Supporting Information to

New Lithium Borates with Bistetrazolato^{2-} and Pyrazinediolato^{2-} Ligands – Potentially Interesting Lithium Electrolyte Additives

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Content:

Single Crystal X-ray Structures

Crystal Data

	TMS_2BT (**2**)	**3**·2 THF	**4**·5 MeCN
Formula	C8 H18 N8 Si2	C10 H16 B F2 Li N8 O2	C14 H15 B2 F2 Li2 N21 O
FW/ g·mol^{-1}	282.48	336.06	566.97
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
Colour, habit	colourless block	colourless block	colourless needle
Crystal size/mm^3	0.12 x 0.08 x 0.06	0.24 x 0.18 x 0.07	0.26 x 0.09 x 0.08
a/ Å	7.113(7)	8.1367(13)	9.6535(14)
b/ Å	11.2141(13)	9.2057(16)	18.036(2)
c/ Å	18.634(2)	11.0783(17)	15.8966(18)
α/°	90	107.287(13)	90
β/°	96.884(9)	101.500(13)	101.860(10)
γ/°	90	97.456(13)	90
V/ Å^3	1475.6(15)	760.4(2)	2708.6(6)
Z	4	2	4
D_{calc}/ g·cm^{-3}	1.272	1.468	1.390
Abs. corr.	multi-scan	none	none
Max./min. Transm.	1.0138 / 0.9586	- / -	- / -
μ/ cm^{-1}	2.39	1.21	1.09
F(000)	600	348	1152
T/ K	100(2)	100(2)	100(2)
θ range/°	2.12 : 25.62	1.99 : 26.83	1.73 to 25.61
range h,k,l	−7:8; −12:13; −22:22	−10:10; −11:11; −14:13	−11:11; −21:21; −19:19
Refl. Coll.	6461	6652	13720
Refl. Indep.	2769	3209	13720
Refl. I > 2σ(I)	1388	1528	2420
Data / restr. / param.	2769 / 0 / 169	3388 / 0 / 217	13720 / 7 / 385
R_{int}	0.0674	0.0599	- (hklf5)
R_1 (obs)	0.0477	0.0401	0.0612
wR_2 (all)	0.1120	0.0915	0.1400
GooF (F_2)	0.824	0.762	0.589
Res. e$^-$ dens. (min./ max.)	−0.267 / 0.376	−0.157 / 0.157	−0.317 / 0.387
CCDC	1484823	1484824	1484825

	H_2OP (**6**)	[EMIm][$(OPN)_2B$] (**7**)	[DMPyr][$(OPN)_2B$] (**8**)
Formula	C4 H4 N2 O2	C58 H39 B3 N32 O12	C18 H14 B N9 O4
FW/ $g \cdot mol^{-1}$	112.09	1408.64	431.19
Crystal system	monoclinic	monoclinic	triclinic
Space group	*P*21/*c*	*C*2/*c*	*P*−1
Colour, habit	colourless needle	colourless plate	colourless block
Crystal size/mm^3	0.37 x 0.11 x 0.10	0.52 x 0.17 x 0.12	0.46 x 0.22 x 0.12
a/ Å	6.1105(3)	15.460(5)	10.1140(6)
b/ Å	10.2259(5)	9.0238(5)	11.7988(7)
c/ Å	6.9669(3)	41.241(5)	17.7771(10)
α/°	90	90	87.703(2)
β/°	93.973(2)	93.289(5)	74.253(2)
γ/°	90	90	79.855(2)
V/ $Å^3$	434.28(4)	6300(4)	2009.8(2)
Z	4	4	4
D_{calc}/ $g \cdot cm^{-3}$	1.714	1.485	1.425
Abs. corr.	multi-scan	multi-scan	multi-scan
Max./min. Transm.	0.7455 / 0.7133	0.7455 / 0.5733	0.7455 / 0.6730
μ/ cm^{-1}	1.41	1.10	1.05
F(000)	232	2888	888
T/ K	100(2)	100(2)	100(2)
θ range/°	3.34 : 27.12	2.45 : 27.16	2.38 : 27.15
range h,k,l	−7:7; −13:13; −8:8	−19:19; −12:12; −52:52	−12:12; −15:15; −22:22
Refl. Coll.	14626	54995	22424
Refl. Indep.	957	6977	8855
Refl. I > 2σ(I)	882	4187	5996
Data / restr. / param.	957 / 0 / 81	6977 / 98 / 516	8855 / 149 / 730
R_{int}	0.0299	0.0961	0.0391
R_1 (obs)	0.0314	0.0623	0.0531
wR_2 (all)	0.0915	0.1526	0.1102
GooF (F_2)	1.062	1.014	1.045
Res. e^- dens. (min./ max.)	−0.241 / 0.393	−0.366 / 0.603	−0.286 / 0.336
CCDC	1527279	1484826	1484827

	TMS_2OP (**10**)	[NBu4][$(OP)_2B$] (**11**)	[$(DME)_3Li$][$(OPN)_2B$] (**12**)
Formula	C10 H20 N2 O2 Si2	C24 H40 B N5 O4	C24 H30 B Li N8 O10
FW/ g·mol^{-1}	256.46	473.42	608.31
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*Pbca*	*P*21/*n*	*C*2/c
Colour, habit	colourless block	colourless block	colourless plate
Crystal size/mm^3	0.47 x 0.28 x 0.22	0.29 x 0.14 x 0.13	0.51 x 0.22 x 0.11
a/ Å	11.2602(6)	10.7012(7)	18.9060(11)
b/ Å	11.0540(5)	16.4098(10)	15.4153(9)
c/ Å	23.4337(11)	15.3653(9)	21.5073(13)
α/°	90	90	90
β/°	90	103.945(2)	96.314(2)
γ/°	90	90	90
V/ Å^3	2916.8(2)	2618.7(3)	6230.1(6)
Z	8	4	8
D_{calc}/ g·cm^{-3}	1.168	1.201	1.297
Abs. corr.	multi-scan	multi-scan	multi-scan
Max./min. Transm.	0.7455 / 0.7040	0.7456 / 0.6758	0.7455 / 0.5921
μ/ cm^{-1}	2.34	0.82	1.01
F(000)	1104	1024	2544
T/ K	100(2)	100(2)	100(2)
θ range/°	2.51 : 27.16	2.32 : 27.96	2.17 : 27.16
range h,k,l	−14:14; −14:13; −30:30	−13:14; −21:21; −20:20	−24:23; −19:19; −27:27
Refl. Coll.	49784	61767	50912
Refl. Indep.	3235	6261	6912
Refl. I > 2σ(I)	2766	4937	5171
Data / restr. / param.	3235 / 0 / 151	6261 / 0 / 311	6912 / 0 / 404
R_{int}	0.0631	0.0636	0.0751
R_1 (obs)	0.0271	0.0477	0.0416
wR_2 (all)	0.0727	0.1181	0.1031
GooF (F_2)	1.037	1.037	1.042
Res. e$^-$ dens. (min./ max.)	−0.317 / 0.348	−0.233 / 0.300	−0.281 / 0.233
CCDC	1527278	1527276	1527277

Data treatment and refinement details

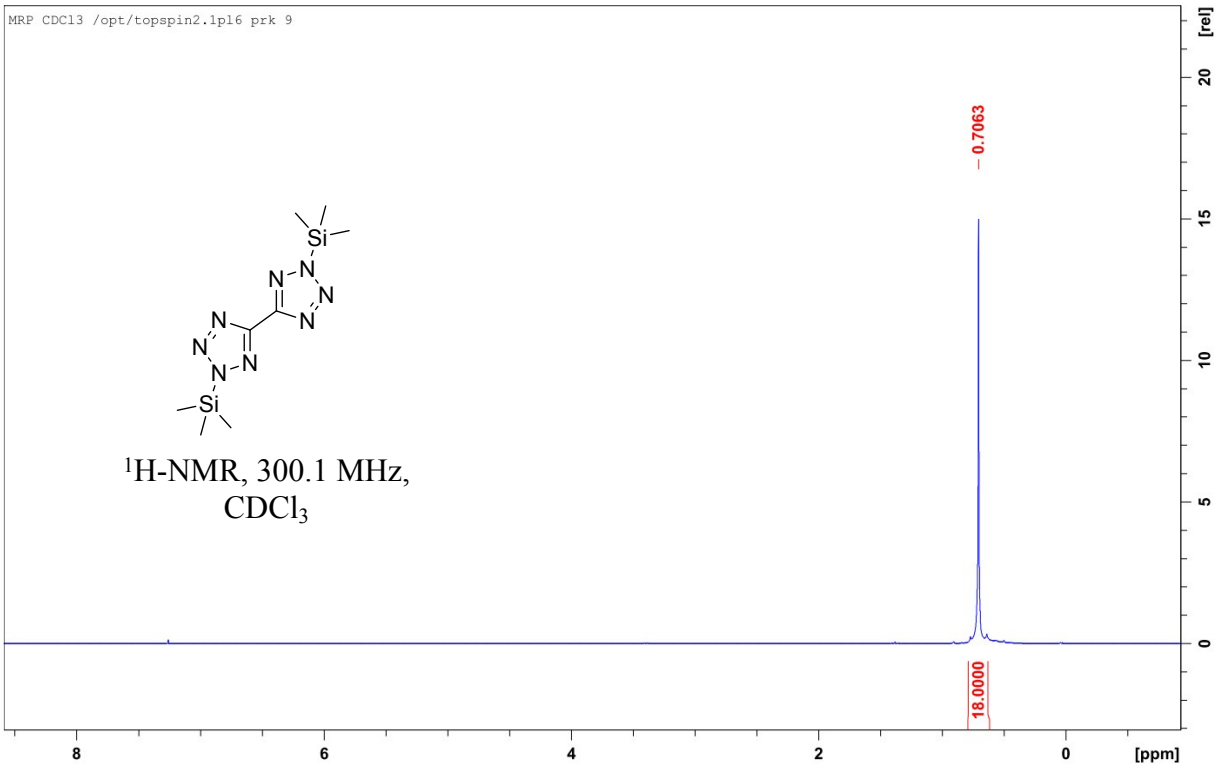
The data of compound **3**·2 THF suffers from comparatively weak scattering also resulting in a low goodness of fit value. Applying numerical or semi-empirical absorption corrections resulted in significant worsening of the refinement results, therefore no absorption correction was applied.

Very weak scattering and non-merohedric twinning complicated solution and refinement of structure **4**. HKLF5 absorption corrections (applied within Stoe X-Area) yielded unsatisfactory results. Best results were obtained, when the advanced integration options of X-Area (merging of Friedel pairs and equivalent reflections) were chosen. Nevertheless only poor bond length accuracy and a very low goodness of fit value could be reached. The model may serve as structural proof, though.

