Supplementary Material

Synthesis of Fluorous Trialkyl Phosphines with the Complete Exlusion of PH_3

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NMR Data of the Isolated and Purified Compounds

$[C_6H_5][R_{F8}(CH_2)_3]_2P$: ^{1}H-NMR (250 MHz, (FC-72): δ 1.55-1.70 (m, 4H), 1.80-2.05 (m, 4H), 2.20-2.40 (m, 4H), 7.40-7.60 (m, 3H), 7.70-7.80 (m, 2H). $^{31}P\{^1H\}$-NMR (101 MHz, FC-72) δ -27.3 (s). ^{19}F-NMR (235 MHz, (CH_2Cl_2) δ -82.2 (t, 6F), -115.3 (m, 4F), -122.6 (m, 4F), -122.8 (m, 4+4F), -123.5 (m, 4F), -124.4 (m, 4F), -127.2 (m, 4F).

$[C_6H_5][R_{F8}(CH_2)_3]_3P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 2.02-2.21 (m, 6H), 2.50-2.75 (m, 6H), 3.27-3.45 (m, 6H), 7.74-7.87 (m, 2H), 7.88-7.97 (m, 1H), 8.29-8.40 (m, 2H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 32.0 (s). ^{19}F-NMR (235 MHz, $(CD_3)_2CO$) δ -81.2 (t, 9F), -114.7 (m, 6F), -122.2 (m, 6F), -122.5 (m, 6+6F), -123.2 (m, 6F), -123.8 (m, 6F), -126.4 (m, 6F).

$[R_{F8}(CH_2)_3]_3P=O$: ^{1}H-NMR (250 MHz, Freon-113): δ 1.59-1.76 (m, 6H), 1.84-2.07 (m, 6H), 2.12-2.42 (m, 6H). $^{31}P\{^1H\}$-NMR (101 MHz, Freon-113) δ 46.1 (s).

$[R_{F8}(CH_2)_3]_3P$: ^{1}H-NMR (250 MHz, FC-72): δ 1.24-1.40 (m, 6H), 1.55-1.76 (m, 6H), 1.88-2.15 (m, 6H). $^{31}P\{^1H\}$-NMR (101 MHz, FC-72) δ -34.6 (s). ^{19}F-NMR (235 MHz, $(CD_3)_2CO$) δ -82.1 (t, 9F), -115.1 (m, 6F), -122.7 (m, 6F), -122.9 (m, 6+6F), -123.9 (m, 6F), -124.5 (m, 6F), -127.1 (m, 6F).

$[C_6H_5][R_{F6}(CH_2)_3]_2P$: ^{1}H-NMR (250 MHz, (FC-72): δ 1.54-1.70 (m, 4H), 1.76-2.02 (m, 4H), 2.10-2.40 (m, 4H), 7.38-7.55 (m, 3H), 7.65-7.80 (m, 2H). $^{31}P\{^1H\}$-NMR (101 MHz, FC-72) δ -26.9 (s).

$[C_6H_5][R_{F6}(CH_2)_3]_3P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 2.02-2.21 (m, 6H), 2.48-2.75 (m, 6H), 3.28-3.46 (m, 6H), 7.75-7.86 (m, 2H), 7.87-7.97 (m, 1H), 8.28-8.41 (m, 2H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 32.0 (s). ^{19}F-NMR (235 MHz, $(CD_3)_2CO$) δ -82.1 (t, 9F), -115.1 (m, 6F), -122.9 (m, 6F), -123.8 (m, 6F), -124.4 (m, 6F), -127.1 (m, 6F).

$[R_{F6}(CH_2)_3]_3P=O$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 1.88-2.09 (m, 12H), 2.34-2.60 (m, 6H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 45.3 (s).

$[R_{F6}(CH_2)_3]_3P$: ^{1}H-NMR (250 MHz, FC-72): δ 1.02-1.20 (m, 6H), 1.33-1.55 (m, 6H), 1.66-1.95 (m, 6H). $^{31}P\{^1H\}$-NMR (101 MHz, FC-72) δ -34.6 (s).

$[C_6H_5][R_{F4}(CH_2)_3]_2P$: ^{1}H-NMR (250 MHz, (FC-72): δ 1.52-1.68 (m, 4H), 1.73-2.00 (m, 4H), 2.05-2.39 (m, 4H), 7.40-7.62 (m, 3H), 7.66-7.80 (m, 2H). $^{31}P\{^1H\}$-NMR (101 MHz, FC-72) δ -26.6 (s).

$[C_6H_5][R_{F8}(CH_2)_3][R_{F4}(CH_2)_3]_2P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 2.00-2.20 (m, 6H), 2.48-2.76 (m, 6H), 3.29-3.48 (m, 6H), 7.73-7.85 (m, 2H), 7.86-7.96 (m, 1H), 8.31-8.43 (m, 2H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 32.1 (s). ^{19}F-NMR (235 MHz, $(CD_3)_2CO$) δ -82.0 (t, 3F), -82.4 (t, 6F), -114.8 (m, 2F), -115.3 (m, 4F), -122.2 (m, 2F), -122.6 (m, 2+2F), -123.2 (m, 2F), -123.8 (m, 2F), -125.4 (m, 4F), -126.3 (m, 2F), -127.1 (m, 4F).

$[R_{F8}(CH_2)_3][R_{F4}(CH_2)_3]_2P=O$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 1.78-2.12 (m, 12H), 2.18-2.50 (m, 6H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 45.0 (s).

$[R_{F8}(CH_2)_3][R_{F4}(CH_2)_3]_2P$: ^{1}H-NMR (250 MHz, FC-72): δ 1.02-1.22 (m, 6H), 1.25-1.48 (m, 6H),1.57-1.87 (m, 6H). $^{31}P\{^1H\}$-NMR (101 MHz, FC-72) δ -33.5 (s).

