

Supporting Information for

Lamellar Structure in Phosphonium Ionic Liquids: the Roles of Fluorination and Chain Length

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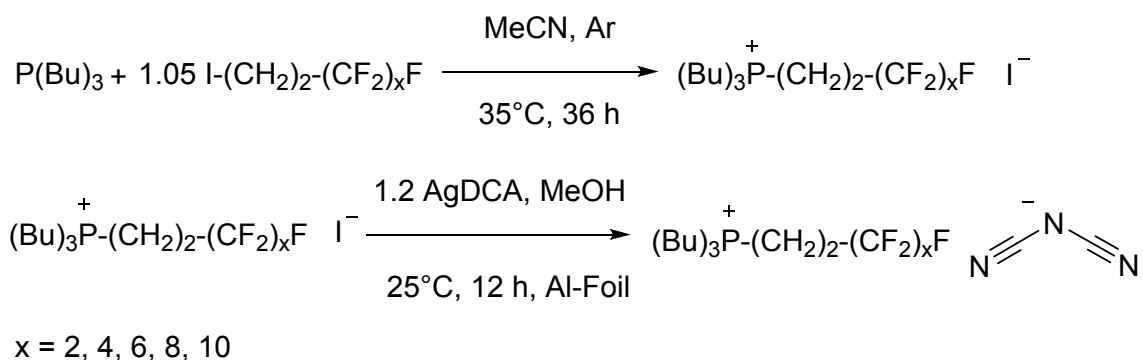
1. Synthesis of the investigated ionic liquids

1.1 NMR-measurements

NMR-spectra were collected on an AV II 400 (Bruker, Billerica, USA) using CDCl₃ as solvent. ¹H-NMR spectra were collected at 400 MHz and ¹³C{¹H}-NMR at 101 MHz and referred to the residual solvent protons and chemical shifts are reported relative to tetramethylsilane. ¹⁹F{¹H}-NMR spectra were recorded at 376 MHz and given in relation to CFCl₃ as reference while ³¹P{¹H} were recorded at 162 MHz relative to 85% aqueous H₃PO₄. The listed data for the chemical shifts δ are given in parts per million (ppm).

1.2 Synthesis of the fluorinated ionic liquids

The tributyl(1*H*,1*H*,2*H*,2*H*-perfluoroalkyl)phosphonium dicyanamides were synthesized following scheme 1 by quarternization reaction of the perfluoroalkyl-iodides with tributylphosphine at slightly elevated temperatures in an inert atmosphere followed by anion exchange reaction with freshly prepared silver dicyanamide in the dark. The quarternization reactions were performed in dried glassware which was evacuated, heated and flushed with argon four times before the reagents were added to prevent to oxidation of tributylphosphine.



Scheme 1: Synthesis of the perfluoro-substituted tributylphosphonium dicyanamide ionic liquids.

1.2.1 Synthesis of the tributyl(1*H*,1*H*,2*H*,2*H*-perfluoroalkyl)phosphonium iodide ionic liquids

1.2.1.1 Tributyl(1*H*,1*H*,2*H*,2*H*-perfluorobutyl)phosphonium iodide

8.19 mL tributylphosphine (1.00 eq, 32.8 mmol, 6.71 g) was dissolved in 150 mL acetonitrile and 4.91 mL 1*H*,1*H*,2*H*,2*H*-perfluorobutyl iodide (1.05 eq, 34.7 mmol, 9.51 g) dissolved in 50 mL acetonitrile added dropwise. The resulting mixture was heated to 35°C and stirred for 36 h. The solvent and excess of reagents were distilled off yielding 15.43 g (32.4 mmol, 98% yield) of a white, slightly yellow solid.

Melting point: 98°C (DSC).

¹H-NMR (400 MHz, CDCl₃): δ[ppm] = 2.80– 2.70 (m, 2H, P-CH₂-CH₂-(CF₂)₂-F), 2.67 – 2.47 (m, 8H, P-CH₂-(CH₂)₃-H and P-CH₂-CH₂-(CF₂)₂-F), 1.61 – 1.47 (m, 12H, P-CH₂-(CH₂)₂-CH₃), 0.95 (t, ²J_{H/H} = 7.0 Hz, 9H, P-(CH₂)₃-CH₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ[ppm] = 23.9 (d, ³J_{C/P} = 15.6 Hz, P-(CH₂)₂-CH₂-CH₃), 23.8 (d, ²J_{C/P} = 4.9 Hz, P-CH₂-CH₂-(CH₂)₂-H), 19.5 (d, ¹J_{C/P} = 46.7 Hz, P-CH₂-(CH₂)₃-H), 13.5 (s, P-(CH₂)₃-CH₃).

¹⁹F{¹H}-NMR (376 MHz, CDCl₃): δ[ppm] = -84.79 (3F, P-(CH₂)₂-CF₂-CF₃), -118.18 (2F, P-(CH₂)₂-CF₂-CF₃).

³¹P{¹H}-NMR (162 MHz, CDCl₃): δ[ppm] = 34.14 (s).

1.2.1.2 Tributyl(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)phosphonium iodide

To 7.31 mL tributylphosphine (1.00 eq, 29.3 mmol, 5.99 g) dissolved in 150 mL acetonitrile was added a solution of 5.94 mL 1*H*,1*H*,2*H*,2*H*-perfluorohexyl iodide (1.05 eq, 30.8 mmol, 11.52 g) dissolved in 50 mL acetonitrile added dropwise. After completion of the addition the reaction mixture was stirred at 35°C for 36 h. The solvent was removed by rotary evaporation and the excess of reagents were distilled off in vacuum yielding 16.23 g (28.2 mmol, 96% yield) of a high viscose, slightly yellow liquid.

Melting point: -17°C (DSC)

¹H-NMR 400 MHz, CDCl₃): δ[ppm] = 2.83 – 2.70 (m, 2H, P-CH₂-CH₂-(CF₂)₄-F), 2.68 – 2.49 (m, 8H, P-CH₂-(CH₂)₃-H and P-CH₂-CH₂-(CF₂)₄-F), 1.61 – 1.46 (m, 12H, P-CH₂-(CH₂)₂-CH₃), 0.95 (t, ²J_{H/H} = 7.0 Hz, 9H, P-(CH₂)₃-CH₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ[ppm] = 23.8 (d, ³J_{C/P} = 15.9 Hz, P-(CH₂)₂-CH₂-CH₃), 23.8 (d, ²J_{C/P} = 4.6 Hz, P-CH₂-CH₂-(CH₂)₂-H), 19.5 (d, ¹J_{C/P} = 46.7 Hz, P-CH₂-(CH₂)₃-H), 13.5 (s, P-(CH₂)₃-CH₃).

¹⁹F{¹H}-NMR (376 MHz, CDCl₃): δ[ppm] = -81.07 (3F, P-(CH₂)₂-(CF₂)₃-CF₃), -114.47 (2F, P-(CH₂)₂-CF₂-(CF₂)₃-F), -123.48 (2F, P-(CH₂)₂-CF₂-CF₂-(CF₂)₂-F), -125.99 (2F, P-(CH₂)₂-(CF₂)₂-CF₂-CF₃).

³¹P{¹H}-NMR (162 MHz, CDCl₃): δ[ppm] = 34.29 (s).

1.2.1.3 Tributyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphonium iodide

To a mixture if In 100 mL acetonitrile and 5.34 mL tributylphosphine (1.00 eq, 21.4 mmol, 4.38 g) was added dropwise a solution of 10.67 g 1*H*,1*H*,2*H*,2*H*-perfluorooctyl iodide (1.05 eq, 22.5 mmol) in 100 mL acetonitrile. The resulting mixture was heated to 35°C and stirred for 36 h at this temperature. The solvent was removed by rotary evaporation and the excess of 1*H*,1*H*,2*H*,2*H*-perfluorooctyl iodide by sublimation to obtain 13.78 g (20.4 mmol, 95% yield) of a white, slightly yellow solid.

Melting point: 54°C (DSC).

¹H-NMR: (400 MHz, CDCl₃): δ[ppm] = 2.86 – 2.78 (m, 2H, P-CH₂-CH₂-(CF₂)₆-F), 2.67 – 2.52 (m, 8H, P-CH₂-(CH₂)₃-H and P-CH₂-CH₂-(CF₂)₆-F), 1.58 – 1.53 (m, 12H, P-CH₂-(CH₂)₂-CH₃), 0.98 (t, ²J_{H/H} = 7.0 Hz, 9H, P-(CH₂)₃-CH₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ[ppm] = 24.0 (d, ³J_{C/P} = 15.6 Hz, P-(CH₂)₂-CH₂-CH₃), 23.9 (d, ²J_{C/P} = 4.8 Hz, P-CH₂-CH₂-(CH₂)₂-H), 19.6 (d, ¹J_{C/P} = 46.8 Hz, P-CH₂-(CH₂)₃-H), 13.6 (s, P-(CH₂)₃-CH₃).

¹⁹F{¹H}-NMR (376 MHz, CDCl₃): δ[ppm] = -80.83 (3F, P-(CH₂)₂-(CF₂)₅-CF₃), -114.08 (2F, P-(CH₂)₂-CF₂-(CF₂)₅-F), -121.80 – -122.87 (6F, P-(CH₂)₂-CF₂-(CF₂)₃-(CF₂)₂-F), -126.19 (2F, P-(CH₂)₂-(CF₂)₄-CF₂-CF₃).

³¹P{¹H}-NMR (162 MHz, CDCl₃): δ[ppm] = 34.24 (s).

1.2.1.4 Tributyl(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phosphonium iodide

4.82 mL tributylphosphine (1.00 eq, 19.4 mmol, 3.97 g) was dissolved in 200 mL acetonitrile and 11.72 g 1*H*,1*H*,2*H*,2*H*-perfluorodecyl iodide (1.05 eq, 20.4 mmol) added in one portion. The resulting suspension was heated to 35°C and stirred for 48 h. The solvent was removed by rotary evaporation and the excess of 1*H*,1*H*,2*H*,2*H*-perfluorodecyl iodide by sublimation yielding 14.49 g (18.7 mmol, 96% yield) of a white, slightly yellow solid

Melting point: 71°C (DSC).

¹H-NMR: (400 MHz, CDCl₃) δ[ppm] = 2.86 – 2.79 (m, 2H, P-CH₂-CH₂-(CF₂)₈-F), 2.65 – 2.58 (m, 8H, P-CH₂-(CH₂)₃-H and P-CH₂-CH₂-(CF₂)₈-F), 1.61 – 1.52 (m, 12H, P-CH₂-(CH₂)₂-CH₃), 0.98 (t, ²J_{H/H} = 7.0 Hz, 9H, P-(CH₂)₃-CH₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ[ppm] = 24.0 (d, ³J_{C/P} = 15.6 Hz, P-(CH₂)₂-CH₂-CH₃), 23.9 (d, ²J_{C/P} = 4.8 Hz, P-CH₂-CH₂-(CH₂)₂-H), 19.6 (d, ¹J_{C/P} = 46.6 Hz, P-CH₂-(CH₂)₃-H), 13.5 (s, P-(CH₂)₃-CH₃).

¹⁹F{¹H}-NMR (376 MHz, CDCl₃) δ[ppm] = -80.86 (3F, P-(CH₂)₂-(CF₂)₇-CF₃), -114.12 (2F, P-(CH₂)₂-CF₂-(CF₂)₇-F), -121.61 – -122.83 (10F, P-(CH₂)₂-CF₂-(CF₂)₅-(CF₂)₂-F), -126.19 (2F, P-(CH₂)₂-(CF₂)₆-CF₂-CF₃).

³¹P{¹H}-NMR (162 MHz, CDCl₃) δ[ppm] = 34.24 (s).

1.2.1.5 Tributyl(1*H*,1*H*,2*H*,2*H*-perfluorododecyl)phosphonium iodide

3.44 mL tributylphosphine (1.00 eq, 13.8 mmol, 2.82 g) was dissolved in 175 mL acetonitrile and 9.78 g 1*H*,1*H*,2*H*,2*H*-perfluorododecyl iodide (1.05 eq, 14.5 mmol) added. The resulting suspension was heated to 35°C and stirred for 60 h. The solvent was removed by rotary evaporation and the excess of 1*H*,1*H*,2*H*,2*H*-perfluorobutyl iodide by sublimation yielding 11.51 g (13.1 mmol, 95% yield) of a white, slightly yellow solid

Melting point: 97°C (DSC).

¹H-NMR (400 MHz, CDCl₃): δ[ppm] = 2.84 – 2.61 (m, 2H, P-CH₂-CH₂-(CF₂)₁₀-F), 2.65 – 2.55 (m, 8H, P-CH₂-(CH₂)₃-H and P-CH₂-CH₂-(CF₂)₁₀-F), 1.60 – 1.51 (m, 12H, P-CH₂-(CH₂)₂-CH₃), 1.60 – 1.51 (m, 12H, P-CH₂-(CH₂)₂-CH₃), 0.96 (t, ²J_{H/H} = 7.0 Hz, 9H, P-(CH₂)₃-CH₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ[ppm] = 23.9 (d, ³J_{C/P} = 15.7 Hz, P-(CH₂)₂-CH₂-CH₃), 23.8 (d, ²J_{C/P} = 5.1 Hz, P-CH₂-CH₂-(CH₂)₂-H), 19.5 (d, ¹J_{C/P} = 46.6 Hz, P-CH₂-(CH₂)₃-H), 13.5 (s, P-(CH₂)₃-CH₃).

¹⁹F{¹H}-NMR (376 MHz, CDCl₃): δ[ppm] = -81.01 (3F, P-(CH₂)₂-(CF₂)₈-CF₃), -114.28 (2F, P-(CH₂)₂-CF₂-(CF₂)₈-F), -121.71 – -122.94 (14F, P-(CH₂)₂-CF₂-(CF₂)₇-(CF₂)₂-F), -126.34 (2F, P-(CH₂)₂-(CF₂)₈-CF₂-CF₃).

³¹P{¹H}-NMR (162 MHz, CDCl₃): δ[ppm] = 34.26 (s).

1.2.2 Synthesis of the tributyl(1*H*,1*H*,2*H*,2*H*-perfluoroalkyl)phosphonium dicyanamide ionic liquids

Freshly prepared silver dicyanamide was used for the anion metathesis of the iodides. For the preparation 1.00 eq. of silver nitrate was dissolved in purified water and aqueous solution of 1.02 eq. sodium dicyanamide added in the dark. The resulting white precipitate was vacuum filtered in the dark, washed three times with purified water and dried in vacuum with exclusion of light to give nearly quantitative yield (>98%). The synthesized silver dicyanamide was used immediately after vacuum drying avoiding any contact with light.

1.2.2.1 Tributyl(1*H*,1*H*,2*H*,2*H*-perfluorobutyl)phosphonium dicyanamide

To flask wrapped in aluminium foil containing a 175 mL methanolic solution of 9.50 g tributyl(1*H*,1*H*,2*H*,2*H*-perfluorobutyl)phosphonium iodide (1.00 eq, 19.9 mmol) was added 4.16 g silver dicyanamide (1.20 eq, 23.9 mmol). The resulting suspension was stirred for 12 h at ambient temperature. The precipitated silver iodide and the excess of silver dicyanamide were filtered off in vacuum and methanol was removed by rotary evaporation. The residue was dissolved in 200 mL dichloromethane and washed four times with 200 mL of water. The organic solvent was dried over MgSO₄, filtered, evaporated and the residue dried on a vacuum line for 48 hours resulting in 8.13 g of a colourless, viscous liquid (19.5 mmol, 96% yield).

Melting point: 26°C (DSC).

¹H-NMR: (400 MHz, CDCl₃): δ[ppm] = 2.54 – 2.40 (m, 4H, P-(CH₂)₂-(CF₂)₂-F), 2.35 – 2.27 (m, 6H, P-CH₂-(CH₂)₃-H), 1.55 – 1.51 (m, 12H, P-CH₂-(CH₂)₂-CH₃), 0.99 (t, ²J_{H/H} = 6.8 Hz, 9H, P-(CH₂)₃-CH₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ[ppm] = 120.0 (s, N-(CN)₂), 23.9 (d, ³J_{C/P} = 15.6 Hz, P-(CH₂)₂-CH₂-CH₃), 23.6 (d, ²J_{C/P} = 4.9 Hz, P-CH₂-CH₂-(CH₂)₂-H), 18.6 (d, ¹J_{C/P} = 47.0 Hz, P-CH₂-(CH₂)₃-H), 13.4 (s, P-(CH₂)₃-CH₃).

¹⁹F{¹H}-NMR (376 MHz, CDCl₃): δ[ppm] = -84.89 (3F, P-(CH₂)₂-CF₂-CF₃), -118.56 (2F, P-(CH₂)₂-CF₂-CF₃).

$^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3): $\delta[\text{ppm}] = 34.75$ (s).

1.2.2.2 Tributyl(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)phosphonium dicyanamide

175 mL methanolic solution of 9.00 g tributyl(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)phosphonium iodide (1.00 eq, 15.6 mmol) was placed in an aluminium foil wrapped flask and 3.26 g silver dicyanamide (1.20 eq, 18.7 mmol) were added. The resulting suspension was stirred for 12 h at ambient temperature. The precipitated silver iodide and the excess of silver dicyanamide were filtered off in vacuum and the organic solvent was removed by rotary evaporation. The residue was dissolved in 200 mL dichloromethane and washed four times with 200 mL of water. The organic solvent was dried over MgSO_4 , filtered, evaporated and the residue dried in oil pump vacuum for 48 hours resulting in 7.89 g of a yellow, viscous liquid (19.5 mmol, 97% yield).

Glass transition point: -55°C (DSC).

^1H -NMR: (400 MHz, CDCl_3): $\delta[\text{ppm}] = 2.55 - 2.43$ (m, 4H, P-(**CH_2**)₂-(CF_2)₄-F), $2.36 - 2.28$ (m, 6H, P- **CH_2** -(CH_2)₃-H), $1.56 - 1.51$ (m, 12H, P- CH_2 -(**CH_2**)₂- CH_3), 0.98 (t, $^2J_{\text{H/H}} = 7.1$ Hz, 9H, P-(CH_2)₃- **CH_3**).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): $\delta[\text{ppm}] = 120.0$ (s, N-(**CN**)₂), 23.9 (d, $^3J_{\text{C/P}} = 15.6$ Hz, P-(CH_2)₂- **CH_2** - CH_3), 23.6 (d, $^2J_{\text{C/P}} = 4.9$ Hz, P- CH_2 - **CH_2** -(CH_2)₂-H), 18.6 (d, $^1J_{\text{C/P}} = 46.9$ Hz, P- **CH_2** -(CH_2)₃-H), 13.3 (s, P-(CH_2)₃- **CH_3**).

$^{19}\text{F}\{^1\text{H}\}$ -NMR (376 MHz, CDCl_3): $\delta[\text{ppm}] = -81.04$ (3F, P-(CH_2)₂-(CF_2)₃- **CF_3**), -114.88 (2F, P-(CH_2)₂- **CF_2** -(CF_2)₃-F), -123.73 (2F, P-(CH_2)₂- CF_2 - **CF_2** -(CF_2)₂-F), -125.98 (2F, P-(CH_2)₂-(CF_2)₂- **CF_2** - CF_3).

$^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3): $\delta[\text{ppm}] = 34.84$ (s).

1.2.2.3 Tributyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphonium dicyanamide

To flask wrapped in aluminium foil containing a 175 mL methanolic solution of 10.00 g tributyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphonium iodide (1.00 eq, 14.8 mmol) was added 3.09 g silver dicyanamide (1.20 eq, 17.7 mmol). The resulting suspension was stirred for 12 h at ambient temperature. The precipitated silver salts were removed by vacuum filtration and methanol was removed by means of rotary evaporation. The residue was dissolved in 200 mL CH_2Cl_2 and washed four times with 200 mL of water. The organic phase was dried over MgSO_4 , filtered, evaporated and the residue dried on a vacuum line for 60 hours to obtain 9.01 g of a yellow, viscous liquid (14.6 mmol, 98% yield).

Glass transition point: -52°C (DSC).

^1H -NMR: (400 MHz, CDCl_3): $\delta[\text{ppm}] = 2.55 - 2.245$ (m, 4H, P-(**CH_2**)₂-(CF_2)₆-F), $2.36 - 2.28$ (m, 6H, P- **CH_2** -(CH_2)₃-H), $1.60 - 1.48$ (m, 12H, P- CH_2 -(**CH_2**)₂- CH_3), 0.98 (t, $^2J_{\text{H/H}} = 7.0$ Hz, 9H, P-(CH_2)₃- **CH_3**).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): $\delta[\text{ppm}] = 120.0$ (s, N-(**CN**)₂), 23.9 (d, $^3J_{\text{C/P}} = 15.6$ Hz, P-(CH_2)₂- **CH_2** - CH_3), 23.6 (d, $^2J_{\text{C/P}} = 4.9$ Hz, P- CH_2 - **CH_2** -(CH_2)₂-H), 18.6 (d, $^1J_{\text{C/P}} = 47.0$ Hz, P- **CH_2** -(CH_2)₃-H), 13.3 (s, P-(CH_2)₃- **CH_3**).

¹⁹F{¹H}-NMR (376 MHz, CDCl₃): δ[ppm] = -80.92 (3F, P-(CH₂)₂-(CF₂)₅-CF₃), -114.69 (2F, P-(CH₂)₂-CF₂-(CF₂)₅-F), -121.88 – -122.93 (6F, P-(CH₂)₂-CF₂-(CF₂)₃-(CF₂)₂-F), -126.21 (2F, P-(CH₂)₂-(CF₂)₄-CF₂-CF₃).

³¹P{¹H}-NMR (162 MHz, CDCl₃): δ[ppm] = 34.84 (s).

1.2.2.4 Tributyl(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phosphonium dicyanamide

To a 175 mL methanolic solution of 9.00 g tributyl(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phosphonium iodide (1.00 eq, 11.6 mmol) placed in a flask wrapped in aluminium foil was added 2.42 g of silver dicyanamide (1.20 eq, 13.9 mmol). The suspension was stirred for 12 h at ambient temperature and the precipitated silver salts were filtered off in vacuum. Methanol was removed by rotary evaporation and the residue dissolved in 200 mL dichloromethane. The CH₂Cl₂ solution was washed four times with 200 mL of water, separated and dried over MgSO₄, filtered and the solvent removed on a rotary evaporator. The residue was finally dried in oil pump vacuum line for 72 hours yielding 8.21 g of a colourless, slightly yellow solid (11.5 mmol, 99% yield).

Melting point: 49°C (DSC).

¹H-NMR: (400 MHz, CDCl₃): δ[ppm] = 2.56 – 2.52 (m, 4H, P-(CH₂)₂-(CF₂)₈-F), 2.37 – 2.30 (m, 6H, P-CH₂-(CH₂)₃-H), 1.60 – 1.53 (m, 12H, P-CH₂-(CH₂)₂-CH₃), 1.00 (t, ²J_{H/H} = 7.0 Hz, 9H, P-(CH₂)₃-CH₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ[ppm] = 120.1 (s, N-(CN)₂), 24.0 (d, ³J_{C/P} = 15.6 Hz, P-(CH₂)₂-CH₂-CH₃), 23.6 (d, ²J_{C/P} = 4.9 Hz, P-CH₂-CH₂-(CH₂)₂-H), 18.7 (d, ¹J_{C/P} = 47.0 Hz, P-CH₂-(CH₂)₃-H), 13.4 (s, P-(CH₂)₃-CH₃).

¹⁹F{¹H}-NMR (376 MHz, CDCl₃): δ[ppm] = -80.92 (3F, P-(CH₂)₂-(CF₂)₇-CF₃), -114.69 (2F, P-(CH₂)₂-CF₂-(CF₂)₇-F), -121.88 – -122.93 (10F, P-(CH₂)₂-CF₂-(CF₂)₅-(CF₂)₂-F), -126.21 (2F, P-(CH₂)₂-(CF₂)₆-CF₂-CF₃).

³¹P{¹H}-NMR (162 MHz, CDCl₃): δ[ppm] = 34.84 (s).

1.2.2.5 Tributyl(1*H*,1*H*,2*H*,2*H*-perfluorododecyl)phosphonium dicyanamide

8.00 g tributyl(1*H*,1*H*,2*H*,2*H*-perfluorododecyl)phosphonium iodide (1.00 eq, 9.13 mmol) was dissolved in 150 mL methanol and the reaction flask protected from light by wrapping in aluminium foil. 1.91 g silver dicyanamide (1.20 eq, 11.0 mmol) were added and the resulting suspension was stirred at ambient temperature for 12 h. After filtering off the precipitated silver salts in vacuum and evaporating methanol by means of rotary evaporation, the residue was dissolved in 200 mL dichloromethane. The organic solution was washed four times with about 200 mL of water and dried over MgSO₄. After filtering, and evaporation of the solvent the residue was dried on a vacuum line for 48 hours to obtain 7.37 g of a colourless, slightly yellow solid (9.04 mmol, 99% yield).

Melting point: 72°C (DSC).

¹H-NMR: (400 MHz, CDCl₃): δ[ppm] = 2.69 – 2.55 (m, 4H, P-(CH₂)₂-(CF₂)₁₀-F), 2.51 – 2.41 (m, 6H, P-CH₂-(CH₂)₃-H), 1.60 – 1.51 (m, 12H, P-CH₂-(CH₂)₂-CH₃), 0.98 (t, ²J_{H/H} = 6.9 Hz, 9H, P-(CH₂)₃-CH₃).

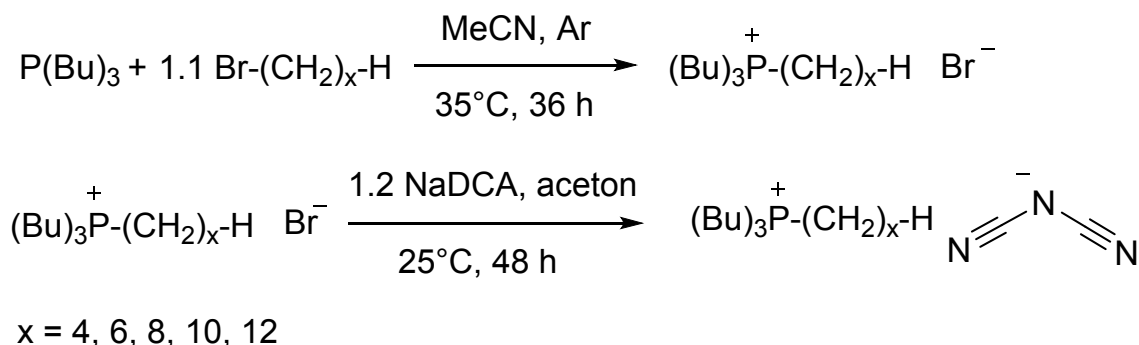
¹³C{¹H}-NMR (101 MHz, CDCl₃): δ[ppm] = 120.1 (s, N-(CN)₂), 24.0 (d, ³J_{C/P} = 15.6 Hz, P-(CH₂)₂-CH₂-CH₃), 23.7 (d, ²J_{C/P} = 4.9 Hz, P-CH₂-CH₂-(CH₂)₂-H), 19.0 (d, ¹J_{C/P} = 46.9 Hz, P-CH₂-(CH₂)₃-H), 13.4 (s, P-(CH₂)₃-CH₃).

¹⁹F{¹H}-NMR (376 MHz, CDCl₃): δ[ppm] = -80.94 (3F, P-(CH₂)₂-(CF₂)₈-CF₃), -114.48 (2F, P-(CH₂)₂-CF₂-(CF₂)₈-F), -121.66 – -122.90 (14F, P-(CH₂)₂-CF₂-(CF₂)₇-(CF₂)₂-F), -126.28 (2F, P-(CH₂)₂-(CF₂)₈-CF₂-CF₃).

³¹P{¹H}-NMR (162 MHz, CDCl₃): δ[ppm] = 34.59 (s).

1.3 Synthesis of the alkylated ionic liquids

The synthesis of the tributyl-alkyl-phosphonium dicyanamides was done after scheme 2 by the reaction tributylphosphine with a slight excess of the corresponding alkyl-bromides at slightly elevated temperatures in an inert atmosphere to give the quarternized phosphonium bromide ILs in the first step. In the second step the anion was exchanged using dicyanamide in acetone.



Scheme 2: Synthesis of the tributyl-alkyl-phosphonium dicyanamide ionic liquids.

1.3.1 Synthesis of the tributyl-alkyl-phosphonium bromide ionic liquids

1.3.1.1 Tetrabutylphosphonium bromide

To a solution of 12.9 mL tributylphosphine (1.00 eq, 52.0 mmol, 10.6 g) in 200 mL acetonitrile was added 6.18 mL of 1-bromobutane (1.1 eq, 57.2 mmol, 7.84 g) in 50 mL acetonitrile dropwise. The resulting mixture was heated to 35°C and stirred at this temperature for 36 h. The solvent was removed by rotary evaporation and the excess of reagents distilled off in vacuum yielding 16.2 g of tetrabutylphosphonium bromide (47.8 mmol, 92% yield) as a white solid.

Melting point: 100°C (DSC).

¹H-NMR: (400 MHz, CDCl₃): δ[ppm] = 2.43 – 2.36 (m, 8H, P-**CH**₂-(CH₂)₃-H), 1.58 – 1.37 (m, 16H, P-CH₂-**(CH₂)₂**-CH₃), 0.91 (t, ²J_{H/H} = 7.0 Hz, 12H, P-(CH₂)₃-**CH**₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ[ppm] = 24.0 (d, ³J_{C/P} = 15.2 Hz, P-(CH₂)₂-**CH**₂-CH₃), 23.8 (d, ²J_{C/P} = 4.9 Hz, P-CH₂-**CH**₂-(CH₂)₂-H), 19.2 (d, ¹J_{C/P} = 46.9 Hz, P-**CH**₂-(CH₂)₃-H), 13.4 (s, P-(CH₂)₃-**CH**₃).

³¹P{¹H}-NMR (162 MHz, CDCl₃): δ[ppm] = 32.79 (s).

1.3.1.2 Tributylhexylphosphonium bromide

In 200 mL acetonitrile were dissolved 11.5 mL of tributylphosphine (1.00 eq, 46.2 mmol, 9.43 g) under argon and 1-bromohexane (1.1 eq, 50.8 mmol, 8.38 g) in 50 mL acetonitrile were dropwise. The mixture was heated to 35°C and for 36 h. The solvent was removed by means of rotary evaporation and the excess of reagents distilled off in oil-pump vacuum yielding 16.3 g of the ionic liquid (44.3 mmol, 96% yield) as a colourless solid.

Melting point: 35°C (DSC).

¹H-NMR: (400 MHz, CDCl₃): δ[ppm] = 2.47 – 2.40 (m, 8H, P-**CH**₂-(CH₂)₃-H and P-**CH**₂-(CH₂)₅-H), 1.54 – 1.46 (m, 16H, P-CH₂-**(CH₂)₂**-CH₃ and P-CH₂-**(CH₂)₂**-(CH₂)₄-H), 1.29 – 1.27 (m, 4H, P-(CH₂)₃-**(CH₂)₂**-CH₃), 0.94 (t, ²J_{H/H} = 7.0 Hz, 9H, P-(CH₂)₃-**CH**₃), 0.86 (t, ²J_{H/H} = 7.0 Hz, 3H, P-(CH₂)₅-**CH**₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ[ppm] = 31.2 (s, P-(CH₂)₃-**CH**₂-(CH₂)₂-H), 30.5 (d, ³J_{C/P} = 14.7 Hz, P-(CH₂)₂-**CH**₂-(CH₂)₃-H), 24.1 (d, ³J_{C/P} = 15.4 Hz, P-(CH₂)₂-**CH**₂-CH₃), 23.9 (d, ²J_{C/P} = 5.2 Hz, P-CH₂-**CH**₂-(CH₂)₄-H), 22.42 (s, P-(CH₂)₄-**CH**₂-CH₃), 22.0 (d, ²J_{C/P} = 4.8 Hz, P-CH₂-**CH**₂-(CH₂)₂-H), 19.5 (d, ¹J_{C/P} = 47.0 Hz, P-**CH**₂-(CH₂)₅-H), 19.3 (d, ¹J_{C/P} = 47.3 Hz, P-**CH**₂-(CH₂)₃-H), 14.0 (s, P-(CH₂)₅-**CH**₃), 13.6 (s, P-(CH₂)₃-**CH**₃).

³¹P{¹H}-NMR (162 MHz, CDCl₃): δ[ppm] = 32.79 (s).

1.3.1.3 Tributylloctylphosphonium bromide

To a solution of 9.95 mL tributylphosphine (1.00 eq, 39.9 mmol, 8.16 g) in 200 mL acetonitrile in an inert atmosphere was added a solution 7.59 mL of 1-bromooctane (1.1 eq, 43.9 mmol, 8.49 g) in 50 mL acetonitrile dropwise. After heating to 35°C for 36 h the solvent was removed on a rotary evaporator, followed distilling off the excess reagents in vacuum to obtain 15.3 g of tributylloctylphosphonium bromide (38.7 mmol, 97% yield) as in the form of a white solid.

Melting point: 31°C (DSC).

¹H-NMR: (400 MHz, CDCl₃): δ[ppm] = 2.48 – 2.38 (m, 8H, P-**CH**₂-(CH₂)₃-H and P-**CH**₂-(CH₂)₇-H), 1.59 – 1.41 (m, 16H, P-CH₂-**(CH₂)₂**-CH₃ and P-CH₂-**(CH₂)₂**-(CH₂)₆-H), 1.31 – 1.24 (m, 8H, P-(CH₂)₃-**(CH₂)₄**-CH₃), 0.95 (t, ²J_{H/H} = 6.6 Hz, 9H, P-(CH₂)₃-**CH**₃), 0.85 (t, ²J_{H/H} = 6.6 Hz, 3H, P-(CH₂)₇-**CH**₃).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): $\delta[\text{ppm}] = 31.8$ (s, P-(CH_2)₅-**CH**₂-(CH_2)₂-H), 31.0 (d, $^3J_{\text{C/P}} = 14.7$ Hz, P-(CH_2)₂-**CH**₂-(CH_2)₅-H), 29.1 (s, P-(CH_2)₄-**CH**₂-(CH_2)₃-H), 29.0 (d, $^4J_{\text{C/P}} = 1.0$ Hz, P-(CH_2)₃-**CH**₂-(CH_2)₄-H), 24.1 (d, $^3J_{\text{C/P}} = 15.5$ Hz, P-(CH_2)₂-**CH**₂-CH₃), 24.0 (d, $^2J_{\text{C/P}} = 4.9$ Hz, P-CH₂-**CH**₂-(CH_2)₆-H), 22.7 (s, P-(CH_2)₆-**CH**₂-CH₃), 22.0 (d, $^2J_{\text{C/P}} = 4.8$ Hz, P-CH₂-**CH**₂-(CH_2)₂-H), 19.5 (d, $^1J_{\text{C/P}} = 47.2$ Hz, P-**CH**₂-(CH_2)₇-H), 19.3 (d, $^1J_{\text{C/P}} = 47.3$ Hz, P-**CH**₂-(CH_2)₃-H), 14.2 (s, P-(CH_2)₇-**CH**₃), 13.6 (s, P-(CH_2)₃-**CH**₃).

