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Synthesis of arsonium salts and betaines based on triphenylarsine and ω-bromoalkanoic acids

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Experimental Section

General remarks. NMR spectra were recorded on the Bruker Avance III instrument with an operating frequency of 122.4 MHz for ^{31}P spectra (external standard 85% H_3PO_4), and an operating frequency of 400 MHz for ^{1}H spectra (internal standard TMS) in a solution of D_2O. IR spectra were recorded on the PerklinElmer UATR Two FT-IR Spectrometer (Spectrum Two). The elemental analysis was carried out on a CHNS analyzer EuroEA3028-HT-OM (Eurovector SpA, Italy). The samples were weighed on Sartorius CP2P (Germany) microbalances in tin capsules. Callidus 4.1 software was used to perform quantitative measurements and evaluate the data received. All chemicals purchased from Sigma-Aldrich were reagent grade and used without purification.

Samples of triphenylarsine and ω-haloalkanoic acids were melted at a temperature 100 °C in a water bath with reflux condenser for 25-55 h. Upon completion of the reaction, the formed oil was washed with diethyl ether. Arsonium salts were dissolved in acetonitrile and titrated with sodium hydroxide solution whose volume was controlled with phenolphthalein. The solvent was distilled in a Schott funnel. The residue was dissolved in acetonitrile, and sodium bromide precipitate was filtered off. The solvent was distilled off from the filtrate, and betaine residue was washed with diethyl ether and dried in vacuum.

Samples of triphenylphosphine and 2,3-dibromopropionic acid were melted at a temperature 100 °C in a water bath with reflux condenser for 1 hour.

(5-Carboxypentyl)trimethylarsonium bromide ***1a***

Colorless crystals, mp 172-177 C, yield: 24%. IR (ν/cm^{-1}): 457, 469, 611, 690, 720, 738, 745, 757, 838, 850, 928, 997, 1021, 1062, 1085, 1106, 1162, 1186, 1206, 1228, 1251, 1309, 1337, 1381, 1437, 1459, 1482, 1705, 2910. ^{1}H NMR spectrum (D_2O) ^{1}H NMR spectrum (D_2O) δ_H, ppm (J/Hz): 1.24–1.43 (m, 4H, $AsCH_2CH_2C\underline{H}_2C\underline{H}_2$), 1.52–1.65 (m, 2H, $AsCH_2C\underline{H}_2$), 2.12 (t, 2H, $As(CH_2)_4C\underline{H}_2$, $^3J_{HH}$ 6.7), 3.20 (t, 2H, $AsCH_2$, $^3J_{HH}$ 6.5), 7.37–7.74 (m, 15H, Ph-As). ^{13}C NMR spectrum (D_2O), δ_C, ppm, 100,6 MHz: 22.29 (s, $As\underline{C}H_2$), 23.37 (s, $AsCH_2\underline{C}H_2$), 23.68 (s, $As(CH_2)_3\underline{C}H_2$), 29.16 (s, $AsCH_2CH_2\underline{C}H_2$), 33.23 (s, $As(CH_2)_4\underline{C}H_2$), 121.06 (s, C^{ipso}), 130.51 (s, C^mH), 132.55 (s, C^oH), 134.01 (s, C^pH), 178.32 (s, COOH). Elemental analysis: Found, %: C 57.65, H 5.46, As 14.76, Br 15.68. $C_{24}H_{26}O_2AsBr$. Calculated, %: C 57.50, H 5.23, As 14.95, Br 15.94.

(7-Carboxyheptyl)triphenylarsonium bromide ***1b***

Colorless crystals, mp 107-112 C, yield: 48%. IR (ν/cm^{-1}): 451, 467, 479, 607, 623, 690, 723, 744, 753, 828, 884, 976, 996, 1022, 1084, 1115, 1163, 1249, 1270, 1289, 1338, 1439, 1460, 1485, 1694, 2011, 2860, 2896, 2935, 3045, 3281. ^{1}H NMR spectrum (D_2O) ^{1}H NMR spectrum (D_2O) δ_H, ppm (J/Hz): 1.06–1.26 (m, 4H, $As(CH_2)_3C\underline{H}_2C\underline{H}_2$), 1.32–1.48 (m, 4H, $AsCH_2C\underline{H}_2C\underline{H}_2$), 1.62–1.73 (m, 2H, $C\underline{H}_2CH_2COOH$), 2.23 (t, 2H, $C\underline{H}_2COOH$, $^3J_{HH}$ 7.5), 3.30 (t, 2H, $AsCH_2$, $^3J_{HH}$ 8.2), 7.59–7.79 (m, 15H, Ph-As). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm, 100,6 MHz: 22.32 (s, $As\underline{C}H_2$), 23.81 (s, $As(CH_2)_5\underline{C}H_2$), 23.94 (s, $AsCH_2\underline{C}H_2$), 27.27 (s, $As(CH_2)_4\underline{C}H_2$), 27.55 (s, $As(CH_2)_3\underline{C}H_2$), 29.36 (s, $AsCH_2CH_2\underline{C}H_2$), 33.68 (s, $As(CH_2)_6\underline{C}H_2$), 121.24 (s, C^{ipso}), 130.34 (s, C^mH), 132.59 (s, C^oH), 133.84 (s, C^pH), 180.03 (s, COOH). Elemental analysis: Found, %: C 59.32, H 5.85, As 14.96, Br 15.15. $C_{26}H_{30}O_2AsBr$. Calculated, %: C 58.99, H 5.71, As 15.16, Br 15.09.

(9-Carboxynonyl)triphenylarsonium bromide ***1c***

Colorless crystals, mp 70 C, yield: 45%. IR (ν/cm^{-1}): 467, 474, 527, 644, 692, 733, 810, 850, 926, 998, 1023, 1066, 1074, 1083, 1101, 1115, 1156, 1185, 1206, 1232, 1258, 1294, 1407, 1431, 1468, 1480, 1578, 1687, 2851, 2916, 2929, 3066. ^{1}H NMR spectrum (D_2O) δ_H, ppm (J/Hz): 0.89–1.06 (m, 8H, As(CH$_2$)$_4$C<u>H$_2$</u>C<u>H$_2$</u>C<u>H$_2$</u>C<u>H$_2$</u>), 1.28 (m, 4H, AsCH$_2$CH$_2$C<u>H$_2$</u>C<u>H$_2$</u>), 1.41 (quintet, 2H, AsCH$_2$C<u>H$_2$</u>, $^3J_{HH}$ 7.8), 1.96 (t, 2H, C<u>H$_2$</u>COOH, $^3J_{HH}$ 7.5), 3.07 (t, 2H, AsC<u>H$_2$</u>, $^3J_{HH}$ 7.9), 7.30 – 7.85 (m, 15H, Ph-As). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm, 100,6 MHz: 21.11 (s, As<u>C</u>H$_2$), 21.48 (s, AsCH$_2$CH$_2$<u>C</u>H$_2$), 25.77 (s, As(CH$_2$)$_3$<u>C</u>H$_2$), 27.69 (s, As(CH$_2$)$_4$<u>C</u>H$_2$), 28.02 (s, As(CH$_2$)$_5$<u>C</u>H$_2$), 28.26 (s, As(CH$_2$)$_6$<u>C</u>H$_2$), 28.60 (s, As(CH$_2$)$_7$<u>C</u>H$_2$), 29.50 (s, AsCH$_2$<u>C</u>H$_2$), 37.57 (s, As(CH$_2$)$_8$<u>C</u>H$_2$), 118.11 (s, C^{ipso}), 130.03 (c, C^{o}H), 133.3 (s, C^{m}H), 134.94 (s, C^{p}H), 183.86 (s, COOH). Elemental analysis: Found, %: C 60.50, H 6.77, As 13.34, Br 14.07. $C_{28}H_{34}O_2AsBr$. Calculated, %: C 60.33, H 6.15, As 13.44, Br 14.34.

6-(Triphenylarsonio)hexanoate ***2a***

Colorless crystals, mp 54 C, yield: 81%. IR (ν/cm^{-1}): 454, 466, 563, 689, 742, 880, 923, 997, 1024, 1045, 1084, 1161, 1186, 1313, 1343, 1393, 1438, 1484, 1563, 2434, 2931, 3180, 3302. ^{1}H NMR spectrum (D_2O) δ_H, ppm (J/Hz): 1.33–1.56 (m, 4H, AsCH$_2$CH$_2$C<u>H$_2$</u>C<u>H$_2$</u>), 1.72 (s, 2H, AsCH$_2$C<u>H$_2$</u>), 1.99–2.15 (m, 2H, C<u>H$_2$</u>COOH), 3.17–3.39 (m, 2H, AsC<u>H$_2$</u>), 7.41–7.90 (m, 15H, Ph-As). ^{13}C NMR spectrum (D_2O), δ_C, ppm, 100,6 MHz: 22.37 (s, As<u>C</u>H$_2$), 23.73 (s, AsCH$_2$CH$_2$<u>C</u>H$_2$), 24.94 (s, As(CH$_2$)$_3$<u>C</u>H$_2$), 29.71 (s, AsCH$_2$<u>C</u>H$_2$), 37.07 (s, As(CH$_2$)$_4$<u>C</u>H$_2$), 121.12 (s, C^6), 130.41 (s, C^{o}H), 132.57 (s, C^{m}H), 133.91 (s, C^{p}H), 183.25 (s, <u>C</u>OOH). Elemental analysis: Found, %: C 69.04, H 6.15, As 17.50. $C_{24}H_{25}O_2As$. Calculated, %: C 68.57, H 5.99, As 17.83.

