Supplementary material

INFLUENCE OF FLUORINE SUBSTITUENTS ON THE PROPERTIES OF PHENYLBORONIC COMPOUNDS

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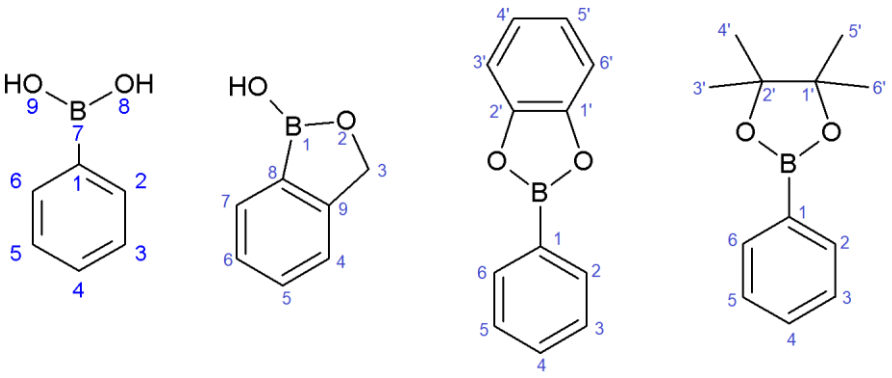

Table 1. ^{1}H NMR chemical shifts of fluorinated phenylboronic acids, benzoxaboroles, boroxines, catechol and pinacol esters

Aryl group	Solvent	Chemical shifts, ppm						Lit.
		OH	H2	H3	H4	H5	H6	
PHENYLBORONIC ACIDS								
2-F [a)]	acetone-d_6	7.2	-	7.06	7.46	7.19	7.76	[1]
3-F	acetone-d_6	7.1	7.57	-	7.18	7.41	7.70	[1]
3-F	20% D_2O/ DMSO-d_6	n.r.[b)]	7.56	-	7.19	7.37	7.46	[2]
4-F	acetone-d_6	7.4	7.93	7.11	-	7.11	7.93	[1]
2,3-F	acetone-d_6	7.5	-	-	7.35	7.18	7.50	[1]
2,4-F	acetone-d_6	7.3	-	6.93	-	7.00	7.91	[1]
2,4-F	acetone-d_6[c)]	n.r.[b)]	-	6.90	-	6.98	7.78	[3]
2,5-F	acetone-d_6	7.6	-	7.11	7.22	-	7.41	[1]
2,6-F	acetone-d_6	7.8	-	6.91	7.41	6.91	-	[1]
2,6-F	acetone-d_6	7.74	-	6.90	7.40	6.90	-	[3]
3,4-F	acetone-d_6	7.4	7.70	-	-	7.30	7.74	[1]

3,5-F	acetone-d_6	7.6	7.43	-	7.06	-	7.43	[1]
2,3,4-F	acetone-d_6	7.5	-	-	-	7.17	7.54	[1]
2,3,5-F	acetone-d_6	7.6	-	-	7.26	-	7.22	[1]
2,3,6-F	acetone-d_6	8.1	-	-	7.33	6.94	-	[1]
2,4,5-F	acetone-d_6	7.4	-	7.17	-	-	7.60	[1]
2,4,6-F	acetone-d_6	7.8	-	6.82	-	6.82	-	[1]
3,4,5-F	acetone-d_6	7.5	7.57	-	-	-	7.41	[1]
3,4,5-F	$CDCl_3$ [d]	4.8	7.35	-	-	-	7.35	[4]
3,4,5-F	ether [d]	6.95	7.38	-	-	-	7.38	[3]
2,3,4,5-F	acetone-d_6	7.5	-	-	-	-	7.41	[1]
2,3,4,5-F	acetone-d_6 [c]	n.r. [b]	-	-	-	-	7.34	[3]
2,3,4,6-F	acetone-d_6	8.0	-	-	-	7.03	-	[1]
2,3,4,6-F	acetone-d_6 [c]	n.r. [b]	-	-	-	7.04	-	[3]
2,3,5,6-F	acetone-d_6	8.2	-	-	7.54	-	-	[1]
2,3,5,6-F	acetone-d_6	8.16	-	-	7.44	-	-	[3]
2,3,5,6-F	ether [d]	7.53	-	-	7.11	-	-	[3]
2,3,4,5,6-F	acetone-d_6	8.3	-	-	-	-	-	[1]
2,3,4,5,6-F	acetone-d_6	8.19	-	-	-	-	-	[3]
				BOROXINES				
3,4,5-F	ether [d]	-	7.67	-	-	-	7.67	[3]
3,4,5-F	$CDCl_3$ [d]	-	7.77	-	-	-	7.77	[4]
2,3,5,6-F	ether [d]	-	-	-	6.74	-	-	[3]
				BENZOXABOROLES				
		OH	**H3**	**H4**	**H5**	**H6**	**H7**	
4-F	DMSO-d_6	9.41	5.06	-	7.26	7.40	7.55	[5]
5-F	DMSO-d_6	9.22	4.95	7.24	-	7.15	7.74	[5]
6-F	DMSO-d_6	9.29	4.95	7.29	7.41	-	7.46	[5]
7-F	DMSO-d_6	9.25	4.99	7.21	7.48	7.00	-	[5]
7-F	acetone-d_6	8.23	5.04	7.24	7.53	7.00	-	[6]
4,5-F	DMSO-d_6	9.47	5.11	-	-	7.42	7.56	[7]
5,6-F	DMSO-d_6	9.34	4.94	7.50	-	-	7.62	[5]
4,5,6-F	DMSO-d_6	9.60	5.10	-	-	-	7.55	[7]
				CATECHOL ESTERS				

