

Supporting Information for:

On the fate of butyl methoxydibenzoylmethane (avobenzone) in coral tissue and its effect on coral metabolome

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Full experimental details

Pocillopora damicornis. Samples of the coral *P. damicornis* were collected in Oman and were acclimated for more than one year in tanks at the Banyuls Oceanological Observatory. Corals were maintained in artificial seawater (ASW) prepared with reverse osmosis purified water and Reef Salt SeaChem salts. Salinity was adjusted to 36 g/L, pH = 8, and the temperature was set at 24 °C. All experiments were conducted with the same ASW.

Preparation of Coral for Exposition to Solar Filters. Coral pieces (1–1.5 cm) were cut from branch tips from the same mother colony. Each piece was attached to a fishing line, and the coral pieces were then suspended each on one ~5–6 cm plastic grid, making sure the lines had the appropriate length so that the coral pieces will stand in the middle of exposure beakers during the assay. Each suspended coral nubbin (five replicates) was clamped to grid above the aquarium of origin, thereby immersing the pieces. The suspended pieces were acclimatized for approximately 1 month before the assay to allow for full healing.

Exposure Setup. Beakers (250 mL) were filled with ASW (200 mL). BM ($\geq 98.0\%$, Sigma-Aldrich) was dissolved in DMSO at concentrations of 400, 120, 20, and 2 $\mu\text{g/mL}$. Each of these solutions (500 μL) was added into separate beakers, resulting in final concentrations of 1000, 300, 50, and 5 $\mu\text{g/L}$. DMSO (500 μL) was used as a negative control, and the DMSO concentration was 0.25% v/v in all beakers. The suspended coral pieces were dipped into the beakers, with the grid positioning the pieces halfway into the water. Gentle bubbling in the beakers was maintained using aquarium air pumps equipped with a Teflon tubing with Pasteur pipettes tips. Homogeneous lighting was set to 250 $\mu\text{mol/m}^2/\text{s}$, with a cycle of 10 h of day and 14 h of night. The corals were transferred every 24 h to a new beaker prepared in the same way. The total exposure lasted for 7 days. Pictures were taken every 24 h to monitor coral polyps. Coral exposure at 1000 $\mu\text{g/L}$ BM was repeated in a separate experiment to confirm the result.

Extraction. After 7 days, the coral pieces were collected and the fishing lines were removed with a scalpel. Each coral piece was placed into a 20 mL test tube, covered with MeOH/ acetonitrile 1/1, and sonicated for 20 min. Once the polyps were dissolved, the solvent was evaporated and the dry samples were kept at $-80\text{ }^{\circ}\text{C}$ until analysis. All solvents used for extraction and profiling were LC-MS gradient grade (Biosolve, Dieuze, France).

UHPLC-HRMS Profiling. High-resolution MS/MS analyses were conducted with a Thermo UHPLC-HRMS system. Analyses were performed in the electrospray positive ionization mode in the range of 133.4–2000 Da in centroid mode. The mass detector was an Orbitrap MS/MS FT Q-Exactive focus mass spectrometer. The analyses were conducted in FullMS data dependent MS² mode. In FullMS, the resolution was set to 70000, and the AGC target was 3×10^6 . In MS², the resolution was 17500, AGC target 10^5 , isolation window 0.4 Da, and stepped normalized collision energy 15/30/45 was used, with 6 s dynamic exclusion. The lock mass option was set for ion at m/z 144.98215, corresponding to $\text{Cu}(\text{CH}_3\text{CN})^{2+}$. The UHPLC column was a Phenomenex Luna Omega polar C-18 150 mm \times 2.1 mm, 1.6 μm . The column temperature was set to 42 °C, and the flow rate was 0.5 mL·min⁻¹. The solvent system was a mixture of water (solution A) with increasing proportions of acetonitrile (solution B), both solvents modified with 0.1% formic acid. The gradient was as follows: 2%

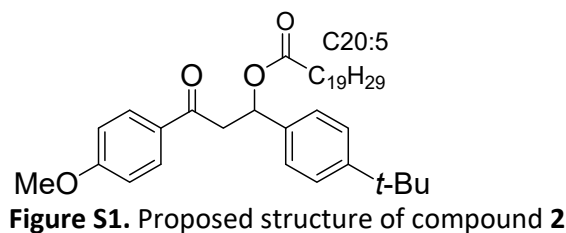
B 3 min before injection, then from 1 to 13 min, a shark fin gradient increase of B up to 100% (curve 2), followed by 100% B for 5 min. The flow was diverted (not injected into the mass spectrometer) before injection, up to 1 min after injection. The coral extracts were dissolved in MeOH (1 mg/mL) by sonication, and 2 μ L was injected onto the column. Standard of sythetic palmitic acid dihydroBM ester (**7**) in acetonitrile (0.1 μ g/mL, 1 μ L injected) was analyzed with the same method.

Metabolomic Analyses. Profiles were analyzed with Compound Discoverer (CD) 2.1 (ThermoFisher, Villebon, France). Coral exposed to DMSO was used as the reference metabolome, and blank injections were used to remove irrelevant ion peaks (ion peak is considered only if the signal is at least 5 times more intense than in the blank). An untargeted metabolomic workflow was used. This workflow finds and identifies the differences between samples and performs retention time alignment, unknown compound detection, and compound grouping across all samples. The workflow predicts elemental compositions for all compounds, fills gaps across all samples, hides chemical background (using Blank samples), identifies compounds using mzCloud (ddMS²) and ChemSpider (formula or exact mass), performs similarity searches for all compounds with ddMS2 data using mzCloud, and calculates a differential analysis (t-test or ANOVA) and determines p values, adjusted p values, ratios, and fold change. The retention time window was set to 2–17 min. The maximum shift for alignment was 0.1 min, the maximum mass tolerance was 2 ppm and the minimum peak intensity was 2×10^6 . Statistical analyses (Principal Component Analysis [PCA], volcano plots) were performed with CD using centered and scaled data.

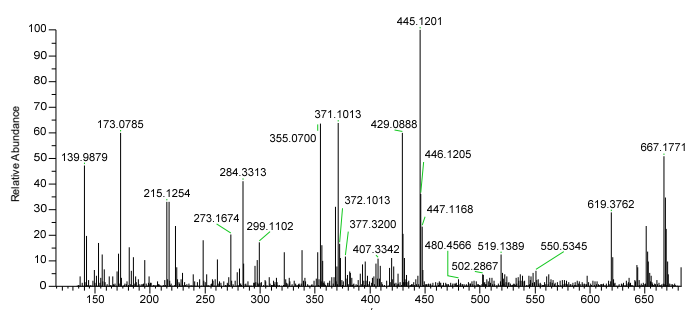
Predicted toxicity of BM derivatives compared to BM. The prediction of BM derivatives toxicity in aquatic organisms was carried out using an ecological structure-activity relationships (ECOSAR) predictive model. This model estimates acute and chronic toxicity concentrations for aquatic organisms by analyzing chemical structure similarity, using data reported to USEPA. To accomplish this task, ECOSAR V 2.2 was utilized in the study, which is distributed by the EPA (<https://www.epa.gov/tsc-screening-tools/ecological-structure-activity-relationships-ecosar-predictive-model>). For acute toxicity, LC₅₀ values on green algae (EC₅₀ at 96 h), daphnids (LC₅₀ at 48 h), and fish (LC₅₀ at 96 h) were considered. ECOSAR also generated predicted chronic toxicity information (Chronic Value, ChV) using the geometric mean of the predicted lowest observed effect concentration (LOEC) and the predicted no observed effect concentration (NOEC). Results for compounds **1**, **4**, **7**, **11** and **12** and reported in Table S1.

Table S1. ECOSAR v2.2 predicted toxicity of BM derivatives compared to BM (**1**)

Cmpd.	Acute (mg/L)			Chronic (mg/L)		
	Fish	Daphnid	Green Algae	Fish	Daphnid	Green Algae
1	0.64	0.71	0.26	0.036	0.034	0.16
4	5.2×10^{-06}	5.1×10^{-06}	2.7×10^{-07}	1.4×10^{-06}	5.6×10^{-06}	2.5×10^{-07}
7	4.6×10^{-05}	5.1×10^{-05}	3.7×10^{-06}	1.0×10^{-05}	4.2×10^{-05}	2.9×10^{-06}
11	4.0×10^{-04}	5.0×10^{-04}	4.9×10^{-05}	7.3×10^{-05}	3.1×10^{-04}	3.3×10^{-05}
12	0.0026	0.0051	0.0039	8.6×10^{-05}	2.7×10^{-04}	0.0055



BM_1mg_R3 #3222 RT: 13.18 AV: 1 NL: 1.48E+007
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]



BM_1mg_R3 #3222 RT: 13.18 AV: 1 NL: 4.29E+006
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

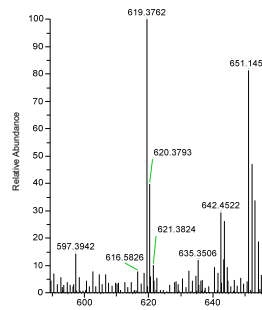


Figure S2. ESI⁺-MS spectrum showing ion [2+Na]⁺ at *m/z* 619.3762, with expansion on the right

Corail_BM1000_R5_17-01-2019_FulIMS-PRM_#2195 RT: 12.47 AV: 1 NL: 5.85E+005
T: FTMS + p ESI Full ms2 619.3758@hcd30.00 [50.0000-650.0000]

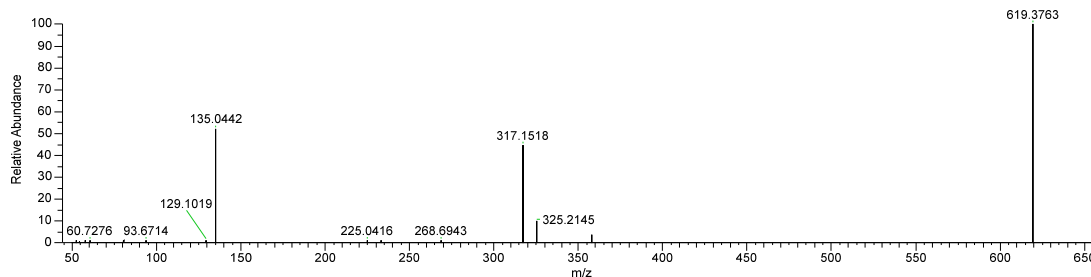
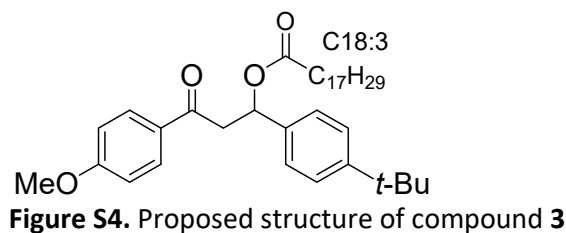


Figure S3. Collision-induced fragmentation spectrum of [2+Na]⁺ at *m/z* 619.3762



BM_1mg_R3 #3305-3320 RT: 13.46-13.51 AV: 8 SB: 9 13.43-13.46, 13.51-13.53 NL: 3.37E+006
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

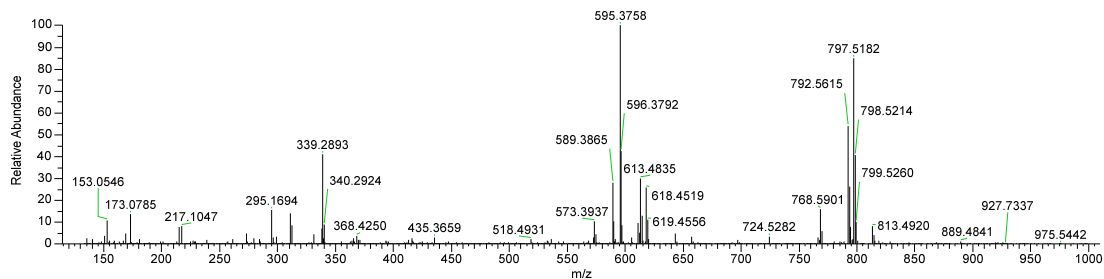


Figure S5. ESI⁺-MS spectrum showing ion [3+Na]⁺ at m/z 595.3758

BM_1mg_R3 #3313 RT: 13.49 AV: 1 NL: 5.54E+005
T: FTMS + c ESI d Full ms2 595.3758@hcd30.00 [50.0000-625.0000]

