Supporting Information

for

Nickel-Catalyzed Direct Methylation of Arylphosphines via Carbon-Phosphorus Bond Cleavage Using $AlMe_3$

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CONTENTS

I. General Information

^{1}H NMR ^{13}C NMR and ^{31}P NMR spectra were recorded on a JEOL ECS-400 spectrometer or VARIAN UNITY INOVA-600 spectrometer in $CDCl_3$ with tetramethylsilane as an internal reference standard, toluene-d_8 or benzene-d_6. The chemical shifts in ^{1}H NMR spectra were recorded relative to $CHCl_3$ (δ 7.26). The chemical shifts in ^{13}C NMR spectra were recorded relative to $CDCl_3$ (δ 77.16). The chemical shifts in ^{31}P NMR spectra were recorded relative to $P(OEt)_3$ (138.8 ppm) as an external standard. Data are reported as follows: chemical shift (δ) in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q= quartet and m = multiplet), coupling constant (*J*) in Hz, and integration. Infrared spectra (IR) were obtained using a JASCO FT/IR-4200 spectrometer; absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra and high resolution mass spectra (HRMS) were obtained on a JEOL JMS-700 spectrometer. Analytical gas chromatography (GC) was carried out on a Shimazu GC-2014 gas chromatograph, equipped with a flame ionization detector. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed with SiO_2 (Silicycle Silica Flash F60 (230-400 mesh)) or NH Silica (Silica Gel 60 (sperical) NH_2 (40-50 μm)).

II. Materials

All commercially available reagents and solvents were supplied from TCI, WAKO and Aldrich. Methyldiphenylphosphine sulfide [CAS: 13639-74-2] was prepared from methyldiphenylphosphine (TCI) and S_8 (Wako). 5-Phenylbenzo[*b*]phosphindole 5-sulfide [CAS: 33771-54-9] was synthesized by using 2,2'-dibromo-1,1'-biphenyl (TCI) and dichloro(phenyl)phosphane (TCI), according to the literature method.[1] 7-Phenylbenzo[*e*]naphtho[2,1-*b*]phosphindole 7-sulfide was synthesized by using 2,2'-dibromo-1,1'-binaphthalene (TCI) and dichloro(phenyl)phosphane (TCI), according to the literature method.[2] Tri([1,1'-biphenyl]-4-yl)phosphane (**6**) was synthesized by using 4-bromobiphenyl (TCI) and trichlorophosphane (TCI), according to the literature method.[3]

III. Optimization Studies

A procedure for optimization studies. In a glovebox filled with nitrogen, $Ni(cod)_2$ (4.1 mg, 0.015

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[1] Kalkeren, H. A.; Leenders, S. H. A. M.; Hommersom, C. R. A.; Ruties, F. P. J. T.; Delft, F. *Chem. Eur. J.* **2011**, *17*, 11290.

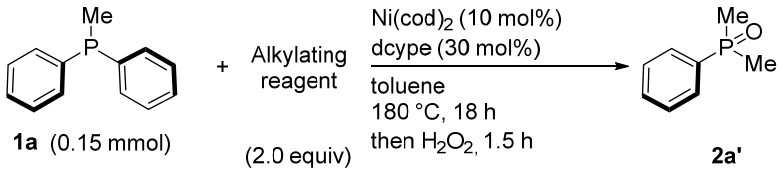
[2] Watson, A. A.; Willis, A. C.; Wild, S. B. *J. Organomet. Chem.* **1993**, *445*, 71.

[3] Song, Z.; Huang, X.; Jiang, S.; He, C.; Tang, L.; Ni, Q. Ma, M.; Chen, B.; Ma, Y. *Org. Lett.* **2022**, *24*, 5573.

mmol, 0.10 equiv), ligand (0.10-0.30 equiv) and toluene (0.30 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap, and stirred for 5 min at rt. A methyldiphenylphosphine (**1a**), methyl(diphenyl)phosphine oxide (**1a'**) or triphenylphosphine (**4**) (0.15 mmol, 1.0 equiv) and $AlMe_3$ (1.8 M in toluene, 0.50-3.0 equiv) (or other methylating reagents) were then added, and the cap was applied to seal the vial. The vial was stirred at 100-180 °C for 18 h. After the reaction mixture was cooled to rt, an aqueous solution of H_2O_2 (30%, 15 drops) were added slowly, and the mixture was stirred at rt for 1.5 h. The crude mixture was filtered through a pad of Celite eluting with EtOAc. The filtrate was analyzed by GC using eicosane as an internal standard.

III-1. Optimization of Reaction Conditions on the Reaction of 1a

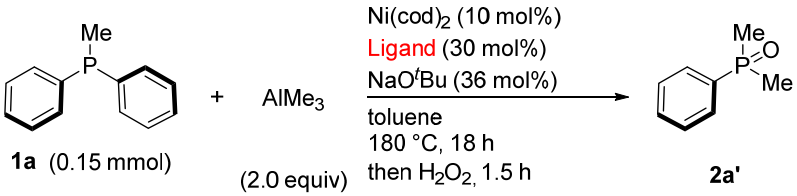
Table S1. Effect of Methylating Reagents



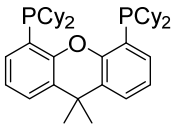
Entry	Alkylating reagent	GC yields (%)		Note
		2a'	**1a'**	
1	$AlMe_3$	58	3	
2	$AlClMe_2$	24	34	
3	MeLi	0	48	
4	MeMgBr	0	35	
5	$ZnMe_2$	0	>99	120 °C
6	$SnMe_4$	0	96	120 °C

The effect of methylating reagents was examined by using **1a** (0.15 mmol), a methylating reagent (0.30 mmol), $Ni(cod)_2$ (0.015 mmol) and dcype (0.045 mmol) in toluene (0.30 mL) at 180 °C for 18 h (Table S1). Under these conditions, $AlMe_3$ was found to be an optimal methylating reagent with a methylated product **2a'** being formed in 58% (Entry 1).

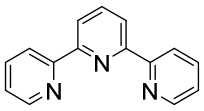
Table S2. Effect of Ligands



Entry	Ligand	GC yields (%)		Note
		2a'	**1a'**	
0	none	46	23	
1	IPr•HCl	48	17	
2	ICy•HCl	42	12	
3	IMes•HCl	40	17	
4	$IMes^{Me}$•HCl	44	19	
5	dcype	58	3	without NaO^{t}Bu
6	Ligand A	42	25	without NaO^{t}Bu
7	dtbpy	35	20	without NaO^{t}Bu
8	Ligand B	29	45	without NaO^{t}Bu



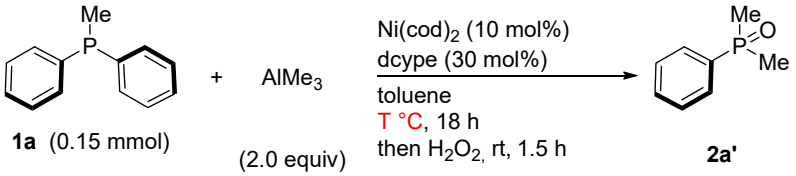
Ligand A



Ligand B

The effect of ligands was examined by using **1a** (0.15 mmol), $AlMe_3$ (0.30 mmol), $Ni(cod)_2$ (0.015 mmol) and ligand (0.045 mmol) in toluene (0.30 mL) at 180 °C for 18 h (Table S2). Under these conditions, dcype was found to be an optimal ligand with a methylated product **2a'** being formed in 58% (Entry 5).

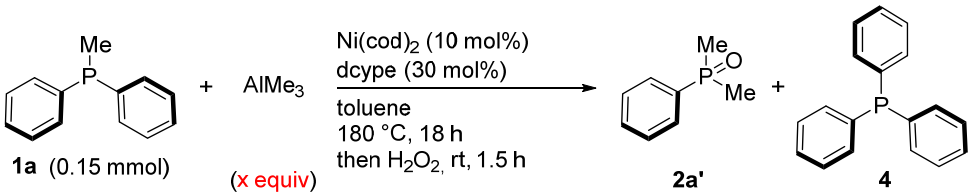
Table S3. Effect of Reaction Temperature



Entry	T (°C)	GC yields (%)	
		2a'	**1a'**
1	180	58	3
2	160	65	15
3	140	42	43
4	120	19	67
5	100	0	51

The effect of the reaction temperature was examined by using **1a** (0.15 mmol), $AlMe_3$ (0.30 mmol), $Ni(cod)_2$ (0.015 mmol) and dcype (0.045 mmol) in toluene (0.30 mL) for 18 h (Table S3). Under these conditions, 180 °C were found to be an optimal reaction temperature with a methylated product **2a'** being formed in 58% (Entry 1).

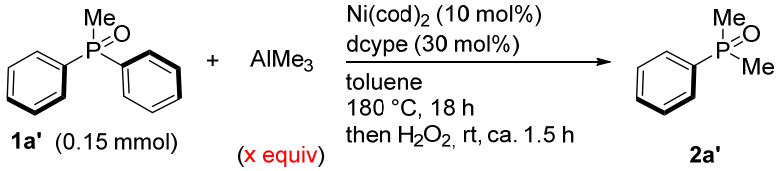
Table S4. Effect of the Amount of $AlMe_3$ Using 1a



Entry	x (equiv)	GC yields (%)		
		2a'	**4**	**1a'**
1	0.50	34	9	31
2	1.0	48	6	31
3	1.2	48	0	16
4	1.5	73	0	7
5	1.8	76	0	6
6	2.0	58	0	3
7	3.0	56	0	3

The effect of the amount of $AlMe_3$ was examined by using **1a** (0.15 mmol), $AlMe_3$, $Ni(cod)_2$ (0.015 mmol) and dcype (0.045 mmol) in toluene (0.30 mL) at 180 °C for 18 h (Table S4). Under these conditions, 1.8 equiv was found to be an optimal amount of $AlMe_3$ with a methylated product **2a'** being formed in 76% (Entry 5).

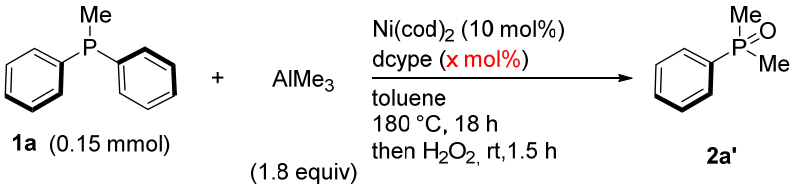
Table S5. Effect of the Amount of $AlMe_3$ Using 1a'



Entry	x (equiv)	GC yields (%)	
		2a'	**1a'**
1	1.5	39	20
2	1.8	42	27
3	2.0	42	19
4	2.5	39	20
5	3.0	34	12

The effect of the amount of $AlMe_3$ was examined by using **1a'** (0.15 mmol), $AlMe_3$, $Ni(cod)_2$ (0.015 mmol) and dcype (0.045 mmol) in toluene (0.30 mL) at 180 °C for 18 h (Table S5). Under these conditions, 1.8 equivalents were found to be an optimal amount of $AlMe_3$ with a methylated product **2a'** being formed in 42% (Entry 2).

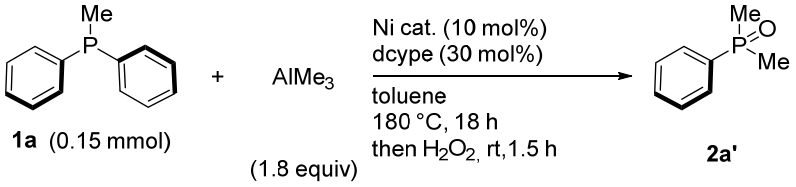
Table S6. Effect of the Amount of dcype



Entry	x (mol%)	GC yields (%)	
		2a'	**1a'**
1	10	43	33
2	20	68	19
3	30	76	6
4	50	61	4

The effect of the amount of dcype was examined by using **1a** (0.15 mmol), $AlMe_3$ (1.8 equiv), $Ni(cod)_2$ (0.015 mmol) and dcype in toluene (0.30 mL) at 180 °C for 18 h (Table S6). Under these conditions, 30 mol% were found to be an optimal amount of dcype with a methylated product **2a'** being formed in 76% (Entry 3).

Table S7. Effect of the Nickel Catalysts

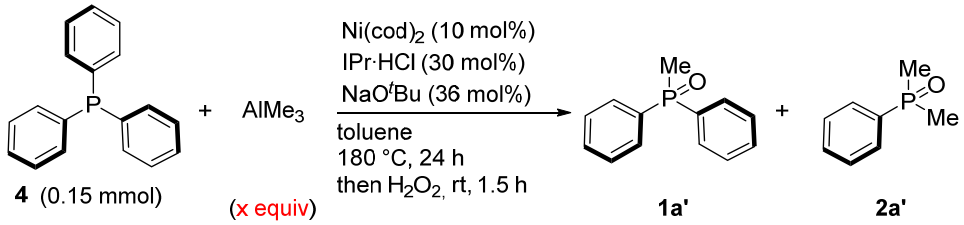


Entry	Ni cat.	GC yields (%)	
		2a'	**1a'**
1	$Ni(cod)_2$	76	6
2	$Ni(OAc)_2$	50	37
3	$NiCl_2$•dme	54	0

The effect of the the Nickel catalysts was examined by using **1a** (0.15 mmol), $AlMe_3$ (1.8 equiv), Ni cat (0.015 mmol) and dcype in toluene (0.30 mL) at 180 °C for 18 h (Table S7).

III-2. Optimization of Reaction Conditions on the Reaction of Triphenylphosphine 4

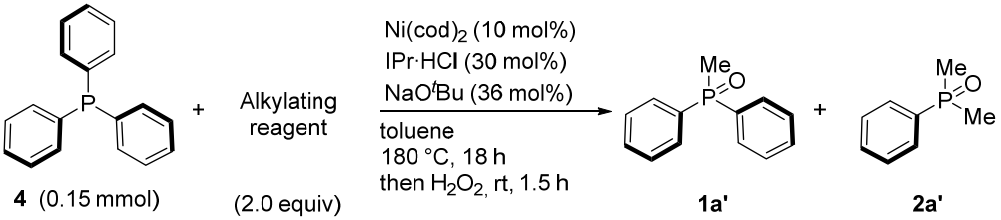
Table S8. Effect of the Amount of $AlMe_3$



Entry	x (equiv)	GC yields (%)		
		1a'	**2a'**	**4'**
1	0.50	22	17	21
2	1.0	23	41	5
3	1.5	13	47	1
4	2.0	21	49	0
5	3.0	26	41	0

The effect of the amount of $AlMe_3$ was examined by using **1a'** (0.15 mmol), $AlMe_3$, $Ni(cod)_2$ (0.015 mmol) and IPr·HCl (0.045 mmol) in toluene (0.30 mL) at 180 °C for 24 h (Table S8). Under these conditions, 2.0 equiv was found to be an optimal amount of $AlMe_3$ (Entry 4).

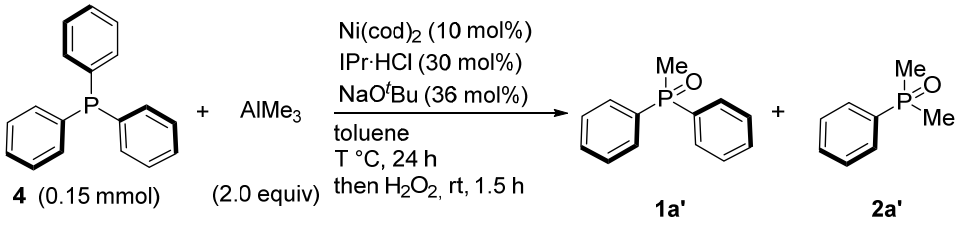
Table S9. Effect of Methylating Reagents in the Reaction of Triphneylphosphine 4



Entry	Alkylating reagent	GC yields (%)		
		1a'	**2a'**	**4'**
1	$AlMe_3$	21	49	0
2	$AlClMe_2$	30	12	30
3	MeMgCl	15	8	35
4	$ZnMe_2$	22	11	53

The effect of methylating reagents was examined by using **4** (0.15 mmol), a methylating reagent (0.30 mmol), $Ni(cod)_2$ (0.015 mmol) and IPr·HCl (0.045 mmol) in toluene (0.30 mL) at 180 °C for 18 h (Table S9). Under these conditions, $AlMe_3$ was found to be an optimal methylating reagent with a mono-methylated product **1a'** and **2a'** being formed in combined yield of 80% (Entry 1).

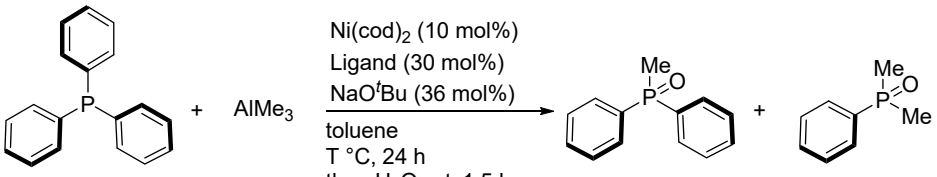
Table S10. Effect of Reaction Temperature



Entry	T (°C)	GC yields (%)		
		1a'	**2a'**	**4'**
1	180	21	49	0
2	160	17	53	0
3	140	24	51	0
4	120	30	55	0
5	100	33	30	15

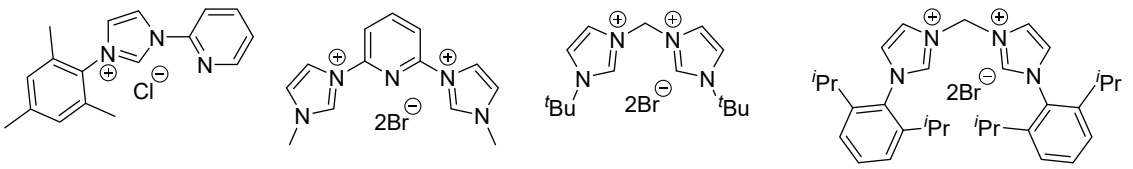
The effect of the reaction temperature was examined by using **4** (0.15 mmol), $AlMe_3$ (2.0 equiv), $Ni(cod)_2$ (0.015 mmol) and IPr·HCl (0.045 mmol) in toluene (0.30 mL) for 24 h (Table S10). Under these conditions, 120 °C were found to be an optimal reaction temperature (Entry 4).

Table S11. Effect of Ligands



4 (0.15 mmol) (2.0 equiv) **1a'** **2a'**

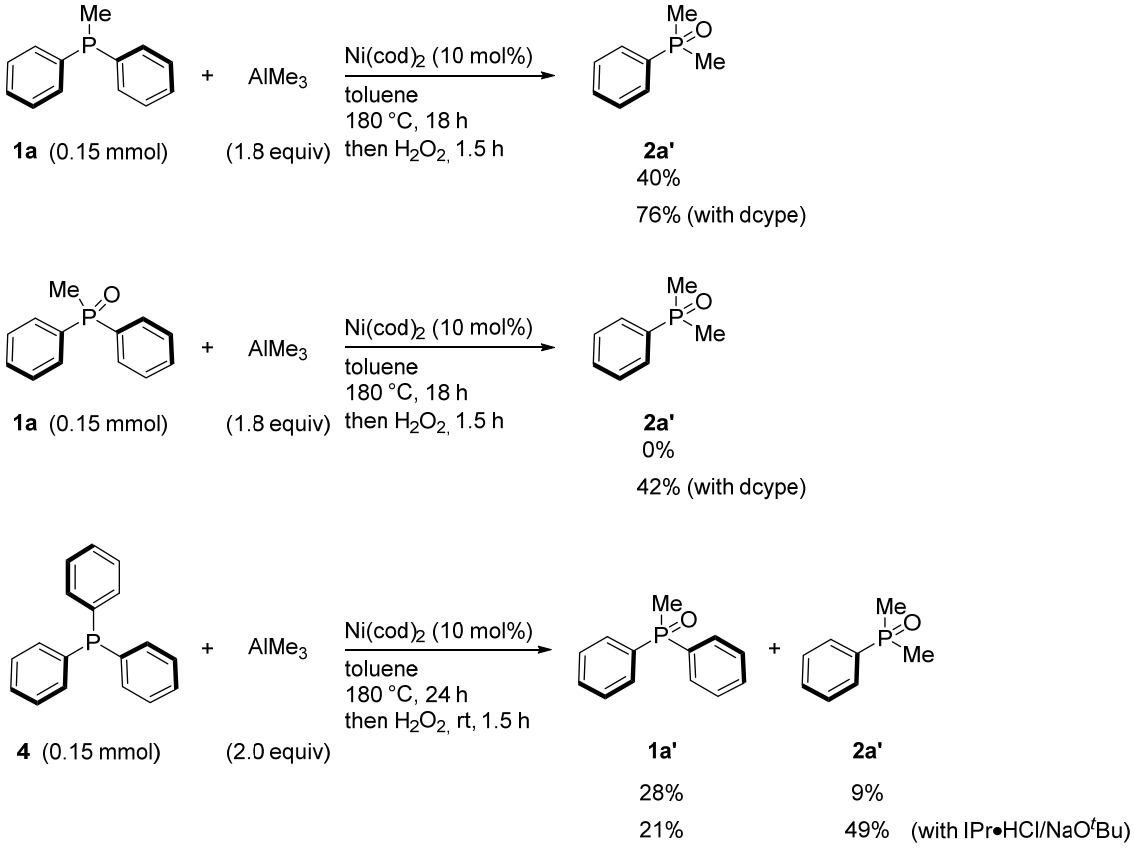
Entry	T (°C)	Ligand	GC yields (%)			Note
			1a'	**2a'**	**4'**	
1	180	-	28	9	0	
2		ICy•HCl	17	53	0	
3		IMes•HCl	13	56	0	
4		IPr•HCl	21	49	0	
5		SIPr•HCl	23	34	5	
6		CAAC•HCl_2	15	8	35	KHMDS (73 mmol) instead of NaO^{t}Bu
7		dcype	30	39	0	without NaO^{t}Bu
8	120	IPr•HCl	30	55	0	
9		I(1-Ad)•HBF_4	23	0	34	
10		I^{i}Pr•HBF_4	15	0	54	
11		IMes^{Me}•HCl	24	44	0	
12		IPr^{Me}•HCl	15	49	0	
13		NHC1•HCl	26	23	7	
14		NHC2•HCl	33	33	6	$AlMe_3$ (2.6 equiv), NaO^{t}Bu (72 mol%)
15		NHC3•HCl	26	48	0	$AlMe_3$ (2.6 equiv), NaO^{t}Bu (72 mol%)
16		NHC4•HCl	32	31	14	$AlMe_3$ (2.6 equiv), NaO^{t}Bu (72 mol%)
17		PCy_3	18	36	4	without NaO^{t}Bu
18		P^tBu_3	24	38	0	without NaO^{t}Bu
19		dcype	6	31	26	without NaO^{t}Bu
20		dtbpy	30	21	12	without NaO^{t}Bu



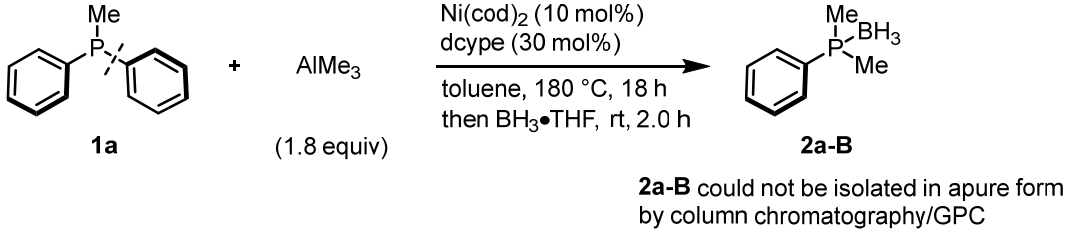
NHC1 NHC2 NHC3 NHC4

The effect of ligands was examined by using **4** (0.15 mmol), $AlMe_3$ (0.30 mmol), $Ni(cod)_2$ (0.015 mmol) and ligand (0.045 mmol) in toluene (0.30 mL) at 120 or 180 °C for 24 h (Table S11). Under these conditions, IPr·HCl was found to be an optimal ligand with a mono-methylated and di-methylated products **1a'** and **2a'** being formed in combined yield of 85% (Entry 8).

Table S12. Summary of the results without ligand



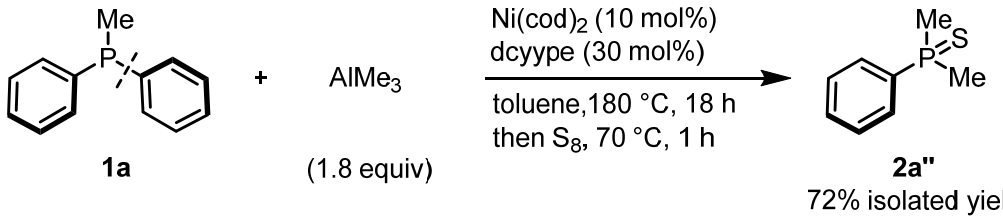
Am attempt to isolate the methylated product as a borane complex



Isolation of the methylated product as a borane complex by treating with BH_3 was examined. However, although the adduct was formed, it cannot be isolated in a pure form even after purification by column chromatography and GPC.

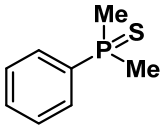
IV. Typical Procedures

Procedure for the Ni-Catalyzed Methylaiton of Methyldiphneylphosphine Using $AlMe_3$



In a glovebox filled with nitrogen, $Ni(cod)_2$ (4.1 mg, 0.015 mmol, 0.10 equiv), dcype (19 mg, 0.045 mmol, 0.30 equiv) and toluene (0.30 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap, and stirred for 5 min at rt. Phosphine **1a** (21 mg, 0.15 mmol, 1.0 equiv) and $AlMe_3$ (1.8 M in toluene, 0.15 mL, 0.27 mmol, 1.8 equiv) were then added, and the cap was applied to seal the vial. The vial was stirred at 180 °C for 18 h. After the reaction mixture was cooled to rt, S_8 (48 mg, 1.5 mmol, 10 equiv) and 1,4-dioxane (1.0 mL) were added in a glovebox, and the mixture was stirred at 70 °C for 1 h. The crude mixture was filtered through a pad of Celite eluting with EtOAc. The crude mixture was concentrated under reduced pressure and purified by flash column chromatography over silica gel eluting with hexane/EtOAc solution. The filtrate was concentrated in vacuo to give a pure methylated phosphine sulfide **2a"** as a colorless oil (17.4 mg, 72%).

Dimethyl(phenyl)phosphine sulfide (2a"). [CAS: 1707-00-2]



R_f 0.17 (hexane/EtOAc = 4/1). Colorless oil (17.4 mg, 72%).

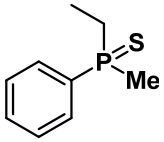
^1H NMR ($CDCl_3$, 399.78 MHz): δ 7.94–7.87 (m, 2H), 7.55–7.47 (m, 3H), 1.99 (d, J = 13.3 Hz, 6H).

^{13}C NMR ($CDCl_3$, 100.53 MHz): δ 133.7 (d, J = 79.5 Hz), 131.7 (d, J = 2.9 Hz), 130.1 (d, J = 10.6 Hz), 128.8 (d, J = 12.5 Hz), 23.0 (d, J = 57.5 Hz).

^{31}P NMR ($CDCl_3$, 161.83 MHz): δ 26.2.

HRMS (EI): Calcd for $C_8H_{11}PS$ 170.0319, Found 170.320.

Ethyl(methyl)(phenyl)phosphine sulfide (2b"). [CAS: 13639-73-1]



R_f 0.23 (hexane/EtOAc = 4/1). Colorless oil (18.1 mg, 66%).

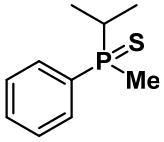
^1H NMR ($CDCl_3$, 399.78 MHz): δ 7.90–7.83 (m, 2H), 7.54–7.45 (m, 3H), 2.09 (dq, J = 11.4, 7.5 Hz, 2H), 1.93 (d, J = 12.8 Hz, 3H), 1.12 (dt, J = 20.2 7.6 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100.53 MHz): 132.2 (d, J = 76.7 Hz) 131.6 (d, J = 2.8 Hz), 130.7 (d, J = 10.5 Hz), 128.7 (d, J = 11.5 Hz), 28.2 (d, J = 55.6 Hz), 20.3 (d, J = 56.5 Hz), δ 6.7 (d, J = 6.3 Hz).

^{31}P NMR ($CDCl_3$, 161.83 MHz): δ 35.4.

HRMS (EI): Calcd for $C_9H_{13}PS$ 184.0476, Found 184.0477.

Isopropyl(methyl)(phenyl)phosphine sulfide (2c")



R_f 0.20 (hexane/EtOAc = 10/1). Colorless oil (13.5 mg, 46%).

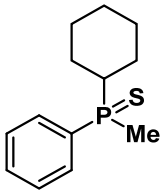
^{1}H NMR ($CDCl_3$, 399.78 MHz): δ 7.90–7.84 (m, 2H), 7.54–7.44 (m, 3H), 2.31–2.18 (m, 1H), 1.93 (d, *J* = 12.4 Hz, 3H), 1.25 (dd, *J* = 18.7, 6.8 Hz, 3H), 0.98 (dd, *J* = 18.7, 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100.53 MHz): δ 131.7 (d, *J* = 74.8 Hz), 131.6 (d, *J* = 1.9 Hz), 131.0 (d, *J* = 9.6 Hz), 128.6 (d, *J* = 11.5 Hz), 31.6 (d, *J* = 53.7 Hz), 18.5 (d, *J* = 54.6 Hz), 15.9 (d, *J* = 8.6 Hz).

^{31}P NMR ($CDCl_3$, 161.83 MHz): δ 43.5.

HRMS (EI): Calcd for $C_{10}H_{15}PS$ 198.0632, Found 198.0631.

Cyclohexyl(methyl)(phenyl)phosphine sulfide (2d") [CAS: 41899-39-2][4]



R_f 0.37 (hexane/EtOAc = 4/1). Colorless oil (17.1 mg, 51%).

^{1}H NMR ($CDCl_3$, 399.78 MHz): δ 7.89–7.83 (m, 2H), 7.54–7.45 (m, 3H), 1.94–1.85 (m, 6H), 1.74–1.67 (m, 2H), 1.51–1.40 (m, 2H), 1.38–1.15 (m, 4H).

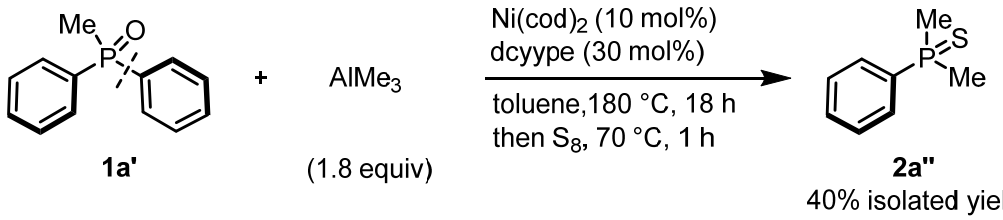
^{13}C NMR ($CDCl_3$, 100.53 MHz): δ 131.6 (d, *J* = 74.7 Hz), 131.5 (d, *J* = 1.9 Hz), 131.1 (d, *J* = 9.6 Hz), 128.6 (d, *J* = 11.5 Hz), 41.5 (d, *J* = 53.7 Hz), 26.3 (d, *J* = 10.5 Hz), 26.2 (d, *J* = 11.5 Hz), 25.7, 25.6, 25.4, 18.0 (d, *J* = 54.6 Hz).

^{31}P NMR ($CDCl_3$, 161.83 MHz): δ 39.8.

HRMS (EI): Calcd for $C_{13}H_{19}PS$ 238.0945, Found 238.0947.

