

SUPPORTING INFORMATION

Transformations of diphenylphosphinothioic acid tertiary amides mediated by the directed ortho metallation

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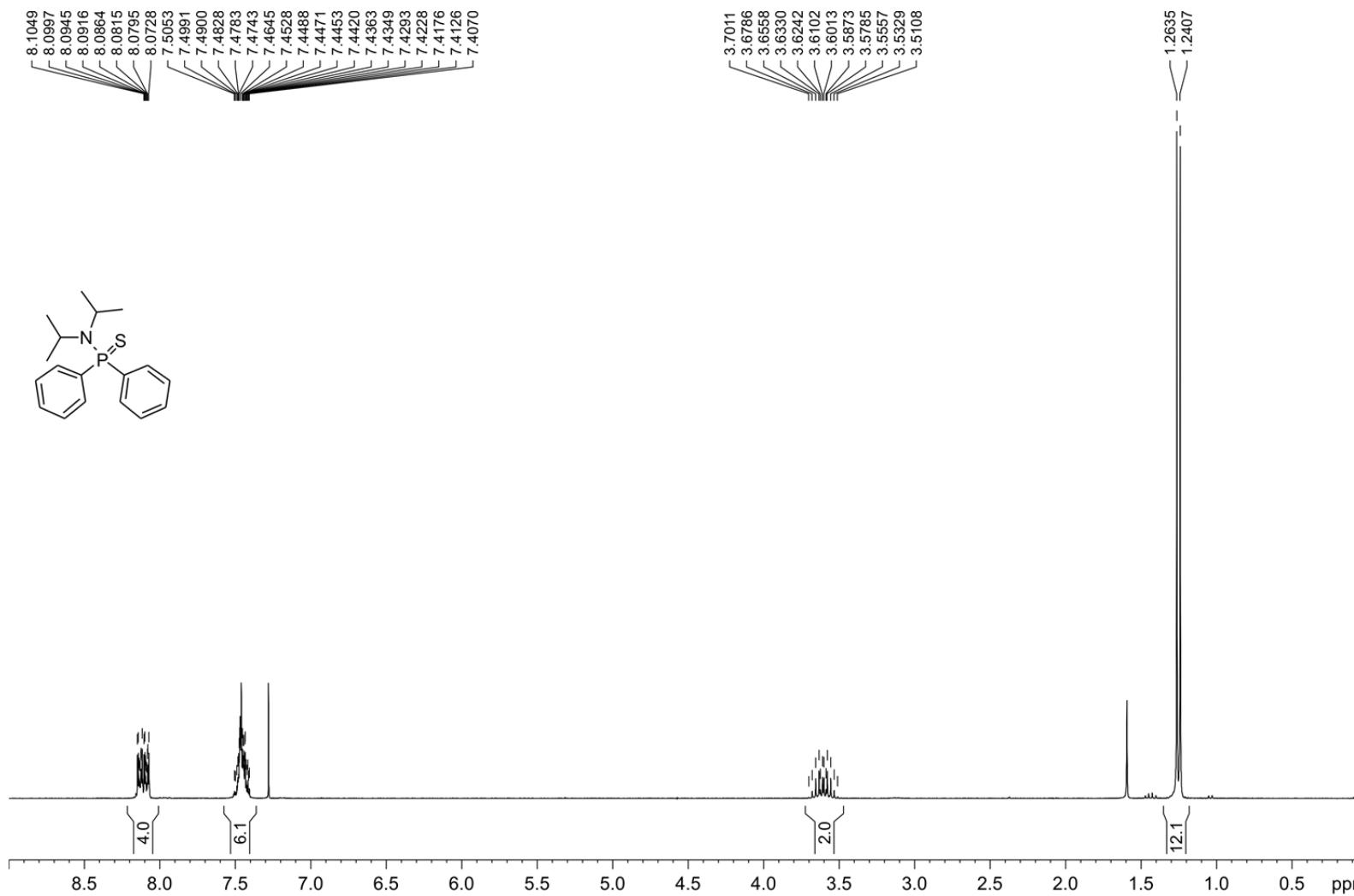


Figure S1. ^1H NMR spectrum (300.13 MHz) of **7** in CDCl_3 .

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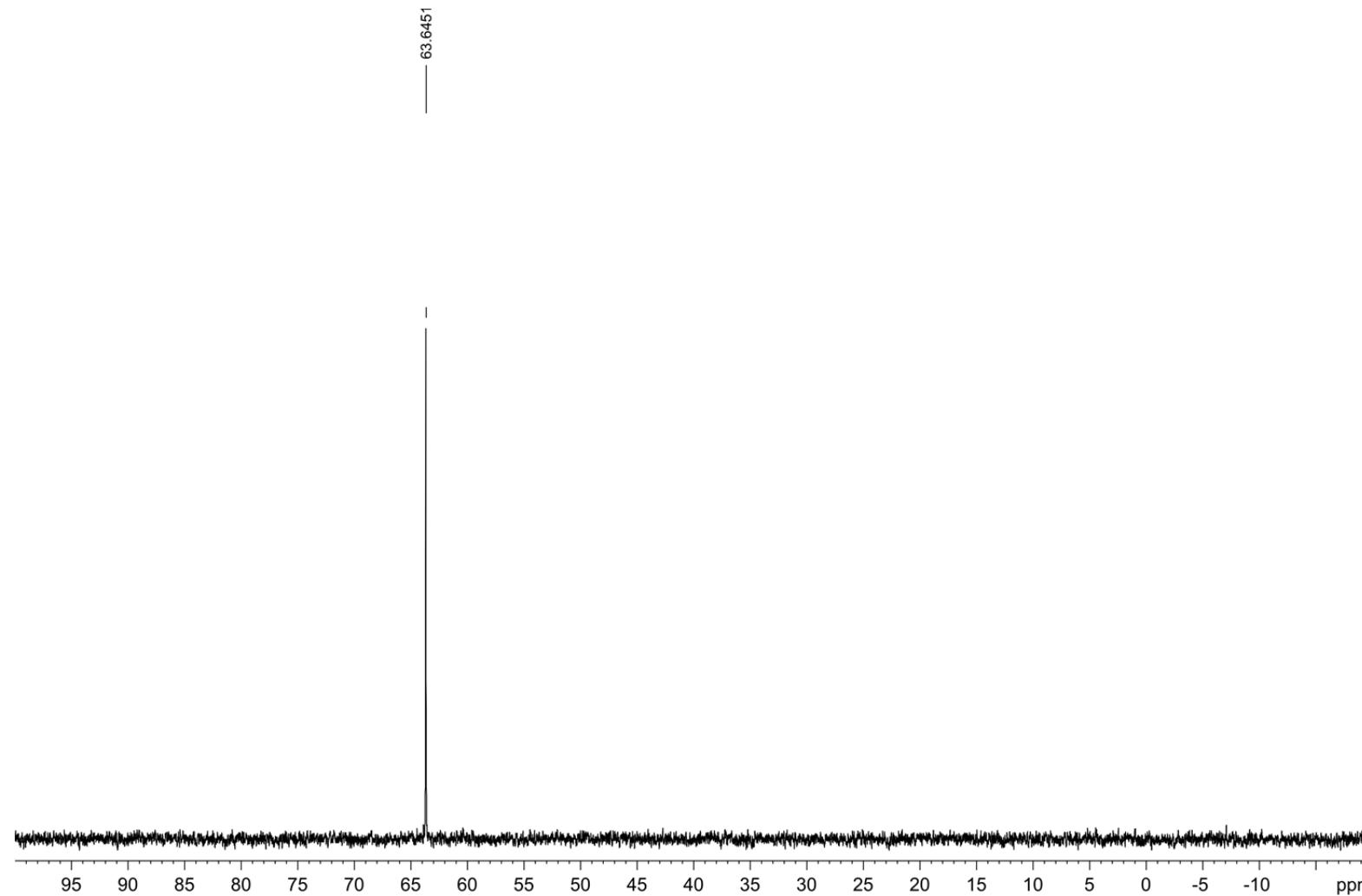


Figure S2. ^{31}P NMR spectrum (121.47 MHz) of **7** in CDCl_3 .

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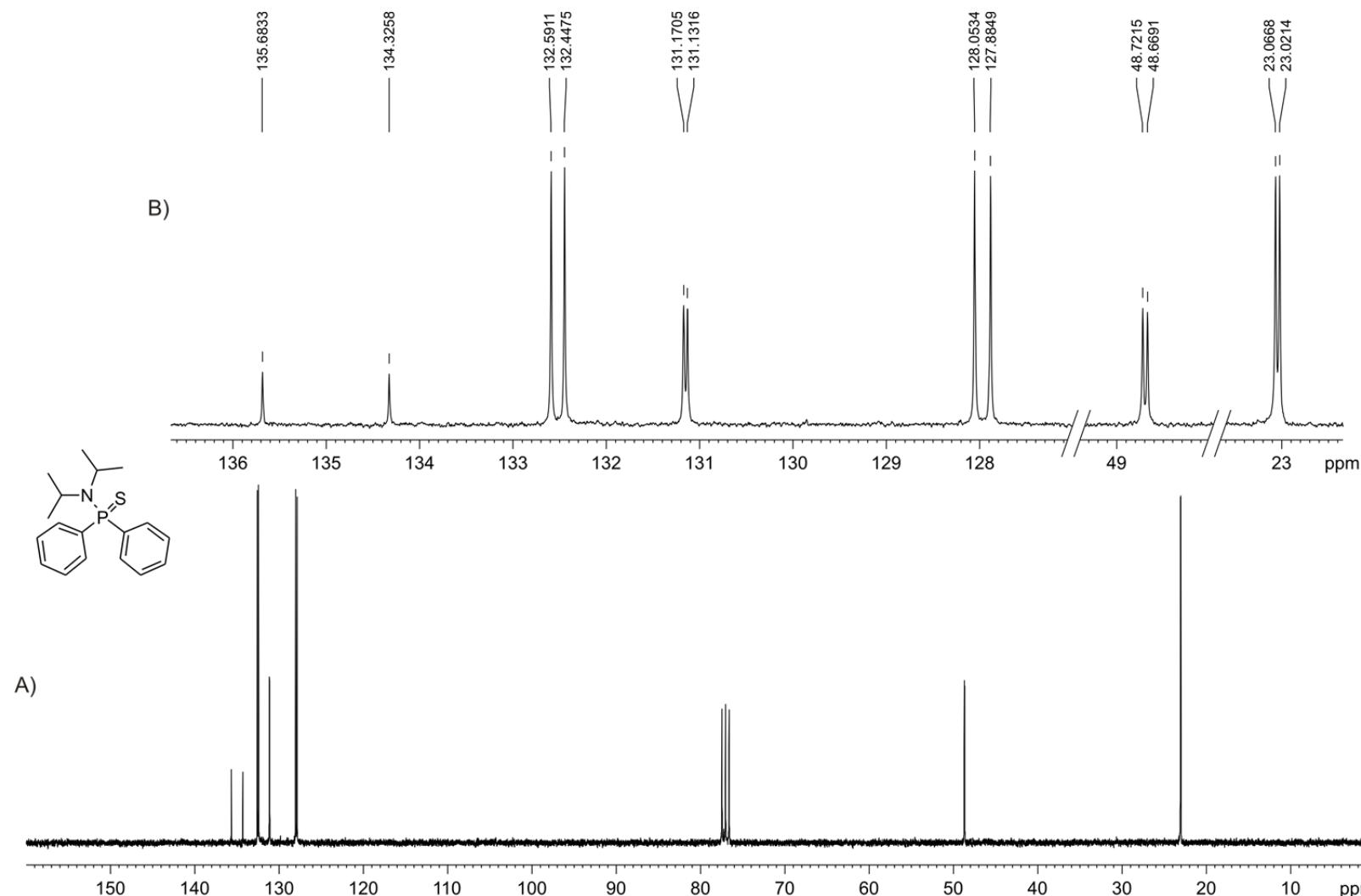


Figure S3. A) ^{13}C NMR spectrum (75.47 MHz) of **7** in CDCl_3 . B) Expansion of A).

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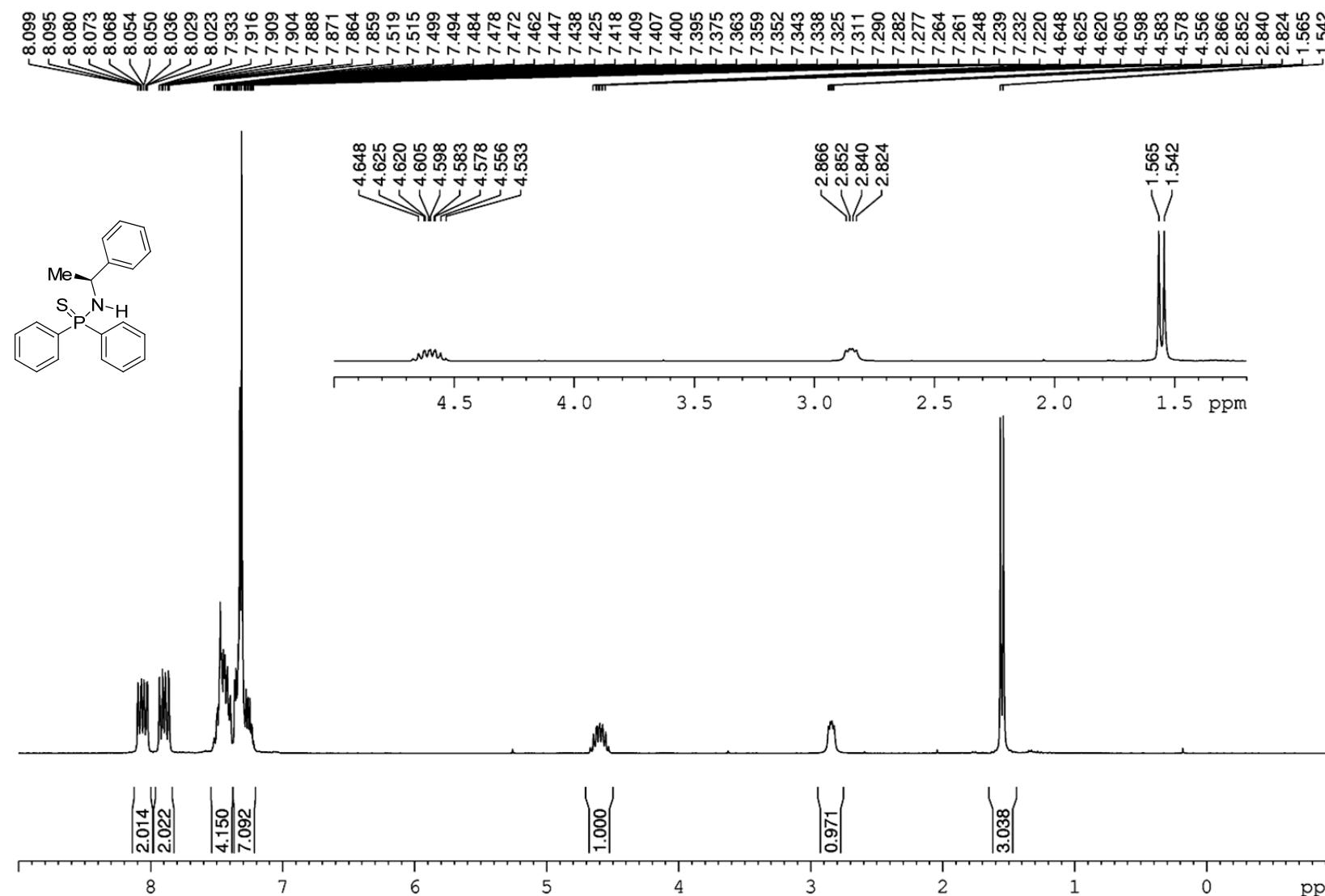


Figure S4. ^1H NMR spectrum (300.13 MHz) of **23** in CDCl_3 .

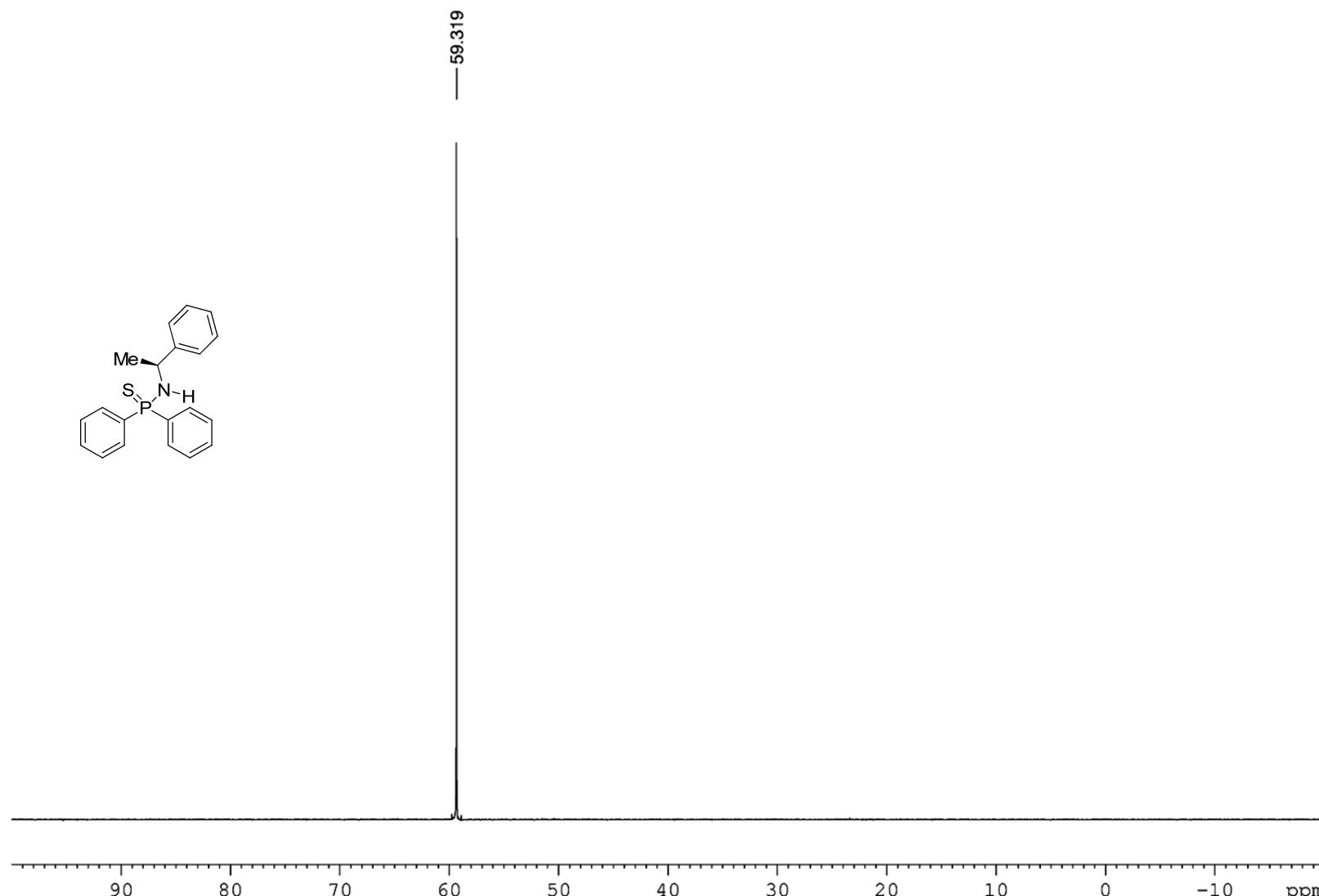


Figure S5. ^{31}P NMR spectrum (121.47 MHz) of **23** in CDCl_3 .

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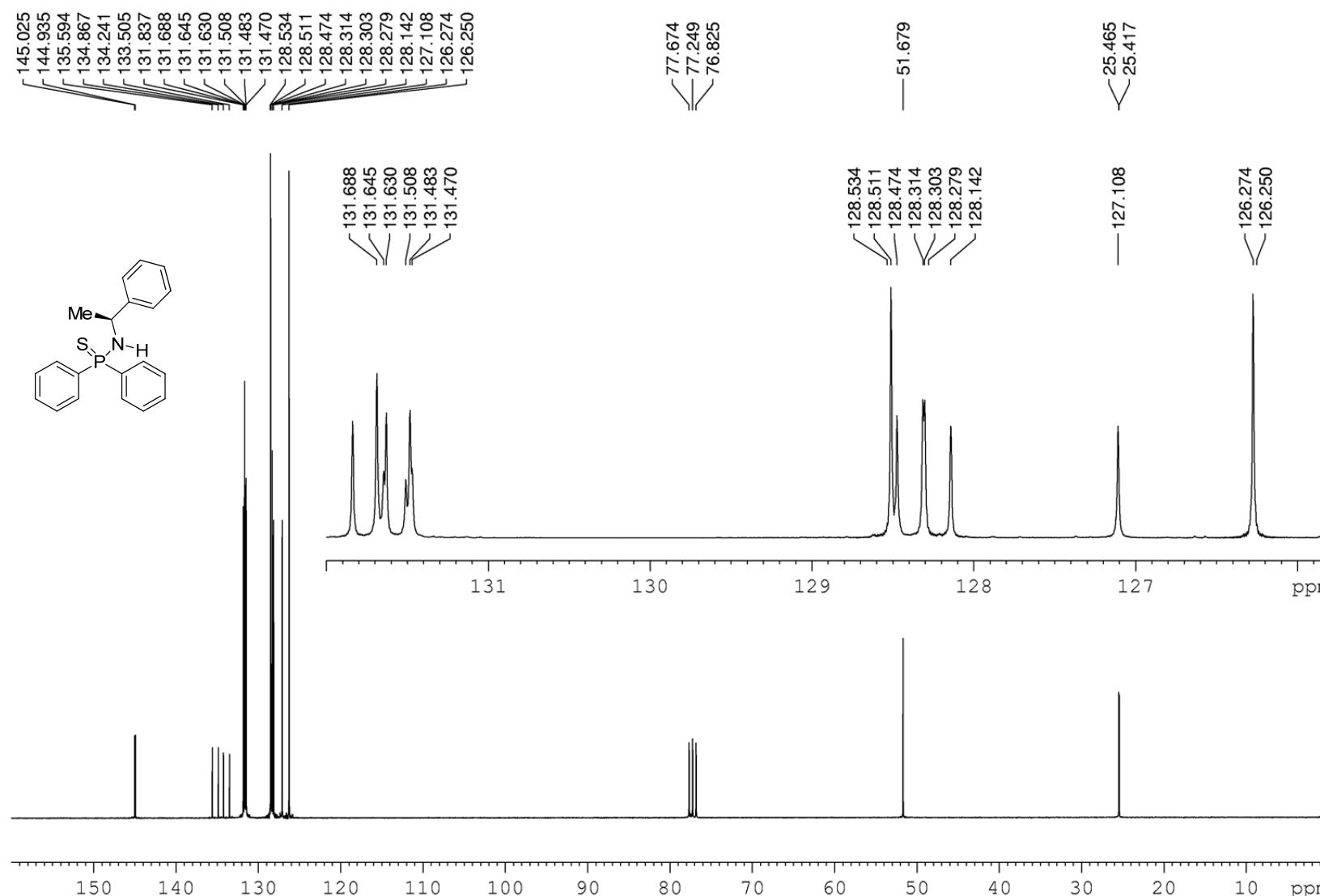


Figure S6. ^{13}C NMR spectrum (75.47 MHz) of **23** in CDCl_3 .

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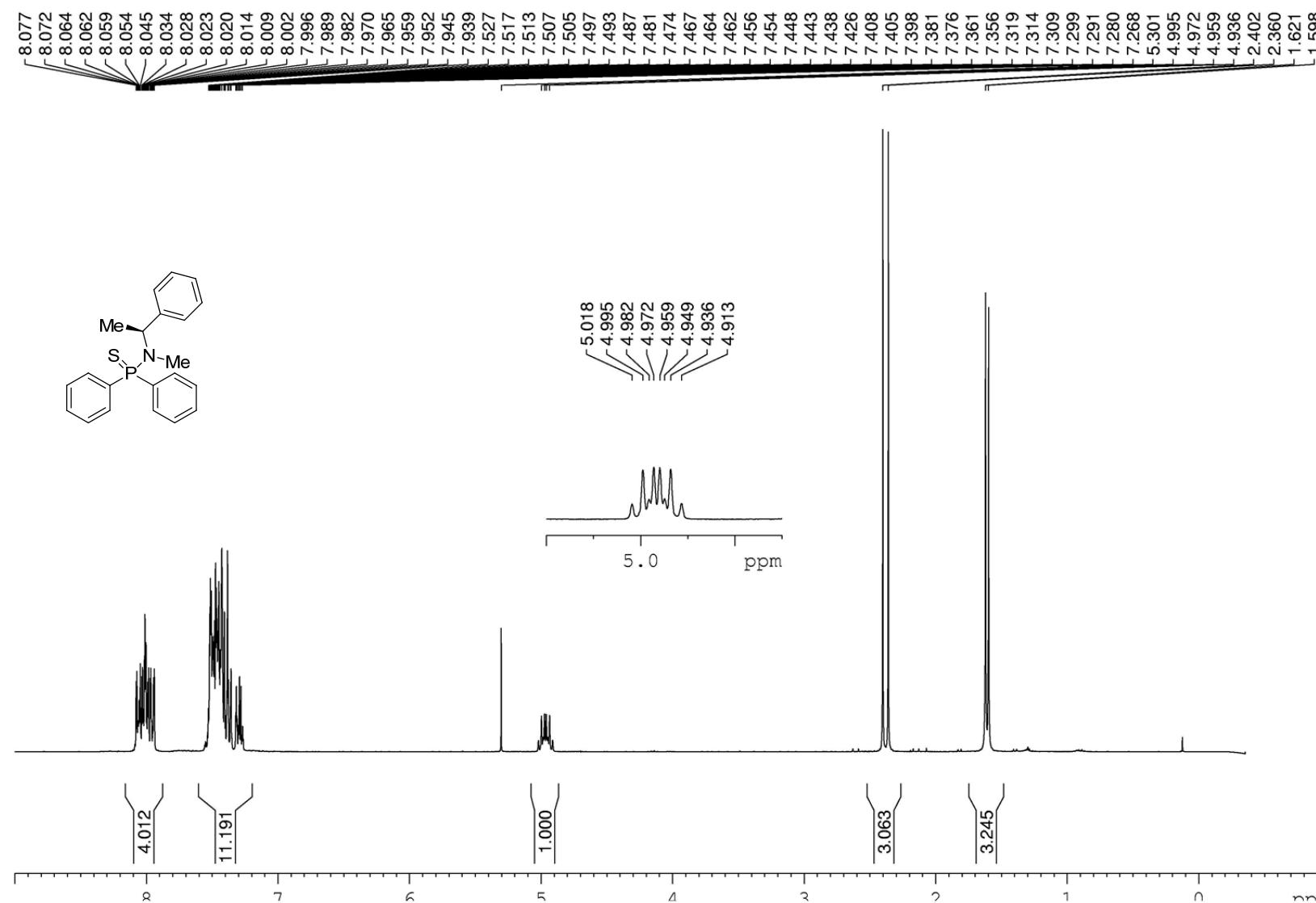


Figure S7. ^1H NMR spectrum (300.13 MHz) of **24** in CDCl_3 .

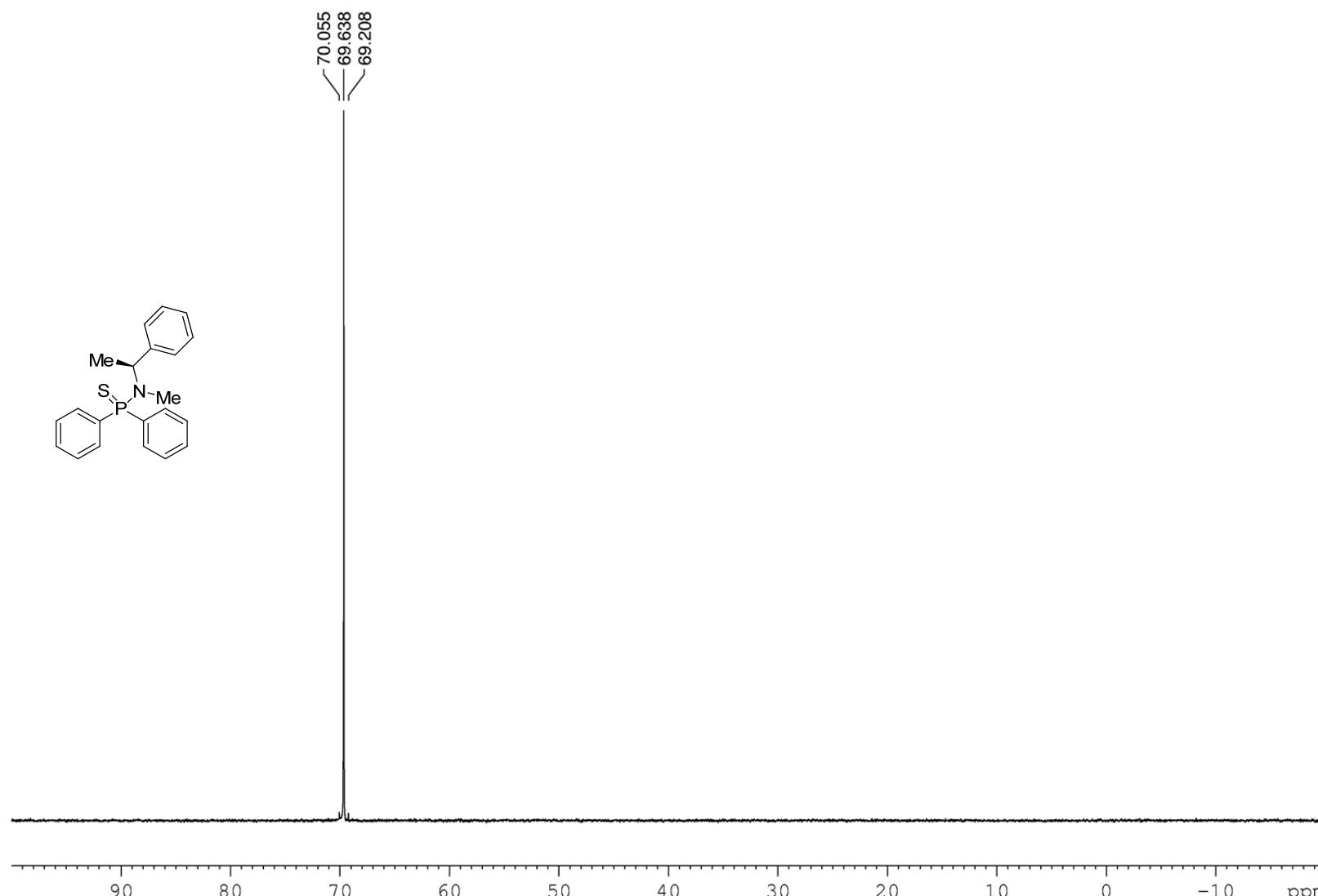


Figure S8. ^{31}P NMR spectrum (121.47 MHz) of **24** in CDCl_3 .

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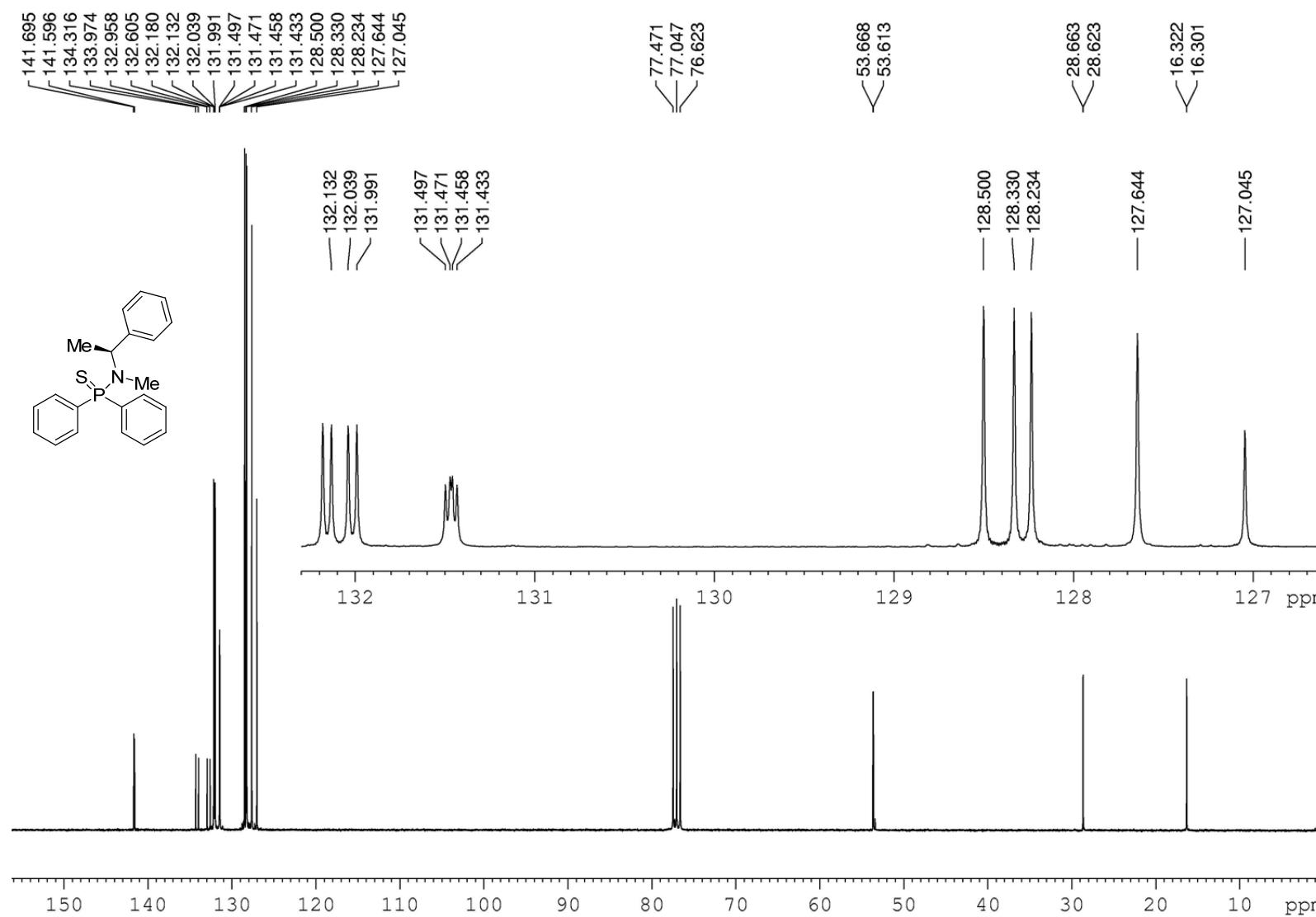


Figure S9. ^{13}C NMR spectrum (75.47 MHz) of **24** in CDCl_3 .

