Electronic Supplementary Material (ESI) for New Journal of Chemistry

^{17}O NMR studies of boronic acids and their derivatives

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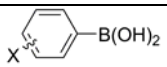
Supplementary Information

Table S1 Values of ^{17}O NMR line halfwidths of substituted phenylboronic acids in [^{2}H]$_6$-acetone (0.01 M, 298 K)



No.	Substituent (X)	$\Delta\nu_{1/2}$ [Hz] of B-**O** oxygen atom and *$\Delta\nu_{1/2}$ of substituent oxygen*		
		ortho **(a)**	*meta* **(b)**	*para* **(c)**
1	**NMe_2**	220	220	220
2	**NH_2**	225	220	220
3	**OMe**	210 *275*	215 *300*	220 *350*
4	**Me**	215	215	205
5	**Ph**	210	215	195
6	**H**	185	185	185
7	**F**	180	200	200
8	**Cl**	180	195	190
9	**Br**	175	200	195
10	**I**	185	195	190
11	**CHO**	190 *315*	200 *320*	195 *350*
12	**COOH**	225 *550*	200 *550*	200 *600*
13	**CF_3**	190	200	195
14	**CN**	200	195	195
15	**NO_2**	215 *600*	200 *620*	205 *590*

Table S2 Values of ^{17}O NMR half line widths of phenylboronic acid esters of monohydroxyl alcohols and phenols in [^{2}H]-chloroform (0.05 M, 298K)

No.	R	$\Delta\nu_{1/2}$ [Hz]
16	CH_3	160
17	CH_2CH_3	180
18	$CH(CH_3)_2$	200
19	$C(CH_3)_3$	210
20	$CH_2CH_2CH_3$	185
21	$CH_2CH(CH_3)_2$	180
22	$CH_2C(CH_3)_3$	205
23	$CH_2C_6H_5$	220
24	$CH(C_6H_5)_2$	230
25	$CH_2CH_2C_6H_5$	210
26	$CH_2CH(C_6H_5)_2$	210
27	$CH_2CH=CH_2$	200
28	$CH(CH_3)CH=CH_2$	210
29	$C(CH_3)_2CH=CH_2$	215
30	C_6H_5	320

Table S3 Values of ^{17}O NMR half line widths of phenylboronic acid esters of aliphatic diols in [^{2}H]-chloroform (0.05 M, 298K)

No.	Compound	$\Delta\nu_{1/2}$ [Hz]	
		O1	O2
31	$R_{1\text{-}4}$ = H		85
32	R_1 = Me, $R_{2\text{-}4}$ = H	125	85
33	$R_{1,2}$ = Me, $R_{3,4}$ = H	140	90
34	$R_{1,3}$ = Me, $R_{2,4}$ = H		115
35	$R_{1,4}$ = Me, $R_{2,3}$ = H		115
36	$R_{1\text{-}3}$ = Me, R_4 = H	145	125
37	$R_{1\text{-}4}$ = Me		155
38	R_1 = Ph, $R_{2\text{-}4}$ = H	140	95
39	$R_{1,2}$ = Ph, $R_{3,4}$ = H	160	100
40	$R_{1,3}$ = Ph, $R_{2,4}$ = H		165
41	$R_{1,4}$ = Ph, $R_{2,3}$ = H		170
42	$R_{1\text{-}3}$ = Ph, R_4 = H	180	165
43	$R_{1\text{-}4}$ = Ph		195
44	$R_{1\text{-}6}$ = H		120
45	R_1 = Me, $R_{2\text{-}6}$ = H	125	120
46	$R_{1,2}$ = Me, $R_{3\text{-}6}$ = H	135	120
47	$R_{1,3}$ = Me, $R_{2,4\text{-}6}$ = H[a]		125
48	R_5 = Me, $R_{1\text{-}4,6}$ = H		120
49	$R_{5,6}$ = Me, $R_{1\text{-}4}$ = H		120
50	$R_{1\text{-}3}$ = Me, $R_{4\text{-}6}$ = H	135	125
51	$R_{1,2,3,4}$ = Me, $R_{5,6}$ = H		140
52	$R_{1\text{-}6}$ = Me		150
53	R_1 = Ph, $R_{2\text{-}6}$ = H	150	120
54	$R_{1,3}$ = Ph, $R_{2,4\text{-}6}$ = H[a]		155
55	n = 2		130
56	n = 3		135
57	n = 4		140
58	n = 6		150
59	n = 8		165
60	n = 1		100
61	n = 2		110
62	n = 3		115
63	n = 5		115
64	n = 7		120

