Supplemental Material for 193 nm Ultraviolet Photodissociation Mass Spectrometry for the Structural Elucidation of Lipid A Compounds in Complex Mixtures

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Figure S-1. MS/MS mass spectra of singly deprotonated wild type *E. coli* lipid A (M_r = 1797.2) using (A) CID, (B) HCD and (C) UVPD. Glucosamine fragment ions are labeled as "ring cleavages".

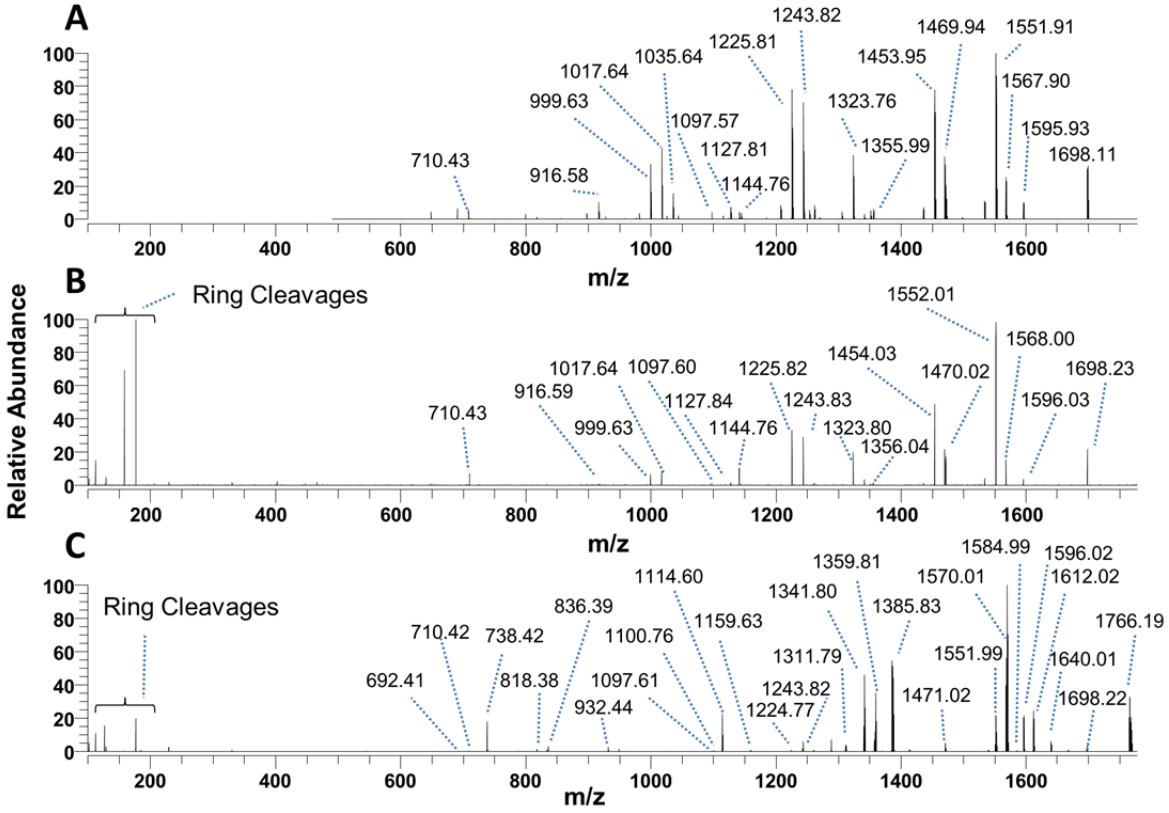
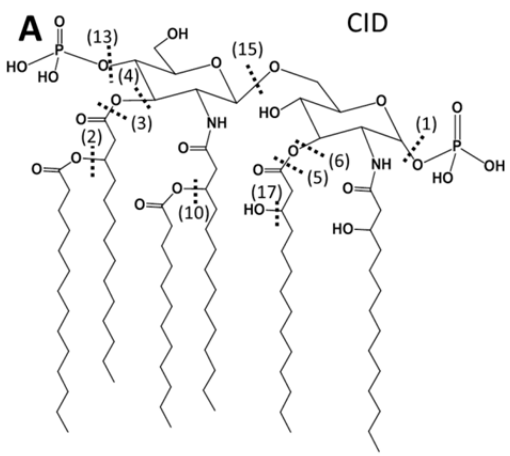
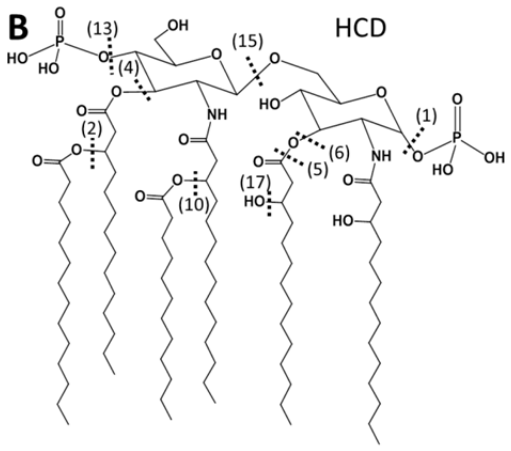


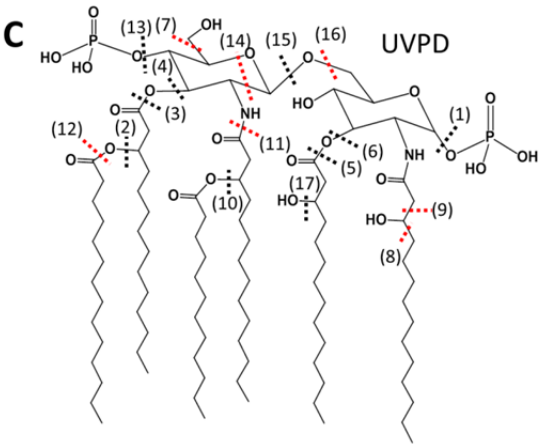
Figure S-2. MS/MS fragmentation maps of singly deprotonated wild type *E. coli* lipid A (M_r = 1797.2) using (A) CID (B) HCD and (C) UVPD. Each cleavage site is numbered, and the m/z values of the fragment ions arising from each cleavage site are listed. Those fragment ions that require multiple cleavages are listed next to each cleavage site. Cleavages marked in red font are unique to UVPD.



1) 1698.11, 1469.94, 1453.95, 1355.99, 1243.82, 1225.81, 1144.76, 1127.81, 1035.64, 1017.64, 999.63, 916.58
2) 1567.90, 1469.94, 1323.76, 1243.82, 1225.81, 1127.81
3) 1035.64
4) 1144.76, 1097.57, 1017.64, 999.64, 916.58
5) 1243.82, 1144.76, 1127.81 1035.64, 1017.64
6) 1551.91, 1453.95, 1323.76, 1255.81, 1097.57, 999.63
7) --
8) --
9) --
10) 1595.93, 916.58
11) --
12) --
13) 1355.99, 1144.76, 916.58
14) --
15) 710.43
16) --
17) 1127.81



1) 1698.23, 1470.02, 1454.03, 1356.04, 1243.83, 1225.82, 1144.76, 1127.84, 1017.64, 999.63, 916.59
2) 1568.00, 1470.02, 1323.80, 1243.83, 1225.82, 1127.84
3) --
4) 1144.76, 1097.60, 1017.64, 999.63, 916.59
5) 1243.83, 1144.76, 1127.84, 1017.64
6) 1552.01, 1454.03, 1323.80, 1225.82,, 1097.60, 999.63
7) --
8) --
9) --
10) 1596.03, 916.59
11) --
12) --
13) 1356.04, 1144.76, 916.59
14) --
15) 710.43
16) --
17) 1127.84



1) 1698.22, 1471.02, 1243.82, 1224.77, 836.39, 818.38
2) 1570.01, 1471.02, 1243.82, 1224.72
3) 1359.81, 836.39, 818.38,
4) 1341.80, 1311.79, 1097.61, 932.44,
5) 1243.82, 836.39, 818.38
6) 1551.99, 1224.77, 1114.60, 1097.61
7) 1766.19, 1311.79, 1114.60
8) 1640.01
9) 1612.02
10) 1596.02, 932.44, 836.39, 818.38
11) 1385.83, 1114.60, 932.44
12) 1584.99
13) --
14) 738.42
15) 710.42
16) 1100.76, 692.41
17) 818.38

Figure S-3. MS/MS mass spectra of doubly deprotonated *V. cholerae* lipid A (M_r = 1757.2 Da) using (A) CID, (B) HCD (C) UVPD. Glucosamine fragment ions are labeled as "ring cleavages".

