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SUPPORTING INFORMATION

Isolation of Ligand-Centered Borocations in Molybdenum Complexes Containing a Triaminoborane-Bridged Diphosphorus Ligand

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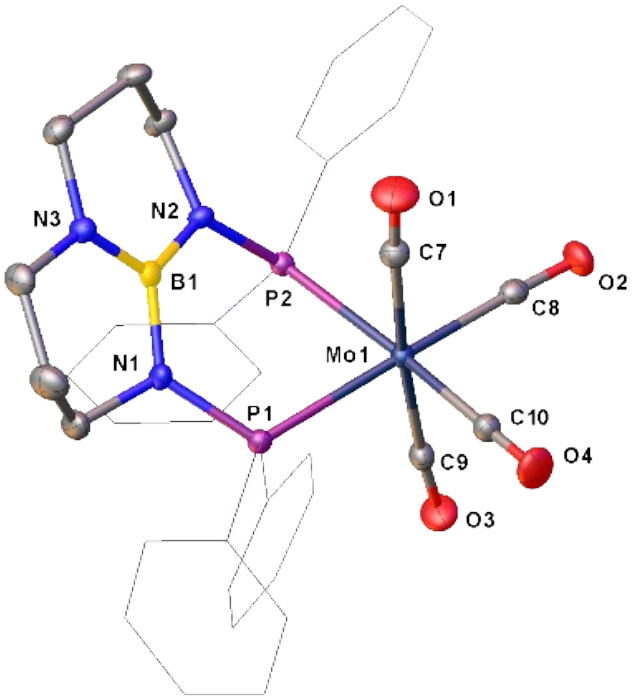

Figure S1. Molecular structure of **1** with thermal ellipsoids at the 35% probability level. Hydrogen atoms were omitted from the figure.

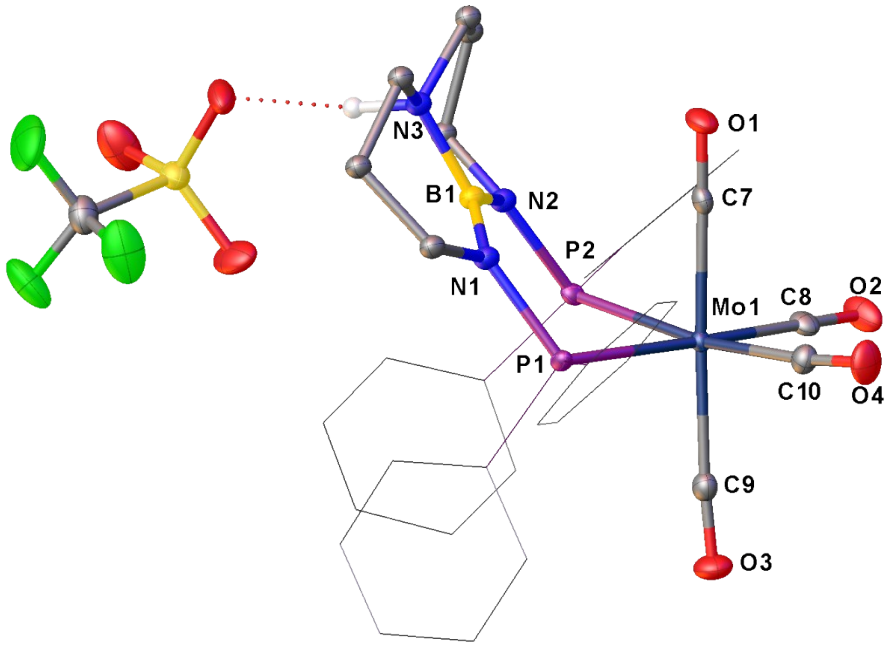

Figure S2. Molecular structure of **1-HOTf** with thermal ellipsoids at the 35% probability level. Hydrogen atoms and co-crystallized solvent molecules were omitted from the figure.

Table S1. Crystallographic data for (^{Ph}TBDPhos)Mo(CO)$_4$ (**1**), [(^{Ph}TBDPhos-H)Mo(CO)$_4$]NTf$_2$ (**1-HNTf$_2$**), [(^{Ph}TBDPhos-H)Mo(CO)$_4$]OTf (**1-HOTf**), and [(^{Ph}TBDPhos-H$_2$F)Mo(CO)$_4$]BF$_4$ (**[1-H$_2$F][BF$_4$]**).

	1	**1-HNTf$_2$**	**1-HOTf**	**[1-H$_2$F][BF$_4$]**
formula	$C_{34}H_{32}BMoN_3O_4P_2$	$C_{34}H_{33}BF_6MoN_4O_8P_2S_2 \cdot 0.5(CH_2Cl_2)$	$C_{34}H_{33}BF_3MoN_3O_7P_2S \cdot (CH_2Cl_2)$	$C_{34}H_{34}B_2F_5MoN_3O_4P_2 \cdot (CH_2Cl_2)$
FW (g mol^{-1})	715.31	1038.93	950.32	908.07
crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic
space group	P-1	Pna2$_1$	P2$_1$/n	P2$_1$/c
a (Å)	10.3852(10)	19.741(2)	15.0807(15)	20.655(2)
b (Å)	15.1206(15)	9.9649(10)	14.2045(14)	11.0271(11)
c (Å)	20.549(2)	44.148(4)	19.3900(19)	17.7885(18)
α (deg)	84.673(5)	90	90	90
β (deg)	85.261(5)	90	105.030(5)	107.133(5)
γ (deg)	84.632(5)	90	90	90
volume (Å^3)	3189.9(5)	8684.6(15)	4011.5(7)	3871.8(7)
Z	4	8	4	4
ρ_{calc} (g cm^{-3})	1.489	1.589	1.574	1.558
μ (mm^{-1})	0.555	0.613	0.657	0.626
F(000)	1464	4200	1928	1840
θ range (deg)	1.00/26.02	2.26/22.19	2.45/26.38	2.20/21.86
R(int)	0.0293	0.0795	0.0338	0.0651
data/restraints/parameters	12584/0/811	17717/80/1116	8196/39/438	7909/0/488
GOF	1.026	1.116	1.023	1.065
R$_1$ [$I > 2\sigma(I)$][a]	0.0343	0.0547	0.0339	0.0733
wR$_2$ (all data)[b]	0.0787	0.1024	0.0807	0.1983
Ext. Coeff	-	-	-	-
Largest Peak/Hole (e·Å^{-3})	0.988/-0.442	1.297/-1.483	0.848/-0.541	2.361/-1.177
Temp (K)	190(2)	150(2)	150(2)	150(2)

[a] $R_1 = \sum |F_o| - |F_c| \, | / | \sum |F_o|$ for reflections with $F_o^2 > 2\,\sigma(F_o^2)$.

[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum (F_o^2)^2]^{1/2}$ for all reflections.

NMR spectra

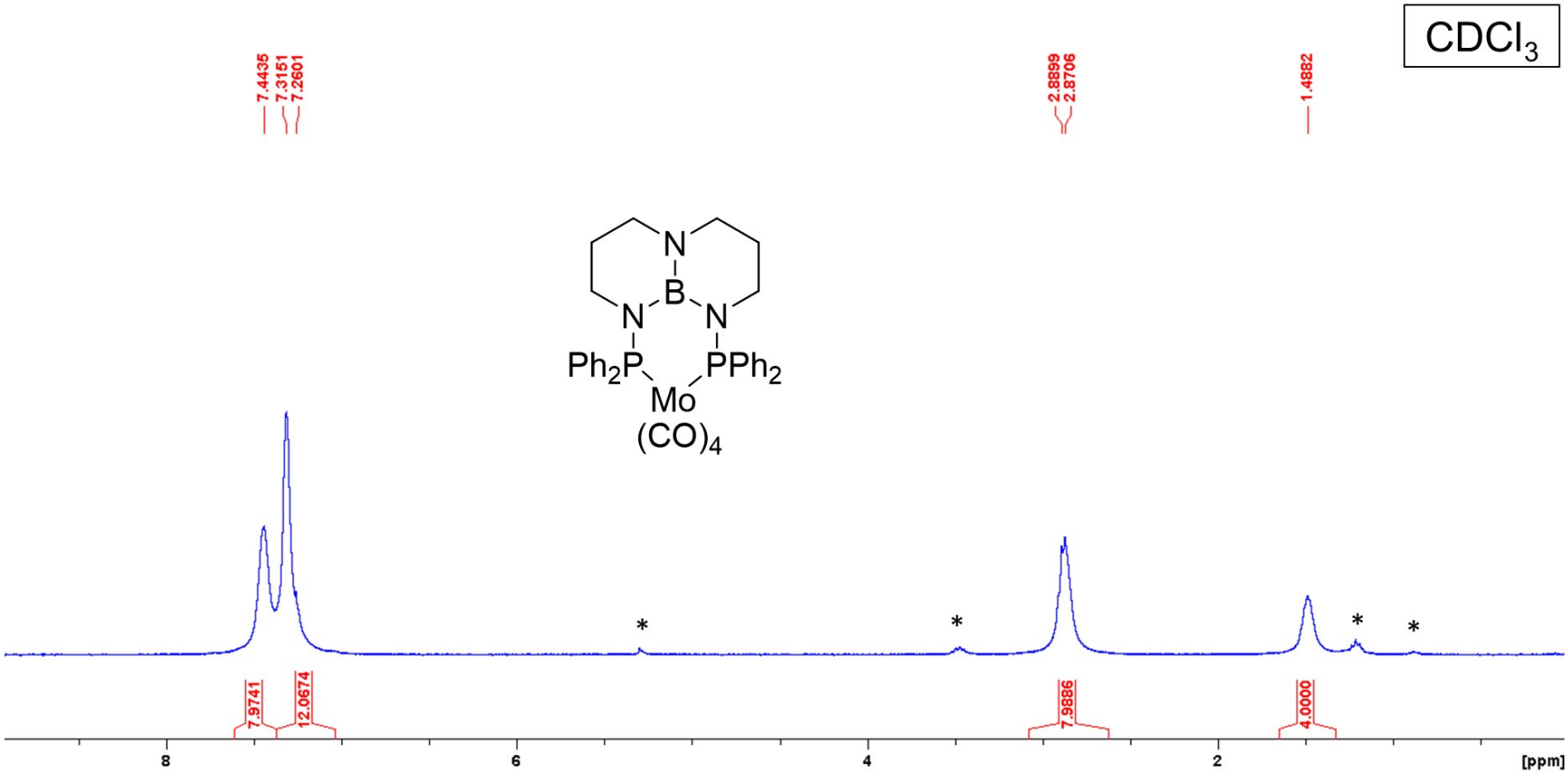

Figure S3. ^{1}H NMR spectrum of (^{Ph}TBDPhos)Mo(CO)$_4$ (**1**). The * symbol indicates resonances assigned to residual pentane, Et_2O, and CH_2Cl_2.