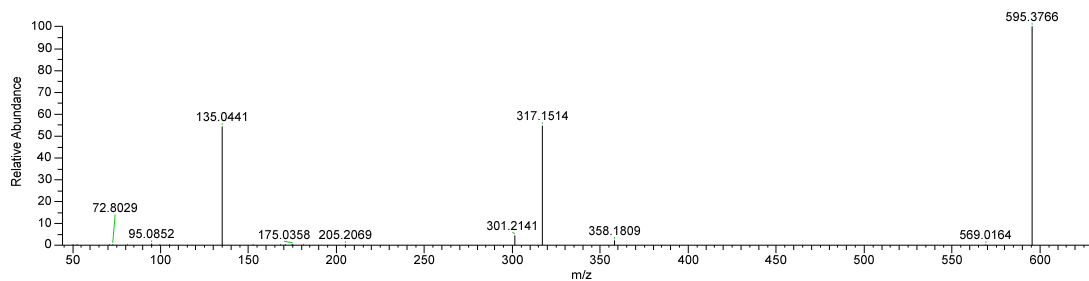


Figure S6. Collision-induced fragmentation spectrum of [3+Na]⁺ at m/z 595.3758

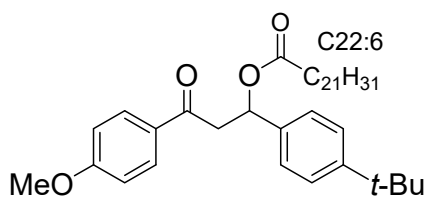


Figure S7. Proposed structure of compound 4

BM_1mg_R3 #3322-3340 RT: 13.52-13.58 AV: 10 SB: 13 13.45-13.51, 13.61-13.64 NL: 4.22E+006
T: FTMS + c ESI d Full lock ms [133.4000-2000.0000]

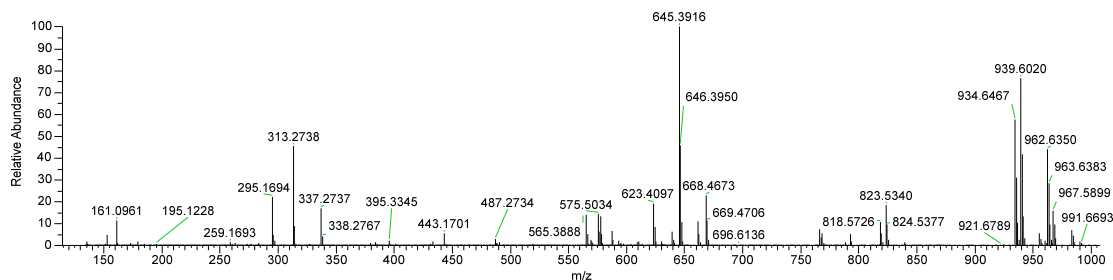


Figure S8. ESI⁺-MS spectrum showing ion [4+Na]⁺ at m/z 645.3916

BM_1mg_R3 #3329 RT: 13.54 AV: 1 NL: 3.00E+005
T: FTMS + c ESI d Full ms2 645.3915@hcd30.00 [50.0000-675.0000]

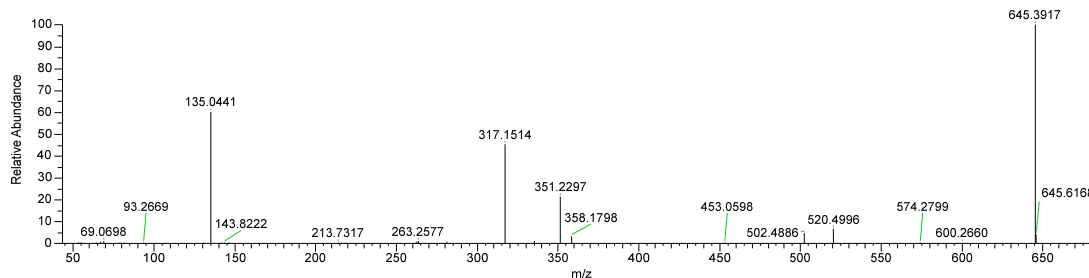


Figure S9. Collision-induced fragmentation spectrum of [4+Na]⁺ at m/z 645.3916

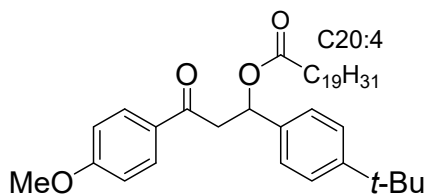


Figure S10. Proposed structure of compound 5

BM_1mg_R3 #3417-3435 RT: 13.84-13.9 AV: 9 SB: 10 13.95-13.99 , 13.80-13.83 NL: 6.65E+006
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

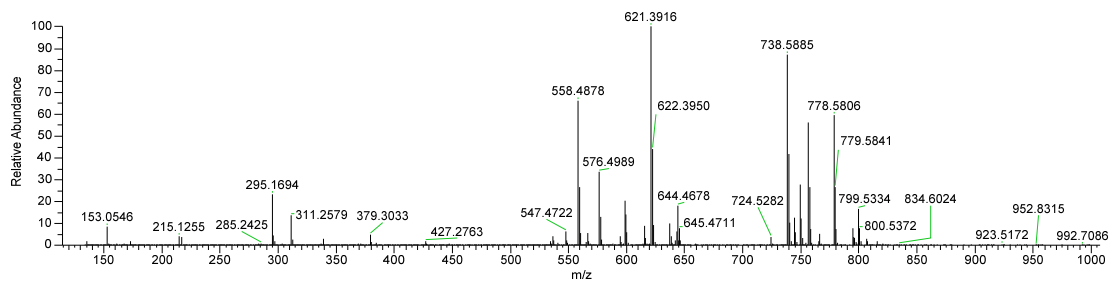


Figure S11. ESI⁺-MS spectrum showing ion [5+Na]⁺ at *m/z* 621.3916

BM_1mg_R3 #3423 RT: 13.86 AV: 1 NL: 8.81E+005
T: FTMS + c ESI d Full ms2 621.3917@hcd30.00 [50.0000-650.0000]

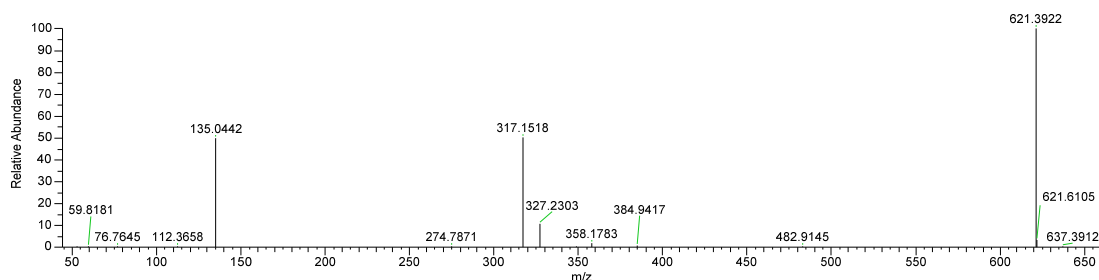


Figure S12. Collision-induced fragmentation spectrum of [5+Na]⁺ at *m/z* 621.3916

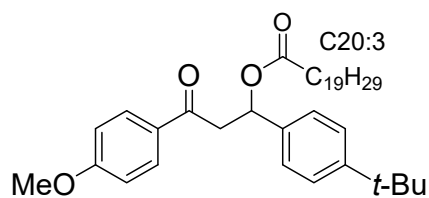


Figure S13. Proposed structure of compound 6

BM_1mg_R3 #3576-3594 RT: 14.38-14.44 AV: 10 SB: 10 14.36-14.38 , 14.49-14.52 NL: 5.49E+006
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

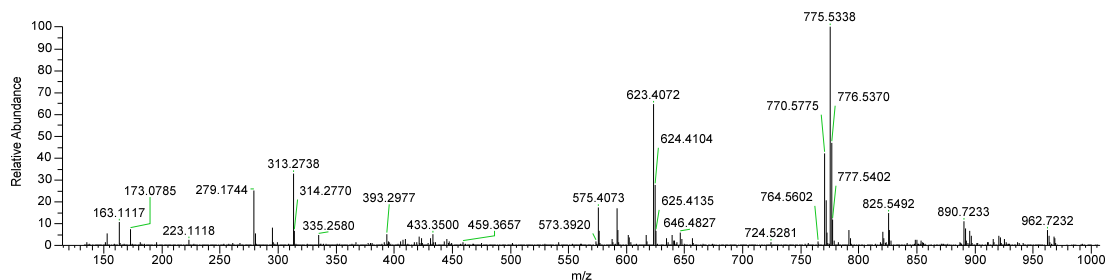


Figure S14. ESI⁺-MS spectrum showing ion [6+Na]⁺ at *m/z* 623.4072

BM_1mg_R3 #3585 RT: 14.41 AV: 1 NL: 5.06E+005
T: FTMS + c ESI d Full ms2 623.4072@hcd30.00 [50.0000-655.0000]

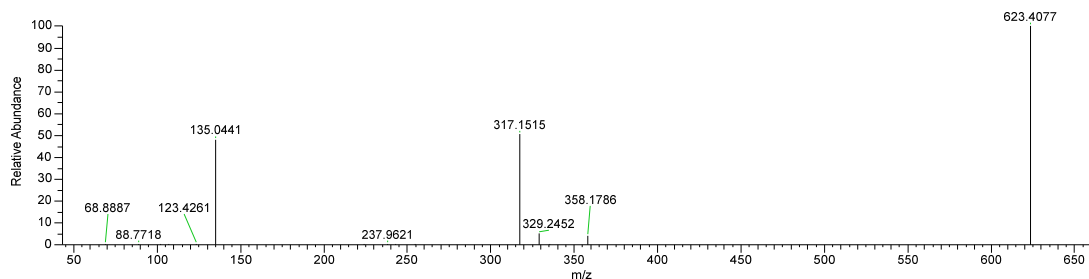


Figure S15. Collision-induced fragmentation spectrum of $[6+Na]^+$ at m/z 623.4072

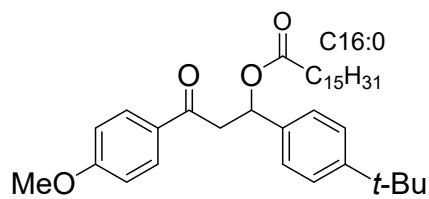


Figure S16. Proposed structure of compound 7

BM_1mg_R3 #3713-3728 RT: 14.84-14.89 AV: 8 SB: 7 14.81-14.84, 14.90-14.92 NL: 5.83E+007
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

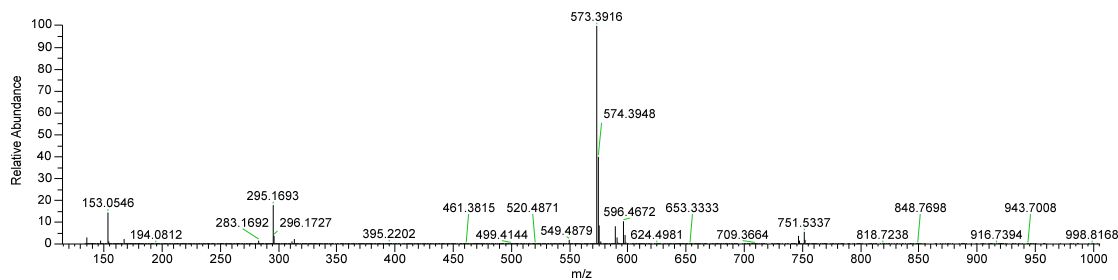


Figure S17. ESI⁺-MS spectrum showing ion $[7+Na]^+$ at m/z 573.3916

BM_1mg_R3 #3711 RT: 14.84 AV: 1 NL: 5.02E+005
T: FTMS + c ESI d Full ms2 573.3914@hcd30.00 [50.0000-605.0000]

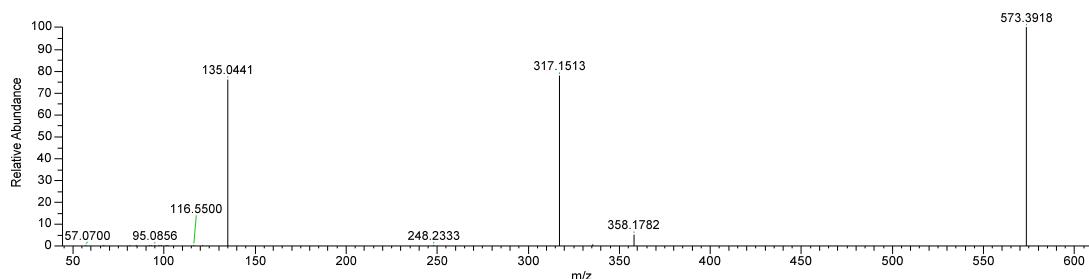


Figure S18. Collision-induced fragmentation spectrum of $[7+Na]^+$ at m/z 573.3916

