Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

The synthesis of tris(perfluoroalkyl)phosphines

Makeba B. Murphy-Jolly, Lesley C. Lewis and Andrew J. M. Caffyn*

Experimental

General

Manipulations were carried out under argon using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents and stored over 4 Å molecular sieves before use. ^{31}P, ^{19}F, ^{13}C and ^{1}H NMR were recorded on a Bruker 400 MHz spectrometer with 85% H_3PO_4, CCl_3F and $SiMe_4$ as external references respectively.

Materials

$P(OPh)_3$ was purchased from Aldrich (3kg, US$103). $PhP(OPh)_2$, Ph_2POPh and $(PhO)_2PCH_2CH_2P(OPh)_2$ were obtained by reaction of $PhPCl_2$ (Strem, 1 kg, US$88), Ph_2PCl (Strem, 1 kg, US$242) and $Cl_2PCH_2CH_2PCl_2$ (Strem, 10 g, US$172) respectively, with phenol in the presence of NEt_3.[1,2] NaOPh was made by reaction of phenol with sodium. Caesium fluoride can be purchased from Apollo (500 g, £130). Tetrabutylammonium triphenyldifluorosilicate (TBAT) was purchased from Aldrich (5 g, US$48.50). $P(OC_6H_4CN)_3$ was made by reaction of PCl_3 with HOC_6H_4CN (Alfa, 100 g, US$70.80) in the presence of NEt_3. The silanes CF_3SiMe_3 (Apollo, 100 g, US$100), $C_2F_5SiMe_3$ (Hansa, 1 g, US$78), $C_3F_7SiMe_3$ (Aldrich, 1 g, US$47.50) are commercially available. We made all the silanes described, from the corresponding perfluoroalkyl iodide and chlorotrimethylsilane in the presence of tetrakis(dimethylamino)ethylene (Lancaster, 50 g, US$30) using Petrov's procedure in 40-75% yields.[3] The cost of the perfluoroalkyl iodides is as follows: CF_3I (Apollo, 500 g, £264), C_2F_5I (Apollo, 500 g, £220), C_3F_7I (Apollo, 100 g, £106), C_4F_9I (Apollo, 100 g, £45) and $C_6F_{13}I$ (Apollo, 500 g, £114).

Synthesis of Ph_2PCF_3

$Ph_2P(OPh)$ (0.049 g, 0.18 mmol) was added to a mixture of dried CsF (0.016 g, 0.1 mmol) in ether (0.4 ml) under argon in an NMR tube. CF_3SiMe_3 (0.038 g, 0.27 mmol) was added, and the reaction closed and sealed. The reaction was monitored by ^{31}P NMR, which showed quantitative yield on completion. ^{31}P NMR: δ 1.7 (q, $^{2}J_{PF}$ =

74 Hz) [lit.[4] ($CDCl_3$) 2.7 (q, ${}^2J_{PF}$ = 73 Hz)]. ^{19}F NMR: δ -56.8 (d, ${}^2J_{PF}$ = 74 Hz) [lit.[4] ($CDCl_3$) -55.3 (d, ${}^2J_{PF}$ = 73 Hz)].

General procedure for the synthesis of $PhP(CF_3)_2$ and $PhP(C_2F_5)_2$

$PhP(OPh)_2$ (0.2 mmol) was added to a mixture of dried CsF (0.1 mmol) in ether (0.4 ml) under argon in an NMR tube. R_fSiMe_3 ($R_f = CF_3, C_2F_5$) (0.54 mmol) was added, and the reaction closed and sealed. The reaction was monitored by ^{31}P NMR, which showed 90% yield on completion. **$PhP(CF_3)_2$:** ^{31}P NMR: δ 3.4 (septet, ${}^2J_{PF}$ = 80 Hz) [lit.[4] ($CDCl_3$) 0.7 (septet, ${}^2J_{PF}$ = 80 Hz)]. ^{19}F NMR: δ -51.8 (d, ${}^2J_{PF}$ = 83 Hz) [lit.[4] ($CDCl_3$) -53.3 (d, ${}^2J_{PF}$ = 80 Hz)]. **$PhP(C_2F_5)_2$:** ^{31}P NMR: δ 3.3 (br, m) [lit.[5] (C_6D_6) 3.5 (m)]. ^{19}F NMR: δ -79.3 (d, ${}^3J_{PF}$ = 17 Hz, CF_3); -108.6 (d, ${}^2J$ = 54 Hz, CF_2) [lit.[5] (C_6D_6) -79.63 (d, ${}^3J_{PF}$ = 18 Hz, CF_3); -108.7, -108.9 (AB portion of ABX spin system, ${}^2J_{FF}$ ~ 300 Hz, ${}^2J_{PF}$(A) = 63 Hz, ${}^2J_{PF}$(B) = 35 Hz, CF_2)].

