Supplementary material

Solubility of Phenylboronic Acid and its Cyclic Esters in Organic Solvents

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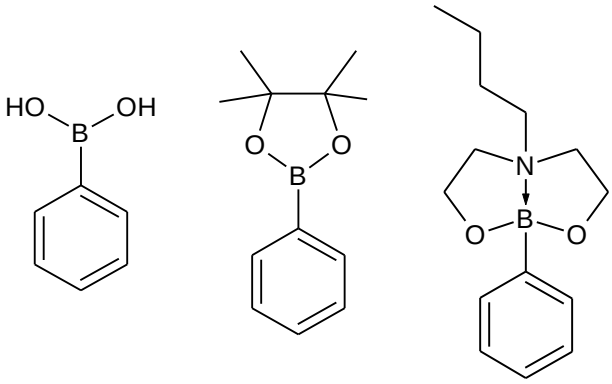
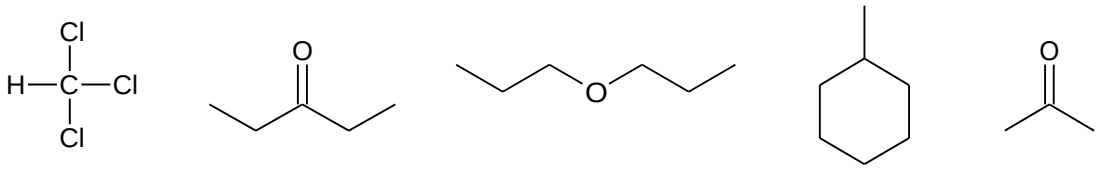
1. Investigated compounds



1 **2** **3**

2. Used solvents



a **b** **c** **d** **e**

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3. Synthesis of compound 3

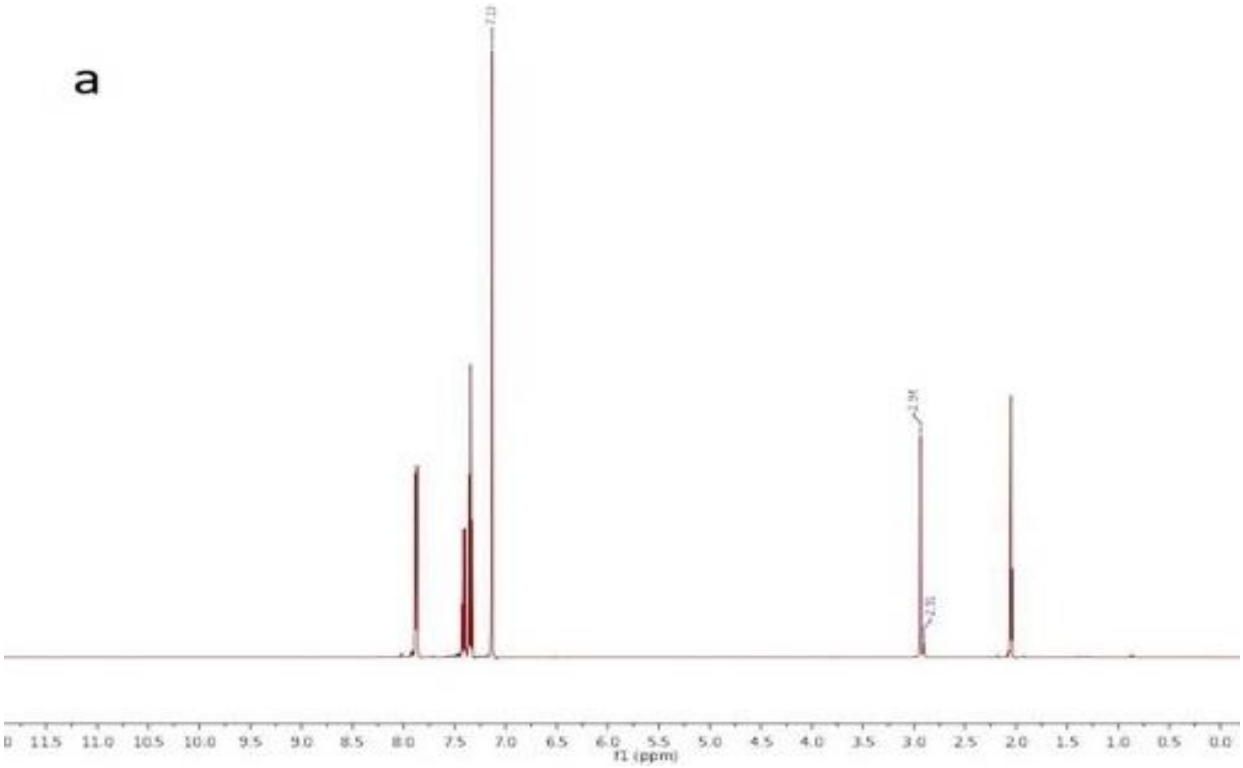
Phenylboronic acid (5.0 g, 0.041 mol) was dissolved in acetone (52.5 ml). Then 2,2'-(butylamino)-diethanol (7.03 g, 0.043 mol) and sodium sulfate (5.1 g) were added. Mixture was stirred for 3 h at room temperature. The solid was filtered and filtrate was concentrated at reduced pressure. Diethyl ether (20 mL) was added to the remaining solid residue, followed by filtration of the resulting slurry, which was washed with diethyl ether (in portions: 10, 5, 3 mL) and dried in vacuum. Product **3** was obtained with 96% yield as a white crystalline solid.