		H2	H3	H4	H5	H6	H3',6'	H4',5'	
3-F	$CDCl_3$	7.75	-	7.26	7.47	7.86	7.32	7.15	[8]
4-F	$CDCl_3$	8.09	7.18	-	7.18	8.09	7.31	7.14	[8]
2,4-F	$CDCl_3$	-	6.90	-	7.01	8.03	7.34	7.15	[8]
2,6-F	$CDCl_3$	-	6.99	7.55	6.99	-	7.38	7.16	[8]
3,4,5-F	$CDCl_3$	7.67	-	-	-	7.67	7.31	7.15	[8]
2,4,6-F	$CDCl_3$	-	6.76	-	6.76	-	7.37	7.16	[8]
2,3,4,5,6-F	$CDCl_3$	-	-	-	-	-	7.40	7.22	[8]
PINACOL ESTERS									
		H2	**H3**	**H4**	**H5**	**H6**	**Hpin**		
2-F	$CDCl_3$	-	7.02	7.43	7.13	7.74	1.36		[8]
3-F	$CDCl_3$	7.49	-	7.14	7.34	7.58	1.35		[9]
4-F	$CDCl_3$	7.74	6.99	-	6.99	7.74	1.26		[2]
2,3-F	$CDCl_3$	-	-	7.22	7.06	7.46	1.36		[9]
2,5-F	$CDCl_3$	-	6.98	7.09	-	7.39	1.36		[9]
3,5-F	$CDCl_3$	7.29	-	6.87	-	7.29	1.34		[9]
2,3,5-F	$CDCl_3$	-	-	6.99	-	7.18	1.36		[9]
2,4,5-F	$CDCl_3$	-	6.88	-	-	7.51	1.35		[9]
2,3,4,5-F	$CDCl_3$	-	-	-	-	7.19	1.04		[9]

[a] notation of aryl group is abbreviated, e.g.: 2-F = 2-C_6H_4F or 3,4,5-F = 3,4,5-$C_6H_2F_3$

[b] n.r.=not reported

[c] recorded in the presence of D_2O (3 equivalents)

[d] recorded in 32°C

Table 3. ^{13}C NMR chemical shifts of fluorinated phenylboronic acids and benzoxaboroles

Aryl group	Solvent	Chemical shifts, ppm						Lit.
		C1	**C2**	**C3**	**C4**	**C5**	**C6**	
PHENYLBORONIC ACIDS								

