Tris(pyrazolyl)phosphines with Copper(I): From Monomers to Polymers

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Crystallographic Details

Details for [C^{H}Cu][PF$_6$]·DCM

In crystal structure **[C^{H}Cu][PF$_6$]·DCM** the molecules of [C^{H}Cu] form a 1-dimensional polymeric chain in the crystallographic *uvw*=[1,-1,1] direction (Fig. S1). The length of *uvw*=[1,-1,1] in the unit cell is 21.1191(12) Å. Because there are four independent monomeric units, the average Cu…Cu distance is consequently 5.2798(3) Å. This Cu coordination polymer shows "whole molecule" disorder with one disorder component running in "up" direction and the other disorder component in "down" direction (Fig. S2). The crystal structure of **[C^{H}Cu][PF$_6$]·DCM** has triclinic P1 (no. 1) symmetry. In the packing of the crystal the polymeric chains form a pseudo-hexagonal arrangement (Fig. S3).

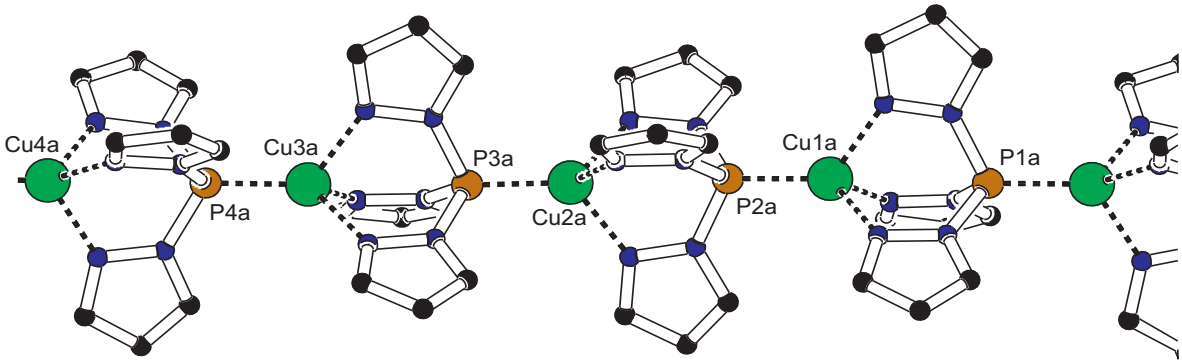


Figure S1. Polymeric coordination chain of ([C^{H}Cu][PF$_6$])$_n$) in crystal structure [C^{H}Cu][PF$_6$]·DCM. Only the major disorder component is shown. Hydrogen atoms, disordered PF$_6$ anions and severely disordered CH$_2$Cl$_2$ solvent molecules are omitted for clarity.

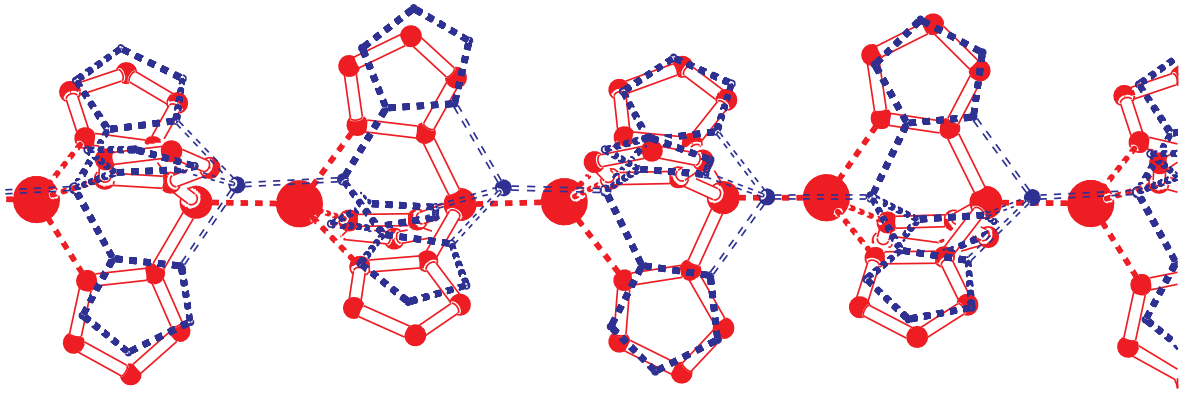


Figure S2. Disorder of the Cu coordination polymer in crystal structure [C^{H}Cu][PF$_6$]·DCM. The major disorder component is drawn in red, the minor component in blue. The ratio between major and minor component is estimated as 89:11%. Hydrogen atoms, disordered PF$_6$ anions and severely disordered CH$_2$Cl$_2$ solvent molecules are omitted for clarity.

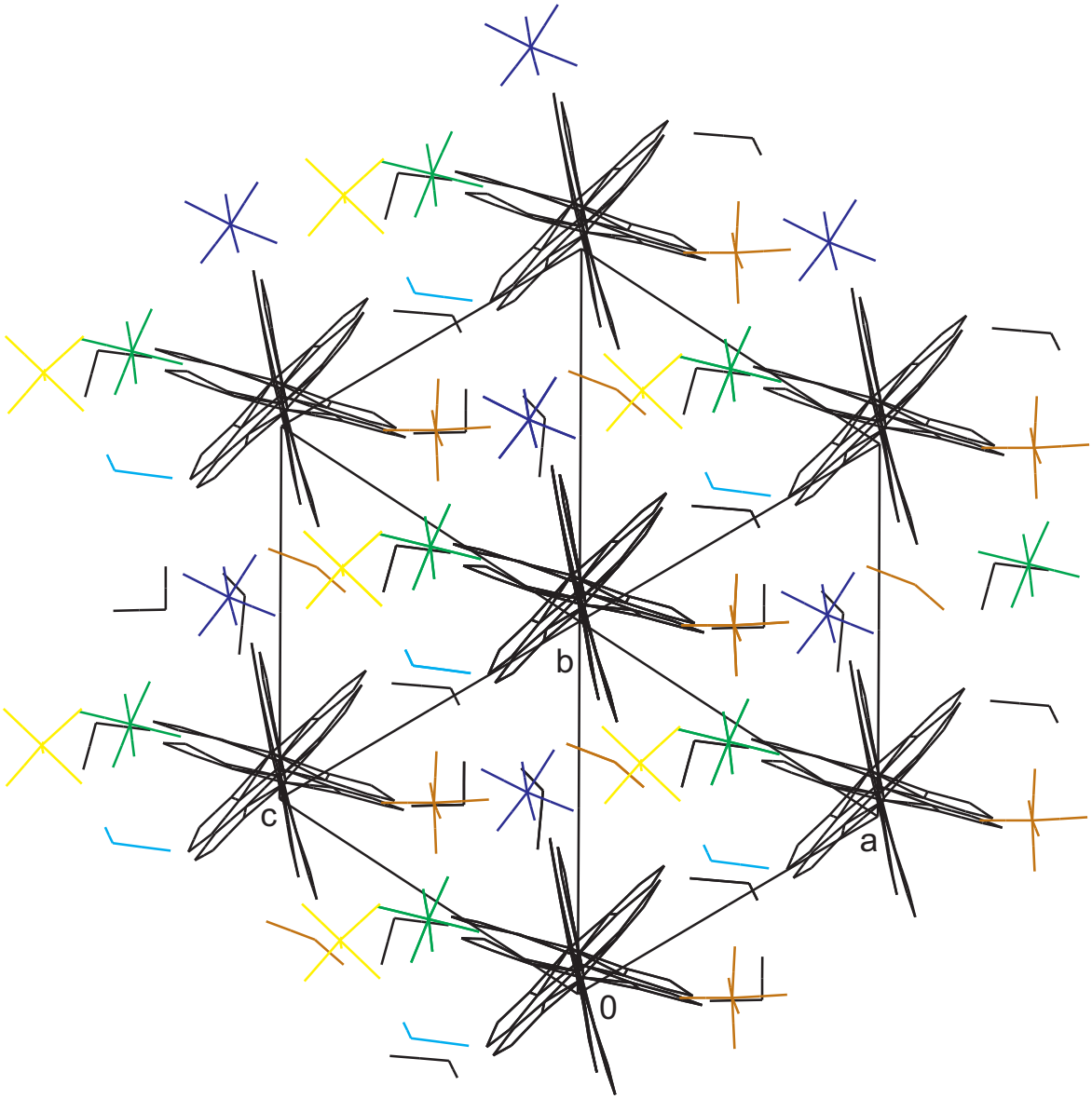


Figure S3. Packing of [C^{H}Cu][PF$_6$]·DCM in the crystal. View along the *uvw* = [1,-1,1] direction. Hydrogen atoms are omitted for clarity. Only the major forms of the disordered molecules are shown. In the final least-squares refinements, the CH_2Cl_2 molecules have been treated with the Squeeze routine.

Details for [C^{H}Cu][PF$_6$]·DCE1 (crystal 1) and [C^{H}Cu][PF$_6$]·DCE2 (crystal 2)

The crystal structure of **[C^{H}Cu][PF$_6$]·DCE1** was merohedrally twinned. The twinning can be detected by comparing the merging R_{int} of the trigonal Laue group -31m with the higher symmetric hexagonal 6/mmm (Table S2). For both symmetries the R_{int} values are similar. As expected, in the case of the non-twinned **[C^{H}Cu][PF$_6$]·DCE2** there is a significant difference between Laue groups -31m and 6/mmm. The twin operation for **[C^{H}Cu][PF$_6$]·DCE1** could be found by a coset decomposition (see Table S1) of point group 6/mmm (symmetry of the lattice) with respect to 31m (symmetry of the crystal).[1] The twin operation used in the refinement was a mirror plane perpendicular to the *c*-axis.

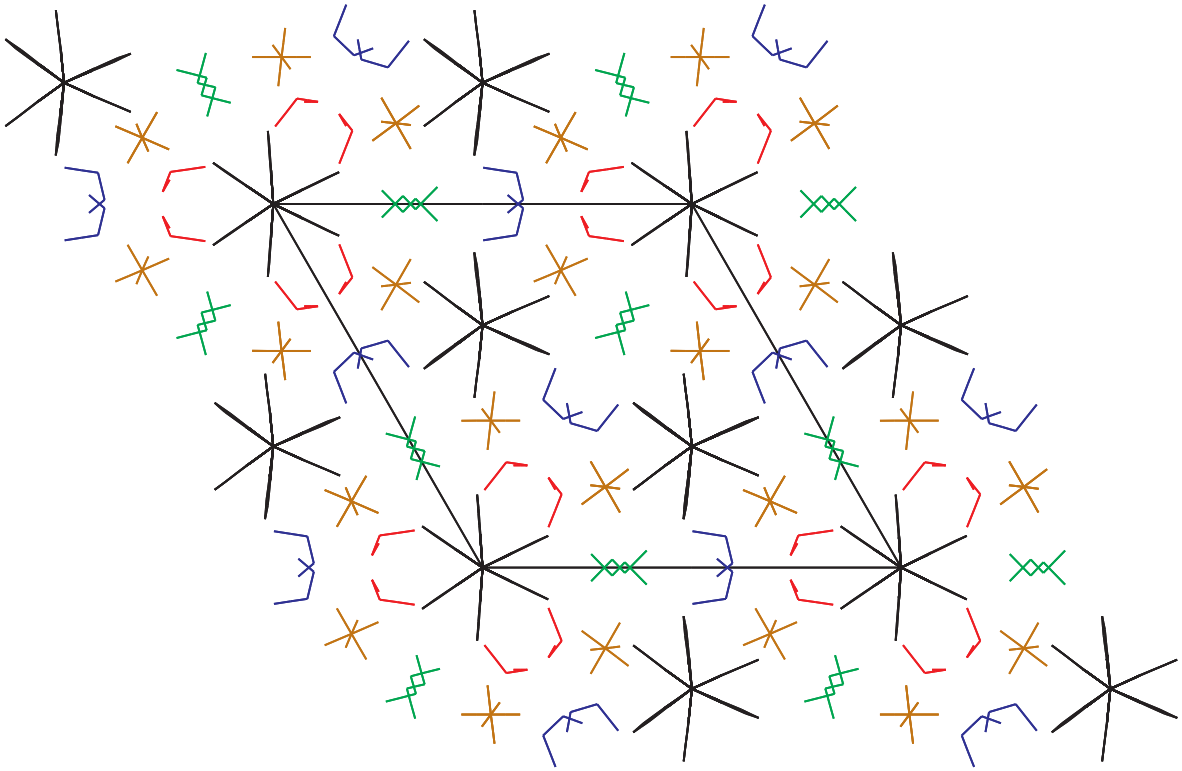


Figure S4. Packing of $[C^{H}Cu][PF_6]\cdot$DCE2 in the crystal. View along the *c*-direction. Hydrogen atoms are omitted for clarity. Only the major forms of the disordered molecules are shown.

Table S1. Coset decomposition of point group 6/mmm to 31m as determined by the Bilbao Crystallographic Server.[2] All symmetry operations of coset 3 are suitable twin operations for the crystal structure of $[C^{H}Cu][PF_6]\cdot$DCE1.

Coset 1	$\{1, 3^{+}_{001}, 3^{-}_{001}, m_{1\text{-}10}, m_{120}, m_{210}\}$
Coset 2	$\{2_{001}, 6^{-}_{001}, 6^{+}_{001}, m_{110}, m_{100}, m_{010}\}$
Coset 3	$\{2_{110}, 2_{100}, 2_{010}, m_{001}, -6^{-}_{001}, -6^{+}_{001}\}$
Coset 4	$\{2_{1\text{-}10}, 2_{120}, 2_{210}, -1, -3^{+}_{001}, -3^{-}_{001}\}$

Table S2. Merging R values R_{int} for the twinned crystal structure $[C^{H}Cu][PF_6]\cdot$DCE1 and the non-twinned $[C^{H}Cu][PF_6]\cdot$DCE2, as determined with the Eval15 software suite.[3]

Laue group	**$[C^{H}Cu][PF_6]\cdot$DCE1**	**$[C^{H}Cu][PF_6]\cdot$DCE2**
-3	0.034	0.053
-3m1	0.037	0.256
-31m	0.035	0.055
6/m	0.037	0.256
6/mmm	0.037	0.257

Table S3. Experimental Details of the Crystal Structure Determinations.

	$[C^{Me2}Cu(NCMe)][PF_6]$	$[C^{Me2}Cu(PPh_3)][PF_6]$	$[(C^{H})_2Cu][PF_6]$	$[C^{H}Cu][PF_6]\cdot DCM$	$[C^{H}Cu][PF_6]\cdot DCE1$	$[C^{H}Cu][PF_6]\cdot DCE2$
formula	$[C_{17}H_{24}CuN_7P](PF_6)$	$[C_{33}H_{36}CuN_6P_2](PF_6)\cdot CH_2Cl_2$	$[C_{18}H_{18}CuN_{12}P_2](PF_6)$ + disordered solvent	$[C_9H_9CuN_6P](PF_6)$ + disordered solvent	$[C_9H_9CuN_6P](PF_6)\cdot 3C_2H_4Cl_2$	$[C_9H_9CuN_6P](PF_6)\cdot 3C_2H_4Cl_2$
fw	565.91	872.05	672.89[4]	440.70[4]	737.56	737.56
crystal size [mm^3]	0.41 × 0.14 × 0.06	0.51 × 0.36 × 0.12	0.41 × 0.17 × 0.15	0.58 × 0.07 × 0.05	0.68 × 0.11 × 0.06	0.40 × 0.13 × 0.06
crystal color	colorless	colorless	colorless	colorless	colorless	colorless
T [K]	150(2)	150(2)	110(2)	150(2)	150(2)	150(2)
crystal system	monoclinic	monoclinic	trigonal	triclinic	trigonal	trigonal
space group	C2/c (no. 15)	$P2_1/n$ (no. 14)	P31c (no. 159)	P1 (no. 1)	P31c (no. 159)	P31c (no. 159)
a [Å]	26.0651(16)	14.3558(1)	19.5288(14)	11.9578(8)	21.2193(6)	21.2337(5)
b [Å]	7.7824(3)	31.5939(2)	-	12.7183(14)	-	-
c [Å]	25.9327(13)	16.7621(1)	18.0311(14)	13.2817(8)	10.6362(5)	10.6155(4)
α [°]	-	-	-	87.521(3)	-	-
β [°]	116.124(3)	90.6316(2)	-	88.058(3)	-	-
γ [°]	-	-	-	84.097(4)	-	-
V [$Å^3$]	4723.0(4)	7602.08(8)	5955.3(10)	2006.5(3)	4147.4(3)	4145.0(3)
Z	8	8	8	4	6	6
d_{calc} [g/cm^3]	1.592	1.524	1.501[4]	1.459[4]	1.772	1.773
μ [mm^{-1}]	1.13	0.91	0.96[4]	1.30[4]	1.55	1.55
abs. corr. type	multiscan[5]	multiscan[5]	multiscan[5]	multiscan[5]	numerical[5]	numerical[5]
abs. corr. range	0.57-0.75	0.54-0.89	0.67-0.75	0.52-0.75	0.60-0.98	0.61-0.94
$(\sin\theta/\lambda)_{max}$ [$Å^{-1}$]	0.65	0.65	0.65	0.65	0.65	0.65
refl. measured / unique / observed	33686 / 5582 / 4261	102481 / 17382 / 12960	83529 / 9095 / 8301	38040 / 17156 / 11100	41758 / 6026 / 5335	46288 / 6330 / 5148
R_{int}	0.057	0.067	0.027	0.064	0.035	0.048
parameters / restraints	306 / 0	1014 / 934	481 / 1	1053 / 9151	381 / 250	394 / 208
R1 / wR2 [$I>2\sigma(I)$]	0.0484 / 0.1198	0.0481 / 0.1134	0.0317 / 0.0799	0.0697 / 0.1768	0.0307 / 0.0646	0.0462 / 0.1100
R1/wR2 [all refl.]	0.0704 / 0.1328	0.0729 / 0.1250	0.0377 / 0.0830	0.1133 / 0.1987	0.0390 / 0.0677	0.0627 / 0.1176
S	1.023	1.026	1.050	1.064	0.944	1.030
Flack[6] x	-	-	0.003(3)	twin	twin	0.03(2)
$\rho_{min/max}$ [$e/Å^3$]	-0.87 / 1.24	-1.31 / 1.39	-1.04 / 0.99	-0.61 / 0.86	-0.57 / 0.30	-0.57 / 2.36

Structure for [C^{H}Cu][PF$_6$]·DCM

[$C_9H_9CuN_6P$](PF_6) + disordered solvent, Fw = 440.70[4], colorless needle, 0.58 × 0.07 × 0.05 mm^3, triclinic, P1 (no. 1), a = 11.9578(8), b = 12.7183(14), c = 13.2817(8) Å, α = 87.521(3), β = 88.058(3), γ = 84.097(4) °, V = 2006.5(3) Å^3, Z = 4, D_x = 1.459 g/cm^3, μ = 1.30 mm^{-1}.* 38040 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. The crystal appeared to be cracked into two fragments related by a 5.2 ° rotation about an arbitrary vector. Two orientation matrices were used for the integration of X-ray intensities with the Eval15 software.[3] Multiscan absorption correction and scaling was performed with TWINABS[5] (correction range 0.52-0.75). 17156 reflections were unique (R_{int} = 0.064), of which 11100 were observed [I>2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT.[7] Least-squares refinement was performed with SHELXL-2014[8] against F^2 of all reflections based on a HKLF-5 file[9] of four components (inclusive Friedel pairs). The crystal structure contains large voids (509 Å^3 / unit cell) filled with disordered CH_2Cl_2 solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation with the Squeeze routine[10] resulting in 255 electrons / unit cell. The Cu coordination polymer and the PF_6 anions were refined with disorder models. The major component of the coordination polymer and the P atoms of PF_6 were refined with anisotropic displacement parameters. The minor disorder component of the coordination polymer was refined with fixed isotropic displacement parameters of U = 0.05. The fluorine atoms of PF_6 were refined with free isotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. 1053 parameters were refined with 9151 restraints (floating origin, distances and angles of the disordered groups). R1/wR2 [I > 2σ(I)]: 0.0697 / 0.1768. R1/wR2 [all refl.]: 0.1133 / 0.1987. S = 1.064. Batch scale factors of the four crystal components: 0.10(3), 0.405(17), 0.05(3). Residual electron density between -0.61 and 0.86 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[11]

Structure for [C^{H}Cu][PF$_6$]·DCE1

[$C_9H_9CuN_6P$](PF_6) · 3$C_2H_4Cl_2$, Fw = 737.56, colorless needle, 0.68 × 0.11 × 0.06 mm^3, trigonal, P31c (no. 159), a = b = 21.2193(6), c = 10.6362(5) Å, V = 4147.4(3) Å^3, Z = 6, D_x = 1.772 g/cm^3, μ = 1.55 mm^{-1}. 41758 reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. X-ray intensities were integrated with the Eval15 software.[3] Numerical absorption correction and scaling was performed with SADABS[5] (correction range 0.60-0.98). 6026 reflections were unique (R_{int} = 0.031), of which 5335 were observed [I>2σ(I)]. The structure was solved with

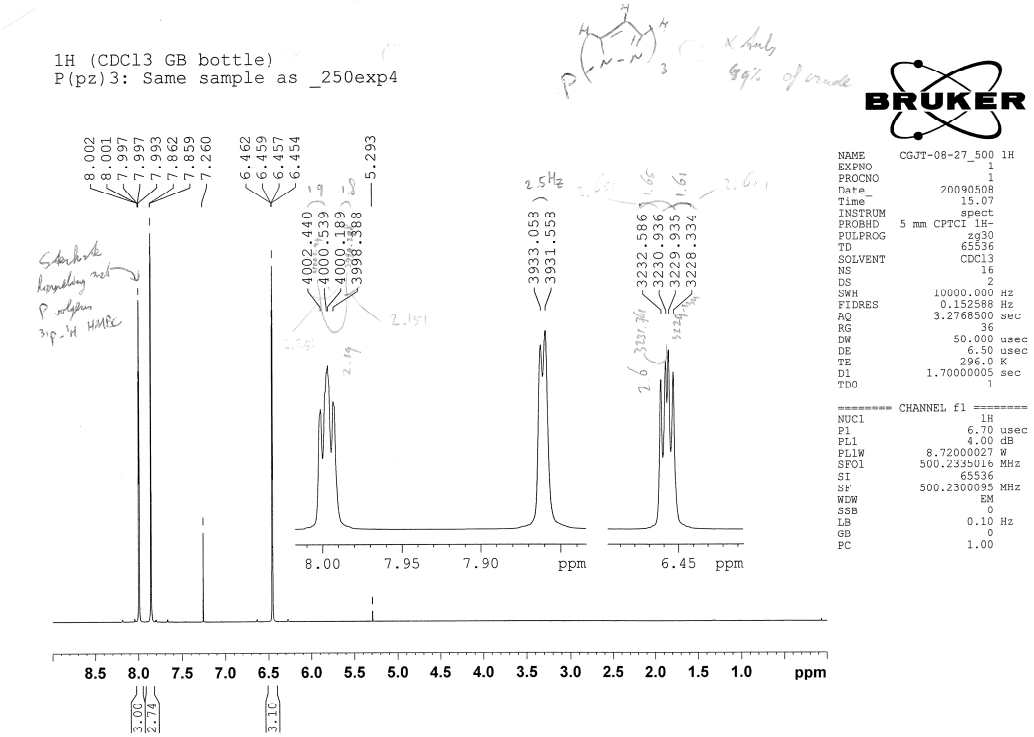
Patterson superposition methods using SHELXT. [7] Least-squares refinement was performed with SHELXL-2014[8] against F^2 of all reflections. The crystal was merohedrally twinned. The twin matrix (1,0,0 / 0,1,0 / 0,0,-1) was used for the refinement, resulting in a twin fraction BASF = 0.4815(14). Additional components for inversion twinning resulted in BASF vales of zero and were omitted subsequently.

