Organocatalytic Asymmetric Hydrophosphination of Nitroalkenes

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General Methods. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 400 MHz, 100 MHz and 162 MHz, respectively. The chemical shifts (δ) are referenced to internal standard TMS (^{1}H NMR), to residual signals of the solvents ($CHCl_3$ - 77.0 ppm for ^{13}C NMR) and to external standard 85% H_3PO_4 (^{31}P NMR). Coupling constants are given in Hz. Carbon types were determined from DEPT ^{13}C NMR experiments. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad signal. Purification of reaction products was carried out by flash chromatography (FC) on silica gel (230-400 mesh) according to the method of Still.[1] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. X-ray structure analysis was carried out at the Department of Organic Chemistry *"A. Mangini"* X-ray Crystallography facility. Mass spectra were obtained from the Alma Mater Studiorum – Bologna University Mass Spectroscopy facilities. Optical rotations are reported as follows: $[\alpha]^{rt}_{D}$ (*c* in g per 100 mL, solvent). All reactions were carried out in oven-dried glassware under a nitrogen atmosphere unless otherwise noted.

Materials. Commercial grade reagents and solvents were used without further purification; otherwise, where necessary, they were purified as recommended.[2]

Diphenyl phosphine **1** and di-*tert*-butyl phosphine were purchased from Aldrich and used as received. CAUTION: Phosphines are highly oxidizable and potentially toxic molecules. All reactions should be carried out in a well-ventilated hood.

Aromatic nitroalkenes were purchased from Aldrich or Lancaster and used as received. Aliphatic nitroalkenes were prepared according to standard literature procedure.[3]

Cinchona alkaloids derivatives such as Quinine and $(DHQ)_2PHAL$ were purchased from Aldrich and used as received.

Thiourea-based bifunctional organocatalysts **A**,[4] **B**,[5] **C**[6] and **D**[7] were prepared following the literature procedures.

Determination of Enantiomeric Purity. Chiral HPLC analysis was performed on an Agilent 1100-series instrumentation. Daicel Chiralpak AD-H with i-PrOH/hexane as the eluent was used.

HPLC traces were compared to racemic samples prepared by uncatalyzed hydrophosphination reactions.

[1] W. C. Still, M. Kahn, A. J. Mitra, *J. Org. Chem.* **1978**, *43*, 2923.
[2] W. L. F. Armarengo, D. D. Perrin, In *Purification of Laboratory Chemicals*, 4th ed.; Butterworth Heinemann: Oxford, 1996.
[3] S. E. Denmark, L. R. Marcin, *J. Org. Chem.* **1993**, *58*, 3850.
[4] T. Marcelli, R.N. S. van der Haas, J. H. van Maarseveen, H. Hiemstra, *Angew. Chem., Int. Ed.* **2006**, *45*, 837.
[5] T. Okino, Y. Hoashi, Y. Takemoto, *J. Am. Chem. Soc.* **2003**, *125*, 12672.
[6] J. Wang, H. Li, X. Yu, L. Zu, W. Wang, *Org. Lett.* **2005**, *7*, 4293.
[7] B. Vakulya, Sz. Varga, A. Csámpai, T. Soos, *Org. Lett.* **2005**, *7*, 1967.

Organocatalytic Asymmetric Hydrophosphination (AHP)

Catalyst Screen.

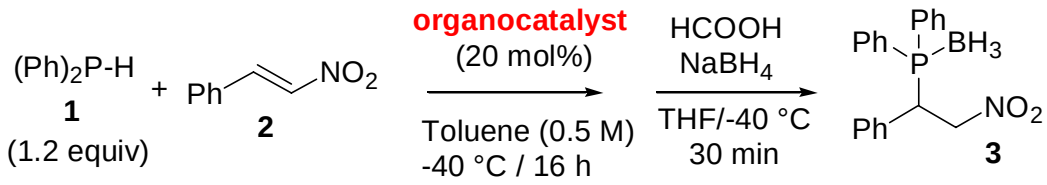
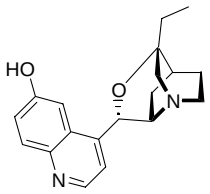
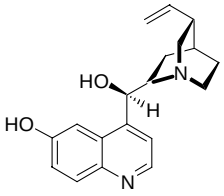
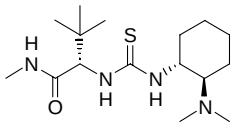
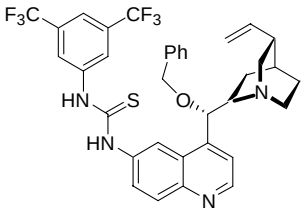
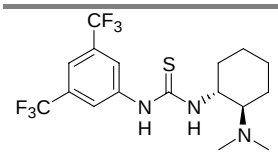
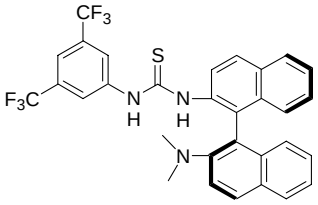
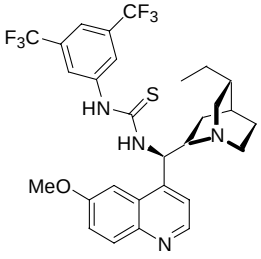
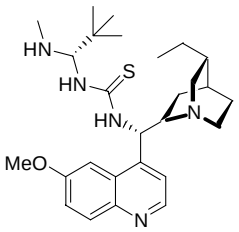
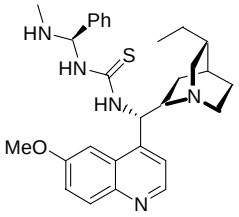
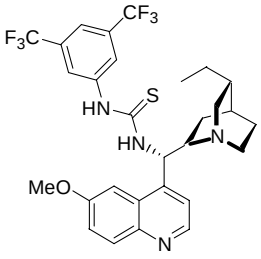


Table S1. Catalyst screen.

Catalyst	Conversion (%)	ee (%)
$(DHQ)_2PYR$	75	0
$(DHQ)_2AQN$	68	0
Quinine	85	0
O-Benzoyl Quinine	80	0
$(DHQ)_2PHAL$	76	18
	60	5
	60	-6
	75	16
	92	15

	80	27
	89	36
	>95%	9
	78	28
	85	22
	**93**	**49**

Reaction Conditions Screen.

a) Solvent Effect

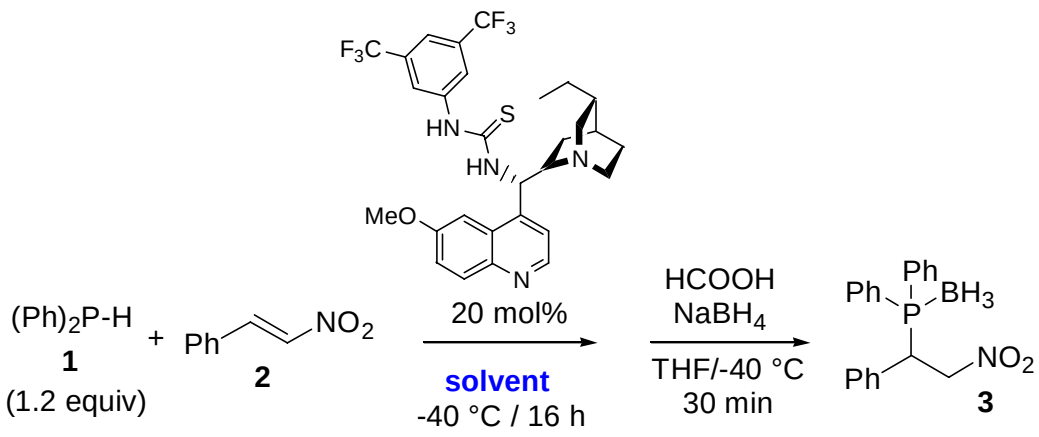


Table S2: Solvent Effect

Solvent	$[\mathbf{2}]_0$	Conversion (%)	ee (%)
toluene	0.2 M		45
TBME	0.2 M		40
THF	0.2 M	30	10
Et_2O	0.2 M		52
toluene	0.5 M	93	49
i-PrOH	0.5 M	>95	13
DCM	0.5 M	>95	34
THF	0.5 M	55	24
AcOEt	0.5 M	74	38
Et_2O	0.5 M	88	60
Et_2O	**1 M**	**92**	**62**

b) Cosolvent and Temperature Effects

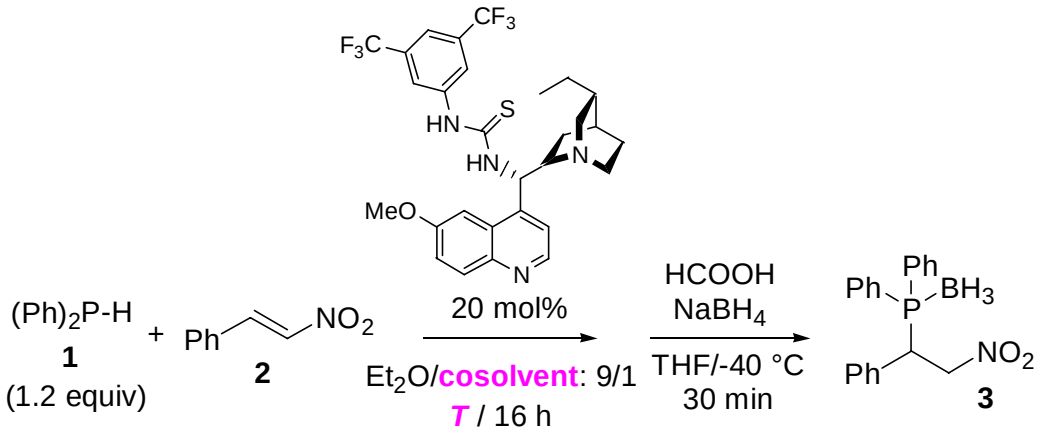


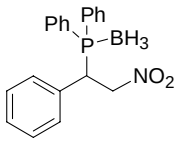
Table S3. Cosolvent and Temperature Effects

cosolvent	$[\mathbf{2}]_0$	T (°C)	Conversion (%)	ee (%)
MeOH	0.5 M	- 40	78	53
HFIP[a]	0.5 M	- 40	>95	50
(+)-Binol[b]	0.5 M	- 40	84	62
Benzoic acid[b]	0.5 M	- 40	82	0
i-PrOH	0.5 M	- 40	80	65
t-BuOH	0.5M	- 40	82	64
i-PrOH	1 M	- 40	>95	67
***i*-PrOH**[c]	**1 M**	**- 40**	**92**	**66**
i-PrOH[c]	1 M	- 10	>95	49
i-PrOH	1 M	- 60	45	46

[a] HFIP = 1,1,1,3,3,3-hexafluor-2-propanol. [b] 20 mol%. [c] 10 mol% of the catalyst.

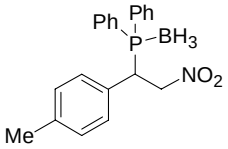
Experimental Procedures

General Procedure for the Organocatalytic AHP of Nitroalkenes. All hydrophosphination reactions were conducted under an atmosphere of nitrogen in flame-dried round bottomed flasks fitted with rubber septa. Stainless steel syringes were used to transfer air and moisture sensitive liquids. Catalyst **D** (0.02 mmol, 12.0 mg) was placed in a 5 mL vial equipped with a Teflon-coated stir bar. Anhydrous Et_2O (180 μL) and *i*-PrOH (20 μL) were added under N_2, followed by the addition of the nitro olefin (0.2 mmol). The vial was capped and the resulting mixture was stirred at RT until homogeneous then cooled to the indicated temperature (generally -40 °C) for 10 minutes. Then diphenyl phosphine **1** (0.24 mmol, 1.2 equiv, 42 μL) was added and stirring was continued for 24 h. Upon complete consumption of the nitro olefin (checked by ^{1}H NMR analysis), the reaction mixture was diluted with 400 μL of anhydrous THF, and solid $NaBH_4$ (0.4 mmol, 2 equiv, 15 mg) was added in one portion followed by a solution of glacial acetic acid (0.5 mmol, 2.5 equiv, 30 mg) in THF (200 μL). Frothing occurs but is readily controllable through magnetic stirring of the solution. The mixture was allowed to warm to RT and, after complete conversion of the free phosphine to the corresponding borane complex (monitored by TLC analysis – generally 30 minutes), quenched with few drops of water. Brine (2 mL) was added and the resulting mixture extracted with AcOEt (3 × 3 mL). The combined organics was washed with brine (5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (FC) to yield the desired β-nitrophosphine-borane complex.

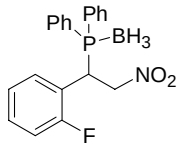


3 – The reaction was carried out at –40 °C for 24 h using 10 mol% of catalyst **D** following the general procedure. The title compound was isolated by column chromatography (hexane/AcOEt = 95/5) as a white solid in 86% yield and 66% ee. The ee was determined by HPLC analysis using a Chiralpak AD-H column (80/20 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 214, 254 nm; τ_{minor} = 6.6 min; τ_{major} = 7.3 min). **Single crystallization from a mixture of hexane/Et_2O afforded the optically pure product (99% ee)** (confirmed by HPLC analysis)**.** $[\alpha]^{rt}_D$= +218.3 (*c* = 0.65, $CHCl_3$, 99% ee). Melting point: 102-104 C°. HRMS: *m/z* calcd for $C_{20}H_{21}B^{11}NO_2P$: 349.140297; found: 349.140100. ESI-MS *m/z* 372 $[M+Na]^+$. ^{31}P NMR (243 MHz, $CDCl_3$): δ = +22.8 (m); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.05 (br q, 3H), 4.60-4.70 (m, 2H), 5.10-5.18 (m, 1H), 7.14-7.30 (m, 7H), 7.33-7.40 (m, 3H), 7.56-7.64 (m, 3H), 7.96-8.03 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 41.7 ($^1J_{C\text{-}P}$ = 30.7 Hz, CH), 75.6 ($^2J_{C\text{-}P}$ = 13.9 Hz, CH_2), 125.865 ($^1J_{C\text{-}P}$ = 56.2 Hz, C), 125.888 ($^1J_{C\text{-}P}$ = 52.8 Hz, C), 128.424 ($^5J_{C\text{-}P}$ = 2.5 Hz, CH), 128.458 ($^4J_{C\text{-}P}$ = 2.1 Hz, CH), 128.500 ($^3J_{C\text{-}P}$ = 10.2 Hz, CH), 129.435 ($^3J_{C\text{-}P}$ = 4.0 Hz, CH), 129.518 ($^3J_{C\text{-}P}$ = 9.8 Hz, CH), 129.390 (C), 131.399 ($^4J_{C\text{-}P}$ = 2.5 Hz, CH), 131.716 ($^4J_{C\text{-}P}$ = 2.5 Hz, CH), 132.785 ($^2J_{C\text{-}P}$ = 9.2 Hz, CH), 132.790 ($^2J_{C\text{-}P}$ = 8.8 Hz, CH).

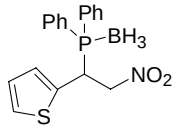
For extensive 2D-NMR studies directed toward the full structural assignment for compound **3**, see the dedicated paragraph at the end of Supporting Information (NMR analysis of **3,** S16).