2-F [a]	acetone-d_6	122	168.19	115.94	133.60	125.04	137.40	[1]
3-F	acetone-d_6	137.1	121.18	163.82	118.13	130.71	131.10	[1]
4-F	acetone-d_6	130.1	137.70	115.47	165.75	115.47	137.70	[1]
4-F	acetone-d_6 [b]	130.72	137.40	115.08	165.31	115.08	137.40	[3]
2,3-F	acetone-d_6	124	154.96	151.33	120.12	125.70	131.80	[1]
2,4-F	acetone-d_6	117.3	168.68	104.25	165.98	112.24	139.02	[1]
2,4-F	acetone-d_6 [b]	117.75	168.33	103.93	165.64	111.90	138.68	[3]
2,5-F	acetone-d_6	123	163.92	117.69	119.86	159.84	122.48	[1]
2,6-F	acetone-d_6	110	166.25	111.90	132.88	111.90	166.25	[1]
2,6-F	acetone-d_6	112.67	166.00	111.64	132.61	111.64	166.00	[3]
3,4-F	acetone-d_6	132.5	123.63	151.09	152.97	117.87	132.36	[1]
3,5-F	acetone-d_6	139.4	117.28	164.01	106.41	164.01	117.28	[1]
2,3,4-F	acetone-d_6	119.2	156.06	140.54	153.57	115.55	131.3	[1]
2,3,5-F	acetone-d_6	125.7	150.77	151.07	107.85	158.44	116.66	[1]
2,3,6-F	acetone-d_6	114.5	152.63	147.92	119.34	112.26	160.92	[1]
2,4,5-F	acetone-d_6	118.7	163.39	105.54	152.70	147.88	124.24	[1]
2,4,6-F	acetone-d_6	108.5	166.72	100.91	165.10	100.91	166.72	[1]
2,4,6-F	acetone-d_6	108.80	166.48	100.54	164.85	100.54	166.48	[3]
3,4,5-F	acetone-d_6	131.9	118.89	151.93	142.09	151.93	118.89	[1]
3,4,5-F	acetone-d_6 [b]	131.98	118.62	151.64	141.77	151.64	118.62	[3]
2,3,4,5-F	acetone-d_6	118.0	152.00	141.35	142.60	148.01	117.21	[1]
2,3,4,5-F	acetone-d_6 [b]	118.76	151.37	140.82	141.96	147.44	116.66	[3]
2,3,4,6-F	acetone-d_6	109.9	153.96	137.93	152.61	102.2	160.24	[1]
2,3,4,6-F	acetone-d_6 [b]	110.20	153.64	137.64	152.90	101.97	159.93	[3]
2,3,5,6-F	acetone-d_6	114.8	148.19	146.83	105.50	146.83	148.19	[1]
2,3,5,6-F	acetone-d_6	116.47	147.92	146.56	107.96	146.56	147.92	[3]
2,3,4,5,6-F	acetone-d_6	109.8	148.69	138.22	142.73	138.22	148.69	[1]
2,3,4,5,6-F	acetone-d_6	110.54	148.45	138.08	142.50	138.08	148.45	[3]

BENZOXABOROLES

		C3	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	
4-F	acetone-d_6	68.85	158.91	118.55	131.37	128.08	136.4	141.21	[6]
5-F	acetone-	70.86	109.16	165.81	115.34	133.32	127.3	158.14	[6]

	d_6								
5-F	DMSO-d_6	70.3	109.2	165.9	115.3	133.3	164.0	157.5	[10]
6-F	acetone-d_6	70.92	123.97	116.61	163.17	118.80	133.9	150.68	[6]
7-F	acetone-d_6	72.16	119.60	135.67	115.03	166.32	119.1	159.38	[6]
				PINACOL ESTERS [c]					
	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C1',C2'**	**C3'-C6'**	
2-F	115.8	167.2	115.2	133.2	123.6	136.8	83.9	24.8	[9]
3-F	131.2	121.0	162.5	118.2	129.4	130.3	84.1	24.8	[9]
4-F	n.r. [d]	137.0	114.9	166.1	114.9	137.0	83.9	24.8	[2]
2,3-F	118.6	131.1	124.0	120.1	150.4	154.5	84.2	24.8	[9]
2,5-F	n.r. [d]	163.0	116.6	119.7	158.4	122.2	84.2	24.8	[9]
3,5-F	n.r. [d]	116.8	162.7	106.5	162.7	116.8	84.4	24.8	[9]
2,3,5-F	n.r. [d]	150.1	150.9	108.3	157.4	116.6	84.5	24.8	[9]
2,4,5-F	112.5	162.5	105.5	152.5	146.8	123.8	84.3	24.8	[9]
2,3,4,5-F	112.2	151.5	140.5	142.6	147.0	116.5	84.6	24.7	[9]

[a] notation of aryl group is abbreviated, e.g.: 2-F = 2-C_6H_4F or 3,4,5-F = 3,4,5-$C_6H_2F_3$

[b] recorded in the presence of D_2O (3 equivalents)

[c] dissolved in $CDCl_3$

[d] not reported

Table 4. ^{11}B NMR chemical shifts of fluorinated phenylboronic acids, benzoxaboroles and boroxines

Aryl group	**Solvent**	**Chemical shifts, ppm**	**Line widths, Hz**	**Lit.**
		PHENYLBORONIC ACIDS		
2-F [a]	acetone-d_6	28.86	120	[1]