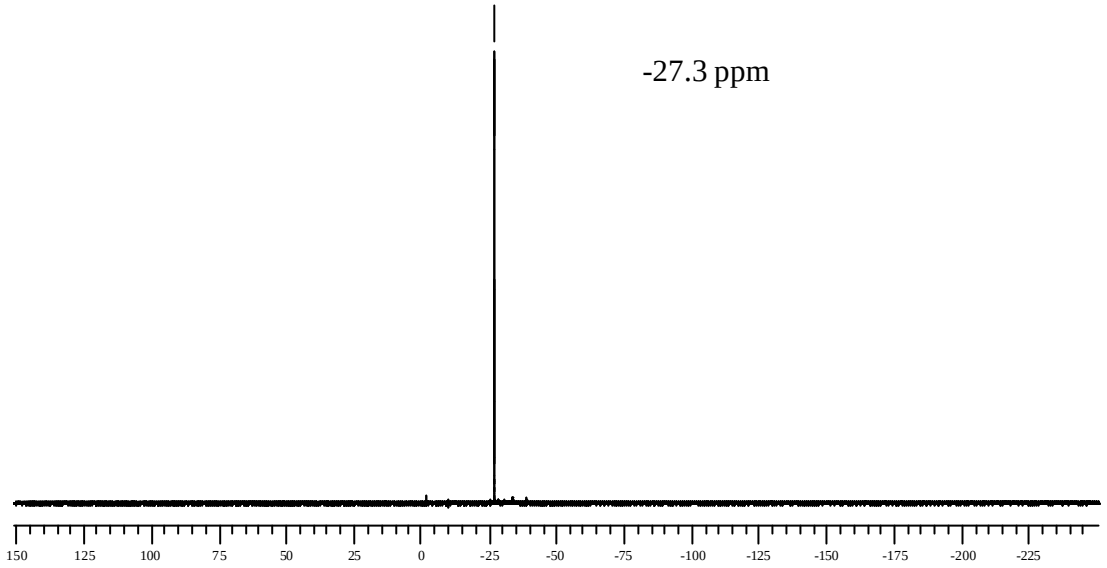
$[C_6H_5][R_{F8}(CH_2)_2]_2P$: ^{1}H-NMR (250 MHz, (FC-72): δ 2.15-2.50 (m, 8H), 7.44-7.56 (m, 3H), 7.68-7.78 (m, 2H). $^{31}P\{^1H\}$-NMR (101 MHz, FC-72) δ -23.3 (s).

$[C_6H_5][R_{F6}(CH_2)_3][R_{F8}(CH_2)_2]_2P^+I^-$: ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 2.10-2.28 (m, 2H), 2.50-3.10 (m, 4+2H), 3.52-3.83 (m, 4+2H), 7.78-7.90 (m, 2H), 7.91-8.02 (m, 1H), 8.37-8.50 (m, 2H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 34.8 (s).

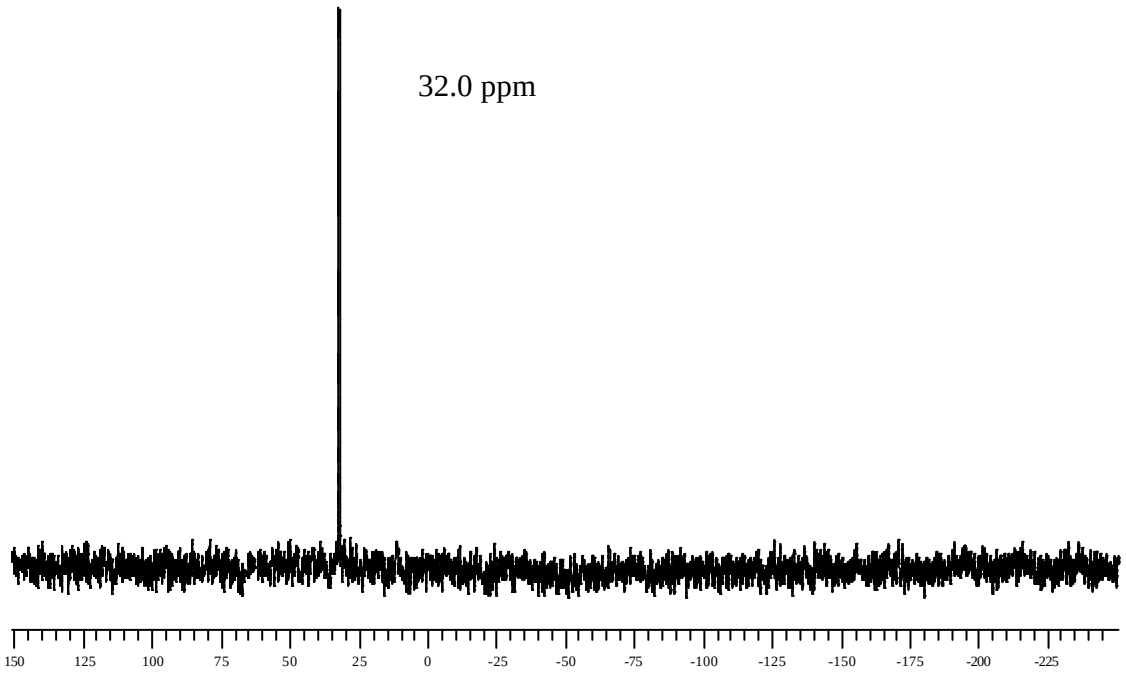
$[R_{F6}(CH_2)_3][R_{F8}(CH_2)_2]_2P=O$: ^{1}H-NMR (250 MHz, FC-72): ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 1.94-2.33 (m, 4+2H), 2.33-2.76 (m, 4+2+2H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ 44.3 (s).

