A Mechanistic Proposal for the Protodeboronation of Neat Boronic Acids: Boronic Acid Mediated Reaction in the Solid State

Gary M. Noonan[†]* *and Andrew G. Leach*[‡†]*.

[†]*Oncology Innovative Medicines, AstraZeneca,*
Alderley Park, Macclesfield, Cheshire, SK10 4TG, UK
g.noonan@redxpharma.com
[‡]*School of Pharmacy and Biomolecular Sciences, Liverpool John Moores University,*
James Parsons Building, Byrom Street, Liverpool, L3 3AF, UK.
A.G.Leach@ljmu.ac.uk

Supporting Information

General Analytical Information

Nuclear Magnetic Resonance spectra were recorded on a Bruker Avance 400 MHz spectrometer at ambient temperature. All ^{1}H NMR spectra were measured in part per million (ppm) relative to, the signals for the residual solvent peak in $CDCl_3$ (7.26 ppm), or where not apparent, relative to the signal for added tetramethylsilane (0.0 ppm); relative to the residual solvent peak in DMSO-d_6 (2.50 ppm); relative to the most 'upfield' residual solvent peak in THF-d_8 (1.73). Data for ^{1}H NMR are reported as: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t= triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), and integration. All ^{13}C NMR spectra are reported in ppm relative to $CDCl_3$ (77.36 ppm) or DMSO-d_6 (39.50) and were obtained with complete ^{1}H decoupling. LC-MS (for qualitative microwave-promoted decomposition studies) was carried out using a Waters Alliance HT (2795), fitted with a Waters ZQ ESCi mass spectrometer, a Waters (2996) Photodiode Array detector, and a Phenomenex Gemini –NX (50x2.1 5mm) column, at a flow rate of 1.1mL/min using a 95% water to 95% acetonitrile solvent gradient over 4 min with a 0.5 min hold. The modifier (50:50 acetonitrile:water 0.1% Formic acid) was kept constant at 5% throughout the solvent gradient. High resolution mass spectrometry (for biaryl compounds) was carried out on a GC-MS, GC: Agilent 6890 with autoinjector injecting 1μL employing a Varian VF-5ms column (30m X 250μm with 0.25μm film thickness), helium at 1ml/min constant flow. GC Method: 50 °C for 4 minutes then ramp 25 °C/min up to 280 °C, then 50 °C/min up to 320 °C, with a total run time of 16 minutes. MS: Waters GCT T.O.F MS with EI^+ ionisation and source scanning from 40 – 800amu. MS: LTQ-FT from Thermo Fisher in negative ion mode scanning from 100-1200 amu with a CTC autosampler and Surveyor PDA. IR spectra were recorded on an Avatar 370 FT-IR Thermo Nicolet Spectrometer. Melting points were obtained on a Buchi B-545 capillary melting point apparatus.

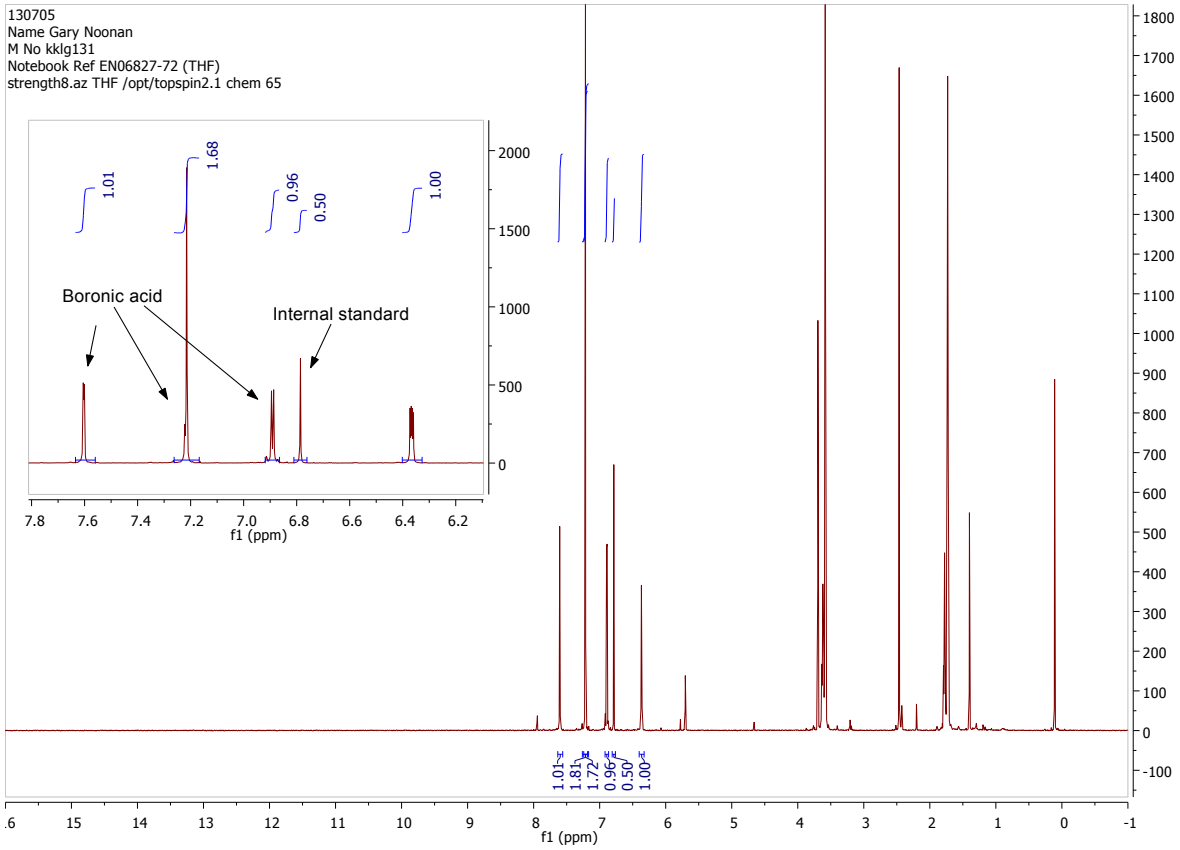
General Reagent Information

Unless otherwise stated, all chemicals were commercially available and were used as received. Unless otherwise stated, reactions were carried out under air and either reagent grade or HPLC grade solvents were used without drying.

Stability studies for boronic acid samples stored in solution

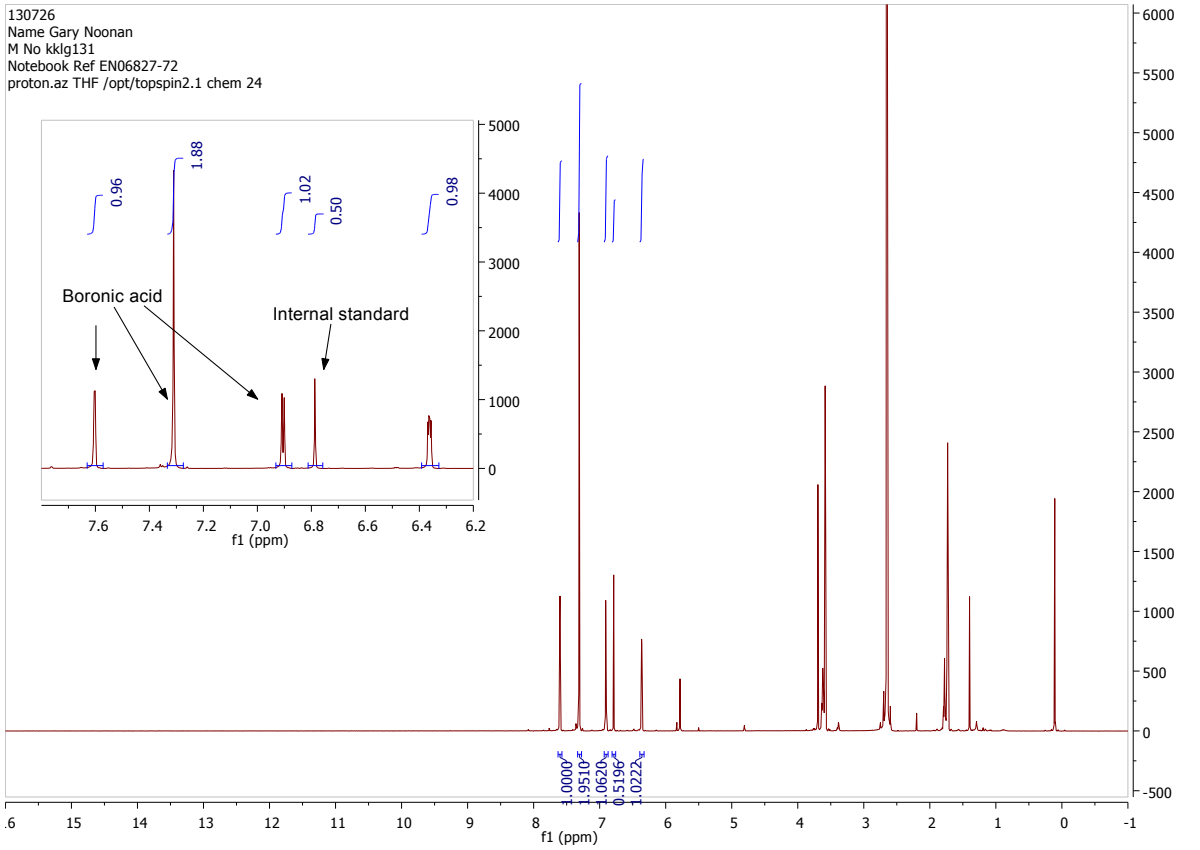
A freshly prepared sample of boronic acid (0.04 mmol), prepared by hydrolysis of the corresponding MIDA-boronate [1] was dissolved in d_8-THF (0.5 mL) together with *para*-dimethoxybenzene (between 0.6 and 5.5 mg depending on the sample) as an internal standard and the ^{1}H NMR was measured (t = 0). The ^{1}H NMR of the same sample was then measured after storage of the NMR tube under ambient conditions i.e. on the bench top at room temperature, under air and with no attempt made to exclude light, for a given period of time. The percentage decomposition was then calculated based on the change in the ratio of the ^{1}H NMR integrals for the boronic acid protons vs. the ^{1}H NMR integral of the internal standard protons over time (see spectra below).

^{1}H NMR of furan-2-boronic acid in d_8-THF t = 0

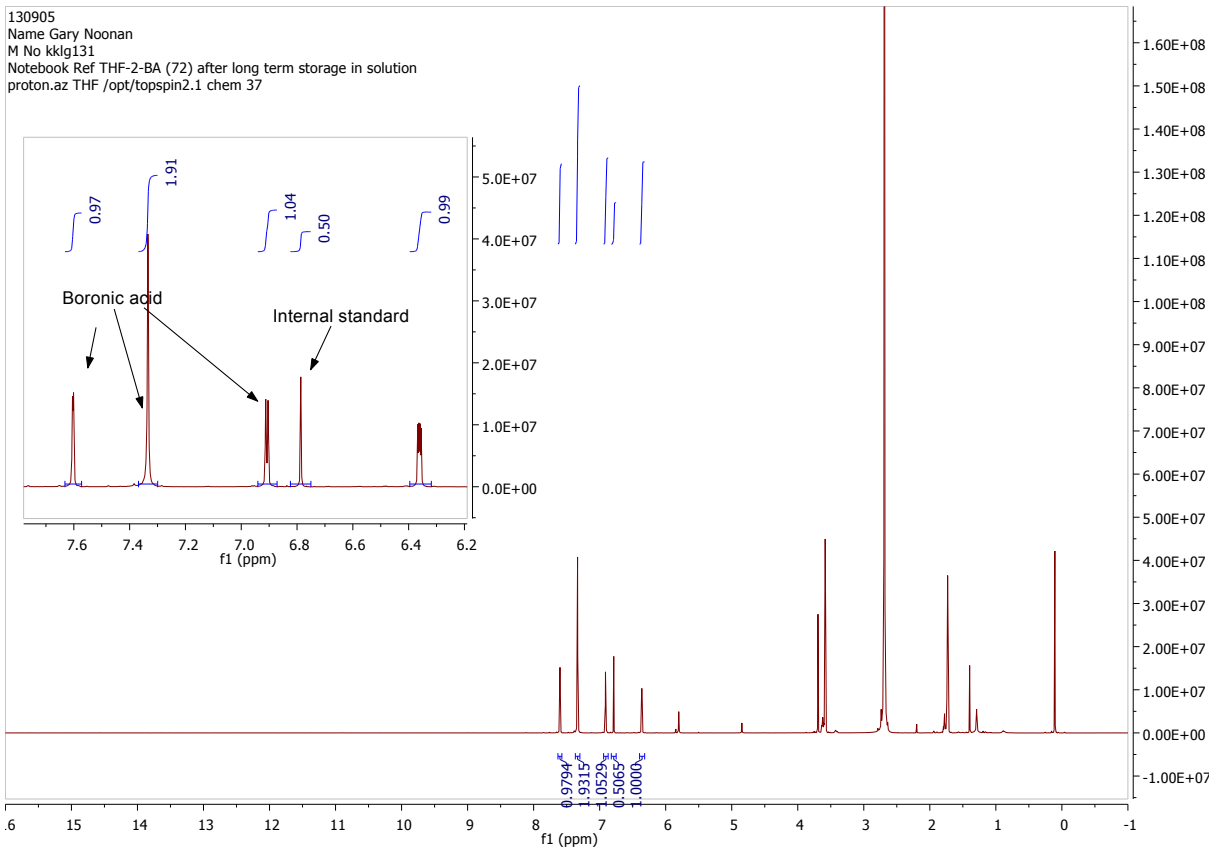


In the series of spectra that follow (see below), the water peak (δ_H ~ 2.5 ppm) can be seen to increase over the time period, but no observable decomposition of boronic acid occurred. Impurities present in the aliphatic region correspond to residual THF (from the work-up in the preparation of the boronic acid sample) and the THF stabilizer, 2,6-di-tert-butyl-4-methylphenol ('butylated-hydroxytoluene') BHT.
Similarly, no decomposition was observed when furan-2-ylboronic acid was stored in d_6-DMSO
(0.08 M) for 2 months.

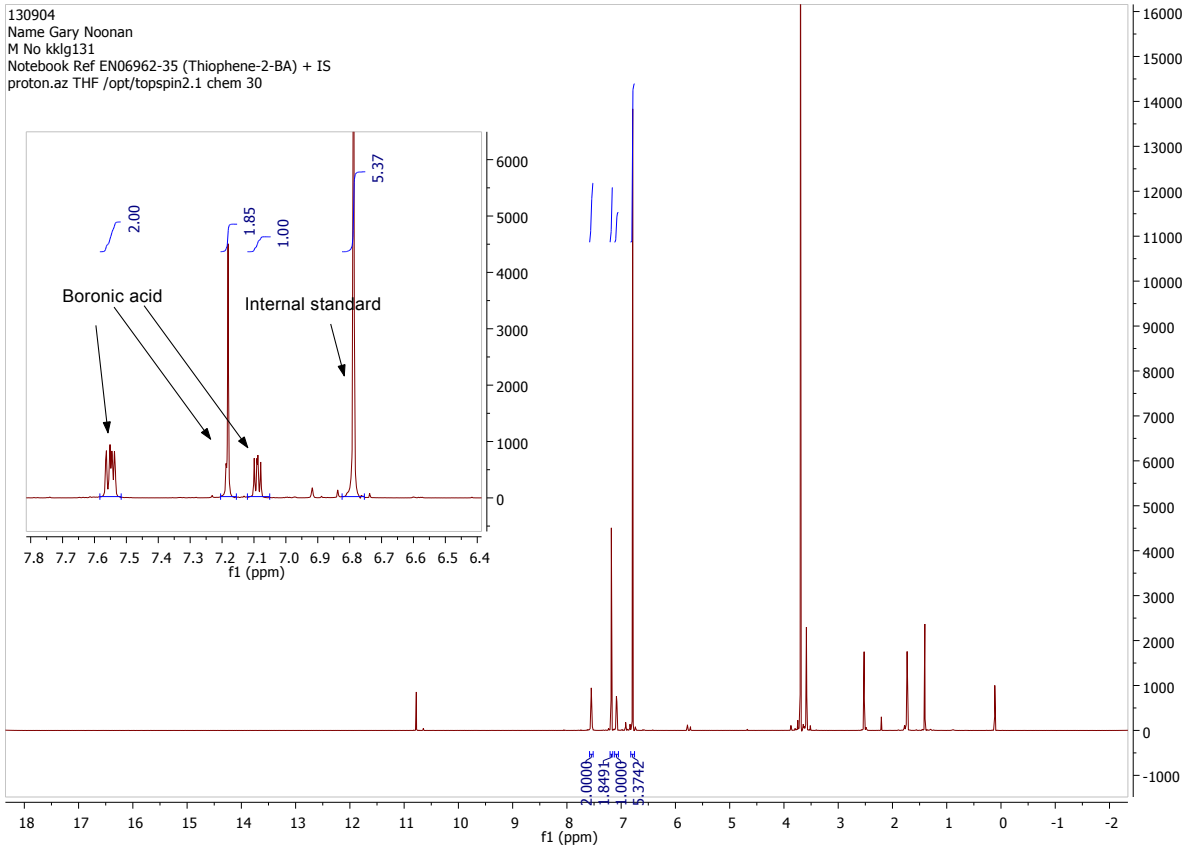
^{1}H NMR of furan-2-boronic acid in d_8-THF t = 3 weeks



