Supporting Information

for

The Bis(biphenyl)phosphorus Fragment in Trivalent and Tetravalent P-Environments

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NMR Spectra

Dichloro-*N*,*N*-diisopropylphosphanamine (**A**)

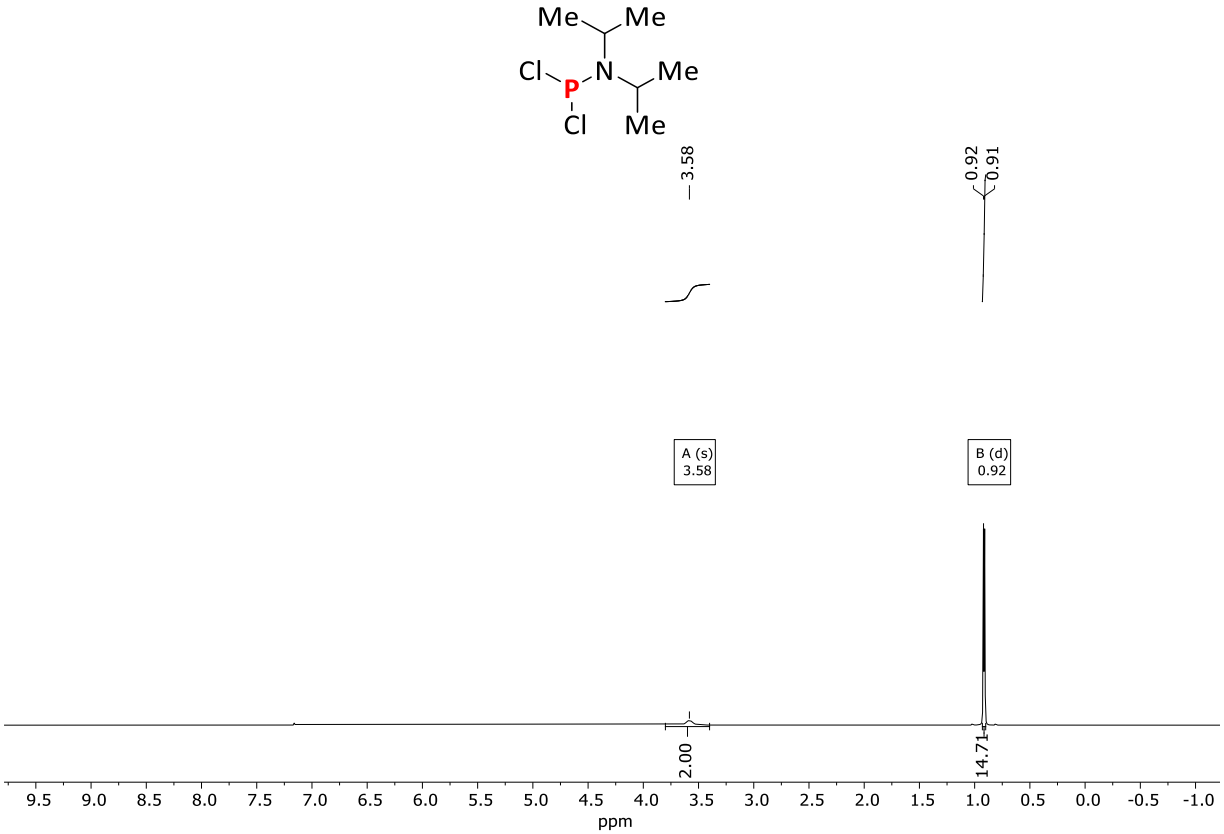

Fig SI 1: ^{1}H NMR (600 MHz) of compound **A** in benzene-d_6.

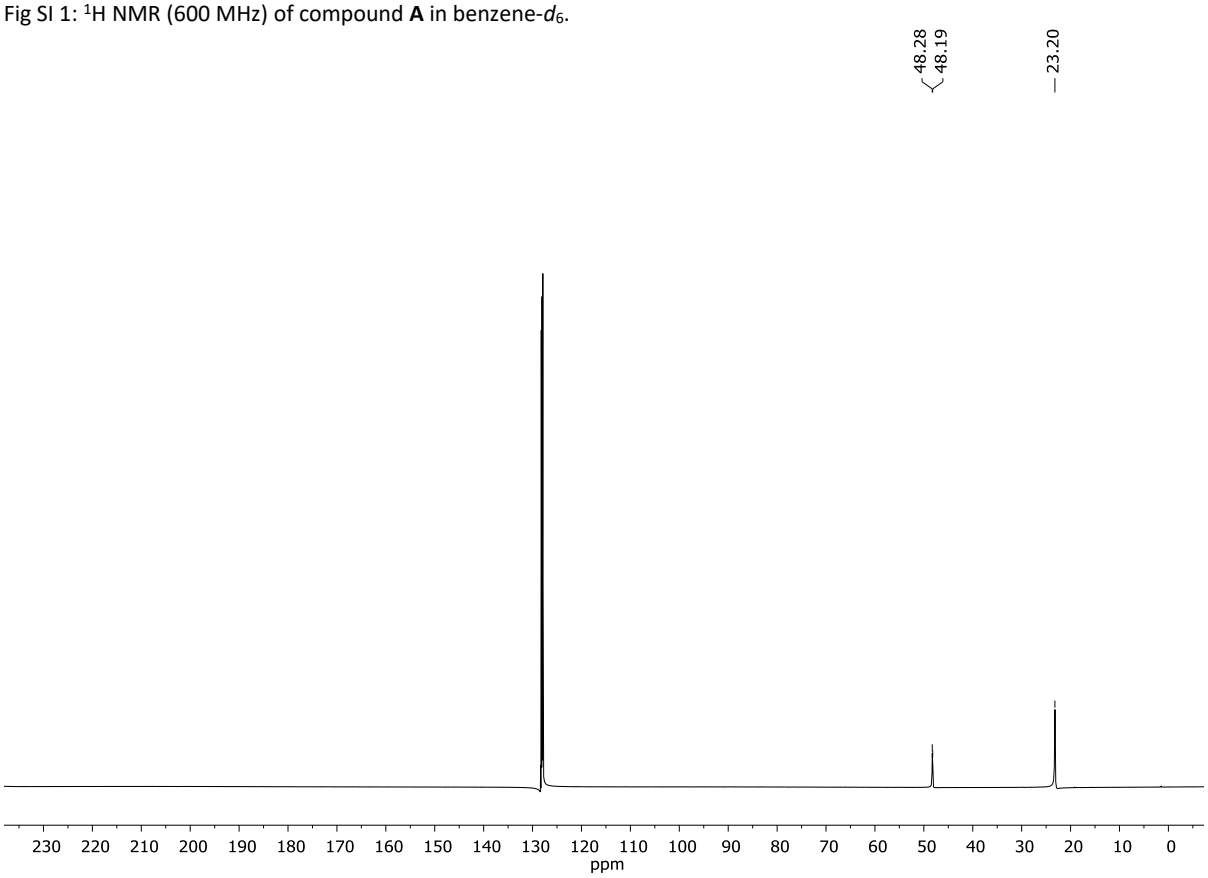

Fig SI 2: ^{13}C{^{1}H} NMR (151 MHz) of compound **A** in benzene-d_6.

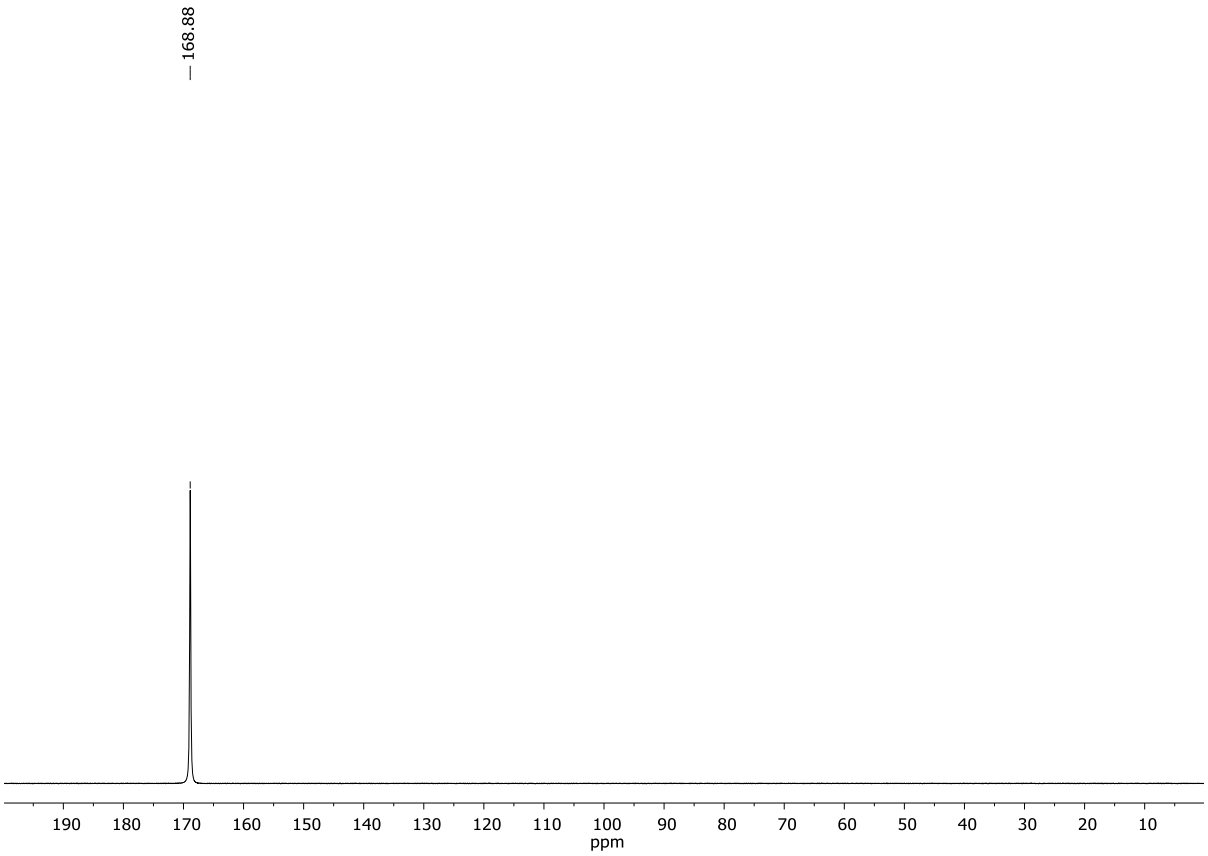

Fig SI 3: $^{31}P\{^{1}H\}$ NMR (243 MHz) of compound **A** in benzene-d_6.

bis(Biphenyl-2-yl)-*N*,*N*-di*iso*propylphosphanamine (**B**)

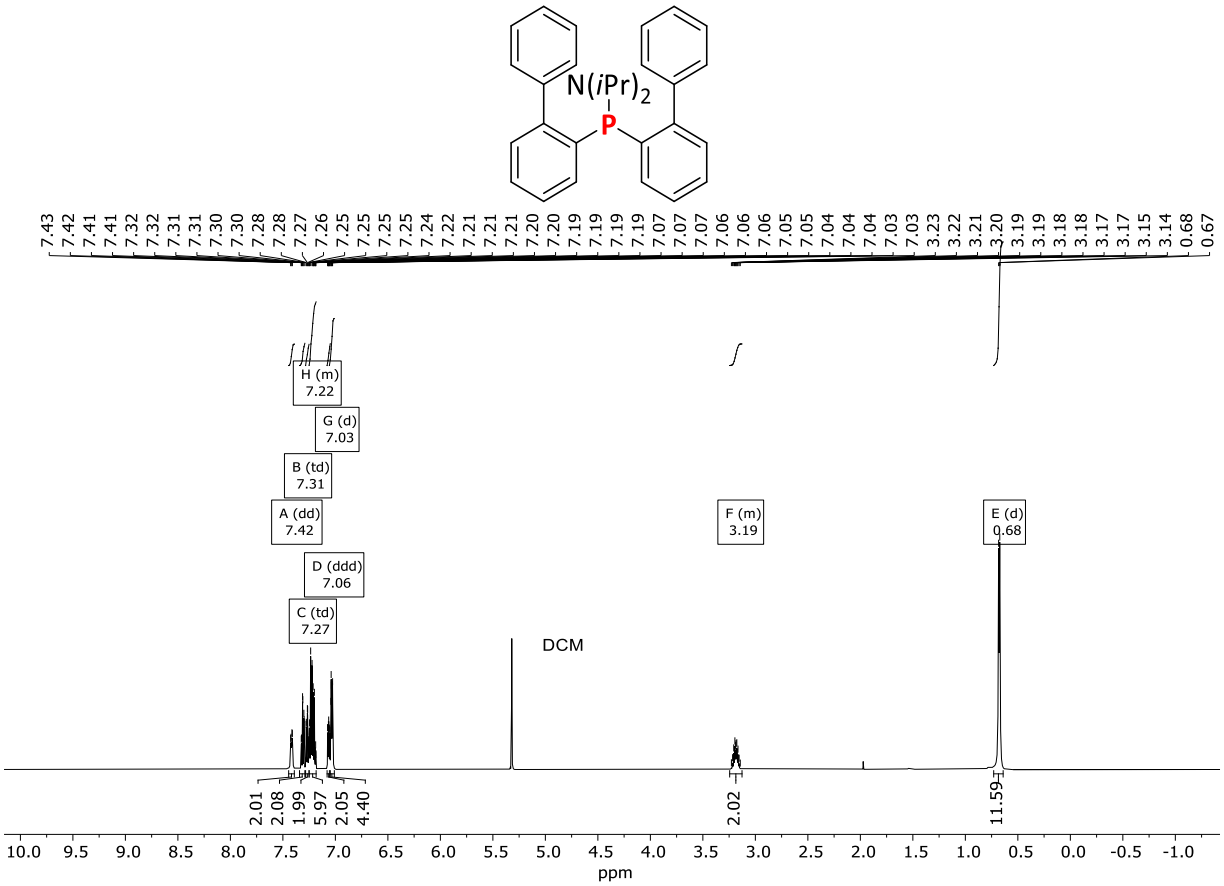

Fig SI 4: ^{1}H NMR (600 MHz) of compound **B** in dichloromethane-d_2.