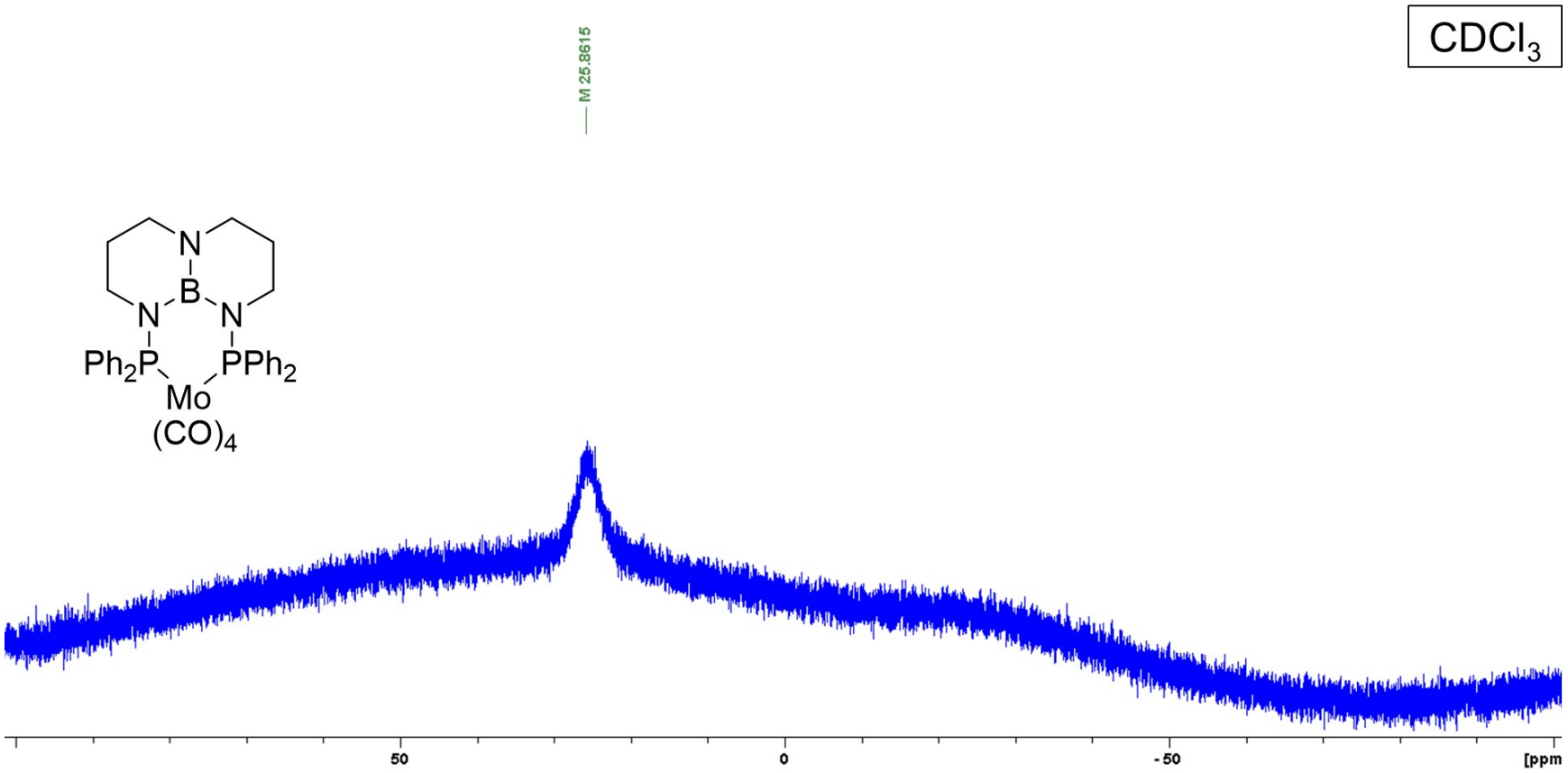

Figure S4. ^{11}B NMR spectrum of (^{Ph}TBDPhos)Mo(CO)$_4$ (**1**).

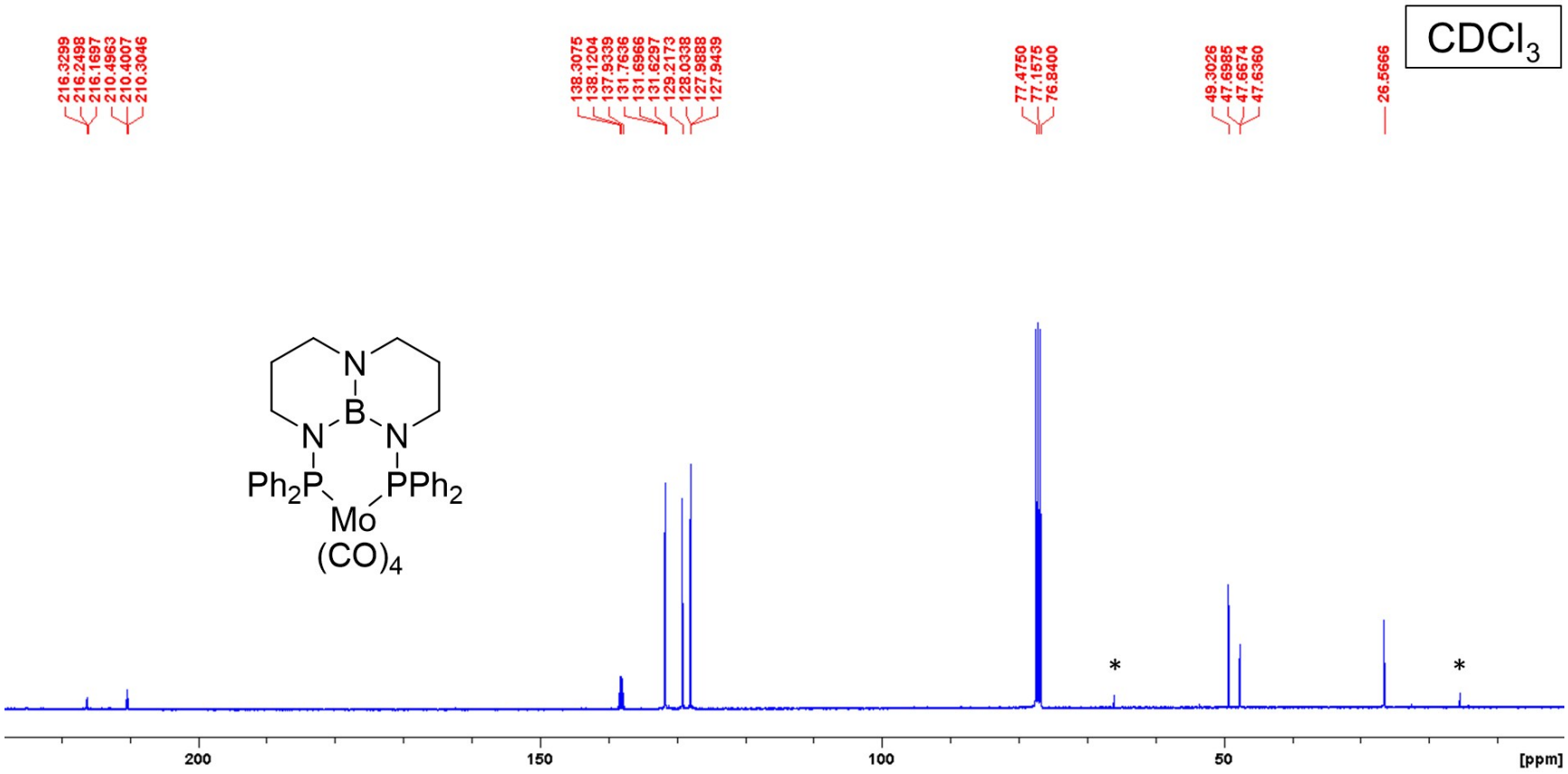

Figure S5. ^{13}C NMR spectrum of (^{Ph}TBDPhos)Mo(CO)$_4$ (**1**). The * symbol indicates resonances assigned to residual Et_2O.

