Detection and quantitation of synthetic cannabinoid receptor agonists in infused papers from prisons in a constantly evolving illicit market

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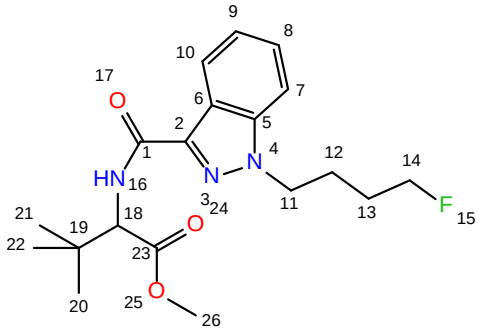
Supplementary Information

SECTION 1: Characterisation (NMR and UPLC-QToF-MS) data for 4F-MDMB-BINACA recovered from a seized sample and used as a reference material.
SECTION 2: Synthesis of (*S*)-enantiomers of 5F-MDMB-PICA and 4F-MDMB-BINACA, and (*S*)-MDMB-4en-PINACA.
SECTION 3: Method development data, quantitative calculations, example calibration curves and quality assurance data.
SECTION 4: SCRA market evolution across three Scottish Prisons.
Total SCRA concentration vs seizure date
SECTION 5: Contextual information and analytical data for paper samples seized in 3 Scottish prisons and found to contain synthetic cannabinoid receptor agonists (SCRAs).
SECTION 6: GC-MS (EI), Low energy (6V) ToF-MS and high energy (10-30V) MS/MS spectra for (a) Cumyl-4CN-BINACA and (b) 4F-PHP identified in seized samples

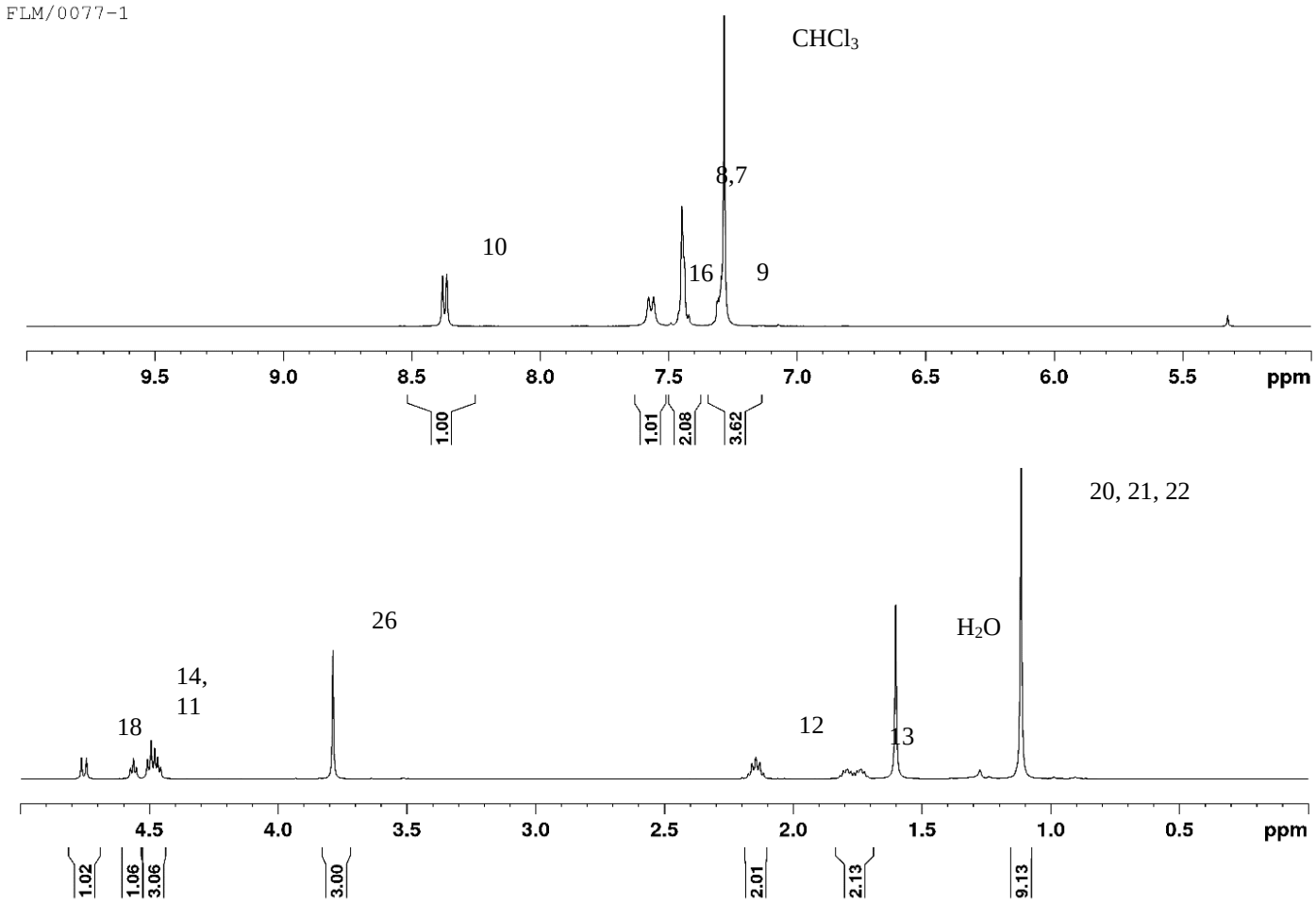
SECTION 1

Analytical data for 4F-MDMB-BINACA Recovered from paper sample FL19/0077-1

(a) NMR data

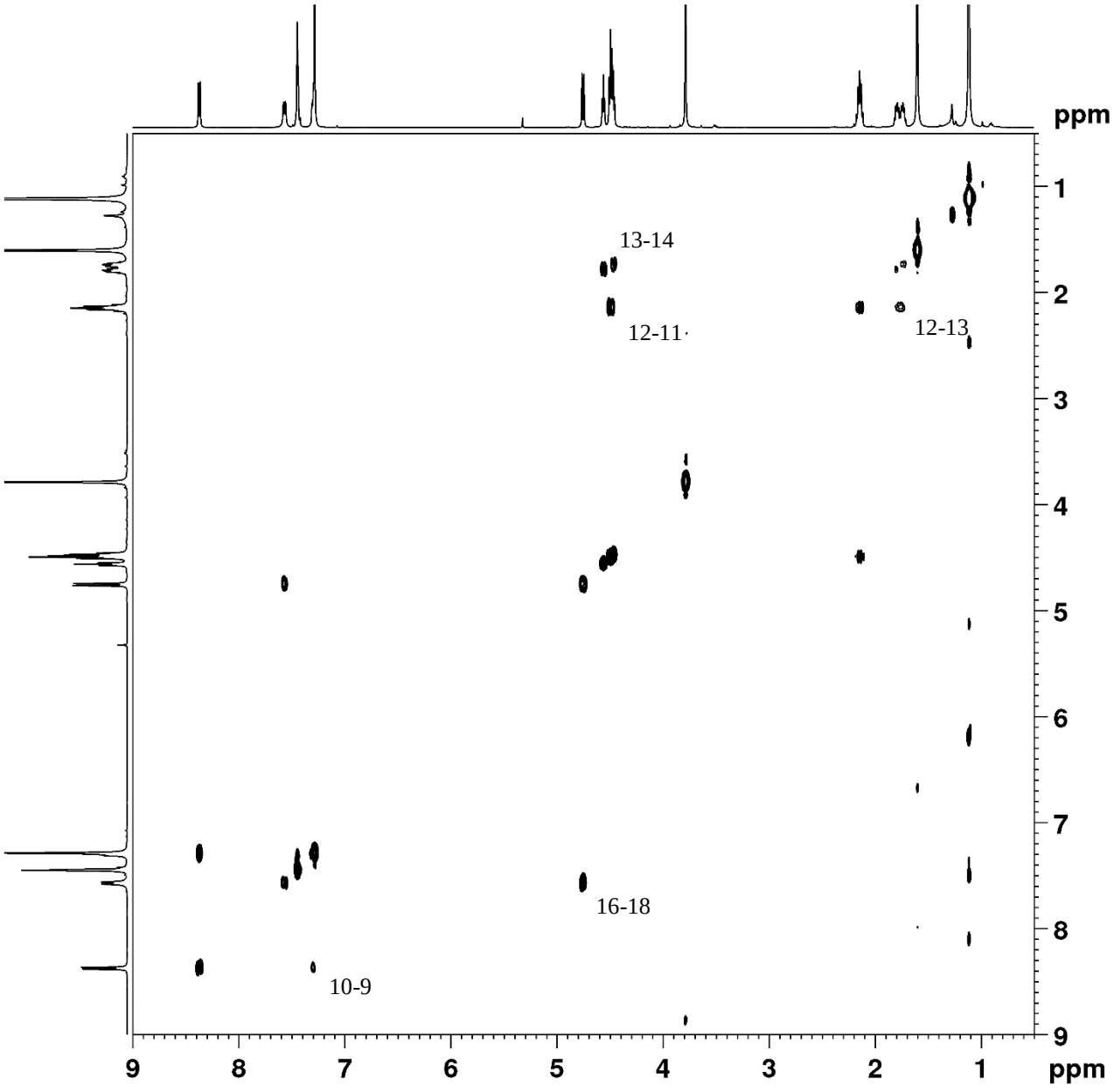


^{1}H Spectrum

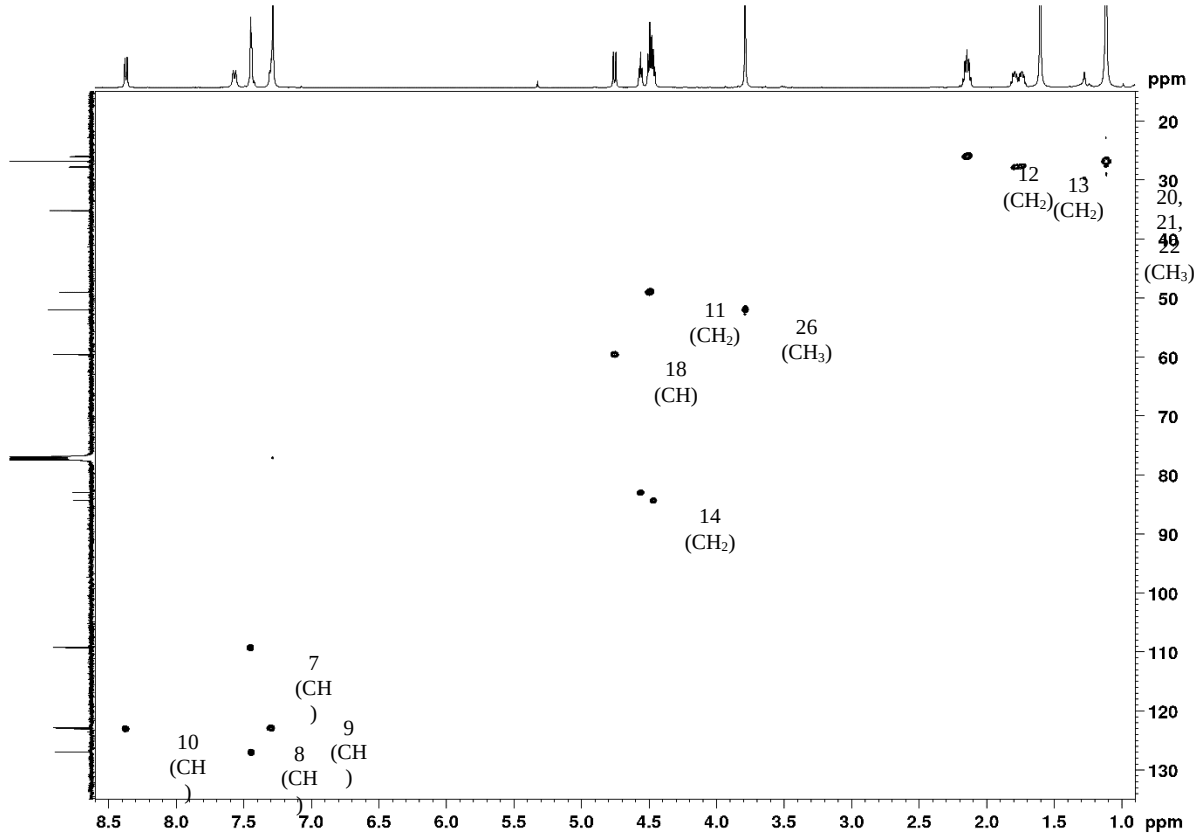


^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 9.7 Hz, 1H), 7.49 – 7.39 (m, 2H), 7.32 – 7.29 (m, 1H), 4.75 (d, *J* = 9.7 Hz, 1H), 4.52 (dt, *J* = 47.2, 5.7 Hz, 2H), 4.50 (t, *J* = 7.0 Hz, 2H), 3.79 (s, 3H), 2.14 (p, *J* = 7.2 Hz, 2H), 1.88 – 1.68 (m, 2H), 1.12 (s, 9H).