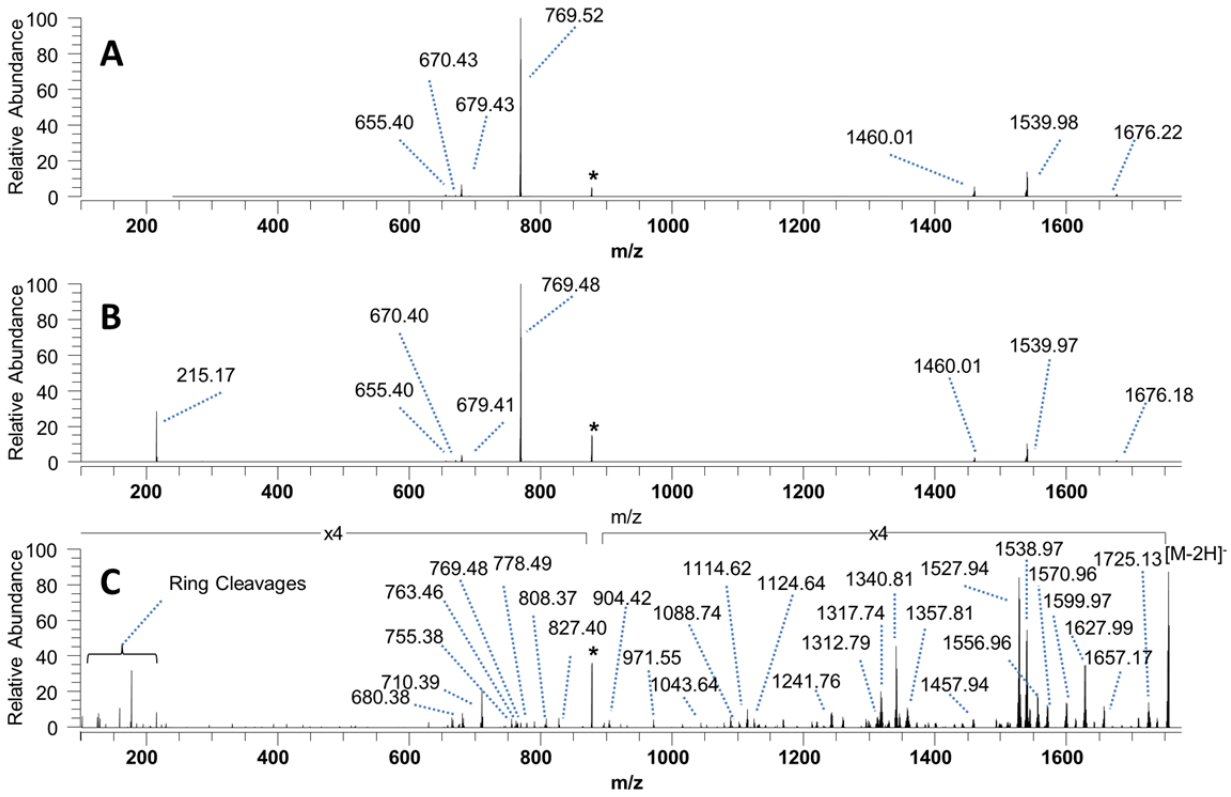


Figure S-4. MS/MS mass spectra of singly deprotonated *V. Cholerae* lipid A (M_r = 1757.2 Da) using (A) CID, (B) HCD (C) UVPD. Glucosamine fragment ions are labeled as "ring cleavages".

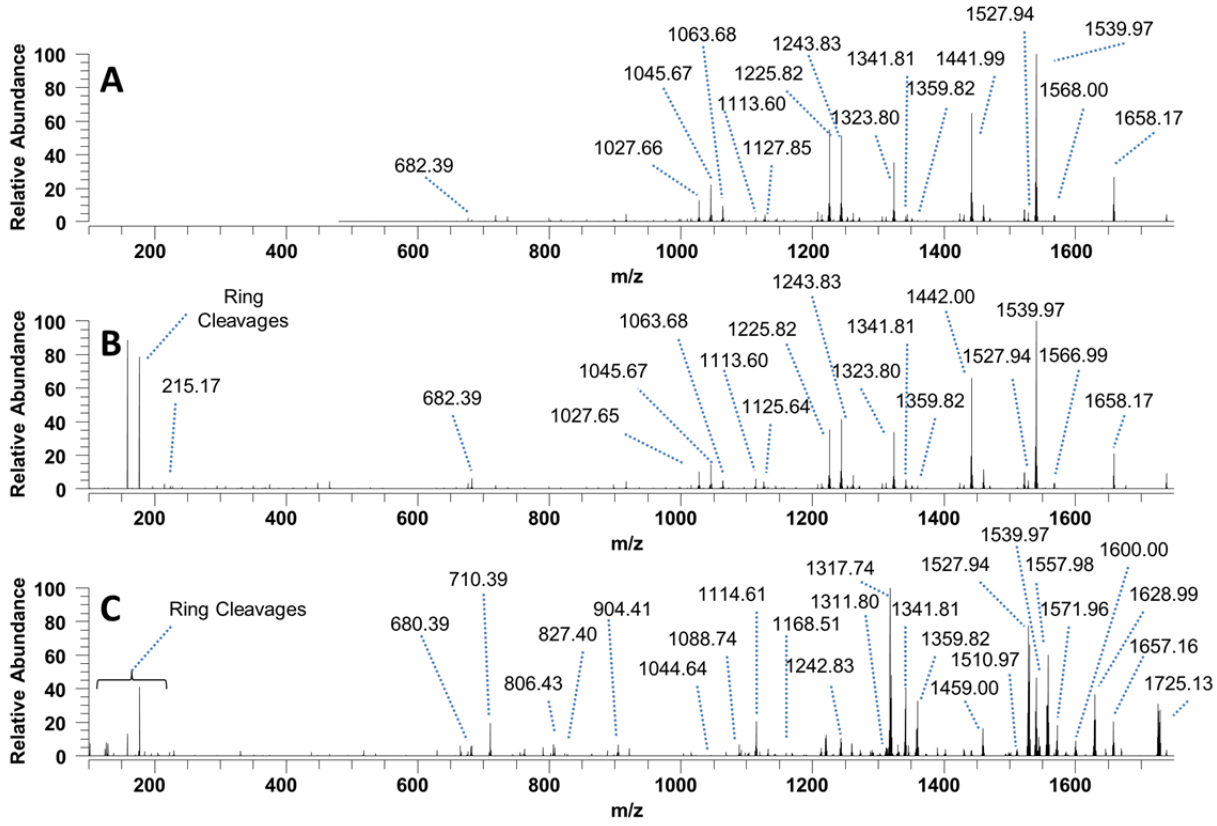


Figure S-5. MS/MS mass spectra of doubly deprotonated *P. aeruginosa* lipid A (M_r = 1617.00 Da) using (A) CID, (B) HCD (C) UVPD. Glucosamine fragment ions are labeled as "ring cleavages".

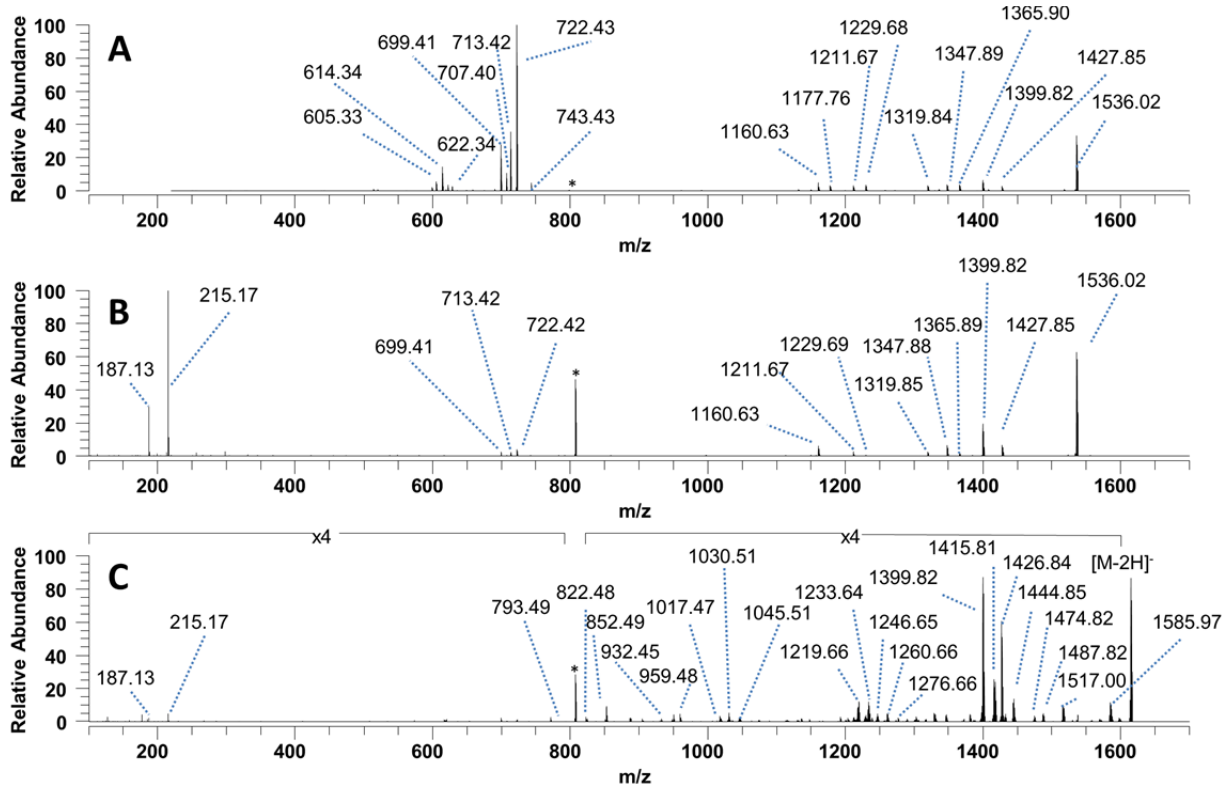


Figure S-6. MS/MS mass spectra of singly deprotonated *P. aeruginosa* lipid A (M_r = 1617.00 Da) using (A) CID, (B) HCD (C) UVPD. Glucosamine fragment ions are labeled as "ring cleavages".