$^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3): $\delta[\text{ppm}] = 32.72$ (s).

1.3.1.4 Tributyldecylphosphonium bromide

For the synthesis of the phosphonium salt 8.15 mL tributylphosphine (1.00 eq, 32.7 mmol, 6.68 g) were dissolved in 200 mL acetonitrile under argon followed by dropwise addition of 7.47 mL of a 1-bromodecane solution (1.1 eq, 36.0 mmol, 7.96 g) in 50 mL acetonitrile. The resulting mixture was heated to 35°C and stirred at this temperature for 36 h. The solvent was removed by rotary evaporation and the excess of reagents by vacuum distillation to obtain 13.3 g of tributyldecylphosphonium bromide (31.4 mmol, 96% yield) as a colourless, highly viscous, supercooled liquid.

Melting point: 28°C (DSC).

^1H -NMR: (400 MHz, CDCl_3): $\delta[\text{ppm}] = 2.48 - 2.38$ (m, 8H, P-**CH**₂-(CH_2)₃-H and P-**CH**₂-(CH_2)₉-H), 1.53 – 1.48 (m, 16H, P-CH₂-(**CH**₂)₂-CH₃ and P-CH₂-(**CH**₂)₂-(CH_2)₈-H), 1.28 – 1.23 (m, 12H, P-(CH_2)₃-(**CH**₂)₆-CH₃), 0.96 (t, $^2J_{\text{H/H}} = 7.1$ Hz, 9H, P-(CH_2)₃-**CH**₃), 0.85 (t, $^2J_{\text{H/H}} = 6.9$ Hz, 3H, P-(CH_2)₉-**CH**₃).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): $\delta[\text{ppm}] = 31.9$ (s, P-(CH_2)₇-**CH**₂-(CH_2)₂-H), 30.9 (d, $^3J_{\text{C/P}} = 14.7$ Hz, P-(CH_2)₂-**CH**₂-(CH_2)₇-H), 29.5 (s, P-(CH_2)₅-**CH**₂-(CH_2)₄-H), 29.4 (s, P-(CH_2)₄-**CH**₂-(CH_2)₅-H), 29.3 (s, P-(CH_2)₆-**CH**₂-(CH_2)₃-H), 29.1 (d, $^4J_{\text{C/P}} = 0.7$ Hz, P-(CH_2)₃-**CH**₂-(CH_2)₆-H), 24.1 (d, $^3J_{\text{C/P}} = 15.0$ Hz, P-(CH_2)₂-**CH**₂-CH₃), 24.0 (d, $^2J_{\text{C/P}} = 4.9$ Hz, P-CH₂-**CH**₂-(CH_2)₈-H), 22.7 (s, P-(CH_2)₈-**CH**₂-CH₃), 22.0 (d, $^2J_{\text{C/P}} = 4.8$ Hz, P-CH₂-**CH**₂-(CH_2)₂-H), 19.5 (d, $^1J_{\text{C/P}} = 47.2$ Hz, P-**CH**₂-(CH_2)₉-H), 19.0 (d, $^1J_{\text{C/P}} = 47.3$ Hz, P-**CH**₂-(CH_2)₃-H), 14.2 (s, P-(CH_2)₉-**CH**₃), 13.6 (s, P-(CH_2)₃-**CH**₃).

$^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3): $\delta[\text{ppm}] = 32.75$ (s).

1.3.1.5 Tributylododecylphosphonium bromide

To a solution of 7.20 mL tributylphosphine (1.00 eq, 28.9 mmol, 5.90 g) in 200 mL acetonitrile was added dropwise a solution of 7.63 mL of 1-bromododecane (1.1 eq, 31.8 mmol, 7.92 g) dissolved in 50 mL acetonitrile. After stirring for 36 h at 35°C the organic solvent was removed using a rotary evaporator. The excess of reagents was distilled off in vacuum yielding 12.4 g of tributylododecylphosphonium bromide (27.5 mmol, 95% yield) in the form of a colourless solid.

Melting point: 40°C (DSC).

¹H-NMR: (400 MHz, CDCl₃) δ[ppm] = 2.49 – 2.39 (m, 8H, P-**CH**₂-(CH₂)₃-H and P-**CH**₂-(CH₂)₁₁-H), 1.55 – 1.49 (m, 16H, P-CH₂-(**CH**₂)₂-CH₃ and P-CH₂-(**CH**₂)₂-(CH₂)₁₀-H), 1.32 – 1.24 (m, 16H, P-(CH₂)₃-(**CH**₂)₈-CH₃), 0.96 (t, ²J_{H/H} = 7.1 Hz, 9H, P-(CH₂)₃-**CH**₃), 0.86 (t, ²J_{H/H} = 6.9 Hz, 3H, P-(CH₂)₁₁-**CH**₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ[ppm] = 32.0 (s, P-(CH₂)₉-**CH**₂-(CH₂)₂-H), 30.9 (d, ³J_{C/P} = 14.7 Hz, P-(CH₂)₂-**CH**₂-(CH₂)₉-H), 29.71 (s, P-(CH₂)₆-**CH**₂-(CH₂)₅-H), 29.70 (s, P-(CH₂)₇-**CH**₂-(CH₂)₄-H), 29.6 (s, P-(CH₂)₅-**CH**₂-(CH₂)₆-H), 29.43 (s, P-(CH₂)₄-**CH**₂-(CH₂)₆-H), 29.42 (s, P-(CH₂)₈-**CH**₂-(CH₂)₃-H), 29.1 (d, ⁴J_{C/P} = 0.7 Hz, P-(CH₂)₃-**CH**₂-(CH₂)₆-H), 24.2 (d, ³J_{C/P} = 15.0 Hz, P-(CH₂)₂-**CH**₂-CH₃), 24.0 (d, ²J_{C/P} = 4.9 Hz, P-CH₂-**CH**₂-(CH₂)₁₀-H), 22.8 (s, P-(CH₂)₁₀-**CH**₂-CH₃), 22.1 (d, ²J_{C/P} = 4.8 Hz, P-CH₂-**CH**₂-(CH₂)₂-H), 19.5 (d, ¹J_{C/P} = 47.2 Hz, P-**CH**₂-(CH₂)₁₁-H), 19.3 (d, ¹J_{C/P} = 47.3 Hz, P-**CH**₂-(CH₂)₃-H), 14.2 (s, P-(CH₂)₁₁-**CH**₃), 13.7 (s, P-(CH₂)₃-**CH**₃).

³¹P{¹H}-NMR (162 MHz, CDCl₃) δ[ppm] = 32.73.

1.3.2 Synthesis of the tributyl-alkyl-phosphonium dicyanamide ionic liquids

1.3.2.1 Tetrabutylphosphonium dicyanamide

3.15 g Sodium dicyanamide (1.2 eq, 35.4 mmol) were added to a solution of 10.0 g tetrabutylphosphonium bromide (1.0 eq., 29.5 mmol) in 200 mL acetone and stirred for 48 h. The solution was filtered, the solvent rotated off and the residue dissolved in dichloromethane and filtered again. The organic solution was washed four times with 150 mL purified water, dried over MgSO₄ and the solvent removed by rotary evaporation. The residue was dried on a vacuum line for 48 hours yielding 9.11 g (28.0 mmol, 95% yield) of a colourless solid.

Melting point: 62°C (DSC).

¹H-NMR: (400 MHz, CDCl₃): δ[ppm] = 2.21 – 2.14 (m, 8H, P-**CH**₂-(CH₂)₃-H), 1.55– 1.48 (m, 16H, P-CH₂-(**CH**₂)₂-CH₃), 0.96 (t, ²J_{H/H} = 7.0 Hz, 12H, P-(CH₂)₃-**CH**₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ[ppm] = 120.0 (s, N-(**CN**)₂), 24.0 (d, ³J_{C/P} = 15.2 Hz, P-(CH₂)₂-**CH**₂-CH₃), 23.6 (d, ²J_{C/P} = 4.7 Hz, P-CH₂-**CH**₂-(CH₂)₂-H), 18.7 (d, ¹J_{C/P} = 47.6 Hz, P-**CH**₂-(CH₂)₃-H), 13.4 (s, P-(CH₂)₃-**CH**₃).

³¹P{¹H}-NMR (162 MHz, CDCl₃) δ[ppm] = 33.20 (s).

1.3.2.2 Tributylhexylphosphonium dicyanamide

To a solution of 10.0 g of tributylhexylphosphonium bromide (1.0 eq., 27.2 mmol) in 200 mL acetone were 2.91 g sodium dicyanamide (1.2 eq, 32.7 mmol). The solutions was stirred for 48 h the the solvent rotated off, the residue dissolved in dichloromethane and filtered again. The organic solution was washed four times with about 150 mL water, dried over MgSO₄ and the solvent removed on a rotary evaporator. The final residue was dried on a vacuum line for 48 hours to obtain 9.24 g of the ionic liquid (26.1 mmol, 96% yield) as a colourless liquid.

Glass transition point: -83°C (DSC).

¹H-NMR: (400 MHz, CDCl₃) δ[ppm] = 2.21 – 2.08 (m, 8H, P-**CH**₂-(CH₂)₃-H and P-**CH**₂-(CH₂)₅-H), 1.48 – 1.46 (m, 16H, P-CH₂-(**CH**₂)₂-CH₃ and P-CH₂-(**CH**₂)₂-(CH₂)₄-H), 1.27 – 1.24 (m, 4H, P-(CH₂)₃-(**CH**₂)₂-CH₃), 0.92 (t, ²J_{H/H} = 7.0 Hz, 9H, P-(CH₂)₃-**CH**₃), 0.82 (t, ²J_{H/H} = 6.9 Hz, 3H, P-(CH₂)₅-**CH**₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ[ppm] = 119.9 (s, N-(**CN**)₂), 30.8 (s, P-(CH₂)₃-**CH**₂-(CH₂)₂-H), 30.3 (d, ³J_{C/P} = 14.7 Hz, P-(CH₂)₂-**CH**₂-(CH₂)₃-H), 23.8 (d, ³J_{C/P} = 15.2 Hz, P-(CH₂)₂-**CH**₂-CH₃), 23.4 (d, ²J_{C/P} = 4.7 Hz, P-CH₂-**CH**₂-(CH₂)₄-H), 22.2 (s, P-(CH₂)₄-**CH**₂-CH₃), 21.5 (d, ²J_{C/P} = 4.8 Hz, P-CH₂-**CH**₂-(CH₂)₂-H), 18.8 (d, ¹J_{C/P} = 47.3 Hz, P-**CH**₂-(CH₂)₅-H), 18.6 (d, ¹J_{C/P} = 47.5 Hz, P-**CH**₂-(CH₂)₃-H), 13.8 (s, P-(CH₂)₅-**CH**₃), 13.3 (s, P-(CH₂)₃-**CH**₃).

³¹P{¹H}-NMR (162 MHz, CDCl₃) δ[ppm] = 33.11 (s).

1.3.2.3 Tributylloctylphosphonium dicyanamide

2.57 g Sodium dicyanamide (1.2 eq, 28.8 mmol) were added to 9.5 g of tributylloctylphosphonium bromide (1.0 eq., 24.0 mmol) dissolved in 200 mL acetone and stirred for 48 h. After filtering off the precipitated sodium bromide, the solvent rotated was rotated off and the residue dissolved in dichloromethane. After additional filtering the organic solution was washed with 150 mL water for four times and dried over MgSO₄. After filtering the solvent was removed by rotary evaporation and the ionic liquids dried on a vacuum line for 48 hours to yield 8.89 g (23.3 mmol, 97% yield) of colourless liquid.

Glass transition point: -84°C (DSC).

¹H-NMR: (400 MHz, CDCl₃) δ[ppm] = 2.23 – 2.14 (m, 8H, P-**CH**₂-(CH₂)₃-H and P-**CH**₂-(CH₂)₇-H), 1.53 – 1.45 (m, 16H, P-CH₂-(**CH**₂)₂-CH₃ and P-CH₂-(**CH**₂)₂-(CH₂)₆-H), 1.31 – 1.25 (m, 8H, P-(CH₂)₃-(**CH**₂)₄-CH₃), 0.97 (t, ²J_{H/H} = 7.0 Hz, 9H, P-(CH₂)₃-**CH**₃), 0.85 (t, ²J_{H/H} = 6.7 Hz, 3H, P-(CH₂)₇-**CH**₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ[ppm] = 120.1 (s, N-(**CN**)₂), 31.7 (s, P-(CH₂)₅-**CH**₂-(CH₂)₂-H), 30.8 (d, ³J_{C/P} = 14.6 Hz, P-(CH₂)₂-**CH**₂-(CH₂)₅-H), 29.0 (s, P-(CH₂)₄-**CH**₂-(CH₂)₃-H), 28.9 (s, P-(CH₂)₃-**CH**₂-(CH₂)₄-H), 24.0 (d, ³J_{C/P} = 15.2 Hz, P-(CH₂)₂-**CH**₂-CH₃), 23.7 (d, ²J_{C/P} = 4.7 Hz, P-CH₂-**CH**₂-(CH₂)₆-H), 22.6 (s, P-(CH₂)₆-**CH**₂-CH₃), 21.7 (d, ²J_{C/P} = 4.7 Hz, P-CH₂-**CH**₂-(CH₂)₂-H), 19.0 (d, ¹J_{C/P} = 47.2 Hz, P-**CH**₂-(CH₂)₇-H), 18.8 (d, ¹J_{C/P} = 47.5 Hz, P-**CH**₂-(CH₂)₃-H), 14.1 (s, P-(CH₂)₇-**CH**₃), 13.5 (s, P-(CH₂)₃-**CH**₃).

³¹P{¹H}-NMR (162 MHz, CDCl₃) δ[ppm] = 33.13 (s).

1.3.2.4 Tributyldecylphosphonium dicyanamide

9.5 g of tributyldecylphosphonium bromide (1.0 eq., 21.0 mmol) was dissolved in 200 mL acetone, 2.25 g sodium dicyanamide (1.2 eq, 25.2 mmol) were added and the mixture was stirred for 48 h. The obtained solution was filtered, the acetone removed on a rotary evaporator and the residue dissolved in CH₂Cl₂. The organic solution was filtered and washed four times with 150 mL water, followed by drying over MgSO₄. After removing the solvent by means of rotary evaporation the residue was finally dried in oil-

pump vacuum line for 48 hours to obtain 8.91 g of ionic liquids (20.4 mmol, 97% yield) as colourless liquid.

Glass transition point: -84°C (DSC).

¹H-NMR: (400 MHz, CDCl₃) δ[ppm] = 2.22 – 2.13 (m, 8H, P-**CH**₂-(CH₂)₃-H and P-**CH**₂-(CH₂)₉-H), 1.51 – 1.42 (m, 16H, P-CH₂-(**CH**₂)₂-CH₃ and P-CH₂-(**CH**₂)₂-(CH₂)₈-H), 1.30 – 1.23 (m, 12H, P-(CH₂)₃-(**CH**₂)₆-CH₃), 0.96 (t, ²J_{H/H} = 6.8 Hz, 9H, P-(CH₂)₃-**CH**₃), 0.83 (t, ²J_{H/H} = 6.7 Hz, 3H, P-(CH₂)₉-**CH**₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ[ppm] = 120.0 (s, N-(**CN**)₂), 31.9 (s, P-(CH₂)₇-**CH**₂-(CH₂)₂-H), 30.8 (d, ³J_{C/P} = 14.7 Hz, P-(CH₂)₂-**CH**₂-(CH₂)₇-H), 29.5 (s, P-(CH₂)₅-**CH**₂-(CH₂)₄-H), 29.31 (s, P-(CH₂)₄-**CH**₂-(CH₂)₅-H), 29.27 (s, P-(CH₂)₆-**CH**₂-(CH₂)₃-H), 28.9 (s, P-(CH₂)₃-**CH**₂-(CH₂)₆-H), 24.0 (d, ³J_{C/P} = 15.2 Hz, P-(CH₂)₂-**CH**₂-CH₃), 23.6 (d, ²J_{C/P} = 4.8 Hz, P-CH₂-**CH**₂-(CH₂)₈-H), 22.7 (s, P-(CH₂)₈-**CH**₂-CH₃), 21.7 (s, P-(CH₂)₈-**CH**₂-CH₃), 19.0 (d, ¹J_{C/P} = 47.2 Hz, P-**CH**₂-(CH₂)₉-H), 18.8 (d, ¹J_{C/P} = 47.5 Hz, P-**CH**₂-(CH₂)₃-H), 14.1 (s, P-(CH₂)₉-**CH**₃), 13.4 (s, P-(CH₂)₃-**CH**₃).

³¹P{¹H}-NMR (162 MHz, CDCl₃) δ[ppm] = 33.12 (s).

1.3.2.5 Tributylidodecylphosphonium dicyanamide

For the anion-metathesis 2.13 g Sodium dicyanamide (1.2 eq, 23.9 mmol) were added to a solution of 9.0 g tributylidodecylphosphonium bromide (1.0 eq., 19.9 mmol) in 200 mL acetone and the mixture stirred for 48 h. After filtration, the solvent was rotated off and the residue dissolved in dichloromethane followed by an additional filtration. After washing the organic solution four times with 150 mL water the organic phase was dried over MgSO₄. Dichloromethane was removed by rotary evaporation and the residue dried for 48 hours in oil-pump vacuum obtaining 8.55 g (20.4 mmol, 98% yield) of a slightly yellow, transparent liquid.

Melting point: -57°C (DSC).

¹H-NMR: (400 MHz, CDCl₃) δ[ppm] = 2.22 – 2.13 (m, 8H, P-**CH**₂-(CH₂)₃-H and P-**CH**₂-(CH₂)₁₁-H), 1.53 – 1.45 (m, 16H, P-CH₂-(**CH**₂)₂-CH₃ and P-CH₂-(**CH**₂)₂-(CH₂)₁₀-H), 1.30 – 1.21 (m, 16H, P-(CH₂)₃-(**CH**₂)₈-CH₃), 0.96 (t, ²J_{H/H} = 7.0 Hz, 9H, P-(CH₂)₃-**CH**₃), 0.83 (t, ²J_{H/H} = 6.8 Hz, 3H, P-(CH₂)₁₁-**CH**₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ[ppm] = 120.0 (s, N-(**CN**)₂), 31.9 (s, P-(CH₂)₉-**CH**₂-(CH₂)₂-H), 30.8 (d, ³J_{C/P} = 14.7 Hz, P-(CH₂)₂-**CH**₂-(CH₂)₉-H), 29.62 (s, s, P-(CH₂)₆-**CH**₂-(CH₂)₅-H), 29.61 (s, P-(CH₂)₇-**CH**₂-(CH₂)₄-H), 29.5 (s, P-(CH₂)₅-**CH**₂-(CH₂)₆-H), 29.33 (s, P-(CH₂)₈-**CH**₂-(CH₂)₃-H), 29.31 (s, P-(CH₂)₈-**CH**₂-(CH₂)₃-H), 28.9 (d, ⁴J_{C/P} = 0.7 Hz, P-(CH₂)₃-**CH**₂-(CH₂)₆-H), 24.0 (d, ³J_{C/P} = 15.2 Hz, P-(CH₂)₂-**CH**₂-CH₃), 23.6 (d, ²J_{C/P} = 4.8 Hz, P-CH₂-**CH**₂-(CH₂)₁₀-H), 22.7 (s, P-(CH₂)₁₀-**CH**₂-CH₃), 21.7 (d, ²J_{C/P} = 4.8 Hz, P-CH₂-**CH**₂-(CH₂)₂-H), 19.0 (d, ¹J_{C/P} = 47.2 Hz, P-**CH**₂-(CH₂)₉-H), 18.8 (d, ¹J_{C/P} = 47.5 Hz, P-**CH**₂-(CH₂)₃-H), 14.1 (s, P-(CH₂)₁₁-**CH**₃), 13.4 (s, P-(CH₂)₃-**CH**₃).

³¹P{¹H}-NMR (162 MHz, CDCl₃) δ[ppm] = 33.11 (s).

2. NMR-spectra

2.1 NMR-spectra of Synthesis of the tributyl(1*H*,1*H*,2*H*,2*H*-perfluoroalkyl)phosphonium iodide ionic liquids

2.1.1 NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorobutyl)phosphonium iodide

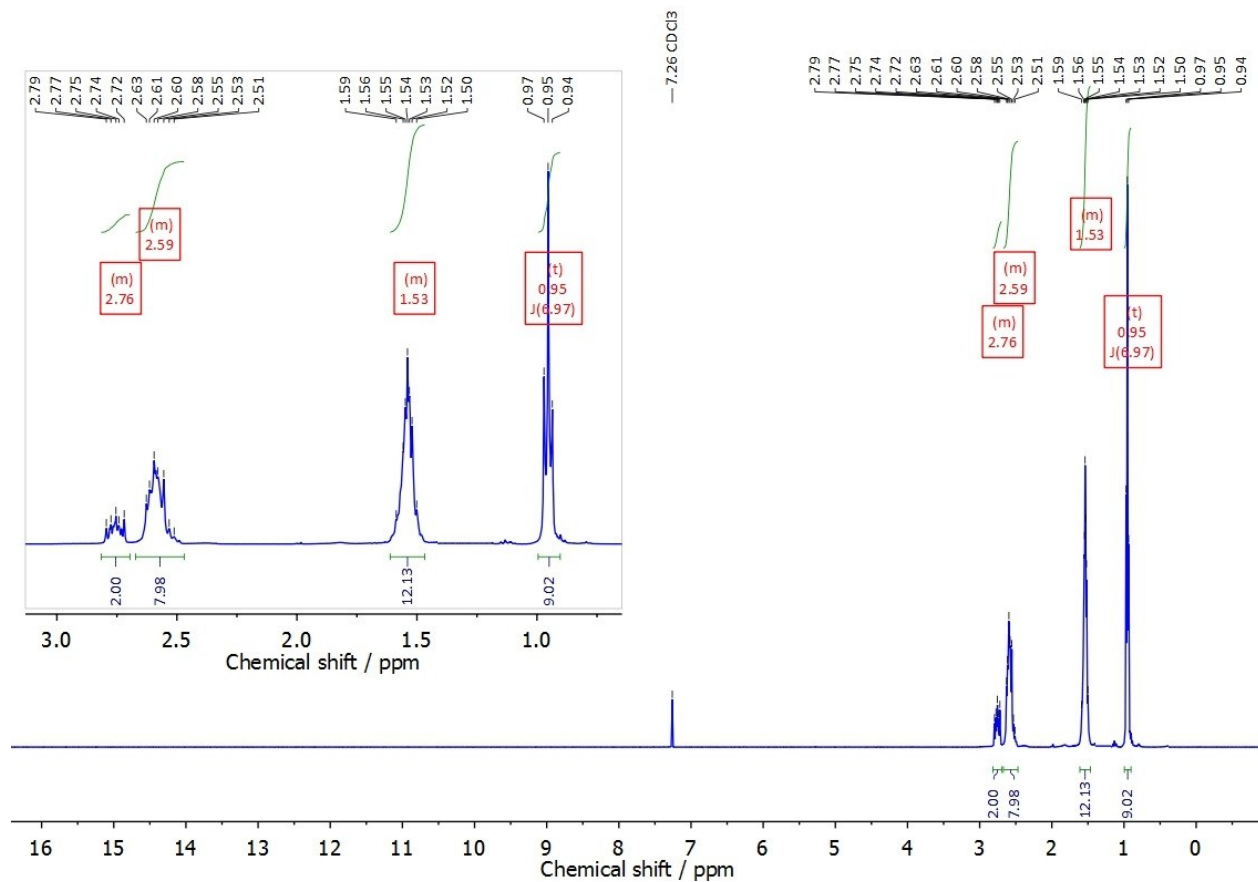


Figure S1. ^1H -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorobutyl)phosphonium iodide.

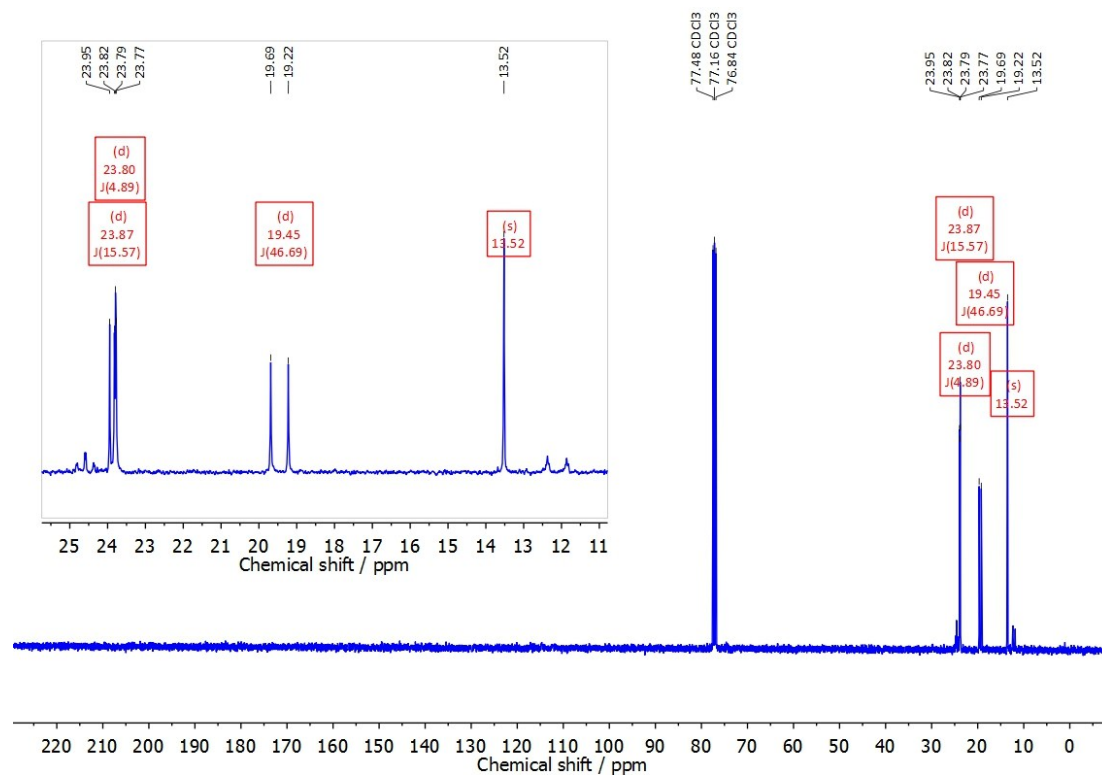


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorobutyl)phosphonium iodide.

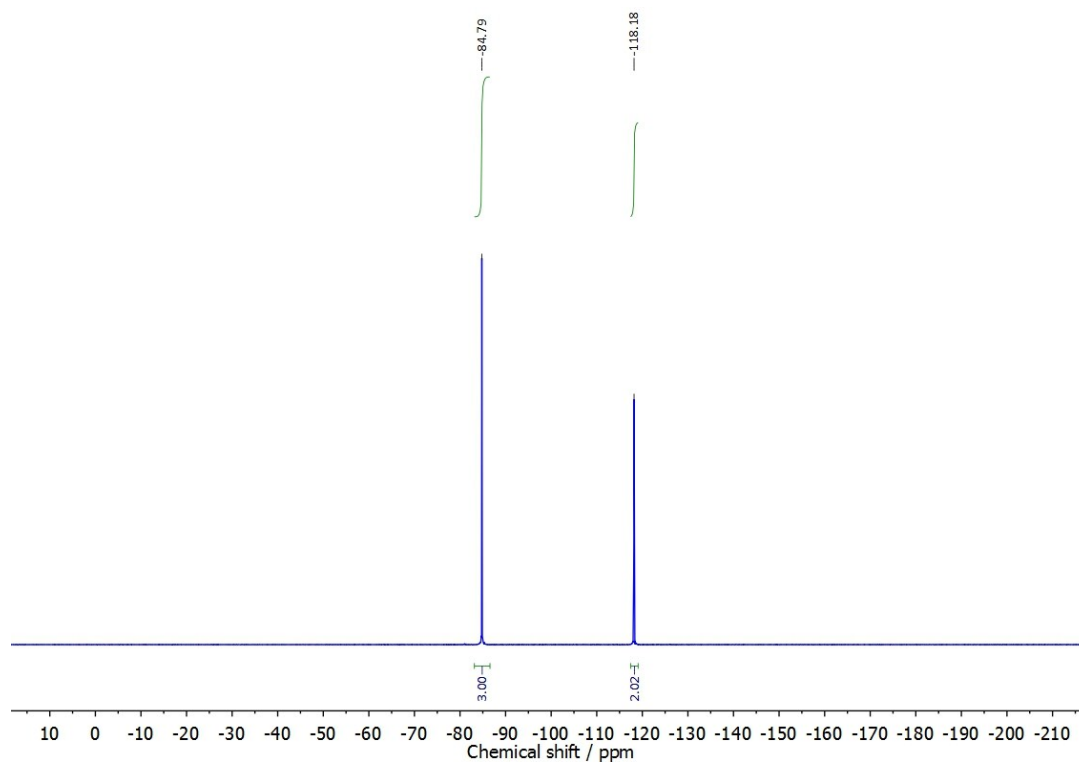


Figure S3. $^{19}\text{F}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorobutyl)phosphonium iodide.

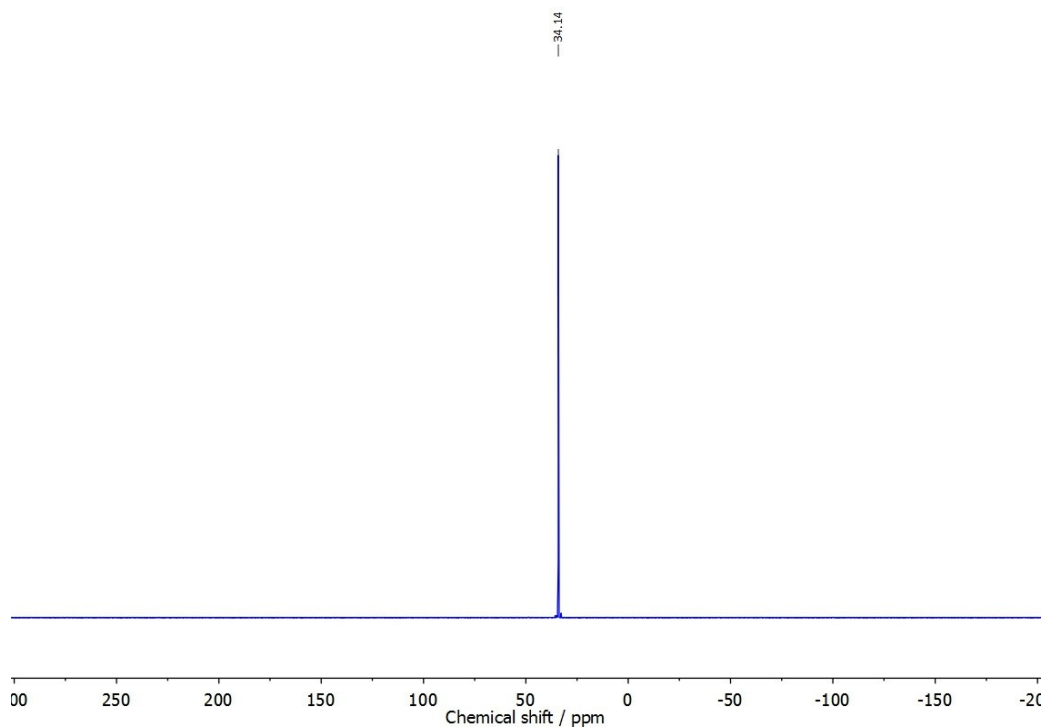


Figure S4. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorobutyl)phosphonium iodide.

2.1.2 NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)phosphonium iodide

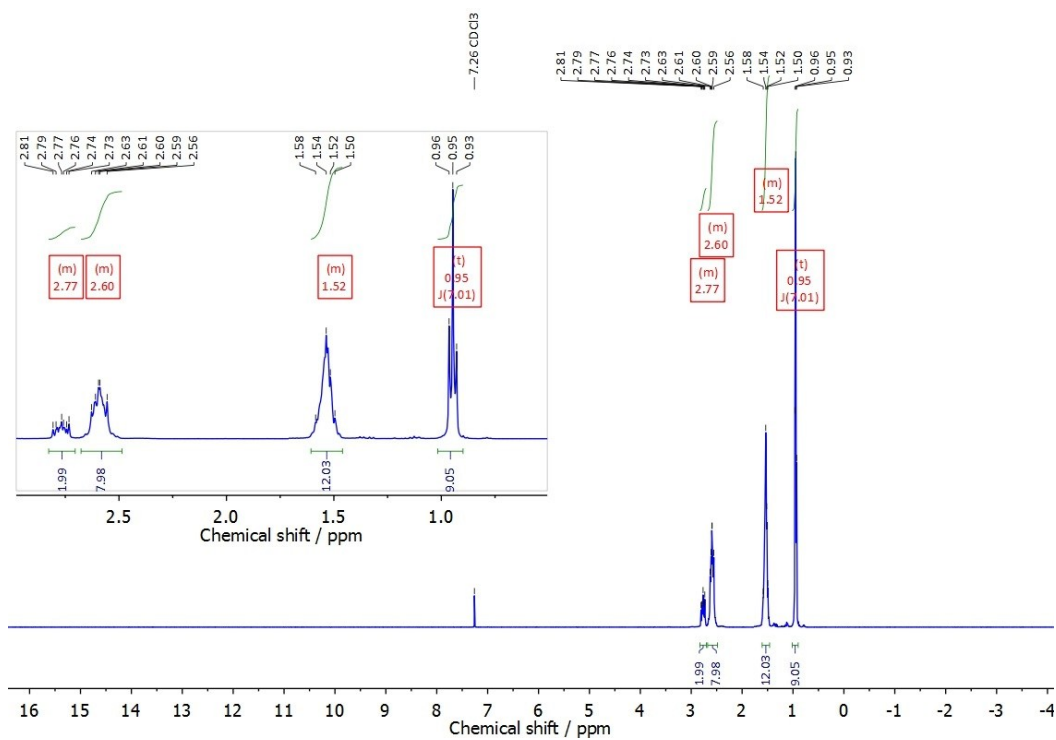


Figure S5. ^1H -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)phosphonium iodide.

