Supporting Information

for

Convergent Synthesis of a

β -(1 $\rightarrow$ 3)-Mannohexaose

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Compound	Spectrum
Phenyl 4,6- <i>O</i> -benzylidene-3- <i>O</i> -(2-naphthylmethyl)-2- <i>O</i> -(prop-2-ynyl)-1-thio- α -D-mannopyranoside (14)	S-3, 4
Phenyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-1-thio- α -D-mannopyranoside (15)	S-5, 6
Methyl 4,6- <i>O</i> -benzylidene-3- <i>O</i> -(2-naphthylmethyl)-2- <i>O</i> -(prop-2-ynyl)- β -D-mannopyranoside (16)	S-7,8
Methyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)- β -D-mannopyranoside (17)	S-9,10
Phenyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-3- <i>O</i> -(2-naphthylmethyl)- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-1-thio- α -D-mannopyranoside (18β)	S-11,12
Phenyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-1-thio- α -D-mannopyranoside (19)	S-13,14
4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-3- <i>O</i> -(2-naphthylmethyl)- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-1-thio- α -D-mannopyranoside (20α)	S-15,16
Phenyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-3- <i>O</i> -(2-naphthylmethyl)- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-1-thio- α -D-mannopyranoside (20β)	S-17,18
Methyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-3- <i>O</i> -(2-naphthylmethyl)- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)- β -D-mannopyranoside (21β)	S-19,20
Methyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)- β -D-mannopyranosyl	S-21,22

-(1→3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -(prop-2-ynyl)-β-D-mannopyranoside (22)	
Methyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-3- <i>O</i> -(3-naphthalen-1-yl-prop-2-ynl)-β-D-mannopyranoside (24)	S-23,24
Methyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-β-D-mannopyranoside (25)	S-25,26
Methyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-3- <i>O</i> -(3-naphthalen-1-yl-prop-2-ynl)-β-D-mannopyranosyl-(1→3)- 4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-β-D-mannopyranoside (26)	S-27,28
Methyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-β-D-mannopyranosyl-(1→3) - 4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-β-D-mannopyranoside (27)	S-29,30
Methyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-3- <i>O</i> -(3-naphthalen-1-yl-prop-2-ynl)-β-D-mannopyranosyl-(1→3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-β-D-mannopyranosyl-(1→3)- 4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-β-D-mannopyranoside (28)	S-31,32
Methyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-β-D-mannopyranosyl-(1→3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-β-D-mannopyranosyl-(1→3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-β-D-mannopyranoside (29)	S-33,34
Phenyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-3- <i>O</i> -(3-naphthalen-1-yl-prop-2-ynl)-β-D-mannopyranosyl-(1→3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-1-thio-α-D-mannopyranoside (31)	S-35,36
Phenyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-β-D-mannopyranosyl-(1→3)- 4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-1-thio-α-D-mannopyranoside (32)	S-37,38
Phenyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-3- <i>O</i> -(3-naphthalen-1-yl-prop-2-ynl)-β-D-mannopyranosyl-(1→3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-β-D-mannopyranosyl-(1→3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-1-thio-α-D-mannopyranoside (33)	S-39,40
Phenyl 4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-3- <i>O</i> -(3-naphthalen-1-yl-prop-2-ynl)-β-D-mannopyranosyl-(1→3)- 4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-β-D-mannopyranosyl-(1→3)-4,6- <i>O</i> -benzylidene-2- <i>O</i> -benzyl-1-thio-α-D-mannopyranoside-S-oxide (34)	S-41,42
Hexasaccharide (35α)	S-44, 45
Hexasaccharide (35β)	S-46,47
Hexasaccharide (36α)	S-49,50
Hexasaccharide (36β)	S-51,52
Hexasaccharide (37)	S-55,56
Hexasaccharide (38)	S-53,54
1-Naphthylpropargylcyclohexyl ether (40)	S-57,58

^1H NMR (500 MHz, CDCl_3)

¹³C NMR (125 MHz, CDCl₃)

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (125 MHz, CDCl_3)

¹³C NMR (125 MHz, CDCl₃)

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (125MHz, CDCl_3)

¹H NMR (500 MHz, CDCl₃)

¹³C NMR (125 MHz, CDCl₃)

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (125 MHz, CDCl_3)

¹H NMR (500 MHz, CDCl₃)

¹H NMR (500 MHz, CDCl₃)

¹³C NMR (125 MHz, CDCl₃)

¹H NMR (500 MHz, CDCl₃)

21β

^{13}C NMR (125 MHz, CDCl_3)

22

^1H NMR (500 MHz, CDCl_3)

22

^{13}C NMR (125 MHz, CDCl_3)

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (125 MHz, CDCl_3)

25

^1H NMR (500 MHz, CDCl_3)

S-25

25

^{13}C NMR (125 MHz, CDCl_3)

27

^1H NMR (500 MHz, CDCl_3)

27

^{13}C NMR (125 MHz, CDCl_3)

¹H NMR (500 MHz, CDCl₃)

^{13}C NMR (125 MHz, CDCl_3)

29

^1H NMR (500 MHz, CDCl_3)

29

^{13}C NMR (125 MHz, CDCl_3)

¹H NMR (500 MHz, CDCl₃)

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (125 MHz, CDCl_3)

1. H

mixture of **35 α** , **35 β**
 ^1H NMR (500 MHz, CDCl_3)

35α

^1H NMR (500 MHz, CDCl_3)

35α

^{13}C NMR (125 MHz, CDCl_3)

mixture of **36 α** , **36 β**
 ^1H NMR (500 MHz, CD_2Cl_2)

36α
 ^1H NMR (500 MHz, CDCl_3)

36α

^{13}C NMR (125 MHz, CDCl_3)

36β

^{13}C NMR (125 MHz, CDCl_3)

^1H NMR (500 MHz, D_2O)

^{13}C NMR (125 MHz, D_2O)

37

^1H NMR (500 MHz, D_2O)

S-55

37

^{13}C NMR (125 MHz, D_2O)

^1H NMR (500MHz, CD_2Cl_2)

^{13}C NMR (125MHz, CD_2Cl_2)