[a] Mixture of diastereoisomers.

Table S4 Values of ^{17}O NMR half line widths of phenylboronic acid esters of aromatic diols in [^2H]-chloroform (0.05 M, 298K)

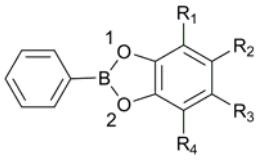
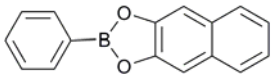
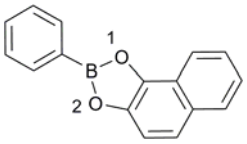
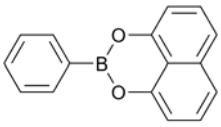
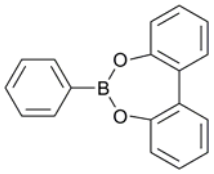
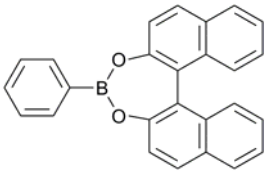
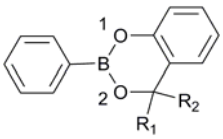
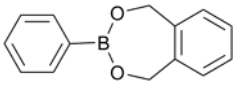
No.	Compound	$\Delta\nu_{1/2}$ [Hz]	
		O1	O2
65	 R_{1-4} = H	180	
66	R_1 = Me, R_{2-4} = H	190	180
67	R_2 = Me, $R_{1,3,4}$ = H	180	180
68	$R_{1,4}$ = Me, $R_{2,3}$ = H	190	
69	$R_{2,3}$ = Me, $R_{1,4}$ = H	185	
70	R_{1-4} = Me	195	
71		185	
72		205	185
73		210	
74		210	
75		220	
76	 $R_{1,2}$ = H	185	110
77	R_1 = Me; R_2 = H	185	125
78	$R_{1,2}$ = Me	185	135
79		155	

Table S5 Values of ^{17}O NMR half line widths of adducts of phenylboronic acid with hydroxy acids in [^{2}H]-chloroform (0.05 M, 298K)

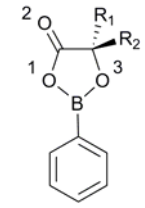
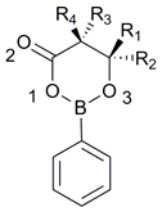
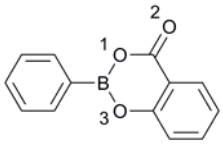
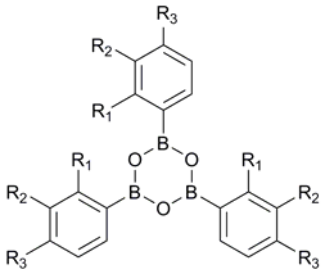
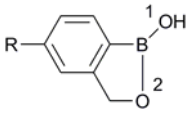
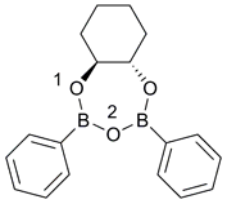
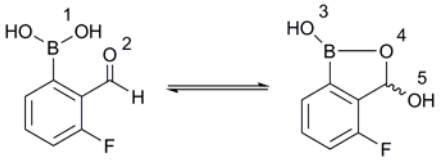
No.	Compound	$\Delta\nu_{1/2}$ [Hz]		
		O1	O2	O3
86	 $R_{1,2}$ = H	100	120	180
87	R_1 = Me, R_2 = H	105	120	190
88	$R_{1,2}$ = Me	110	120	195
89	$R_{1\text{-}4}$ = H	120	125	190
90	R_1 = Me, $R_{2\text{-}6}$ = H	120	125	195
91	 $R_{1,2}$ = Me, $R_{3,4}$ = H	120	125	205
92	R_3 = Me, $R_{1,2,4}$ = H	125	135	190
93	$R_{3,4}$ = Me, $R_{1,2}$ = H	130	135	195
94	$R_{1\text{-}4}$ = Me	135	140	210
95		155	125	190

