Supplementary Material

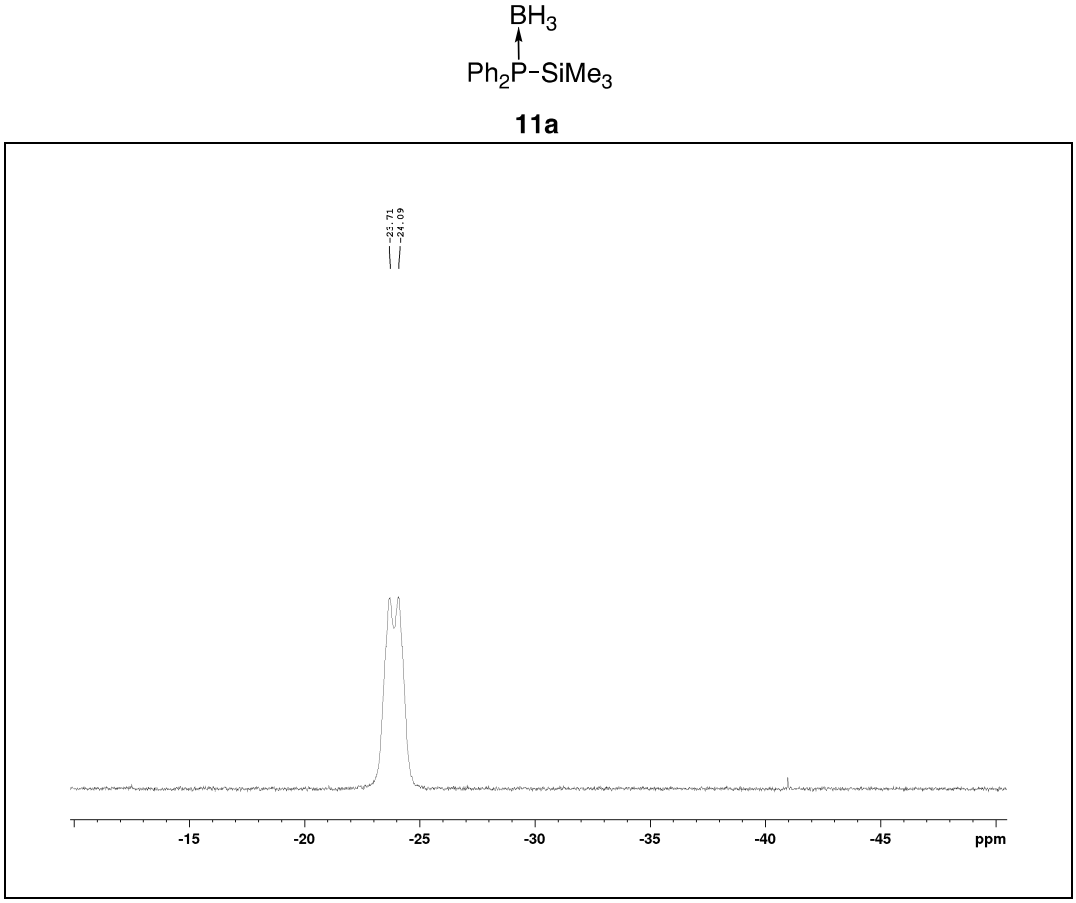
P-Chirogenic silylphosphine-boranes: synthesis and phospha-Michael reactions

Eric Bonnefille, Arnaud Tessier,[†]* Hélène Cattey, Pierre Le Gendre and Sylvain Jugé*

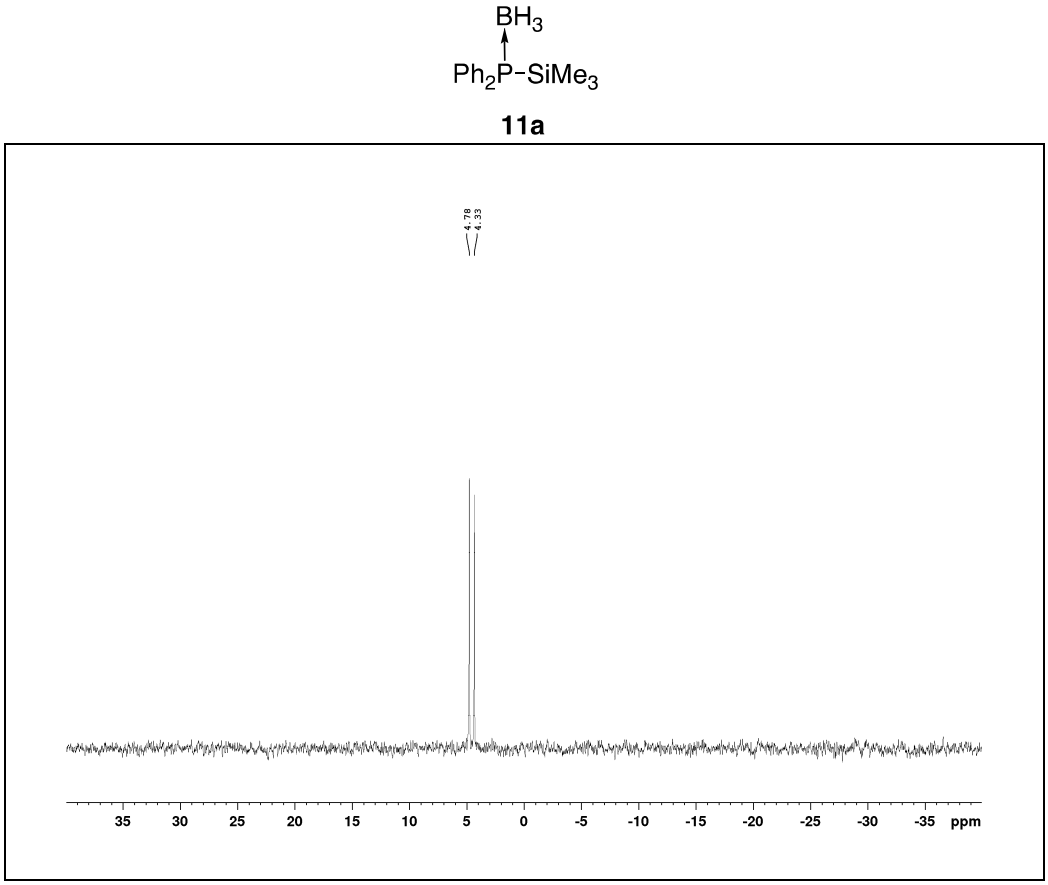
Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB- StéréochIM-UMR CNRS 6302), 9 avenue A. Savary BP47870, 21078 Dijon Cedex, France
[†] Present adress: Université de Nantes, CNRS, CEISAM, UMR CNRS 6230, Faculté des Sciences et des Techniques, 2 rue de la Houssinière, BP 92208, 44322 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

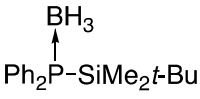
^{31}P NMR (121.4 MHz, C_6D_6) spectrum for **11a**



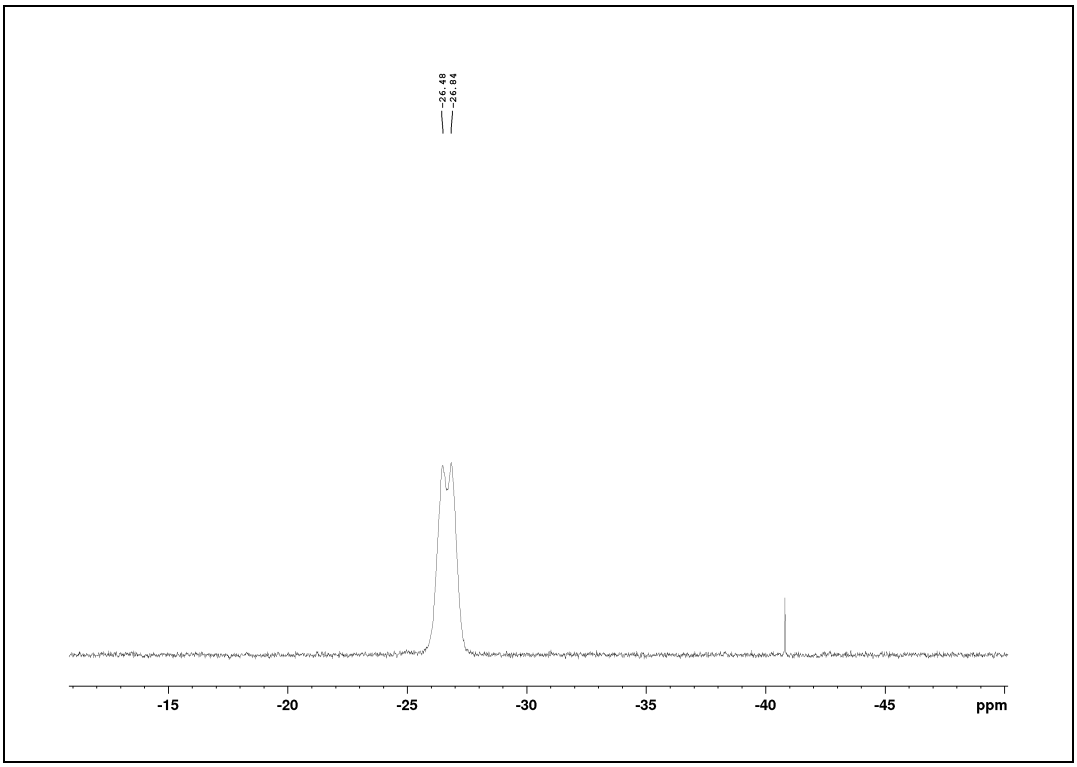
^{29}Si NMR (99.4 MHz, C_6D_6) spectrum for **11a**



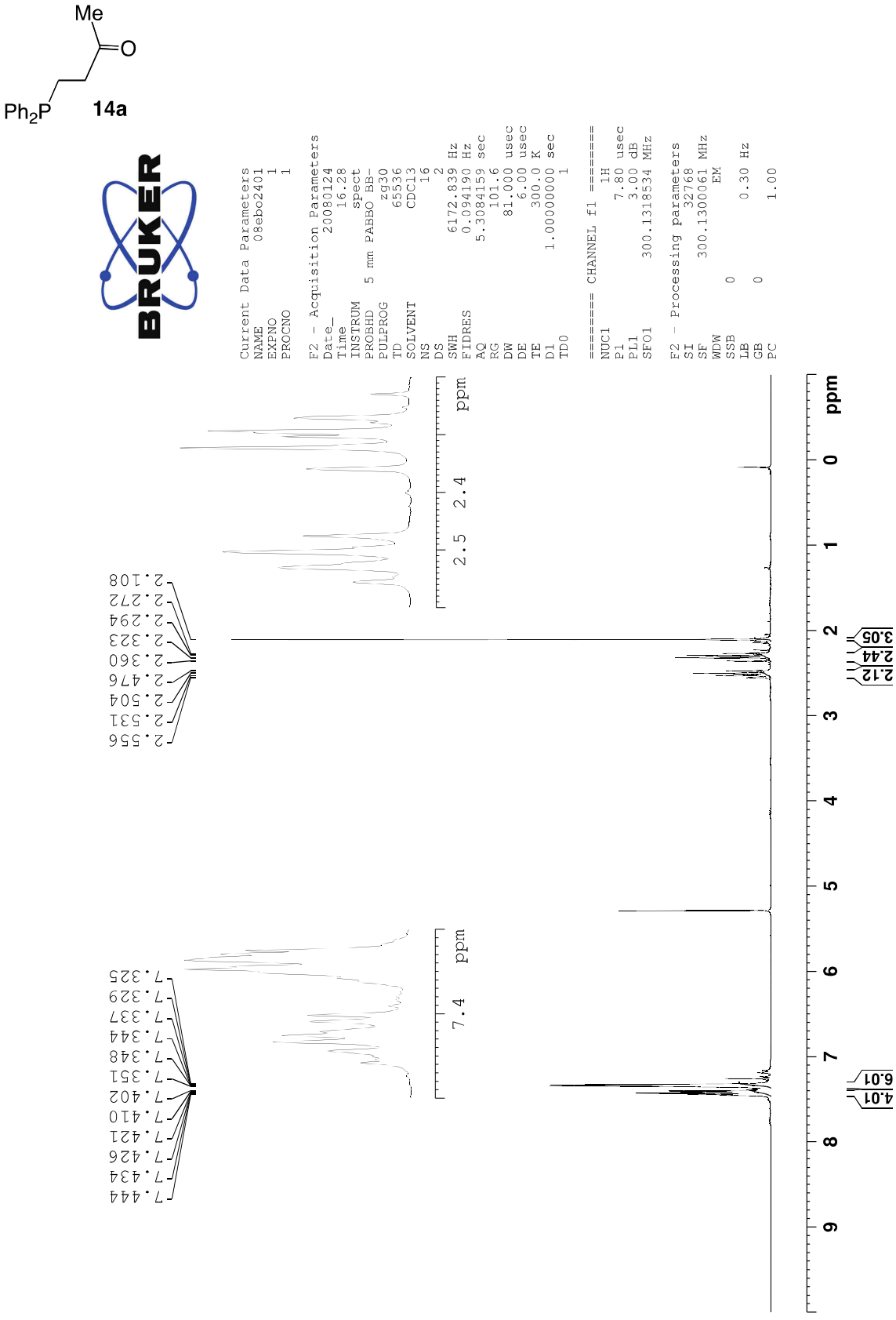
^{31}P NMR (121.4 MHz, C_6D_6) spectrum for **11b**



