

Supporting Information: Ionic Liquid Adsorption at the Silica–Oil Interface Revealed by Neutron Reflectivity

*Peter K. Cooper,^a Hua Li,^a Nageshwar Rao Yepuri,^{b,c} Andrew Nelson,^c Grant B. Webber,^d
Anton P. Le Brun,^c Tamim A. Darwish,^{b,c} Gregory G. Warr,^e Rob Atkin^{a,*}*

^a School of Molecular Sciences, University of Western Australia, 35 Stirling Highway,
Crawley, WA 6009, Australia

^b National Deuteration Facility, Australian Nuclear Science and Technology Organisation,
Locked Bag 2001, Kirrawee DC, NSW 2232, Australia

^c Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW 2234,
Australia

^d Priority Research Centre for Advanced Fluids and Interfaces, University of Newcastle,
Callaghan, NSW 2308, Australia

^e School of Chemistry and Australian Institute for Nanoscale Science and Technology,
University of Sydney, Sydney, NSW 2006, Australia

* Corresponding author e-mail: rob.atkin@uwa.edu.au

Table S1. Scattering length densities, ρ , and molecular volumes M_V .

Species	ρ ($\times 10^{-6} \text{ \AA}^{-2}$)			M_V (\AA^3)		
	25 °C	60 °C	80 °C	25 °C	60 °C	80 °C
Si	2.07	2.07	2.07	-	-	-
SiO ₂	3.47	3.47	3.47	38	38	38
<i>h</i> -octane	-0.52	-0.50	-0.49	272	283	290
<i>d</i> -octane	6.32 ^a	6.09	5.91	272	283	290
P_{6,6,6,14} (^{<i>i</i>}C₈)₂PO₂	-0.28	-0.27	-0.27	1450	1485	1505
P_{6,6,6,14}⁺	-0.38	-0.38	-0.37	950	973	986
(^{<i>i</i>}C₈)₂PO₂⁻	-0.08	-0.08	-0.08	490	501	508
<i>d</i>-P_{6,6,6,14} (^{<i>i</i>}C₈)₂PO₂	4.41 ^b	4.30	4.25	1450	1485	1505
<i>d</i>-P_{6,6,6,14}⁺	6.77 ^b	6.61	6.52	950	973	986

^a Based on 99.4% isotopic purity of *d*-octane. Pure value 6.36.

^b Based on 96% isotopic purity of *d*-P_{6,6,6,14}⁺.

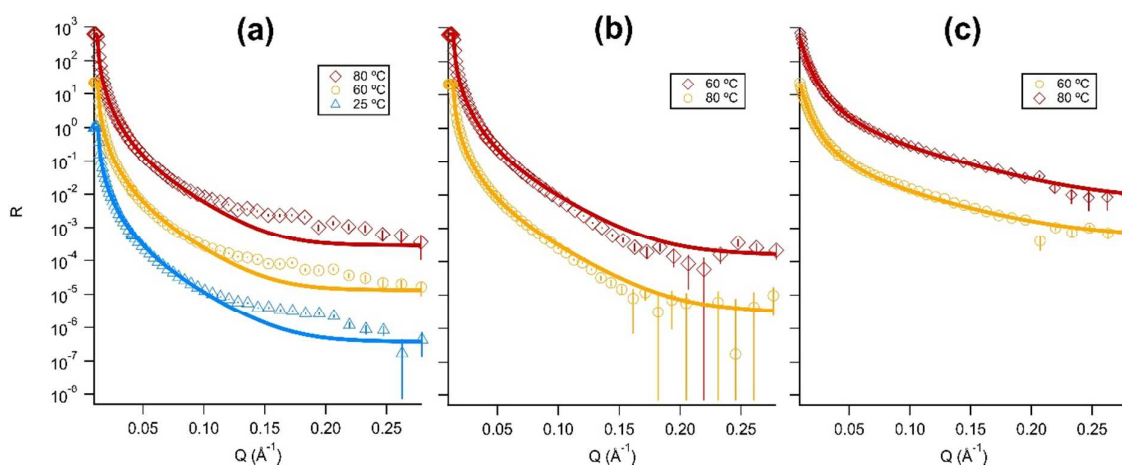
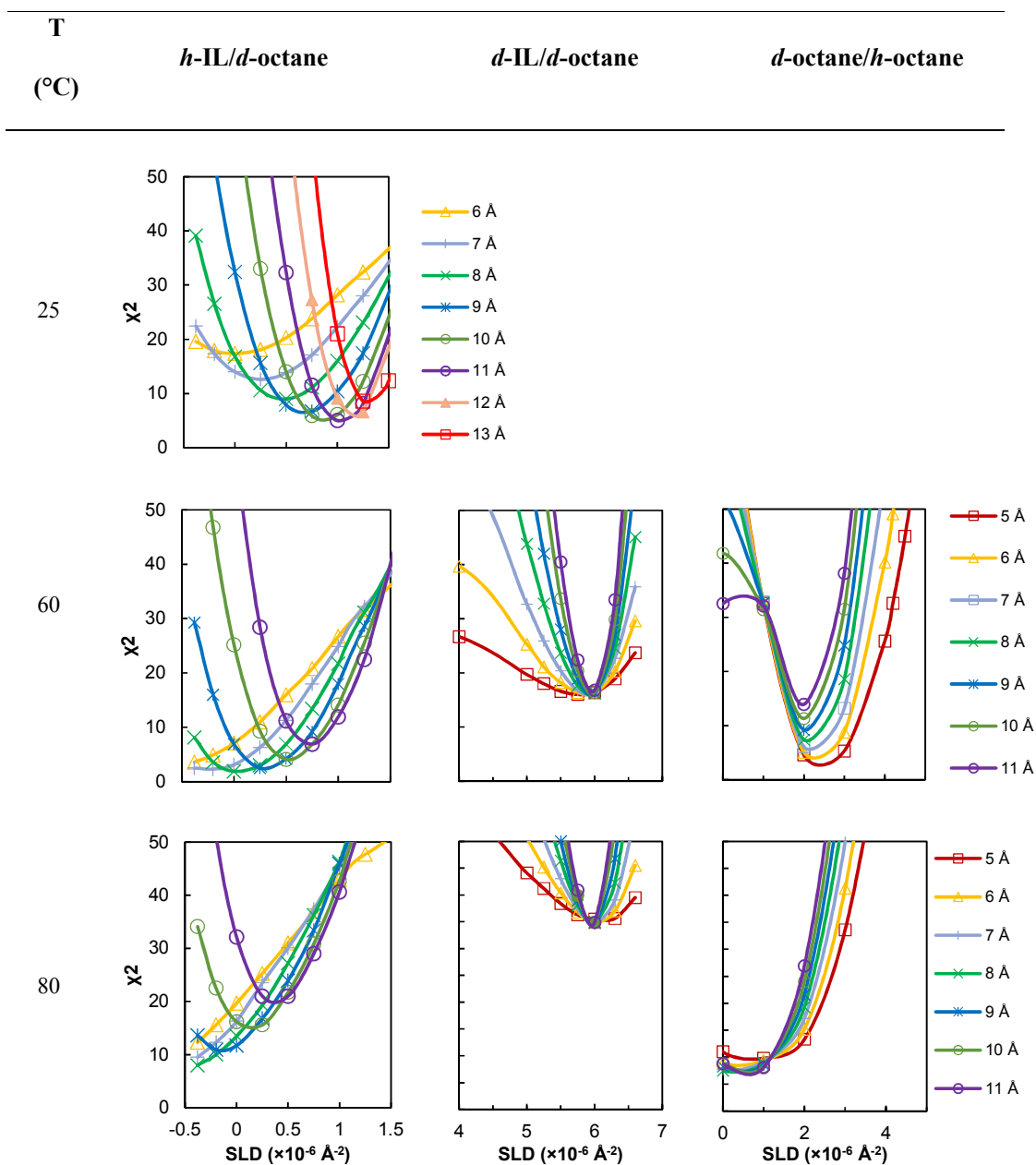


Figure S1. R vs Q as a function of temperature for three different contrast conditions (a) *h*-P_{6,6,6,14} (^{*i*}C₈)₂PO₂ in *d*-octane; (b) *d*-P_{6,6,6,14} (^{*i*}C₈)₂PO₂ in *d*-octane; (c) *d*-P_{6,6,6,14} (^{*i*}C₈)₂PO₂ in *h*-octane. The data for 60 °C and 80 °C have been vertically offset for clarity. The solid lines show the fits to the data modeled without an adsorbed layer.