Procedure for the Ni-Catalyzed Methylaiton of 1a' Using $AlMe_3$

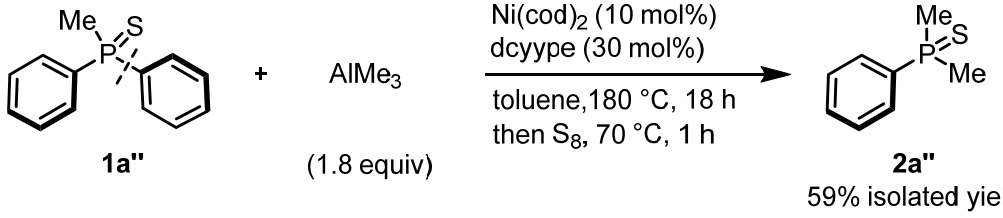
[4] Woznicki, P.; Korzeniowska, E.; Stankevic, M. *J. Org. Chem.* **2017**, *82*, 10271.



1a' (1.8 equiv) **2a"** 40% isolated yield

In a glovebox filled with nitrogen, $Ni(cod)_2$ (4.1 mg, 0.015 mmol, 0.10 equiv), dcype (19 mg, 0.045 mmol, 0.30 equiv) and toluene (0.30 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap, and stirred for 5 min at rt. Phosphine oxide **1a'** (32 mg, 0.15 mmol, 1.0 equiv) and $AlMe_3$ (1.8 M in toluene, 0.15 mL, 0.27 mmol, 1.8 equiv) were then added, and the cap was applied to seal the vial. The vial was stirred at 180 °C for 18 h. After the reaction mixture was cooled to rt, S_8 (48 mg, 1.5 mmol, 10 equiv) and 1,4-dioxane (1.0 mL) were added in a glovebox, and the mixture was stirred at 70 °C for 1 h. The crude mixture was filtered through a pad of Celite eluting with EtOAc. The crude mixture was concentrated under reduced pressure and purified by flash column chromatography over silica gel eluting with hexane/EtOAc solution. The filtrate was concentrated in vacuo to give a pure methylated phosphine sulfide **2a"** as a colorless oil (10.2 mg, 40%).

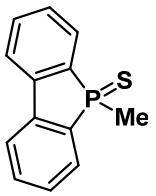
Procedure for the Ni-Catalyzed Methylaiton of 1a" Using $AlMe_3$



1a" (1.8 equiv) **2a"** 59% isolated yield

In a glovebox filled with nitrogen, $Ni(cod)_2$ (4.1 mg, 0.015 mmol, 0.10 equiv), dcype (19 mg, 0.045 mmol, 0.30 equiv) and toluene (0.30 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap, and stirred for 5 min at rt. Phosphine sulfide **1a"** (39 mg, 0.15 mmol, 1.0 equiv) and $AlMe_3$ (1.8 M in toluene, 0.15 mL, 0.27 mmol, 1.8 equiv) were then added, and the cap was applied to seal the vial. The vial was stirred at 180 °C for 18 h. After the reaction mixture was cooled to rt, S_8 (48 mg, 1.5 mmol, 10 equiv) and 1,4-dioxane (1.0 mL) were added in a glovebox, and the mixture was stirred at 70 °C for 1 h. The crude mixture was filtered through a pad of Celite eluting with EtOAc. The crude mixture was concentrated under reduced pressure, and purified by flash column chromatography over silica gel eluting with hexane/EtOAc solution. The filtrate was concentrated in vacuo to give a pure methylated phosphine sulfide **2a"** as a colorless oil (15.1 mg, 59%).

5-Methylbenzo[*b*]phosphindole 5-sulfide (2e"). [CAS: 33771-53-8]



R_f 0.23 (hexane/EtOAc = 10/1). White solid (30.8 mg, 89%).

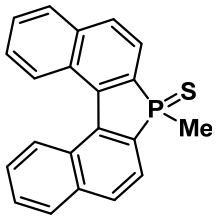
^{1}H NMR ($CDCl_3$, 399.78 MHz): δ 7.89 (dddd, *J* =10.6, 7.4, 1.3, 0.64 Hz, 2H), 7.81 (dd, *J* = 7.7, 0.72 Hz, 2H), 7.58 (tt, *J* = 7.7, 1.6 Hz, 2H), 7.47 (tdd, *J* = 7.4, 3.8, 0.96 Hz, 2H), 2.01 (d, *J* = 13.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100.53 MHz): δ 140.5 (d, *J* = 18.2 Hz), 135.4 (d, *J* = 87.2 Hz), 132.8 (d, *J* = 1.9 Hz), 129.7 (d, *J* = 11.5 Hz), 128.9 (d, *J* = 10.5 Hz), 121.5 (d, *J* = 9.6 Hz), 23.0 (d, *J* = 54.6 Hz).

^{31}P NMR ($CDCl_3$, 161.83 MHz): δ 32.2.

HRMS (EI): Calcd for $C_{13}H_{11}PS$ 230.0319, Found 230.0317.

7-Methylbenzo[*e*]naphtho[2,1-*b*]phosphindole 7-sulfide. (2f") [CAS: 92-52-4]



R_f 0.17 (hexane/EtOAc = 10/1). Pale yellow solid (30.3 mg,61%).

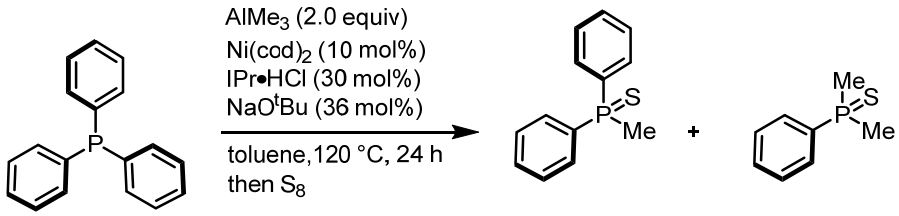
^{1}H NMR ($CDCl_3$, 399.78 MHz): δ 8.24–8.22 (d, *J* = 8.2 Hz, 2H), 8.09–8.06 (m, 2H), 8.02–7.98 (m, 4H), 7.65–7.61 (m, 2H), 7.56–7.51 (m, 2H), 2.06 (d, *J* = 13.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100.53 MHz): δ 139.8–139.5 (m), 137.0, 130.9 (bs), 129.1, 129.0, 128.9, 128.2, 127.6, 125.9, 124.0–123.1 (m), 22.5 (d, *J* = 53.6 Hz).

^{31}P NMR ($CDCl_3$, 161.83 MHz): δ 34.5.

HRMS (EI): Calcd for $C_{21}H_{15}PS$ 330.0632, Found 330.0631.

Procedure for the Ni-Catalyzed Methylaiton of 4 Using $AlMe_3$

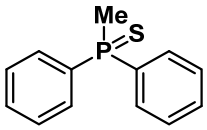


4a **5a** 28% **2a"** 53%

In a glovebox filled with nitrogen, $Ni(cod)_2$ (4.1 mg, 0.015 mmol, 0.10 equiv), IPr·HCl (19 mg,

0.045 mmol, 0.30 equiv), NaO^{t}Bu (5.2 mg, 0.054 mmol, 0.36 equiv) toluene (0.30 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap, and stirred for 5 min at rt. Pohosphine **4** (0.15 mmol, 39 mg, 1.0 equiv) and $AlMe_3$ (1.8 M in toluene, 0.17 mL, 0.30 mmol, 2.0 equiv) were then added, and the cap was applied to seal the vial. The vial was stirred at 120 °C for 24 h. After the reaction mixture was cooled to rt, S_8 (48 mg, 1.5 mmol, 10 equiv) and 1,4-dioxane (1.0 mL) were added in a glovebox, and the mixture was stirred at 70 °C for 1 h. The crude mixture was filtered through a pad of Celite eluting with EtOAc. The crude mixture was concentrated under reduced pressure, and purified by flash column chromatography over silica gel eluting with hexane/EtOAc solution. The filtrate was concentrated in vacuo to give a pure mono-methylated (**5**) and di-methylated (**2a"**) phosphine sulfide (28% and 53%, respectively).

Methyldiphenylphosphine sulfide (5a). [CAS: 13639-74-2]



R_f 0.20 (hexane/EtOAc = 10/1). Colorless oil (9.7 mg, 28%).

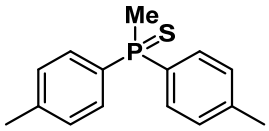
^{1}H NMR ($CDCl_3$, 399.78 MHz): δ 7.85–7.78 (m, 4H), 7.52–7.43 (m, 6H), 2.27 (d, *J* = 13.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100.53 MHz): 134.0 (d, *J* = 82.4 Hz), 131.6 (d, *J* = 2.9 Hz), 130.9 (d, *J* = 10.5 Hz), 128.8 (d, *J* = 11.5 Hz), 21.8 (d, *J* = 59.4 Hz).

^{31}P NMR ($CDCl_3$, 161.83 MHz): δ 29.4.

HRMS (EI): Calcd for $C_{13}H_{13}PS$ 232.0476, Found 232.0474.

Methyldi-*p*-tolylphosphine sulfide (5b). [CAS: 54844-87-0]



R_f 0.25 (hexane/EtOAc = 9/1). Colorless oil (23 mg, 59%).

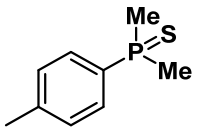
^{1}H NMR ($CDCl_3$, 399.78 MHz): δ 7.68 (dd, *J* = 13.3, 8.2 Hz, 2H), 7.26–7.24 (m, 2H), 2.38 (s, 3H), 2.23 (d, *J* = 13.3 Hz, 2H)

^{13}C NMR ($CDCl_3$, 100.53 MHz): δ 142.0 (d, *J* = 2.9 Hz), 131.0 (d, *J* = 84.4 Hz), 130.9 (d, *J* = 11.5 Hz), 129.5 (d, *J* = 12.5 Hz), 22.0 (d, *J* = 60.4 Hz), 21.6.

^{31}P NMR ($CDCl_3$, 161.83 MHz): δ 28.7.

HRMS (EI): Calcd for $C_{15}H_{18}PS$ 261.0861, Found 261.0871.

Dimethyl(*p*-tolyl)phosphine sulfide (2g"). [CAS: 54844-89-2]



R_f 0.12 (hexane/EtOAc = 10/1). Colorless oil (5.0 mg, 18%).

^{1}H NMR ($CDCl_3$, 399.78 MHz): 7.78 (dd, *J* = 13.0, 8.0 Hz, 2H), 7.30 (dd, *J* = 8.0, 2.5 Hz, 2H), 2.41 (s, 3H), 1.96 (d, *J* = 12.8 Hz, 6H)

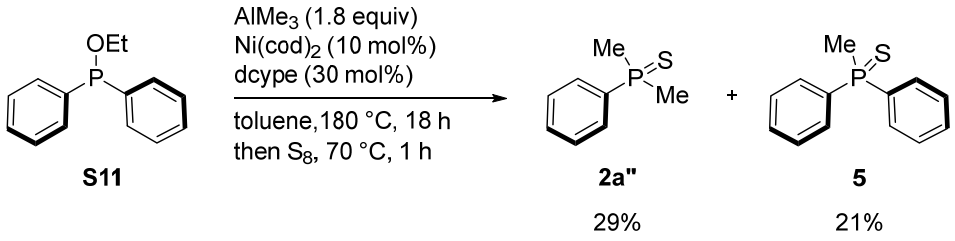
^{13}C NMR ($CDCl_3$, 100.53 MHz): 142.2 (d, *J* = 2.9 Hz), 130.5 (d, *J* = 82.4 Hz), 130.2 (d, *J* = 10.5 Hz), 129.5 (d, *J* = 12.5 Hz), 23.1 (d, *J* = 57.5 Hz), 21.6.

^{31}P NMR ($CDCl_3$, 161.83 MHz): δ 25.8.

HRMS (EI): Calcd for $C_9H_{14}PS$ 185.0548, Found 185.0549.

V. Additional Scope and Limitations

Diethoxyphenylphosphine.



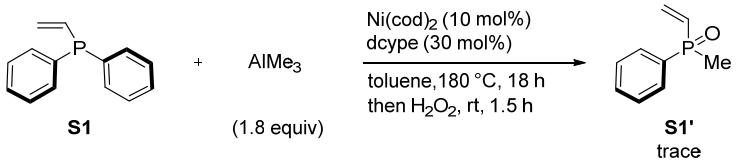
S11 **2a"** **5**

29% 21%

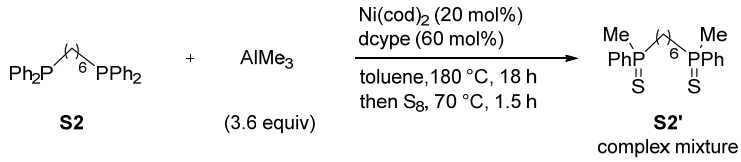
The reaction of $PPh_2(OEt)$ as the substrate under the standard reaction conditions afforded $PhMe_2P{=}S$ (**2a"**, 29%) and $Ph_2MeP{=}S$ (**5**, 21%), probably through the formation of PPh_2Me.[5]

Unsuccessful substrates.

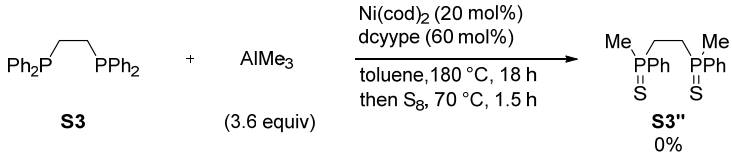
[5] Liu, Q.; Lu, Y.; Sheng, H.; Zhang, C.; Su, X.; Wang, Z.; Chen, X. *Angew Chem Int Ed* **2021**, *60*, 25477–25484.



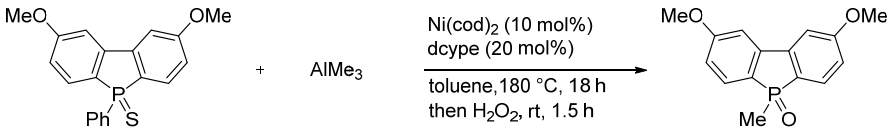
S1 → **S1'** trace



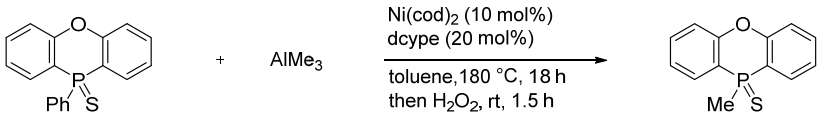
S2 → **S2'** complex mixture



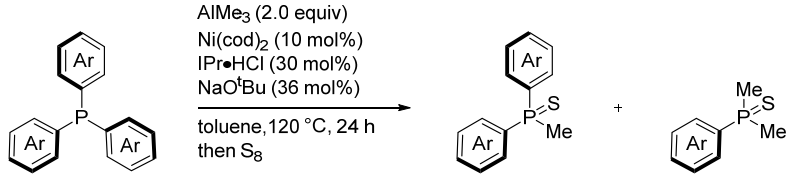
S3 → **S3''** 0%

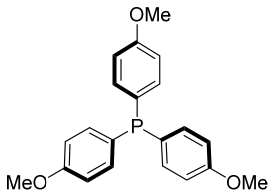


S4 → **S4'** 0%

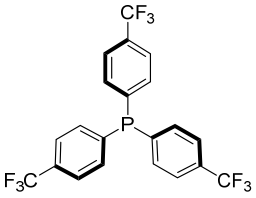


S5 → **S5'** 0%

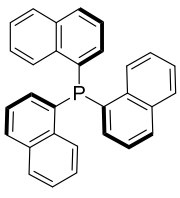


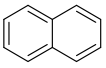


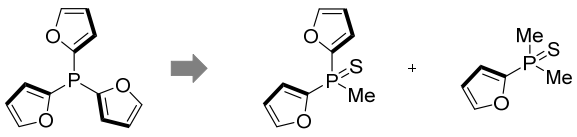
S6
complex mixture



S7
0%



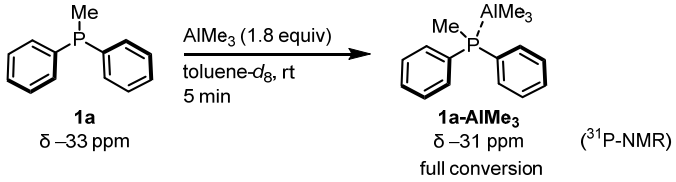
S8
complex mixture +  was observed.



S9 → **S9-1''** ca. 20% + **S9-2''** 0%

VI. Mechanistic Studies

VI-1. Observation of the Complexation between 1a and $AlMe_3$ Using NMR.



In a glovebox filled with nitrogen, **1a** (21 mg, 0.15 mmol, 1.0 equiv), $AlMe_3$ (1.8 M in toluene, 0.15 mL, 0.27 mmol) and toluene-d_8 (0.30 mL) were added to a J-Young NMR tube. The mixture was stirred at rt for 5 min and the reaction was monitored by NMR spectroscopy. ^{31}P NMR spectra revealed that **1a** was converted completely into a different species (δ = - 31 ppm), which is in agreement with the shift reported for phosphine-aluminum adduct **1a-AlMe$_3$**.[6]

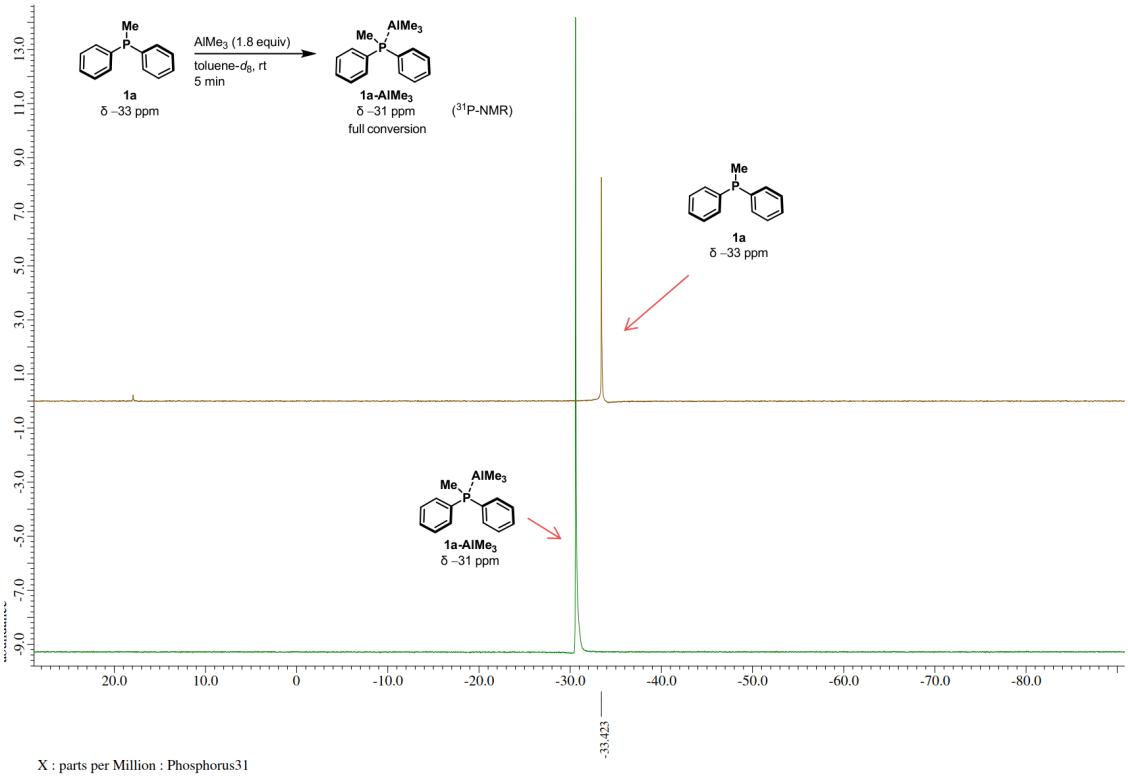
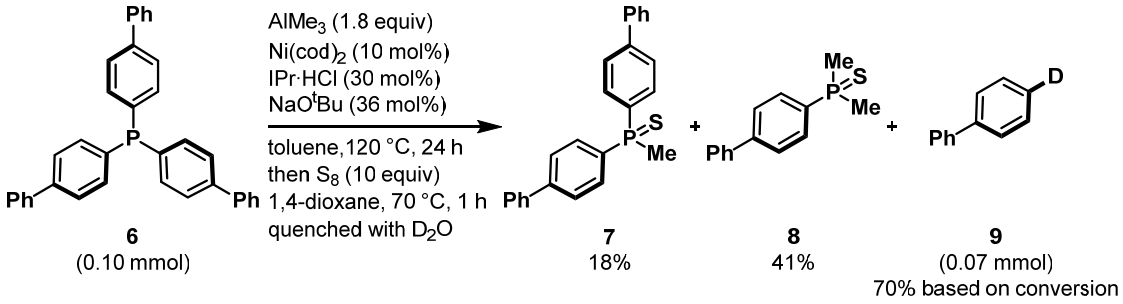


Figure S1. ^{31}P NMR spectra of **1a** and **1a-AlMe$_3$** in toluene-d_8

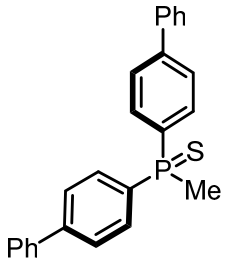
VI-2. Examination of the Fate of the Eliminated Aryl Fragment.

[6] R. Barron, *J. Chem. Soc., Dalton Trans.*, **1988**, 3047.



In a glovebox filled with nitrogen, $Ni(cod)_2$ (2.8 mg, 0.010 mmol, 0.10 equiv), IPr·HCl (13 mg, 0.030 mmol, 0.30 equiv), NaO^{t}Bu (3.5 mg, 0.036 mmol, 0.36 equiv) toluene (0.60 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap, and stirred for 5 min at rt. Tri([1,1'-biphenyl]-4-yl)phosphane (**6**) (0.10 mmol, 49 mg, 1.0 equiv) and $AlMe_3$ (1.8 M in toluene, 0.12 mL, 0.20 mmol, 2.0 equiv) were then added, and the cap was applied to seal the vial. The vial was stirred at 120 °C for 24 h. After the reaction mixture was cooled to rt, S_8 (32 mg, 1.0 mmol, 10 equiv) and 1,4-dioxane (0.65 mL) were added in a glovebox, and the mixture was stirred at 70 °C for 1 h. The crude mixture was the quenched with D_2O (0.20 mL) and filtered through a pad of Celite eluting with EtOAc. The filtrate was concentrated under reduced pressure, and purified by flash column chromatography over silica gel eluting with hexane/EtOAc solution. The filtrate was concentrated in vacuo to give a pure mono-methylated (**7**) di-methylated (**8**) phosphine sulfide and 4-deuterated biphenyl **9** [18%, 41%, and 70%, respectively (based on the converted biphenyl group)]. In addition, it should be noted that 4-methyl-1,1'-biphenyl was observed by GC-MS in the reaction mixture.

Di([1,1'-biphenyl]-4-yl)(methyl)phosphine sulfide (7).



R_f 0.13(hexane/EtOAc = 3/1). Colorless oil (7.0 mg, 18%).

^{1}H NMR ($CDCl_3$, 399.78 MHz): δ 7.92 (dd, *J* = 13.1, 8.5 Hz, 4H), 7.71–7.68 (m, 4H), 7.61–7.59 (m, 4H), 7.49–7.45 (m, 4H), 7.41 (d, *J* = 7.3 Hz, 2H), 2.35 (d, *J* = 13.3 Hz, 3H).

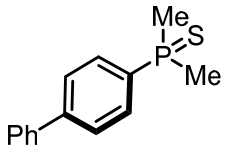
^{13}C NMR ($CDCl_3$, 100.53 MHz): δ 144.6 (d, *J* = 2.9 Hz), 140.1, 132.7 (d, *J* = 83.4 Hz), 131.5 (d, *J* = 11.5 Hz), 129.2, 128.4, 127.6 (d, *J* = 12.5 Hz), 127.5, 22.1 (d, *J* = 59.4 Hz).

^{31}P NMR ($CDCl_3$, 161.83 MHz): δ 29.8.

IR (KBr, cm^{-1}): 3750 w, 3649 m, 1558 m, 1540 s, 1508 m, 885 w, 757 s, 698 m, 665 s, 612 m, 420 w.

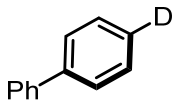
MS, m/z (relative intensity, %): 384 (M^+, 100), 383 (32), 370 (11), 369 (41), 353 (14), 352 (45), 351 (12), 337 (20), 215 (13), 199 (32), 183 (14), 165 (16), 152 (12).
HRMS (DART): Calcd for $C_{25}H_{22}PS$ 385.1174, Found 385.1177.

[1,1'-Biphenyl]-4-yldimethylphosphine sulfide (8).



R_f 0.40 (hexane/EtOAc = 3/1). White solid (10 mg, 41%). M.p. xx °C
^{1}H NMR ($CDCl_3$, 399.78 MHz): δ 7.99–7.94 (m, 2H), 7.71 (td, *J* = 4.2, 2.3 Hz, 2H), 7.62–7.60 (m, 2H), 7.47 (td, *J* = 6.5, 1.7 Hz, 2H), 7.42–7.40 (m, 1H), 2.03 (d, *J* = 12.8 Hz, 6H).
^{13}C NMR ($CDCl_3$, 100.53 MHz): δ 144.6 (d, *J* = 2.9 Hz), 139.3, 132.3 (d, *J* = 81.5 Hz), 130.7 (d, *J* = 10.5 Hz), 129.1, 128.3, 127.6, 127.4, 23.1 (d, *J* = 57.5 Hz).
^{31}P NMR ($CDCl_3$, 161.83 MHz): δ 25.9.
IR (KBr, cm^{-1}): 3855 w, 1597 w, 1482 m, 1288 w, 1118 m, 945 m, 912 s, 867 w, 833 m, 762 s, 736 m, 588 m.
MS, m/z (relative intensity, %): 246 (M^+, 90), 232 (16), 231 (100), 198 (18), 167 (10), 152 (91).
HRMS (DART): Calcd for $C_{14}H_{16}PS$ 247.0705, Found 247.0712.

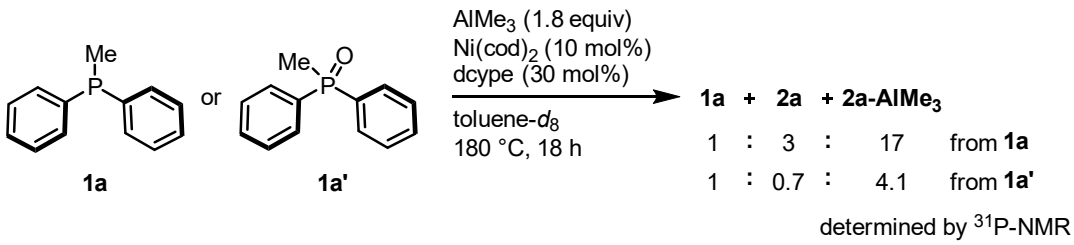
1,1'-Biphenyl-4-d (9). [CAS: 4819-98-1][7]



R_f 0.82 (hexane/EtOAc = 3/1). White solid (11 mg, 70%: based on the converted biphenyl group).
^{1}H NMR ($CDCl_3$, 399.78 MHz): δ 7.62 (d, *J* = 7.3 Hz, 4H), 7.48–7.44 (m, 4H), 7.37 (t, *J* = 7.3 Hz, 1H).
^{13}C NMR ($CDCl_3$, 100.53 MHz): δ 141.4, 128.9 (two overlapping peak), 128.8, 127.4, 127.3 (two overlapping peak), 127.0 (t, *J* = 24.0 Hz).
^{2}H NMR ($CHCl_3$, 161.83 MHz): δ 7.09.
HRMS (DART): Calcd for $C_{12}H_9D$ 155.08398, Found 155.08397.

VI-3. Monitoring the crude reaction mixture using 1a and 1a'

[7] Lin, Z.-H.; Yao, Y.-F.; Zhang, C.-P. *Org. Lett.* **2022**, *24*, 8417.



In a glovebox filled with nitrogen, $Ni(cod)_2$ (4.1 mg, 0.015 mmol, 0.10 equiv), dcype (19 mg, 0.045 mmol, 0.30 equiv) and toluene-d_8 (0.30 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap, and stirred for 5 min at rt. Phosphine **1a** (21 mg, 0.15 mmol, 1.0 equiv) and $AlMe_3$ (1.8 M in toluene, 0.15 mL, 0.27 mmol, 1.8 equiv) were then added, and the cap was applied to seal the vial. The vial was stirred at 180 °C for 18 h. After the reaction mixture was cooled to rt, the reaction was monitored by NMR spectroscopy. When arylphosphine **1a** was used as a substrate, most of methylated product **2a** was present as its aluminum adduct **2a-AlMe$_3$**. And when the corresponding oxide **1a'** was used as the substrate, a mixture of **1a**/**2a**/**2a-AlMe$_3$** (1/0.7/4.1) was formed.