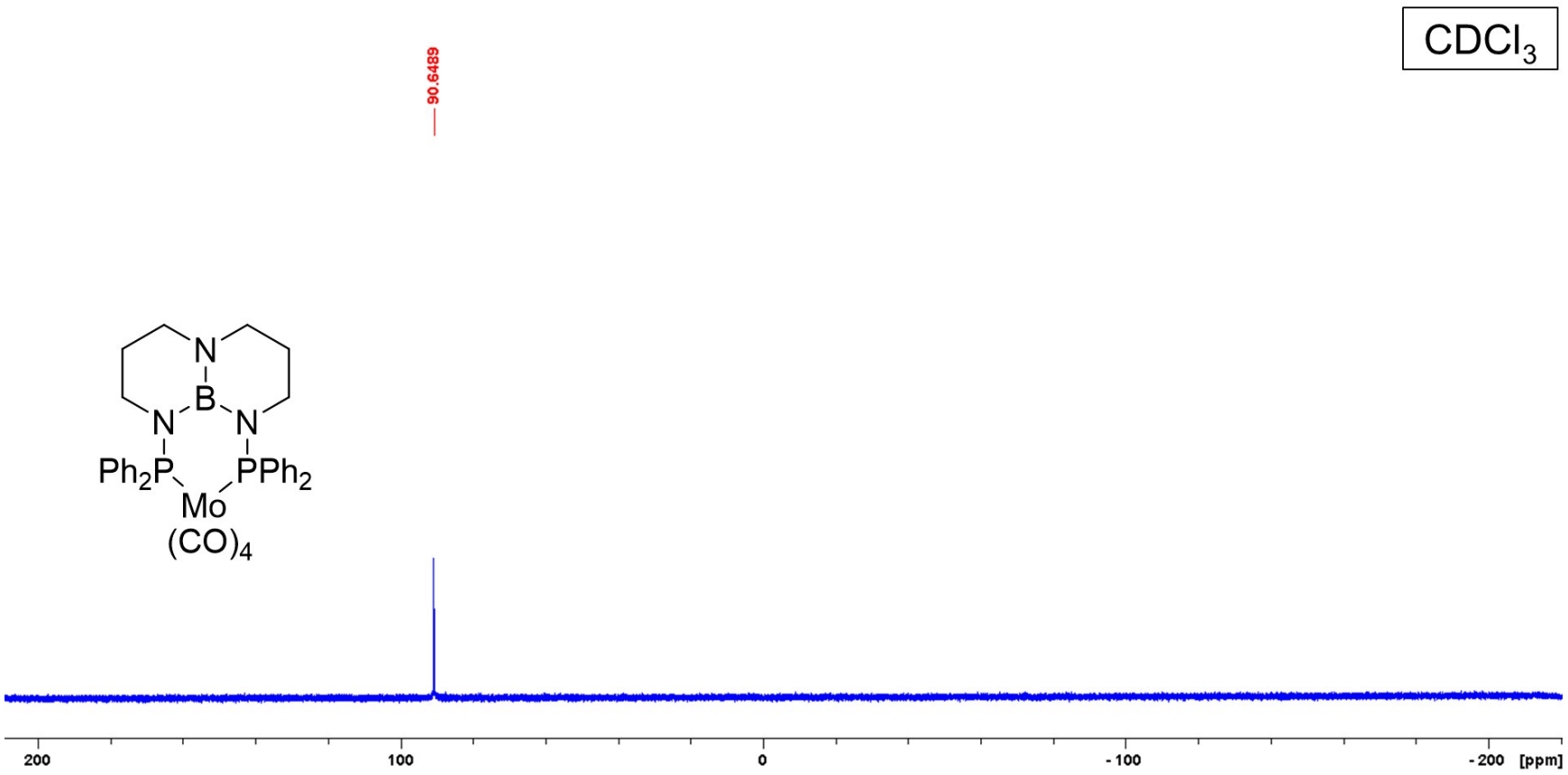

Figure S6. ^{31}P NMR spectrum of (^{Ph}TBDPhos)Mo(CO)$_4$ (**1**).

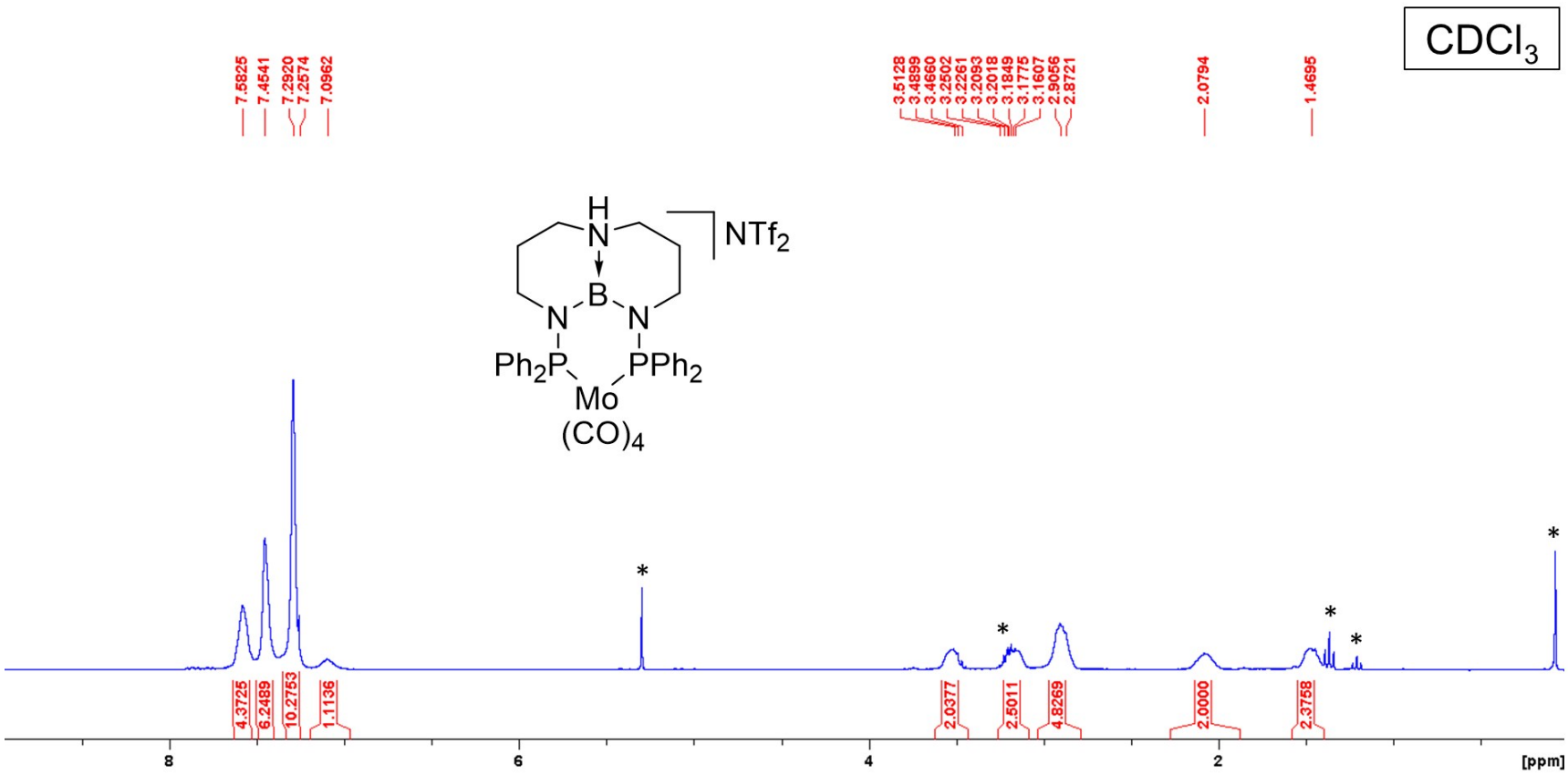

Figure S7. ^{1}H NMR spectrum of [(^{Ph}TBDPhos-H)Mo(CO)$_4$]NTf$_2$ (**1-HNTf$_2$**). The * symbol indicates resonances assigned to residual grease, pentane, Et_2O, and CH_2Cl_2.