8-(Triphenylarsonio)octanoate ***2b***

Colorless crystals, mp 79-90 °C, yield: 75%. IR (ν/cm^{-1}): 468, 614, 689, 741, 883, 996, 1024, 1083, 1161, 1186, 1313, 1409, 1436, 1484, 1558, 1564, 2856, 2926, 3397. ^{1}H NMR spectrum (D_2O) ^{1}H NMR spectrum (D_2O) δ_H, ppm (J/Hz): 1.01–1.23 (m, 4H, $As(CH_2)_3C\underline{H}_2C\underline{H}_2$), 1.28–1.48 (m, 4H, $AsCH_2C\underline{H}_2C\underline{H}_2$), 1.59–1.74 (m, 2H, $C\underline{H}_2CH_2COOH$), 2.05 (t, 2H, $C\underline{H}_2COOH$, $^{3}J_{HH}$ 7.5), 3.19–3.34 (m, 2H, $AsCH_2$), 7.24–7.89 (m, 15H, Ph-As). ^{13}C NMR spectrum (D_2O), δ_C, ppm, 100,6 MHz: 22.43 (s, $As\underline{C}H_2$), 23.75 (s, $AsCH_2\underline{C}H_2$), 25.55 (s, $As(CH_2)_5\underline{C}H_2$), 27.52 (s, $As(CH_2)_4\underline{C}H_2$), 28.15 (s, $As(CH_2)_3\underline{C}H_2$), 29.53 (s, $AsCH_2CH_2\underline{C}H_2$), 37.42 (s, $As(CH_2)_6\underline{C}H_2$), 121.13 (s, C^{ipso}), 130.44 (s, C^{m}), 132.50 (s, C^{o}), 133.93 (s, C^{p}), 183.83 (s, $\underline{C}OOH$). Elemental analysis: Found, %: C 70.13, H 6.87, As 16.01. $C_{26}H_{29}O_2As$. Calculated, %: C 69.64, H 6.52, As 16.71.

10-(Triphenylarsonio)decanoate ***2c***

Colorless oil, yield: 76%. IR (ν/cm^{-1}): 468, 614, 689, 741, 883, 996, 1024, 1083, 1161, 1186, 1313, 1409, 1436, 1484, 1558, 1564, 2856, 2926, 3397. ^{1}H NMR spectrum (D_2O) δ_H, ppm (J/Hz): 0.89–1.06 (m, 8H, $As(CH_2)_4C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2$), 1.28 (m, 4H, $As(CH_2)_2C\underline{H}_2C\underline{H}_2$), 1.41 (п, 2H, $AsCH_2C\underline{H}_2$, $^{3}J_{HH}$ 7.8), 1.96 (t, 2H, $C\underline{H}_2COOH$, $^{3}J_{HH}$ 7.5), 3.07 (t, 2H, $AsC\underline{H}_2$, $^{3}J_{HH}$ 7.9), 7.30–7.85 (m, 15H, Ph-As). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm, 100,6 MHz: 21.11 (s, $As\underline{C}H_2$), 21.48 (s, $AsCH_2CH_2\underline{C}H_2$), 25.77 (s, $As(CH_2)_3\underline{C}H_2$), 27.69 (s, $As(CH_2)_4\underline{C}H_2$), 28.02 (s, $As(CH_2)_5\underline{C}H_2$), 28.26 (s, $As(CH_2)_6\underline{C}H_2$), 28.60 (s, $As(CH_2)_7\underline{C}H_2$), 29.50 (s, $AsCH_2\underline{C}H_2$), 37.57 (s, $As(CH_2)_8\underline{C}H_2$), 118.11 (s, C^{ipso}), 130.03 (s, $C^{o}H$), 133.3 (s, $C^{m}H$), 134.94 (s, $C^{p}H$), 183.86 (s, $\underline{C}OOH$). Elemental analysis: Found, %: C 70.93, H 6.72, As 16.14. $C_{28}H_{33}AsO_2$. Calculated, %: C 70.58, H 6.98, As 15.72.

(2-Carboxyethyl)triphenylarsonium bromide ***1d***

Colorless crystals, yield: 43%. ^{1}H NMR spectrum (D_2O) δ_H, ppm (*J*/Hz): 2.95 (m, 2H, AsC<u>H$_2$</u>), 3.57 (t, 2H, AsCH$_2$<u>C</u>H$_2$, $^{3}J_{HH}$ 7.0), 7.63 (t, 6H, C^{p}H, $^{3}J_{HH}$ 7.7), 7.70 (t, 6H, C^{o}H, $^{3}J_{HH}$ 7.2), 7.76 (t, 3H, C^{m}H, $^{3}J_{HH}$ 7.6). Elemental analysis: Found, %: C 55.31, H 4.72, As 16.08, Br 18.11. $C_{21}H_{20}O_2AsBr$. Calculated, %: C 54.93, H 4.39, As 16.32, Br 17.40.

Hydrogen-bonded adduct of triphenylphosphine oxide and 2,3-dibromopropanoic acid ***4***

Colorless crystals, mp 104 C, yield: 45%. IR (ν/cm^{-1}): 539, 693, 721, 1118, 1146, 1435, 1715, 1926, 2384. ^{1}H NMR spectrum (D_2O) δ_H, ppm (*J*/Hz): 3.69 (dd, 1H, , ^{3}J 1.13 Hz, ^{3}J 2.45 Hz), 3.78 (t, 1H, ^{3}J 10.3 Hz), 4.44 (dd, 1H, ^{3}J 10.9 Hz, ^{3}J 4.7 Hz), 7.42-7.61 (m, 15H, Ph-P). ^{13}C NMR spectrum (D_2O), δ_C, ppm, 100.6 MHz: 29.71 (s, <u>CH$_2$</u>-CH-COOH), 41.69 (s, <u>CH</u>-COOH), 128.66 (d, C^{o}, $^{2}J_{PC}$ 12.3 Hz), 130.53 (s, C^{ipso}), 131.68 (d, C^{m}, $^{3}J_{PC}$ 10.2 Hz), 132.51 (d, C^{p}, $^{4}J_{PC}$ 2.7), 169.66 (s, <u>C</u>OOH). ^{31}P NMR spectrum (D_2O): δ_P 32.88 ppm. Elemental analysis: Found, %: C 50.11, H 4.07, Br 31.54, P 6.41. $C_{21}H_{19}Br_2O_3P$. Calculated, %: C 49.44, H 3.75, Br 31.32, P 6.07.

(2-Carboxyethyl)triphenylphosphonium bromide ***5***

Colorless crystals, mp 209-215 C, yield: 40%. IR (ν/cm^{-1}): 505, 687, 1109, 1436, 1728, 2890. ^{1}H NMR spectrum (D_2O) δ_H, ppm (*J*/Hz): 2.42 (s, 2H, <u>CH$_2$</u>-COOH), 3.26 (s, 2H, <u>CH$_2$</u>-P), 6.73-7.98 (m, 15H, Ph-P). ^{13}C NMR spectrum (D_2O), δ_C, ppm, 100,6 MHz: 17.21 (d, <u>CH$_2$</u>-P, $^{1}J_{PC}$ 55.1 Hz), 26.40 (s, <u>CH$_2$</u>-COOH), 117.03 (d, C^{ipso}, $^{1}J_{PC}$ 87.1 Hz), 130.11 (d, C^{o}, $^{2}J_{PC}$ 12.7 Hz), 133.3 (d, C^{m}, $^{3}J_{PC}$ 9.2 Hz), 135.2 (d, C^{p}, $^{4}J_{PC}$ 2.2 Hz), 173.63 (s, <u>C</u>OOH). ^{31}P NMR spectrum (D_2O): δ_P 22.88 ppm. Elemental analysis: Found, %: C 60.91, H 4.51, Br 19.63, P 7.19. $C_{21}H_{20}BrO_2P$. Calculated, %: C 60.74, H 4.85, Br 19.24, P 7.46.

X-Ray Crystallography. Data set for single crystal of compound **4** ($C_{21}H_{19}Br_2O_3P$) was collected on a Rigaku XtaLab Synergy S instrument with a HyPix detector and a PhotonJet microfocus X-ray tube using Cu Kα (λ = 1.54184 Å) radiation at low temperature. Images were indexed and integrated using the CrysAlisPro data reduction package. Data were corrected for systematic errors and absorption using the ABSPACK module: numerical absorption correction based on Gaussian integration over a multifaceted crystal model and empirical absorption correction based on spherical harmonics according to the point group symmetry using equivalent reflections. The GRAL module was used for analysis of systematic absences and space group determination. The structure was solved by direct methods using SHELXT[S1] and refined by the full-matrix least-squares on F^2 using SHELXL.[S2] Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were inserted at the calculated positions and refined as riding atoms. The figures were generated using Mercury 4.1 program.[S3] Crystals were obtained by slow evaporation method.