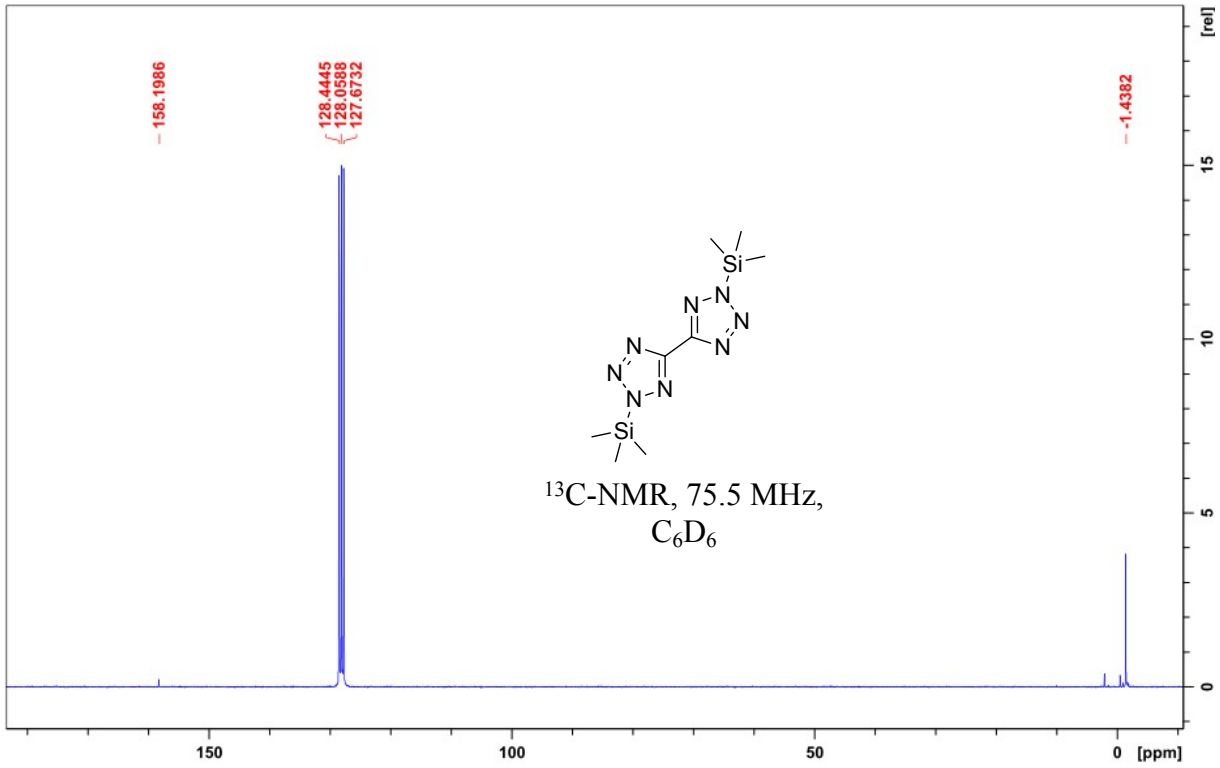
The structures of compounds **7** and **8** suffer from significant disorder especially in the respective cation part. In case of **7** SAME, DELU, RIGU, FLAT and DFIX restraints had to be applied to reach convergence on a chemically justifiable model. In case of **8** DELU, RIGU and SAME had to be applied for the same cause.

NMR Spectra

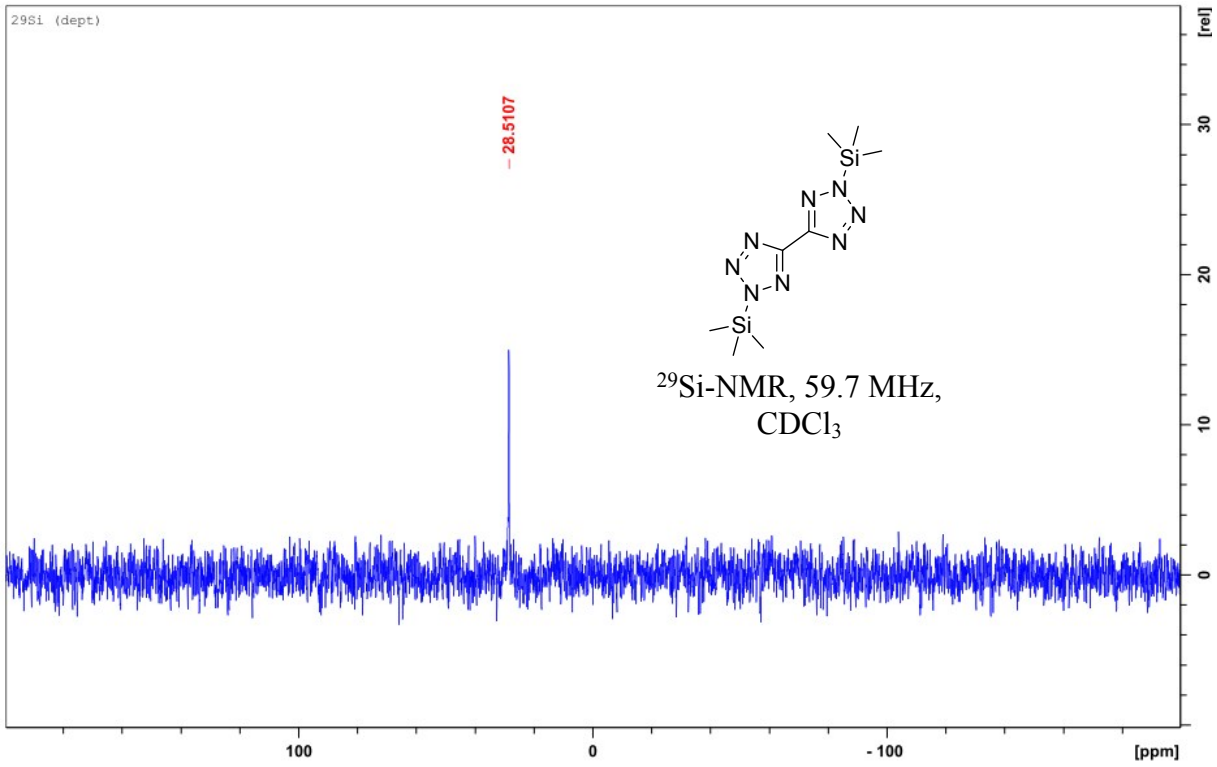
TMS_2BT (2)