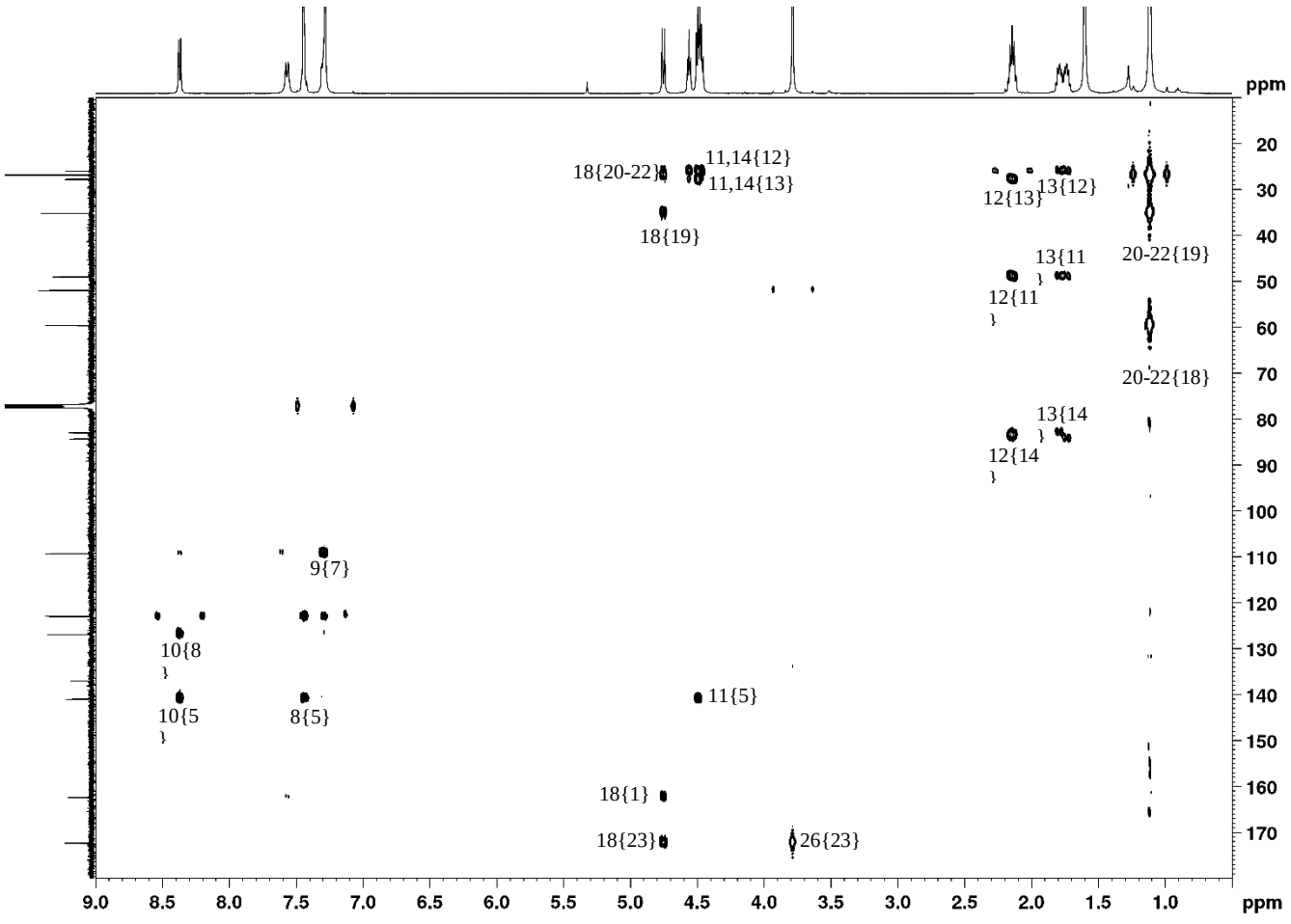
COSY spectrum



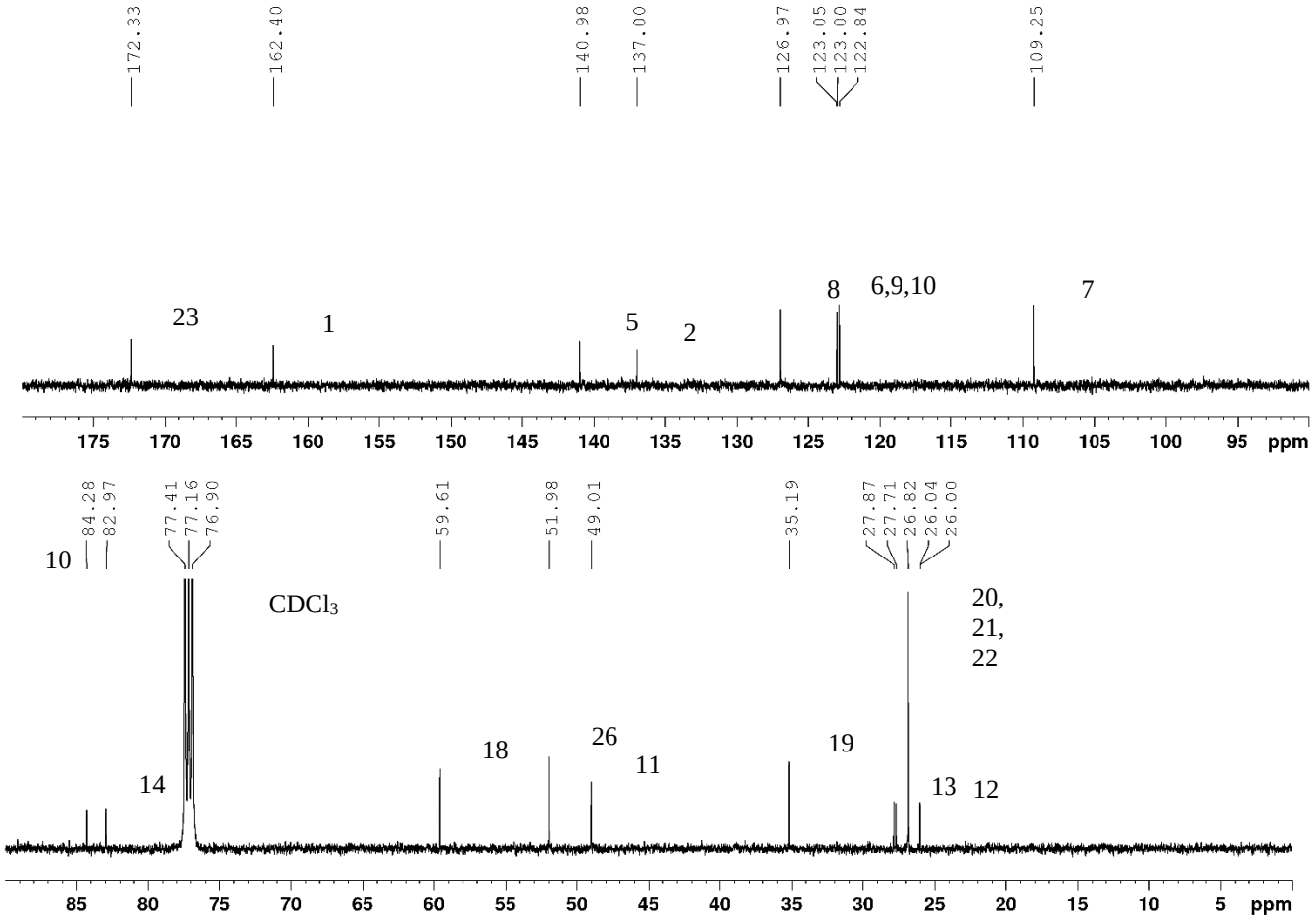
HSQC-DEPT



HMBC - $^{1}H\{^{13}C\}$



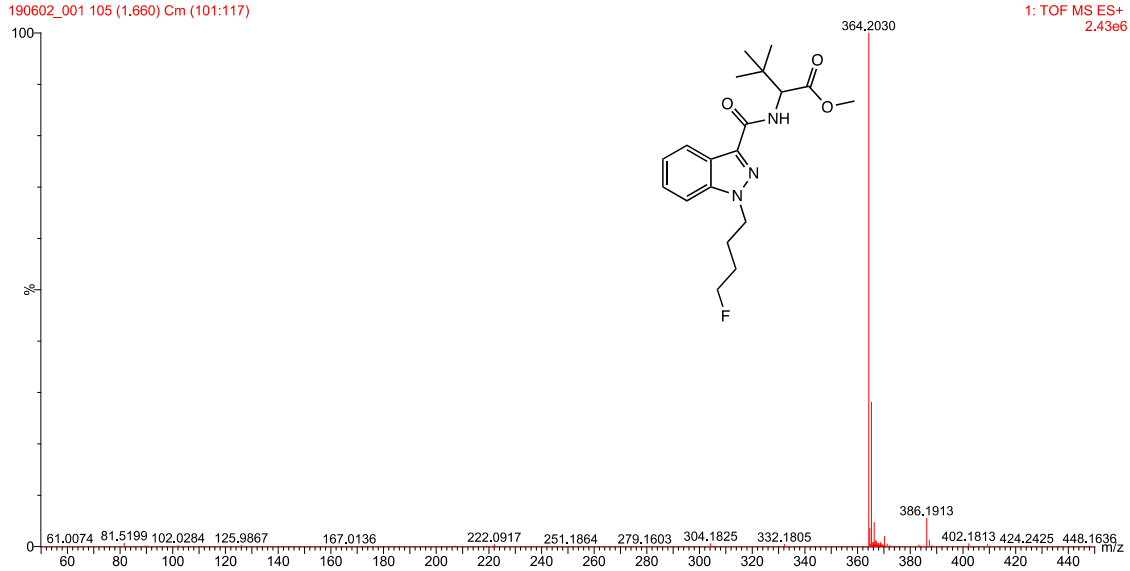
^{13}C Spectrum



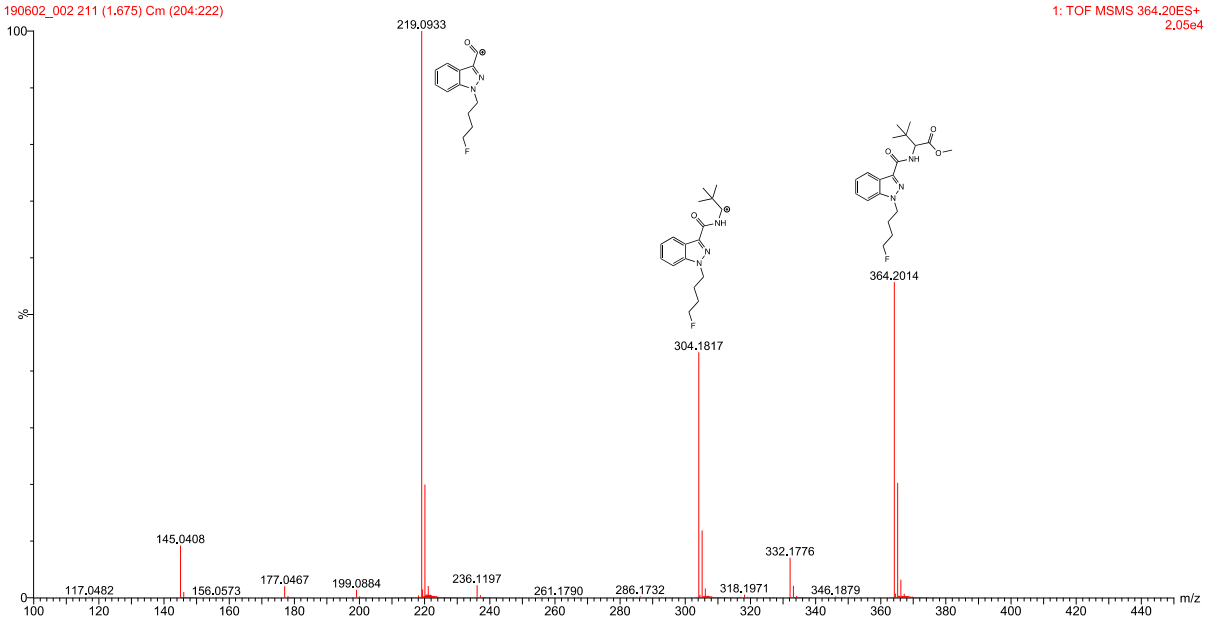
^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.33, 162.40, 140.98, 137.00, 126.97, 123.05, 123.00, 122.84, 109.25, 83.63 (d, *J* = 165.3 Hz), 59.61, 51.98, 49.01, 35.19, 27.79 (d, *J* = 20.1 Hz), 26.82, 26.02 (d, *J* = 4.3 Hz).

(b) UPLC-QToF-MS Data – Recovered 4F-MDMB-BINACA

(i) Low energy (6V) TOF-MS spectrum



(ii) High Energy (10-30V) MS/MS Fragmentation pattern



SECTION 2

A: Synthesis of (*S*)- 4F-MDMB-BINACA

Synthesis of the first intermediate

The first intermediate was prepared using the method reported by Banister et al.[1,2]. Methyl-1H-indazole-3-carboxylate (5.68 mmol) was dissolved in tetrahydrofuran (30 mL) in a dried and ice-cooled round-bottom flask. To this was added potassium tert-butoxide (6.24 mmol, 1.1 eq). The ice bath was removed, and the mixture was stirred for 1 hour. Subsequently, the mixture was cooled again, and pre-requisite alkyl halide was dropwise added (5.96 mmol, 1.05 eq). The resulting solution was stirred for 48 hours at ambient temperature. Hereafter, the reaction was quenched with water (100 mL) and extracted with ethyl acetate (3 x 100 mL). The organic layers were combined, washed with brine (150 mL), dried with magnesium sulfate and concentrated *in vacuo*. The resulting yellow-orange oil (which crystallised upon standing), was purified using flash column chromatography, using a mobile phase of hexane-ethyl acetate (80:20 v/v).

Synthesis of the second intermediate

The second intermediate was prepared using the method reported by Banister et al.[1,2]. The first intermediate (2.58 mmol) was dissolved in methanol (20 mL) and a 1 M aqueous sodium hydroxide solution (3.78 mmol, 1.5 eq) was added. The resulting solution was heated to a reflux and stirred for 18 hours. Here after, the mixture was cooled to room temperature, and concentrated *in vacuo*. The remaining solid was suspended it a saturated aqueous sodium bicarbonate solution (75 mL) and washed with diethyl ether (75 mL). Subsequently, the pH of the aqueous phase was adjusted to 2 with a 1M aqueous hydrochloric acid solution. The acidified aqueous phase was extracted with diethyl ether (3 x 75 mL). The organic layers were combined, washed with brine (150 mL), dried with magnesium sulfate and concentrated *in vacuo*. If necessary, the resulting solid was recrystallised from isopropanol.

Synthesis of the final compounds

(*S*)-4F-MDMB-BINACA were prepared using the method reported by Banister et al.[1,2]. The second intermediate (0.78 mmol) was dissolved in dimethylsulfoxide (10 mL) in a round-bottom flask. To this was added (*S*)-*tert* leucine methyl ester (0.82 mmol, 1.05 eq), EDC*HCl (1.56 mmol, 2 eq), HOBt, (1.56 mmol, 2 eq) and finally, DIPEA (3.9 mmol, 5 eq) was dropwise added. The resulting solution was stirred for 14 hours at ambient temperature. Hereafter, the reaction was quenched with a saturated aqueous sodium bicarbonate solution (75 mL), and extracted with ethyl acetate (3 x 75 mL). The organic layers were combined, washed with brine (100 mL), dried with magnesium sulfate and concentrated *in vacuo*. The resulting yellow-orange oil was purified using flash column chromatography, using a mobile phase of hexane-ethyl acetate (80:20 v/v).