General procedure for the synthesis of $P(C_3F_7)_3$ and $P(C_6F_{13})_3$

$P(OC_6H_4CN)_3$ (0.23mmol) was added to dried CsF (0.70mmol) in a 1:1 mixture of benzonitrile/ether (0.6 ml) under argon in an NMR tube. R_fSiMe_3 ($R_f = C_4F_9, C_6F_{13}$) (0.70mmol) was added. The reaction was exothermic and a separate layer of product was observed almost immediately. This was separated by syringe to give crude product. **$P(C_3F_7)_3$:** ^{31}P NMR: δ 21.6 (m) [lit.[6] 23.3(m)]. ^{19}F NMR: δ -79.6 (s); -101.1 (d, ${}^3J_{PF}$ = 38 Hz); -120.5 (d, ${}^2J_{PF}$ = 34 Hz) [lit.[6] -81.0 (s); -103.2 (d, ${}^2J_{PF}$ = 37 Hz); -122.7 (d, ${}^3J_{PF}$ = 30 Hz)]. **$P(C_6F_{13})_3$:** ^{31}P NMR: δ 27.9 (br) [lit.[6] 25.0 (m)]. ^{19}F NMR: δ -78.1 (s, CF_3); -98.1(d, ${}^2J_{PF}$ = 34 Hz, PCF_2); -114.1 (d, ${}^3J_{PF}$ unresolved, CF_2); -118.4(s); -119.4 (s); -123.1 (s) [lit.[6] -83.2 (s); -102.8 (d, ${}^2J_{PF}$ = 25 Hz); -118.8 (d, ${}^3J_{PF}$ = 11 Hz); -123.2 (s); 124.3 (s); -128.0 (s)].

General procedure for the synthesis of $(CF_3)_2PCH_2CH_2P(CF_3)_2$ and $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$

R_fSiMe_3 ($R_f = CF_3, C_2F_5$) (0.6mmol) was added to a mixture of dried CsF (0.3mmol), $(PhO)_2PCH_2CH_2P(OPh)_2$ (0.15mmol) and ether (0.5 ml) in an NMR tube. The mixture was shaken intermittently and allowed to stand overnight. The reaction was monitored by ^{31}P NMR, which showed 95% ($R_f = CF_3$) and 90% yield ($R_f = C_2F_5$) on completion. **$(CF_3)_2PCH_2CH_2P(CF_3)_2$:** ^{31}P NMR: δ -1.0 (m) [lit.[7] -3.2 (m)]. ^{19}F NMR: δ -54.5 (d, $^2J_{PF}$ = 83 Hz) [lit.[8] -54.9 (d, $^2J_{PF}$ = 74 Hz)]. **$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$:** ^{31}P NMR: δ 6.41 (m) [lit.[9] (C_6D_6) 7.4 (m)]. ^{19}F NMR: δ -85.0 (s, CF_3); -110.7 (m, $^2J_{PF}$ = 45 Hz) [lit.[9] (C_6D_6) -82.3 (s, CF_3); -112.1 (tm, $^2J_{PF}$ = 43 Hz, CF_2)].

