

Supplementary Material

P-Chirogenic silylphosphine-boranes: synthesis and phospha-Michael reactions

Eric Bonnefille, Arnaud Tessier,^{†*} Hélène Cattey, Pierre Le Gendre and Sylvain Jugé*

*Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB- StéréochIM-UMR
CNRS 6302), 9 avenue A. Savary BP47870, 21078 Dijon Cedex, France*

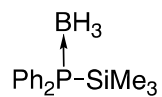
[†] *Present adress: Université de Nantes, CNRS, CEISAM, UMR CNRS 6230, Faculté des
Sciences et des Techniques, 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3,
France*

E-mail: Arnaud.Tessier@univ-nantes.fr, sylvain.juge@u-bourgogne.fr

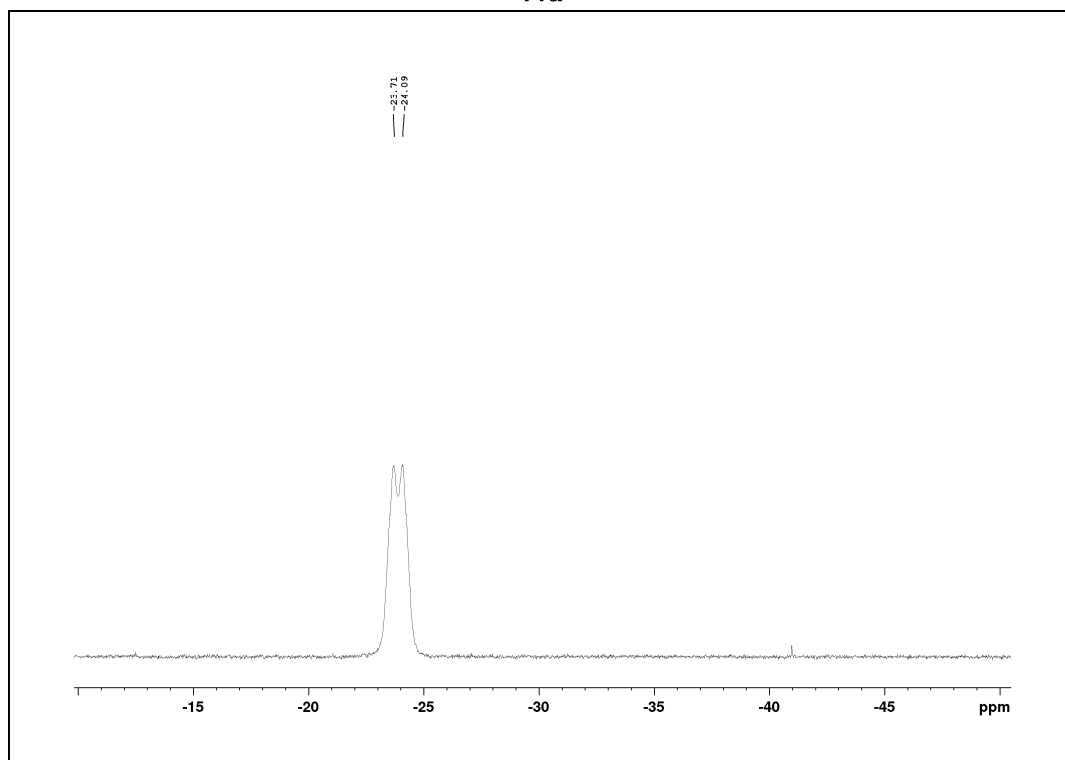
Dedicated to Prof. Jürgen Martens for his 65th birthday

³¹ P, ²⁹ Si NMR spectra, compound 11a	S2
³¹ P NMR spectra, compound 11b	S3
¹ H, ¹³ C, ³¹ P NMR spectra, compound 14a	S4
¹ H, ³¹ P NMR spectra, compound 14b	S7
¹ H, ¹³ C, ³¹ P NMR spectra, compound 14c	S8
¹ H, ¹³ C, ³¹ P NMR spectra, compound 14d	S11
¹ H, ¹³ C, ³¹ P NMR spectra, compound 15a	S13
¹ H, ¹³ C, ³¹ P NMR spectra, compound 15c	S15
¹³ C, ³¹ P NMR spectra, compound 15d	S17
¹ H, ¹³ C, ³¹ P NMR spectra, compound 15e	S19
¹ H, ¹³ C, ³¹ P NMR spectra, compound 18	S21
¹ H, ¹³ C, ³¹ P NMR spectra for compound 19a	S24
¹ H, ³¹ P NMR spectra for compound 19b	S26
¹³ C, ³¹ P NMR spectra, compound 20a	S27
¹³ C, ³¹ P NMR spectra, compound 20b	S28
¹ H, ¹³ C, ³¹ P NMR spectra, compound 21	S30
X-ray data for compounds 19a and 21	S32

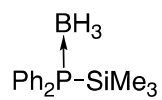
^{31}P NMR (121.4 MHz, C_6D_6) spectrum for **11a**



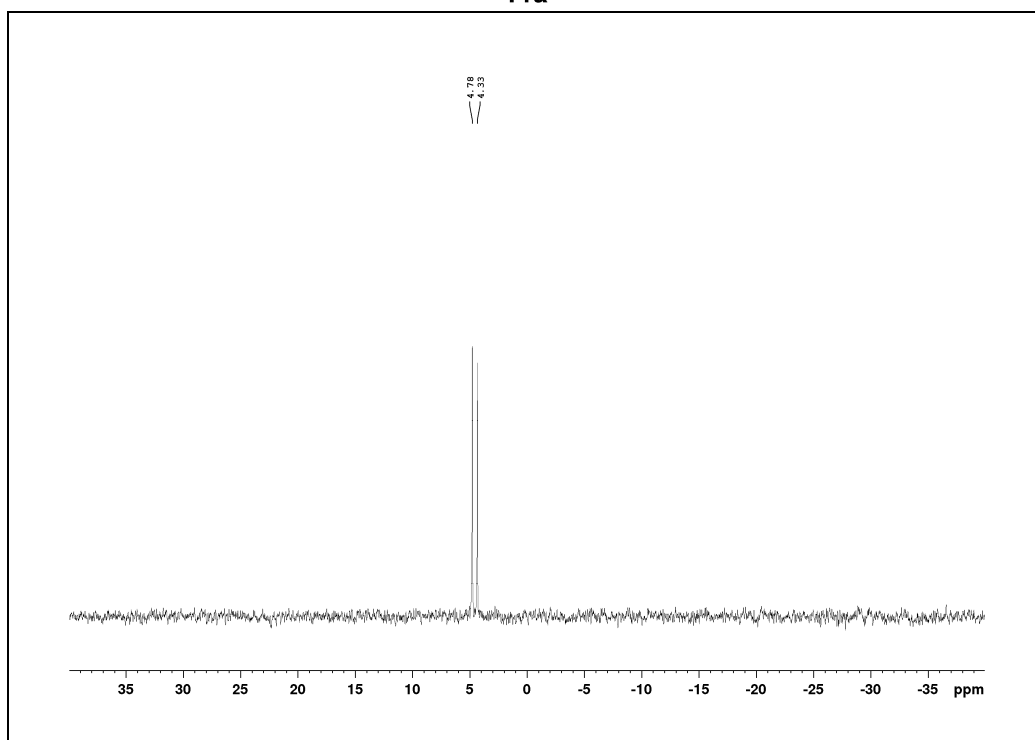
11a



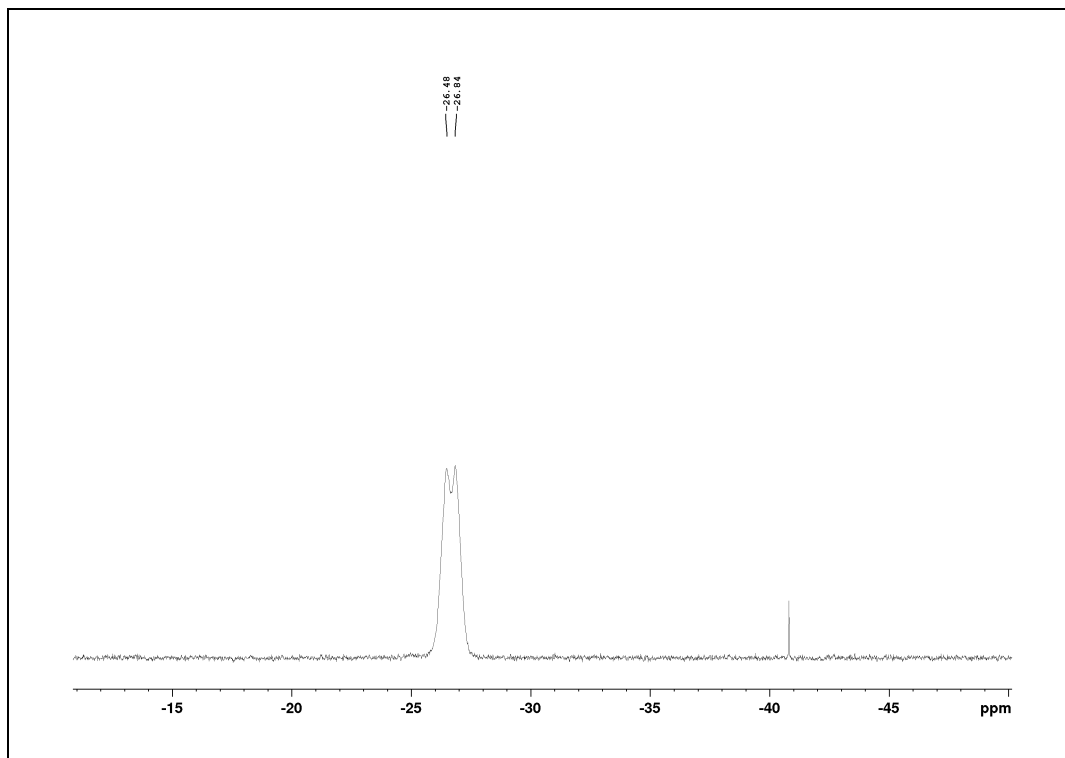
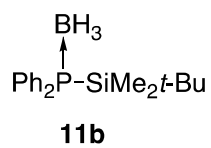
^{29}Si NMR (99.4 MHz, C_6D_6) spectrum for **11a**

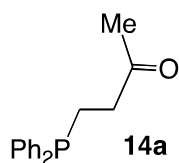


11a



^{31}P NMR (121.4 MHz, C_6D_6) spectrum for **11b**



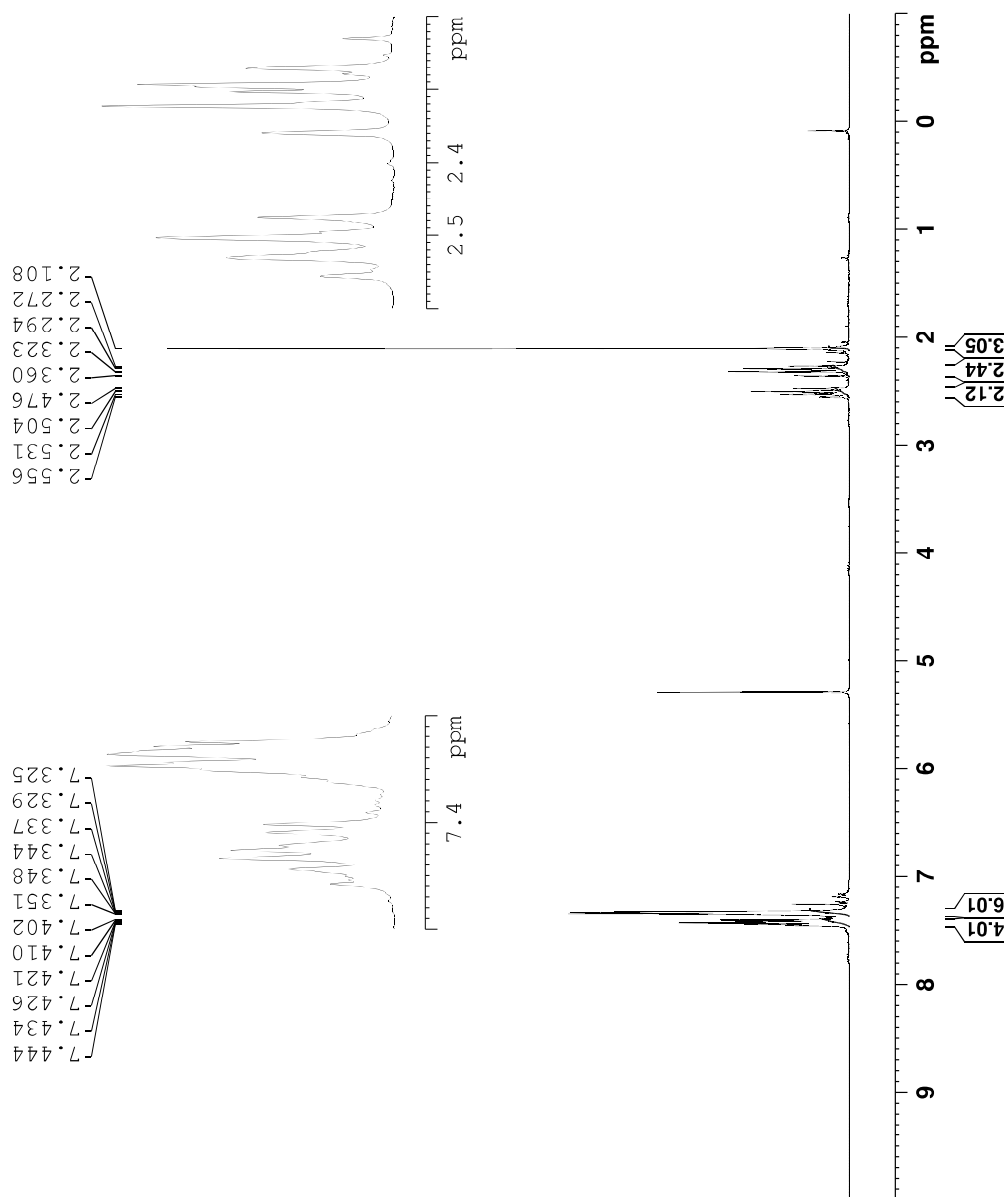
¹H NMR (300 MHz, C₆D₆) spectrum for **14a**

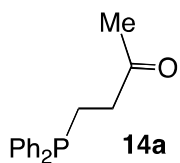
Current Data Parameters
 NAME 08ebc2401
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080124
 Time 16.28
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084159 sec
 RG 101.6
 DW 81.000 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 7.80 usec
 PL1 3.00 dB
 SFO1 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300061 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



¹³C NMR (75.4 MHz, CDCl₃) spectrum for **14a**

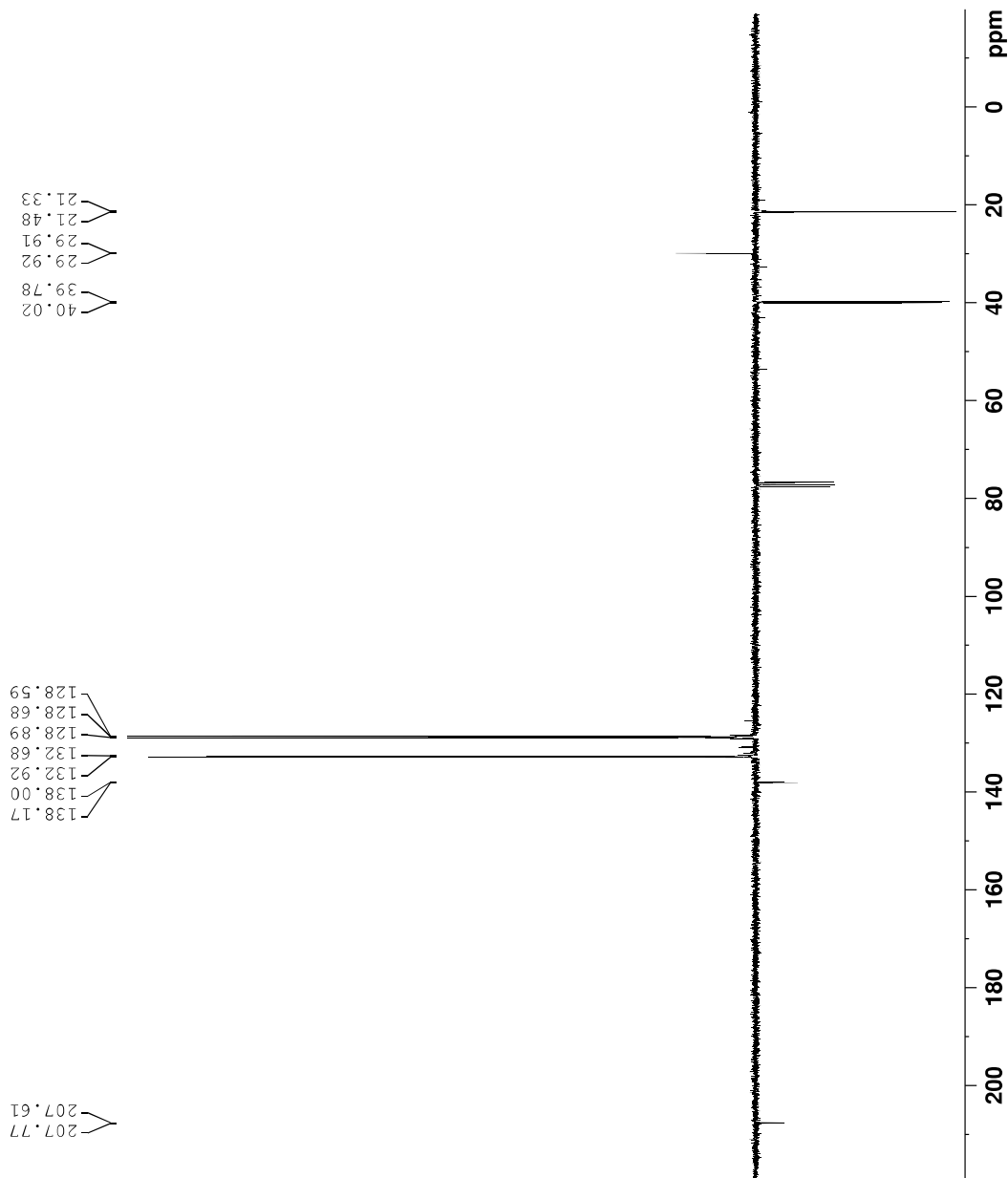
Current Data Parameters
 NAME 08ebo2401
 EXPNO 6
 PROCNO 1