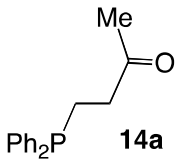
11b

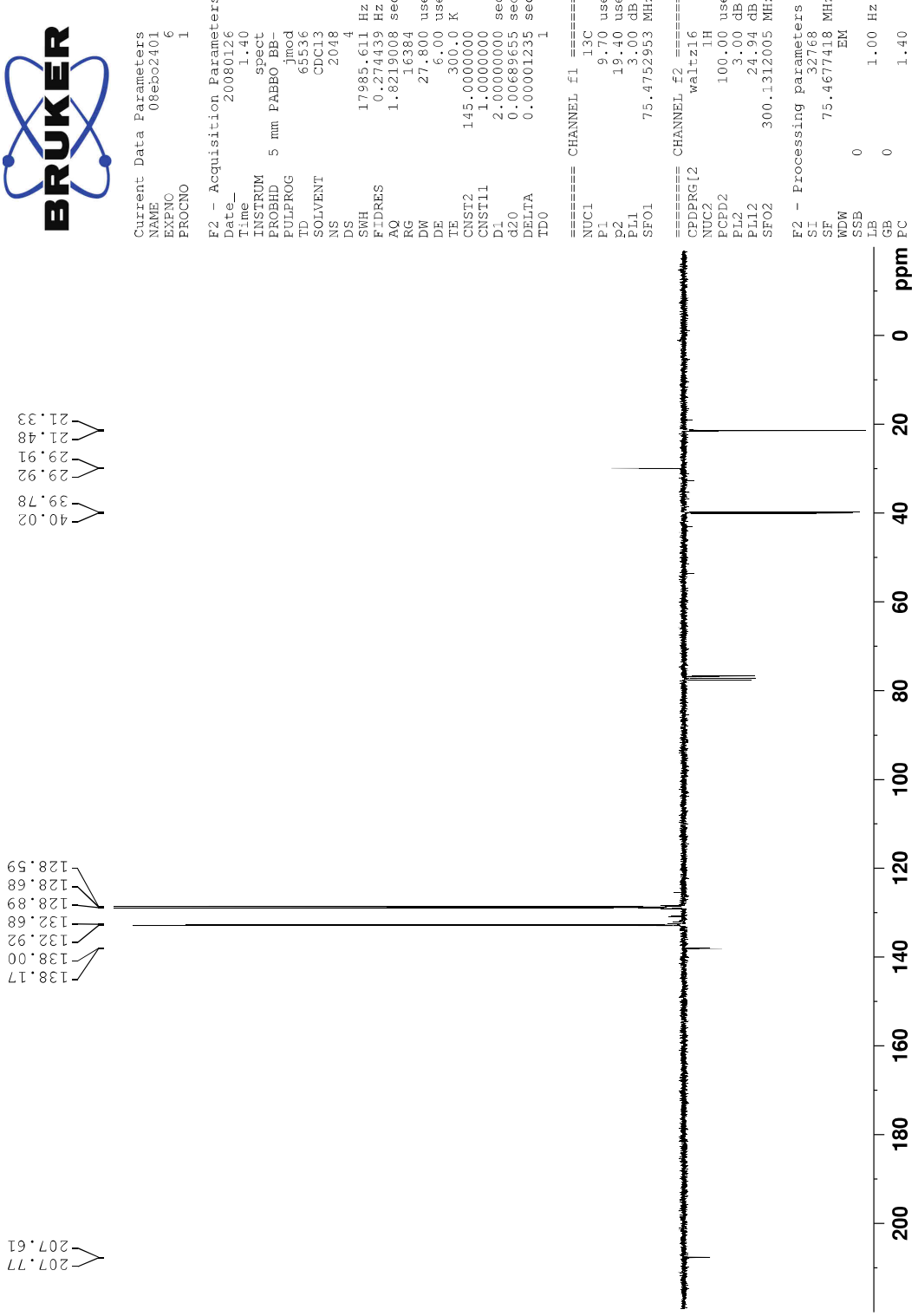


^{1}H NMR (300 MHz, C_6D_6) spectrum for **14a**

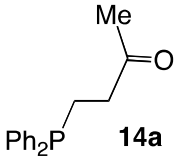


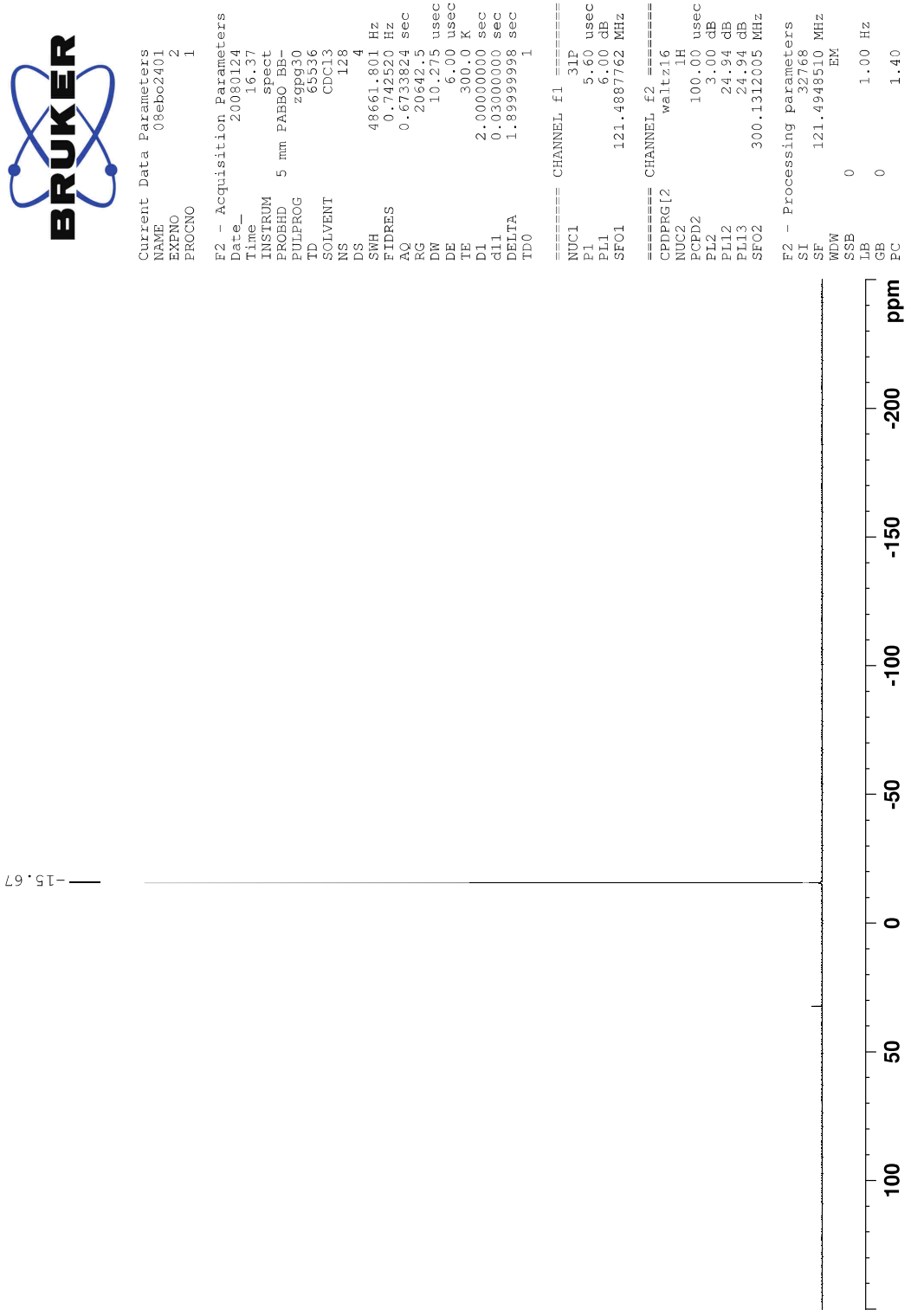
^{13}C NMR (75.4 MHz, $CDCl_3$) spectrum for **14a**



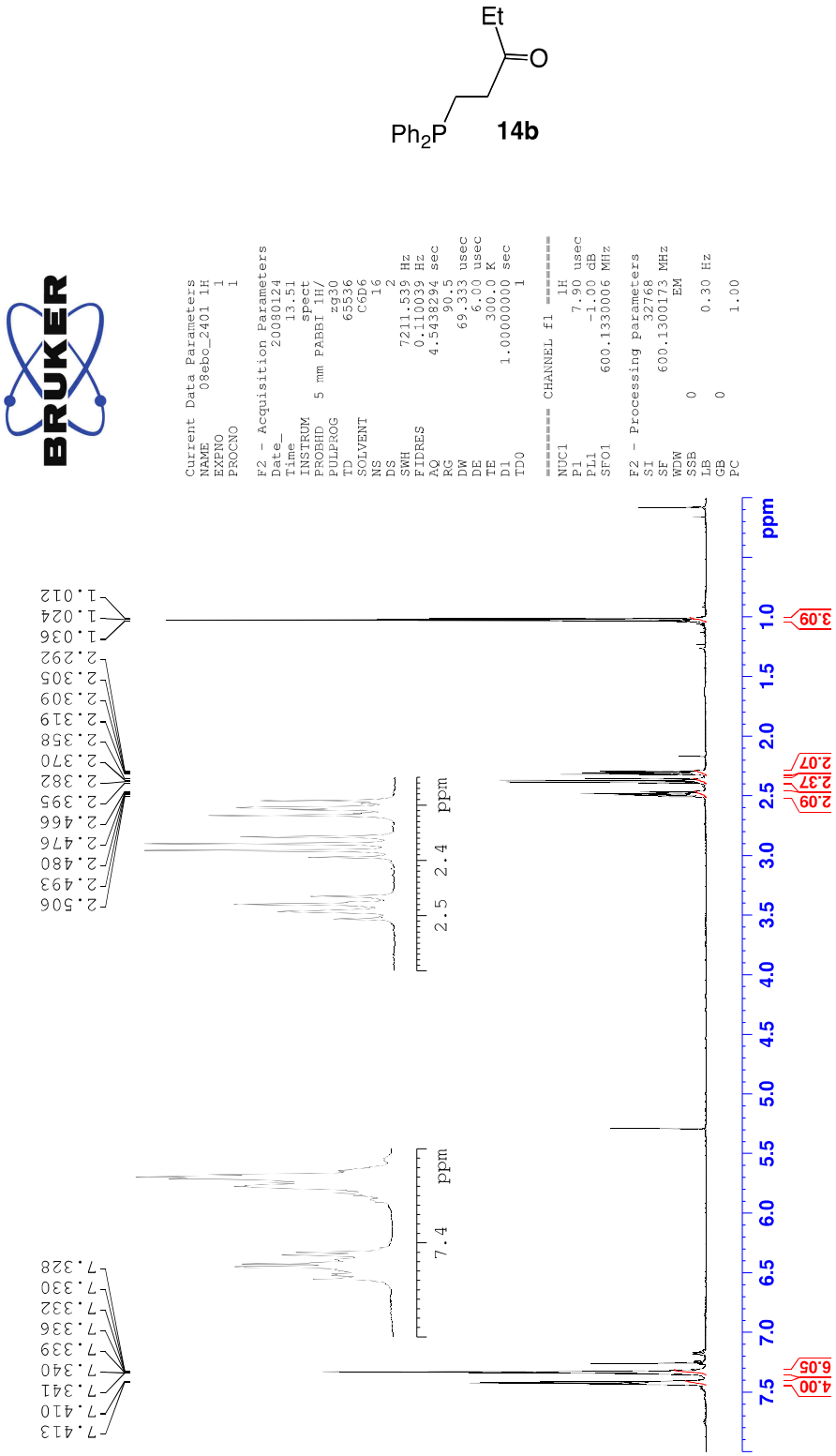


^{31}P NMR (121.4 MHz, $CDCl_3$) spectrum for **14a**

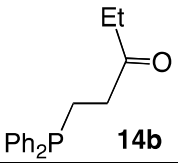




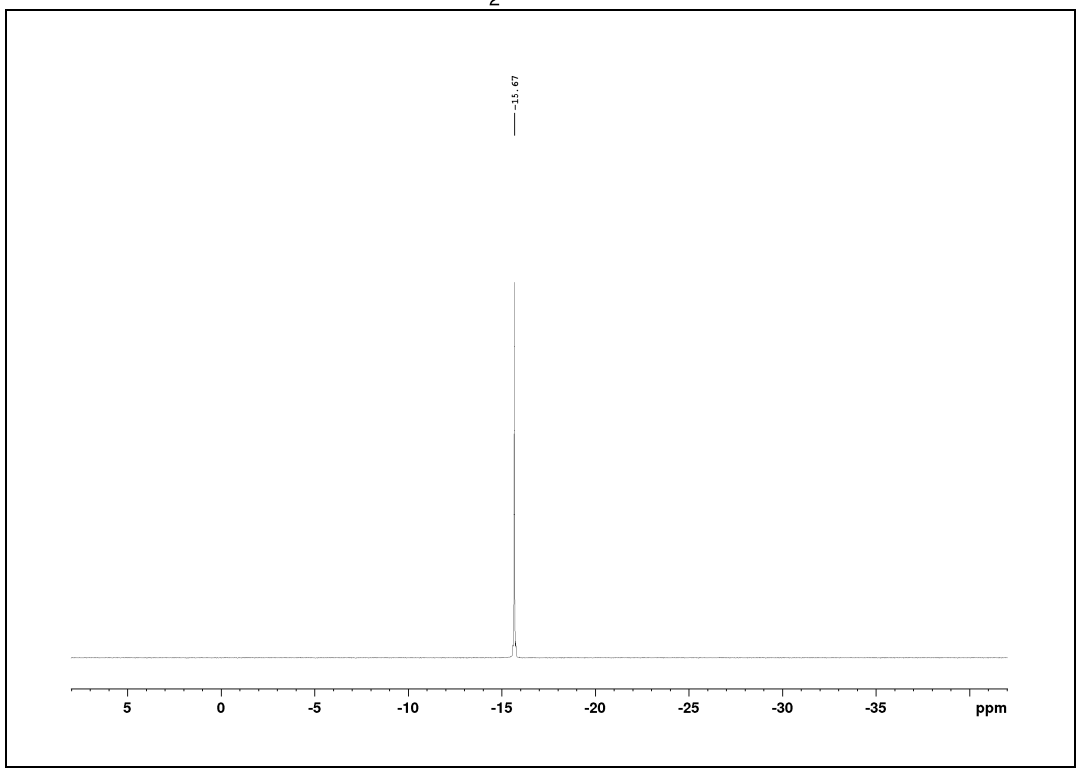
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **14b**



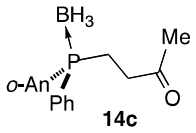
^{31}P NMR (121.4 MHz, $CDCl_3$) spectrum for **14b**



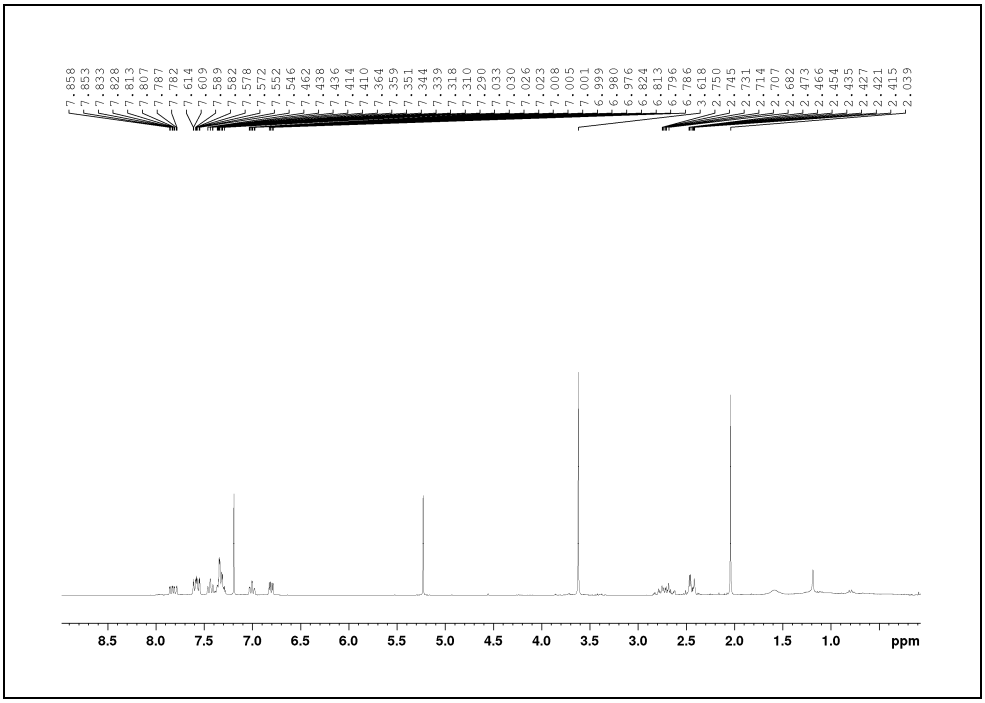
14b



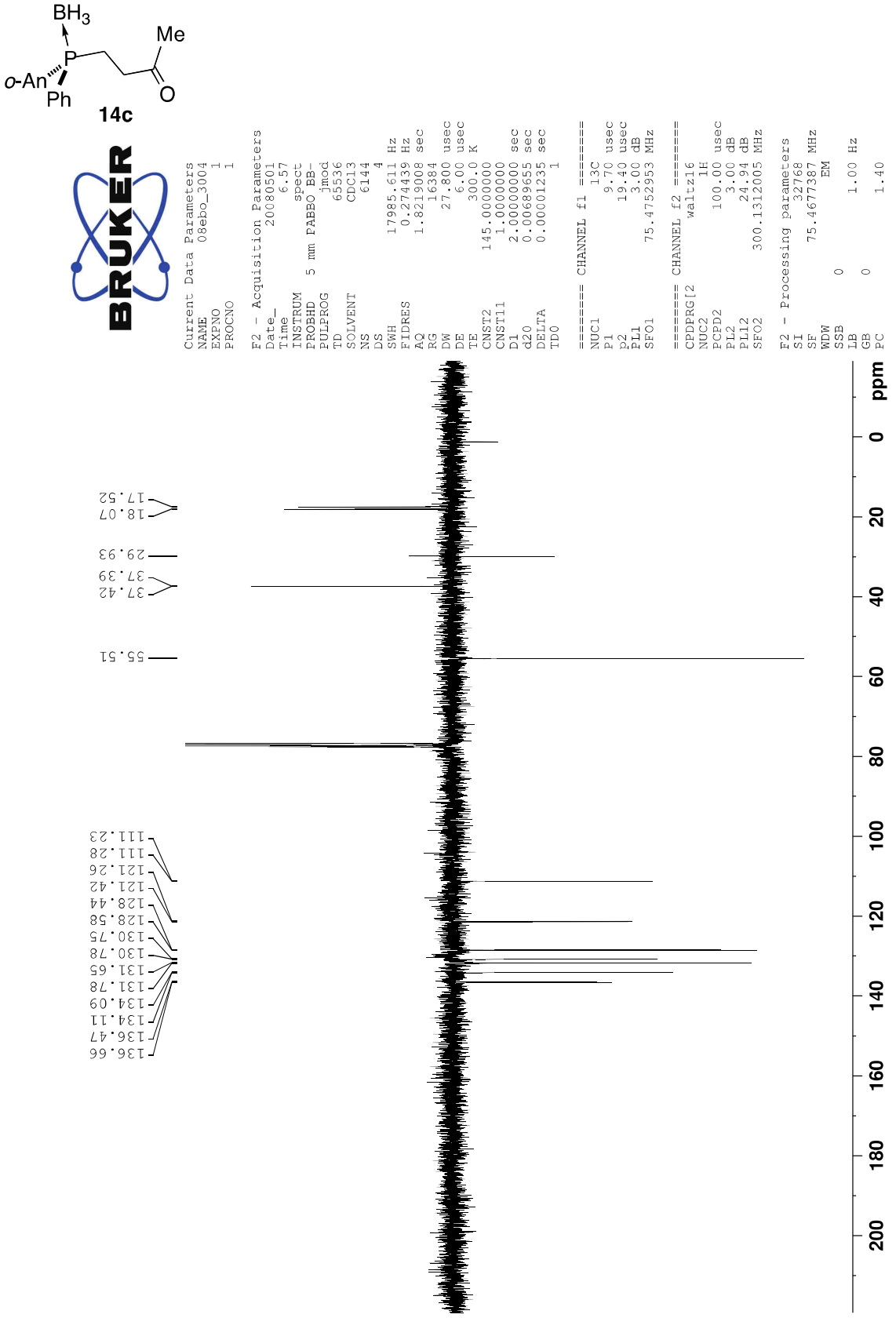
^{1}H NMR (300 MHz, $CDCl_3$) spectrum for **14c**



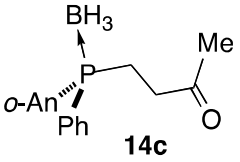
14c



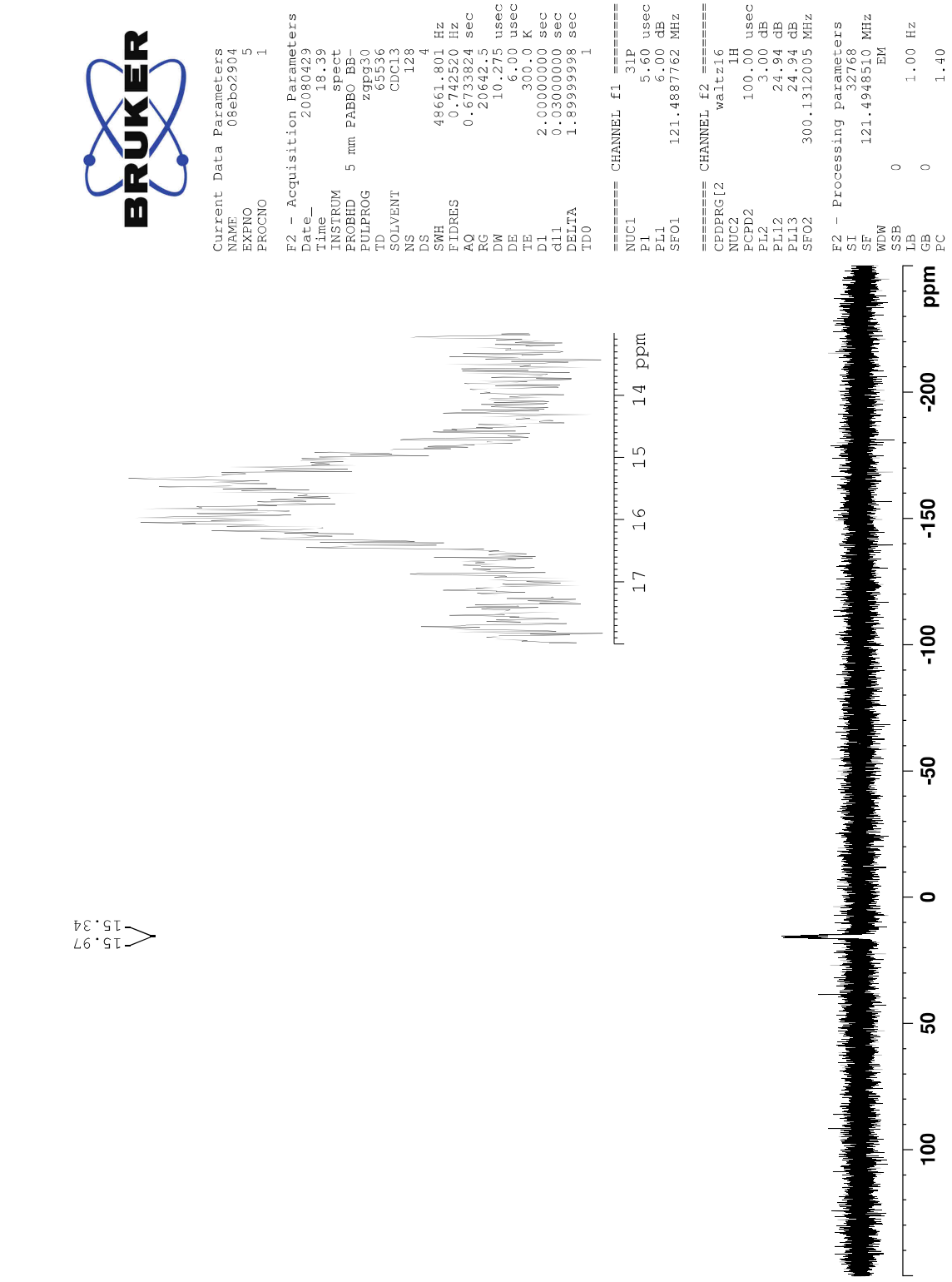
^{13}C NMR (75.4 MHz, $CDCl_3$) spectrum for **14c**



