

Supplementary Materials

Sulfation of Phenolic Acids: Chemoenzymatic vs. Chemical Synthesis

Viola Kolaříková¹, Katerina Brodský^{1,2}, Lucie Petrášková¹, Helena Pelantová¹, Josef Cvačka³, Libor Havlíček⁴, Vladimír Křen¹ and Kateřina Valentová^{1,*}

¹ Institute of Microbiology of the Czech Academy of Sciences, Vídeňská 1083, CZ 142 20 Prague, Czech Republic

² Department of Biochemistry and Microbiology, University of Chemistry and Technology Prague Technická 5, CZ 16628 Prague 6 (Czech Republic)

³ Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Flemingovo nám. 2, CZ 166 10 Prague, Czech Republic

⁴ Institute of Experimental Botany of the Czech Academy of Sciences, Vídeňská 1083, 14220 Prague, Czech Republic

* Correspondence: kata.valentova@email.cz

Contents

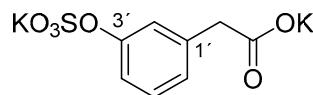
Potassium 2-(3-(sulfonatoxy)phenyl)acetate (K₂ 3-HPA-S)	6
Figure S1. HPLC chromatogram of K ₂ 3-HPA-S	6
Table S1. ¹ H and ¹³ C NMR data for K ₂ 3-HPA-S.....	6
Figure S2. ¹ H NMR spectrum of K ₂ 3-HPA-S.....	7
Figure S3. ¹³ C NMR spectrum of K ₂ 3-HPA-S.....	8
Figure S4. IR spectrum of K ₂ 3-HPA-S.....	8
Figure S5. MS (ESI ⁻) spectrum of K ₂ 3-HPA-S.....	9
Figure S6. HRMS (ESI ⁻) spectrum of K ₂ 3-HPA-S.....	9
Sodium 2-(3-(sulfonatoxy)phenyl)acetate (Na₂ 3-HPA-S)	9
Figure S7. HPLC chromatogram of Na ₂ 3-HPA-S.....	10
Table S2. ¹ H and ¹³ C NMR data for Na ₂ 3-HPA-S	10
Figure S8. ¹ H NMR spectrum of Na ₂ 3-HPA-S	11
Figure S9. ¹³ C NMR spectrum of Na ₂ 3-HPA-S	11
Figure S10. IR spectrum of Na ₂ 3-HPA-S.....	12
Figure S11. MS (ESI ⁻) spectrum of Na ₂ 3-HPA-S.....	12
Figure S12. HRMS (ESI ⁻) spectrum of Na ₂ 3-HPA-S.....	13
Potassium 2-(4-(sulfonatoxy)phenyl)acetate (K₂ 4-HPA-S)	13
Figure S13. HPLC chromatogram of K ₂ 4-HPA-S	13
Table S3. ¹ H and ¹³ C NMR data for K ₂ 4-HPA-S	14
Figure S14. ¹ H NMR spectrum of K ₂ 4-HPA-S.....	14
Figure S15. ¹³ C NMR spectrum of K ₂ 4-HPA-S.....	15
Figure S16. IR spectrum of K ₂ 4-HPA-S	15
Figure S17. MS (ESI ⁻) spectrum of K ₂ 4-HPA-S.....	16
Figure S18. HRMS (ESI ⁻) spectrum of K ₂ 4-HPA-S.....	16
Sodium 2-(4-(sulfonatoxy)phenyl)acetate (Na₂ 4-HPA-S)	16
Figure S19. HPLC chromatogram of Na ₂ 4-HPA-S.....	17
Table S4. ¹ H and ¹³ C NMR data for Na ₂ 4-HPA-S	17
Figure S20. ¹ H NMR spectrum of Na ₂ 4-HPA-S	17
Figure S21. ¹³ C NMR spectrum of Na ₂ 4-HPA-S	18
Figure S22. IR spectrum of Na ₂ 4-HPA-S.....	18
Figure S23. MS (ESI ⁻) spectrum of Na ₂ 4-HPA-S	19
Figure S24. HRMS (ESI ⁻) spectrum of Na ₂ 4-HPA-S.....	19
Potassium 3-(4-(sulfonatoxy)phenyl)propanoate (K₂ 4-HPP-S).....	19
Figure S25. HPLC chromatogram of K ₂ 4-HPP-S	20

Table S5. ^1H and ^{13}C NMR data for K_2 4-HPP-S.....	20
Figure S26. ^1H NMR spectrum of K_2 4-HPP-S	21
Figure S27. ^{13}C NMR spectrum of K_2 4-HPP-S	21
Figure S28. IR spectrum of K_2 4-HPP-S.....	22
Figure S29. MS (ESI $^-$) spectrum of K_2 4-HPP-S.....	22
Figure S30. HRMS (ESI $^-$) spectrum of K_2 4-HPP-S.	23
Sodium 3-(4-(sulfonatoxy)phenyl)propanoate (Na₂ 4-HPP-S).....	23
Figure S31. HPLC chromatogram of Na ₂ 4-HPP-S.....	23
Table S6. ^1H and ^{13}C NMR data for Na ₂ 4-HPP-S	24
Figure S32. ^1H NMR spectrum of Na ₂ 4-HPP-S	24
Figure S33. ^{13}C NMR spectrum of Na ₂ 4-HPP-S	25
Figure S34. IR spectrum of Na ₂ 4-HPP-S.....	25
Figure S35. MS (ESI $^-$) spectrum of Na ₂ 4-HPP-S.	26
Figure S36. HRMS (ESI $^-$) spectrum of Na ₂ 4-HPP-S.....	26
Potassium 2-(2-hydroxyphenyl)acetate (K 2-HPA) and potassium 2-(2-hydroxy-5-sulfonatophenyl)acetate (K₂ 2-HPA-CS).....	26
Figure S37. HPLC chromatogram of K 2-HPA and K ₂ 2-HPA-CS	27
Table S7. ^1H and ^{13}C NMR data for K 2-HPA.....	27
Table S8. ^1H and ^{13}C NMR data for K ₂ 2-HPA-CS.	28
Figure S38. ^1H NMR spectrum of K 2-HPA and K ₂ 2-HPA-CS.....	28
Figure S39. ^{13}C NMR spectrum of K 2-HPA and K ₂ 2-HPA-CS.....	29
3-(4,5-Dihydroxy-2-sulfophenyl)propanoic acid (DHPP-CS).....	29
Figure S40. HPLC chromatogram of DHPP-CS	29
Table S9. ^1H and ^{13}C NMR data for DHPP-CS.....	30
Figure S41. ^1H NMR spectrum of DHPP-CS.	30
Figure S42. ^{13}C NMR spectrum of DHPP-CS	31
Figure S43. MS (ESI $^-$) spectrum of DHPP-CS.	31
Figure S44. HRMS (ESI $^-$) spectrum of DHPP-CS.....	32
3,4-dihydroxyphenylacetic acid 3-O-sulfate (DHPA-3'-S) and 3,4-dihydroxyphenylacetic acid 4-O-sulfate (DHPA-4'-S).....	32
Figure S45. HPLC chromatogram of DHPA-3'-S and DHPA-4'-S.....	32
Table S10. ^1H and ^{13}C NMR data for DHPA-3'-S and DHPA-4'-S	33
Figure S46. ^1H NMR spectrum of DHPA-3'-S and DHPA-4'-S	34
Figure S47. ^{13}C NMR spectrum of DHPA-3'-S and DHPA-4'-S.....	34
Figure S48. IR spectrum of DHPA-3'-S and DHPA-4'-S.....	35
Figure S49. MS (ESI $^-$) spectrum of DHPA-S.	35

Figure S50. HRMS (ESI ⁻) spectrum of compound DHPA-S	36
3,4-Dihydroxyphenylpropionic acid sulfates (DHPP-S): 3,4-dihydroxyphenylpropionic acid 3'-O-sulfate (DHPP-3'-S) and 3,4-dihydroxyphenylpropionic acid 4'-O-sulfate (DHPP-4'-S).....	36
Figure S51. HPLC chromatogram of DHPP-3'-S and DHPP-4'-S	37
Table S11. ¹ H and ¹³ C NMR data of DHPP-3'-S and DHPP-4'-S	37
Figure S52. ¹ H NMR spectrum of DHPP-3'-S and DHPP-4'-S	38
Figure S53. ¹³ C NMR spectrum of DHPP-3'-S and DHPP-4'-S	39
Figure S54. IR spectrum of DHPP-3'-S and DHPP-4'-S	39
Figure S55. MS (ESI ⁻) spectrum of DHPP-S	40
Figure S56. HRMS (ESI ⁻) spectrum of DHPP-S	40
Sodium dihydroxyphenylacetate sulfates (Na₂ DHPA-S): sodium 2-(4-hydroxy-3-(sulfonatoxy)phenyl)acetate (DHPA-3'-S) and sodium 2-(3-hydroxy-4-(sulfonatoxy)phenyl)acetate (DHPA-4'-S)	40
Figure S57. HPLC chromatogram of Na₂ DHPA-3'-S and Na₂ DHPA-4'-S	41
Table S12. ¹ H and ¹³ C NMR data of Na₂ DHPA-3'-S and Na₂ DHPA-4'-S	41
Figure S58. ¹ H NMR spectrum of Na₂ DHPA-3'-S and Na₂ DHPA-4'-S	42
Figure S59. ¹³ C NMR spectrum of Na₂ DHPA-3'-S and Na₂ DHPA-4'-S	43
Figure S60. IR spectrum of compound Na₂ DHPA-3'-S and Na₂ DHPA-4'-S	43
Figure S61. MS (ESI ⁻) spectrum of Na₂ DHPA-S	44
Figure S62. HRMS (ESI ⁻) spectrum of Na₂ DHPA-S	44
Sodium phenylpropanoate sulfates (DHPP-S): sodium 3-(4-hydroxy-3-(sulfonatoxy)phenyl)propanoate (DHPP-3'-S) and sodium 2-(3-hydroxy-4-(sulfonatoxy)phenyl)propanoate (DHPP-4'-S).....	45
Figure S63. HPLC chromatogram of Na₂ DHPP-3'-S and Na₂ DHPP-4'-S	45
Table S13. ¹ H and ¹³ C NMR data of Na₂ DHPP-3'-S and Na₂ DHPP-4'-S	45
Figure S64. ¹ H NMR spectrum of Na₂ DHPP-3'-S and Na₂ DHPP-4'-S	46
Figure S65. ¹³ C NMR spectrum of Na₂ DHPP-3'-S and Na₂ DHPP-4'-S	47
Figure S66. IR spectrum of compound Na₂ DHPP-3'-S and Na₂ DHPP-4'-S	47
Figure S67. MS (ESI ⁻) spectrum of Na₂ DHPP-S	48
Figure S68. HRMS (ESI ⁻) spectrum of Na₂ DHPP-S	48
(Trioxomethyl)methylammonium (2-hydroxyphenyl)acetate (2-HPA-Tris).....	48
Figure S69. HPLC chromatogram of 2-HPA-Tris	49
Table S14. ¹ H and ¹³ C NMR data for compound 2-HPA-Tris	49
Figure S70. ¹ H NMR spectrum of 2-HPA-Tris	50
Figure S71. ¹³ C NMR spectrum of 2-HPA-Tris	50
Figure S72. IR spectrum of 2-HPA-Tris	51
(Trioxomethyl)methylammonium (3-hydroxyphenyl)acetate (3-HPA-Tris).....	51

Figure S73. HPLC chromatogram of 3 -HPA-Tris	51
Table S15. ^1H and ^{13}C NMR data for 3 -HPA-Tris.....	52
Figure S74. ^1H NMR spectrum of 3 -HPA-Tris.....	52
Figure S75. ^{13}C NMR spectrum of 3 -HPA-Tris.....	53
Figure S76. IR spectrum of 3 -HPA-Tris	53
(Trioxomethyl)methylammonium (4-hydroxyphenyl)acetate (4-HPA-Tris).....	54
Figure S77. HPLC chromatogram of 4 -HPA-Tris	54
Table S16. ^1H and ^{13}C NMR data for 4 -HPA-Tris.....	54
Figure S78. ^1H NMR spectrum of 4 -HPA-Tris.....	55
Figure S79. ^{13}C NMR spectrum of 4 -HPA-Tris.....	55
Figure S80. IR spectrum of 4 -HPA-Tris	56
(Trioxomethyl)methylammonium (4-hydroxyphenyl)propanoate (4-HPP-Tris)	56
Figure S81. HPLC chromatogram of 4 -HPA-Tris	56
Table S17. ^1H and ^{13}C NMR data for 4 -HPP-Tris	57
Figure S82. ^1H NMR spectrum of 4 -HPP-Tris.....	57
Figure S83. ^{13}C NMR spectrum of 4 -HPP-Tris.....	58
Figure S84. IR spectrum of 4 -HPP-Tris	58

Potassium 2-(3-(sulfonatoxy)phenyl)acetate (K_2 3-HPA-S)



mAU

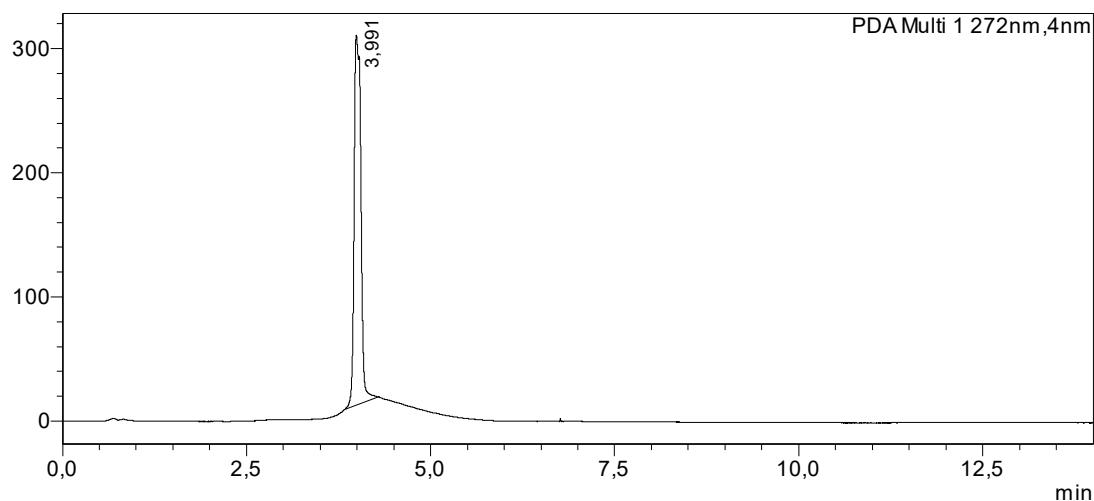


Figure S1. HPLC chromatogram of K_2 3-HPA-S

(RT= 3.991 min, 99% purity)

Table S1. ^1H and ^{13}C NMR data for K_2 3-HPA-S

(700.13 MHz for ^1H , 176.05 MHz for ^{13}C , DMSO-*d*₆)

Atom	δ_{C}	m.	δ_{H}	n _H	m.	J [Hz]	$\delta_{\text{C}}^{\text{HPA}}$	$\delta_{\text{C}} - \delta_{\text{C}}^{\text{HPA}}$
1	173.95	S	-	0	-	-	172.52	1.43
2	45.29	T	3.243	2	s	-	40.72	4.57
1'	140.04	S	-	0	-	-	136.11	3.93
2'	121.45	D	7.084	1	dd	2.4, 1.5	116.12	5.33
3'	152.88	S	-	0	-	-	157.16	-4.28
4'	117.54	D	6.936	1	ddd	8.1, 2.4, 1.0	113.51	4.03
5'	127.73	D	7.101	1	dd	8.1, 7.5	129.08	-1.35
6'	124.16	D	6.908	1	ddd	7.5, 1.5, 1.0	119.83	4.33

Minority K 3-HPA:

Atom	δ_c	m.	δ_h	n_H	m.	J [Hz]	δ_c^{HPA}	$\delta_c - \delta_c^{\text{HPA}}$
1	174.10	S	-	0	-	-	172.52	1.58
2	45.19	T	3.191	2	s	-	40.72	4.47
1'	139.98	S	-	0	-	-	136.11	3.87
2'	116.32	D	6.726	1	dd	2.5, 1.4	116.12	0.2
3'	157.30	S	-	0	-	-	157.16	0.14
4'	112.32	D	6.525	1	ddd	8.0, 2.5, 0.9	113.51	-1.19
5'	128.23	D	6.963	1	dd	8.0, 7.5	129.08	-0.85
6'	119.49	D	6.584	1	ddd	7.5, 1.4, 0.9	119.83	-0.34

approximate molar ratio **K₂ 3-HPA-S : K 3-HPA** = 88 : 12

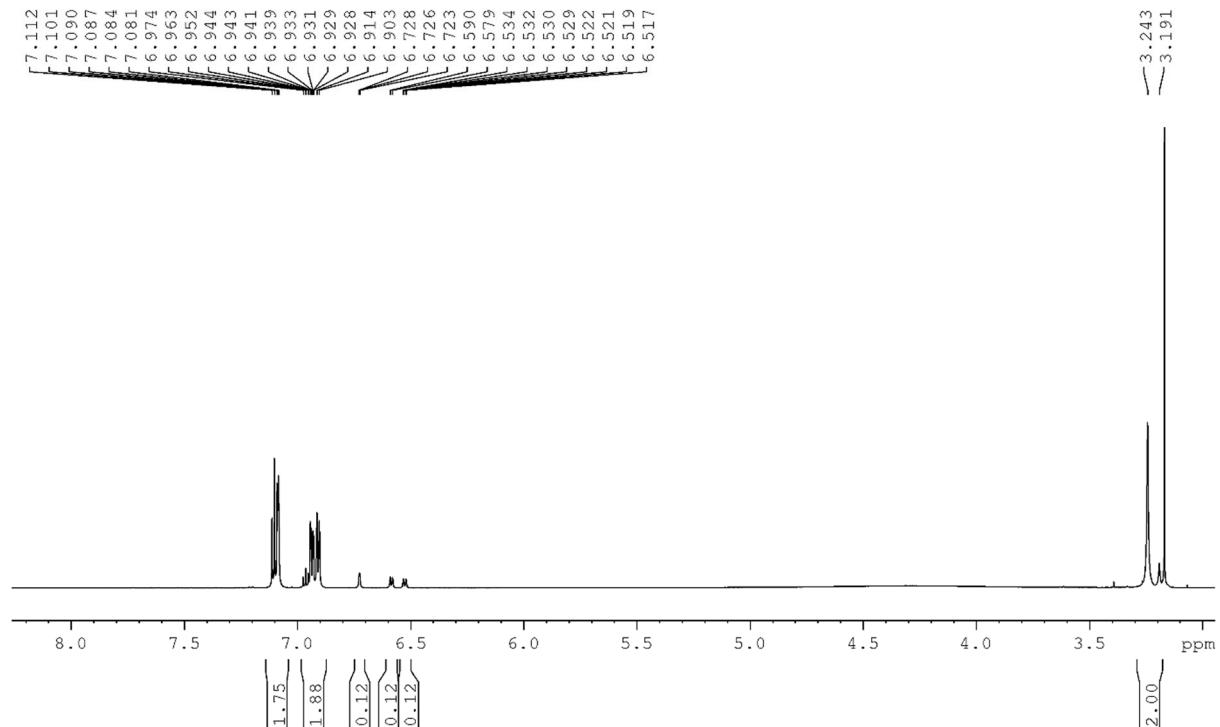


Figure S2. ¹H NMR spectrum of **K₂ 3-HPA-S**

(700.13 MHz, DMSO-*d*₆)

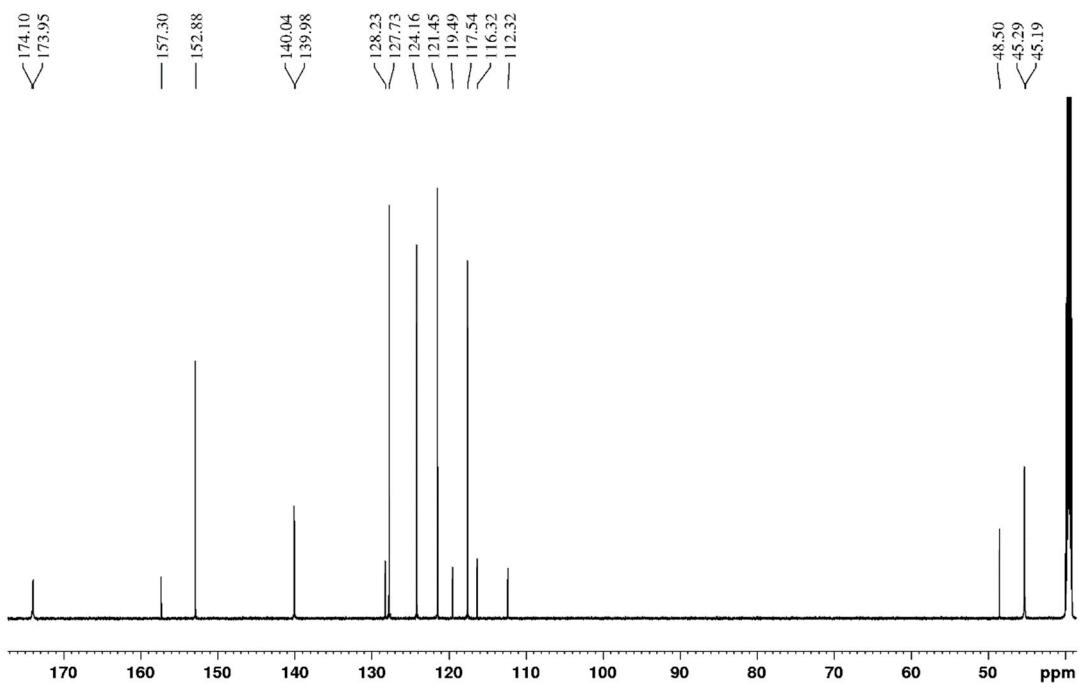


Figure S3. ^{13}C NMR spectrum of **K₂ 3-HPA-S**

(176.05 MHz, DMSO-*d*₆)

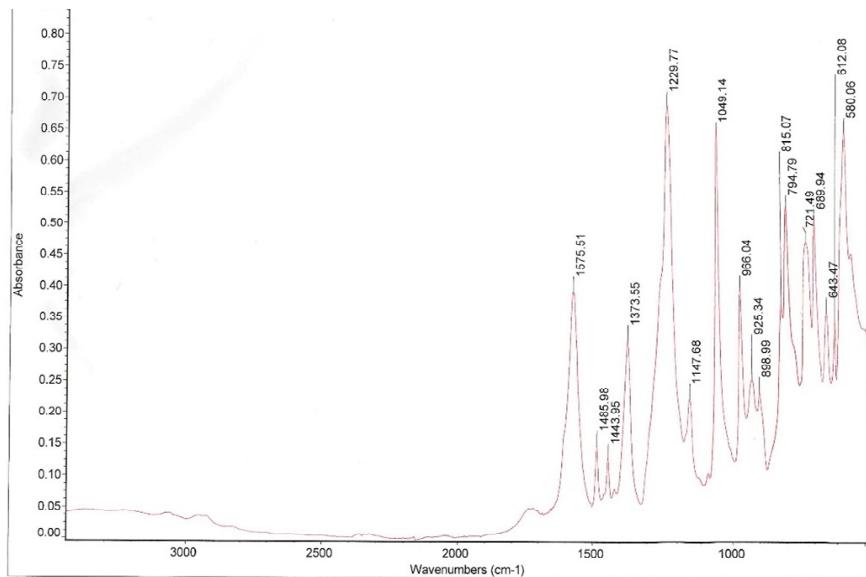


Figure S4. IR spectrum of **K₂ 3-HPA-S**.

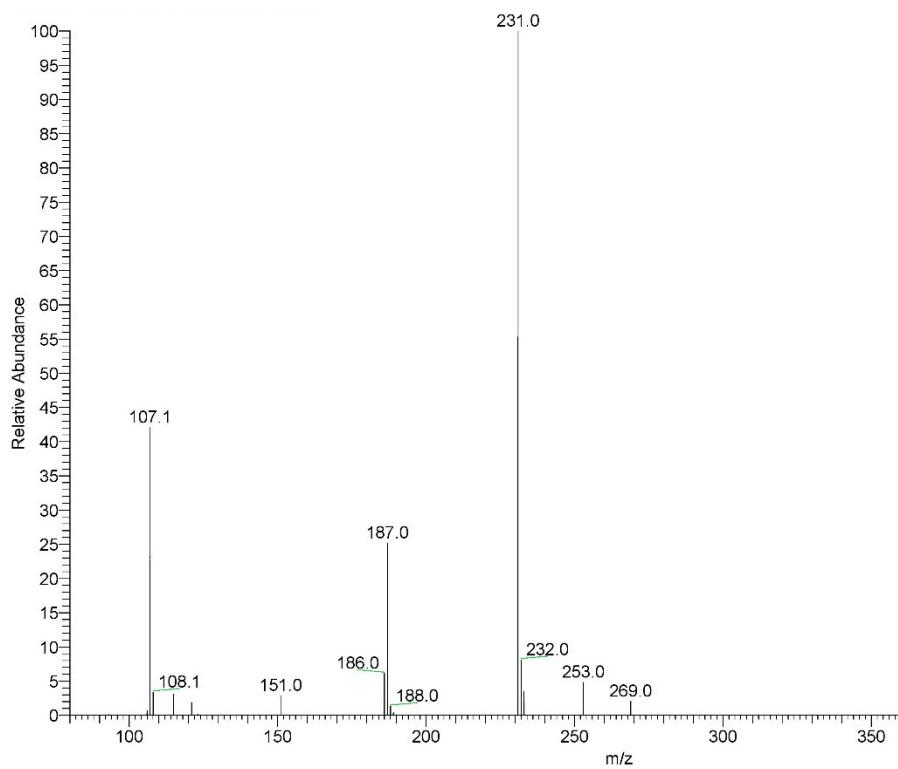


Figure S5. MS (ESI⁻) spectrum of K₂ 3-HPA-S.

([M - 2K + H]⁻, *m/z* 231.0).

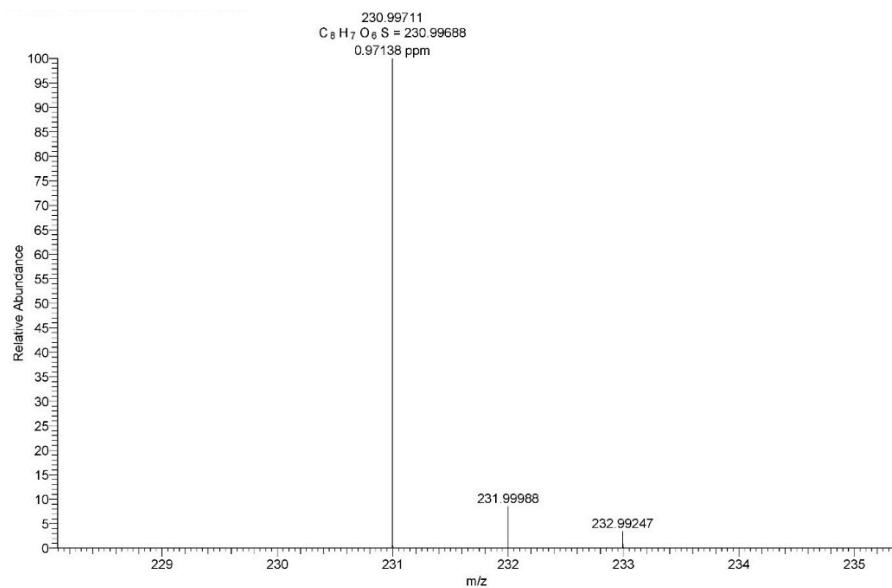


Figure S6. HRMS (ESI⁻) spectrum of K₂ 3-HPA-S.

Calculated (for C₈H₇O₆S⁻) 230.99688, measured 230.99711 (1.0 ppm).