$[R_{F6}(CH_2)_3][R_{F8}(CH_2)_2]_2P$: ^{1}H-NMR (250 MHz, FC-72): ^{1}H-NMR (250 MHz, $(CD_3)_2CO$): δ 1.08-1.24 (m, 2H), 1.25-1.39 (m, 4H), 1.39-1.56 (m, 4H), 1.69-2.00 (m, 4+2H). $^{31}P\{^1H\}$-NMR (101 MHz, $(CD_3)_2CO$) δ -27.8 (s). ^{19}F-NMR (235 MHz, $(CD_3)_2CO$) δ -82.2 (t, 6+3F), -115.1 (t, 4+2F), -122.7 (m, 4F), -122.9 (m, 4+4+2F), -123.9 (m, 4+2F), -124.5 (m, 4+2F), -127.2 (m, 4+2F).

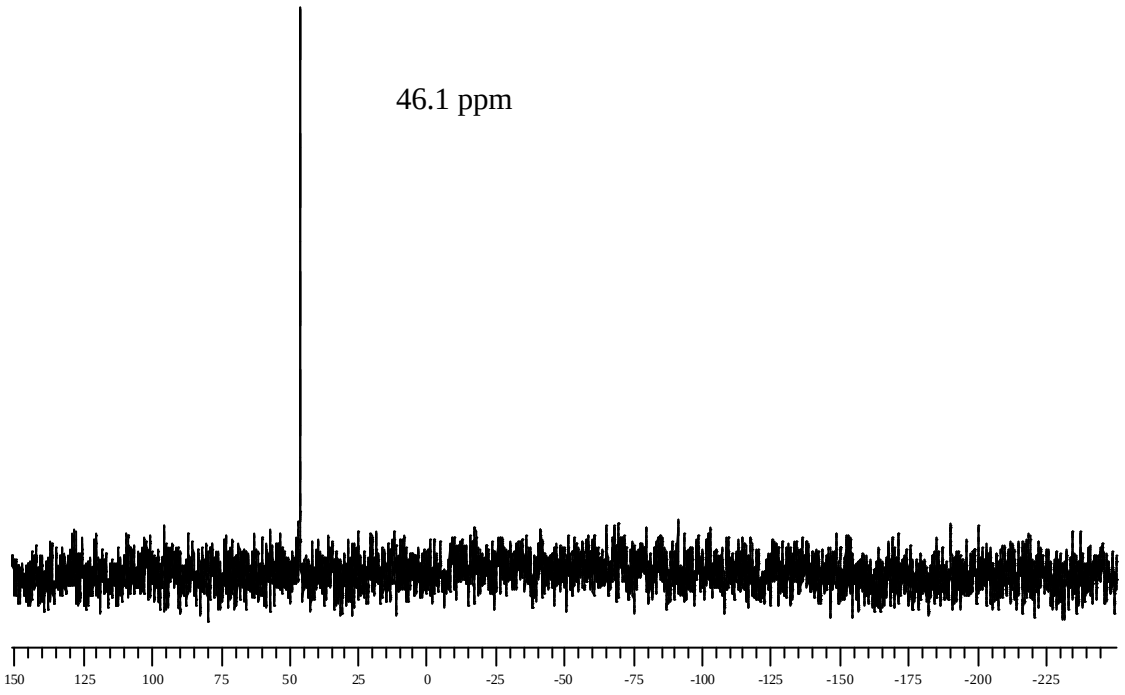
$^{31}P\{^{1}H\}$-NMR spectrum of $[C_6H_5][R_{F8}(CH_2)_3]_2P$



$^{31}P\{^{1}H\}$-NMR spectrum of $[C_6H_5][R_{F8}(CH_2)_3]_3P^+I^-$



$^{31}P\{^{1}H\}$-NMR spectrum of $[R_{F8}(CH_2)_3]_3P=O$



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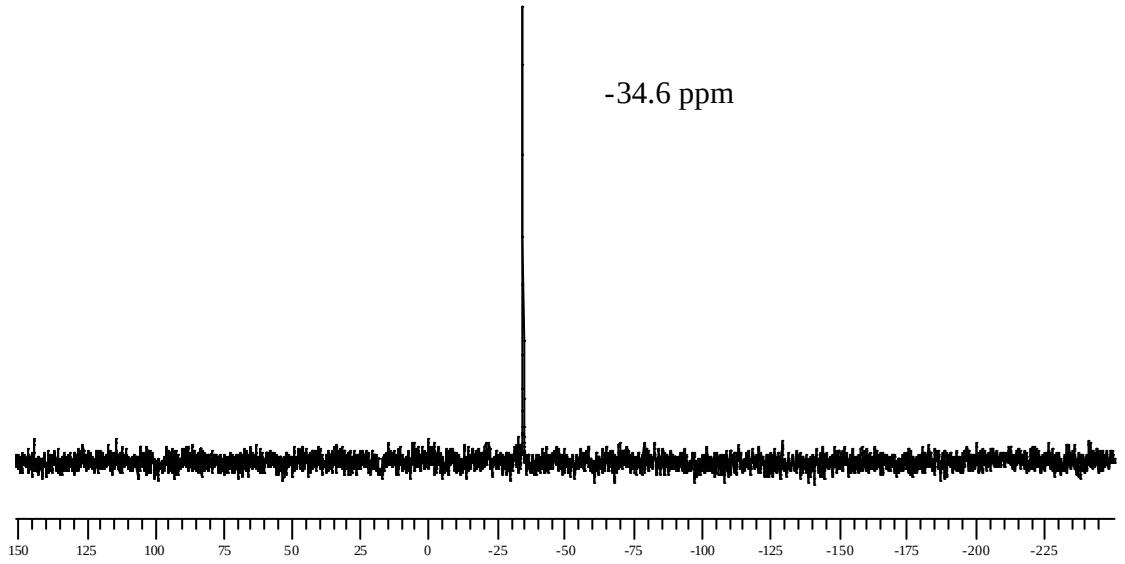