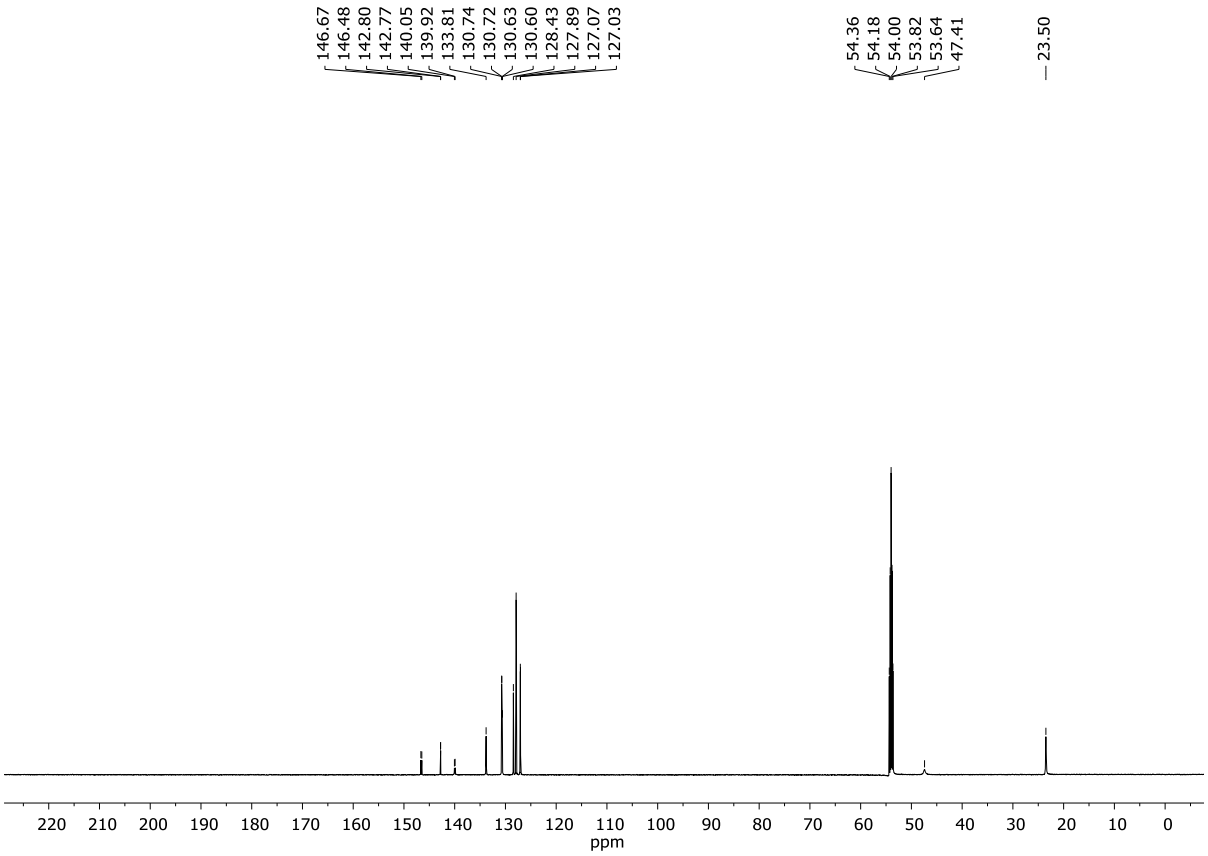

Fig SI 5: $^{13}C\{^{1}H\}$ NMR (151 MHz) of compound **B** in dichloromethane-d_2.

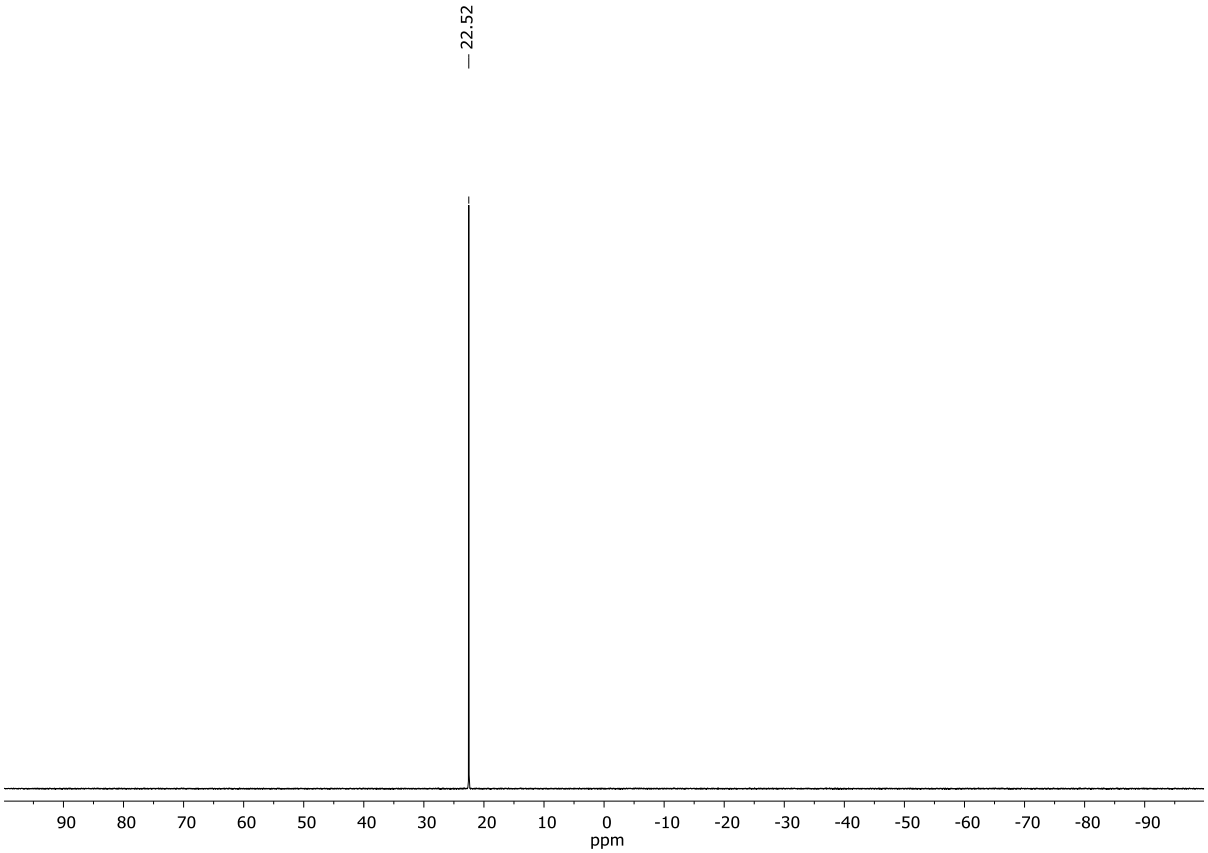

Fig SI 6: $^{31}P\{^{1}H\}$ NMR (243 MHz) of compound **B** in dichloromethane-d_2.

bis(Biphenyl-2-yl)chlorophosphine (**C**)

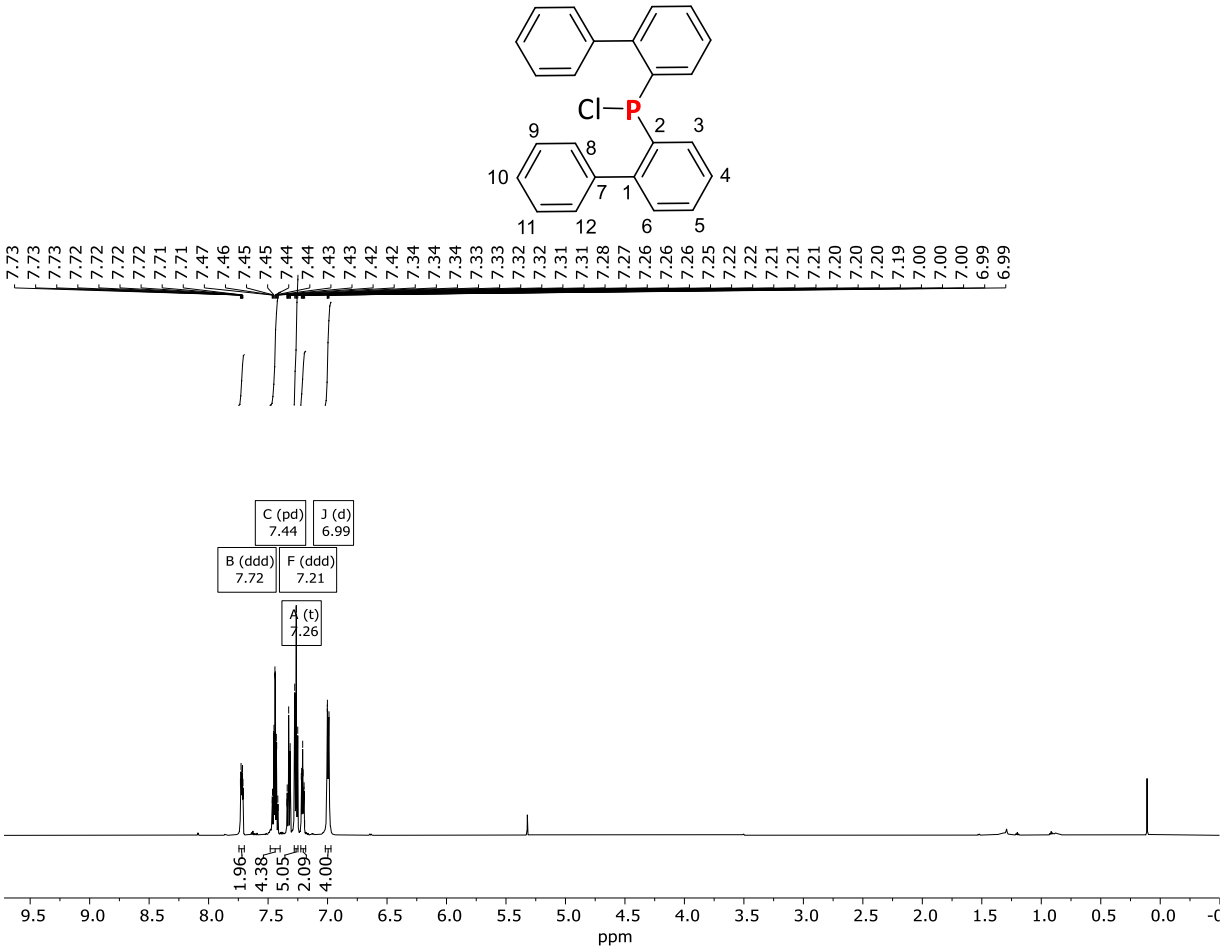

Fig SI 7: ^{1}H NMR (600 MHz) of compound **C** in benzene-d_6.

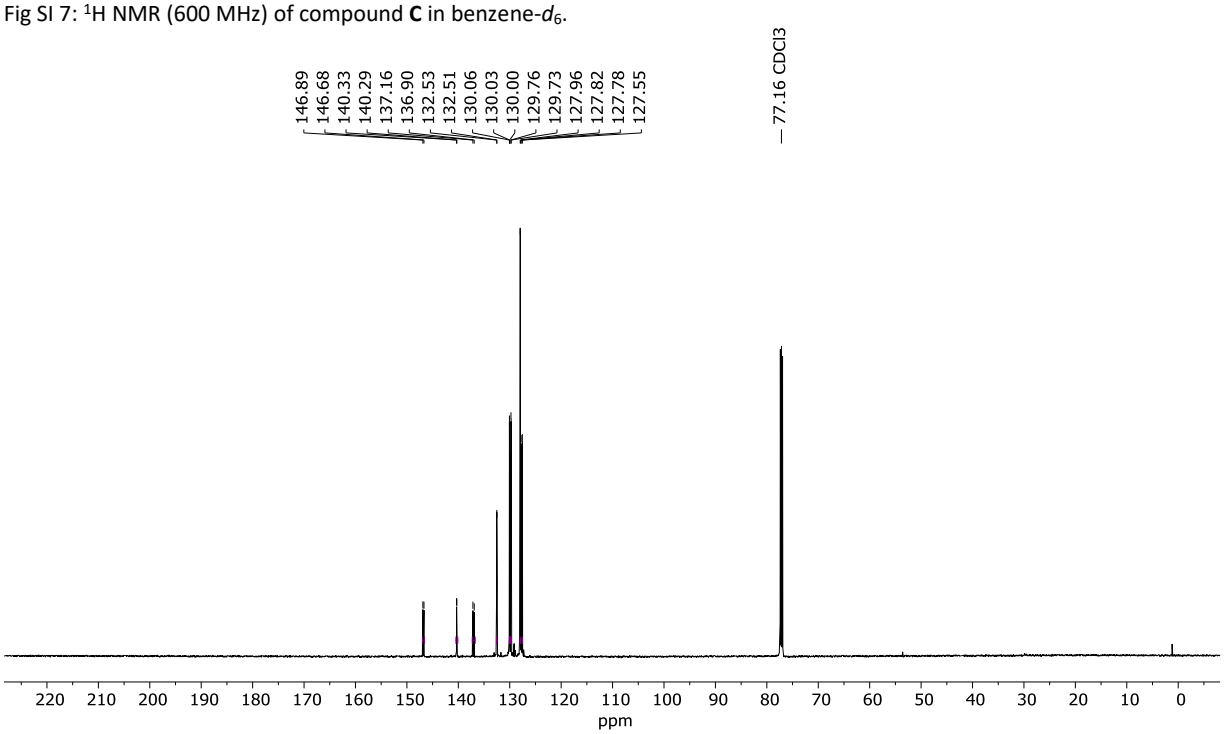

Fig SI 8: ^{13}C{^{1}H} NMR (151 MHz) of compound **C** in chloroform-*d*.