Isolation of $Ph_2PC_2F_5$

$Ph_2P(OPh)$ (4.5 g, 16.3 mmol) was added to a mixture of dried CsF (1.09 g, 7.18 mmol) in ether (20 ml) under argon in an NMR tube. $C_2F_5SiMe_3$ (3.4 g, 17.5 mmol) was added, and the reaction sealed. The reaction was monitored by ^{31}P NMR, which showed quantitative yield overnight. Volatiles were pumped off to reduce the volume of the mixture. The crude product was removed by cannula filtration. Vacuum distillation of the filtrate at 89-93°C and 0.075Torr (104-107°C and 0.2Torr[10]) gave $Ph_2PC_2F_5$ (4.0 g, 80%). ^{1}H NMR (C_6D_6): δ 7.60 (m, 2H); 7.02 (m, 3H) (Figure 1) [lit.[10] (C_6D_6) 7.59 (m, 2H), 7.01 (m, 3H)]. ^{31}P NMR (C_6D_6) : δ -2.4 (t, $^2J_{PF}$ = 65 Hz) [lit.[10] (C_6D_6) -1.41 (tq, $^2J_{PF}$ = 58.0 Hz, $^3J_{PF}$ = 17 Hz]. ^{19}F NMR δ -80.7 (d, $^3J_{PF}$ = 16.2 Hz); -112.9 (d, $^2J_{PF}$ = 57.2 Hz) [lit.[10] (C_6D_6) -80.4 (dt, $^3J_{PF}$ = 16.5 Hz, $^3J_{FF}$ = 3.1 Hz); -112.6 (tq, $^2J_{PF}$ = 57.0 Hz, $^3J_{FF}$ = 3.1 Hz)]. ^{13}C NMR: ($CDCl_3$) δ 135.3 (d, $^1J_{PC}$ = 22 Hz); 131.0 (s); 129.0 (s); 128.9 (s); 120.8 (tdq, $^1J_{CF}$ = 288 Hz, $^1J_{CP}$ = 53 Hz, $^2J_{CF}$ = 37 Hz, CF_2); 120.1 (qtd, $^1J_{CF}$ = 287 Hz, $^2J_{CF}$ = 33 Hz, $^2J_{CP}$ = 21 Hz, CF_3) (Figure 2).

Isolation of $P(CF_3)_3$

A mixture of $P(OPh)_3$ (2.9 ml, 0.011 mol), CsF (1.08 g, 0.007 mol) and PhCN (3 ml) was de-aerated by three freeze, pump, thaw degas cycles. CF_3SiMe_3 (5 ml, 0.03 mol) was then added at -196°C. The mixture was warmed slowly to room temperature, at which time a vigorous reaction occurred. The mixture was stirred for 1 hour. Trap to trap condensation using a vacuum line gave $P(CF_3)_3$ (1.91 g, 80%). ^{31}P NMR: δ -3.6 (dectet, $^2J_{PF}$ = 83 Hz) [lit.[11] -2.5(dectet, $^2J_{PF}$ = 85 Hz)]. ^{19}F NMR: δ -51.6 (d) [lit.[11] -50.7 (d)]. ^{13}C NMR (d_8-toluene) δ 125.7 (qm, $^1J_{CF}$ = 309 Hz) (Figures 3a & 3b) [lit.[11] (C_6D_6) 125.9 (q, $^1J_{CF}$ = 318 Hz)]. **Caution:** $P(CF_3)_3$ is a spontaneously flammable gas (bp = 17 °C).[12]

It can be conveniently stored under air-free conditions in a radical inhibiting solvent such as toluene.[13]

Isolation of $P(C_2F_5)_3$

$P(OPh)_3$ (5.68 g, 18.2 mmol) was added to a mixture of dried CsF (2.31 g, 15.2 mmol) in benzonitrile (25 ml) under argon. $C_2F_5SiMe_3$ (9.02 g, 46.9 mmol) was added. The reaction was shaken intermittently over 10 minutes and left for 1 hour, during which a bottom layer of product separated from the mixture. The bottom layer was removed and distilled, at 60-62 °C, to give $P(C_2F_5)_3$ (5.18 g, 85%). ^{31}P NMR: δ 12.7 (septet of dectets) [lit.[6] 13.7 (septet of dectets)]. ^{19}F NMR: δ -82.6 (d, $^3J_{PF} = 15$ Hz, CF_3); -106.7 (d, $^2J_{PF} = 53$ Hz, CF_2) [lit.[6] -84.5 (d, $^3J_{PF} = 16$ Hz, CF_3); -107.9(d, $^2J_{PF} = 48$ Hz, CF_2)]. ^{13}C NMR: ($CDCl_3$) δ 118.2 (qm, $^1J_{CF} = 287$ Hz, CF_3); 117.6 (tq, $^1J_{CF} = 298$ Hz, $^2J_{CF} = 45$ Hz, CF_2) (Figure 4).