Table S2. The χ^2 best fit values as a function of IL layer SLD for different IL layer thicknesses at 25 °C, 60 °C and 80 °C. The legend shows which IL layer thickness the data correspond to.



Deuterated P_{6,6,6,14} (¹³C)₈PO₂ synthesis details

General

Chemicals and reagents of the highest grade were purchased from Sigma-Aldrich and were used without further purification. Solvents were purchased from Sigma-Aldrich Chemical Co., Merck and Fronine Laboratory Supplies and were purified by literature methods. When solvent mixtures were used as an eluent, the proportions are given by volume. NMR spectroscopy solvents were purchased from Cambridge Isotope Laboratories Inc. and were used without further purification. Thin-layer chromatography (TLC) was performed on Fluka Analytical silica gel aluminium sheets (25 F254). Davisil® silica gel (LC60Å 40-63 micron) was used for bench-top flash column chromatography and prepacked silica cartridges were used for REVELERIS™ flash chromatography.

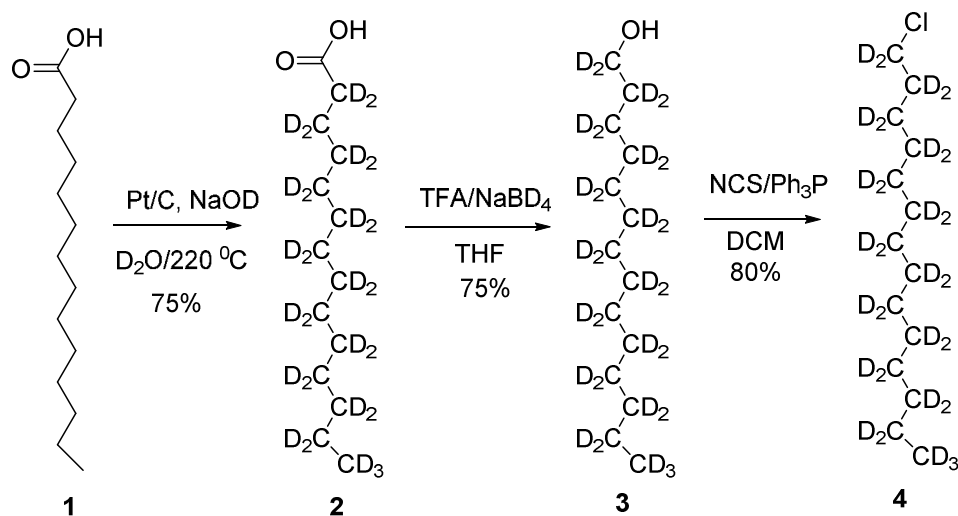
Methods and Data Analysis

Electrospray ionisation mass spectra (ESI-MS) were recorded on a 4000 QTrap AB SCIEX Mass Spectrometer. The overall percent deuteration of the molecules was calculated by ER-MS (enhanced resolution – MS) using the isotope distribution analysis of the different isotopologues by analysing the area under each MS peak which corresponds to a defined number of deuterium atoms. The contribution of the carbon-13 (natural abundance) to the value of the area under each [X^{+1}] MS signal is subtracted based on the relative amount found in the protonated version. In a typical analysis we measure the C-13 natural abundance contribution by running ER-MS of the protonated version (or estimate it by ChemDraw software) and use this value in our calculation using an in-house developed method that subtracts this contribution from each MS signal constituting the isotope distribution. ¹H NMR (400 MHz), ¹³C NMR (100 MHz), and ²H NMR (61.4 MHz) spectra were recorded on a

Bruker 400 MHz spectrometer at 298 K. Chemical shifts, in ppm, were referenced to the residual signal of the corresponding solvent. Deuterium NMR spectroscopy was performed using the probe's lock channel for direct observation.

Synthesis of trihexyl tetradecyl phosphonium-*d*₆₈bis (2,4,4-trimethylpentyl) phosphinate:

Synthesis of 1-tetradecylchloride-*d*₂₉:



Scheme S1. Synthesis of 1-tetradecylchloride-*d*₂₉

Deuteration of tetradecanoic acid-*d*₂₇ (2)

A mixture of tetradecanoic acid **1** (13 g, 56.92 mmol), 10% Pt/C catalyst (1.62 g, 0.83 mmol) and 40% NaOD solution (2.49 g, 60.74 mmol or 6.22 mL of 40% NaOD in D₂O) in D₂O (120 mL) was stirred under hydrothermal conditions for 72 hours at 220 °C in a Mini Benchtop 4560 Parr reactor (600 mL vessel capacity, 206 bar max. pressure, 350 °C max. temperature). At 220°C and with these reagents, the Parr reactor reached 25 bar in pressure. After cooling, the reaction mixture was diluted with dichloromethane (200 mL) and the mixture filtered

through Celite to remove the catalyst. The filtered catalyst was washed with water (3 × 100 mL) and the filtrate acidified to pH 2 with dilute HCl. The product was extracted with dichloromethane (100 mL × 3) and the combined organic phases were dried over Na₂SO₄, filtered and concentrated in *vacuo* to give a white solid (12.5 g). The product was then run through a second cycle in the Parr reactor with fresh Pt/C catalyst, NaOD and D₂O under the same conditions as above. Following extraction and evaporation of solvent, the final product was obtained as a white solid **2** (10.9 g, 42.75 mmol, 75.1% yield, deuteration level: 97%). ESI-MS [M⁺] m/z 254, isotopic distribution *d*₂₄ 3.4%, *d*₂₅ 10.0%, *d*₂₆ 33.6%, *d*₂₇ 52.9%.

Synthesis of 1-tetradecanol-d₂₉ (**3**)

To a cold (0°C) suspension of sodium borodeuteride (1.29 g, 30.70 mole) and tetradecanoic acid-*d*₂₇ **2** (7.0 g, 27.74 mmol) in dry THF (20 ml) was added CF₃COOH (3.5 g, 30.7 mole) slowly over 15 min period. The reaction mixture was allowed gradually to warm to room temperature. The reaction mixture was left to stir for further 4 hr at the same temperature. The mixture was quenched with dilute HCl (5 ml, 3N), extracted with ether (3 x 10 ml), the ether extract was further washed with water, brine and dried over anhydrous MgSO₄. The corresponding alcohol was purified by column chromatography (*n*-hexane:ethyl acetate; 96:4) to yield compound **3** (5g, 20.57 mmol, 75% yield, deuteration level: 97%) as a colourless liquid.

¹H NMR (CDCl₃) residual protons δ 0.84 (m), 1.23 (m), 1.61 (m), 3.63 (m)

²H NMR (CDCl₃) δ 0.78 (s, 3D), 1.16 (m, 22.4D), 1.49 (m, 2.12D), 3.57 (m, 2.0D)

¹³C NMR (CDCl₃) δ 12.9 (m), 21.4 (m), 24.5 (m), 28.3 (m), 30.2 (m), 31.6 (m), 62.3 (m).