Sodium 2-(3-(sulfonatoxy)phenyl)acetate (Na₂ 3-HPA-S)

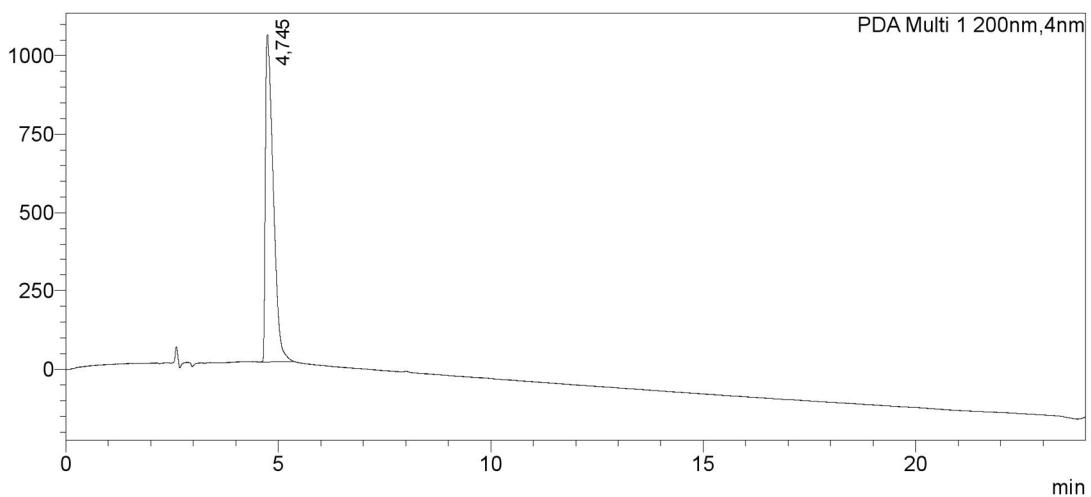
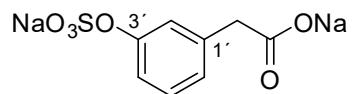


Figure S7. HPLC chromatogram of **Na₂ 3-HPA-S**
(RT= 4.745 min, 99% purity)

Table S2. ¹H and ¹³C NMR data for **Na₂ 3-HPA-S**

(600.23 MHz for ¹H, 150.93 MHz for ¹³C, DMSO-*d*₆)

Atom	δ_c	m.	δ_h	n _h	m.	J [Hz]	δ_c^{HPA}	$\delta_c - \delta_c^{HPA}$
1	174.97	S	-	0	-	-	172.52	2.45
2	45.76	T	3.214	2	s	-	40.72	5.04
1'	140.33	S	-	0	-	-	136.11	4.22
2'	121.44	D	7.048	1	dd	$\Sigma J = 3.9$	116.12	5.32
3'	152.82	S	-	0	-	-	157.16	-4.34
4'	117.30	D	6.945	1	ddd	8.1, 2.4, 1.1	113.51	3.79
5'	127.59	D	7.088	1	dd	$\Sigma J = 15.6$	129.08	-1.49
6'	124.08	D	6.931	1	ddd	7.5, $\Sigma J = 2.5$	119.83	4.25

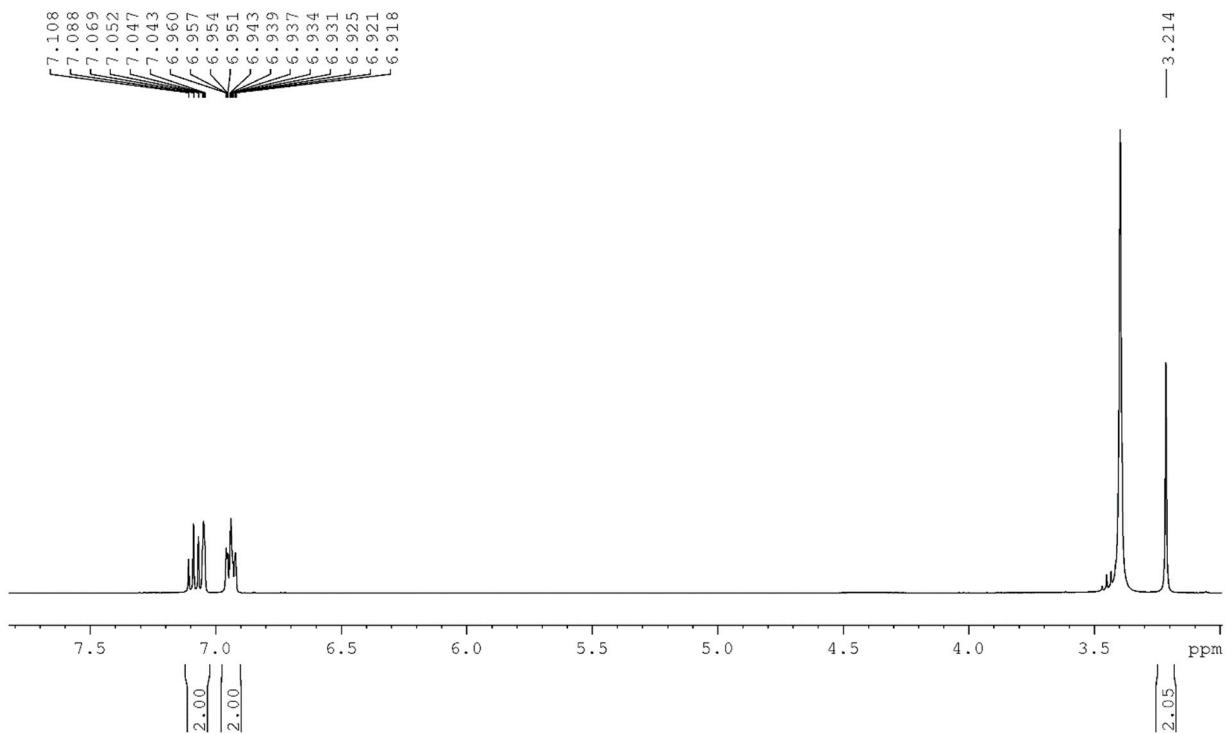


Figure S8. ^1H NMR spectrum of Na_2 3-HPA-S

(600.23 MHz, $\text{DMSO}-d_6$)

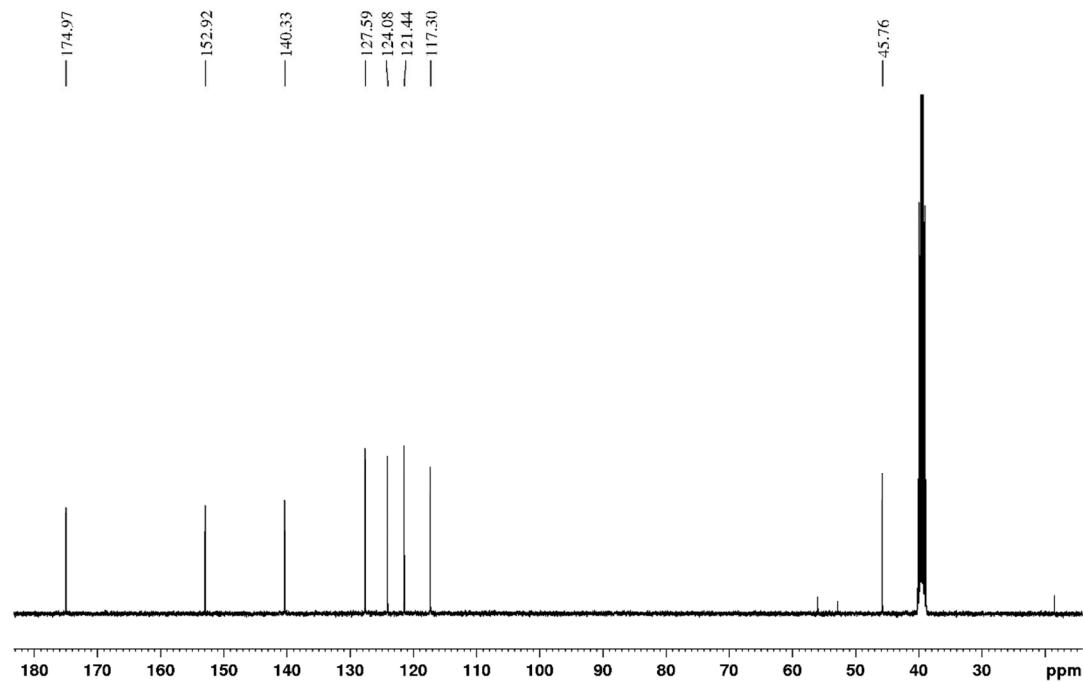


Figure S9. ^{13}C NMR spectrum of Na_2 3-HPA-S

(150.93 MHz, $\text{DMSO}-d_6$)

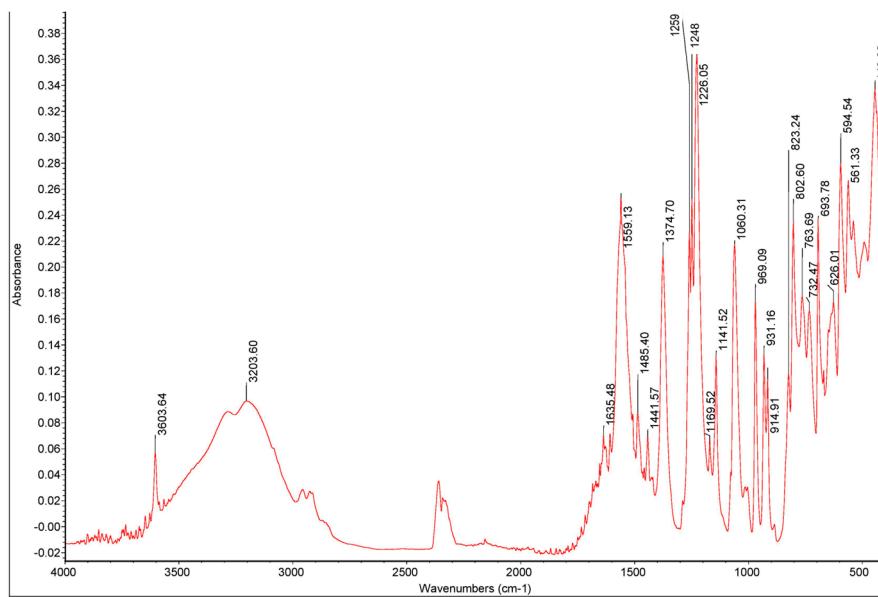


Figure S10. IR spectrum of Na_2 3-HPA-S.

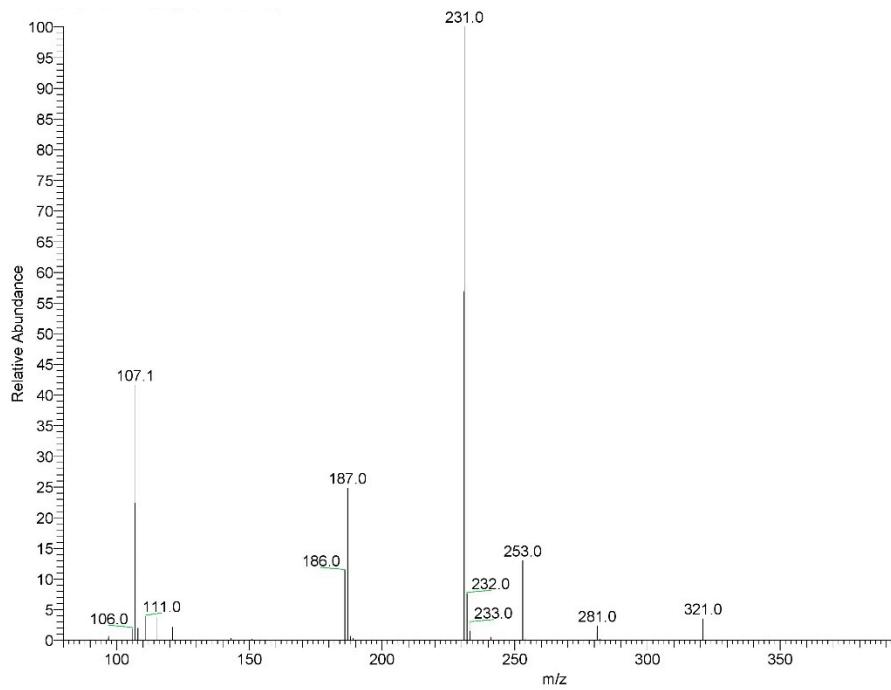


Figure S11. MS (ESI^-) spectrum of Na_2 3-HPA-S.

($[\text{M} - 2\text{Na} + \text{H}]^-, m/z 231.0$; $[\text{M} - \text{Na}]^-, m/z 253.0$).

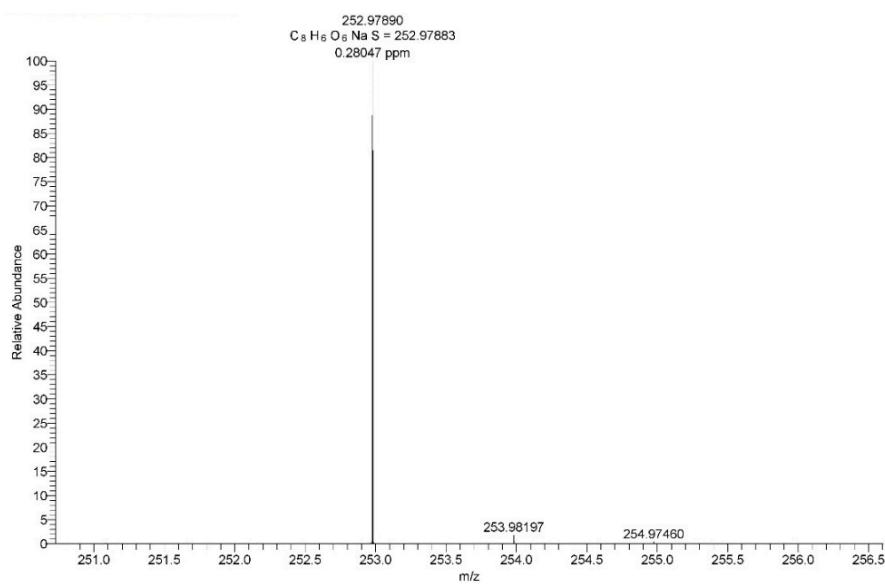


Figure S12. HRMS (ESI⁻) spectrum of Na₂ 3-HPA-S.

Calculated (for C₈H₆O₆NaS⁻) 252.97883, measured 252.97890 (0.3 ppm).

Potassium 2-(4-(sulfonatoxy)phenyl)acetate (K₂ 4-HPA-S)

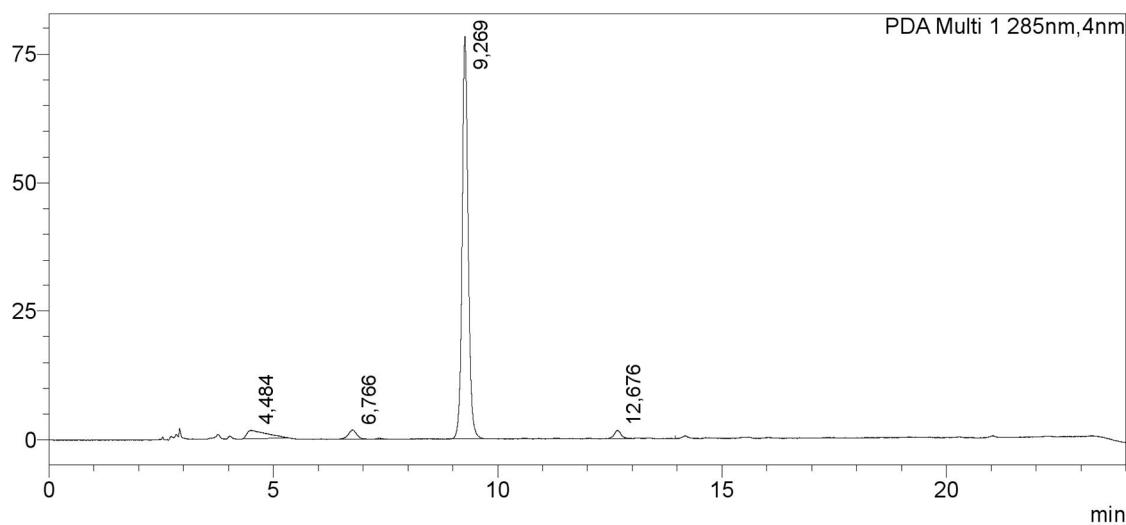
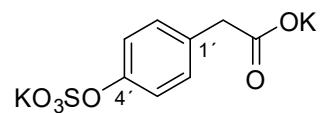


Figure S13. HPLC chromatogram of K₂ 4-HPA-S

(RT = 9.269 min, 89% purity)

Table S3. ^1H and ^{13}C NMR data for **K₂ 4-HPA-S**

(399.83 MHz for ^1H , 100.54 MHz for ^{13}C , DMSO-*d*₆)

Atom	δ_{C}	m.	δ_{H}	n _H	m.	$\delta_{\text{C}}^{4\text{HPA}}$	$\delta_{\text{C}} - \delta_{\text{C}}^{4\text{HPA}}$
1	173.96	S	-	0	-	172.99	0.97
2	45.86	T	3.131	2	s	39.79	6.07
1'	135.10	S	-	0	-	125.03	10.07
2'	129.13	D	7.086	2	m	130.13	-1.00
3'	119.80	D	6.982	2	m	114.92	4.88
4'	150.79	S	-	0	-	155.95	-5.16

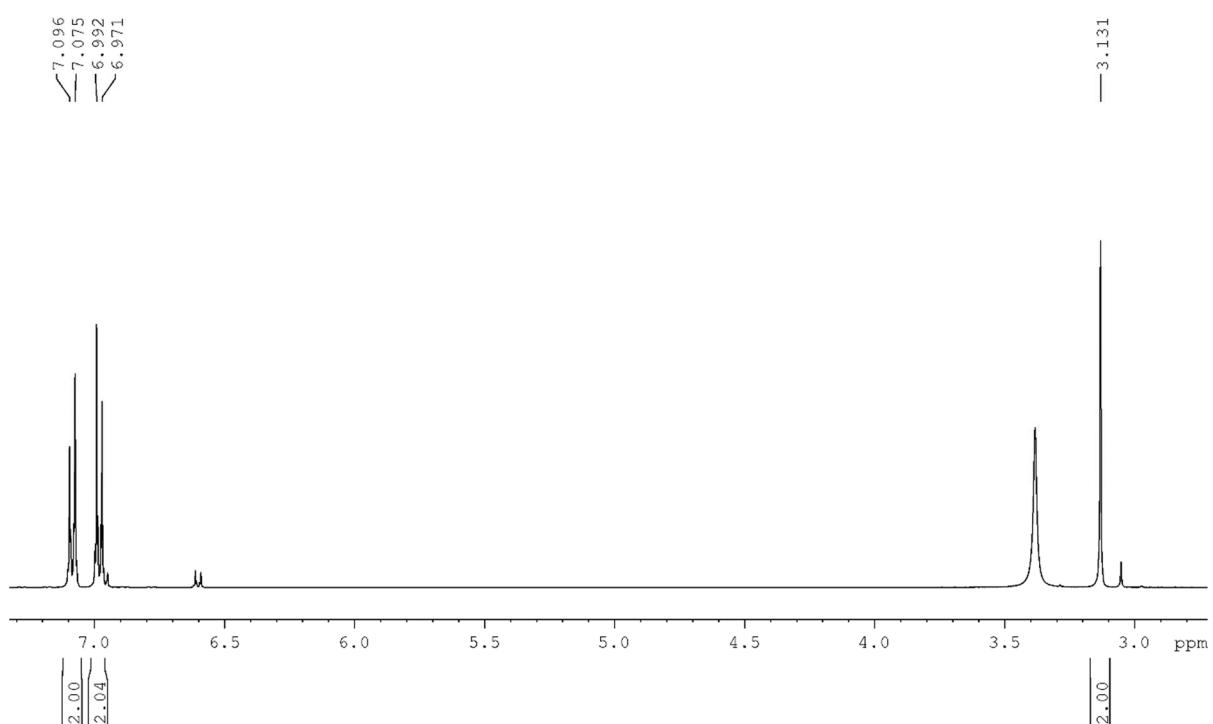


Figure S14. ^1H NMR spectrum of **K₂ 4-HPA-S**

(399.83 MHz, DMSO-*d*₆)

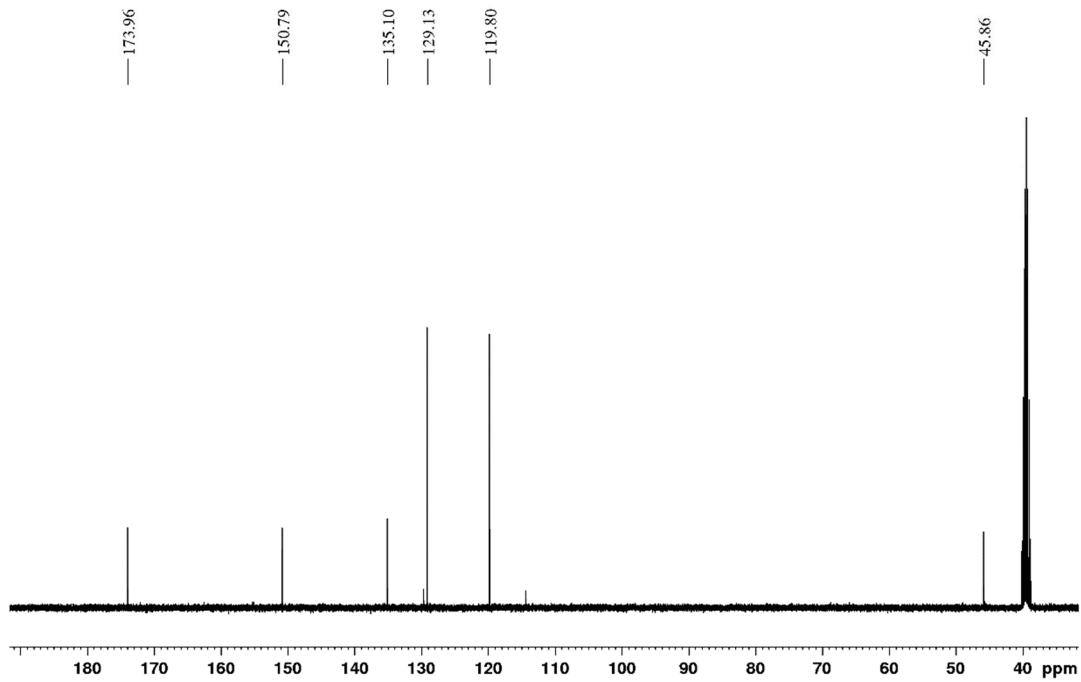


Figure S15. ^{13}C NMR spectrum of K_2 4-HPA-S
(100.54 MHz, $\text{DMSO}-d_6$)

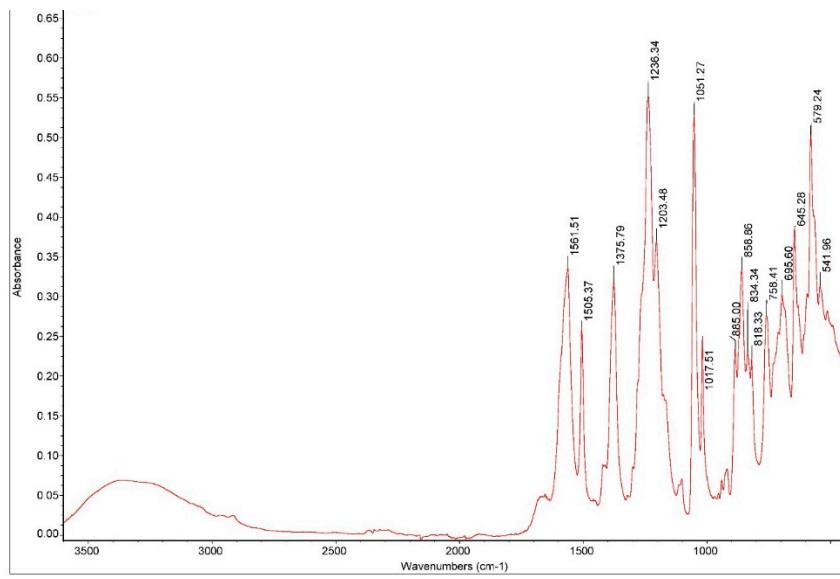


Figure S16. IR spectrum of K_2 4-HPA-S.

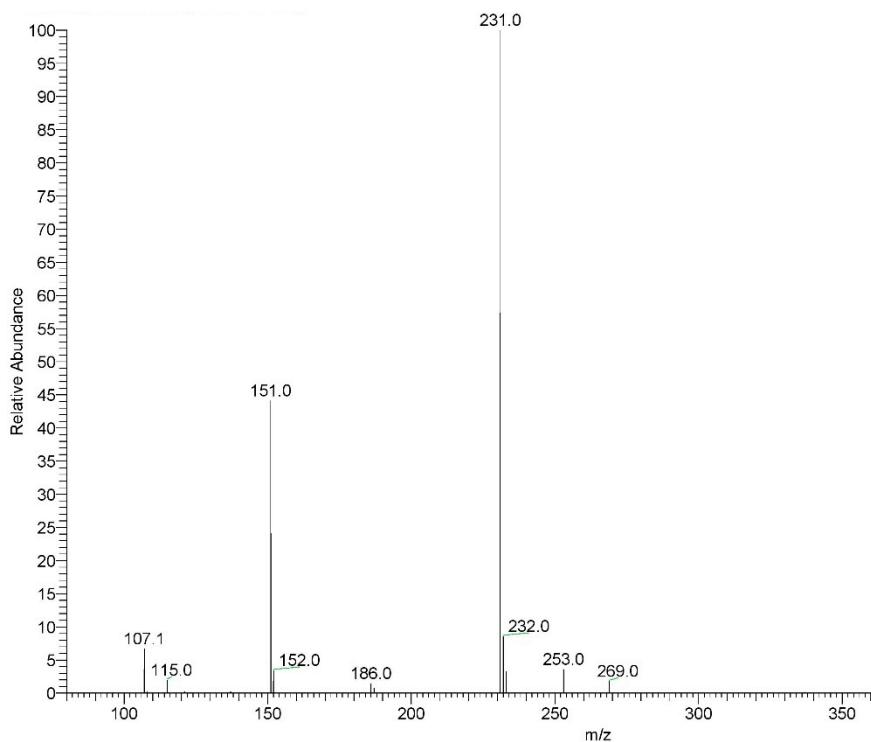


Figure S17. MS (ESI⁻) spectrum of K₂ 4-HPA-S.

([M - 2K + H]⁻, *m/z* 231.0).

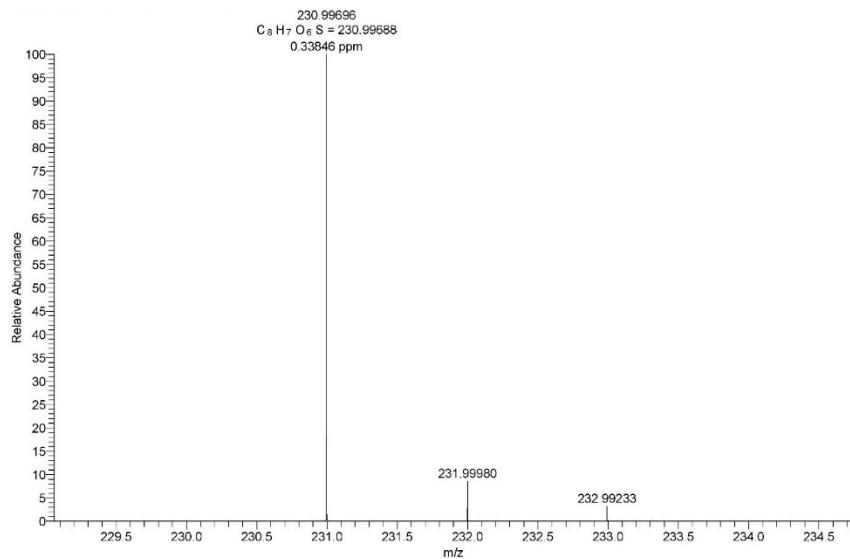
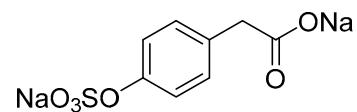


Figure S18. HRMS (ESI⁻) spectrum of K₂ 4-HPA-S.

Calculated (for C₈H₇O₆S⁻) 230.99688, measured 230.99696 (0.3 ppm).

