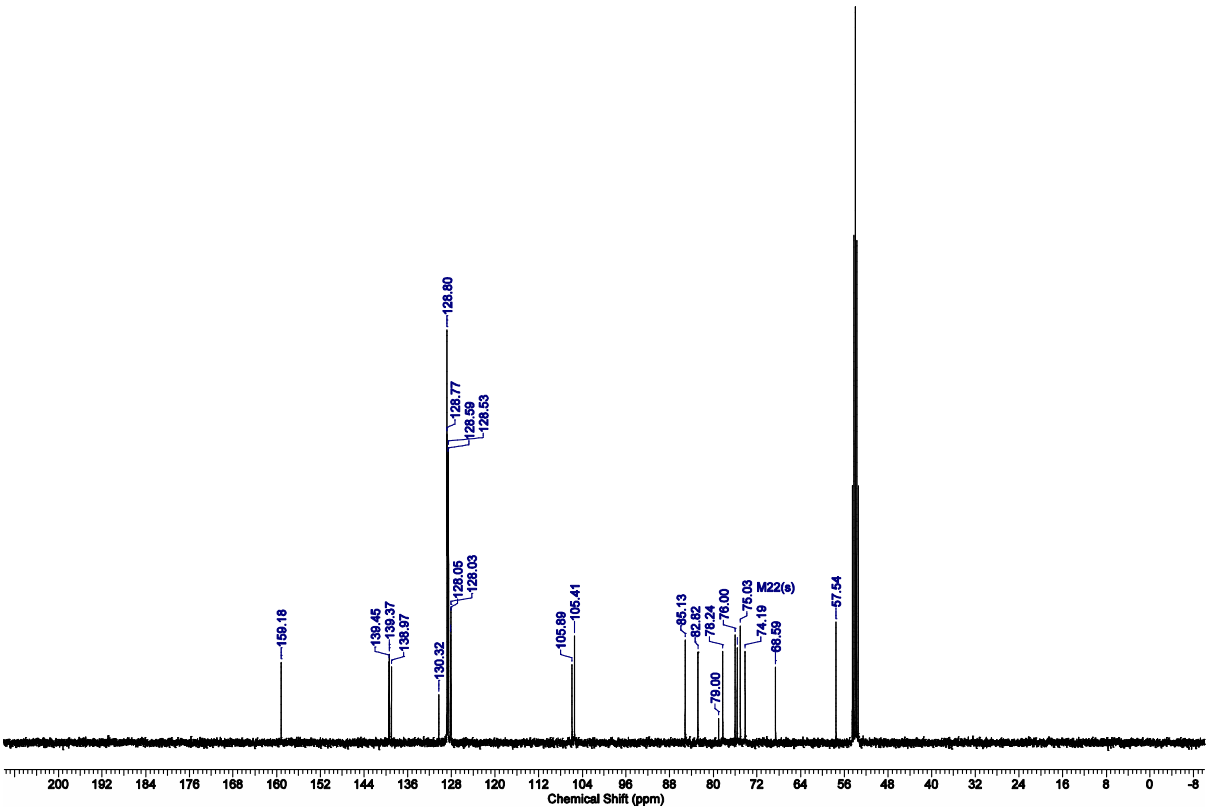

OBn
BnO
OBn
MeO
O
O
I
O
OBn
BnO
OBn
O
OMe

34

3.57
7.33
7.33
7.31
7.24
7.37
7.37
7.24
7.21
7.20
7.39
7.19
6.50
6.46
4.93
4.92
4.86
4.85
4.95
4.76
4.67
4.40
4.38
4.31
4.31
3.95
3.92
3.70
3.50
3.48
3.48
3.46
31.00
2.02
6.09 2.03 2.02 2.00 2.00 2.00 2.02 2.02 2.03 2.04 6.01 2.02
Chemical Shift (ppm)


128.80
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139.45
139.37
138.97
130.32
105.89
105.41
85.13
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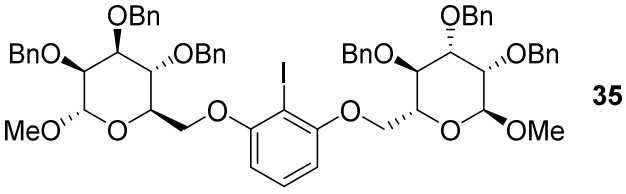
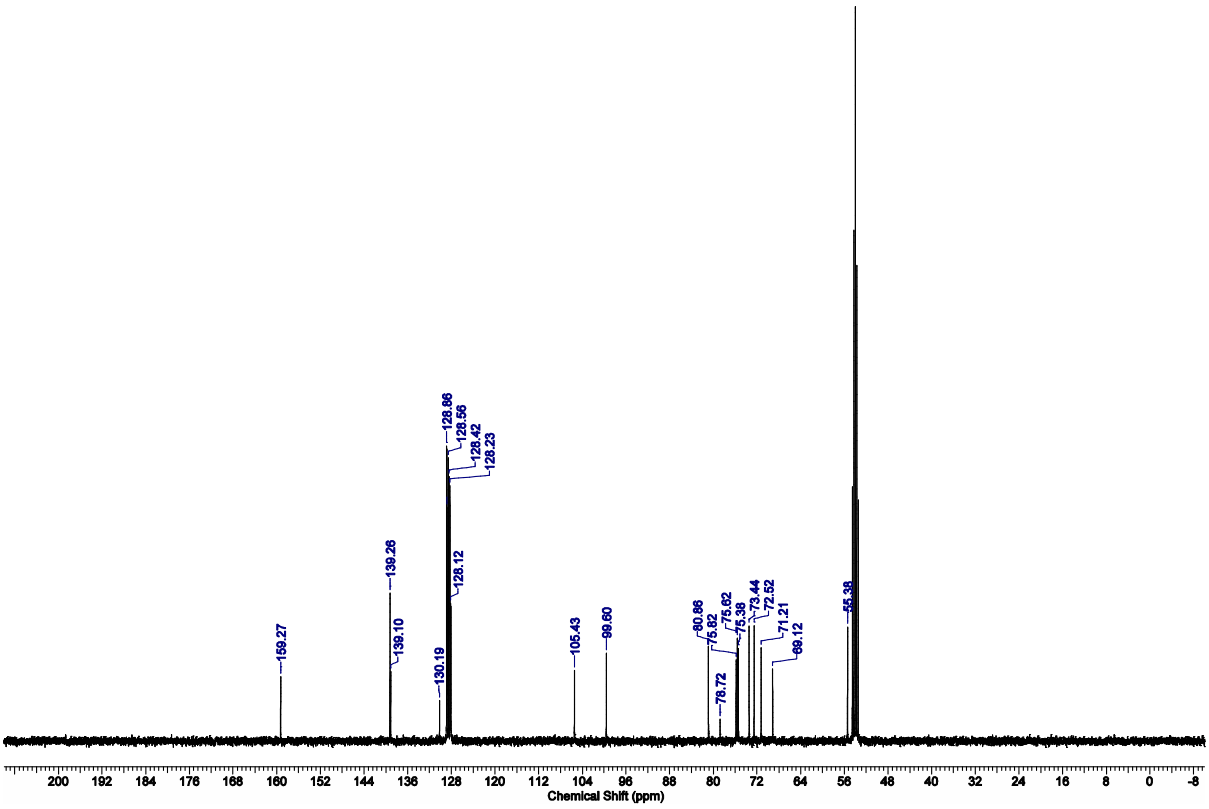
78.00
76.00
75.03
74.19
68.59
M22(s)
57.54
Chemical Shift (ppm)


OBn
BnO
OBn
MeO
O
O
I
O
OBn
BnO
OBn
O
OMe

35

3.40
7.25
7.26
7.35
7.33
7.42
7.39
7.44
7.44
7.24
7.23
7.20
7.18
6.44
6.42
4.95
4.83
4.82
4.76
4.72
4.69
4.68
4.64
4.61
4.25
4.21
4.18
4.16
3.95
3.92
3.88
3.88
3.87
31.34
2.02
2.03 2.03 8.03 2.04 2.04 4.05 6.06
6.00
Chemical Shift (ppm)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128.23
128.12
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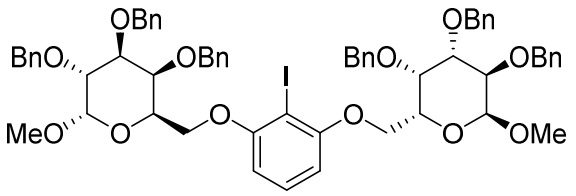
71.21
69.12
55.38
Chemical Shift (ppm)