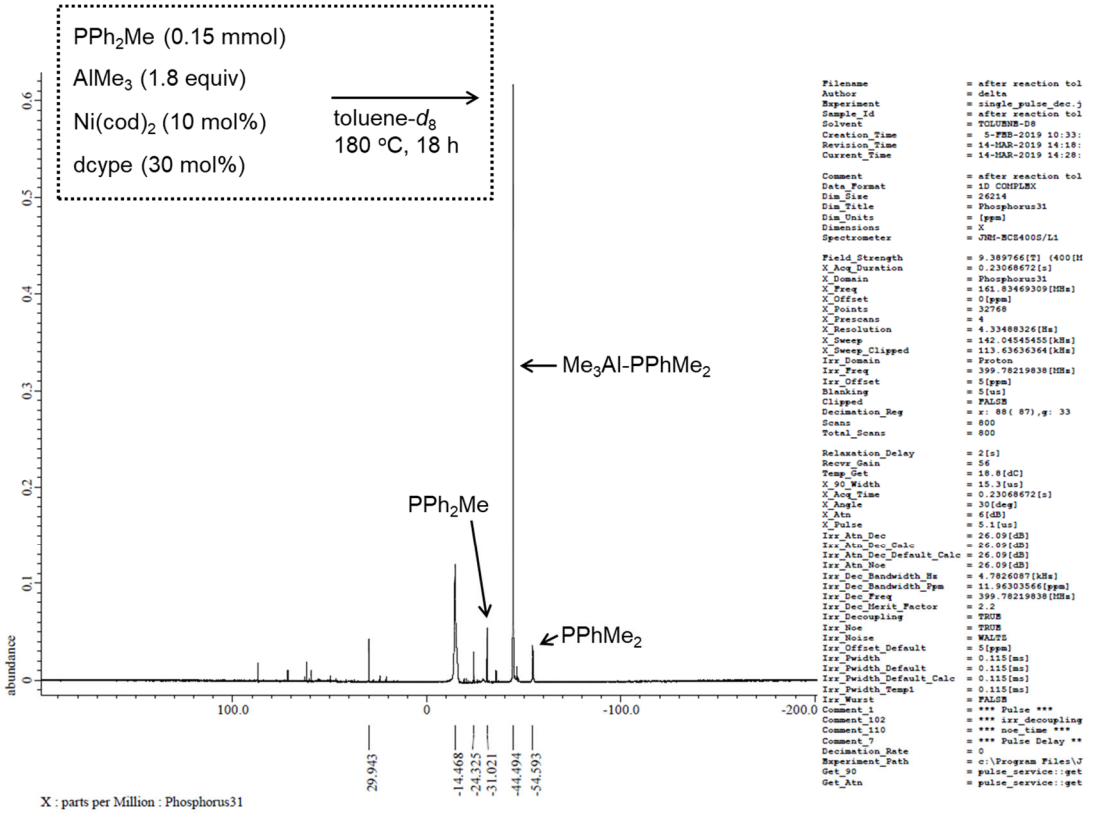


Figure S2. ^{31}P NMR spectrum in the reaction mixture of **1a** in toluene-d_8

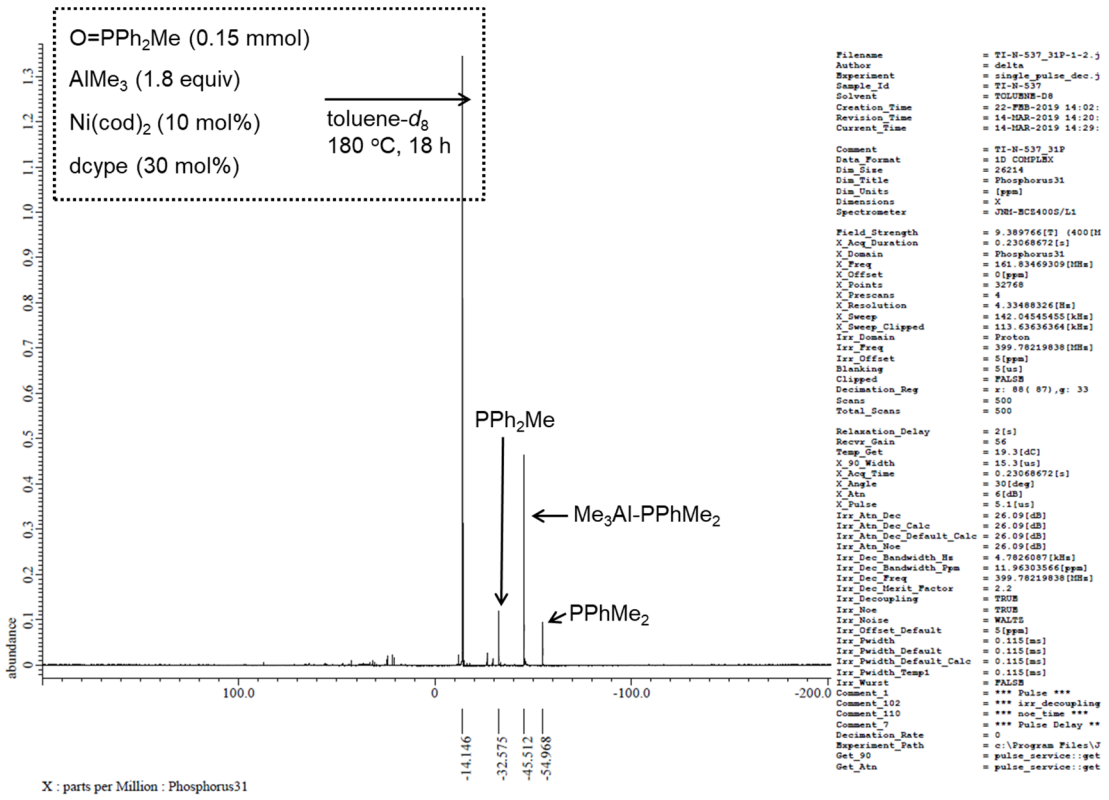
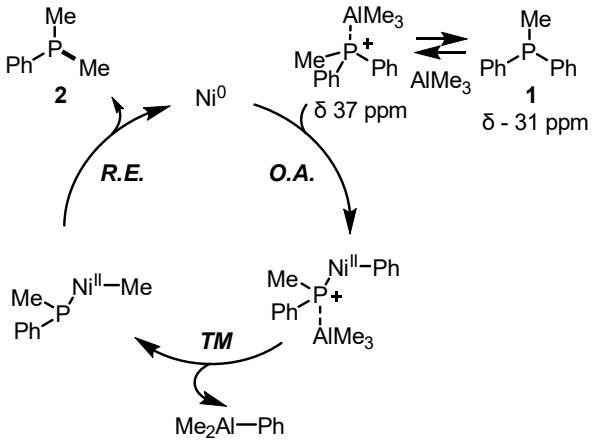


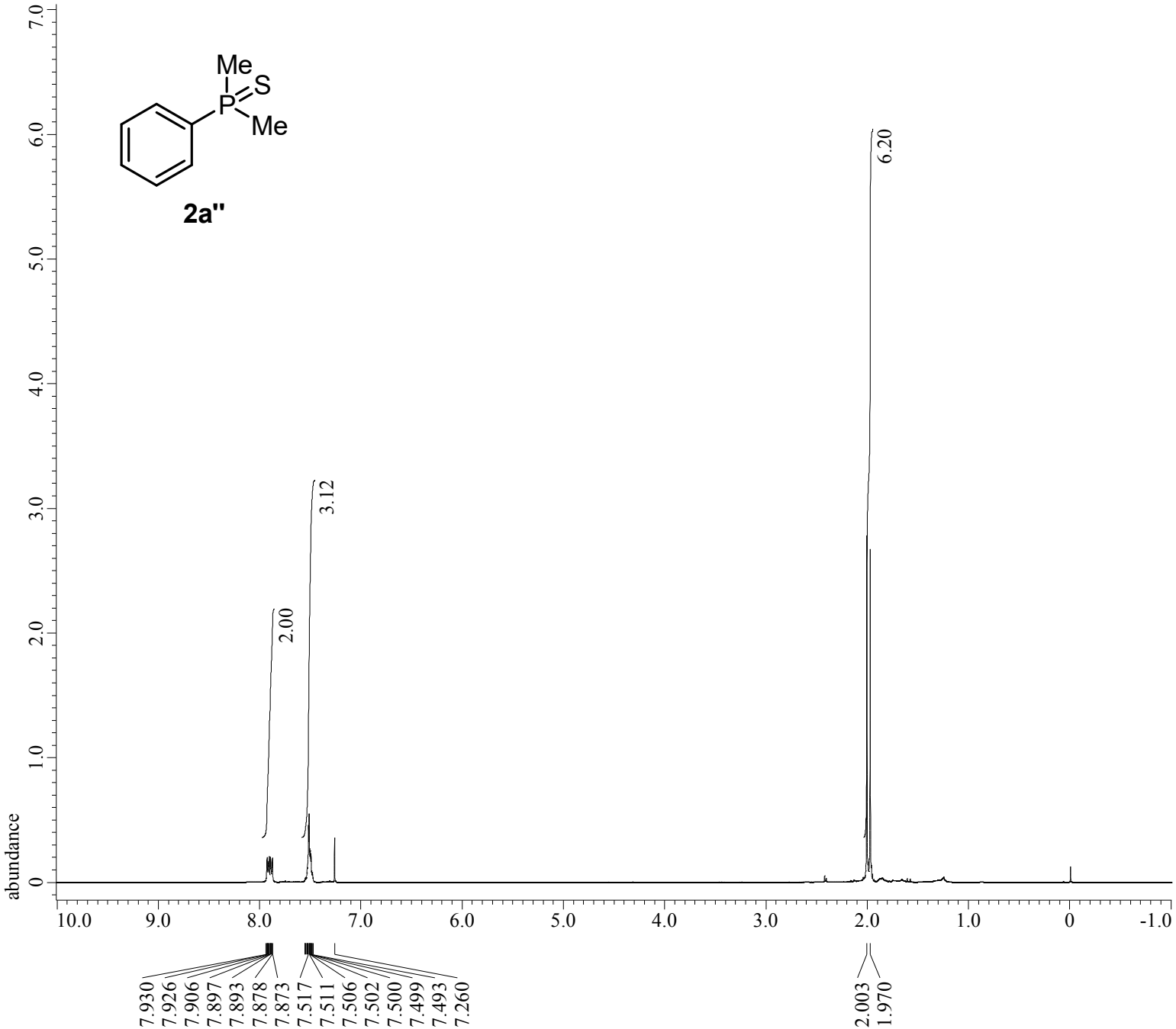
Figure S3. ^{31}P NMR spectrum in the reaction mixture of **1a'** in toluene-d_8

VII. Alternative mechanism

An alternative mechanism



VIII. Copies of ^{1}H, ^{13}C and ^{31}P NMR Spectra



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Revision_Time	= 13-MAR-2019 19:13:49
Current_Time	= 15-MAR-2019 17:08:23
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X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.22869888[Hz]
X_Sweep	= 7.4940048[kHz]
X_Sweep_Clipped	= 5.99520384[kHz]
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Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
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Tri_Freq	= 399.78219838[MHz]
Tri_Offset	= 5[ppm]
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Clipped	= FALSE
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X_Pulse	= 3.2[us]
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Tri_Mode	= Off
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Comment_201	= *** obs_dante_presatu
Comment_202	= *** irr_ presaturatio
Comment_203	= *** tri_ presaturatio
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Dante_Presat	= FALSE
Decimation_Rate	= 0
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Get_Freq	= pulse_service::get_fr
Get_Gamma	= pulse_service::get_ga
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Get_Spin	= pulse_service::get_sp
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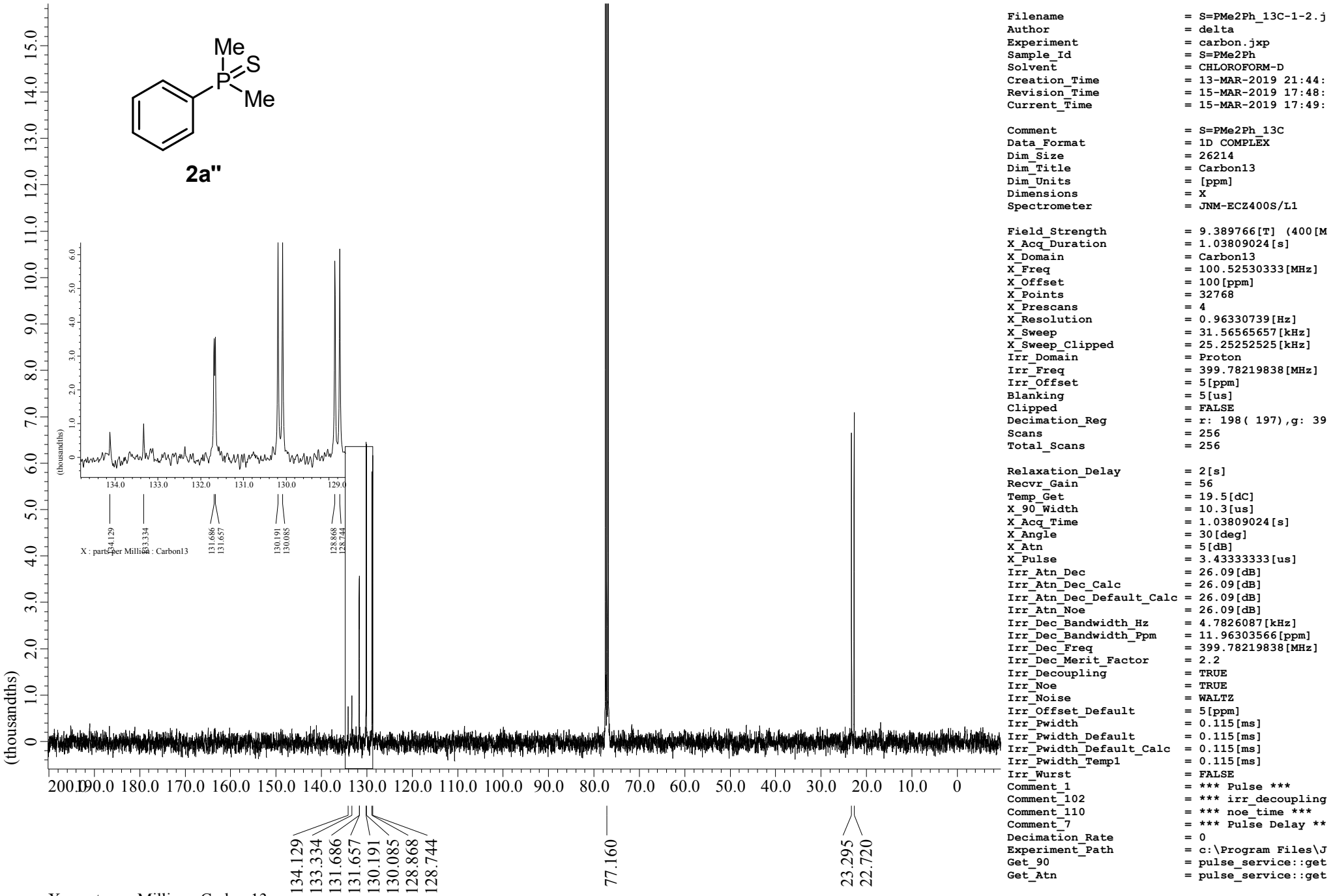
^{1}H NMR Spectrum of **2a"** ($CDCl_3$)

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Revision_Time               = 15-MAR-2019 17:48:
Current_Time                = 15-MAR-2019 17:49:

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X_Sweep                     = 31.56565657[kHz]
X_Sweep_Clipped             = 25.25252525[kHz]
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Irr_Freq                    = 399.78219838[MHz]
Irr_Offset                  = 5[ppm]
Blanking                    = 5[us]
Clipped                     = FALSE
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Temp_Get                    = 19.5[dC]
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Irr_Atn_Dec_Calc            = 26.09[dB]
Irr_Atn_Dec_Default_Calc    = 26.09[dB]
Irr_Atn_Noe                 = 26.09[dB]
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Irr_Dec_Bandwidth_Ppm       = 11.96303566[ppm]
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Irr_Noe                     = TRUE
Irr_Noise                   = WALTZ
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Comment_110                 = *** noe_time ***
Comment_7                   = *** Pulse Delay **
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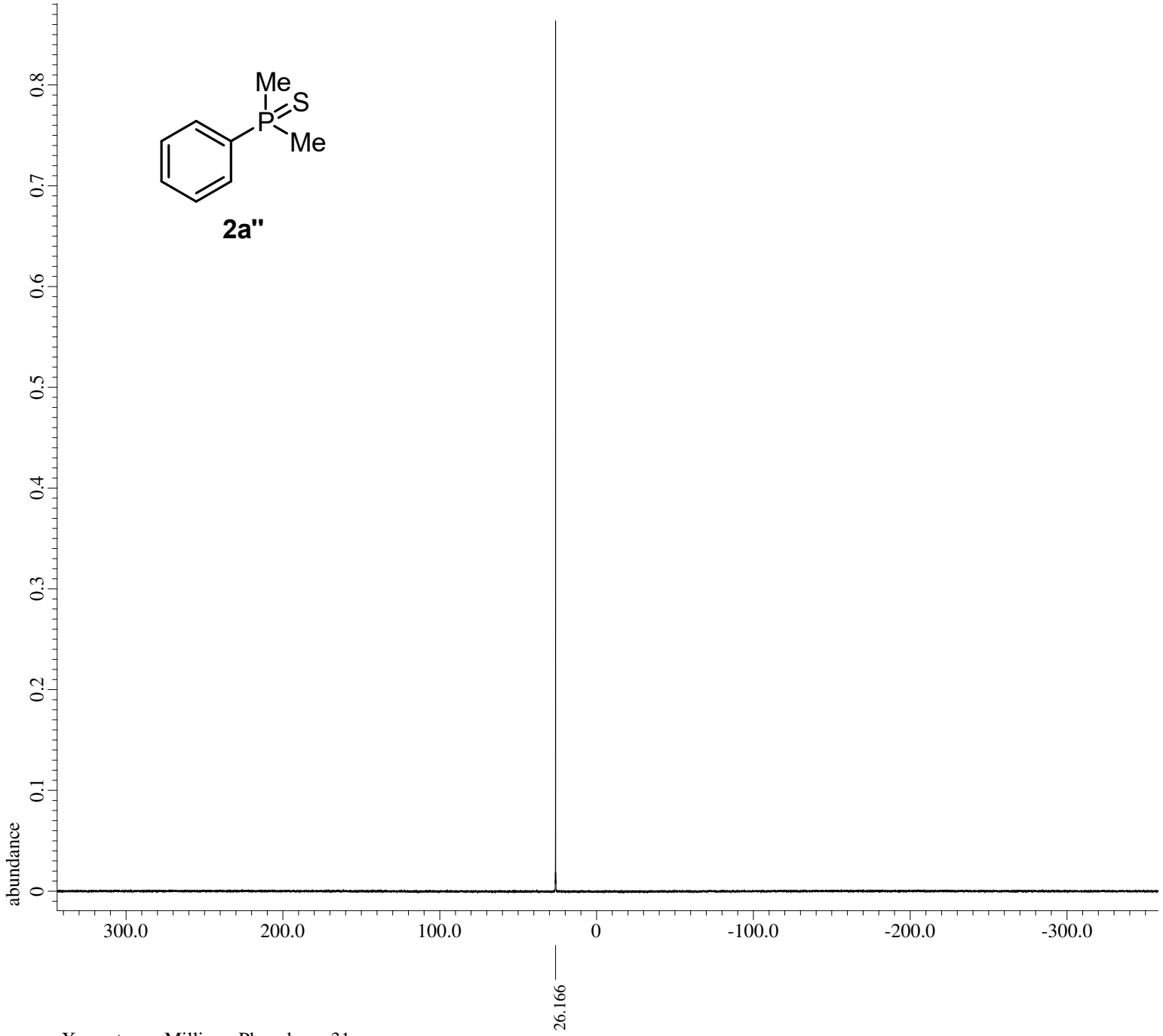
X : parts per Million : Carbon13

^{13}C NMR Spectrum of **2a"** ($CDCl_3$)

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Solvent                   = CHLOROFORM-D
Actual_Start_Time         = 13-MAR-2019 21:32:
Revision_Time             = 13-MAR-2019 21:40:

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Dim_Title                 = Phosphorus31
Dim_Units                 = [ppm]
Dimensions                = X
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X_Freq                    = 161.83469309[MHz]
X_Offset                  = 0[ppm]
X_Points                  = 32768
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X_Resolution              = 4.33488326[Hz]
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X_Sweep_Clipped           = 113.63636364[kHz]
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Irr_Freq                  = 399.78219838[MHz]
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Blanking                  = 5[us]
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Relaxation_Delay          = 2[s]
Recvr_Gain                = 56
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X_Angle                   = 30[deg]
X_Atn                     = 6[dB]
X_Pulse                   = 5.1[us]
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Irr_Atn_Dec_Calc          = 26.09[dB]
Irr_Atn_Dec_Default_Calc  = 26.09[dB]
Irr_Atn_Noe               = 26.09[dB]
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Irr_Dec_Bandwidth_Ppm     = 11.96303566[ppm]
Irr_Dec_Freq              = 399.78219838[MHz]
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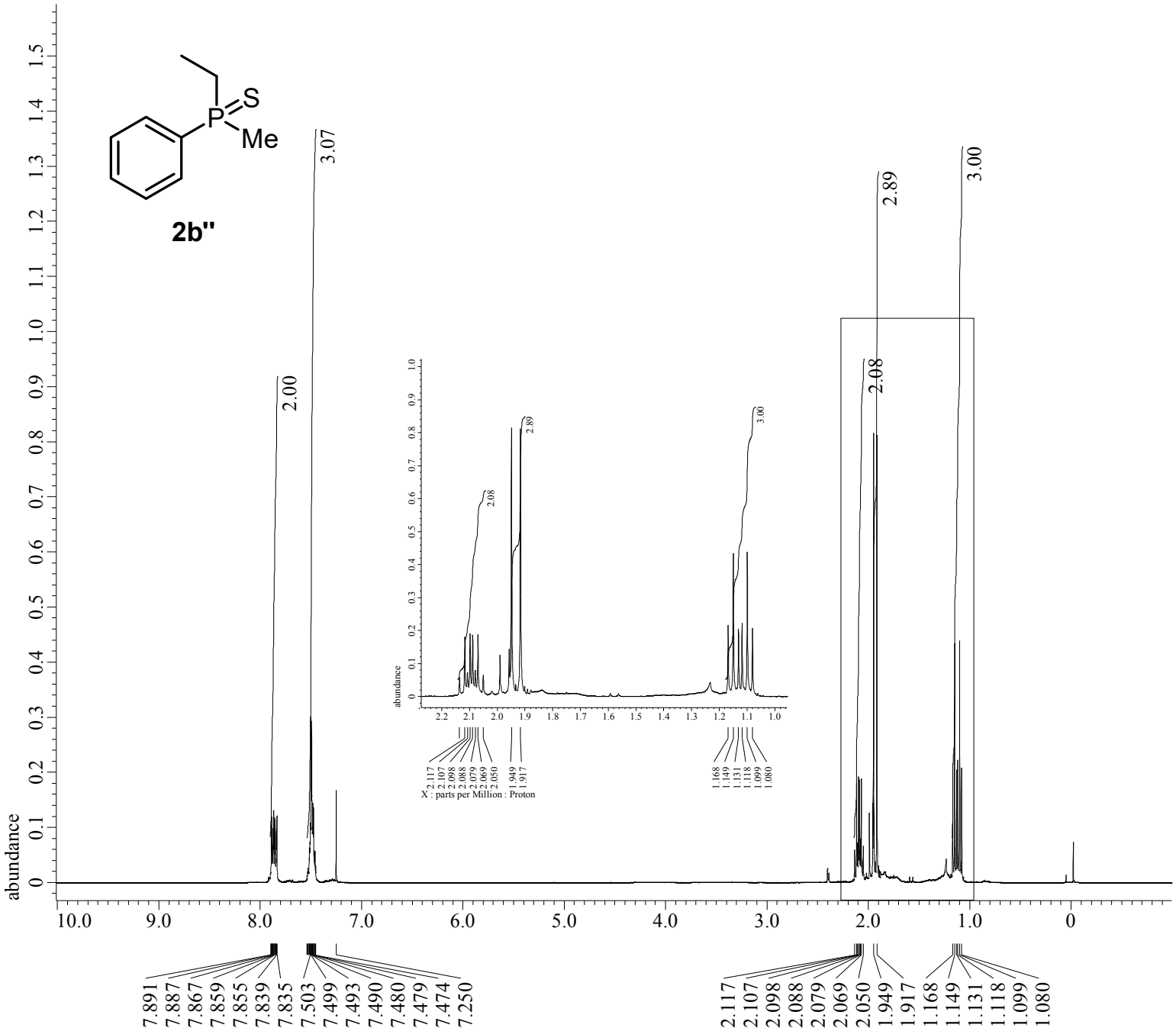
^{31}P NMR Spectrum of **2a"** ($CDCl_3$)



X : parts per Million : Proton

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X_Freq	= 399.78219838[MHz]
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X_Prescans	= 1
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X_Sweep	= 7.4940048[kHz]
X_Sweep_Clipped	= 5.99520384[kHz]
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Irr_Freq	= 399.78219838[MHz]
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Tri_Freq	= 399.78219838[MHz]
Tri_Offset	= 5[ppm]
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Clipped	= FALSE
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X_Acq_Time	= 4.37256192[s]
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Comment_202	= *** irr_ presaturatio
Comment_203	= *** tri_ presaturatio
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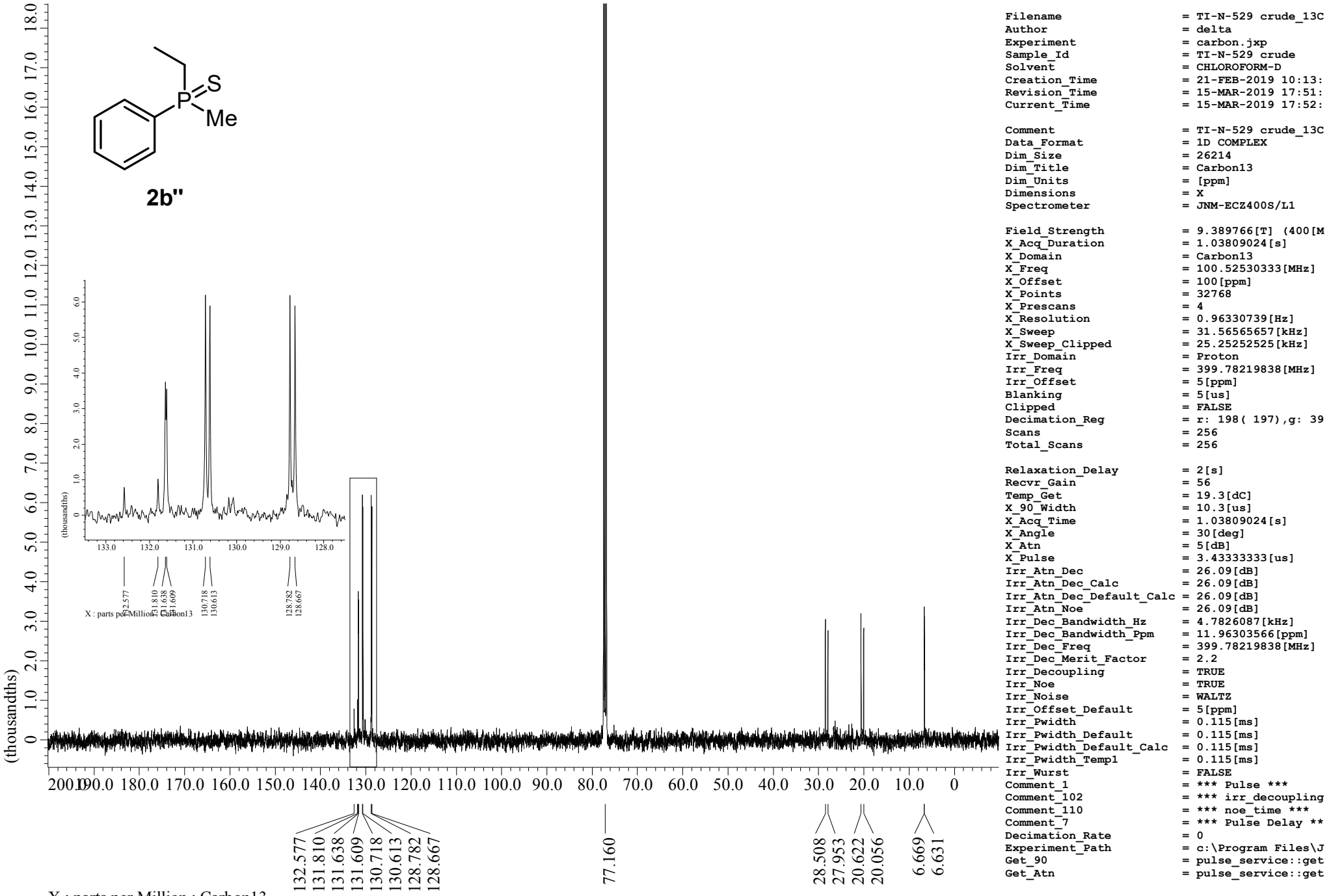
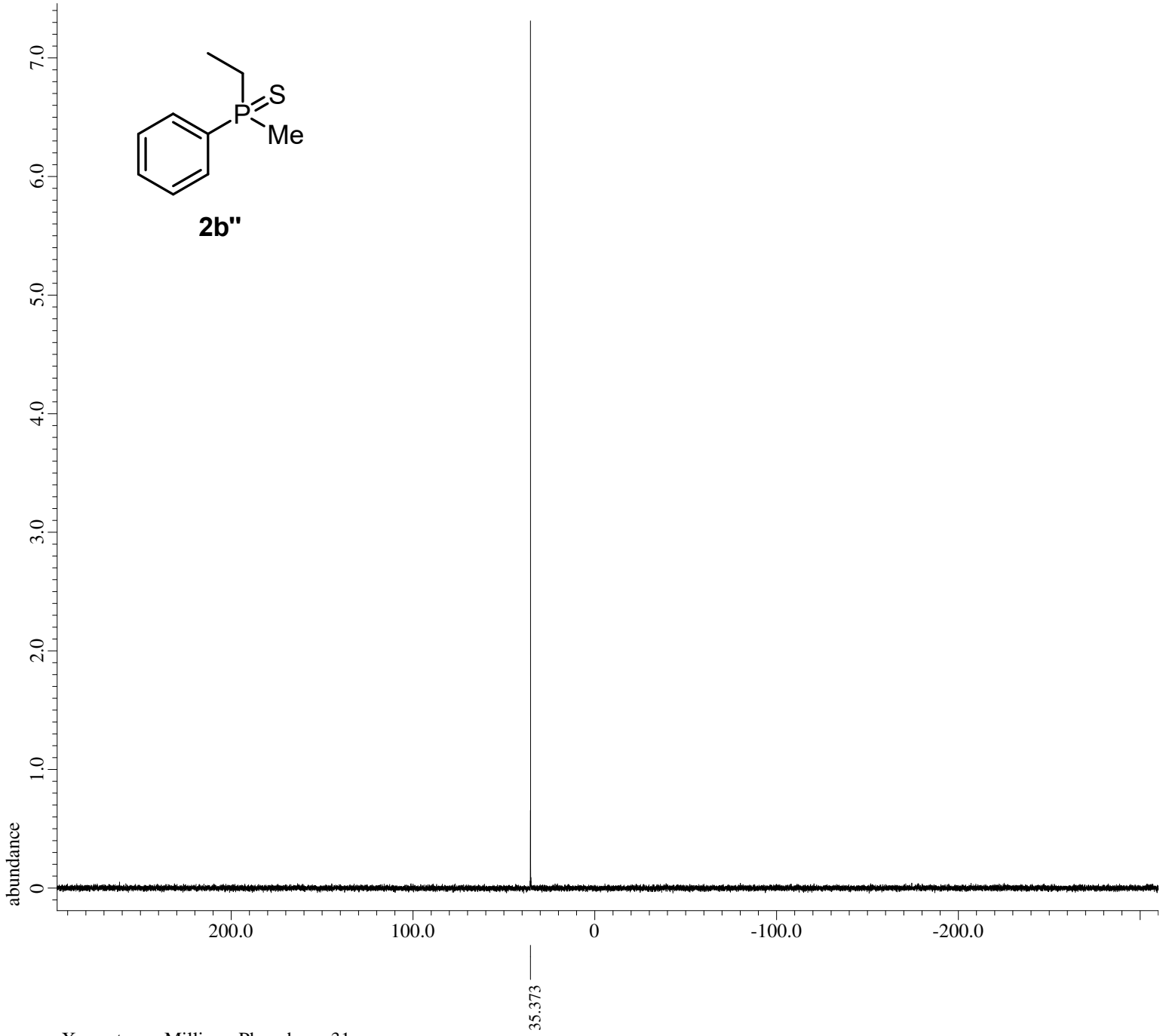
^{1}H NMR Spectrum of **2b"** ($CDCl_3$)



X : parts per Million : Carbon13

^{13}C NMR Spectrum of **2b"** ($CDCl_3$)

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Dimensions        = X
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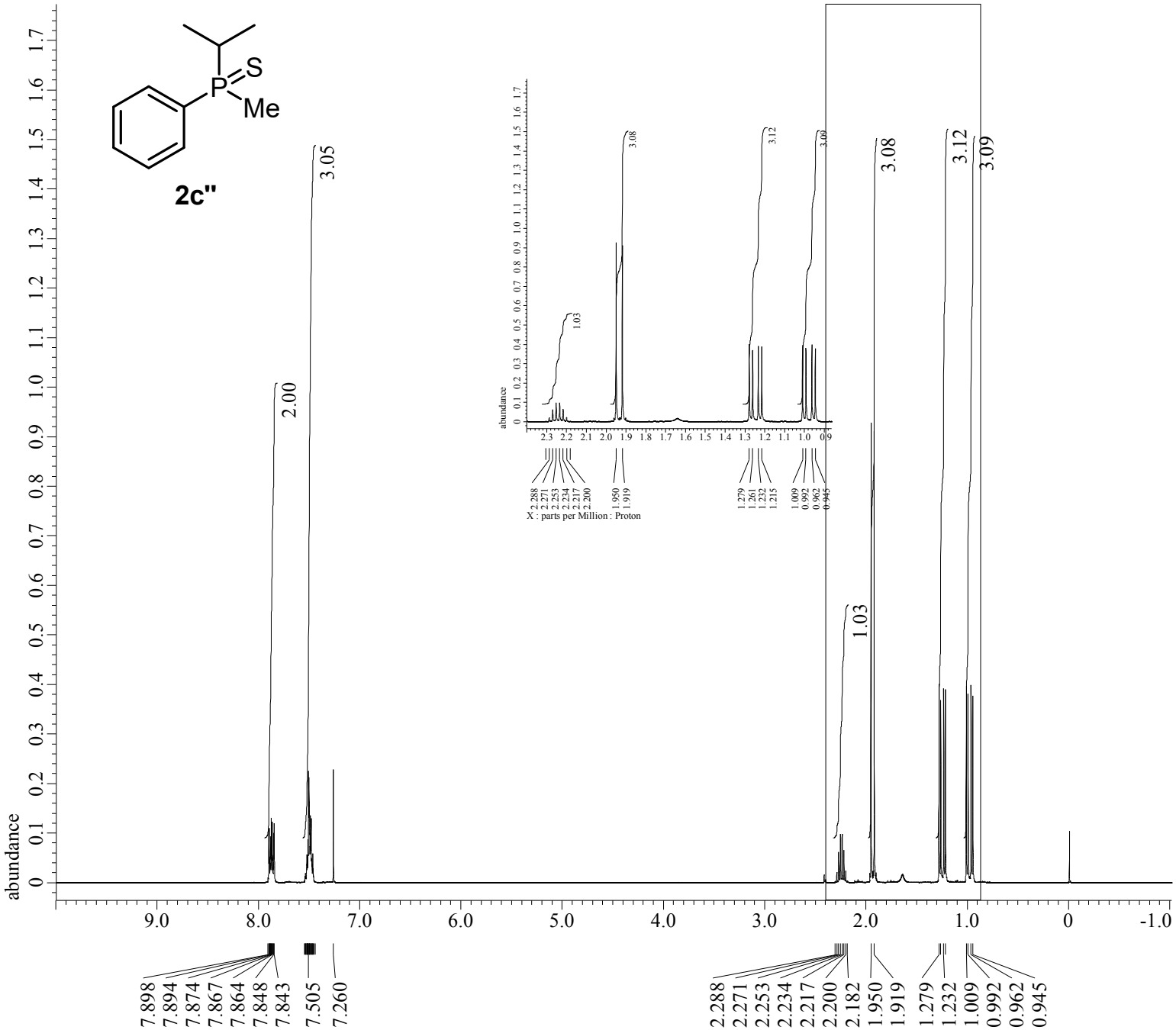
^{31}P NMR Spectrum of **2b"** ($CDCl_3$)