^{1}H NMR of furan-2-boronic acid in d_8-THF t = 2 months

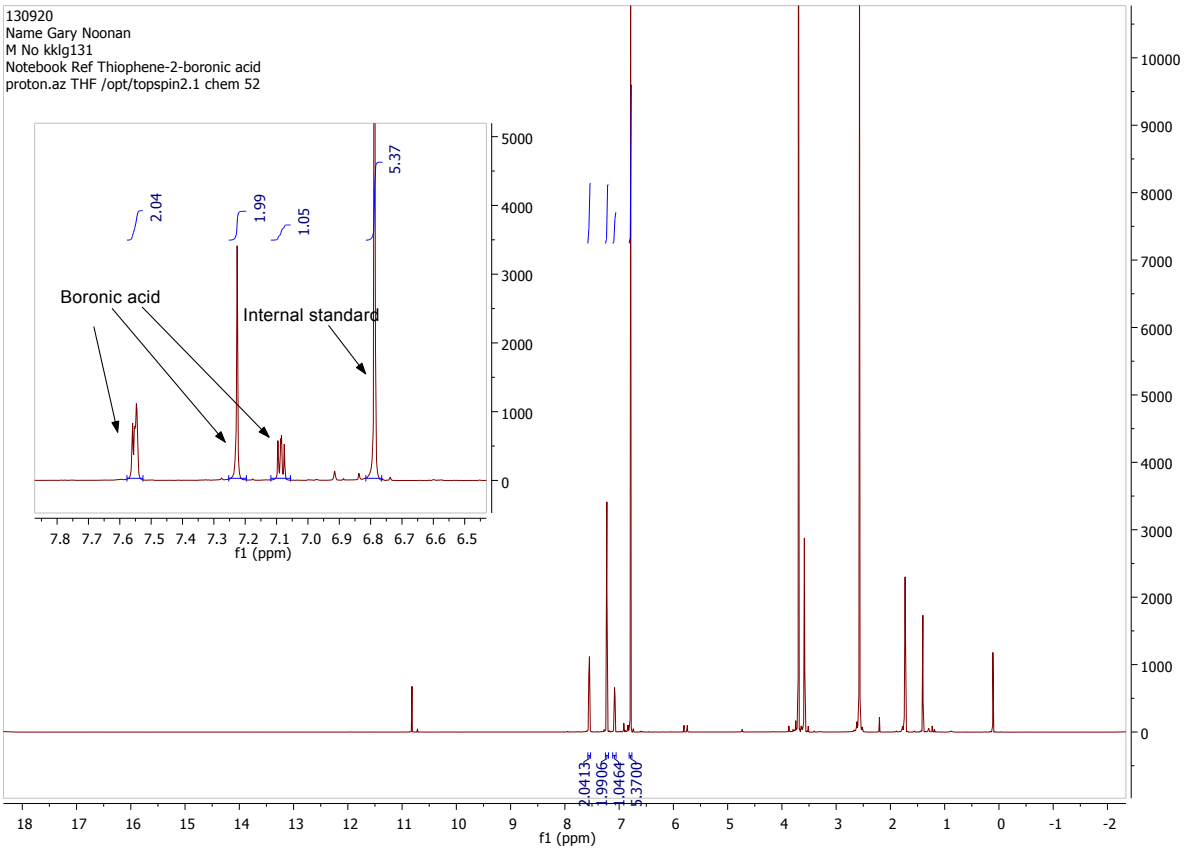


^{1}H NMR of thiophene-2-ylboronic acid in d_8-THF t = 0

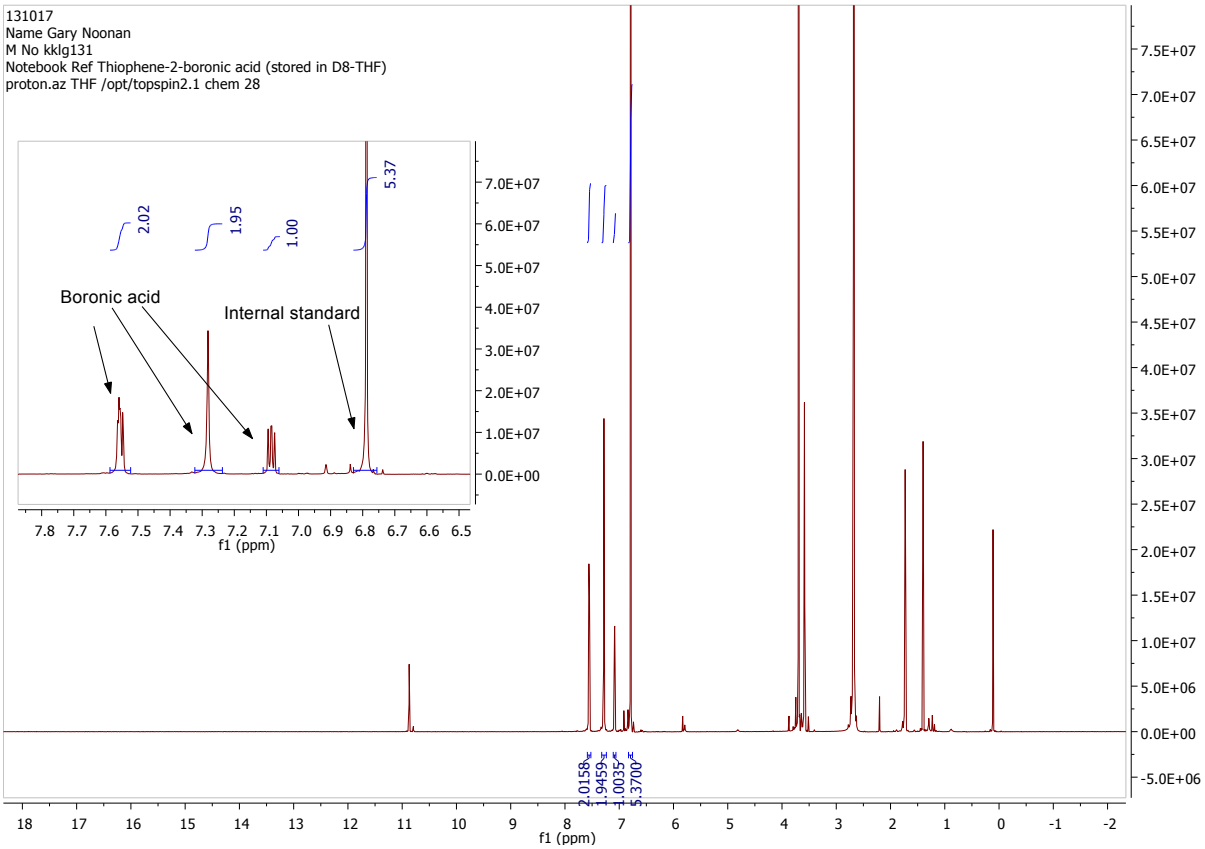


In the series of spectra that follow (see below), the water peak (δ_H ~ 2.5 ppm) can be seen to increase over the time period, but again, no observable decomposition was apparent. Impurities present in the aliphatic region correspond to residual THF (from the work-up in the preparation of the boronic acid sample) and the THF stabilizer, 2,6-di-tert-butyl-4-methylphenol ('butylated hydroxytoluene') BHT.

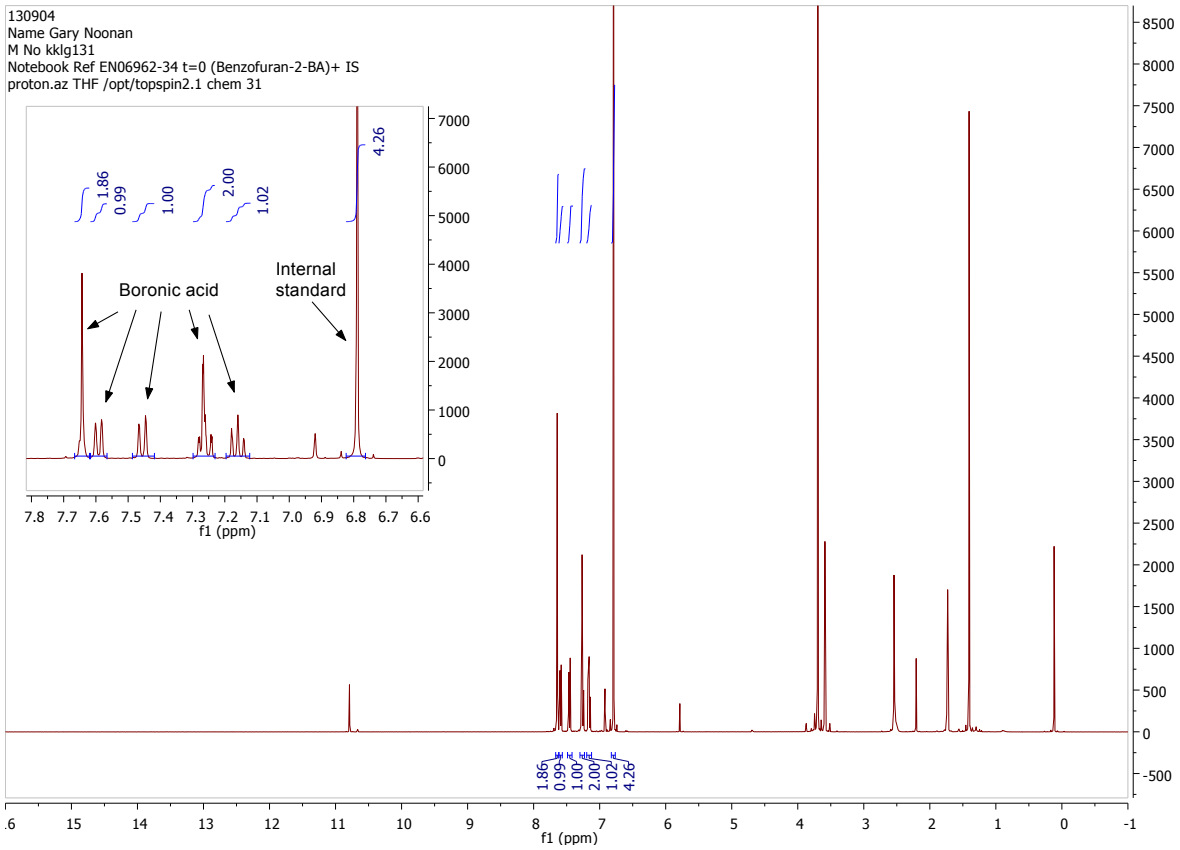
^{1}H NMR of thiophen-2yl-boronic acid in d_8-THF t = 16 days



^{1}H NMR of thiophen-2-ylboronic acid in d_8-THF t = 1 month 13 days

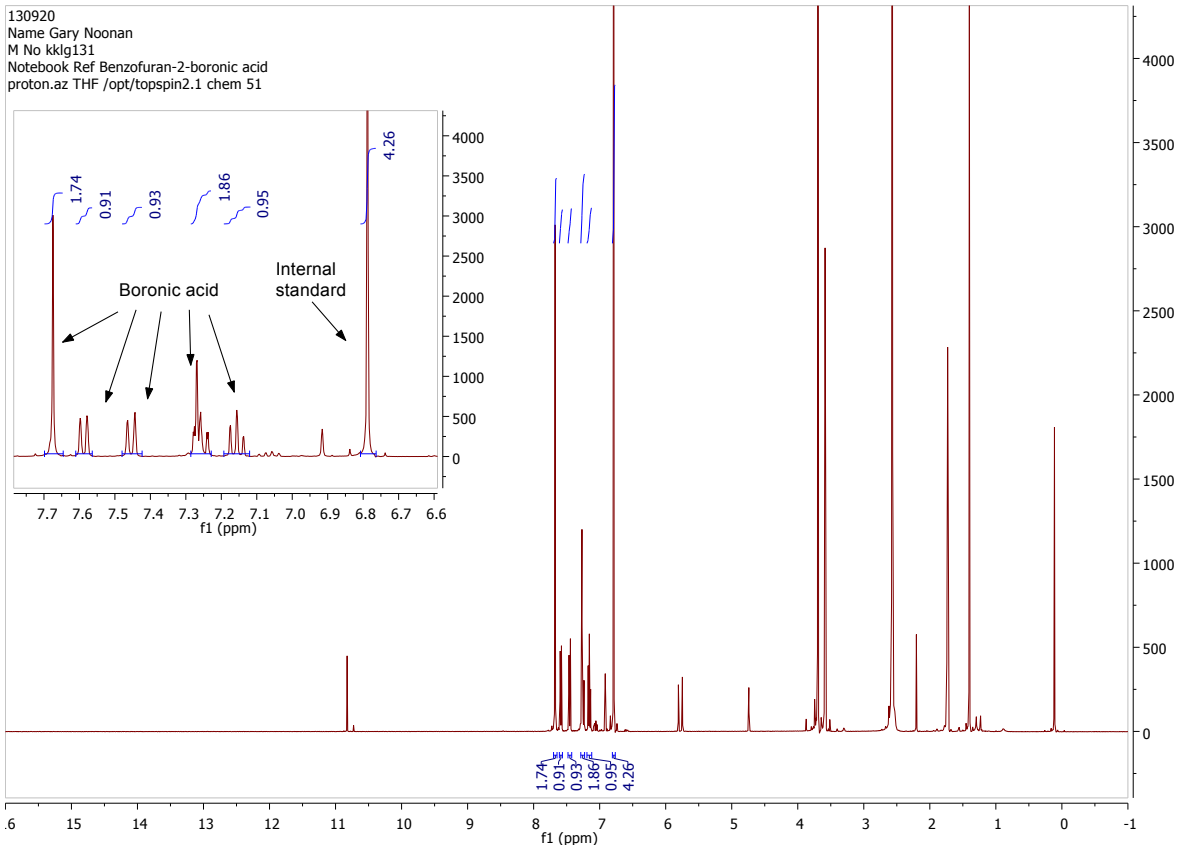


^{1}H NMR of benzofuran-2-ylboronic acid in d_8-THF t = 0

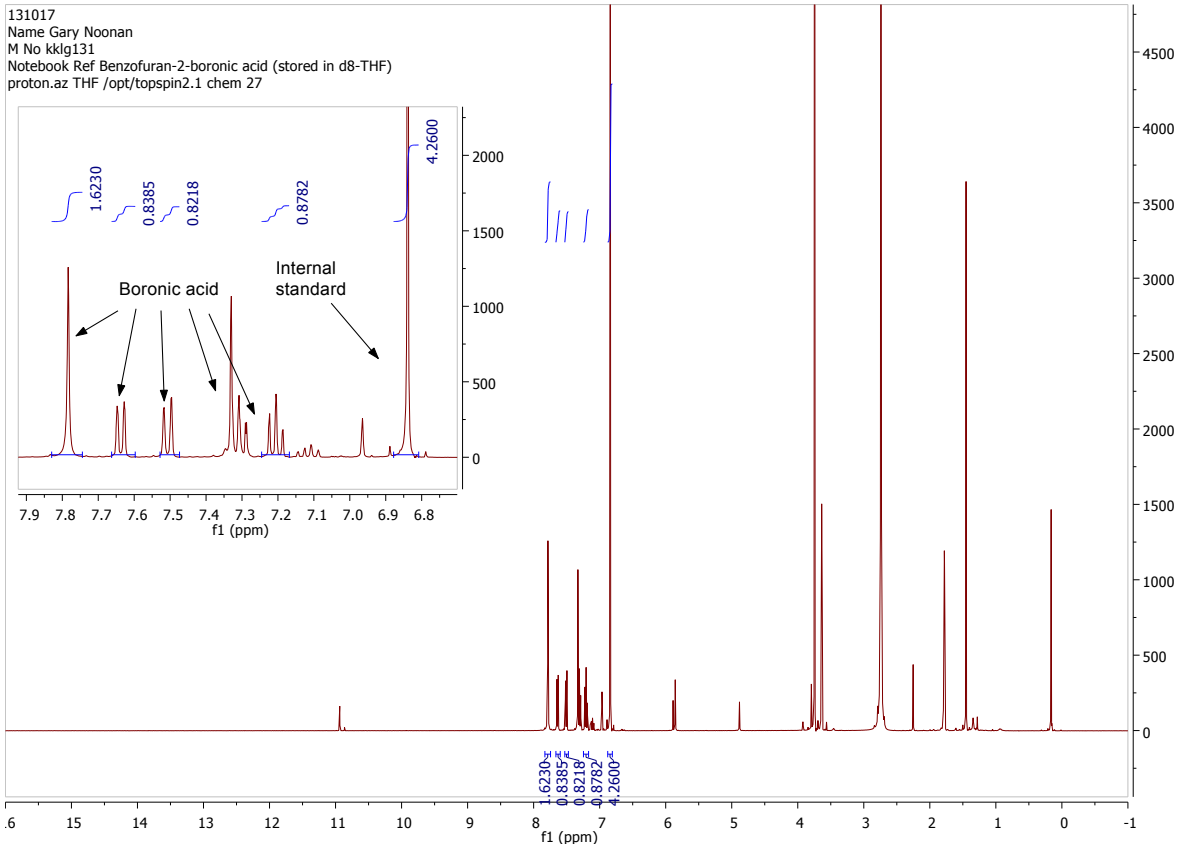


In the spectra which follow (see below), the water peak (δ_H ~ 2.5 ppm) can be seen to increase over the time period, but a relatively small amount of decomposition was apparent. Burke and co-workers observed 12% decomposition in 15 days when the reagent was stored in the solid state. [1] Interestingly, this boronic acid appears to be more unstable in solution than furan-2-ylboronic acid; the opposite behaviour has been observed for the storage of the neat reagents. Impurities present in the aliphatic region correspond to residual THF (from the work-up in the preparation of the boronic acid sample) and the THF stabilizer, 2,6-di-tert-butyl-4-methylphenol ('butylated hydroxytoluene') BHT.

^{1}H NMR of benzofuran-2-ylboronic acid in d_8-THF t = 16 days (91% remaining)



^{1}H NMR of benzofuran-2-ylboronic acid in d_8-THF t = 1 month 13 days (84% remaining)



LCMS data for qualitative microwave promoted decomposition studies

All experiments were carried out using 0.05 mmol of freshly prepared boronic acid, prepared *via* MIDA boronate hydrolysis. [1] Dimethoxybenzene was employed as an LCMS internal standard. The mol-ratio of internal standard to substrate was varied for each boronic acid to provide appropriate UV absorbance ratios of the protodeboronated products vs. the internal standard in the LCMS of the crude reaction mixtures.

Mol-ratio of boronic acid to internal standard: furan-2-ylboronic acid (10:1), benzofuran-2-ylboronic acid (1:1) thiophene-2-boronic acid (7:1).