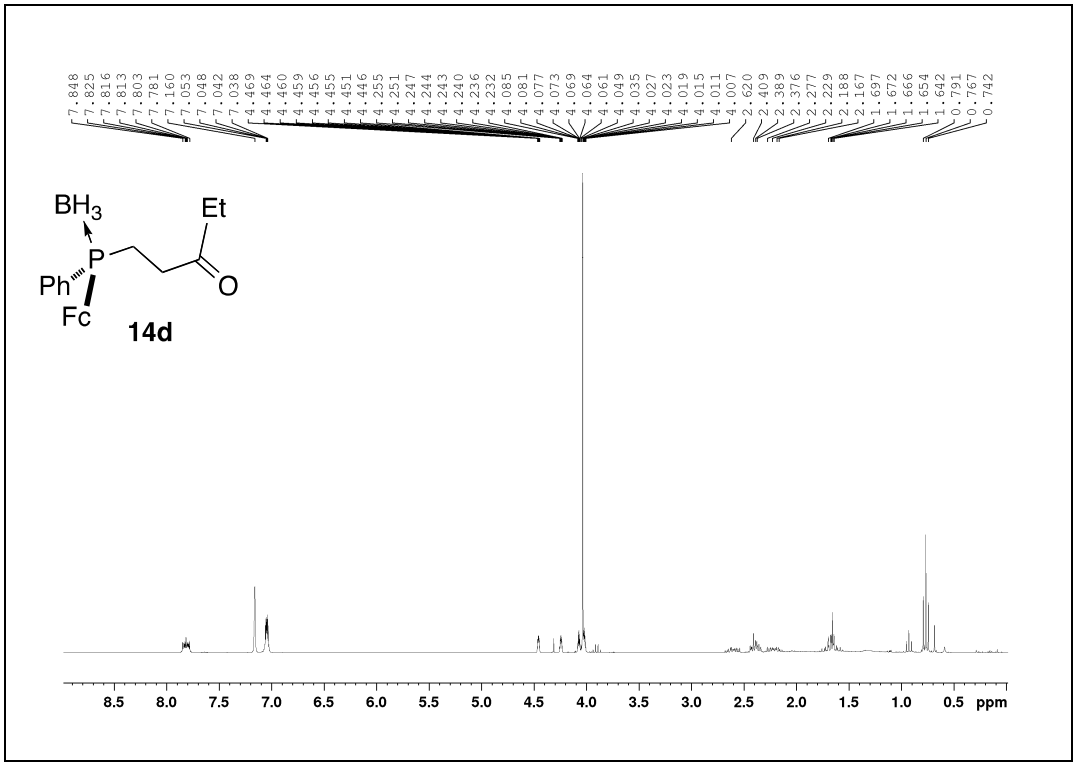
^{31}P NMR (121.4 MHz, $CDCl_3$) spectrum for **14c**



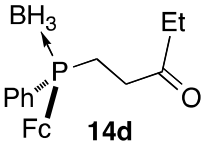
14c

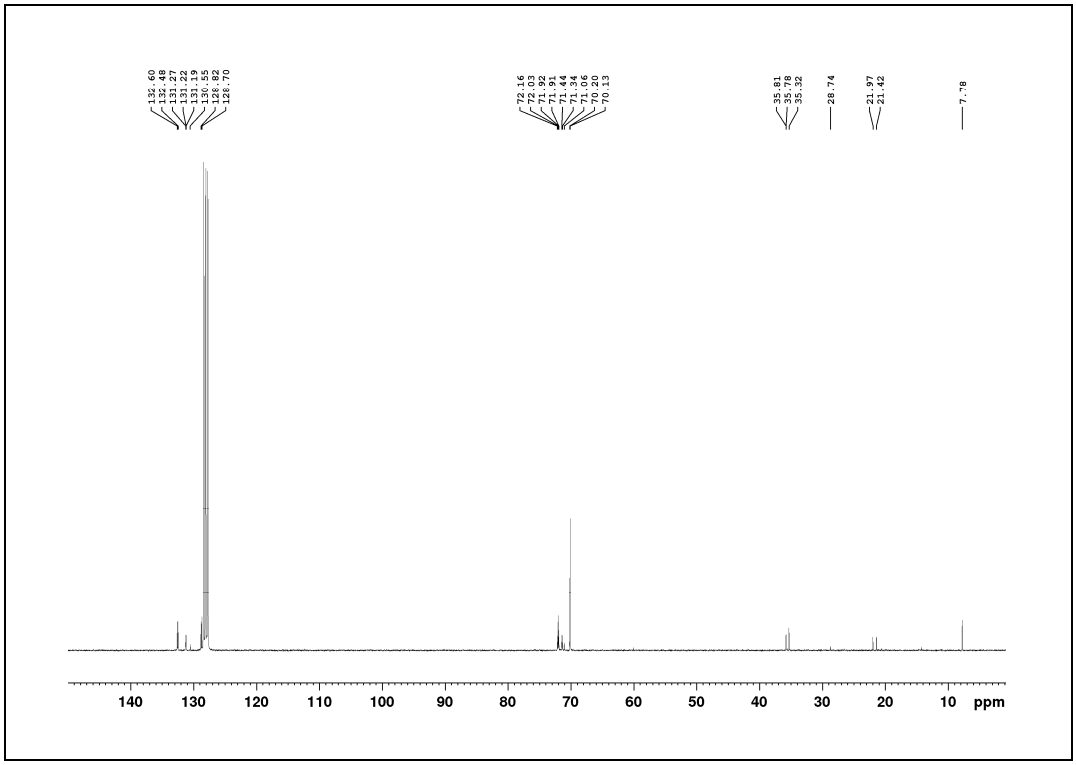


^{1}H NMR (300 MHz, C_6D_6) spectrum for **14d**

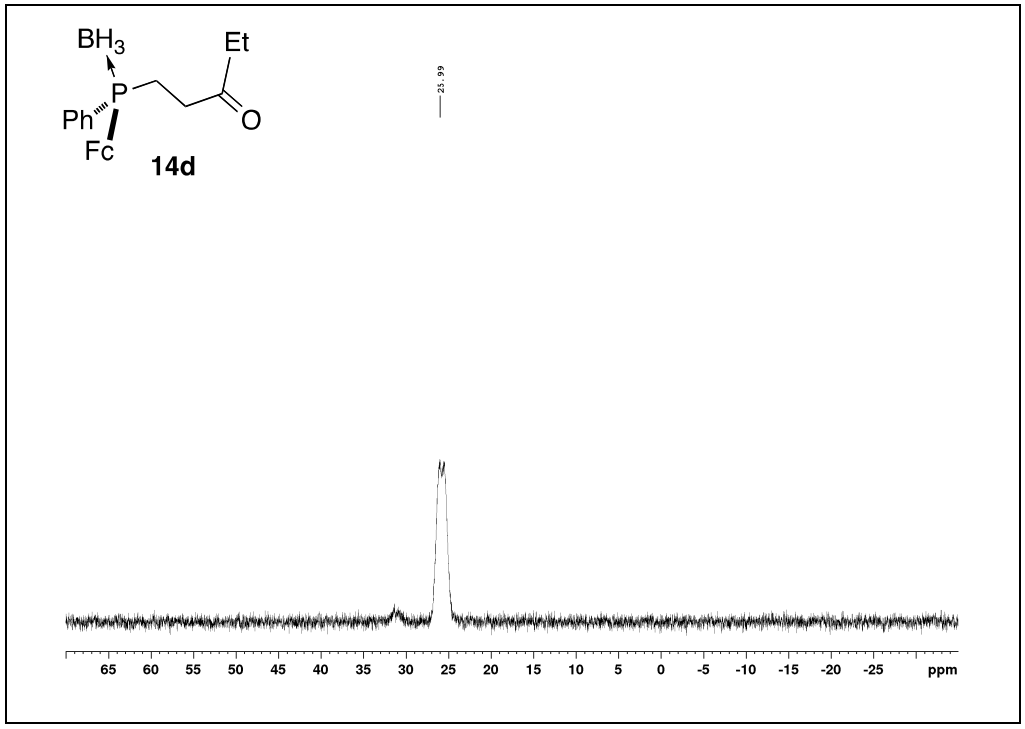


^{13}C NMR (75.4 MHz, C_6D_6) spectrum for **14d**

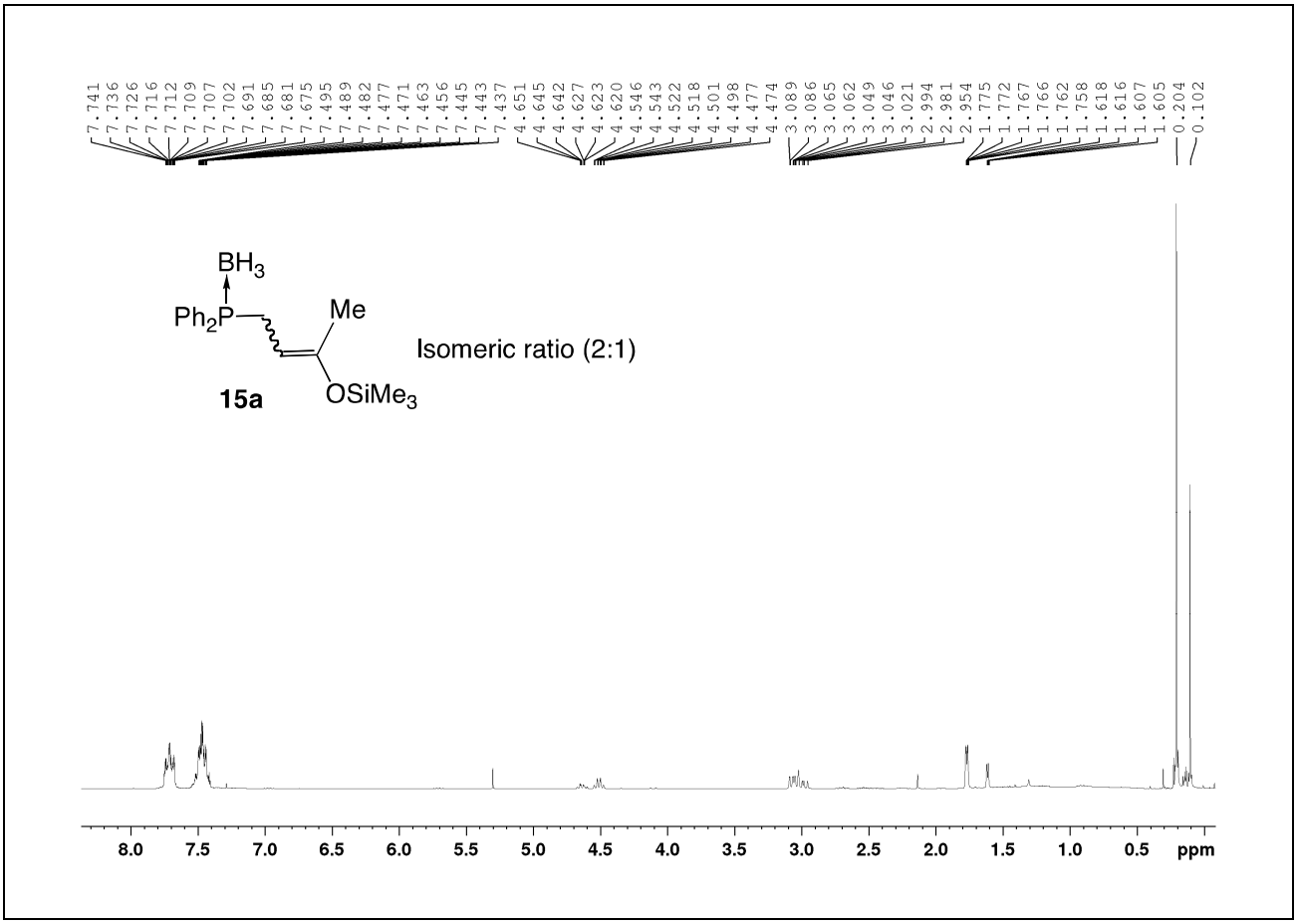




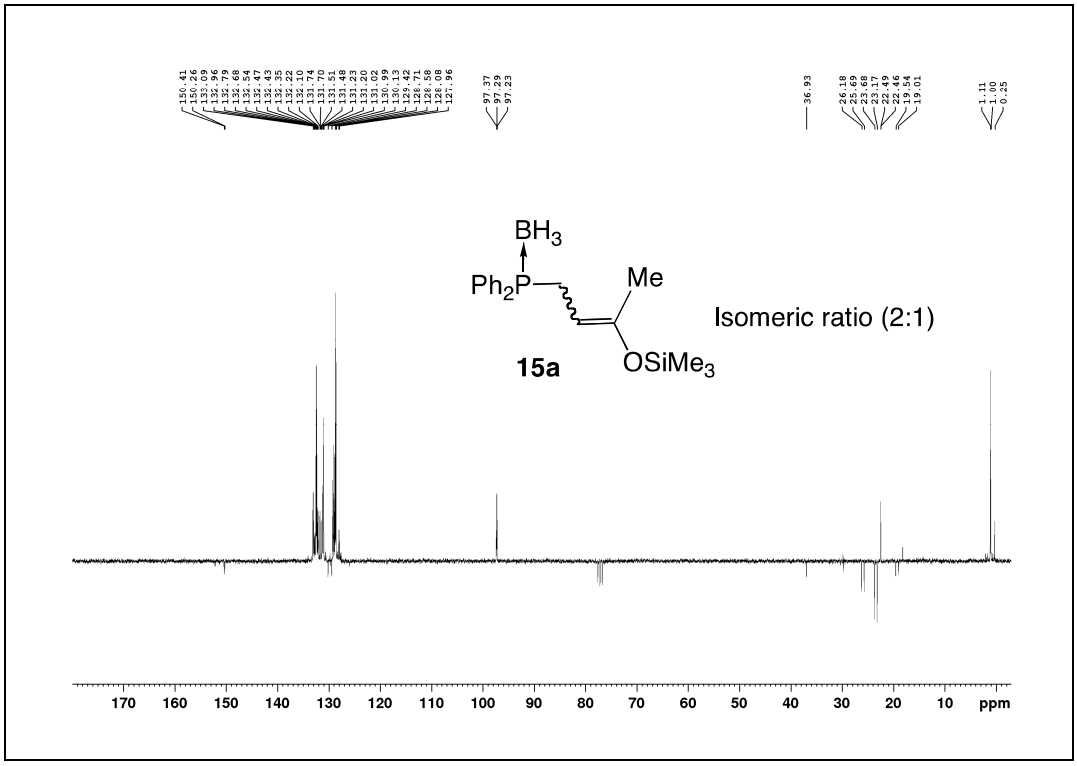
^{31}P NMR (121.4 MHz, C_6D_6) spectrum for **14d**



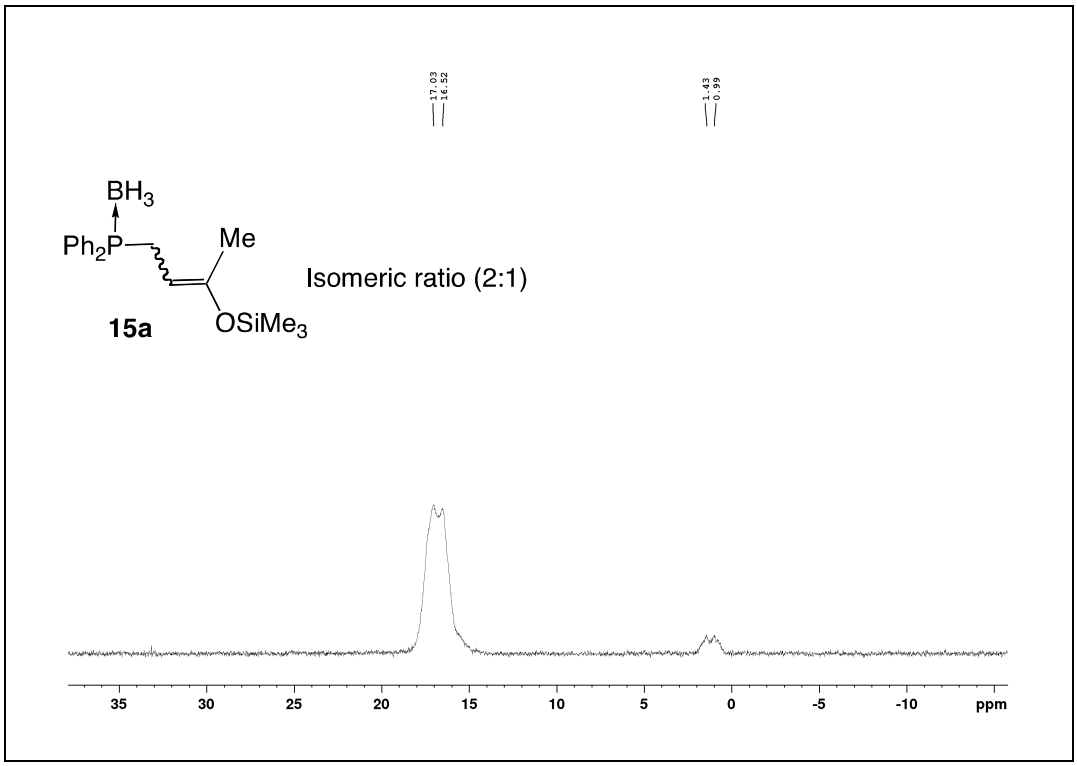
^{1}H NMR (300 MHz, $CDCl_3$) spectrum for **15a**