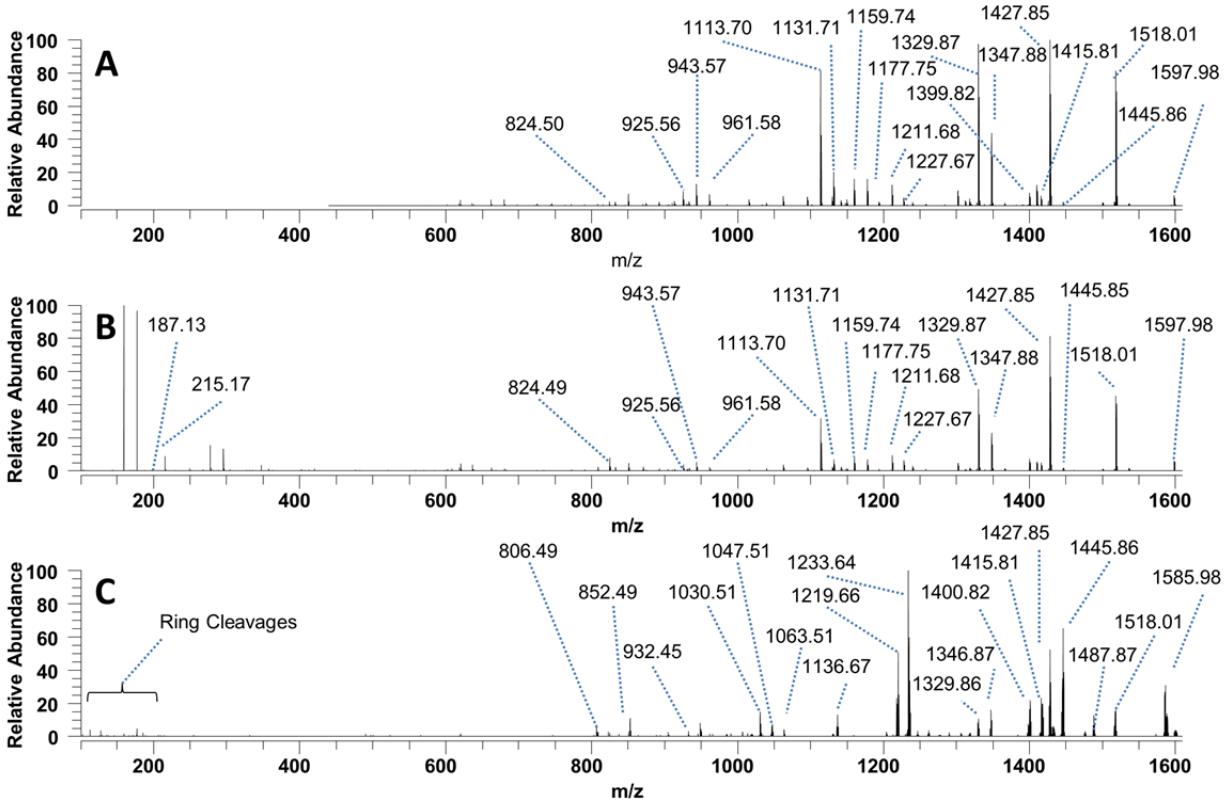
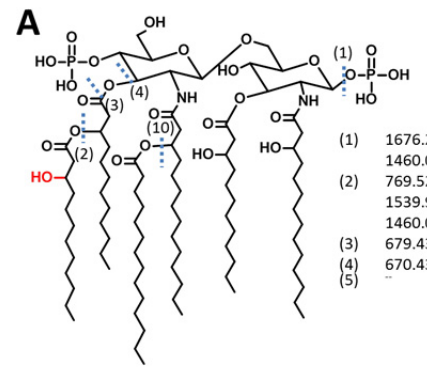
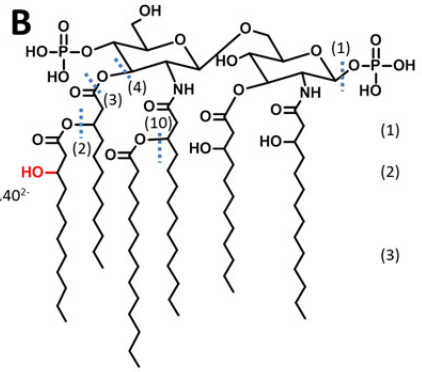


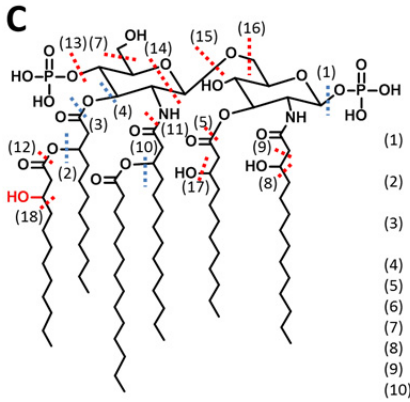
Figure S-7. MS/MS fragmentation maps of doubly deprotonated *V. cholerae* lipid A (M_r = 1757.2 Da) using (A) CID, (B) HCD, and (C) UVPD. Each cleavage site is numbered, and the m/z values of the fragment ions arising from each cleavage site are listed. Those fragment ions that require multiple cleavages are listed next to each cleavage site. Cleavages marked in red font are unique to UVPD.



(1) 1676.22, 1460.01
(2) 769.52^{2-}, 1539.98, 1460.01
(3) 679.43^{2-}
(4) 670.43^{2-}
(5) --
(6) --
(7) --
(8) --
(9) --
(10) 655.40^{2-}

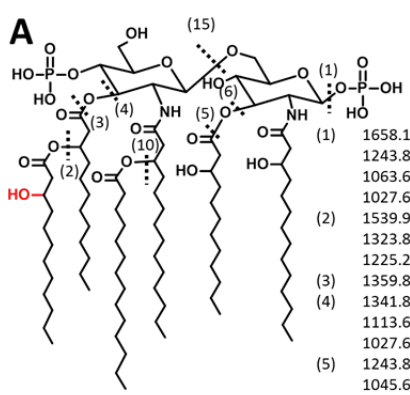


(1) 1676.18, 1460.01
(2) 769.48^{2-}, 1539.97, 1460.01, 215.15
(3) 679.41^{2-}
(4) 670.40^{2-}
(5) --
(6) --
(7) --
(8) --
(9) --
(10) 655.40^{2-}

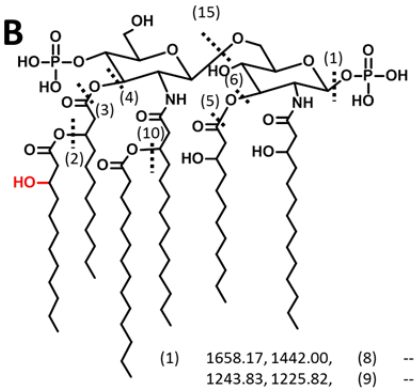


(1) 1657.17, 1457.94, 1241.76, 1169.72
(2) 769.48^{2-}, 1538.97, 1241.46, 215.15
(3) 778.49^{2-}, 1357.81, 1169.72
(4) 1340.81, 904.42
(5) 1457.94, 1241.76
(6) ---
(7) 1725.13
(8) 1599.97
(9) 1570.96
(10) 763.46^{2-}, 1527.94, 1114.62, 904.42,
(11) 1317.74
(12) 1556.96
(13) 1169.72
(14) 1043.64, 710.39
(15) 680.38
(16) 1088.74
(17) 755.38^{2-}
(18) 1627.99
755.38^{2-}

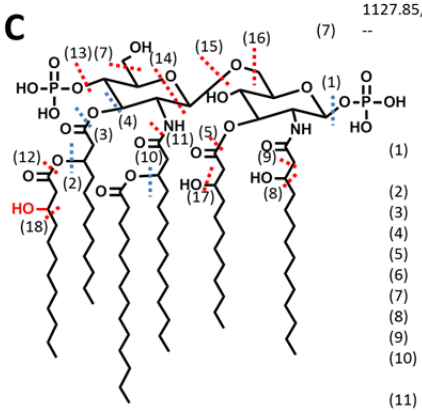
Figure S-8. MS/MS fragmentation maps of singly deprotonated *V. Cholerae* lipid A (M_r = 1757.2 Da) using (A) CID, (B) HCD, and (C) UVPD. Each cleavage site is numbered, and the m/z values of the fragment ions arising from each cleavage site are listed. Those fragment ions that require multiple cleavages are listed next to each cleavage site. Cleavages marked in red font are unique to UVPD.



(1)	1658.17, 1441.99, 1243.83, 1225.82, 1063.68, 1045.67, 1027.66	(8)	--
		(9)	--
		(10)	1527.94, 1113.60
		(11)	--
(2)	1539.97, 1441.99, 1323.80, 1243.83, 1225.23	(12)	--
		(13)	--
		(14)	--
(3)	1359.82, 1063.68	(15)	682.39
(4)	1341.81, 1127.85, 1113.60, 1045.67, 1027.66	(16)	--
		(17)	--
		(18)	--
(5)	1243.83, 1063.68, 1045.67		
(6)	1323.80, 1225.82, 1127.85, 1027.66		
(7)	--		

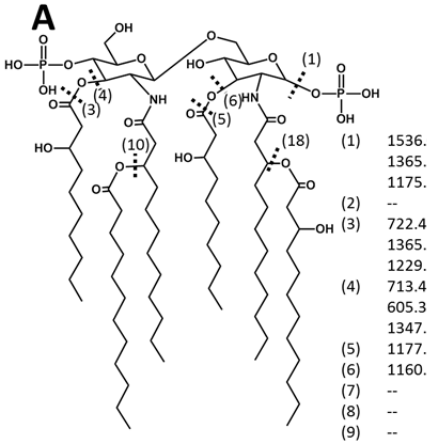


(1)	1658.17, 1442.00, 1243.83, 1225.82, 1063.68, 1045.67, 1027.65	(8)	--
		(9)	--
		(10)	1527.94, 1113.60
		(11)	--
(2)	1539.97, 1442.00, 1323.80, 1243.83, 1225.82, 215.17	(12)	--
		(13)	--
		(14)	--
(3)	1359.82, 1063.68	(15)	682.39
(4)	1341.81, 1125.64, 1113.60, 1045.67, 1027.66	(16)	--
		(17)	--
		(18)	--
(5)	1243.83, 1063.68, 1045.67		
(6)	1323.80, 1225.82, 1125.64, 1027.65		
(7)	--		

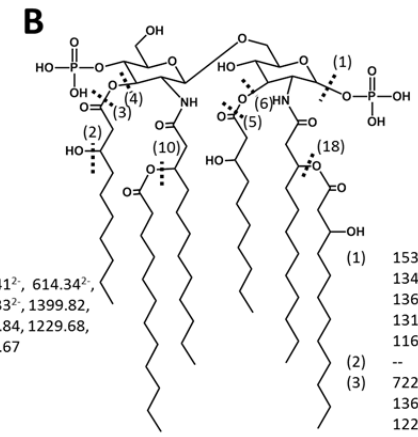


(1)	1657.16, 1459.00, 1242.83, 1169.72	(13)	1168.51
		(14)	1044.64, 710.39
(2)	1538.97, 1241.46,	(15)	680.39
(3)	1357.81, 1168.51	(16)	1088.74
(4)	1341.81, 904.41	(17)	1510.97
(5)	1459.00, 1242.83	(18)	1628.99
(6)	---		
(7)	1725.13		
(8)	1600.00		
(9)	1571.96		
(10)	1527.94, 1114.61, 904.41		
(11)	1317.74		
(12)	1557.98		

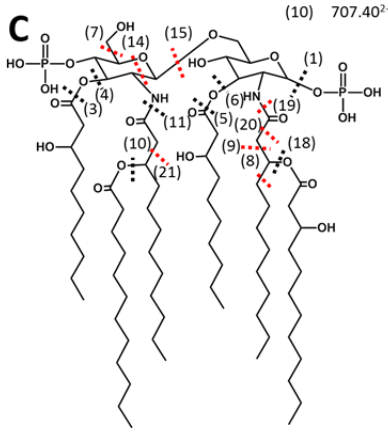
Figure S-9. MS/MS fragmentation maps of doubly deprotonated *P. aeruginosa* lipid A (M_r = 1617.00 Da Da) using (A) CID, (B) HCD, and (C) UVPD-MS. Each cleavage site is numbered, and the m/z values of the fragment ions arising from each cleavage site are listed. Those fragment ions that require multiple cleavages are listed next to each cleavage site. Cleavages marked in red font are unique to UVPD.



