Supporting Information

Calcium Complexes with Imino-phosphinanilido Chalcogenide Ligands for Heterofunctionalisation Catalysis

Srinivas Anga,† Jean-François Carpentier,*§ Tarun K. Panda,*† Thierry Roisnel,§ and Yann Sarazin*§

S20. ^{1}H NMR spectrum (C_6D_6, 500.13 MHz, 298 K) of [{L^3}Ca{N($SiMe_3$)$_2$}(thf)] (**3**)

S21. $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 161.9 MHz, 298 K) of [{L^3}Ca{N($SiMe_3$)$_2$}(thf)] (**3**)

S22. $^{77}Se\{^{1}H\}$ NMR spectrum (C_6D_6, 76.31 MHz, 298 K) of [{L^3}Ca{N($SiMe_3$)$_2$}(thf)] (**3**)

S23. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 125.76 MHz, 298 K) of [{L^3}Ca{N($SiMe_3$)$_2$}(thf)] (**3**)

Table TS1. Crystallographic data and refinement parameters of L^3H, 3 and 5.

Crystal	**{L^3H}**	**3**	**5**
CCDC No.	1479903	1479904	1479905
Empirical formula	$C_{31}H_{33}N_2PSe$	$C_{41}H_{58}CaN_3OPSeSi_2$	$C_{62}H_{64}CaN_4P_2S_2$
Formula weight	543.52	815.09	1031.31
T (K)	150(2)	150(2)	150(2)
λ (Å)	1.54184	0.71073	1.54184 A
Crystal system	monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	P-1	C_2/c
a (Å)	13.4929(2)	10.204(4)	22.6518(6)
b (Å)	15.45835(19)	16.193(7)	10.3398(2)
c (Å)	14.4620(2)	17.708(7)	25.6988(7)
α (°)	90	65.515(14)	90
β (°)	107.1086(16)	85.943(12)	115.912(3)
γ (°)	90	73.318(14)	90
V (Å^3)	2882.97(8)	2546.8(18)	5413.9(3)
Z	4	2	4
D_{calc} g cm^{-3}	1.252	1.063	1.265
μ (mm^{-1})	3.513	0.945	2.609
F (000)	2004.0	860.0	2184
Theta range for data collection	8.582 to 142.26	5.9 to 52.9	4.796 to 71.411
Limiting indices	$-15 \leq h \leq 16$, $-8 \leq k \leq 18$, $-17 \leq l \leq 17$	$-12 \leq h \leq 12$, $-17 \leq k \leq 20$, $0 \leq l \leq 22$	-27<=h<=18 -12<=k<=12 -30<=l<=31
Reflections collected / unique	10969	10155	14668 / 5081
Completeness to theta = 71.25	99%	98%	98.0 %
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5496/0/320	10155/0/461	5081/0/325
Goodness-of-fit on F^2	1.047	1.148	1.050
Final R indices [I>2sigma(I)]	$R_1 = 0.0574$, $wR_2 = 0.1494$	$R_1 = 0.0879$, $wR_2 = 0.2587$	$R_1 = 0.0372$, $wR_2 = 0.0967$
R indices (all data)	$R_1 = 0.0500$, $wR_2 = 0.1407$	$R_1 = 0.1289$, $wR_2 = 0.2821$	$R_1 = 0.0421$, $wR_2 = 0.1017$
Largest diff. peak and hole	0.53/-0.79 e.A^{-3}	3.38/-0.86 e.A^{-3}	0.230/-0.459 e.A^{-3}

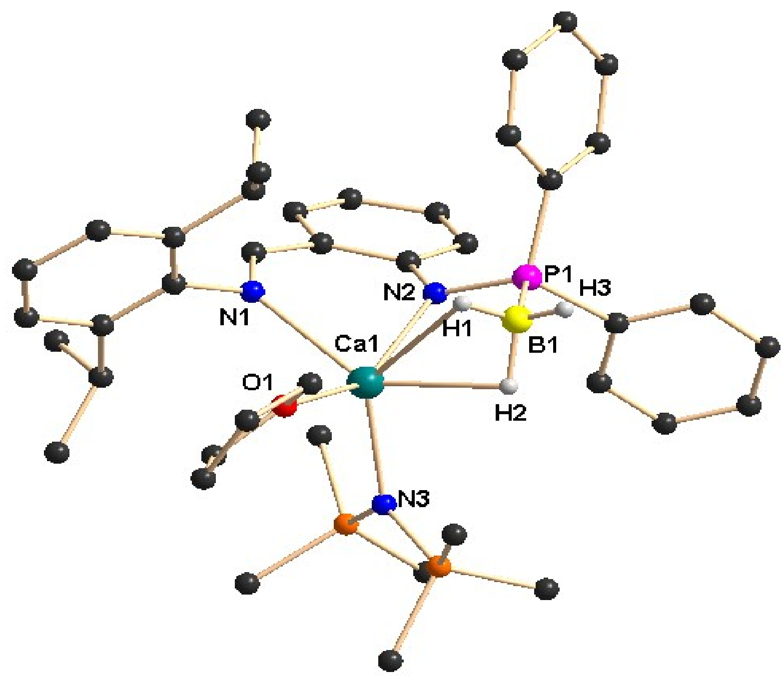
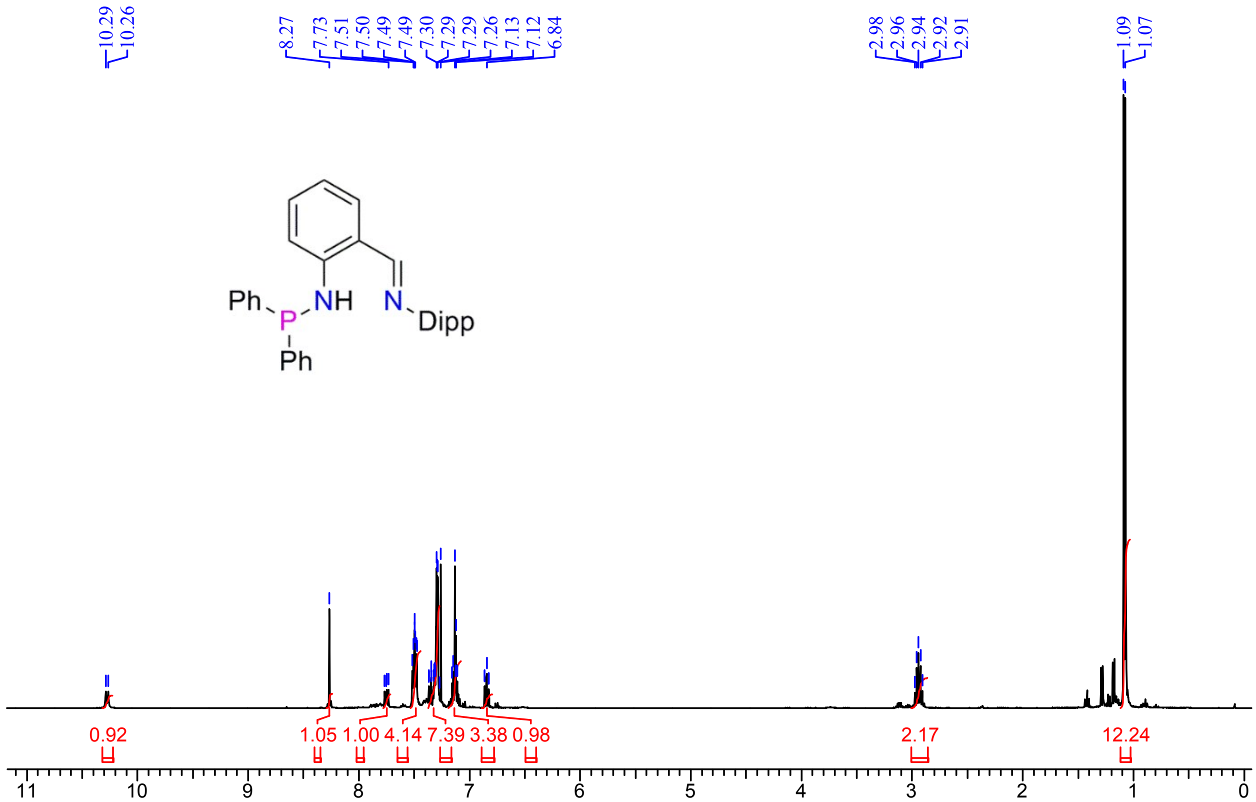
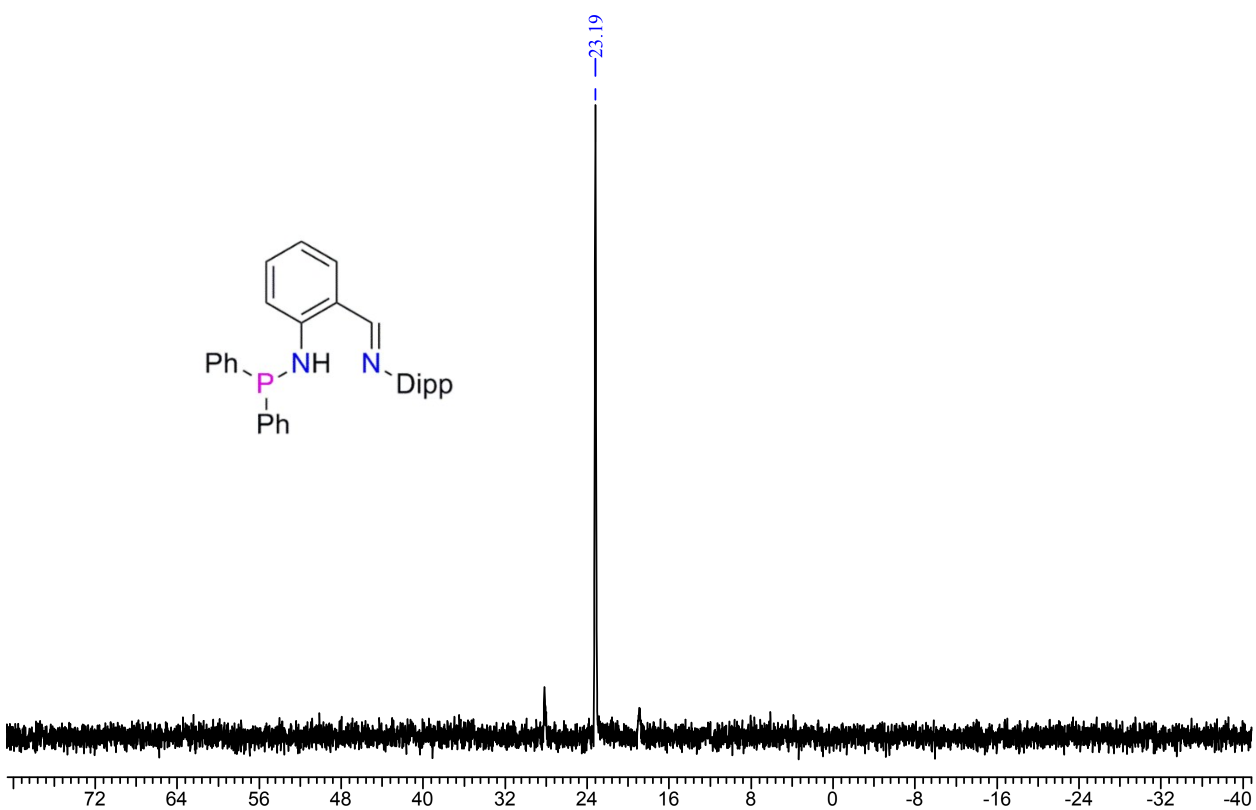