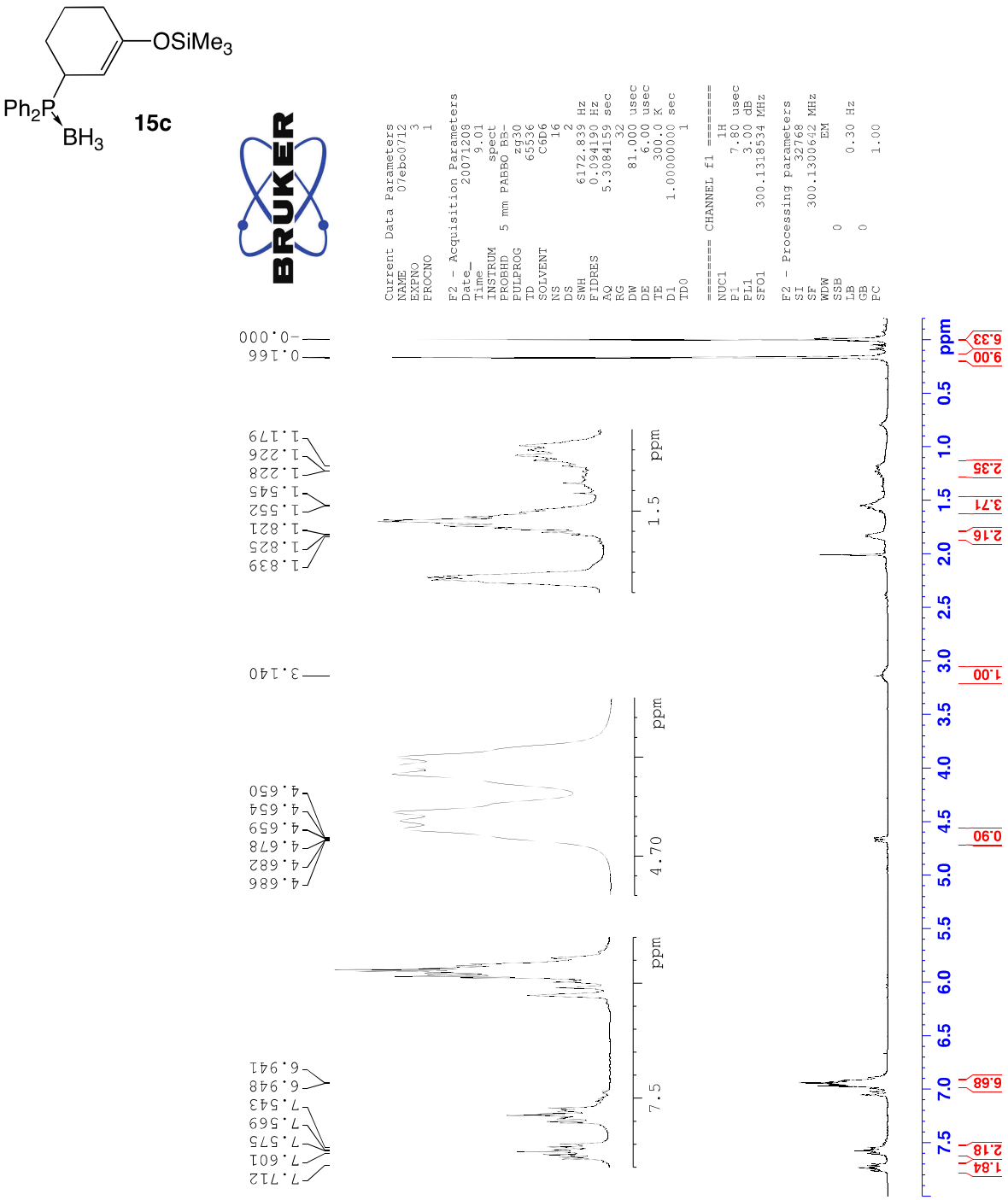
^{13}C NMR (75.4 MHz, $CDCl_3$)) spectrum for **15a**



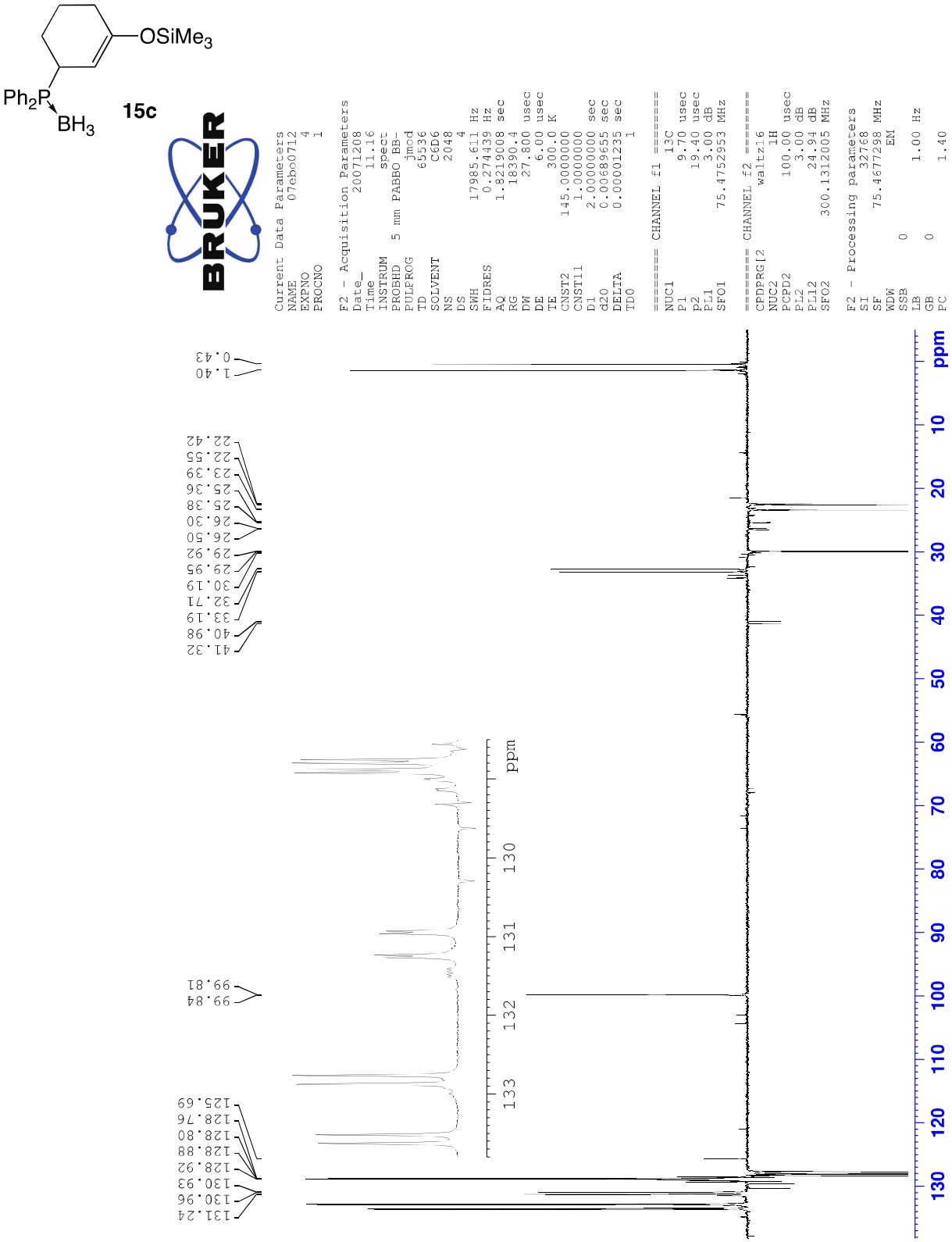
^{31}P NMR (121.4 MHz, $CDCl_3$) spectrum for **15a**



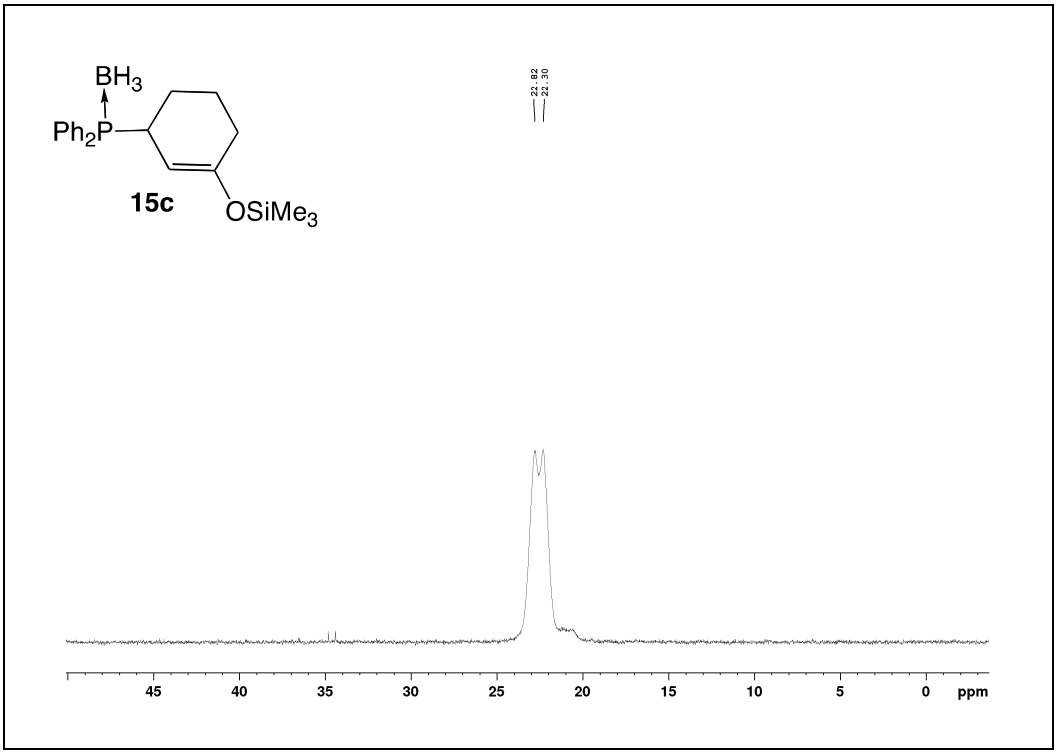
^{1}H NMR (300 MHz, C_6D_6) spectrum for **15c**



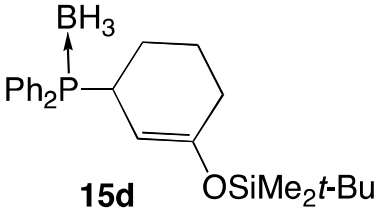
^{13}C NMR (75.4 MHz, C_6D_6) spectrum for **15c**

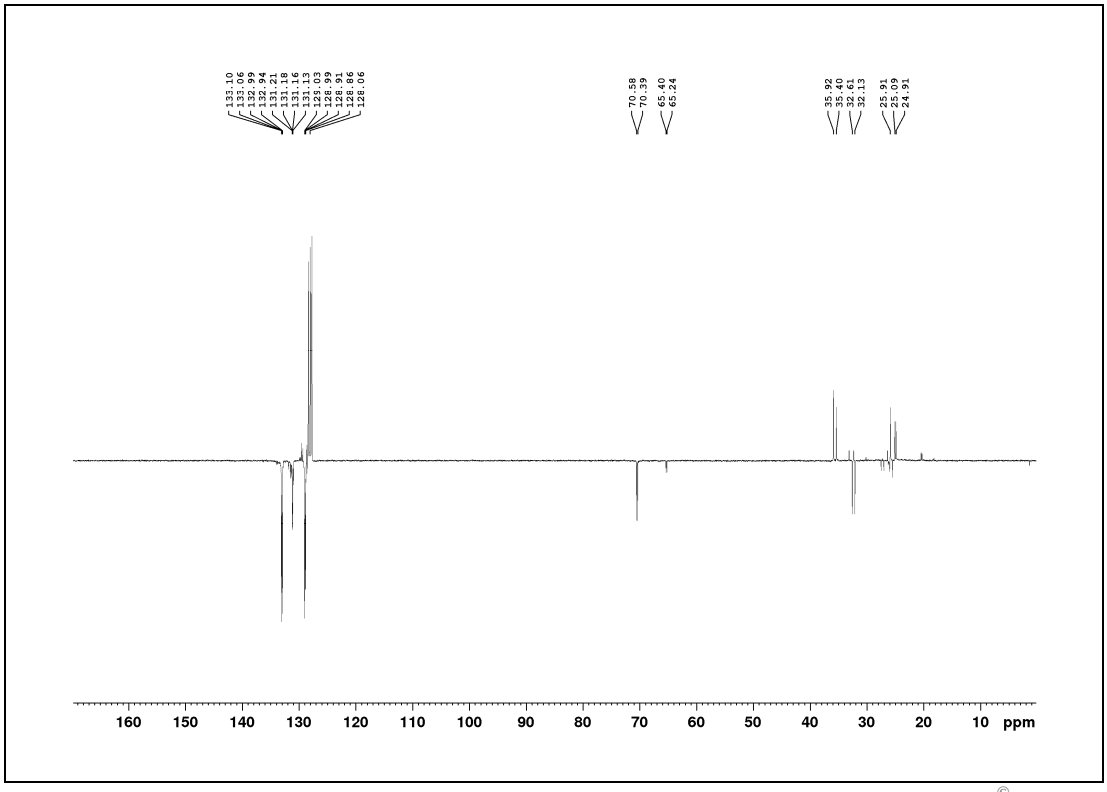


^{31}P NMR (121.4 MHz, C_6D_6) spectrum for **15c**

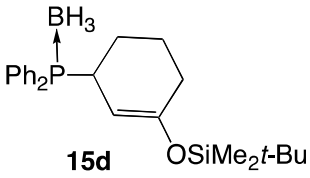


^{13}C NMR (75.4 MHz, C_6D_6) spectrum for **15d**

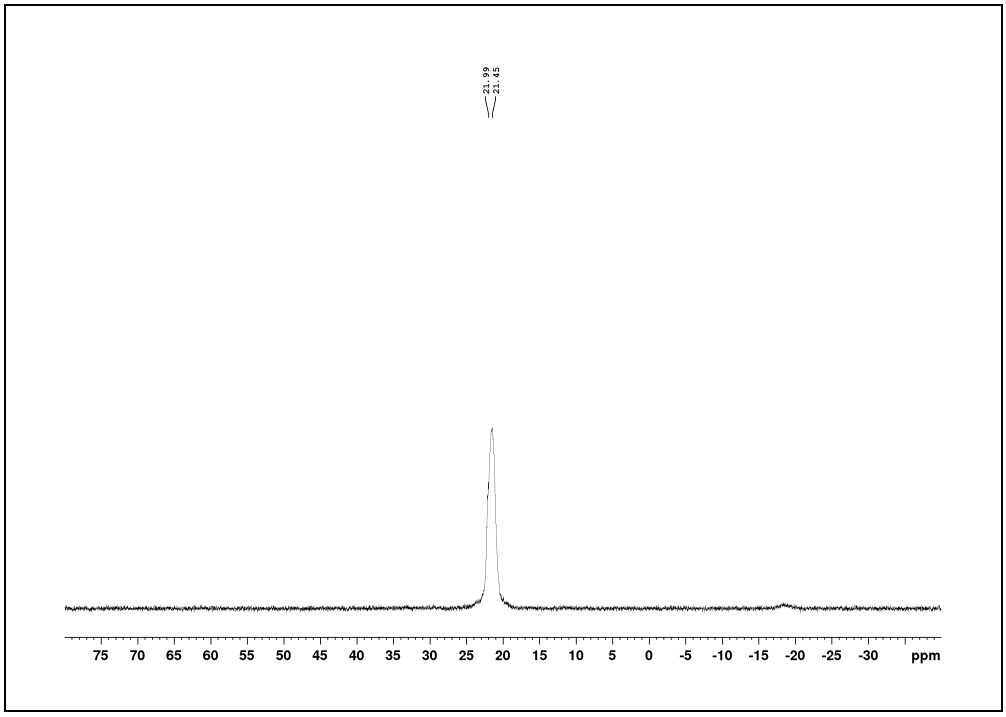




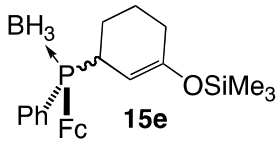
^{31}P NMR (121.4 MHz, C_6D_6) spectrum for **15d**