6-Butyl-2-(phenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (**3**):

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.61 (m, 2H, Ph), 7.27 (m, 3H, Ph), 4.15 (m, 4H, OCH_2), 3.03 (m, 4H, CH_2N), 2.31 (m, 2H, $N\mathbf{CH_2}CH_2CH_2CH_3$), 1.49 (m, 2H, $NCH_2\mathbf{CH_2}CH_2CH_3$), 1.12 (sext, 2H, $NCH_2CH_2\mathbf{CH_2}CH_3$, J = 7.5 Hz), 0.808 (t, 3H, CH_3, J = 7.5 Hz) ppm.

^{11}B NMR ($CDCl_3$, 96 MHz): δ = 12.76 ppm

4. NMR spectra



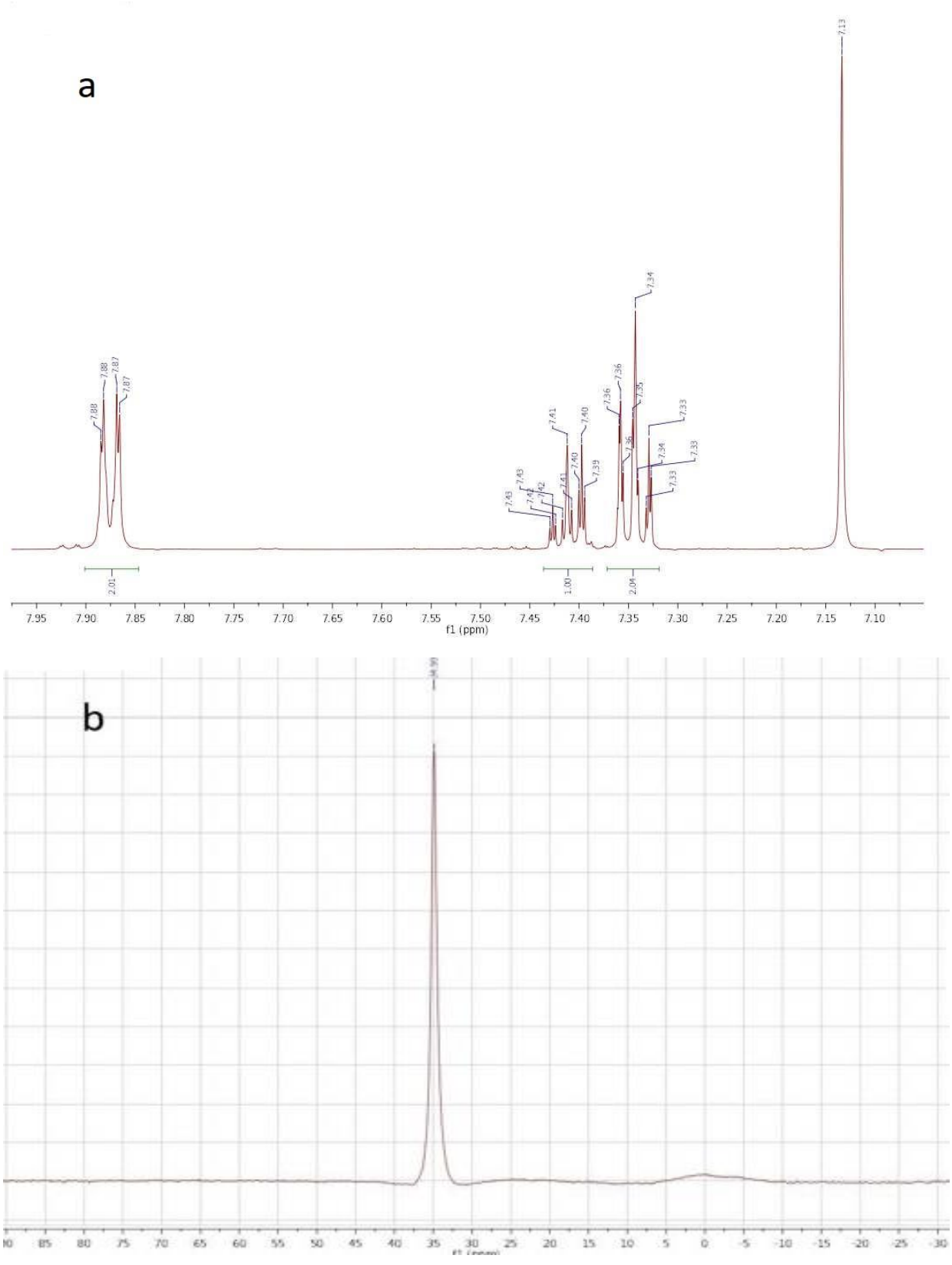
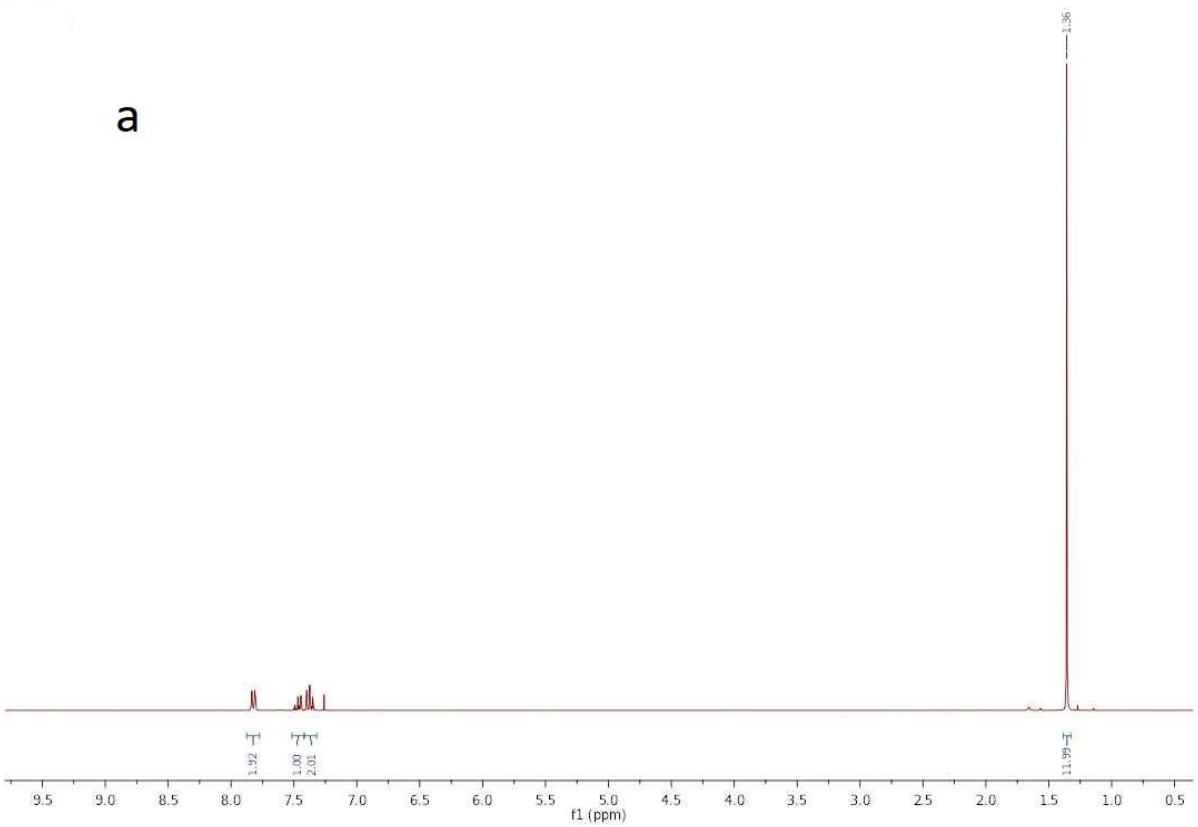
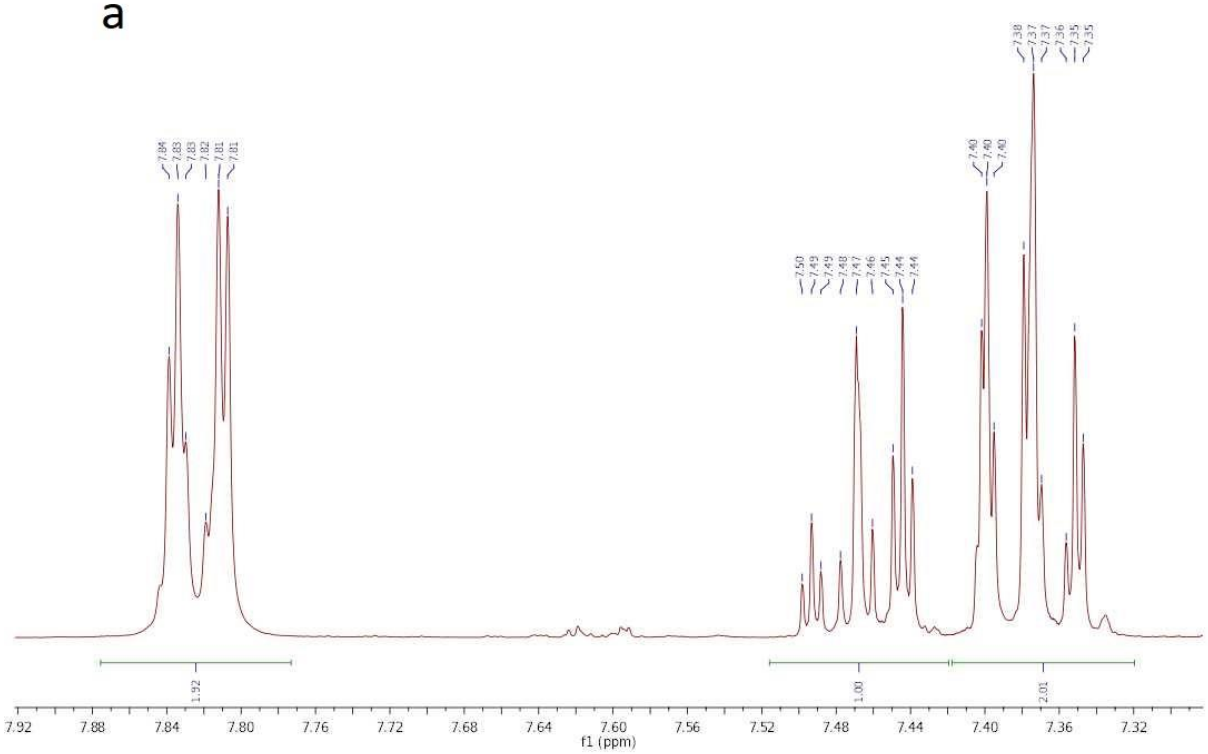


Figure S1 ^{1}H NMR (a) and ^{11}B (b) NMR spectra of compound **1** (in acetone-d6).

a


1.36
1.92
1.00
2.01
11.99
f1 (ppm)

a


7.84
7.83
7.83
7.82
7.81
7.81
7.50
7.49
7.49
7.48
7.47
7.46
7.45
7.44
7.44
7.40
7.40
7.40
7.38
7.37
7.37
7.36
7.35
7.35
1.92
1.00
2.01
f1 (ppm)