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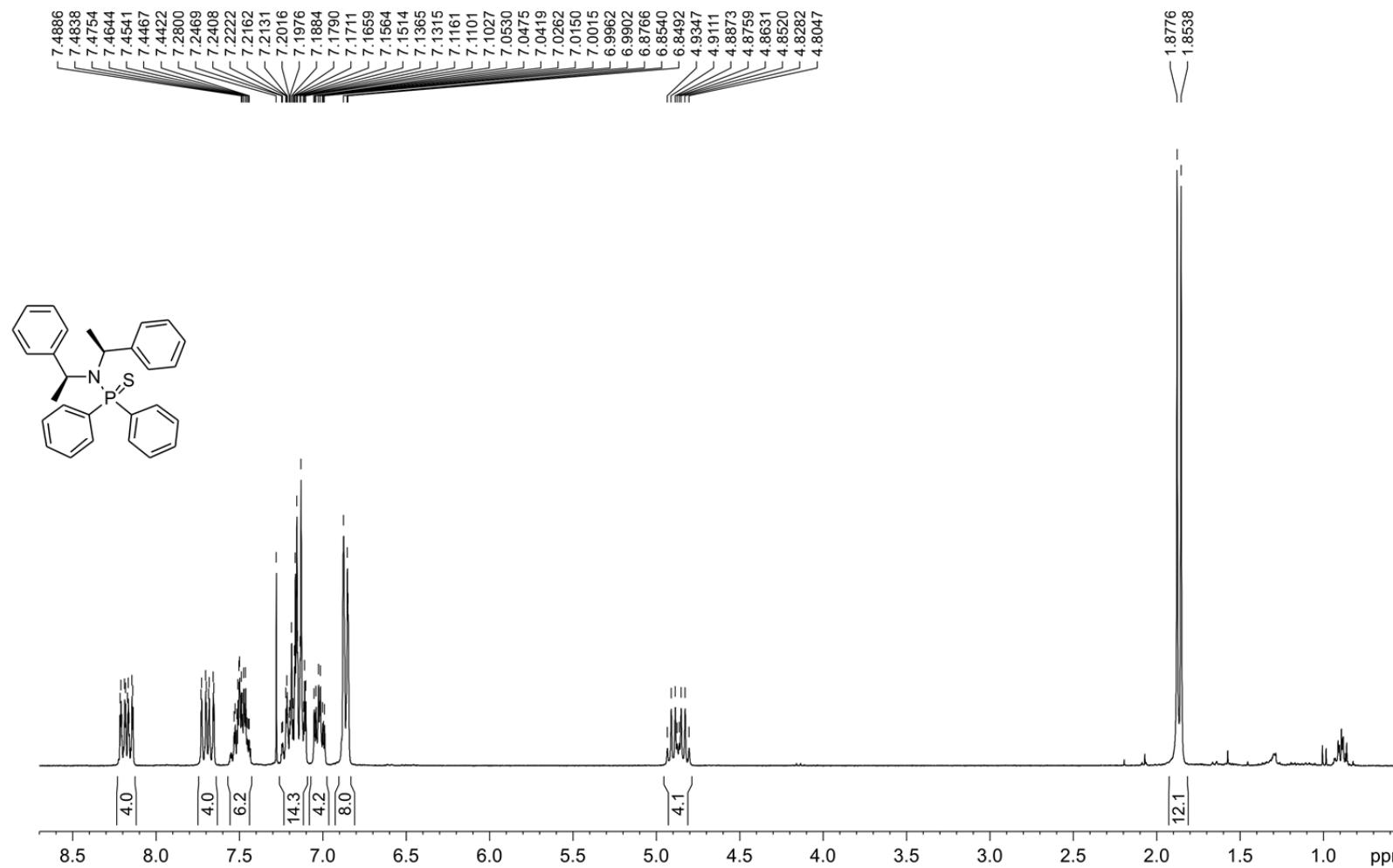


Figure S10. ^1H NMR spectrum (300.13 MHz) of **26** in CDCl_3 .

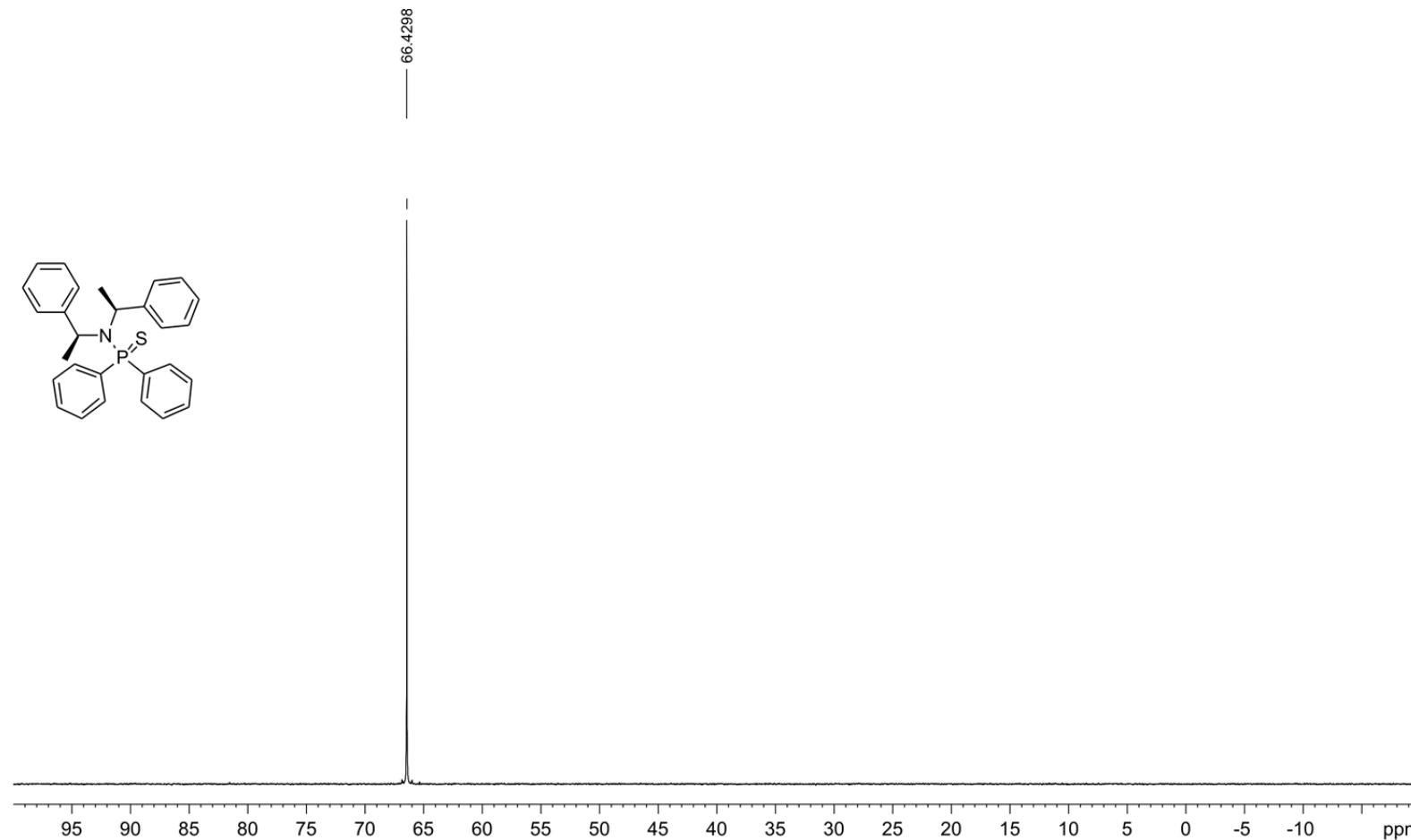


Figure S11. ^{31}P NMR spectrum (121.47 MHz) of **26** in CDCl_3 .

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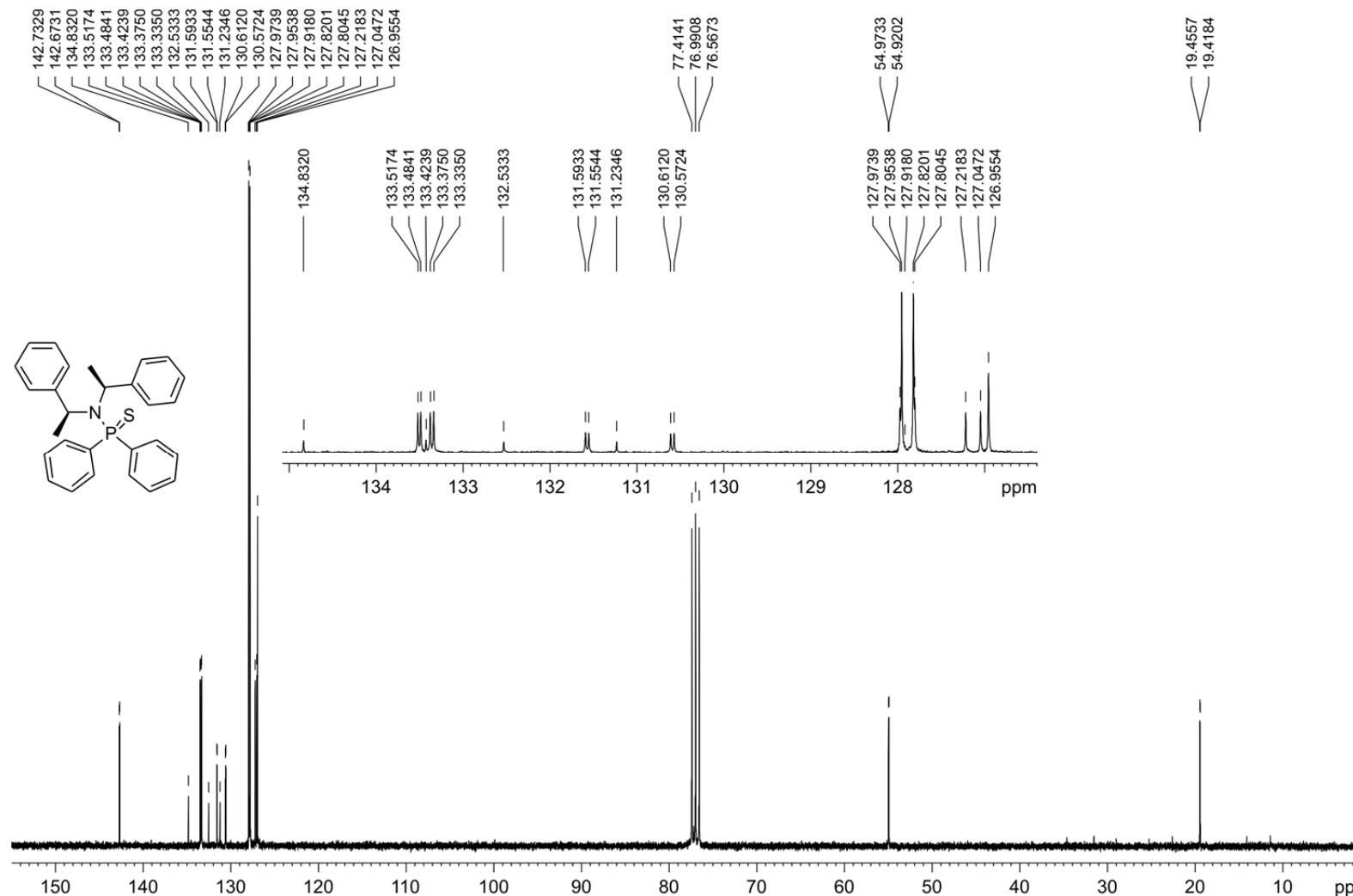


Figure S12. ^{13}C NMR spectrum (75.47 MHz) of **26** in CDCl_3 .

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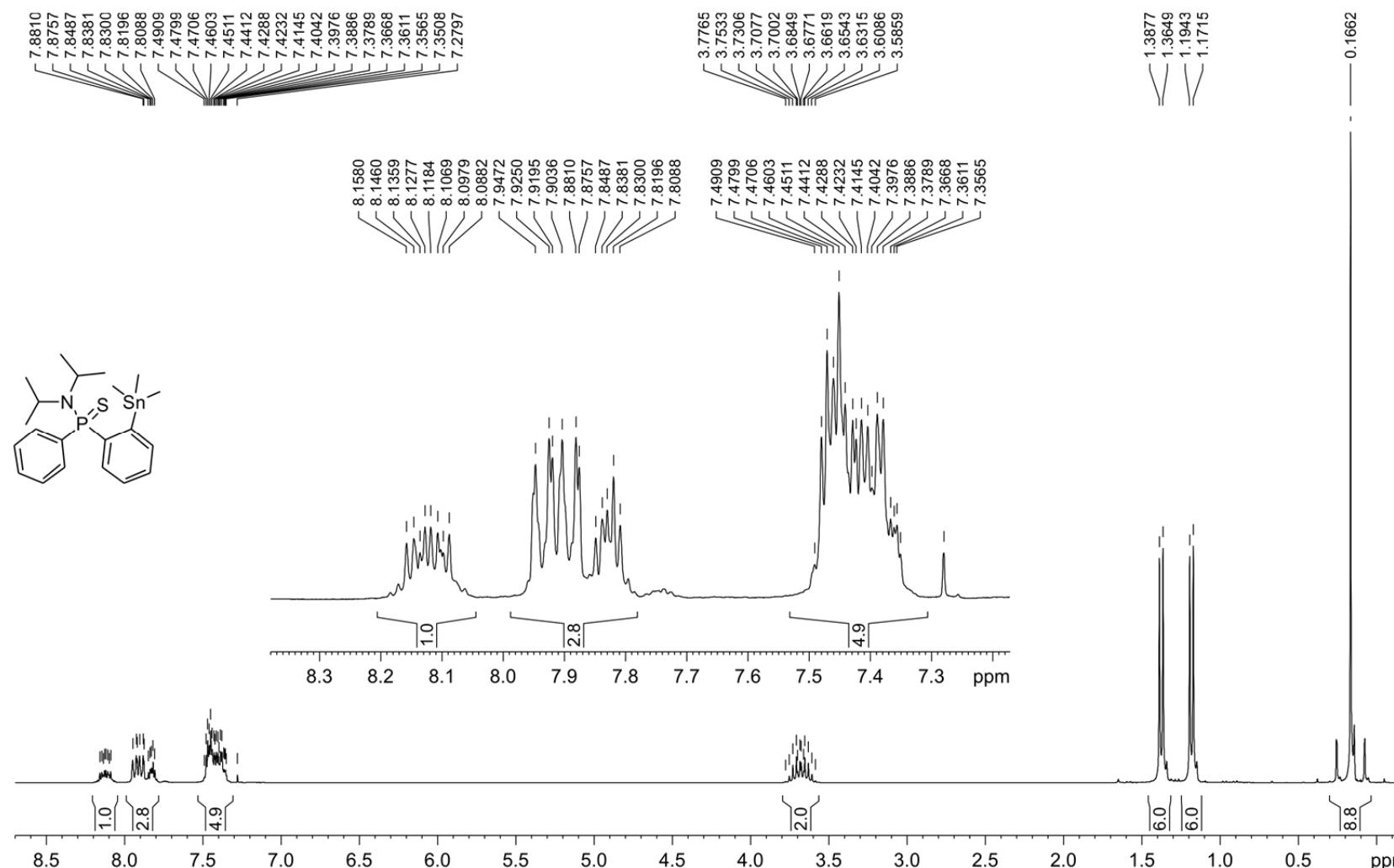


Figure S13. ^1H NMR spectrum (300.13 MHz) of **9** in CDCl_3 .

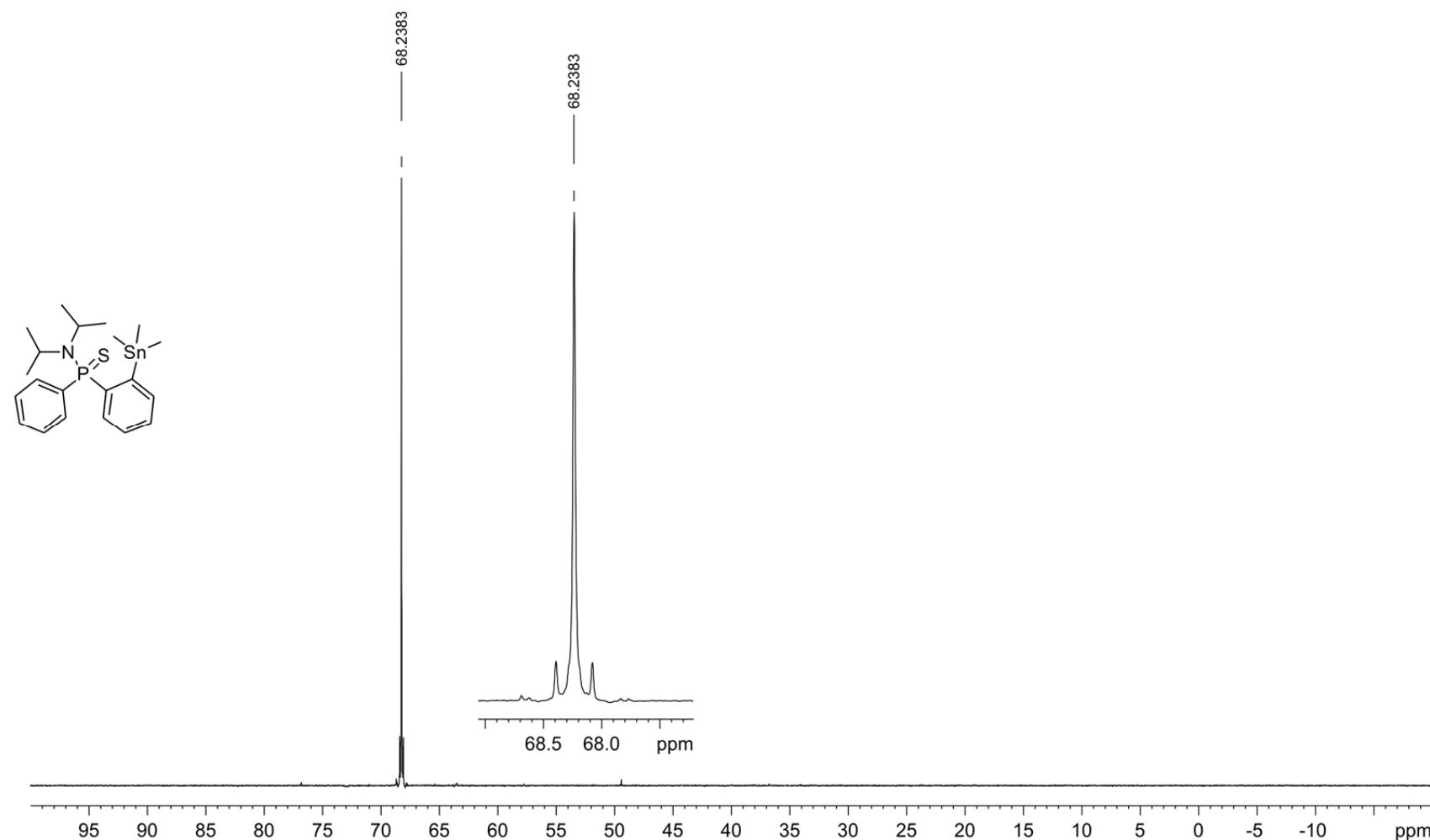


Figure S14. ^{31}P NMR spectrum (121.47 MHz) of **9** in CDCl_3 .

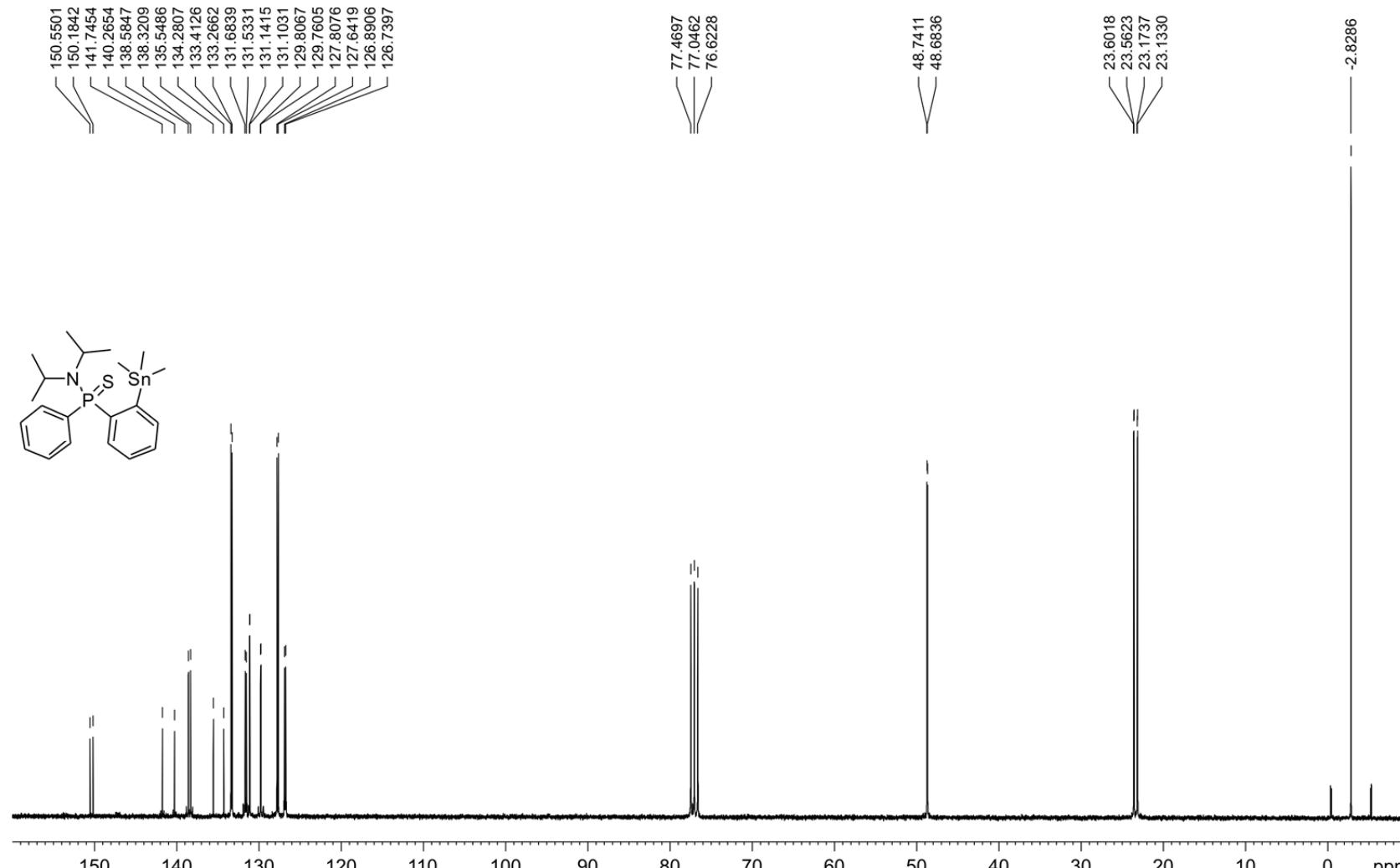


Figure S15. ^{13}C NMR spectrum (75.47 MHz) of **9** in CDCl_3 .

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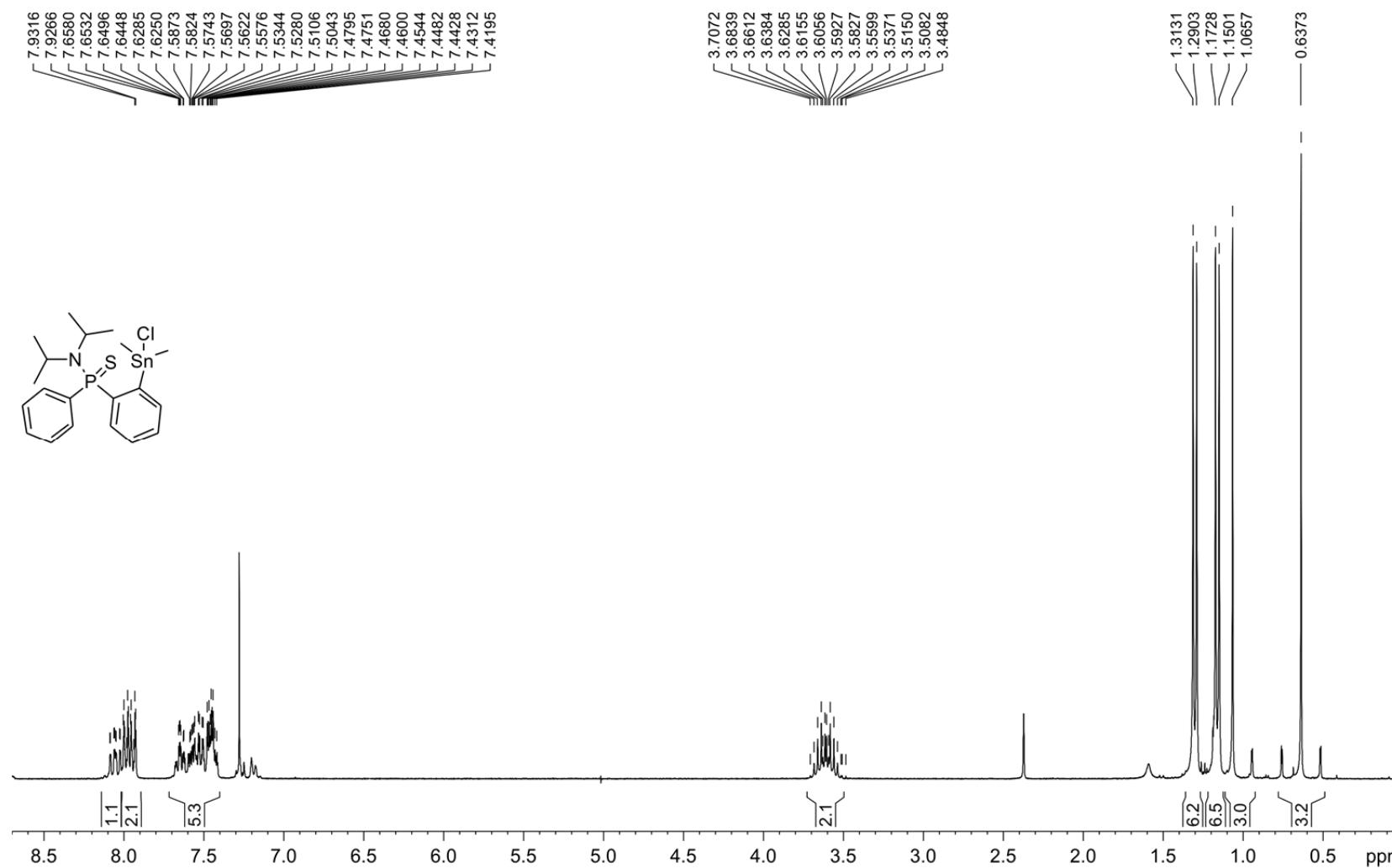


Figure S16. ¹H NMR spectrum (300.13 MHz) of **10** in CDCl_3 .

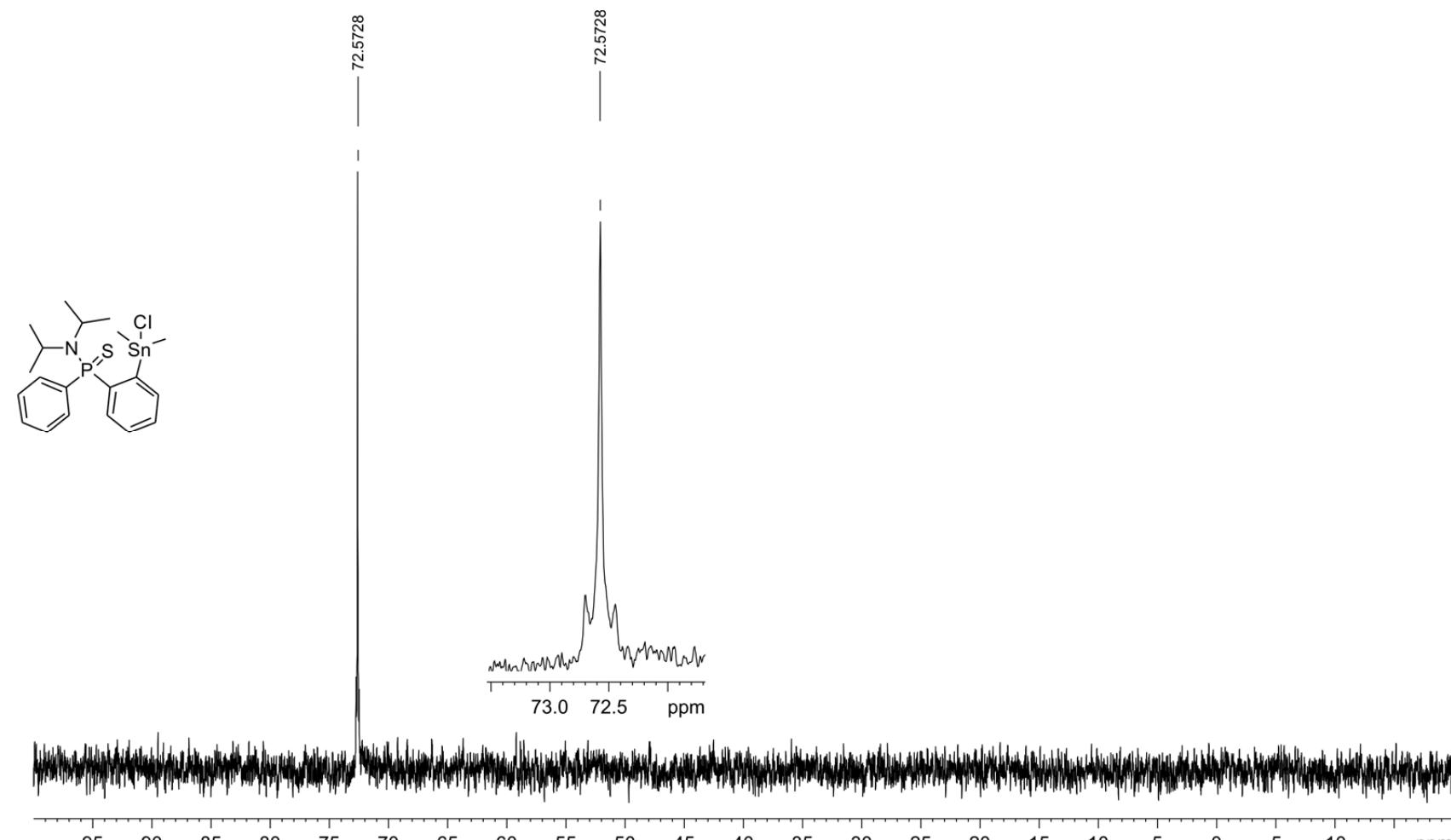


Figure S17. ^{31}P NMR spectrum (121.47 MHz) of **10** in CDCl_3 .

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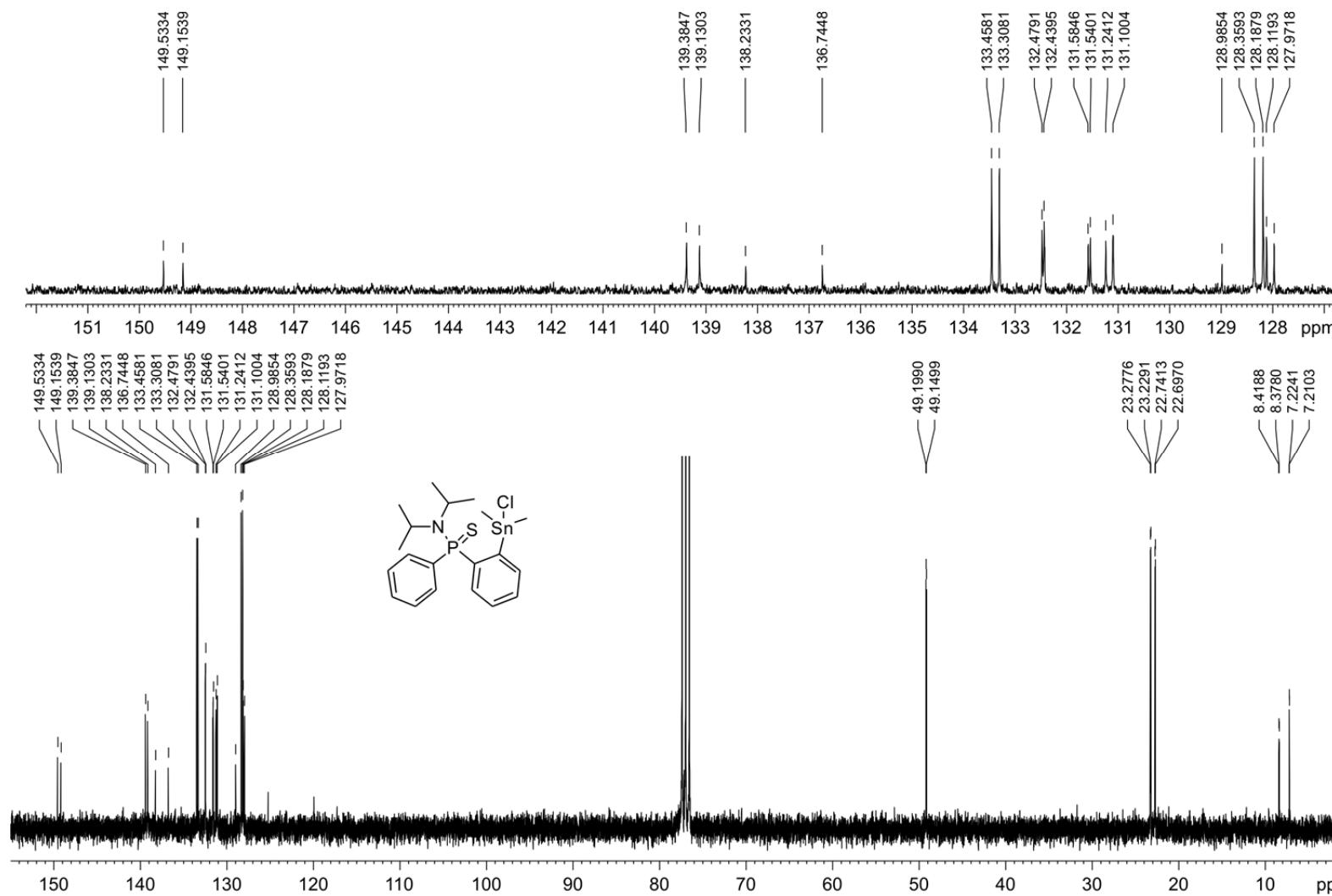


Figure S18. ^{13}C NMR spectrum (75.47 MHz) of **10** in CDCl_3 .