(1)	1536.02, 1347.89, 1365.90, 1319.84, 1175.76, 1160.63	(11)	--
(2)	--	(12)	--
(3)	722.43^{2-}, 614.34^{2-} 1365.90, 1177.75, 1229.68, 1160.63	(13)	--
(4)	713.42^{2-}, 622.34^{2-} 605.33^{2-}, 1427.85, 1347.89, 1211.67,	(14)	--
(5)	1177.76	(15)	--
(6)	1160.63, 622.34^{2-}	(16)	--
(7)	--	(17)	--
(8)	--	(18)	699.41^{2-}, 614.34^{2-}, 605.33^{2-}, 1399.82, 1319.84, 1229.68, 1211.67
(9)	--		
(10)	707.40^{2-}		

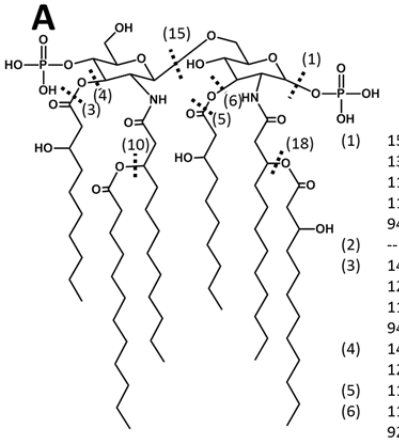


(1)	1536.02, 1347.88, 1365.89, 1319.85, 1160.63	(9)	--
(2)	--	(10)	--
(3)	722.42^{2-}, 1365.89, 1229.69, 1160.63	(11)	--
(4)	713.42^{2-}, 1427.85, 1347.88, 1211.67, 187.13	(12)	--
(5)	--	(13)	--
(6)	1160.63	(14)	--
(7)	--	(15)	--
(8)	--	(16)	--
		(17)	--
		(18)	699.41^{2-}, 1399.82, 1319.85, 1229.69, 1211.67, 215.17

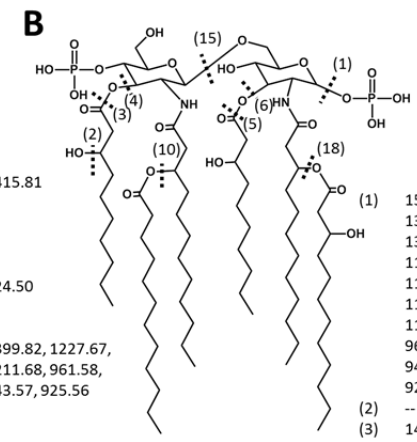


(1)	1517.00, 1346.87, 1328.87, 959.48, 932.45	(12)	--
(2)	--	(13)	--
(3)	1444.85, 1346.87	(14)	852.49
(4)	1426.84, 1328.87, 1046.51, 1017.47, 1030.51, 959.48, 932.45	(15)	822.48, 793.49
(5)	--	(16)	--
(6)	--	(17)	--
(7)	1585.97, 1017.49	(18)	1399.82
(8)	1487.82	(19)	1219.66, 1030.51, 932.45
(9)	1260.66	(20)	1246.65
(10)	1415.81	(21)	1276.66
(11)	1233.64, 1046.51, 1017.47, 959.48		

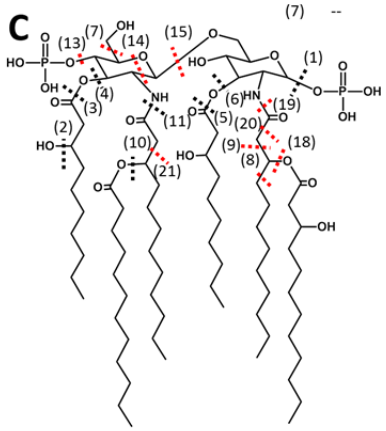
Figure S-10. MS/MS fragmentation maps of singly deprotonated *P. aeruginosa* lipid A (M_r = 1617.00 Da Da) using (A) CID, (B) HCD, and (C) UVPD. Each cleavage site is numbered, and the m/z values of the fragment ions arising from each cleavage site are listed. Those fragment ions that require multiple cleavages are listed next to each cleavage site. Cleavages marked in red font are unique to UVPD.



(1)	1518.01, 1347.88, 1329.87, 1177.75, 1159.74, 1131.71, 1113.70, 961.58, 943.57, 925.56
(2)	--
(3)	1445.86, 1347.88, 1227.67, 1159.74, 1177.75 961.58, 943.57
(4)	1427.85, 1329.87, 1211.68, 925.56
(5)	1177.75, 961.58
(6)	1159.74, 943.57, 925.56
(7)	--
(8)	--
(9)	--
(10)	1415.81
(11)	--
(12)	--
(13)	--
(14)	--
(15)	824.50
(16)	--
(17)	--
(18)	1399.82, 1227.67, 1211.68, 961.58, 943.57, 925.56



(1)	1518.01, 1347.88, 1329.87, 1177.75, 1159.74, 1131.71, 1113.70, 961.58, 943.57, 925.56	(6)	1159.74, 943.57, 925.56
(2)	--	(7)	--
(3)	1445.85, 1347.88, 1227.67, 1159.74, 1177.75, 961.58, 943.57	(8)	--
(4)	1427.85, 1329.87, 1211.68, 925.56	(9)	--
(5)	1177.75, 961.58	(10)	1415.81
		(11)	--
		(12)	--
		(13)	--
		(14)	--
		(15)	824.49
		(16)	--
		(17)	--
		(18)	1399.82, 1227.67, 1211.68, 961.58, 943.57, 925.56



(1)	1518.01, 1346.87, 1329.86, 932.45	(14)	852.49
(2)	--	(15)	822.48
(3)	1445.86, 1346.87	(16)	806.49
(4)	1427.85, 1329.86, 1047.51, 1018.51, 1030.51, 932.45	(17)	--
		(18)	1400.82
		(19)	1219.66, 1030.51, 932.45
(5)	--	(20)	1246.64
(6)	--	(21)	1277.66
(7)	1585.98, 1018.51		
(8)	1487.87		
(9)	1261.64		
(10)	1415.81		
(11)	1233.64, 1047.51, 1018.51		
(12)	--		
(13)	--		

Figure S-11. Extracted ion chromatograms (EIC) of the major lipid A species observed upon combinatorial modification of BN2 expressed in the presence of the active enzymes LpxF, PagL and PagP. Each EIC is aligned with the corresponding schematic structure.

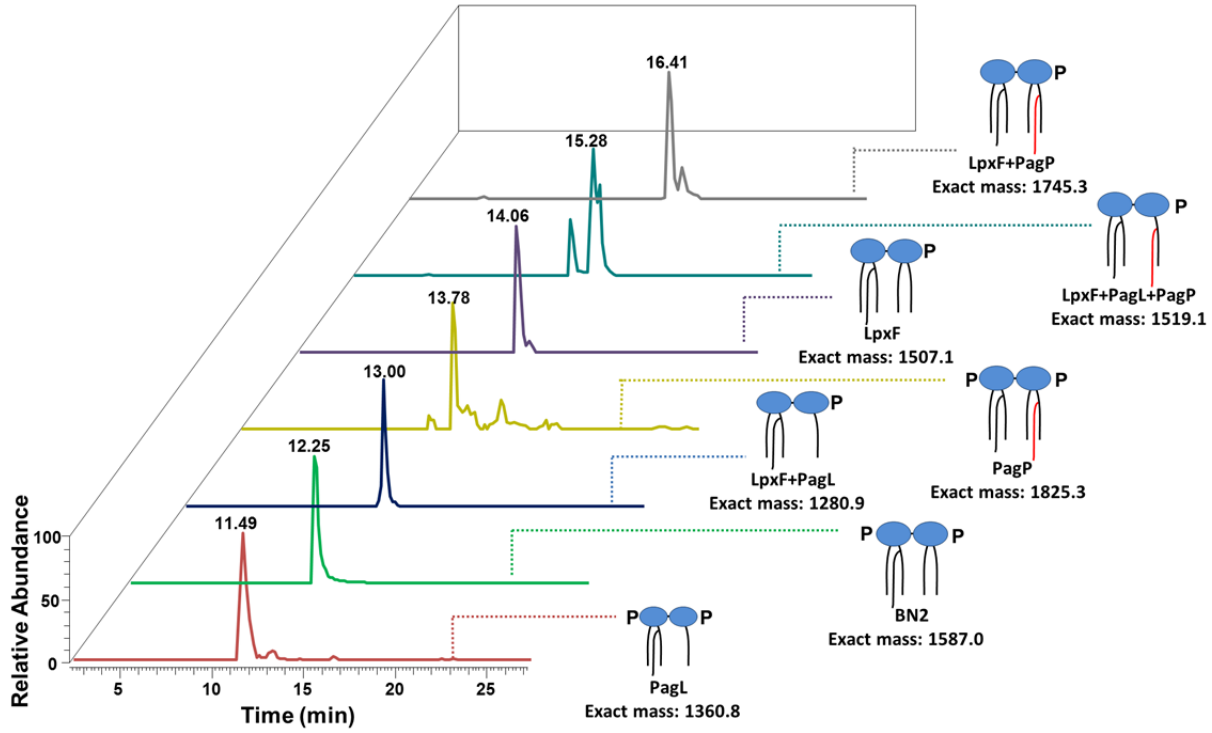


Figure S-12. Survey ESI mass spectra of the major lipid A species observed upon combinatorial modification of BN2 expressed in the presence of the active enzymes LpxE, PagL and PagP.