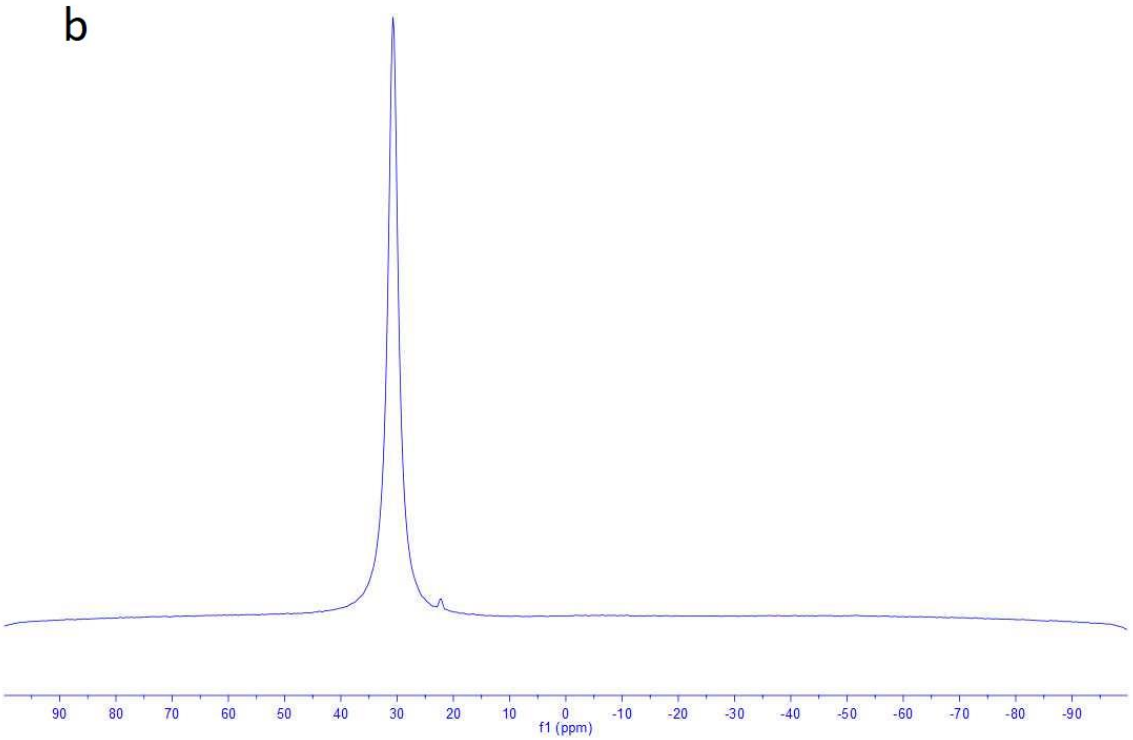
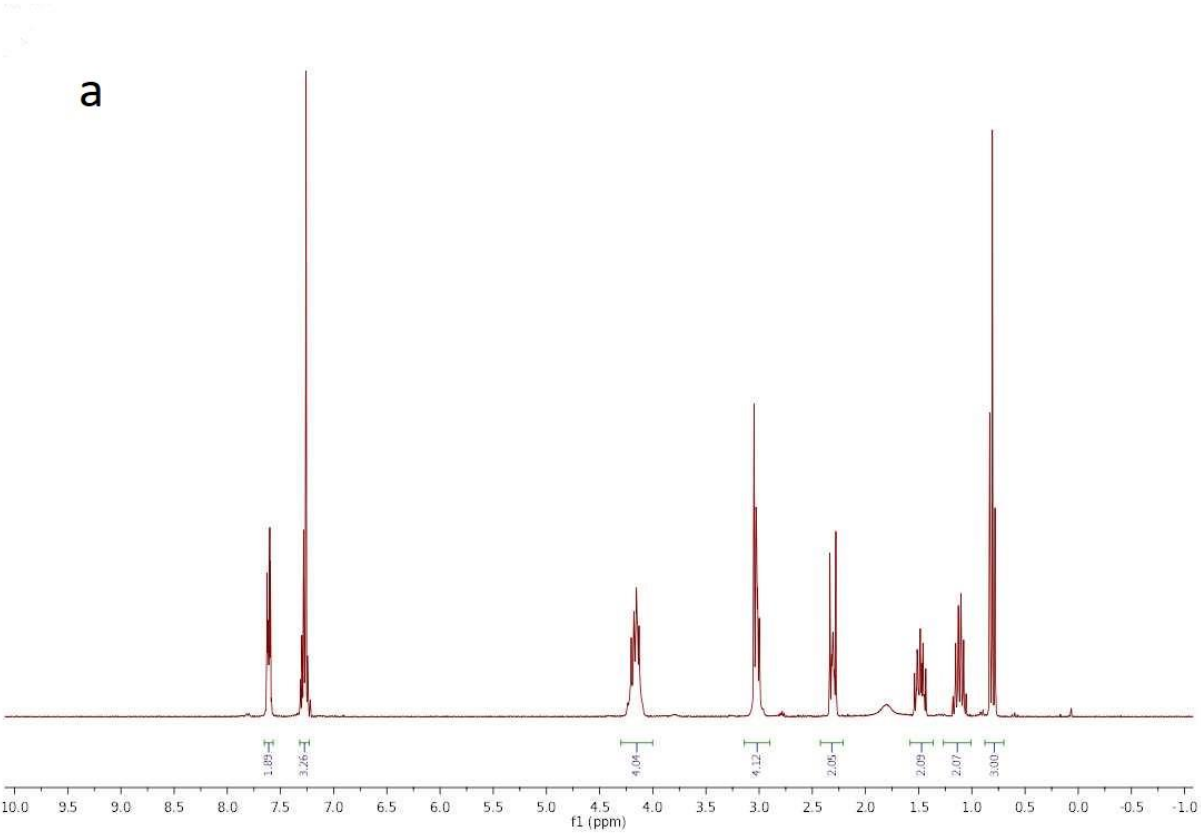


Figure S2 ^{1}H NMR (a) and ^{11}B (b) NMR spectra of compound **2** (in $CDCl_3$).