Representative procedure for boronic acid decomposition studies:

To a microwave vial containing thiophen-2-ylboronic acid (6.40 mg, 0.05 mmol) and 1,4-dimethoxybenzene (1 mg, 7.24 μmol) as a solution in THF (0.1 mL) was added H_2O (0.4 mL) and potassium phosphate (31.8 mg, 0.15 mmol). The vial was then capped and the sample was heated to 130 °C for 30 min under microwave irradiation. MeCN (0.5 mL) was then added to the crude reaction mixture and the resulting solution was transferred to an LCMS sample vial prior to immediate analysis (see chromatograms below).

Notes:

The same stock solution of boronic acid and internal standard was used for the reactions containing no additive and those containing K_3PO_4, thus insuring that the level of decomposition observed relative to the internal standard could be compared under the various conditions. Each reaction was also carried out in duplicate demonstrating reproducible decomposition or lack of decomposition under the various reaction conditions.

For reactions involving potassium phosphate, three equivalents-relative to boronic acid-were added to the aqueous portion of the reaction solvent.

Retention times (Rt) for the presented LCMS data are as follows:

1,4-dimethoxybenzene (internal standard): 1.89 min, BHT (THF stabiliser): 3.43 min, furan: 1.06 min, furan-2-ylboronic acid: 0.56 min, benzofuran: 2.38 min, benzofuran-2-ylboronic acid: 1.48 min, thiophene: 1.75 min, thiophen-2-ylboronic acid: 0.99 min (Note: The retention times shown are based on LCMS data measured for authentic samples of each of the above compounds prior to carrying out these decomposition studies).

Results: The chromatograms below show that trace/small amounts of protodeboronation were observed when the boronic acid samples were heated in the presence of excess water. For comparison complete protodeboronation was carried out using K_3PO_4 to promote the reaction.

Furan-2-ylboronic acid in water alone

Retention times: 1,4-dimethoxybenzene: 1.89 min., furan: 1.06 min., furan-2-boronic acid: 0.56 min.

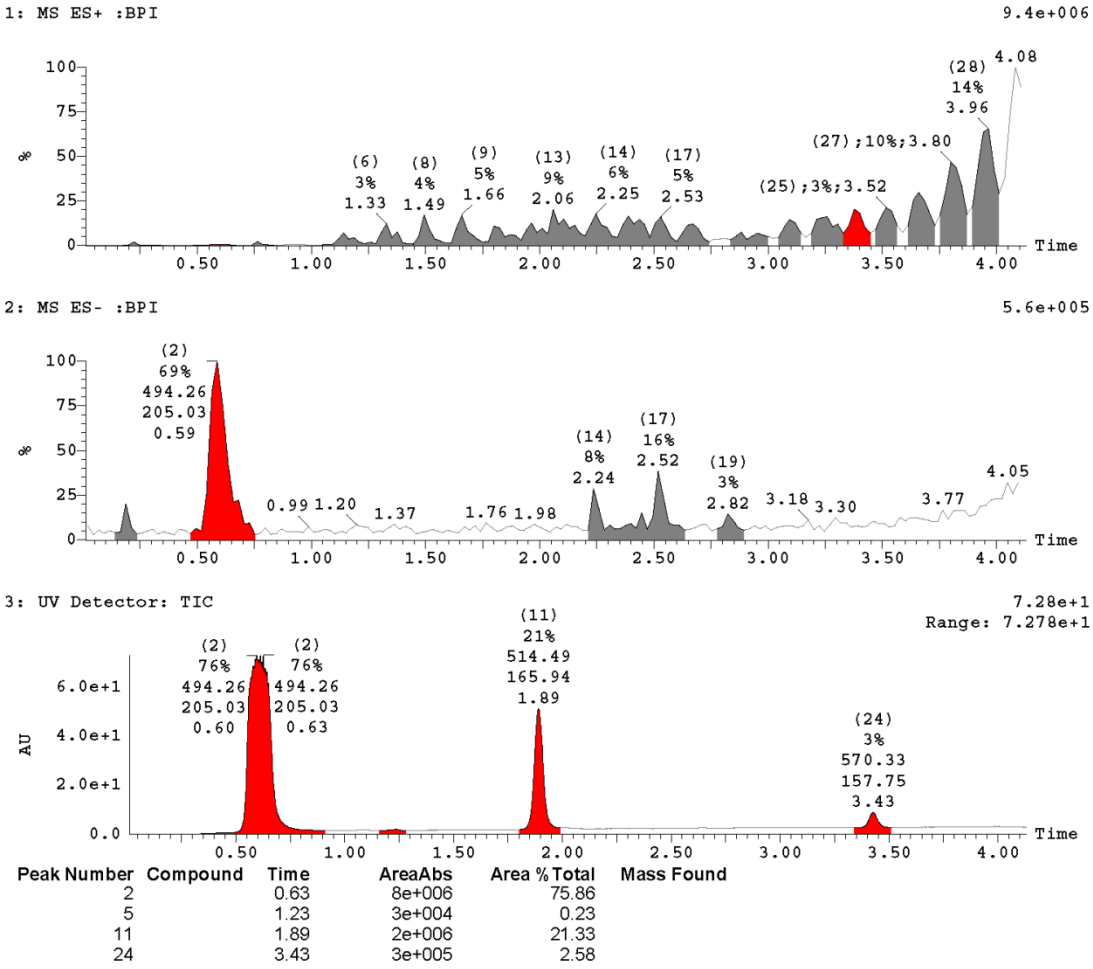
Openlynx Report - kklg131 Page 1

Sample: 1 Vial:1:31 ID:EN06827-75 t= 390 min 130 degrees
File:Noonan Gary452-1 Method:C:\MassLynx\5MIN.olp Date:05-Jul-2013
Time:16:55:35 SIGNED BY Description:EN06827-75 t= 390 min 130 degrees
33S38E lcms

Printed: Fri Jul 05 17:19:23 2013

Typo in title, should read:
EN06827-75 t = 30 min 130 degrees

Sample Report:



Peak Number	Compound	Time	AreaAbs	Area % Total	Mass Found
2		0.63	8e+006	75.86	
5		1.23	3e+004	0.23	
11		1.89	2e+006	21.33	
24		3.43	3e+005	2.58	

Furan-2-ylboronic acid in Water:THF 4:1

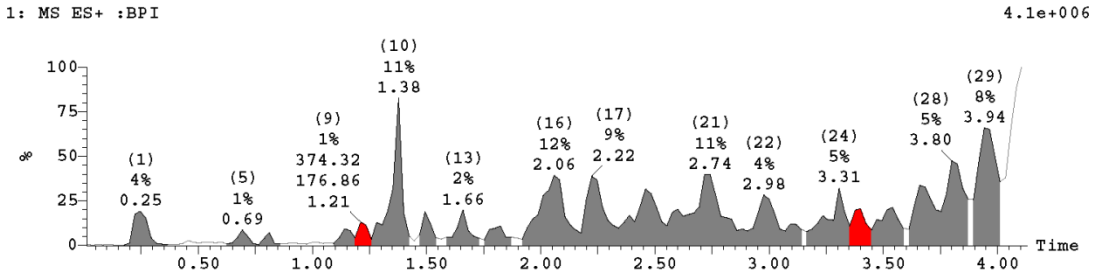
Retention times: 1,4-dimethoxybenzene: 1.89 min., furan: 1.06 min., furan-2-boronic acid: 0.56 min**.**

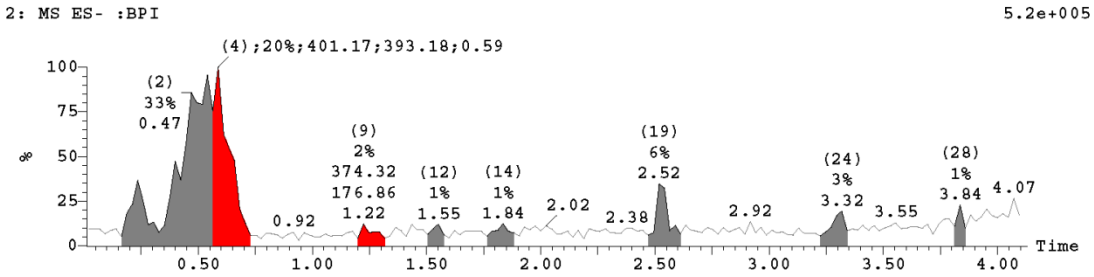
Openlynx Report - kklg131 Page 1

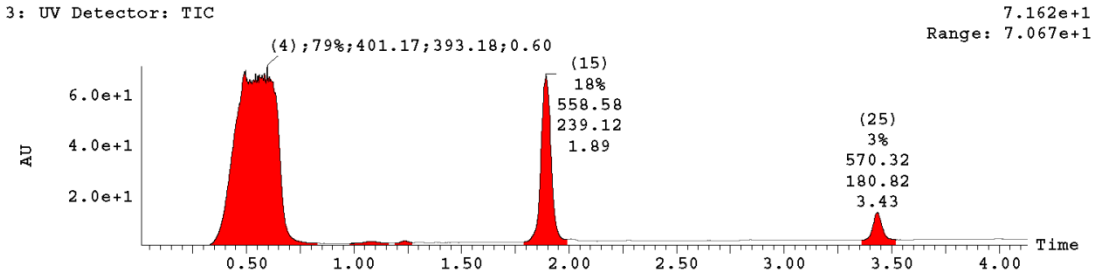
Sample: 1 Vial:1:26 ID:EN06827-73 t= 390 min 130 degrees
File:Noonan Gary450-1 Method:C:\MassLynx\5MIN.olp Date:05-Jul-2013
Time:16:24:10 SIGNED BY Description:EN06827-73 t= 390 min 130 degrees
33S38E lcms

Printed: Fri Jul 05 16:30:10 2013

Sample Report:







Peak Number	Compound	Time	AreaAbs	Area % Total	Mass Found
4		0.60	2e+007	79.15	
7		1.08	4e+004	0.23	
9		1.24	3e+004	0.14	
15		1.89	3e+006	17.86	
25		3.43	5e+005	2.62	

Furan-2-ylboronic acid in water:THF 4:1 + 3 eq. of potassium phosphate

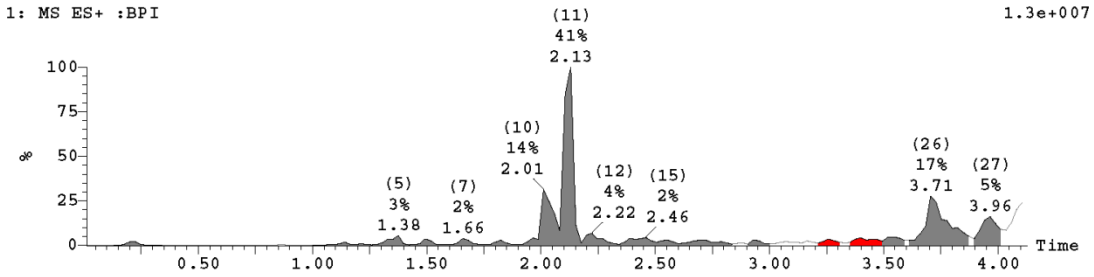
Retention times: 1,4-dimethoxybenzene: 1.89 min., furan: 1.06 min., furan-2-boronic acid: 0.56 min.

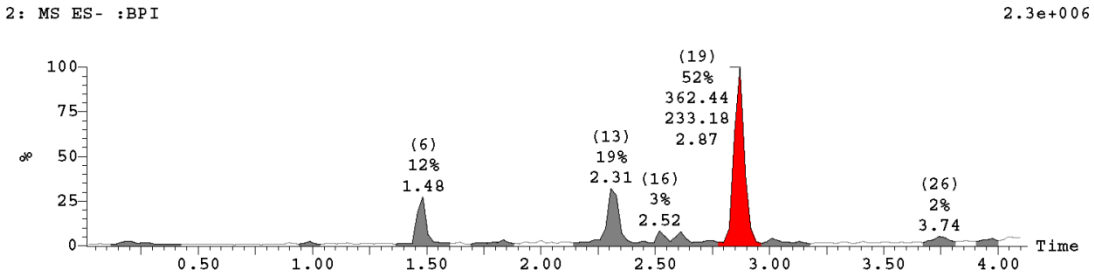
Openlynx Report - kklg131 Page 1

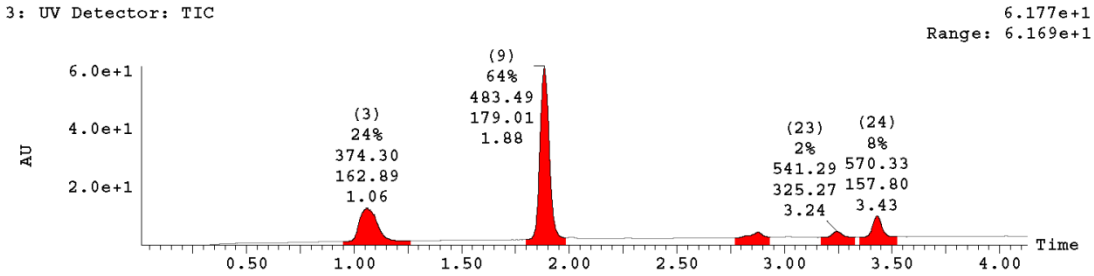
Sample: 1 Vial:1:30 ID:EN06827-74 t= 390 min 130 degrees
File:Noonan Gary451-1 Method:C:\MassLynx\5MIN.olp Date:05-Jul-2013
Time:16:49:27 SIGNED BY Description:EN06827-74 t= 390 min 130 degrees
33S38E lcms

Printed: Fri Jul 05 16:55:34 2013

Sample Report:







Peak Number	Compound	Time	AreaAbs	Area % Total	Mass Found
3		1.06	1e+006	23.69	
9		1.89	3e+006	64.21	
19		2.88	1e+005	2.28	
23		3.25	1e+005	2.26	
24		3.43	3e+005	7.56	

Benzofuran-2-ylboronic acid in water alone

Retention times: 1,4-dimethoxybenzene: 1.89 min., benzofuran: 2.22 min., benzofuran-2-ylboronic acid: 1.48 min.

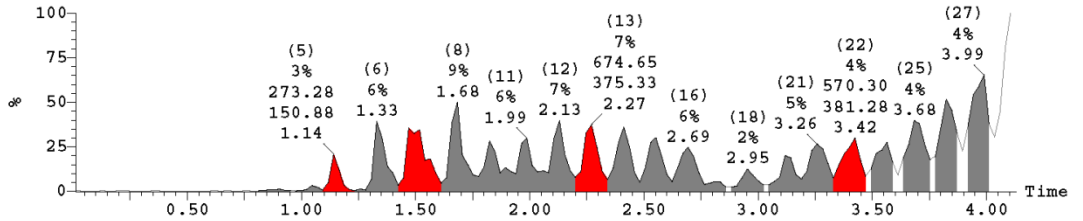
Openlynx Report - kklg131 Page 1

Sample: 1 Vial:1:39 ID:EN06827-94 crude t= 30 min at 130 degrees
File:Noonan Gary482-1 Method:C:\MassLynx\5MIN.olp Date:26-Jul-2013
Time:15:42:22 SIGNED BY Description:EN06827-94 crude t= 30 min at 130 degrees
33S38E lcms

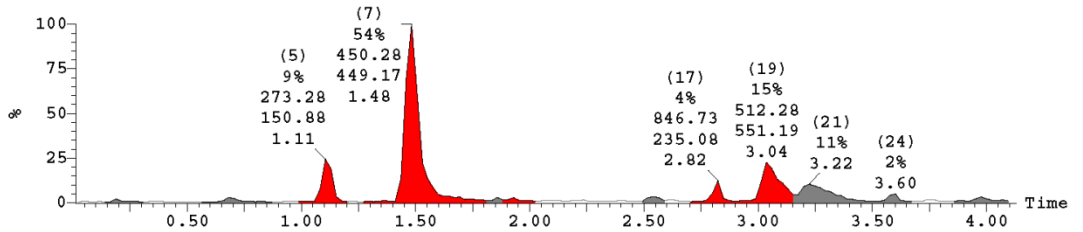
Printed: Fri Jul 26 15:52:59 2013

Sample Report:

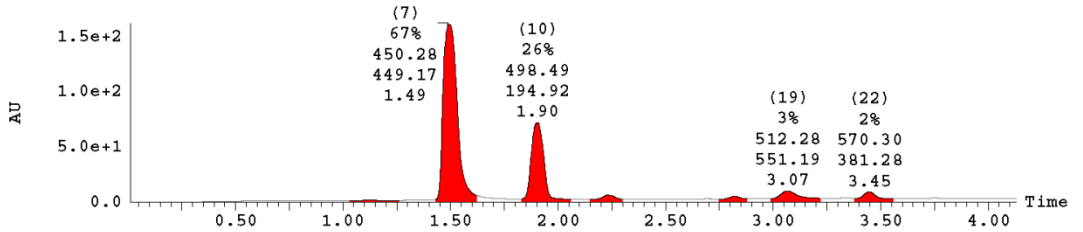
1: MS ES+ :BPI 4.1e+006



2: MS ES- :BPI 4.4e+006



3: UV Detector: TIC 1.615e+2
Range: 1.615e+2



Peak Number	Compound	Time	AreaAbs	Area % Total	Mass Found
5		1.12	3e+004	0.19	
7		1.49	1e+007	67.07	
10		1.90	4e+006	25.69	
13		2.23	2e+005	1.20	
17		2.82	1e+005	0.64	
19		3.07	6e+005	3.29	
22		3.45	3e+005	1.91	