One Cu coordination polymer was refined with a disorder model. The estimated ratio between major and minor disorder component is 85:15%. The slight disorder in the other independent coordination chain has been ignored. All non-hydrogen atoms were refined with anisotropic displacement parameters with the exception of the minor disorder component (isotropic, constrained to the same value with EADP instruction). One of the $C_2H_4Cl_2$ solvent molecules was also refined with a disorder model. All hydrogen atoms were introduced in calculated positions and refined with a riding model. 381 parameters were refined with 250 restraints (floating origin, distances and angles of the disordered groups). R1/wR2 [$I > 2\sigma(I)$]: 0.0307 / 0.0646. R1/wR2 [all refl.]: 0.0390 / 0.0677. S = 0.944. Residual electron density between -0.57 and 0.30 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[11]

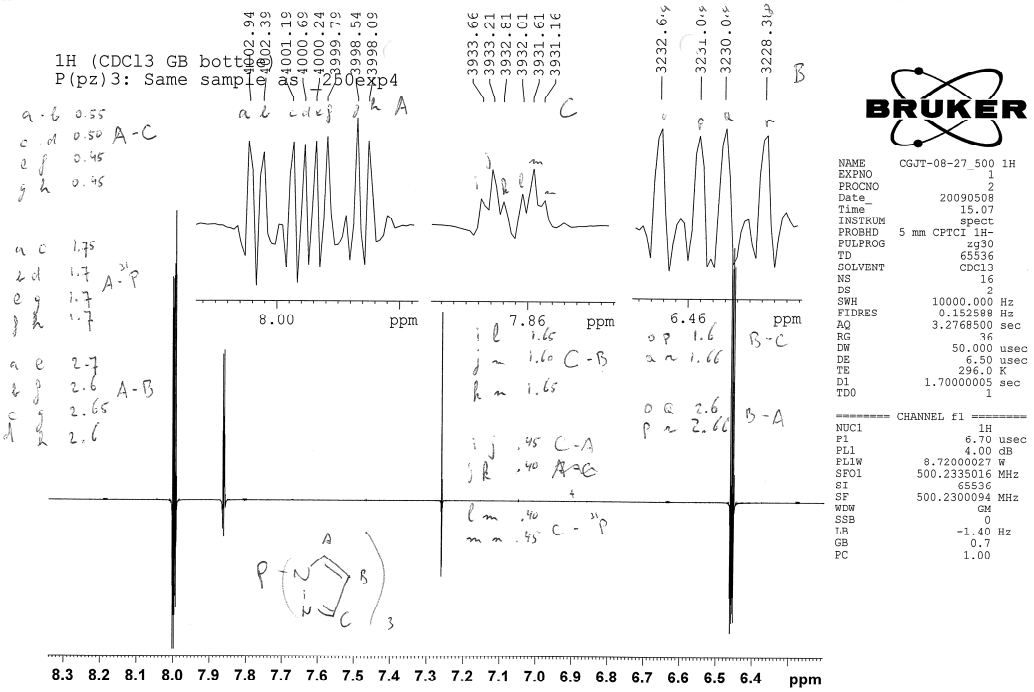
NMR spectra

NMR spectra of tris(pyrazolyl)phosphine (C^H)

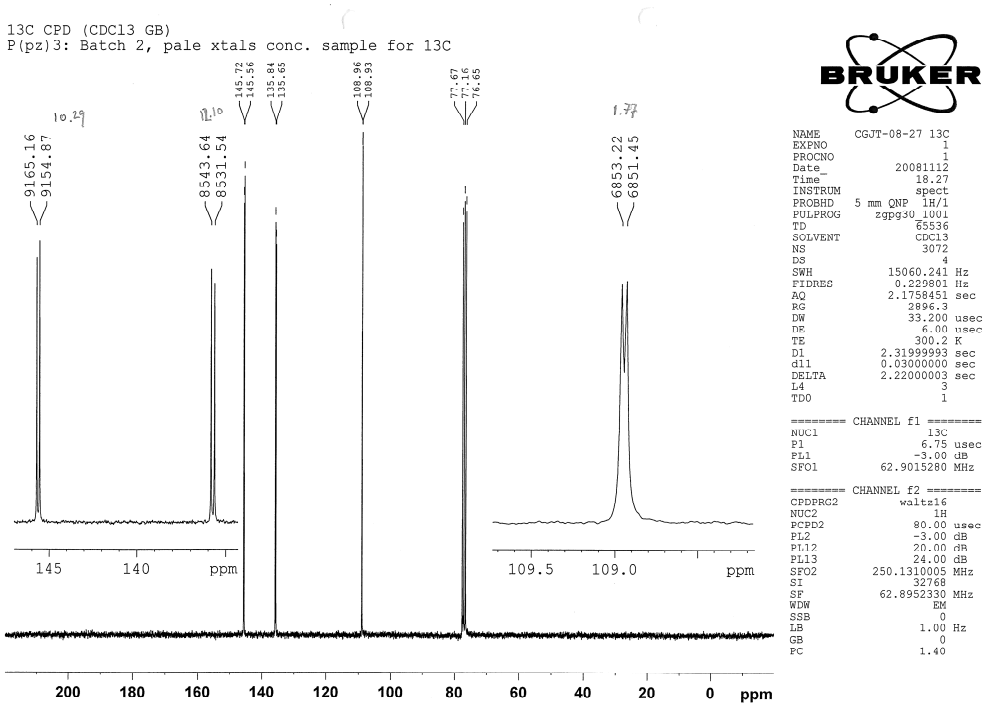
^{1}H NMR of $\mathbf{C^H}$ (500.2 MHz, $CDCl_3$)



^{1}H NMR of $\mathbf{C^H}$ (500.2 MHz, $CDCl_3$) after line narrowing



$^{13}C\{^{1}H\}$ NMR of $\mathbf{C^H}$ (62.9 MHz, $CDCl_3$)

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TE                 300.2 K
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L4                        3
TD0                       1

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PL13                  24.00 dB
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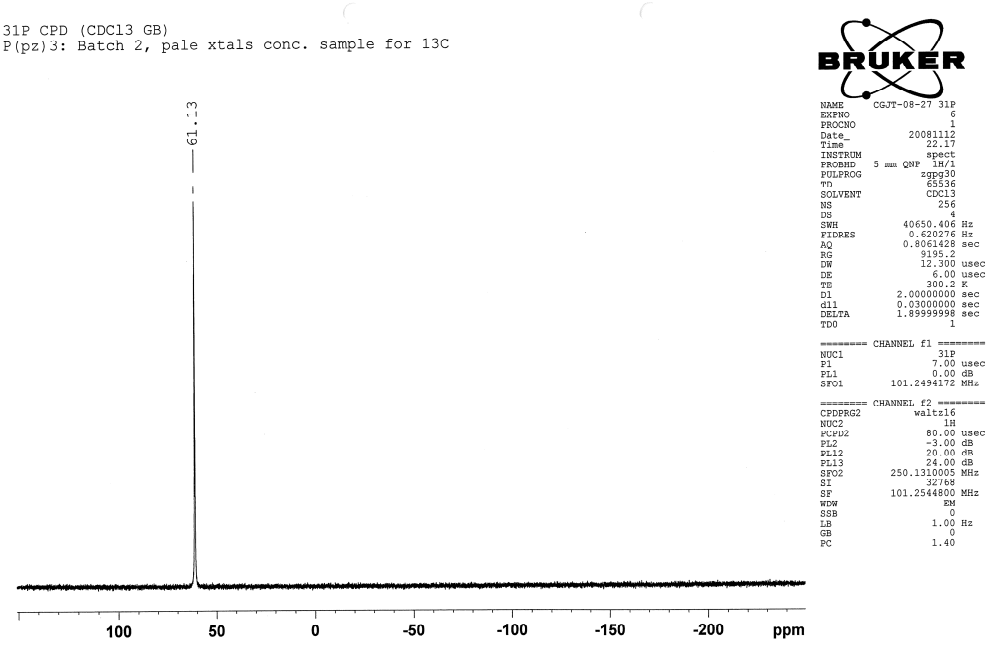
$^{31}P\{^{1}H\}$ NMR of $\mathbf{C^H}$ (101.3 MHz, $CDCl_3$)

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TD0                       1

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PL1                    0.00 dB
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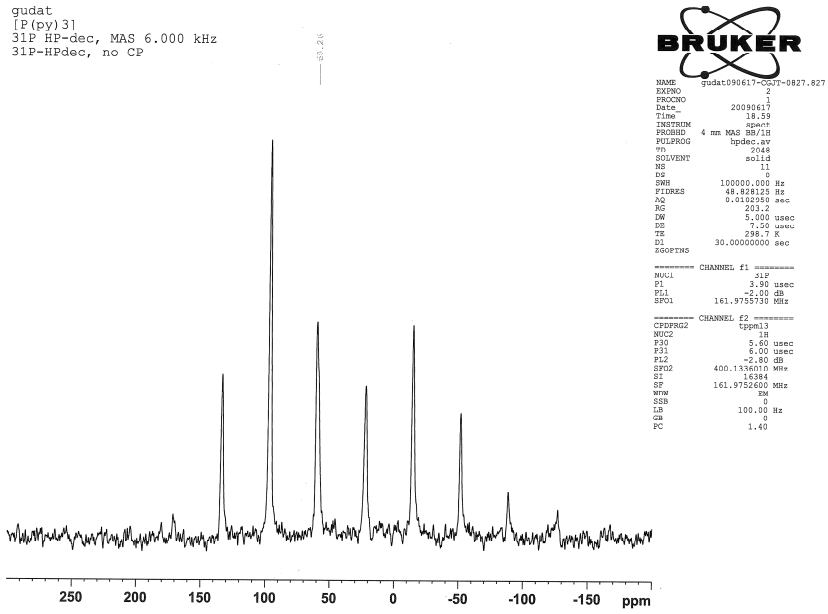
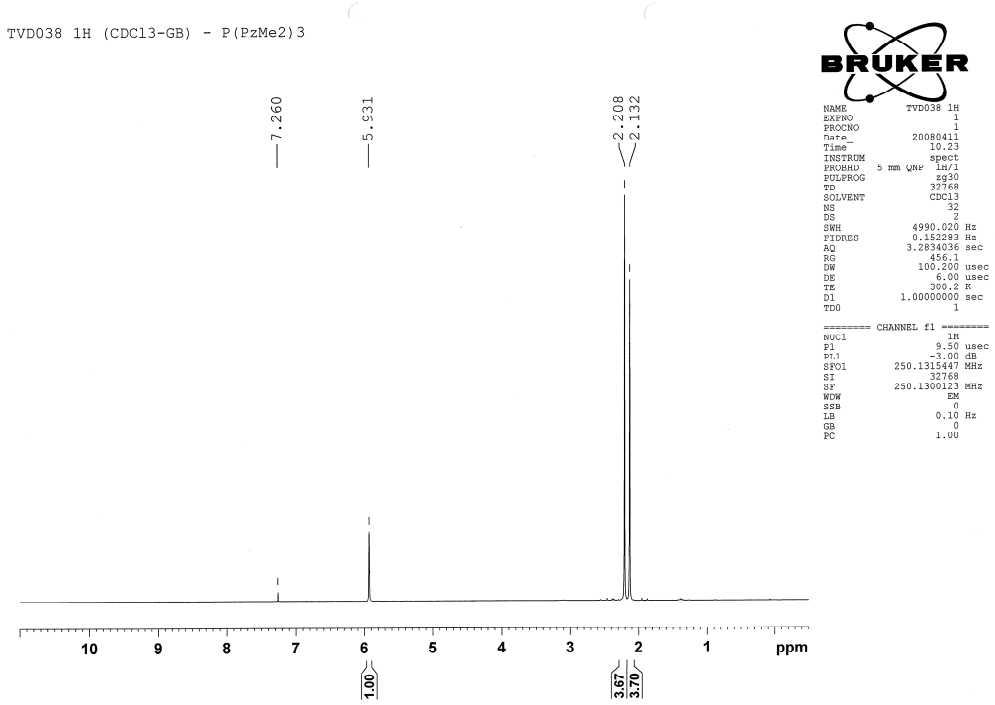
$^{31}P\{^{1}H\}$ MAS NMR of $\mathbf{C^{H}}$ (162.0 MHz)

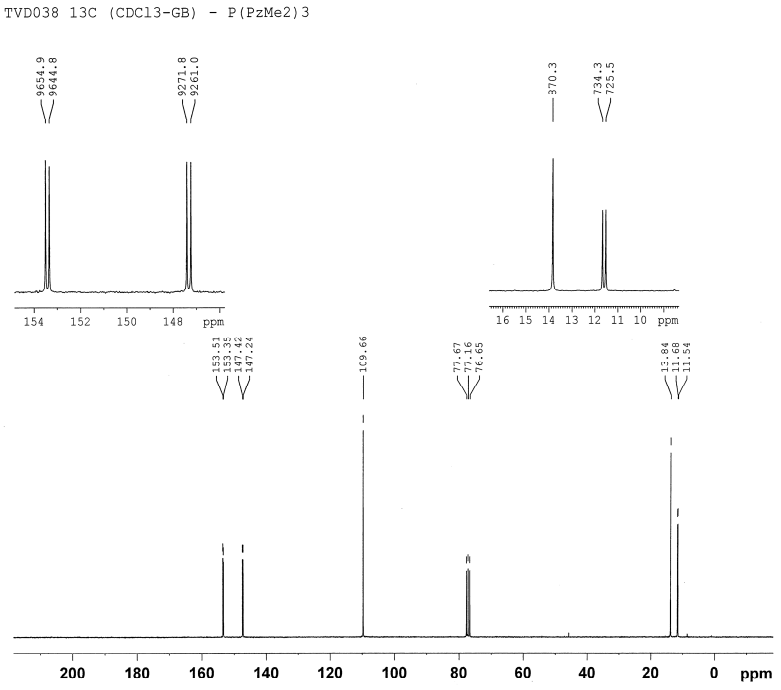


NMR spectra of tris(3,5-dimethylpyrazolyl)phosphine (C^{Me2})

^{1}H NMR of $\mathbf{C^{Me2}}$ (250.1 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR of $\mathbf{C^{Me2}}$ (62.9 MHz, $CDCl_3$)

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FIDRES           0.229801 Hz
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DE                    6.00 usec
TE                  300.2 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
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P1                    6.75 usec
PL1                  -3.00 dB
SFO1            62.9015280 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -3.00 dB
PL12                 20.00 dB
PL13                 24.00 dB
SFO2           250.1310005 MHz
SI                    65536
SF             62.8952425 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
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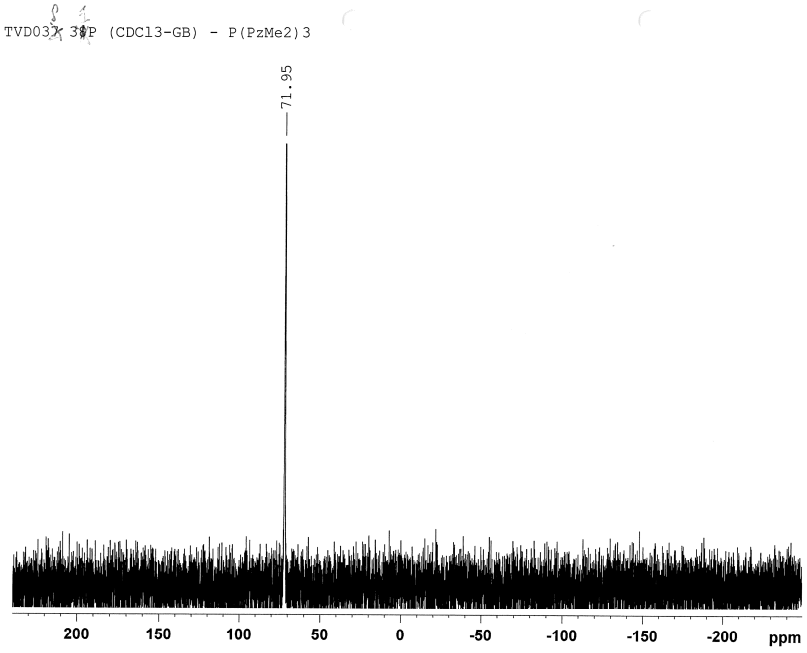
^{31}P NMR of $\mathbf{C^{Me2}}$ (101.3 MHz, $CDCl_3$)

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TE                  300.2 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                      1

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P1                   7.00 usec
PL1                  0.00 dB
SFO1           101.2544800 MHz

======== CHANNEL f2 ========
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NUC2                    1H
PCPD2                80.00 usec
PL2                  -3.00 dB
PL12                 20.00 dB
PL13                 24.00 dB
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SF             101.2544800 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    1.40
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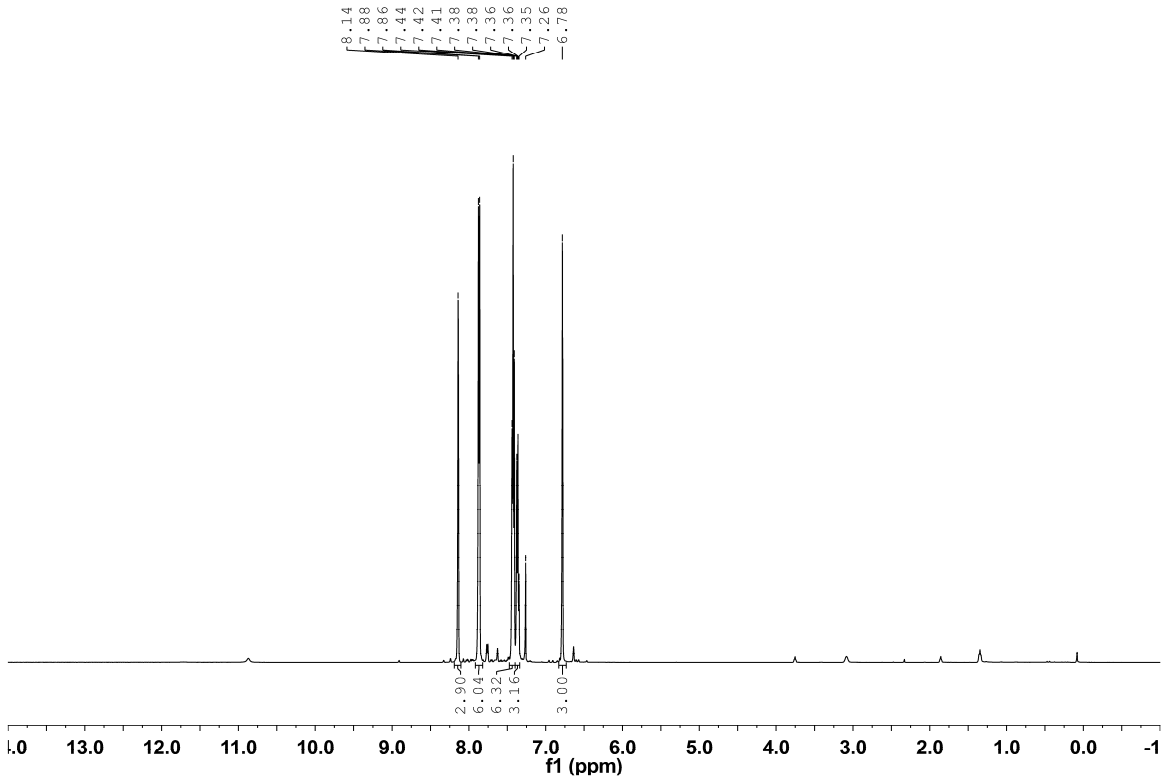
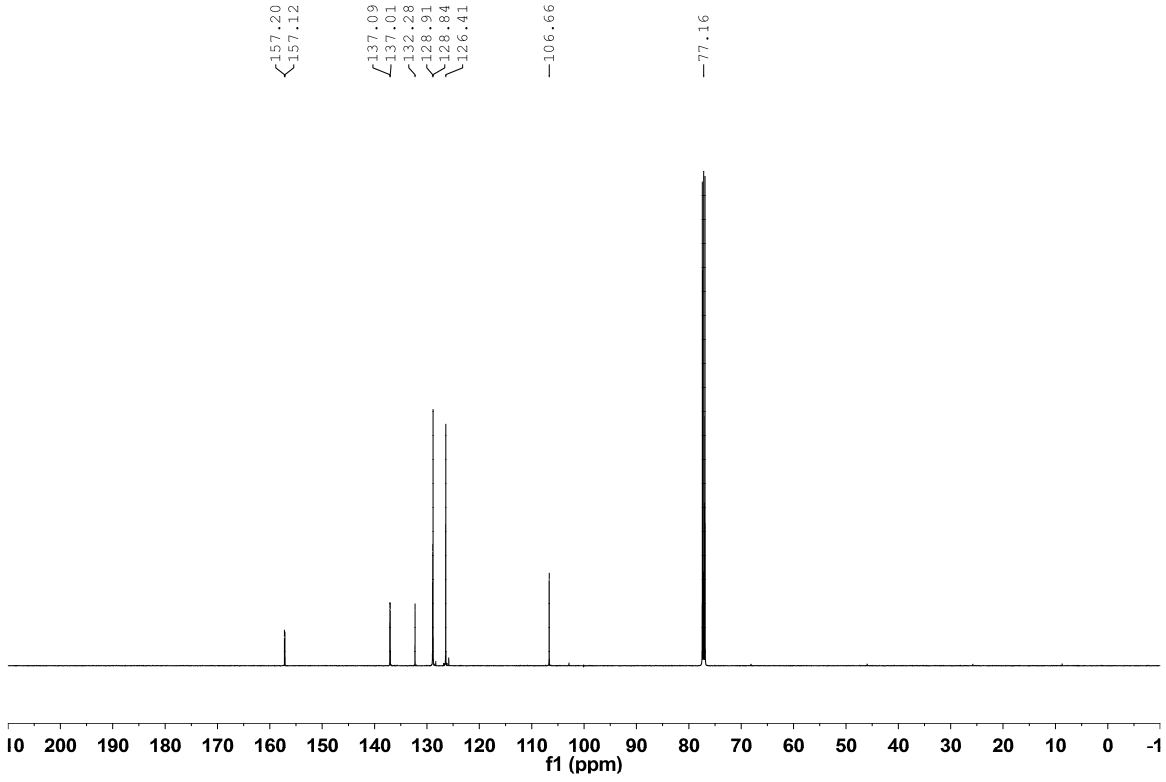
NMR spectra of tris(3-phenylpyrazol-1-yl)phosphine (C^{Ph})

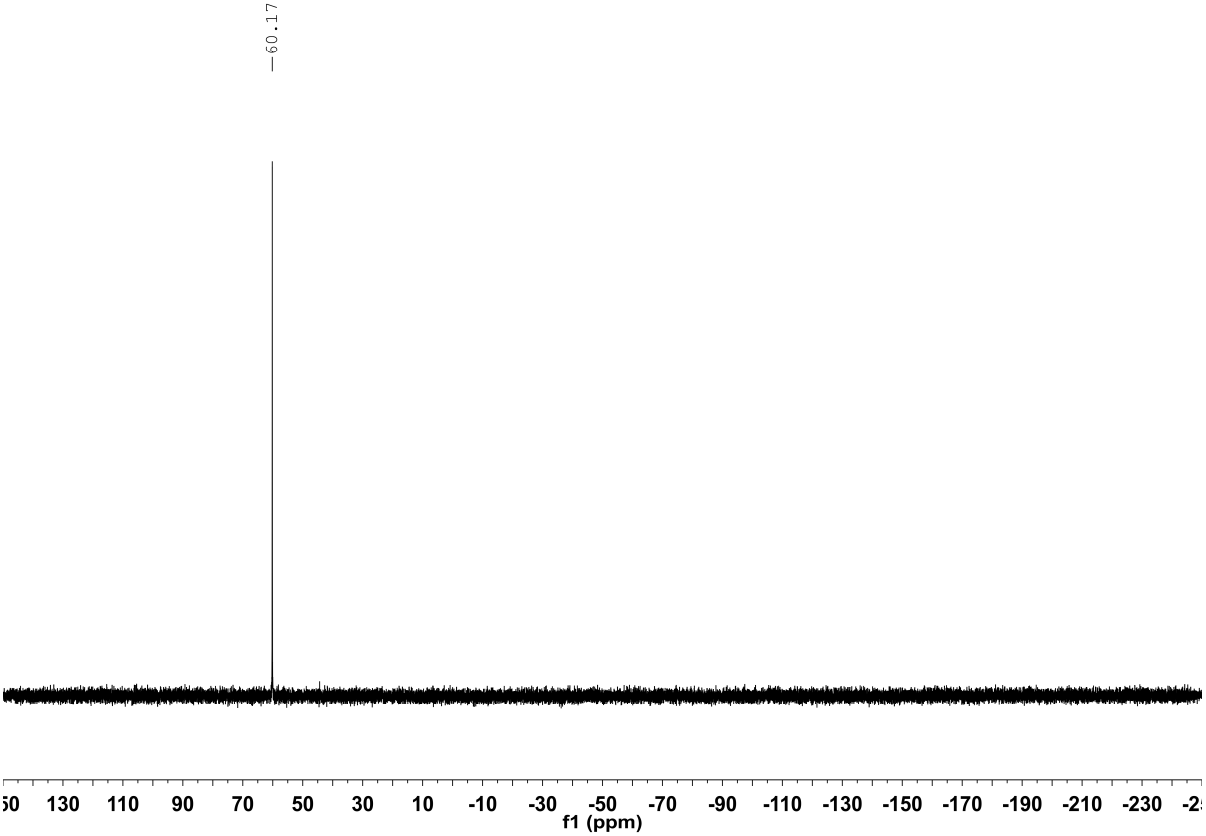
^{1}H-NMR of **C**^{Ph} (500.2 MHz, $CDCl_3$)



^{13}C-NMR of **C**^{Ph} (125.8 MHz, $CDCl_3$)

