Electronic Supporting Material

π-Excess σ^2P ligands: Synthesis of biaryl-type 1,3-benzazaphosphole hybrid ligands and formation of P^P'-M(CO)$_4$ chelate complexes

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1. Detection of 2-thiophenmethanol as side product in the synthesis of 2e
2. ^{31}P and ^{13}C NMR spectra of new compounds
3. Tables with atomic coordinates, bond lengths and angles of 9a

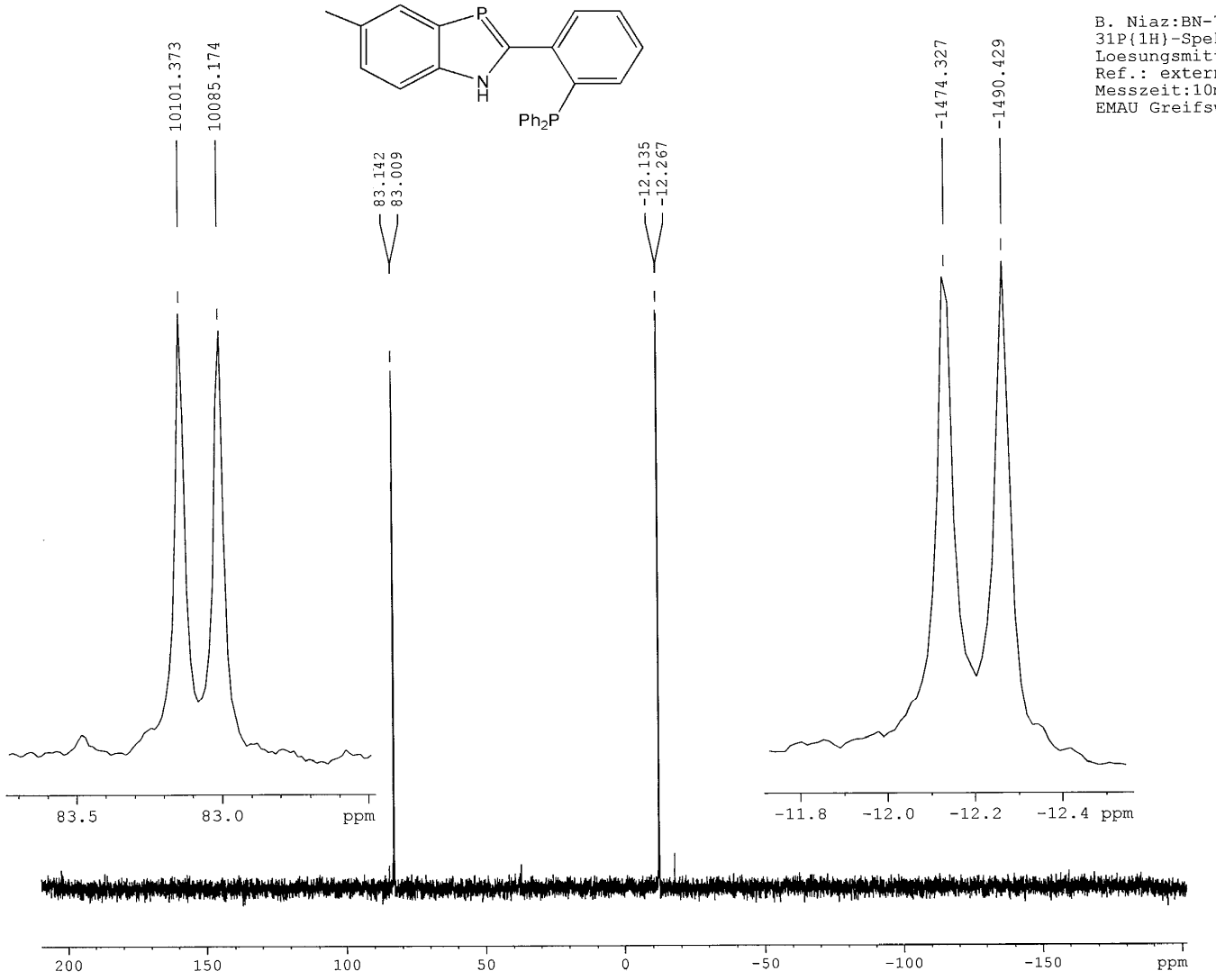
1. Detection of 2-thiophenmethanol as side product in the synthesis of 2e.

After refluxing 2-phosphanyl-4-methylaniline (**1**) and thiophen-2-carboxaldehyde in xylene in the presence of *p*-toluene sulfonic acid the solvent and volatiles were condensed in vacuum into a cooling trap. In the condensate a small amount of 2-thiophenmethanol was detected by GC-MS measurements of the condensate and a reference sample, synthesized according to ref. [1]. The assignment was confirmed additionally by good accordance of the characteristic mass spectra with those of the library spectrum. We thank P. Gierok and Prof. Dr. M. Lalk (Institut für Biochemie, Ernst-Moritz-Arndt-Universität Greifswald) for the measurements, using GC Agilent 6890N, MS Agilent 5973, Software MS-Chemstation, inlet temperature 280°C, oven 70°C 1min, 1.5°C/min to 76°C, 5°C/min to 330°C for 10min; 1mL/min, column DB-5ms from Agilent (30m x i.d. 0.25mm x 0.25µm film).

[1] M. D'Auria, A. De Mico, F. D'Onofrio, G. Piancatelli, *J. Org. Chem.* **1987**, *52*, 5243-5247.

1. NMR-Spectra

^{31}P NMR spectrum **2a**.



B. Niaz:BN-71e
31P{1H}-Spektrum
Loesungsmittel: CDCl3
Ref.: extern, H3PO4 = 0.0 ppm (+/- 0.3)
Messzeit:10min.
EMAU Greifswald - Avance II - 300

Current Data Parameters

NAME	NI_BN-71e
EXPNO	31
PROCNO	1

F2 - Acquisition Parameters

Date_	20100719
Time	9.04
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PROBHD	5 mm PABBO BB-
PULPROG	zqpg30
TD	32768
SOLVENT	CDCl3
NS	256
DS	4
SWH	50000.000 Hz
FIDRES	1.525879 Hz
AQ	0.3277300 sec
RG	23100
DW	10.000 usec
DE	6.00 usec
TE	299.4 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1

======== CHANNEL f1 ========

NUC1	31P
P1	10.25 usec
PL1	2.00 dB
SFO1	121.4953510 MHz

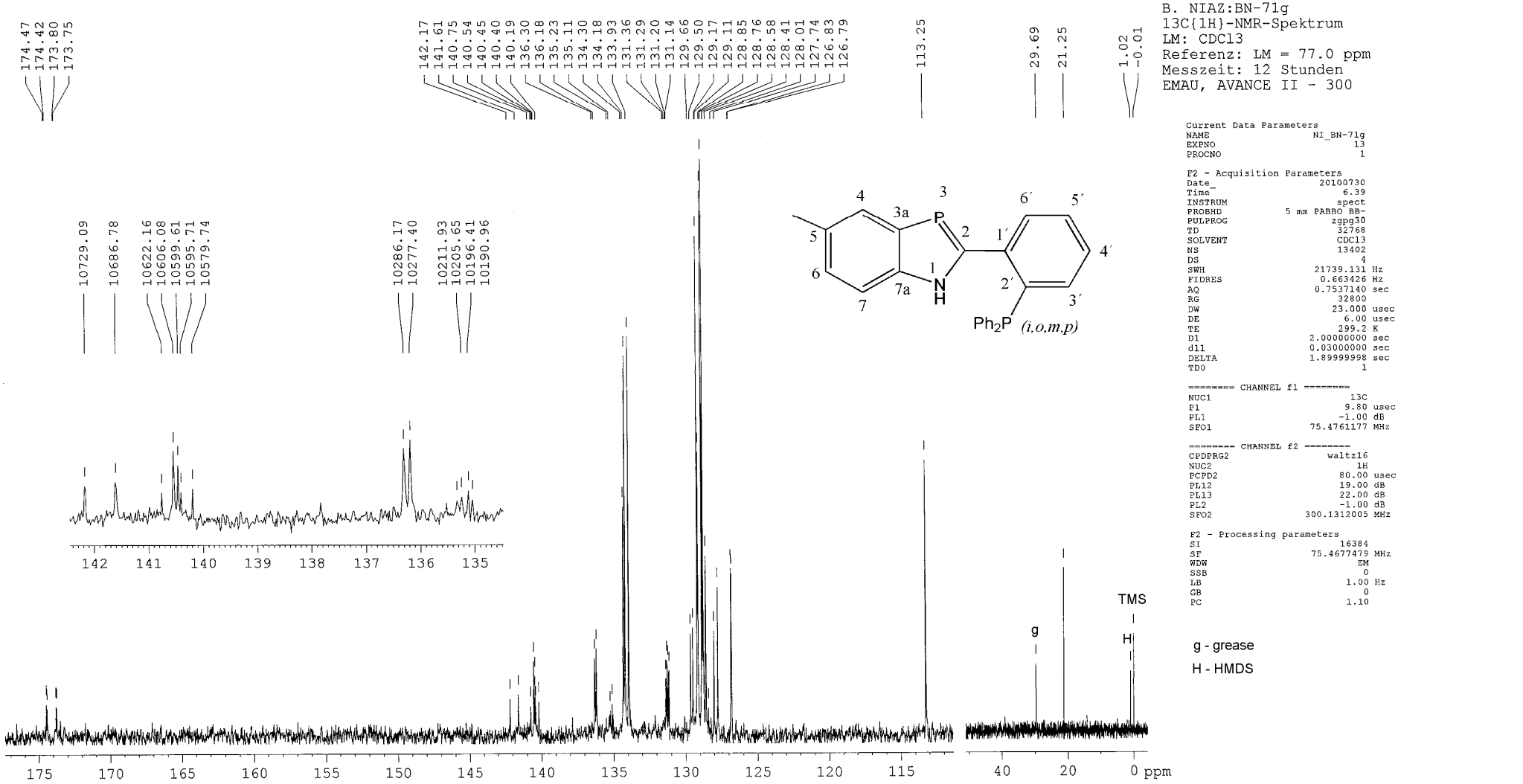
======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	19.00 dB
PL13	22.00 dB
PL2	-1.00 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

SI	32768
SF	121.4948510 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

^{13}C NMR spectrum (aryl and methyl range) of **2a**.



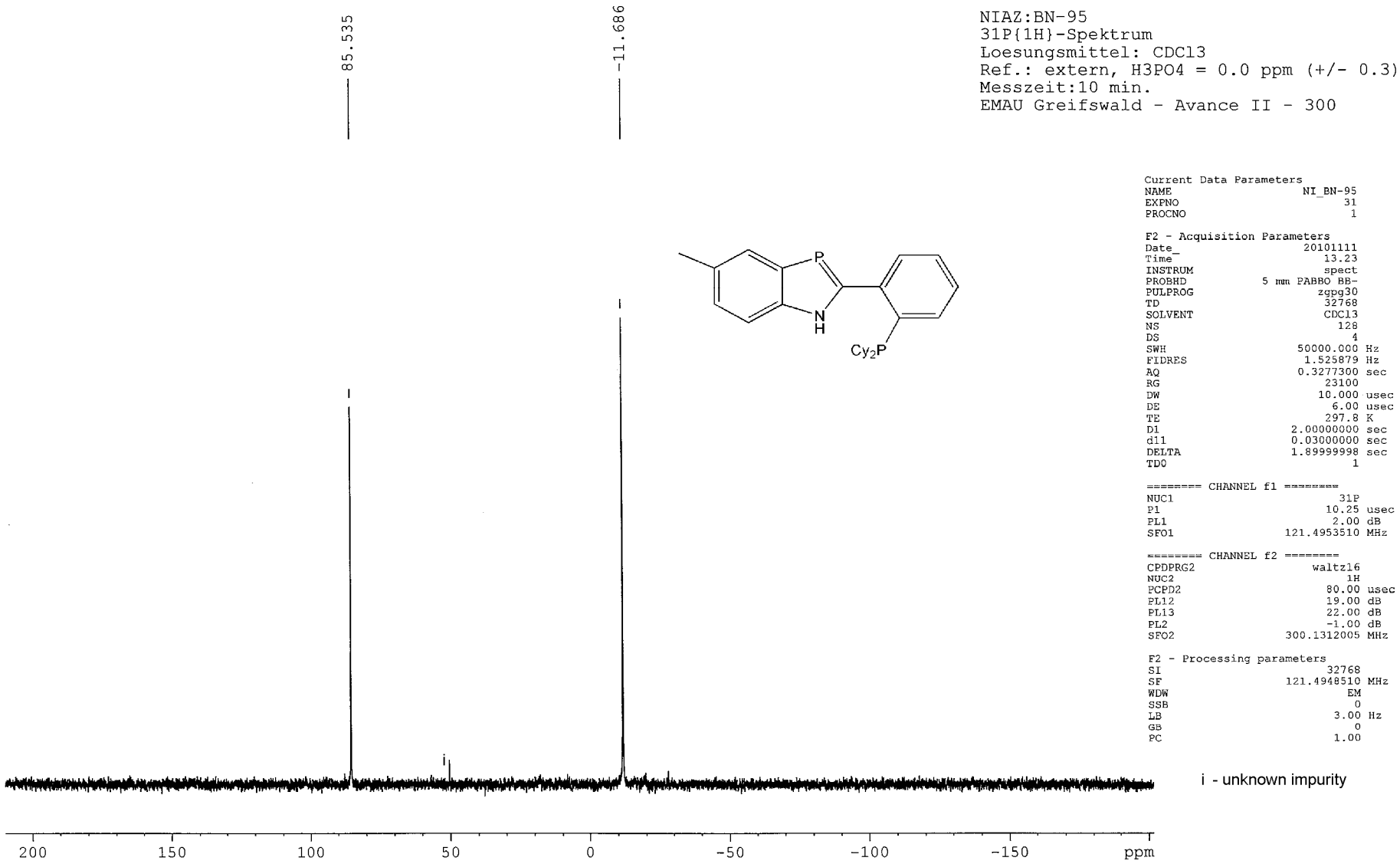
B. NIAZ:BN-71g
13C{1H}-NMR-Spektrum
LM: CDCl3
Referenz: LM = 77.0 ppm
Messzeit: 12 Stunden
EMAU, AVANCE II - 300