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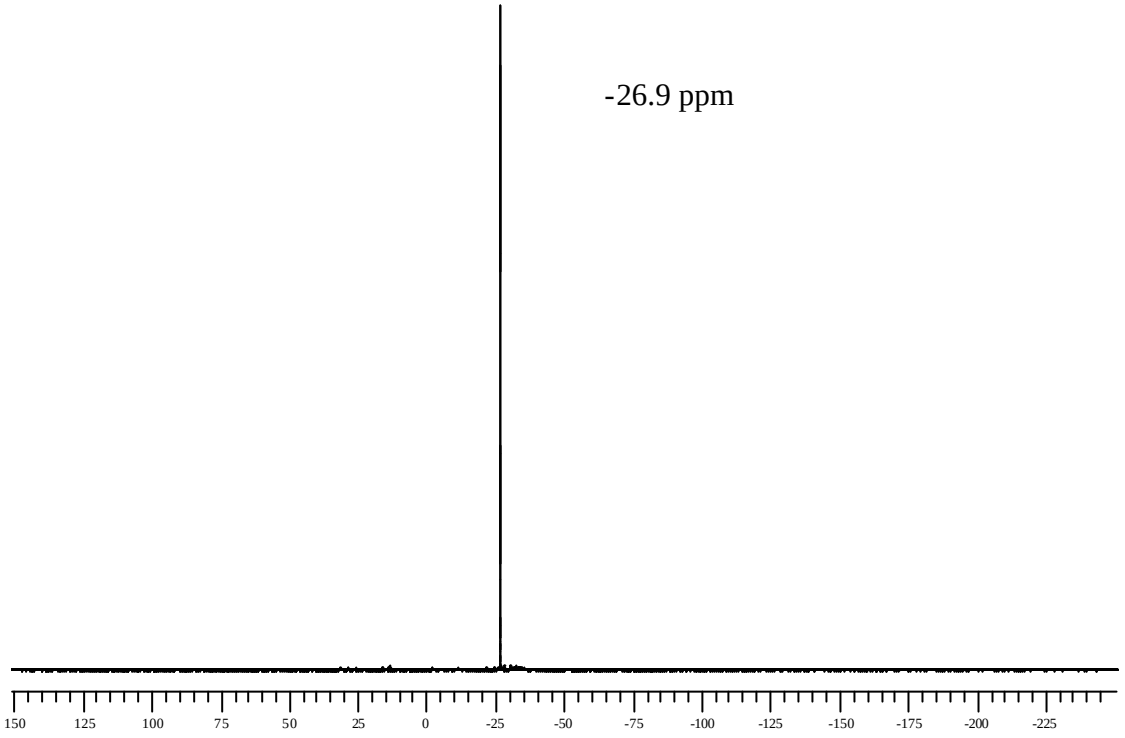