Table S6 Values of ^{17}O NMR half line widths of representative arylboronic acid derivatives belonging to other classes in [^2H]-chloroform (0.05 M, 298K)

No.	Compound		$\Delta\nu_{1/2}$ [Hz]				
			O^1				O^R
96		R_{1-3} = H	220				-
97		R_1 = Me, $R_{2,3}$ = H	250				-
98		R_1 = OMe, $R_{2,3}$ = H	300				365
99		R_1 = NO_2, $R_{2,3}$ = H	300				620
100		R_2 = Me, $R_{1,3}$ = H	230				-
101		R_2 = OMe, $R_{1,3}$ = H	230				310
102		R_2 = NO_2, $R_{1,3}$ = H	300				580
103		R_3 = Me, $R_{1,2}$ = H	220				-
104		R_3 = OMe, $R_{1,2}$ = H	220				325
105		R_3 = NO_2, $R_{1,2}$ = H	280				570
			O^1		O^2		O^R
106		R = H	170		190		-
107		R = OMe	165		190		330
108		R = NO_2	165		195		590
109			210		250		-
			O^1	O^2	O^3	O^4	O^5
110[a]			155	300	180	195	100

[a] In [^2H]$_3$-acetone at 298 K (c = 0.1 M).

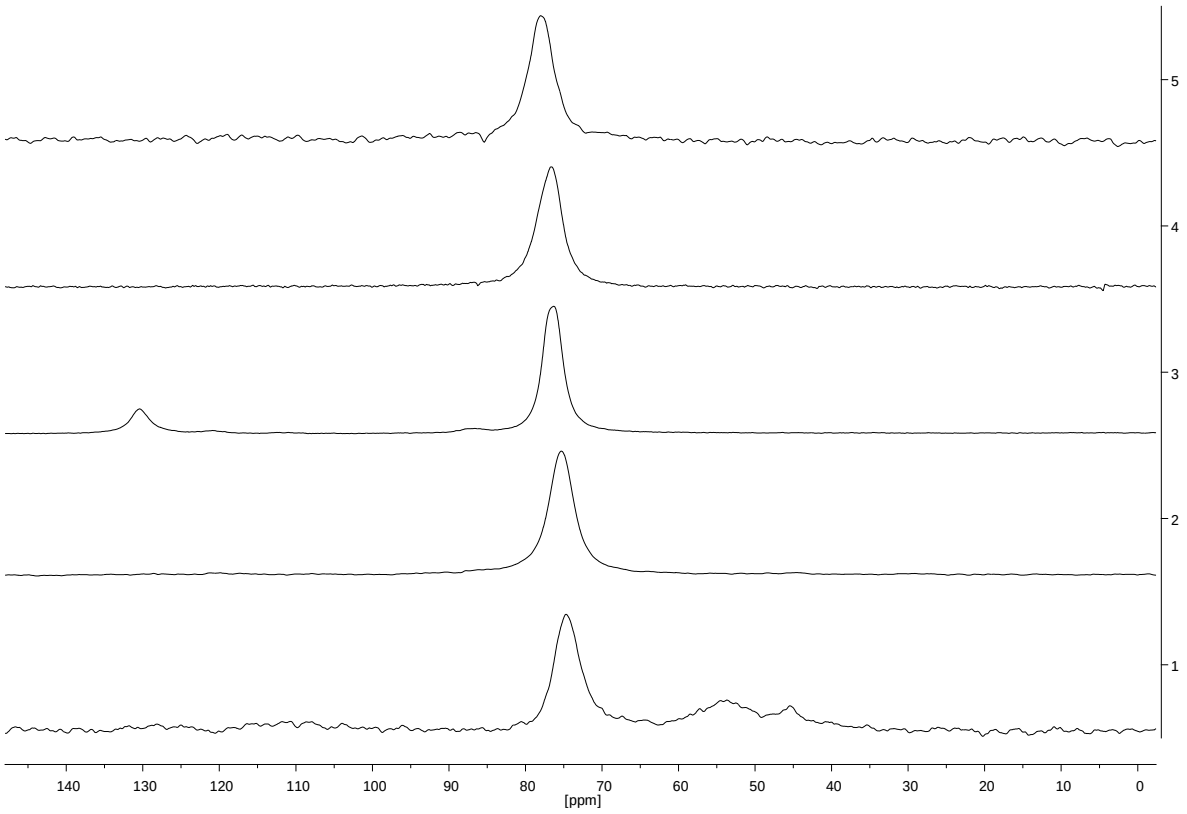


Fig. S1. Selected ^{17}O NMR spectra of *para* substituted phenylboronic acids (from the bottom): 4-methoxyphenylboronic acid, phenylboronic acid (signal at *ca.* 130 ppm is assigned to boroxine), 4-bromophenylboronic acid, 4-methylphenylboronic acid and 4-cyanophenylboronic acid (all spectra measured in acetone-d_6 at 298 K for unlabeled compounds).