OBn
BnO
OBn
MeO
O
O
I
O
OBn
BnO
OBn
O
OMe

36

7.25
3.43
7.37
7.37
7.44
7.45
6.42
6.40
4.97
4.87
4.83
4.80
4.79
4.69
4.56
4.53
4.17
4.02
4.01
4.01
4.00
3.98
3.94
3.94
7.23
7.22
7.19
7.19
7.18
7.17
3.93
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2.06
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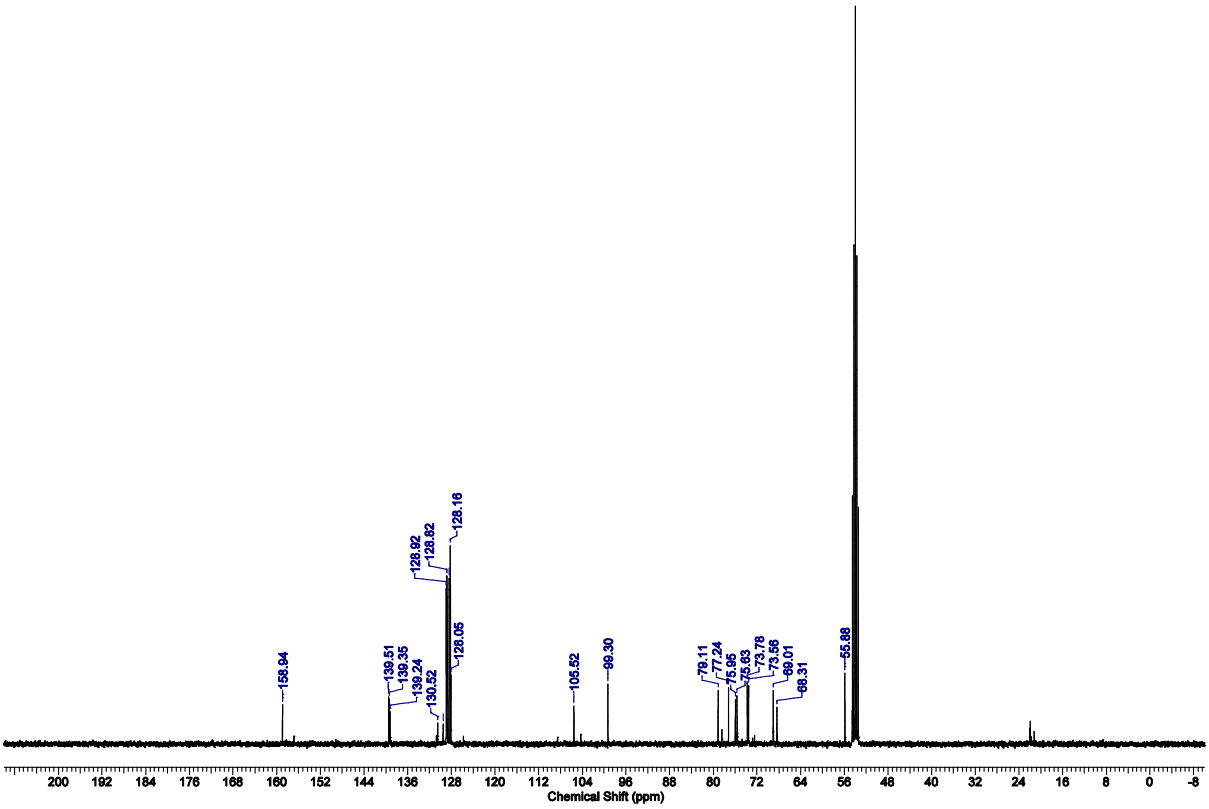
3.99
8.00
5.94
Chemical Shift (ppm)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158.94
139.51
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139.24
130.52
105.52
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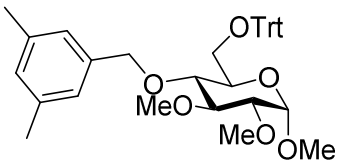
77.24
75.95
75.63
73.78
73.56
69.01
68.31
55.88
Chemical Shift (ppm)


OTrt
O
MeO
O
MeO
OMe

38

2.16
3.50
3.59
3.37
7.43
7.41
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7.43
7.19
7.22
7.17
7.15
6.50
6.79
7.14
7.13
4.87
4.86
4.51
4.49
4.16
4.13
3.68
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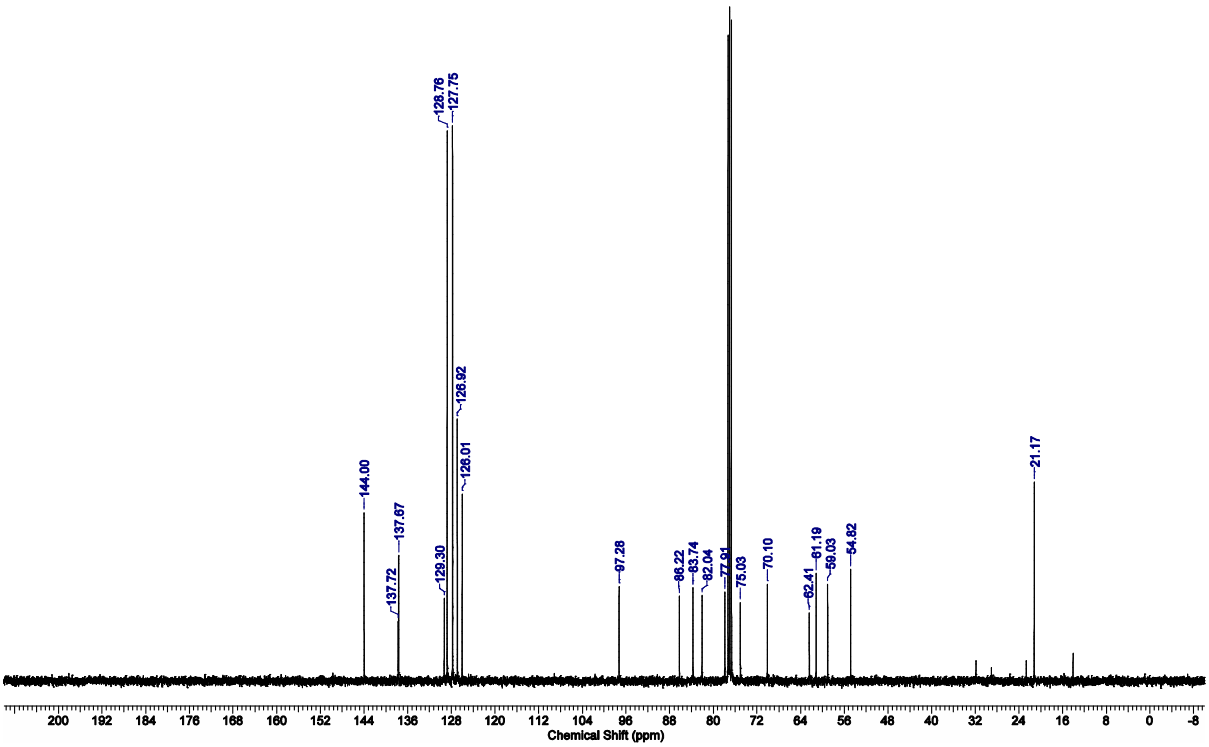
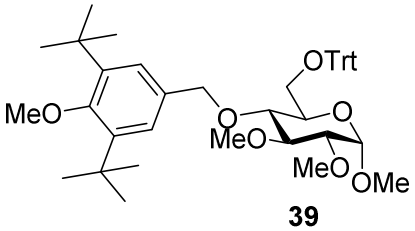
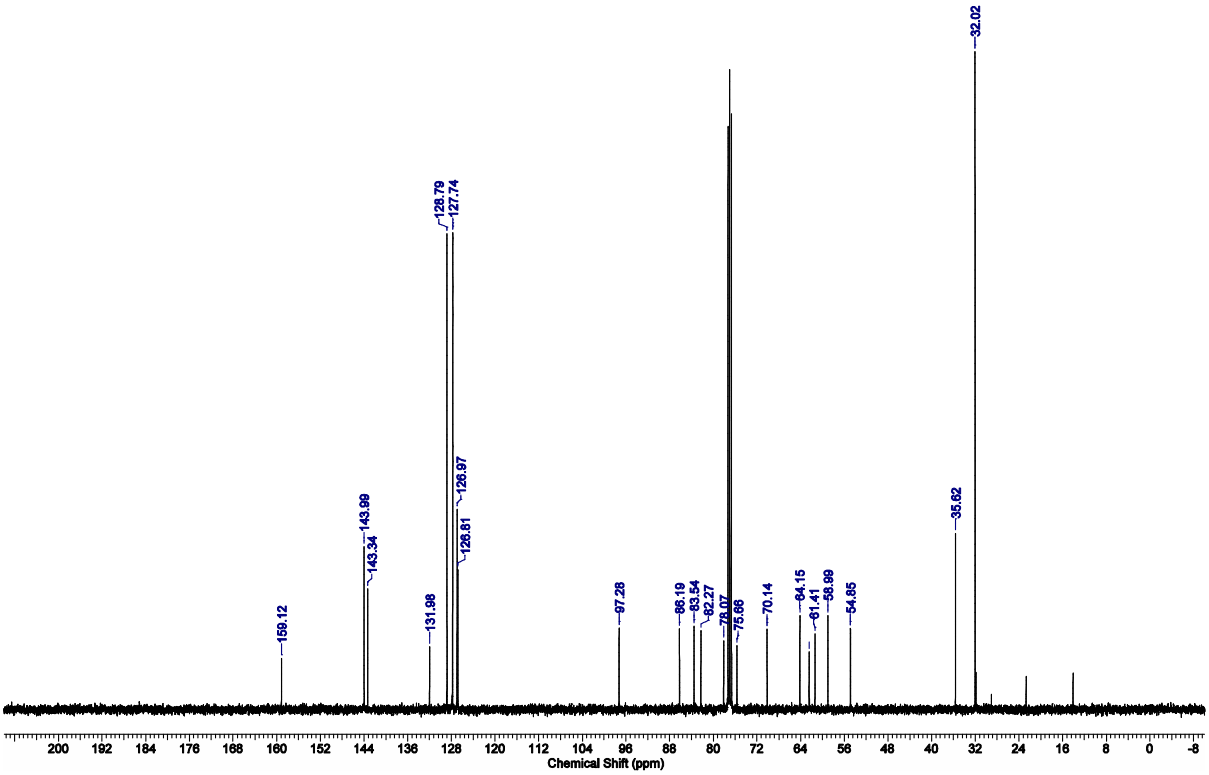
3.12
3.11
6.03 9.73
1.00 2.03
1.03 1.03 1.03 1.00 3.03 5.01 1.00 3.03 1.01 1.01 6.04
Chemical Shift (ppm)