Current Data Parameters	
NAME	NI_BN-71g
EXPNO	13
PROCNO	1
F2 - Acquisition Parameters	
Date_	20100730
Time	6.39
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	13402
DS	4
SWH	21739.131 Hz
FIDRES	0.663426 Hz
AQ	0.7537140 sec
RG	32800
DW	23.000 usec
DE	6.00 usec
TE	299.2 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.80 usec
PL1	-1.00 dB
SFO1	75.4761177 MHz
-------- CHANNEL f2 --------	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	19.00 dB
PL13	22.00 dB
PL2	-1.00 dB
SFO2	300.1312005 MHz
F2 - Processing parameters	
SI	16384
SF	75.4677479 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.10

g - grease

H - HMDS

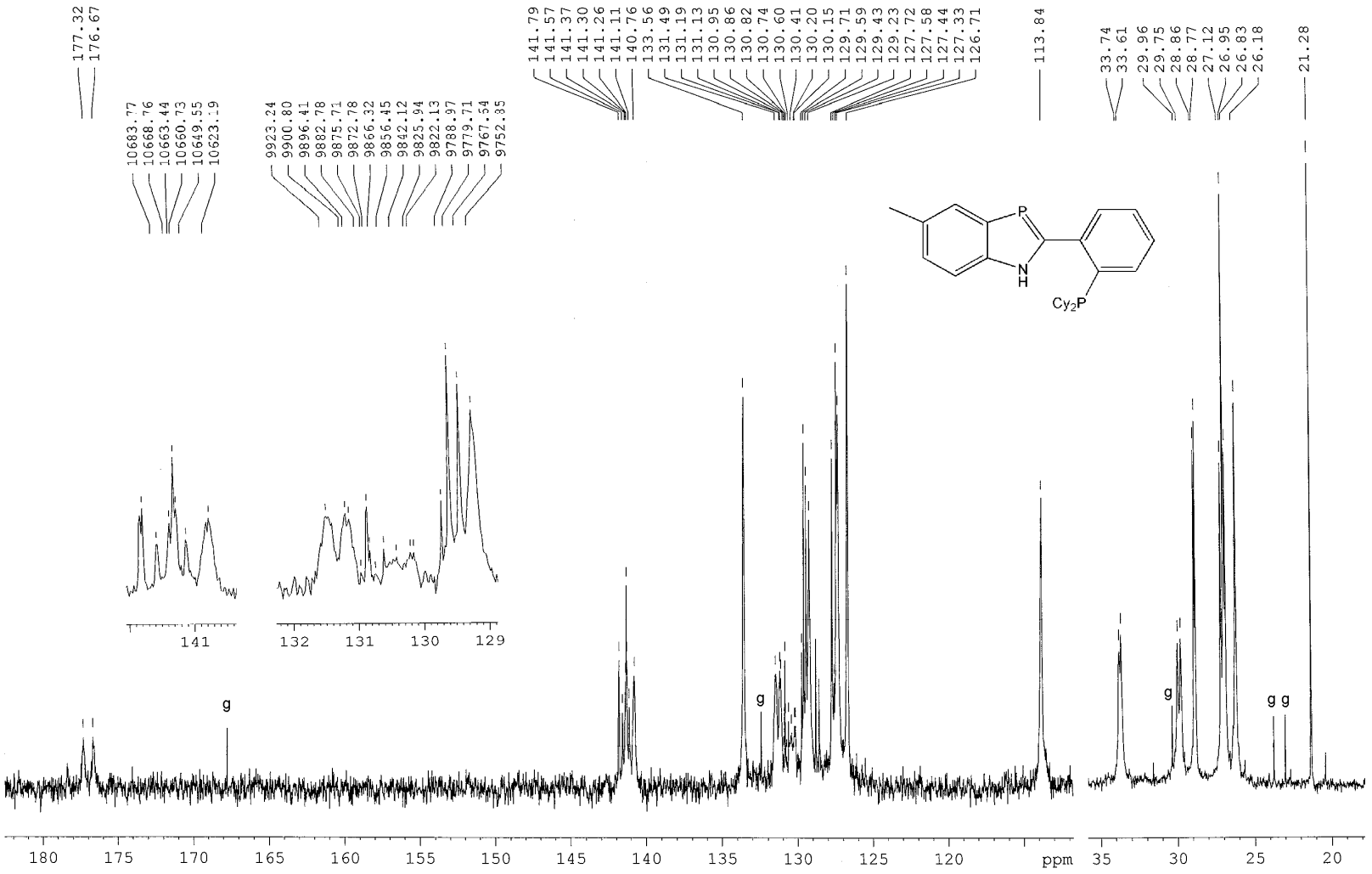
^{31}P NMR spectrum of **2b**.



Current Data Parameters	
NAME	NI_BN-95
EXPNO	31
PROCNO	1
F2 - Acquisition Parameters	
Date_	20101111
Time	13.23
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	128
DS	4
SWH	50000.000 Hz
FIDRES	1.525879 Hz
AQ	0.3277300 sec
RG	23100
DW	10.000 usec
DE	6.00 usec
TE	297.8 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	31P
P1	10.25 usec
PL1	2.00 dB
SFO1	121.4953510 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	19.00 dB
PL13	22.00 dB
PL2	-1.00 dB
SFO2	300.1312005 MHz
F2 - Processing parameters	
SI	32768
SF	121.4948510 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.00

i - unknown impurity

^{13}C NMR spectrum of **2b**.

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Niaz:BN-95c
13C{1H}-NMR-Spektrum
LM:CDCl3
Referenz:LM=77,0 ppm
Messzeit: 2,5 d
EMAU, AVANCE II - 300

Current Data Parameters
NAME                  NI_BN-95c
EXPNO                        13
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20101129
Time                       8.50
INSTRUM                   spect
PROBHD  5 mm PABBO BB-
PULPROG                 zgpg30
TD                        32768
SOLVENT                   CDCl3
NS                        71304
DS                            4
SWH                  21739.131 Hz
FIDRES                0.663426 Hz
AQ                    0.7537140 sec
RG                        32800
DW                       23.000 usec
DE                        6.00 usec
TE                       297.4 K
D1                    2.00000000 sec
d11                   0.03000000 sec
DELTA                 1.89999998 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        13C
P1                         9.80 usec
PL1                       -1.00 dB
SFO1                75.4761177 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                     80.00 usec
PL12                      19.00 dB
PL13                      22.00 dB
PL2                       -1.00 dB
SFO2               300.1312005 MHz

F2 - Processing parameters
SI                        16384
SF                 75.4677492 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         0.30
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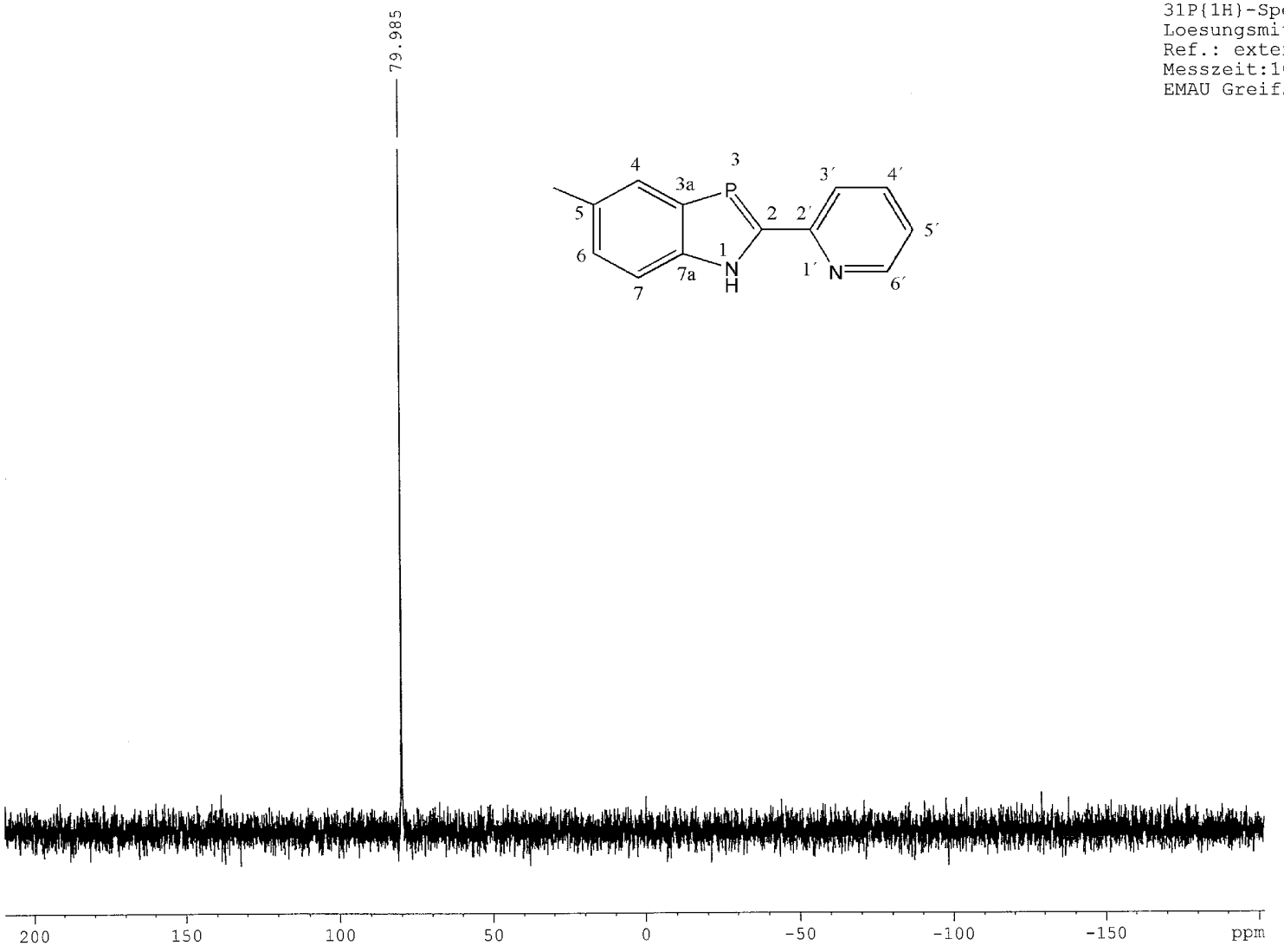
g - phthalate grease contamination

^{31}P NMR spectrum of **2c.**

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NIAZ:BN-61
31P{1H}-Spektrum
Loesungsmittel: CDCl3
Ref.: extern, H3PO4 = 0.0 ppm (+/-0.3)
Messzeit:10min.
EMAU Greifswald - Avance II - 300
```

```
Current Data Parameters
NAME                   NI_BN-61
EXPNO                        31
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20100114
Time                       9.11
INSTRUM                   spect
PROBHD  5 mm PABBO BB-
PULPROG                 zgpg30
TD                       32768
SOLVENT                  CDCl3
NS                         256
DS                           4
SWH                  50000.000 Hz
FIDRES                1.525879 Hz
AQ                   0.3277300 sec
RG                       23100
DW                    10.000 usec
DE                     6.00 usec
TE                     297.6 K
D1                   2.00000000 sec
d11                  0.03000000 sec
DELTA                1.89999998 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       31P
P1                    10.25 usec
PL1                    2.00 dB
SFO1                121.4953510 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 80.00 usec
PL12                  19.00 dB
PL13                  22.00 dB
PL2                   -1.00 dB
SFO2                300.1312005 MHz

F2 - Processing parameters
SI                       32768
SF                  121.4948510 MHz
WDW                         EM
SSB                          0
LB                    3.00 Hz
GB                           0
PC                    1.20
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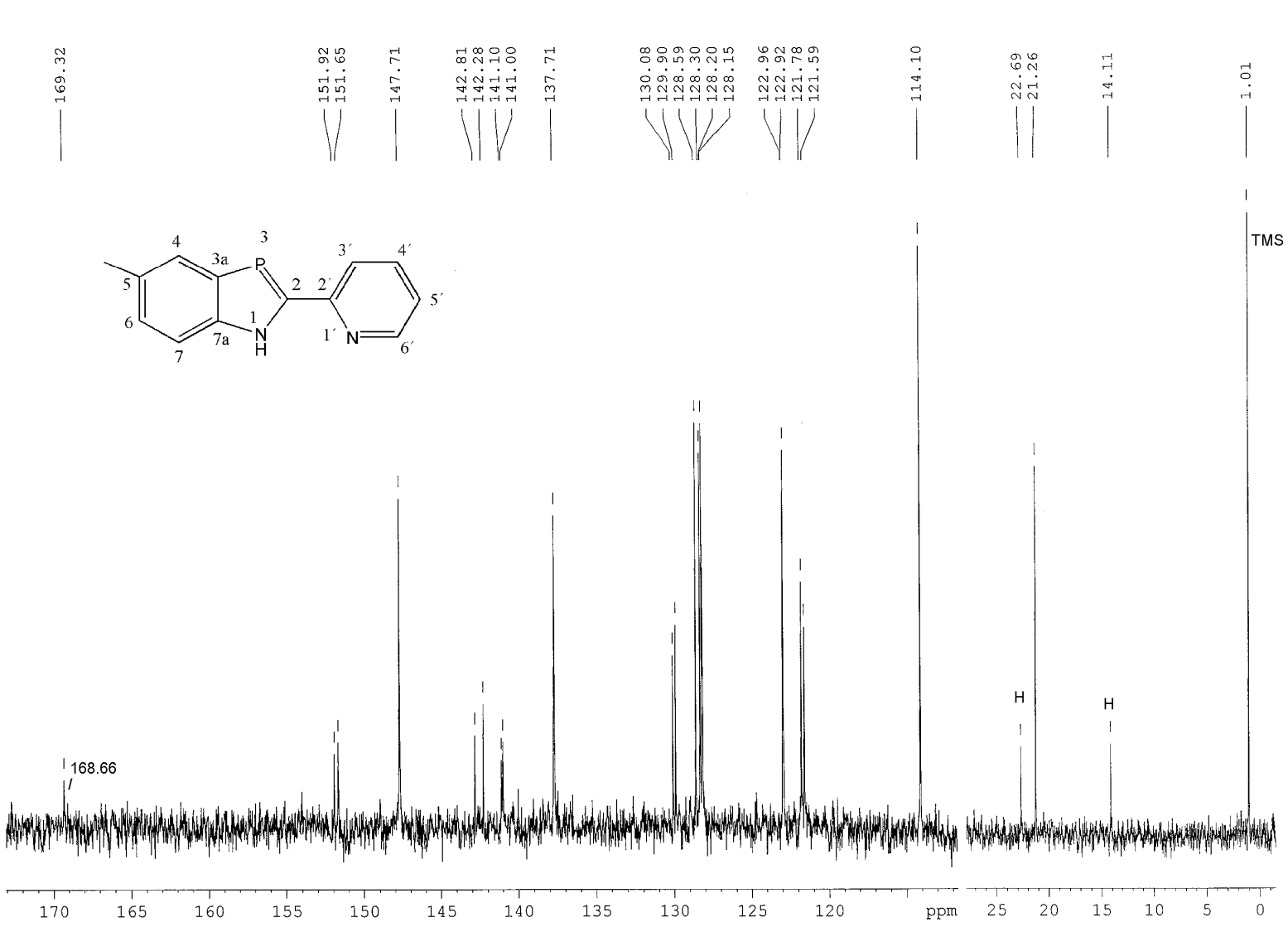
^{13}C NMR spectrum of **2c.**



NIAZ:BN-61
13C{1H}-NMR-Spektrum
LM:CDCl3
Referenz::LM=77ppm
Messzeit: 48 h
EMAU, AVANCE II - 300

Current Data Parameters

NAME	NI_BN-61
EXPNO	13
PROCNO	1

F2 - Acquisition Parameters

Date_	20100118
Time	9.04
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	58069
DS	4
SWH	21739.131 Hz
FIDRES	0.663426 Hz
AQ	0.7537140 sec
RG	32800
DW	23.000 usec
DE	6.00 usec
TE	297.0 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1