Isolation of $P(C_4F_9)_3$

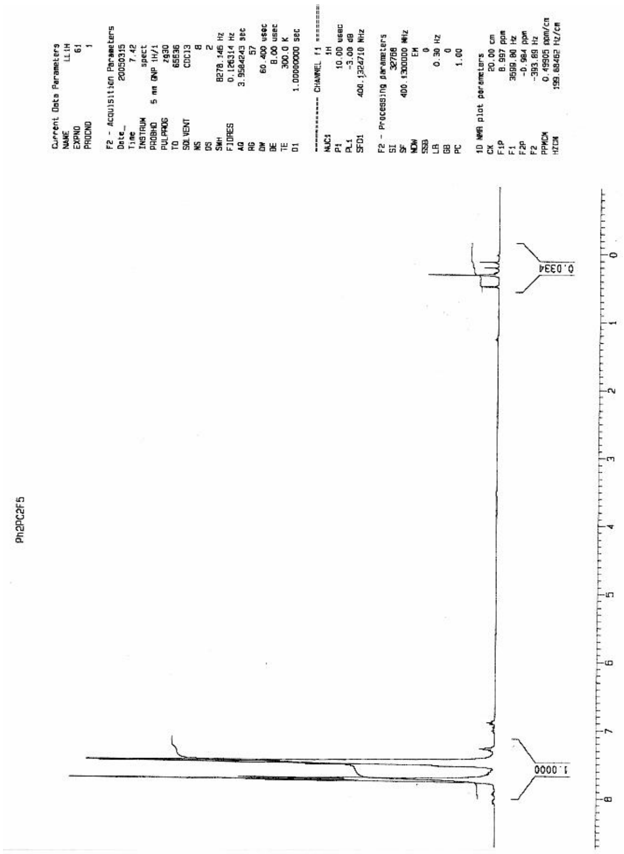
$P(OC_6H_4CN)_3$ (1.21 g, 3.1 mmol) was added to dried CsF (2.95 g, 19.4 mmol) in a Schlenk under argon. Benzonitrile (10 ml) and ether (10 ml) were added. $C_4F_9SiMe_3$ (6 ml, 19.7 mmol) was added by syringe and the mixture stirred rapidly. A colourless bottom layer of crude product separated from the mixture. This layer (1.5 g, 0.75 ml) was removed by syringe and distilled using a Hickman still to give $P(C_4F_9)_3$ (0.80 g, 40%). ^{31}P NMR: δ 21.8 (m) [lit.[6] 23.7 (m)]. ^{19}F NMR: δ -83.7 (s, CF_3); -103.6 (d, $^2J_{PF} = 33$ Hz, PCF_2); -120.6 (d, $^3J_{PF} = 30$ Hz, $C\mathit{F_2}CF_2CF_3$); -128.5 (s, $C\mathit{F_2}CF_3$) [lit.[6] -83.7(s); -103.3(d, $^2J_{PF} = 32$ Hz); -120.1(d, $^3J_{PF} = 30$ Hz); -128.0(s)]. ^{13}C NMR: δ 127-108 (m, CF_2's); 119.5 (qt, $^1J_{CF} = 287$ Hz, $^2J_{CF} = 33$ Hz, CF_3) (Figure 5).

References

1. T. J. Hall and J. H. Hargis, *J. Org. Chem.,* 1986, **51**, 4185.
2. J. Chatt, W. Hussain, G. J. Leigh, M. Hapipah, C. J. Pickett and D. A. Rankin, *J. Chem. Soc., Dalton Trans.,*1985, 1131.
3. V. A. Petrov, *Tetrahedron Lett.,* 2001, **42**, 3267.
4. P. Panne, D. Naumann and B. Hoge, *J. Fluorine Chem.*, 2001, **112**, 283.