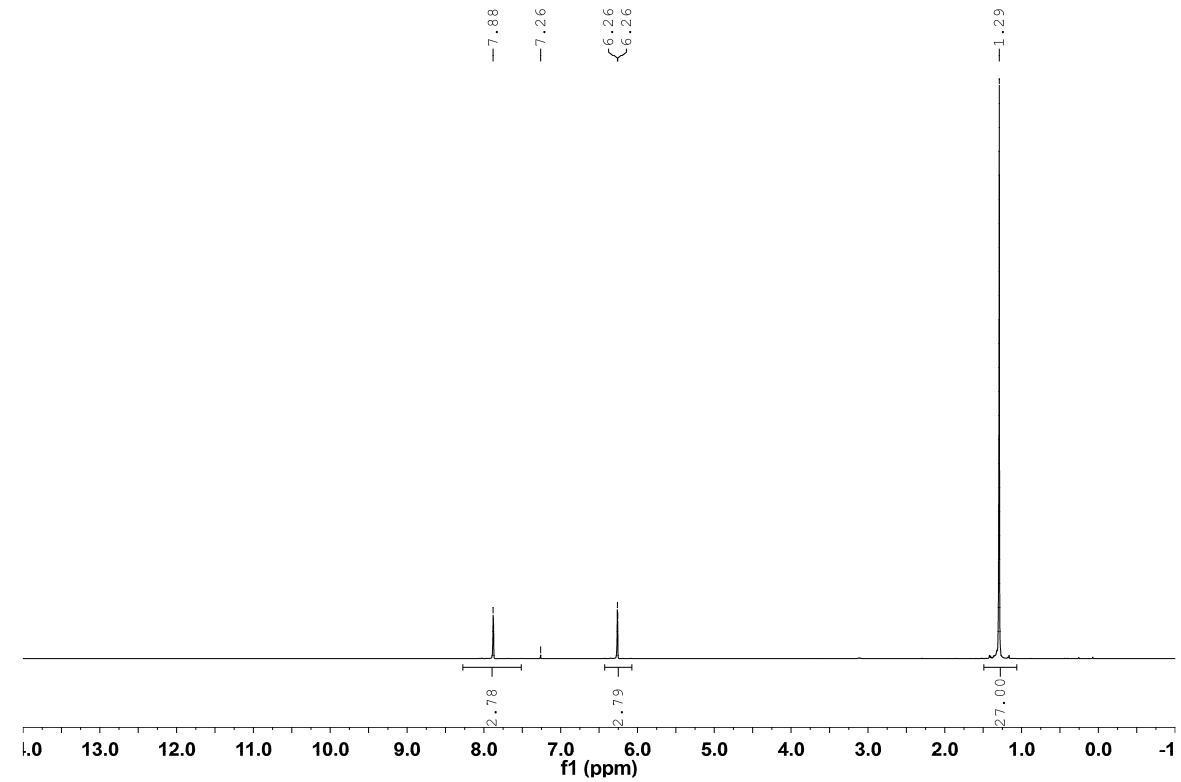


^{31}P-NMR of $\mathbf{C}^{\mathbf{Ph}}$ (162.0 MHz, $CDCl_3$)

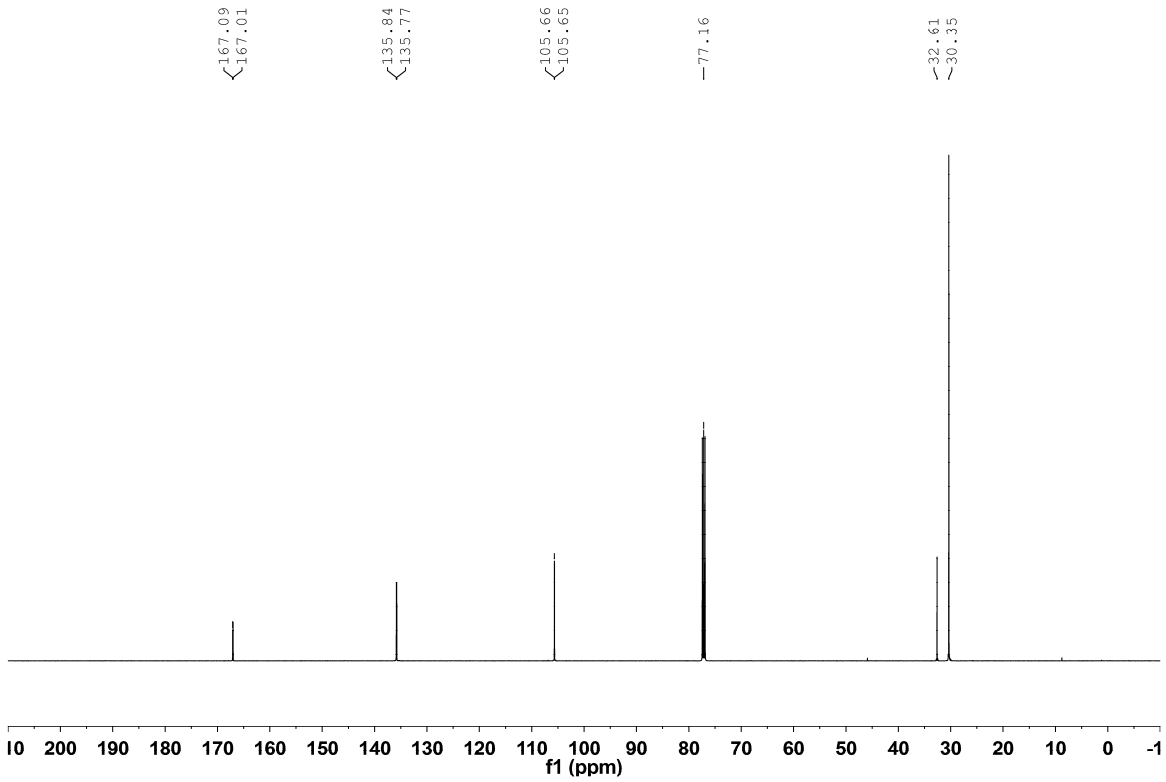


NMR spectra of tris(3-*tert*-butylpyrazol-1-yl)phosphine ($\mathbf{C}^{t\text{-}\mathbf{Bu}}$)

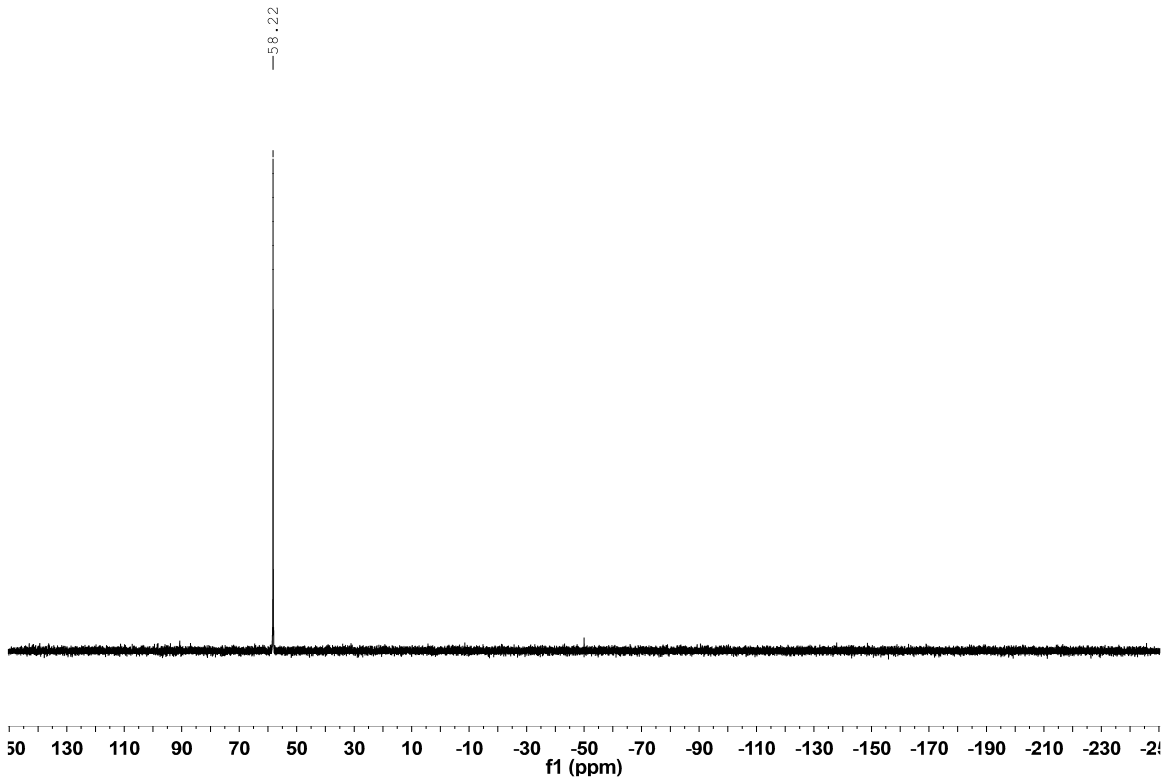
^{1}H-NMR of $\mathbf{C}^{t\text{-}\mathbf{Bu}}$ (500.2 MHz, $CDCl_3$)



^{13}C-NMR of **C**$^{t\text{-Bu}}$ (125.8 MHz, $CDCl_3$)

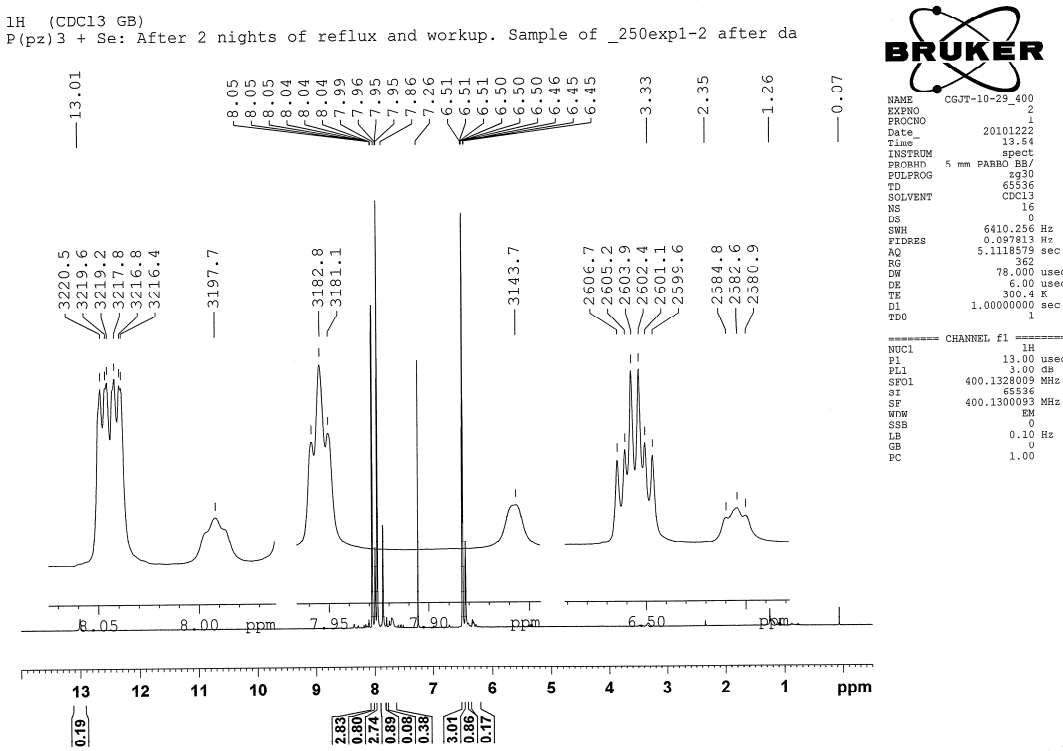


^{31}P-NMR of **C**$^{t\text{-Bu}}$ (162.0 MHz, $CDCl_3$)

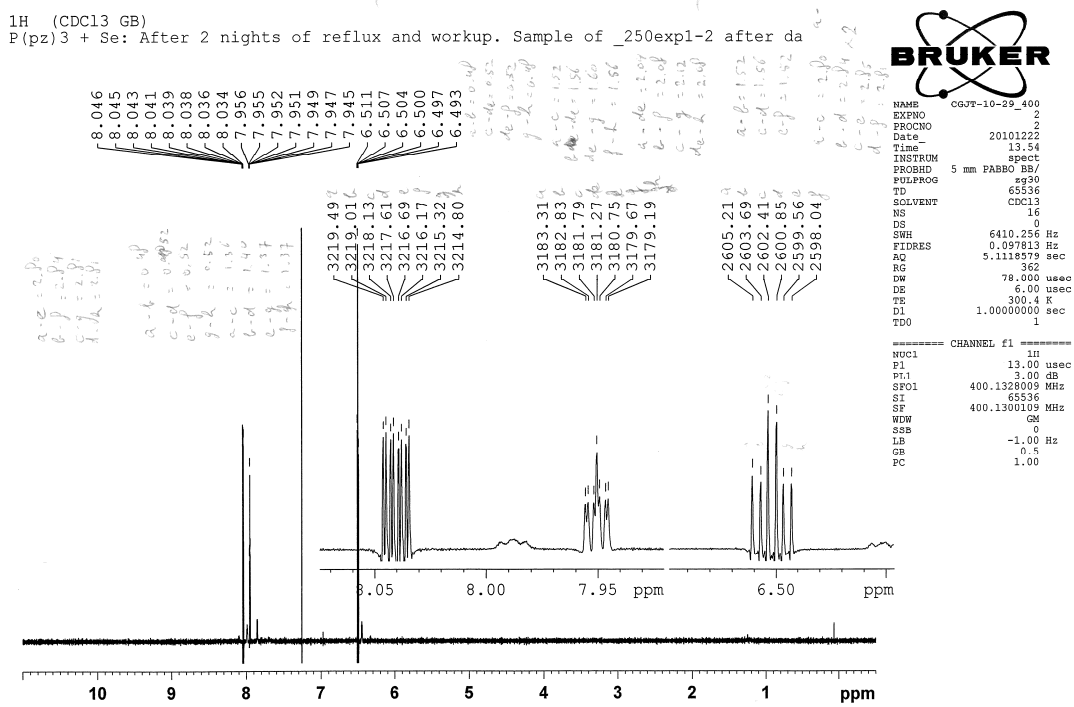


NMR spectra of tris(pyrazolyl)phosphine selenide (SeC^H)

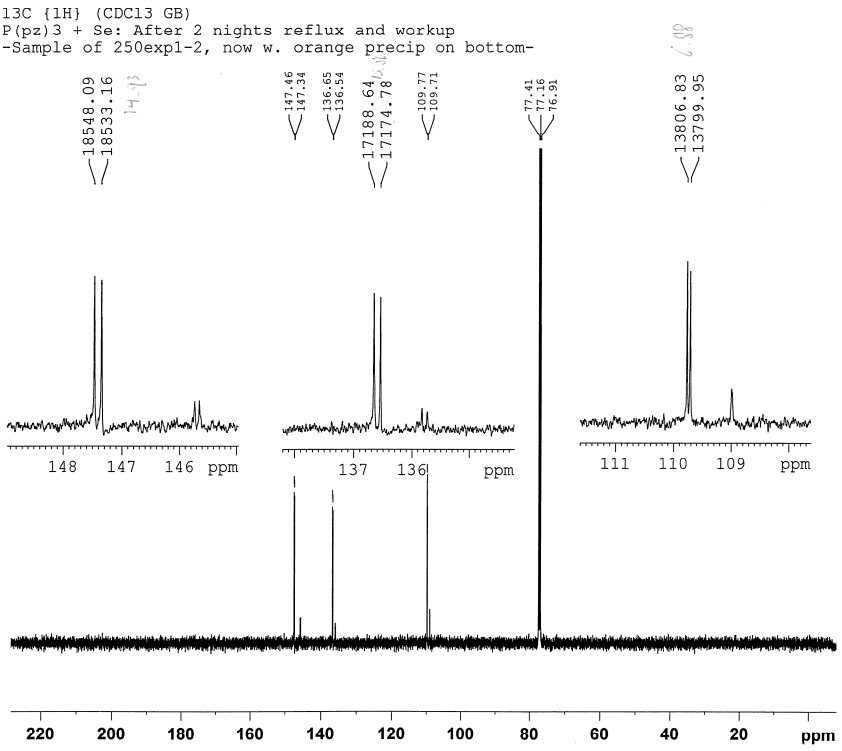
^{1}H NMR of Se$\mathbf{C}^{\mathbf{H}}$ (400.1 MHz, $CDCl_3$)



^{1}H NMR of Se$\mathbf{C}^{\mathbf{H}}$ (400.1 MHz, $CDCl_3$) after line narrowing



$^{13}C\{^{1}H\}$ NMR of Se**C**^{H} (125.8 MHz, $CDCl_3$)

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PROCNO                     1
Date_               20101222
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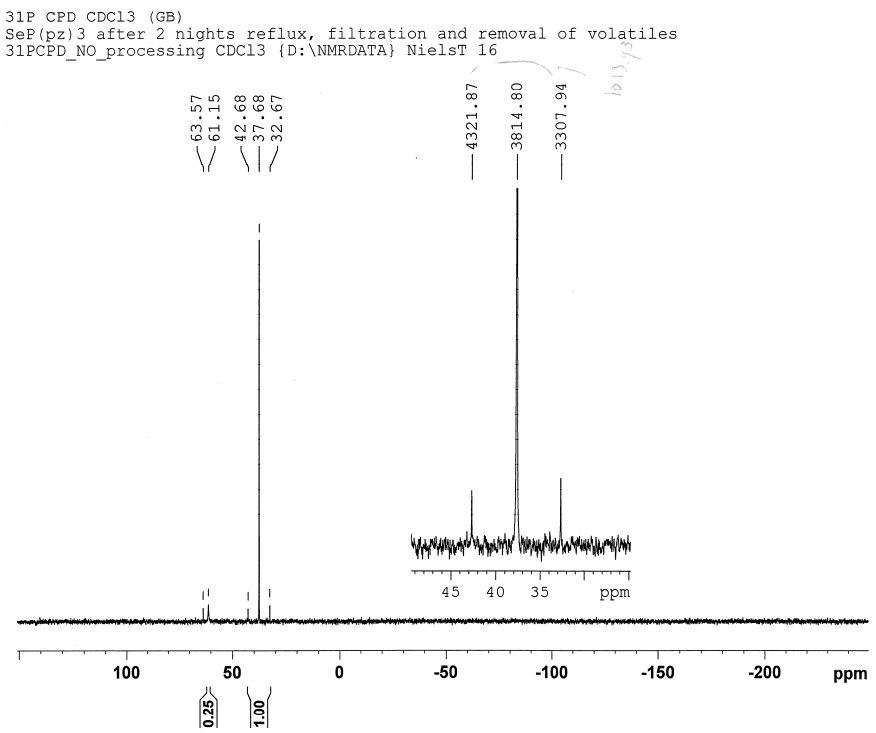
INSTRUM                spect
PROBHD   5 mm CPTCI 1H-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       20
DS                        2
SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                1.1010548 sec
RG                     2050
DW                   16.800 usec
DE                    6.50 usec
TE                   296.0 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     11.20 usec
PL1                    -2.00 dB
PL1W           88.77790070 W
SFO1          125.7967701 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                80.00 usec
PL2                    4.00 dB
PL12                  25.28 dB
PL13                  28.00 dB
PL2W           8.72000027 W
PL12W          0.06494062 W
PL13W          0.03471494 W
SFO2          500.2320009 MHz
SI                    65536
SF            125.7829181 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

$^{31}P\{^{1}H\}$ NMR of Se**C**^{H} (101.3 MHz, $CDCl_3$)

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PROCNO                     1
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Time                   17.58
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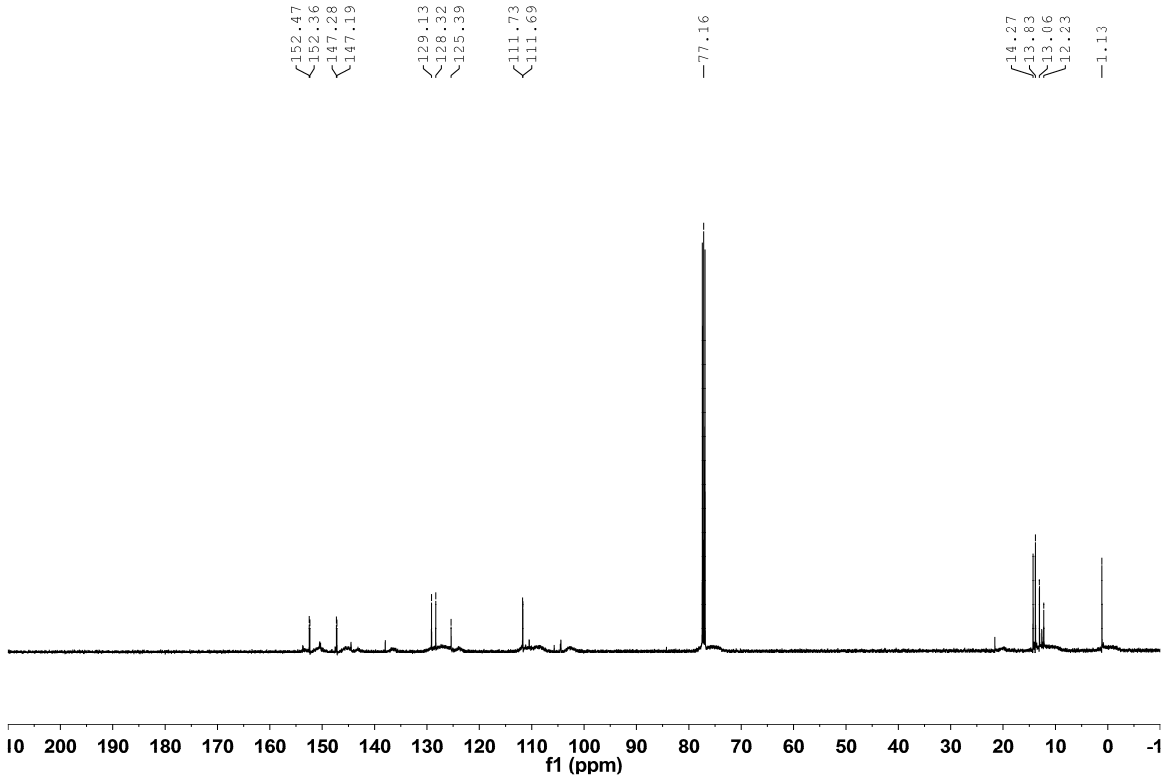
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       64
DS                        4
SWH               40650.406 Hz
FIDRES             0.620276 Hz
AQ                0.8061428 sec
RG                   20642.5
DW                   12.300 usec
DE                    6.00 usec
TE                   300.2 K
D1                2.00000000 sec
D11               0.03000000 sec
DELTA             1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     31P
P1                     7.00 usec
PL1                    0.00 dB
SFO1         101.2494172 MHz