Synthesis of 1-tetradecylchloride-d₂₉ (**4**)

To a cold (0 °C) solution of 1-tetradecanol-*d*₂₉ (**3**) (5.0 g, 20.57 mmol) and triphenyl phosphine (5.77 g, 22.02 mmol) in dichlormethane (100 mL) was added slowly *n*-

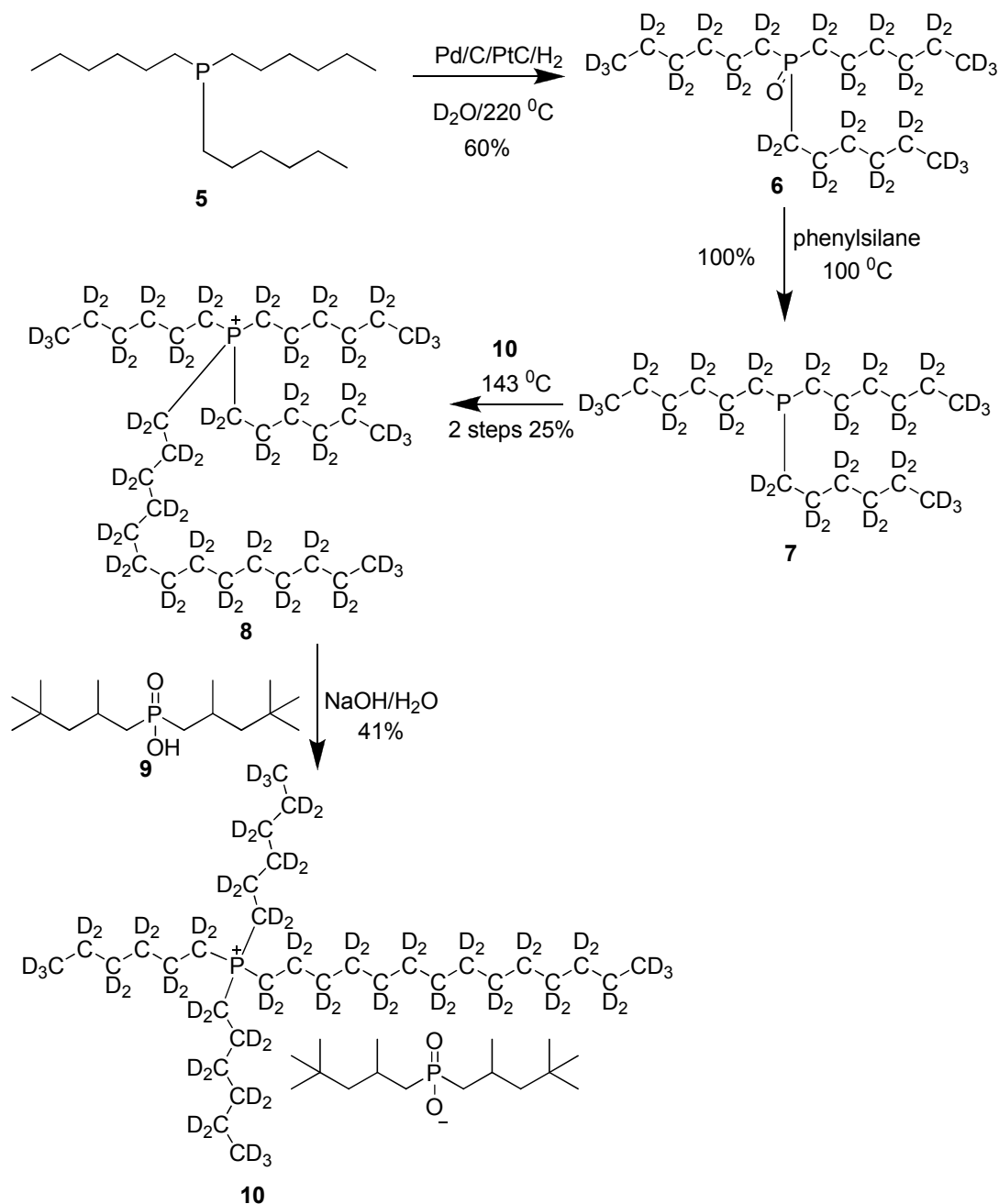
chlorosuccinimide (2.9 g, 22.02 mmol). The reaction mixture was brought to room temperature and stirring was continued for 45 minutes, washed with sodium thiosulfate saturated solution (150 mL). The reaction was monitored by TLC using 100% hexane as a solvent system. The organic layer was evaporated to give a solid. The solid was taken into a mortar and it was triturated with hexane (200 mL \times 5), and the combined hexane portions were evaporated. The residue was purified by flash chromatography on silica column using 100% petroleum ether to give a colourless liquid **4** (4.3 g, 16.47 mmol, yield 80%) (Scheme 1).

¹H NMR (CDCl₃) residual protons δ 0.88 (m), 1.23 (m), 1.38 (m), 1.58 (m), 1.75 (m), 3.52 (m)

²H NMR (CDCl₃) δ 0.82(s, 3D), 1.19 (m, 19D), 1.35 (m, 2.5D), 1.70 (m, 2D), 3.48 (m, 2.0D)

¹³C NMR (CDCl₃) δ 13.1 (m), 21.4 (m), 25.8 (m), 28.4 (m), 30.04 (m), 31.8 (m), 44.2 (m).

Synthesis of trihexyl-tetradecyl-phosphonium chloride-*d*₆₈ (10):



Scheme S2. Synthesis of trihexyl-tetradecyl-phosphonium chloride- d_{68}

Deuteration of trihexyphosphineoxide- d_{39} (6):

A mixture of trihexylphosphine **5** (7 g, 24.47 mmol), 10% Pt/C catalyst (1.5 g), and 10% Pd/C catalyst (1.5 g) in D_2O (135 mL) was stirred under N_2 bubbling for 2 min followed by H_2

bubbling for 2 min at RT. The reaction mixture was heated at 220 °C for 1 day. After cooling, the reaction mixture was diluted with DCM, filtered through Celite, washed with DCM and then the aqueous phase was extracted with dichloromethane (3 x 50 mL). The combined extracts were dried over MgSO₄ and then evaporated to give **6** as a colourless liquid (4.8 g, 14.07 mmol, 60% yield, deuteration level: 93%).

¹H NMR (CDCl₃) residual protons δ 0.81 (m), 0.87 (m), 1.23 (m), 1.29 (m), 1.32 (m), 1.49 (m), 1.62 (m).

²H NMR (CDCl₃) δ 0.78 (m, 6.7D), 1.18 (m, 8.2D), 1.28 (m, 4.0D), 1.44 (m, 4D), 1.58 (m, 3.57D)

¹³C NMR (CDCl₃) δ 12.7 (m), 21.1 (m), 26.9 (m), 29.7 (m).

³¹P NMR (CDCl₃) δ 50.

ESI-MS [M^{+Na}] m/z 364, isotopic distribution with 93% D level, *d*₃₃ 1.5%, *d*₃₄ 10.5%, *d*₃₅ 13.5%, *d*₃₆ 17.7%, *d*₃₇ 21.0%, *d*₃₈ 21.6%, *d*₃₉ 14.2%.

Synthesis of deuterated trihexylphosphine-d₃₉ (7):

A solution of trihexylphosphineoxide-*d*₃₉ **6** (3.0 g, 8.79 mmol) in phenylsilane (4 mL) was heated to 100 °C in a sealed tube under nitrogen for overnight. The reaction was monitored by ³¹P NMR in degassed CDCl₃ through the disappearance of the starting material peak at 50.8 ppm and the appearance of trihexylphosphine peak at -33.65 ppm (Figure 12).

Phenylsilane was removed under reduced pressure to give pale yellow residue, which is used in the next step without further purification.

Synthesis of deuterated trihexyltetradecylphosphine chloride-d₆₈ (8):

Trihexylphosphine-*d*₃₉ **7** (2.85 g, 8.79 mmol) neat was heated to 143 °C before tetradecylchloride-*d*₂₉ (3.03 g 12.30 mmol) was added slowly. The temperature was maintained at 143 °C for 24 hrs. The progress of the reaction was monitored by ³¹P NMR

spectroscopy in CDCl_3 (^{31}P peak at at -33.65 ppm disappeared to give a peak at 32 ppm, Figure 16). After the completion of the reaction, the compound was purified on 10 cm silica bed using a gradient solvent system, 100 mL hexane, 100 mL of 25% ethyl acetate in hexane and 100 mL 100% ethyl acetate. Trihexyltetradecylphosphine chloride- d_{68} **8** was eluted in 100% ethyl acetate and the solvent was evaporated under reduced pressure to give compound **8** as a colourless liquid (4.8 g, 8.71 mmol, quantitative, deuteration level 96%).

$^1\text{H NMR}$ (CDCl_3) residual protons δ 0.88 (m), 0.91 (m), 1.21 (m), 1.27 (m), 1.34 (m), 1.44 (m), 1.49 (m), 1.77 (m), 2.16 (m), 2.20 (m).

$^2\text{H NMR}$ (CDCl_3) δ 0.78 (m, 6.7D), 1.18 (m, 8.2D), 1.28 (m, 4.0D), 1.44 (m, 4D), 1.58 (m, 3.57D), 2.14 (3.0D).

$^{13}\text{C NMR}$ (CDCl_3) δ 12.7 (m), 21.1 (m), 26.9 (m), 29.7 (m).