======== CHANNEL f1 ========

NUC1	13C
P1	9.80 usec
PL1	-1.00 dB
SFO1	75.4761177 MHz

======== CHANNEL f2 ========

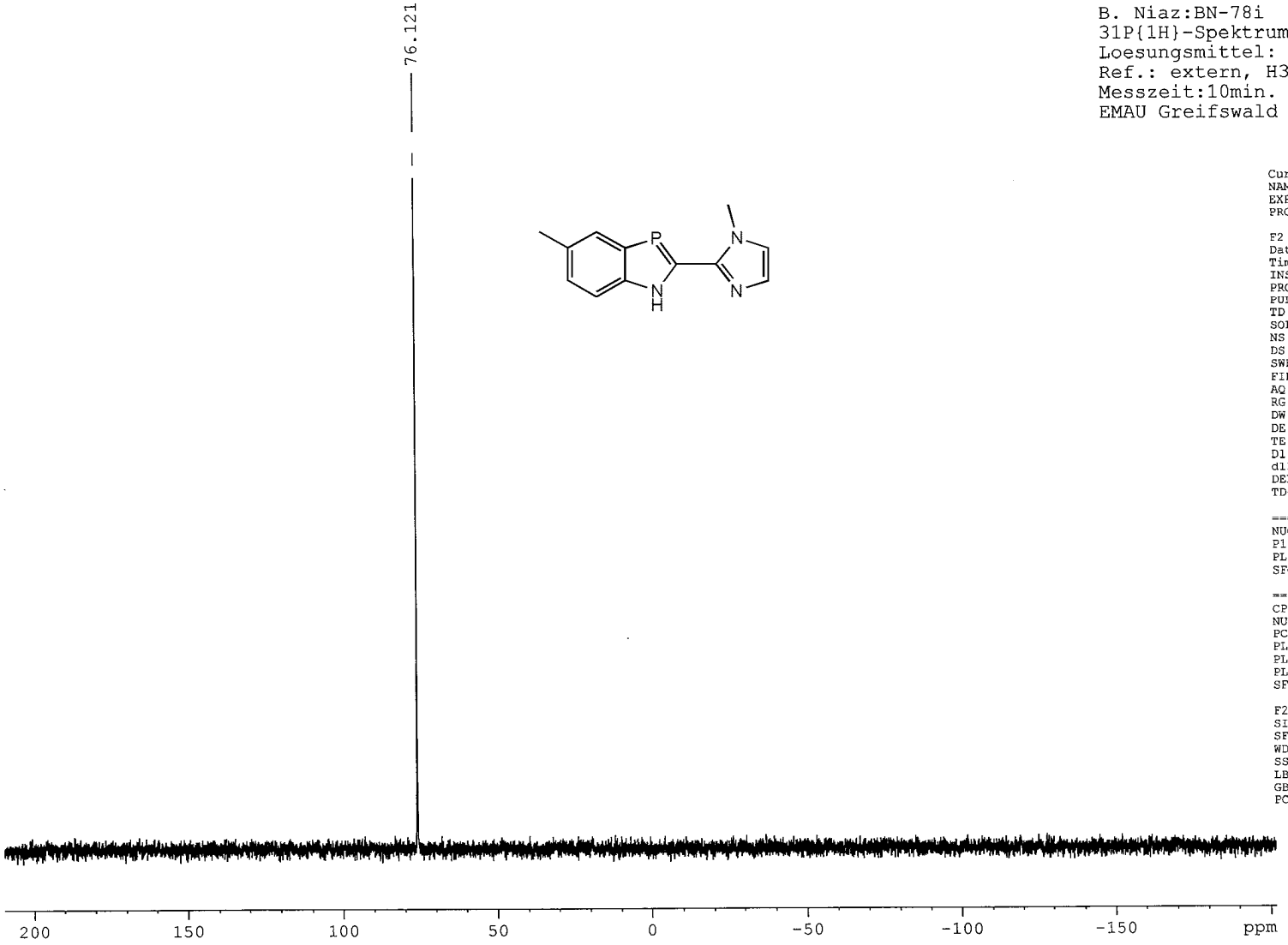
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	19.00 dB
PL13	22.00 dB
PL2	-1.00 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

SI	16384
SF	75.4677479 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.20

H - n-Hexane

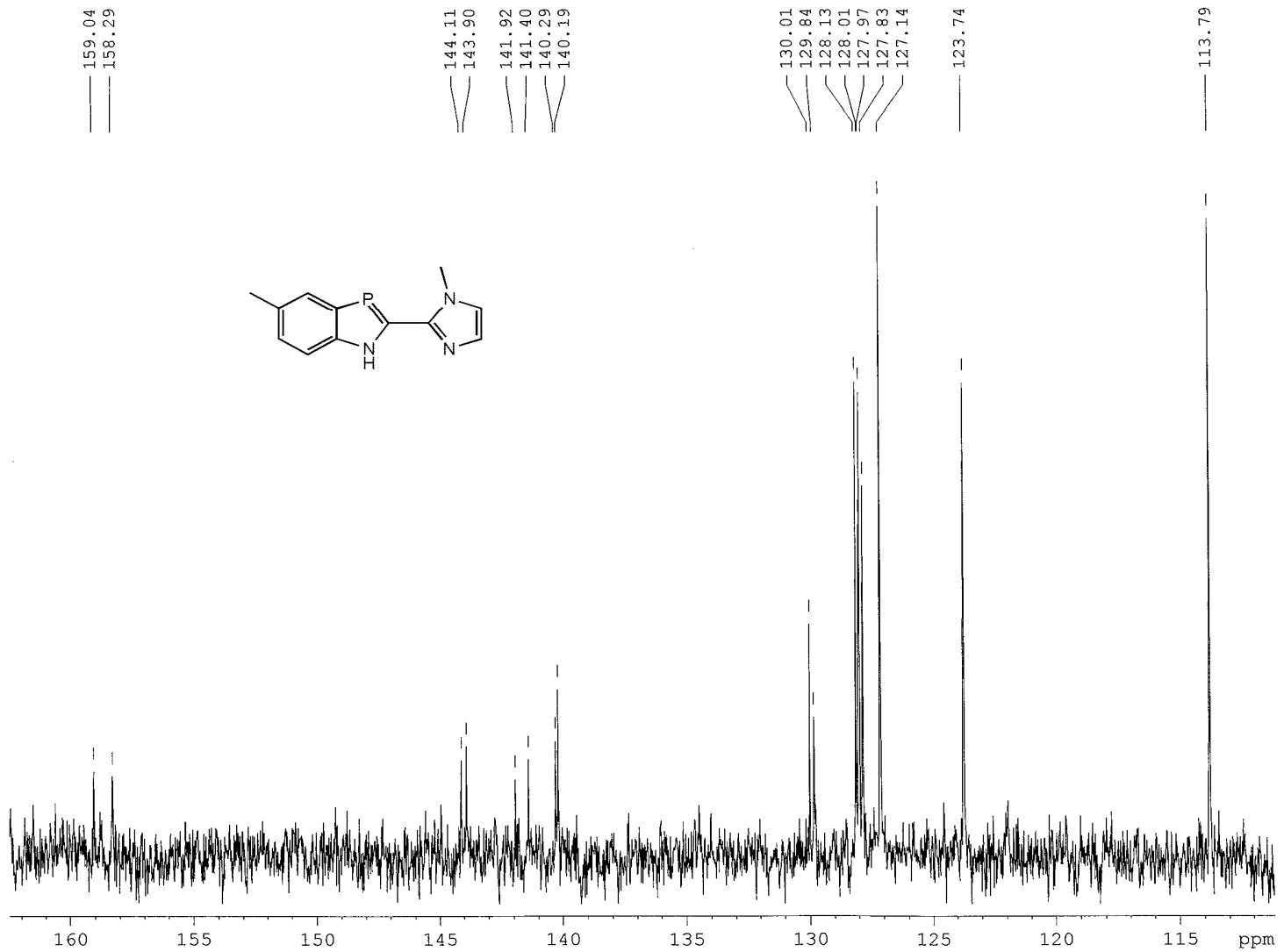
^{31}P NMR spectrum of **2d**.



B. Niaz:BN-78i
31P{1H}-Spektrum
Loesungsmittel: CDCl3
Ref.: extern, H3PO4 = 0.0 ppm (+/- 0.3)
Messzeit:10min.
EMAU Greifswald - Avance II - 300

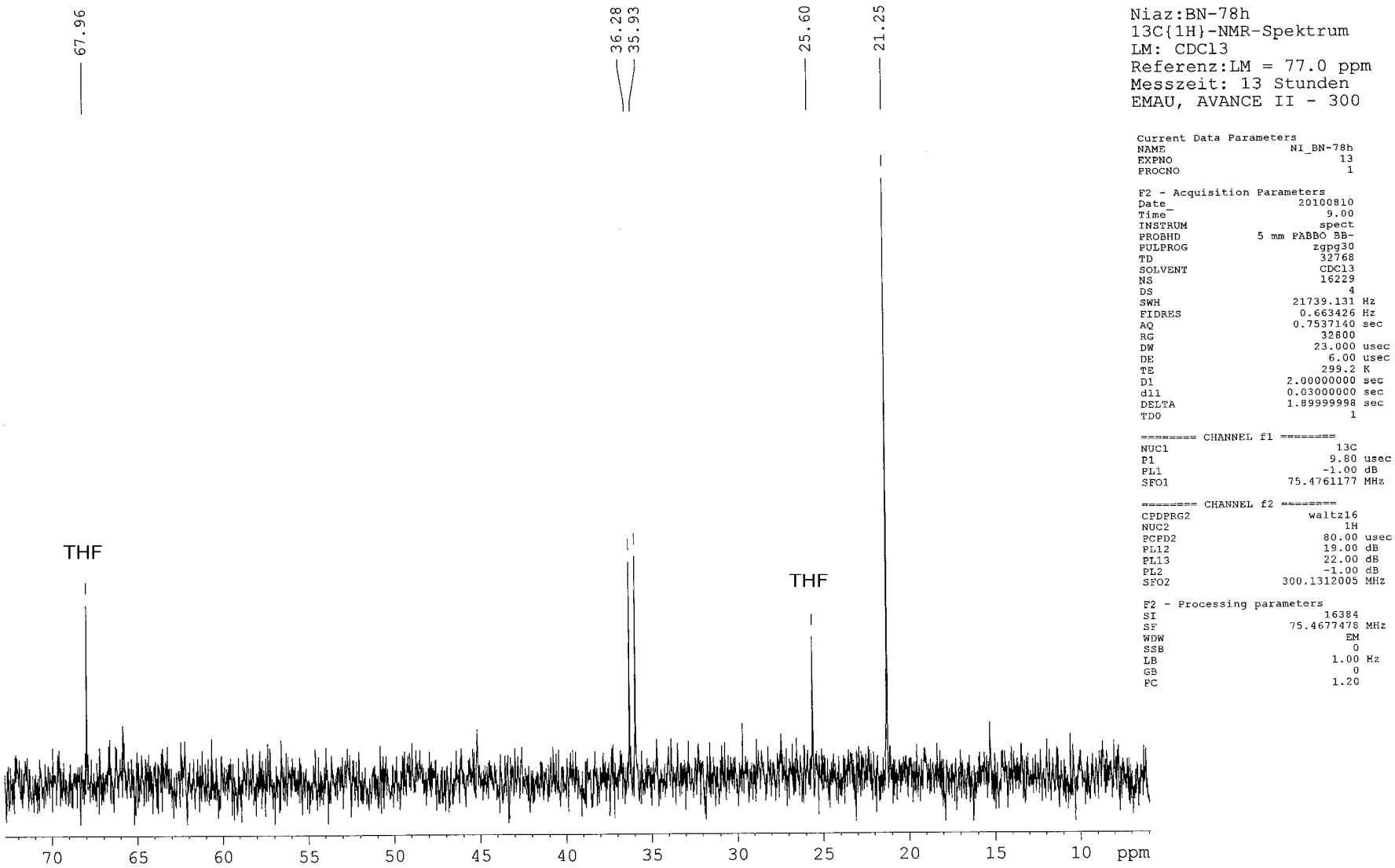
Current Data Parameters	
NAME	NI_BN-78i
EXPNO	31
PROCNO	1
F2 - Acquisition Parameters	
Date_	20100806
Time	9.51
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	256
DS	4
SWH	50000.000 Hz
FIDRES	1.525879 Hz
AQ	0.3277300 sec
RG	23100
DW	10.000 usec
DE	6.00 usec
TE	299.4 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	31P
P1	10.25 usec
PL1	2.00 dB
SFO1	121.4953510 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	19.00 dB
PL13	22.00 dB
PL2	-1.00 dB
SFO2	300.1312005 MHz
F2 - Processing parameters	
SI	32768
SF	121.4948510 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

^{13}C NMR spectrum (aryl range) of **2d**.




```
Niaz:BN-78h
13C{1H}-NMR-Spektrum
LM: CDCl3
Referenz:LM = 77.0 ppm
Messzeit: 13 Stunden
EMAU, AVANCE II - 300

Current Data Parameters
NAME                      NI_BN-78h
EXPNO                            13
PROCNO                            1

F2 - Acquisition Parameters
Date_                      20100810
Time                           9.00
INSTRUM                       spect
PROBHD     5 mm PABBO BB-
PULPROG                     zgpg30
TD                           32768
SOLVENT                      CDCl3
NS                           16229
DS                               4
SWH                      21739.131 Hz
FIDRES                    0.663426 Hz
AQ                        0.7537140 sec
RG                           32800
DW                          23.000 usec
DE                           6.00 usec
TE                          299.2 K
D1                     2.00000000 sec
d11                    0.03000000 sec
DELTA                  1.89999998 sec
TD0                              1

======== CHANNEL f1 ========
NUC1                           13C
P1                            9.80 usec
PL1                          -1.00 dB
SFO1                  75.4761177 MHz

======== CHANNEL f2 ========
CPDPRG2                   waltz16
NUC2                           1H
PCPD2                        80.00 usec
PL12                         19.00 dB
PL13                         22.00 dB
PL2                          -1.00 dB
SFO2                 300.1312005 MHz

F2 - Processing parameters
SI                           16384
SF                    75.4677478 MHz
WDW                            EM
SSB                             0
LB                           1.00 Hz
GB                              0
PC                           1.20
```

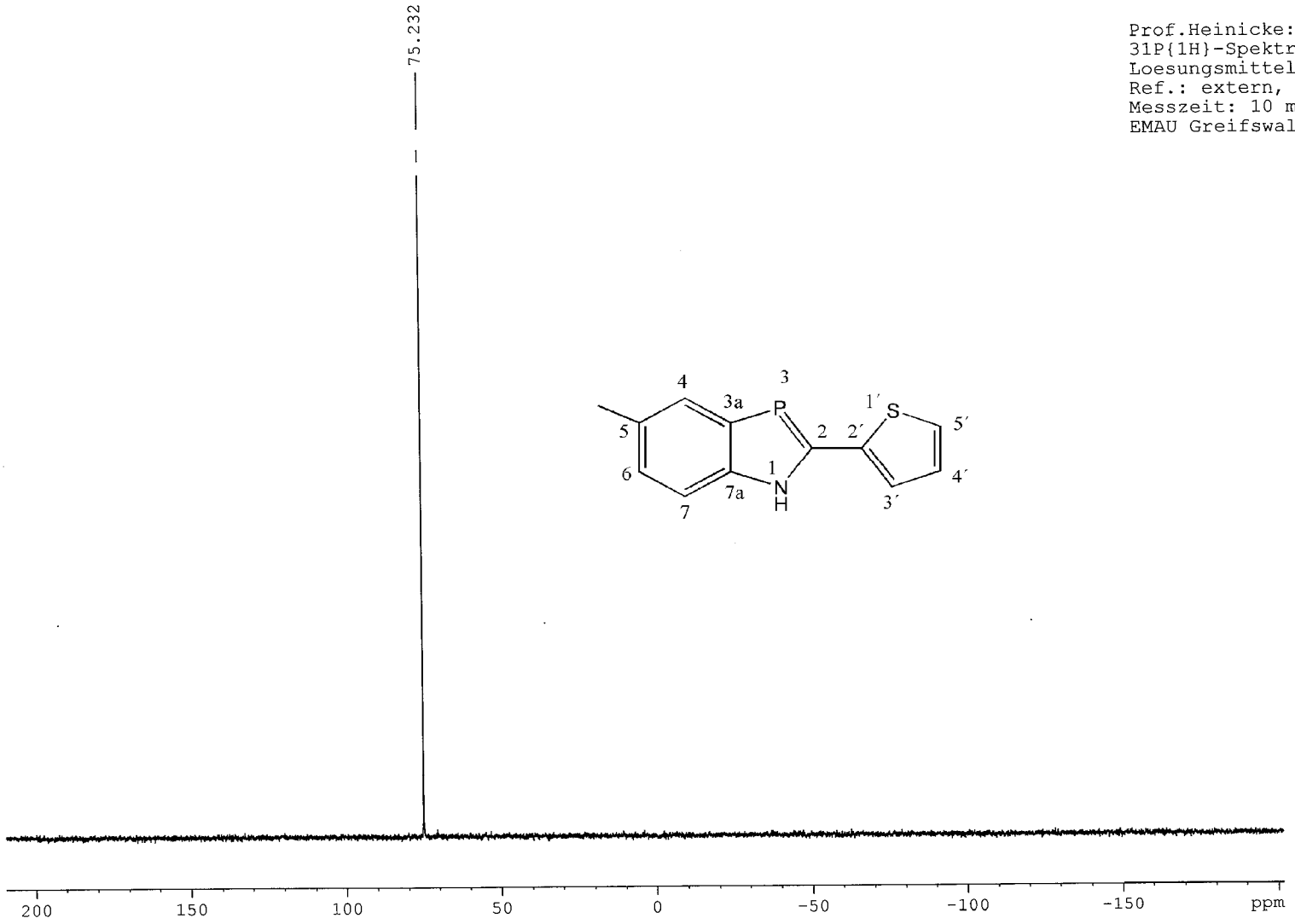
^{13}C NMR spectrum (alkyl range) of **2d**.



