Supporting Information to:

Trends in Hydrophilicity/Lipophilicity of Phosphonium Ionic Liquids as Determined by Ion-Transfer Electrochemistry

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Micropipette fabrication: An electric puller (Narishige, Model #PP-83, Japan) was used to pull a hollow borosilicate glass capillary (1.0 mm internal and 2.0 mm external diameter, Sutter Instrument Co., Navato, CA, USA) towards its center, thus generating two tapered ends. The ends were then flame annealed with a Bunsen burner. Afterwards a 1.0 to 1.5 cm long, 25 µm diameter platinum wire (Goodfellow Cambridge Ltd., Huntingdon, United Kingdom) was pushed down the length of the capillary through its open end to finally rest in the pulled portion by dropping the capillary (tapered end down) through a large hollow glass tube; if done correctly this should result in a straight wire supported by the pulled glass walls. A vacuum line was affixed to the capillaries open end and, under reduced pressure, the Pt-wire was sealed in place utilizing the electric puller. A series of grinding/polishing pads (Buehler Canada, Markham, ON) were employed to polish the tapered ends until the surface of the glass was smooth, as observed through an optical microscope, and the R_g, the ratio of external (r_g) to internal (a) diameter ($R_g = r_g / a$), was greater than 50. The finished capillary was then placed in a solution of 3:1 HCl:HNO$_3$ (aqua regia) which etched the Pt-wire leaving a microchannel of uniform diameter (~25 µm).

The pipette tips were then silanized by passing argon gas through the back of the capillary while it was immersed in a trimethylchlorosilane solution for 5 min; once dry, the capillaries were placed in an oven over night at 100°C.

$$\mathrm{Ag}\left|\,\mathrm{Ag_2SO_4}\,\right|\underset{(aq)}{\mathrm{10\ mM\ Li_2SO_4}}\Big\|\underset{(DCE)}{\mathrm{5\ mM\ P_{8888}TB}}\Big|\,\mathrm{AgTB}\,\Big|\,\mathrm{Ag} \qquad \text{[Cell S1]}$$

$$\mathrm{Ag}\,\Big|\,\mathrm{AgI}\,\Big|\,\begin{array}{c}2\ \mathrm{mM\ N(CH_3)_4}\\ 10\ \mathrm{mM\ LiI}\\ (aq)\end{array}\Big\|\,\begin{array}{c}5\ \mathrm{mM\ P_{8888}TB}\\ (DCE)\end{array}\Big|\,\mathrm{AgTB}\,\Big|\,\mathrm{Ag} \qquad \text{[Cell S2]}$$

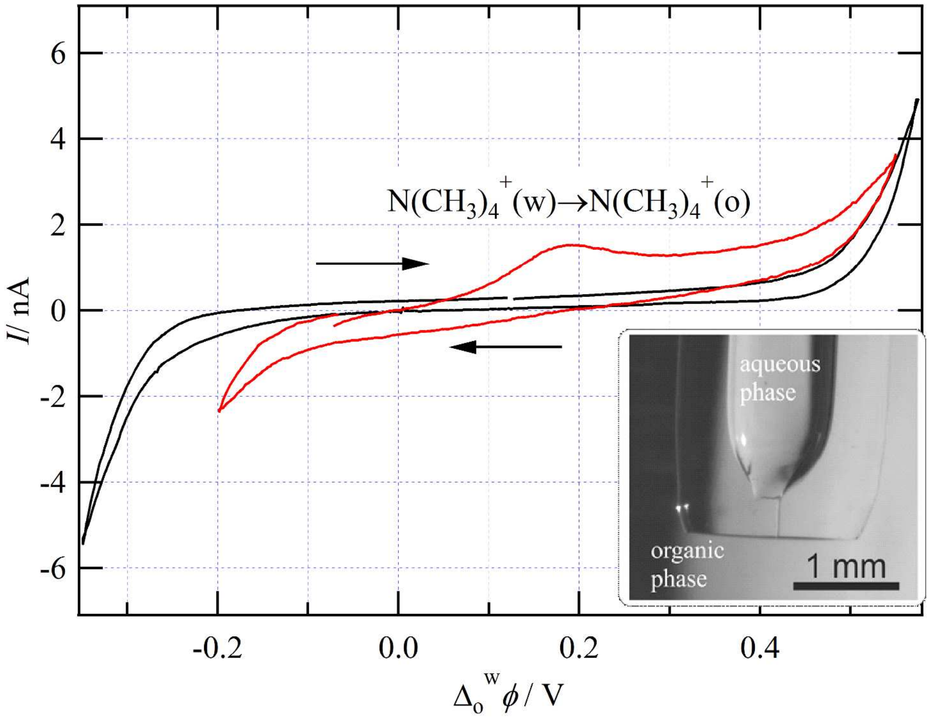

Figure S1: Cyclic voltammograms acquired using Cell S1 (black trace) and Cell S2 (red, dashed trace), with a scan rate of 0.020 V s^{-1}. Inset: photo taken using a CCD camera equipped with a 12× zoom lens assembly (Navitar, Rochester, NY) of the micro-pipette tip with the microchannel filled with the aqueous phase. The size of the interface was determined through optical measurements to be 25 μm.

Synthesis

Synthesis of tributyl(hexyl)phosphonium iodide

Tributylphosphine (4.00 g, 19.6 mmol) and 1-iodohexane (6.3 g, 29.7 mmol) were combined in a pressure tube. Acetonitrile (10 mL) was added to the mixture and stirred for 24 hours. The solution was then poured in to a round bottom flask and volatiles were removed using a rotary evaporator. The viscous solution was then precipitated in diethyl ether (150 mL) and stirred for one hour. The top layer was then decanted, leaving a viscous white residue. Volatiles were then evaporated *in vacuo* and the resulting white powder was identified as tributyl(hexyl)phosphonium iodide (5.12 g, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82 (t, 3H, J = 8 Hz, CH_3), 0.91 (t, 9H, J = 8 Hz, CH_3), 1.24 (m, 4H, $P(C_3H_6)\mathit{CH_2CH_2}CH_3$)), 1.49 (m, 16H, $PCH_2\mathit{CH_2CH_2}$*)*, 2.36 (m, 8H, PCH_2). $^{31}P\{^1H\}$ NMR (161.82 MHz, $CDCl_3$): δ 33.46 (s). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ 13.44 (s, 3C), 13.85 (s, 1C), 19.30 (d, 3C, $^1J_{P\text{-}C}$ = 47 Hz), 19.50 (d, 1C, $^1J_{P\text{-}C}$ = 47 Hz), 21.77 (d, 1C, $^3J_{P\text{-}C}$ = 5 Hz), 22.25 (s, 1C), 23.71 (d, 3C, $^3J_{P\text{-}C}$ = 4 Hz), 23.72 (d, 3C $^2J_{P\text{-}C}$ = 16 Hz), 30.28 (d, 1C, $^2J_{P\text{-}C}$ = 14 Hz), 30.94 (s, 1C). TOF-MS-ES+: *m/z* observed 287 $(M)^+$, 702 $(2M + I)^+$, 1116 $(3M + 2I)^+$. TOF-MS-ES-: *m/z* observed 541 $(M + 2I)^-$, 955 $(2M + 3I)^-$, 1370 $(3M + 4I)^-$.