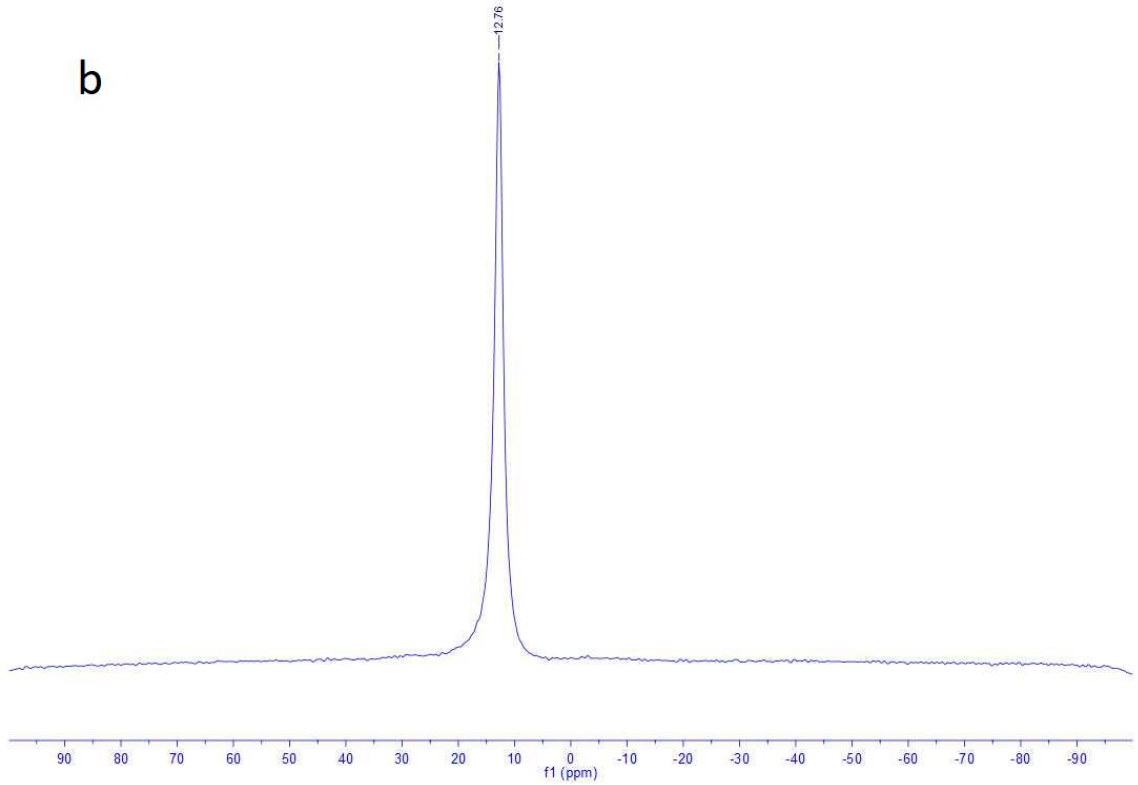


Figure S3 ^{1}H NMR (a) and ^{11}B (b) NMR spectra of compound **3** (in $CDCl_3$).

5. Typical luminescence vs. temperature curve

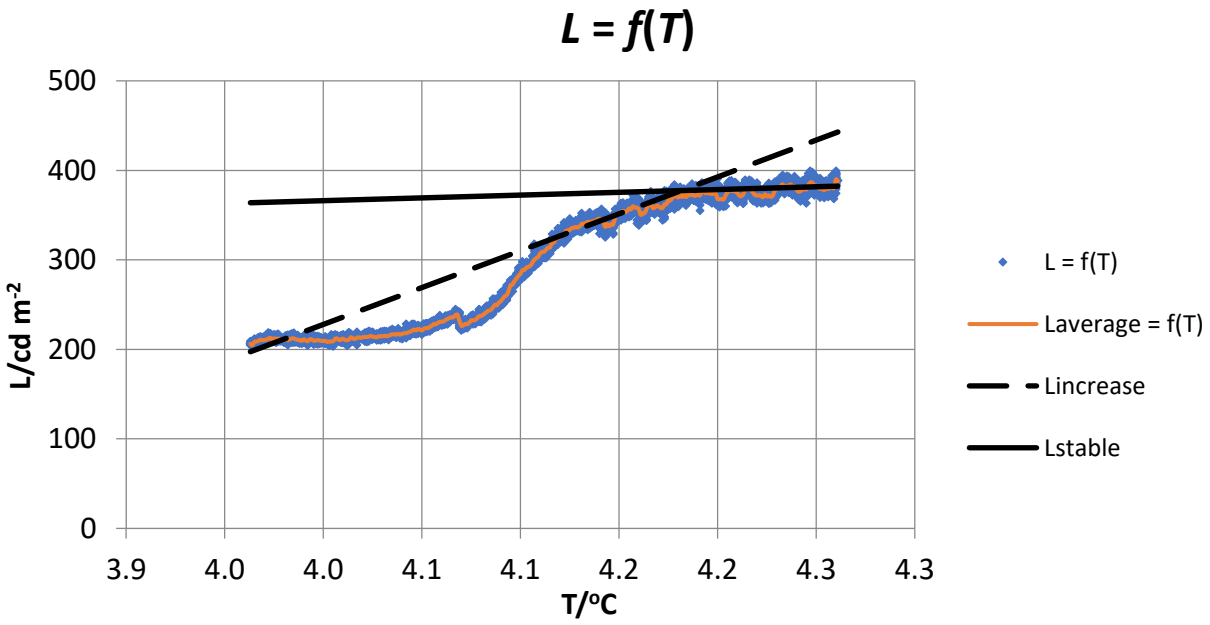
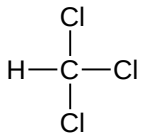