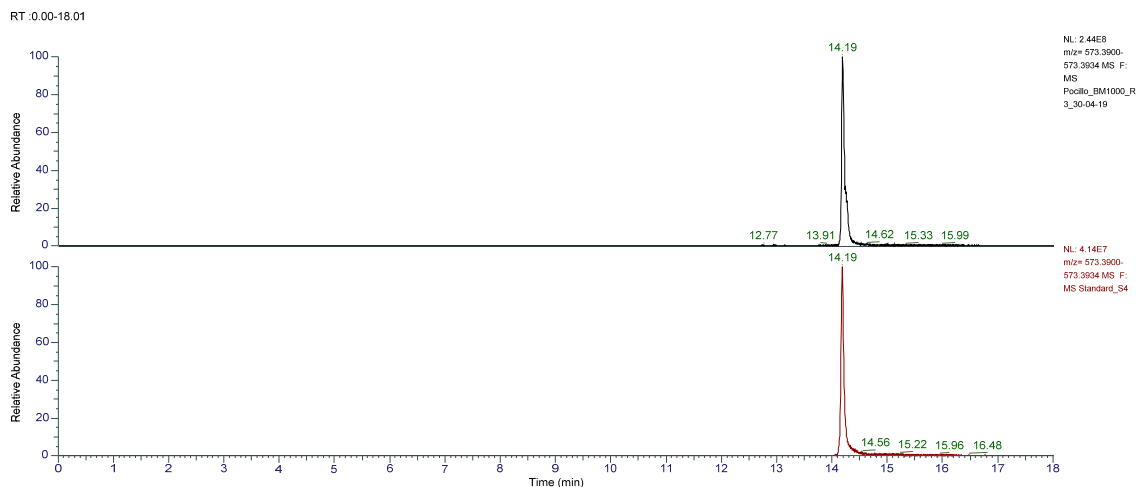


Figure S19. Compared extracted ion chromatograms at m/z 573.3914 ($[7+Na]^+$) in an extract of BM-exposed coral (top) and synthetic analytical standard of compound **7** (bottom)

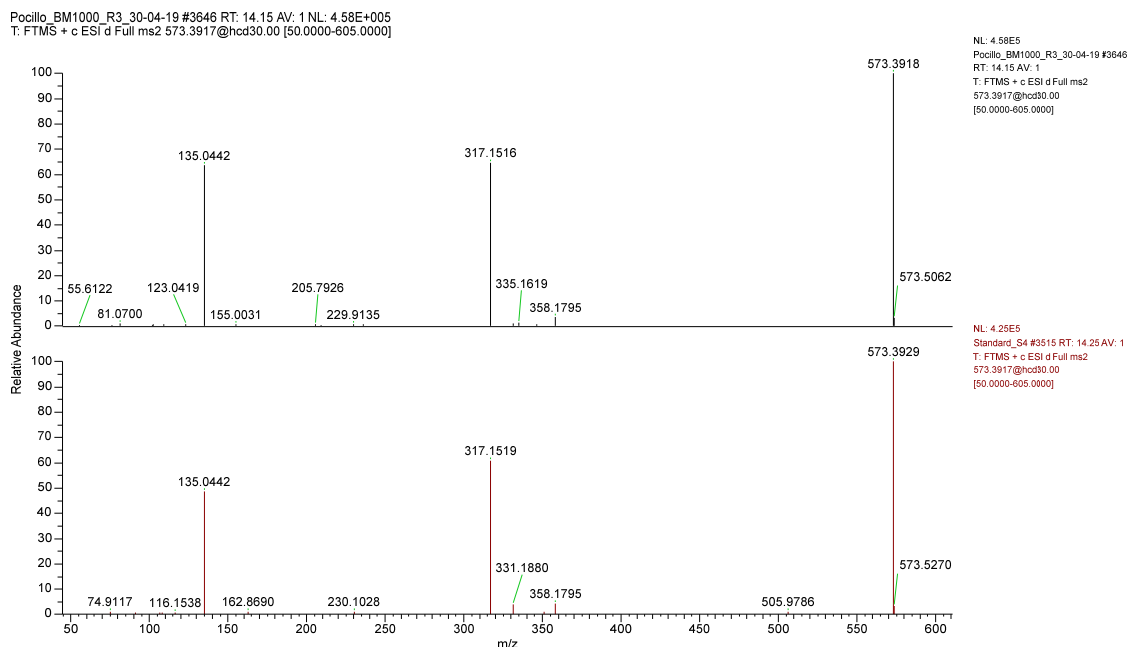


Figure S20. Compared collision-induced fragmentation spectra of $[7+Na]^+$ ion at m/z 573.3914 in an extract of BM-exposed coral (top) and synthetic analytical standard of compound **7** (bottom)

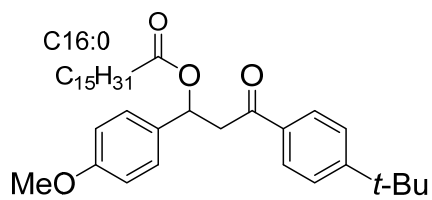


Figure S21. Proposed structure of compound **8**

BM_1mg_R3 #3737-3749 RT: 14.92-14.96 AV: 6 SB: 8 14.90-14.92 , 14.97-15.00 NL: 2.70E+007
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

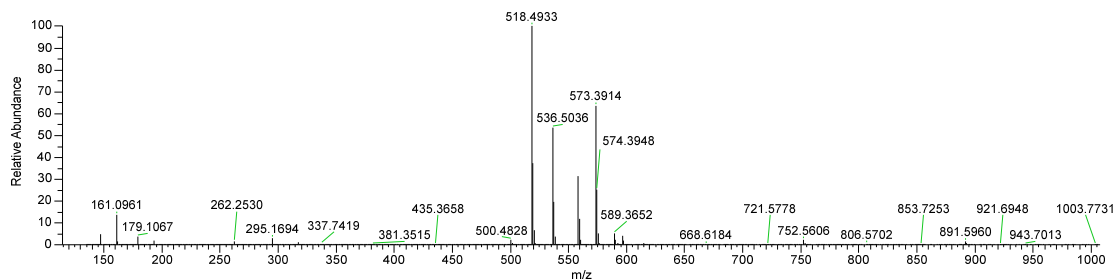


Figure S22. ESI⁺-MS spectrum showing ion [8+Na]⁺ at m/z 573.3916

Corail_BM1000_R5_17-01-2019_FulIMS-PRM_#2598-2611 RT: 14.23-14.27 AV: 7 SB: 3 14.14-14.16 NL: 2.75E6
T: FTMS + p ESI Full ms2 573.3914@hcd30.00 [50.0000-605.0000]

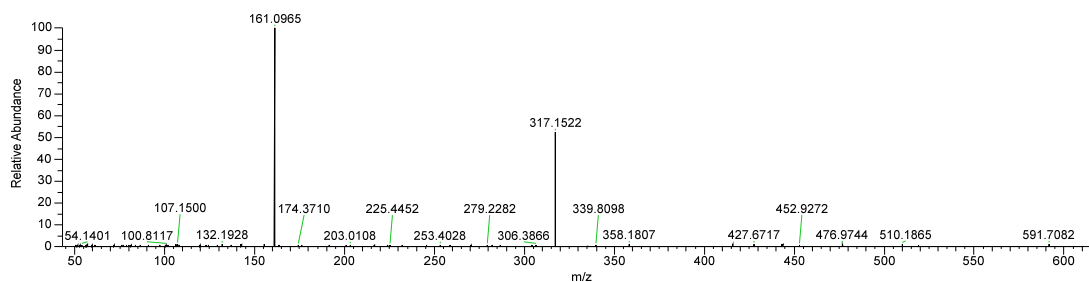


Figure S23. Collision-induced fragmentation spectrum of [8+Na]⁺ at m/z 573.3916

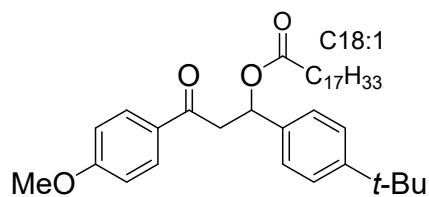


Figure S24. Proposed structure of compound 9

BM_1mg_R3 #3746-3761 RT: 14.95-15 AV: 8 SB: 8 15.00-15.02 , 14.92-14.94 NL: 7.53E+006
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

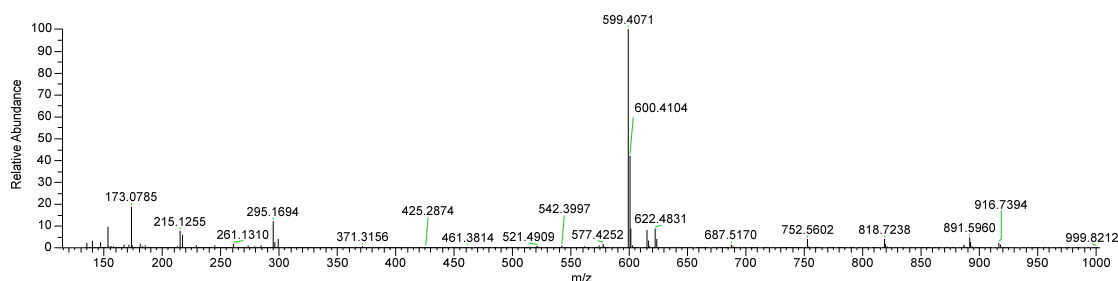


Figure S25. ESI⁺-MS spectrum showing ion [9+Na]⁺ at m/z 599.4071

BM_1mg_R3 #3751 RT: 14.97 AV: 1 NL: 9.35E+005
T: FTMS + c ESI d Full ms2 599.4069@hcd30.00 [50.0000-630.0000]

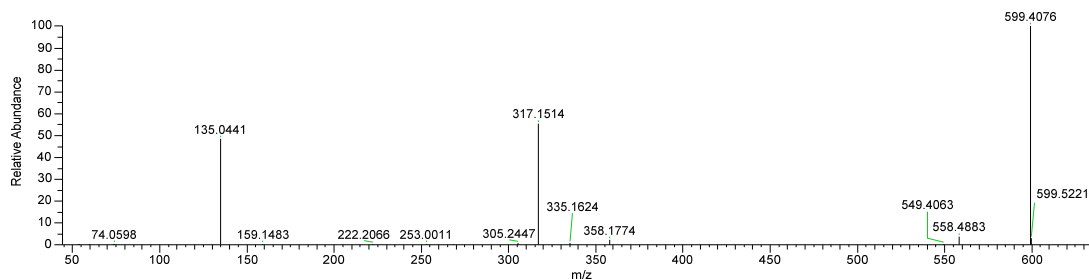


Figure S26. Collision-induced fragmentation spectrum of $[9+Na]^+$ at m/z 599.4071

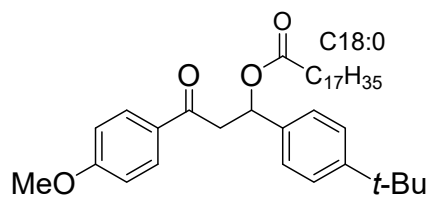


Figure S27. Proposed structure of compound **10**

BM_1mg_R3 #4017-4029 RT: 15.88-15.92 AV: 6 SB: 8 15.94-15.96, 15.86-15.88 NL: 8.93E+006
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

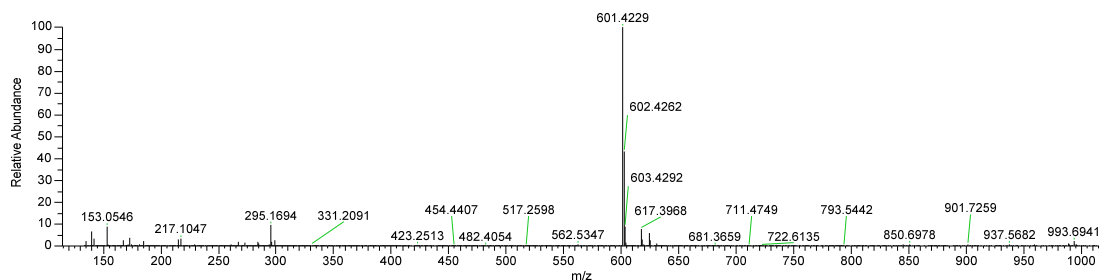


Figure S28. ESI⁺-MS spectrum showing ion $[10+Na]^+$ at m/z 601.4229

BM_1mg_R3 #4021 RT: 15.89 AV: 1 NL: 6.26E+005
T: FTMS + c ESI d Full ms2 601.4229@hcd30.00 [50.0000-630.0000]

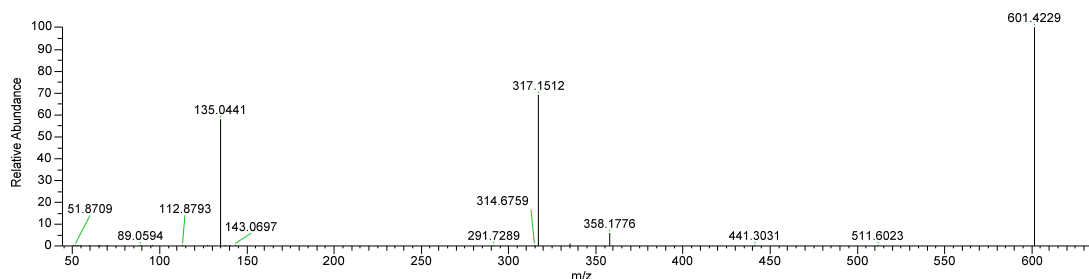


Figure S29. Collision-induced fragmentation spectrum of $[10+Na]^+$ at m/z 601.4229

