Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary information

Synthesis of phosphonosulfonic acid building block as linkers for coordination polymers

O. Beyer,[a] T. Homburg,[b] M. Albat,[b] N. Stock,[b] and U. Lüning*[a]

[a]Otto-Diels-Institut für Organische Chemie, Christian-Albrechts-Universität zu Kiel, Otto-Hahn-Platz 4, 24118 Kiel, Germany

[b]Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, Max-Eyth-Str. 2, 24118 Kiel, Germany

*Correspondence to:

luening@oc.uni-kiel.de

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1. Linker Synthesis

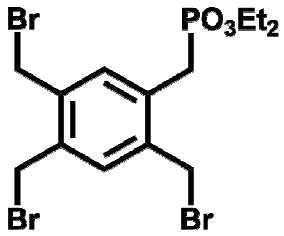
General remarks: All commercially available reagents were used without further purification: benzene-1,3-disulfonic acid disodium salt (94 %, Alfa Aesar), *N*-bromosuccinimide (99 %, Alfa Aesar), 1,3-dibromobenzene (97 %, chemPUR), 1,4-dibromobenzene (98 %, Alfa Aesar), 3,5-dibromo-1-(trimethylsilyl)benzene (97 %, TCI), 1,2-dichloroethane (anhydrous 99.8 %, VWR), calcium hydroxide (95 %, Alfa Aesar), Dowex 50WX8 hydrogen form (200-400 mesh, Sigma Aldrich), fuming sulfuric acid 20 - 30 % SO_3 (abcr), fuming sulfuric acid 65 % SO_3 (VWR), palladium(II) chloride (99.9 %, Alfa Aesar), sodium iodide (99+%, Alfa Aesar), sodium sulfite (98 %, Sigma Aldrich), tetra-*n*-butylammonium bromide (99 %, Sigma Aldrich), tetra-*n*-butylammonium hydroxide 40 % in water (Sigma Aldrich), tetra-*n*-butylammonium iodide (98 %, Alfa Aesar), triethyl phosphite (98 %, Alfa Aesar), trimethylsilyl chlorosulfonate (99 %, Sigma Aldrich). 1,2,4,5-Tetrakis(bromomethyl)benzene (**1**) was prepared according to a literature procedure.[1] Solvents were distilled before use. Column chromatography was carried out with silica gel (Macherey-Nagel, particle size 0.04–0.063 mm). Melting points were measured with a Gallenkamp MPD350.BM2.5 instrument. NMR spectra were recorded with a Bruker DRX 500 instrument and assignments were supported by COSY, HSQC and HMBC. ^{1}H-NMR signals of acidic protons were listed with the expected number of protons, even if the integral was much larger due to moisture. Even when spectra were obtained as broad-band decoupled ^{13}C-NMR, the type of ^{13}C signal is always listed as singlet, doublet, etc. Additionally, the multiplicities for ^{31}P-coupled ^{1}H-decoupled ^{13}C signals are given in square brackets and the coupling constants were assigned if possible. All chemical shifts are referenced to the residual proton or carbon of the solvent. EI mass spectra and HRMS were recorded with a JEOL AccuTOF GCV 4G. ESI mass spectra were recorded with an Applied Biosystems Mariner 5280. IR spectra were recorded with a Perkin-Elmer Spectrum 100 spectrometer equipped with a Golden Gate Diamond ATR unit A-531-G. All IR spectra containing sulfonic acids were dominated by three typical broad bands besides the fingerpint section. Elemental analyses (EA) were carried out with a Euro EA 3000 Elemental Analyzer from Euro Vector. For Microwave synthesis, a CEM Discover SP was used.

Procedure for the syntheses of phosphonic acid diethyl esters 2, 4, 5 and 6

To a solution of 1,2,4,5-tetrakis(bromomethyl)benzene (**1**, 15.0 g. 33.33 mmol) in toluene (400 mL) was added triethyl phosphite (11.4 mL, 66.66 mmol) and the mixture was heated to reflux for 12 h. The solvent was evaporated in vacuo. To obtain the desired products, the residue was purified by column chromatography using a gradient of three different solvents. Starting with cyclohexane/ethyl acetate (2:1) as eluant, the unreacted starting material **1** was separated. By slowly switching to cyclohexane/ethyl acetate (1:2), the mono-substituted product **5** was eluated. The gradient was changed to pure ethyl acetate and ethanol was

gradually added to eluate the di-substituted products **2**, **3** and **4** with ethyl acetate/ethanol (95:5). Tri-substituted product **6** was obtained with ethyl acetate/ethanol (65:35) as eluant. Solvents were removed in vacuo and the residue of the di-substituted products **2**, **3** and **4** were dissolved with *tert*-butyl methyl ether (10 mL) and kept at 5°C for 7 d. Colourless crystals, a mixture of **2** and **4**, were obtained by filtration. The mixture was purified by column chromatography (ethyl acetate/ethanol 98:2). **2, 4** and **5** were obtained as colourless solids and **6** as a colourless oil.

[2,4,5-Tris(bromomethyl)phenyl]methylphosphonic acid diethyl ester (5)



Yield: 4.61 g (9.09 mmol, 27 %)

M. p.: 76 °C

^{1}H-NMR (500 MHz, 300 K, $CDCl_3$): δ = 7.35 (s, 1H, Ar-3-*H*), 7.30 (d, $^{4}J_{H\text{-}P}$ = 2.8 Hz, 1H, Ar-6-*H*), 4.65 (s, 2H, Ar-2-C*H*$_2$), 4.61 (s, 2H, Ar-5-C*H*$_2$), 4.60 (s, 2H, Ar-4-C*H*$_2$), 4.04 (m_c, 4H, P-O-C*H*$_2$), 3.31 (d, $^{2}J_{H\text{-}P}$ = 22.0 Hz, 2H, Ar-1-C*H*$_2$), 1.27 (t, ^{3}J = 7.1 Hz, 6H, C*H*$_3$) ppm.

^{13}C-NMR (125 MHz, 300 K, $CDCl_3$): δ = 138.0 (s[d_P], $^{3}J_{C\text{-}P}$ = 6.3 Hz, Ar-2-*C*), 137.3 (s[d_P], $^{4}J_{C\text{-}P}$ = 3.8 Hz, Ar-5-*C*), 136.0 (s[d_P], $^{5}J_{C\text{-}P}$ = 4.0 Hz, Ar-4-*C*), 134.5 (d[d_P], $^{3}J_{C\text{-}P}$ = 5.6 Hz, Ar-6-*C*), 133.5 (d[d_P], $^{4}J_{C\text{-}P}$ = 3.2 Hz, Ar-3-*C*), 132.7 (s[d_P], $^{2}J_{C\text{-}P}$ = 9.5 Hz, Ar-1-*C*), 62.6 (t[d_P], $^{2}J_{C\text{-}P}$ = 6.8 Hz, P-O-*C*H$_2$), 31.1 (t, Ar-2-*C*H$_2$), 30.8 (t[d_P], $^{1}J_{C\text{-}P}$ = 137.6 Hz, Ar-1-*C*H$_2$), 29.2 (t, Ar-4,5-*C*H$_2$), 16.6 (q[d_P], $^{3}J_{C\text{-}P}$ = 6.0 Hz, *C*H$_3$) ppm.

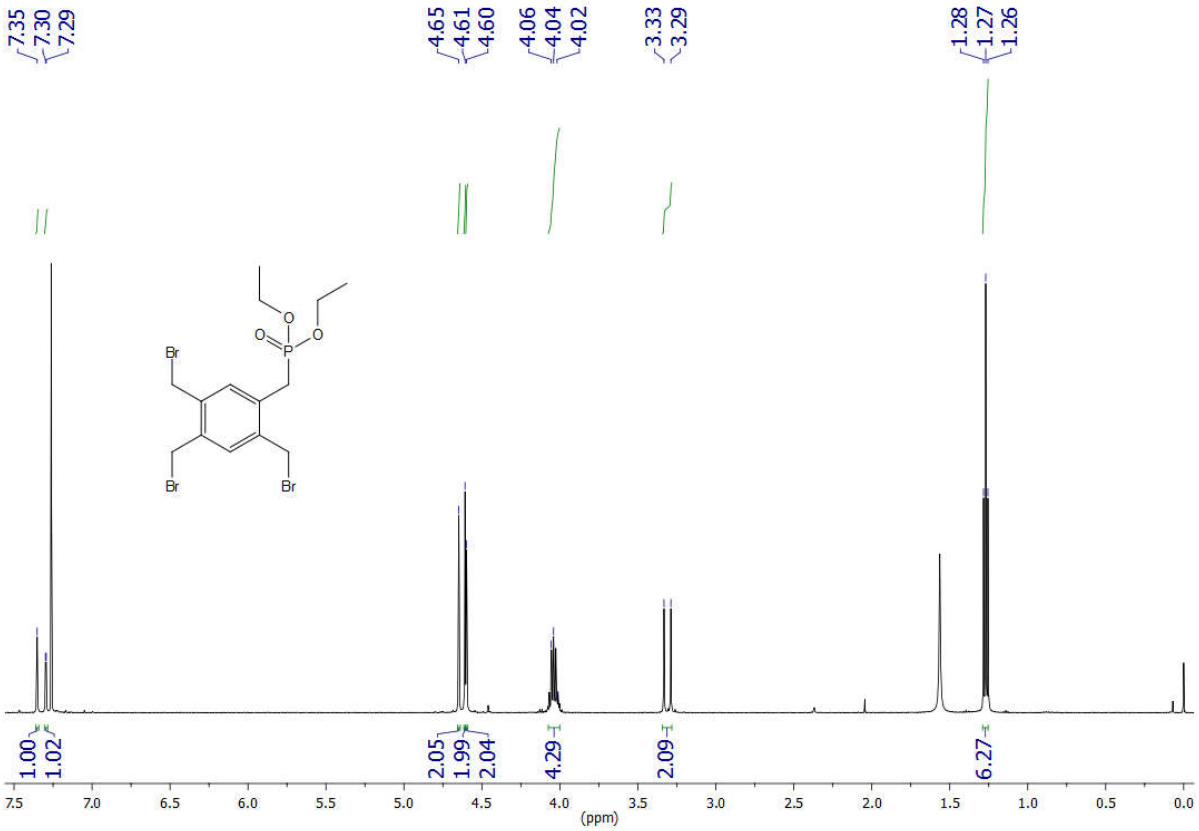
^{31}P-NMR (202 MHz, 300 K, $CDCl_3$): 24.4 (s, 1P, *P*O$_3$Et$_2$) ppm.

MS (EI): *m/z* = 510, 508, 506, 504 (1.2, 3.6, 3.7, 1.3) $[M]^{+\cdot}$, 429, 427, 425 (27.5, 56.1, 28.6) [M -Br]$^{+\cdot}$, 347, 345 (94.1, 77.9) [M -H -2Br]$^{+\cdot}$, 267 (80.8) [M -3Br]$^{+\cdot}$, 211 (100) [M -3Br -C_4H_8]$^{+\cdot}$.

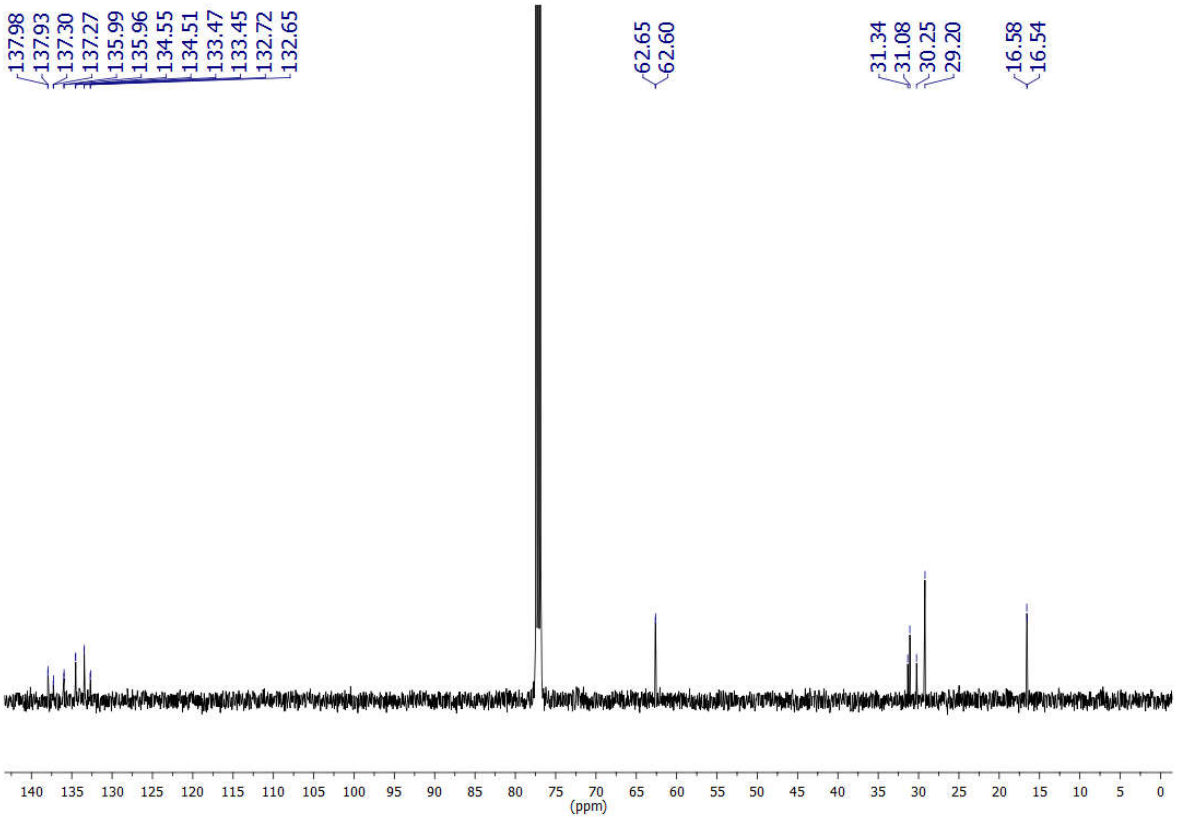
HRMS (EI): *m/z* = $C_{14}H_{20}{}^{79}Br_2{}^{81}BrO_3P$ calcd. 505.8680; found 505.8682 (Δ <0.4 ppm); $C_{14}H_{20}{}^{79}Br{}^{81}Br_2O_3P$ calcd. 507.8659; found 507.8664 (Δ 0.9 ppm).

IR (ATR): $\tilde{\nu}$ = 3044 (aryl-H val.), 2978, 2903 (CH_2-val.), 1508 (arom. C=C), 1439 (CH_2-def.) cm^{-1}.

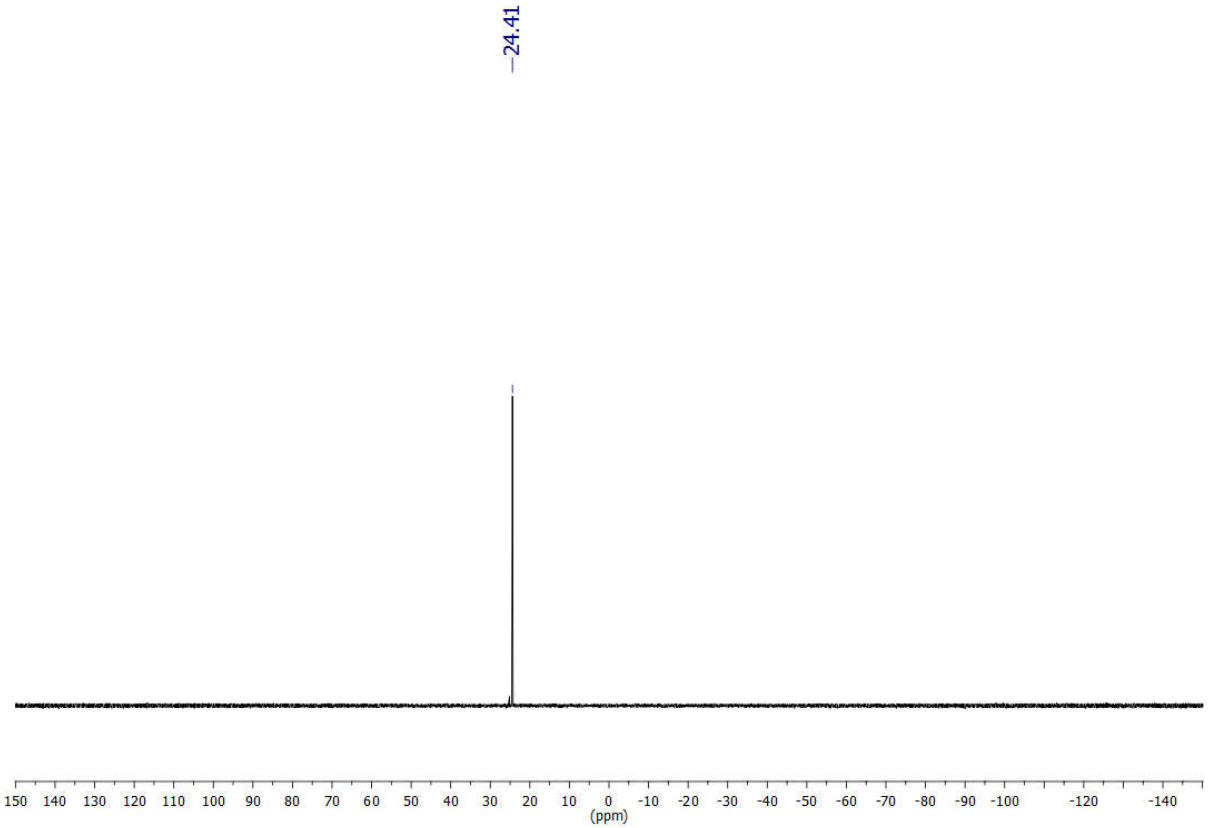
EA ($C_{14}H_{20}Br_3O_3P$) (506.99): calcd. C 33.17 H 3.98;
($C_{14}H_{20}Br_3O_3P \cdot 0.166\ C_4H_8O_2$) (521.68): calcd. C 33.77 H 4.12;
found C 33.78 H 4.05.



^{1}H-NMR (500 MHz, 300 K, $CDCl_3$) of **5**

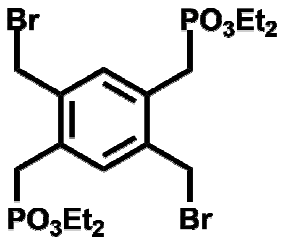


^{13}C-NMR (125 MHz, 300 K, $CDCl_3$) of **5**



^{31}P-NMR (202 MHz, 300 K, $CDCl_3$) of **5**

[2,5-Bis(bromomethyl)-benzene-1,4-diyl]bis(methylphosphonic acid diethyl ester) (2)



Yield: 602 mg (1.07 mmol, 3 %)

M. p.: 115 °C

^{1}H-NMR (500 MHz, 300 K, CD_2Cl_2): δ = 7.28 (d, $^{4}J_{H\text{-}P}$ = 1.8 Hz, 2H, Ar-3,6-*H*), 4.68 (s, 4H, Ar-2,5-C*H*$_2$), 4.00 (m_c, 8H, P-O-C*H*$_2$), 3.31 (d, $^{2}J_{H\text{-}P}$ = 20.4 Hz, 4H, Ar-1,4-C*H*$_2$), 1.24 (t, ^{3}J = 7.1 Hz, 12H, C*H*$_3$) ppm.

^{13}C-NMR (125 MHz, 300 K, CD_2Cl_2): δ = 138.0 (s, Ar-2,5-*C*), 134.5 (d, Ar-3,6-*C*), 131.3 (s, Ar-1,4-*C*), 62.9 (t[m_P], P-O-*C*H$_2$), 32.1 (t, Ar-2,5-*C*H$_2$), 31.0 (t[d_P], $^{1}J_{C\text{-}P}$ = 137.9 Hz, Ar-1,4-*C*H$_2$), 16.8 (q[m_P], *C*H$_3$) ppm.

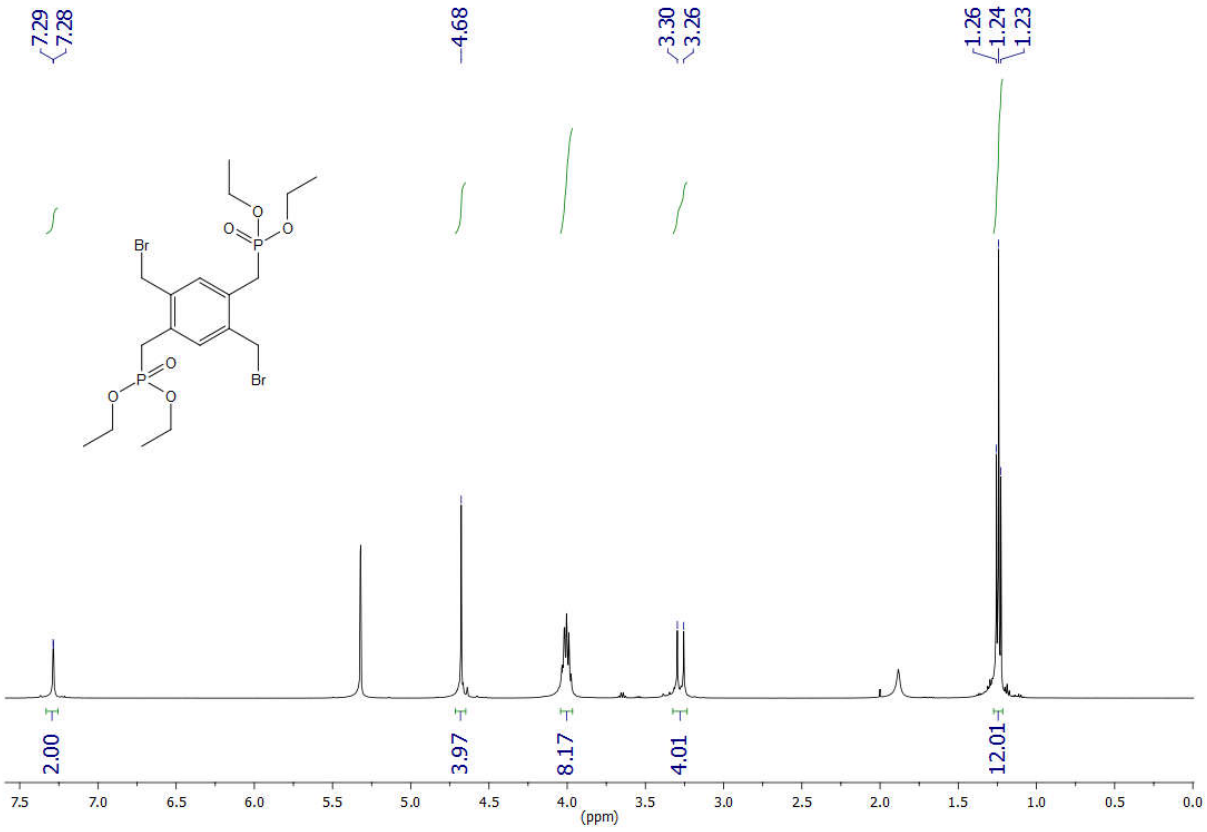
^{31}P-NMR (202 MHz, 300 K, CD_2Cl_2): 24.4 (s, 2P, *P*O$_3$Et$_2$) ppm.

MS (EI): *m/z* = 566, 564, 562 (0.9, 1.9, 1.0) $[M]^{+\cdot}$, 485, 483 (21.0, 21.4) $[M\text{ -Br}]^{+\cdot}$, 403 (86.7) $[M\text{ -H -2Br}]^{+\cdot}$, 375 (100) $[M\text{ -2Br -C}_2H_5]^{+\cdot}$.

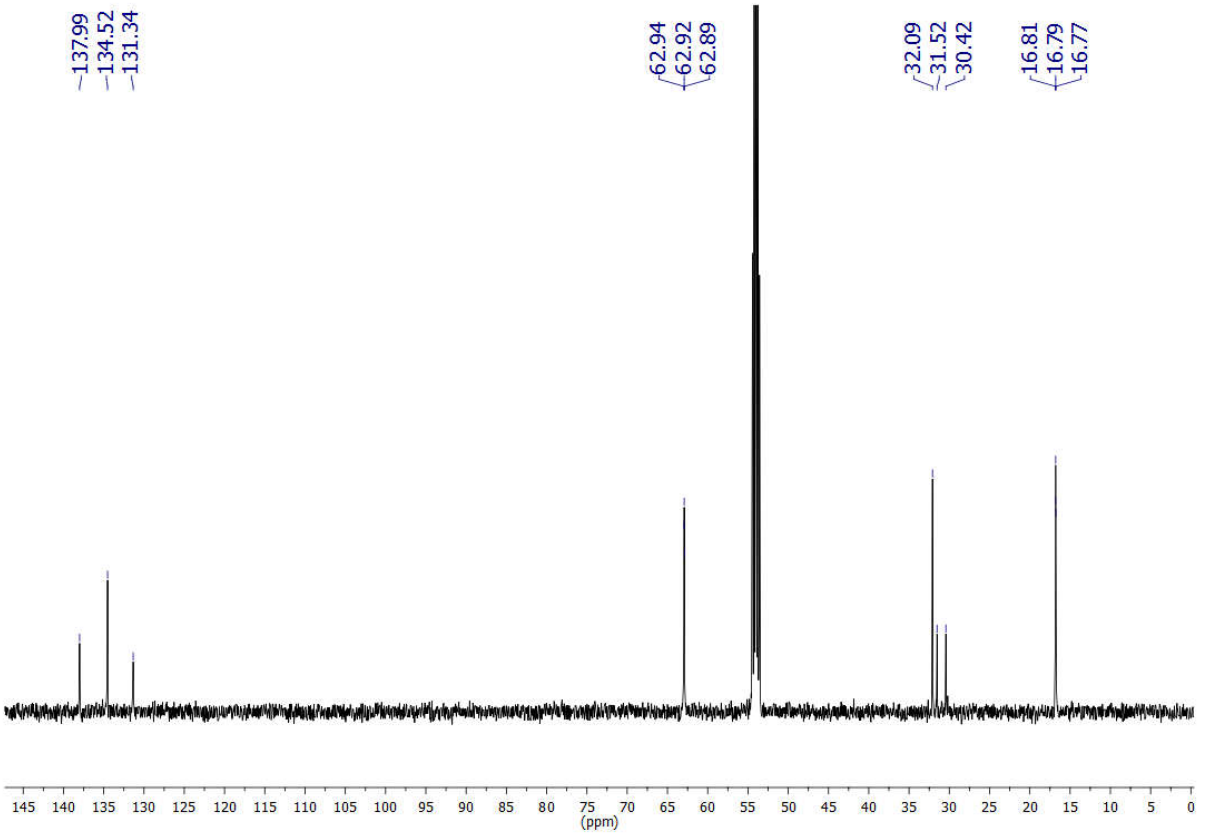
HRMS (EI): *m/z* = $C_{18}H_{30}{}^{79}Br^{81}BrO_6P_2$ calcd. 563.9864; found 553.9838 (Δ 4.6 ppm).

IR (ATR): $\tilde{\nu}$ = 2980, 2905 (CH_2-val.), 1508 (arom. C=C), 1440 (CH_2-def.) cm^{-1}.

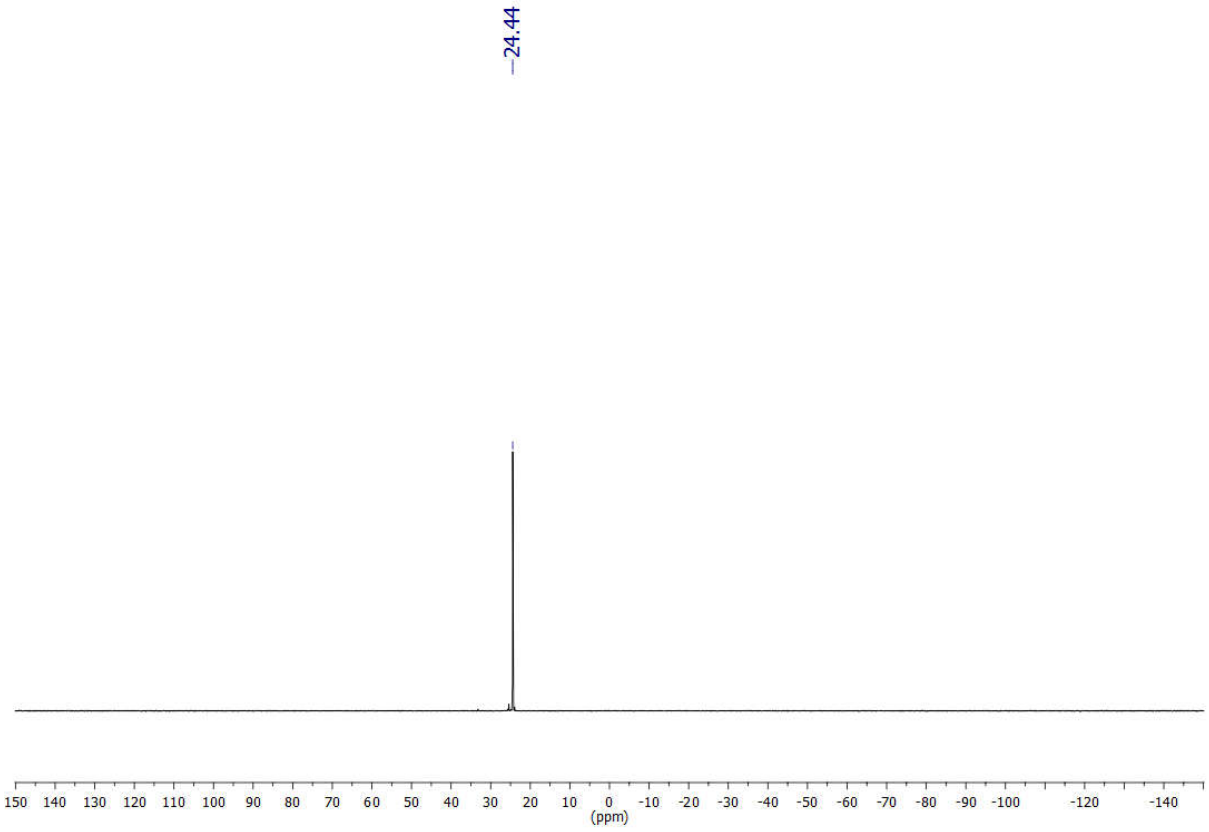
EA ($C_{18}H_{30}Br_2O_6P_2$) (564.18): calcd. C 38.32 H 5.36;
found C 38.71 H 5.52.



^{1}H-NMR (500 MHz, 300 K, CD_2Cl_2) of **2**

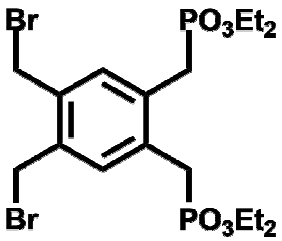


^{13}C-NMR (125 MHz, 300 K, CD_2Cl_2) of **2**



^{31}P-NMR (202 MHz, 300 K, CD_2Cl_2) of **2**

[4,5-Bis(bromomethyl)-benzene-1,2-diyl]bis(methylphosphonic acid diethyl ester) (4)



Yield: 584 mg (1.04 mmol, 3 %)

M. p.: 107 °C

^{1}H-NMR (500 MHz, 300 K, CD_2Cl_2): δ = 7.27 (d, $^4J_{H\text{-}P}$ = 1.9 Hz, 2H, Ar-3,6-*H*), 4.64 (s, 4H, Ar-4,5-C*H*$_2$), 4.00 (m$_c$, 8H, P-O-C*H*$_2$), 3.37 (d, $^2J_{H\text{-}P}$ = 20.4 Hz, 4H, Ar-1,2-C*H*$_2$), 1.24 (t, ^3J = 7.1 Hz, 12H, C*H*$_3$) ppm.

^{13}C-NMR (125 MHz, 300 K, CD_2Cl_2): δ = 135.9 (s, Ar-4,5-*C*), 134.7 (d, Ar-3,6-*C*), 133.6 (s[m$_P$], Ar-1,2-*C*), 62.8 (t[m$_P$], P-O-*C*H$_2$), 32.5 (t[d$_P$d$_P$], $^1J_{C\text{-}P}$ = 137.1 Hz, $^4J_{C\text{-}P}$ = 1.5 Hz, Ar-1,2-*C*H$_2$), 30.2 (t, Ar-4,5-*C*H$_2$), 16.8 (q[m$_P$], *C*H$_3$) ppm.