B: Synthesis of (*S*)-5F-MDMB-PICA and (*S*)-AMB-CHMICA

Synthesis of the first intermediate

The first intermediate of the indole carboxamide type SCRAs were prepared using the method reported by Banister et al. [(1,2)] Sodium hydride (60% dispersion in mineral oil, 1.37 g, 34.2 mmol, 2 eq) was suspended in cooled (0 °C) dimethylformamide (60 mL). Indole (2 g, 17.1 mmol) was portion wise added. This mixture was stirred for 10 minutes at ambient temperature. Hereafter, the mixture was cooled again and the appropriate bromoalkane (18.0 mmol, 1.05 eq) was dropwise added after which the mixture was stirred for 1 hour at ambient temperature. The mixture was cooled again and trifluoroacetic anhydride (5.9 mL, 42.8 mmol, 2.5 eq) was dropwise added and was stirred for 1 hour at ambient temperature. To quench the reaction, the mixture was poured onto ice water (150 mL) and extracted with dichloromethane (3 x 100 mL). The organic phase was washed with water (2 x 100 mL) and brine (150 mL), dried using magnesium sulfate and concentrated *in vacuo*. The resulting oil was purified using flash column chromatography, using a mobile phase of hexane-ethyl acetate (90:10 v/v).

Synthesis of the second intermediate
The second intermediate of indole carboxamide-type SCRAs were prepared using an adaptation of the method reported Corbet (patent US20040067939). The first intermediate (the alkyl indole) (4.98 mmol) was dissolved in an aqueous sodium hydroxide solution (20%, 20 mL). The mixture was heated till reflux and stirred for 18 hour. The resulting mixture was cooled the reaction was quenched by adding water (150 mL). The pH was adjusted to 1 using 1 M aqueous hydrochloric acid (10 mL). The water phase was extracted using ethyl acetate (2 x 150 mL). The combined organic layers were washed with saturated aqueous sodium hydrogen carbonate (100 mL), water (100 mL) and brine (100 mL), then dried using magnesium sulfate and concentrated *in vacuo*. The resulting solid was recrystallized from diethyl ether.

Synthesis of the final compound
The final compound of indole carboxamide-type SCRAs were prepared using the method reported by Banister et al.[1,2].The second intermediate (0.78 mmol) was dissolved in dimethylsulfoxide (10 mL) in a round-bottom flask. To this was added the pre-requisite amino acid derivative (0.82 mmol, 1.05 eq), EDC*HCl (1.56 mmol, 2 eq), HOBt, (1.56 mmol, 2 eq) and finally, DIPEA (3.9 mmol, 5 eq) was dropwise added. The resulting solution was stirred for 14 hours at ambient temperature. Hereafter, the reaction was quenched with a saturated aqueous sodium bicarbonate solution (75 mL), and extracted with ethyl acetate (3 x 75 mL). The organic layers were combined, washed with brine (100 mL), dried with magnesium sulfate and concentrated *in vacuo*. The resulting yellow-orange oil was purified using flash column chromatography, using a mobile phase of hexane-ethyl acetate (80:20 v/v) for 5F-MDMB-PICA. The compound AMB-CHMICA was purified with hexane-ethyl acetate (90:10 v/v).

References
[1]Banister SD, Longworth M, Kevin R, Sachdev S, Santiago M, Stuart J, et al. Pharmacology of Valinate and tert-Leucinate Synthetic Cannabinoids 5F-AMBICA, 5F-AMB, 5F-ADB, AMB-FUBINACA, MDMB-FUBINACA, MDMB-CHMICA, and Their Analogues. ACS Chemical Neuroscience. 2016;7(9):1241-54.

[2]Banister SD, Moir M, Stuart J, Kevin RC, Wood KE, Longworth M, et al. Pharmacology of Indole and Indazole Synthetic Cannabinoid Designer Drugs AB-FUBINACA, ADB-FUBINACA, AB-PINACA, ADB-PINACA, 5F-AB-PINACA, 5F-ADB-PINACA, ADBICA, and 5F-ADBICA. ACS Chemical Neuroscience. 2015;6(9):1546-59.

C: Analytical characterisation data

(*S*)-4F-MDMB-BINACA
1H-NMR (400 MHz, CHLOROFORM-D) δ 8.32-8.35 (m, 1H), 7.53 (d, J = 9.6 Hz, 1H), 7.41 (td, J = 2.4, 1.1 Hz, 2H), 7.27 (q, J = 2.6 Hz, 1H), 4.72 (d, J = 9.6 Hz, 1H), 4.54 (t, J = 5.7 Hz, 1H), 4.46 (t, J = 7.1 Hz, 2H), 4.42 (t, J = 5.7 Hz, 1H), 3.75 (s, 3H), 2.07-2.15 (m, 2H), 1.68-1.78 (m, 2H), 1.10 (d, J = 13.3 Hz, 9H)
13C-NMR (101 MHz, CHLOROFORM-D) δ 172.26 (s, 1C), 162.34 (s, 1C), 140.94 (s, 1C), 136.97 (s, 1C), 126.91 (s, 1C), 123.05-122.98 (1C), 122.95 (s, 1C), 122.78 (s, 1C), 109.18 (s, 1C), 83.55 (d, J = 165.3 Hz, 1C), 59.57 (s, 1C), 51.89 (s, 1C), 48.95 (s, 1C), 35.13 (s, 1C), 27.73 (d, 1C), 26.76 (s, 3C), 25.95 (d, 1C)
GC-MS tR = 15.42 min, *m/z* = 363[M+], 219 (100%), 145 (31%), 275 (26%), 307 (25%), 131 (23%)
Yield: 91.0%, purity: 99.7 %

(*S*)-5F-MDMB-PICA
[1]H-NMR (400 MHz, CHLOROFORM-D) δ (ppm) 7.95-7.98 (m, 1H), 7.74 (s, 1H), 7.37-7.39 (m, 1H), 7.27-7.30 (m, 2H), 6.52 (d, J = 9.2 Hz, 1H), 4.77 (d, J = 9.2 Hz, 1H), 4.41 (dt, J = 47.2,

6.0 Hz, 2H), 4.16 (t, J = 7.1 Hz, 2H), 3.75 (s, 3H), 1.87-1.95 (m, 2H), 1.66-1.76 (m, 2H), 1.43-1.49 (m, 2H), 1.08 (s, 9H)
^{13}C-NMR (101 MHz, CHLOROFORM-D) δ (ppm) 172.82 (s, 1C), 164.81 (s, 1C), 136.65 (s, 1C), 131.98 (s, 1C), 125.32 (s, 1C), 122.62 (s, 1C), 121.78 (s, 1C), 120.07 (s, 1C), 110.75 (s, 1C), 110.41 (s, 1C), 83.76 (d, J = 165.3 Hz, 1C), 59.78 (s, 1C), 51.96 (s, 1C), 46.83 (s, 1C), 35.16 (s, 1C), 30.04 (d, 1C), 29.74 (s, 1C), 26.85 (s, 3C), 22.92 (d, 1C)
GC-MS t_R = 17.02 min, *m/z* = 376[M+], 232 (100%), 144 (20%), 233 (17%), 260 (10%), 288 (8%)
Yield: 87.9%, purity: 98.7+%

(*S*)-AMB-CHMICA
^{1}H-NMR (400 MHz, CHLOROFORM-D) δ (ppm) 7.95-7.99 (m, 1H), 7.70 (s, 1H), 7.37 (td, J = 4.5, 3.1 Hz, 1H), 7.25-7.29 (m, 2H), 6.47 (d, J = 8.7 Hz, 1H), 4.86 (q, J = 4.4 Hz, 1H), 3.95 (d, J = 6.9 Hz, 2H), 3.78 (s, 3H), 2.27-2.32 (m, 1H), 1.82-1.88 (m, 1H), 1.64-1.71 (m, 5H), 1.15 (dd, J = 17.6, 9.4 Hz, 3H), 0.94-1.19 (m, 11H), 1.03 (dd, J = 9.6, 6.9 Hz, 6H)
^{13}C-NMR (101 MHz, CHLOROFORM-D) δ (ppm) 173.27 (s, 1C), 165.04 (s, 1C), 137.03 (s, 1C), 132.67 (s, 1C), 122.44 (s, 1C), 121.59 (s, 1C), 120.05 (s, 2C), 110.73 (s, 2C), 56.94 (s, 1C), 53.49 (s, 1C), 52.30 (s, 1C), 38.61 (s, 1C), 31.82 (s, 1C), 31.07 (s, 2C), 26.27 (s, 1C), 25.71 (s, 2C), 19.20 (s, 1C), 18.17 (s, 1C)
GC-MS t_R = 18.16 min, *m/z* = 370[M+], 240 (100%), 256 (61%), 144 (31%), 207 (17%), 55 (15%)
Yield: 87.3%, purity: 99.6 %

(*S*)-MDMB-4en-PINACA
^{1}H-NMR (400 MHz, CHLOROFORM-D) δ (ppm) 8.33 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 9.6 Hz, 1H), 7.47-7.32 (m, 2H), 7.32-7.16 (m, 1H), 5.91-5.70 (m, 1H), 5.14-4.95 (m, 2H), 4.72 (d, J = 9.6 Hz, 1H), 4.40 (t, J = 6.6 Hz, 2H), 3.75 (s, 3H), 2.19-2.04 (m, 4H), 1.08 (s, 9H)
^{13}C-NMR (400 MHz, CHLOROFORM-D) δ (ppm) 172.28 (s, 1C), 162.42 (s, 1C), 140.93 (s, 1C), 137.14 (s, 1C), 136.78 (s, 1C), 126.73 (s, 1C), 122.97 (s, 1C), 122.87 (s, 1C), 122.69 (s, 1C), 116.02 (s, 1C), 109.31 (s, 1C), 59.53 (s, 1C), 51.92 (s, 1C), 48.69 (s, 1C), 35.14 (s, 1C), 30.82 (s, 1C), 28.81 (s, 1C), 26.77 (s, 3C)
GC-MS t_R: 15.38 min, *m/z* = 356[M+], 213 (100%), 145 (28%), 171 (17%), 214 (17%), 301 (16%).
Yield: 87.8 %. Purity: 98.6 %

SECTION 3
Method development data, quantitative calculations, example calibration curves and quality assurance data.

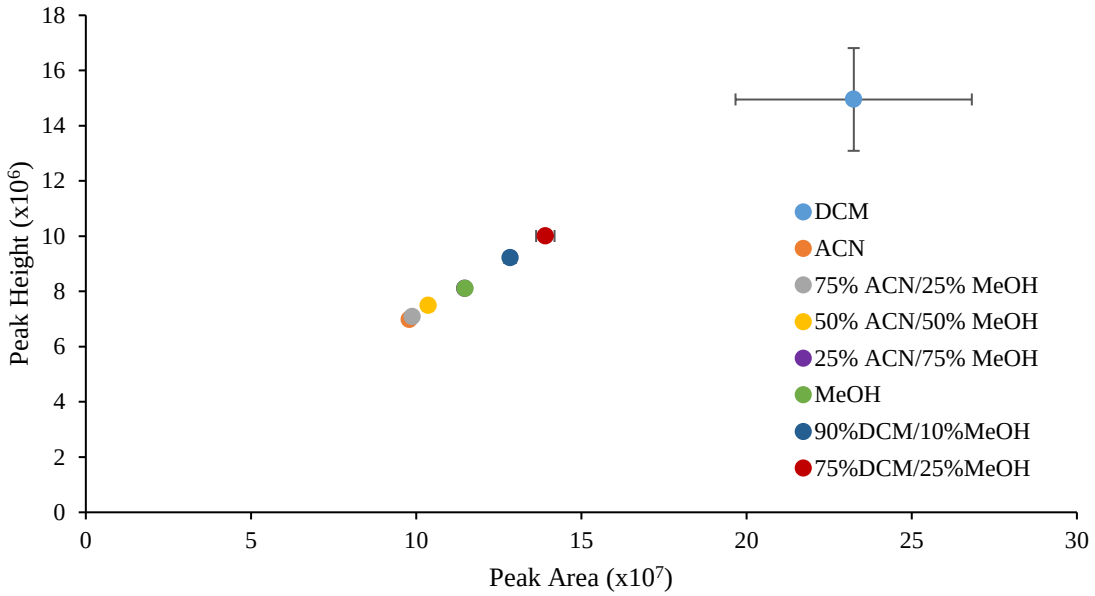


Figure S3.1a Analysis of SCRAs using a variety of solvents on GC-MS fitted with a HP-5MS column (n=10). 0.2 mg/mL solutions of an AMB-FUBINACA reference standard were made in each solvent. Hexane was immediately eliminated as the SCRA was not soluble in hexane. The remaining standards were injected ten times with the samples mixed up in the sequence in order to better account for the variability of the GC-MS, such as variability in the injection, inlet, solid phase, or MS source. The samples were run using a 1:20 split injection. Error bars reflect the calculated standard error of the mean.

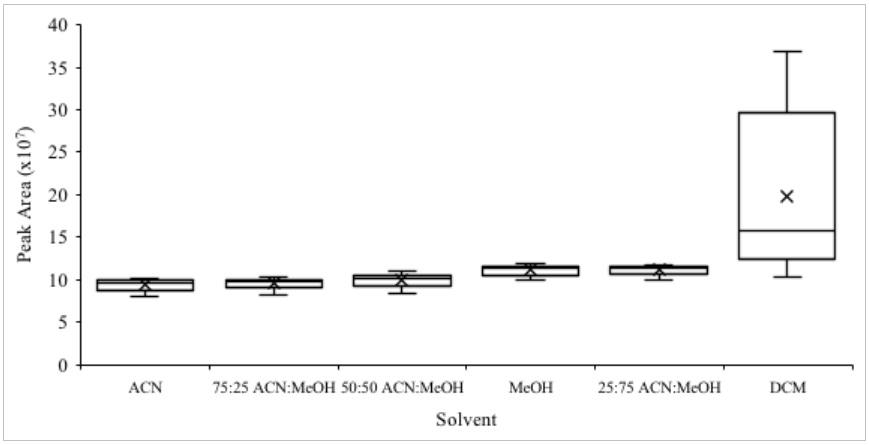


Figure S3.1b Variation of GC-MS response to the use of different injection solvents (n=10).