5 – The reaction was carried out at –40 °C for 24 h using 15 mol% of catalyst **D** following the general procedure. The title compound was isolated by column chromatography (hexane/AcOEt = 9/1) as a white solid in 67% yield and 52% ee. The ee was determined by HPLC analysis using a Chiralpak AD-H column (80/20 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 214, 254 nm; τ_{minor} = 9.5 min; τ_{major}= 10.2 min). $[\alpha]^{rt}_{D}$= +96.8 (*c* = 1.25, $CHCl_3$, 52% ee). HRMS: *m/z* calcd for $C_{21}H_{23}B^{10}FNO_2P$: 362.159581; found: 362.15930. ESI-MS *m/z* 386 $[M+Na]^+$. Melting point: 128-129 C°. ^{31}P NMR (162 MHz, $CDCl_3$): δ = +21.8 (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (br q, 3H), 2.24 (s, 3H), 4.56-4.68 (m, 2H), 5.06-5.14 (m, 1H), 6.94-7.03 (m, 4H), 7.23-7.29 (m, 2H), 7.32-7.40 (m, 3H), 7.54-7.62 (m, 3H), 7.94-8.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0 (CH_3), 41.4 ($^{1}J_{C\text{-}P}$ = 30.6 Hz, CH), 75.8 ($^{2}J_{C\text{-}P}$ = 13.7 Hz, CH_2), 126.0 ($^{1}J_{C\text{-}P}$ = 55.6 Hz, C), 126.1 ($^{1}J_{C\text{-}P}$ = 52.3 Hz, C), 128.1 ($^{2}J_{C\text{-}P}$ = 1.6 Hz, C), 128.5 ($J_{C\text{-}P}$ = 10.4 Hz, CH), 129.1 ($J_{C\text{-}P}$ = 2.4 Hz, CH), 129.3 ($J_{C\text{-}P}$ = 4.0 Hz, CH), 129.4 ($J_{C\text{-}P}$ = 9.7 Hz, CH), 131.6 ($J_{C\text{-}P}$ = 2.4 Hz, CH), 132.3 ($J_{C\text{-}P}$ = 2.4 Hz, CH), 132.7 ($J_{C\text{-}P}$ = 8.8 Hz, CH), 132.8 ($J_{C\text{-}P}$ = 8.8 Hz, CH), 138.2 ($^{5}J_{C\text{-}P}$ = 2.4 Hz, C).

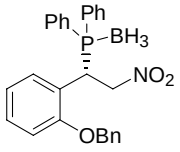


6 – The reaction was carried out at –10 °C for 24 h using 10 mol% of catalyst **D** following the general procedure. The title compound was isolated by column chromatography (hexane/AcOEt = 9/1) as a white solid in 83% yield and 45% ee. The ee was determined by HPLC analysis using a Chiralpak AD-H column (80/20 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 230, 254 nm; τ_{minor} = 6.4 min; τ_{major}= 6.9 min). **Single crystallization from a mixture of hexane/*i*PrOH afforded the optically pure product** (confirmed by HPLC analysis) **in 24% yield.** $[\alpha]^{rt}_{D}$= +326.7 (*c* = 0.44, $CHCl_3$, 99% ee). HRMS: *m/z* calcd for $C_{20}H_{20}B^{11}FNO_2P$: 367.130877; found: 367.12900. ESI-MS *m/z* 390 $[M+Na]^+$. Melting point: 115-118 C°. ^{31}P NMR (162 MHz, $CDCl_3$): δ = +22.9 (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (br q, 3H), 4.59-4.67 (m, 1H), 5.12-5.24 (m, 2H), 6.74-6.80 (m, 1H), 7.11-7.25 (m, 4H), 7.34-7.41 (m, 3H), 7.59-7.66 (m, 4H), 8.02-8.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.7 ($^{1}J_{C\text{-}P}$ = 31.4 Hz, $J_{C\text{-}F}$ = 2.5 Hz, CH), 74.8 ($^{2}J_{C\text{-}P}$ = 13.7 Hz, CH_2), 115.3 ($J_{C\text{-}P}$ = 1.7 Hz, $J_{C\text{-}F}$ = 22.6 Hz, CH), 119.4 ($J_{C\text{-}P}$ = 12.1 Hz, C), 124.4 ($J_{C\text{-}P}$ = 2.4 Hz, $J_{C\text{-}F}$ = 4.0 Hz, CH), 125.5 ($^{1}J_{C\text{-}P}$ = 56.4 Hz, C), 125.7 ($^{1}J_{C\text{-}P}$ = 51.5 Hz, C), 128.4 ($J_{C\text{-}P}$ = 10.5 Hz, CH), 129.2 ($J_{C\text{-}P}$ = 2.4 Hz, $J_{C\text{-}F}$ = 3.2 Hz, CH), 129.6 ($J_{C\text{-}P}$ = 10.4 Hz, CH), 130.1 ($J_{C\text{-}P}$ = 8.9 Hz, $J_{C\text{-}F}$ = 2.4 Hz, CH), 131.7 ($J_{C\text{-}P}$ = 2.4 Hz, CH), 132.5 ($^{3}J_{C\text{-}P}$ = 2.4 Hz, CH), 132.6 ($J_{C\text{-}P}$ = 9.6 Hz, CH), 132.8 ($J_{C\text{-}P}$ = 8.8 Hz, CH), 138.2 ($^{5}J_{C\text{-}P}$ = 2.4 Hz, C), 160.5 ($J_{C\text{-}P}$ = 4.9 Hz, $J_{C\text{-}F}$ = 246.3 Hz, CF), .



7 – The reaction was carried out at –40 °C for 24 h using 15 mol% of catalyst **D** following the general procedure. The title compound was isolated by column chromatography (hexane/AcOEt = 95/5) as a white solid in 71% yield and 36% ee. The ee was determined by HPLC analysis using a Chiralpak AD-H column (80/20 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 214, 254 nm; τ_{minor} = 6.9 min; τ_{major}= 7.6 min). $[\alpha]^{rt}_{D}$= +58.5 (*c* = 0.71, $CHCl_3$, 36% ee). HRMS: *m/z* calcd for $C_{18}H_{19}B^{11}NO_2PS$: 355.09672; found:

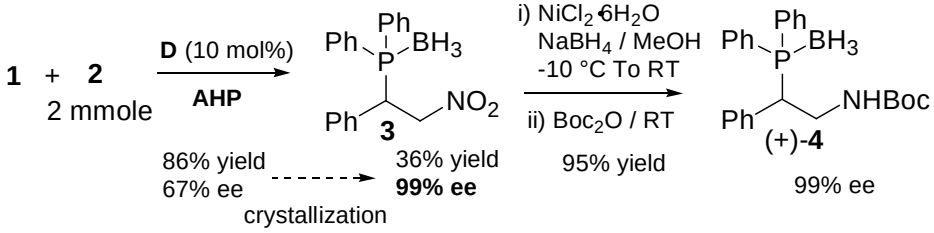
355.09700. ESI-MS *m/z* 378 $[M+Na]^+$. Melting point: 126-128 C°. ^{31}P NMR (162 MHz, $CDCl_3$): δ = +23.0 (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.07 (br q, 3H), 4.67-4.73 (m, 1H), 4.93-5.07 (m, 2H), 6.84-6.87 (m, 1H), 6.93-6.97 (m, 1H), 7.10-7.12 (m, 1H), 7.30-7.35 (m, 2H), 7.42-7.50 (m, 3H), 7.55-7.65 (m, 3H), 7.92-7.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.3 ($^1J_{C\text{-}P}$ = 32.2 Hz, CH), 76.6 ($^2J_{C\text{-}P}$ = 16.1 Hz, CH_2), 125.6 ($^1J_{C\text{-}P}$ = 55.5 Hz, C), 125.9 ($^1J_{C\text{-}P}$ = 52.3 Hz, C), 126.0 ($J_{C\text{-}P}$ = 3.2 Hz, CH), 126.9 ($J_{C\text{-}P}$ = 1.6 Hz, CH), 128.1 ($J_{C\text{-}P}$ = 4.8 Hz, CH), 128.7 ($J_{C\text{-}P}$ = 10.5 Hz, CH), 129.5 ($J_{C\text{-}P}$ = 9.7 Hz, CH), 131.9 ($J_{C\text{-}P}$ = 2.4 Hz, CH), 132.4 ($J_{C\text{-}P}$ = 2.4 Hz, CH), 132.7 ($J_{C\text{-}P}$ = 8.9 Hz, CH), 132.8 ($J_{C\text{-}P}$ = 8.9 Hz, CH), 133.7 (C).



(*S*)-**8** – The reaction was carried out at –40 °C for 30 h using 15 mol% of catalyst **D** following the general procedure. The title compound was isolated by column chromatography (hexane/AcOEt = 9/1) as a white solid in 90% yield and 60% ee. The ee was determined by HPLC analysis using a Chiralpak AD-H column (80/20 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = λ = 214, 254 nm; τ_{minor} = 6.2 min; τ_{major} = 7.4 min). **Single crystallization from a mixture of hexane/Et_2O afforded the optically pure product** (confirmed by HPLC analysis) **in 37% yield.** $[\alpha]^{rt}_D$ = +121.9 (*c* = 0.51, $CHCl_3$, 99% ee). HRMS: *m/z* calcd for $C_{27}H_{27}B^{10}NO_3P$: 454.18579; found: 454.18500. ESI-MS *m/z* 478 $[M+Na]^+$. Melting point: 87-89 C°. ^{31}P NMR (162 MHz, $CDCl_3$): δ = +22.6 (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.03 (br q, 3H), 4.40 (d, *J* = 11.2 Hz, 1H), 4.58 (ddd, J_1 = 3.6, J_2 = 6.0, $J_{H\text{-}P}$ = 14.0 Hz, 1H), 4.81 (d, *J* = 11.2 Hz, 1H), 5.23 (ddd, J_1 = 3.6, J_2 = 12.4, $J_{H\text{-}P}$ = 14.0 Hz, 1H), 5.54 (ddd, J_1 = 3.6, J_2 = 12.4, $J_{H\text{-}P}$ = 16.4 Hz, 1H), 6.57 (d, *J* = 8.4, 1H), 7.00 (t, *J* = 7.6, 1H), 7.07-7.12 (m, 4H), 7.14-7.19 (m, 1H), 7.28-7.50 (m, 8H), 7.56-7.63 (m, 2H), 7.90-7.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.8 ($^1J_{C\text{-}P}$ = 31.4 Hz, CH), 69.9 (CH_2), 75.0 ($^2J_{C\text{-}P}$ = 16.1 Hz, CH_2), 111.4 ($J_{C\text{-}P}$ = 1.6 Hz, CH), 120.7 ($^1J_{C\text{-}P}$ = 2.4 Hz, C), 120.9 ($^1J_{C\text{-}P}$ = 2.4 Hz, CH), 125.7 ($J_{C\text{-}P}$ = 52.3 Hz, C), 126.3 ($^1J_{C\text{-}P}$ = 57.1 Hz, C), 127.4 (CH), 127.6 ($J_{C\text{-}P}$ = 10.4 Hz, CH), 128.1 (CH), 128.3 ($J_{C\text{-}P}$ = 3.2 Hz, CH), 128.6 (CH), 129.3 ($J_{C\text{-}P}$ = 9.7 Hz, CH), 129.4 ($J_{C\text{-}P}$ = 2.4 Hz, CH), 130.9 ($J_{C\text{-}P}$ = 2.4 Hz, CH), 132.2 ($J_{C\text{-}P}$ = 2.4 Hz, CH), 132.7 ($J_{C\text{-}P}$ = 8.9 Hz, CH), 133.2 ($J_{C\text{-}P}$ = 8.9 Hz, CH), 136.6 (C).

The absolute configuration of 8 was assigned to be (*S*) by X-ray crystallographic analysis, see S14 for details.

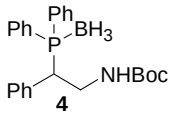
2 mmol-scale experiment and synthesis of enantiopure β-aminophosphine (+)-4.



Catalyst **D** (10 mol%, 0.2 mmol, 119.2 mg) was placed in a 10 mL vial equipped with a Teflon-coated stir bar. Anhydrous Et_2O (1.8 mL) and *i*-PrOH (0.2 mL) were added under N_2, followed by the

addition of the β-nitrostyrene **2** (2 mmol, 298 mg). The vial was capped and the resulting mixture was stirred at RT until homogeneous then cooled to - 40 °C for 10 minutes. Then diphenyl phosphine **1** (2.4 mmol, 1.2 equiv, 415 μL) was added and stirring was continued for 24 h. Upon complete consumption of **2** (checked by TLC analysis), the reaction mixture was diluted with 4 mL of anhydrous THF, and solid $NaBH_4$ (4 mmol, 2 equiv, 148 mg) was added in one portion followed by a solution of glacial acetic acid (5 mmol, 2.5 equiv, 286 μL) in THF (2 mL). Frothing occurs but is readily controllable through magnetic stirring of the solution. The mixture was allowed to warm to RT and, after complete conversion of the free phosphine to the corresponding borane complex **3** (30 minutes), quenched with water. Brine (15 mL) was added and the resulting mixture extracted with AcOEt (3 × 15 mL). The combined organics was washed with brine (15 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (FC) to yield the desired β-nitrophosphine-borane complex **3** in 86% yield (600 mg) and 67% ee.

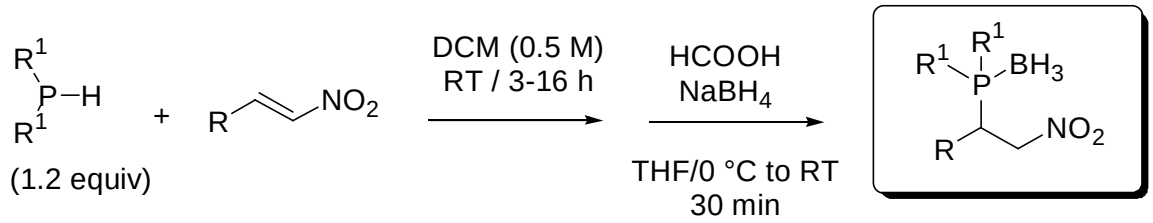
Single crystallization from a mixture of hexane/Et_2O afforded the optically pure product 3 in 36% overall yield (250 mg) and 99% ee (confirmed by HPLC analysis)**.** $[\alpha]^{rt}_D$= +218.3 (*c* = 0.65, $CHCl_3$, 99% ee).