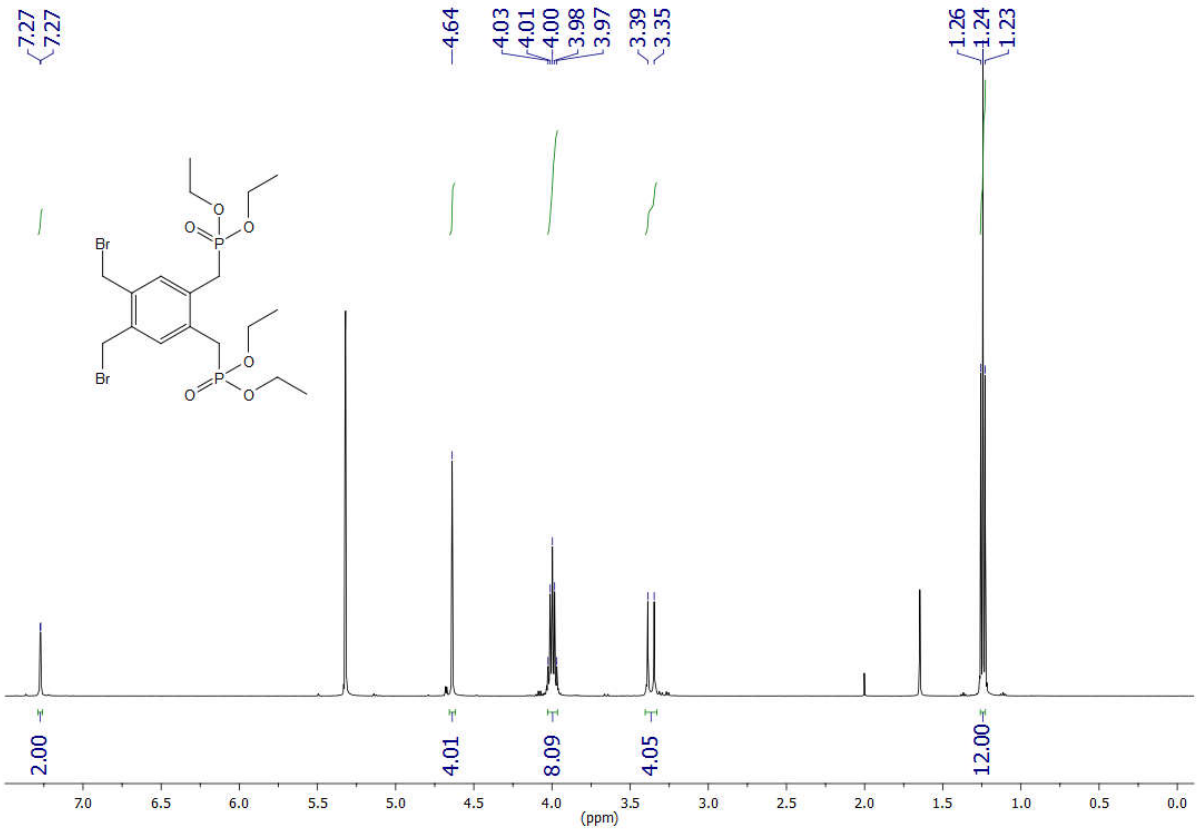
^{31}P-NMR (202 MHz, 300 K, CD_2Cl_2): 25.4 (s, 2P, PO_3Et_2) ppm.

MS (EI): *m/z* = 566, 564, 562 (3.4, 7.0, 3.6) $[M]^{+\cdot}$, 485, 483 (100, 99.3) $[M\text{ -Br}]^{+\cdot}$.

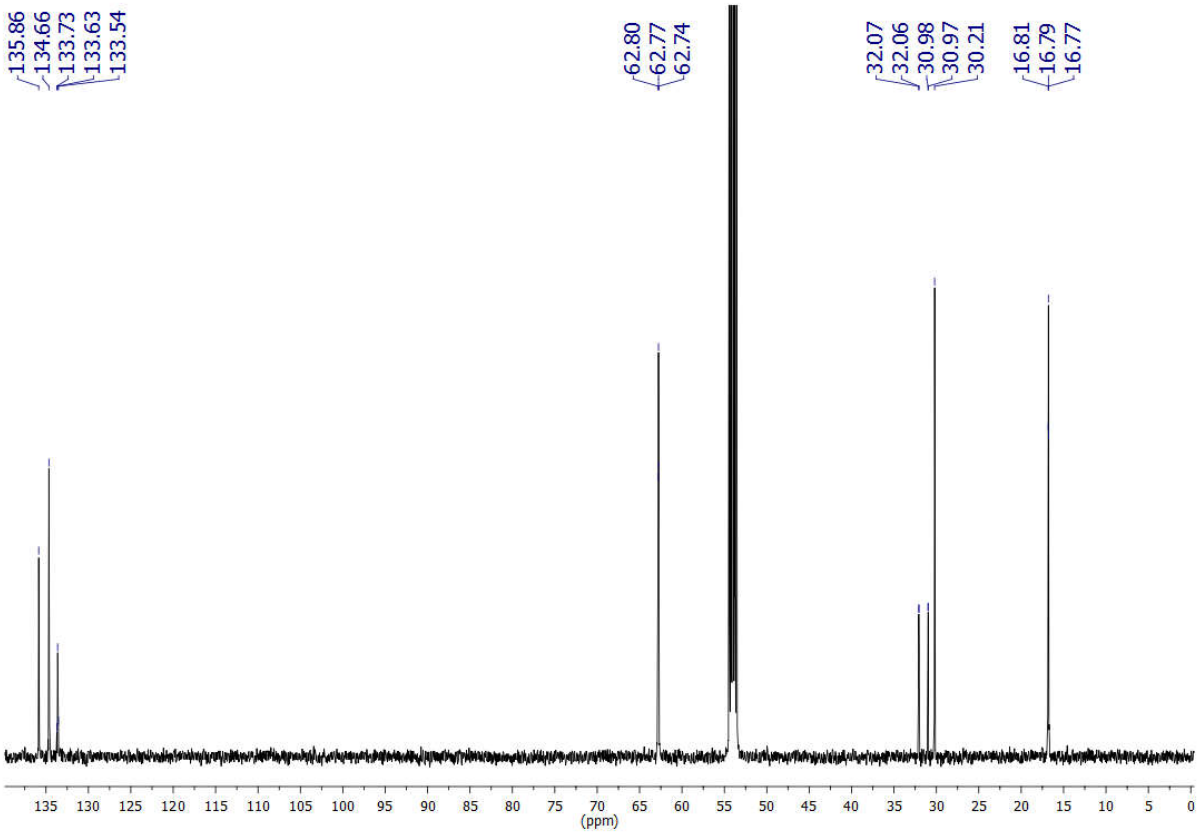
HRMS (EI): *m/z* = $C_{18}H_{30}{}^{79}Br_2O_6P_2$ calcd. 561.9884; found 561.9882 (Δ 0.5 ppm);
$C_{18}H_{30}{}^{79}Br^{81}BrO_6P_2$ calcd. 563.9864; found 563.9864 (Δ <0.1 ppm);
$C_{18}H_{30}{}^{81}Br_2O_6P_2$ calcd. 565.9843; found 565.9849 (Δ 1.0 ppm).

IR (ATR): $\tilde{\nu}$ = 2979, 2926 (CH_2-val.), 1508 (arom. C=C), 1474, 1441 (CH_2-def.) cm^{-1}.

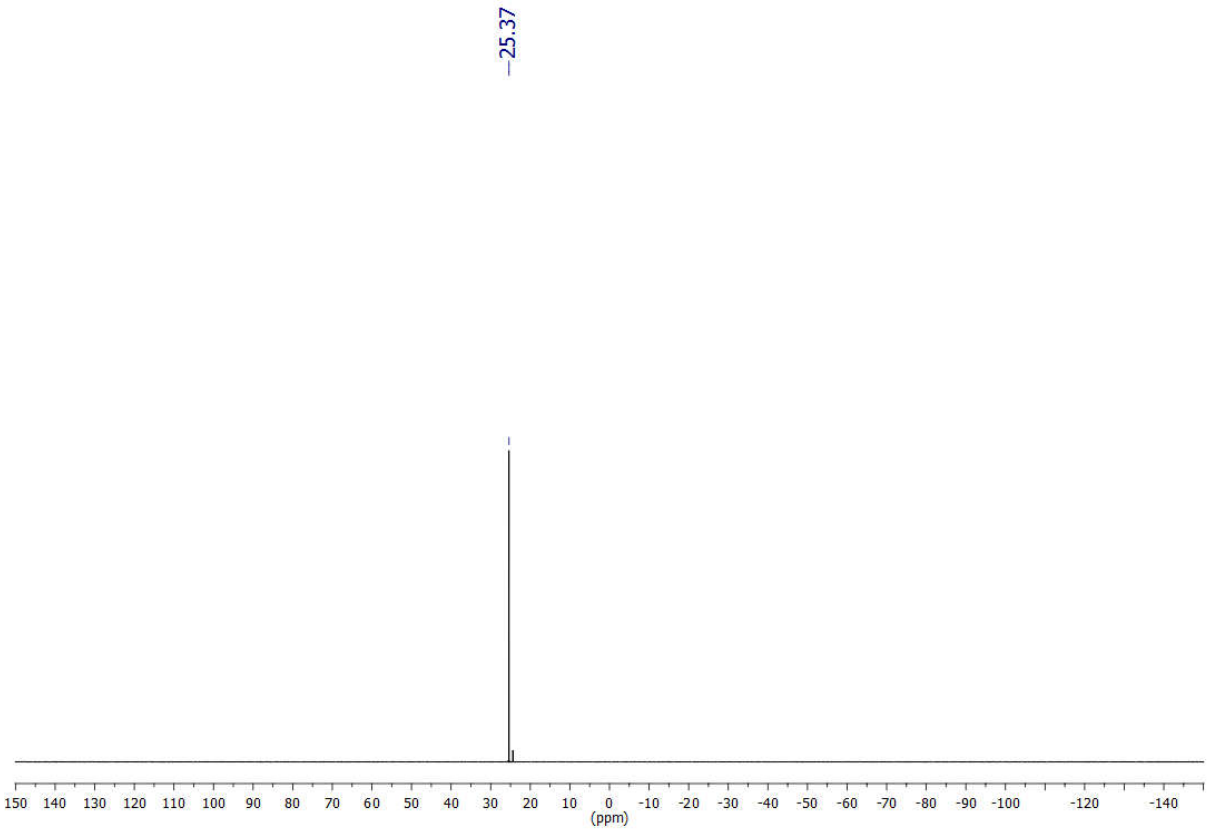
EA ($C_{18}H_{30}Br_2O_6P_2$) (564.18): calcd. C 38.32 H 5.36;
found C 38.51 H 5.58.



^{1}H-NMR (500 MHz, 300 K, CD_2Cl_2) of **4**

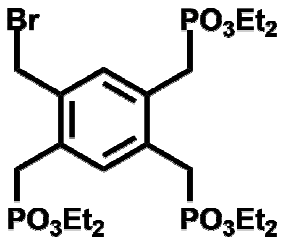


^{13}C-NMR (125 MHz, 300 K, CD_2Cl_2) of **4**



^{31}P-NMR (202 MHz, 300 K, CD_2Cl_2) of **4**

[5-(Bromomethyl)-benzene-1,2,4-triyl]tris(methylphosphonic acid diethyl ester) (6)



Yield: 3.52 g (5.66 mmol, 17 %)

M. p.: Oil

^{1}H-NMR (500 MHz, 300 K, CD_2Cl_2): δ = 7.25 (m_c, 1H, Ar-6-*H*), 7.18 (m_c, 1H, Ar-3-*H*), 4.67 (s, 2H, Ar-5-C*H*$_2$), 4.00 (m_c, 12H, P-O-C*H*$_2$), 3.36 (d, $^{2}J_{H\text{-}P}$ = 20.7 Hz, 2H, Ar-2-C*H*$_2$), 3.34 (d, $^{2}J_{H\text{-}P}$ = 20.2 Hz, 2H, Ar-1-C*H*$_2$), 3.27 (d, $^{2}J_{H\text{-}P}$ = 21.7 Hz, 2H, Ar-4-C*H*$_2$), 1.26-1.21 (m, 18H, C*H*$_3$) ppm.

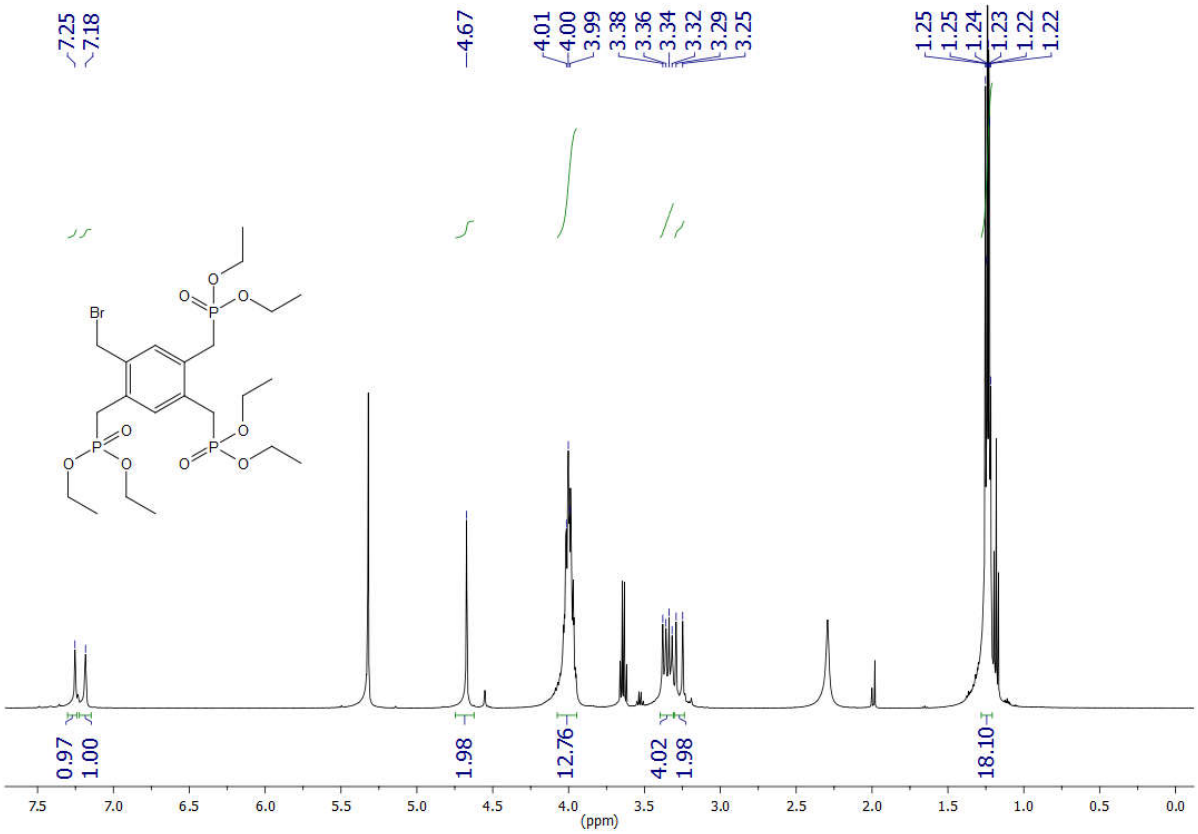
^{13}C-NMR (125 MHz, 300 K, CD_2Cl_2): δ = 136.1 (s[m_P], Ar-5-*C*), 135.2 (d[m_P], Ar-3-*C*), 134.3 (d[m_P], Ar-6-*C*), 133.0 (s[m_P], Ar-2-*C*), 131.5 (s[m_P], Ar-1-*C*), 130.7 (s[m_P], Ar-4-*C*), 63.0-62.7 (t[m_P], P-O-*C*H$_2$), 32.5 (t, Ar-5-*C*H$_2$), 31.5 (t[d_P], $^{1}J_{C\text{-}P}$ = 135.9 Hz, Ar-1-*C*H$_2$), 31.3 (t[d_P], $^{1}J_{C\text{-}P}$ = 136.7 Hz, Ar-2-*C*H$_2$), 30.9 (t[d_P], $^{1}J_{C\text{-}P}$ = 137.3 Hz, Ar-4-*C*H$_2$), 16.8 (q[m_P], *C*H$_3$) ppm.

^{31}P-NMR (202 MHz, 300 K, CD_2Cl_2): 25.9 (dd, ^{5}J = 9.0 Hz, ^{7}J = 2.7 Hz, 1P, Ar-1-CH$_2$-*P*), 25.9 (dd, ^{5}J = 9.0 Hz, ^{6}J = 8.5 Hz, 1P, Ar-2-CH$_2$-*P*), 24.9 (dd, ^{6}J = 8.5 Hz, ^{7}J = 2.7 Hz, 1P, Ar-4-CH$_2$-*P*) ppm.

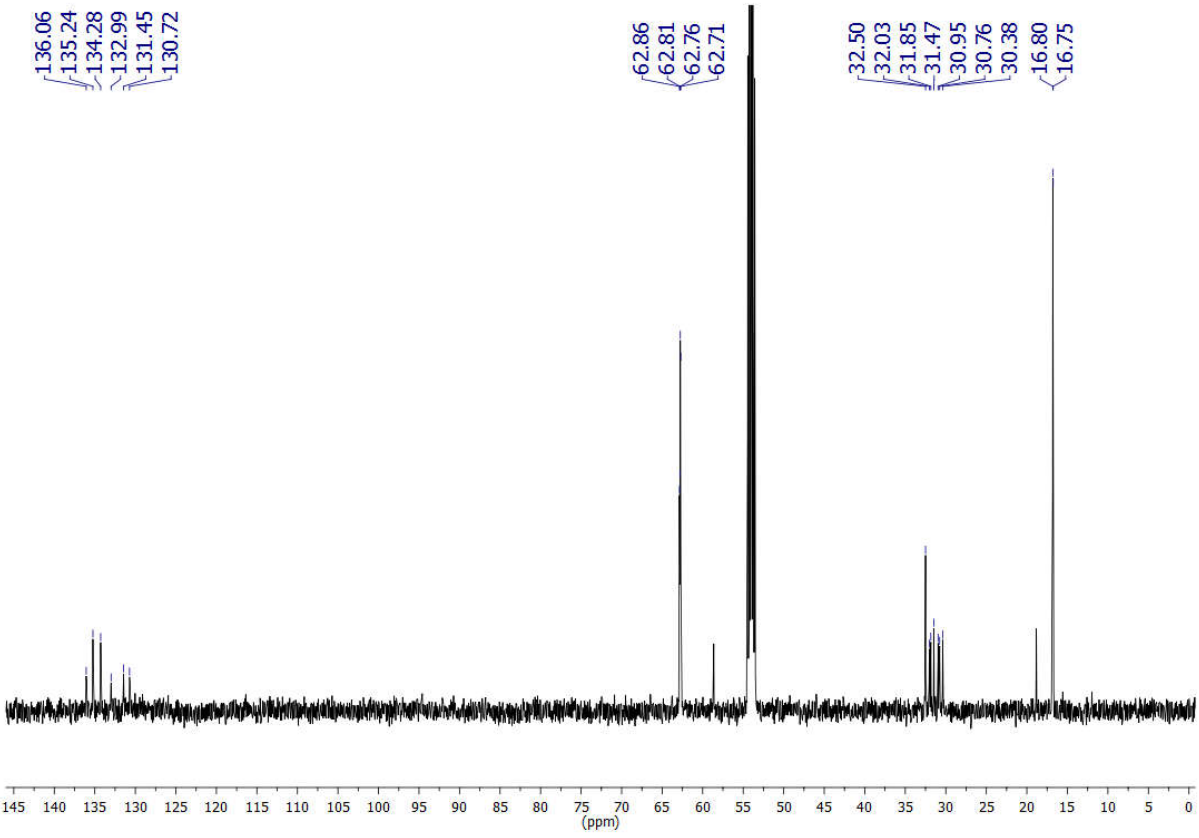
MS (EI): *m/z* = 622, 620 (0.1, 0.1) $[M]^{+\cdot}$, 586 (5.5) $[M - Br + C_2H_5O]^{+\cdot}$, 557 (100) $[(M - Br + C_2H_5O) - C_2H_5]^{+\cdot}$, 529 (79.3) $[(M - Br + C_2H_5O) - C_4H_9]^{+\cdot}$.

IR (ATR): $\tilde{\nu}$ = 2980, 2930 (CH$_2$-val.), 1507 (arom. C=C), 1478, 1443 (CH$_2$-def.) cm^{-1}.

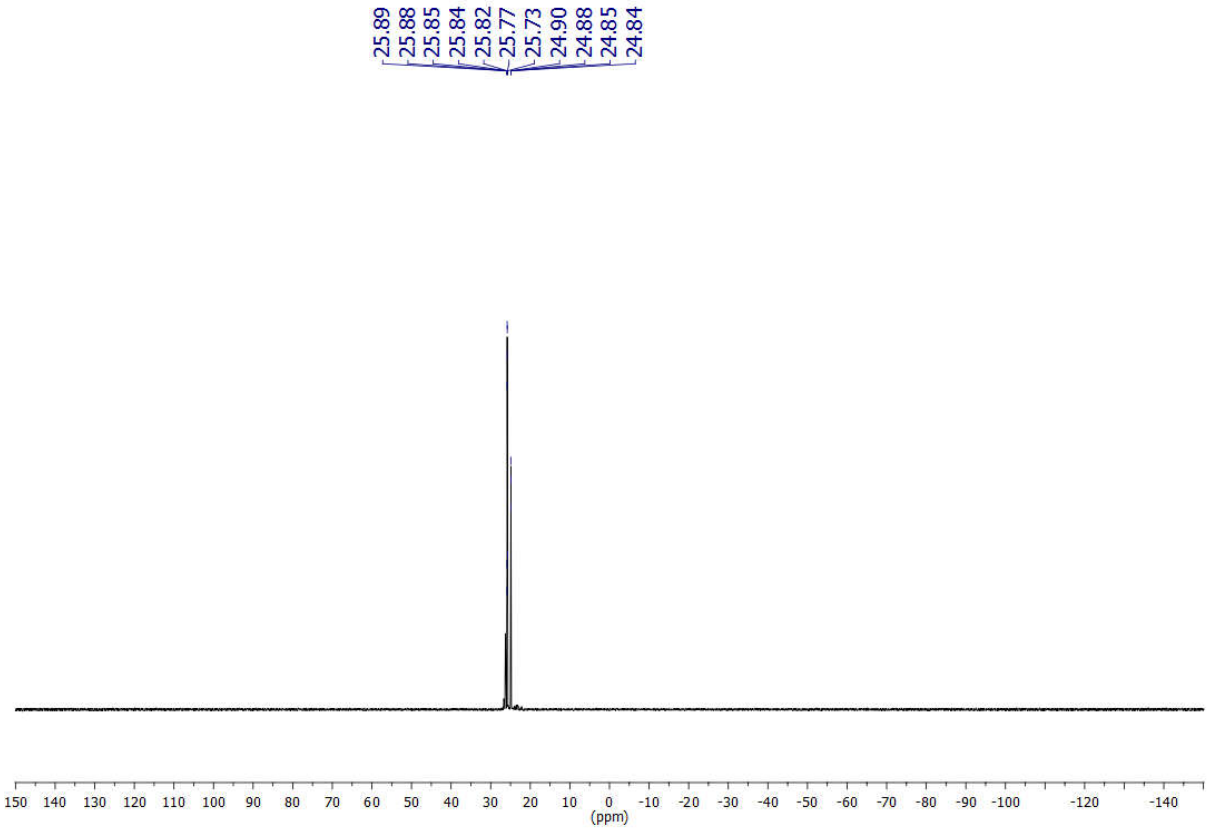
EA ($C_{22}H_{40}BrO_9P_3$) (621.37): calcd. C 42.52 H 6.49;
($C_{22}H_{40}BrO_9P_3 \cdot 2\ C_2H_6O$) (713.51): calcd. C 43.77 H 7.35;
found C 44.00 H 7.45.



^{1}H-NMR (500 MHz, 300 K, CD_2Cl_2) of **6**

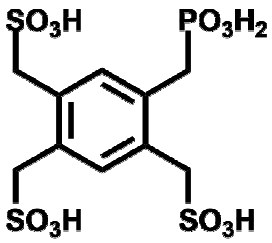


^{13}C-NMR (125 MHz, 300 K, CD_2Cl_2) of **6**



^{31}P-NMR (202 MHz, 300 K, CD_2Cl_2) of **6**

[5-(Phosphonomethyl)benzene-1,2,4-triyl]tris(methylsulfonic acid) (8)



To a saturated aqueous solution of sodium sulfite (100 mL) was added water (25 mL) and [2,4,5-tris(bromomethyl)phenyl]methylphosphonic acid diethyl ester (**5**, 6.30 g, 12.43 mmol) dissolved in acetone (20 mL). The reaction mixture was stirred at 100 °C for 12 h. Acetone was removed in vacuo and conc. hydrochloric acid (100 mL) was added to the aqueous solution and the mixture was stirred at 120 °C for 2 d. The solvent was removed in vacuo and the residue was treated with dimethyl sulfoxide (200 mL) to dissolve the product. Undissolved sodium chloride was separated by filtration. The solution was poured into dichloromethane (2000 mL) and the precipitate was collected by filtration. To exchange the sodium ions, the residue was dissolved in water and rinsed over a column filled with ion-exchange resin (Dowex 50WX8 hydrogen form). The eluate was concentrated and dried for 24 h at 60 °C in a vacuum oven, to yield a colourless solid.

Yield: 3.59 g (7.91 mmol, 64 %)

M. p.: 250 °C (decomposition)

^{1}H-NMR (500 MHz, 300 K, DMSO-d6): δ = 8.80 (br. s, 5H, SO_3H, PO_3H_2), 7.09 (s, 1H, Ar-3-*H*), 7.08 (d, $^{4}J_{H\text{-}P}$ = 2.6 Hz, 1H, Ar-6-*H*), 4.09 (s, 2H, Ar-1-CH_2), 4.05 (s, 2H, Ar-2-CH_2), 4.00 (s, 2H, Ar-4-CH_2), 3.25 (d, $^{2}J_{H\text{-}P}$ = 21.0 Hz, 2H, Ar-5-CH_2) ppm.

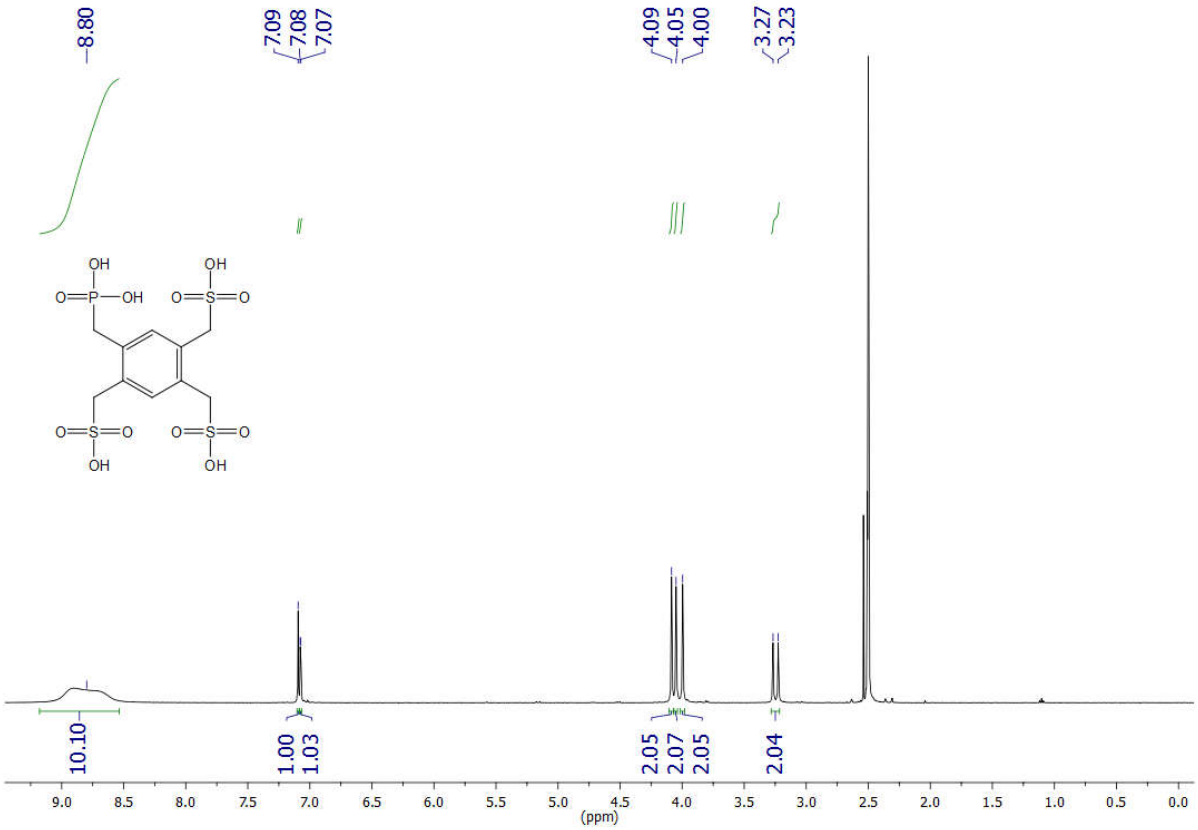
^{13}C-NMR (125 MHz, 300 K, DMSO-d6): δ = 135.7 (d[d_P], $^{4}J_{C\text{-}P}$ = 2.0 Hz, Ar-3-*C*), 134.5 (d[d_P], $^{3}J_{C\text{-}P}$ = 4.9 Hz, Ar-6-*C*), 132.3 (s[d_P], $^{5}J_{C\text{-}P}$ = 3.1 Hz, Ar-2-*C*), 131.9 (s[d_P], $^{4}J_{C\text{-}P}$ = 3.8 Hz, Ar-1-*C*), 131.5 (s[d_P], $^{2}J_{C\text{-}P}$ = 9.0 Hz, Ar-5-*C*), 131.4 (s[d_P], $^{3}J_{C\text{-}P}$ = 5.7 Hz, Ar-4-*C*), 54.7 (t, Ar-4-*C*H_2), 54.6 (t, Ar-1-*C*H_2, Ar-2-*C*H_2), 32.3 (t[d_P], $^{1}J_{C\text{-}P}$ = 130.0 Hz, Ar-5-*C*H_2) ppm.

^{31}P-NMR (202 MHz, 300 K, DMSO-d6): 22.6 (s, 1P, *P*O_3H_2) ppm.

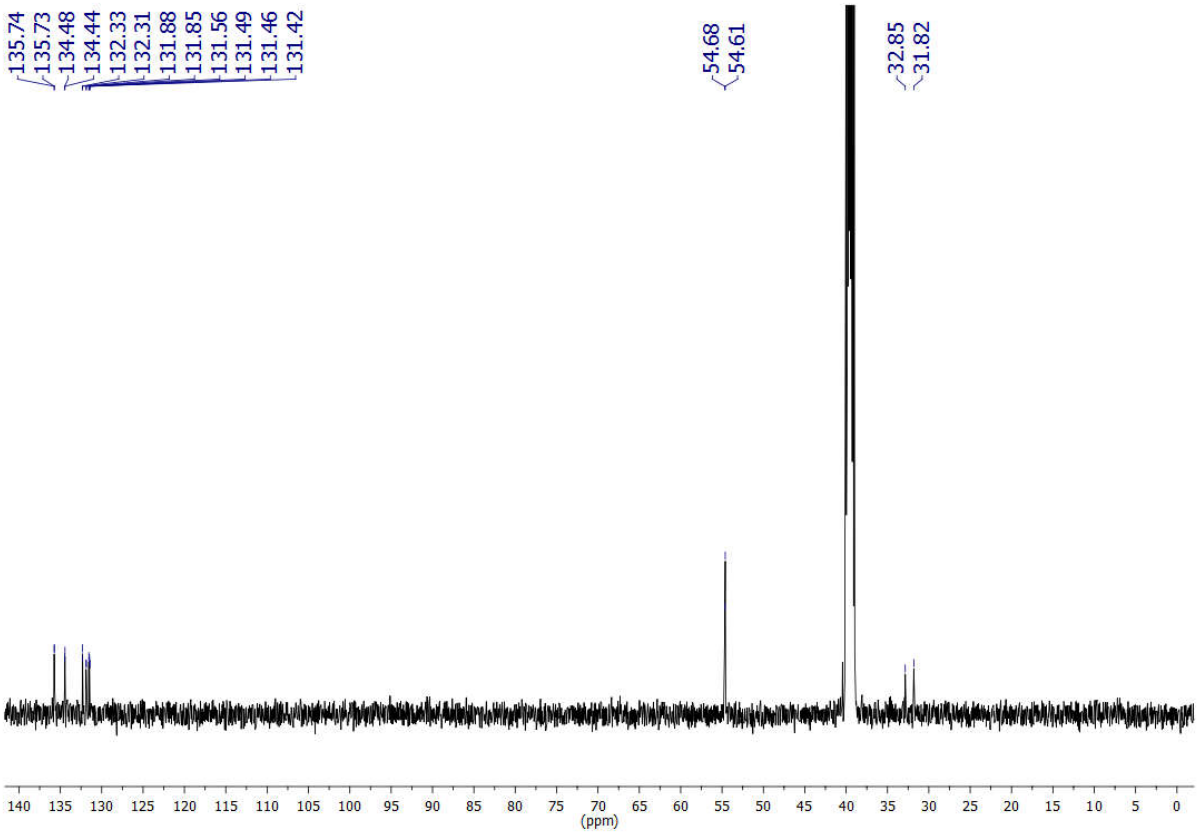
MS (ESI_{neg}): *m/z* = 453 $[M-H]^-$, 435 $[M-H_3O]^-$.