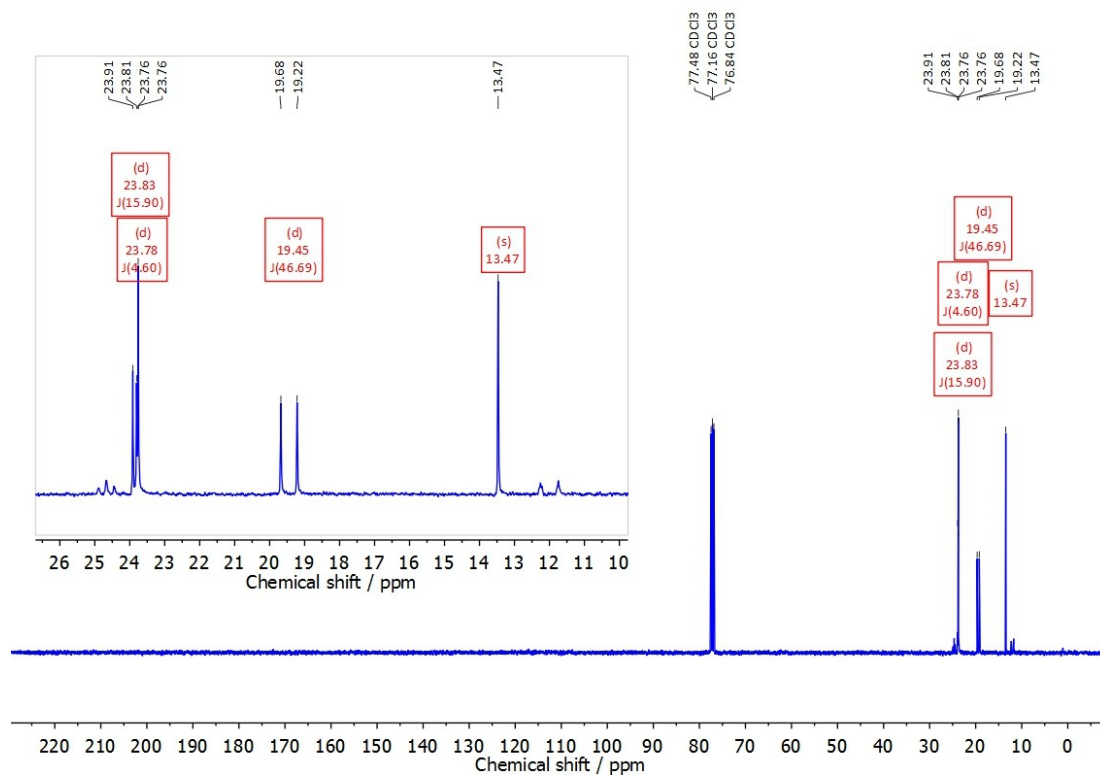


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)phosphonium iodide.

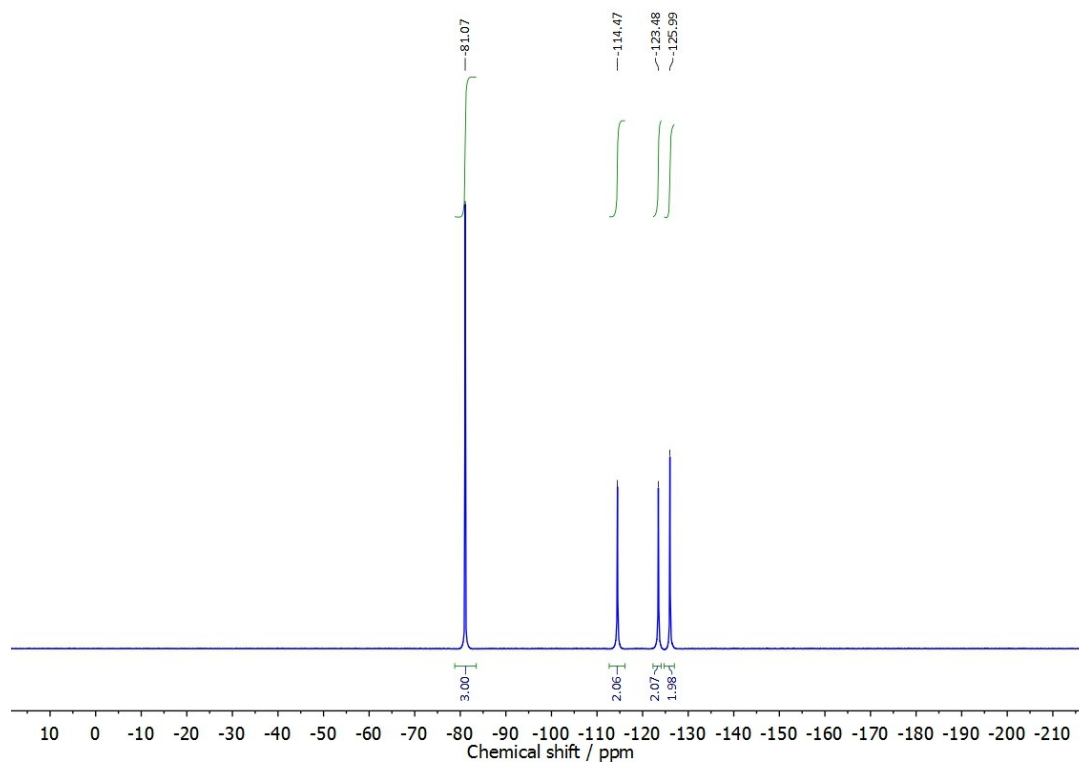


Figure S7. $^{19}\text{F}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)phosphonium iodide.

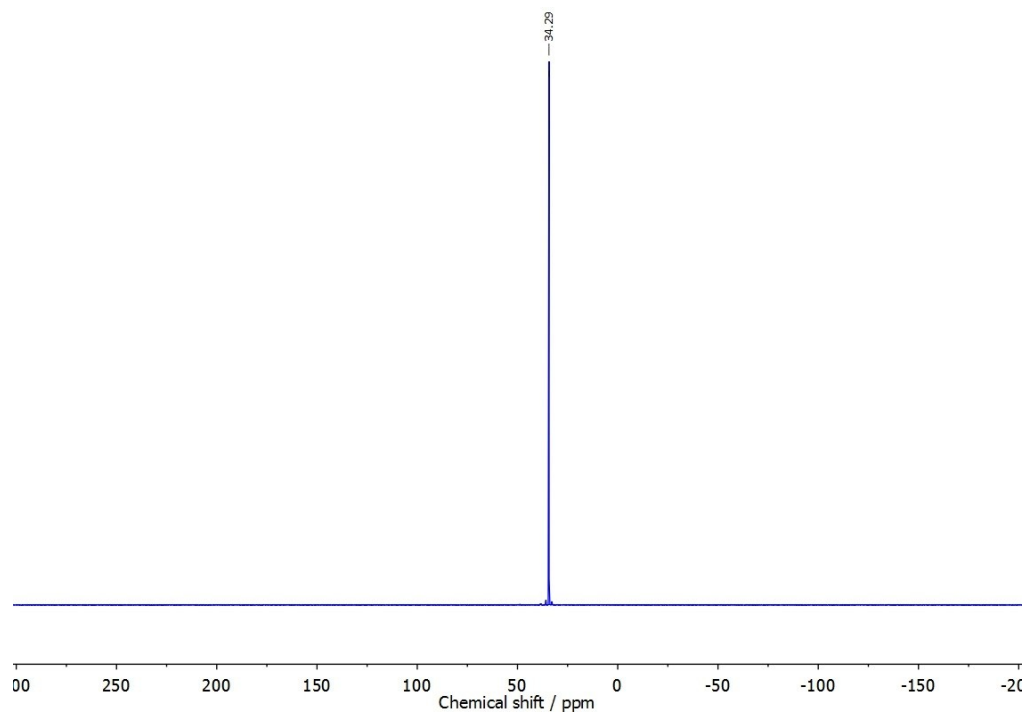


Figure S8. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)phosphonium iodide.

2.1.3 NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphonium iodide

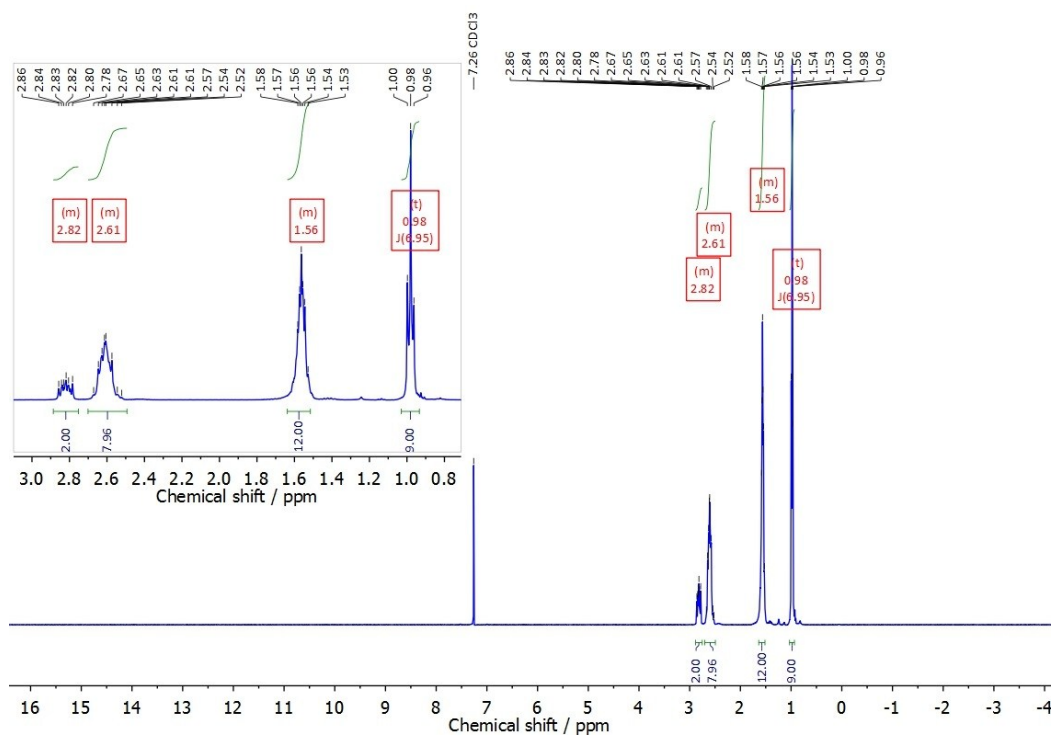


Figure S9. ^1H -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphonium iodide.

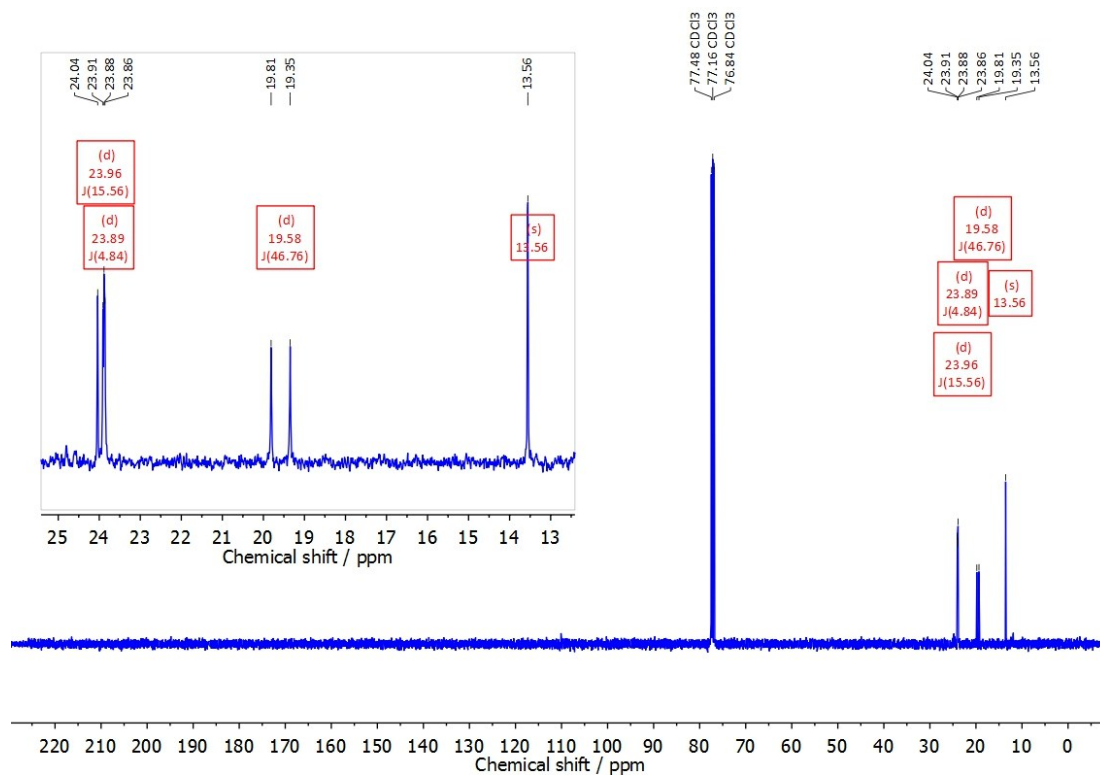


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphonium iodide.

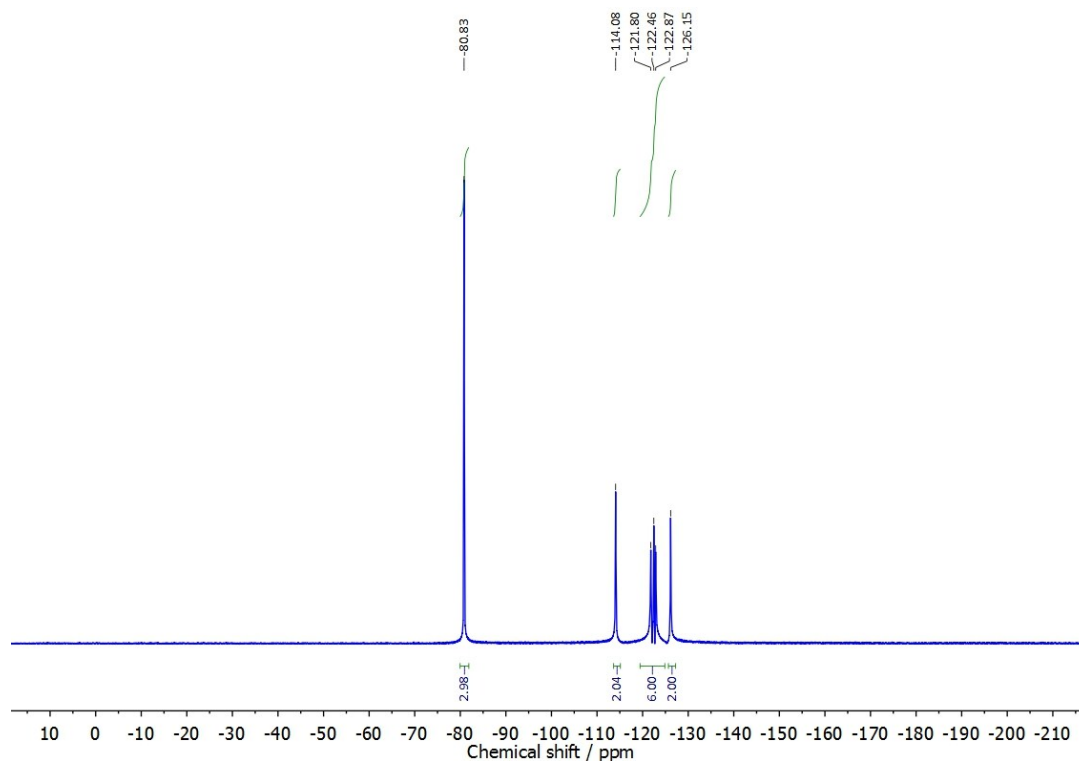


Figure S11. $^{19}\text{F}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphonium iodide.

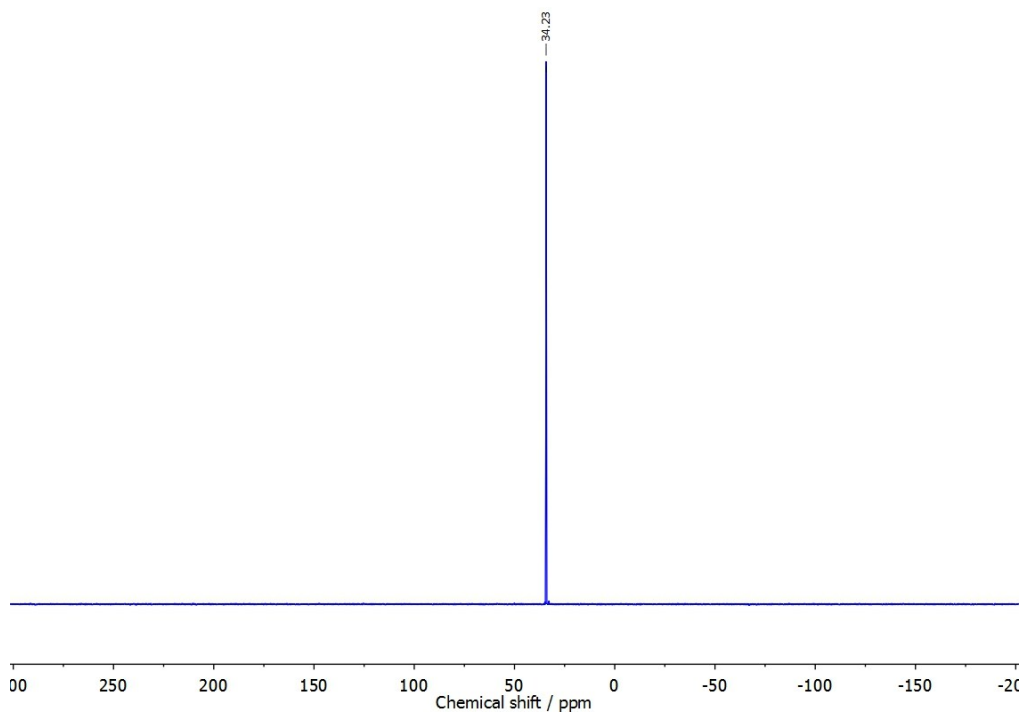


Figure S12. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphonium iodide.

2.1.4 NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phosphonium iodide

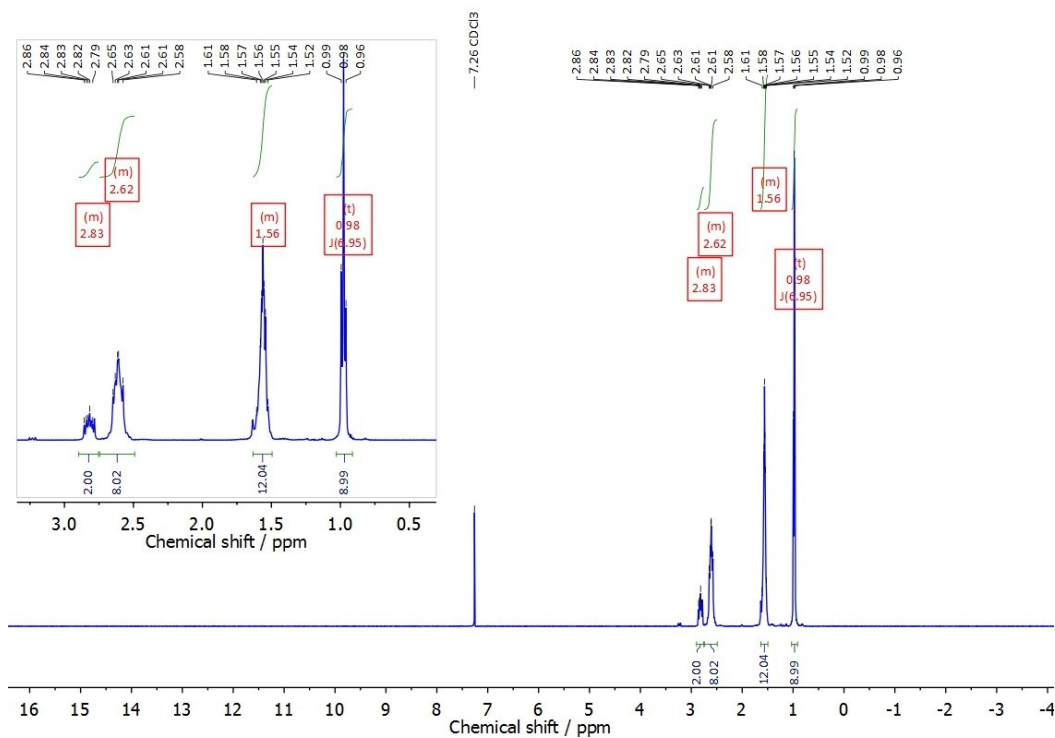


Figure S13. ^1H -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phosphonium iodide.

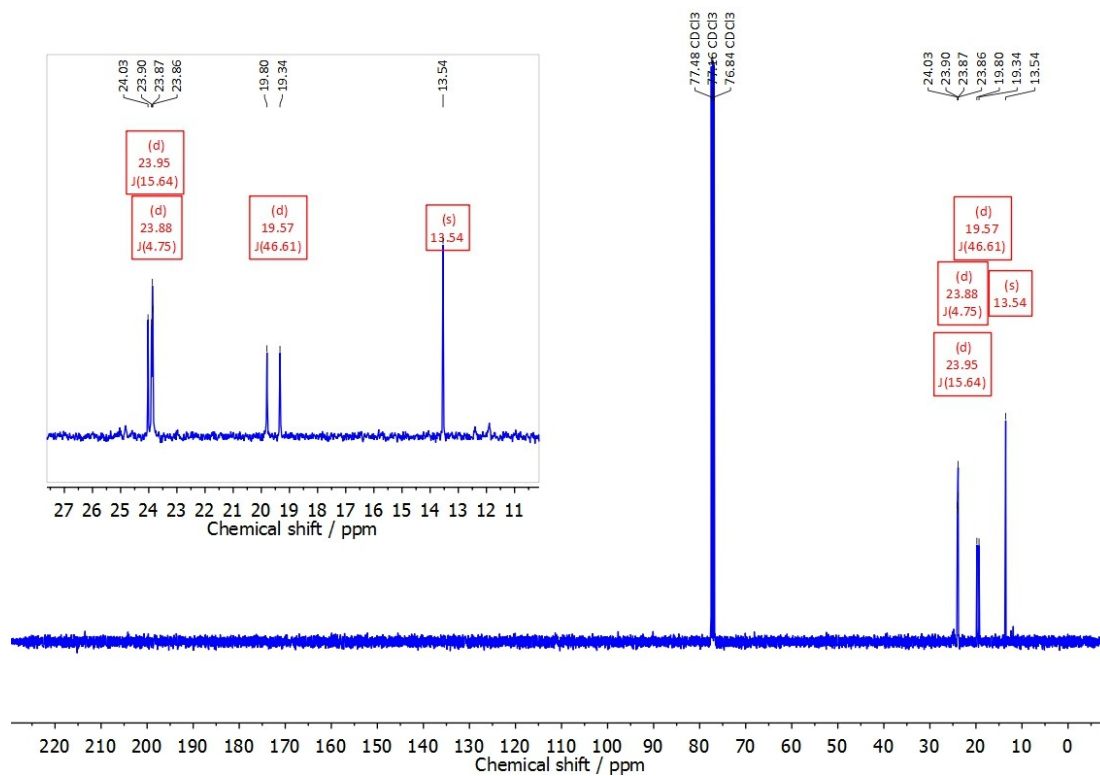


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phosphonium iodide.

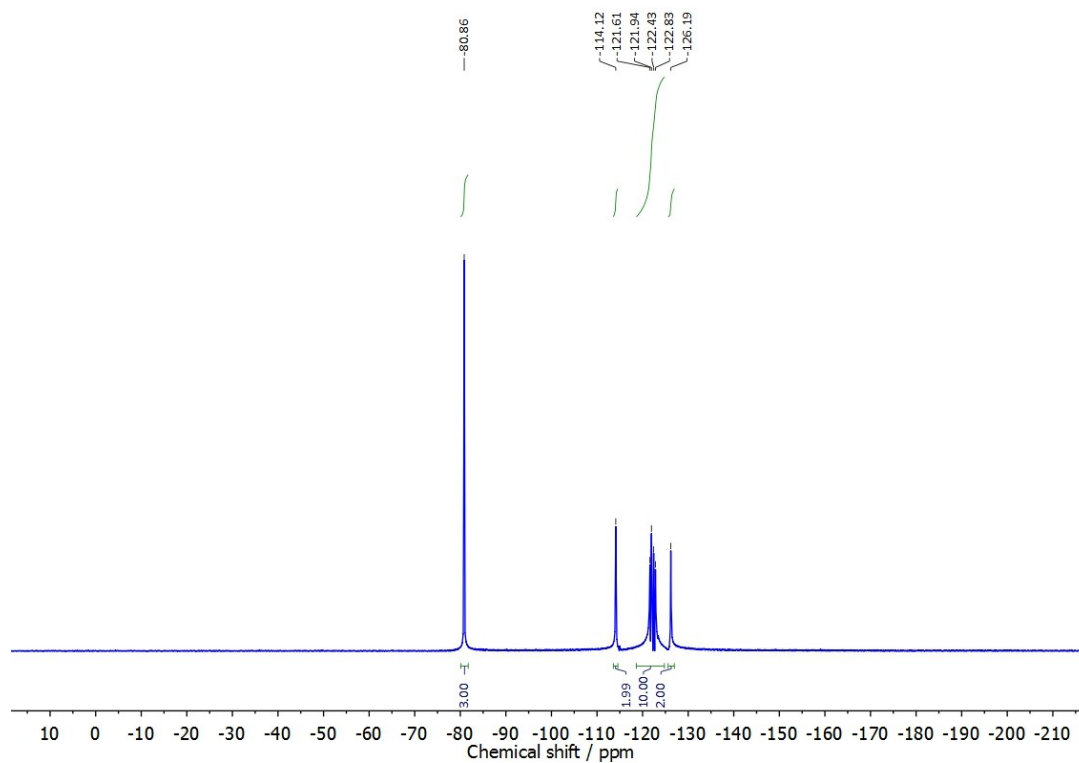


Figure S15. $^{19}\text{F}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phosphonium iodide.

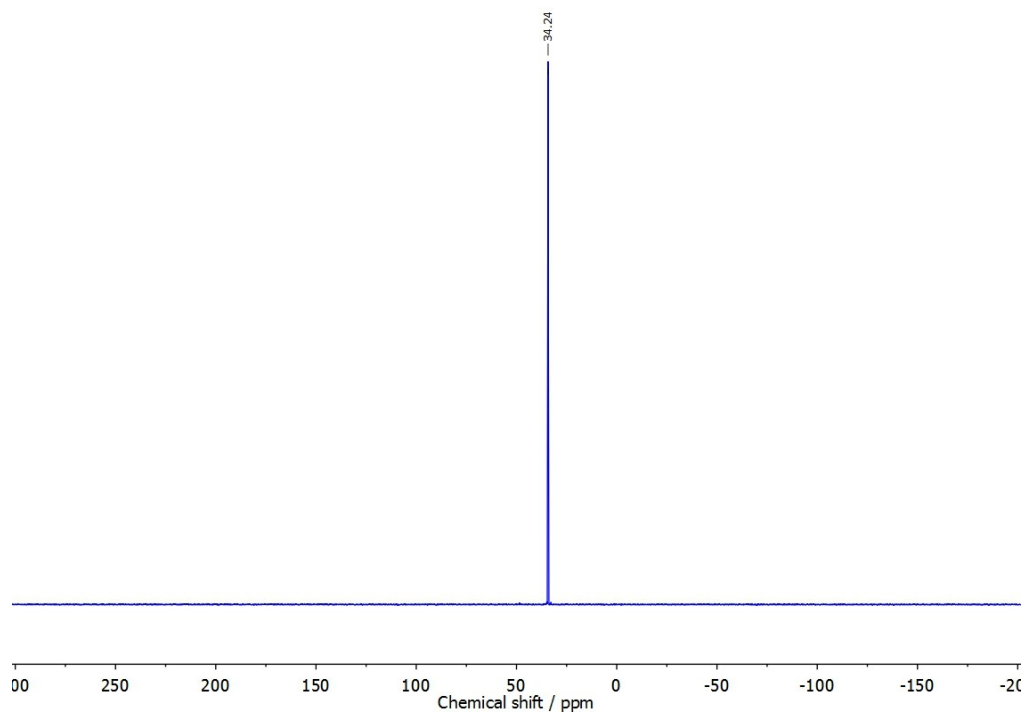


Figure S16. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phosphonium iodide.

2.1.5 NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorododecyl)phosphonium iodide

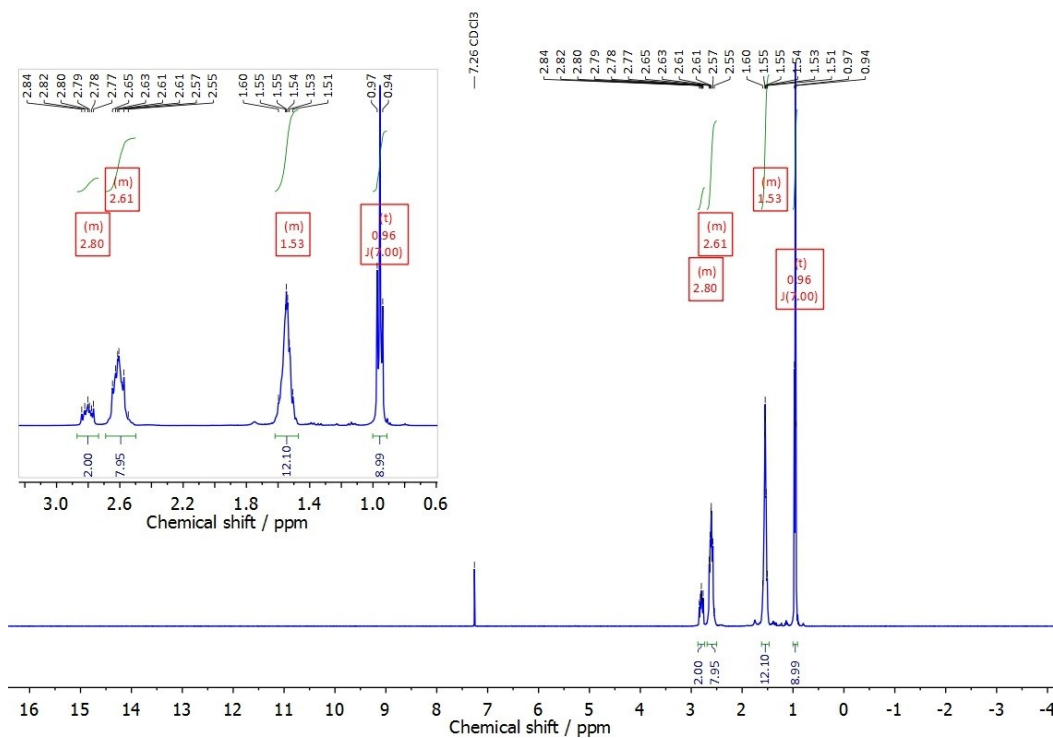


Figure S17. ^1H -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorododecyl)phosphonium iodide.

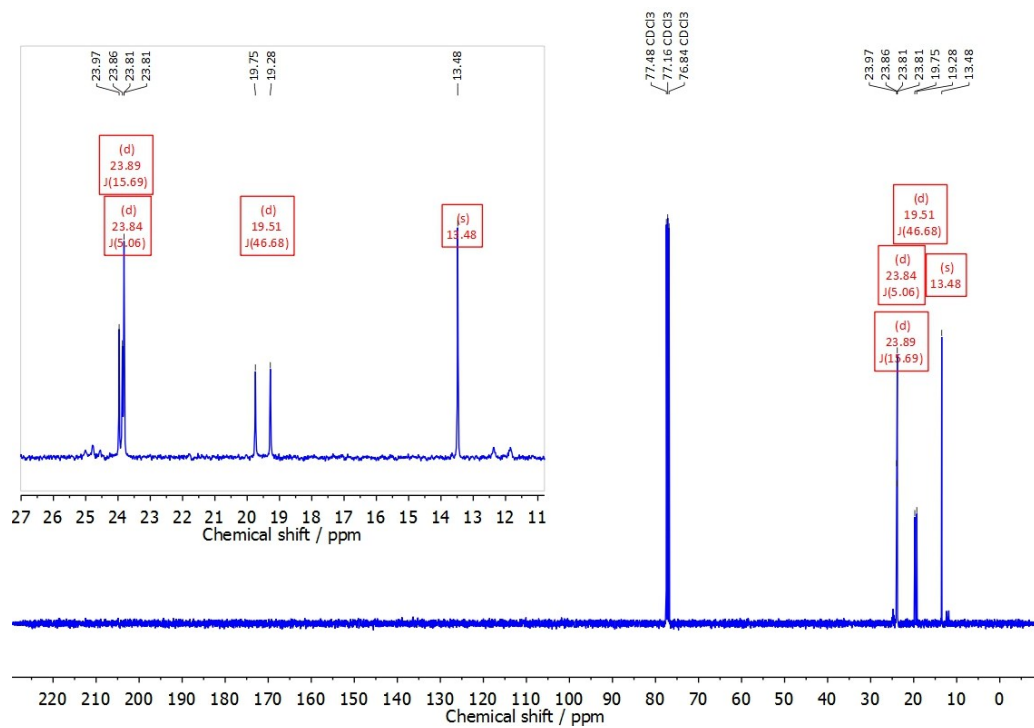


Figure S18. ¹³C{¹H}-NMR-spectra of tributyl(1H,1H,2H,2H-perfluorododecyl)phosphonium iodide.