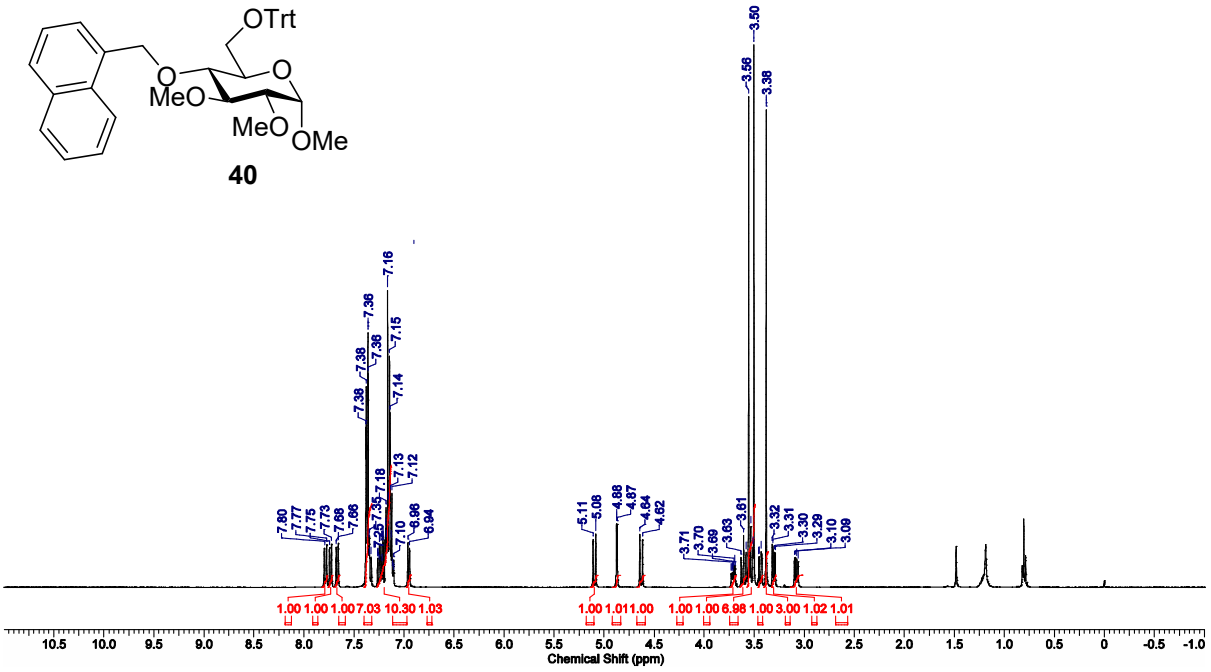

128.76
127.75
126.92
126.01
144.00
137.87
137.72
129.30
97.28
86.22
83.74
82.04
77.04
75.03
70.10
62.41
61.19
59.03
54.82
21.17
Chemical Shift (ppm)

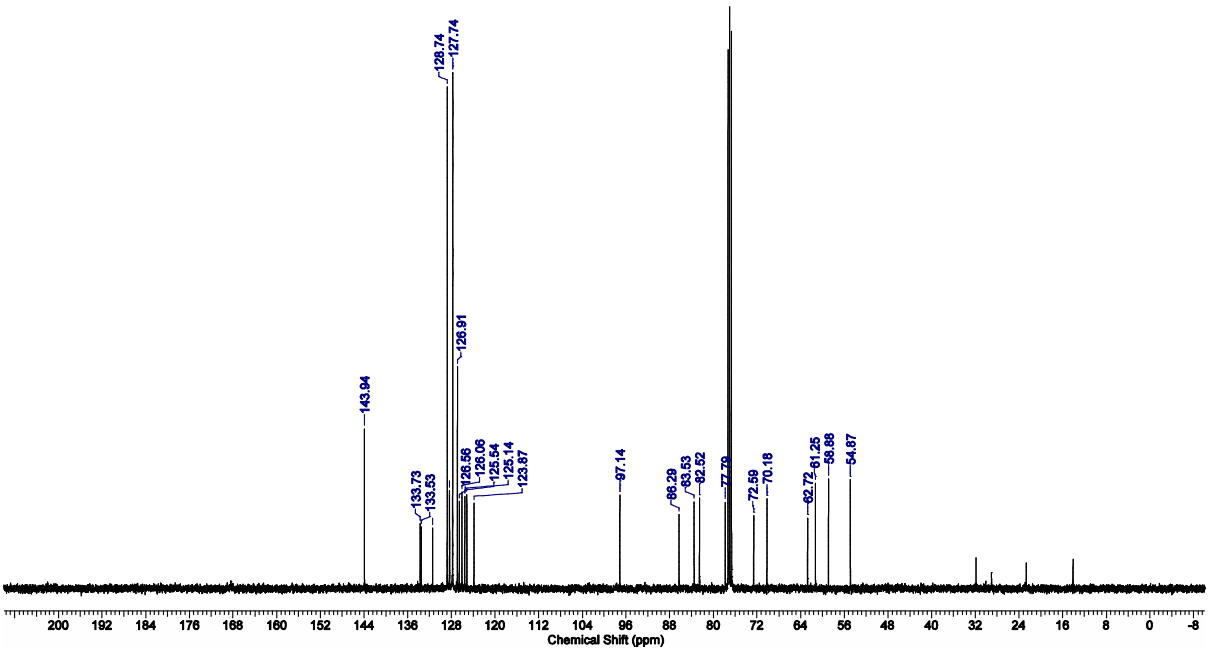

OTrt
MeO
O
O
MeO
MeO
OMe

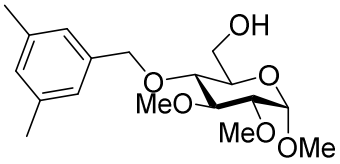
39

1.29
3.62
3.56
3.51
3.36
7.45
7.45
7.43
7.21
7.20
6.88
4.88
4.87
4.44
4.07
4.04
5.94 9.42 1.97
0.97 0.95 0.96 1.02 3.04 7.98 1.02 2.99 1.05 1.03
18.00
Chemical Shift (ppm)


32.02
128.79
127.74
126.97
126.61
143.99
143.34
159.12
131.98
97.28
86.19
83.54
82.27
78.07
75.66
70.14
64.15
61.41
58.99
54.85
35.62
Chemical Shift (ppm)

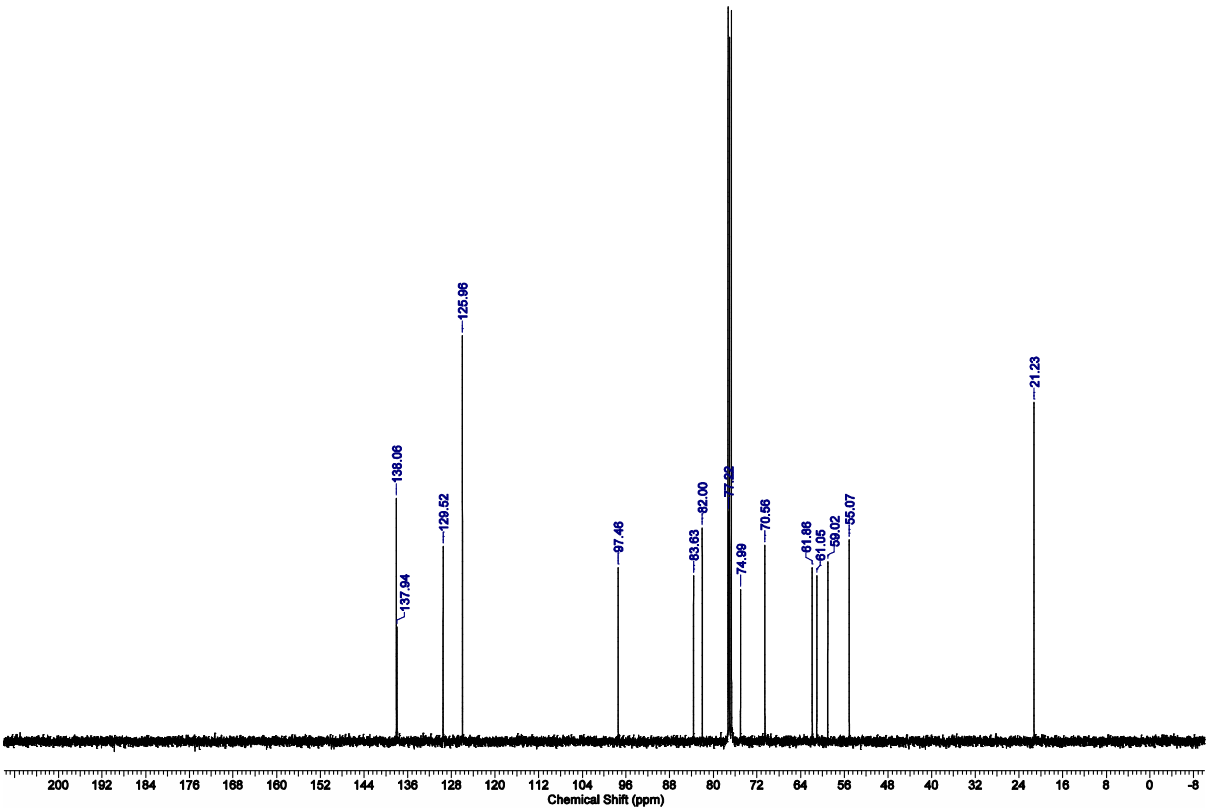

OTrt
O
MeO
O
MeO
OMe
40
Chemical Shift (ppm)

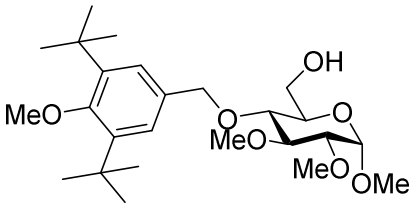

Chemical Shift (ppm)