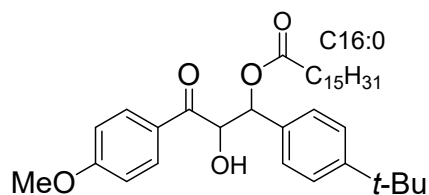


Figure S30. Proposed structure of compound **11**

BM_1mg_R3 #3094 RT: 12.74 AV: 1 SB: 20 12.67-12.73, 12.80-12.87 NL: 8.78E+006
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

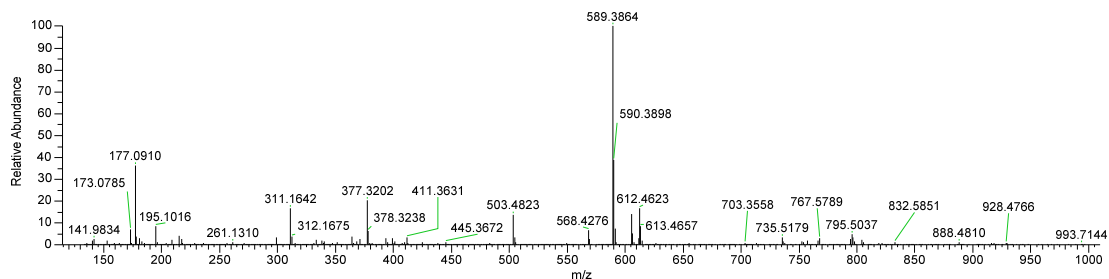


Figure S31. ESI⁺-MS spectrum showing ion [11+Na]⁺ at m/z 589.3864

BM_1mg_R3 #3095 RT: 12.75 AV: 1 NL: 1.09E+006
T: FTMS + c ESI d Full ms2 589.3864@hcd30.00 [50.0000-620.0000]

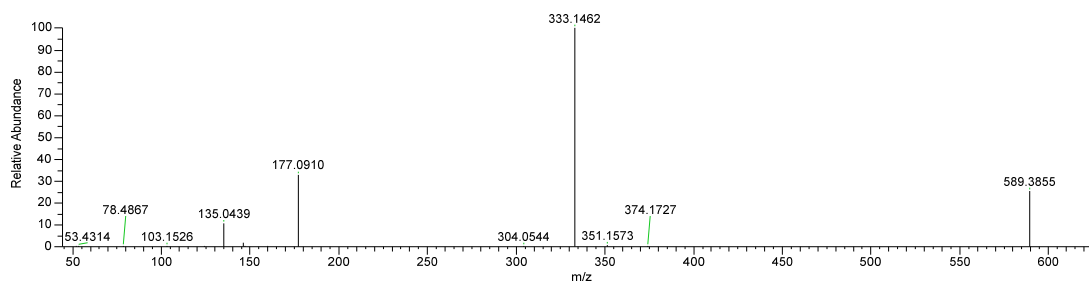


Figure S32. Collision-induced fragmentation spectrum of [11+Na]⁺ at m/z 589.3864

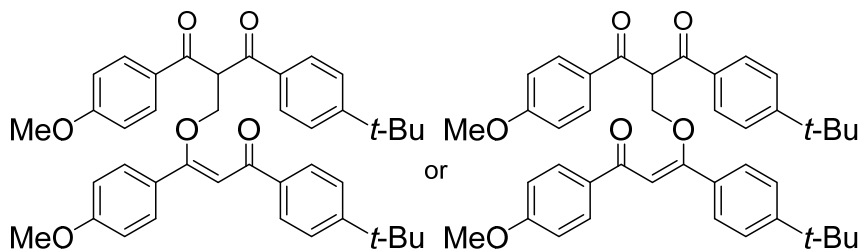


Figure S33. Proposed structure of compound **12**

BM_1mg_R3 #2388-2400 RT: 10.37-10.41 AV: 7 SB: 7 10.35-10.37, 10.41-10.43 NL: 1.17E+007
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

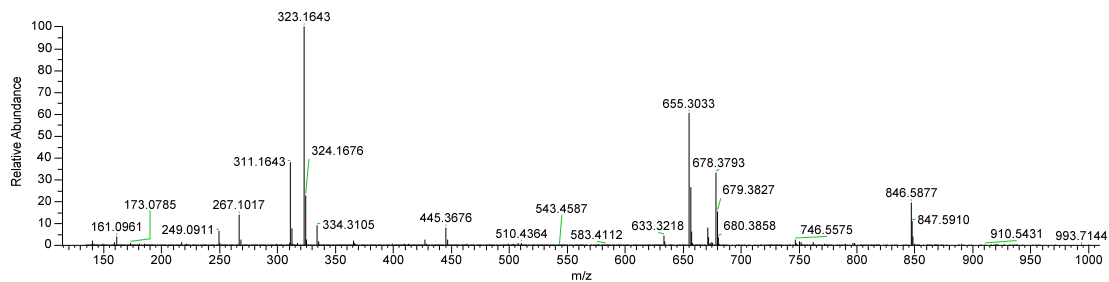


Figure S34. ESI⁺-MS spectrum showing ion [12+Na]⁺ at m/z 655.3033

BM_1mg_R3 #2393 RT: 10.39 AV: 1 NL: 1.49E+006
T: FTMS + c ESI d Full ms2 655.3032@hcd30.00 [50.0000-685.0000]

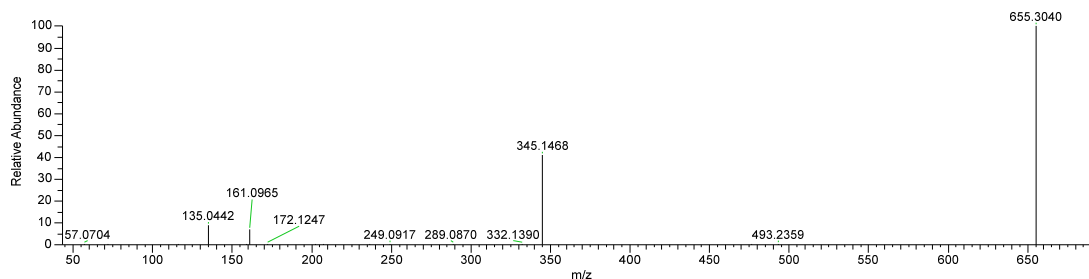


Figure S35. Collision-induced fragmentation spectrum of $[12+Na]^+$ at m/z 655.3033

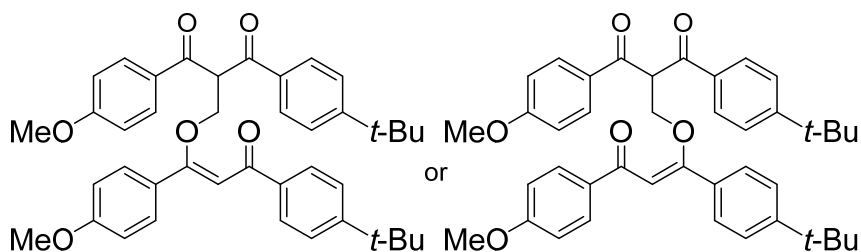


Figure S36. Proposed structure of compound **13**

BM_1mg_R3 #2411-2423 RT: 10.45-10.49 AV: 6 SB: 10 10.42-10.44 10.50-10.54 NL: 1.33E7
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

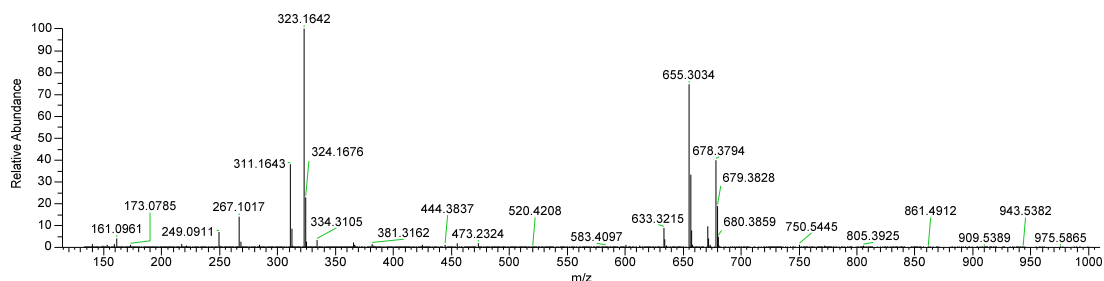


Figure S37. ESI⁺-MS spectrum showing ion $[13+Na]^+$ at m/z 655.3034

Corail_BM1000_R5_17-01-2019_FulIMS-PRM_#1715 RT: 10.02 AV: 1 NL: 2.31E+005
T: FTMS + p ESI Full ms2 655.3030@hcd30.00 [50.0000-685.0000]

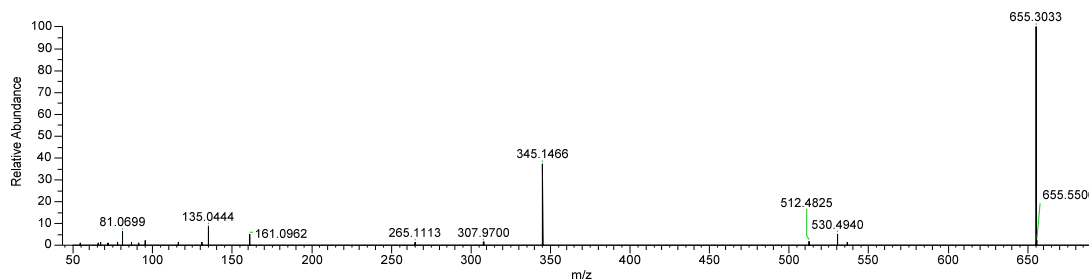


Figure S38. Collision-induced fragmentation spectrum of $[13+Na]^+$ at m/z 655.3034

BM_1mg_R3 #2397 RT: 10.40 AV: 1 NL: 6.83E+005
T: FTMS + c ESI d Full ms2 311.1643@hcd30.00 [50.0000-335.0000]

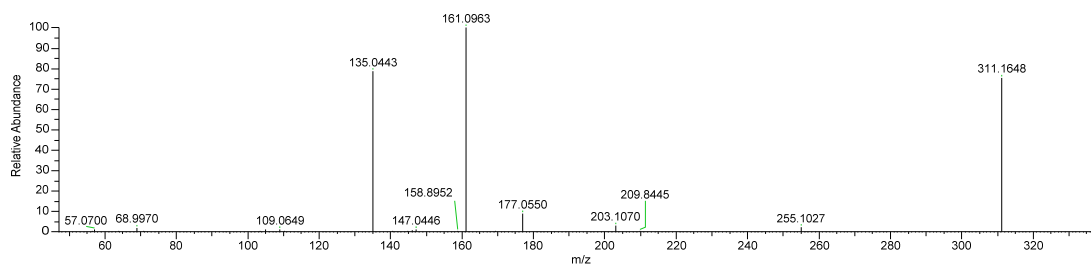


Figure S39. Collision-induced fragmentation spectrum of Frag. 1 at m/z 311.1643

BM_1mg_R3 #2391 RT: 10.38 AV: 1 NL: 1.36E+006
T: FTMS + c ESI d Full ms2 323.1643@hcd30.00 [50.0000-345.0000]

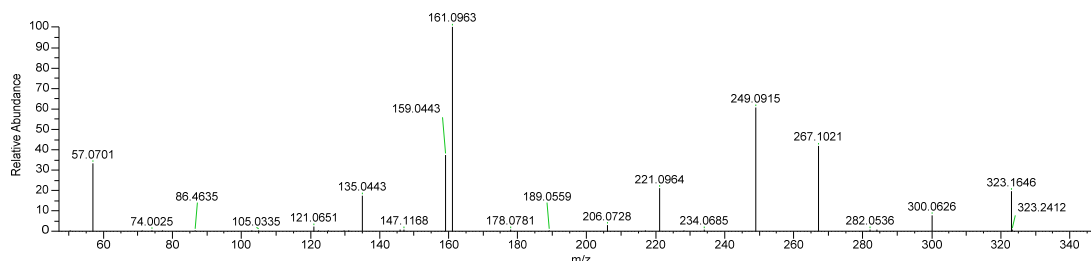


Figure S40. Collision-induced fragmentation spectrum of Frag. 2 at m/z 323.1643

BM_1mg_R3 #2076 RT: 9.30 AV: 1 NL: 3.57E+008
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