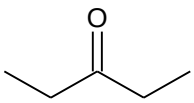
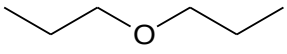
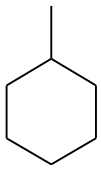
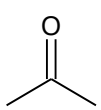
Figure S4 Typical luminescence vs. temperature curve.

6. Primary experimental data

Table S1 Experimental solid-liquid equilibrium data for the compounds **1** – **3** and the solvents **a** – **e**

solvent	**1**		**2**		**3**	
	x_1	T/°C	x_1	T/°C	x_1	T/°C
a 	0.24207	72.73	0.89490	17.70	0.60718	98.02
	0.18030	62.94	0.85800	15.22	0.55574	90.41
	0.13912	58.35	0.82130	12.29	0.50636	82.85
	0.11400	52.92	0.79408	10.27	0.46669	78.18
	0.09137	49.45	0.76948	8.42	0.43699	71.31
	0.07970	46.28	0.74280	5.80	0.39716	65.57
	0.06848	43.27	0.71976	3.18	0.36190	56.18
	0.05850	38.97	0.69847	1.53	0.34322	47.83
	0.04882	34.79	0.67219	-3.22	0.33514	49.71
	0.03304	33.48	0.65991	-4.90	0.33239	46.28
					0.31816	41.82
		-		-	0.30926	38.60
					0.27511	24.32

(continued)

solvent	1		2		3	
	x_1	T/°C	x_1	T/°C	x_1	T/°C
b 			0.92402	20.09	0.46030	89.37
			0.89095	17.84	0.43057	88.24
			0.79593	12.32	0.40467	85.26
			0.75234	9.14	0.35112	82.42
			0.71041	6.12	0.34481	80.43
			0.65208	1.65	0.33576	79.17
		-	0.61530	-1.25	0.31831	77.10
			0.58771	-3.77	0.29023	73.90
			0.56905	-5.80	0.26365	70.76
			0.56660	-5.13	0.23340	66.15
			0.53657	-7.90	0.21517	63.38
				-	0.20253	61.53
c 	0.46327	51.43	0.97515	24.69	0.14777	91.38
	0.30313	45.04	0.87010	19.68	0.12694	90.55
	0.27828	41.97	0.82986	17.61	0.12093	90.18
	0.23061	32.97	0.77867	14.62	0.11312	89.87
	0.20628	27.00	0.71853	10.96	0.10941	89.67
			0.61925	1.70	0.10287	89.36
			0.60631	1.05	0.09742	89.03
			0.58645	-1.10	0.09268	88.69
			0.55969	-3.07	0.08121	87.91
		-	0.54746	-4.30	0.07176	87.09
					0.05676	85.40
					0.03179	79.39
				-	0.02589	76.48
					0.02033	73.92
d 	0.04927	70.38	0.88500	18.54	0.02189	87.92
	0.03036	68.21	0.82503	14.98	0.01778	86.34
	0.02406	64.57	0.77049	11.59	0.01433	84.79
	0.02099	60.92	0.70460	7.67	0.01158	81.69
	0.01768	57.93	0.65800	4.84	0.00993	81.70
	0.01629	55.88	0.61048	1.80	0.00773	77.73
	0.01322	49.74	0.58154	0.02	0.00597	74.18
	0.01121	45.80	0.54648	-2.49	0.00419	69.04
	0.00966	43.71	0.52604	-4.23	0.00328	67.73
	0.00847	37.56	0.50456	-5.27	0.00274	65.28
e 	0.14624	65.99				
	0.12977	57.82				
	0.11983	51.20				
	0.11127	44.28				
	0.10509	38.82		-		-
	0.10227	36.25				
	0.09963	33.59				
	0.09741	30.70				

Approximated error of mole fraction: 0.00016.