OH
O
MeO
O
MeO
OMe

41

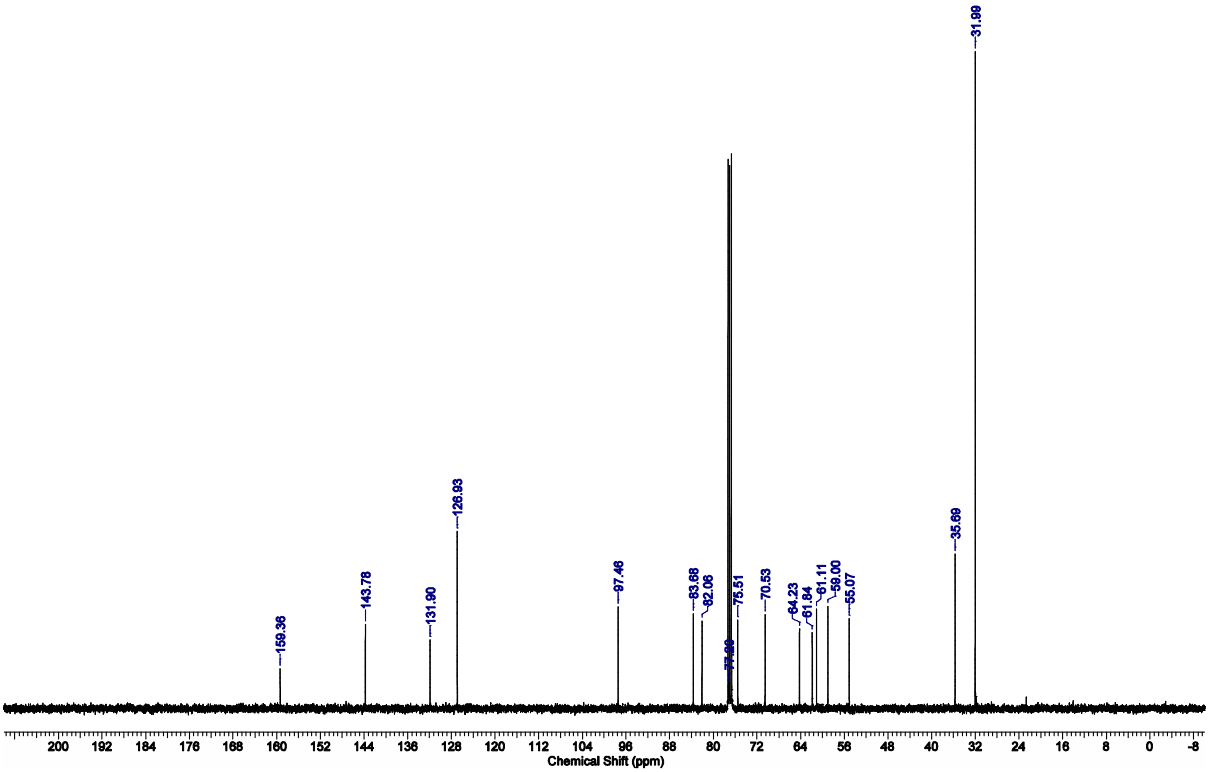
3.67
3.54
3.40
2.32
6.97
6.95
4.83
4.82
4.80
4.59
4.56
3.81
3.79
3.78
3.74
3.24
3.23
3.21
3.21
2.95
2.01
1.02
1.03
1.05
5.05
3.02
4.07
1.03
6.00
Chemical Shift (ppm)

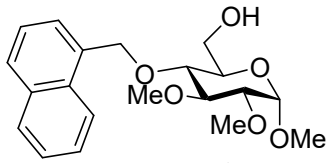

138.06
137.94
129.52
125.96
97.46
83.63
82.00
77.03
74.99
70.56
61.86
61.05
59.02
55.07
21.23
Chemical Shift (ppm)


OH
MeO
O
O
MeO
MeO
OMe

42

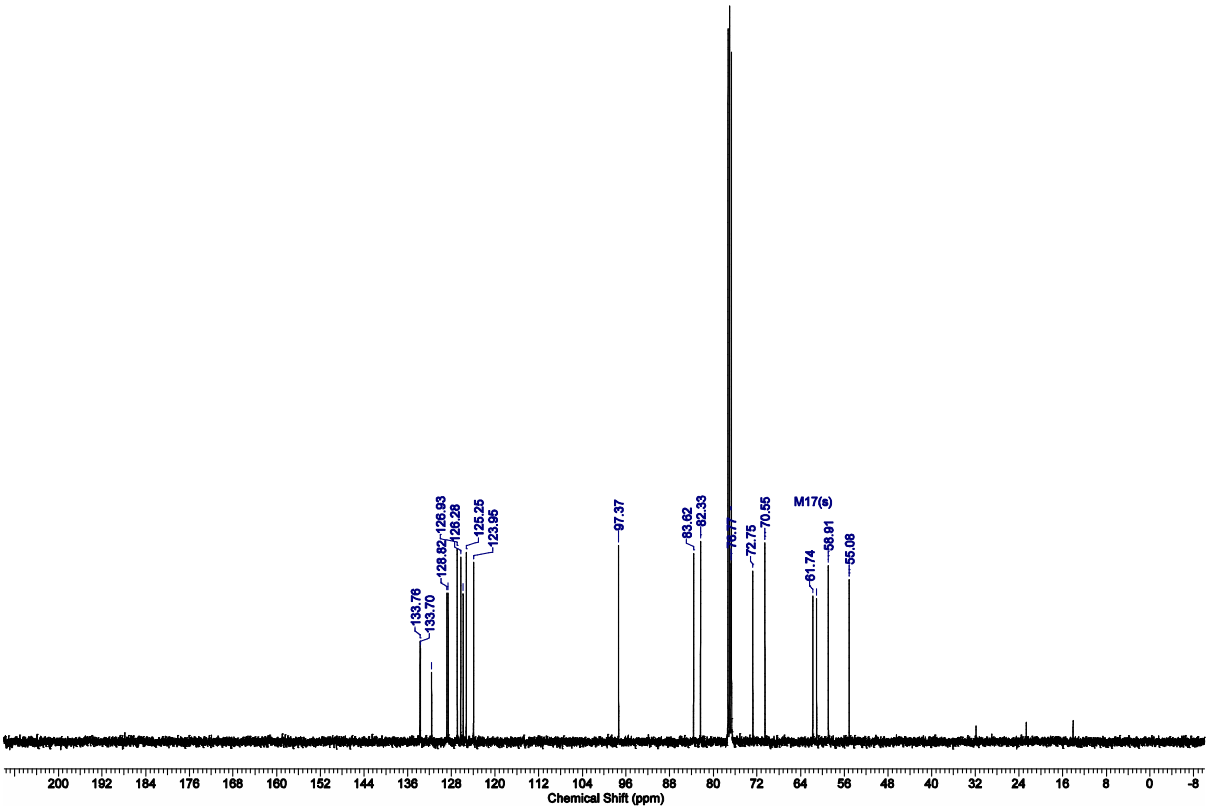
1.43
7.24
3.70
3.68
3.55
3.40
4.83
4.82
4.82
4.79
4.57
4.55
3.79
3.77
3.76
3.73
1.98
2.01
1.00
1.02
9.02
3.00
4.04
1.03
18.04
Chemical Shift (ppm)

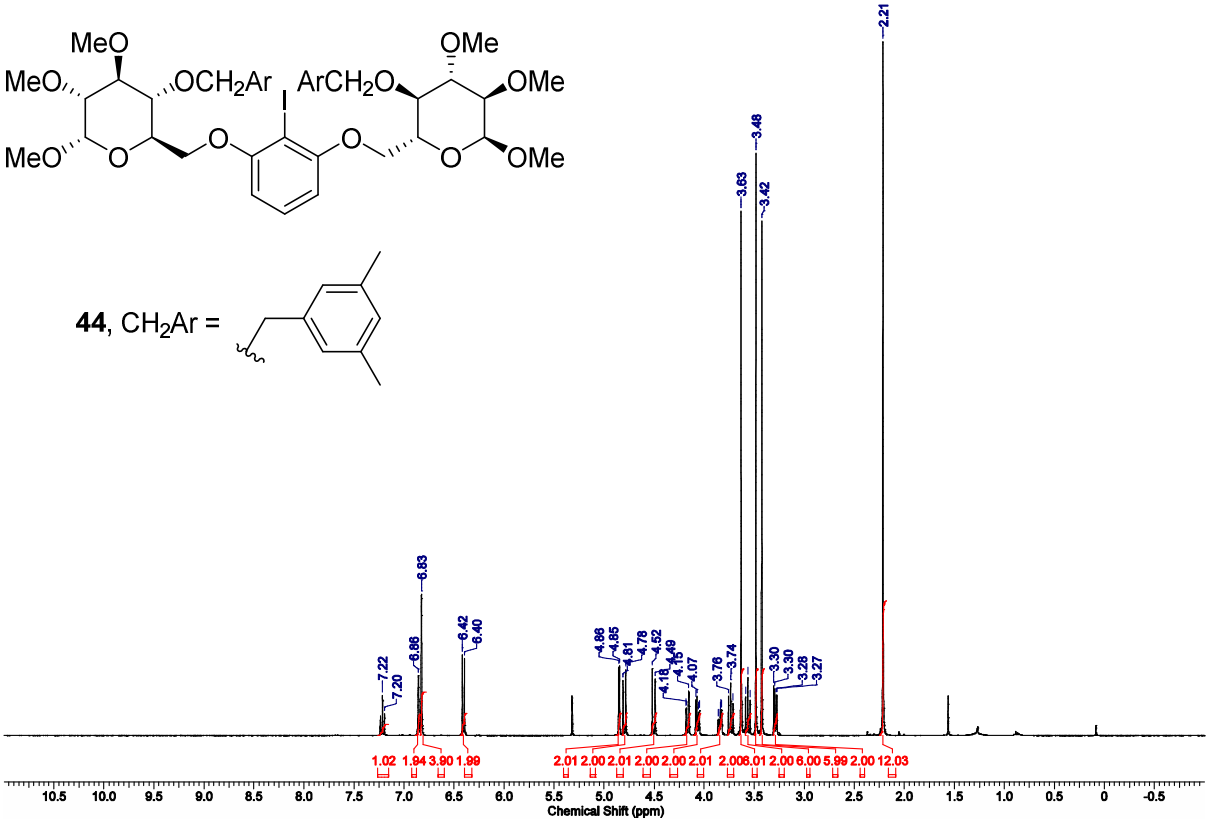

31.99
128.93
143.78
159.36
131.90
97.46
63.68
62.06
75.51
70.53
64.23
61.84
61.11
58.00
55.07
35.69
Chemical Shift (ppm)