Benzofuran-2-ylboronic acid in water:THF 4:1

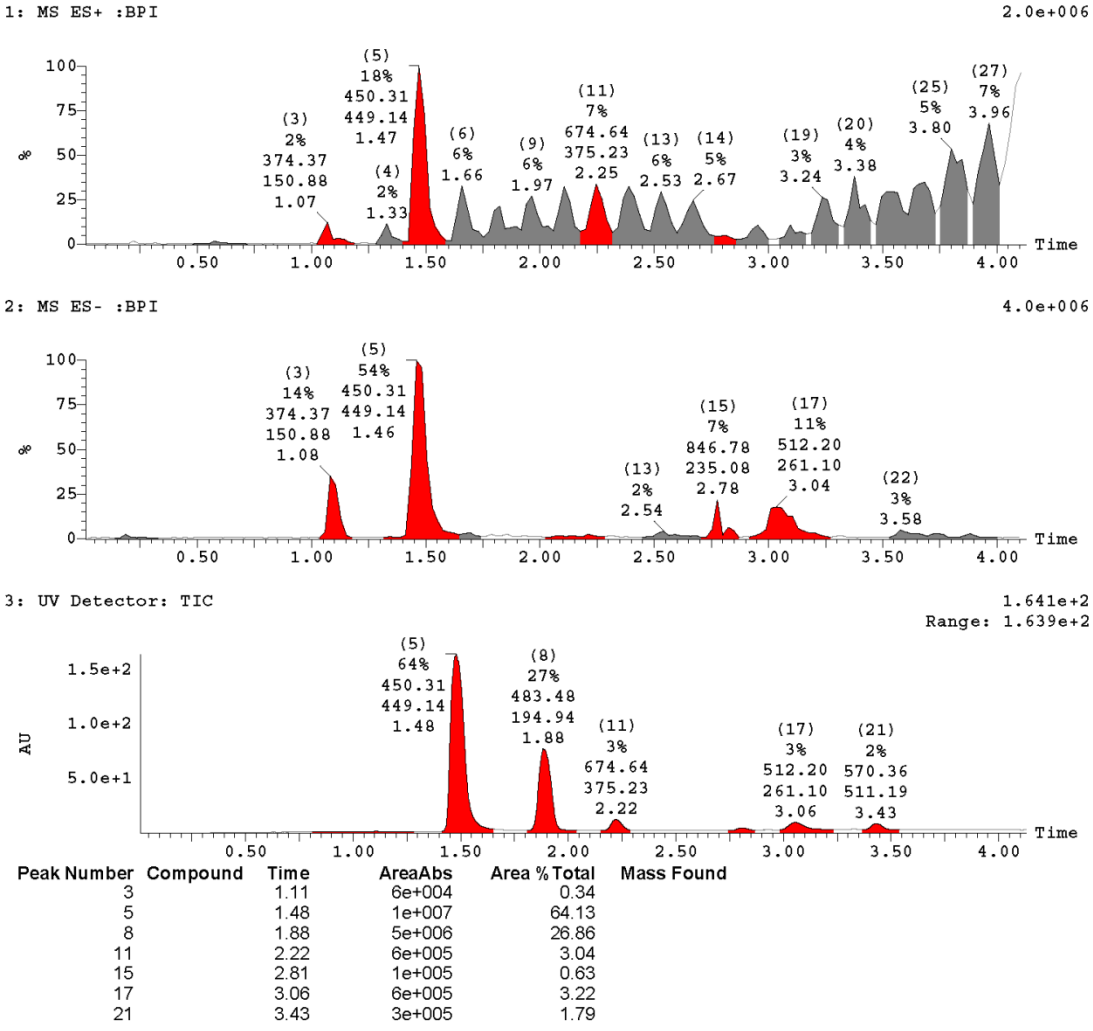
Retention times: 1,4-dimethoxybenzene: 1.89 min., benzofuran: 2.22 min., benzofuran-2-ylboronic acid: 1.48 min.

Openlynx Report - kklg131 Page 1

Sample: 1 Vial:1:38 ID:EN06827-93 crude t= 30 min at 130 degrees
File:Noonan Gary481-1 Method:C:\MassLynx\5MIN.olp Date:26-Jul-2013
Time:15:36:14 SIGNED BY Description:EN06827-93 crude t= 30 min at 130 degrees
33S38E lcms

Printed: Fri Jul 26 15:42:21 2013

Sample Report:



Peak Number	Compound	Time	AreaAbs	Area % Total	Mass Found
3		1.11	6e+004	0.34	
5		1.48	1e+007	64.13	
8		1.88	5e+006	26.86	
11		2.22	6e+005	3.04	
15		2.81	1e+005	0.63	
17		3.06	6e+005	3.22	
21		3.43	3e+005	1.79	

Benzofuran-2-ylboronic acid in water:THF 4:1 + 3 Eq. of potassium phosphate

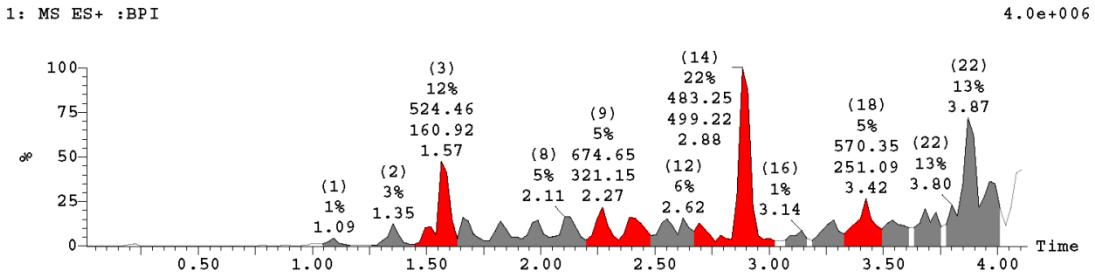
Retention times: 1,4-dimethoxybenzene: 1.89 min., benzofuran: 2.22 min., benzofuran-2-ylboronic acid: 1.48 min**.**

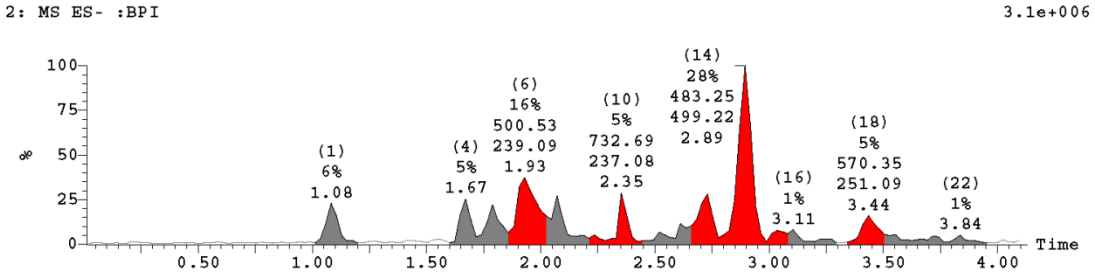
Openlynx Report - kklg131 Page 1

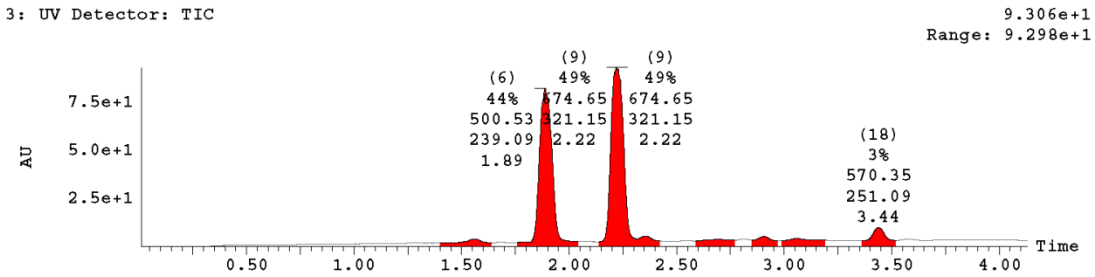
Sample: 1 Vial:1:40 ID:EN06827-95 crude t= 30 min at 130 degrees
File:Noonan Gary483-1 Method:C:\MassLynx\5MIN.olp Date:26-Jul-2013
Time:15:59:04 SIGNED BY Description:EN06827-95 crude t= 30 min at 130 degrees
33S38E lcms

Printed: Fri Jul 26 16:05:10 2013

Sample Report:







Peak Number	Compound	Time	AreaAbs	Area % Total	Mass Found
3		1.56	1e+005	1.21	
6		1.89	5e+006	43.51	
9		2.22	6e+006	49.11	
10		2.35	9e+004	0.75	
13		2.69	7e+004	0.61	
14		2.90	1e+005	0.92	
15		3.06	9e+004	0.74	
18		3.44	4e+005	3.16	

Thiophene-2-ylboronic acid in water alone

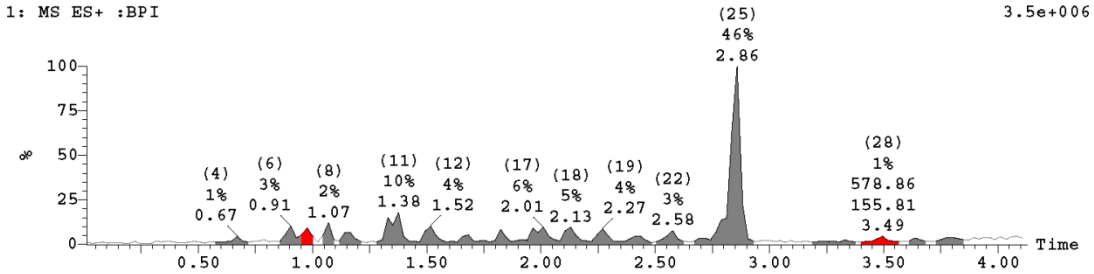
Retention times: 1,4-dimethoxybenzene: 1.95 min., thiophene: 1.75 min., thiophen-2-ylboronic acid: 0.99 min.

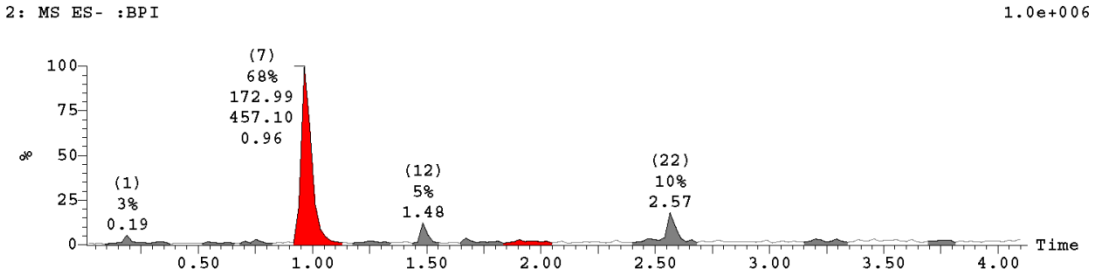
Openlynx Report - kklg131 Page 1

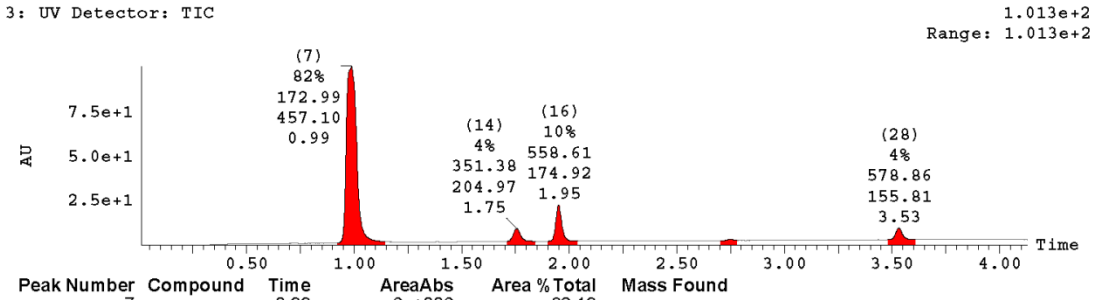
Sample: 1 Vial:3:20 ID:EN06962-36a (water only)
File:Noonan Gary570-1 Method:C:\MassLynx\5MIN.olp Date:04-Sep-2013
Time:18:05:48 SIGNED BY Description:EN06962-36a (water only)
33S38E lcms

Printed: Wed Sep 04 18:17:19 2013

Sample Report:







Peak Number	Compound	Time	AreaAbs	Area % Total	Mass Found
7		0.99	6e+006	82.13	
14		1.76	3e+005	4.20	
16		1.95	7e+005	9.87	
24		2.75	2e+004	0.29	
28		3.53	2e+005	3.51	

Thiophene-2-boronic acid in water:THF 4:1

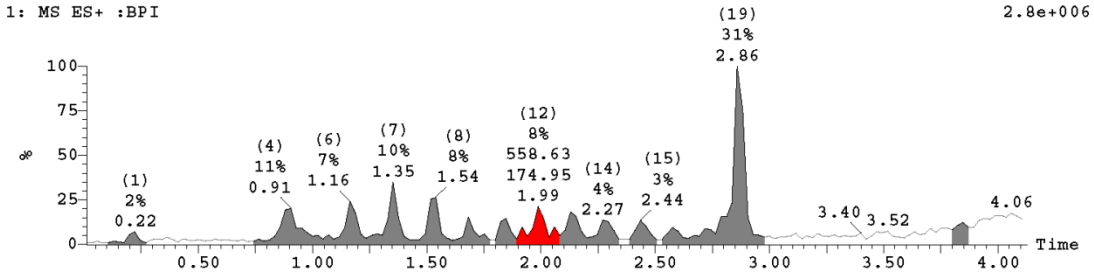
Retention times: 1,4-dimethoxybenzene: 1.95 min., thiophene: 1.75 min., thiophen-2-ylboronic acid: 0.99 min.

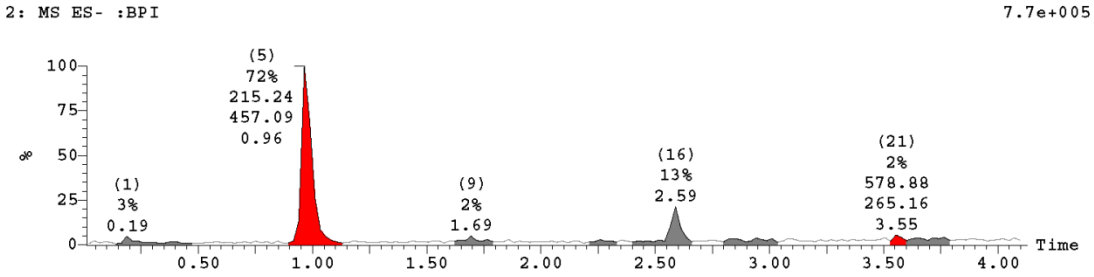
Openlynx Report - kklg131 Page 1

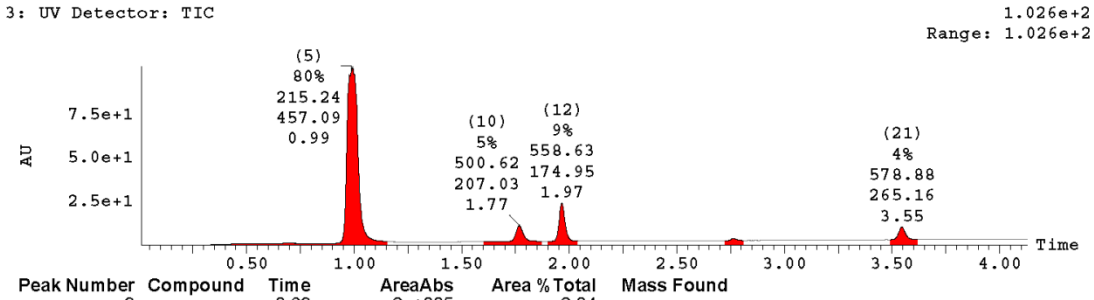
Sample: 1 Vial:3:22 ID:EN06962-33a (water:thf 4:1)
File:Noonan Gary571-1 Method:C:\MassLynx\5MIN.olp Date:04-Sep-2013
Time:18:23:07 SIGNED BY Description:EN06962-33a (water:thf 4:1)
33S38E lcms

Printed: Wed Sep 04 18:29:14 2013

Sample Report:







Peak Number	Compound	Time	AreaAbs	Area % Total	Mass Found
3		0.69	2e+005	2.04	
5		0.99	6e+006	79.55	
10		1.77	4e+005	4.96	
12		1.97	7e+005	9.46	
18		2.77	3e+004	0.44	
21		3.55	3e+005	3.55	

Thiophene-2-ylboronic acid in water:THF 4:1 + 3 Eq. of potassium phosphate

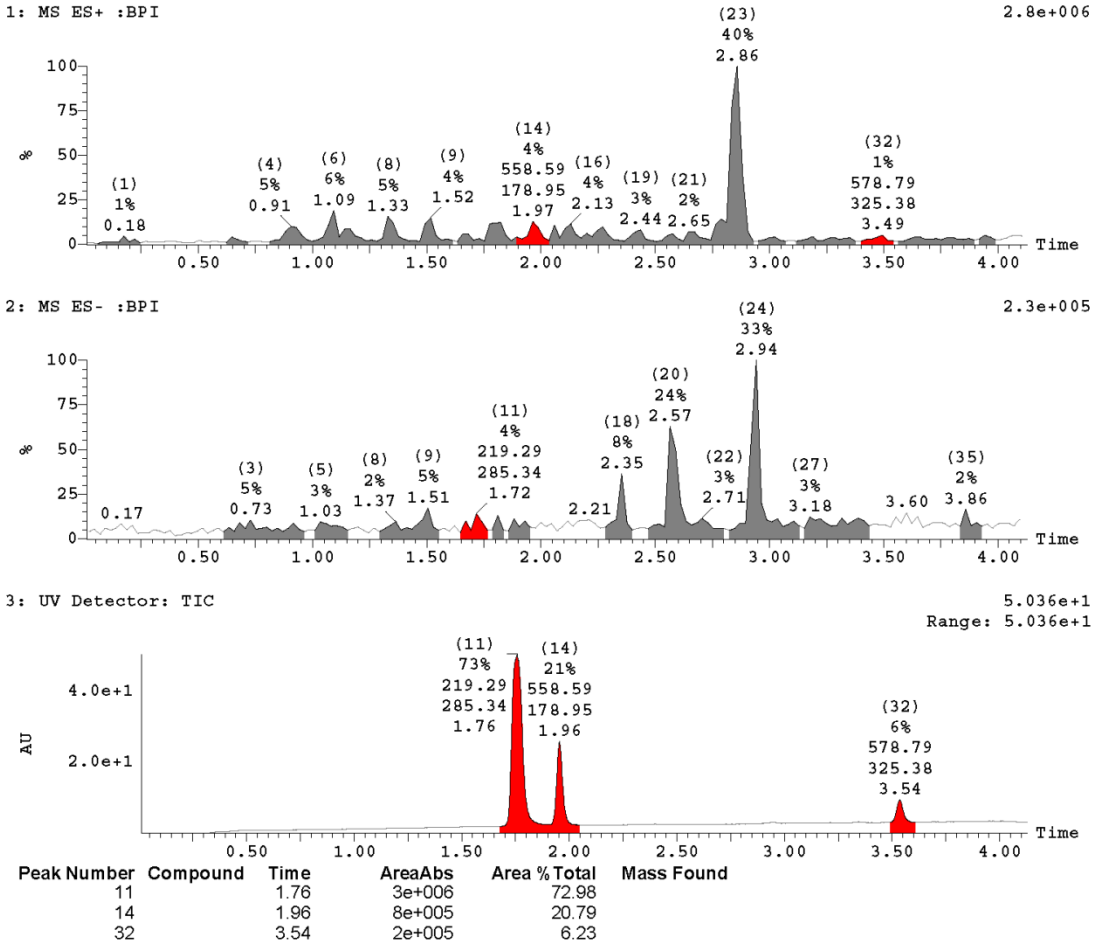
Retention times: 1,4-dimethoxybenzene: 1.95 min., thiophene: 1.75 min., thiophen-2-ylboronic acid: 0.99 min.