^{1}H-NMR, 300.1 MHz,
$CDCl_3$

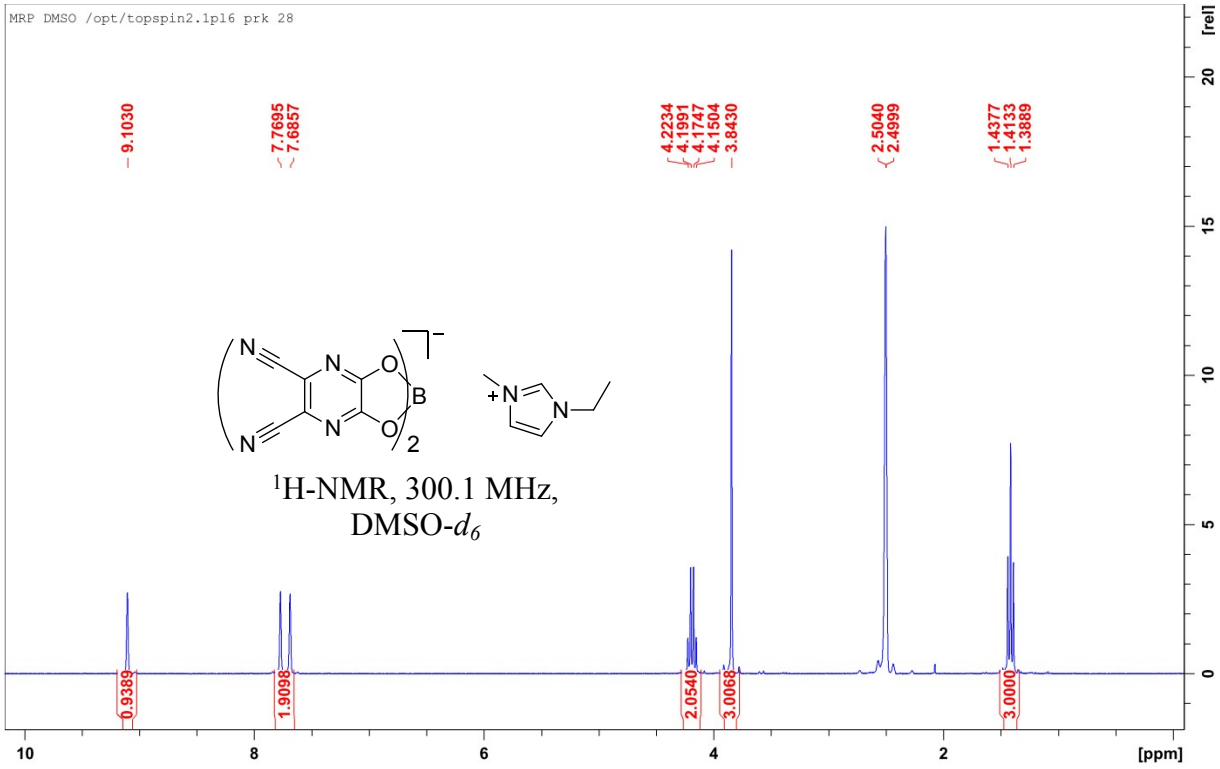


^{13}C-NMR, 75.5 MHz,
C_6D_6

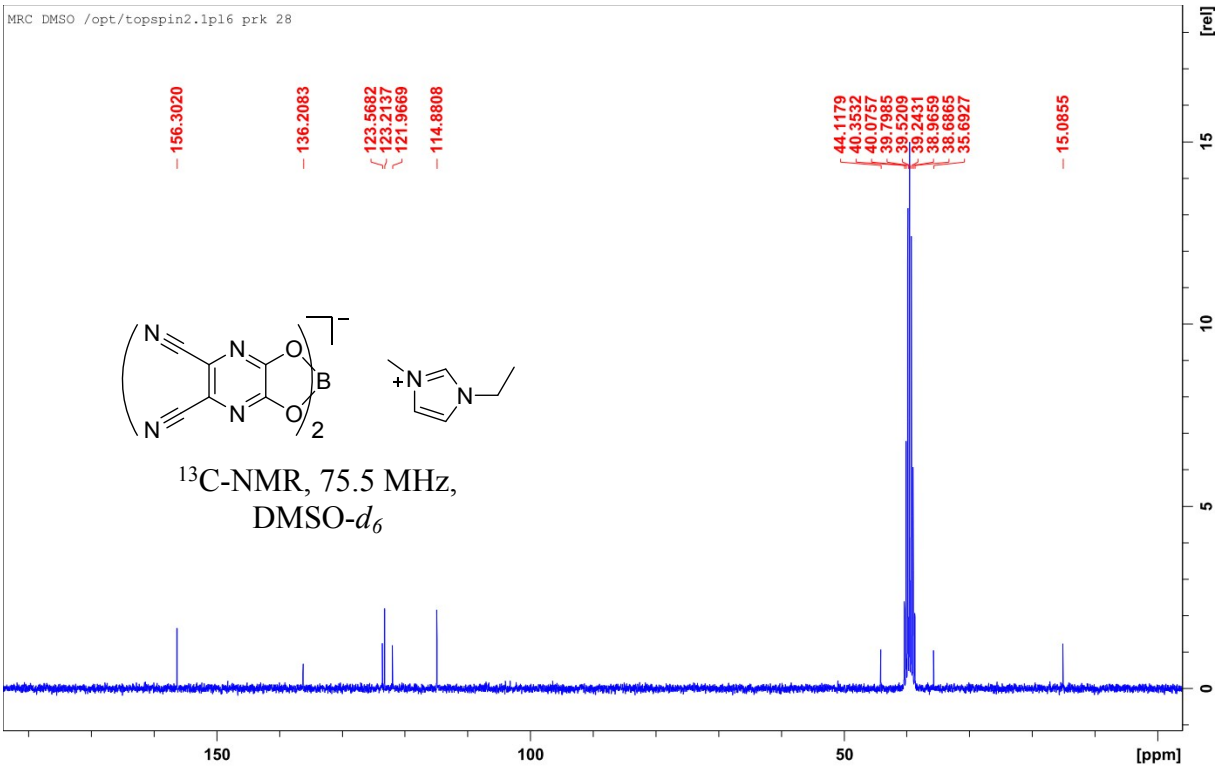


^{29}Si-NMR, 59.7 MHz,
$CDCl_3$

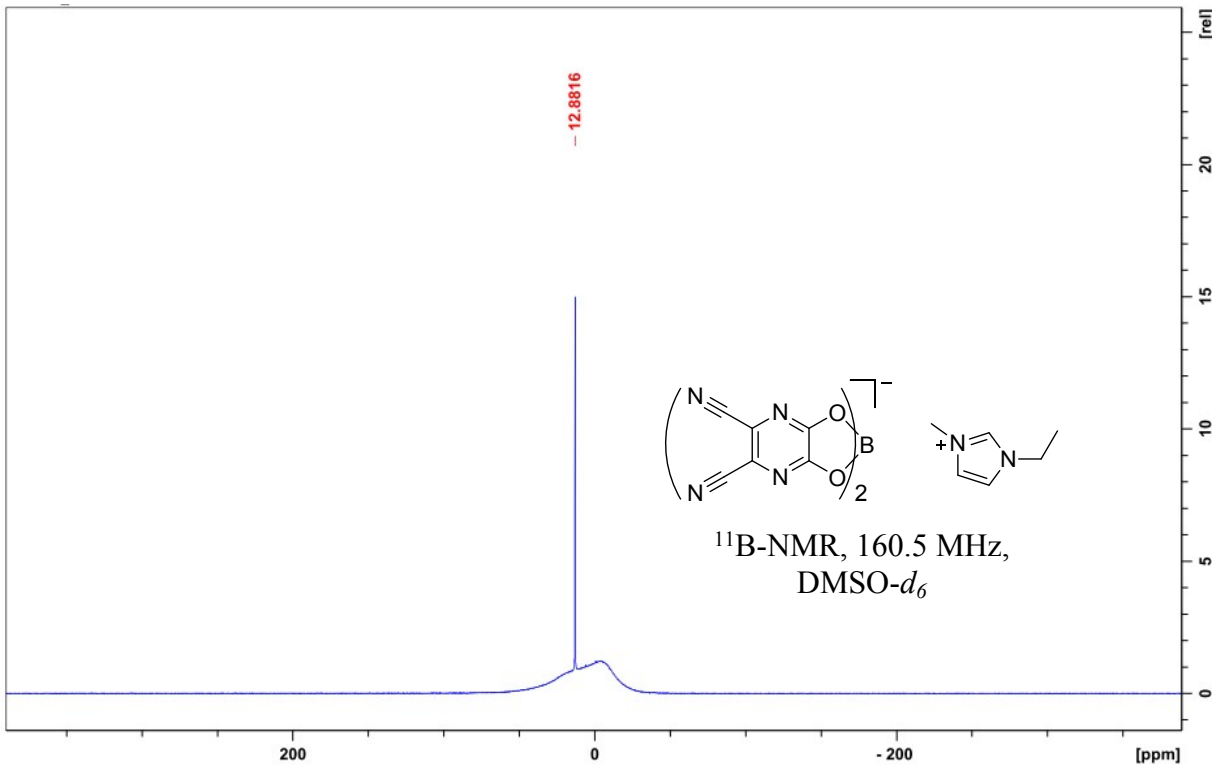
[EMIm][(OPN)$_2$B] (7)



^{1}H-NMR, 300.1 MHz,
DMSO-d_6

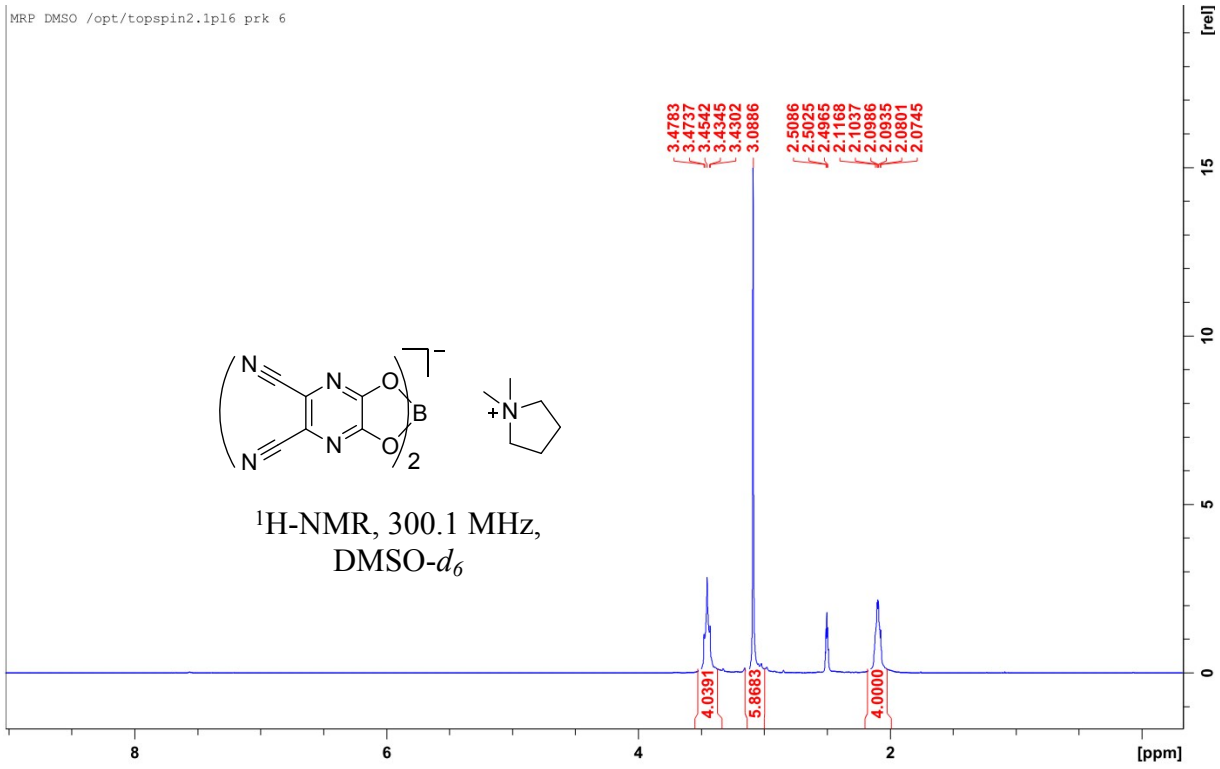


^{13}C-NMR, 75.5 MHz,
DMSO-d_6

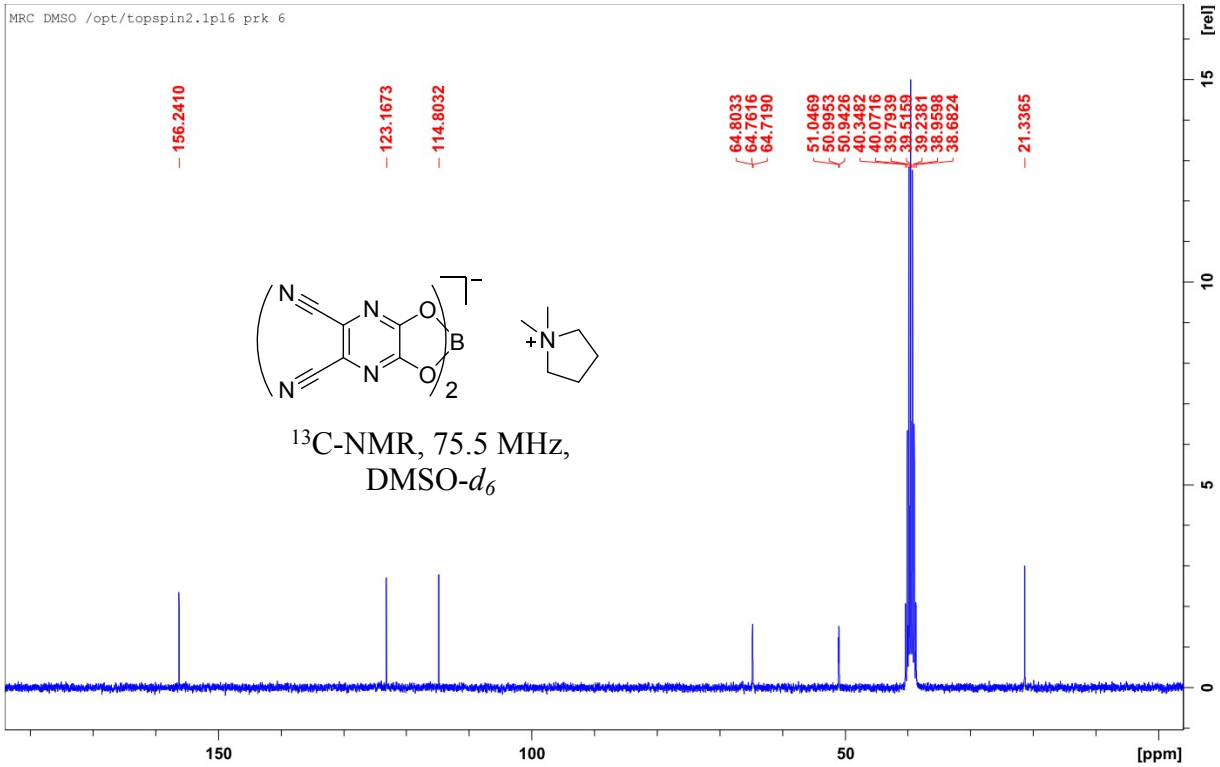


^{11}B-NMR, 160.5 MHz,
DMSO-d_6

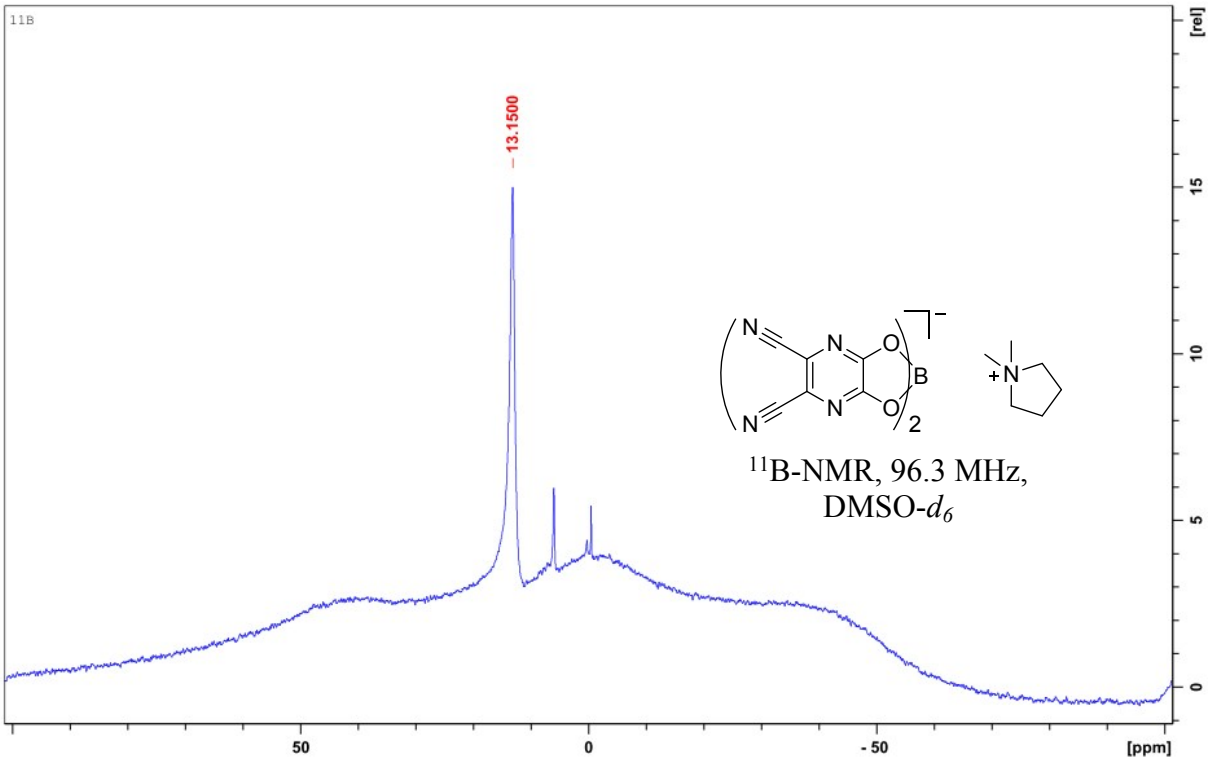
[DMPyr][(OPN)$_2$B] (8)