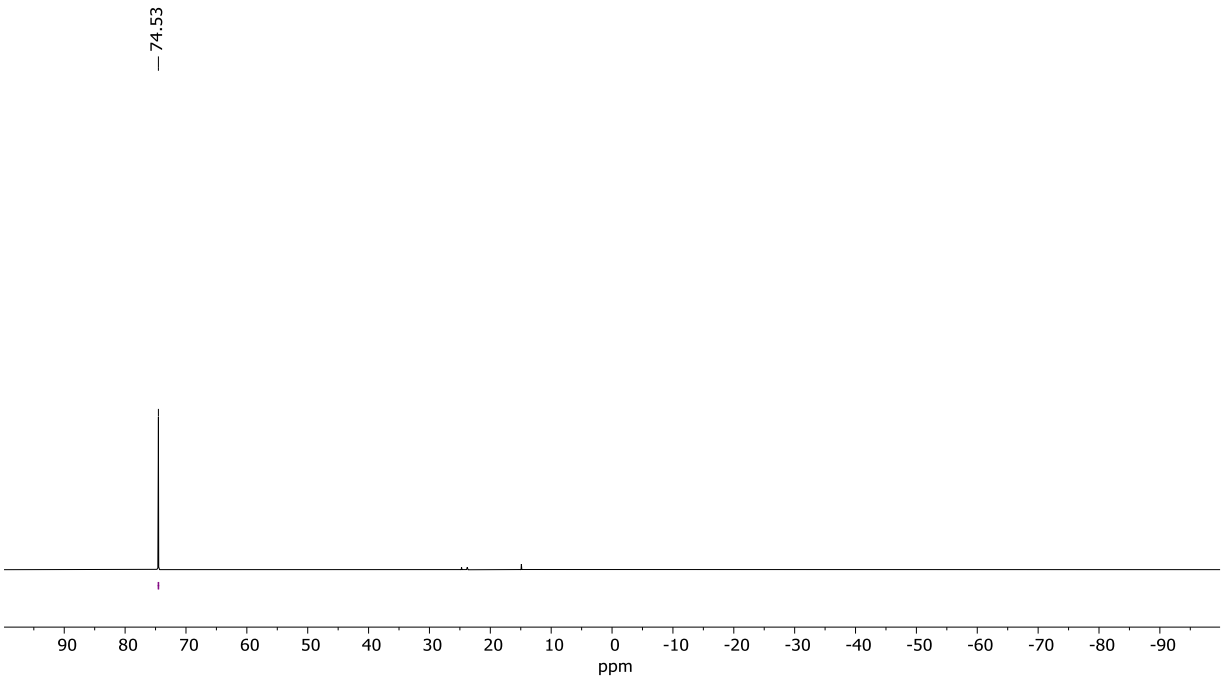

Fig SI 9: $^{31}P\{^{1}H\}$ NMR (243 MHz) of compound **D** in chloroform-*d*.

bis(Biphenyl-2-yl)phosphine (**D**)

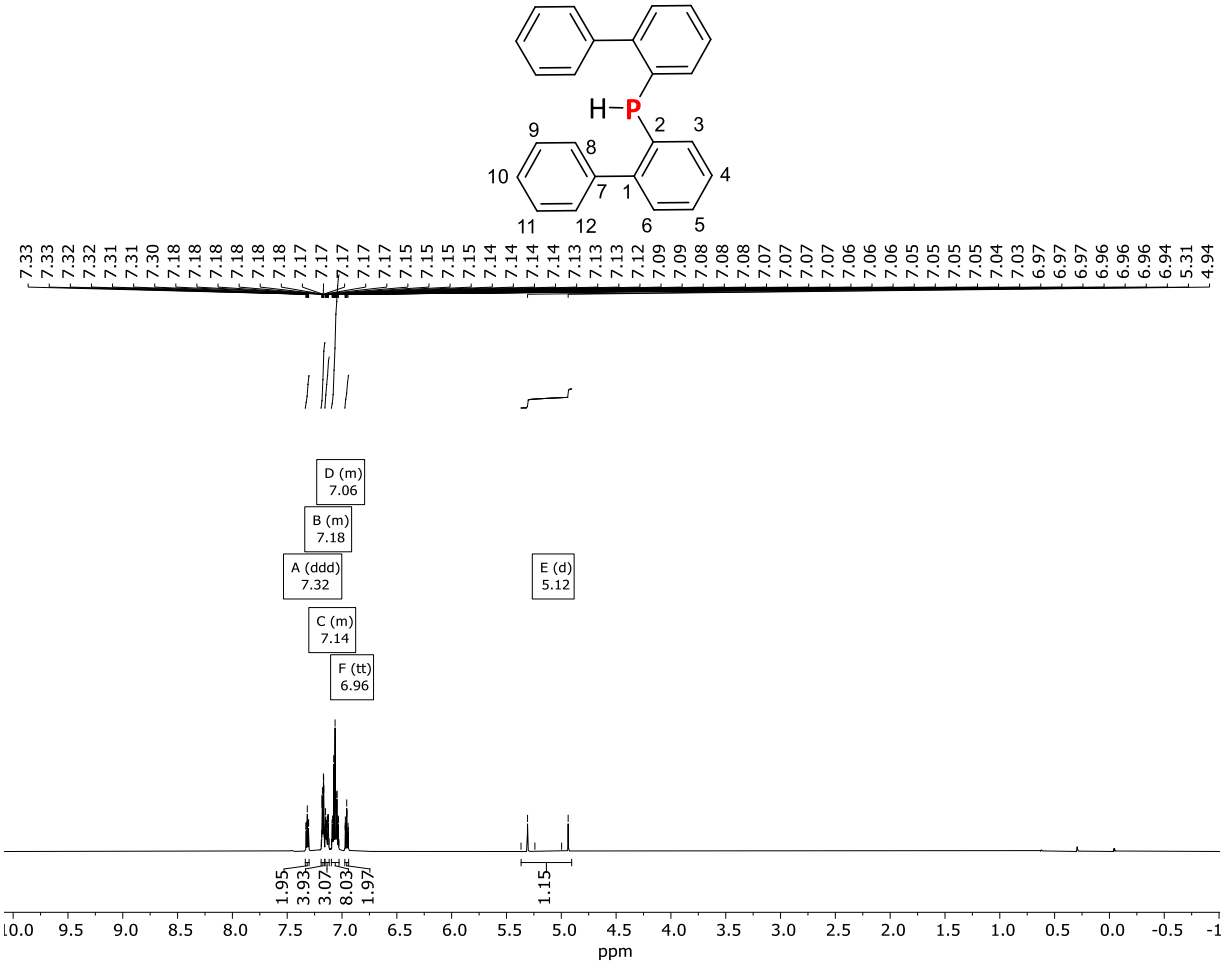

Fig SI 10: ^{1}H NMR (600 MHz) of compound **D** in benzene-d_6.

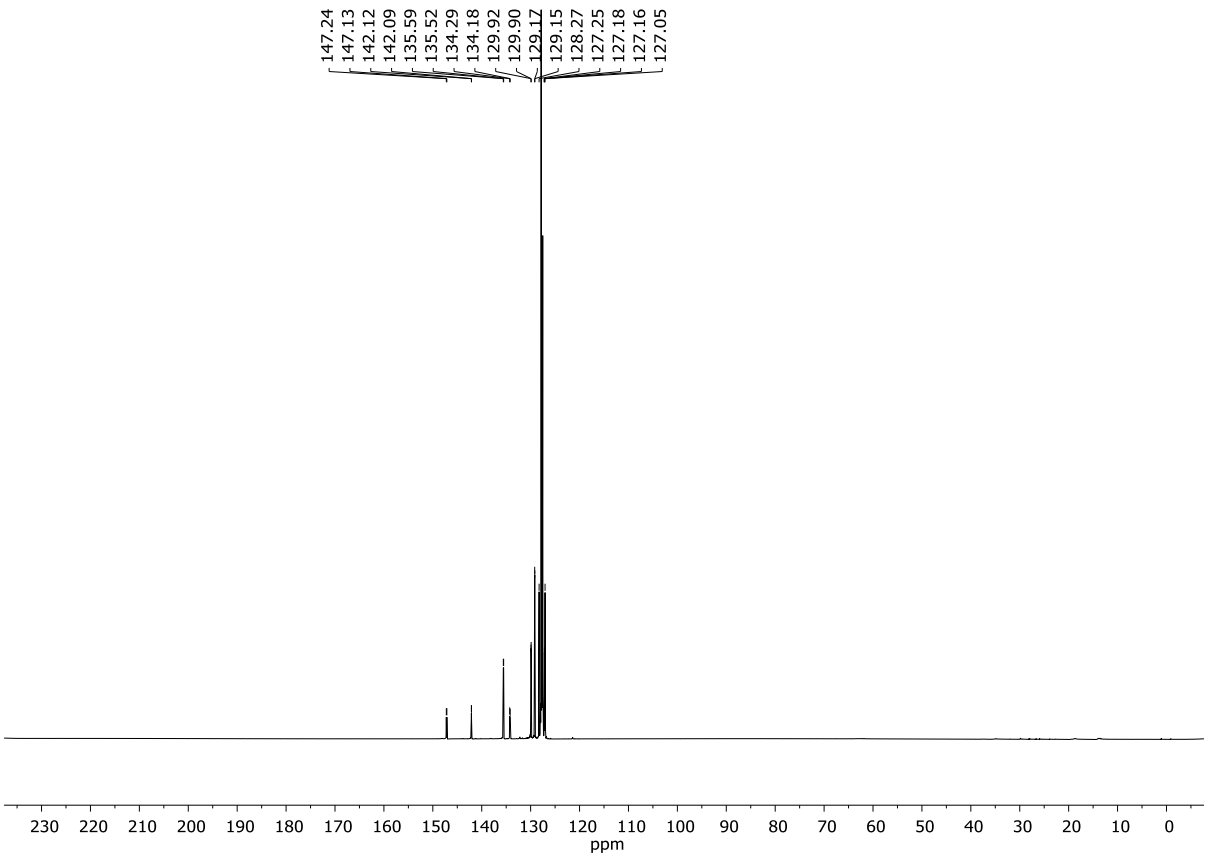

Fig SI 11: $^{13}C\{^{1}H\}$ NMR (151 MHz) of compound **D** in benzene-d_6.

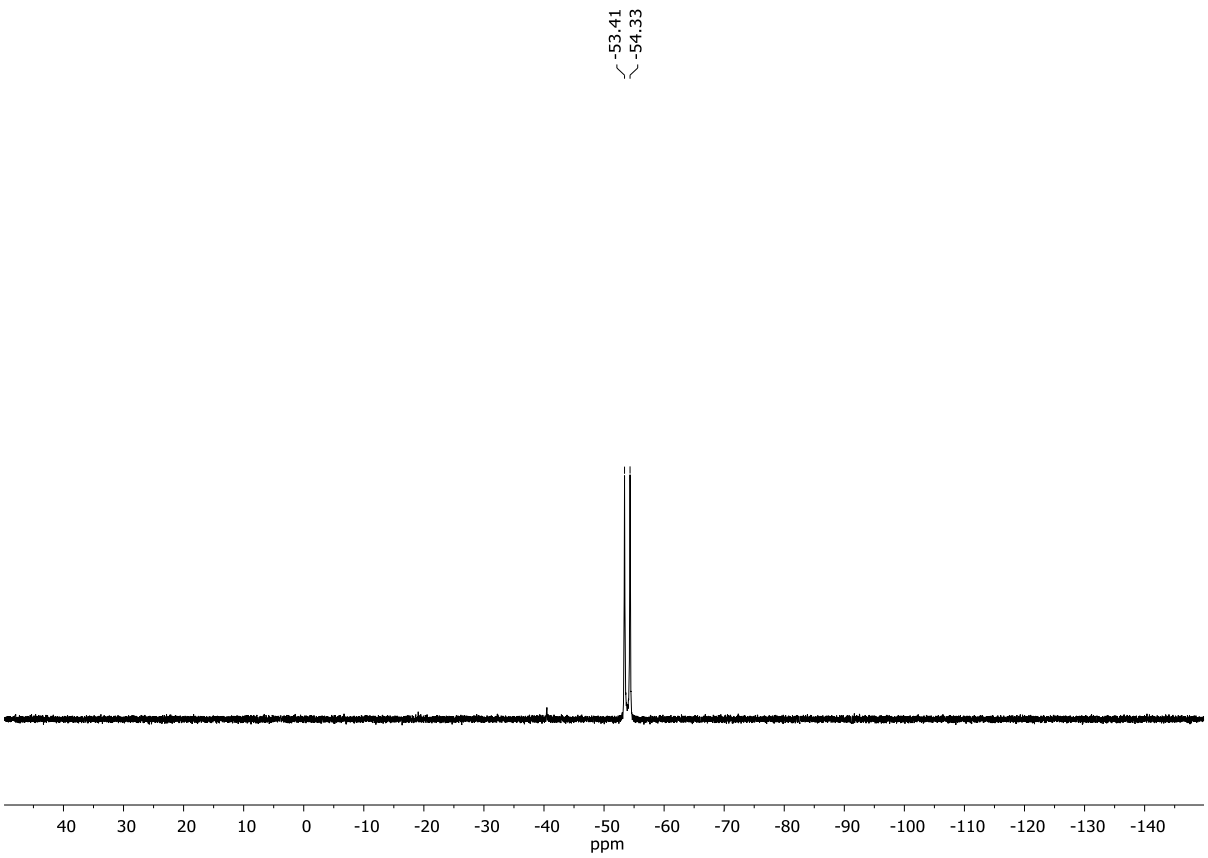

Fig SI 12: ^{31}P NMR (243 MHz) of compound **D** in benzene-d_6.

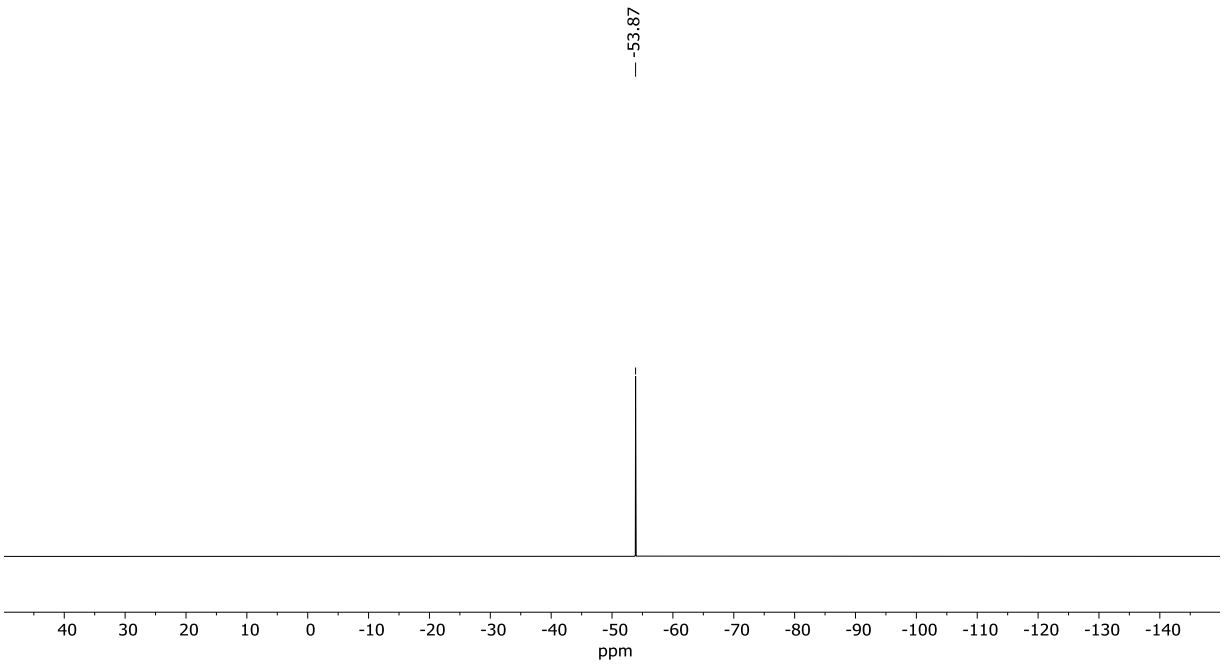

Fig SI 13: $^{31}P\{^{1}H\}$ NMR (243 MHz) of compound **D** in benzene-d_6.