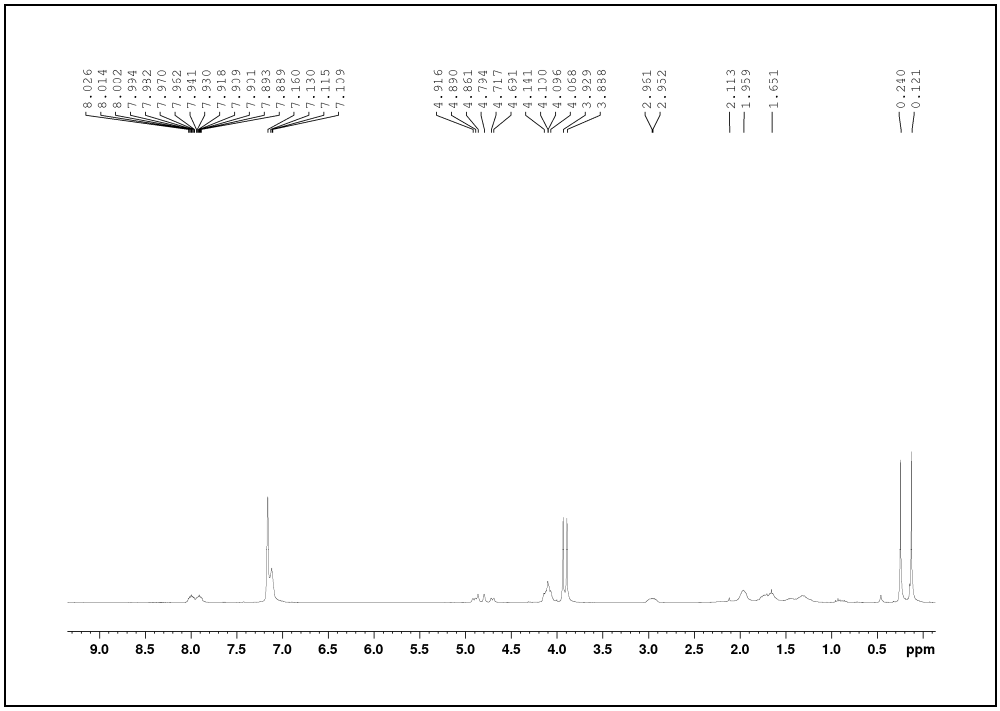
15d



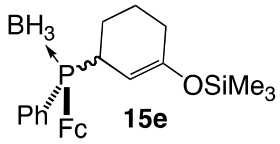
^{1}H NMR (300 MHz, C_6D_6) spectrum for **15e**

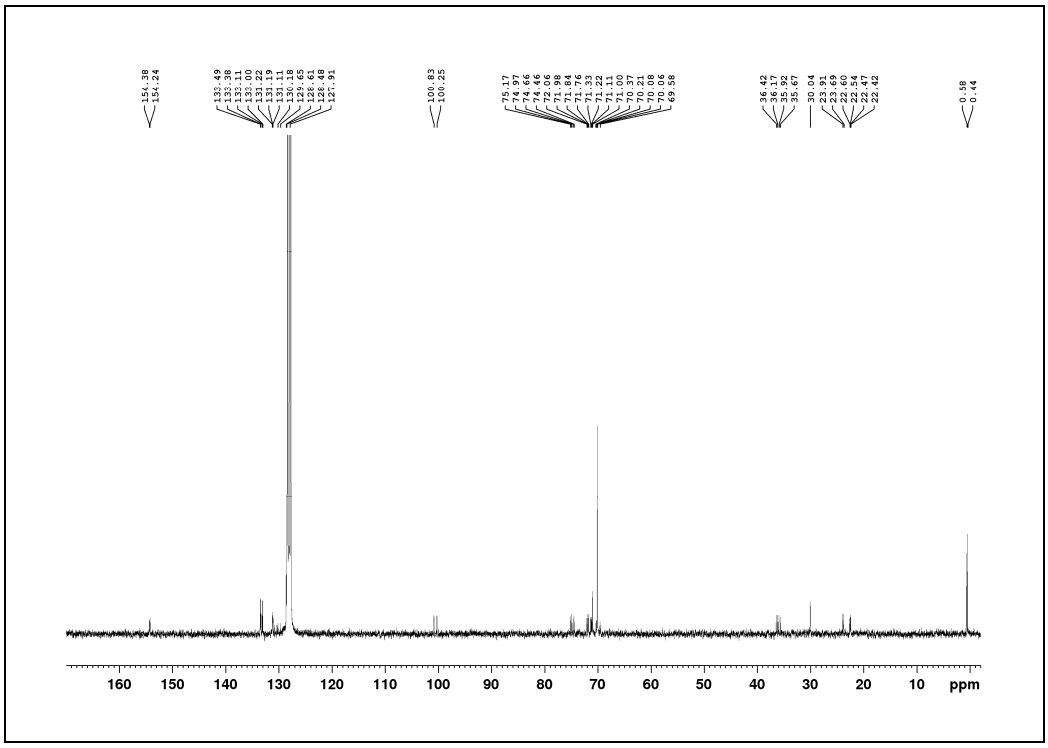


15e

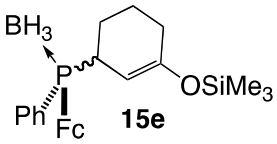


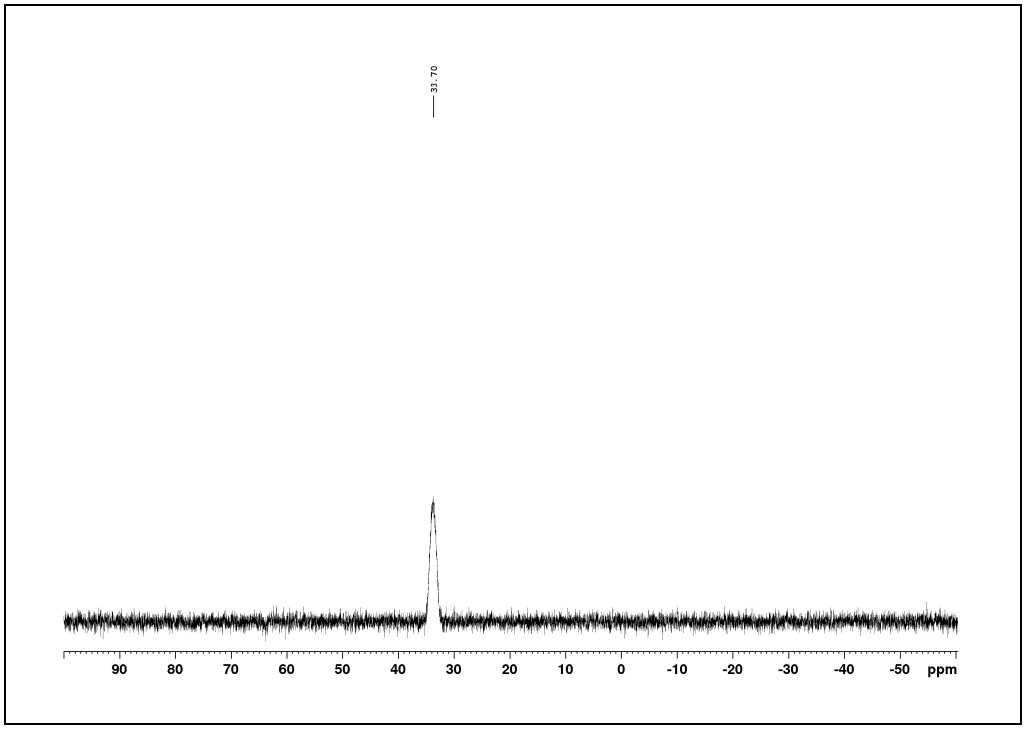
^{13}C NMR (75.4 MHz, C_6D_6) spectrum for **15e**



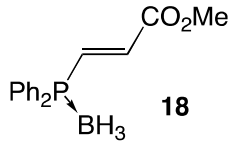


^{31}P NMR (121.4 MHz, $CDCl_3$) spectrum for **15e**





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



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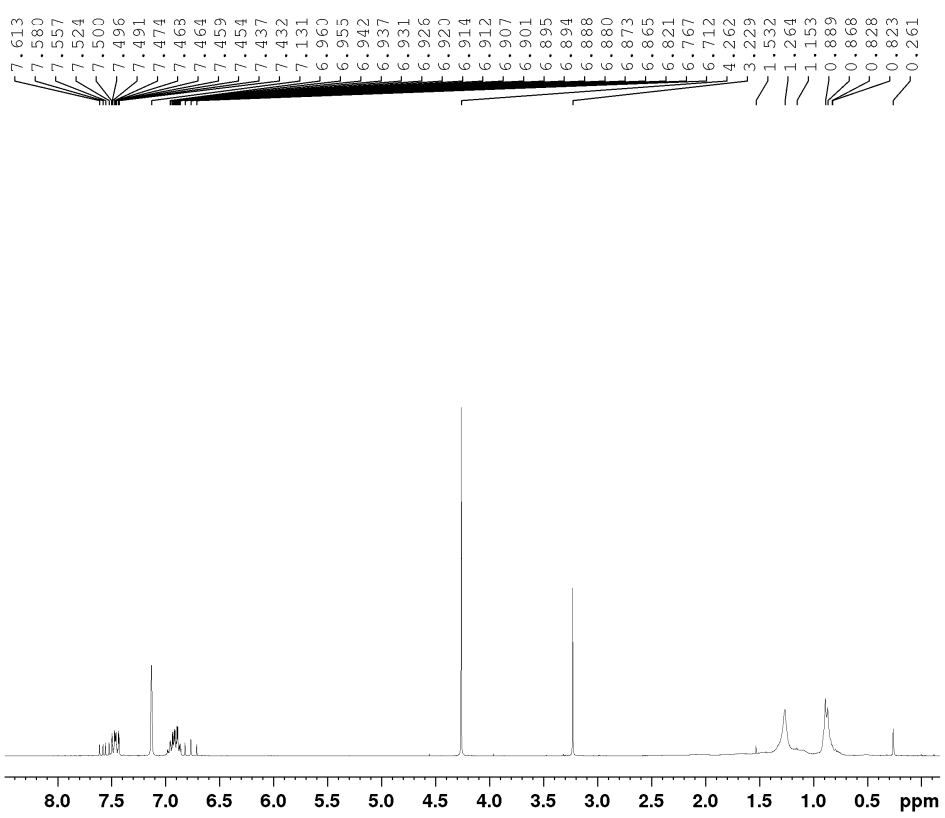


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PL1                3.00 dB
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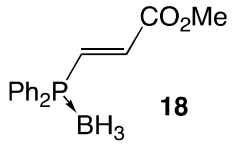
^{13}C NMR (75.4 MHz, C_6D_6) spectrum for **18**



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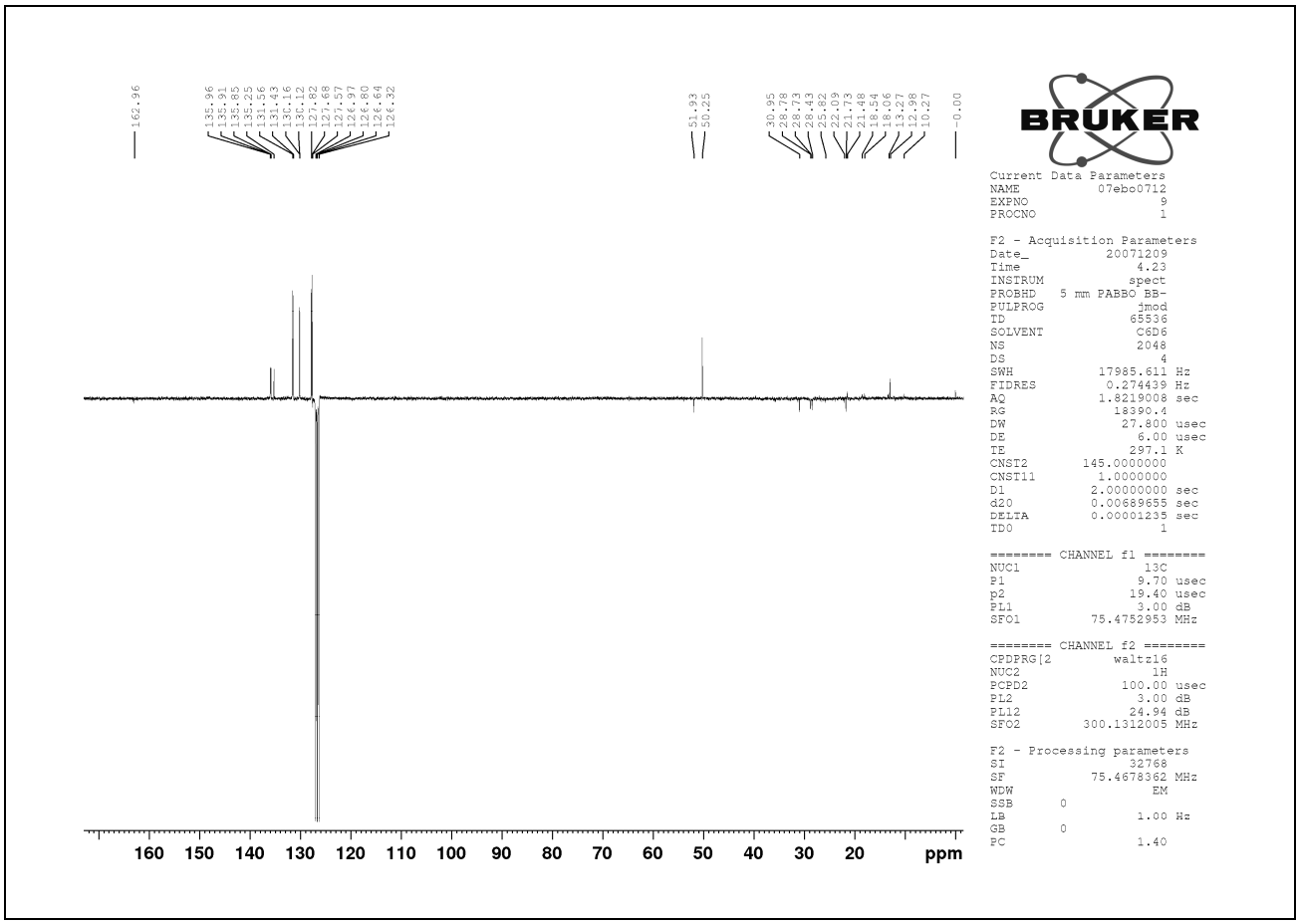
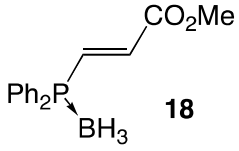


^{31}P NMR (202.4 MHz, $CDCl_3$) spectrum for **18**



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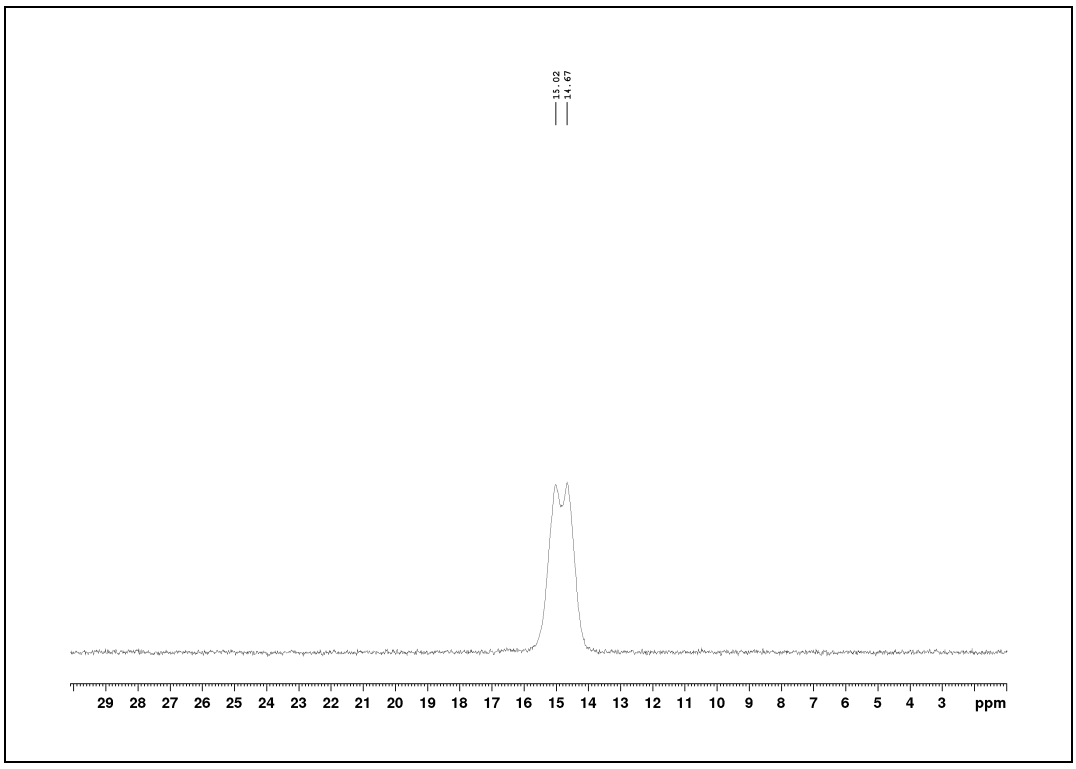
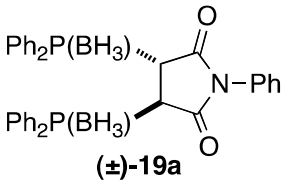
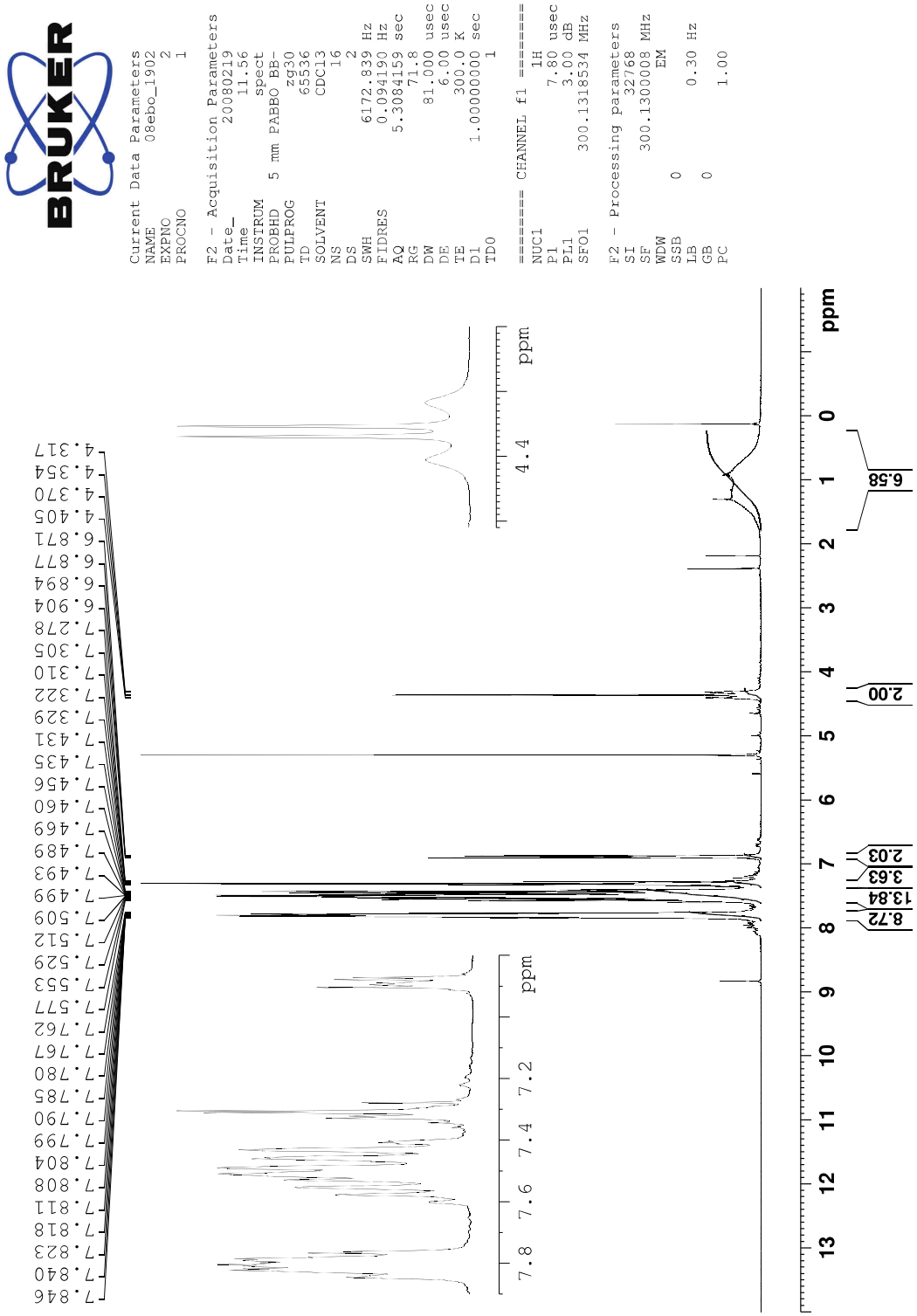