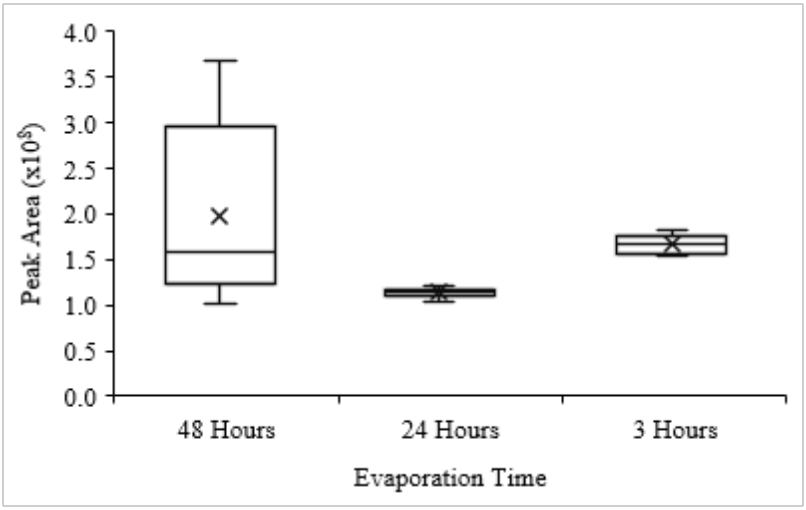


Figure S3.2. Variability of GC-MS peak area of SCRAs in DCM based on period of time (evaporation time) between first and last injection of a 0.2 mg/mL AMB-FUBINACA reference standard (n=10).

Table S3.1. Determination of the number of extractions required to remove 100% of the SCRAs from paper using spiked paper samples.

		4F-MDMB-BINACA		5F-MDMB-PINACA		AMB-FUBINACA		5F-MDMB-PICA		AMB-CHMICA	
Sample	**Extraction**	**Peak Area**	**% of Total Peak Area**	**Peak Area**	**% of Total Peak Area**	**Peak Area**	**% of Total Peak Area**	**Peak Area**	**% of Total Peak Area**	**Peak Area**	**% of Total Peak Area**
1	1	6199921	98.19	6477579	98.43	6623660	98.43	6888002	95.42	8007152	95.09
	2	114177	1.81	99324	1.51	102438	1.52	311600	4.32	397461	4.72
	3	0	0.00	3897	0.06	2983	0.04	19374	0.27	16351	0.19
	4	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00
	5	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00
2	1	6120132	96.51	7144536	94.16	7356744	94.32	5549749	96.50	6652830	96.52
	2	205353	3.24	420607	5.54	420591	5.39	196400	3.41	237924	3.45
	3	15902	0.25	22145	0.29	22594	0.29	5080	0.09	2085	0.03
	4	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00
	5	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00
3	1	5854229	96.77	6783245	98.29	7044574	98.29	6224384	97.29	7346622	97.28
	2	187689	3.10	110705	1.60	115883	1.62	166643	2.60	202063	2.68
	3	7407	0.12	7159	0.10	6681	0.09	6861	0.11	3625	0.05
	4	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00
	5	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00
Average	1		97.16		96.96		97.01		96.40		96.29
	2		2.72		2.89		2.84		3.45		3.62
	3		0.12		0.15		0.14		0.15		0.09
	4		0.00		0.00		0.00		0.00		0.00
	5		0.00		0.00		0.00		0.00		0.00

Calculations for the Quantitation of SCRA Paper Samples

CALIBRATION STANDARD CONCENTRATION CALCULATIONS

1. Calculate the 1 mg/mL SCRA Concentration

MeOH Volume = $\frac{g\ of\ MeOH}{\rho\ of\ MeOH}$

[mg/mL SCRA] = $\frac{mg\ of\ SCRA}{MeOH\ Volume}$

2. Calculate the Internal Standard (IS) Concentration

[IS Stock] = $\frac{g\ of\ Tridecane}{\frac{g\ of\ Tridecane}{\rho\ of\ Tridecane}+\frac{g\ of\ solvent}{\rho\ of\ solvent}}$

[378 μg/mL IS] = $\frac{(g\ of\ IS\ Stock)\times[IS\ Stock]}{[IS\ Stock]+\rho\ of\ solvent} \div \left(\frac{g\ of\ IS\ Stock}{[IS\ Stock]+\rho\ of\ solvent}+\frac{g\ of\ solvent}{\rho\ of\ solvent}\right)$

3. Calculate the Calibration Standards Volumes

SCRA Volume = $\frac{g\ of\ SCRA}{[mg/mL\ SCRA]+\rho\ of\ MeOH}$

IS Volume = $\frac{g\ of\ 378\ \mu g/mL\ IS}{[378\ \mu g/mL\ IS]+\rho\ of\ solvent}$

DCM Volume = $\frac{g\ of\ DCM}{\rho\ of\ DCM}$

Solvent Volume = $\frac{g\ of\ solvent}{\rho\ of\ solvent}$

Total Volume = SCRA Volume + IS Volume + DCM Volume + Solvent Volume

4. Calculate the Calibration Standards Actual Concentrations

[SCRA] = $\frac{Volume\ of\ SCRA}{Total\ Volume}\times[mg/mL\ SCRA]$

[IS] = $\frac{Volume\ of\ IS}{Total\ Volume}\times[378\ \mu g/mL\ IS]$

5. Calculate the Average Internal Standards Concentration for All Standards

6. Calculate the Response Ratio and Concentration Ratio of Calibration Responses

Response Ratio = $\frac{SCRA\ Response}{IS\ Response}$

Concentration Ratio = $\frac{[SCRA]}{Average\ [IS]}$

7. Calculate the Average Response Ratios of Each Calibration Standard

8. Calculate a Quadratic Regression for the Calibration Curve Using Average Response Ratios

For ease, c = Concentration Ratio and r = Average Response Ratio

$$\begin{bmatrix}\Sigma c_i^4 & \Sigma c_i^3 & \Sigma c_i^2\\ \Sigma c_i^3 & \Sigma c_i^2 & \Sigma c_i\\ \Sigma c_i^2 & \Sigma c_i & n\end{bmatrix}[\Sigma c_i^2 r_i \quad \Sigma c_i r_i \quad \Sigma r_i] = [a \quad b \quad c]$$

where $y = ax^2 + bx + c$

9. Calculate the Coefficient of Determination (R^2)

$R^2 = 1 - \frac{SSE}{SSTO} = 1 - \frac{\Sigma(predictions - r)^2}{\Sigma(r - mean(r))^2}$

where predictions are found by inputting each concentration ratio value into the quadratic regression.

Method Validation Calculations

10. Calculate the Check Standards Volumes

Same as for Calibration Standards (Step 3)

11. Calculate the Check Standards Actual Concentrations

Same as for Calibration Standards (Step 4)

12. Calculate the Response Ratios of Check Standards and Spiked Sample

Response Ratio = $\frac{SCRA\ Response}{IS\ Response}$

13. Calculate the Concentration Ratios of Check Standards and Spiked Sample

Concentration Ratio = $\frac{-b+\sqrt{b^2-4a(c-r)}}{2a}$

For the check standards, use the average response ratio of the three runs of each standard.

14. Calculate the µg/mL Concentration of Check Standards and Spiked Sample

[Check Standard] = $(Concentration\ Ratio) \times [IS]$

[Spiked Sample] = $(Concentration\ Ratio) \times [IS] \times 2$, where 2 is the dilution factor

15. Calculate the µg/cm^2 Concentration of the Spiked Sample

[µg/cm^2] = $[\mu g/mL] \times \frac{Volume\ of\ solvent\ in\ mL}{Area\ of\ paper\ sample\ in\ cm^2} = [\mu g/mL] \times \frac{Volume\ of\ solvent\ in\ mL}{(1\ cm)^2}$

16. Calculate the Percent Error of Check Standards and Spiked Sample

% Error = $\left|\frac{theoretical-actual}{actual}\right| \times 100$

C: Calculating SCRA concentrations in paper samples (3mm hole punched samples)

17. Calculate the Response Ratio and Concentration Ratio

Same as for Check Standards (Step 9)

18. Calculate the µg/mL Concentration

[µg/mL] = $(Concentration\ Ratio) \times [IS] \times 2$

where 2 is the dilution factor

19. Calculate the mg/cm^2 Concentration

[mg/cm^2] = $[\mu g/mL] \times \frac{Volume\ of\ solvent\ in\ mL}{Area\ of\ paper\ sample\ in\ mm^2} \times 0.1 = [\mu g/mL] \times \frac{Volume\ of\ solvent\ in\ mL}{\pi(1.5\ mm)^2} \times 0.1$,

where 0.1 is the conversion factor from µg/mm^2 to mg/cm^2

Example Calibration Data

Table S3.2. 4F-MDMB-BINACA calibration curve data.

Concentration	Response	IS Response	Average Response Ratio	Concentration Ratio
109.19	1249771, 3103518, 2523605	98512, 202606, 170785	14.26	2.62
74.48	1278751, 1025183, 685048	134233, 132818, 91085	8.26	1.97
51.58	296334, 362262, 888534	68128, 105013, 192918	4.14	1.31
27.43	184634, 222240, 127724	109788, 142966, 81597	1.60	0.66
9.69	32166, 30236, 28872	77759, 77208, 77613	0.39	0.26
5.09	10248, 11622, 18659	54155, 73407, 128807	0.16	0.13

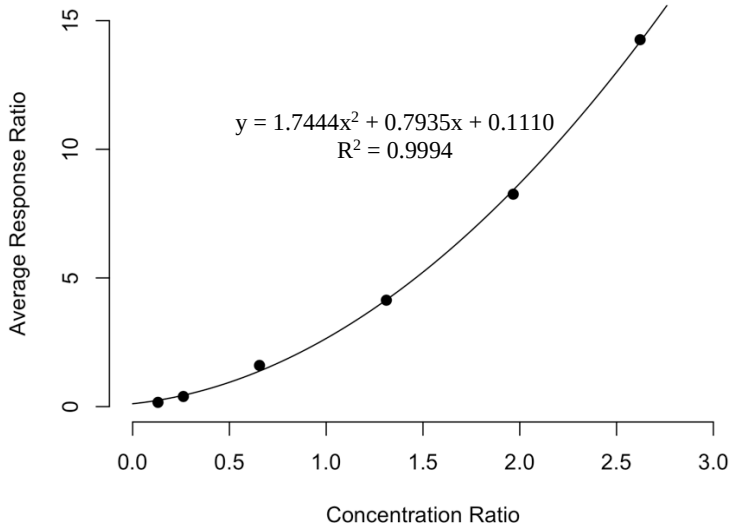


Figure S3.4. 4F-MDMB-BINACA calibration curve from 29/10/19.

Table S3.3. 4F-MDMB-BINACA quality assurance data

Response	IS Response	Response Ratio	Concentration Ratio	Actual Concentration	Concentration	% Bias
Calibration curve check standards						
196485	105292	1.87	0.80	32.19 μg/mL	32.54 μg/mL	+1.07
1150246	110959	10.37	2.21	93.85 μg/mL	92.18 μg/mL	-1.78
Batch SCRA spiked paper sample						
365151	81348	4.49	1.37	72.44 μg/cm^2	64.06 μg/cm^2	-11.57

Table S3.4. Example 4F-MDMB-BINACA batch quantitation data.

Sample	Response	IS Response	Response Ratio	Concentration Ratio	Concentration (μg/mL)	Concentration (mg/cm^2)
FL19/0077	313670	71416	4.39	1.36	109.13	0.94 ± 0.14
FL19/0078-2	0	69191	<0.16	<0.13	<10.18	<0.09 ± 0.01
FL19/0081	57441	62783	0.91	0.49	39.33	0.33 ± 0.05
FL19/0082	281894	64073	4.40	1.36	109.24	0.90 ± 0.14
FL19/0083	241088	68491	3.52	1.19	95.71	0.83 ± 0.13
FL19/0119	29976	66388	0.45	0.27	21.70	0.19 ± 0.03
FL19/0126	66435	63814	1.04	0.54	43.26	0.37 ± 0.06
FL19/0129	96584	67650	1.43	0.67	53.99	0.47 ± 0.07
FL19/0132-1	0	63337	<0.16	<0.13	<10.18	<0.09 ± 0.01
FL19/0133-1	0	66109	<0.16	<0.13	<10.18	<0.09 ± 0.01
FL19/0135-1	62014	66419	0.93	0.50	39.93	0.36 ± 0.05
FL19/0135-3	5050	64561	<0.16	<0.13	<10.18	<0.09 ± 0.01
FL19/0146	49574	68638	0.72	0.41	32.74	0.29 ± 0.04
FL19/0151	39514	67049	0.59	0.34	27.65	0.24 ± 0.04
FL19/0164-3	98224	64081	1.53	0.70	56.64	0.51 ± 0.08
FL19/0180	16418	71040	<0.16	<0.13	<10.18	<0.09 ± 0.01
FL19/0181-2	10857	64388	<0.16	<0.13	<10.18	<0.09 ± 0.01
FL19/0183	22660	67766	0.33	0.20	15.83	0.14 ± 0.02
FL19/0184	228078	66859	3.41	1.17	93.93	0.81 ± 0.12
FL19/0185	117058	72951	1.60	0.73	58.40	0.52 ± 0.08

Table S3.5. Quantitation method validation data: 4F-MDMB-BINACA spiked papers

Sample	Extractions Volume	Response	IS Response	Response Ratio	Concentration Ratio	Concentration (μg/mL)	Concentration (μg/cm^2)	% bias
Mock 1 Quant 1	0.4754	547021	181021	3.02	1.86	147.36	70.00	-8.14
Mock 2 Quant 1	0.4944	529416	177535	2.98	1.85	146.16	72.20	-5.25
Mock 3 Quant 1	0.4654	559426	184730	3.03	1.86	147.56	68.62	-9.95
Mock 4 Quant 1	0.5341	464751	167040	2.78	1.77	140.00	74.76	-1.89
Mock 5 Quant 1	0.5401	446877	181100	2.47	1.64	129.87	70.13	-7.97
Mock 6 Quant 1	0.5259	499954	173270	2.89	1.81	143.2	75.33	+1.15
Mock 1 Quant 2	0.4754	498758	184251	2.71	1.74	137.63	65.37	-14.21
Mock 2 Quant 2	0.4944	515625	169538	3.04	1.87	147.95	73.09	-4.08
Mock 3 Quant 2	0.4654	557757	172617	3.23	1.94	153.58	71.42	-6.28
Mock 4 Quant 2	0.5341	460152	162756	2.83	1.79	141.40	75.51	+0.91
Mock 5 Quant 2	0.5401	457474	179634	2.55	1.67	132.47	71.53	-6.12
Mock 6 Quant 2	0.5259	472585	173275	2.73	1.75	138.27	72.73	-4.55
Mock 1 Quant 3	0.4754	503264	165992	3.03	1.86	147.67	70.14	-7.95
Mock 2 Quant 3	0.4944	499954	168617	2.97	1.84	145.64	71.95	-5.58
Mock 3 Quant 3	0.4654	542747	167067	3.25	1.95	154.09	71.65	-5.97
Mock 4 Quant 3	0.5341	453218	161254	2.81	1.78	140.88	75.23	+1.27
Mock 5 Quant 3	0.5401	430453	147758	2.91	1.82	144.06	77.79	+2.09
Mock 6 Quant 3	0.5259	459411	165096	2.78	1.77	140.01	73.65	-3.35

*****There was an error with the extraction of one of the spiked samples because the glass vial used for extraction had chemical residue remaining from the glass washing processed used, which resulted in a cloudy extraction solution and poor quantitation. For that reason, those sample quantitations were removed from this dataset.