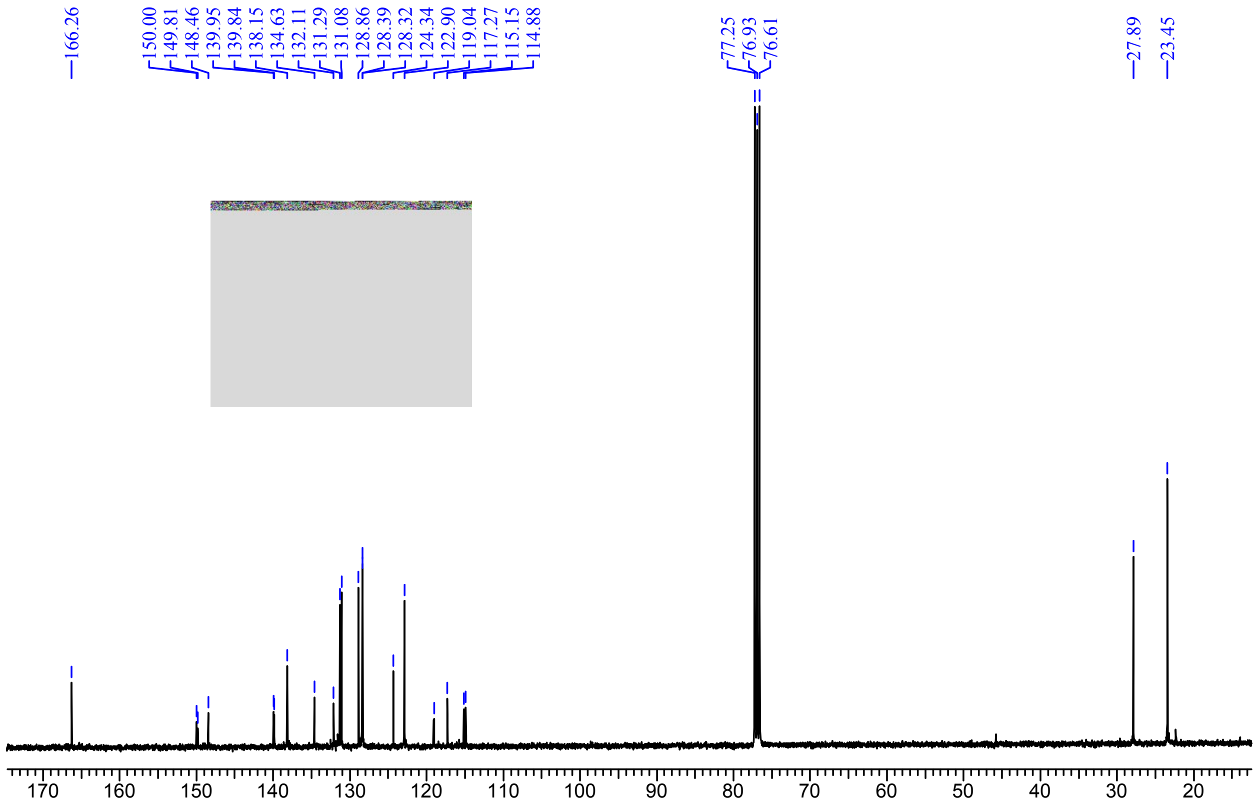
Figure FS1. Solid-state structure of [{L[4]}CaN(SiMe$_3$)$_2$·(THF)] (**4**). All hydrogen atoms (except H1, H2 and H3) are omitted for clarity. Selected bond lengths (Å) and angles (°): Ca1–N1 2.3668(18), Ca1–N2 2.5156(18), Ca1–N3 2.298(2), Ca1–O1 2.3553(16), Ca1–H1 2.49(3), Ca1–H2 2.55(3), N1–Ca1–N2 74.08(6), N1–Ca1–N3 115.38(7), N1–Ca1–O1 146.76(6), N2–Ca1–N3 128.91(7), N2-Ca1-O1 87.28(6), N3–Ca1–O1 97.78(7).



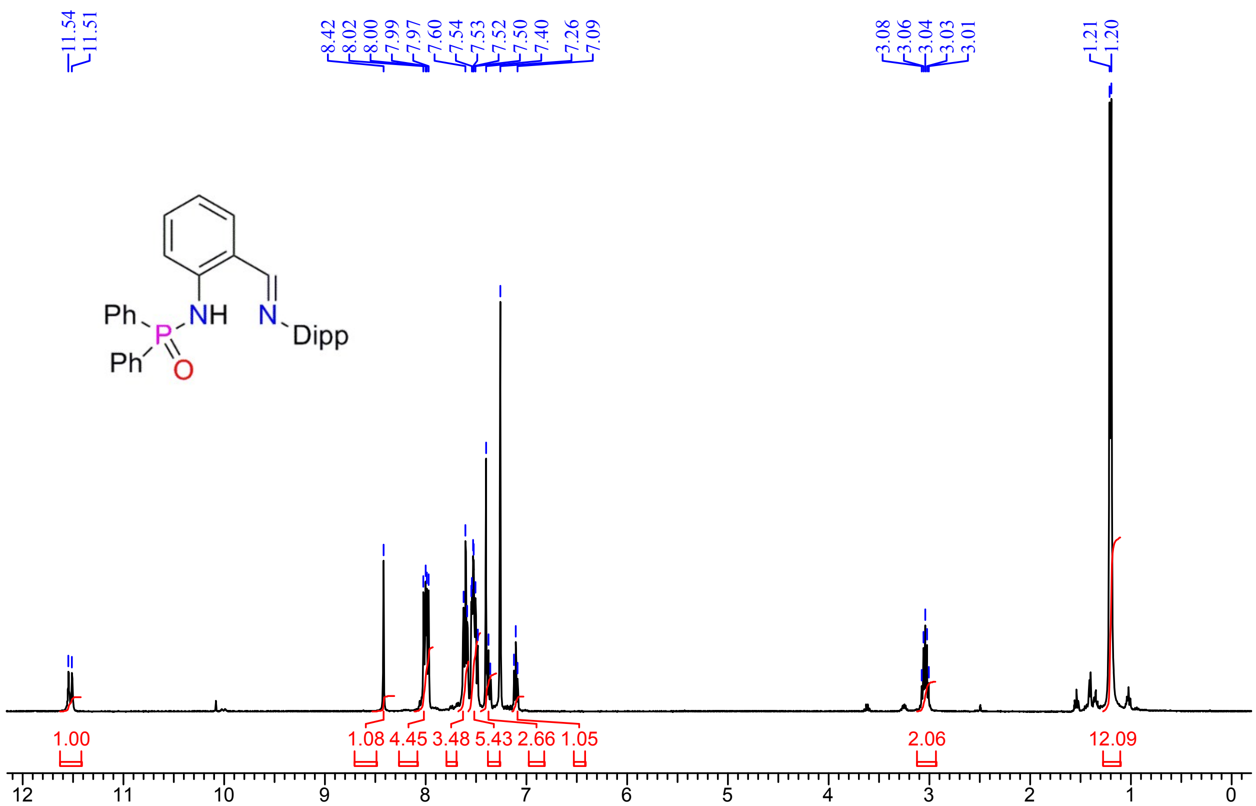
S1. ^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, 298 K) of $Ph_2PHNC_6H_4CH$=N(Dipp) (**L^{0}}H**)