Sodium 2-(4-(sulfonatoxy)phenyl)acetate (Na₂ 4-HPA-S)



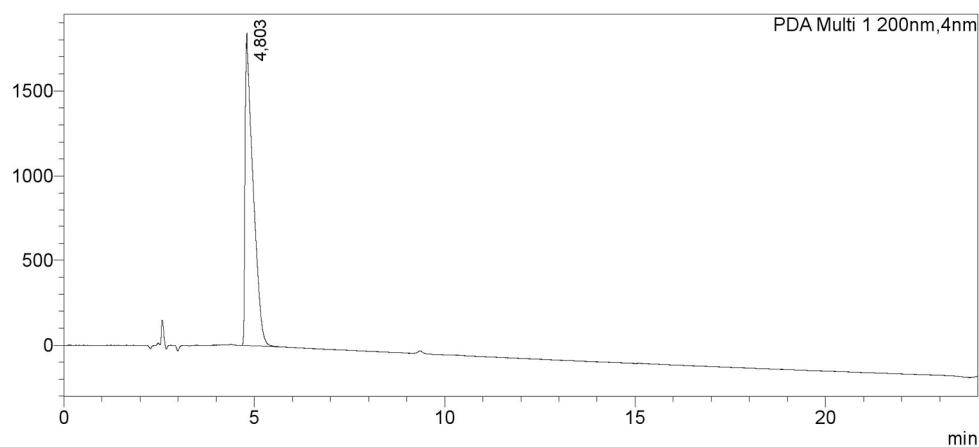


Figure S19. HPLC chromatogram of **Na₂ 4-HPA-S**

(RT= 4.803 min, 99% purity)

Table S4. ¹H and ¹³C NMR data for **Na₂ 4-HPA-S**

(399.83 MHz for ¹H, 100.54 MHz for ¹³C, DMSO-*d*₆)

Atom	δ_c	m.	δ_h	n _H	m.	$\delta_c^{4\text{HPA}}$	$\delta_c - \delta_c^{4\text{HPA}}$
1	174.79	S	-	0	-	172.99	1.80
2	45.33	T	3.155	2	s	39.79	5.54
1'	134.60	S	-	0	-	125.03	9.57
2'	129.14	D	7.093	2	m	130.13	-0.99
3'	119.82	D	6.979	2	m	114.92	4.90
4'	150.96	S	-	0	-	155.95	-4.99

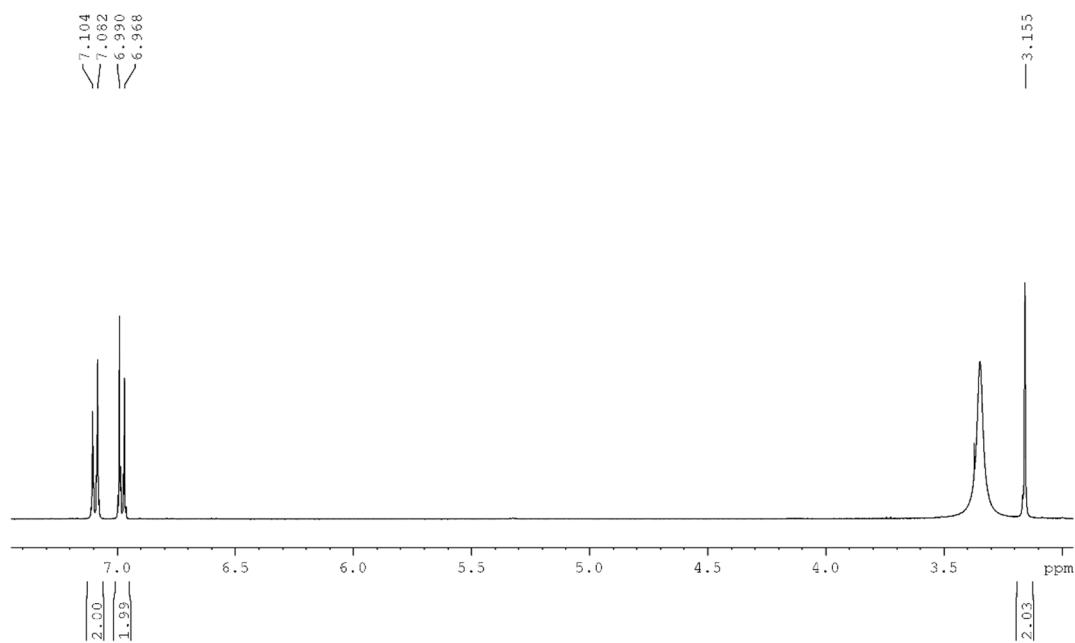


Figure S20. ¹H NMR spectrum of **Na₂ 4-HPA-S**

(399.83 MHz, DMSO-*d*₆)

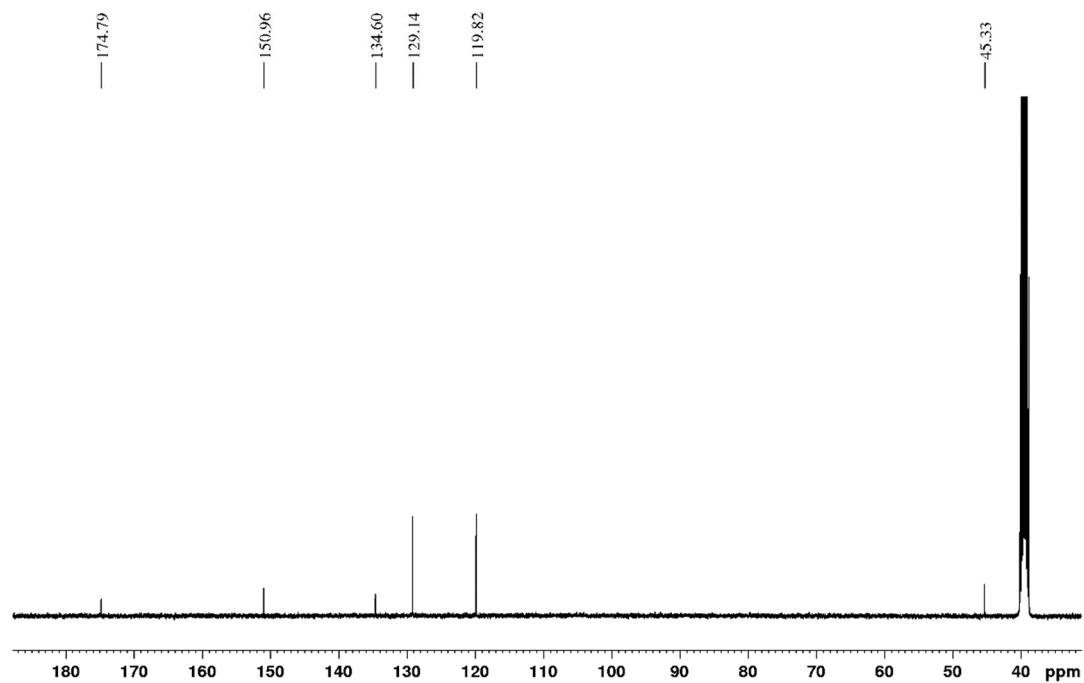


Figure S21. ¹³C NMR spectrum of Na₂ 4-HPA-S

(100.54 MHz, DMSO-*d*₆)

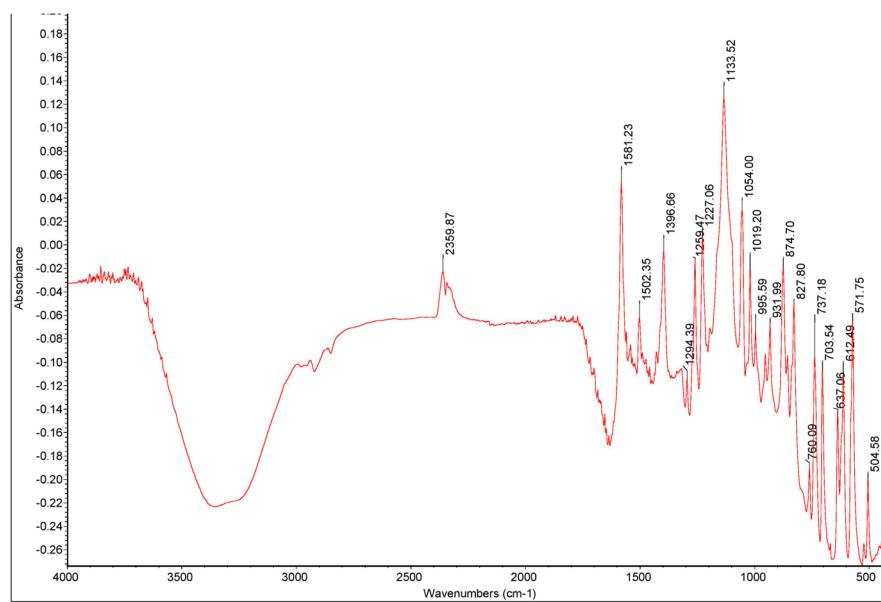


Figure S22. IR spectrum of Na₂ 4-HPA-S.

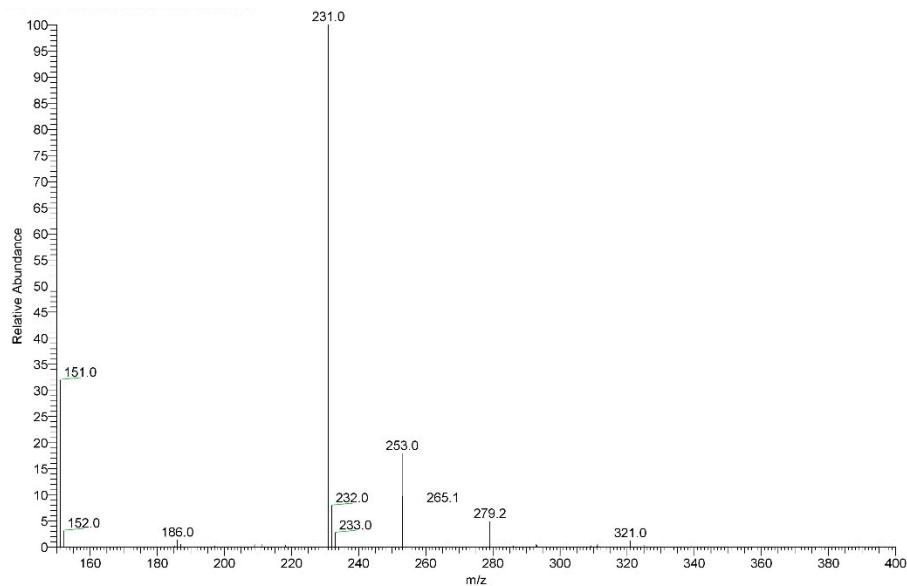


Figure S23. MS (ESI⁻) spectrum of Na₂ 4-HPA-S.

([M - 2Na + H]⁻, *m/z* 231.0).

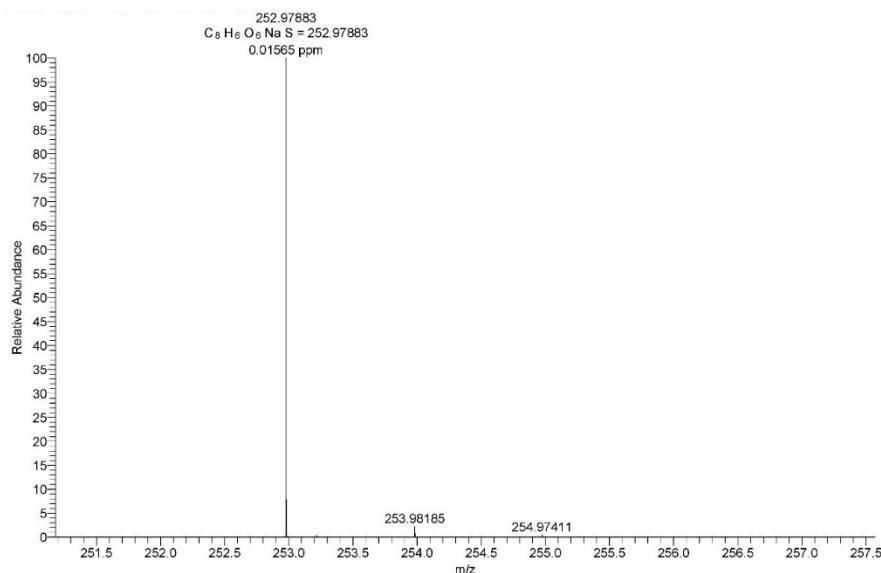
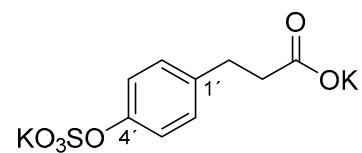


Figure S24. HRMS (ESI⁻) spectrum of Na₂ 4-HPA-S.

Calculated (for C₈H₆O₆NaS⁻) 252.97883, measured 252.97883 (0.0 ppm).

Potassium 3-(4-(sulfonatoxy)phenyl)propanoate (K₂ 4-HPP-S)



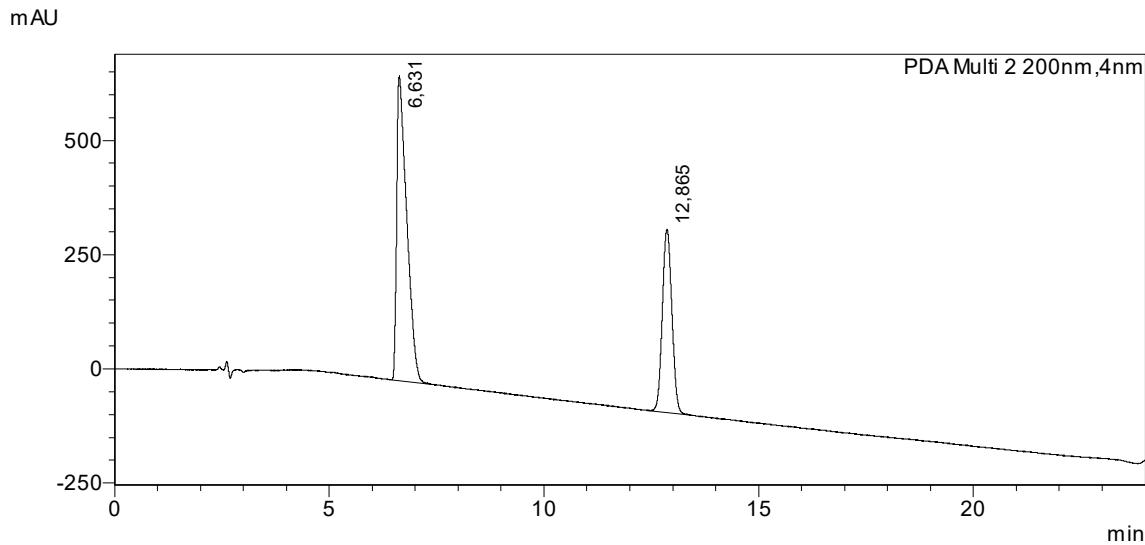


Figure S25. HPLC chromatogram of **K₂ 4-HPP-S**

(RT= 6.631 min, 64% purity, the peak at 12.865 min belongs to the starting 4-HPP and might be partially enhanced by degradation during HPLC analysis under acidic conditions)

Table S5. ¹H and ¹³C NMR data for **K₂ 4-HPP-S**

(700.13 MHz for ¹H, 176.05 MHz for ¹³C, DMSO-*d*₆)

Atom	δ_c	m.	δ_h	n _h	m.	J [Hz]	δ_c^{HPP}	$\delta_c - \delta_c^{HPP}$
1	174.85	S	-	0	-	-	173.76	1.09
2	37.28	T	2.369	2	m	-	35.64	1.64
3	30.50	T	2.736	2	m	-	29.50	1
1'	136.35	S	-	0	-	-	130.84	5.51
2'6'	128.28	D	7.089	2	m	$\Sigma J = 8.6$	128.97	-0.69
3'5'	120.34	D	7.042	2	m	$\Sigma J = 8.6$	114.97	5.37
4'	151.44	S	-	0	-	-	155.43	-3.99

Minority K 4-HPP

Atom	δ_c	m.	δ_h	n _h	m.	J [Hz]	δ_c^{HPP}	$\delta_c - \delta_c^{HPP}$
1	174.9	S	-	0	-	-	173.76	1.14
2	37.42	T	2.331	2	m	-	35.64	1.78
3	30.28	T	2.667	2	m	-	29.50	0.78
1'	131.64	S	-	0	-	-	130.84	0.8
2'6'	128.86	D	6.973	2	m	$\Sigma J = 8.5$	128.97	-0.11
3'5'	114.92	D	6.643	2	m	$\Sigma J = 8.5$	114.97	-0.05
4'	155.36	S	-	0	-	-	155.43	-0.07

approximate molar ratio **K₂ 4-HPP-S : K 4-HPP** = 87 : 13

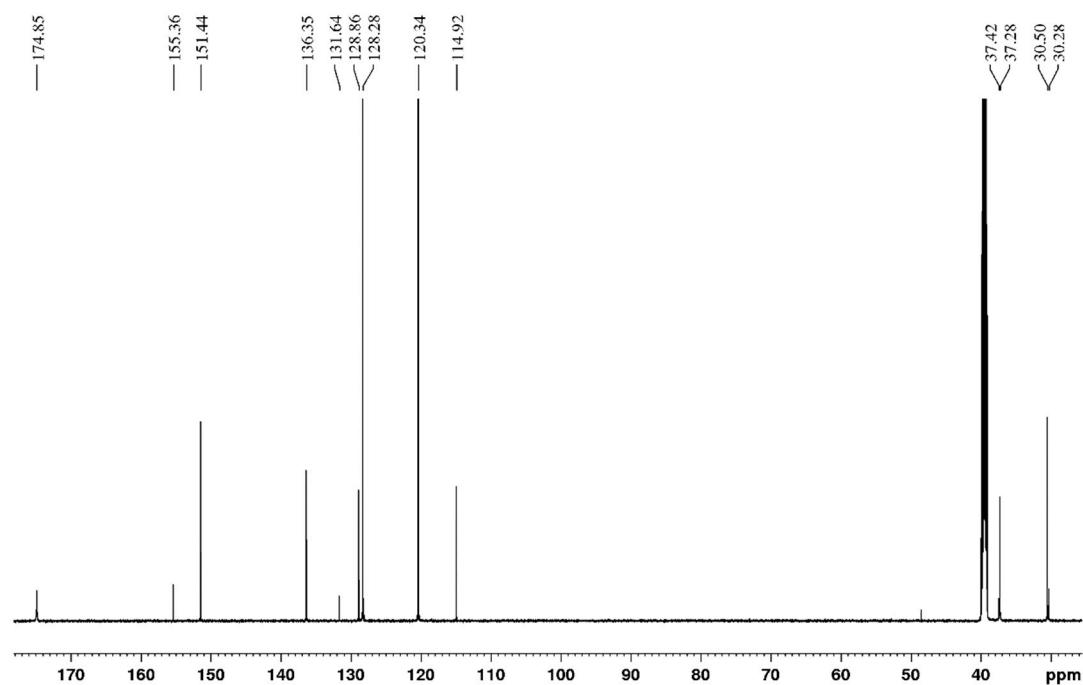
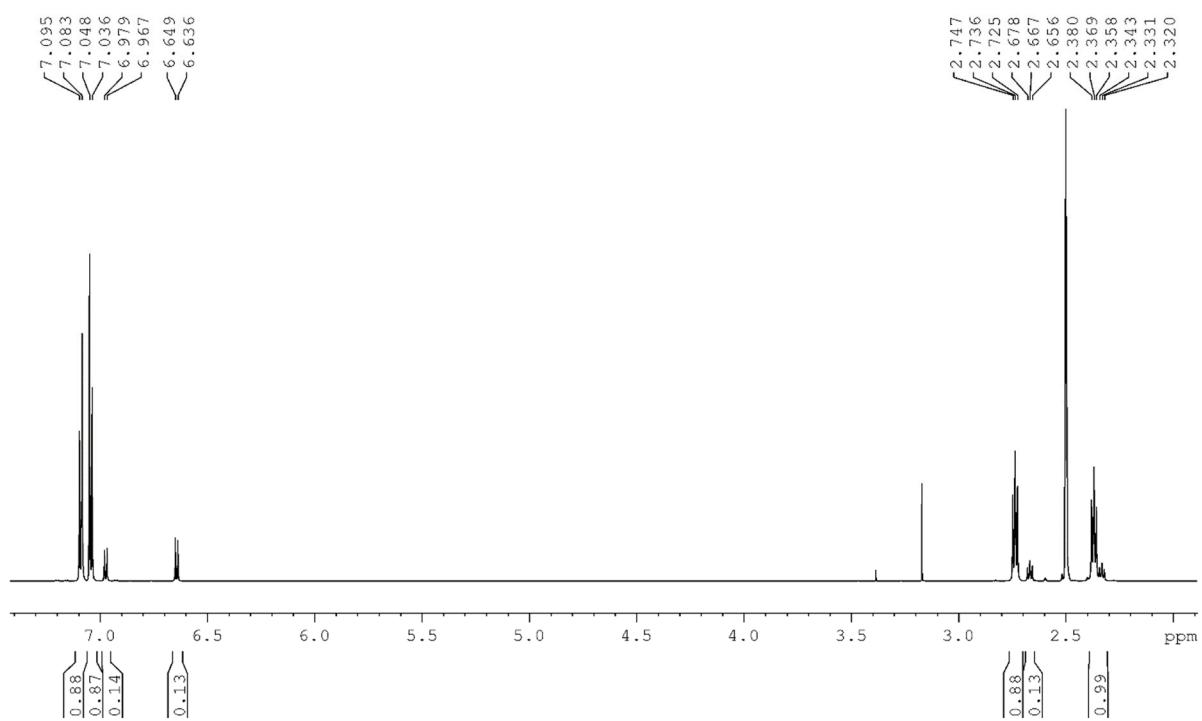


Figure S27. ^{13}C NMR spectrum of K_2 4-HPP-S

(176.05 MHz, DMSO-*d*₆)

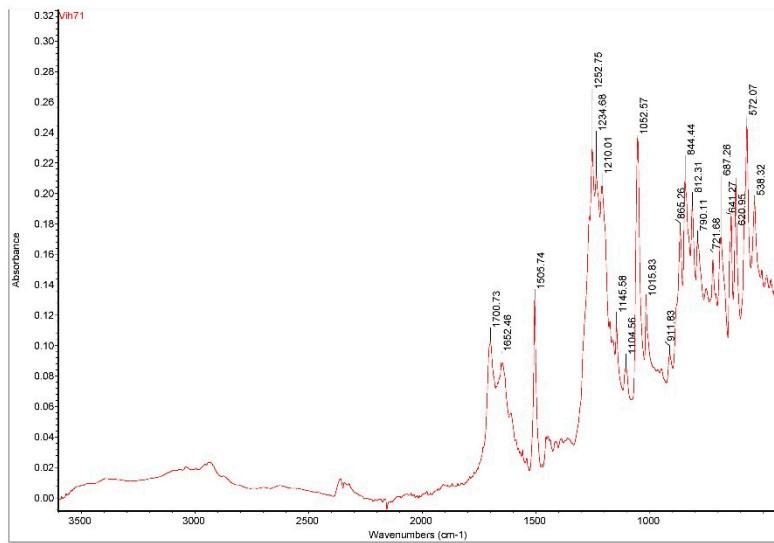


Figure S28. IR spectrum of K₂ 4-HPP-S.

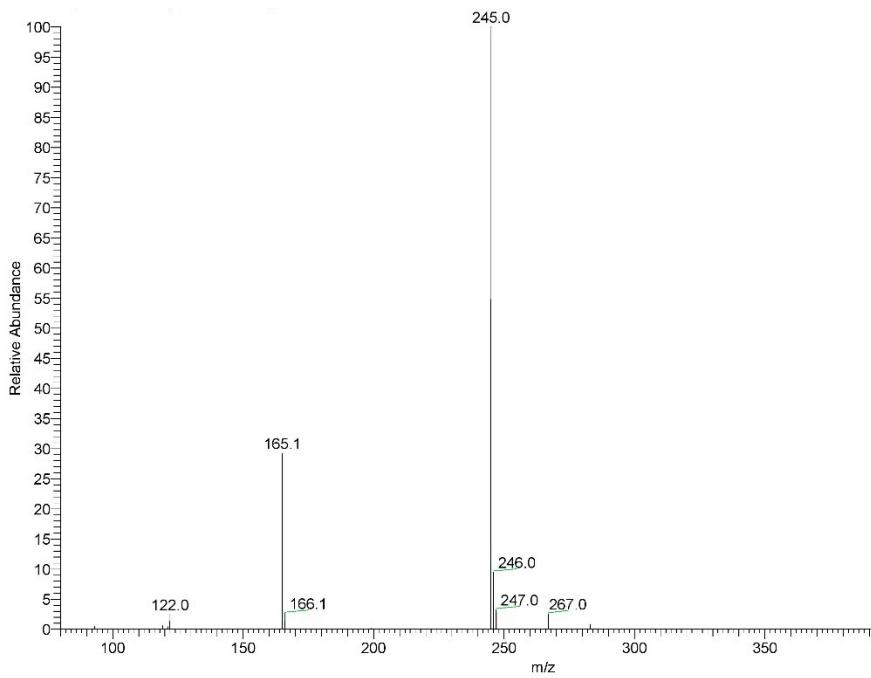


Figure S29. MS (ESI⁻) spectrum of K₂ 4-HPP-S.

([M - 2K + H]⁻, *m/z* 245.0).

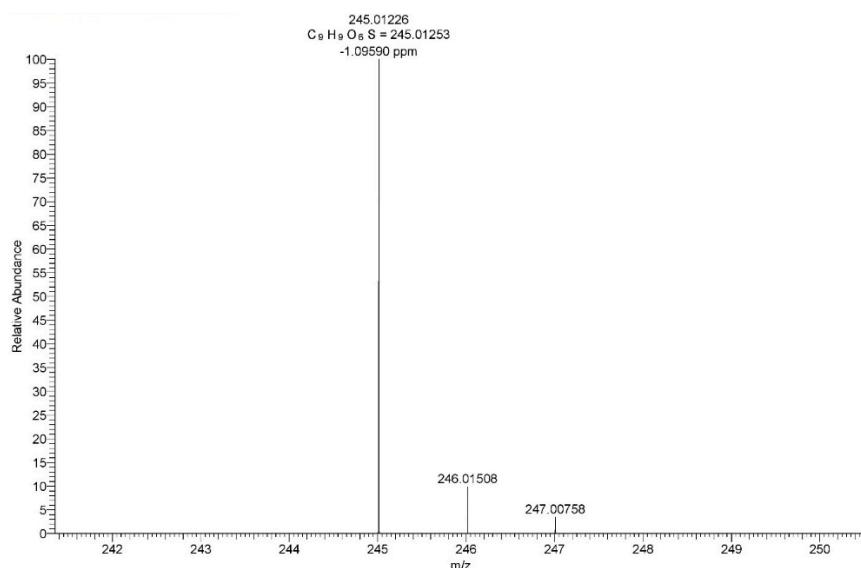


Figure S30. HRMS (ESI⁻) spectrum of K₂ 4-HPP-S.

Calculated (for C₉H₉O₆S⁻) 245.01253, measured 245.01226 (-1.1 ppm).