4

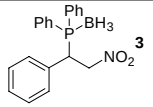
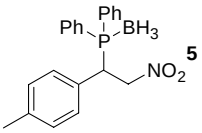
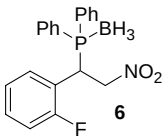
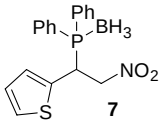
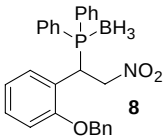
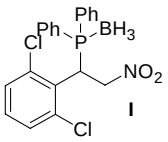
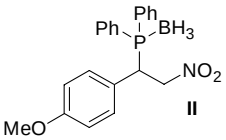
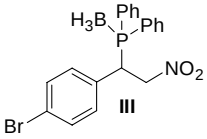
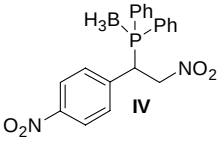
Enantiomerically pure (+)-**3** (250 mg, 0.716 mmol) was dissolved in MeOH (10 mL) and stirred at –10 °C for 5 minutes. Then, $NiCl_2 \cdot 6H_2O$ (425 mg, 1.79 mmol - 2.5 equiv) was added in one portion and stirring continued for 10 minutes, at which time $NaBH_4$ (268 mg, 7.16 mmol - 10 equiv) was added in small doses. After 30 minutes stirring, the reaction mixture was allowed to worm to RT, and di-*tert*-butyl dicarbonate (Boc_2O, 470 mg, 2.15 mmol - 3 equiv) was added. Stirring was continued for 2.5 hours and then the reaction mixture was diluted with a saturated solution of $NaHCO_3$ (20 mL): the aqueous layer was separated and extracted with AcOEt (3 times) and DCM (1 time). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (FC) eluting with hexane/AcOEt 9/1 to yield the desired *N*-Boc β-aminophosphine-borane complex **4** as a white solid in 95% yield (285 mg – 34% yield over two steps) and 99% ee. The ee was determined by HPLC analysis using a Chiralpak AD-H column (95/5 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 214, 254 nm; τ_{minor} = 10.9 min; τ_{major}= 11.9 min). $[\alpha]^{rt}_D$= +92.0 (*c* = 0.71, $CHCl_3$, 99% ee). HRMS: *m/z* calcd for $C_{25}H_{31}B^{11}NO_2P$: 419.21855; found: 419.21800. ESI-MS *m/z* 442 $[M+Na]^+$. Melting point: 132-134 C°. ^{31}P NMR (162 MHz, $CDCl_3$): δ = +20.8 (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.20 (br q, 3H), 1.33 (s, 9H), 3.61-3.71 (m, 1H), 3.80-3.90 (m, 1H), 4.15-4.25 (m, 1H), 4.53-4.58 (br, 1H), 7.09-7.21 (m, 7H), 7.27-7.32 (m, 3H), 7.52-7.57 (m, 3H), 7.99-8.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.2 (3 CH_3), 41.6 ($^2J_{C\text{-}P}$ = 8.1 Hz, CH_2), 42.1 ($^1J_{C\text{-}P}$ = 29.7 Hz, CH), 79.3 (C), 127.4 (CH), 127.6 ($^1J_{C\text{-}P}$ = 46.7 Hz, C), 128.1 ($J_{C\text{-}P}$ = 10.4 Hz, CH), 128.2 (CH), 129.0 ($J_{C\text{-}P}$ = 9.7 Hz, CH), 129.8 ($J_{C\text{-}P}$ = 4.0 Hz, CH), 130.8 (CH), 131.5 (CH), 132.6 ($J_{C\text{-}P}$ = 8.9 Hz, CH), 132.9 ($J_{C\text{-}P}$ = 8.9 Hz, CH), 134.3 (C), 155.6 (C).

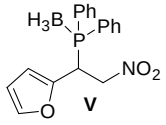
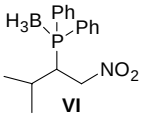
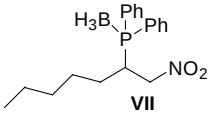
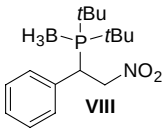
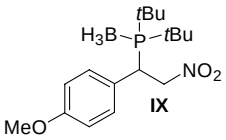
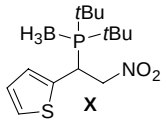
Uncatalyzed Hydrophosphination of Nitroalkenes



General Procedure for the Uncatalyzed Hydrophosphination of Nitroalkenes. All hydrophosphination reactions were conducted under an atmosphere of nitrogen in flame-dried round bottomed flasks fitted with rubber septa. Stainless steel syringes were used to transfer air and moisture sensitive liquids. Anhydrous DCM (600 μL) was added under N_2, followed by the addition of the nitro olefin (0.3 mmol) and the secondary phosphines (Diphenyl or di-*tert*-butyl phosphine). The vial was capped and the resulting mixture was stirred for 3-16 h (see Table S4 for details). Upon complete consumption of the nitro olefin (checked by ^{1}H NMR TLC analyses), the reaction mixture was cooled to 0 °C and diluted with 400 μL of anhydrous THF. Solid $NaBH_4$ (0.4 mmol, 2 equiv, 15 mg) was added in one portion followed by a solution of glacial acetic acid (0.5 mmol, 2.5 equiv, 30 mg) in THF (200 μL). Frothing occurs but is readily controllable through magnetic stirring of the solution. The mixture was allowed to warm to RT and, after complete conversion of the free phosphine to the corresponding borane complex (monitored by TLC analysis), quenched with few drops of water. Brine (3 mL) was added and the resulting mixture extracted with AcOEt (3 × 5 mL). The combined organics was washed with brine (10 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (FC) to yield the desired β-nitrophosphine-borane complex.

Table S4. Uncatalyzed hydrophosphination of nitroalkenes

Phosphine	Product	Time	Isolated Yield
$(Ph)_2PH$	 **3**	3 h	93 % [A]
$(Ph)_2PH$	 **5**	3 h	91% [A]
$(Ph)_2PH$	 **6**	3 h	88% [A]
$(Ph)_2PH$	 **7**	3 h	86% [A]
$(Ph)_2PH$	 **8**	3 h	94% [A]
$(Ph)_2PH$	 **I**	3 h	90%
$(Ph)_2PH$	 **II**	3 h	92% [A]
$(Ph)_2PH$	 **III**	3 h	91%
$(Ph)_2PH$	 **IV**	3h	75% [A]

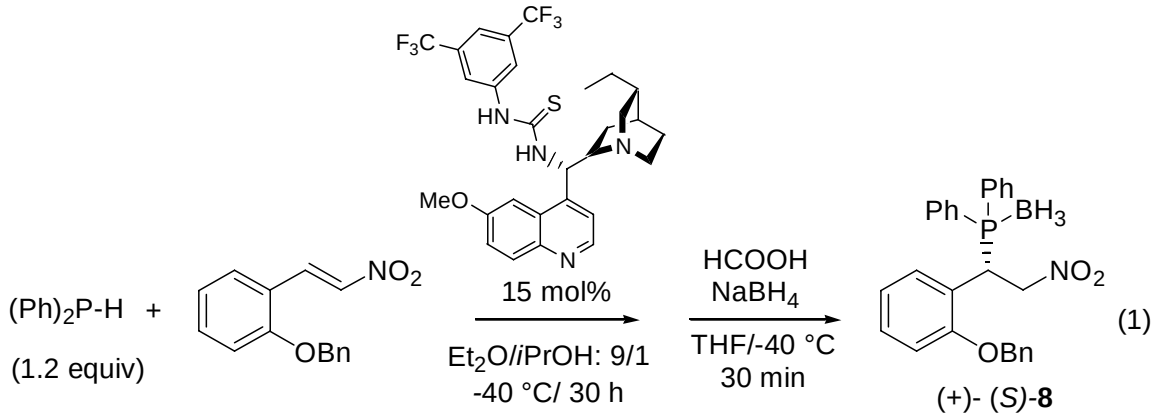
$(Ph)_2PH$	 **V**	8h	70% [A]
$(Ph)_2PH$	 **VI**	16 h	74%
$(Ph)_2PH$	 **VII**	16 h	82% [A]
$(t\text{-}Bu)_2PH$	 **VIII**	16 h	76% [A]
$(t\text{-}Bu)_2PH$	 **IX**	16 h	64%
$(t\text{-}Bu)_2PH$	 **X**	16 h	74% [A]

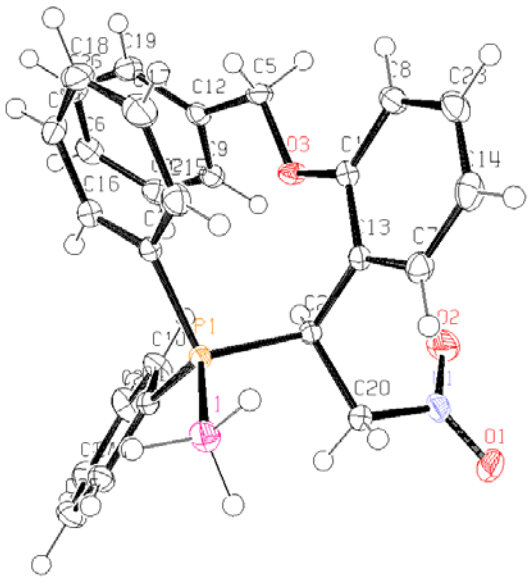
[A] ^{1}H NMR and ^{13}C NMR spectra for these compounds are provided in the final section of Supporting Information

X-Ray Structure Analysis.

Determination of Absolute configuration of Compound 8.

The absolute configurations of compound (+)-**8** was assigned by X-ray crystallographic analysis. Crystallization from a mixture of Hexane/Et_2O afforded a single enantiopure isomer (confirmed by HPLC analysis) as fine colourless needles suitable for X-ray diffraction measurements with the absolute configuration as shown in Equation 1.





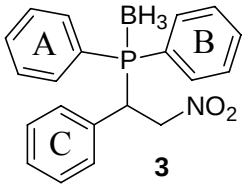
Molecular formula: $C_{27}H_{27}BNO_3P$, M_r = 455.29, monoclinic, space group $P2_1$ (No. 4), a = 9.7738(12), b = 13.1358(16), c = 9.8656(12) Å, β =109.146(2), V = 1196.5(3) Å^3, **T = 100(2) K**, Z = 2, ρ_c = 1.264 g cm^{-3}, F(000) = 480, graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), $\mu(Mo_{K\alpha})$ = 0.144 mm^{-1}, colourless brick (1.0 × 0.7 × 0.6 mm^3), empirical absorption correction with SADABS (transmission factors: 0.8694 – 0.9315), 2400 frames, exposure time 10 s, $2.19 \le \theta \le 28.63$, $-12 \le h \le 12$, $-17 \le k \le 17$, $-13 \le l \le 12$, 13673 reflections collected, 5605 independent reflections (R_{int} =

0.0277), solution by direct methods (SHELXS97)[8] and subsequent Fourier syntheses, full-matrix least-squares on F_o^2 (SHELX97)[8], hydrogen atoms refined with a riding model excepted for the three hydrogens bonded to the boron atom. data / parameters = 5605 / 310, $S(F^2)$ = 1.077, $R(F)$ = 0.0269 and $wR(F^2)$ = 0.0779 on all data, $R(F)$ = 0.0266 and $wR(F^2)$ = 0.711 for 5533 reflections with $I > 2\sigma(I)$, weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 0.000P]$ where $P = (F_o^2 + 2F_c^2)/3$, largest difference peak and hole 0.202 and –0.261 e Å^{-3}. Flack parameter: -0.03(4).[9]

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-615184. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] Sheldrick, G. M. *SHELX97*; Universität Göttingen, Germany, 1997.
[9] Flack, H. D. , Acta Cryst. **1983**, *A39*, 876-881

NMR Analysis of Compound 3



3

signal	^{1}H	^{13}C
BH_3	1.05 (broad m)	
CH	4.65 (m)	41.7 ($^{1}J_{C\text{-}P}$ = 30.7 Hz)
CH_2	4.66 (m) and 5.14 (m)	75.6 ($^{2}J_{C\text{-}P}$ = 13.9 Hz)
Cq (A)		125.865 ($^{1}J_{C\text{-}P}$ = 56.2 Hz)
Ortho CH (A)	7.33 (m)	137.790 ($^{2}J_{C\text{-}P}$ = 8.8 Hz)
Meta CH (A)	7.24 (m)	129.518 ($^{3}J_{C\text{-}P}$ = 9.8 Hz)
Para CH (A)	7.37 (m)	131.716 ($^{4}J_{C\text{-}P}$ = 2.5 Hz)
Cq (B)		125.888 ($^{1}J_{C\text{-}P}$ = 52.8 Hz)
Ortho CH (B)	7.99 (m)	132.785 ($^{2}J_{C\text{-}P}$ = 9.2 Hz)
Meta CH (B)	7.57 (m)	128.500 ($^{3}J_{C\text{-}P}$ = 10.2 Hz)
Para CH (B)	7.61 (m)	131.399 ($^{4}J_{C\text{-}P}$ = 2.5 Hz)
Cq (C)		131.390
Ortho CH (C)	7.14 (m)	129.435 ($^{3}J_{C\text{-}P}$ = 4.0 Hz)
Meta CH (C)	7.16 (m)	128.458 ($^{4}J_{C\text{-}P}$ = 2.1 Hz)
Para CH (C)	7.19 (m)	128.424 ($^{5}J_{C\text{-}P}$ = 2.5 Hz)

Full structural assignment of compound **3** was obtained by extensive 2D-NMR.

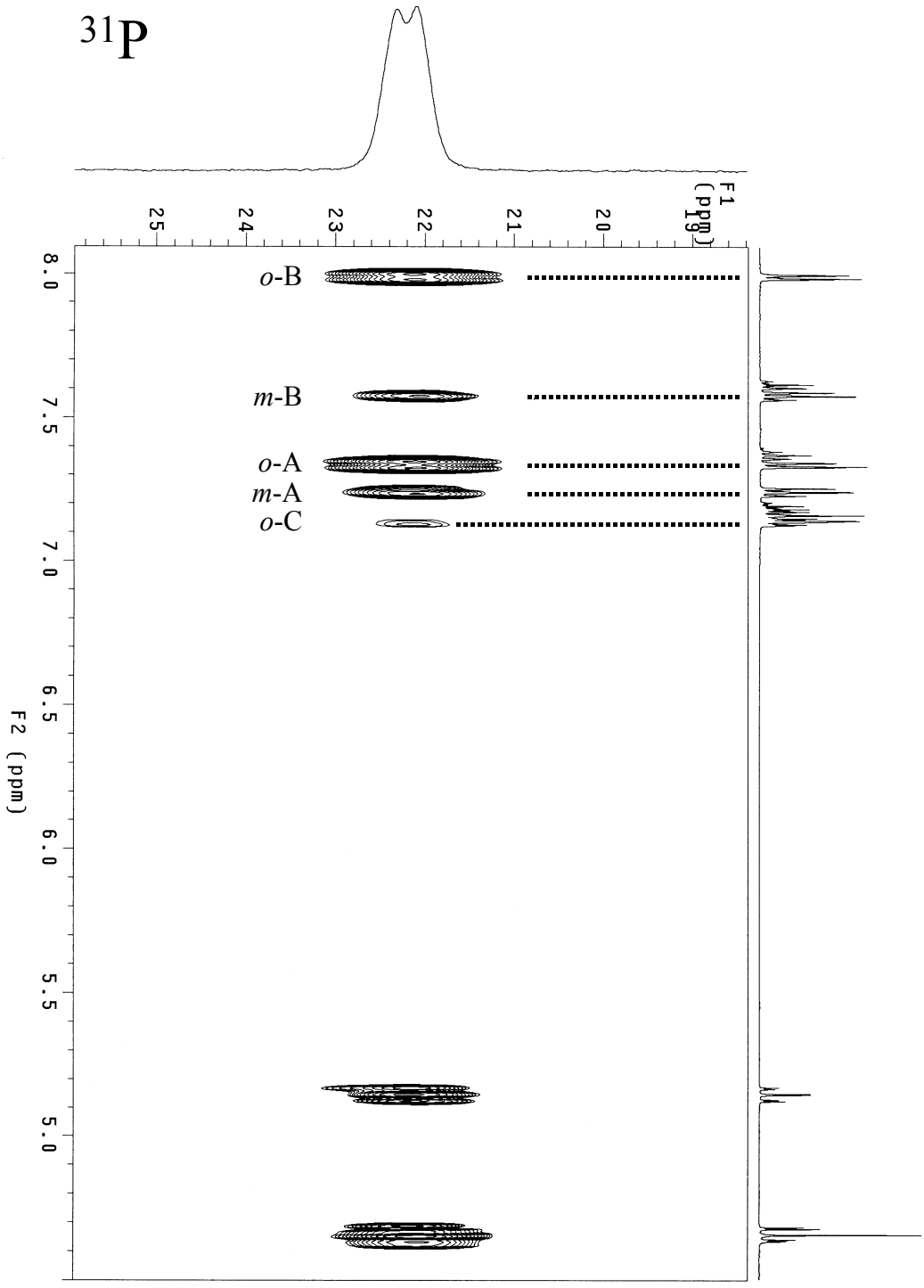
First of all, ^{1}H-NMR spectra was obtained with ^{31}P-selective decoupling, in order to reduce the spectral complexity due to ^{1}H-^{31}P coupling. The ^{31}P-NMR spectrum shows a single broad doublet at 22.8 ppm. The very large line width id due to fast T2 relaxation, owing to the presence of the borane moiety.