$^{31}\text{P NMR}$ (CDCl_3) δ 32.

ESI-MS [M^{+1}] m/z 552. Isotopic distribution 96% D level, d_{63} 6.7%, d_{64} 14.8%, d_{65} 23.0%, d_{66} 25.9%, d_{67} 20.3%, d_{68} 9.2%.

Synthesis of deuterated trihexyl(tetradecyl)phosphonium- d_{68} bis(2,4,4-trimethylpentyl)phosphinate (10):

To a warm (55 °C) mixture of trihexyltetradecyl phosphonium chloride- d_{68} **8** (6.2 g, 11.25 mmol) and bis(2,4,4-trimethylpentyl)phosphinic acid **9** (3.5 g, 12.06 mmol, 85% pure supplied by CYANEX[®] 272 {Cytect Industries}, prewashed with 20% NaOH followed by 20% H_2SO_4 and dried) in water (10 ml deionised water) was added slowly NaOH (0.450 g, 11.25 mmol of 25% aqueous solution) and the reaction mixture was stirred for 1 hr at the same temperature. Hexane (30 mL) was added to the reaction and left to stir for another 5 min. Organic layer was separated and evaporated under vacuum to give pale yellow coloured liquid, which was purified on 10 cm silica bed using a gradient solvent system, 100 ml of hexane, 100 ml of 25% ethyl acetate in hexane and 100 ml of 100% ethyl acetate. Pure

compound was eluted in 100% ethyl acetate, solvent evaporated under reduced pressure to give colourless liquid **10** (3.6 g, 4.28 mmol, 38% yield, deuteration level 96%).

¹H NMR (CDCl₃) δ 0.85 (m, 0.6H), 0.93 (s, 9H), 0.94 (s), 1.12 (m, 4H), 1.20-1.39 (m, 3.17H), 1.46 (m, 0.6H), 1.57 (m, 1H), 1.99 (m, 1H), 2.40 (d, 3H), 3.56 (m, 1H).

²H NMR (CDCl₃) δ 0.81 (m), 1.19 (m), 1.43 (m), 2.38 (m).

¹³C NMR (CDCl₃) δ 13.0 (m), 18.52 (s), 18.97 (s), 28.36 (m), 29.78 (m), 30.36 (s), 31.21 (s), 41.93 (s), 42.79 (s), 50.31 (s), 58.2 (s).

³¹P NMR (CDCl₃) δ 36.5 (m), 32.8 (s).

ESI-MS [M⁺] m/z 552. Isotopic distribution 96% D level, *d*₆₃ 6.7%, *d*₆₄ 14.8%, *d*₆₅ 23.0%, *d*₆₆ 25.9%, *d*₆₇ 20.3%, *d*₆₈ 9.2%.

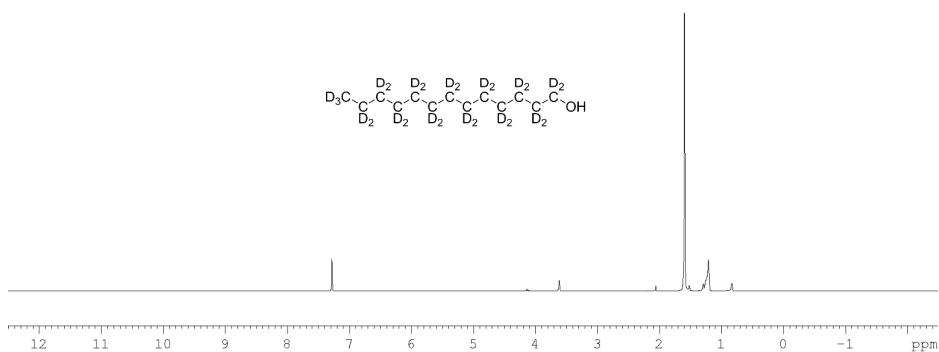


Figure S3. ¹H NMR of compound **3** in CDCl₃.

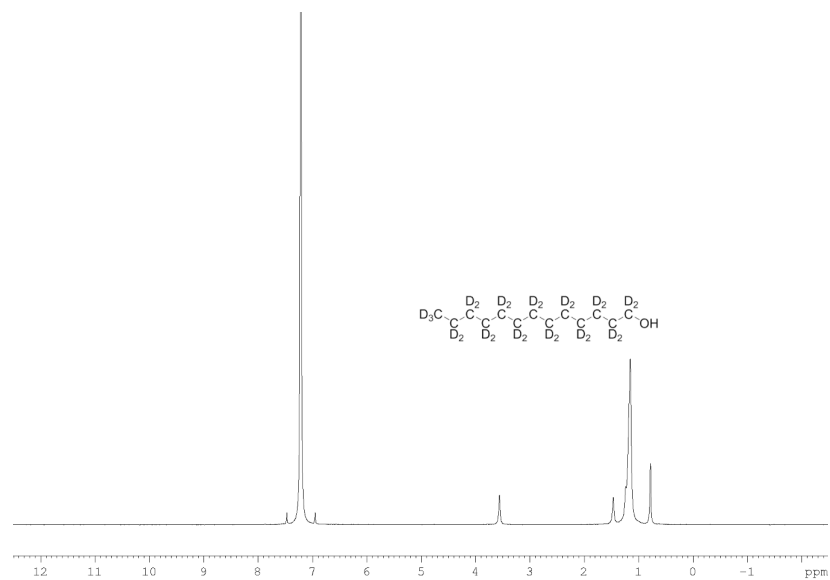


Figure S4. ^2H NMR of compound **3** in CDCl_3 .

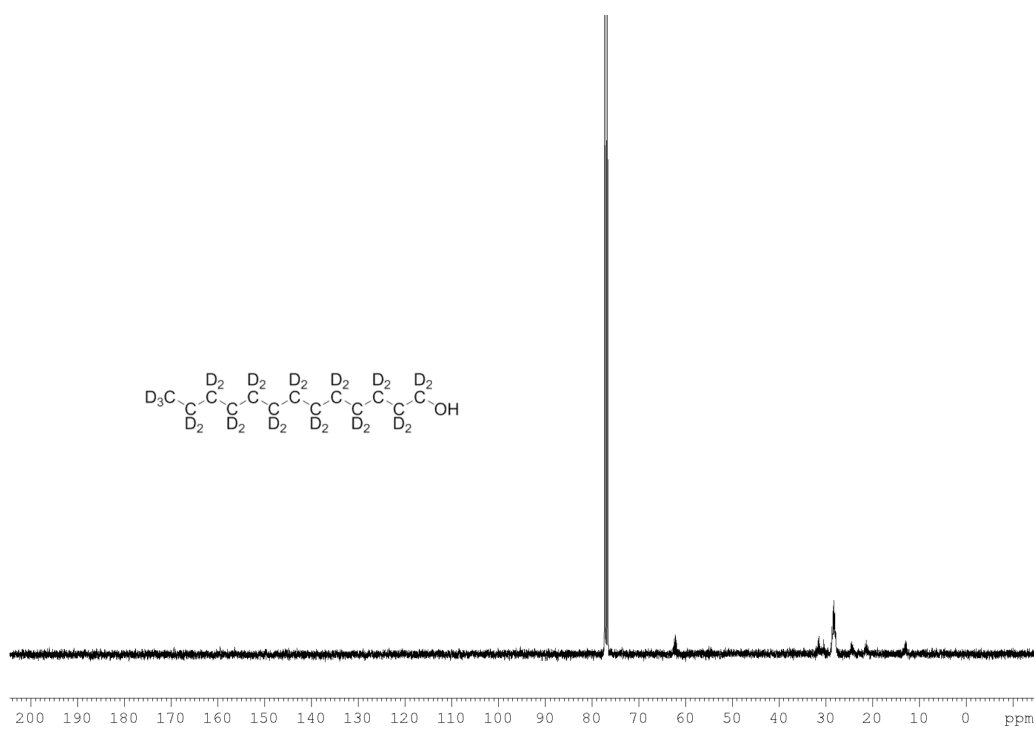


Figure S5. ^{13}C NMR of compound **3** in CDCl_3 .