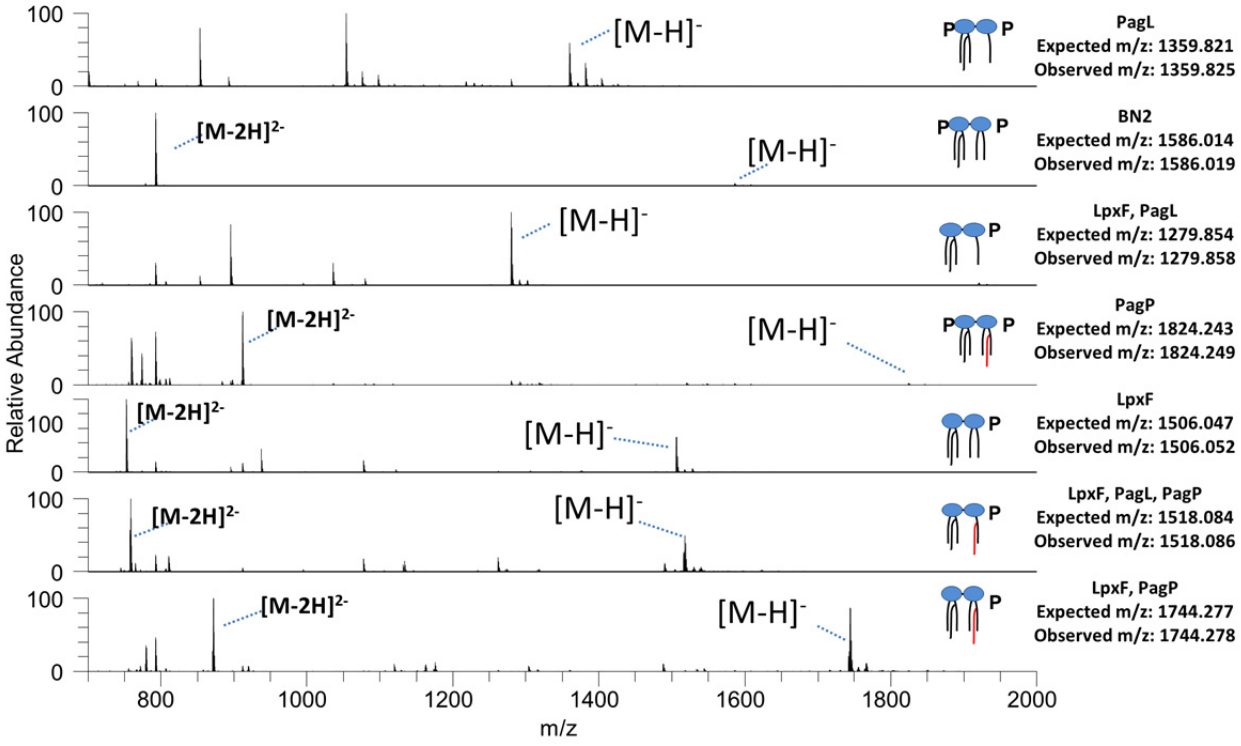


Figure S-13 Cleavage site histograms for doubly and singly deprotonated *E. coli* BN2 lipid (M_r = 1587.0 Da) using (A) CID, and (B) UVPD. Black bars represent fragment ions from the doubly deprotonated precursor. Blue bars represent fragments from the singly deprotonated precursor. Relative frequencies for all cleavage sites were calculated using equation 1. The numbers representing the cleavage sites are shown in the structure.

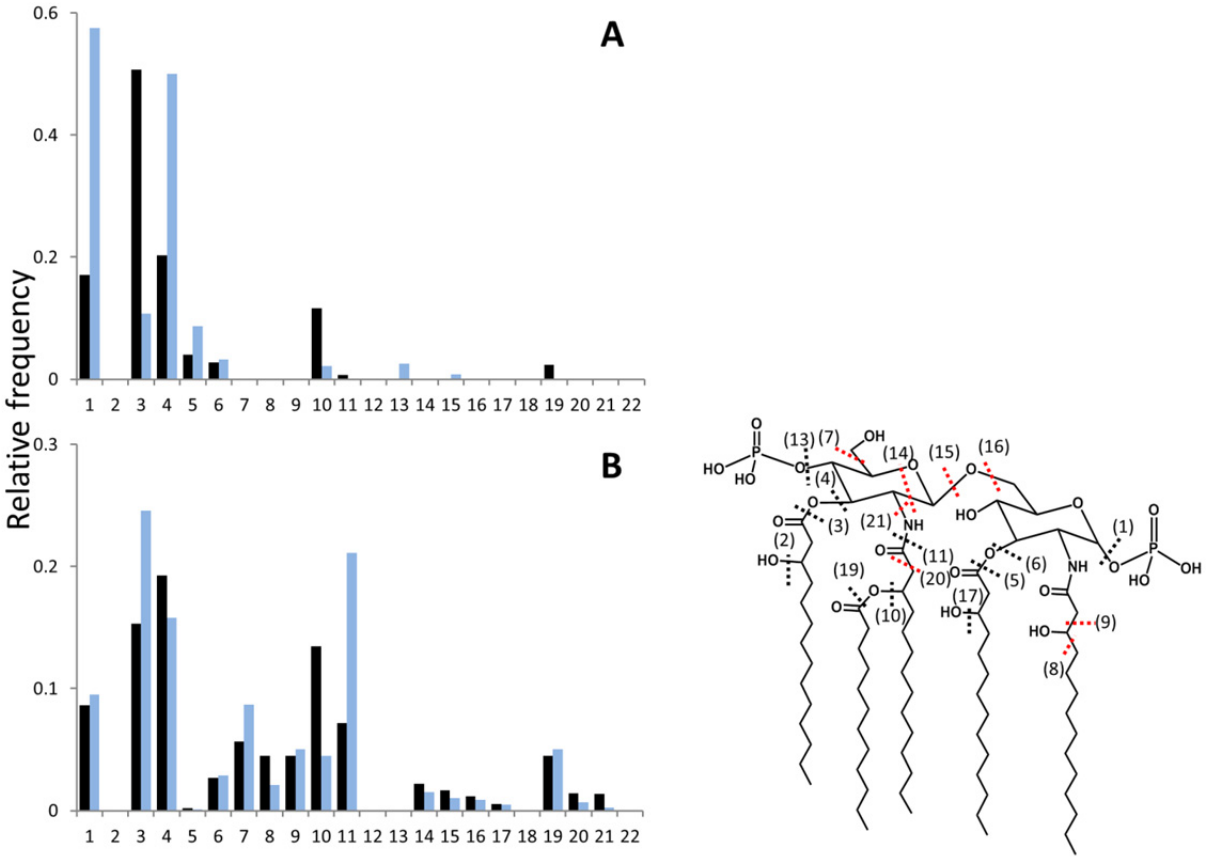
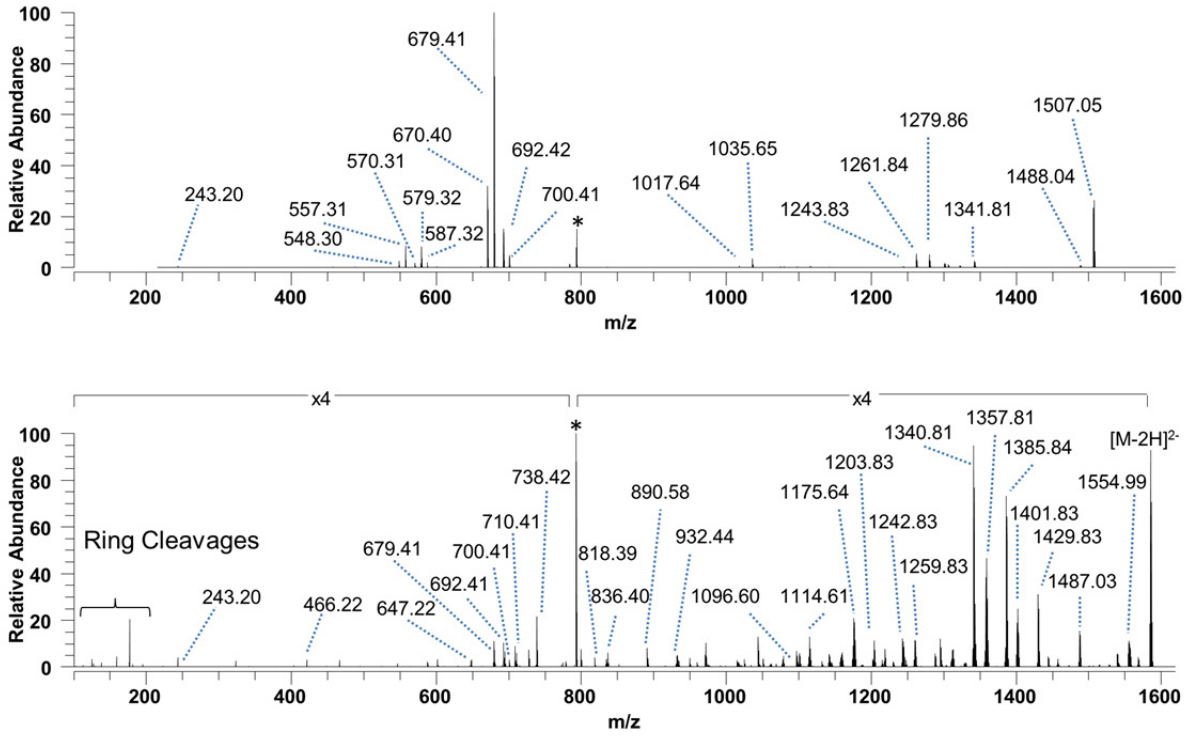
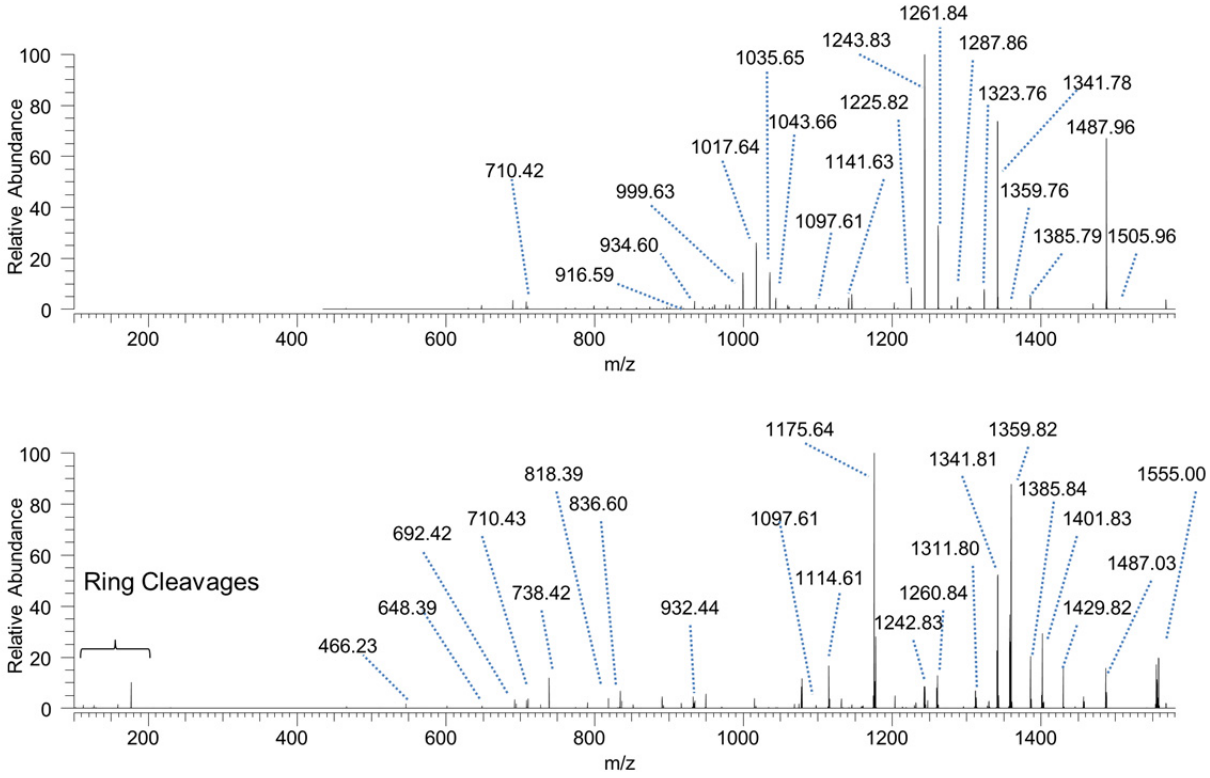