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X_Domain	= Proton
X_Freq	= 399.78219838[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.22869888[Hz]
X_Sweep	= 7.4940048[kHz]
X_Sweep_Clipped	= 5.99520384[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
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Total_Scans	= 8
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Recvr_Gain	= 46
Temp_Get	= 19.1[dC]
X_90_Width	= 6.4[us]
X_Acq_Time	= 4.37256192[s]
X_Angle	= 45[deg]
X_Atn	= 1[dB]
X_Pulse	= 3.2[us]
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Tri_Mode	= Off
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Comment_201	= *** obs_dante_presatu
Comment_202	= *** irr_ presaturatio
Comment_203	= *** tri_ presaturatio
Comment_7	= *** Pulse Delay ***
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Dante_Presat	= FALSE
Decimation_Rate	= 0
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Get_Freq	= pulse_service::get_fr
Get_Gamma	= pulse_service::get_ga
Get_Probe_Parameter	= probe_service::get_pr
Get_Spin	= pulse_service::get_sp
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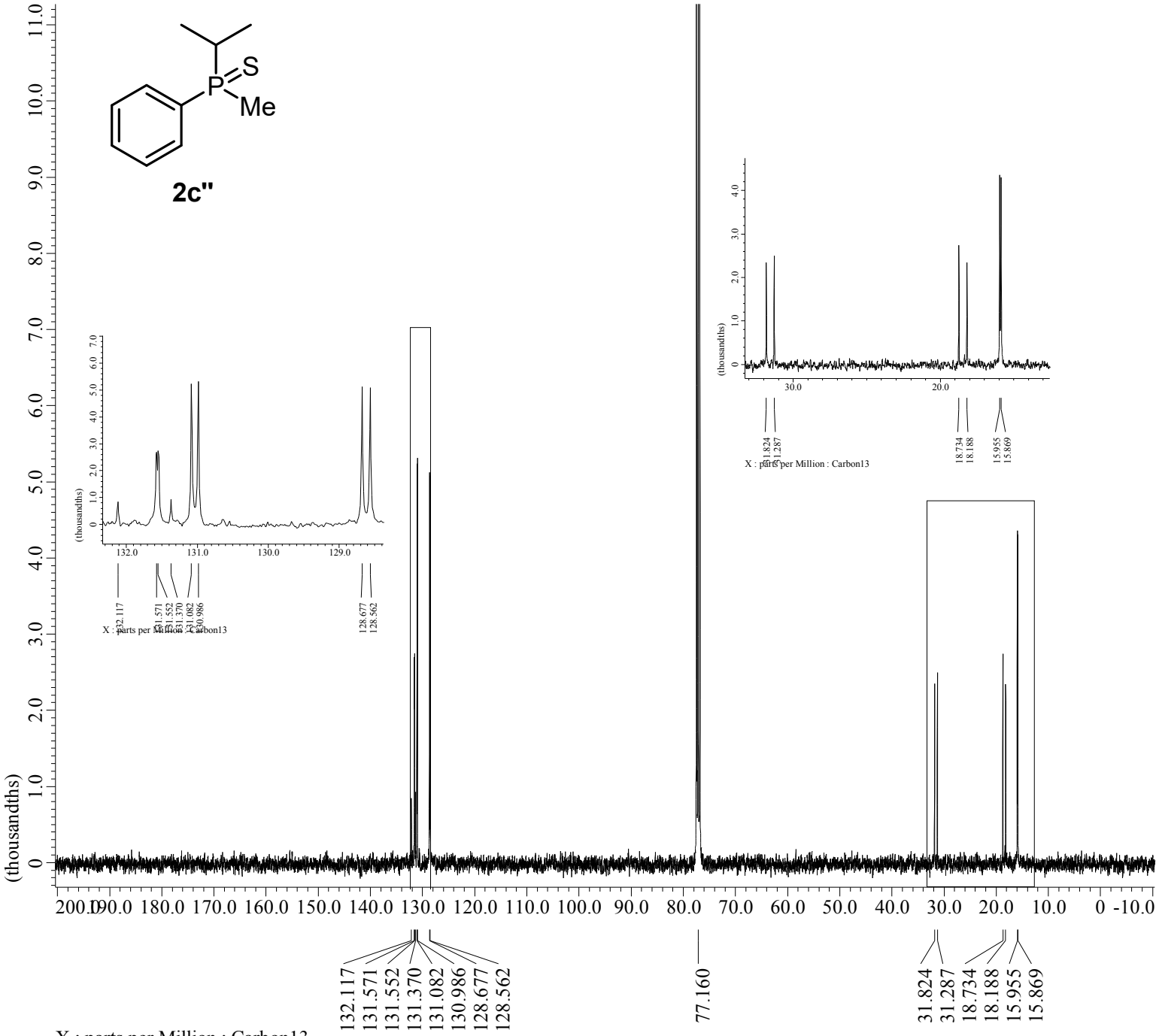
X : parts per Million : Proton

^{1}H NMR Spectrum of **2c"** ($CDCl_3$)

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Creation_Time           = 20-MAR-2019 05:03:
Revision_Time           = 20-MAR-2019 09:15:
Current_Time            = 20-MAR-2019 14:30:

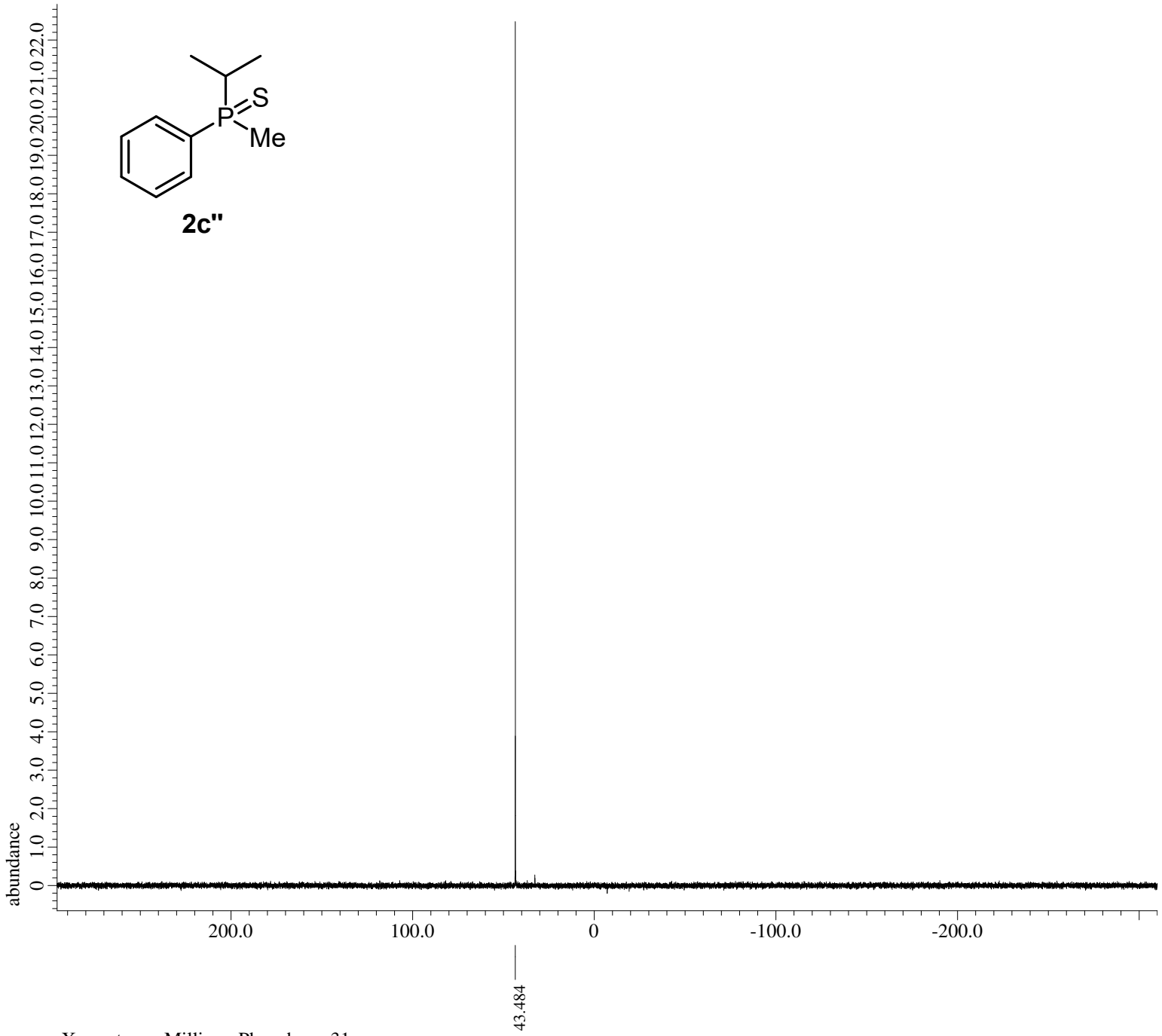
Comment                 = TI-N-577 GPC_13C
Data_Format             = 1D COMPLEX
Dim_Size                = 26214
Dim_Title               = Carbon13
Dim_Units               = [ppm]
Dimensions              = X
Spectrometer            = JNM-ECZ400S/L1

Field_Strength          = 9.389766[T] (400[M
X_Acq_Duration          = 1.03809024[s]
X_Domain                = Carbon13
X_Freq                  = 100.52530333[MHz]
X_Offset                = 100[ppm]
X_Points                = 32768
X_Prescans              = 4
X_Resolution            = 0.96330739[Hz]
X_Sweep                 = 31.56565657[kHz]
X_Sweep_Clipped         = 25.25252525[kHz]
Irr_Domain              = Proton
Irr_Freq                = 399.78219838[MHz]
Irr_Offset              = 5[ppm]
Blanking                = 5[us]
Clipped                 = TRUE
Decimation_Reg          = r: 198( 197),g: 39
Scans                   = 1024
Total_Scans             = 1024

Relaxation_Delay        = 2[s]
Recvr_Gain              = 56
Temp_Get                = 19.2[dC]
X_90_Width              = 10.3[us]
X_Acq_Time              = 1.03809024[s]
X_Angle                 = 30[deg]
X_Atn                   = 5[dB]
X_Pulse                 = 3.43333333[us]
Irr_Atn_Dec             = 26.09[dB]
Irr_Atn_Dec_Calc        = 26.09[dB]
Irr_Atn_Dec_Default_Calc = 26.09[dB]
Irr_Atn_Noe             = 26.09[dB]
Irr_Dec_Bandwidth_Hz    = 4.7826087[kHz]
Irr_Dec_Bandwidth_Ppm   = 11.96303566[ppm]
Irr_Dec_Freq            = 399.78219838[MHz]
Irr_Dec_Merit_Factor    = 2.2
Irr_Decoupling          = TRUE
Irr_Noe                 = TRUE
Irr_Noise               = WALTZ
Irr_Offset_Default      = 5[ppm]
Irr_Pwidth              = 0.115[ms]
Irr_Pwidth_Default      = 0.115[ms]
Irr_Pwidth_Default_Calc = 0.115[ms]
Irr_Pwidth_Temp1        = 0.115[ms]
Irr_Wurst               = FALSE
Comment_1               = *** Pulse ***
Comment_102             = *** irr_decoupling
Comment_110             = *** noe_time ***
Comment_7               = *** Pulse Delay **
Decimation_Rate         = 0
Experiment_Path         = c:\Program Files\J
Get_90                  = pulse_service::get
Get_Atn                 = pulse_service::get
```

X : parts per Million : Carbon13

^{13}C NMR Spectrum of **2c"** ($CDCl_3$)



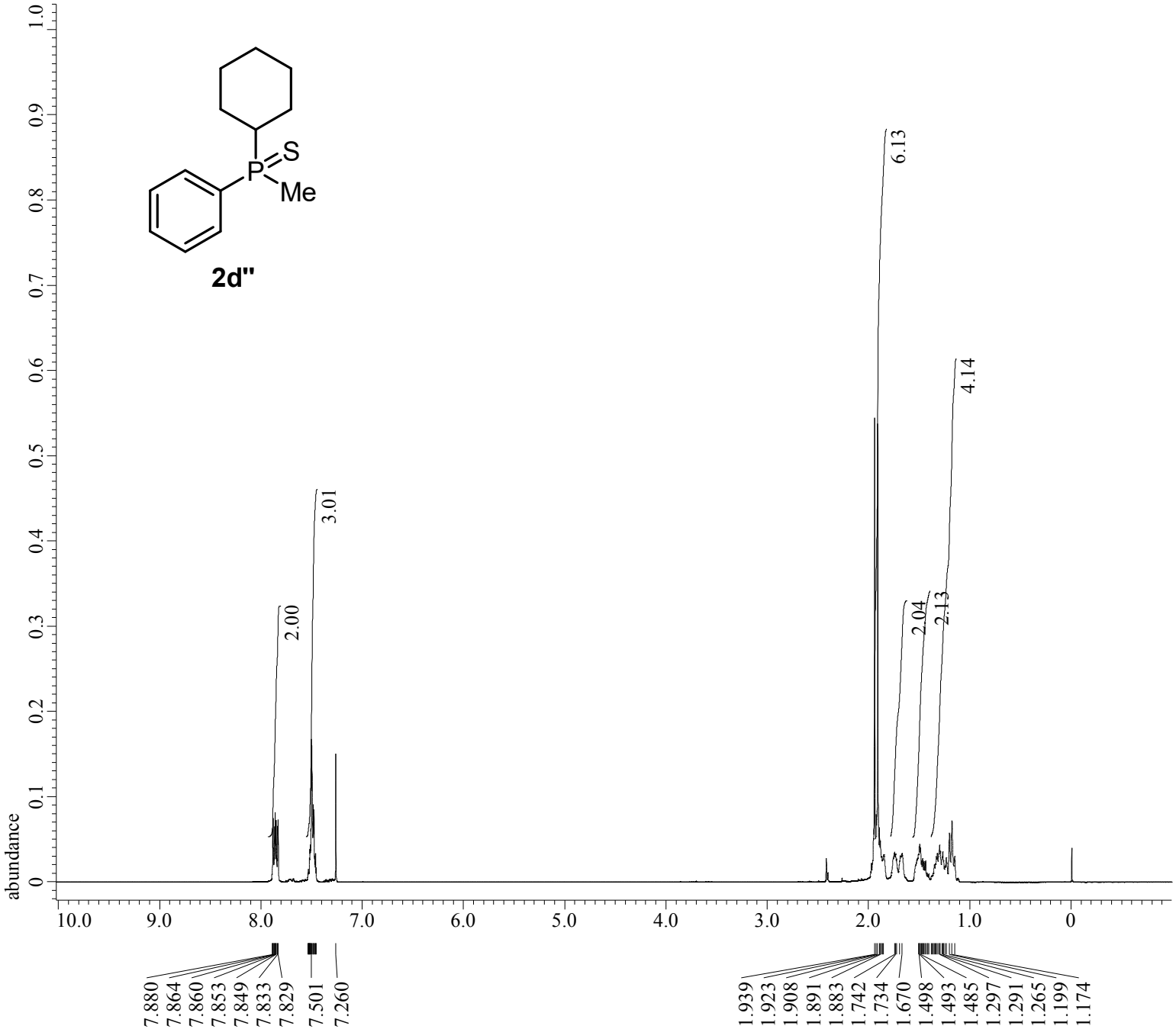

```
Filename           = TI-N-577_31P-1-2.jdf
Author             = delta
Experiment         = single_pulse_dec.jxp
Sample_Id          = TI-N-577
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 18-APR-2023 18:14:53
Revision_Time      = 19-APR-2023 08:57:03

Comment            = TI-N-577_31P
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Phosph
Dim_Title          = Phosphorus31
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECS400
Spectrometer       = DELTA2_NMR

Field_Strength     = 9.389766[T] (400[MHz])
X_Acq_Duration     = 0.26738688[s]
X_Domain           = 31P
X_Freq             = 161.83469309[MHz]
X_Offset           = 0[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 3.73989928[Hz]
X_Sweep            = 122.54901961[kHz]
X_Sweep_Clipped    = 98.03921569[kHz]
Irr_Domain         = Proton
Irr_Freq           = 399.78219838[MHz]
Irr_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 18
Total_Scans        = 18

Relaxation_Delay   = 2[s]
Recvr_Gain         = 56
Temp_Get           = 20.3[dC]
X_90_Width         = 14.5[us]
X_Acq_Time         = 0.26738688[s]
X_Angle            = 30[deg]
X_Atn              = 4.1[dB]
X_Pulse            = 4.83333333[us]
Irr_Atn_Dec        = 20.9[dB]
Irr_Atn_Noe        = 20.9[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 0.115[ms]
Decoupling         = TRUE
Initial_Wait       = 1[s]
Noe                = TRUE
Noe_Time           = 2[s]
Repetition_Time    = 2.26738688[s]
```

^{31}P NMR Spectrum of **2c"** ($CDCl_3$)



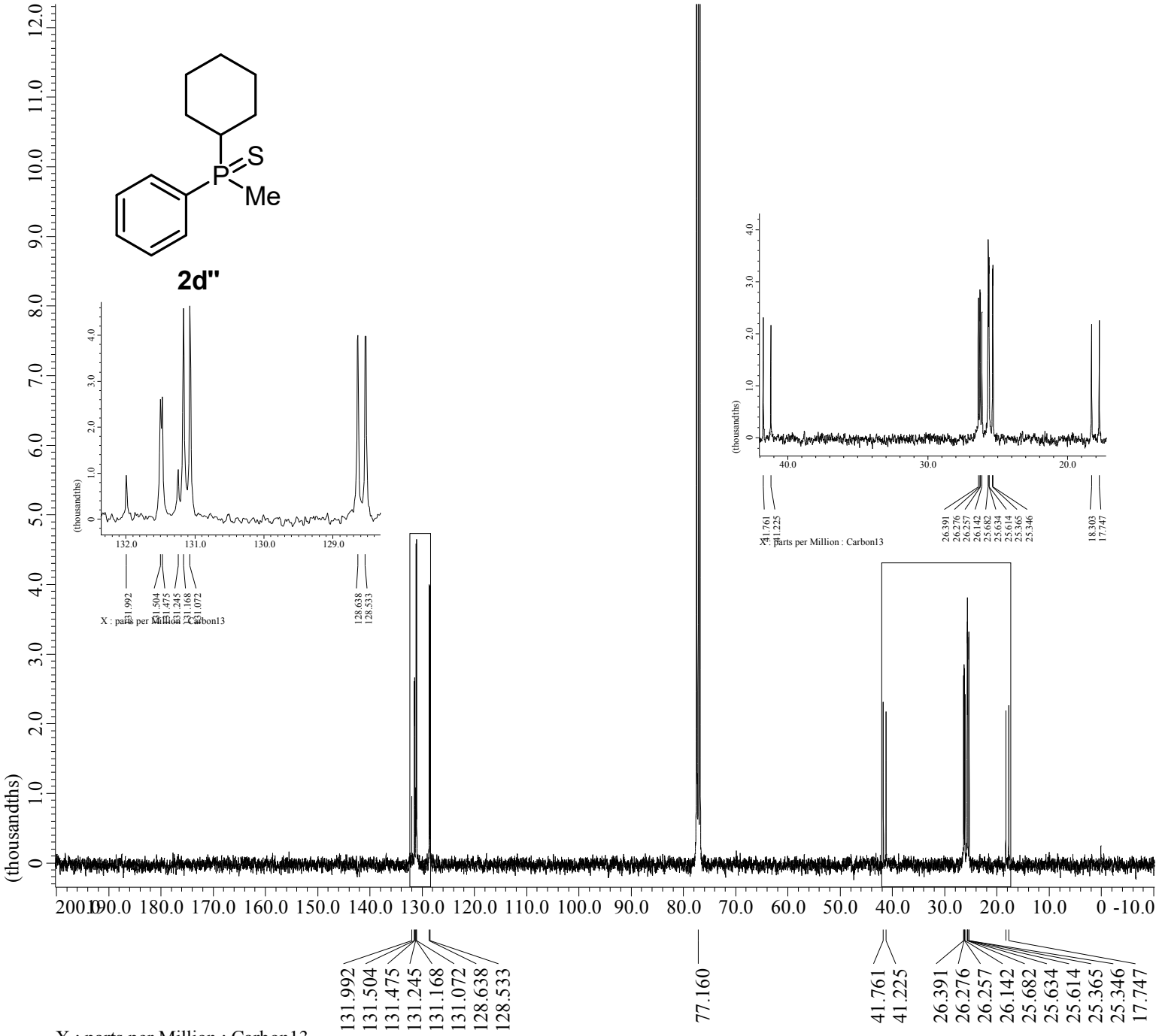

```
Filename              = TI-N-575 GPC_1H-1-1.j
Author                = delta
Experiment            = proton.jxp
Sample_Id             = TI-N-575 GPC
Solvent               = CHLOROFORM-D
Creation_Time         = 13-MAR-2019 14:10:38
Revision_Time         = 13-MAR-2019 14:38:26
Current_Time          = 15-MAR-2019 17:12:35

Comment               = TI-N-575 GPC_1H
Data_Format           = 1D COMPLEX
Dim_Size              = 26214
Dim_Title             = Proton
Dim_Units             = [ppm]
Dimensions            = X
Spectrometer          = JNM-ECZ400S/L1

Field_Strength        = 9.389766[T] (400[MHz]
X_Acq_Duration        = 4.37256192[s]
X_Domain              = Proton
X_Freq                = 399.78219838[MHz]
X_Offset              = 5[ppm]
X_Points              = 32768
X_Prescans            = 1
X_Resolution          = 0.22869888[Hz]
X_Sweep               = 7.4940048[kHz]
X_Sweep_Clipped       = 5.99520384[kHz]
Irr_Domain            = Proton
Irr_Freq              = 399.78219838[MHz]
Irr_Offset            = 5[ppm]
Tri_Domain            = Proton
Tri_Freq              = 399.78219838[MHz]
Tri_Offset            = 5[ppm]
Blanking              = 2[us]
Clipped               = FALSE
Decimation_Reg        = r: 834( 833),g: 49
Scans                 = 8
Total_Scans           = 8

Relaxation_Delay      = 5[s]
Recvr_Gain            = 46
Temp_Get              = 19.7[dC]
X_90_Width            = 6.4[us]
X_Acq_Time            = 4.37256192[s]
X_Angle               = 45[deg]
X_Atn                 = 1[dB]
X_Pulse               = 3.2[us]
Irr_Mode              = Off
Tri_Mode              = Off
Comment_1             = *** Pulse ***
Comment_111           = *** presat_time ***
Comment_201           = *** obs_dante_presatu
Comment_202           = *** irr_ presaturatio
Comment_203           = *** tri_ presaturatio
Comment_7             = *** Pulse Delay ***
Dante_Loop            = 500
Dante_Presat          = FALSE
Decimation_Rate       = 0
Experiment_Path       = c:\Program Files\JEOL
Get_90                = pulse_service::get_90
Get_Atn               = pulse_service::get_at
Get_Freq              = pulse_service::get_fr
Get_Gamma             = pulse_service::get_ga
Get_Probe_Parameter   = probe_service::get_pr
Get_Spin              = pulse_service::get_sp
Initial_Wait          = 1[s]
Phase                 = {0, 90, 270, 180, 180
Phase_Acq             = {0, 90, 270, 180, 180
Presat_Time           = 5[s]
```

^{1}H NMR Spectrum of **2d"** ($CDCl_3$)



Filename = TI-N-575 S=PCy 13C
Author = delta
Experiment = carbon.jxp
Sample_Id = TI-N-575 S=PCy 13C
Solvent = CHLOROFORM-D
Creation_Time = 20-MAR-2019 09:40:
Revision_Time = 20-MAR-2019 11:15:
Current_Time = 20-MAR-2019 14:32:

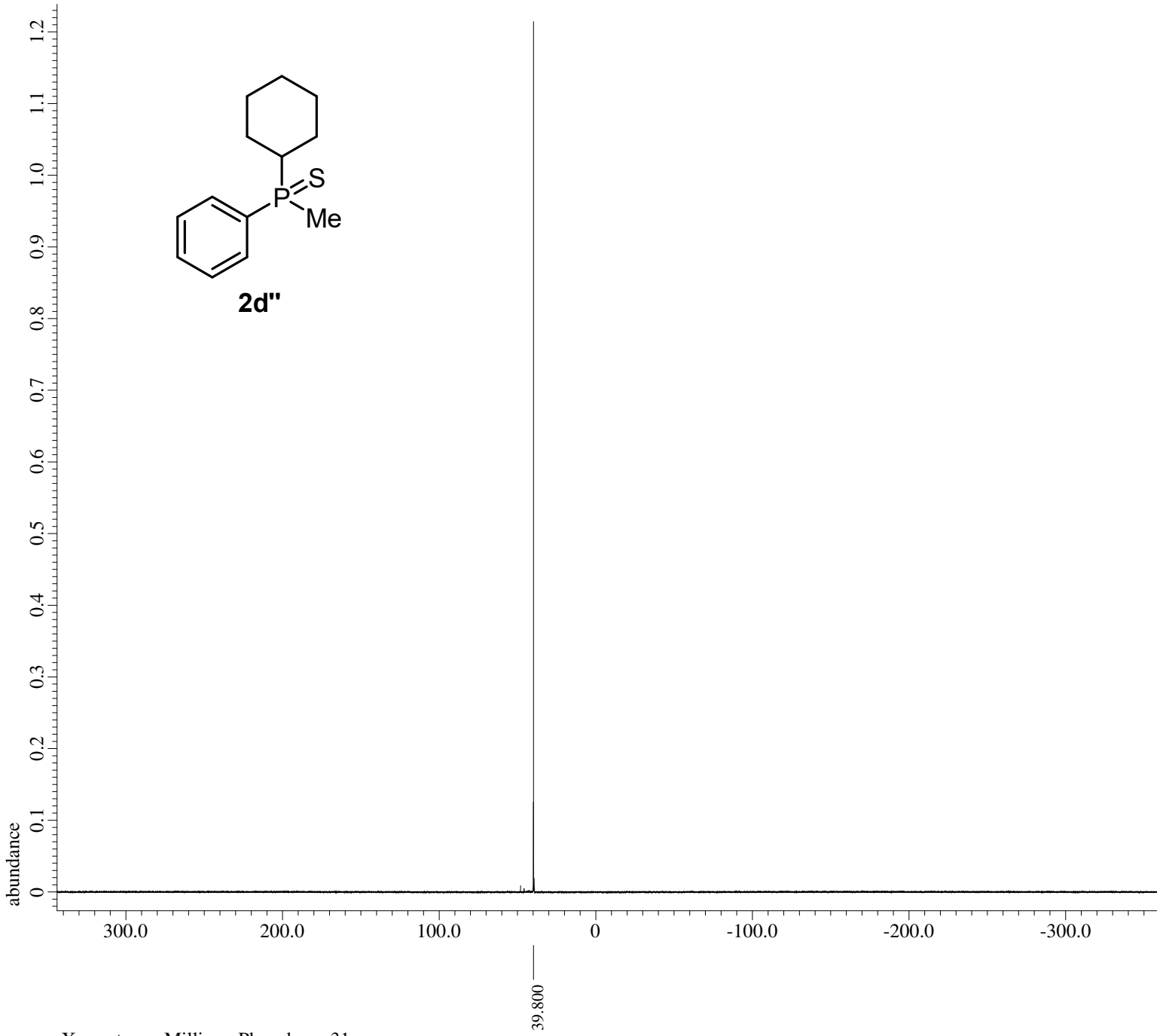
Comment = TI-N-575 S=PCy 13C
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Spectrometer = JNM-ECZ400S/L1

Field_Strength = 9.389766[T] (400[M
X_Acq_Duration = 1.03809024[s]
X_Domain = Carbon13
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.96330739[Hz]
X_Sweep = 31.56565657[kHz]
X_Sweep_Clipped = 25.25252525[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Blanking = 5[us]
Clipped = TRUE
Decimation_Reg = r: 198(197),g: 39
Scans = 1024
Total_Scans = 1024

Relaxation_Delay = 2[s]
Recvr_Gain = 56
Temp_Get = 19.3[dC]
X_90_Width = 10.3[us]
X_Acq_Time = 1.03809024[s]
X_Angle = 30[deg]
X_Atn = 5[dB]
X_Pulse = 3.43333333[us]
Irr_Atn_Dec = 26.09[dB]
Irr_Atn_Dec_Calc = 26.09[dB]
Irr_Atn_Dec_Default_Calc = 26.09[dB]
Irr_Atn_Noe = 26.09[dB]
Irr_Dec_Bandwidth_Hz = 4.7826087[kHz]
Irr_Dec_Bandwidth_Ppm = 11.96303566[ppm]
Irr_Dec_Freq = 399.78219838[MHz]
Irr_Dec_Merit_Factor = 2.2
Irr_Decoupling = TRUE
Irr_Noe = TRUE
Irr_Noise = WALTZ
Irr_Offset_Default = 5[ppm]
Irr_Pwidth = 0.115[ms]
Irr_Pwidth_Default = 0.115[ms]
Irr_Pwidth_Default_Calc = 0.115[ms]
Irr_Pwidth_Temp1 = 0.115[ms]
Irr_Wurst = FALSE
Comment_1 = *** Pulse ***
Comment_102 = *** irr_decoupling
Comment_110 = *** noe_time ***
Comment_7 = *** Pulse Delay **
Decimation_Rate = 0
Experiment_Path = c:\Program Files\J
Get_90 = pulse_service::get
Get_Atn = pulse_service::get

X : parts per Million : Carbon13

^{13}C NMR Spectrum of **2d"** ($CDCl_3$)



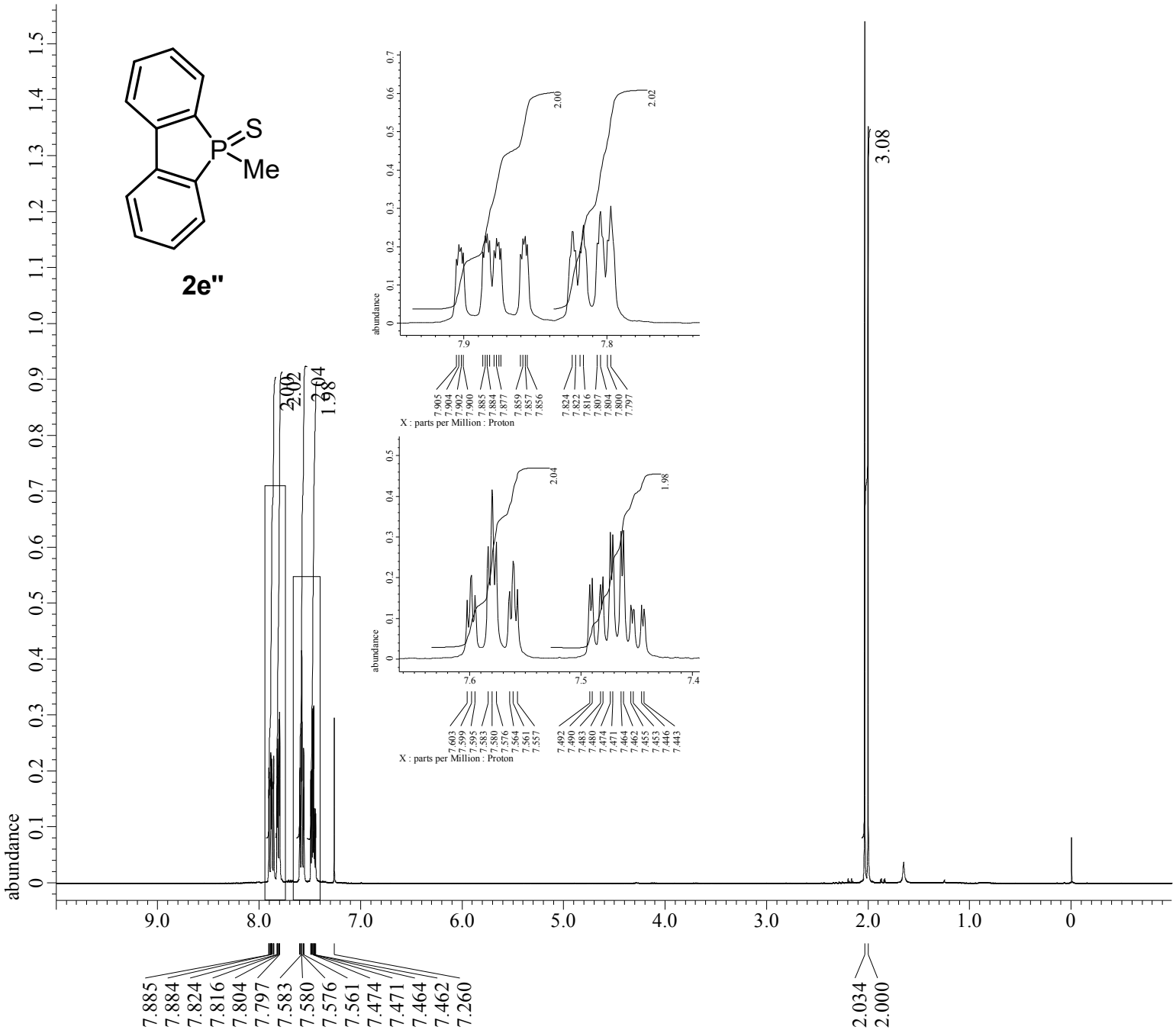