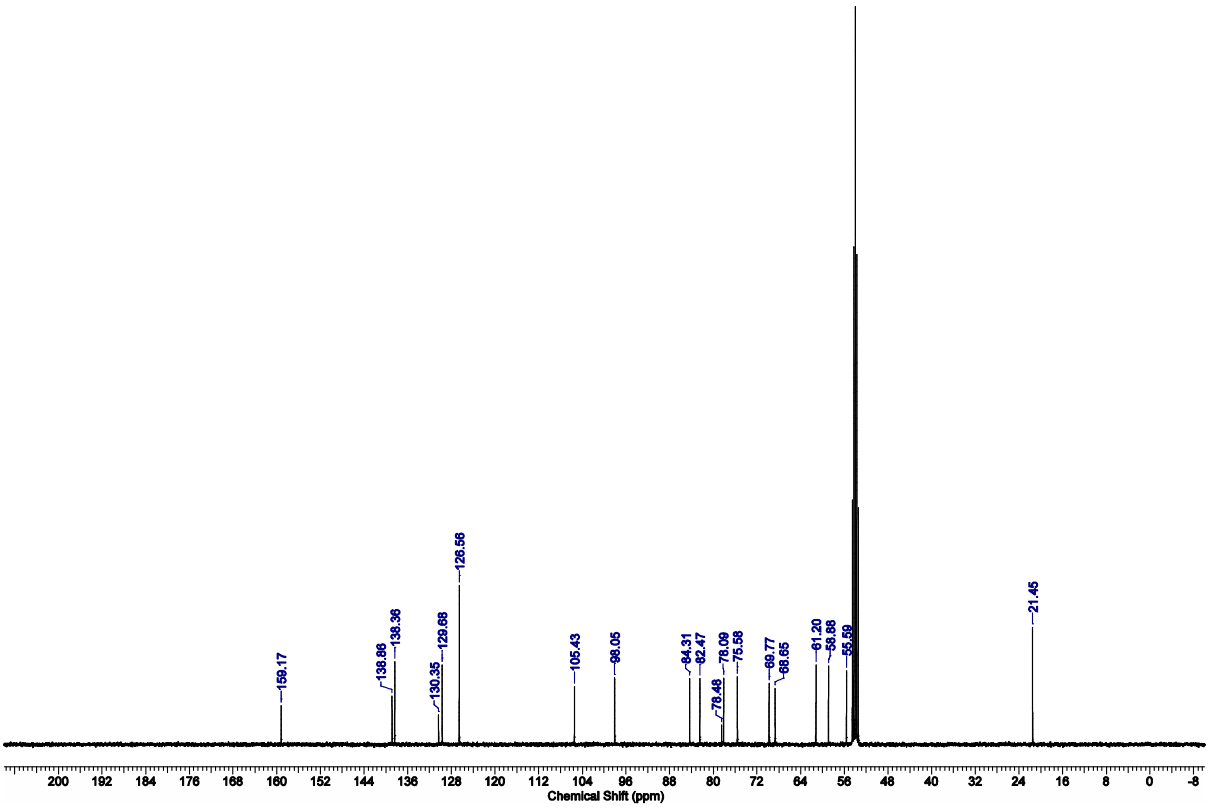

OH
O
MeO
O
MeO
OMe

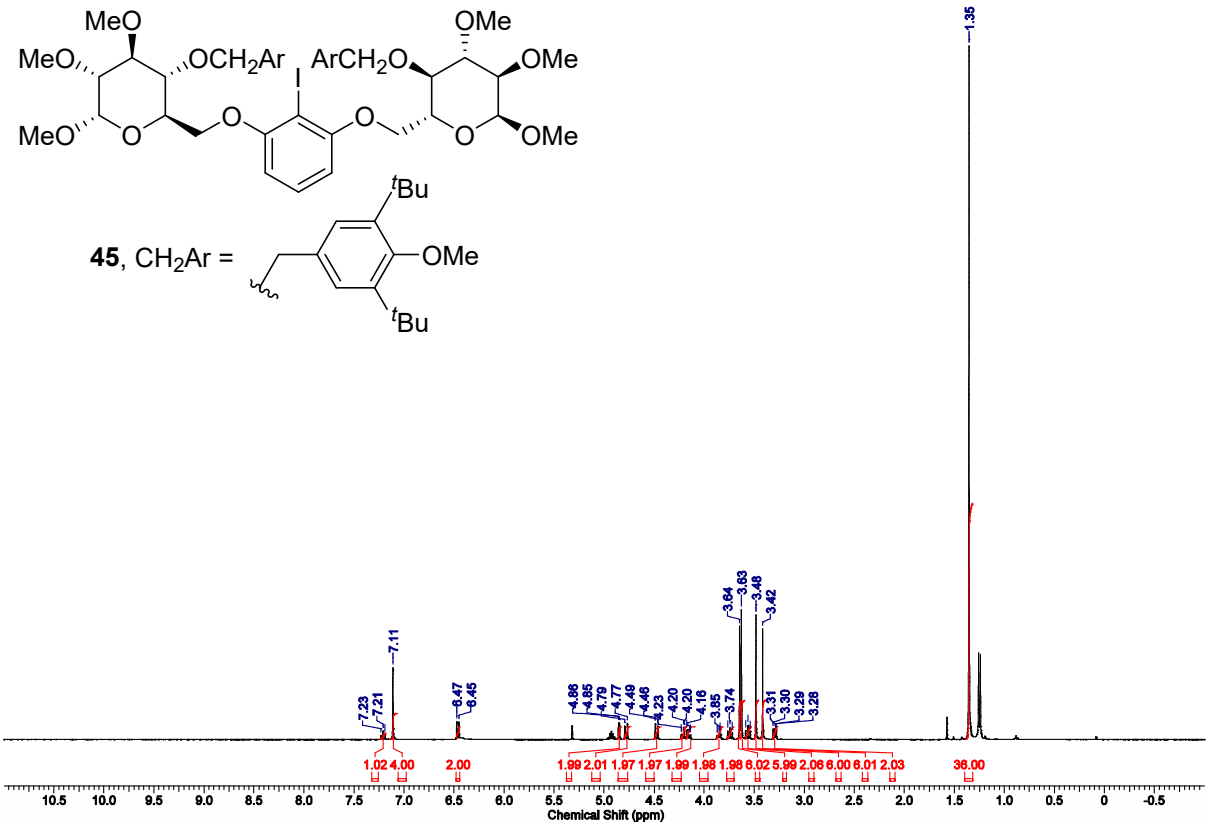
43

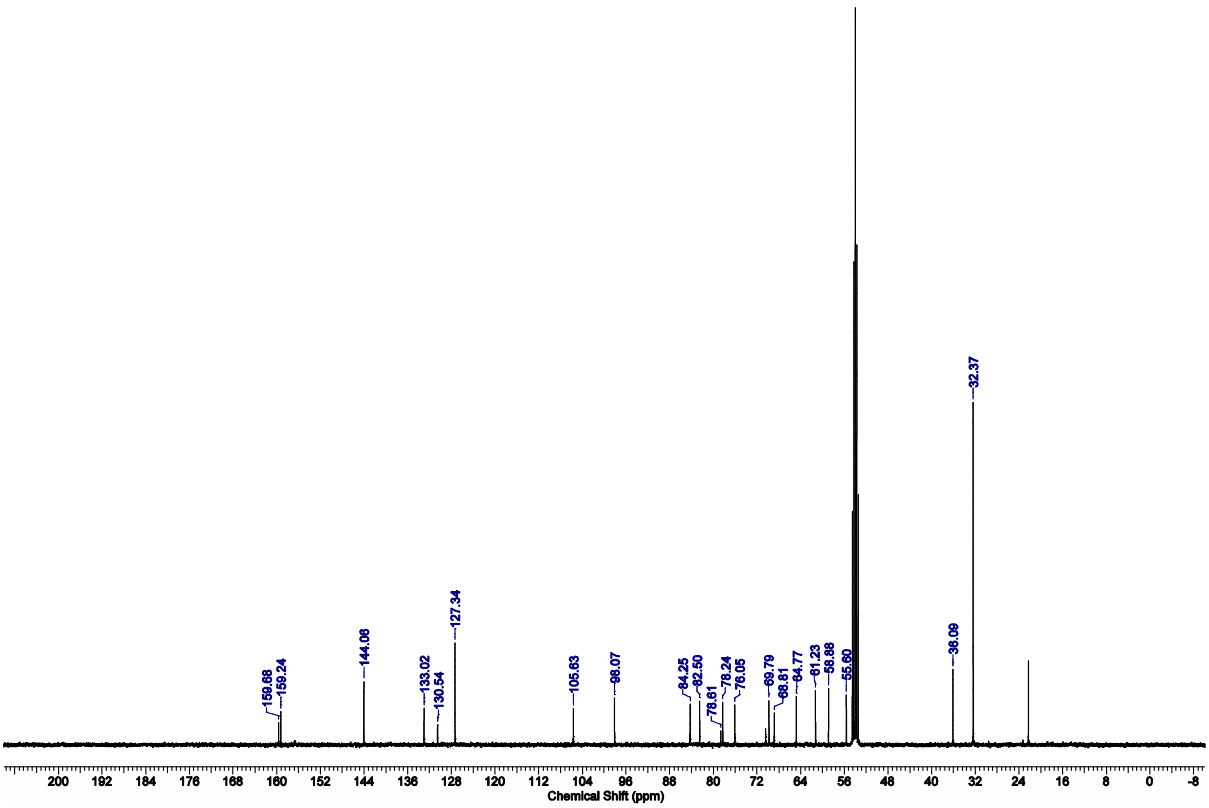
3.70
3.55
3.39
8.17
8.15
7.87
7.85
7.83
7.56
7.53
7.51
7.47
7.45
5.42
5.39
5.09
5.06
4.84
4.83
3.71
3.54
3.29
3.28
3.25
1.00 1.96 3.97
0.99 0.99 1.00
11.03 3.00 1.00
Chemical Shift (ppm)

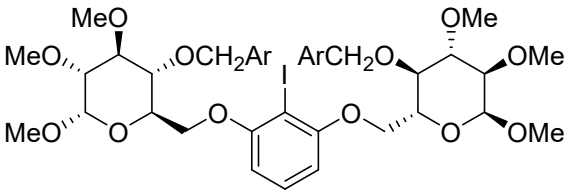

133.78
133.70
128.82
126.93
126.28
125.25
123.96
97.37
83.62
82.33
76.77
72.75
70.55
M17(s)
61.74
58.81
55.08
Chemical Shift (ppm)


MeO
MeO
OCH2Ar
ArCH2O
OMe
OMe
MeO
O
O
O
O
OMe
44, CH2Ar =
2.21
3.48
3.63
3.42
6.83
6.86
6.42
6.40
7.22
7.20
4.88
4.85
4.81
4.78
4.52
4.49
4.15
4.13
4.07
3.76
3.74
3.30
3.30
3.28
3.27
1.02 1.94 3.90 1.99
2.01 2.00 2.01 2.00 2.00 2.01 2.00 8.01 2.00 6.00 5.99 2.00 12.03
Chemical Shift (ppm)