Crystal data: formula ($C_{21}H_{19}Br_2O_3P$), M = 510.15 g mol^{-1}, monoclinic, space group $P2_1/n$ (No. 14), Z = 4, a = 13.5085(3) Å, b = 9.73571(17) Å, c = 17.0492(4) Å, α = 90.000°, β = 110.342(3)°, γ = 90.000°, V = 2102.37(8) $Å^3$, ρ_{calc} = 1.612 g/cm^3, μ = 5.763 mm^{-1}, 24710 reflections collected ($-17 \leq h \leq 17, -12 \leq k \leq 12, -21 \leq l \leq 21$), 2θ range = 7.242 to 154.222, 4352 independent (R_{int} = 0.0483) and 4018 observed reflections [$I \geq 2\ \sigma(I)$], 263 refined parameters, R_1 = 0.0521, wR_2 = 0.1323, goodness of fit S = 1.095. R_{sigma} = 0.0304.

References

S1. G. M. Sheldrick, *Acta Crystallogr*., 2015, **C71**, 3.

S2. G.M. Sheldrick, *Acta Crystallogr*., 2007, **A64**, 112.

S3. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor; M. Towler and J. van de Streek, *J. Appl. Crystallogr*., 2006, **39**, 453.

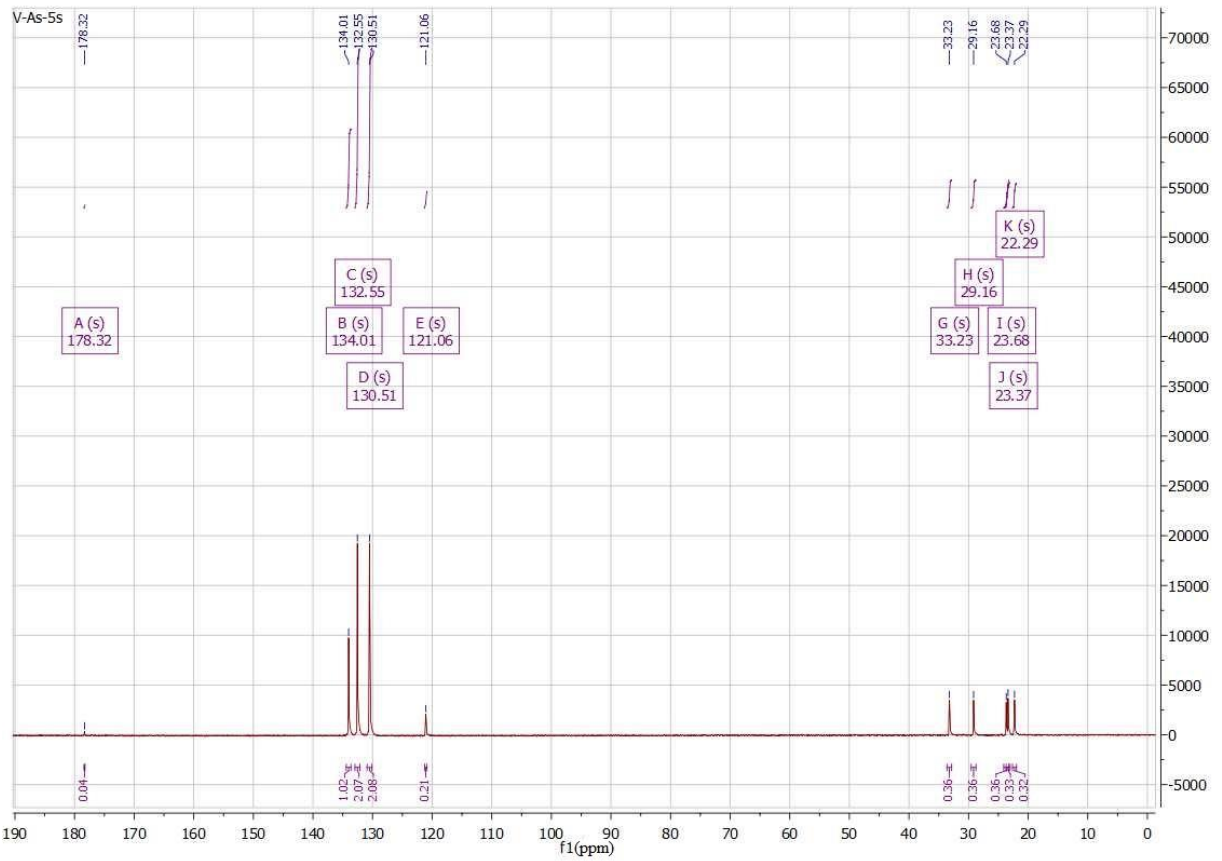

Figure S1 $^{13}C\{^{1}H\}$ NMR spectrum of arsonium salt **1a** (100.6 MHz, D_2O).

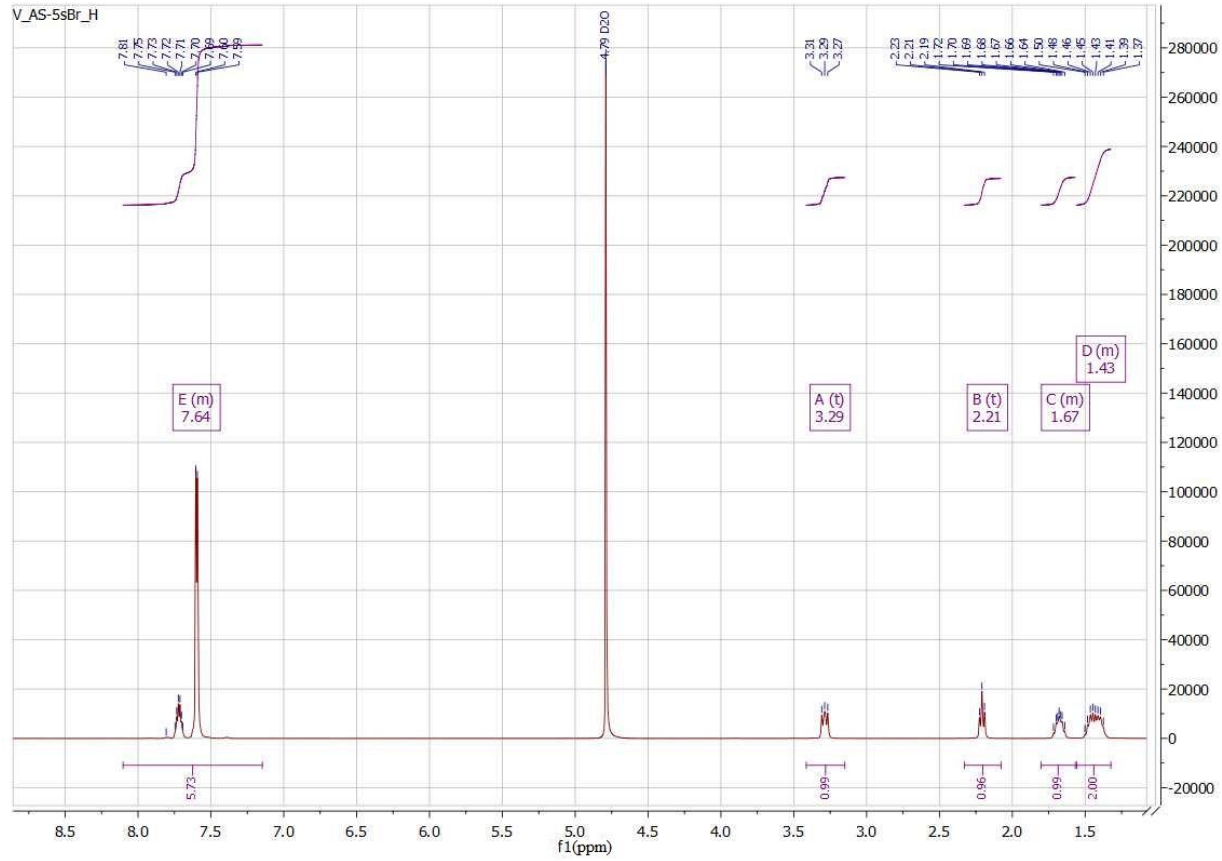

Figure S2 ^{1}H NMR spectrum of arsonium salt **1a** (400 MHz, D_2O).