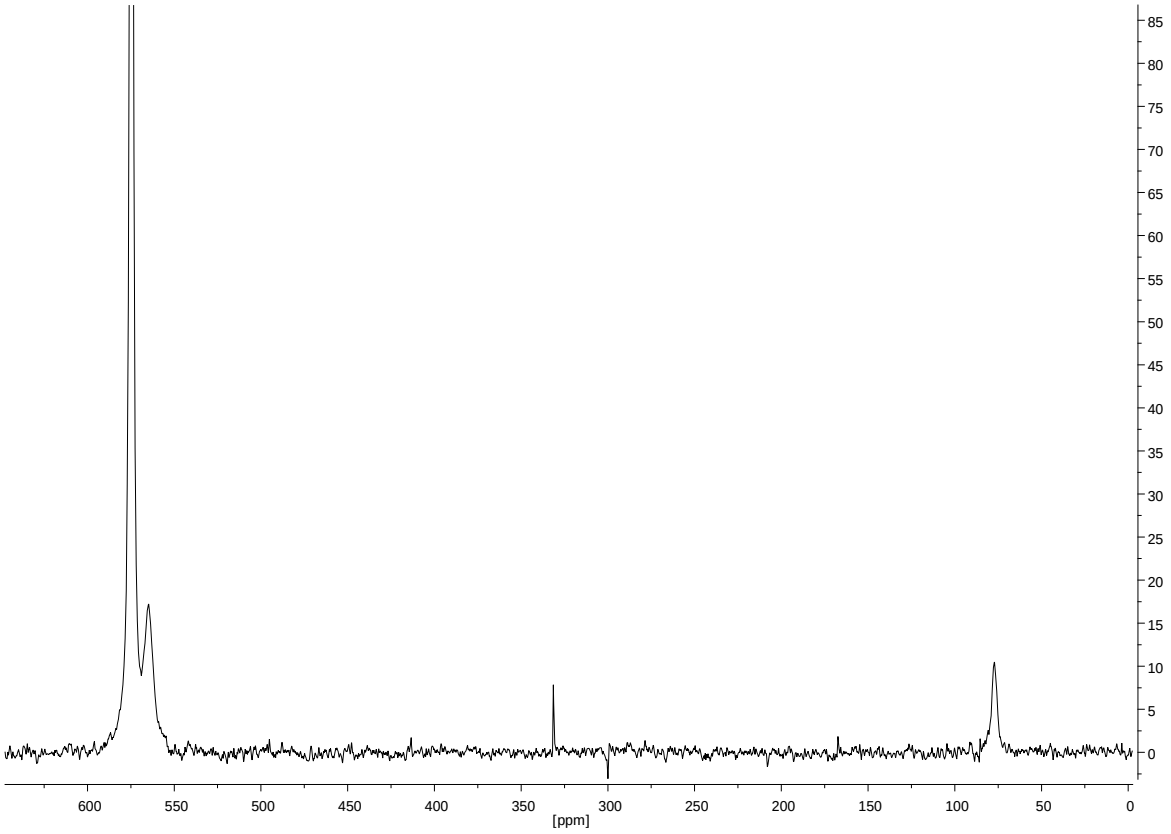


Fig. S2. The ^{17}O NMR spectrum of 3-formylphenylboronic acid (in acetone-d_6, at 298 K, unlabeled compound; the signal at 575 ppm is assigned to the solvent)