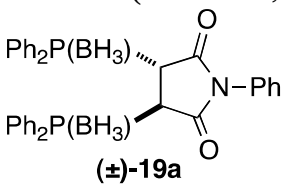
^{1}H NMR (300 MHz, $CDCl_3$) spectrum for **19a**



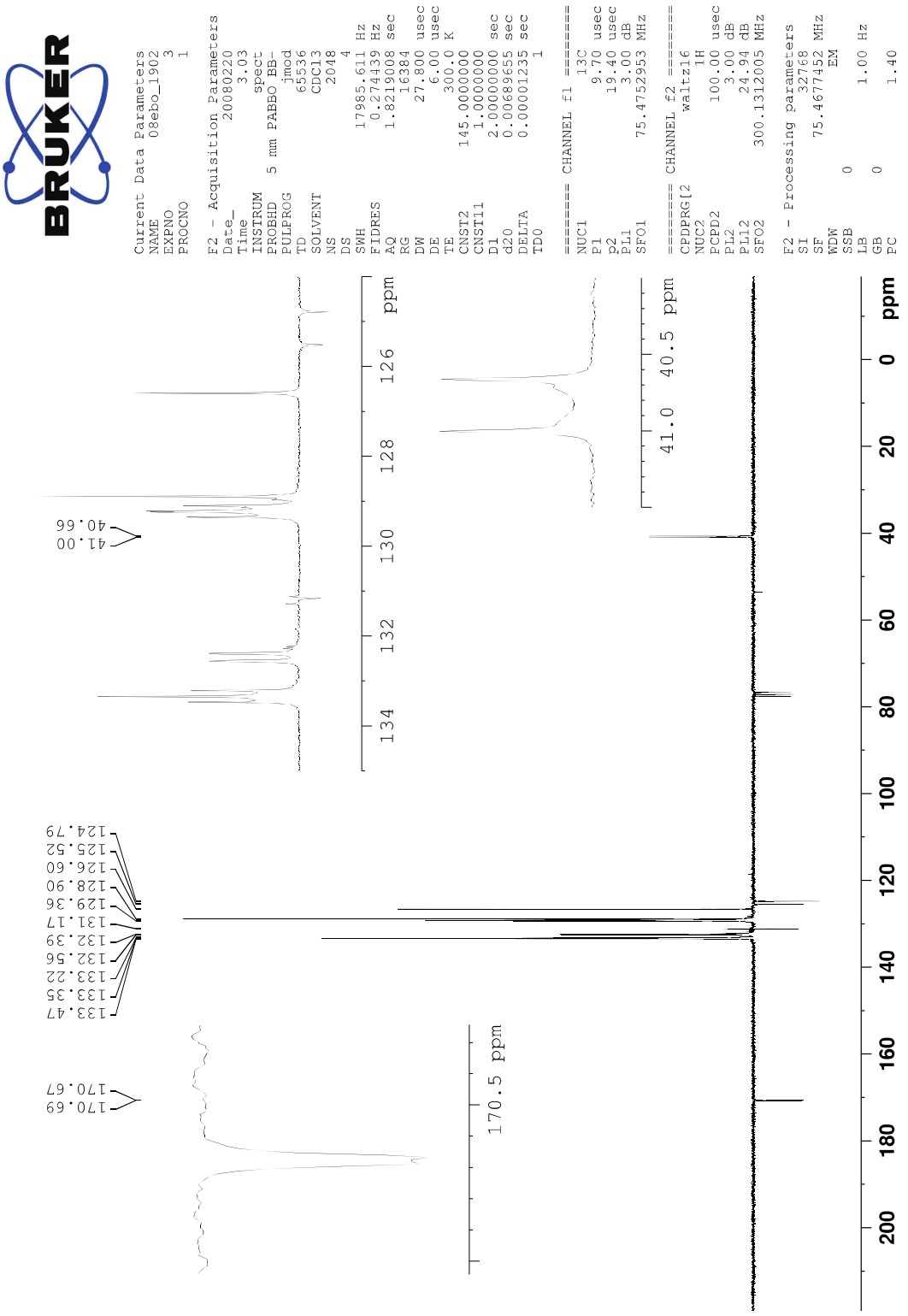
(±)-19a



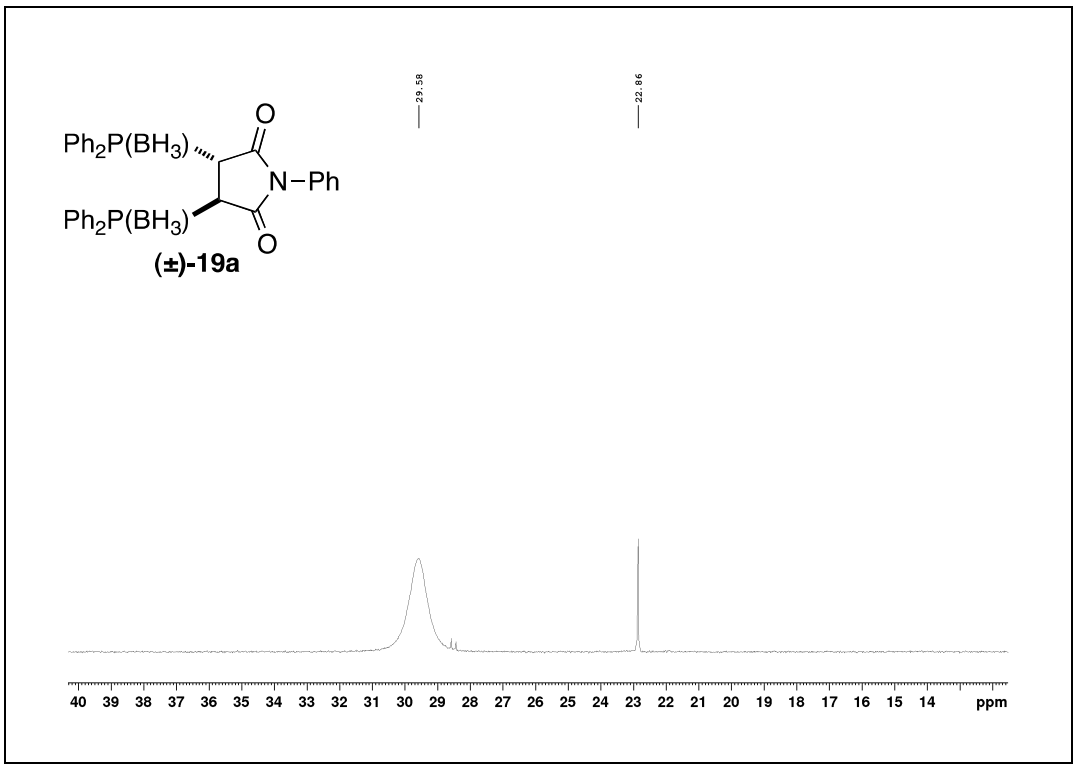
^{13}C NMR (75.4 MHz, $CDCl_3$) spectrum for **19a**



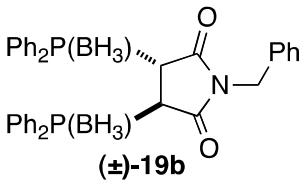
(±)-19a



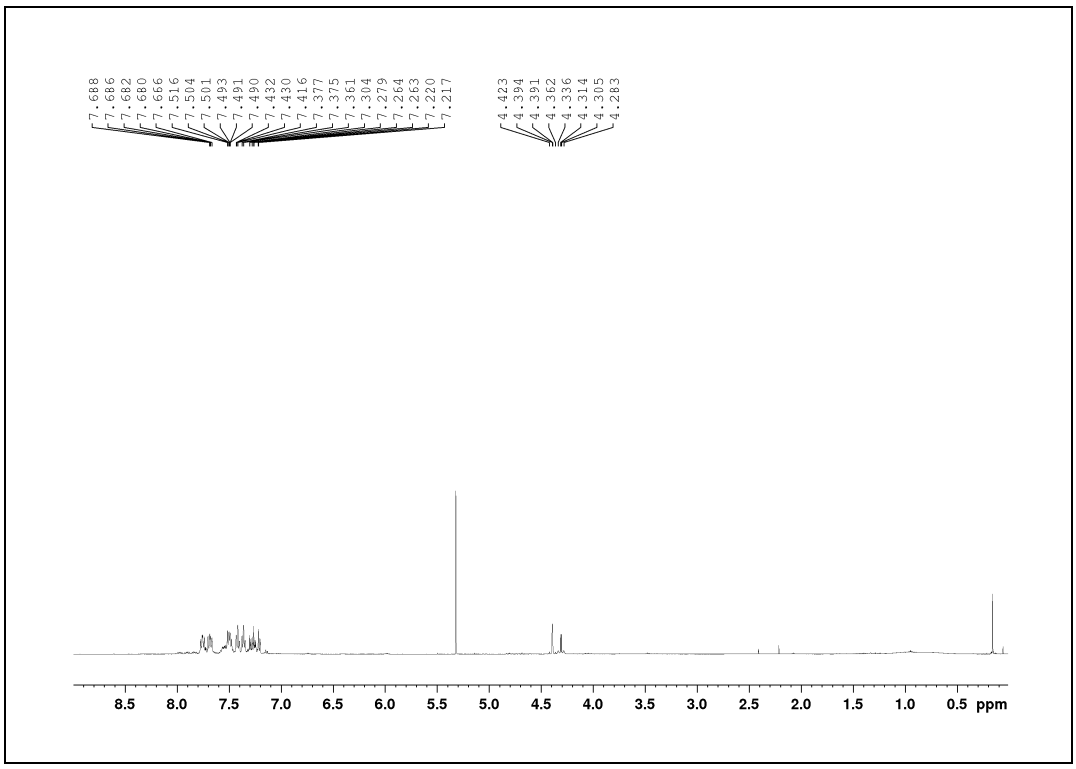
^{31}P NMR (121.4 MHz, $CDCl_3$) spectrum for **19a**



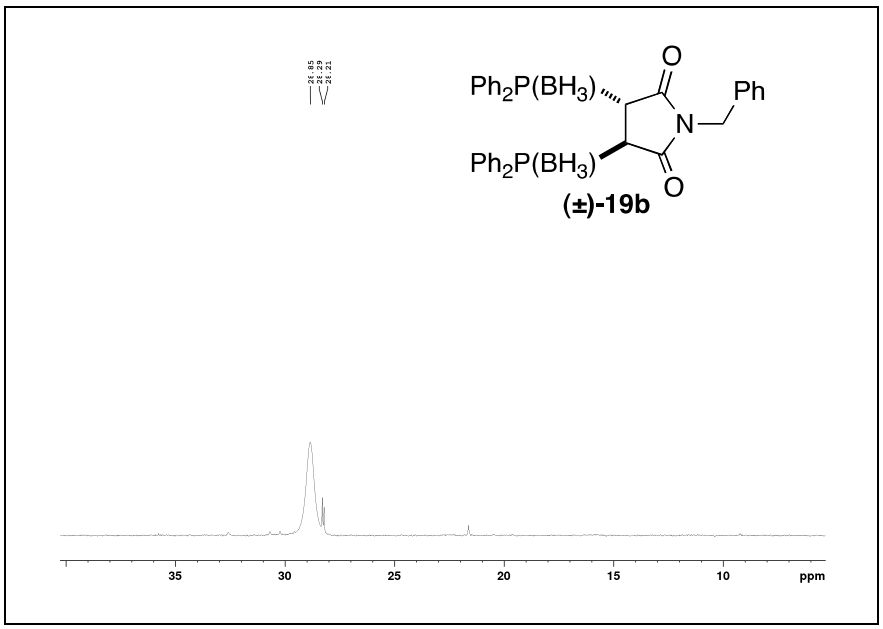
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **19b**



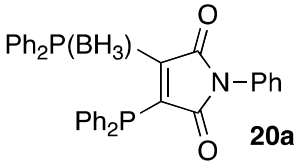
(±)-19b



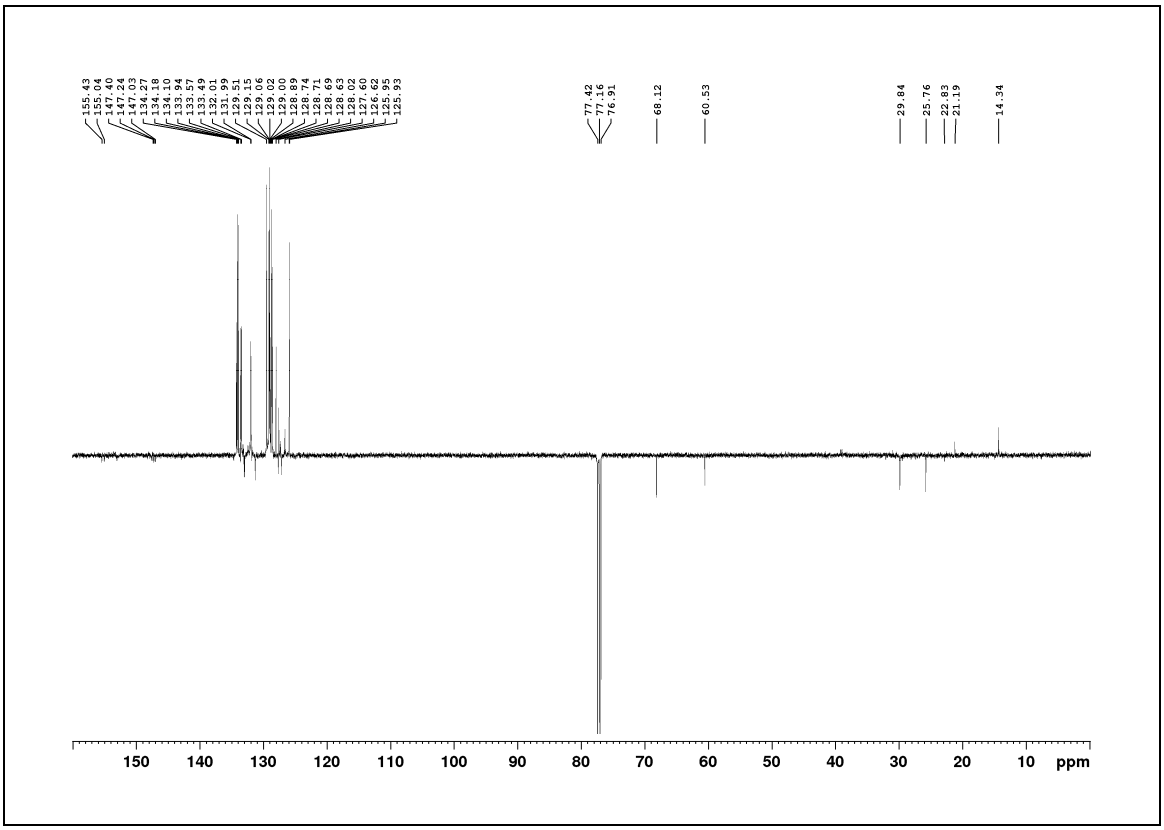
^{31}P NMR (202.4 MHz, $CDCl_3$) spectrum for **19b**