Openlynx Report - kklg131 Page 1

Sample: 1 Vial:3:43 ID:EN06962-38(water:thf 4:1+ K3PO4 3 eq.)
File:Noonan Gary575-1 Method:C:\MassLynx\5MIN.olp Date:05-Sep-2013
Time:17:19:38 SIGNED BY Description:EN06962-38(water:thf 4:1+ K3PO4 3 eq.)
33S38E lcms

Printed: Thu Sep 05 17:25:38 2013

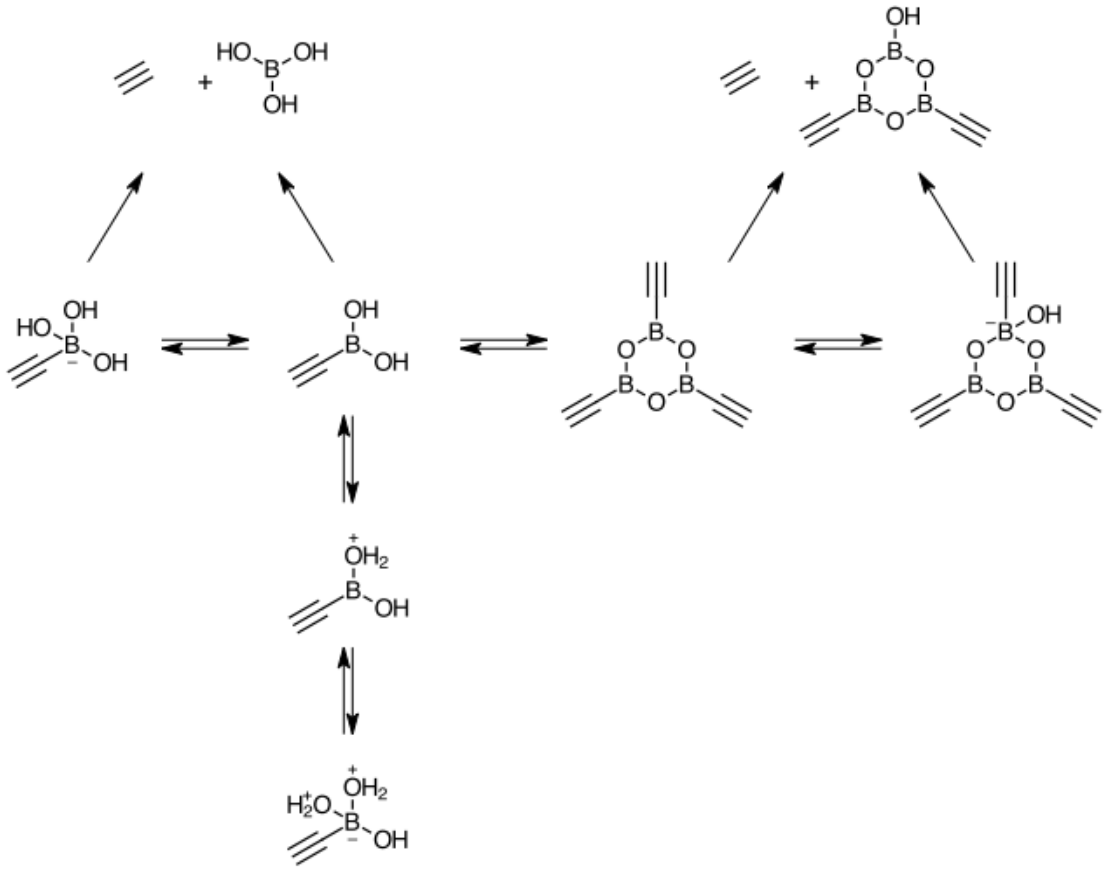
Sample Report:



Peak Number	Compound	Time	AreaAbs	Area % Total	Mass Found
11		1.76	3e+006	72.98	
14		1.96	8e+005	20.79	
32		3.54	2e+005	6.23	

Benchmarking of levels of computational theory

The Evanseck group described the challenge of correctly treating the Lewis acidity of boron and proposed the use of the M06 functional. [2-4] Recent studies on boron mediated aldol reactions by the Wiest group also suggest that M06 single point energy calculations combined with a B3LYP geometry optimization provide adequate levels of accuracy. [5] A range of single point and geometry optimisation combinations were considered as part of this work and applied to a small system involving alkynyl boronic acid. The absolute energies of each species are provided in Table S79-S80 and the species involved are shown in Figure S78 (below).



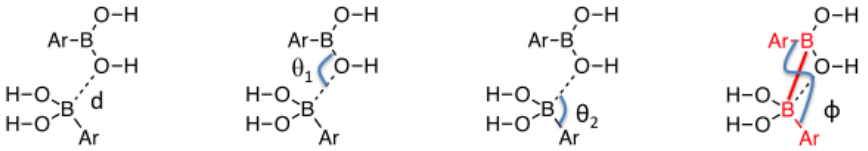
	WATER IEFPCM with B3LYP/6-31+G*	B3LYP/6-31G*//B3LYP/6-31+G**	B3LYP/6-31+G**//B3LYP/6-31+G**	M06/6-31G*//B3LYP/6-31+G**	M06/6-311+G**//B3LYP/6-31+G**	M062X/6-31G*//B3LYP/6-31+G**
ALKYNYL_1WATERTS	-10.30	-329.716342	-329.852837	-329.548317	-329.666688	-329.587832
ALKYNYL_2WATERTS_1	-9.67	-406.158879	-406.333760	-405.958654	-406.110470	-405.998540
ALKYNYL_ATE_PLUS_WATER_TS_FIX	-52.53	-405.634980	-405.829262	-405.439637	-405.608636	-405.480691
ALKYNYL_BORONIC_ACID_PROT_3	-67.86	-253.653466	-253.748228	-253.513042	-253.595655	-253.549528
ALKYNYL_BORONIC_ACID_PROT_PLUS_WATER_2	-74.25	-330.087396	-330.220510	-329.915963	-330.031354	-329.956791
ALKYNYL_BORONIC_ACID_PROT_PLUS_WATER_TS	-64.70	-330.043146	-330.174787	-329.873589	-329.988306	-329.912765
ALKYNYL_BORONIC_ACID	-7.14	-253.355823	-253.454292	-253.217365	-253.302619	-253.255084
ALKYNYL_BOROXINE_1WATERTS	-1.11	-607.172727	-607.361803	-606.827484	-606.993736	-606.949635
ALKYNYL_BOROXINE_2WATERTS_1	-1.67	-683.623525	-683.852698	-683.246962	-683.448097	-683.369561
ALKYNYL_BOROXINE_ATE_PLUS_WATER_TS	-42.99	-683.102786	-683.347714	-682.730325	-682.945617	-682.854578
ALKYNYL_BOROXINE_ATE	-45.69	-606.711592	-606.916579	-606.368284	-606.547887	-606.496080
ALKYNYL_BOROXINE	3.60	-530.802218	-530.954627	-530.486945	-530.621442	-530.607434
ALKYNYL_DIMER_6MR_PROTMIGRAT_TS_FIX	-14.37	-506.642233	-506.829683	-506.367630	-506.531284	-506.447026
ALKYNYL_DIMER_6MRTS	-14.37	-506.642233	-506.829682	-506.367631	-506.531284	-506.447025
ALKYNYL_DIMER_TS_ONEOH_1	-6.00	-506.655721	-506.842471	-506.382636	-506.546149	-506.463000
ALKYNYL_MANXATE_2	-63.94	-329.211428	-329.369961	-329.044113	-329.181638	-329.089831
HYDRONIUM	-108.02	-76.689085	-76.730838	-76.655019	-76.690901	-76.652316
HYDROXIDE	-102.23	-75.720773	-75.826945	-75.687739	-75.782946	-75.689636
WATER	-7.27	-76.408953	-76.458353	-76.375859	-76.417620	-76.373352

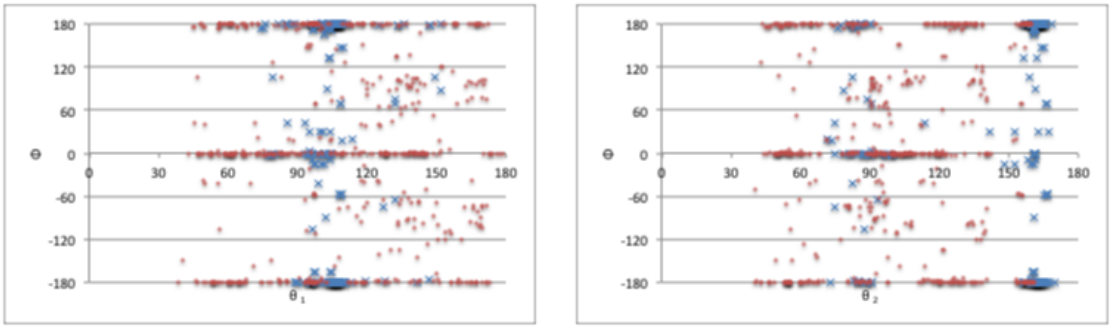
	M062X/6-311+G**//B3LYP/6-31+G**	M06HF/6-31G*//B3LYP/6-31+G**	M06HF/6-311+G**//B3LYP/6-31+G**	MP2/6-31G*//B3LYP/6-31+G**	MP2/6-311+G**//B3LYP/6-31+G**
ALKYNYL_1WATERTS	-329.723147	-329.614848	-329.766190	-328.768590	-329.000247
ALKYNYL_2WATERTS_1	-406.171734	-406.024953	-406.220141	-404.998774	-405.299245
ALKYNYL_ATE_PLUS_WATER_TS_FIX	-405.670487	-405.508817	-405.722078	-404.481390	-404.794495
ALKYNYL_BORONIC_ACID_PROT_3	-253.643672	-253.570966	-253.675233	-252.916719	-253.075083
ALKYNYL_BORONIC_ACID_PROT_PLUS_WATER_2	-330.088822	-329.983020	-330.130600	-329.142766	-329.371594
ALKYNYL_BORONIC_ACID_PROT_PLUS_WATER_TS	-330.044895	-329.939860	-330.087610	-329.091844	-329.322890
ALKYNYL_BORONIC_ACID	-253.352087	-253.276558	-253.384467	-252.622763	-252.781543
ALKYNYL_BOROXINE_1WATERTS	-607.139472	-607.029831	-607.238980	-605.401839	-605.720894
ALKYNYL_BOROXINE_2WATERTS_1	-683.599012	-683.449243	-683.704378	-681.641575	-682.030812
ALKYNYL_BOROXINE_ATE_PLUS_WATER_TS	-683.097178	-682.937202	-683.206321	-681.125539	-681.525674
ALKYNYL_BOROXINE_ATE	-606.698232	-606.580776	-606.802923	-604.952048	-605.278787
ALKYNYL_BOROXINE	-530.760165	-530.682817	-530.849357	-529.244795	-529.492080
ALKYNYL_DIMER_6MR_PROTMIGRAT_TS_FIX	-506.633308	-506.499102	-506.707222	-505.177683	-505.490899
ALKYNYL_DIMER_6MRTS	-506.633306	-506.499100	-506.707220	-505.177681	-505.490899
ALKYNYL_DIMER_TS_ONEOH_1	-506.649032	-506.515814	-506.722420	-505.190245	-505.504521
ALKYNYL_MANXATE_2	-329.242860	-329.122003	-329.291467	-328.273326	-328.519769
HYDRONIUM	-76.693593	-76.650382	-76.697250	-76.475077	-76.549500
HYDROXIDE	-75.784074	-75.690625	-75.790510	-75.513104	-75.639559
WATER	-76.420616	-76.369942	-76.423087	-76.196845	-76.274554

The MP2/6-311+G** level of theory was taken as the best available but is impractical for any larger species than those studied in this benchmarking exercise. Energy changes (for the various processes shown in Figure S78) computed at the various levels were compared with those computed at the benchmark level. The RMSE was computed for each level of theory (including RHF which is excluded from the Table for the sake of space). This data clearly support the earlier findings of Plumley et al. and of Lee et al. and suggest that M06 with a large basis set is suitable for studying these systems.

Level of theory	RMSE (kcal/mol)
B3LYP/6-31G*	11.0
B3LYP/6-311+G**	4.1
M06/6-31G*	12.9
M06/6-311+G**	2.6
M062X/6-31G*	15.2
M062X/6-311+G**	3.7
M06HF/6-31G*	19.4
M06HF/6-311+G**	8.2
RHF/6-31G*	13.2
RHF/6-311+G**	15.4
MP2/6-31G*	11.5

Crystal structure geometrical parameter analysis





DIST1 = d
TOR1 = ϕ
ANG1 = θ_1
ANG2 = θ_2

REFCOD	DIST1	TOR1	ANG1	ANG2
GISVIO	3.004	-179.98	92.777	88.622
BEWYAE01	3.128	180	88.733	90.188
BEWYAE01	3.136	-180	90.229	90.544
BEWYAE	3.172	-180	89.656	90.595
BEWYAE	3.18	180	87.872	90.146
CITNOJ	3.228	-106.806	96.371	87.668
GENTOJ	3.232	-180	88.744	84.88
AVOTIO	3.261	0	94.643	82.258
EFIDON	3.274	179.98	85.808	81.281
PAXTEO	3.276	180	85.254	85.913
KEGNEQ	3.297	174	75.355	82.231
KEGNEQ	3.319	174	74.198	75.929
AFOLUC	3.325	-3.316	100.533	87.12
WIYNAU	3.392	178.817	146.965	77.168
XETLOY	3.418	41.689	93.04	74.709
IGERAO	3.432	-180	110.309	167.988
XETLOY	3.441	-41.449	98.929	82.718
MUWYUZ	3.443	-180	108.993	164.75
GODGUC	3.45	180	107.474	161.687
XOSDUF	3.456	-179.98	110.845	166.824
FEJGIL	3.463	180	110.049	164.789
REHDOY	3.464	0	104.711	87.123
KUGBUK	3.469	180	107.879	164.733
BAGYOZ	3.471	-180	107.026	163.622
WAJXEL	3.471	86.529	151.821	78.725
XUVBAR	3.474	-179.98	105.903	165.309
PHBORA01	3.475	2.37	95.526	90.53

AFOLUC	3.476	-57.203	109.252	166.481
DEWYAG	3.479	179.98	109.467	162.773
WIYNAU	3.48	29.666	104.064	162.755
XOSDUF	3.481	147.227	109.949	165.041
QACYIE	3.482	180	108.363	168.726
FUZLES	3.483	-179.98	107.507	164.84
DIXTOU	3.483	180	103.84	160.142
PHBORA01	3.484	68.44	108.786	165.69
NUPQIZ	3.484	106.391	149.373	158.806
DIXTUA	3.489	-178.528	127.54	84.944
PHBORA01	3.492	68.44	108.419	166.382
AFOLUC	3.492	-57.203	108.186	166.567
WAPDIB	3.495	0	98.992	88.047
DEWYEK	3.496	180	107.055	163.132
DIXVAI	3.497	0	95.749	87.51
BAJTEM01	3.498	-180	107.334	163.973
WAJXEL	3.499	180	106.248	164.035
WEJCIY	3.5	-180	104.978	159.992
NIQYUI	3.5	75.74	132.462	88.849
NIQYUI	3.5	180	108.402	163.646
NEYVIX	3.5	180	111.141	165.888
KUGBOE	3.5	180	107.134	164.021
GISVIO	3.501	-180	106.26	164.401
OLIDOC	3.502	180	107.666	163.095
PHBORA	3.503	-2.168	94.402	90.036
ETOLAA	3.503	180	108.387	165
YESZAY	3.504	-180	109.664	160.205
PHBORA	3.504	-59.601	108.838	165.208
BAJTEM02	3.504	180	107.385	164.191
XOSDUF	3.507	147.227	108.634	163.864
FAKTER	3.507	-164.79	104.939	160.649
PHBORA	3.508	-59.601	108.812	166.337
PAXSUD	3.509	-180	108.229	163.023
EFIDIH	3.509	180	107.513	163.108
HUXXII	3.511	180	109.286	161.909
GODHAJ	3.515	-15.357	101.308	159.892
FAKTER	3.515	170.877	104.846	160.525
ROGKUU	3.517	-180	106.264	163.75
FAKTER	3.521	170.877	104.557	161.233
WEJCIY	3.522	-75.51	127.304	75.008
ROGMEF	3.523	180	106.341	164.102
LABCUM	3.525	180	106.22	165.418
XOSDOZ	3.526	179.98	107.935	164.307
REHDOY	3.526	180	107.632	164.916
EFIDON	3.526	180	105.453	163.722
BAJTEM	3.526	-180	107.925	163.894
TUNGAK	3.527	-180	109.283	166.758