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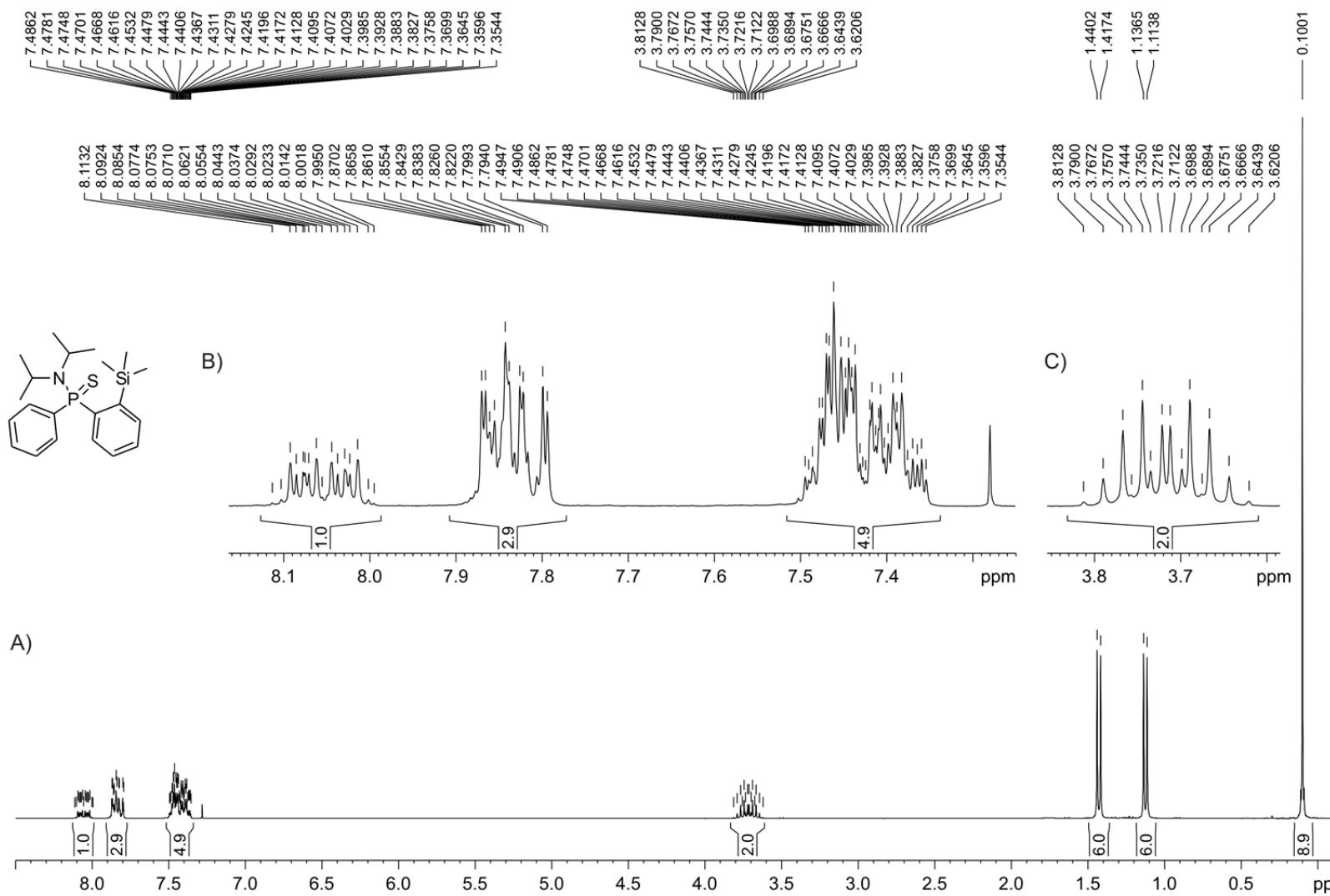


Figure S19. ^1H NMR spectrum (300.13 MHz) of **11** in CDCl_3 .

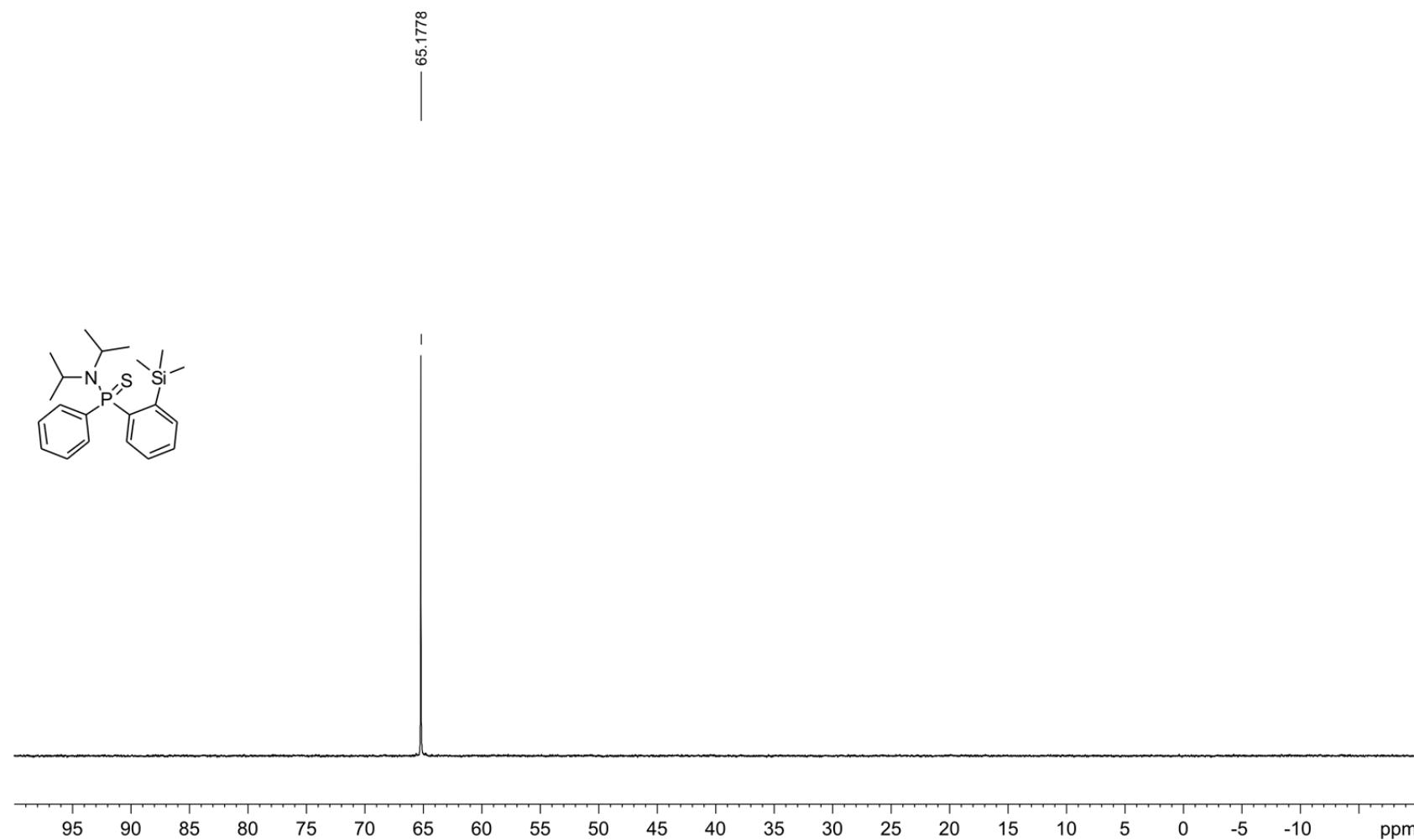


Figure S20. ^{31}P NMR spectrum (121.47 MHz) of **11** in CDCl_3 .

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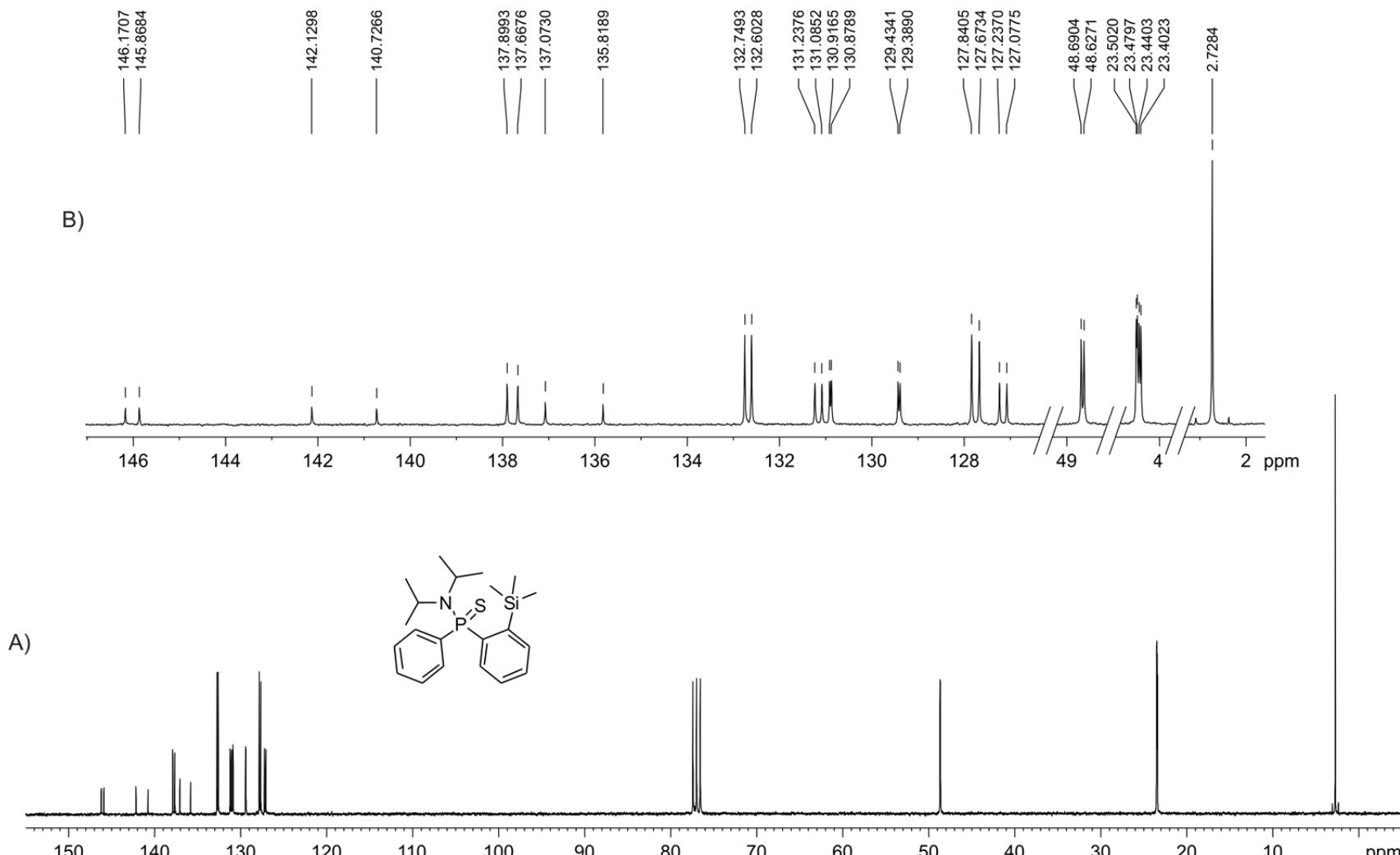


Figure S21. ^{13}C NMR spectrum (75.47 MHz) of **11** in CDCl_3 .

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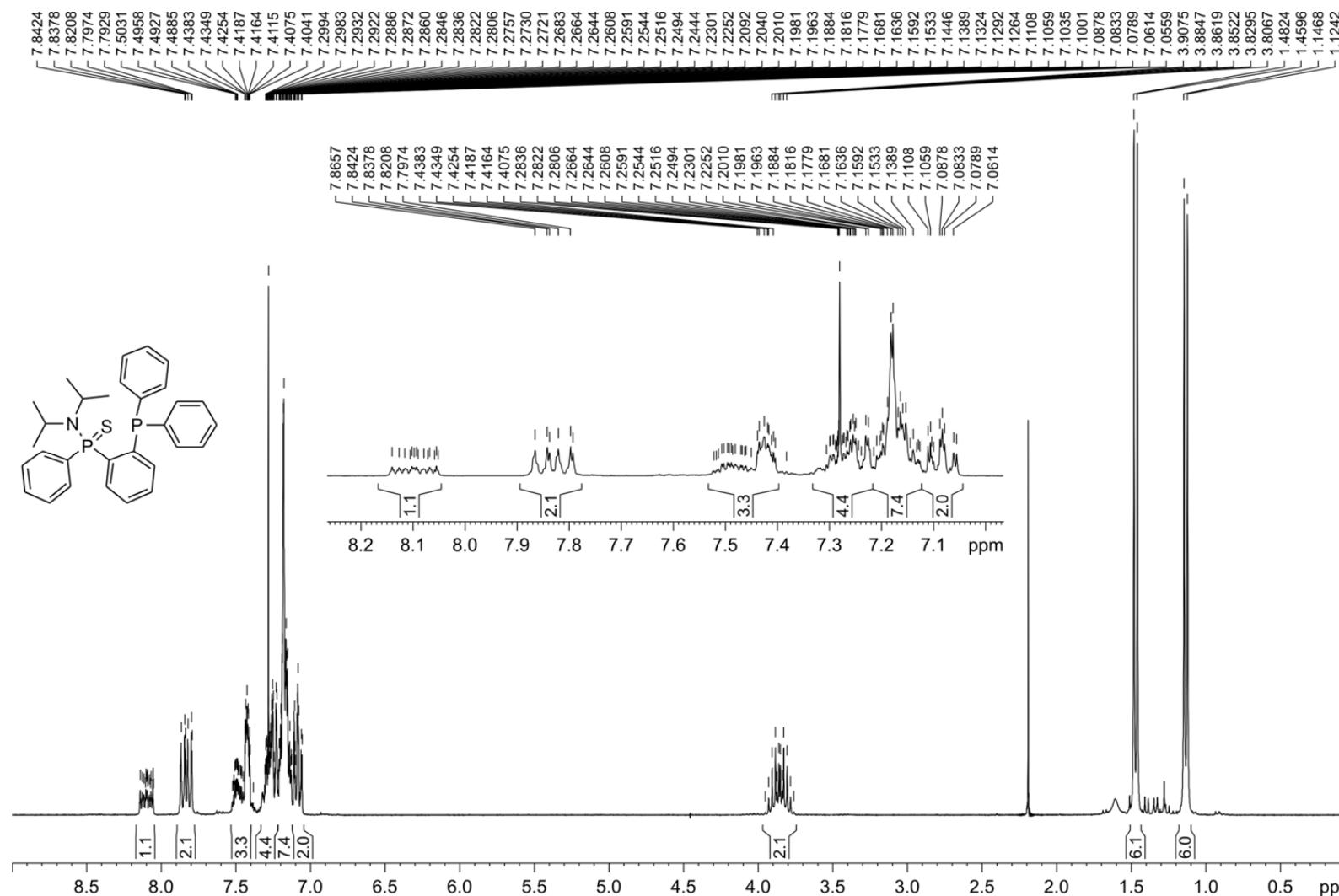


Figure S22. ¹H NMR spectrum (300.13 MHz) of **12** in CDCl_3 .

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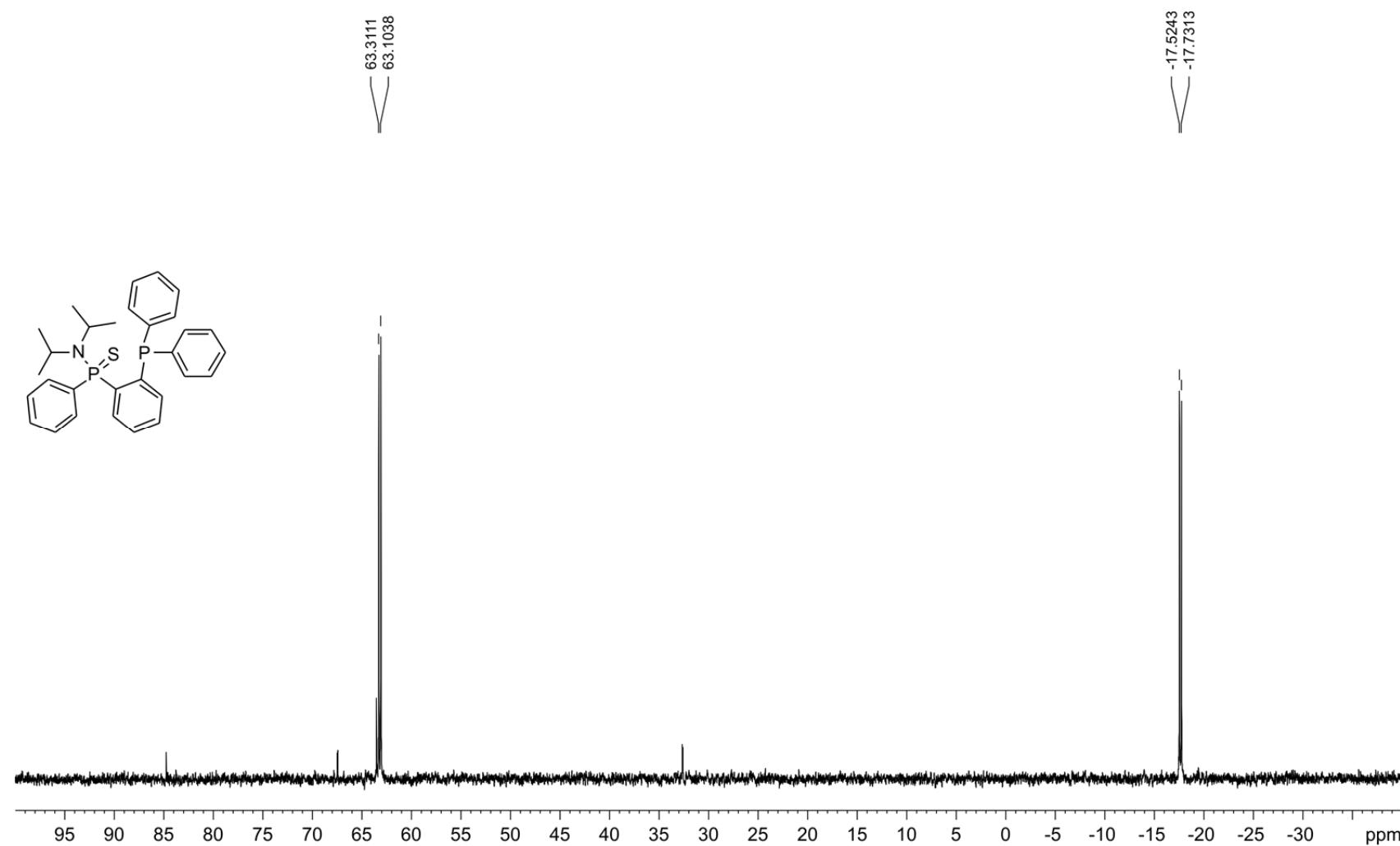


Figure S23. ^{31}P NMR spectrum (121.47 MHz) of **11** in CDCl_3 .

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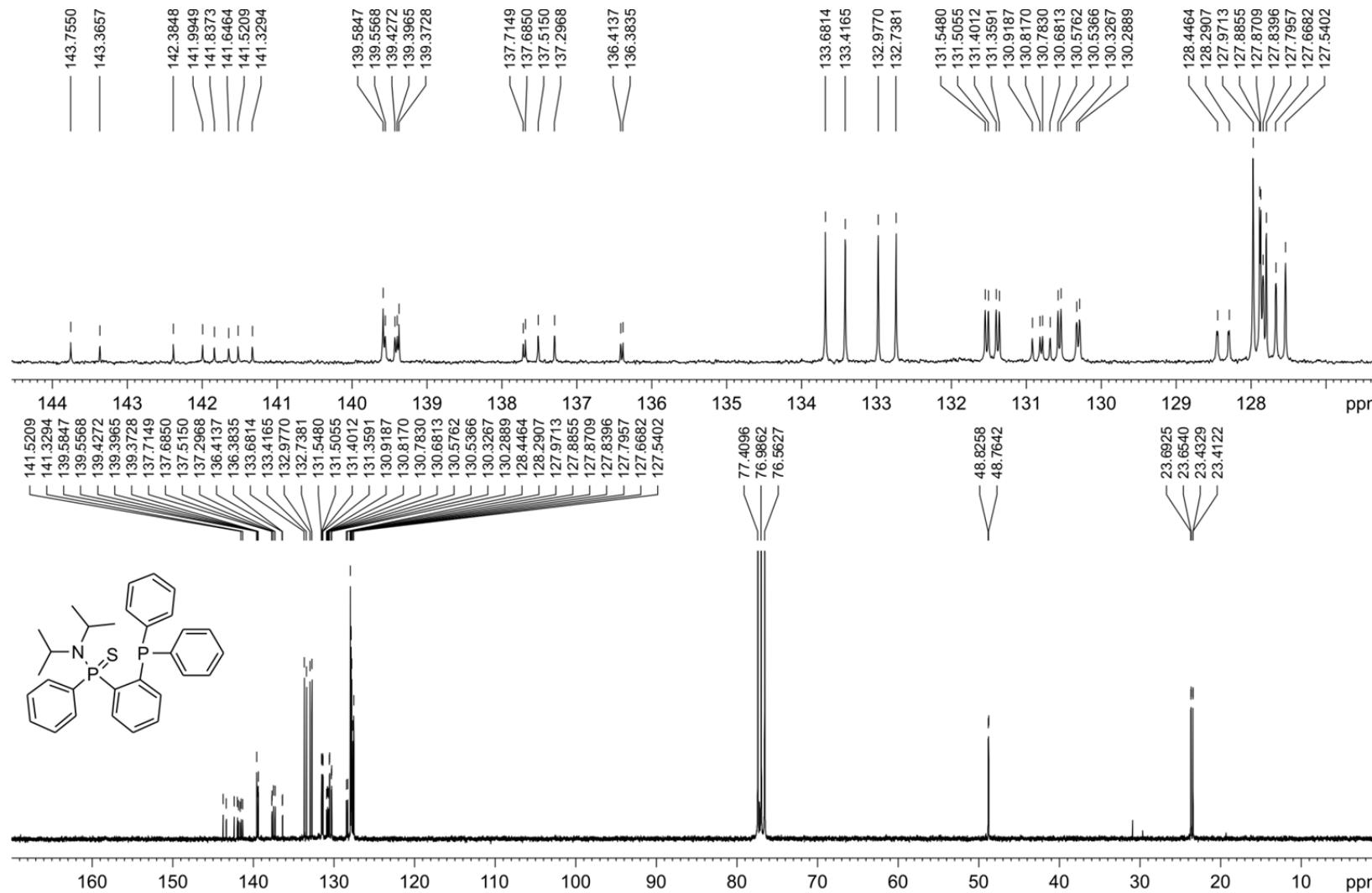


Figure S24. ^{13}C NMR spectrum (75.47 MHz) of **12** in CDCl_3

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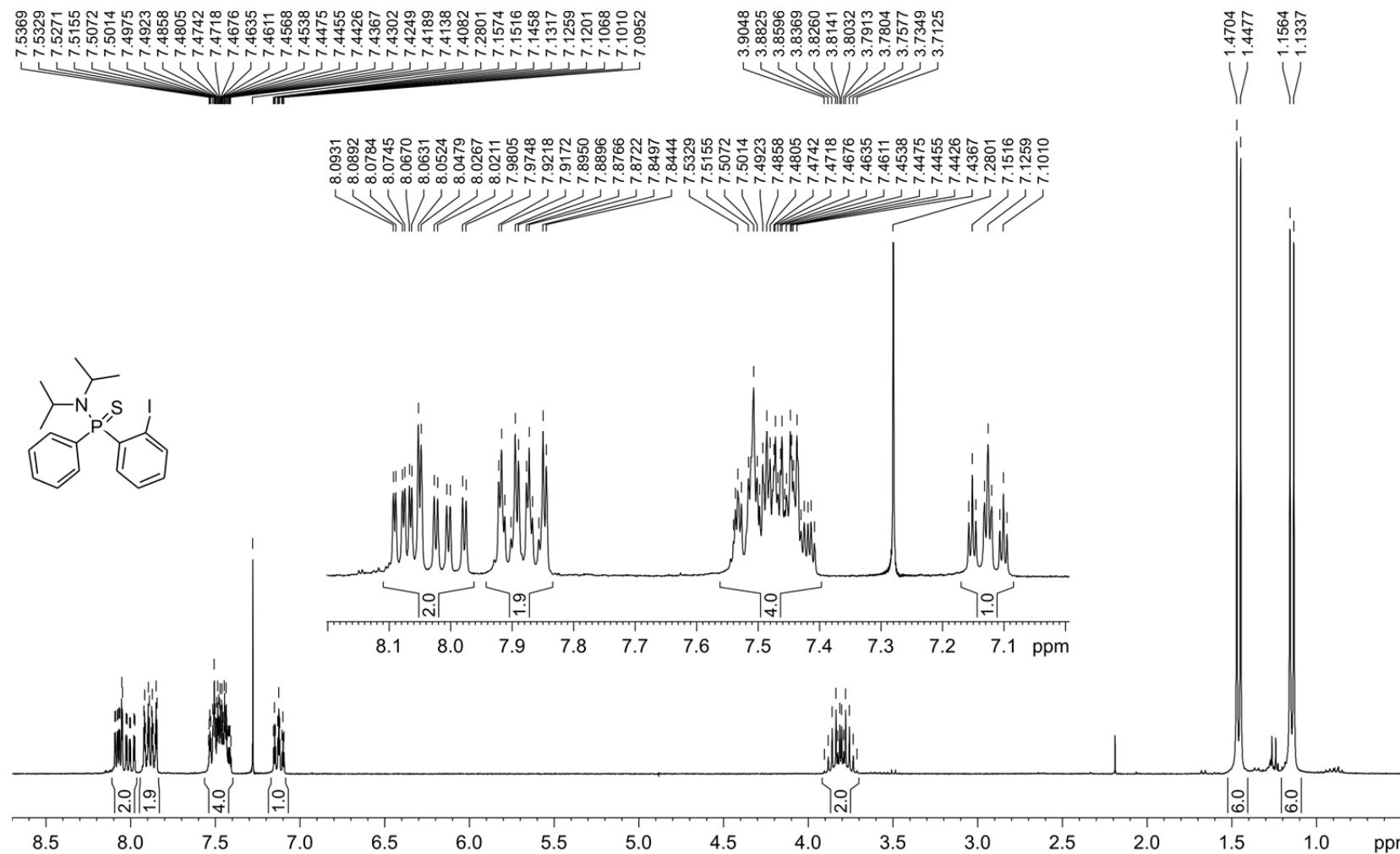


Figure S25. ^1H NMR spectrum (300.13 MHz) of **13** in CDCl_3 .

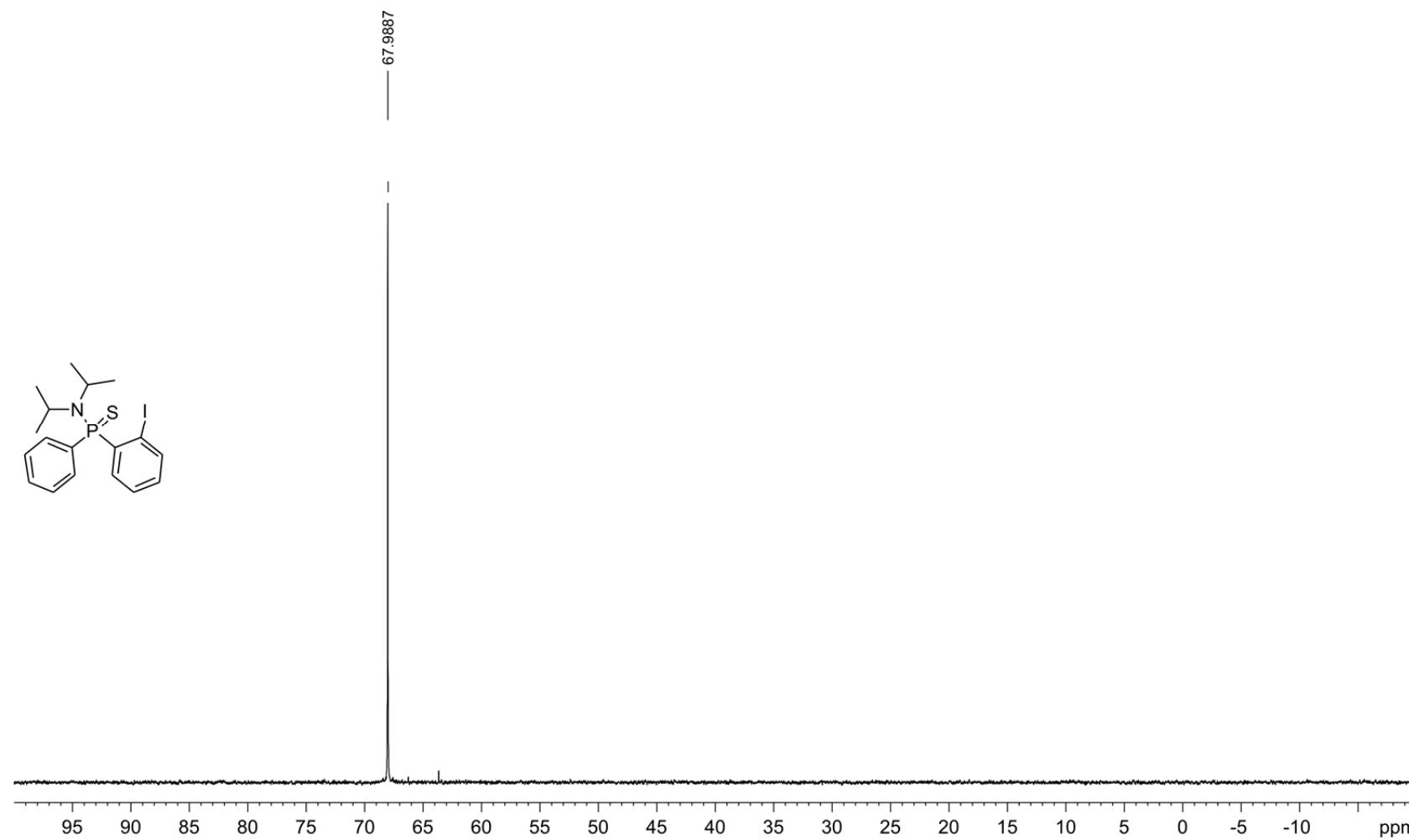


Figure S26. ^{31}P NMR spectrum (121.47 MHz) of **13** in CDCl_3 .

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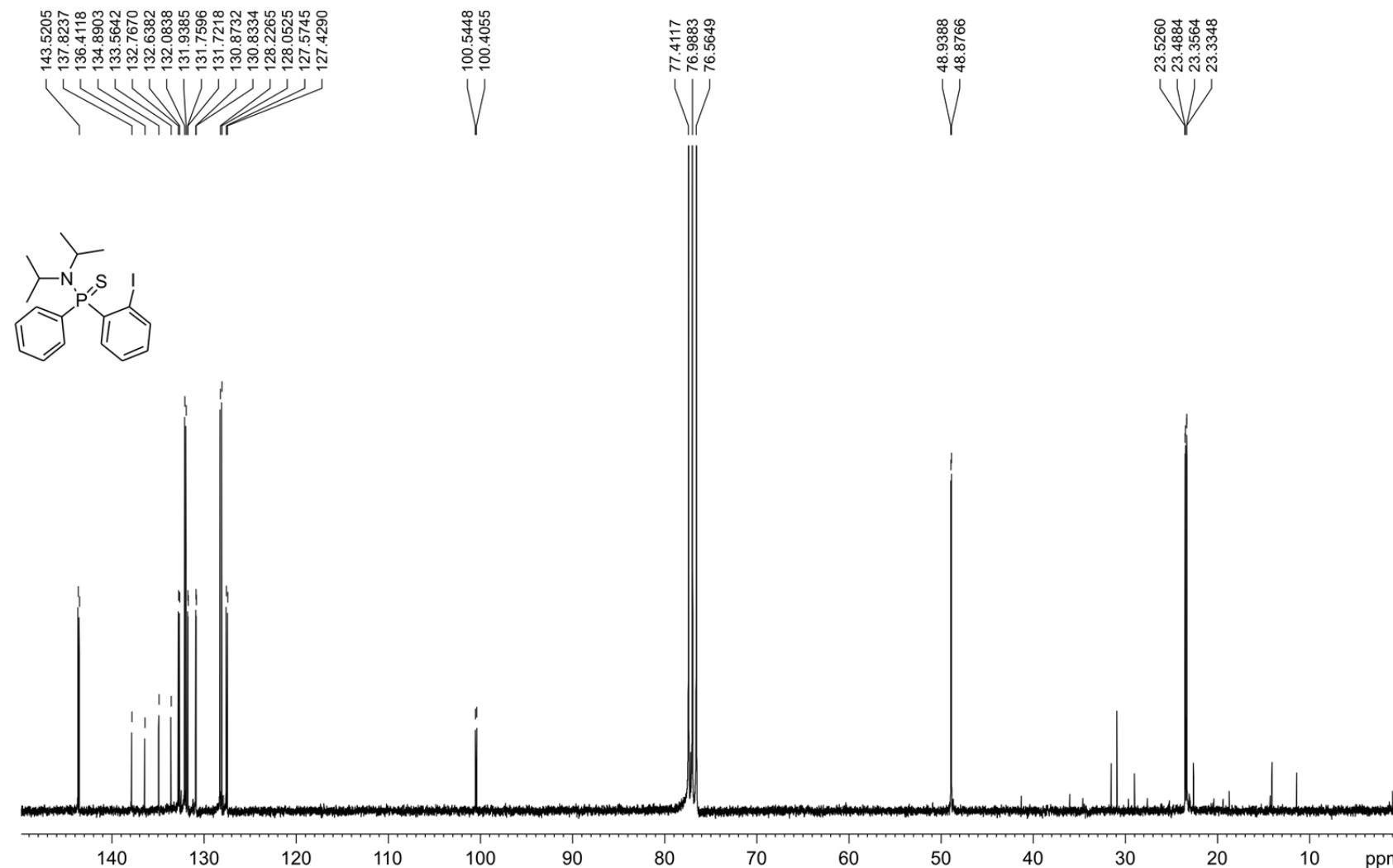


Figure S27. ^{13}C NMR spectrum (75.47 MHz) of **13** in CDCl_3 .