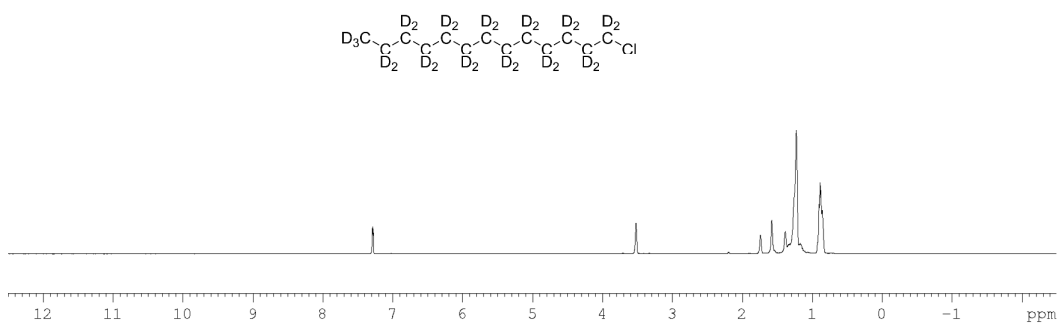


Figure S6. ^1H NMR of compound **4** in CDCl_3 .

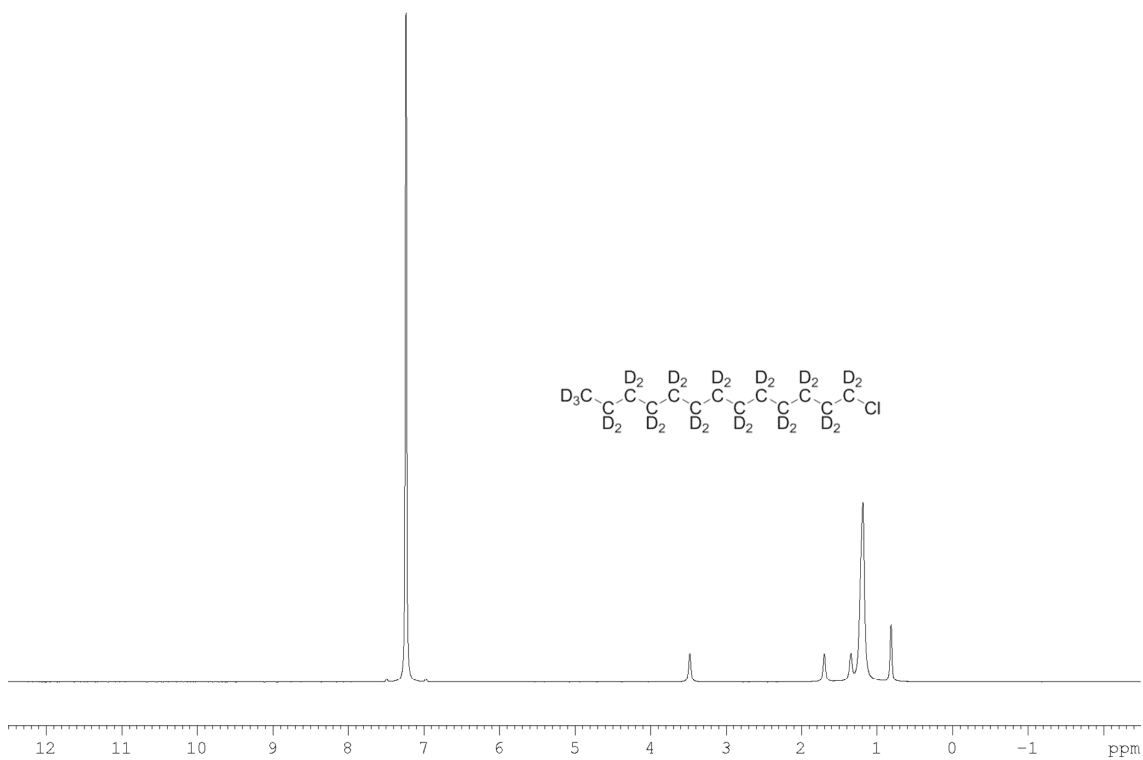


Figure S7. ^2H NMR of compound **4** in CDCl_3 .

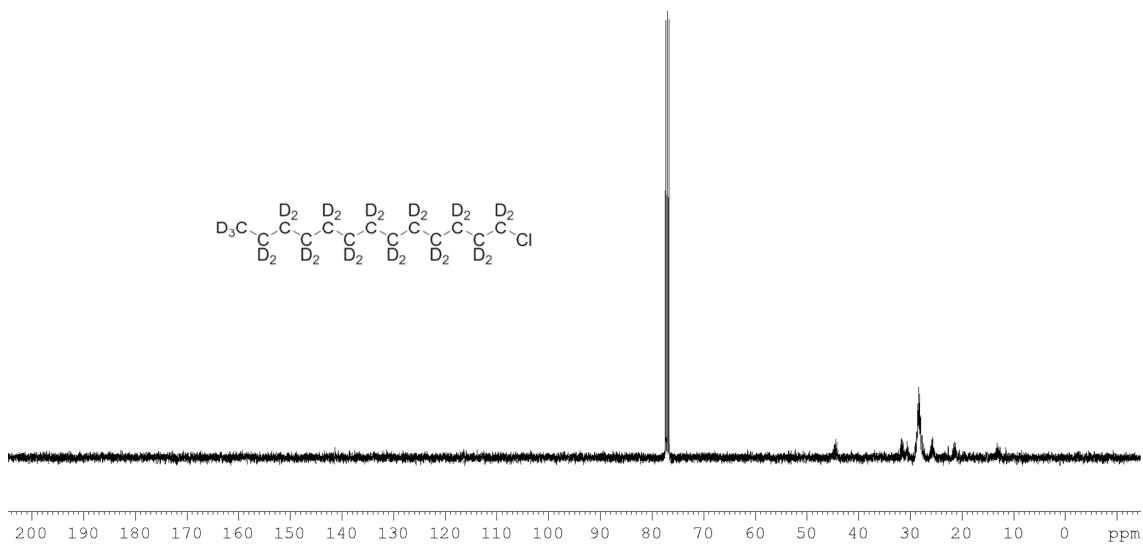


Figure S8. ^{13}C NMR of compound **4** in CDCl_3 .

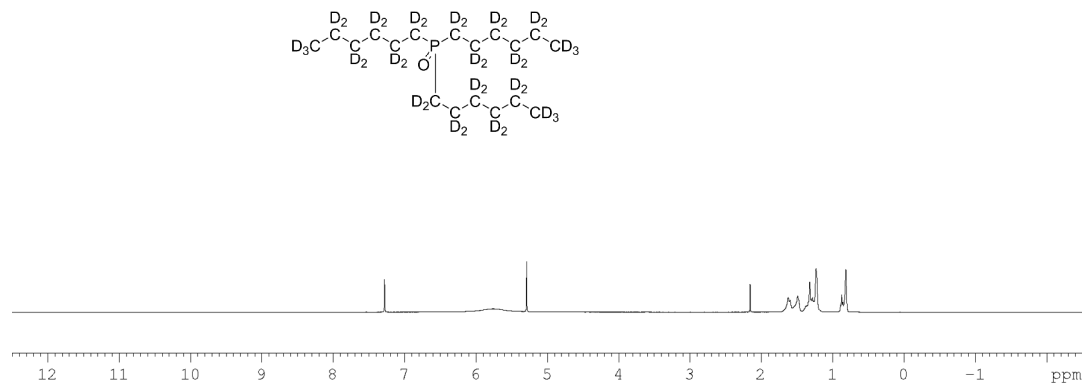


Figure S9. ^1H NMR of compound **6** in CDCl_3 .