IR (ATR): $\tilde{\nu}$ = 2655, 2166 (br. O-H), 1655 (H_3O^+), 1508 (arom. C=C) cm^{-1}.

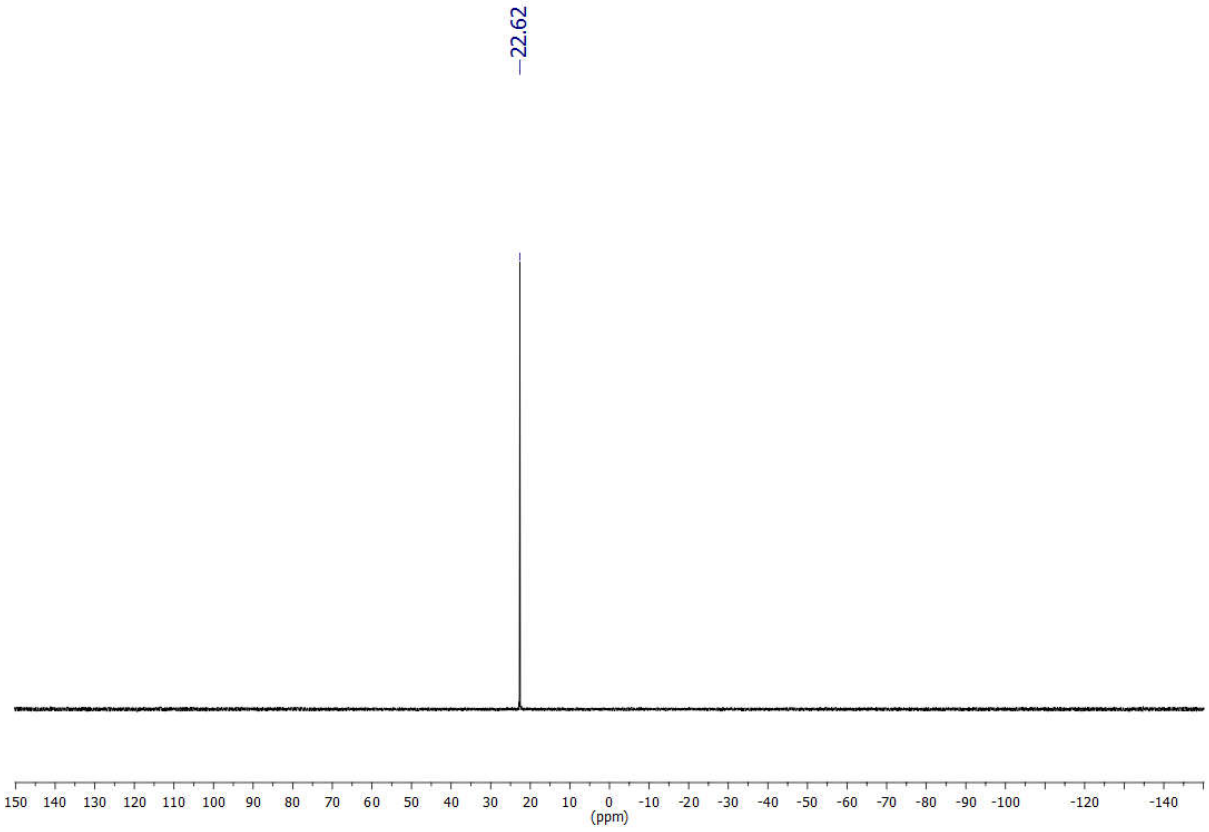
EA ($C_{10}H_{15}O_{12}PS_3$) (454.39): calcd. C 26.43 H 3.33 S 21.17;
($C_{10}H_{15}O_{12}PS_3 \cdot 4\ H_2O$) (526.45): calcd. C 22.81 H 4.40 S 18.27;
found C 22.61 H 4.55 S 18.40.



^{1}H-NMR (500 MHz, 300 K, DMSO-d6) of **8**

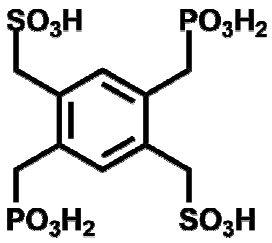


^{13}C-NMR (125 MHz, 300 K, DMSO-d6) of **8**



^{31}P-NMR (202 MHz, 300 K, DMSO-d6) of **8**

[2,5-Bis(phosphonomethyl)-benzene-1,4-diyl]bis(methylsulfonic acid) (9)



To a saturated aqueous solution of sodium sulfite (20 mL) was added water (5 mL) and [2,5-bis(bromomethyl)-benzene-1,4-diyl]bis(methylphosphonic acid diethyl ester) (**2**, 878 mg, 1.56 mmol) dissolved in acetone (15 mL). The reaction mixture was stirred at 100 °C for 12 h. Acetone was removed in vacuo and conc. hydrochloric acid (40 mL) was added to the aqueous solution and the mixture was stirred at 120 °C for 2 d. The solvent was removed in vacuo and the residue was treated with dimethyl sulfoxide (50 mL) to dissolve the product. Undissolved sodium chloride was separated by filtration. The solution was poured into dichloromethane (500 mL) and the precipitate was collected by filtration. To exchange the sodium ions, the residue was dissolved in water and rinsed over a column filled with ion-exchange resin (Dowex 50WX8 hydrogen form). The eluate was concentrated to give yellow oil which was dissolved in ethanol (3 mL). Acetonitrile (20 mL) was added and the solution was kept at 5 °C for 2 h.

The precipitate was filtered and dried for 24 h at 60 °C in a vacuum oven, to yield a colourless solid.

Yield: 532 mg (1.17 mmol, 75 %)

M. p.: 285 °C (decomposition)

^{1}H-NMR (500 MHz, 300 K, DMSO-d6): δ = 10.46 (br. s, 6H, SO_3H, PO_3H_2), 7.08 (s, 2H, Ar-3,6-*H*), 3.97 (s, 4H, Ar-1,4-CH_2), 3.21 (d, $^{2}J_{H\text{-}P}$ = 19.7 Hz, 4H, Ar-2,5-CH_2) ppm.

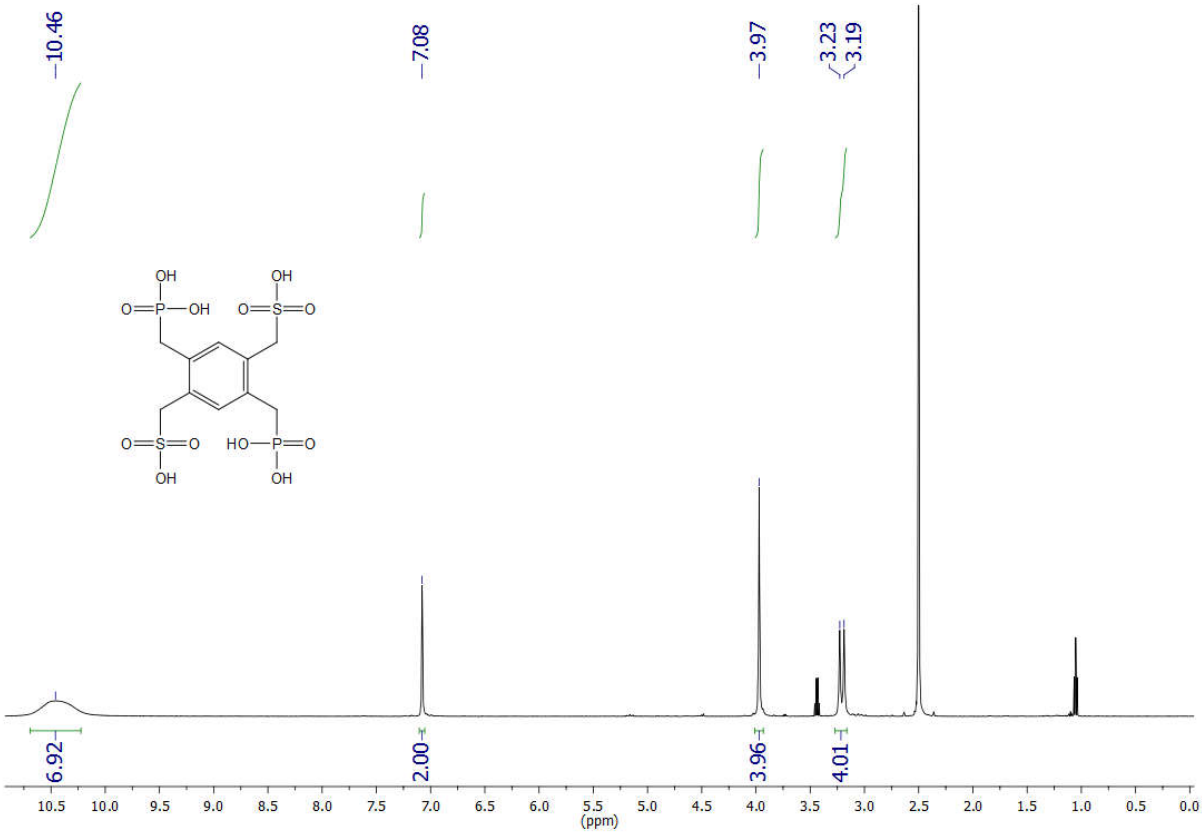
^{13}C-NMR (125 MHz, 300 K, DMSO-d6): δ = 134.6 (d[m_P], Ar-3,6-*C*), 131.6 (s[m_P], Ar-2,5-*C*), 131.1 (s[m_P], Ar-1,4-*C*), 54.7 (t, Ar-1,4-*C*H_2), 32.3 (t[d_P], $^{1}J_{C\text{-}P}$ = 130.6 Hz, Ar-2,5-*C*H_2) ppm.

^{31}P-NMR (202 MHz, 300 K, DMSO-d6): 22.0 (s, 2P, *P*O_3H_2) ppm.

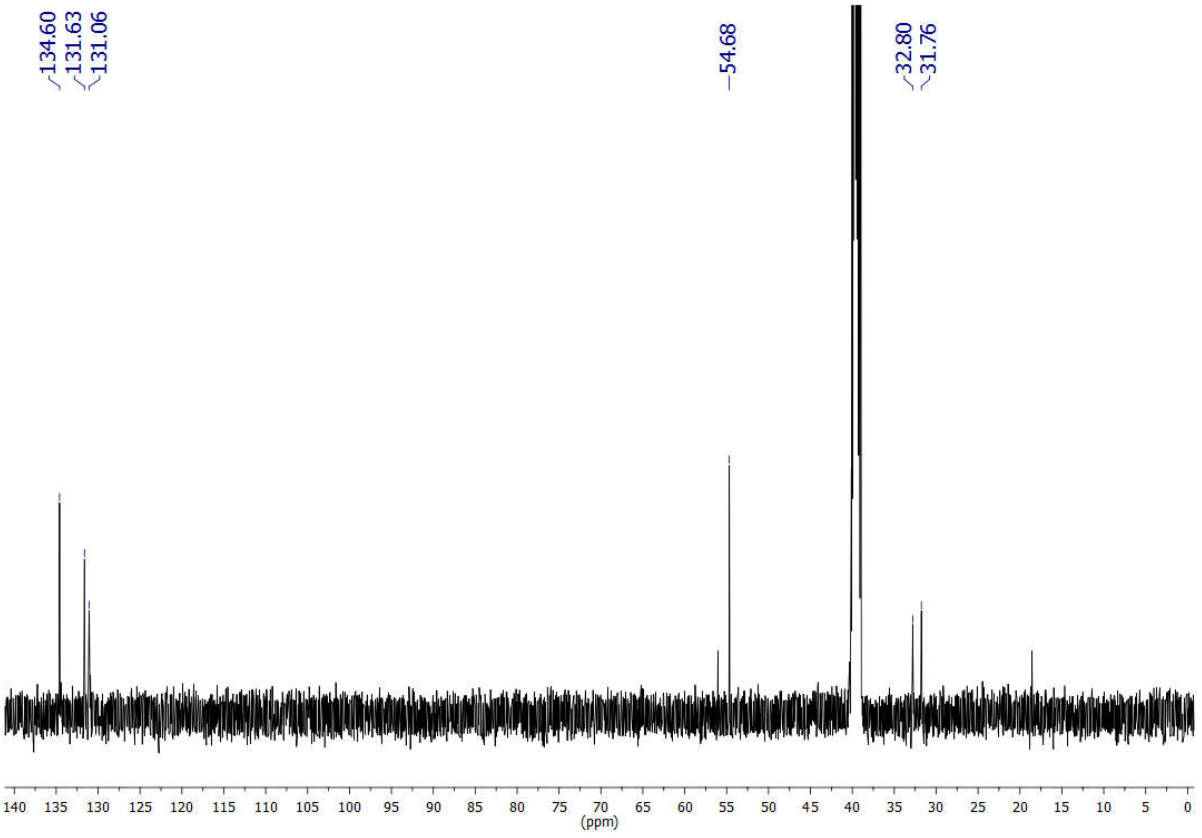
MS (ESI_{neg}): *m/z* = 453 $[M-H]^-$, 435 $[M-H_3O]^-$.

IR (ATR): $\tilde{\nu}$ = 2753, 2249 (br. O-H), 1667 (H_3O^+), 1510 (arom. C=C) cm^{-1}.

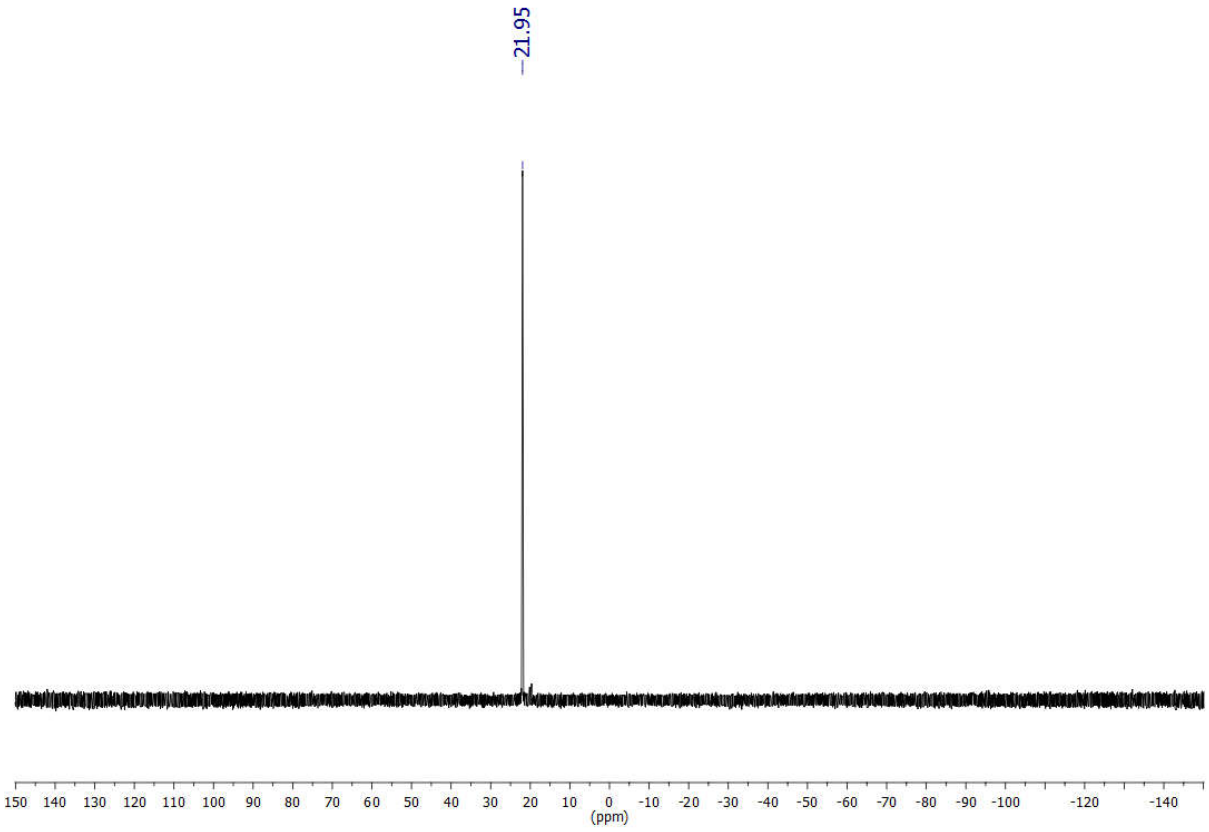
EA ($C_{10}H_{16}O_{12}P_2S_2$) (454.30): calcd. C 26.44 H 3.55 S 14.12;
($C_{10}H_{16}O_{12}P_2S_2 \cdot 0.33\ C_2H_6O \cdot 0.33\ H_2O$) (475.66): calcd. C 26.93 H 3.96 S 13.48;
found C 27.29 H 4.03 S 13.34.



^{1}H-NMR (500 MHz, 300 K, DMSO-d6) of **9**

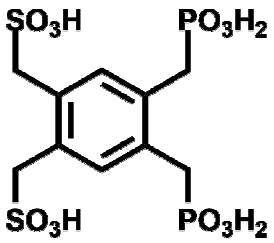


^{13}C-NMR (125 MHz, 300 K, DMSO-d6) of **9**



^{31}P-NMR (202 MHz, 300 K, DMSO-d6) of **9**

[4,5-Bis(phosphonomethyl)-benzene-1,2-diyl]bis(methylsulfonic acid) (10)



To a saturated aqueous solution of sodium sulfite (10 mL) was added water (2.5 mL) and [4,5-bis(bromomethyl)-benzene-1,2-diyl]bis(methylphosphonic acid diethyl ester) (**4**, 342 mg, 606 µmol) dissolved in acetone (10 mL). The reaction mixture was stirred at 100 °C for 12 h. Acetone was removed in vacuo and conc. hydrochloric acid (30 mL) was added to the aqueous solution and the mixture was stirred at 120 °C for 2 d. The solvent was removed in vacuo and the residue was treated with dimethyl sulfoxide (50 mL) to dissolve the product. Undissolved sodium chloride was separated by filtration. The solution was poured into dichloromethane (500 mL) and the precipitate was collected by filtration. To exchange the sodium ions, the residue was dissolved in water and rinsed over a column filled with ion-exchange resin (Dowex 50WX8 hydrogen form). The eluate was concentrated to give yellow oil, which was dissolved in ethanol (3 mL). Acetonitrile (20 mL) was added and the solution was kept at 5 °C for 2 h.

The precipitate was filtered and dried for 24 h at 60 °C in a vacuum oven, to yield a colourless solid.

Yield: 225 mg (495 µmol, 82 %)

M. p.: >300 °C

^{1}H-NMR (500 MHz, 300 K, DMSO-d6): δ = 9.95 (br. s, 6H, SO_3H, PO_3H_2), 7.07 (s, 2H, Ar-3,6-*H*), 4.03 (s, 4H, Ar-1,2-CH_2), 3.13 (d, $^{2}J_{H\text{-}P}$ = 20.3 Hz, 4H, Ar-4,5-CH_2) ppm.

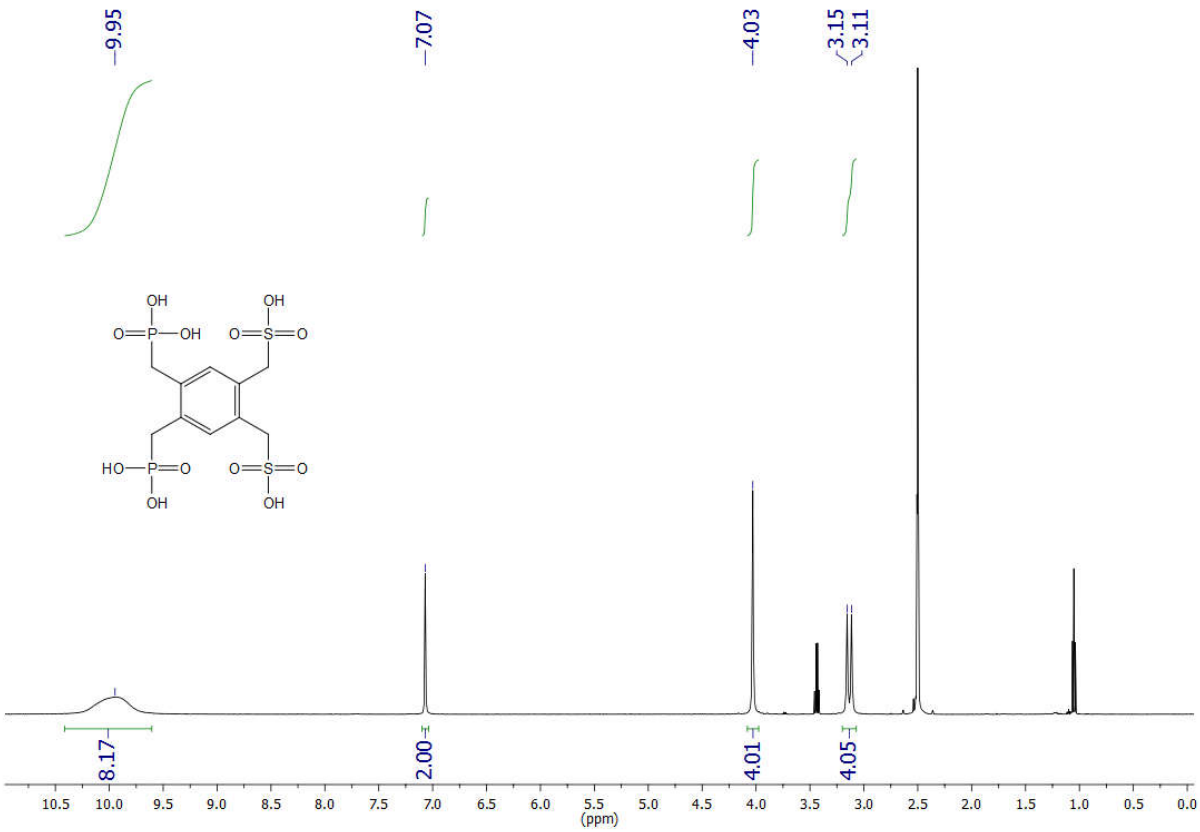
^{13}C-NMR (125 MHz, 300 K, DMSO-d6): δ = 134.6 (d[m_P], Ar-3,6-*C*), 132.2 (s[m_P], Ar-1,2-*C*), 130.4 (s[m_P], Ar-4,5-*C*), 54.7 (t, Ar-1,2-*C*H_2), 32.3 (t[d_P], $^{1}J_{C\text{-}P}$ = 131.5 Hz, Ar-4,5-*C*H_2) ppm.

^{31}P-NMR (202 MHz, 300 K, DMSO-d6): 22.2 (s, 2P, *P*O_3H_2) ppm.

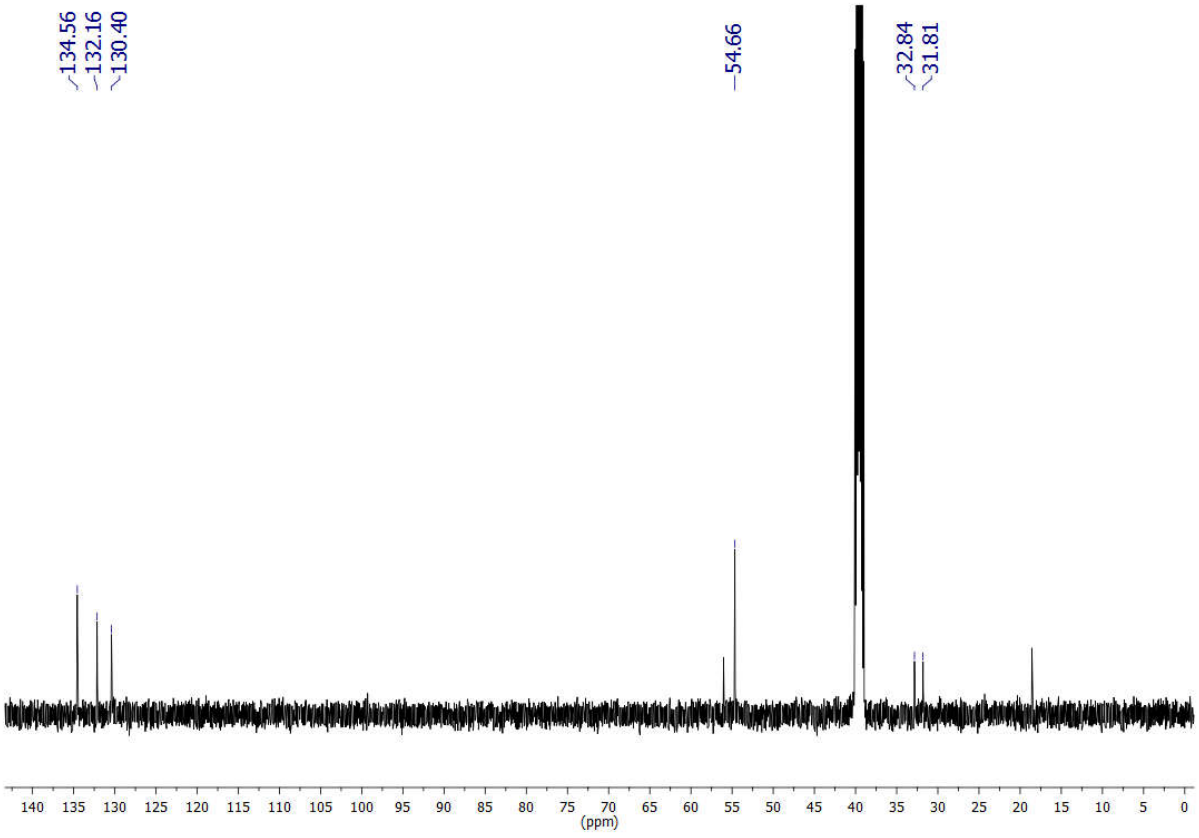
MS (ESI_{neg}): *m/z* = 453 $[M-H]^-$, 435 $[M-H_3O]^-$.

IR (ATR): $\tilde{\nu}$ = 2957 (br. O-H), 1657 (H_3O^+), 1513 (arom. C=C) cm^{-1}.

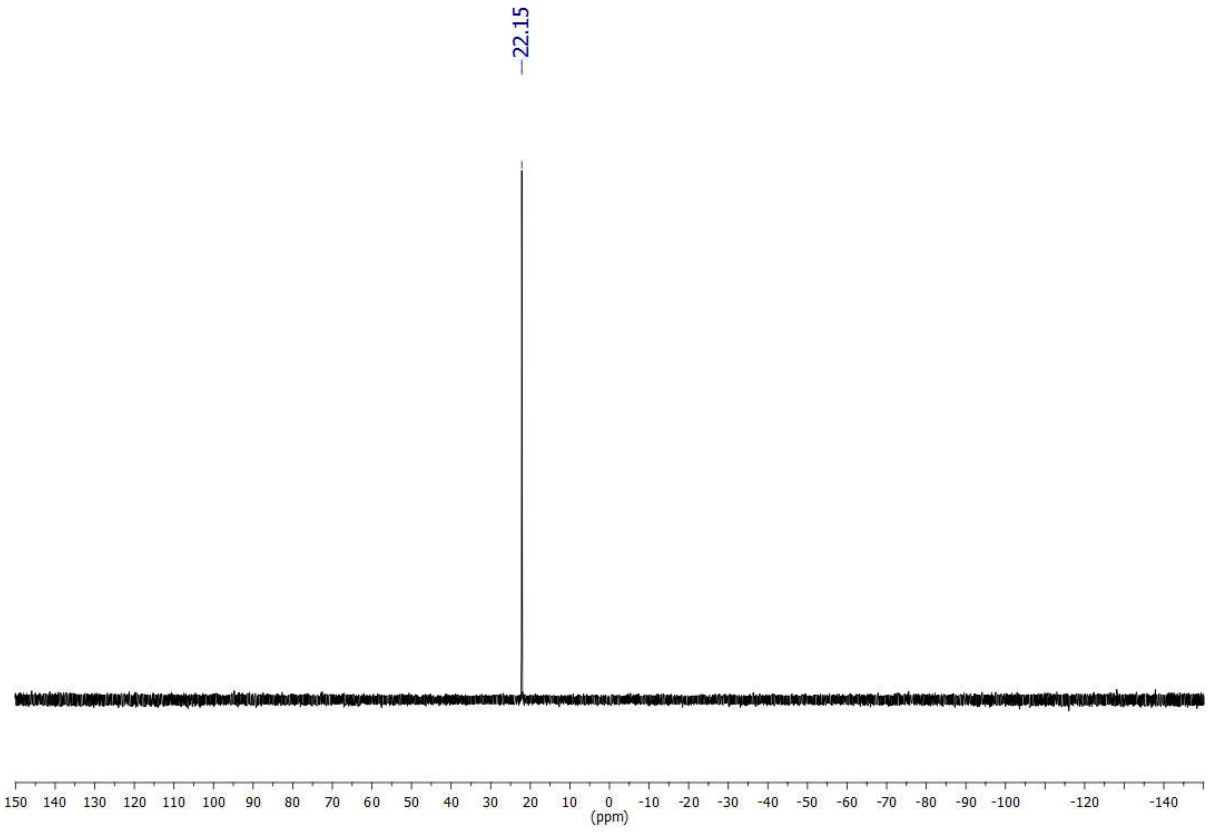
EA ($C_{10}H_{16}O_{12}P_2S_2$) (454.30): calcd. C 26.44 H 3.55 S 14.12;
($C_{10}H_{16}O_{12}P_2S_2 \cdot 0.2\ C_2H_6O \cdot 0.2\ H_2O$) (467.12): calcd. C 26.74 H 3.80 S 13.73;
found C 26.47 H 3.77 S 13.36.



^{1}H-NMR (500 MHz, 300 K, DMSO-d6) of **10**

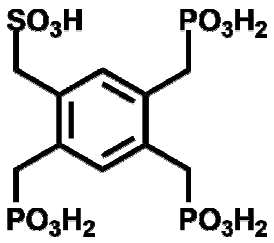


^{13}C-NMR (125 MHz, 300 K, DMSO-d6) of **10**



^{31}P-NMR (202 MHz, 300 K, DMSO-d6) of **10**

[2,4,5-Tris(phosphonomethyl)phenyl]methylsulfonic acid (11)



To a saturated aqueous solution of sodium sulfite (40 mL) was added water (10 mL) and [5-(bromomethyl)-benzene-1,2,4-triyl]tris(methylphosphonic acid diethyl ester) (**6**, 2.39 g, 3.85 mmol) dissolved in acetone (15 mL). The reaction mixture was stirred at 100 °C for 12 h. Acetone was removed in vacuo and conc. hydrochloric acid (40 mL) was added to the aqueous solution and the mixture was stirred at 120 °C for 2 d. The solvent was removed in vacuo and the residue was treated with dimethyl sulfoxide (100 mL) to dissolve the product. Undissolved sodium chloride was separated by filtration. The solution was poured into dichloromethane (1000 mL) and the precipitate was collected by filtration. To exchange the sodium ions, the residue was dissolved in water and rinsed over a column filled with ion-exchange resin (Dowex 50WX8 hydrogen form). The eluate was concentrated and dried for 24 h at 60 °C in a vacuum oven, to yield a colourless solid.

Yield: 1.52 g (3.35 mmol, 87 %)

M. p.: 246 °C

^{1}H-NMR (500 MHz, 300 K, DMSO-d6): δ = 8.08 (br. s, 7H, SO_3H, PO_3H_2), 7.09 (s, 1H, Ar-6-*H*), 7.06 (m_c, 1H, Ar-3-*H*), 3.90 (s, 2H, Ar-1-CH_2), 3.19 (d, $^{2}J_{H\text{-}P}$ = 20.3 Hz, 2H, Ar-2-CH_2), 3.11 (d, $^{2}J_{H\text{-}P}$ = 20.3 Hz, 4H, Ar-4,5-CH_2) ppm.