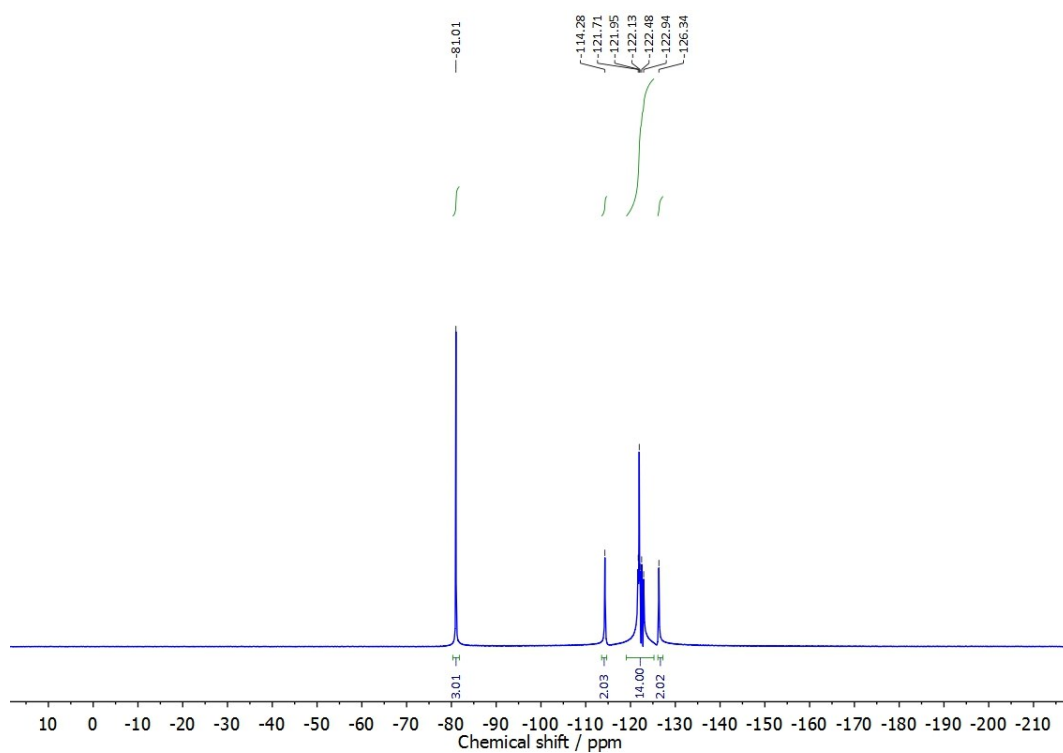


Figure S19. ¹⁹F{¹H}-NMR-spectra of tributyl(1H,1H,2H,2H-perfluorododecyl)phosphonium iodide.

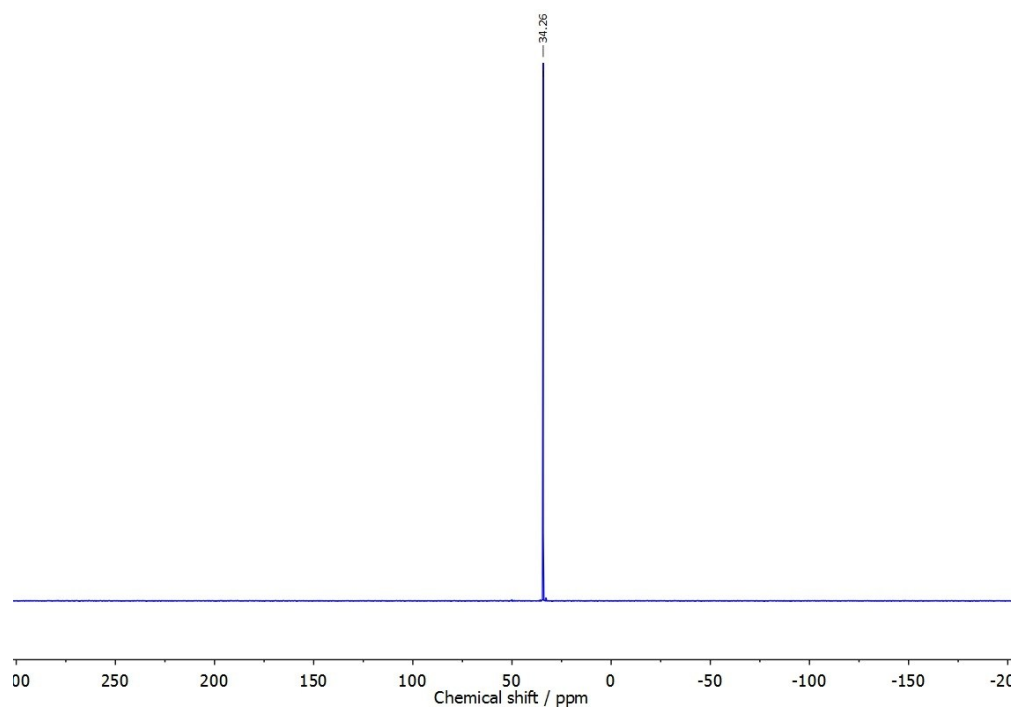


Figure S20. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorododecyl)phosphonium iodide.

2.2 NMR-spectra of the tributyl(1*H*,1*H*,2*H*,2*H*-perfluoroalkyl)phosphonium dicyanamide ionic liquids

2.2.1 NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorobutyl)phosphonium dicyanamide F2

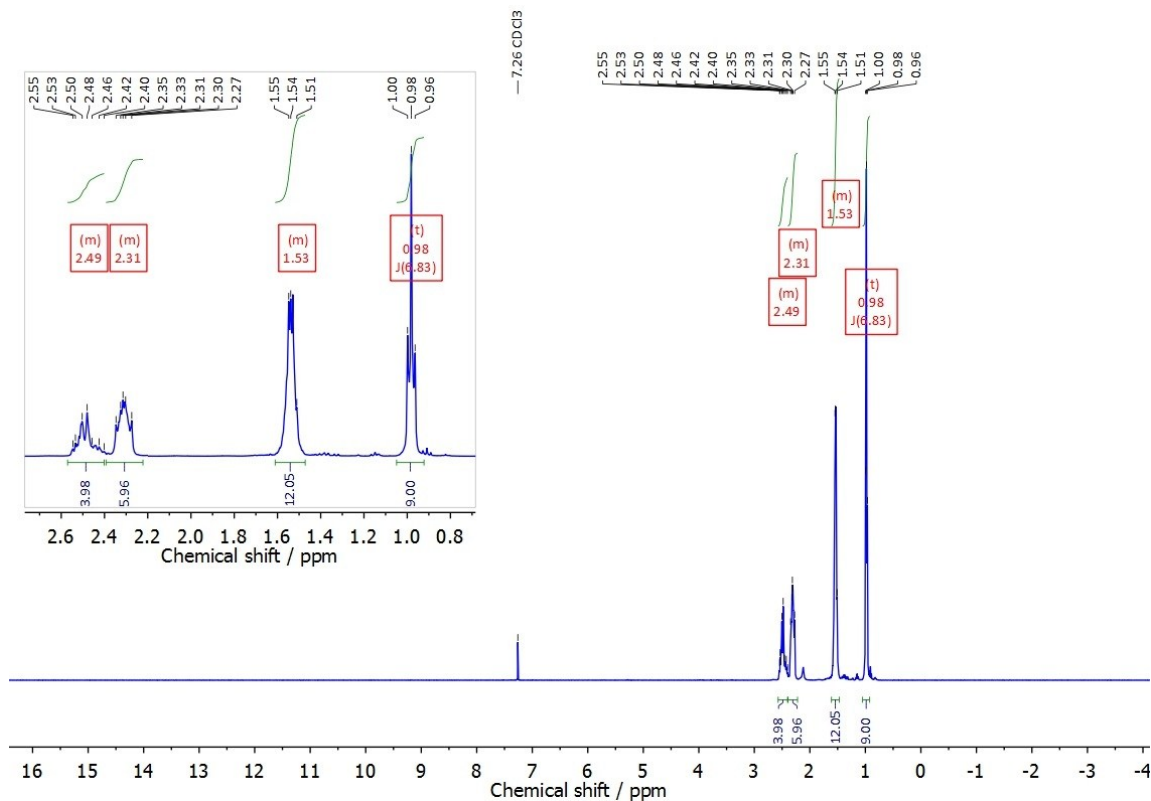


Figure S21. ^1H -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorobutyl)phosphonium dicyanamide.

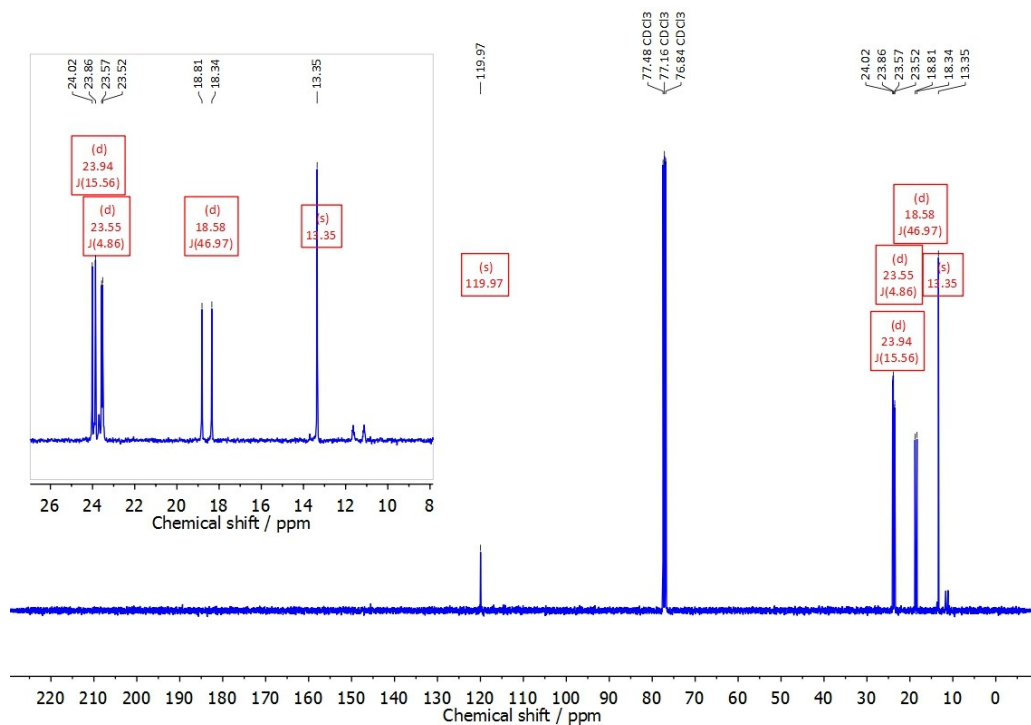


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorobutyl)phosphonium dicyanamide.

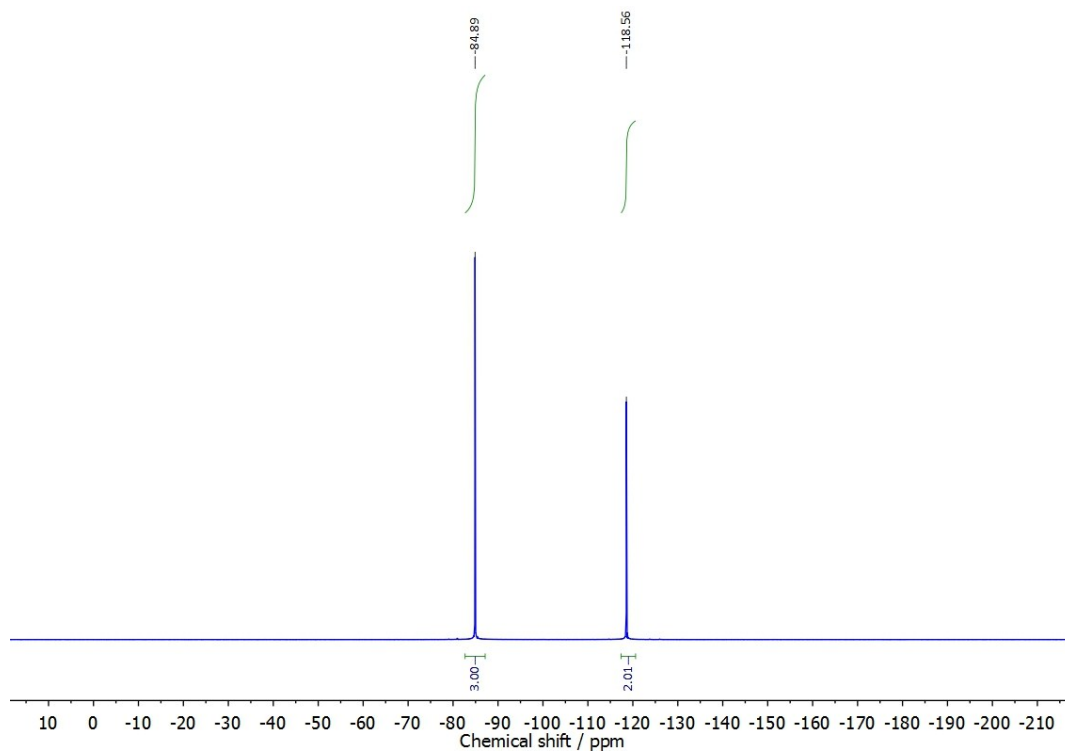


Figure S23. $^{19}\text{F}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorobutyl)phosphonium dicyanamide.

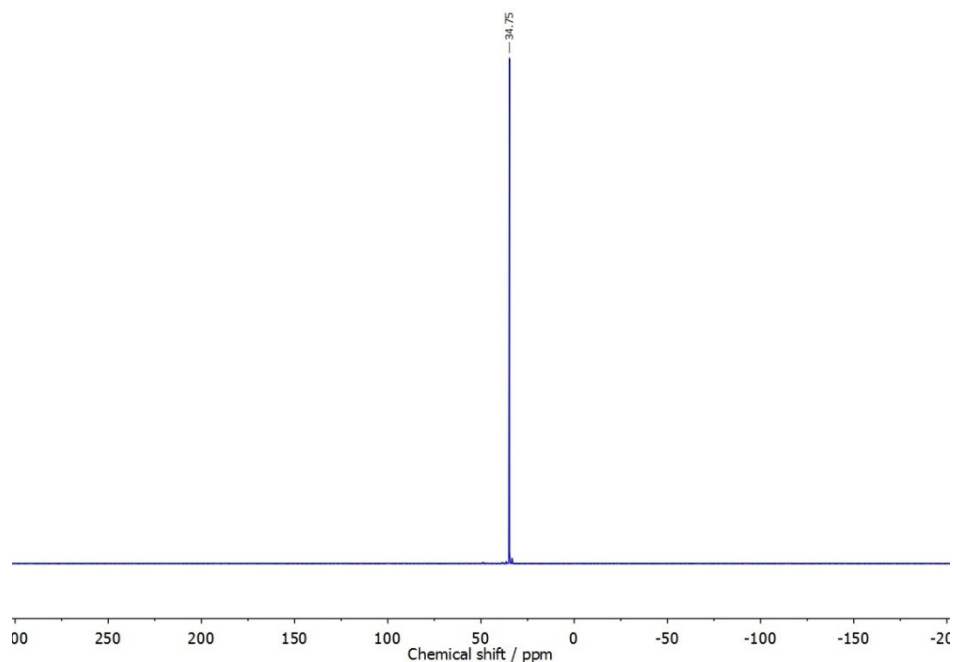


Figure S24. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorobutyl)phosphonium dicyanamide.

2.2.2 NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)phosphonium dicyanamide F4

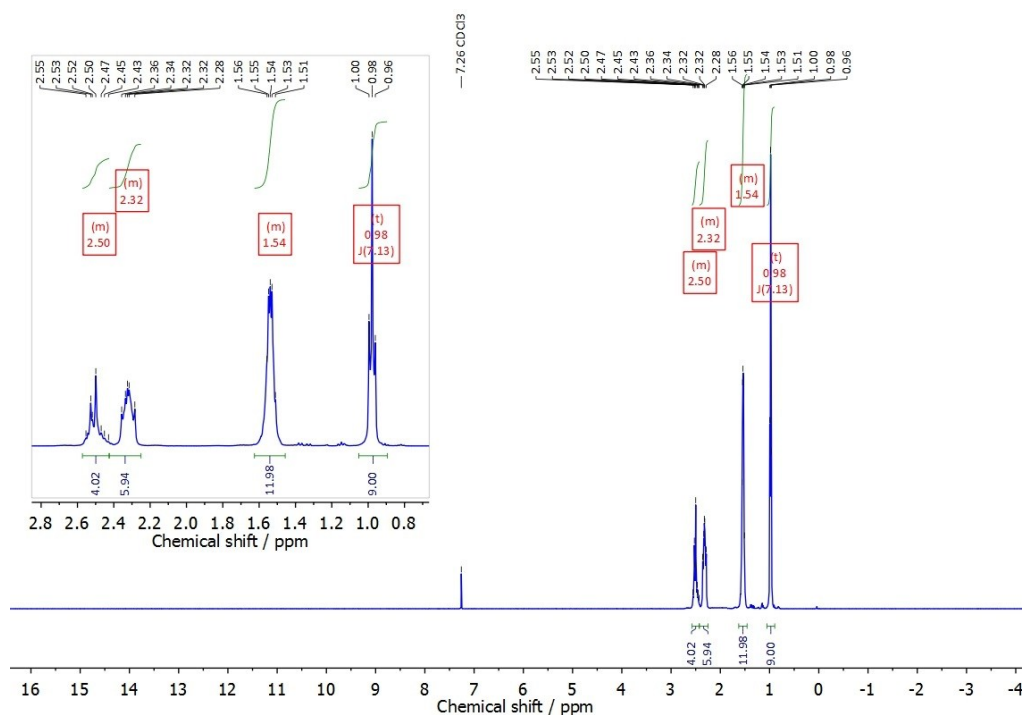


Figure S25. ^1H -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)phosphonium dicyanamide.

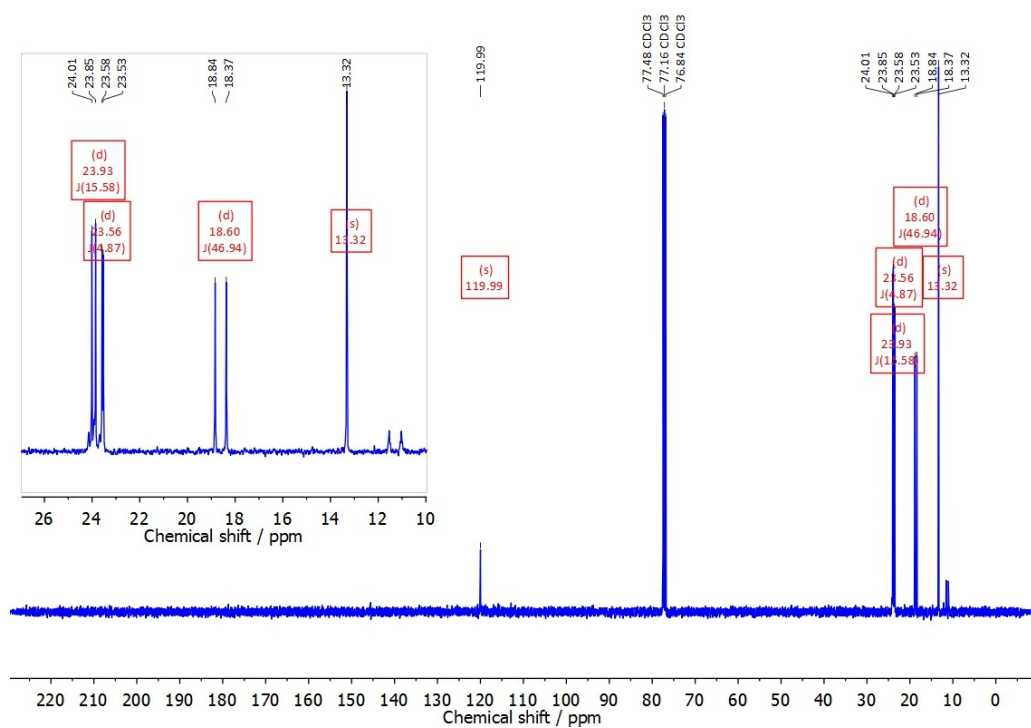


Figure S26. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)phosphonium dicyanamide.

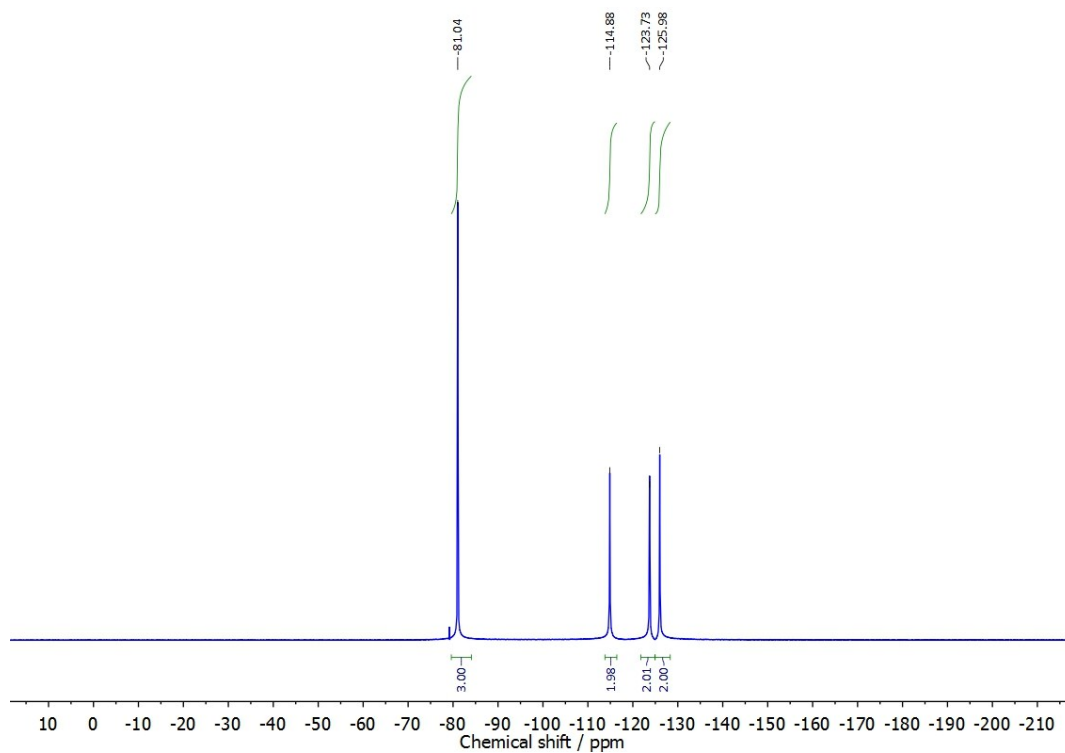


Figure S27. $^{19}\text{F}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)phosphonium dicyanamide.

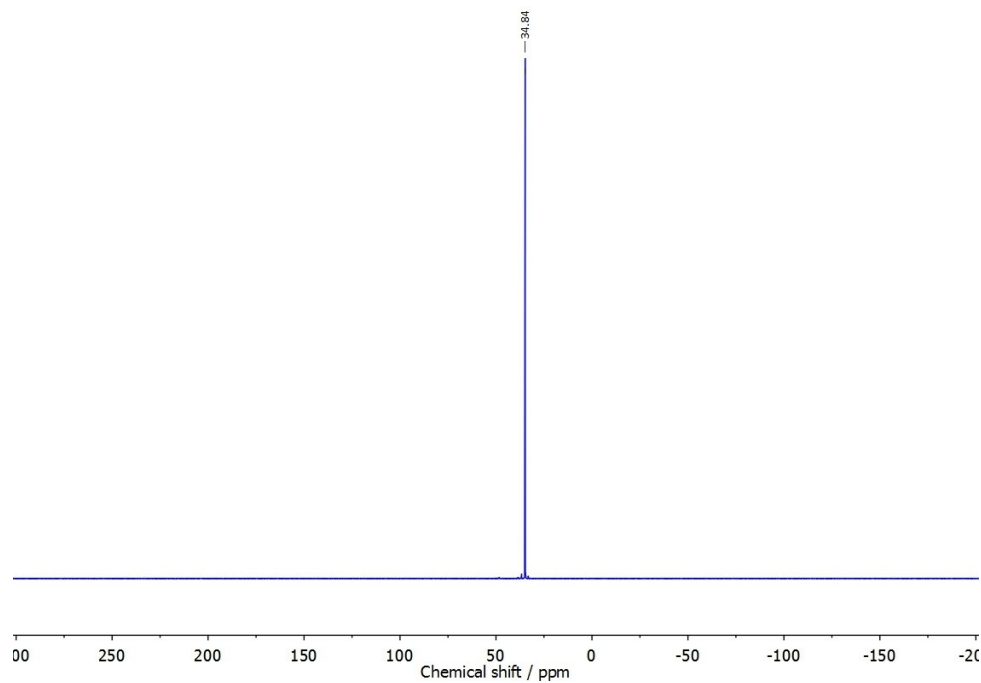


Figure S28. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)phosphonium dicyanamide.

2.2.3 NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphonium dicyanamide F6

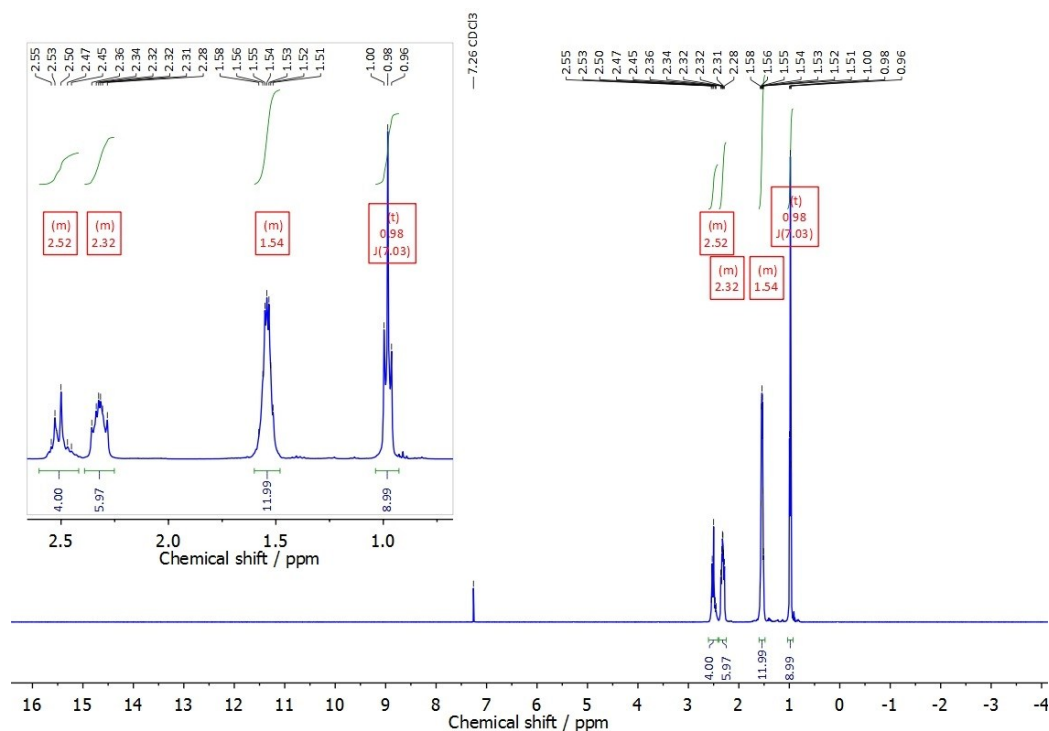


Figure S29. ^1H -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphonium dicyanamide.

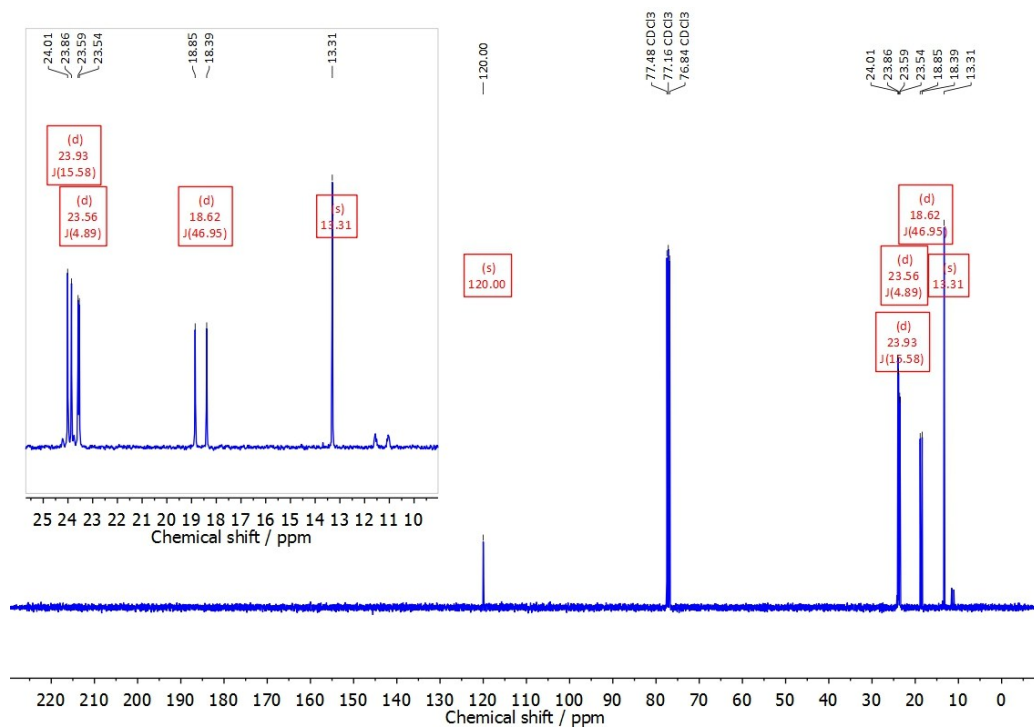


Figure S30. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphonium dicyanamide.

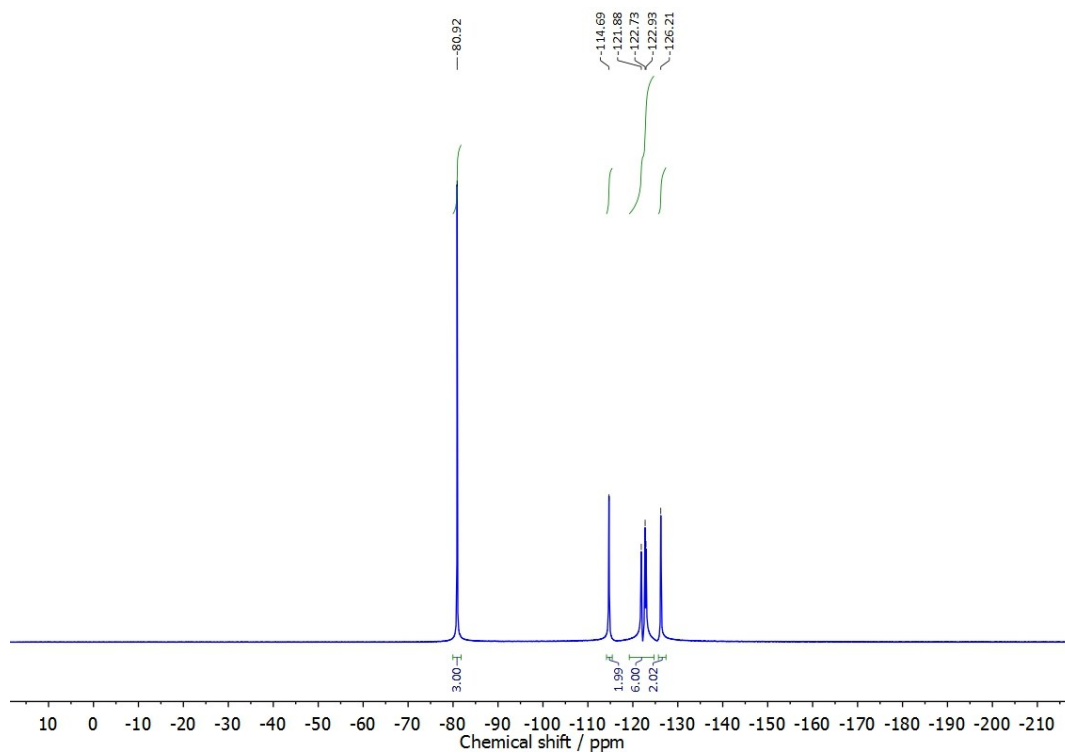


Figure S31. $^{19}\text{F}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphonium dicyanamide.

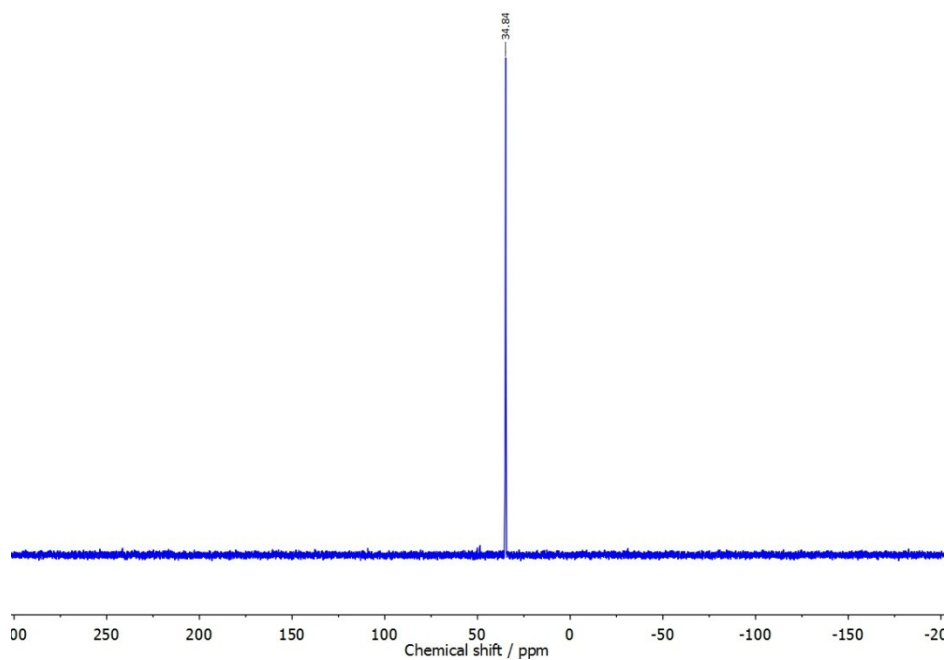


Figure S32. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphonium dicyanamide.