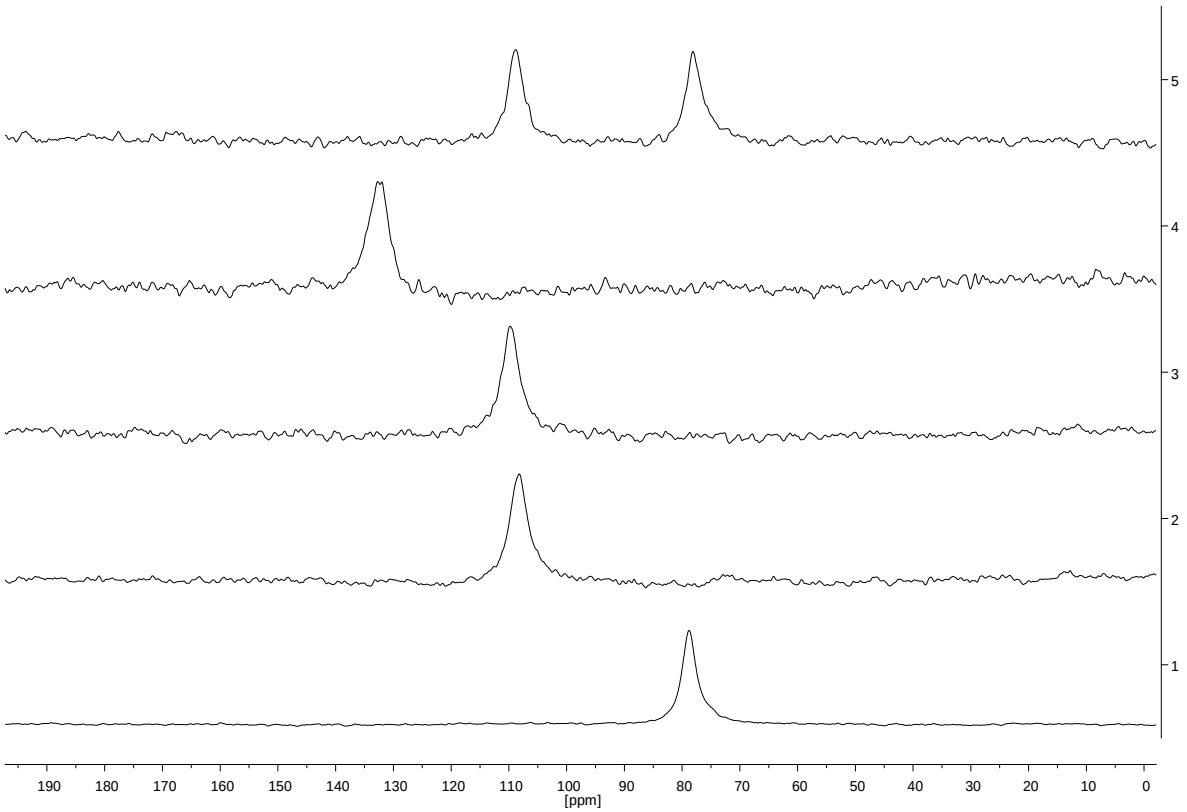


Fig. S3. Selected ^{17}O NMR spectra of phenylboronic acid esters with 1,2-aliphatic diols (from the bottom): 1,2-ethanediol, 2R,3R-butanediol, *meso*-2,3-butanediol, 2,3-dimethyl-2,3-butanediol, 1,2-propanediol (all spectra measured in chloroform-*d* at 298 K for unlabeled compounds)