Sodium 3-(4-(sulfonatoxy)phenyl)propanoate (Na₂ 4-HPP-S)

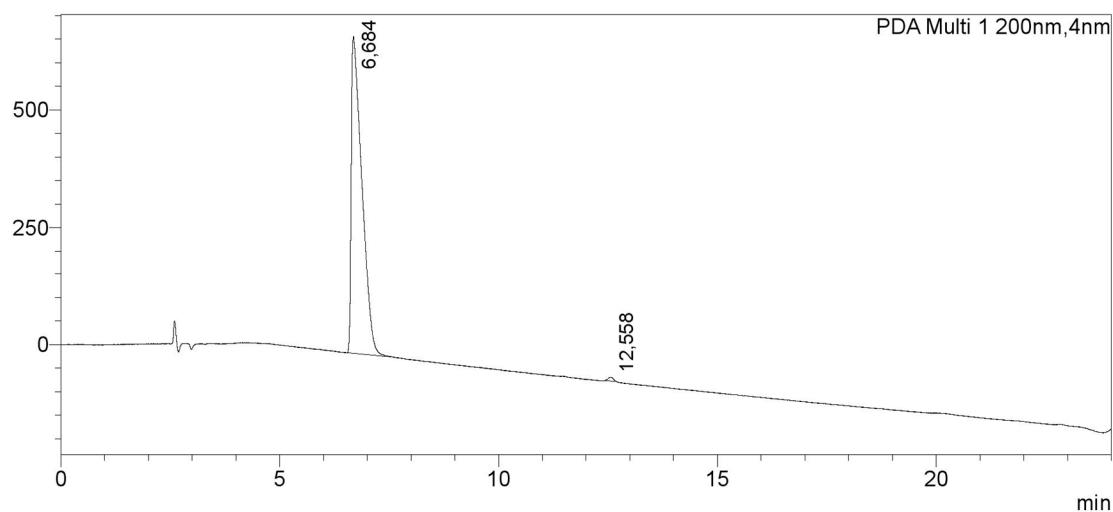
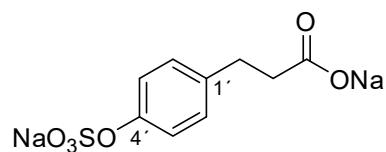


Figure S31. HPLC chromatogram of Na₂ 4-HPP-S
(RT= 6.684 min, 99% purity)

Table S6. ^1H and ^{13}C NMR data for Na_2 4-HPP-S

(600.23 MHz for ^1H , 150.93 MHz for ^{13}C , DMSO- d_6)

Atom	δ_c	m.	δ_h	n _H	m.	J [Hz]	δ_c^{HPP}	$\delta_c - \delta_c^{\text{HPP}}$
1	176.36	S	-	0	-	-	173.76	2.60
2	40.06	T	2.153	2	m	-	35.64	4.42
3	31.90	T	2.704	2	m	-	29.50	2.40
1'	137.93	S	-	0	-	-	130.84	7.09
2'6'	128.16	D	7.067	2	m	$\Sigma J = 8.7$	128.97	-0.81
3'5'	120.24	D	7.007	2	m	$\Sigma J = 8.7$	114.97	5.27
4'	151.09	S	-	0	-	-	155.43	-4.34

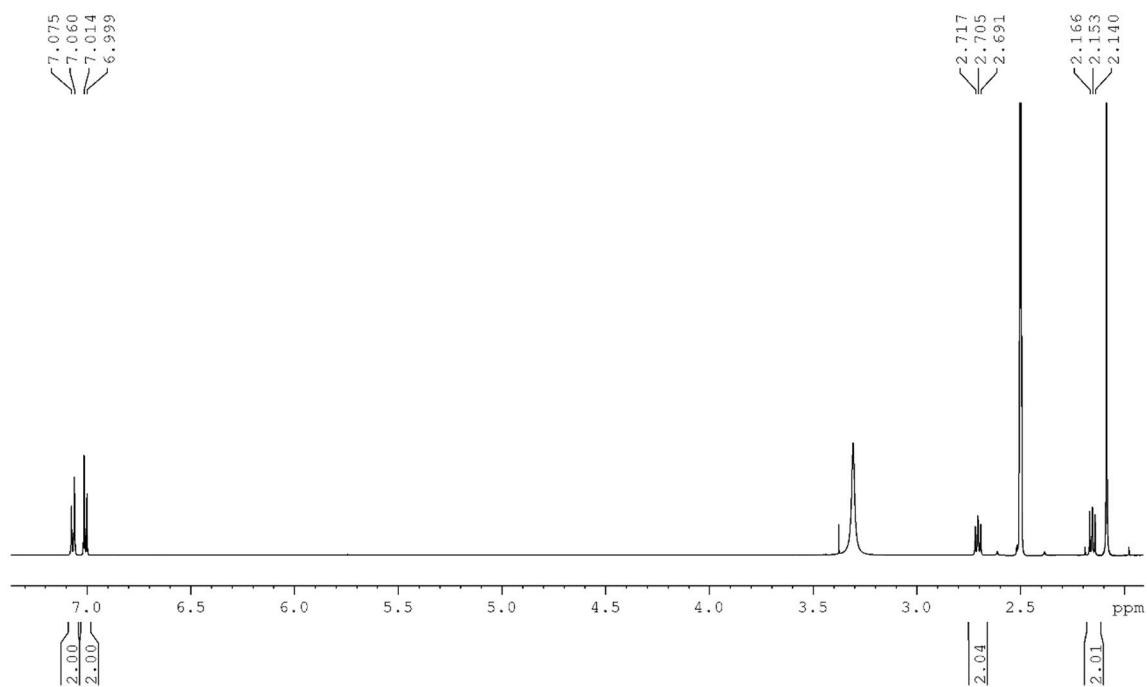


Figure S32. ^1H NMR spectrum of Na_2 4-HPP-S

(600.23, DMSO- d_6)

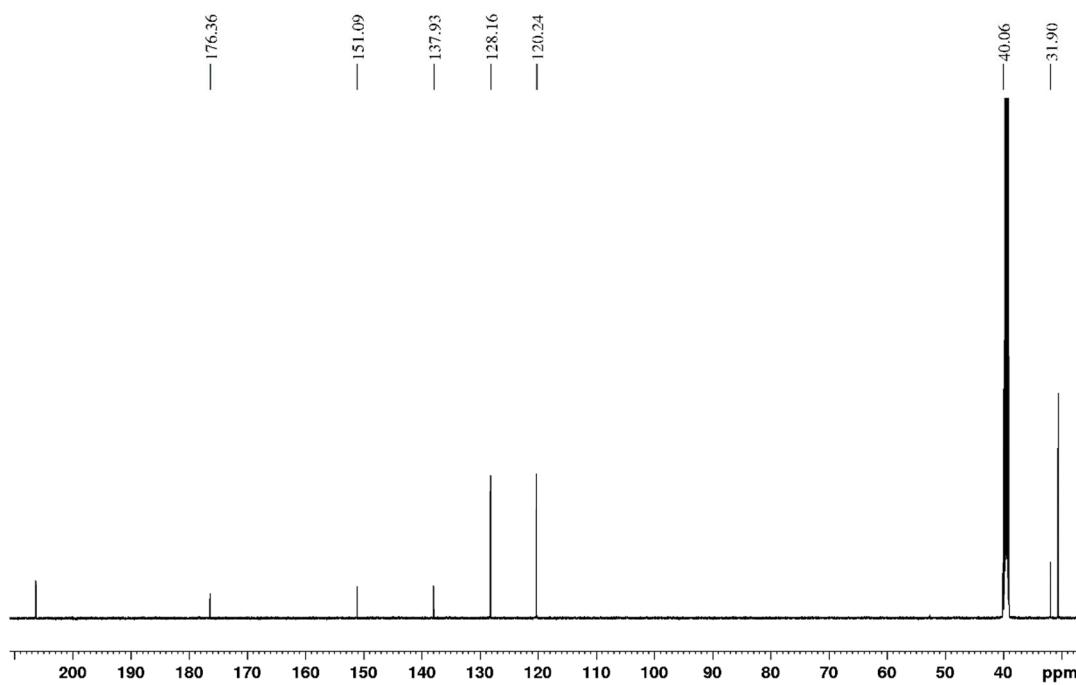


Figure S33. ^{13}C NMR spectrum of Na_2 4-HPP-S
(150.93 MHz, $\text{DMSO}-d_6$)

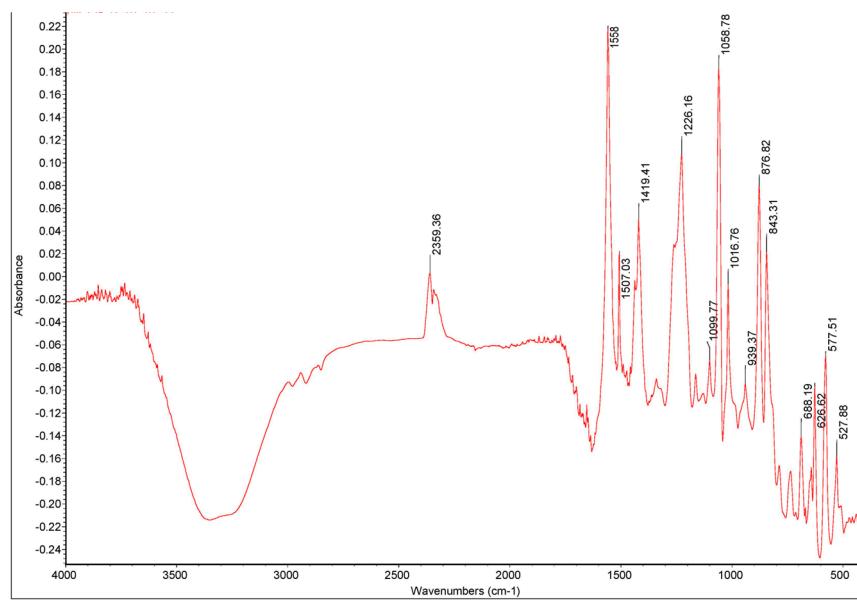


Figure S34. IR spectrum of Na_2 4-HPP-S.

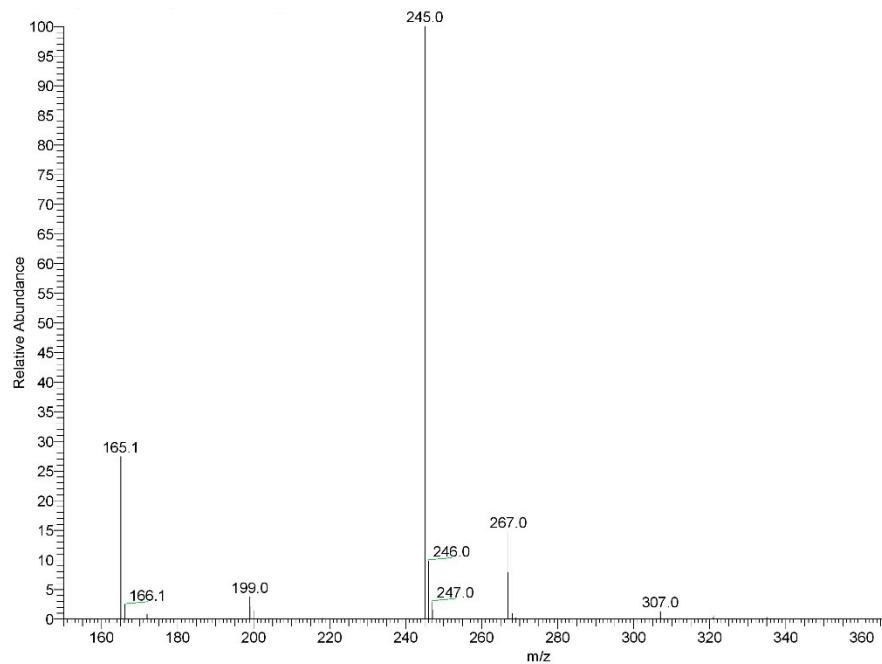


Figure S35. MS (ESI^-) spectrum of $\text{Na}_2\text{4-HPP-S}$.

($[\text{M} - 2\text{Na} + \text{H}]^-, m/z 245.0$; $[\text{M} - \text{Na}]^-, m/z 267.0$).

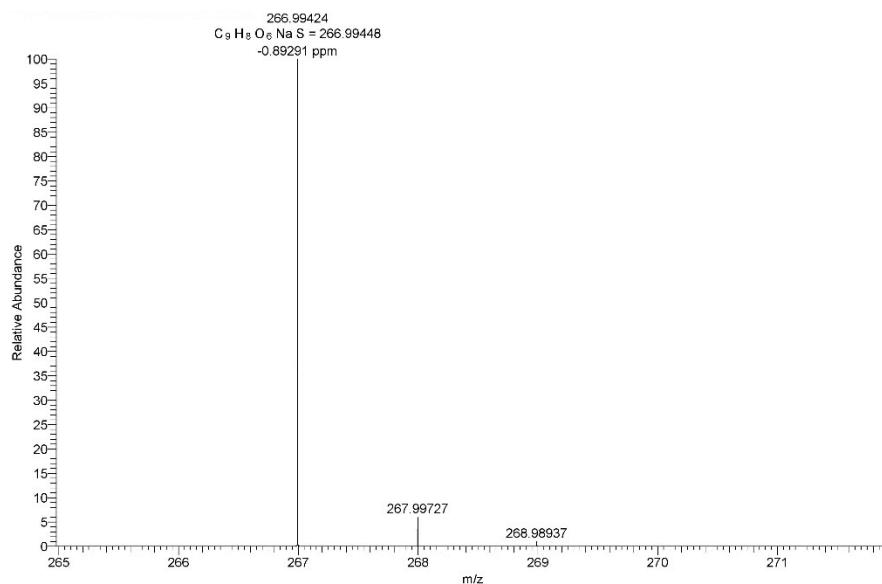


Figure S36. HRMS (ESI^-) spectrum of $\text{Na}_2\text{4-HPP-S}$.

Calculated (for $\text{C}_9\text{H}_8\text{O}_6\text{NaS}^-$) 266.99448, measured 266.99424 (-0.9 ppm).

Potassium 2-(2-hydroxyphenyl)acetate (K 2-HPA) and potassium 2-(2-hydroxy-5-sulfonatophenyl)acetate (K₂ 2-HPA-CS)

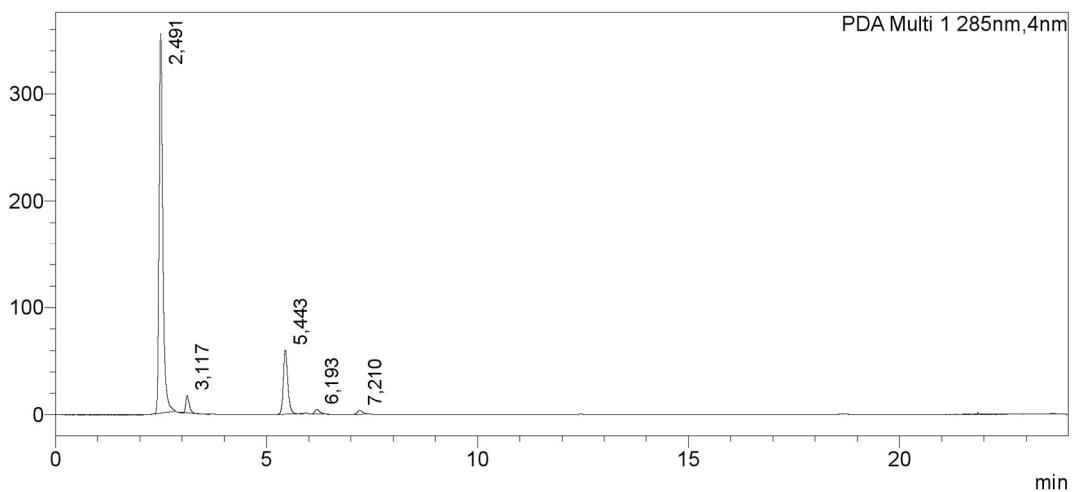


Figure S37. HPLC chromatogram of **K 2-HPA** and **K₂ 2-HPA-CS**
(RT= 2.491 min, 79%; RT= 5.443 min, 16%)

Potassium 2-(2-(sulfonatoxy)phenyl)acetate (K 2-HPA)

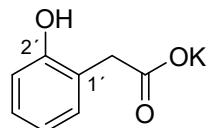


Table S7. ¹H and ¹³C NMR data for **K 2-HPA**.

(399.83 MHz for ¹H, 100.54 MHz for ¹³C, DMSO-*d*₆)

Atom	δ_c	m.	δ_h	n _H	m.	J [Hz]	$\delta_c^{2\text{HPA}}$	$\delta_c - \delta_c^{2\text{HPA}}$
1	174.24	S	-	0	-	-	172.63	1.61
2	40.88	T	3.352	2	s	-	35.23	5.65
1'	123.774	S	-	0	-	-	121.75	2.02
2'	157.14	S	-	0		-	155.26	1.88
3'	115.94	D	6.688	1	dd	8.0, 1.3	114.68	1.26
4'	127.15	D	6.987	1	ddd	n.e.	127.67	-0.52
5'	117.89	D	6.633	1	ddd	1.3, $\Sigma J = 14.7$	118.58	-0.69
6'	130.25	D	6.960	1	dd	n.e.	130.92	-0.67

n.e. ... not extracted

Potassium 2-(2-hydroxy-5-sulfonatophenyl)acetate (K₂ 2-HPA-CS)

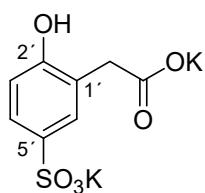


Table S8. ^1H and ^{13}C NMR data for K_2 2-HPA-CS.

(399.83 MHz for ^1H , 100.54 MHz for ^{13}C , DMSO- d_6)

Atom	δ_{c}	m.	δ_{H}	n _H	m.
1	174.13	S	-	0	-
2	40.95	T	3.347	2	s
1'	122.42	S	-	0	-
2'	157.51	S	-	0	-
3'	114.65	D	6.593	1	m
4'	124.89	D	7.267	1	m
5'	138.25	S	-	0	-
6'	128.00	D	7.26 ^H	1	m

^H ... HSQC readout

approximate molar ratio **K 2-HPA : K₂ 2-HPA-CS** = 1 : 1

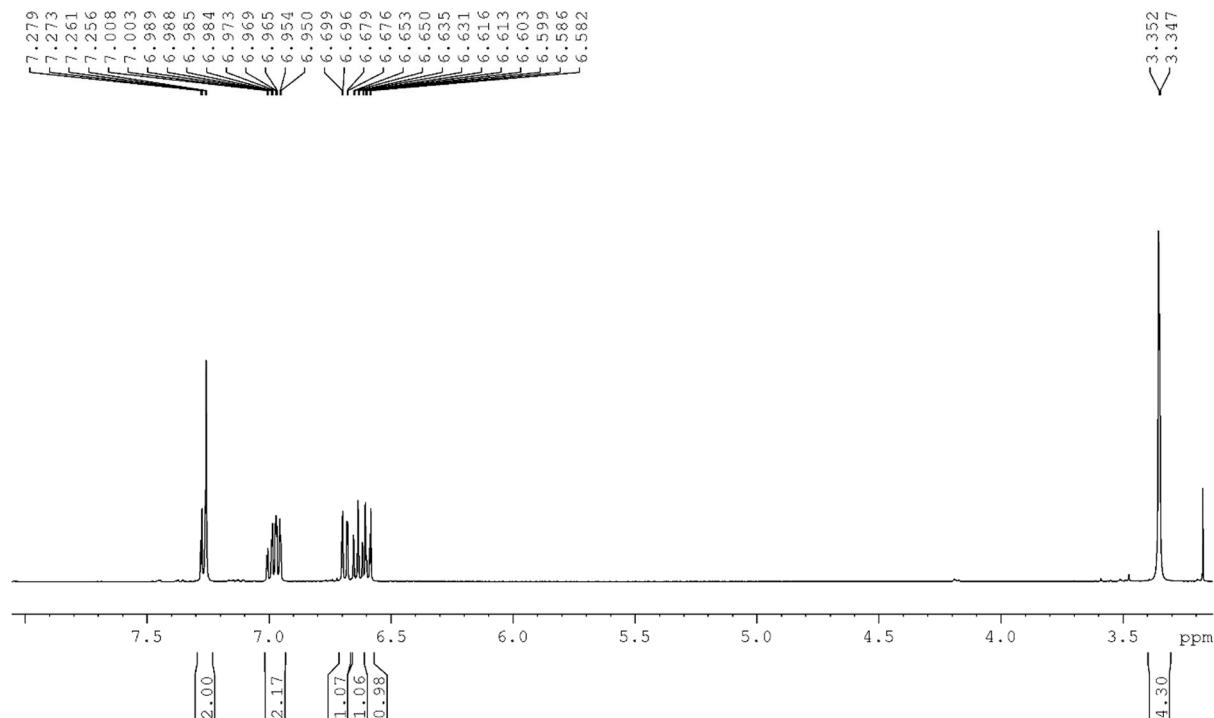


Figure S38. ^1H NMR spectrum of **K 2-HPA** and **K₂ 2-HPA-CS**.

(399.83 MHz, DMSO- d_6)

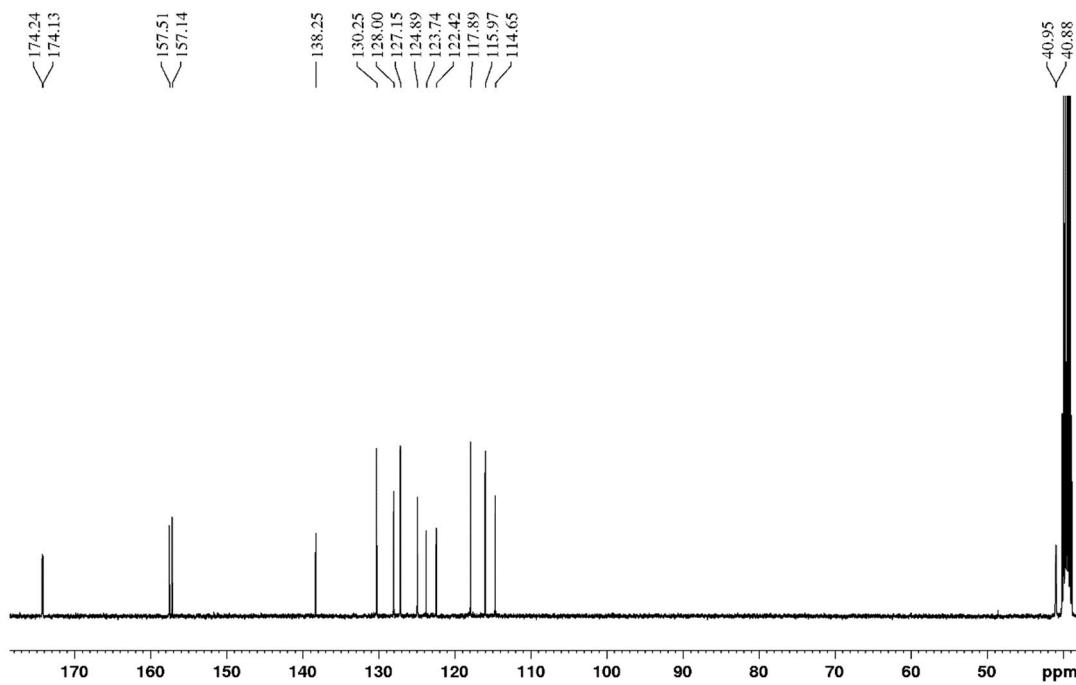


Figure S39. ^{13}C NMR spectrum of **K 2-HPA** and **K₂ 2-HPA-CS**.

(100.54 MHz, DMSO-*d*₆)

3-(4,5-Dihydroxy-2-sulfophenyl)propanoic acid (DHPP-CS)

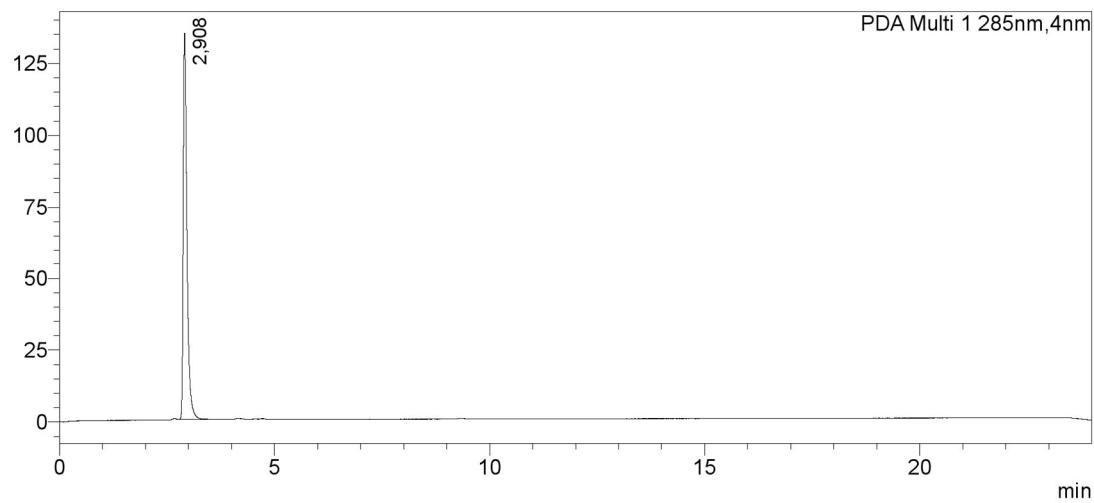
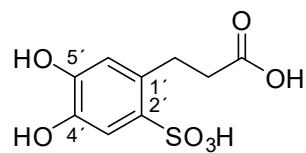


Figure S40. HPLC chromatogram of **DHPP-CS**

(RT= 2.908 min, 99% purity)

Table S9. ^1H and ^{13}C NMR data for **DHPP-CS**.

(399.83 MHz for ^1H , 100.54 MHz for ^{13}C , DMSO- d_6)

Atom	δ_{C}	m.	δ_{H}	n _H	m.	J [Hz]
1	174.39	S	-	0	-	-
2	35.53	T	2.489	2	m	$\Sigma J = 15.9$
3	27.30	T	3.015	2	m	$\Sigma J = 15.9$
1'	129.33	S	-	0	-	-
2'	116.21	D	6.517	1	s	-
3'	157.04	S	-	0	-	-
4'	112.64	S	-	0	-	-
5'	128.55	D	7.210	1	s	-
6'	119.76	S	-	0	-	-

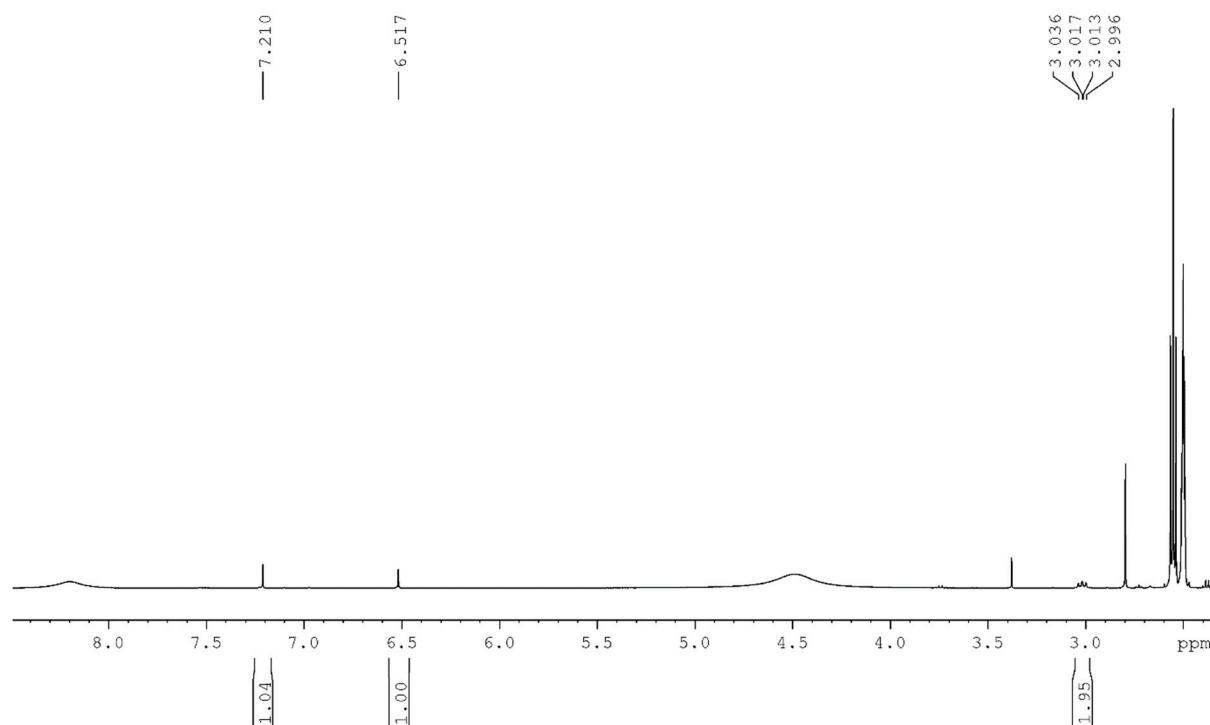


Figure S41. ^1H NMR spectrum of **DHPP-CS**.