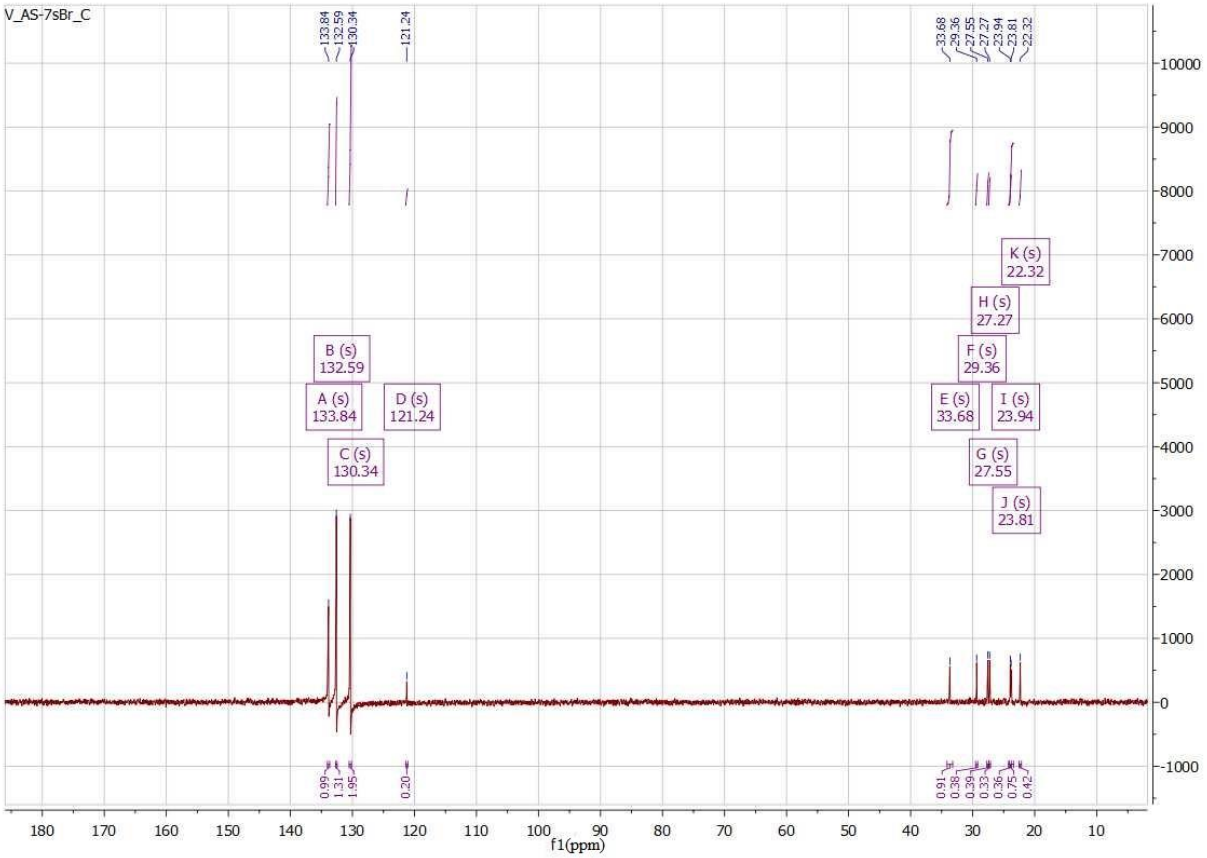

Figure S3 $^{13}C\{^{1}H\}$ NMR spectrum of arsonium salt **1b** (100.6 MHz, D_2O).

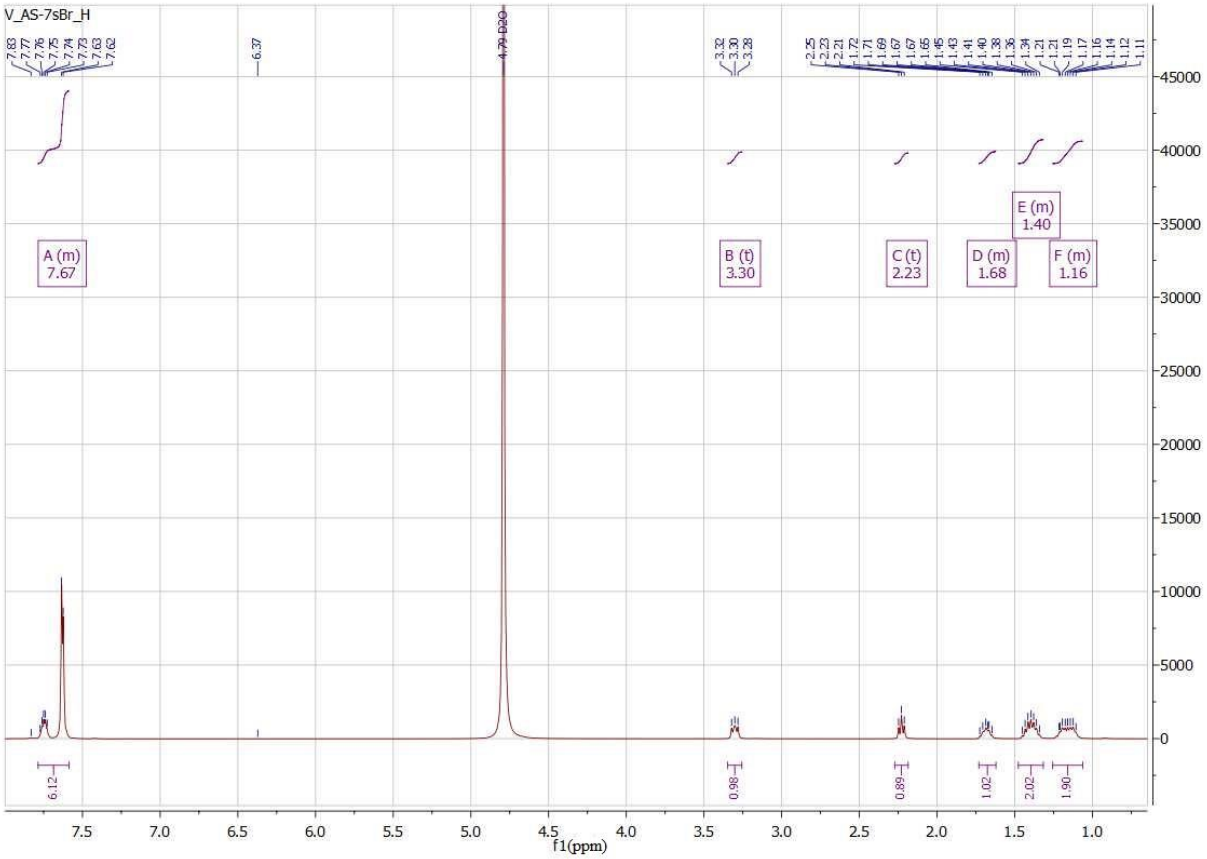

Figure S4 ^{1}H NMR spectrum of arsonium salt **1b** (400 MHz, D_2O).

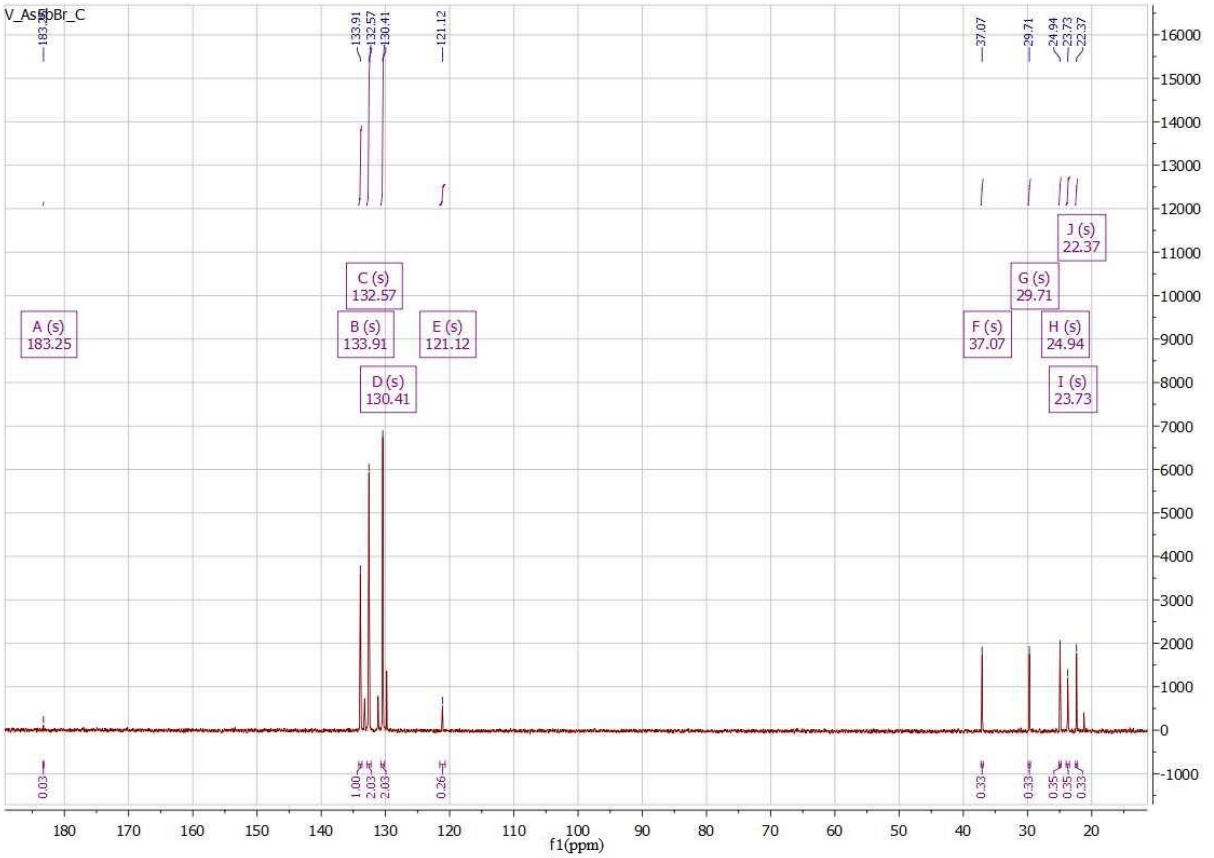

Figure S5 $^{13}C\{^{1}H\}$ NMR spectrum of betaine **2a** (100.6 MHz, D_2O).