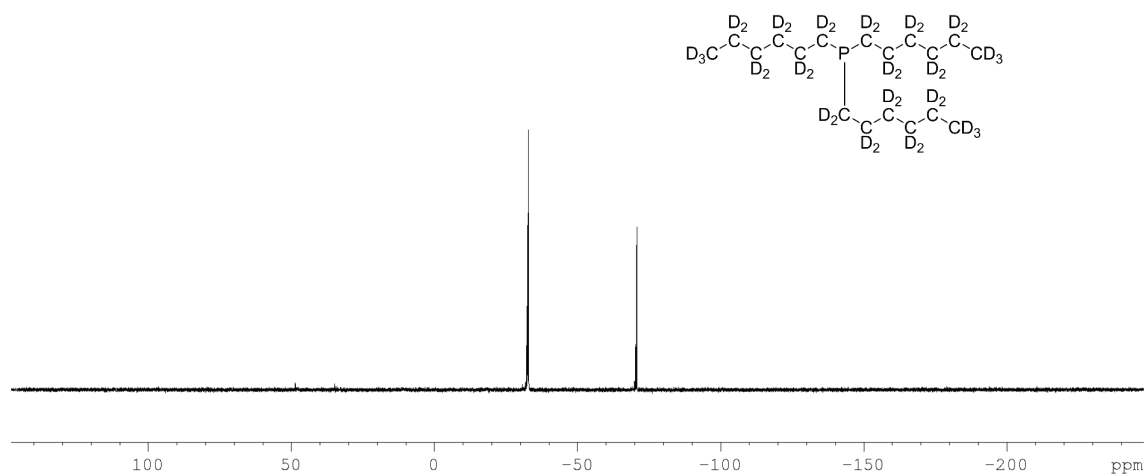


Figure S14. ^{31}P NMR of compound 7 in CDCl_3 showing the product peak at -33.6 ppm and some impurity peak at -70.5 ppm.

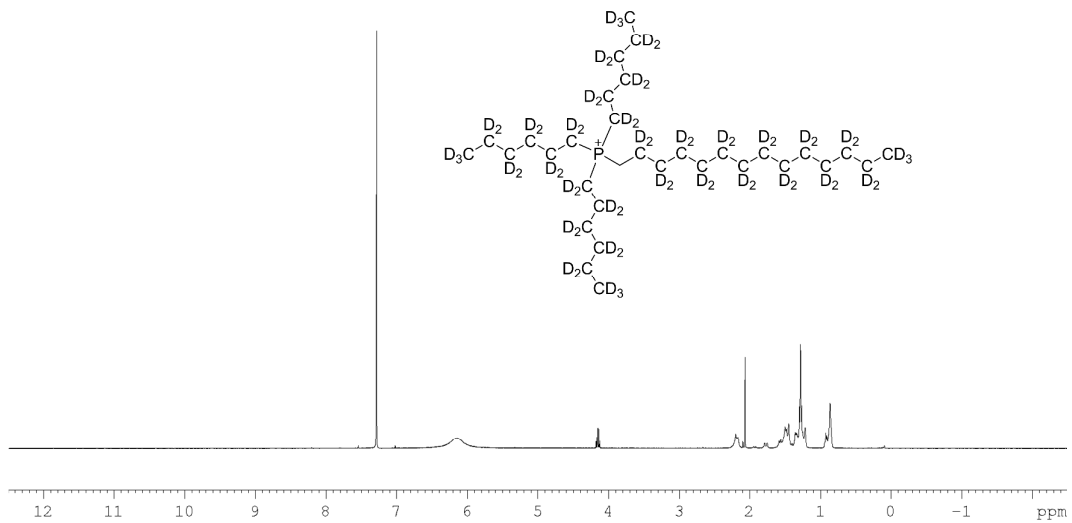


Figure S15. ^1H NMR of compound **8** in CDCl_3 .

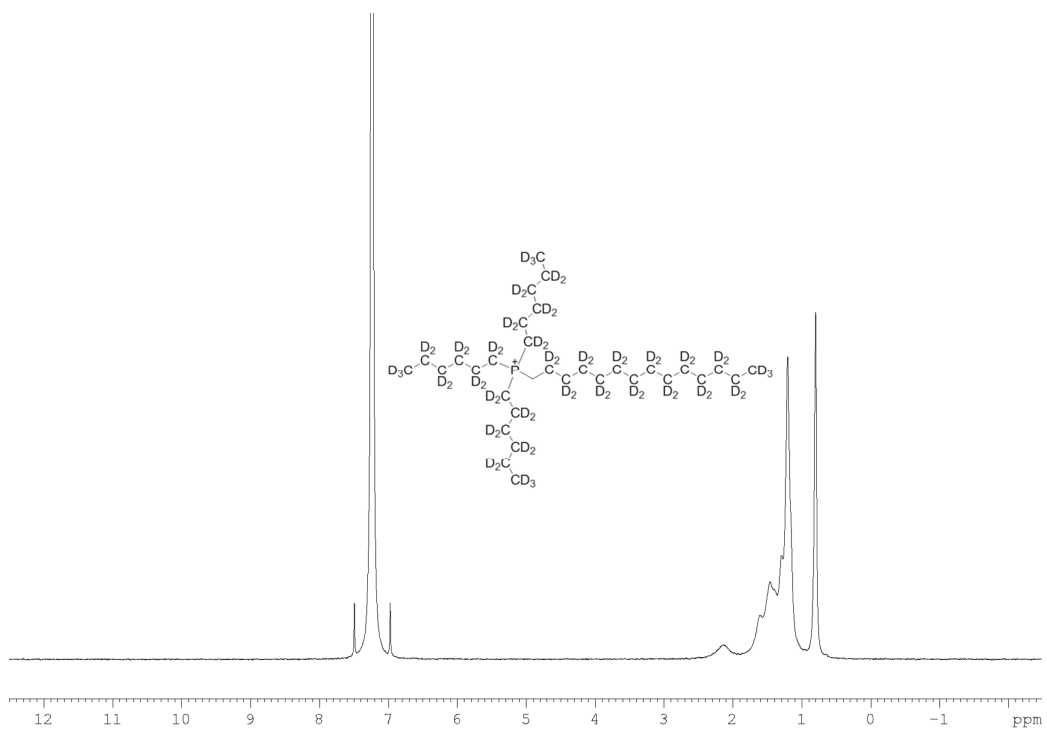


Figure S16. ^2H NMR of compound **8** in CDCl_3 .

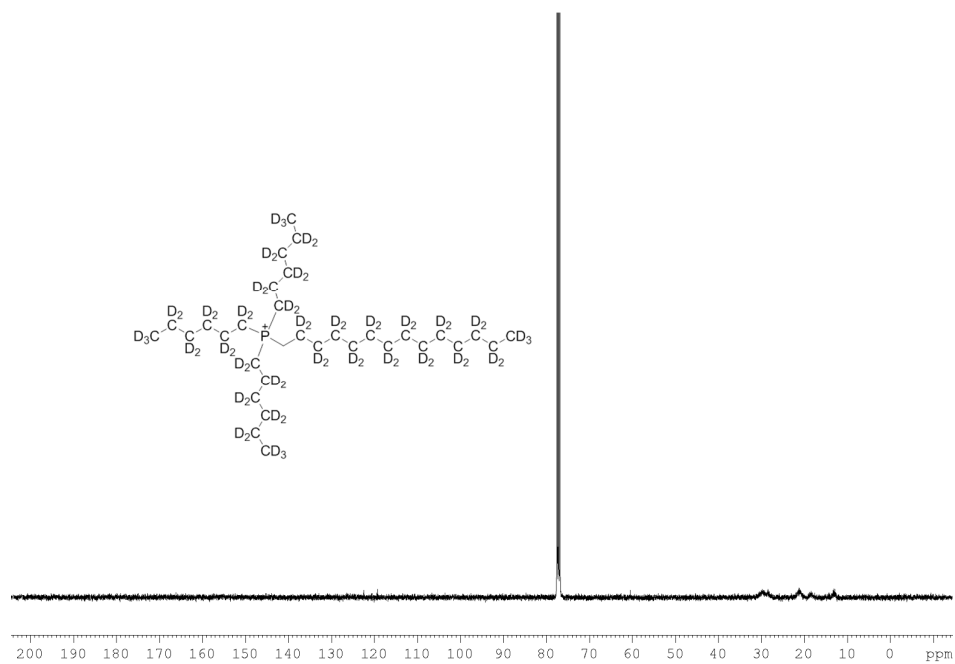


Figure S17. ^{13}C NMR of compound **8** in CDCl_3 .