Lithium *bis*(biphenyl-2-yl)phosphide (**E**)

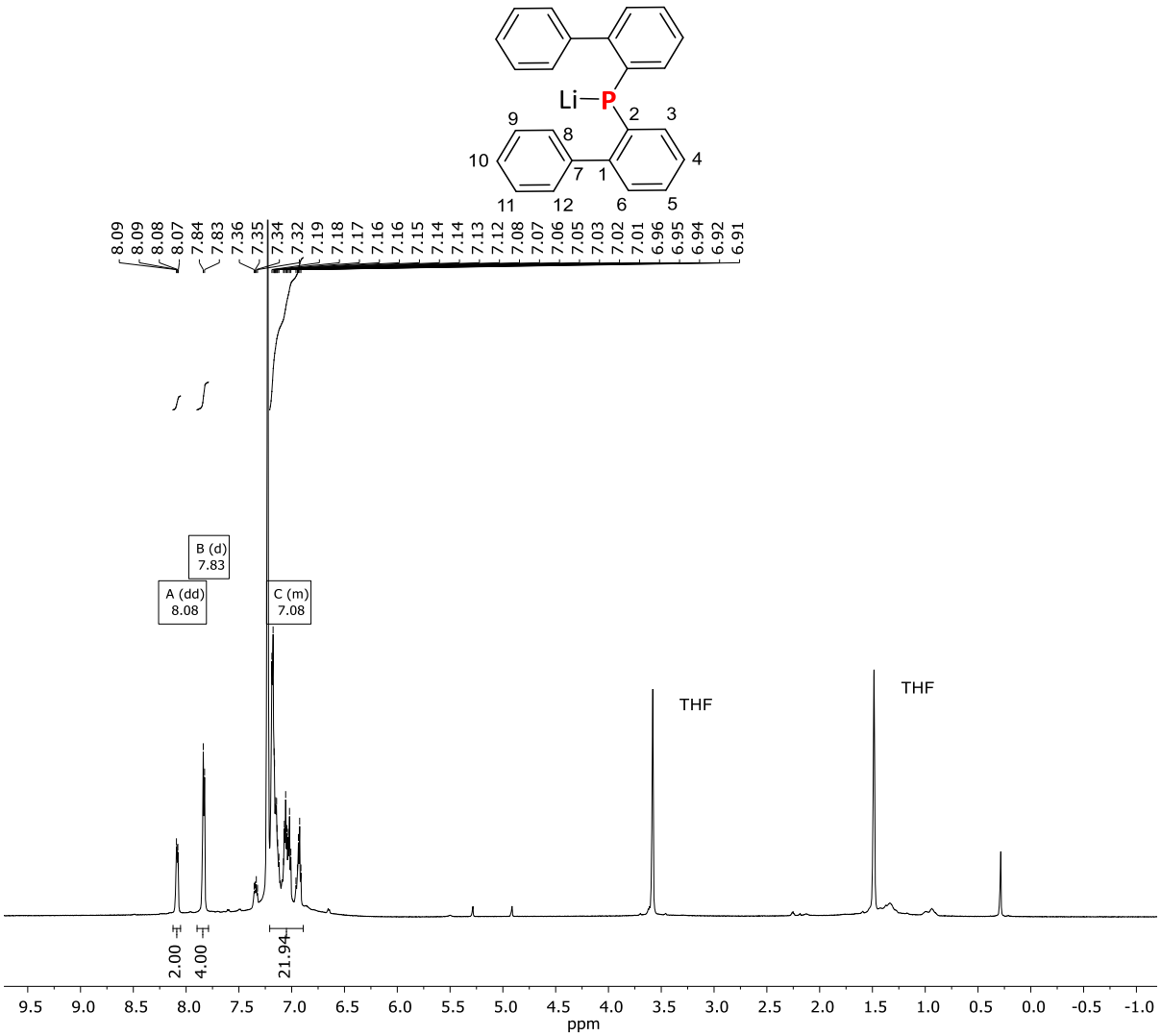

Fig SI 14: ^{1}H NMR (600 MHz) of compound **E** in benzene-d_6/tetrahydrofuran-d_8 (80:20).

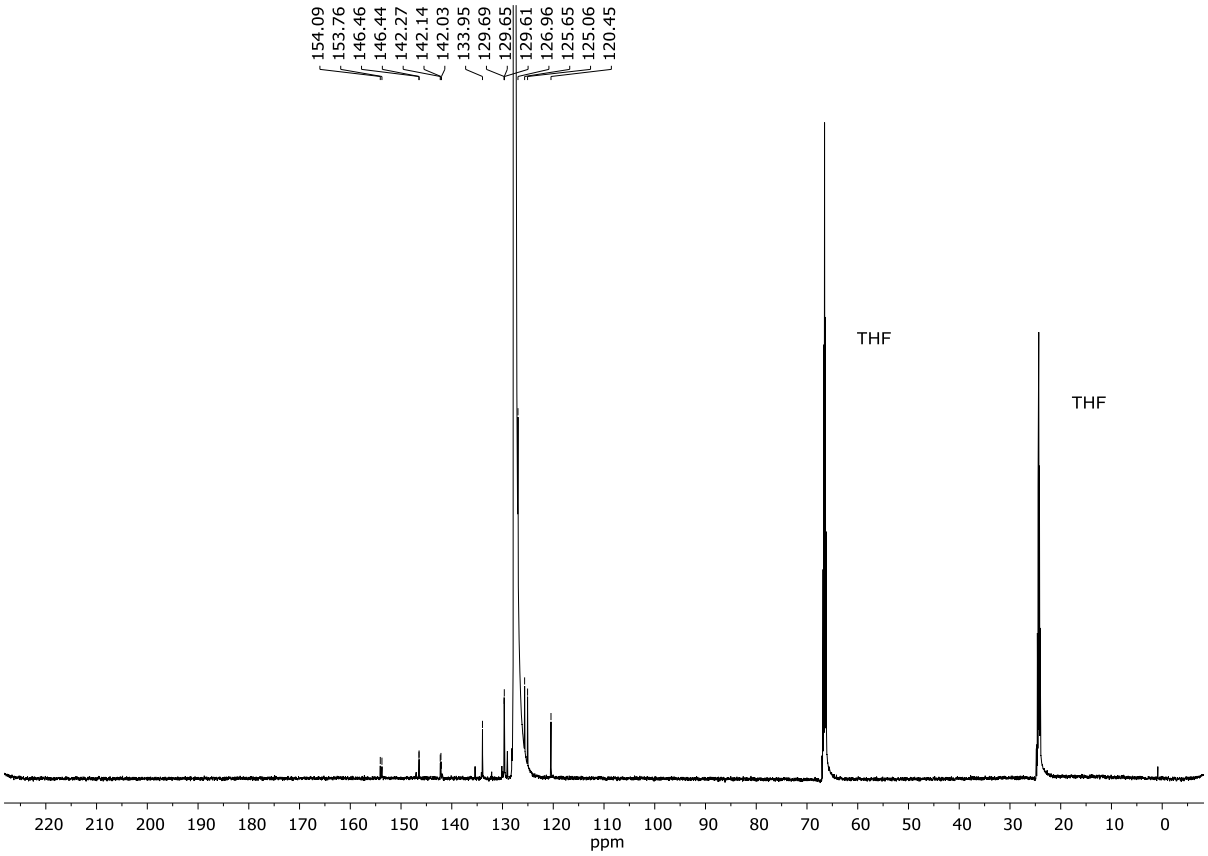

Fig SI 15: $^{13}C\{^{1}H\}$ NMR (151 MHz) of compound **E** in benzene-d_6/tetrahydrofuran-d_8 (80:20).

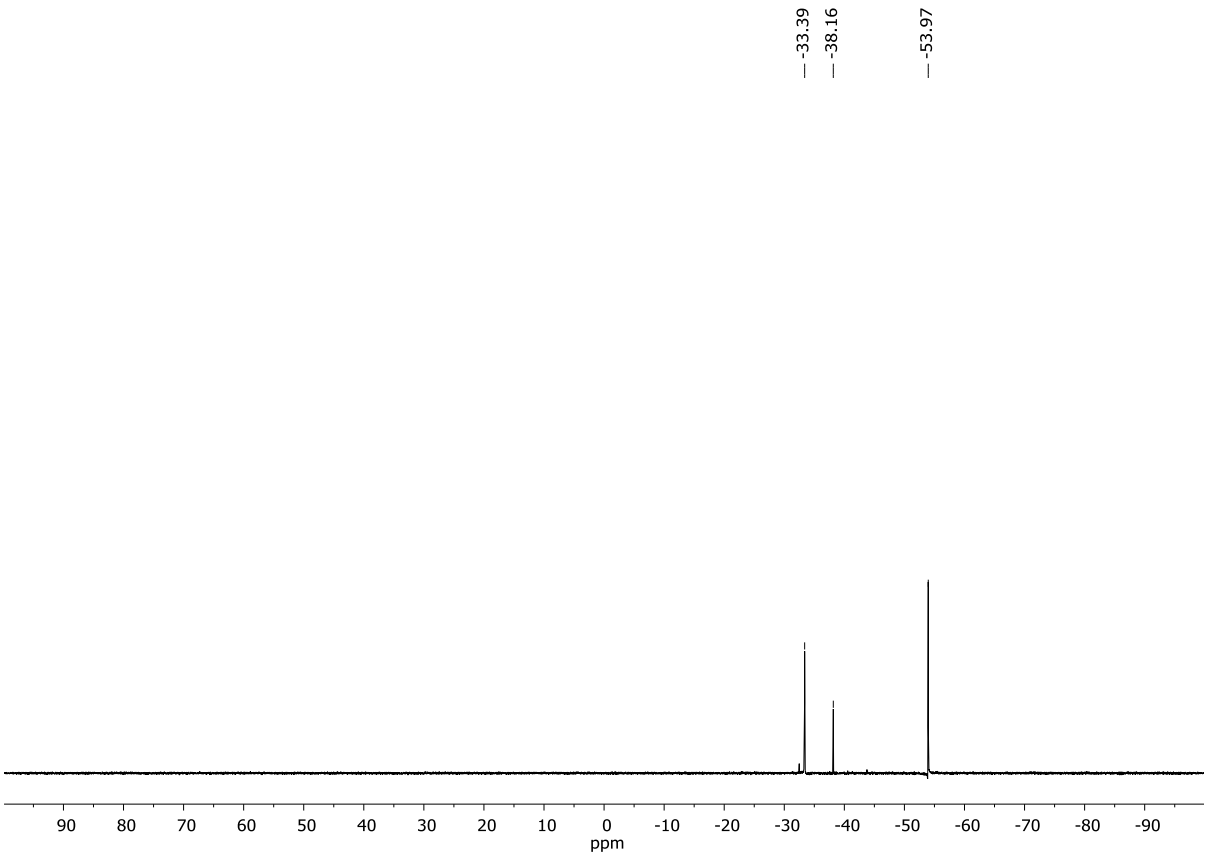

Fig SI 16: $^{31}P\{^{1}H\}$ NMR (243 MHz) of compound **E** in benzene-d_6/tetrahydrofuran-d_8 (80:20).

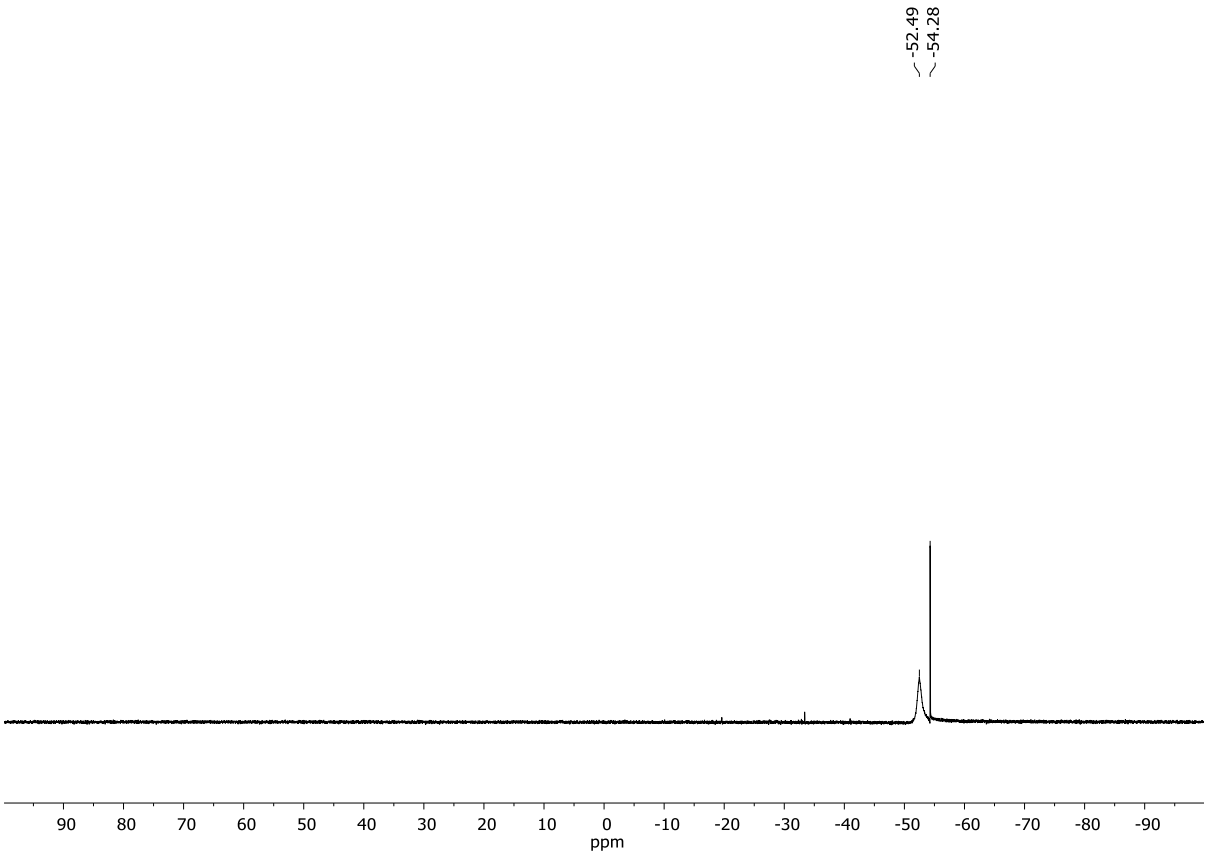

Fig SI 17: $^{31}P\{^{1}H\}$ NMR (243 MHz) of compound **E** in benzene-d_6.