^{1}H-NMR, 300.1 MHz,
DMSO-d_6

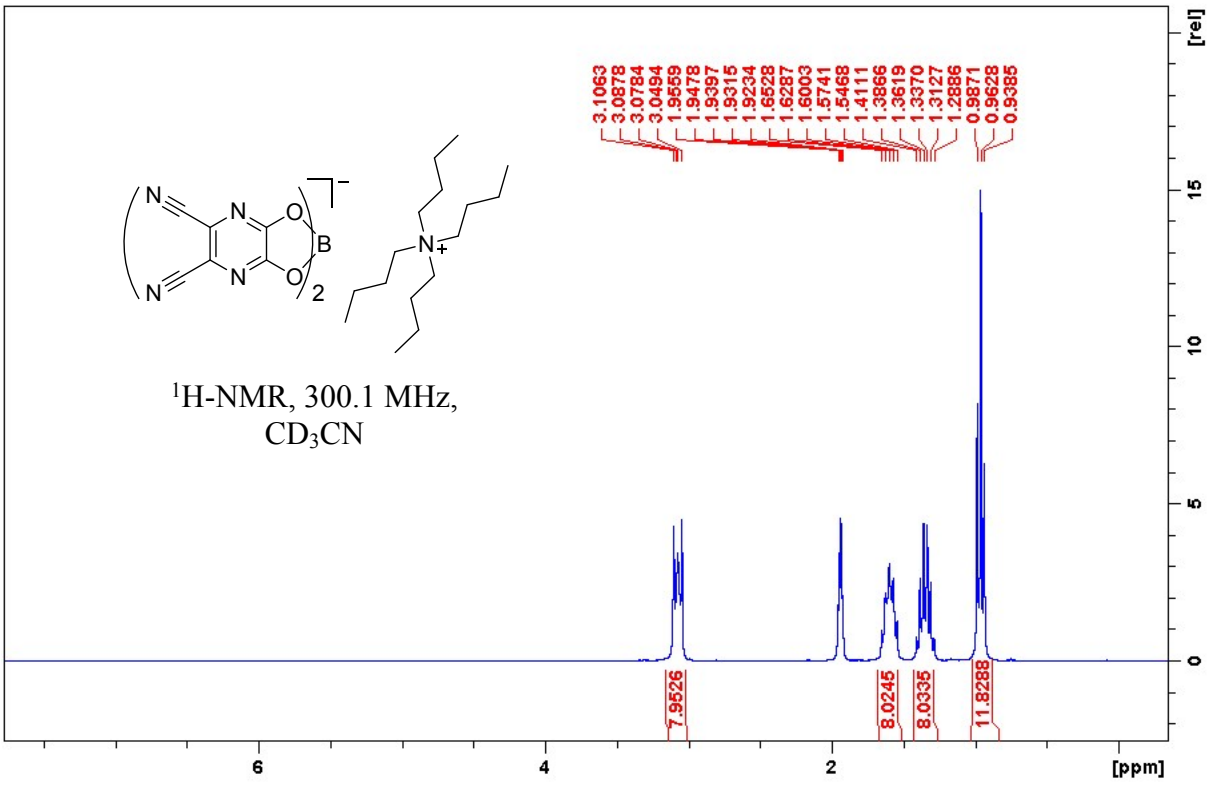


^{13}C-NMR, 75.5 MHz,
DMSO-d_6

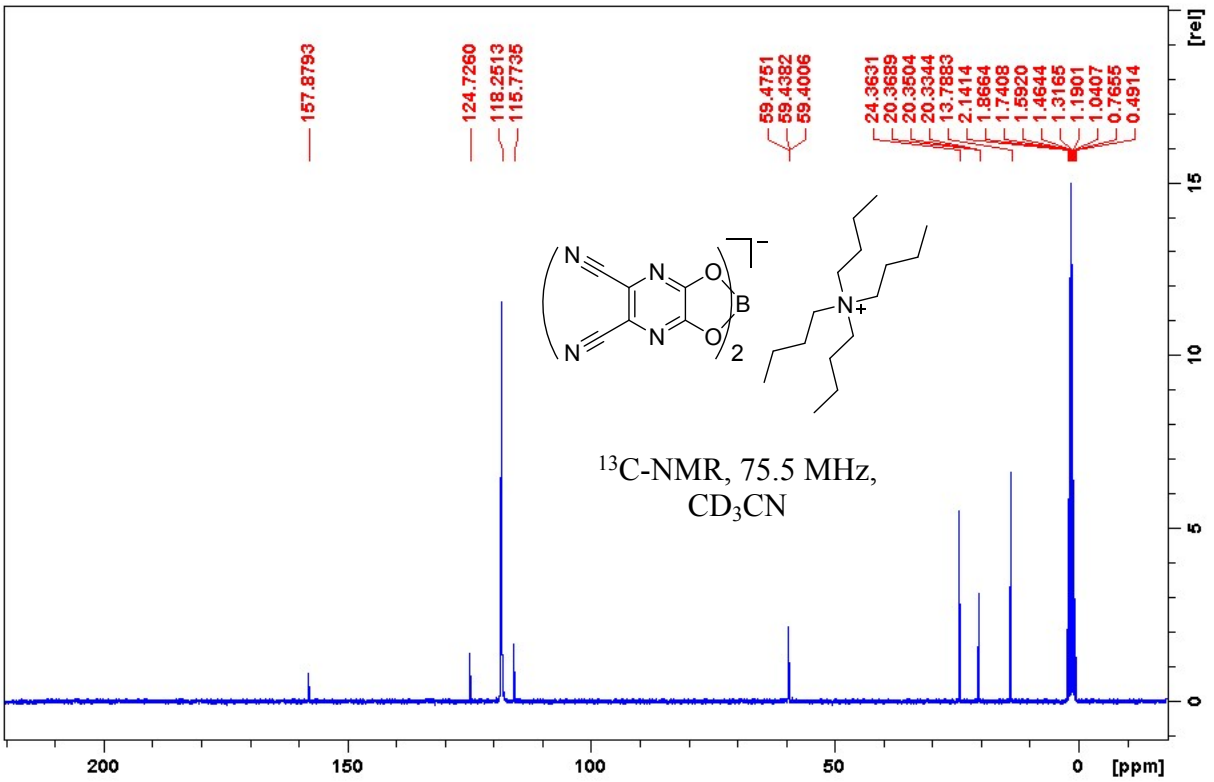


^{11}B-NMR, 96.3 MHz,
DMSO-d_6

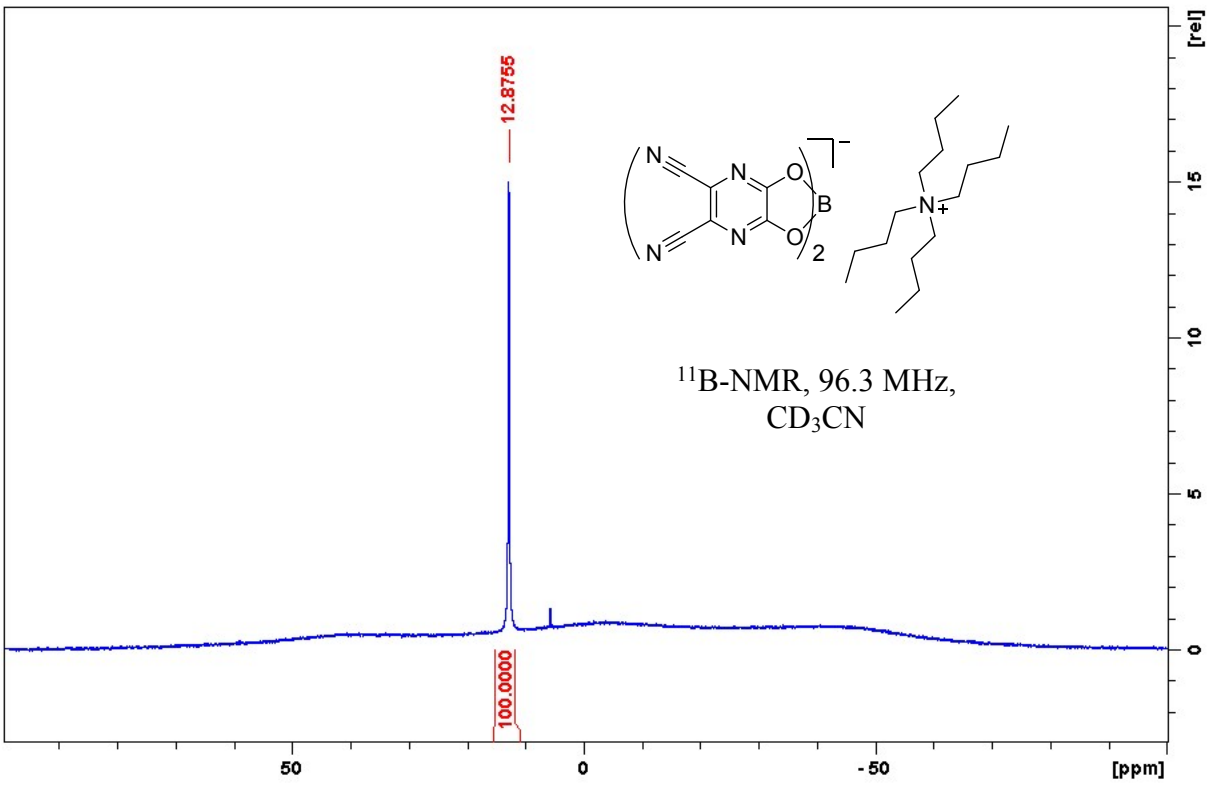
[NBu$_4$][(OPN)$_2$B] (9)