```
Filename                 = TI-N-575 GPC_31P-1
Author                   = delta
Experiment               = single_pulse_dec.j
Sample_Id                = TI-N-575 GPC
Solvent                  = CHLOROFORM-D
Actual_Start_Time        = 13-MAR-2019 14:14:
Revision_Time            = 13-MAR-2019 16:25:

Comment                  = TI-N-575 GPC_31P
Data_Format              = 1D COMPLEX
Dim_Size                 = 26214
X_Domain                 = Phosphorus31
Dim_Title                = Phosphorus31
Dim_Units                = [ppm]
Dimensions               = X
Spectrometer             = JNM-ECZ400S/L1

Field_Strength           = 9.389766[T] (400[M
X_Acq_Duration           = 0.23068672[s]
X_Domain                 = Phosphorus31
X_Freq                   = 161.83469309[MHz]
X_Offset                 = 0[ppm]
X_Points                 = 32768
X_Prescans               = 4
X_Resolution             = 4.33488326[Hz]
X_Sweep                  = 142.04545455[kHz]
X_Sweep_Clipped          = 113.63636364[kHz]
Irr_Domain               = Proton
Irr_Freq                 = 399.78219838[MHz]
Irr_Offset               = 5[ppm]
Blanking                 = 5[us]
Clipped                  = FALSE
Scans                    = 300
Total_Scans              = 300

Relaxation_Delay         = 2[s]
Recvr_Gain               = 56
Temp_Get                 = 19.8[dC]
X_90_Width               = 15.3[us]
X_Acq_Time               = 0.23068672[s]
X_Angle                  = 30[deg]
X_Atn                    = 6[dB]
X_Pulse                  = 5.1[us]
Irr_Atn_Dec              = 26.09[dB]
Irr_Atn_Dec_Calc         = 26.09[dB]
Irr_Atn_Dec_Default_Calc = 26.09[dB]
Irr_Atn_Noe              = 26.09[dB]
Irr_Dec_Bandwidth_Hz     = 4.7826087[kHz]
Irr_Dec_Bandwidth_Ppm    = 11.96303566[ppm]
Irr_Dec_Freq             = 399.78219838[MHz]
Irr_Dec_Merit_Factor     = 2.2
Irr_Decoupling           = TRUE
Irr_Noe                  = TRUE
Irr_Noise                = WALTZ
Irr_Offset_Default       = 5[ppm]
Irr_Pwidth               = 0.115[ms]
Irr_Pwidth_Default       = 0.115[ms]
Irr_Pwidth_Default_Calc  = 0.115[ms]
Irr_Pwidth_Templ         = 0.115[ms]
Irr_Wurst                = FALSE
Decimation_Rate          = 0
Experiment_Path          = c:\Program Files\J
```

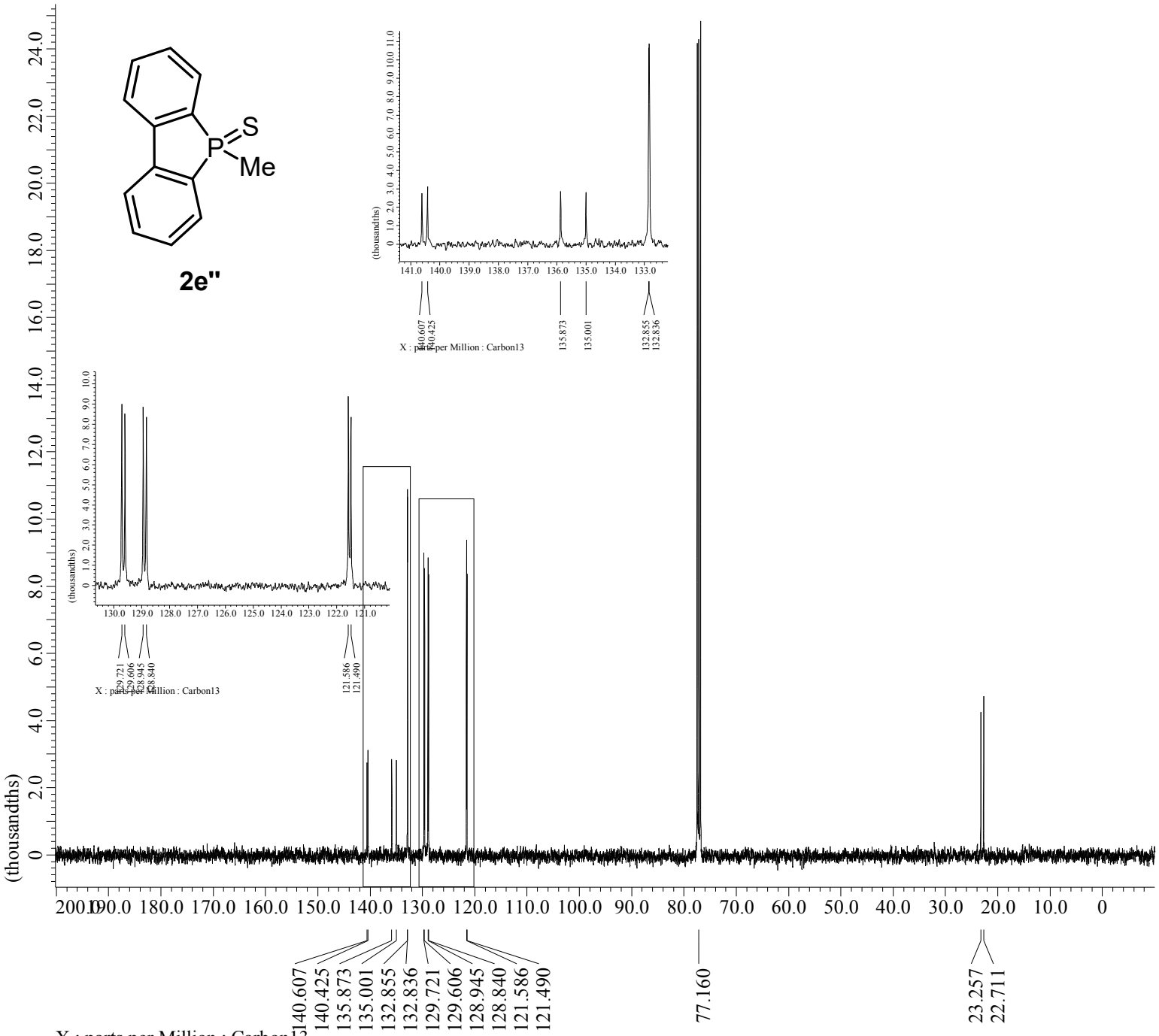
^{31}P NMR Spectrum of **2d"** ($CDCl_3$)



Filename	= TI-N-559 GPC_1H-1-1.j
Author	= delta
Experiment	= proton.jxp
Sample_Id	= TI-N-559 GPC
Solvent	= CHLOROFORM-D
Creation_Time	= 28-FEB-2019 12:27:00
Revision_Time	= 13-MAR-2019 15:03:25
Current_Time	= 15-MAR-2019 17:18:19
Comment	= TI-N-559 GPC_1H
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Spectrometer	= JNM-ECZ400S/L1
Field_Strength	= 9.389766[T] (400[MHz]
X_Acq_Duration	= 3.12475648[s]
X_Domain	= Proton
X_Freq	= 399.78219838[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.32002494[Hz]
X_Sweep	= 10.48657718[kHz]
X_Sweep_Clipped	= 8.38926174[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 399.78219838[MHz]
Tri_Offset	= 5[ppm]
Blanking	= 2[us]
Clipped	= FALSE
Decimation_Reg	= r: 596(595),g: 47
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 46
Temp_Get	= 19.6[dC]
X_90_Width	= 6.4[us]
X_Acq_Time	= 3.12475648[s]
X_Angle	= 45[deg]
X_Atn	= 1[dB]
X_Pulse	= 3.2[us]
Irr_Mode	= Off
Tri_Mode	= Off
Comment_1	= *** Pulse ***
Comment_111	= *** presat_time ***
Comment_201	= *** obs_dante_presatu
Comment_202	= *** irr_ presaturatio
Comment_203	= *** tri_ presaturatio
Comment_7	= *** Pulse Delay ***
Dante_Loop	= 500
Dante_Presat	= FALSE
Decimation_Rate	= 0
Experiment_Path	= c:\Program Files\JEOL
Get_90	= pulse_service::get_90
Get_Atn	= pulse_service::get_at
Get_Freq	= pulse_service::get_fr
Get_Gamma	= pulse_service::get_ga
Get_Probe_Parameter	= probe_service::get_pr
Get_Spin	= pulse_service::get_sp
Initial_Wait	= 1[s]
Phase	= {0, 90, 270, 180, 180
Phase_Acq	= {0, 90, 270, 180, 180
Presat_Time	= 5[s]

X : parts per Million : Proton

^{1}H NMR Spectrum of **2e"** ($CDCl_3$)

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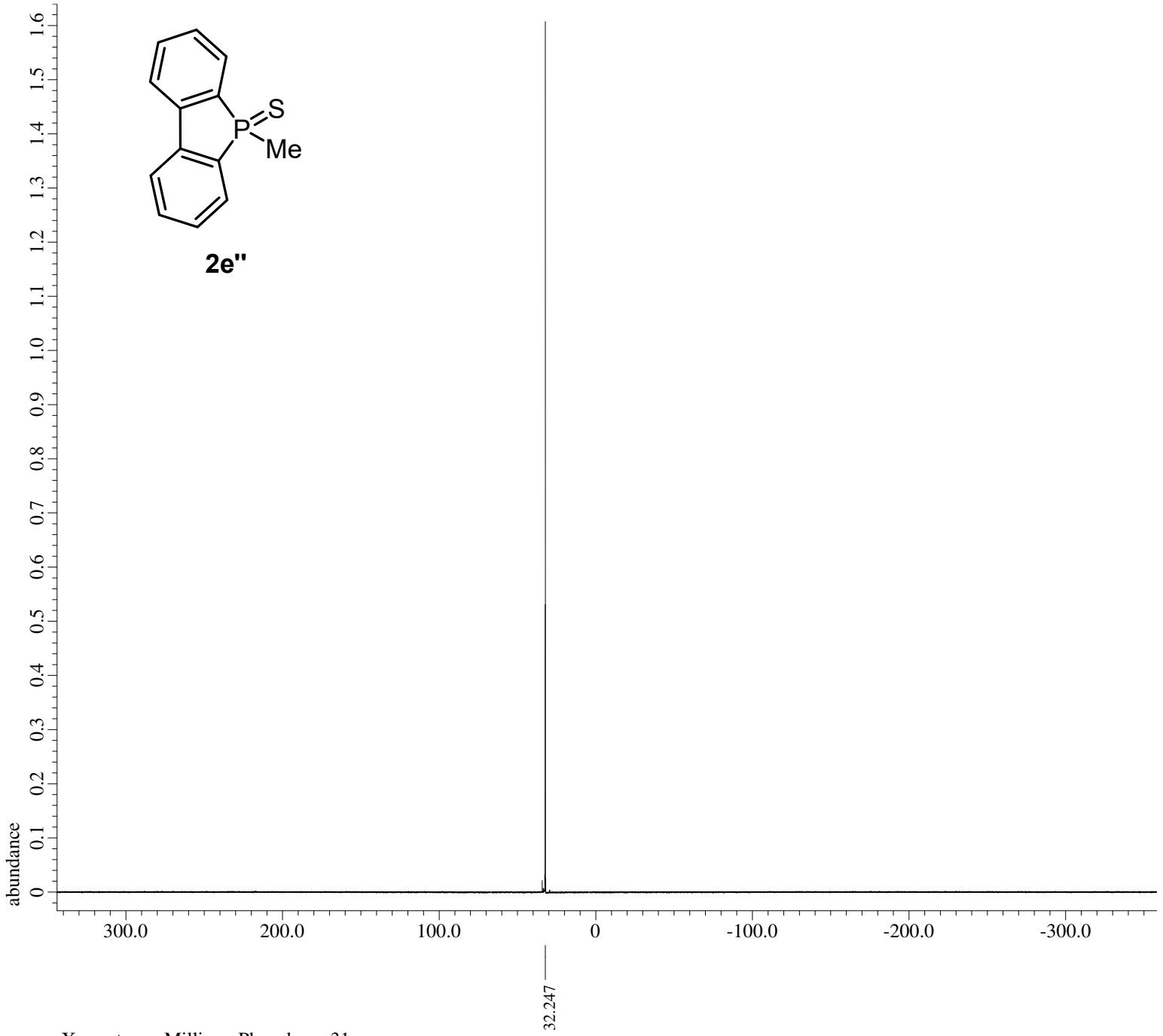
Filename                    = TI-N-559 GPC 1_13C
Author                      = delta
Experiment                  = carbon.jxp
Sample_Id                   = TI-N-559 GPC 1
Solvent                     = CHLOROFORM-D
Creation_Time               = 28-FEB-2019 15:55:
Revision_Time               = 13-MAR-2019 19:24:
Current_Time                = 15-MAR-2019 17:20:

Comment                     = TI-N-559 GPC 1_13C
Data_Format                 = 1D COMPLEX
Dim_Size                    = 26214
Dim_Title                   = Carbon13
Dim_Units                   = [ppm]
Dimensions                  = X
Spectrometer                = JNM-ECZ400S/L1

Field_Strength              = 9.389766[T] (400[M
X_Acq_Duration              = 1.03809024[s]
X_Domain                    = Carbon13
X_Freq                      = 100.52530333[MHz]
X_Offset                    = 100[ppm]
X_Points                    = 32768
X_Prescans                  = 4
X_Resolution                = 0.96330739[Hz]
X_Sweep                     = 31.56565657[kHz]
X_Sweep_Clipped             = 25.25252525[kHz]
Irr_Domain                  = Proton
Irr_Freq                    = 399.78219838[MHz]
Irr_Offset                  = 5[ppm]
Blanking                    = 5[us]
Clipped                     = TRUE
Decimation_Reg              = r: 198( 197),g: 39
Scans                       = 256
Total_Scans                 = 256

Relaxation_Delay            = 2[s]
Recvr_Gain                  = 56
Temp_Get                    = 20[dC]
X_90_Width                  = 10.3[us]
X_Acq_Time                  = 1.03809024[s]
X_Angle                     = 30[deg]
X_Atn                       = 5[dB]
X_Pulse                     = 3.43333333[us]
Irr_Atn_Dec                 = 26.09[dB]
Irr_Atn_Dec_Calc            = 26.09[dB]
Irr_Atn_Dec_Default_Calc    = 26.09[dB]
Irr_Atn_Noe                 = 26.09[dB]
Irr_Dec_Bandwidth_Hz        = 4.7826087[kHz]
Irr_Dec_Bandwidth_Ppm       = 11.96303566[ppm]
Irr_Dec_Freq                = 399.78219838[MHz]
Irr_Dec_Merit_Factor        = 2.2
Irr_Decoupling              = TRUE
Irr_Noe                     = TRUE
Irr_Noise                   = WALTZ
Irr_Offset_Default          = 5[ppm]
Irr_Pwidth                  = 0.115[ms]
Irr_Pwidth_Default          = 0.115[ms]
Irr_Pwidth_Default_Calc     = 0.115[ms]
Irr_Pwidth_Temp1            = 0.115[ms]
Irr_Wurst                   = FALSE
Comment_1                   = *** Pulse ***
Comment_102                 = *** irr_decoupling
Comment_110                 = *** noe_time ***
Comment_7                   = *** Pulse Delay **
Decimation_Rate             = 0
Experiment_Path             = c:\Program Files\J
Get_90                      = pulse_service::get
Get_Atn                     = pulse_service::get
```

^{13}C NMR Spectrum of **2e"** ($CDCl_3$)



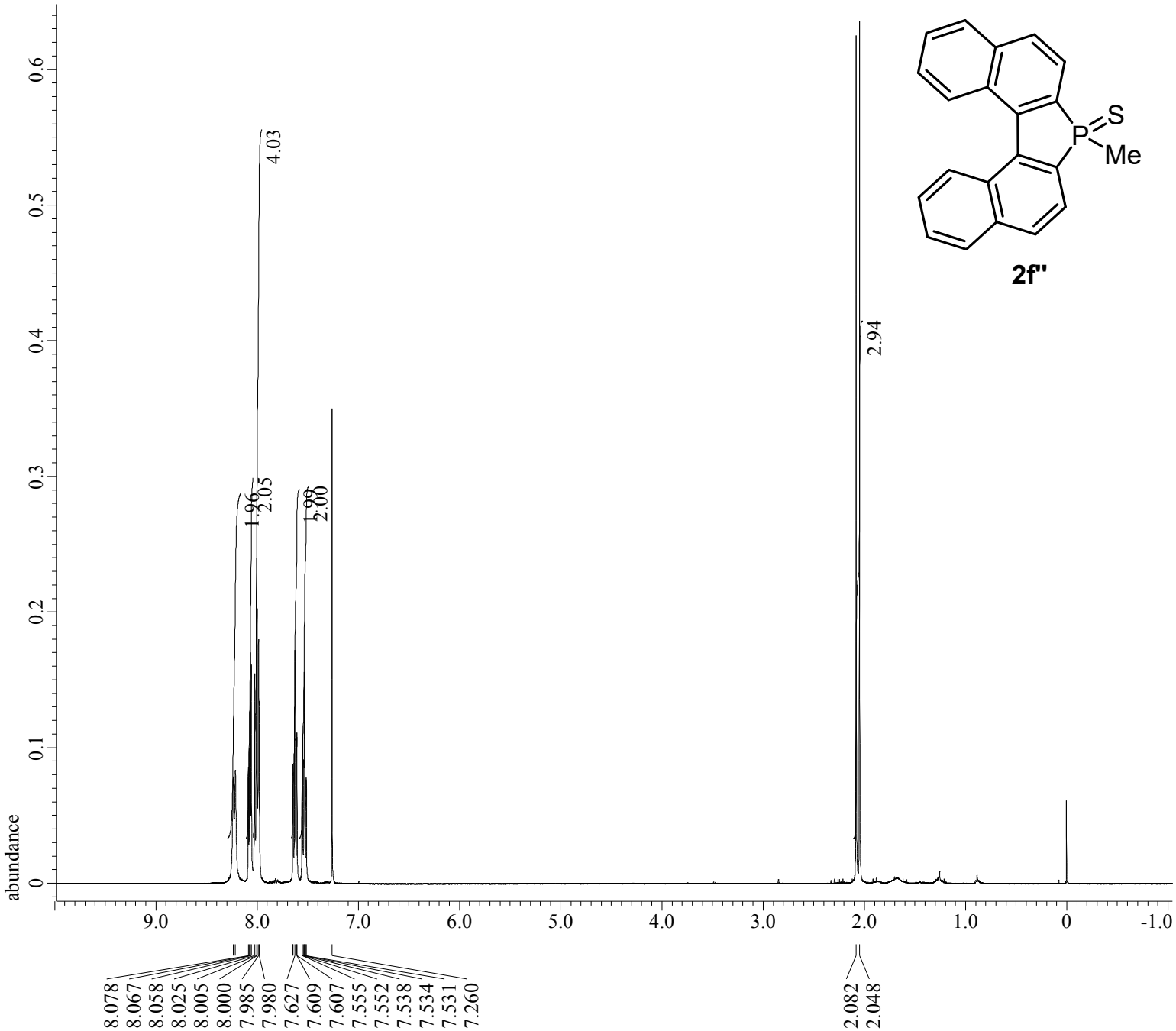

```
Filename                  = TI-N-559 GPC_31P-1
Author                    = delta
Experiment                = single_pulse_dec.j
Sample_Id                 = TI-N-559 GPC
Solvent                   = CHLOROFORM-D
Actual_Start_Time         = 28-FEB-2019 13:08:
Revision_Time             = 13-MAR-2019 23:09:

Comment                   = TI-N-559 GPC_31P
Data_Format               = 1D COMPLEX
Dim_Size                  = 26214
X_Domain                  = Phosphorus31
Dim_Title                 = Phosphorus31
Dim_Units                 = [ppm]
Dimensions                = X
Spectrometer              = JNM-ECZ400S/L1

Field_Strength            = 9.389766[T] (400[M
X_Acq_Duration            = 0.23068672[s]
X_Domain                  = Phosphorus31
X_Freq                    = 161.83469309[MHz]
X_Offset                  = 0[ppm]
X_Points                  = 32768
X_Prescans                = 4
X_Resolution              = 4.33488326[Hz]
X_Sweep                   = 142.04545455[kHz]
X_Sweep_Clipped           = 113.63636364[kHz]
Irr_Domain                = Proton
Irr_Freq                  = 399.78219838[MHz]
Irr_Offset                = 5[ppm]
Blanking                  = 5[us]
Clipped                   = FALSE
Scans                     = 300
Total_Scans               = 300

Relaxation_Delay          = 2[s]
Recvr_Gain                = 56
Temp_Get                  = 19.8[dC]
X_90_Width                = 15.3[us]
X_Acq_Time                = 0.23068672[s]
X_Angle                   = 30[deg]
X_Atn                     = 6[dB]
X_Pulse                   = 5.1[us]
Irr_Atn_Dec               = 26.09[dB]
Irr_Atn_Dec_Calc          = 26.09[dB]
Irr_Atn_Dec_Default_Calc  = 26.09[dB]
Irr_Atn_Noe               = 26.09[dB]
Irr_Dec_Bandwidth_Hz      = 4.7826087[kHz]
Irr_Dec_Bandwidth_Ppm     = 11.96303566[ppm]
Irr_Dec_Freq              = 399.78219838[MHz]
Irr_Dec_Merit_Factor      = 2.2
Irr_Decoupling            = TRUE
Irr_Noe                   = TRUE
Irr_Noise                 = WALTZ
Irr_Offset_Default        = 5[ppm]
Irr_Pwidth                = 0.115[ms]
Irr_Pwidth_Default        = 0.115[ms]
Irr_Pwidth_Default_Calc   = 0.115[ms]
Irr_Pwidth_Templ          = 0.115[ms]
Irr_Wurst                 = FALSE
Decimation_Rate           = 0
Experiment_Path           = c:\Program Files\J
```

^{31}P NMR Spectrum of **2e''** ($CDCl_3$)



2f'

```
Filename              = TI-N-574 GPC_1H-1-2.j
Author                = delta
Experiment            = proton.jxp
Sample_Id             = TI-N-574 GPC
Solvent               = CHLOROFORM-D
Creation_Time         = 14-MAR-2019 09:40:58
Revision_Time         = 14-MAR-2019 09:47:47
Current_Time          = 15-MAR-2019 17:22:04

Comment               = TI-N-574 GPC_1H
Data_Format           = 1D COMPLEX
Dim_Size              = 26214
Dim_Title             = Proton
Dim_Units             = [ppm]
Dimensions            = X
Spectrometer          = JNM-ECZ400S/L1

Field_Strength        = 9.389766[T] (400[MHz]
X_Acq_Duration        = 4.37256192[s]
X_Domain              = Proton
X_Freq                = 399.78219838[MHz]
X_Offset              = 5[ppm]
X_Points              = 32768
X_Prescans            = 1
X_Resolution          = 0.22869888[Hz]
X_Sweep               = 7.4940048[kHz]
X_Sweep_Clipped       = 5.99520384[kHz]
Irr_Domain            = Proton
Irr_Freq              = 399.78219838[MHz]
Irr_Offset            = 5[ppm]
Tri_Domain            = Proton
Tri_Freq              = 399.78219838[MHz]
Tri_Offset            = 5[ppm]
Blanking              = 2[us]
Clipped               = FALSE
Decimation_Reg        = r: 834( 833),g: 49
Scans                 = 8
Total_Scans           = 8

Relaxation_Delay      = 5[s]
Recvr_Gain            = 46
Temp_Get              = 19.5[dC]
X_90_Width            = 6.4[us]
X_Acq_Time            = 4.37256192[s]
X_Angle               = 45[deg]
X_Atn                 = 1[dB]
X_Pulse               = 3.2[us]
Irr_Mode              = Off
Tri_Mode              = Off
Comment_1             = *** Pulse ***
Comment_111           = *** presat_time ***
Comment_201           = *** obs_dante_presatu
Comment_202           = *** irr_ presaturatio
Comment_203           = *** tri_ presaturatio
Comment_7             = *** Pulse Delay ***
Dante_Loop            = 500
Dante_Presat          = FALSE
Decimation_Rate       = 0
Experiment_Path       = c:\Program Files\JEOL
Get_90                = pulse_service::get_90
Get_Atn               = pulse_service::get_at
Get_Freq              = pulse_service::get_fr
Get_Gamma             = pulse_service::get_ga
Get_Probe_Parameter   = probe_service::get_pr
Get_Spin              = pulse_service::get_sp
Initial_Wait          = 1[s]
Phase                 = {0, 90, 270, 180, 180
Phase_Acq             = {0, 90, 270, 180, 180
Presat_Time           = 5[s]
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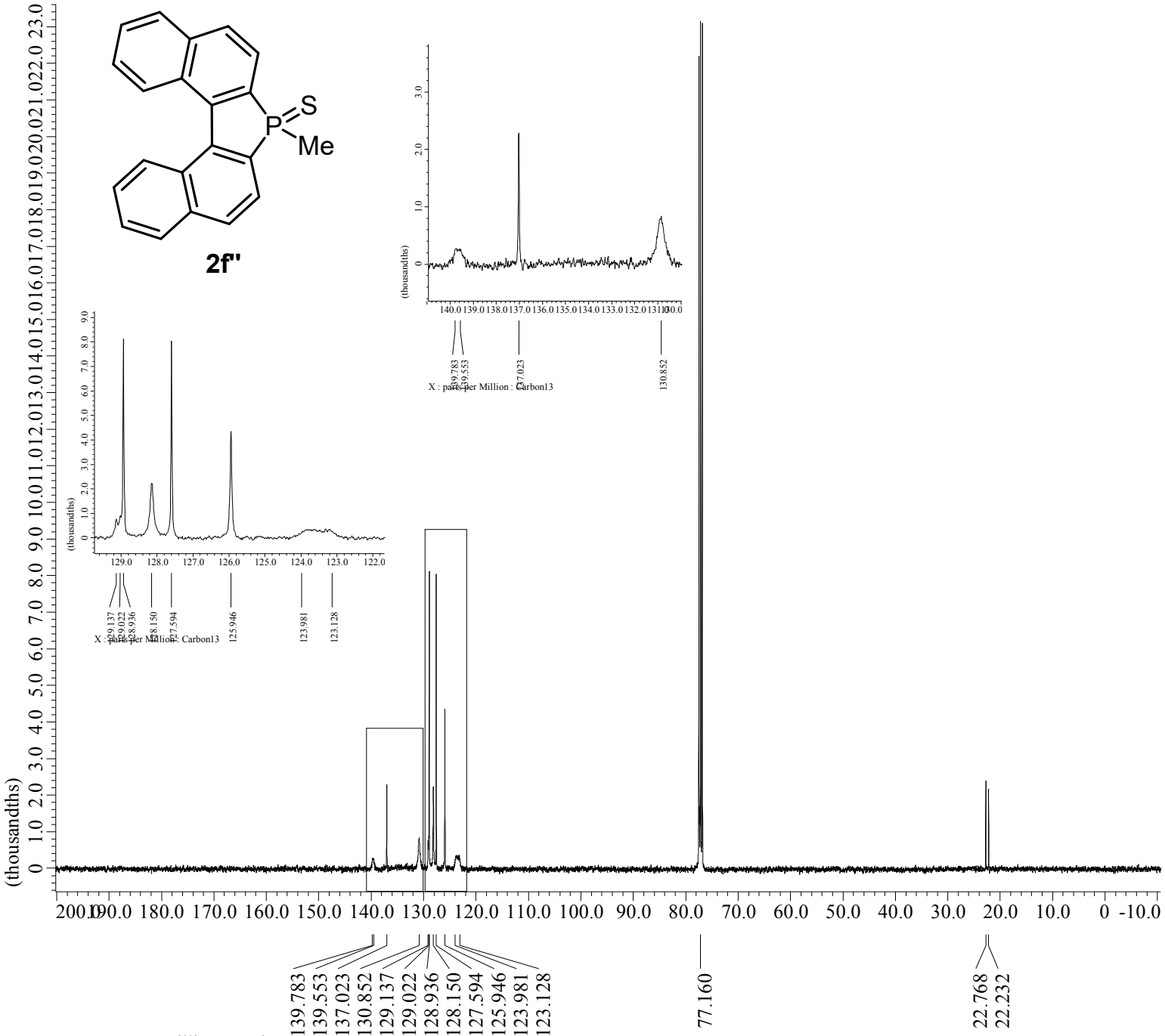
X : parts per Million : Proton

^{1}H NMR Spectrum of **2f"** ($CDCl_3$)



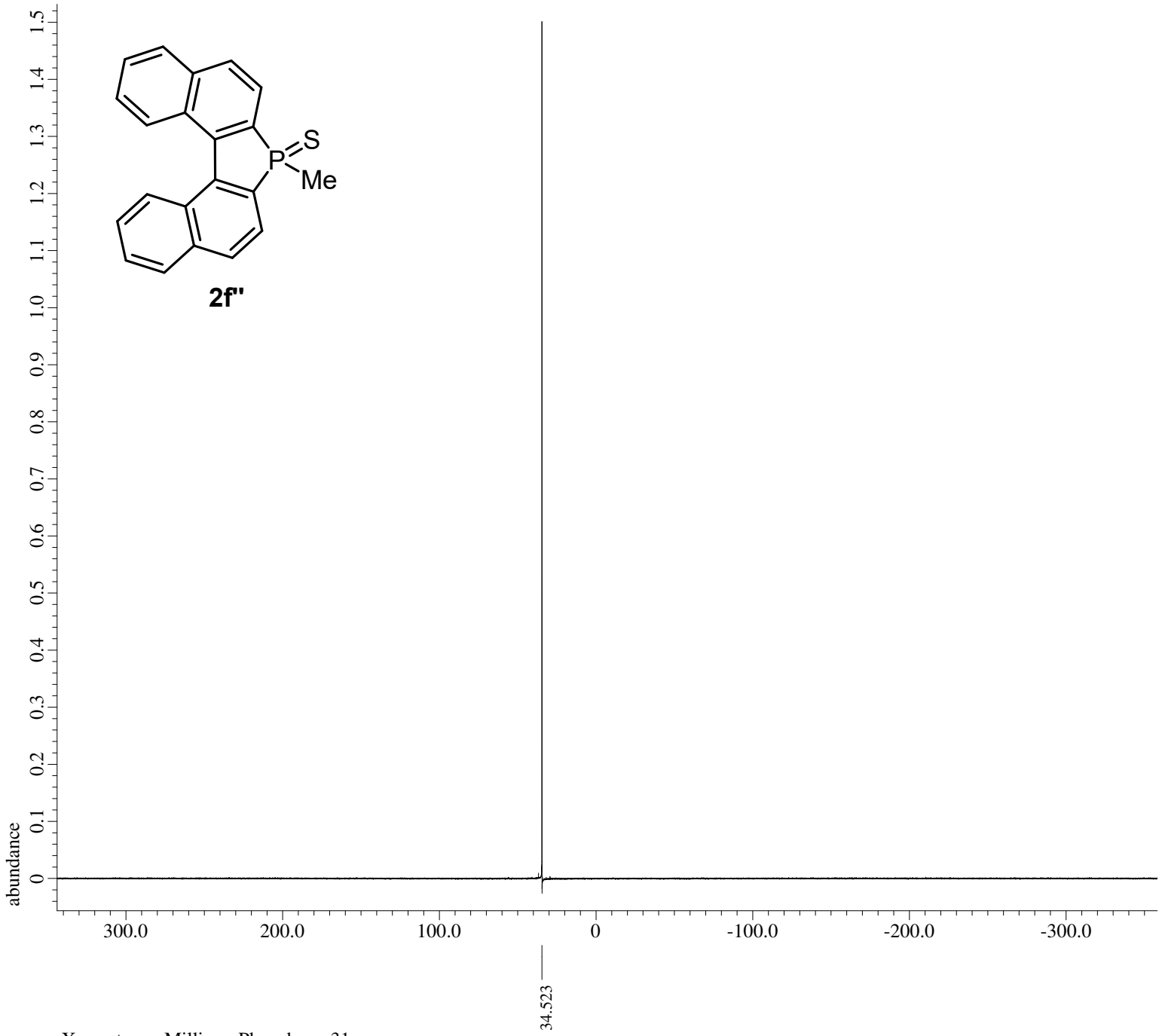