Then, a ^{1}H-^{31}P long range correlation (g-HMBC sequence) was acquired to assign the proton signals of the two couples of ortho hydrogens of ring A and B. These signals were located at 7.33 and 7.95 ppm. (from the NMR point of view the two aromatic rings named A and B are different, due to the presence of the chiral center, but the assignment is not possible. Thus the A and B labels are arbitrarily indicated).

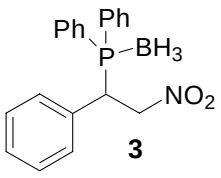
^{1}H-^{1}H gCOSY spectrum, obtained with selective ^{31}P-decoupling, allowed the assignment of the other aromatic hydrogens of A and B rings, and the assignment of the hydrogens belonging to ring C.

^{1}H-^{13}C direct correlation (gHSQC sequence) allowed the full assignment of the protonated carbons.

^{1}H-^{13}C long range correlation (g-HMBC sequence) allowed the unambiguous assignment of the quaternary carbon of ring C, because of the long range coupling with the two CH_2 protons.
Both HSQC and HMBC were acquired without ^{13}P decoupling and with very high resolution in F1 (2048 increments) in order to obtain sufficient resolution.



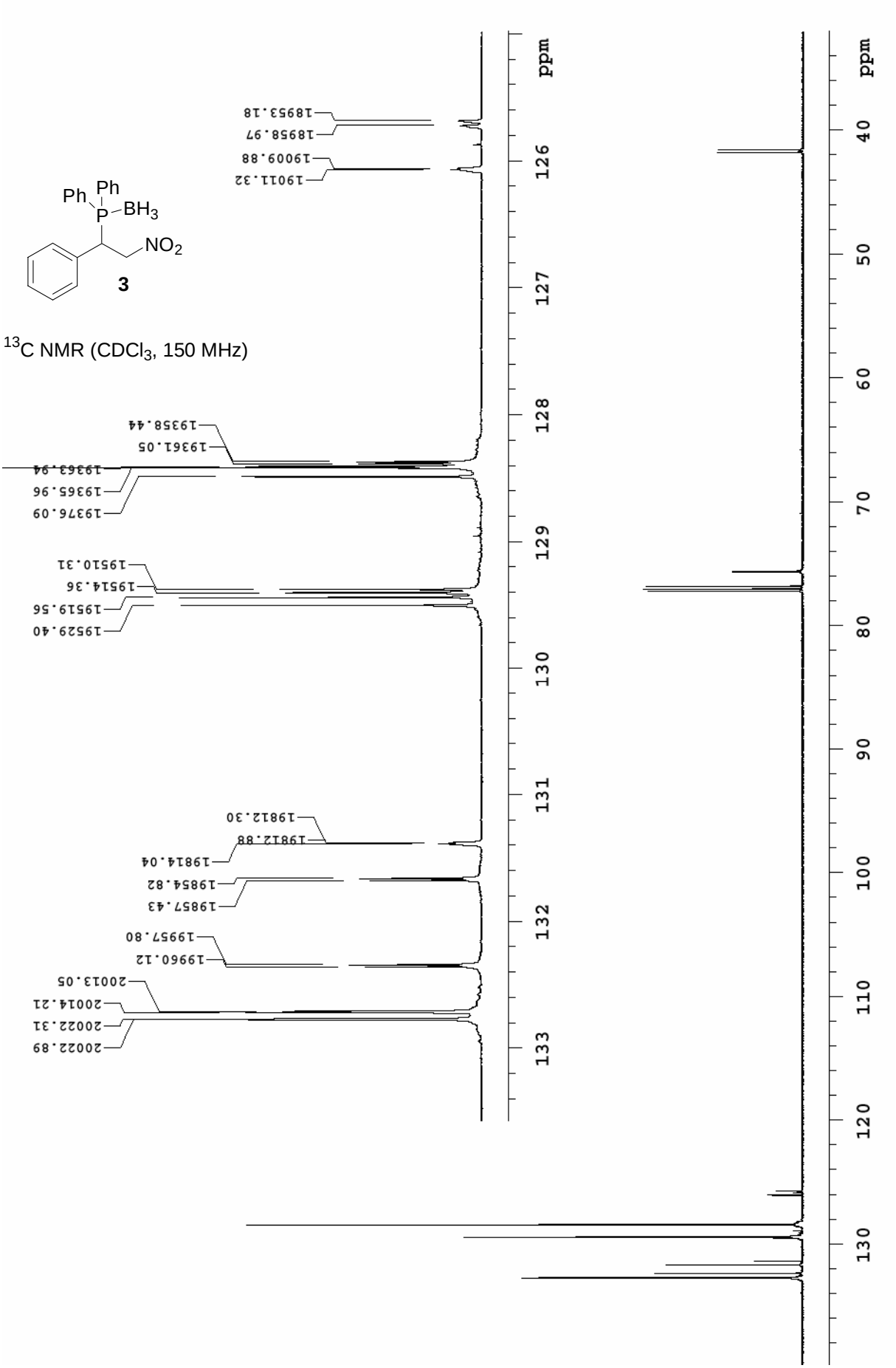
^{1}H NMR ($CDCl_3$, 600 MHz)



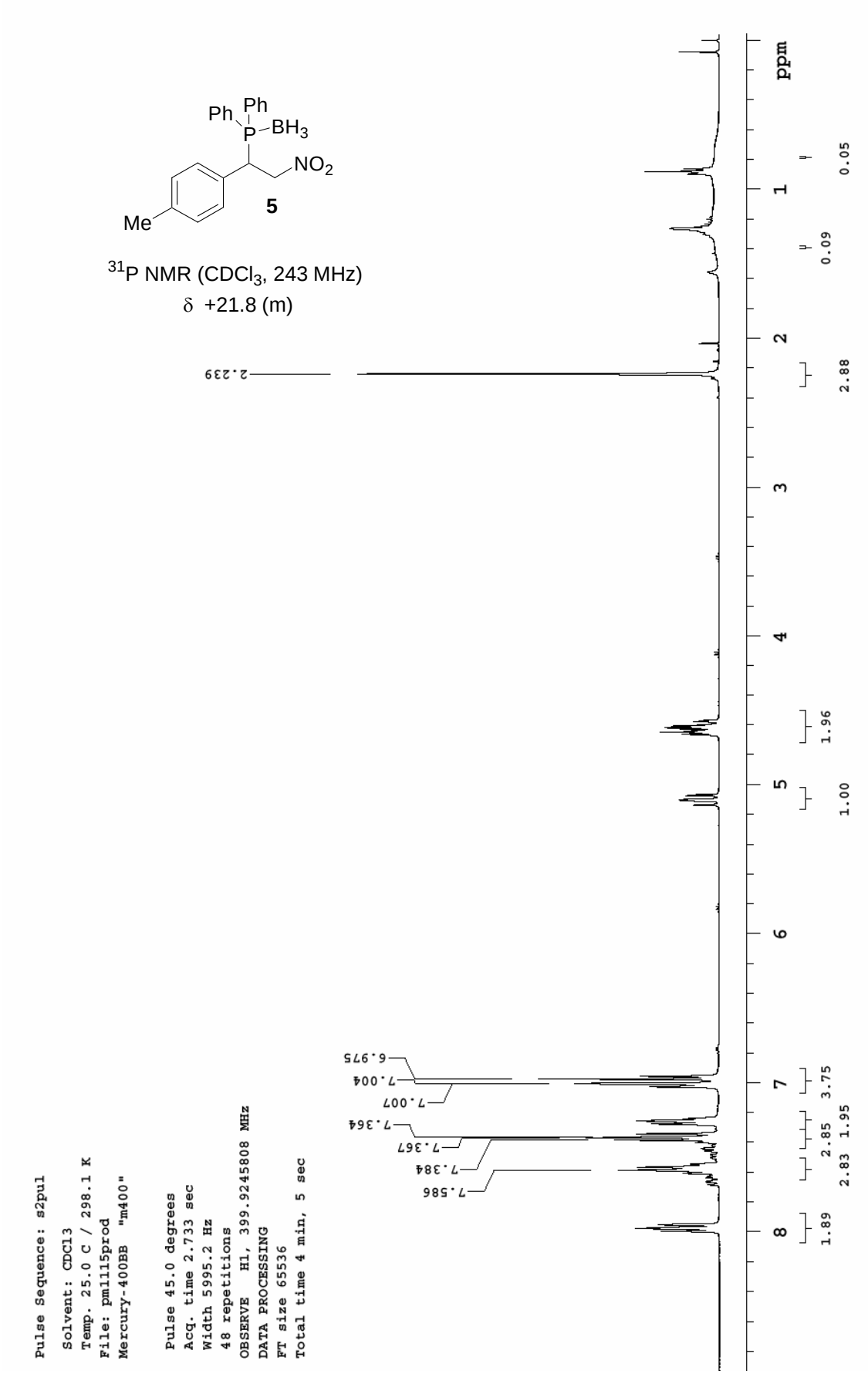
3

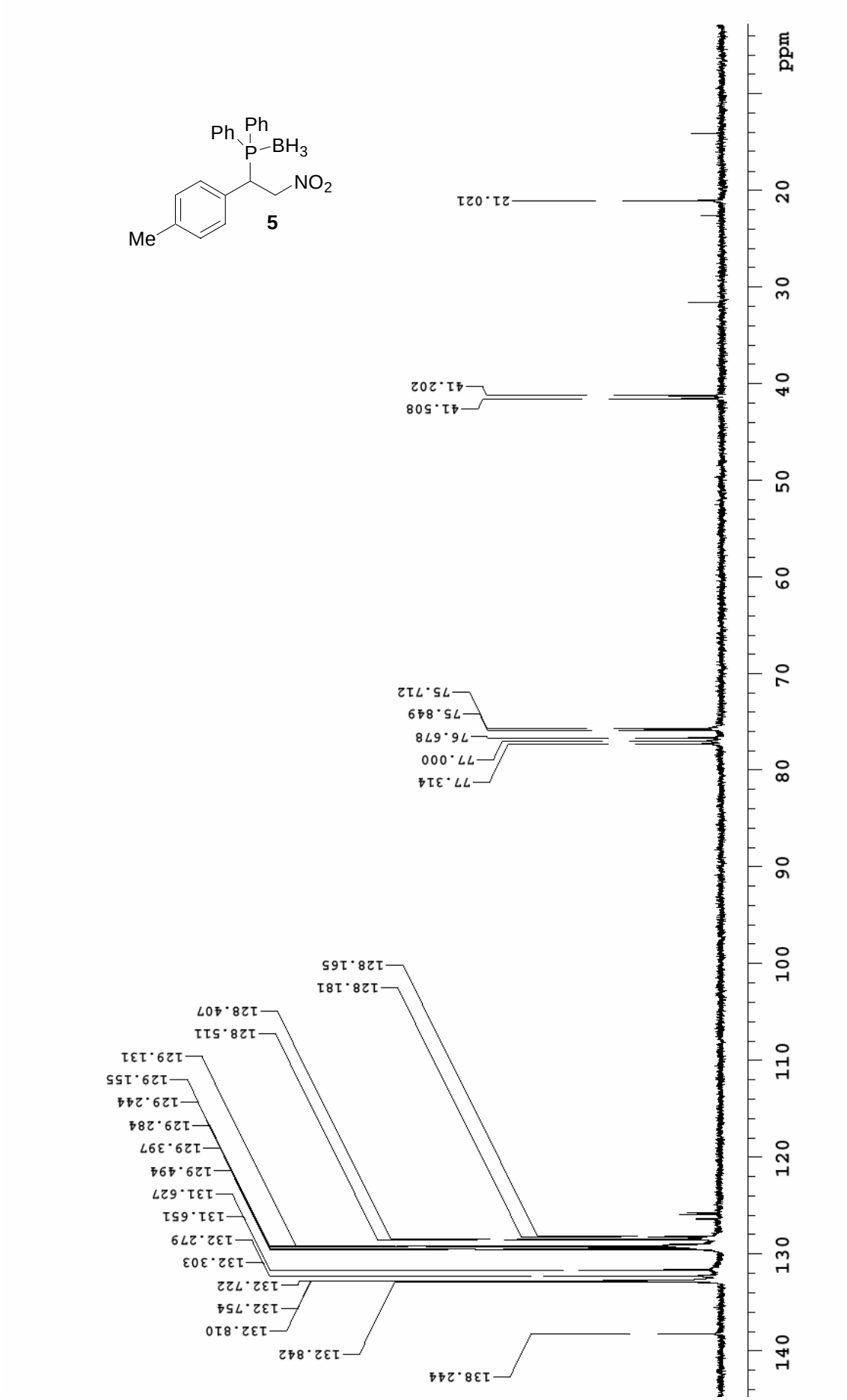
^{31}P NMR ($CDCl_3$, 243 MHz)

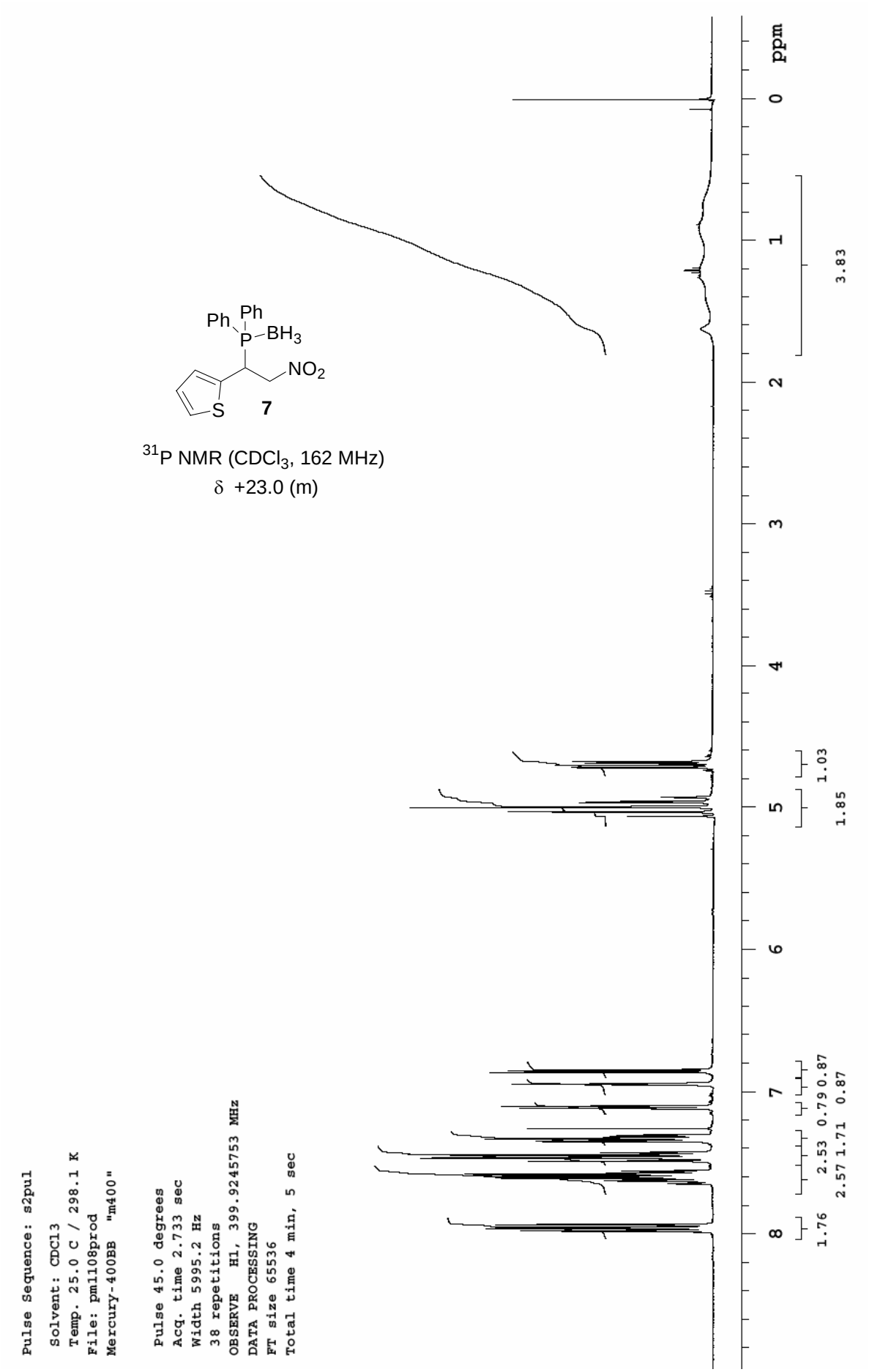
δ +22.8 (m)