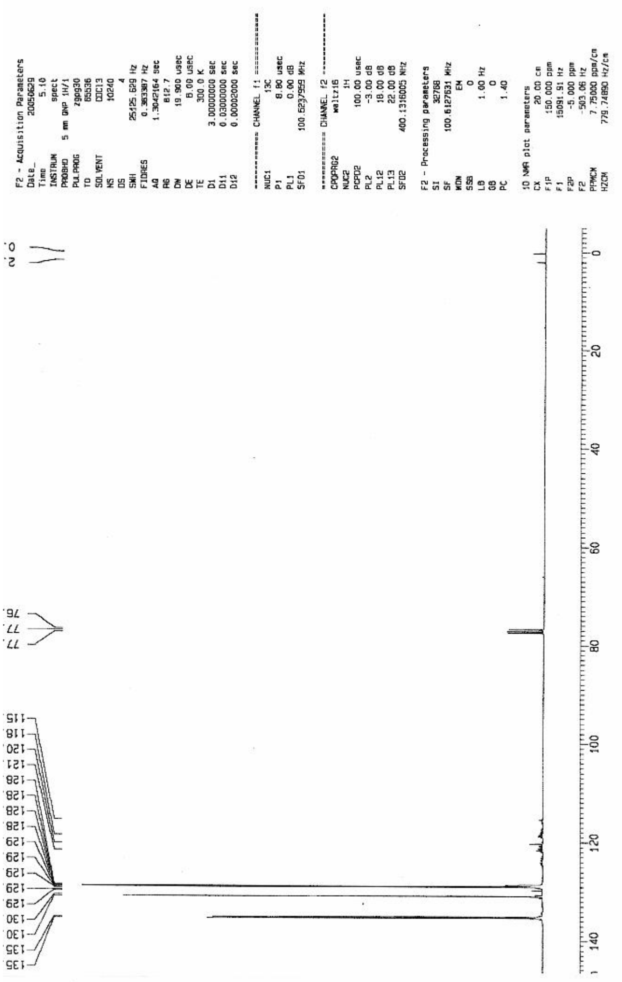
5. J. D. Palcic, P. N. Kapoor, D. M. Roddick and R. G. Peters, *Dalton Trans.,* 2004, 1644.
6. J. J. Kampa, J. W. Nail and R. J. Lagow, *Angew. Chem. Int. Ed.*, 1995, **34**, 1241.
7. B. Hoge and C. Thösen, *Inorg. Chem.*, 2001, **40**, 3113.
8. I. G. Phillips, R. G. Ball and R. G. Cavell, *Inorg. Chem.*, 1988, **27**, 4038.
9. M. F. Ernst and D. M. Roddick, *Inorg. Chem.*, 1989, **28**, 1624.
10. R. G. Peters, B. L. Bennett, R. C. Schnabel and D. M. Roddick, *Inorg. Chem.*, 1997, **36**, 5962.
11. A. B. Burg, *Inorg. Nucl. Chem. Lett.,* 1977, **13**, 199.
12. F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.,* 1953, 1565.
13. W. Mahler, *Inorg. Chem.,* 1979, **18**, 352.

Figure 1. ^{1}H NMR spectrum of $Ph_2PC_2F_5$ in $CDCl_3$



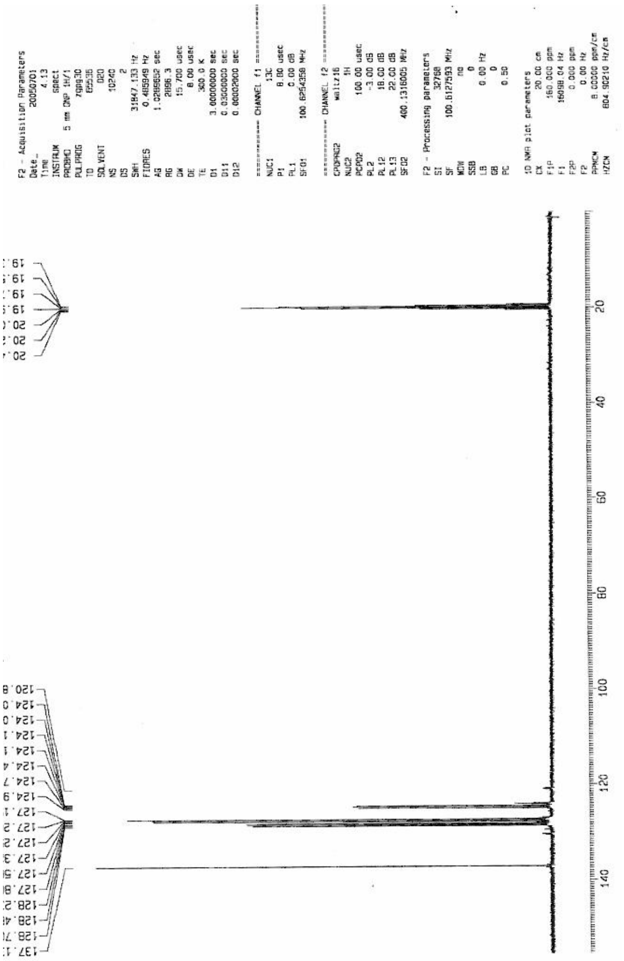
```
Current Data Parameters
NAME              LL1H
EXPNO               61
PROCNO               1

F2 - Acquisition Parameters
Date_         20050315
Time              7.42
INSTRUM          spect
PROBHD   5 mm QNP 1H/1
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   8
DS                   2
SWH          8278.146 Hz
FIDRES       0.126314 Hz
AQ          3.9584243 sec
RG                  57
DW              60.400 usec
DE                8.00 usec
TE               300.0 K
D1          1.00000000 sec

============= CHANNEL f1 ========
NUC1                1H
P1               10.00 usec
PL1              -3.00 dB
SFD1       400.1324710 MHz

F2 - Processing parameters
SI               32768
SF         400.1300000 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX               20.00 cm
F1P              8.997 ppm
F1             3599.80 Hz
F2P             -0.984 ppm
F2             -393.89 Hz
PPMCM          0.49905 ppm/cm
HZCM         199.68462 Hz/cm
```