^{1}H-NMR, 300.1 MHz,
CD_3CN

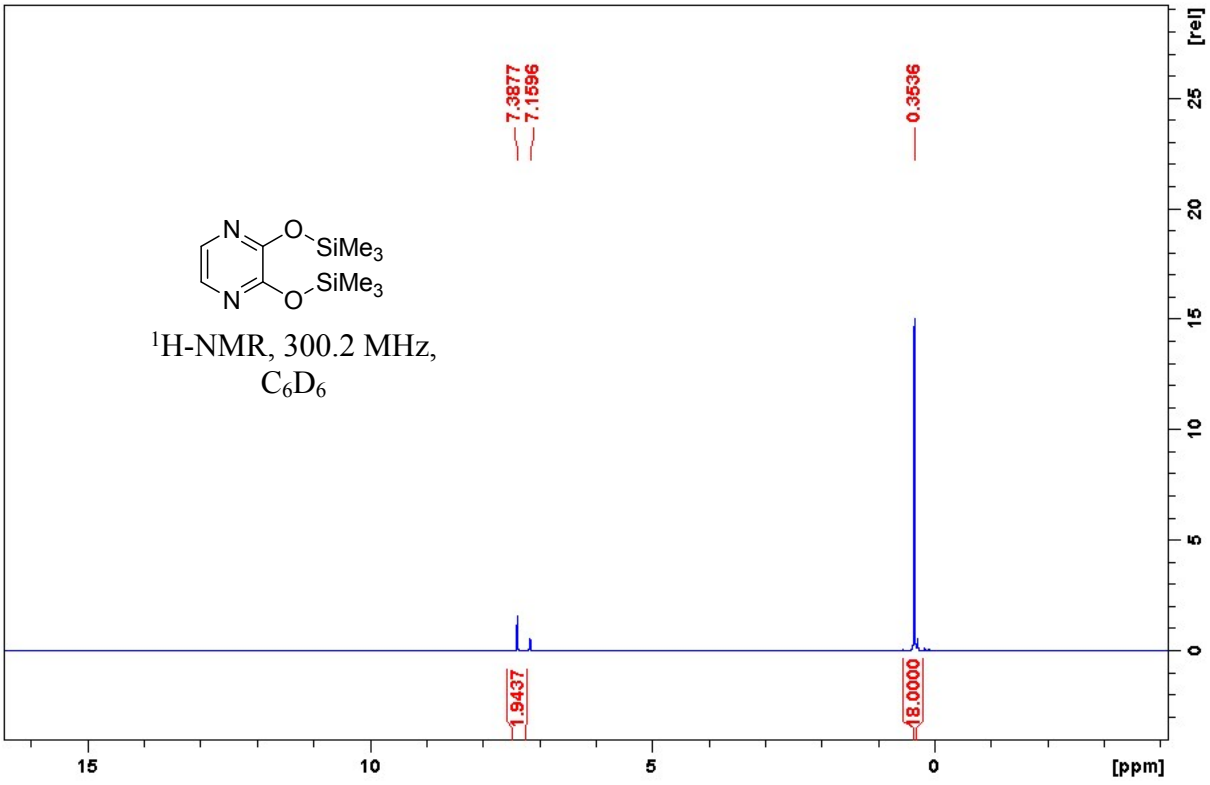


^{13}C-NMR, 75.5 MHz,
CD_3CN

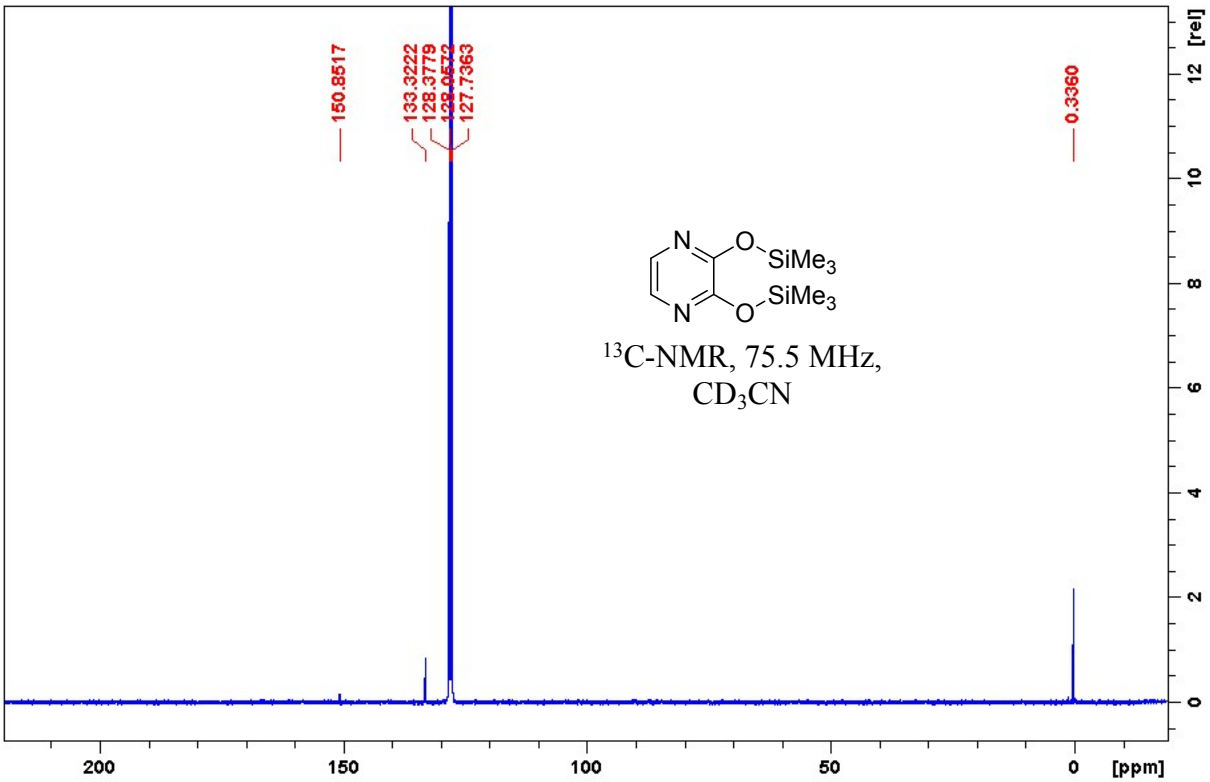


^{11}B-NMR, 96.3 MHz,
CD_3CN

TMS_2OP (10)