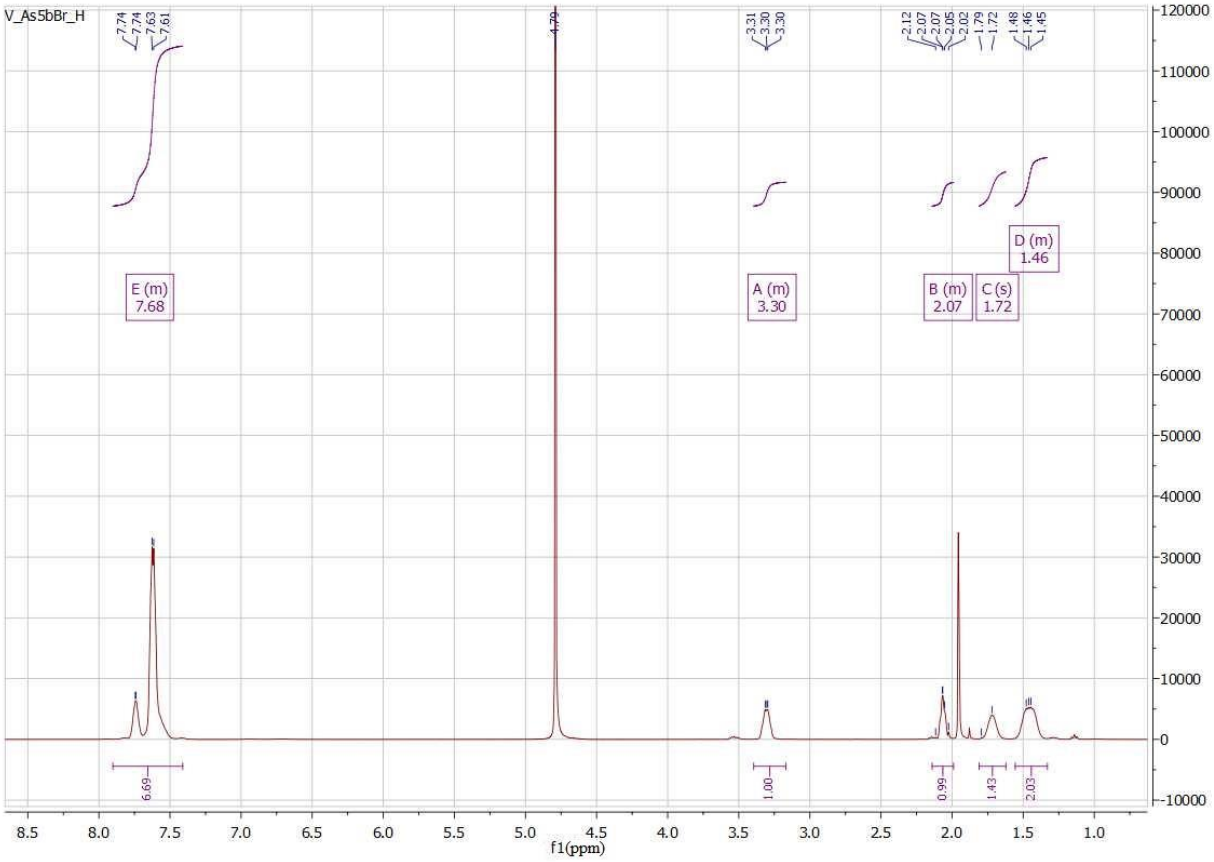

Figure S6 ^{1}H NMR spectrum of betaine **2a** (400 MHz, D_2O).

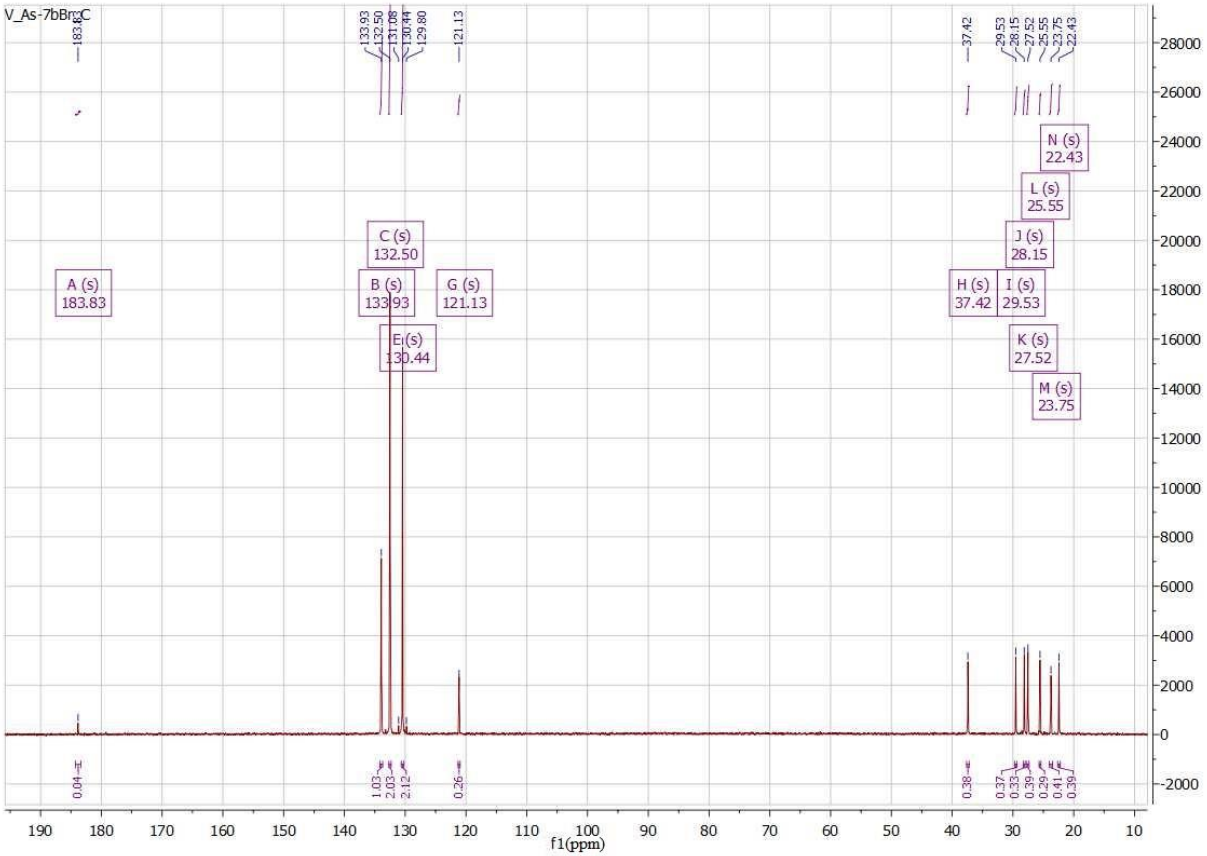

Figure S7 $^{13}C\{^{1}H\}$ NMR spectrum of betaine **2b** (100.6 MHz, D_2O).

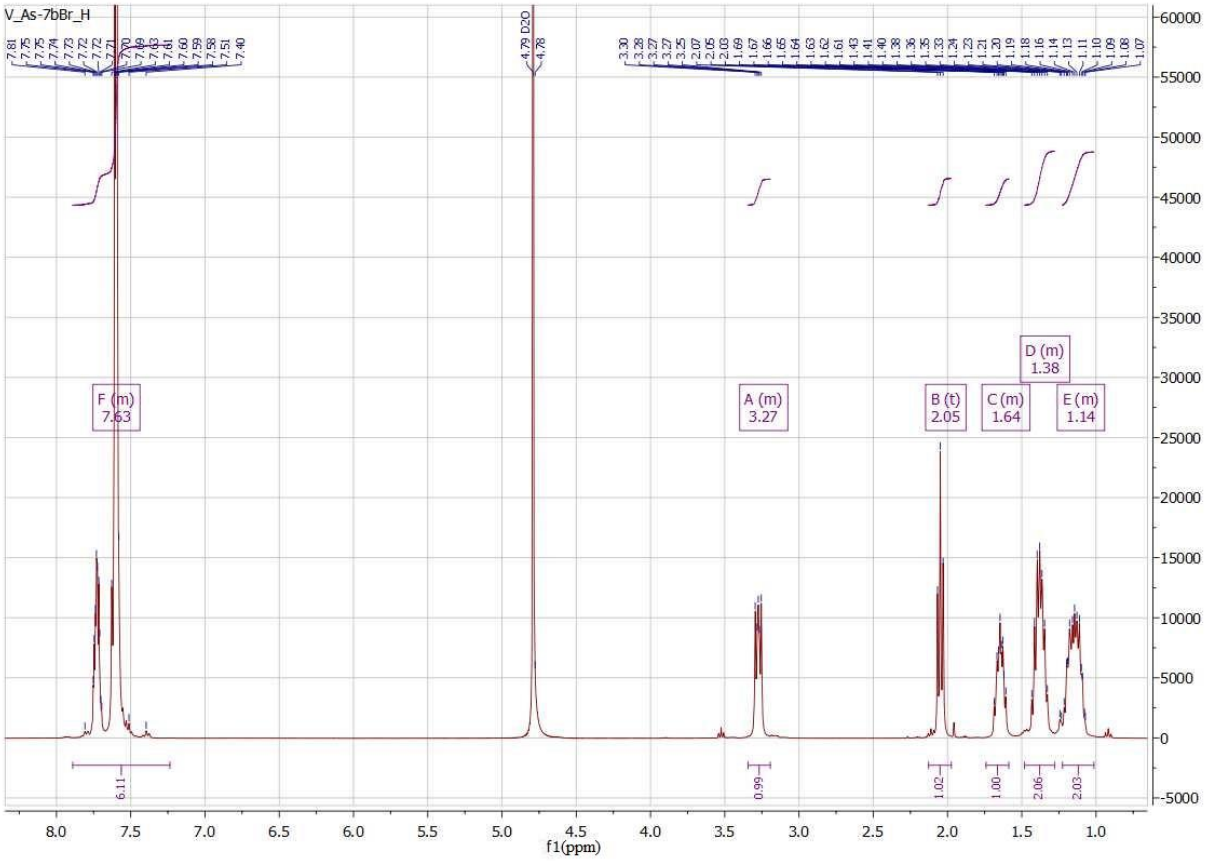

Figure S8 ^{1}H NMR spectrum of betaine **2b** (400 MHz, D_2O).