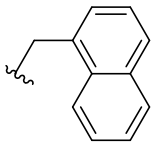

159.17
138.86
138.36
130.35
129.68
126.56
105.43
98.05
84.31
82.47
78.48
78.09
75.58
69.77
68.65
61.20
59.88
55.69
21.45
Chemical Shift (ppm)


MeO
MeO
OCH2Ar
ArCH2O
OMe
OMe
MeO
O
O
O
O
OMe
tBu
45, CH2Ar =
OMe
tBu
1.35
7.11
7.23
7.21
6.47
6.45
4.86
4.85
4.79
4.77
4.49
4.46
4.23
4.20
4.20
4.16
3.85
3.74
3.84
3.63
3.48
3.42
3.31
3.30
3.29
3.28
1.02 4.00
2.00
1.99 2.01 1.97 1.97 1.99 1.98 1.98 6.02 5.99 2.06 6.00 6.01 2.03
36.00
Chemical Shift (ppm)

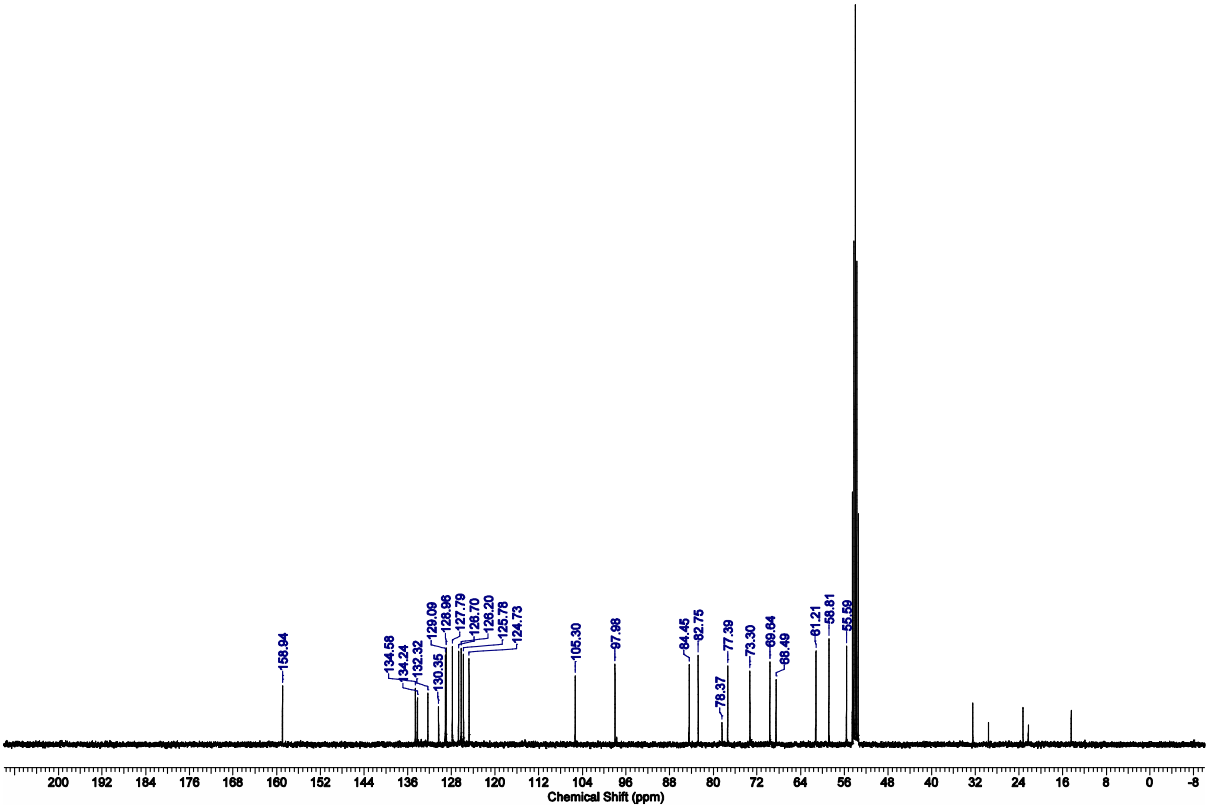

32.37
159.68
159.24
144.06
133.02
130.54
127.34
105.63
98.07
84.25
82.50
78.61
78.24
76.05
69.79
68.81
64.77
61.23
58.88
55.60
36.09
Chemical Shift (ppm)

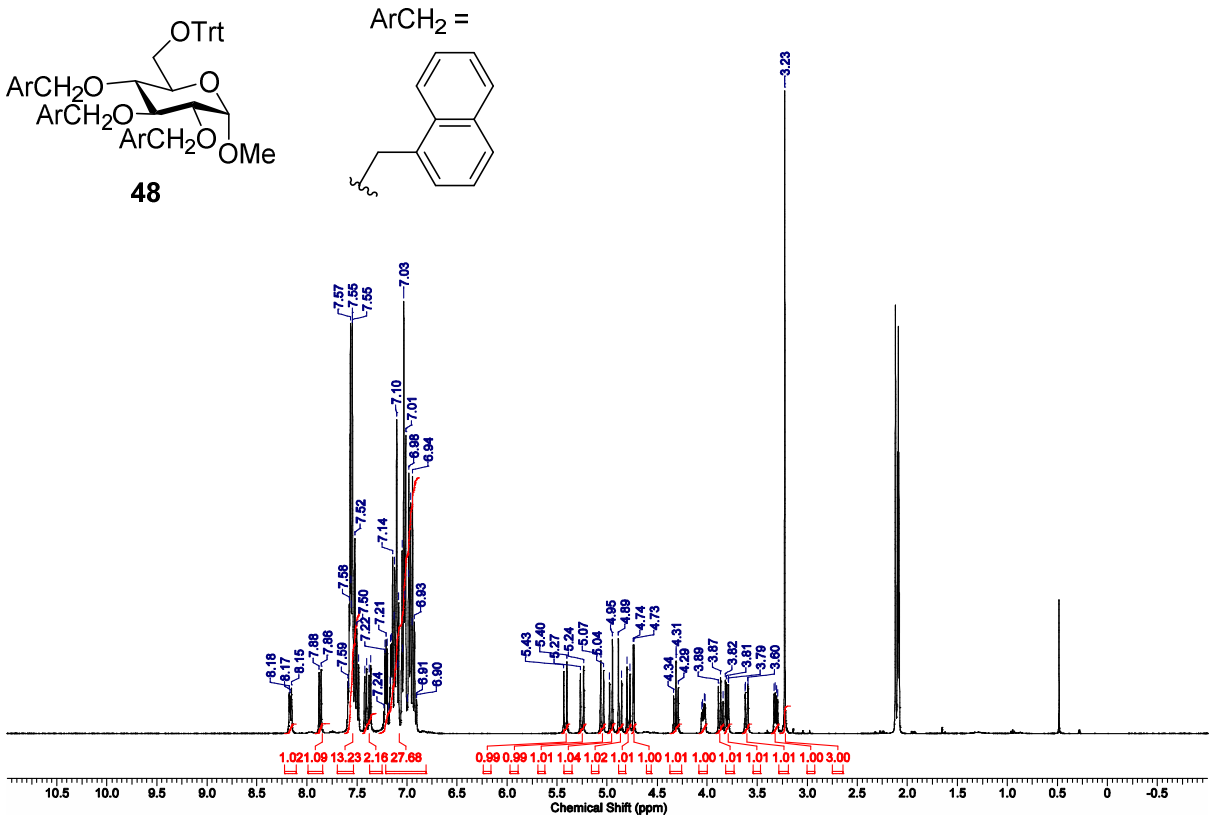

MeO
MeO
OCH2Ar
ArCH2O
OMe
OMe
MeO
O
O
O
O
OMe

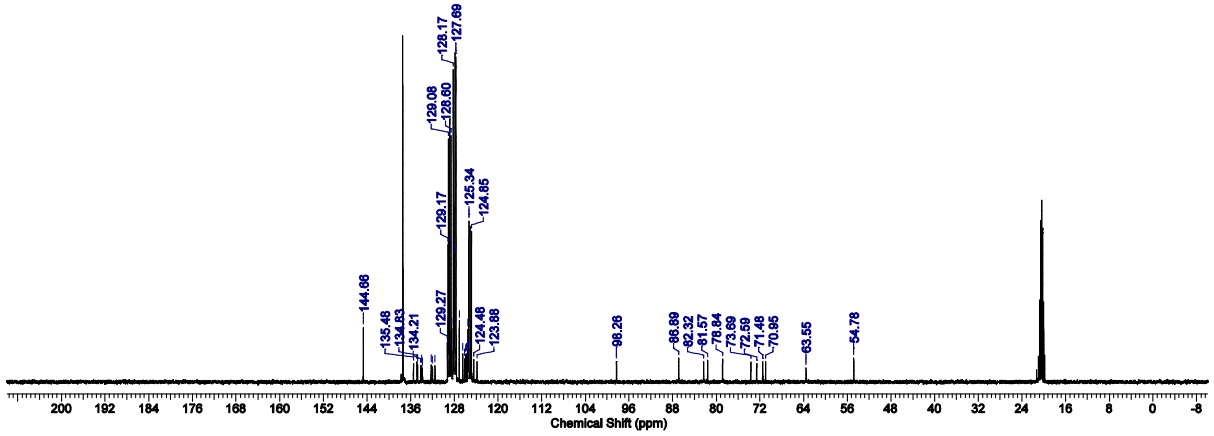
46, CH_2Ar =

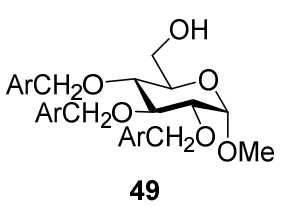


Chemical Shift (ppm)


Chemical Shift (ppm)

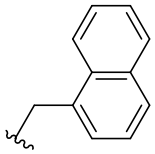

OTrt
ArCH2O
ArCH2O
ArCH2O
OMe
48
ArCH2 =
Chemical Shift (ppm)


Chemical Shift (ppm)