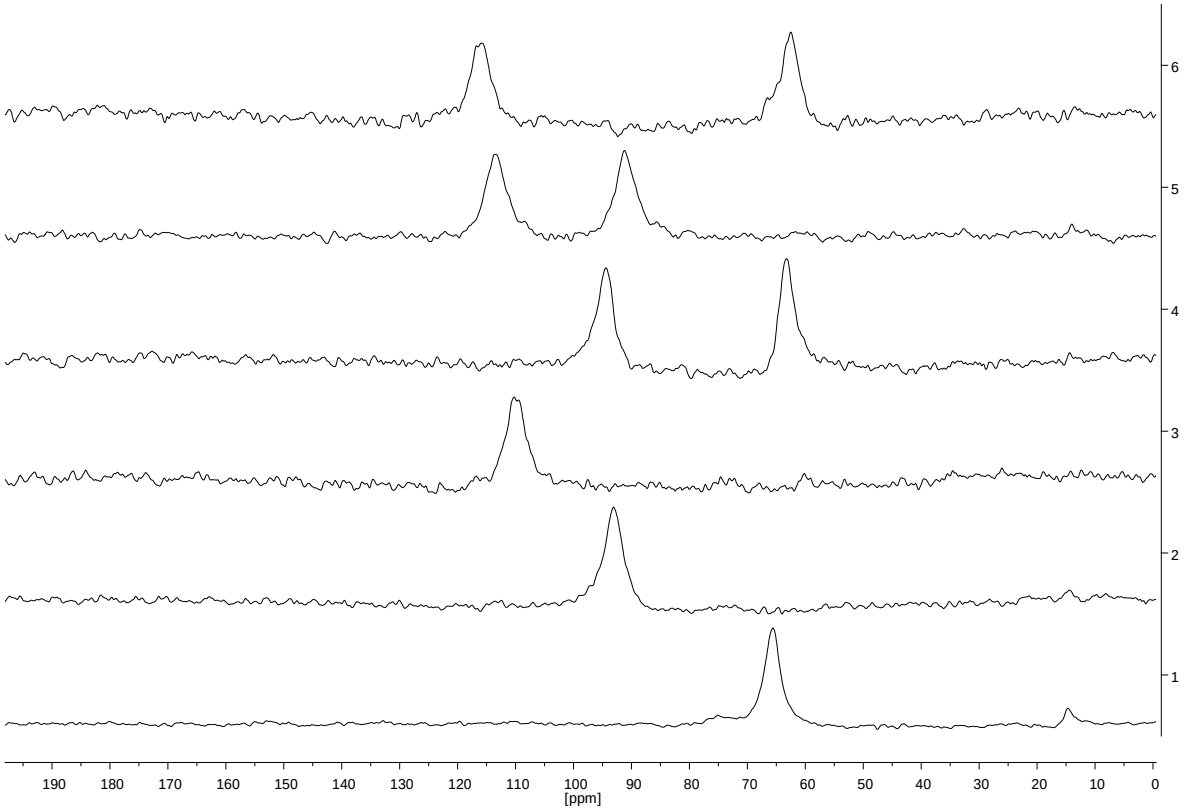


Fig. S4. Selected ^{17}O NMR spectra of phenylboronic acid esters with 1,3-aliphatic diols (from the bottom): 1,3-propanediol, 2,4-pentanediol, 2,4-dimethyl-2,4-pentanediol, 1,3-butanediol, 2-methyl-2,4-pentanediol, 2-methyl-2,4-butanediol (all spectra measured in chloroform-*d* at 298 K for unlabeled compounds)