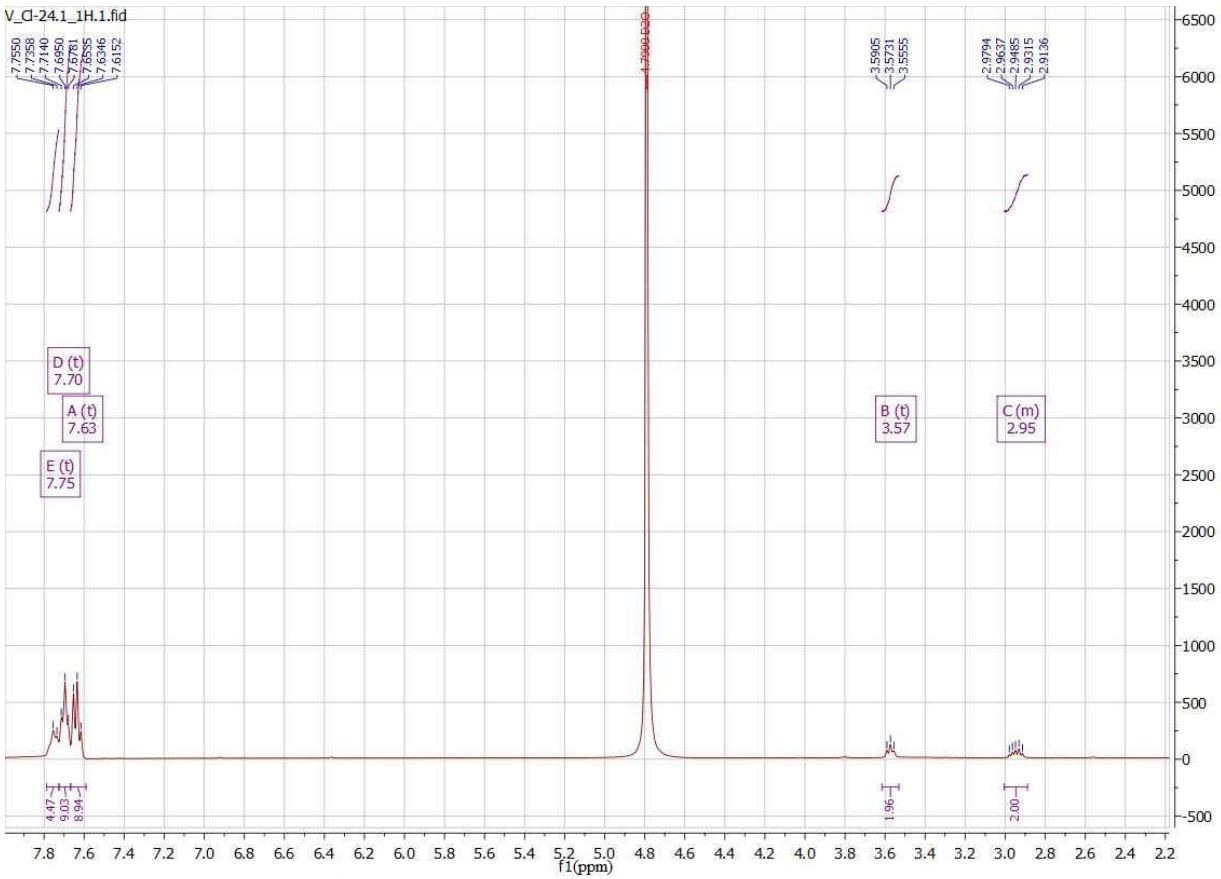

Figure S9 ^{1}H NMR spectrum of arsonium salt **1d** (400 MHz, D_2O).

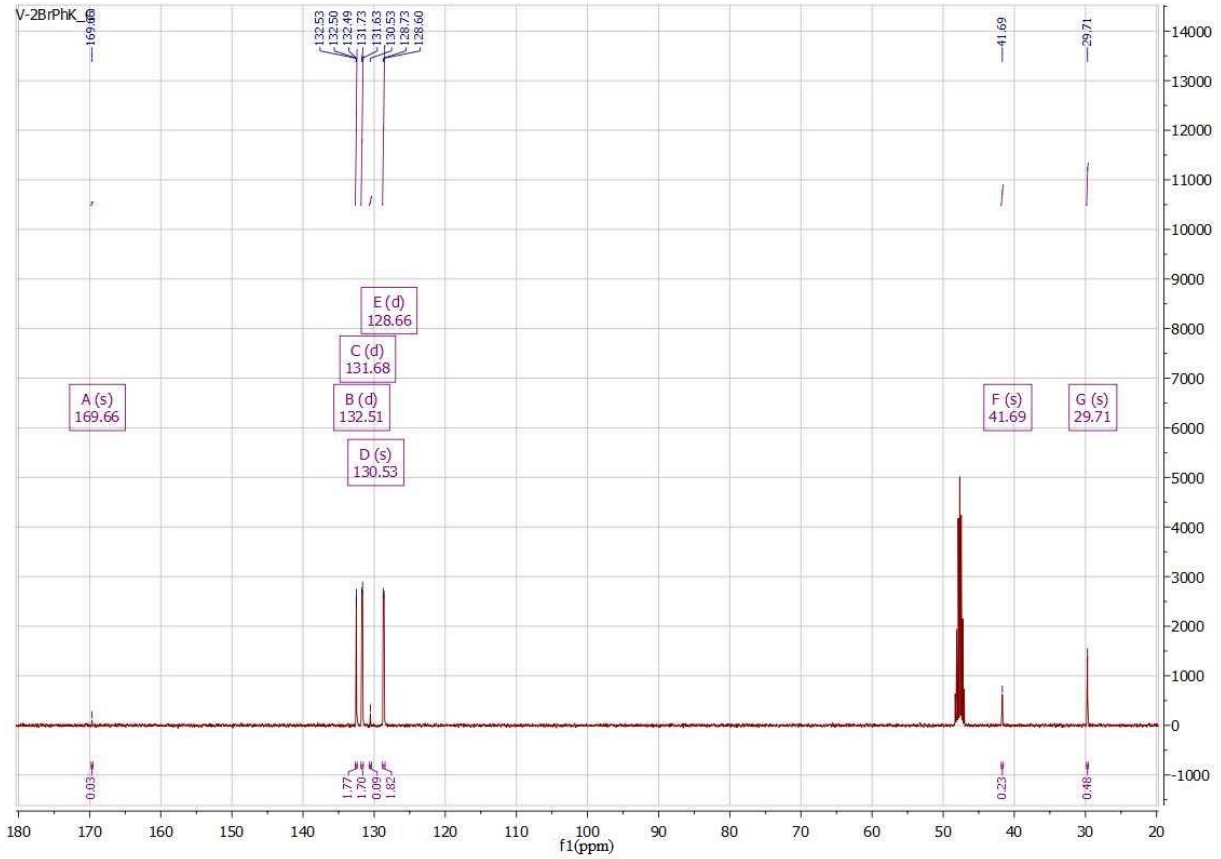

Figure S10 $^{13}C\{^{1}H\}$ NMR spectrum of complex **4** (100.6 MHz, CD_3OD).