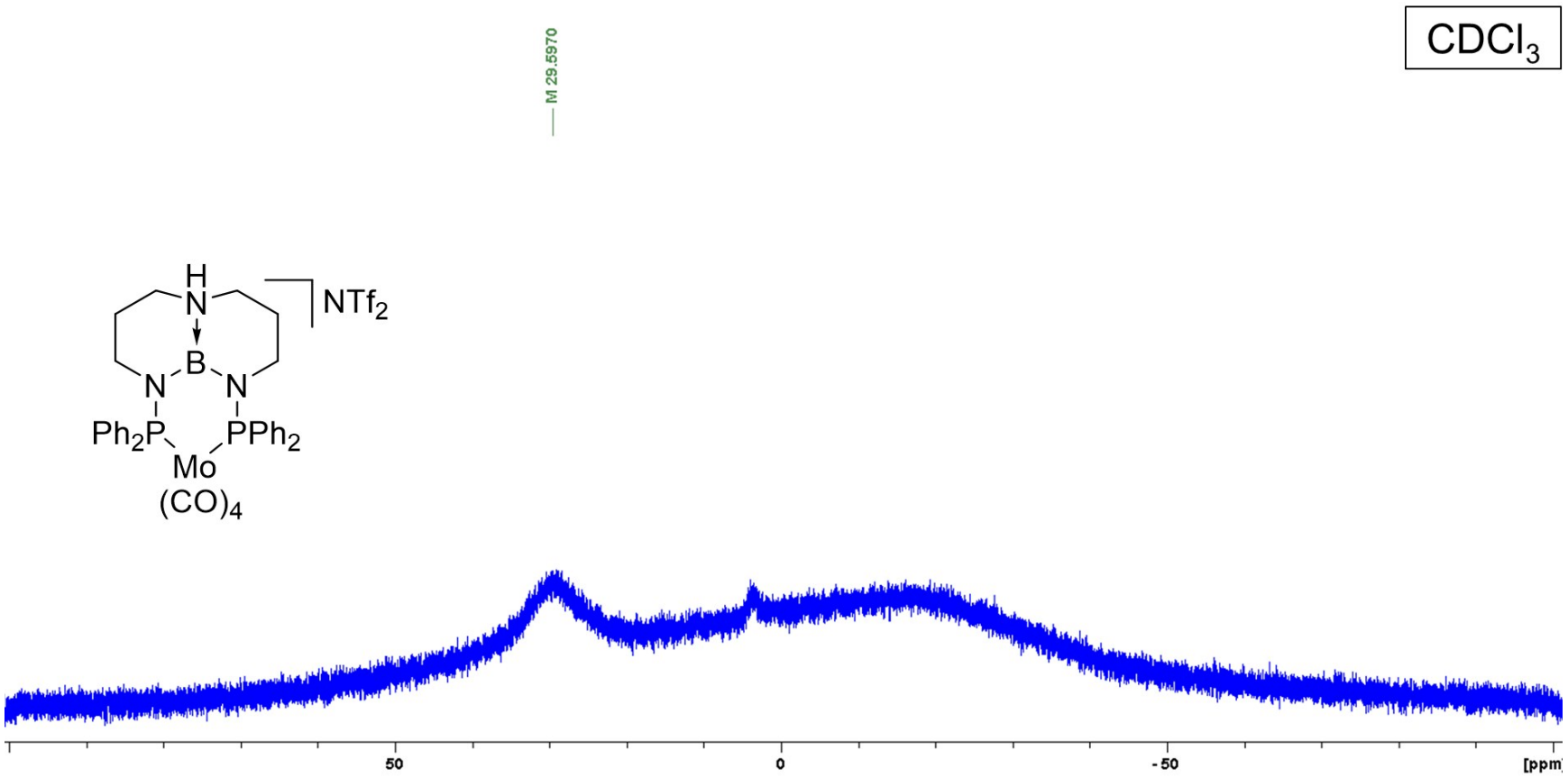

Figure S8. ^{11}B NMR spectrum of [(^{Ph}TBDPhos-H)Mo(CO)$_4$]NTf$_2$ (**1-HNTf$_2$**).

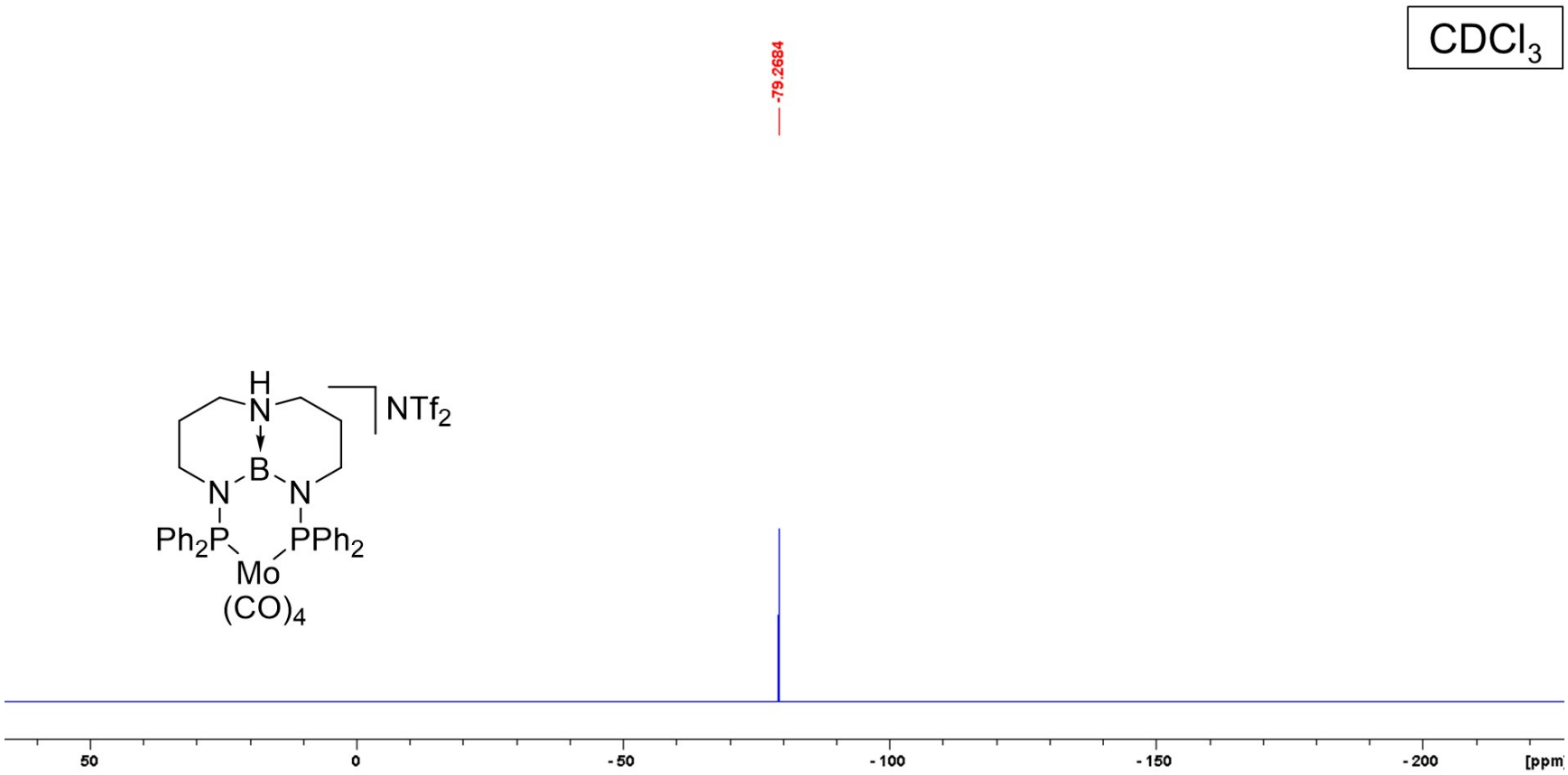

Figure S9. ^{19}F NMR spectrum of [(^{Ph}TBDPhos-H)Mo(CO)$_4$]NTf$_2$ (**1-HNTf$_2$**).

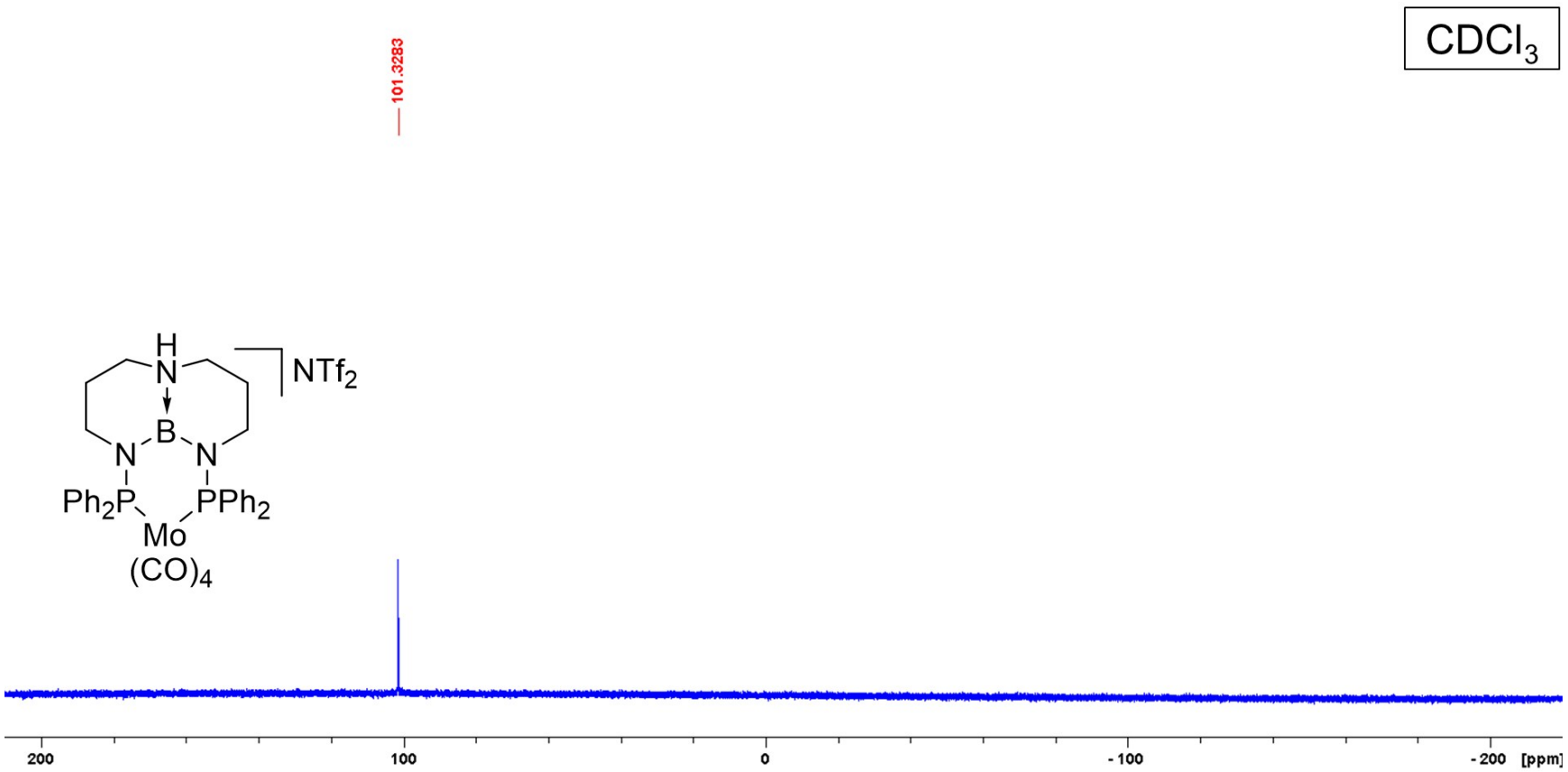

Figure S10. ^{31}P NMR spectrum of [(^{Ph}TBDPhos-H)Mo(CO)$_4$]NTf$_2$ (**1-HNTf$_2$**).