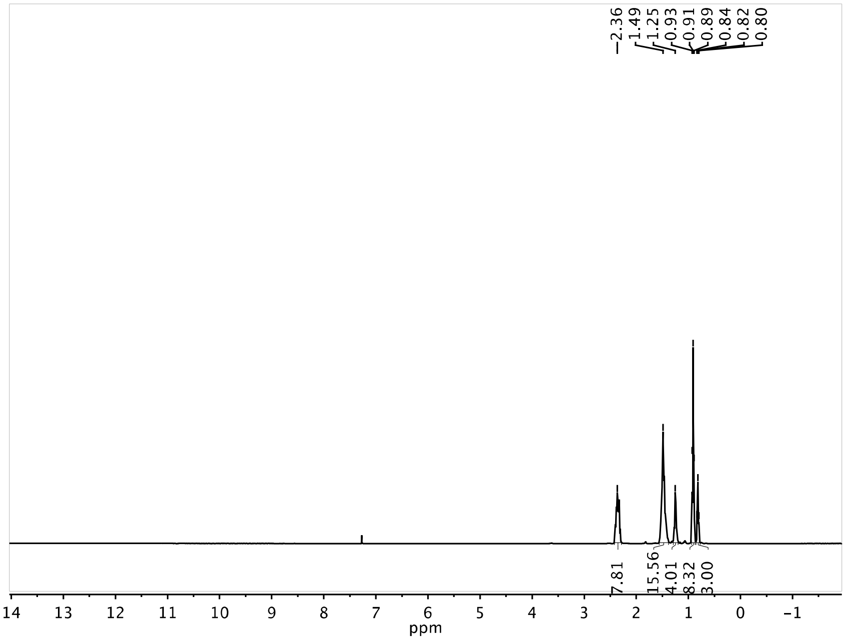

Figure S2: ^{1}H NMR spectrum of tributyl(hexyl)phosphonium iodide

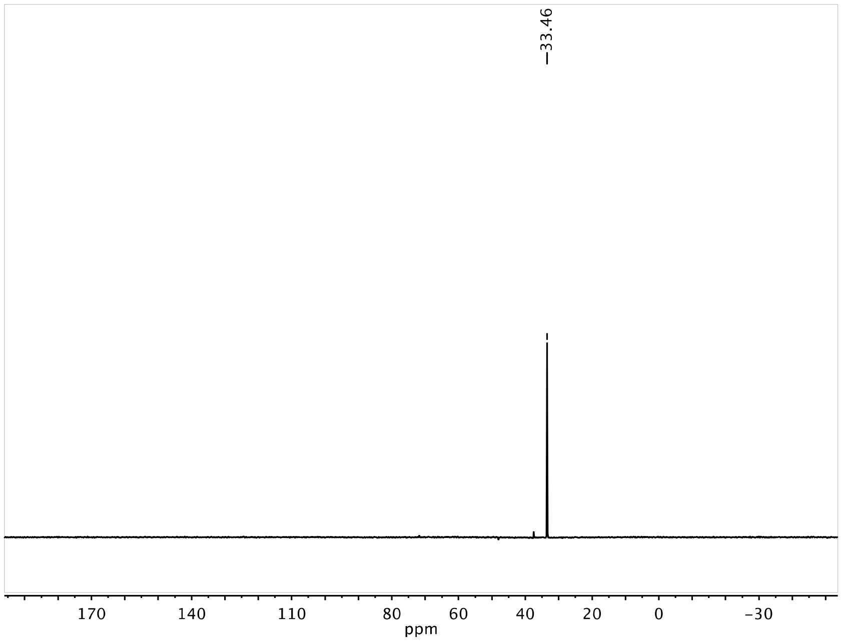

Figure S3: $^{31}P\{^{1}H\}$ NMR spectrum of tributyl(hexyl)phosphonium iodide

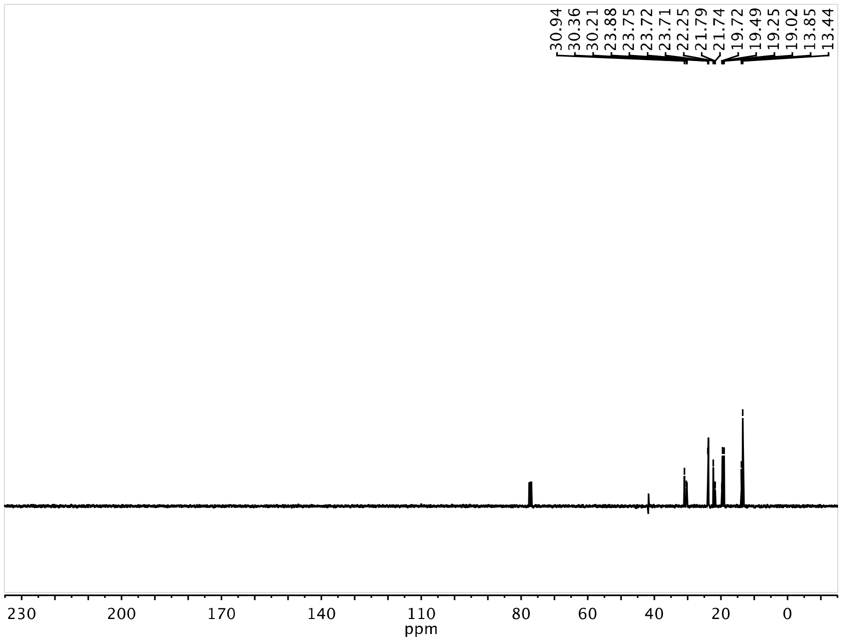

Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum of tributyl(hexyl)phosphonium iodide

Synthesis of tributyl(1H,1H,2H,2H-perfluorohexyl)phosphonium iodide

Tributylphosphine (5.00 g, 24.5 mmol) and 1,1,1,2,2,3,3,4,4-Nonafluoro-6-iodohexane (14 g, 37.43 mmol) were combined in a pressure tube. Acetonitrile (10 mL) was added to the mixture and stirred for 24 hours. The solution was then poured in to a round bottom flask and volatiles were removed using a rotary evaporator. The viscous solution was then precipitated in diethyl ether (150 mL) and stirred for one hour. The top layer was then decanted, leaving a viscous yellow oil which was dried *in vacuo* and identified as tributyl(1H,1H,2H,2H-perfluorohexyl)phosphonium iodide (9.2 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (t, 9H, *J* = 8 Hz, CH_3), 1.55 (m, 12H, $PCH_2\mathit{CH_2CH_2}CH_3$), 2.6 (m, 8H, PCH_2), 2.78 (m, 2H, $PCH_2\mathit{CH_2}(C_4F_9)$). $^{31}P\{^{1}H\}$ NMR (161.82 MHz, $CDCl_3$): δ 34.23 (s). ^{19}F NMR (376.15 MHz, $CDCl_3$): δ -126.0 (m, 2F, CF_2), -123.5 (m, 2F, CF_2), -114.6 (m, 2F, CF_2), -81.1 (m, 3F, CF_3). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, $CDCl_3$): δ 12.1 (d, 1C, $^{1}J_{P\text{-}C}$ = 54 Hz), 13.57 (s, 3C), 19.5 (d, 3C, $^{1}J_{P\text{-}C}$ = 46 Hz), 23.85 (s, 3C), 23.95 (d, 3C, $^{2}J_{P\text{-}C}$ = 12 Hz), 24.74 (t, $^{2}J_{F\text{-}C}$ = 45 Hz). TOF-MS-ES+: *m/z* observed 449 $(M)^+$, 1025 $(2M + I)^+$, 1601 $(3M + 2I)^+$. TOF-MS-ES-: *m/z* observed 703 $(M + 2I)^-$, 1279 $(2M + 3I)^-$, 1855 $(3M + 4I)^-$.

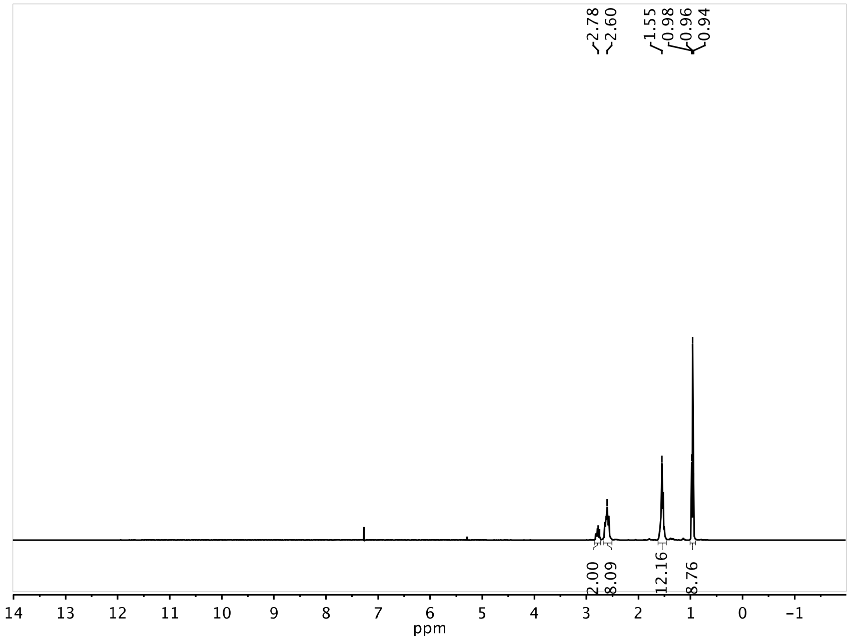

Figure S5: ^{1}H NMR spectrum of tributyl(1H,1H,2H,2H-perfluorohexyl)phosphonium iodide

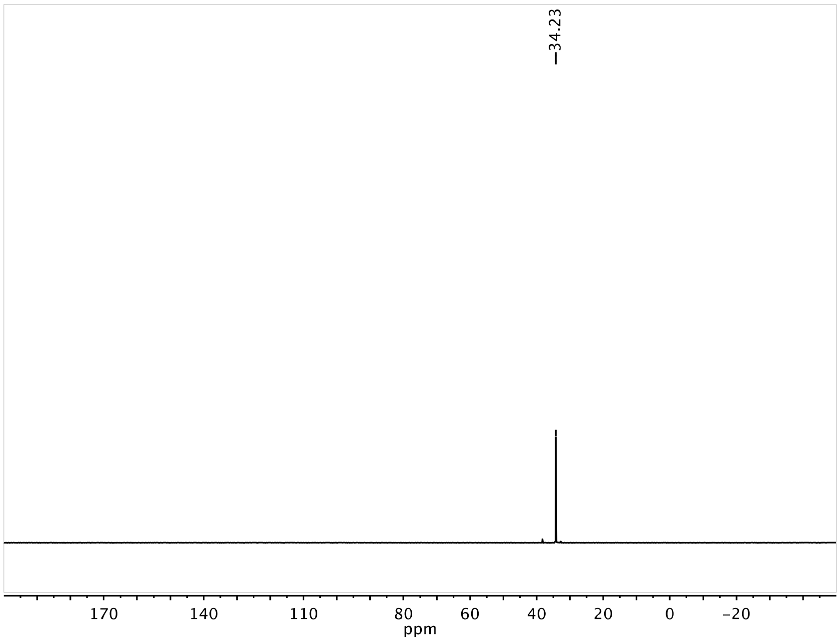

Figure S6: $^{31}P\{^{1}H\}$ NMR spectrum of tributyl(1H,1H,2H,2H-perfluorohexyl)phosphonium iodide

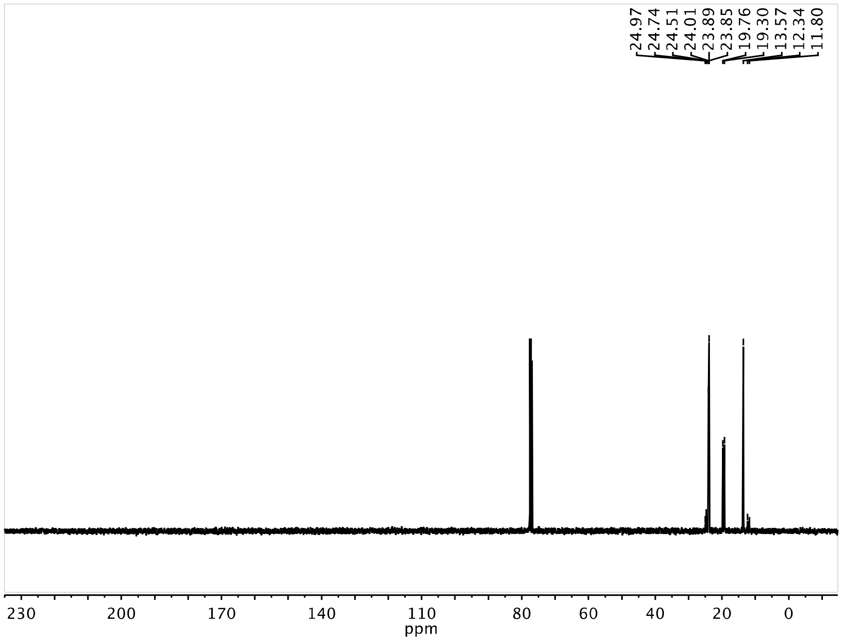

Figure S7: $^{13}C\{^{1}H\}$ NMR spectrum of tributyl(1H,1H,2H,2H-perfluorohexyl)phosphonium iodide

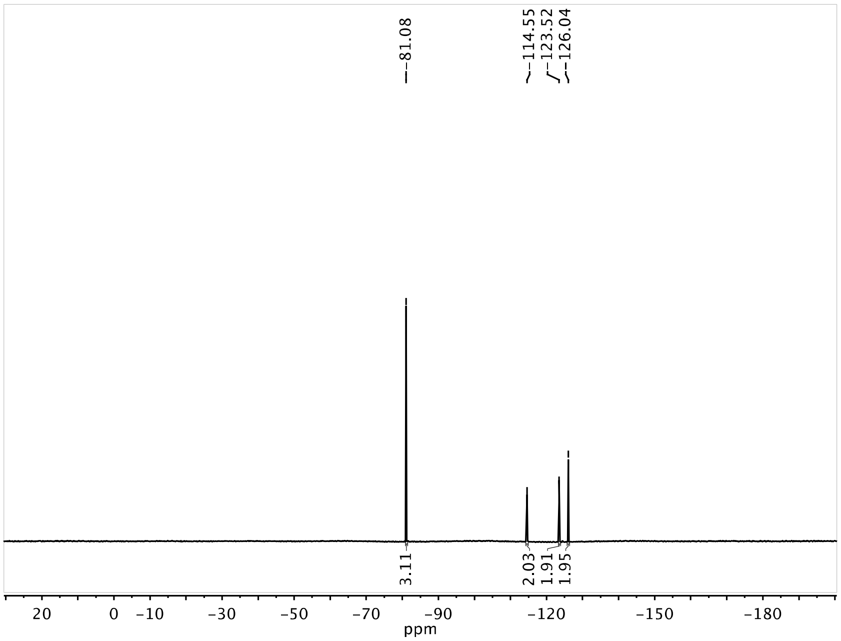

Figure S8: $^{19}F\{^1H\}$ NMR spectrum of tributyl(1H,1H,2H,2H-perfluorohexyl)phosphonium iodide