7. DSC curves

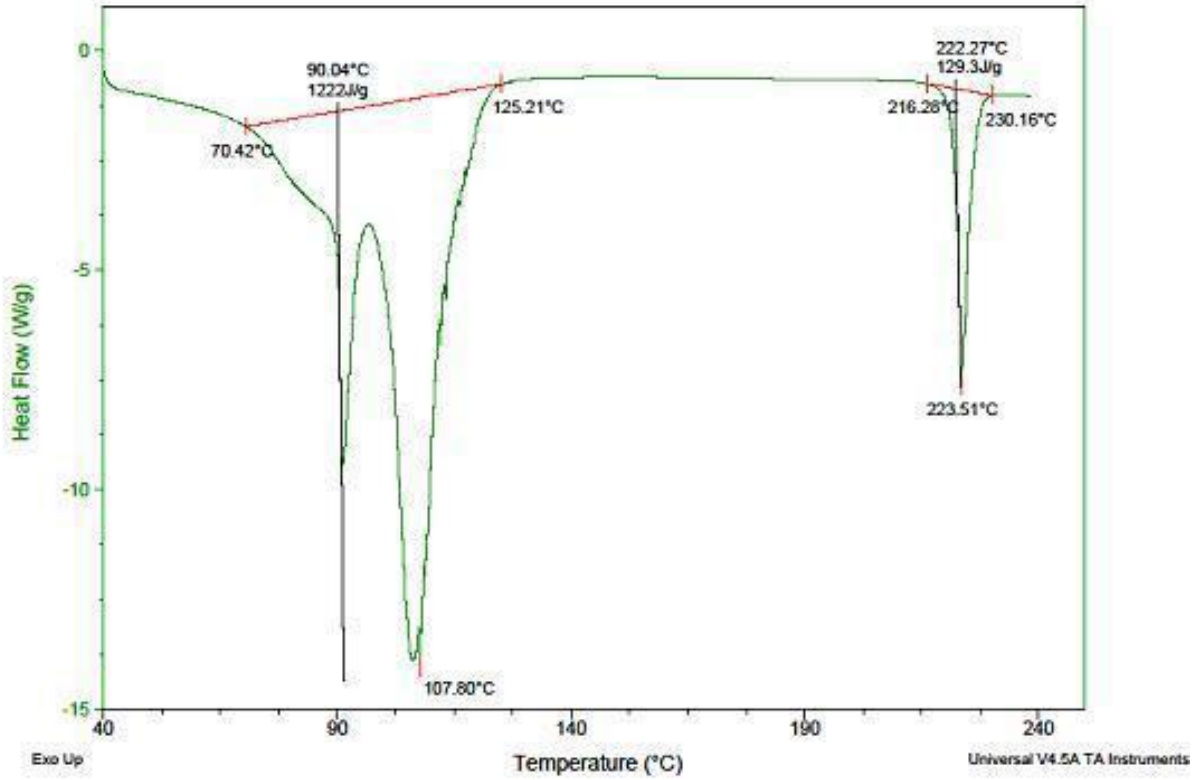


Figure S5 DSC curve of **1**.

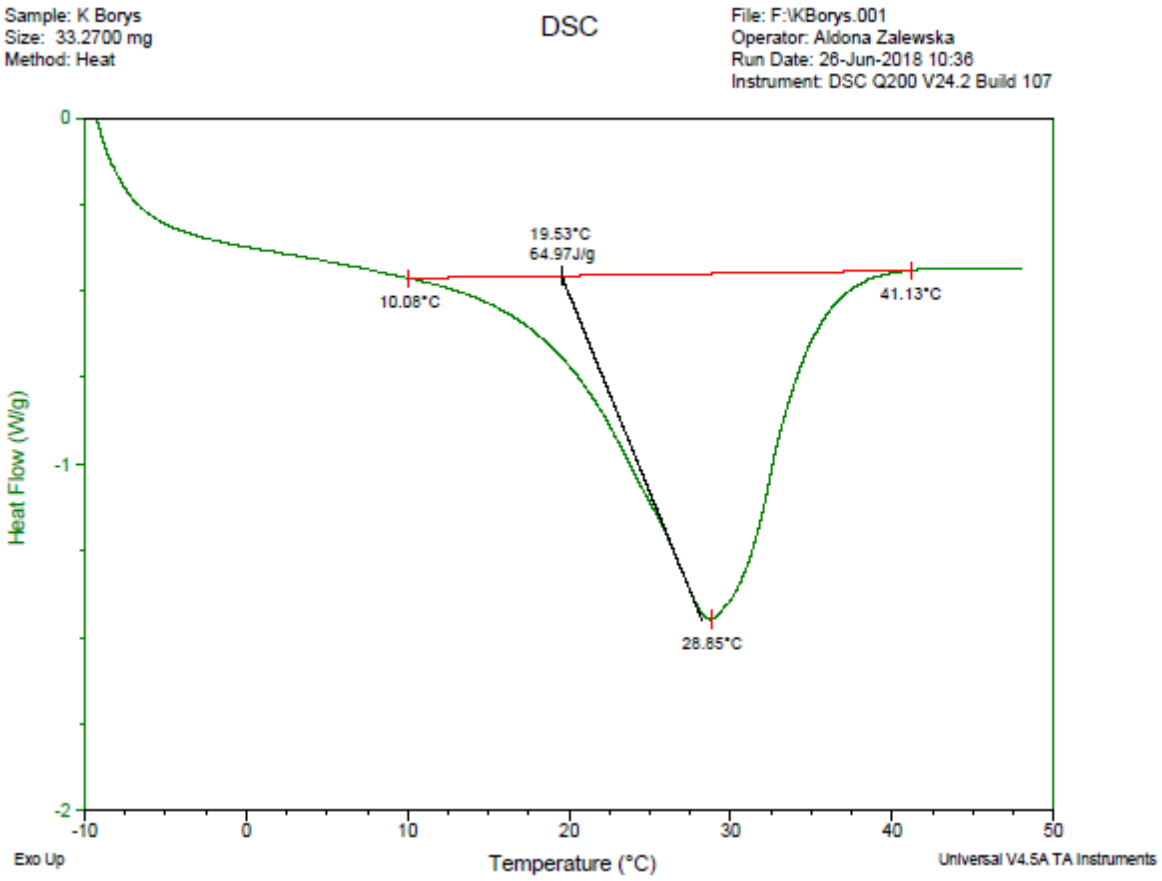


Figure S6 DSC curve of **2**.