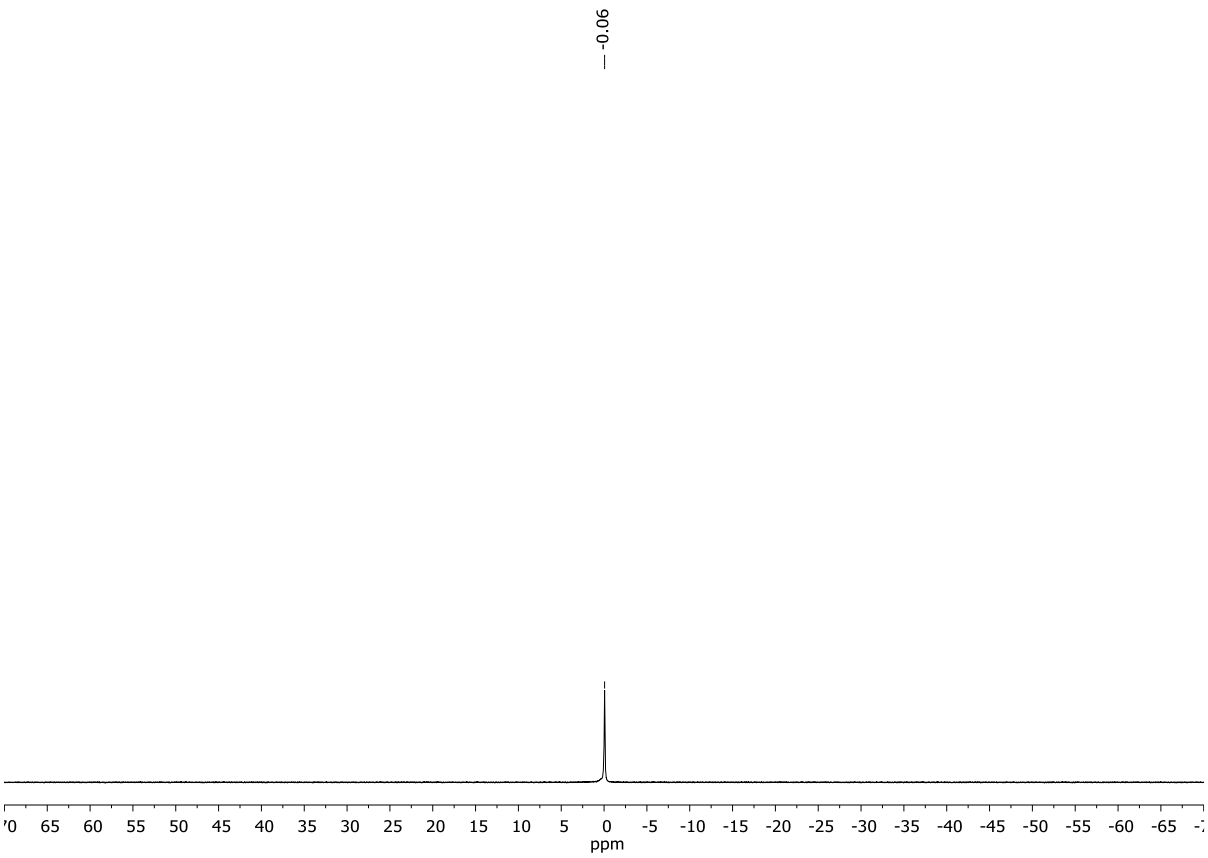

Fig SI 18: ^{7}Li NMR (233 MHz) of compound **E** in benzene-d_6/tetrahydrofuran-d_8 (80:20).

bis(Biphenyl-2-yl)phosphine borane (**F**)

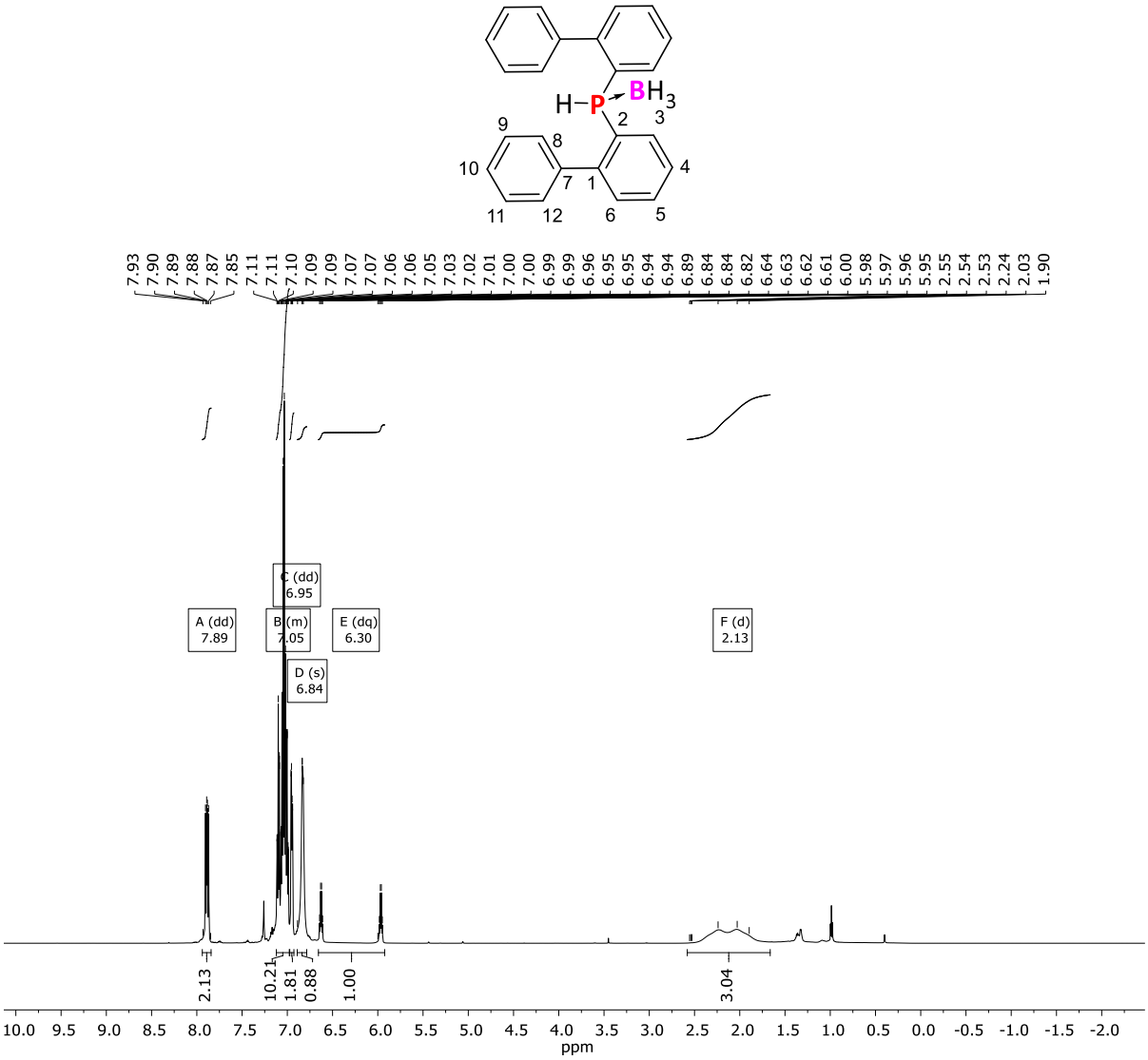

Fig SI 19: ^{1}H NMR (600 MHz) of compound **F** in benzene-d_6.

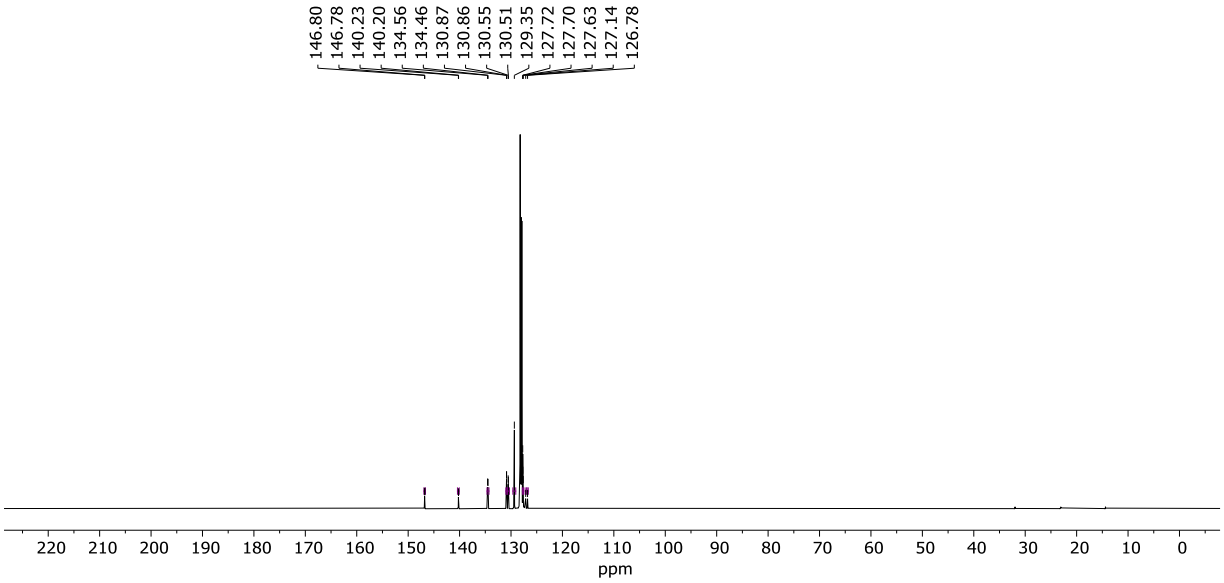

Fig SI 20: ^{13}C{^{1}H} NMR (151 MHz) of compound **F** in benzene-d_6.

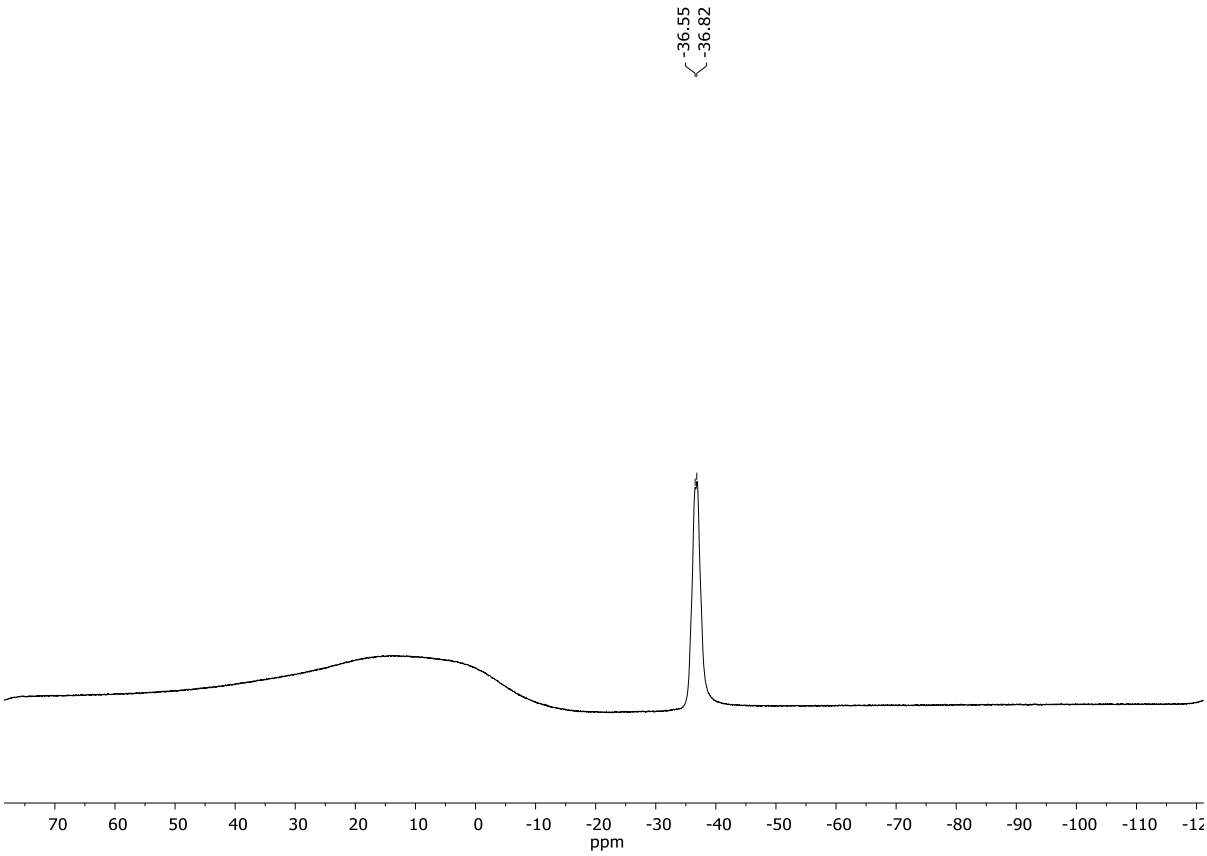

Fig SI 21: ^{11}B NMR (193 MHz) of compound **F** in benzene-d_6.