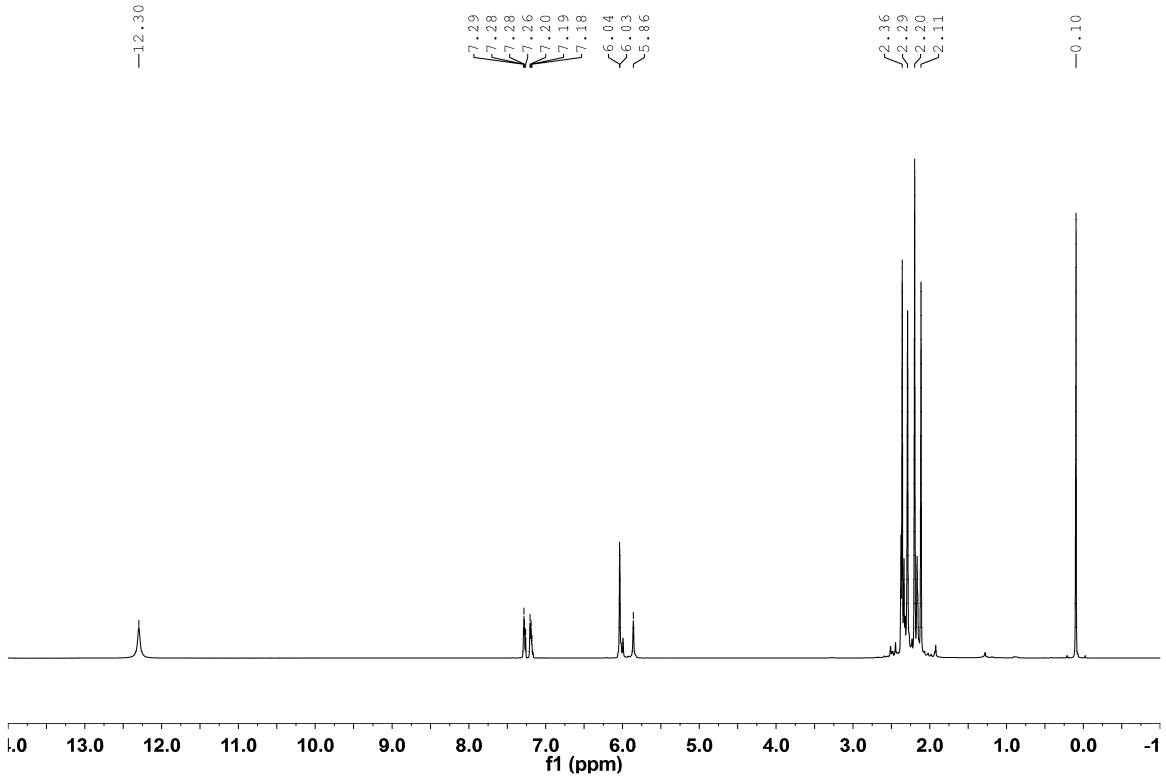
======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                80.00 usec
PL2                   -3.00 dB
PL12                  20.00 dB
PL13                  24.00 dB
SFO2          250.1310005 MHz
SI                    65536
SF            101.2544800 MHz
WDW                      EM
SSB                       0
LB                     3.00 Hz
GB                        0
PC                     1.40
```

NMR spectra of tris(3,5-dimethylpyrazolyl)phosphine selenide (SeC^{Me2})

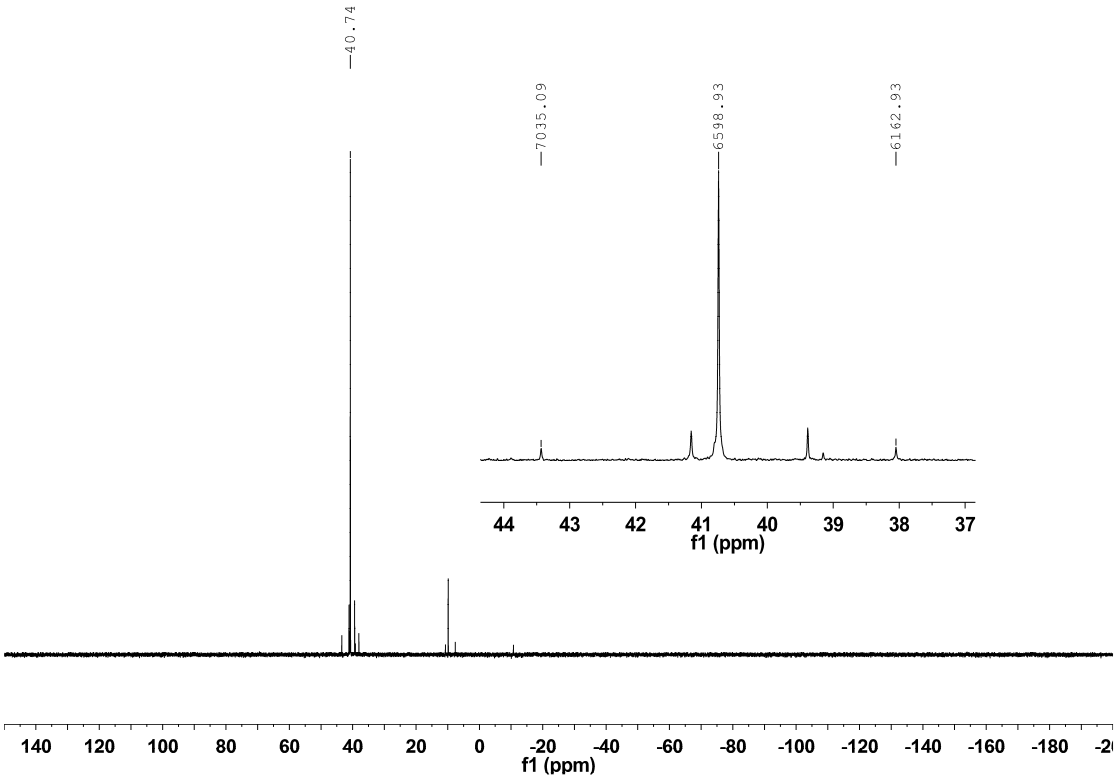
^{1}H NMR of Se$\mathbf{C}^{Me2}$ (500.2 MHz, $CDCl_3$)



^{13}C NMR of Se$\mathbf{C}^{Me2}$ (125.8 MHz, $CDCl_3$)

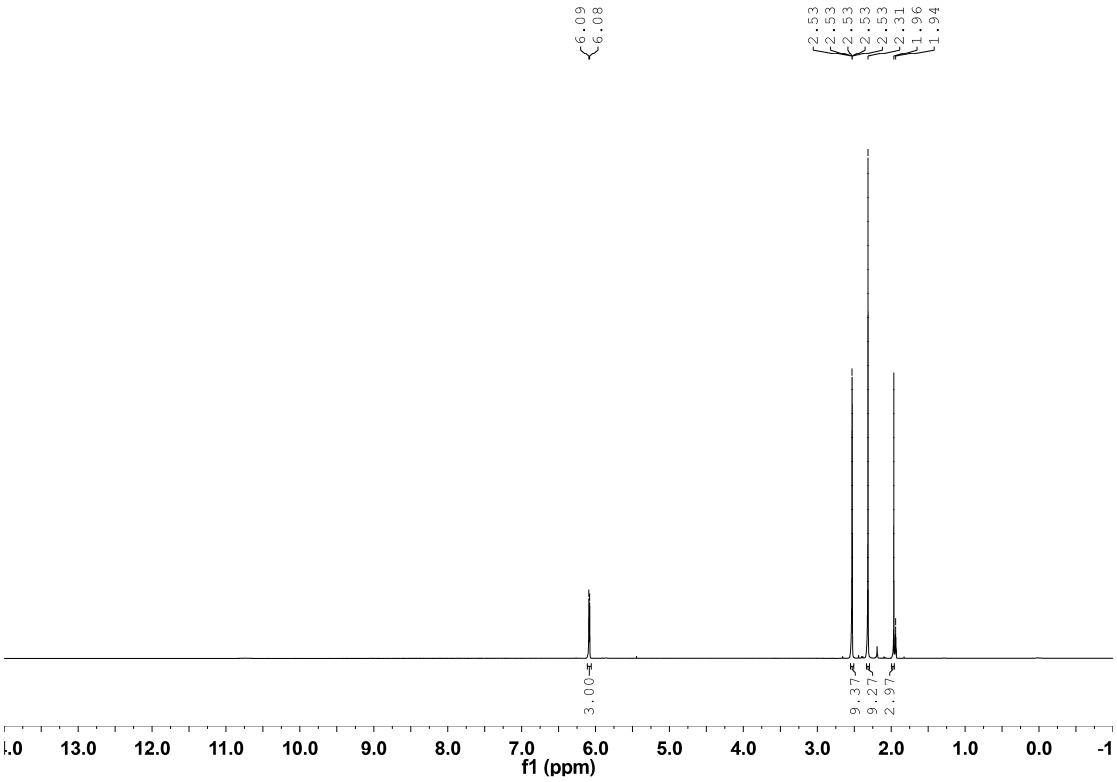


$^{31}P\{^{1}H\}$ NMR of Se**C**^{Me2} (162.0 MHz, $CDCl_3$)

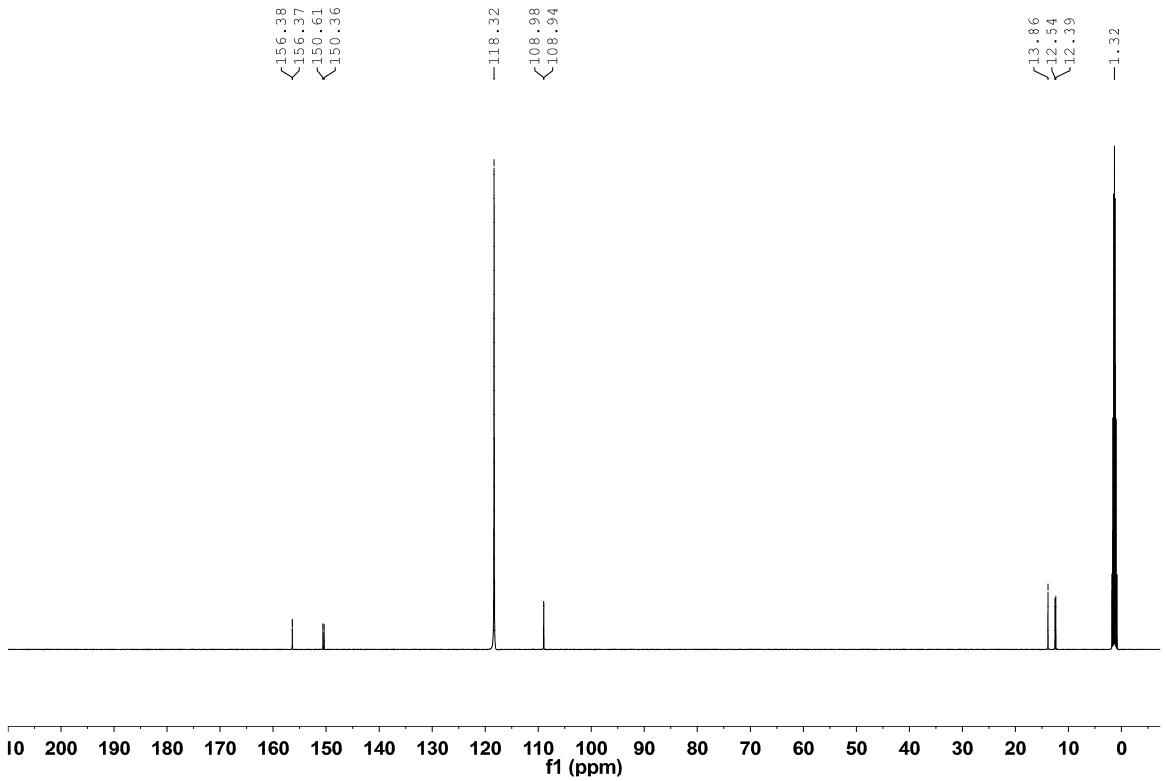


NMR spectra of acetonitrile tris(3,5-dimethylpyrazolyl)phosphine copper(I) hexafluorophosphate ([C^{Me2}Cu(NCMe)][PF_6])

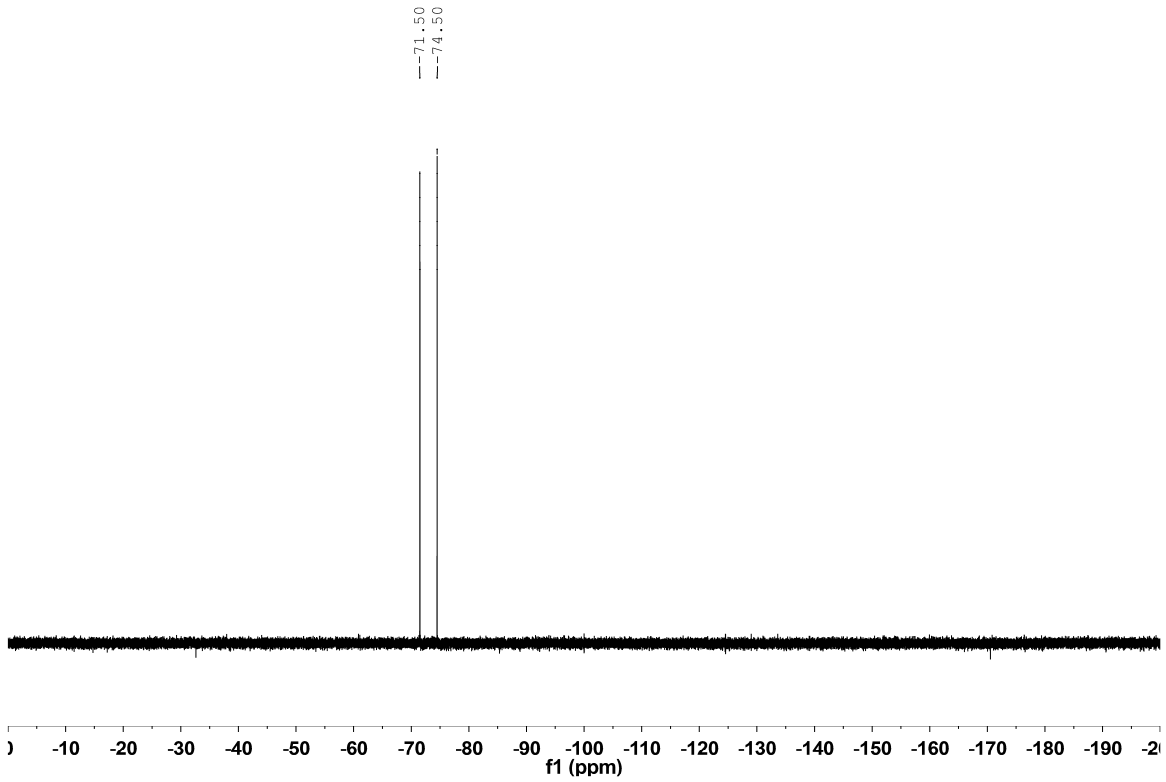
^{1}H NMR of [**C**^{Me2}Cu(NCMe)][PF_6] (500.2 MHz, CD_3CN)



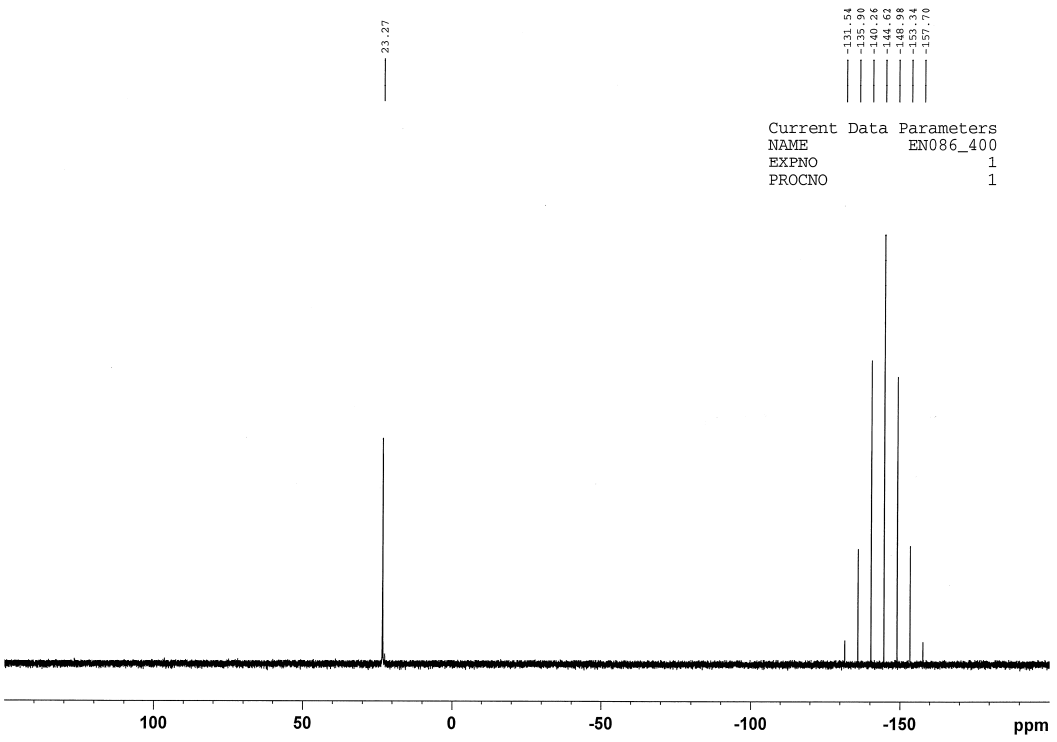
^{13}C NMR of [**C**$^{\mathbf{Me2}}$Cu(NCMe)][PF_6] (125.8 MHz, CD_3CN)



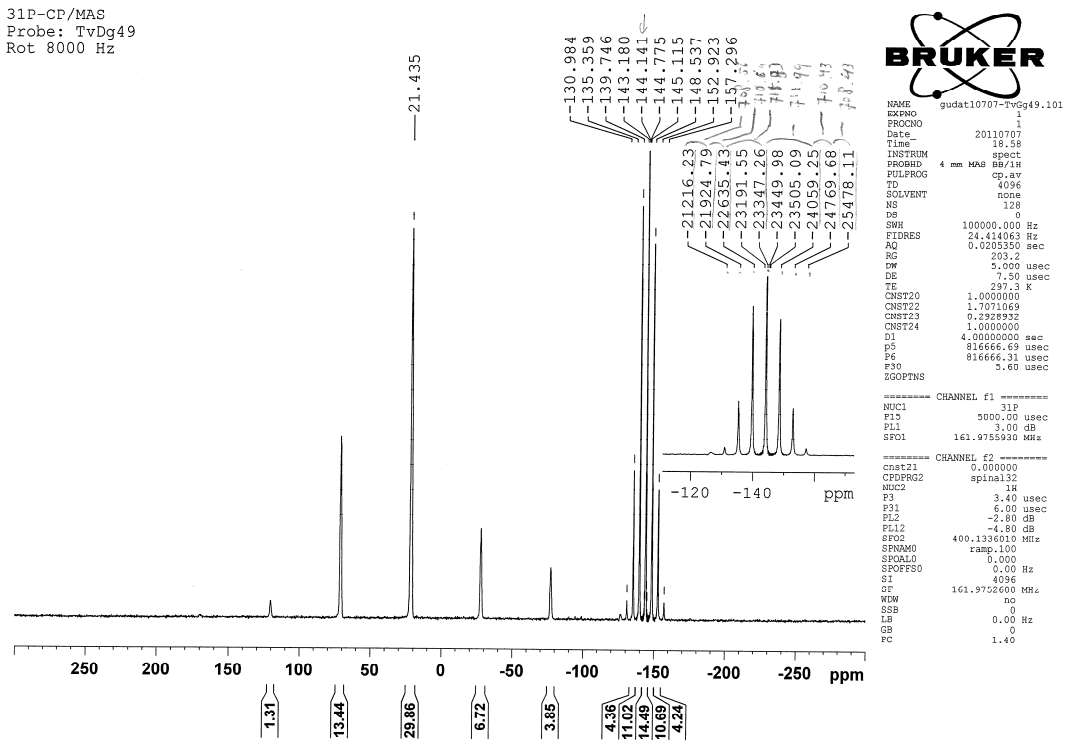
^{19}F NMR of [**C**$^{\mathbf{Me2}}$Cu(NCMe)][PF_6] (235.3 MHz, CD_3CN)



^{31}P NMR of [**C**$^{\mathbf{Me2}}$Cu(NCMe)][PF_6] (162.0 MHz, CD_3CN)

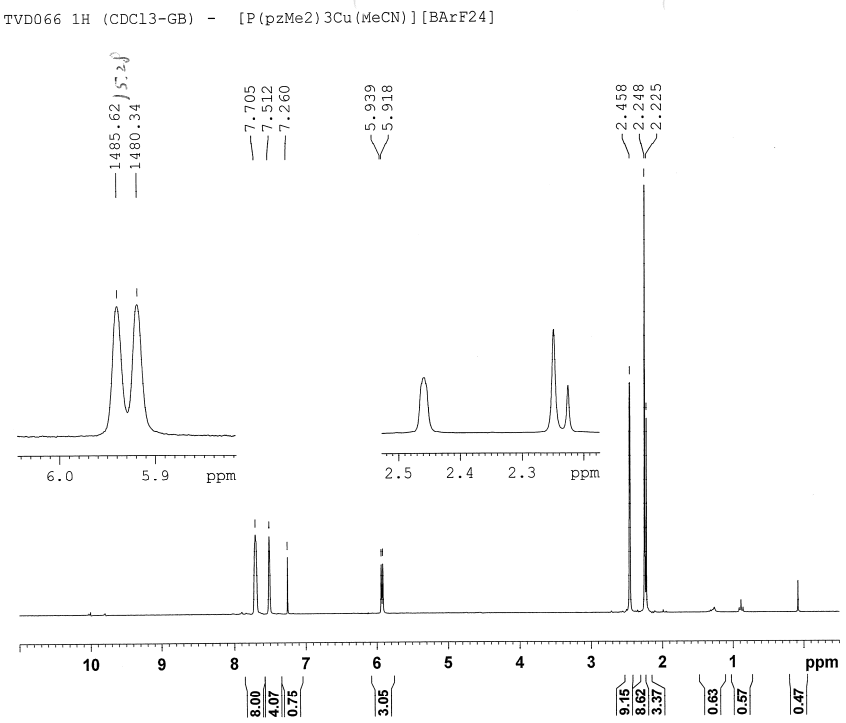


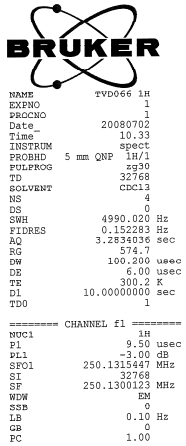
^{31}P{^{1}H} CP/MAS NMR of [**C**$^{\mathbf{Me2}}$Cu(NCMe)][PF_6] (162.0 MHz)



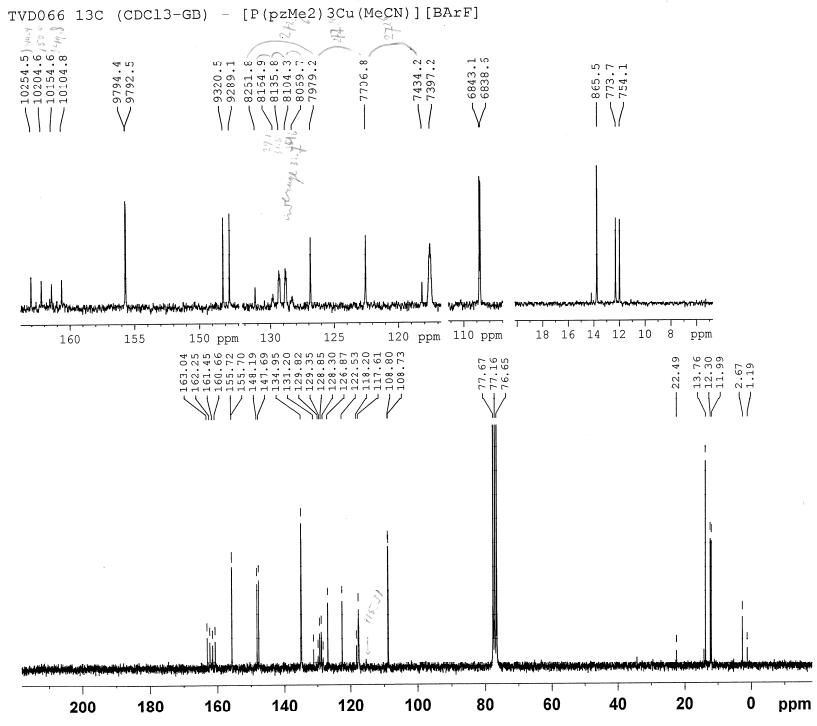
NMR spectra of acetonitrile tris(3,5-dimethylpyrazolyl)phosphine copper(I) tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate ([C^{Me2}Cu(NCMe)][$BArF_{24}$])

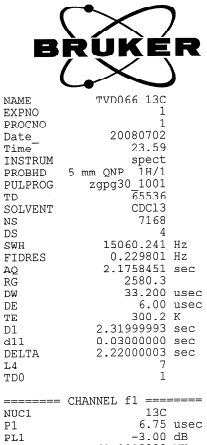
^{1}H NMR of [C^{Me2}Cu(NCMe)][$BArF_{24}$] (250.1 MHz, $CDCl_3$)



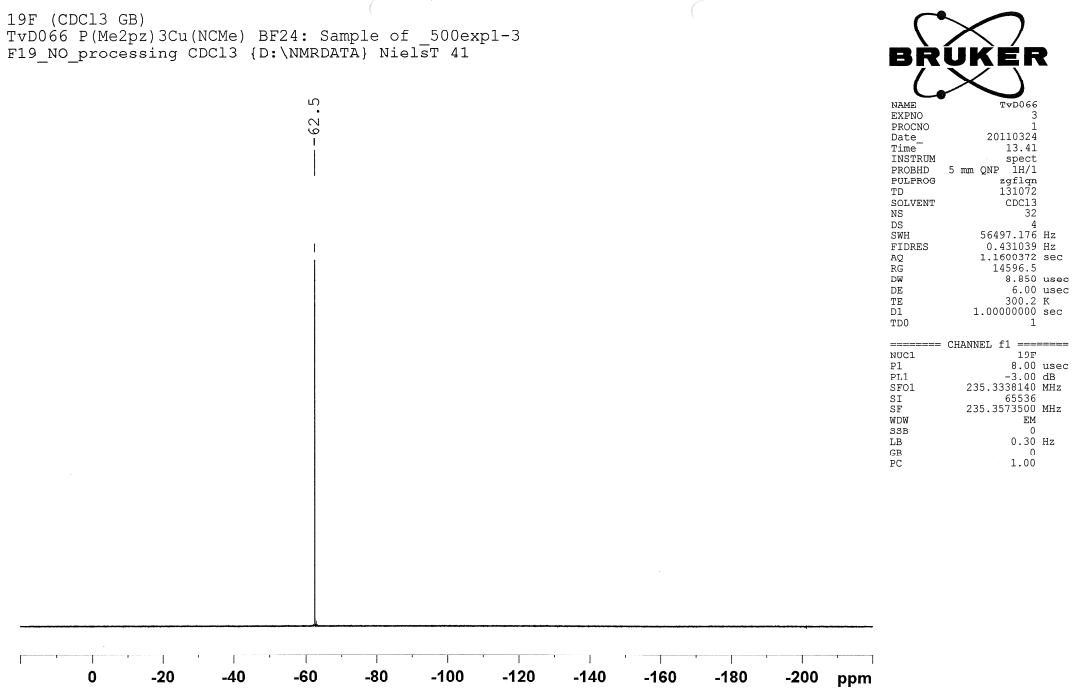


^{13}C{^{1}H} NMR of [C^{Me2}Cu(NCMe)][$BArF_{24}$] (62.9 MHz, $CDCl_3$)

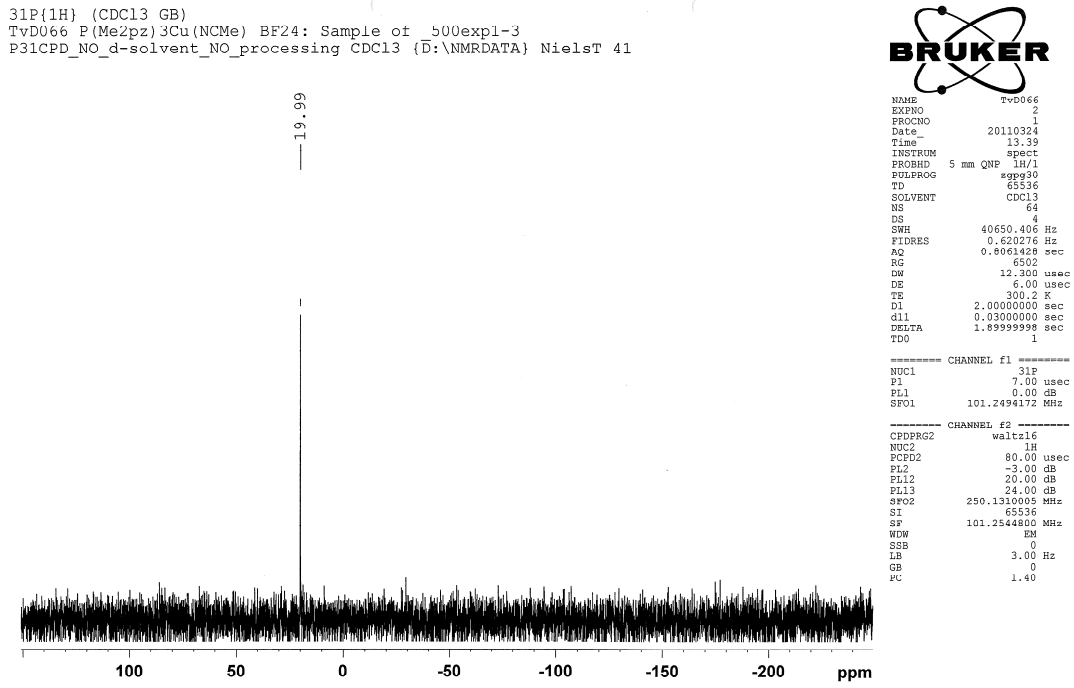




^{19}F NMR of [$\mathbf{C}^{\mathbf{Me2}}$Cu(NCMe)][BArF$_{24}$] (235.3 MHz, $CDCl_3$)

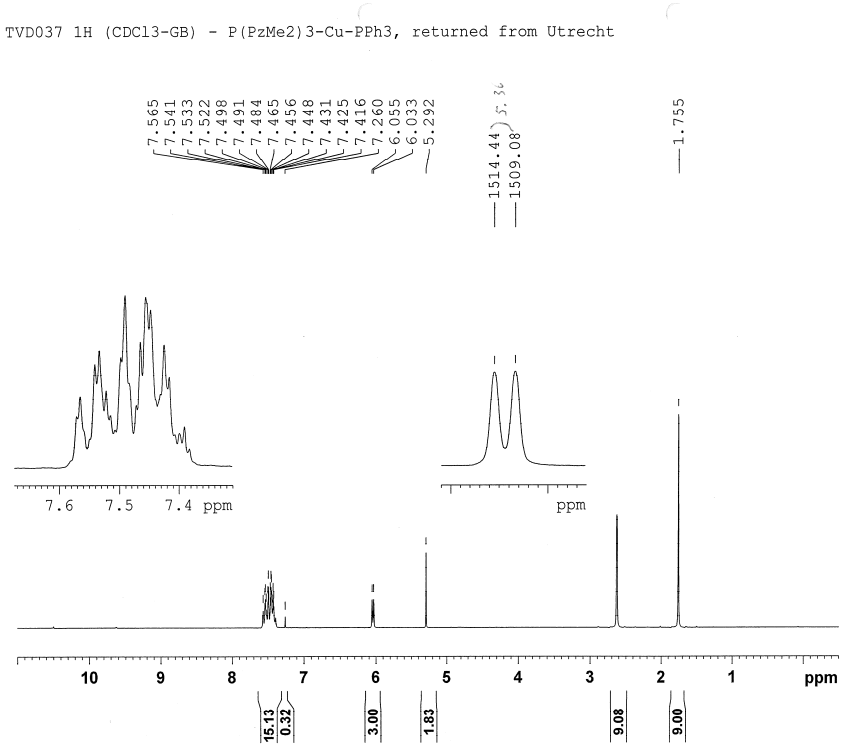


^{31}P NMR of [$\mathbf{C}^{\mathbf{Me2}}$Cu(NCMe)][BArF$_{24}$] (101.3 MHz, $CDCl_3$)



NMR spectra of tris(3,5-dimethylpyrazolyl)phosphine triphenylphosphine copper(I) hexafluorophosphate ([C^{Me2}Cu(PPh_3)][PF_6])

^{1}H NMR of [C^{Me2}Cu(PPh_3)][PF_6] (250.1 MHz, $CDCl_3$)

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PROCNO                      1
Date_                20080617
Time                    13.51
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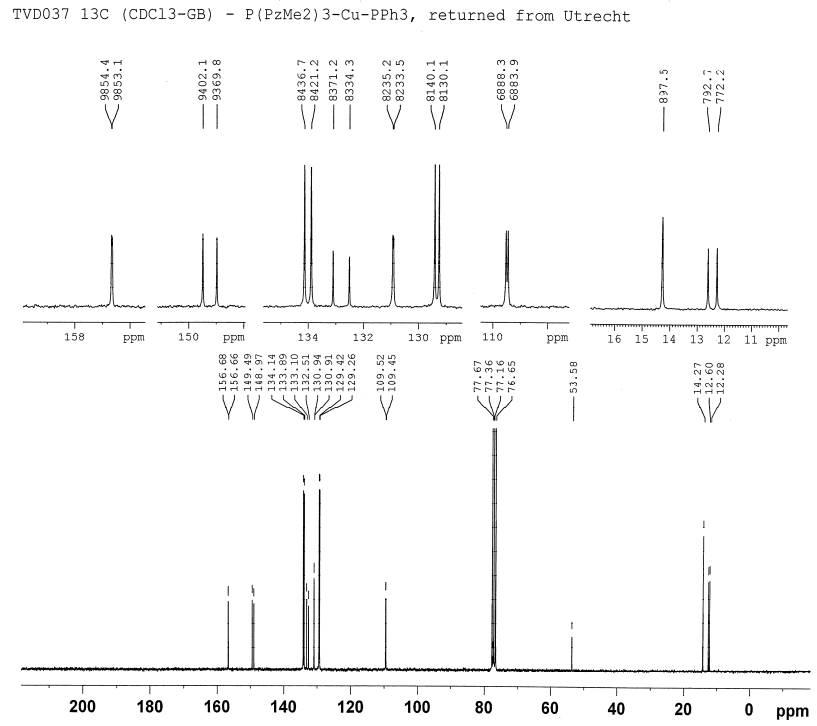
PROBHD   5 mm QNP  1H/1
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                          4
DS                          0
SWH                4990.020 Hz
FIDRES             0.152283 Hz
AQ                 3.2834036 sec
RG                     287.4
DW                   100.200 usec
DE                     6.00 usec
TE                     300.2 K
D1                20.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                       9.50 usec
PL1                     -3.00 dB
SFO1            250.1315447 MHz
SI                       32768
SF              250.1300122 MHz
WDW                         EM
SSB                         0
LB                       0.10 Hz
GB                          0
PC                       1.00
```