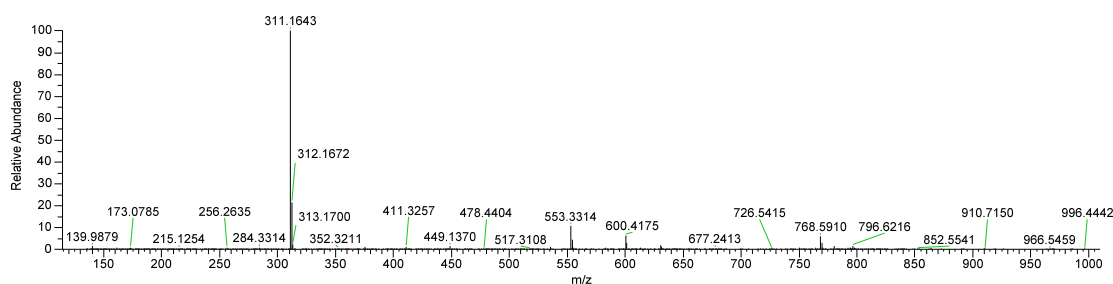


Figure S41. ESI⁺-MS spectrum showing the undetermined ion at m/z 449.1370 corresponding to compound **14**

BM_1mg_R3 #2079 RT: 9.31 AV: 1 NL: 2.85E+005
T: FTMS + c ESI d Full ms2 449.1370@hcd30.00 [50.0000-475.0000]

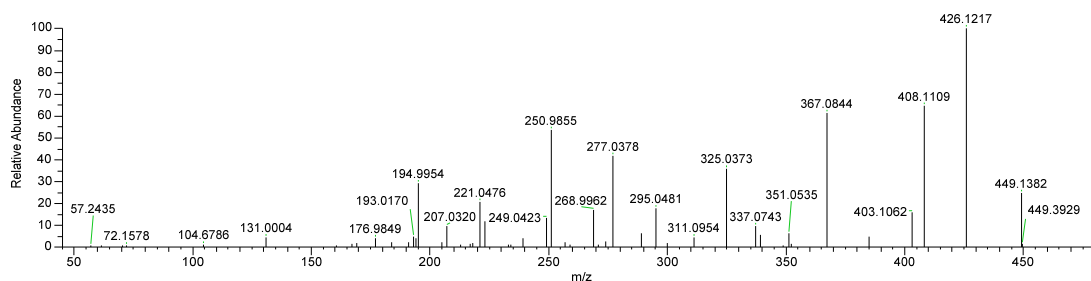


Figure S42. Collision-induced fragmentation spectrum of ion at m/z 449.1370

BM_1mg_R3 #3364-3382 RT: 13.66-13.72 AV: 10 SB: 13 13.62-13.65 , 13.72-13.77 NL: 7.36E+006
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

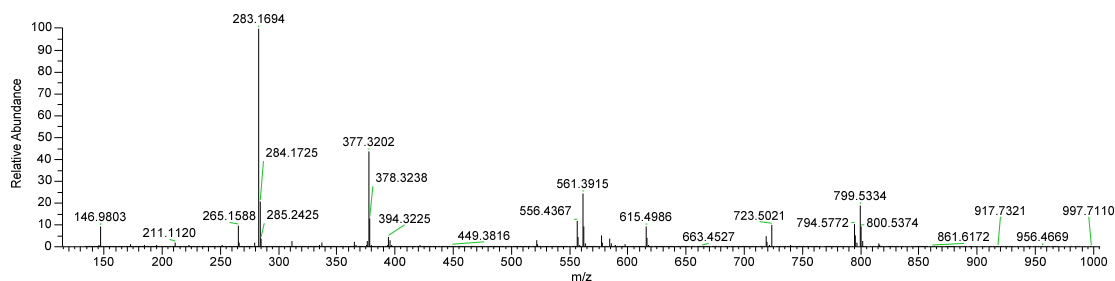


Figure S43. ESI⁺-MS spectrum showing ion [15+H]⁺ at m/z 283.1694

BM_1mg_R3 #3371 RT: 13.68 AV: 1 NL: 6.04E+005
T: FTMS + c ESI d Full ms2 283.1694@hcd30.00 [50.0000-305.0000]

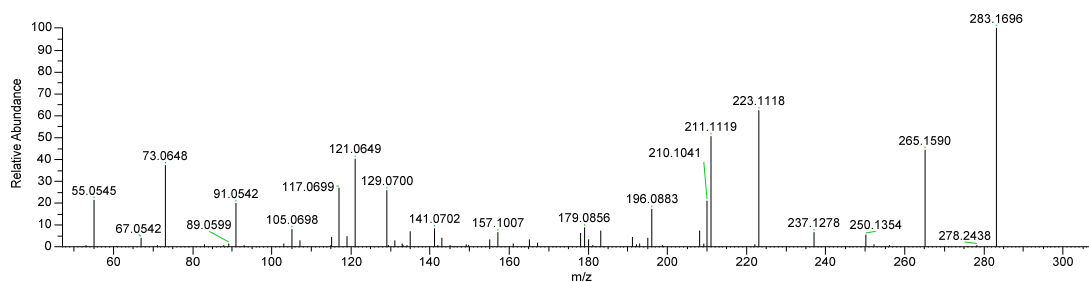


Figure S44. Collision-induced fragmentation spectrum of [15+H]⁺ at m/z 283.1694

BM_1mg_R3 #3555-3567 RT: 14.31-14.35 AV: 6 SB: 6 14.35-14.37 , 14.29-14.31 NL: 1.46E+006
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

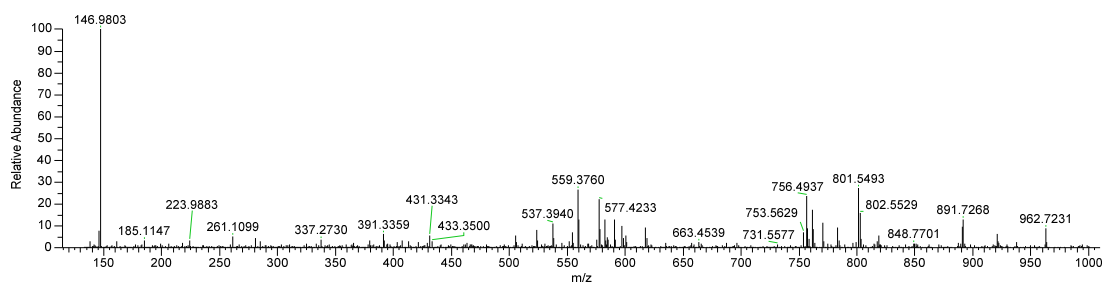


Figure S45. ESI⁺-MS spectrum showing ion [16+Na]⁺ at m/z 559.3760

BM_1mg_R5 #3587 RT: 14.36 AV: 1 NL: 1.01E+006
T: FTMS + c ESI d Full ms2 559.3761@hcd30.00 [50.0000-590.0000]

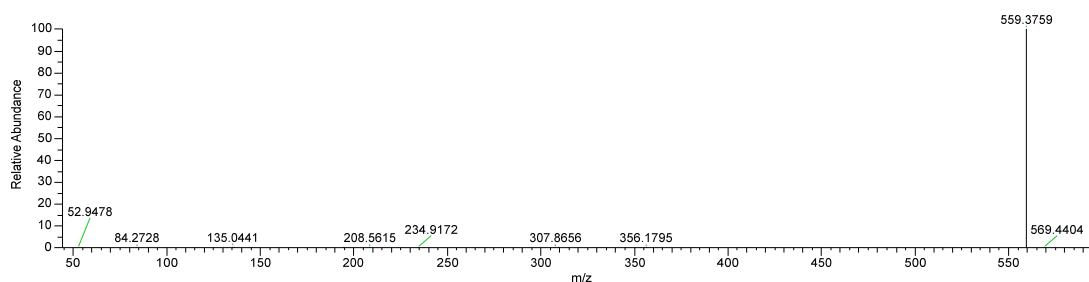


Figure S46. Collision-induced fragmentation spectrum of [16+Na]⁺ at m/z 559.3760

BM_1mg_R3 #3591-3605 RT: 14.43-14.48 AV: 7 SB: 12 14.39-14.43, 14.48-14.52 NL: 8.46E+006
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

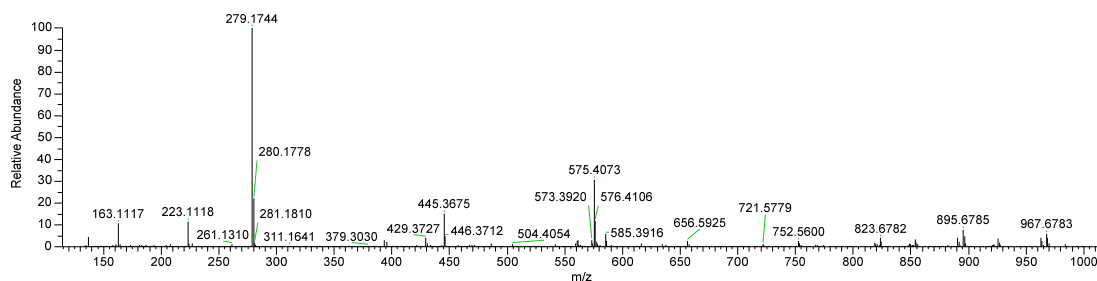


Figure S47. ESI⁺-MS spectrum showing ion [17+H]⁺ at m/z 279.1744

BM_1mg_R5 #3611 RT: 14.44 AV: 1 NL: 1.01E+006
T: FTMS + c ESI d Full ms2 279.1744@hcd30.00 [50.0000-300.0000]

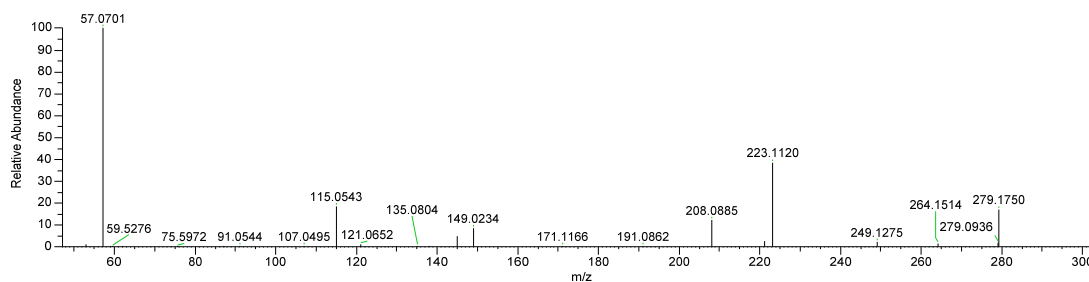


Figure S48. Collision-induced fragmentation spectrum of [17+H]⁺ at m/z 279.1744

Table S2. Compared ESI⁺-MS response of [BM+H]⁺ and [7+Na]⁺ ions, full data

	BM	C16:0-dihydroBM
Ion	[M+H] ⁺ , major tautomer	[M+Na] ⁺
m/z	311.1642	573.3914
Initial mass (mg)	2.8	2.1
Relative mass	1	0.75
Concentration in S2 (μg/mL)	14.7	11.1
Area in S2	6.52E+09	4.96E+09
Relative response in MS at ~ 12 μg/mL	1	1.02
Concentration in S3 (μg/mL)	1.47	1.11
Area in S3	5.62E+08	1.22E+09
Relative response in MS at ~ 1.2 μg/mL	1	2.90
Concentration in S4 (μg/mL)	0.147	0.111
Area in S4	5.36E+07	1.74E+08
Relative response in MS at ~ 0.12 μg/mL	1	4.33
Concentration in S5 (μg/mL)	0.0147	0.0111
Area in S4	7.49E+06	1.79E+07
Relative response in MS at ~ 0.012 μg/mL	1	3.18

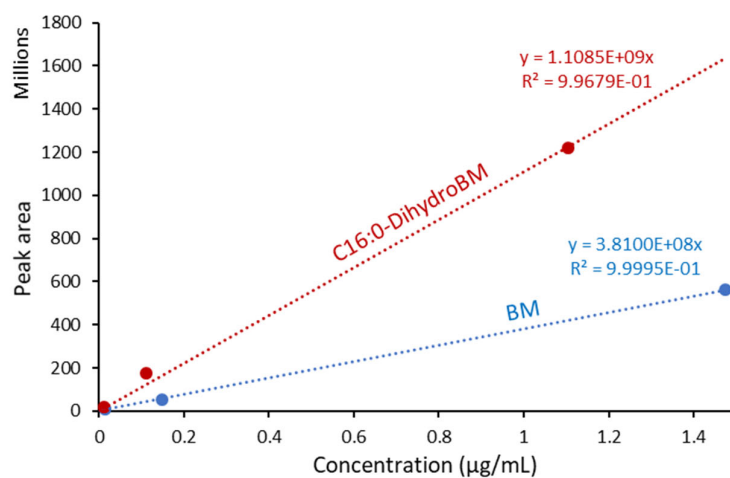


Figure S49. Compared ESI⁺-MS response of [BM+H]⁺ and [7+Na]⁺ ions in the range of concentration for which the response is linear

