Modular Synthesis of Fluorous Trialkylphosphines

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Supporting Information

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Detailed Synthetic Protocol

Typical procedure for the preparation of $[R_{F8}(CH_2)_3]_3P$: Tris(2-cyanoethyl)phosphine (5.257 g, 27.21 mmol) and $R_{F8}(CH_2)_3I$ (27.00 g, 45.91 mmol) was placed into a round-bottomed flask, closed with a stop-cock, clamped, heated with vigorous stirring at 130°C for 1 hour, and then at 160°C 10 hours. After cooling to 35°C, 50 ml of CH_2Cl_2 was added to the yellowish-brown solid, the mixture finely powdered in a mortar, and filtered through a Büchner-funnel. Washing with 2x40 ml of CH_2Cl_2 and drying in vacuo gave 21.22 g (99.8%) of $[R_{F8}(CH_2)_3P(CH_2CH_2CN)_3]^+I^-$ as a white powder. 21.00 g (26.88 mmol) of this salt was weighted into a heavy-walled round-bottomed flask and treated with NaOMe (30 w/w% solution in methanol, 9.68 g, 53.76 mmol) and MeOH (28 ml, <0.1% water). The flask was closed with a stop-cock, clamped, and heated to 70°C with vigorous stirring. The initial suspension turned into solution after about 30 minutes. After 12 hours the reaction mixture was evaporated to dryness at room temperature using rotary evaporator combined with water-vacuo. The brown residue was then suspended in water (100 ml) and filtered through a Büchner-funnel. The remaining solid was suspended again in 50 ml of water, filtered, dissolved in 250 ml of $CHCl_3$:CH_3OH(10:1) and dried over desiccated $MgSO_4$. The solution was then filtered, evaporated to dryness and the residue was finally dried in vacuo (80°C, 0.05 mbar) giving 13.19 g (81.8%) of $R_{F8}(CH_2)_3P(CH_2CH_2CN)_2$ as a white powder. The alkylation of this phosphine (12.40 g, 20.66 mmol) was carried out similarly to the first alkylation step with (18.22 g, 30.98 mmol) of $R_{F8}(CH_2)_3I$ and resulted in 24.06 g (98.0%) of $\{[R_{F8}(CH_2)_3]_2 P(CH_2CH_2CN)_2\}^+I^-$ as a white powder. Dealkylation was performed with (20.00 g, 16.83 mmol) of this salt and (6.06 g, 33.66 mmol) of a NaOMe-solution in 18 ml of MeOH:EtOH (2:1) at 80°C. The same work-up procedure as used for the previous dealkylation gave 13.40 g (79.1%) of $[R_{F8}(CH_2)_3]_2PCH_2CH_2CN$ as an off-white powder. This phosphine showed no air-sensitivity after a week at room-temperature. Next, 14.60 g (87.8%) of $\{[R_{F8}(CH_2)_3]_3 PCH_2CH_2CN\}^+I^-$ was obtained from this phosphine (10.50 g, 10.42 mmol) and $R_{F8}(CH_2)_3I$ (12.26 g, 20.84 mmol) applying the general alkylation procedure, after purification by flash chromatography on alumina and

a small amount of carbon-black (eluted with acetone). This chromatography is needed to get out the traces of inpurities, which are difficult to be removed from the final fluorous phosphine. During the last step, all manipulations were performed strictly under nitrogen. This salt (14.00 g, 8.775 mmol) was dealkylated with (3.16 g, 17.55 mmol) of a NaOMe-solution in 14 ml of MeOH:EtOH (1:1) at 80°C for 14 hours in the general way. After cooling to room temperature O_2-free methanol (25ml) and FC-72 (40 ml) was added to the mixture. The extraction at 30°C was followed by further 40 ml of O_2-free FC-72. All fluorous phases were combined and the solution was evaporated to dryness at atmospheric pressure. Drying in high-vacuum at 80°C gave 12.05 g (97.1%) of $[R_{F8}(CH_2)_3]_3P$ as an off-white powder.

In the case of $[R_{F4}(CH_2)_3]_3P$ and $[R_{F6}(CH_2)_3]_3P$, the bis-perfluoroalkyl-phosphine intermediates were liquids, while in the case of $[R_{F4}(CH_2)_3]_3P$ the mono perfluoroalkyl-phosphine was liquid too. The intermediate phosphine, $[R_{F6}(CH_2)_3][R_{F8}(CH_2)_3]P(CH_2CH_2CN)$ was also a liquid. Therefore, the work-up procedure in these cases after the appropriate dealkylation steps was different from the general. The crude reaction mixture was also evaporated to dryness, treated with water, but after the separation of the phases the water was removed and the organic oil was extracted again with water. After the removal of the aqueous phase, the oil was dissolved in chloroform, dried over desiccated $MgSO_4$, filtered, and evaporated to dryness using rotary evaporator. Finally, the residual oil was heated with stirring under vacuo (0.1 mbar) at 60-70°C to remove the traces of 2-methoxypropionitrile. The corresponding phosphines were obtained as light yellow or brown oils.

NMR Data of Prepared Compounds

$[R_{F8}(CH_2)_3](NC\text{-}CH_2CH_2)_3P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 2.24-2.36 (m, 2H), 2.51-2.68 (m, 2H), 3.20-3.29 (m, 2H), 3.31-3.40 (m, 6H), 3.40-3.50 (m, 6H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 38.7 (s). ^{19}F-NMR (235 MHz, $(CD_3)_2CO$) δ -82.1 (t, 3F), -115.1 (m, 2F), -122.6 (m, 2F), -122.9 (m, 2+2F), -123.7 (m, 2F), -124.5 (m, 2F), -127.2 (m, 2F).

$[R_{F8}(CH_2)_3](NC\text{-}CH_2CH_2)_2P$: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.64-1.71 (m, 2H), 1.76-1.92 (m, 2+4H), 2.15-2.32 (m, 2H), 2.53-2.61 (m, 4H). $^{31}P\{^1H\}$-NMR (101 MHz, $CDCl_3$) δ -24.4 (s). ^{19}F-NMR (235 MHz, $CDCl_3$) δ -81.2 (t, 3F), -114.6 (m, 2F), -122.1 (m, 2F), -122.3 (m, 2+2F), -123.1 (m, 2F), -123.9 (m, 2F), -126.5 (m, 2F).

$[R_{F8}(CH_2)_3]_2(NC\text{-}CH_2CH_2)_2P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 2.08-2.21 (m, 4H), 2.38-2.55 (m, 4H), 2.98-3.11 (m, 4H), 3.15-3.30 (m, 4+4H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 37.1 (s). ^{19}F-NMR (235 MHz, $(CD_3)_2CO$) δ -82.1 (t, 6F), -115.0 (m, 4F), -122.7 (m, 4F), -122.9 (m, 4+4F), -123.7 (m, 4F), -124.4 (m, 4F), -127.2 (m, 4F).

$[R_{F8}(CH_2)_3]_2(NC\text{-}CH_2CH_2)P$: ^{1}H-NMR (250 MHz, $CDCl_3$:CD_3OD (9:1)): δ 1.59-1.66 (m, 4H), 1.73-1.85 (m, 2+4H), 2.17-2.35 (m, 4H), 2.55-2.64 (m, 2H). $^{31}P\{^1H\}$-NMR (101 MHz, $CDCl_3$:CD_3OD (9:1)) δ -29.2 (s). ^{19}F-NMR (235 MHz, $CDCl_3$:CD_3OD (9:1)) δ -82.1 (t, 6F), -115.1(m, 4F), -122.7 (m, 4F), -122.9 (m, 4+4F), -123.8 (m, 4F), -124.5 (m, 4F), -127.2 (m, 4F).

$[R_{F8}(CH_2)_3]_3(NC\text{-}CH_2CH_2)P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 2.04-2.19 (m, 6H), 2.38-2.56 (m, 6H), 2.91-3.03 (m, 6H), 3.12-3.25 (m, 2+2H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 36.2 (s). ^{19}F-NMR (235 MHz, $(CD_3)_2CO$) δ -82.1 (t, 9F), -114.9 (m, 6F), -122.7 (m, 6F), -122.9 (m, 6+6F), -123.8 (m, 6F), -124.4 (m, 6F), -127.2 (m, 6F).

$[R_{F8}(CH_2)_3]_3P$: ^{1}H-NMR (250 MHz, FC-72): δ 1.50-1.63 (m, 6H), 1.80-2.00 (m, 6H), 2.14-2.40 (m, 6H). $^{31}P\{^1H\}$-NMR (101 MHz, FC-72) δ -34.4 (s). ^{19}F-NMR (235 MHz, $(CD_3)_2CO$) δ -82.2 (t, 9F), -115.2 (m, 6F), -122.7 (m, 6F), -122.9 (m, 6+6F), -123.8 (m, 6F), -124.5 (m, 6F), -127.2 (m, 6F).

$[R_{F6}(CH_2)_3](NC\text{-}CH_2CH_2)_3P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): 2.20-2.38 (m, 2H), 2.46-2.72 (m, 2H), 3.17-3.32 (m, 2H), 3.32-3.40 (m, 6H), 3.40-3.53 (m, 6H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 38.6 (s).

$[R_{F6}(CH_2)_3](NC\text{-}CH_2CH_2)_2P$: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.59-1.69 (m, 2H), 1.71-1.91 (m, 2+4H), 2.09-2.33 (m, 2H), 2.48-2.62 (m, 4H). $^{31}P\{^1H\}$-NMR (101 MHz, $CDCl_3$) δ -23.6 (s).

$[R_{F6}(CH_2)_3]_2(NC\text{-}CH_2CH_2)_2P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 2.16-2.35 (m, 4H), 2.46-2.71 (m, 4H), 3.09-3.25 (m, 4H), 3.26-3.45 (m, 4+4H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 37.8 (s). ^{19}F-NMR (235 MHz, $(CD_3)_2CO$) δ -82.2 (t, 6F), -115.0 (m, 4F), -122.9 (m, 4F), -123.9 (m, 4F), -124.5 (m, 4F), -127.2 (m, 4F).

$[R_{F6}(CH_2)_3]_2(NC\text{-}CH_2CH_2)P$: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.51-1.62 (m, 4H), 1.68-1.87 (m, 2+4H), 2.07-2.33 (m, 4H), 2.44-2.57 (m, 2H). $^{31}P\{^1H\}$-NMR (101 MHz, $CDCl_3$) δ -27.4 (s).

$[R_{F6}(CH_2)_3]_3(NC\text{-}CH_2CH_2)P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 2.12-2.32 (m, 6H), 2.46-2.71 (m, 6H), 3.02-3.19 (m, 6H), 3.22-3.46 (m, 2+2H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 37.0 (s).

$[R_{F6}(CH_2)_3]_3P$: ^{1}H-NMR (250 MHz, FC-72): δ 1.52-1.63 (m, 6H), 1.82-2.01 (m, 6H), 2.16-2.41 (m, 6H). $^{31}P\{^1H\}$-NMR (101 MHz, FC-72) δ -36.0 (s).

$[R_{F4}(CH_2)_3](NC\text{-}CH_2CH_2)_3P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 2.18-2.36 (m, 2H), 2.45-2.70 (m, 2H), 3.14-3.29 (m, 2H), 3.29-3.39 (m, 6H), 3.39-3.52 (m, 6H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 38.6 (s). ^{19}F-NMR (235 MHz, $(CD_3)_2CO$) δ -82.4 (t, 3F), -115.3 (m, 2F), -125.5 (m, 2F), -127.1 (m, 2F).

$[R_{F4}(CH_2)_3](NC\text{-}CH_2CH_2)_2P$: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.59-1.68 (m, 2H), 1.69-1.89 (m, 2+4H), 2.08-2.33 (m, 2H), 2.47-2.61 (m, 4H). $^{31}P\{^1H\}$-NMR (101 MHz, $CDCl_3$) δ -23.7 (s).

$[R_{F4}(CH_2)_3]_2(NC\text{-}CH_2CH_2)_2P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 2.15-2.35 (m, 4H), 2.45-2.71 (m, 4H), 3.07-3.23 (m, 4H), 3.26-3.44 (m, 4+4H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 37.8 (s). ^{19}F-NMR (235 MHz, $(CD_3)_2CO$) δ -82.4 (t, 6F), -115.3 (m, 4F), -125.5 (m, 4F), -127.2 (m, 4F).

$[R_{F4}(CH_2)_3]_2(NC\text{-}CH_2CH_2)P$: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.51-1.61 (m, 4H), 1.66-1.86 (m, 2+4H), 2.07-2.30 (m, 4H), 2.44-2.56 (m, 2H). $^{31}P\{^1H\}$-NMR (101 MHz, $CDCl_3$) δ -27.5 (s).

$[R_{F4}(CH_2)_3]_3(NC\text{-}CH_2CH_2)P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 2.14-2.32 (m, 6H), 2.45-2.70 (m, 6H), 3.01-3.17 (m, 6H), 3.21-3.42 (m, 2+2H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 37.0 (s).

$[R_{F4}(CH_2)_3]_3P$: ^{1}H-NMR (250 MHz, FC-72): δ 1.51-1.64 (m, 6H), 1.81-2.01 (m, 6H), 2.15-2.40 (m, 6H). $^{31}P\{^1H\}$-NMR (101 MHz, FC-72) δ -34.5 (s).

$[R_{F8}(CH_2)_4](NC\text{-}CH_2CH_2)_3P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 1.83-1.99 (m, 2H), 2.03-2.21 (m, 2H), 2.26-2.52 (m, 2H), 3.04-3.19 (m, 2H), 3.25-3.36 (m, 6H), 3.36-3.48 (m, 6H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 38.4 (s).

$[R_{F8}(CH_2)_4](NC\text{-}CH_2CH_2)_2P$: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.52-1.62 (m, 2+2H), 1.67-1.79 (m, 2H), 1.78-1.89 (t, 4H), 1.99-2.24 (m, 2H), 2.46-2.60 (m, 4H). $^{31}P\{^1H\}$-NMR (101 MHz, $CDCl_3$) δ -23.3 (s).

$[R_{F8}(CH_2)_4]_2(NC\text{-}CH_2CH_2)_2P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 1.82-1.97 (m, 4H), 1.99-2.17 (m, 4H), 2.25-2.51 (m, 4H), 2.91-3.07 (m, 4H), 3.18-3.36 (m, 4+4H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 37.5 (s).