```
Filename                    = TI-N-574 GPC_13C-2
Author                      = delta
Experiment                  = carbon.jxp
Sample_Id                   = TI-N-574 GPC
Solvent                     = CHLOROFORM-D
Creation_Time               = 15-MAR-2019 01:03:
Revision_Time               = 15-MAR-2019 13:47:
Current_Time                = 15-MAR-2019 17:23:

Comment                     = TI-N-574 GPC_13C
Data_Format                 = 1D COMPLEX
Dim_Size                    = 26214
Dim_Title                   = Carbon13
Dim_Units                   = [ppm]
Dimensions                  = X
Spectrometer                = JNM-ECZ400S/L1

Field_Strength              = 9.389766[T] (400[M
X_Acq_Duration              = 1.03809024[s]
X_Domain                    = Carbon13
X_Freq                      = 100.52530333[MHz]
X_Offset                    = 100[ppm]
X_Points                    = 32768
X_Prescans                  = 4
X_Resolution                = 0.96330739[Hz]
X_Sweep                     = 31.56565657[kHz]
X_Sweep_Clipped             = 25.25252525[kHz]
Irr_Domain                  = Proton
Irr_Freq                    = 399.78219838[MHz]
Irr_Offset                  = 5[ppm]
Blanking                    = 5[us]
Clipped                     = TRUE
Decimation_Reg              = r: 198( 197),g: 39
Scans                       = 2048
Total_Scans                 = 2048

Relaxation_Delay            = 2[s]
Recvr_Gain                  = 56
Temp_Get                    = 19.3[dC]
X_90_Width                  = 10.3[us]
X_Acq_Time                  = 1.03809024[s]
X_Angle                     = 30[deg]
X_Atn                       = 5[dB]
X_Pulse                     = 3.43333333[us]
Irr_Atn_Dec                 = 26.09[dB]
Irr_Atn_Dec_Calc            = 26.09[dB]
Irr_Atn_Dec_Default_Calc    = 26.09[dB]
Irr_Atn_Noe                 = 26.09[dB]
Irr_Dec_Bandwidth_Hz        = 4.7826087[kHz]
Irr_Dec_Bandwidth_Ppm       = 11.96303566[ppm]
Irr_Dec_Freq                = 399.78219838[MHz]
Irr_Dec_Merit_Factor        = 2.2
Irr_Decoupling              = TRUE
Irr_Noe                     = TRUE
Irr_Noise                   = WALTZ
Irr_Offset_Default          = 5[ppm]
Irr_Pwidth                  = 0.115[ms]
Irr_Pwidth_Default          = 0.115[ms]
Irr_Pwidth_Default_Calc     = 0.115[ms]
Irr_Pwidth_Temp1            = 0.115[ms]
Irr_Wurst                   = FALSE
Comment_1                   = *** Pulse ***
Comment_102                 = *** irr_decoupling
Comment_110                 = *** noe_time ***
Comment_7                   = *** Pulse Delay **
Decimation_Rate             = 0
Experiment_Path             = c:\Program Files\J
Get_90                      = pulse_service::get
Get_Atn                     = pulse_service::get
```


^{13}C NMR Spectrum of **2f''** ($CDCl_3$)



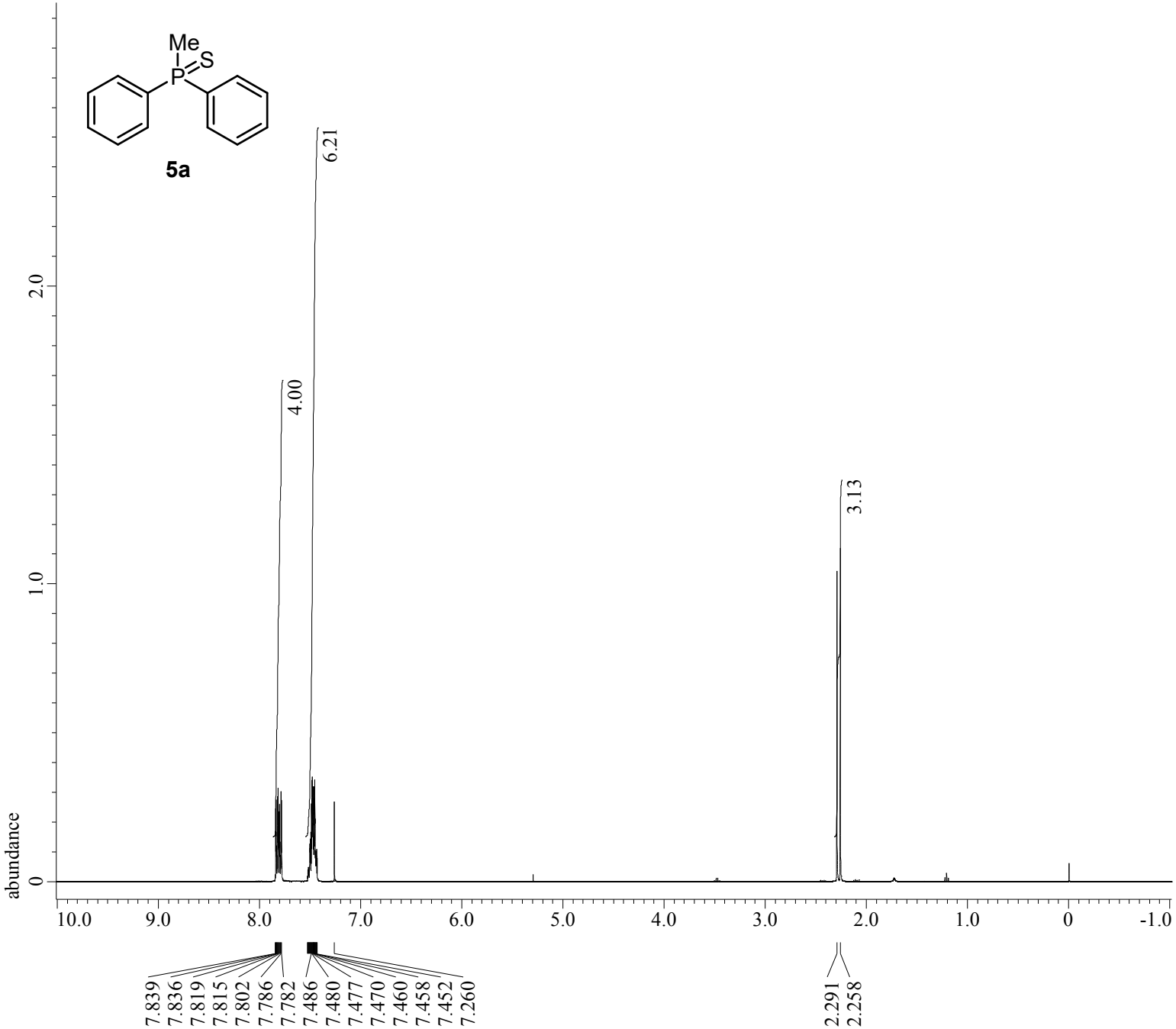

```
Filename                = TI-N-574 GPC_31P-1
Author                  = delta
Experiment              = single_pulse_dec.j
Sample_Id               = TI-N-574 GPC
Solvent                 = CHLOROFORM-D
Actual_Start_Time       = 14-MAR-2019 09:43:
Revision_Time           = 14-MAR-2019 10:55:

Comment                 = TI-N-574 GPC_31P
Data_Format             = 1D COMPLEX
Dim_Size                = 26214
X_Domain                = Phosphorus31
Dim_Title               = Phosphorus31
Dim_Units               = [ppm]
Dimensions              = X
Spectrometer            = JNM-ECZ400S/L1

Field_Strength          = 9.389766[T] (400[M
X_Acq_Duration          = 0.23068672[s]
X_Domain                = Phosphorus31
X_Freq                  = 161.83469309[MHz]
X_Offset                = 0[ppm]
X_Points                = 32768
X_Prescans              = 4
X_Resolution            = 4.33488326[Hz]
X_Sweep                 = 142.04545455[kHz]
X_Sweep_Clipped         = 113.63636364[kHz]
Irr_Domain              = Proton
Irr_Freq                = 399.78219838[MHz]
Irr_Offset              = 5[ppm]
Blanking                = 5[us]
Clipped                 = FALSE
Scans                   = 300
Total_Scans             = 300

Relaxation_Delay        = 2[s]
Recvr_Gain              = 56
Temp_Get                = 19.5[dC]
X_90_Width              = 15.3[us]
X_Acq_Time              = 0.23068672[s]
X_Angle                 = 30[deg]
X_Atn                   = 6[dB]
X_Pulse                 = 5.1[us]
Irr_Atn_Dec             = 26.09[dB]
Irr_Atn_Dec_Calc        = 26.09[dB]
Irr_Atn_Dec_Default_Calc = 26.09[dB]
Irr_Atn_Noe             = 26.09[dB]
Irr_Dec_Bandwidth_Hz    = 4.7826087[kHz]
Irr_Dec_Bandwidth_Ppm   = 11.96303566[ppm]
Irr_Dec_Freq            = 399.78219838[MHz]
Irr_Dec_Merit_Factor    = 2.2
Irr_Decoupling          = TRUE
Irr_Noe                 = TRUE
Irr_Noise               = WALTZ
Irr_Offset_Default      = 5[ppm]
Irr_Pwidth              = 0.115[ms]
Irr_Pwidth_Default      = 0.115[ms]
Irr_Pwidth_Default_Calc = 0.115[ms]
Irr_Pwidth_Templ        = 0.115[ms]
Irr_Wurst               = FALSE
Decimation_Rate         = 0
Experiment_Path         = c:\Program Files\J
```

^{31}P NMR Spectrum of **2f''** ($CDCl_3$)




```
Filename              = S=PPh2Me_1H-2-1.jdf
Author                = delta
Experiment            = proton.jxp
Sample_Id             = S=PPh2Me
Solvent               = CHLOROFORM-D
Creation_Time         = 13-MAR-2019 22:57:57
Revision_Time         = 13-MAR-2019 22:58:07
Current_Time          = 15-MAR-2019 17:24:59

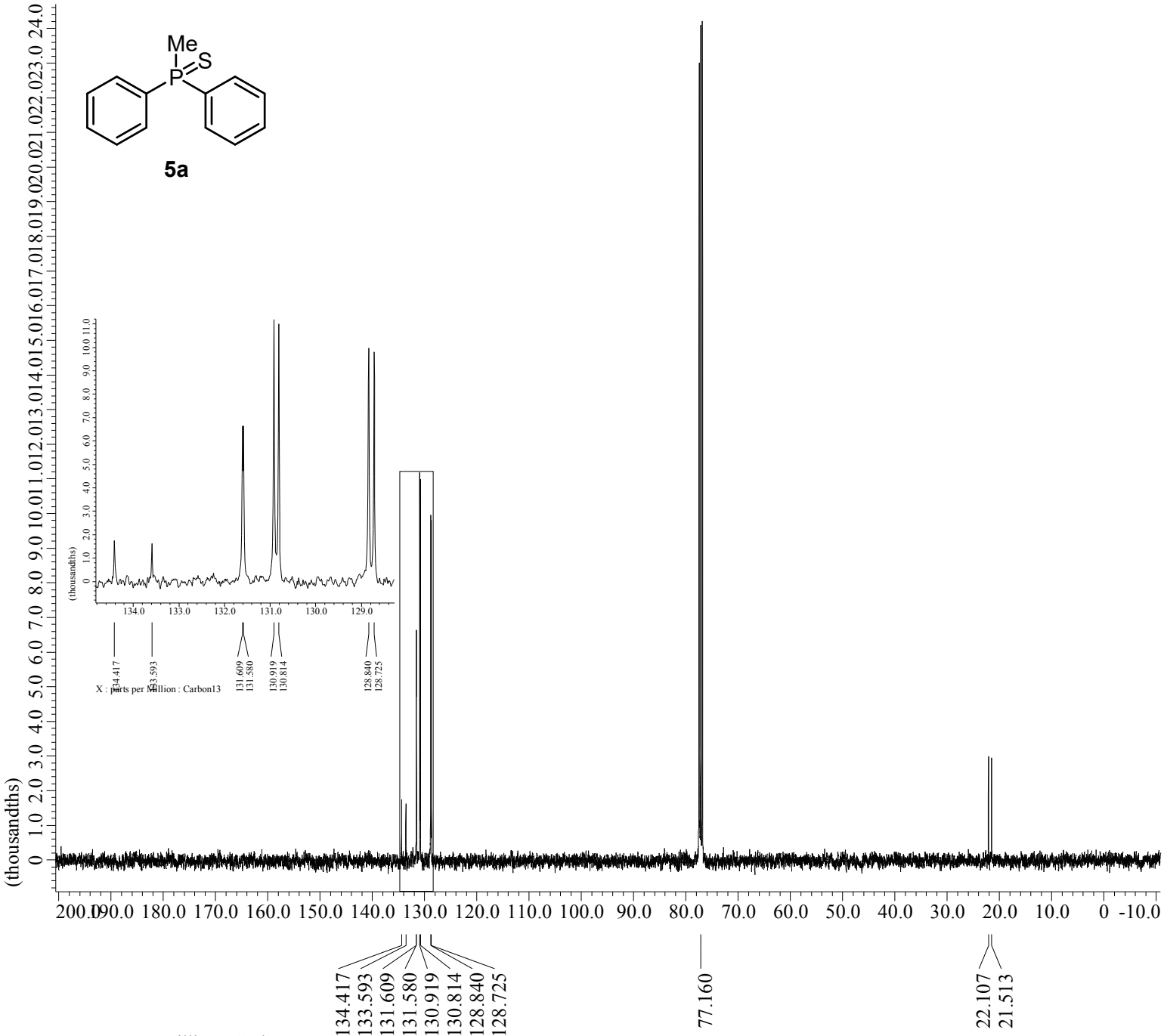
Comment               = S=PPh2Me_1H
Data_Format           = 1D COMPLEX
Dim_Size              = 26214
Dim_Title             = Proton
Dim_Units             = [ppm]
Dimensions            = X
Spectrometer          = JNM-ECZ400S/L1

Field_Strength        = 9.389766[T] (400[MHz]
X_Acq_Duration        = 4.37256192[s]
X_Domain              = Proton
X_Freq                = 399.78219838[MHz]
X_Offset              = 5[ppm]
X_Points              = 32768
X_Prescans            = 1
X_Resolution          = 0.22869888[Hz]
X_Sweep               = 7.4940048[kHz]
X_Sweep_Clipped       = 5.99520384[kHz]
Irr_Domain            = Proton
Irr_Freq              = 399.78219838[MHz]
Irr_Offset            = 5[ppm]
Tri_Domain            = Proton
Tri_Freq              = 399.78219838[MHz]
Tri_Offset            = 5[ppm]
Blanking              = 2[us]
Clipped               = FALSE
Decimation_Reg        = r: 834( 833),g: 49
Scans                 = 8
Total_Scans           = 8

Relaxation_Delay      = 5[s]
Recvr_Gain            = 46
Temp_Get              = 19.5[dC]
X_90_Width            = 6.4[us]
X_Acq_Time            = 4.37256192[s]
X_Angle               = 45[deg]
X_Atn                 = 1[dB]
X_Pulse               = 3.2[us]
Irr_Mode              = Off
Tri_Mode              = Off
Comment_1             = *** Pulse ***
Comment_111           = *** presat_time ***
Comment_201           = *** obs_dante_presatu
Comment_202           = *** irr_ presaturatio
Comment_203           = *** tri_ presaturatio
Comment_7             = *** Pulse Delay ***
Dante_Loop            = 500
Dante_Presat          = FALSE
Decimation_Rate       = 0
Experiment_Path       = c:\Program Files\JEOL
Get_90                = pulse_service::get_90
Get_Atn               = pulse_service::get_at
Get_Freq              = pulse_service::get_fr
Get_Gamma             = pulse_service::get_ga
Get_Probe_Parameter   = probe_service::get_pr
Get_Spin              = pulse_service::get_sp
Initial_Wait          = 1[s]
Phase                 = {0, 90, 270, 180, 180
Phase_Acq             = {0, 90, 270, 180, 180
Presat_Time           = 5[s]
```

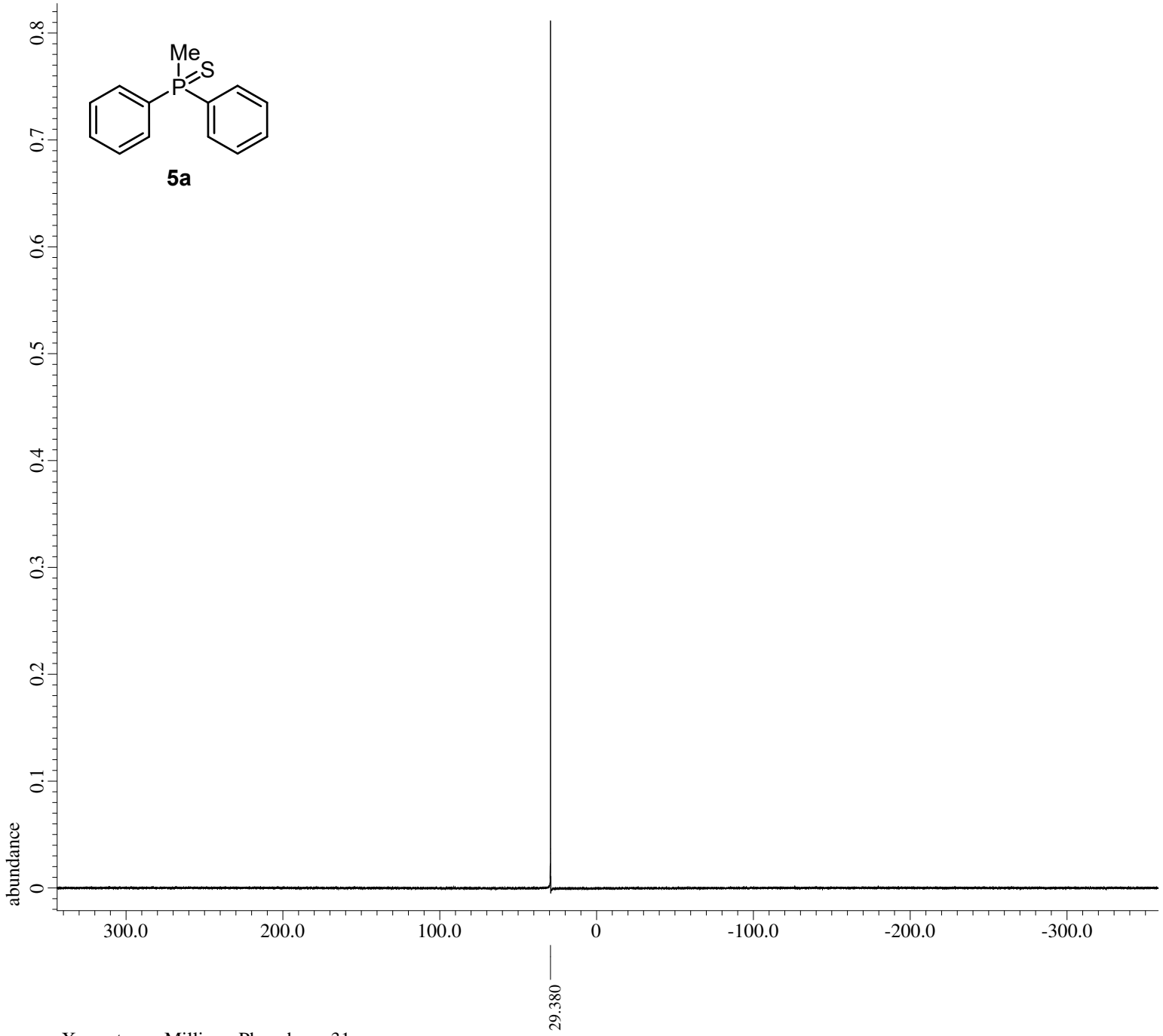
X : parts per Million : Proton

^{1}H NMR Spectrum of **5a** ($CDCl_3$)



Filename	= S=PPh2Me_13C-1-1.j
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= S=PPh2Me
Solvent	= CHLOROFORM-D
Creation_Time	= 13-MAR-2019 23:13:
Revision_Time	= 14-MAR-2019 09:25:
Current_Time	= 15-MAR-2019 17:26:
Comment	= S=PPh2Me_13C
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= Carbon13
Dim_Units	= [ppm]
Dimensions	= X
Spectrometer	= JNM-ECZ400S/L1
Field_Strength	= 9.389766[T] (400[M
X_Acq_Duration	= 1.03809024[s]
X_Domain	= Carbon13
X_Freq	= 100.52530333[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 0.96330739[Hz]
X_Sweep	= 31.56565657[kHz]
X_Sweep_Clipped	= 25.25252525[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Blanking	= 5[us]
Clipped	= FALSE
Decimation_Reg	= r: 198(197),g: 39
Scans	= 256
Total_Scans	= 256
Relaxation_Delay	= 2[s]
Recvr_Gain	= 56
Temp_Get	= 19.5[dC]
X_90_Width	= 10.3[us]
X_Acq_Time	= 1.03809024[s]
X_Angle	= 30[deg]
X_Atn	= 5[dB]
X_Pulse	= 3.43333333[us]
Irr_Atn_Dec	= 26.09[dB]
Irr_Atn_Dec_Calc	= 26.09[dB]
Irr_Atn_Dec_Default_Calc	= 26.09[dB]
Irr_Atn_Noe	= 26.09[dB]
Irr_Dec_Bandwidth_Hz	= 4.7826087[kHz]
Irr_Dec_Bandwidth_Ppm	= 11.96303566[ppm]
Irr_Dec_Freq	= 399.78219838[MHz]
Irr_Dec_Merit_Factor	= 2.2
Irr_Decoupling	= TRUE
Irr_Noe	= TRUE
Irr_Noise	= WALTZ
Irr_Offset_Default	= 5[ppm]
Irr_Pwidth	= 0.115[ms]
Irr_Pwidth_Default	= 0.115[ms]
Irr_Pwidth_Default_Calc	= 0.115[ms]
Irr_Pwidth_Temp1	= 0.115[ms]
Irr_Wurst	= FALSE
Comment_1	= *** Pulse ***
Comment_102	= *** irr_decoupling
Comment_110	= *** noe_time ***
Comment_7	= *** Pulse Delay **
Decimation_Rate	= 0
Experiment_Path	= c:\Program Files\J
Get_90	= pulse_service::get
Get_Atn	= pulse_service::get

^{13}C NMR Spectrum of **5a** ($CDCl_3$)



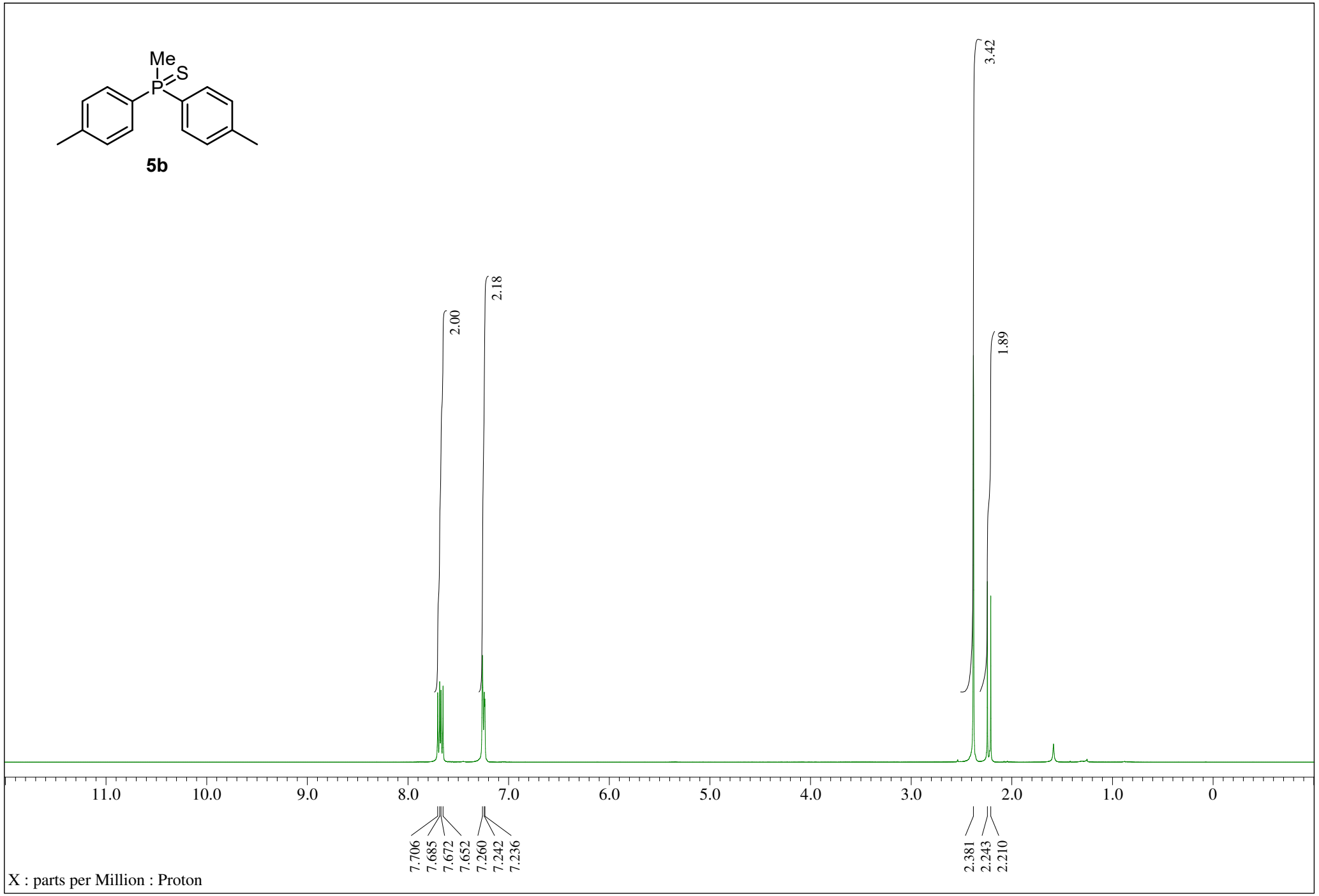

```
Filename                 = S=PPh2Me_31P-1-1.j
Author                   = delta
Experiment               = single_pulse_dec.j
Sample_Id                = S=PPh2Me
Solvent                  = CHLOROFORM-D
Actual_Start_Time        = 13-MAR-2019 23:00:
Revision_Time            = 13-MAR-2019 23:10:

Comment                  = S=PPh2Me_31P
Data_Format              = 1D COMPLEX
Dim_Size                 = 26214
X_Domain                 = Phosphorus31
Dim_Title                = Phosphorus31
Dim_Units                = [ppm]
Dimensions               = X
Spectrometer             = JNM-ECZ400S/L1

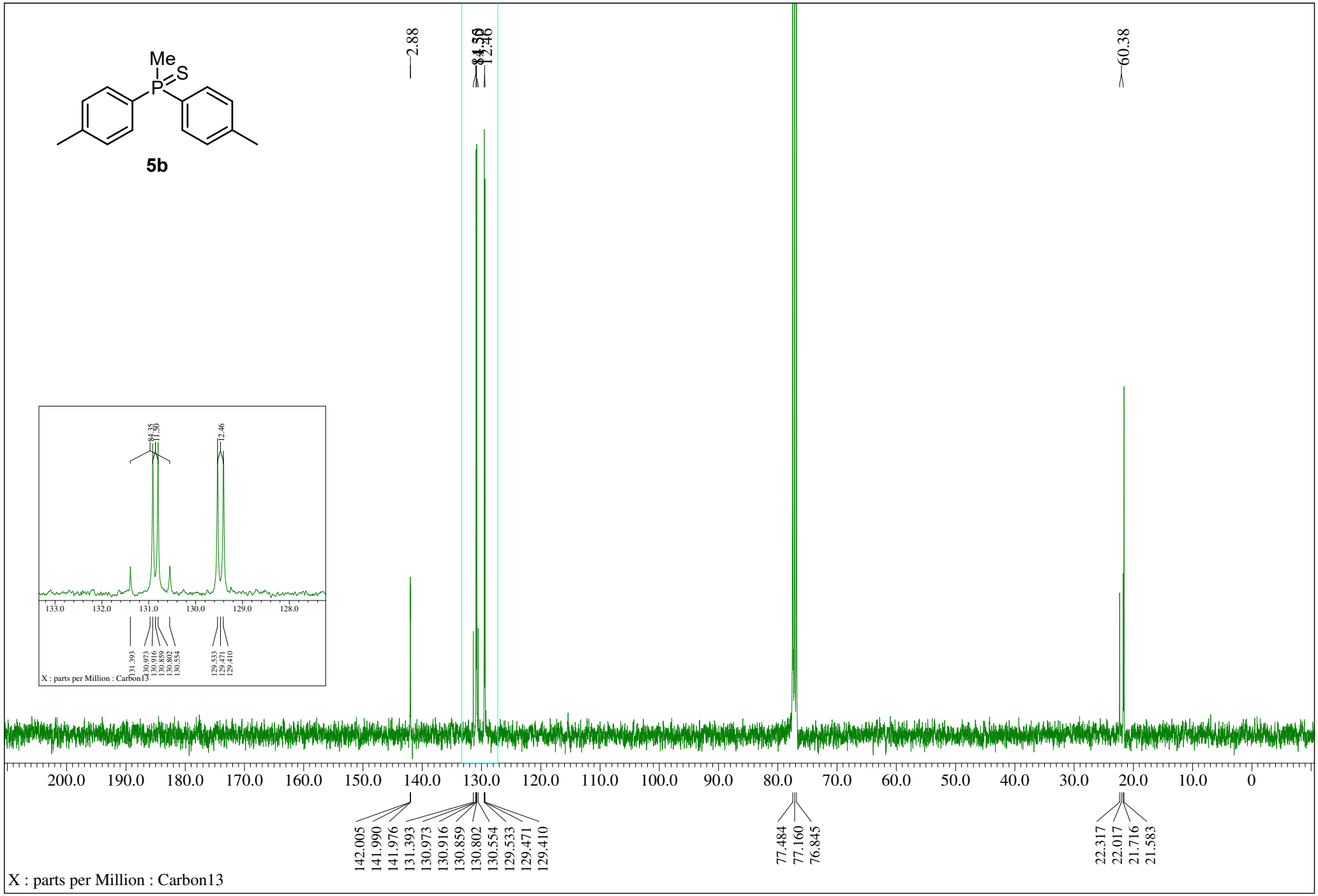
Field_Strength           = 9.389766[T] (400[M
X_Acq_Duration           = 0.23068672[s]
X_Domain                 = Phosphorus31
X_Freq                   = 161.83469309[MHz]
X_Offset                 = 0[ppm]
X_Points                 = 32768
X_Prescans               = 4
X_Resolution             = 4.33488326[Hz]
X_Sweep                  = 142.04545455[kHz]
X_Sweep_Clipped          = 113.63636364[kHz]
Irr_Domain               = Proton
Irr_Freq                 = 399.78219838[MHz]
Irr_Offset               = 5[ppm]
Blanking                 = 5[us]
Clipped                  = FALSE
Scans                    = 300
Total_Scans              = 300