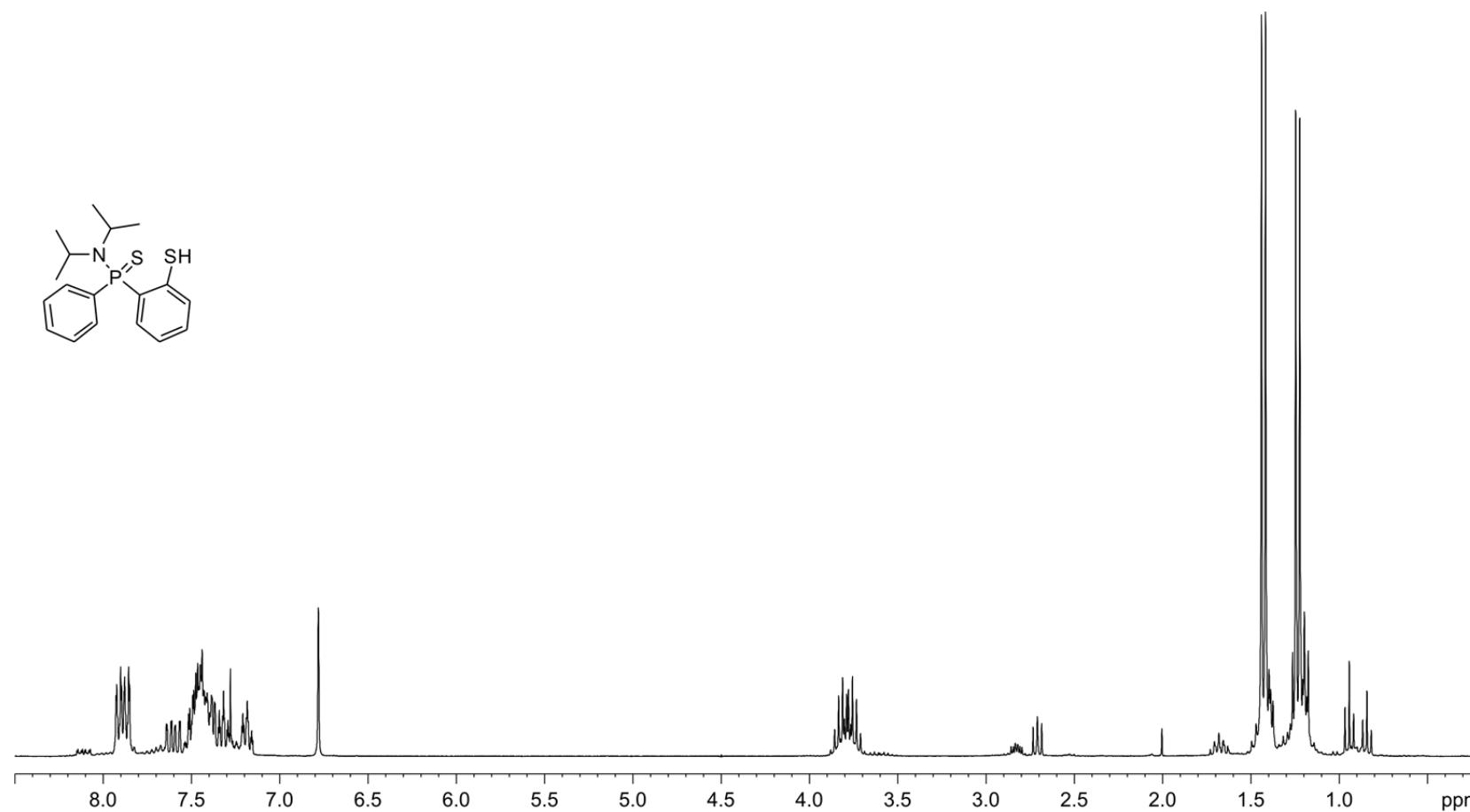


Figure S28. ¹H NMR spectrum (300.13 MHz) of the crude reaction affording **14** in CDCl₃.

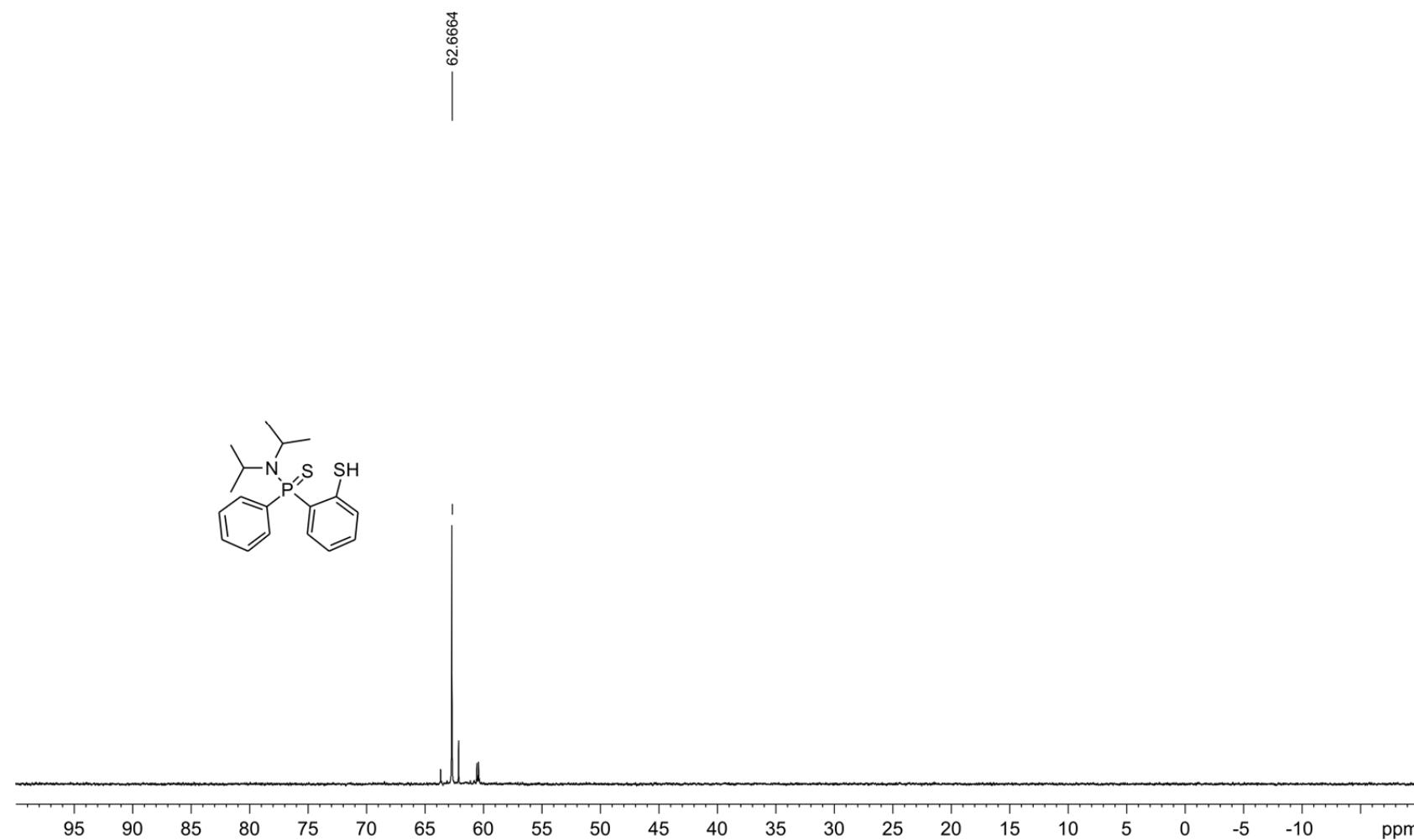


Figure S29. ^{31}P NMR spectrum (121.47 MHz) of the crude reaction affording **14** in CDCl_3 .

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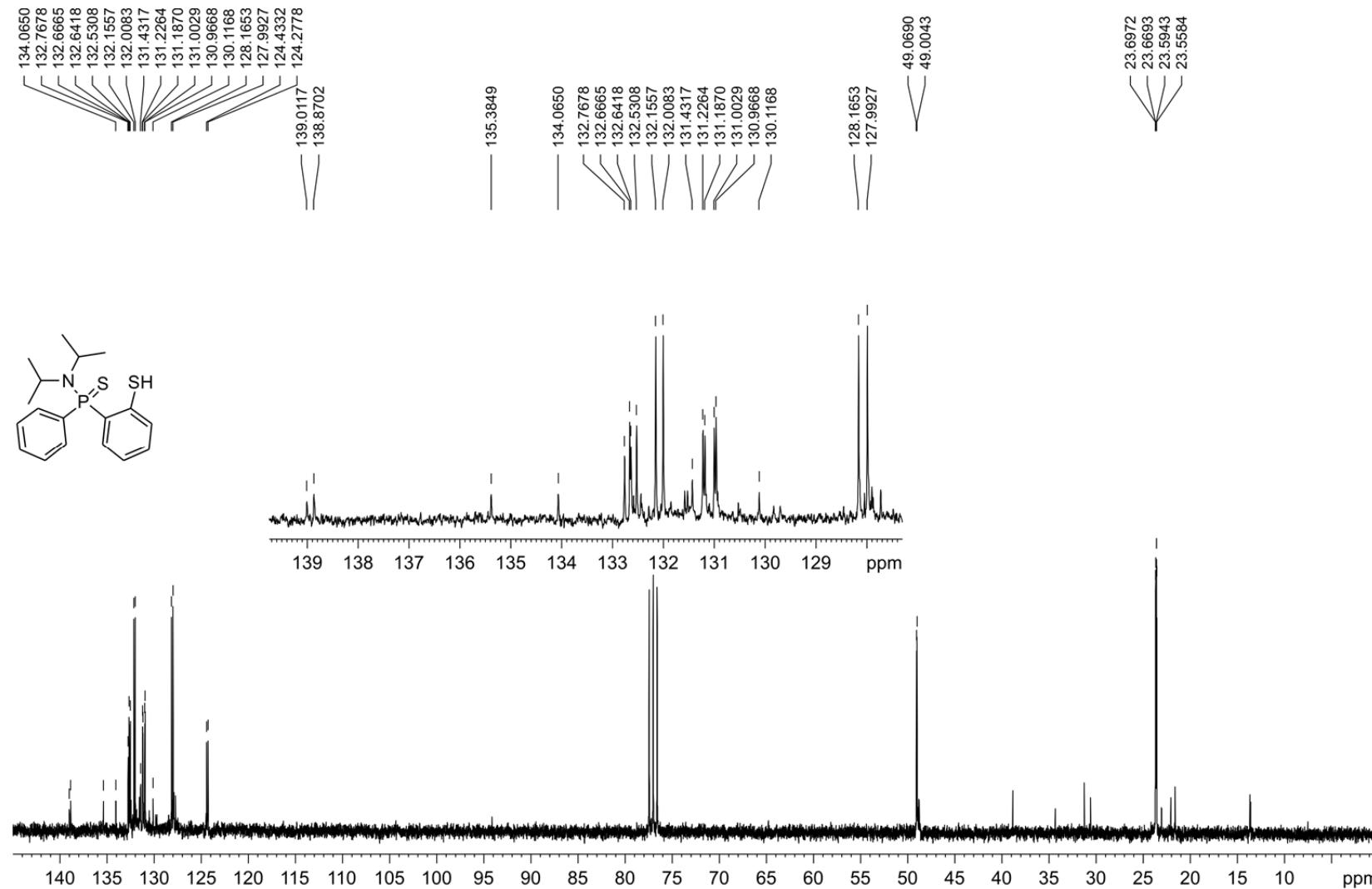


Figure S30. ^{13}C NMR spectrum (75.47 MHz) of the crude reaction affording **14** in CDCl_3 .

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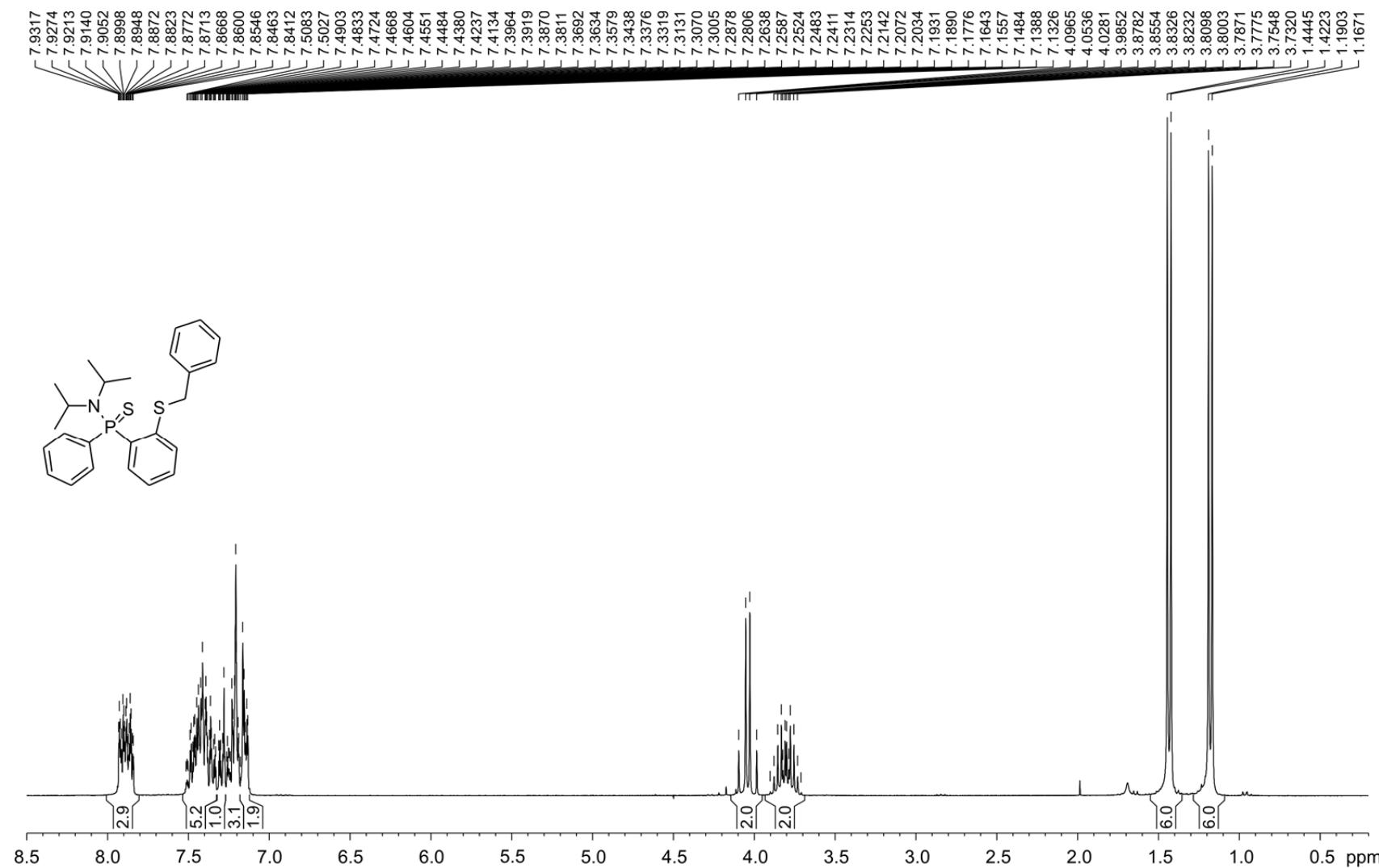


Figure S31. ^1H NMR spectrum (300.13 MHz) of **15** in CDCl_3 .

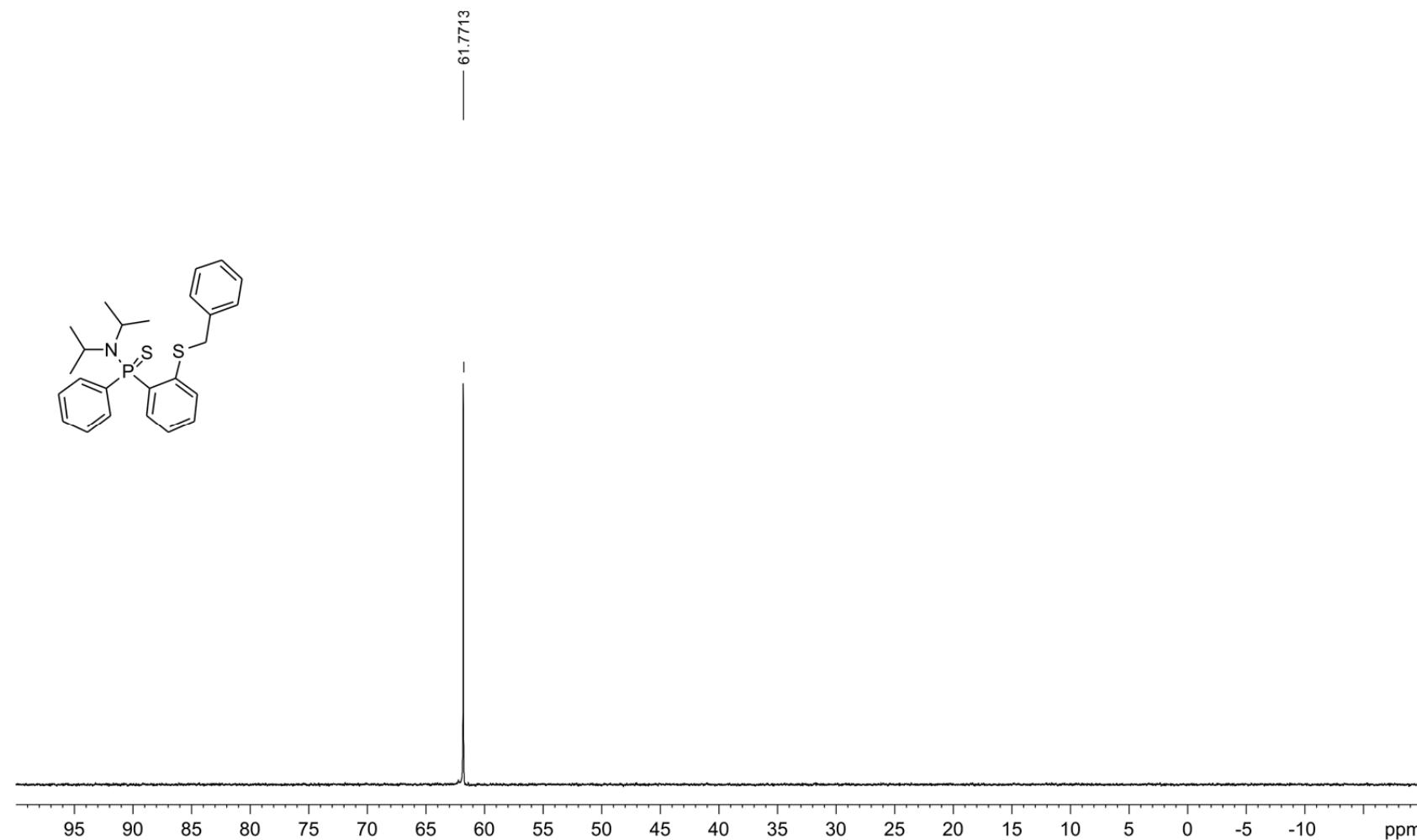


Figure S32. ^{31}P NMR spectrum (121.47 MHz) of **15** in CDCl_3 .

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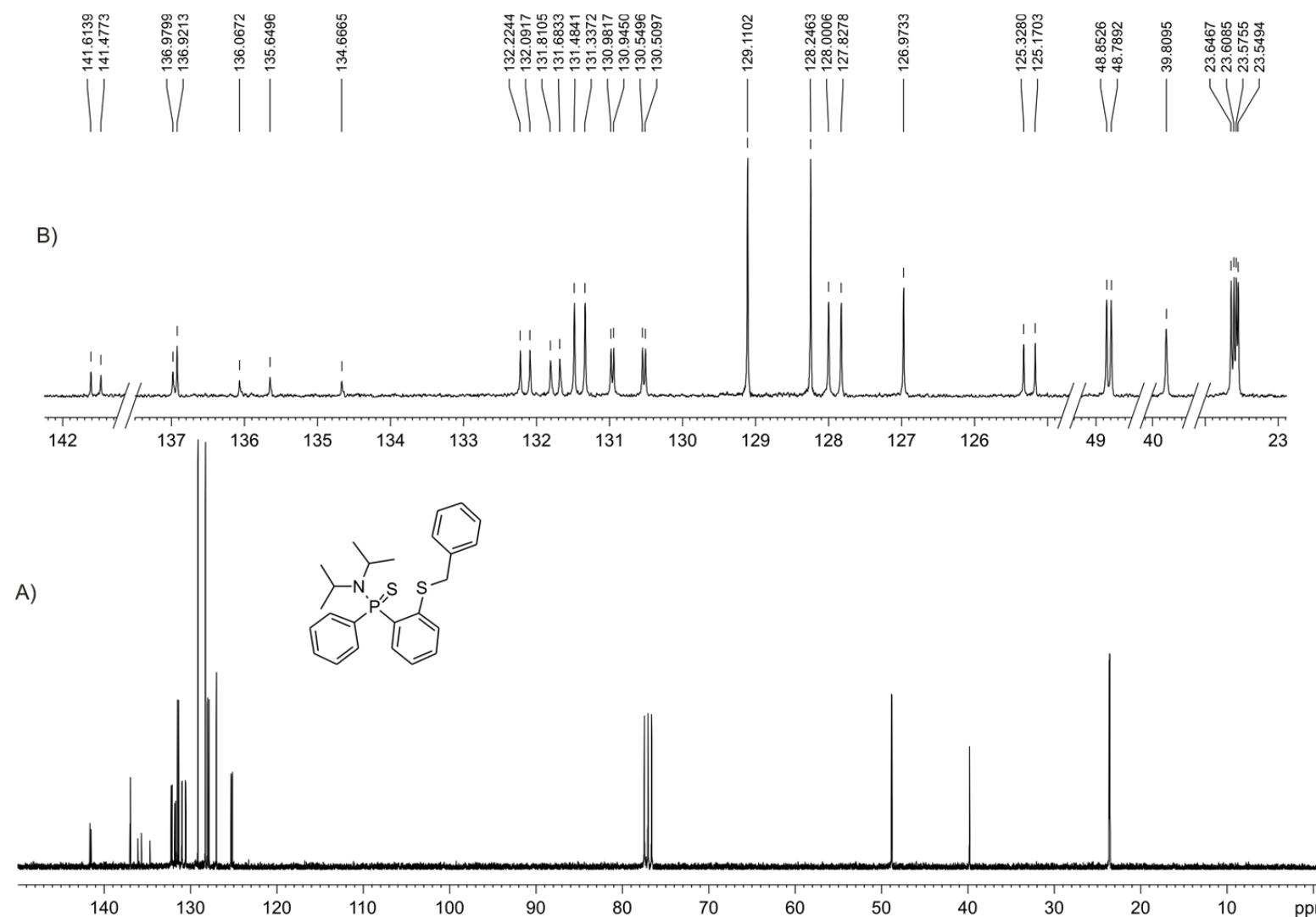


Figure S33. ^{13}C NMR spectrum (75.47 MHz) of **15** in CDCl_3 .

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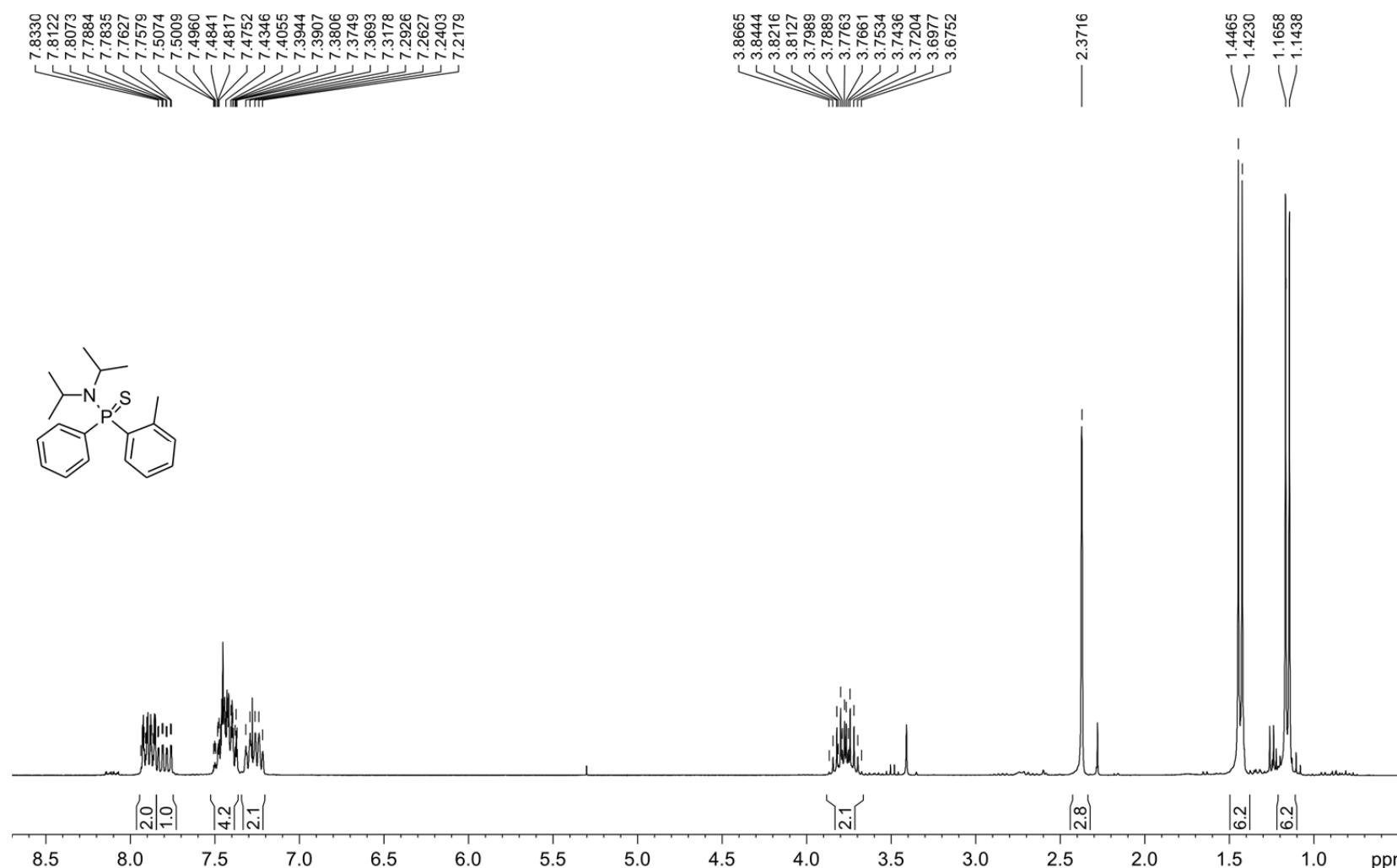


Figure S34. ^1H NMR spectrum (300.13 MHz) of **16** in CDCl_3 .

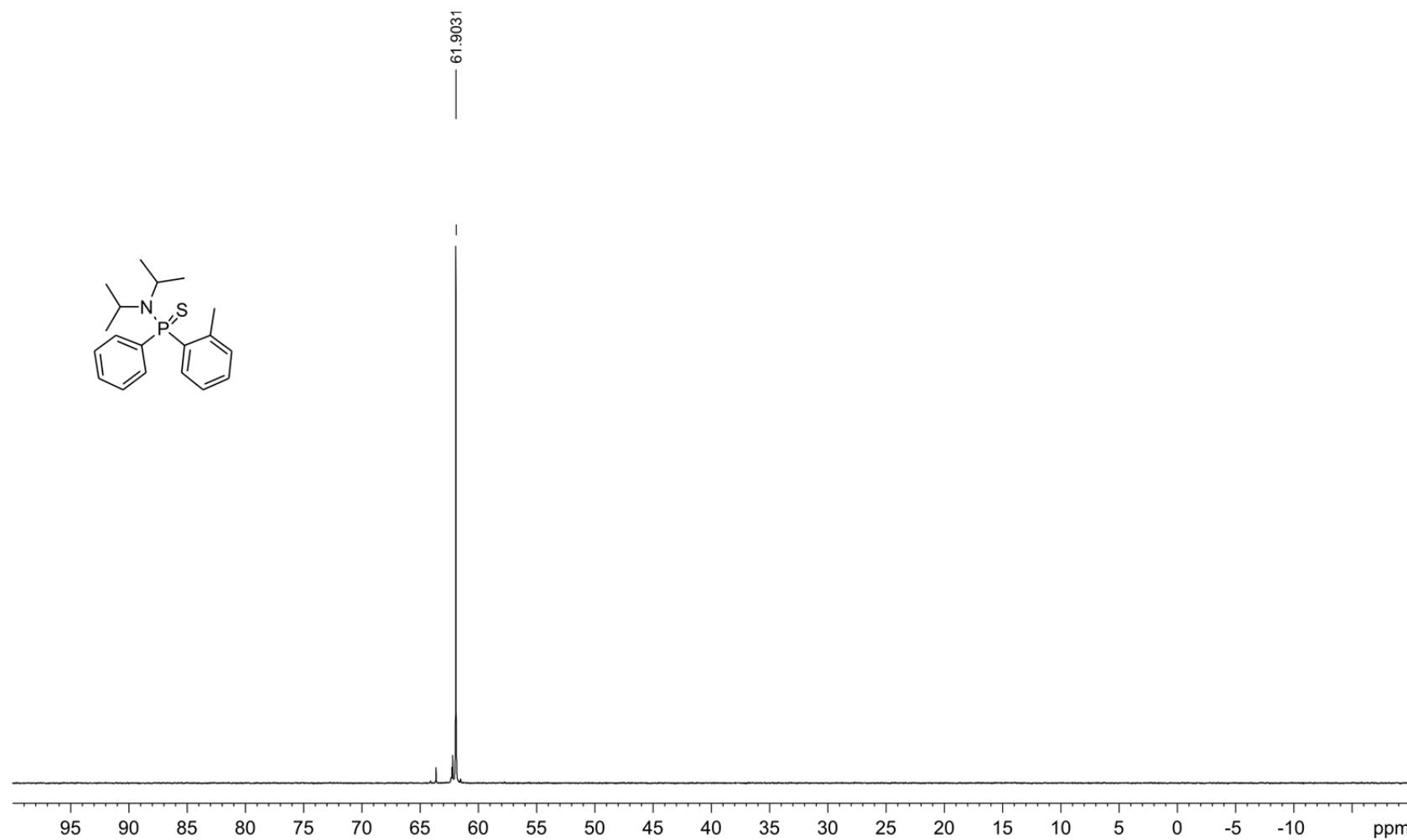


Figure S35. ^{31}P NMR spectrum (121.47 MHz) of **16** in CDCl_3 .

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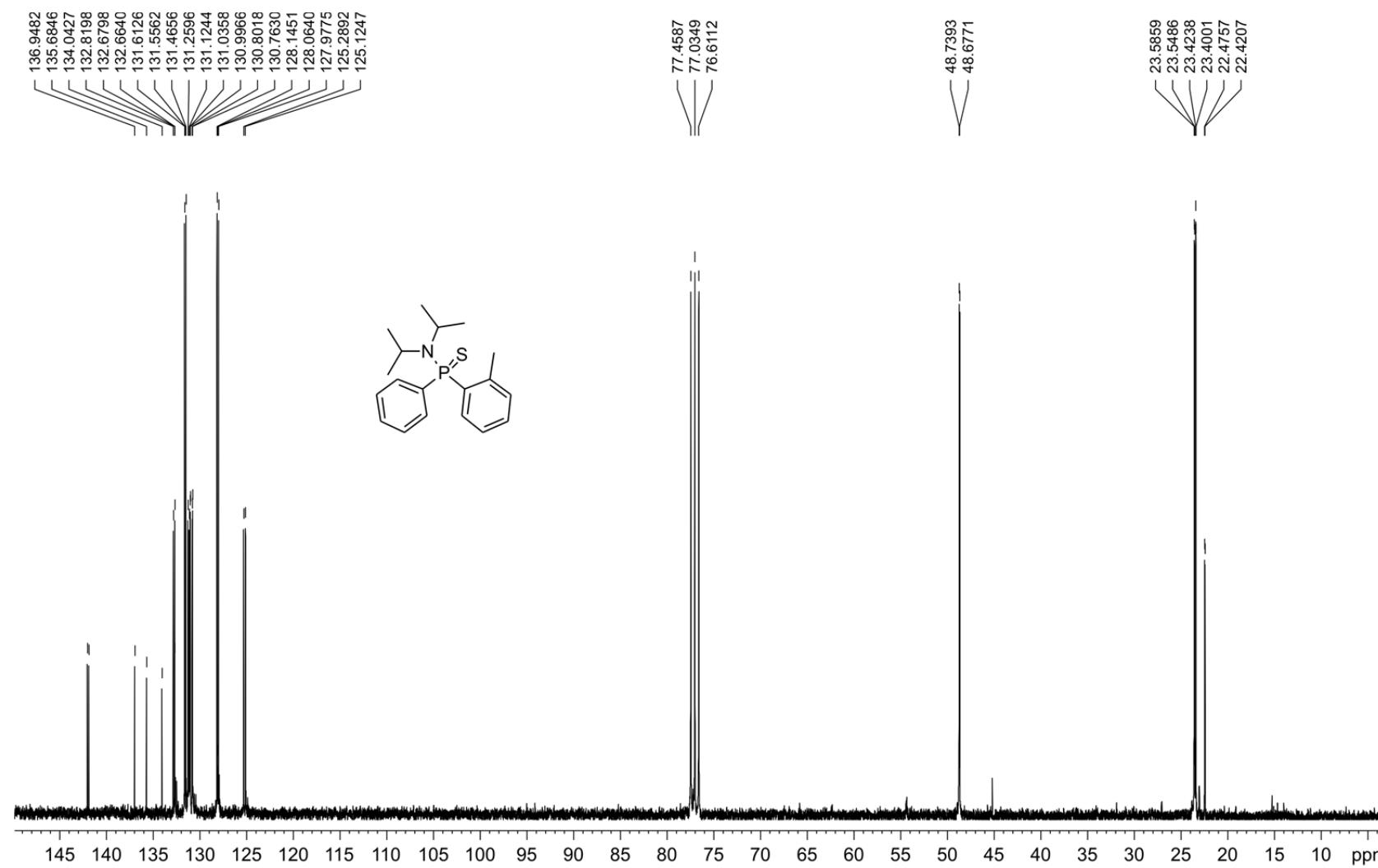


Figure S36. ¹³C NMR spectrum (75.47 MHz) of **16** in CDCl₃.