Synthesis of tributyl(decyl)phosphonium iodide

Tributylphosphine (3.50 g, 17.1 mmol) and 1-iododecane (5.57g, 20.8 mmol) were combined in a pressure tube. Acetonitrile (10 mL) was added to the mixture and stirred for 24 hours. The solution was then poured in to a round bottom flask and volatiles were removed using a rotary evaporator. The viscous solution was then precipitated in a solution of hexanes (50 mL) and diethyl ether (2 mL) and stirred for one hour. The top later was then decanted, leaving a white residue, which was redissolved in a small amount of acetonitrile (3 mL), followed by precipitation in a solution of hexanes and diethyl ether. The top layer was decanted and volatiles were then evaporated *in vacuo* leaving a white oil which was identified as tributyl(decyl)phosphonium iodide (2.31 g, 28%). ^1H NMR (400 MHz, $CDCl_3$): δ 0.84 (t, 3H, J = 8 Hz, CH_3), 0.95 (t, 9H, J = 8 Hz, CH_3), 1.22 (m, 12H, $PCH_2\mathit{CH_2CH_2}$), 1.52 (m, 16H, $PCH_2(\mathit{C_8H_{16}})CH_3$), 2.40 (m, 8H, PCH_2). $^{31}P\{^1H\}$ NMR (161.82 MHz, $CDCl_3$): δ 32.67 (s). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): 13.95 (s, 3C), 14.51 (s, 1C), 19.52 (d, 3C, $^1J_{P\text{-}C}$ = 47 Hz), 19.72 (d, 1C, $^1J_{P\text{-}C}$ = 47 Hz), 22.29 (d, 1C, $^2J_{P\text{-}C}$ = 5 Hz), 23.05 (s, 1C), 24.22 (d, 3C, $^2J_{P\text{-}C}$ = 5 Hz), 24.27 (d, 3C, $^3J_{P\text{-}C}$ = 14 Hz), 29.37 (s, 1C), 29.66 (s, 1C), 29.72 (s, 1C), 29.86 (s, 1C), 31.08 (d, 1C, $^3J_{P\text{-}C}$ = 15 Hz), 32.24 (s, 1C). TOF-MS-ES+: *m/z* observed 343 $(M)^+$, 814 $(2M + I)^+$, 1284 $(3M + 2I)^+$. TOF-MS-ES-: *m/z* observed 597 $(M + 2I)^-$, 1067 $(2M + 3I)^-$.

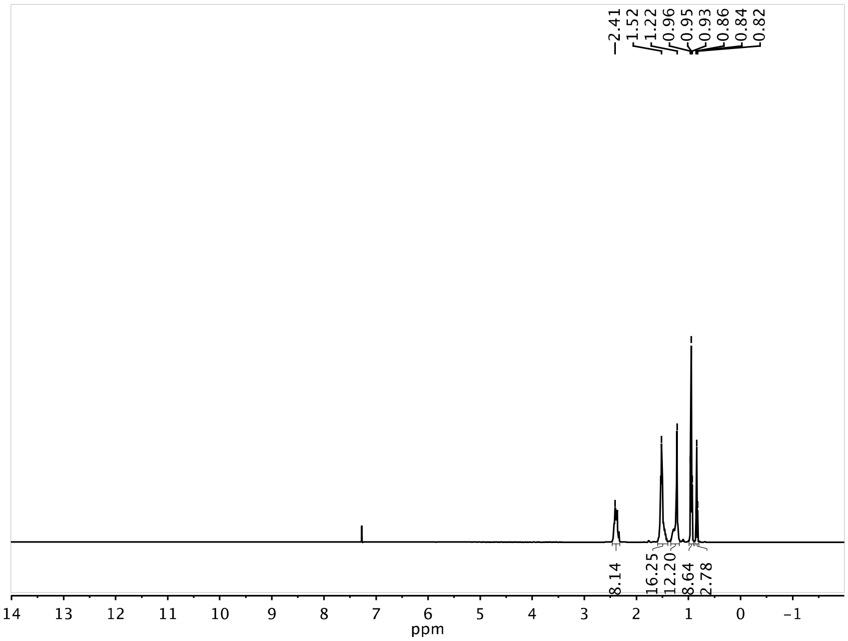

Figure S9: ^{1}H NMR spectrum of tributyl(decyl)phosphonium iodide

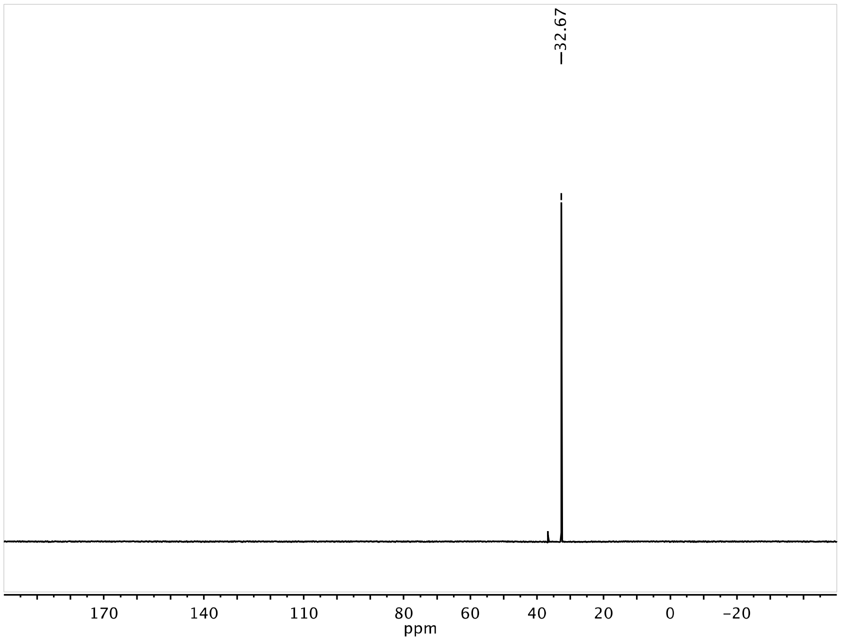

Figure S10: ^{31}P{^{1}H} NMR spectrum of tributyl(decyl)phosphonium iodide

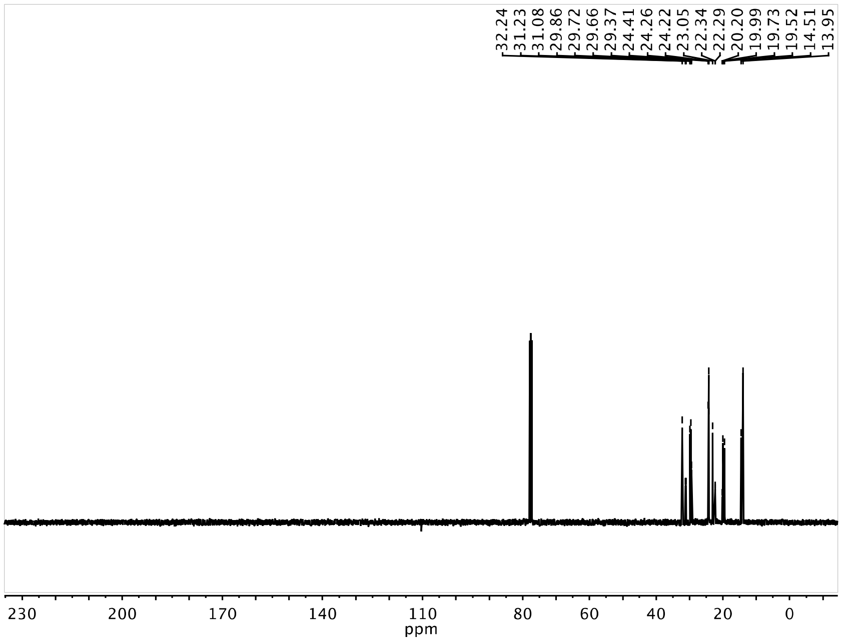

Figure S11: $^{13}C\{^1H\}$ NMR spectrum of tributyl(decyl)phosphonium iodide

Synthesis of **1a** (tributyl(hexyl)phosphonium tetrakis(pentafluorophenyl) borate)

Tributyl(hexyl)phosphonium iodide (0.680 g, 1.60 mmol) was dissolved in 4 mL of DCM, follow by the addition of solid potassium tetrakis(pentafluorophenyl) borate (1.27 g, 1.76 mmol). The mixture was stirred for 24 hours and then filtered to remove insoluble material. The solution was extracted with water (4 x 5 mL) and each extraction was tested for the presence halogen anions using silver nitrate solutions. After four extractions, there were no detectable halogens in the aqueous fraction. The organic layer was dried (Na_2SO_4), and volatiles were evaporated leaving a white solid which was identified as **1a** (1.4 g, 89%). ^1H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, 3H, J = 8 Hz, CH_3), 0.93 (t, 9H, J = 8 Hz, CH_3), 1.26 (m, 4H, $P(C_3H_6)\mathit{CH_2CH_2}CH_3)$), 1.45 (m, 16H, $PCH_2\mathit{CH_2CH_2})$, 1.94 (m, 8H, PCH_2). $^{31}P\{^1H\}$ NMR (161.82 MHz, $CDCl_3$): δ 33.13 (s). ^{19}F NMR (376.15 MHz, $CDCl_3$): δ -166.69 (t, 8F, J = 15 Hz, Ar-F), -162.74 (t, 4F, J = 23 Hz, Ar-F), -132.53 (t, 8F, J = 11 Hz, Ar-F). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ 13.16 (s, 3C), 13.85 (s, 1C), 18.37 (d, 3C, $^1J_{P\text{-}C}$ = 48 Hz), 18.64 (d, 1C, $^1J_{P\text{-}C}$ = 47), 21.49 (d, 1C, $^2J_{P\text{-}C}$ = 5 Hz), 22.36 (s, 1C), 23.43 (d, 3C, $^2J_{P\text{-}C}$ = 4 Hz), 23.95 (d, 3C, $^3J_{P\text{-}C}$ = 14 Hz), 30.40 (d, 1C, $^3J_{P\text{-}C}$ = 14 Hz), 30.96 (s, 1C), 135.33 (d, $^1J_{F\text{-}C}$ = 232 Hz, C_{meta}), 137.16 (d, $^1J_{F\text{-}C}$ = 242 Hz, C_{para}), 148.36 (d, $^1J_{F\text{-}C}$ = 241, C_{ortho}). TOF-MS-ES+: *m/z* observed 288 $(M)^+$. TOF-MS-ES-: *m/z* observed 1645 $(M + 2A)^-$.