Figure S-14. The following compilation of spectra and fragmentation maps were used in the identification of BN2 pFLP lipid A species shown in Figure 5.

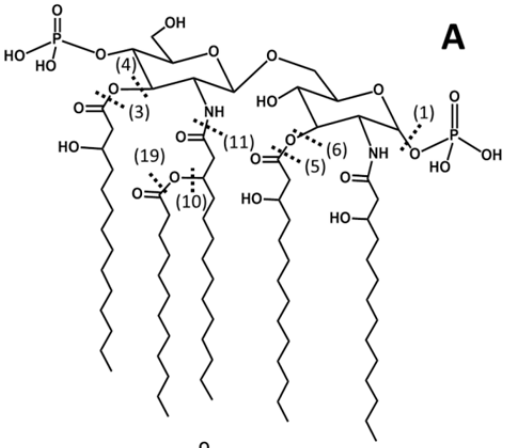
MS/MS mass spectra of doubly deprotonated penta-acylated BN2 *E. coli* lipid A (M_r = 1587.0 Da) using (A) CID or (B) UVPD. Glucosamine fragment ions are labeled as "ring cleavages".



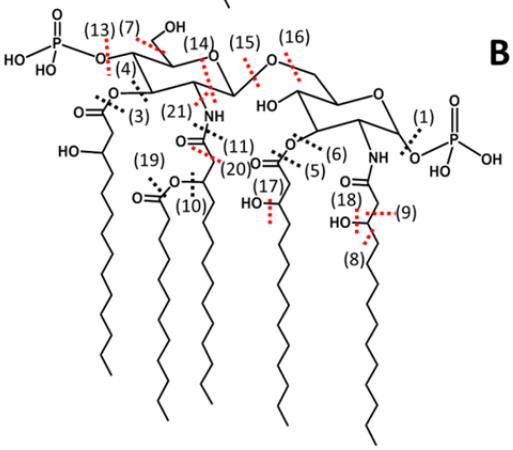
MS/MS mass spectra of singly deprotonated penta-acylated BN2 *E. coli* lipid A (M_r = 1587.0 Da) using (A) CID and (B) UVPD. Glucosamine fragment ions are labeled as "ring cleavages."



MS/MS fragmentation maps of doubly deprotonated BN2 *E. coli* lipid A (M_r = 1587.0 Da) using (A) CID and (B) UVPD. Each cleavage site is numbered, and the m/z values of the fragment ions arising from each cleavage site are listed. Those fragment ions that require multiple cleavages are listed next to each cleavage site. Cleavages marked in red font are unique to UVPD. The companion MS/MS spectra are shown in Supplemental Figure 14.

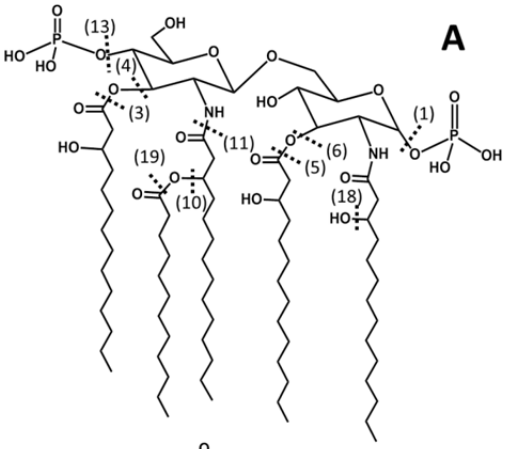


1) 1507.05, 1488.05, 1261.84, 1243.83, 1035.65, 1017.64
2) --
3) 679.41^{2-}, 579.32^{2-}, 1261.84, 1035.65, 1017.64
4) 670.39^{2-}, 570.31^{2-}, 557.31^{2-}, 548.30^{2-}, 1341.81, 1243.83, 1035.65
5) 1017.64, 1035.65, 557.31^{2-}
6) 548.30^{2-}
7) --
8) --
9) --
10) 692.42^{2-}, 579.32^{2-}, 570.31^{2-}
11) 587.32^{2-}
12) --
13) --
14) --
15) --
16) --
17) --
18) --
19) 700.41^{2-}
20) --
21) --

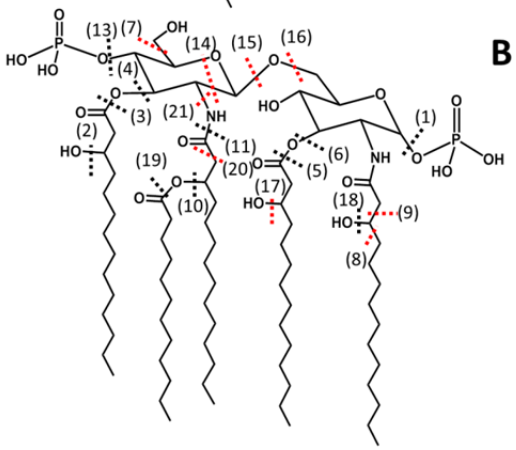


1) 1487.03, 1259.83, 1242.83, 836.40, 818.39
2) --
3) 679.41^{2-}, 1358.81, 1259.83, 836.40, 818.39, 647.22
4) 1340.81, 1242.83, 1114.61, 1096.60, 932.44 243.20
5) 466.22
6) 1114.62, 1096.60
7) 1554.99, 1312.80, 1114.62
8) 1429.83
9) 1401.83
10) 692.41^{2-}, 1385.84, 836.40
11) 1175.64, 1114.62, 932.44
12) --
13) --
14) 738.42
15) 710.42, 647.22
16) 890.58, 466.22
17) 818.39.
18) --
19) 700.42^{2-}, 1401.83
20) 1203.63
21) 1159.63

MS/MS fragmentation maps of singly deprotonated BN2 *E. coli* lipid A (M_r = 1587.0 Da) using (A) CID and (B) UVPD. Each cleavage site is numbered, and the m/z values of the fragment ions arising from each cleavage site are listed. Those fragment ions that require multiple cleavages are listed next to each cleavage site. Cleavages marked in red font are unique to UVPD. The companion MS/MS spectra are shown in Supplemental Figure 15.