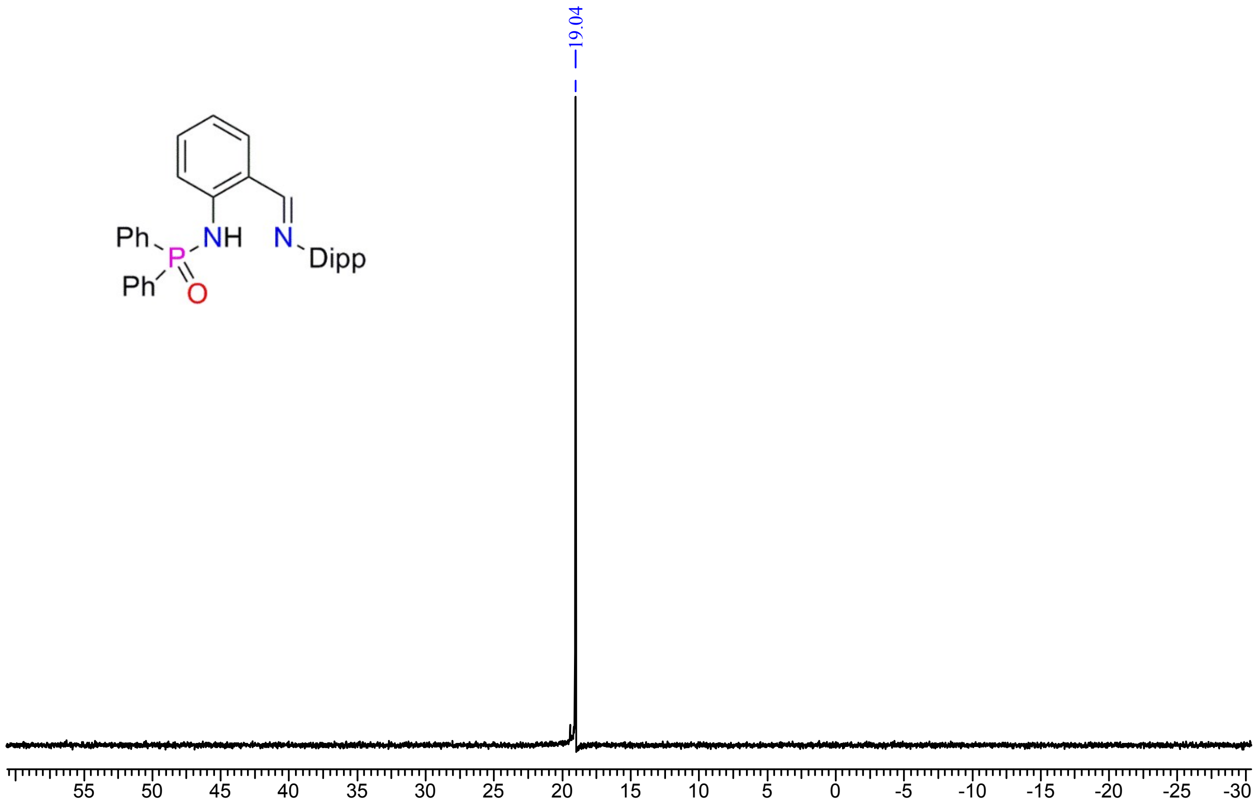
S2. ^{31}P{^{1}H} NMR spectrum ($CDCl_3$, 161.9 MHz, 298 K) of $Ph_2PHNC_6H_4CH$=N(Dipp) (**L^{0}}H**)



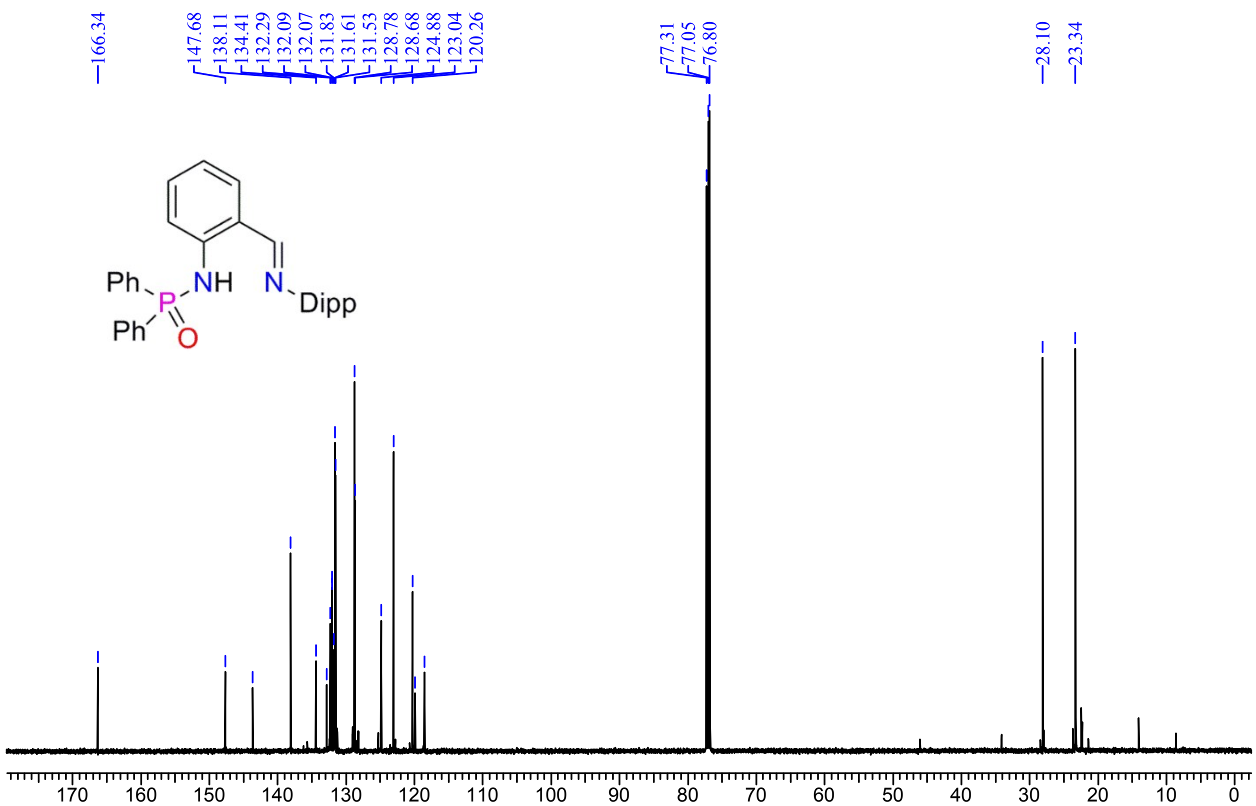
S3. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 125.76 MHz, 298 K) of $Ph_2PHNC_6H_4CH{=}N(Dipp)$ (**L^0}H**)



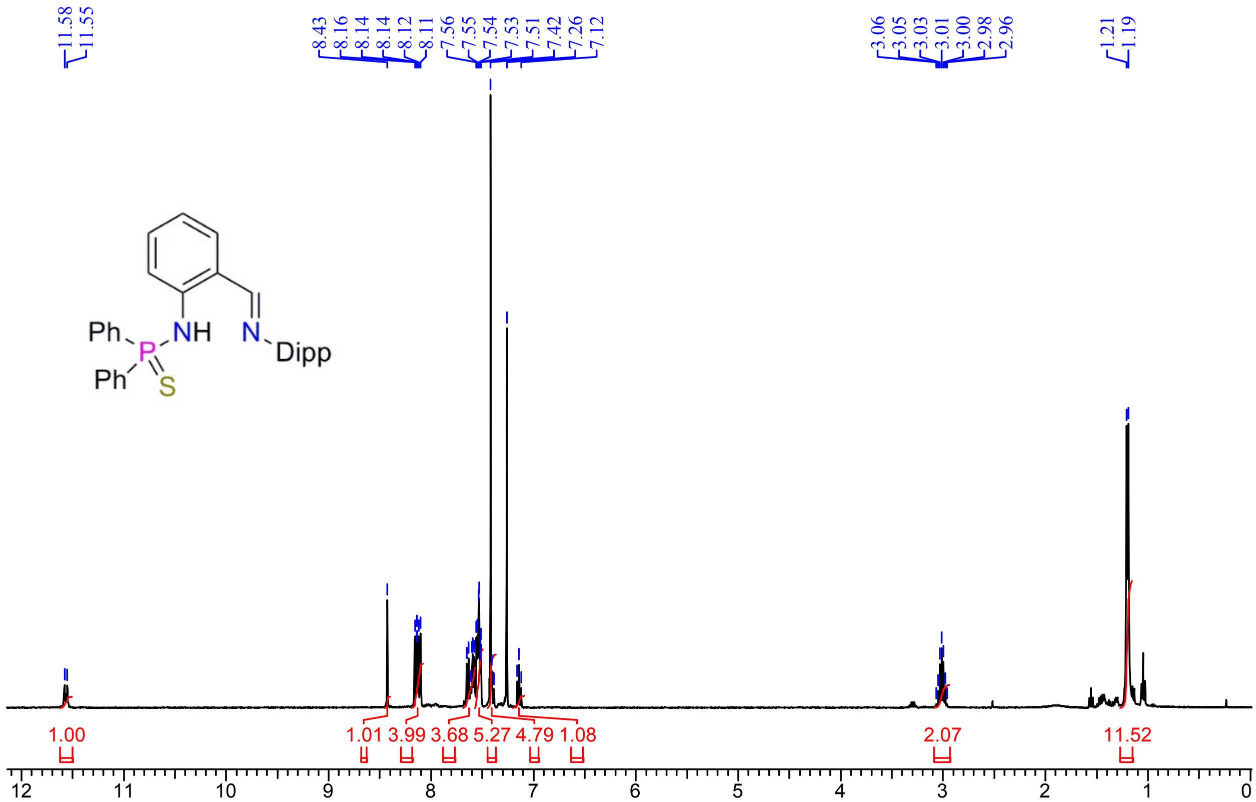
S4. ^1H NMR spectrum ($CDCl_3$, 500.13 MHz, 298 K) of $Ph_2P(O)HNC_6H_4CH{=}N(Dipp)$ (**L^1}H**)