Table S3.6. Quantitation method validation data: 5F-MDMB-PINACA spiked papers

Sample	Extractions Volume	Response	IS Response	Response Ratio	Concentration Ratio	Concentration (μg/mL)	Concentration (μg/cm^2)	% bias
Mock 1 Quant 1	0.5112	403021	120729	3.34	1.81	143.41	73.31	-4.55
Mock 2 Quant 1	0.5623	335781	144061	2.33	1.47	116.32	65.40	-14.8
Mock 3 Quant 1	0.5271	382317	126481	3.02	1.71	135.45	71.40	-7.03
Mock 4 Quant 1	0.5307	392857	147556	2.66	1.59	125.81	66.77	-13.1
Mock 5 Quant 1	0.5706	328676	137089	2.40	1.49	118.28	67.50	-12.1
Mock 6 Quant 1	0.5409	361873	115708	3.13	1.74	138.14	74.71	-2.72
Mock 1 Quant 2	0.5112	380711	138428	2.75	1.62	128.22	65.54	-14.7
Mock 2 Quant 2	0.5623	360432	137415	2.62	1.57	124.72	70.13	-8.69
Mock 3 Quant 2	0.5271	391140	136648	2.86	1.66	131.24	69.18	-9.92
Mock 4 Quant 2	0.5307	400168	140578	2.85	1.65	130.82	69.43	-9.59
Mock 5 Quant 2	0.5706	341613	139421	2.45	1.51	119.82	68.37	-11.0
Mock 6 Quant 2	0.5409	349628	128349	2.72	1.61	127.51	68.96	-10.2
Mock 1 Quant 3	0.5112	394140	131869	2.99	1.70	134.57	68.79	-10.4
Mock 2 Quant 3	0.5623	361310	109071	3.31	1.80	142.78	80.28	+4.53
Mock 3 Quant 3	0.5271	385529	140884	2.74	1.61	127.85	67.39	-12.3
Mock 4 Quant 3	0.5307	397447	131533	3.02	1.71	135.42	71.87	-6.41
Mock 5 Quant 3	0.5706	337505	139064	2.43	1.50	119.14	67.99	-11.5
Mock 6 Quant 3	0.5409	372661	131374	2.84	1.65	130.55	70.61	-8.06

*There was an error with one of the spiked samples, which was clear from the significantly low SCRA responses in all three replicates of the sample extraction. In addition, the same error in the spiked sample was seen in those samples with AMB-FUBINACA. Since there was one 1 mg/mL solution for 5F-MDMB-PINACA and AMB-FUBINACA combined, the consistency in the low concentration of SCRAs in this sample provides confidence that there was an error with the infusion of the spiked paper or the extraction of that sample. For that reason, those sample quantitations were removed from this dataset.

Table S3.7. Quantitation method validation data: AMB-FUBINACA

Sample	Extractions Volume	Response	IS Response	Response Ratio	Concentration Ratio	Concentration (μg/mL)	Concentration (μg/cm^2)	% bias
Mock 1 Quant 1	0.5112	513529	120729	4.25	1.94	153.37	78.40	+4.11
Mock 2 Quant 1	0.5623	427255	144061	2.97	1.54	121.76	68.47	-9.08
Mock 3 Quant 1	0.5271	501451	126481	3.96	1.85	146.74	77.36	+2.73
Mock 4 Quant 1	0.5307	501659	147556	3.40	1.68	133.06	70.62	-6.21
Mock 5 Quant 1	0.5706	433039	137089	3.16	1.60	126.88	72.41	-3.84
Mock 6 Quant 1	0.5409	480202	115708	4.15	1.91	151.02	81.68	+8.48
Mock 1 Quant 2	0.5112	506673	138428	3.66	1.76	139.50	71.31	-5.30
Mock 2 Quant 2	0.5623	475371	137415	3.46	1.70	134.56	75.66	+0.48
Mock 3 Quant 2	0.5271	513971	136648	3.76	1.79	141.94	74.82	-0.64
Mock 4 Quant 2	0.5307	536327	140578	3.82	1.81	143.22	76.01	+0.95
Mock 5 Quant 2	0.5706	455589	139421	3.27	1.64	129.70	74.01	-1.71
Mock 6 Quant 2	0.5409	465099	128349	3.62	1.75	138.61	74.97	-0.44
Mock 1 Quant 3	0.5112	521026	131869	3.95	1.85	146.43	74.85	-0.60
Mock 3 Quant 3	0.5271	511705	140884	3.63	1.75	138.82	73.18	-2.82
Mock 4 Quant 3	0.5307	534080	131533	4.06	1.88	148.97	79.06	+5.00
Mock 5 Quant 3	0.5706	452291	139064	3.25	1.63	129.31	73.79	-2.01
Mock 6 Quant 3	0.5409	510582	131374	3.89	1.83	144.91	78.38	+4.09

*There was an error with one of the spiked samples, which was clear from the significantly low SCRA responses in all three replicates of the sample extraction. In addition, the same error in the spiked sample was seen in those samples with 5F-MDMB-PINACA. Since there was one 1 mg/mL solution for AMB-FUBINACA and 5F-MDMB-PINACA combined, the consistency in the low concentration of SCRAs in this sample provides confidence that there was an error with the infusion of the spiked paper or the extraction of that sample. For that reason, those sample quantitations were removed from this dataset.

**There was an error in the two-fold dilution with the third quantitation sample of the second spiked paper (Mock 2) that resulted in abnormally low internal standard concentration, leading to high errors in the concentration calculated. For that reason, those sample quantitations were removed from this dataset.

Table S3.8. Quantitation method validation data: 5F-MDMB-PICA spiked papers

Sample	Extractions Volume	Response	IS Response	Response Ratio	Concentration Ratio	Concentration (μg/mL)	Concentration (μg/cm^2)	% bias
Mock 1 Quant 1	0.5261	273797	101753	2.69	1.81	143.35	75.41	+1.36
Mock 2 Quant 1	0.5353	288632	124669	2.32	1.65	131.02	70.13	-5.74
Mock 3 Quant 1	0.5543	271490	110996	2.45	1.71	135.42	75.07	+0.89
Mock 4 Quant 1	0.5757	247955	121982	2.03	1.53	121.08	69.71	-6.30
Mock 5 Quant 1	0.5158	268730	125702	2.14	1.58	124.85	64.40	-13.5
Mock 1 Quant 2	0.5261	295037	139197	2.12	1.57	124.20	65.34	-12.2
Mock 2 Quant 2	0.5353	286167	149330	1.92	1.47	116.79	62.51	-16.0
Mock 3 Quant 2	0.5543	283231	139217	2.03	1.53	121.15	67.15	-9.74
Mock 4 Quant 2	0.5757	263728	135132	1.95	1.49	118.11	68.00	-8.60
Mock 5 Quant 2	0.5158	278020	123184	2.26	1.63	129.02	66.54	-10.6
Mock 1 Quant 3	0.5261	295270	143929	2.05	1.54	121.76	64.05	-13.9
Mock 2 Quant 3	0.5353	299923	144158	2.08	1.55	122.81	65.73	-11.7
Mock 3 Quant 3	0.5543	352296	163205	2.16	1.59	125.59	69.62	-6.43
Mock 4 Quant 3	0.5757	258767	134187	1.93	1.48	117.24	67.50	-9.27
Mock 5 Quant 3	0.5158	272206	112288	2.42	1.70	134.69	69.47	-6.63

*There was an error with two of the spiked samples, which was clear from the significantly low response ratios in all three replicates of the sample extraction. In addition, the same error in the spiked sample was seen in those samples with AMB-CHMICA. Since there was one 1 mg/mL solution for 5F-MDMB-PICA and AMB-CHMICA combined, the consistency in the low concentration of SCRAs in this sample provides confidence that there was an error with the infusion of the spiked paper or the extraction of that sample. For that reason, those sample quantitations were removed from this dataset.

Table S3.9. Quantitation method validation data: AMB-CHMICA spiked papers

Sample	Extractions Volume	Response	IS Response	Response Ratio	Concentration Ratio	Concentration (μg/mL)	Concentration (μg/cm^2)	% bias
Mock 1 Quant 1	0.5261	361764	101753	3.56	1.98	160.64	84.51	+11.3
Mock 2 Quant 1	0.5353	383912	124669	3.08	1.81	147.25	78.82	+3.84
Mock 3 Quant 1	0.5543	368311	110996	3.32	1.90	154.08	85.41	+12.5
Mock 4 Quant 1	0.5757	332465	121982	2.73	1.68	136.65	78.67	+3.66
Mock 5 Quant 1	0.5158	357237	125702	2.84	1.73	140.20	72.31	-4.73
Mock 1 Quant 2	0.5261	390985	139197	2.81	1.72	139.20	73.23	-3.52
Mock 2 Quant 2	0.5353	378113	149330	2.53	1.61	130.58	69.89	-7.91
Mock 3 Quant 2	0.5543	378921	139217	2.72	1.68	136.53	75.69	+0.28
Mock 4 Quant 2	0.5757	346660	135132	2.57	1.62	131.64	75.79	+0.14
Mock 5 Quant 2	0.5158	369579	123184	3.00	1.79	144.93	74.75	-1.51
Mock 1 Quant 3	0.5261	393031	143929	2.73	1.69	136.81	71.97	-5.18
Mock 2 Quant 3	0.5353	408121	144158	2.83	1.72	139.88	74.87	+1.36
Mock 3 Quant 3	0.5543	452074	163205	2.77	1.70	138.02	76.51	+0.80
Mock 4 Quant 3	0.5757	343294	134187	2.56	1.62	131.42	75.66	+0.31
Mock 5 Quant 3	0.5158	358040	112288	3.19	1.85	150.41	77.57	+2.21

*There was an error with two of the spiked samples, which was clear from the significantly low response ratios in all three replicates of the sample extraction. In addition, the same error in the spiked sample was seen in those samples with 5F-MDMB-PICA. Since there was one 1 mg/mL solution for AMB-CHMICA and 5F-MDMB-PICA combined, the consistency in the low concentration of SCRAs in this sample provides confidence that there was an error with the infusion of the spiked paper or the extraction of that sample. For that reason, those sample quantitations were removed from this dataset.

Table S3.10. Quantitation method validation data: Statistical analysis overview.

SCRA	p-value	Sample	Mean	Minimum	Maximum	SEM
4F-MDMB-BINACA	0.54	Mock 1	68.50	65.37	70.14	1.57
		Mock 2	72.41	71.95	73.09	0.35
		Mock 4	70.56	68.62	71.65	0.97
		Mock 5	75.17	74.76	75.51	0.22
		Mock 6	73.15	70.13	77.79	2.35
		Mock 7	73.90	72.73	75.33	0.76
		Total	72.28	65.37	77.79	0.69
5F-MDMB-PICA	0.07	Mock 1	68.27	64.05	75.41	3.59
		Mock 2	66.13	62.51	70.13	2.21
		Mock 3	70.61	67.15	75.07	2.34
		Mock 6	68.40	67.50	69.71	0.67
		Mock 7	66.80	64.40	69.47	1.47
		Total	68.04	62.51	75.41	0.95
AMB-CHMICA	0.05	Mock 1	76.57	71.97	84.51	3.99
		Mock 2	74.53	69.89	78.82	2.58
		Mock 3	79.20	75.69	85.41	3.12
		Mock 6	76.71	75.66	78.67	0.98
		Mock 7	74.88	72.31	77.57	1.52
		Total	76.38	69.89	85.41	1.10
AMB-FUBINACA	0.16	Mock 1	74.85	71.31	78.40	2.05
		Mock 3	72.06	68.47	75.66	3.60
		Mock 4	75.12	73.18	77.36	1.22
		Mock 5	75.23	70.62	79.06	2.47
		Mock 6	73.40	72.41	74.01	0.50
		Mock 7	78.34	74.97	81.68	1.94
		Total	75.00	68.47	81.68	0.81
5F-MDMB-PINACA	0.50	Mock 1	69.21	65.54	73.31	2.25
		Mock 3	71.94	65.40	80.28	4.39
		Mock 4	69.33	67.39	71.40	1.16
		Mock 5	69.36	66.77	71.87	1.47
		Mock 6	67.95	67.50	68.37	0.25
		Mock 7	71.43	68.96	74.71	1.71
		Total	69.87	65.40	80.28	0.87

*The p-value is from the single factor ANOVA comparing the three consecutive sets of the spiked paper samples run for each SCRA, where the alpha value was 0.05.