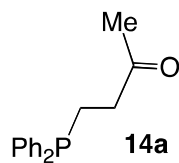
F2 - Acquisition Parameters
 Date_ 20080126
 Time 1.40
 INSTRUM spect
 PROBHD 5 mm F4BBO1B-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 2048
 DS 4
 SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219008 sec
 RG 16384
 DW 27.800 usec
 DE 6.00 usec
 TE 300.0 K
 CNST2 145.000000
 CNST1 1.000000
 D1 2.0000000 sec
 d20 0.00689655 sec
 DELTA 0.00001235 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 13C
 P1 9.70 usec
 P2 19.40 usec
 PL1 3.00 dB
 SFO1 75.4752953 MHz

==== CHANNEL f2 =====
 CPDPRG2 walzr16
 NUC2 1H
 FCFD2 100.00 usec
 PL2 3.00 dB
 PL12 24.94 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677418 MHz
 SSB EM
 MDW 0
 LB 0
 GB 1.00 Hz
 PC 1.40



³¹P NMR (121.4 MHz, CDCl₃) spectrum for **14a**

```

Current Data Parameters
NAME      08ebc2401
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_     20080124
Time      16.37
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         128
DS         4
SWH        48661.801 Hz
FIDRES     0.742520 Hz
AQ         0.6733824 sec
RG         20642.5
DW         10.275 usec
DE         6.00 usec
TE         300.0 K
D1         2.00000000 sec
GL1        0.03000000 sec
DELTA     1.89999998 sec
TD0        1

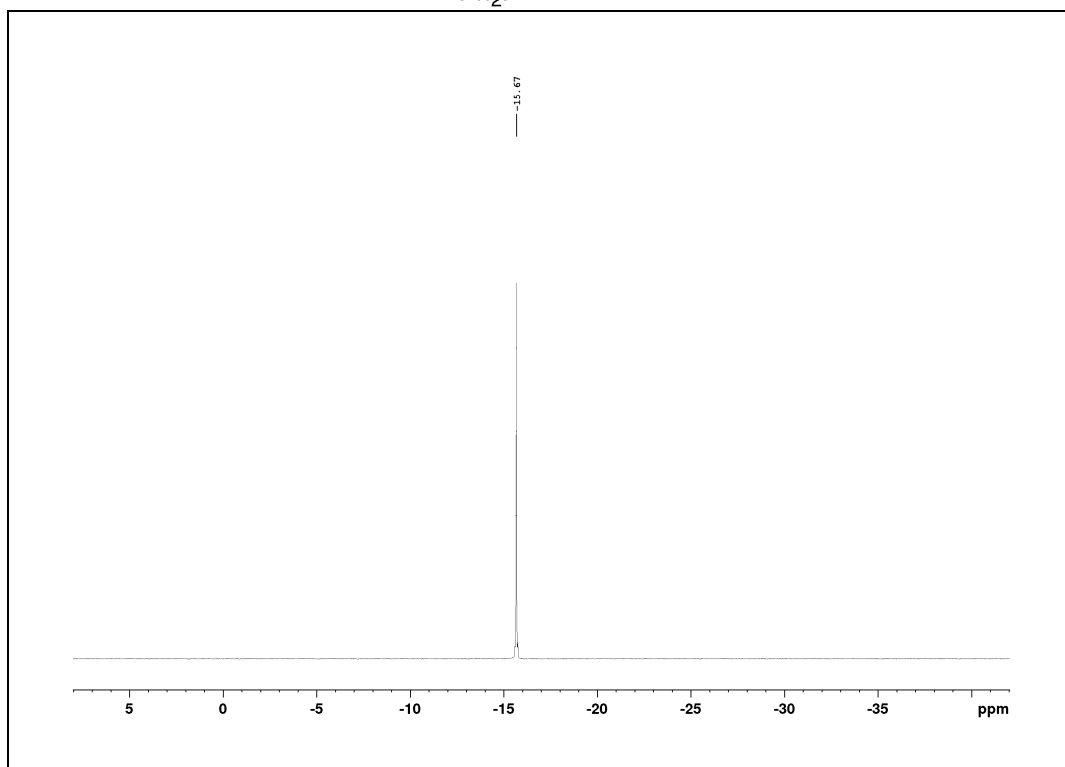
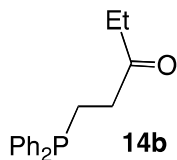
===== CHANNEL f1 =====
NUC1      31P
P1        5.60 usec
PL1       6.00 dB
SFO1      121.4887762 MHz

===== CHANNEL f2 =====
CPDPRG[2] waltz16
NUC2      1H
PCPD2     100.00 usec
PL2       3.00 dB
PL12      24.94 dB
PL13      24.94 dB
SFO2      300.1312005 MHz

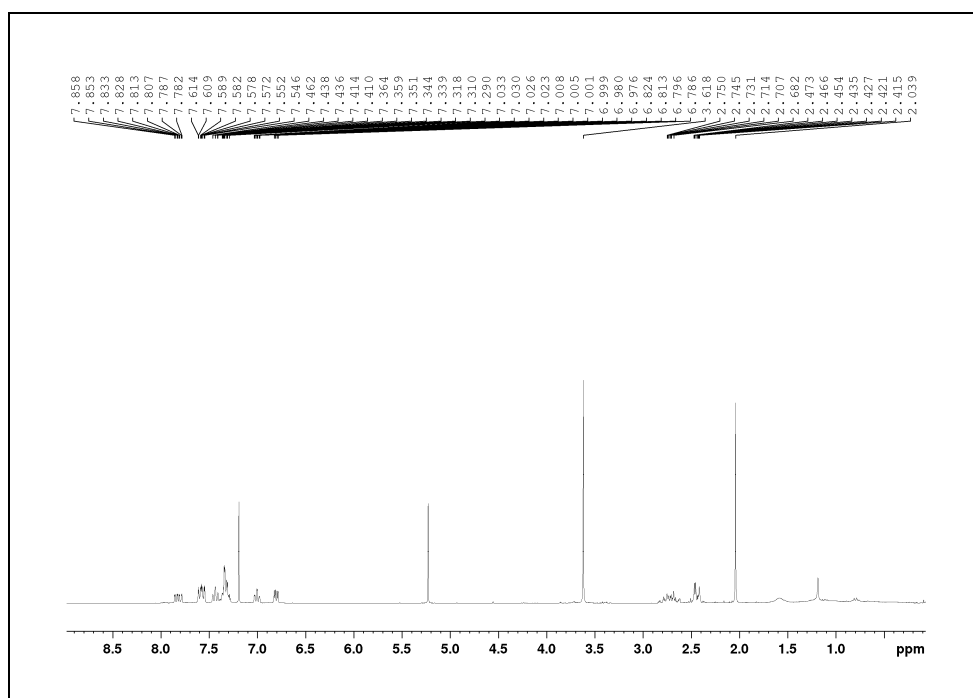
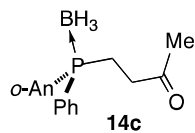
F2 - Processing parameters
SI        32768
SF        121.4948510 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
  
```

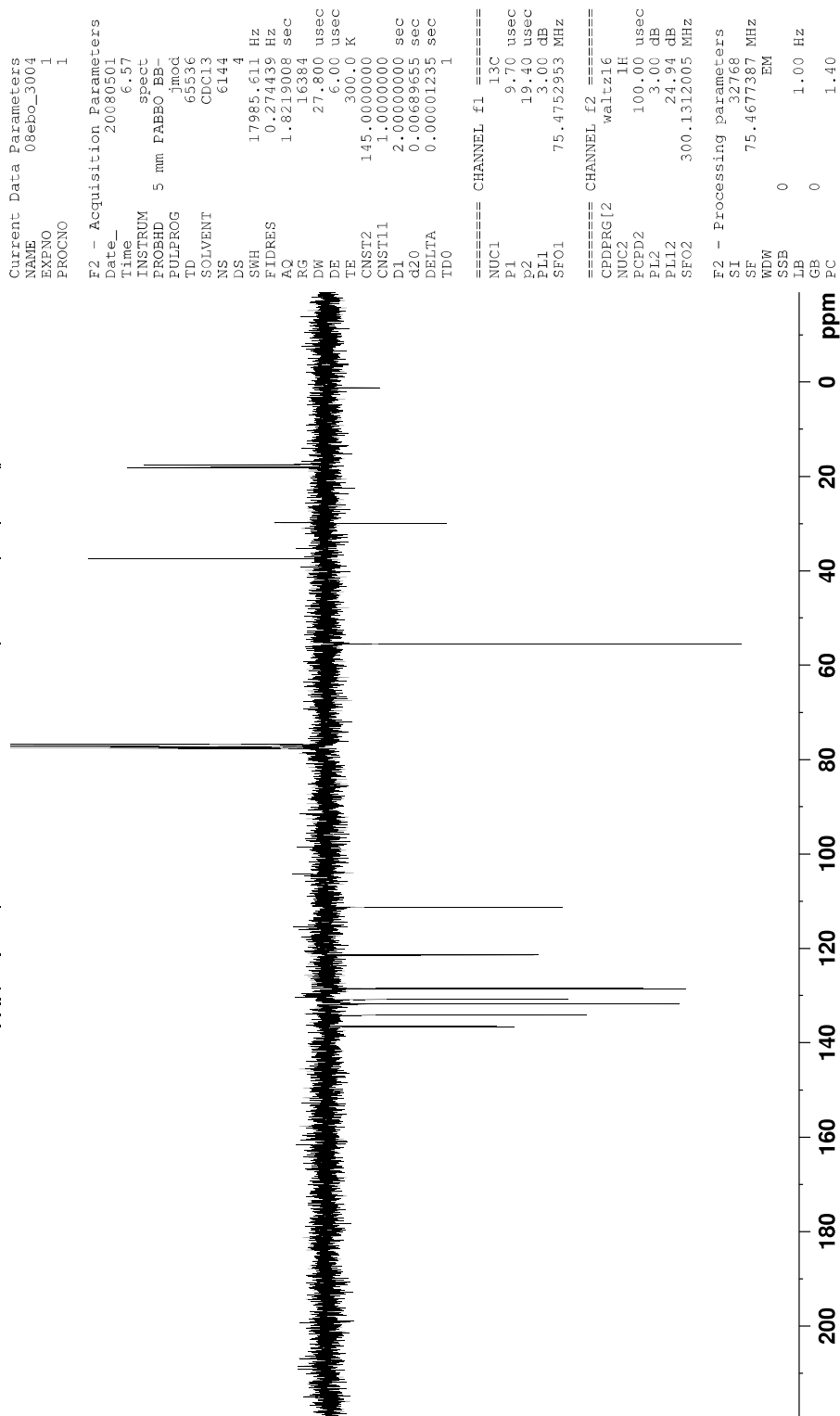
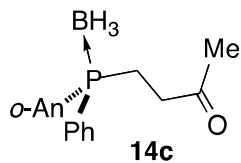


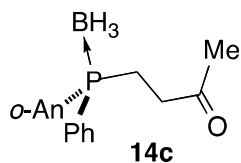
^{31}P NMR (121.4 MHz, CDCl_3) spectrum for **14b**