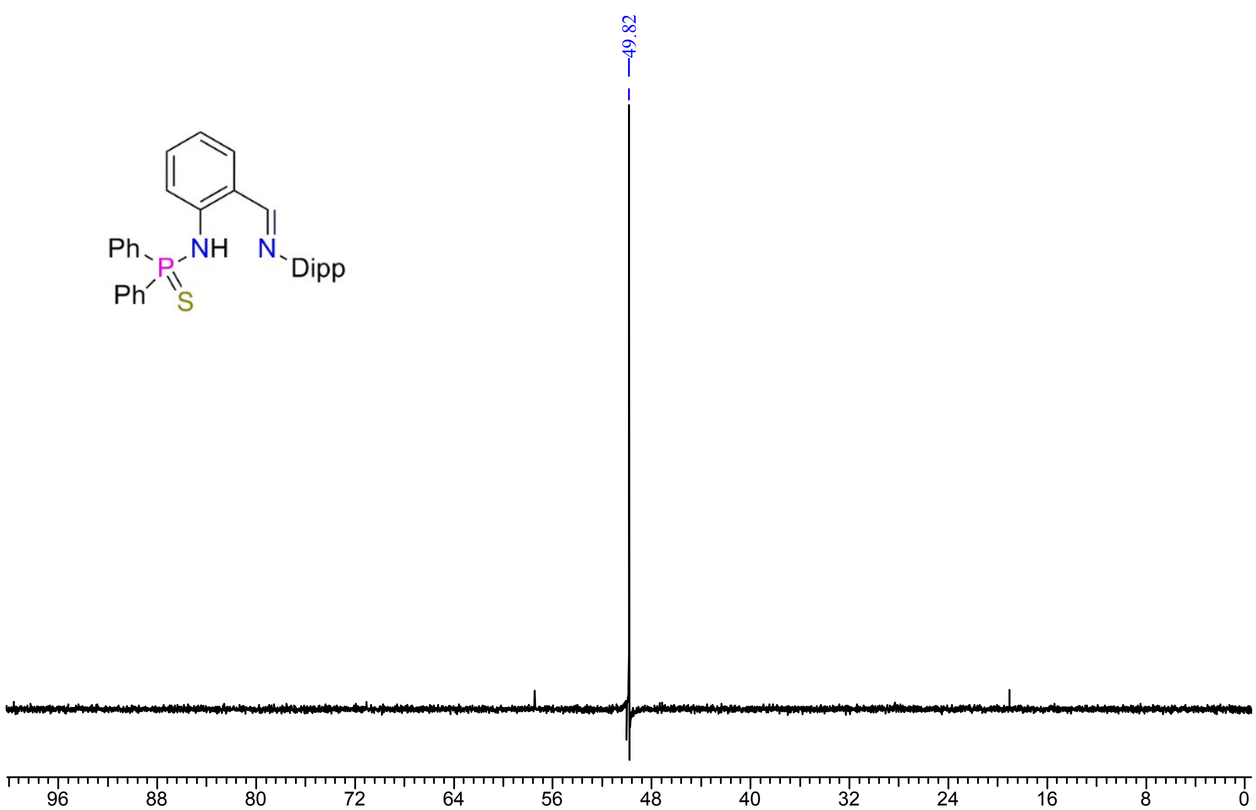
S5. $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$, 161.9 MHz, 298 K) of $Ph_2P(O)HNC_6H_4CH{=}N(Dipp)$ (**L^1}H**)



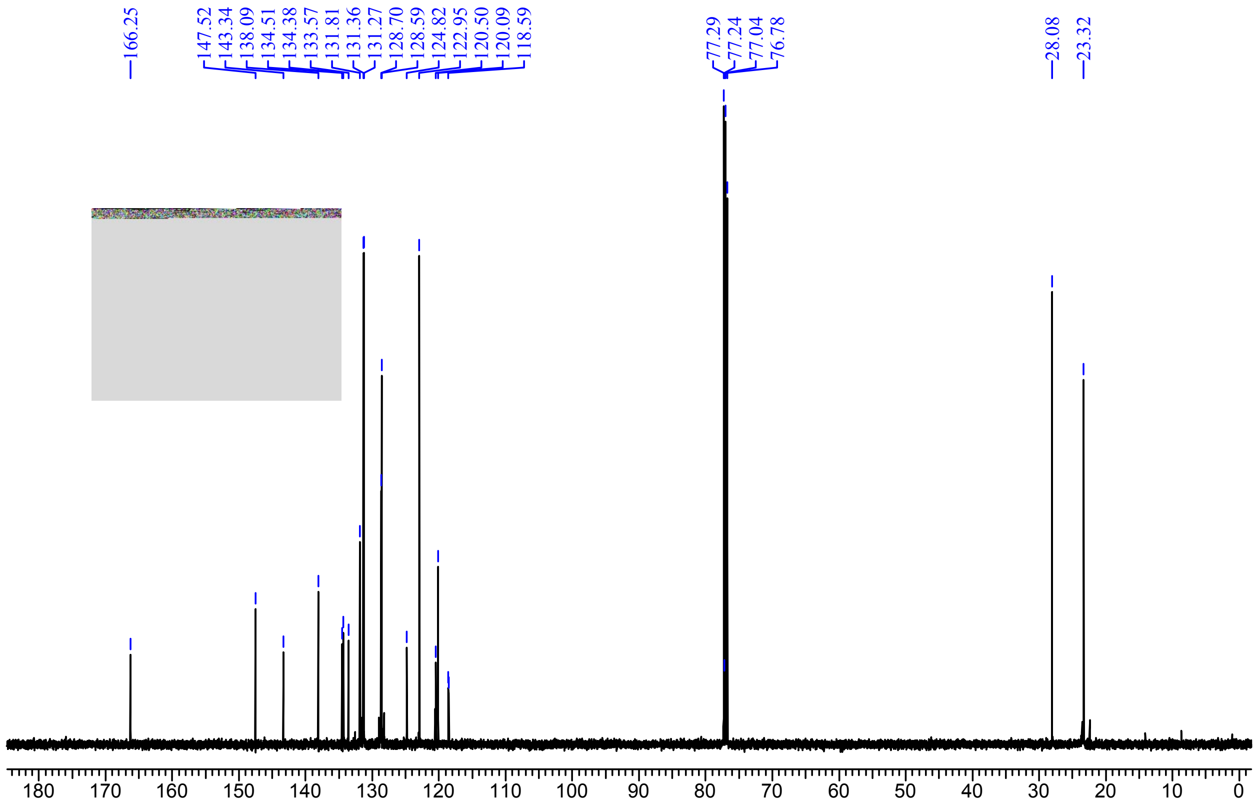
S6. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 125.76 MHz, 298 K) of $Ph_2P(O)HNC_6H_4CH{=}N(Dipp)$ (**L^1}H**)