SECTION 4

SCRA market evolution across three Scottish Prisons
Total SCRA concentration vs seizure date

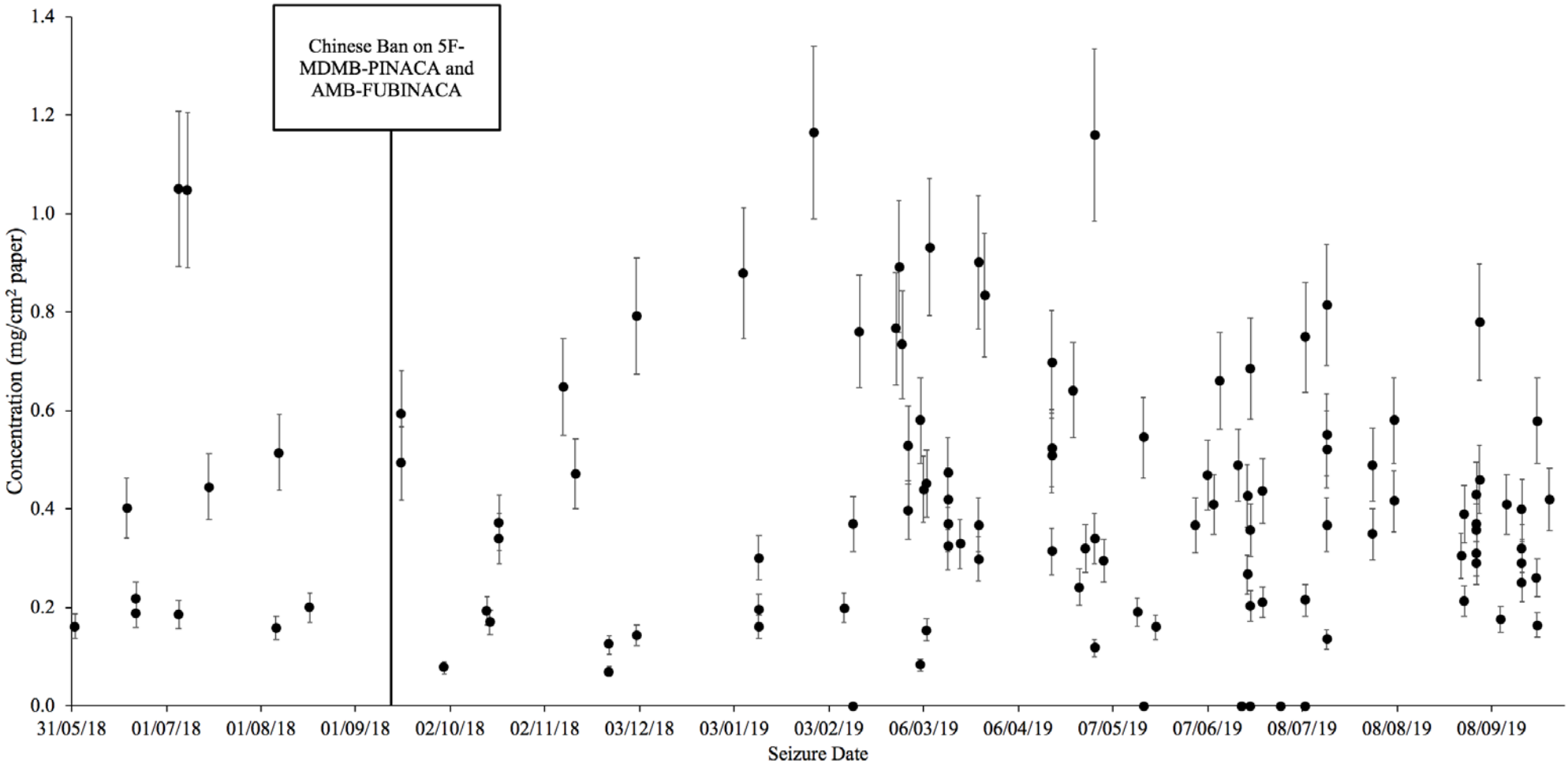


Figure S4.1. Timeline of the total synthetic cannabinoid receptor agonist concentrations of all quantitated samples with a seizure date from three Scottish prisons (n=137) where error bars represent the 15% error determined from the series of spiked samples run for method validation. Any samples on the x-axis (indicating a concentration of 0) had concentrations below the limit of quantitation (<0.05-0.09 mg/cm^2).

SECTION 5

Contextual information and analytical data for infused paper samples seized in 3 Scottish prisons and found to contain synthetic cannabinoid receptor agonists (SCRAs)

Prison	Date	Sample ID	GC-MS					UPLC-QToF-MS/MS				
			SCRA Identified	Retention Time (mins)	MS library R-match (x/1000)	m/z (a.m.u)	Conc. mg/cm^2	λmax (nm)	$[M+H]^+$ ToF-MS	Theoretical Monoisotopic Mass (amu)	Mass Error (ppm)	MS/MS Fragments
1	01/06/18	FL19/0002-2	5F-MDMB-PINACA	9.36	935	377	0.16	303	378.2190	378.2193	-0.8	346.1941, 318.1986, 233.1101(base peak), 177.0472, 145.0404
1	08/06/19	FL19/0003-1	AMB-FUBINACA	10.02	945	383	NA	302	384.1725	384.1723	0.5	352.1480, 324.1527, 281.1523, 253.0800(base peak), 225.0850
			EMB-FUBINACA	10.15	862	397	NA	301	398.1890	398.1880	2.5	352.1482, 324.15067, 253.0782(base peak), 225.0847, 109.0451
			4F-PHP	7.25	934	263	NA	NA	264.1765	264.1764	0.4	193.1042, 140.1448, 123.0250, 109.0454
1	12/06/18	FL19/0004-2	5F-MDMB-PINACA	9.42	940	377	NA	303	378.2192	378.2193	-0.3	346.1937, 318.1995, 233.1104(base peak), 177.0482, 145.0413
1	21/06/18	FL19/0006-1	5F-MDMB-PINACA	9.36	924	377	0.22	303	378.2195	378.2193	-0.5	346.1950, 318.2008, 233.1115(base peak), 177.0482, 145.0417
		FL19/0006-2	5F-MDMB-PINACA	9.35	923	377	0.19	303	378.2188	378.2193	-1.3	346.1947, 318.1990, 233.1101(base peak), 177.0469, 145.0407
1	05/07/18	FL19/0007-1	AMB FUBINACA	10.00	941	383	1.05	303	384.1719	384.1723	-1.0	352.1446, 324.1527, 281.1558, 253.0797(base peak), 225.0854
			EMB-FUBINACA	10.23	903	397	NA	301	398.1890	398.1880	2.5	352.1465, 324.1503, 253.0779(base peak), 225.0847, 109.0455
		FL19/0007-2	5F-MDMB-PINACA	9.45	932	377	0.19	303	378.2209	378.2193	4.2	346.1923, 318.1992, 233.1109(base peak), 145.0421, 121.0479
1	15/07/18	FL19/0012-3	5F-MDMB-PINACA	9.49	931	377	0.44	303	378.2202	378.2193	2.4	346.1936, 318.2013, 233.1120(base peak), 177.0493, 145.0424
1	06/08/18	FL19/0013-1	5F-MDMB-PINACA	9.42	933	377	0.16	303	378.2193	378.2193	0.0	346.1949, 318.1999, 233.1109(base peak), 177.0475, 145.0409
1	07/08/18	FL19/0014	5F-MDMB-PINACA	9.41	940	377	0.52	303	378.2201	378.2193	2.1	346.1932, 318.1985, 233.1100(base peak), 177.0474, 145.0413
1	30/09/18	FL19/0020	5F-MDMB-PINACA	9.36	935	377	0.08	303	378.2194	378.2193	0.3	346.1938, 318.1990, 233.1103(base peak), 177.0473, 145.0407
1	16/09/18	FL19/0022-4	5F-MDMB-PINACA	9.32	937	377	0.59	303	378.2203	378.2193	2.7	346.1938, 318.1990, 233.1103(base peak), 177.0473, 145.0408
		FL19/0022-5	5F-MDMB-PINACA	9.34	930	377	0.49	303	378.2186	378.2193	-1.8	346.1938, 318.1990, 233.1103(base peak), 177.0473, 145.0409
1	14/10/18	FL19/0023-2	5F-MDMB-PINACA	9.38	927	377	0.19	303	378.2193	378.2193	0.0	346.1929, 317.1983, 233.1105(base peak), 177.0490, 145.0426
1	15/10/18	FL19/0024	5F-MDMB-PINACA	9.37	937	377	0.17	303	378.2190	378.2193	-0.8	346.1939, 318.1985, 233.1103(base peak), 145.0399
1	18/10/18	FL19/0025-1	5F-MDMB-PINACA	9.47	931	377	0.34	303	378.2198	378.2193	1.3	346.1922, 318.2207, 233.1107(base peak), 177.0473, 145.0402
1	18/10/18	FL19/0027-1	5F-MDMB-PINACA	9.38	927	377	0.37	303	378.2206	378.2193	3.4	346.1945, 318.1996, 233.1112(base peak), 177.0481, 145.0421
1	12/11/18	FL19/0034	5F-MDMB-PINACA	9.35	919	377	0.47	303	378.2196	378.2193	0.8	346.1960, 318.1999, 233.1113(base peak), 177.0483, 145.0423
1	02/12/18	FL19/0039	5F-MDMB-PINACA	9.44	934	377	0.79	303	378.2197	378.2193	1.1	346.1929, 318.2005, 233.1120(base peak), 177.0490, 145.0429
1	02/12/18	FL19/0040	5F-MDMB-PINACA	9.38	939	377	0.14	303	378.2198	378.2193	1.3	346.1950, 318.1994, 233.1103(base peak), 145.0396
1	06/01/19	FL19/0043	5F-MDMB-PINACA	9.38	934	377	0.88	303	378.2201	378.2193	2.1	346.1960, 318.2005, 233.1111(base peak), 177.0485, 145.0417
1	26/01/19	FL19/0052-2	5F-MDMB-PICA	10.17	927	376	NA	292	377.2250	377.224	2.7	232.1152 (base peak), 144.0462
1	02/02/19	FL19/0057-2	5F-MDMB-PICA	10.13	931	376	NA	292	377.2249	377.224	2.4	232.1146 (base peak), 144.0448
1	29/01/19	FL19/0059-1	5F-MDMB-PINACA	9.52	933	377	1.17	303	378.2199	378.2193	1.6	346.1915, 318.2001, 233.1121(base peak), 177.0497, 145.0431
1	08/02/19	FL19/0060	5F-MDMB-PICA	10.16	929	376	0.20	292	377.2257	377.224	4.5	232.1153 (base peak), 144.0461
1	13/02/19	FL19/0061-1	5F-MDMB-PICA	10.24	929	376	0.76	292	377.2266	377.224	6.9	232.1151 (base peak), 144.0461

Prison	Date	Sample ID	GC-MS					UPLC-QToF-MS/MS				
			SCRA Identified	Retention Time (mins)	MS library R-match (x/1000)	m/z (a.m.u)	Conc. mg/cm^2	λmax (nm)	$[M+H]^+$ ToF-MS	Theoretical Monoisotopic Mass (amu)	Mass Error (ppm)	MS/MS Fragments
1	NA	FL19/0064	5F-MDMB-PICA	10.15	930	376	0.30	292	377.2253	377.224	3.4	232.1155 (base peak), 144.0461
1	N/A	FL19/0066-4	5F-MDMB-PICA	10.24	927	376	0.62	292	377.2249	377.224	2.4	232.1145 (base peak), 144.0450
		FL19/0066-5	5F-MDMB-PICA	10.23	932	376	0.61	292	377.2253	377.224	3.4	232.1160 (base peak), 144.0464
		FL19/0066-8	5F-MDMB-PICA	10.21	931	376	0.73	292	377.2261	377.224	5.6	232.1155 (base peak), 144.0464
		FL19/0066-9	5F-MDMB-PICA	10.19	934	376	0.44	292	377.2270	377.224	8.0	232.1148 (base peak), 144.0455
1	23/11/18	FL19/0067-2	CUMYL-4CN-BINACA	11.42	897	361	NA	303	361.2027	361.2028	-0.3	243.1261, 226.0999(base peak), 145.0421, 119.0879
			5F-MDMB-PICA	10.13	784	376	NA	292	377.2234	377.224	-1.6	232.1145 (base peak), 144.0478
			AMB-FUBINACA	9.95	934	383	NA	303	384.1717	384.1723	-1.6	352.1475, 324.1536, 281.1567, 253.0800(base peak), 225.0854
			5F-MDMB-PINACA	9.44	933	377	0.07	303	378.2206	378.2193	3.5	346.1932, 318.2001, 233.1120(base peak), 177.0491, 145.0432
1	23/11/18	FL19/0067-1	5F-MDMB-PINACA	9.44	938	377	0.12	303	378.2200	378.2193	1.9	346.1931, 318.1997, 233.1102(base peak), 145.0410
1	N/A	FL19/0070-1	5F-MDMB-PINACA	9.37	932	377	0.24	303	378.2196	378.2193	0.8	346.1953, 318.1993, 233.1117(base peak), 177.0488, 145.0424
		FL19/0070-2	5F-MDMB-PINACA	9.34	923	377	0.05	303	378.2195	378.2193	0.5	346.1946, 318.1996, 233.1107(base peak), 177.0477, 145.0409
1	18/06/18	FL19/0071	5F-MDMB-PINACA	9.35	918	377	0.40	303	378.2195	378.2193	0.5	346.1942, 318.1989, 233.1108(base peak), 177.0477, 145.0420
1	11/01/19	FL19/0072-1	5F-MDMB-PINACA	9.36	911	377	0.20	303	378.2184	378.2193	-2.4	346.2447, 318.2460, 233.1444(base peak), 177.0735, 145.0623
		FL19/0072-2	5F-MDMB-PICA	10.06	913	376	0.16	292	377.2227	377.224	-3.4	232.1142 (base peak), 144.0452
		FL19/0072-3	5F-MDMB-PINACA	9.38	941	377	0.30	303	378.2193	378.2193	0.0	346.1943, 318.1985, 233.1104(base peak), 177.0473, 145.0407
1	13/02/19	FL19/0074-2	5F-MDMB-PICA	10.20	931	376	NA	292	377.2259	377.224	5.0	232.1159 (base peak), 144.0473
1	08/07/19	FL19/0075-3	5F-MDMB-PINACA	9.48	933	377	1.05	303	378.2189	378.2193	-1.1	346.1918, 318.2005, 233.1112(base peak), 177.0485, 145.0421
2	N/A	FL19/0077-1	4F-MDMB-BINACA	9.27	931	363	NA	303	364.2014	364.2043	-8.0	332.1737, 304.1848, 219.0951(base peak), 177.0489, 145.0417
		FL19/0077-2	4F-MDMB-BINACA	9.13	911	363	0.94	303	364.2041	364.2043	-0.5	332.1737, 304.1848, 219.0951(base peak), 177.0489, 145.0417
2	11/02/19	FL19/0078-2	4F-MDMB-BINACA	9.11	948	363	<0.09	303	364.2039	364.2043	-1.1	332.1769, 304.1818, 219.0945(base peak), 177.0477, 145.0407
2	11/02/19	FL19/0079	5F-MDMB-PICA	10.17	933	376	0.37	291	377.2249	377.224	2.4	232.1155 (base peak), 144.0470
2	18/03/19	FL19/0081	4F-MDMB-BINACA	9.10	920	364	0.33	302	364.2034	364.2043	-2.5	332.1787, 304.1846, 219.0955(base peak), 177.0486, 145.0424
2	24/03/19	FL19/0082	4F-MDMB-BINACA	9.11	932	364	0.90	303	364.2036	364.2043	1.9	332.1759, 304.2268, 219.1258(base peak), 177.0737, 145.0627
2	26/03/19	FL19/0083	4F-MDMB-BINACA	9.20	933	364	0.83	303	364.2043	364.2043	0.0	332.1745, 304.1852, 219.0952(base peak), 177.0492, 145.0424
1	25/02/19	FL19/0091-2	5F-MDMB-PINACA	9.34	924	377	0.77	303	378.2206	378.2193	3.4	346.1928, 318.2007, 233.1116(base peak), 177.0486, 145.0425
		FL19/0091-3	5F-MDMB-PINACA	9.34	921	377	0.89	303	378.2203	378.2193	2.6	346.1931, 318.1996, 233.1100(base peak), 177.0467, 145.0408
		FL19/0091-4	5F-MDMB-PINACA	9.35	927	377	0.73	303	378.2207	378.2193	3.7	346.1926, 318.2004, 233.1107(base peak), 177.0481, 145.0415
1	01/03/19	FL19/0095-1	5F-MDMB-PINACA	9.39	929	377	0.40	303	378.2207	378.2193	3.7	346.1931, 318.1993, 233.1110(base peak), 177.0479, 145.0420
		FL19/0095-2	5F-MDMB-PINACA	9.33	919	377	NA	303	378.2200	378.2193	1.9	346.1944, 318.1989, 233.1102(base peak), 177.0463, 145.0396