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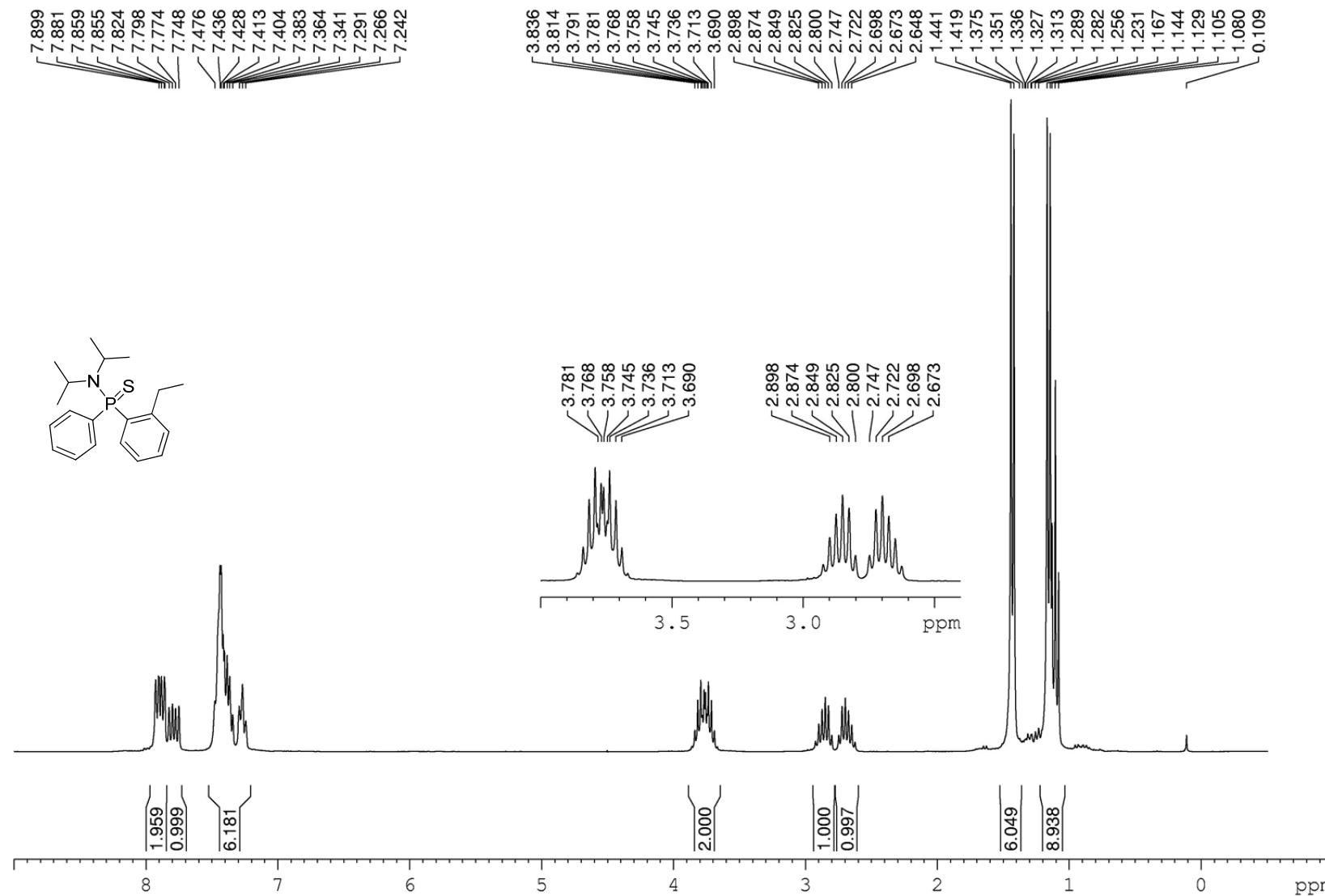


Figure S37. ¹H NMR spectrum (300.13 MHz) of **17** in CDCl_3 .

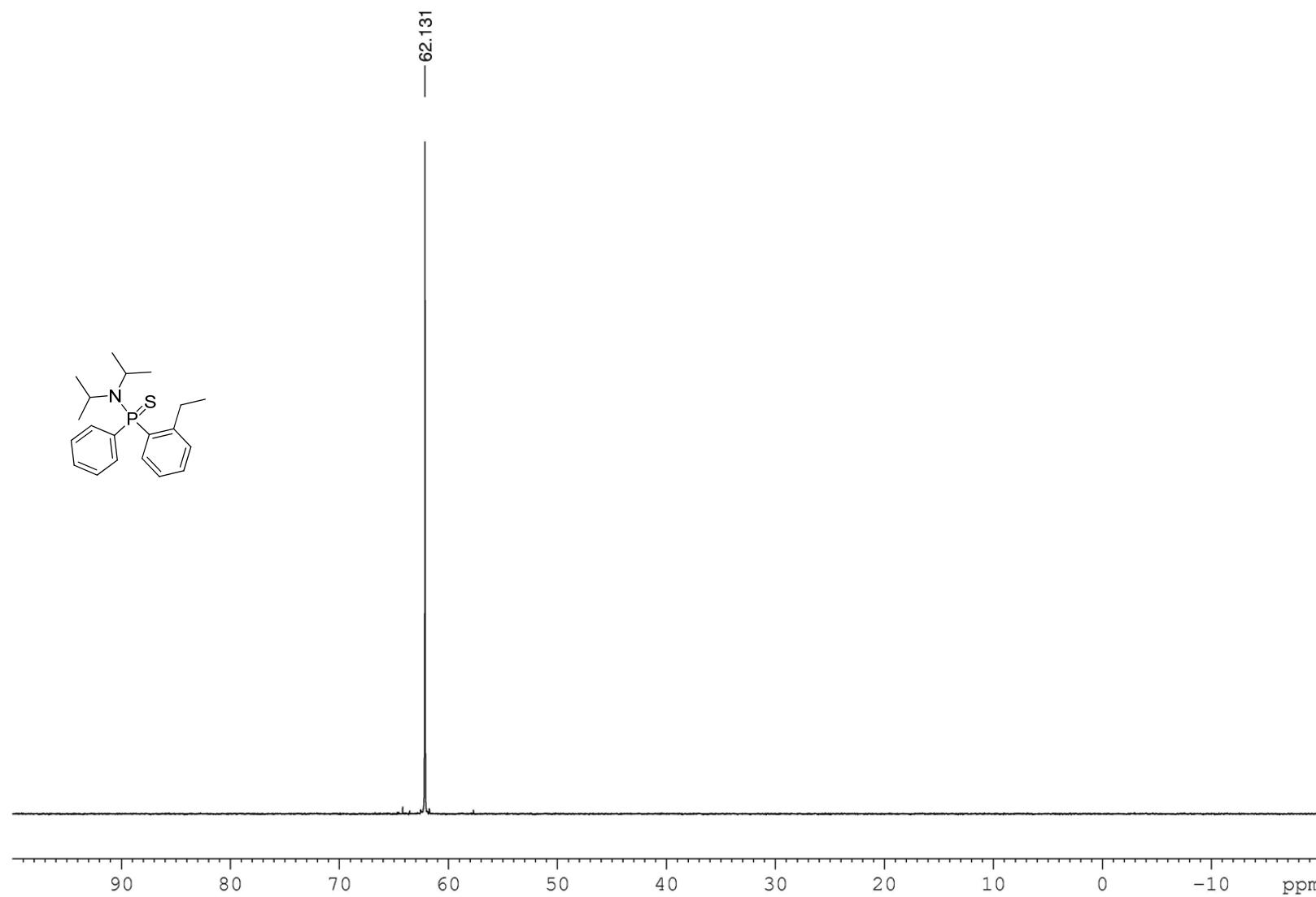


Figure S38. ^{31}P NMR spectrum (121.47 MHz) of **17** in CDCl_3 .

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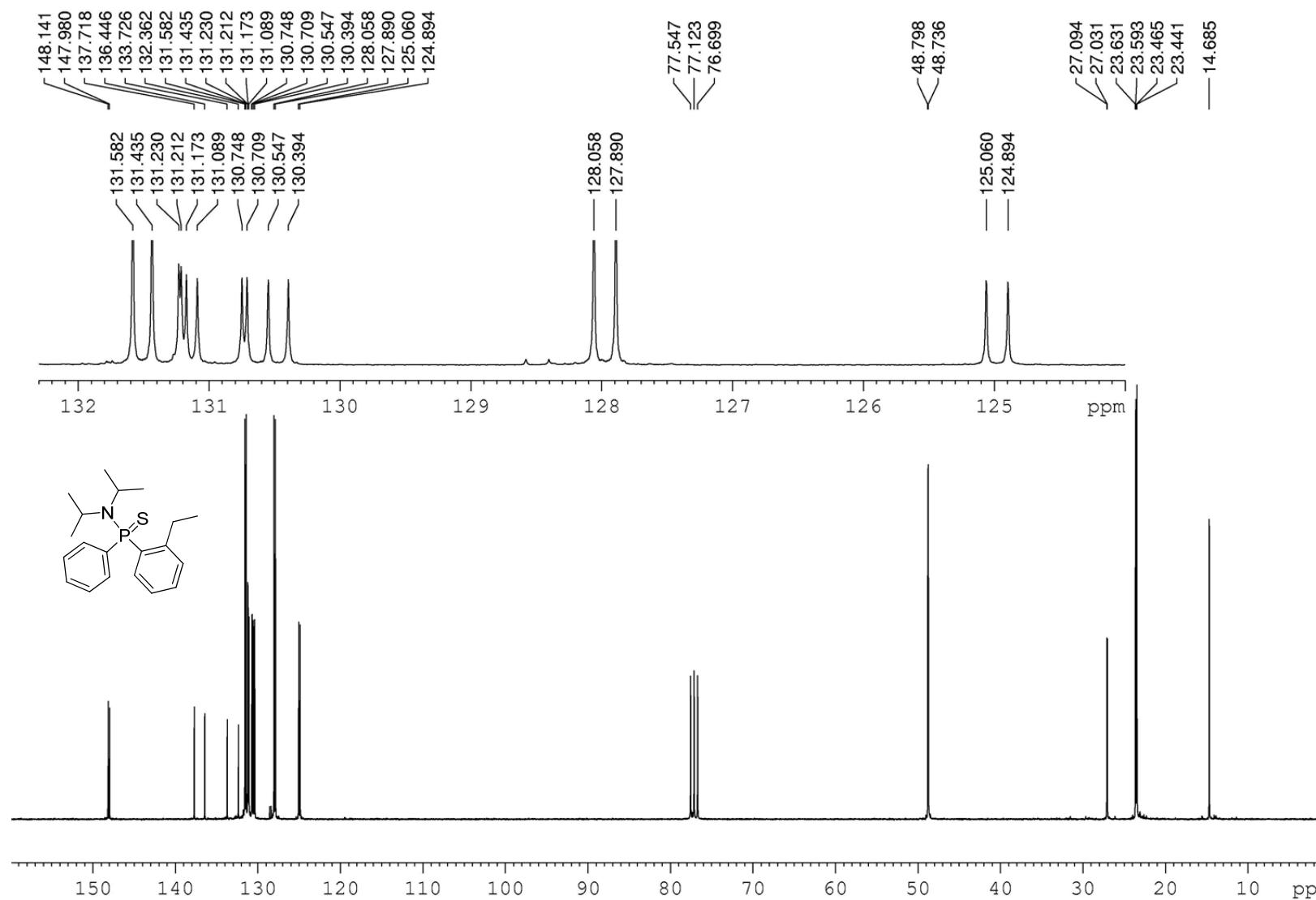


Figure S39. ^{13}C NMR spectrum (75.47 MHz) of **17** in CDCl_3 .

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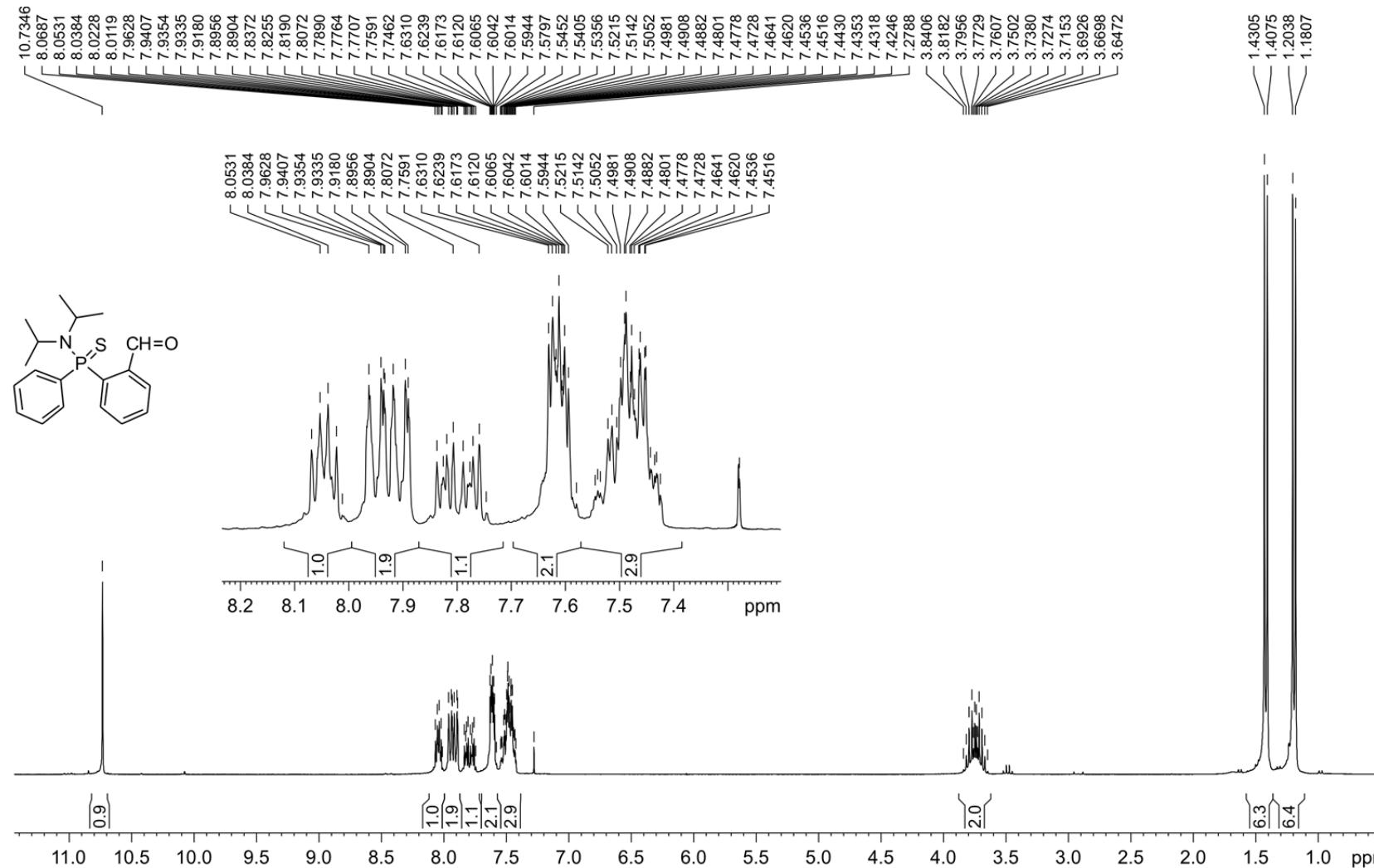


Figure S40. ^1H NMR spectrum (300.13 MHz) of **18** in CDCl_3 .

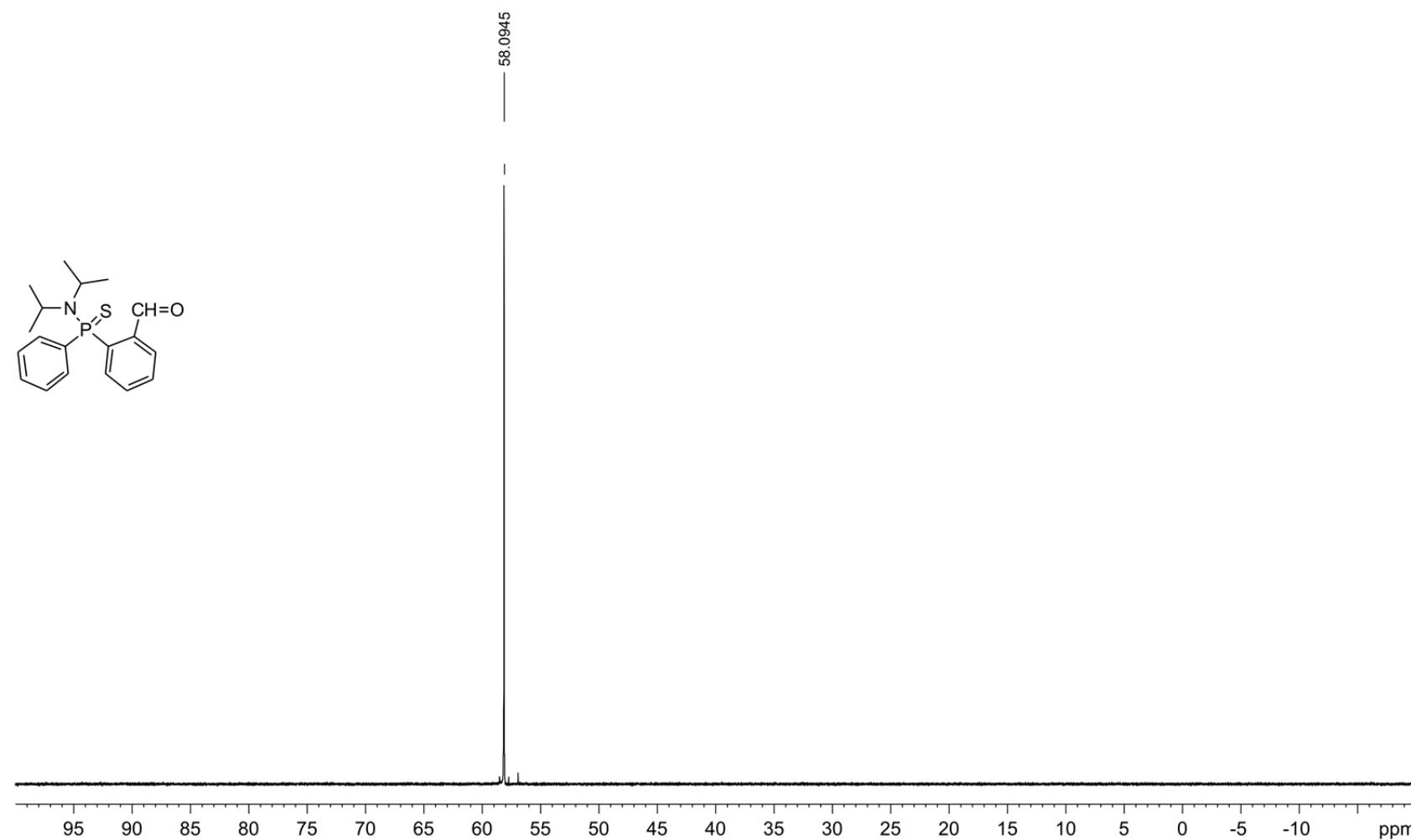


Figure S41. ^{31}P NMR spectrum (121.47 MHz) of **18** in CDCl_3 .

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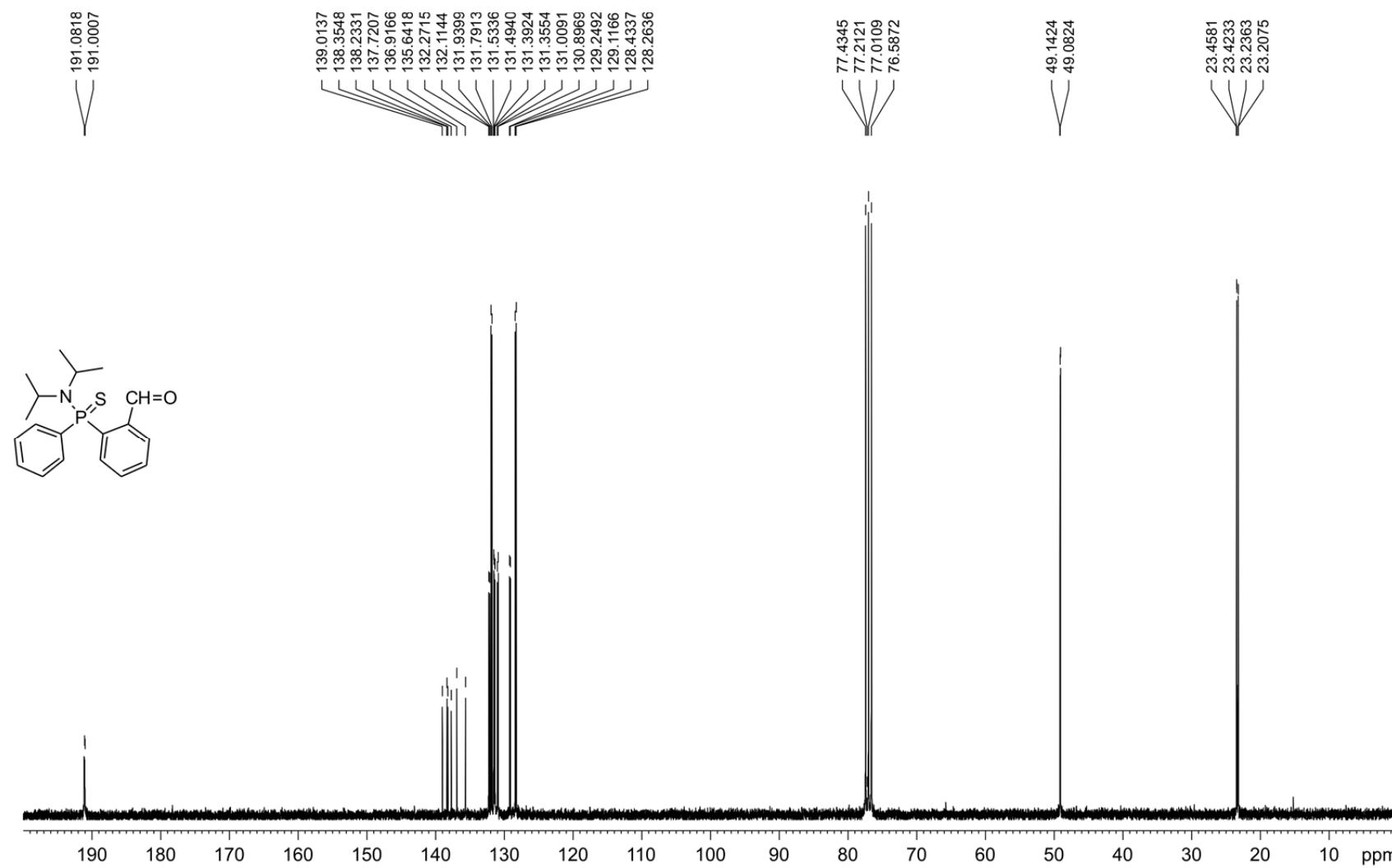


Figure S42. ^{13}C NMR spectrum (75.47 MHz) of **18** in CDCl_3 .

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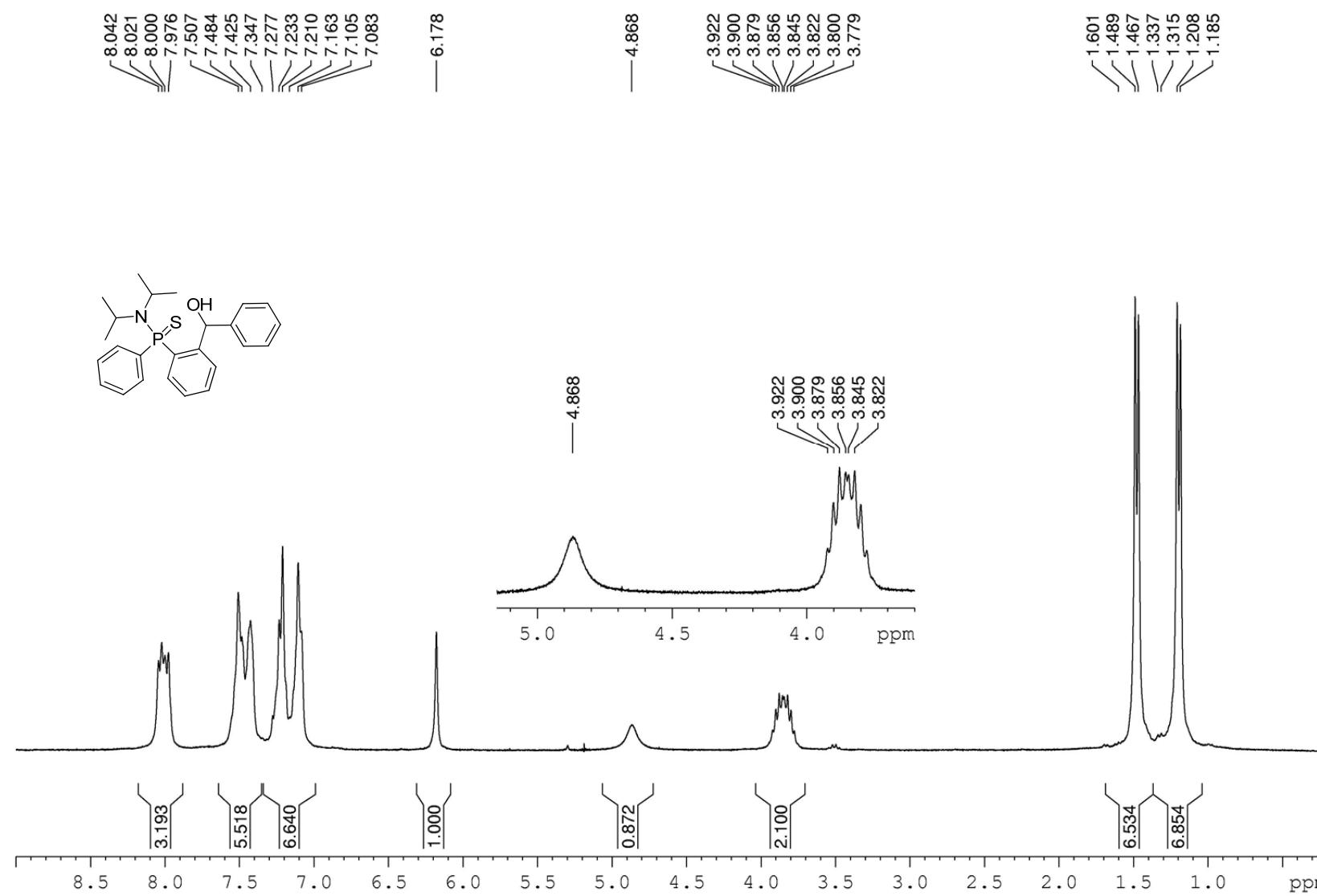


Figure S43. ^1H NMR spectrum (300.13 MHz) of **19** in CDCl_3 .

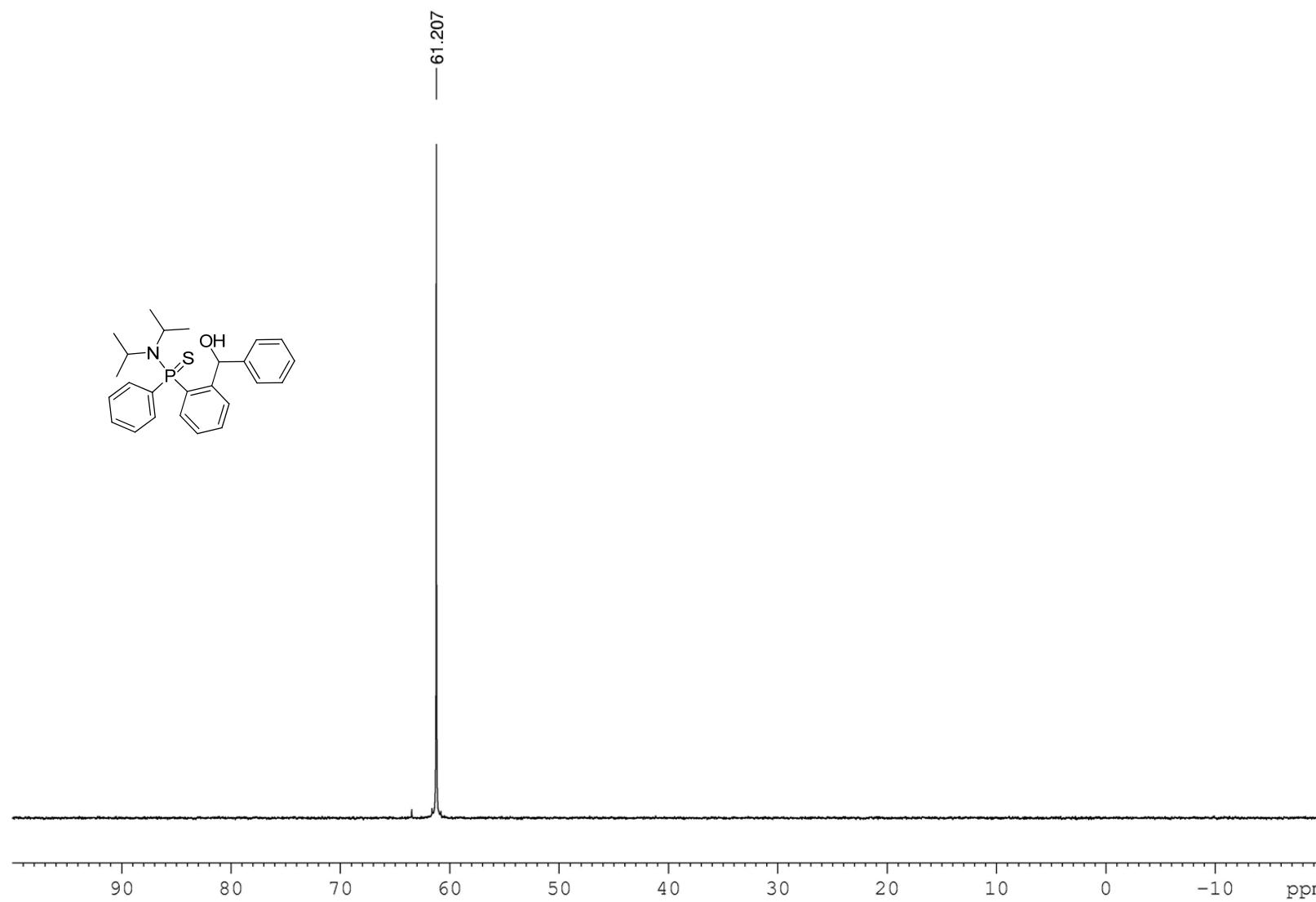


Figure S44. ^{31}P NMR spectrum (121.47 MHz) of **19** in CDCl_3 .

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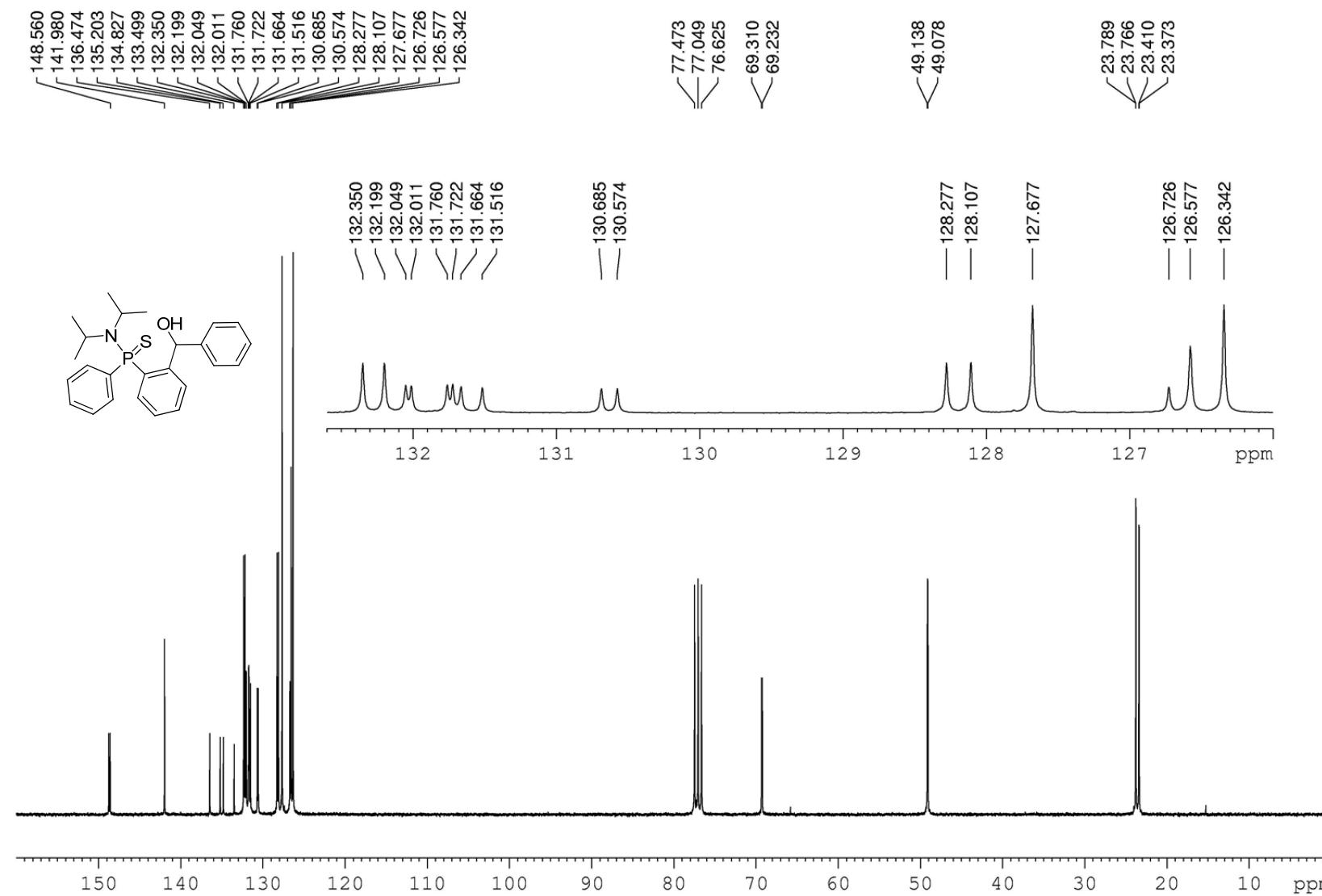


Figure S45. ^{13}C NMR spectrum (75.47 MHz) of **19** in CDCl_3 .