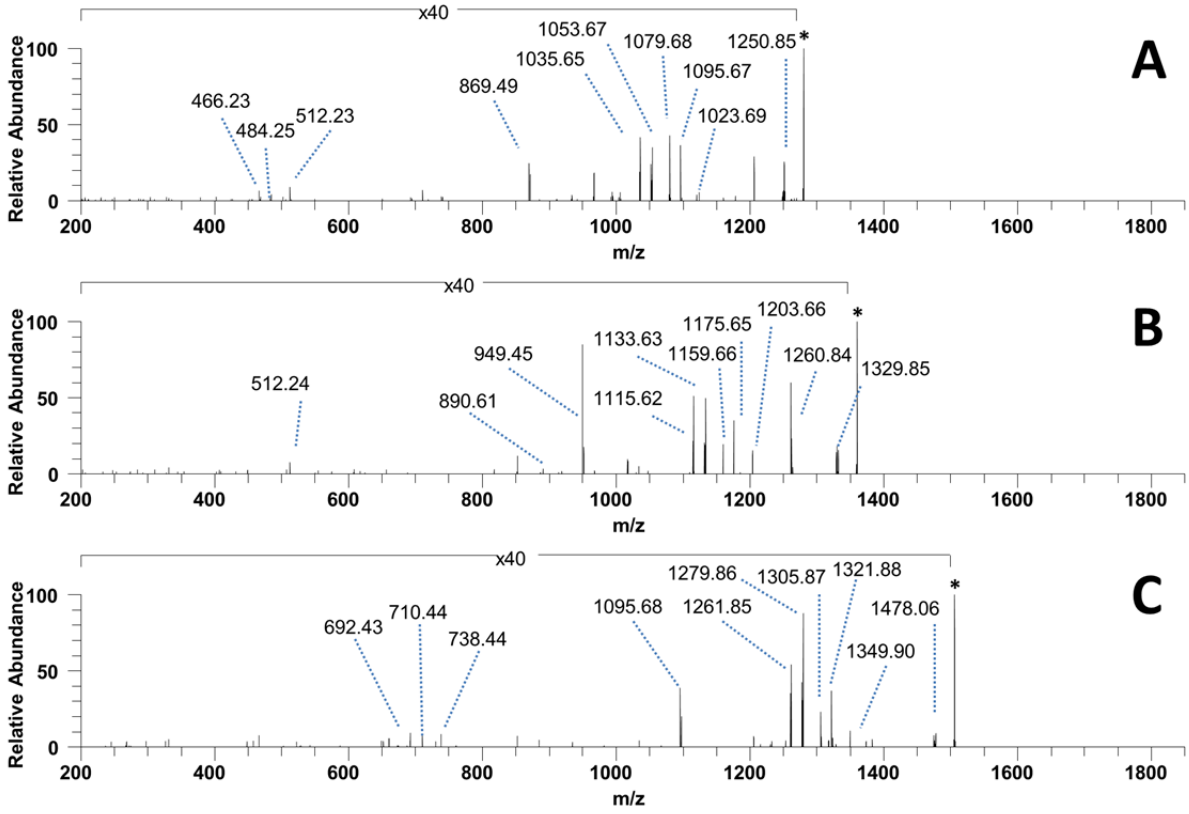


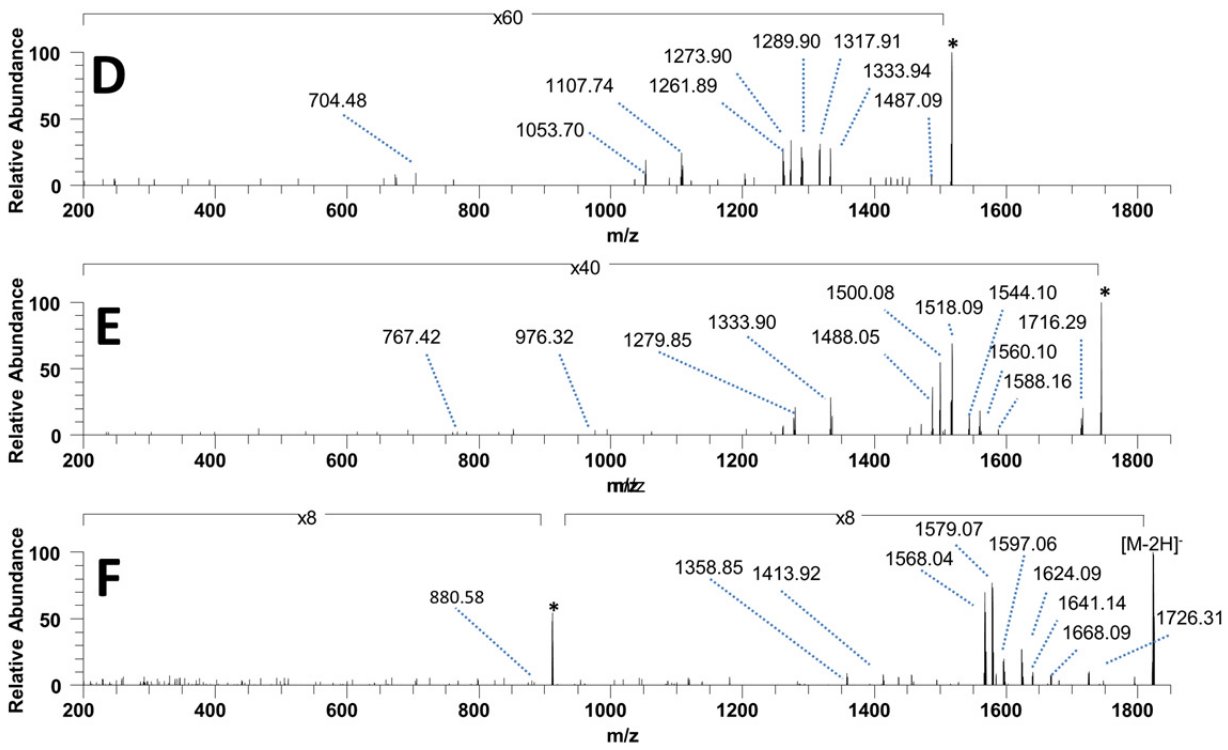
1) 1505.96, 1487.96, 1261.84, 1243.83, 1225.82, 1035.65, 1017.64, 999.63, 934.60, 916.59
2) --
3) 1359.76, 1261.84, 1035.65, 934.60
4) 1341.78, 1323.76, 1243.83, 1141.63, 1097.61, 1017.64, 999.63, 916.59
5) 1035.65, 1017.64, 934.60
6) 1097.61, 999.63
7) --
8) --
9) --
10) 1385.79, 1141.63, 916.59
11) --
12) --
13) 1225.82, 934.60, 916.59
14) --
15) 710.42
16) --
17) 1323.76
18) --
19) --
20) --
21) --



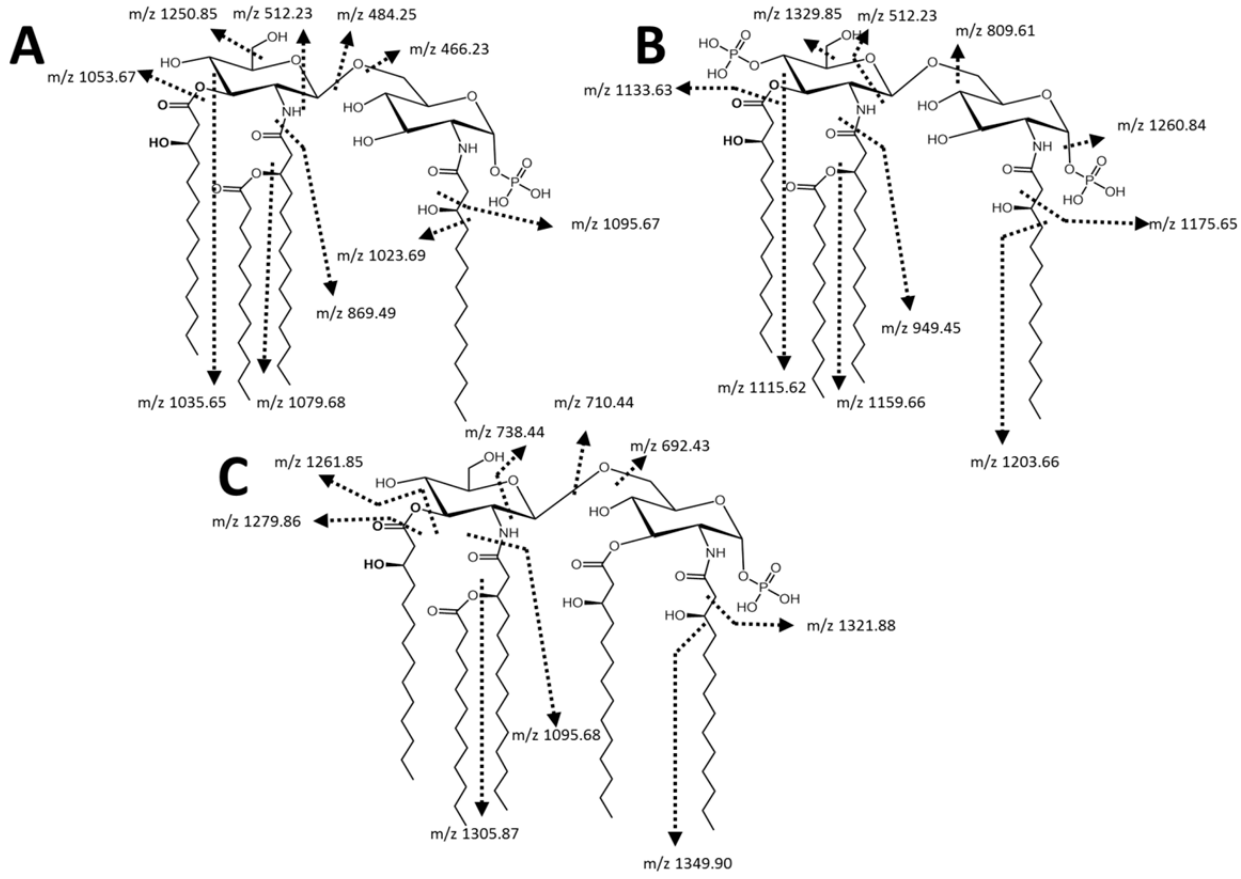
1) 1487.03, 1260.84, 1242.83, 836.60, 818.39
2) --
3) 1359.82, 1311.80 1260.84, 834.47, 818.39, 648.39
4) 1341.81, 1242.83, 932.44, 1097.61
5) 466.23
6) 1097.61, 1114.61
7) 1555.00, 1311.80, 1114.61
8) 1429.82
9) 1401.83
10) 1385.84, 836.60
11) 1175.64, 1114.61, 932.44
12) --
13) --
14) 738.42
15) 710.42, 648.39
16) 890.58, 466.23
17) 818.39
18) --
19) 1401.84
20) 1203.64
21) 1160.63

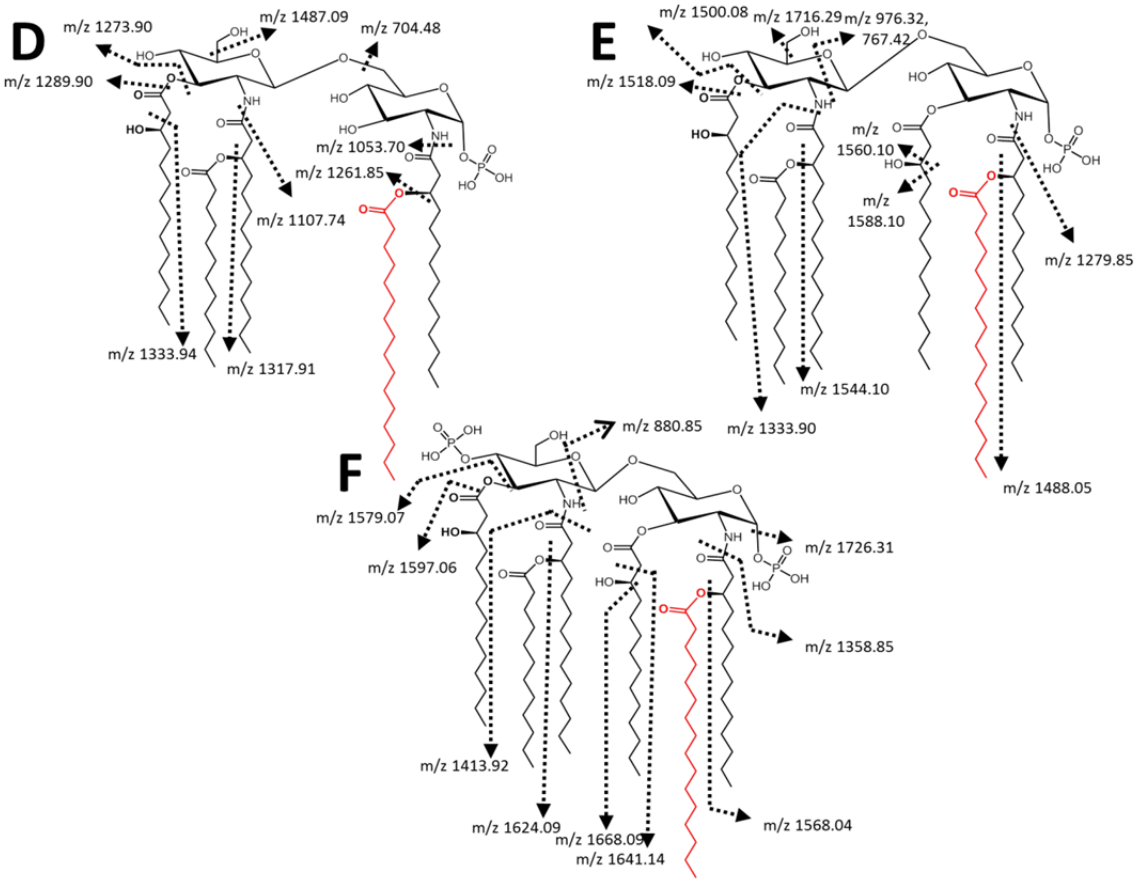
UVPD mass spectra of deprotonated BN2 lipid A modified with (A) LpxF+PagL (M_r = 1280.9 Da), (B) PagL (M_r = 1360.8 Da), (C) LpxF (M_r = 1507.1 Da) , (D) LpxF+PagL+PagP (M_r = 1519.1 Da) , (E) LpxF+PagP (M_r = 1745.3 Da) , and (F) PagP (M_r = 1825.3 Da) .