Prison	Date	Sample ID	GC-MS					UPLC-QToF-MS/MS				
			SCRA Identified	Retention Time (mins)	MS library R-match (x/1000)	m/z (a.m.u)	Conc. mg/cm^2	λmax (nm)	$[M+H]^+$ ToF-MS	Theoretical Monoisotopic Mass (amu)	Mass Error (ppm)	MS/MS Fragments
1	05/03/19	FL19/0096-2	5F-MDMB-PICA	9.71	899	376	0.08	292	377.2244	377.224	1.1	377.2206, 232.1147 (base peak), 144.0447
1	05/03/19	FL19/0097	AMB-CHMICA	10.83	899	370	0.58	292	371.2346	371.2334	3.2	371.2173, 240.1396 (base peak), 144.0453
1	07/03/19	FL19/0100	5F-MDMB-PICA	10.03	913	376	0.45	292	377.2246	377.224	1.6	377.2091, 232.1151(base peak), 144.0470
1	07/03/19	FL19/0102-2	5F-MDMB-PICA	9.98	899	376	0.16*	292	377.2244	377.224	1.1	377.2183, 232.1146(base peak), 144.0444
1	08/03/19	FL19/0104	5F-MDMB-PINACA	9.36	928	377	0.93	303	378.2210	378.2193	4.5	346.1941, 318.2016, 233.1127(base peak), 177.0495, 145.0433
1	14/03/19	FL19/0105-3A	5F-MDMB-PICA	9.82	932	376	0.42	291	377.2257	377.224	4.5	232.1164 (base peak), 144.0471
		FL19/0105-3D	5F-MDMB-PICA	9.82	932	376	0.47	291	377.2258	377.224	4.8	232.1153 (base peak), 144.0463
		FL19/0105-3G	5F-MDMB-PICA	9.82	932	376	0.37	291	377.2249	377.224	2.4	232.1151 (base peak), 144.0453
		FL19/0105-3I	5F-MDMB-PICA	9.82	932	376	NA	291	377.2242	377.224	0.5	232.1146 (base peak), 144.0461
		FL19/0105-3J	5F-MDMB-PICA	9.82	932	376	0.32	291	377.2244	377.224	1.1	232.1155 (base peak), 144.0479
1	24/03/19	FL19/0107-1	5F-MDMB-PICA	9.99	919	376	0.30	292	377.2239	377.224	-0.3	377.2131, 232.1146(base peak), 144.0426
		FL19/0107-2	5F-MDMB-PICA	9.99	903	376	0.37	292	377.2243	377.224	0.8	377.2140, 232.1140(base peak), 144.0452
1	28/04/19	FL19/0110	5F-MDMB-PINACA	9.34	931	377	0.13	303	378.2185	378.2193	-2.1	346.1942, 318.1991, 233.1103(base peak), 177.0472, 145.0406
			5F-MDMB-PICA	10.02	918	376	0.19	292	377.2244	377.224	1.1	377.2243, 232.1130(base peak), 144.0449
1	01/05/19	FL19/0111-5	5F-MDMB-PINACA	9.31	916	377	0.12	303	378.2196	378.2193	0.8	346.1943, 318.1988, 233.1096(base peak), 177.0460, 145.0399
			5F-MDMB-PICA	9.99	911	376	0.22	292	377.2246	377.224	1.6	377.2249, 232.1153(base peak), 144.0481
		FL19/0111-6	AMB-FUBINACA	9.90	947	383	1.16	302	384.1724	384.1723	0.3	352.1463, 342.1522, 253.0796 (base peak), 109.0463
			EMB-FUBINACA	10.02	900	397	NA	301	398.1889	398.1880	2.3	352.1484, 324.1511, 253.0790(base peak), 225.0820, 109.0456
			4F-PHP	7.20	924	263	NA	NA	264.1772	264.1764	3.0	193.1051, 140.1460, 123.0262, 109.0469
		FL19/0111-7	5F-MDMB-PINACA	9.31	919	377	0.12	303	378.2192	378.2193	-0.3	346.1942, 318.1995, 233.1105(base peak), 177.0471, 145.0405
1	NA	FL19/0115-3	5F-MDMB-PICA	10.04	915	376	0.36	292	377.2249	377.224	2.4	377.2094, 232.1150 (base peak), 144.0461
		FL19/0115-4	5F-MDMB-PICA	10.01	915	376	0.27	292	377.2246	377.224	1.6	377.2107, 232.1145 (base peak), 144.0464
		FL19/0115-5	5F-MDMB-PINACA	9.35	930	377	0.19	303	378.2207	378.2193	3.7	346.1928, 318.1992, 233.1108(base peak), 177.0480, 145.0409
		FL19/0115-7	5F-MDMB-PICA	9.98	905	376	0.29	292	377.2239	377.224	-0.3	377.2131, 232.1138 (base peak), 144.0445
		FL19/0115-8	5F-MDMB-PICA	10.01	904	376	0.67	292	377.2239	377.224	-0.3	377.2107, 232.1140 (base peak), 144.0454
1	NA	FL19/0116	5F-MDMB-PINACA	9.28	882	377	<0.05	303	378.2176	378.2193	-4.5	346.1941, 318.1982, 233.1096(base peak), 177.0482, 145.0415
3	15/05/19	FL19/0119	4F-MDMB-BINACA	9.40	938	363	0.19	302	364.2038	364.2043	-1.4	332.1770, 304.1849, 219.0952(base peak), 177.0485, 145.0416
3	17/05/19	FL19/0120	5F-MDMB-PICA	10.39	906	376	0.55	292	377.2242	377.224	0.5	232.1141 (base peak), 144.0457
3	17/05/19	FL19/0123	5F-MDMB-PINACA	9.63	934	377	<0.05	302	378.2192	378.2193	-0.3	346.1945, 318.1990, 233.1111(base peak), 177.0477, 145.0416
3	03/06/19	FL19/0126	4F-MDMB-BINACA	9.36	923	363	0.37	303	364.2042	364.2043	-0.3	332.1763, 304.1846, 219.0958(base peak), 177.0493, 145.0427

Prison	Date	Sample ID	GC-MS					UPLC-QToF-MS/MS				
			SCRA Identified	Retention Time (mins)	MS library R-match (x/1000)	m/z (a.m.u)	Conc. mg/cm^2	λmax (nm)	$[M+H]^+$ ToF-MS	Theoretical Monoisotopic Mass (amu)	Mass Error (ppm)	MS/MS Fragments
3	07/06/19	FL19/0127	4F-MDMB-BINACA	9.27	907	363	NA	303	364.2032	364.2043	-3.0	332.1782, 304.1840, 219.0947(base peak), 177.0469, 145.0422
			MDMB-FUBINACA	10.23	803	397	NA	ND	ND	ND	ND	ND
			MMB-CHMICA	11.23	849	371	NA	ND	ND	ND	ND	ND
3	07/06/19	FL19/0129	4F-MDMB-BINACA	9.38	872	363	0.47	303	364.2033	364.2043	-2.7	332.1753, 304.1844, 219.0948(base peak), 177.0486, 145.0409
3	11/06/19	FL19/0131	5F-MDMB-PICA	9.22	883	376	0.66	292	377.2252	377.224	3.2	232.1141 (base peak), 144.0455
3	18/06/19	FL19/0132-1	4F-MDMB-BINACA	9.29	942	363	<0.09	303	364.2033	364.2043	-2.7	332.1759, 304.2268, 219.1258(base peak), 177.0737, 145.0627
3	18/06/19	FL19/0133-1	4F-MDMB-BINACA	9.28	852	363	<0.09	303	364.2022	364.2043	-5.8	332.1765, 304.1813, 219.0932(base peak), 177.0468, 145.0401
3	21/06/19	FL19/0135-1	4F-MDMB-BINACA	9.32	919	363	0.36	303	364.2027	364.2043	-4.4	332.2277, 304.2282, 219.1266(base peak), 177.0743, 145.0629
		FL19/0135-2	5F-MDMB-PICA	10.44	925	376	0.69	292	377.2251	377.224	2.9	232.1137 (base peak), 144.0446
		FL19/0135-3	4F-MDMB-BINACA	9.29	942	363	<0.09	303	364.2029	364.2043	-3.8	332.1779, 304.1830, 219.0942(base peak), 177.0477, 145.0404
3	21/06/19	FL19/0136	5F-MDMB-PICA	10.44	923	376	0.20	292	377.2251	377.224	2.9	232.1157 (base peak), 144.0473
3	25/06/19	FL19/0138-1	5F-MDMB-PICA	10.39	922	376	0.21	292	377.2242	377.224	0.5	232.1490 (base peak), 144.0676
3	21/05/19	FL19/0141	5F-MDMB-PICA	9.72	930	376	0.16	292	377.2253	377.224	3.4	232.1142 (base peak), 144.0457
3	17/06/19	FL19/0142-1	MDMB-4en-PINACA	8.84	938	357	0.38	302	358.2132	358.2131	0.3	326.1877, 298.1921, 213.1033(base peak), 171.0581, 145.0404
			4F-MDMB-BINACA	8.94	702	363	0.11	303	364.2027	364.2018	2.5	332.1783, 304.1830, 219.0950(base peak), 177.0485, 145.0415
3	20/06/19	FL19/0143-5	5F-MDMB-PICA	9.75	923	376	0.27	292	377.2254	377.224	3.7	232.1150 (base peak), 144.0470
		FL19/0143-8	5F-MDMB-PICA	9.71	932	376	NA	292	377.2251	377.224	2.9	232.1189 (base peak), 144.0676
3	24/04/19	FL19/0145-1	5F-MDMB-PICA	9.81	929	376	0.64	NA	NA	NA	NA	NA
3	04/05/19	FL19/0146	4F-MDMB-BINACA	8.94	936	363	0.29	303	364.2018	364.2043	-6.9	332.1743, 304.1847, 219.0946(base peak), 177.0487, 145.0413
			5F-MDMB-PICA	9.85	928	376	NA	292	377.2250	377.224	2.7	232.1143 (base peak), 144.0455
3	06/03/19	FL19/0148-1	5F-MDMB-PICA	9.68	934	376	NA	292	377.2254	377.224	3.7	232.1153 (base peak), 144.0466
3	17/08/18	FL19/0149	AMB-FUBINACA	9.60	940	383	0.20	302	384.1740	384.1723	4.4	352.1474, 342.152217, 253.0798 (base peak), 109.0464
			4F-PHP	**7.05**	957	263	NA	NA	264.1772	264.1764	1.9	193.1015, 140.1449, 123.0253, 109.0460
3	09/06/19	FL19/0150	MDMB-4en-PINACA	8.86	948	357	0.25	303	358.2130	358.2131	-0.3	326.1844, 298.1916, 213.1048(base peak), 171.0602, 145.0427
			4F-MDMB-BINACA	8.88	894	363	0.15	303	364.2042	364.2043	-0.3	332.1738, 304.1835, 219.0948(base peak), 177.0482, 145.0422
3	26/04/19	FL19/0151	4F-MDMB-BINACA	8.88	928	363	0.24	303	364.2039	364.2043	-1.1	332.2257, 304.2274, 219.1268(base peak), 177.0740, 145.0626
3	08/11/18	FL19/0157-1	5F-MDMB-PINACA	9.20	932	377	0.65	303	378.2188	378.2193	-1.3	346.1932, 318.2004, 233.1112(base peak), 177.0481, 145.0421
3	NA	FL19/0158	5F-MDMB-PICA	9.70	932	376	<0.09	292	377.2249	377.224	2.4	232.1489 (base peak), 144.00679
3	17/04/19	FL19/0164-1`	5F-MDMB-PICA	9.76	932	376	0.31	292	377.2264	377.224	6.4	232.1154 (base peak), 144.0470
		FL19/0164-2	5F-MDMB-PICA	9.79	926	376	0.52	292	377.2260	377.224	5.3	232.1149 (base peak), 144.0462