Niaz:BN-78h
13C{1H}-NMR-Spektrum
LM: CDCl3
Referenz:LM = 77.0 ppm
Messzeit: 13 Stunden
EMAU, AVANCE II - 300

Current Data Parameters	
NAME	NI_BN-78h
EXPNO	13
PROCNO	1
F2 - Acquisition Parameters	
Date_	20100810
Time	9.00
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	16229
DS	4
SWH	21739.131 Hz
FIDRES	0.663426 Hz
AQ	0.7537140 sec
RG	32800
DW	23.000 usec
DE	6.00 usec
TE	299.2 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.80 usec
PL1	-1.00 dB
SFO1	75.4761177 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	19.00 dB
PL13	22.00 dB
PL2	-1.00 dB
SFO2	300.1312005 MHz
F2 - Processing parameters	
SI	16384
SF	75.4677478 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.20

^{31}P NMR spectrum of **2e**.



Prof.Heinicke: BN103SC4
31P{1H}-Spektrum
Loesungsmittel: CDCl3
Ref.: extern, H3PO4 = 0.0 ppm (+/- 0.3)
Messzeit: 10 min.
EMAU Greifswald - Avance II - 300

Current Data Parameters

NAME	HE_BN103SC4
EXPNO	31
PROCNO	1

F2 - Acquisition Parameters

Date_	20110826
Time	8.02
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PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	256
DS	4
SWH	50000.000 Hz
FIDRES	1.525879 Hz
AQ	0.3277300 sec
RG	23100
DW	10.000 usec
DE	6.00 usec
TE	296.9 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1

======== CHANNEL f1 ========

NUC1	31P
P1	10.25 usec
PL1	2.00 dB
SFO1	121.4953510 MHz

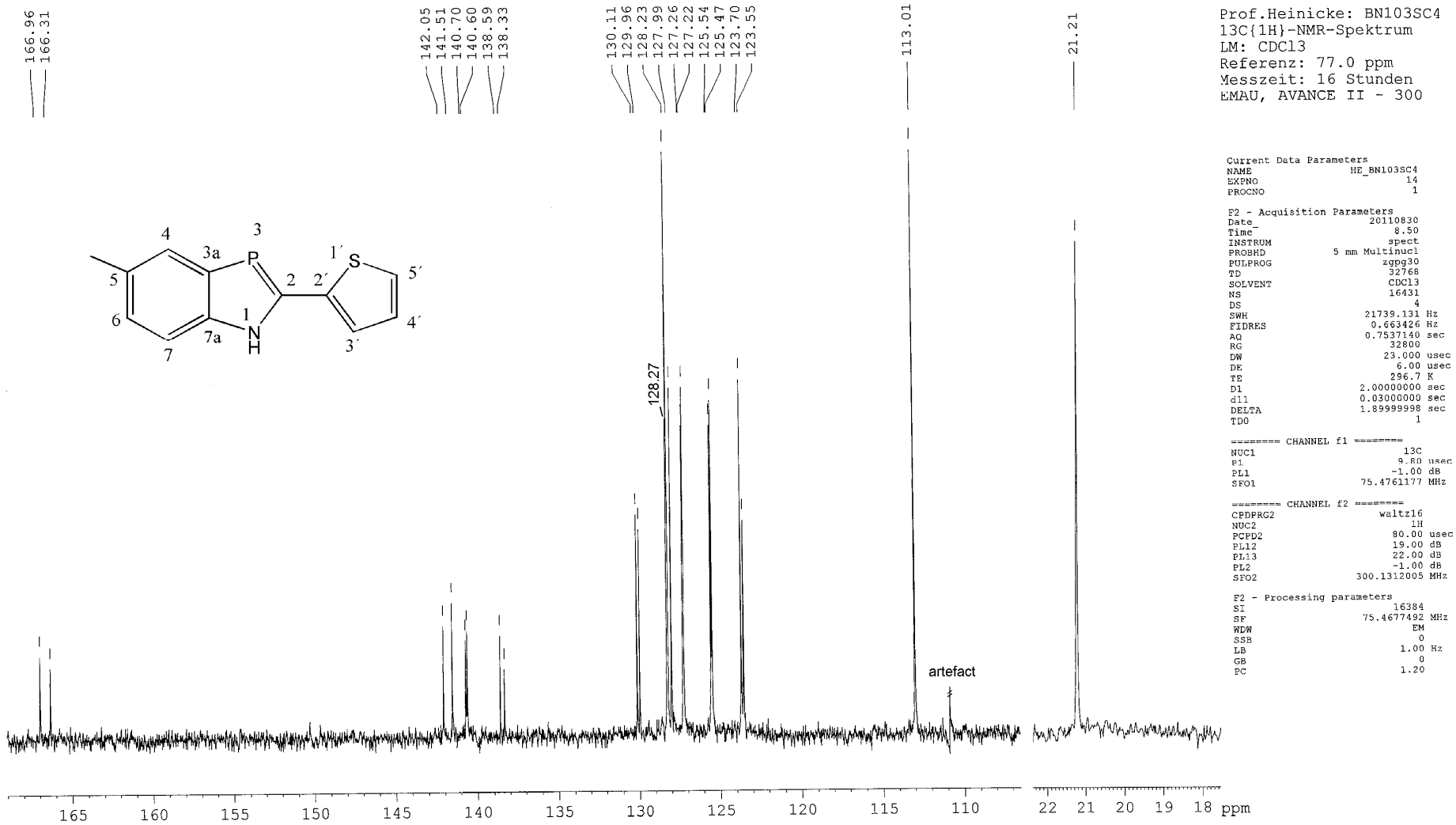
======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	19.00 dB
PL13	22.00 dB
PL2	-1.00 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

SI	32768
SF	121.4948510 MHz
WDW	EM
SSB	0
LB	4.00 Hz
GB	0
PC	1.40

^{13}C NMR spectrum (aryl and methyl range) of **2e**.



Prof.Heinicke: BN103SC4
13C{1H}-NMR-Spektrum
LM: CDCl3
Referenz: 77.0 ppm
Messzeit: 16 Stunden
EMAU, AVANCE II - 300

Current Data Parameters

NAME	HE_BN103SC4
EXPNO	14
PROCNO	1

F2 - Acquisition Parameters

Date_	20110830
Time	8.50
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	16431
DS	4
SWH	21739.131 Hz
FIDRES	0.663426 Hz
AQ	0.7537140 sec
RG	32800
DW	23.000 usec
DE	6.00 usec
TE	296.7 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1

======== CHANNEL f1 ========

NUC1	13C
P1	9.80 usec
PL1	-1.00 dB
SFO1	75.4761177 MHz

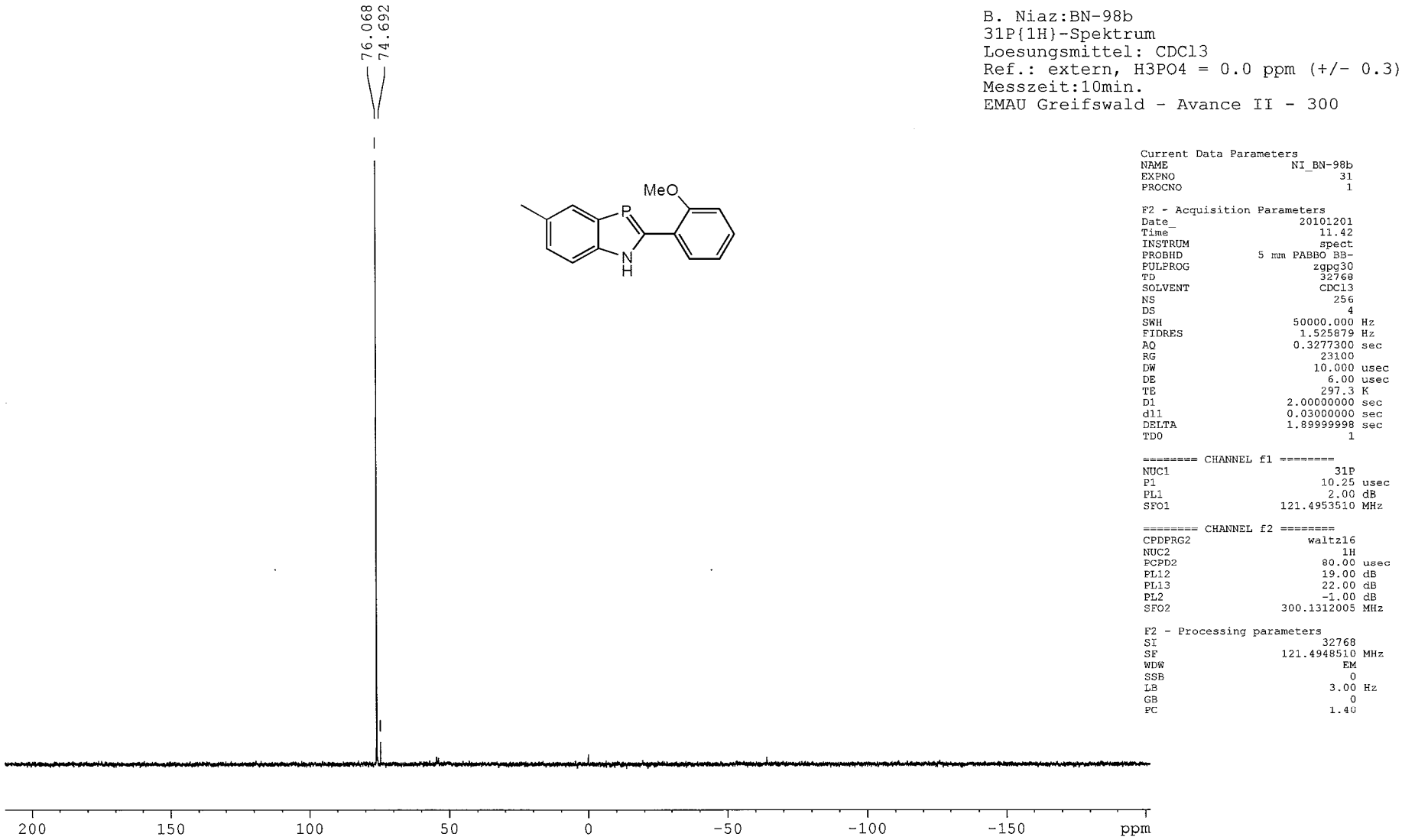
======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	19.00 dB
PL13	22.00 dB
PL2	-1.00 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

SI	16384
SF	75.4677492 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.20

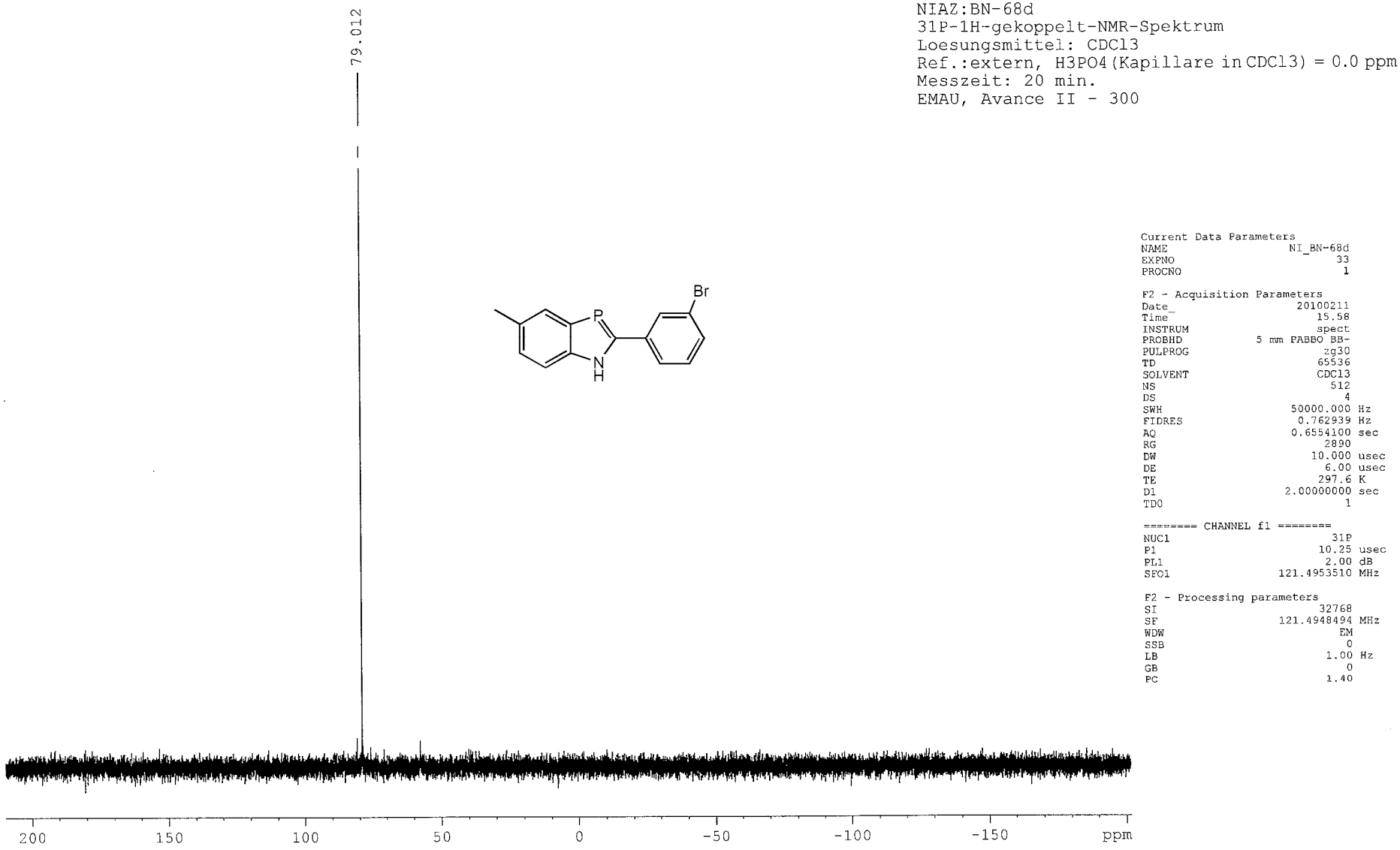
^{31}P NMR spectrum of **2f**.