2.2.4 NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phosphonium dicyanamide F8

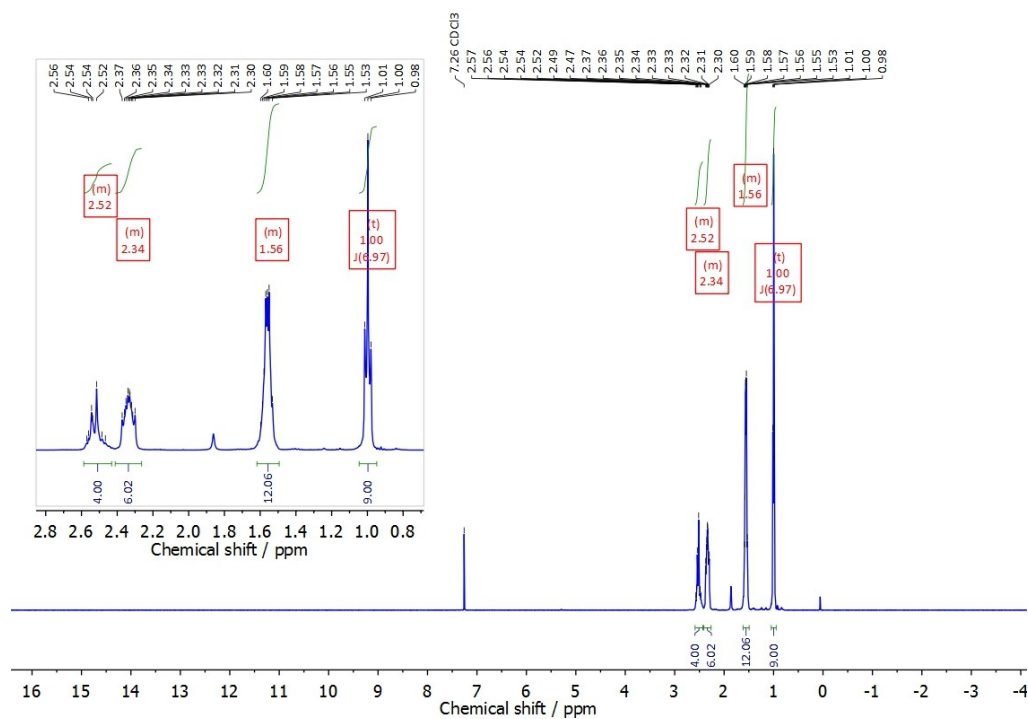


Figure S33. ^1H -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phosphonium dicyanamide.

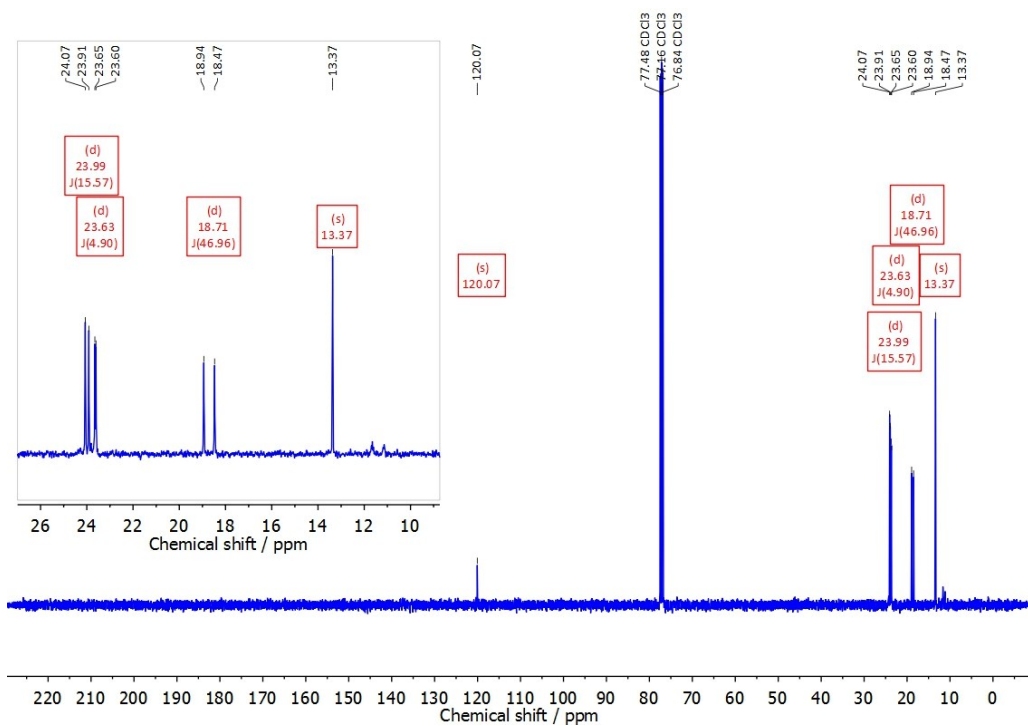


Figure S34. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phosphonium dicyanamide.

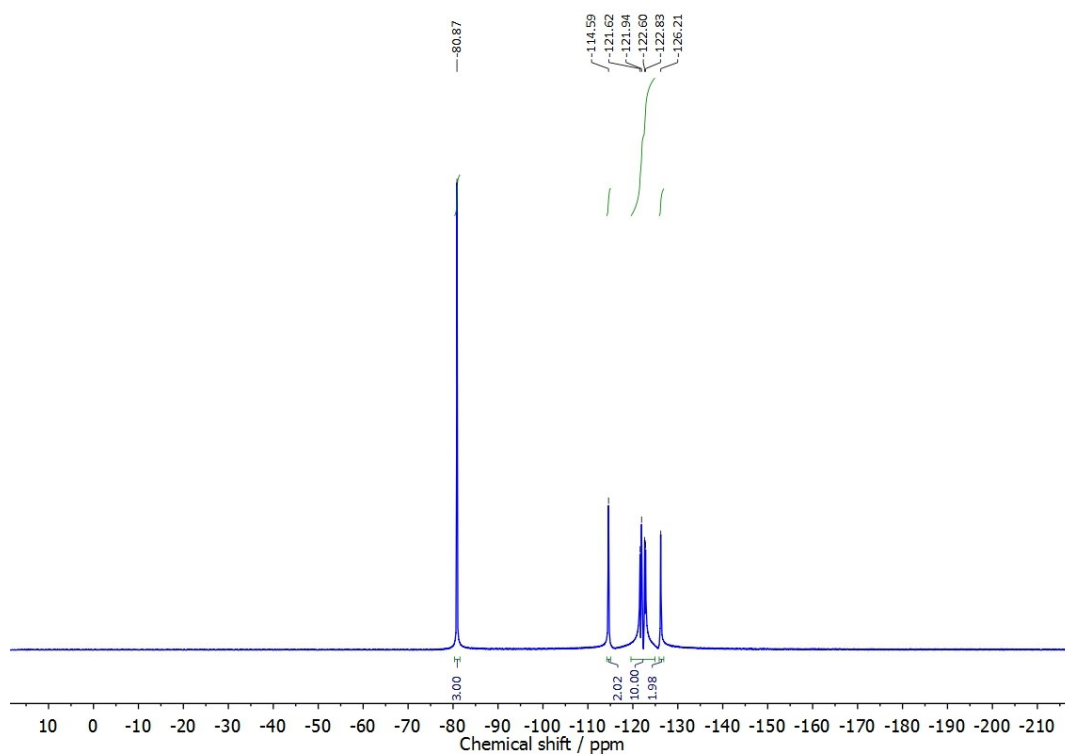


Figure S35. $^{19}\text{F}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phosphonium dicyanamide.

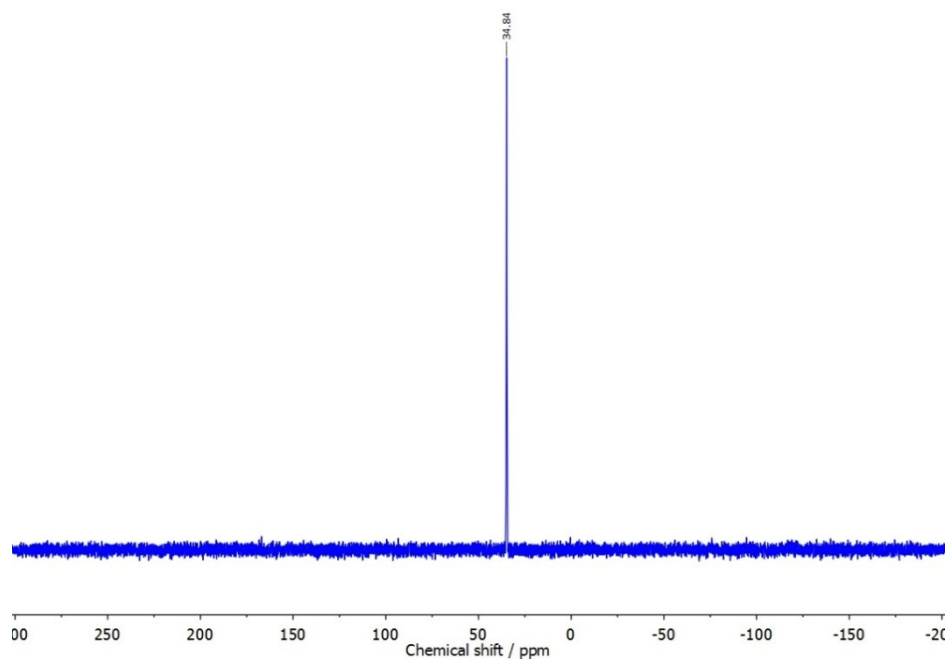


Figure S36. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phosphonium dicyanamide.

2.2.5 NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorododecyl)phosphonium dicyanamide F10

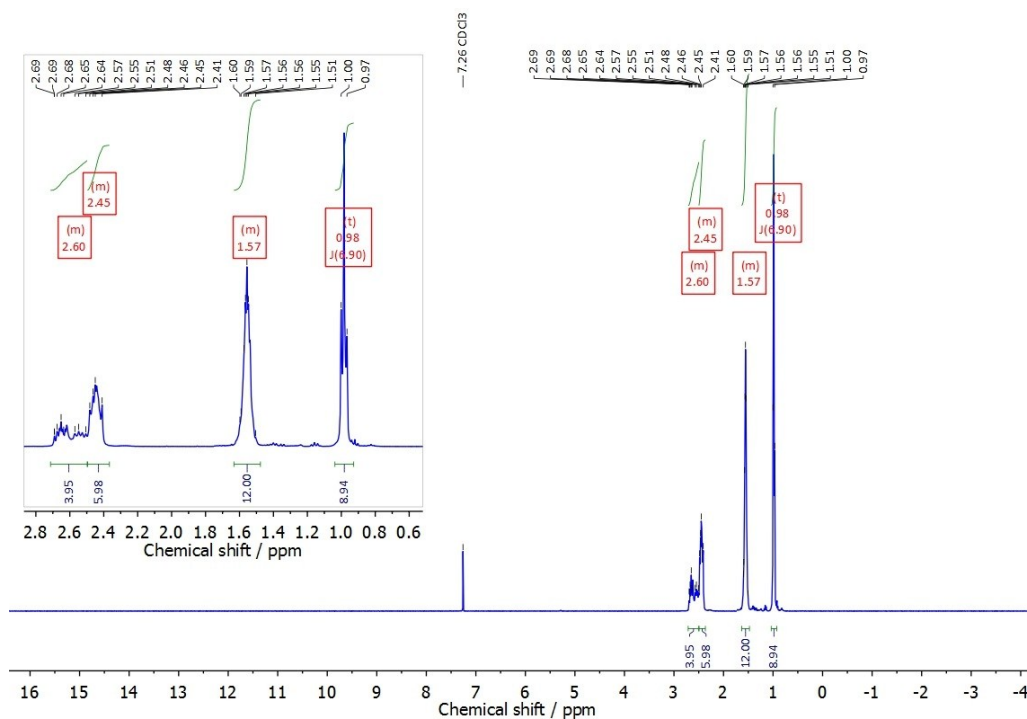


Figure S37. ^1H -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorododecyl)phosphonium dicyanamide.

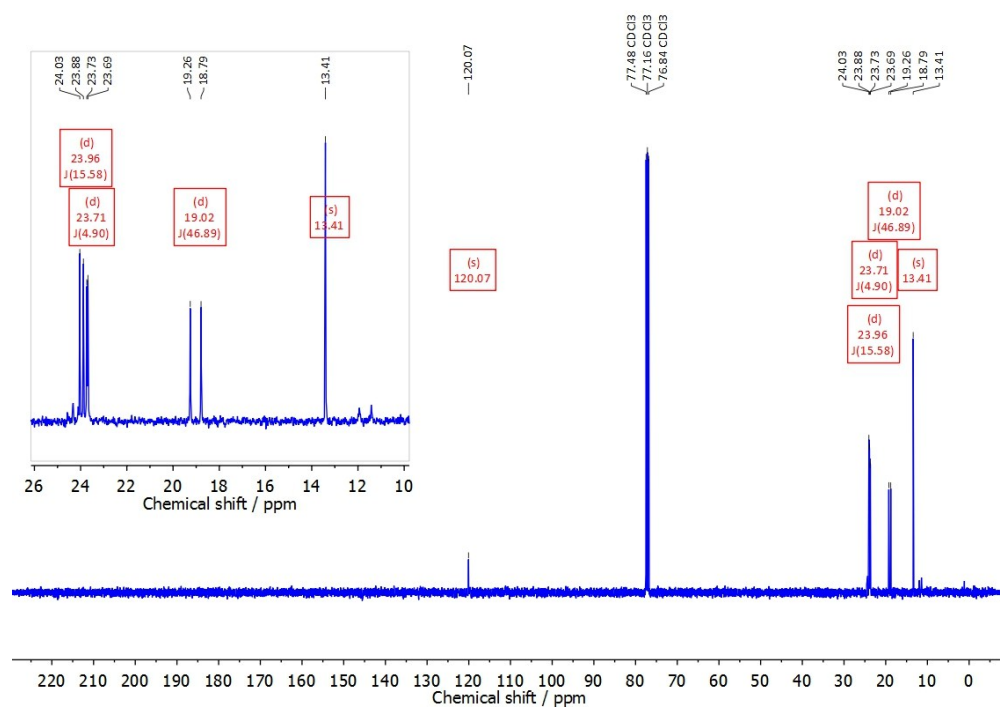


Figure S38. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorododecyl)phosphonium dicyanamide.

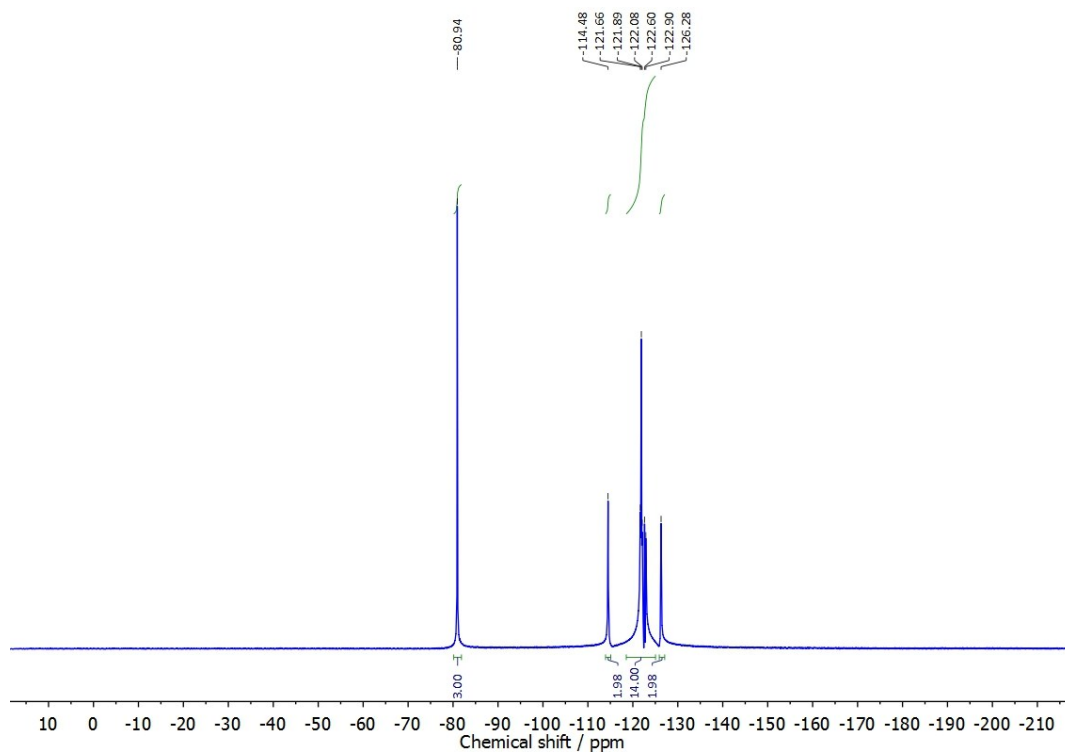


Figure S39. $^{19}\text{F}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorododecyl)phosphonium dicyanamide.

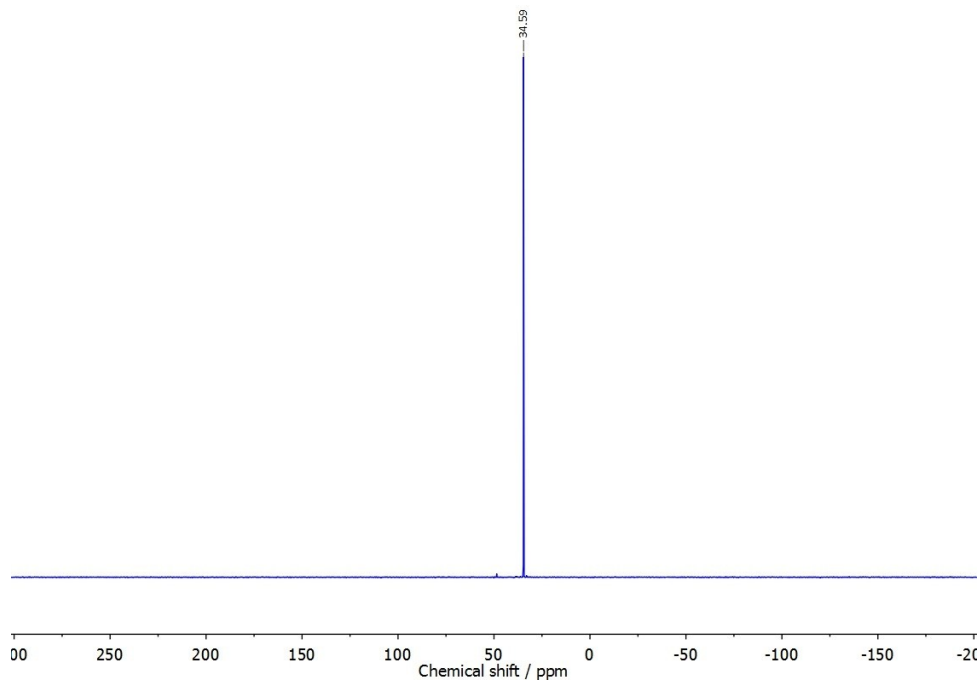


Figure S40. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributyl(1*H*,1*H*,2*H*,2*H*-perfluorododecyl)phosphonium dicyanamide.

2.3 NMR-spectra of the tributyl-alkyl-phosphonium bromide ionic liquids

2.3.1 NMR-spectra of tetrabutylphosphonium bromide

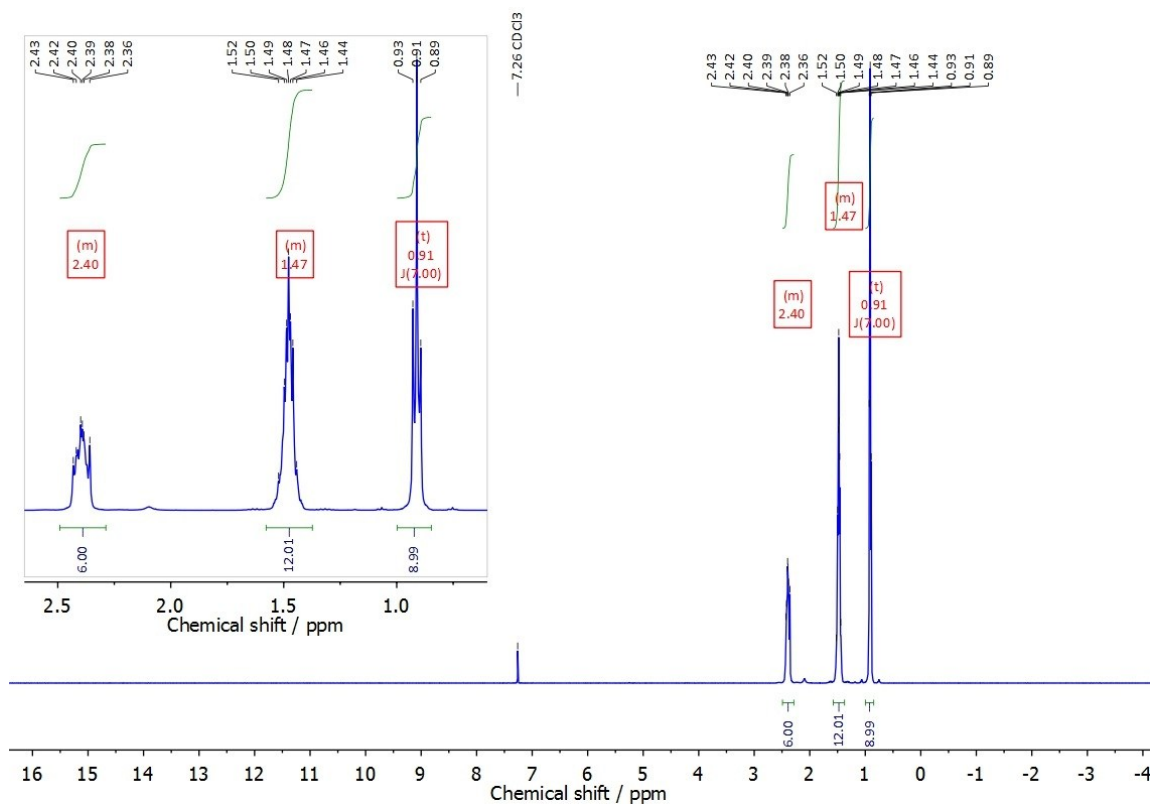


Figure S41. ^1H -NMR-spectra of tetrabutylphosphonium bromide.

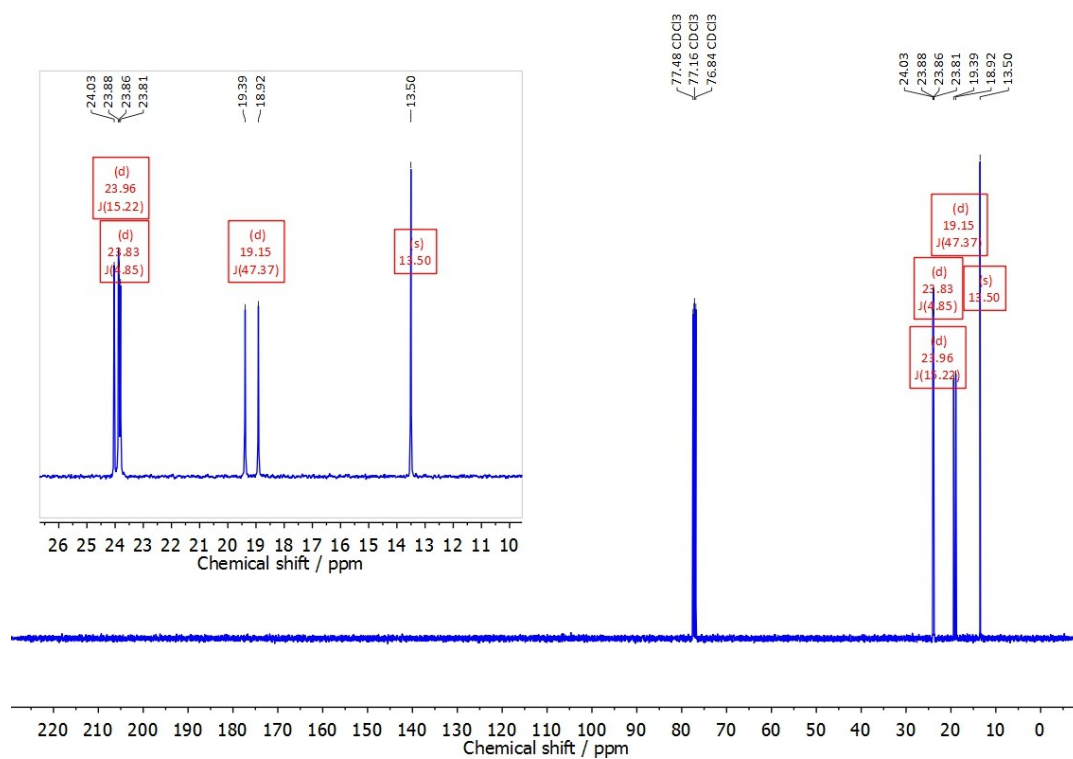


Figure S42. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tetrabutylphosphonium bromide.

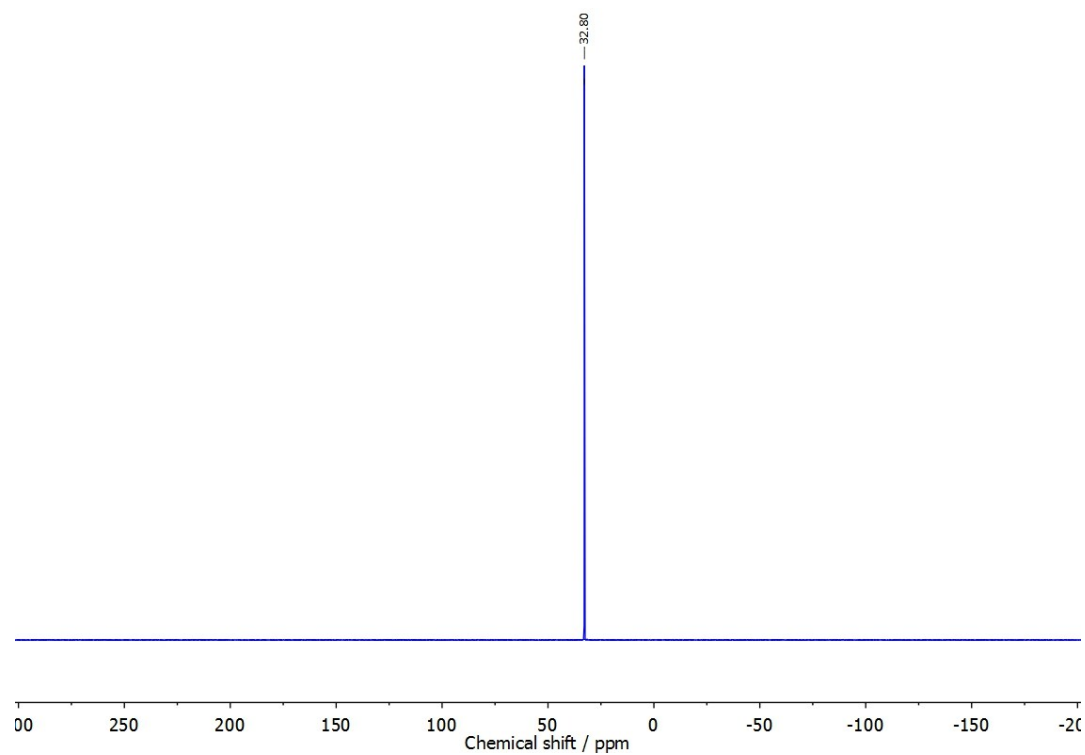


Figure S43. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tetrabutylphosphonium bromide.

2.3.2 NMR-spectra of tributylhexylphosphonium bromide

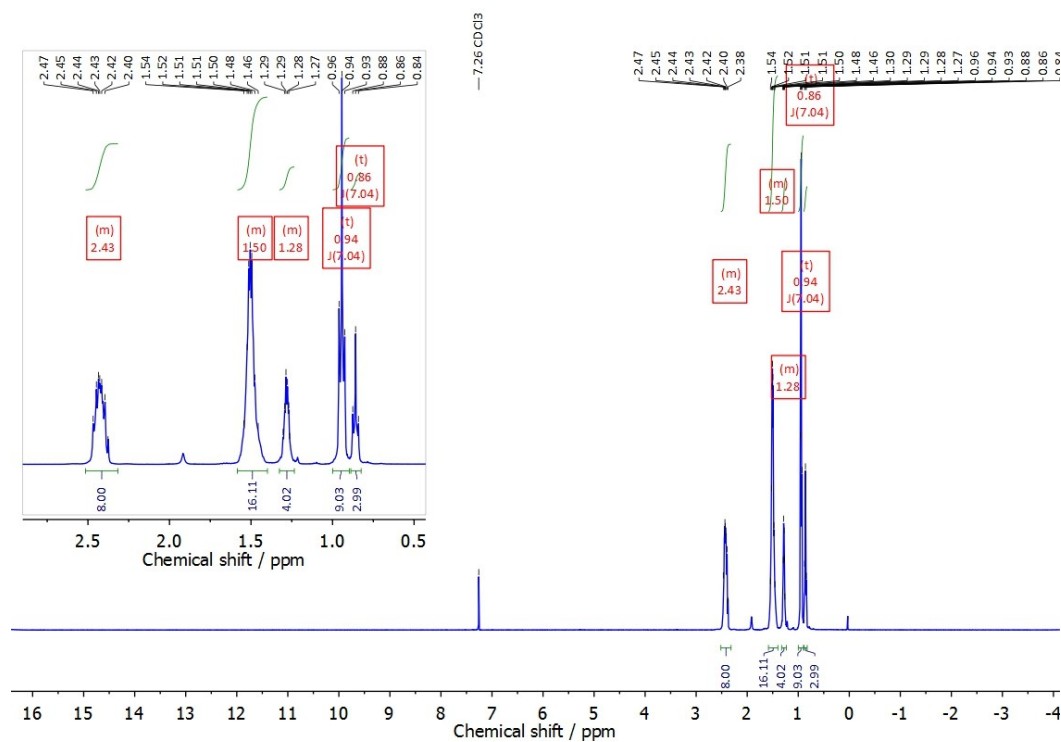


Figure S44. ^1H -NMR-spectra of tributylhexylphosphonium bromide.

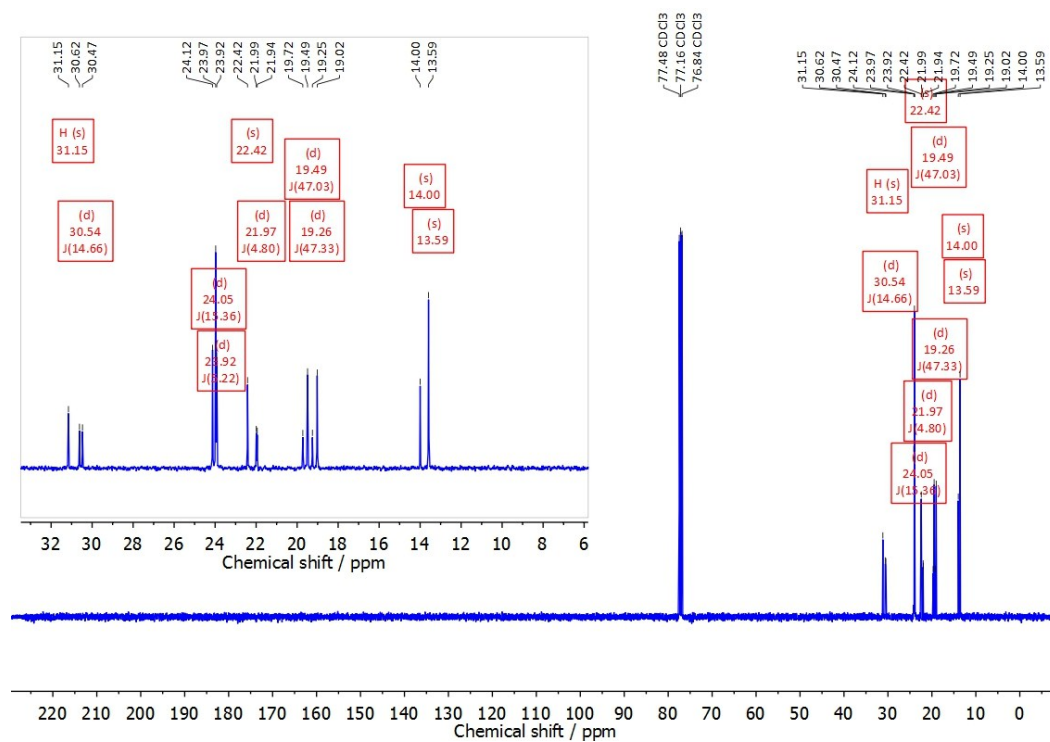


Figure S45. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributylhexylphosphonium bromide.