GODHAJ	3.527	-8.559	103.9	161.717
FAKTER	3.527	-164.79	104.091	160.548
GITLAX	3.528	-180	107.175	164.431
FECSEM	3.528	180	105.998	161.702
BUDREY	3.529	-180	108.575	163.596
BAJTIQ	3.529	-180	106.678	163.275
XOSFAN	3.531	180	106.341	163.245
TASCEW	3.531	-180	105.537	163.504
WIYMUN	3.532	180	107.545	160.751
GODHAJ	3.533	-15.357	100.276	161.079
TUNNEW	3.535	-180	107.581	162.303
OCEFAF	3.537	180	107.206	165.441
VIVQAT	3.537	-180	104.146	161.771
VEFCOZ	3.54	-180	105.258	161.296
PAXSUD	3.54	69.231	131.968	90.921
WIYMOH01	3.541	180	107.917	162.572
FUBKOD	3.541	-180	105.992	161.888
UCETUS	3.543	180	108.714	165.161
XUVBEV	3.544	180	103.767	164.84
WIYPEA	3.544	-180	108.038	162.189
DIXTIO	3.544	179.378	107.038	163.583
SAFSID	3.546	-180	107.649	165.346
WIYNAU	3.546	29.666	101.275	142.036
USALAC	3.546	180	103.772	161.144
KEGNAM	3.546	-179.98	113.21	170.019
DIXTIO	3.548	179.378	106.689	164.554
FOVMOT	3.549	-179.98	106.351	162.839
MIDZAB	3.55	-180	103.515	162.211
WIYMUN	3.551	180	105.784	157.078
OLEXAF	3.551	180	105.949	162.248
REHDOY	3.553	180	107.155	164.23
OLEXOT	3.553	-180	106.908	162.566
FEJGUX	3.555	180	107.976	162.559
BPHBAC01	3.557	180	107.342	163.661
IYAXAH	3.558	180	106.299	163.099
KOJQAC	3.559	-180	104.92	161.876
RONLIP	3.561	-180	107.379	160.851
WIYMUN01	3.562	180	108.063	160.652
FUBLIY	3.562	-179.845	141.97	72.899
VIVPUM	3.563	179.98	104.102	162.533
LEYNAF	3.563	165.373	101.438	161.02
DECROT	3.563	-180	104.138	160.789
WIYMOH	3.564	180	107.694	162.494
WENZUL	3.566	179.98	106.986	163.68
LEYNAF	3.567	165.373	101.331	160.646
MUCJUQ	3.569	-180	104.371	160.603
VEFCIT	3.571	-180	105.177	161.541

TITDEG	3.572	-179.98	107.455	163.934
ZAPDAV	3.573	-180	105.578	160.787
HOXPIU	3.574	-180	105.451	162.809
GISVIO	3.575	180	105.791	162.812
MOKKON	3.58	-179.98	106.669	162.689
WIYNAU	3.582	29.666	99.769	167.149
ZILBEB	3.583	180	105.479	161.782
WIYMUN01	3.583	179.98	106.975	158.225
OCAJUY	3.584	-180	107.848	157.944
XECHUJ	3.586	-180	109.337	166.079
GODHAJ	3.588	-15.357	98.078	148.012
XETLOY	3.591	41.689	85.736	113.493
MUCJUQ	3.591	0	98.133	95.93
BEWYAE	3.596	180	103.86	160.04
NIQZAP	3.601	0	103.951	161.28
BEWYAE	3.602	180	103.977	160.826
GODHAJ	3.608	-15.357	97.245	152.297
NIQZET01	3.609	90.039	103.057	161.221
DIXTUA	3.61	-178.528	119.718	83.048
BEWYAE01	3.611	180	103.971	159.689
WIYMEX	3.613	131.923	104.475	156.713
FETZUA	3.615	0	103.562	161.178
NIQZET	3.616	0	103.851	161.443
BEWYAE01	3.616	180	103.928	160.436
ROKJUX	3.62	17.983	109.043	73.429
MIDZAB	3.621	-180	100.228	156.57
FUBLIY	3.621	179.845	135.782	86.42
SOWJAQ	3.63	-180	94.962	87.972
VEFCUF	3.632	178.608	147.307	159.878
PAXTIS	3.634	0	93.544	75.078
CITNOJ	3.635	106.806	79.559	82.295
ROKJUX	3.636	20.121	113.705	71.348
LIXLAG	3.636	180	151.945	165.812
UMUHOZ	3.637	172.852	102.354	161.289
FETZUA	3.638	180	103.112	161.315
UMUHOZ	3.639	172.852	102.153	161.235
FETZUA	3.639	-180	103.418	161.329
REHDOY	3.64	0	96.304	98.005
NIQZET01	3.64	-90.039	101.953	160.985
WIYMEX	3.642	131.923	103.239	162.246
QACYEA	3.643	178.715	133.384	82.906
HIRGEV	3.643	173.548	103.038	161.209
FETZUA	3.643	0	102.378	161.444
FAKTER	3.645	-3.443	78.991	96.874
XUVBAR	3.646	-179.98	98.362	156.99
HIRGEV	3.646	173.548	102.752	160.945
NIQZET	3.652	0	102.338	160.886

BEWYAE	3.652	180	101.185	162.099
XUVBEV	3.653	180	100.126	157.522
NIQZAP	3.656	0	101.677	161.11
OLIDOC	3.658	-65.004	132.312	93.5
NIQZET01	3.658	0	79.834	81.13
USALAC	3.659	180	100.765	160.194
FECSEM	3.66	-180	101.961	156.429
BEWYAE	3.661	180	101.353	161.415
QACYEA	3.662	178.715	133.23	85.285
DIXTOU	3.663	180	95.566	159.423
FAKTER	3.664	-164.79	97.849	160.946
ITIRAE	3.666	-176.476	146.666	159.344
IYAXAH	3.67	180	76.349	86.137
ETOLAA	3.672	0	82.051	78.511
FECSEM	3.674	-180	101.596	165.449
WIYNAU	3.675	178.817	125.312	83.864
BEWYAE01	3.676	180	100.858	162.045
FAKTER	3.677	-164.79	97.331	160.956
WENZUL	3.681	180	81.893	81.105
BEWYAE01	3.681	180	101.026	161.445
FAKTER	3.683	-3.443	77.494	99.944
NIQZET	3.684	0	78.75	85.821
GODHAJ	3.684	-8.559	96.789	158.377
WIYNAU	3.685	29.666	95.365	152.825
FAKTER	3.691	170.877	97.25	160.72
ZILBEB	3.696	180	100.398	160.726
WEJCIY	3.696	-180	96.159	156.106
VIVQAT	3.699	-180	96.653	159.951
FAKTER	3.699	170.877	96.737	161.083
VIVPUM	3.7	179.98	97.69	159.368
WIYMUN	3.701	180	98.503	157.367
MOKKON	3.703	0	82.159	77.972
DECROT	3.703	-180	97.462	160.674
FETZUA	3.71	0	80.159	83.026
VEFCOZ	3.711	-180	97.768	159.17
PAXSUD	3.713	-69.231	120.361	90.4
NIQYUI	3.713	-75.74	118.653	89.512
WAJXEL	3.716	180	96.369	158.109
AFOLUC	3.716	-57.203	97.38	154.184
VEFCIT	3.717	-180	98.875	161.087
KOJQAC	3.717	-180	97.993	160.547
PHBORA01	3.719	68.44	97.69	155.287
PHBORA01	3.72	68.44	97.641	155.932
AVOTIO	3.721	0	75.843	118.294
ROGKUU	3.722	-180	96.724	158.321
NUPQIZ	3.723	96.595	137.611	80.98
ROKJUX	3.724	17.983	104.053	152.129

NIQZAP	3.724	0	78.846	82.531
ZAPDAV	3.725	-180	98.728	160.029
USAKOP	3.725	64.981	129.535	95.829
FETZUA	3.725	0	79.789	82.472
FAKTER	3.727	-2.642	79.682	96.471
IYAXAH	3.728	180	98.632	158.568
AFOLUC	3.729	-57.203	97.3	154.803
FECSEM	3.73	180	97.08	158.692
BAGYOZ	3.731	-180	95.105	157.207
TASCEW	3.731	-180	96.891	158.005
OLIDOC	3.731	180	97.185	158.377
ROGKUU	3.732	0.02	140.497	83.201
DEWYEK	3.732	180	96.115	156.494
ROGMEF	3.733	180	96.95	158.021
GODGUC	3.733	180	94.607	155.093
GISVIO	3.733	180	98.66	159.258
EFIDON	3.733	180	96.33	158.097
PAXSUD	3.734	-180	97.419	158.547
GISVIO	3.736	-180	95.985	157.128
NIQYUI	3.738	180	97.096	158.238
PHBORA	3.741	-59.601	97.646	155.999
EFIDIH	3.741	180	96.927	158.943
MIDZAB	3.742	-18.047	118.643	95.326
DIXTOU	3.745	-167.159	150.175	92.814
PHBORA	3.746	-59.601	97.277	156.038
REHDOY	3.747	0	91.679	103.049
KUGBUK	3.747	180	95.267	157.545
FEJGUX	3.747	180	99.261	158.753
BAJTIQ	3.747	-180	96.692	159.115
FUZLES	3.748	-179.98	95.518	157.151
FEJGIL	3.748	180	96.518	156.784
BPHBAC01	3.748	180	98.713	158.226
USAKOP	3.749	-64.981	127.201	88.169
MUCJUQ	3.749	-180	96.548	157.925
YESZAY	3.75	-180	97.753	156.71
FUBKOD	3.75	-180	96.655	160.631
FOVMOT	3.75	-179.98	97.408	159.108
WIYMUN	3.752	180	97.579	155.882
WIYMOH01	3.753	180	98.153	159.584
XOSFAN	3.753	180	96.691	158.952
WIYMUN01	3.754	179.98	99.15	156.858
PHBORA01	3.754	91.701	138.911	91.744
WIYPEA	3.755	-180	98.129	160.178
TUNNEW	3.755	-180	97.17	158.603
HOXPIU	3.758	-180	97.192	159.754
MUCJUQ	3.759	0	91.15	104.919
LABCUM	3.759	180	95.887	156.904

DIXTIO	3.76	179.378	97.253	157.671
KUGBOE	3.762	180	95.31	158.362
WIYPEA	3.763	0	142.394	96.341
VEXFUZ02	3.765	178.55	146.04	86.81
AFOLUC	3.765	-93.072	137.199	92.109
AFOLUC	3.765	93.072	138.877	90.927
ETOLAA	3.766	0	78.115	80.348
BAJTEM01	3.766	-180	95.159	158.395
KEGNEQ	3.769	174	56.629	78.426
WIYMOH	3.77	180	98.103	159.816
QACYIE	3.771	180	95.516	153.483
PHBORA01	3.771	-91.701	137.835	91.895
OLIDOC	3.771	65.004	125.114	91.002
BAJTEM02	3.774	180	95.074	158.393
MUWYUZ	3.776	-180	93.526	155.048
WENZUL	3.777	179.98	97.728	158.311
MOKKON	3.777	0	78.985	80.393
ETOLAA	3.777	180	96.119	157.272
GITLAX	3.778	-180	96.108	157.283
KEGNEQ	3.779	174	55.899	82.365
PHBORA	3.78	-92.07	140.237	92.016
MOKKON	3.78	-179.98	97.891	160.33
FETZUA	3.78	104.536	141.059	90.677
XOSDOZ	3.782	179.98	96.564	158.139
DIXTIO	3.782	179.378	96.301	158.713
PHBORA01	3.783	64.384	136.462	93.826
SAFSID	3.785	-180	96.95	157.907
WIYMUN01	3.785	180	97.845	156.023
FETZUA	3.786	104.536	142.019	91.135
TITDEG	3.788	-179.98	98.153	159.292
PEYLOV	3.789	-177.666	142.212	86.98
BAJTEM	3.789	-180	95.621	158.951
OLEXAF	3.79	180	96.217	155.985
XUVBAR	3.792	97.776	143.25	92.89
IGERAO	3.792	-180	94.263	154.628
DEWYAG	3.792	179.98	94.878	158.202
NUPQIZ	3.794	106.391	125.518	98.613
HUXXII	3.794	180	96.229	156.035
WIYMUN	3.795	-38.888	124.672	94.029
WIYMOH01	3.796	0	142.637	95.461
WIYMOH	3.797	0	142.852	95.506
WEJCIY	3.797	-75.51	111.517	85.718
OCEFAF	3.799	180	95.889	157.284
WIYMUN	3.799	39.412	125.065	92.315
DIXVAI	3.799	0	82.878	113.166
REHDOY	3.8	180	94.942	157.426
REHDOY	3.801	180	96.341	158.342

AFOLUC	3.802	-54.861	135.987	96.044
NIQZET01	3.803	-103.892	140.559	90.94
NIQZET01	3.803	-69.043	142.194	96.987
RONLIP	3.804	-180	96.574	156.215
FETZUA	3.805	69.108	139.859	96.212
XOSDUF	3.806	147.227	95.298	150.938
BUDREY	3.807	-180	96.067	157.107
TUNGAK	3.808	-180	96.248	156.734
AFOLUC	3.808	54.861	134.851	98.506
REHDOY	3.809	0	88.8	113.939
NEYVIX	3.81	180	95.846	157.591
FETZUA	3.811	-69.108	139.316	96.48
FAKTER	3.811	-2.642	76.21	101.149
VEFCUF	3.812	178.607	133.283	154.686
PHBORA01	3.812	-64.384	134.447	97.936
PHBORA	3.813	-62.462	137.983	94.163
IGERAO	3.815	0	101.091	87.981
NIQZET	3.816	70.102	142.638	97.368
ROKJUX	3.818	20.121	104.735	153.222
NIQZAP	3.82	-67.002	142.37	96.497
IYAXAH	3.82	180	70.444	87.272
UCETUS	3.821	180	96.28	155.541
PHBORA	3.825	92.07	137.66	91.666
OCAJUY	3.825	-180	96.902	153.472
XUVBEV	3.827	88.276	141.968	90.313
OLEXOT	3.828	-180	94.23	156.736
NIQZET	3.828	96.787	139.643	91.039
IYAXAH	3.83	0	144.363	93.395
WAPDIB	3.832	0	84.342	112.68
GISVIO	3.833	0	146.407	90.335
XOSDUF	3.835	147.227	93.951	156.952
DIXTOU	3.835	167.159	143.157	84.767
BPHBAC01	3.835	0	145.011	91.963
NIQZAP	3.836	103.569	139.583	90.649
VEXFUZ02	3.839	-178.55	139.989	84.537
XOSDUF	3.841	-179.98	93.489	153.885
WIYMEX	3.843	0	136.901	97.373
WIYMUN01	3.847	-39.422	125.454	92.694
WIYMEX	3.85	0	136.038	104.452
MIDYOO	3.851	180	109.593	120.498
BEWYAE	3.851	180	61.104	88.704
PHBORA	3.852	62.462	135.035	97.979
ITIRAE	3.853	-176.476	132.219	153.509
BEWYAE01	3.86	180	60	88.52
WIYMUN01	3.863	38.985	126.023	93.946
XECHUJ	3.866	-180	96.627	156.353
TUNGAK	3.88	0.02	144.609	92.564

ITIRAE	3.89	0	145.323	91.176
VEFCUF	3.891	0	145.485	92.91
PEYLOV	3.891	177.666	134.222	83.048
TUNGAK	3.894	-179.98	82.692	84.399
BEWYAE	3.897	-180	60.628	89.49
OCAJUY	3.898	-177.913	148.694	86.231
UMUHOZ	3.902	0.02	138.579	100.232
UMUHOZ	3.905	0.02	138.639	100.355
BEWYAE01	3.908	-180	59.778	89.22
AFOLUC	3.913	-3.316	75.945	127.111
HUXXII	3.914	0.02	140.027	98.795
ZAPDAV	3.916	0	143.571	95.084
WIYMUN	3.916	-38.888	117.838	113.178
WIYMUN	3.924	39.412	117.708	111.864
WENZUL	3.929	0	139.601	97.44
OLIDOC	3.933	-179.98	103.053	97.848
NUPQIZ	3.937	96.595	122.344	91.323
PAYYAP	3.94	-87.419	148.604	85.825
XETLOY	3.943	41.689	71.753	98.791
WIYPEA	3.949	0	128.46	104.762
EFIDIH	3.951	0	141.527	95.575
PAXTEO	3.956	180	58.355	84.77
KEGNAM	3.958	-179.98	94.262	153.845
WAJXEL	3.959	-86.529	115.525	95.751
WIYMUN01	3.96	-39.422	118.566	111.93
PHBORA01	3.96	2.37	75.578	121.083
HIRGEV	3.963	0	137.634	100.21
HIRGEV	3.964	0	137.923	100.435
GISVIO	3.964	-179.98	54.426	87.944
WIYMUN01	3.969	38.985	119.401	112.75
DISSAA	3.969	-177.47	143.116	127.442
XAVHUZ	3.974	0.249	119.043	107.474
WIYMOH01	3.976	0	128.587	105.442
PHBORA	3.983	-2.168	74.698	122.337
WIYMOH	3.989	0	128.459	105.385
ITIQUX	3.991	0	151.554	89.992
MOKKON	4.004	-180	95.554	120.473
HUXXII	4.007	0	132.638	101.88
ZILBEB	4.013	0	140.258	99.087
WENZUL	4.014	0	131.703	102.672
EFIDON	4.022	179.98	56.066	84.048
ZILBEB	4.024	0.648	117.507	82.167
AVOTIO	4.026	0	63.663	81.476
NIQZET01	4.027	180	92.356	122.338
IYAXAH	4.031	0	128.281	106.933
SOWJIY	4.033	-180	115.446	130.121
GENTOJ	4.058	-180	55.661	85.908