Relaxation_Delay         = 2[s]
Recvr_Gain               = 56
Temp_Get                 = 19.7[dC]
X_90_Width               = 15.3[us]
X_Acq_Time               = 0.23068672[s]
X_Angle                  = 30[deg]
X_Atn                    = 6[dB]
X_Pulse                  = 5.1[us]
Irr_Atn_Dec              = 26.09[dB]
Irr_Atn_Dec_Calc         = 26.09[dB]
Irr_Atn_Dec_Default_Calc = 26.09[dB]
Irr_Atn_Noe              = 26.09[dB]
Irr_Dec_Bandwidth_Hz     = 4.7826087[kHz]
Irr_Dec_Bandwidth_Ppm    = 11.96303566[ppm]
Irr_Dec_Freq             = 399.78219838[MHz]
Irr_Dec_Merit_Factor     = 2.2
Irr_Decoupling           = TRUE
Irr_Noe                  = TRUE
Irr_Noise                = WALTZ
Irr_Offset_Default       = 5[ppm]
Irr_Pwidth               = 0.115[ms]
Irr_Pwidth_Default       = 0.115[ms]
Irr_Pwidth_Default_Calc  = 0.115[ms]
Irr_Pwidth_Templ         = 0.115[ms]
Irr_Wurst                = FALSE
Decimation_Rate          = 0
Experiment_Path          = c:\Program Files\J
```

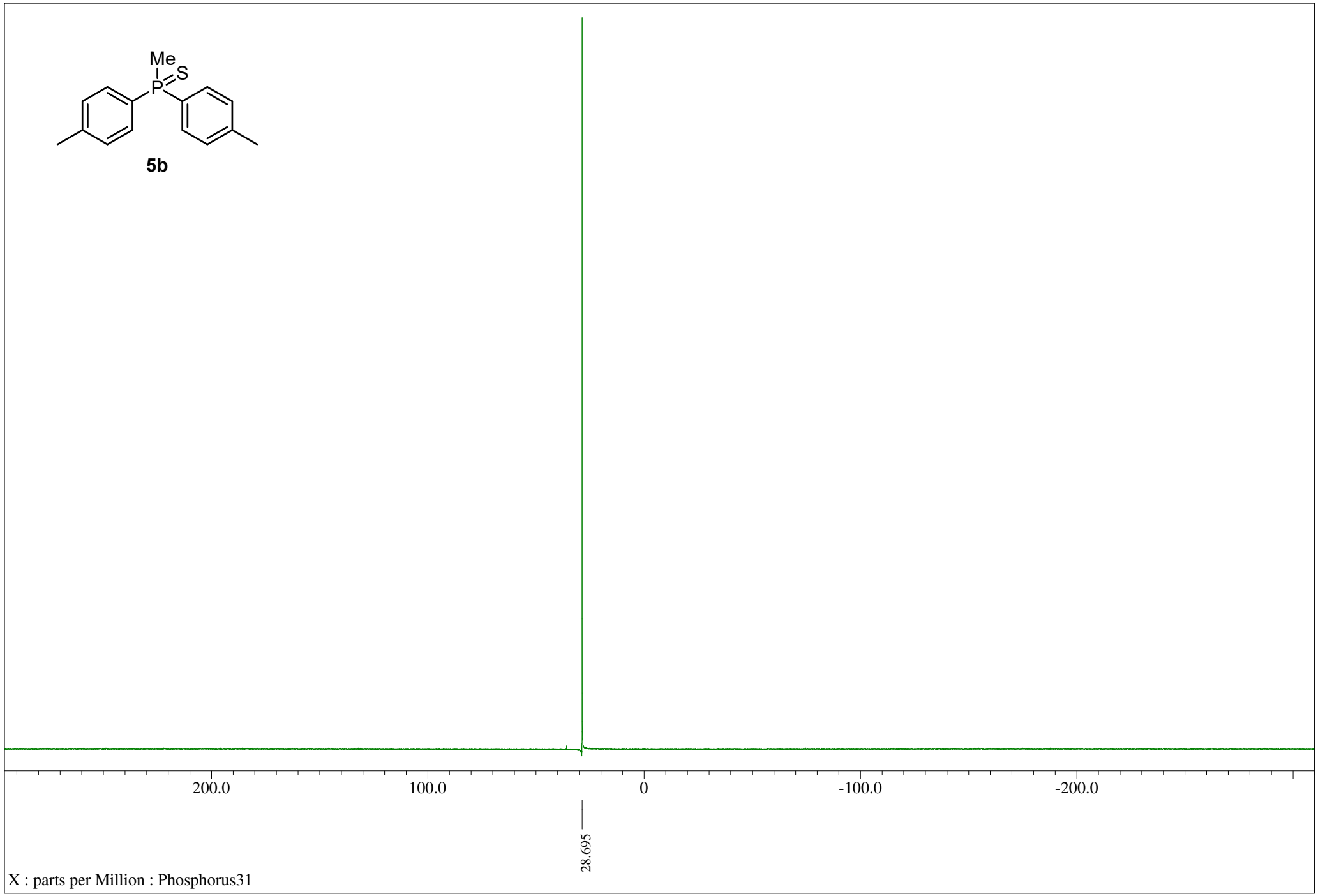
^{31}P NMR Spectrum of **5a** ($CDCl_3$)



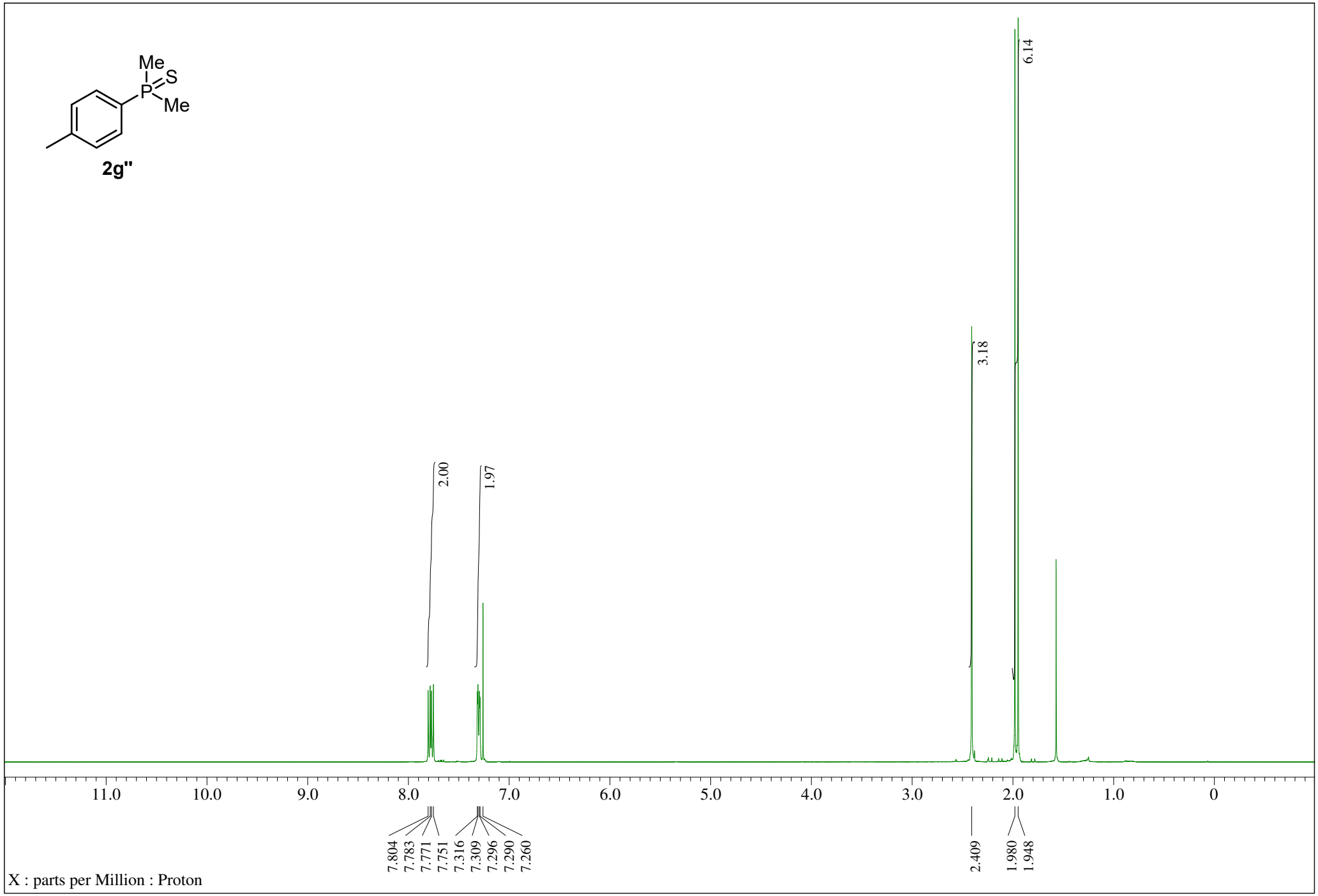
^{1}H NMR Spectrum of **5b** ($CDCl_3$)



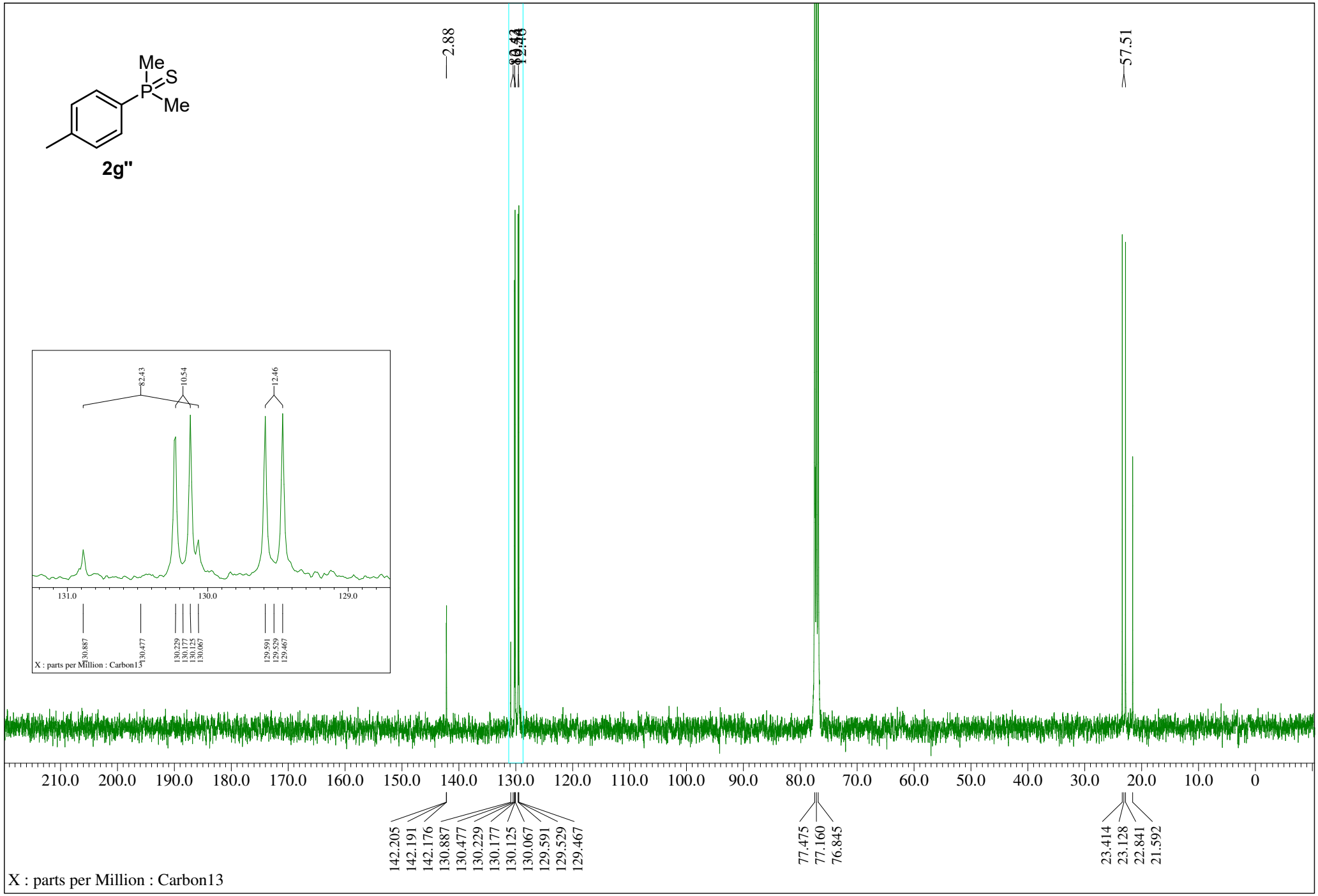
^{13}C NMR Spectrum of **5b** ($CDCl_3$)



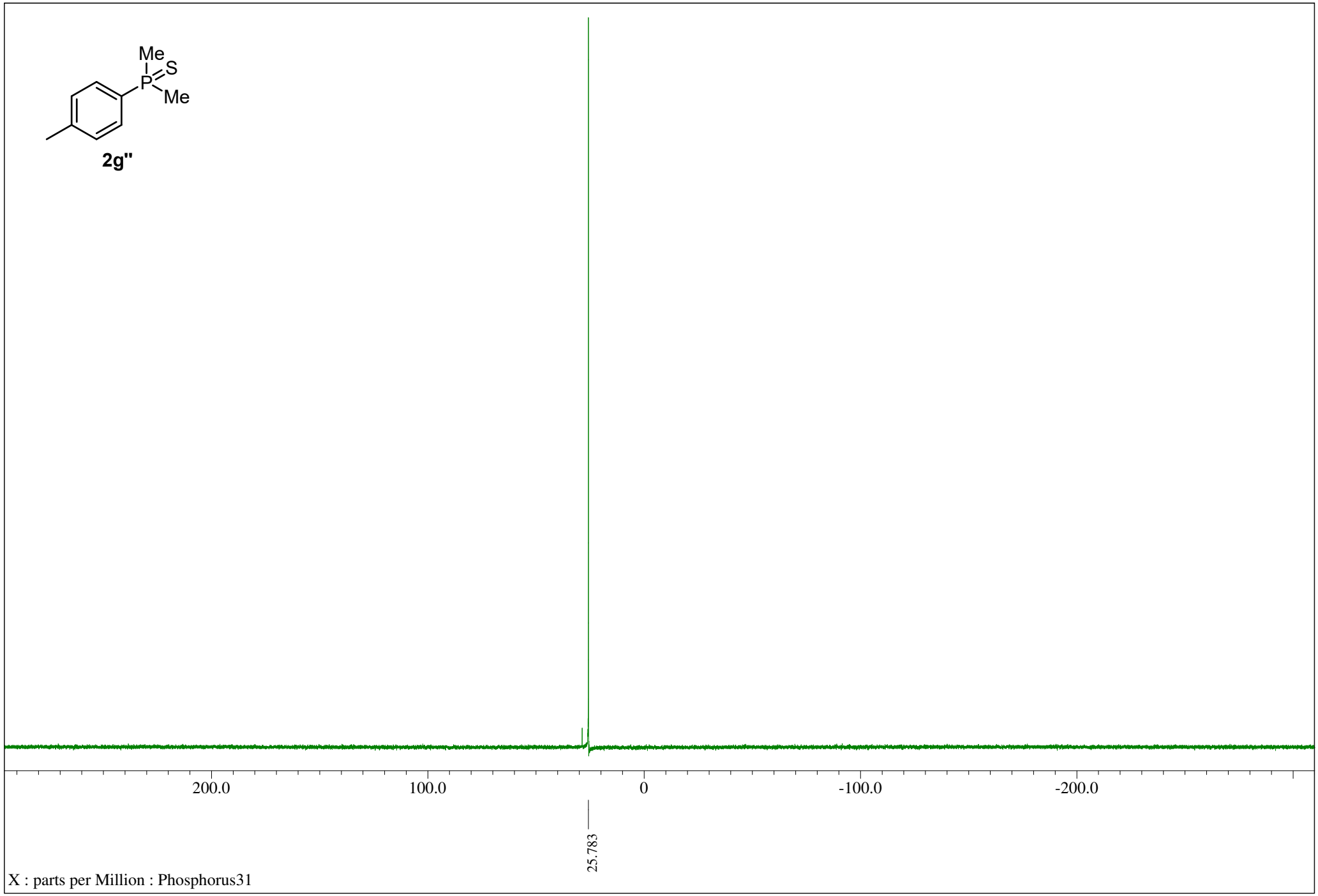
^{31}P NMR Spectrum of **5b** ($CDCl_3$)



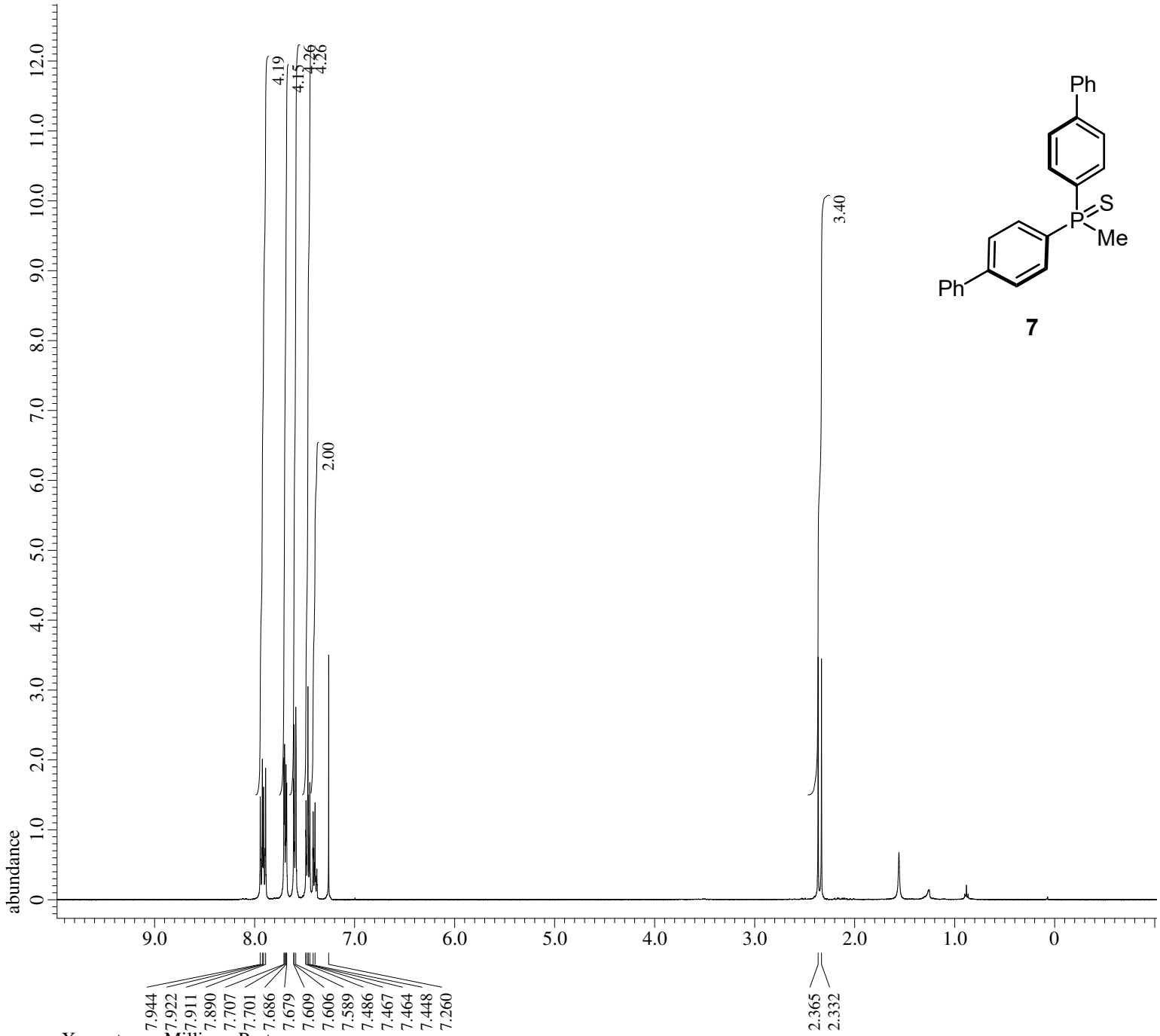
^{1}H NMR Spectrum of **2g"** ($CDCl_3$)



^{13}C NMR Spectrum of **2g"** ($CDCl_3$)



^{31}P NMR Spectrum of **2g"** ($CDCl_3$)



7

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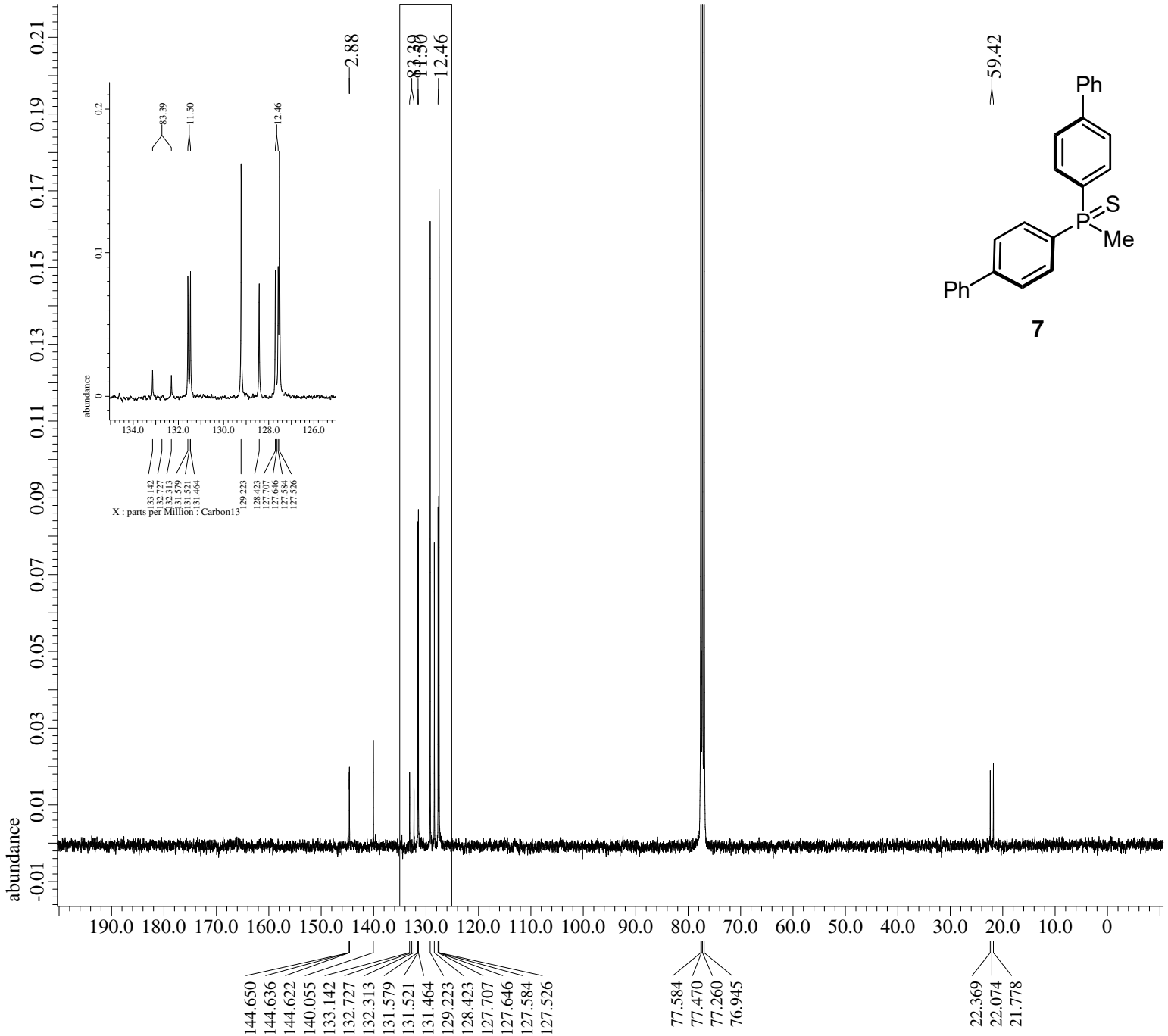
Filename           = RS-23-009-3_Proton-1-2.jd
Author             = delta
Experiment         = proton.jxp
Sample_Id          = RS-23-009-3
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 18-APR-2023 19:59:22
Revision_Time      = 19-APR-2023 09:03:10

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 13107
X_Domain           = Proton
Dim_Title          = Proton
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECS400
Spectrometer       = DELTA2_NMR

Field_Strength     = 9.389766[T] (400[MHz])
X_Acq_Duration     = 2.18365952[s]
X_Domain           = 1H
X_Freq             = 399.78219838[MHz]
X_Offset           = 5[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.45794685[Hz]
X_Sweep            = 7.5030012[kHz]
X_Sweep_Clipped    = 6.00240096[kHz]
Irr_Domain         = Proton
Irr_Freq           = 399.78219838[MHz]
Irr_Offset         = 5[ppm]
Tri_Domain         = Proton
Tri_Freq           = 399.78219838[MHz]
Tri_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 8
Total_Scans        = 8

Relaxation_Delay   = 2[s]
Recvr_Gain         = 50
Temp_Get           = 20.1[dC]
X_90_Width         = 11.9[us]
X_Acq_Time         = 2.18365952[s]
X_Angle            = 45[deg]
X_Atn              = 1.2[dB]
X_Pulse            = 5.95[us]
Irr_Mode           = Off
Tri_Mode           = Off
Dante_Presat       = FALSE
Initial_Wait       = 1[s]
Repetition_Time    = 4.18365952[s]
```

^{1}H NMR Spectrum of **7** ($CDCl_3$)

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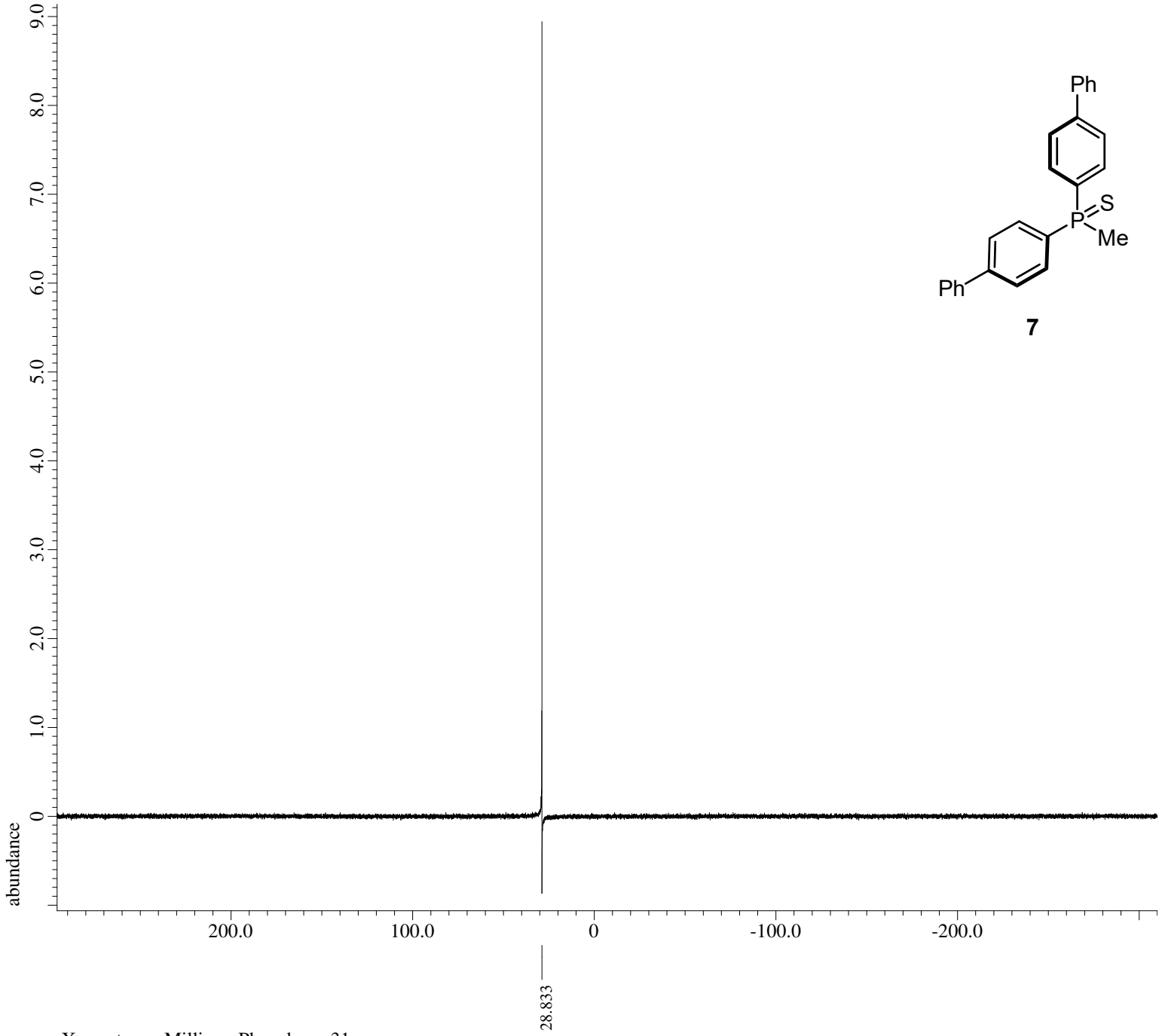
Filename          = RS-23-009-3_13C-1-5.jdf
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = RS-23-009-3
Solvent           = CHLOROFORM-D
Actual_Start_Time = 19-APR-2023 02:07:39
Revision_Time     = 19-APR-2023 08:28:15

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 1.04333312[s]
X_Domain          = 13C
X_Freq            = 100.52530333[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.95846665[Hz]
X_Sweep           = 31.40703518[kHz]
X_Sweep_Clipped   = 25.12562814[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 5120
Total_Scans       = 5120