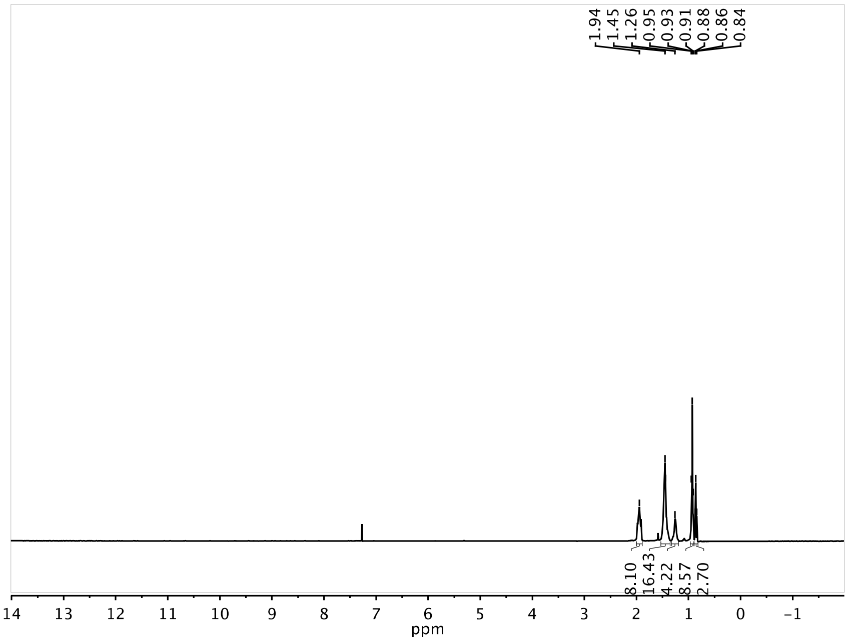

Figure S12: ^{1}H NMR spectrum of **1a**

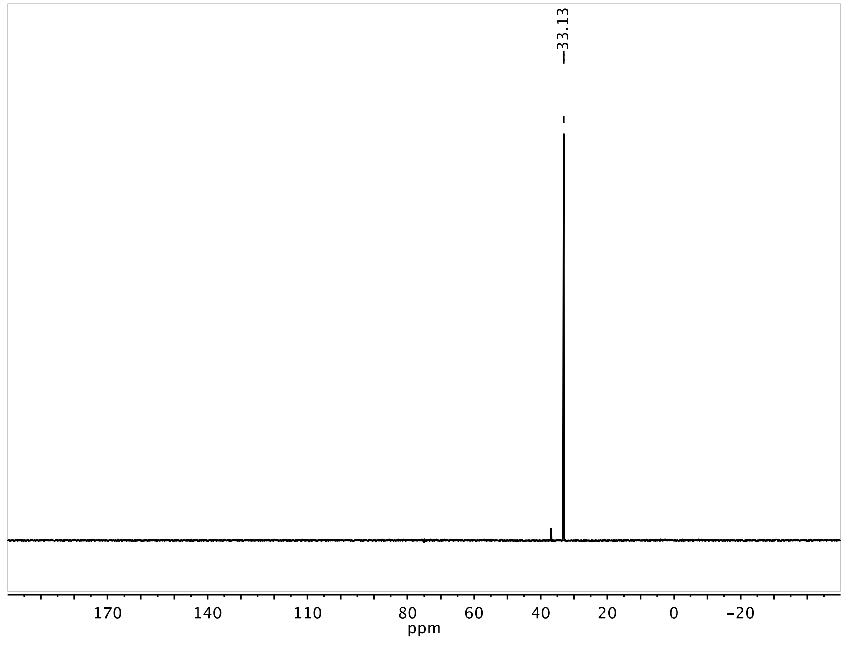

Figure S13: ^{31}P{^{1}H} NMR spectrum of **1a**.

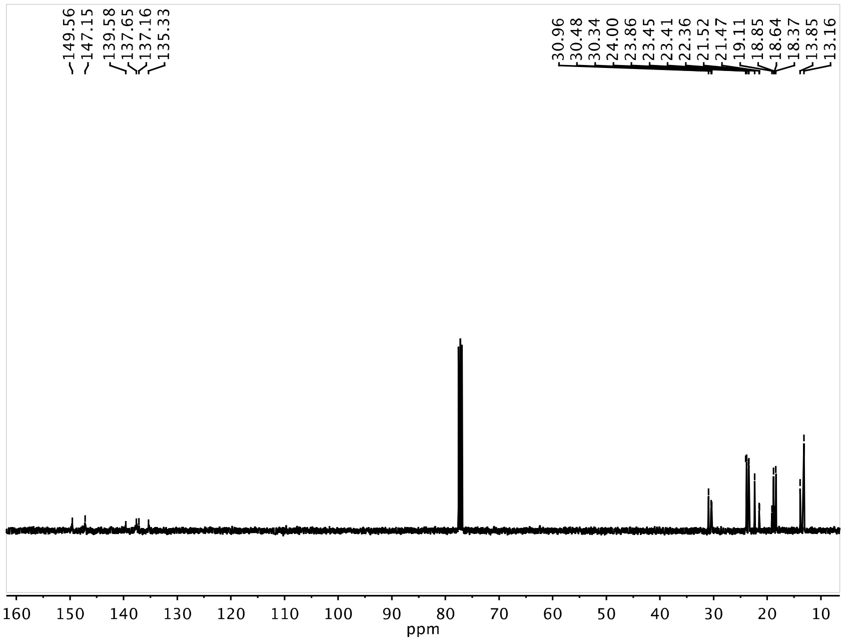

Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum of **1a**.

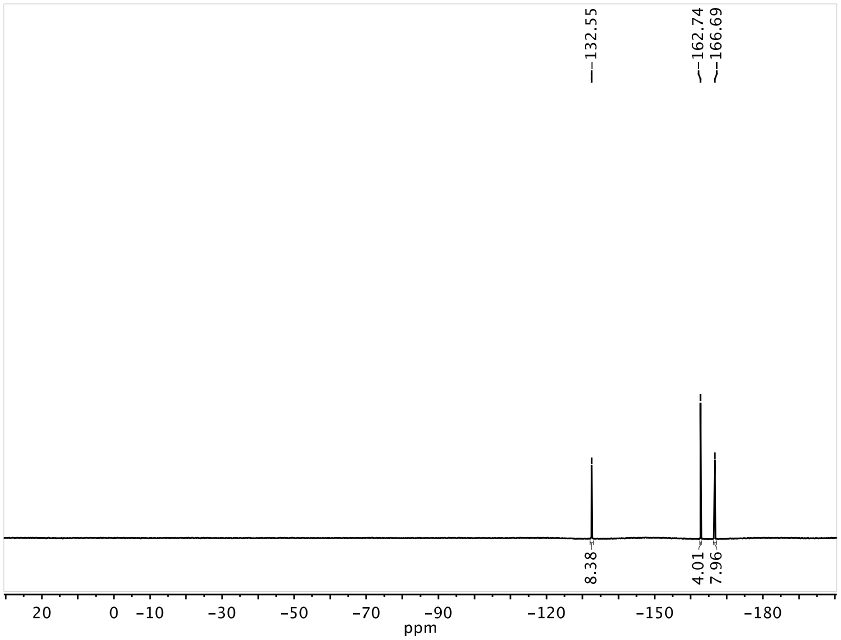

Figure S15: $^{19}F\{^{1}H\}$ NMR spectrum of **1a**.

Synthesis of **2a** (tributyl(1H,1H,2H,2H-perfluorohexyl)phosphonium tetrakis(pentafluorophenyl) borate)

Tributyl(1H,1H,2H,2H-perfluorohexyl)phosphonium (0.340 g, 0.580 mmol) was dissolved in 2 mL of DCM, follow by the addition of solid potassium tetrakis(pentafluorophenyl) borate (0.46 g, 0.64 mmol). The mixture was stirred for 24 hours and then filtered to remove insoluble material. The solution was extracted with water (4 x 5 mL) and each extraction was tested for the presence halogen anions using silver nitrate solutions. After four extractions, there were no detectable halogens in the aqueous fraction. The organic layer was dried (Na_2SO_4), and volatiles were evaporated leaving a white solid identified as **2a** (0.36 g, 50 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, 9H, *J* = 8 Hz, CH_3), 1.44 (m, 12H, $PCH_2\mathit{CH_2CH_2}CH_3$)), 2.01 (m, 6H, P*CH₂)*, 2.29 (m, 4H, $P\mathit{CH_2CH_2}C_4F_9$). $^{31}P\{^1H\}$ NMR (161.82 MHz, $CDCl_3$): 34.80 (s). ^{19}F NMR (376.15 MHz, $CDCl_3$): δ -166.50 (t, 8F, *J* = 15 Hz, Ar-F), -162.63, (t, 4F, *J* = 20 Hz, Ar-F), -132.76 (t, 8F, *J* = 10 Hz, Ar-F), -126.23 (s, 2F), -124.13 (s, 2F), 115.30 (s, 2F), 81.21 (s, 3F). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ 10.70 (d, 1C, $^1J_{P\text{-}C}$ = 52 Hz), 12.74 (s, 3C), 18.25 (d, 3C $^1J_{P\text{-}C}$ = 47 Hz), 23.07 (d, 3C, $^2J_{P\text{-}C}$ = 5 Hz), 23.59 (d, 3C, $^3J_{P\text{-}C}$ = 15 Hz), 135.60 (d, $^1J_{F\text{-}C}$ = 240 Hz, C_{meta}), 137.16 (d, $^1J_{F\text{-}C}$ = 251 Hz, C_{para}), 148.36 (d, $^1J_{F\text{-}C}$ = 235, C_{ortho}). TOF-MS-ES+: *m/z* observed 287 $(M)^+$. TOF-MS-ES-: *m/z* observed 1645 $(M + 2A)^-$.