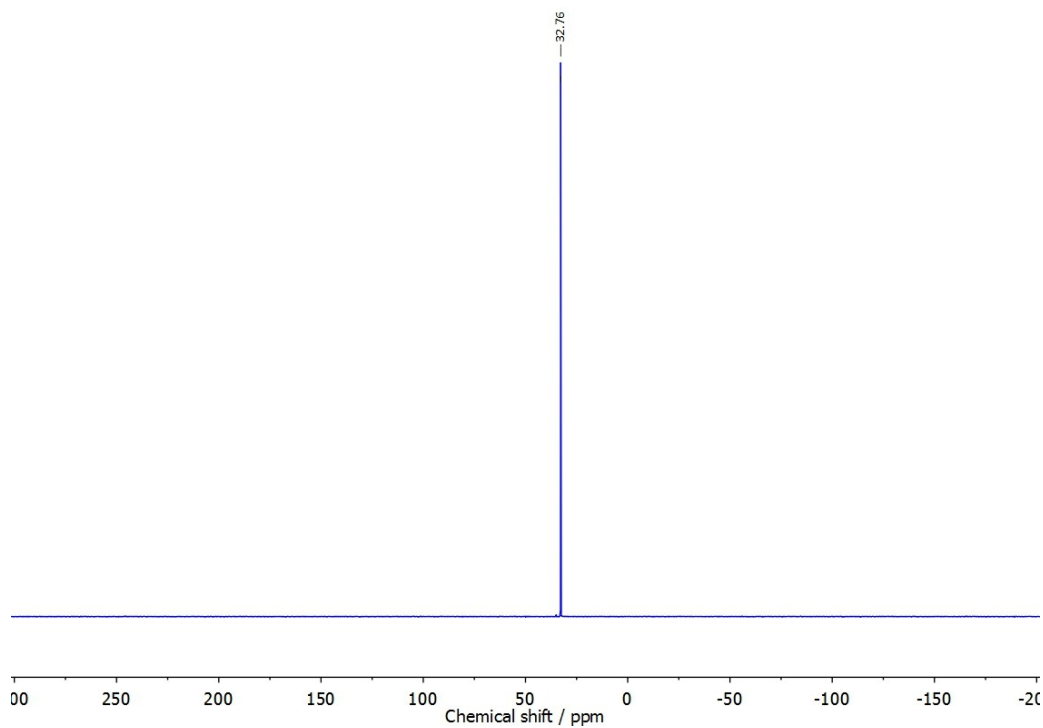


Figure S46. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributylhexylphosphonium bromide.

2.3.3 NMR-spectra of tributylhexylphosphonium bromide

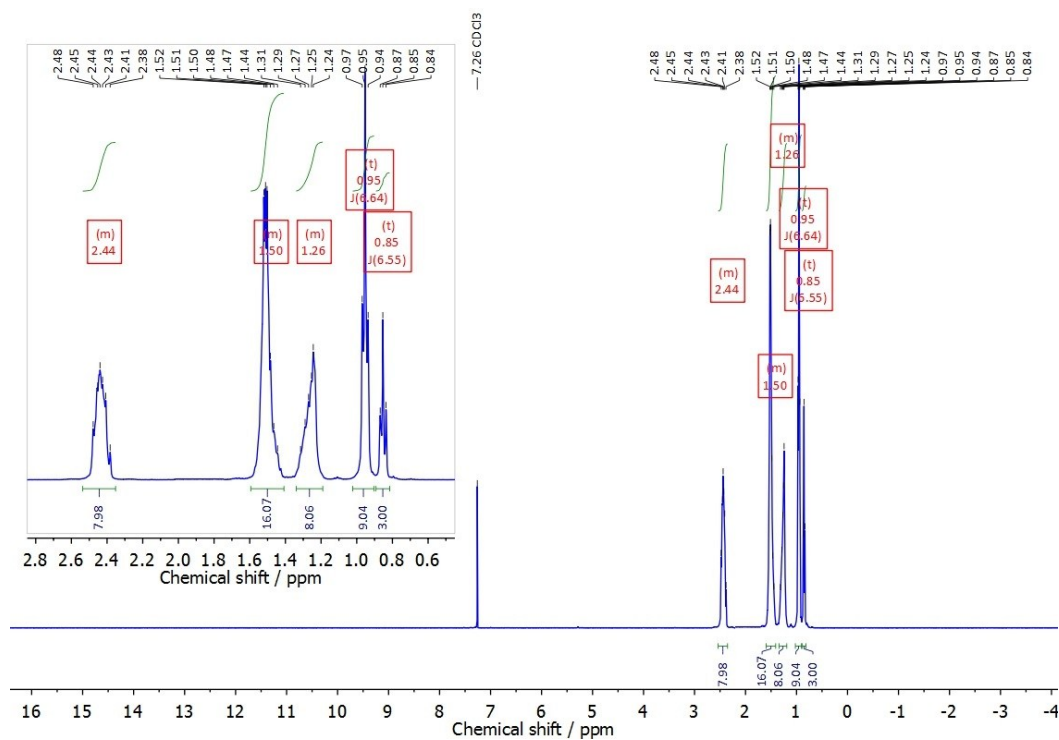


Figure S47. ^1H -NMR-spectra of tributylhexylphosphonium bromide.

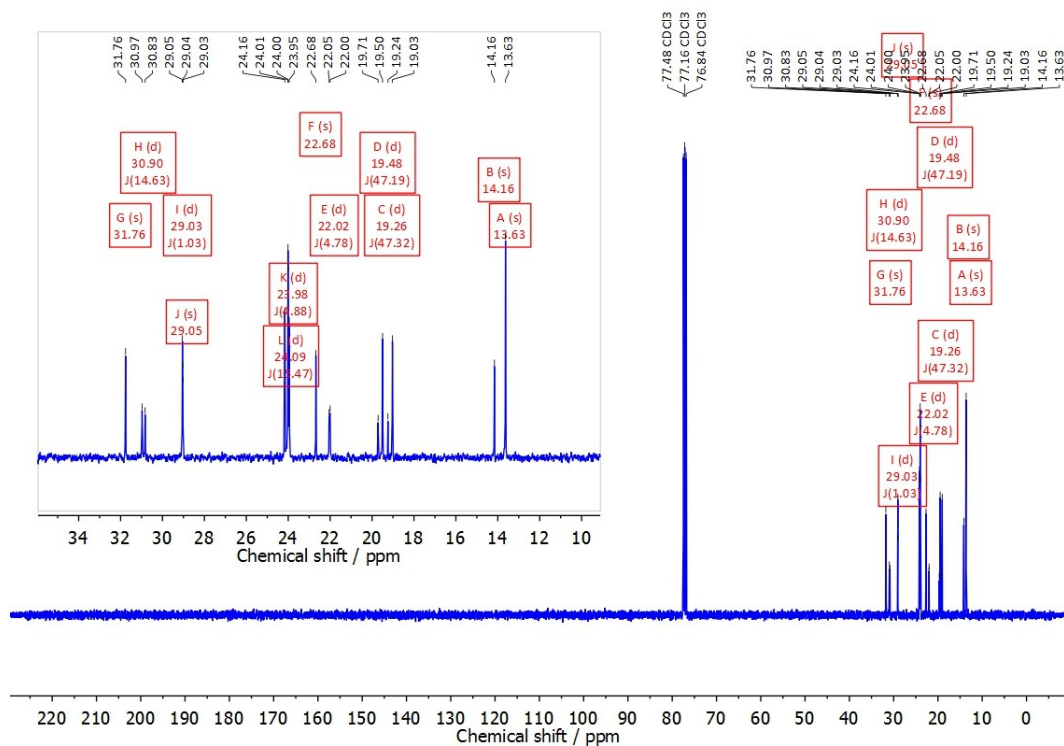


Figure S48. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributylmethylphosphonium bromide.

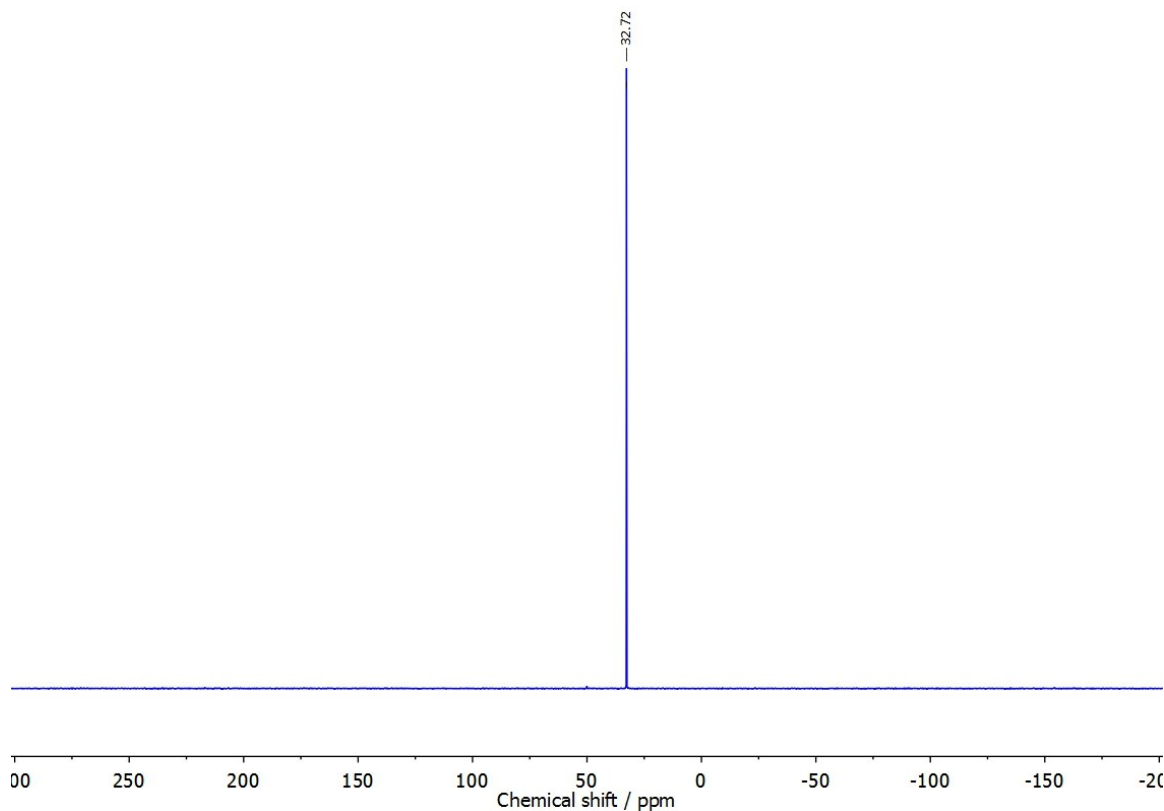


Figure S49. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributylmethylphosphonium bromide.

2.3.4 NMR-spectra of tributyldecylphosphonium bromide

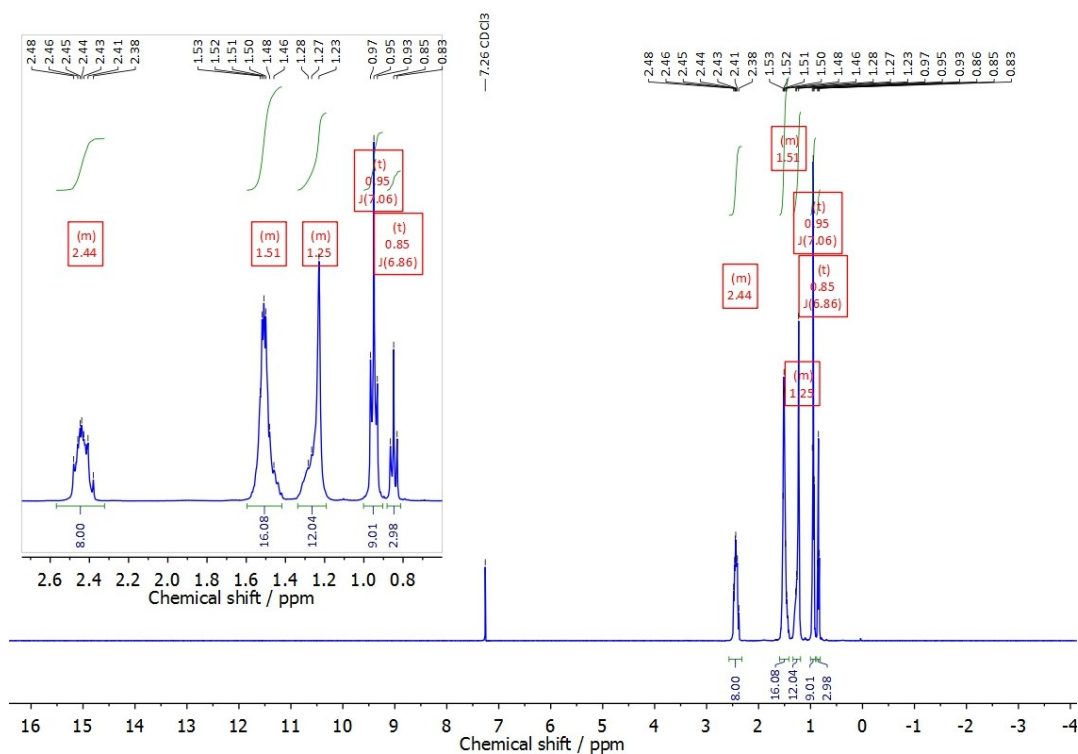


Figure S50. ^1H -NMR-spectra of tributyldecylphosphonium bromide.

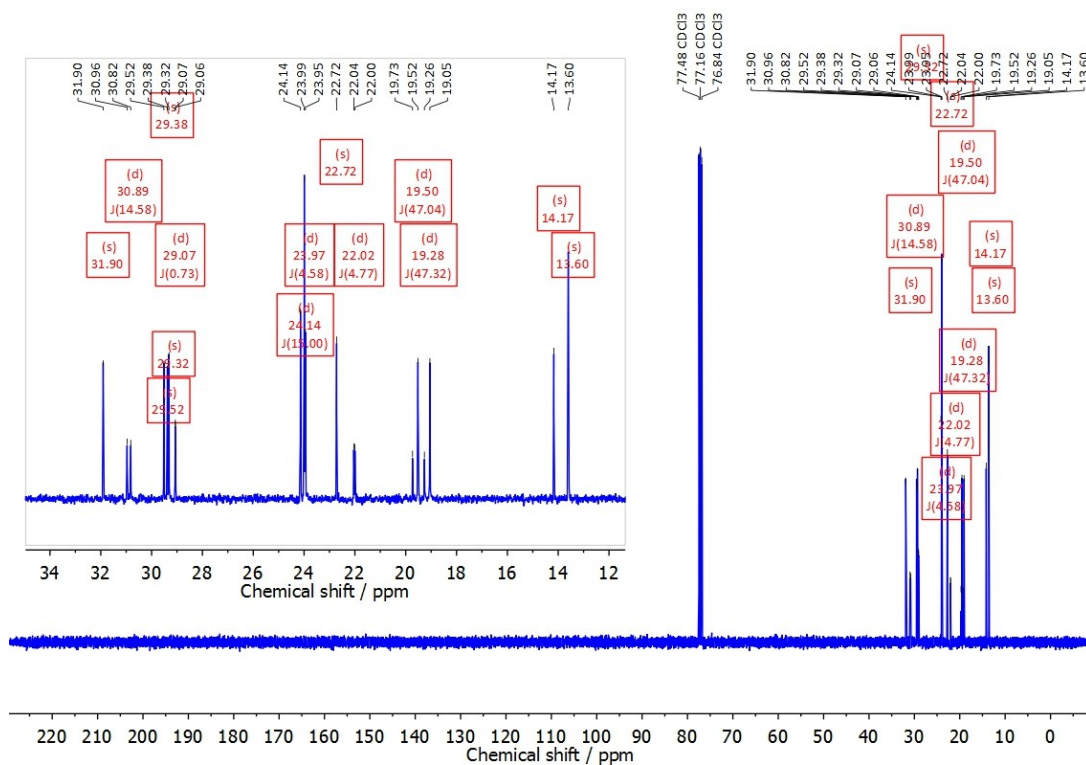


Figure S51. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributyldecylphosphonium bromide.

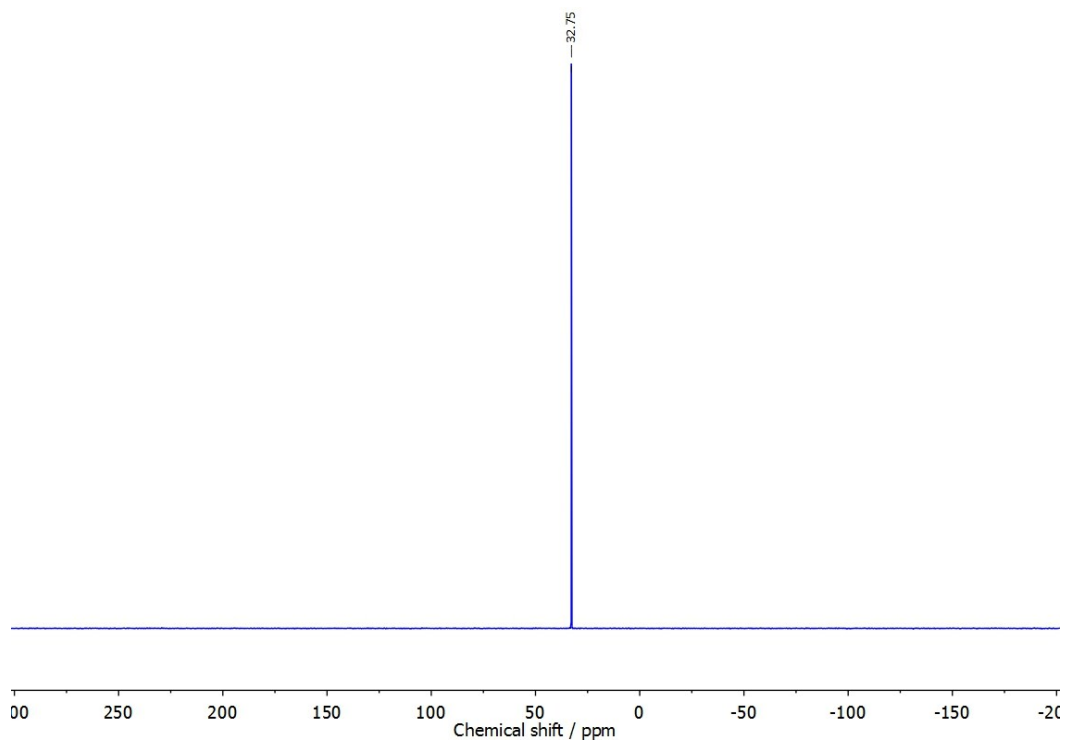


Figure S52. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributyldecylphosphonium bromide.

2.3.5 NMR-spectra of tributyldecylphosphonium bromide

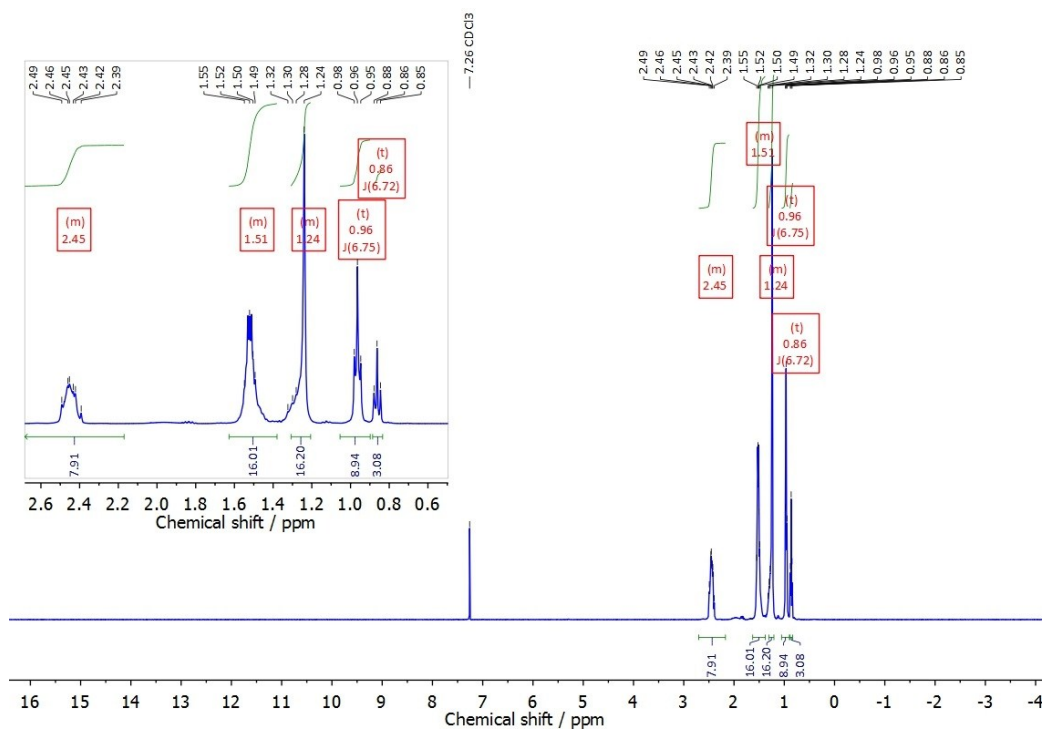


Figure S53. ^1H -NMR-spectra of tributyldecylphosphonium bromide.

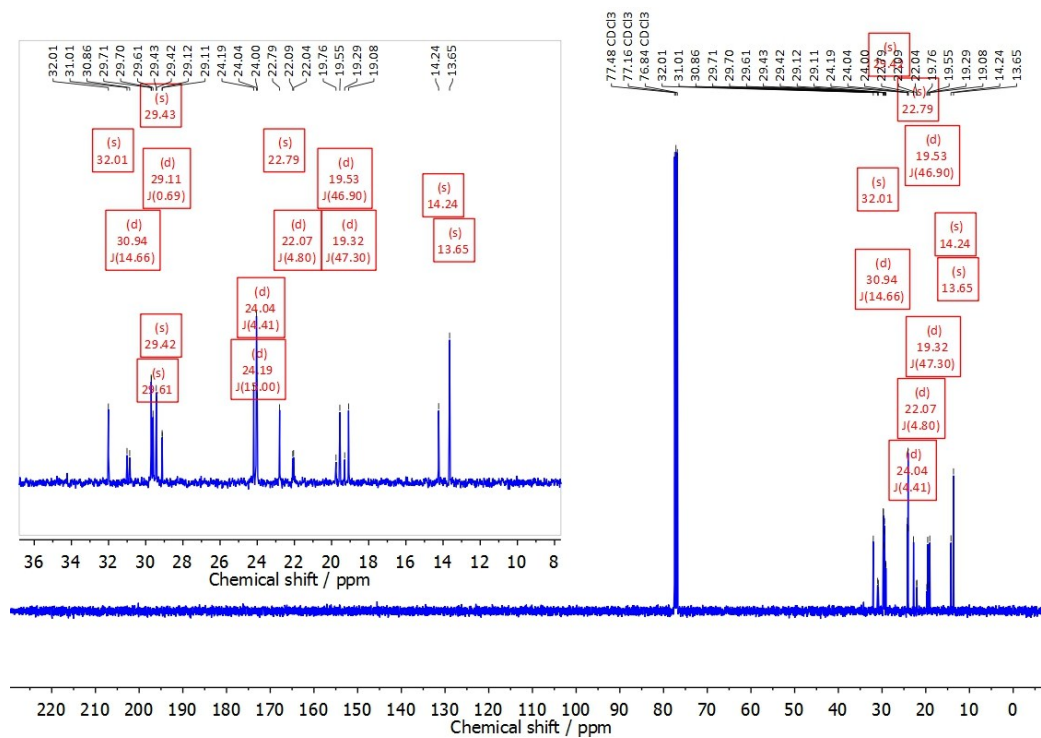


Figure S54. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributyldecylphosphonium bromide.

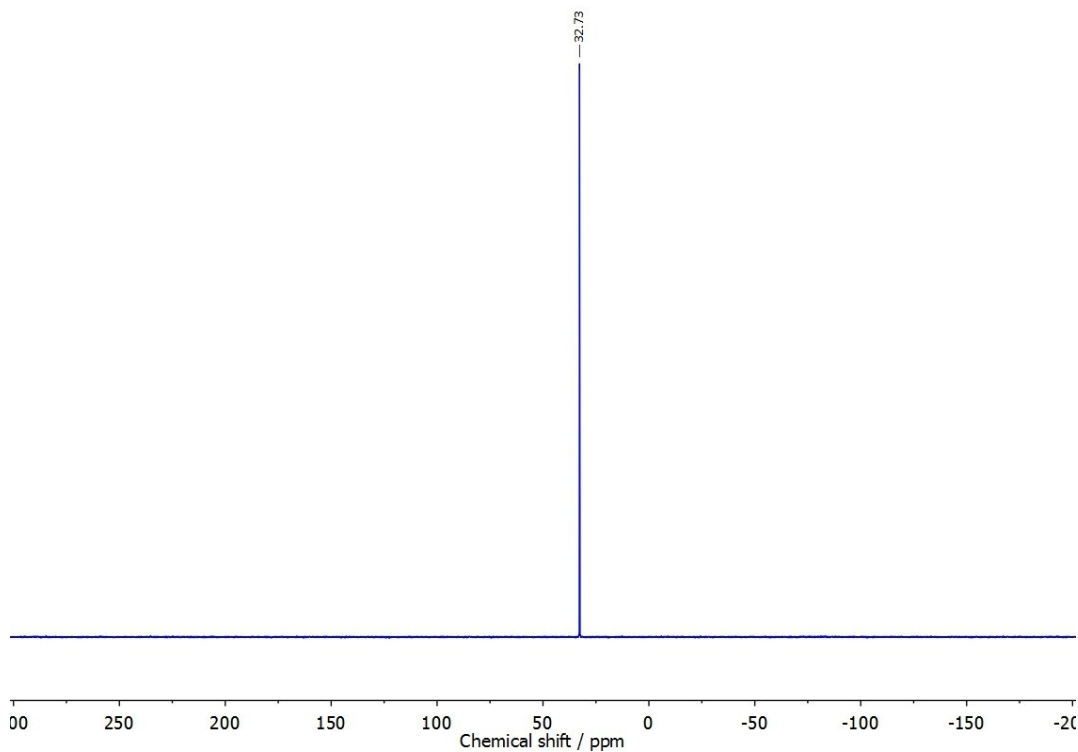


Figure S55. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributyldecylphosphonium bromide.

2.4 NMR-spectra of the tributyl-alkyl-phosphonium dicyanamide ionic liquids

2.4.1 NMR-spectra of tetrabutylphosphonium dicyanamide C4

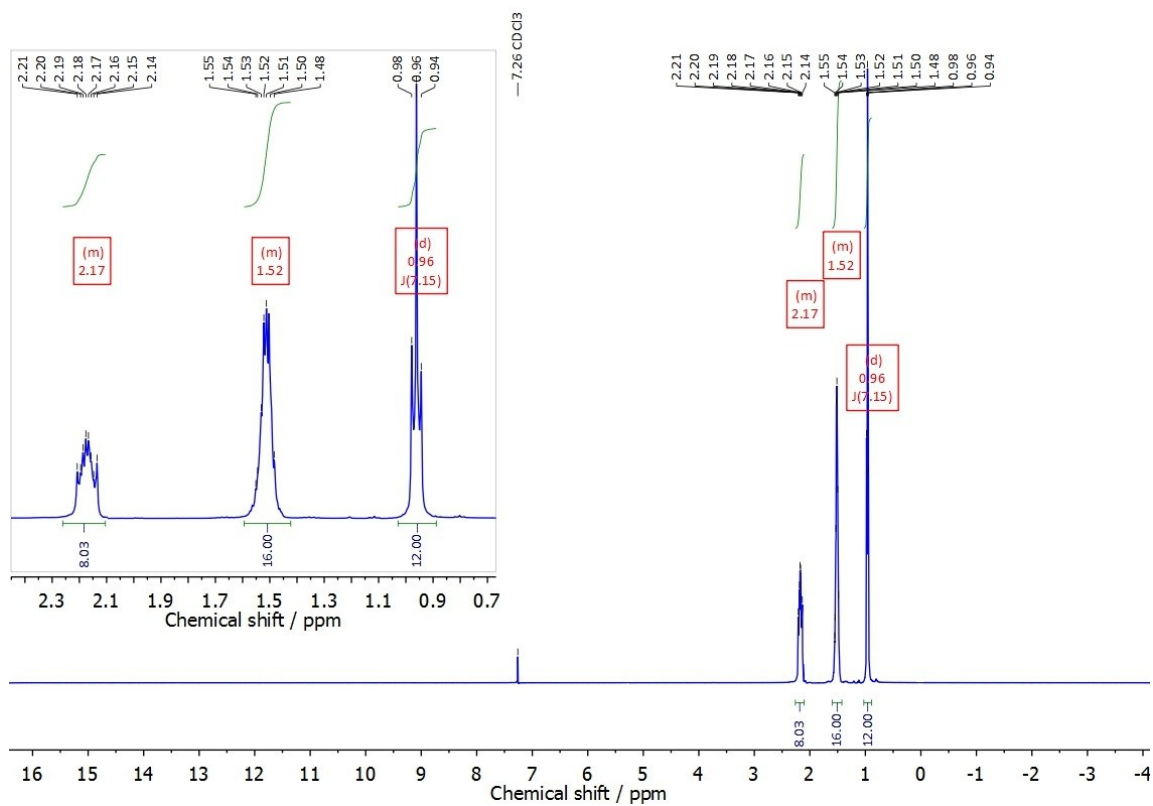


Figure S56. ^1H -NMR-spectra of tetrabutylphosphonium dicyanamide.

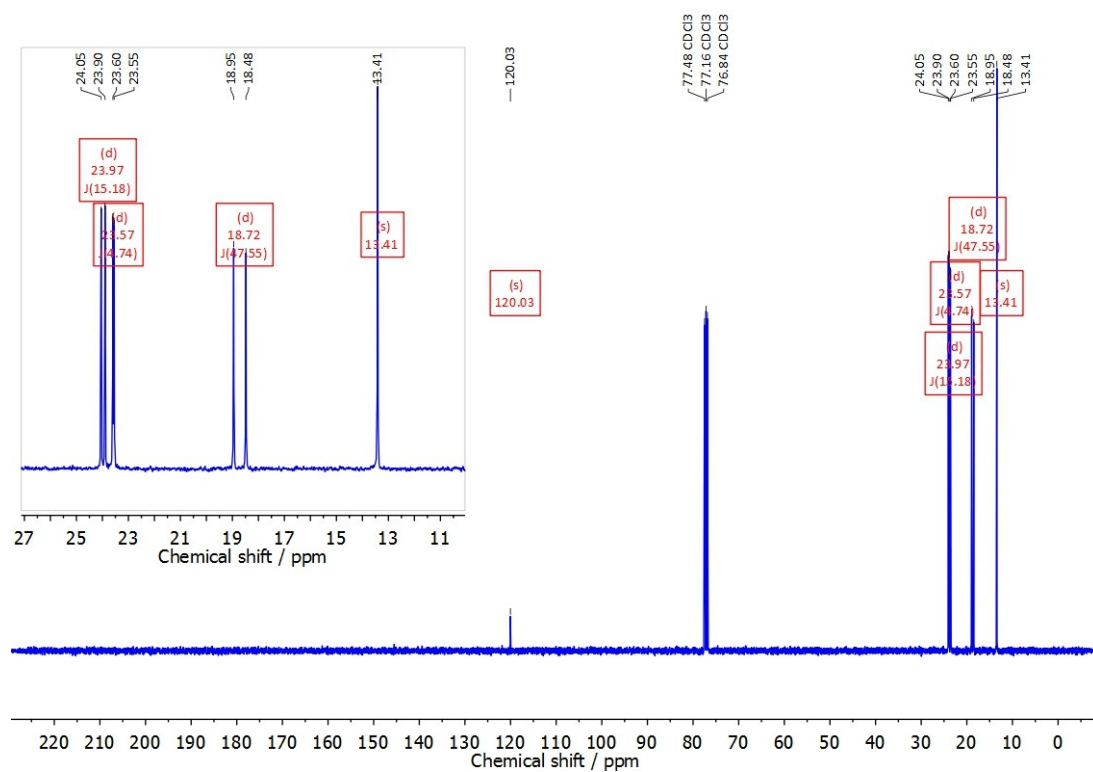


Figure S57. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tetrabutylphosphonium dicyanamide.

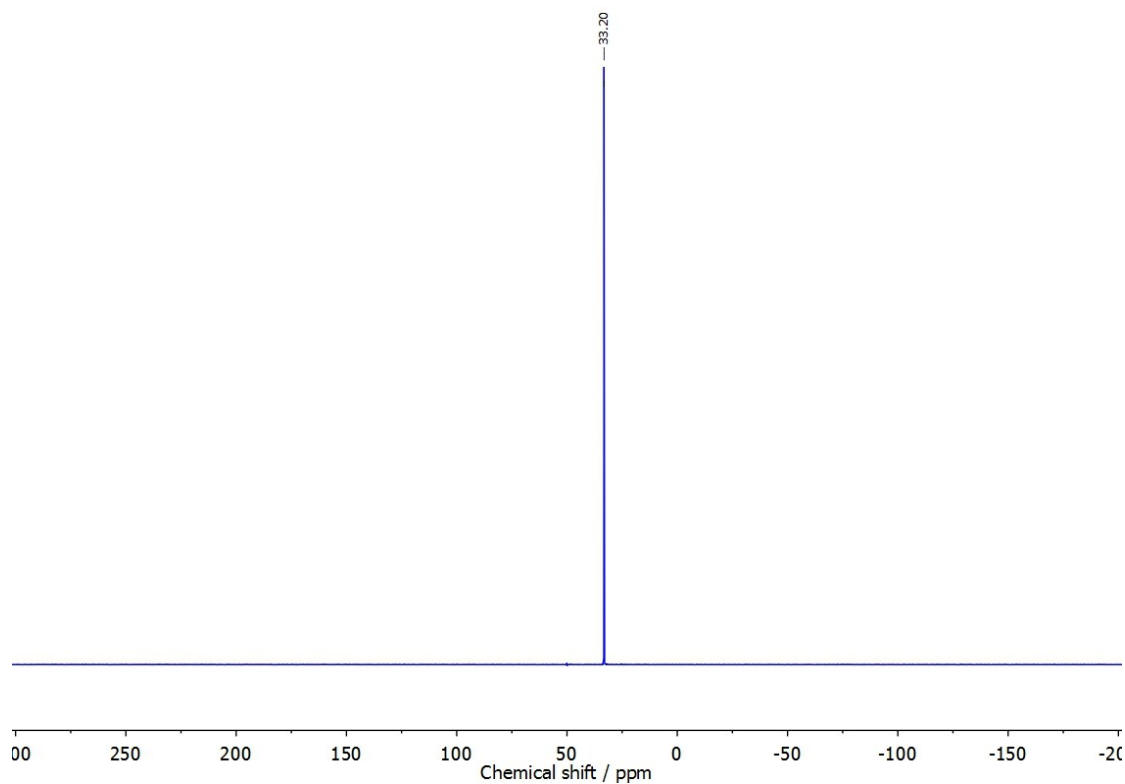


Figure S58. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tetrabutylphosphonium dicyanamide.