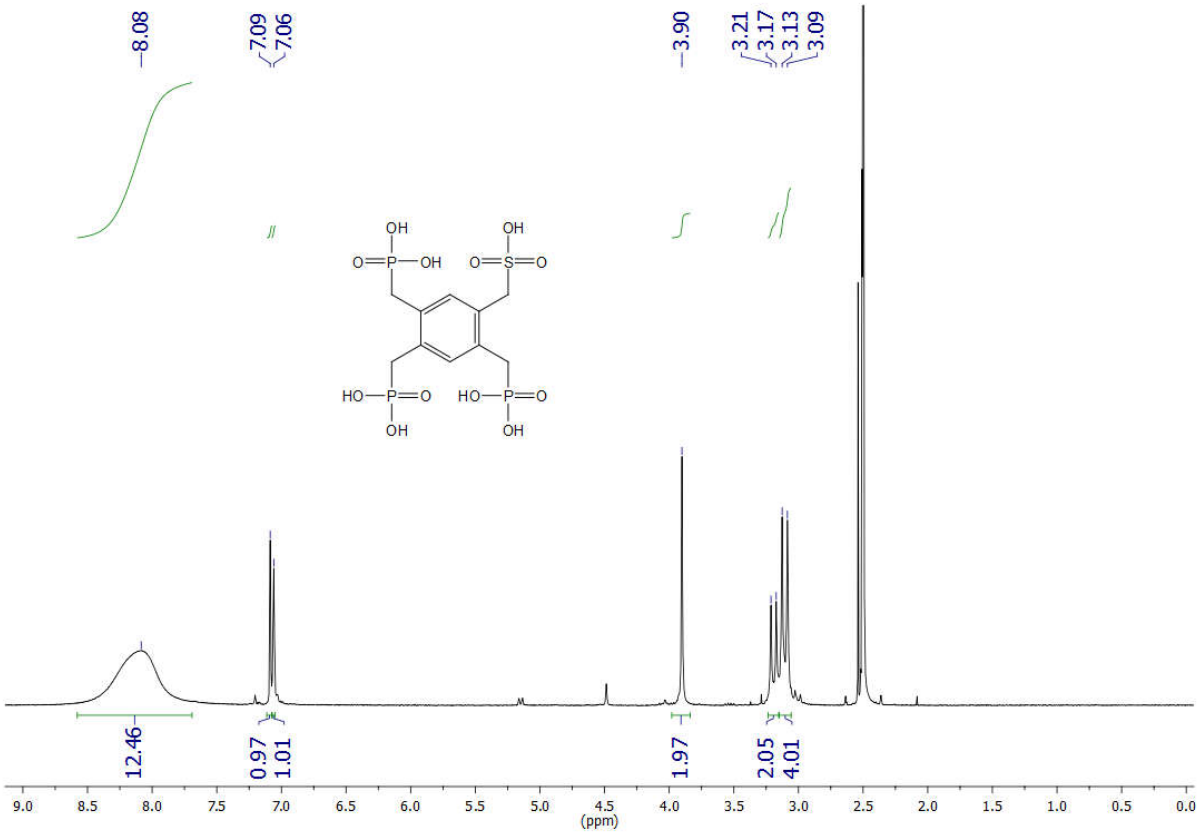
^{13}C-NMR (125 MHz, 300 K, DMSO-d6): δ = 134.8 (d[m_P], Ar-6-*C*), 133.4 (d[m_P], Ar-3-*C*), 131.6 (s[m_P], Ar-1-*C*), 131.3 (s[m_P], Ar-2-*C*), 130.6 (s[m_P], Ar-4-*C*), 129.9 (s[m_P], Ar-5-*C*), 54.7 (t, Ar-1-*C*H_2), 32.3 (t[d_P], $^{1}J_{C\text{-}P}$ = 129.8 Hz, Ar-2-*C*H_2), 32.2 (t[d_P], $^{1}J_{C\text{-}P}$ = 132.8 Hz, Ar-4,5-*C*H_2) ppm.

^{31}P-NMR (202 MHz, 300 K, DMSO-d6): 21.9 (m_c, 3P, *P*O_3H_2) ppm.

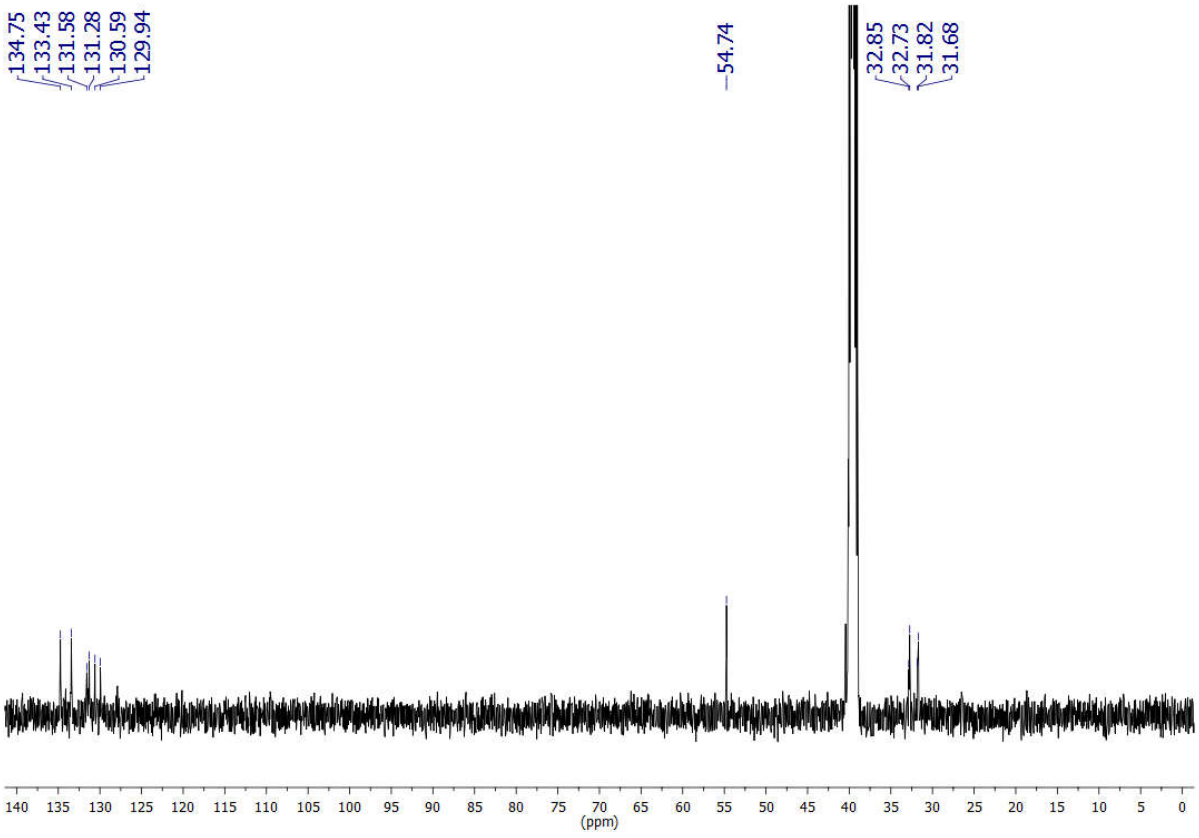
MS (ESI_{neg}): *m/z* = 453 [M -H]$^-$, 435 [M -H_3O]$^-$.

IR (ATR): $\tilde{\nu}$ = 2752, 2291 (br. O-H), 1505 (arom. C=C) cm^{-1}.

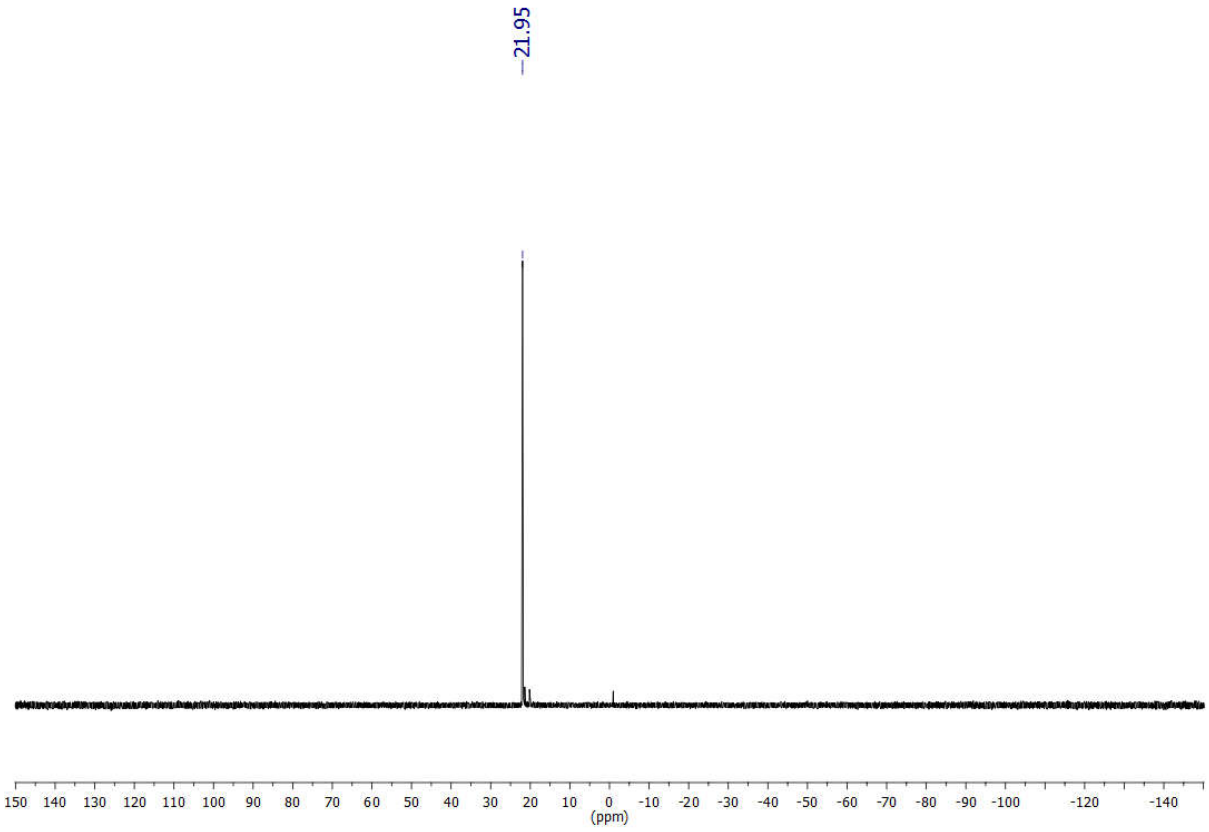
EA ($C_{10}H_{17}O_{12}P_3S$) (454.22): calcd. C 26.44 H 3.77 S 7.06;
found C 26.53 H 3.76 S 7.20.



^{1}H-NMR (500 MHz, 300 K, DMSO-d6) of **11**

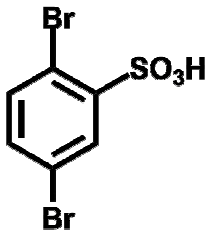


^{13}C-NMR (125 MHz, 300 K, DMSO-d6) of **11**



^{31}P-NMR (202 MHz, 300 K, DMSO-d6) of **11**

2,5-Dibromobenzenesulfonic acid (18)



Fuming sulfuric acid (20 - 30 % SO_3) (10 mL) was added to 1,4-dibromobenzene (**17**, 5.0 g, 21.2 mmol) under nitrogen atmosphere. The suspension was stirred at 150 °C until it became a dark brown solution (ca. 2 h). The reaction mixture was poured carefully into ice-cold water (100 mL). After treating the mixture with saturated aqueous sodium hydrogen carbonate solution until pH = 7 was reached, the water was evaporated in vacuo and the residue was dried for 2 d at 60 °C in a vacuum oven. Methanol (1000 mL) was added to the dry solid and the suspension was heated to 60 °C. Undissolved sodium sulfate was separated by filtration and the solvent was evaporated in vacuo. The residue was mixed with 2 M aqueous sodium hydroxide (200 mL) and water (50 mL) to give a suspension, which was stirred at 50 °C for 1 h. After 15 h at room temp., the undissolved solid was filtered off to give the sodium salt as a colourless solid (2.60 g). Concentration of the mother liquor to 50 % of the volume led to precipitation. Filtration gave about 800 mg of additional product. To exchange the sodium ion, the combined residue was dissolved in water and rinsed over a column filled with ion-exchange

resin (Dowex 50WX8 hydrogen form). The eluate was concentrated and dried for 24 h at 60 °C in a vacuum oven, to yield a colourless solid.

Yield: 3.01 g (9.53 mmol, 45 %) (Lit.[2]: 86 % of the sodium salt)

M. p.: 138 °C

^{1}H-NMR (500 MHz, 300 K, DMSO-d6): δ = 8.00 (d, ^{4}J = 2.6 Hz, 1H, Ar-6-*H*), 7.53 (d, ^{3}J = 8.4 Hz, 1H, Ar-3-*H*), 7.42 (dd, ^{3}J = 8.4 Hz, ^{4}J = 2.6 Hz, 1H, Ar-4-*H*), 6.67 (br. s, 1H, SO_3H) ppm.

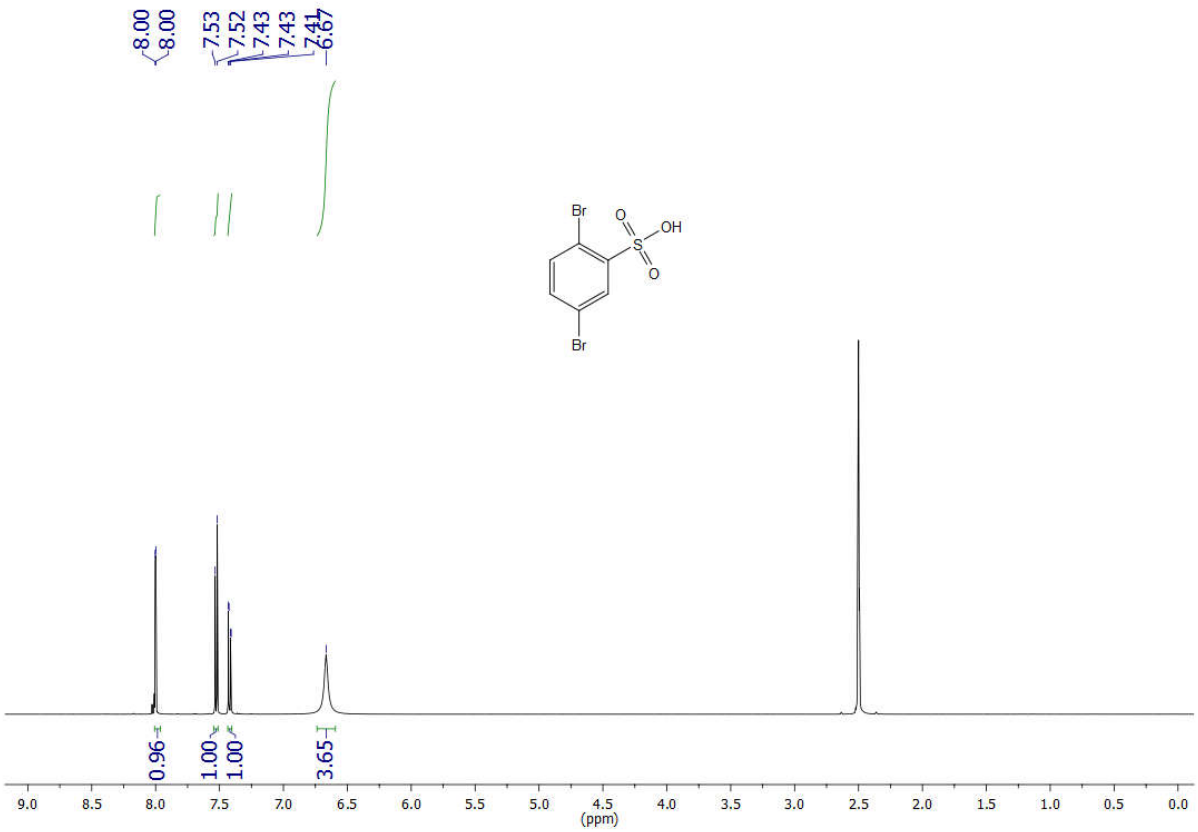
^{13}C-NMR (125 MHz, 300 K, DMSO-d6): δ = 148.8 (s, Ar-1-*C*), 135.9 (d, Ar-3-*C*), 132.8 (d, Ar-4-*C*), 131.4 (d, Ar-6-*C*), 119.8 (s, Ar-5-*C*), 118.7 (s, Ar-2-*C*) ppm.

MS (EI): *m/z* = 318, 316, 314 (52, 100, 50) $[M]^{+\cdot}$.

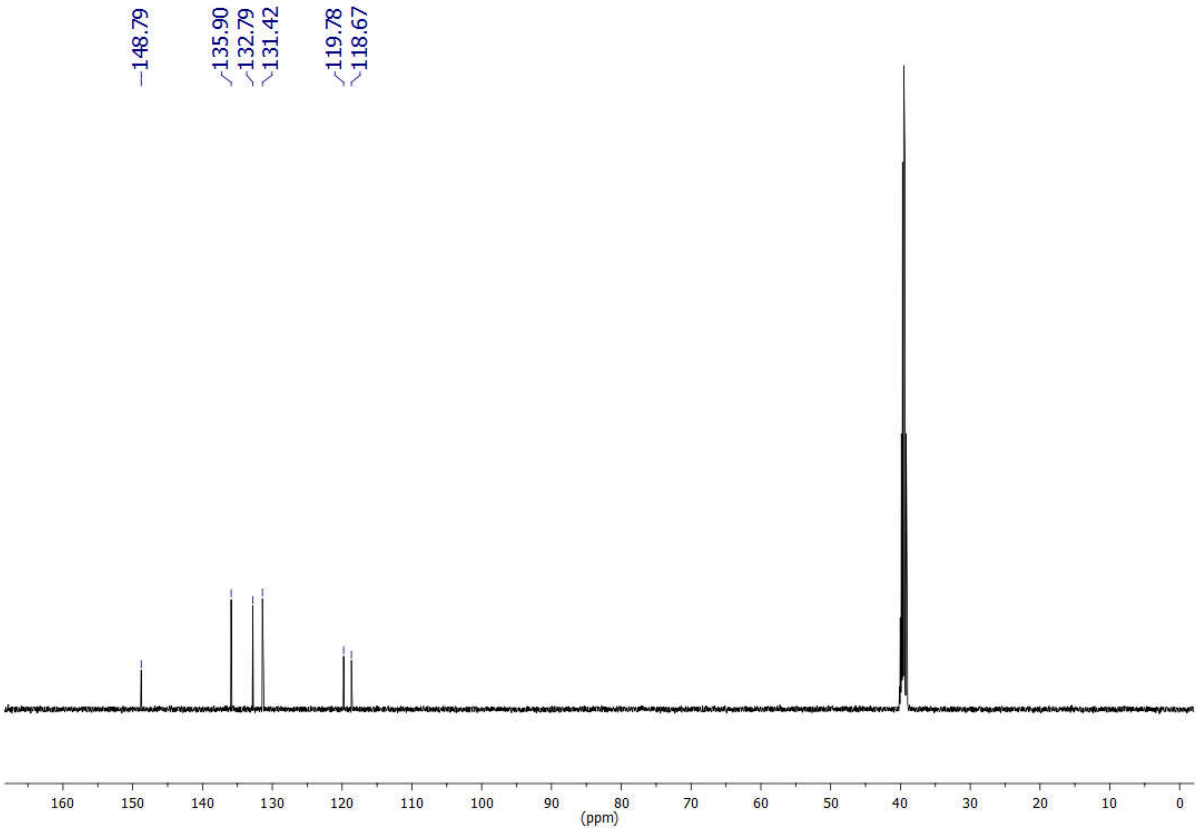
HRMS (EI): *m/z* = $C_6H_4{}^{79}Br_2O_3S$ calcd. 313.8248; found 313.8243 (Δ 1.5 ppm);
$C_6H_4{}^{79}Br^{81}BrO_3S$ calcd. 315.8227; found 315.8222 (Δ 1.7 ppm);
$C_6H_4{}^{81}Br_2O_3S$ calcd. 317.8207; found 317.8202 (Δ 1.6 ppm).

IR (ATR): $\tilde{\nu}$ = 3087 (aryl-H val.), 2900, 2169 (br., OH), 1673 (H_3O^+) cm^{-1}.

EA ($C_6H_4Br_2O_3S$) (315.97): calcd. C 22.81 H 1.28 S 10.15;
($C_6H_4Br_2O_3S \cdot 1\ H_2O$) (333.98): calcd. C 21.58 H 1.81 S 9.60;
found C 21.19 H 2.20 S 9.83.

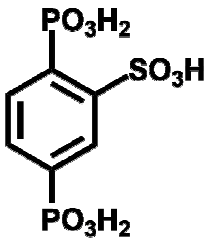


^{1}H-NMR (500 MHz, 300 K, DMSO-d6) of **18**



^{13}C-NMR (125 MHz, 300 K, DMSO-d6) of **18**

2,5-Diphosphonobenzenesulfonic acid (25)



A solution of 2,5-dibromobenzenesulfonic acid (**18**, 1.93 g, 6.12 mmol) in water (50 mL) was treated with aqueous tetra-*n*-butylammonium hydroxide (40 % in water) until pH = 7 was reached. The solvent was removed in vacuo and the residue was dried in a vacuum oven at 60 °C for 12 h to obtain the respective tetra-*n*-butylammonium salt. Three microwave vials were charged each with salt (3 x 1.13 g, 3 x 2.03 mmol), palladium(II) chloride (3 x 36 mg, 3 x 203 µmol) and triethyl phosphite (3 x 4 mL, 3 x 16.7 mmol). The vials were irradiated in a microwave oven (max. 200 W, 220 °C) for 1 h. The combined dark brown solution was added to a mixture of ethyl acetate (100 mL) and water (100 mL) in a separatory funnel. The aqueous layer was washed with ethyl acetate (3 x 100 mL) and water was removed in vacuo. The residue was dissolved in a mixture of water (50 mL) and conc. hydrochloric acid (100 mL) and stirred for 12 h at 120 °C. After removing the solvent in vacuo, the residue was dissolved in acetone (50 mL) and mixed with four equivalents of sodium iodide (3.67 g, 24.5 mmol) dissolved in acetone (30 mL). The precipitate was collected by filtration and recrystallized from a mixture of ethanol and water. To exchange the sodium ions, the residue was dissolved in water and rinsed over a column filled with ion-exchange resin (Dowex 50WX8 hydrogen form). The eluate was concentrated and dried for 24 h at 60 °C in a vacuum oven, to yield a colourless solid.

Yield: 922 mg (2.90 mmol, 47 %)

M. p.: 172 °C

^{1}H-NMR (500 MHz, 300 K, DMSO-d6): δ = 8.26 (ddd, $J_{H\text{-}P}$ = 13.2 Hz, $J_{H\text{-}P}$ = 4.8 Hz, ^{4}J = 1.3 Hz, 1H, Ar-6-*H*), 8.04 (ddd, $J_{H\text{-}P}$ = 13.9 Hz, ^{3}J = 7.6 Hz, $J_{H\text{-}P}$ = 3.7 Hz, 1H, Ar-3-*H*), 7.79 (m_c, H, Ar-4-*H*), 6.79 (br. s, 5H, PO_3H_2, SO_3H) ppm.

^{13}C-NMR (125 MHz, 300 K, DMSO-d6): δ = 146.6 (s[$d_P d_P$], $J_{C\text{-}P}$ = 13.4 Hz, $J_{C\text{-}P}$ = 9.3 Hz, Ar-1-*C*), 137.0 (s[$d_P d_P$], $^{1}J_{C\text{-}P}$ = 137.0 Hz, $^{4}J_{C\text{-}P}$ = 2.6 Hz, Ar-5-*C*), 133.1 (d[$d_P d_P$], $J_{C\text{-}P}$ = 13.6 Hz, $J_{C\text{-}P}$ = 7.0 Hz, Ar-3-*C*), 132.5 (s[$d_P d_P$], $^{1}J_{C\text{-}P}$ = 164.3 Hz, $^{4}J_{C\text{-}P}$ = 2.9 Hz, Ar-2-*C*), 131.2 (d[$d_P d_P$], $J_{C\text{-}$

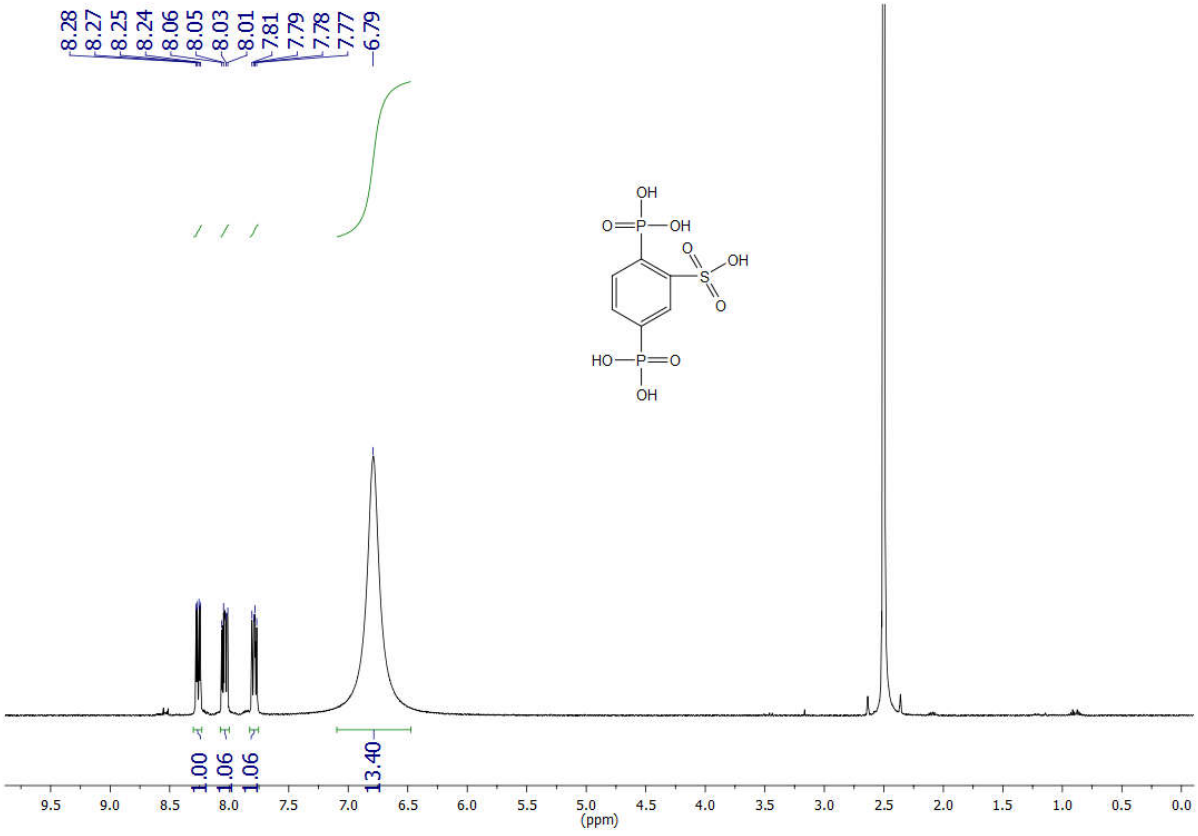
$_P$ = 12.3 Hz, $J_{C\text{-}P}$ = 9.5 Hz, Ar-4-*C*), 129.4 (d[$d_P d_P$], $^2J_{C\text{-}P}$ = 11.5 Hz, $^3J_{C\text{-}P}$ = 11.5 Hz, Ar-6-*C*) ppm.

^{31}P-NMR (202 MHz, 300 K, DMSO-d6): 10.5 (d, $^5J_{P\text{-}P}$ = 3.2 Hz, 1P, PO_3H_2), 9.3 (d, $^5J_{P\text{-}P}$ = ca. 3 Hz, 1P, PO_3H_2) ppm.

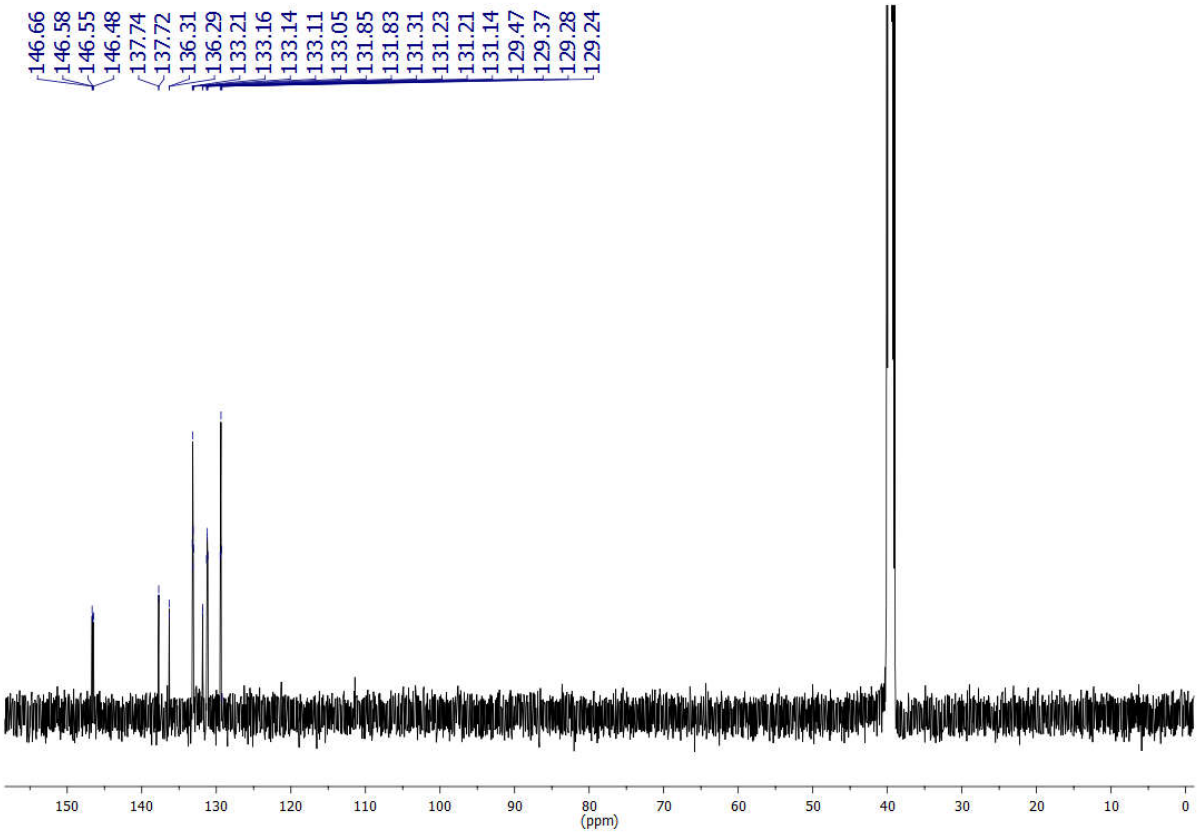
MS (ESI_{neg}): *m/z* = 953 [3M -H]$^-$, 635 [2M -H]$^-$, 317 [M -H]$^-$, 299 [M -H_3O]$^-$.

IR (ATR): $\tilde{\nu}$ = 2758, 2290 (br., OH), 1684 (H_3O^+) cm^{-1}.