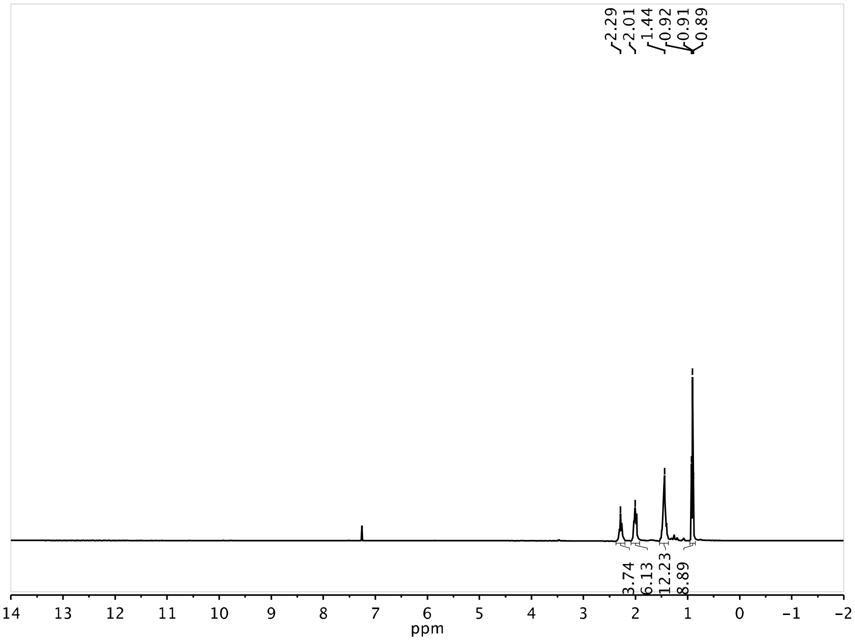

Figure S16: ^{1}H NMR spectrum of **2a**

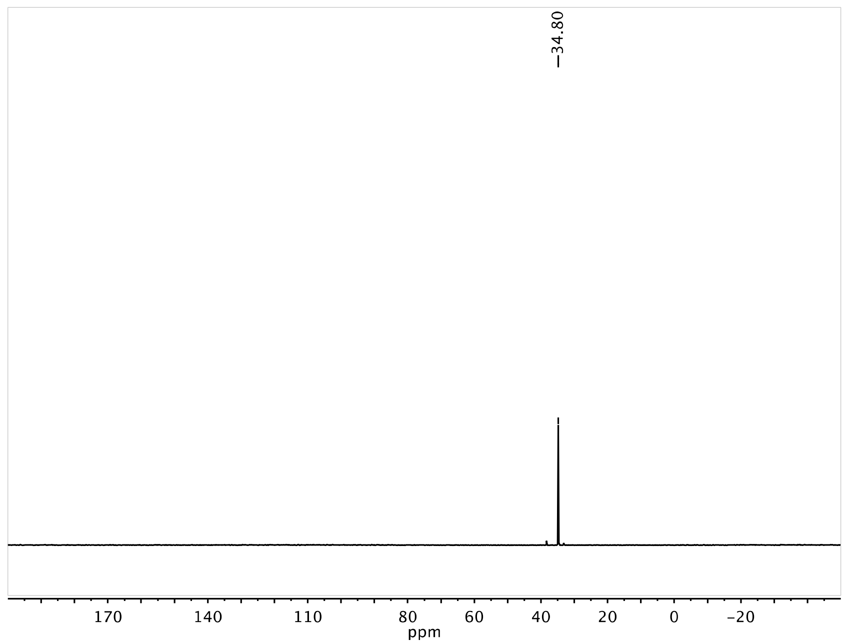

Figure S17: $^{31}P\{^1H\}$ NMR spectrum of **2a**

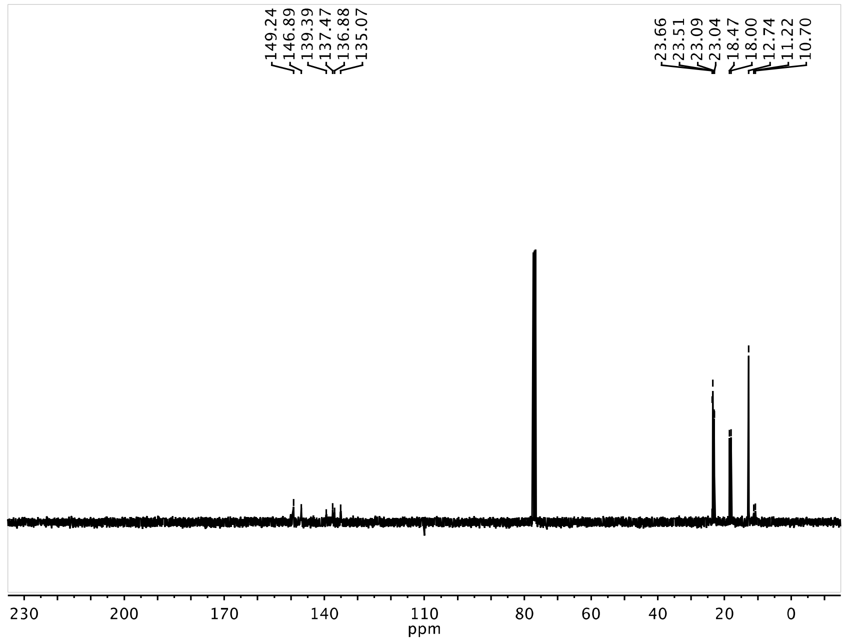

Figure S18: $^{13}C\{^1H\}$ NMR spectrum of **2a**

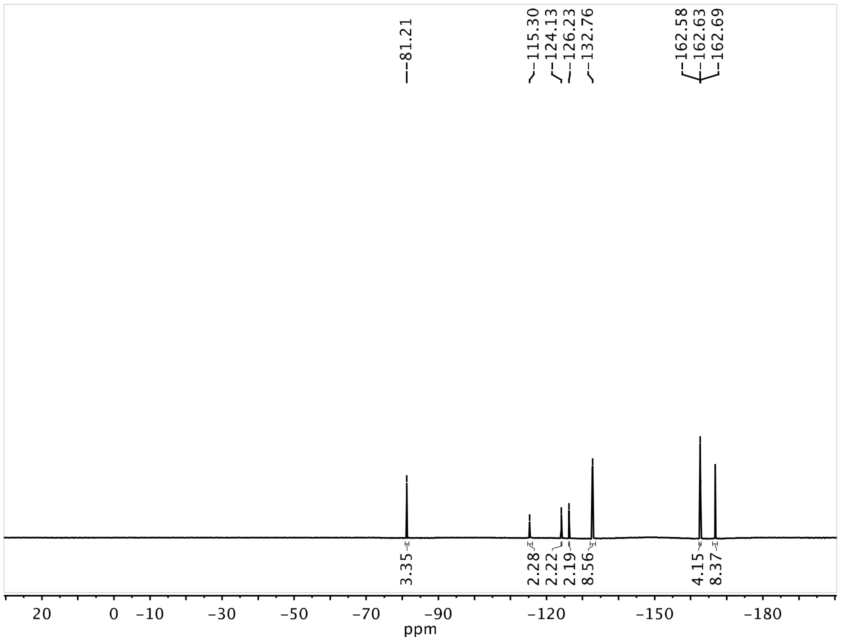

Figure S19: $^{19}F\{^1H\}$ NMR spectrum of **2a**

Synthesis of **3a** (tributyl(decyl)phosphonium tetrakis(pentafluorophenyl) borate)

Tributyl(decyl)phosphonium iodide (0.87 g, 1.80 mmol) was dissolved in 5 mL of DCM, followed by the addition of solid potassium tetrakis(pentafluorophenyl) borate (1.42 g, 1.98 mmol). The mixture was stirred for 24 hours and then filtered to remove insoluble material. The solution was extracted with water (4 x 5 mL) and each extraction was tested for the presence of halogen ions using silver nitrate solutions. After four extractions, there were no detectable halogens in the aqueous fraction. The organic layer was dried (Na_2SO_4), and volatiles were evaporated leaving a yellow viscous oil which was identified as **3a** (0.81 g, 43%). ^1H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, 3H, J = 8 Hz, CH_3), 0.93 (t, 9H, J = 8 Hz, CH_3), 1.22 (m, 12H, $PCH_2\mathit{CH_2CH_2}$), 1.45 (m, 16H, $PCH_2(\mathit{C_8H_{16}})CH_3$), 1.95 (m, 8H, PCH_2). $^{31}P\{^1H\}$ NMR (161.82 MHz, $CDCl_3$): δ 33.13 (s). ^{19}F NMR (376.15 MHz, $CDCl_3$): δ -166.68 (t, 8F, J = 15 Hz, Ar-F), -162.73 (t, 4F, J = 23 Hz, Ar-F), -132.52 (t, 8F, J = 11 Hz, Ar-F). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ 13.13 (s, 3C), 14.21 (s, 1C), 18.36 (d, 3C, $^1J_{P\text{-}C}$ = 47 Hz), 18.61 (d, 1C, $^1J_{P\text{-}C}$ = 48 Hz), 21.50 (d, 1C, $^2J_{P\text{-}C}$ = 5 Hz), 22.81 (s, 1C), 22.42 (d, 3C, $^2J_{P\text{-}C}$ = 5 Hz), 23.90 (d, 3C, $^3J_{P\text{-}C}$ = 15 Hz), 28.88 (s, 1C), 29.33 (s, 1C), 29.37(s, 1C), 29.54 (s, 1C), 30.66 (d, 1C, $^3J_{P\text{-}C}$ = 14 Hz), 31.98 (s, 1C), 136.50 (d, $^1J_{F\text{-}C}$ = 243, C_{meta}), 138.37 (d, $^1J_{F\text{-}C}$ = 246, C_{para}), 148.35 (d, $^1J_{F\text{-}C}$ = 240 Hz, C_{ortho}) . TOF-MS-ES+: *m/z* observed 343 $(M)^+$. TOF-MS-ES-: *m/z* observed 1701 $(M + 2A)^-$.