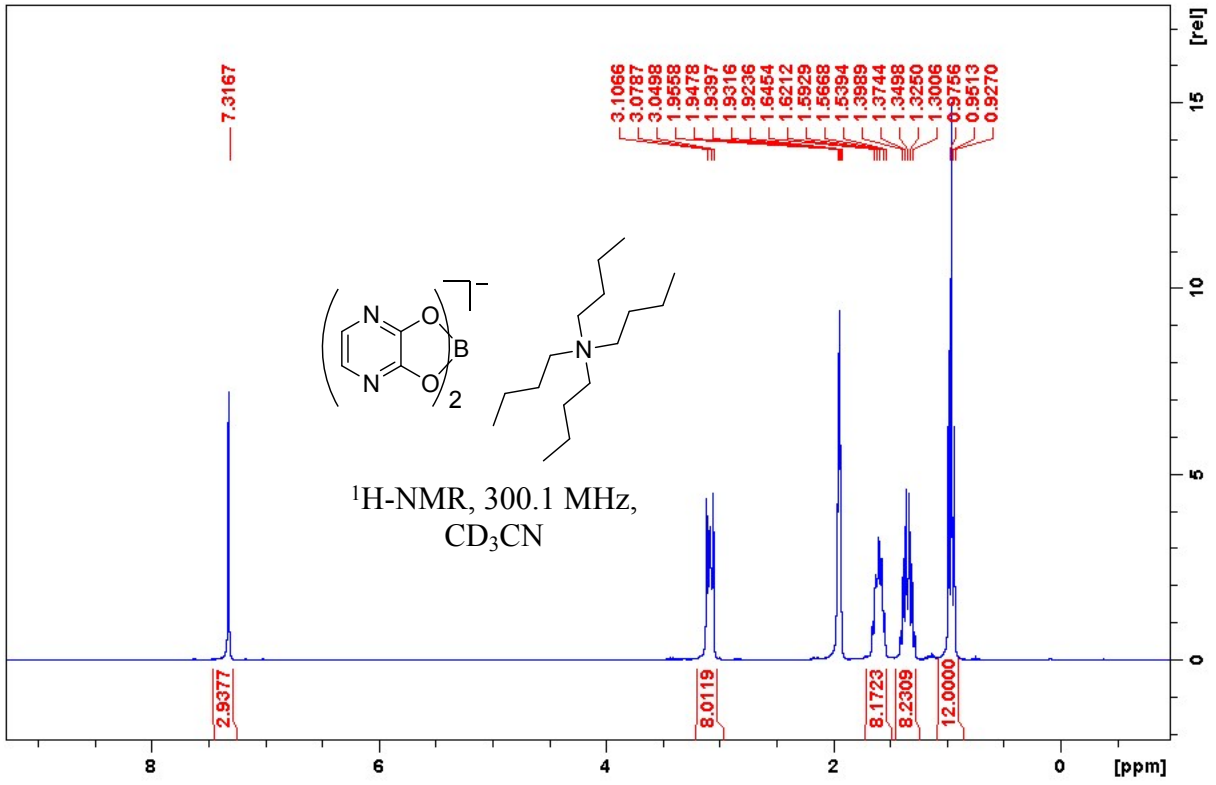


^{1}H-NMR, 300.2 MHz,
C_6D_6

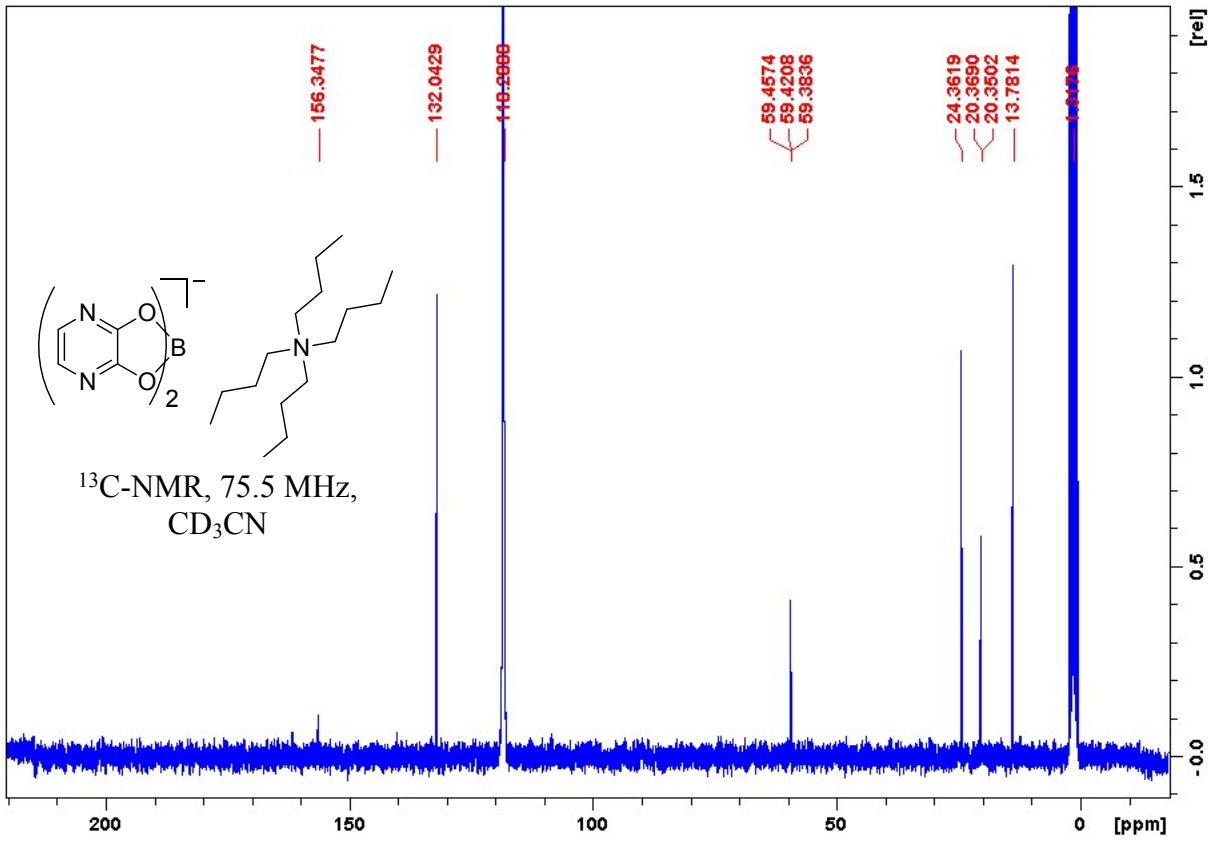


^{13}C-NMR, 75.5 MHz,
CD_3CN

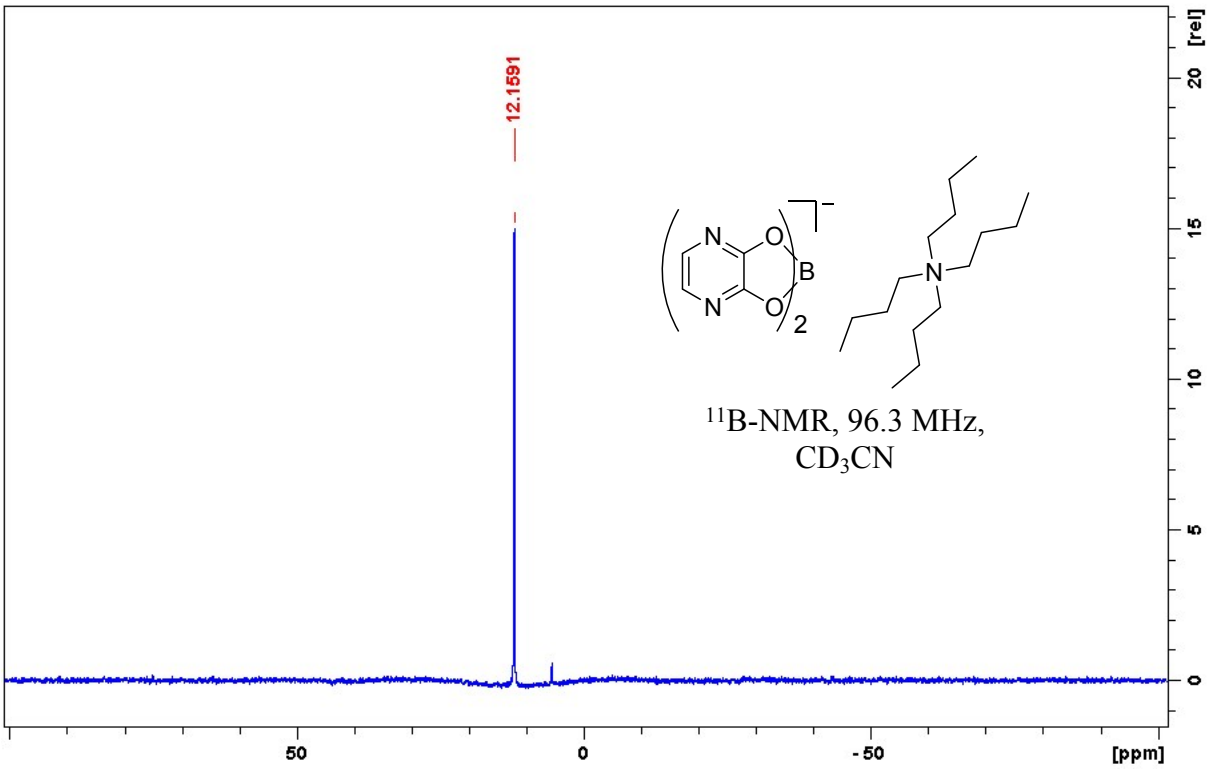
[NBu$_4$][(OP)$_2$B] (11)



^{1}H-NMR, 300.1 MHz,
CD_3CN

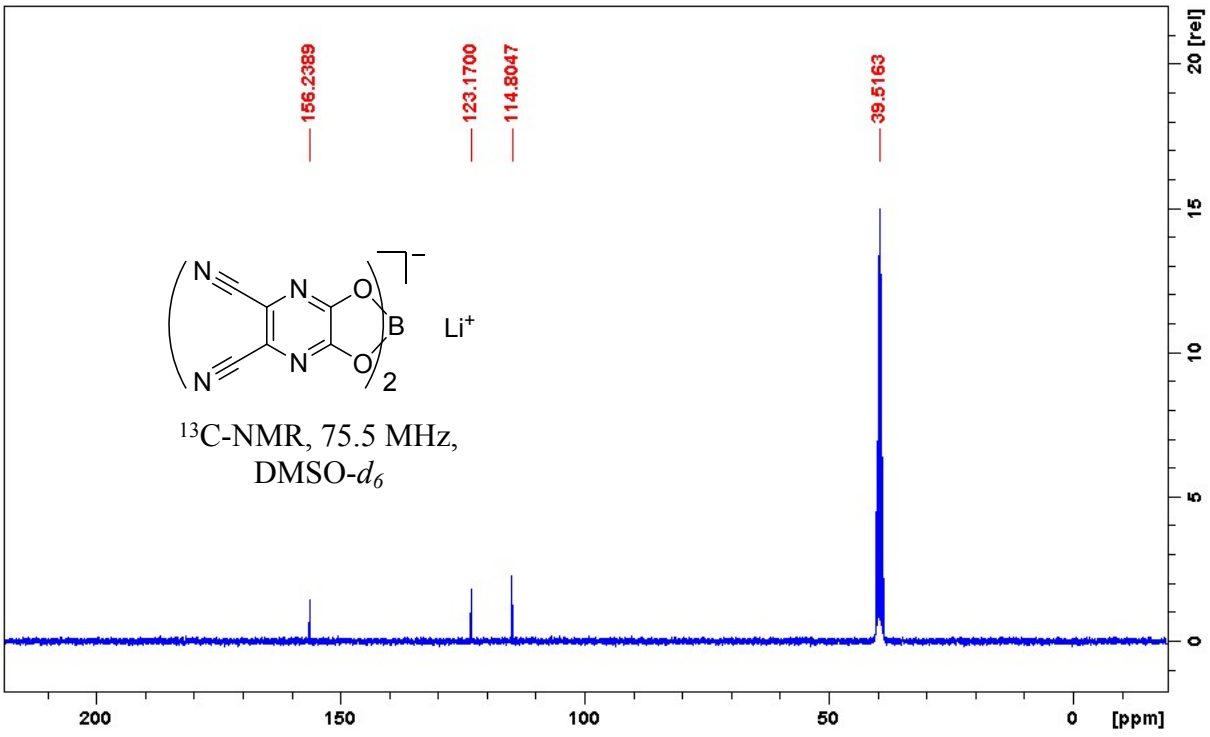


^{13}C-NMR, 75.5 MHz,
CD_3CN

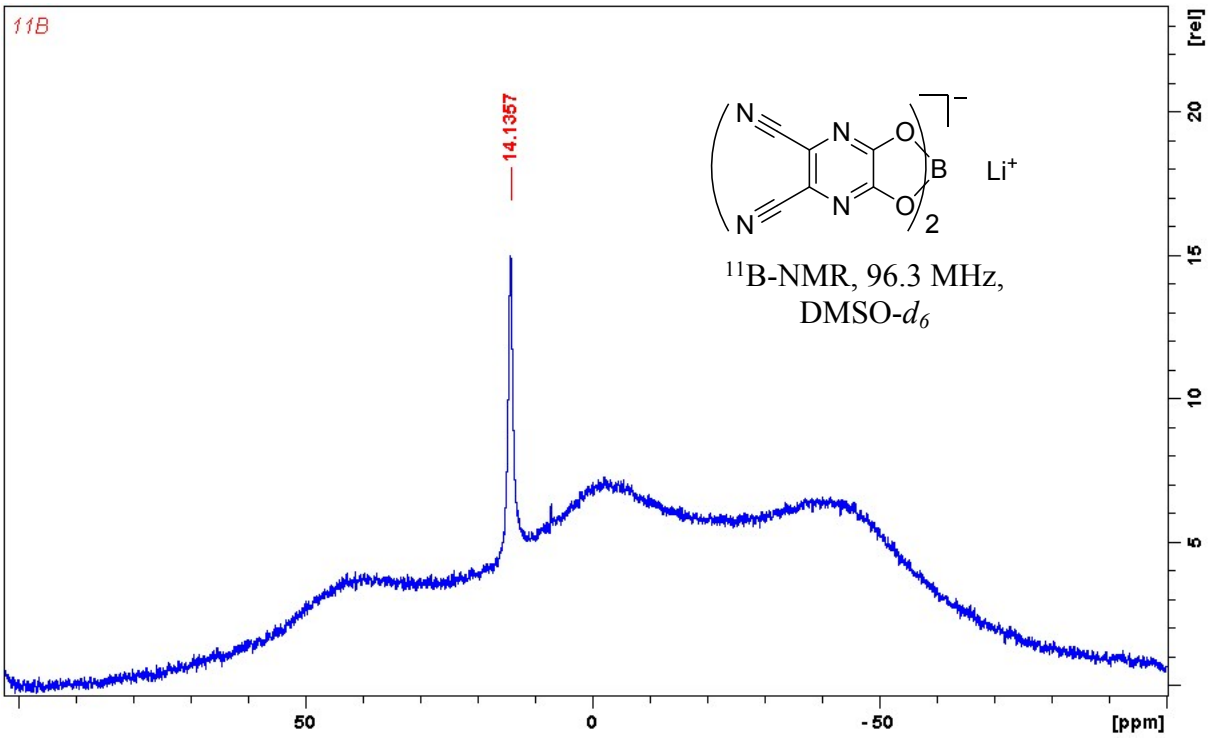


^{11}B-NMR, 96.3 MHz,
CD_3CN

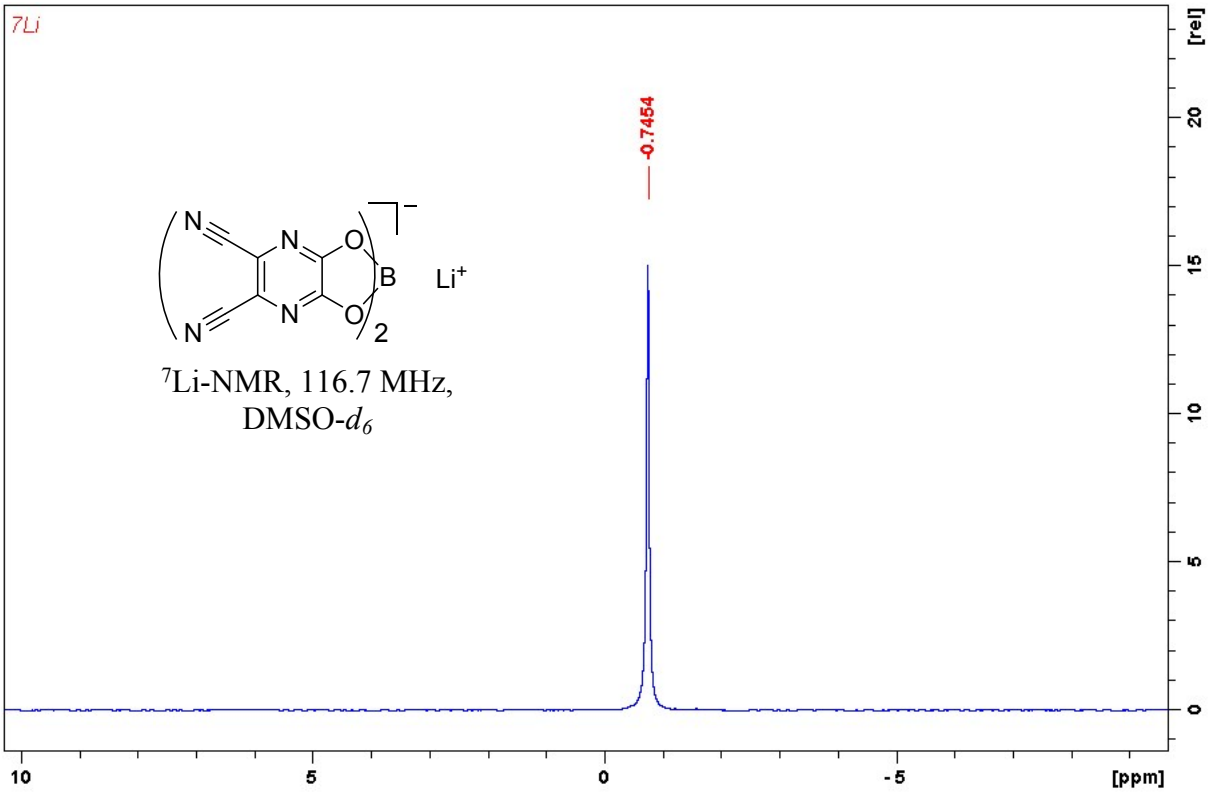
[Li][(OPN)$_2$B] (12)