^1H NMR (300 MHz, CDCl_3) spectrum for **14c**



^{13}C NMR (75.4 MHz, CDCl_3) spectrum for **14c**

³¹P NMR (121.4 MHz, CDCl₃) spectrum for **14c**

```

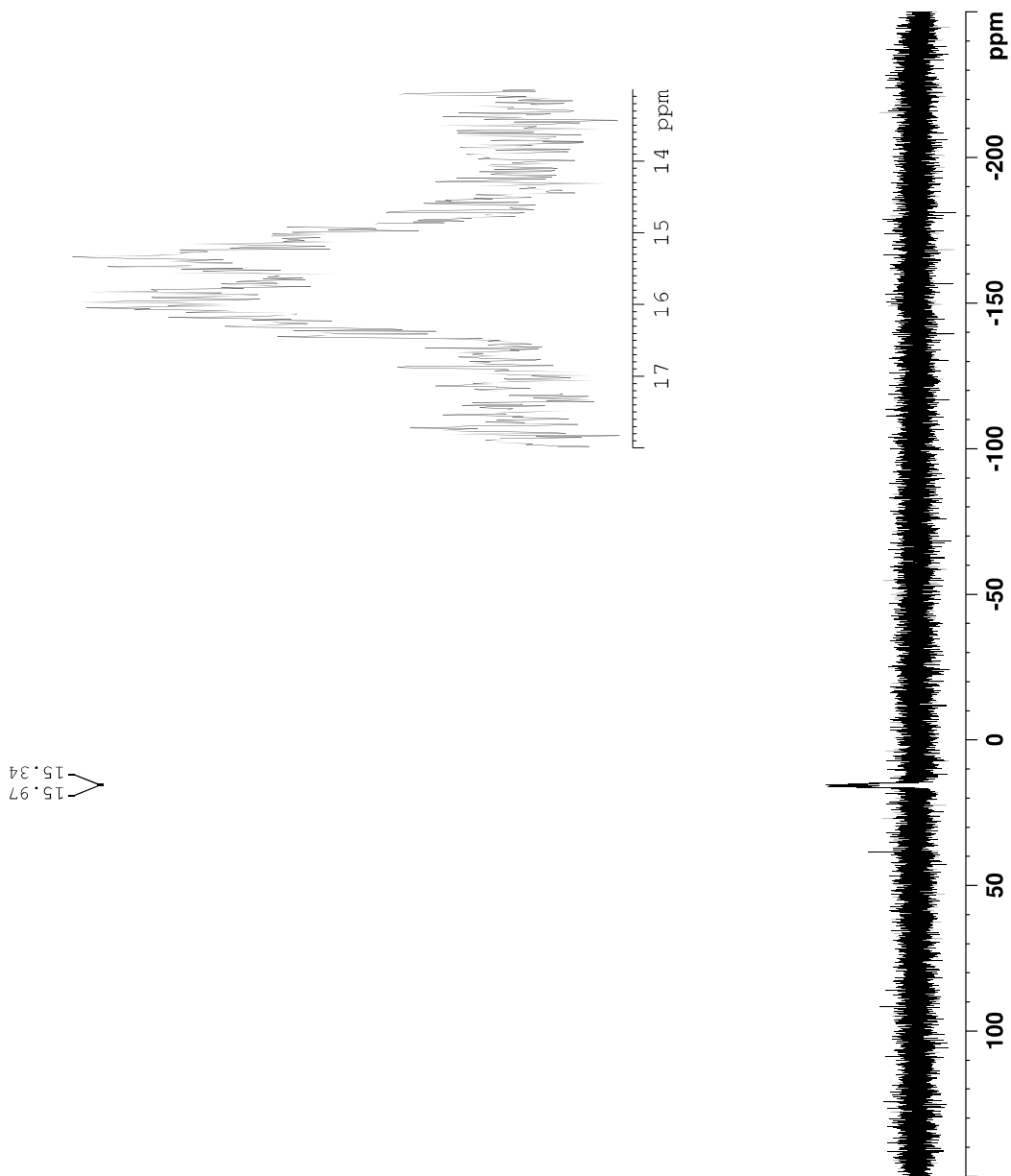
Current Data Parameters
NAME_      08ebo2904
EXNO       5
PROCNO     1

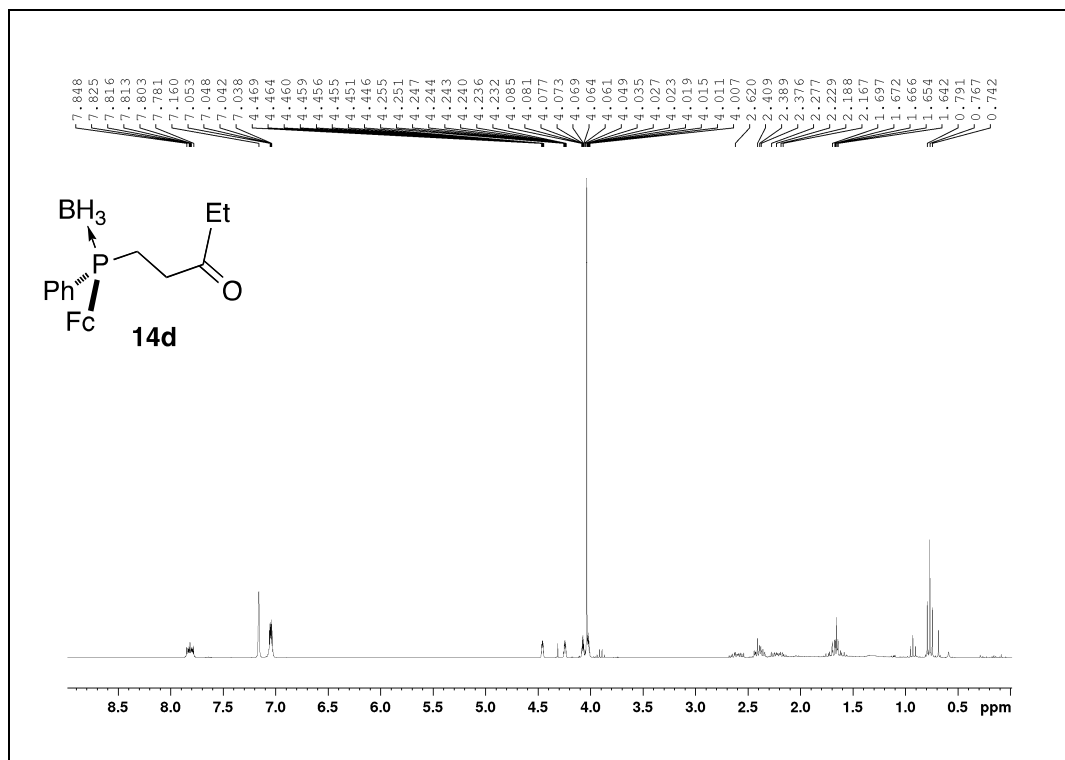
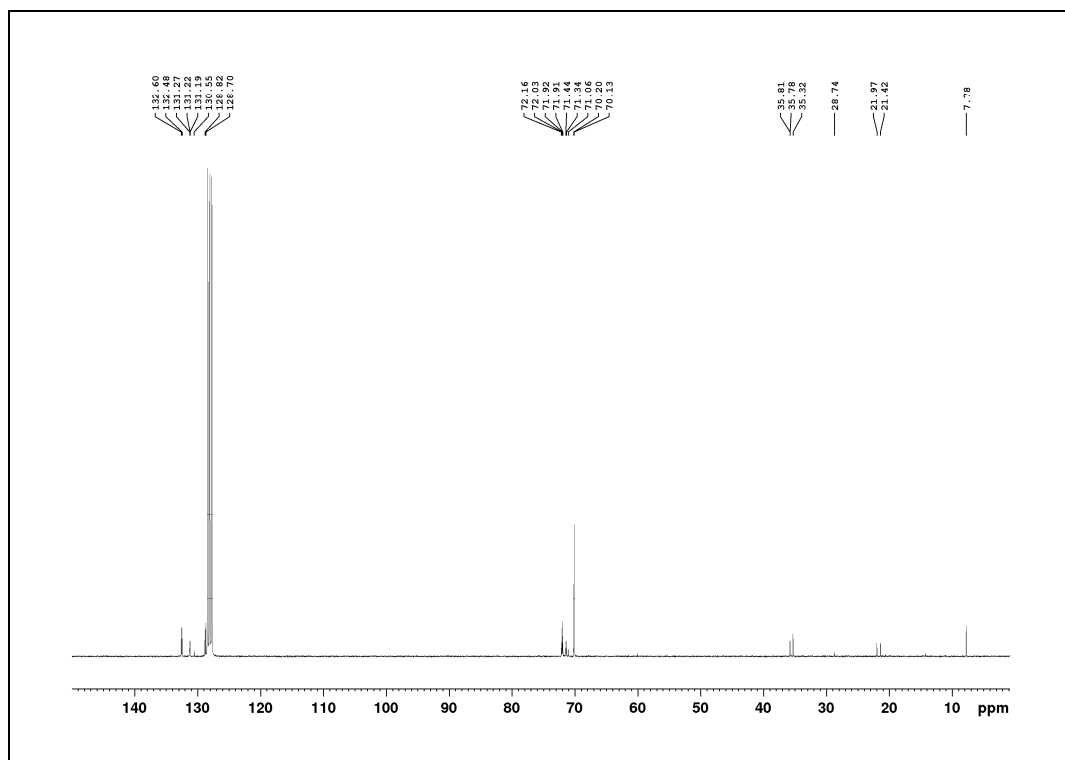
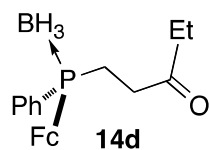
F2 - Acquisition Parameters
Date_      20080429
Time       18.39
INSTRUM    spect
PROBHD     5 mm PABBO BB-
PULPROG    zgpg30
TD         65536
SOLVENT    CDCl3
NS         128
DS         4
SMH        48661.801 Hz
FIDRES     0.748520 Hz
AQ         0.6733824 sec
RG         20642.5
DW         10.275 usec
DE         6.00 usec
TE         300.0 K
D1         2.00000000 sec
d11        0.03000000 sec
DELTA     1.89999998 sec
TD0        1

===== CHANNEL f1 =====
NUC1       31P
PI         5.60 usec
PL1        6.00 dB
SFO1       121.4887762 MHz

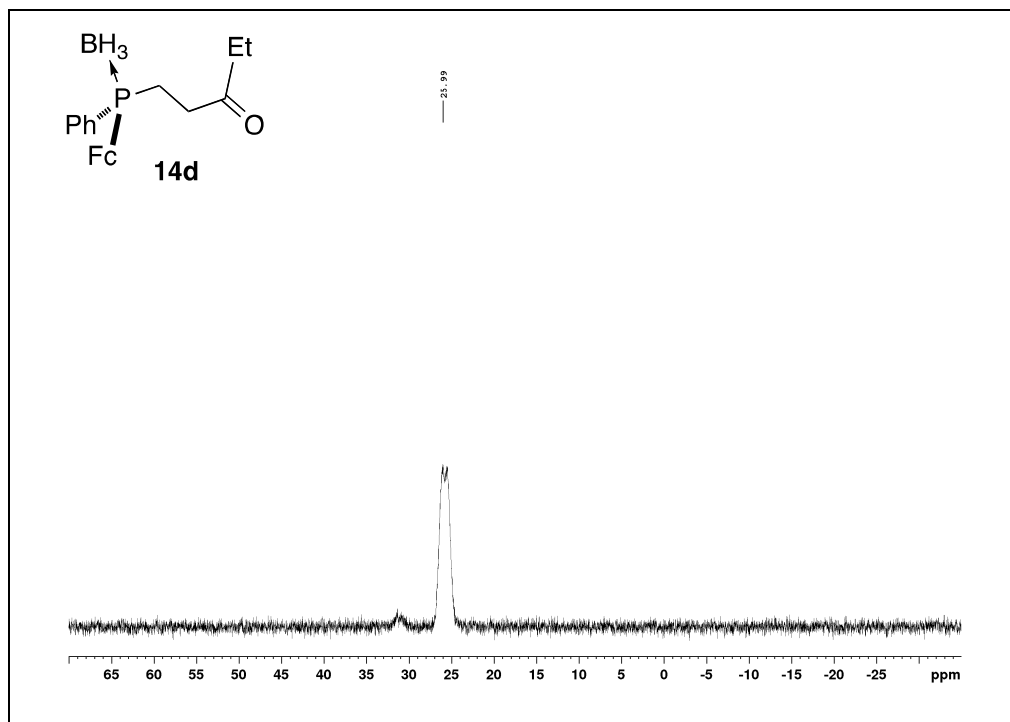
===== CHANNEL f2 =====
CPDPRG[2]  waltz16
NUC2       1H
PCPD2      100.00 usec
PL2        3.00 dB
PL12       24.94 dB
PL13       24.94 dB
SFO2       300.1312005 MHz

F2 - Processing parameters
SI         32768
SF         121.4948510 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```

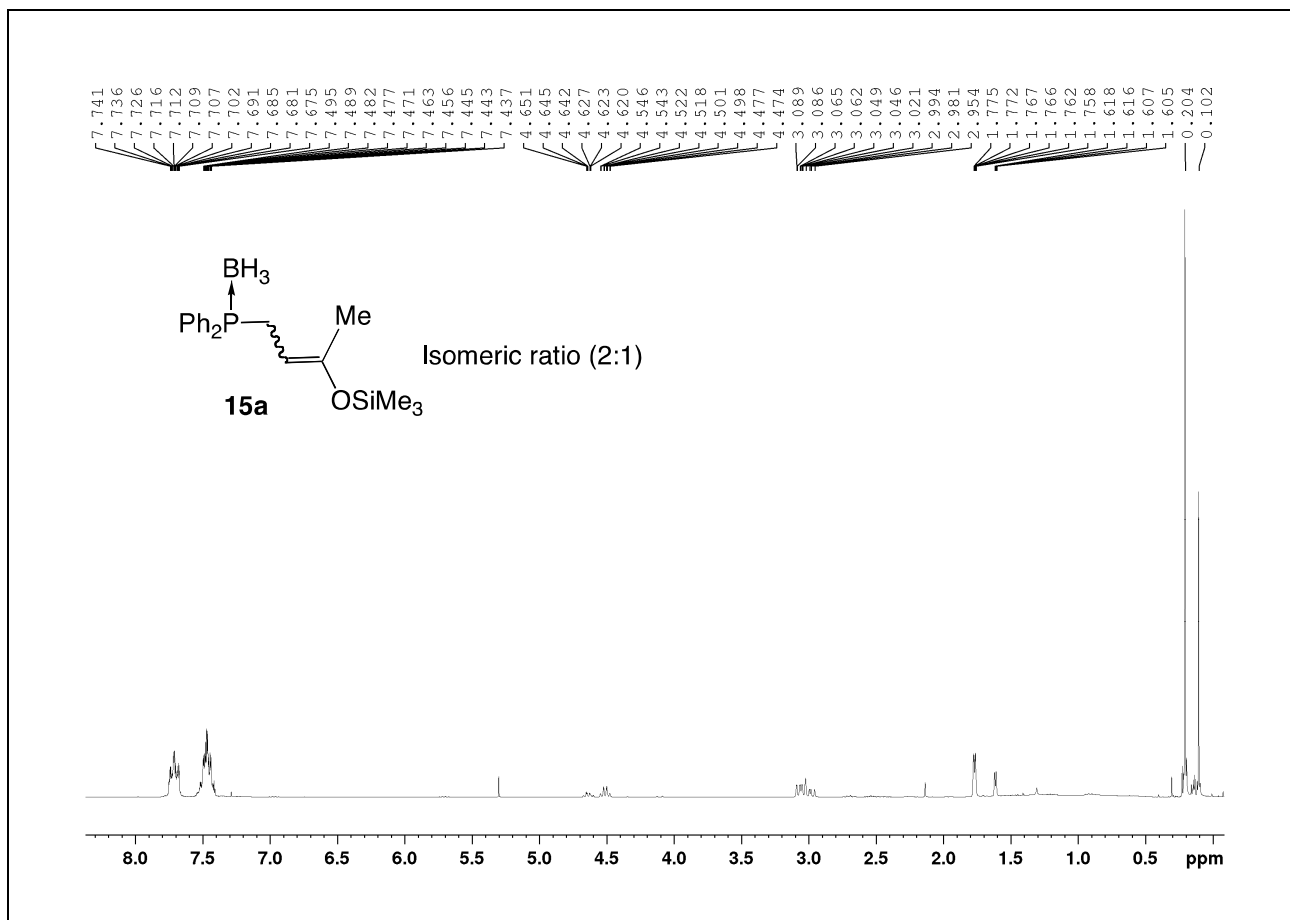


^1H NMR (300 MHz, C_6D_6) spectrum for **14d** ^{13}C NMR (75.4 MHz, C_6D_6) spectrum for **14d**

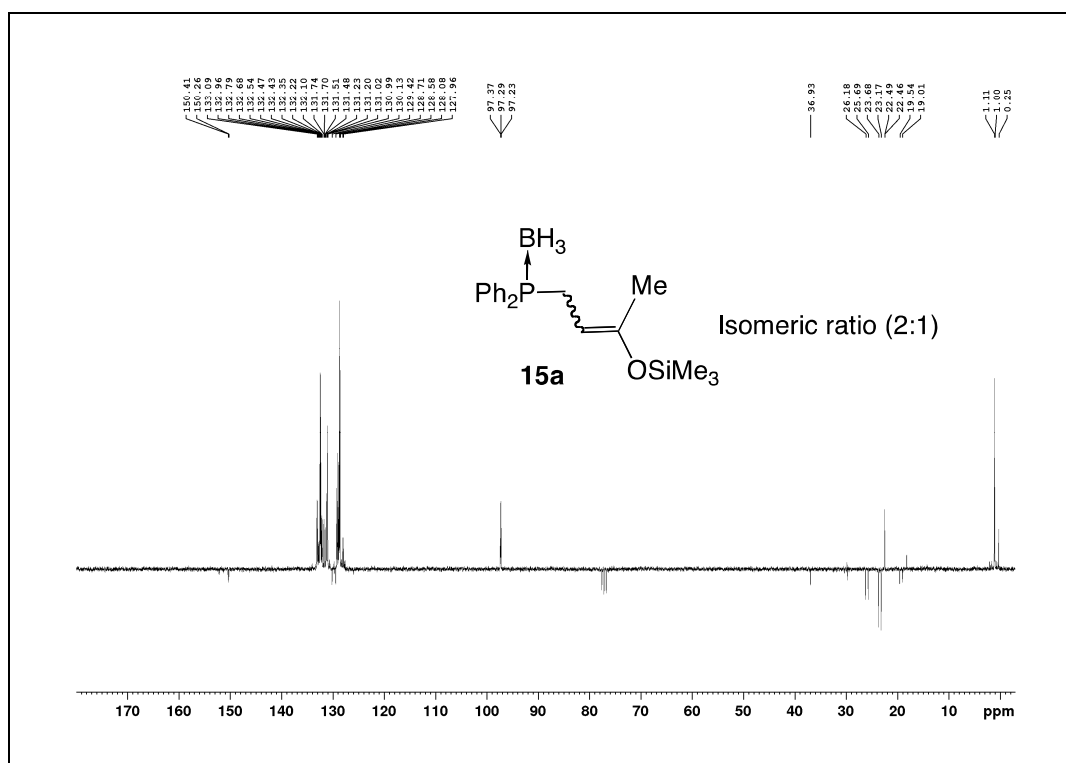
^{31}P NMR (121.4 MHz, C_6D_6) spectrum for **14d**



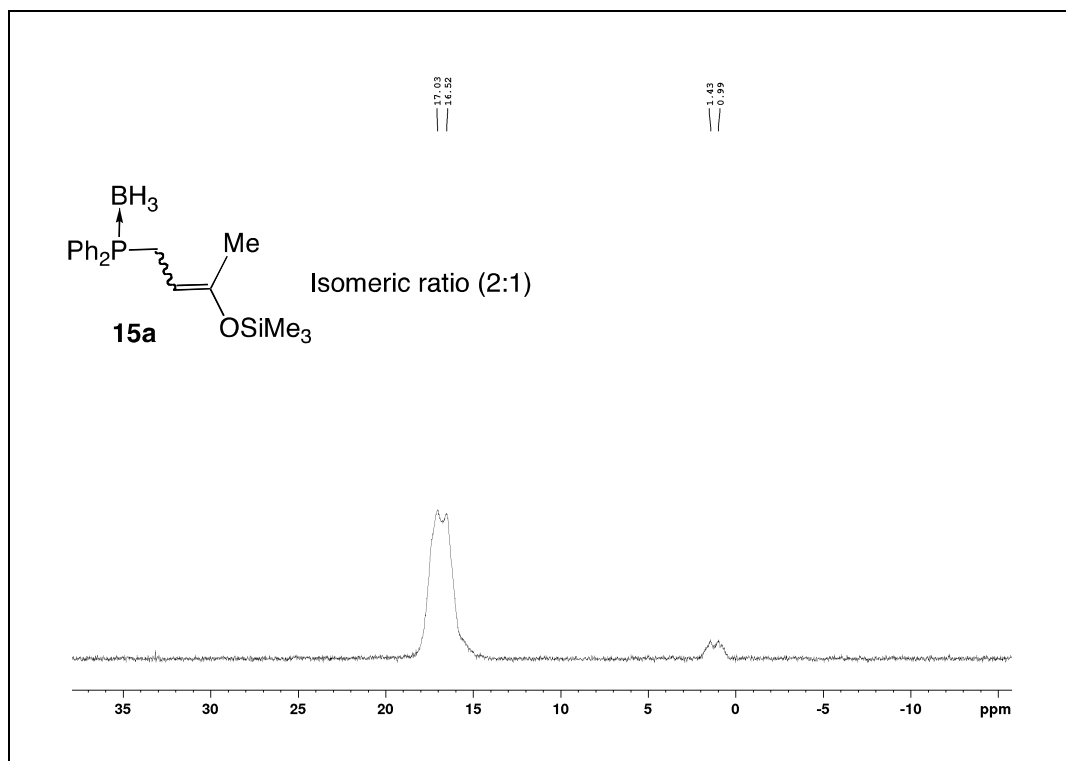
^1H NMR (300 MHz, CDCl_3) spectrum for **15a**

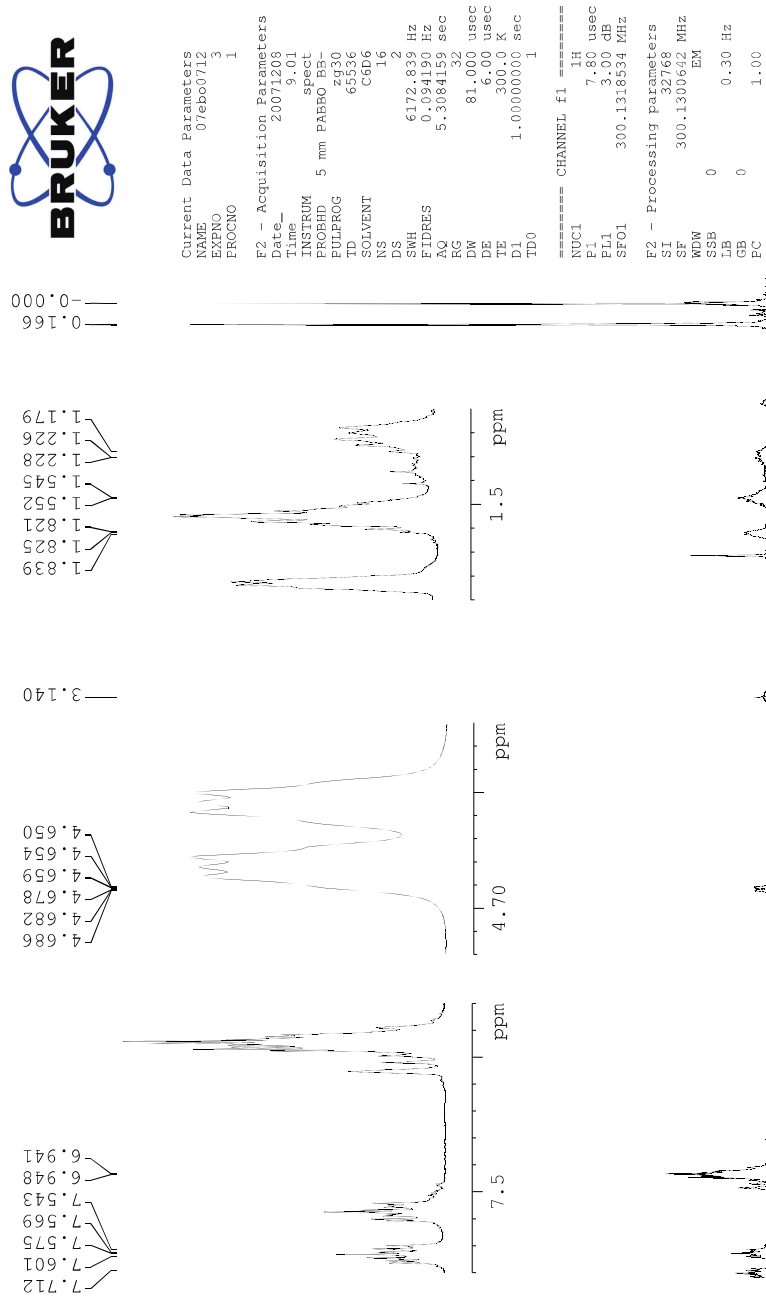
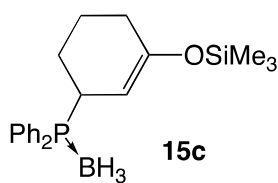


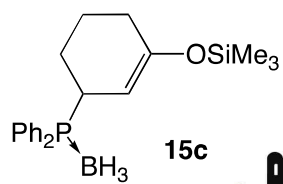
^{13}C NMR (75.4 MHz, CDCl_3) spectrum for **15a**



^{31}P NMR (121.4 MHz, CDCl_3) spectrum for **15a**



^1H NMR (300 MHz, C_6D_6) spectrum for **15c**

^{13}C NMR (75.4 MHz, C_6D_6) spectrum for **15c**