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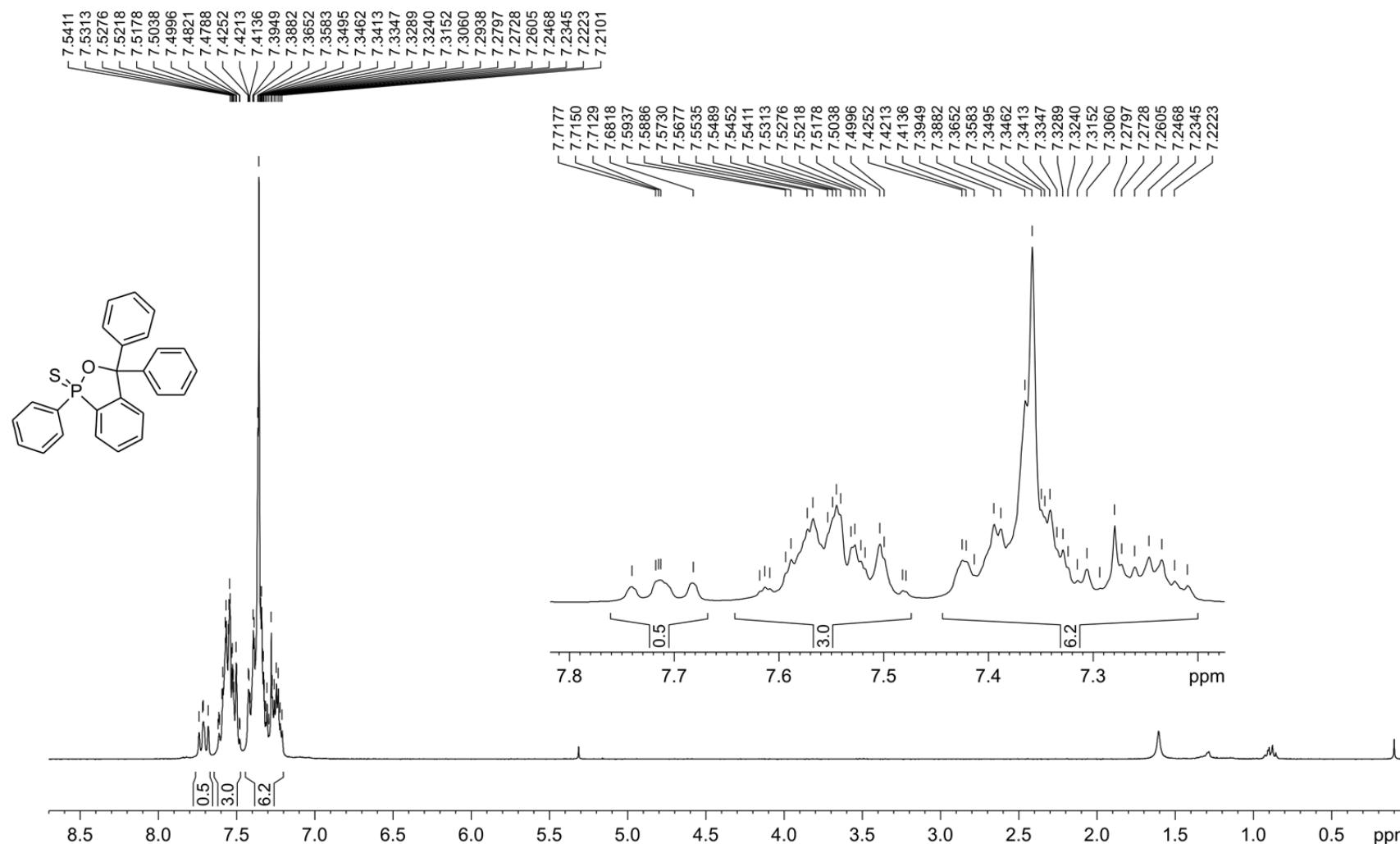


Figure S46. ^1H NMR spectrum (300.13 MHz) of **20** in CDCl_3 .

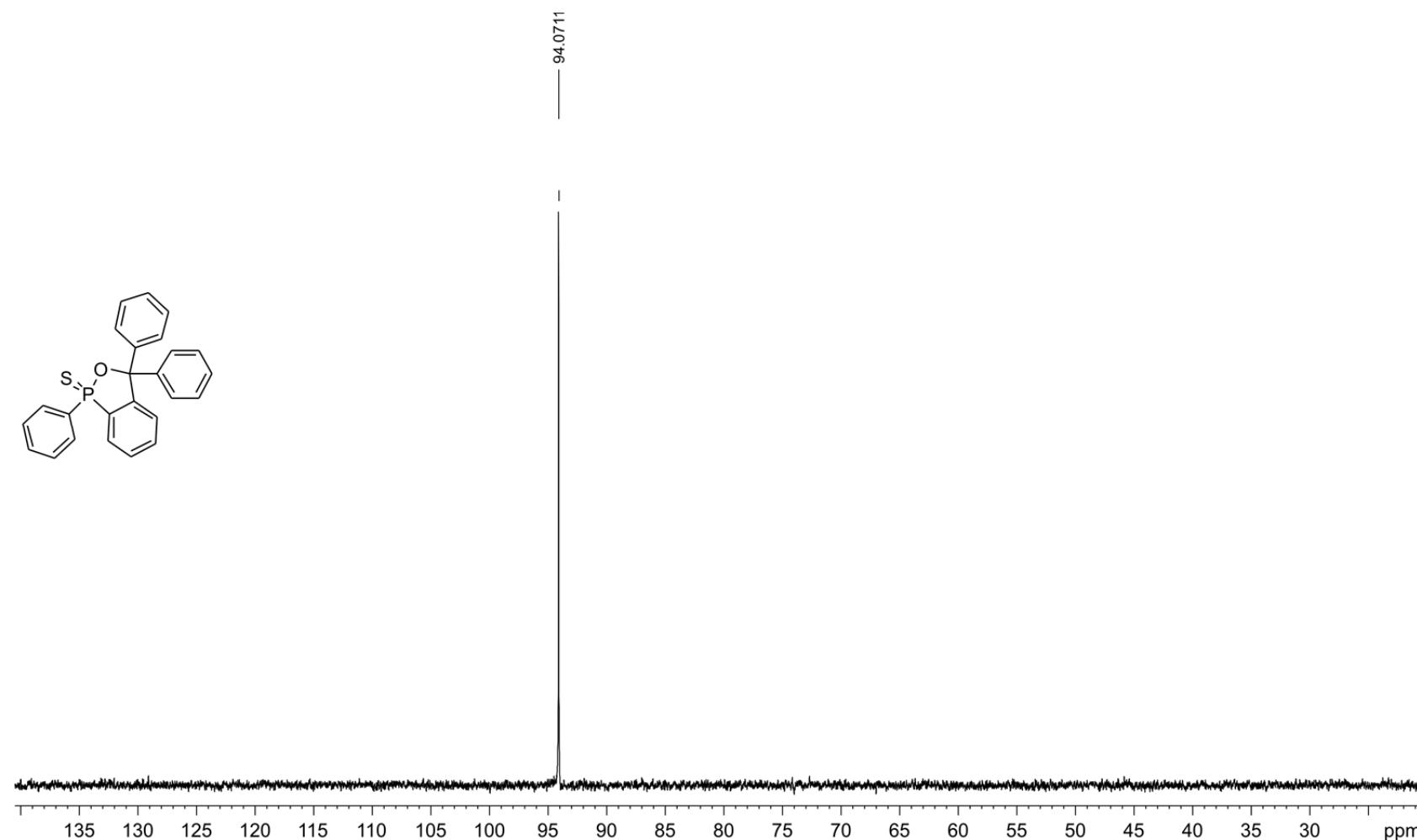


Figure S47. ^{31}P NMR spectrum (121.47 MHz) of **20** in CDCl_3 .

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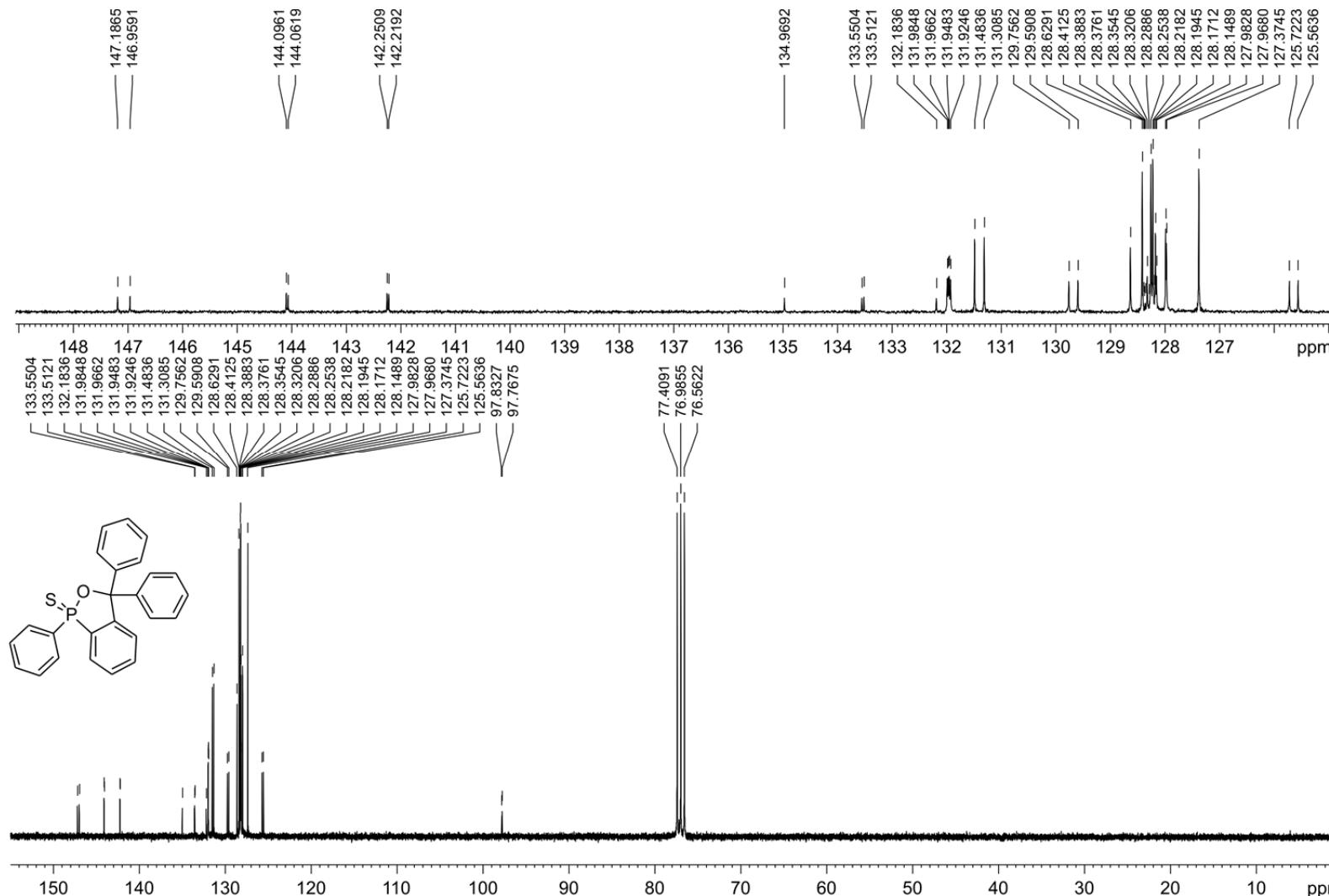


Figure S48. ^{13}C NMR spectrum (75.47 MHz) of **20** in CDCl_3 .

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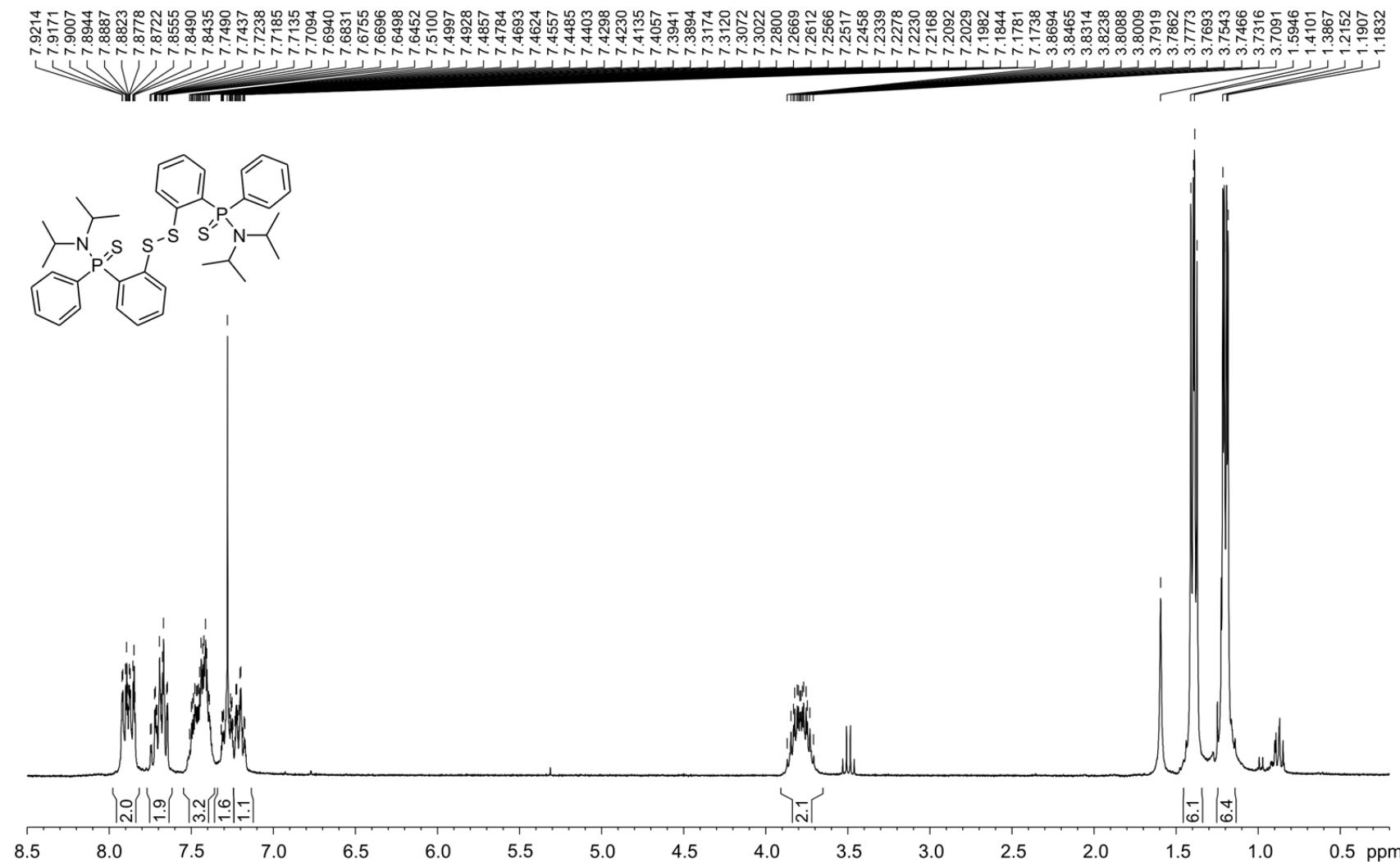


Figure S49. ^1H NMR spectrum (300.13 MHz) of **21** in CDCl_3 .

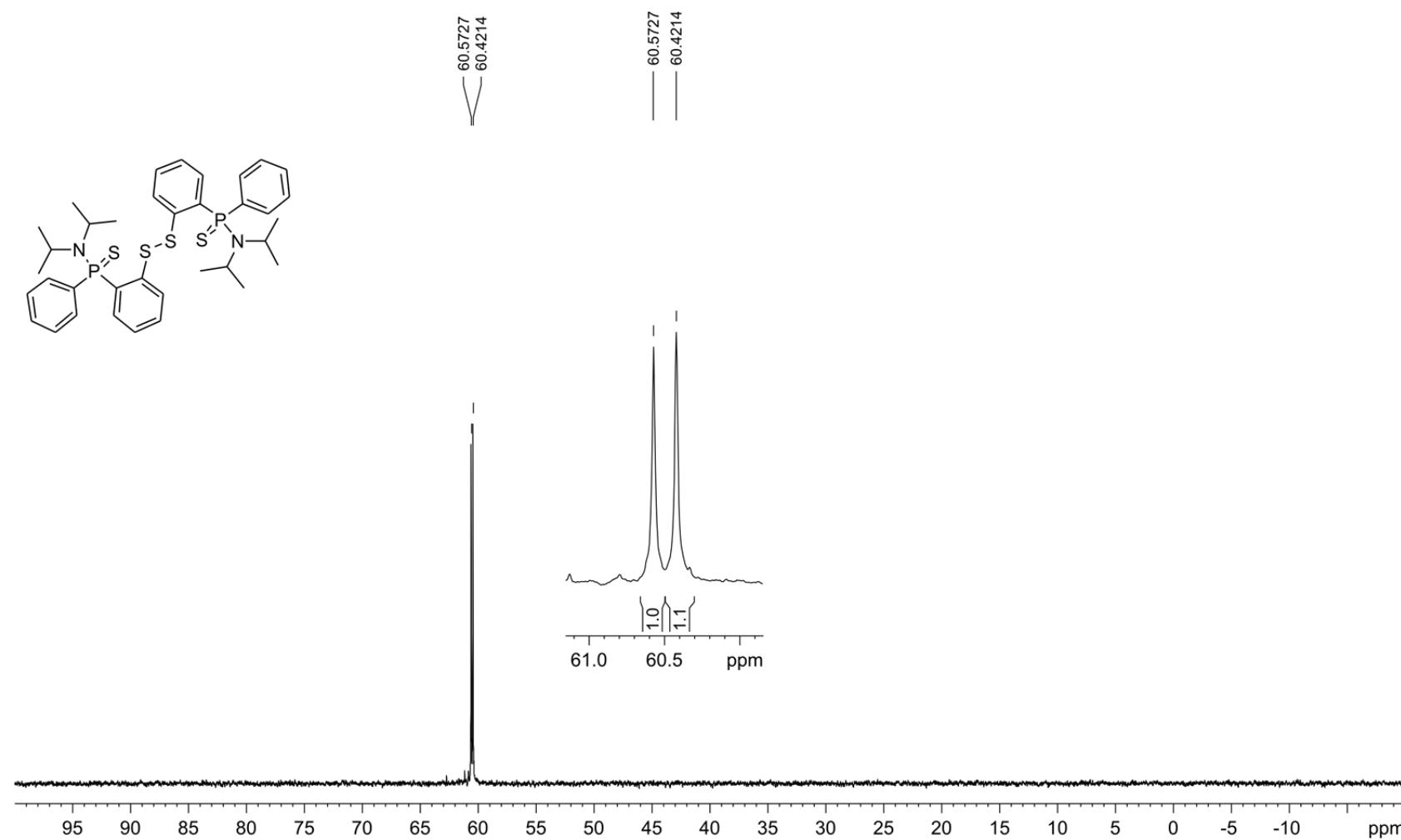


Figure S50. ^{31}P NMR spectrum (121.47 MHz) of **21** in CDCl_3 .

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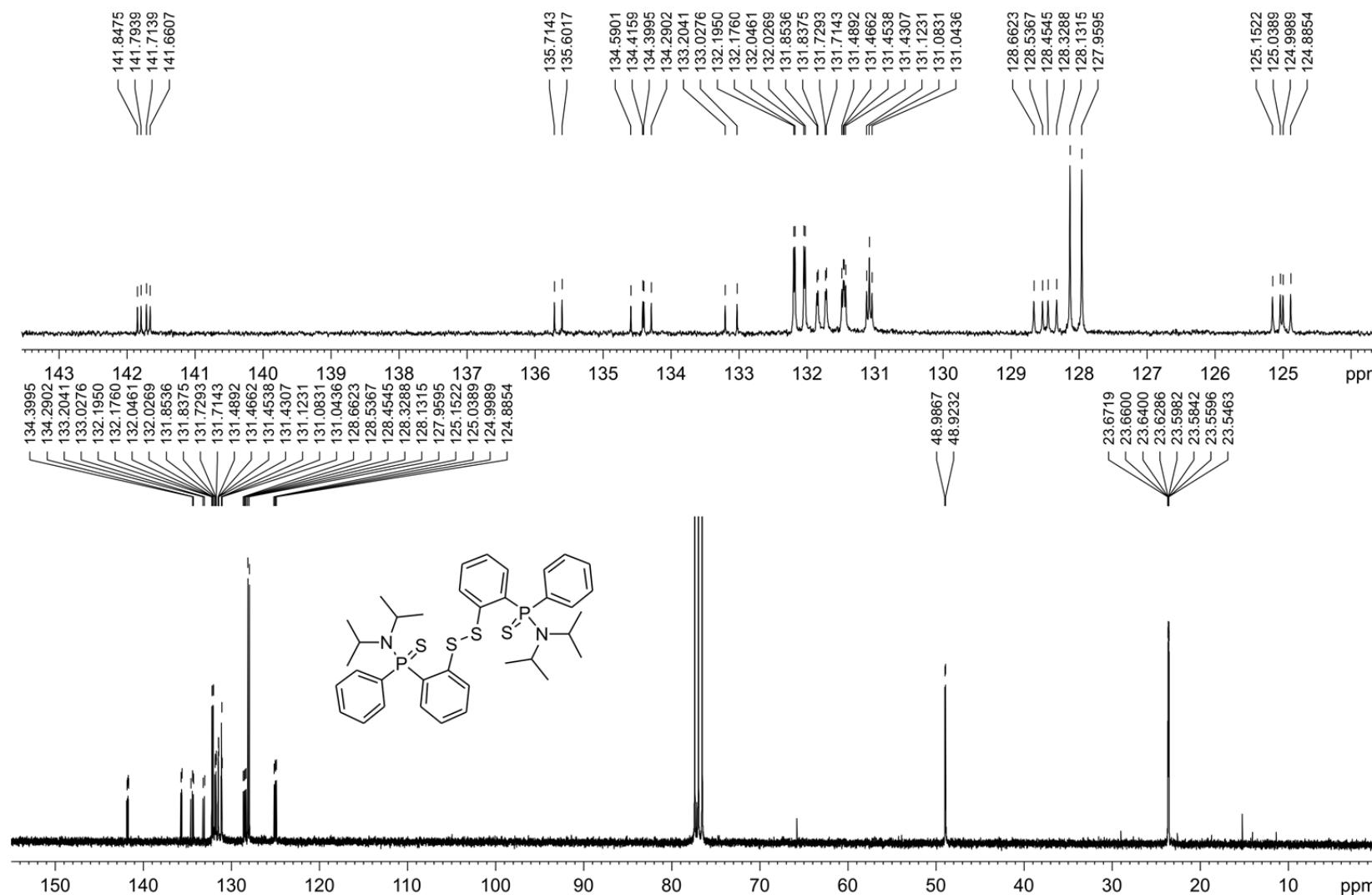


Figure S51. ^{13}C NMR spectrum (75.47 MHz) of **21** in CDCl_3 .

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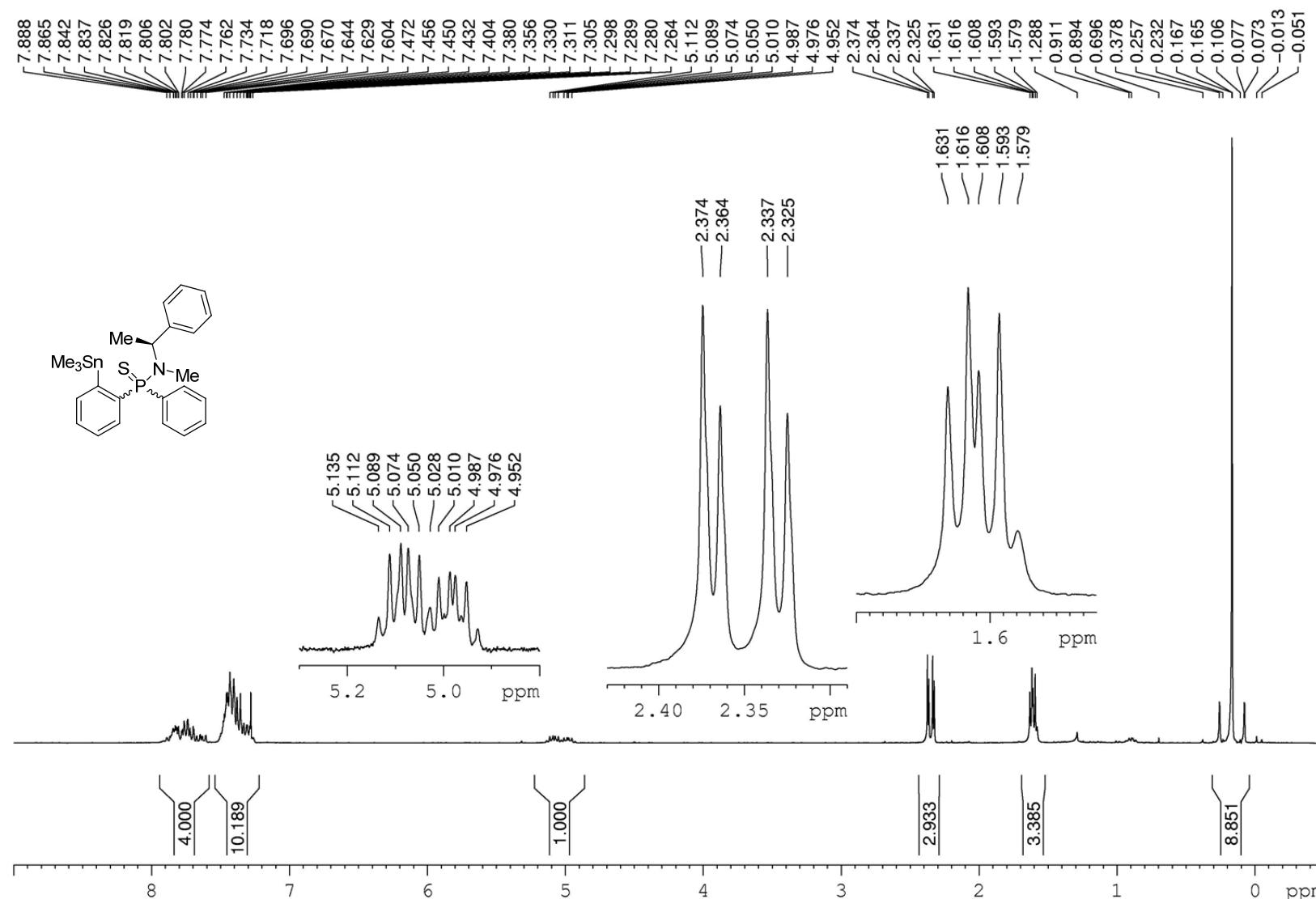


Figure S52. ^1H NMR spectrum (300.13 MHz) of **27** in CDCl_3 .

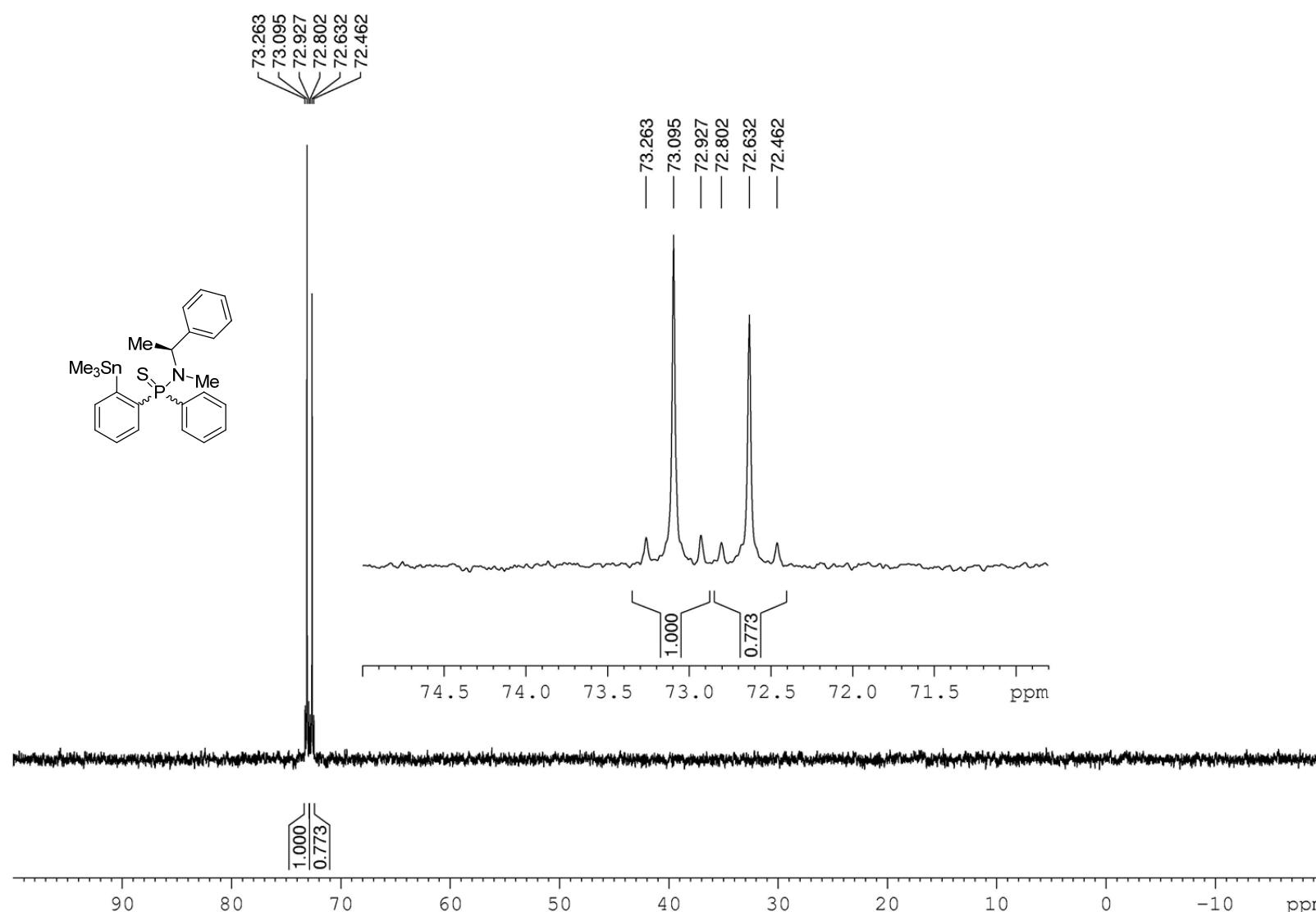


Figure S53. ^{31}P NMR spectrum (121.47 MHz) of **27** in CDCl_3 .

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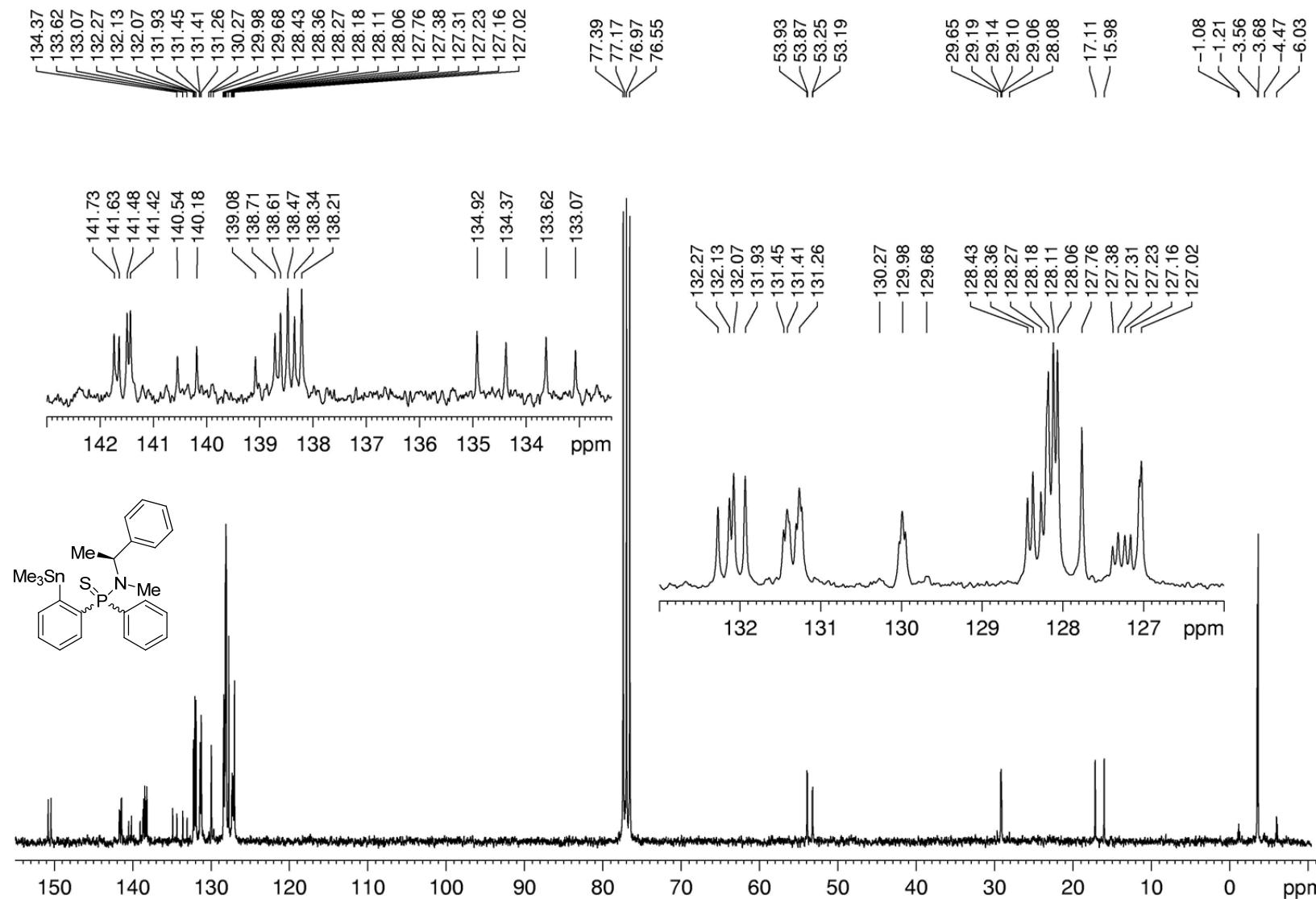


Figure S54. ^{13}C NMR spectrum (75.47 MHz) of **27** in CDCl_3 .