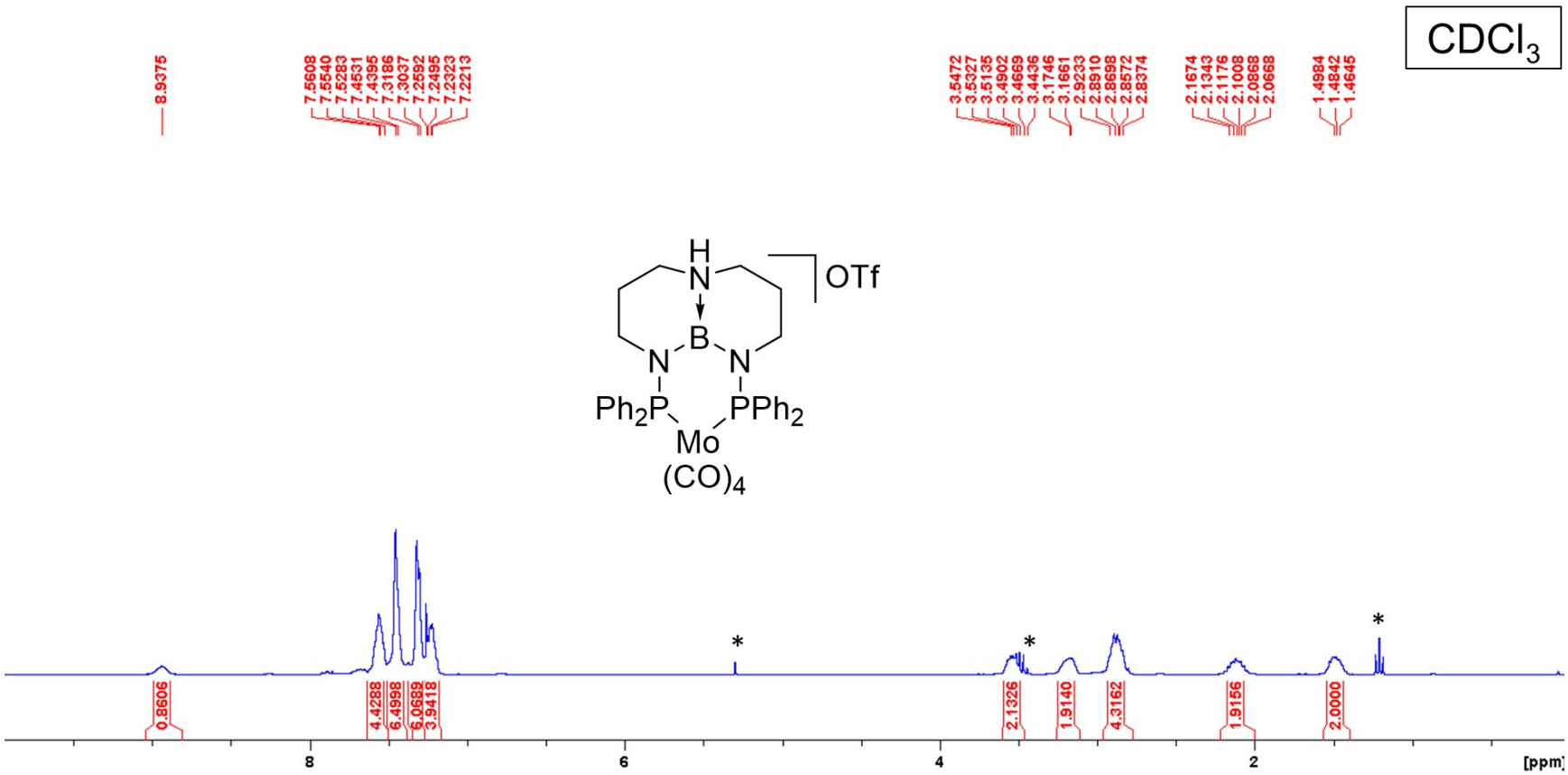

Figure S11. ^{1}H NMR spectrum of [(^{Ph}TBDPhos-H)Mo(CO)$_4$]OTf (**1-HOTf**). The * symbol indicates resonances assigned to residual Et_2O and CH_2Cl_2.

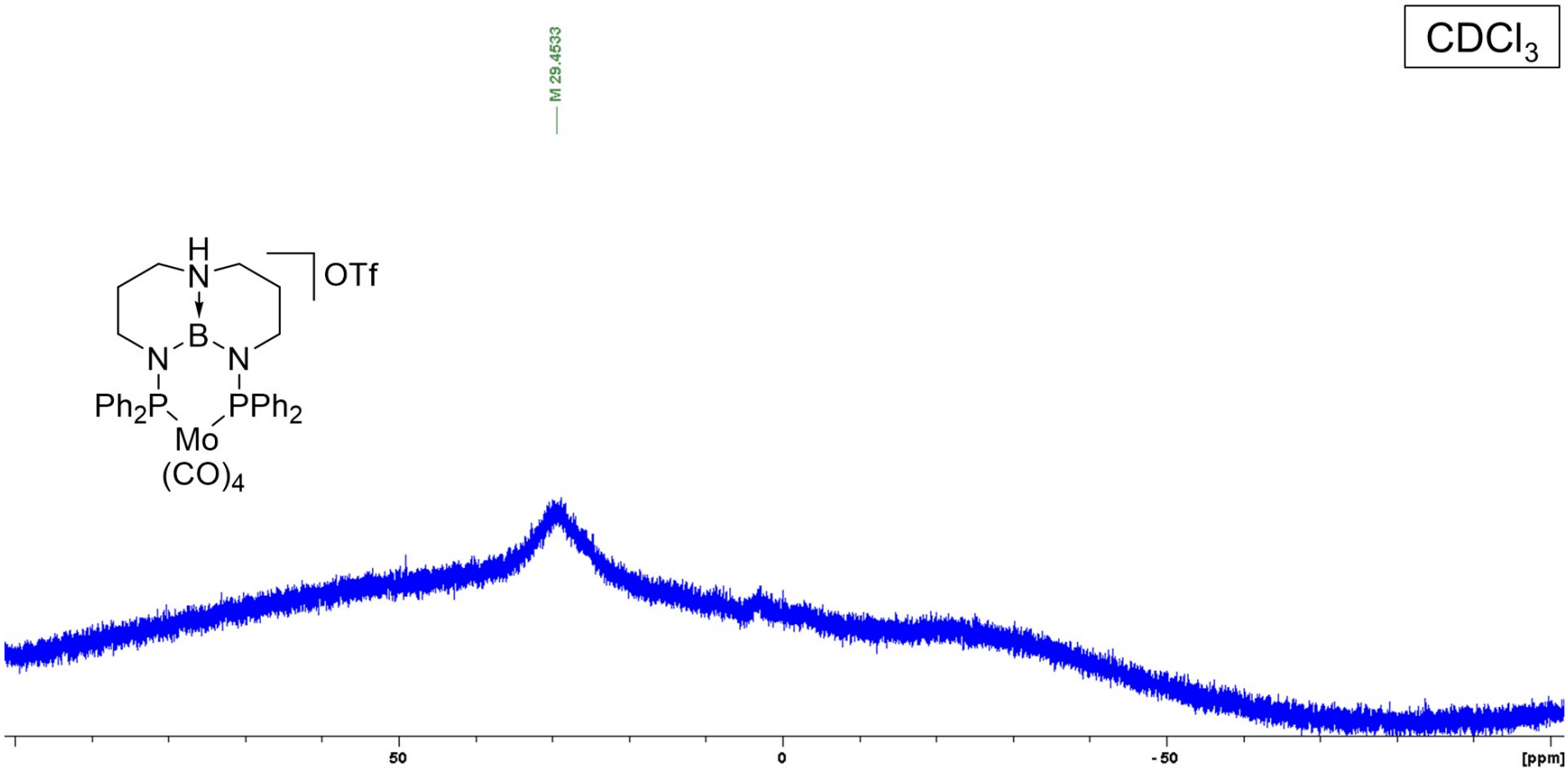

Figure S12. ^{11}B NMR spectrum of [(^{Ph}TBDPhos-H)Mo(CO)$_4$]OTf (**1-HOTf**).