^{13}C{^{1}H} NMR of [C^{Me2}Cu(PPh_3)][PF_6] (62.9 MHz, $CDCl_3$)

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PROCNO                   1
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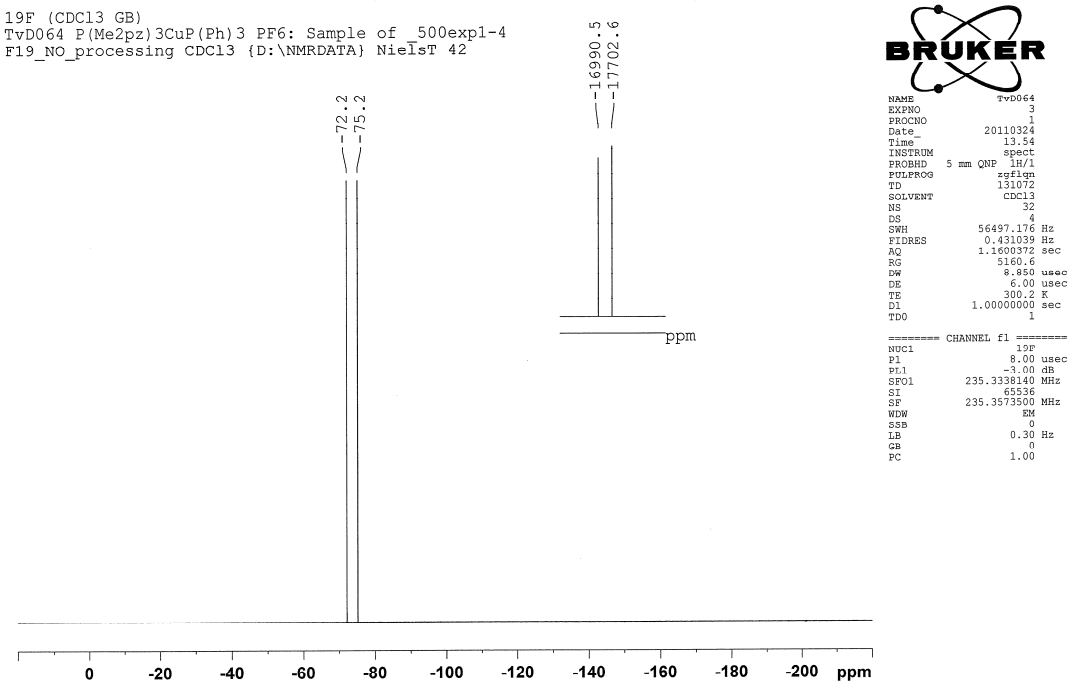
PULPROG      zgpg30_1001
TD                   65536
SOLVENT              CDCl3
NS                    4096
DS                       4
SWH             15060.241 Hz
FIDRES           0.229801 Hz
AQ               2.1758451 sec
RG                    1024
DW                 33.200 usec
DE                 6.00 usec
TE                 300.2 K
D1              2.31999993 sec
d11             0.03000000 sec
DELTA           2.22000003 sec
L4                       4
TD0                      1

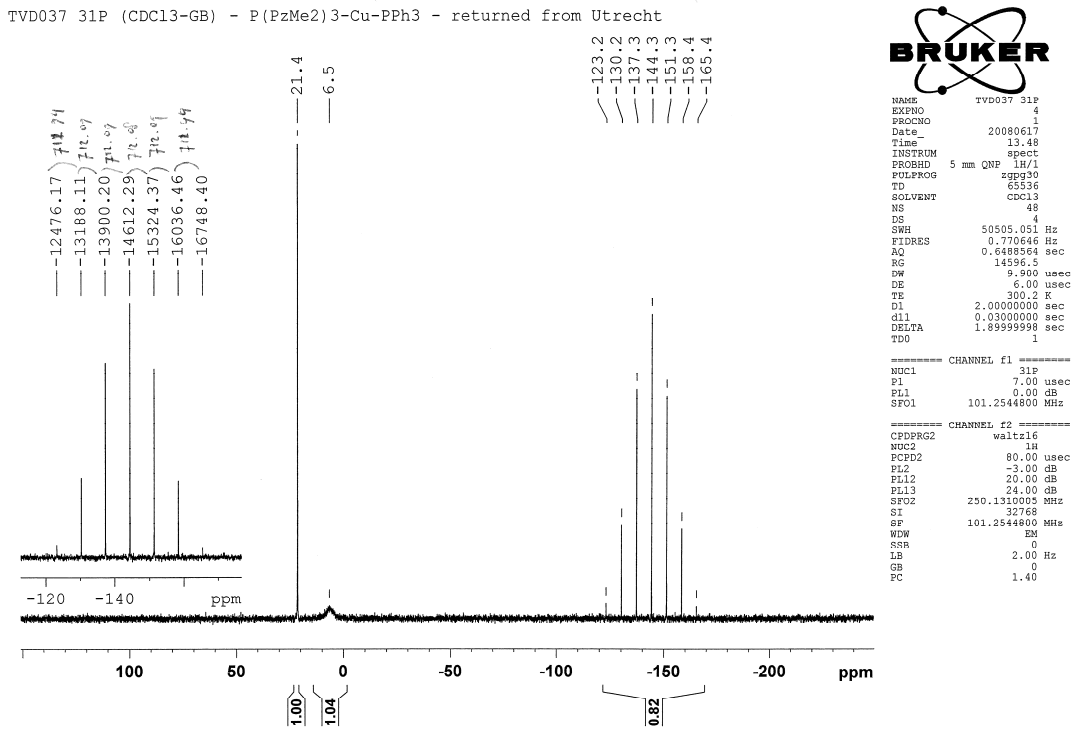
======== CHANNEL f1 ========
NUC1                    13C
P1                    6.75 usec
PL1                  -3.00 dB
SFO1         62.9015280 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -3.00 dB
PL12                 20.00 dB
PL13                 24.00 dB
SFO2         250.1310005 MHz
SI                   65536
SF           62.8952339 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

^{19}F NMR of [**C**$^{\mathbf{Me2}}$Cu(PPh$_3$)][PF$_6$] (235.3 MHz, CDCl$_3$)

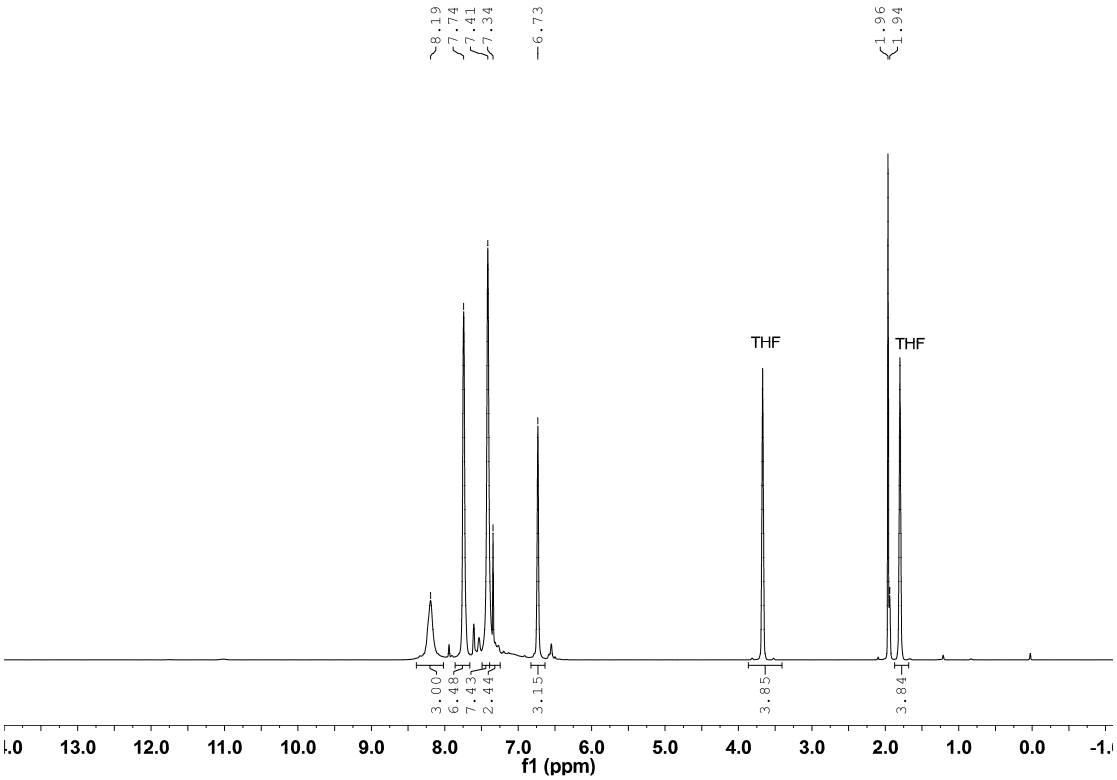


^{31}P NMR of [**C**$^{\mathbf{Me2}}$Cu(PPh$_3$)][PF$_6$] (101.3 MHz, CDCl$_3$)

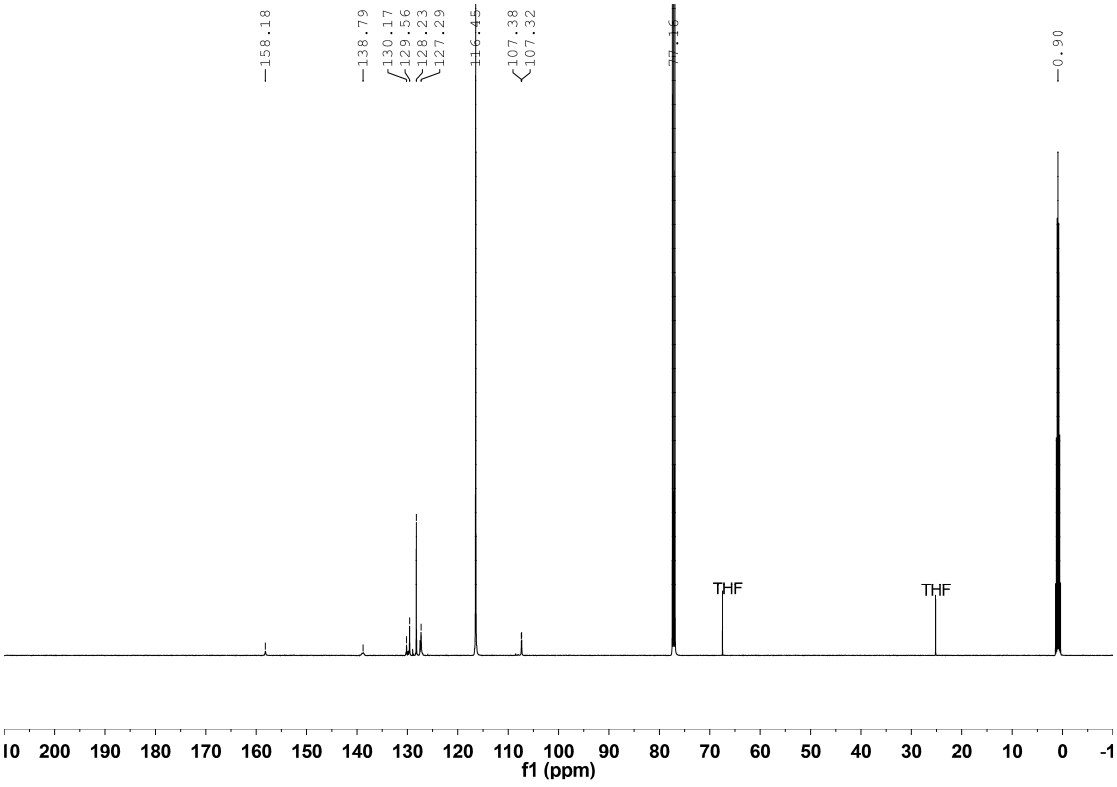


NMR spectra of acetonitrile tris(3-phenylpyrazolyl)phosphine copper(I) hexafluorophosphate ([C^{Ph}Cu(NCMe)][PF$_6$])

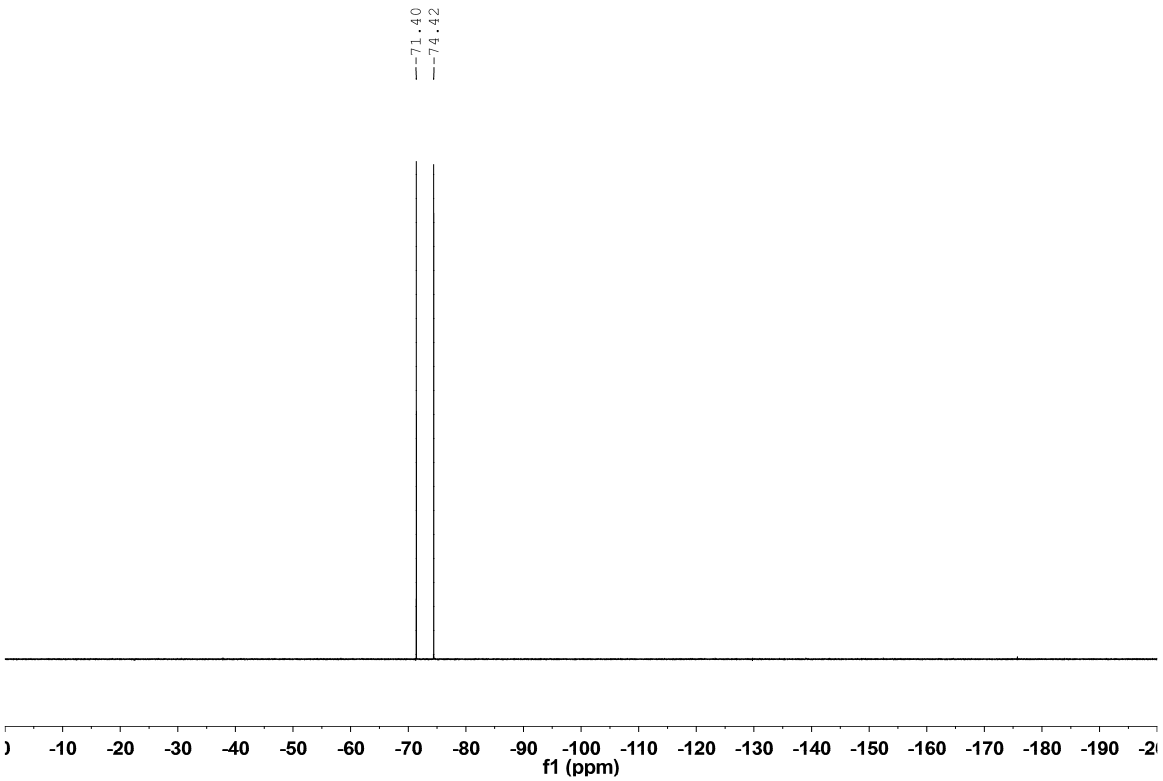
^{1}H NMR of [**C^{Ph}**Cu(NCMe)][PF$_6$] (500.2 MHz, $CDCl_3$+CD_3CN)



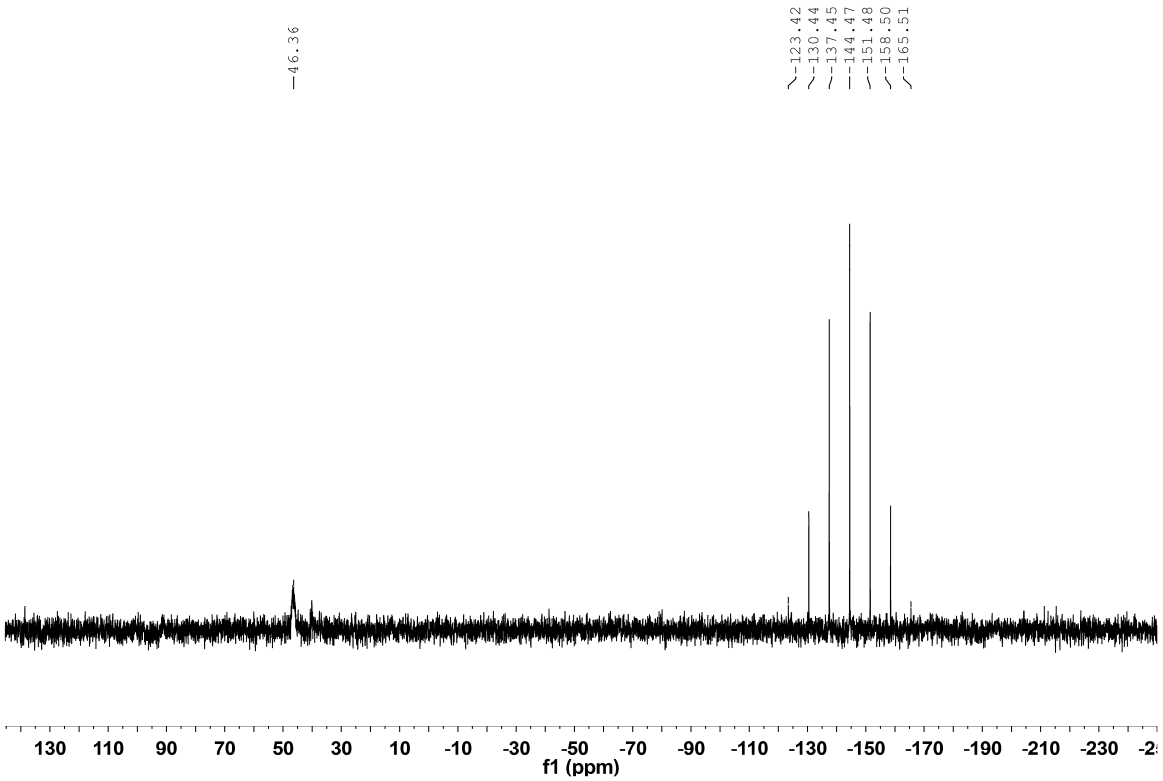
^{13}C{^{1}H} NMR of [**C^{Ph}**Cu(NCMe)][PF$_6$] (125.8 MHz, $CDCl_3$+CD_3CN)