```

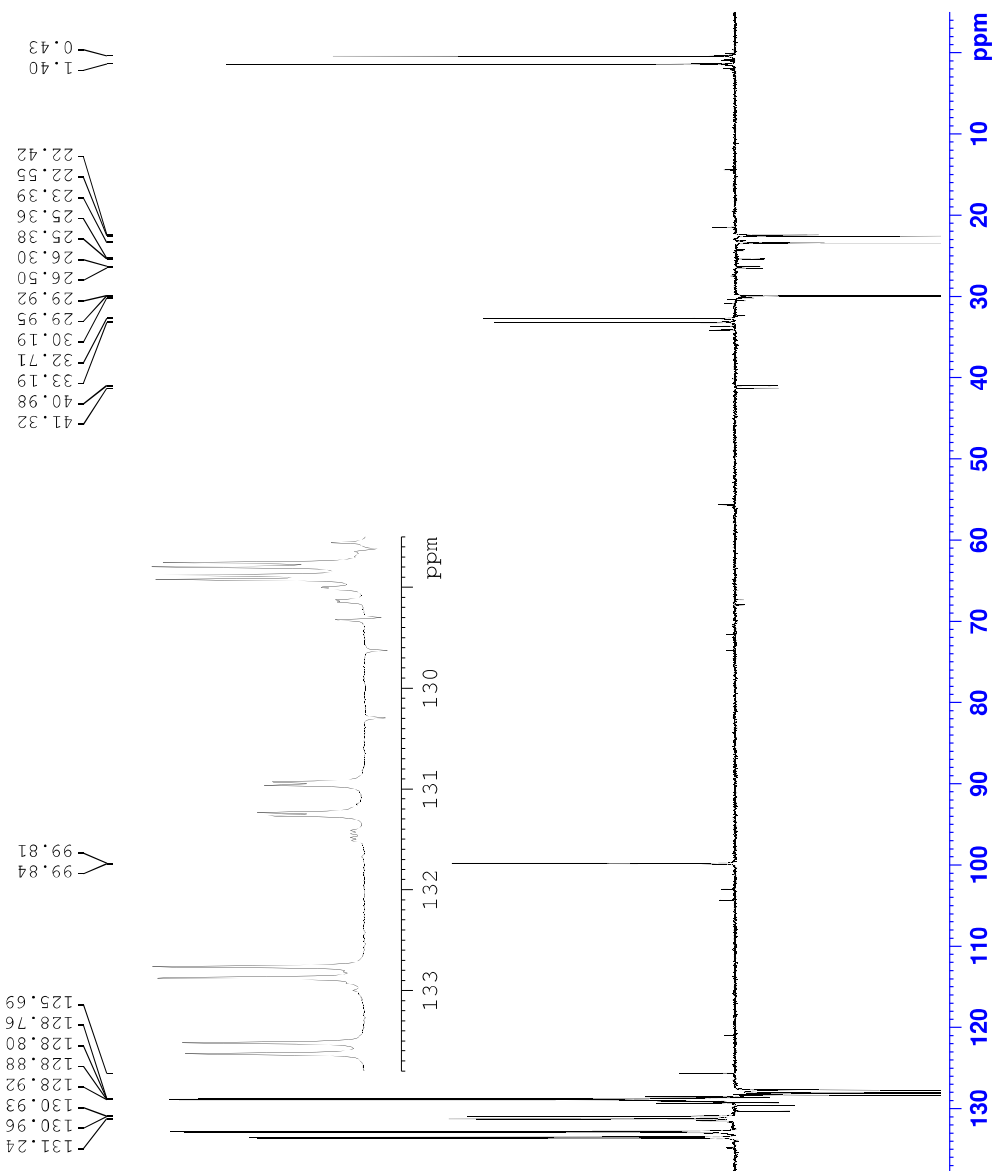
Current Data Parameters
NAME      07ebc0712
EXPNO     4
PROCNO    1

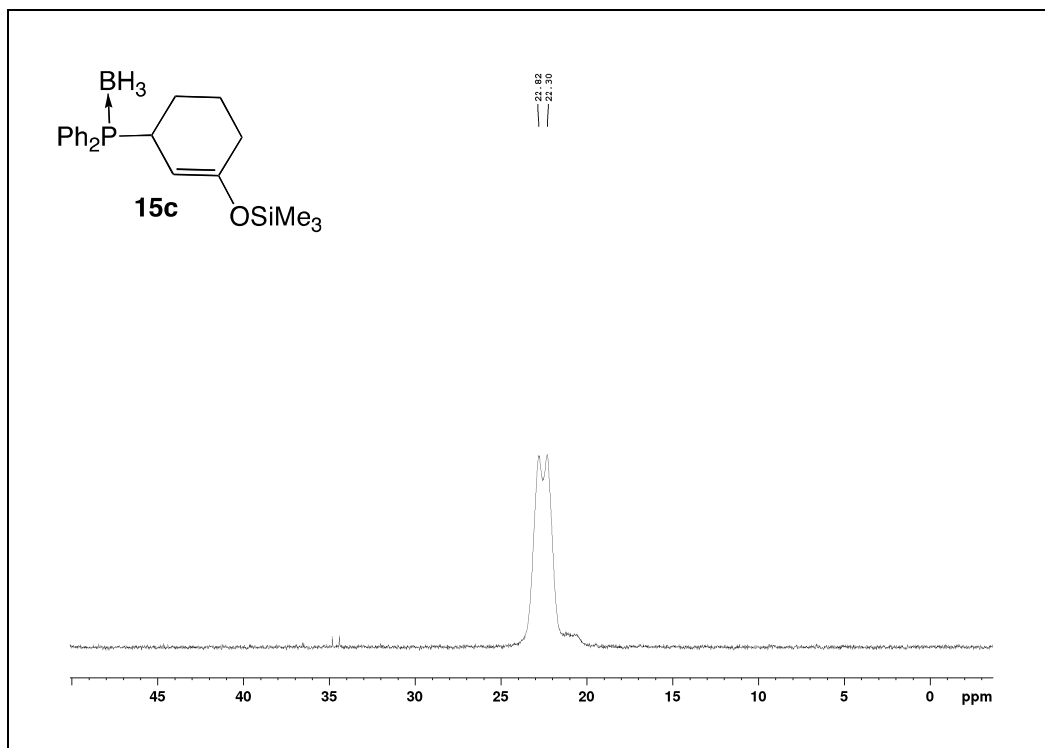
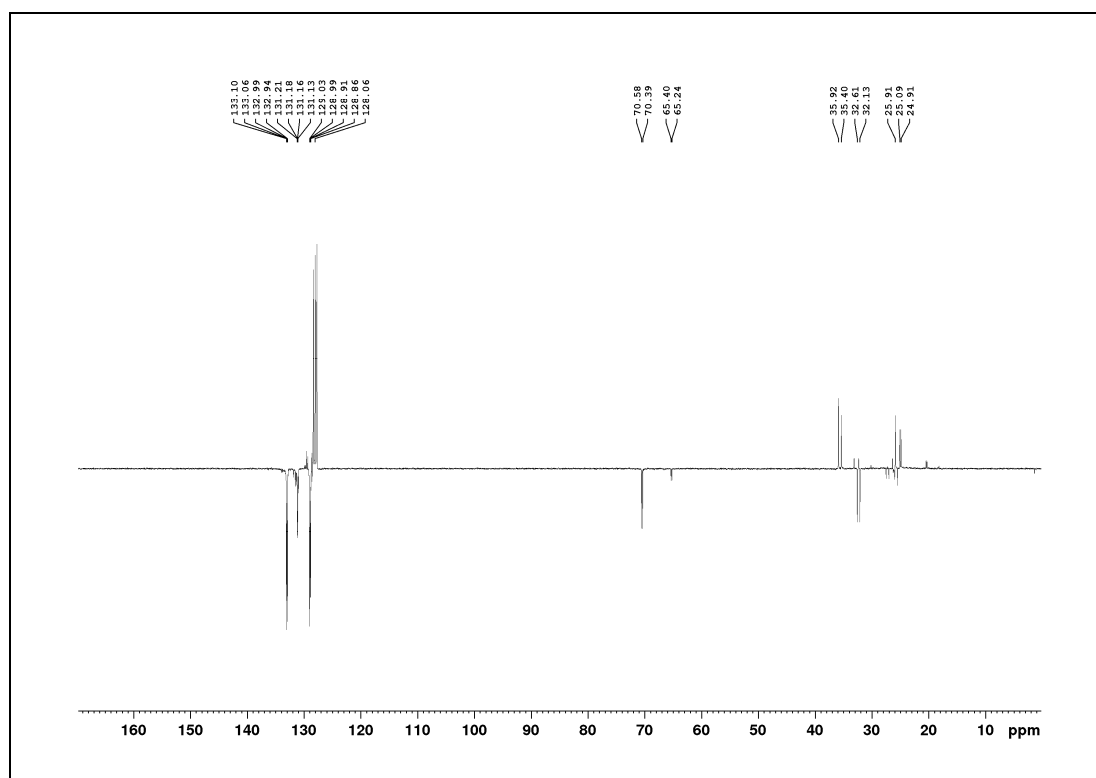
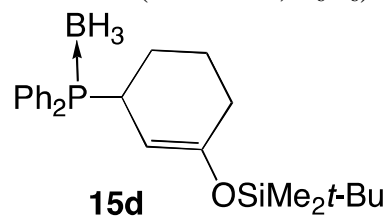
F2 - Acquisition Parameters
Date_     20071208
Time      11.16
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   jmcD
TD         65536
SOLVENT   C6D6
NS         2048
DS         4
SWH        17985.611 Hz
FIDRES     0.374439 Hz
AQ         1.831908 sec
RG         18390.4
DW         27.600 usec
DE         6.00 usec
TE         300.0 K
CNS1       145.0000000
CNS2       1.0000000
D1         2.0000000 sec
d2         0.00689655 sec
DELTA     0.00001235 sec
TD0        1

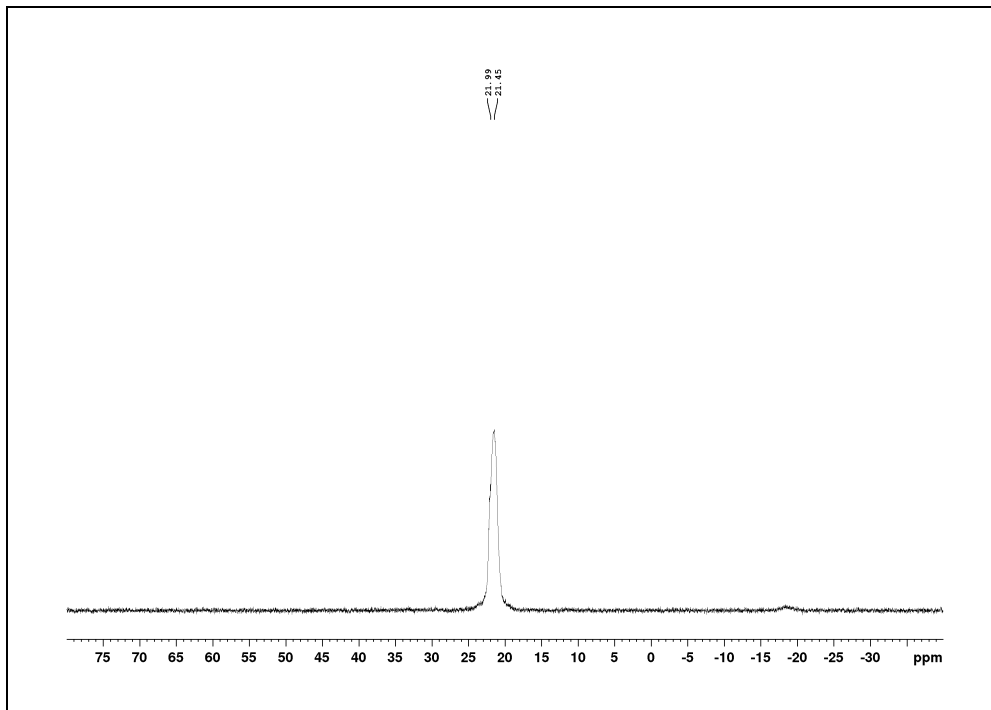
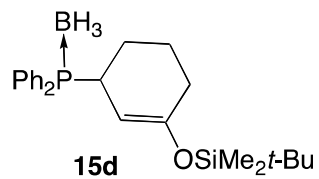
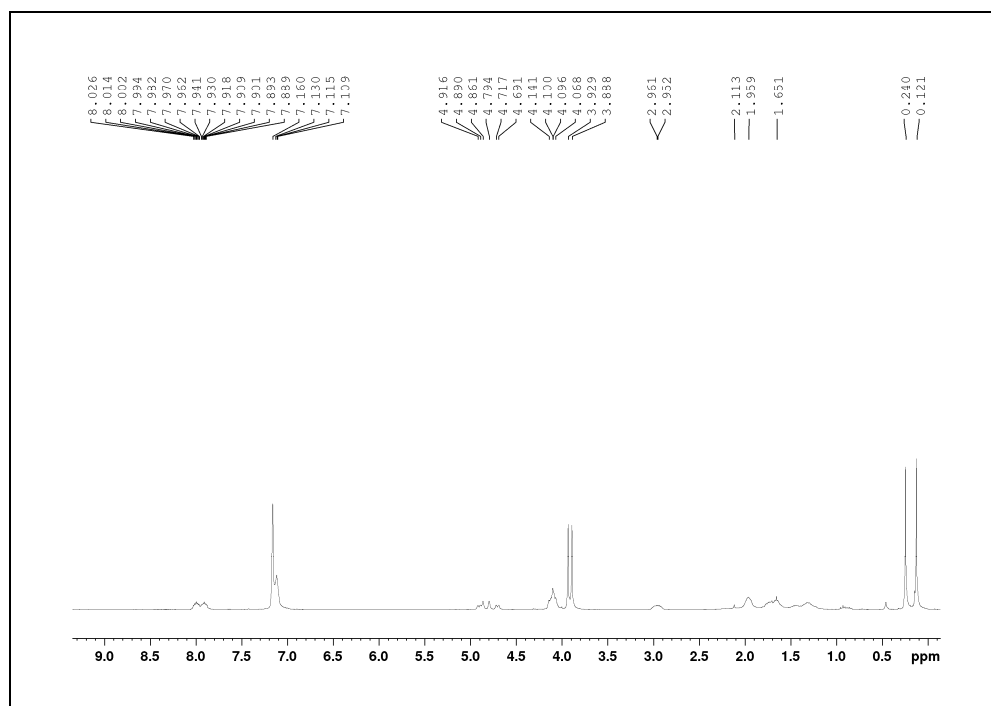
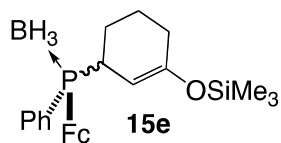
===== CHANNEL f1 =====
NUC1       13C
P1         9.70 usec
P2         19.40 usec
PL1        3.00 dB
SFO1       75.4752953 MHz

===== CHANNEL f2 =====
CPDPRG[2] waitz16
NUC2       1H
PCPD2      100.00 usec
PL2        3.00 dB
PL12       24.94 dB
SFO2       300.1312005 MHz

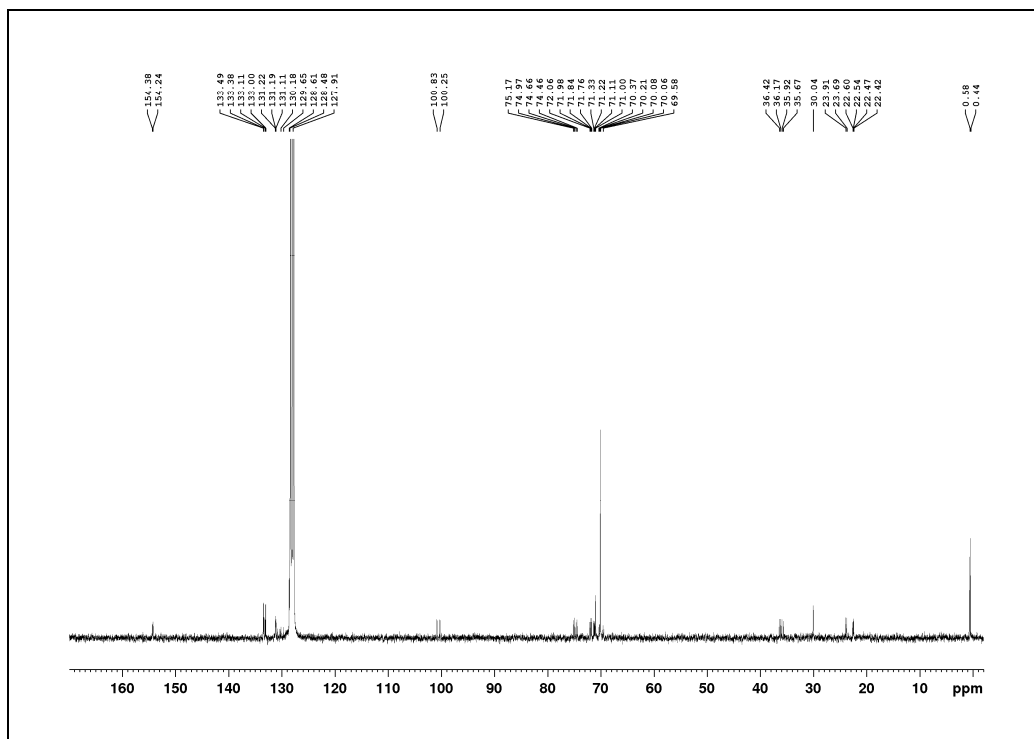
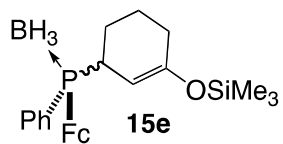
F2 - Processing parameters
SI         32768
SF         75.4677298 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```



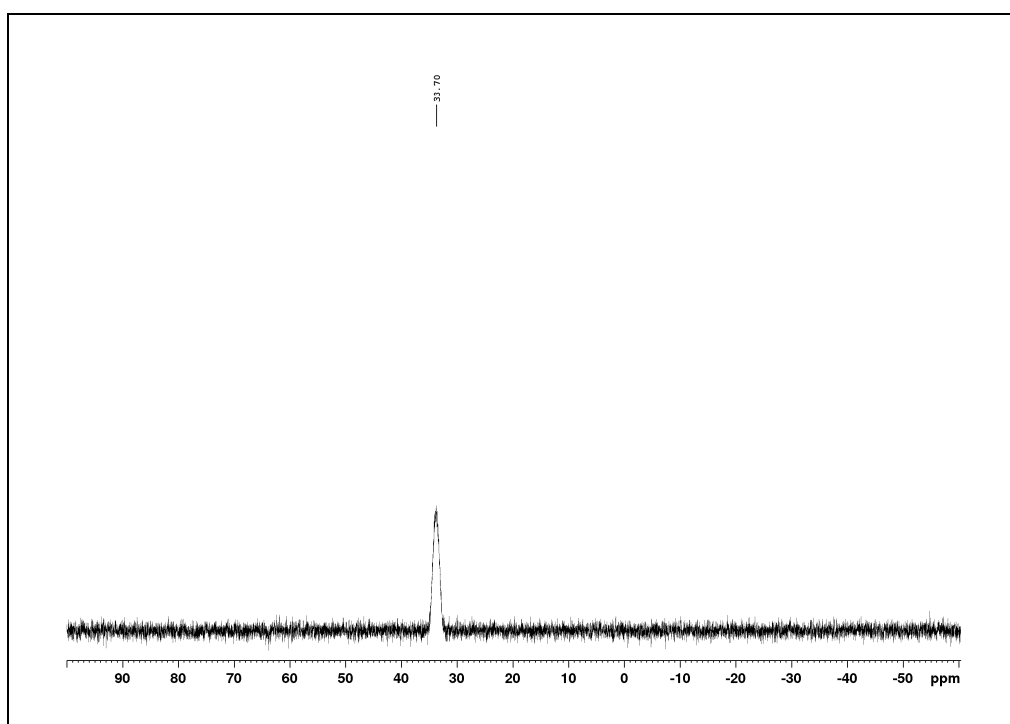
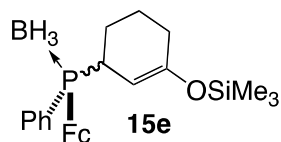
^{31}P NMR (121.4 MHz, C_6D_6) spectrum for **15c** ^{13}C NMR (75.4 MHz, C_6D_6) spectrum for **15d**