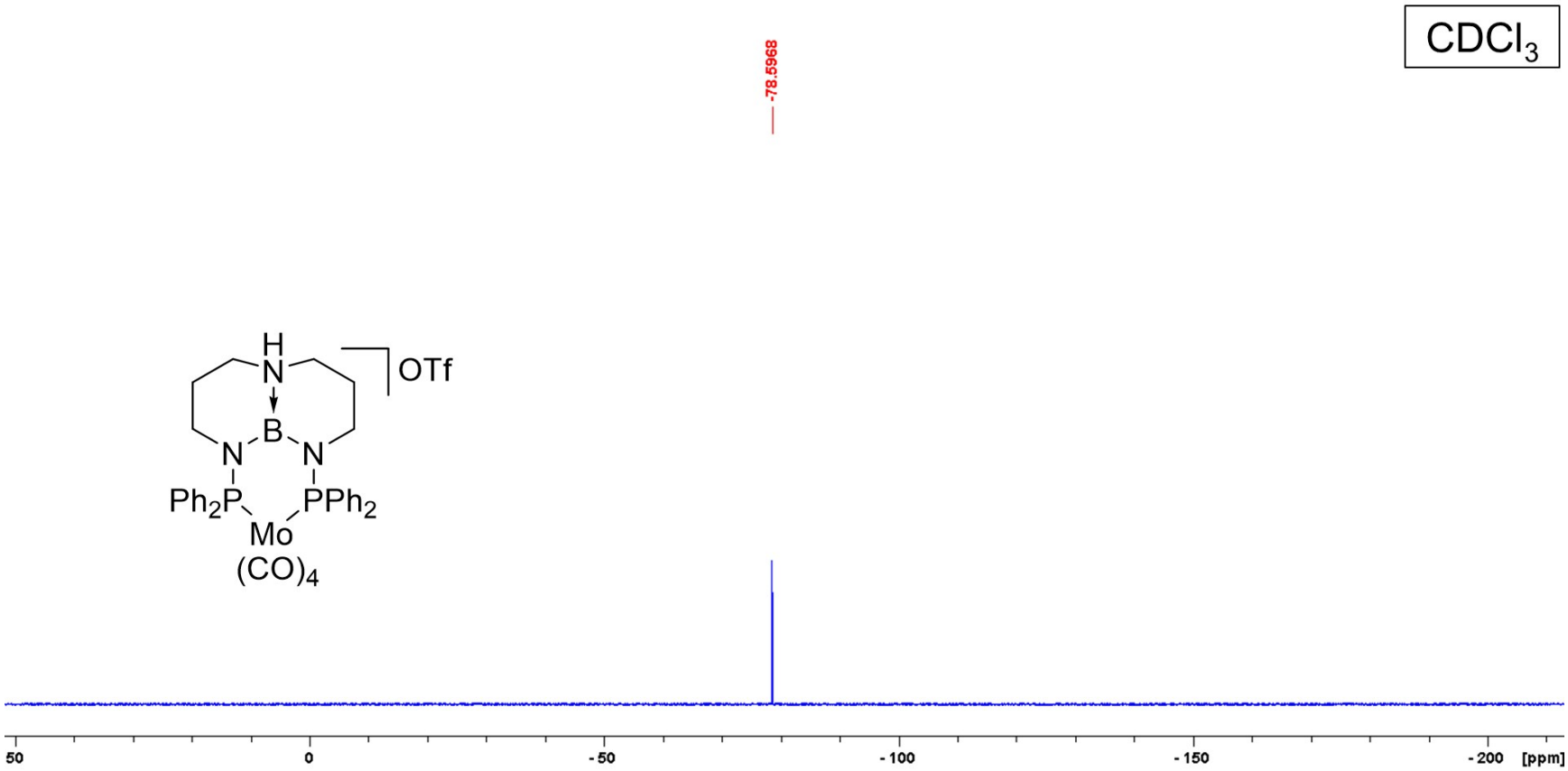

Figure S13. ^{19}F NMR spectrum of [(^{Ph}TBDPhos-H)Mo(CO)$_4$]OTf (**1-HOTf**).

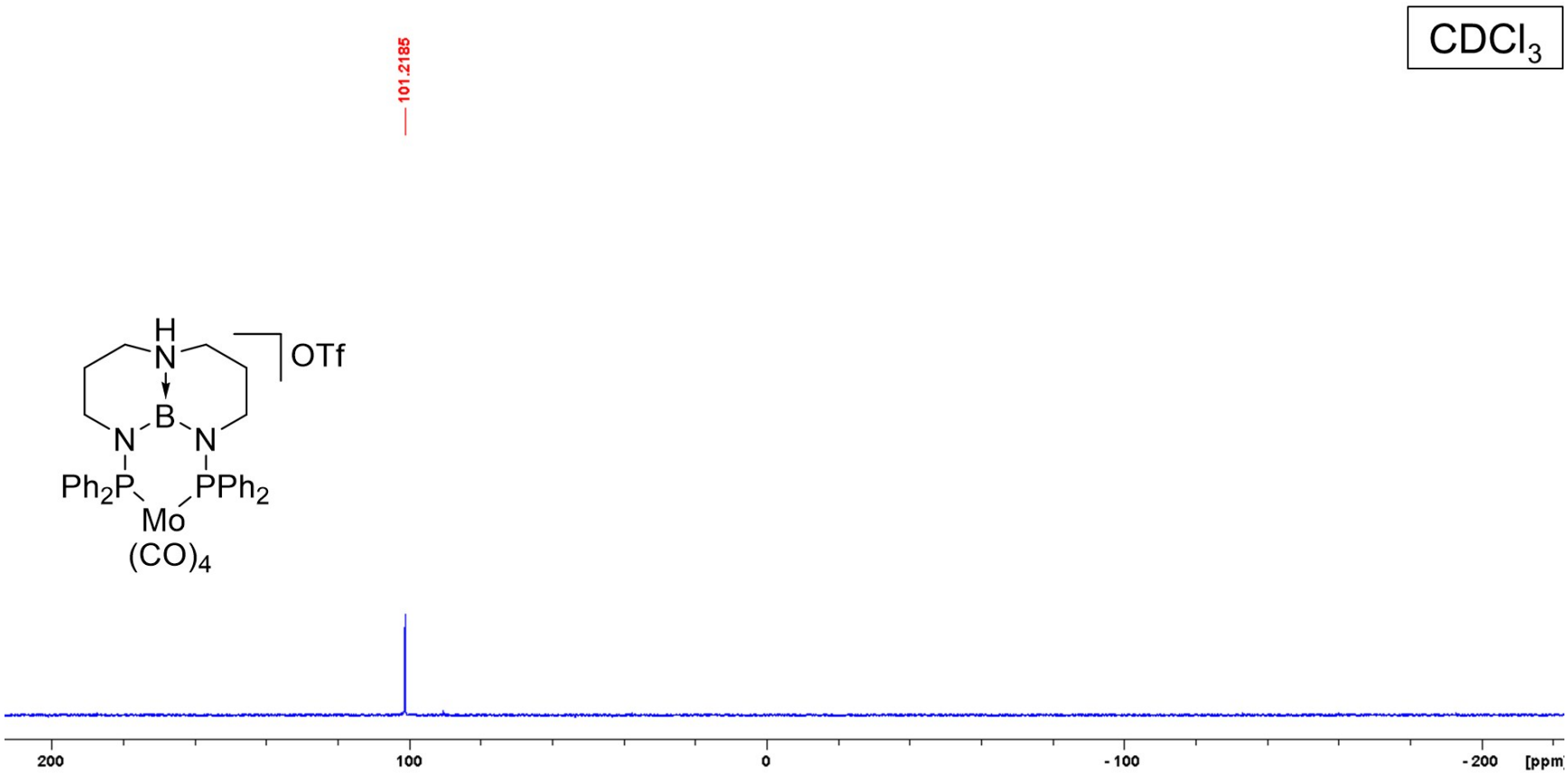

Figure S14. ^{31}P NMR spectrum of [(^{Ph}TBDPhos-H)Mo(CO)$_4$]OTf (**1-HOTf**).