$[R_{F8}(CH_2)_4]_2(NC\text{-}CH_2CH_2)P$: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.39-1.64 (m, 4+4H), 1.64-1.82 (m, 4+2H), 1.95-2.23 (m, 4H), 2.40-2.55 (m, 2H). $^{31}P\{^1H\}$-NMR (101 MHz, $CDCl_3$) δ -26.6 (s).

$[R_{F8}(CH_2)_4]_3(NC\text{-}CH_2CH_2)P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 1.82-1.95 (m, 6H), 1.96-2.11 (m, 6H), 2.25-2.50 (m, 6H), 2.76-2.94 (m, 6H), 3.06-3.31 (m, 2+2H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 36.5 (s).

$[R_{F8}(CH_2)_4]_3P$: ^{1}H-NMR (250 MHz, FC-72): δ 1.36-1.49 (m, 6H), 1.49-1.67 (m, 6H), 1.67-1.87 (m, 6H), 1.93-2.23 (m, 6H). $^{31}P\{^1H\}$-NMR (101 MHz, FC-72) δ -32.4 (s).

$[R_{F8}(CH_2)_3](NC\text{-}CH_2CH_2)_3P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 2.24-2.36 (m, 2H), 2.51-2.68 (m, 2H), 3.20-3.29 (m, 2H), 3.31-3.40 (m, 6H), 3.40-3.50 (m, 6H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 38.7 (s).

$[R_{F8}(CH_2)_3](NC\text{-}CH_2CH_2)_2P$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 1.64-1.71 (m, 2H), 1.76-1.92 (m, 2+4H), 2.15-2.32 (m, 2H), 2.53-2.61 (m, 4H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ -24.4 (s).

$[R_{F8}(CH_2)_3][R_{F8}(CH_2)_4](NC\text{-}CH_2CH_2)_2P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 1.85-1.97 (m, 2H), 1.98-2.70 (m, 2+2+2+2H), 2.95-3.19 (m, 2+2H), 3.20-3.40 (m, 4+4H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 37.7 (s).

$[R_{F8}(CH_2)_3][R_{F8}(CH_2)_4](NC\text{-}CH_2CH_2)P$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 1.45-1.64 (m, 2+2+2H), 1.65-1.87 (m, 2+2+2H), 2.96-2.32 (m, 2+2H), 2.43-2.57 (m, 2H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ -27.1 (s).

$[R_{F8}(CH_2)_3][R_{F8}(CH_2)_4]_2(NC\text{-}CH_2CH_2)P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 1.83-1.97 (m, 4H), 1.97-2.70 (m, 2+2+4+4H), 2.73-3.07 (m, 2+4H), 3.11-3.34 (m, 2+2H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 36.8 (s).

$[R_{F8}(CH_2)_3][R_{F8}(CH_2)_4]_2P$: ^{1}H-NMR (250 MHz, FC-72): δ 1.39-1.52 (m, 2+4H), 1.52-1.68 (m, 4H), 1.69-1.92 (m, 2+4H), 1.97-2.33 (m, 2+4H). $^{31}P\{^1H\}$-NMR (101 MHz, FC-72) δ -34.7 (s).

$[R_{F6}(CH_2)_3](NC\text{-}CH_2CH_2)_3P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 2.20-2.38 (m, 2H), 2.46-2.72 (m, 2H), 3.17-3.32 (m, 2H), 3.32-3.40 (m, 6H), 3.40-3.53 (m, 6H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 38.6 (s).

$[R_{F6}(CH_2)_3](NC\text{-}CH_2CH_2)_2P$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 1.59-1.69 (m, 2H), 1.71-1.91 (m, 2+4H), 2.09-2.33 (m, 2H), 2.48-2.62 (m, 4H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ -23.6 (s).

$[R_{F6}(CH_2)_3][R_{F8}(CH_2)_3](NC\text{-}CH_2CH_2)_2P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 2.16-2.35 (m, 2+2H), 2.47-2.72 (m, 2+2H), 3.09-3.25 (m, 2+2H), 3.26-3.46 (m, 4+4H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 37.8 (s). ^{19}F-NMR (235 MHz, $(CD_3)_2CO$) δ -82.1-(-82.3) (m, 3+3F), -114.9-(-115.1) (m, 2+2F), -122.5-(-123.1) (m, 2+2+2+2F), -123.6-(-124.1) (m, 2+2F), -124.3-(-124.7) (m, 2+2F), -127.1-(-127.4) (m, 2+2F).

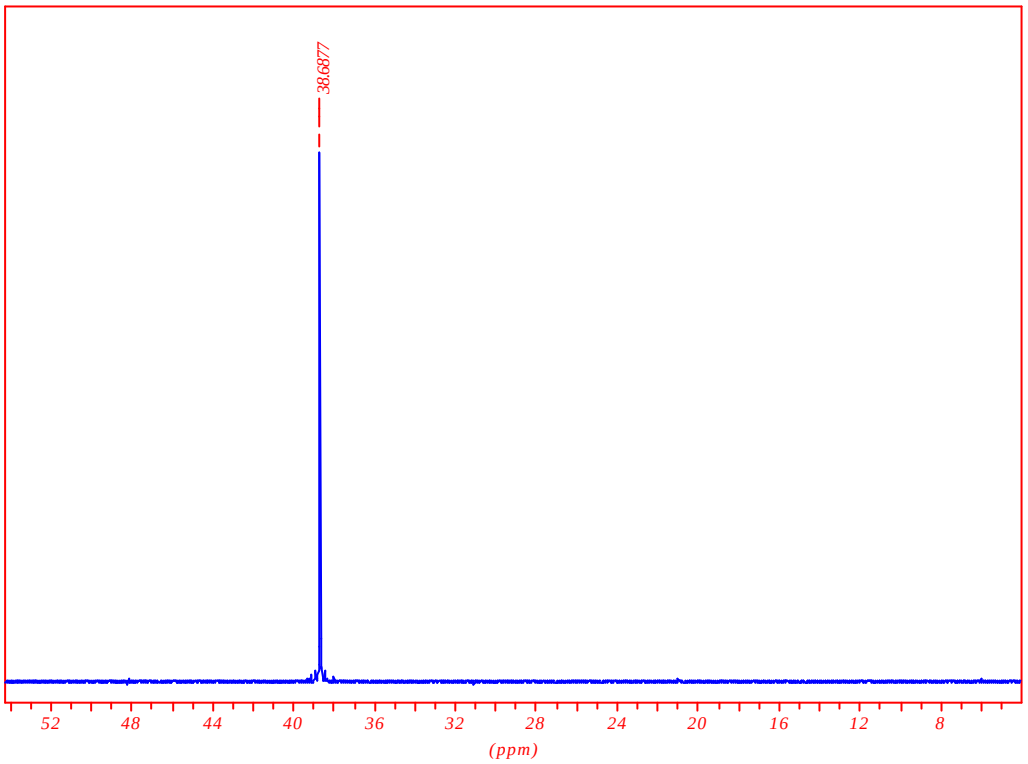
$[R_{F6}(CH_2)_3][R_{F8}(CH_2)_3](NC\text{-}CH_2CH_2)P$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 1.52-1.63 (m, 2+2H), 1.70-1.87 (m, 2+2+2H), 2.07-2.33 (m, 2+2H), 2.44-2.57 (m, 2H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ -27.5 (s).

$[R_{F6}(CH_2)_3][R_{F8}(CH_2)_3][R_{F8}(CH_2)_4](NC\text{-}CH_2CH_2)P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 1.82-1.98 (m, 2H), 2.00-2.72 (m, 2+2+2+2+2+2H), 2.89-3.18 (m, 2+2+2H), 3.18-3.45 (m, 2+2H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 36.8 (s). ^{19}F-NMR (235 MHz, $(CD_3)_2CO$) δ -82.2-(-82.4) (m, 3+3+3F), -114.8-(-115.3) (m, 2+2+2F), -122.6-(-123.2) (m, 2+2+2+2+2+2+2F), -123.6-(-124.2) (m, 2+2+2F), -124.3-(-124.7) (m, 2+2+2F), -127.2-(-127.5) (m, 2+2+2F).

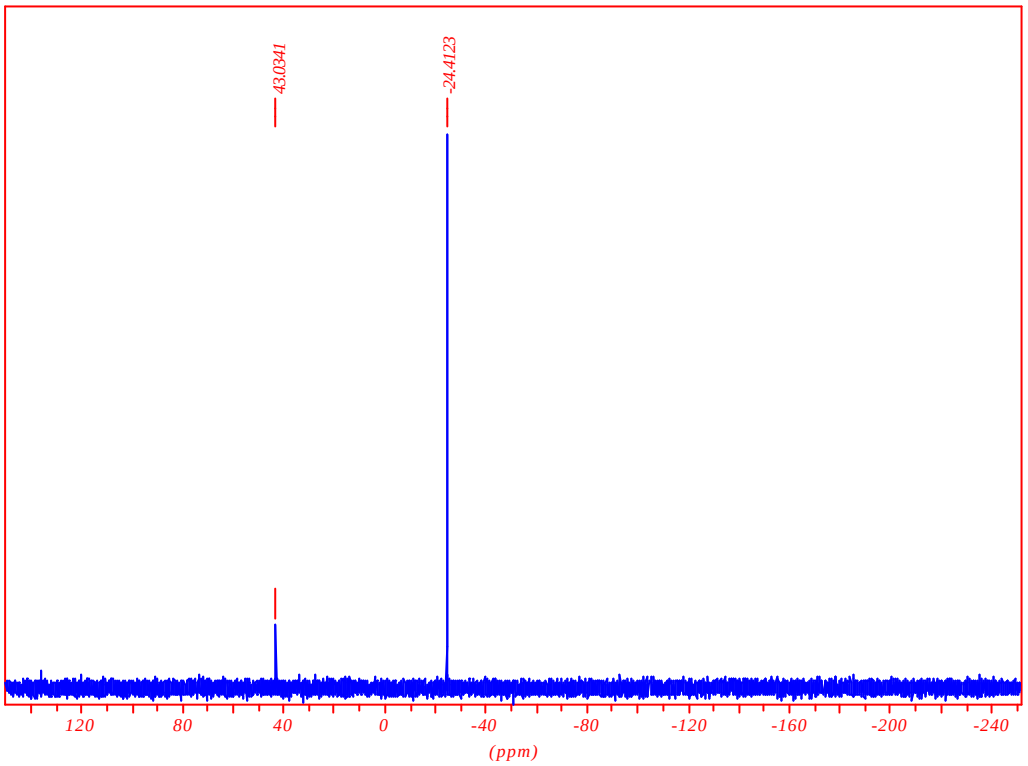
$[R_{F6}(CH_2)_3][R_{F8}(CH_2)_3][R_{F8}(CH_2)_4]P$: ^{1}H-NMR (250 MHz, FC-72): δ 1.46-1.75 (m, 2+2+2+2H), 1.75-2.00 (m, 2+2+2H), 2.02-2.54 (m, 2+2+2H). $^{31}P\{^1H\}$-NMR (101 MHz, FC-72) δ -34.0 (s). ^{19}F-NMR (235 MHz, $(CD_3)_2CO$) δ -82.1-(-82.3) (m, 3+3+3F), -114.9-(-115.2) (m, 2+2+2F), -122.6-(-123.2) (m, 2+2+2+2+2+2+2F), -123.6-(-124.2) (m, 2+2+2F), -124.4-(-124.8) (m, 2+2+2F), -127.1-(-127.5) (m, 2+2+2F).

$^{31}P\{^{1}H\}$-NMR Spectra of Prepared Compounds

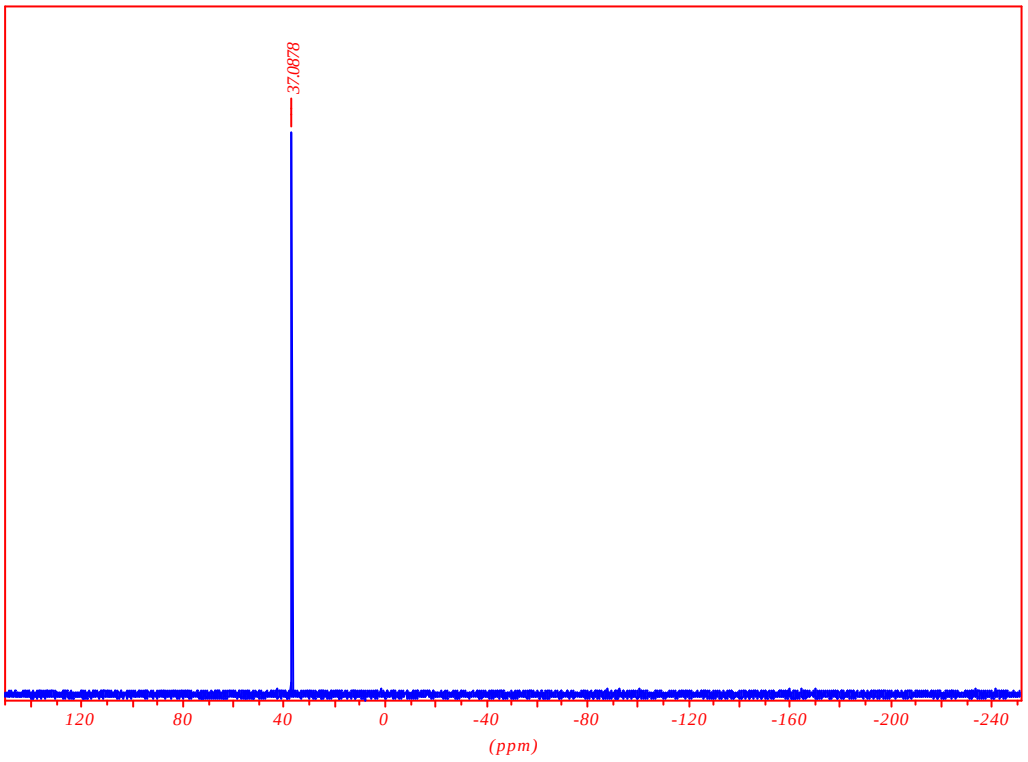
$[R_{F8}(CH_2)_3](NC\text{-}CH_2CH_2)_3P^+I^-$