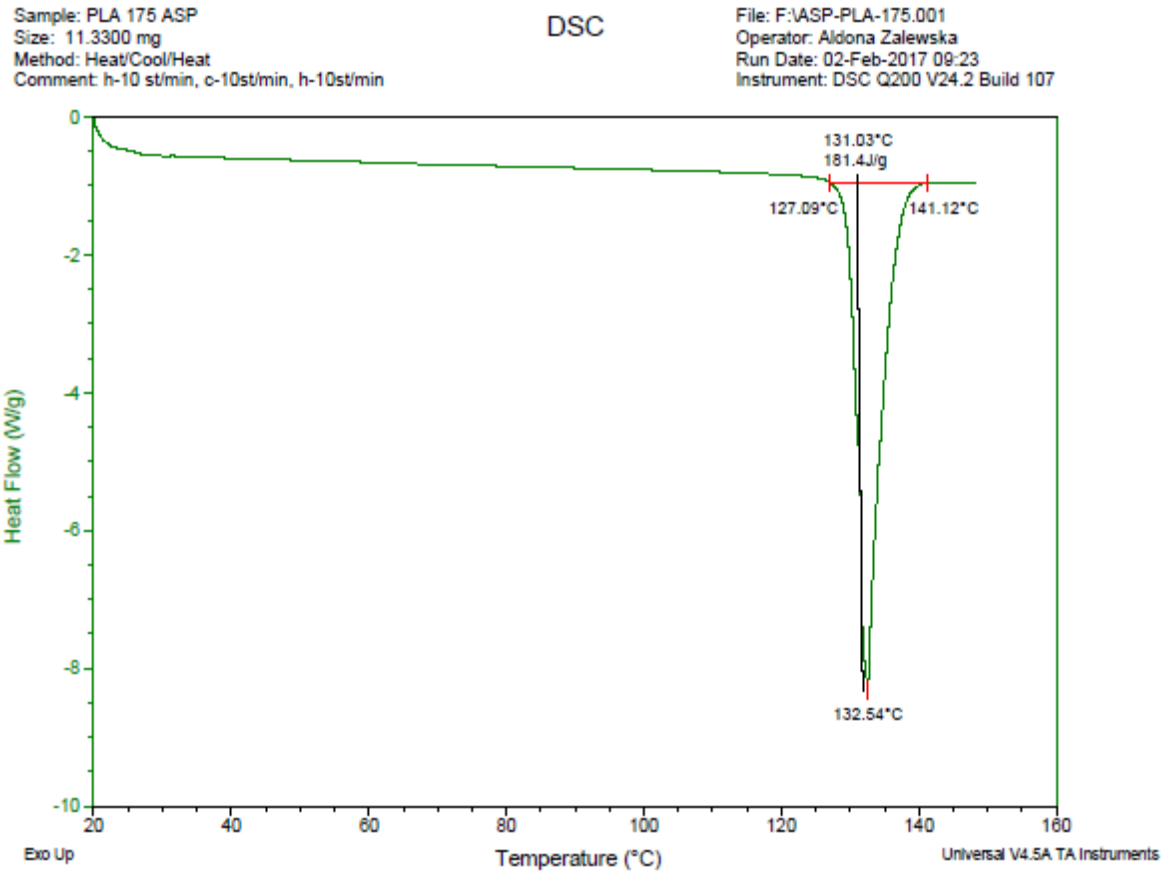


Figure S7 DSC curve of **3**.

8. Correlation parameters:

Table S2. Adjusted parameters of the solubility curves and the standard deviations (σ)[a].

System	Redlich-Kister		Wilson		NRTL[b]	
	a_0, a_1, (a_2) / kJ·mol^{-1}	σ /K	Δg_{12}, Δg_{21} /kJ·mol^{-1}	σ /K	Δg_{12}, Δg_{12} /kJ·mol^{-1}	σ /K
Pinacol ester (**2**) +						
Chloroform	-3.2233	0.80	-1.4750	0.79	-2.1513	0.80
	-0.20520		-1.4914		-0.83611	
3-Pentanone	0.48939	0.67	-1.4611	0.81	1.5563	0.84
	-0.94857		1.2755		-1.9562	
Dipropyl ether	-2.3217	0.46	-2.4388	0.32	8.2515	0.38
	1.8268		5.4831		-5.0394	
Methylocyclohexane	1.3161	0.36	7.8173	0.59	-2.6444	0.43
	-0.74883		-1.3116		10.144	
Azaester (**3**) +						
Chloroform	-19.265	1.2	-4.3150	2.3	-9.3504	2.0
	6.3197		-26.747		-3.3504	
	-8.0958					
3-Pentanone	-5.3169	1.1	-4.5104	0.95	5.0651	1.2
	-1.8504		0.71753		-7.6532	
Dipropyl ether	-0.91905	0.65	9.4355	0.74	-5.9670	0.24
	-6.3648		-1.7652		14.905	
Methylcyclohexane	-16.235	1.1	11.216	0.69	-8.0595	1.3
	-25.505		-1.0697		2.3838	

	Polynomial	
	a_0, a_1, a_2, (a_3) /K	σ /K
Phenylboronic acid (**1**) +		
Chloroform	295.69 323.73 -491.60	1.2
Acetone	135.19 2415.2 -6980.9	0.18
Dipropyl ether	225.32 483.59 -581.46	0.21
Methylcyclohexane	282.56 4302.4 -103950 -334540	0.75

[a] $\sigma = \left[\sum_{i=1}^{n}\left(T_i^{exp} - T_i^{calc}\right)^2 / n\right]^{1/2}$. [b] The nonrandomness parameter (α) was set equal to 0.2.