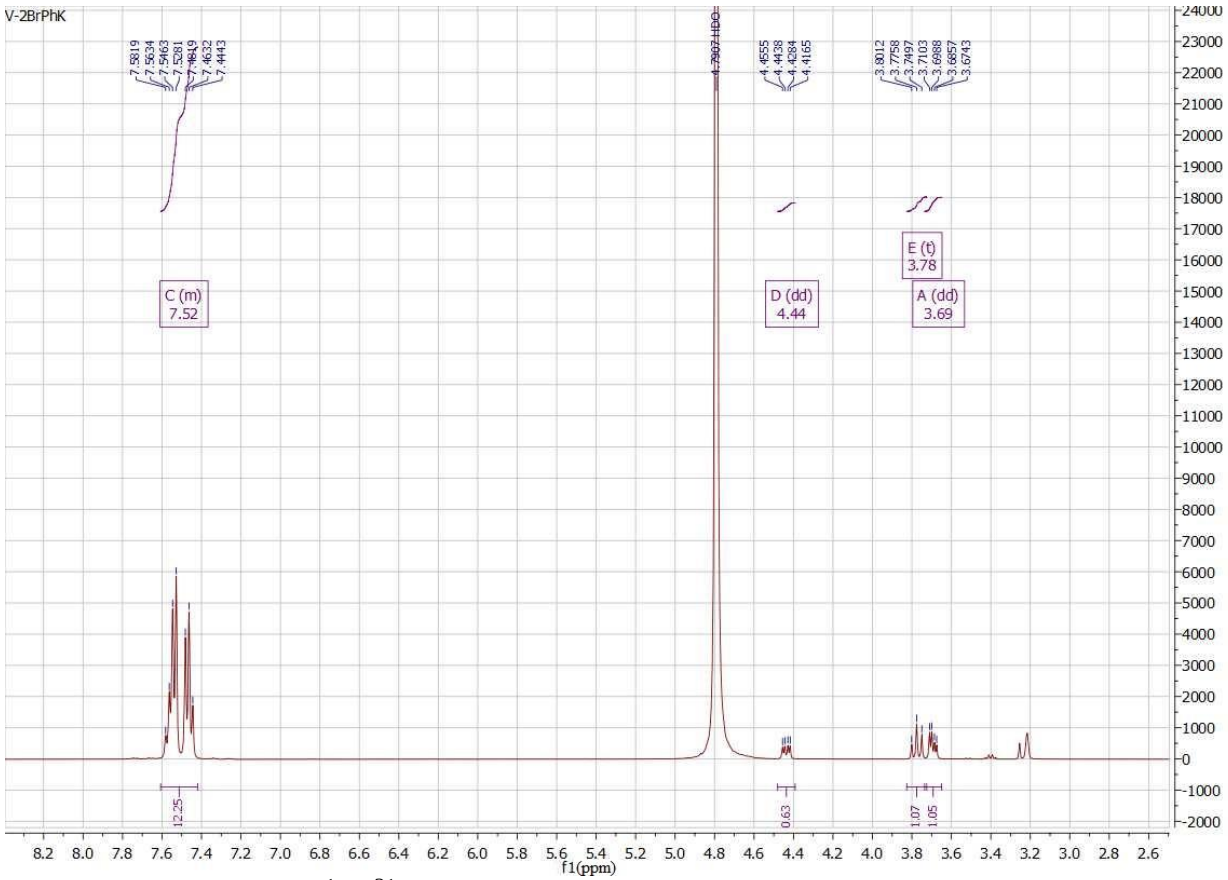

Figure S11 $^{1}H\{^{31}P\}$ NMR spectrum of complex **4** (400 MHz, CD_3OD).

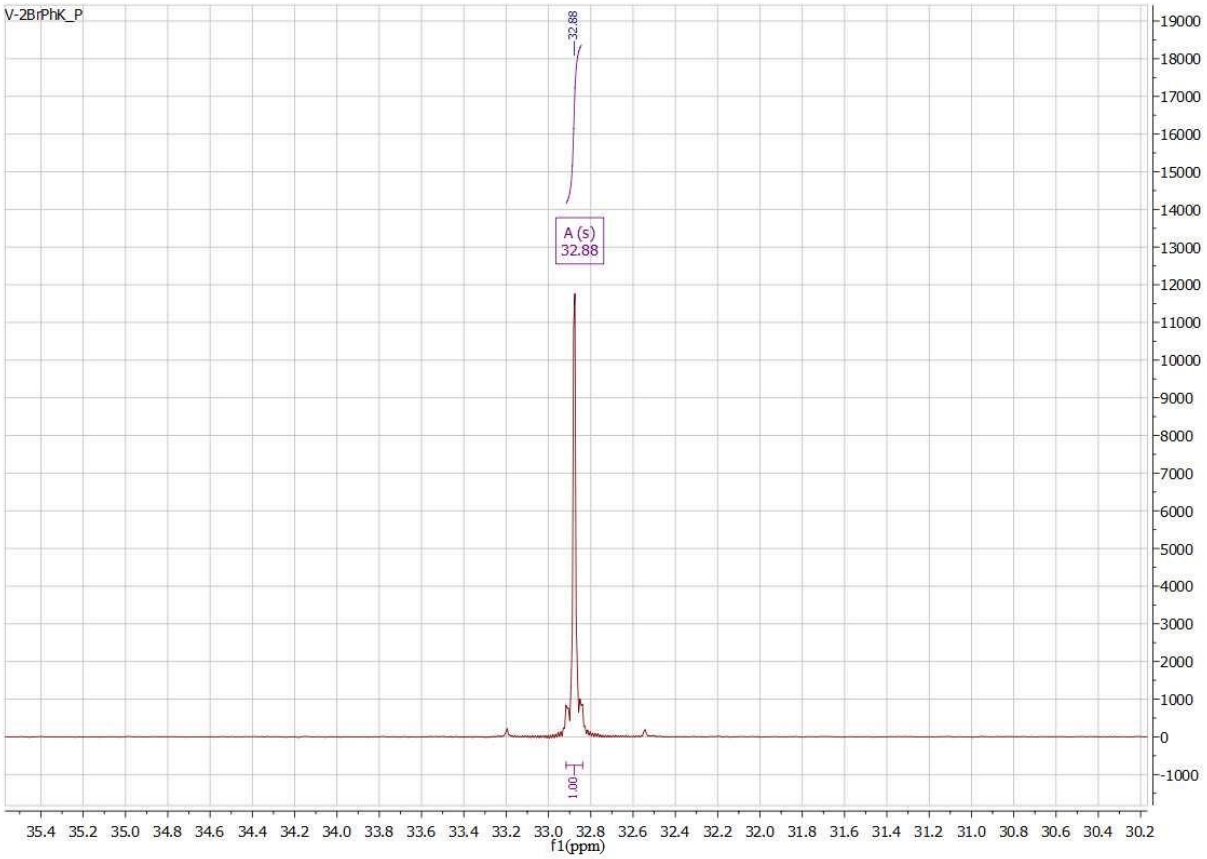

Figure S12 $^{31}P\{^{1}H\}$ NMR spectrum of complex **4** (122.4 MHz, CD_3OD).

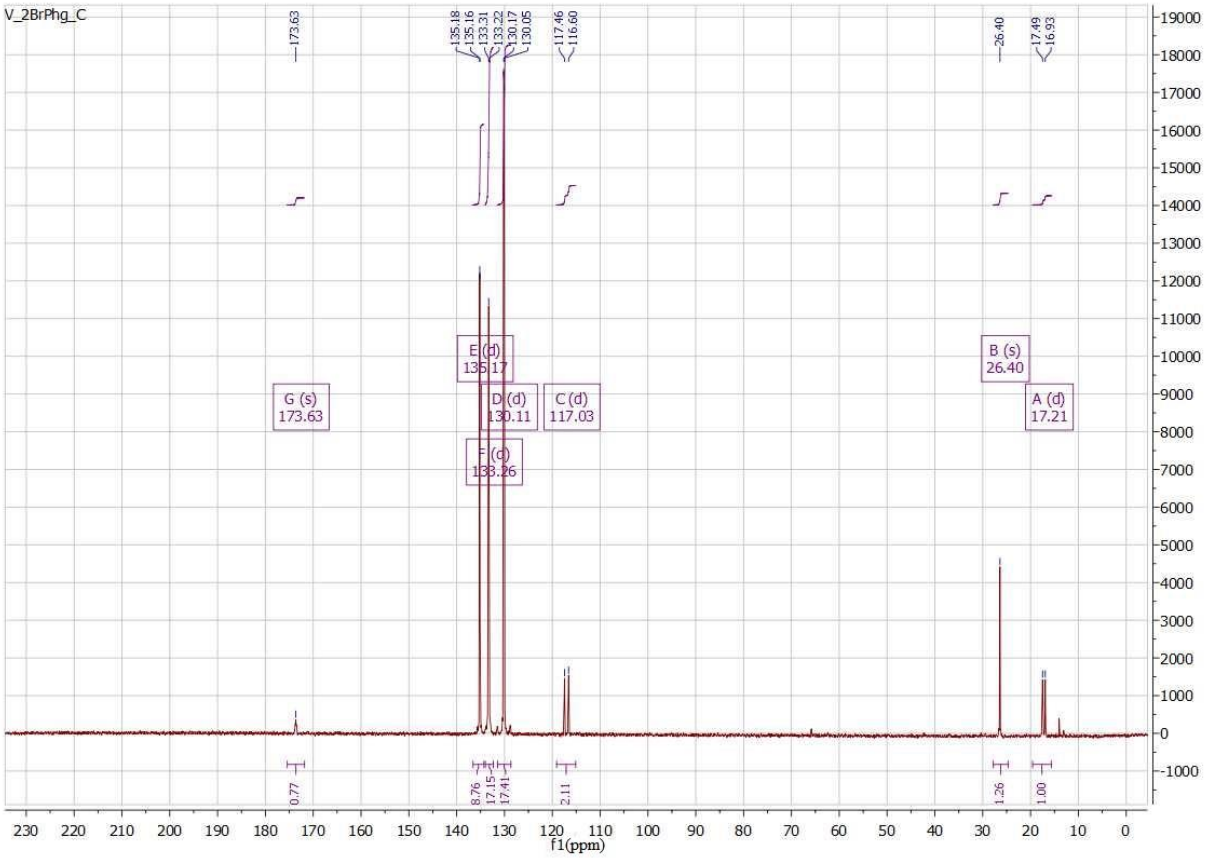

Figure S13 $^{13}C\{^{1}H\}$ NMR spectrum of phosphonium salt **5** (100.6 MHz, D_2O).