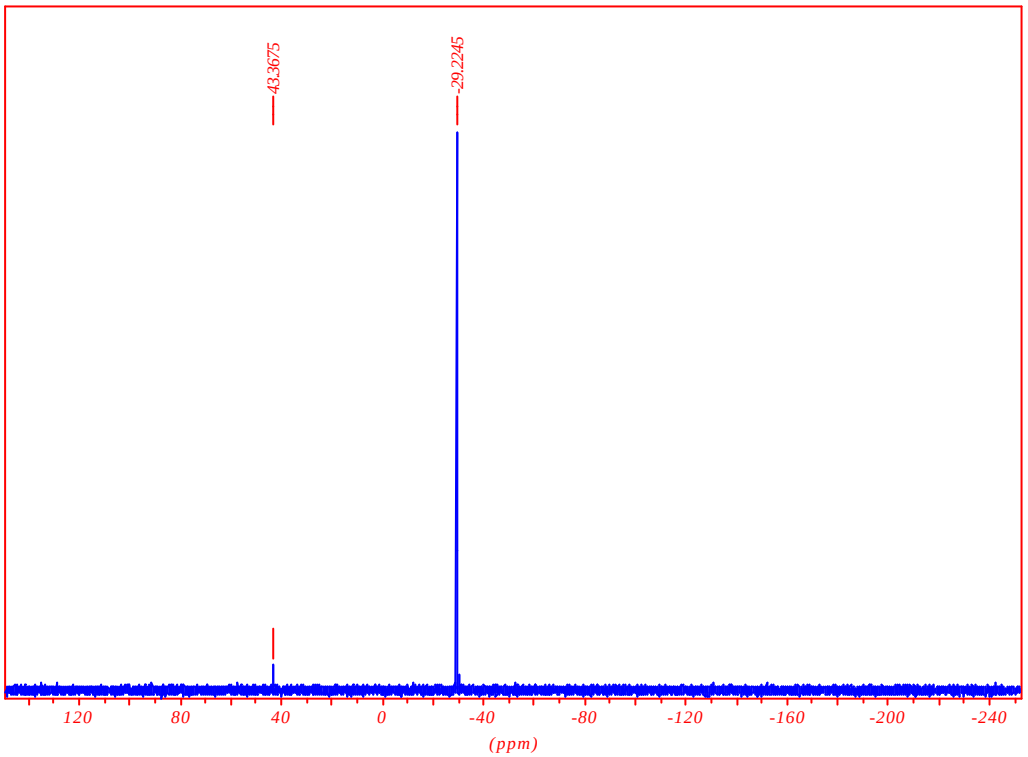
$[R_{F8}(CH_2)_3](NC\text{-}CH_2CH_2)_2P$



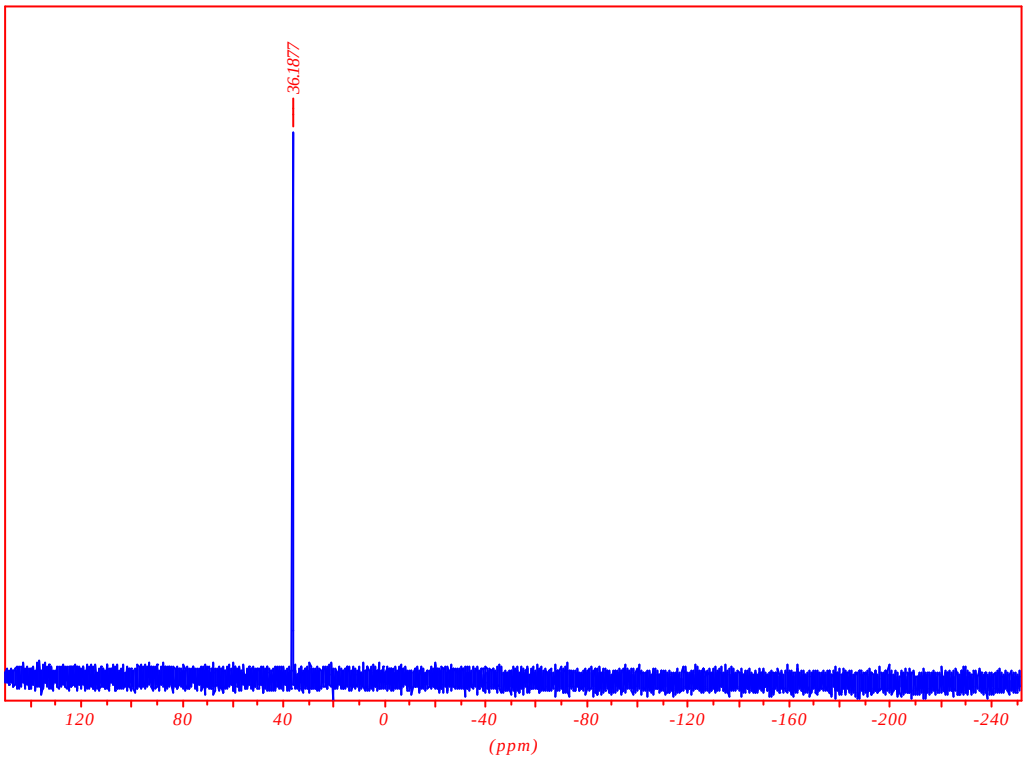
$[R_{F8}(CH_2)_3]_2(NC\text{-}CH_2CH_2)_2P^+I^-$



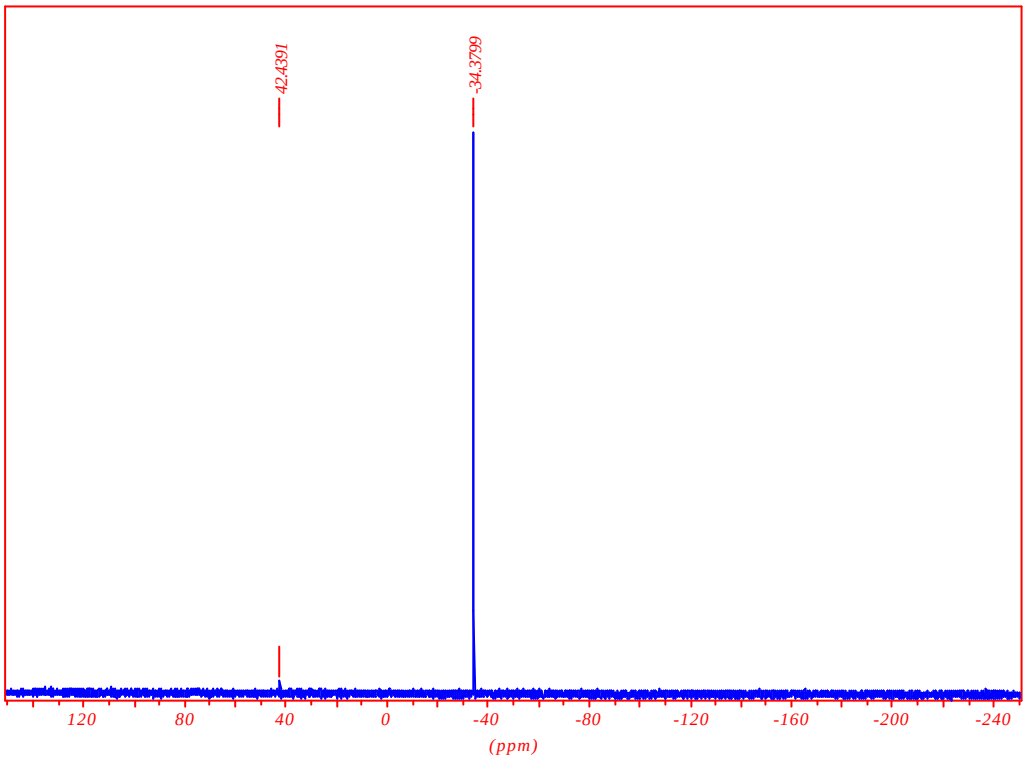
$[R_{F8}(CH_2)_3]_2(NC\text{-}CH_2CH_2)P$



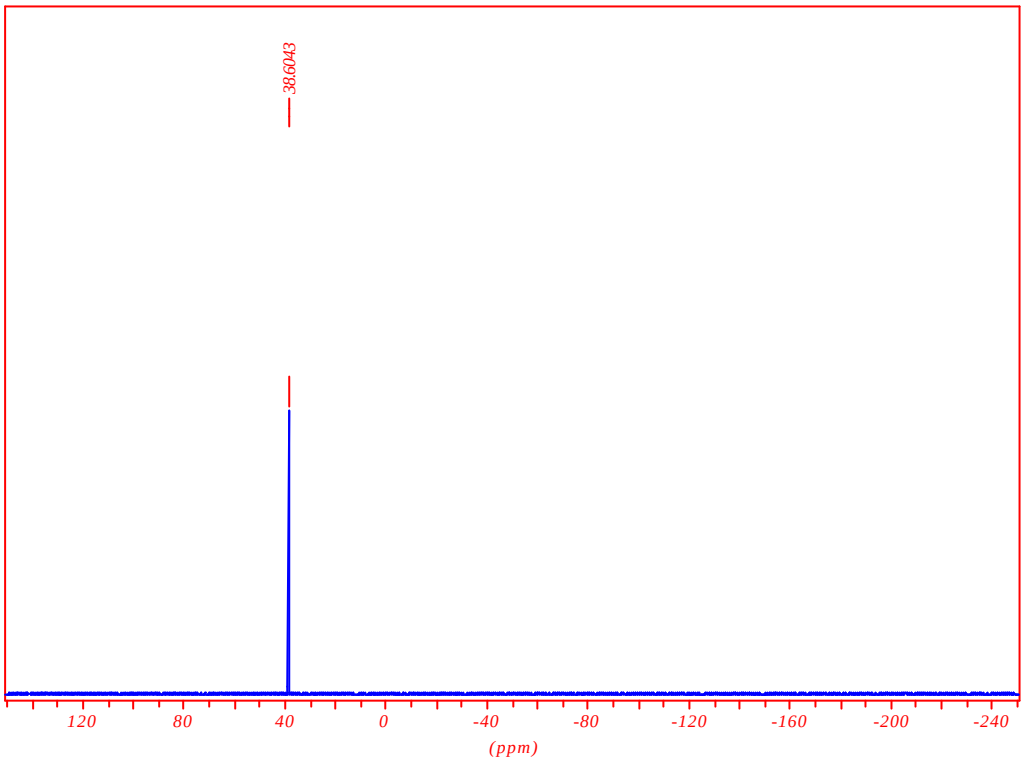
$[R_{F8}(CH_2)_3]_3(NC\text{-}CH_2CH_2)P^+I^-$



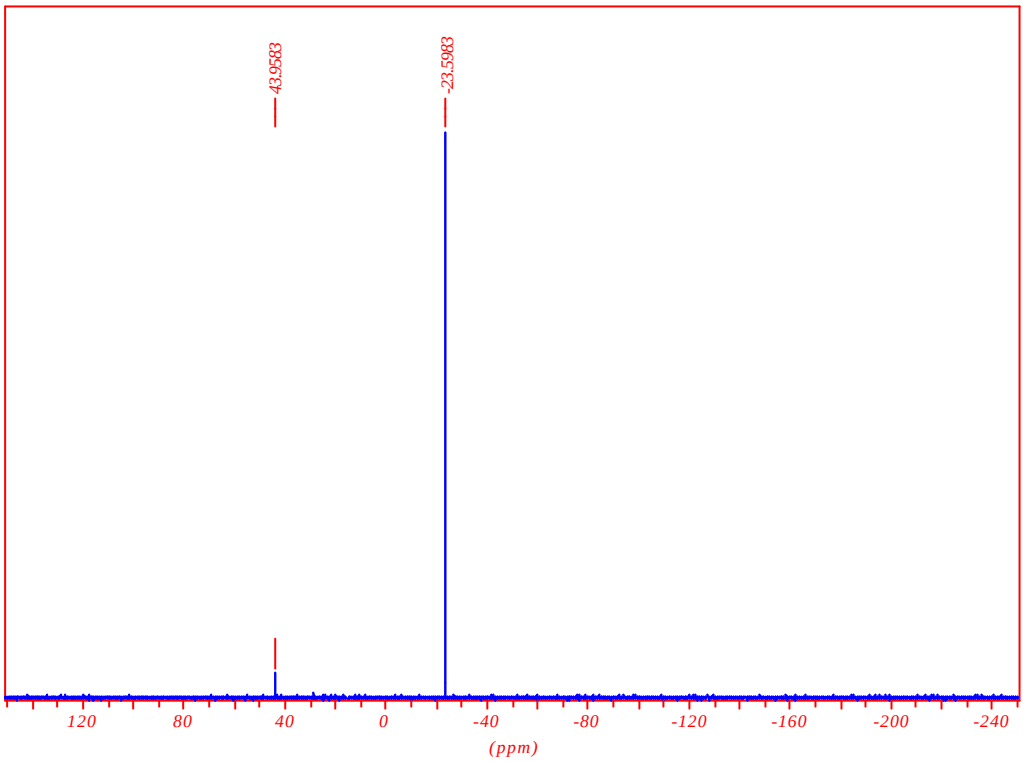
$[R_{F8}(CH_2)_3]_3P$



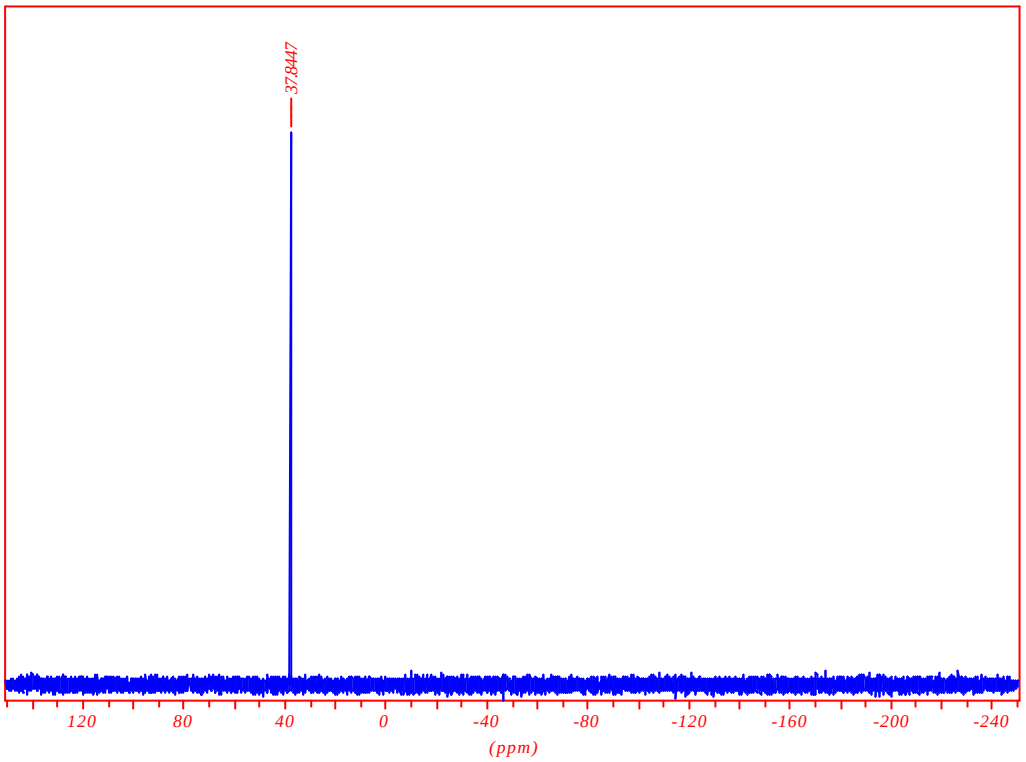
$[R_{F6}(CH_2)_3](NC\text{-}CH_2CH_2)_3P^+I^-$