Ph
Ph
P
BH3
NO2
3
13C NMR (CDCl3, 150 MHz)
ppm

NMR Spectra

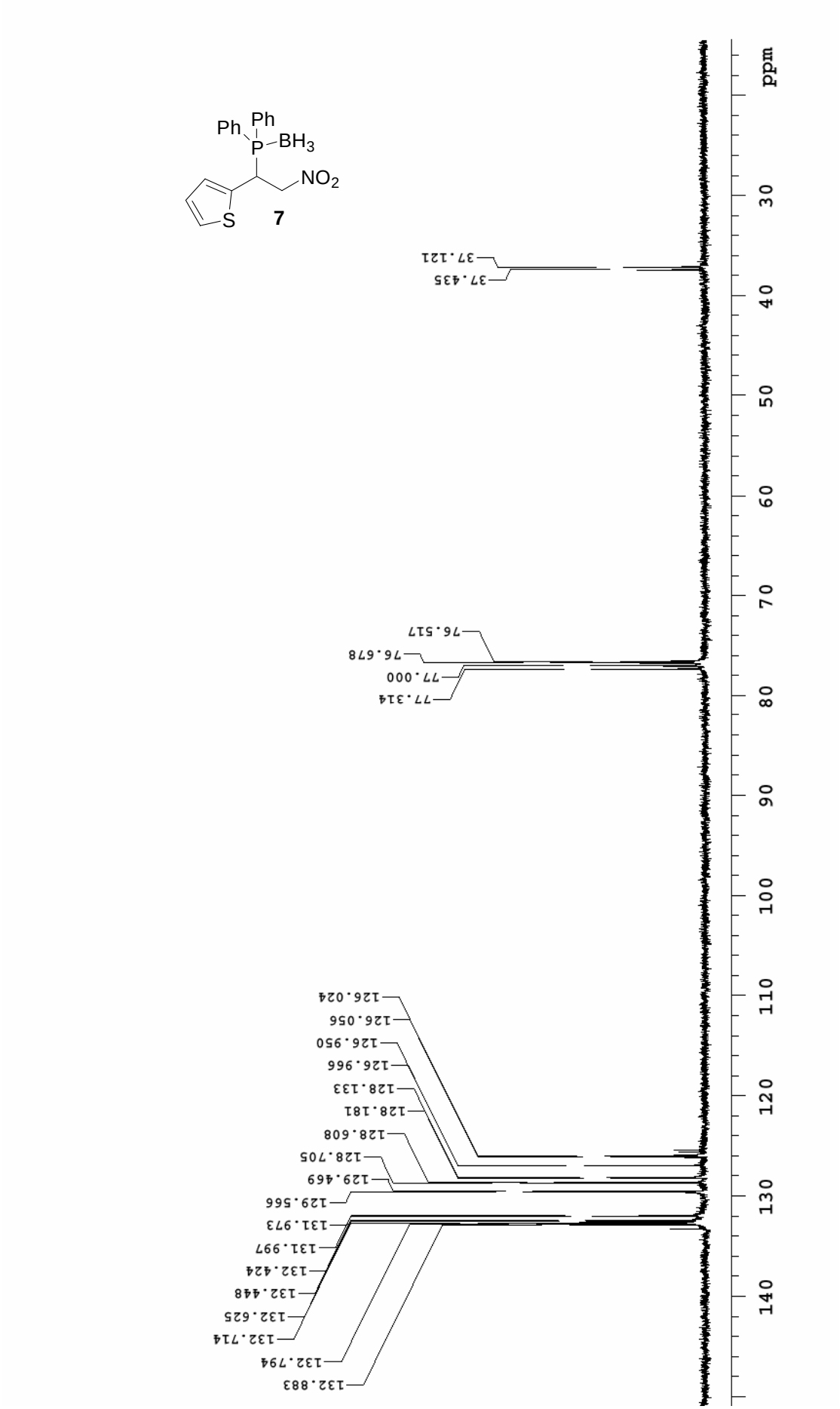

Ph
Ph
P
BH3
NO2
Me
5
31P NMR (CDCl3, 243 MHz)
δ +21.8 (m)
2.239
7.586
7.384
7.367
7.364
7.007
7.004
6.975
ppm
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
File: pm1115prod
Mercury-400BB "m400"
Pulse 45.0 degrees
Acq. time 2.733 sec
Width 5995.2 Hz
48 repetitions
OBSERVE H1, 399.9245808 MHz
DATA PROCESSING
FT size 65536
Total time 4 min, 5 sec

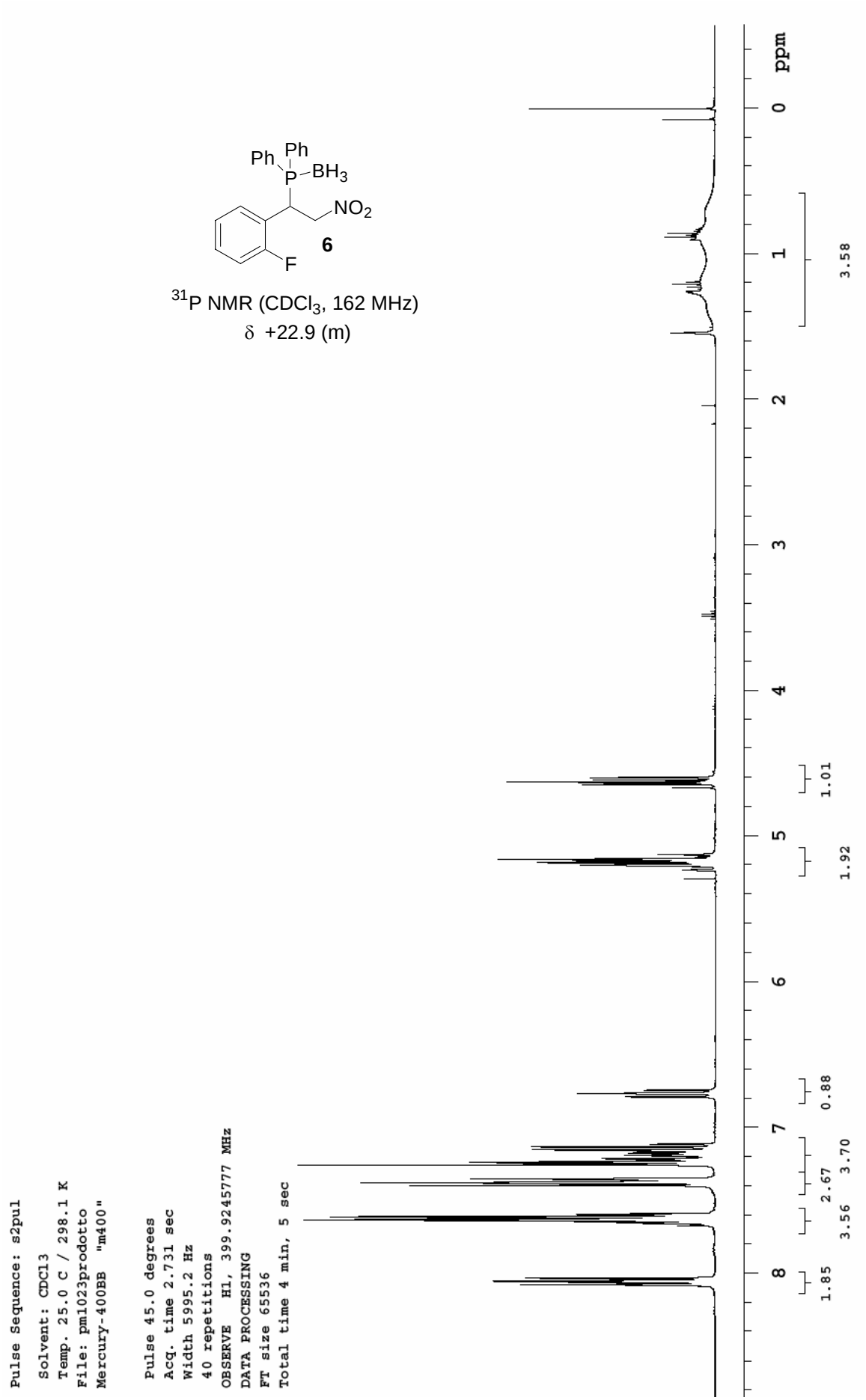

Ph
Ph
P
BH3
NO2
Me
5
ppm
21.021
41.202
41.508
75.712
75.849
76.678
77.000
77.314
128.165
128.181
128.407
128.511
129.131
129.155
129.244
129.284
129.397
129.494
131.627
131.651
132.279
132.303
132.722
132.754
132.810
132.842
138.244



^{31}P NMR ($CDCl_3$, 162 MHz)

δ +23.0 (m)

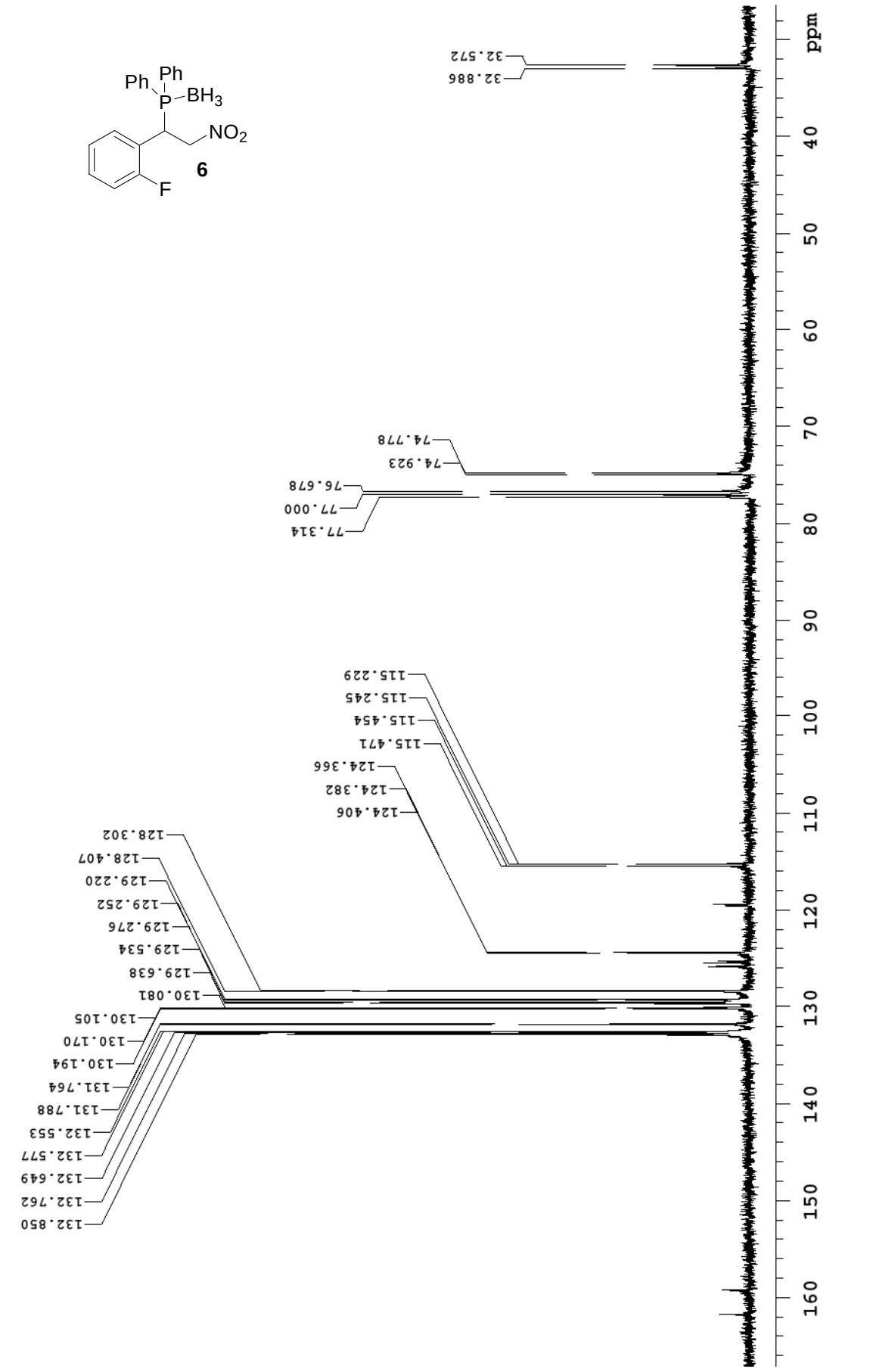

Ph
Ph
P
BH3
NO2
S
7
ppm
37.121
37.435
76.517
76.678
77.000
77.314
126.024
126.056
126.950
126.966
128.133
128.181
128.608
128.705
129.469
129.566
131.973
131.997
132.424
132.448
132.625
132.714
132.794
132.883