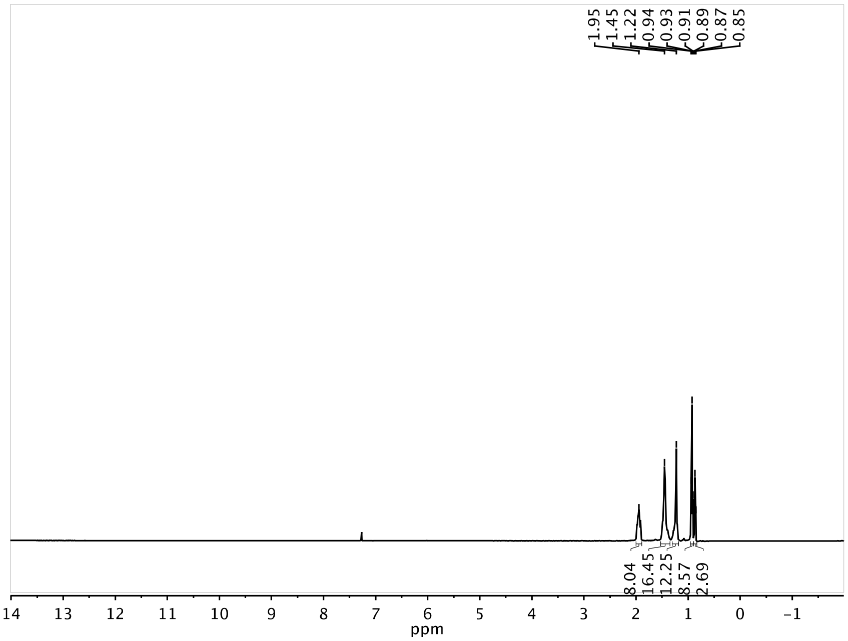

Figure S20: ^{1}H NMR spectrum of **3a**

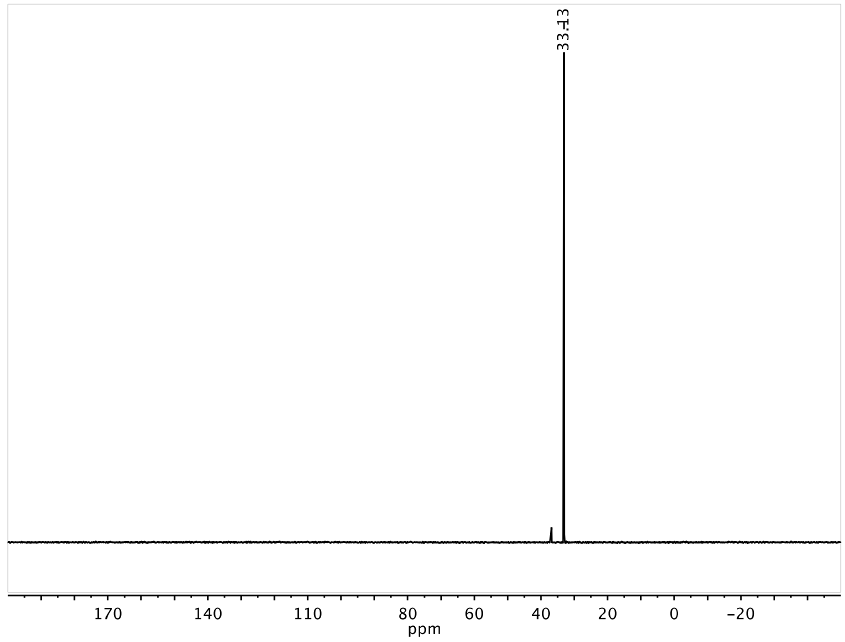

Figure S21: ^{31}P{^{1}H} NMR spectrum of **3a**

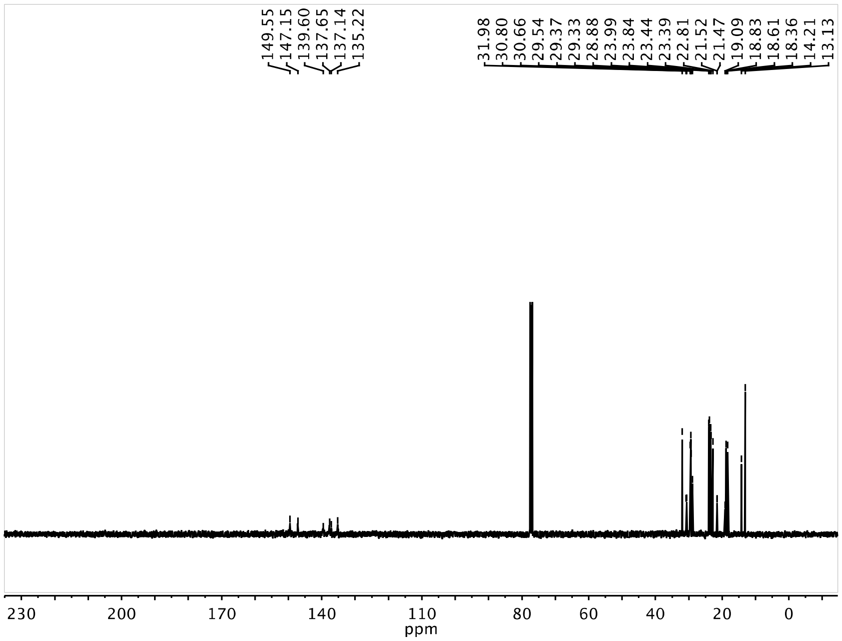

Figure S22: $^{13}C\{^1H\}$ NMR spectrum of **3a**

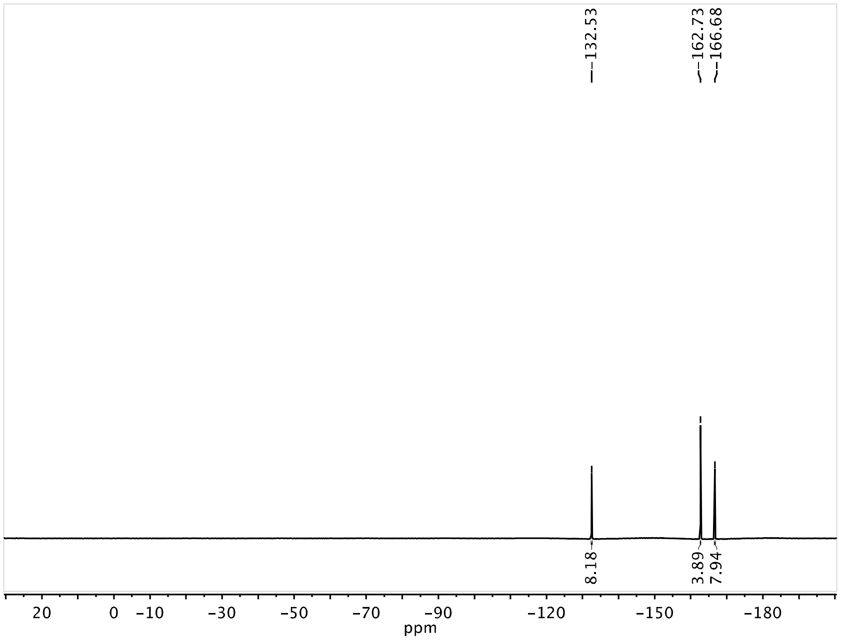

Figure S23: $^{19}F\{^1H\}$ NMR spectrum of **3a**

Synthesis of **1b** (tris(3-hydroxypropyl)hexylphosphonium iodide)

Tris(3-hydroxypropyl)phosphine (2.13 g, 10.2 mmol) and 1-iodohexane (2.21 g, 10.4 mmol) were combined in a pressure tube. DMF (6 mL) was added to the mixture and stirred for 24 hours. The solution was then poured in to diethyl ether (200 mL) and stirred for one hour. The top layer was decanted leaving a white oily residue. Volatiles were removed *in vacuo* at 100 °C for 16 hours. A colourless oil remained and was identified as **1b** (3.51 g, 82%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.85 (t, 3H, J = 8 Hz), 1.28 (m, 4H, $PCH_2CH_2CH_2\mathit{CH_2CH_2}CH_3$), 1.38 (m, 2H, $PCH_2CH_2\mathit{CH_2}CH_2CH_2CH_2$), 1.48 (m, 2H, $PCH_2\mathit{CH_2}CH_2CH_2CH_2CH_2$), 1.64 (m, 6H, $PCH_2\mathit{CH_2}$), 2.24 (m, 6H, $P\mathit{CH_2}$), 3.45 (dt, 6H, J = 4 Hz, $PCH_2CH_2\mathit{CH_2}$), 4.73 (t, 3H, J = 8 Hz, OH). $^{31}P\{^1H\}$ NMR (161.82 MHz, DMSO-d_6): δ 36.66 (s), 36.92 (s), 39.15 (s).* $^{13}C\{^1H\}$ NMR (100.5 MHz, DMSO-d_6): δ 13.86 (s, 1C), 14.7 (d, 3C, $^1J_{P\text{-}C}$ = 49 Hz), 17.8 (d, 1C,$^1J_{P\text{-}C}$ = 47), 20.53 (d, 1C, $^2J_{P\text{-}C}$ = 4 Hz), 21.8 (s, 1C), 24.07 (d, 3C, $^2J_{P\text{-}C}$ = 4 Hz), 29.74 (d, 1C, $^3J_{P\text{-}C}$ = 15 Hz), 30.4 (s, 1C), 60.37 (d, 3C, $^3J_{P\text{-}C}$ = 15 Hz). TOF-MS-ES+: *m/z* observed 293 $(M)^+$, 713 $(2M + I)^+$. TOF-MS-ES-: *m/z* observed 547 $(M + 2I)^-$, 967 $(2M + 3I)^-$.

*Three signals were observed in the product, at a 0.03:1:0.05 ratio for the signals at 36.66, 36.92, and 39.15 ppm respectively. The two minor peaks are isomers that are were carried over in the starting phosphine and are a result of the reaction conditions required to make tri(hydroxypropyl)phosphine from PH_3 gas.

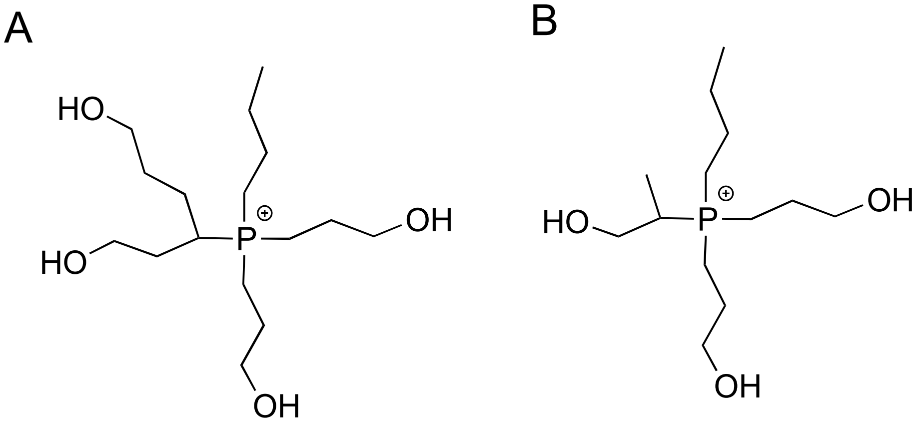

Figure S24: Structures of isomeric phosphonium cations. Ion **A** δ = 36.66 and ion **B** δ = 39.15.

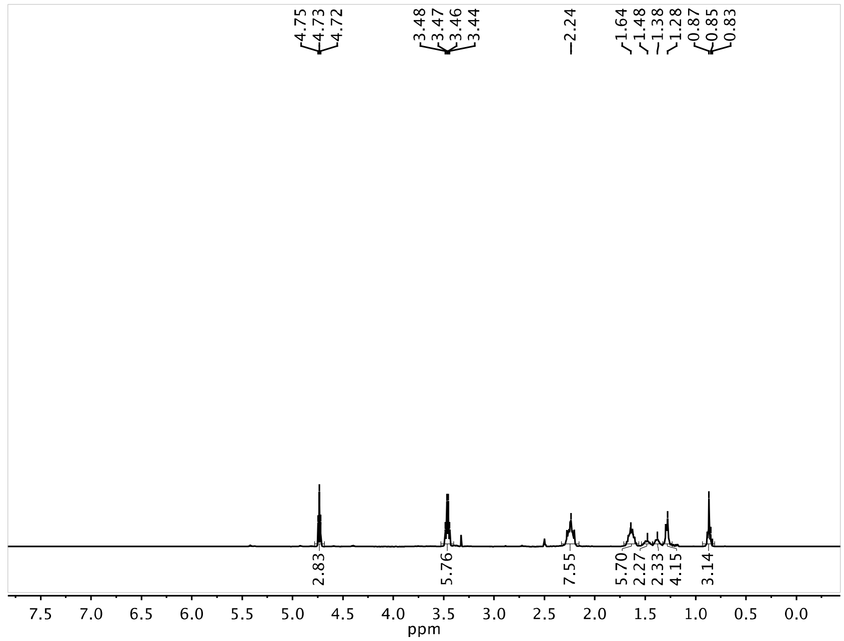

Figure S25: ^{1}H NMR spectrum of **1b**.