2.4.2 NMR-spectra of tributylhexylphosphonium dicyanamide C6

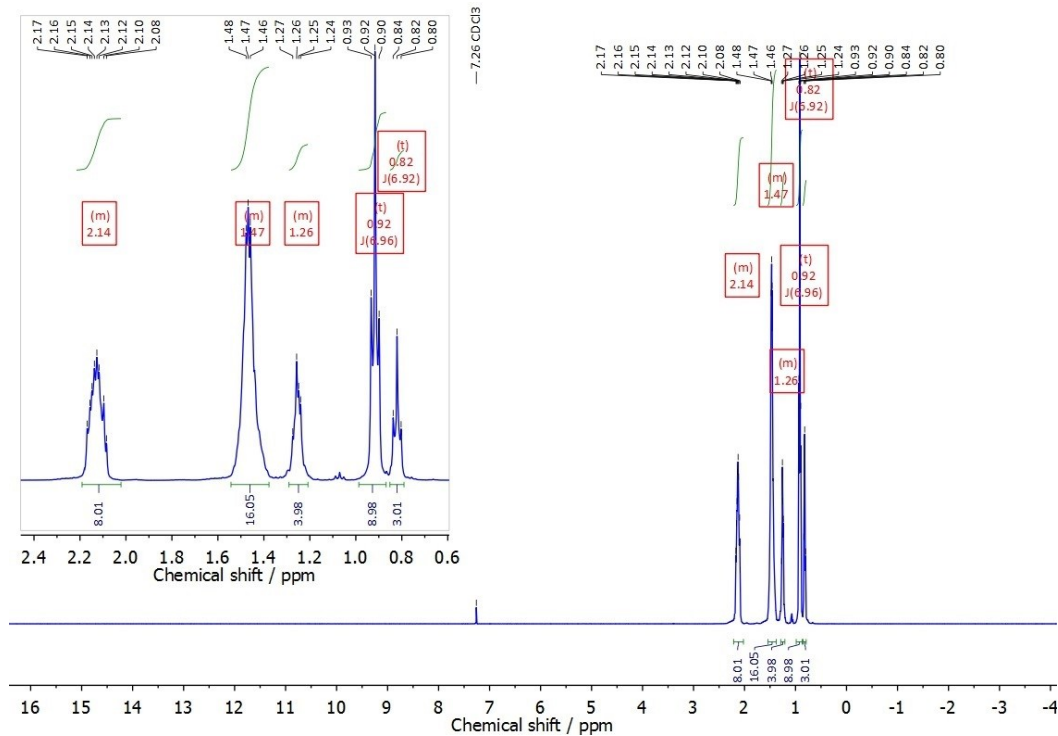


Figure S59. ^1H -NMR-spectra of tributylhexylphosphonium dicyanamide.

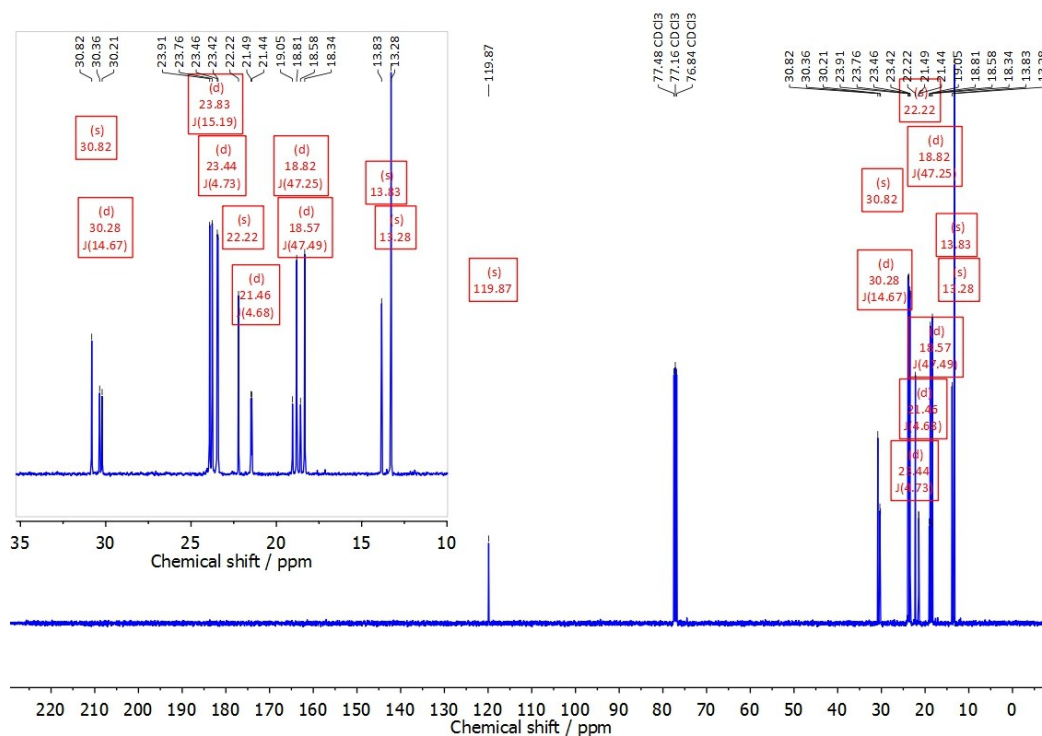


Figure S60. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributylhexylphosphonium dicyanamide.

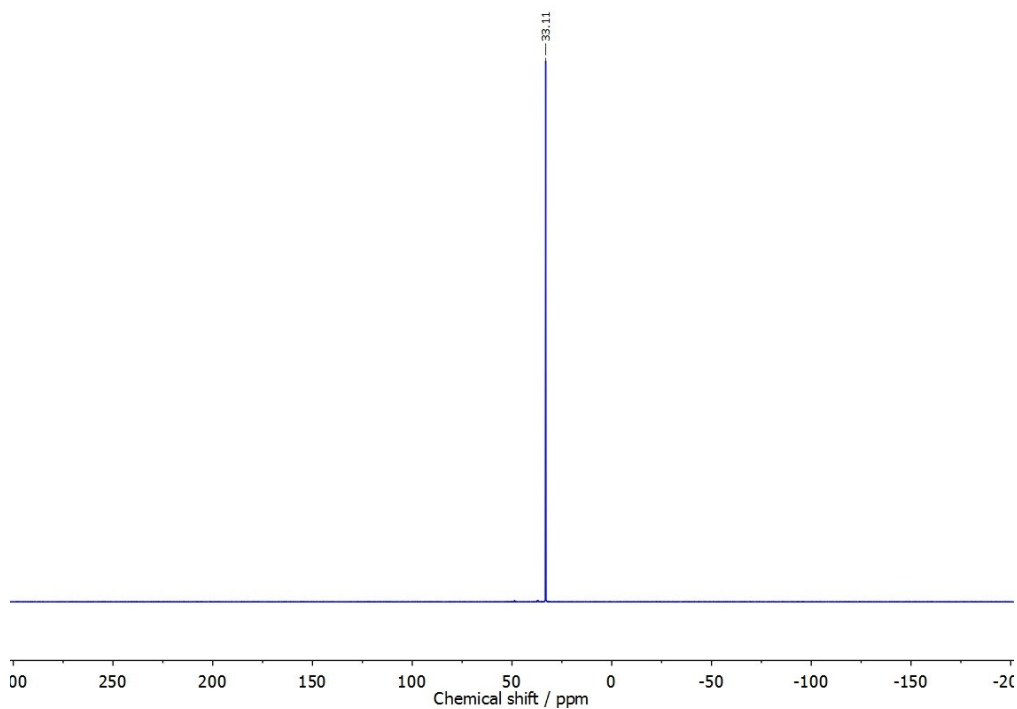


Figure S61. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributylhexylphosphonium dicyanamide.

2.4.3 NMR-spectra of tributyloctylphosphonium dicyanamide C8

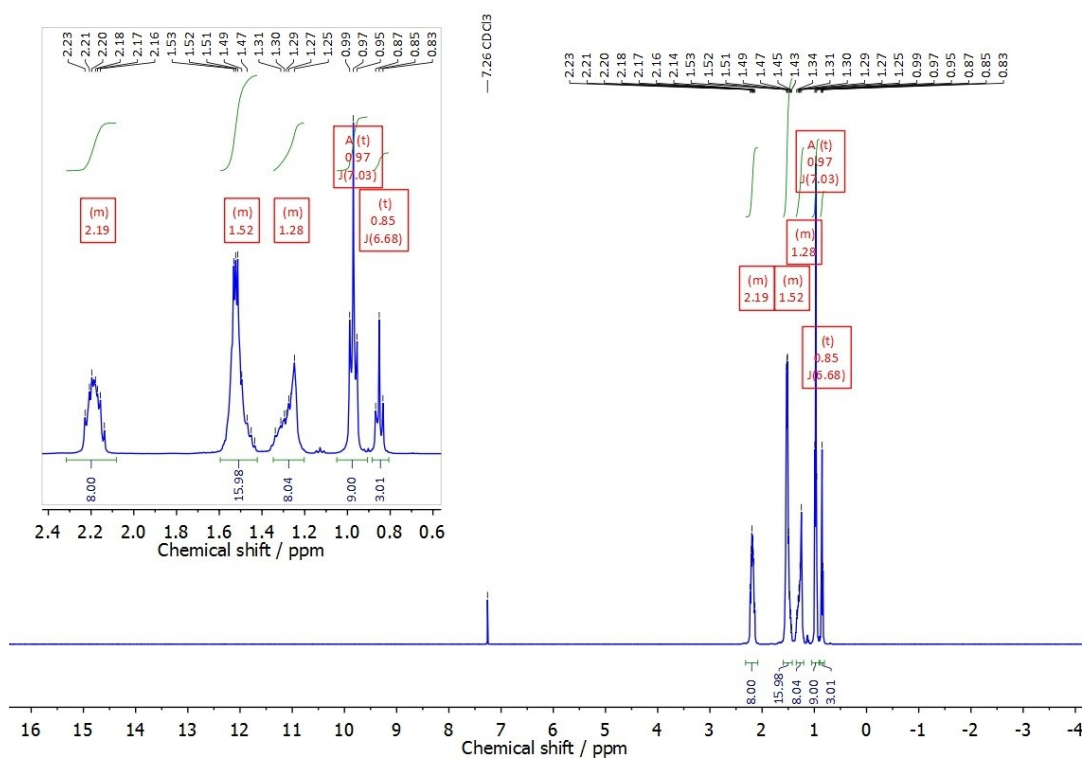


Figure S62. ^1H -NMR-spectra of tributyloctylphosphonium dicyanamide.

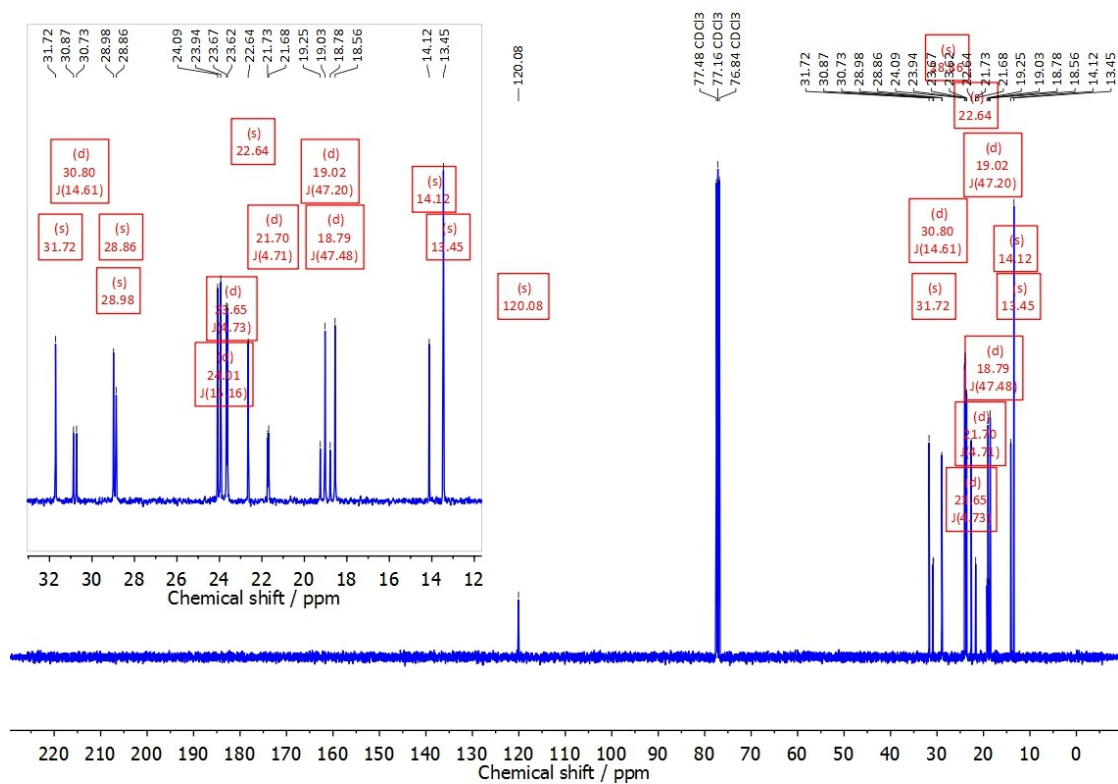


Figure S63. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributyl-octylphosphonium dicyanamide.

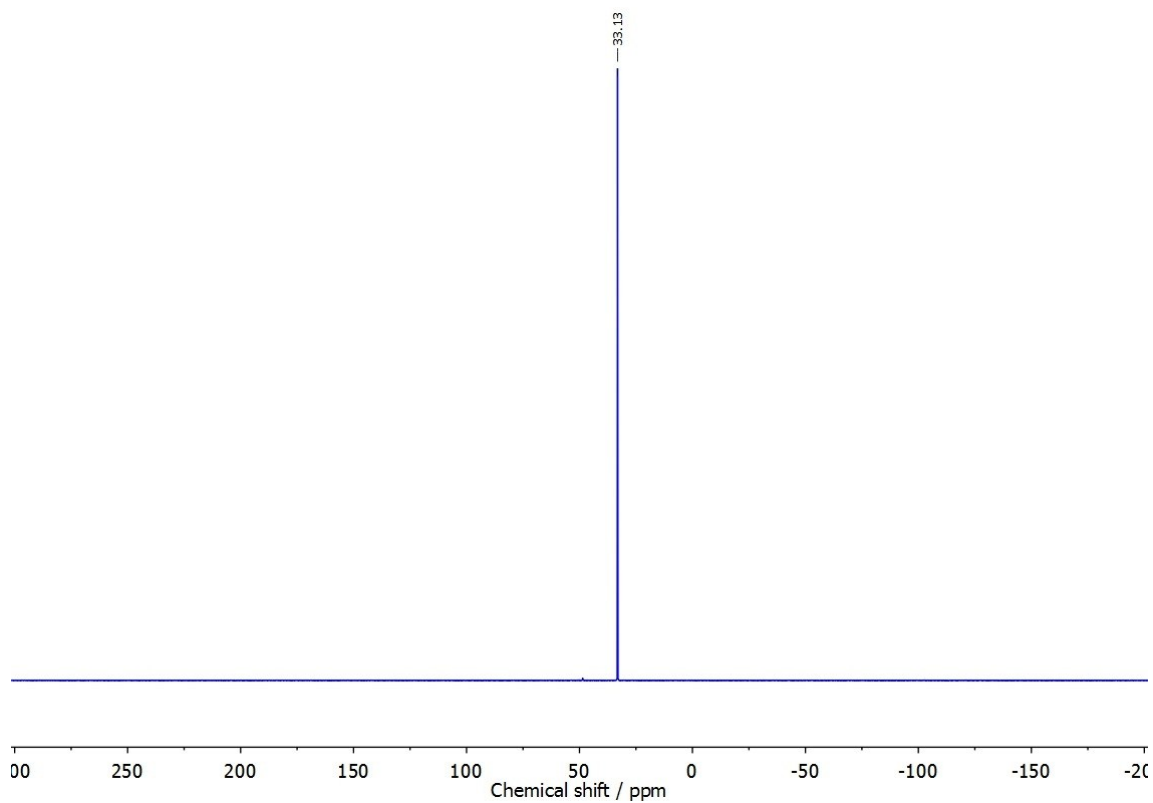


Figure S64. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributyl-octylphosphonium dicyanamide.

2.4.4 NMR-spectra of tributyldecylphosphonium dicyanamide C10

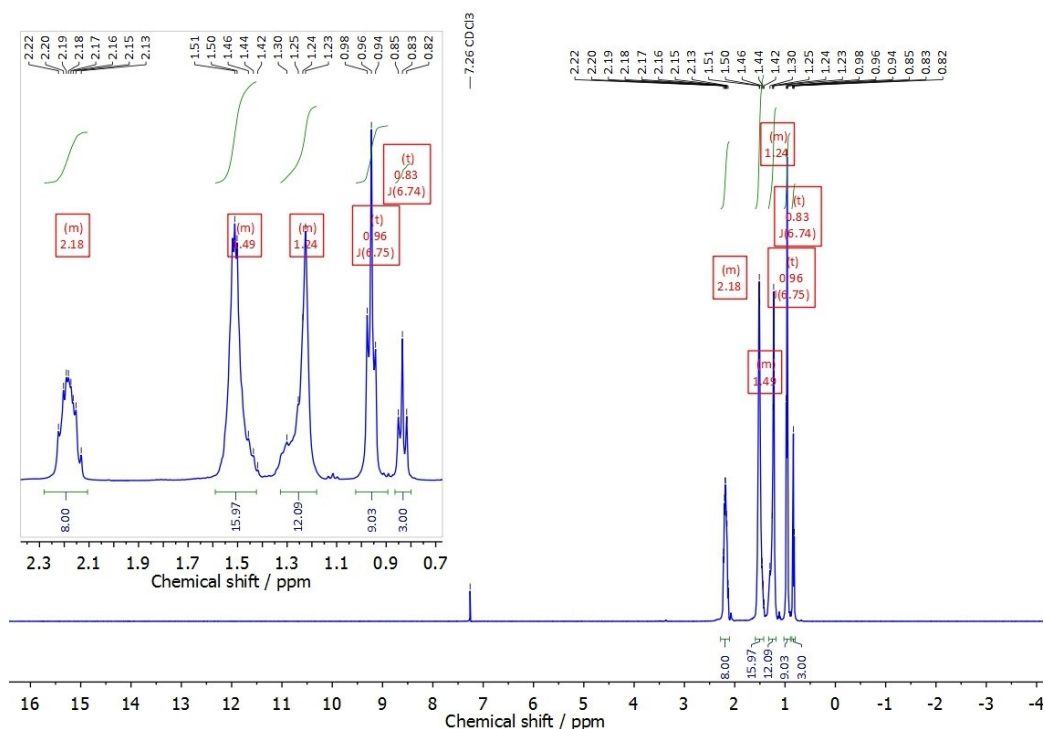


Figure S65. ^1H -NMR-spectra of tributyldecylphosphonium dicyanamide.

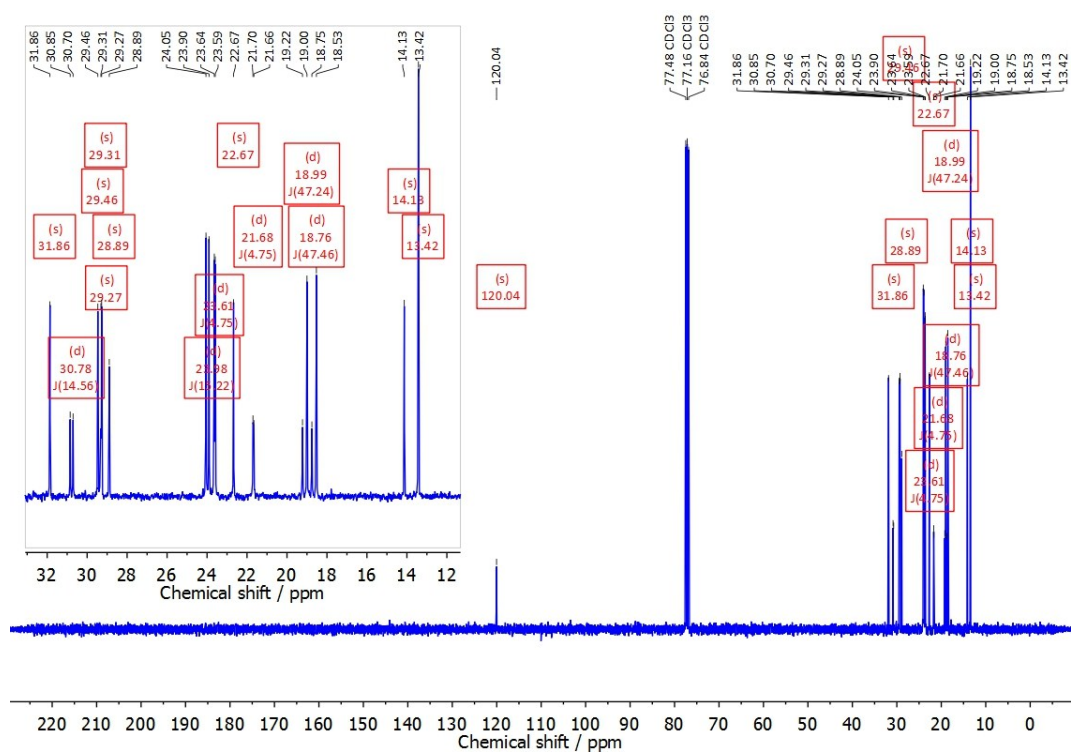


Figure S66. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributyldecylphosphonium dicyanamide.

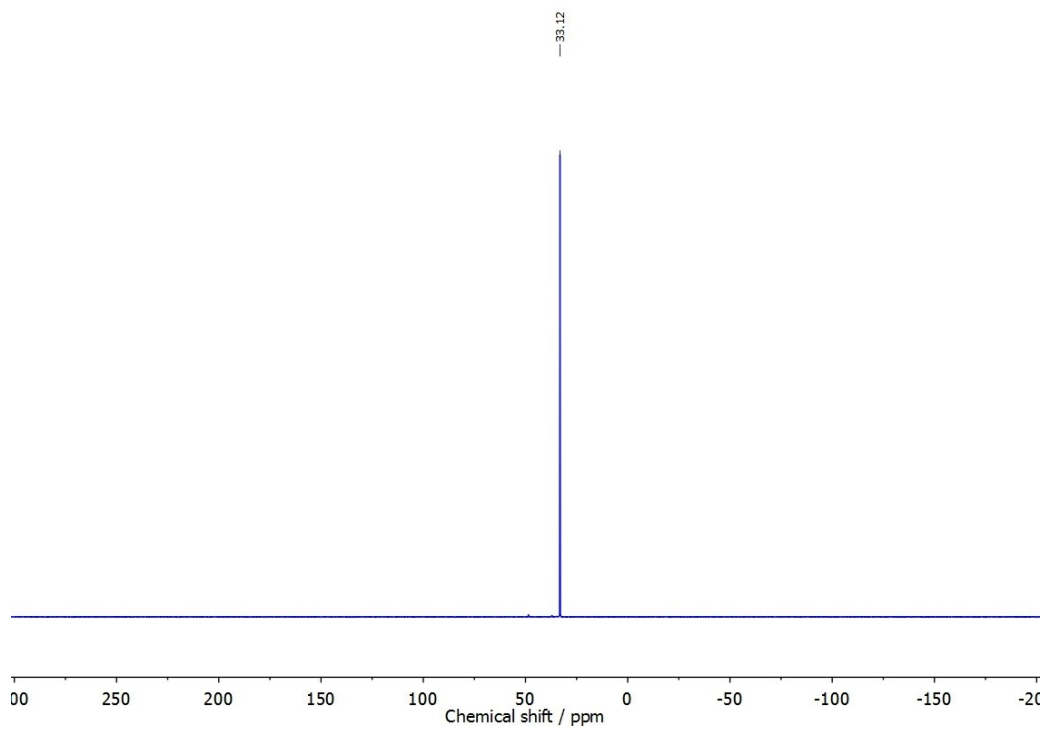


Figure S67. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributyldecylphosphonium dicyanamide.

2.4.5 NMR-spectra of tributyldecylphosphonium dicyanamide C12

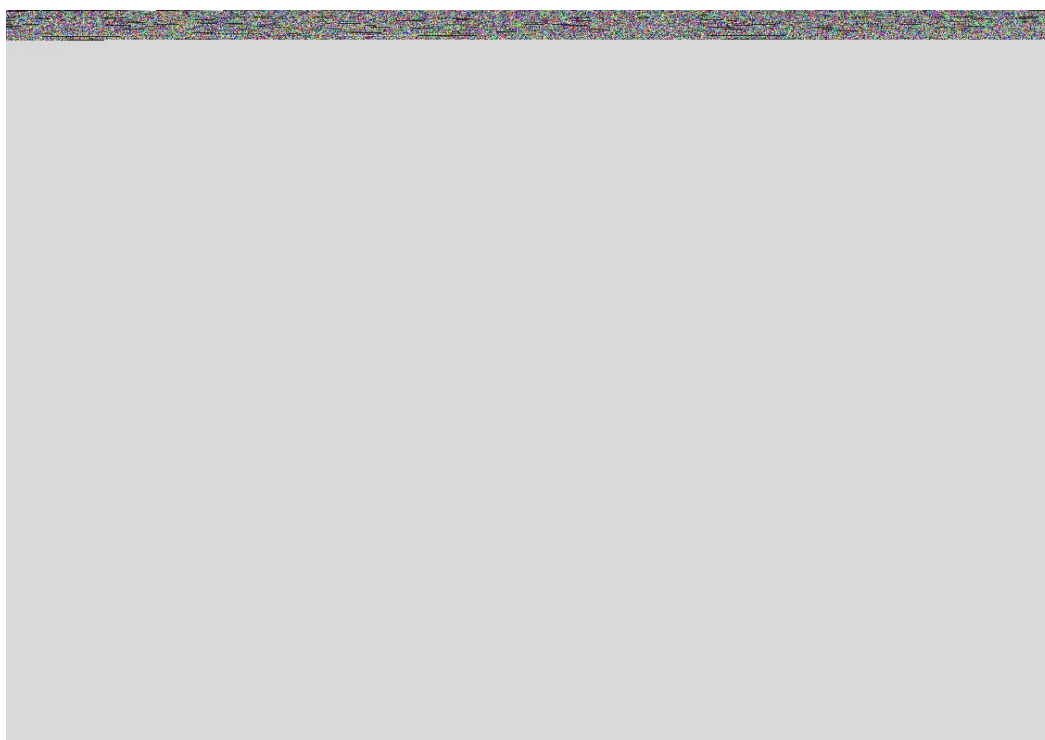


Figure S68. ^1H -NMR-spectra of tributyldecylphosphonium dicyanamide.

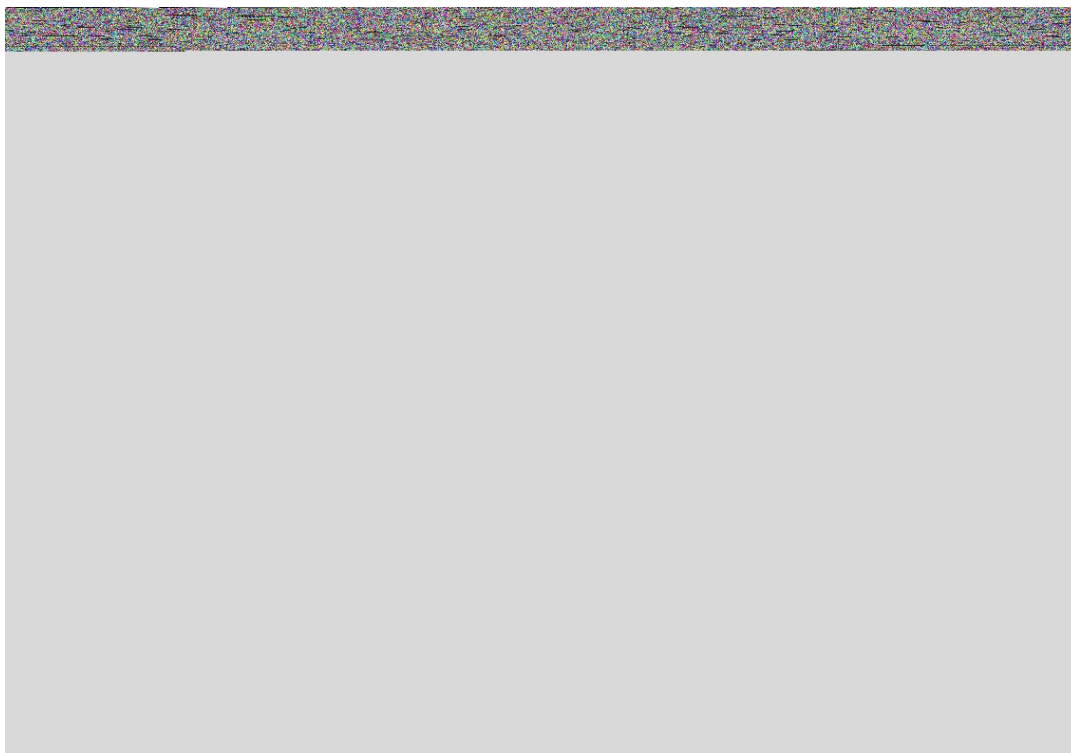


Figure S69. $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra of tributyldecylphosphonium dicyanamide.



Figure S70. $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of tributyldecylphosphonium dicyanamide.

3. Molecular Interactions in Ionic Liquids

We excluded the existence of hydrogen bonding of the type C-H...F-C in our ILs by comparing the van der Waals radii of hydrogen (d_H) and fluorine (d_F) with the minimum distance (D_{HF}) of hydrogen and fluorine in the F8 single crystal. Figure S71 shows the distance between hydrogen and fluorine and C-H...F angles in F8 single crystal. There is general agreement that $d_H + d_F > D_{HF}$ is necessary for the formation of hydrogen bonds.¹ In Figure S71, $d_H + d_F = 2.67 \text{ \AA}$, below the minimum value of D_{HF} ($2.93 \text{ \AA}$) in the F8 single crystal. An additional structural aspect that speaks against hydrogen bonds is the angle of C-H...F that is 121° here, below the ideal angle (180°) of hydrogen bonding. Therefore we conclude that our ILs do not exhibit C-H...F-C hydrogen bonding.

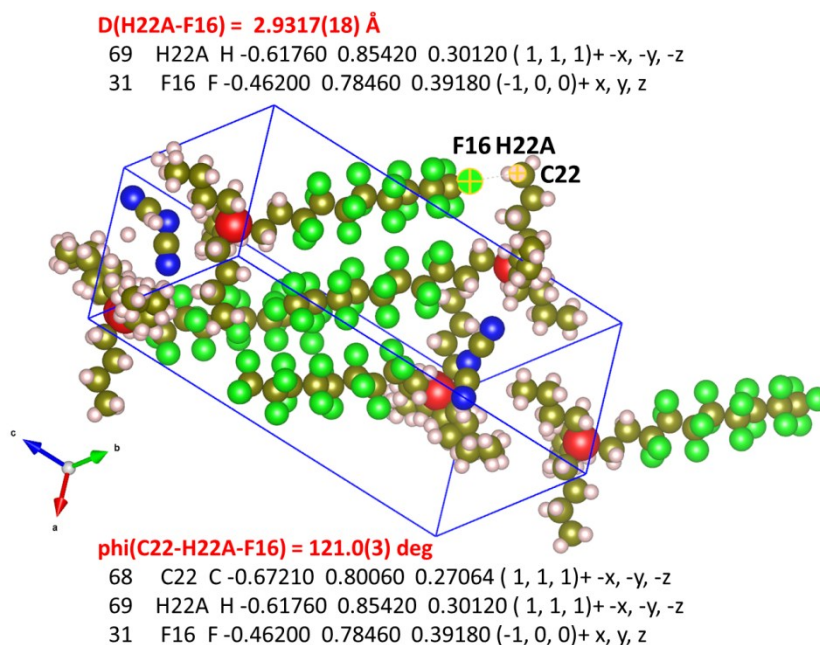


Figure S71. Illustration of the distances and angles among carbon, hydrogen, and fluorine atoms in the F8 single crystal. C22-H22A...F16 is taken as an example to show the minimum value of H...F distance and C-H...F angle.

4. Thermogravimetric Analysis

TGA curves of the fluorinated DCA-ILs and the corresponding alkylated IL are given in figure S71 and figure S72. The fluorinated ILs showed overall decomposition temperatures that are about 150°C lower than the comparable non-fluorinated. Furthermore the residual weight for the fluorinated ILs is with values of about 30% much higher than for the alkyl-ILs were the values are around 15% of the initial weight. This indicated a different decomposition mechanism for the perfluoroalkyl substituted ILs which

may result from the higher charge localization at the phosphonium core which is a result of the strong electron withdrawing effect of the fluorine-atoms.

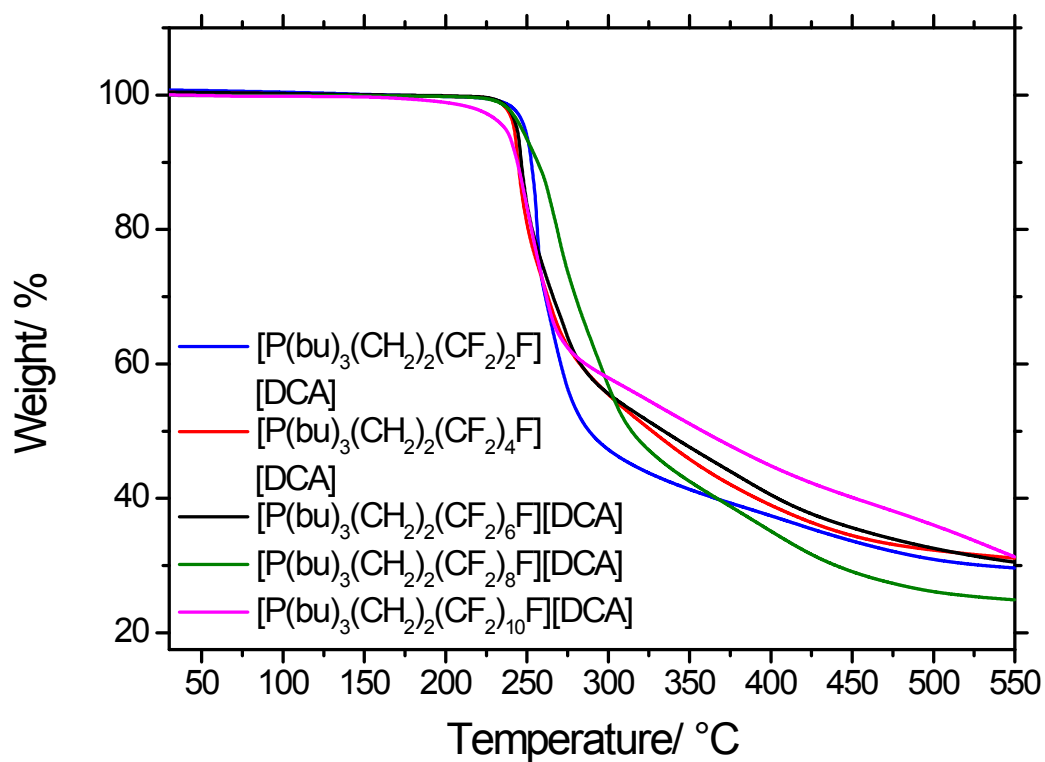


Figure S72. Thermogravimetric analysis for the fluorinated tributylphosphonium ILs [P(bu)₃(CH₂)₂(CF₂)_xF][DCA].