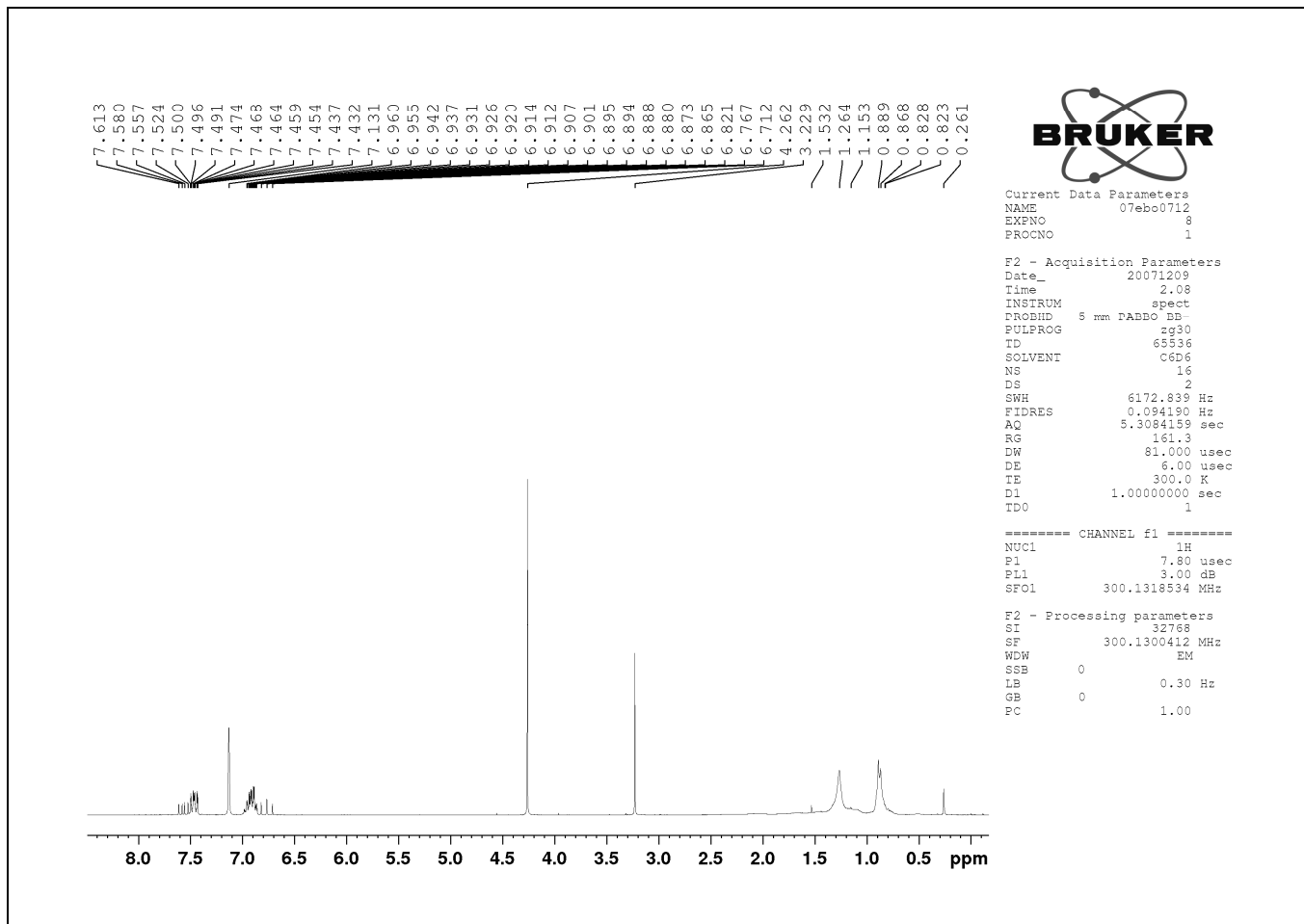
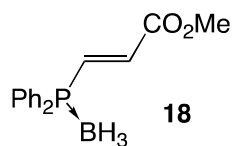
^{31}P NMR (121.4 MHz, C_6D_6) spectrum for **15d** ^1H NMR (300 MHz, C_6D_6) spectrum for **15e**

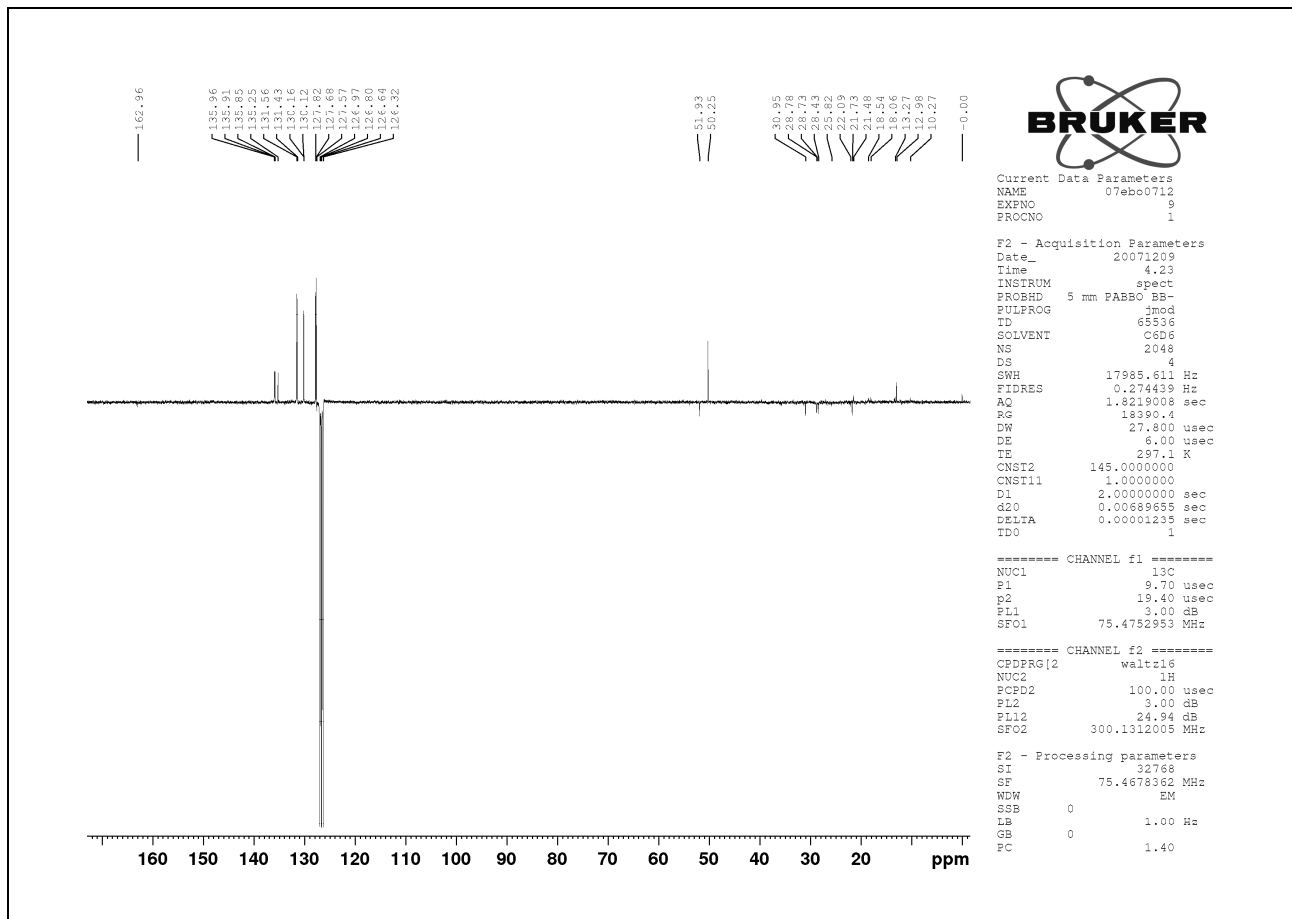
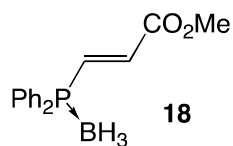
^{13}C NMR (75.4 MHz, C_6D_6) spectrum for **15e**



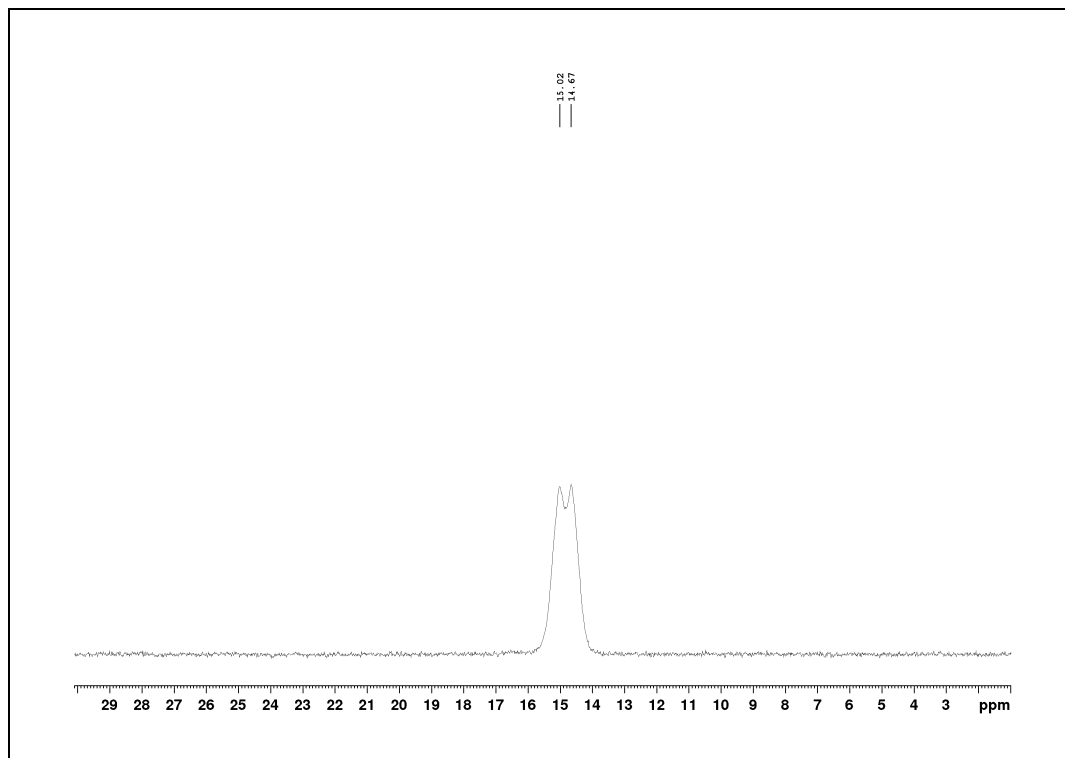
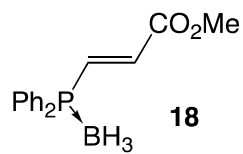
^{31}P NMR (121.4 MHz, CDCl_3) spectrum for **15e**

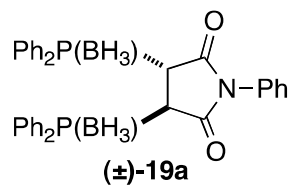


^1H NMR (300 MHz, C_6D_6) spectrum for **18**

^{13}C NMR (75.4 MHz, C_6D_6) spectrum for **18**

^{31}P NMR (202.4 MHz, CDCl_3) spectrum for **18**



^1H NMR (300 MHz, CDCl_3) spectrum for **19a**

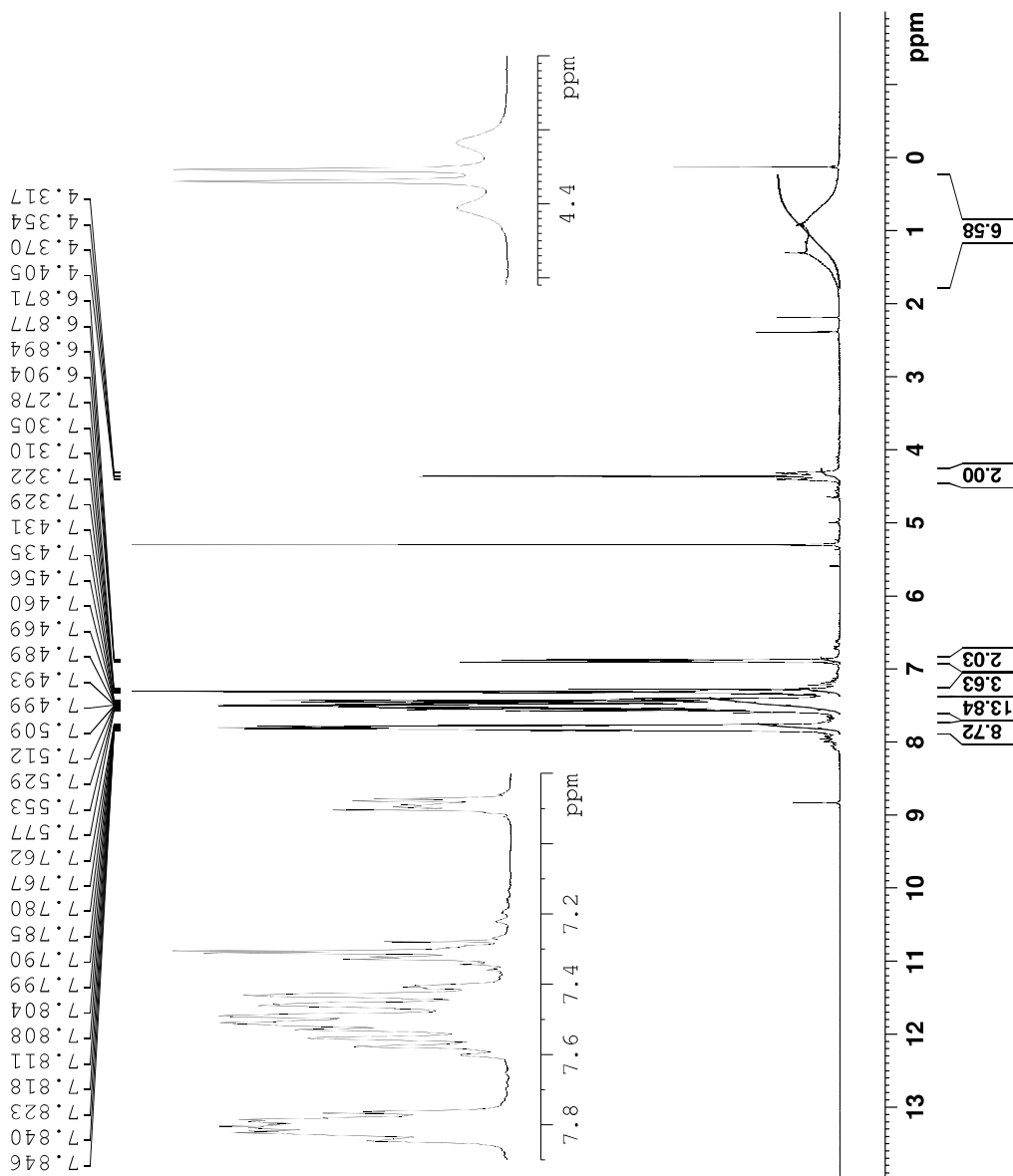
```

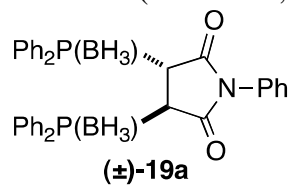
Current Data Parameters
NAME      08ebo_1902
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_     20080219
Time      11.56
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        6172.839 Hz
FIDRES     0.094190 Hz
AQ         5.3084159 sec
RG         71.8
DE         81.000 usec
TE         300.0 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1      1H
PI        7.80 usec
PL1       3.00 dB
SFO1      300.1318534 MHz

F2 - Processing parameters
SI         32768
SF         300.1300008 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
  
