## **Supplemental Material**

# Electrospray ionisation mass spectrometric studies of *N*-substituted 10-(aminosulfonyl)bornyl acrylate derivatives

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### I Mass Spectrometry (MS) Methodology

#### Direct injection MS analysis

1 mg of each sample was dissolved in 1 ml methanol (Romil), followed by a further 10-fold dilution into methanol. 2  $\mu$ L of sample was injected into a stream of methanol flowing at 0.3 ml/min, using a Waters ultra pressure liquid chromatograph (UPLC) (Waters, Midford, USA) which conveyed the sample to a Waters Synapt G2 quadrupole time-of-flight (QTOF) mass spectrometer used for high-resolution accurate mass analysis.

Data was acquired in resolution mode, the mass spectrometer was optimized for best sensitivity, a cone voltage of 15 V, desolvation gas was nitrogen at 650 L/hr and desolvation temperature 275 <sup>o</sup>C. The instrument was operated with an electrospray ionization probe in the positive mode. Sodium formate was used for calibration and leucine encephalin was infused in the background as lock mass for accurate mass determinations.

### LC-MS/MS analysis

The MS/MS experiments were conducted with liquid chromatographic separation using a Waters BEH C18, 2.1 x 100 mm, 1.7  $\mu$ m particle size column kept at 50 °C and the same instrument as above, A generic gradient starting at 100% mobile phase A (0.1% formic acid in MilliQ water) to 100% mobile phase B (acetonitrile with 0.1% formic acid) over 12 minutes using a flow rate of 0.4 mL/min.

The MS/MS experiments were conducted by collision-induced dissociation of selected parent ions by accelerating these ions to high kinetic energy using an electrical potential followed by collision with argon gas molecules in the Trap collision cell at a collision energy of 30 V.

### II HRMS ESI MS Spectra

Elemental composition fit of 4a-NH<sub>4</sub><sup>+</sup> (m/z 395 ion) with its HRMS ESI Mass Spectrum :



Elemental composition fit of  $4a-H^+$  (m/z 378 ion) with its HRMS ESI Mass Spectrum:

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378.1743	378.1746	-0.3	-0.8	3.5	C13 H28 N7 O2 52	31.7	3.879	2.07	13	28	7	2	2	2	P
	378.1737 378.1752 378.1752 378.1733 378.1724 378.1764 378.1719 378.1771	0.6 -0.9 1.0 1.9 -2.1 2.4 -2.8	1.6 -2.4 2.6 5.0 -5.6 6.3 -7.4	4.5 12.5 -1.5 -0.5 3.5 17.5 -0.5	C12 H24 N7 07 C21 H24 N5 5 C12 H32 N3 06 52 C11 H28 N3 011 C16 H28 N 09 C24 H20 N5 C9 H28 N7 07 5	31.5 31.8 31.6 31.3 31.6 31.9 31.4	3.684 4.066 3.812 3.562 3.806 4.147 3.624	2.51 1.71 2.21 2.84 2.22 1.58 2.67	12 21 12 11 16 24 9	24 24 32 28 28 20 28	7 5 3 1 5 7	7 6 11 9 7	1 2 1	1 2 2 1	>
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### Elemental composition fit of 4a-Na<sup>+</sup> (m/z 400 ion) with the HRMS ESI Mass Spectrum

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	400.1559 400.1552 400.1549	-0.2 0.5 0.8	-0.5 1.2 2.0	0.5 -1.5 15.5	C14 H28 N O9 Na2 C12 H31 N3 O6 52 Na C25 H22 N O4	30.9 27.2 31.2	19.217 15.498 19.475	0.00 0.00 0.00	14 12 25	28 31 22	1 3 1	9 6 4	2	2 1				
	400.1567 400.1568	-1.0	-2.5 -2.7	2.5 -0.5	C13 H26 N3 O11 C15 H32 N O4 52 Na2	30.6 26.6	18.871 14.901	0.00	13 15	26 32	3	11	2	2				
	400.1543	1.4	3.5	-0.5	C11 H27 N3 O11 Na	31.4	19.673	0.00	11	27	3	11		1				
	400.1576	-1.9	-4.7	1.5	C14 H30 N3 O6 52	26.5	14.786	0.00	14	30	3	6	2					<b>~</b>
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Elemental composition fit of 4ai (m/z 306 ion) with the HRMS ESI Mass Spectrum:

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Elements Used:																		
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306.1528 306	.1528	0.0	0.0	6.5	C17 H24 N O2 5	22.6	4.273	1.39		17	24	1	2	1				
306	.1535	-0.7	-2.3	2.5	C10 H24 N7 52	33.1	14,724	0.00		10	24	ź	5	2				
306	.1513	1.5	4.9	-1.5	C8 H24 N3 O9	38.7	20.311	0.00		8	24	з	9					
306	.1553	-2.5	-8.2	2.5	C13 H24 N 07	37.4	19.056	0.00		13	24	1	7					
306	.1501	-3.2	-10.5	-1.5	C13 H2U N7 5 C6 H24 N7 O5 5	20.1	1.694	18.38		13	20	4	=	1				
306	.1561	-3.3	-10.8	1.5	C14 H28 N O2 52	31.6	13.226	0.00		14	28	í	2	2				
306	.1494	3.4	11.1	11.5	C20 H20 N O2	38.0	19.666	0.00		20	20	1	2					
PK_RU_220315_ 100- - - - - - - - - - - - - - - - - -	1 1151 (8.	.818) Cr	m (1143	::1157)					30	3	28	61						
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### ESI MS/MS Spectrum of $4a-H^+$ (*m*/*z* 378)



### ESI MS/MS Spectrum of 4a-NH<sub>4</sub><sup>+</sup> (*m*/z 395)



MS-MS ESI Mass Spectrum of fragment 4al (m/z 306: "base peak") in spectra of 4al-H<sup>+</sup> (m/z 378) and 4a-NH<sub>4</sub><sup>+</sup> (m/z 395)



### Elemental composition fit of 4b (m/z 398 ion) with the HRMS ESI Mass Spectrum

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Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
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398.1200 -0.5 -1.3 3.5 C12.H25.N7 02.52 CI 54.4 9.286 0.01 12 25 7 2 2 1
396.1189 0.07 1.8 1.75 C21 Hb 07 5 6.15 16.303 0.00 13 27 7 2 1
399.1104 1.1 2.8 -1.5 C15 H35 O 52 Rh 57.2 12.073 0.00 15 35 1 2 1 398.1206 -1.1 -2.8 1.2 C20 H25 C21 H25 C1 48.1 2.002 5.49 20 21 5 1 1
3961207 -1.2 -3.0 -0.5 CI + H32 NZ O2 CI N 52.2 7.079 0.08 14 32 2 2 1 1
398.128 -1.3 -3.3 7.5 C17 H24 N3 O4 52 56.9 11.784 0.00 17 24 3 4 2 398.1181 1.4 3.5 C15 C28 H6 Nº 2 67.5 22.329 0.00 28 16 1 2
LM14MPL0F2
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201.0774 201.0274 420 278.04 279.0955 320.1714 201.0062 201.06
220 240 250 560 560 560 560 560 560 560 560 560 5

### Elemental composition fit of 4c (m/z 344 ion) with the HRMS ESI Mass Spectrum



### Elemental composition fit of 5a (m/z 414 ion) with the HRMS ESI Mass Spectrum

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	414.1502	2 -0.4	-1.0	3.5	C16 H31 N4 O2 Rh	127.2	20.814	0.00	16	31	4	2	1								
	414.149	0.4	1.0	-0.5	C11 H32 N8 CI Rh	118.2	11.851	0.00	11	32	8 .	2	1 1								
	414.1506	5 -0.8	-1.9	6.5	C20 H29 N O4 5 Cl	112.5	6.135	0.22	20	29	1 ·	<del>1</del> 1	1								
	414.148	3 1.0 - 1.2	2.4	11.5	C21 H24 N3 O4 5	123.3	16.976	0.00	21	24	3 '	4 1	1								
	414.1513	3 -1.5	-3.6	2.5	C13 H29 N7 O2 52 C	116.9	10.547	0.00	13	29	7 3	2 2	1								_
	414.1479	9 1.9	4.6	7.5	C16 H25 N7 O2 5 C	114.9	8.610	0.02	16	25	7 3	2 1	1								~
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### II NMR Spectra for compound 4a

**Note**: Extraneous signals at *ca*. 1.26, 2.05 and 4.12 ppm in the <sup>1</sup>H NMR spectra and at *ca*. 14.2, 21.0, 60.5 and 171.4 ppm in the <sup>13</sup>C NMR spectra are attributed to the presence of residual ethyl acetate.