^{13}C-NMR, 75.5 MHz,
DMSO-d_6

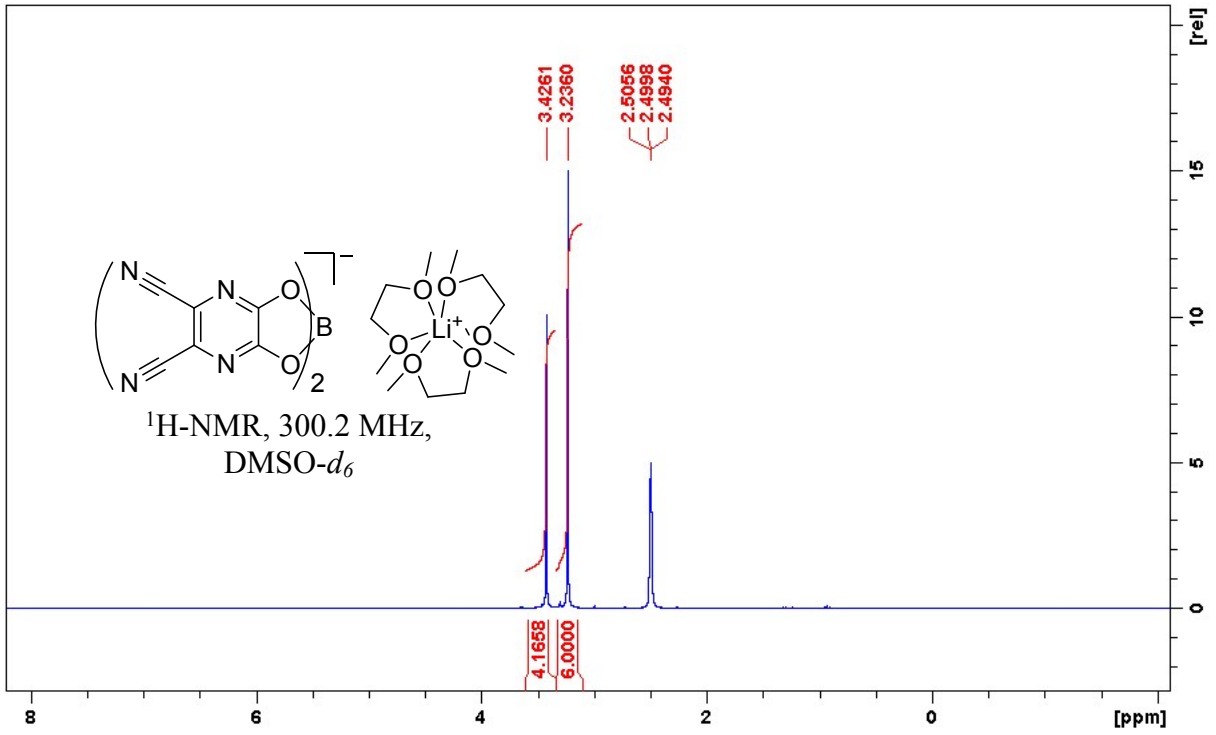


^{11}B-NMR, 96.3 MHz,
DMSO-d_6

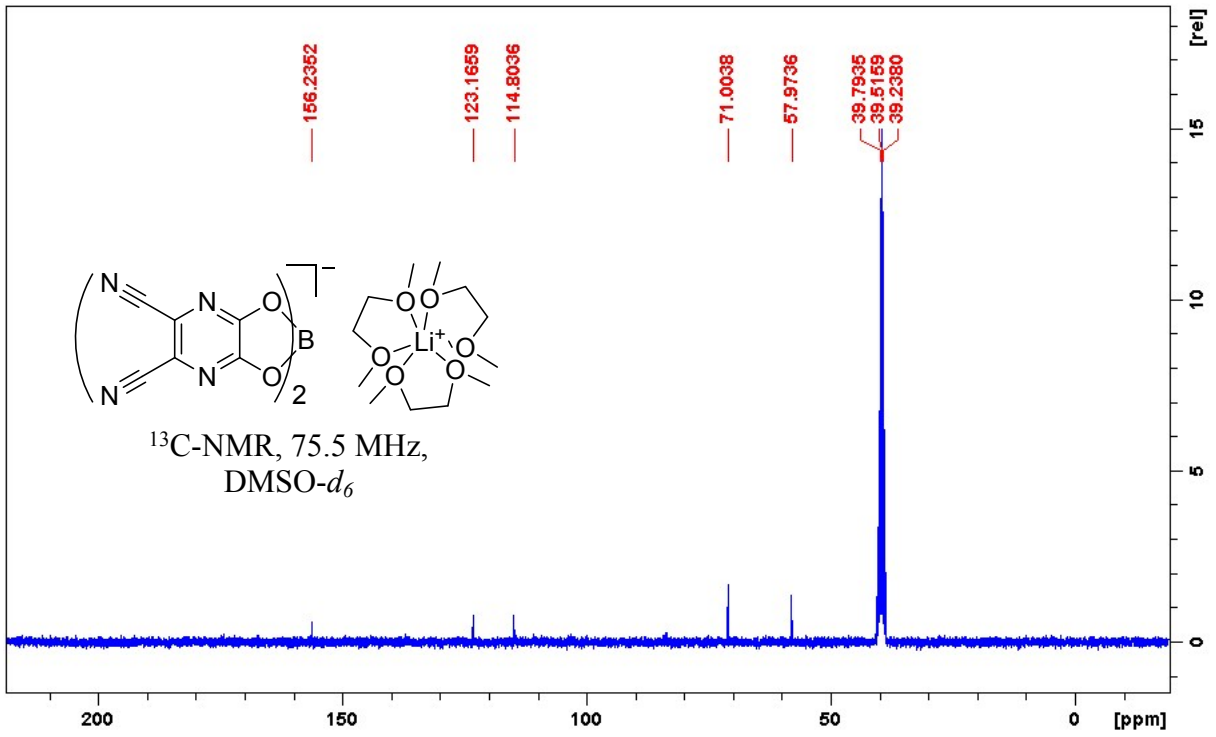


^{7}Li-NMR, 116.7 MHz,
DMSO-d_6

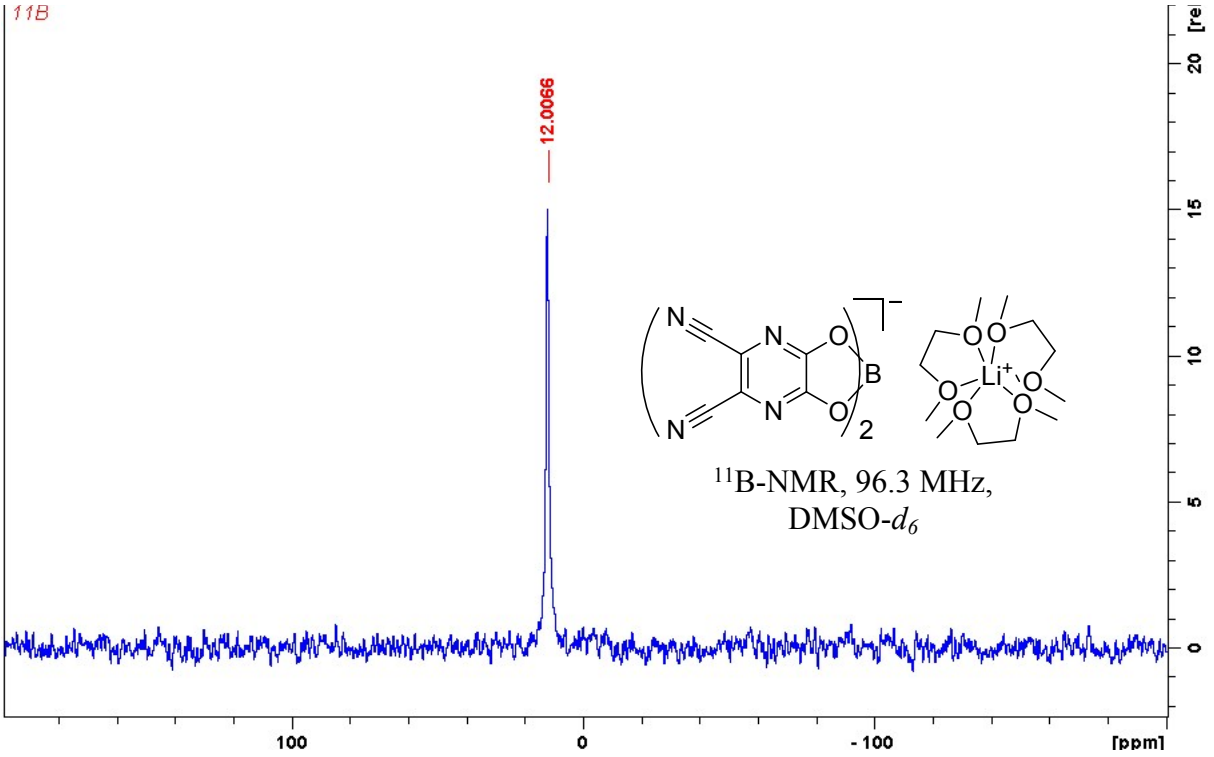
[(DME)$_3$Li][(OPN)$_2$B] (12·3 DME)