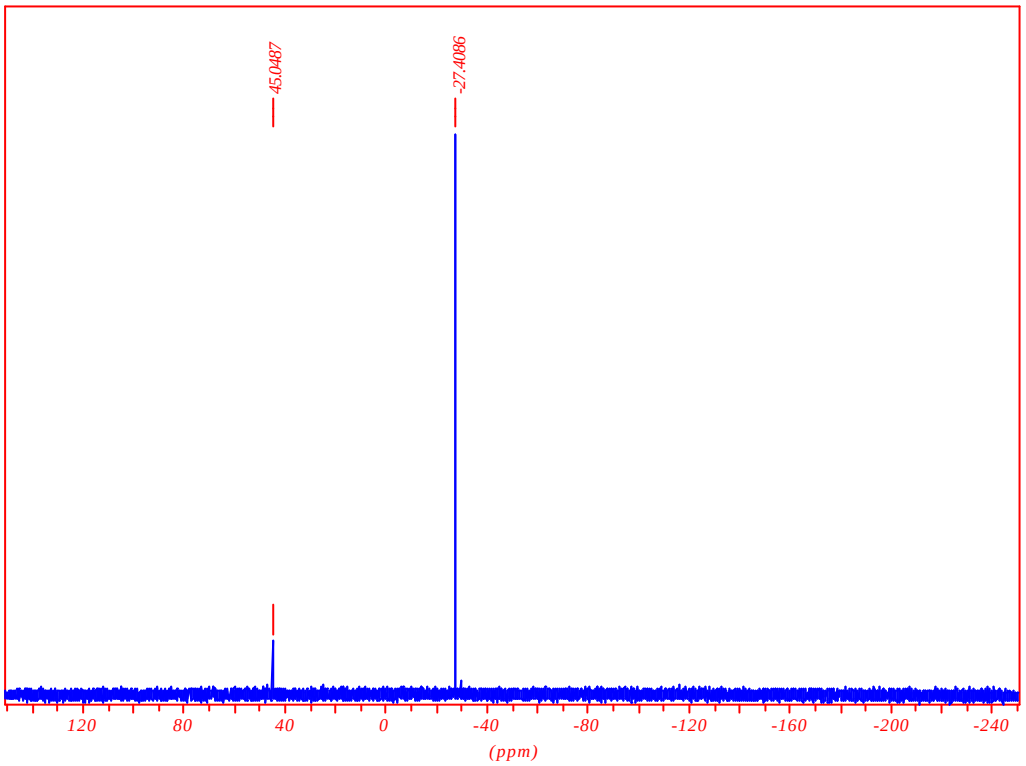
$[R_{F6}(CH_2)_3](NC\text{-}CH_2CH_2)_2P$



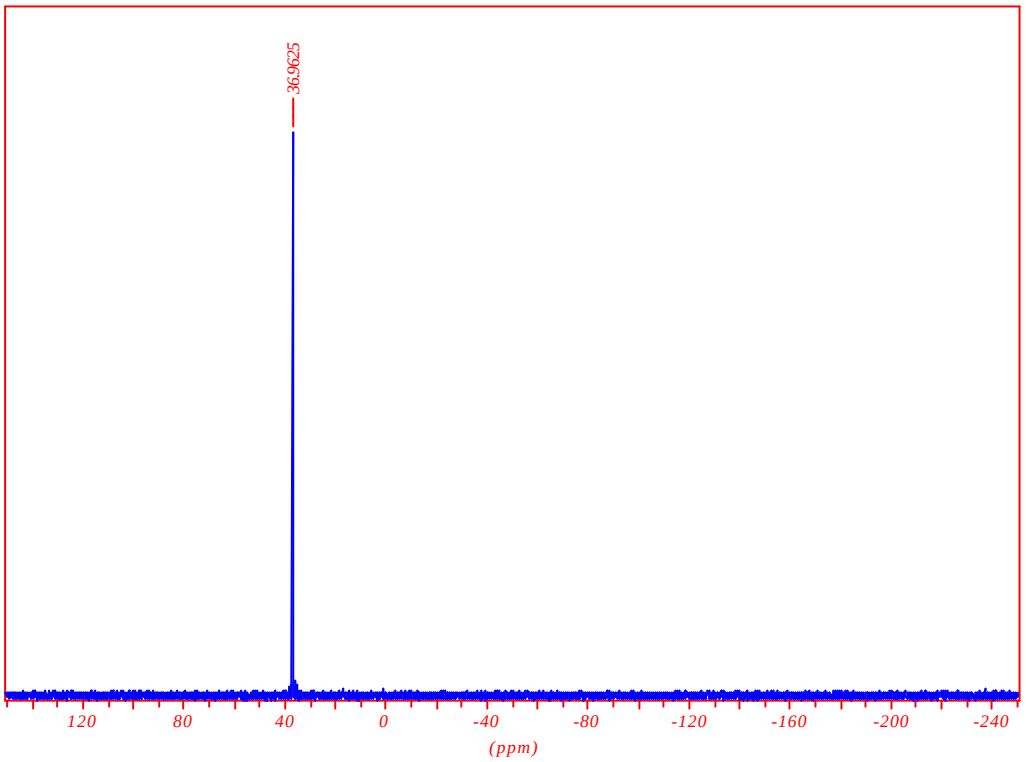
$[R_{F6}(CH_2)_3]_2(NC\text{-}CH_2CH_2)_2P^+I^-$



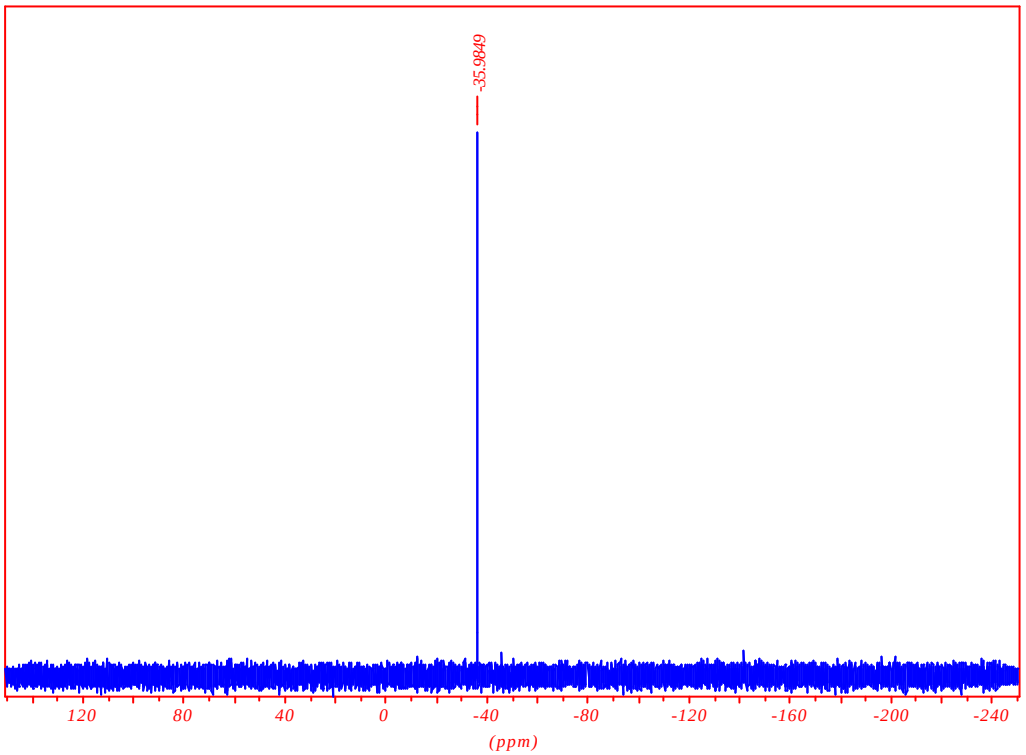
$[R_{F6}(CH_2)_3]_2(NC\text{-}CH_2CH_2)P$



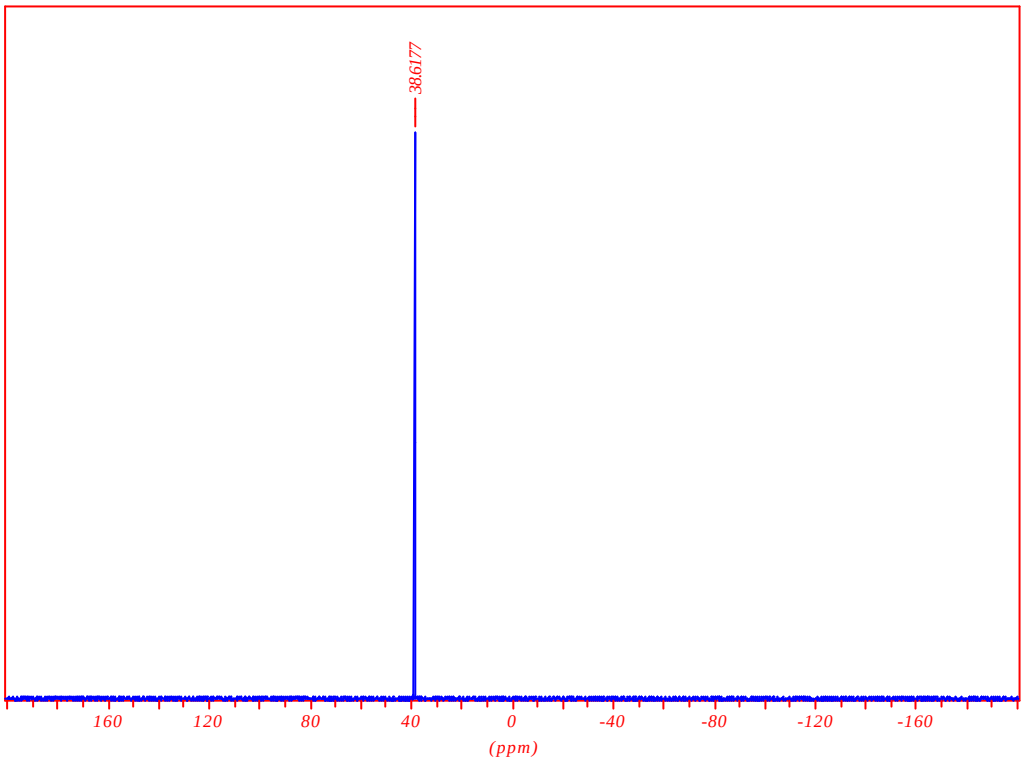
$[R_{F6}(CH_2)_3]_3(NC\text{-}CH_2CH_2)P^+I^-$