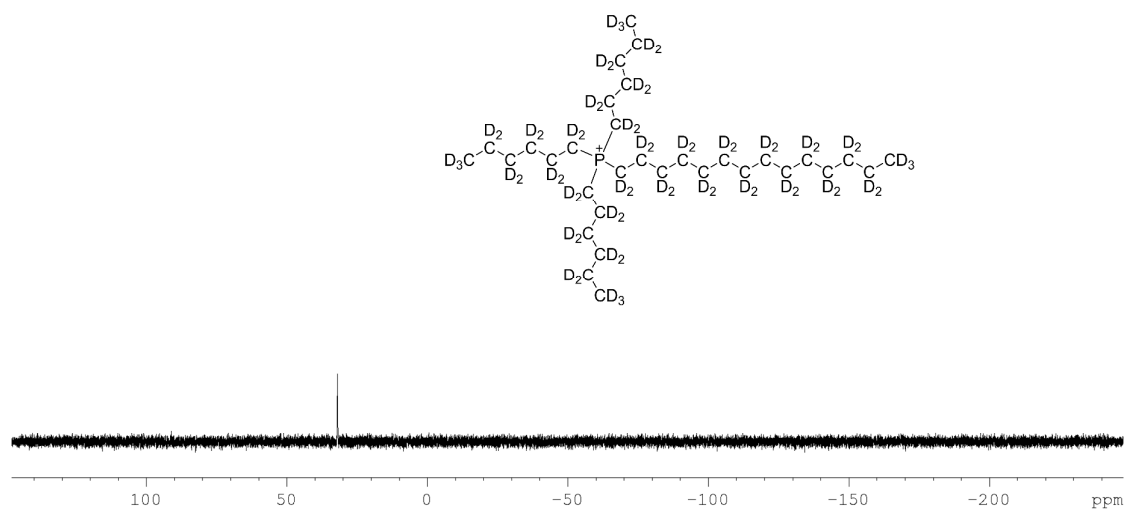


Figure S18. ^{31}P NMR of compound **8** in CDCl_3 .

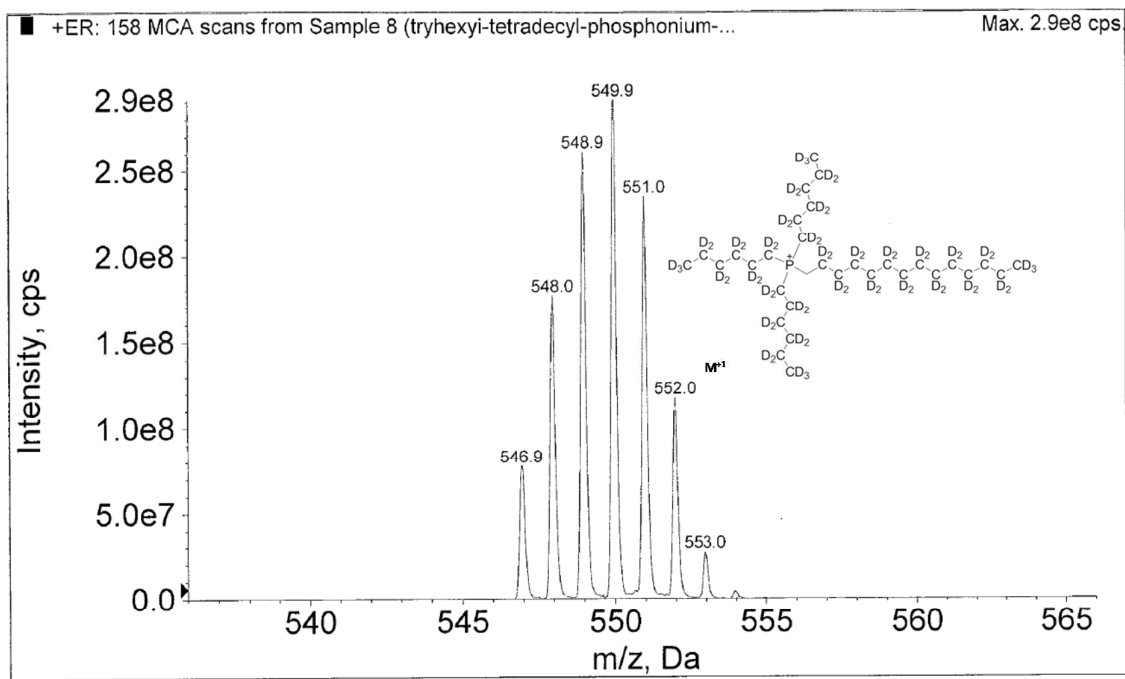


Figure S19. ESMS m/z 552 [M^{+1}] of compound **8**.

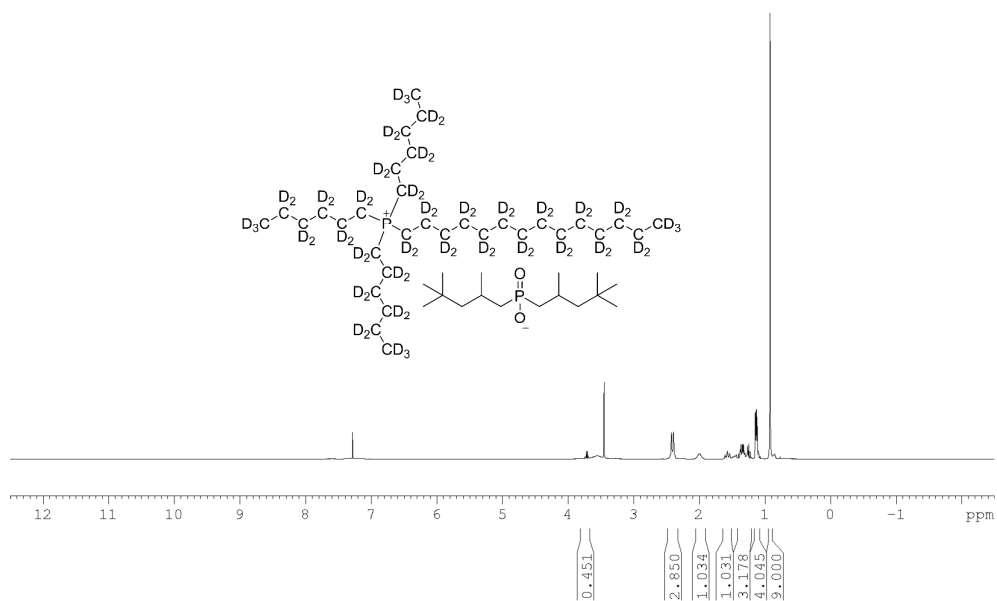


Figure S20. ^1H NMR of compound **10** in CDCl_3 .

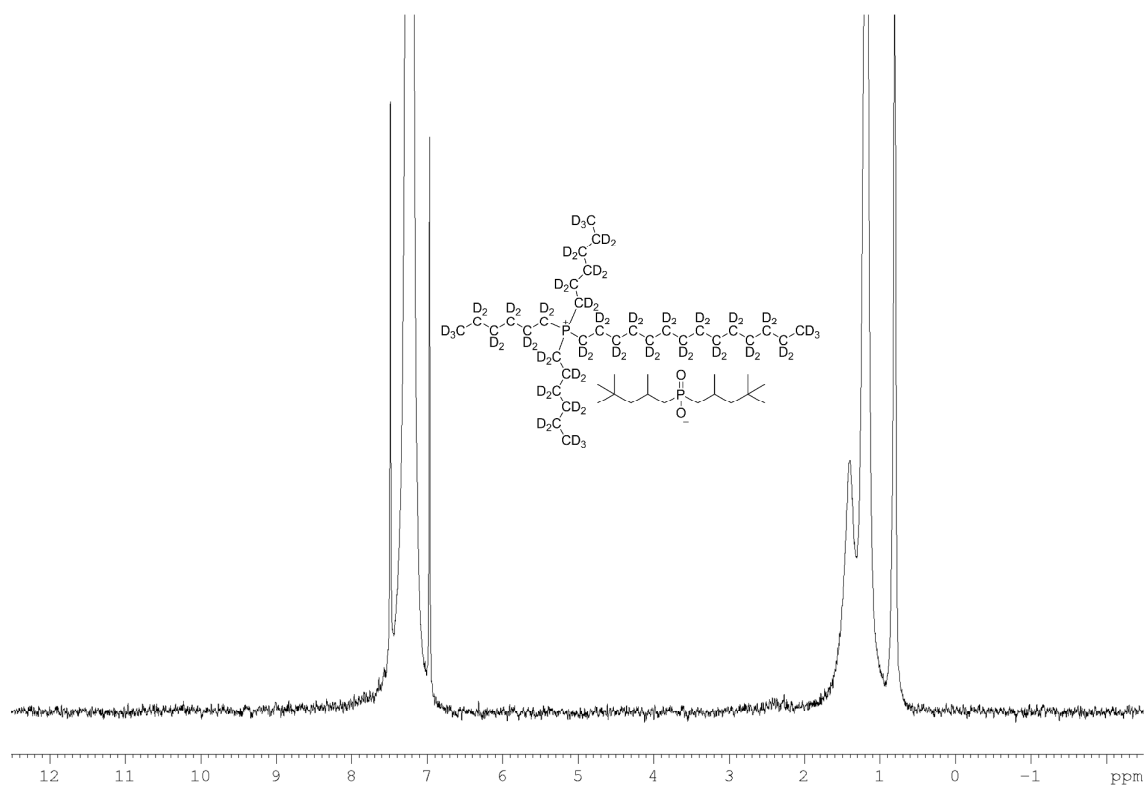


Figure S21. ^2H NMR of compound **10** in CDCl_3 .