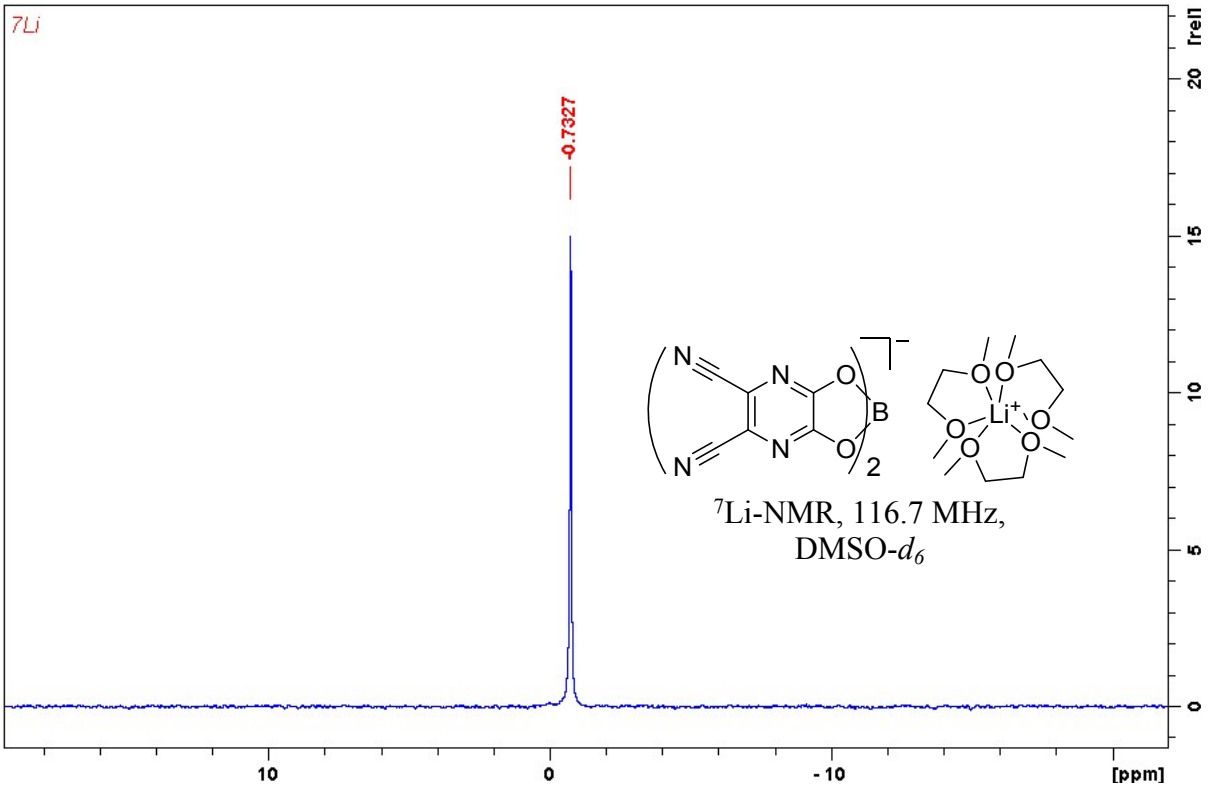
^{1}H-NMR, 300.2 MHz,
DMSO-d_6



^{13}C-NMR, 75.5 MHz,
DMSO-d_6

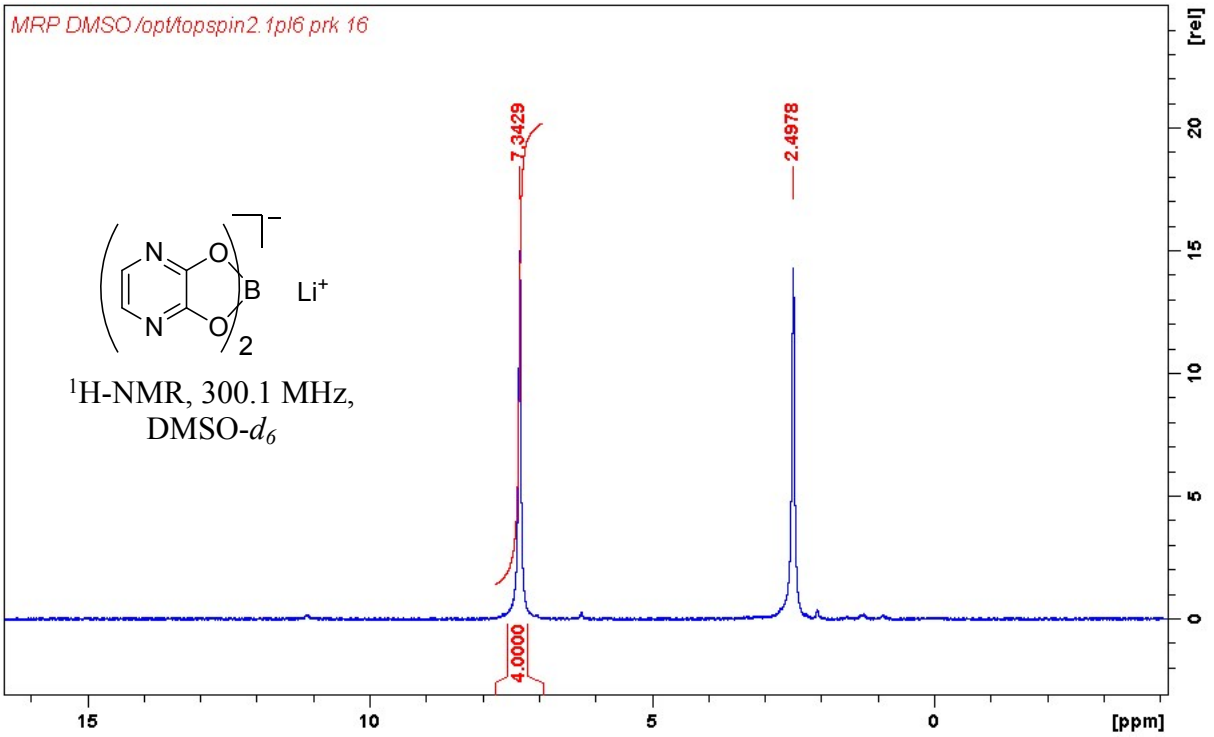


^{11}B-NMR, 96.3 MHz,
DMSO-d_6



^{7}Li-NMR, 116.7 MHz,
DMSO-d_6

[Li][(OP)$_2$B] (13)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4.0000
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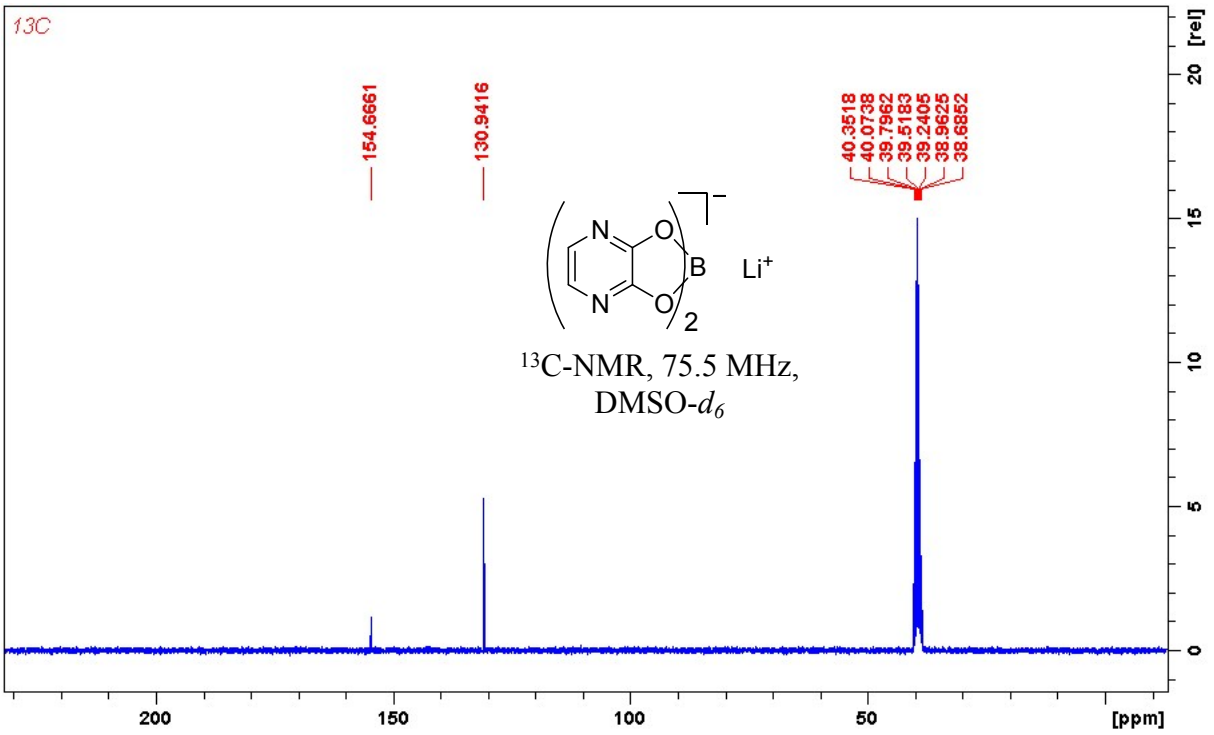
[ppm]
Li+
^{1}H-NMR, 300.1 MHz,
DMSO-d_6


13C
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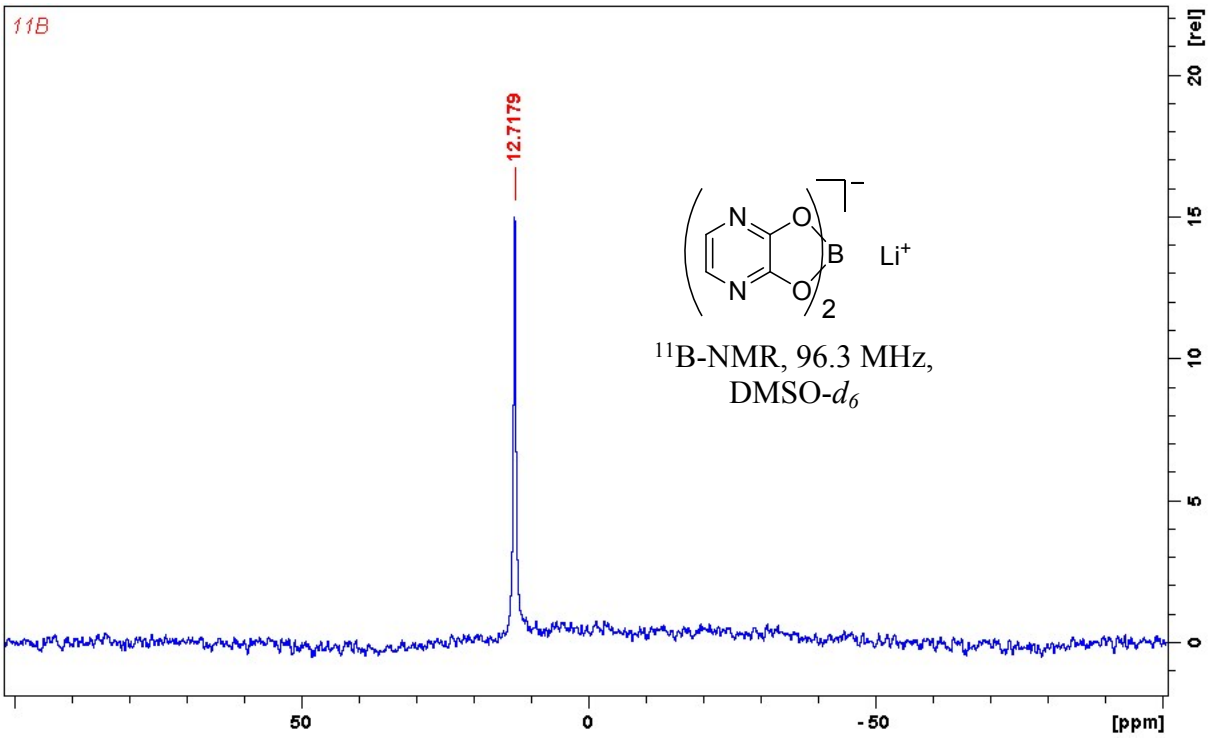
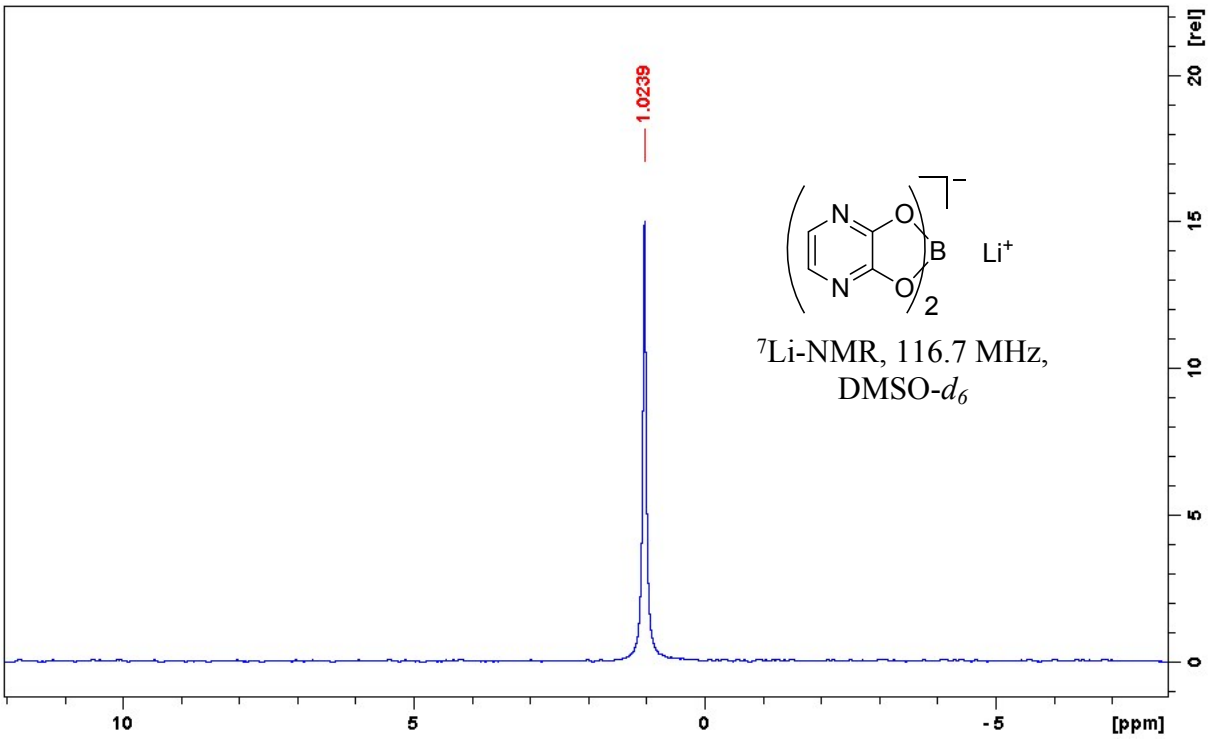
[ppm]
Li+
^{13}C-NMR, 75.5 MHz,
DMSO-d_6



^{11}B-NMR, 96.3 MHz,
DMSO-d_6



^{7}Li-NMR, 116.7 MHz,
DMSO-d_6