(399.83 MHz, DMSO- d_6)

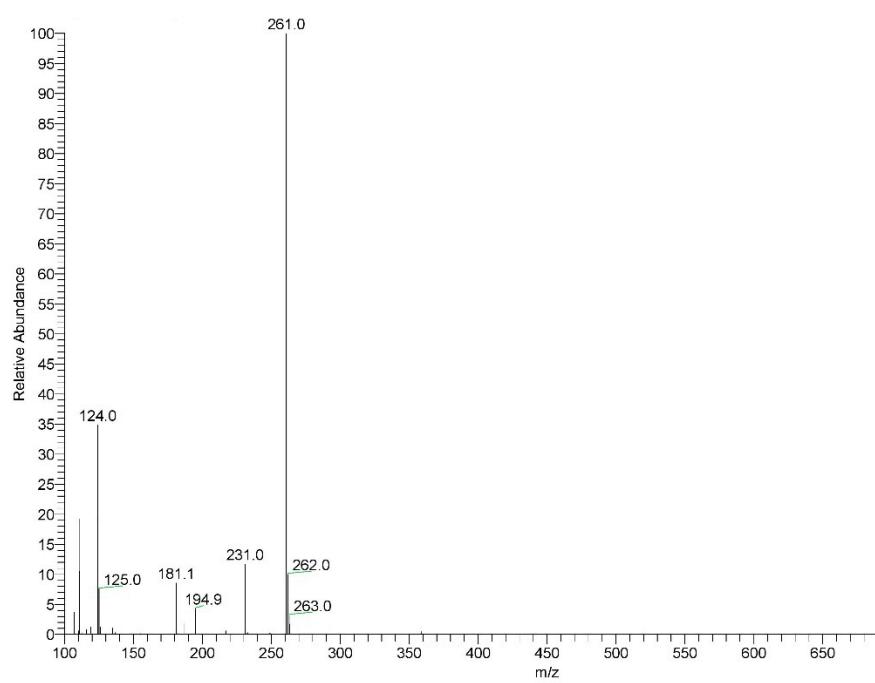
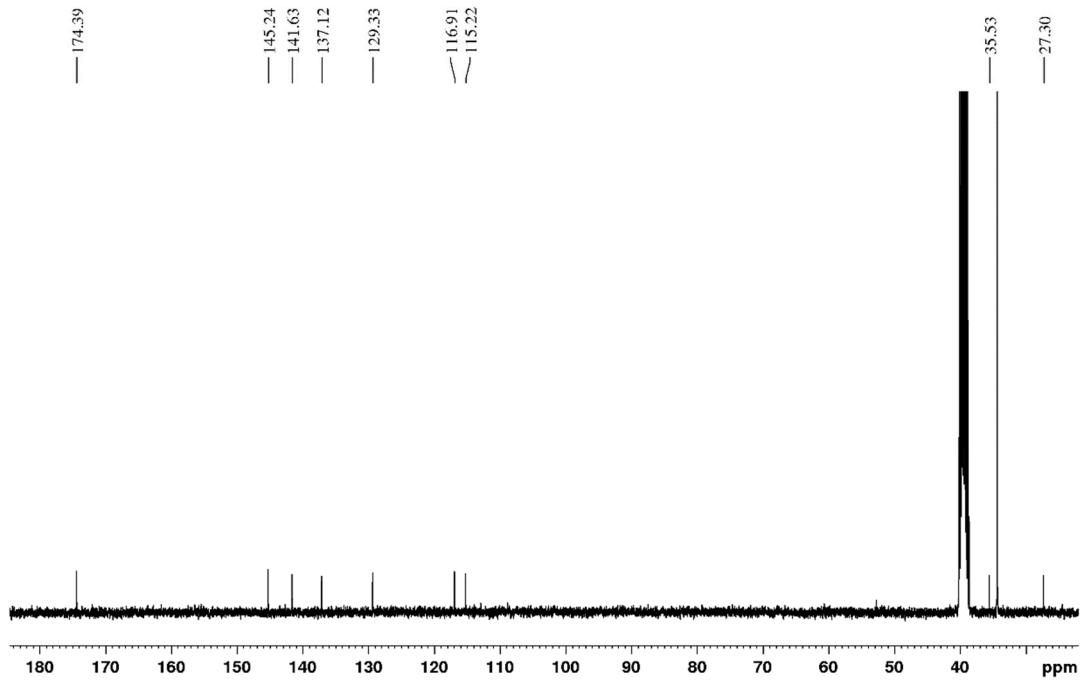


Figure S43. MS (ESI⁻) spectrum of DHPP-CS.
([M - H]⁻, *m/z* 261.0).

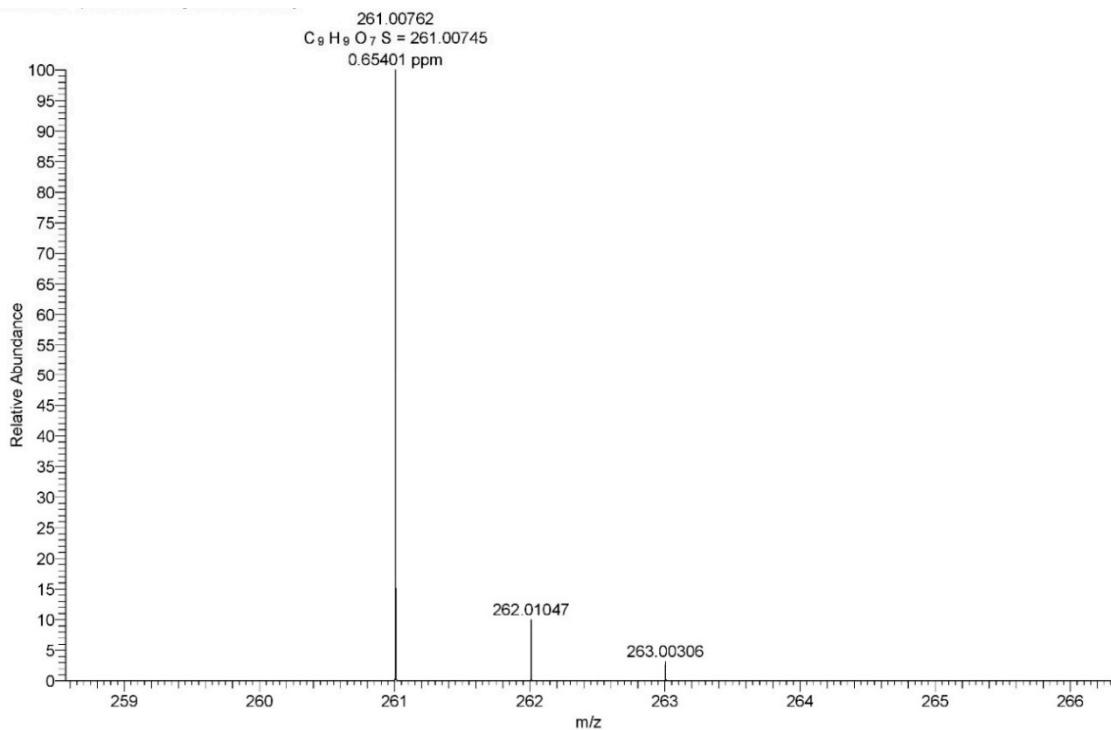


Figure S44. HRMS (ESI⁻) spectrum of **DHPP-CS**.

Calculated (for C₉H₉O₇S⁻) 261.00745, measured 261.00762 (0.7 ppm).

3,4-dihydroxyphenylacetic acid 3-O-sulfate (DHPA-3'-S) and 3,4-dihydroxyphenylacetic acid 4-O-sulfate (DHPA-4'-S)

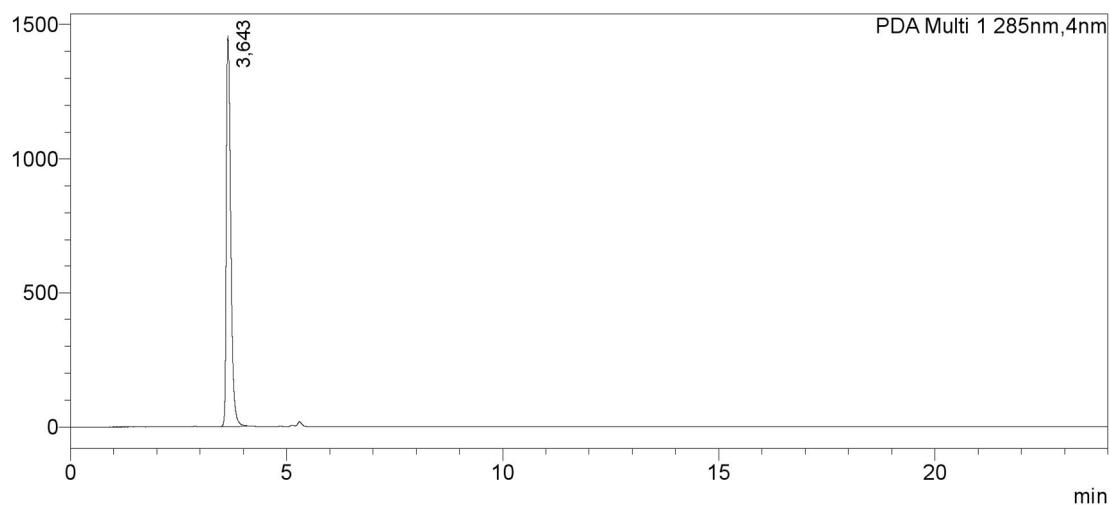
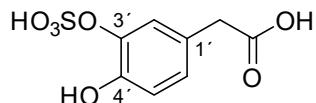


Figure S45. HPLC chromatogram of **DHPA-3'-S** and **DHPA-4'-S**

(RT= 3.643 min, 99%)

Table S10. ^1H and ^{13}C NMR data for **DHPA-3'-S** and **DHPA-4'-S**(600.23 MHz for ^1H , 150.93 MHz for ^{13}C , DMSO- d_6)**DHPA-3'-S**

Atom	δ_c	m.	δ_h	n _H	m.	J [Hz]	δ_c^{DHPA}	$\delta_c - \delta_c^{\text{DHPA}}$
1	173.74	S	-	0	-	-	173.00	0.74
2	41.13 ^x	T	3.33 ^H	2	m	-	40.14	0.99
1'	127.17 ^x	S	-	0	-	-	125.60	1.57
2'	123.88	D	6.980	1	d	2.2	116.58	7.30
3'	140.32	S	-	0	-	-	144.91	-4.59
4'	147.55	S	-	0	-	-	143.94	3.61
5'	116.76	D	6.724	1	d	8.2	115.28	1.48
6'	127.17	D	6.829	1	dd	8.2, 2.2	119.94	7.23

^H ... HSQC readout, ^x ... broad signal**DHPA-4'-S**

Atom	δ_c	m.	δ_h	n _H	m.	J [Hz]	δ_c^{DHPA}	$\delta_c - \delta_c^{\text{DHPA}}$
1	173.74	S	-	0	-	-	173.00	0.74
2	41.49 ^x	T	3.33 ^H	2	m	-	40.14	1.35
1'	133.13 ^x	S	-	0	-	-	125.60	7.53
2'	118.14	D	6.710	1	d	2.1	116.58	1.56
3'	148.66	S	-	0	-	-	144.91	3.75
4'	139.22	S	-	0	-	-	143.94	-4.72
5'	122.60	D	6.975	1	d	8.1	115.28	7.32
6'	120.19	D	6.598	1	dd	8.1, 2.1	119.94	0.25

^H ... HSQC readout, ^x ... broad signalapproximate molar ratio **DHPA-3'-S : DHPP-A'-S = 85 : 15**

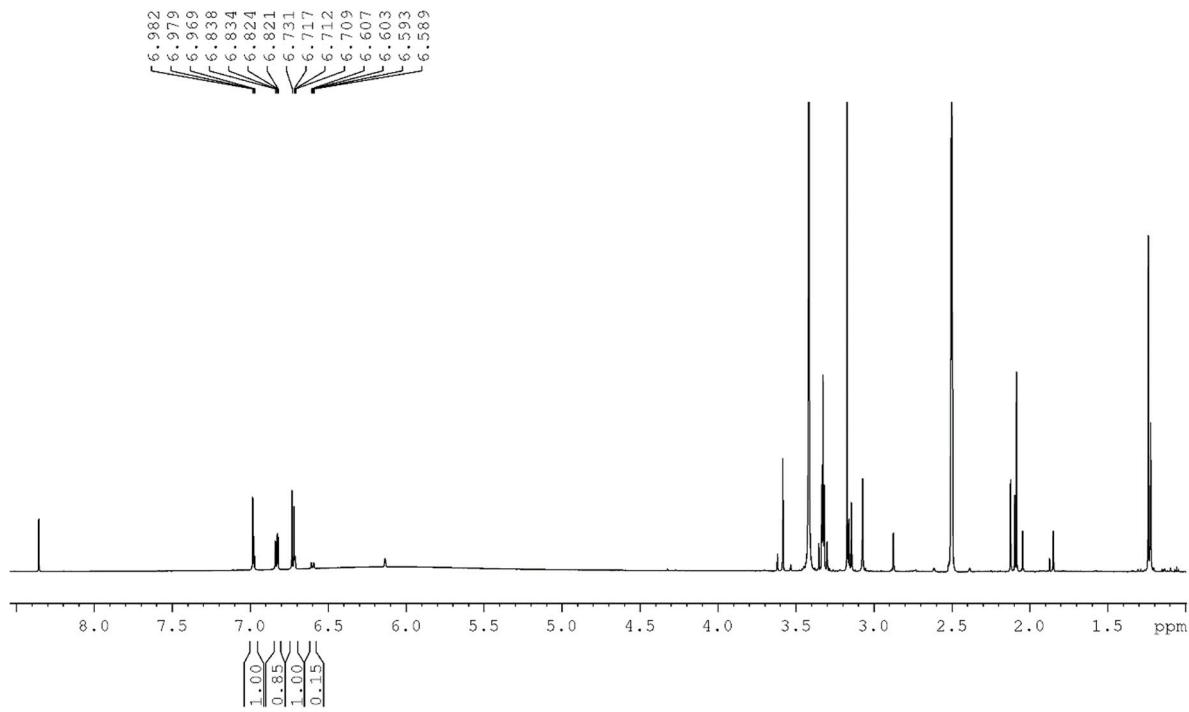


Figure S46. ^1H NMR spectrum of DHPA-3'-S and DHPA-4'-S (600.23 MHz, $\text{DMSO}-d_6$)

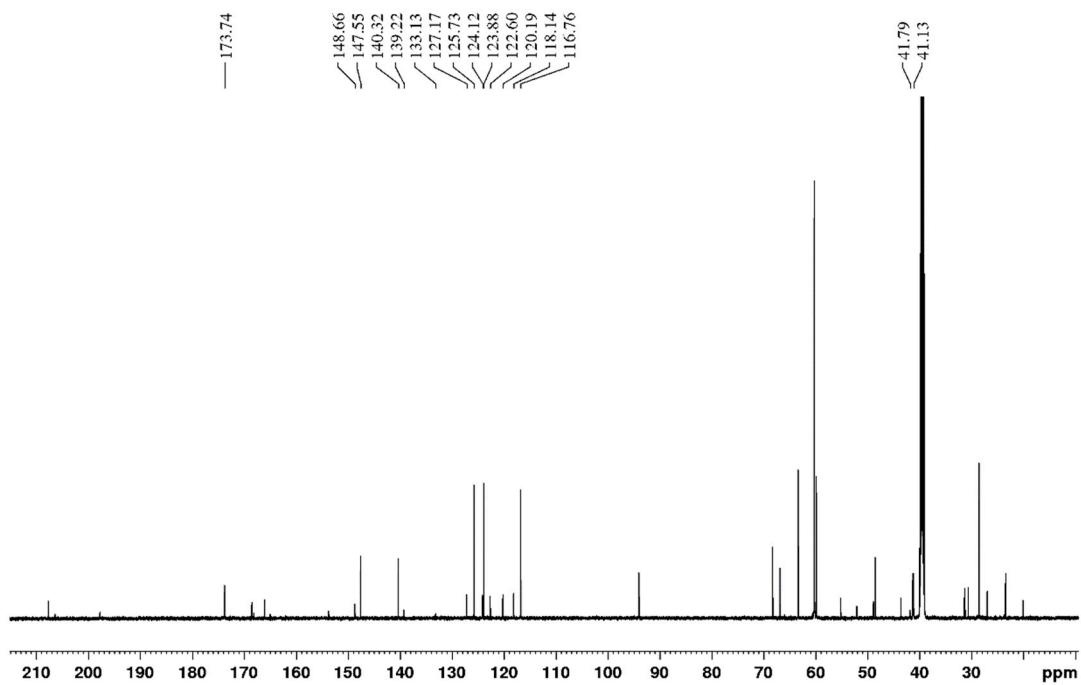


Figure S47. ^{13}C NMR spectrum of DHPA-3'-S and DHPA-4'-S.
(150.93 MHz, $\text{DMSO}-d_6$)

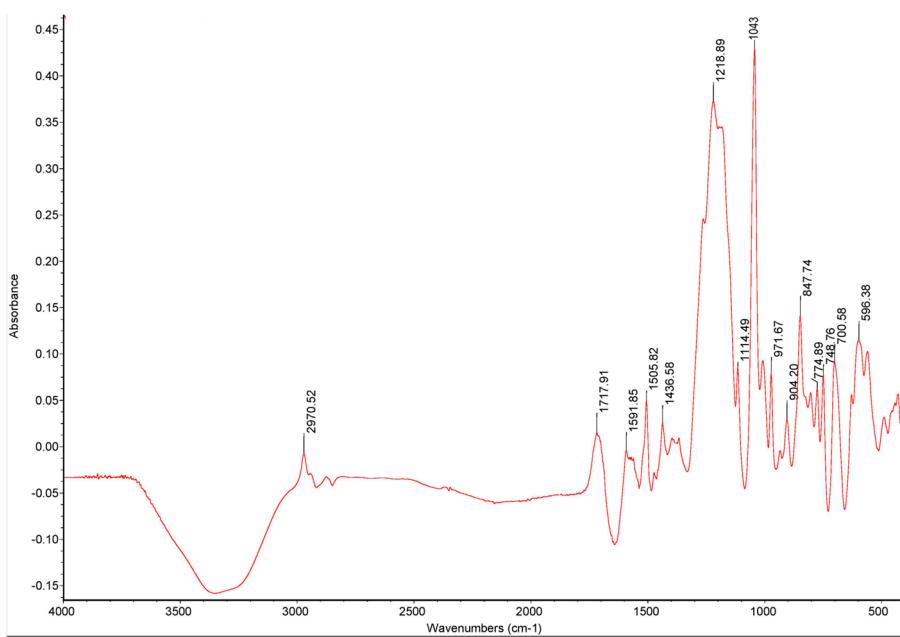


Figure S48. IR spectrum of **DHPA-3'-S** and **DHPA-4'-S**.

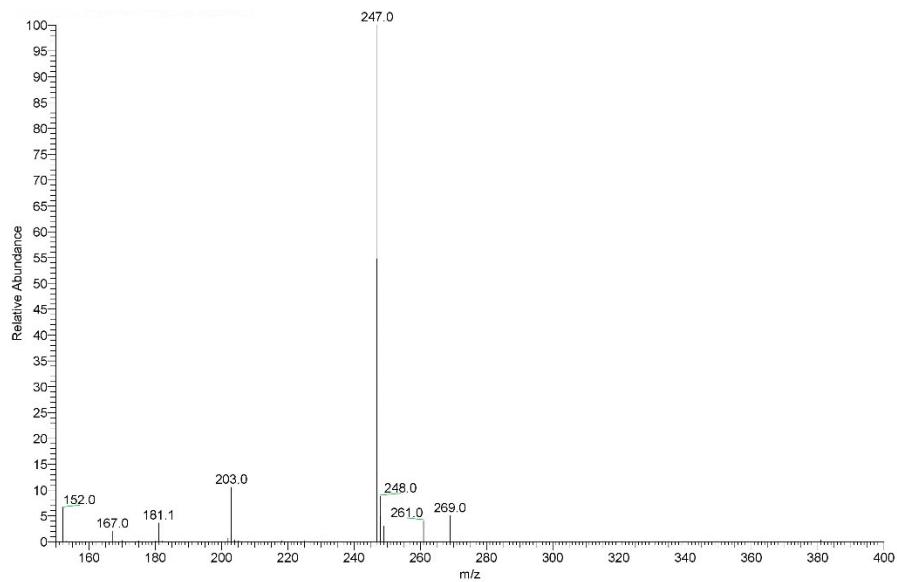


Figure S49. MS (ESI⁻) spectrum of **DHPA-S**.

([M - H]⁻, m/z 247.0).

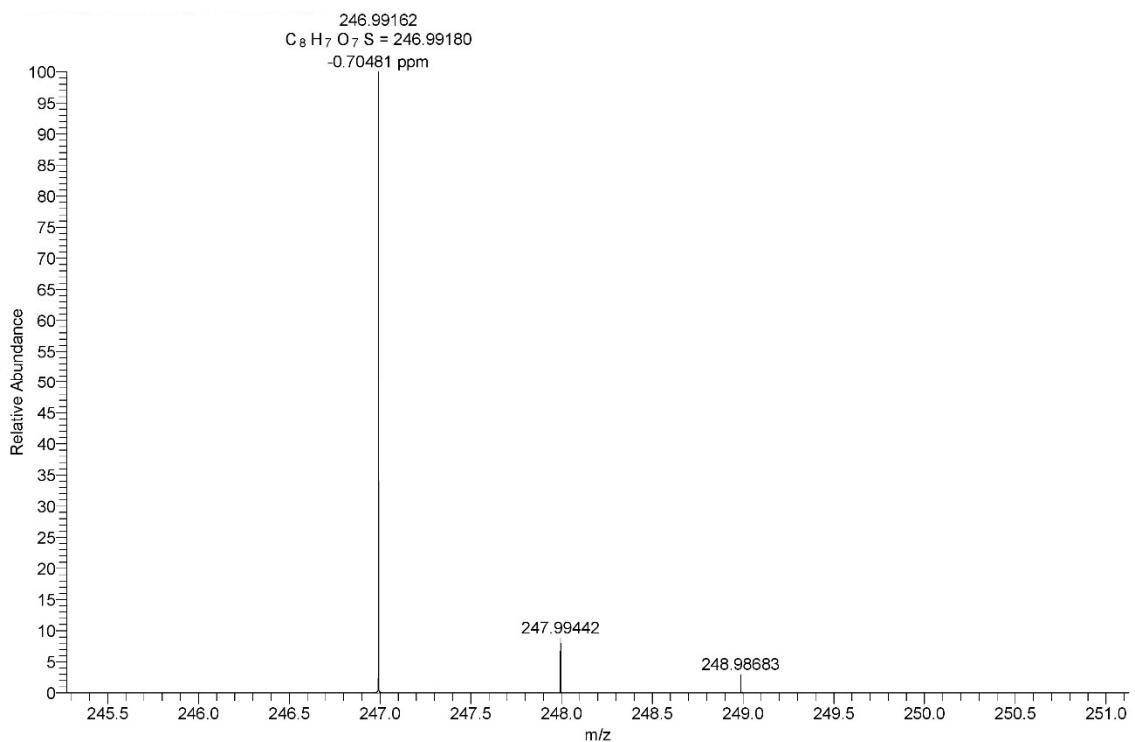
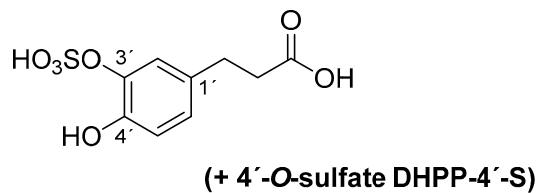


Figure S50. HRMS (ESI^-) spectrum of compound **DHPA-S**.
 Calculated (for $C_8H_7O_7S^-$) 246.99180, measured 246.99162 (-0.7 ppm).

3,4-Dihydroxyphenylpropionic acid sulfates (DHPP-S): 3,4-dihydroxyphenylpropionic acid 3'-*O*-sulfate (DHPP-3'-S) and 3,4-dihydroxyphenylpropionic acid 4'-*O*-sulfate (DHPP-4'-S)



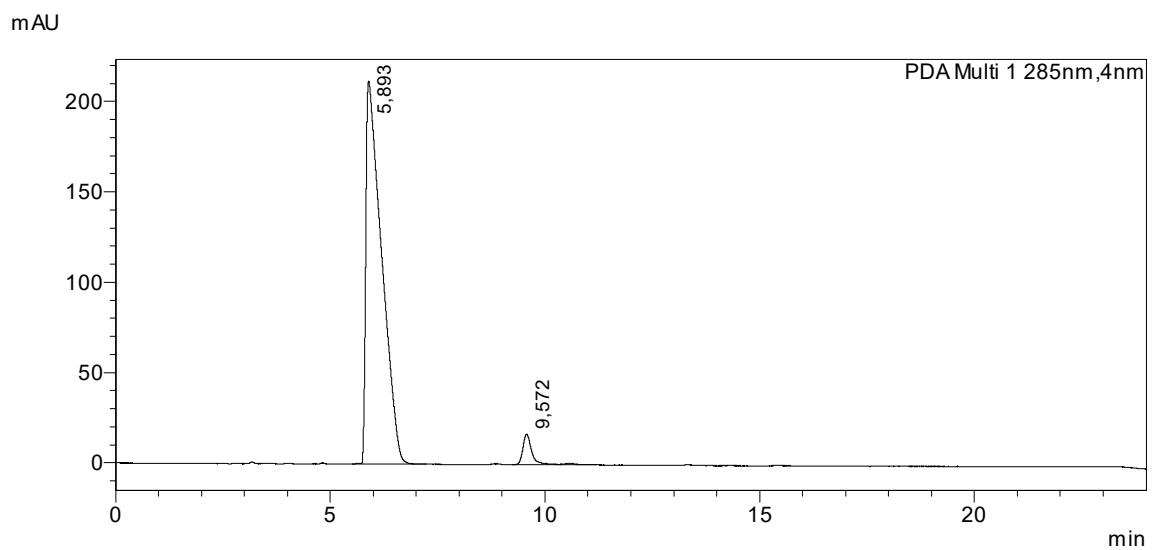


Figure S51. HPLC chromatogram of **DHPP-3'-S** and **DHPP-4'-S**
(RT= 5.839 min, 96%; the peak at 9.572 min belongs to the starting DHPP)

Table S11. ^1H and ^{13}C NMR data of **DHPP-3'-S** and **DHPP-4'-S**

(399.83 MHz for ^1H , 100.54 MHz for ^{13}C , DMSO- d_6)

DHPP-3'-S

Atom	δ_{C}	m.	δ_{H}	n _H	m.	J [Hz]	$\delta_{\text{C}}^{\text{DHPP}}$	$\delta_{\text{c}} - \delta_{\text{C}}^{\text{DHPP}}$
1	174.54	S	-	0	-	-	173.76	0.78
2	36.42	T	2.377	2	m	-	35.61	0.81
3	29.85	T	2.676	2	m	-	29.68	0.17
1'	132.37	S	-	0	-	-	131.60	0.77
2'	122.89	D	6.925	1	d	2.1	115.55	7.34
3'	140.46	S	-	0	-	-	144.90	-4.44
4'	147.23	S	-	0	-	-	143.30	3.93
5'	116.95	D	6.706	1	d	8.2	115.36	1.59
6'	124.52	D	6.797	1	dd	8.2, 2.2	118.65	5.87

DHPP-4'-S

Atom	δ_c	m.	δ_h	n _H	m.	J [Hz]	δ_c^{DHPP}	$\delta_c - \delta_c^{\text{DHPP}}$
1	174.54	S	-	0	-	-	173.76	0.78
2	36.42	T	2.396	2	m	-	35.61	0.81
3	30.26	T	2.676	2	m	-	29.68	0.58
1'	138.3 ^x	S	-	0	-	-	131.60	6.7
2'	117.00	D	6.666	1	d	2.1	115.55	1.45
3'	148.85	S	-	0	-	-	144.90	3.95
4'	138.9 ^x	S	-	0	-	-	143.30	-4.4
5'	122.92	D	6.952	1	d	8.2	115.36	7.56
6'	119.06	D	6.579	1	dd	8.2, 2.1	118.65	0.41

approximate molar ratio **DHPP-3'-S : DHPP-4'-S** = 87 : 13

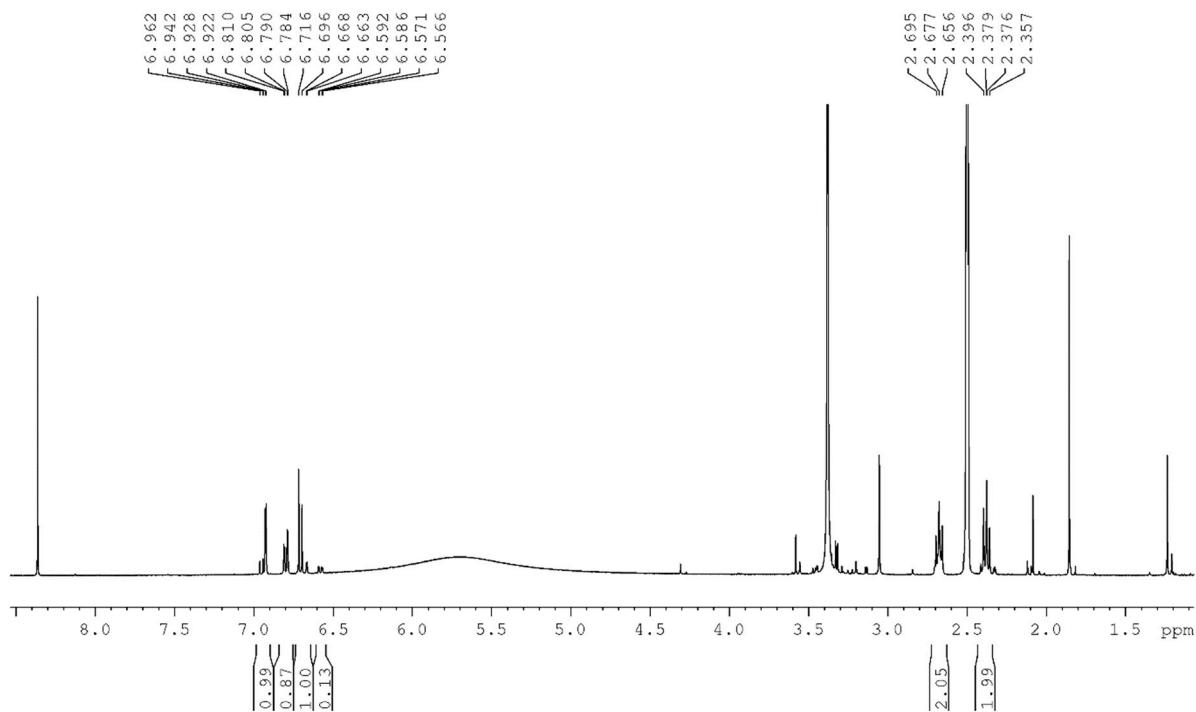


Figure S52. ^1H NMR spectrum of **DHPP-3'-S** and **DHPP-4'-S**.