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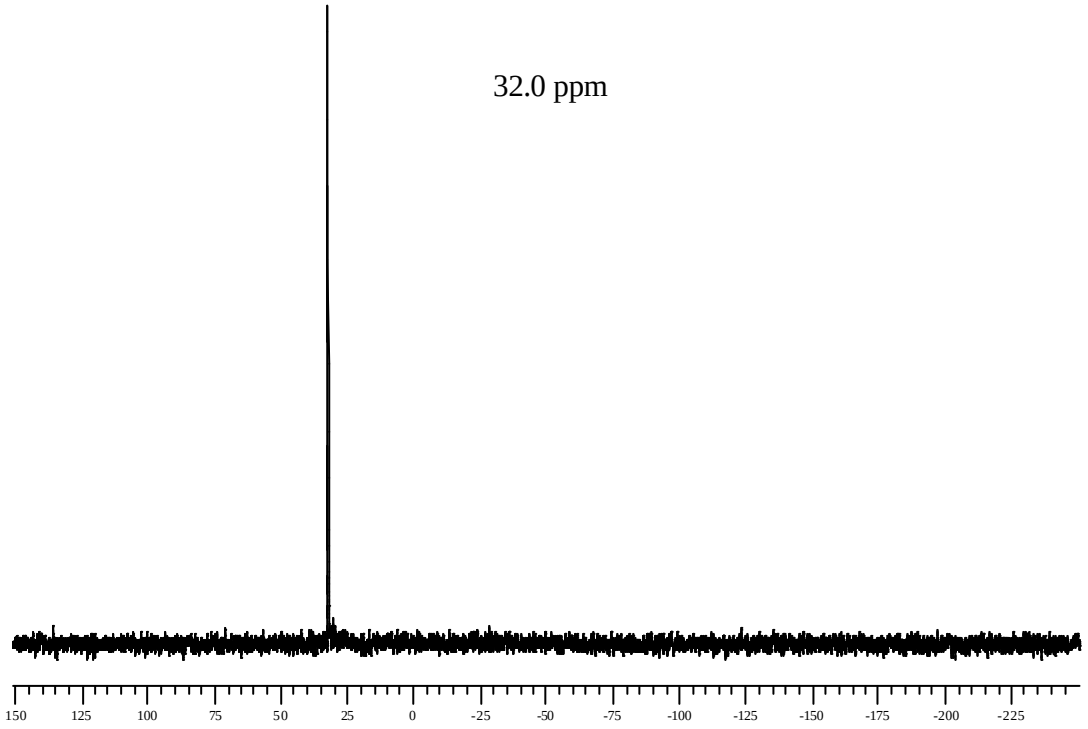
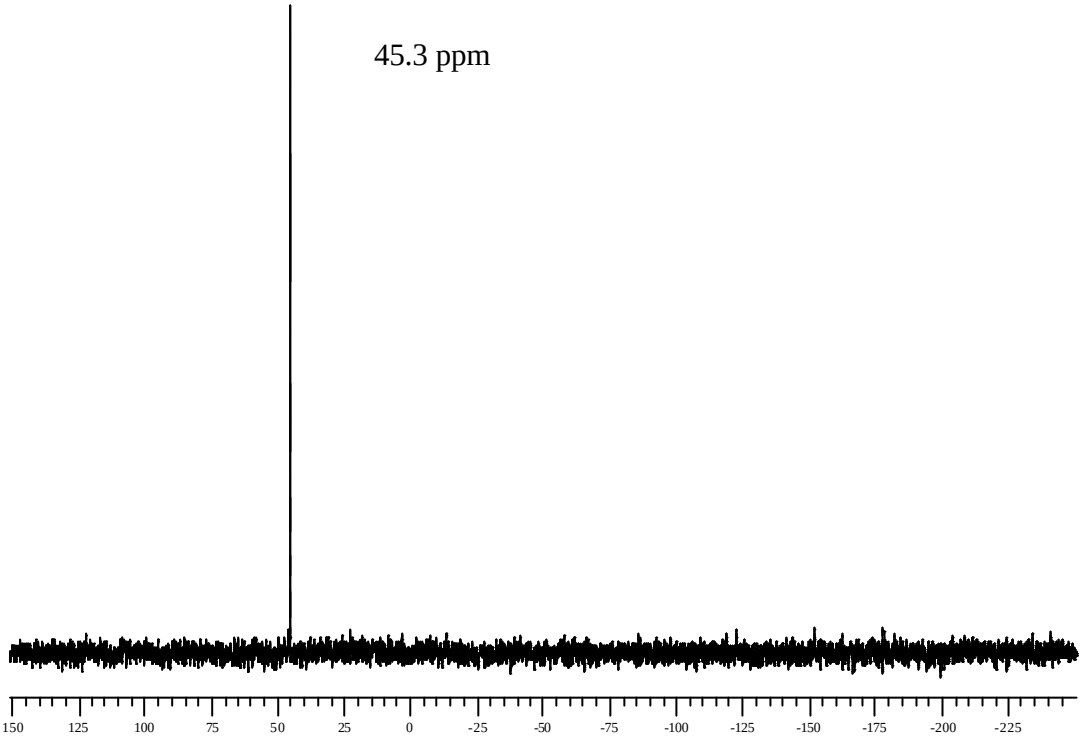
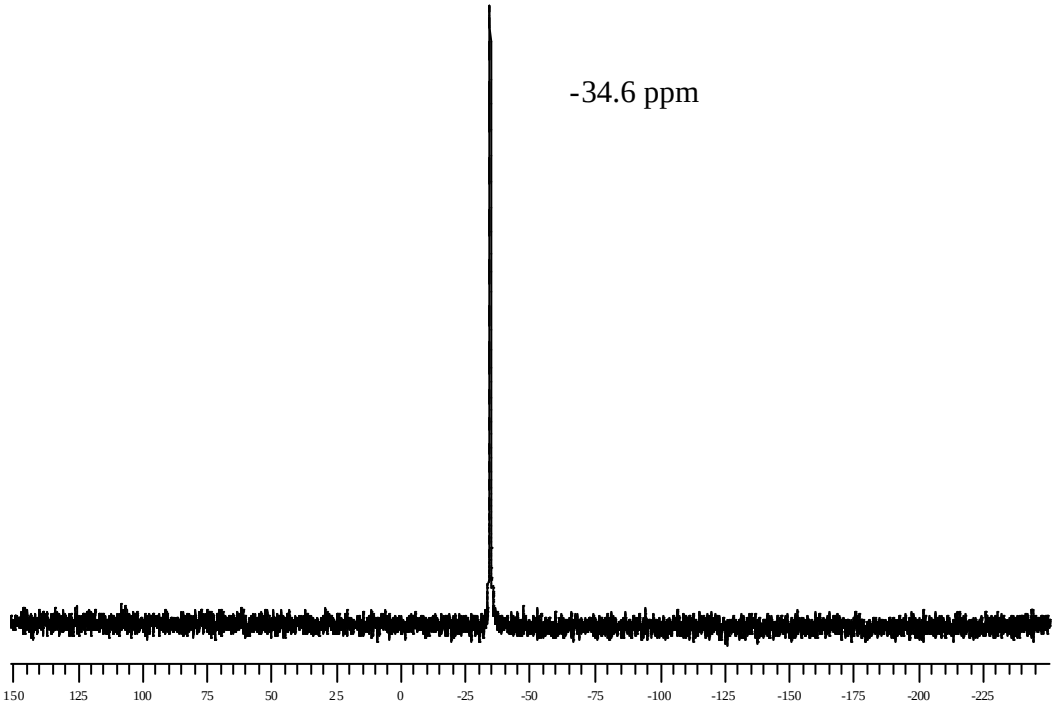


$^{31}P\{^{1}H\}$-NMR spectrum of $[R_{F6}(CH_2)_3]_3P=O$



$^{31}P\{^{1}H\}$-NMR spectrum of $[R_{F6}(CH_2)_3]_3P$



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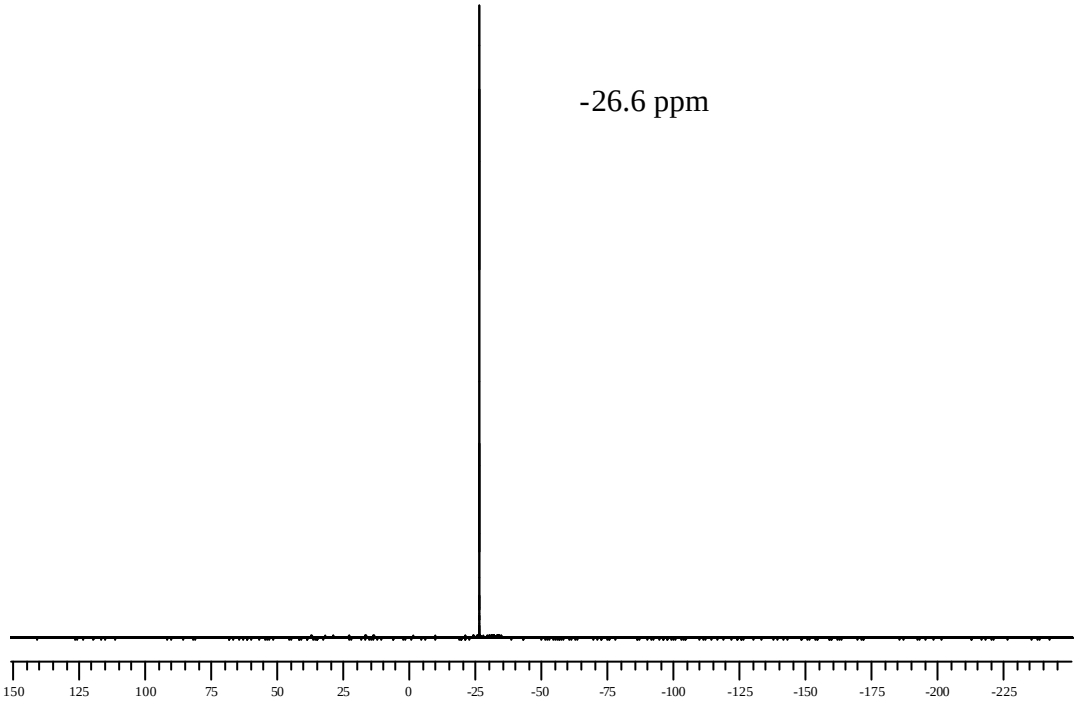