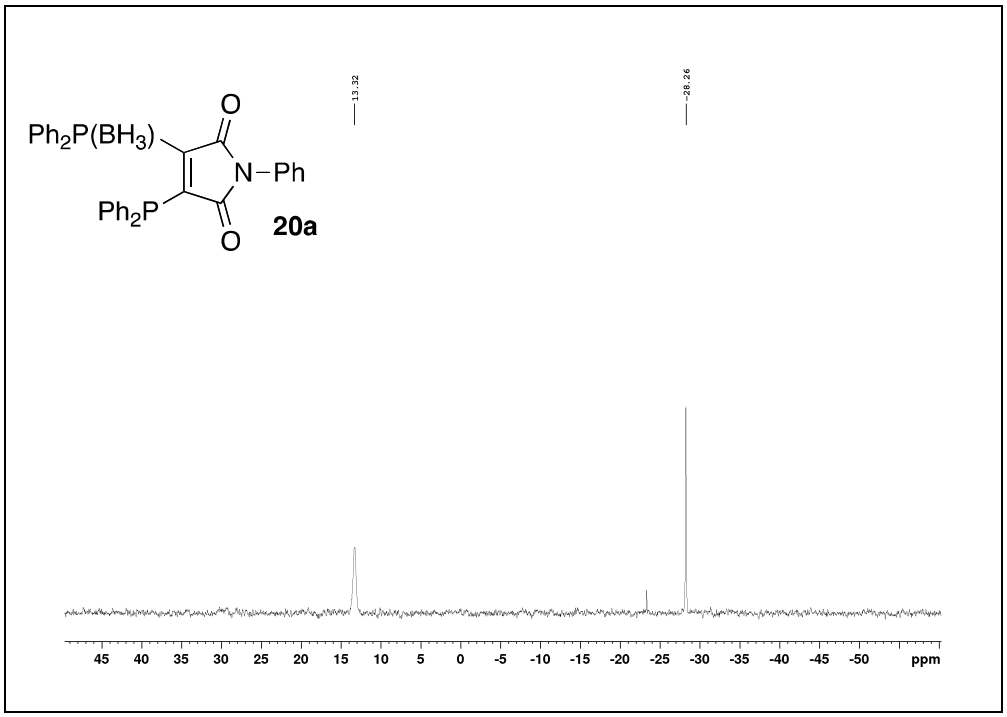
^{13}C NMR (125.8 MHz, $CDCl_3$) spectrum for **20a**



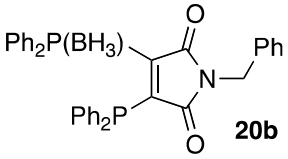
20a

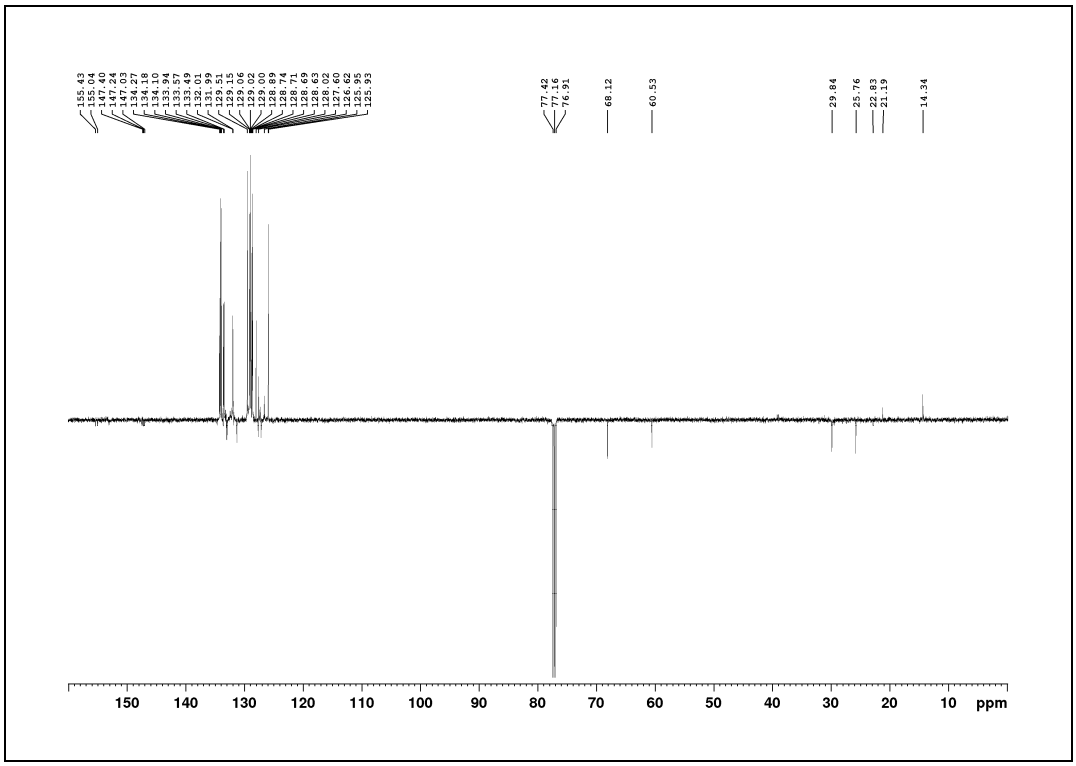


^{31}P NMR (202.4 MHz, $CDCl_3$) spectrum for **20a**

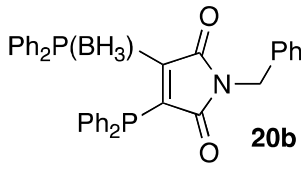


^{13}C NMR (150.9 MHz, $CDCl_3$) spectrum for **20b**

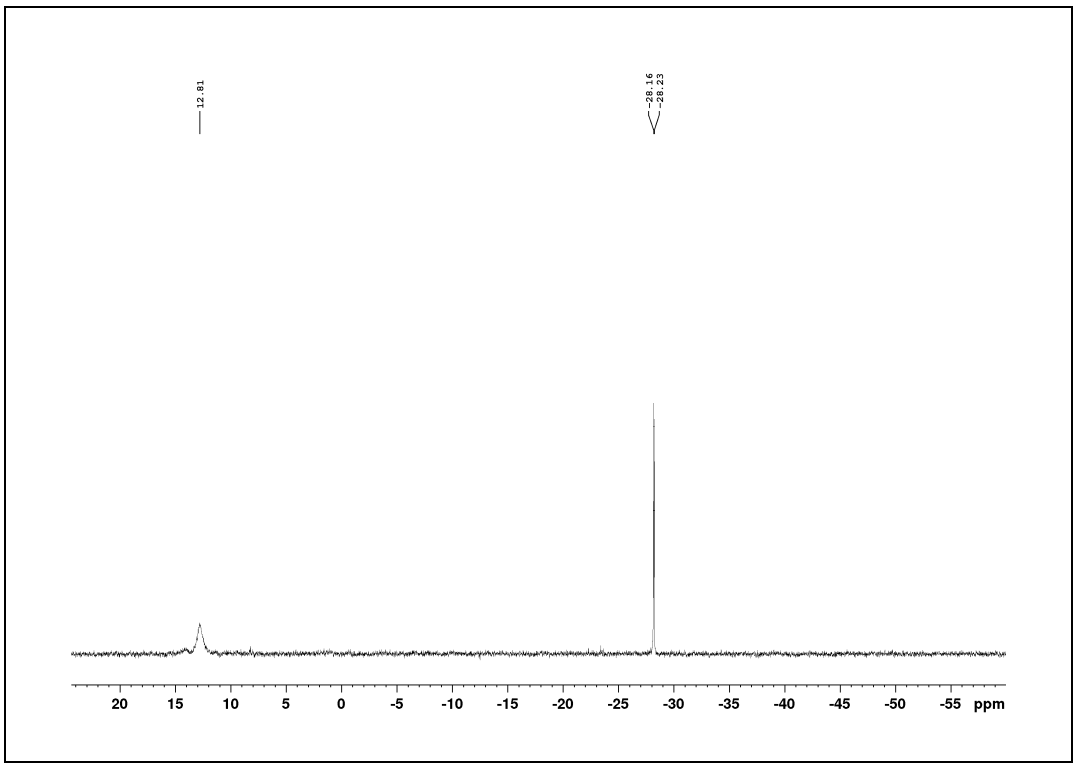




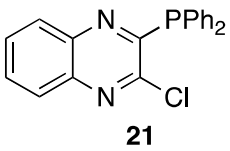
^{31}P NMR (121.4 MHz, $CDCl_3$) spectrum for **20b**



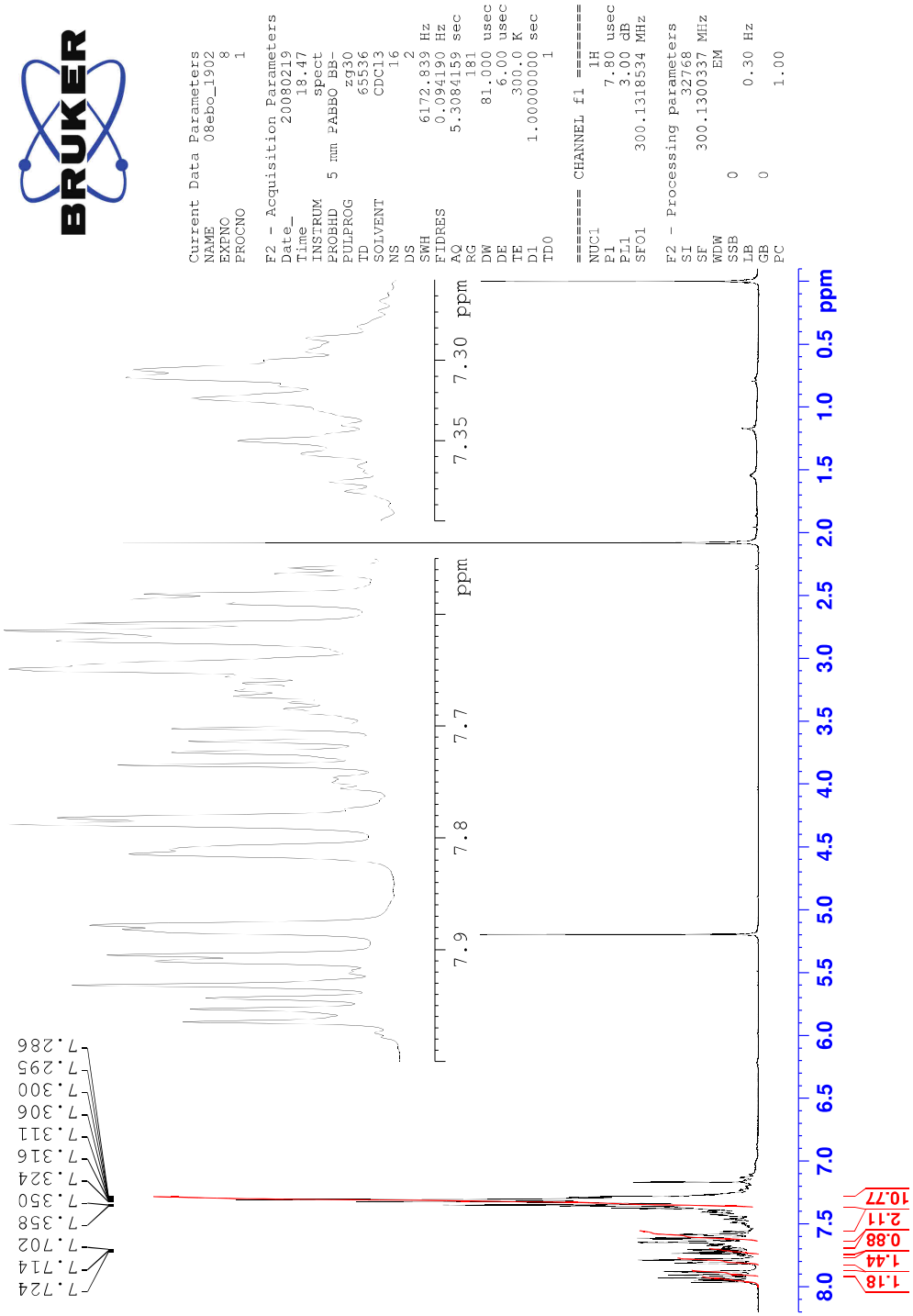
20b



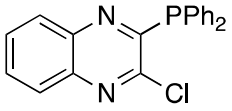
^{1}H NMR (300 MHz, $CDCl_3$) spectrum for **21**



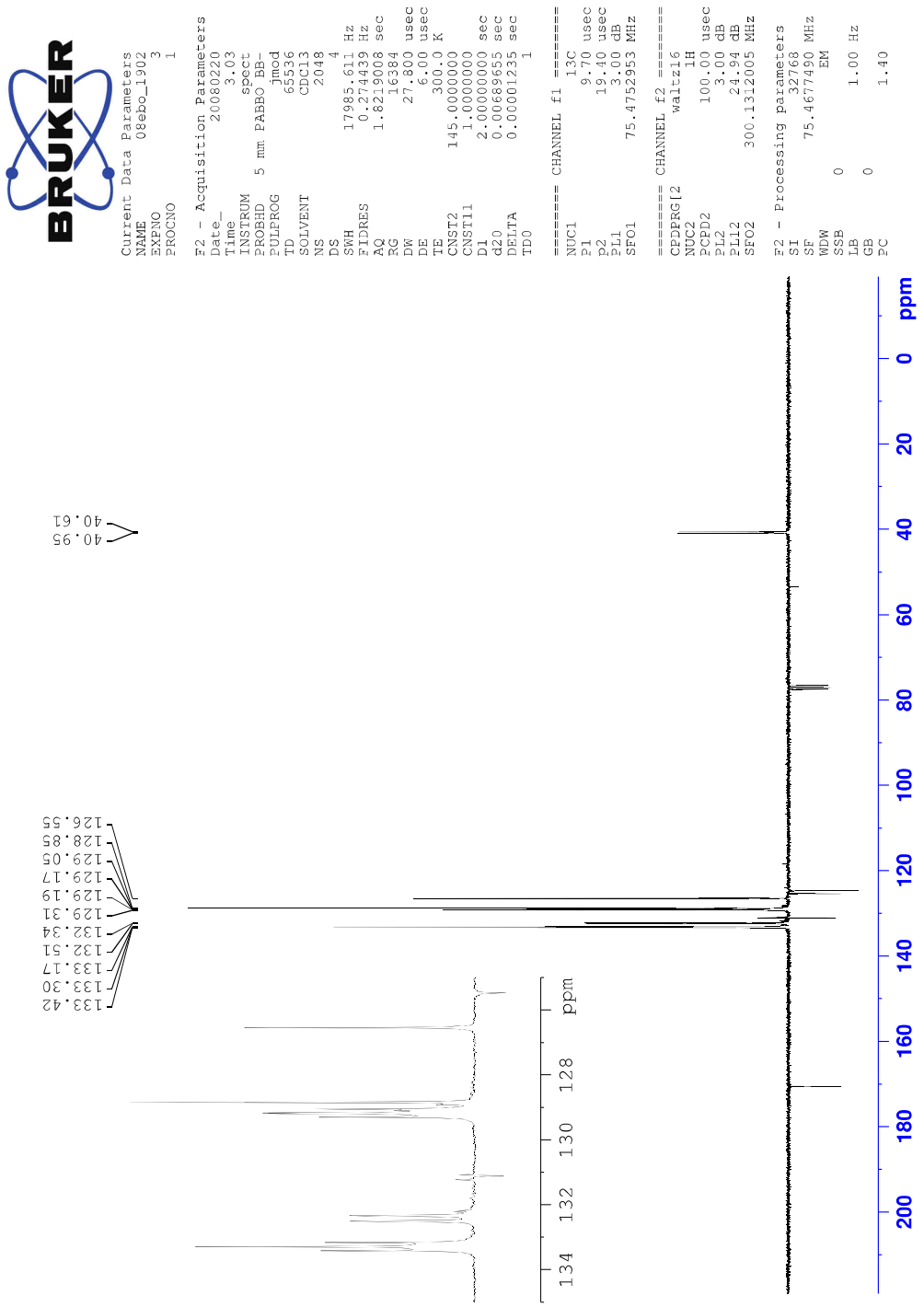
21



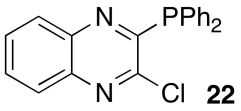
^{13}C NMR (75.4 MHz, $CDCl_3$) spectrum for **21**