(399.83 MHz, DMSO-*d*₆)

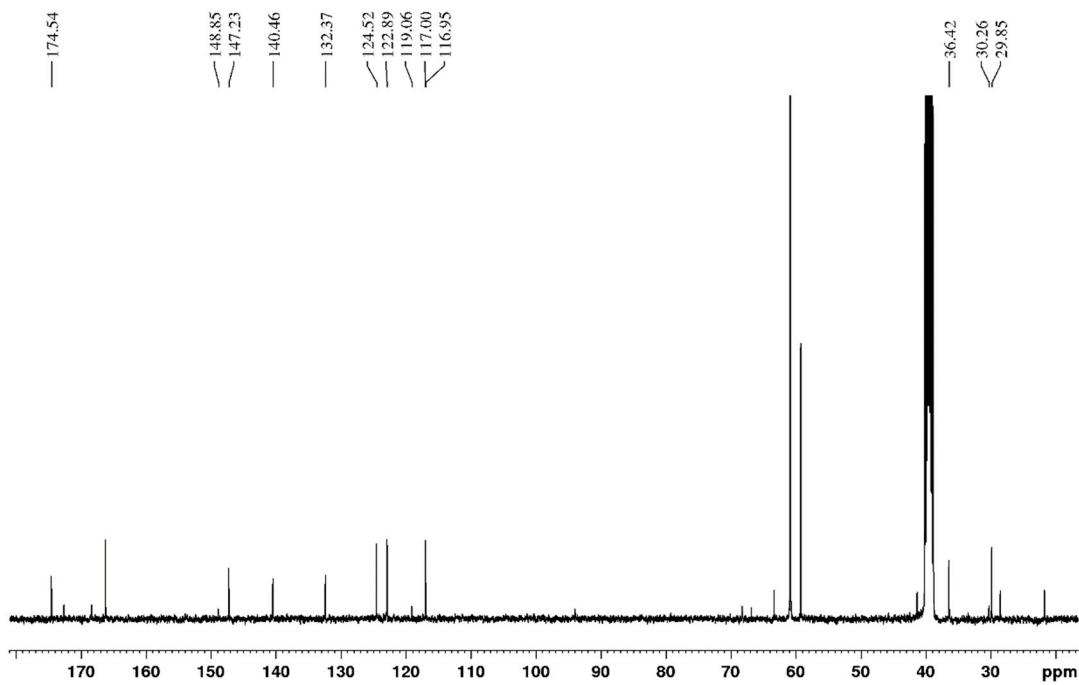


Figure S53. ^{13}C NMR spectrum of **DHPP-3'-S** and **DHPP-4'-S**.

(100.54 MHz, DMSO- d_6)

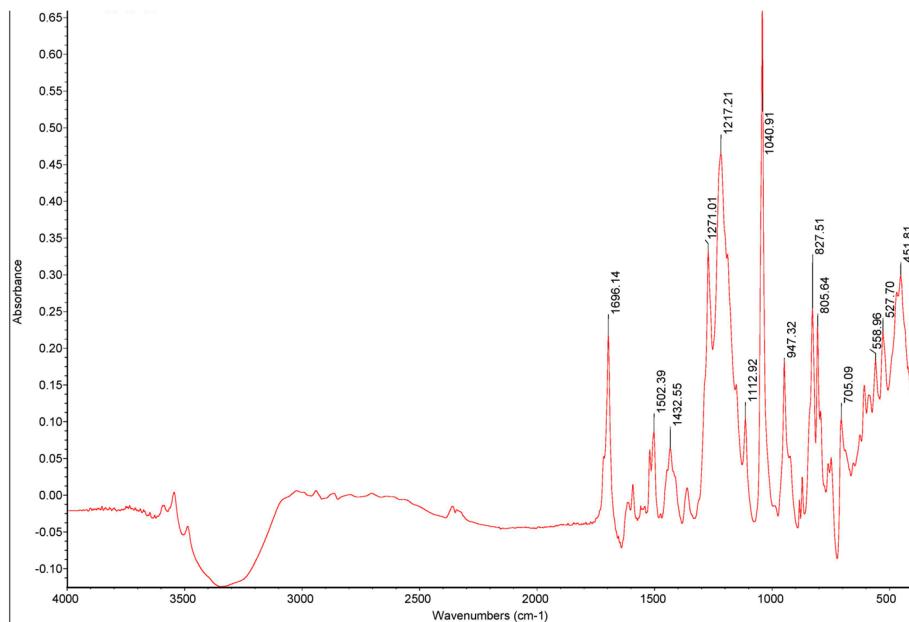


Figure S54. IR spectrum of **DHPP-3'-S** and **DHPP-4'-S**.

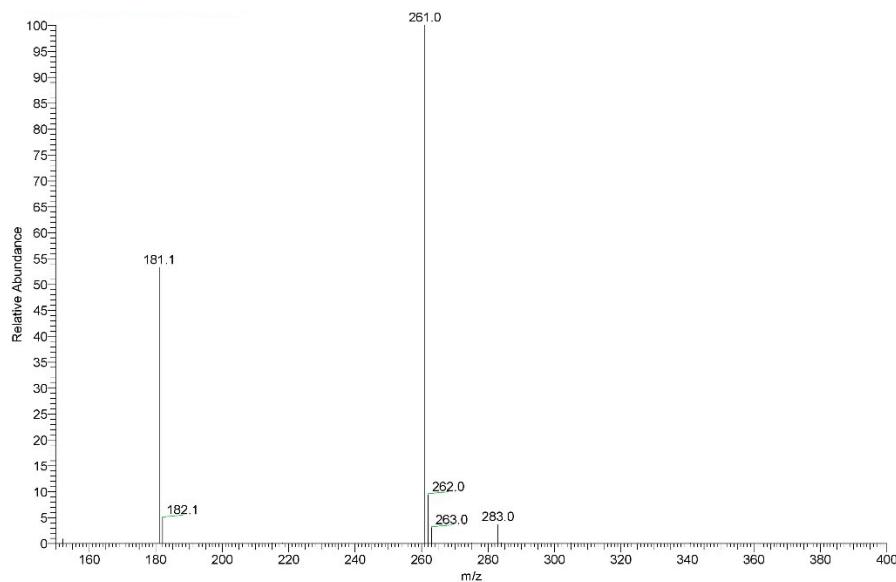


Figure S55. MS (ESI⁻) spectrum of **DHPP-S**.

([M - H]⁻, *m/z* 261.0).

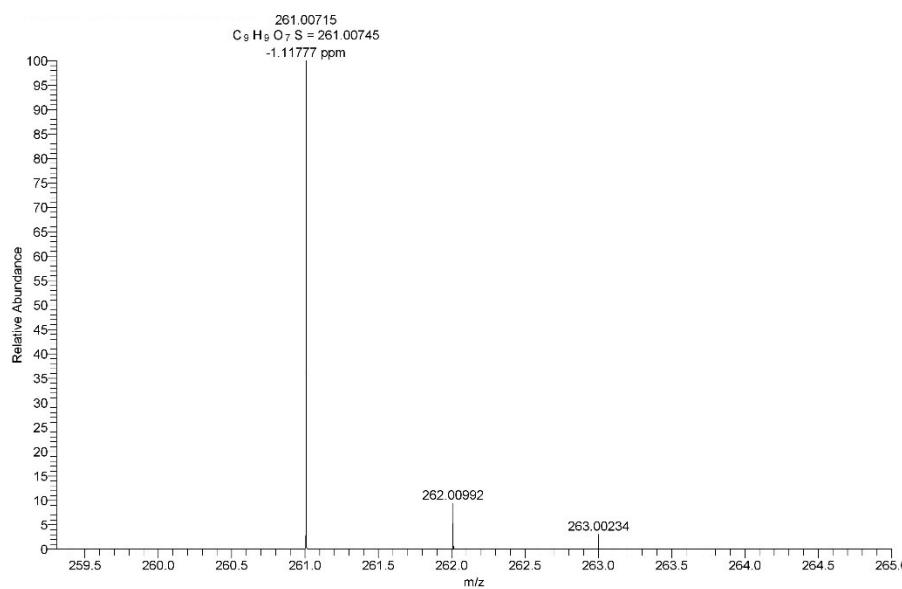
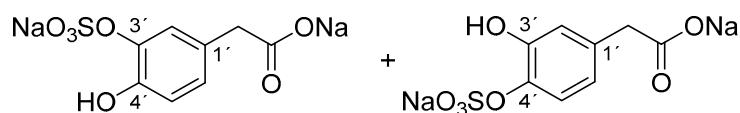


Figure S56. HRMS (ESI⁻) spectrum of **DHPP-S**.

Calculated (for C₉H₉O₇S⁻) 261.00745, measured 261.00715 (-1.1 ppm).

Sodium dihydroxyphenylacetate sulfates (Na₂ DHPA-S): sodium 2-(4-hydroxy-3-(sulfonatoxy)phenyl)acetate (DHPA-3'-S) and sodium 2-(3-hydroxy-4-(sulfonatoxy)phenyl)acetate (DHPA-4'-S)



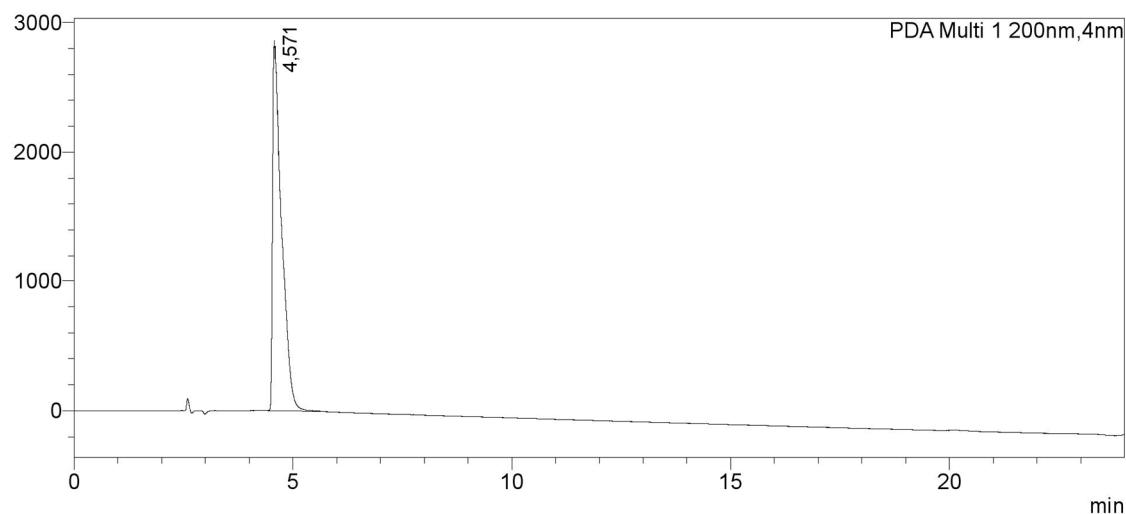


Figure S57. HPLC chromatogram of **Na₂DHPA-3'-S** and **Na₂DHPA-4'-S**
(RT= 4.571 min, 99%)

Table S12. ¹H and ¹³C NMR data of **Na₂DHPA-3'-S** and **Na₂DHPA-4'-S**

(600.23 MHz for ¹H, 150.93 MHz for ¹³C, DMSO-*d*₆)

Na₂DHPA-3'-S

Atom	δ_c	m.	δ_h	n _H	m.	J [Hz]	δ_c^{DHPA}	$\delta_c - \delta_c^{\text{DHPA}}$
1	175.27	S	-	0	-	-	173.00	2.27
2	44.90	T	3.101	2	br s	-	40.14	4.76
1'	130.76 ^x	S	-	0	-	-	125.60	5.16
2'	123.95	D	6.950	1	d	2.2	116.58	7.37
3'	139.97	S	-	0	-	-	144.91	-4.94
4'	146.99 ^x	S	-	0	-	-	143.94	3.05
5'	116.36	D	6.649	1	d	8.2	115.28	1.08
6'	125.74	D	6.824	1	dd	8.2, 2.2	119.94	5.80

^x ... broad signal

Na₂DHPA-4'-S

Atom	δ_c	m.	δ_H	n _H	m.	J [Hz]	δ_c^{DHPA}	$\delta_c - \delta_c^{DHPA}$
1	175.07	S	-	0	-	-	173.00	2.07
2	45.52	T	3.110	2	br s	-	40.14	5.38
1'	136.77	S	-	0	-	-	125.60	11.17
2'	118.19	D	6.737	1	d	2.1	116.58	1.61
3'	148.87	S	-	0	-	-	144.91	3.96
4'	138.38	S	-	0	-	-	143.94	-5.56
5'	122.26	D	6.869	1	d	8.1	115.28	6.98
6'	119.72	D	6.563	1	dd	8.1, 2.1	119.94	-0.22

approximate molar ratio **Na₂DHPA-3'-S**: **Na₂DHPA-4'-S** = 9 : 91

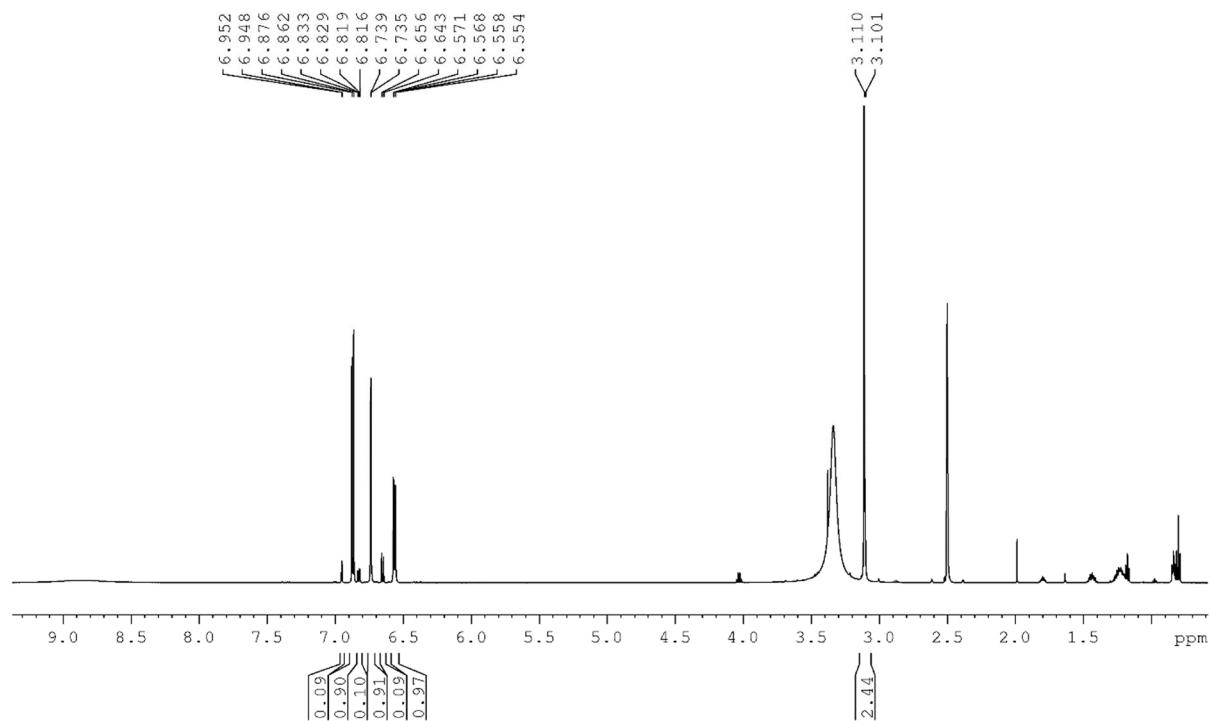


Figure S58. ^1H NMR spectrum of **Na₂DHPA-3'-S** and **Na₂DHPA-4'-S**. (600.23 MHz, DMSO-*d*₆)

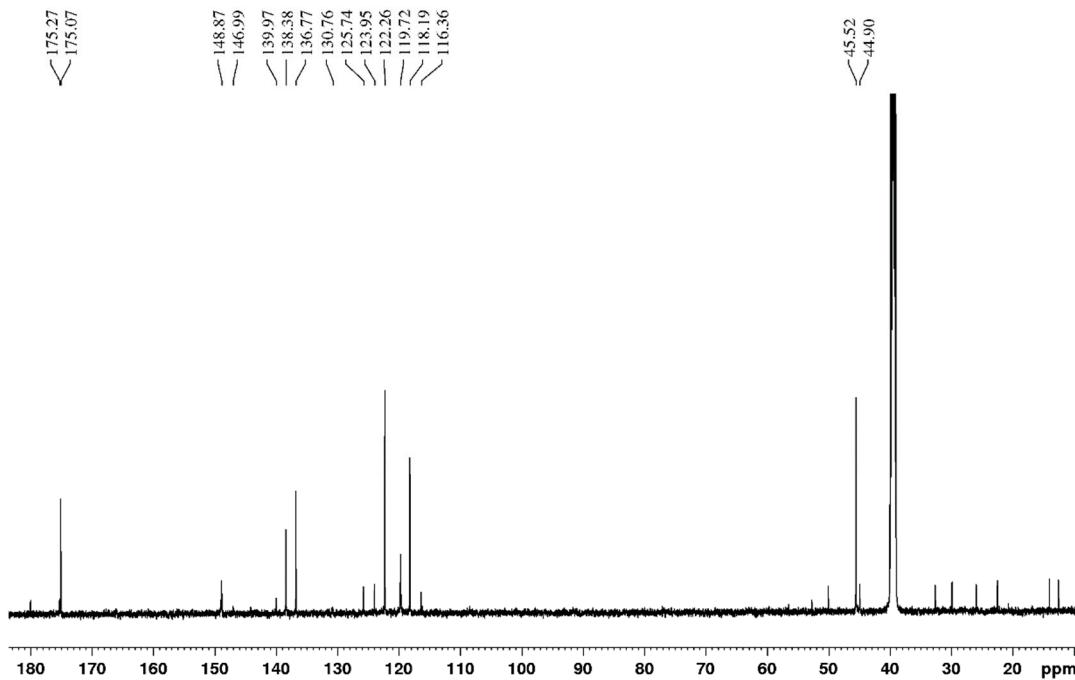


Figure S59. ^{13}C NMR spectrum of $\text{Na}_2 \text{DHPA-3}'\text{-S}$ and $\text{Na}_2 \text{DHPA-4}'\text{-S}$.
(150.93 MHz, $\text{DMSO}-d_6$)

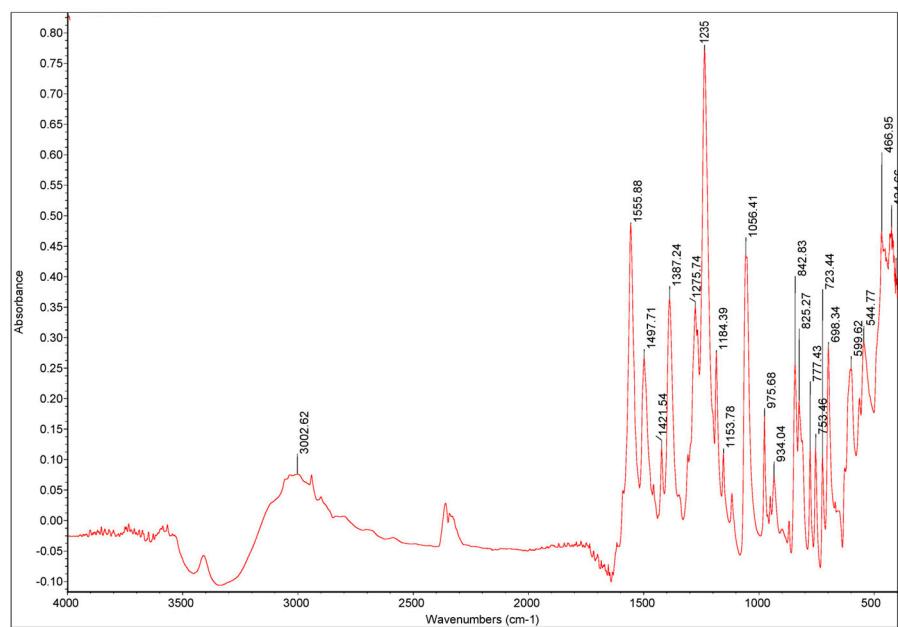


Figure S60. IR spectrum of compound $\text{Na}_2 \text{DHPA-3}'\text{-S}$ and $\text{Na}_2 \text{DHPA-4}'\text{-S}$.

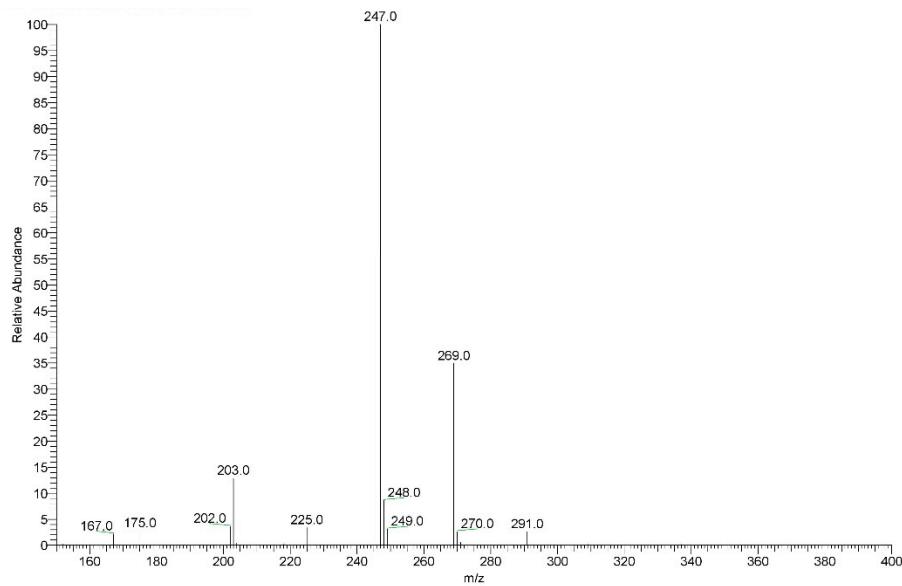


Figure S61. MS (ESI⁻) spectrum of Na₂ DHPA-S.

([M – 2Na + H]⁻, *m/z* 247.0; [M – Na]⁻, *m/z* 269.0; [M – H]⁻, *m/z* 291.0).

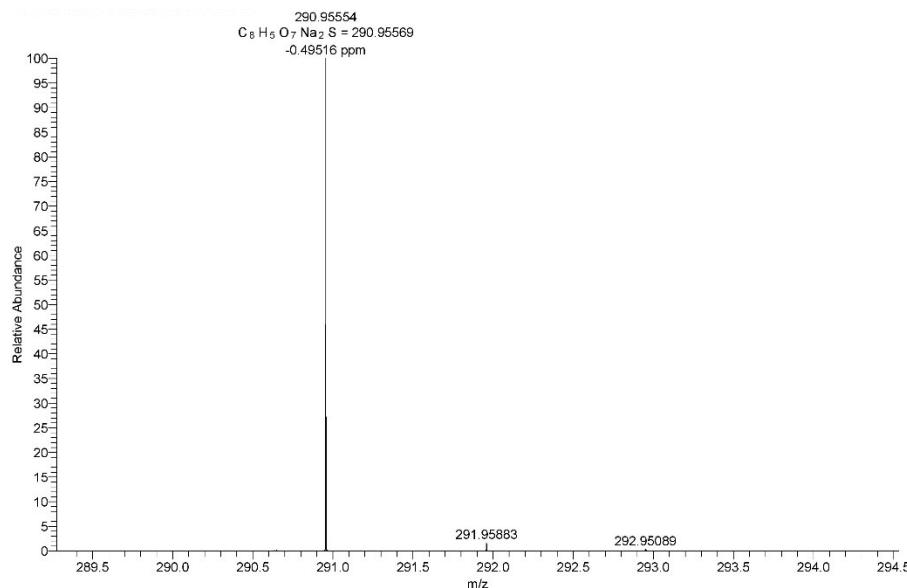


Figure S62. HRMS (ESI⁻) spectrum of Na₂ DHPA-S.

Calculated (for C₈H₅O₇Na₂S⁻) 290.95569, measured 290.95554 (-0.5 ppm).