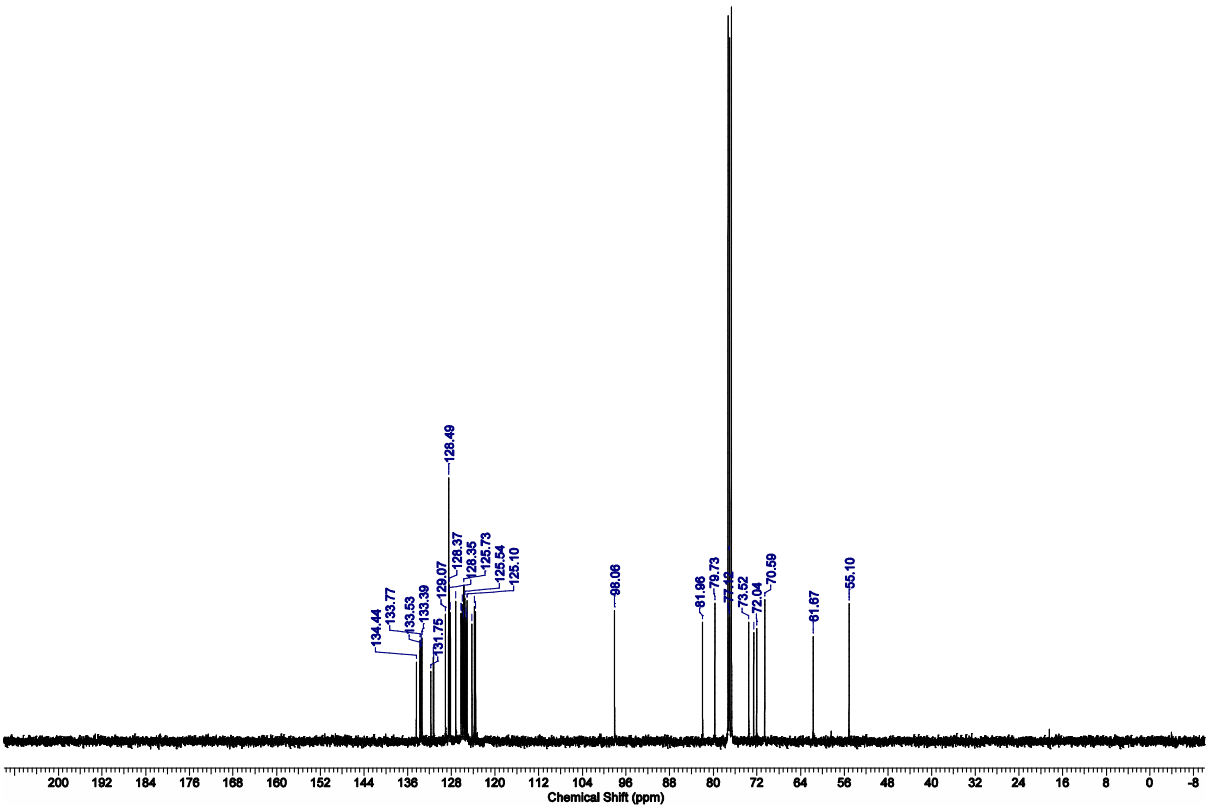

OH
ArCH2O
O
ArCH2O
ArCH2O
OMe

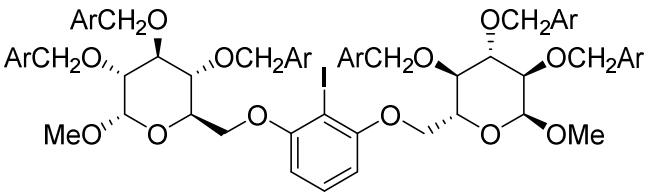
49

$ArCH_2$ =



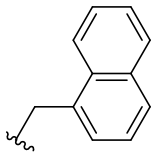
3.07
7.32
7.30
7.73
7.72
7.71
7.28
7.15
7.38
7.34
7.14
7.14
8.13
8.11
7.97
7.95
7.79
7.74
5.46
5.43
5.26
5.24
5.23
5.21
5.18
4.98
4.95
4.94
4.91
4.24
4.23
4.12
4.10
3.62
3.60
3.59
3.58
3.57
3.56
3.48
3.43
1.01 1.02 1.02 6.02 12.48
1.00 3.02 2.01
0.99 1.02 3.10 1.02 1.02 3.01
Chemical Shift (ppm)


128.49
128.37
128.35
125.73
125.54
125.10
134.44
133.77
133.53
133.39
131.75
129.07
98.06
81.96
79.73
77.49
73.52
72.04
70.59
61.67
55.10
Chemical Shift (ppm)

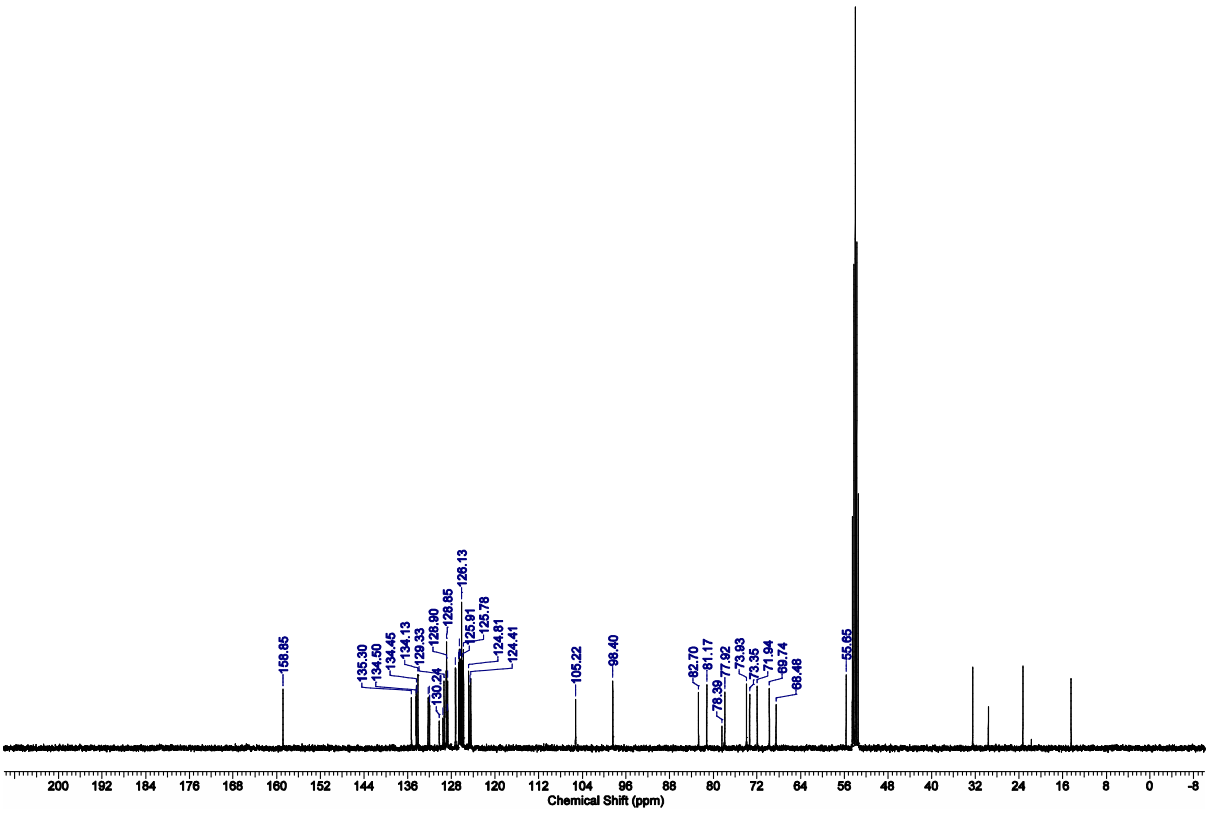

ArCH2O
ArCH2O
OCH2Ar
ArCH2O
OCH2Ar
MeO
O
O
O
O
OMe

50

$ArCH_2$ =



3.31
7.27
7.26
7.85
7.84
7.82
7.55-7.53
7.41
7.81
7.18
7.17
7.16
7.00
6.98
8.20
8.18
8.09
8.07
7.88
5.97
5.95
5.53
5.50
5.36
5.33
5.27
5.24
5.21
5.14
5.04
4.72
4.71
4.23
4.20
4.04
4.01
3.94
3.83
3.82
3.81
3.80
1.99 2.01 12.01 1.99 4.00 12.03 6.07 2.99 1.02 1.97 2.00 2.02 3.99 2.01 2.00 2.00 2.01 6.02 3.99 6.00
Chemical Shift (ppm)


158.85
135.30
134.50
134.45
134.13
129.33
128.90
128.85
126.13
125.91
125.78
124.81
124.41
105.22
98.40
82.70
81.17
78.39
77.92
73.93
73.35
71.94
69.74
68.48
55.65
Chemical Shift (ppm)

1 Crystallographic Data

Crystals of **8c** were prepared by slow evaporation of a saturated solution of **8c** in CH_2Cl_2 and *n*-heptane at room temperature. Single crystals were selected, coated with Parabar 10312 (previously known as Paratone N, Hampton Research) and fixed on a microloop. Data were collected on a Bruker APEX II DUO instrument equipped with an IμS microfocus sealed tube and QUAZAR optics for Mo K_α radiation (λ = 0.71073 Å). The Data collection strategy was determined using COSMO [1] employing ω-scans. Raw data were processed using APEX [2] and SAINT [3], corrections for absorption effects were applied using SADABS [4]. The structure was solved by direct methods and refined against all data by full-matrix least-squares methods on F^2 using SHELXTL [5] and Shelxle [6]. All atoms were refined anisotropically, hydrogen atoms were placed in calculated positions and refined isotropically.