^{19}F-NMR of [**C**$^{\mathbf{Ph}}$Cu(NCMe)][PF_6] (235.4 MHz, $CDCl_3$+CD_3CN)

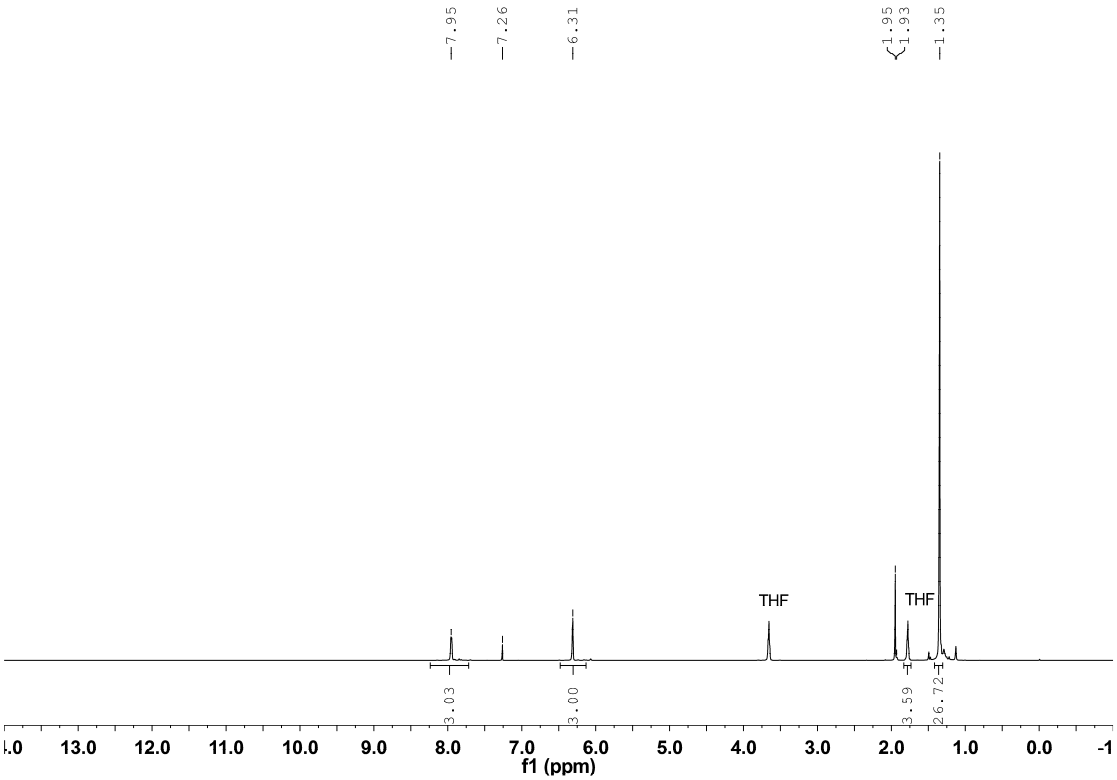


^{31}P-NMR of [**C**$^{\mathbf{Ph}}$Cu(NCMe)][PF_6] (162.0 MHz, $CDCl_3$+CD_3CN)

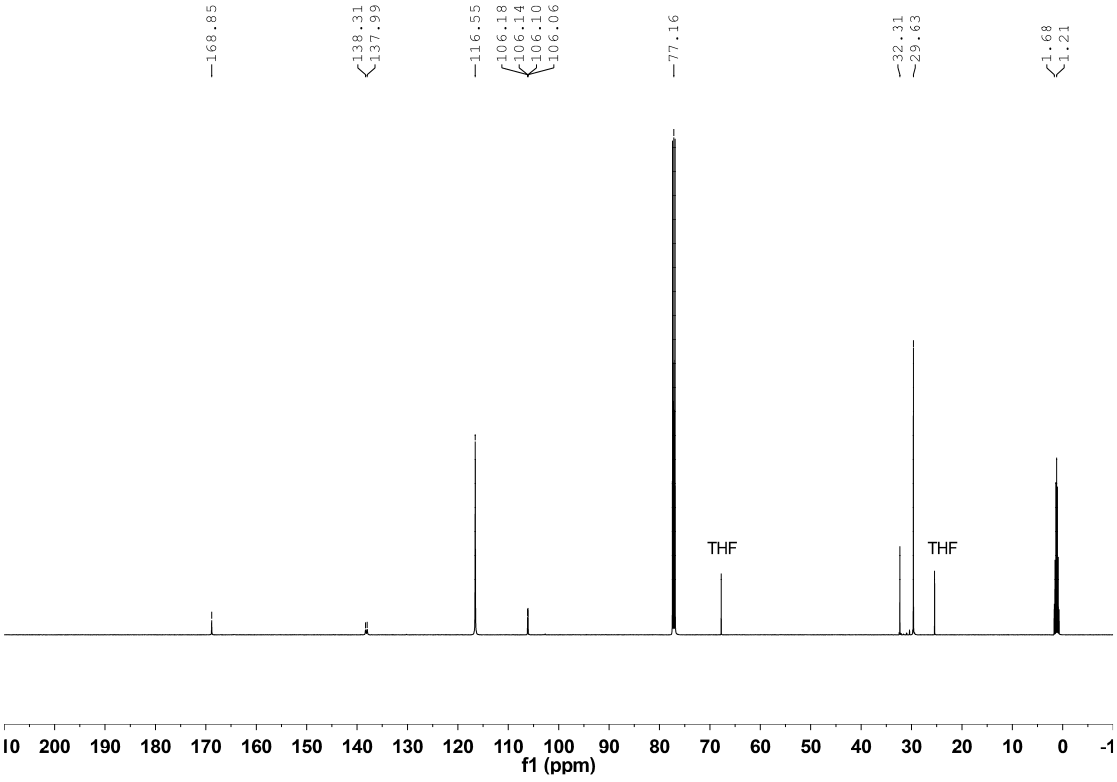


NMR spectra of acetonitrile tris(3-*tert*-butylpyrazolyl)phosphine copper(I) hexafluorophosphate ([C$^{t\text{-Bu}}$Cu(NCMe)][PF$_6$])

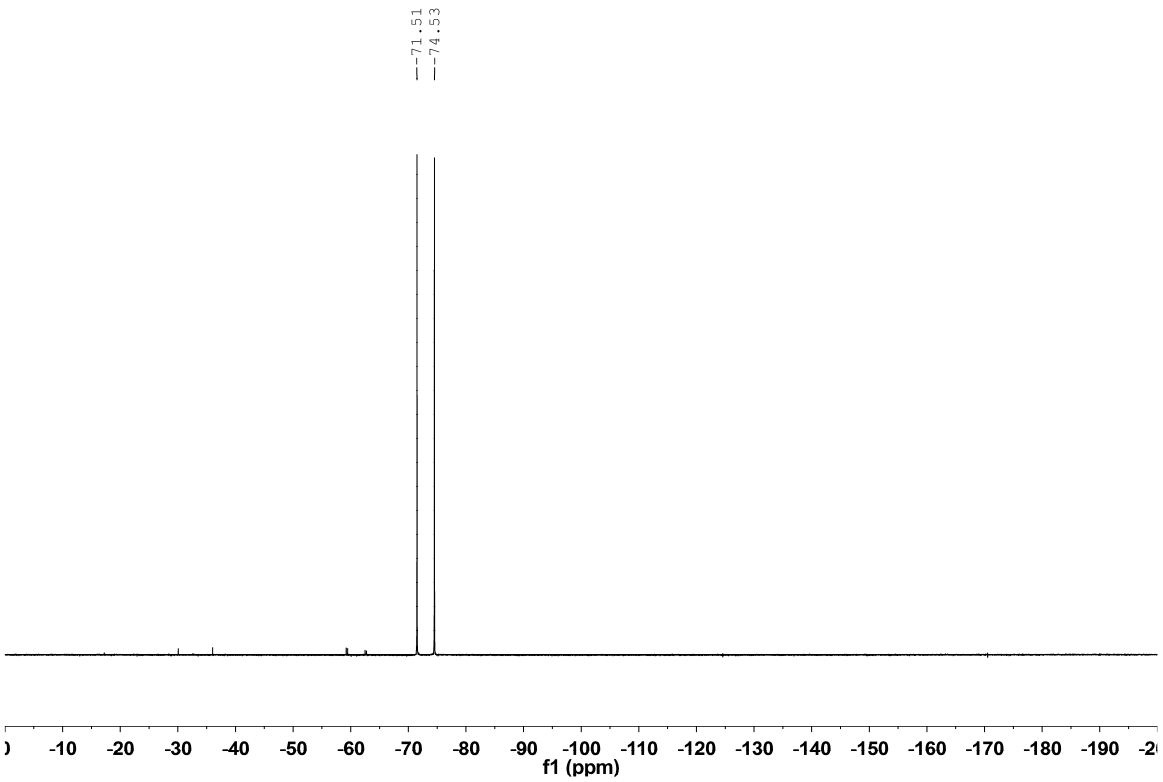
^{1}H-NMR of [**C**$^{t\text{-Bu}}$Cu(NCMe)][PF$_6$] (500.2 MHz, $CDCl_3$+CD_3CN)



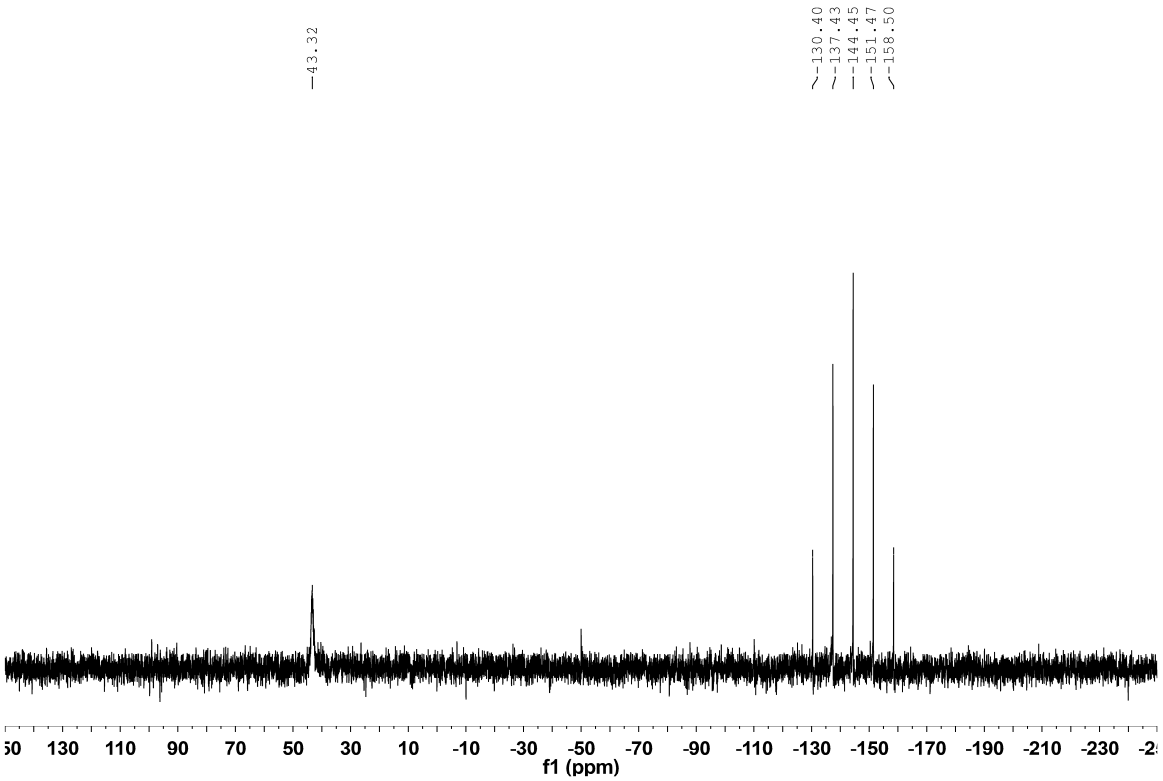
^{13}C-NMR of [**C**$^{t\text{-Bu}}$Cu(NCMe)][PF$_6$] (125.8 MHz, $CDCl_3$+CD_3CN)



^{19}F-NMR (235.4 MHz, $CDCl_3$+CD_3CN)

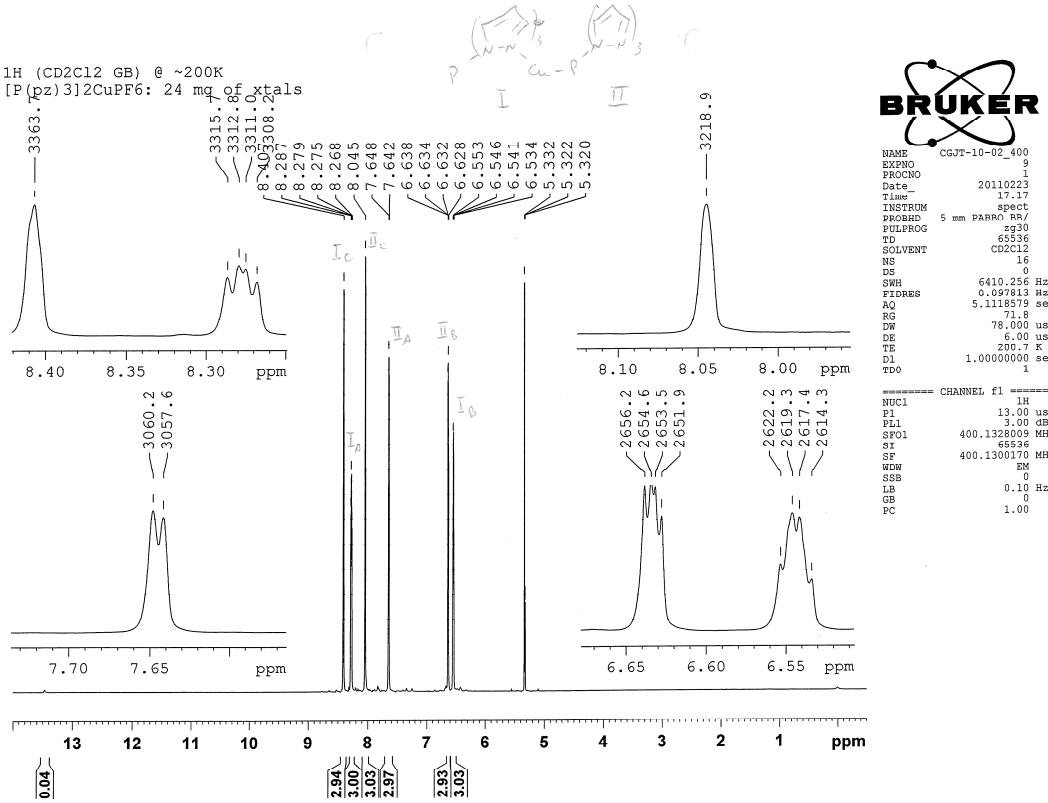


^{31}P-NMR (162.0 MHz, $CDCl_3$+CD_3CN)



NMR spectra of bis(tris(pyrazolyl)phosphine)copper(I) hexafluorophosphate ([(C^{H})$_2$Cu][PF$_6$])

^{1}H NMR of [(**C^{H}**)$_2$Cu][PF$_6$] (400.1 MHz, 201 K, CD_2Cl_2)



BRUKER

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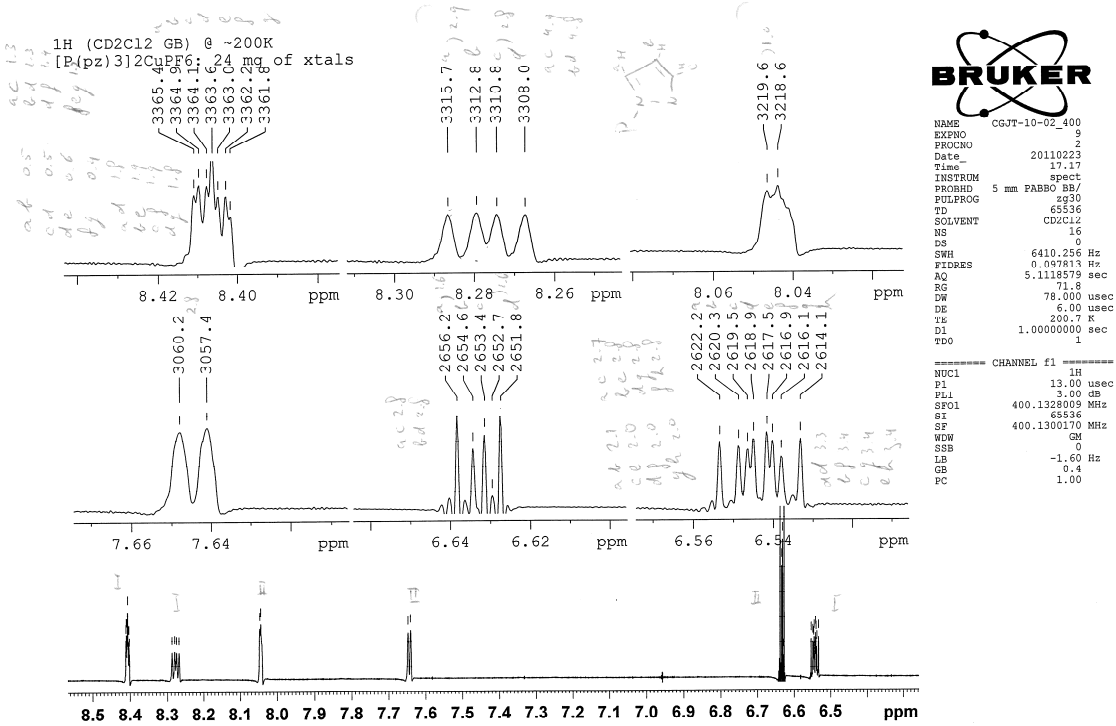
PULPROG	zg30
TD	65536
SOLVENT	CD2Cl2
NS	16
DS	0
SWH	6410.256 Hz
FIDRES	0.097813 Hz
AQ	5.1118579 sec
RG	71.8
DW	78.000 usec
DE	6.00 usec
TE	200.7 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	13.00 usec
PL1	3.00 dB
SFO1	400.1328009 MHz
SI	65536
SF	400.1300170 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

^{1}H NMR of [(**C^{H}**)$_2$Cu][PF$_6$] (400.1 MHz, 201 K, CD_2Cl_2) after line narrowing



BRUKER

NAME	CGJT-10-02_400
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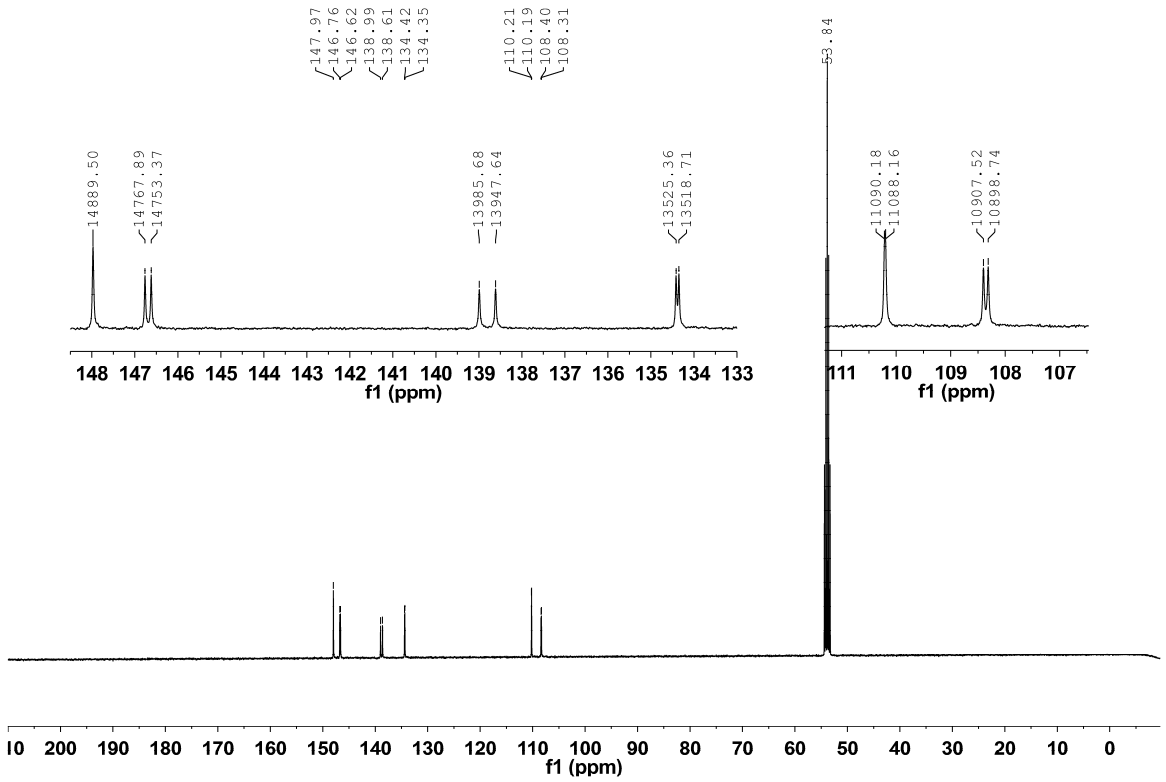
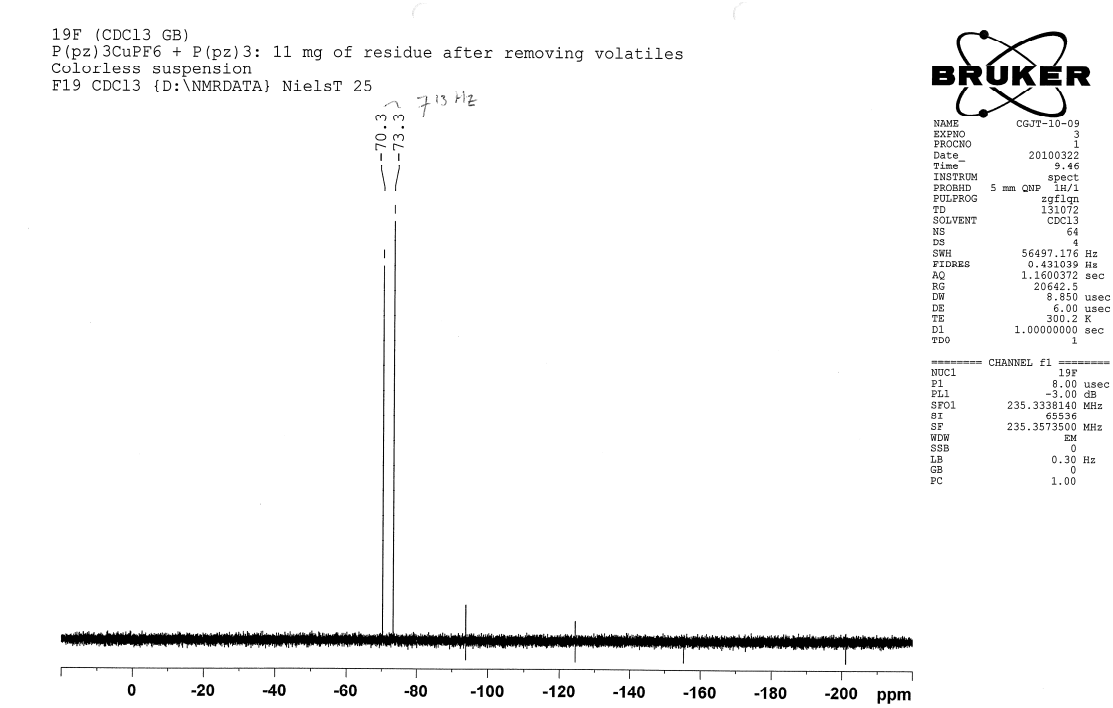
PROCNO	2
Date_	20110223
Time	17.17
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CD2Cl2
NS	16
DS	0
SWH	6410.256 Hz
FIDRES	0.097813 Hz
AQ	5.1118579 sec
RG	71.8
DW	78.000 usec
DE	6.00 usec
TE	200.7 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	13.00 usec
PL1	3.00 dB
SFO1	400.1328009 MHz
SI	65536
SF	400.1300170 MHz
WDW	GM
SSB	0
LB	-1.60 Hz
GB	0.4
PC	1.00