Sodium phenylpropanoate sulfates (DHPP-S): sodium 3-(4-hydroxy-3-(sulfonatoxy)phenyl)propanoate (DHPP-3'-S) and sodium 2-(3-hydroxy-4-(sulfonatoxy)phenyl)propanoate (DHPP-4'-S)

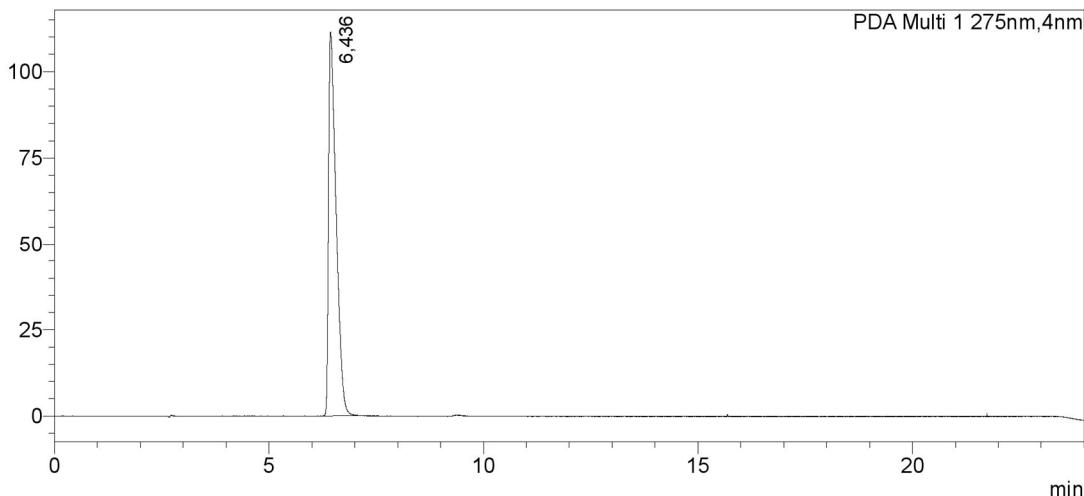
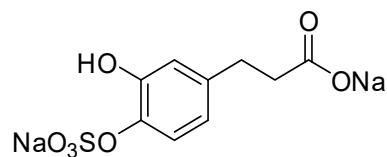
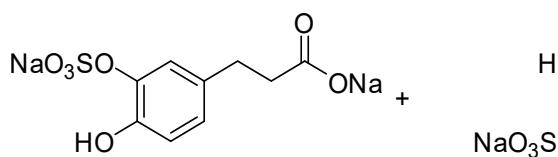


Figure S63. HPLC chromatogram of **Na₂ DHPP-3'-S** and **Na₂ DHPP-4'-S**

(RT= 6.436 min, 99%)

Table S13. ¹H and ¹³C NMR data of **Na₂ DHPP-3'-S** and **Na₂ DHPP-4'-S**.

(600.23 MHz for ¹H, 150.93 MHz for ¹³C, DMSO-*d*₆)

Na₂ DHPP-3'-S

Atom	δ_c	m.	δ_h	n _h	m.	J [Hz]	δ_c^{DHPP}	$\delta_c - \delta_c^{\text{DHPP}}$
1	177.01	S	-	0	-	-	173.76	3.25
2	39.77	T	2.152	2	m	-	35.61	4.16
3	31.6	T	2.651	2	m	-	29.68	1.92
1'	134.25	S	-	0	-	-	131.60	2.65
2'	122.86	D	6.925	1	d	2.2	115.55	7.31
3'	140.30	S	-	0	-	-	144.90	-4.60
4'	146.84	S	-	0	-	-	143.30	3.54
5'	116.76	D	6.686	1	d	8.2	115.36	1.40
6'	124.47	D	6.781	1	dd	8.2, 2.2	118.65	5.82

Na₂ DHPP-4'-S

Atom	δ_c	m.	δ_h	n _H	m.	J [Hz]	δ_c^{DHPP}	$\delta_c - \delta_c^{\text{DHPP}}$
1	176.90	S	-	0	-	-	173.76	3.14
2	39.88	T	2.168	2	m	-	35.61	4.27
3	31.99	T	2.660	2	m	-	29.68	2.31
1'	140.27	S	-	0	-	-	131.60	8.67
2'	117.01	D	6.670	1	d	2.1	115.55	1.46
3'	148.87	S	-	0	-	-	144.90	3.97
4'	138.43	S	-	0	-	-	143.30	-4.87
5'	122.82	D	6.920	1	d	8.1	115.36	7.46
6'	118.94	D	6.557	1	dd	8.1, 2.1	118.65	0.29

approximate molar ratio Na₂ DHPP-3'-S: Na₂ DHPP-4'-S = 14 : 86

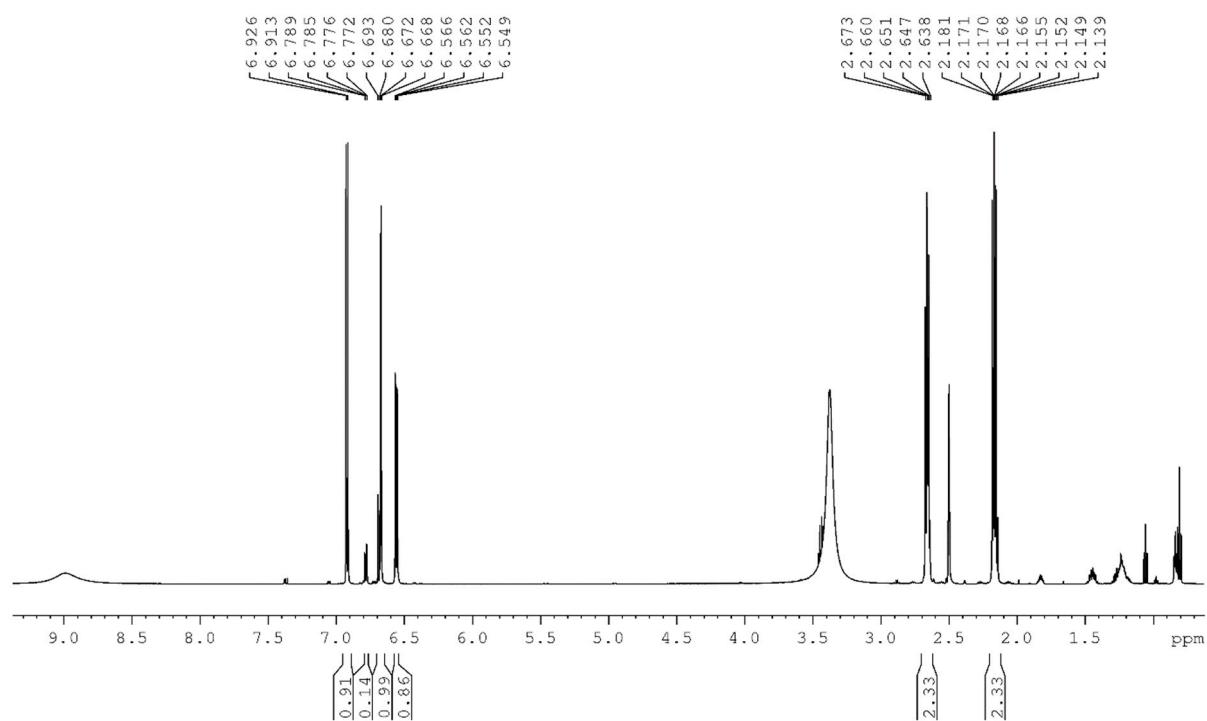


Figure S64. ¹H NMR spectrum of Na₂ DHPP-3'-S and Na₂ DHPP-4'-S.

(600.23 MHz, DMSO-*d*₆)

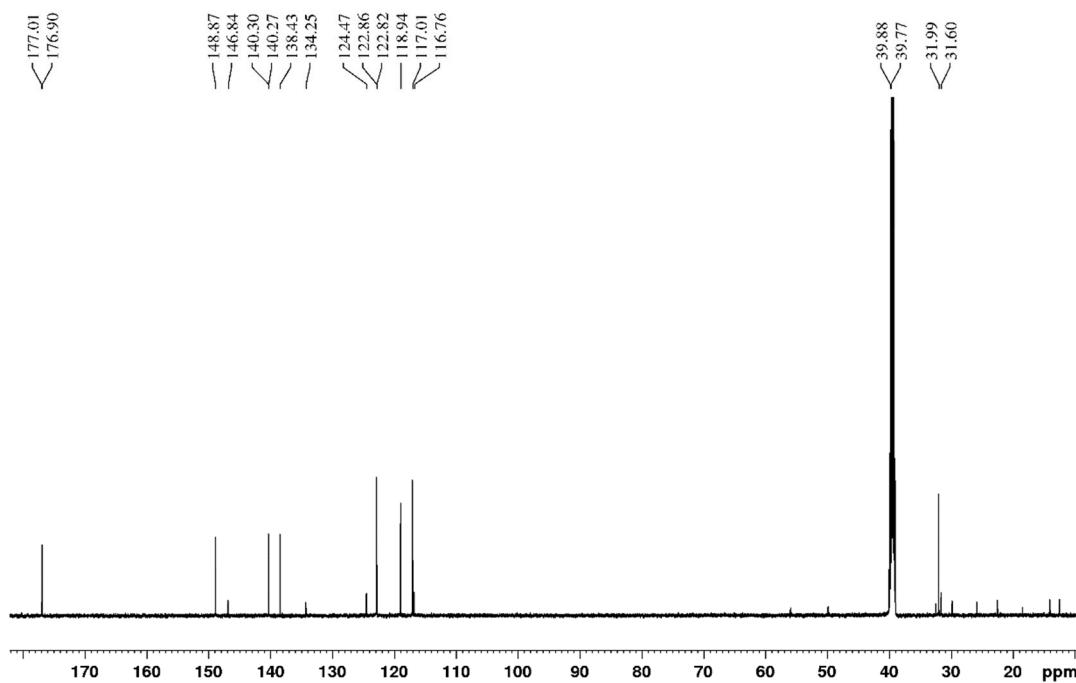


Figure S65. ^{13}C NMR spectrum of $\text{Na}_2 \text{DHPP-3}'\text{-S}$ and $\text{Na}_2 \text{DHPP-4}'\text{-S}$.
(150.93 MHz, $\text{DMSO}-d_6$)

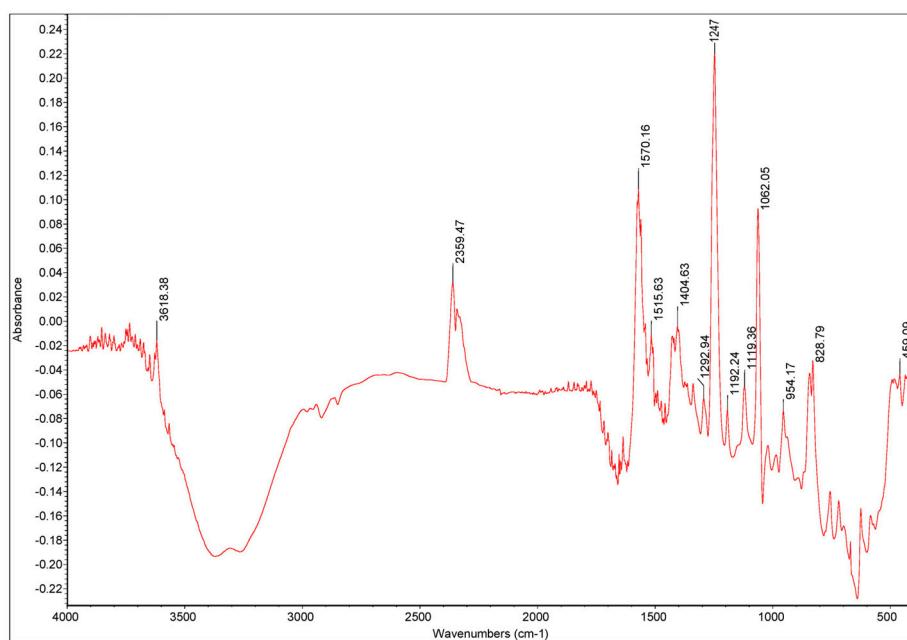


Figure S66. IR spectrum of compound $\text{Na}_2 \text{DHPP-3}'\text{-S}$ and $\text{Na}_2 \text{DHPP-4}'\text{-S}$.

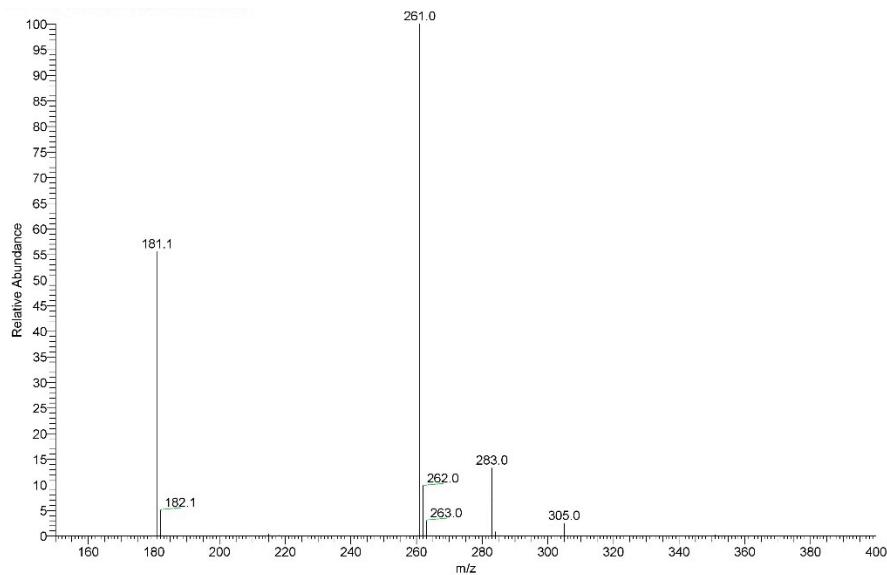


Figure S67. MS (ESI⁻) spectrum of Na₂ DHPP-S.

([M - 2Na + H]⁻, *m/z* 261.0; [M - Na]⁻, *m/z* 283.0; [M - H]⁻, *m/z* 305.0).

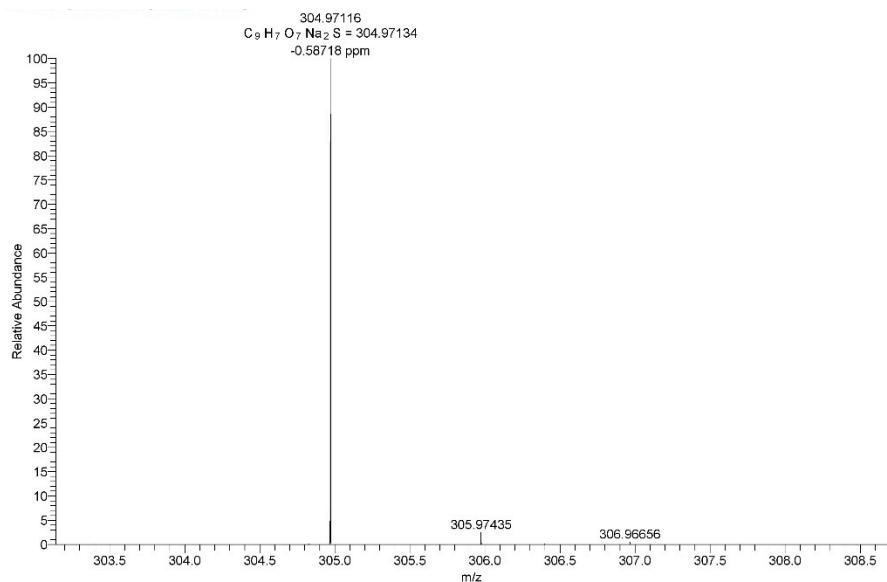


Figure S68. HRMS (ESI⁻) spectrum of Na₂ DHPP-S.

Calculated (for C₉H₇O₇Na₂S⁻) 304.97134, measured 304.97116 (-0.6 ppm).

(Trioxomethyl)methylammonium (2-hydroxyphenyl)acetate (2-HPA-Tris)

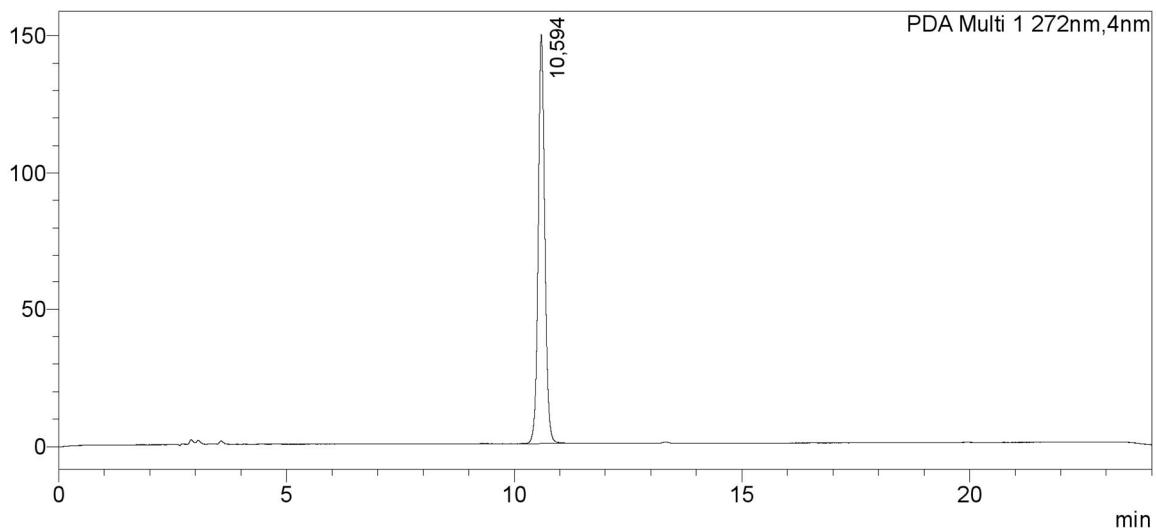
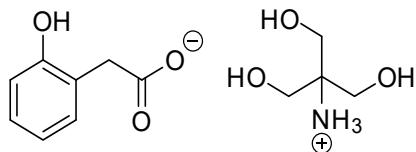


Figure S69. HPLC chromatogram of **2-HPA·Tris**.

(RT= 10.594 min, 99%)

Table S14. ^1H and ^{13}C NMR data for compound **2-HPA·Tris**.

(399.83 MHz for ^1H , 100.54 MHz for ^{13}C , DMSO- d_6)

Atom	δ_{C}	m.	δ_{H}	n _H	m.	J [Hz]	$\delta_{\text{C}}^{\text{2HPA}}$	$\delta_{\text{C}} - \delta_{\text{C}}^{\text{2HPA}}$
1	175.48	S	-	0	-	-	172.63	2.85
2	43.53	T	3.301	2	s	-	35.23	8.30
1'	124.63	S	-	0	-	-	121.75	2.88
2'	157.74	S	-	0	-	-	155.26	2.48
3'	116.63	D	6.644	1	dd	8.0, 1.3	114.68	1.95
4'	127.00	D	6.972	1	ddd	8.0, 7.3, 1.8	127.67	-0.67
5'	117.84	D	6.612	1	ddd	7.4, 7.3, 1.3	118.58	-0.74
6'	130.02	D	6.919	1	dd	7.4, 1.8	130.92	-0.90

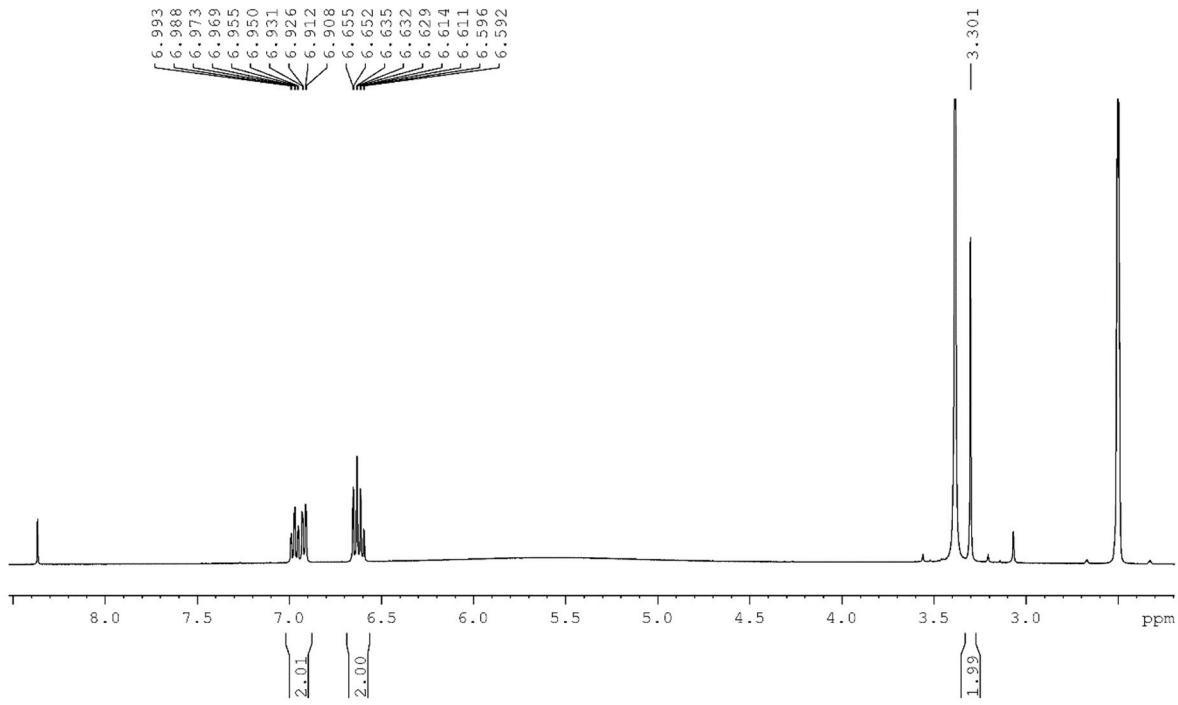


Figure S70. ^1H NMR spectrum of **2**-HPA·Tris.

(399.83 MHz, DMSO)

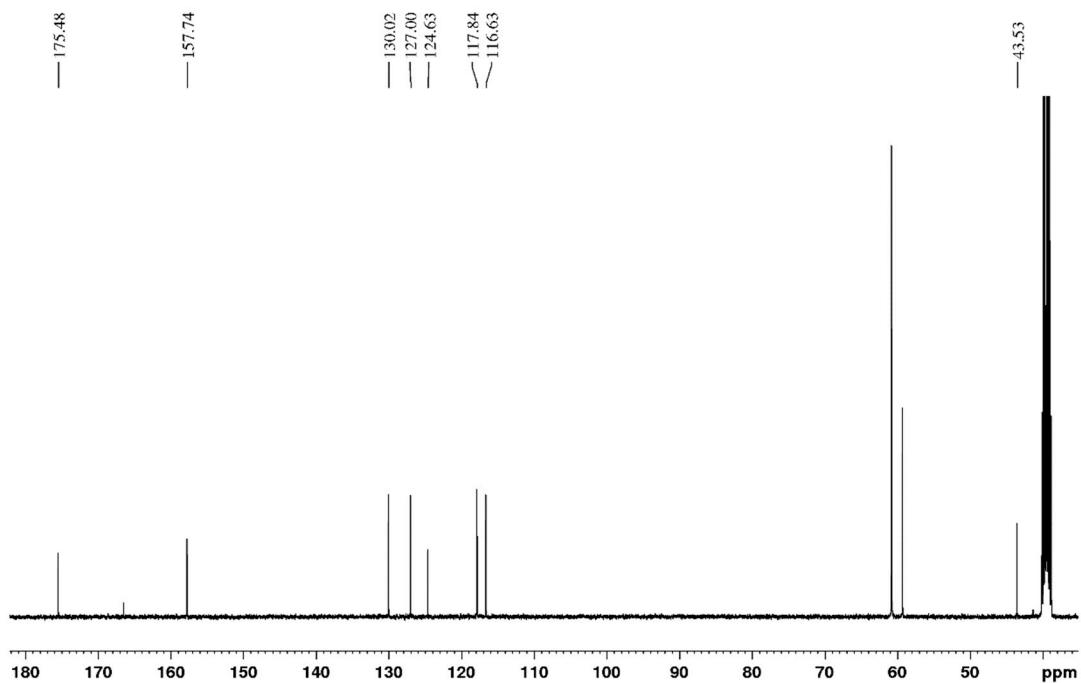


Figure S71. ^{13}C NMR spectrum of **2**-HPA·Tris.

(100.54 MHz, DMSO)

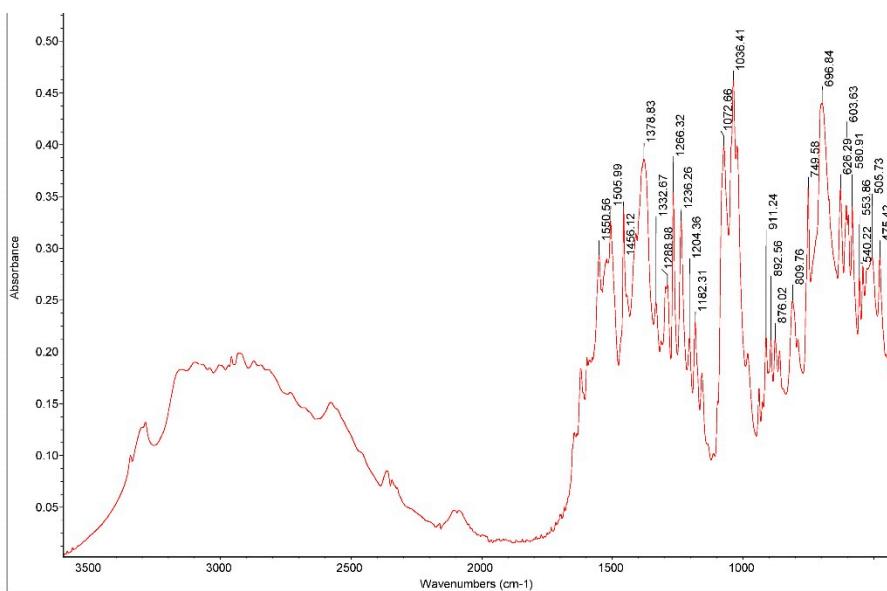


Figure S72. IR spectrum of 2-HPA·Tris.

(Trioxomethyl)methylammonium (3-hydroxyphenyl)acetate (3-HPA·Tris)

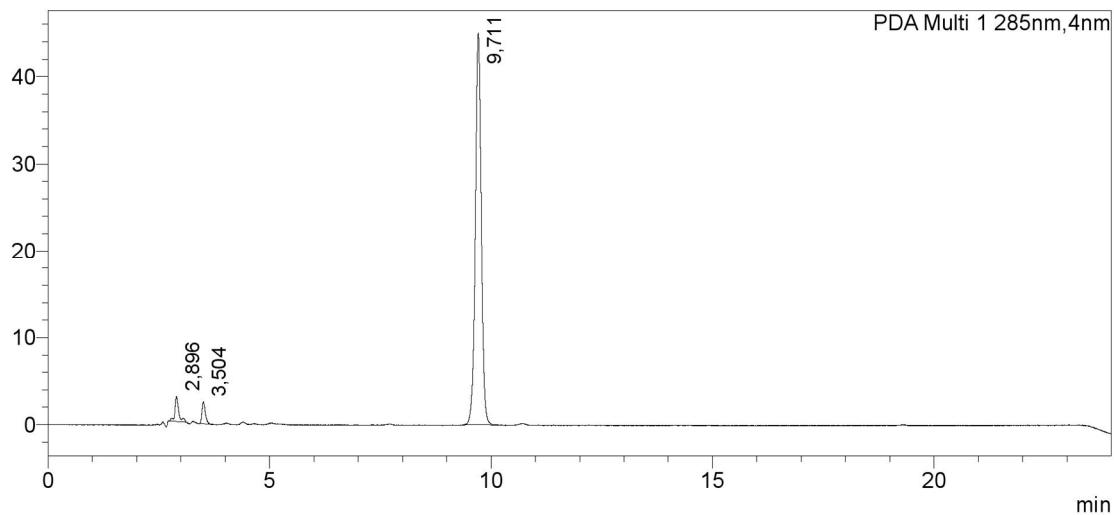
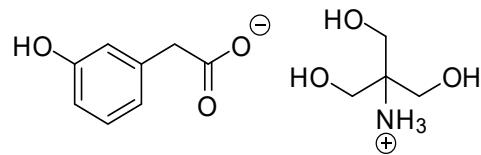


Figure S73. HPLC chromatogram of 3-HPA·Tris.

(RT= 9.711 min, 93.2%)

Table S15. ^1H and ^{13}C NMR data for **3**-HPA·Tris.