Aryl group	Solvent	Chemical shifts, ppm	Line widths, Hz	Lit.
3-F	acetone-d_6	28.84	130	[1]
3-F	CD_3OD	27.7	n.r.[b)]	[2]
4-F	acetone-d_6	29.06	100	[1]
4-F	acetone-d_6 [c)]	28.53	195	[3]
4-F	ether	28.08	141	[3]
4-F	$CDCl_3$	27.5	n.r.[b)]	[11]
2,3-F	acetone-d_6	28.40	110	[1]
2,4-F	acetone-d_6	28.46	120	[1]
2,4-F	acetone-d_6 [c)]	28.01	136	[3]
2,4-F	ether	27.36	86	[3]
2,4-F	CH_2Cl_2/CD_2Cl_2	27.96	74	[3]
2,5-F	acetone-d_6	28.30	115	[1]
2,6-F	acetone-d_6	28.46	105	[1]
2,6-F	acetone-d_6	28.06	105	[3]
2,6-F	ether	27.37	67	[3]
3,4-F	acetone-d_6	28.46	100	[1]
3,5-F	acetone-d_6	28.21	110	[1]
2,3,4-F	acetone-d_6	28.00	110	[1]
2,3,5-F	acetone-d_6	27.96	100	[1]
2,3,6-F	acetone-d_6	28.02	120	[1]
2,4,5-F	acetone-d_6	27.84	120	[1]
2,4,6-F	acetone-d_6	27.98	110	[1]
2,4,6-F	acetone-d_6	27.76	119	[3]
3,4,5-F	acetone-d_6	27.95	100	[1]
3,4,5-F	acetone-d_6 [c)]	27.59	161	[3]
3,4,5-F	ether	27.18	97	[3]
2,3,4,5-F	acetone-d_6	27.58	120	[1]
2,3,4,5-F	acetone-d_6 [c)]	27.08	165	[3]
2,3,4,6-F	acetone-d_6	27.63	120	[1]
2,3,4,6-F	acetone-d_6 [c)]	27.24	116	[3]
2,3,5,6-F	acetone-d_6	27.64	115	[1]

Aryl group	Solvent	Chemical shifts, ppm	Line widths, Hz	Lit.
2,3,5,6-F	acetone-d_6	27.21	124	[3]
2,3,5,6-F	ether	26.61	105	[3]
2,3,4,5,6-F	acetone-d_6	27.40	105	[1]
2,3,4,5,6-F	acetone-d_6	26.93	112	[3]
2,3,4,5,6-F	ether	26.21	98	[3]
BOROXINES				
4-F	ether	28.08	141	[3]
2,4-F	ether	19.10	104	[3]
2,6-F	ether	19.02	96	[3]
2,6-F	acetonitrile-d_3	28.5	n.r.[b)]	[12]
2,4,6-F	acetonitrile-d_3	28.0	n.r.[b)]	[12]
3,4,5-F	ether	27.18	97	[3]
2,3,5,6-F	ether	19.51	142	[3]
2,3,4,5,6-F	ether	18.58	255	[3]
2,3,4,5,6-F	toluene-d_7	20.1	n.r.[b)]	[11]
2,3,4,5,6-F	acetonitrile-d_3	20.4	n.r.[b)]	[12]
BENZOXABOROLES				
5-F	acetone-d_6	31.3	n.r.[b)]	[2]
5-F	DMSO-d_6	31.8	n.r.[b)]	[60]
CATECHOL ESTERS				
2-F	$CDCl_3$	30.7	n.r.[b)]	[8]
3-F	$CDCl_3$	31.3	n.r.[b)]	[8]
4-F	$CDCl_3$	31.4	n.r.[b)]	[8]
2,4-F	$CDCl_3$	30.6	n.r.[b)]	[8]
2,6-F	$CDCl_3$	29.9	n.r.[b)]	[8]
3,4,5-F	$CDCl_3$	30.8	n.r.[b)]	[8]
2,4,6-F	$CDCl_3$	29.7	n.r.[b)]	[8]
2,3,4,5,6-F	$CDCl_3$	29.1	n.r.[b)]	[8]
PINACOL ESTERS				
2-F	$CDCl_3$	29.7	n.r.[b)]	[8]
2-F	$CDCl_3$	30.2	n.r.[b)]	[9]

Aryl group	Solvent	Chemical shifts, ppm	Line widths, Hz	Lit.
3-F	$CDCl_3$	30.6	n.r.[b)]	[9]
4-F	$CDCl_3$	28.9	n.r.[b)]	[2]
2,3-F	$CDCl_3$	30.0	n.r.[b)]	[9]
2,5-F	$CDCl_3$	29.9	n.r.[b)]	[9]
3,5-F	$CDCl_3$	30.3	n.r.[b)]	[9]
2,3,5-F	$CDCl_3$	29.6	n.r.[b)]	[9]
2,4,5-F	$CDCl_3$	29.6	n.r.[b)]	[9]
2,3,4,5-F	$CDCl_3$	29.5	n.r.[b)]	[9]

[a)] notation of aryl group is abbreviated, e.g.: 2-F = 2-C_6H_4F or 3,4,5-F = 3,4,5-$C_6H_2F_3$

[b)] n.r. = not reported

[c)] recorded in the presence of D_2O (3 equivalents)

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