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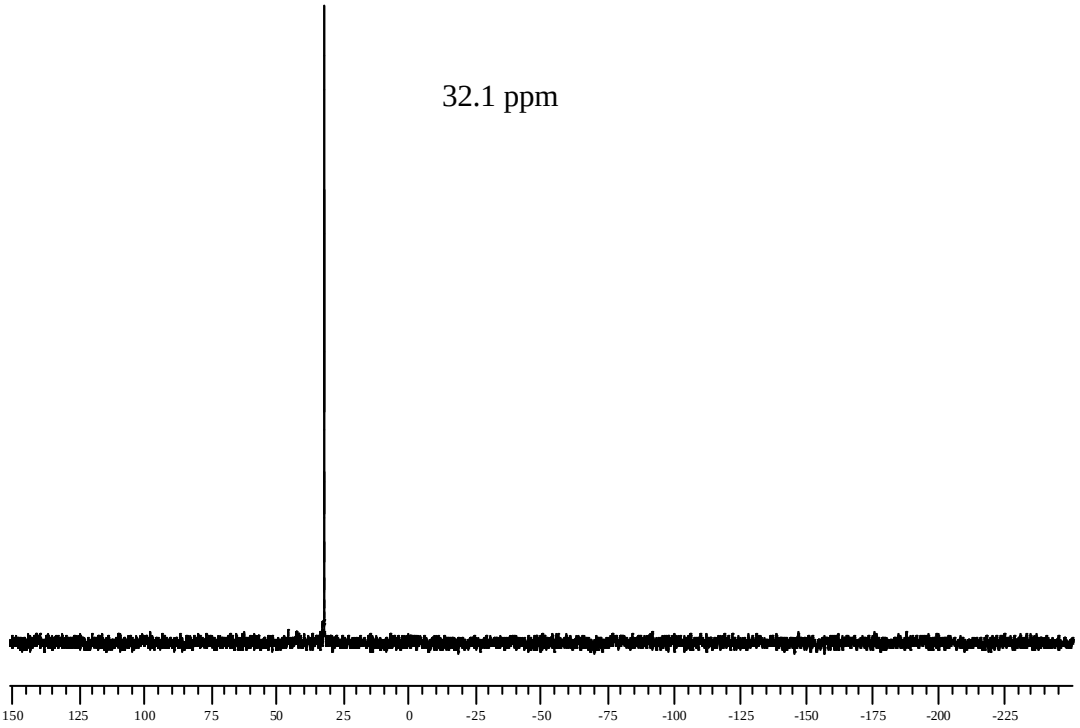
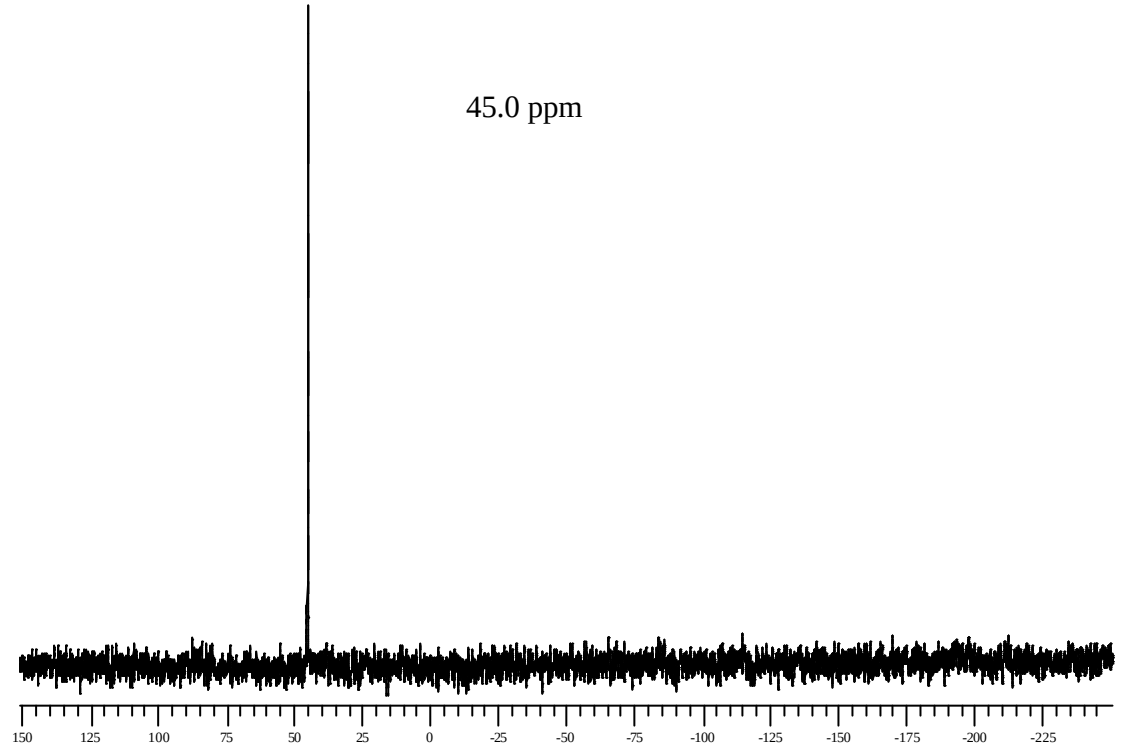
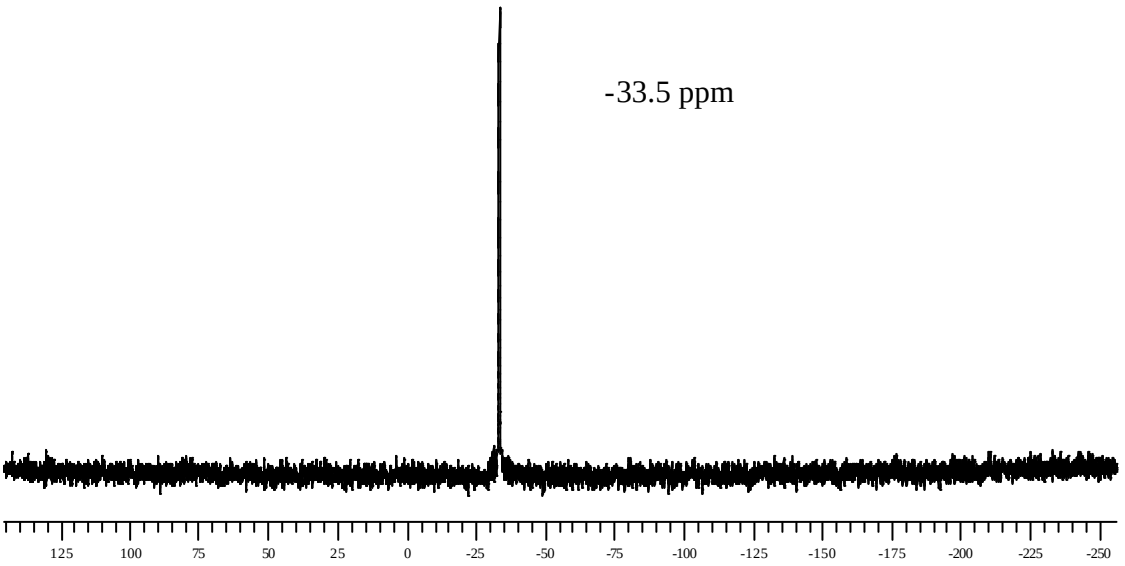