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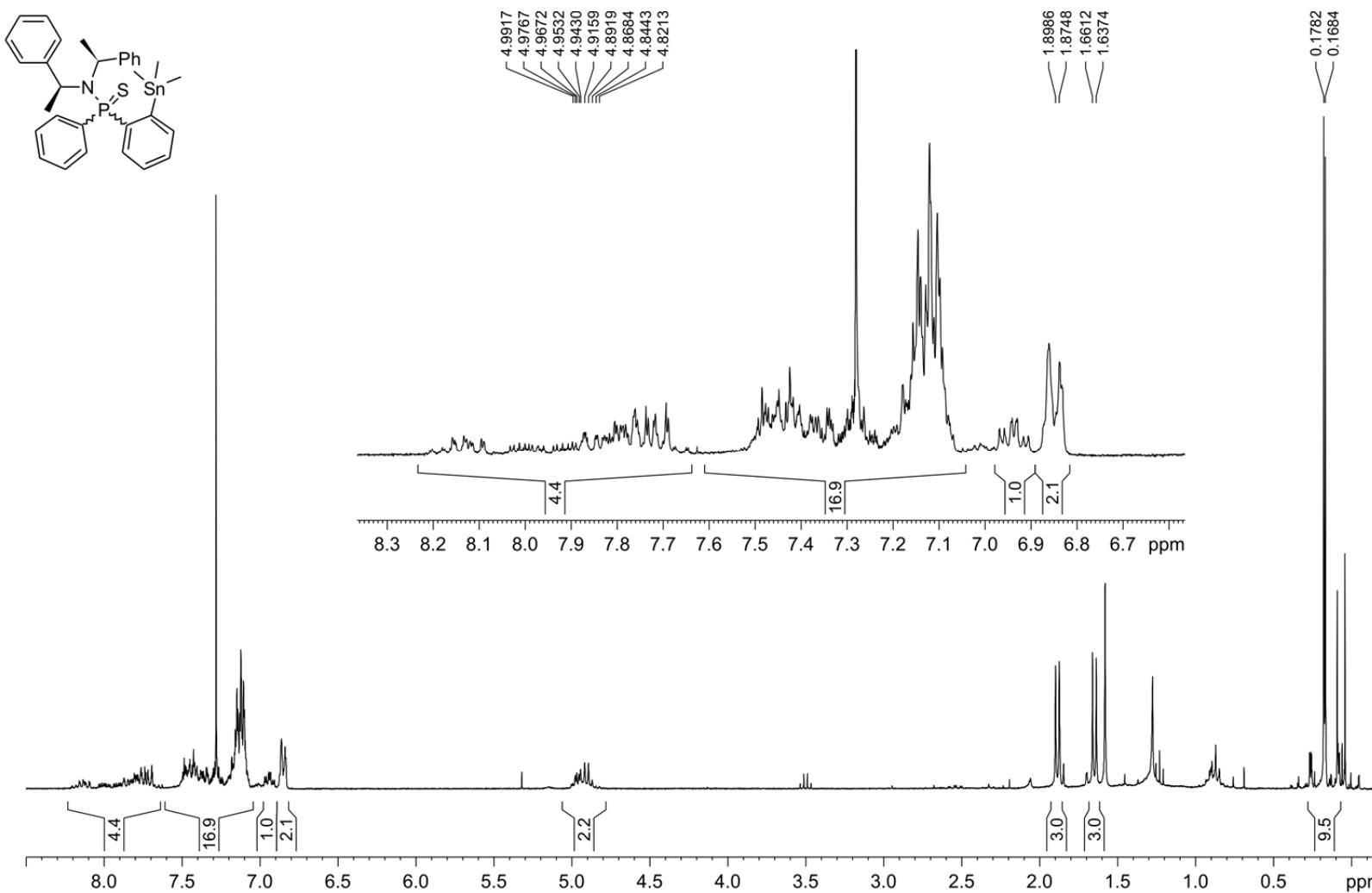


Figure S55. ^1H NMR spectrum (300.13 MHz) of **29** in CDCl_3 .

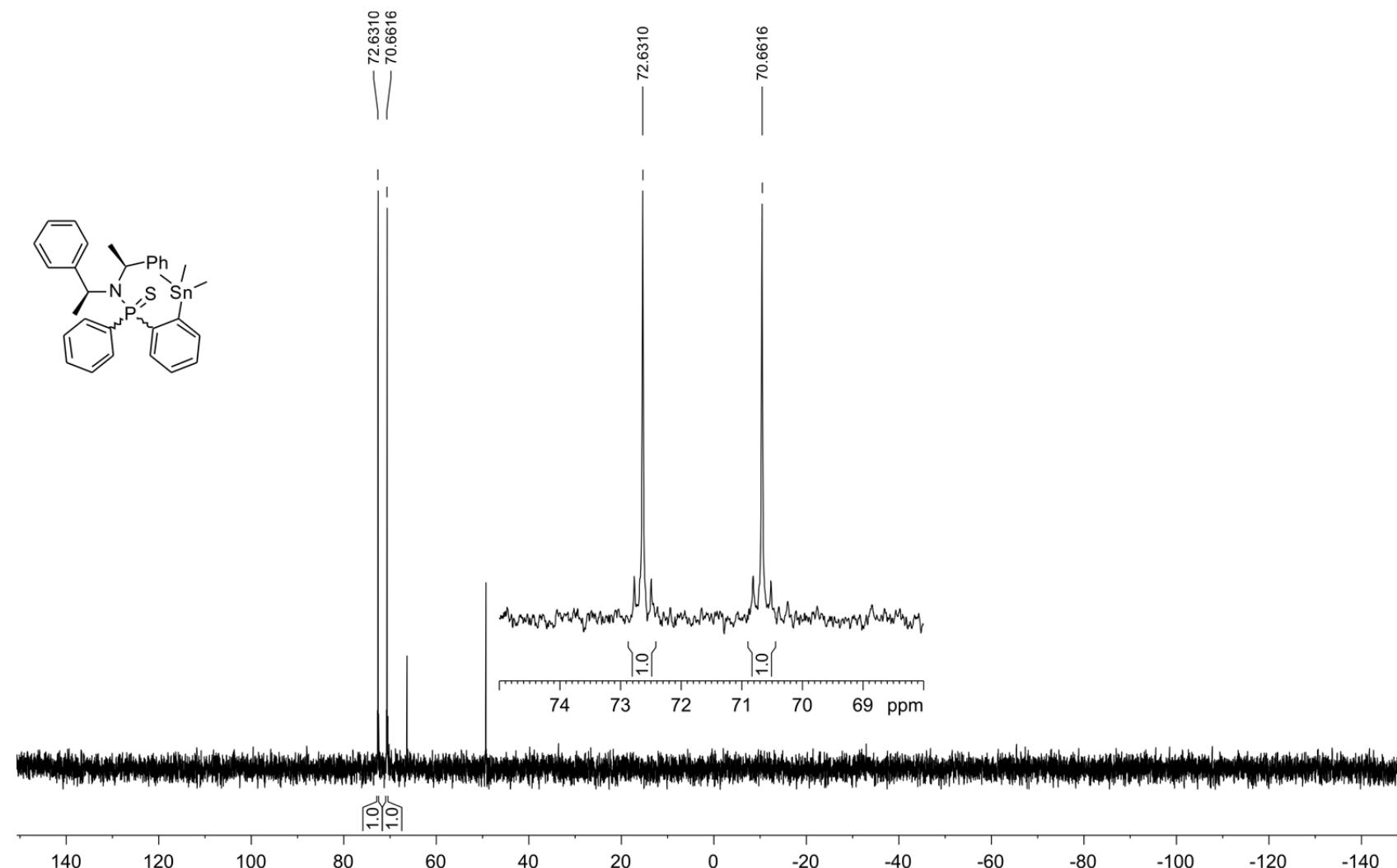


Figure S56. ^{31}P NMR spectrum (121.47 MHz) of **29** in CDCl_3 .

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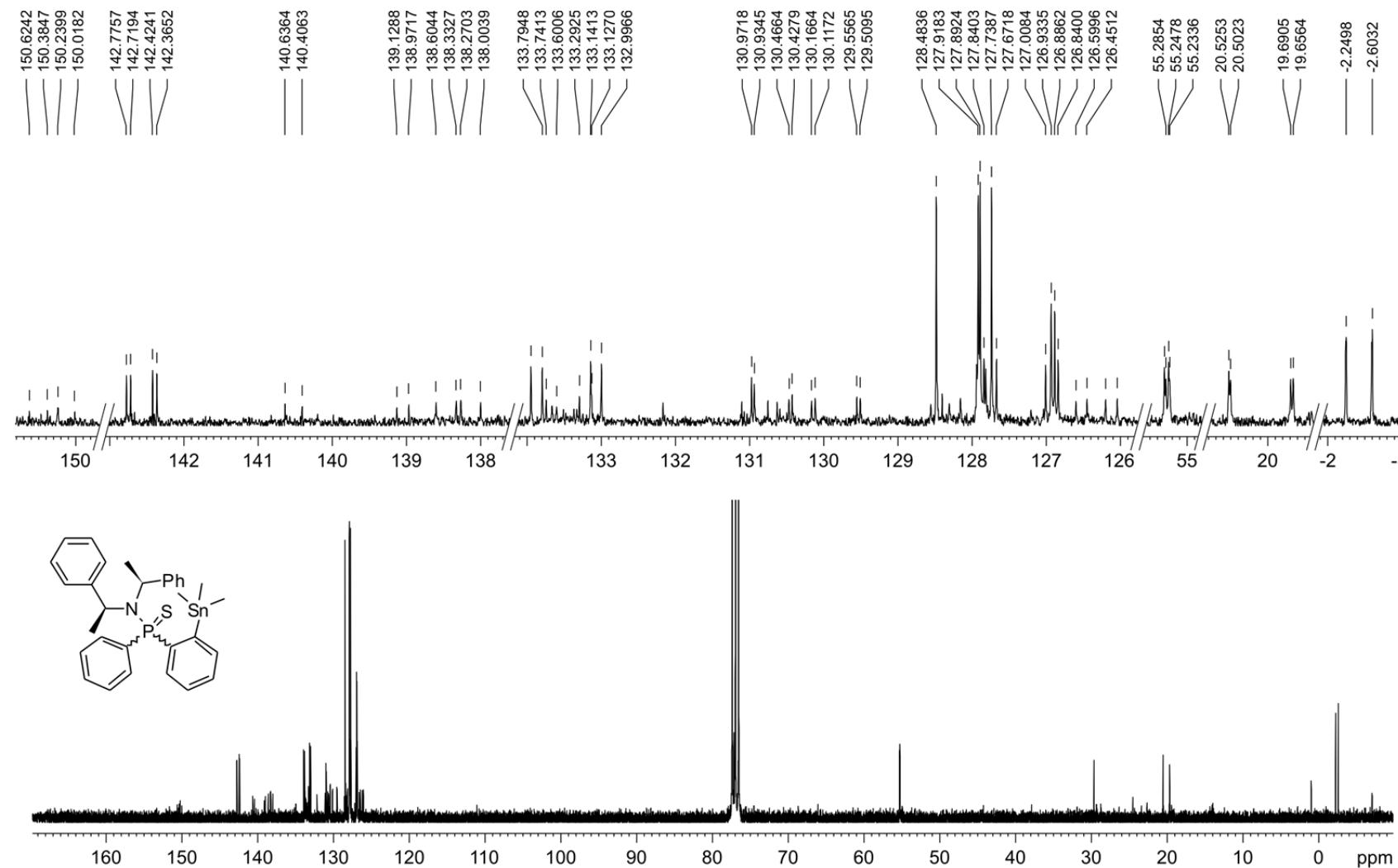


Figure S57. ^{13}C NMR spectrum (75.47 MHz) of **29** in CDCl_3 .

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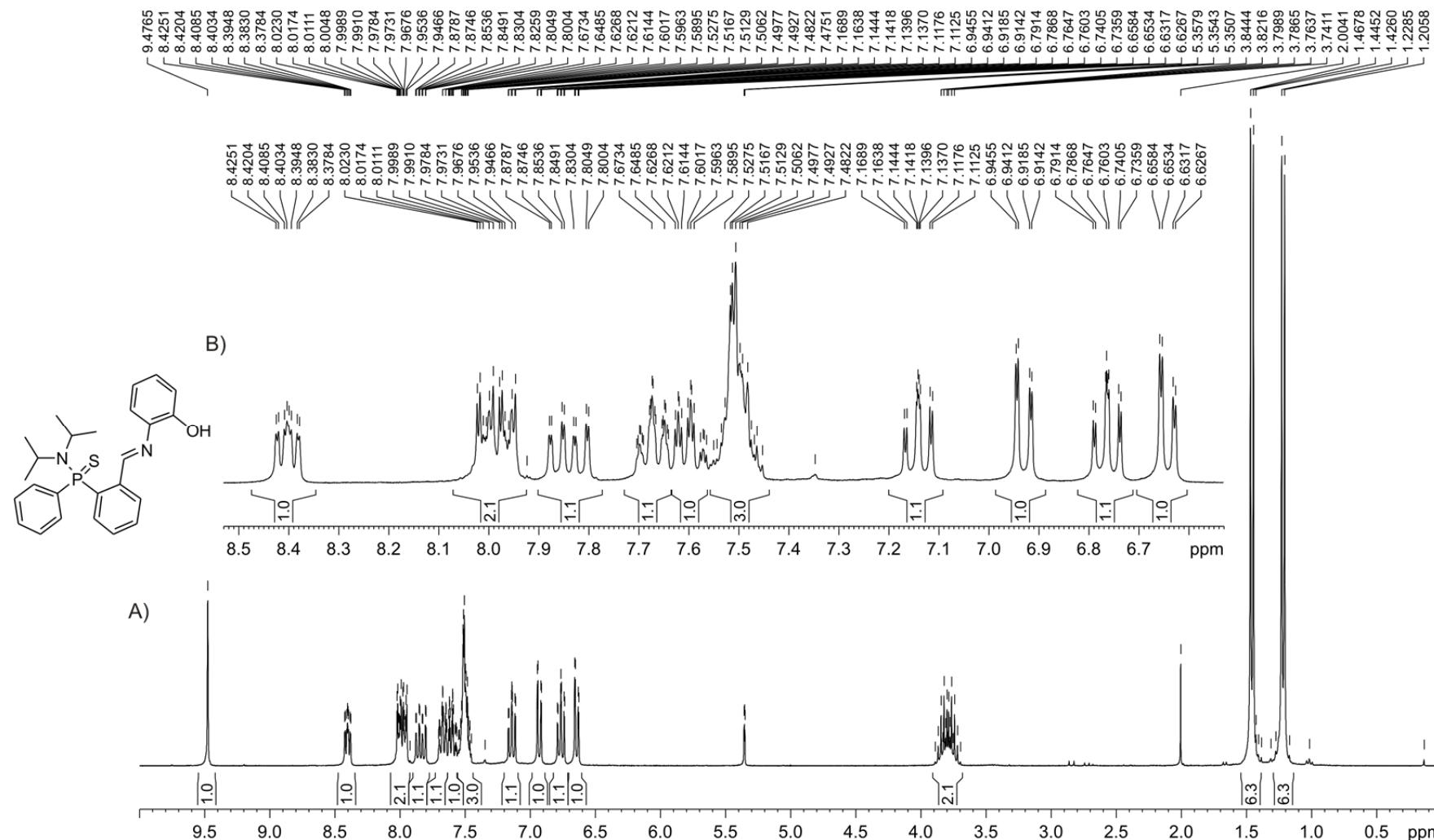


Figure S58. ¹H NMR spectrum (300.13 MHz) of **31** in CD₂Cl₂.

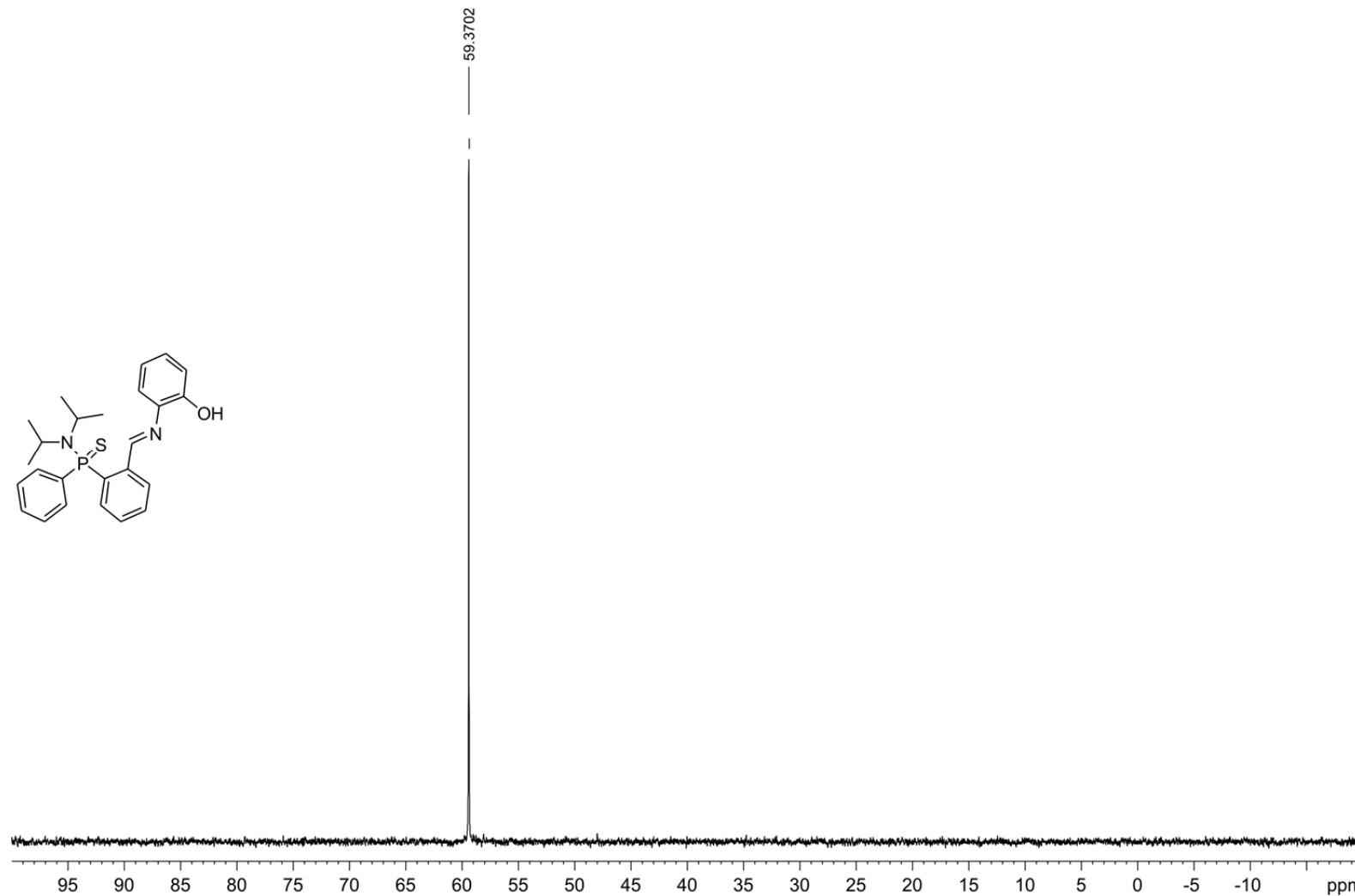


Figure S59. ^{31}P NMR spectrum (121.47 MHz) of **31** in CD_2Cl_2 .

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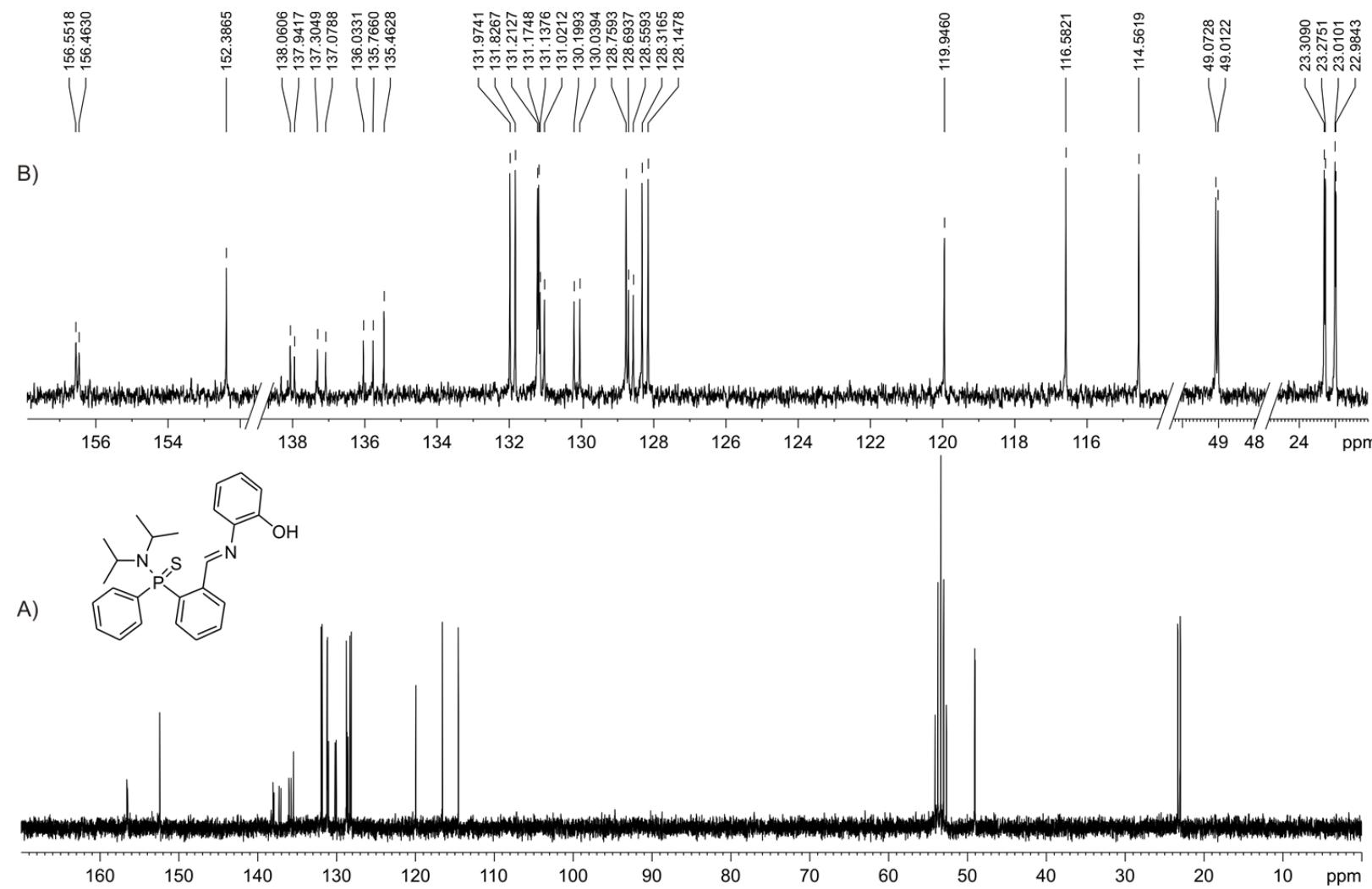


Figure S60. ^{13}C NMR spectrum (75.47 MHz) of **31** in CD_2Cl_2 .

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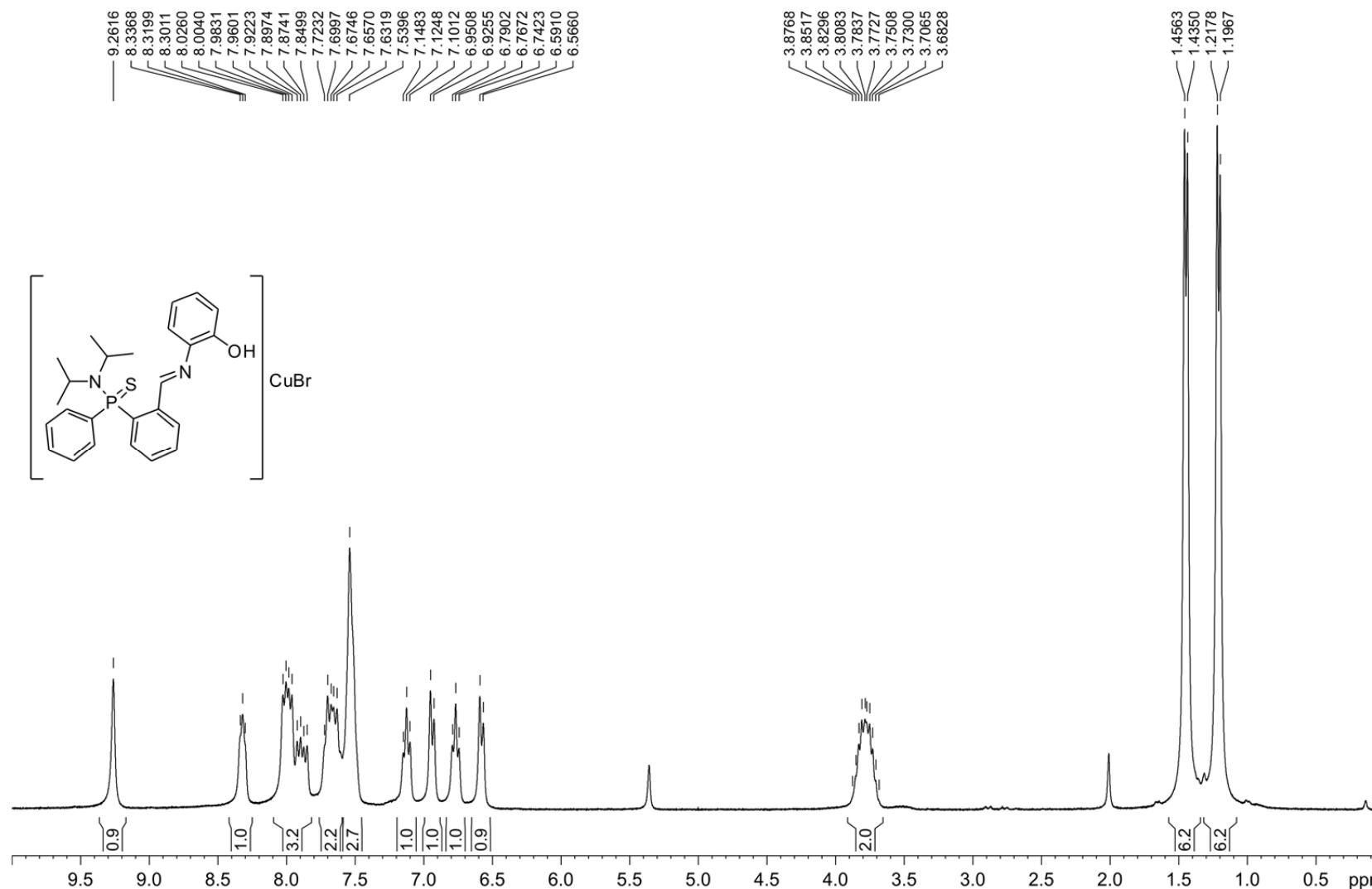


Figure S61. ¹H NMR spectrum (300.13 MHz) of **32** in CD_2Cl_2 .

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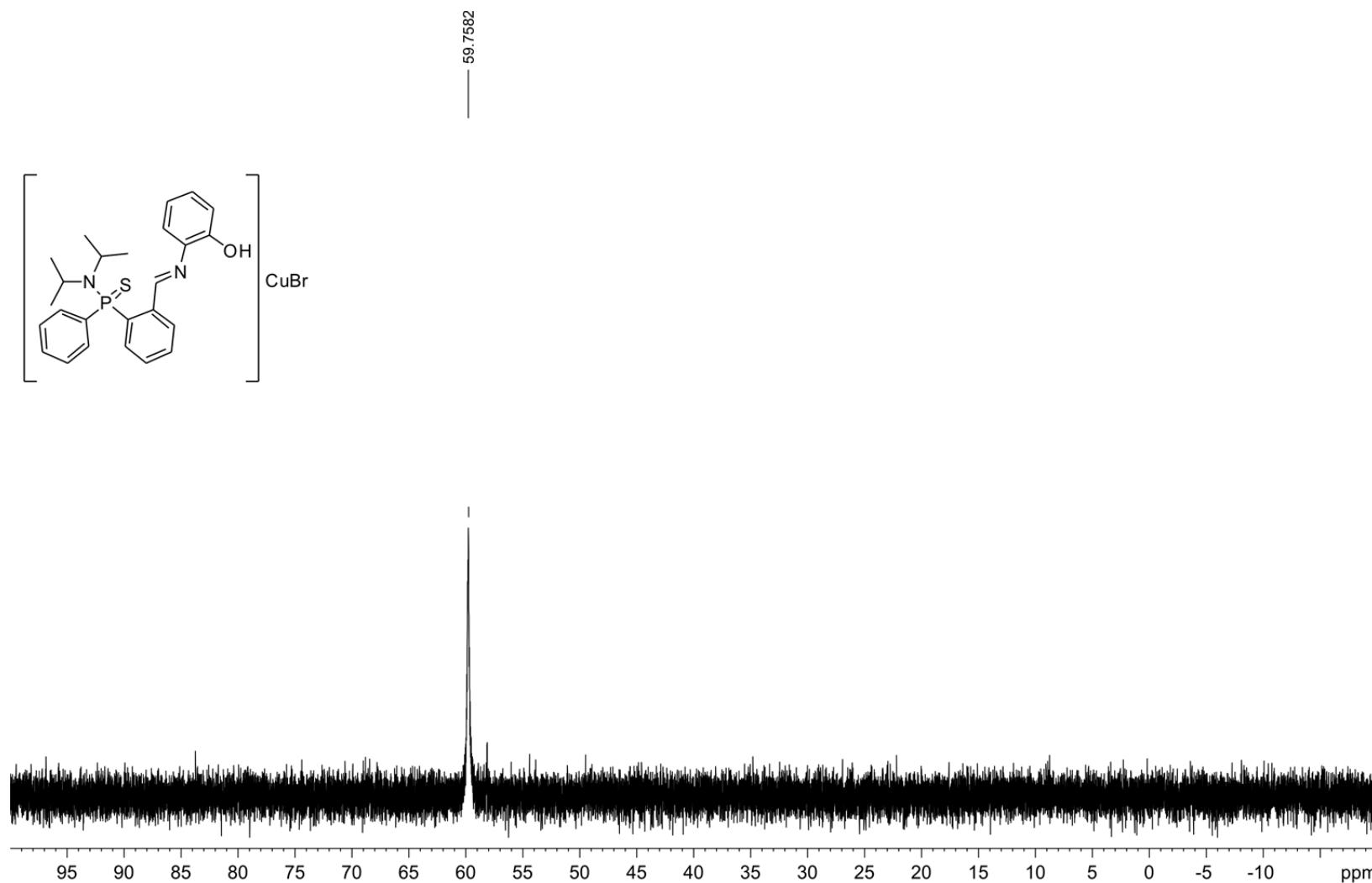


Figure S62. ³¹P NMR spectrum (121.47 MHz) of **32** in CD₂Cl₂

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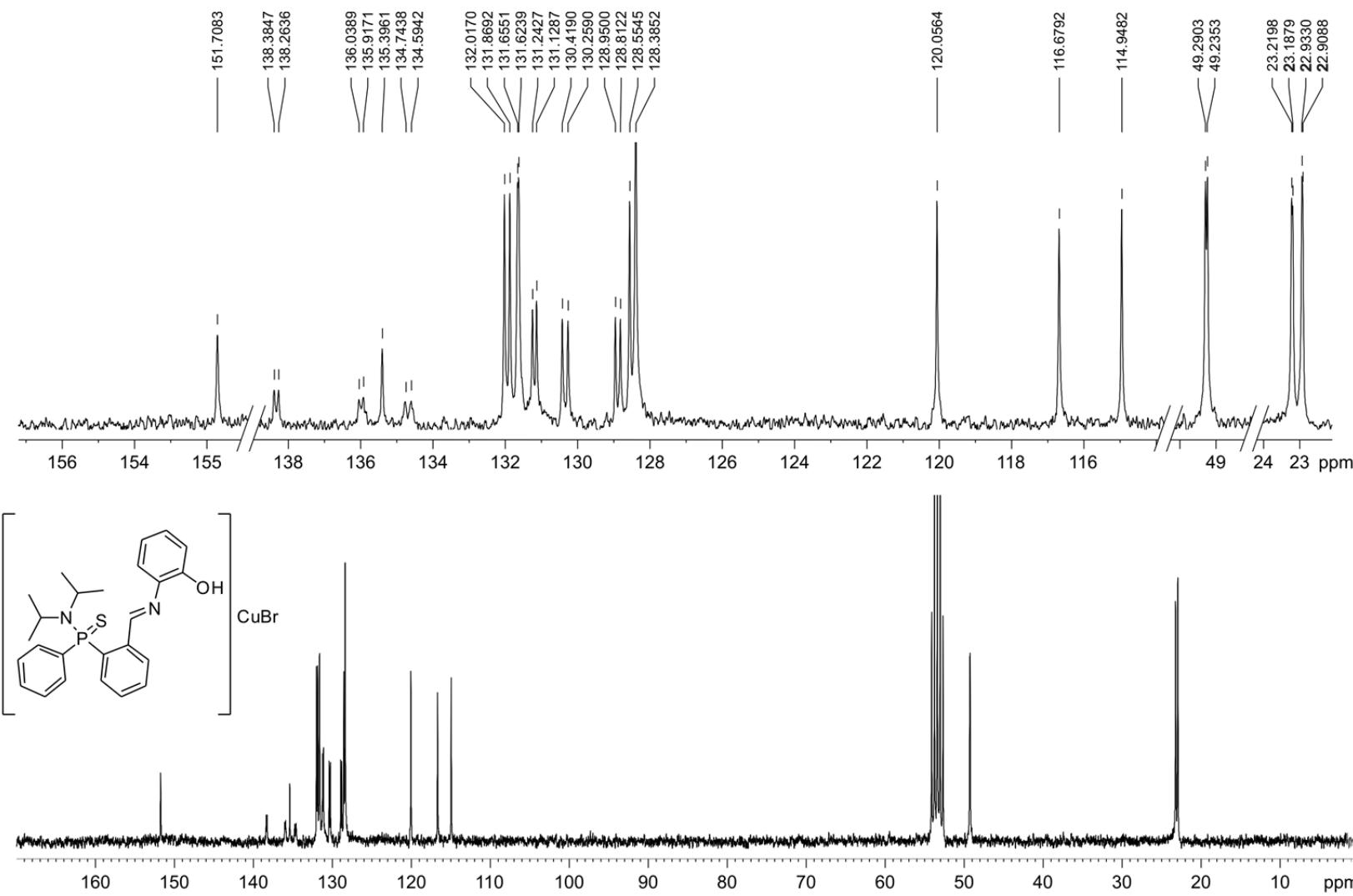


Figure S63. ¹³C NMR spectrum (75.47 MHz) of 32 in CD₂Cl₂.