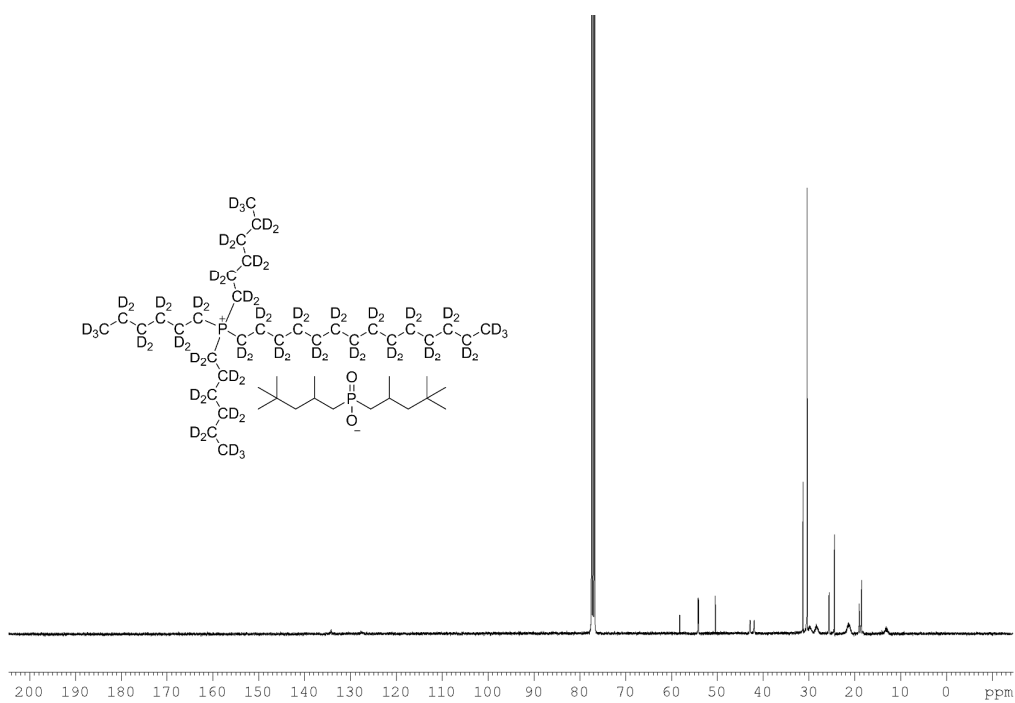


Figure S22. ^{13}C NMR of compound **10** in CDCl_3 .

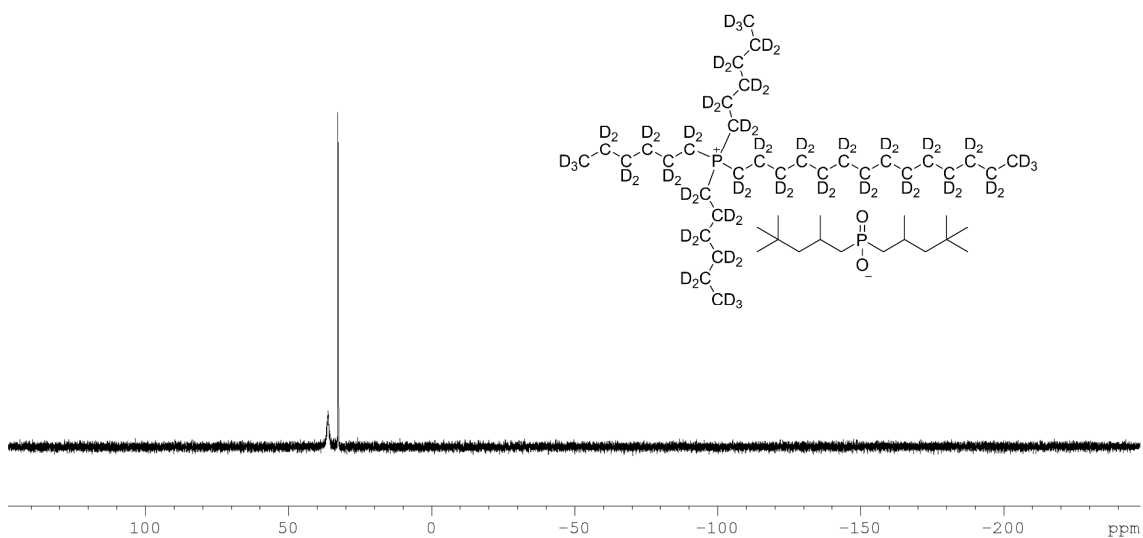


Figure S23. ^{31}P NMR of compound **10** in CDCl_3 .

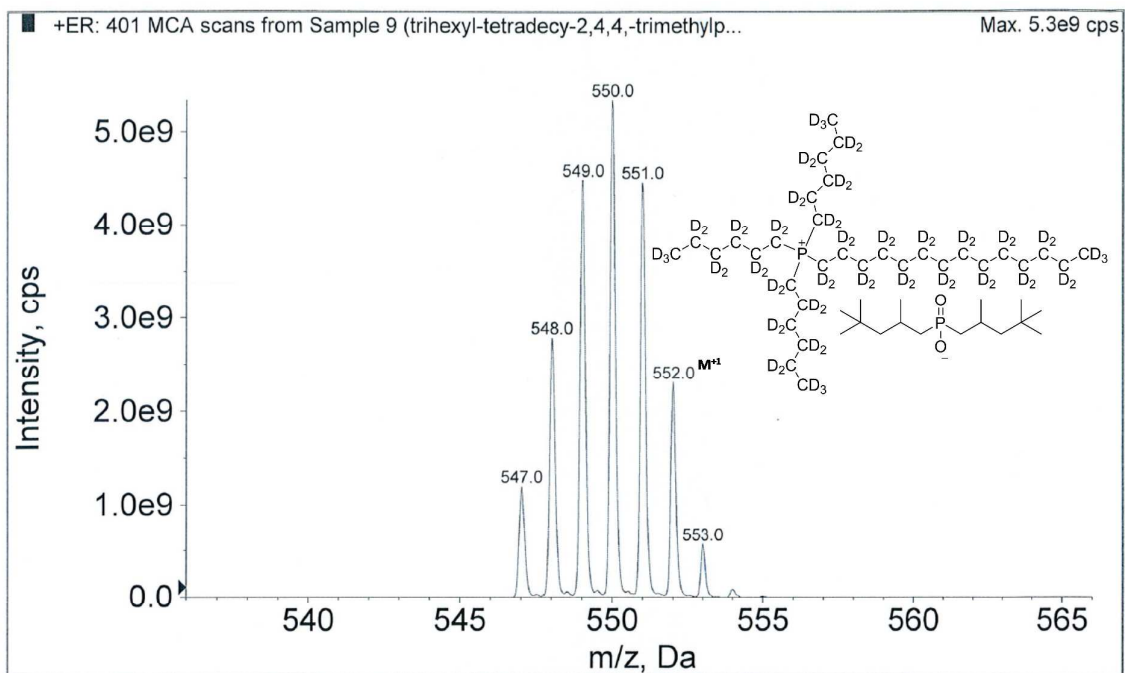


Figure S24. ESMS m/z 552 $[\text{M}^{+1}]$ cationic part of the compound **10**.