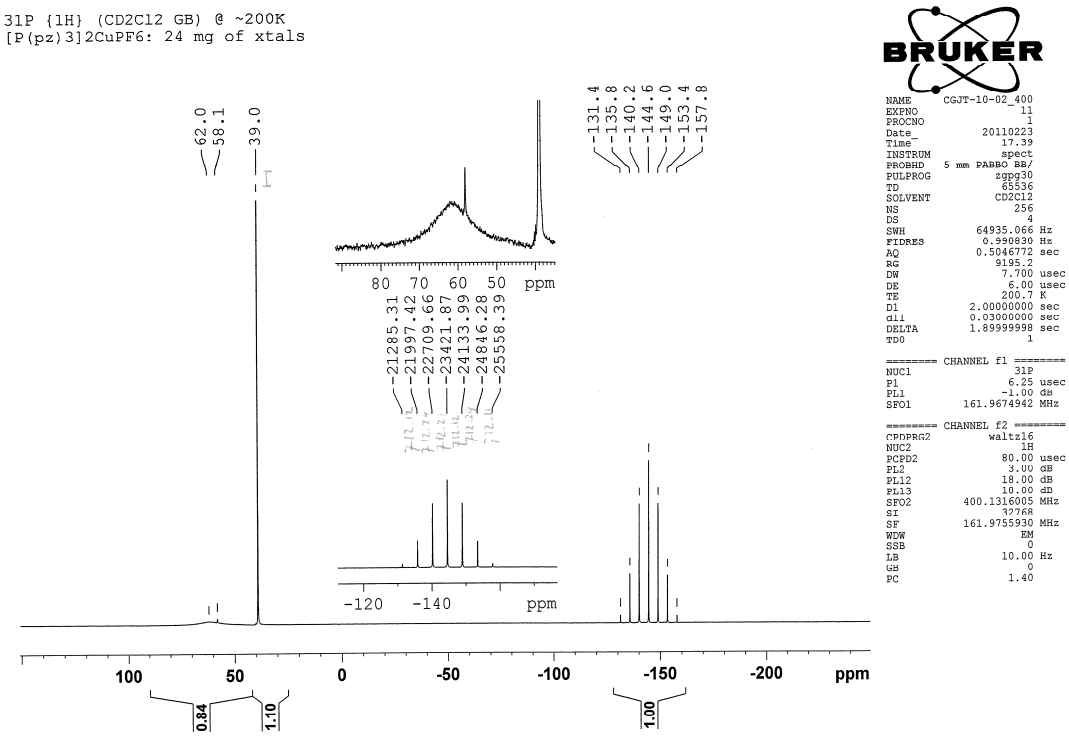
$^{13}C\{^{1}H\}$ NMR of $[(\mathbf{C}^{\mathbf{H}})_2Cu][PF_6]$ (100.6 MHz, 201 K, CD_2Cl_2)



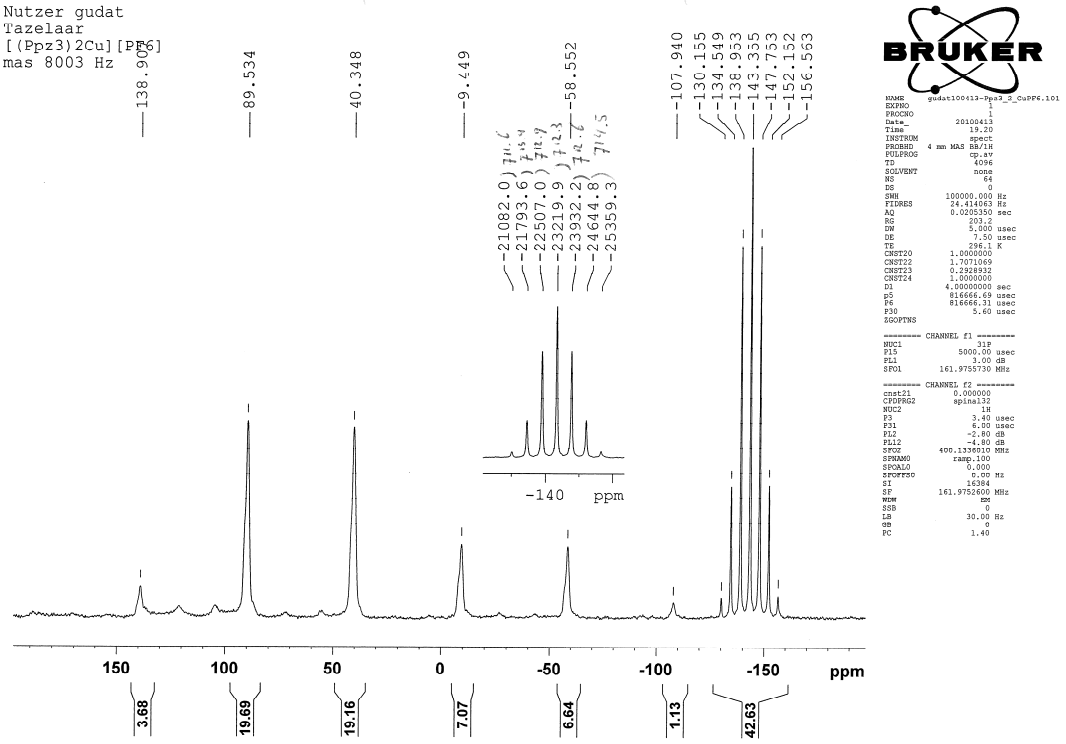
^{19}F NMR of $[(\mathbf{C}^{\mathbf{H}})_2Cu][PF_6]$ (235.3 MHz, $CDCl_3$)



$^{31}P\{^{1}H\}$ NMR of $[(\mathbf{C}^{\mathbf{H}})_2Cu][PF_6]$ (162.0 MHz, 201 K, CD_2Cl_2)

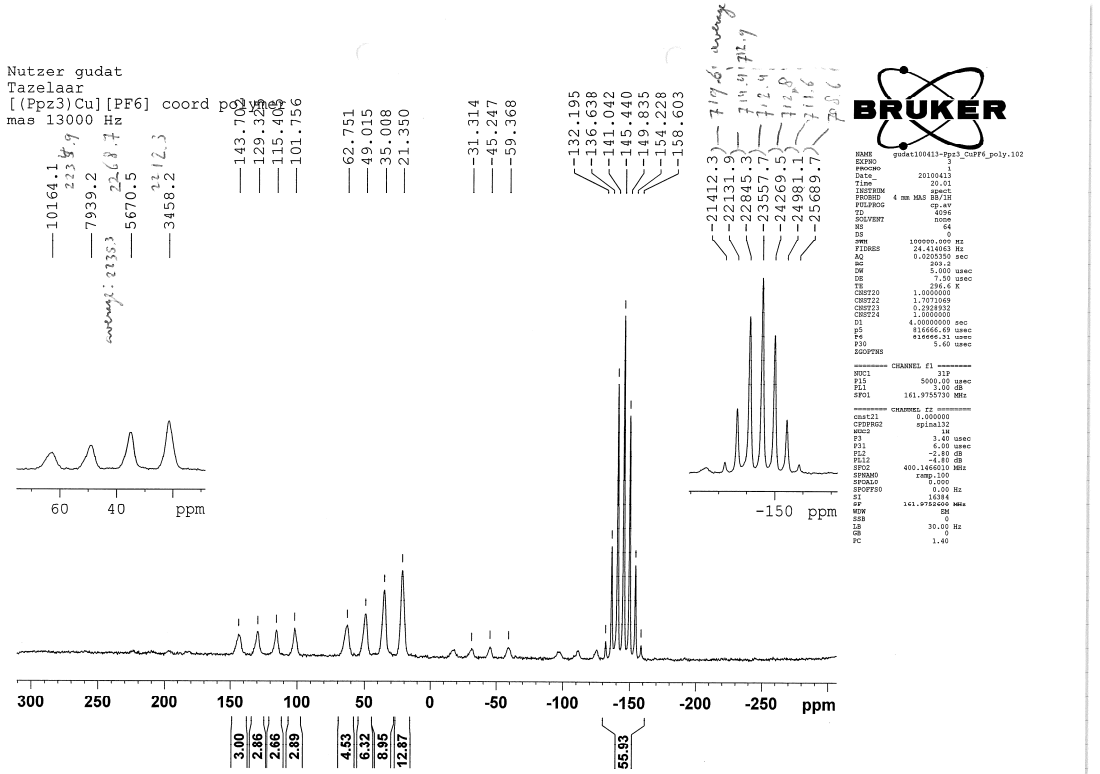


$^{31}P\{^{1}H\}$ CP/MAS NMR of $[(\mathbf{C}^{\mathbf{H}})_2Cu][PF_6]$ (162.0 MHz)

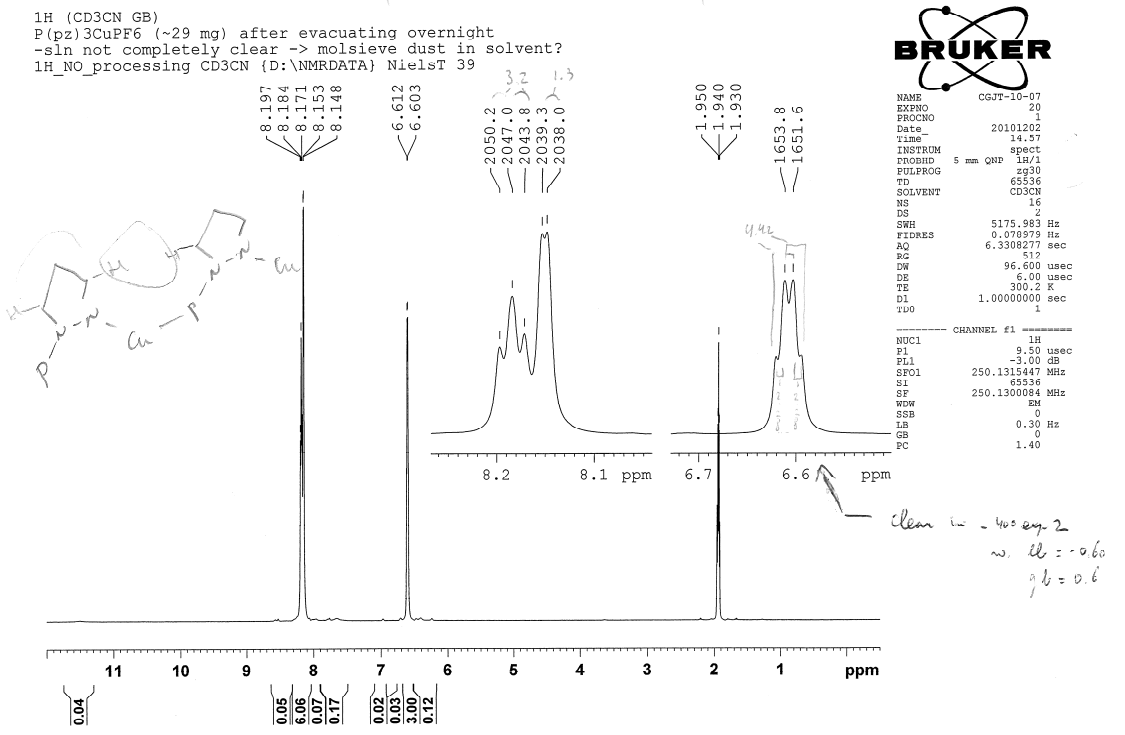


NMR spectra of tris(pyrazolyl)phosphine copper(I) hexafluorophosphate (([C^{H}Cu][PF$_6$])$_n$)

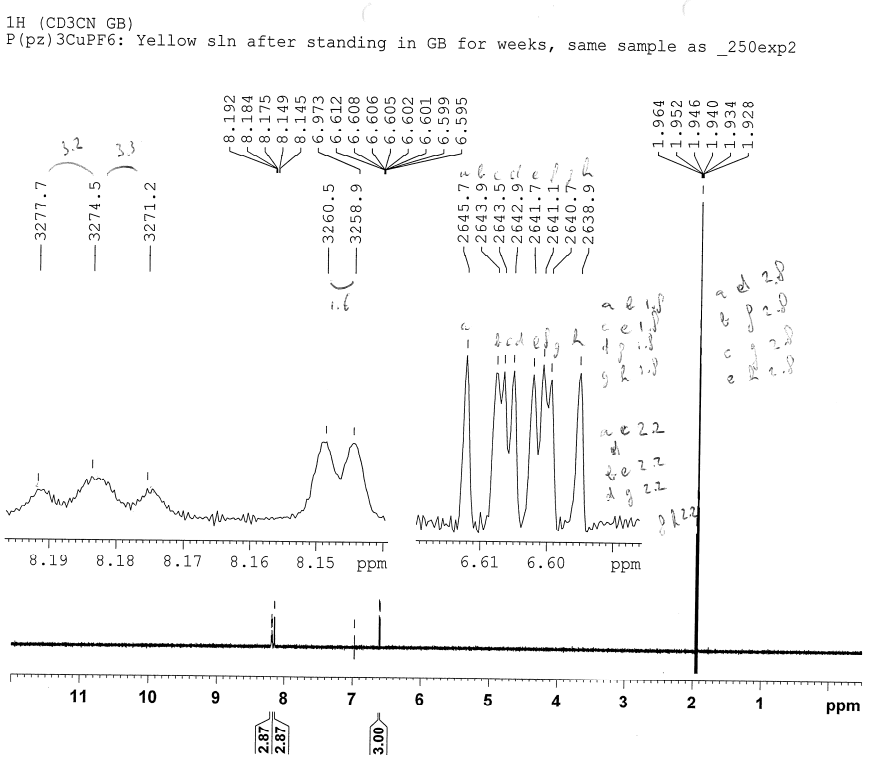
^{31}P{^{1}H} MAS NMR of ([C^{H}Cu][PF$_6$])$_n$ (162.0 MHz)

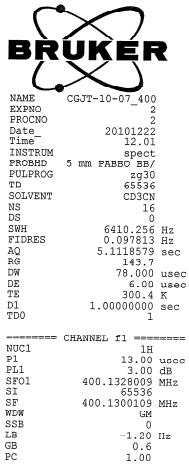


^{1}H NMR of ([C^{H}Cu][PF$_6$])$_n$ (400.1 MHz, CD$_3$CN)

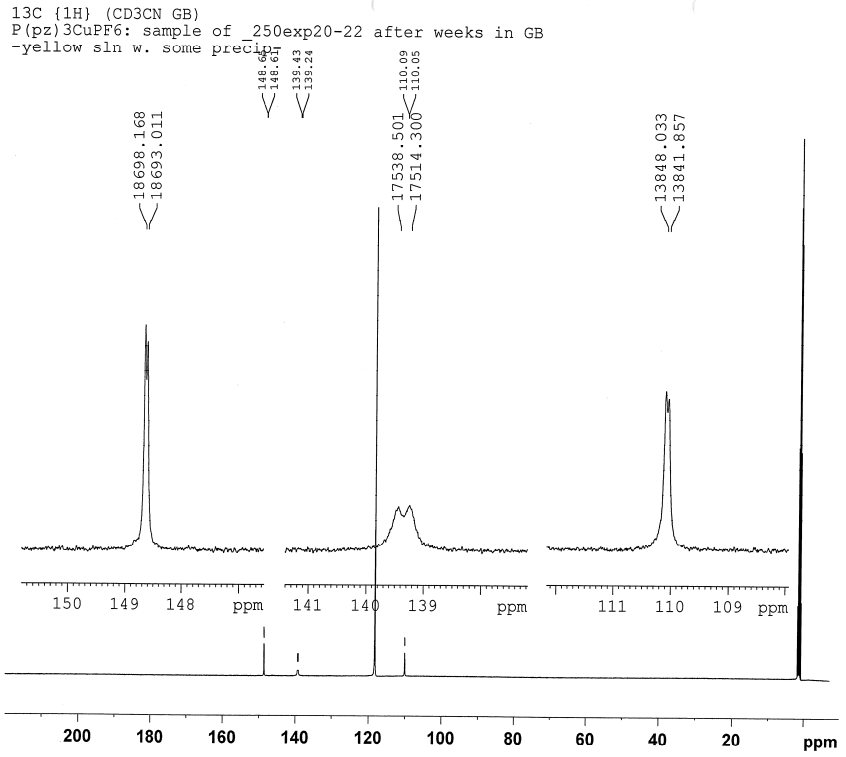


^{1}H NMR of ([**C^{H}**Cu][PF$_6$])$_n$ (400.1 MHz, CD$_3$CN) after line narrowing





^{13}C{^{1}H} NMR of ([**C^{H}**Cu][PF$_6$])$_n$ (125.8 MHz, CD$_3$CN)

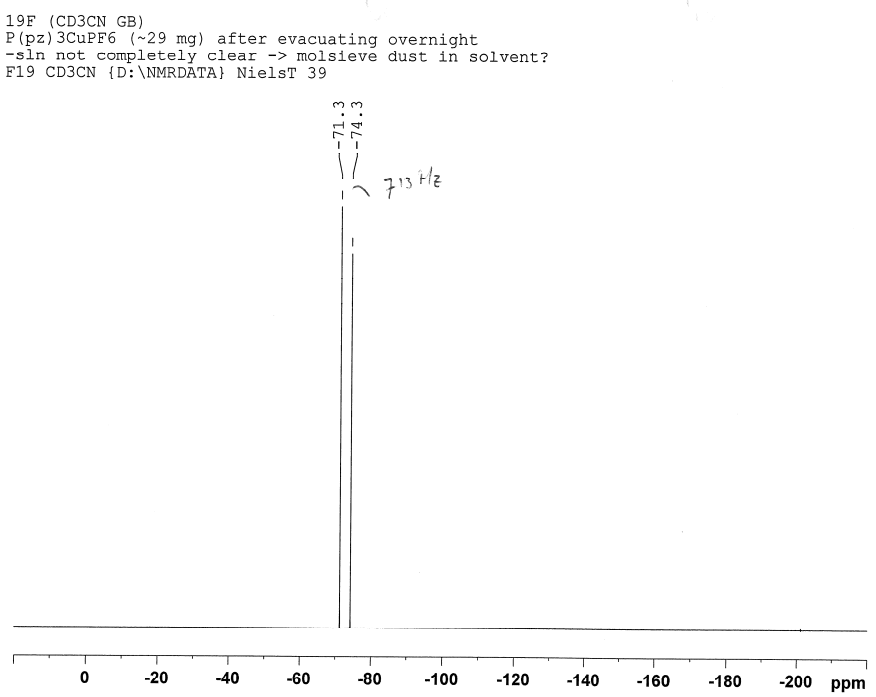


NAME CGJT-10-07_500
EXPNO 2
PROCNO 1
Date_ 20101222
Time 14.17
INSTRUM spect
PROBHD 5 mm CPTCI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 371
DS 2
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 296.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 11.20 usec
PL1 -2.00 dB
PL1W 88.77790070 W
SFO1 125.7967701 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 25.28 dB
PL13 28.00 dB
PL2W 8.72000027 W
PL12W 0.06494062 W
PL13W 0.03471494 W
SFO2 500.2320009 MHz
SI 65536
SF 125.7828098 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{19}F NMR of $([\mathbf{C}^{\mathbf{H}}Cu][PF_6])_n$ (235.3 MHz, CD_3CN)

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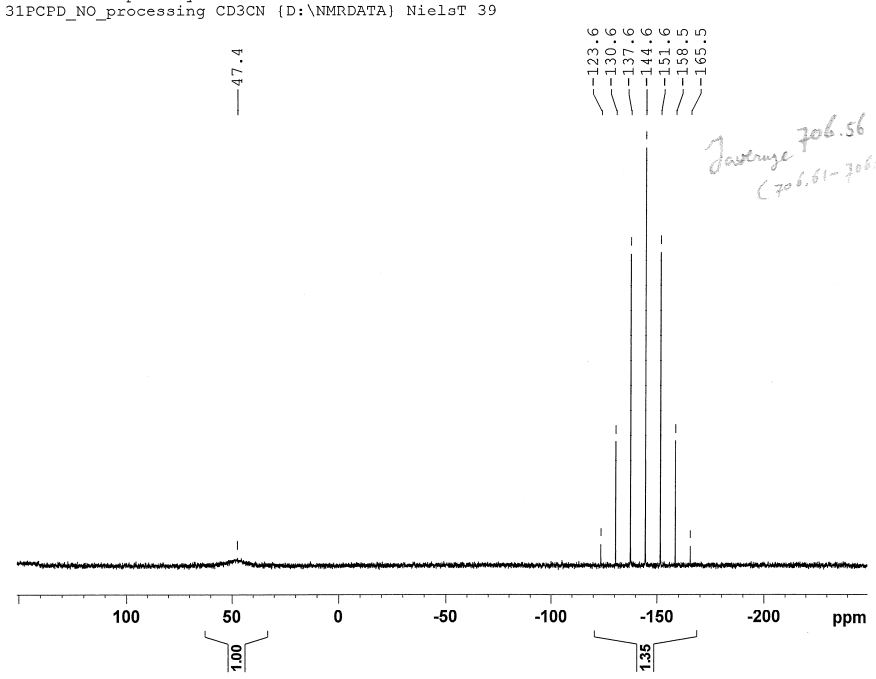
NAME                CGJT-10-07
EXPNO                       22
PROCNO                       1
Date_                 20101202
Time                     15.05
INSTRUM                  spect
PROBHD   5 mm QNP  1H/1
PULPROG                 zgflqn
TD                      131072
SOLVENT                   CD3CN
NS                           32
DS                            4
SWH                  56497.176 Hz
FIDRES                0.431039 Hz
AQ                    1.1600372 sec
RG                       2298.8
DW                        8.850 usec
DE                        6.00 usec
TE                       300.2 K
D1                    1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       19F
P1                        8.00 usec
PL1                      -3.00 dB
SFO1               235.3338140 MHz
SI                         65536
SF                 235.3573500 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```

$^{31}P\{^{1}H\}$ NMR of $([\mathbf{C}^{\mathbf{H}}Cu][PF_6])_n$ (101.3 MHz, CD_3CN)



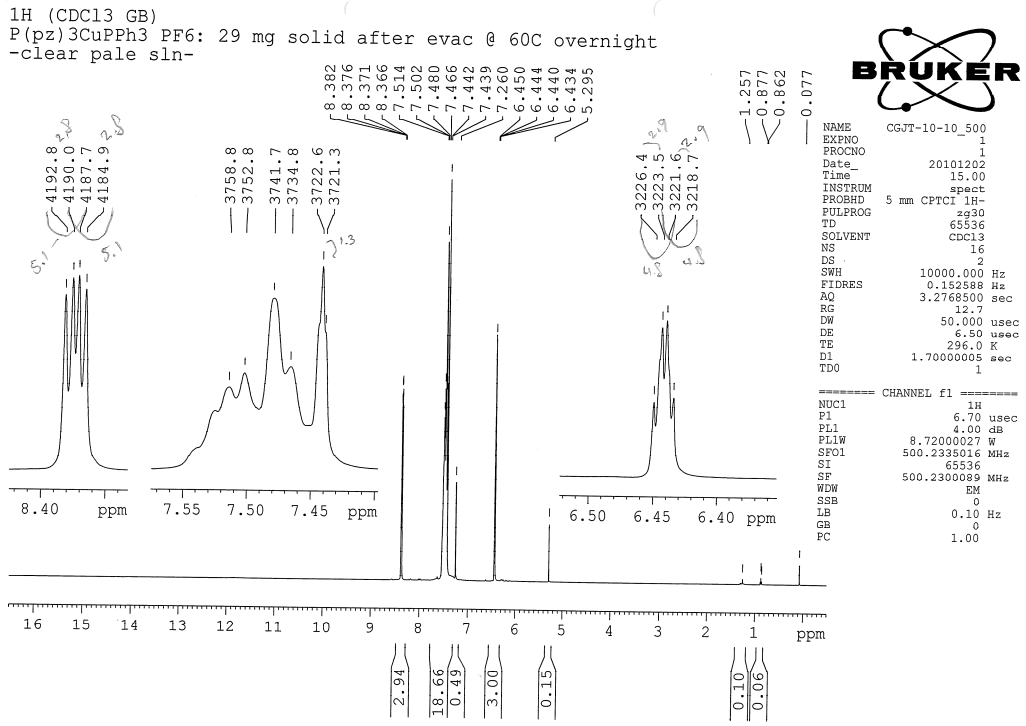

```
NAME                CGJT-10-07
EXPNO                       21
PROCNO                       1
Date_                 20101202
Time                     15.03
INSTRUM                  spect
PROBHD   5 mm QNP  1H/1
PULPROG                 zgpg30
TD                       65536
SOLVENT                   CD3CN
NS                           96
DS                            4
SWH                  40650.406 Hz
FIDRES                0.620276 Hz
AQ                    0.8061428 sec
RG                       20642.5
DW                       12.300 usec
DE                        6.00 usec
TE                       300.2 K
D1                    2.00000000 sec
d11                   0.03000000 sec
DELTA                 1.89999998 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       31P
P1                        7.00 usec
PL1                       0.00 dB
SFO1               101.2494172 MHz

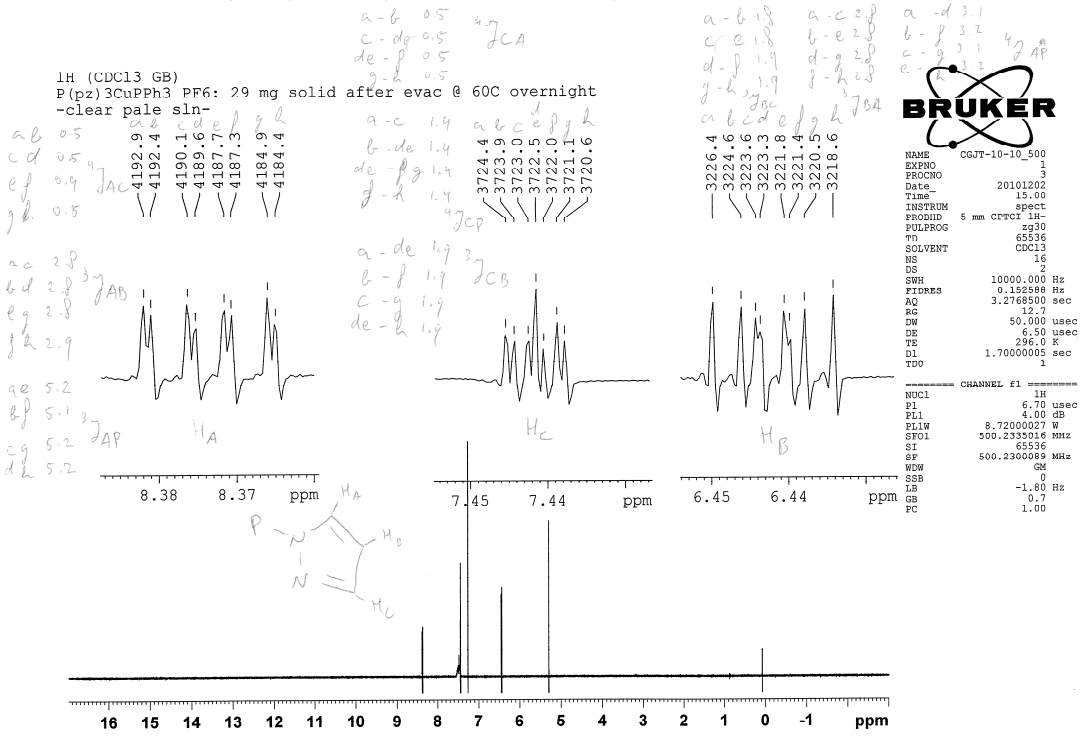
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                    80.00 usec
PLZ                      -3.00 dB
PL12                     20.00 dB
PL13                     24.00 dB
SFO2               250.1310005 MHz
SI                         65536
SF                 101.2544800 MHz
WDW                           EM
SSB                            0
LB                          3.00 Hz
GB                             0
PC                          1.40
```