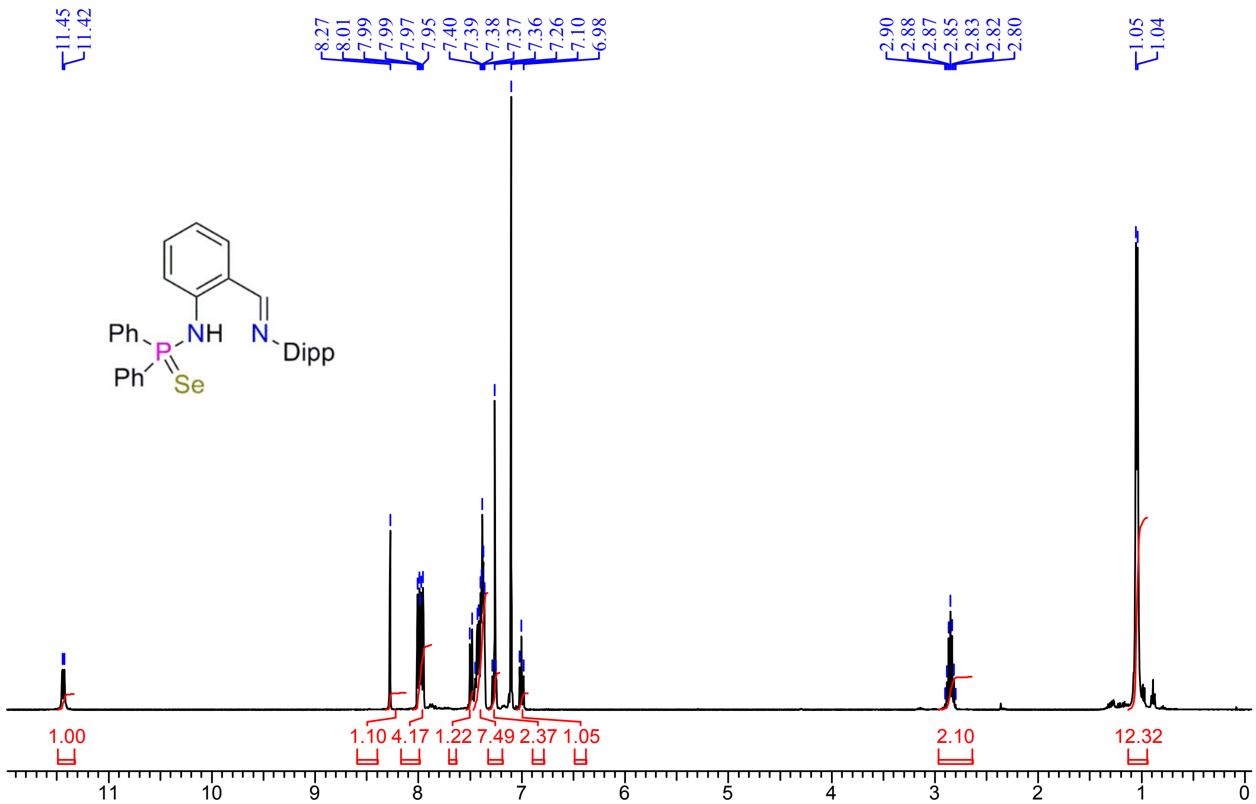
S7.^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, 298 K) of $Ph_2P(S)HNC_6H_4CH{=}N(Dipp)$ (**L^2}H**)



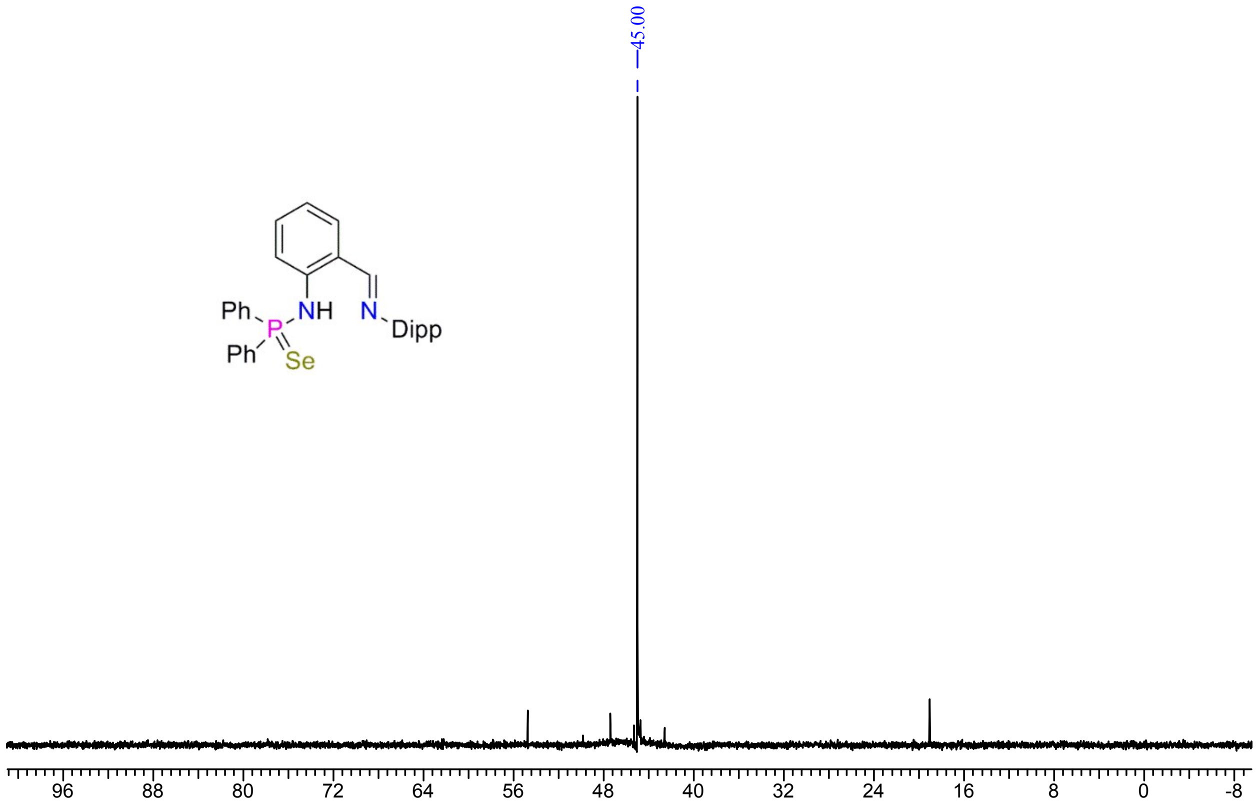
S8. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 161.9 MHz, 298 K) of $Ph_2P(S)HNC_6H_4CH{=}N(Dipp)$ (**L^2}H**)



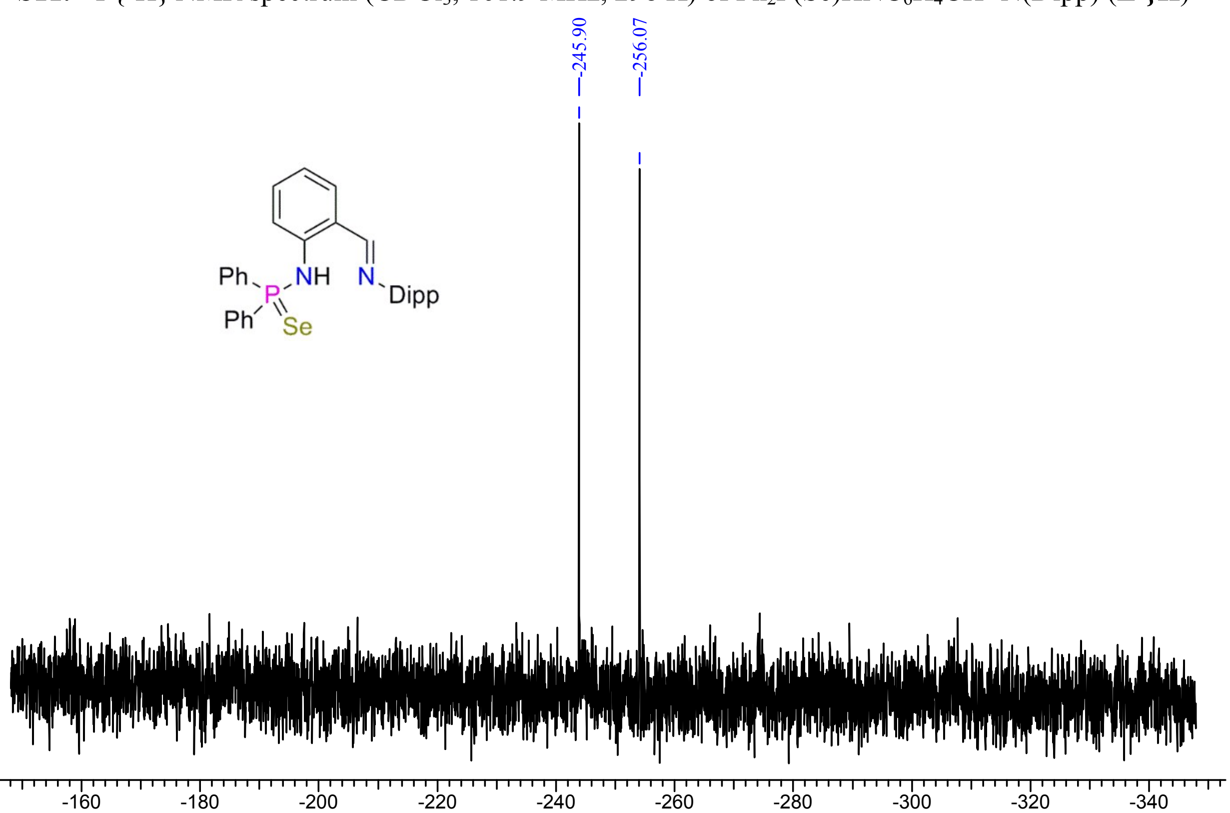
S9. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 125.76 MHz, 298 K) of $Ph_2P(S)HNC_6H_4CH{=}N(Dipp)$ (**L^2}H**)