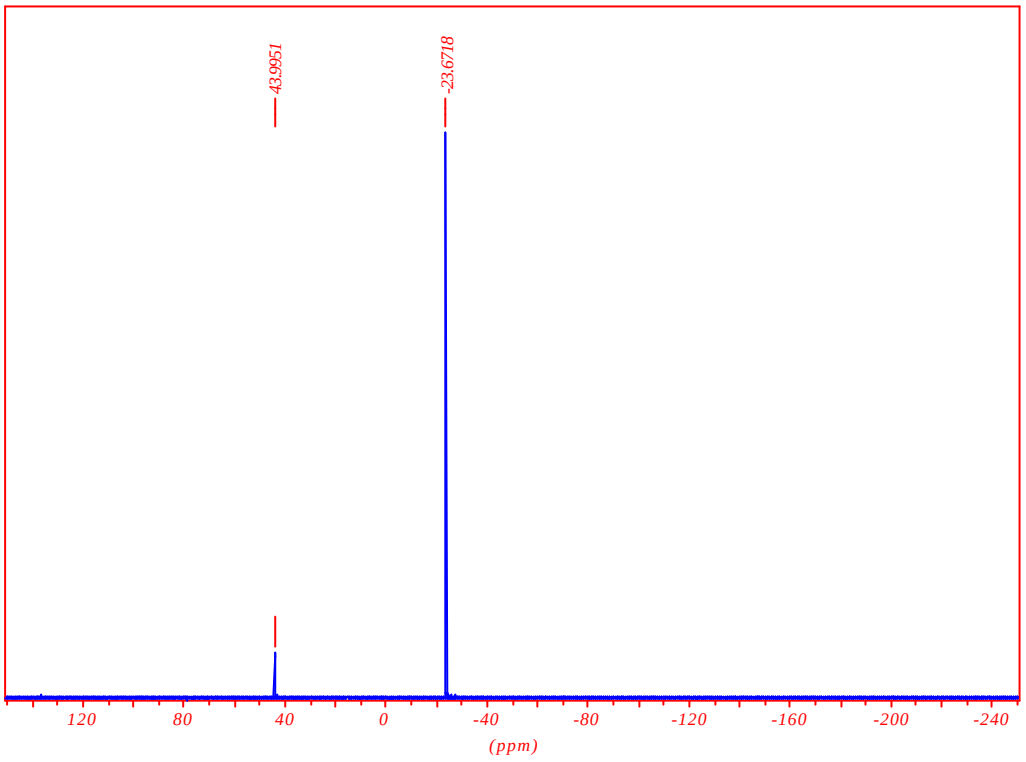
$[R_{F6}(CH_2)_3]_3P$



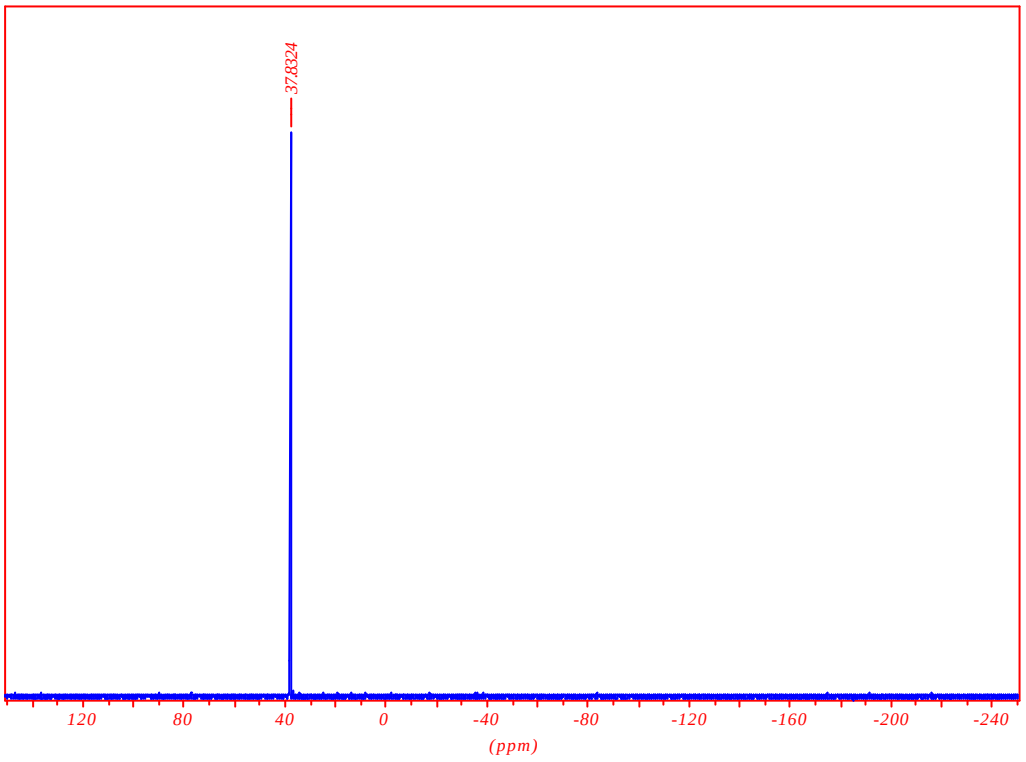
$[R_{F4}(CH_2)_3](NC\text{-}CH_2CH_2)_3P^+I^-$



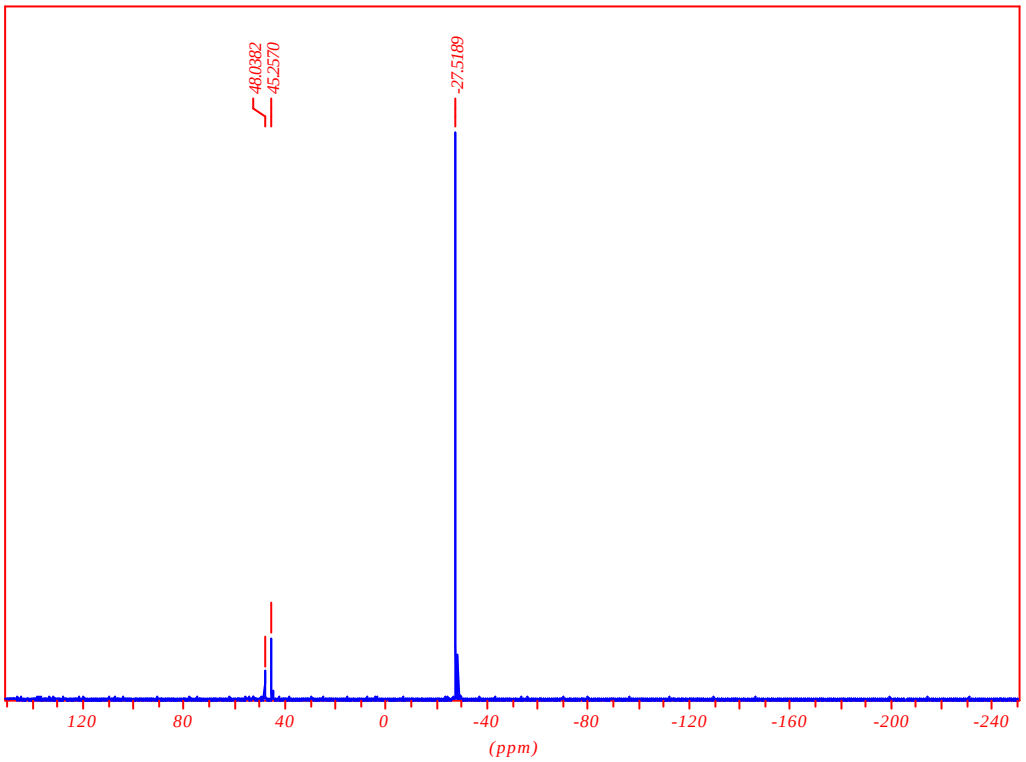
$[R_{F4}(CH_2)_3](NC\text{-}CH_2CH_2)_2P$



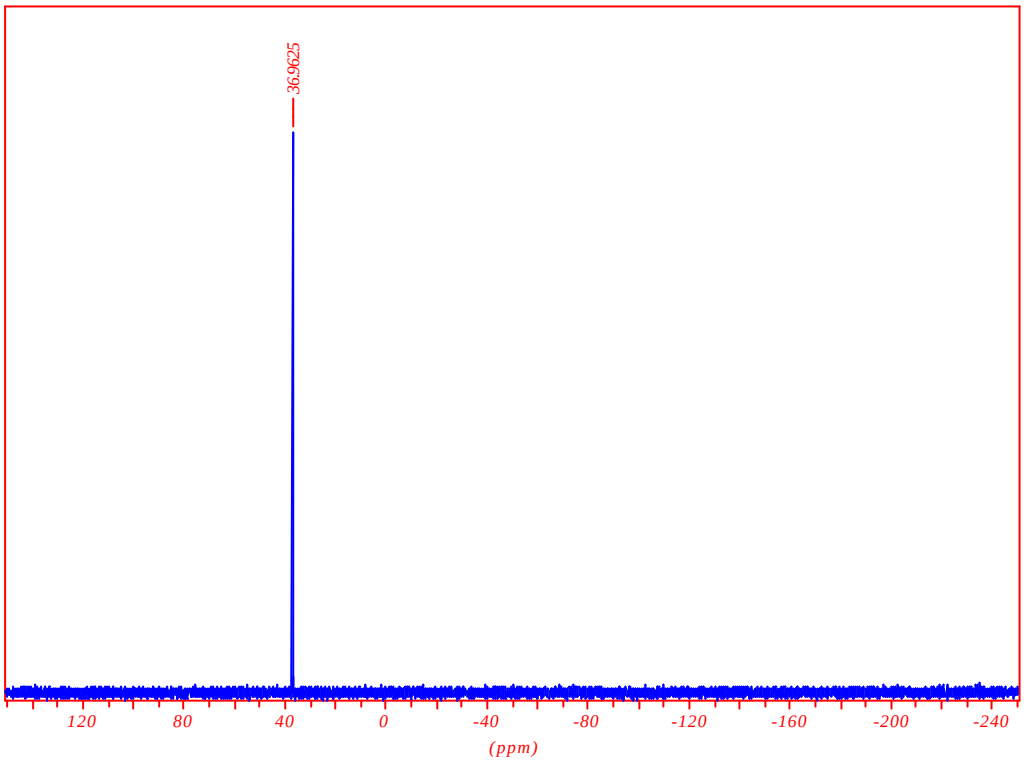
$[R_{F4}(CH_2)_3]_2(NC\text{-}CH_2CH_2)_2P^+I^-$



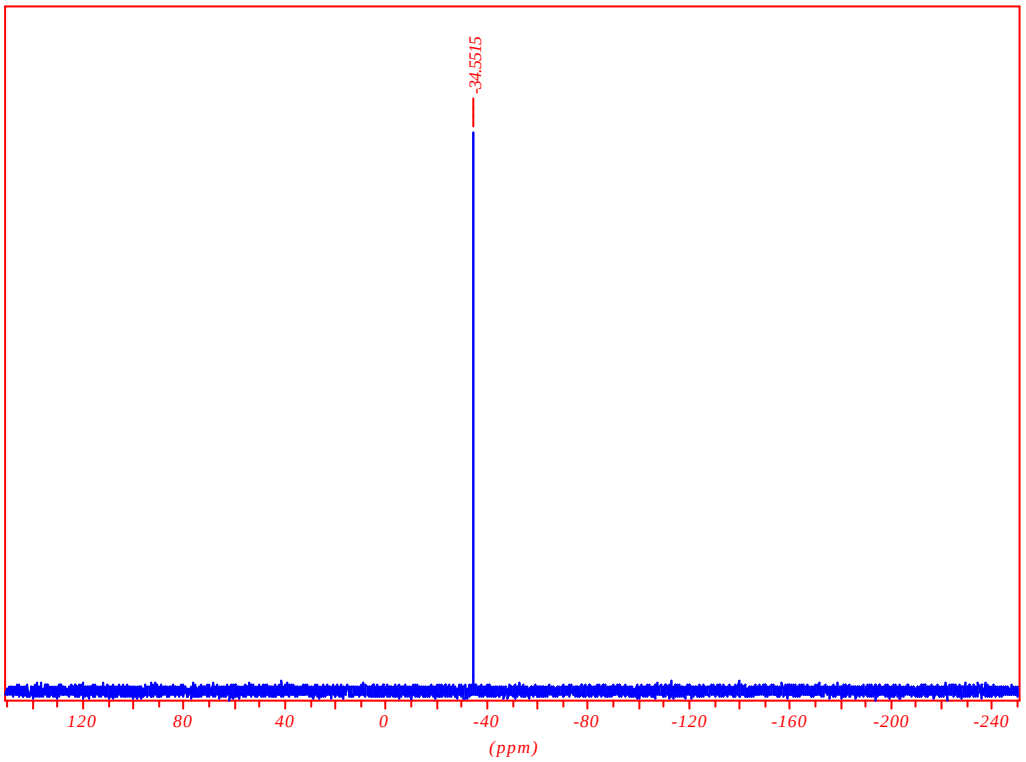
$[R_{F4}(CH_2)_3]_2(NC\text{-}CH_2CH_2)P$



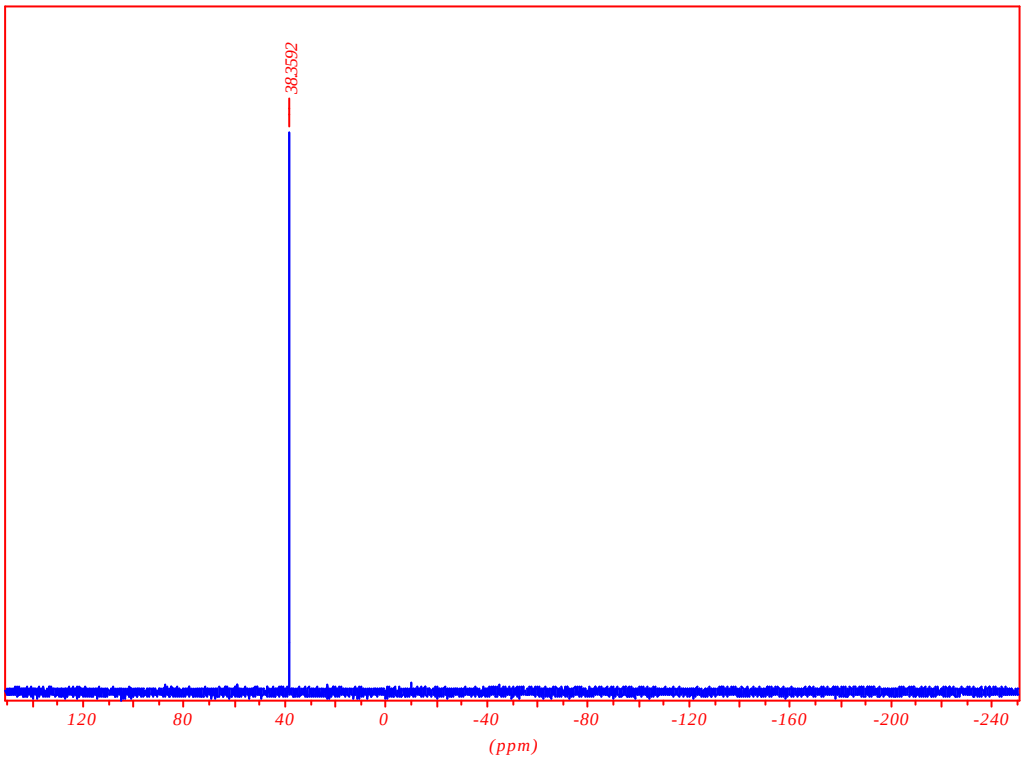
$[R_{F4}(CH_2)_3]_3(NC\text{-}CH_2CH_2)P^+I^-$