Figure 2. ^{13}C NMR spectrum of $Ph_2PC_2F_5$ in $CDCl_3$



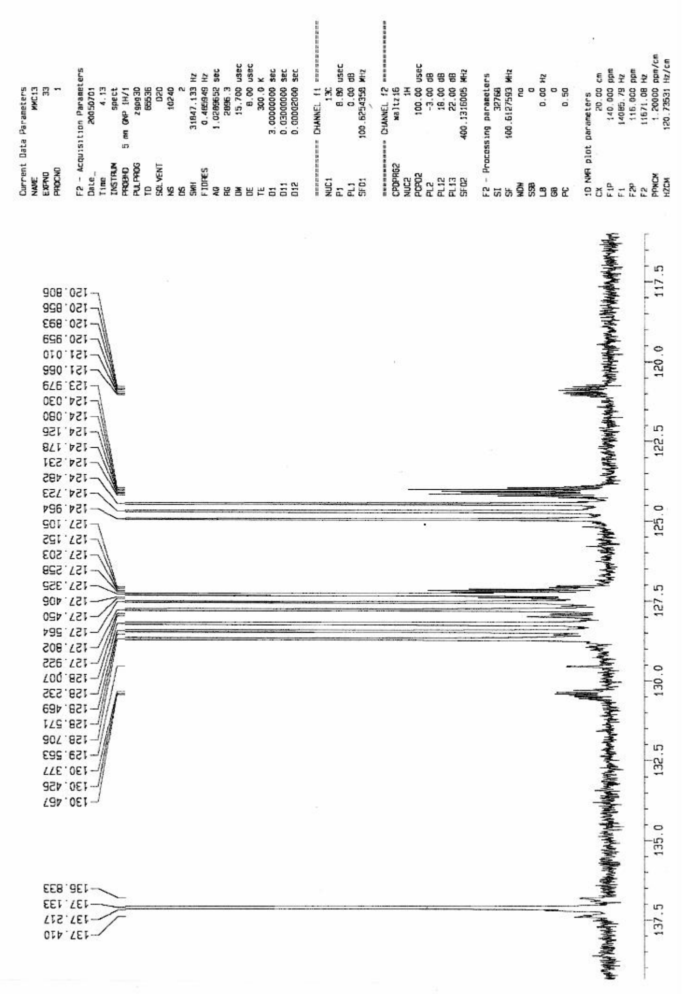
```
F2 - Acquisition Parameters
Date_          20050629
Time               5.10
INSTRUM           spect
PROBHD   5 mm QNP 1H/1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                10240
DS                    4
SWH          25125.629 Hz
FIDRES        0.383387 Hz
AQ           1.3042164 sec
RG                812.7
DW              19.900 usec
DE                6.00 usec
TE               300.0 K
D1          3.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec

============ CHANNEL f1 ============
NUC1                13C
P1                 8.80 usec
PL1                0.00 dB
SFO1        100.6237959 MHz

============ CHANNEL f2 ------------
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              18.00 dB
PL13              22.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127631 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P             150.000 ppm
F1             15091.91 Hz
F2P              -5.000 ppm
F2              -503.06 Hz
PPMCM           7.75000 ppm/cm
HZCM          779.74890 Hz/cm
```