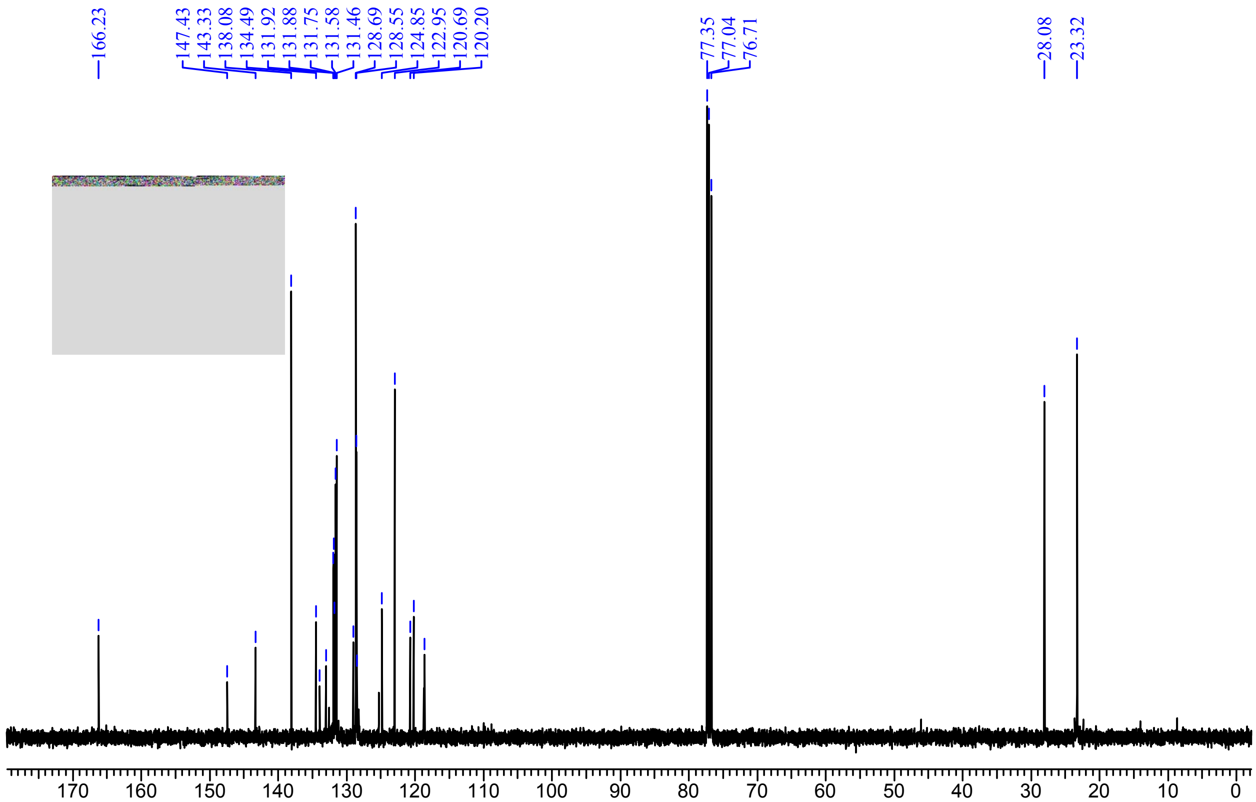
S10. ^1H NMR spectrum ($CDCl_3$, 500.13 MHz, 298 K) of $Ph_2P(Se)HNC_6H_4CH{=}N(Dipp)$ (**L^3}H**)



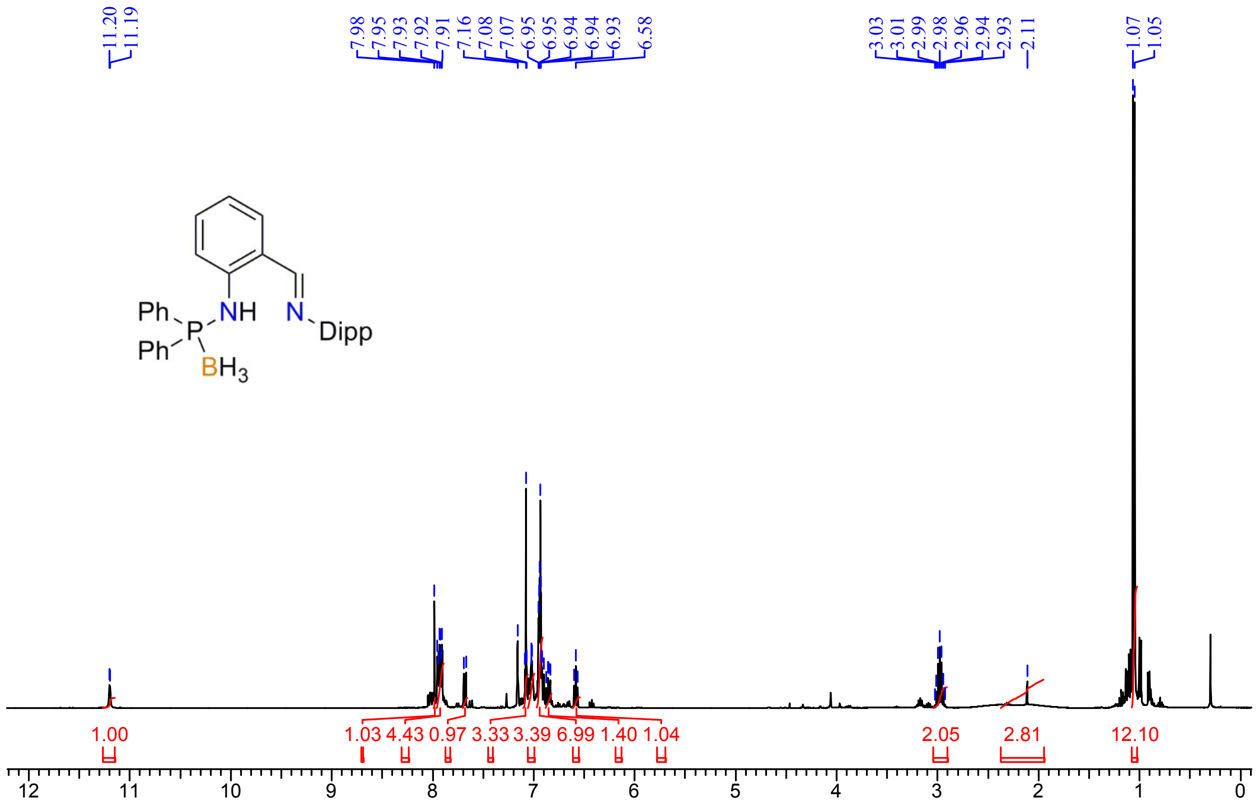
S11. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 161.9 MHz, 298 K) of $Ph_2P(Se)HNC_6H_4CH{=}N(Dipp)$ (**L^3}H**)



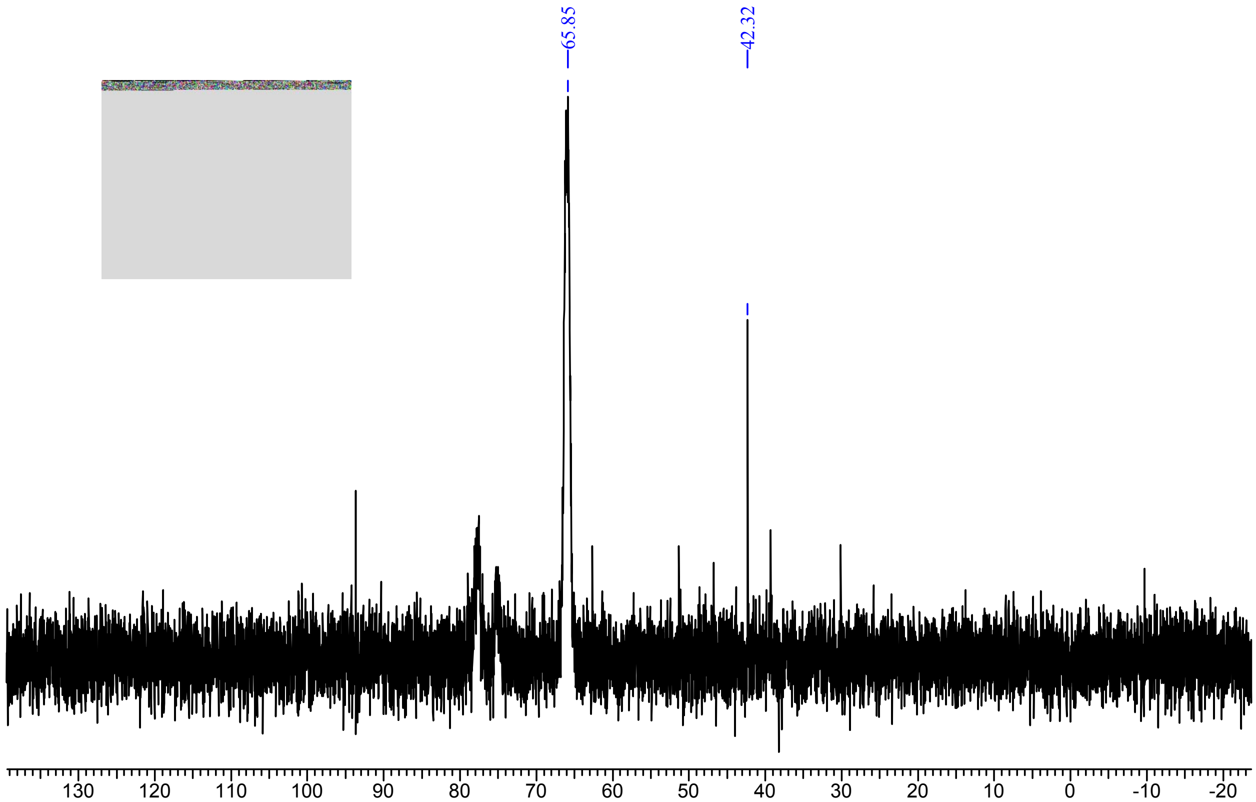
S12. $^{77}Se\{^{1}H\}$ NMR spectrum ($CDCl_3$, 76.31 MHz, 298 K) of $Ph_2P(Se)HNC_6H_4CH{=}N(Dipp)$ (**L^3}H**)