Table S3. Extracted ion chromatogram peak areas for compounds **1-11** in coral exposed to BM (data provided by Compound Discoverer), corrected peak areas to report on mass relative proportions, and relative corrected peak areas

	[BM] (µg/L)	Cmpd. #											Total 2-11
		1 (BM)	2	3	4	5	6	7	8	9	10	11	
Peak area in coral exposed to BM	5	26138	2610	3311	2736	2217	2778	52070	20102	2508	4270	5460	98063
	50	14927	5450	3825	8771	20132	6028	429584	13318	4464	32055	11363	534990
	300	60696	98042	81898	182842	140004	63314	4423157	50338	85529	450488	338275	5913886
	1000	434362	224511	440193	584738	592647	334674	16668663	342890	415686	1154072	1035388	21793462
Corrected peak area in coral exposed to BM (For compounds 2-11 , Peak area/3)	5	26138	870	1104	912	739	926	17357	6701	836	1423	1820	32688
	50	14927	1817	1275	2924	6711	2009	143195	4439	1488	10685	3788	178330
	300	60696	32681	27299	60947	46668	21105	1474386	16779	28510	150163	112758	1971295
	1000	434362	74837	146731	194913	197549	111558	5556221	114297	138562	384691	345129	7264487
Relative corrected peak area (in relation to BM peak area) in coral exposed to BM	5		0.03	0.04	0.03	0.03	0.04	0.66	0.26	0.03	0.05	0.07	1.3
	50		0.12	0.09	0.20	0.45	0.13	9.59	0.30	0.10	0.72	0.25	12
	300		0.54	0.45	1.00	0.77	0.35	24.29	0.28	0.47	2.47	1.86	32
	1000		0.17	0.34	0.45	0.45	0.26	12.79	0.26	0.32	0.89	0.79	17

BM_1mg_R3 #3046-3063 RT: 12.58-12.64 AV: 9 SB: 14 12.56-12.58 , 12.64-12.70 NL: 2.02E+007
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

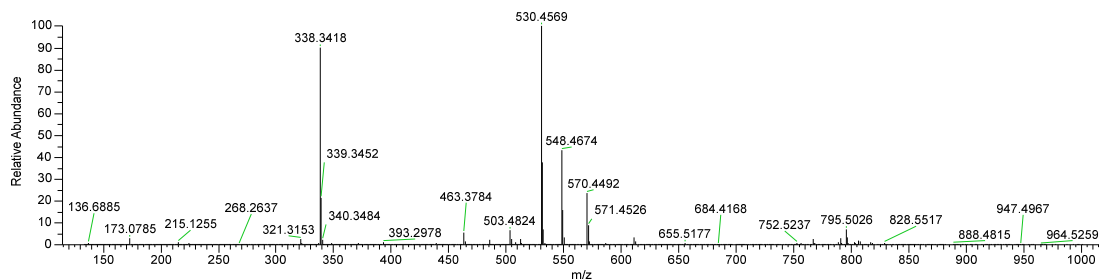


Figure S50. ESI⁺-MS spectrum showing ion [18+H]⁺ at m/z 548.4674

BM_1mg_R3 #3051 RT: 12.60 AV: 1 NL: 2.86E+005
T: FTMS + c ESI d Full ms2 548.4675@hcd30.00 [50.0000-575.0000]

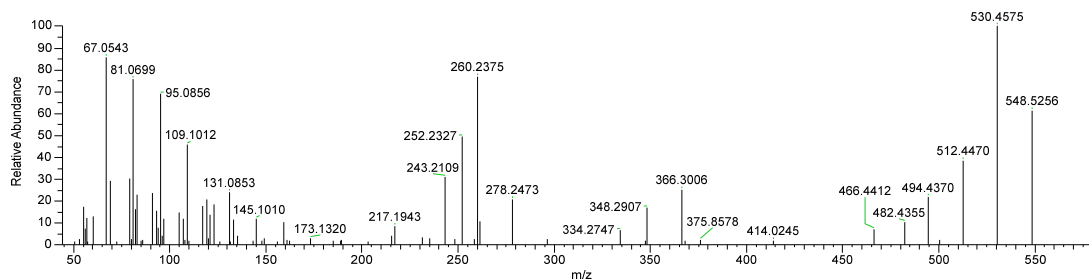


Figure S51. Collision-induced fragmentation spectrum of [18+H]⁺ at m/z 548.4674

BM_1mg_R3 #3184-3205 RT: 13.05-13.12 AV: 11 SB: 25 12.99-13.04 , 13.11-13.22 NL: 3.44E+007
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

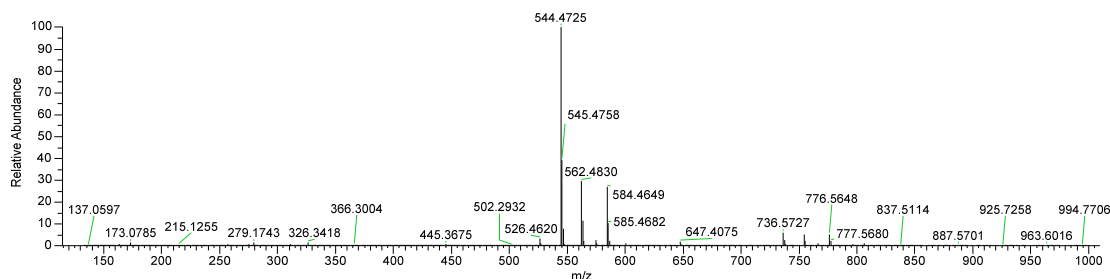


Figure S52. ESI⁺-MS spectrum showing ion [19+H]⁺ at m/z 562.4830

BM_1mg_R3 #3187 RT: 13.06 AV: 1 NL: 3.34E+005
T: FTMS + c ESI d Full ms2 562.4830@hcd30.00 [50.0000-590.0000]

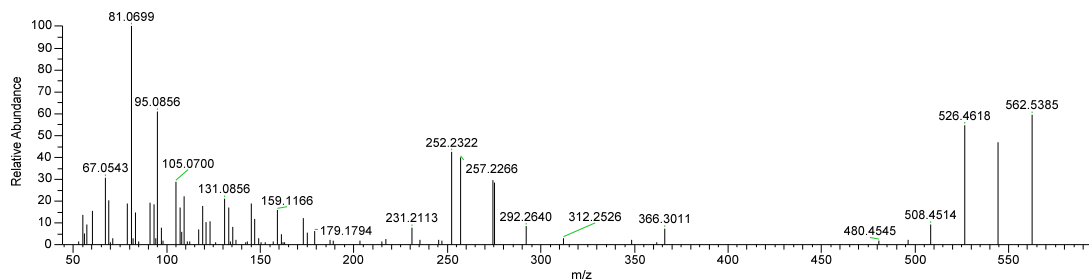


Figure S53. Collision-induced fragmentation spectrum of [19+H]⁺ at m/z 562.4830

BM_1mg_R3 #3273-3290 RT: 13.35-13.41 AV: 9 SB: 13 13.29-13.34, 13.41-13.45 NL: 1.29E+007
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

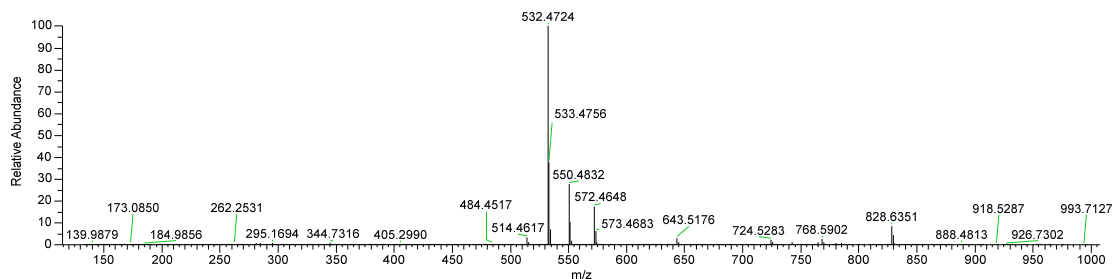


Figure S54. ESI⁺-MS spectrum showing ion [20+H]⁺ at m/z 550.4832

BM_1mg_R3 #3279 RT: 13.37 AV: 1 NL: 3.64E+005
T: FTMS + c ESI d Full ms2 550.4830@hcd30.00 [50.0000-580.0000]

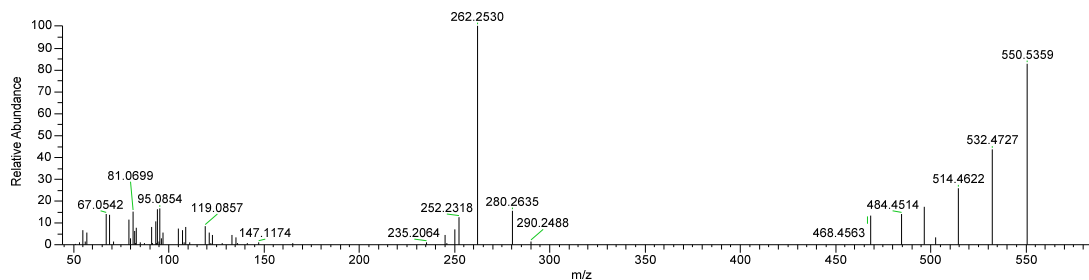


Figure S55. Collision-induced fragmentation spectrum of [20+H]⁺ at m/z 550.4832

BM_1mg_R3 #1909-1923 RT: 8.72-8.77 AV: 7 SB: 18 8.67-8.72, 8.77-8.84 NL: 4.12E+006
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

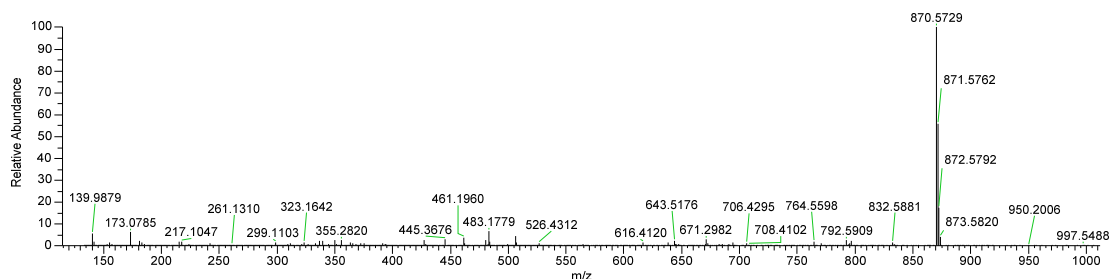


Figure S56. ESI⁺-MS spectrum showing ion [21+H]⁺ at m/z 870.5731

BM_1mg_R3 #1915 RT: 8.74 AV: 1 NL: 2.04E+006
T: FTMS + c ESI d Full ms2 870.5729@hcd30.00 [60.3333-905.0000]

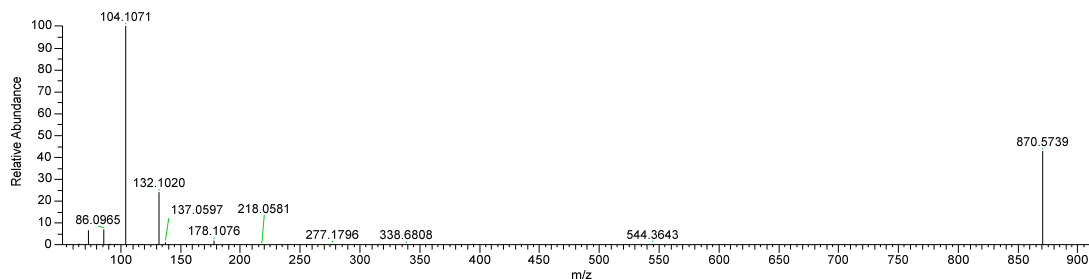


Figure S57. Collision-induced fragmentation spectrum of [21+H]⁺ at m/z 870.5731

BM_1mg_R3 #2096 RT: 9.37 AV: 1 SB: 8 9.33-9.36 , 9.40-9.42 NL: 2.15E+006
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