Figure 3a. ^{13}C NMR spectrum of $P(CF_3)_3$ in d_8-toluene



```
F2 - Acquisition Parameters
Date_          20050701
Time               4.13
INSTRUM           spect
PROBHD   5 mm DNP 1H/1
PULPROG          zgpg30
TD                65536
SOLVENT             D20
NS                10240
DS                    2
SWH          31847.133 Hz
FIDRES        0.485949 Hz
AQ           1.0289652 sec
RG               2896.3
DW              15.700 usec
DE                8.00 usec
TE               300.0 K
D1          3.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec

============ CHANNEL f1 ============
NUC1                13C
P1                 8.80 usec
PL1                0.00 dB
SFO1       100.6254358 MHz

============ CHANNEL f2 ============
CPDPRG2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              18.00 dB
PL13              22.00 dB
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127593 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 0.50

1D NMR plot parameters
CX                20.00 cm
F1P             160.000 ppm
F1             16098.04 Hz
F2P               0.000 ppm
F2                 0.00 Hz
PPMCM           8.00000 ppm/cm
HZCM          804.90210 Hz/cm
```

Figure 3b. Expansion of ^{13}C NMR spectrum of $P(CF_3)_3$ in *d_8*-toluene



```
Current Data Parameters
NAME              MMC13
EXPNO                33
PROCNO                1

F2 - Acquisition Parameters
Date_          20050701
Time               4.13
INSTRUM           spect
PROBHD   5 mm QNP 1H/1
PULPROG          zgpg30
TD                65536
SOLVENT             D20
NS                10240
DS                    2
SWH           31847.133 Hz
FIDRES         0.485949 Hz
AQ            1.0289652 sec
RG               2896.3
DW               15.700 usec
DE                 8.00 usec
TE                300.0 K
D1           3.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec

============ CHANNEL f1 =============
NUC1                13C
P1                 8.80 usec
PL1                0.00 dB
SFO1        100.6254358 MHz

============ CHANNEL f2 =============
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              18.00 dB
PL13              22.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127593 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 0.50

1D NMR plot parameters
CX                20.00 cm
F1P             140.000 ppm
F1             14085.79 Hz
F2P             116.000 ppm
F2             11671.08 Hz
PPMCM           1.20000 ppm/cm
HZCM          120.73531 Hz/cm
```

Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2005

Figure 4. ^{13}C NMR spectrum of $P(C_2F_5)_3$ in $CDCl_3$

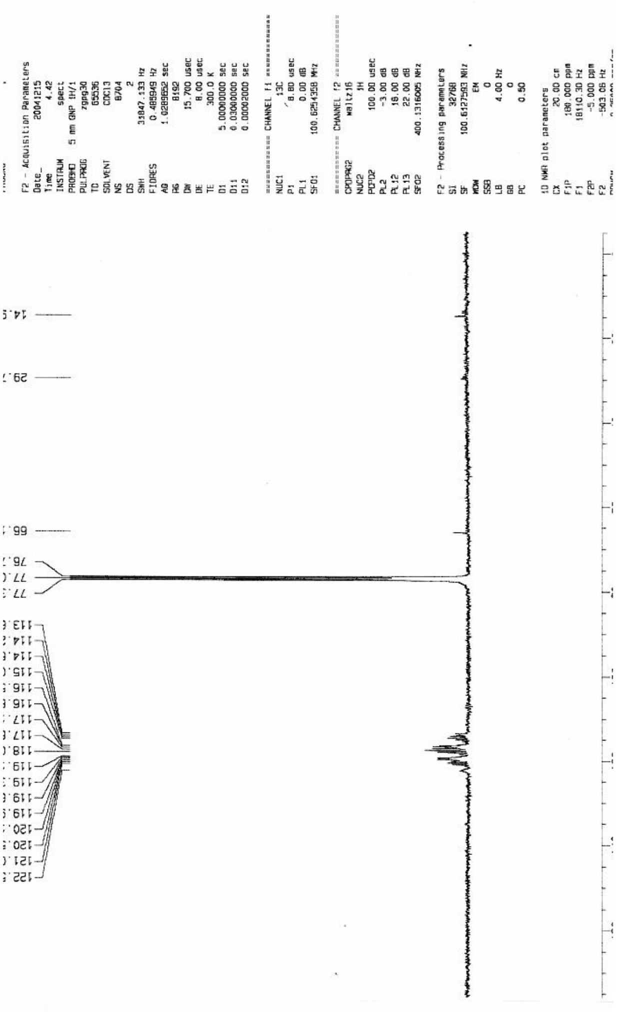


Figure 5. ^{13}C NMR spectrum of neat $P(C_4F_9)_3$