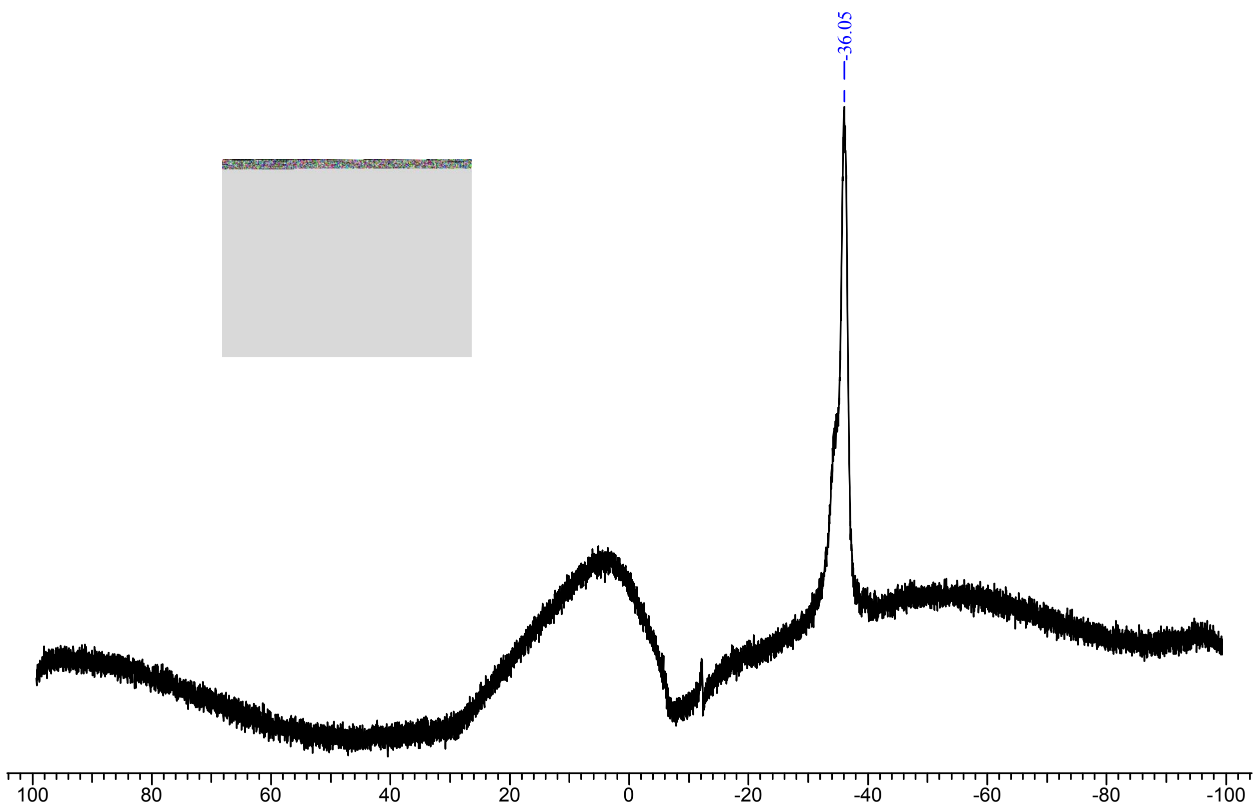
S13. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125.76 MHz, 298 K) of $Ph_2P(Se)HNC_6H_4CH{=}N(Dipp)$ (**L**[3]**}H**)



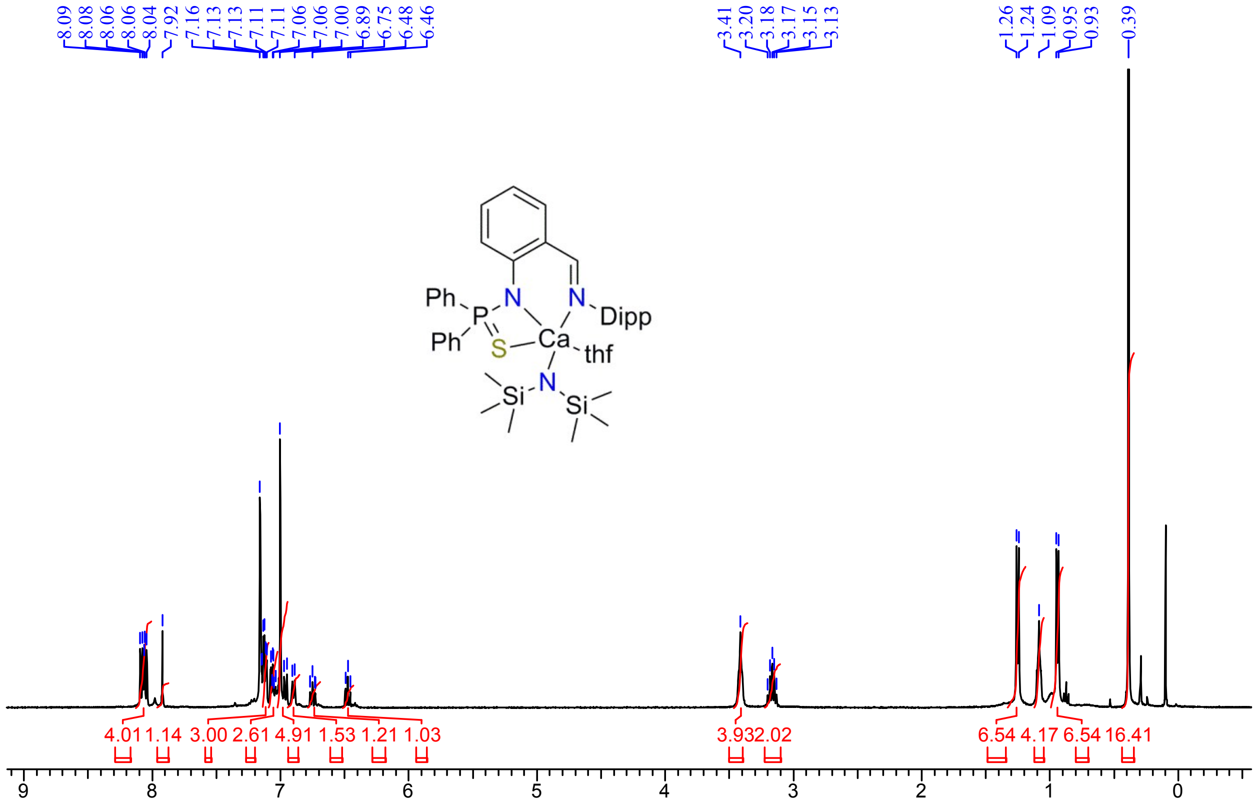
S14. ^{1}H NMR spectrum (C_6D_6, 400.13 MHz, 298 K) of $Ph_2P(BH_3)HNC_6H_4CH{=}N(Dipp)$ (**L**[4]**}H**)