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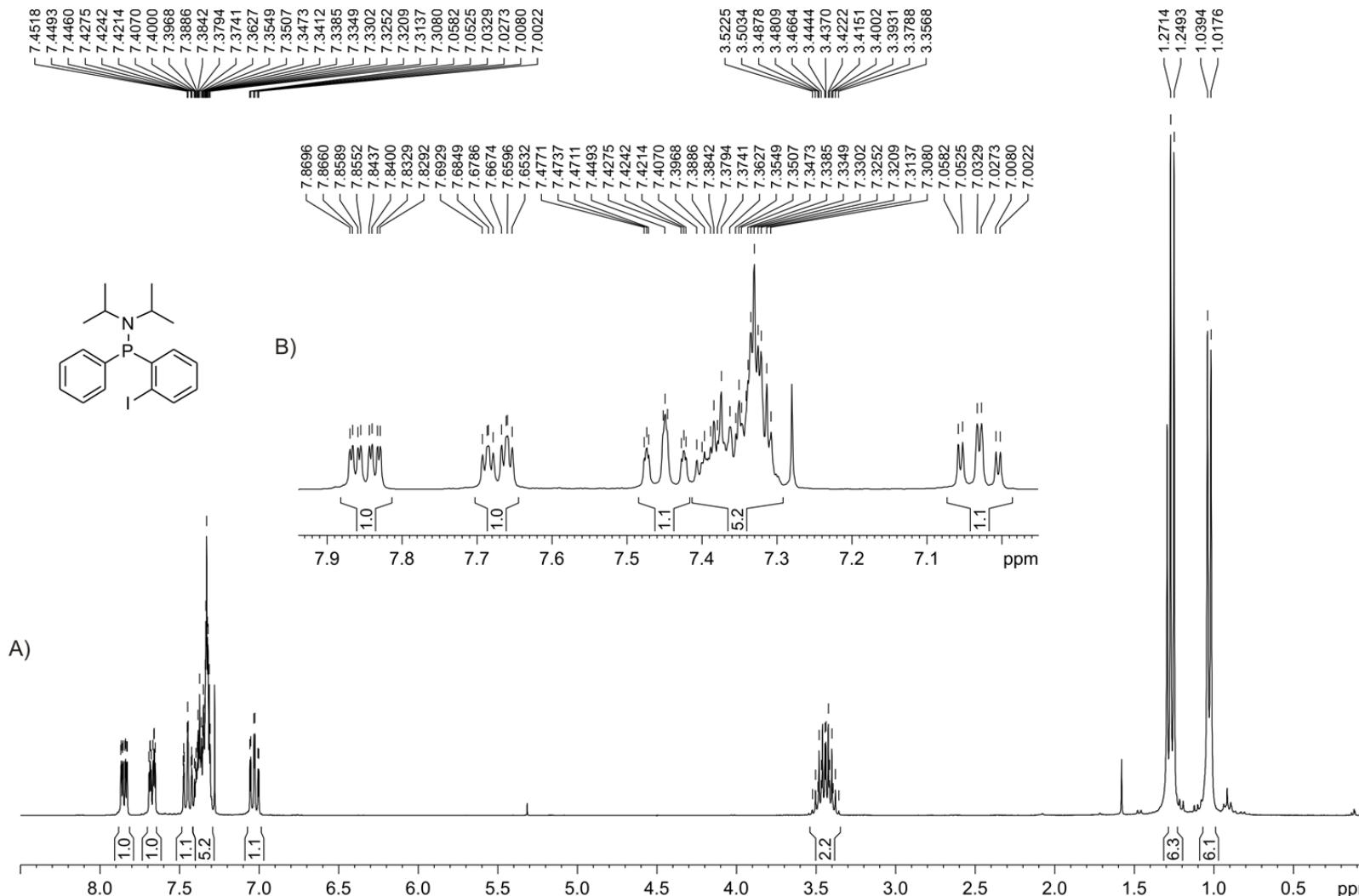


Figure S64. A) ^1H NMR spectrum (300.13 MHz) of **33** in CDCl_3 . B) Expansion of the aromatic region of A).

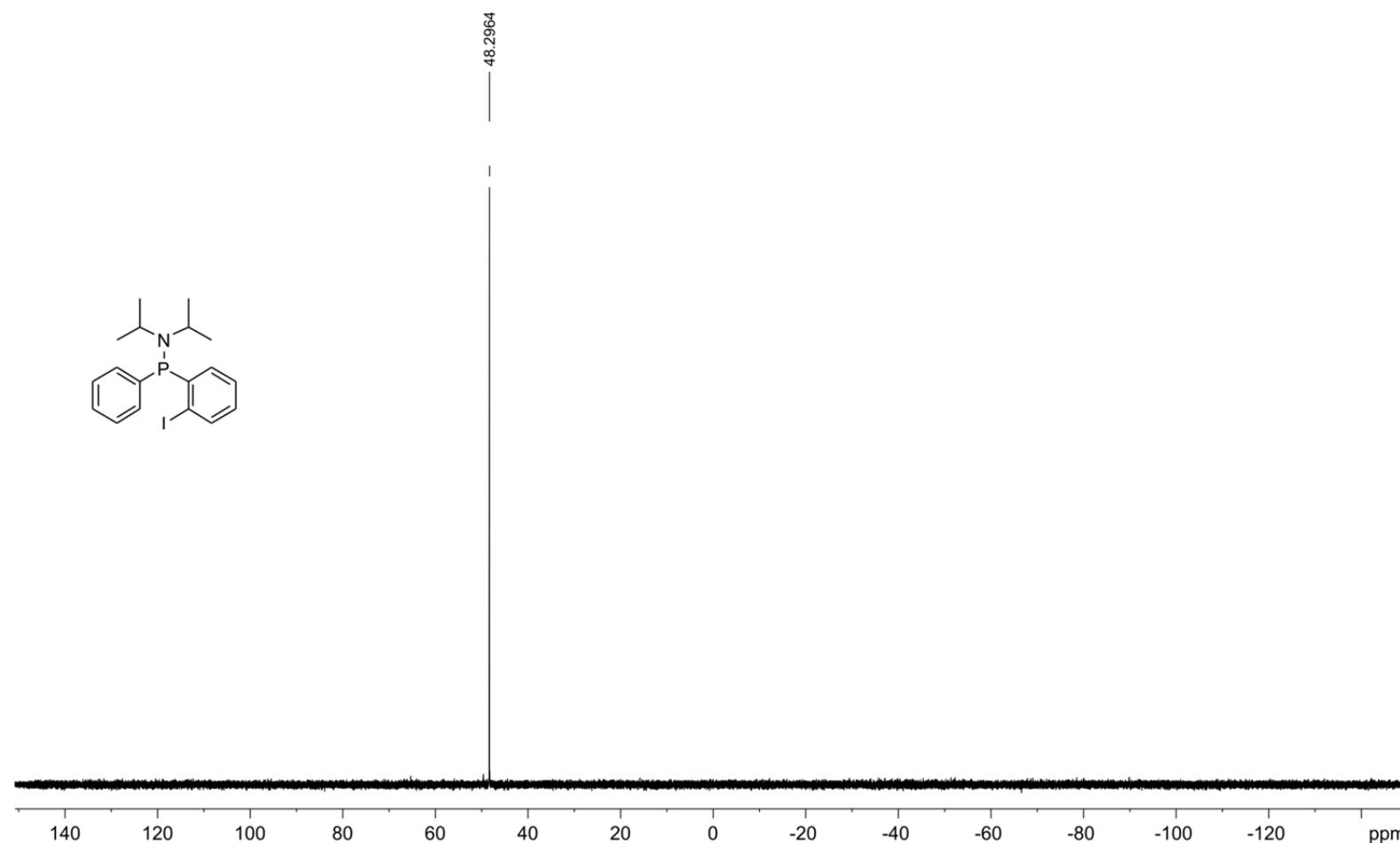


Figure S65. ^{31}P NMR spectrum (121.47 MHz) of **33** in CDCl_3 .

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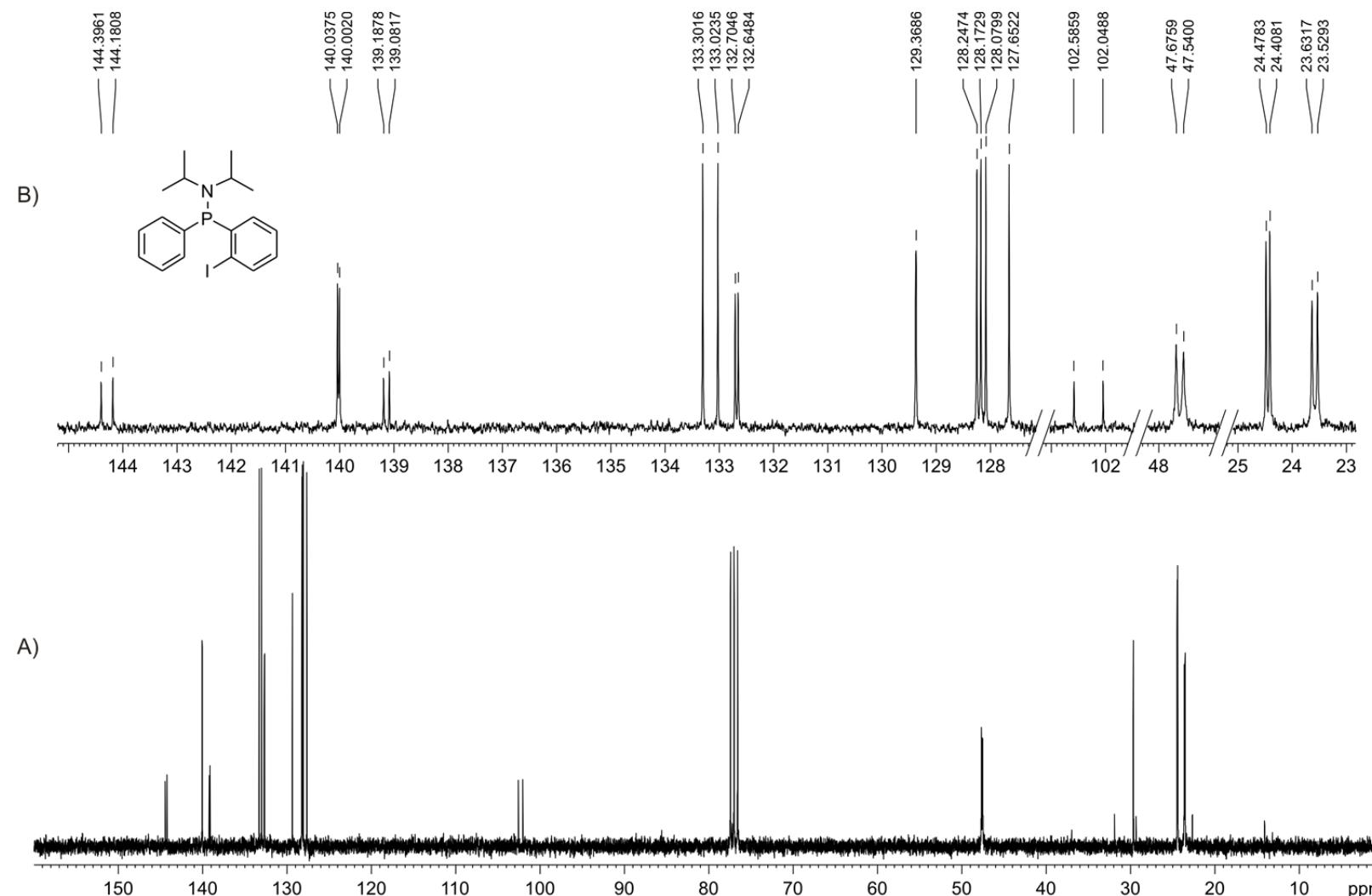


Figure S66. A) ^{13}C NMR spectrum (75.47 MHz) of **33** in CDCl_3 . B) Expansion of A).

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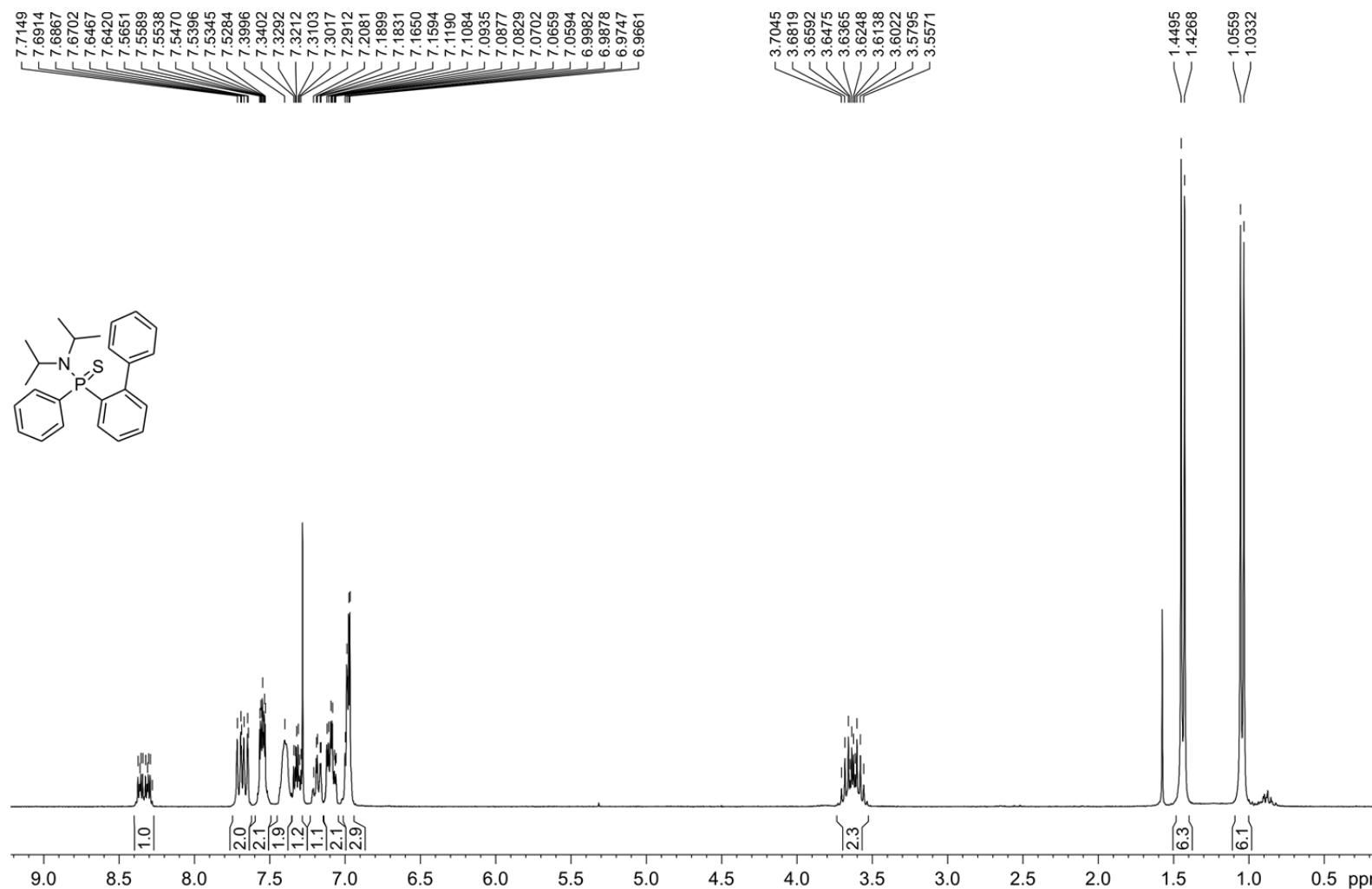


Figure S67. ^1H NMR spectrum (300.13 MHz) of **35** in CDCl_3 .

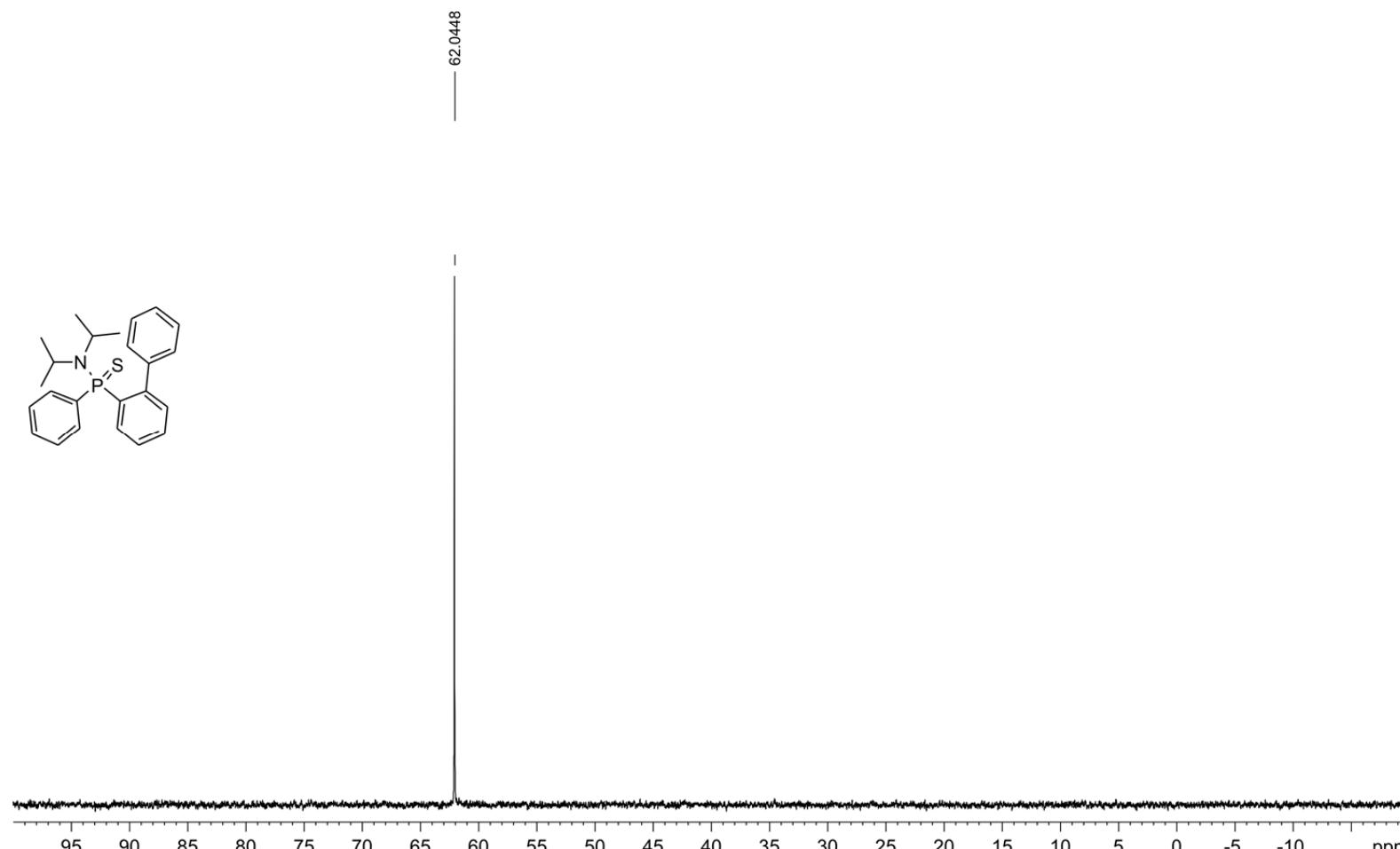


Figure S68. ^{31}P NMR spectrum (121.47 MHz) of **35** in CDCl_3 .

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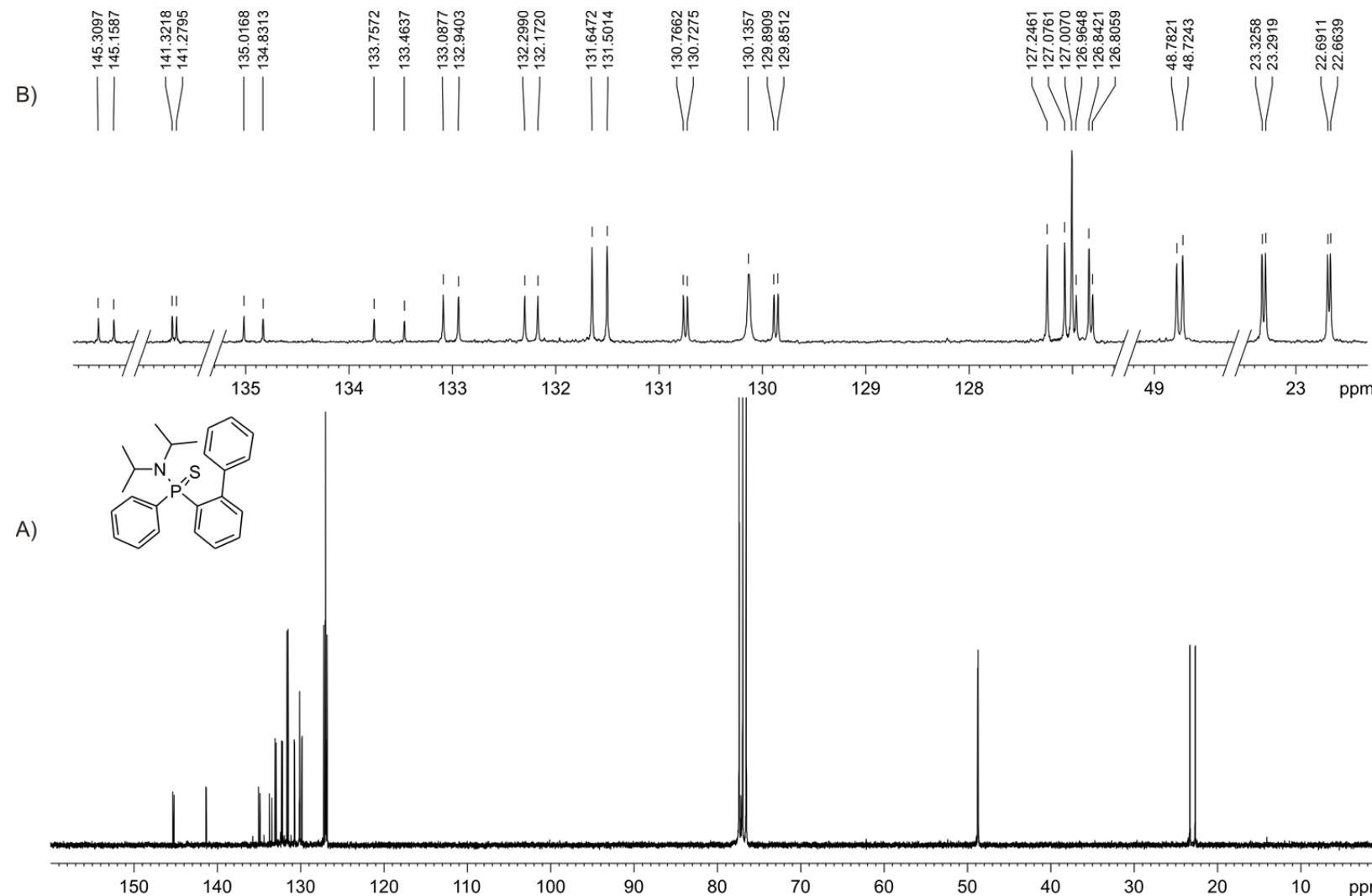


Figure S69. A) ^{13}C NMR spectrum (75.47 MHz) of **35** in CDCl_3 . B) Expansion of A).

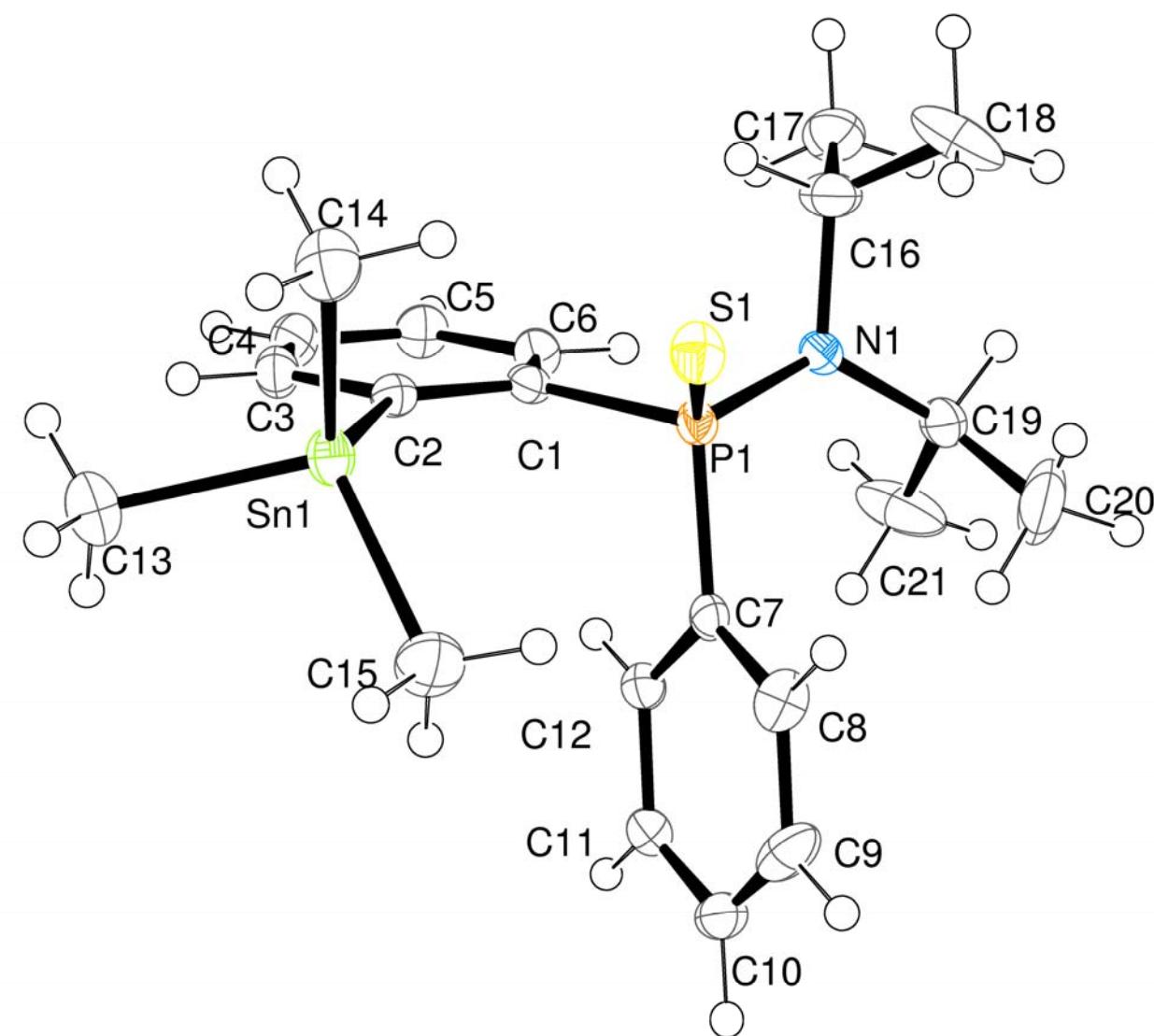


Figure S70. X-ray crystal structure of **9** (thermal ellipsoids shown at 50% probability) including atomic numbering.

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Table S1. Crystal data and structure refinement for **9**.

Empirical formula	C ₂₁ H ₃₂ NPSn		
Formula weight	480.20		
Temperature	100(2) K		
Wavelength	1.54184 Å		
Crystal system	P2 ₁ /c		
Space group	monoclinic		
Unit cell dimensions	a = 10.6237(1) Å	α= 90°.	
	b = 16.3773(2) Å	β= 125.406(1)°.	
	c = 15.8989(2) Å	γ = 90°.	
Volume	2254.65(4) Å ³		
Z	4		
Density (calculated)	1.415 Mg/m ³		
Absorption coefficient	10.562 mm ⁻¹		
F(000)	984		
Crystal size	0.27 x 0.14 x 0.13 mm ³		
Theta range for data collection	4.35 to 68.55°.		
Index ranges	-12<=h<=12, -18<=k<=19, -19<=l<=18		
Reflections collected	14406		
Independent reflections	4097 [R(int) = 0.0327]		
Completeness to theta = 67.50°	99.6 %		
Absorption correction	Empirical		
Max. and min. transmission	1.000 and 0.5559		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	4097 / 0 / 226		
Goodness-of-fit on F ²	1.045		
Final R indices [I>2sigma(I)]	R1 = 0.0272, wR2 = 0.0686		
R indices (all data)	R1 = 0.0301, wR2 = 0.0708		
Largest diff. peak and hole	0.439 and -0.931 e.Å ⁻³		

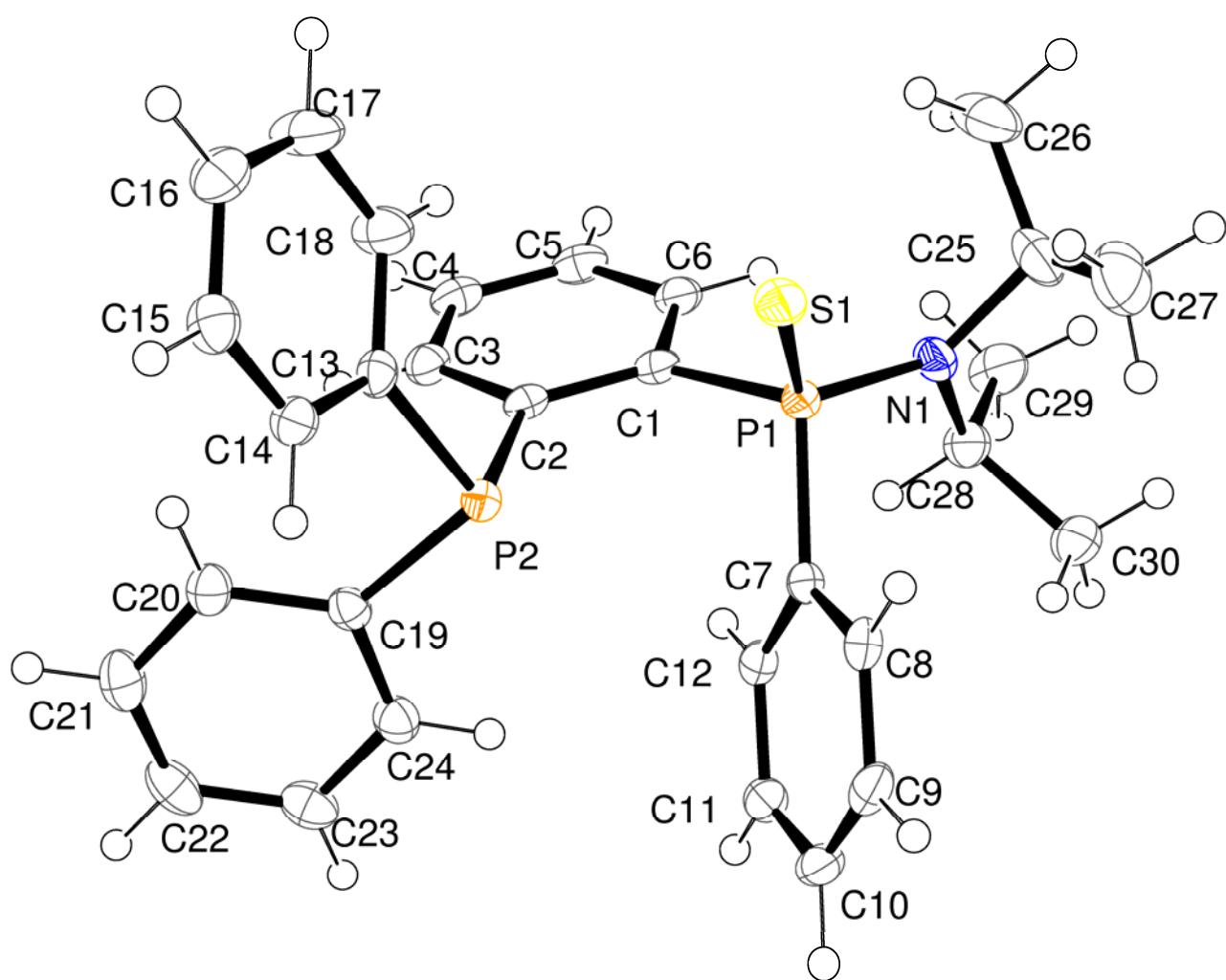


Figure S71. X-ray crystal structure of **12** (thermal ellipsoids shown at 50% probability) including atomic numbering.

Transformations of diphenylphosphinothioic acid...

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Table S2. Crystal data and structure refinement for compound **12**.

Empirical formula	C ₃₀ H ₃₃ N P ₂ S		
Formula weight	501.57		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P 21/c		
Unit cell dimensions	a = 13.6300(5) Å	α= 90°.	
	b = 10.2681(3) Å	β= 119.548(2)°.	
	c = 22.3237(6) Å	γ = 90°.	
Volume	2717.96(15) Å ³		
Z	4		
Density (calculated)	1.226 Mg/m ³		
Absorption coefficient	0.256 mm ⁻¹		
F(000)	1064		
Crystal size	1.41 x 0.429 x 0.339 mm ³		
Theta range for data collection	1.72 to 24.42°.		
Index ranges	-15<=h<=15, -11<=k<=11, -25<=l<=22		
Reflections collected	13903		
Independent reflections	4468 [R(int) = 0.0906]		
Completeness to theta = 24.42°	99.9 %		
Absorption correction	Refined		
Max. and min. transmission	1.0473 and 0.6756		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	4468 / 0 / 311		
Goodness-of-fit on F ²	1.027		
Final R indices [I>2sigma(I)]	R1 = 0.0423, wR2 = 0.1080		
R indices (all data)	R1 = 0.0443, wR2 = 0.1095		
Largest diff. peak and hole	0.620 and -0.377 e.Å ⁻³		