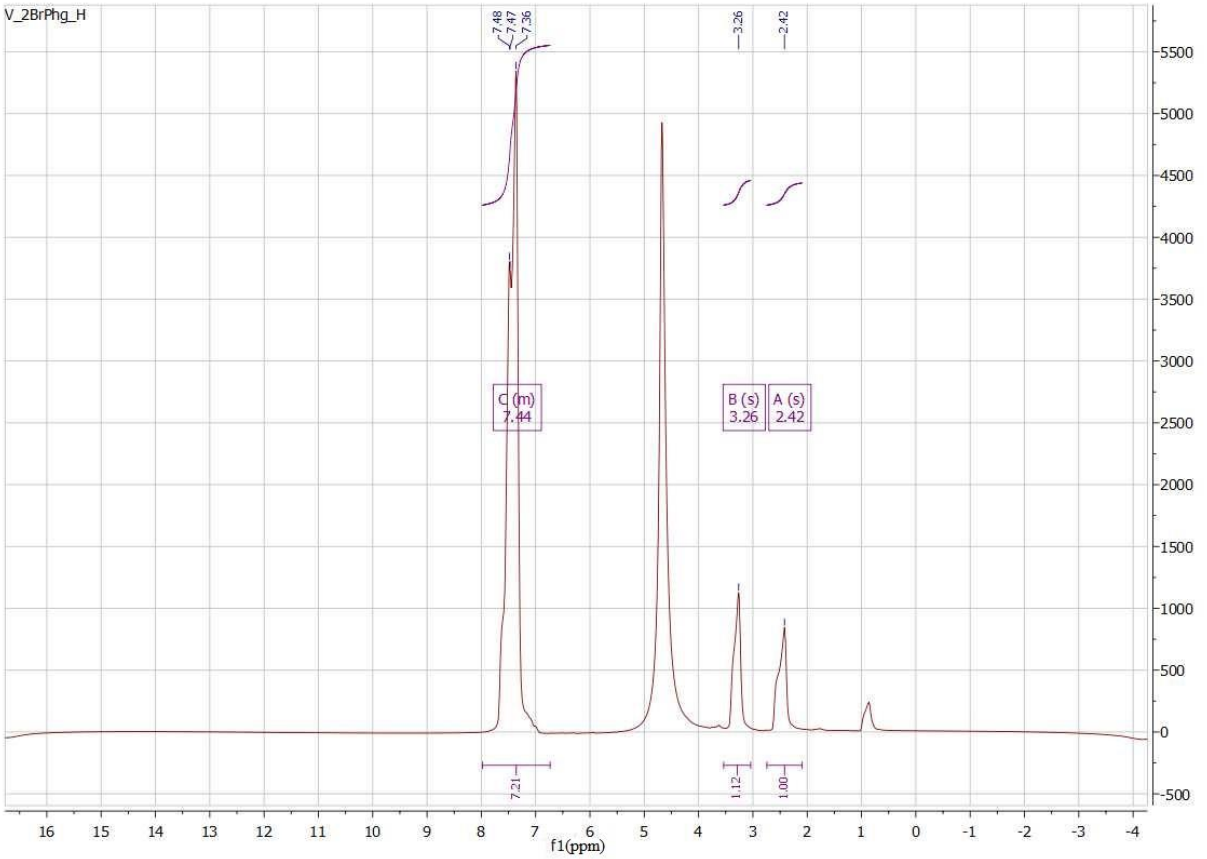

Figure S14 $^{1}H\{^{31}P\}$ NMR spectrum of phosphonium salt **5** (400 MHz, D_2O).

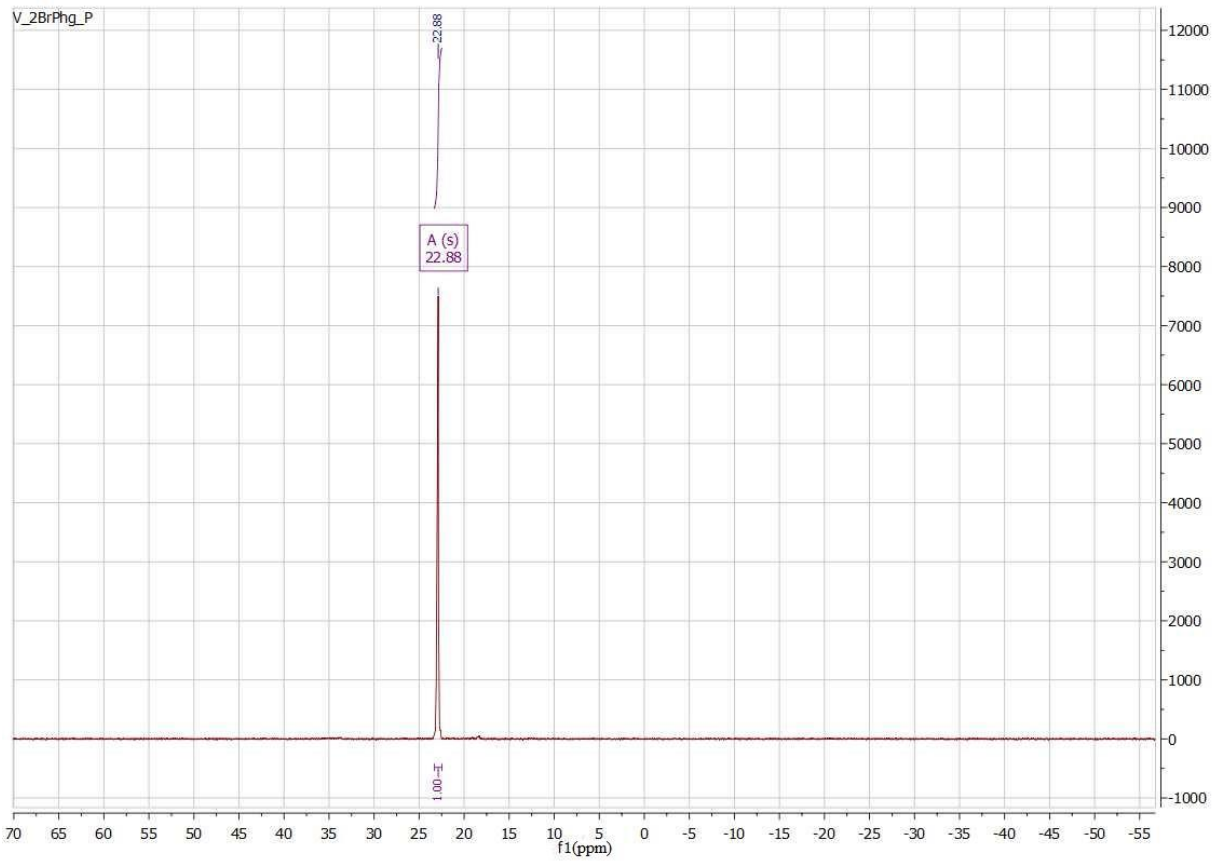

Figure S15 $^{31}P\{^{1}H\}$ NMR spectrum of phosphonium salt **5** (122.4 MHz, D_2O).

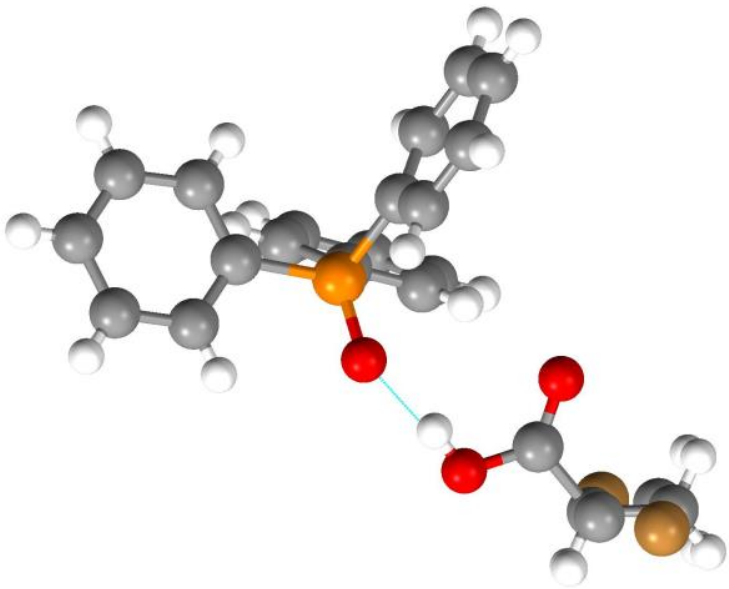

Figure S16 A fragment of crystal packing of complex **4**.

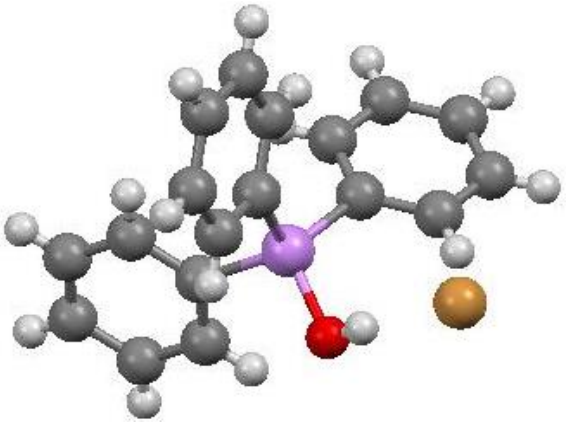

Figure S17 The structure of compound **3** (CCDC number 1228478).