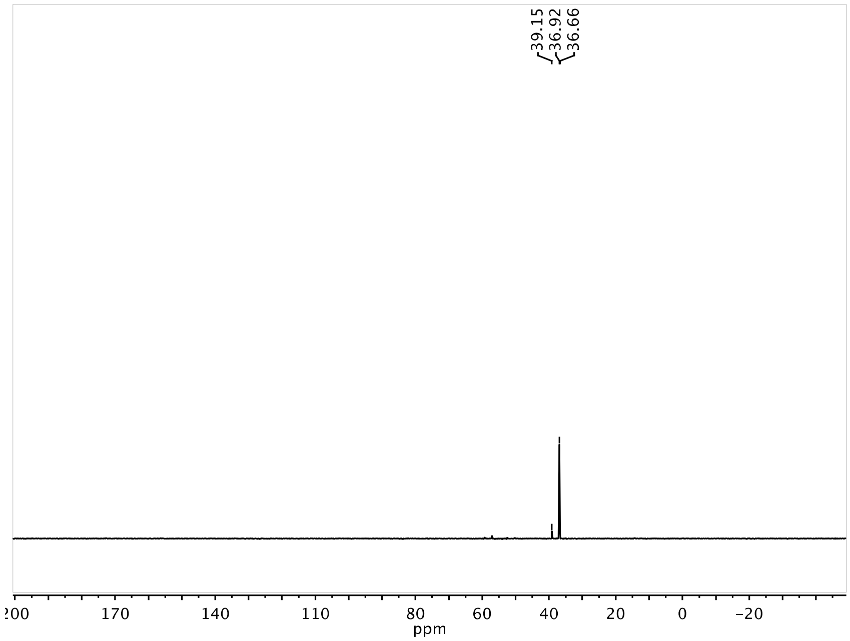

Figure S26: ^{31}P{^{1}H} NMR spectrum of **1b**.

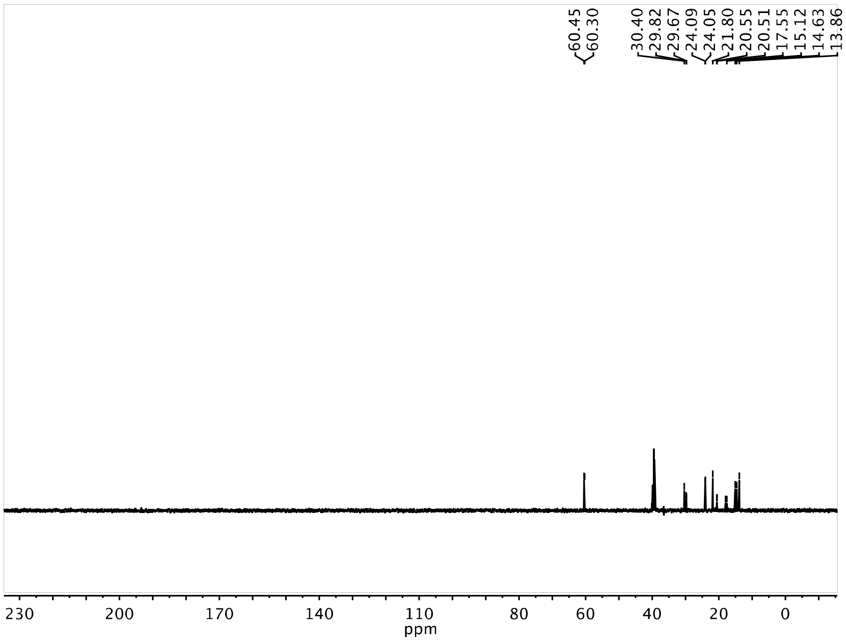

Figure S27: $^{13}C\{^{1}H\}$ NMR spectrum of **1b**

Synthesis of **2b** (tris(3-hydroxypropyl)(1H,1H,2H,2H-perfluorohexyl)phosphonium iodide)

Tris(3-hydroxypropyl) phosphine (11.06 g, 53.14 mmol) and 1,1,1,2,2,3,3,4,4-Nonafluoro-6-iodohexane (29 g, 77.54 mmol) were combined in a pressure tube. DMF (10 mL) was added to the mixture and stirred for 24 hours. The solution was then poured in to diethyl ether (200 mL) and stirred for one hour. The top layer was decanted leaving a white oily residue, which was precipitated in diethyl ether (200 mL) two additional times. The white residue was heated (100 °C) *in vacuo* for 16 hours to remove volatiles leaving a colourless oil, which was identified as **2b** (6.75 g, 22%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.84 (m, 6H, $PCH_2\mathit{CH_2}CH_2OH$), 2.5 (m, 6H, $P\mathit{CH_2}$), 2.69 (m, 4H, $P\mathit{CH_2CH_2}(C_4F_9)$), 3.67 (t, 2H, J = 8 Hz, $\mathit{CH_2}OH$), 4.77 (s, 1H, OH). $^{31}P\{^{1}H\}$ NMR (161.82 MHz, DMSO-d_6): δ 38.76 (s), 39.15(s), 41.98 (s). ^{19}F NMR (376.15 MHz, DMSO-d_6): δ -126.8 (m, 2F), -124.3 (s, 2F), -115.6 (m, 2F), -82.3 (m, 3F). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, DMSO-d_6): δ 7.3 (d, $^{1}J_{P\text{-}C}$ = 49 Hz), 15.9 (d, 3C, $^{2}J_{P\text{-}C}$ = 4 Hz), 52.5 (d, 3C, $^{3}J_{P\text{-}C}$ = 15 Hz). TOF-MS-ES+: *m/z* observed 455 $(M)^{+}$, 1037 $(2M + I)^{+}$. TOF-MS-ES-: *m/z* observed 709 $(M + 2I)^{-}$.

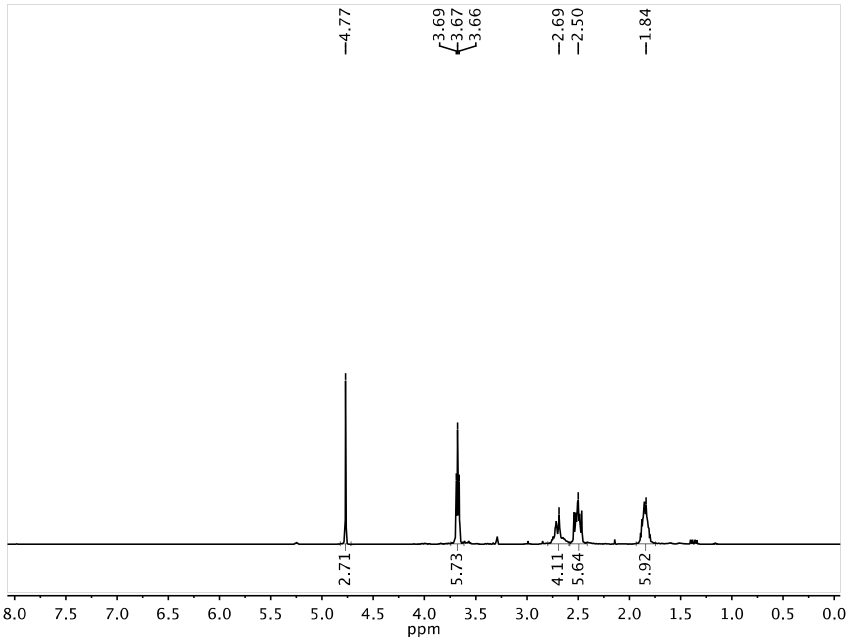

Figure S28: ^{1}H NMR spectrum of **2b**.

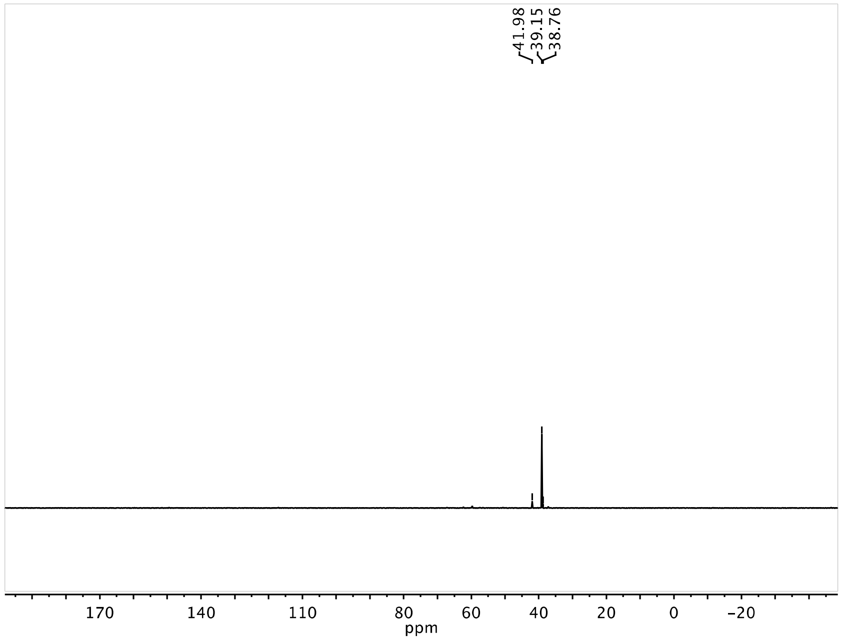

Figure S29: ^{31}P{^{1}H} NMR spectrum of **2b**.

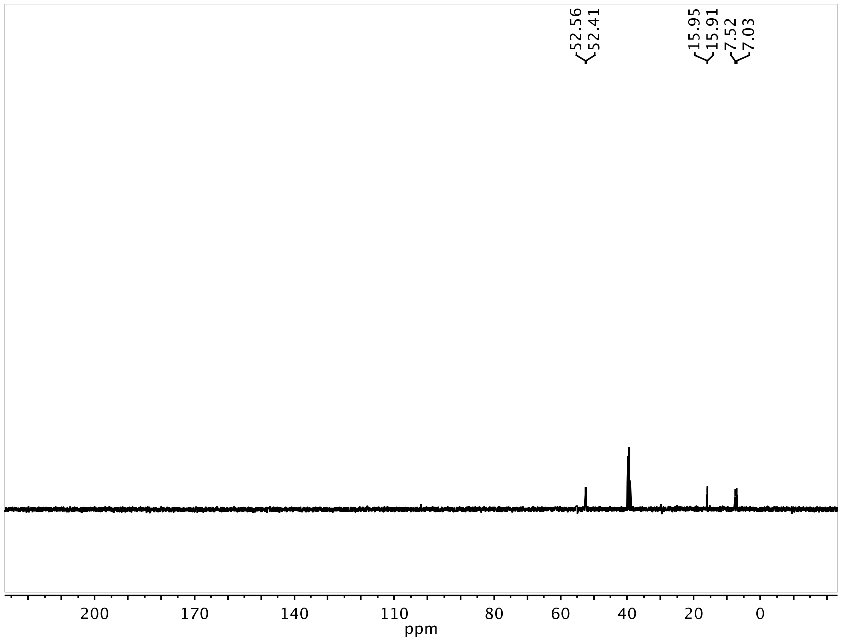

Figure S30: $^{13}C\{^1H\}$ NMR spectrum of **2b**.