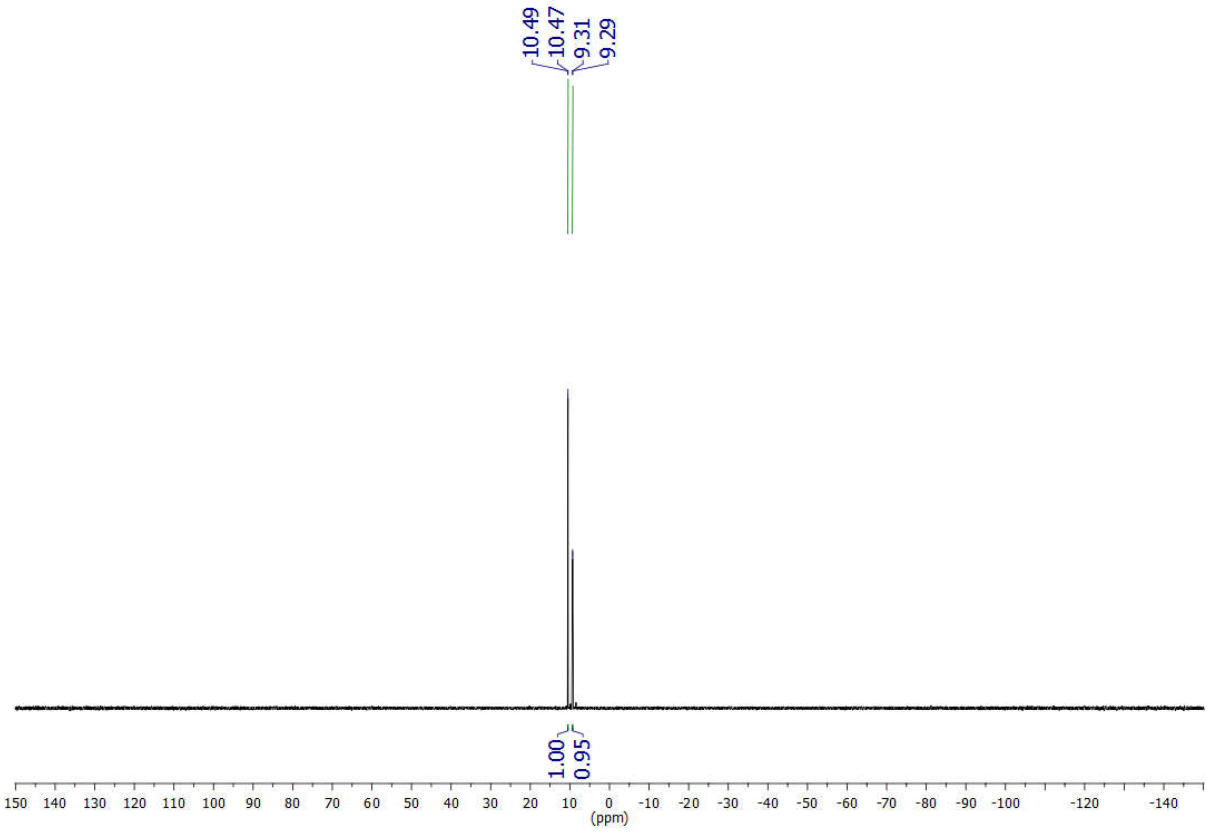
EA ($C_6H_8O_9P_2S$) (318.13): calcd. C 22.65 H 2.53 S 10.08;
($C_6H_8O_9P_2S \cdot 2\ H_2O$) (354.17): calcd. C 20.35 H 3.42 S 9.05;
found C 20.53 H 3.21 S 9.26.



^{1}H-NMR (500 MHz, 300 K, DMSO-d6) of **25**

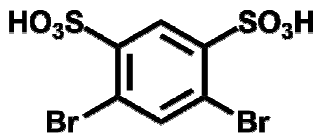


^{13}C-NMR (125 MHz, 300 K, DMSO-d6) of **25**



^{31}P-NMR (202 MHz, 300 K, DMSO-d6) of **25**

4,6-Dibromobenzene-1,3-disulfonic acid (22)



1,3-Dibromobenzene (**21**, 9.2 mL, 76.13 mmol) was added in portions to fuming sulfuric acid (65 % SO_3) (60 mL) and the reaction mixture was stirred for 5 h at 120 °C followed by 12 h at room temp. The mixture was poured carefully into ice-cold water (300 mL) and treated with sodium hydroxide until pH = 7 was reached. The water was removed in vacuo and the residue was dried for 2 d at 60 °C in a vacuum oven. Dimethyl sulfoxide (150 mL) was added to the dried solid and the suspension was stirred for 1 h at 60 °C. Undissolved sodium sulfate was removed by filtration and the filtrate was poured into dichloromethane (800 mL). Filtration of the precipitate and washing with dichloromethane (200 mL) gave a colourless solid. To exchange the sodium ions, the residue was dissolved in water and rinsed over a column filled with ion-exchange resin (Dowex 50WX8 hydrogen form). The eluate was concentrated and dried for 24 h at 60 °C in a vacuum oven, to yield a colourless solid.

Yield: 23.57 g (59.52 mmol, 78 %)

M. p.: 200 °C

^{1}H-NMR (500 MHz, 300 K, DMSO-d6): δ = 8.44 (s, 1H, Ar-2-*H*), 7.74 (s, 1H, Ar-5-*H*), 5.70 (br. s, 2H, SO_3*H*) ppm.

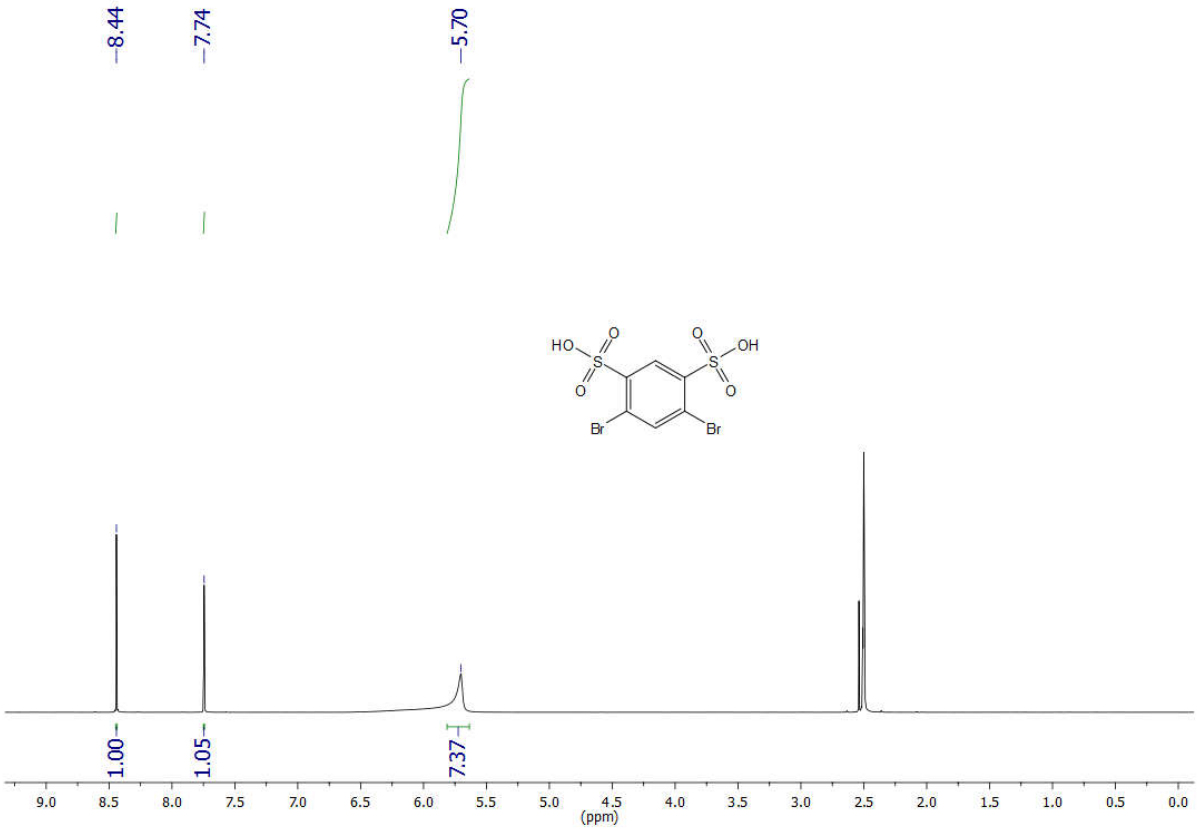
^{13}C-NMR (125 MHz, 300 K, DMSO-d6): δ = 145.4 (s, Ar-1,3-*C*), 137.6 (d, Ar-5-*C*), 129.4 (d, Ar-2-*C*), 119.9 (s, Ar-4,6-*C*) ppm.

MS (EI): *m/z* = 398, 396, 394 (56, 100, 49) $[M]^{+\cdot}$.

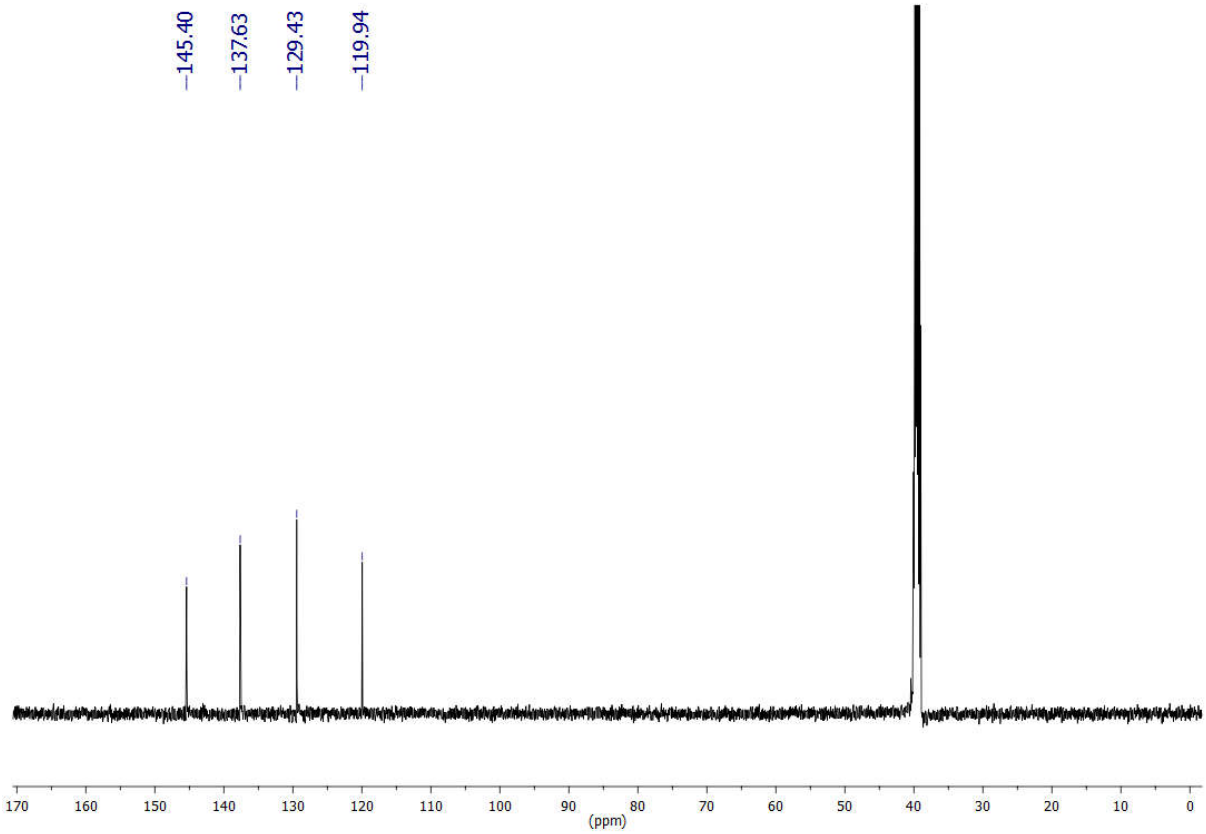
HRMS (EI): *m/z* = $C_6H_3{}^{79}Br_2O_6{}^{33}S^{34}S$ calcd. 395.7689; found 395.7686 (Δ 0.9 ppm).

IR (ATR): $\tilde{\nu}$ = 3101 (aryl-H val.), 2170 (br., OH), 1684 (H_3O^+), 1559, 1528 (arom. C=C) cm^{-1}.

EA ($C_6H_4Br_2O_6S_2$) (396.03): calcd. C 18.20 H 1.02 S 16.19;
($C_6H_4Br_2O_6S_2 \cdot 2\ H_2O$) (432.06): calcd. C 16.68 H 1.87 S 14.84;
found C 16.65 H 1.79 S 15.14.

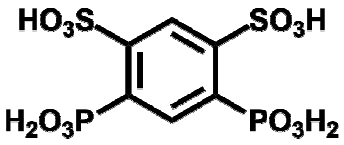


^{1}H-NMR (500 MHz, 300 K, DMSO-d6) of **22**



^{13}C-NMR (125 MHz, 300 K, DMSO-d6) of **22**

4,6-Diphosphonobenzene-1,3-disulfonic acid (27)



4,6-Dibromobenzene-1,3-disulfonic acid (**22**, 3.00 g, 7.57 mmol) dissolved in water (50 mL) was treated with aqueous tetra-*n*-butylammonium hydroxide (40 % in water) until pH = 7 was reached. The solvent was removed in vacuo and the residue was dried in a vacuum oven at 60 °C for 12 h to obtain the respective tetra-*n*-butylammonium salt. Four microwave vials were charged each with salt (4 x 1.66 g, 4 x 1.89 mmol), palladium(II) chloride (4 x 34 mg, 4 x 189 µmol) and triethyl phosphite (4 x 5 mL, 4 x 20.9 mmol). The vials were irradiated in a microwave oven (max. 200 W, 220 °C) for 60 min. The combined dark brown solution was added to a mixture of ethyl acetate (150 mL) and water (150 mL) in a separatory funnel. The aqueous layer was washed with ethyl acetate (3 x 150 mL) and water was removed in vacuo. The residue was dissolved in a mixture of water (100 mL) and conc. hydrochloric acid (200 mL) and stirred for 12 h at 120 °C. After removing the solvent in vacuo, the residue was dissolved in acetone (100 mL) and mixed with five equivalents of sodium iodide (5.67 g, 37.85 mmol) dissolved in acetone (50 mL). The precipitate was collected by filtration and recrystallized from a mixture of ethanol and water. To exchange the sodium ions, the residue was dissolved in water and rinsed over a column filled with ion-exchange resin (Dowex 50WX8 hydrogen form). The eluate was concentrated and dried for 24 h at 60 °C in a vacuum oven, to yield a colourless solid.

Yield: 987 mg (2.48 mmol, 33 %)

M. p.: >300 °C

^{1}H-NMR (500 MHz, 300 K, DMSO-d6): δ = 8.61 (t, $^{3}J_{H\text{-}P}$ = 13.9 Hz, 1H, Ar-5-*H*), 8.47 (t, $^{4}J_{H\text{-}P}$ = 4.6 Hz, 1H, Ar-2-*H*), 6.31 (br. s, 6H, PO_3H_2, SO_3H) ppm.

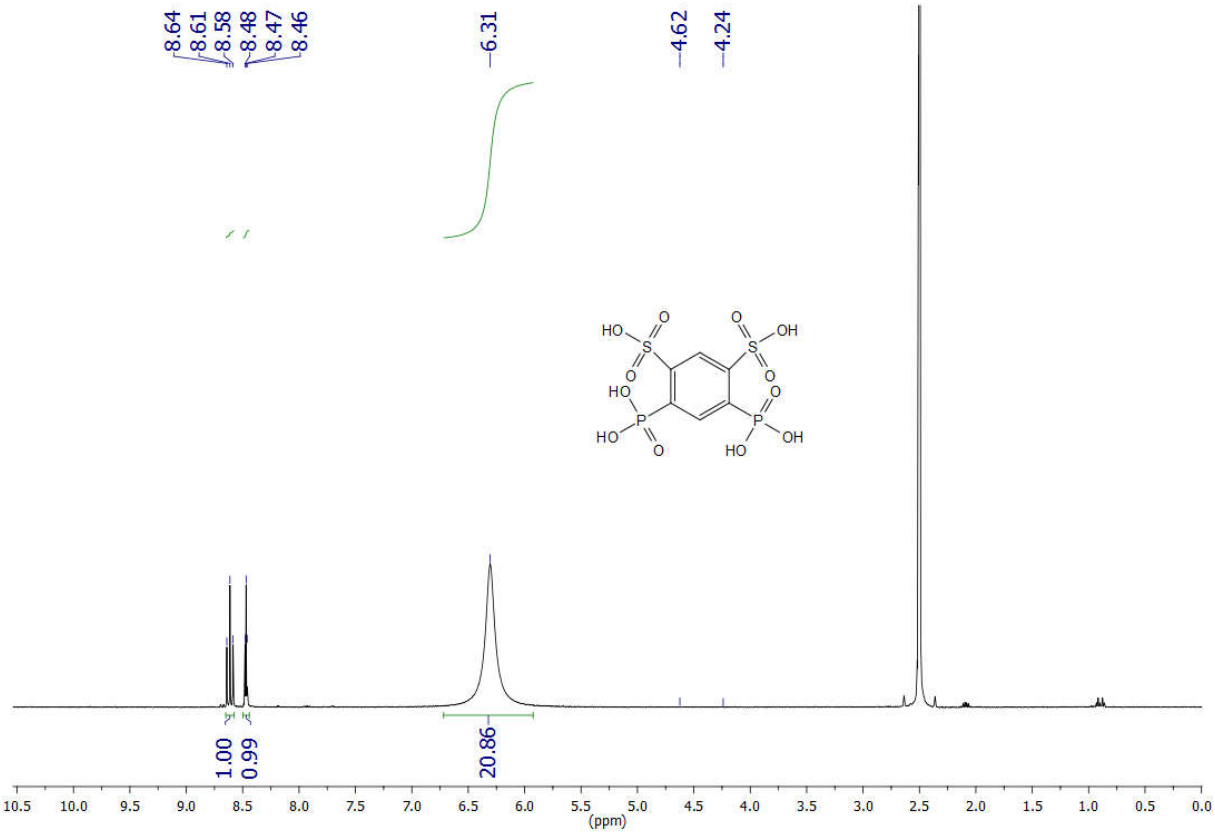
^{13}C-NMR (125 MHz, 300 K, DMSO-d6): δ = 149.0 (s[$d_P d_P$], $J_{C\text{-}P}$ = 9.9 Hz, $J_{C\text{-}P}$ = 3.5 Hz, Ar-1,3-*C*), 138.8 (d[t_P], $^{2}J_{C\text{-}P}$ = 8.9 Hz, Ar-5-*C*), 130.8 (s[$d_P d_P$], $^{1}J_{C\text{-}P}$ = 166.3 Hz, $^{3}J_{C\text{-}P}$ = 11.3 Hz, Ar-4,6-*C*), 126.8 (d[t_P], $^{3}J_{C\text{-}P}$ = 10.8 Hz, Ar-2-*C*) ppm.

^{31}P-NMR (202 MHz, 300 K, DMSO-d6): 8.6 (s, 2P, PO_3H_2) ppm.

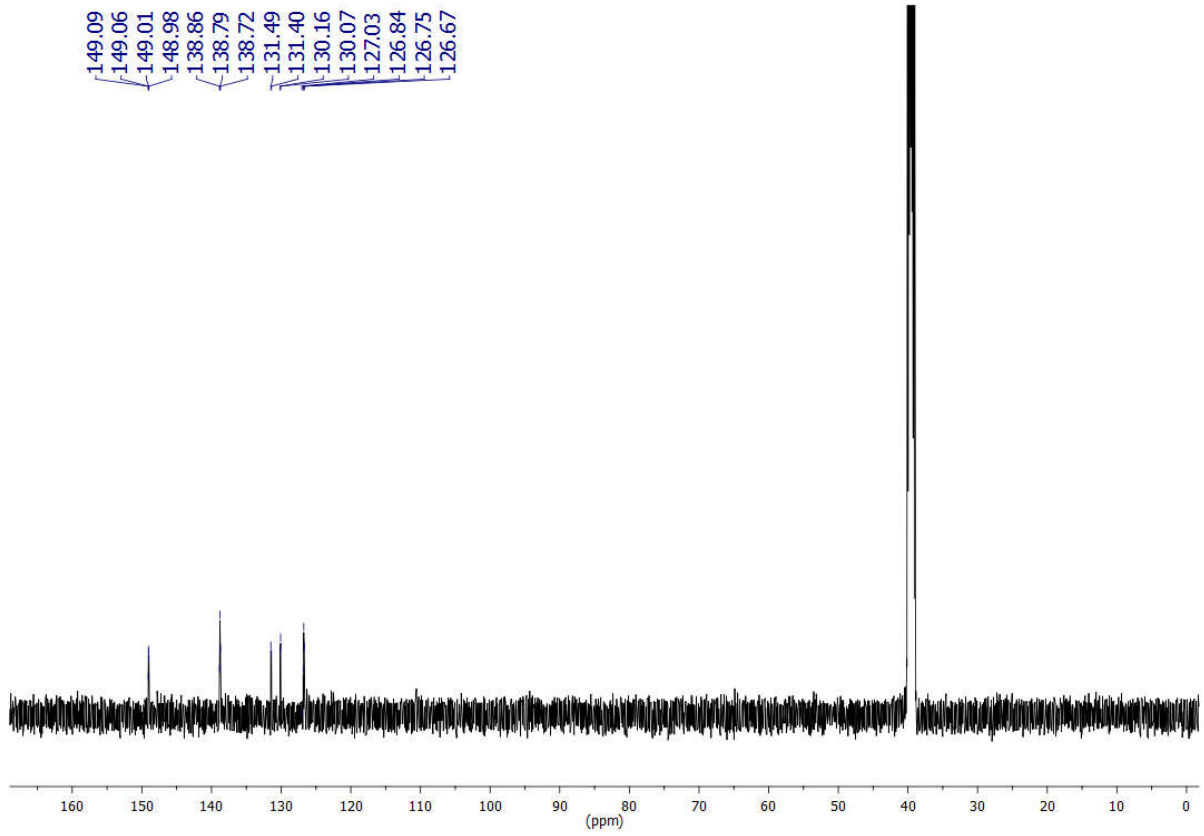
MS (ESI_{neg}): *m/z* = 795 $[2M-H]^-$, 397 $[M-H]^-$, 379 $[M-H_3O]^-$.

IR (ATR): $\tilde{\nu}$ = 3127 (aryl-H val.), 2753, 2257, (br., OH), 1654 (H_3O^+) cm^{-1}.

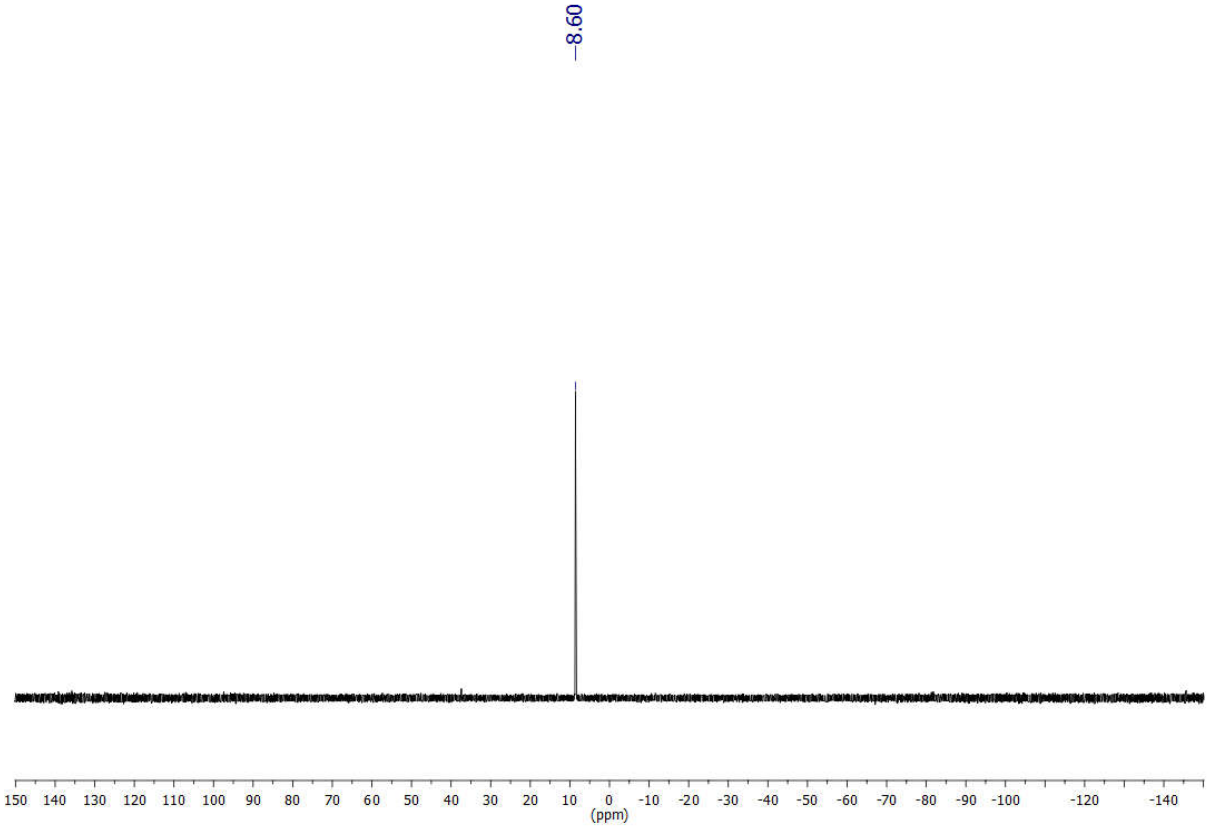
EA ($C_6H_8O_{12}P_2S_2$) (398.20): calcd. C 18.10 H 2.03 S 16.11;
($C_6H_8O_{12}P_2S_2 \cdot 3\ H_2O$) (452.24): calcd. C 15.93 H 3.12 S 14.18;
found C 16.28 H 3.30 S 13.85.



^{1}H-NMR (500 MHz, 300 K, DMSO-d6) of **27**



^{13}C-NMR (125 MHz, 300 K, DMSO-d6) of **27**

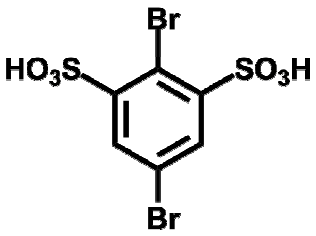


^{31}P-NMR (202 MHz, 300 K, DMSO-d6) of **27**

Procedure for the synthesis of disulfonic acids 19 and 20

A suspension of 1,4-dibromobenzene (**17**, 10.00 g, 42.39 mmol) and fuming sulfuric acid (20 - 30 % SO_3) (40 mL) was stirred for 24 h at 200 °C. The brown solution was poured into ice-cold water (300 mL) and treated with sodium carbonate until pH = 7 was reached. Water was removed in vacuo and the residue was dried for 2 d at 60 °C in a vacuum oven. *N*,*N*-Dimethylformamide (200 mL) was added to the dried solid and the suspension was stirred for 6 h at 60 °C. Undissolved sodium sulfate was removed by filtration and the DMF was evaporated in vacuo. The obtained solid was dried for 5 d at 60 °C in a vacuum oven. The residue, which is a mixture of 2,5-dibromobenzene-1,3-disulfonic acid disodium salt and 2,5-dibromobenzene-1,4-disulfonic acid disodium salt, was extracted with ethanol using Soxhlet extraction. Because the 2,5-dibromobenzene-1,4-disulfonic acid sodium salt is insoluble in ethanol, it stayed in the extraction thimble and was investigated by ^{1}H- and ^{13}C-NMR to determine the extraction time. When only pure 2,5-dibromobenzene-1,4-disulfonic acid sodium salt was left in the thimble, the extraction was stopped. The colourless solid in the thimble was dried for 1 d at 60 °C in a vacuum oven. Evaporation of ethanol in vacuo from the filtrate gave pure 2,5-dibromobenzene-1,3-disulfonic acid sodium salt. The residue was dried for 1 d at 60 °C in a vacuum oven to give a colourless solid. To exchange the sodium ions, the respective sodium salt was dissolved in water and rinsed over a column filled with ion-exchange resin (Dowex 50WX8 hydrogen form). The eluate was concentrated and dried for 24 h at 60 °C in a vacuum oven, to yield a colourless solid in both cases.

2,5-Dibromobenzene-1,3-disulfonic acid (19)



Yield: 10.64 g (26.9 mmol, 63 %)

M. p.: 220 °C

^{1}H-NMR (500 MHz, 300 K, DMSO-d6): δ = 8.02 (s, 2H, Ar-4,6-*H*), 5.29 (br. s, 2H, SO_3*H*) ppm.

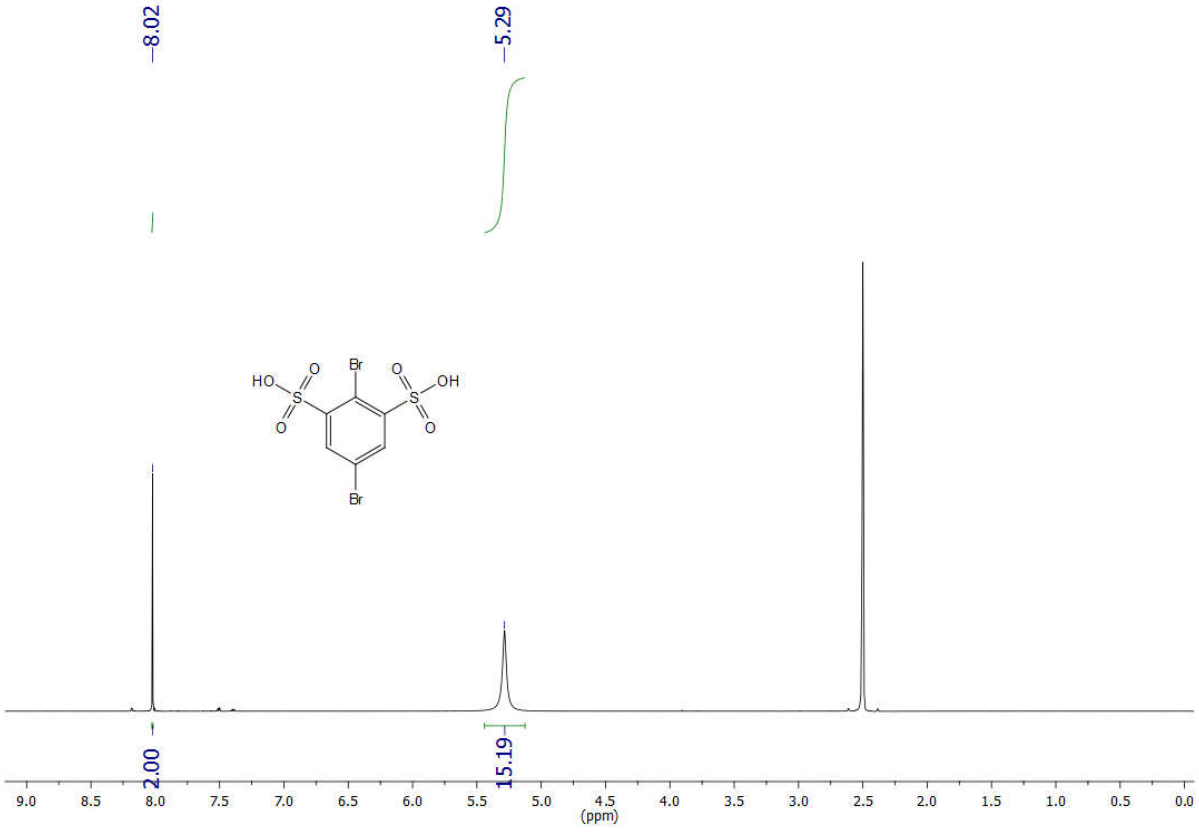
^{13}C-NMR (125 MHz, 300 K, DMSO-d6): δ = 150.4 (s, Ar-1,3-*C*), 131.4 (d, Ar-4,6-*C*), 118.3 (s, Ar-5-*C*), 117.2 (s, Ar-2-*C*) ppm.

MS (EI): *m/z* = 398, 396, 394 (56, 100, 49) $[M]^{+\cdot}$, 316, 314, 312 (74, 94, 36) $[M - H_2O_3S]^{+\cdot}$, 235, 233 (79, 47) $[M - H_2O_3S - Br]^{+\cdot}$.