```



^{13}C NMR (75.4 MHz, CDCl_3) spectrum for **19a**

```

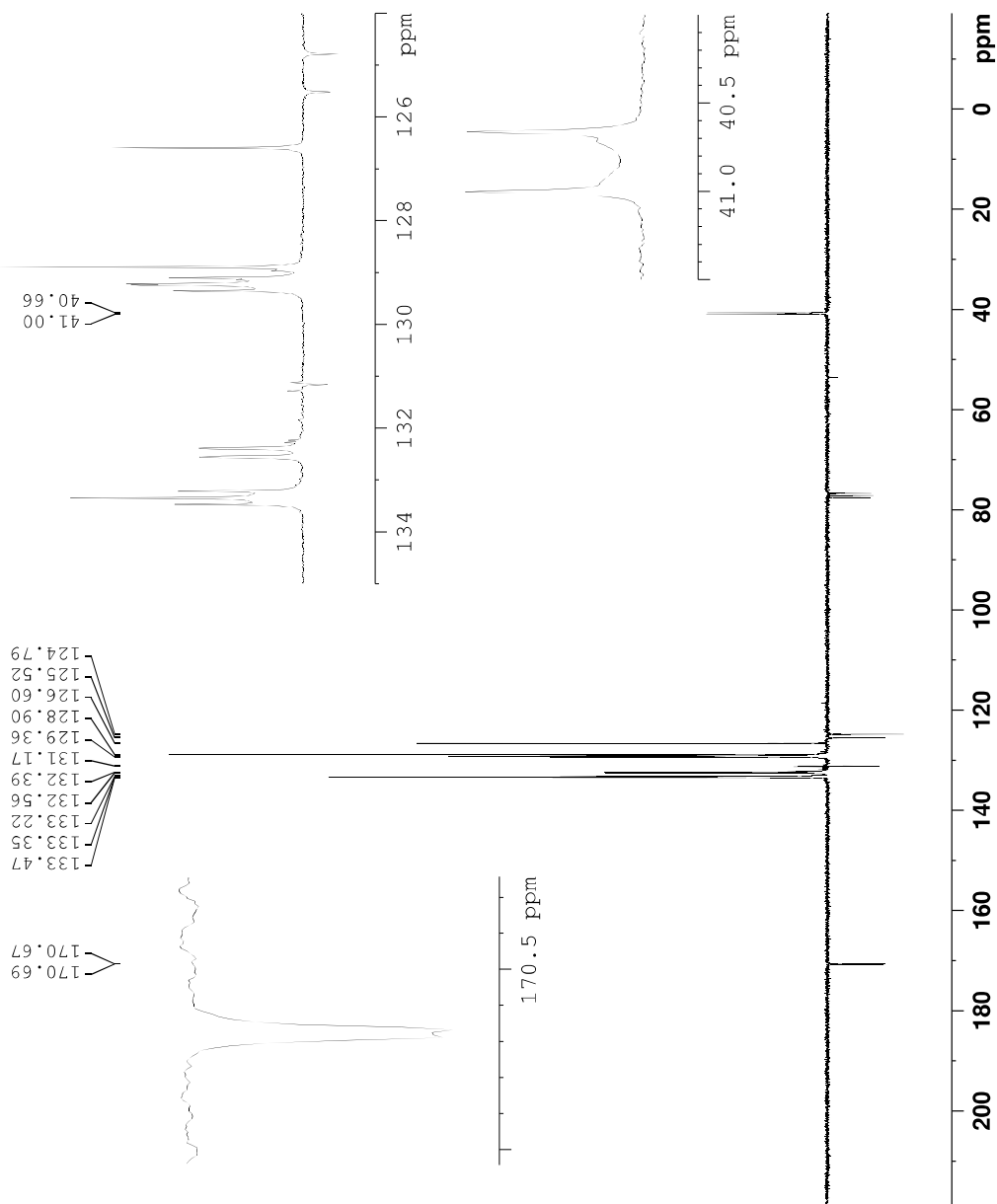
Current Data Parameters
NAME      08ebo_1902
EXPNO     3
PROCNO    1

F2 - Acquisition Parameters
Date_     20080220
Time      3.03
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   jmod
TD         65536
SOLVENT   CDCl3
NS         2048
DS         4
SWH        17985.611 Hz
FIDRES     0.274439 Hz
AQ         1.8219008 sec
RG         16384
DE         27.800 usec
TE         300.0 K
CNST2     145.0000000
CNST11    1.0000000
D1         2.00000000 sec
d20        0.00689655 sec
DELTA     0.00001235 sec
TD0        1

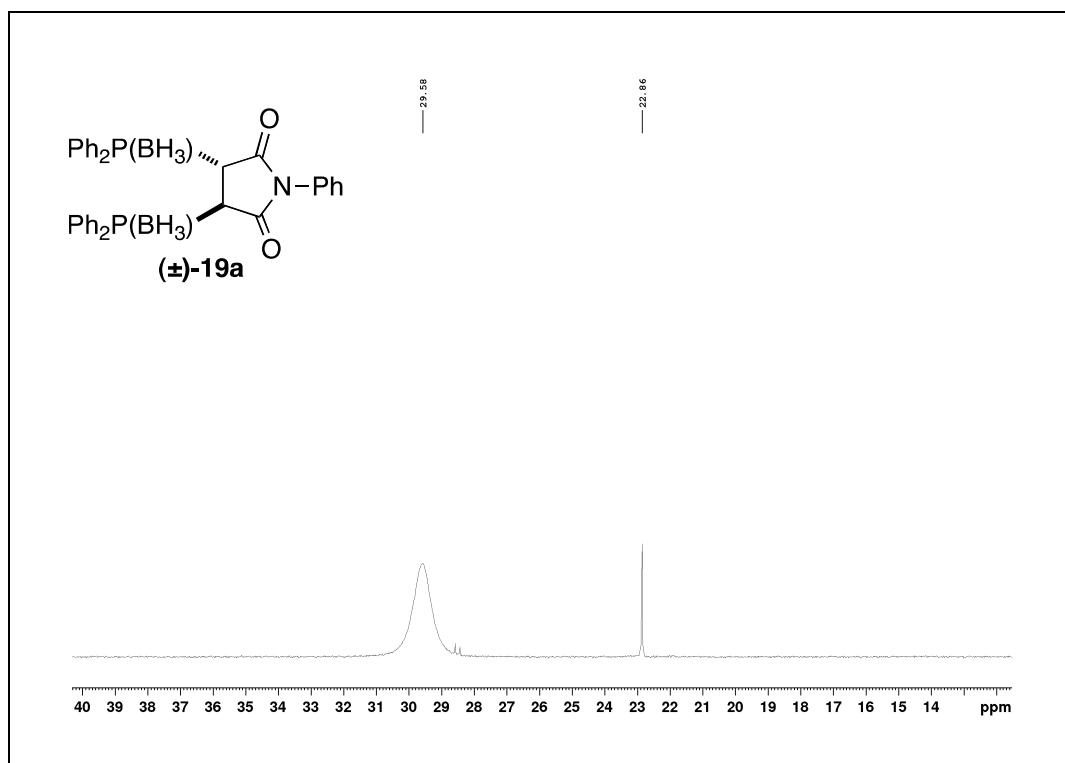
===== CHANNEL f1 =====
NUC1       13C
P1         9.70 usec
P2         19.40 usec
PL1        3.00 dB
PL12       75.4752953 MHz
SF01

===== CHANNEL f2 =====
CPDPRG[2] walzr16
NUC2       1H
PCPD2     100.00 usec
PL2        3.00 dB
PL12       24.94 dB
SF02     300.1312005 MHz

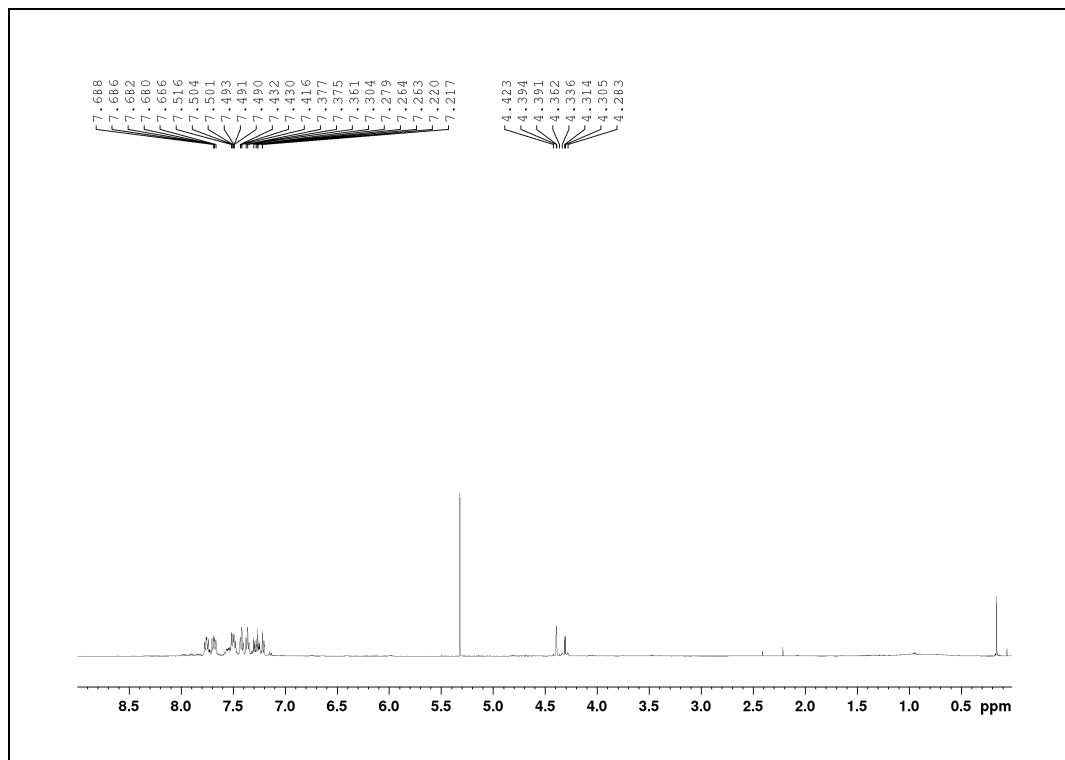
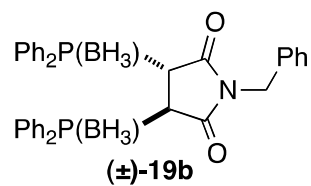
F2 - Processing parameters
SI         32768
SF         75.4677452 MHz
WDW        0
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```



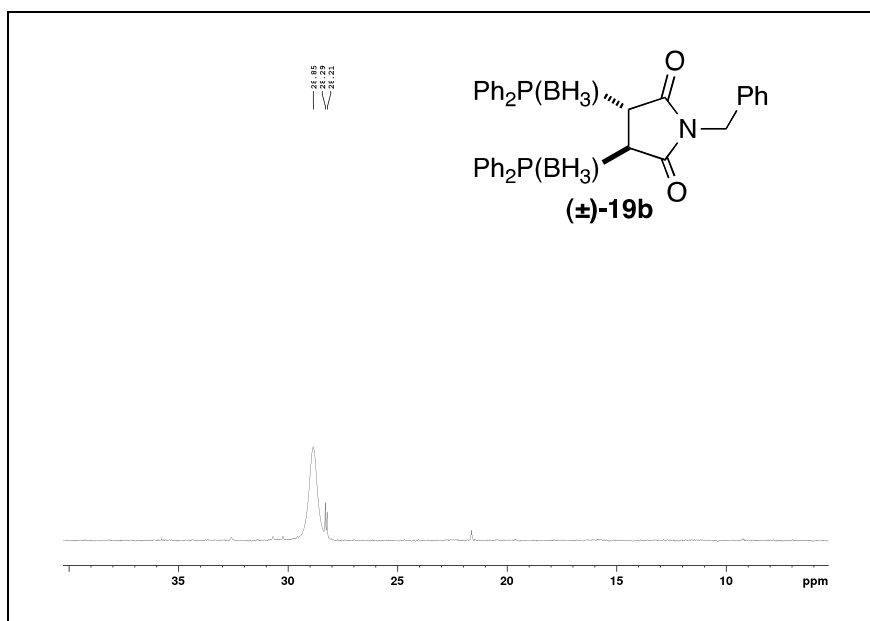
^{31}P NMR (121.4 MHz, CDCl_3) spectrum for **19a**

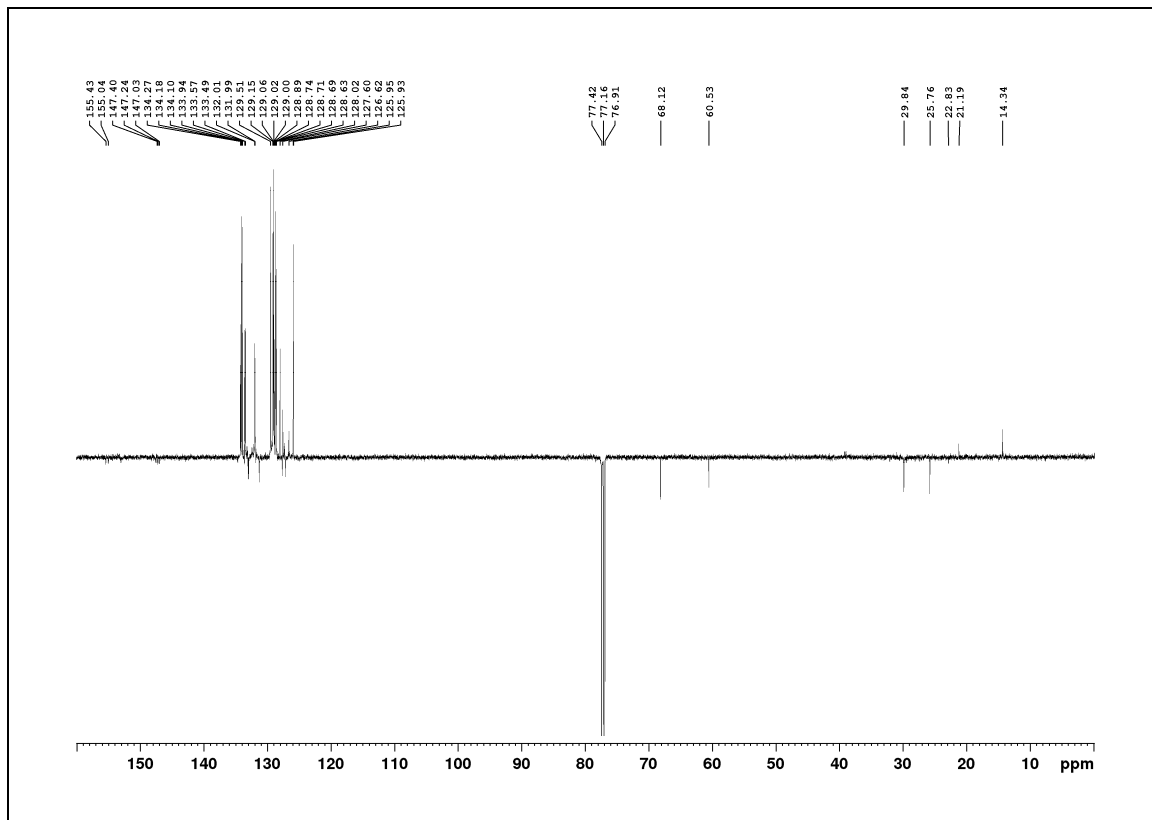
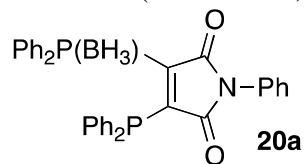


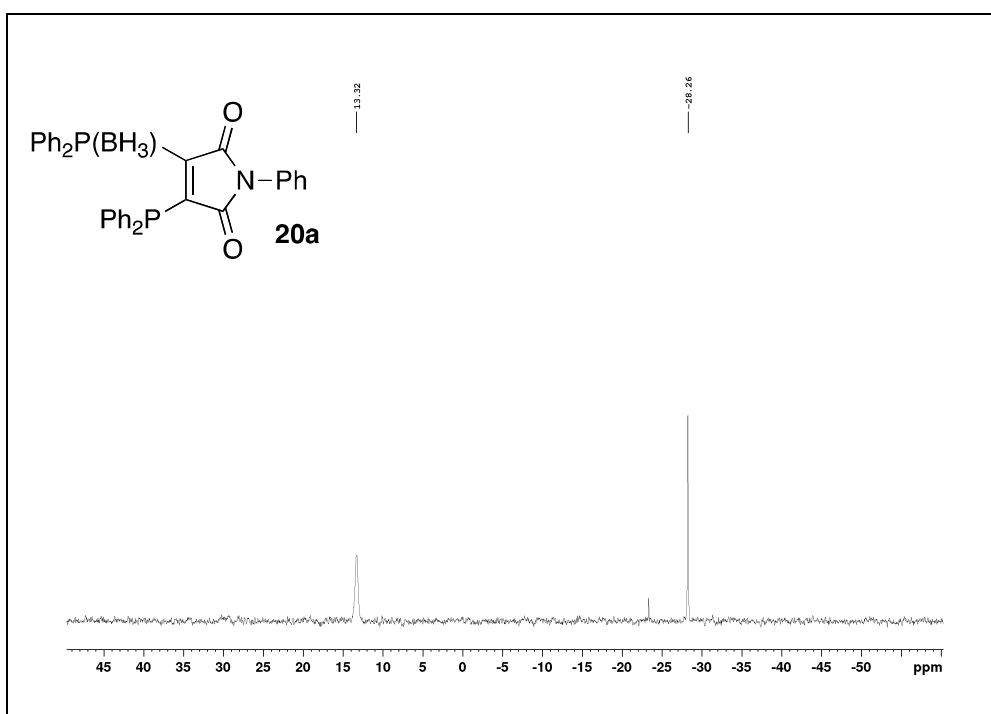
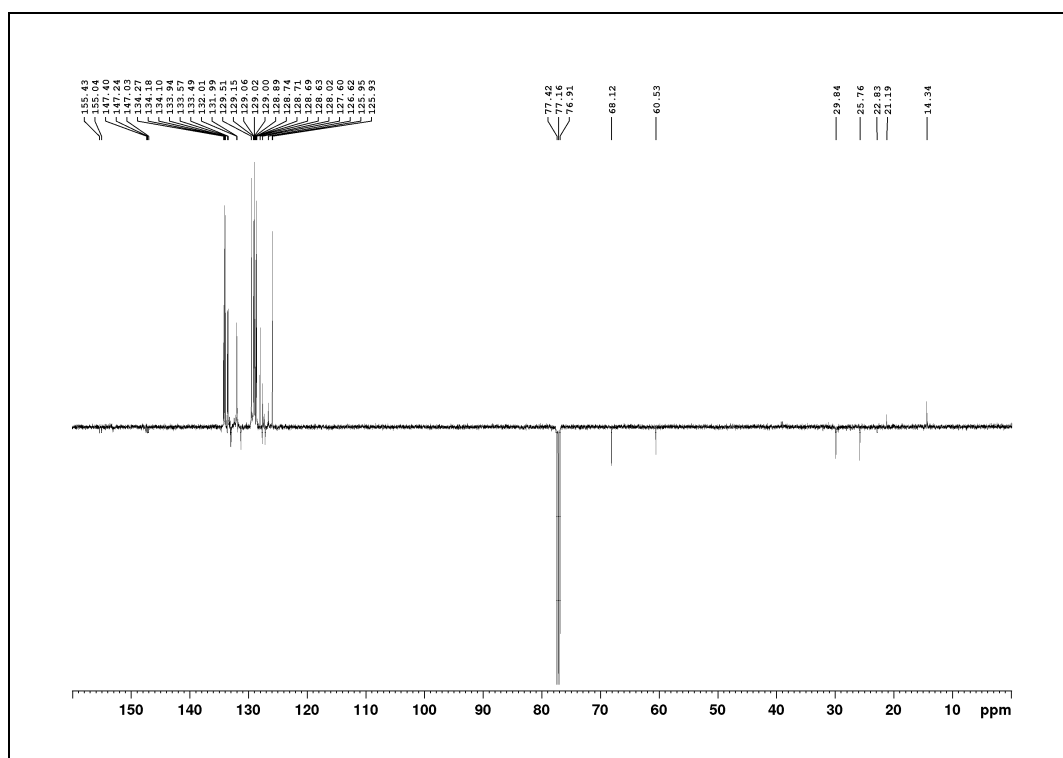
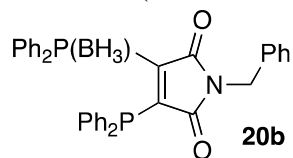
^1H NMR (500 MHz, CDCl_3) spectrum for **19b**



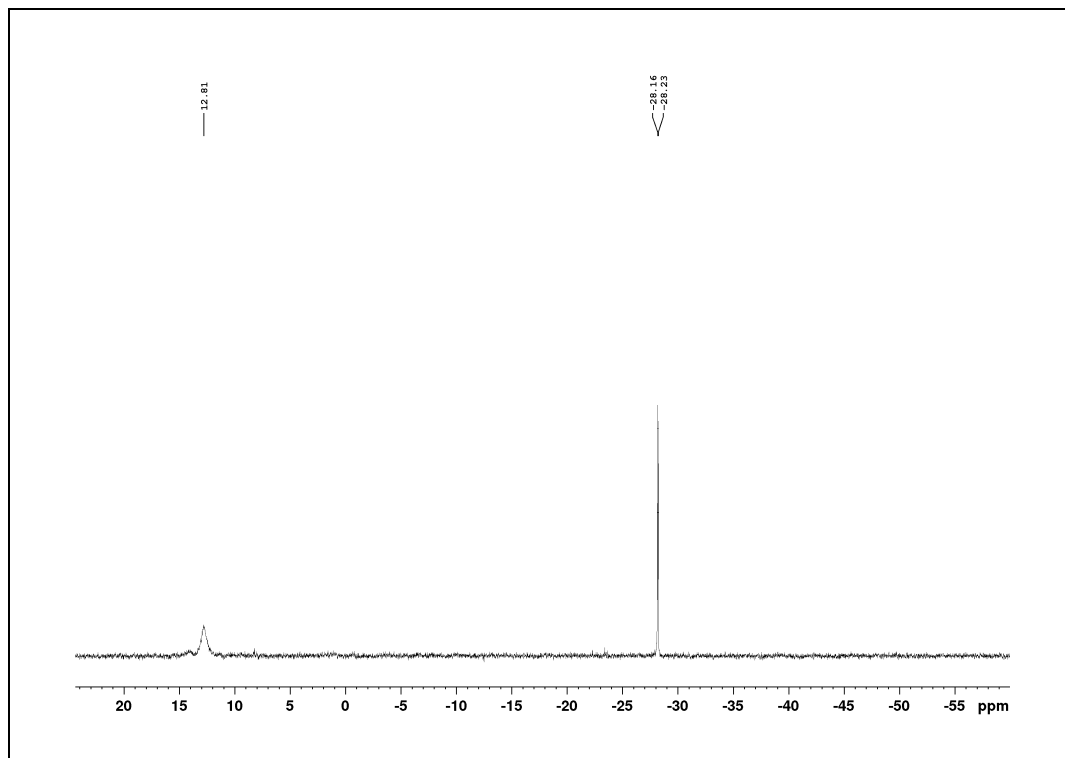
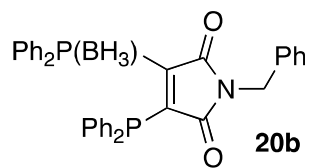
^{31}P NMR (202.4 MHz, CDCl_3) spectrum for **19b**

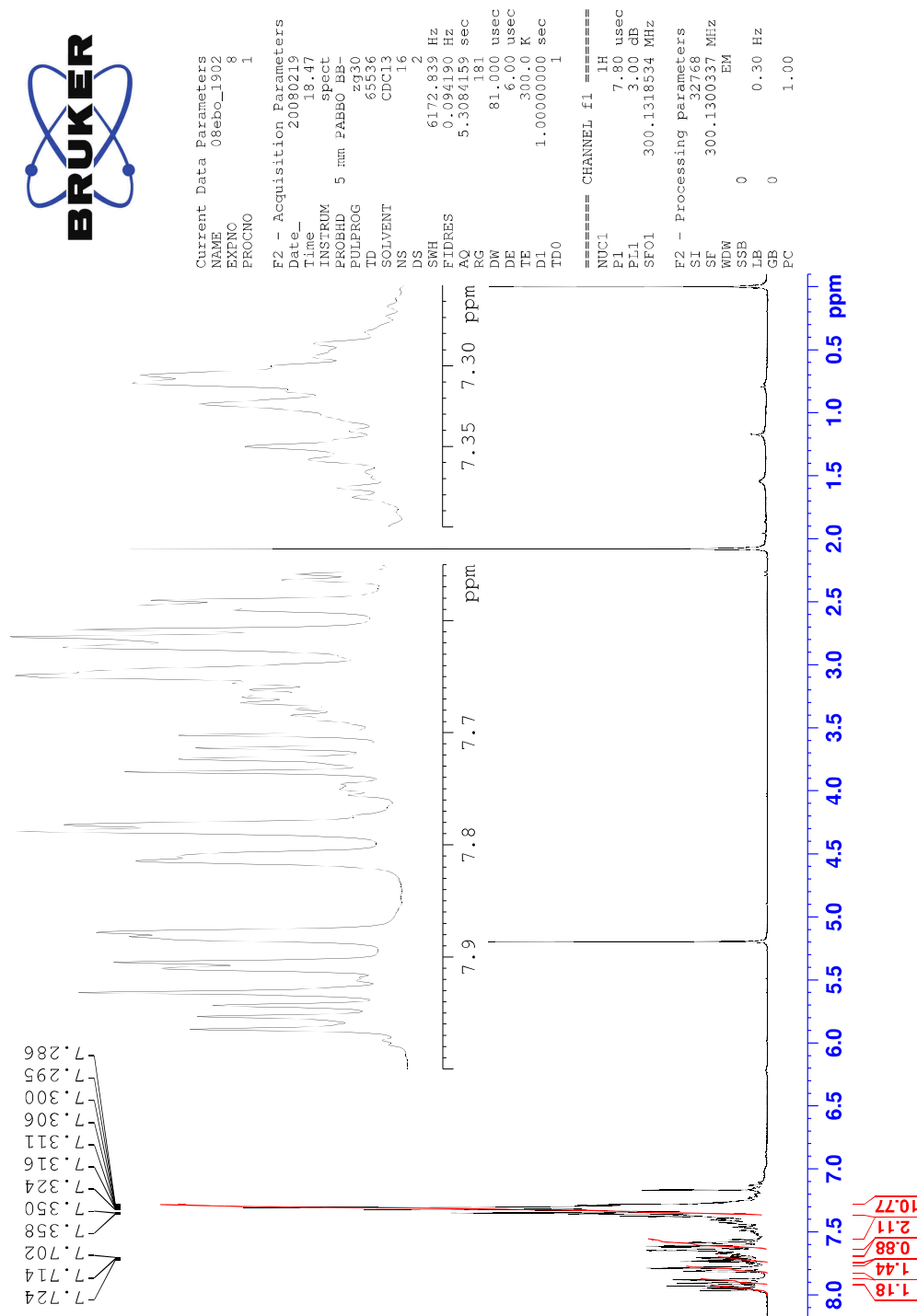
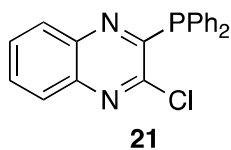


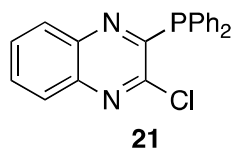
^{13}C NMR (125.8 MHz, CDCl_3) spectrum for **20a**

^{31}P NMR (202.4 MHz, CDCl_3) spectrum for **20a** ^{13}C NMR (150.9 MHz, CDCl_3) spectrum for **20b**

^{31}P NMR (121.4 MHz, CDCl_3) spectrum for **20b**



^1H NMR (300 MHz, CDCl_3) spectrum for **21**

^{13}C NMR (75.4 MHz, CDCl_3) spectrum for **21**

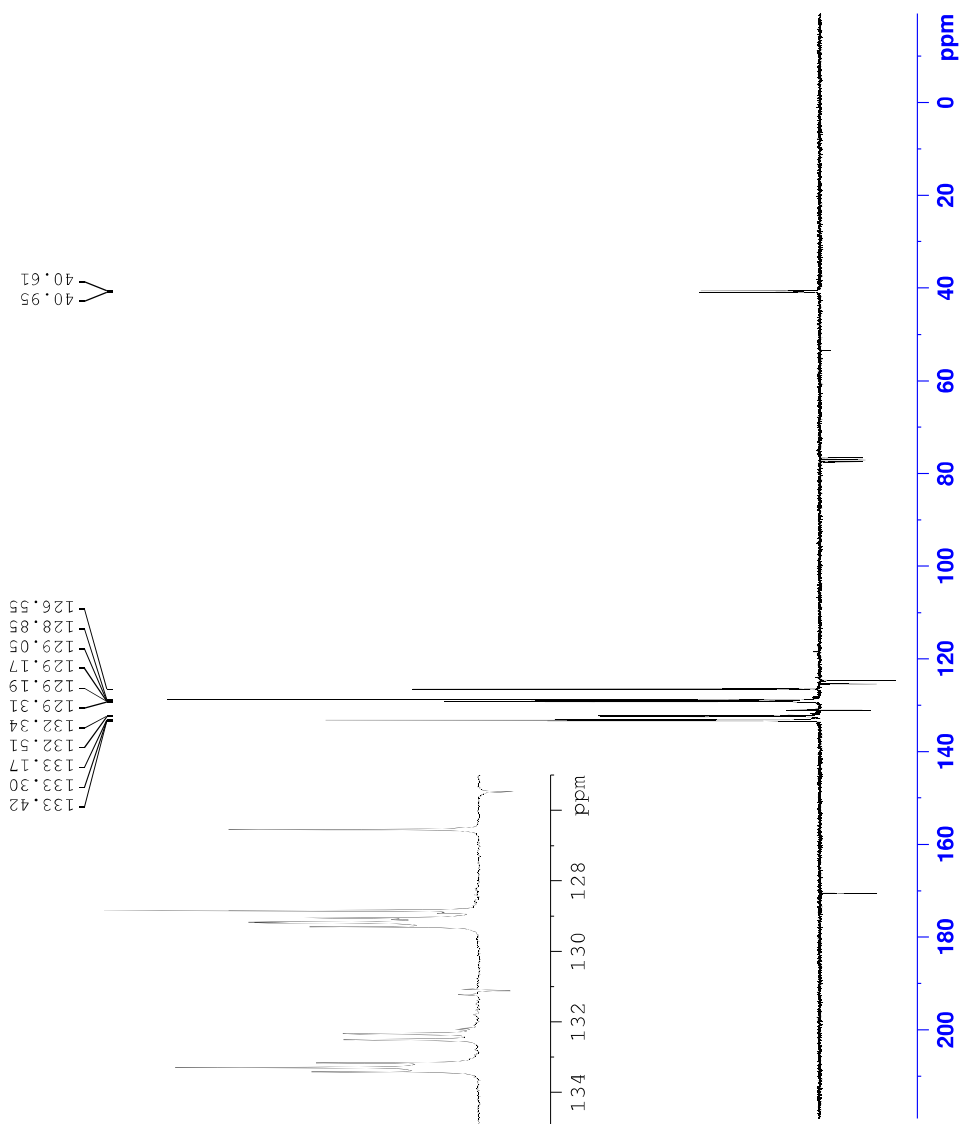
Current Data Parameters
 NAME 08ebo_1902
 EXPNO 3
 PROCNO 1

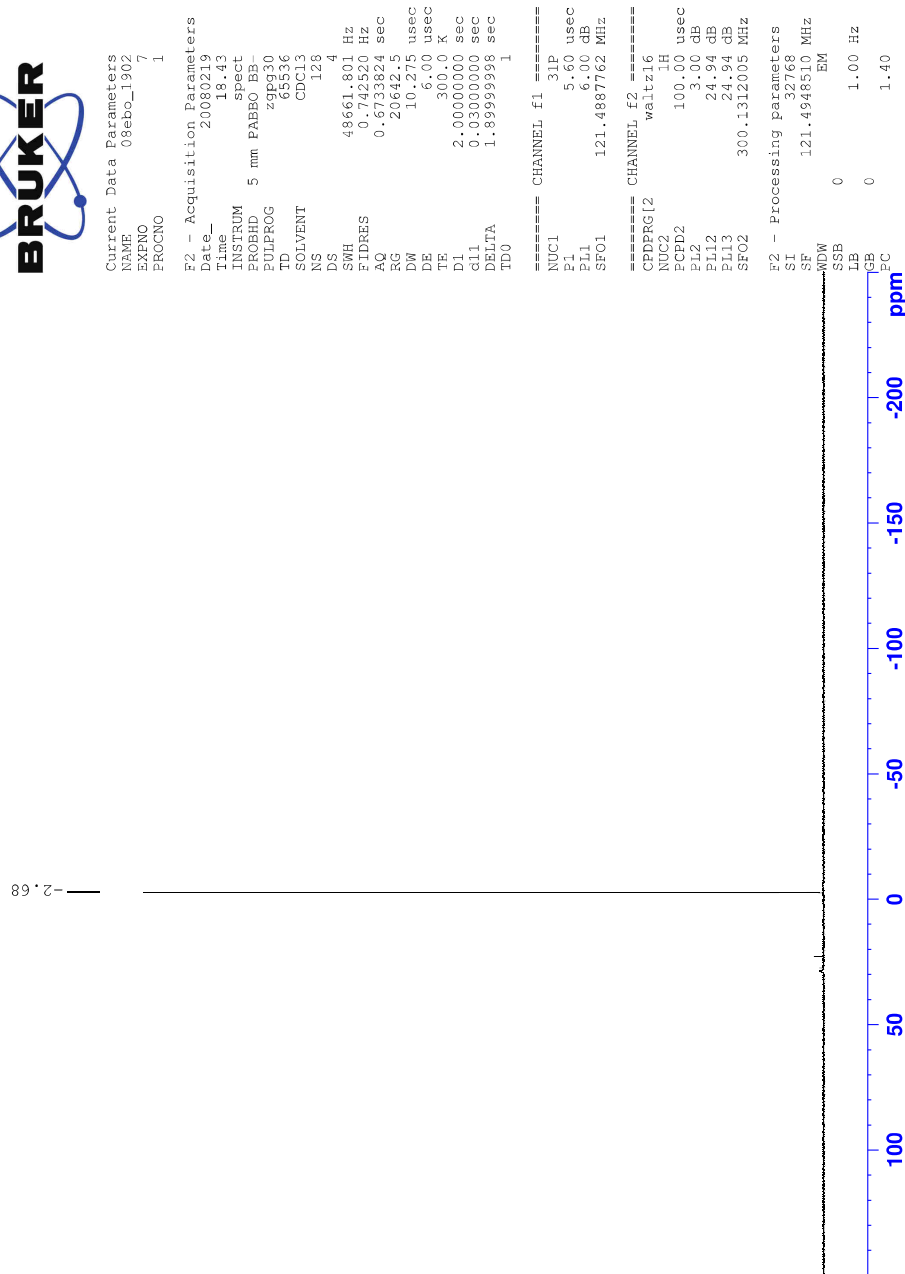
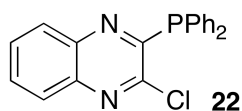
F2 - Acquisition Parameters
 Date_ 20080220
 Time 3.03
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG jmod
 TD 65536
 SOLVENT CDCl_3
 NS 2048
 DS 4
 SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219008 sec
 RG 16384
 DW 27.800 usec
 DE 6.00 usec
 TE 300.0 K
 CNST2 145.000000
 CNST1 1.000000
 D1 2.0000000 sec
 d2 0.00689655 sec
 DELTA 0.00001235 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.70 usec
 P2 18.60 usec
 SFL 3.00 dB
 SFO1 75.4752953 MHz

===== CHANNEL f2 =====
 CPDPRG2 waitz16
 NUC2 1H
 P1 100.00 usec
 P2 3.00 dB
 SFL 24.94 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677450 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

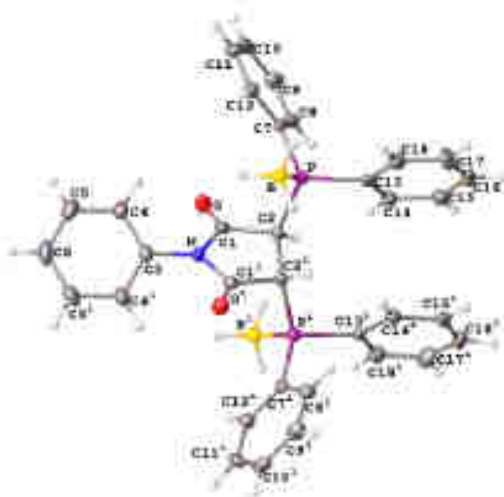


³¹P NMR (121.4 MHz, CDCl₃) spectrum for **21**

X-ray data for compounds **19a** and **21**Compound **19a**

Olex2

Crystal Data and Experimental



Experimental. A single colourless prism-shaped crystal (**19a**) was selected and mounted on a glass fiber with grease on a Nonius Kappa CCD diffractometer. The crystal ($0.25 \times 0.17 \times 0.05 \text{ mm}^3$) was kept at $T = 115 \text{ K}$ during data collection. Using Olex2 (Dolomanov et al., 2009), the structure was solved with the SIR92 program (Altomare, 1993) structure solution program, using the direct methods solution method. The model was refined with version of XL (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $\text{C}_{34}\text{H}_{33}\text{B}_2\text{NO}_2\text{P}_2$, $M_r = 571.17$, monoclinic, $C2/c$ (No. 15), $a = 9.093(5) \text{ \AA}$, $b = 16.643(5) \text{ \AA}$, $c = 19.794(5) \text{ \AA}$, $\beta = 98.166(5)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 2965(2) \text{ \AA}^3$, $T = 115 \text{ K}$, $Z = 4$, $Z' = 0.5$, $\mu (\text{MoK}\alpha) = 0.179$, 6019 reflections measured, 3387 unique ($R_{int} = 0.0465$) which were used in all calculations. The final wR_2 was 0.1015 (all data) and R_1 was 0.0443 ($I > 2(I)$).

Compound	19a
CCDC number	1048105
Formula	$\text{C}_{34}\text{H}_{33}\text{B}_2\text{NO}_2\text{P}_2$
$D_{calc} / \text{g cm}^{-3}$	1.279
μ / mm^{-1}	0.179
Formula Weight	571.17
Colour	colourless
Shape	prism
Max Size/mm	0.25
Mid Size/mm	0.17
Min Size/mm	0.05
T/K	115
Crystal System	monoclinic
Space Group	$C2/c$
$a/\text{Å}$	9.093(5)
$b/\text{Å}$	16.643(5)
$c/\text{Å}$	19.794(5)
$\alpha/^\circ$	90
$\beta/^\circ$	98.166(5)
$\gamma/^\circ$	90
$V/\text{Å}^3$	2965(2)
Z	4
Z'	0.5
$\Theta_{min}/^\circ$	3.100
$\Theta_{max}/^\circ$	27.453
Measured Refl.	6019
Independent Refl.	3387
Reflections Used	2254
R_{int}	0.0465
Parameters	189
Restraints	0
Largest Peak	0.320
Deepest Hole	-0.383
GooF	1.028
wR_2 (all data)	0.1015
wR_2	0.0897
R_1 (all data)	0.0854
R_1	0.0443

Experimental Extended. A colourless prism-shaped crystal with dimensions $0.25 \times 0.17 \times 0.05 \text{ mm}^3$ was mounted on a glass fibre with grease. Data were collected using a Nonius Kappa CCD diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at $T = 115 \text{ K}$. Data were measured using ω and θ scans using MoK α radiation (X-ray tube, 50 kV, 32 mA). The total number of runs and images was based on the strategy calculation from the program Collect (Nonius BV, 1997-2000). The actually achieved resolution was $Q = 27.453$. Cell parameters were retrieved using the SCALEPACK (Otwinowski, 1997) software and refined using DENZO (Otwinowski, 1997). Data reduction was performed using the DENZO software (Otwinowski, 1997) which corrects for Lorentz polarisation. The final completeness is 99.70 out to 27.453 in θ . No absorption correction was performed. The absorption coefficient (MU) of this material is 0.179. The structure was solved by Direct Methods with the SIR92 program (Altomare, 1993) structure solution program and refined by Least Squares using version of the ShelXL (Sheldrick, 2008). The structure was solved in the space group C2/c (# 15). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