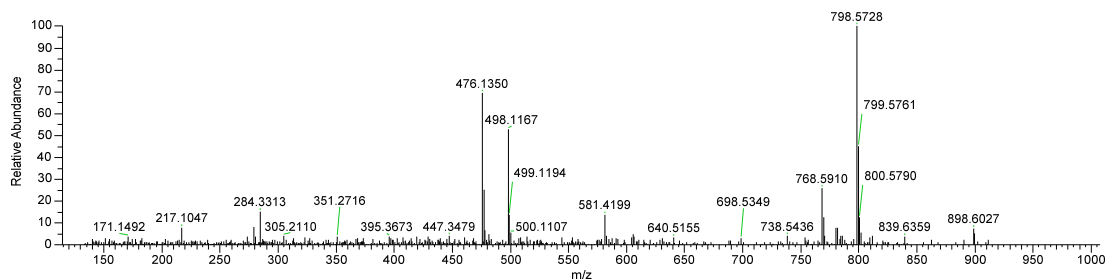


Figure S58. ESI⁺-MS spectrum showing ion [22+H]⁺ at m/z 798.5731

BM_1mg_R3 #2093 RT: 9.36 AV: 1 NL: 1.54E+006
T: FTMS + c ESI d Full ms2 798.5731@hcd30.00 [55.3333-830.0000]

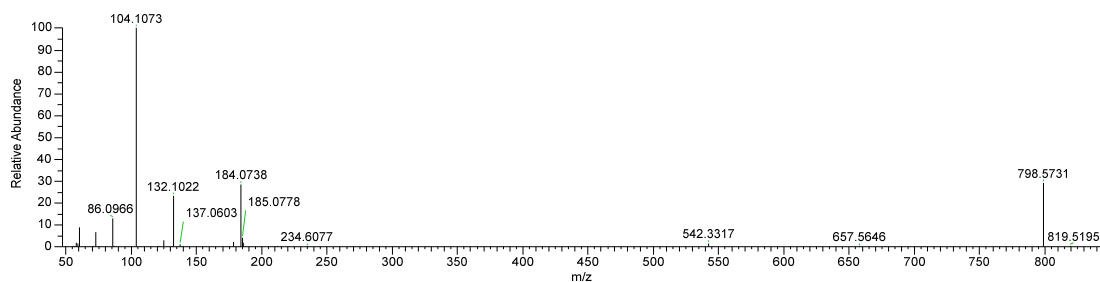


Figure S59. Collision-induced fragmentation spectrum of [22+H]⁺ at m/z 798.5731

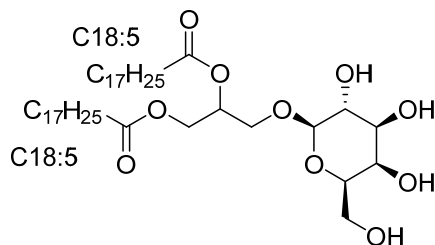


Figure S60. Proposed structure of compound **23**

BM_1mg_R3 #2544-2561 RT: 10.9-10.96 AV: 9 SB: 17 10.85-10.89 , 10.97-11.04 NL: 3.04E+006
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

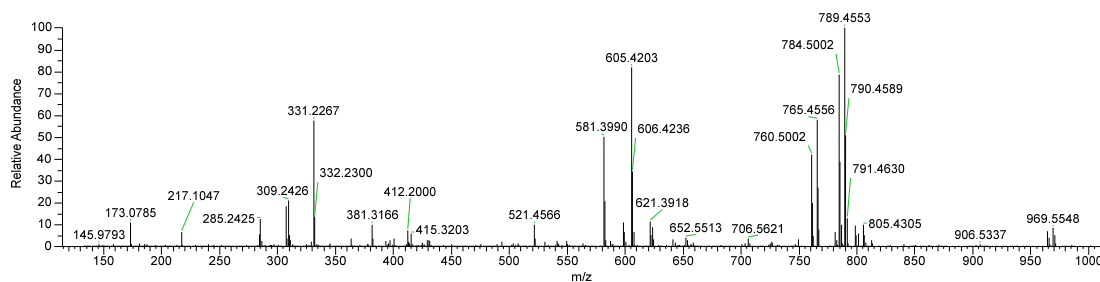


Figure S61. ESI⁺-MS spectrum showing ion [23+Na]⁺ at m/z 789.4553

BM_1mg_R3 #2553 RT: 10.93 AV: 1 NL: 3.67E+005
T: FTMS + c ESI d Full ms2 789.4554@hcd30.00 [55.0000-825.0000]

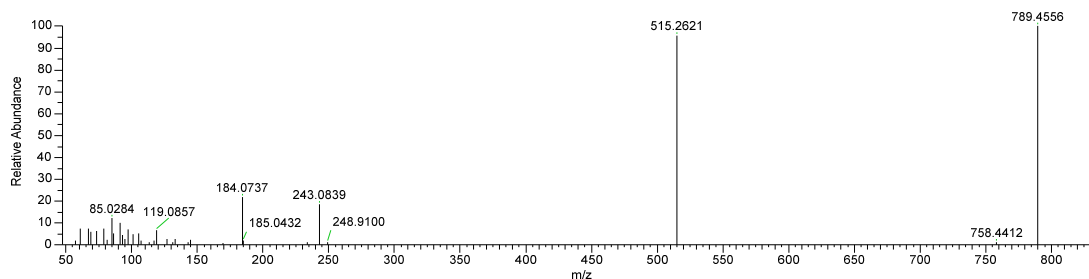


Figure S62. Collision-induced fragmentation spectrum of $[23+Na]^+$ at m/z 789.4553

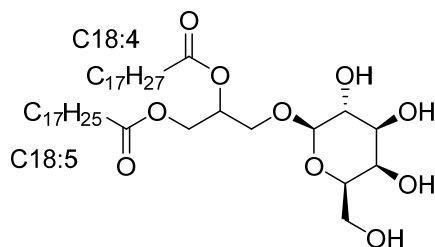


Figure S63. Proposed structure of compound **24**

BM_1mg_R3 #2633 RT: 11.21 AV: 1 NL: 1.46E+008
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

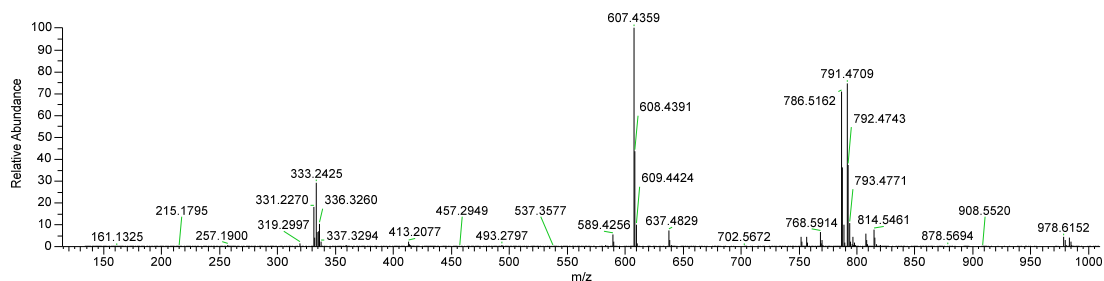


Figure S64. ESI+-MS spectrum showing ion $[24+Na]^+$ at m/z 791.4709

BM_1mg_R3 #2633 RT: 11.21 AV: 1 NL: 2.47E+006
T: FTMS + c ESI d Full ms2 791.4711@hcd30.00 [55.0000-825.0000]

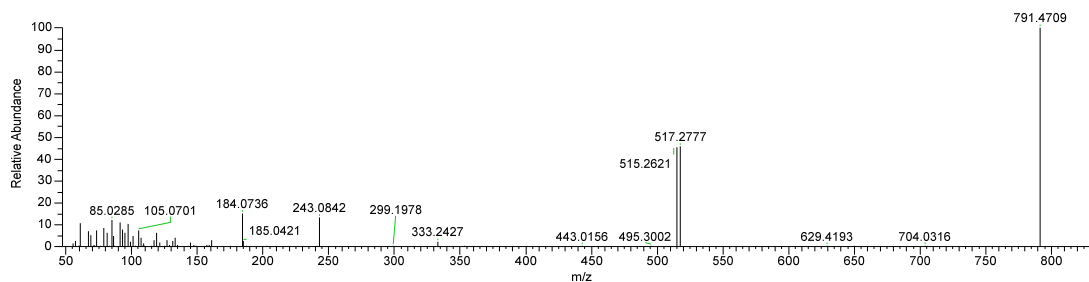


Figure S65. Collision-induced fragmentation spectrum of $[24+Na]^+$ at m/z 791.4709

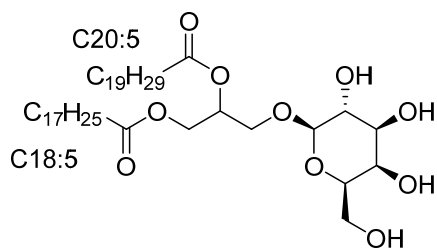


Figure S66. Proposed structure of compound **25**

BM_1mg_R3 #2753-2771 RT: 11.61-11.67 AV: 9 SB: 53 11.53-11.59, 11.69-11.97 NL: 1.25E+008
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

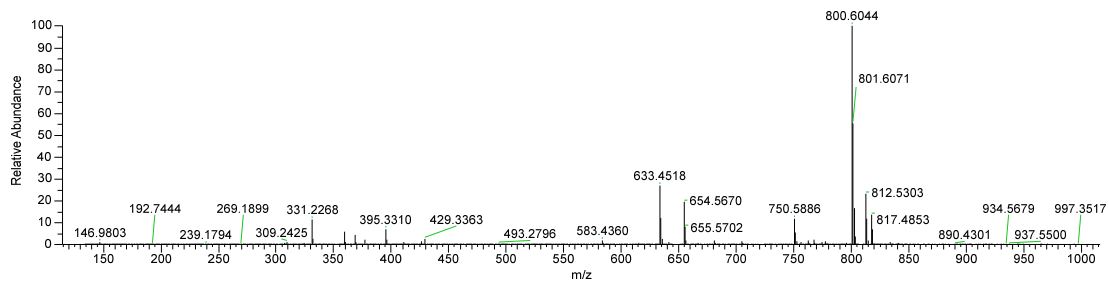


Figure S67. ESI⁺-MS spectrum showing ion $[25+Na]^+$ at m/z 817.4853

BM_1mg_R3 #2769 RT: 11.66 AV: 1 NL: 2.60E+006
T: FTMS + c ESI d Full ms2 817.4851@hcd30.00 [56.6667-850.0000]

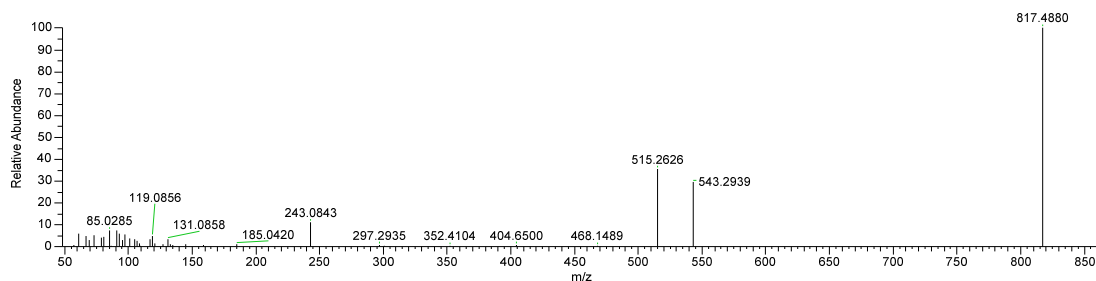


Figure S68. Collision-induced fragmentation spectrum of $[25+Na]^+$ at m/z 817.4866

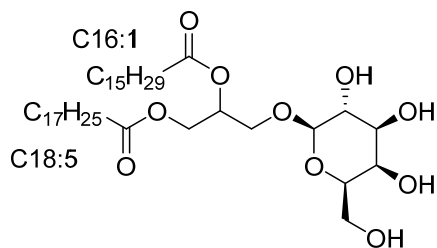


Figure S69. Proposed structure of compound **26**

BM_1mg_R3 #2955-2977 RT: 12.28-12.35 AV: 11 SB: 16 12.23-12.28 , 12.35-12.39 NL: 1.28E+007
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

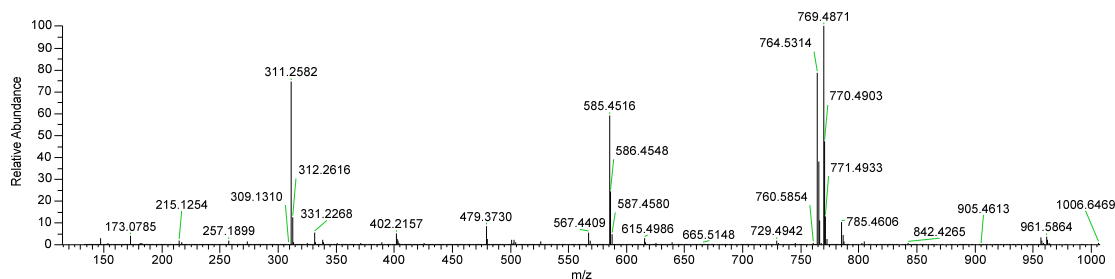


Figure S70. ESI⁺-MS spectrum showing ion [26+Na]⁺ at *m/z* 769.4871

BM_1mg_R3 #2961 RT: 12.30 AV: 1 NL: 3.15E+006
T: FTMS + c ESI d ms2 769.4872@hcd30.00 [53.6667-805.0000]