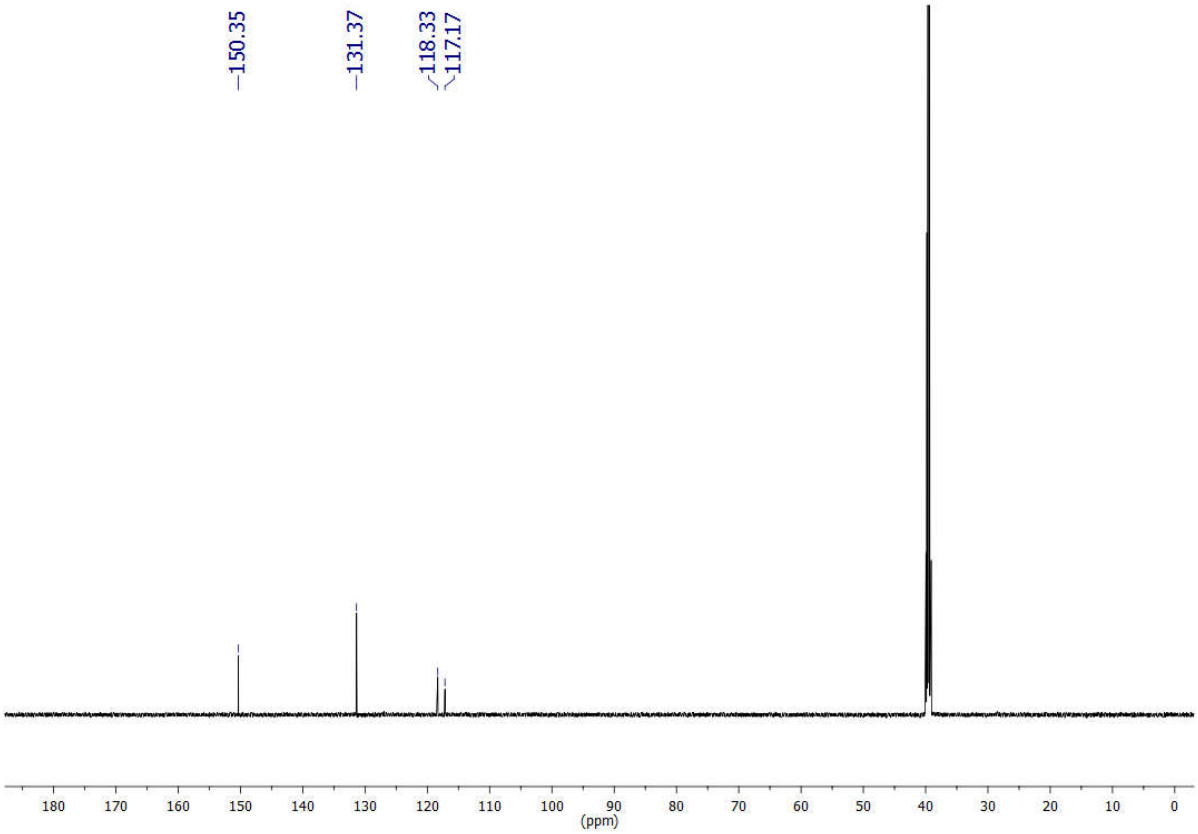
HRMS (EI): *m/z* = $C_6H_4{}^{79}Br_2O_6S_2$ calcd. 393.7816; found 393.7813 (Δ 0.8 ppm);
$C_6H_4{}^{79}Br^{81}BrO_6S_2$ calcd. 395.7796; found 395.7795 (Δ 0.2 ppm);
$C_6H_4{}^{81}Br_2O_6S_2$ calcd. 397.7775; found 317.7774 (Δ 0.3 ppm).

IR (ATR): $\tilde{\nu}$ = 2518, 2163 (br., OH), 1749, 1630 (H_3O^+), 1548 (arom. C=C) cm^{-1}.

EA ($C_6H_4Br_2O_6S_2$) (396.03): calcd. C 18.20 H 1.02 S 16.19;
($C_6H_4Br_2O_6S_2 \cdot 2\ H_2O$) (432.06): calcd. C 16.68 H 1.87 S 14.84;
found C 17.05 H 1.89 S 15.09.

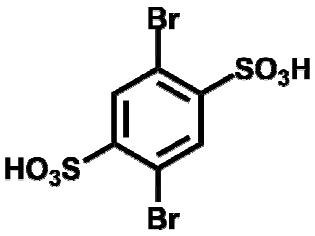


^{1}H-NMR (500 MHz, 300 K, DMSO-d6) of **19**



^{13}C-NMR (125 MHz, 300 K, DMSO-d6) of **19**

2,5-Dibromobenzene-1,4-disulfonic acid (20)



Yield: 4.56 g (11.5 mmol, 27 %) (Lit.[3]: 38 % of the sodium salt)

M. p.: >300 °C

^{1}H-NMR (500 MHz, 300 K, DMSO-d6): δ = 8.00 (s, 2H, Ar-3,6-*H*), 4.59 (br. s, 2H, SO_3H) ppm.

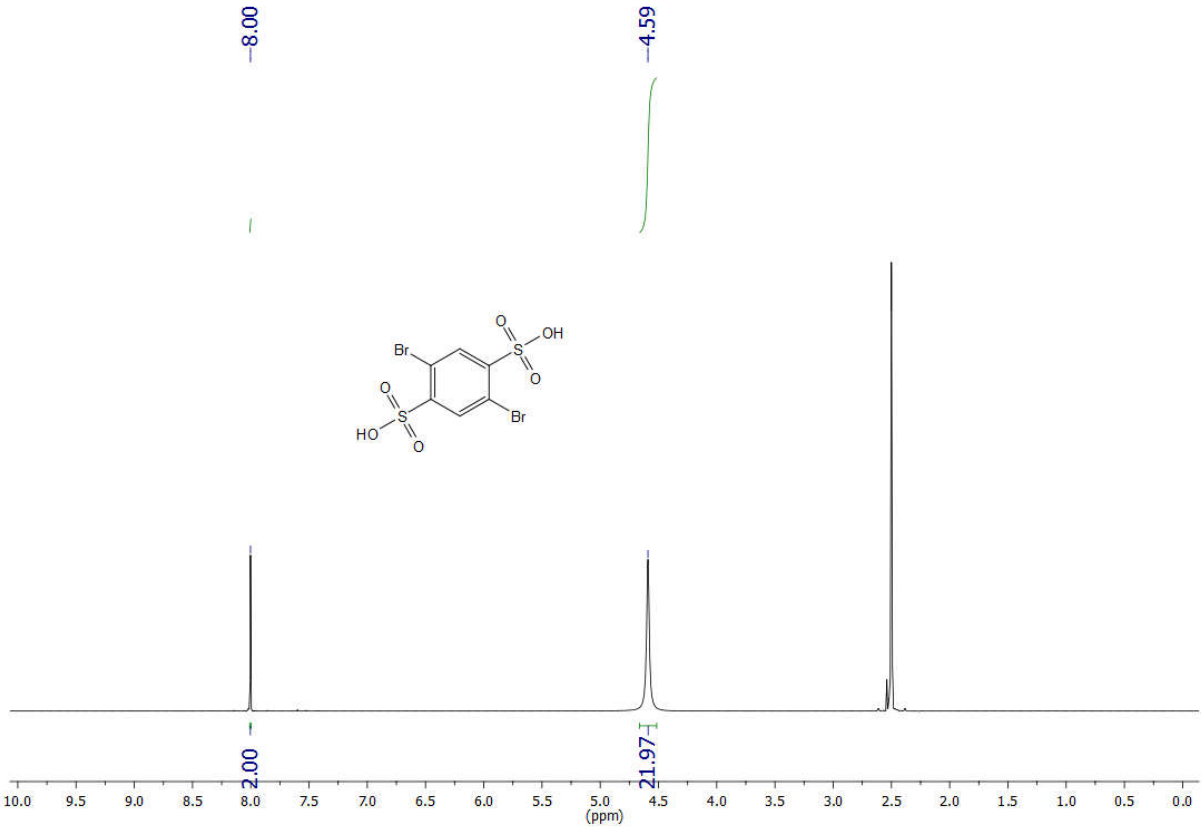
^{13}C-NMR (125 MHz, 300 K, DMSO-d6): δ = 148.0 (s, Ar-1,4-*C*), 134.0 (d, Ar-3,6-*C*), 117.5 (s, Ar-2,5-*C*) ppm.

MS (EI): *m/z* = 398, 396, 394 (40, 71, 35) $[M]^{+\cdot}$, 318, 316, 314 (18, 23, 12) $[M - O_3S]^{+\cdot}$, 157 (100) $[MH - O_3S - 2Br]^{+\cdot}$.

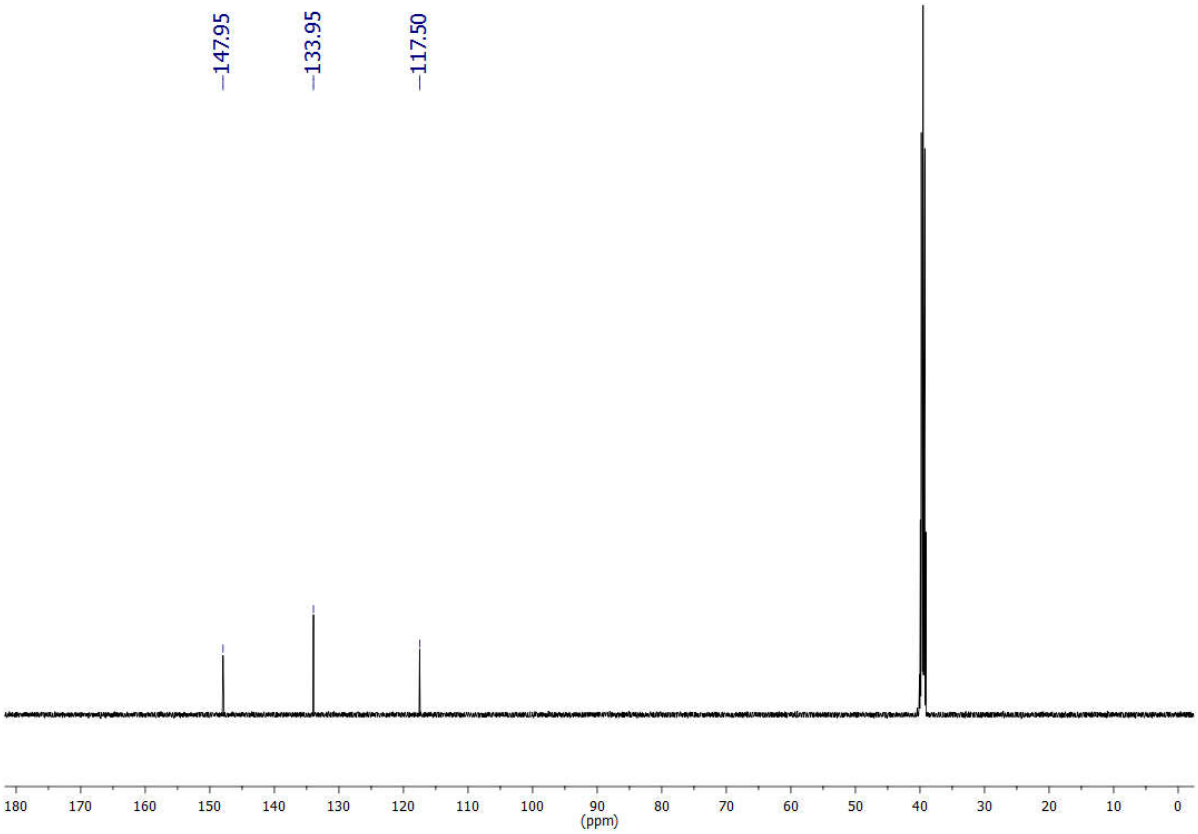
HRMS (EI): *m/z* = $C_6H_4{}^{79}Br_2O_6S_2$ calcd. 393.7816; found 393.7803 (Δ 3.3 ppm);
$C_6H_4{}^{79}Br^{81}BrO_6S_2$ calcd. 395.7796; found 395.7786 (Δ 2.5 ppm);
$C_6H_4{}^{81}Br_2O_6S_2$ calcd. 397.7775; found 317.7767 (Δ 2.0 ppm).

IR (ATR): $\tilde{\nu}$ = 3112 (aryl-H val.), 2480, 2082 (br., OH), 1697 (H_3O^+) cm^{-1}.

EA ($C_6H_4Br_2O_6S_2$) (396.03): calcd. C 18.20 H 1.02 S 16.19;
($C_6H_4Br_2O_6S_2 \cdot 2\ H_2O$) (432.06): calcd. C 16.68 H 1.87 S 14.84;
found C 16.99 H 1.90 S 14.92.

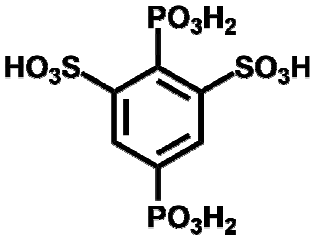


^{1}H-NMR (500 MHz, 300 K, DMSO-d6) of **20**



^{13}C-NMR (125 MHz, 300 K, DMSO-d6) of **20**

2,5-Diphosphonobenzene-1,3-disulfonic acid (28)



A solution of 2,5-dibromobenzene-1,3-disulfonic acid (**19**, 861 mg, 2.17 mmol) in water (20 mL) was treated with aqueous tetra-*n*-butylammonium hydroxide (40 % in water) until pH = 7 was reached. The solvent was removed in vacuo and the residue was dried in a vacuum oven at 60 °C for 12 h to obtain the respective tetra-*n*-butylammonium salt. Two microwave vials were charged each with salt (2 x 955 mg, 2 x 1.09 mmol), palladium(II) chloride (2 x 19 mg, 2 x 109 µmol) and triethyl phosphite (2 x 4 mL, 2 x 16.7 mmol). The vials were irradiated in a microwave oven (max. 200 W, 220 °C) for 60 min. The combined dark brown solution was added to a mixture of ethyl acetate (100 mL) and water (100 mL) in a separatory funnel. The aqueous layer was washed with ethyl acetate (3 x 100 mL) and water was removed in vacuo. The residue was dissolved in a mixture of water (50 mL) and conc. hydrochloric acid (100 mL) and stirred for 12 h at 120 °C. After removing the solvent in vacuo, the residue was

dissolved in acetone (50 mL) and mixed with five equivalents of sodium iodide (1.63 g, 10.9 mmol) dissolved in acetone (30 mL). The precipitate was collected by filtration and recrystallized two times from a mixture of ethanol and water. To exchange the sodium ions, the residue was dissolved in water and rinsed over a column filled with ion-exchange resin (Dowex 50WX8 hydrogen form). The eluate was concentrated and dried for 24 h at 60 °C in a vacuum oven, to yield a colourless solid.

Yield: 42 mg (105 µmol, 5 %)

M. p.: 158 °C

^{1}H-NMR (500 MHz, 300 K, DMSO-d6): δ = 8.48 (dd, $^{3}J_{H\text{-}P}$ = 13.1 Hz, $^{4}J_{H\text{-}P}$ = 3.6 Hz, 2H, Ar-4,6-*H*), 5.78 (br. s, 6H, PO_3H_2, SO_3H) ppm.

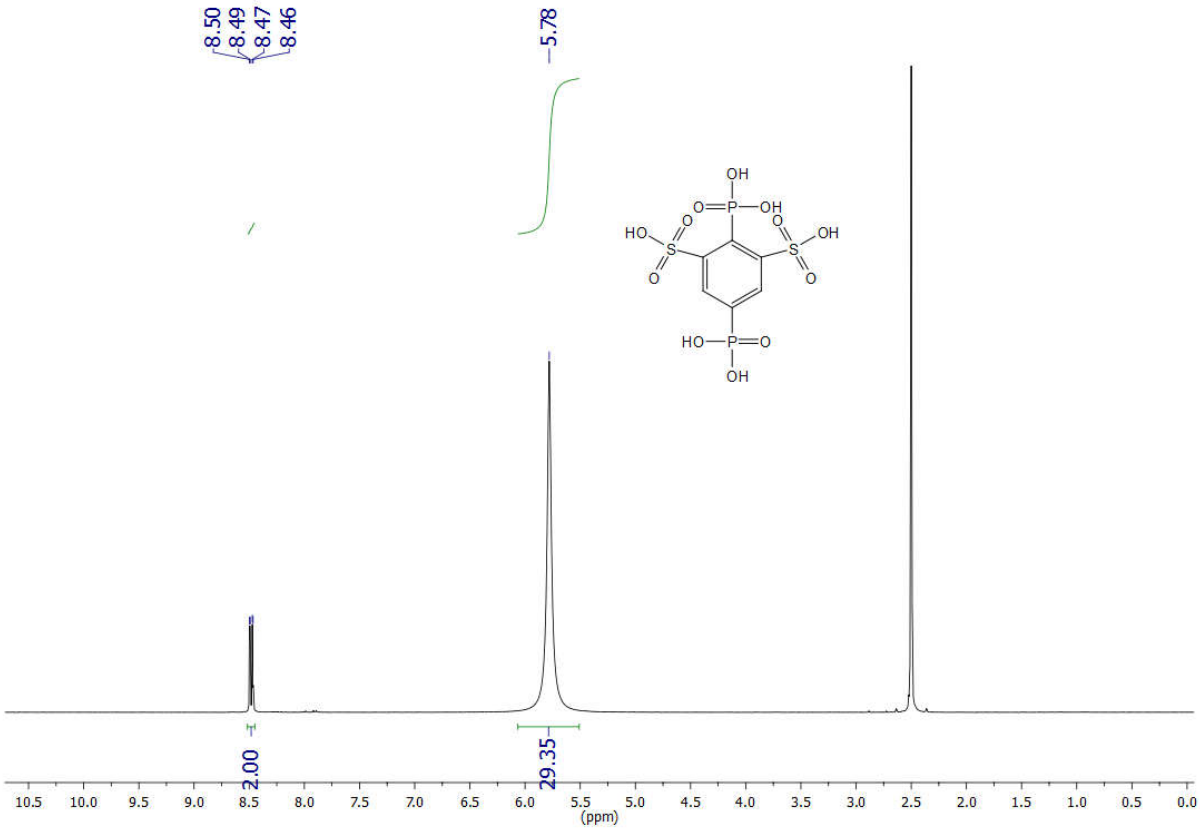
^{13}C-NMR (125 MHz, 300 K, DMSO-d6): δ = 148.6 (s[$d_P d_P$], $J_{C\text{-}P}$ = 12.8 Hz, $J_{C\text{-}P}$ = 8.3 Hz, Ar-1,3-*C*), 136.3 (s[$d_P d_P$], $^{1}J_{C\text{-}P}$ = 180.6 Hz, $^{4}J_{C\text{-}P}$ = 2.7 Hz, Ar-5-*C*), 131.9 (d[$d_P d_P$], $^{2}J_{C\text{-}P}$ = 11.1 Hz, $^{3}J_{C\text{-}P}$ = 11.1 Hz, Ar-4,6-*C*), 129.5 (s[$d_P d_P$], $^{1}J_{C\text{-}P}$ = 161.1 Hz, $^{4}J_{C\text{-}P}$ = 2.9 Hz, Ar-2-*C*) ppm.

^{31}P-NMR (202 MHz, 300 K, DMSO-d6): 9.2 (d, $^{5}J_{P\text{-}P}$ = 3.7 Hz, 1P, PO_3H_2), 7.2 (m_c, 1P, PO_3H_2) ppm.

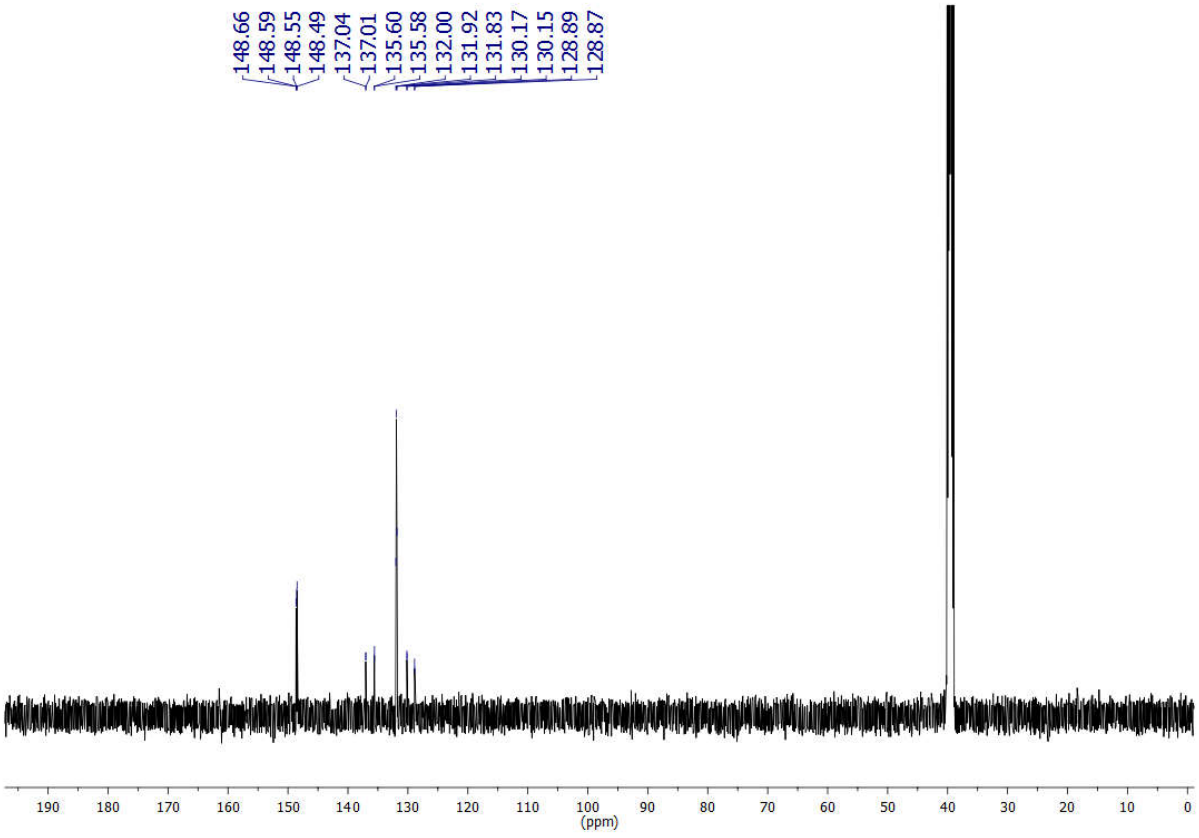
MS (ESI_{neg}): *m/z* = 795 $[2M - H]^-$, 397 $[M - H]^-$, 379 $[M - H_3O]^-$.

IR (ATR): $\tilde{\nu}$ = 2785, 2219 (br., OH), 1694 (H_3O^+) cm^{-1}.

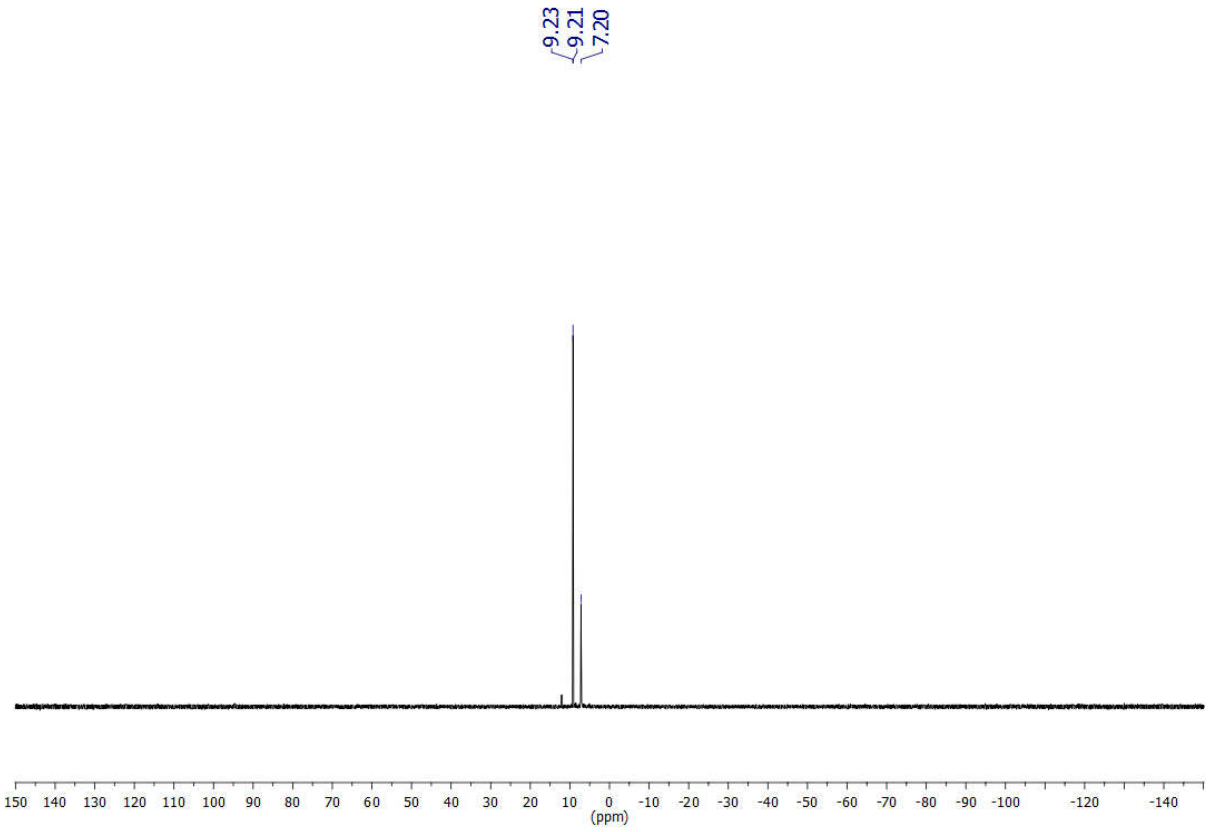
EA ($C_6H_8O_{12}P_2S_2$) (398.20): calcd. C 18.10 H 2.03 S 16.11;
($C_6H_8O_{12}P_2S_2 \cdot 1\ H_2O$) (416.21): calcd. C 17.31 H 2.42 S 15.41;
found C 17.66 H 2.45 S 15.11.



^{1}H-NMR (500 MHz, 300 K, DMSO-d6) of **28**

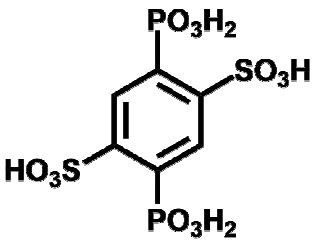


^{13}C-NMR (125 MHz, 300 K, DMSO-d6) of **28**



^{31}P-NMR (202 MHz, 300 K, DMSO-d6) of **28**

2,5-Diphosphonobenzene-1,4-disulfonic acid (26)



2,5-Dibromobenzene-1,4-disulfonic acid (**20**, 469 mg, 1.18 mmol) dissolved in water (20 mL) was treated with aqueous tetra-*n*-butylammonium hydroxide (40 % in water) until pH = 7 was reached. The solvent was removed in vacuo and the residue was dried in a vacuum oven at 60 °C for 12 h to obtain the respective tetra-*n*-butylammonium salt. A microwave vial was charged with salt (1.04 g, 1.18 mmol), palladium(II) chloride (21 mg, 118 µmol) and triethyl phosphite (4 mL, 16.7 mmol). The vial was irradiated in a microwave oven (max. 200 W, 220 °C) for 60 min. The dark brown solution was added to a mixture of ethyl acetate (100 mL) and water (100 mL) in a separatory funnel. The aqueous layer was washed with ethyl acetate (3 x 100 mL) and water was removed in vacuo. The residue was dissolved in a mixture of water (15 mL) and conc. hydrochloric acid (30 mL) and stirred for 12 h at 120 °C. After removing the solvent in vacuo, the residue was dissolved in acetone (15 mL) and mixed with five equivalents

of sodium iodide (884 mg, 5.90 mmol) dissolved in acetone (10 mL). The precipitate was collected by filtration and recrystallized from a mixture of ethanol and water. To exchange the sodium ions, the residue was dissolved in water and rinsed over a column filled with ion-exchange resin (Dowex 50WX8 hydrogen form). The eluate was concentrated and dried for 24 h at 60 °C in a vacuum oven, to yield a colourless solid.

Yield: 187 mg (470 µmol, 40 %)

M. p.: >300 °C

^{1}H-NMR (500 MHz, 300 K, DMSO-d6): δ = 9.35 (br. s, 6H, PO_3H_2, SO_3H), 8.53 (m_c, 2H, Ar-3,6-*H*) ppm.

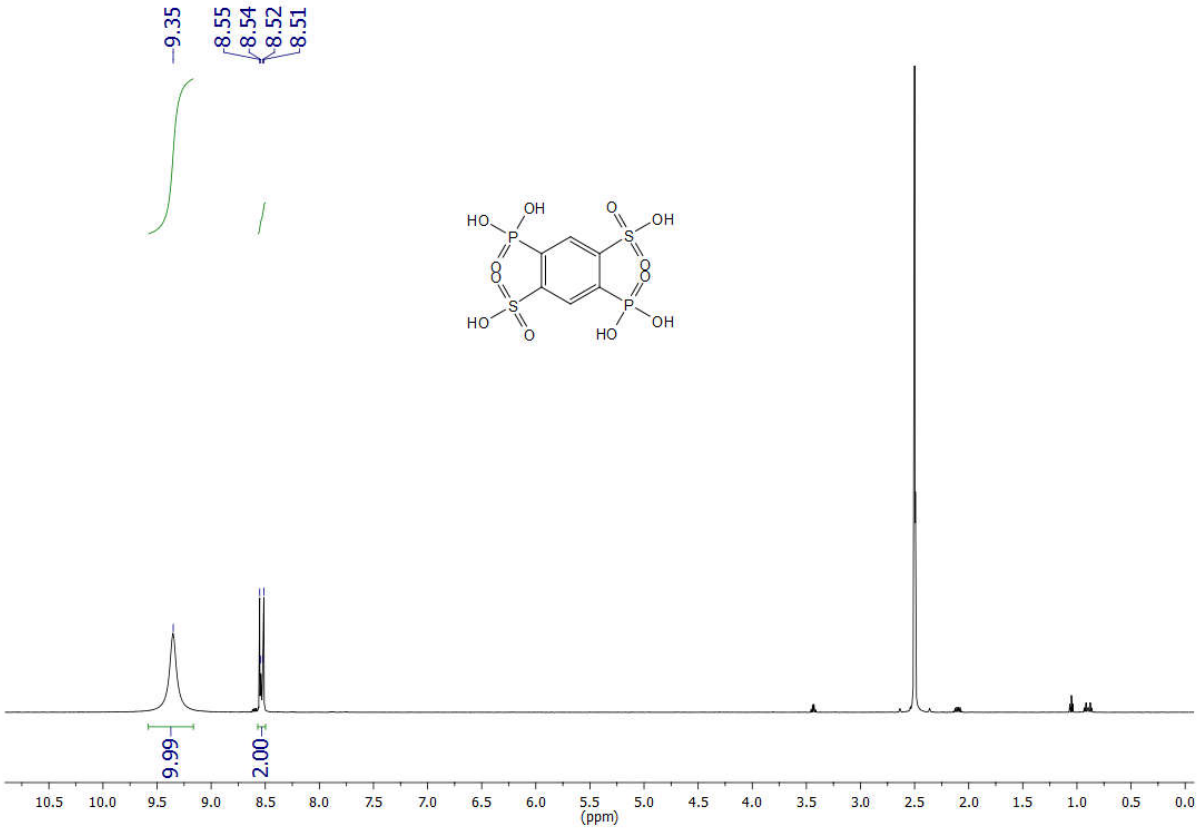
^{13}C-NMR (125 MHz, 300 K, DMSO-d6): δ = 147.7 (s[m_P], Ar-1,4-*C*), 133.06 (s[d_Pd_P], $^{1}J_{C\text{-}P}$ = 165.4 Hz, $^{4}J_{C\text{-}P}$ = 2.8 Hz, Ar-2,5-*C*), 133.05 (d[t_P], $^{2}J_{C\text{-}P}$ = 9.8 Hz, Ar-3,6-*C*) ppm.

^{31}P-NMR (202 MHz, 300 K, DMSO-d6): 8.5 (s, 2P, PO_3H_2) ppm.