B. Niaz:BN-98b
31P{1H}-Spektrum
Loesungsmittel: CDCl3
Ref.: extern, H3PO4 = 0.0 ppm (+/- 0.3)
Messzeit:10min.
EMAU Greifswald - Avance II - 300

Current Data Parameters	
NAME	NI_BN-98b
EXPNO	31
PROCNO	1
F2 - Acquisition Parameters	
Date_	20101201
Time	11.42
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	256
DS	4
SWH	50000.000 Hz
FIDRES	1.525879 Hz
AQ	0.3277300 sec
RG	23100
DW	10.000 usec
DE	6.00 usec
TE	297.3 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	31P
P1	10.25 usec
PL1	2.00 dB
SFO1	121.4953510 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	19.00 dB
PL13	22.00 dB
PL2	-1.00 dB
SFO2	300.1312005 MHz
F2 - Processing parameters	
SI	32768
SF	121.4948510 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

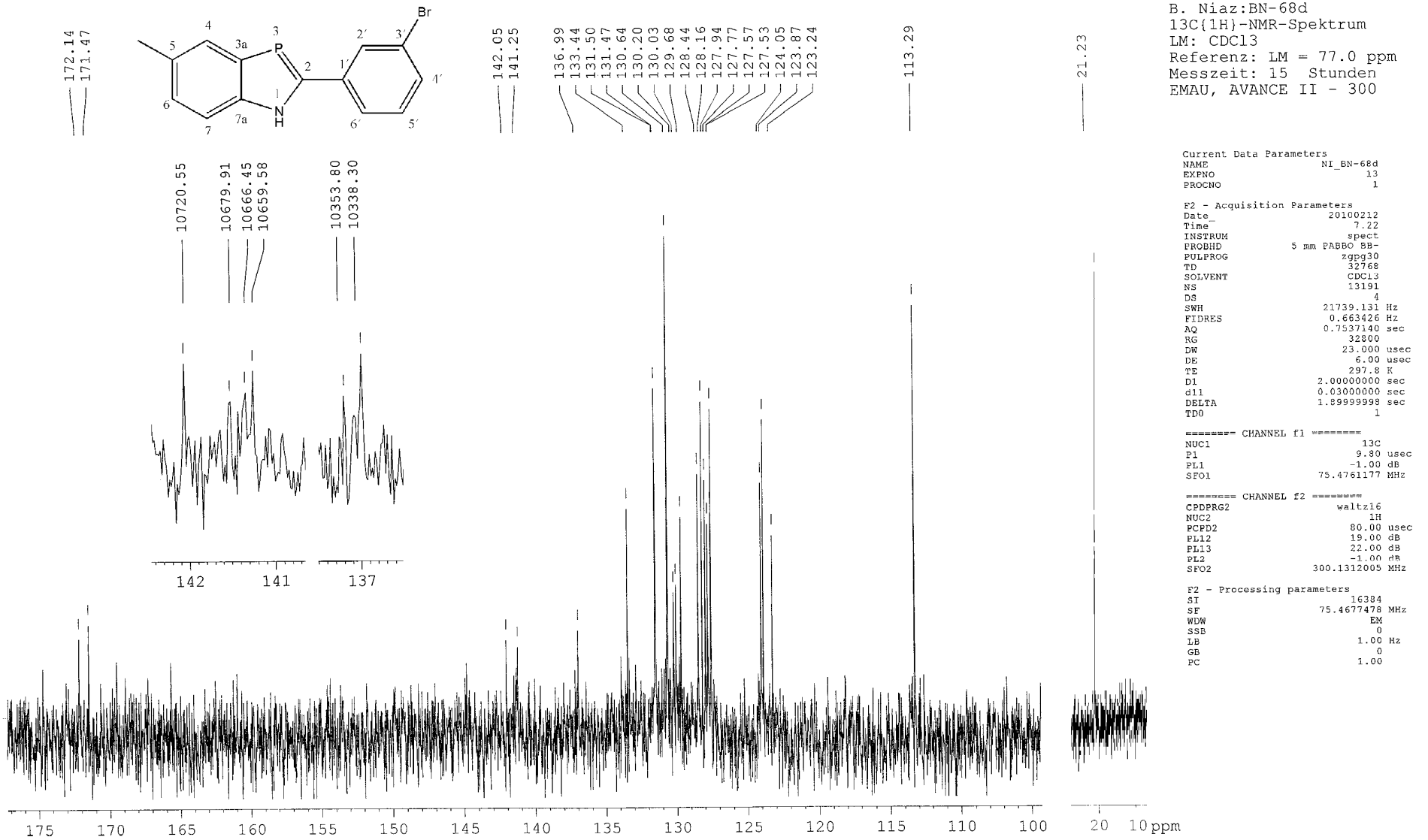
^{31}P NMR spectrum of **2g**.



NIAZ:BN-68d
31P-1H-gekoppelt-NMR-Spektrum
Loesungsmittel: CDCl3
Ref.:extern, H3PO4(Kapillare in CDCl3) = 0.0 ppm
Messzeit: 20 min.
EMAU, Avance II - 300

Current Data Parameters	
NAME	NI_BN-68d
EXPNO	33
PROCNO	1
F2 - Acquisition Parameters	
Date_	20100211
Time	15.58
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	512
DS	4
SWH	50000.000 Hz
FIDRES	0.762939 Hz
AQ	0.6554100 sec
RG	2890
DW	10.000 usec
DE	6.00 usec
TE	297.6 K
D1	2.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	31P
P1	10.25 usec
PL1	2.00 dB
SFO1	121.4953510 MHz
F2 - Processing parameters	
SI	32768
SF	121.4948494 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

^{13}C NMR spectrum (aryl and methyl range) of **2g**.



B. Niaz:BN-68d
13C{1H}-NMR-Spektrum
LM: CDCl3
Referenz: LM = 77.0 ppm
Messzeit: 15 Stunden
EMAU, AVANCE II - 300

Current Data Parameters

NAME	NI_BN-68d
EXPNO	13
PROCNO	1

F2 - Acquisition Parameters

Date_	20100212
Time	7.22
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	13191
DS	4
SWH	21739.131 Hz
FIDRES	0.663426 Hz
AQ	0.7537140 sec
RG	32800
DW	23.000 usec
DE	6.00 usec
TE	297.8 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1

======== CHANNEL f1 ========

NUC1	13C
P1	9.80 usec
PL1	-1.00 dB
SFO1	75.4761177 MHz

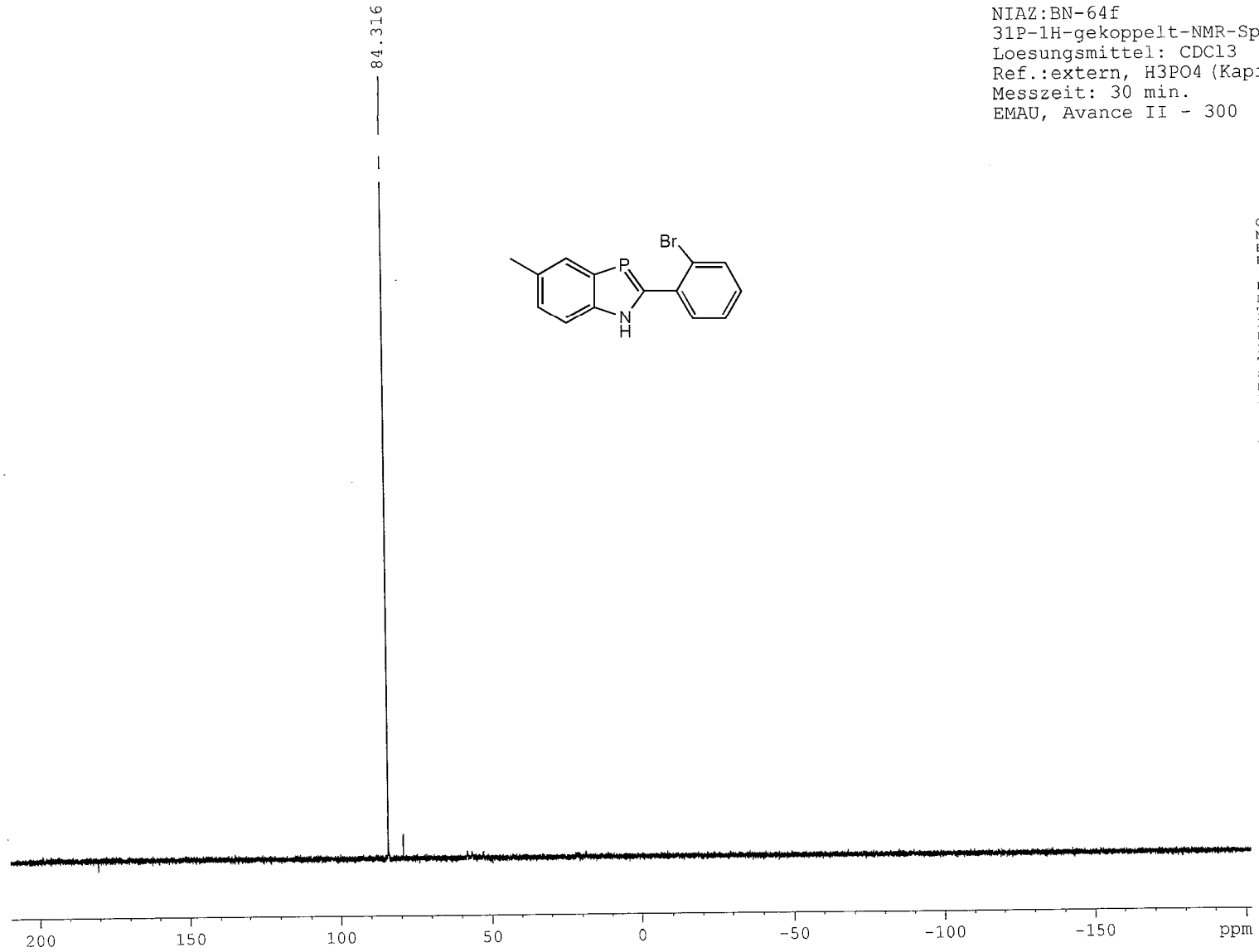
======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	19.00 dB
PL13	22.00 dB
PL2	-1.00 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

SI	16384
SF	75.4677478 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

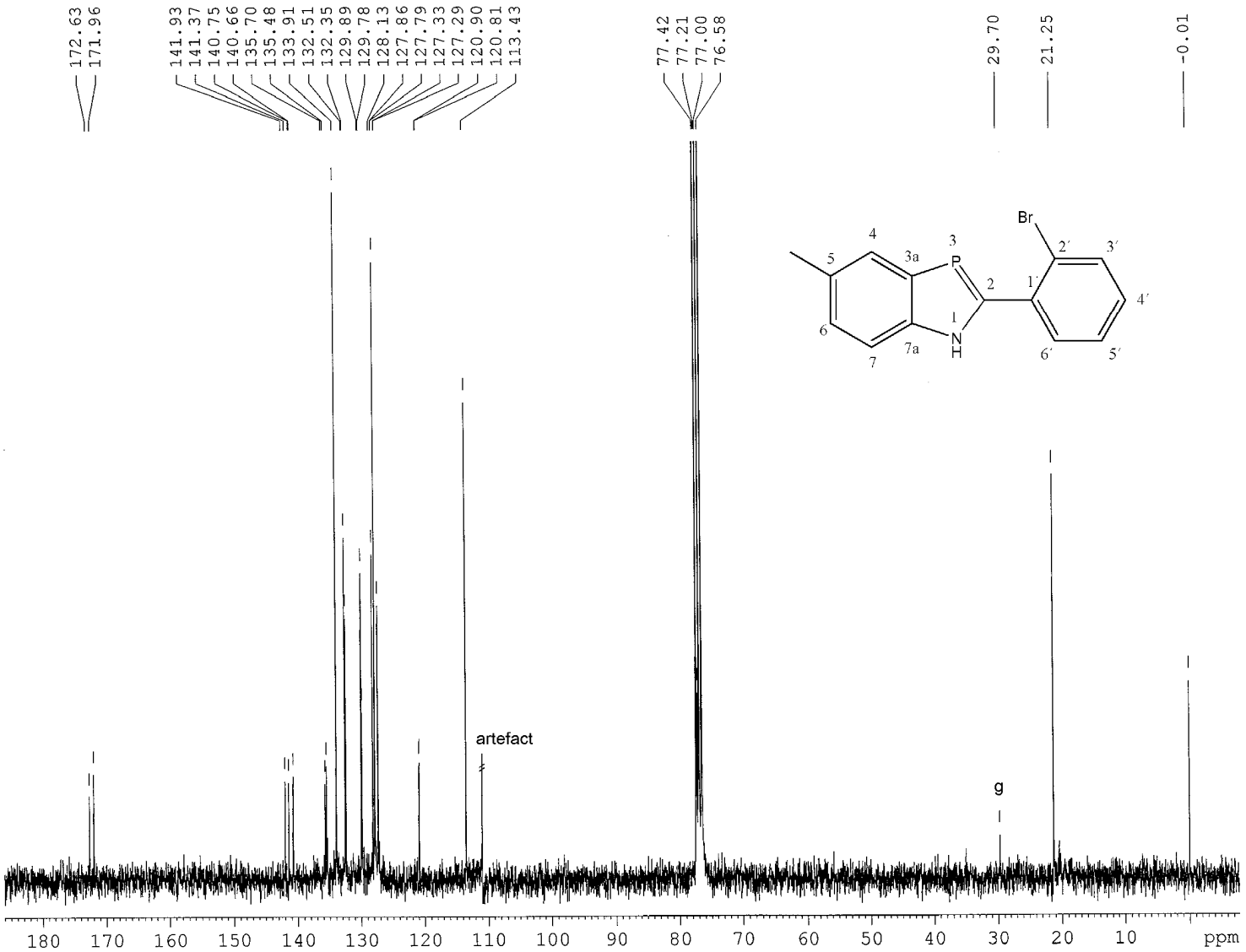
^{31}P NMR spectrum of **2h**.



NIAZ:BN-64f
31P-1H-gekoppelt-NMR-Spektrum
Loesungsmittel: CDCl3
Ref.:extern, H3PO4 (Kapillare in CDCl3) = 0.0 ppm
Messzeit: 30 min.
EMAU, Avance II - 300

Current Data Parameters	
NAME	NI_BN-64f
EXPNO	33
PROCNO	1
F2 - Acquisition Parameters	
Date_	20100203
Time	17.10
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	716
DS	4
SWH	50000.000 Hz
FIDRES	0.762939 Hz
AQ	0.6554100 sec
RG	2890
DW	10.000 usec
DE	6.00 usec
TE	297.6 K
D1	2.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	31P
P1	10.25 usec
PL1	2.00 dB
SFO1	121.4953510 MHz
F2 - Processing parameters	
SI	32768
SF	121.4948502 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

^{13}C NMR spectrum of **2h**.