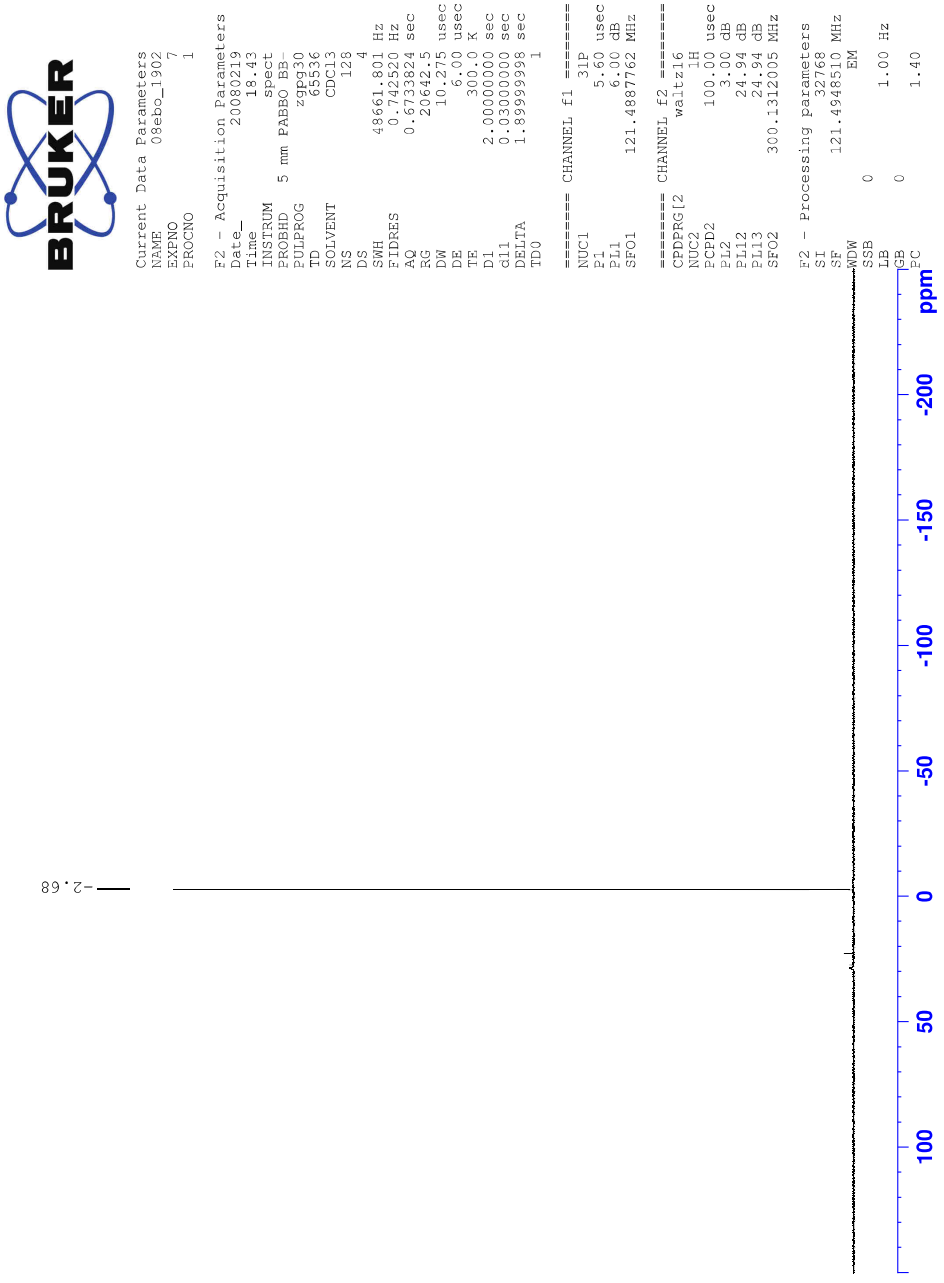
21



^{31}P NMR (121.4 MHz, $CDCl_3$) spectrum for **21**



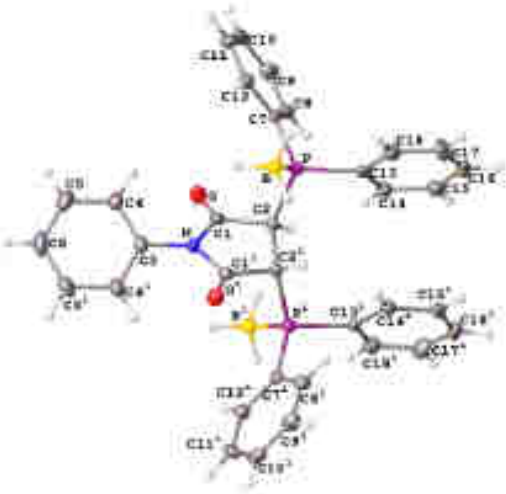
22



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 × 0.17 × 0.05 mm³) was kept at T = 115 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. $C_{34}H_{33}B_2NO_2P_2$, M_r = 571.17, monoclinic, C2/c (No. 15), a = 9.093(5) Å, b = 16.643(5) Å, c = 19.794(5) Å, β = 98.166(5)°, α = γ = 90°, V = 2965(2) Å³, T = 115 K, Z = 4, Z' = 0.5, μ (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	$C_{34}H_{33}B_2NO_2P_2$
$D_{calc.}$/ 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/Å	9.093(5)
b/Å	16.643(5)
c/Å	19.794(5)
α/°	90
β/°	98.166(5)
γ/°	90
V/Å³	2965(2)
Z	4
Z'	0.5
Θ_{min}/°	3.100
Θ_{max}/°	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 × 0.17 × 0.05 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 φ and ω 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 $\theta = 27.453$. 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 (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **19a**. U_{eq} is defined as 1/3 of 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 (×10⁴) **19a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka^*b^*U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	21.1(10)	19.9(11)	15.6(9)	1.6(8)	3.9(8)	0.5(9)
C2	18(1)	15.6(10)	16.9(9)	-0.8(8)	3.5(8)	-2.6(8)
C3	21.7(15)	16.0(15)	24.7(13)	0	0.8(12)	0
C4	26.8(12)	20.5(11)	25.3(11)	-2.8(9)	1.3(9)	0.6(9)
C5	29.5(12)	24.7(12)	36.2(12)	-10.2(10)	-0.2(10)	1.5(10)
C6	26.5(17)	16.8(15)	49(2)	0	-6.6(15)	0
C7	23.8(10)	14.8(10)	15.5(9)	1.0(8)	3.7(8)	3.0(9)
C8	23.5(10)	23.9(11)	19.1(10)	-1.1(9)	4.9(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)	-3.7(9)	6.9(10)	4.2(11)
C12	26.6(11)	21.6(11)	20.5(10)	-0.6(8)	4.0(9)	-0.1(9)
C13	17.8(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)	3.9(8)	-0.7(9)
C15	34.4(13)	20.3(11)	23.6(11)	-1.9(9)	8.8(10)	-5(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(13)	10.6(10)	5.9(10)	7.6(10)
C18	16.3(10)	25.8(11)	26.2(11)	1.0(9)	2.9(8)	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(6)	6.6(6)
F	16.7(3)	16.6(3)	16.0(2)	-0.2(2)	2.45(19)	0.1(2)
B	18.6(12)	23.1(13)	18.6(11)	-1.6(9)	2.5(9)	-0.5(10)

Table 3: Bond Lengths in Å for **19a**.

Atom	Atom	Length/Å
C1	C2	1.516(3)
C1	N	1.401(2)
C1	O	1.203(2)
C2	C2^1	1.545(3)
C2	F	1.3877(18)
C3	C4	1.387(2)
C3	C8	1.387(2)
C3	N	1.436(3)
C4	C5	1.389(3)
C5	C6	1.381(2)
C6	C5^1	1.381(2)
C7	C8	1.394(3)
C7	C12	1.397(3)
C7	F	1.3897(18)
C9	C9	1.384(2)
C9	C10	1.384(3)
C10	C11	1.389(3)
C11	C12	1.388(3)
C13	C14	1.394(3)
C13	C18	1.393(3)
C13	F	1.3806(17)
C14	C15	1.385(3)
C15	C16	1.375(3)
C16	C17	1.376(3)
C17	C18	1.385(3)
N	C1^1	1.401(2)
F	B	1.510(2)

^{1}-X,+Y,3/2-Z

Table 4: Bond Angles in ° for **19a**.

Atom	Atom	Atom	Angle/°
N	C1	C2	107.91(15)
O	C1	C2	126.61(16)
O	C1	N	125.46(18)
C1	C2	C2^1	103.62(9)
C1	C2	F	109.47(12)
C2^1	C2	F	111.36(16)
C4^1	C3	C4	120.5(3)
C4^1	C3	N	119.77(15)
C4	C3	N	119.77(13)
C3	C4	C5	119.32(19)
C6	C5	C4	120.7(2)
C5^1	C6	C5	119.5(3)
C8	C7	C12	119.36(17)
C8	C7	F	121.83(14)
C12	C7	F	118.87(15)
C9	C8	C7	120.54(19)
C10	C9	C8	119.76(19)
C11	C10	C9	120.30(18)
C10	C11	C12	120.40(19)
C11	C12	C7	119.70(19)
C14	C13	F	123.51(15)
C18	C13	C14	118.79(18)
C18	C13	F	117.57(15)
C15	C14	C13	120.34(19)
C16	C15	C14	120.2(2)
C15	C16	C17	120.1(2)

Atom	Atom	Atom	Angle/°
C16	C17	C18	120.3(2)
C17	C18	C13	120.25(19)
C1	N	C1'	112.1(2)
C1	N	C3	123.93(11)
C1'	N	C3	123.93(11)
C2	F	H	110.54(9)
C7	F	C2	105.82(8)

Atom	Atom	Atom	Angle/°
C7	F	N	113.10(10)
C13	F	C2	104.54(8)
C13	F	C7	106.48(8)
C13	F	H	115.58(9)

[1] -X,+Y,3/2-Z

Table 3. Hydrogen Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 19a. U_{eq} is defined as 1/3 of of the trace of the orthogonalized U_{ij}

Atom	x	y	z	U_{eq}
H2	6441	2005	7429	28
H4	5737	-684	6580	30
H5	5749	-2089	6590	37
H6	5000	-2792	7500	39
H8	7852	2332	6297	26
H9	9550	1964	5584	33
H10	8834	1057	4685	34
H11	6415	376	4491	35
H12	4700	94]	5289	37
H14	6619	3257	7070	26
H15	4524	4627	7013	31
H16	4625	5272	6300	33
H17	2788	4517	5655	36
H18	2839	3118	5716	29
HA	2427(7)	1619(5)	5630(5)	30
HB	2152(8)	1015(5)	6474(4)	30
HC	3814(3)	812(6)	6145(3)	30

Citations

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

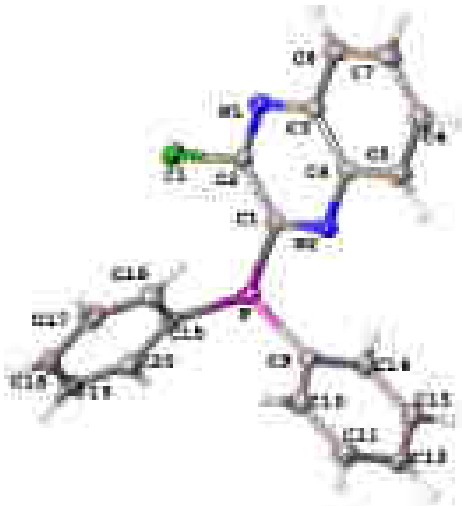
O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, OlexZ: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.* (2009), 42, 339-341.

Sheldrick, G.M., A short history of SheIX. *Acta Cryst.* (2008). A64, 112-122.

Compound 21

Olex2

Crystal Data and Experimental



Compound	21
CCDC Number	1048106
Formula	$C_{20}H_{14}ClN_2P$
$D_{calc.}$/ g cm^{-3}	1.356
μ/mm^{-1}	0.320
Formula Weight	348.75
Colour	clear light yellow
Shape	prism
Max Size/mm	0.17
Mid Size/mm	0.15
Min Size/mm	0.10
T/K	115
Crystal System	triclinic
Space Group	P-1
a/Å	9.3698(3)
b/Å	10.0995(3)
c/Å	10.4743(4)
α/°	82.6270(10)
β/°	85.0880(10)
γ/°	76.188(2)
V/Å^3	854.42(5)
Z	2
Z'	1
θ_{min}/°	3.177
θ_{max}/°	27.495
Measured Refl.	7339
Independent Refl.	3893
Reflections Used	2953
R_{int}	0.0310
Parameters	217
Restraints	0
Largest Peak	2.348
Deepest Hole	-0.359
GooF	1.052
wR2 (all data)	0.1433
wR2	0.1310
R1 (all data)	0.0754
R1	0.0529

Experimental. A Single clear light yellow prism-shaped crystal of (21) was selected and mounted on a glass fibre with grease on a Nonius Kappa CCD diffractometer. The crystal (0.17 × 0.15 × 0.10 mm^3) was kept at T = 115 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. $C_{20}H_{14}ClN_2P$, M_r = 348.75, triclinic, P-1 (No. 2), a = 9.3698(3) Å, b = 10.0995(3) Å, c = 10.4743(4) Å, α = 82.6270(10)°, β = 85.0880(10)°, γ = 76.188(2)°, V = 854.42(5) Å^3, T = 115 K, Z = 2, Z' = 1, μ(MoK$_\alpha$) = 0.320, 7339 reflections measured, 3893 unique (R_{int} = 0.0310) which were used in all calculations. The final wR2 was 0.1433 (all data) and R1 was 0.0529 (I > 2(I)).

Experimental Extended. A clear light yellow prism-shaped crystal with dimensions 0.17 × 0.15 × 0.10 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 K. Data were measured using φ and ω 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 the program Collect (Nonius BV, 1997-2000). The actually achieved resolution was ϑ = 27.491. 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 27.491 in ϑ. No absorption correction was performed. The absorption coefficient ($M\mu$) of this material is 0.329. 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 SheIXL (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 (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 21. U_{eq} is defined as 1/3 of 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)	-68(3)	6716(2)	20.9(5)
C5	223(3)	1078(3)	6863(3)	24.2(6)
C6	717(3)	2174(3)	6409(3)	27.9(6)
C7	2122(3)	2322(3)	5798(3)	30.5(6)
C8	3010(3)	1360(3)	5649(3)	28.8(6)
C9	1049(3)	3364(3)	8060(3)	19.8(5)
C10	-1436(3)	2496(3)	9462(3)	25.8(6)
C11	-2986(3)	2547(3)	9816(3)	27.6(6)
C12	-3996(3)	3479(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)	8208(3)	20.5(5)
C16	2594(3)	1382(3)	8996(3)	26.3(6)
C17	3378(3)	869(3)	11256(3)	30.7(6)
C18	3380(3)	1922(3)	11736(3)	28.7(6)
C19	2617(3)	3421(3)	10974(3)	28.6(6)
C20	1861(3)	3870(3)	9706(3)	25.7(6)
N1	3422(2)	715(3)	5999(2)	23.3(5)
N2	606(2)	1025(2)	7178(2)	20.6(5)
P	825.8(7)	3528.5(8)	7508.7(7)	21.50(16)
Cl	4049.9(6)	2888.7(7)	6876.0(7)	24.96(18)

Table 7. Anisotropic Displacement Parameters (×10⁴) **21**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	19.8(12)	22.1(12)	15.9(11)	-4.9(10)	1.8(9)	-1.9(10)
C2	17.2(12)	24.6(13)	17.5(12)	-7.6(10)	0.7(9)	-4.7(10)
C3	20.9(12)	23.5(13)	19.0(12)	-6.4(10)	1.2(9)	-0.5(10)
C4	20.8(12)	22.0(12)	14.1(11)	-5.8(10)	1.6(9)	-1(1)
C5	23.4(13)	26.2(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	35.7(15)	27.8(15)	29.5(15)	-16.9(12)	1.9(12)	-1.8(12)
C8	25.5(14)	38.8(14)	27.9(14)	-15.9(12)	2.5(11)	0.8(11)
C9	19.2(12)	19.6(12)	20.4(12)	-9.8(10)	0.3(9)	-1.8(9)
C10	22.9(13)	28.4(14)	20.6(13)	-8.3(11)	-1.7(10)	-1.8(11)
C11	28.3(14)	31.8(15)	20.3(13)	-8.7(11)	3.4(10)	-8.8(11)
C12	19.2(13)	33.8(15)	38.4(14)	-16.8(12)	4.8(10)	-8.8(11)
C13	21.9(13)	32.3(15)	24.2(14)	-9.7(12)	-4.1(10)	-5.4(11)
C14	22.1(12)	26.8(13)	19.9(13)	-9.5(11)	0.9(10)	-6(1)
C15	16.1(11)	21.7(12)	21.7(12)	-9.2(10)	2.9(9)	-3.2(9)
C16	26.8(14)	24.2(13)	25.2(14)	-12.1(11)	-0.4(11)	-2.4(11)
C17	28.2(14)	28.7(15)	24.9(14)	-6.8(12)	2.8(11)	1.7(11)
C18	20.8(13)	43.1(17)	21.6(13)	-15.3(13)	0.5(10)	-9.0(12)
C19	26.3(14)	36.2(16)	35.3(15)	-22.8(13)	4.7(11)	10.6(12)
C20	22.4(13)	23.8(13)	29.7(14)	-12.3(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)	16.3(10)	-8.4(9)	0.5(8)	-2.9(8)
F	18.3(3)	24.8(4)	19.7(3)	-10.3(3)	0.1(2)	-0.6(3)
O	18.8(3)	28.8(3)	26.7(3)	-12.1(3)	2.7(2)	-6.1(2)

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

Atom	Atom	Length/Å
C1	C2	1.433(3)
C1	N2	1.313(2)
C1	F	1.344(2)
C2	N1	1.298(3)
C2	C1	1.761(3)
C3	C4	1.418(3)
C3	C8	1.414(4)
C3	N1	1.374(3)
C4	C5	1.412(4)
C4	N2	1.370(3)
C5	C6	1.366(4)
C6	C7	1.419(4)
C7	C8	1.372(4)
C9	C10	1.391(3)
C9	C14	1.394(3)
C9	F	1.822(2)
C10	C11	1.389(4)
C11	C12	1.379(4)
C12	C13	1.394(4)
C13	C14	1.381(4)
C15	C16	1.396(4)
C15	C20	1.395(4)
C15	F	1.829(3)
C16	C17	1.394(4)
C17	C18	1.378(4)
C18	C19	1.382(4)
C19	C20	1.387(4)

Table 9: Bond Angles in ° for **21**.

Atom	Atom	Atom	Angle/°
C2	C1	F	119.66(19)
N2	C1	C2	119.5(2)
N2	C1	F	120.78(18)
C1	C2	O	118.4(2)
N1	C2	C1	125.1(2)
N1	C2	O	116.56(18)
C8	C3	C4	120.1(2)
N1	C3	C4	120.5(2)
N1	C3	C8	119.4(2)
C5	C4	C3	119.2(2)
N2	C4	C3	121.2(2)
N2	C4	C5	119.6(2)
C6	C5	C4	120.9(2)
C5	C6	C7	120.8(3)
C8	C7	C6	120.5(3)
C7	C8	C3	119.5(2)
C10	C9	C14	118.8(2)
C10	C9	F	124.29(18)
C14	C9	F	116.74(18)
C11	C10	C9	120.4(2)
C12	C11	C10	120.3(2)
C11	C12	C13	119.8(2)
C14	C13	C12	119.8(2)
C13	C14	C9	120.9(2)

Atom	Atom	Atom	Angle/°
C16	C15	F	123.9(2)
C20	C15	C16	118.7(2)
C20	C15	F	117.51(19)
C17	C16	C15	120.1(3)
C18	C17	C16	120.5(3)
C17	C18	C19	119.9(2)
C18	C19	C20	120.1(3)

Atom	Atom	Atom	Angle/°
C10	C20	C15	120.8(2)
C2	N1	C1	115.8(2)
C1	N2	C4	117.3(2)
C9	F	C1	102.30(11)
C9	F	C15	103.87(11)
C15	F	C1	101.91(11)

Table 10. Hydrogen Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 28. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{ij}

Atom	x	y	z	U_{eq}
H5	-887	-997	7267	29
H6	-126	-2831	6501	34
H7	2444	-3075	5497	37
H8	3928	-1457	5344	34
H10	-707	1878	10171	31
H11	-3156	1977	10754	38
H12	-4579	3466	8959	32
H13	-4332	4898	6639	35
H14	-1913	4841	6067	28
H16	2589	881	9674	32
H17	3885	-140	11765	37
H18	3898	1625	12501	34
H19	2611	4124	11310	35
H20	1367	4885	9187	31

Citations

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