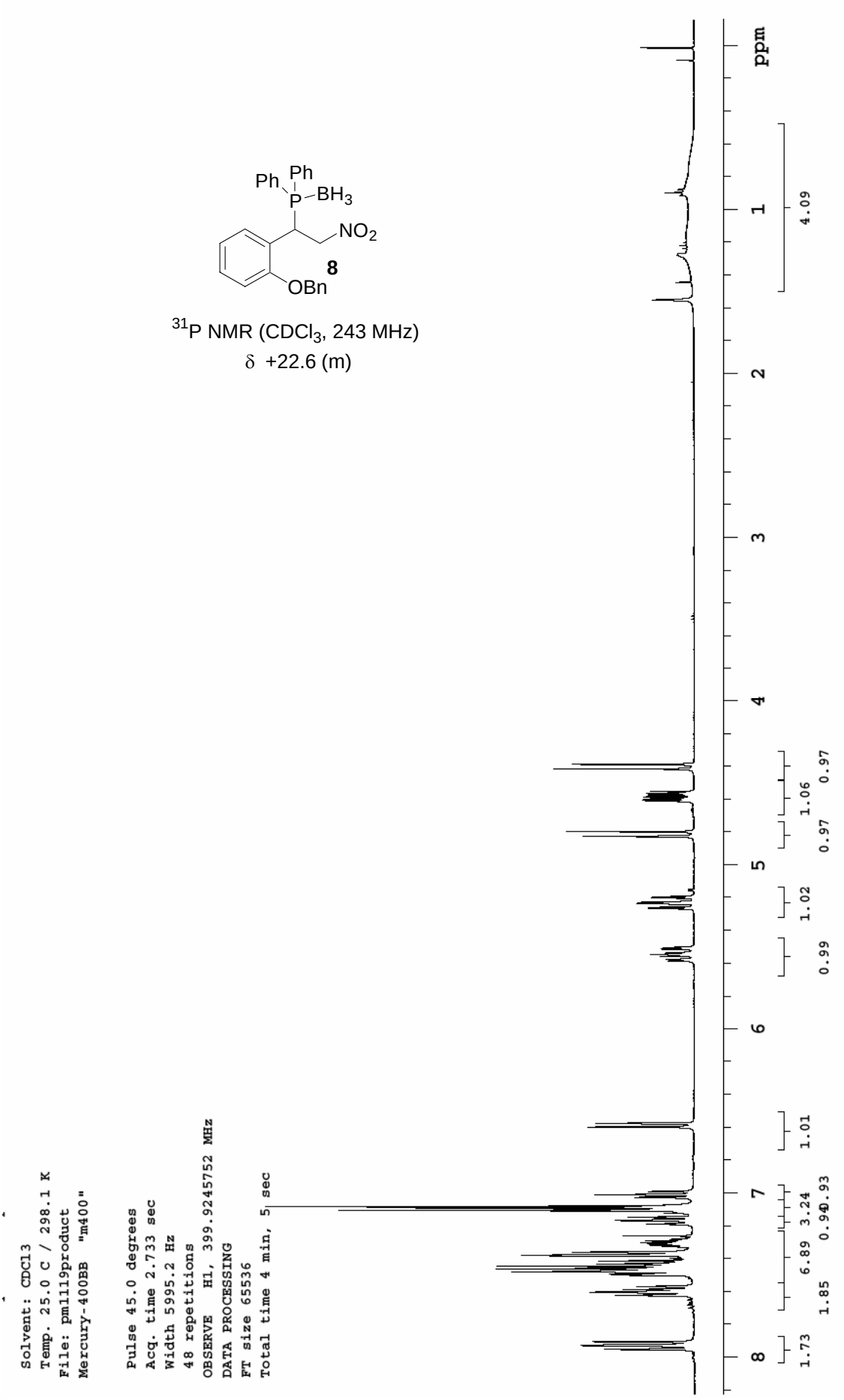


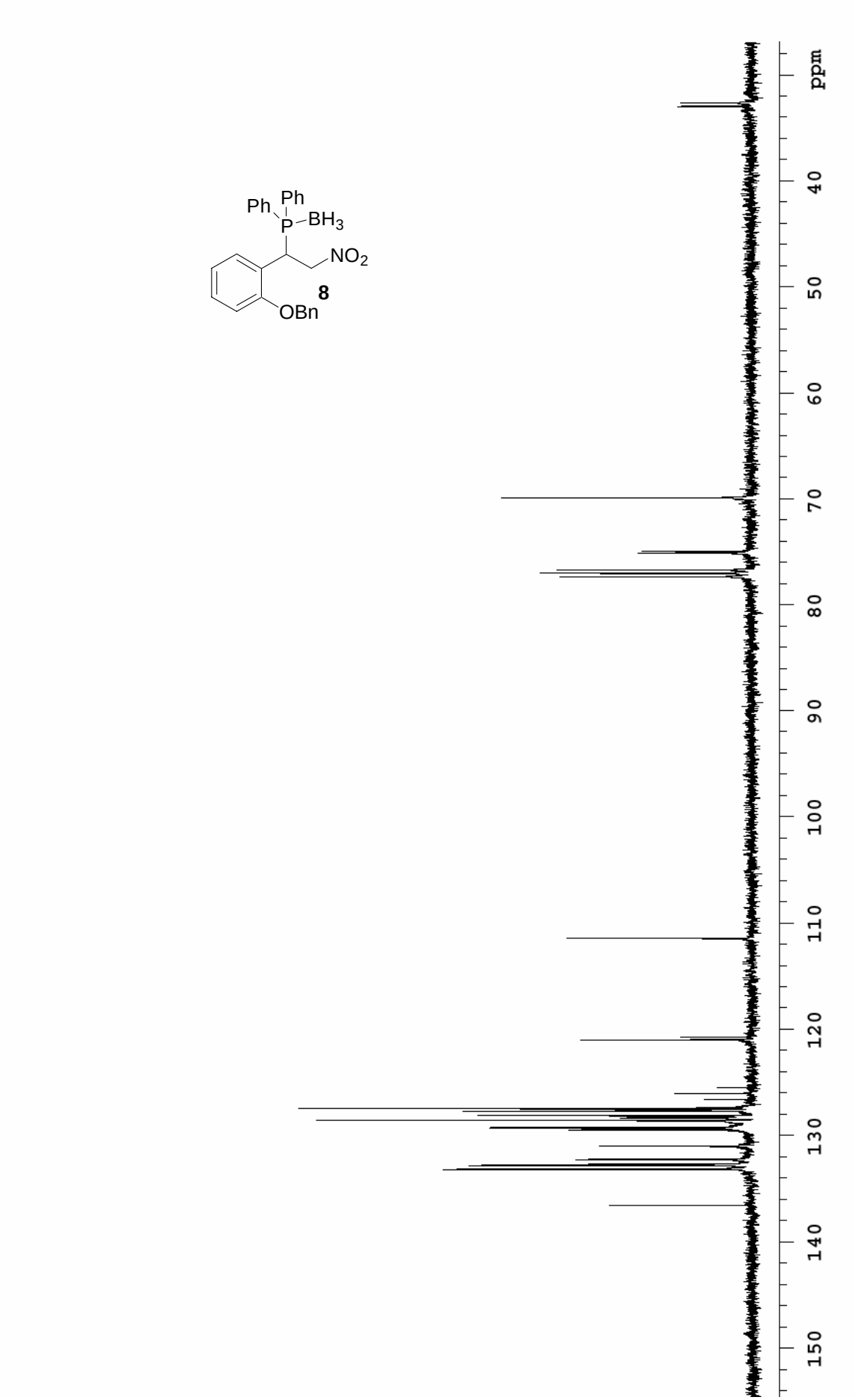
6

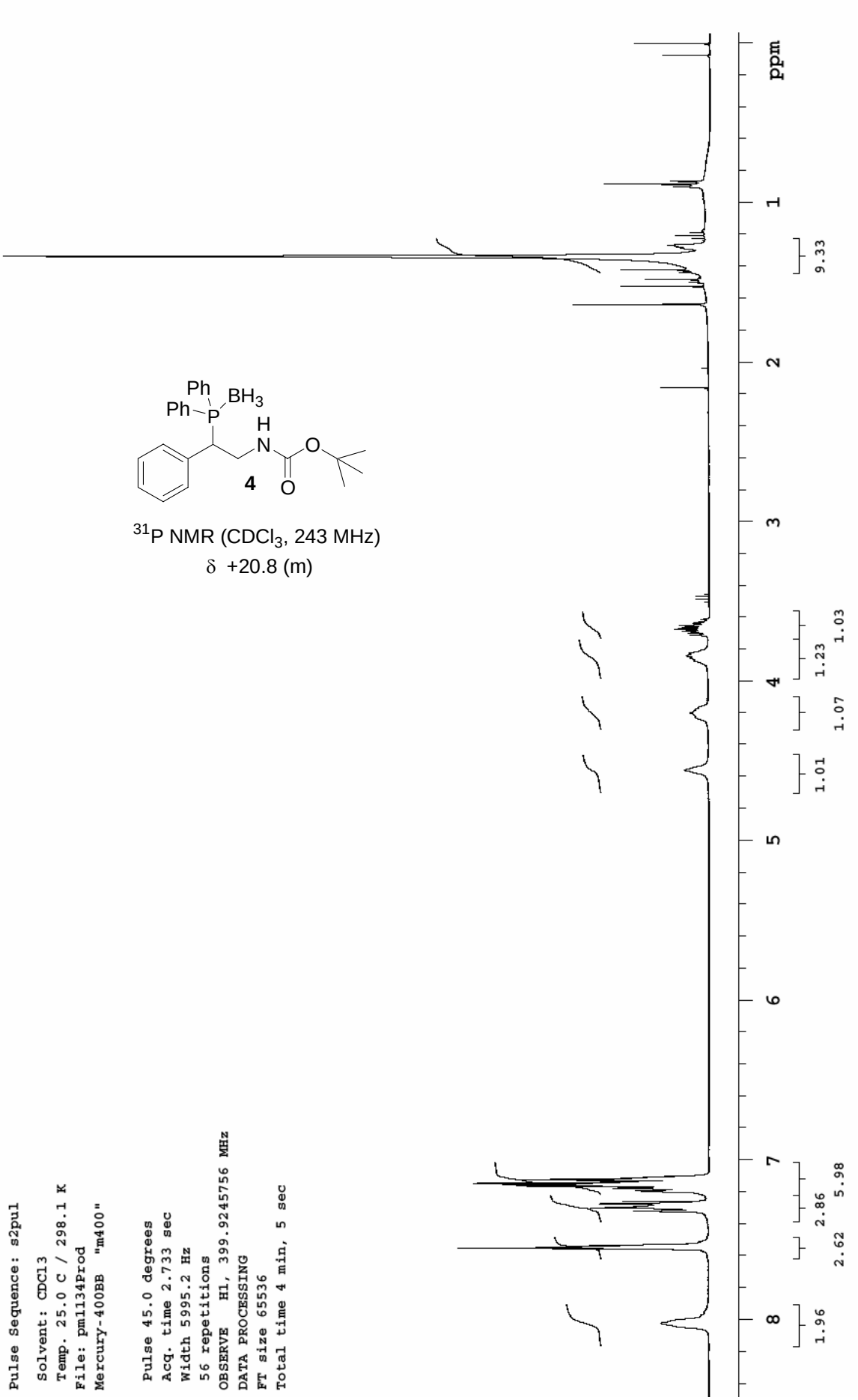
^{31}P NMR ($CDCl_3$, 162 MHz)

δ +22.9 (m)


Ph
Ph
P
BH3
NO2
F
6
32.572
32.886
74.778
74.923
76.678
77.000
77.314
115.229
115.245
115.454
115.471
124.366
124.382
124.406
128.302
128.407
129.220
129.252
129.276
129.534
129.638
130.081
130.105
130.170
130.194
131.764
131.788
132.553
132.577
132.649
132.762
132.850
ppm
40
50
60
70
80
90
100
110
120
130
140
150
160


Ph
Ph
P
BH3
NO2
OBn
8
31P NMR (CDCl3, 243 MHz)
δ +22.6 (m)
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
File: pm1119product
Mercury-400BB "m400"
Pulse 45.0 degrees
Acq. time 2.733 sec
Width 5995.2 Hz
48 repetitions
OBSERVE H1, 399.9245752 MHz
DATA PROCESSING
FT size 65536
Total time 4 min, 5 sec
ppm
1.73
6.89
3.24
1.01
1.85
0.94
0.93
0.99
1.02
0.97
1.06
0.97
0.97
4.09