BPHBAC01	4.065	0	126.933	108.618
OCAJUY	4.066	-177.913	133.792	90.242
PAXSUD	4.069	179.98	103.449	92.066
ZILBEB	4.08	0	134.536	101.097
TUNGAK	4.086	0.02	128.102	107.255
ZAPDAV	4.096	0	129.499	105.057
ROKJUX	4.099	17.983	88.124	71.914
EFIDIH	4.101	0	129.722	104.191
GISVIO	4.102	0	125.679	109.688
FAKTER	4.102	-3.443	60.872	100.105
VEFCUF	4.103	0	128.229	106.889
NIQZET	4.119	0	61.423	120.256
NIQYUI	4.123	-180	102.555	86.199
ROGKUU	4.133	0	114.294	115.709
NIQZET01	4.137	0	60.814	121.756
FAKTER	4.138	-3.443	59.467	103.2
AFOLUC	4.138	170.967	99.457	129.856
XETLOY	4.141	-41.449	69.819	117.414
AFOLUC	4.142	-3.316	66.792	91.362
ITIRAE	4.144	0	125.523	108.592
IGERAO	4.148	0	86.118	111.638
PAXTIS	4.153	0	72.205	78.95
PHBORA	4.156	-2.168	67.799	92.072
FAKTER	4.162	-2.642	62.303	104.073
FETZUA	4.168	0	61.849	120.138
NIQZAP	4.171	0	61.106	121.578
FAKTER	4.171	-2.642	61.964	99.445
PAYYAP	4.172	87.419	129.642	93.949
NIQZAP	4.174	180	93.042	122.402
ETOLAA	4.176	0	61.948	120.621
FETZUA	4.182	180	92.284	122.954
KEGNIU	4.189	180	152.563	124.839
PHBORA01	4.19	2.37	66.495	92.805
FOVMOT	4.19	0.02	140.877	92.948
XAVHUZ	4.193	-0.02	121.63	90.906
CITNOJ	4.197	-106.806	56.463	55.568
FETZUA	4.201	0	60.903	119.631
FETZUA	4.201	180	92.093	122.166
WENZUL	4.206	180	60.852	81.023
PAXTIS	4.211	0	69.868	123.565
MOKKON	4.212	0	61.644	120.613
LIXLAG	4.216	180	110.996	114.223
NIQZET	4.221	180	93.465	125.562
ETOLAA	4.227	180	96.943	118.31
MOKKON	4.241	-180	85.763	120.805
ETOLAA	4.246	0	58.917	118.515
ROKJUX	4.254	20.121	86.136	70.992

GISVIO	4.255	0	116.666	48.962
MOKKON	4.262	0	59.396	118.041
XOSDOZ	4.269	0	132.176	99.065
ITIQUX	4.272	0	128.284	108.782
DOBKUA	4.274	0	135.792	77.968
REHDOY	4.277	180	123.209	127.715
PHBORA	4.297	173.448	100.691	129.998
BEWYAE01	4.302	0.02	109.847	51.038
VEFCIT	4.305	-180	119.71	80.626
PHBORA01	4.307	-173.514	100.609	130.203
ZILBEB	4.311	0.644	104.388	81.601
BEWYAE01	4.315	-0.02	109.373	50.927
XOSDOZ	4.324	0	127.548	99.732
BEWYAE	4.324	0	109.223	51.373
WAJXEL	4.334	180	90.308	79.729
SOWJIY	4.339	180	108.962	76.022
TUNGAK	4.342	-179.98	64.561	85.846
BEWYAE	4.344	0	108.384	51.248
ITIGEY	4.347	179.98	98.777	87.967
BAJTEM01	4.353	-179.98	64.318	54.098
AFOLUC	4.356	170.967	89.643	124.825
BAJTEM02	4.361	-180	64.773	55.309
BAJTEM	4.365	-180	65.011	55.563
MUCJUQ	4.374	-179.98	115.128	135.525
VEFCOZ	4.381	179.98	122.463	81.757
TASCEW	4.388	180	66.508	50.016
FOVMOT	4.388	0.02	126.072	105.536
ZILBEB	4.393	-179.273	127.621	119.883
DIXVAI	4.394	0	59.068	88.799
LABCUM	4.411	180	118.453	82.767
AVOTIO	4.415	0	47.415	115.794
MORTET	4.425	0	99.195	50.197
ZILBEB	4.428	-0.644	99.037	116.378
CITNOJ	4.428	106.806	46.776	113.344
PHBORA	4.437	-2.168	56.455	119.883
FUBKOD	4.437	-179.98	65	55.595
NIQYUI	4.438	-108.552	155.615	96.776
PHBORA01	4.453	2.37	55.813	118.94
BAGFAS	4.474	-180	172.027	111.39
WAPDIB	4.483	0	58.284	90.092
XETLOY	4.492	-41.449	55.641	64.263
AFOLUC	4.494	-3.316	52.564	125.066
WAJXEL	4.497	-103.469	169.94	83.254
WIYNAU	4.499	-49.671	145.41	40.381
KECJIM	4.501	-176.806	159.504	113.323
PAXSUD	4.514	-112.724	156.247	101.427
LIXLAG	4.521	180	96.922	83.054

MIDZAB	4.522	-148.517	78.598	56.52
PHBORA	4.525	173.448	90.483	126.626
AFOLUC	4.525	-72.351	165.682	79.2
ETOLAA	4.529	180	84.43	117.693
PHBORA01	4.535	-173.514	90.645	126.53
AFOLUC	4.535	-100.929	168.623	107.888
XETLOY	4.566	41.689	45.624	130.184
KEGNEQ	4.566	-179.363	141.894	83.85
KECJIM	4.578	-176.806	150.936	114.748
KUGBUK	4.58	21.729	99.712	82.603
GISVIO	4.587	126.906	110.799	42.917
KEGNIU	4.597	180	113.065	73.004
ZILBEB	4.605	-179.273	115.185	117.234
ROGKUU	4.607	-180	151.068	119.96
PHBORA01	4.607	77.661	165.477	81.148
SOWJAQ	4.613	-180	54.672	90.164
KUGBUK	4.613	-157.028	105.815	113.667
AVOTIO	4.616	-141.249	125.351	66.825
BAJTEM02	4.619	-180	54.12	55.441
BAGFAS	4.621	176.944	111.599	47.271
BAJTEM01	4.621	-179.98	53.26	54.355
XETLOY	4.624	-41.449	49.914	94.999
KEGNEQ	4.626	179.363	135.996	82.988
DIXVAI	4.63	0	48.733	108.05
FETDEO	4.631	178.498	134.01	74.406
BAJTEM	4.633	-180	53.823	55.611
PEPNUU	4.634	0	178.719	68.273
OLIDOC	4.64	0	108.984	62.222
MIDYOO	4.641	180	73.207	114.9
XOSFAN	4.647	180	92.887	60.373
REHDOY	4.65	0	54.983	89.259
OLIDOC	4.65	114.247	157.196	105.461
KECJIM	4.65	-178.633	100.508	117.81
PHBORA01	4.653	96.378	167.543	104.339
NUPQIZ	4.657	106.391	83.386	109.737
PAXTIS	4.662	0	51.078	117.997
BEWYAE	4.664	176.497	68.072	46.862
KOJQAC	4.668	-180	74.176	43.289
PHBORA	4.674	-76.334	165.966	81.281
MUCJUQ	4.678	0	53.464	93.226
KUGBUK	4.68	-21.729	95.132	118.621
FETDEO	4.681	178.498	126.38	73.962
XUVBAR	4.684	-80.993	167.591	89.905
BEWYAE01	4.685	176.363	67.937	46.311
REHDOY	4.692	0	52.947	94.916
PAYYAP	4.693	0	103.934	48.51
DISSAA	4.697	-177.47	100.653	119.312

FUBKOD	4.702	-179.98	54.099	55.257
MORTET	4.709	0	86.387	52.91
FETDIS	4.711	0.02	143.525	85.195
PHBORA	4.714	-97.219	167.082	105.482
EFIDON	4.716	0.02	106.087	46.531
DOBKUA	4.717	0	110.911	118.849
ZILBEB	4.725	-0.648	85.236	115.691
WAPDIB	4.743	0	46.69	106.552
REHDOY	4.747	-180	112.231	133.825
XAVHUZ	4.748	0.249	83.003	95.11
VEFCUF	4.76	-180	61.65	55.021
BEWYAE	4.76	176.497	64.108	45.544
FECSEM	4.766	180	62.385	52.872
IYAXAH	4.774	180	128.798	81.713
REHDOY	4.775	0	49.259	101.483
QUSPAW	4.78	0	106.75	44.142
BEWYAE01	4.78	176.362	64.079	44.938
IGERAO	4.788	-180	118.492	122.317
NUPQIZ	4.791	0	107.397	45.783
CITNOJ	4.793	136.874	138.317	59.561
KECJIM	4.8	-178.633	93.817	120.437
TASCEW	4.802	180	48.913	55.124
ITIRAE	4.809	-180	65.439	53.024
WIYMUN	4.811	135.672	132.598	122.548
SOWHUI	4.816	180	112.175	135.631
MUCJUQ	4.817	0	47.558	102.902
IGERAO	4.818	0	59.201	89.235
NUPQIZ	4.84	0	104.691	61.019
GENTOJ	4.848	-0.02	148.559	56.611
WIYMOH	4.854	180	67.305	61.501
WIYMUN	4.855	-135.672	130.515	121.688
FECSEM	4.876	180	57.62	55.658
ITIRAE	4.877	-176.476	81.57	125.78
VEFCUF	4.884	-180	56.641	54.875
DOBKUA	4.885	-178.262	95.096	40.911
WADQIC	4.887	150.382	118.156	102.732
XUVBEV	4.89	-90.201	169.137	93.271
VEFCUF	4.892	178.607	79.929	127.138
GISVIO	4.896	-180	165.28	124.498
REHDOY	4.897	0	43.174	107.001
BEWYAE	4.899	0	83.816	54.937
WIYMOH01	4.909	-180	67.134	61.3
WIYMUN01	4.915	-135.56	133.919	122.326
BEWYAE01	4.921	-0.02	82.828	54.9
BEWYAE	4.923	0	82.849	55.801
FETZUA	4.926	-73.904	171.684	80.72
MOYLES	4.927	180	102.883	117.422

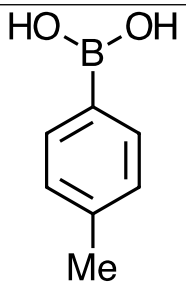
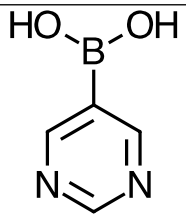
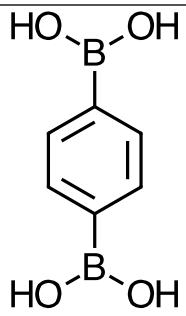
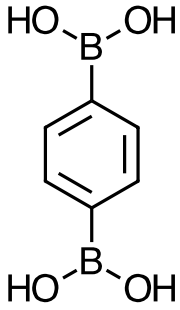
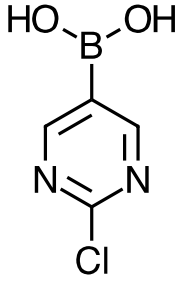
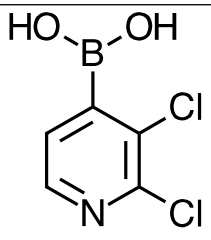
WIYMUN01	4.929	135.56	132.978	121.681
FETZUA	4.931	75.356	171.465	80.806
DIXTIO	4.935	-178.888	128.702	67.593
NIQZET	4.937	95.84	170.76	105.949
BEWYAE01	4.94	0.02	82.085	55.645
NIQZET01	4.944	-75.063	170.123	80.56
NIQZET01	4.948	-100.067	169.44	107.492
BAJTIQ	4.949	-144.28	141.634	66.919
OLIDOC	4.95	-179.98	60.868	97.594
SOWJIY	4.953	-180	74.726	119.349
DIXTIO	4.955	178.888	127.368	67.925
ZAPDAV	4.974	-180	172.849	128.245
NIQZAP	4.976	-73.487	169.762	81.146
NIQZAP	4.977	101.322	171.037	106.909
FETZUA	4.978	101.609	169.987	106.46
PAXSUD	4.981	0	113.579	59.136
BPHBAC01	4.983	180	62.358	55.896
XAVHUZ	4.984	0.249	73.555	94.593
KECJOS	4.984	178.299	113.893	54.887
SOWHUI	4.986	-39.073	165.451	66.605
NIQZET	4.987	77.669	169.963	84.203
IYAXAH	4.992	0.02	95.802	54.22
IYAXAH	4.996	-180	60.859	53.556
HUXXII	4.998	-180	162.869	134.695
FETZUA	4.998	100.222	168.688	106.372
WIYMOH	5	180	61.332	60.588
OLEXAF	5	180	66.129	43.795
IYAXAH	5	0.02	95.606	53.36
BPHBAC01	5.008	180	166.701	124.88
KECJIM	5.01	-178.633	85.27	119.031
FETDIS	5.013	0	122.654	109.724
WIYPEA	5.014	-179.98	67.989	60.161
QUSPAW	5.023	94.298	163.07	94.805
BPHBAC01	5.023	180	60.59	57.121
PAYYAP	5.029	0	89.2	53.702
WIYMOH01	5.03	-180	62.227	60.236
DISSAA	5.038	-177.47	85.839	113.999
ROGKUU	5.039	180	72.892	49.895
KEGNIU	5.04	44.777	130.835	134.02
WIYPEA	5.043	-180	167.114	128.777
QUSPAW	5.044	0	145.172	58.515
CAKZAR	5.047	180	125.392	64.498
IYAXAH	5.049	180	164.113	125.946
USAKEF	5.05	180	130.412	69.016
MIDYOO	5.055	180	103.976	54.182
WIYMOH01	5.056	-180	167.448	127.804
WIYMOH	5.061	180	167.045	128.08

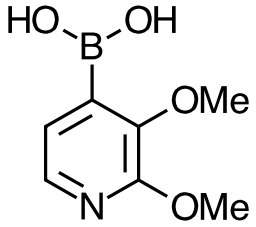
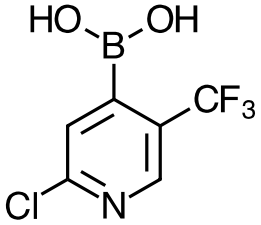
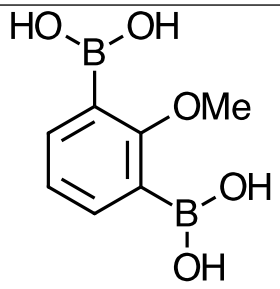
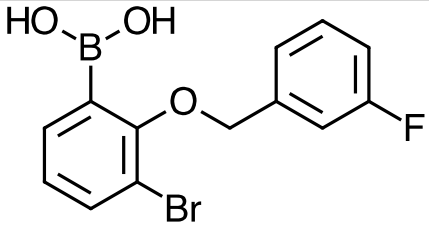
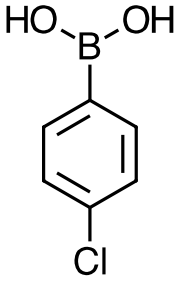
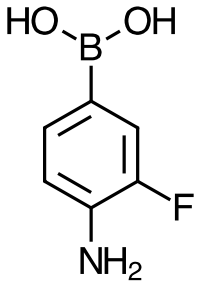
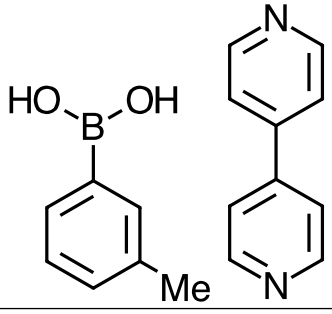
USAKEF	5.067	-179.45	129.586	65.831
OLEXOT	5.068	-180	64.733	42.834
IGERAO	5.068	0	47.625	106.737
KECJIM	5.075	-178.633	82.51	115.983
IYAXAH	5.078	-180	57.521	53.318
TUNNEW	5.079	-180	62.838	40.716
FETDEO	5.079	-178.518	125.465	63.85
FETDEO	5.081	-178.518	125.217	63.284
BEWYAE	5.083	176.497	50.246	51.963
KECJOS	5.086	177.856	113.805	53.277
ROGKUU	5.09	180	122.589	64.77
TUNGAK	5.091	0.02	100.627	51.726
OCAJUY	5.101	4.24	156.043	55.037
WIYMEX	5.102	178.967	170.629	135.136
ITIRAE	5.103	-180	53.201	54.314
USAKEF	5.109	-179.45	127.546	67.168
MIDZAB	5.111	-178.03	124.111	69.981
CAKZAR	5.118	-179.98	118.245	60.31
WIYMEX	5.118	178.967	167.4	128.289
EFIDON	5.123	0.02	87.888	51.835
BUDREY	5.123	-180	77.534	54.748
OCAJUY	5.125	-180	60.414	45.861
KUQYEB	5.125	180	112.861	115.634
BEWYAE01	5.125	176.362	49.52	51.901
AFOLUC	5.126	100.93	118.496	137.71
QUSPAW	5.132	0	90.987	50.204
GISVIO	5.142	0	77.507	56.155
DIXTOU	5.142	-173.052	95.405	83.253
DIXTUA	5.148	6.987	114.959	91.605
WENZUL	5.153	0	109.547	49.588
UMUHOZ	5.159	180	168.277	131.783
UMUHOZ	5.162	180	168.833	131.983
WAJXEL	5.164	180	56.118	80.445
TUNGAK	5.168	-180	167.094	124.767
FUWHIP	5.168	-179.339	156.24	63.525
MUCJUQ	5.182	-179.98	78.942	125.563
VEFCUF	5.188	178.608	67.92	138.777
BEWYAE	5.189	176.497	45.231	51.587
WENZUL	5.192	180	167.956	129.18
FUWHIP	5.192	179.98	153.744	63.73
XUVBAR	5.197	80.993	119.793	137.827
PAXSUD	5.197	179.98	56.32	92.938
WIYPEA	5.198	-179.98	60.373	59.306
BPHBAC01	5.202	-180	113.029	65.259
HIRGEV	5.209	179.98	169.441	131.693
EFIDIH	5.209	-180	165.269	126.7
HIRGEV	5.21	179.98	167.968	131.175