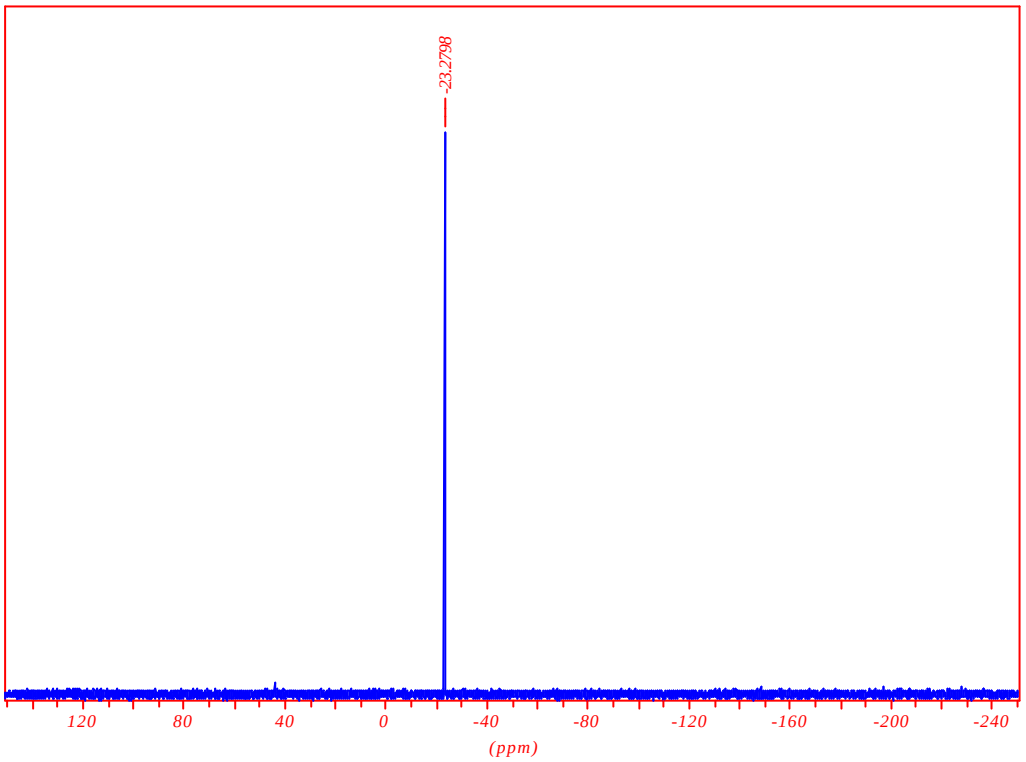
$[R_{F4}(CH_2)_3]_3P$



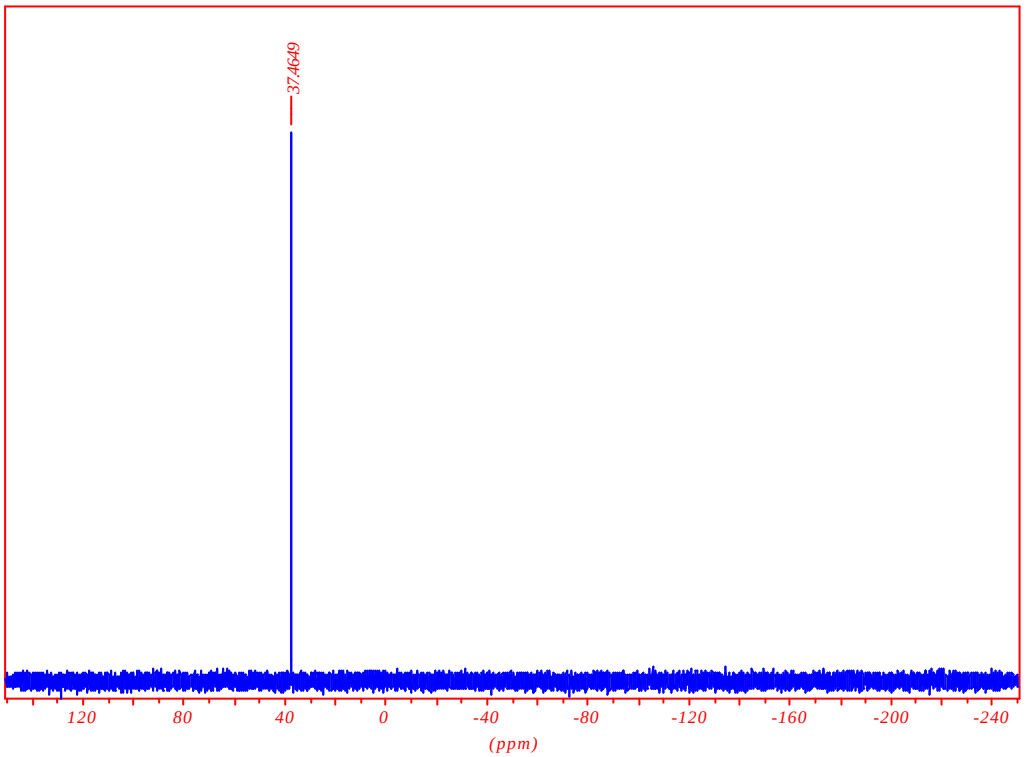
$[R_{F8}(CH_2)_4](NC\text{-}CH_2CH_2)_3P^+I^-$



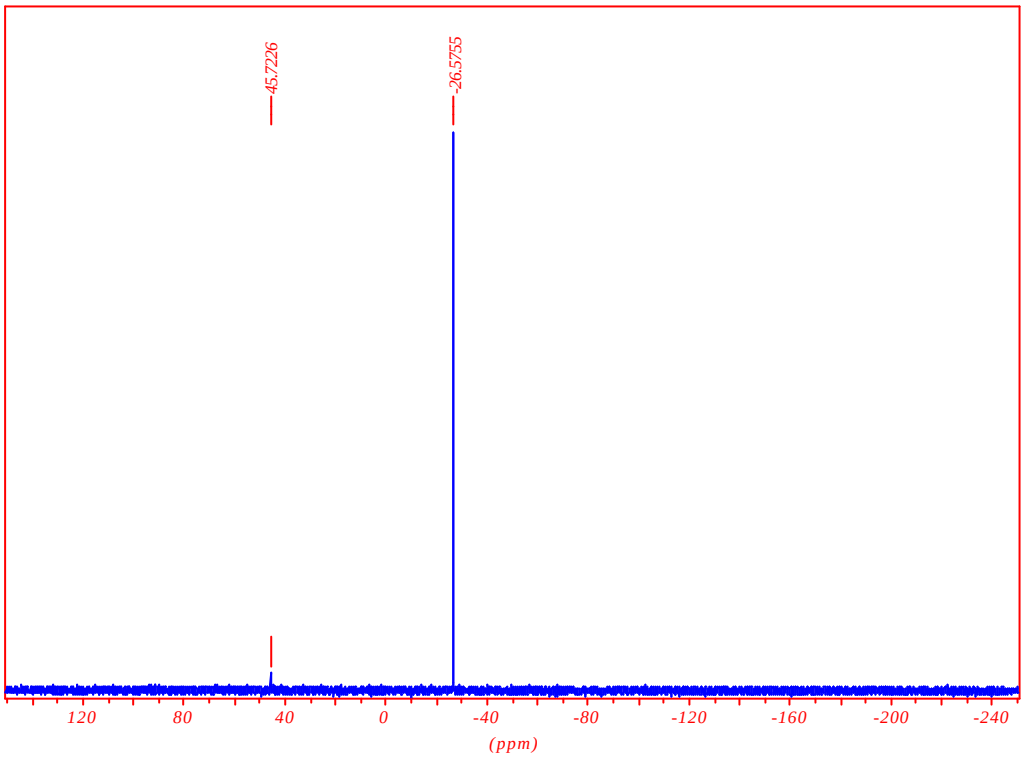
$[R_{F8}(CH_2)_4](NC\text{-}CH_2CH_2)_2P$



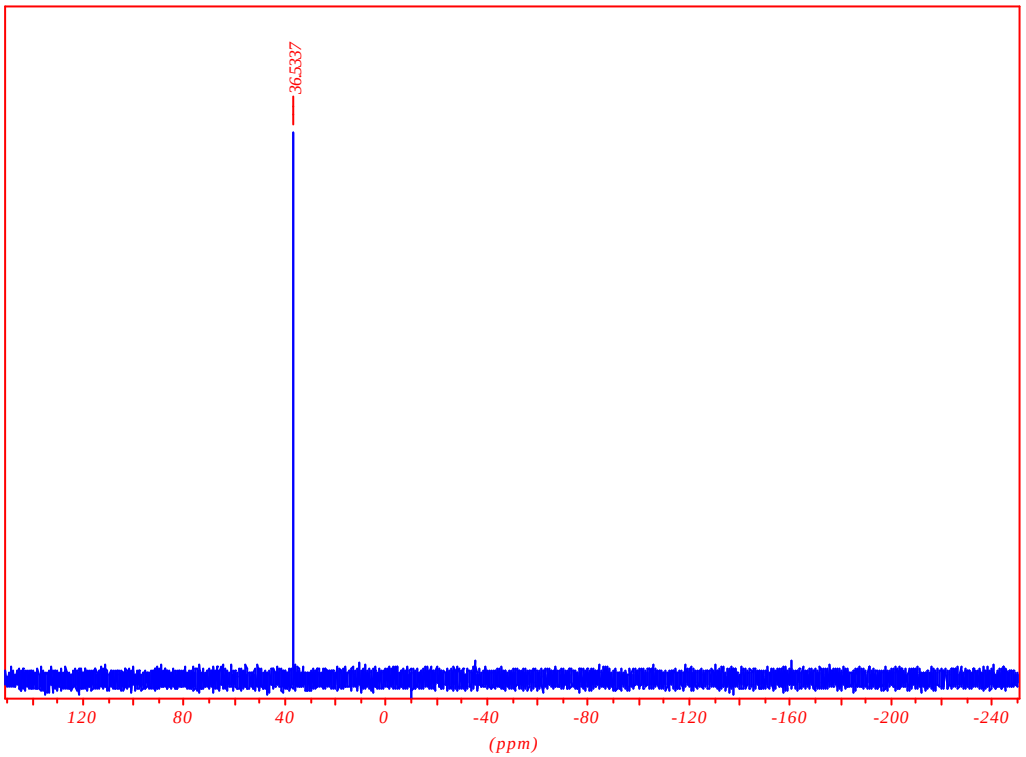
$[R_{F8}(CH_2)_4]_2(NC\text{-}CH_2CH_2)_2P^+I^-$



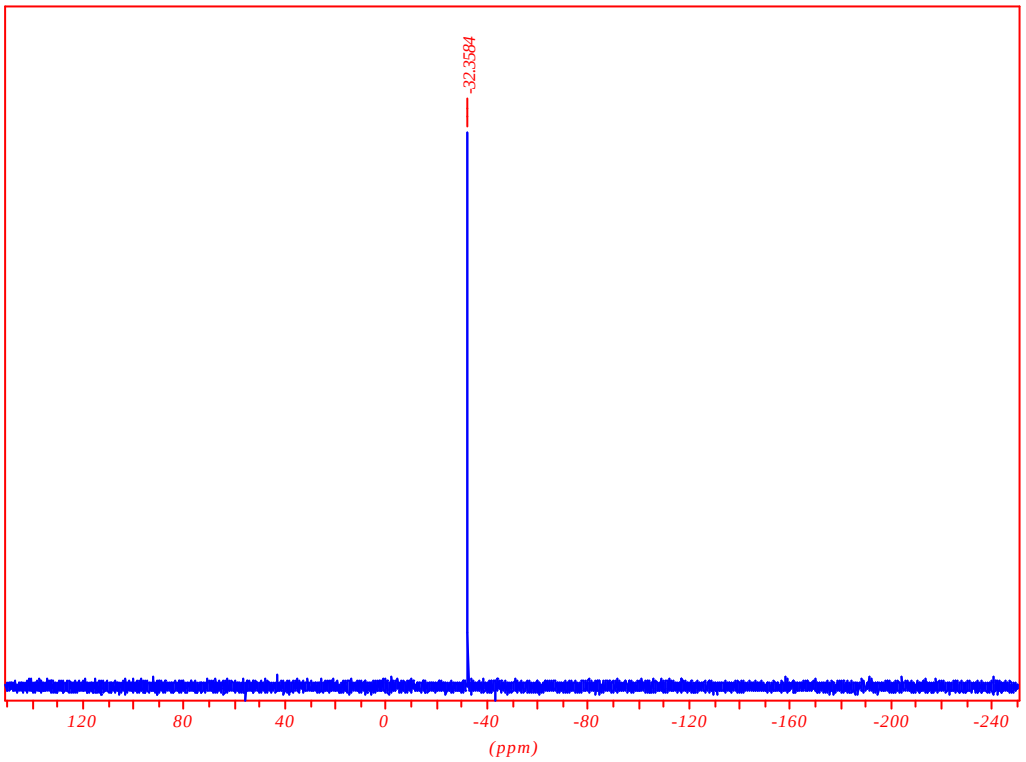
$[R_{F8}(CH_2)_4]_2(NC\text{-}CH_2CH_2)P$