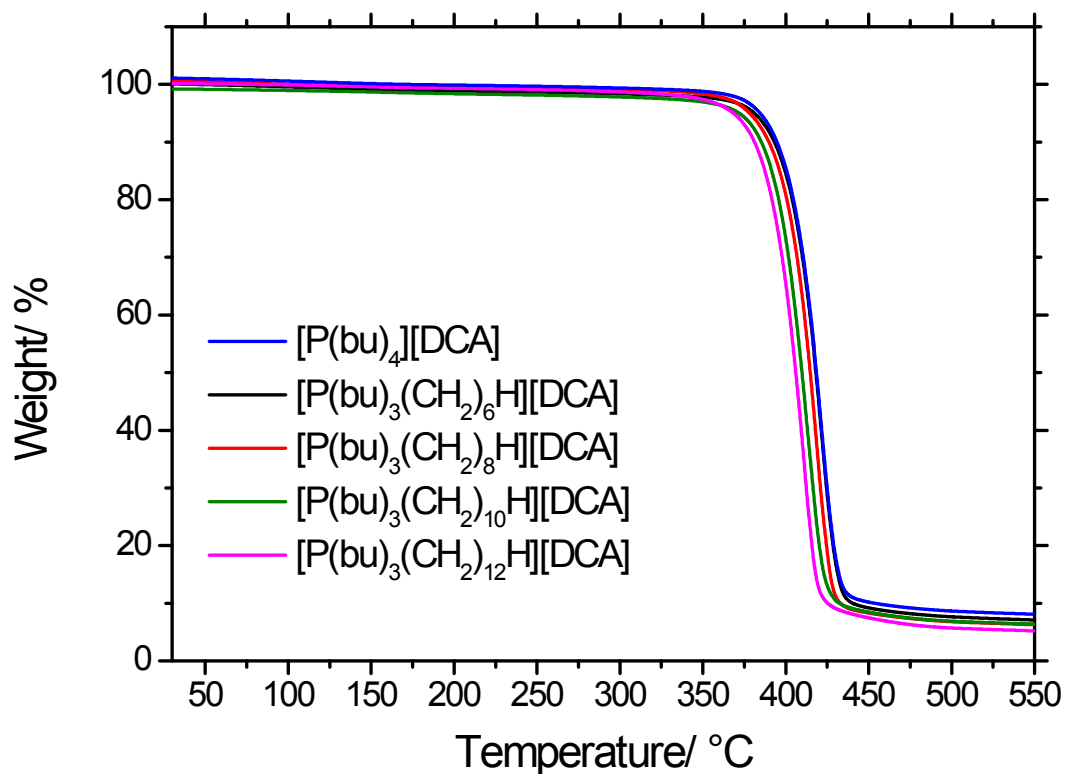


Figure S73. Thermogravimetric analysis for the alkylated tributylphosphonium ILs $[P(bu)_3(CH_2)_yH][DCA]$.

5. Obtaining peak positions of SAXS data

We obtained peak positions from SAXS data (Figure 3) using the fitting functions of Origin 9.1. Whenever possible, peaks were fit using the

Gauss fit:

$$I = I_0 + \frac{A}{w\sqrt{\pi/2}} e^{-2\frac{(q - q_c)^2}{w^2}}$$

Where I is the intensity, I_0 the intensity offset, A the area, w the peak width, q the scattering vector, and q_c the scattering vector of the peak centre. The fitted peak values for alkylated and fluorinated ILs are summarized in Table S1 and S2, respectively. In cases where this was not possible because the peak was too broad, or obscured by other peaks, we use the

First derivative zero-crossing

The first derivative of the scattering signal was calculated using Origin, and zero-crossings were identified automatically by the software. If there were multiple zero-crossings in the region of interest, the region of interest was narrowed down until only one remained.

Table S1. Peak positions of SAXS data of alkylated ILs (Figure 3a) fitted by Gauss function.

Sample	Peak	Peak center ($\text{\AA}^{-1}$)	Start point [§] ($\text{\AA}^{-1}$)	End point [§] ($\text{\AA}^{-1}$)
C4	Polarity	0.69	0.48	0.74
	Charge	0.85 [¥]	0.76	0.96
	Adjacency	1.49	1.28	1.70
C6	Polarity	0.63	0.48	0.70
	Charge	0.85	0.78	1.00
	Adjacency	1.51	1.28	1.70
C8	Polarity	0.60	0.41	0.63
	Charge	0.89	0.78	1.00
	Adjacency	1.49	1.28	1.70
C10	Polarity	0.50	0.35	0.57
	Charge	0.89	0.73	0.95
	Adjacency	1.49	1.28	1.70
C12	Polarity	0.39	0.24	0.46
	Charge	0.88	0.73	0.95
	Adjacency	1.49	1.28	1.70

[§]start point and end point define the selected q range for peak fitting.

Table S2. Peak positions of SAXS data of fluorinated ILs (Figure 3b) fitted by Gauss function.

Sample	Peak	Peak center ($\text{\AA}^{-1}$)	Start point [§] ($\text{\AA}^{-1}$)	End point [§] ($\text{\AA}^{-1}$)
F2	Lamellar 1 st order scattering	0.37 [¥]	0.21	0.43
	Lamellar 2 nd order scattering			
	Polarity	0.66	0.50	0.72
	Charge	0.82	0.78	1.00
	Adjacency	1.43	1.18	1.60
F4	Lamellar 1 st order scattering	0.34	0.18	0.40
	Lamellar 2 nd order scattering			
	Polarity	0.62 [¥]	0.50	0.72
	Charge	0.89 [¥]	0.77	0.98

	Adjacency	1.29	1.18	1.60
F6	Lamellar 1 st order scattering	0.26	0.18	0.40
	Lamellar 2 nd order scattering			
	Polarity			
	Charge	0.89 [‡]	0.77	0.98
	Adjacency	1.29	1.18	1.60
F8	Lamellar 1 st order scattering	0.22	0.12	0.34
	Lamellar 2 nd order scattering	0.42 [‡]	0.38	0.50
	Polarity			
	Charge	0.82	0.70	0.92
	Adjacency	1.17	1.02	1.44
F10	Lamellar 1 st order scattering	0.20	0.12	0.34
	Lamellar 2 nd order scattering	0.37 [‡]	0.33	0.45
	Polarity			
	Charge	0.84 [‡]	0.70	0.92
	Adjacency	1.11	1.02	1.44

[§]start point and end point define the selected q range for peak fitting.

[‡] The peak was fitted with another gadget (quick peaks) of software Origin 9.1 with following parameters: both direction, 1st derivative method, 1 polynomial order of Savitzky-Golay smooth derivative, 40 points of window and the others are set to be auto.

6. Single crystal structure analysis of [P(bu₃)R_{f8}][DCA]

Single crystals of [P(bu)₃(CH₂)₂C₈F₁₇][DCA] (F8) suitable for structure analysis could be obtained by dissolving in a 1:1 mixture of dichloromethane and heptane and slow solvent evaporation at 25°C until crystals formed. The data was recorded at 142 K using Mo-K α radiation in the Theta range of 0.840 to 26.722° on an AXS X8 Apex 2 diffractometer (Bruker, Billerica, USA) collecting 39865 reflexes. The data was refined by full-matrix least-squares on F². Final R-index with SHELX² using anisotropic refinements of the hydrogen atoms resulted in R1 = 0.05943. The cif file of F8 single crystal data with name “F8 single crystal” is included as a separate file.

Table S3: Single crystal X-ray data collection and structure solution refinement for [P(bu)₃(CH₂)₂C₈F₁₇][DCA].

CCDC	1503513
Empirical formula	C ₂₄ H ₃₁ F ₁₇ N ₃ P
Formula weight	715.49
Temperature	142(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 10.1936(7) Å a = 102.184(4)°. b = 12.6081(10) Å b = 97.398(4)°. c = 25.0746(17) Å g = 94.832(5)°.
Volume	3103.1(4) Å ³
Z	4
Density (calculated)	1.531 Mg/m ³
Absorption coefficient	0.211 mm ⁻¹
F(000)	1456
Crystal size	0.559 x 0.407 x 0.046 mm ³
Theta range for data collection	0.840 to 26.722°.
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 14, -31 ≤ l ≤ 29
Reflections collected	39865
Independent reflections	12493 [R(int) = 0.0302]
Completeness to theta = 25.242°	97.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6972
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	12493 / 257 / 897
Goodness-of-fit on F ²	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0593, wR2 = 0.1470
R indices (all data)	R1 = 0.0947, wR2 = 0.1679
Largest diff. peak and hole	0.929 and -0.578 e.Å ⁻³

7. Rheological Measurements

7.1 Shear dependent viscosities

The Ostwald-de Waele power law describes the shear thinning in the fluorinated ionic liquids with increasing side chain length and temperature in the linear regime:

$$\tau = k \dot{\gamma}^n \quad (1)$$

with τ : shear stress
k: consistency index
 $\dot{\gamma}$: shear force
n: flow behaviour index

A flow behaviour index of $n = 1$ indicates Newtonian behaviour, while values $n < 1$ are observed in shear thinning fluids. The difference from unity is a measure for the shear thinning in the liquid. Increasing the number of carbon atoms in the perfluoro-alkyl side chain increased the minimum shear rate of shear thinning and reduced the region of Newtonian flow. Longer fluorinated side chains led to a higher degree of shear thinning, indicated by lower flow behaviour indices and higher maximal temperatures for shear thinning. With increasing temperature the region of linear shear thinning is expanded to higher shear rates while at the same time the flow behaviour index decreases. No shear thinning behaviour was observed for the non-fluorinated ILs at any of the measured temperatures or shear rates. The Ostwald-de Waele parameters for the different ranges of the shear rates and temperatures are given in table S4-S6, the plots of the shear dependent viscosities in dependence of temperature are given in figure S73-79.

Table S4: Shear dependent rheological properties of [P(bu)₃(CH₂)₂(CF₂)₂F][DCA] (F2).

T/ °C	Newtonian region			shear thinning region		
	$\dot{\gamma}/s^{-1}$	n	R ²	$\dot{\gamma}/s^{-1}$	n	R ²
25	50- 3235	1.00	0.999	5609-10000	0.77	0.997
30	50- 4232	1.00	0.999	6606-10000	0.79	0.998
40	50- 5264	1.00	0.999	6957-10000	0.91	0.999
50	50- 5942	1.00	0.999	7303-10000	0.95	0.999
60	50-10000	1.00	0.999	not observed		
70	50-10000	1.00	0.999	not observed		
80	50-10000	1.00	0.999	not observed		
90	50-10000	1.00	0.999	not observed		
100	50-10000	1.00	0.999	not observed		

Table S5: Shear dependent rheological properties of [P(bu)₃(CH₂)₂(CF₂)₄F][DCA] (F4).

T/ °C	Newtonian region			Shear thinning region		
	$\dot{\gamma}/s^{-1}$	n	R ²	$\dot{\gamma}/s^{-1}$	n	R ²
25	50-873	0.99	0.999	4930-10000	0.58	0.982
30	50-1553	1.00	0.999	4930-10000	0.68	0.994
40	50-2587	1.00	0.999	6606-10000	0.79	0.999
50	50-3595	1.00	0.999	6957-10000	0.88	0.998
60	50-3926	1.00	0.999	7303-10000	0.97	0.999
70	50-10000	1.00	0.999	not observed		
80	50-10000	1.00	0.999	not observed		
90	50-10000	1.00	0.999	not observed		
100	50-10000	1.00	0.999	not observed		

Table S6: Shear dependent rheological properties of [P(bu)₃(CH₂)₂(CF₂)₆F][DCA] (F6).

T/ °C	Newtonian region			Shear thinning region		
	$\dot{\gamma}/ \text{s}^{-1}$	n	R ²	$\dot{\gamma}/ \text{s}^{-1}$	n	R ²
25	50-873	1.00	0.999	4611-10000	0.46	0.967
30	50-873	1.00	0.999	4611-10000	0.54	0.984
40	50-873	1.00	0.999	4930-10000	0.70	0.994
50	50-1213	1.00	0.999	4930-10000	0.81	0.998
60	50-1887	1.00	0.999	5964-10000	0.84	0.999
70	50-2912	1.00	0.999	6237-10000	0.88	0.999
80	50-10000	1.00	0.999	not observed		
90	50-10000	1.00	0.999	not observed		
100	50-10000	1.00	0.999	not observed		

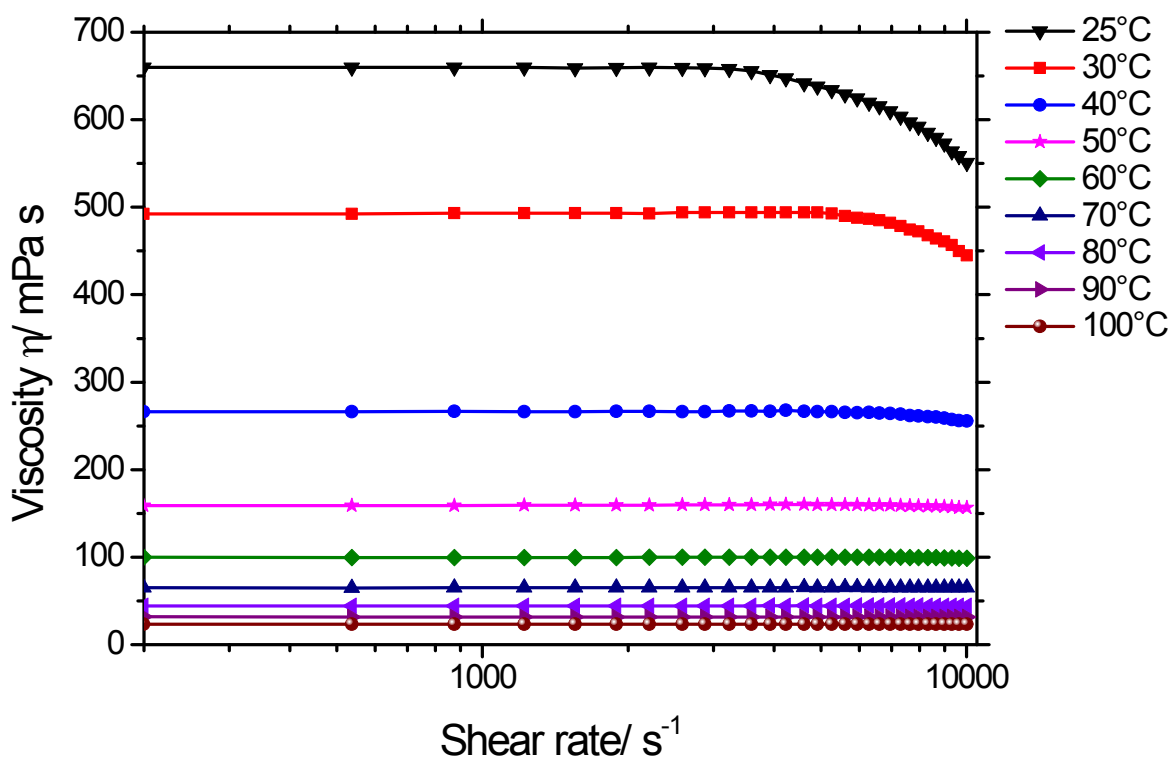


Figure S74. Shear rate dependent viscosity of [P(bu)₃(CH₂)₂(CF₂)₂F][DCA] (F2) at different temperatures.

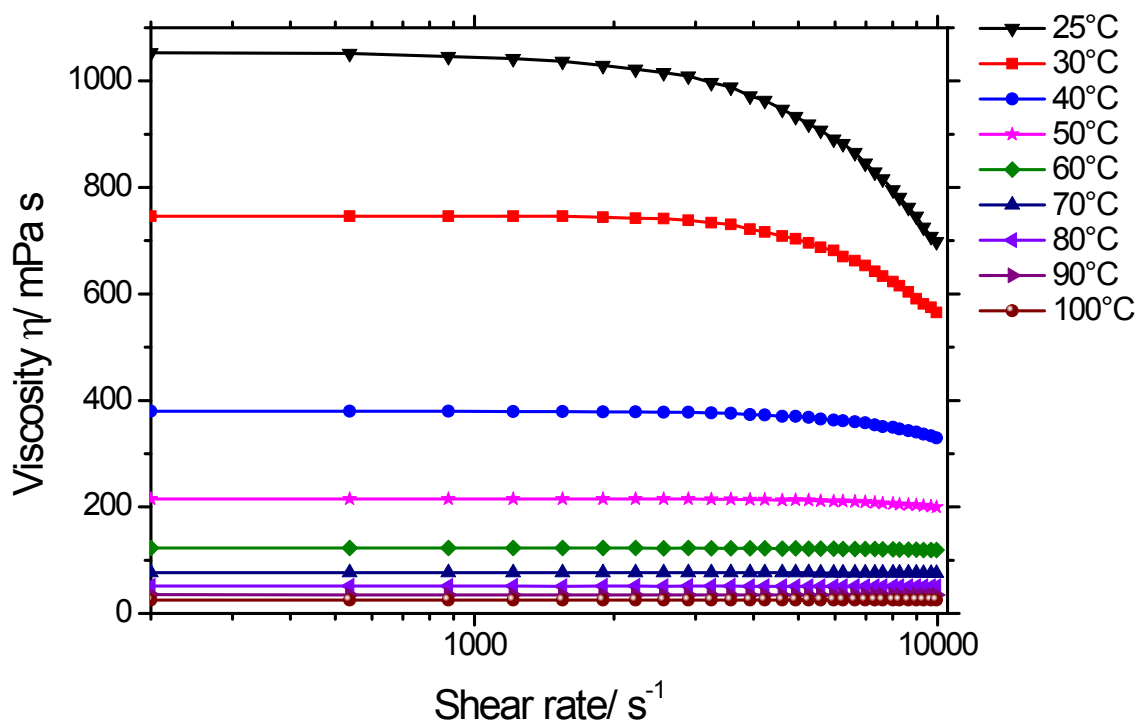


Figure S75. Shear rate dependent viscosity of [P(bu)₃(CH₂)₂(CF₂)₄F][DCA] (F4) at different temperatures.

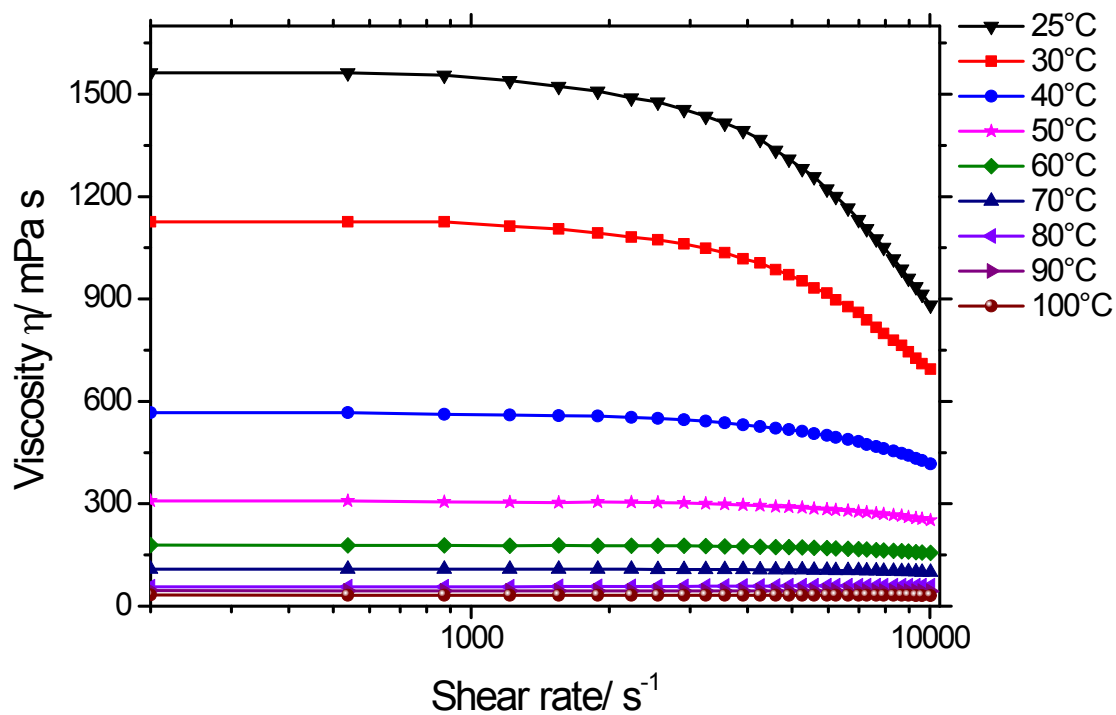


Figure S76. Shear rate dependent viscosity of [P(bu)₃(CH₂)₂(CF₂)₆F][DCA] (F6) at different temperatures.

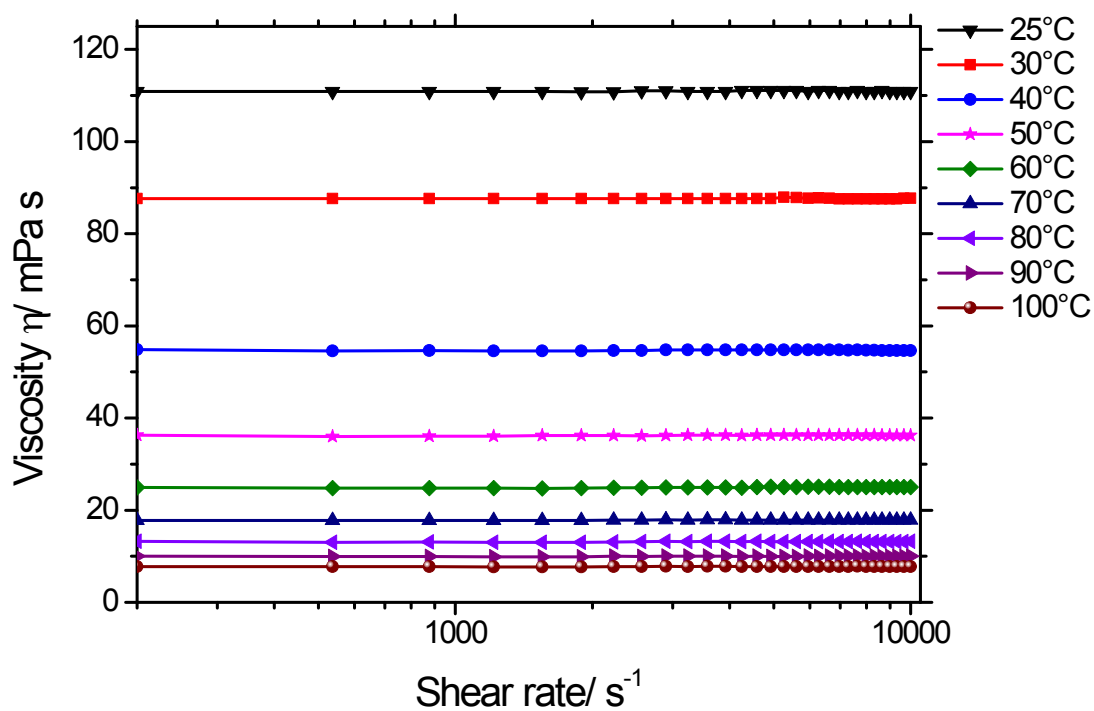


Figure S77. Shear rate dependent viscosity of $[P(bu)_3(CH_2)_6H][DCA]$ (C6) at different temperatures.

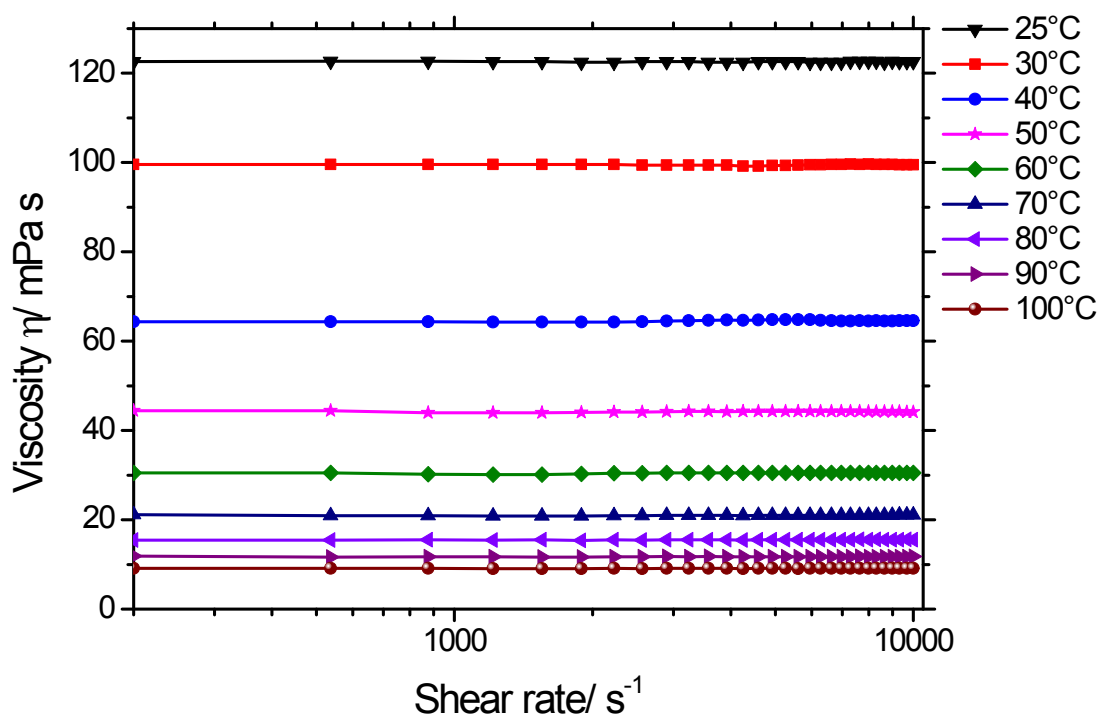


Figure S78. Shear rate dependent viscosity of $[P(bu)_3(CH_2)_8H][DCA]$ (C8) at different temperatures.

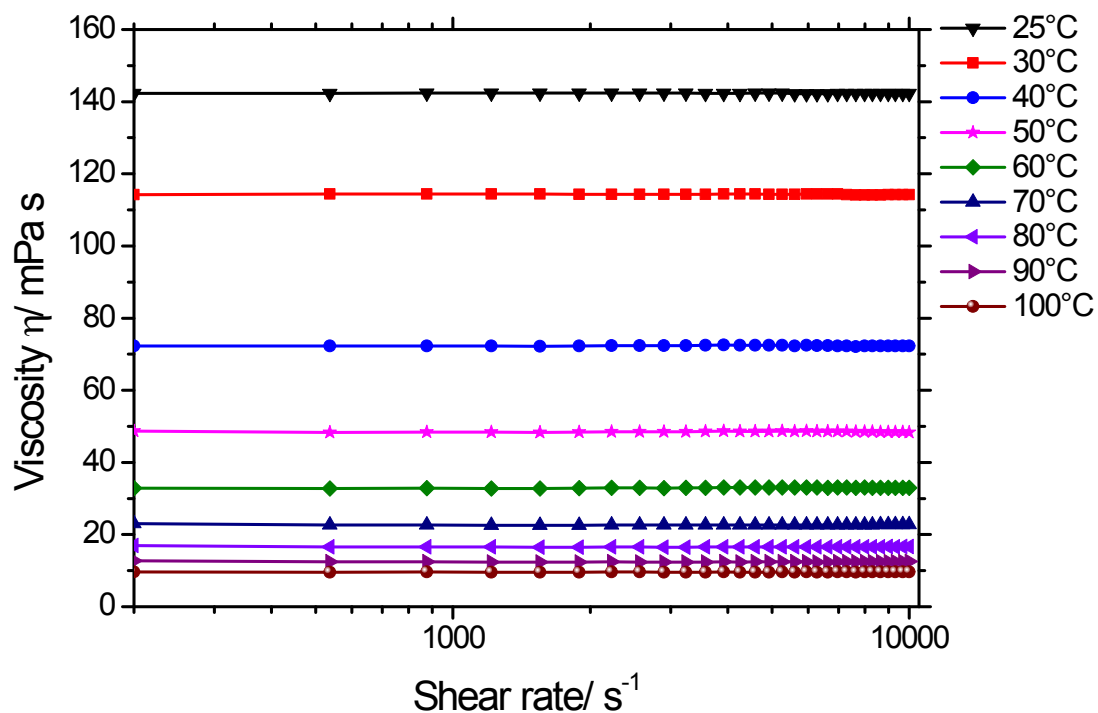


Figure S79. Shear rate dependent viscosity of [P(bu)₃(CH₂)₁₀H][DCA] (C10) at different temperatures.

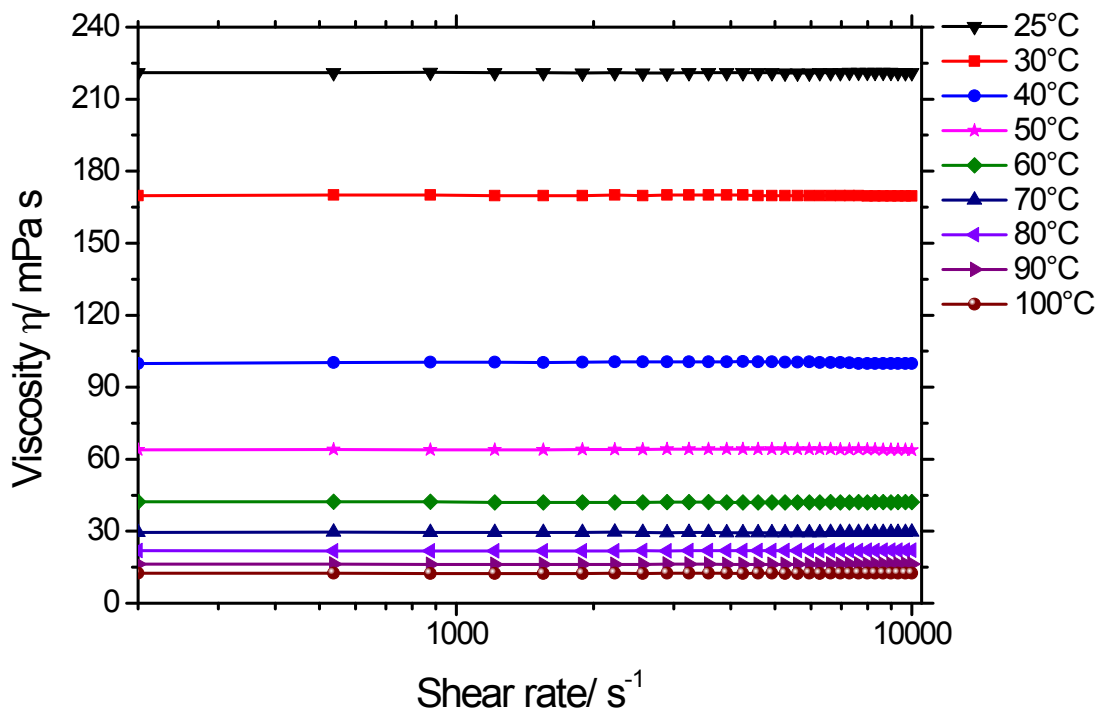


Figure S80. Shear rate dependent viscosity of [P(bu)₃(CH₂)₁₂H][DCA] (C12) at different temperatures.

7.2 Temperature dependent viscosities

Zero-shear viscosity data for the fluorinated and non-fluorinated phosphonium DCA ILs were obtained by fitting the Vogel-Fulcher-Tammann equation (2) to the measured data, a procedure that has been successfully applied for describing the temperature dependent viscosity of a very wide range of ionic liquids.³

$$\eta_o = \eta_{\infty} e^{\frac{B}{T - T_0}} \quad (2)$$

with η_o : Zero-shear viscosity
 η_{∞} : Viscosity at infinite temperature
 B: specific constant
 T : Absolute temperature
 T_0 : Vogel temperature $T_0 < T_g$

The resulting fit-parameters are listed in Table S7.

Table S7: Resulting values of the fit parameters for the Vogel-Fulcher-Tammann equation.

Ionic Liquid	η_o / mPa s ⁻¹	B/ K	T_0 / K	R ²
[P(bu) ₃ (CH ₂) ₂ (CF ₂) ₂ F][DCA] (F2)	0.0051	2152	115.5	0.9997
[[P(bu) ₃ (CH ₂) ₂ (CF ₂) ₄ F][DCA] (F4)	0.0026	2290	120.8	0.9999
[P(bu) ₃ (CH ₂) ₂ (CF ₂) ₆ F][DCA] (F6)	0.0022	2348	119.6	0.9994
[P(bu) ₃ (CH ₂) ₆ H][DCA] (C4)	0.0124	1625	119.6	0.9998
[P(bu) ₃ (CH ₂) ₈ H][DCA] (C6)	0.0236	1503	122.3	0.9994
[P(bu) ₃ (CH ₂) ₁₀ H][DCA] (C8)	0.0259	1467	129.5	0.9993
[P(bu) ₃ (CH ₂) ₁₂ H][DCA] (C12)	0.0268	1414	141.3	0.9998

8. References

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- 3 A. Rupp, N. Roznyatovskaya, H. Scherer, W. Beichel, P. Klose, C. Sturm, A. Hoffmann, J. Tübke, T. Koslowski and I. Krossing, *Chem. - A Eur. J.*, 2014, **20**, 9794–9804.