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 20.2[dC]
X_90_Width        = 9.73[us]
X_Acq_Time        = 1.04333312[s]
X_Angle           = 30[deg]
X_Atn             = 5.1[dB]
X_Pulse           = 3.24333333[us]
Irr_Atn_Dec       = 20.9[dB]
Irr_Atn_Noe       = 20.9[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 0.115[ms]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.04333312[s]
```

^{13}C NMR Spectrum of **7** ($CDCl_3$)



7

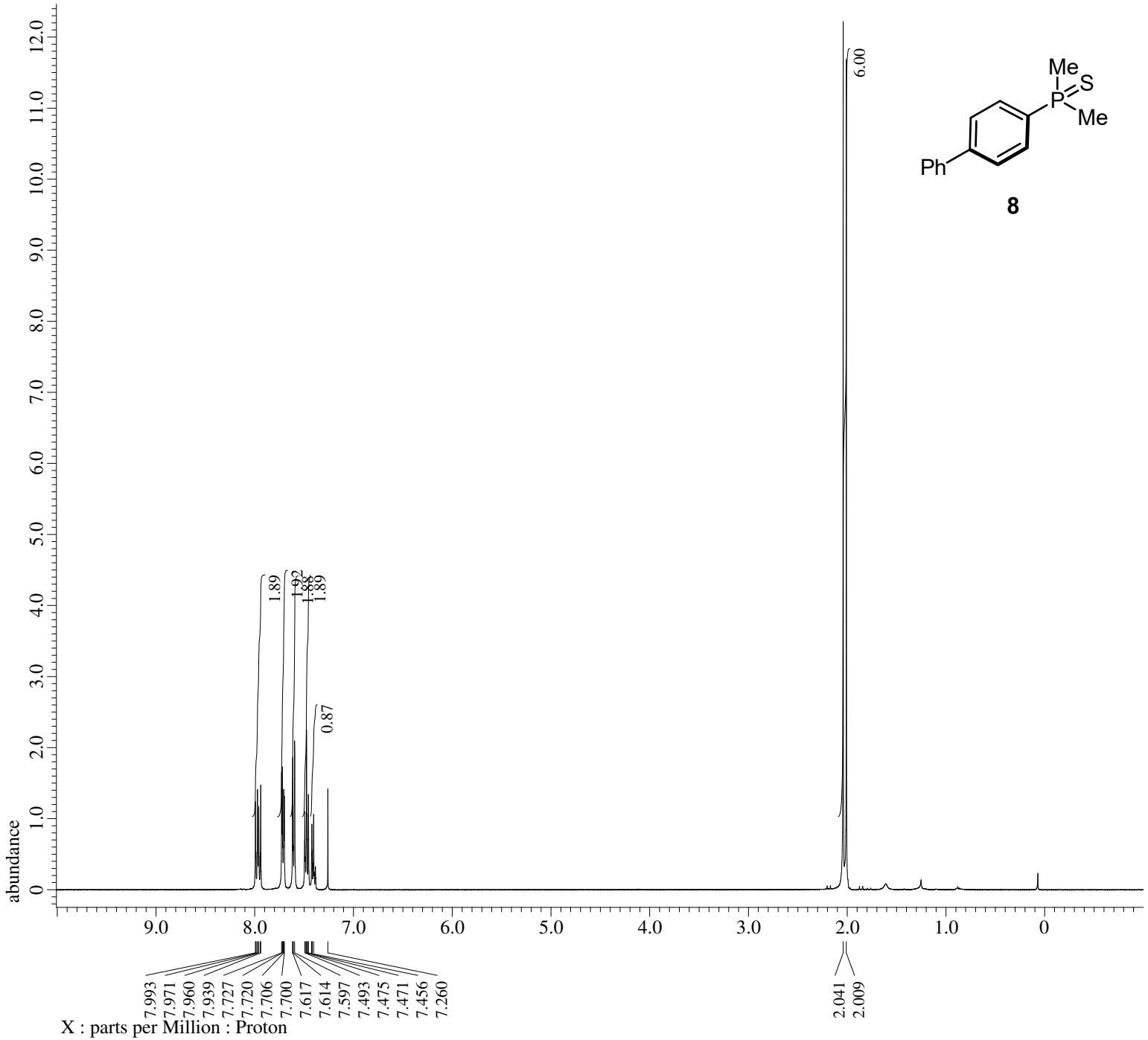
```
Filename           = RS-23-008-2-f17_31P-1-2.j
Author             = delta
Experiment         = single_pulse_dec.jxp
Sample_Id          = RS-23-008-2-f17
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 29-MAR-2023 15:02:01
Revision_Time      = 19-APR-2023 09:11:33

Comment            = RS-23-008-2-f17_31P
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Phosph
Dim_Title          = Phosphorus31
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECS400
Spectrometer       = DELTA2_NMR

Field_Strength     = 9.389766[T] (400[MHz])
X_Acq_Duration     = 0.26738688[s]
X_Domain           = 31P
X_Freq             = 161.83469309[MHz]
X_Offset           = 0[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 3.73989928[Hz]
X_Sweep            = 122.54901961[kHz]
X_Sweep_Clipped    = 98.03921569[kHz]
Irr_Domain         = Proton
Irr_Freq           = 399.78219838[MHz]
Irr_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 256
Total_Scans        = 256

Relaxation_Delay   = 2[s]
Recvr_Gain         = 58
Temp_Get           = 19.7[dC]
X_90_Width         = 14.5[us]
X_Acq_Time         = 0.26738688[s]
X_Angle            = 30[deg]
X_Atn              = 4.1[dB]
X_Pulse            = 4.83333333[us]
Irr_Atn_Dec        = 20.9[dB]
Irr_Atn_Noe        = 20.9[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 0.115[ms]
Decoupling         = TRUE
Initial_Wait       = 1[s]
Noe                = TRUE
Noe_Time           = 2[s]
Repetition_Time    = 2.26738688[s]
```

^{31}P NMR Spectrum of **7** ($CDCl_3$)



8

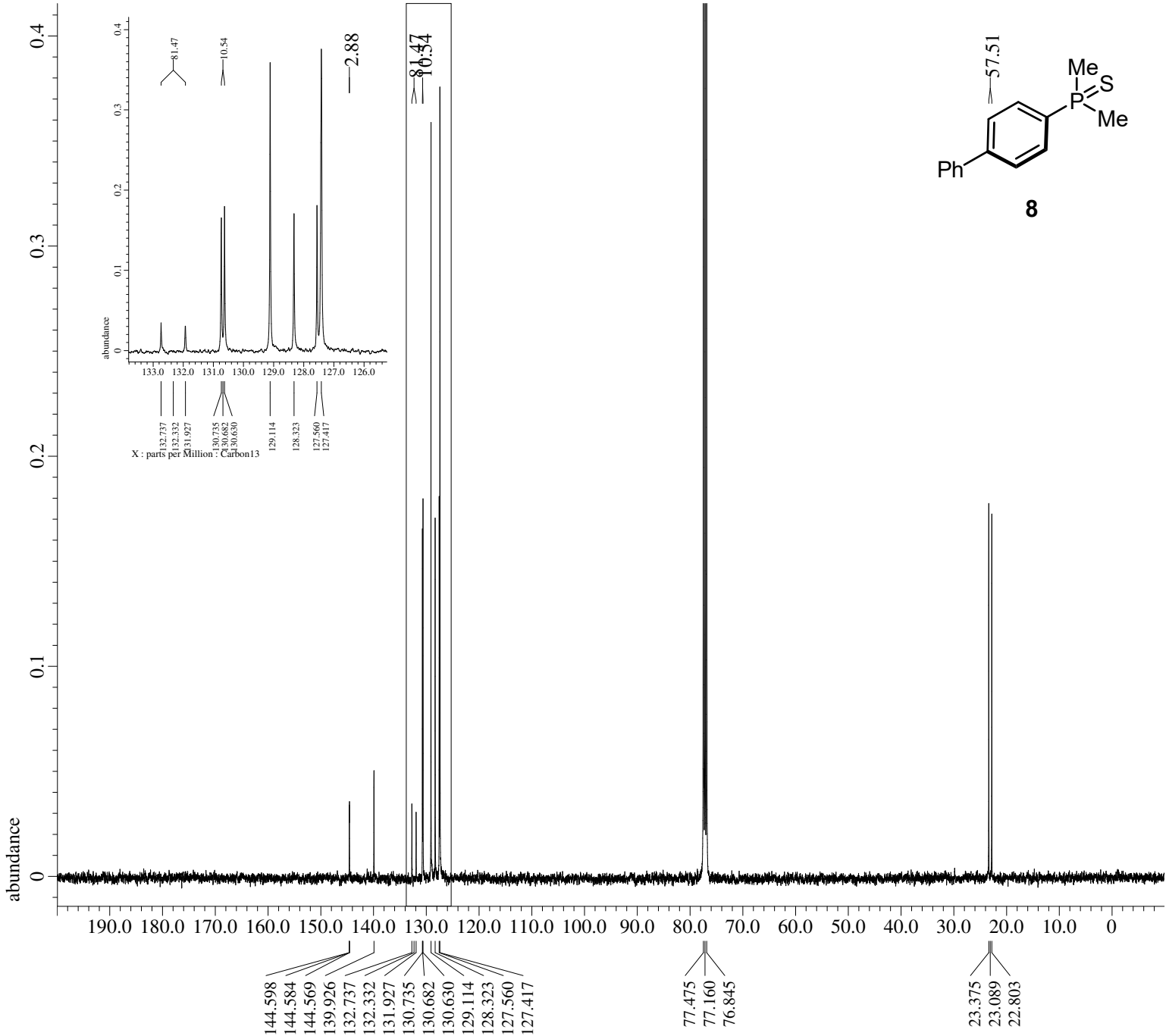
```
Filename           = RS-23-009-2_Proton-1-2.jd
Author             = delta
Experiment         = proton.jxp
Sample_Id          = RS-23-009-2
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 18-APR-2023 19:53:54
Revision_Time      = 19-APR-2023 09:13:44

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 13107
X_Domain           = Proton
Dim_Title          = Proton
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECS400
Spectrometer       = DELTA2_NMR

Field_Strength     = 9.389766[T] (400[MHz])
X_Acq_Duration     = 2.18365952[s]
X_Domain           = 1H
X_Freq             = 399.78219838[MHz]
X_Offset           = 5[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.45794685[Hz]
X_Sweep            = 7.5030012[kHz]
X_Sweep_Clipped    = 6.00240096[kHz]
Irr_Domain         = Proton
Irr_Freq           = 399.78219838[MHz]
Irr_Offset         = 5[ppm]
Tri_Domain         = Proton
Tri_Freq           = 399.78219838[MHz]
Tri_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 8
Total_Scans        = 8

Relaxation_Delay   = 2[s]
Recvr_Gain         = 42
Temp_Get           = 20.1[dC]
X_90_Width         = 11.9[us]
X_Acq_Time         = 2.18365952[s]
X_Angle            = 45[deg]
X_Atn              = 1.2[dB]
X_Pulse            = 5.95[us]
Irr_Mode           = Off
Tri_Mode           = Off
Dante_Presat       = FALSE
Initial_Wait       = 1[s]
Repetition_Time    = 4.18365952[s]
```

^{1}H NMR Spectrum of **8** ($CDCl_3$)



8

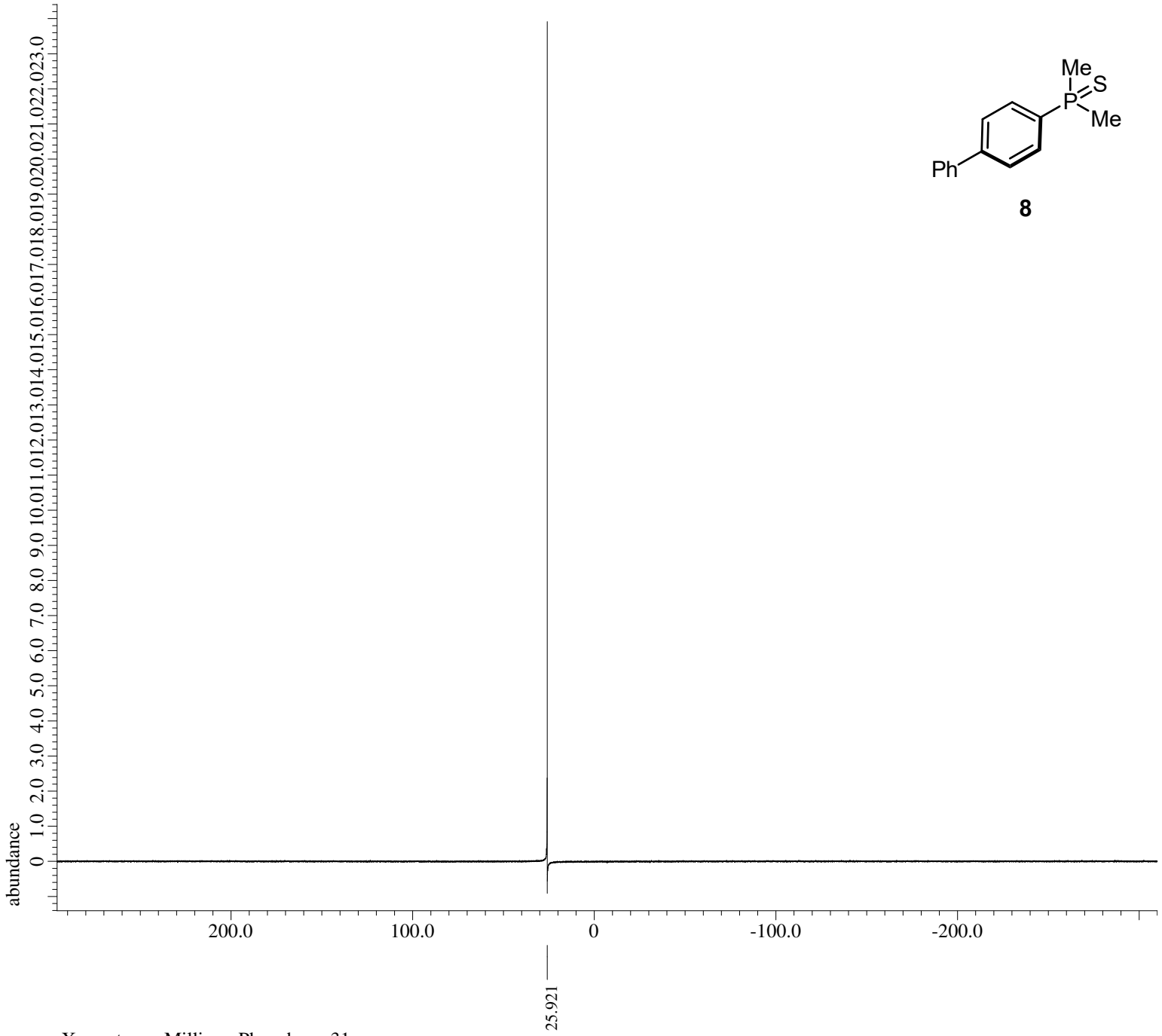
```
Filename            = RS-23-009-2_13C-1-3.jdf
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = RS-23-009-2
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 19-APR-2023 00:07:19
Revision_Time       = 19-APR-2023 09:37:43

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.04333312[s]
X_Domain            = 13C
X_Freq              = 100.52530333[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 0.95846665[Hz]
X_Sweep             = 31.40703518[kHz]
X_Sweep_Clipped     = 25.12562814[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 2048
Total_Scans         = 2048

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 20.4[dC]
X_90_Width          = 9.73[us]
X_Acq_Time          = 1.04333312[s]
X_Angle             = 30[deg]
X_Atn               = 5.1[dB]
X_Pulse             = 3.24333333[us]
Irr_Atn_Dec         = 20.9[dB]
Irr_Atn_Noe         = 20.9[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 0.115[ms]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 3.04333312[s]
```

^{13}C NMR Spectrum of **8** ($CDCl_3$)



8

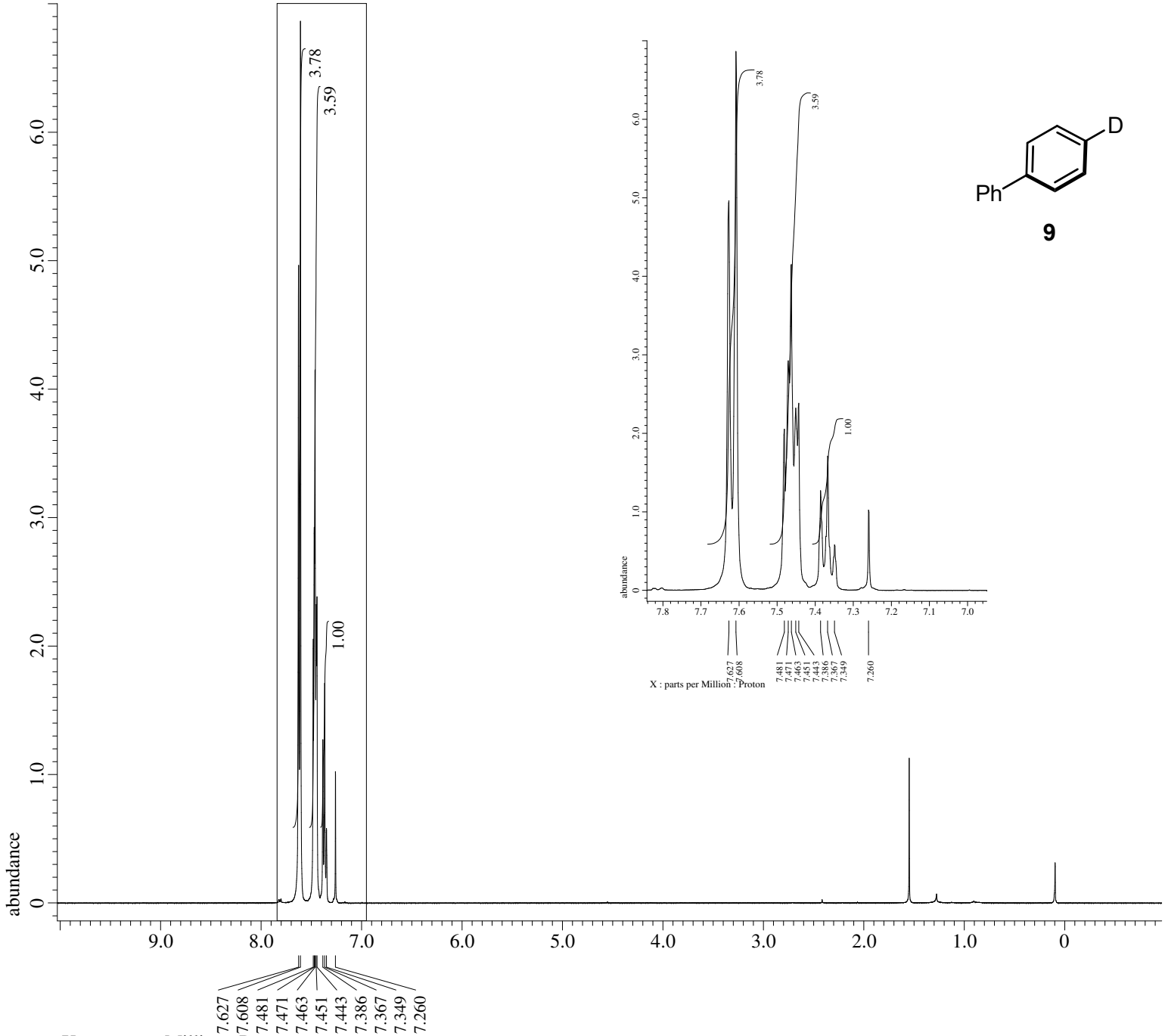
```
Filename           = RS-23-008-f23-26_31P-1-2.
Author             = delta
Experiment         = single_pulse_dec.jxp
Sample_Id          = RS-23-008-f23-26
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 29-MAR-2023 14:45:27
Revision_Time      = 19-APR-2023 09:42:45

Comment            = RS-23-008-f23-26_31P
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Phosph
Dim_Title          = Phosphorus31
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECS400
Spectrometer       = DELTA2_NMR

Field_Strength     = 9.389766[T] (400[MHz])
X_Acq_Duration     = 0.26738688[s]
X_Domain           = 31P
X_Freq             = 161.83469309[MHz]
X_Offset           = 0[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 3.73989928[Hz]
X_Sweep            = 122.54901961[kHz]
X_Sweep_Clipped    = 98.03921569[kHz]
Irr_Domain         = Proton
Irr_Freq           = 399.78219838[MHz]
Irr_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 256
Total_Scans        = 256

Relaxation_Delay   = 2[s]
Recvr_Gain         = 56
Temp_Get           = 19.6[dC]
X_90_Width         = 14.5[us]
X_Acq_Time         = 0.26738688[s]
X_Angle            = 30[deg]
X_Atn              = 4.1[dB]
X_Pulse            = 4.83333333[us]
Irr_Atn_Dec        = 20.9[dB]
Irr_Atn_Noe        = 20.9[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 0.115[ms]
Decoupling         = TRUE
Initial_Wait       = 1[s]
Noe                = TRUE
Noe_Time           = 2[s]
Repetition_Time    = 2.26738688[s]
```

^{31}P NMR Spectrum of **8** ($CDCl_3$)



9

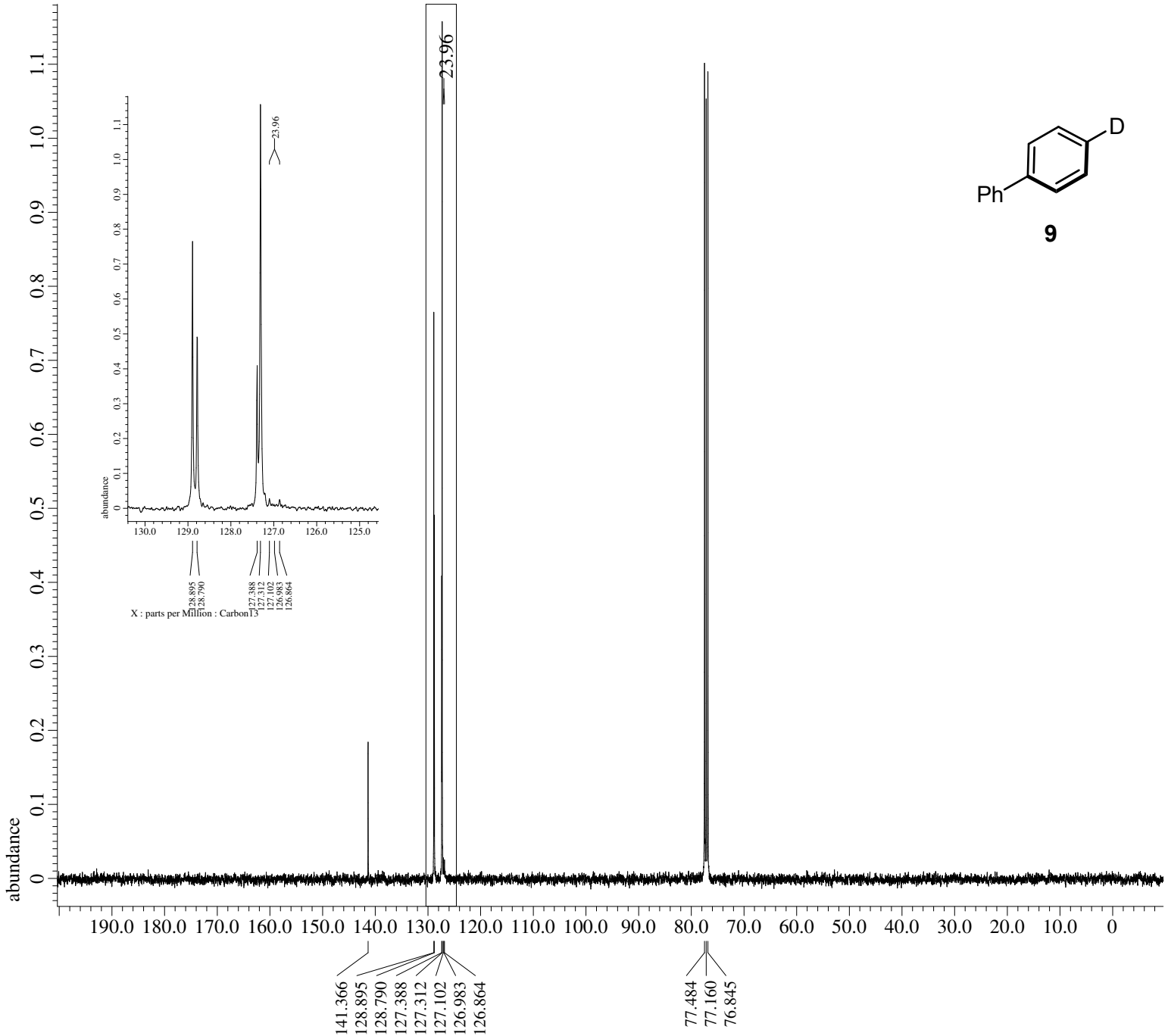
```
Filename          = RS-23-008-f4-6_Proton-1-6
Author            = delta
Experiment        = proton.jxp
Sample_Id         = RS-23-008-f4-6
Solvent           = CHLOROFORM-D
Actual_Start_Time = 29-MAR-2023 10:14:29
Revision_Time     = 19-APR-2023 16:30:42

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 2.18365952[s]
X_Domain          = 1H
X_Freq            = 399.78219838[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.45794685[Hz]
X_Sweep           = 7.5030012[kHz]
X_Sweep_Clipped   = 6.00240096[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 399.78219838[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 2[s]
Recvr_Gain        = 40
Temp_Get          = 18.9[dC]
X_90_Width        = 11.9[us]
X_Acq_Time        = 2.18365952[s]
X_Angle           = 45[deg]
X_Atn             = 1.2[dB]
X_Pulse           = 5.95[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 4.18365952[s]
```

^{1}H NMR Spectrum of **9** ($CDCl_3$)



X : parts per Million : Carbon13

9

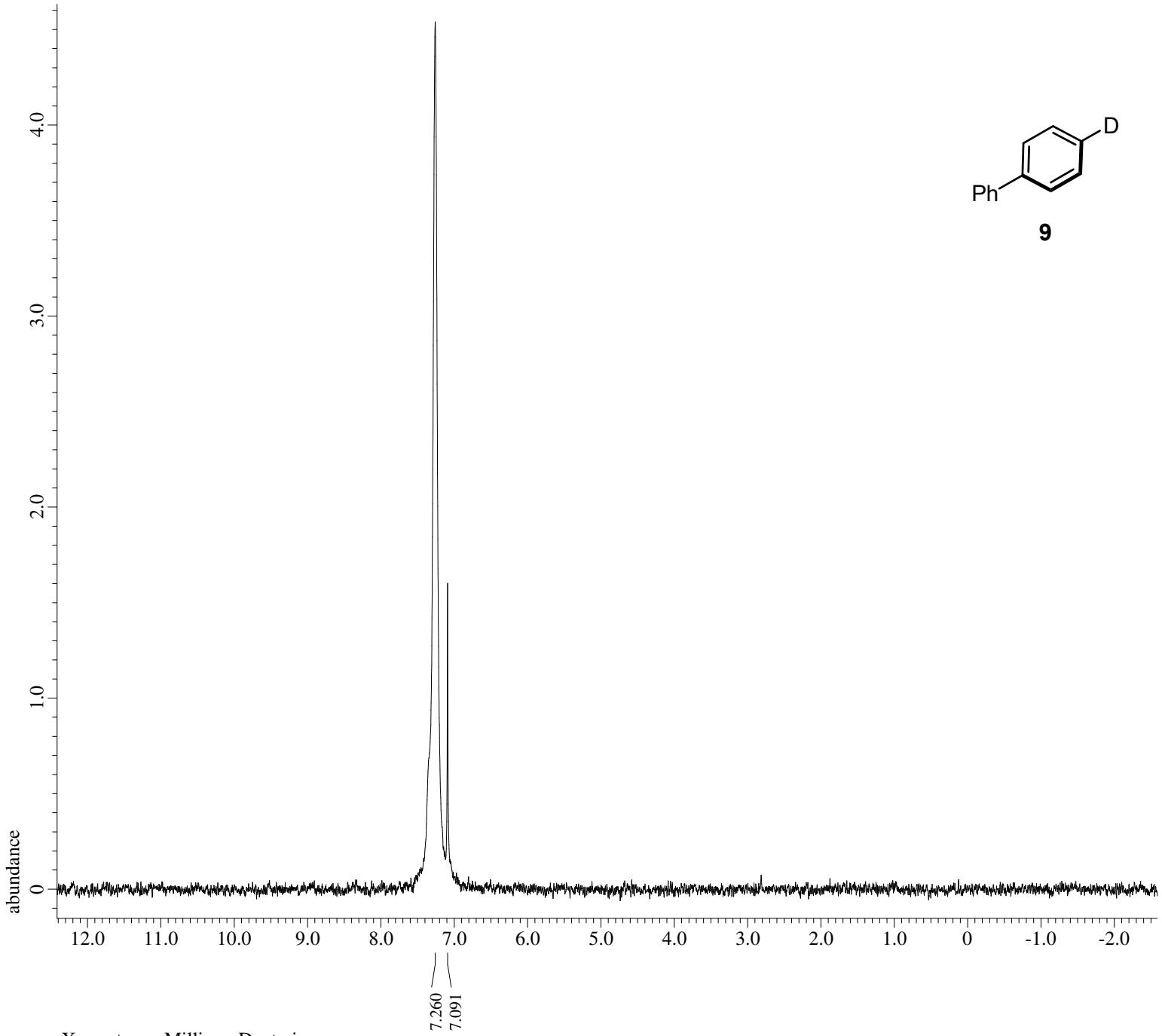
```
Filename          = RS-23-008-f4-6_Carbon-1-2
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = RS-23-008-f4-6
Solvent           = CHLOROFORM-D
Actual_Start_Time = 29-MAR-2023 11:04:54
Revision_Time     =  8-APR-2023 12:15:34

Comment           = RS-23-008-f4-6
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 1.04333312[s]
X_Domain          = 13C
X_Freq            = 100.52530333[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.95846665[Hz]
X_Sweep           = 31.40703518[kHz]
X_Sweep_Clipped   = 25.12562814[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Clipped           = TRUE
Scans             = 256
Total_Scans       = 256

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 19.4[dC]
X_90_Width        = 9.73[us]
X_Acq_Time        = 1.04333312[s]
X_Angle           = 30[deg]
X_Atn             = 5.1[dB]
X_Pulse           = 3.24333333[us]
Irr_Atn_Dec       = 20.9[dB]
Irr_Atn_Noe       = 20.9[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 0.115[ms]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.04333312[s]
```

^{13}C NMR Spectrum of **9** ($CDCl_3$)



9

```
Filename          = RS-23-009-1_single_pulse-
Author            = delta
Experiment        = single_pulse.jxp
Sample_Id         = RS-23-009-1
Solvent           = NONE
Actual_Start_Time = 19-APR-2023 18:04:45
Revision_Time     = 19-APR-2023 18:04:55

Comment           = RS-23-009-1_2D
Data_Format       = 1D COMPLEX
Dim_Size          = 6554
X_Domain          = Deuter
Dim_Title         = Deuterium
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 7.11852032[s]
X_Domain          = 2H
X_Freq            = 61.36899787[MHz]
X_Offset          = 5[ppm]
X_Points          = 8192
X_Prescans        = 1
X_Resolution      = 0.14047863[Hz]
X_Sweep           = 1.15080096[kHz]
X_Sweep_Clipped   = 920.64076597[Hz]
Irr_Domain        = Deuterium
Irr_Freq          = 61.36899787[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Deuterium
Tri_Freq          = 61.36899787[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 0.2[s]
Recvr_Gain        = 66
Temp_Get          = 20.4[dC]
X_90_Width        = 12.4[us]
X_Acq_Time        = 7.11852032[s]
X_Angle           = 45[deg]
X_Atn             = 3.9[dB]
X_Pulse           = 6.2[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 7.31852032[s]
```

^{2}H NMR Spectrum of **9** ($CDCl_3$)