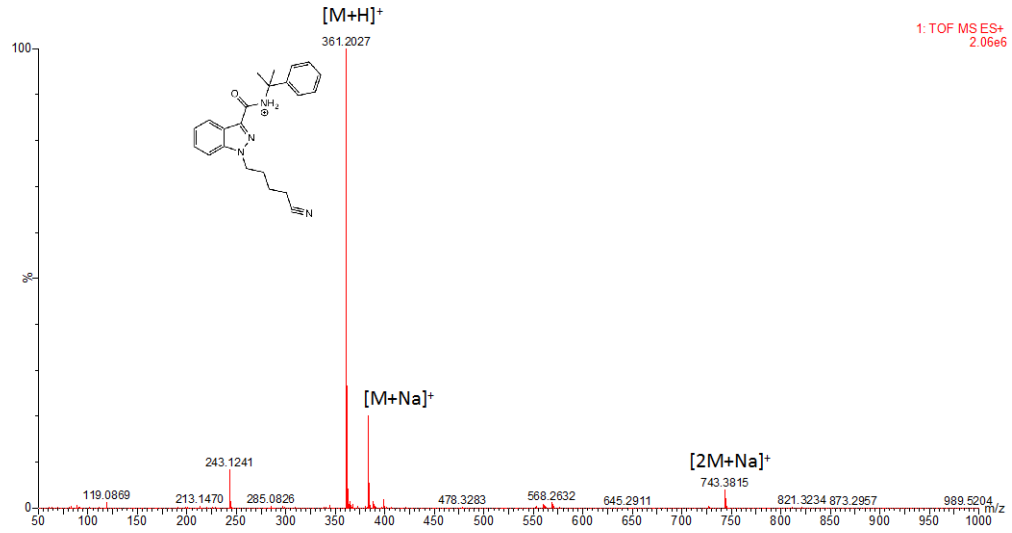
Prison	Date	Sample ID	GC-MS					UPLC-QToF-MS/MS				
			SCRA Identified	Retention Time (mins)	MS library R-match (x/1000)	m/z (a.m.u)	Conc. mg/cm^2	λmax (nm)	$[M+H]^+$ ToF-MS	Theoretical Monoisotopic Mass (amu)	Mass Error (ppm)	MS/MS Fragments
3	17/04/19	FL19/0164-3	4F-MDMB-BINACA	8.94	941	363	0.51	303	364.2038	364.2043	-1.4	332.1740, 304.1846, 219.0947(base peak), 177.0493, 145.0421
		FL19/0164-4	5F-MDMB-PICA	9.77	926	376	0.70	292	377.2264	377.224	6.4	232.1150 (base peak), 144.0467
1	05/07/19	FL19/0178-3	AMB-FUBINACA	9.58	941	383	NA	301	384.1720	378.2193	0.8	352.1441, 225.0854, 253.0797(base peak), 334.1526, 109.0471
			EMB-FUBINACA	9.68	898	397	NA	NA	NA	NA	NA	NA
1	01/07/19	FL19/0180	4F-MDMB-BINACA	8.80	938	363	NA	303	364.2033	364.2043	2.7	332.1776, 304.1829, 219.0947(base peak), 177.0482, 145.0430
1	09/07/19	FL19/0181-1	5F-MDMB-PICA	9.66	919	376	0.75	291	377.2238	377.2240	0.5	232.1147(base peak), 144.0461
		FL19/0181-2	4F-MDMB-BINACA	8.79	940	363	<0.09	303	364.2032	364.2043	3.0	332.1776, 304.1829, 219.0947(base peak), 177.0482, 145.0430
		FL19/0181-3	MDMB-4en-PINACA	8.77	927	357	NA	303	358.2129	358.2131	0.6	326.1866, 298.1914, 213.1040(base peak), 171.0585, 145.0410
			5F-MDMB-PICA	9.63	918	376	0.22	302	377.2245	377.2240	-1.3	232.1150(base peak), 144.0467
1	16/07/19	FL19/0183	4F-MDMB-BINACA	8.81	942	363	0.14	303	364.2034	364.2043	2.5	332.1758, 304.1835, 219.0949(base peak), 177.0455, 145.0411
1	16/07/19	FL19/0184	4F-MDMB-BINACA	8.80	945	363	0.81	303	364.2029	364.2043	3.8	332.1736, 304.1836, 219.0947(base peak), 177.0488, 145.0417
1	16/07/19	FL19/0185	4F-MDMB-BINACA	8.81	940	363	0.52	303	364.2032	364.2043	3.0	332.1760, 304.1838, 219.0956(base peak), 177.0495, 145.0430
1	16/07/19	FL19/0186	4F-MDMB-BINACA	8.82	937	363	0.37	303	264.2032	364.2043	3.0	332.1787, 304.1841, 219.0950(base peak), 177.0485, 145.0419
1	NA	FL19/0188	5F-MDMB-PICA	9.69	916	376	0.52	292	377.2237	377.2240	0.8	232.1156(base peak), 144.0466
1	31/07/19	FL19/0189-1	5F-MDMB-PICA	9.67	914	376	0.49	292	377.2240	377.2240	0.0	232.1156(base peak), 144.0467
		FL19/0189-2	5F-MDMB-PICA	9.65	917	376	0.35	292	377.2241	377.2240	-0.3	232.1152(base peak), 144.0466
1	25/06/19	FL19/0190	4F-MDMB-BINACA	8.82	940	363	0.44	303	364.2031	364.2043	4.7	332.1749, 304.1834, 219.0954(base peak), 177.0484, 145.0422
1	16/07/19	FL19/0191	4F-MDMB-BINACA	8.82	941	363	0.55	303	364.2031	364.2043	3.3	332.1754, 304.1837, 219.0956(base peak), 177.0487, 145.0424
1	N/A	FL19/0194	5F-MDMB-PICA	9.67	925	376	0.21	292	377.2240	377.2240	0.0	232.1146(base peak), 144.0450
1	N/A	FL19/0196	4F-MDMB-BINACA	8.81	931	363	0.24	303	364.2029	364.2043	3.8	332.1743, 304.1840, 219.0962(base peak), 177.0494, 145.0427
			MDMB-4en-PINACA	8.79	941	357	0.15	303	358.2123	358.2131	2.2	326.1847, 298.1933, 213.1040(base peak), 171.0607, 145.0424
1	29/08/19	FL19/0197-2	4F-MDMB-BINACA	8.81	941	363	0.31	303	364.2030	364.2043	3.6	332.1755, 304.1839, 219.0950(base peak), 177.0480, 145.0418
1	13/09/19	FL19/0205	MDMB-4en-PINACA	9.15	896	357	0.16	303	358.2133	358.2131	-0.6	326.1887, 298.1935, 213.1039(base peak), 171.0580, 145.0412
			4F-MDMB-BINACA	9.19	928	363	0.25	303	364.2034	364.2043	2.5	332.1744, 304.1843, 219.0954(base peak), 177.0491, 145.0427
1	03/09/19	FL19/206-B	MDMB-4en-PINACA	9.14	906	357	0.36	303	358.2132	358.2131	-0.3	326.1877, 298.1936, 213.1046(base peak), 171.0612, 145.0430
		FL19/206-C	MDMB-4en-PINACA	9.12	883	357	0.16	303	358.2130	358.2131	0.3	326.1878, 298.1941, 213.1039(base peak), 171.0595, 145.0413
			4F-MDMB-BINACA	9.15	899	363	0.21	303	364.2037	364.2043	1.6	332.1771, 304.1831, 219.0942(base peak), 177.0473, 145.0406
		FL19/206-D	MDMB-4en-PINACA	9.13	868	357	0.21	303	358.2131	358.2131	0.0	326.1875, 298.1927, 213.1040(base peak), 171.0576, 145.0402
			4F-MDMB-BINACA	9.16	930	363	0.22	303	364.2036	364.2043	1.9	332.1778, 304.1840, 219.0948(base peak), 177.0484, 145.0409
		FL19/206-E	MDMB-4en-PINACA	9.13	906	357	0.29	303	358.2130	358.2131	0.3	326.1877, 298.1928, 213.1034(base peak), 171.0579, 145.0401

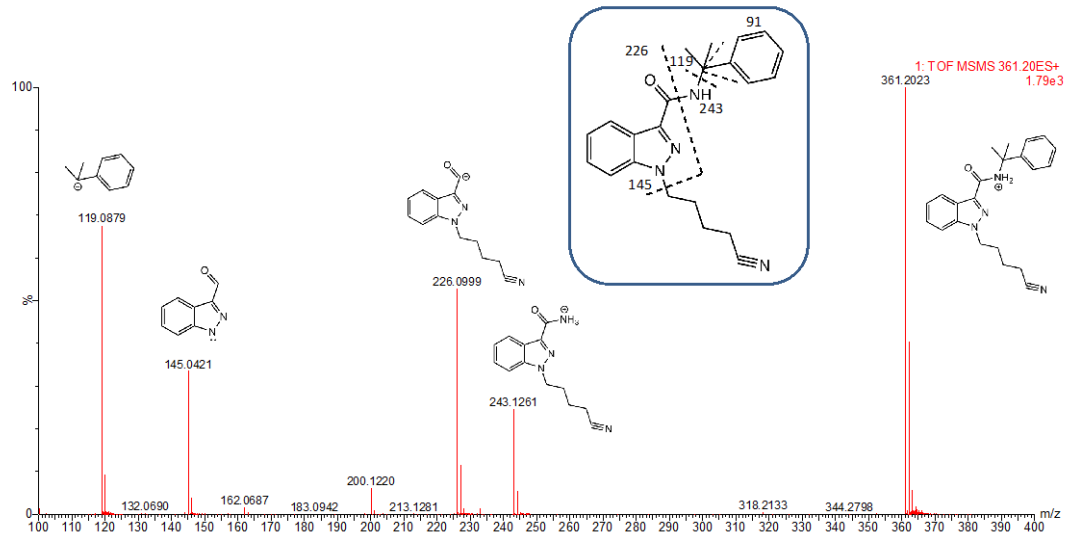
Prison	Date	Sample ID	GC-MS					UPLC-QToF-MS/MS				
			SCRA Identified	Retention Time (mins)	MS library R-match (x/1000)	m/z (a.m.u)	Conc. mg/cm^2	λmax (nm)	$[M+H]^+$ ToF-MS	Theoretical Monoisotopic Mass (amu)	Mass Error (ppm)	MS/MS Fragments
1	03/09/19	FL19/206-F	MDMB-4en-PINACA	9.12	919	357	0.10	303	358.2129	358.2131	0.6	326.1874, 298.1922, 213.1037(base peak), 171.0601, 145.0421
			4F-MDMB-BINACA	9.16	931	363	0.21	303	364.2035	364.2043	2.2	332.1768, 304.1841, 219.0951(base peak), 177.0485, 145.0430
		FL19/206-G	MDMB-4en-PINACA	9.12	891	357	NA	303	358.2126	358.2131	1.4	326.1873, 298.1928, 213.1032(base peak), 171.0571, 145.0400
1	07/08/19	FL19/0207-1	5F-MDMB-PICA	10.18	930	376	0.42	292	377.2237	377.2240	0.8	232.1156(base peak), 144.0466
		FL19/0207-2	5F-MDMB-PICA	10.20	930	376	0.47	292	377.2234	377.2240	1.6	232.1157(base peak), 144.0467
			4F-MDMB-BINACA	9.13	926	363	0.11	303	364.2027	364.2043	4.4	332.1779, 304.1834, 219.0952(base peak), 177.0489, 145.0419
1	18/09/19	FL19/0210	MDMB-4en-PINACA	9.12	926	357	<0.07	303	358.2130	358.2131	0.3	326.1884, 298.1925, 213.1033(base peak), 171.0575, 145.0404
			4F-MDMB-BINACA	9.15	924	363	0.15	303	364.2033	364.2043	2.7	332.1788, 304.1841, 219.0954(base peak), 177.0482, 145.0416
			5F-MDMB-PICA	10.2	913	376	<0.08	292	377.2236	377.2240	1.1	232.1145(base peak), 144.0449
1	18/09/19	FL19/0215-E	MDMB-4en-PINACA	9.12	903	357	0.13	303	358.2126	358.2131	1.4	326.1883, 298.1933, 213.1036(base peak), 171.0599, 145.0413
			4F-MDMB-BINACA	9.16	948	363	0.19	303	364.2033	364.2043	2.7	332.1768, 304.1843, 219.0942(base peak), 177.0482, 145.0422
			5F-MDMB-PICA	10.11	927	376	<0.08	292	377.2240	377.2240	0.0	232.1150(base peak), 144.0458
		FL19/0215-F	MDMB-4en-PINACA	9.129	932	357	0.15	303	358.2125	358.2131	1.7	326.1881, 298.1934, 213.1044(base peak), 171.0613, 145.0433
			4F-MDMB-BINACA	9.164	934	363	0.20	303	364.2035	364.2043	2.2	332.1755, 304.1841, 219.0945(base peak), 177.0487, 145.0421
			5F-MDMB-PICA	10.108	924	376	<0.09	292	377.2237	377.2240	0.8	232.1139(base peak), 144.0457
		FL19/0215-G	MDMB-4en-PINACA	9.118	920	357	0.15	303	358.2127	358.2131	1.1	326.1878, 298.1939, 213.1047(base peak), 171.0604, 145.0437
			4F-MDMB-BINACA	9.152	944	363	0.18	303	364.2035	364.2043	2.2	332.1778, 304.1835, 219.0952(base peak), 177.0486, 145.0418
		FL19/0215-H	MDMB-4en-PINACA	9.106	909	357	NA	303	358.2119	358.2131	3.3	326.1879, 298.1932, 213.1036(base peak), 171.0593, 145.0402
			4F-MDMB-BINACA	9.135	912	363	NA	303	364.2029	364.2043	3.8	332.1788, 304.1832, 219.0941(base peak), 177.0478, 145.0404
1	11/09/19	FL19/0219	MDMB-4en-PINACA	9.124	942	357	0.18	303	358.2126	358.2131	1.4	326.1871, 298.1937, 213.1046(base peak), 171.0580, 145.0423
1	04/09/19	FL19/0224-1	MDMB-4en-PINACA	9.138	922	357	0.29	303	358.2126	358.2131	1.4	326.1871, 298.1935, 213.1036(base peak), 171.0767, 145.0416
			4F-MDMB-BINACA	9.18	941	363	0.44	303	364.2032	364.2043	3.0	332.1739, 304.1843, 219.0955(base peak), 177.0491, 145.0429
			5F-MDMB-PICA	10.09	869	376	<0.10	292	377.2240	377.2240	0.0	232.1138(base peak), 144.0448
		FL19/0224-1	4F-MDMB-BINACA	9.169	943	363	0.36	303	364.2029	364.2043	3.8	332.1742, 304.1841, 219.0943(base peak), 177.0484, 145.0415
			5F-MDMB-PICA	10.079	802	376	<0.09	292	377.2230	377.2240	2.7	232.1136(base peak), 144.0451
1	27/09/19	FL19/0226	MDMB-4en-PINACA	9.141	943	357	0.42	303	358.2123	358.2131	2.2	326.1871, 298.1924, 213.1032(base peak), 171.0571, 145.0408
1	23/09/19	FL19/0232-2	MDMB-4en-PINACA	9.107	915	357	0.09	303	358.2127	358.2131	1.1	326.1887, 298.1943, 213.1046(base peak), 171.0596, 145.0423
			4F-MDMB-BINACA	9.135	935	363	0.17	303	364.2037	364.2043	1.6	332.1791, 304.1851, 219.0955(base peak), 177.0495, 145.0424
		FL19/0232-3	4F-MDMB-BINACA	9.114	942	357	0.16	303	364.2039	364.2043	1.1	332.1773, 304.1845, 219.0944(base peak), 177.0480, 145.0408
1	23/09/19	FL19/0233-1A	MDMB-4en-PINACA	9.141	939	357	0.58	303	358.2123	358.2131	2.2	326.1887, 298.1934, 213.1040(base peak), 171.0593, 145.0428

SECTION 6

Low energy (6V) ToF-MS and high energy (10-30V) MS/MS spectra for tentative confirmation of Cumyl-4CN-BINACA and 4F-PHP identified in seized samples

(a) Sample FL19/0067-2: HRMS spectrum of Cumyl-4CN-BINACA and product ion spectra





(b) HRMS spectrum of 4F-PHP and proposed product ion fragments
Example: sample FL19/0003