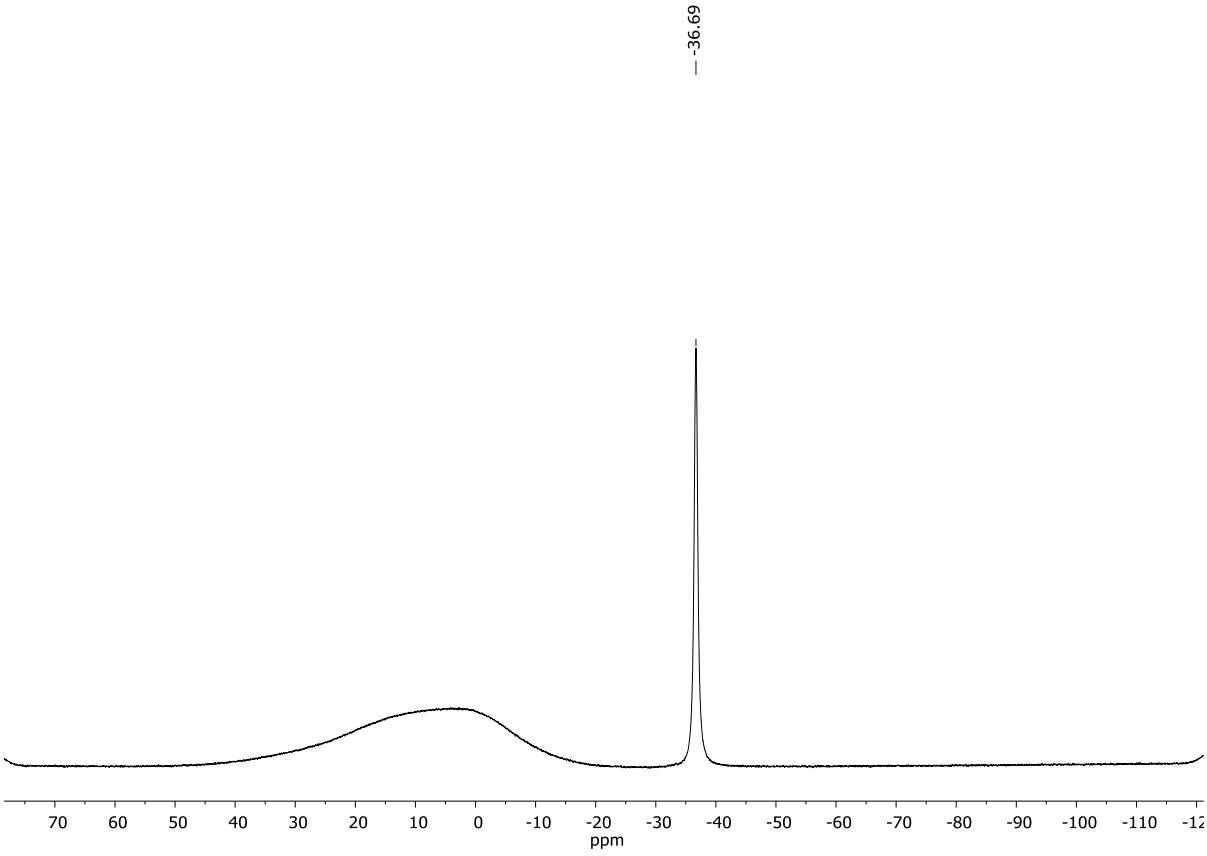

Fig SI 22: ^{11}B{^{1}H} NMR (193 MHz) of compound **F** in benzene-d_6.

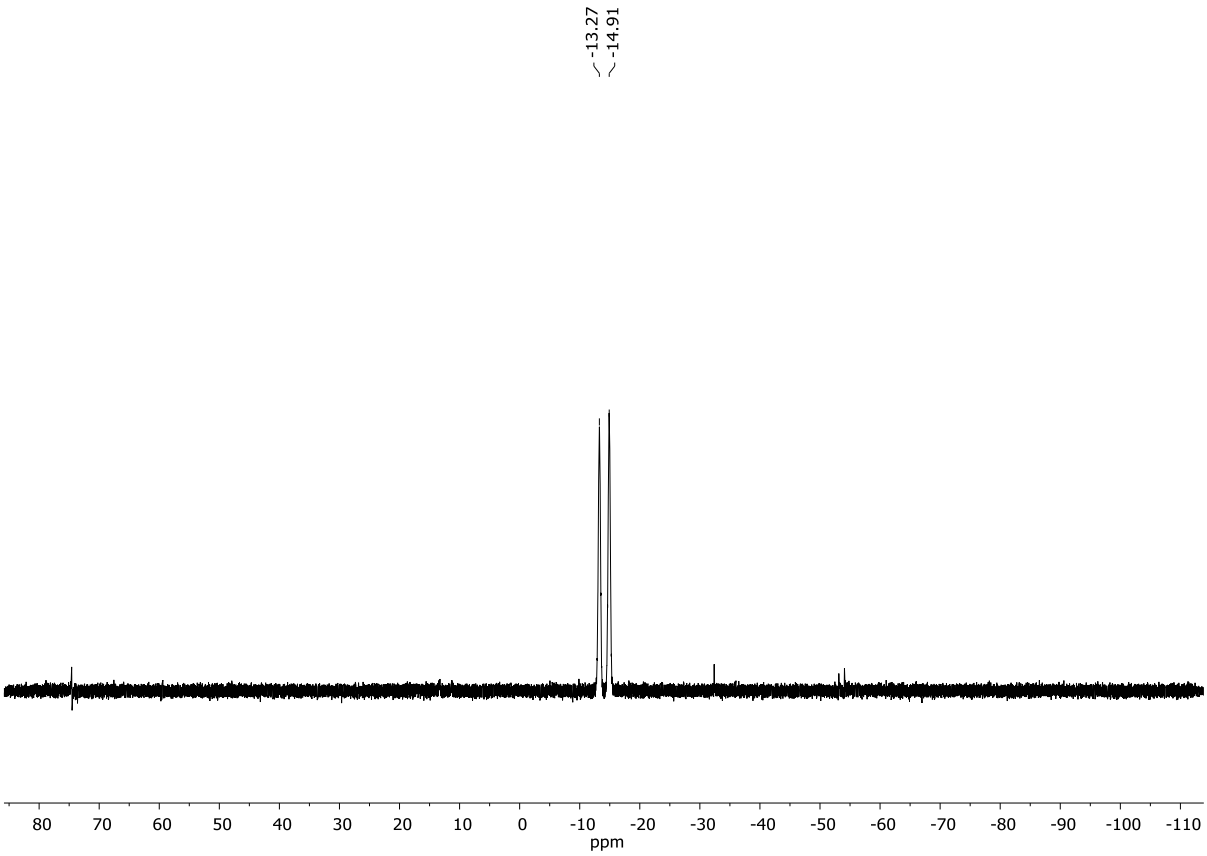

Fig SI 23: ^{31}P NMR (243 MHz) of compound **F** in benzene-d_6.

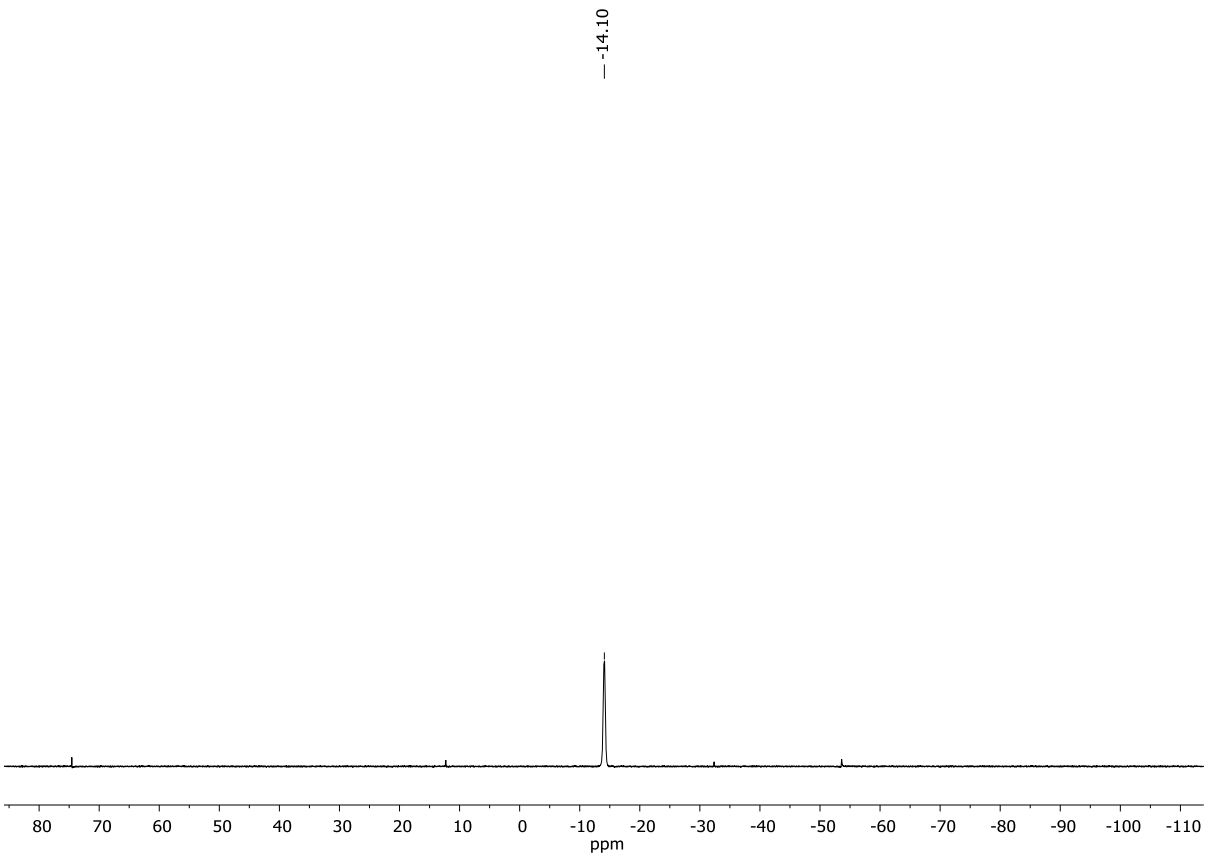

Fig SI 24: ^{31}P{^{1}H} NMR (243 MHz) of compound **F** in benzene-d_6.

bis(Biphenyl-2-yl)(trimethylsilyl)phosphine (**G**)

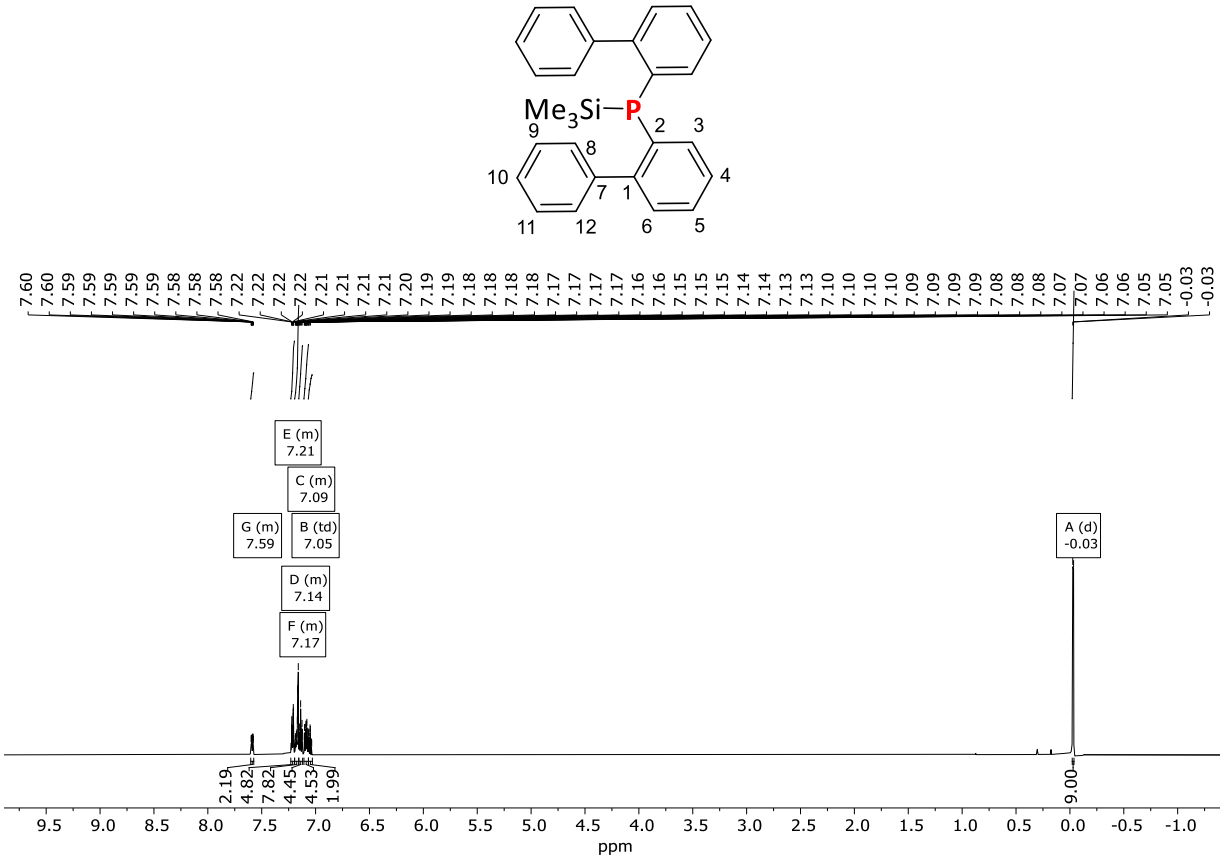

Fig SI 25: ^{1}H NMR (600 MHz) of compound **G** in benzene-d_6.