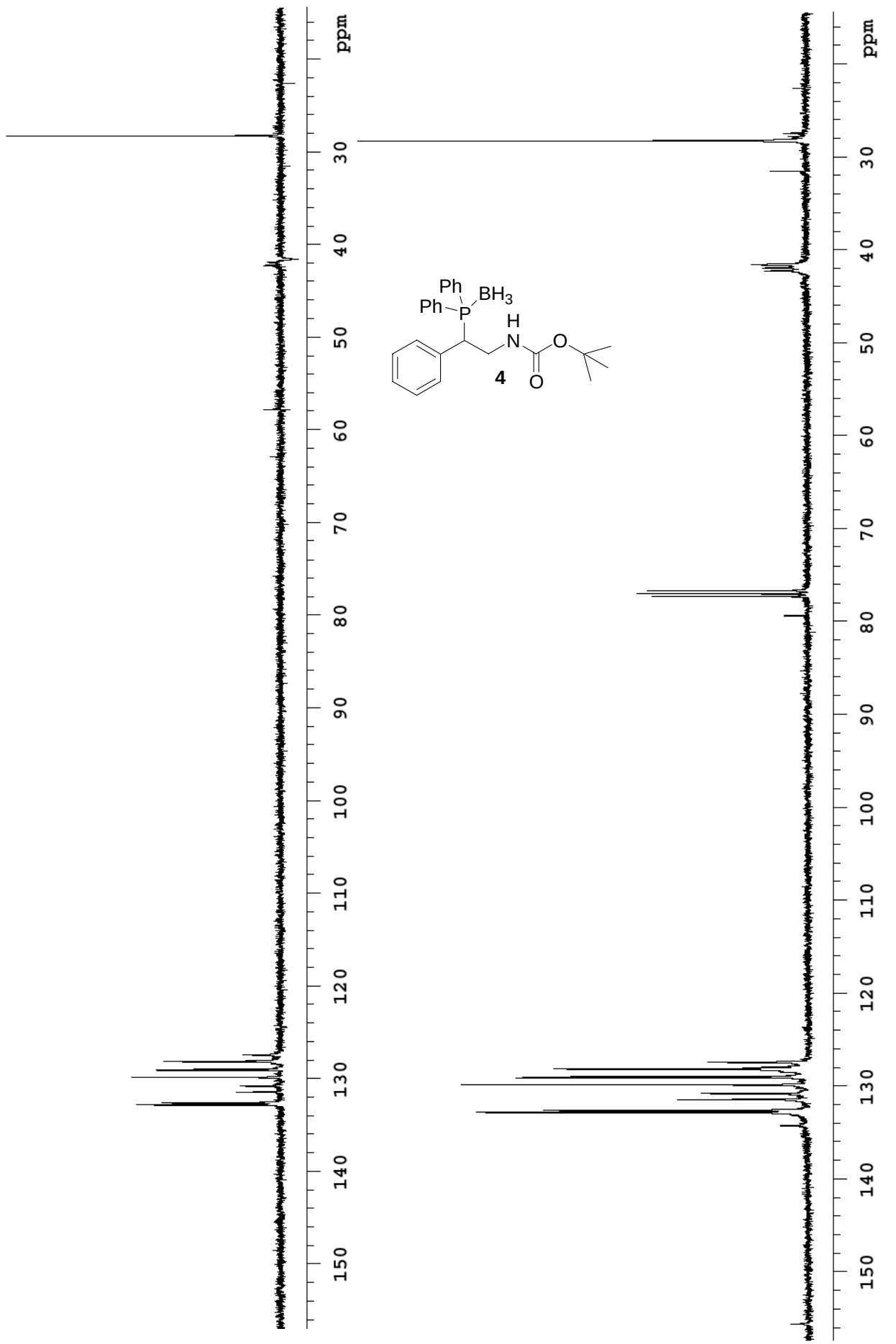

Ph
Ph
P
BH3
NO2
OBn
8
ppm
40
50
60
70
80
90
100
110
120
130
140
150

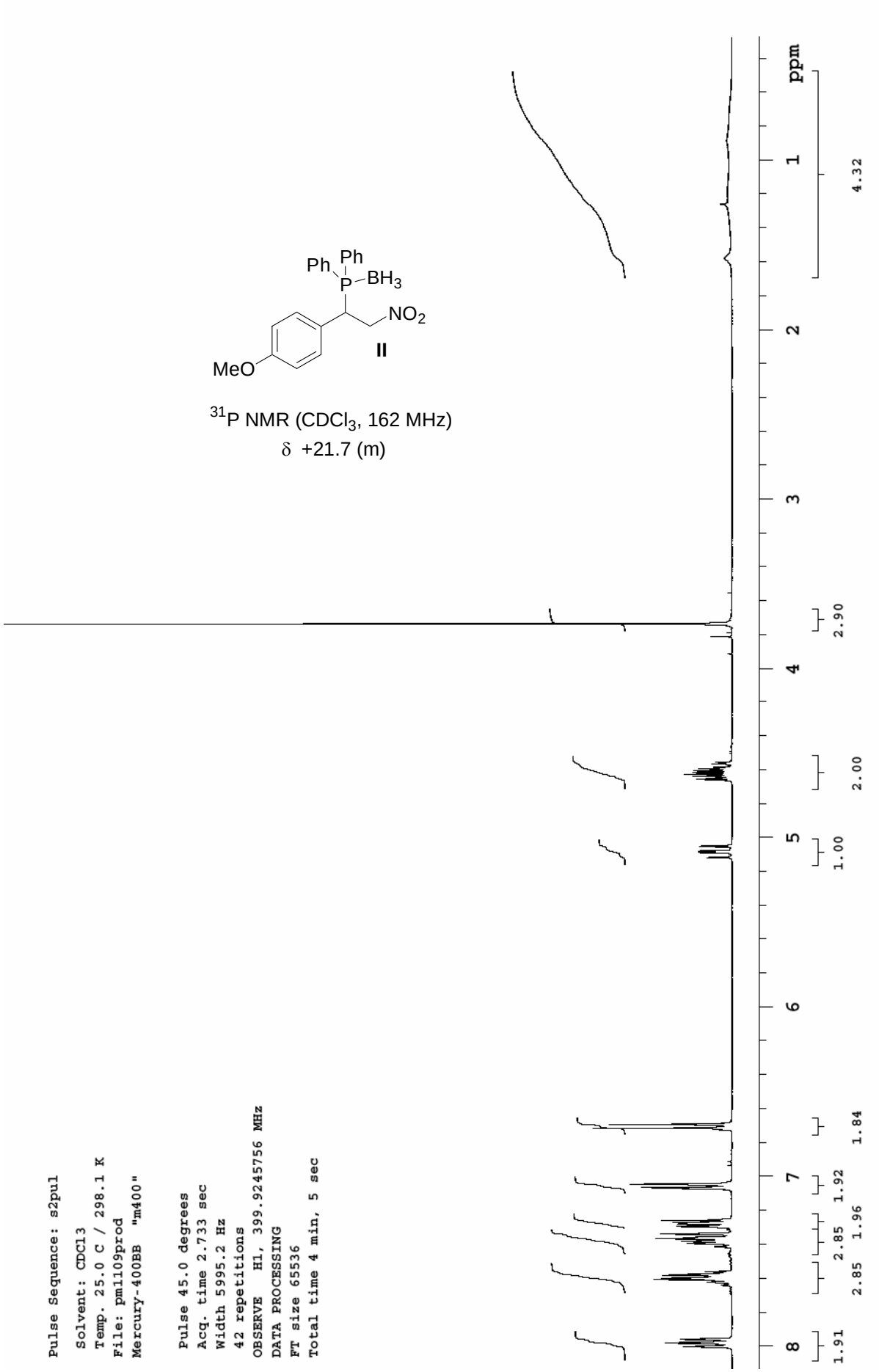


4

^{31}P NMR ($CDCl_3$, 243 MHz)

δ +20.8 (m)

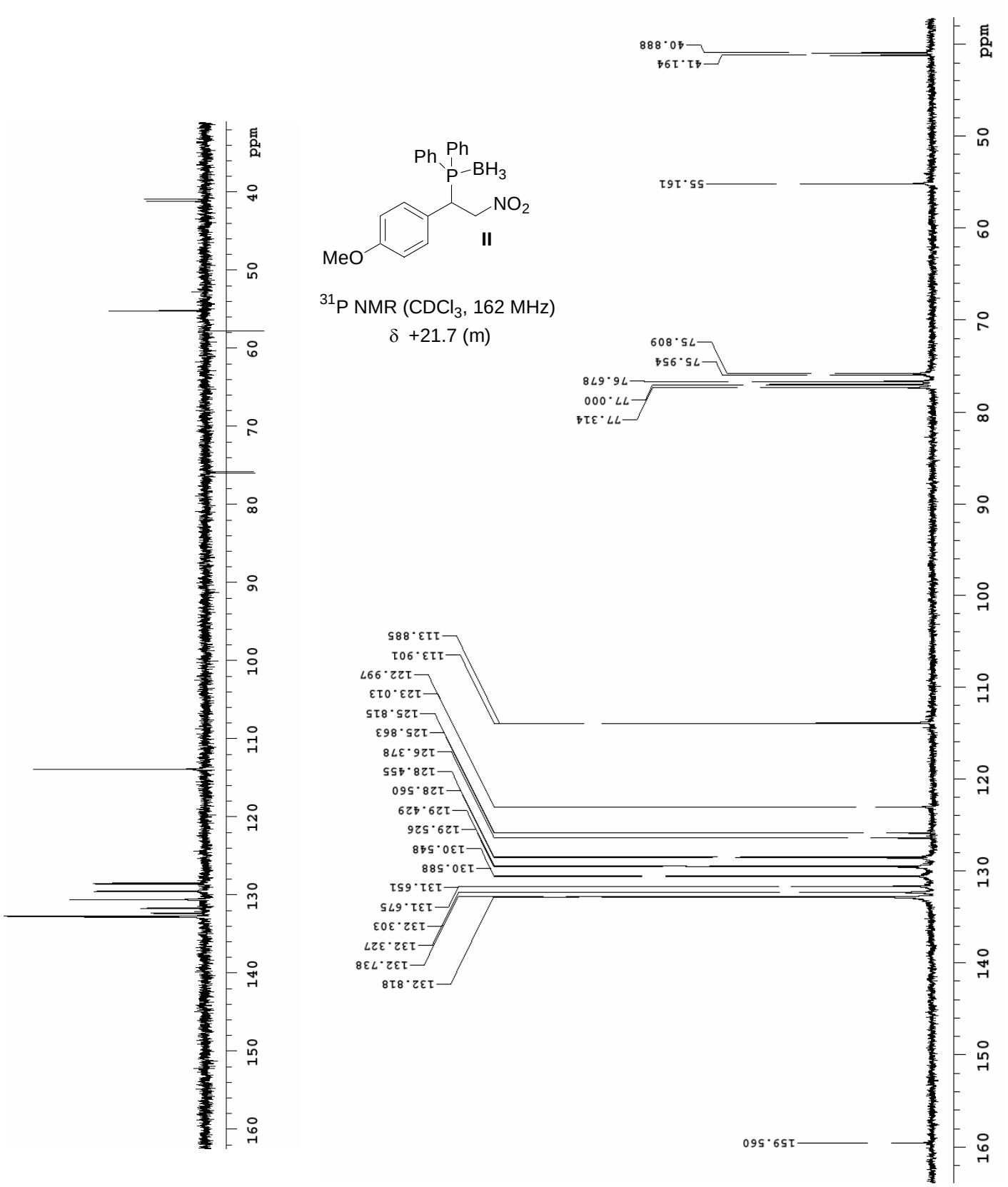

ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
Ph
Ph
P
BH3
H
N
O
O
4

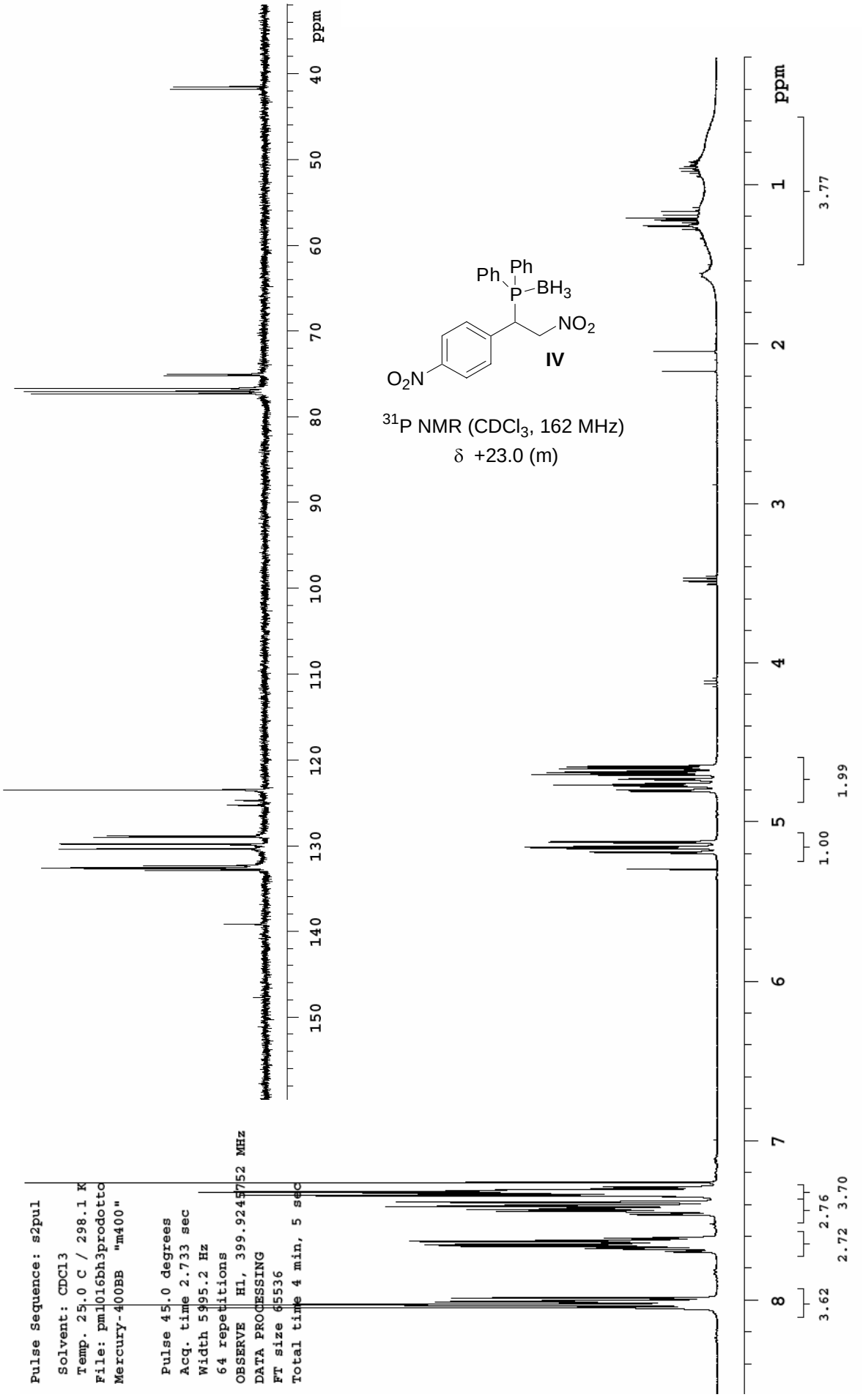


II

^{31}P NMR ($CDCl_3$, 162 MHz)

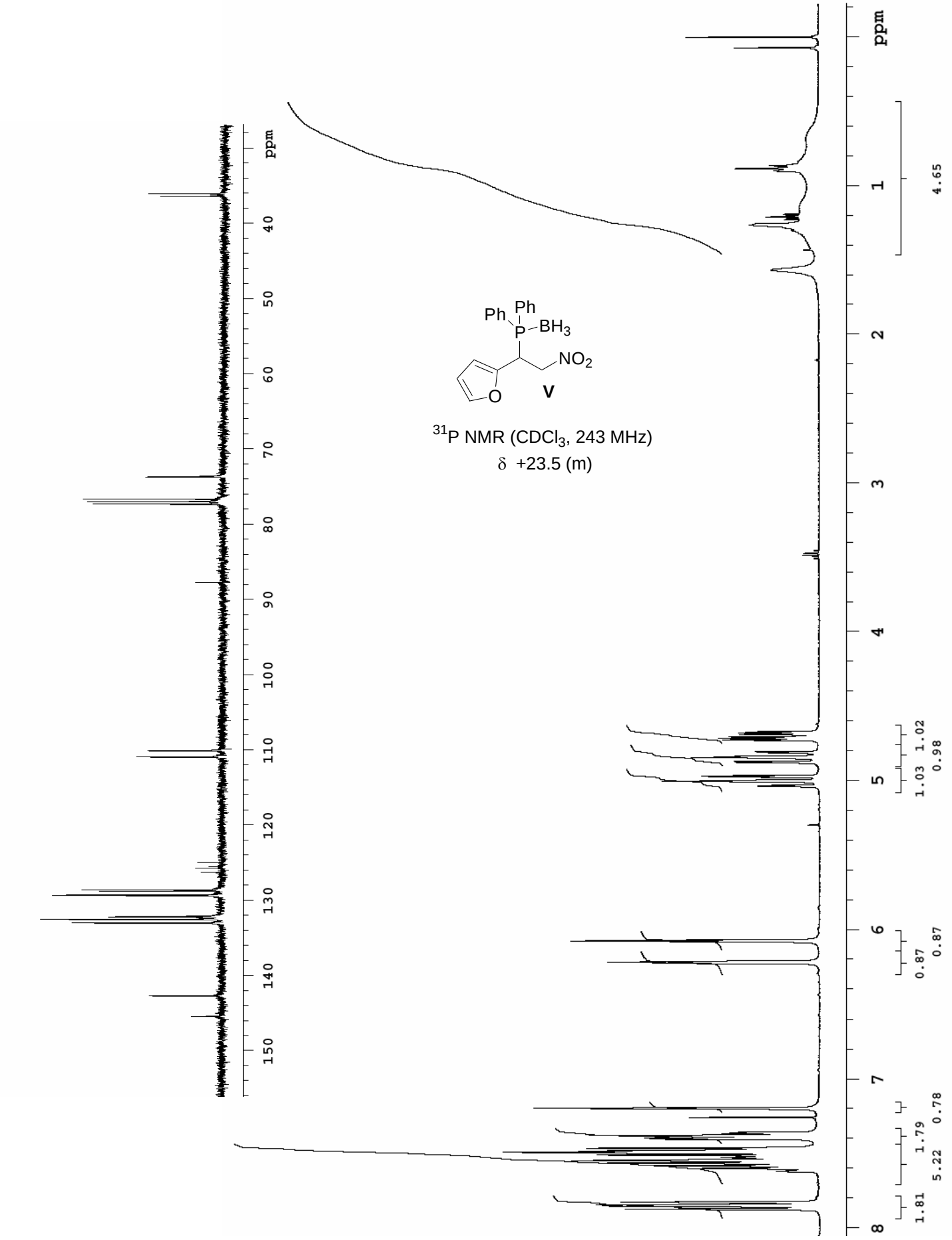
δ +21.7 (m)

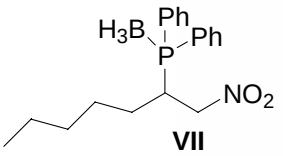

Ph
Ph
P
BH3
NO2
MeO
II
31P NMR (CDCl3, 162 MHz)
δ +21.7 (m)
ppm



^{31}P NMR ($CDCl_3$, 162 MHz)