B. Niaz:BN-64f
13C{1H}-NMR-Spektrum
LM: CDCl3
Referenz: LM = 77.0 ppm
Messzeit: 15 Stunden
EMAU, AVANCE II - 300

Current Data Parameters

NAME	NI_BN-64f
EXPNO	13
PROCNO	1

F2 - Acquisition Parameters

Date_	20100204
Time	8.56
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	14740
DS	4
SWH	21739.131 Hz
FIDRES	0.663426 Hz
AQ	0.7537140 sec
RG	32800
DW	23.000 usec
DE	6.00 usec
TE	297.7 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1

======== CHANNEL f1 ========

NUC1	13C
P1	9.80 usec
PL1	-1.00 dB
SFO1	75.4761177 MHz

======== CHANNEL f2 ========

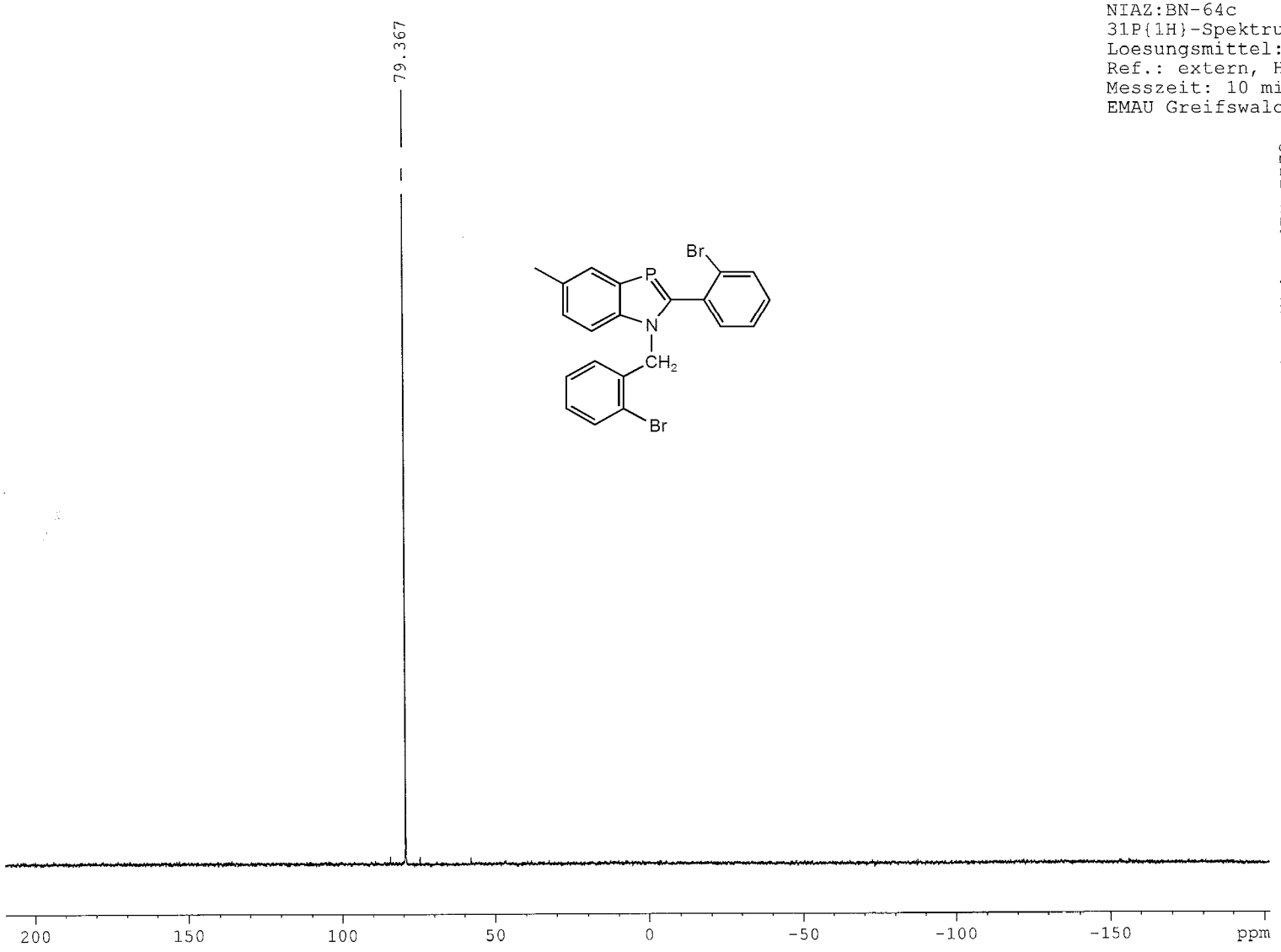
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	19.00 dB
PL13	22.00 dB
PL2	-1.00 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

SI	16384
SF	75.4677478 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

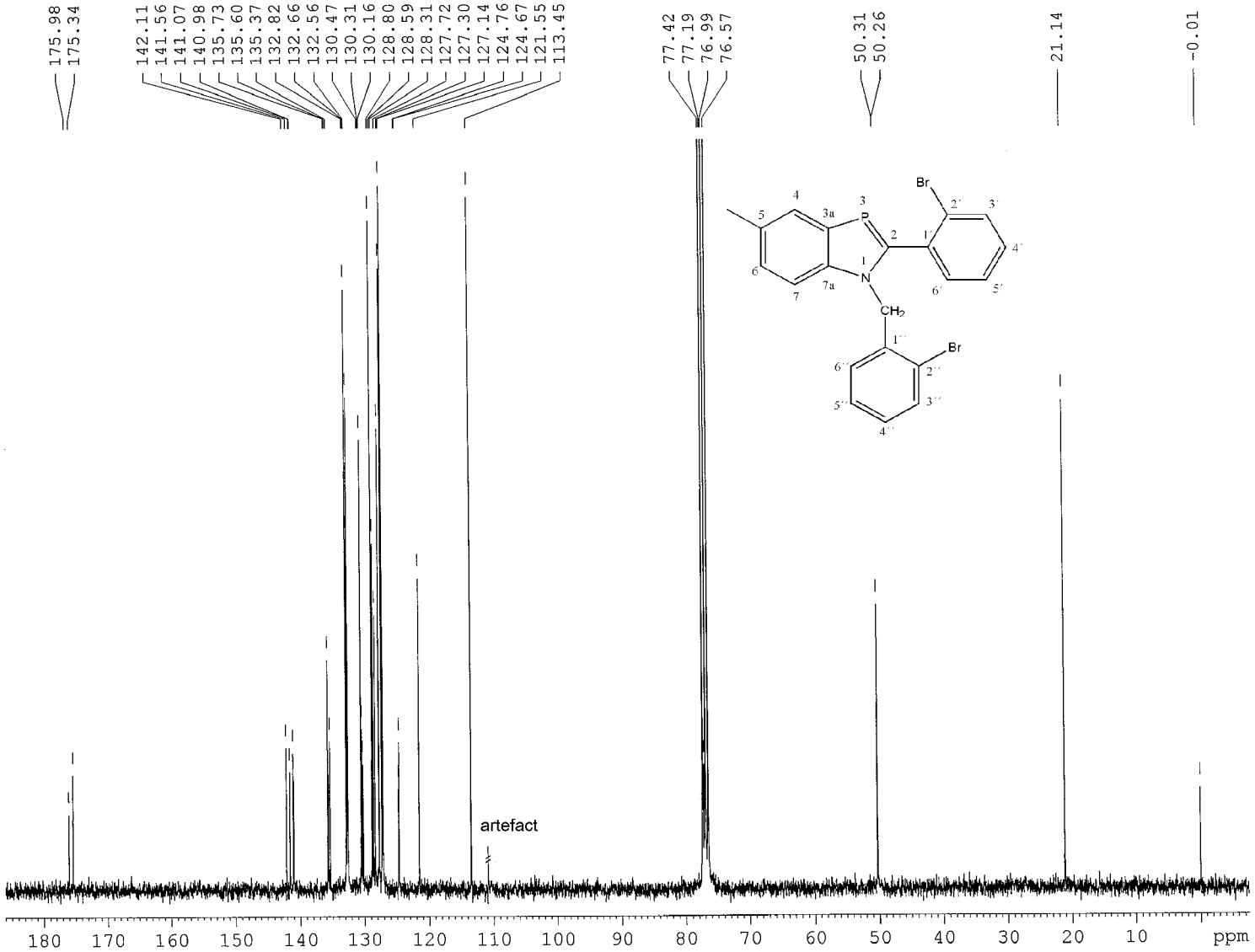
g - grease

^{31}P NMR spectrum of **3h**.




```
NIAZ:BN-64c
31P{1H}-Spektrum Spektrum
Loesungsmittel: CDCl3
Ref.: extern, H3PO4 = 0.0 ppm (+/- 0.3)
Messzeit: 10 min.
EMAU Greifswald - Avance II - 300

Current Data Parameters
NAME                  NI_BN-64c
EXPNO                        31
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20100127
Time                       9.21
INSTRUM                   spect
PROBHD  5 mm PABBO BB-
PULPROG                 zgpg30
TD                       32768
SOLVENT                  CDCl3
NS                          87
DS                           4
SWH                50000.000 Hz
FIDRES              1.525879 Hz
AQ                  0.3277300 sec
RG                       23100
DW                     10.000 usec
DE                      6.00 usec
TE                     297.6 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       31P
P1                    10.25 usec
PL1                    2.00 dB
SFO1          121.4953510 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 80.00 usec
PL12                  19.00 dB
PL13                  22.00 dB
PL2                   -1.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                       32768
SF            121.4948510 MHz
WDW                         EM
SSB                          0
LB                    4.00 Hz
GB                           0
PC                        1.40
```

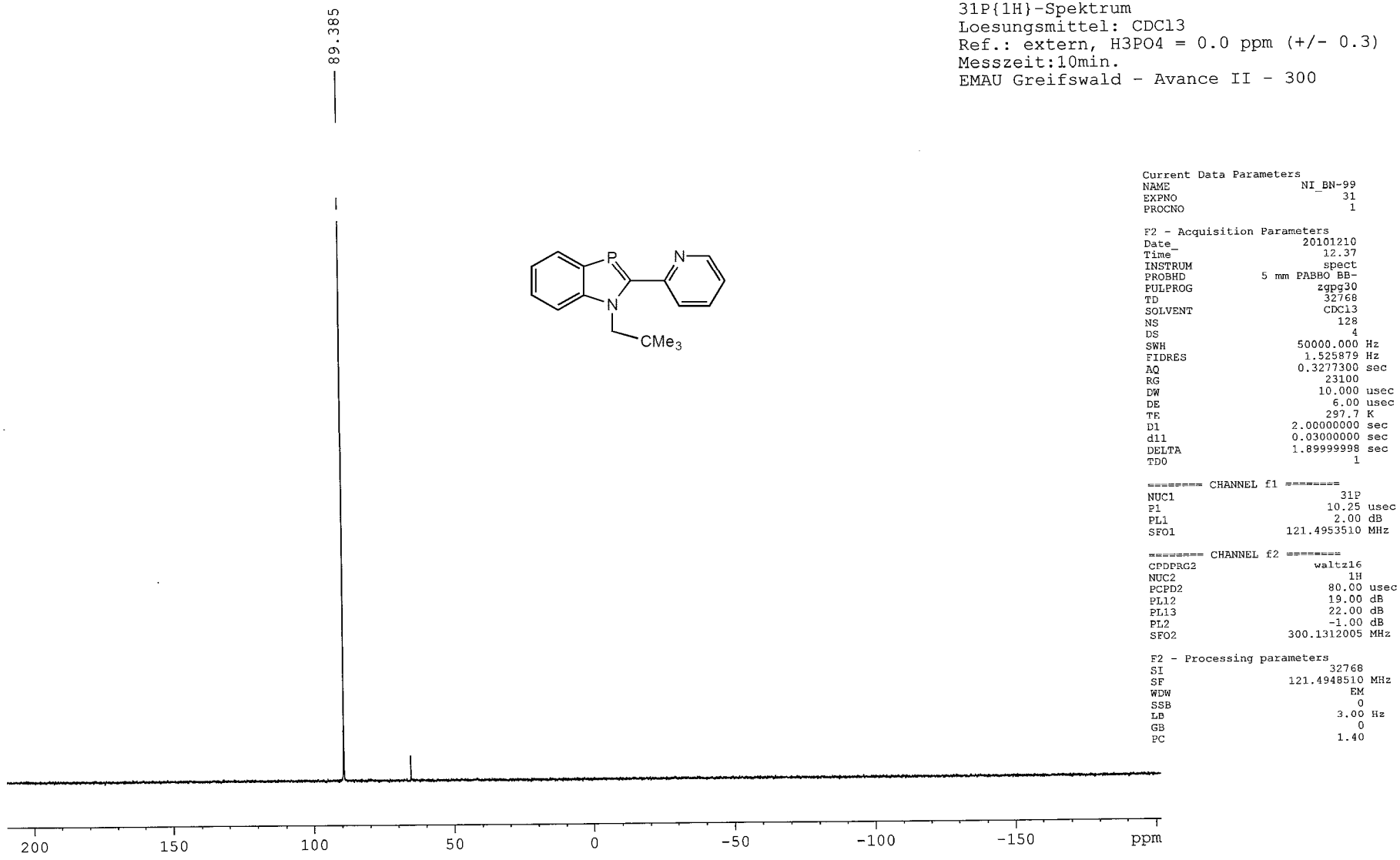
^{13}C NMR spectrum of **3h**.



B. Niaz:BN-64c
13C{1H}-NMR-Spektrum
LM: CDCl3
Referenz: LM = 77.0 ppm
Messzeit: 15 Stunden
EMAU, AVANCE II - 300

Current Data Parameters	
NAME	NI_BN-64c
EXPNO	13
PROCNO	1
F2 - Acquisition Parameters	
Date_	20100128
Time	9.13
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	18866
DS	4
SWH	21739.131 Hz
FIDRES	0.663426 Hz
AQ	0.7537140 sec
RG	32800
DW	23.000 usec
DE	6.00 usec
TE	297.8 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.80 usec
PL1	-1.00 dB
SFO1	75.4761177 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	19.00 dB
PL13	22.00 dB
PL2	-1.00 dB
SFO2	300.1312005 MHz
F2 - Processing parameters	
SI	16384
SF	75.4677491 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

^{31}P NMR spectrum of **6a**.