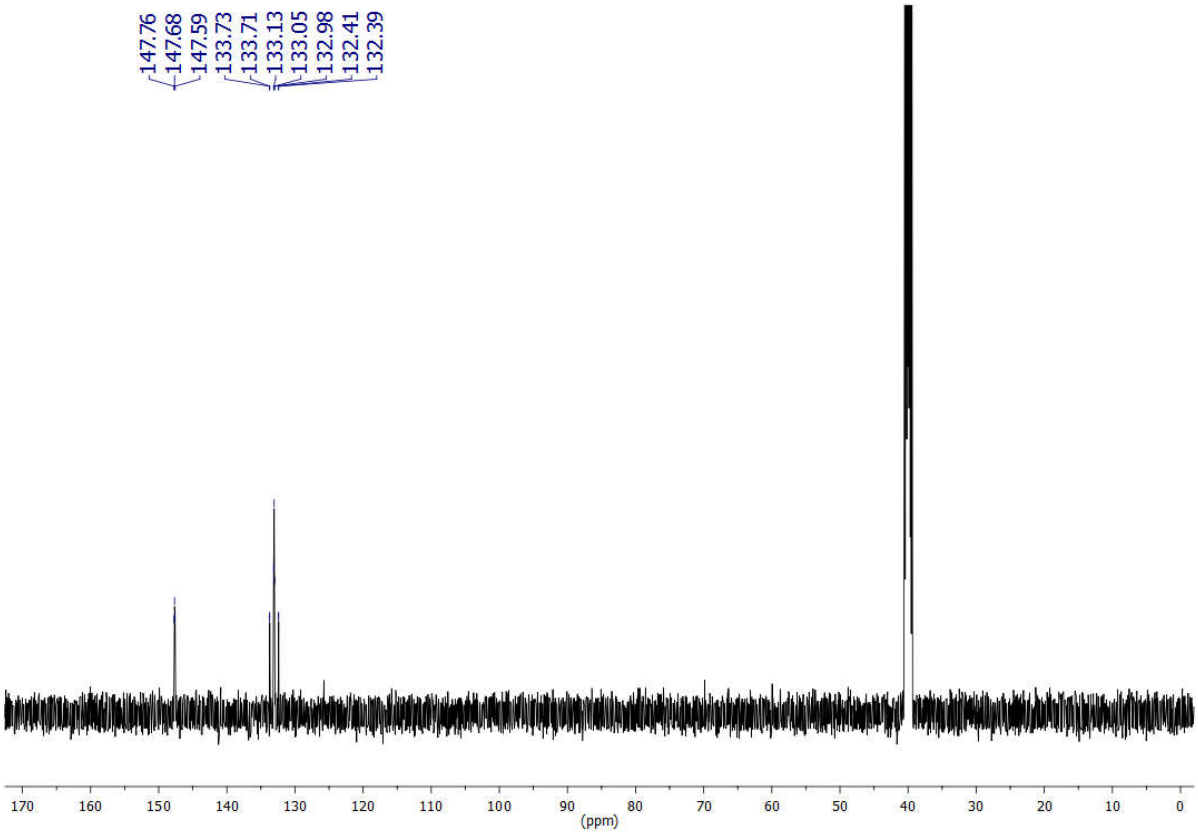
MS (ESI_{neg}): *m/z* = 795 $[2M-H]^-$, 397 $[M-H]^-$, 379 $[M-H_3O]^-$.

IR (ATR): $\tilde{\nu}$ = 2796, 2250, (br., OH), 1683 (H_3O^+) cm^{-1}.

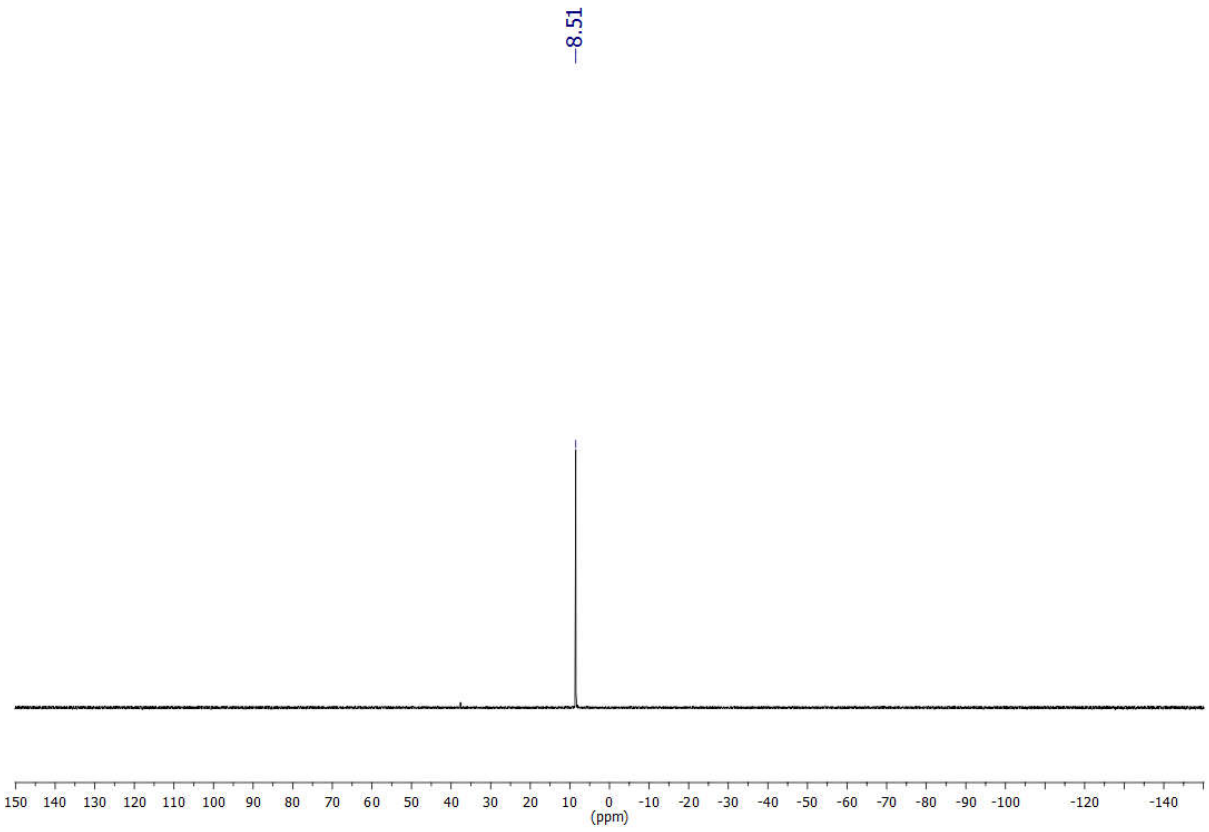
EA ($C_6H_8O_{12}P_2S_2$) (398.20): calcd. C 18.10 H 2.03 S 16.11;
($C_6H_8O_{12}P_2S_2 \cdot 0.4H_2O \cdot 0.2C_2H_6O$) (414.62): calcd. C 18.54 H 2.43 S 15.47;
found C 18.67 H 2.30 S 15.58.



^{1}H-NMR (500 MHz, 300 K, DMSO-d6) of **26**

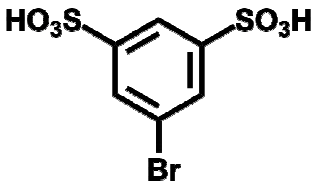


^{13}C-NMR (125 MHz, 300 K, DMSO-d6) of **26**



^{31}P-NMR (202 MHz, 300 K, DMSO-d6) of **26**

5-Bromobenzene-1,3-disulfonic acid (13)



To conc. sulfuric acid (40 mL) was added benzene-1,3-disulfonic acid disodium salt (**12**, 10.0 g, 35.44 mmol) and the suspension was stirred until everything was dissolved. *N*-bromosuccinimide (6.94 g, 38.98 mmol) was added in portions and the reaction mixture was stirred for 12 h at room temp..The solution was poured into water (500 mL) and neutralized with calcium hydroxide. Undissolved calcium sulfate was removed by filtration. After removing the water in vacuo, the residue was dried in a vacuum oven at 60 °C for 12 h. To remove impurities of unreacted benzene-1,3-disulfonic acid disodium salt, the residue was dissolved in water (250 mL) and tetra-*n*-butylammonium bromide (25.1 g, 77.88 mmol) was added. The aqueous solution was extracted with dichloromethane (3 x 150 mL) and the organic layer was dried with magnesium sulfate. After removing the solvent in vacuo, the residue was dissolved in acetone (50 mL) and mixed with four equivalents of sodium iodide (21.22 g, 141.6 mmol) dissolved in acetone (100 mL). The precipitate was collected by filtration and washed with

acetone (250 mL). To exchange the sodium ions, the residue was dissolved in water and rinsed over a column filled with ion-exchange resin (Dowex 50WX8 hydrogen form). The eluate was concentrated and dried for 24 h at 60 °C in a vacuum oven, to yield a colourless solid.

Yield: 9.34 g (29.5 mmol, 83 %)

M. p.: 134 °C

^{1}H-NMR (500 MHz, 300 K, DMSO-d6): δ = 7.84 (t, ^{4}J = 1.4 Hz, 1H, Ar-2-*H*), 7.63 (d, ^{4}J = 1.4 Hz, 2H, Ar-4,6-*H*), 6.80 (br. s, 2H, SO_3H) ppm.

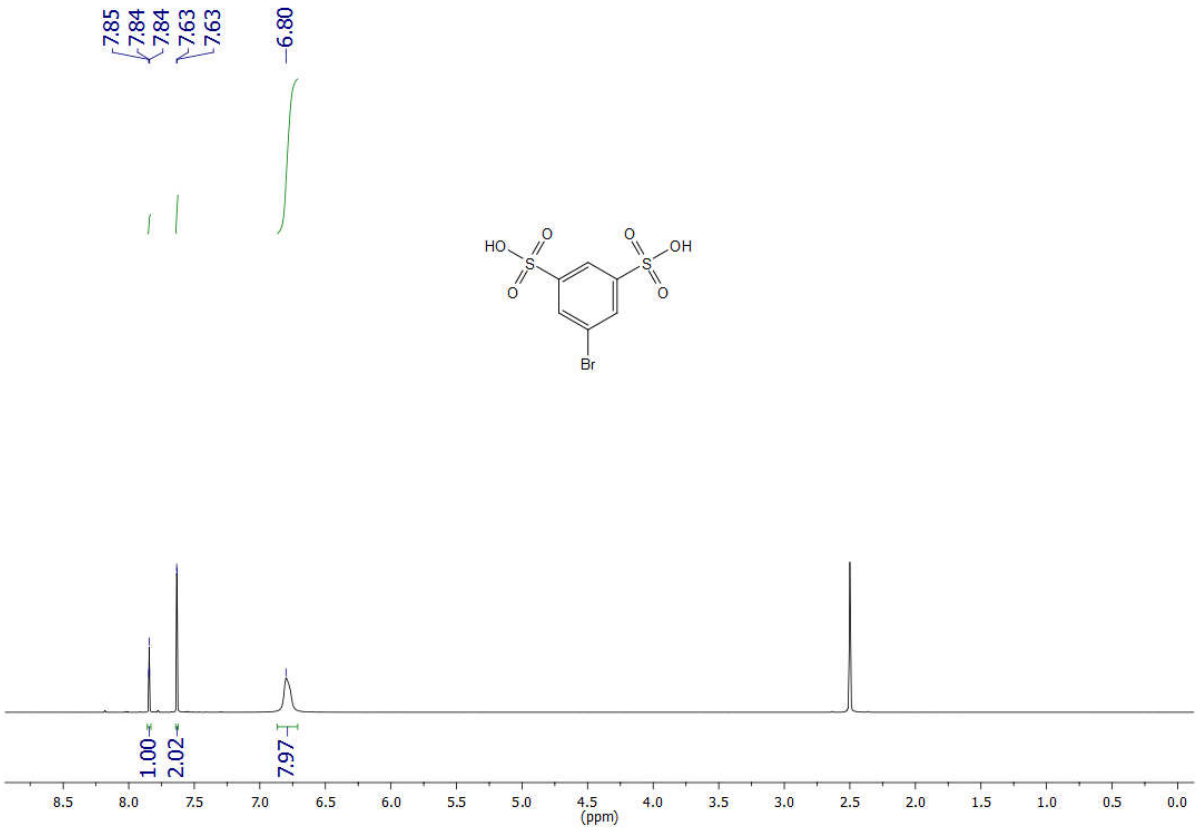
^{13}C-NMR (125 MHz, 300 K, DMSO-d6): δ = 150.0 (s, Ar-1,3-*C*), 128.1 (d, Ar-4,6-*C*), 122.0 (d, Ar-2-*C*), 120.1 (s, Ar-5-*C*) ppm.

MS (EI): *m/z* = 318, 316 (100, 94) $[M]^{+\cdot}$.

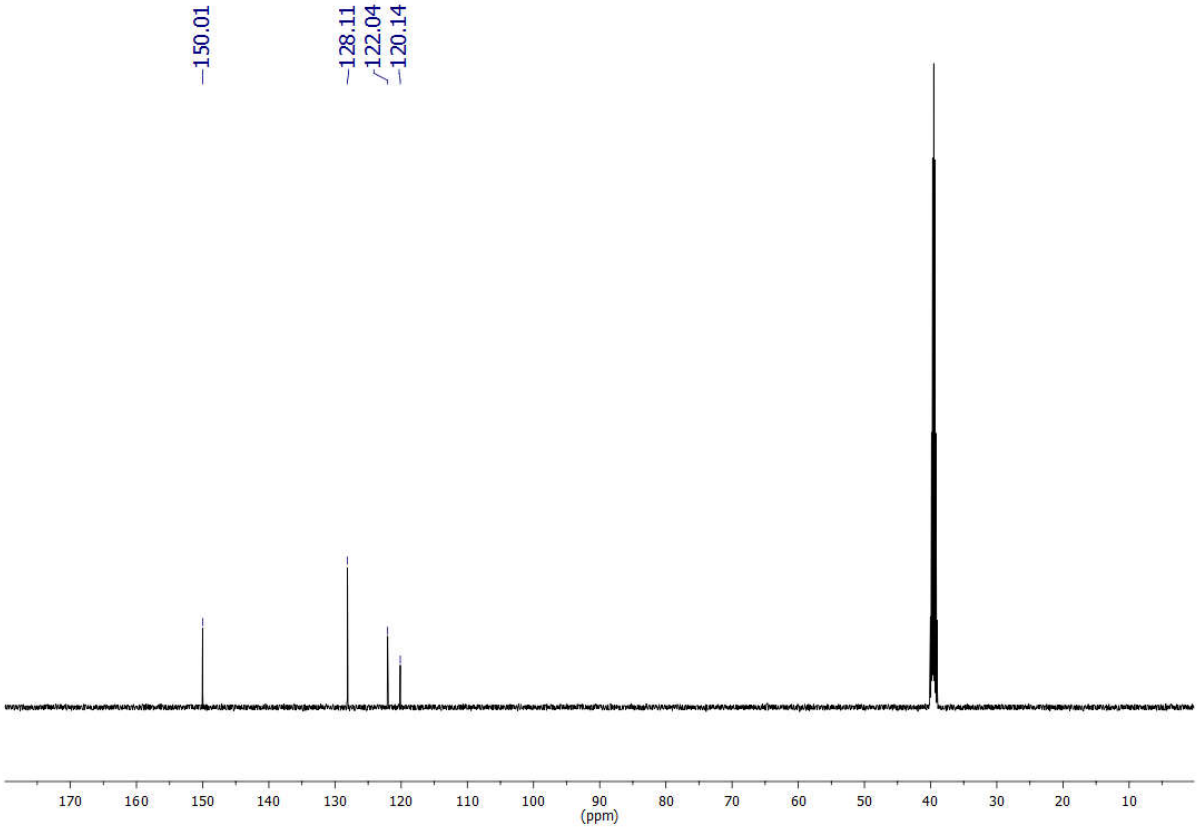
HRMS (EI): *m/z* = $C_6H_5{}^{79}BrO_6S_2$ calcd. 315.8711; found 315.8705 (Δ 1.8 ppm);
$C_6H_5{}^{81}BrO_6S_2$ calcd. 317.8690; found 317.8686 (Δ 1.5 ppm).

IR (ATR): $\tilde{\nu}$ = 3081 (aryl-H val.), 2634, 2187, (br., OH), 1685 (H_3O^+) 1568 (arom. C=C) cm^{-1}.

EA ($C_6H_5BrO_6S_2$) (317.13): calcd. C 22.72 H 1.59 S 20.22;
($C_6H_5BrO_6S_2 \cdot 2\ H_2O$) (353.16): calcd. C 20.41 H 2.57 S 18.16;
found C 20.58 H 2.49 S 17.98.

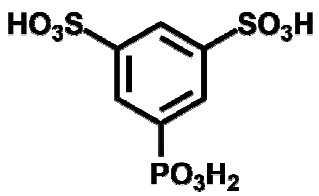


^{1}H-NMR (500 MHz, 300 K, DMSO-d6) of **13**



^{13}C-NMR (125 MHz, 300 K, DMSO-d6) of **13**

5-Phosphonobenzene-1,3-disulfonic acid (23)



5-Bromobenzene-1,3-disulfonic acid (**13**, 992 mg, 2.75 mmol) dissolved in water (20 mL) was treated with aqueous tetra-*n*-butylammonium hydroxide (40 % in water) until pH = 7 was reached. The solvent was removed in vacuo and the residue was dried in a vacuum oven at 60 °C for 12 h to obtain the respective tetra-*n*-butylammonium salt. Two microwave vials were charged with salt (2 x 1.09 g, 2 x 1.37 mmol), palladium(II) chloride (2 x 24 mg, 2 x 137 µmol) and triethyl phosphite (2 x 4 mL, 2 x 16.7 mmol). The vials were irradiated in a microwave oven (max. 200 W, 220 °C) for 60 min. The combined solution was added to a mixture of ethyl acetate (100 mL) and water (100 mL) in a separatory funnel. The aqueous layer was washed with ethyl acetate (3 x 100 mL) and water was removed in vacuo. The residue was dissolved in a mixture of water (20 mL) and conc. hydrochloric acid (40 mL) and stirred for 12 h at 120 °C. After removing the solvent in vacuo, the residue was dissolved in acetone (25 mL) and mixed with five equivalents of sodium iodide (1.65 g, 10.99 mmol) dissolved in acetone (20 mL). The precipitate was collected by filtration and washed with ethanol (150 mL). To exchange the sodium ions, the residue was dissolved in water and rinsed over a column filled with ion-exchange resin (Dowex 50WX8 hydrogen form). The eluate was concentrated and dried for 24 h at 60 °C in a vacuum oven, to yield a colourless solid.

Yield: 684 mg (2.15 mmol, 78 %)

M. p.: 225 °C

^{1}H-NMR (500 MHz, 300 K, DMSO-d6): δ = 8.76 (br. s, 4H, PO_3H_2, SO_3H), 7.99 (dt, ^{4}J = 1.7 Hz, $^{5}J_{H\text{-}P}$ = 1.0 Hz, 1H, Ar-2-*H*), 7.91 (dd, $^{3}J_{H\text{-}P}$ = 13.0 Hz, ^{4}J = 1.7 Hz, 1H, Ar-4,6-*H*) ppm.

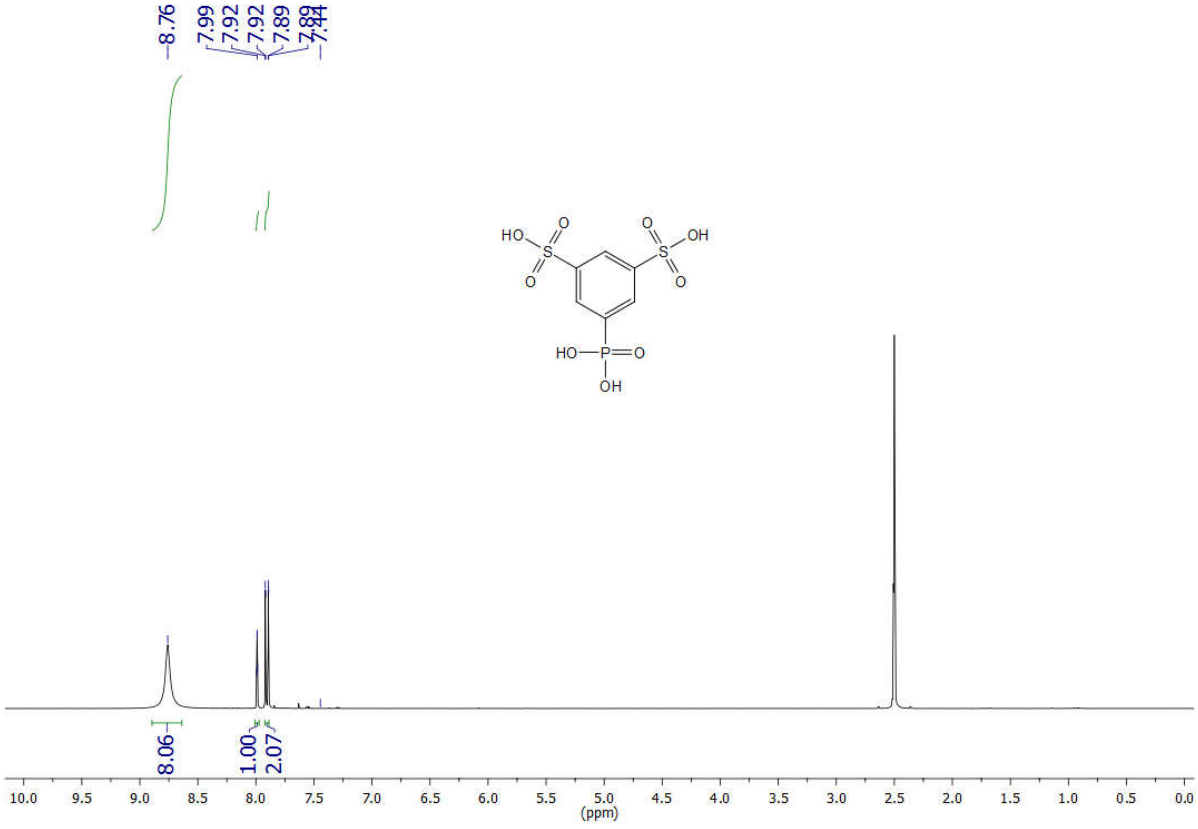
^{13}C-NMR (125 MHz, 300 K, DMSO-d6): δ = 147.5 (s[d_P], $^{3}J_{C\text{-}P}$ = 13.8 Hz, Ar-1,3-*C*), 133.06 (s[d_P], $^{1}J_{C\text{-}P}$ = 180.0 Hz, Ar-5-*C*), 127.9 (d[d_P], $^{2}J_{C\text{-}P}$ = 11.2 Hz, Ar-4,6-*C*), 125.4 (d[d_P], $^{4}J_{C\text{-}P}$ = 2.5 Hz, Ar-2-*C*) ppm.

^{31}P-NMR (202 MHz, 300 K, DMSO-d6): 12.2 (s, 1P, PO_3H_2) ppm.

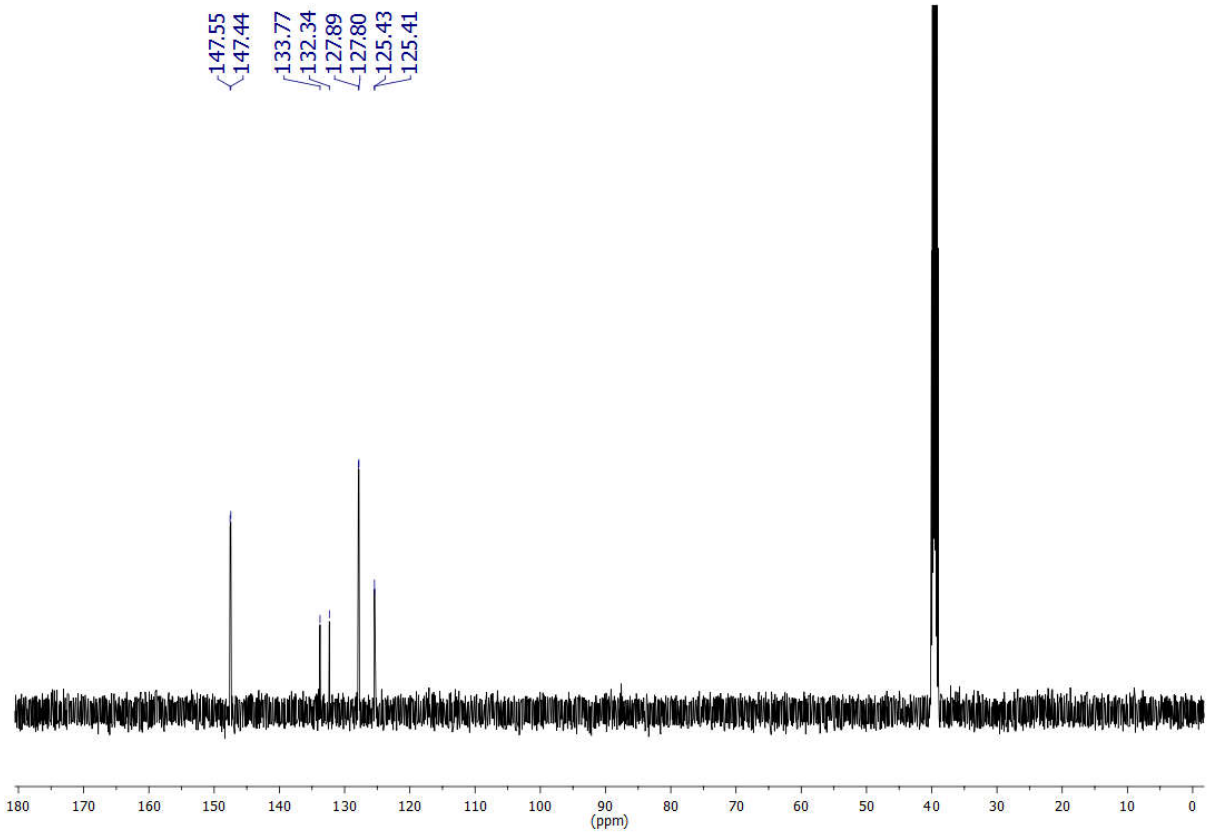
MS (ESI_{neg}): *m/z* = 635 $[2M - H]^-$, 317 $[M - H]^-$, 299 $[M - H_3O]^-$.

IR (ATR): $\tilde{\nu}$ = 2743, 2198 (br., OH), 1684 (H_3O^+), 1588 (arom. C=C) cm^{-1}.

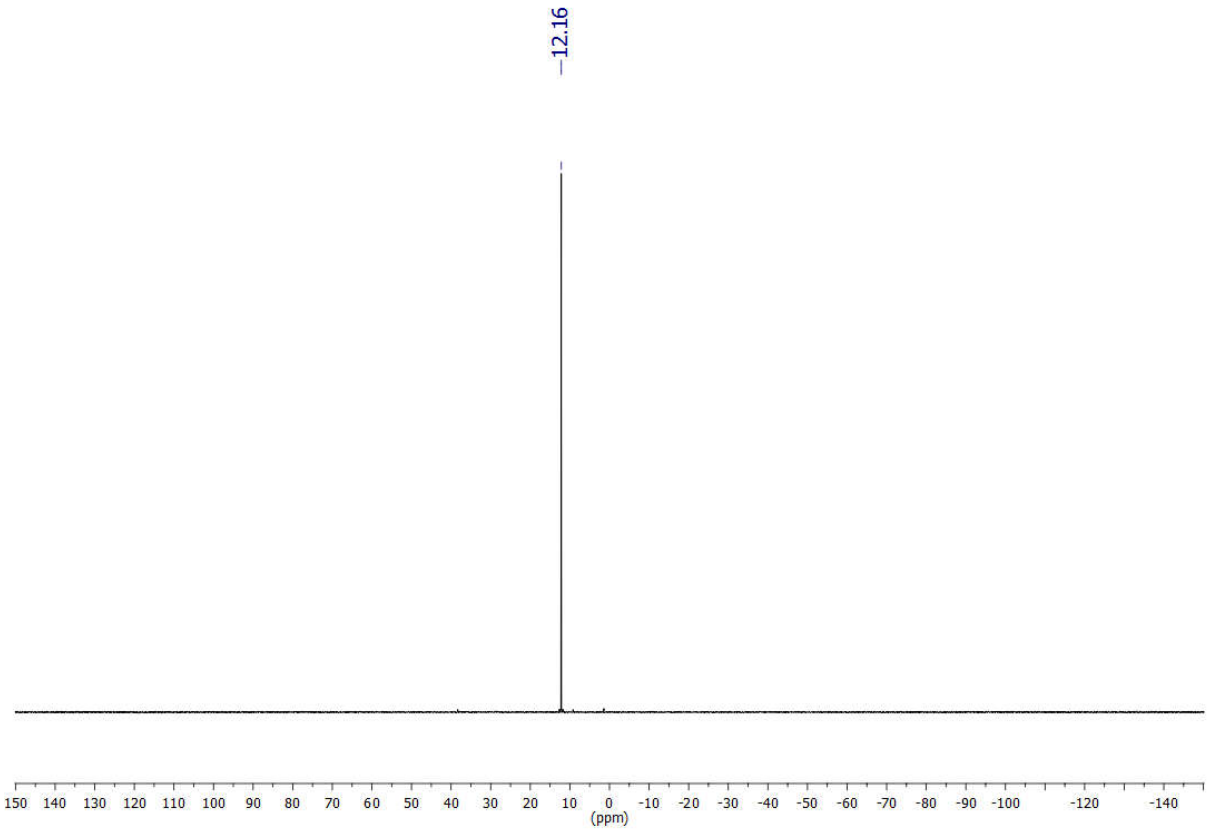
EA ($C_6H_7O_9PS_2$) (318.22): calcd. C 22.65 H 2.22 S 20.15;
($C_6H_7O_9PS_2 \cdot 1\ H_2O$) (336.23): calcd. C 21.43 H 2.70 S 19.07;
found C 21.25 H 2.63 S 18.94.



^{1}H-NMR (500 MHz, 300 K, DMSO-d6) of **23**

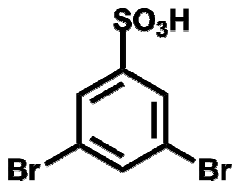


^{13}C-NMR (125 MHz, 300 K, DMSO-d6) of **23**



^{31}P-NMR (202 MHz, 300 K, DMSO-d6) of **23**

3,5-Dibromobenzenesulfonic acid (16)



Under nitrogen, 3,5-dibromo-1-(trimethylsilyl)benzene (**14**, 2.86 g, 9.28 mmol) was dissolved in 1,2-dichloroethane (20 mL) and trimethylsilyl chlorosulfonate (1.86 mL, 12.08 mmol) was added. The reaction mixture was stirred for 2 d at 90 °C. After adding 2 M aqueous sodium hydroxide (15 mL), the mixture was stirred at room temp. for 1 h. Water (100 mL) and dichloromethane (100 mL) were added and the aqueous layer was washed with dichloromethane (3 x 100 mL). The aqueous layer was treated with conc. sulfuric acid until pH = 7 was reached. Tetra-*n*-butylammonium iodide (5.15 g, 13.9 mmol) was dissolved in the aqueous layer to transfer the product ions into the organic layer by extraction with dichloromethane (3 x 100 mL). After drying with magnesium sulfate, the solvent was removed in vacuo. The residue was dissolved in acetone (20 mL) and mixed with two equivalents of sodium iodide (2.78 g, 18.58 mmol) dissolved in acetone (30 mL). A precipitate formed within 12 h and was separated by filtration. To exchange the sodium ion, the residue was dissolved in water and rinsed over a column filled with ion-exchange resin (Dowex 50WX8 hydrogen form). The eluate was concentrated and dried for 24 h at 60 °C in a vacuum oven, to yield a colourless solid.

Yield: 2.49 g (7.88 mmol, 85 %)

M. p.: 133 °C

^{1}H-NMR (500 MHz, 300 K, DMSO-d6): δ = 7.80 (t, ^{4}J = 1.8 Hz, 1H, Ar-4-*H*), 7.68 (d, ^{4}J = 1.8 Hz, 2H, Ar-2,6-*H*), 7.66 (br. s, 1H, SO_3H) ppm.

^{13}C-NMR (125 MHz, 300 K, DMSO-d6): δ = 151.9 (s, Ar-1-*C*), 133.4 (d, Ar-4-*C*), 127.5 (d, Ar-2,6-*C*), 122.0 (s, Ar-3,5-*C*) ppm.

MS (EI): *m/z* = 318, 316, 314 (52, 100, 50) $[M]^{+\cdot}$, 237, 235, 233 (13, 31, 16) $[M - HO_3S]^{+\cdot}$.