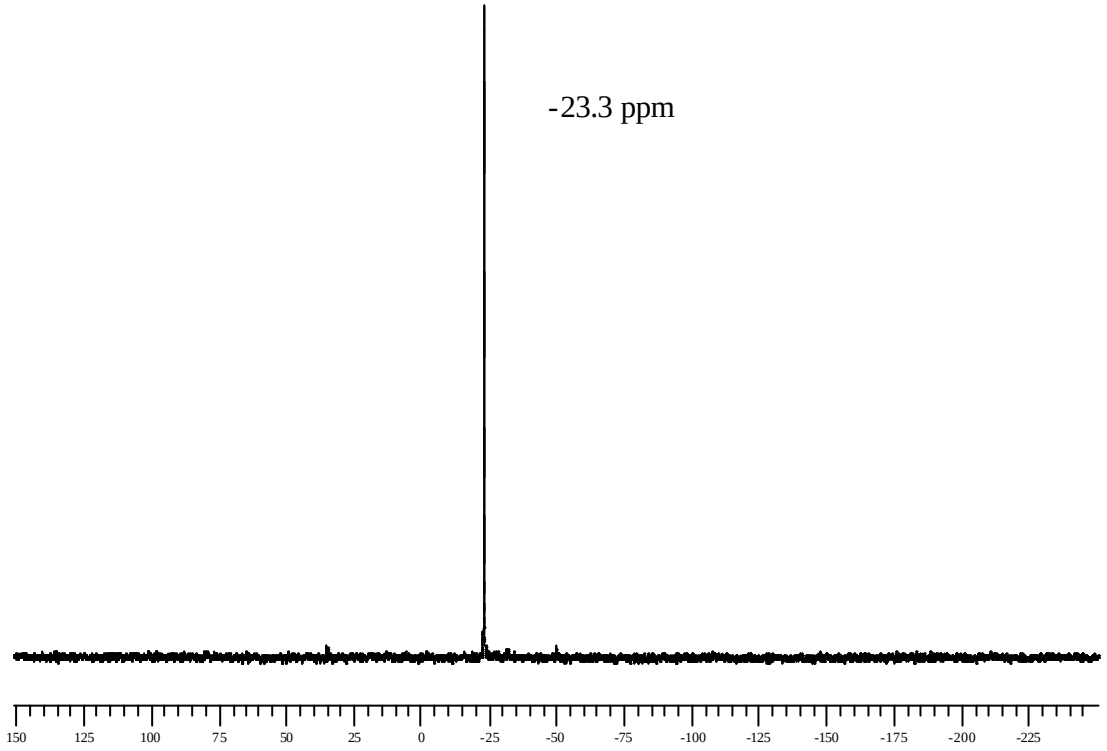
$^{31}P\{^{1}H\}$-NMR spectrum of $[R_{F8}(CH_2)_3][R_{F4}(CH_2)_3]_2P{=}O$