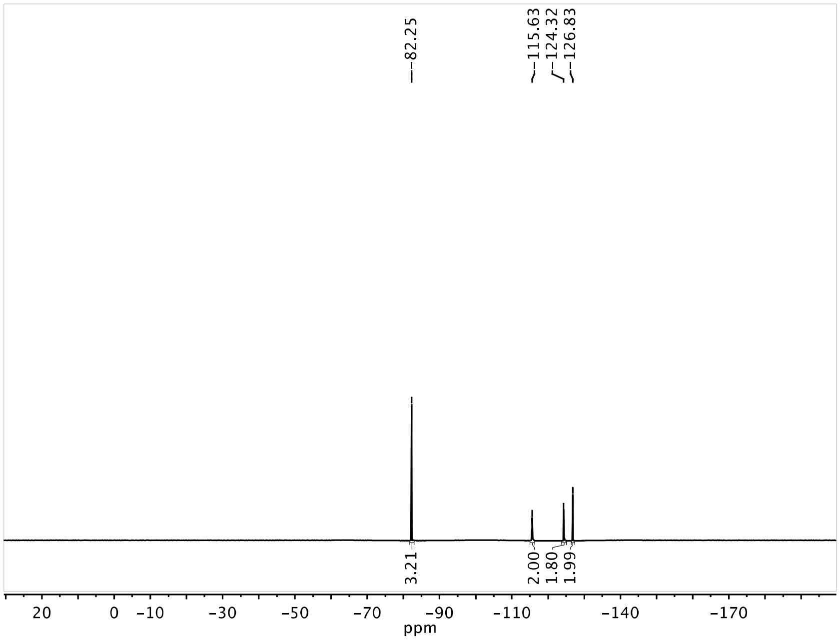

Figure S31: $^{19}F\{^1H\}$ NMR spectrum of **2b**.

Synthesis of **3b** (tris(3-hydroxypropyl)decylphosphonium iodide)

Tri(hydroxypropyl) phosphine (2.88 g, 13.84 mmol) and 1-iododecane (3.74 g, 13.94 mmol) were combined in a pressure tube. DMF (6 mL) was added to the mixture and stirred for 24 hours. The solution was then poured in to diethyl ether (250 mL) and stirred for one hour. The top layer was decanted leaving behind a white oily residue. The residue was then rinsed with diethyl ether (200 mL) two times. Volatiles were removed *in vacuo* at 100 °C for 16 hours. A colourless oil remained and was identified as **3b** (1.7 g, 45%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.84 (t, 3H, J = 8 Hz), 1.23 (m, 12H, $\mathrm{PCH_2CH_2CH_2}(CH_2CH_2)_3\mathrm{CH_3}$), 1.36 (m, 2H, $\mathrm{PCH_2CH_2}CH_2\mathrm{(CH_2)_6CH_3}$), 1.47 (m, 2H, $\mathrm{PCH_2}CH_2\mathrm{(CH_2)_7CH_3}$)), 1.65 (m, 6H, $\mathrm{PCH_2}CH_2$), 2.24 (m, 6H, $\mathrm{P}CH_2$), 3.46 (bs, 6H, $\mathrm{PCH_2CH_2}CH_2$), 4.73 (bs, 3H, OH). ^{31}P{^{1}H} NMR (161.82 MHz, DMSO-d_6): δ 36.66 (s), 36.92 (s), 39.15 (s). ^{13}C{^{1}H} NMR (100.5 MHz, DMSO-d_6): δ 13.95 (s, 1C), 14.9 (d, 3C, $^1J_{\mathrm{P\text{-}C}}$ = 49 Hz), 17.9 (d, 1C, $^1J_{\mathrm{P\text{-}C}}$ = 48), 20.59 (d, 1C, $^2J_{\mathrm{P\text{-}C}}$ = 4 Hz), 22.4 (s, 1C), 24.07 (d, 3C, $^2J_{\mathrm{P\text{-}C}}$ = 4 Hz), 28.22 (s, 1C), 28.61 (s, 1C), 28.73 (s, 1C), 28.90 (s, 1C), 30.01 (d, 1C, $^3J_{\mathrm{P\text{-}C}}$ = 15 Hz), 31.23 (s, 1C), 60.27 (d, 3C, $^3J_{\mathrm{P\text{-}C}}$ = 15 Hz). TOF-MS-ES+: *m/z* observed 349 $(\mathrm{M})^+$, 826 $(2\mathrm{M} + \mathrm{I})^+$. TOF-MS-ES-: *m/z* observed 603 $(\mathrm{M} + 2\mathrm{I})^-$, 1079 $(2\mathrm{M} + 3\mathrm{I})^-$.

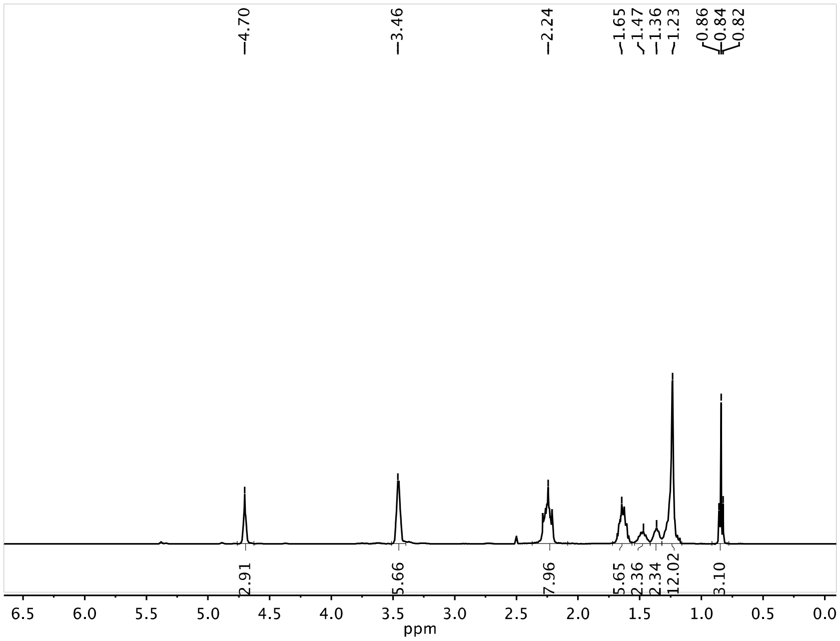

Figure S32: ^{1}H NMR spectrum of **3b**.

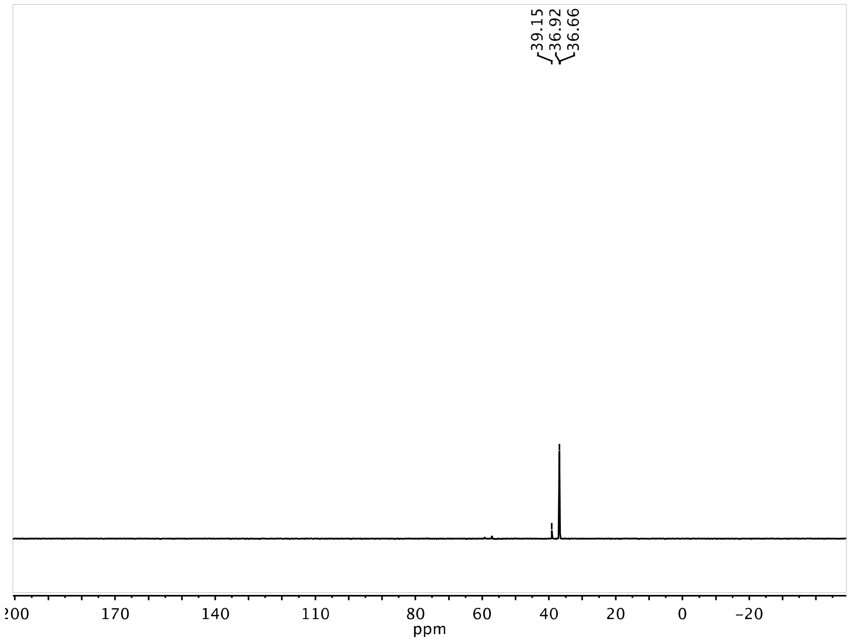

Figure S33: $^{31}P\{^{1}H\}$ NMR spectrum of **3b**.

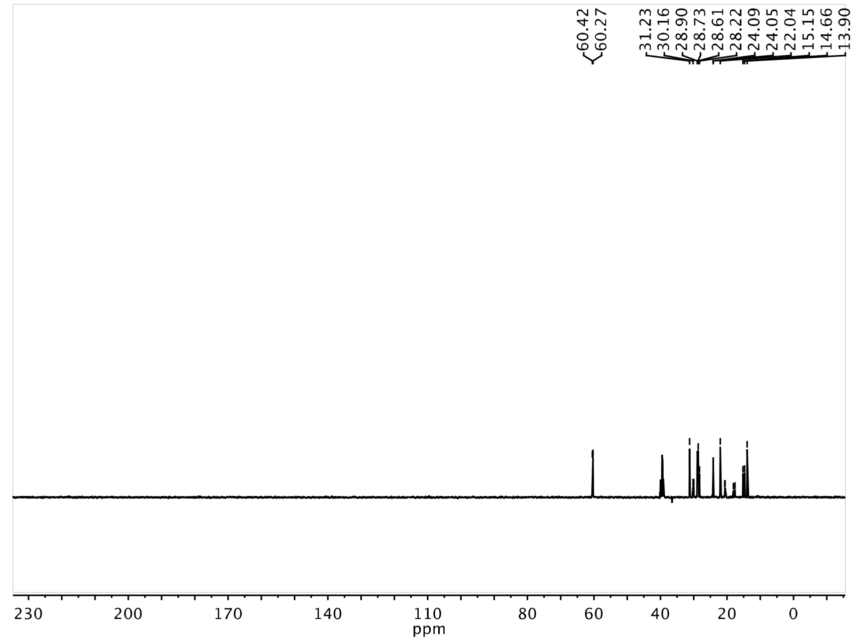

Figure S34: $^{13}C\{^{1}H\}$ NMR spectrum of **3b**.