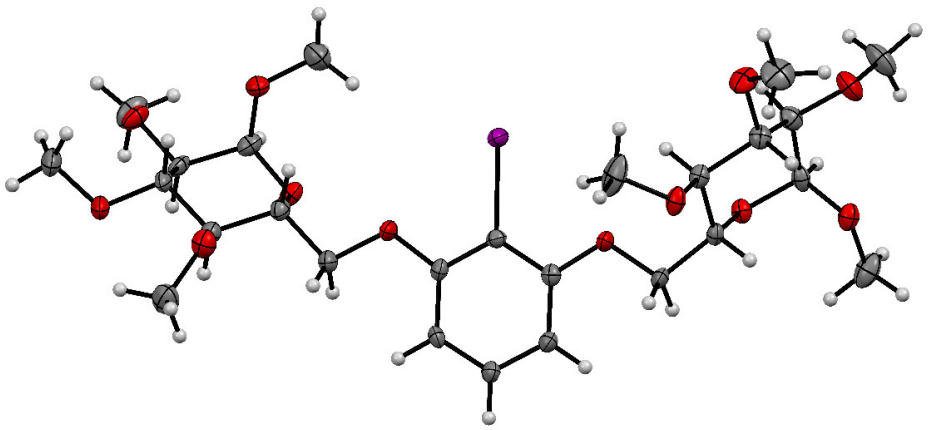


Figure S 1. Molecular structure of **8c**.

Table S 1. Crystal data and structure refinement for **8c**. (CCDC **1952578**)

Identification code	mo_MI215_0m_a	
Empirical formula	C_{26} H_{41} I O_{12}	
Formula weight	672.49	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.5931(10) Å	α= 90°.
	b = 10.3571(12) Å	β= 90°.
	c = 35.008(4) Å	γ = 90°.
Volume	3115.7(6) $Å^3$	
Z	4	
Density (calculated)	1.434 Mg/m^3	
Absorption coefficient	1.084 mm^{-1}	
F(000)	1384	
Crystal size	0.511 x 0.094 x 0.050 mm^3	

Theta range for data collection	2.051 to 28.298°.
Index ranges	-11<=h<=11, -13<=k<=12, -46<=l<=36
Reflections collected	33670
Independent reflections	7702 [R(int) = 0.0588]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.4422
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7702 / 0 / 360
Goodness-of-fit on F2	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0328, wR2 = 0.0673
R indices (all data)	R1 = 0.0358, wR2 = 0.0685
Absolute structure parameter	-0.028(10)
Extinction coefficient	n/a
Largest diff. peak and hole	1.138 and -0.617 e.Å-3

2 HPLC

Chiral HPLC was performed at a Synkam "S1121" chromatograph equipped with a Dr Maisch "Reprosil Chiral-OM, 5 µm, 125 × 4.6 mm" column (eluent *n*-hexanes/*i*-PrOH, 85/15, flow rate: 0.7 ml/min, $t_r(S)$ = 9.5 – 9.8 min, $t_r(R)$ = 11.1 – 11.2 min). For detection a uv-detector at 230 nm was used.

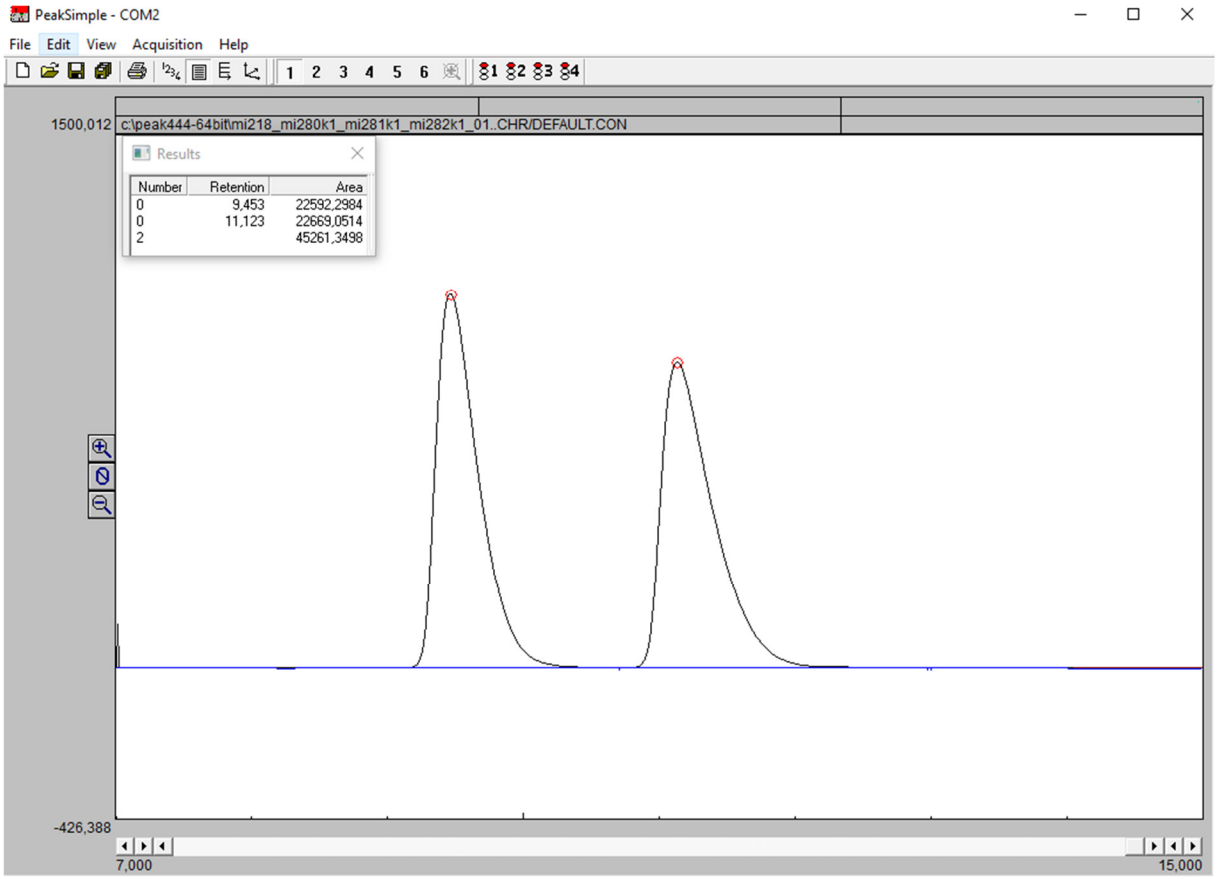


Figure S 2. Chiral HPLC chromatogram of racemic **2**.

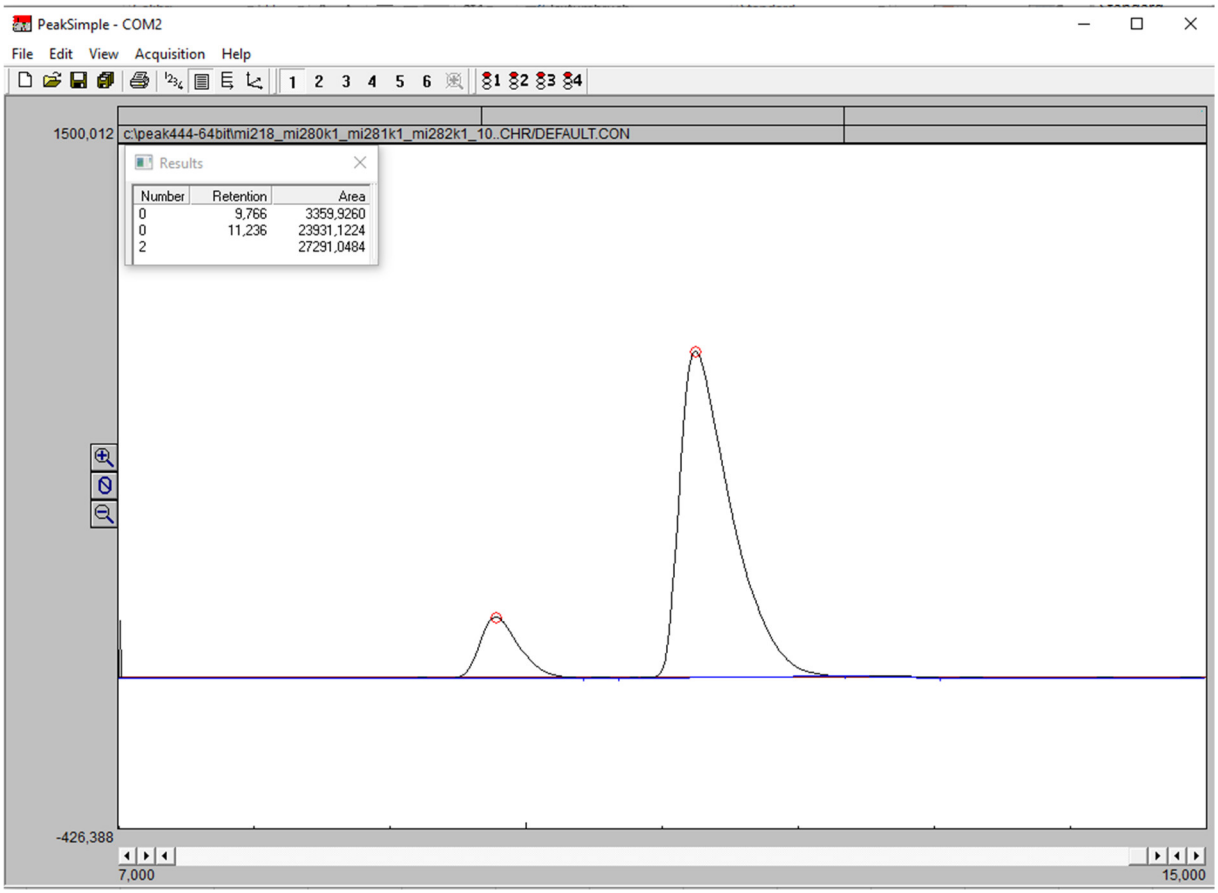


Figure S 3. Chiral HPLC chromatogram of Table 1, entry 19.

3 References

[1] *COSMO v. 1.61*, Bruker AXS Inc., Madison, WI, **2012**.

[2] APEX 3 V. 2017.3-0, Bruker AXS Inc., Madison, WI, **2017**.

[3] *SAINT v. 8.38A*, Bruker AXS Inc., Madison, WI, **2017**.

[4] L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Cryst.* **2015**, *48*, 3-10.

[5] G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3-8.

[6] C. B. Hubsche, G. M. Sheldrick, B. Dittirich, *J. Apll. Crystallogr.***2011**, *44*, 1281-1284.