Table 1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 19a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
C1	6082(2)	777.8(11)	7250.1(9)	18.7(4)
C2	5588(2)	1647.6(11)	7254.1(8)	16.7(4)
C3	5000	-554.5(16)	7500	20.7(6)
C4	5440(2)	-968.2(12)	6954.4(10)	25.2(5)
C5	5441(2)	-1802.7(12)	6960.5(11)	30.6(5)
C6	5000	-2220.7(18)	7500	32.7(8)
C7	6111(2)	1671.5(11)	5829.6(9)	17.9(4)
C8	7558(2)	1970.1(12)	5932.8(9)	22.1(4)
C9	8570(2)	1741.5(12)	5508.9(10)	27.2(5)
C10	8139(2)	1217.0(12)	4975(1)	28.0(5)
C11	6705(2)	924.8(12)	4861.8(10)	29.0(5)
C12	5684(2)	1146.2(12)	5286.8(9)	22.9(5)
C13	4732.7(19)	3033.2(11)	6401.4(8)	16.2(4)
C14	5831(2)	3494.3(11)	6783.1(9)	21.7(5)
C15	5779(2)	4326.4(12)	6746.9(10)	25.7(5)
C16	4653(2)	4702.3(12)	6326.6(10)	27.8(5)
C17	3564(2)	4254.4(12)	5944.4(11)	30.2(5)
C18	3596(2)	3423.3(12)	5979.9(10)	23.2(5)
N	5000	308.1(13)	7500	19.3(5)
O	7186.8(14)	525.7(8)	7053.4(6)	25.3(3)
P	4762.0(5)	1948.4(3)	6378.1(2)	16.41(14)
B	2878(2)	1441.9(14)	6128.8(11)	20.1(5)

Table 2. Anisotropic Displacement Parameters ($\times 10^3$) 19a. The anisotropic displacement factor exponent takes the form: $-2\pi^2(h^2 a^2 \sigma_{11} + \dots + 2hka^2 c^2 \sigma_{13} + \dots)$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	21.1(10)	18.9(11)	15.6(9)	1.6(8)	3.9(8)	0.5(9)
C2	19(1)	15.6(10)	16.8(9)	-0.6(8)	3.6(8)	-2.6(8)
C3	21.7(15)	16.0(15)	23.7(15)	0	0.6(12)	0
C4	28.9(17)	20.5(11)	25.5(11)	2.8(9)	13(9)	0.6(9)
C5	29.5(12)	24.7(12)	36.2(12)	-10.2(10)	-0.2(10)	1.5(10)
C6	28.3(17)	16.8(15)	49(2)	0	-6.4(15)	0
C7	23.8(10)	14.8(10)	15.5(9)	1.0(8)	1.7(8)	1.0(9)
C8	23.5(10)	23.9(11)	19.1(10)	-1.1(9)	4.8(8)	1.9(9)
C9	23.2(11)	32.6(13)	29.8(11)	5.1(10)	-8.7(9)	-4.2(10)
C10	34.0(13)	27.1(12)	26.1(11)	7.1(9)	15.4(10)	11.1(10)
C11	43.5(14)	26.3(12)	17.9(10)	-1.7(9)	6.9(10)	4.2(11)
C12	24.6(11)	21.6(11)	20.5(10)	-0.6(9)	4.0(9)	-0.1(9)
C13	17.9(9)	17.9(10)	14.3(9)	1.5(8)	6.8(7)	1.4(9)
C14	24.7(11)	21.2(11)	19.2(10)	0.3(8)	3.0(8)	-0.7(9)
C15	34.4(13)	28.3(11)	23.6(11)	1.9(9)	8.8(10)	-0(1)
C16	35.1(13)	17.3(11)	34.8(12)	-2.9(10)	17.9(10)	2.4(10)
C17	25.2(12)	24.5(12)	41.2(15)	10.6(10)	5.9(10)	7.6(10)
C18	18.3(10)	25.0(11)	26.2(11)	1.0(9)	2.9(9)	1.0(9)
N	25.0(13)	14.3(12)	19.6(12)	0	6.2(10)	0
O	24.6(8)	24.0(8)	29.4(8)	3.5(6)	11.4(8)	6.6(8)
F	16.7(3)	16.6(3)	16.0(3)	-0.2(2)	2.45(19)	0.1(2)
H	18.6(12)	21.1(13)	18.4(11)	1.5(9)	2.3(9)	-0.5(10)

Table 3. Bond Lengths in Å for 19a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.516(3)	C9	C10	1.384(3)
C1	N	1.401(2)	C10	C11	1.380(3)
C1	O	1.203(2)	C11	C12	1.388(3)
C2	C2'	1.545(3)	C13	C14	1.394(3)
C2	F	1.8677(18)	C15	C18	1.384(3)
C3	C9	1.387(2)	C15	F	1.806(2)
C3	C4	1.387(2)	C16	C15	1.387(3)
C3	N	1.435(3)	C15	C16	1.375(2)
C4	C5	1.389(3)	C16	C17	1.376(3)
C5	C6	1.381(2)	C17	C18	1.385(3)
C6	C6'	1.381(2)	N	C15	1.401(2)
C7	C8	1.394(3)	F	H	1.510(2)
C7	C12	1.397(3)			
C7	F	1.8097(18)			
C8	C9	1.384(2)			

^a1-3,+1,3/2-2

Table 4. Bond Angles in ° for 19a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N	C1	C2	107.91(13)	C8	C7	F	121.83(14)
O	C1	C2	126.51(14)	C12	C7	F	116.87(15)
O	C1	N	125.46(18)	C9	C8	C7	120.34(19)
C1	C2'	C2	103.62(9)	C10	C9	C8	119.76(19)
C1	C2	F	109.47(12)	C11	C10	C9	120.30(18)
C2'	C2'	F	111.36(16)	C10	C11	C12	120.40(19)
C4'	C3	C4	120.5(3)	C11	C12	C7	116.70(19)
C4	C3	N	119.77(13)	C14	C13	F	123.51(15)
C4	C3	N	119.77(13)	C18	C13	C14	118.79(18)
C5	C4	C5	119.12(19)	C19	C13	F	117.57(15)
C6	C5	C4	120.7(2)	C15	C14	C13	120.34(19)
C6'	C6	C5	119.5(3)	C16	C15	C14	120.2(2)
C8	C7	C12	119.30(17)	C15	C16	C17	120.1(2)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C16	C17	C18	120.3(2)	C7	F	H	113.12(18)
C17	C18	C19	120.25(19)	C8	F	C2	104.54(8)
C1	N	C1'	112.1(2)	C9	F	C7	106.48(8)
C2	N	C2	123.93(11)	C10	F	H	115.50(9)
C1'	N	C3	121.93(11)				
C2	F	H	110.34(9)				
C7	F	C2	105.82(9)				

$$^{\circ}1-X+Y, X/2-Z$$

Table 3: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 19a. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} .

Atom	x	y	z	U_{eq}
H2	6441	2005	7429	20
H4	5737	484	6580	35
H5	5749	2089	6590	37
H6	5000	2792	7500	29
H8	7852	3323	6297	26
H9	9550	1944	5584	23
H10	6834	1057	6685	34
H11	6415	576	4491	35
H12	4700	941	5209	27
H14	6619	3237	7070	26
H15	4524	4627	7013	31
H16	4625	3272	6300	33
H17	2780	4517	5655	36
H18	2839	3118	5716	28
HA	2427(7)	1619(5)	5630(5)	30
HB	2152(8)	1015(5)	6474(4)	30
HC	3014(3)	812(8)	6145(3)	20

Citations

Altomare, A.; Carrararo, G.; Giacovazzo, C.; Guagliardi, A., Completion and refinement of crystal structures with SHELX. *J. Appl. Cryst.* 1999, 26(5), 343-350.

O.V. Dolomanov and I. Bourhis and E. Sheldrick and J.A.K. Howard and H. Puschmann, Coot: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* (2009), 42, 339-341.

Sheldrick, G.M., A short history of SHELX. *Acta Cryst.* (2008), A64, 339-341.