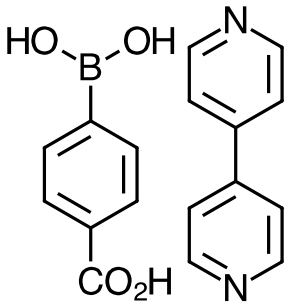
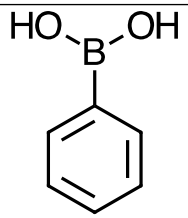
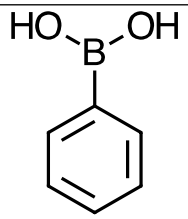
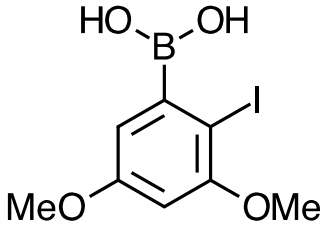
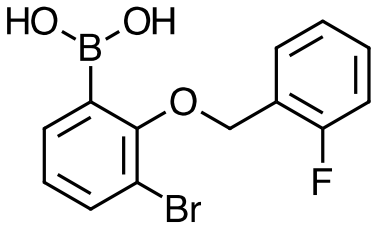
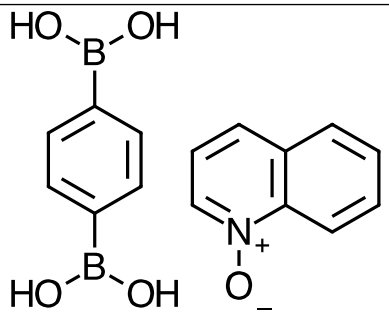
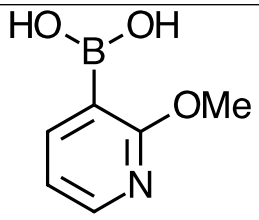
WENZUL	5.214	180	137.032	85.304
ITIRAE	5.215	-176.476	67.853	140.542
NIQYUI	5.216	0	116.5	55.165
WIYPEA	5.222	180	158.982	135.879
KUGBUK	5.225	21.729	72.655	76.388
BEWYAE01	5.227	176.363	44.632	51.405
PHBORA01	5.234	-96.378	117.843	138.417
DEWYAG	5.234	180	118.506	64.778
MOYLIW	5.236	180	116.36	113.969
ZILBEB	5.237	-180	171.538	130.059
DIXTOU	5.248	179.98	89.008	66.336
WIYMOH01	5.251	-180	159.163	136.303
TUNGAK	5.251	0.02	93.372	53.979
KUQYEB	5.251	-180	118.724	112.406
WIYMUN	5.252	120.617	152.318	138.573
PHBORA	5.26	97.219	119.962	137.72
PHBORA01	5.266	-74.711	162.093	90.747
DIXTUA	5.268	-178.528	45.981	80.815
NIQZET01	5.269	100.067	134.845	134.426
GISVIO	5.269	0	72.319	142.235
WIYMUN	5.273	-120.617	150.769	135.846
XAVHUZ	5.276	-0.02	73.191	100.41
NIQZET	5.276	-95.84	133.378	134.315
GISVIO	5.279	180	111.528	62.624
WIYMOH	5.28	179.98	158.917	136.276
WENZUL	5.282	-180	156.446	133.738
PHBORA	5.282	73.415	163.422	90.294
ZILBEB	5.283	0.644	63.408	84.405
EFIDIH	5.283	180	157.959	134.988
REHDOY	5.285	180	122.325	133.322
MORTET	5.285	0	62.779	139.662
BAGFAS	5.286	176.944	81.925	58.255
NUPQIZ	5.29	0	85.582	50.469
GISVIO	5.29	180	61.621	53.518
VEFCUF	5.294	180	115.795	64.583
WIYMUN01	5.295	-120.592	153.629	138.122
OCAJUY	5.296	4.059	152.07	59.975
CITNOJ	5.297	0	172.951	49.557
PHBORA01	5.301	-95.818	164.979	107.831
ZILBEB	5.304	-179.98	164.325	131.602
BEWYAE01	5.31	0	67.136	141.094
WIYMUN01	5.311	120.592	151.96	136.326
NIQYUI	5.312	-180	52.557	88.27
BEWYAE	5.314	-0.02	66.812	140.618
GISVIO	5.315	180	60.473	54.723
SOWJIY	5.317	0	173.128	57.23
FETZUA	5.32	-100.222	133.29	134.951

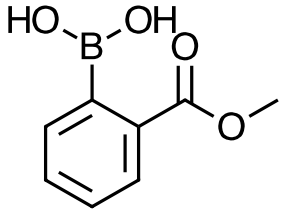
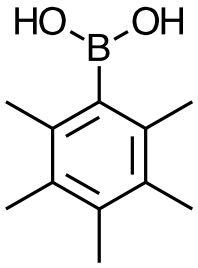
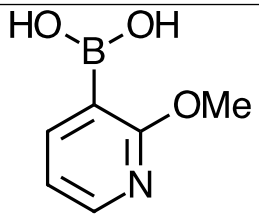
NIQZAP	5.321	101.322	133.556	134.669
IYAXAH	5.321	-180	160.692	137.308
GISVIO	5.321	126.906	79.071	64.067
FETZUA	5.321	101.609	133.464	134.863
PHBORA	5.324	96.843	165.574	108.286
TUNGAK	5.326	179.98	157.44	138.443
BEWYAE01	5.33	0	66.356	141.017
FOVMOT	5.331	180	158.354	123.821
BEWYAE	5.336	0	65.88	140.536
GISVIO	5.337	144.894	106.4	66.032
WEJCIY	5.342	-119.371	160.578	77.134
AFOLUC	5.342	72.351	104.632	140.765
OCAJUY	5.348	-180	50.839	46.688
SOWHUI	5.352	180	87.354	131.323
WADQIC	5.354	150.382	95.892	102.191
AFOLUC	5.355	68.066	158.78	91.018
ITIGEY	5.362	179.98	56.479	88.311
WIYNAU	5.366	51.643	148.63	58.385
KECJOS	5.366	177.856	100.28	57.479
RONLIP	5.372	0	137.785	80.543
AFOLUC	5.372	99.788	164.378	112.048
ZAPDAV	5.374	180	59.11	48.865
OLIDOC	5.379	0	77.144	67.648
PHBORA01	5.381	-77.661	107.715	140.635
XUVBEV	5.385	90.201	119.996	138.979
WADQIC	5.387	150.382	94.451	152.581
DIXTOU	5.388	173.052	85.201	94.665
XOSDOZ	5.396	179.98	149.647	130.177
BPHBAC01	5.397	-180	159.928	138.309
NUPQIZ	5.398	180	119.092	61.654
LIXLAG	5.398	0	170.415	50.945
WIYMOH	5.401	-179.98	117.839	67.822
MIDZAB	5.402	-148.517	40.486	49.329
OLEXAF	5.404	180	48.066	49.234
XAVHUZ	5.405	-0.02	68.059	100.416
WIYMOH01	5.409	180	117.143	67.403
USAKIJ	5.41	-65.119	93.305	59.591
REHDOY	5.412	-180	82.674	126.015
PAYYAP	5.412	107.181	137.024	50.363
IYAXAH	5.412	-180	112.022	62.165
NIQZET01	5.413	60.996	141.324	121.331
PHBORA	5.416	76.334	109.057	140.417
HUXXII	5.42	180	165.365	127.359
TUNGAK	5.424	180	128.503	80.809
MIDZAB	5.427	16.791	151.349	104.036
OLIDOC	5.43	114.247	105.053	138.292
ZAPDAV	5.432	180	56.535	51.135

OLEXOT	5.437	-180	49.149	48.687
KUGBUK	5.438	-157.028	70.844	102.874
FECSEM	5.44	-126.362	146.004	61.479
PAXSUD	5.441	-112.724	98.111	138.951
VEFCIT	5.442	0	140.476	50.539
LEYNAF	5.446	-180	66.399	60.073
REHDOY	5.447	180	70.638	120.081
TUNNEW	5.448	-180	46.787	46.918
NUPQIZ	5.453	0	78.897	63.933
SOWJAQ	5.454	0	173.854	58.762
AFOLUC	5.455	-69.179	149.987	121.265
NIQYUI	5.456	-108.552	93.685	139.605
ITIRAE	5.458	180	117.927	64.914
AFOLUC	5.463	-99.788	150.808	132.109
PHBORA01	5.465	95.818	144.888	132.843
OLIDOC	5.467	0	73.573	130.945
KOJQAC	5.467	-180	38.587	53.185
KUQYEB	5.472	0	177.643	60.565
KUQYEB	5.478	0	174.334	63.796
MOYLIW	5.479	0	176.101	59.947
OLIDOC	5.481	-110.119	153.707	101.388
ITIGEY	5.482	90.334	132.976	57.174
WIYMUN	5.483	-38.888	49.435	85.009
WIYMUN	5.486	39.412	49.719	83.446
SOWJAQ	5.492	-179.98	138.519	128.879
PHBORA	5.495	-96.842	144.108	133.003
LABCUM	5.496	0.02	127.87	52.909
GENTOJ	5.5	-180	170.04	123.391
ZAPDAV	5.502	180	157.428	133.627
WADQIC	5.505	180	172.543	119.434
MORTET	5.509	0	52.444	137.094
FECSEM	5.51	-71.594	134.399	53.956
ZILBEB	5.514	0.648	52.34	83.093
BAJTIQ	5.514	-144.28	107.952	98.089
SOWJIY	5.517	-180	119.318	55.407

Yields of boronic acids with crystal structures consistent with proposed mechanism compared with other yields from the same reports.				
CCDC code	Boronic acid	% Yield of boronic acid shown	Average % yield of other boronic acids in same paper (original values in parentheses)	Ref
AFOLUC		71		6
AVOTIO		45	61 (61)	7
BEWYAE				8
BEWYAE01				N/A
CITNOJ		85	46 (46)	9
DIXTUA		56	79 (82, 82, 73)	10

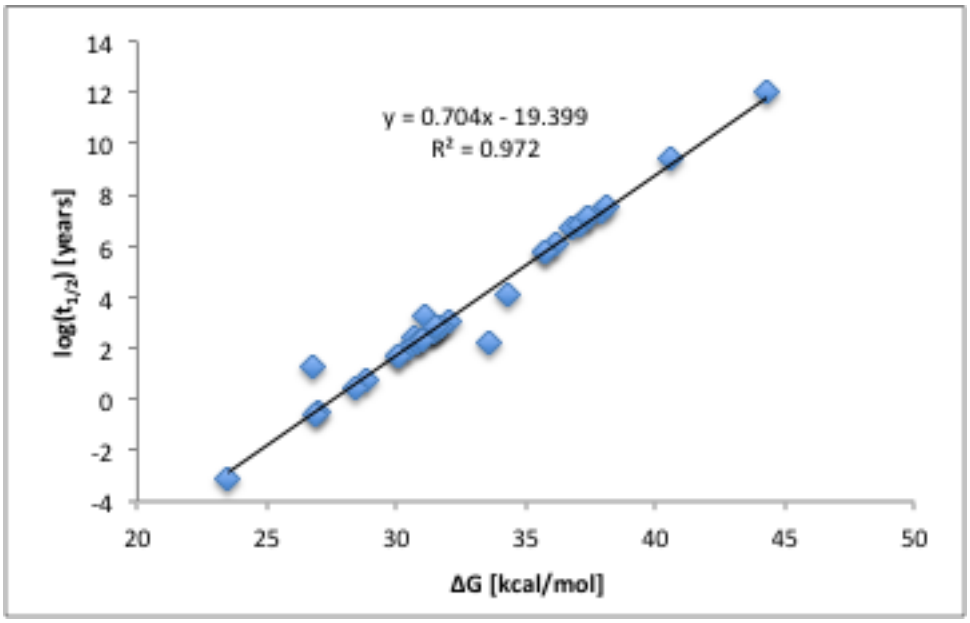
DIXVAI		12	79 (82, 82, 73)	10
FUBLIY		42	71 (95, 94, 25)	11
GISVIO		43		12
MUCJUQ				13
NIQYUI				14
OLIDOC		47		15
PAXSUD		84	83 (83)	16

PAXTIS		59	83 (83)	16
PHBORA				17
PHBORA01				18
QACYEA		75	65 (82, 78, 45, 51, 43, 88, 75, 52, 51, 95, 95, 61, 62, 59, 57, 46)	19
REHDOY				20
SOWJAQ		26	43 (46, 2, 82)	21
WAPDIB		48		22

WEJCIY				23
WIYNAU		87	70 (66, 81, 64, 69)	24
XETLOY				25

Aqueous free energy of activation compared with $t_{1/2}$

Data are taken from the review of Wolfenden. [26]



References

1. Knapp, D. M., Gillis, E. P. & Burke, M. D. A General Solution for Unstable Boronic Acids: Slow-Release Cross-Coupling from Air-Stable MIDA Boronates. *J. Am. Chem. Soc.* **131**, 6961-6963 (2009).

2. Plumley, J. A. & Evanseck, J. D. Covalent and ionic nature of the dative bond and account of accurate ammonia borane binding enthalpies. *The Journal of Physical Chemistry A* **111**, 13472-13483 (2007).

3. Plumley, J. A. & Evanseck, J. D. Hybrid Meta-Generalized Gradient Functional Modeling of Boron− Nitrogen Coordinate Covalent Bonds. *Journal of Chemical Theory and Computation* **4**, 1249-1253 (2008).

4. Plumley, J. A. & Evanseck, J. D. Periodic Trends and Index of Boron Lewis Acidity. *The Journal of Physical Chemistry A* **113**, 5985-5992 (2009).

5. Lee, J. M., Helquist, P. & Wiest, O. Diastereoselectivity in Lewis-Acid-Catalyzed Mukaiyama Aldol Reactions: A DFT Study. *J. Am. Chem. Soc.* **134**, 14973-14981 (2012).

6. Zheng, C., Spielvogel, B., Smith, R. & Hosmane, N. Crystal structure of 4-methylphenylboronic acid, C7H9BO2. *Zeitschrift für Kristallographie-New Crystal Structures* **216**, 363-364 (2001).

7. Saygili, N., Batsanov, A. S. & Bryce, M. R. 5-Pyrimidylboronic acid and 2-methoxy-5-pyrimidylboronic acid: new heteroarylpyrimidine derivatives via Suzuki cross-coupling reactions. *Organic & biomolecular chemistry* **2**, 852-857 (2004).

8. Rodríguez-Cuamatzi, P., Vargas-Díaz, G. & Höpfl, H. Modification of 2D water that contains hexameric units in chair and boat conformations—a contribution to the structural elucidation of bulk water. *Angewandte Chemie* **116**, 3103-3106 (2004).

9. Clapham, K. M. *et al*. New Pyrimidylboronic Acids and Functionalized Heteroarylpyrimidines by Suzuki Cross-Coupling Reactions. *European Journal of Organic Chemistry* **2007**, 5712-5716 (2007).

10. Smith, A. E., Clapham, K. M., Batsanov, A. S., Bryce, M. R. & Tarbit, B. (Dimethoxy-and Dihalopyridyl) boronic Acids and Highly Functionalized Heteroarylpyridines by Suzuki Cross-Coupling Reactions. *European Journal of Organic Chemistry* **2008**, 1458-1463 (2008).

11. Clapham, K. M., Batsanov, A. S., Bryce, M. R. & Tarbit, B. Trifluoromethyl-substituted pyridyl-and pyrazolylboronic acids and esters: synthesis and Suzuki–Miyaura cross-coupling reactions. *Organic & biomolecular chemistry* **7**, 2155-2161 (2009).

12. Dabrowski, M., Lulinski, S. & Serwatowski, J. (2-Methoxy-1, 3-phenylene) diboronic acid. *Acta Crystallographica Section E: Structure Reports Online* **64**, o414-o415 (2008).

13. Kacprzak, K., Klis, T. & Serwatowski, J. [3-Bromo-2-(3-fluorobenzyloxy) phenyl] boronic acid. *Acta Crystallographica Section E: Structure Reports Online* **65**, o2250-o2250 (2009).

14. Shimpi, M. R., SeethaLekshmi, N. & Pedireddi, V. R. Supramolecular architecture in some 4-halophenylboronic acids. *Crystal Growth & Design* **7**, 1958-1963 (2007).

15. Das, S., Alexeev, V. L., Sharma, A. C., Geib, S. J. & Asher, S. A. Synthesis and crystal structure of 4-amino-3-fluorophenylboronic acid. *Tetrahedron Lett.* **44**, 7719-7722 (2003).

16. Aakeröy, C. B., Desper, J., Levin, B. & Salmon, D. J. Boronic Acids As Versatile Supramolecular Reagents. *ACA Trans.* **39**, 123-129 (2004).

17. Rettig, S. J. & Trotter, J. Crystal and molecular structure of phenylboronic acid, C6H5B(OH)2. *Can. J. Chem.* **55**, 3071-3075 (1977).

18. Cyrański, M. K., Jezierska, A., Klimentowska, P., Panek, J. J. & Sporzyński, A. Impact of intermolecular hydrogen bond on structural properties of phenylboronic acid: quantum chemical and X-ray study. *Journal of Physical Organic Chemistry* **21**, 472-482 (2008).

19. Al-Zoubi, R. M. & Hall, D. G. Mild silver (I)-mediated regioselective iodination and bromination of arylboronic acids. *Org. Lett.* **12**, 2480-2483 (2010).

20. Serwatowski, J., Klis, T. & Kacprzak, K. 3-Bromo-2-(2-fluorobenzyloxy) phenylboronic acid. *Acta Crystallographica Section E: Structure Reports Online* **62**, o1308-o1309 (2006).

21. Sarma, R. & Baruah, J. B. B··· π-aromatic and C–H··· B interactions in co-crystals of aromatic amine< i> N-oxides with< i> p-phenylenediboronic acid. *J. Mol. Struct.* **920**, 350-354 (2009).

22. Thompson, A. E. *et al*. 2-Ethoxy-3-pyridylboronic acid: a versatile reagent for the synthesis of highly-functionalised 3-aryl/heteroaryl-pyridines via Suzuki cross-coupling reactions. *Tetrahedron* **61**, 5131-5135 (2005).

23. Lulinski, S. & Serwatowski, J. 2-(Methoxycarbonyl) phenylboronic acid. *Acta Crystallographica Section C: Crystal Structure Communications* **62**, o301-o303 (2006).

24. Filthaus, M., Oppel, I. M. & Bettinger, H. F. Supramolecular structures and spontaneous resolution: the case of ortho-substituted phenylboronic acids. *Organic & biomolecular chemistry* **6**, 1201-1207 (2008).

25. Dabrowski, M., Lulinski, S., Serwatowski, J. & Szczerbinska, M. (2-Methoxy-3-pyridyl) boronic acid. *Acta Crystallographica Section C: Crystal Structure Communications* **62**, o702-o704 (2006).

26. Wolfenden, R. Benchmark reaction rates, the stability of biological molecules in water, and the evolution of catalytic power in enzymes. *Annu. Rev. Biochem.* **80**, 645-667 (2011).