D
x60
Relative Abundance
m/z
704.48
1053.70
1107.74
1261.89
1273.90
1289.90
1317.91
1333.94
1487.09
*
E
x40
767.42
976.32
1279.85
1333.90
1488.05
1500.08
1518.09
1544.10
1560.10
1588.16
1716.29
*
F
x8
x8
880.58
*
1358.85
1413.92
1568.04
1579.07
1597.06
1624.09
1641.14
1668.09
[M-2H]-
1726.31

UVPD fragment ion cleavage maps for BN2 Lipid A modified with (A) LpxF+PagL (M_r = 1280.9 Da), (B) PagL (M_r = 1360.8 Da), (C) LpxF (M_r = 1507.1 Da), (D) LpxF+PagL+PagP (M_r = 1519.1 Da), (E) LpxF+PagP (M_r = 1745.3 Da), and (F) PagP (M_r = 1825.3 Da). The UVPD-MS spectra are shown in Supplemental Figure 19.




D
m/z 1273.90
m/z 1487.09
m/z 704.48
m/z 1289.90
m/z 1053.70
m/z 1261.85
m/z 1107.74
m/z 1333.94
m/z 1317.91
E
m/z 1500.08
m/z 1716.29
m/z 976.32,
767.42
m/z 1518.09
m/z
1560.10
m/z
1588.10
m/z 1279.85
m/z 1544.10
m/z 1333.90
m/z 1488.05
F
m/z 880.85
m/z 1579.07
m/z 1597.06
m/z 1726.31
m/z 1358.85
m/z 1413.92
m/z 1624.09
m/z 1668.09
m/z 1641.14
m/z 1568.04

Supplemental Table 1. (Table S-1) CID, HCD and UVPD fragment ions of doubly deprotonated *E. coli* lipid A (M_r = 1797.2). The spectra are shown in Figure 1 and fragmentation maps are shown in Figure 2.

Cleavage	Theoretical m/z	Experimental m/z	Formula	Error (ppm)	H Migration
	CID Fragment Ions				
1	1717.253	1717.243	$C_{94}H_{177}N_2O_{22}P$	-5.8	
2	783.498	783.499	$C_{80}H_{148}N_2O_{23}P_2$	1.3	
2	1568.003	1567.999	$C_{80}H_{149}N_2O_{23}P_2$	-2.6	
3	679.407	679.405	$C_{66}H_{124}N_2O_{22}P_2$	-2.9	
4	670.401	670.401	$C_{66}H_{122}N_2O_{21}P_2$	0.0	
1+2	1488.037	1488.035	$C_{80}H_{148}N_2O_{20}P$	-1.3	
	HCD Fragment Ions				
1	1717.253	1717.245	$C_{94}H_{177}N_2O_{22}P$	-4.7	
2	783.498	783.497	$C_{80}H_{148}N_2O_{23}P_2$	-1.3	
2	1568.003	1568.003	$C_{80}H_{149}N_2O_{23}P_2$	0.0	
2	227.202	227.202	$C_{14}H_{27}O_2$	0.0	
3	679.407	679.406	$C_{66}H_{124}N_2O_{22}P_2$	-1.5	
4	670.402	670.401	$C_{66}H_{122}N_2O_{21}P_2$	-1.5	
1+2	1488.037	1488.043	$C_{80}H_{148}N_2O_{20}P$	4.1	
1+2+5	1243.833	1243.831	$C_{66}H_{120}N_2O_{17}P$	-1.6	
1+2+6	1225.822	1225.820	$C_{66}H_{118}N_2O_{16}P$	-1.6	
1+3+5	1035.650	1035.646	$C_{52}H_{96}N_2O_{16}P$	-3.9	
1+4+5	1017.640	1017.638	$C_{52}H_{94}N_2O_{15}P$	-2.0	
	UVPD Fragment Ions				
1	1698.235	1697.218	$C_{94}H_{174}N_2O_{21}P$	-5.4	-H
2	1568.003	1569.000	$C_{80}H_{149}N_2O_{23}P_2$	-6.9	+H
2	783.498	783.494	$C_{80}H_{148}N_2O_{23}P_2$	-5.1	
2	227.202	227.201	$C_{14}H_{27}O_2$	-4.4	
3	1359.821	1357.801	$C_{66}H_{125}N_2O_{22}P_2$	-2.9	-2H
4	1341.810	1340.798	$C_{66}H_{123}N_2O_{21}P_2$	-3.1	-H
6	1552.008	1550.997	$C_{80}H_{149}N_2O_{22}P_2$	-2.1	-H
7	1765.193	1765.191	$C_{93}H_{174}N_2O_{24}P_2$	-1.1	
8	1640.024	1640.017	$C_{83}H_{153}N_2O_{25}P_2$	-4.3	
9	1612.029	1612.020	$C_{82}H_{153}N_2O_{24}P_2$	-5.6	
10	1596.035	1596.025	$C_{82}H_{153}N_2O_{23}P_2$	-6.3	
11	1387.852	1386.833	$C_{68}H_{129}N_2O_{22}P_2$	-8.1	-H
12	1583.998	1584.999	$C_{80}H_{149}N_2O_{24}P_2$	-4.3	+H
14	738.420	738.420	$C_{35}H_{65}NO_{13}P$	0.0	
15	710.425	710.422	$C_{34}H_{65}NO_{12}P$	-4.2	
16	1100.775	1100.771	$C_{60}H_{111}NO_{14}P$	-3.6	
16	692.414	692.412	$C_{34}H_{63}NO_{11}P$	-2.9	
1+3+5+10+17	817.462	818.420	C40H70N2O13P	-61.0	
1+3+5+10	836.480	836.393	C40H73N2O14P	-104.0	
4+11	932.442	932.437	C40H74N2O18P2	-5.4	
7+11+6	1114.645	1114.605	C53H100N2O18P2	-35.9	
1+2+5	1243.833	1242.818	C66H120N2O17P	-5.8	-H
1+2+6	1225.822	1224.763	C66H118N2O16P	-41.8	-H
1+2	1470.026	1470.003	C80H146N2O19P	-15.6	

Supplemental Table 2. (Table S-2) UVPD fragment ions of singly deprotonated BN2 penta-acyl *E. coli* lipid A (M_r = 1587.0 Da) . The spectrum is shown in Supplemental Figure 15B and fragmentation map is shown in Supplemental Figure 16B.

Cleavage	Theoretical m/z	Experimental m/z	Formula	Error (ppm)	H Migration
1	1488.037	1487.027	$C_{80}H_{148}N_2O_20P$	-1.5	-H
3	1359.821	1359.823	$C_{66}H_{125}N_2O_{22}P_2$	1.5	
4	1341.81	1341.813	$C_{66}H_{123}N_2O_{21}P_2$	2.2	
6	1097.6061	1097.613	$C_{52}H_{95}N_2O_{18}P_2$	6.3	+H
7	1554.996	1554.995	$C_{79}H_{148}N_2O_{23}P_2$	-0.6	
8	1429.826	1429.824	$C_{69}H_{127}N_2O_{24}P_2$	-1.4	
9	1401.831	1401.832	$C_{68}H_{127}N_2O_{23}P_2$	0.7	
10	1385.836	1385.838	$C_{68}H_{127}N_2O_{22}P_2$	1.4	
11	1175.638	1175.639	$C_{54}H_{101}N_2O_{21}P_2$	0.9	
14	738.417	738.421	$C_{35}H_{65}NO_{13}P$	5.4	
15	710.425	710.432	$C_{34}H_{65}NO_{12}P$	9.9	
16	890.576	890.58	$C_{46}H_{85}NO_{13}P$	4.5	
19	1401.831	1401.832	$C_{68}H_{127}N_2O_{23}P_2$	0.7	
20	1203.633	1203.636	$C_{55}H_{101}N_2O_{22}P_2$	2.5	
21	1160.627	1160.625	$C_{54}H_{100}NO_{21}P_2$	-1.7	
5+16	466.221	466.226	$C_{20}H_{37}NO_9P$	10.7	
3+15	648.388	648.392	$C_{32}H_{59}NO_{10}P$	6.2	
1+3+5+17	817.462	818.391	$C_{40}H_{70}N_2O_{13}P$	-96.3	+H
4+11	932.442	932.445	$C_{40}H_{74}N_2O_{18}P_2$	3.2	
6+7+11	1114.645	1114.610	$C_{53}H_{100}N_2O_{18}P_2$	-31.4	
1+3	1260.835	1260.836	$C_{66}H_{121}N_2O_{18}P$	0.8	
1+4	1243.833	1242.827	$C_{66}H_{120}N_2O_{17}P$	1.4	-H
4+7	1310.791	1311.800	$C_{65}H_{120}N_2O_{20}P_2$	0.9	+H