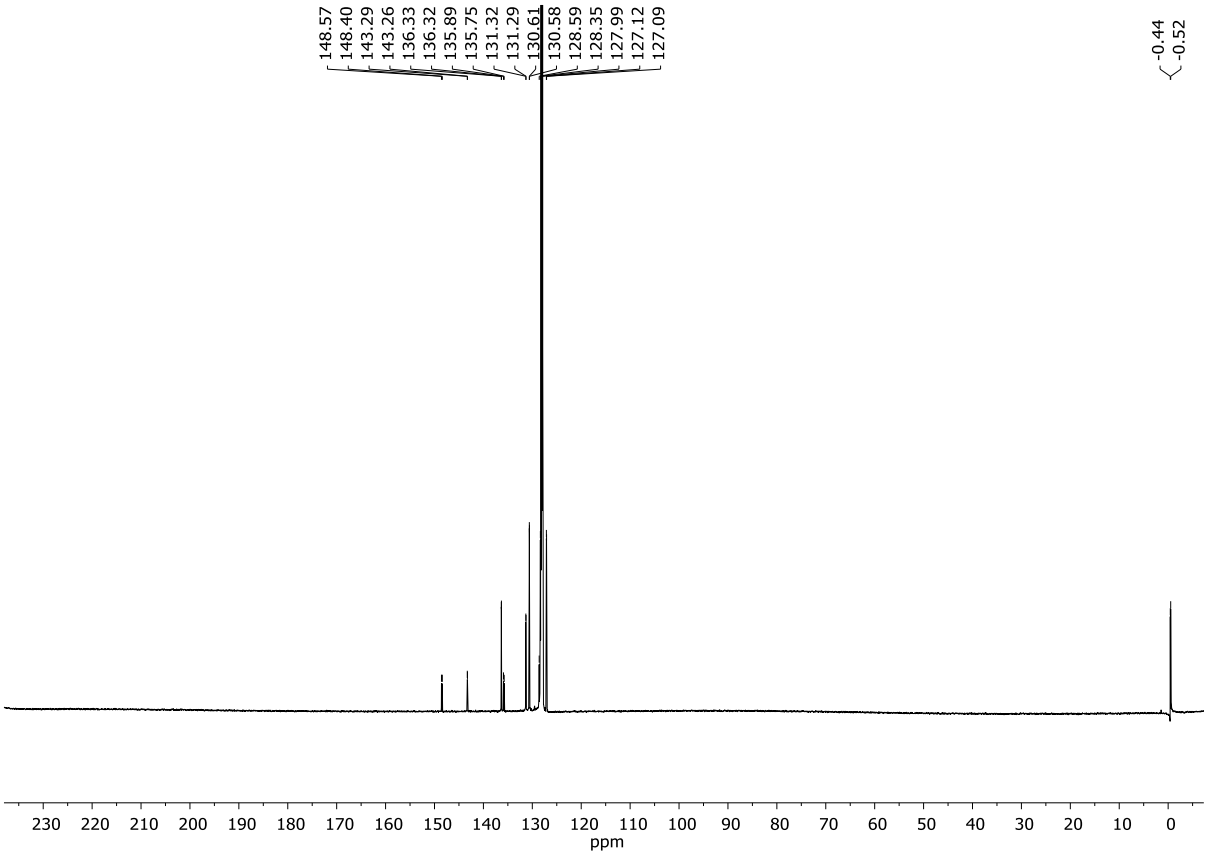

Fig SI 26: ^{13}C{^{1}H} NMR (151 MHz) of compound **G** in benzene-d_6.

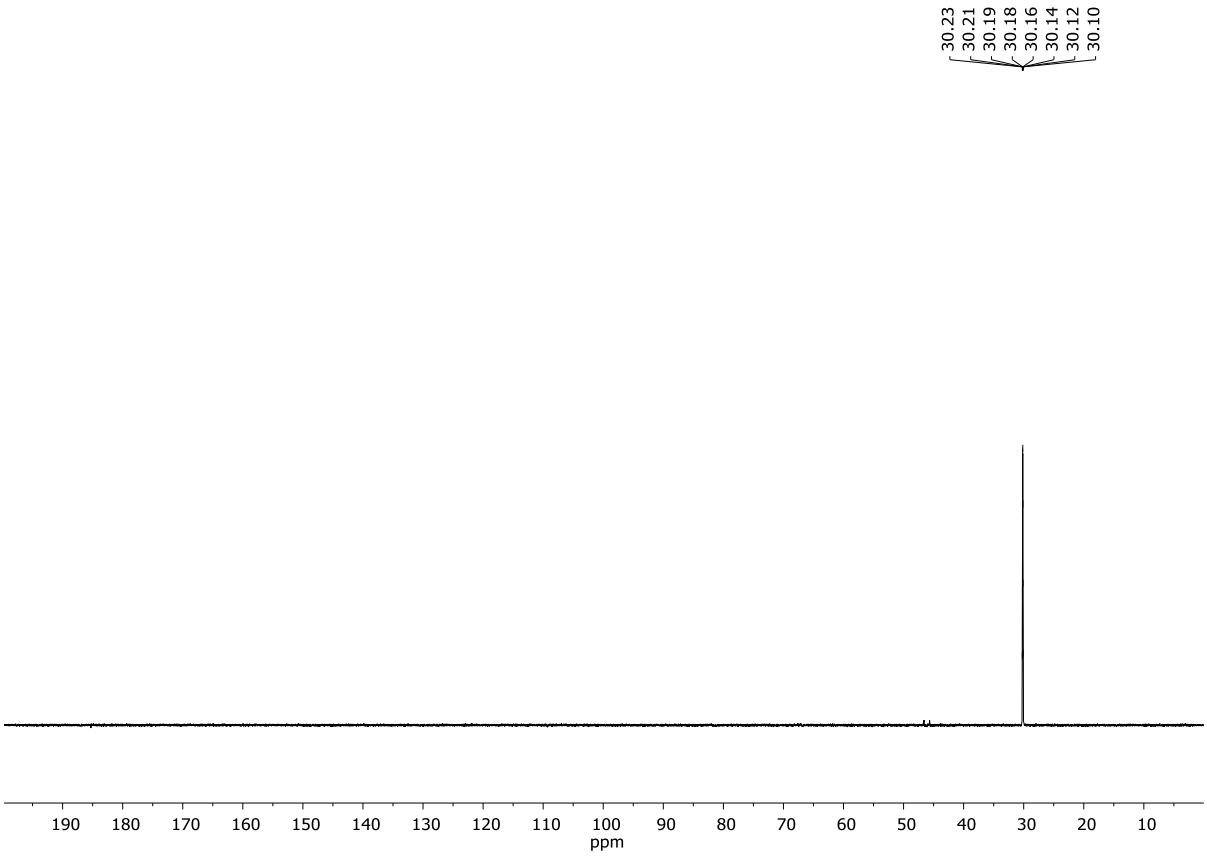

Fig SI27: ^{31}P NMR (243 MHz) of compound **G** in benzene-d_6.

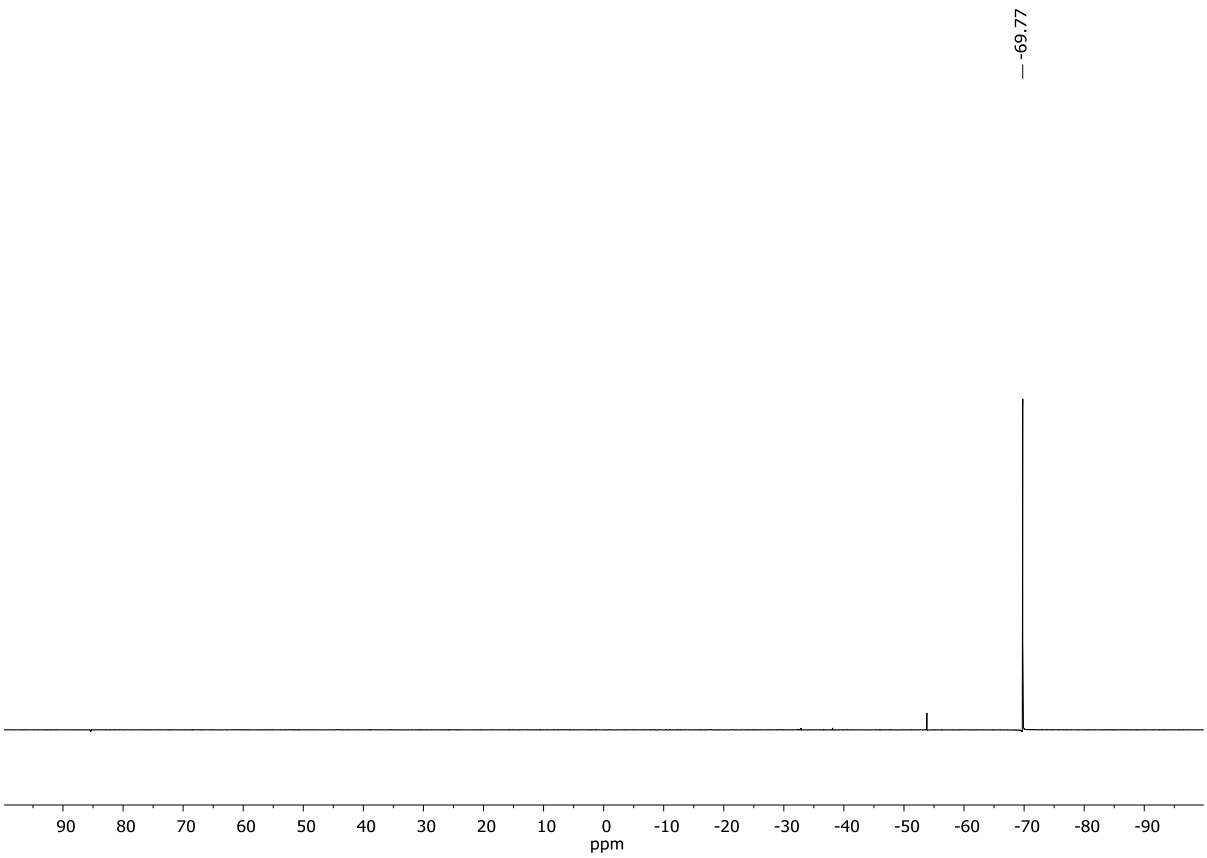

Fig SI28: ^{31}P{^{1}H} NMR (243 MHz) of compound **G** in benzene-d_6.

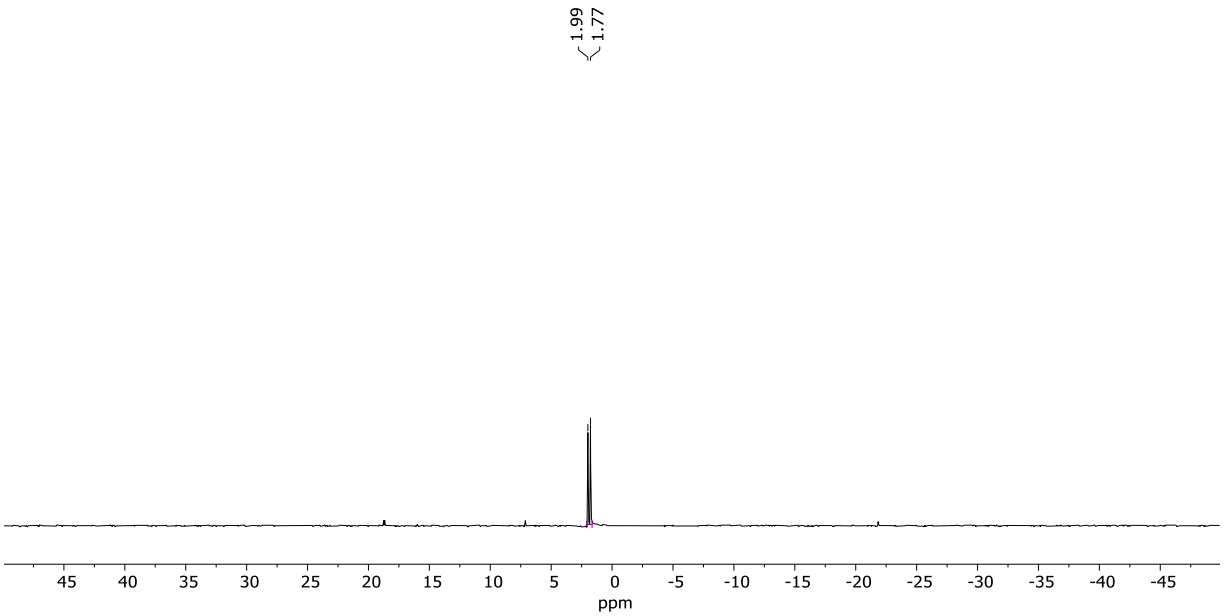

Fig SI29: ^{29}Si{^{1}H} DEPT NMR (119 MHz) of compound **G** in benzene-d_6.

bis(Biphenyl-2-yl)(trimethyltin)phosphine (**H**)

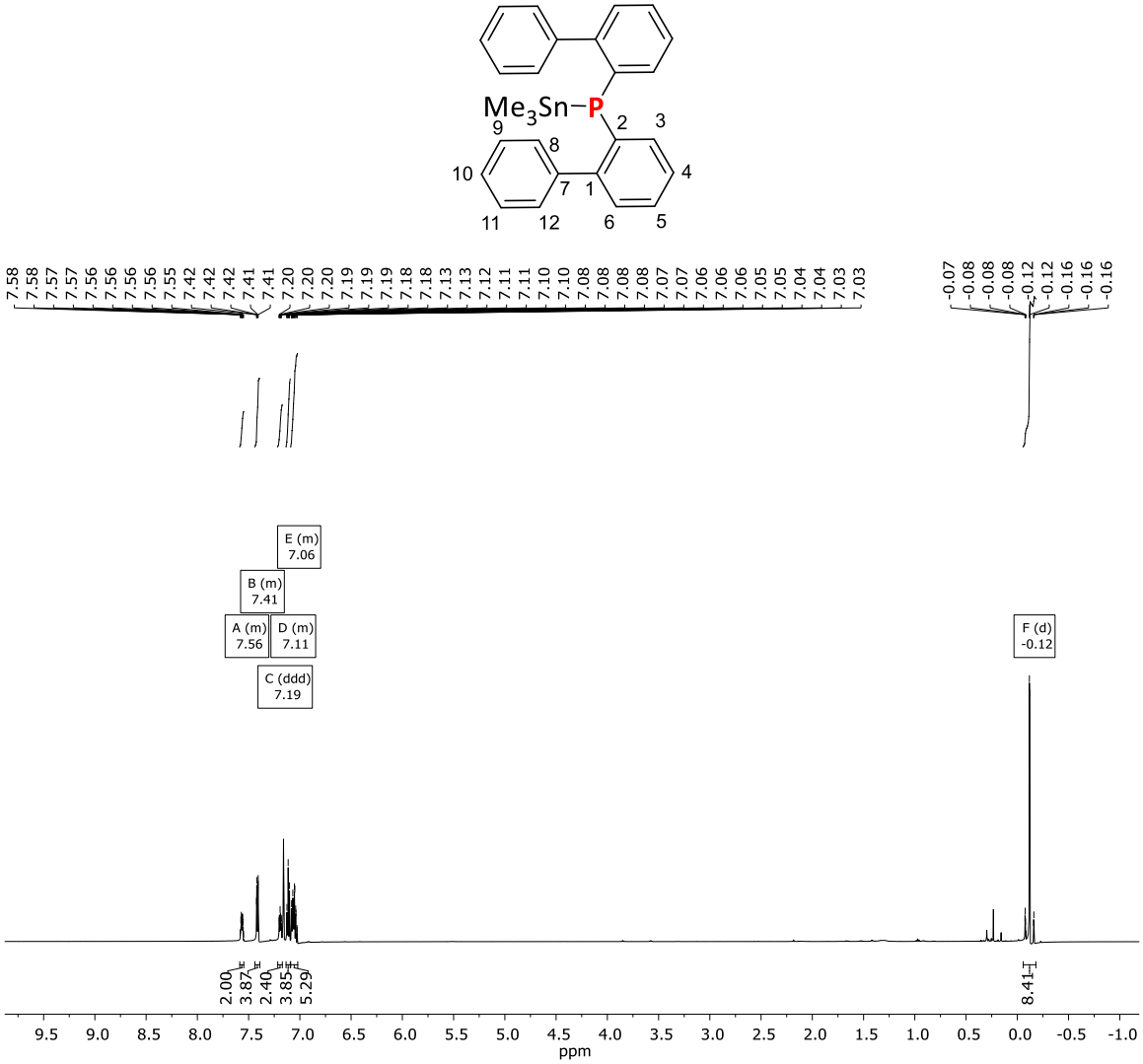

Fig SI 30: ^{1}H NMR (600 MHz) of compound **H** in benzene-d_6.