δ +23.0 (m)

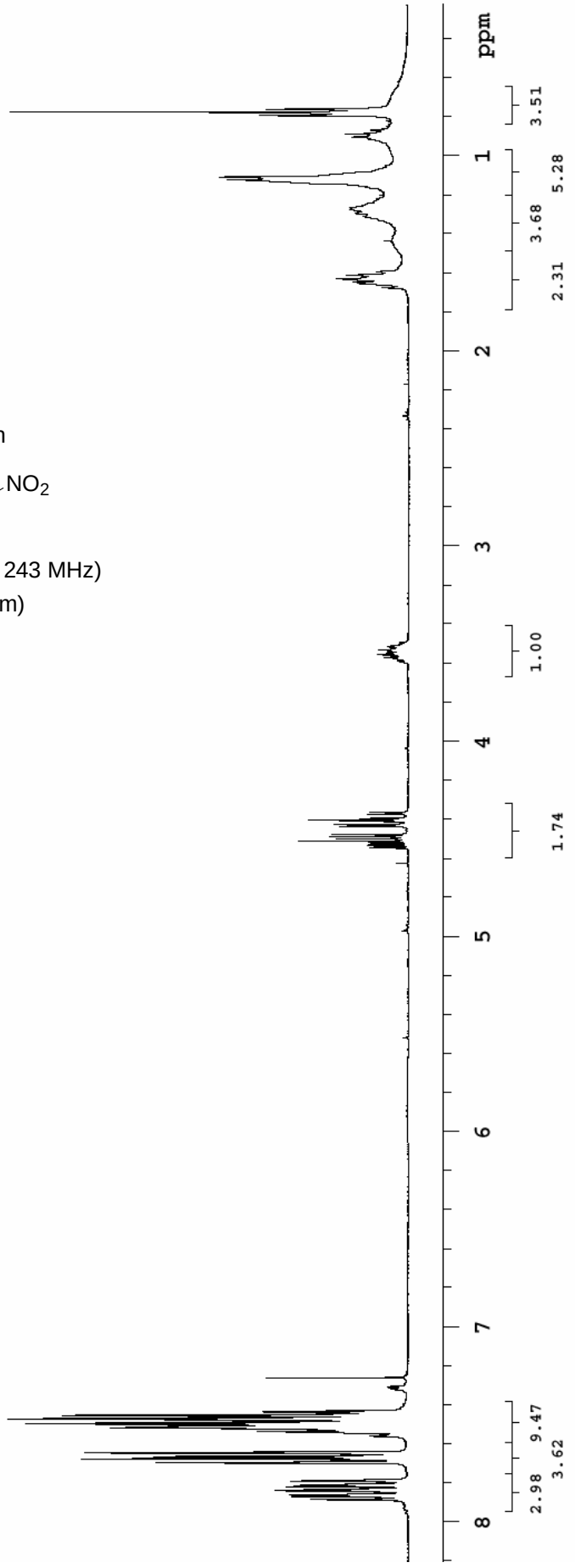

Ph
Ph
P
BH3
NO2
O
V
31P NMR (CDCl3, 243 MHz)
δ +23.5 (m)
ppm
4.65
1.03 1.02
0.98
0.87
0.87
1.81
1.79
5.22
0.78

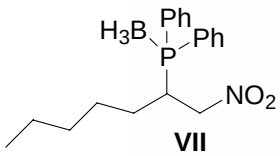


VII

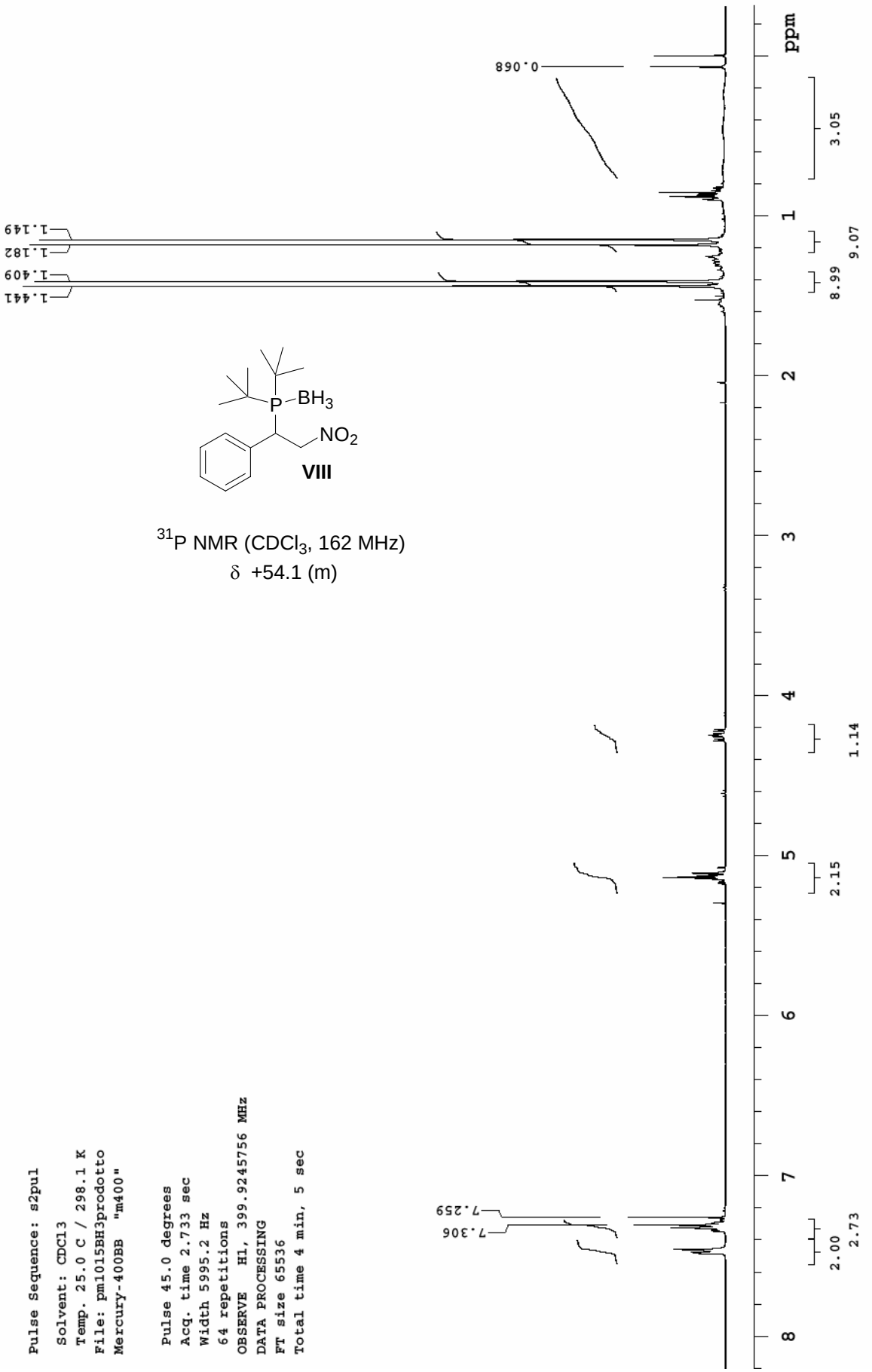
^{31}P NMR ($CDCl_3$, 243 MHz)

δ +21.9 (m)





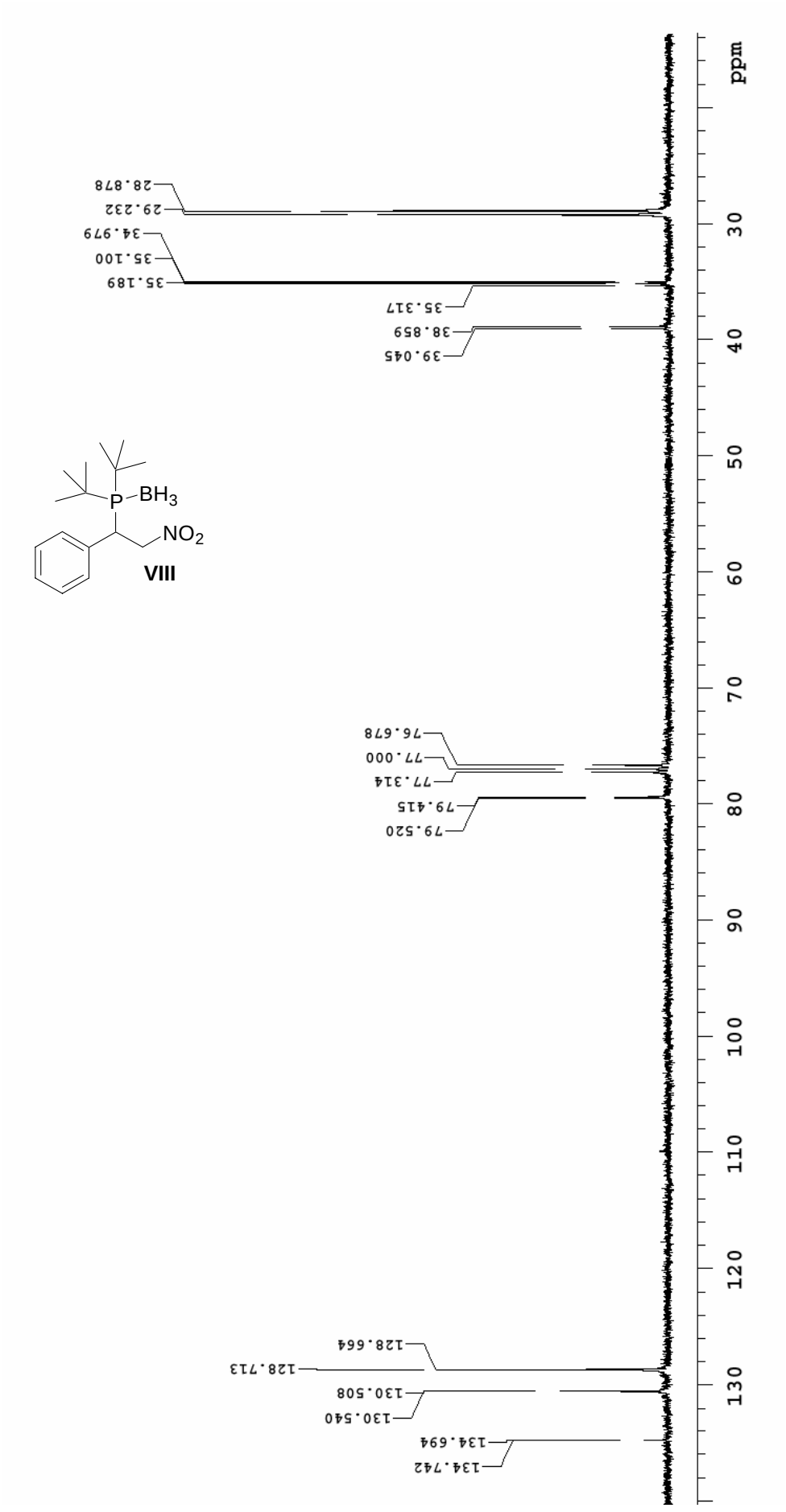
VII



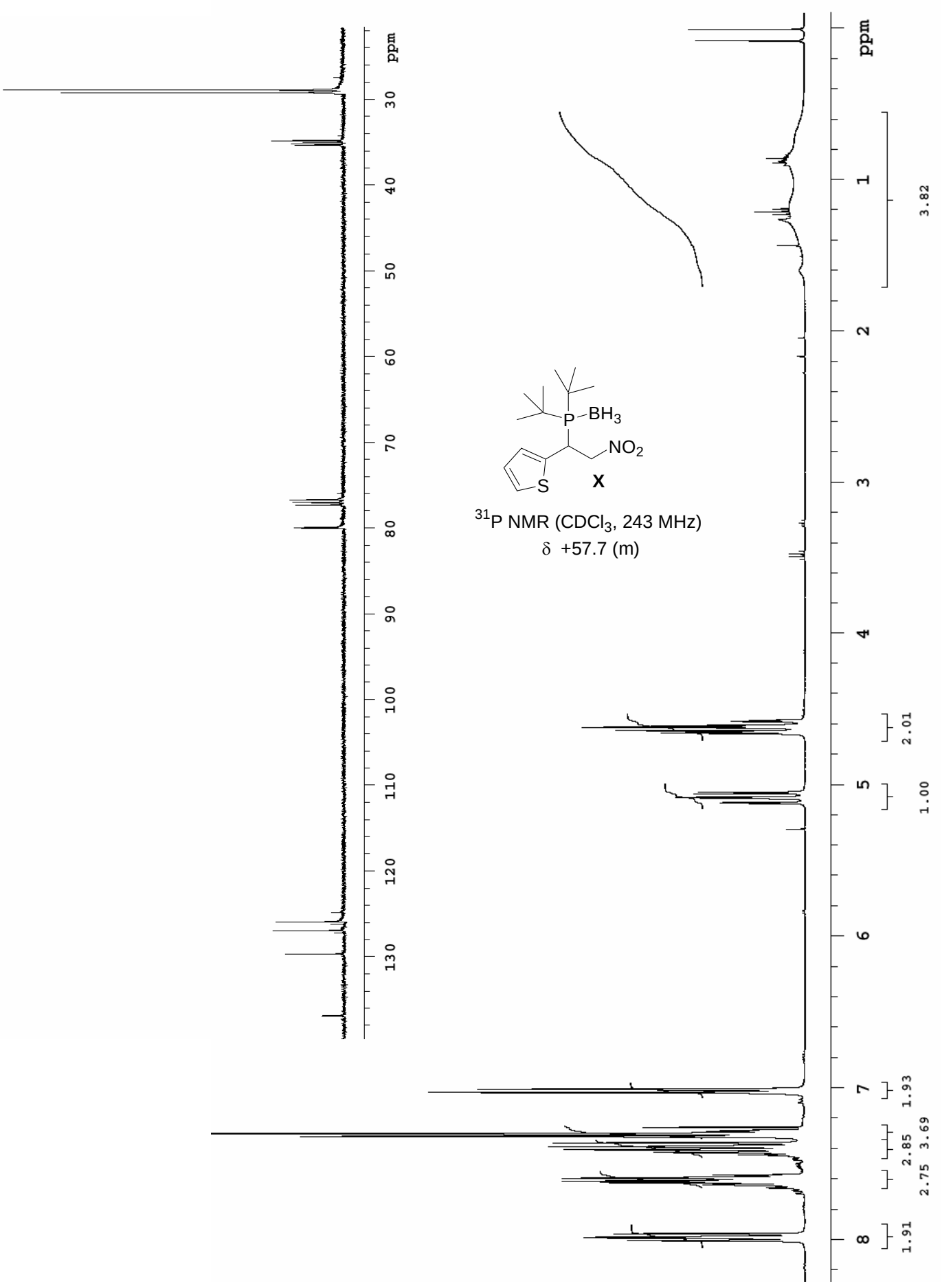
VIII

^{31}P NMR ($CDCl_3$, 162 MHz)

δ +54.1 (m)


ppm
30
40
50
60
70
80
90
100
110
120
130
28.878
29.232
34.979
35.100
35.189
35.317
38.859
39.045
76.678
77.000
77.314
79.415
79.520
128.664
128.713
130.508
130.540
134.694
134.742
P
BH3
NO2

VIII


P
BH3
NO2
S
X
31P NMR (CDCl3, 243 MHz)
δ +57.7 (m)
ppm
3.82
2.01
1.00
1.93
2.85
3.69
2.75
1.91