Experimental Extended. A clear light yellow prism-shaped crystal with dimensions $0.17 \times 0.15 \times 0.10$ mm³ was mounted on a glass fibre with grease. Data were collected using a Nonius Kappa CCD diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at $T = 115$ K. Data were measured using ω - and ϕ -scans using MoK α radiation (λ -ray tube, 50 kV, 22 mA). The total number of runs and images was based on the strategy calculation the program Collect (Nonius BV, 1997–2000). The actually achieved resolution was $\theta = 27.44^\circ$. Cell parameters were retrieved using the SCALEPACK (Otwinowski, 1997) software and refined using DENZO (Otwinowski, 1997). Data reduction was performed using the DENZO software (Otwinowski, 1997) which corrects for Lorentz polarization. The final completeness is 99.40 out to 27.44° in θ . No absorption correction was performed. The absorption coefficient (M) of this material is 0.220. The structure was solved by Direct Methods with the SRS2 program (Altomari, 1990) structure solution program and refined by Least Squares using version of the ShelXL (Sheldrick, 2008). The structure was solved in the space group $P-1$ ($\# 2$). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

Table 6. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 21. U_{eq} is defined as $1/3$ of the trace of the orthogonalized U_{ij} .

Atom	x	y	z	U_{eq}
C1	1472(3)	1925(3)	7051(2)	20.0(5)
C2	2897(3)	1725(3)	6458(3)	20.5(5)
C3	2517(3)	-222(3)	6116(3)	22.4(5)
C4	1109(3)	48(3)	6718(3)	20.5(5)
C5	223(3)	1076(3)	6863(3)	24.2(6)
C6	717(3)	2174(3)	6409(3)	27.9(6)
C7	2100(3)	-2522(3)	5798(3)	30.5(6)
C8	3018(3)	-1360(3)	5649(3)	28.0(6)
C9	-1049(3)	3364(3)	8060(3)	19.8(5)
C10	-1436(3)	2496(3)	8462(3)	25.8(6)
C11	-2096(3)	2547(3)	8610(3)	27.6(6)
C12	-3996(3)	3629(3)	8763(3)	26.6(6)
C13	-3620(3)	4380(3)	7850(3)	27.2(6)
C14	-2159(3)	4261(3)	7009(3)	23.3(5)
C15	1834(3)	2817(3)	8206(3)	20.5(5)
C16	2594(3)	1302(3)	8996(3)	26.3(6)
C17	3370(3)	888(3)	11256(3)	30.7(6)
C18	3380(3)	1922(3)	11738(3)	28.7(6)
C19	2617(3)	3421(3)	10974(3)	28.6(6)
C20	1861(3)	3670(3)	9706(3)	25.7(6)
N1	3422(2)	715(3)	5999(2)	23.3(5)
N2	595(2)	1025(2)	7178(2)	20.6(5)
F	825.8(7)	3524.5(8)	7586.7(7)	21.50(16)
Cl	4049.9(6)	2888.7(7)	6276.3(7)	24.96(18)

Table 7: Anisotropic Displacement Parameters ($\times 10^3$) **21**. The anisotropic displacement factor exponent takes the form: $-2z^2[a^2 \times h^2 + b^2 \times k^2 + c^2 \times l^2]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	19.0(12)	22.1(12)	15.9(11)	-4.9(10)	-1.8(9)	-1.9(10)
C2	17.2(12)	24.6(13)	12.5(12)	-7.6(10)	0.7(9)	-4.7(10)
C3	20.9(12)	23.5(13)	19.0(12)	-8.4(10)	-1.2(9)	-0.5(10)
C4	20.8(12)	22.0(12)	14.1(11)	-5.8(10)	-1.5(9)	-1(1)
C5	23.4(13)	24.2(13)	19.2(12)	-7.4(11)	0.2(10)	-4.5(10)
C6	32.9(15)	23.5(13)	24.7(14)	-8.1(11)	3.4(11)	-6.4(11)
C7	38.7(15)	27.8(15)	29.5(15)	-16.8(12)	-1.9(12)	-1.0(12)
C8	25.5(14)	38.0(14)	27.9(14)	-15.9(12)	2.5(11)	0.0(11)
C9	19.2(12)	19.0(12)	20.4(12)	-8.0(10)	0.3(9)	-1.0(9)
C10	22.9(13)	28.4(14)	20.6(13)	-8.3(11)	-1.7(10)	-1.0(11)
C11	20.5(14)	31.0(15)	20.5(13)	-8.7(11)	3.4(10)	-0.8(11)
C12	19.2(13)	33.8(15)	18.4(14)	-16.8(12)	4.8(10)	-8.9(11)
C13	21.9(13)	32.3(15)	14.2(14)	-8.7(12)	-4.1(10)	-5.4(11)
C14	22.1(13)	26.8(13)	19.9(13)	-9.5(11)	8.9(10)	-6(1)
C15	16.1(11)	21.7(12)	21.7(12)	-8.2(10)	3.9(9)	-3.2(9)
C16	28.8(14)	34.2(15)	25.2(14)	-12.1(11)	-0.4(11)	-2.4(11)
C17	28.2(14)	28.7(15)	24.9(14)	-4.8(12)	3.8(11)	1.7(11)
C18	20.8(13)	45.1(17)	21.6(13)	-15.3(13)	-0.5(10)	-0.0(12)
C19	26.3(14)	36.3(16)	15.3(15)	-22.8(13)	6.7(11)	-10.6(12)
C20	22.4(13)	23.8(13)	29.7(14)	-12.2(12)	2.5(10)	-3.9(10)
N1	20.2(10)	27.5(12)	20.0(11)	-10.4(9)	1.7(8)	-2.6(9)
N2	19.6(10)	23.8(11)	18.3(10)	-8.4(9)	0.5(8)	-2.9(8)
F	18.8(3)	24.8(4)	19.7(3)	-18.3(3)	0.1(2)	-0.6(3)
O	18.8(3)	28.0(3)	26.7(3)	-12.1(3)	2.7(2)	-6.1(3)

Table 8: Bond Lengths in Å for **21**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.453(3)	C9	C14	1.394(3)
C1	N2	1.312(2)	C9	F	1.622(2)
C1	F	1.594(2)	C10	C11	1.385(4)
C2	N1	1.298(2)	C11	C12	1.379(4)
C2	Cl	1.761(3)	C12	C13	1.394(4)
C3	C4	1.418(3)	C13	C14	1.381(4)
C3	Cl	1.814(4)	C15	C16	1.396(4)
C3	N1	1.374(2)	C15	C20	1.385(4)
C4	C5	1.412(4)	C15	F	1.638(3)
C4	N2	1.370(2)	C16	C17	1.394(4)
C5	C6	1.366(4)	C17	C18	1.378(4)
C6	C7	1.419(4)	C18	C19	1.382(4)
C7	C8	1.372(4)	C19	C20	1.387(4)
C9	C19	1.391(3)			

Table 9: Bond Angles in ° for **21**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	F	110.66(19)	C6	C5	C4	126.0(2)
N2	C1	C2	119.5(2)	C5	C6	C7	120.8(3)
N2	C1	F	120.78(18)	C6	C7	C8	120.5(3)
C1	C2	C3	118.4(2)	C7	C8	C9	119.5(2)
N1	C2	C3	125.1(2)	C10	C9	C14	118.8(2)
C9	C2	C3	114.54(18)	C10	C9	F	124.29(18)
C9	C2	C4	120.1(2)	C16	C9	F	116.74(18)
N1	C2	C4	120.5(2)	C11	C10	C9	120.4(2)
N1	C2	C8	119.4(2)	C12	C11	C10	120.3(2)
C5	C4	C3	116.2(2)	C11	C12	C13	119.8(2)
N2	C4	C3	121.2(2)	C14	C13	C12	119.8(2)
N2	C4	C5	119.5(2)	C13	C14	C9	120.9(2)

Atom1	Atom2	Atom3	Angle/°	Atom1	Atom2	Atom3	Angle/°
C16	C15	F	123.8(2)	C19	C20	C15	120.8(2)
C20	C19	C16	118.7(2)	C2	N1	C1	115.8(2)
C20	C15	F	117.51(19)	C1	N2	C4	117.9(2)
C17	C16	C15	120.1(3)	C9	F	C1	102.35(11)
C18	C17	C16	120.5(3)	C9	F	C15	103.87(11)
C17	C18	C19	119.9(2)	C15	F	C1	101.91(11)
C18	C19	C20	120.1(3)				

Table 10: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 21. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} .

Atom	x	y	z	U_{eq}
H5	-897	-897	7267	29
H6	326	-2831	6501	34
H7	2444	-3075	5497	37
H8	3920	-1457	5344	34
H10	-707	1978	10171	31
H11	-3158	1977	10754	33
H12	-4579	3465	8959	32
H13	-4352	4898	6684	35
H14	-1913	4841	6067	29
H16	2583	581	9674	32
H17	3885	-140	11765	37
H18	3930	1625	12501	34
H19	2811	4124	11310	33
H20	1367	4085	9187	31

Citations

Altomare, A.; Cammino, G.; Giacovazzo, C.; Guagliardi, A. Completion and refinement of crystal structures with SIR92. *J. Appl. Cryst.* 1993, 26 (3), 343-350.

©K. Dolomanov and L.J. Bourhis and R.J. Gilhe and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* (2009), 42, 339-341.

Sheldrick, G.M. A short history of SHELX. *Acta Cryst.* (2004), A60, 3-14.