NMR spectra of triphenylphosphine tris(pyrazolyl)phosphine copper(I) hexafluorophosphate ([C^{H}Cu(PPh$_3$)][PF$_6$])

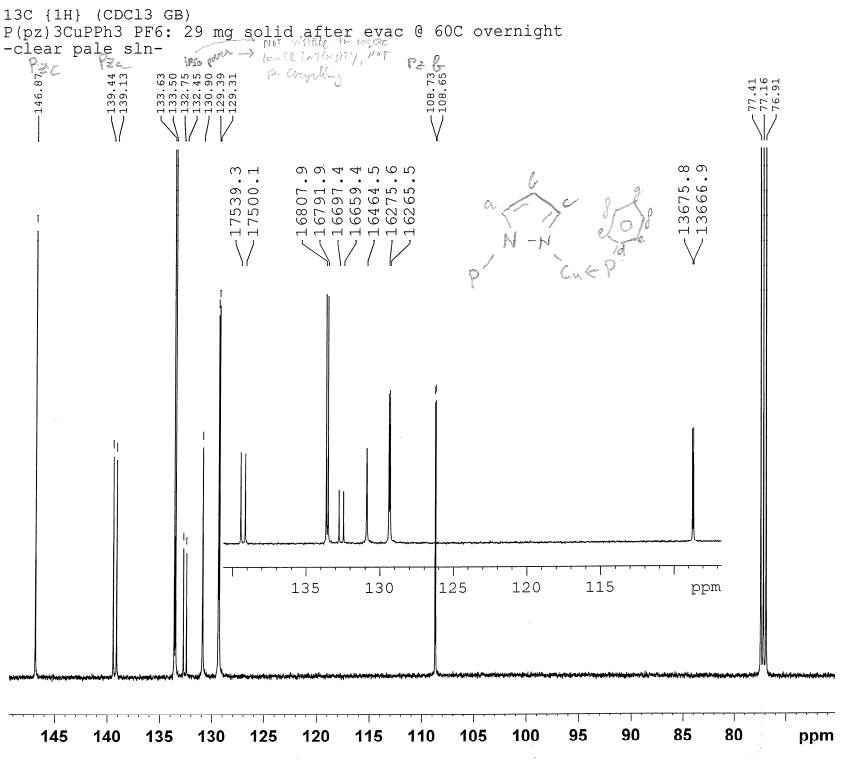
^{1}H NMR of [**C^{H}**Cu(PPh$_3$)][PF$_6$] (500.2 MHz, CDCl$_3$)



^{1}H NMR of [**C^{H}**Cu(PPh$_3$)][PF$_6$] (500.2 MHz, CDCl$_3$)

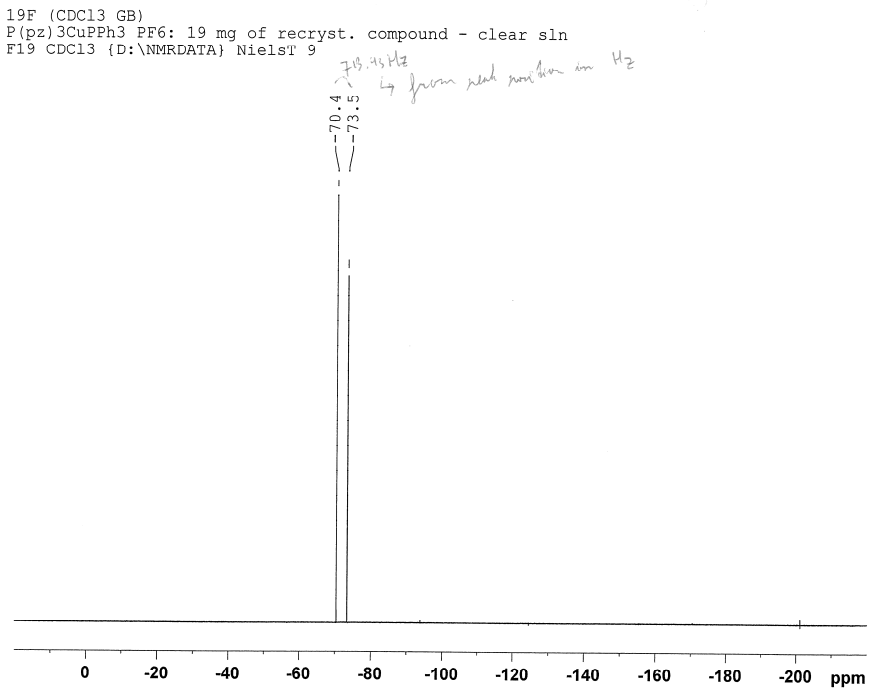


$^{13}C\{^{1}H\}$ NMR of $[\mathbf{C^{H}}Cu(PPh_3)][PF_6]$ (125.8 MHz, $CDCl_3$)



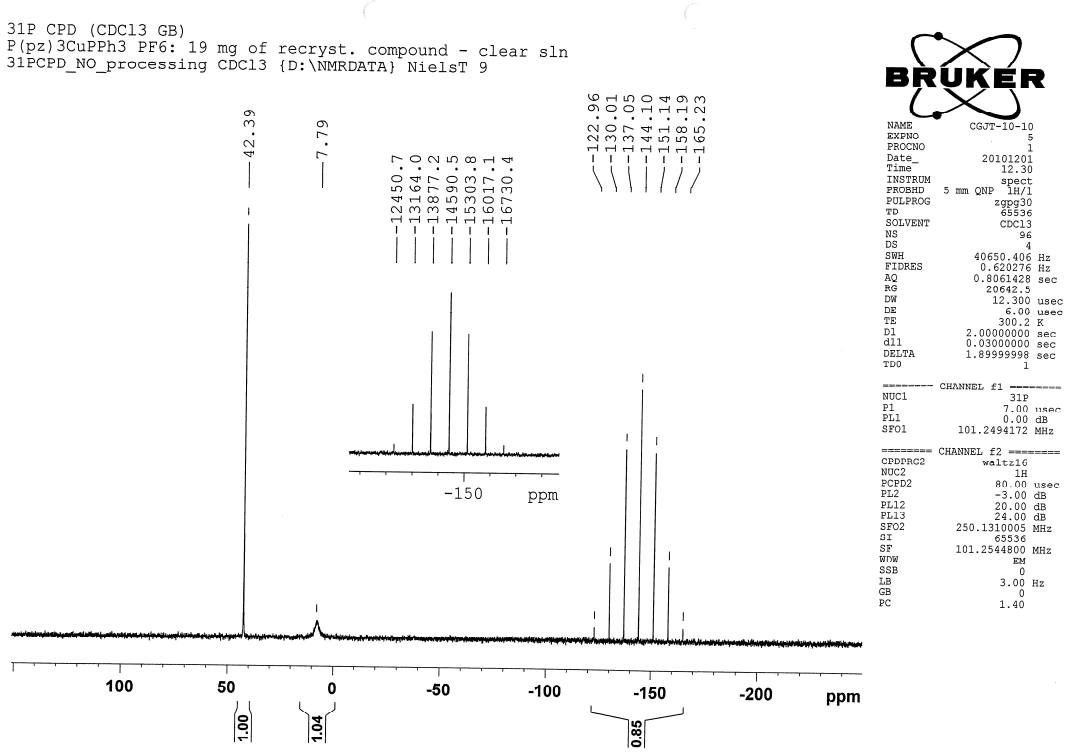
NAME	CGJT-10-10_500
EXPNO	2
PROCNO	1
Date_	20101202
Time_	15.03
INSTRUM	spect
PROBHD	5 mm CPTCI 1H-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	240
DS	2
SWH	29761.904 Hz
FIDRES	0.454131 Hz
AQ	1.1010548 sec
RG	2050
DW	16.800 usec
DE	6.50 usec
TE	296.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	11.20 usec
PL1	-2.00 dB
PL1W	88.77790070 W
SFO1	125.7967701 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	4.00 dB
PL12	25.28 dB
PL13	20.00 dB
PL2W	8.72000027 W
PL12W	0.06494062 W
PL13W	0.03471494 W
SFO2	500.2320009 MHz
SI	65536
SF	125.7829203 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

^{19}F NMR of $[\mathbf{C^{H}}Cu(PPh_3)][PF_6]$ (235.3 MHz, $CDCl_3$)

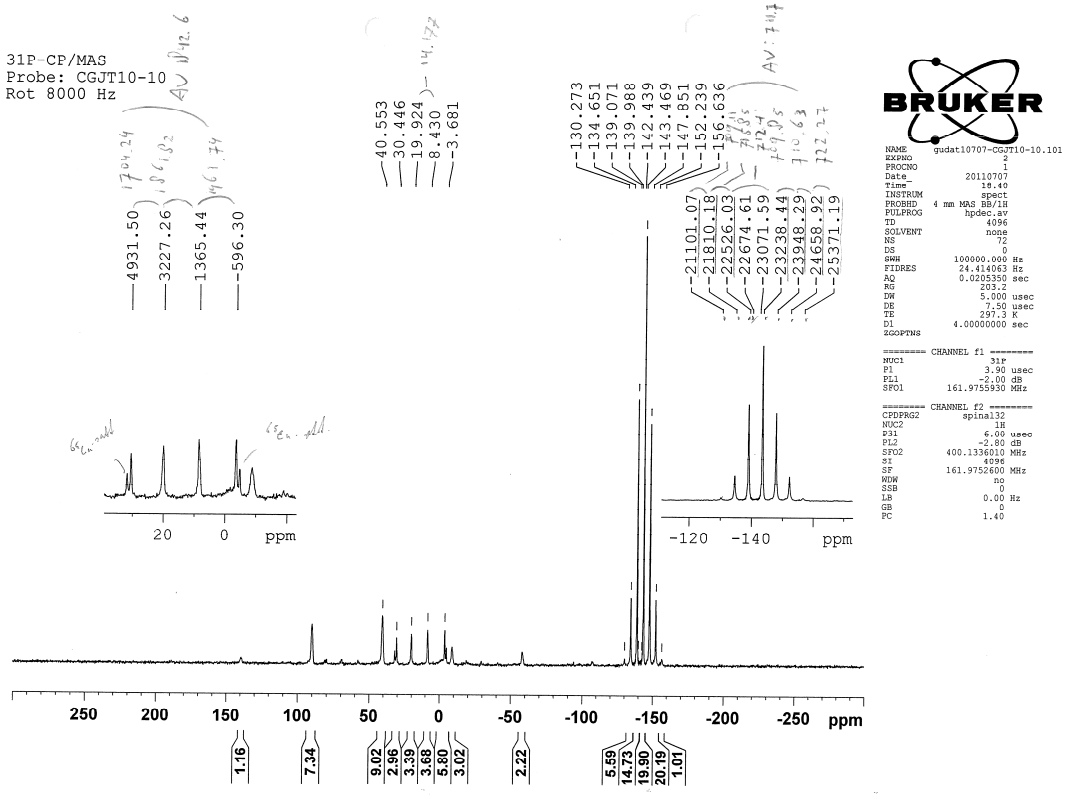


NAME	CGJT-10-10
EXPNO	6
PROCNO	1
Date_	20101201
Time_	12.31
INSTRUM	spect
PROBHD	5 mm QNP 1H/1
PULPROG	zgflqn
TD	131072
SOLVENT	CDCl3
NS	32
DS	4
SWH	56497.176 Hz
FIDRES	0.431039 Hz
AQ	1.1600372 sec
RG	9195.2
DW	8.850 usec
DE	6.00 usec
TE	300.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	19F
P1	8.00 usec
PL1	-3.00 dB
SFO1	235.3338140 MHz
SI	65536
SF	235.3573500 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

$^{31}P\{^{1}H\}$ NMR of $[\mathbf{C}^{\mathbf{H}}Cu(PPh_3)][PF_6]$ (101.3 MHz, $CDCl_3$)



$^{31}P\{^{1}H\}$ CP/MAS NMR of $[\mathbf{C}^{\mathbf{H}}Cu(PPh_3)][PF_6]$ (162.0 MHz)



Computational Details

Calculations were performed with the Gaussian09 series of programs.[12] The B3PW91[13-15] functional was used in combination with the 6-31G* basis set for all non-metal-atoms[16,17] (C, H, N, P) and the Lanl2dz for copper.[18,19] The stationary points were characterized as minima by full vibration frequencies calculations (no imaginary frequency).

Cartesian coordinates, three lowest frequencies and thermochemistry of PCuN3

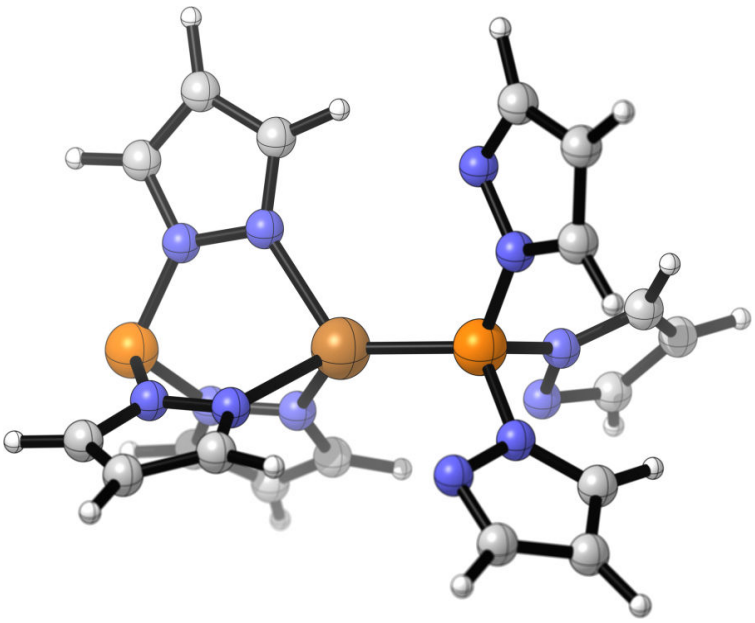


Figure S5. View of the optimized Structure of PCuN3

Element	X	Y	Z
Cu	0.00000000	0.00000000	0.47629201
P	0.00000000	0.00000000	3.84177899
P	0.00000000	0.00000000	-1.72650504
N	-0.13529100	1.53601801	3.04646993
N	-0.13052100	1.72376001	1.69552195
N	0.67523599	1.37541795	-2.52436495
N	0.46389800	2.57785511	-1.91693294
C	-0.24147400	3.02989888	1.51232505
C	-0.32127100	3.71720195	2.74373794
C	-0.24989800	2.73771095	3.70113993
C	1.01969504	3.46328402	-2.72665095
C	1.60362399	2.85307693	-3.86354303
C	1.36488199	1.51181698	-3.70460391
H	-0.25200200	3.41232204	0.49994501
H	-0.41671300	4.78109980	2.90331006
H	-0.26941100	2.78515291	4.78139400
H	0.99458098	4.51442003	-2.46866012
H	2.13827395	3.32930994	-4.67287111
H	1.64058495	0.65519100	-4.30293322

N	1.39787602	-0.65084398	3.04646993
N	-1.26258504	-0.88517398	3.04646993
N	1.55808103	-0.74884498	1.69552195
N	-1.42755997	-0.97491503	1.69552195
N	0.85352898	-1.27248096	-2.52436495
N	-1.52876496	-0.10293700	-2.52436495
N	2.00053906	-1.69067395	-1.91693294
N	-2.46443605	-0.88717997	-1.91693294
C	2.74470592	-1.30582702	1.51232505
C	-2.50323296	-1.72407198	1.51232505
C	3.37982702	-1.58037198	2.74373794
C	-3.05855489	-2.13683009	2.74373794
C	2.49587607	-1.15243697	3.70113993
C	-2.24597812	-1.58527398	3.70113993
C	2.48944402	-2.61472392	-2.72665095
C	-3.50913906	-0.84855998	-2.72665095
C	1.66902602	-2.81531811	-3.86354303
C	-3.27264905	-0.03776000	-3.86354303
C	0.62683100	-1.93793094	-3.70460391
C	-1.99171305	0.42611399	-3.70460391
H	3.08115792	-1.48792005	0.49994501
H	-2.82915592	-1.92440104	0.49994501
H	4.34890985	-2.02966595	2.90331006
H	-3.93219709	-2.75143409	2.90331006
H	2.54671907	-1.15926003	4.78139400
H	-2.27730799	-1.62589300	4.78139400
H	3.41231203	-3.11854291	-2.46866012
H	-4.40689278	-1.39587796	-2.46866012
H	1.81412995	-3.51645494	-4.67287111
H	-3.95240402	0.18714499	-4.67287111
H	-0.25288001	-1.74838400	-4.30293322
H	-1.38770497	1.09319305	-4.30293322

	1	2	3
	A	E	E
Frequencies --	17.1501	35.1384	35.1399
Red. masses --	6.2167	6.0041	6.0041
Frc consts --	0.0011	0.0044	0.0044
IR Inten --	0.0283	0.2349	0.2350

Sum of electronic and zero-point Energies= -2231.436297
Sum of electronic and thermal Energies= -2231.406638
Sum of electronic and thermal Enthalpies= -2231.405694
Sum of electronic and thermal Free Energies= -2231.499929

HF = -2231.81196597

Cartesian coordinates, three lowest frequencies and thermochemistry of N4Cu

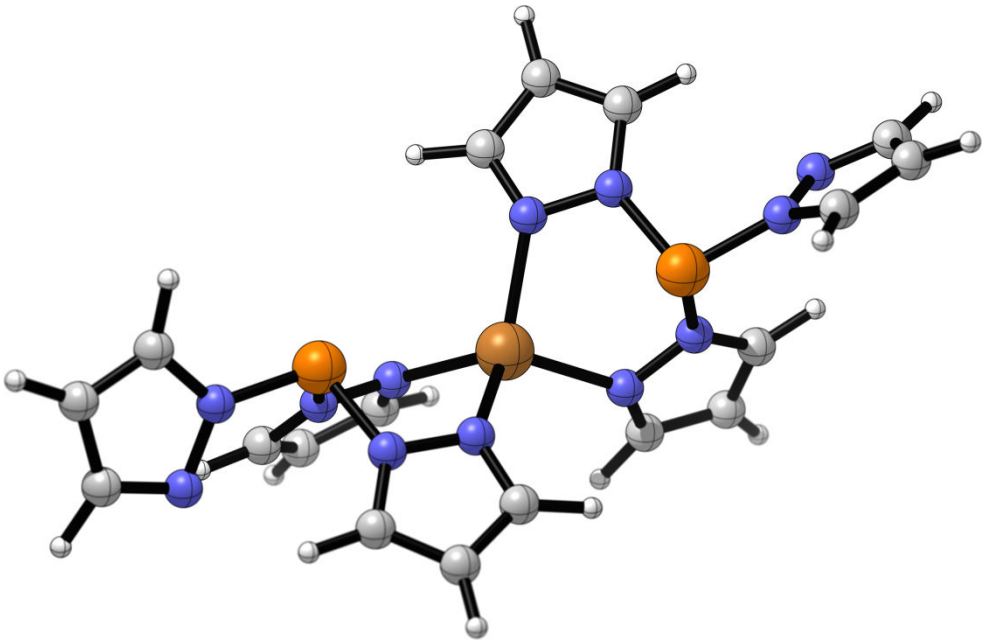


Figure S6. View of the optimized structure of N4Cu

Element	X	Y	Z
H	4.49372292	2.49232507	-0.85563999
C	3.43850803	2.27642703	-0.77130401
C	2.39855289	3.17254901	-0.88055199
H	2.37613201	4.24003077	-1.03838694
N	1.24521506	2.46304893	-0.72504002
N	1.50547695	1.14185703	-0.50878298
C	2.82936192	1.03041601	-0.53019297
H	1.37241602	-3.57283807	4.12619686
C	1.17356801	-3.12672901	3.16249990
C	0.92904198	-3.78638601	1.97819495
H	1.24407196	-0.89857101	3.48488808
H	0.85526103	-4.83576488	1.73647201
N	0.74456102	-2.83288598	1.02235901
N	0.85698700	-1.57962000	1.54849398
C	1.11013901	-1.75780106	2.84115291
H	-0.85526103	4.83576488	1.73647201
C	-0.92904198	3.78638601	1.97819495
C	-1.17356801	3.12672901	3.16249990
H	-1.37241602	3.57283807	4.12619686
C	-1.11013901	1.75780106	2.84115291
H	-1.24407196	0.89857101	3.48488808
N	-0.85698700	1.57962000	1.54849398
N	-0.74456102	2.83288598	1.02235901
H	-3.28811598	-0.06400000	-0.37125501
C	-2.82936192	-1.03041601	-0.53019297
N	-1.50547695	-1.14185703	-0.50878298
H	-4.49372292	-2.49232507	-0.85563999
N	-1.24521506	-2.46304893	-0.72504002
C	-2.39855289	-3.17254901	-0.88055199
H	-2.37613201	-4.24003077	-1.03838694
C	-3.43850803	-2.27642703	-0.77130401
Cu	0.00000000	0.00000000	0.39265999
H	3.28811598	0.06400000	-0.37125501

P	-0.47604999	2.80806899	-0.71737599
P	0.47604999	-2.80806899	-0.71737599
N	0.45613301	-4.49424219	-1.05054200
N	-0.29526299	-5.42293310	-0.38070601
C	0.00000000	-6.57081509	-0.96741199
C	0.93827498	-6.41813993	-2.01870894
C	1.21010900	-5.07743406	-2.04752493
H	-0.47110501	-7.48095989	-0.61661798
H	1.35039902	-7.18453693	-2.65872693
H	1.86247802	-4.48771906	-2.67725801
N	-0.45613301	4.49424219	-1.05054200
N	0.29526299	5.42293310	-0.38070601
C	0.00000000	6.57081509	-0.96741199
C	-0.93827498	6.41813993	-2.01870894
C	-1.21010900	5.07743406	-2.04752493
H	0.47110501	7.48095989	-0.61661798
H	-1.35039902	7.18453693	-2.65872693
H	-1.86247802	4.48771906	-2.67725801

	1	2	3
	A	B	A
Frequencies --	12.6514	14.6593	17.6812
Red. masses --	6.8231	6.7914	5.8908
Frc consts --	0.0006	0.0009	0.0011
IR Inten --	0.0758	0.2026	0.0702

Sum of electronic and zero-point Energies= -2231.432543
Sum of electronic and thermal Energies= -2231.402532
Sum of electronic and thermal Enthalpies= -2231.401588
Sum of electronic and thermal Free Energies= -2231.498536

HF = -2231.80742390

References

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