Current Data Parameters

NAME	NI_BN-99
EXPNO	31
PROCNO	1

F2 - Acquisition Parameters

Date_	20101210
Time	12.37
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	128
DS	4
SWH	50000.000 Hz
FIDRES	1.525879 Hz
AQ	0.3277300 sec
RG	23100
DW	10.000 usec
DE	6.00 usec
TE	297.7 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1

======== CHANNEL f1 ========

NUC1	31P
P1	10.25 usec
PL1	2.00 dB
SFO1	121.4953510 MHz

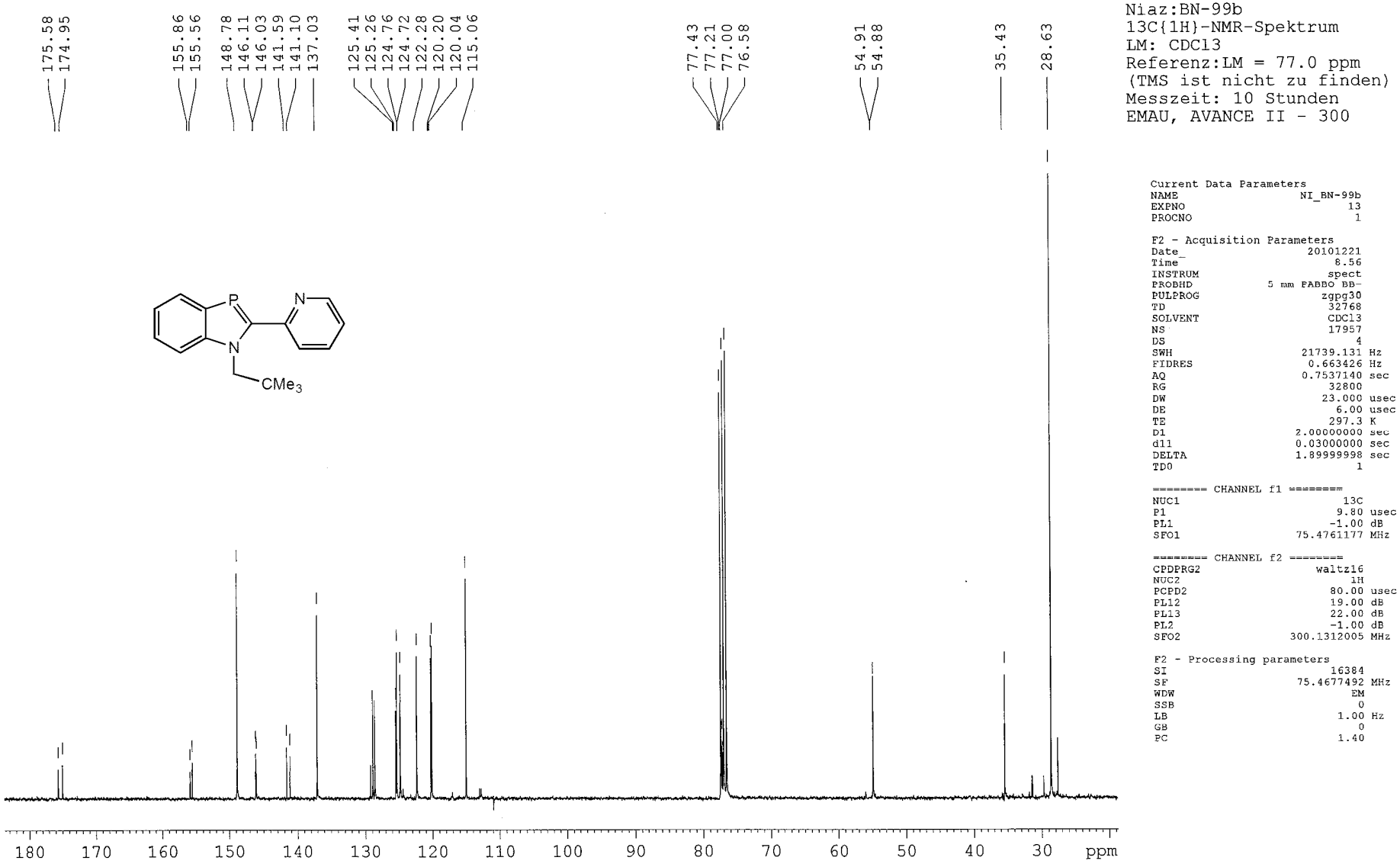
======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	19.00 dB
PL13	22.00 dB
PL2	-1.00 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

SI	32768
SF	121.4948510 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

^{13}C NMR spectrum of **6a**.



Niaz:BN-99b
13C{1H}-NMR-Spektrum
LM: CDCl3
Referenz:LM = 77.0 ppm
(TMS ist nicht zu finden)
Messzeit: 10 Stunden
EMAU, AVANCE II - 300

Current Data Parameters

NAME	NI_BN-99b
EXPNO	13
PROCNO	1

F2 - Acquisition Parameters

Date_	20101221
Time	8.56
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	17957
DS	4
SWH	21739.131 Hz
FIDRES	0.663426 Hz
AQ	0.7537140 sec
RG	32800
DW	23.000 usec
DE	6.00 usec
TE	297.3 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1

======== CHANNEL f1 ========

NUC1	13C
P1	9.80 usec
PL1	-1.00 dB
SFO1	75.4761177 MHz

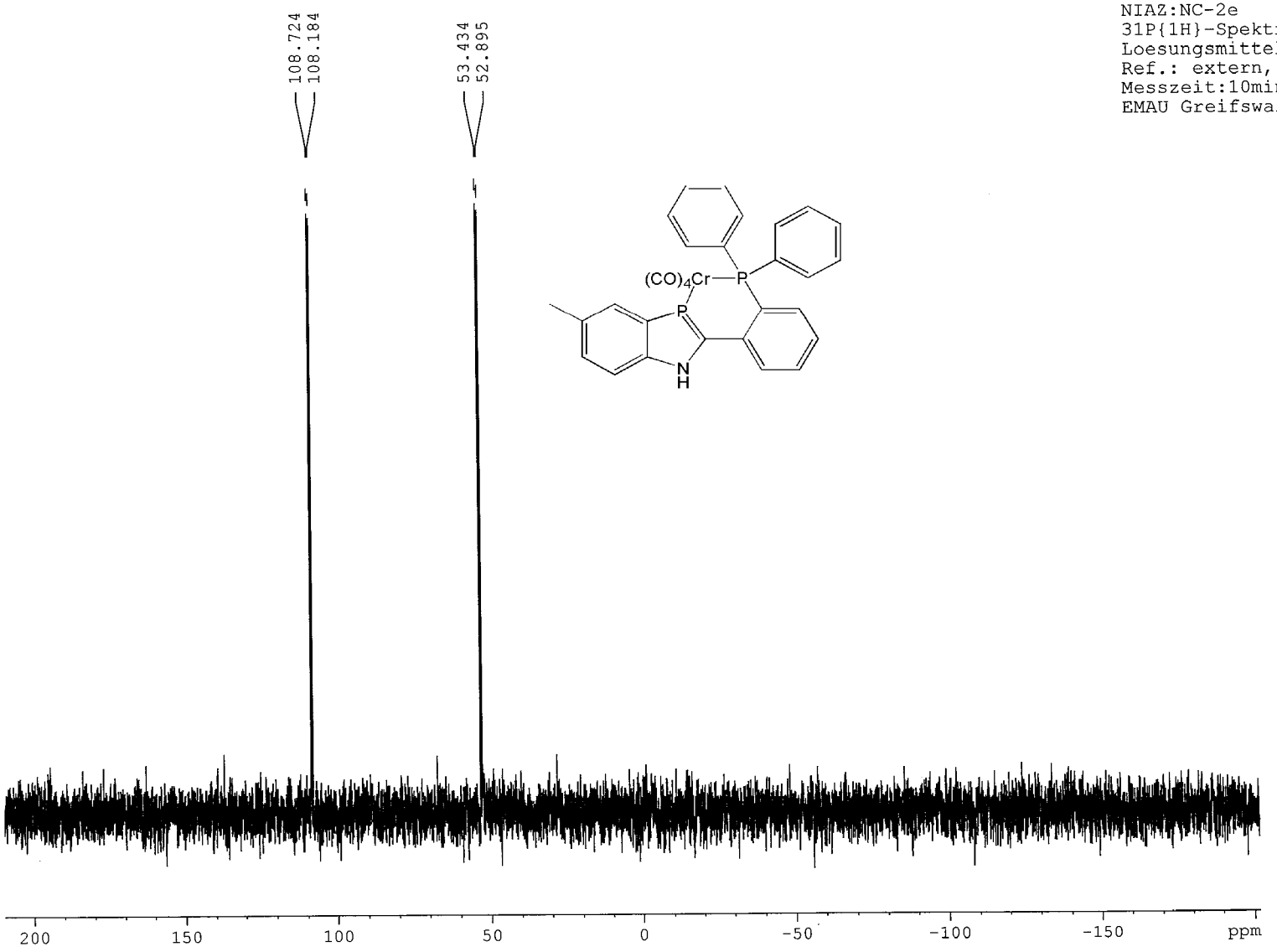
======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	19.00 dB
PL13	22.00 dB
PL2	-1.00 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

SI	16384
SF	75.4677492 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

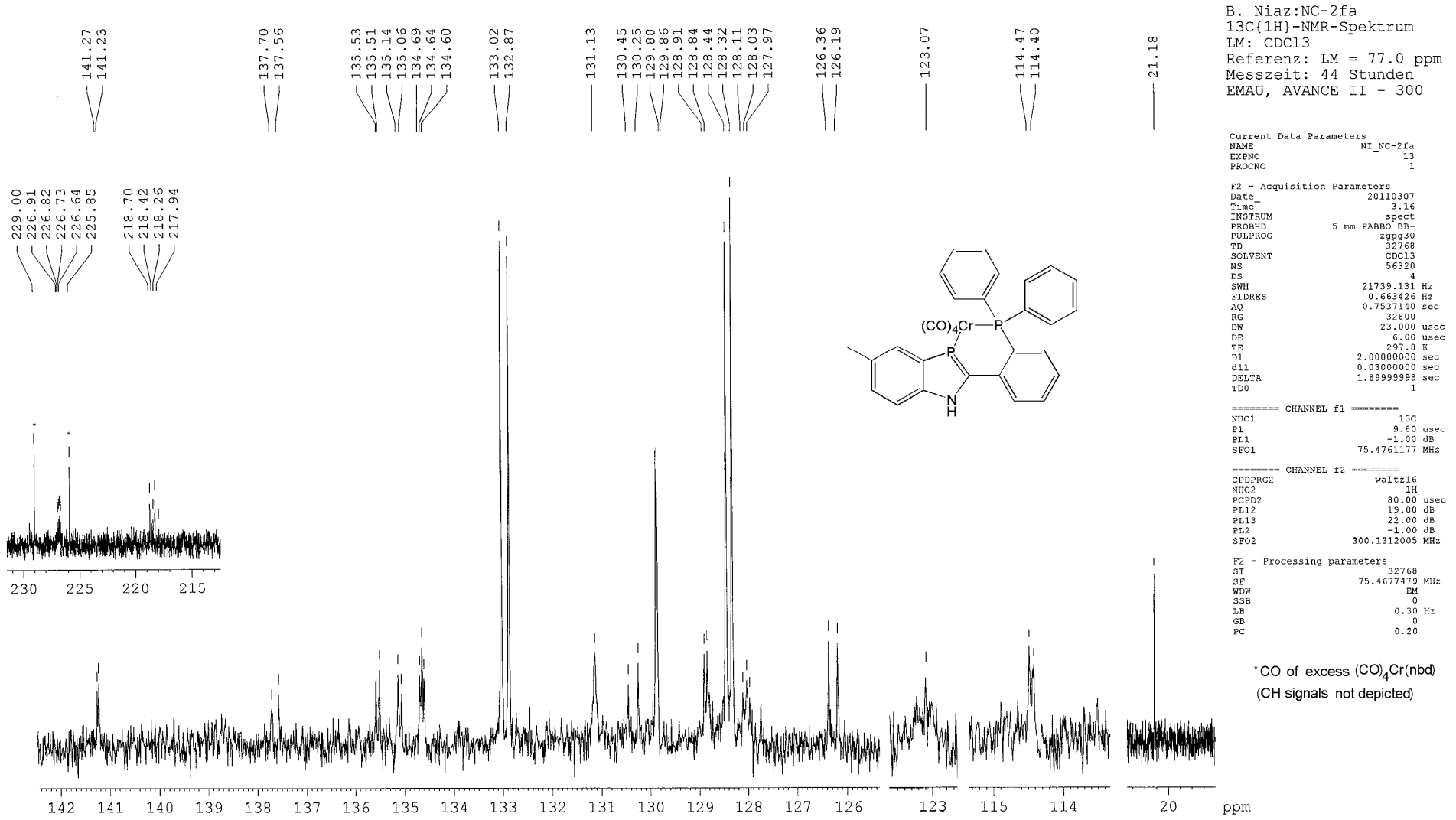
^{31}P NMR spectrum of **8a**.




```
NIAZ:NC-2e
31P{1H}-Spektrum
Loesungsmittel: CD2Cl2
Ref.: extern, H3PO4 = 0.0 ppm (+/- 0.3)
Messzeit:10min.
EMAU Greifswald - Avance II - 300
```

```
Current Data Parameters
NAME                   NI_NC-2e
EXPNO                        32
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20100908
Time                      15.10
INSTRUM                   spect
PROBHD  5 mm PABBO BB-
PULPROG                 zgpg30
TD                       32768
SOLVENT                  CD2Cl2
NS                          256
DS                            4
SWH                50000.000 Hz
FIDRES             1.525879 Hz
AQ                 0.3277300 sec
RG                        23100
DW                    10.000 usec
DE                     6.00 usec
TE                     298.2 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        31P
P1                    10.25 usec
PL1                    2.00 dB
SFO1             121.4953510 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                 80.00 usec
PL12                  19.00 dB
PL13                  22.00 dB
PL2                   -1.00 dB
SFO2             300.1312005 MHz

F2 - Processing parameters
SI                       32768
SF               121.4948510 MHz
WDW                         EM
SSB                          0
LB                    3.00 Hz
GB                           0
PC                    3.00
```

^{13}C NMR spectrum of **8a**.

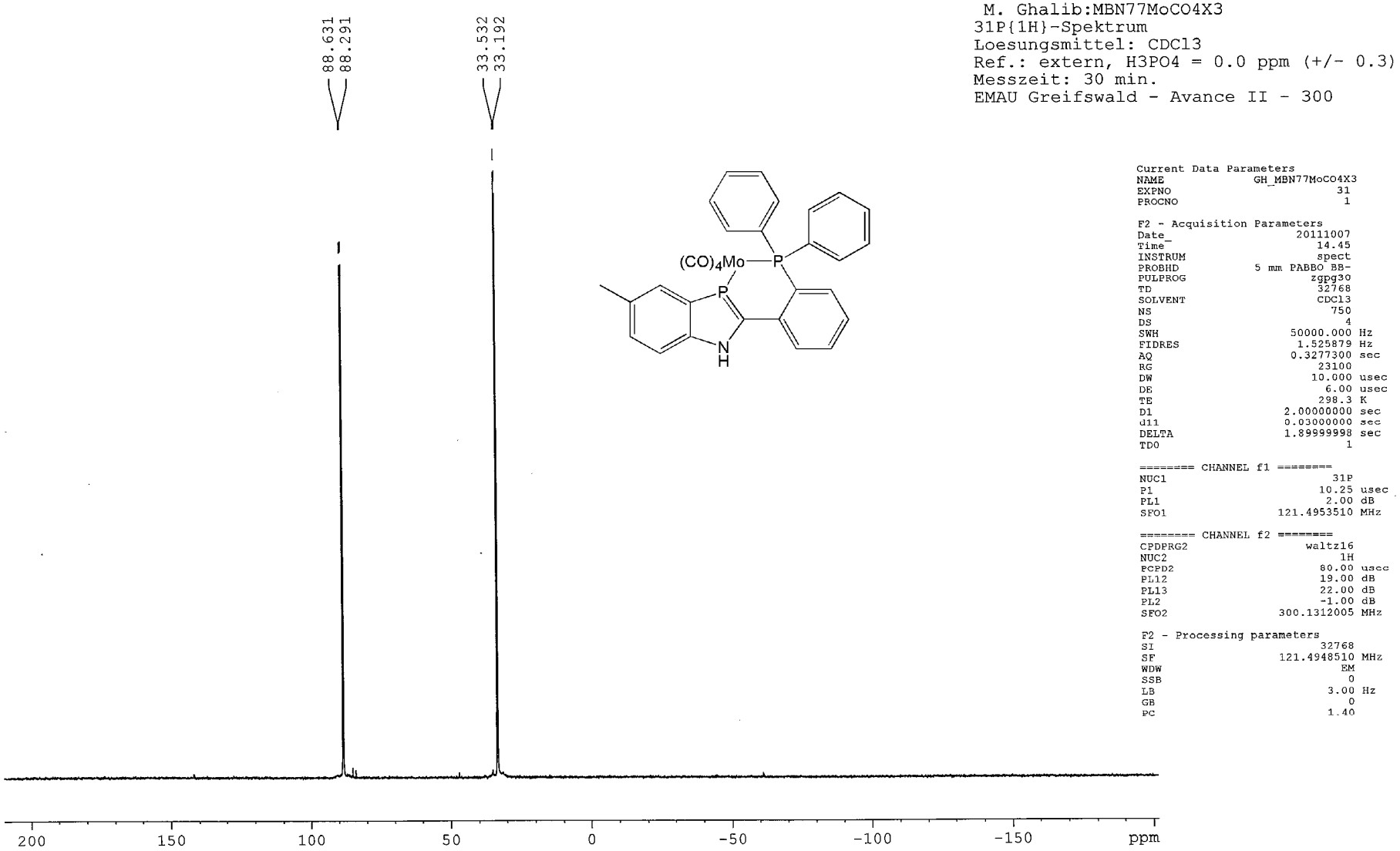


B. Niaz:NC-2fa
13C{1H}-NMR-Spektrum
LM: CDCl3
Referenz: LM = 77.0 ppm
Messzeit: 44 Stunden
EMAU, AVANCE II - 300

Current Data Parameters	
NAME	NI_NC-2fa
EXPNO	13
PROCNO	1
F2 - Acquisition Parameters	
Date_	20110307
Time	3.16
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	56320
DS	4
SWH	21739.131 Hz
FIDRES	0.663426 Hz
AQ	0.7537140 sec
RG	32800
DW	23.000 usec
DE	6.00 usec
TE	297.8 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.80 usec
PL1	-1.00 dB
SFO1	75.4761177 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	19.00 dB
PL13	22.00 dB
PL2	-1.00 dB
SFO2	300.1312005 MHz
F2 - Processing parameters	
SI	32768
SF	75.4677479 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	0.20

*CO of excess $(CO)_4Cr(nbd)$
(CH signals not depicted)

^{31}P NMR spectrum of **9a**.