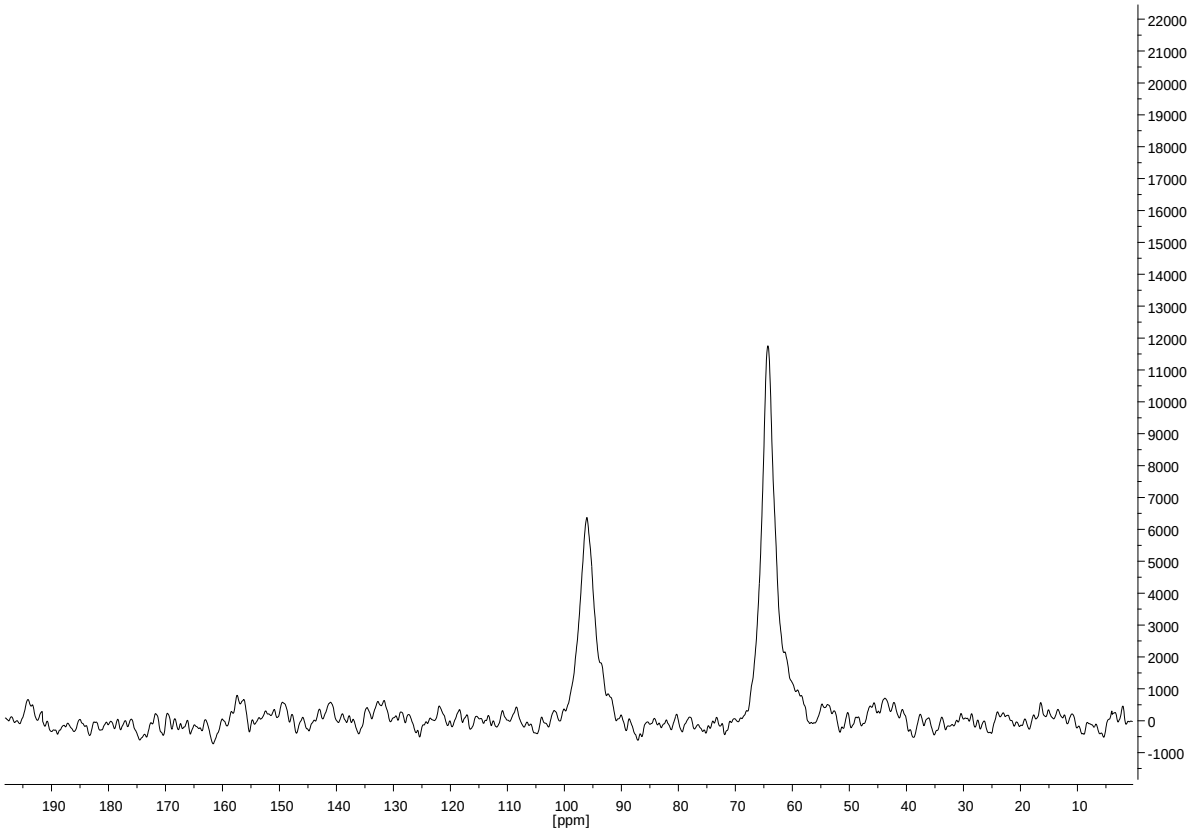


Fig. S5. The ^{17}O NMR spectrum of compound **106** (in chloroform-*d*, at 298 K, unlabeled compound)