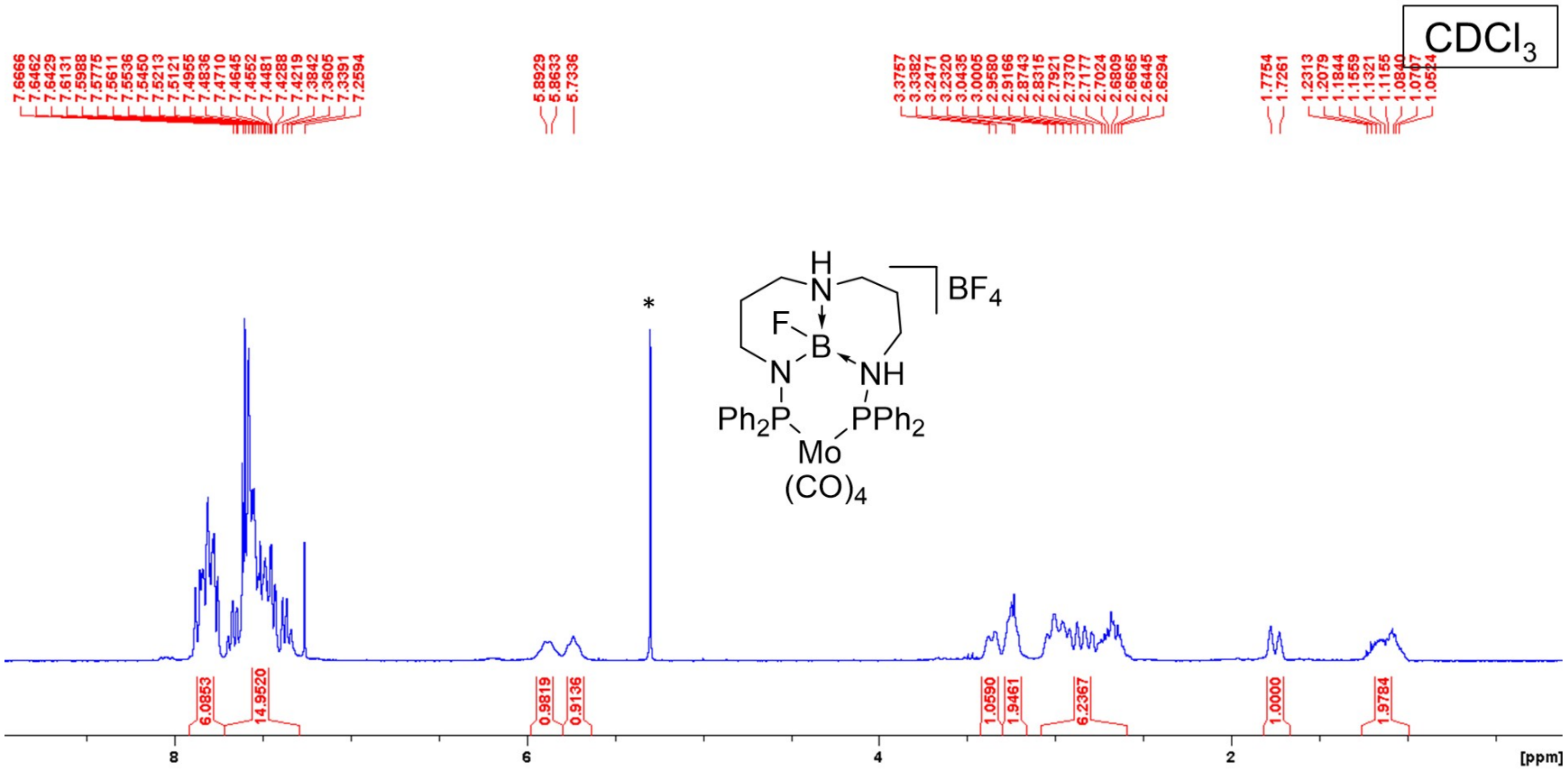

Figure S15. ^{1}H NMR spectrum of [(^{Ph}TBDPhos-H_2F)Mo(CO)$_4$]BF_4 (**[1-H_2F][BF_4]**). The * symbol indicates resonances assigned to residual CH_2Cl_2.

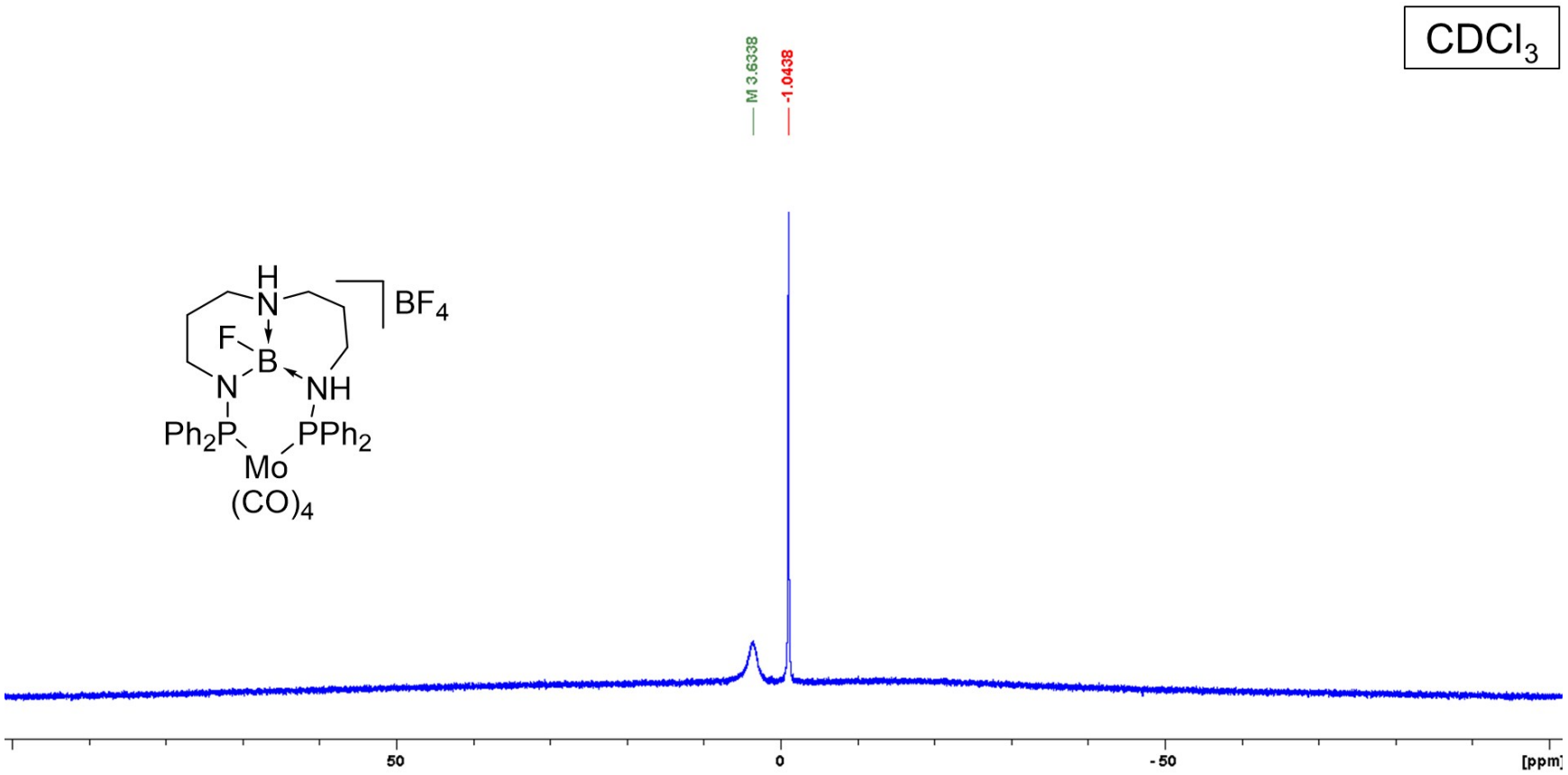

Figure S16. ^{11}B NMR spectrum of [(^{Ph}TBDPhos-H_2F)Mo(CO)$_4$]BF_4 (**[1-H_2F][BF_4]**).

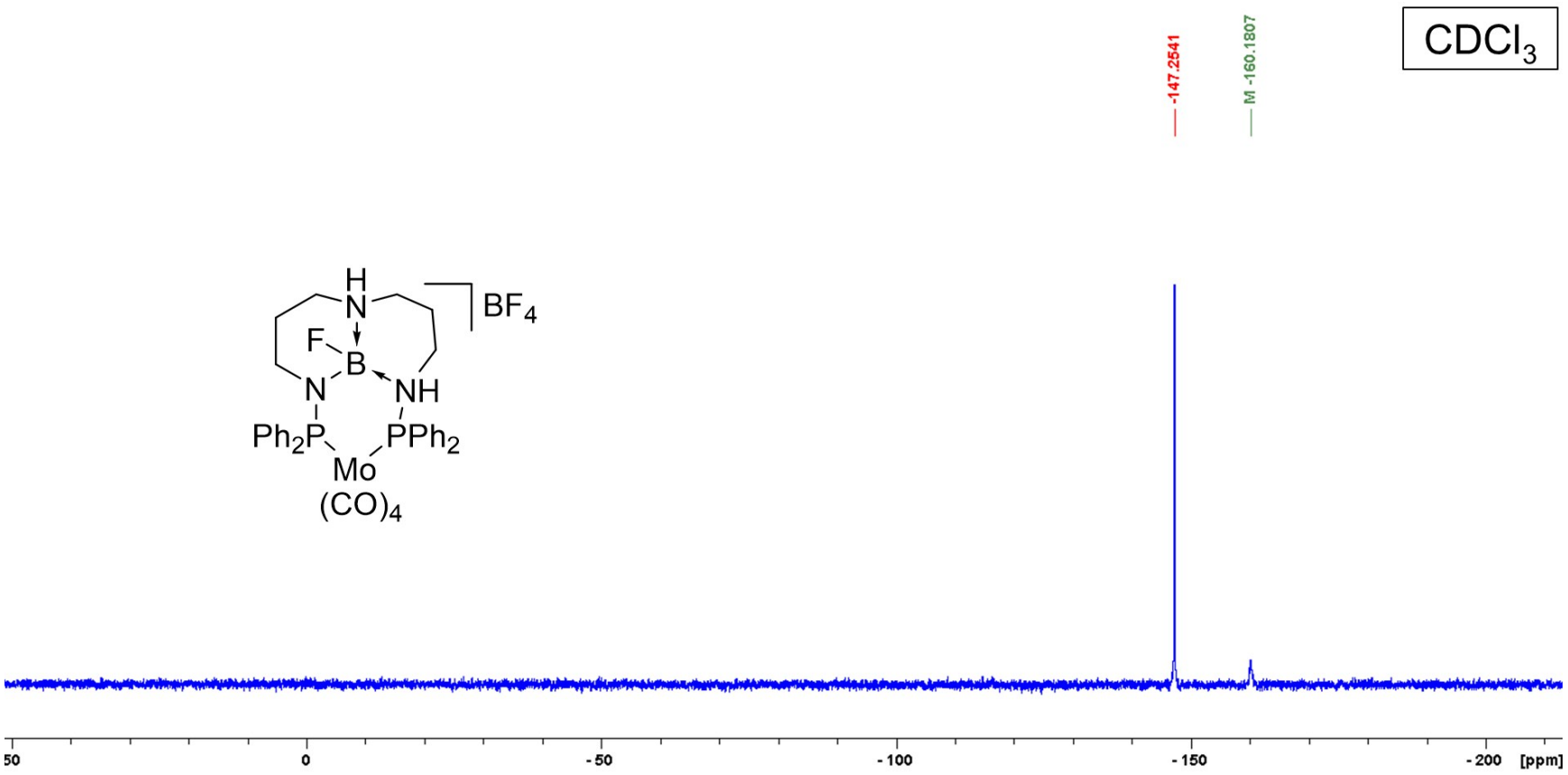

Figure S17. ^{19}F NMR spectrum of [(^{Ph}TBDPhos-H_2F)Mo(CO)$_4$]BF_4 (**[1-H_2F][BF_4]**).