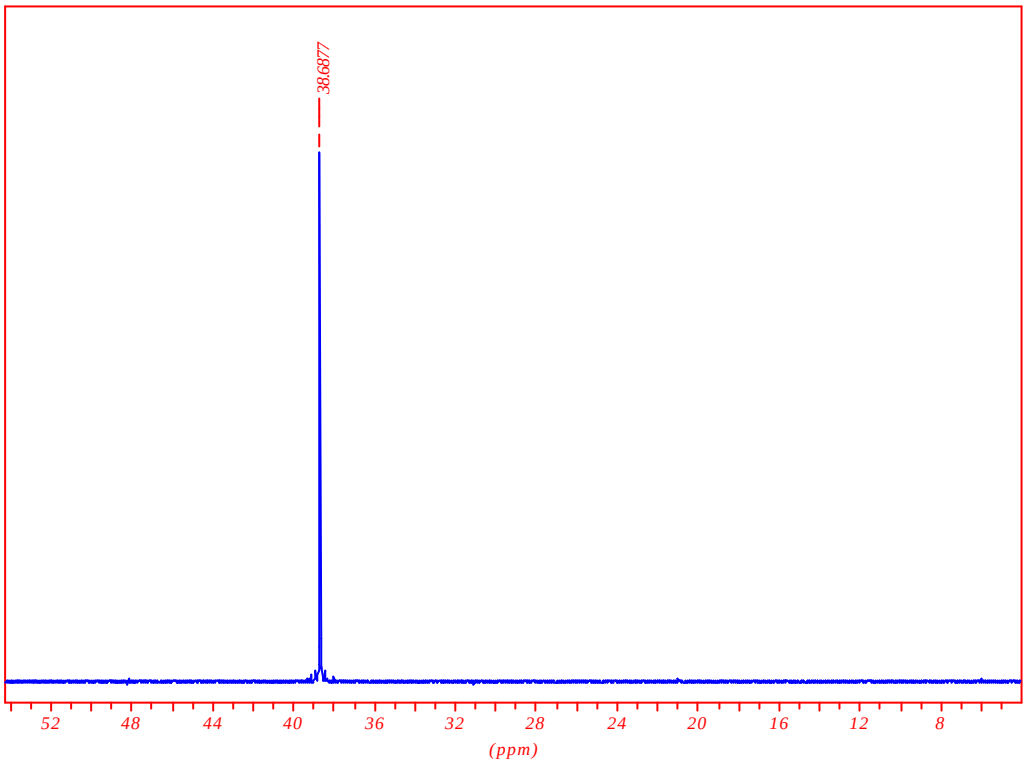
$[R_{F8}(CH_2)_4]_3(NC\text{-}CH_2CH_2)P^+I^-$



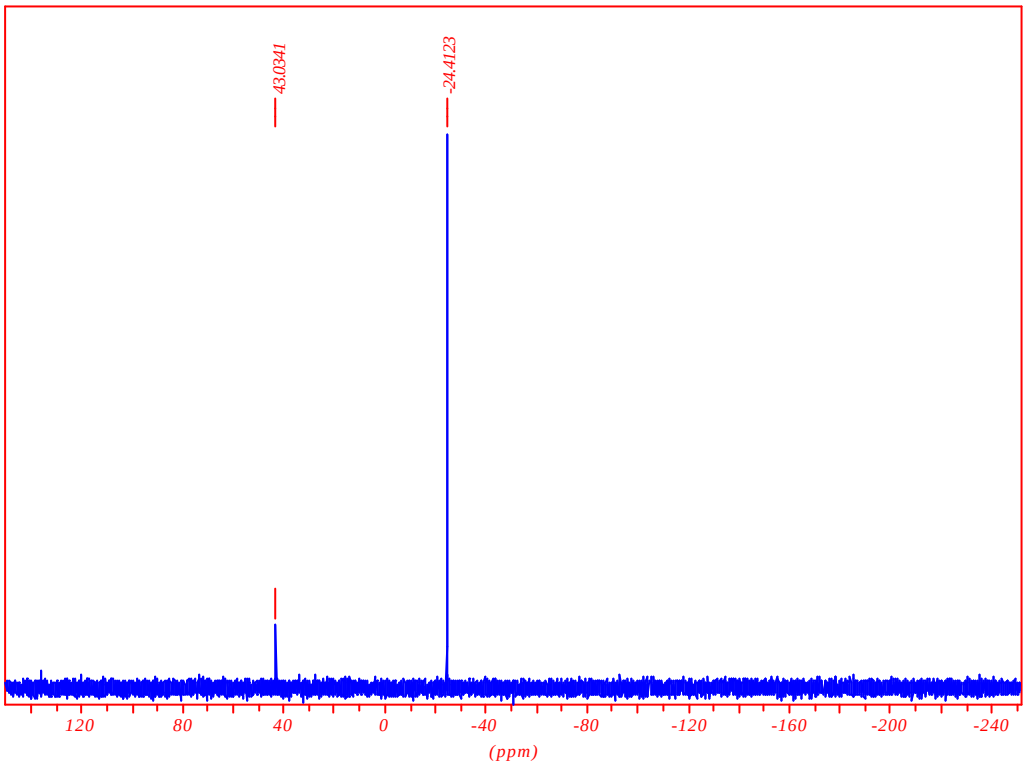
$[R_{F8}(CH_2)_4]_3P$



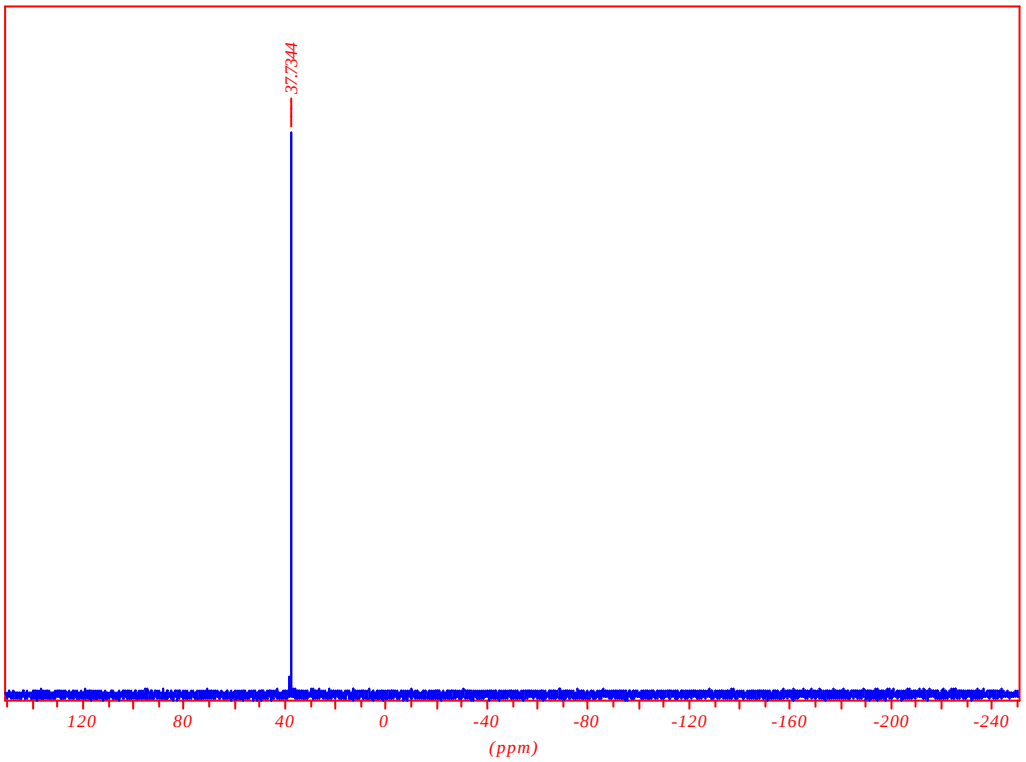
$[R_{F8}(CH_2)_3](NC\text{-}CH_2CH_2)_3P^+I^-$



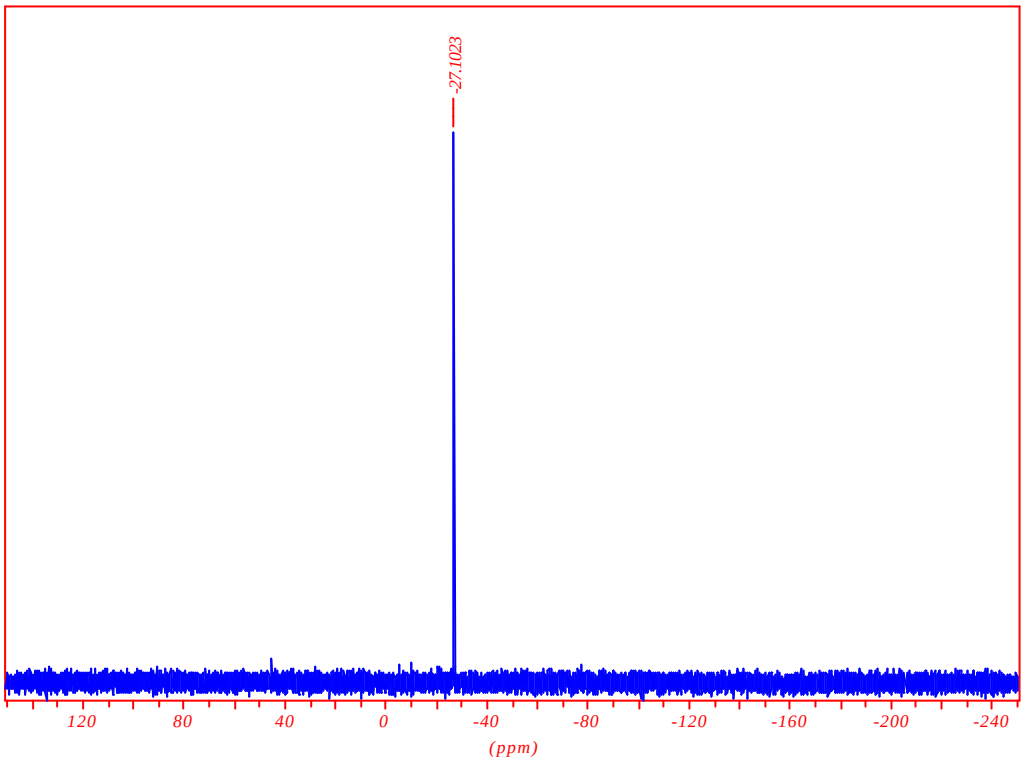
$[R_{F8}(CH_2)_3](NC\text{-}CH_2CH_2)_2P$



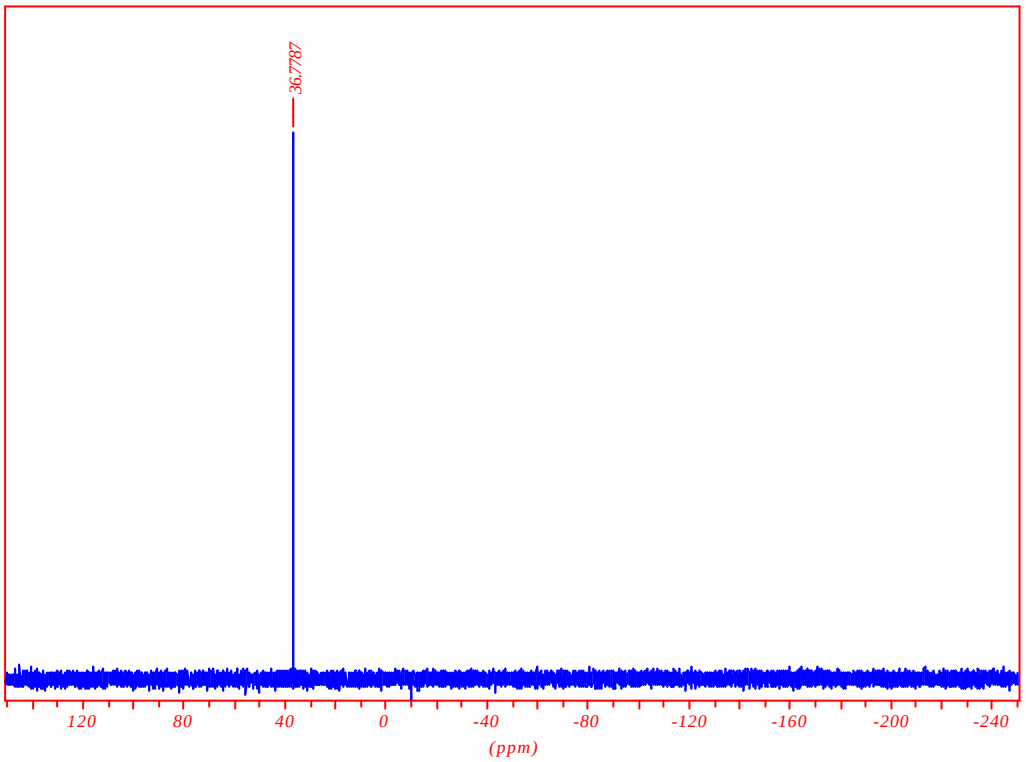
$[R_{F8}(CH_2)_3][R_{F8}(CH_2)_4](NC\text{-}CH_2CH_2)_2P^+I^-$



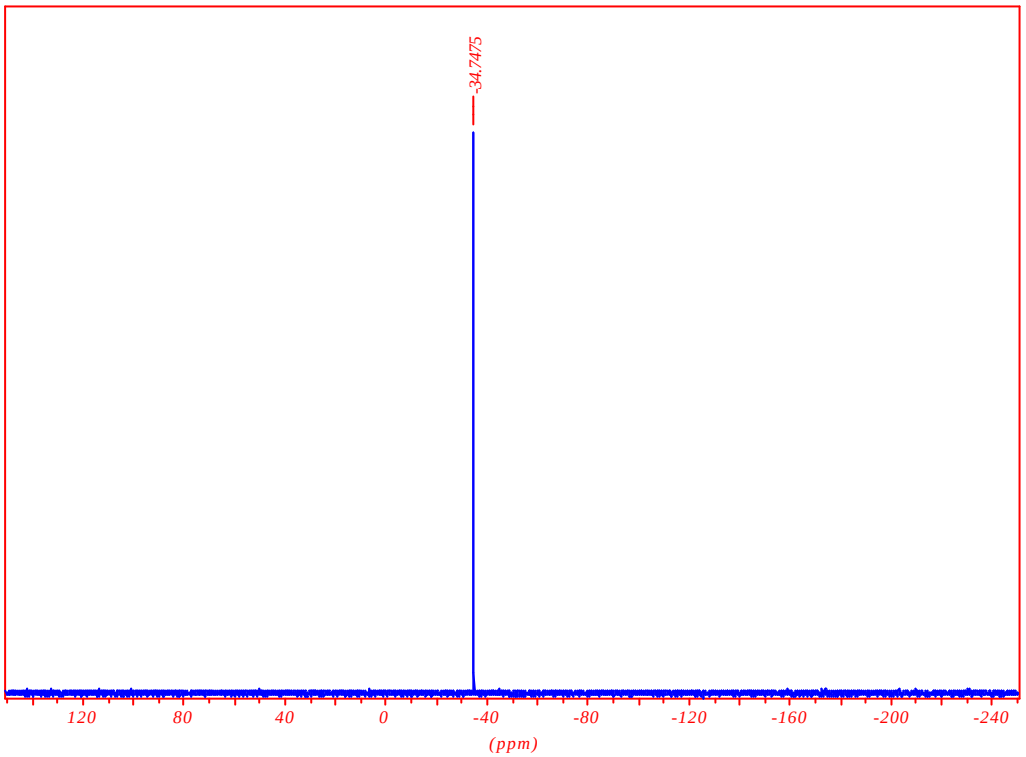
$[R_{F8}(CH_2)_3][R_{F8}(CH_2)_4](NC\text{-}CH_2CH_2)P$