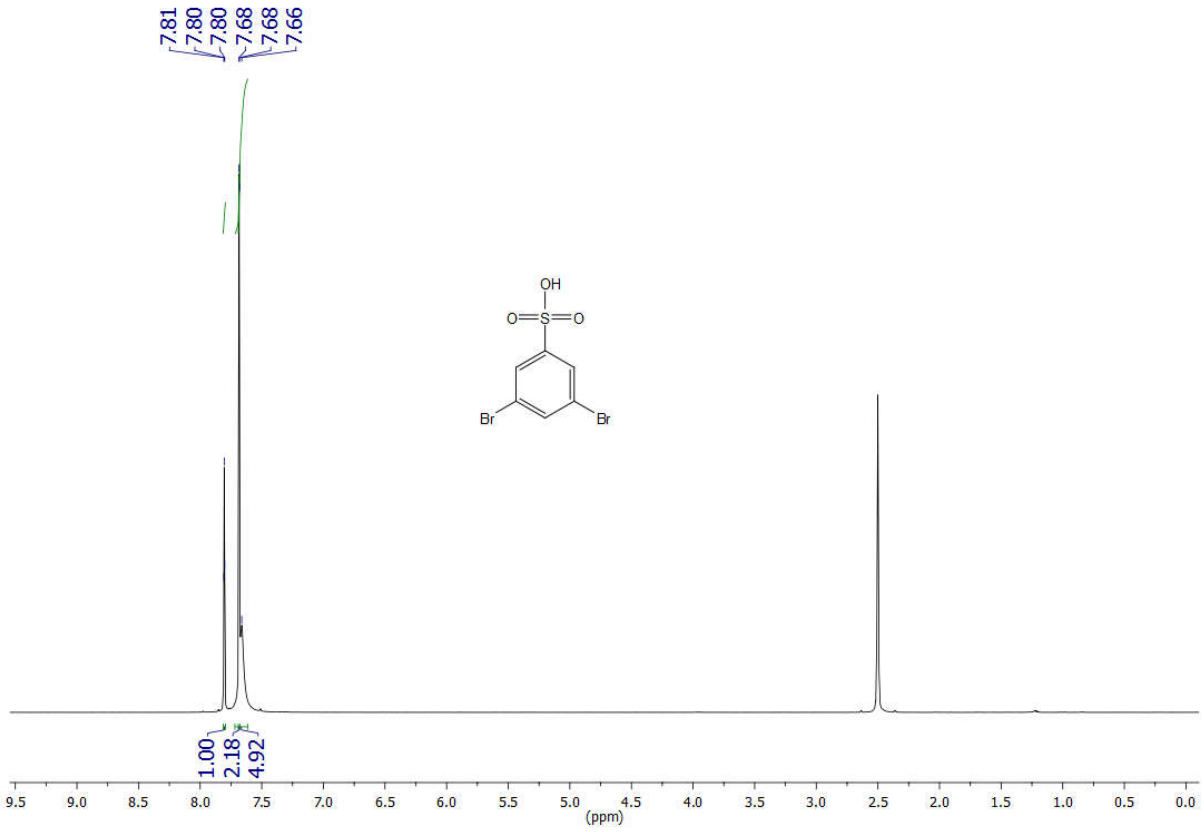
HRMS (EI): *m/z* = $C_6H_4{}^{79}Br_2O_3{}^{34}S$ calcd. 315.8206; found 315.8212 (Δ 1.8 ppm);
$C_6H_4{}^{79}Br\,{}^{81}BrO_3S$ calcd. 315.8227; found 315.8212 (Δ 5.0 ppm).

IR (ATR): $\tilde{\nu}$ = 3065 (aryl-H val.), 2554, 2187 (br., OH), 1666 (H_3O^+), 1560 (arom. C=C) cm^{-1}.

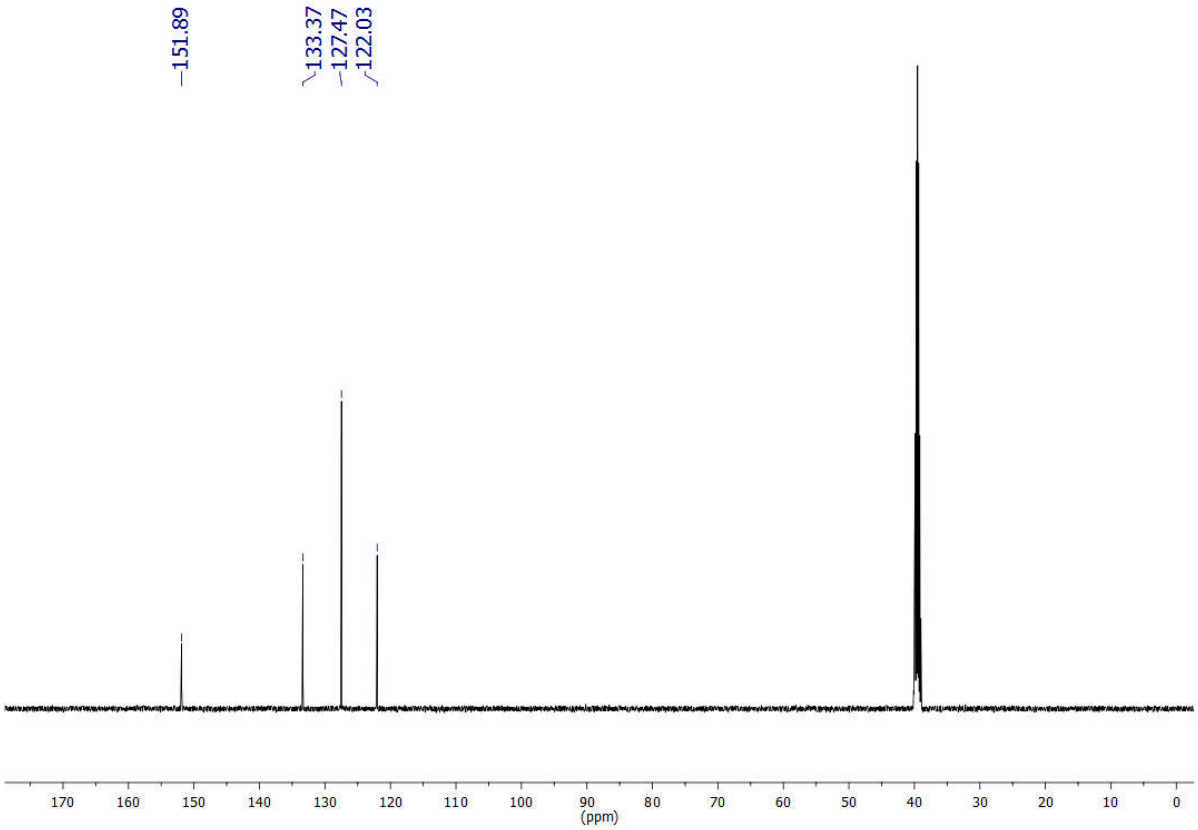
EA ($C_6H_4Br_2O_3S$) (315.97): calcd. C 22.81 H 1.28 S 10.15;

($C_6H_4Br_2O_3S \cdot 1\ H_2O$) (333.98): calcd. C 21.58 H 1.81 S 9.60;

found C 21.82 H 1.69 S 9.77.

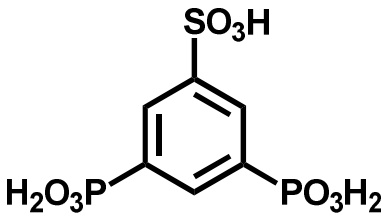


^{1}H-NMR (500 MHz, 300 K, DMSO-d6) of **16**



^{13}C-NMR (125 MHz, 300 K, DMSO-d6) of **16**

3,5-Diphosphonobenzenesulfonic acid (24)



3,5-Dibromobenzenesulfonic acid (**16**, 1.76 g, 5.59 mmol) dissolved in water (40 mL) was treated with aqueous tetra-*n*-butylammonium hydroxide (40 % in water) until pH = 7 was reached. The solvent was removed in vacuo and the residue was dried in a vacuum oven at 60 °C for 12 h to obtain the respective tetra-*n*-butylammonium salt. Three microwave vials were charged with salt (3 x 1.03 g, 3 x 1.86 mmol), palladium(II) chloride (3 x 33 mg, 3 x 186 µmol) and triethyl phosphite (3 x 4 mL, 3 x 16.7 mmol). The vials were irradiated in a microwave oven (max. 200 W, 220 °C) for 60 min. The combined solution was added to a mixture of ethyl acetate (100 mL) and water (100 mL) in a separatory funnel. The aqueous layer was washed with ethyl acetate (3 x 100 mL) and water was removed in vacuo. The residue was dissolved in a mixture of water (40 mL) and conc. hydrochloric acid (80 mL) and stirred for 12 h at 120 °C. After removing the solvent in vacuo, the residue was dissolved in acetone (40 mL) and mixed with four equivalents of sodium iodide (3.35 g, 22.38 mmol)

dissolved in acetone (20 mL). The precipitate was collected by filtration and washed with ethanol (150 mL). To exchange the sodium ions, the residue was dissolved in water and rinsed over a column filled with ion-exchange resin (Dowex 50WX8 hydrogen form). The eluate was concentrated and dried for 24 h at 60 °C in a vacuum oven, to yield a colourless solid.

Yield: 1.11 g (3.49 mmol, 62 %)

M. p.: 292 °C

^{1}H-NMR (500 MHz, 300 K, DMSO-d6): δ = 9.91 (br. s, 5H, PO_3H_2, SO_3H), 8.06 (m_c, 2H, Ar-2,6-*H*), 7.96 (tt, $^{3}J_{H\text{-}P}$ = 12.6 Hz, ^{4}J = 1.4 Hz, 1H, Ar-4-*H*) ppm.

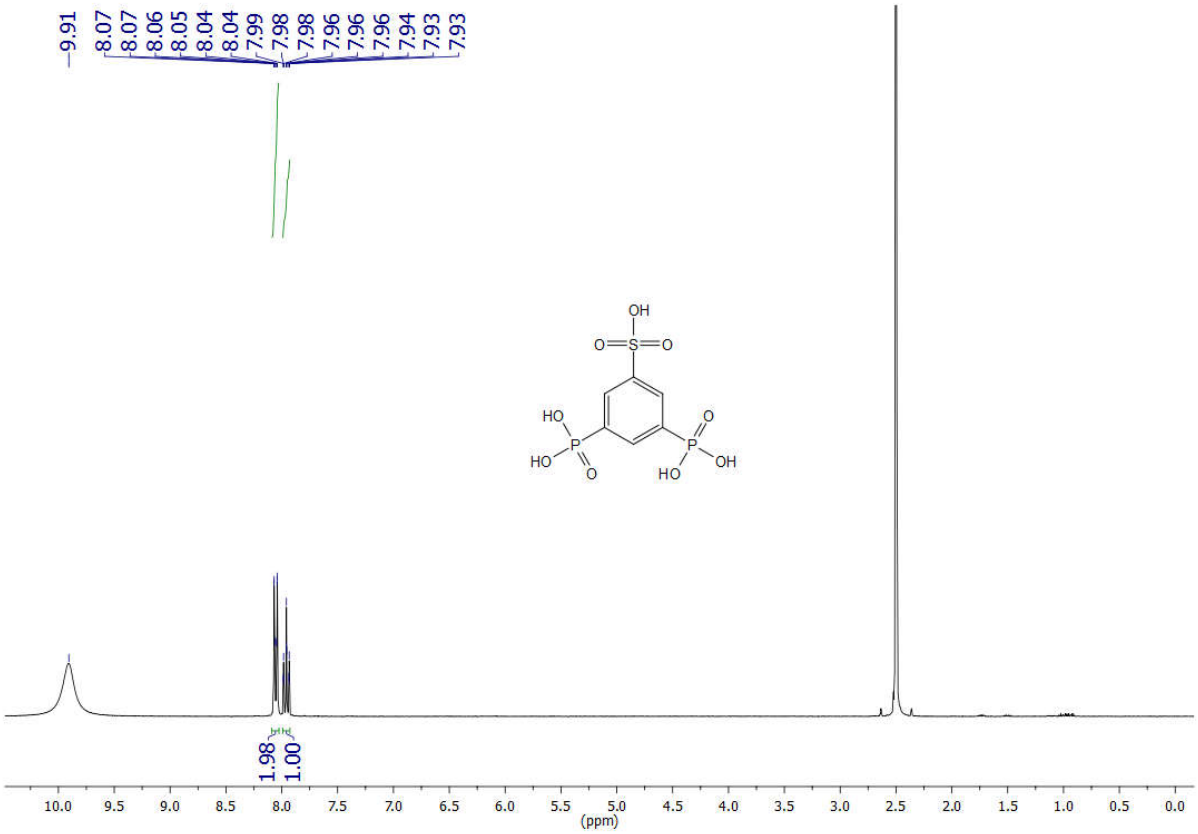
^{13}C-NMR (125 MHz, 300 K, DMSO-d6): δ = 147.8 (s[t_P], $^{3}J_{C\text{-}P}$ = 13.2 Hz, Ar-1-*C*), 133.7 (s[d_Pd_P], $^{1}J_{C\text{-}P}$ = 180.1 Hz, $^{3}J_{C\text{-}P}$ = 12.7 Hz, Ar-3,5-*C*), 132.6 (d[t_P], $^{2}J_{C\text{-}P}$ = 10.8 Hz, Ar-4-*C*), 130.0 (d[m_P], Ar-2,6-*C*) ppm.

^{31}P-NMR (202 MHz, 300 K, DMSO-d6): 11.6 (s, 2P, PO_3H_2) ppm.

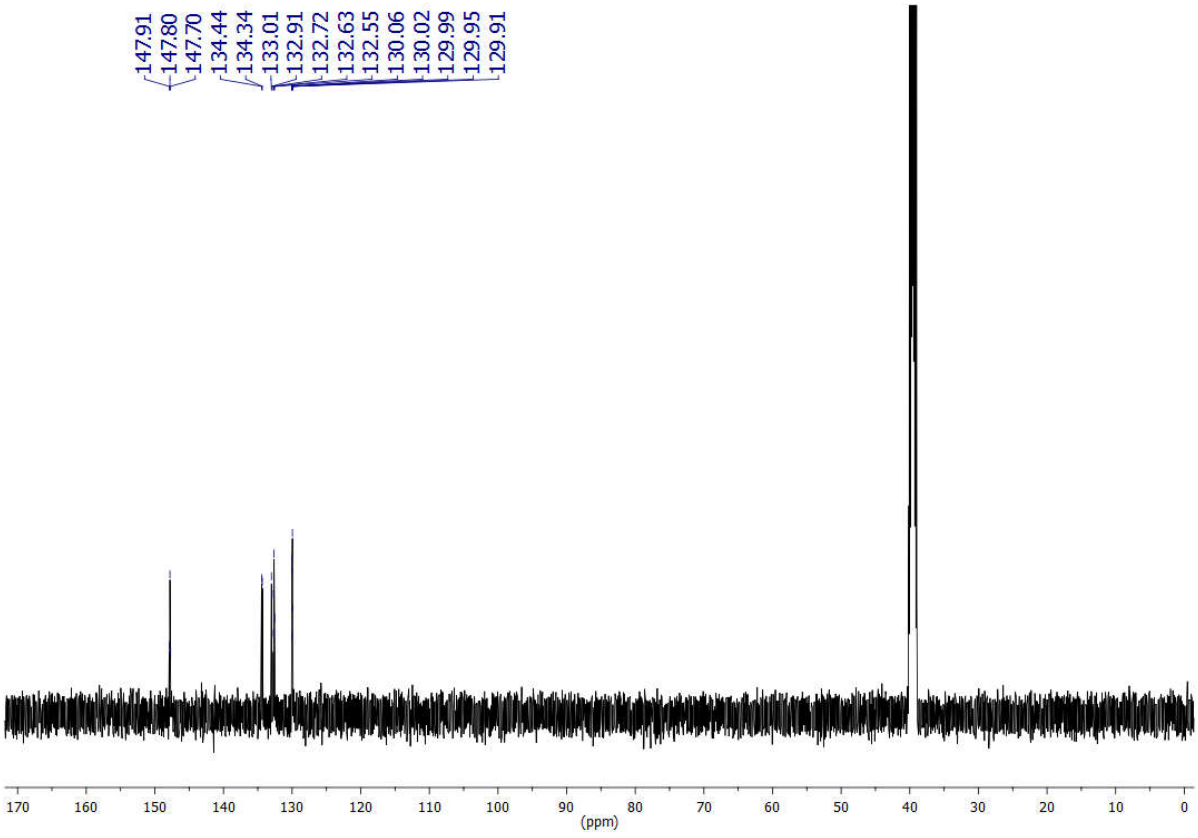
MS (ESI_{neg}): *m/z* = 317 $[M-H]^-$.

IR (ATR): $\tilde{\nu}$ = 3074 (aryl-H val.), 2657, 2226 (br., OH), 1587 (arom. C=C) cm^{-1}.

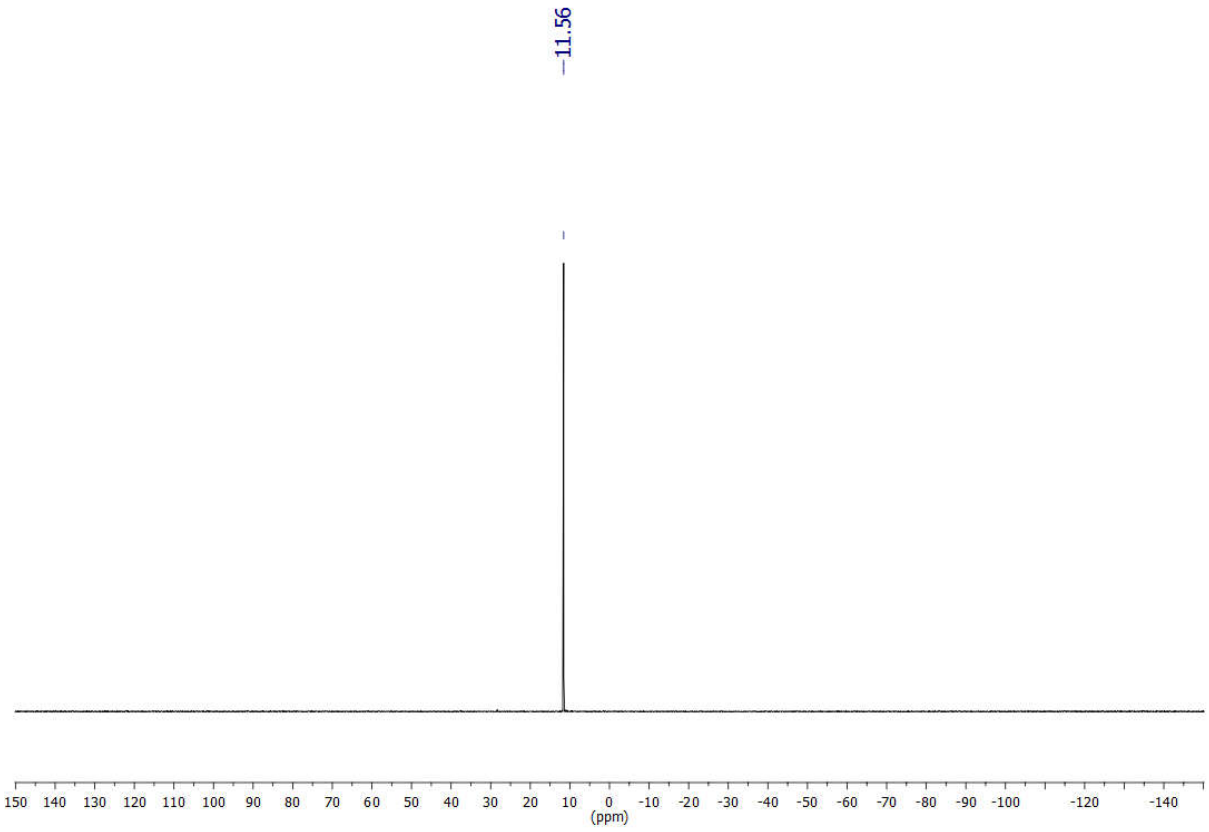
EA ($C_6H_8O_9P_2S$) (318.13): calcd. C 22.65 H 2.53 S 10.08;
found C 22.70 H 2.54 S 10.03.



^{1}H-NMR (500 MHz, 300 K, DMSO-d6) of **24**



^{13}C-NMR (125 MHz, 300 K, DMSO-d6) of **24**



^{31}P-NMR (202 MHz, 300 K, DMSO-d6) of **24**

2. Synthesis and characterization of $[La_4(H_2L)_3(H_2O)_8]$

Synthesis procedure

The system La^{3+}/ 2,5-bis(phosphonomethyl)-benzene-1,4-diyl-bis(methylsulfonic acid) (H_6L, compound (**9**)/ H_2O was investigated under solvothermal reaction conditions using a custom made multiclave reactor containing 24 PTFE vessels each with a maximum volume of 2 mL.[4] The multiclave reactor was heated in a Memmert UFP400 oven (forced air circulation). In total, 120 experiments were performed varying the metal source as well as the metal to linker ratio and the reaction temperature. The optimized reaction procedure is as following: a mixture of $La(NO_3)_3$ $6H_2O$ (14.7 mg, 340 µmol) and 5-bis(phosphonomethyl)-benzene-1,4-diyl-bis(methylsulfonic acid) (**9**, 15.4 mg, 340 µmol) in 1.0 mL H_2O was heated to 160 °C in 2 h. After 84 h at the desired reaction temperature, the oven was cooled down to room temperature within 12 h. This procedure led to single crystals of $[La_4(H_2L)_3(H_2O)_8]$. The reaction products were filtered off, washed with water and dried in air.

Structure solution and refinement

The crystal structure of $[La_4(H_2L)_3(H_2O)_8]$ was determined from single-crystal X-ray diffraction data. X-ray diffraction measurements were performed on a Stoe IPDS diffractometer equipped with an image-plate detector using Mo-K_α radiation (λ=71.073 pm). The crystal structure was solved in the space group *C2/m* by direct methods with the program SHELXT-2014 and refined using the program SHELXL-2014[5]. The functional groups $–SO_3^-$ and $–PO_3H^-$ have very similar coordination properties and in addition, phosphorus and sulfur can hardly be distinguished by X-ray diffraction due to the very similar scattering power. In our structure refinement, the linker molecules are located on special positions (Wyckoff letter 4i and 2a with site symmetry *m* and *2/m*, respectively) and thus the atomic positions of the P/S atoms were refined with an occupancy of 0.5 each, utilizing the EADP and EXYZ commands. Numerical absorption correction was carried out by using XShape and XRed[6]. The pores contained continuous ribbons of diffuse electron density, probably from disordered water molecules. The electron density inside the pores (285 electrons) was removed via the SQUEEZE command using Platon[7]. Hydrogen atoms could not be localized and were refined using a riding model.

Table S1 Results of the crystal structure determination of $[La_4(H_2L)_3(H_2O)_8]$.

Crystal system	monoclinic
Space group	*C2/m*
a (Å)	20.047(4)
b (Å)	11.357(2)
c (Å)	18.677(4)
α (°)	90
β (°)	118.51(3)
γ (°)	90
V (Å³)	3736.3(16)
Z	4
Abs. coeff. (mm^{-1})	2.626
Crystal size (mm)	0.133 x 0.106 x 0.06
Reflections collected Symmetry independent	19490 / 4470
R_{int}	0.0691
No. of parameters	217
R1 [$I > 2\sigma(I)$], R1 (all data)	0.0667, 0.0724
wR2 [$I > 2\sigma(I)$], *wR2* (all data)	0.1654, 0.1685
Largest diff. peak (e $Å^{-1}$)	-1.91 / 1.52

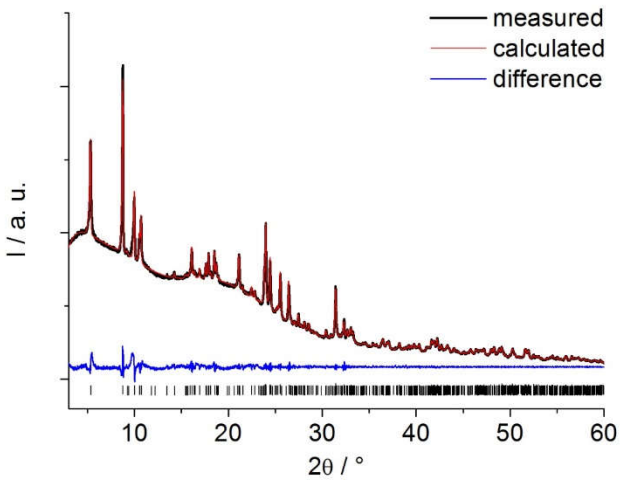


Figure S1: Pawley-Fit of $[La_4(H_2L)_3(H_2O)_8]$. Measured and calculated PXRD data, the difference of both and the allowed reflections are shown in black, red, blue and as black bars, respectively.

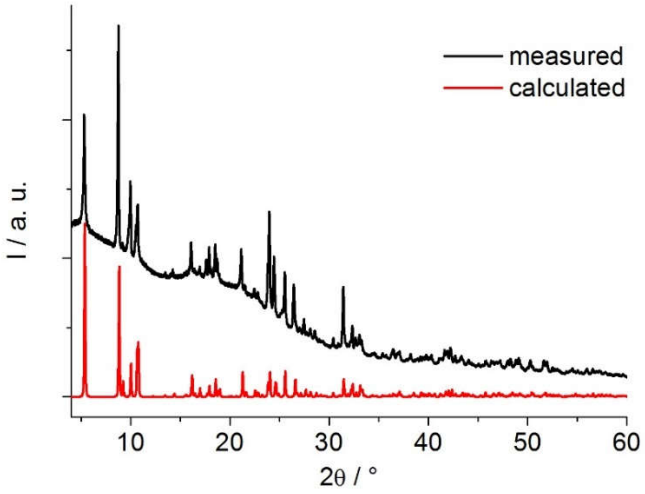


Figure S2: Comparison of the theoretical with the measured PXRD pattern $[La_4(H_2L)_3(H_2O)_8]$.

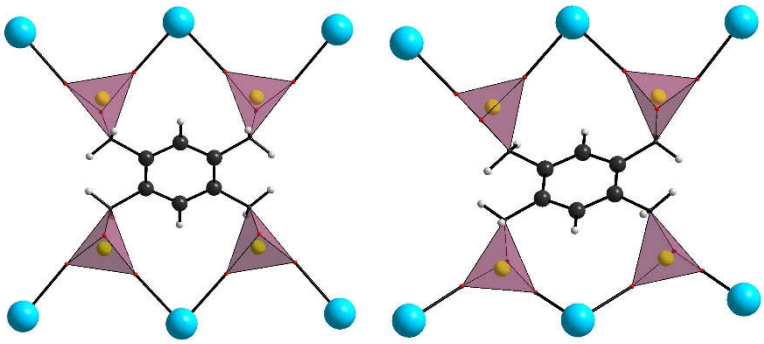


Figure S3: Representation of the two crystallographically independent linker molecules connecting six La^{3+} ions each via sulfonate/phosphonate groups. Lanthanum atoms are shown in teal, oxygen atoms in red, sulfur / phosphor in yellow, carbon atoms in black and hydrogen in white.

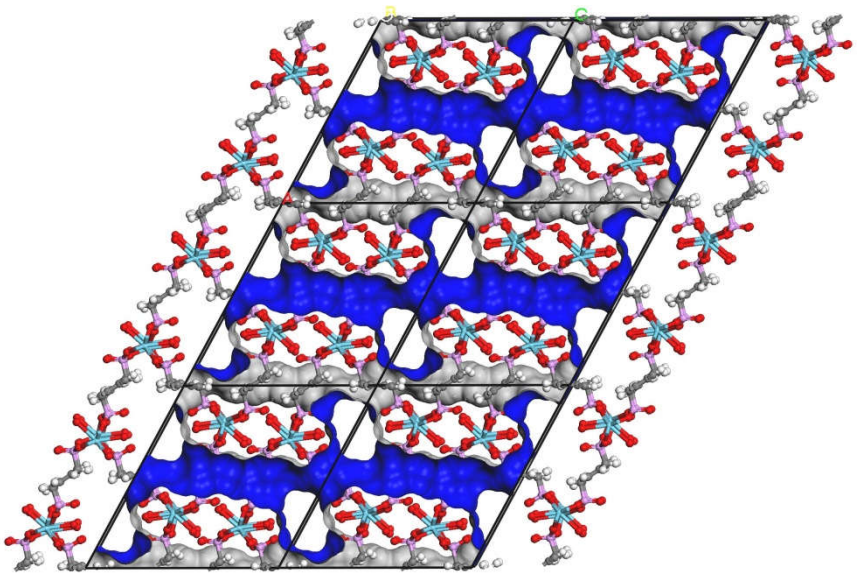


Figure S4: Representation of 1D channels in [$La_4(H_2L)_3(H_2O)_8$**]** along the *b* axis and *c* axis and their connection. Lanthanum atoms are shown in teal, oxygen atoms in red, and carbon atoms in gray (view along [001]. The Connolly surface was calculated with a probe diameter of 2.6 Å (kinetic diameter of H_2O) using the program Materials Studio and is shown in blue/gray.[8]

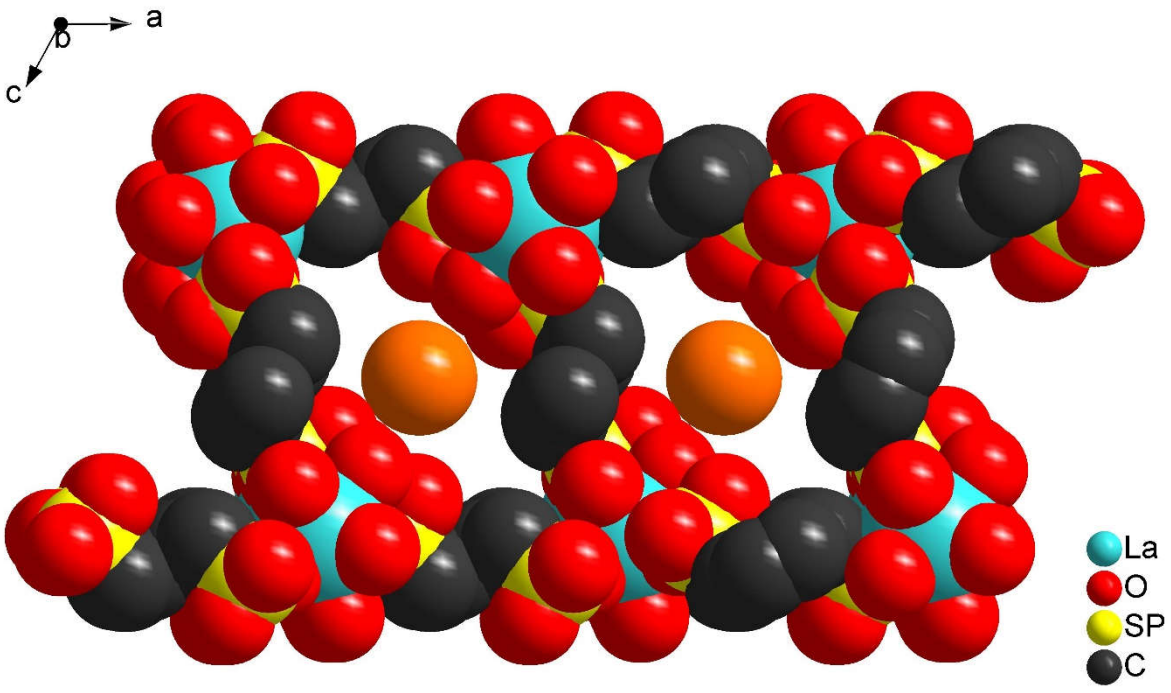


Figure S5: Space filling representation of 1D channels in [$La_4(H_2L)_3(H_2O)_8$]. along the *b* axis. The orange sphere with a diameter of 3.8 Å is used for easier visualisation. Lanthanum atoms are shown in teal, oxygen atoms in red, sulfur and phosphor in yellow and carbon atoms in black.

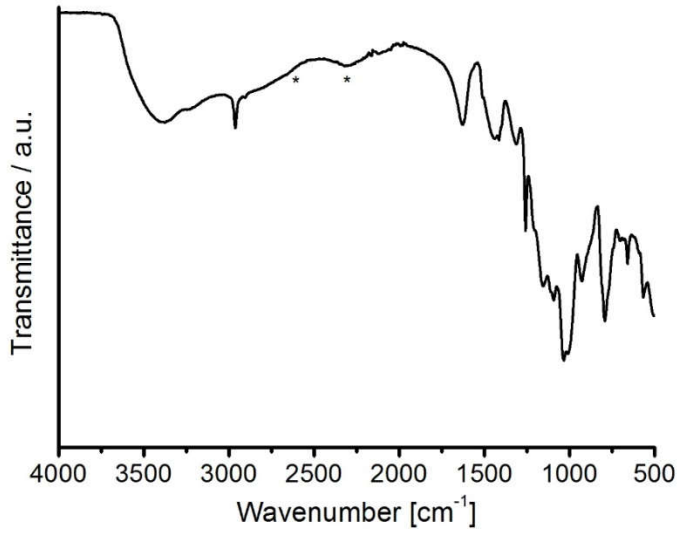


Figure S6: IR spectrum of $[La_4(H_2L)_3(H_2O)_8]$. A broad band between 4000 and ~2500 cm^{-1} is visible and most likely attributed to water molecules as suggested by single-crystal X-ray diffraction. In addition, C-H stretching vibrations of the CH_2 groups are around ~2970 and ~2910 cm^{-1} Within the region of 2650 and 2300 cm^{-1} pronounced signals for the presence of protonated phosphonate groups can be found (marked with a *), which supports the finding of the single-crystal X-ray diffraction data.[9] The sharp Signal at 1630 cm^{-1} is assigned to the deformation vibration of water.

Table S2: Possible hydrogen bonds (D/A distance) within the crystal structure of $[La_4(H_2L)_3(H_2O)_8]$.

Atoms	Atomic distance [Å]
La1-O1・・O10	3.082
La2-O2・・O10	2.976

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