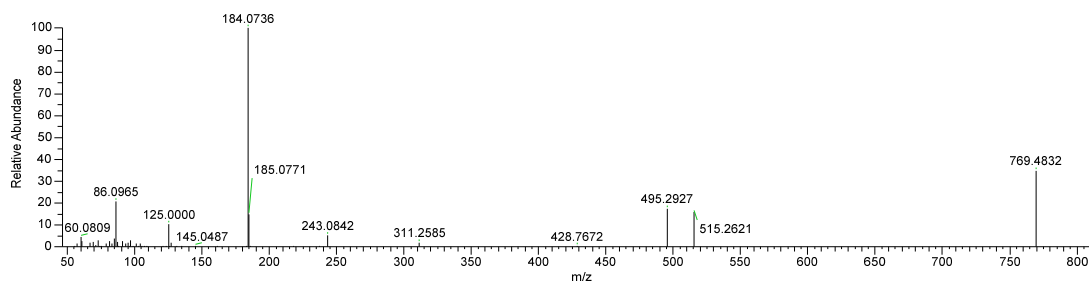


Figure S71. Collision-induced fragmentation spectrum of [26+Na]⁺ at *m/z* 769.4871

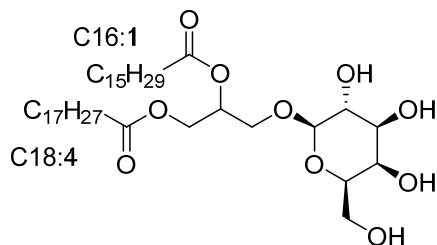


Figure S72. Proposed structure of compound **27**

BM_1mg_R3 #3063-3078 RT: 12.64-12.69 AV: 8 SB: 16 12.57-12.63 , 12.69-12.73 NL: 8.77E+006
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

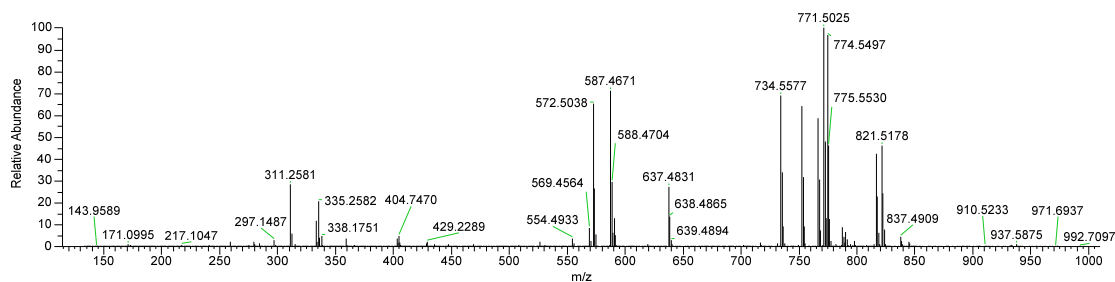


Figure S73. ESI⁺-MS spectrum showing ion [27+Na]⁺ at *m/z* 771.5025

BM_1mg_R3 #3067 RT: 12.65 AV: 1 NL: 5.65E+005
T: FTMS + c ESI d Full ms2 771.5024@hcd30.00 [53.6667-805.0000]

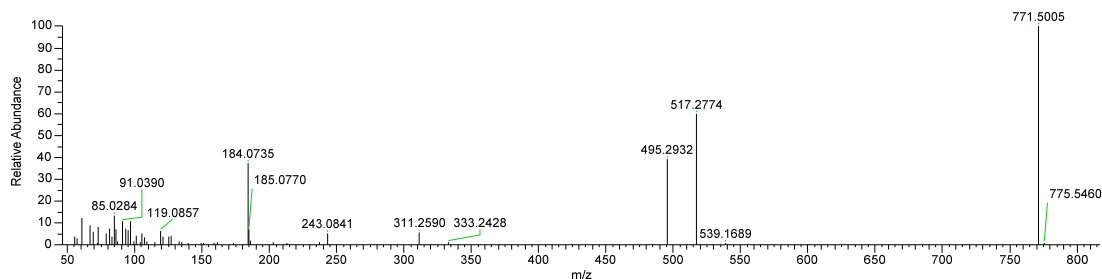


Figure S74. Collision-induced fragmentation spectrum of $[27+Na]^+$ at m/z 771.5025

BM_1mg_R3 #2602-2620 RT: 11.1-11.16 AV: 10 SB: 12 11.06-11.10, 11.17-11.20 NL: 3.22E+006
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

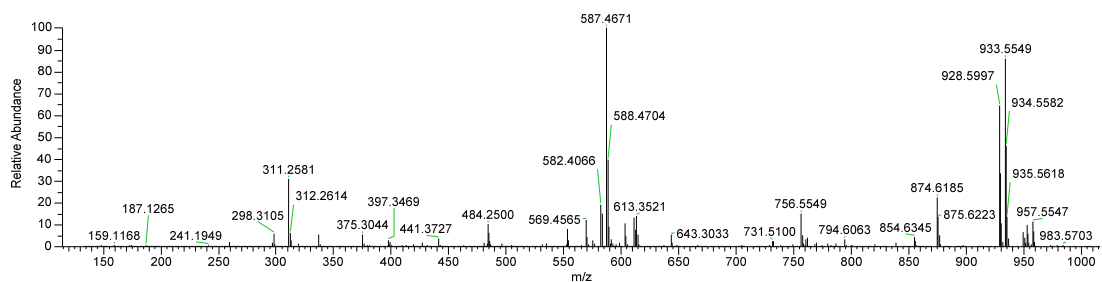


Figure S75. ESI+-MS spectrum showing ion $[28+H]^+$ at m/z 613.3521

Corail_BM1000_R5_17-01-2019_FullIMS-PRM_2 #1847 RT: 10.50 AV: 1 NL: 3.18E+004
T: FTMS + p ESI Full ms2 613.3524@hcd30.00 [50.0000-645.0000]

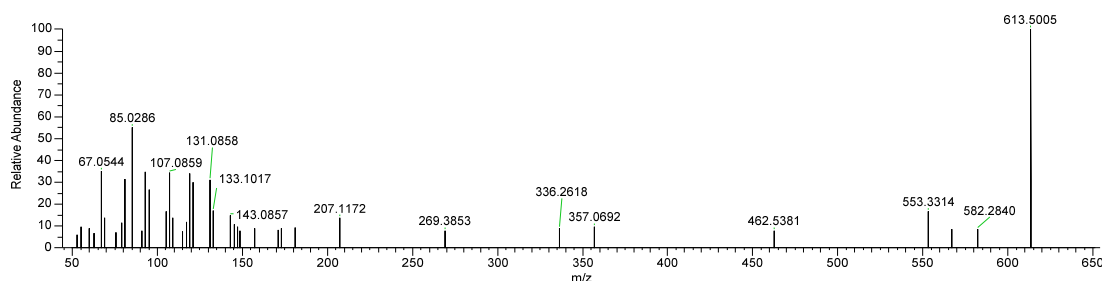


Figure S76. Collision-induced fragmentation spectrum of $[28+H]^+$ at m/z 613.3521

BM_1mg_R3 #2653-2668 RT: 11.27-11.32 AV: 8 SB: 29 11.22-11.27, 11.32-11.46 NL: 9.90E+006
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

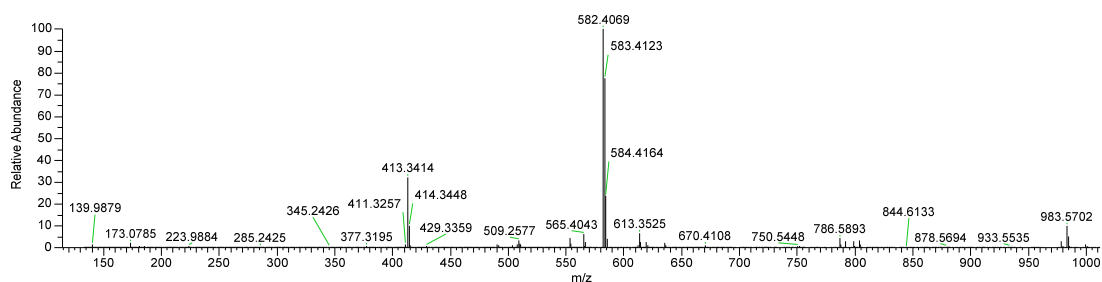


Figure S77. ESI+-MS spectrum showing ion $[29+H]^+$ at m/z 613.3525

BM_1mg_R4 #2715 RT: 11.37 AV: 1 NL: 1.90E+005
T: FTMS + c ESI d Full ms2 613.4830@hcd30.00 [50.0000-645.0000]

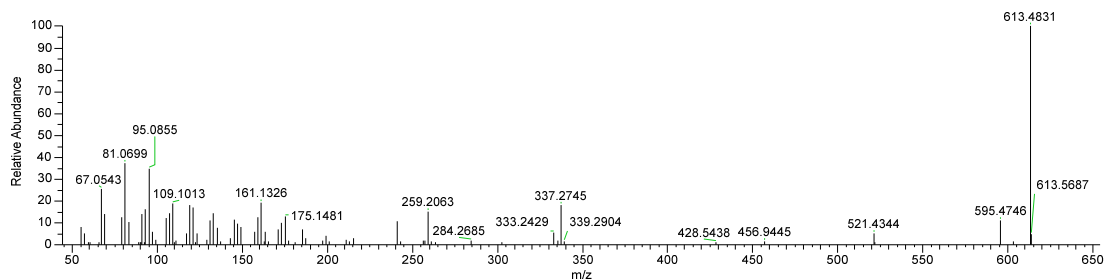


Figure S78. Collision-induced fragmentation spectrum of $[29+H]^+$ at m/z 613.3521

BM_1mg_R3 #2931-2952 RT: 12.2-12.27 AV: 11 SB: 19 12.27-12.33 12.14-12.20 NL: 1.60E7
T: FTMS + c ESI Full lock ms [133.4000-2000.0000]

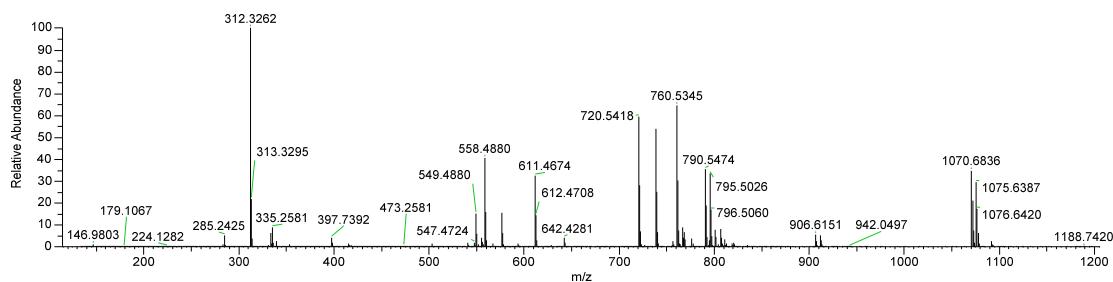


Figure S79. ESI+-MS spectrum showing ion $[30+NH_4]^+$ at m/z 1070.6836

BM_1mg_R1 #2948 RT: 12.22 AV: 1 NL: 1.28E+006
T: FTMS + c ESI d Full ms2 1070.6836@hcd30.00 [74.0000-1110.0000]

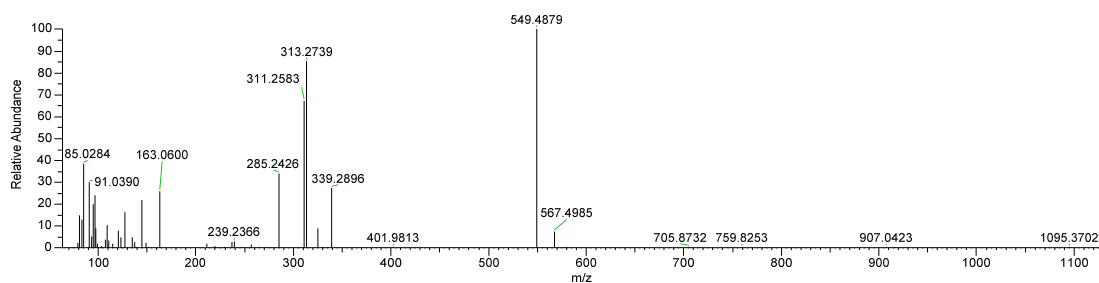


Figure S80. Collision-induced fragmentation spectrum of $[30+NH_4]^+$ at m/z 1070.6836