M. Ghalib:MBN77MoCO4X3
31P{1H}-Spektrum
Loesungsmittel: CDCl3
Ref.: extern, H3PO4 = 0.0 ppm (+/- 0.3)
Messzeit: 30 min.
EMAU Greifswald - Avance II - 300

Current Data Parameters

NAME	GH_MBN77MoCO4X3
EXPNO	31
PROCNO	1

F2 - Acquisition Parameters

Date_	20111007
Time	14.45
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	750
DS	4
SWH	50000.000 Hz
FIDRES	1.525879 Hz
AQ	0.3277300 sec
RG	23100
DW	10.000 usec
DE	6.00 usec
TE	298.3 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1

======== CHANNEL f1 ========

NUC1	31P
P1	10.25 usec
PL1	2.00 dB
SFO1	121.4953510 MHz

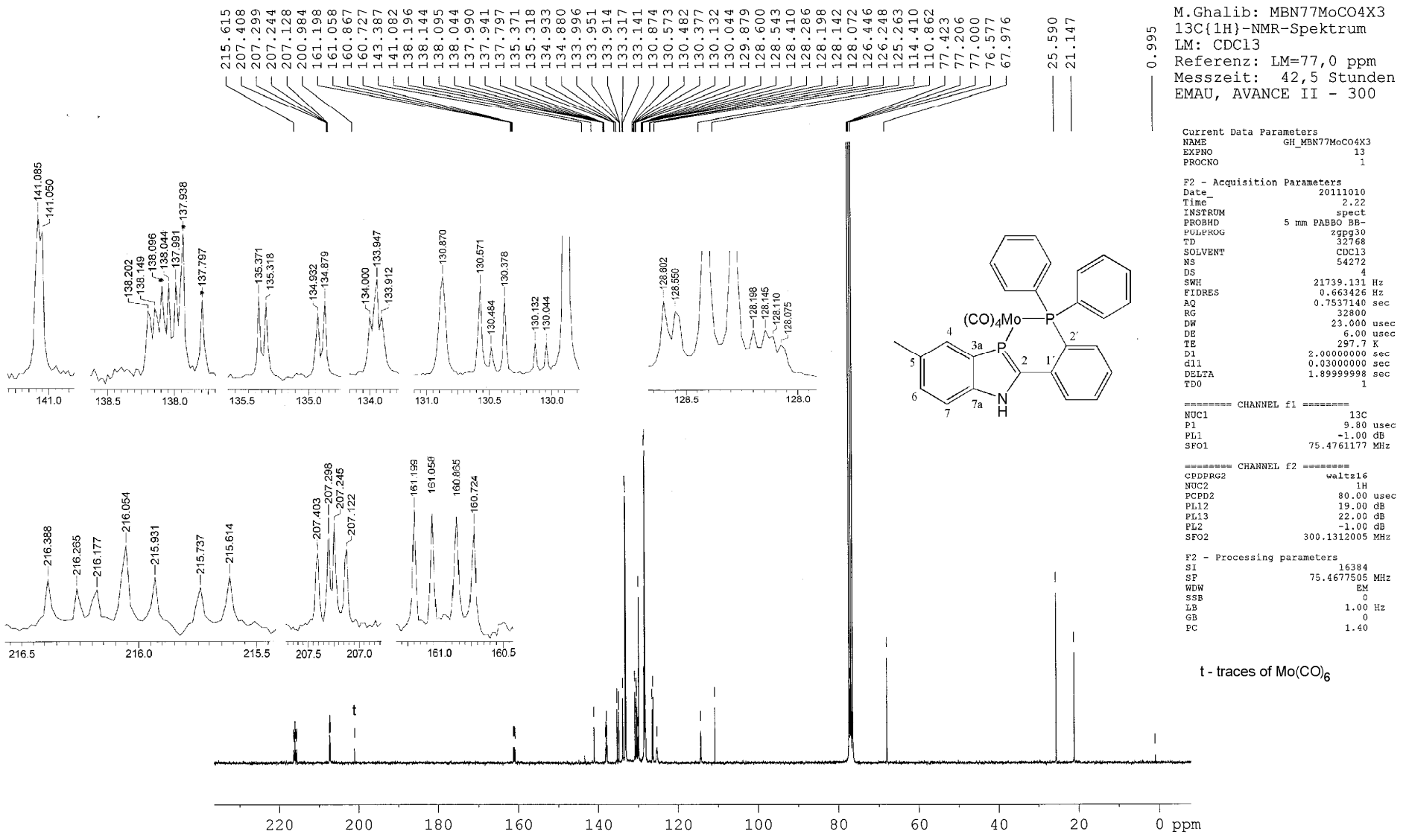
======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	19.00 dB
PL13	22.00 dB
PL2	-1.00 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

SI	32768
SF	121.4948510 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

^{13}C NMR spectrum of **9a**.



3. Tables with atomic coordinates, bond lengths and angles of 9a

Table 3.1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Mo	6418.1(1)	3096.4(1)	2203.6(1)	12.4(1)
N(1)	7092.9(10)	7708.4(16)	3168.2(8)	14.6(3)
C(2)	6558.4(11)	6828.2(18)	2799.9(9)	11.9(3)
P(3)	6834.9(3)	5088.0(5)	2929.3(2)	12.0(1)
C(3A)	7717.2(11)	5554.1(18)	3456.7(9)	13.1(3)
C(4)	8330.7(12)	4713.1(19)	3803.9(9)	14.4(3)
C(5)	8959.0(12)	5342(2)	4211.6(10)	17.4(4)
C(6)	8962.3(13)	6837(2)	4284.1(11)	19.5(4)
C(7)	8369.5(13)	7684(2)	3952.1(10)	19.1(4)
C(7A)	7744.0(12)	7039.9(18)	3532.7(9)	14.2(3)
C(8)	9637.8(13)	4463(2)	4562.5(11)	23.3(4)
C(9)	6789.4(15)	1660(2)	2892.9(11)	22.1(4)
O(1)	7010.2(12)	825.7(16)	3302.4(8)	33.6(4)
C(10)	6153.6(15)	1592(2)	1487.7(11)	22.3(4)
O(2)	6037.2(13)	720.2(17)	1078.0(9)	37.8(4)
C(11)	5219.2(14)	3021(2)	2646.0(10)	21.0(4)
O(3)	4573.7(11)	2956.0(18)	2927.7(9)	36.1(4)
C(12)	7661.9(13)	3178(2)	1871.7(10)	18.7(4)
O(4)	8373.3(10)	3240.5(17)	1733.5(8)	29.5(4)
P(1)	5985.6(3)	5141.3(5)	1408.2(2)	10.7(1)
C(21)	5795.1(12)	7347.9(18)	2432.0(9)	13.0(3)
C(22)	5452.4(12)	6671.5(19)	1829.2(9)	13.7(3)
C(23)	4700.0(12)	7210(2)	1531.2(10)	18.8(4)
C(24)	4297.0(13)	8402(2)	1801.3(11)	21.9(4)
C(25)	4638.0(12)	9078(2)	2384.6(9)	18.9(4)
C(26)	5375.4(12)	8550.7(19)	2696.7(10)	16.6(4)
C(31)	6853.8(11)	5974.2(19)	910.7(9)	13.4(3)
C(32)	7351.5(12)	5095(2)	484.6(9)	17.0(4)
C(33)	7978.2(13)	5657(2)	45.6(11)	23.4(4)
C(34)	8119.3(14)	7106(2)	33.7(11)	26.4(5)
C(35)	7637.3(14)	7983(2)	463.0(11)	24.5(4)
C(36)	7002.5(13)	7427(2)	897.4(10)	18.8(4)
C(41)	5241.8(11)	4683.0(19)	695.9(9)	13.2(3)

C(42)	4610.0(12)	3671(2)	828.7(10)	17.8(4)
C(43)	4022.1(13)	3307(2)	312.4(10)	20.9(4)
C(44)	4060.0(13)	3933(2)	-344.7(10)	19.4(4)
C(45)	4686.2(13)	4937(2)	-484.6(10)	19.4(4)
C(46)	5273.1(13)	5312(2)	31.5(10)	16.0(4)

Table 3.2 Bond lengths [Å] and angles [°].

Mo-C(9)	1.973(2)	P(1)-C(31)	1.8284(18)
Mo-C(10)	2.011(2)	P(1)-C(41)	1.8340(18)
Mo-C(12)	2.039(2)	P(1)-C(22)	1.8496(18)
Mo-C(11)	2.050(2)	C(21)-C(26)	1.404(2)
Mo-P(3)	2.4219(5)	C(21)-C(22)	1.417(2)
Mo-P(1)	2.5442(5)	C(22)-C(23)	1.398(3)
N(1)-C(2)	1.369(2)	C(23)-C(24)	1.387(3)
N(1)-C(7A)	1.381(2)	C(24)-C(25)	1.386(3)
C(2)-C(21)	1.464(2)	C(25)-C(26)	1.386(3)
C(2)-P(3)	1.7173(17)	C(31)-C(36)	1.393(3)
P(3)-C(3A)	1.7574(18)	C(31)-C(32)	1.396(3)
C(3A)-C(4)	1.407(2)	C(32)-C(33)	1.390(3)
C(3A)-C(7A)	1.412(2)	C(33)-C(34)	1.387(3)
C(4)-C(5)	1.383(3)	C(34)-C(35)	1.385(3)
C(5)-C(6)	1.419(3)	C(35)-C(36)	1.391(3)
C(5)-C(8)	1.501(3)	C(41)-C(42)	1.396(3)
C(6)-C(7)	1.376(3)	C(41)-C(46)	1.396(3)
C(7)-C(7A)	1.399(2)	C(42)-C(43)	1.386(3)
C(9)-O(1)	1.160(2)	C(43)-C(44)	1.383(3)
C(10)-O(2)	1.148(2)	C(44)-C(45)	1.387(3)
C(11)-O(3)	1.141(3)	C(45)-C(46)	1.387(2)
C(12)-O(4)	1.140(3)		
C(9)-Mo-C(10)	91.33(7)	P(3)-Mo-P(1)	79.598(13)
C(9)-Mo-C(12)	87.31(9)	C(2)-N(1)-C(7A)	115.17(15)
C(10)-Mo-C(12)	90.70(9)	N(1)-C(2)-C(21)	122.29(15)
C(9)-Mo-C(11)	88.32(9)	N(1)-C(2)-P(3)	110.84(13)
C(10)-Mo-C(11)	93.81(9)	C(21)-C(2)-P(3)	126.38(13)
C(12)-Mo-C(11)	173.79(8)	C(2)-P(3)-C(3A)	92.17(8)
C(9)-Mo-P(3)	94.45(6)	C(2)-P(3)-Mo	126.51(6)
C(10)-Mo-P(3)	171.81(7)	C(3A)-P(3)-Mo	136.83(6)
C(12)-Mo-P(3)	83.80(5)	C(4)-C(3A)-C(7A)	119.56(16)
C(11)-Mo-P(3)	92.15(6)	C(4)-C(3A)-P(3)	131.09(14)
C(9)-Mo-P(1)	174.05(6)	C(7A)-C(3A)-P(3)	109.31(13)
C(10)-Mo-P(1)	94.61(6)	C(5)-C(4)-C(3A)	120.06(17)
C(12)-Mo-P(1)	92.23(5)	C(4)-C(5)-C(6)	119.00(17)
C(11)-Mo-P(1)	91.66(6)	C(4)-C(5)-C(8)	120.64(18)

C(6)-C(5)-C(8)	120.34(17)	C(43)-C(44)-C(45)	119.73(17)
C(7)-C(6)-C(5)	122.17(18)	C(44)-C(45)-C(46)	120.18(16)
C(6)-C(7)-C(7A)	118.40(17)	C(45)-C(46)-C(41)	120.54(16)
N(1)-C(7A)-C(7)	126.76(16)		
N(1)-C(7A)-C(3A)	112.43(16)		
C(7)-C(7A)-C(3A)	120.79(17)		
O(1)-C(9)-Mo	179.34(18)		
O(2)-C(10)-Mo	177.2(2)		
O(3)-C(11)-Mo	176.06(18)		
O(4)-C(12)-Mo	175.24(17)		
C(31)-P(1)-C(41)	100.79(8)		
C(31)-P(1)-C(22)	102.68(8)		
C(41)-P(1)-C(22)	102.73(8)		
C(31)-P(1)-Mo	116.00(6)		
C(41)-P(1)-Mo	115.26(6)		
C(22)-P(1)-Mo	117.09(6)		
C(26)-C(21)-C(22)	118.64(16)		
C(26)-C(21)-C(2)	118.59(16)		
C(22)-C(21)-C(2)	122.76(15)		
C(23)-C(22)-C(21)	118.66(16)		
C(23)-C(22)-P(1)	119.07(14)		
C(21)-C(22)-P(1)	122.24(13)		
C(24)-C(23)-C(22)	121.67(17)		
C(25)-C(24)-C(23)	119.79(18)		
C(26)-C(25)-C(24)	119.63(17)		
C(25)-C(26)-C(21)	121.59(17)		
C(36)-C(31)-C(32)	118.95(17)		
C(36)-C(31)-P(1)	123.83(14)		
C(32)-C(31)-P(1)	117.06(14)		
C(33)-C(32)-C(31)	120.73(18)		
C(34)-C(33)-C(32)	119.91(19)		
C(35)-C(34)-C(33)	119.70(19)		
C(34)-C(35)-C(36)	120.61(19)		
C(35)-C(36)-C(31)	120.09(19)		
C(42)-C(41)-C(46)	118.67(16)		
C(42)-C(41)-P(1)	118.28(14)		
C(46)-C(41)-P(1)	123.04(14)		
C(43)-C(42)-C(41)	120.53(17)		
C(44)-C(43)-C(42)	120.34(18)		

Electronic Supplementary Material (ESI) for Dalton Transactions

Table 3.3 Hydrogen bonds [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(01)...O(1)#1	0.808(16)	2.167(17)	2.959(2)	167(2)
C(42)-H(42)...O(4)#2	0.95	2.50	3.151(2)	126.2
C(43)-H(43)...O(4)#2	0.95	2.67	3.234(3)	118.8

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z

#2 x-1/2,-y+1/2,z