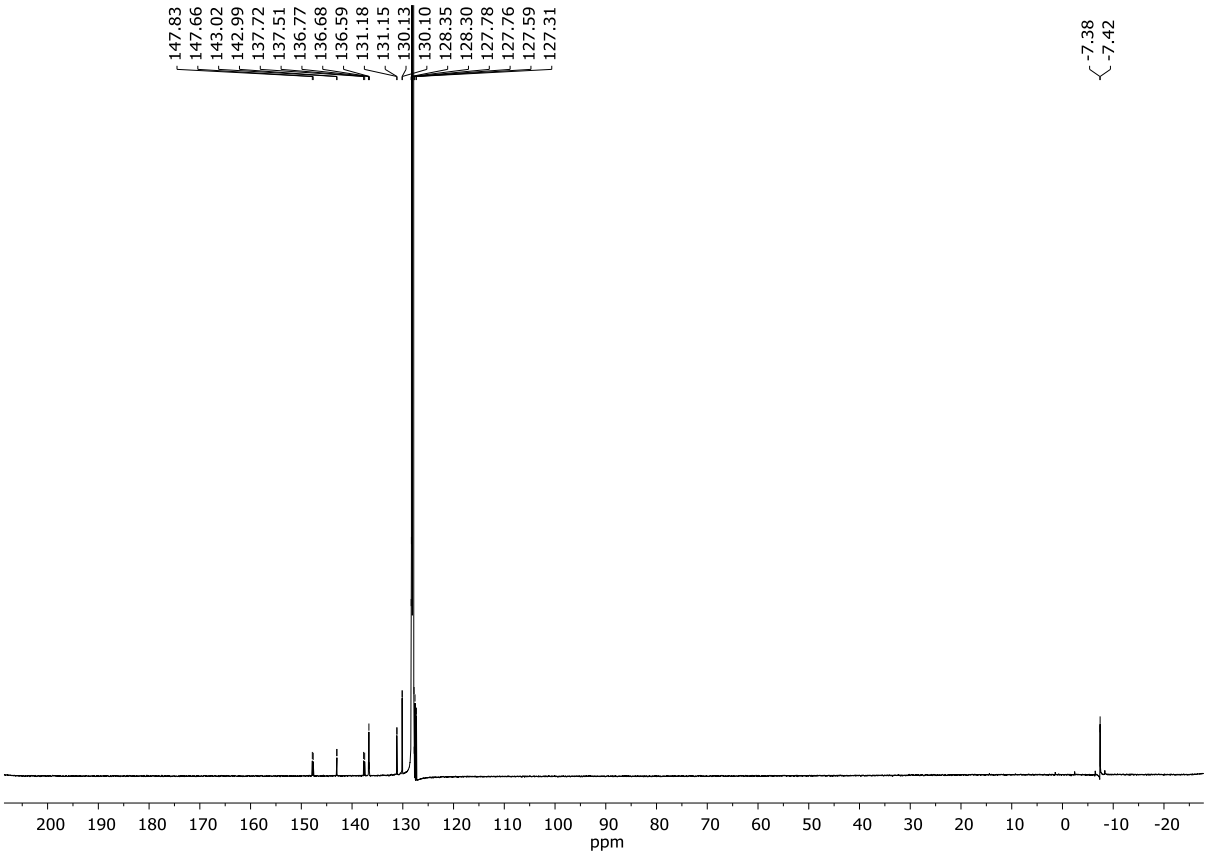

Fig SI 31: $^{13}C\{^{1}H\}$ NMR (151 MHz) of compound **H** in benzene-d_6.

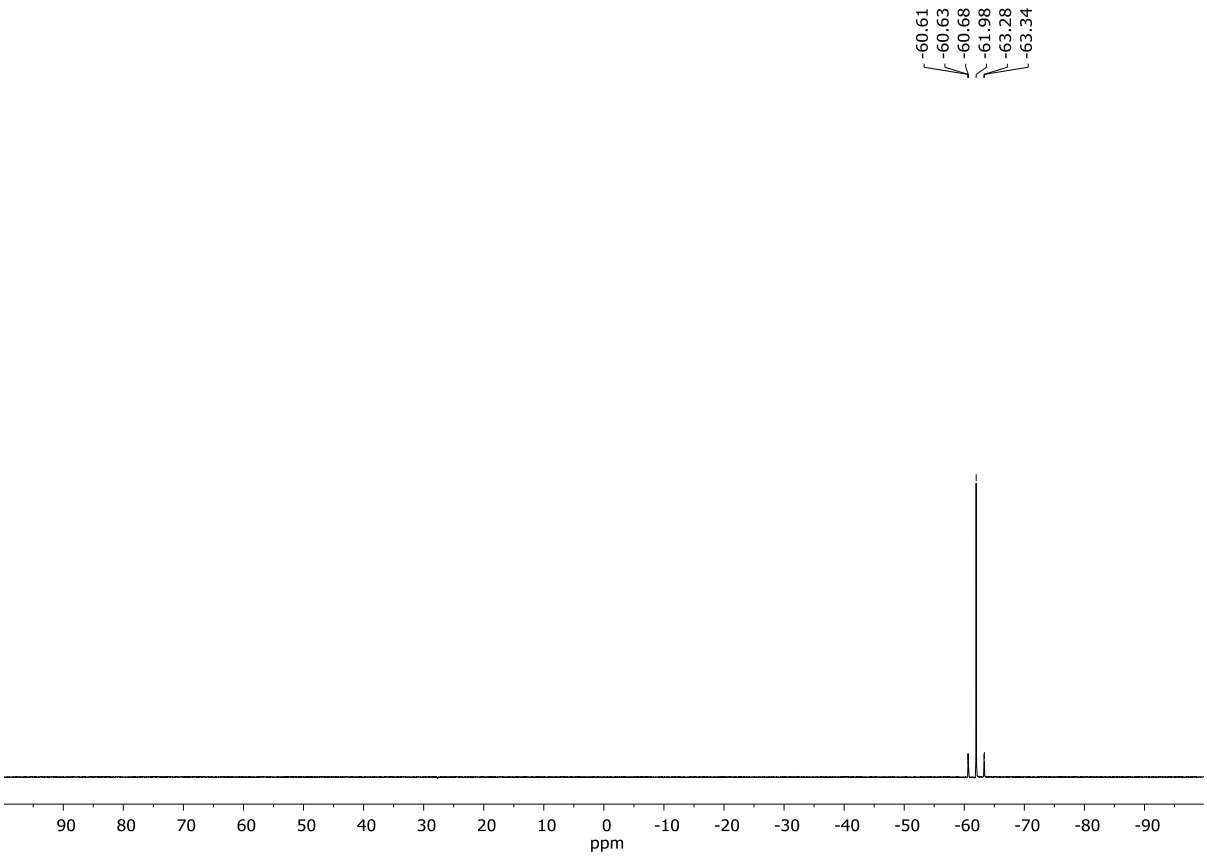

Fig SI 32: $^{31}P\{^{1}H\}$ NMR (243 MHz) of compound **H** in benzene-d_6.

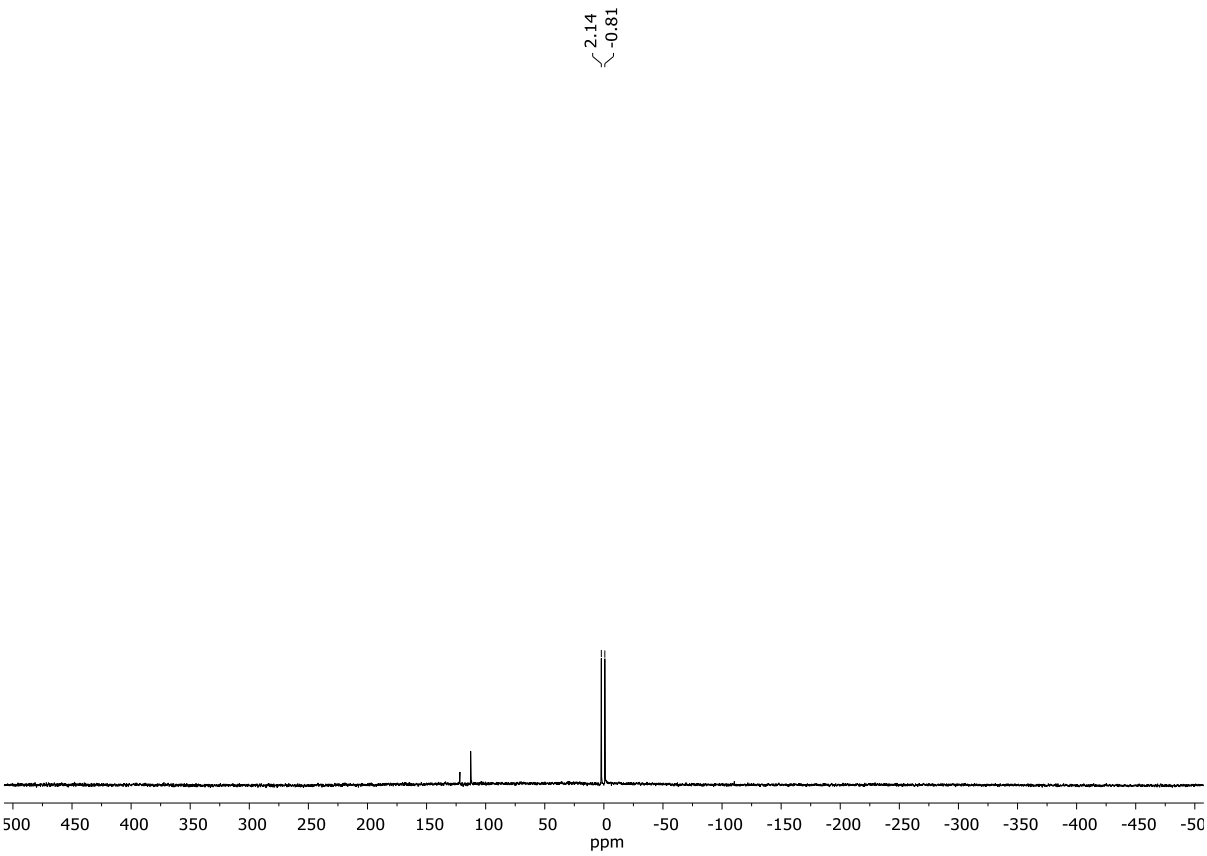

Fig SI 33: $^{119}Sn\{^{1}H\}$ NMR (119 MHz) of compound **H** in benzene-d_6.

Single crystal analysis

Tabl. SI1: Overview of essential crystal structure details for B, D, E and F.

	B	**D**	**E**	**F**
CCDC	2106887	2106888	2108753	2106889
Empirical formula	$C_{30}H_{32}NP$	$C_{24}H_{19}P$	$C_{24}H_{18}LiP$	$C_{27}H_{25}BP$
Formula weight	437.53	338.36	344.29	391.25
Temperature/K	100.0	100.0	100.0	100.0
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	9.4189(3)	7.5529(2)	12.6051(9)	11.8705(5)
b/Å	11.1819(4)	20.0280(6)	16.0123(12)	10.2205(4)
c/Å	12.7140(4)	11.7785(3)	18.4340(12)	17.8670(7)
α/°	89.0990(10)	90	90	90
β/°	76.1210(10)	94.2750(10)	104.712(2)	93.7090(10)
γ/°	70.6150(10)	90	90	90
Volume/$Å^3$	1223.28(7)	1776.77(8)	3598.7(4)	2163.13(15)
Z	2	4	8	4
ρ_{calc}g/cm^3	1.188	1.265	1.271	1.201
μ/mm^{-1}	0.130	0.157	0.156	0.137
F(000)	468.0	712.0	1440.0	828.0
Crystal size/mm^3	0.23 × 0.21 × 0.18	0.28 × 0.19 × 0.16	0.24 × 0.23 × 0.21	0.26 × 0.2 × 0.19
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.472 to 66.998	5.346 to 57	4.2 to 61.016	4.594 to 59.996
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19	-10 ≤ h ≤ 9, -26 ≤ k ≤ 26, -15 ≤ l ≤ 15	-18 ≤ h ≤ 18, -22 ≤ k ≤ 22, -26 ≤ l ≤ 26	-16 ≤ h ≤ 16, -14 ≤ k ≤ 14, -25 ≤ l ≤ 25
Reflections collected	102866	36505	108594	78277
Independent reflections	9585 [R_{int} = 0.0282, R_{sigma} = 0.0149]	4485 [R_{int} = 0.0402, R_{sigma} = 0.0225]	10966 [R_{int} = 0.0504, R_{sigma} = 0.0288]	6303 [R_{int} = 0.0291, R_{sigma} = 0.0146]
Data/restraints/parameters	9585/0/293	4485/0/231	10966/0/469	6303/3/277
Goodness-of-fit on F^2	1.050	1.040	1.035	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0333, wR_2 = 0.0922	R_1 = 0.0389, wR_2 = 0.0874	R_1 = 0.0447, wR_2 = 0.1085	R_1 = 0.0352, wR_2 = 0.0927
Final R indexes [all data]	R_1 = 0.0381, wR_2 = 0.0960	R_1 = 0.0466, wR_2 = 0.0912	R_1 = 0.0603, wR_2 = 0.1170	R_1 = 0.0403, wR_2 = 0.0974
Largest diff. peak/hole / e $Å^{-3}$	0.48/-0.29	0.38/-0.32	0.50/-0.36	0.38/-0.31