(600.23 MHz for ^1H , 150.93 MHz for ^{13}C , DMSO- d_6)

Atom	δ_{C}	m.	δ_{H}	n _H	m.	J [Hz]	$\delta_{\text{C}}^{\text{HPA}}$	$\delta_{\text{C}} - \delta_{\text{C}}^{\text{HPA}}$
1	174.60	S	-	0	-	-	172.52	2.08
2	43.89	T	3.251	2	s	-	40.72	3.17
1'	138.81	S	-	0	-	-	136.11	2.7
2'	116.21	D	6.663	1	dd	2.5, 1.6	116.12	0.09
3'	157.04	S	-	0	-	-	157.16	-0.12
4'	112.64	D	6.555	1	ddd	8.1, 2.5, 1.0	113.51	-0.87
5'	128.55	D	7.006	1	dd	8.1, 7.5	129.08	-0.53
6'	119.76	D	6.612	1	ddd	7.5, 1.6, 1.0	119.83	-0.07

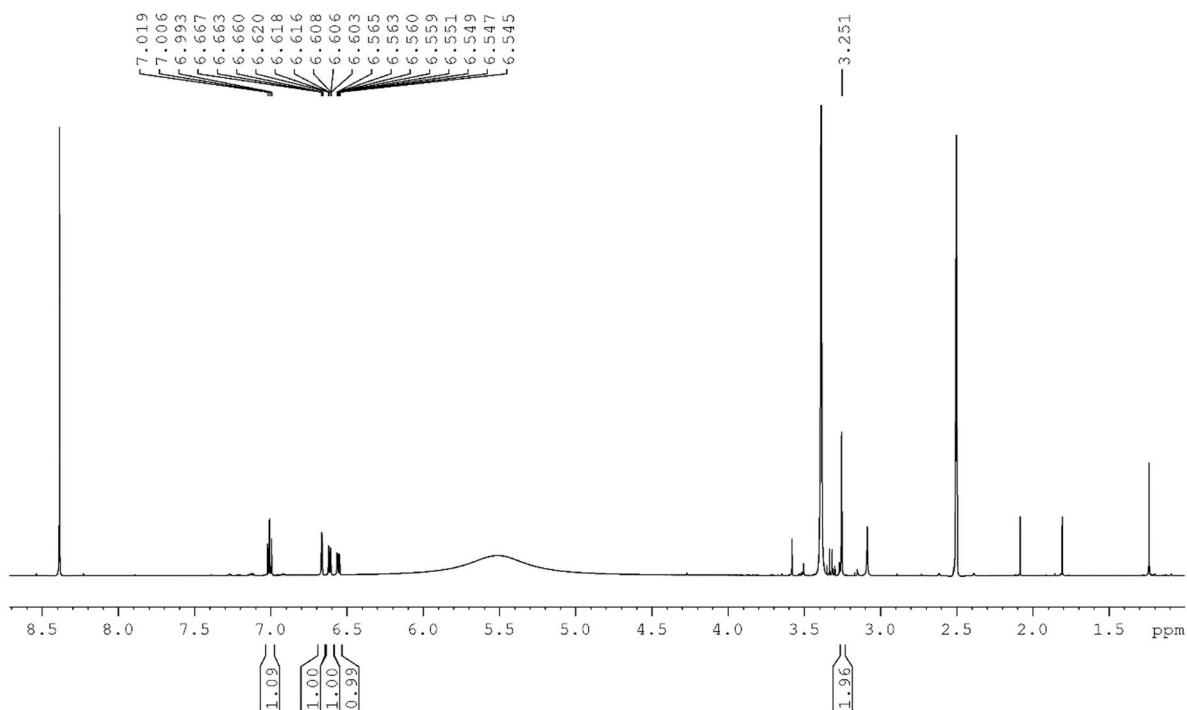


Figure S74. ^1H NMR spectrum of **3**-HPA·Tris.

(600.23 MHz, DMSO- d_6)

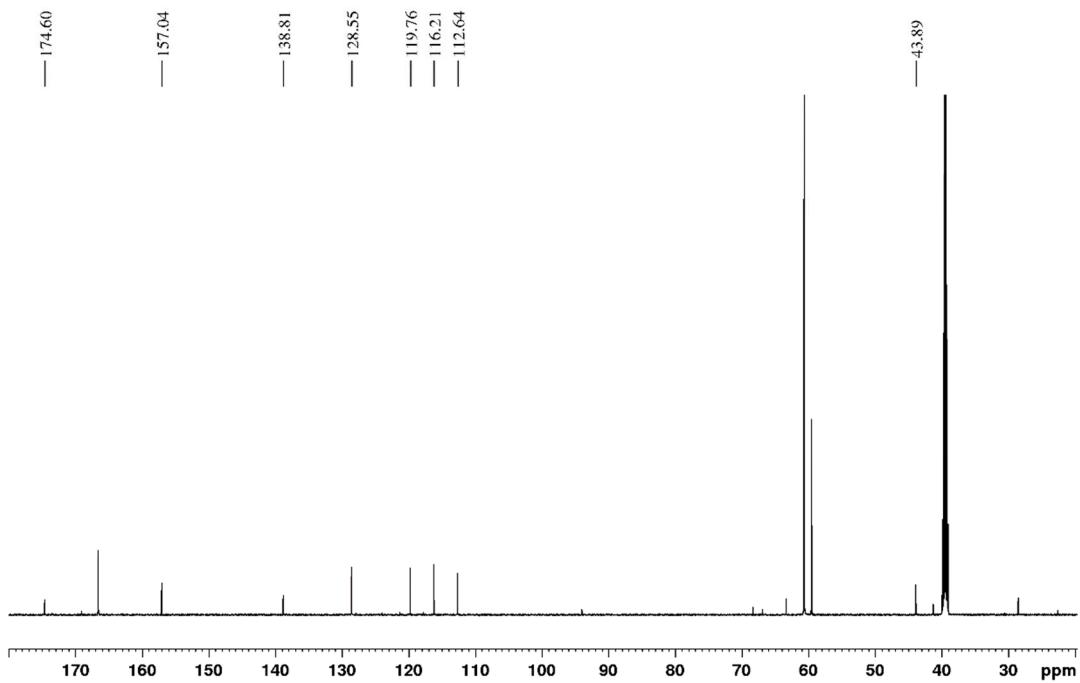


Figure S75. ^{13}C NMR spectrum of 3-HPA-Tris.

(150.93 MHz for ^{13}C , DMSO- d_6)

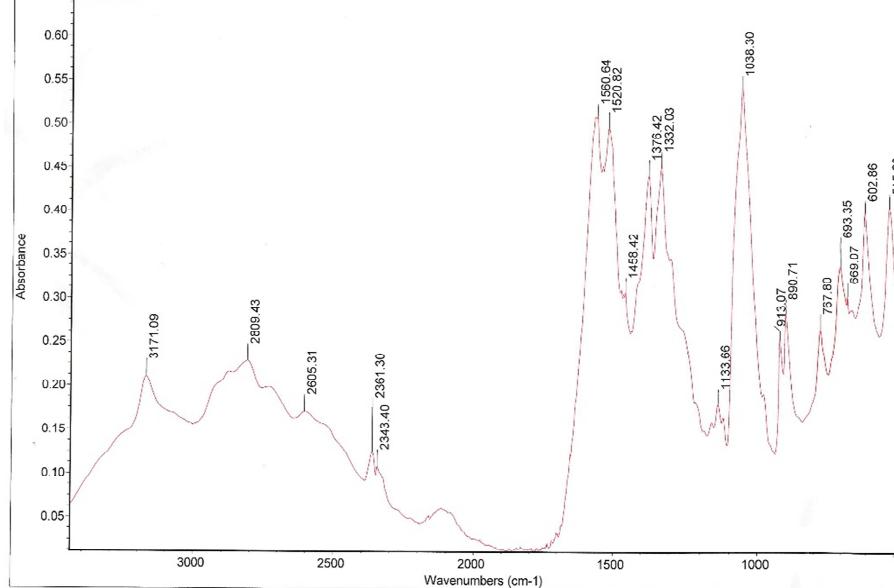


Figure S76. IR spectrum of 3-HPA-Tris.

(Trioxomethyl)methylammonium (4-hydroxyphenyl)acetate (4-HPA·Tris)

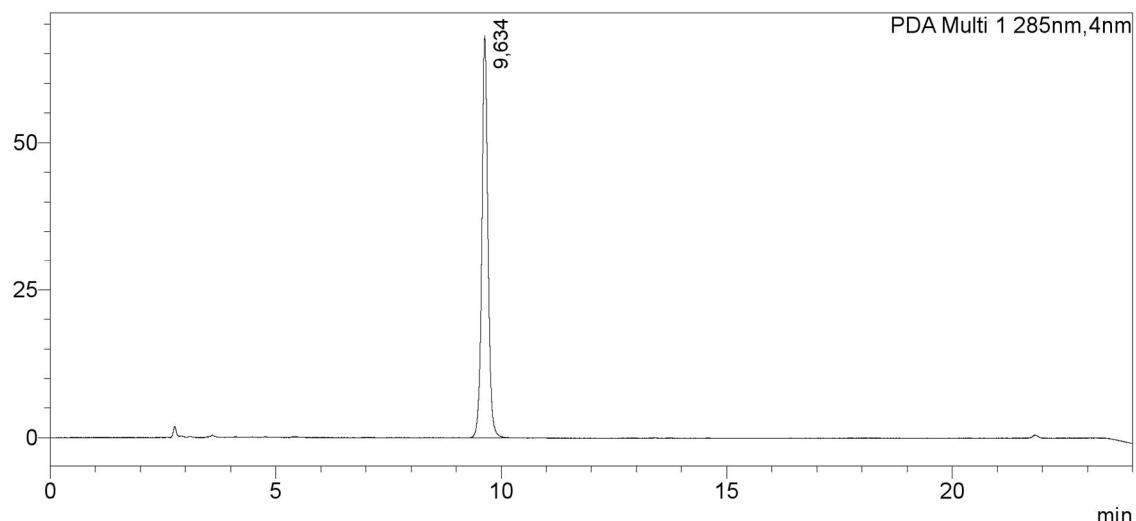
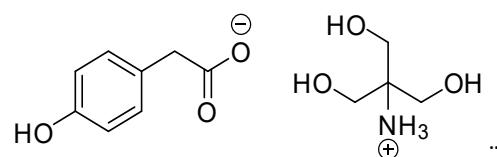


Figure S77. HPLC chromatogram of **4-HPA·Tris**.

(RT= 9.634 min, 99%)

Table S16. ¹H and ¹³C NMR data for **4-HPA·Tris**.
(399.83 MHz for ¹H, 100.54 MHz for ¹³C, DMSO-*d*₆)

Atom	δ_c	m.	δ_h	n _H	m.	$\delta_c^{2\text{HPA}}$	$\delta_c - \delta_c^{2\text{HPA}}$
1	174.55	S	-	0	-	172.99	1.56
2	42.05	T	3.268	2	s	39.79	2.26
1'	127.02	S	-	0	-	125.03	1.99
2'	129.97	D	7.003	2	m	130.13	-0.16
3'	114.67	D	6.647	2	m	114.92	-0.25
4'	155.51	S	-	0	-	155.95	-0.44

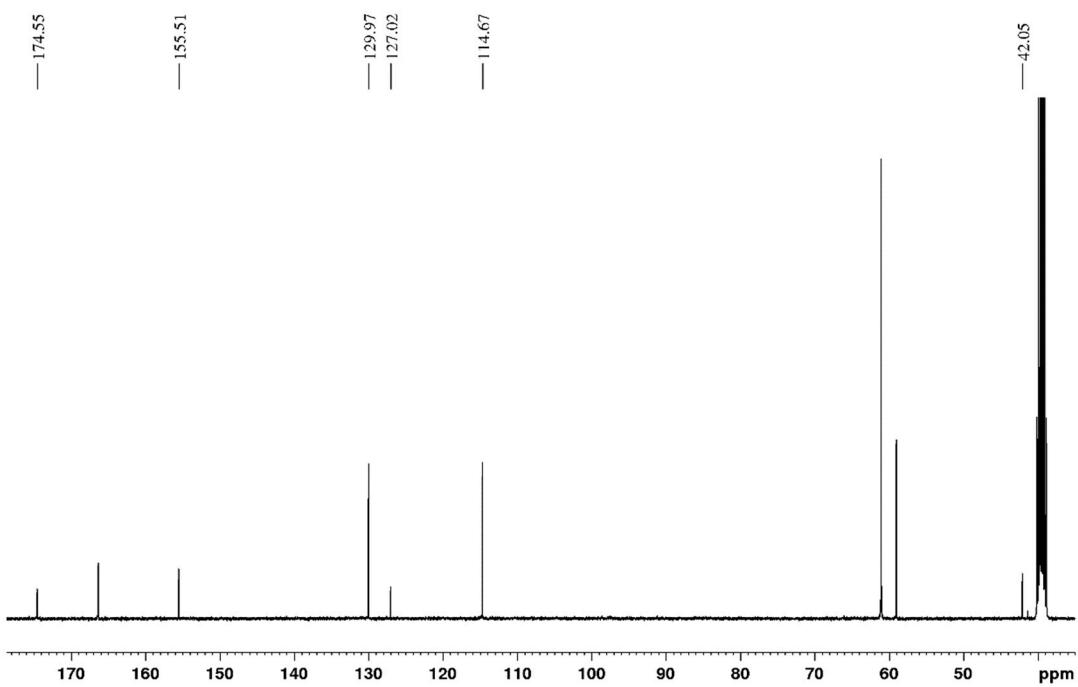
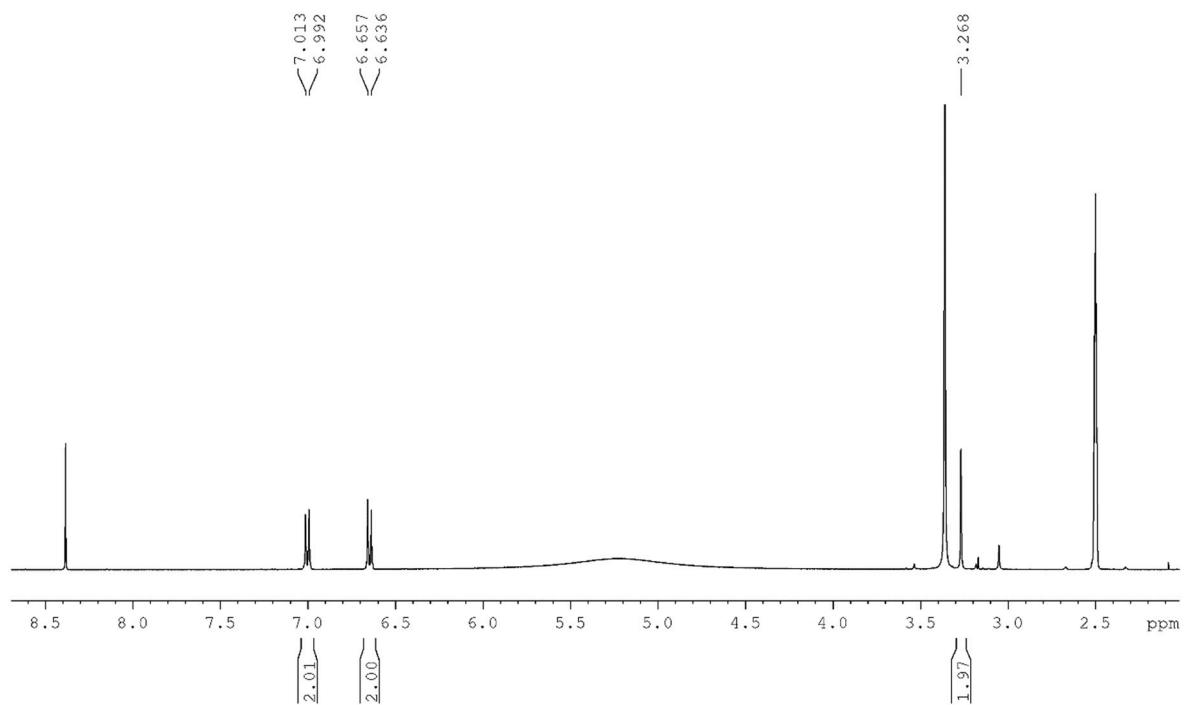


Figure S78. ¹H NMR spectrum of 4-HPA·Tris.
(399.83 MHz, DMSO-*d*₆)

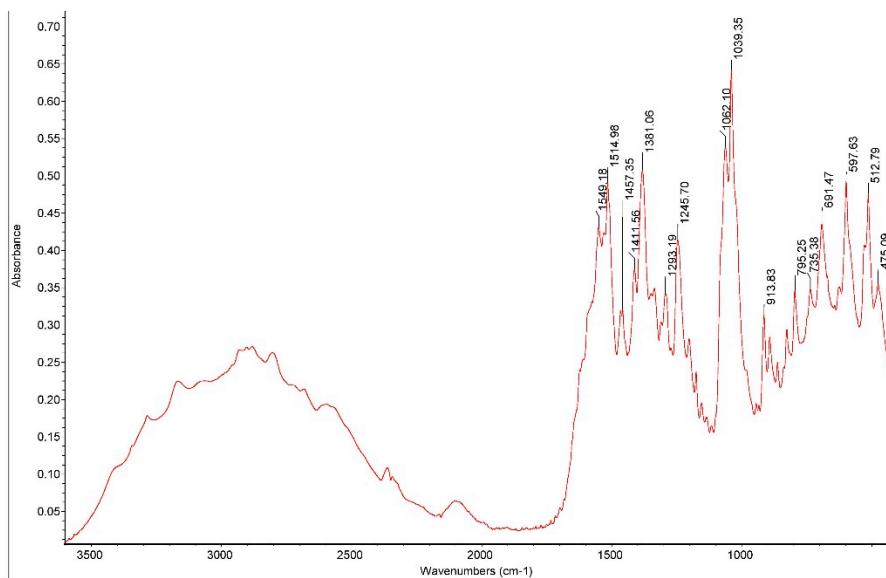


Figure S80. IR spectrum of 4-HPA-Tris.

(Trioxomethyl)methylammonium (4-hydroxyphenyl)propanoate (4-HPP-Tris)

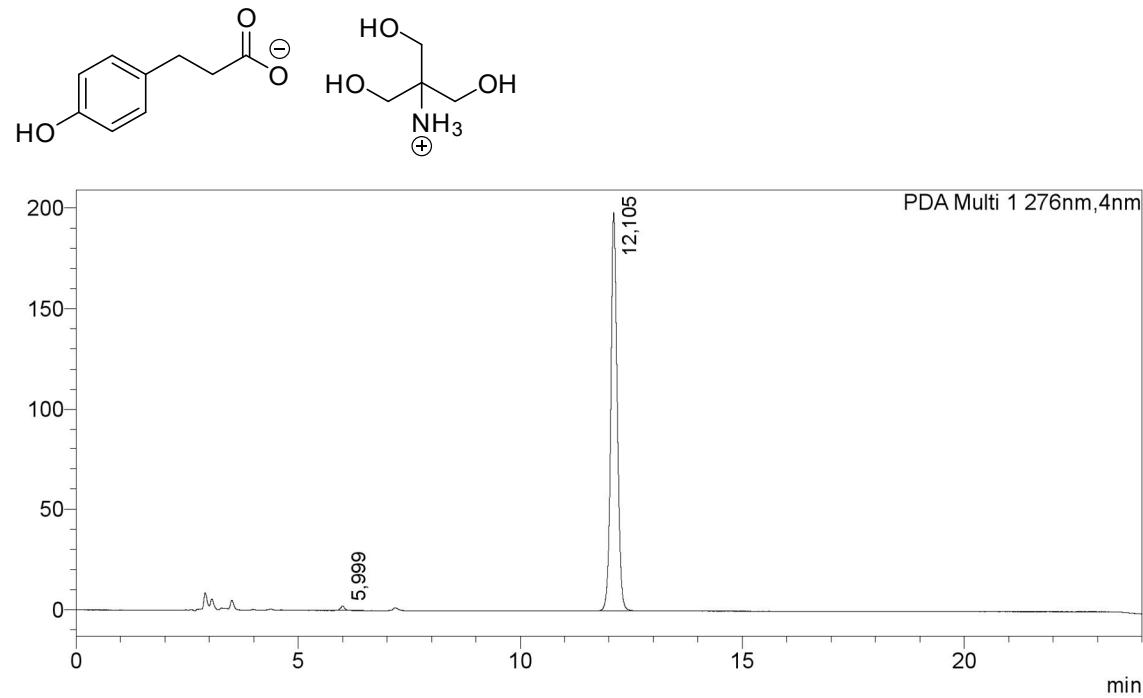


Figure S81. HPLC chromatogram of 4-HPA-Tris.

(RT= 12.105 min, 99%)

Table S17. ^1H and ^{13}C NMR data for **4-HPP-Tris**.

(600.23 MHz for ^1H , 150.93 MHz for ^{13}C , DMSO- d_6)

Atom	δ_{C}	m.	δ_{H}	n _H	m.	J [Hz]	$\delta_{\text{C}}^{\text{HPP}}$	$\delta_{\text{C}} - \delta_{\text{C}}^{\text{HPP}}$
1	175.46	S	-	0	-	-	173.76	1.7
2	37.39	T	2.289	2	m	-	35.64	1.75
3	30.50	T	2.657	2	m	-	29.50	1
1'	131.80	S	-	0	-	-	130.84	0.96
2'6'	128.84	D	6.966	2	m	$\Sigma J = 8.6$	128.97	-0.13
3'5'	114.91	D	6.640	2	m	$\Sigma J = 8.6$	114.97	-0.06
4'	155.34	S	-	1	-	-	155.43	-0.09

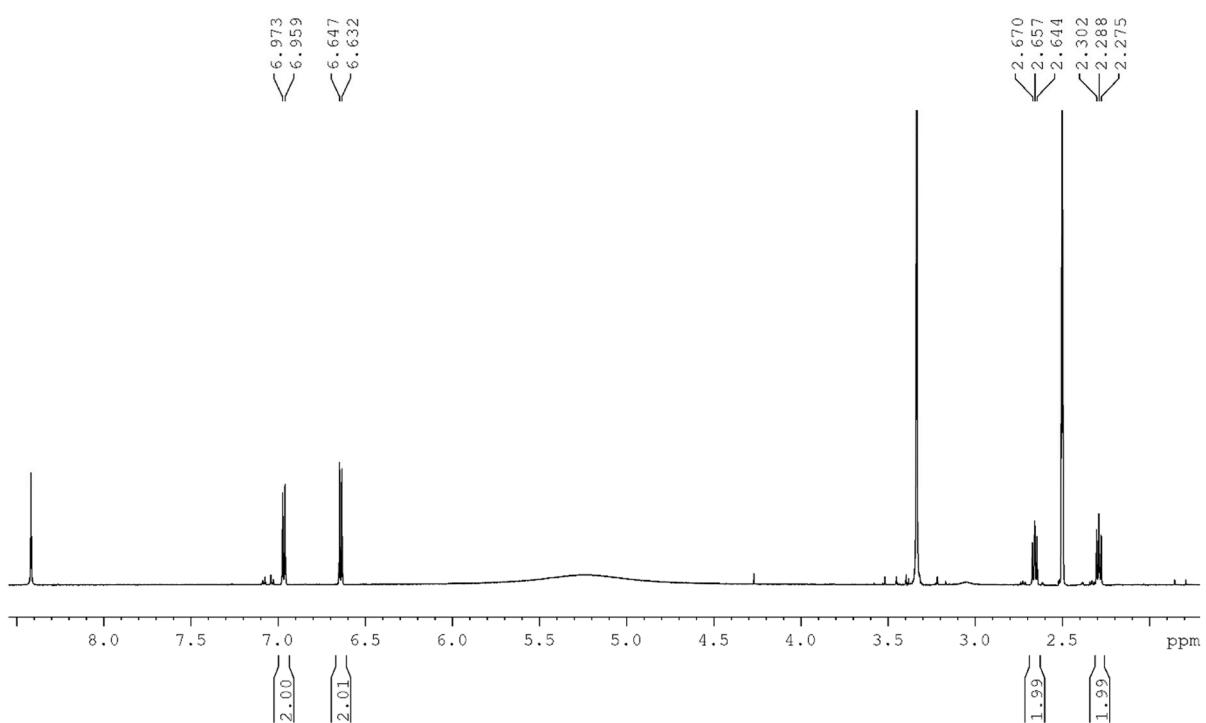


Figure S82. ^1H NMR spectrum of **4-HPP-Tris**

(600.23 MHz, DMSO- d_6)

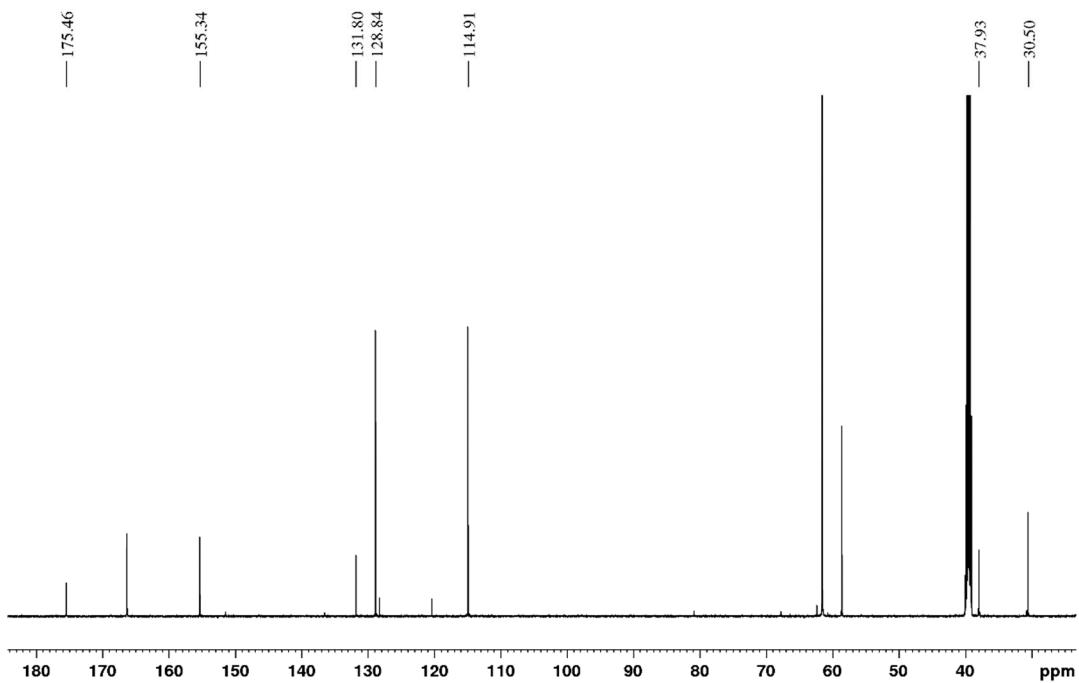


Figure S83. ¹³C NMR spectrum of 4-HPP·Tris.

(150.93 MHz, DMSO-*d*₆)

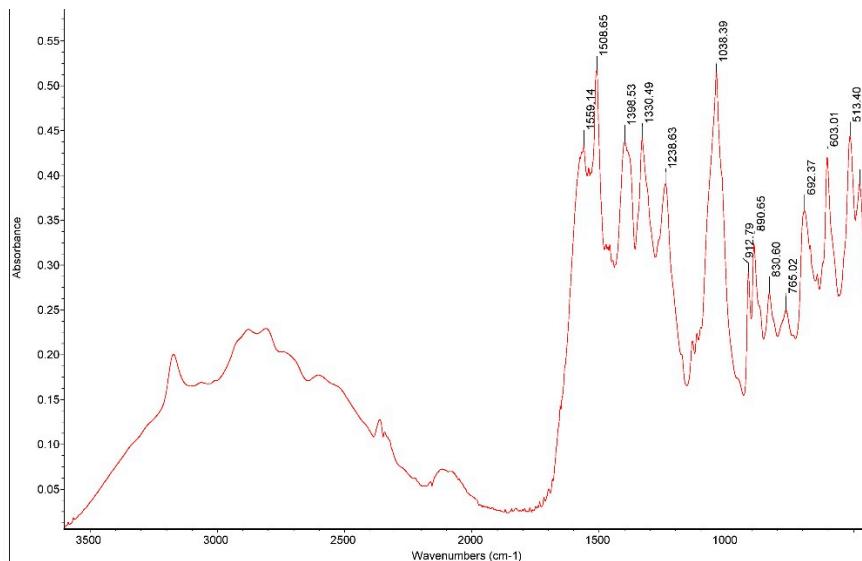


Figure S84. IR spectrum of 4-HPP·Tris.