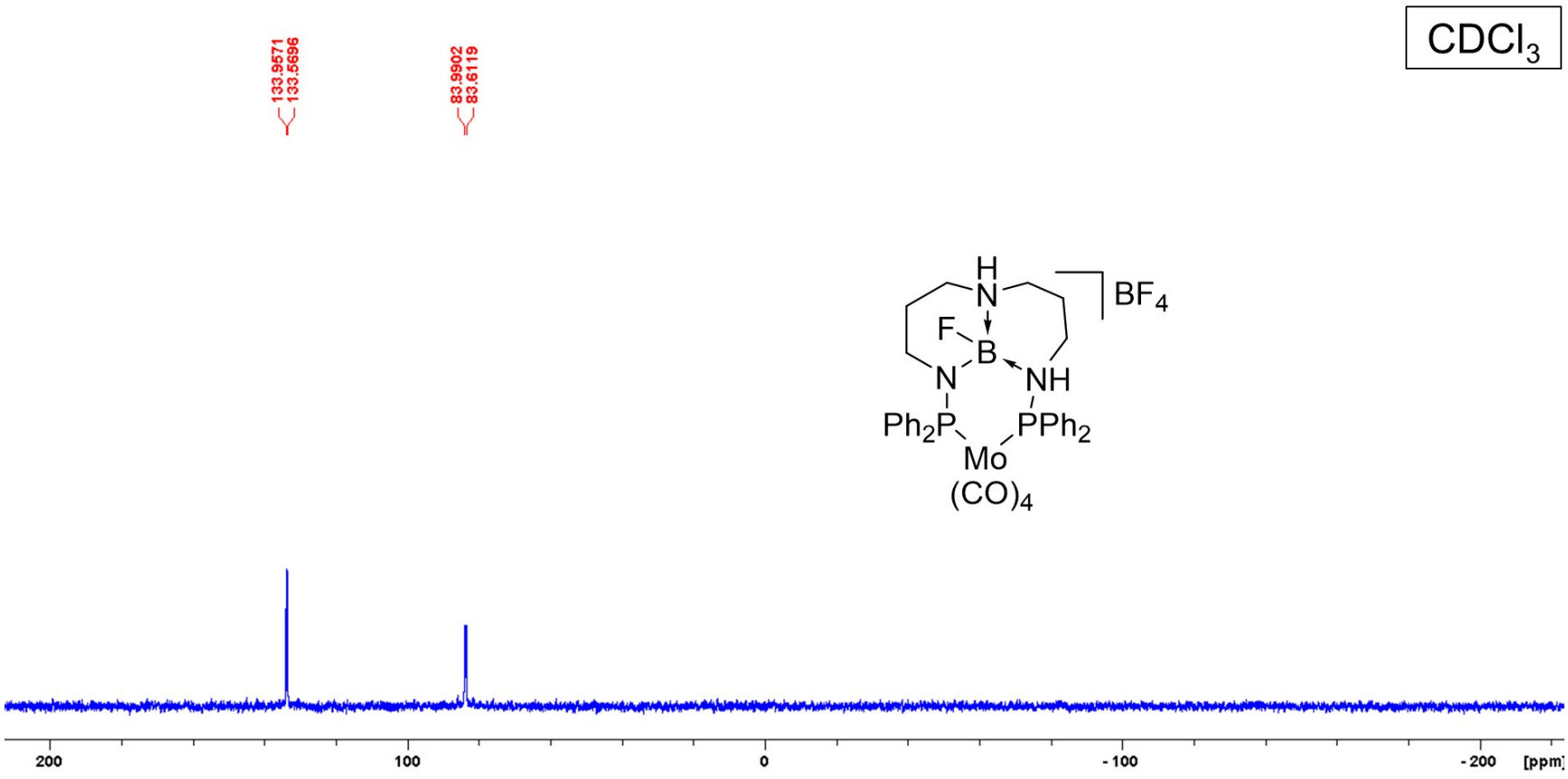

Figure S18. ^{31}P NMR spectrum of [(^{Ph}TBDPhos-H_2F)Mo(CO)$_4$]BF_4 (**[1-H_2F][BF_4]**).

Density Functional Theory Calculations

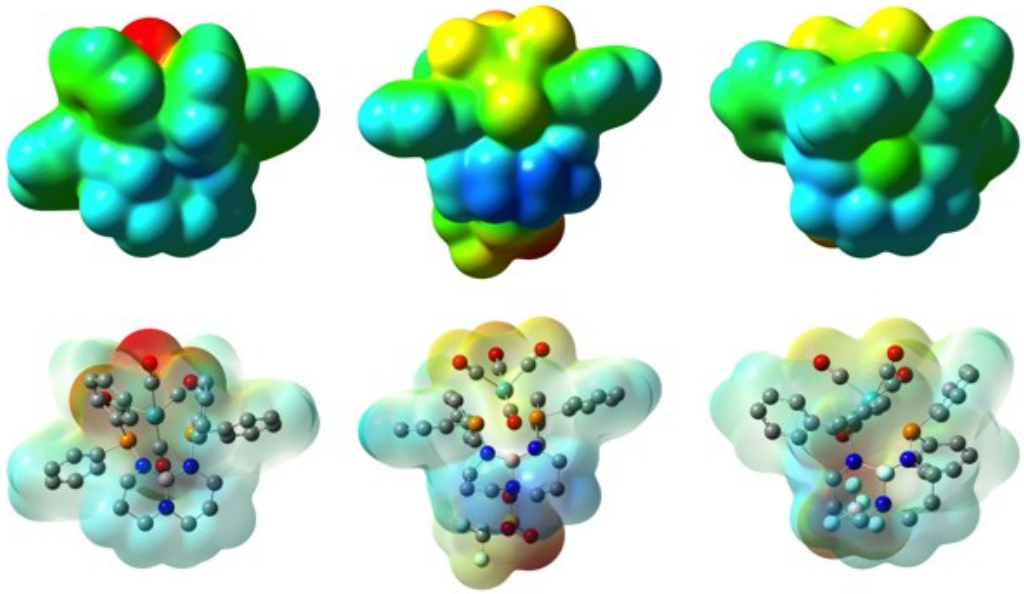

Figure S19. Electrostatic potential for species **1** (left), **1-HOTf** (center), and **[1-H_2F][BF_4]** (right). The electron density is plotted at an isovalue of Density = 0.0008. Top is the solid surface and bottom is the transparent surface. Hydrogen atoms are omitted in the ball and stick representations for clarity. Red coloring of the surface corresponds to a negative potential while blue indicates a positive region.

Table S2. Total calculated energies in Hartrees on the optimized DFT geometries.

Structure	M06, def2-TZVP/def2-SV(P)	M06, def2-TZVP
1	-2553.691413	-3624.52360352
1-HOTf	-3515.543961	-4586.67716660
[1-H_2F][BF_4]	-3079.306731	-4150.34655267
2	--	-1044.22947294
2-HOTf	--	-1044.66397500

Table S3. Select bond distances (Å) and angles (deg) from the M06 optimized geometries of **1**, **1-HOTf**, and **[1-H_2F][BF_4]**.

Structure	Mo-P	Mo-CO_{ax}	Mo-CO_{eq}	B-N	B-N(P)	P-N	X---HN	P-Mo-P	OC-Mo-CO	∑ NBN
1	2.520	2.036	1.995	1.422	1.459	1.686	-	83.3	178.1	359.6
	2.535	2.054	1.999		1.471	1.695			91.8	
1-HOTf	2.510	2.033	1.999	1.554	1.416	1.710	1.754	82.3	177.1	360.0
	2.523	2.056	2.002		1.428	1.739			90.5	
[1-H_2F][BF_4]	2.485	2.048	1.997	1.638	1.496	1.681	1.908	86.7	169.0	329.2
	2.542	2.052	2.003		1.634	1.836	1.988		92.5	

Table S4. Calculated Mo-CO stretching frequencies in cm^{-1}. Calculated intensities are shown in parentheses.

Structure	CO stretches
1	1972 (2381), 1975 (3488), 2008 (1825), 2109 (652)
1-HOTf	1976 (3517), 1988 (2263), 2019 (1627), 2114 (811)
[1-H_2F][BF_4]	1991 (2363),2003 (3611), 2021 (1091), 2121 (845)