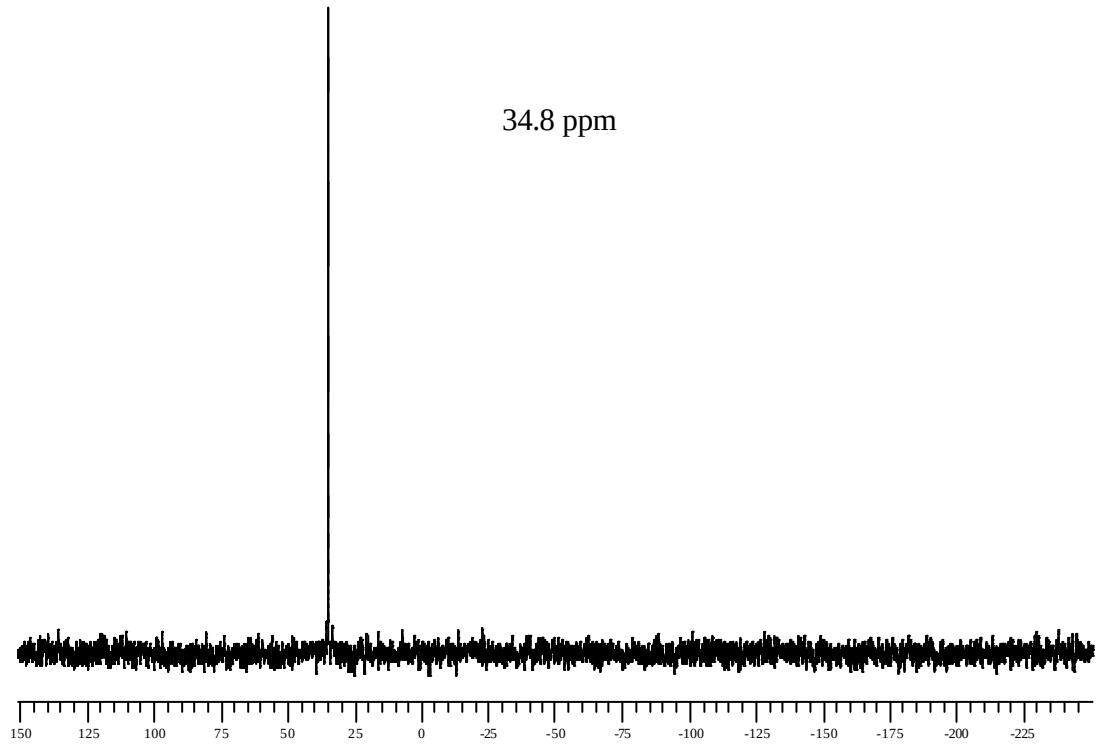
$^{31}P\{^{1}H\}$-NMR spectrum of $[R_{F8}(CH_2)_3][R_{F4}(CH_2)_3]_2P$



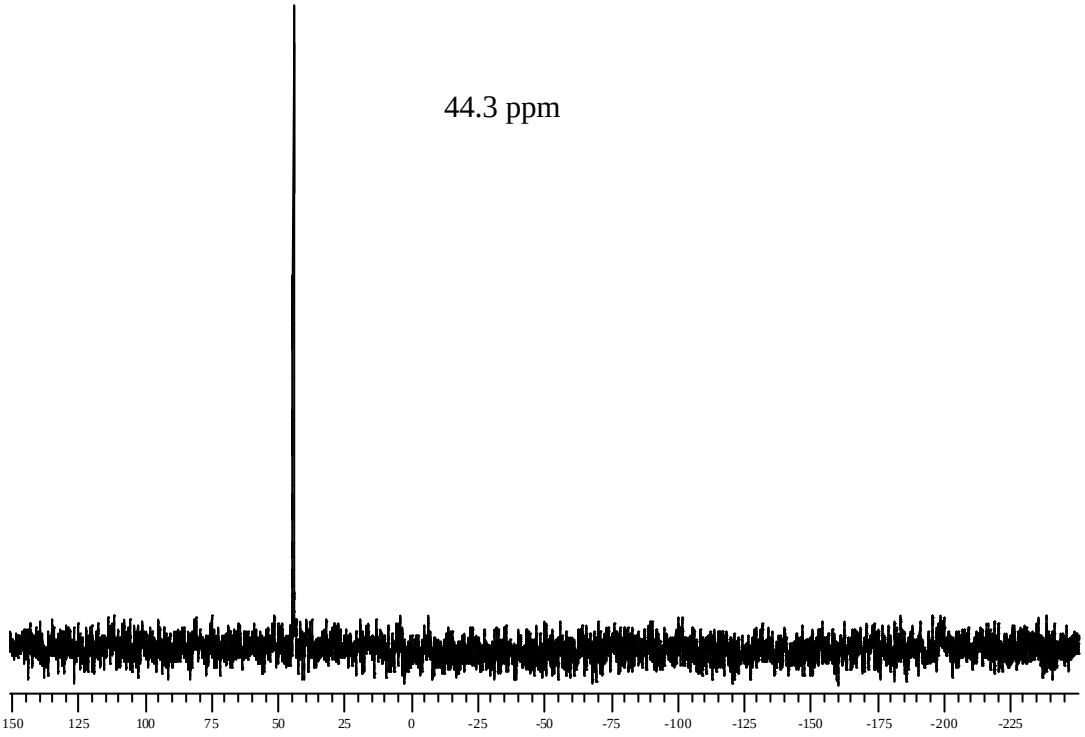
$^{31}P\{^{1}H\}$-NMR spectrum of $[C_6H_5][R_{F8}(CH_2)_2]_2P$



$^{31}P\{^{1}H\}$-NMR spectrum of $[C_6H_5][R_{F6}(CH_2)_3][R_{F8}(CH_2)_2]_2P^{+}I^{-}$



$^{31}P\{^{1}H\}$-NMR spectrum of $[R_{F6}(CH_2)_3][R_{F8}(CH_2)_2]_2P{=}O$



$^{31}P\{^{1}H\}$-NMR spectrum of $[R_{F6}(CH_2)_3][R_{F8}(CH_2)_2]_2P$