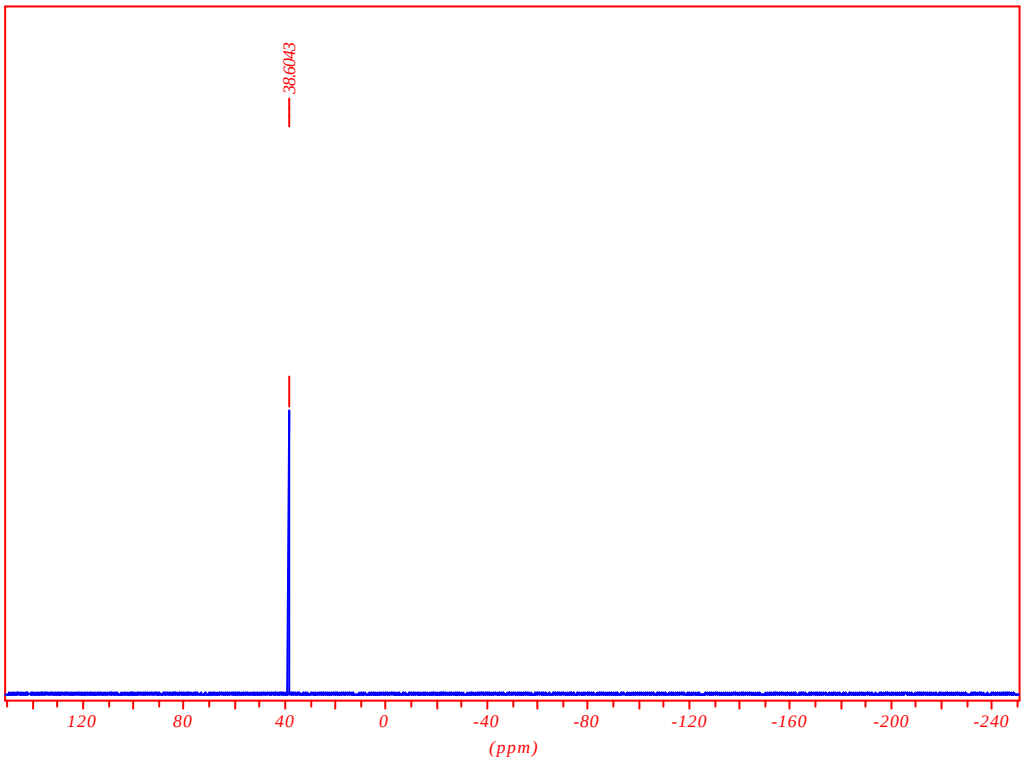
$[R_{F8}(CH_2)_3][R_{F8}(CH_2)_4]_2(NC\text{-}CH_2CH_2)P^+I^-$



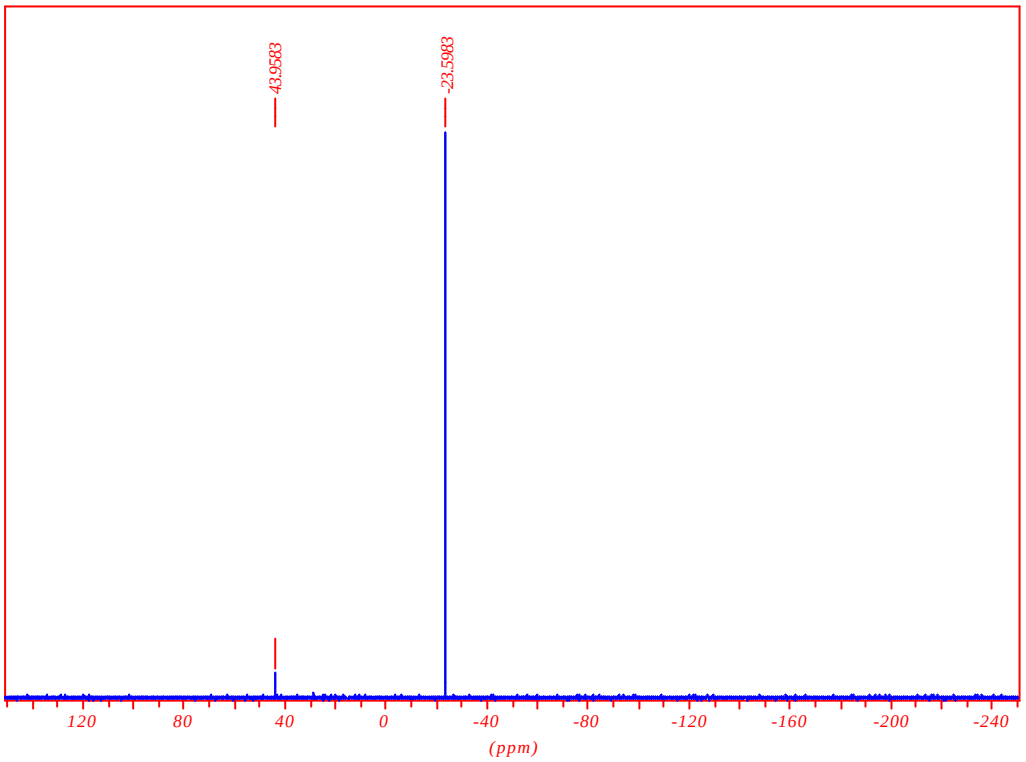
$[R_{F8}(CH_2)_3][R_{F8}(CH_2)_4]_2P$



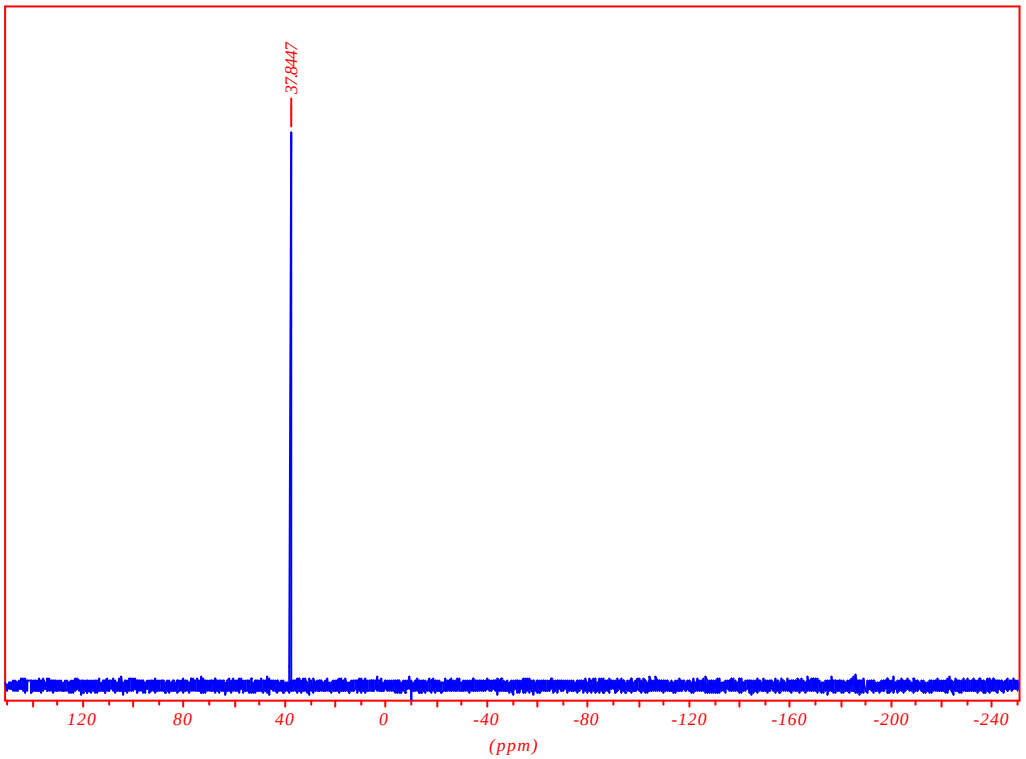
$[R_{F6}(CH_2)_3](NC\text{-}CH_2CH_2)_3P^+I^-$



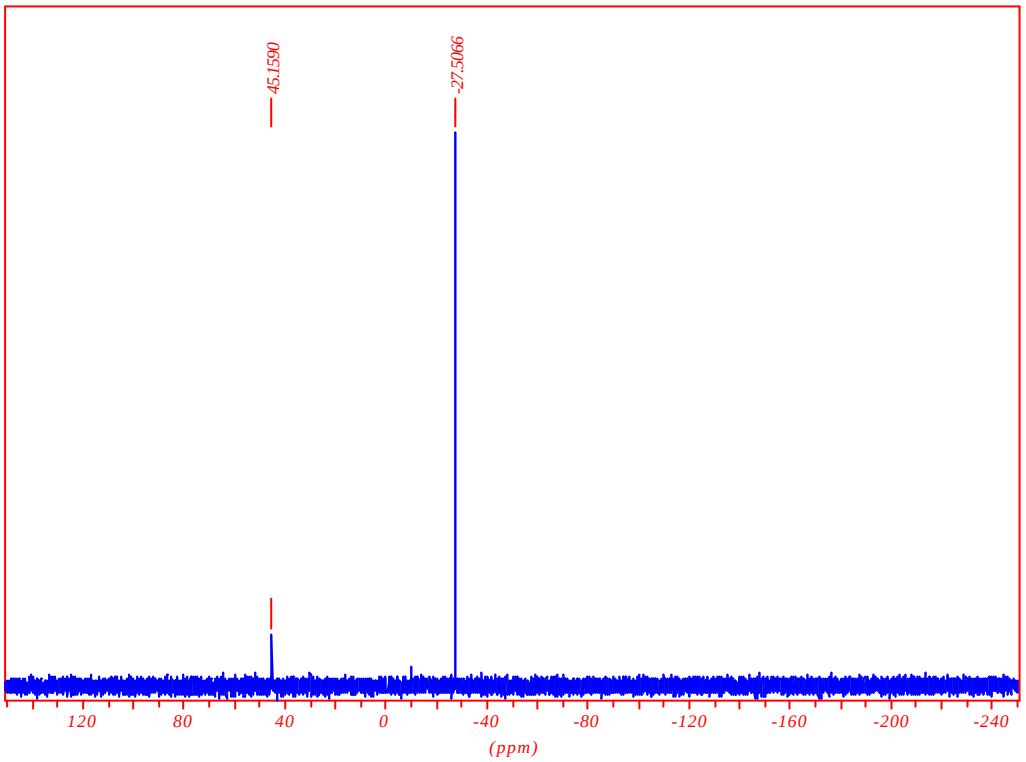
$[R_{F6}(CH_2)_3](NC\text{-}CH_2CH_2)_2P$



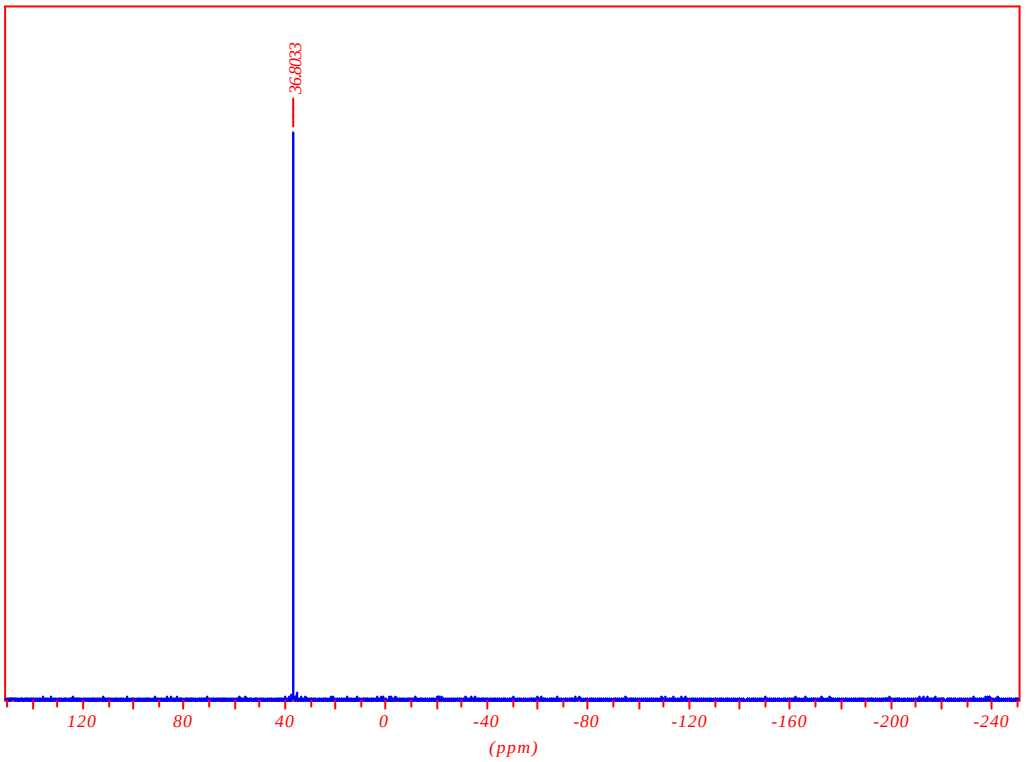
$[R_{F6}(CH_2)_3][R_{F8}(CH_2)_3](NC\text{-}CH_2CH_2)_2P^+I^-$



$[R_{F6}(CH_2)_3][R_{F8}(CH_2)_3](NC\text{-}CH_2CH_2)P$



$[R_{F6}(CH_2)_3][R_{F8}(CH_2)_3][R_{F8}(CH_2)_4](NC\text{-}CH_2CH_2)P^+I^-$



$[R_{F6}(CH_2)_3][R_{F8}(CH_2)_3][R_{F8}(CH_2)_4]P$