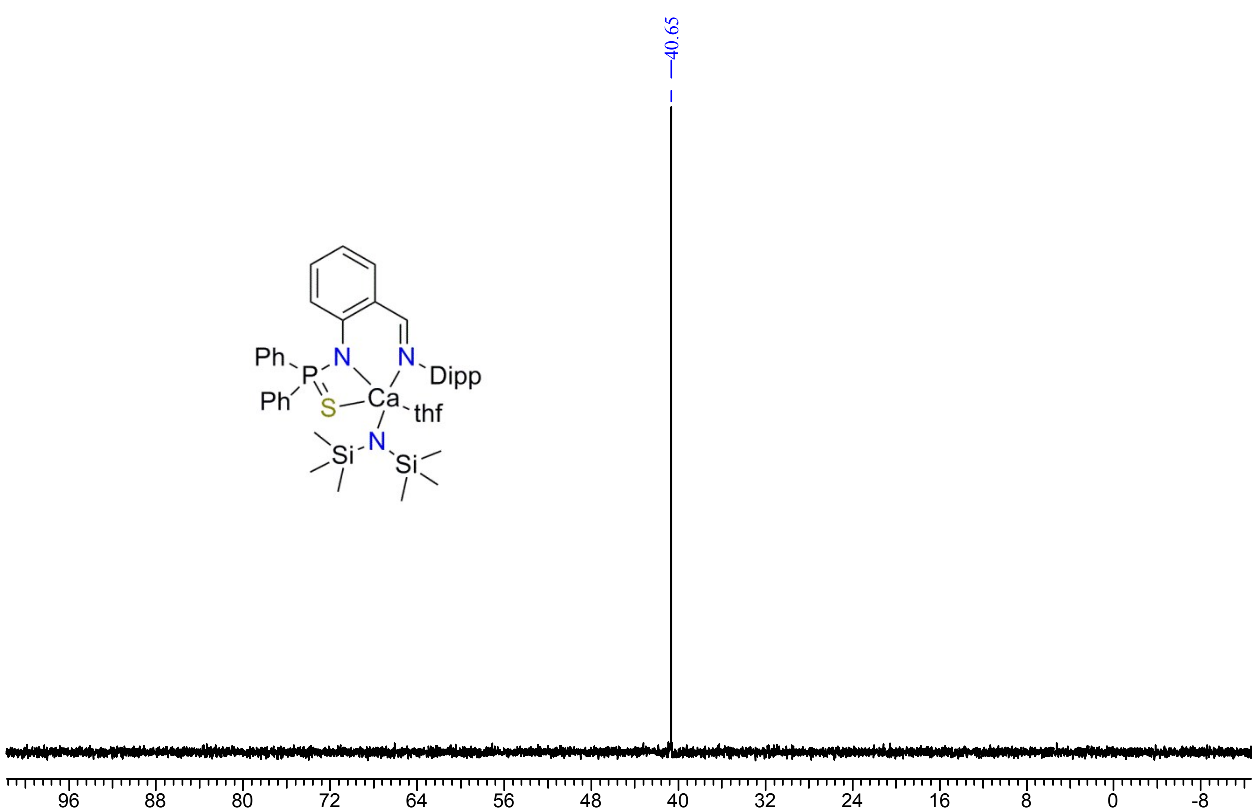
S15. $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 161.9 MHz, 298 K) of $Ph_2P(BH_3)HNC_6H_4CH{=}N(Dipp)$ (**L[4]}H**)



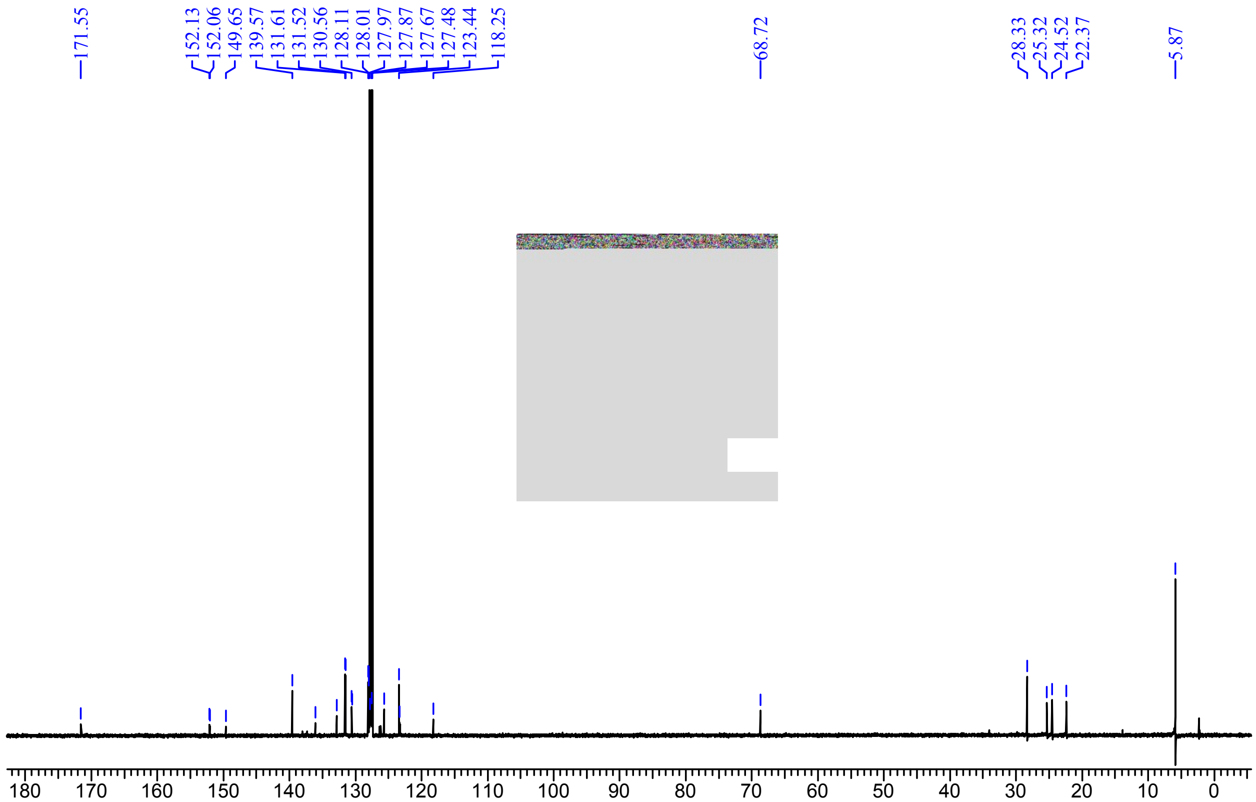
S16. $^{11}B\{^{1}H\}$ NMR spectrum (C_6D_6, 128.4 MHz, 298 K) of $Ph_2P(BH_3)HNC_6H_4CH{=}N(Dipp)$ (**L[4]}H**)



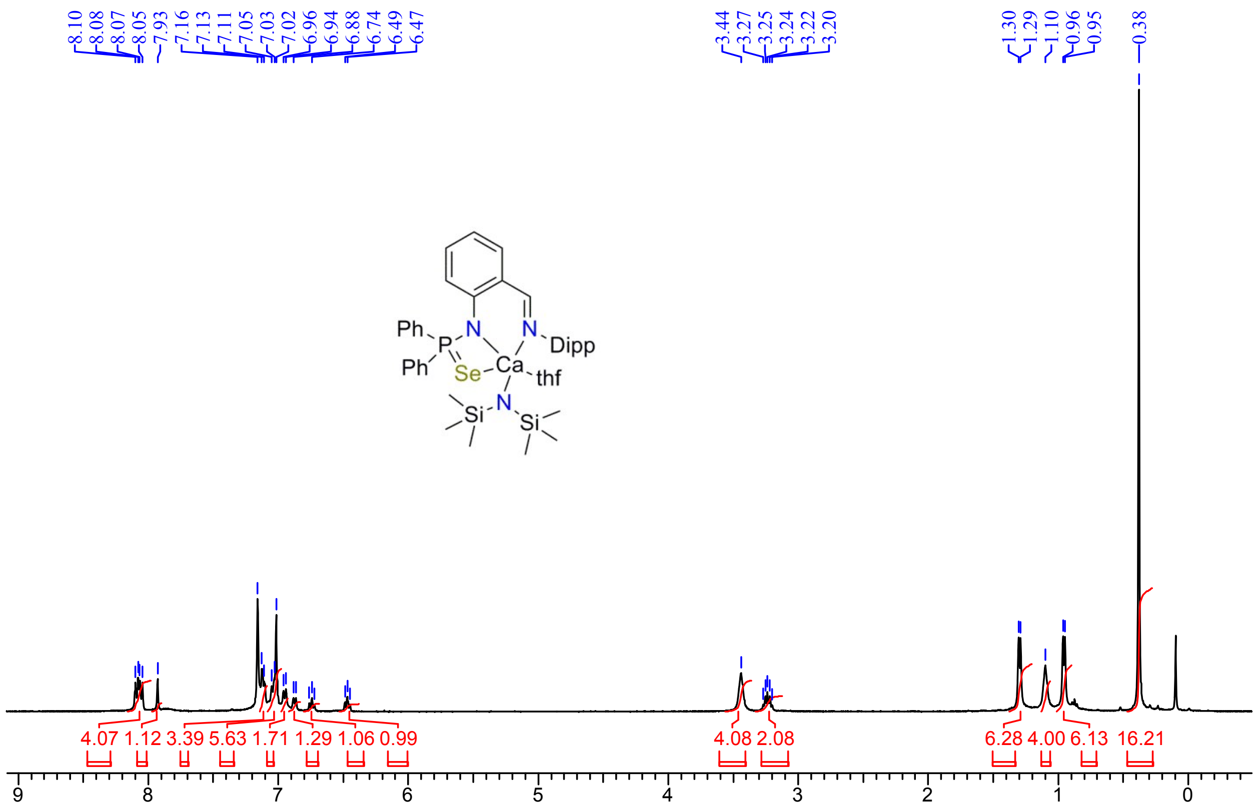
S17. ^{1}H NMR spectrum (C_6D_6, 500.13 MHz, 298 K) of [{L^2}Ca{N($SiMe_3$)$_2$}(thf)] (**2**)



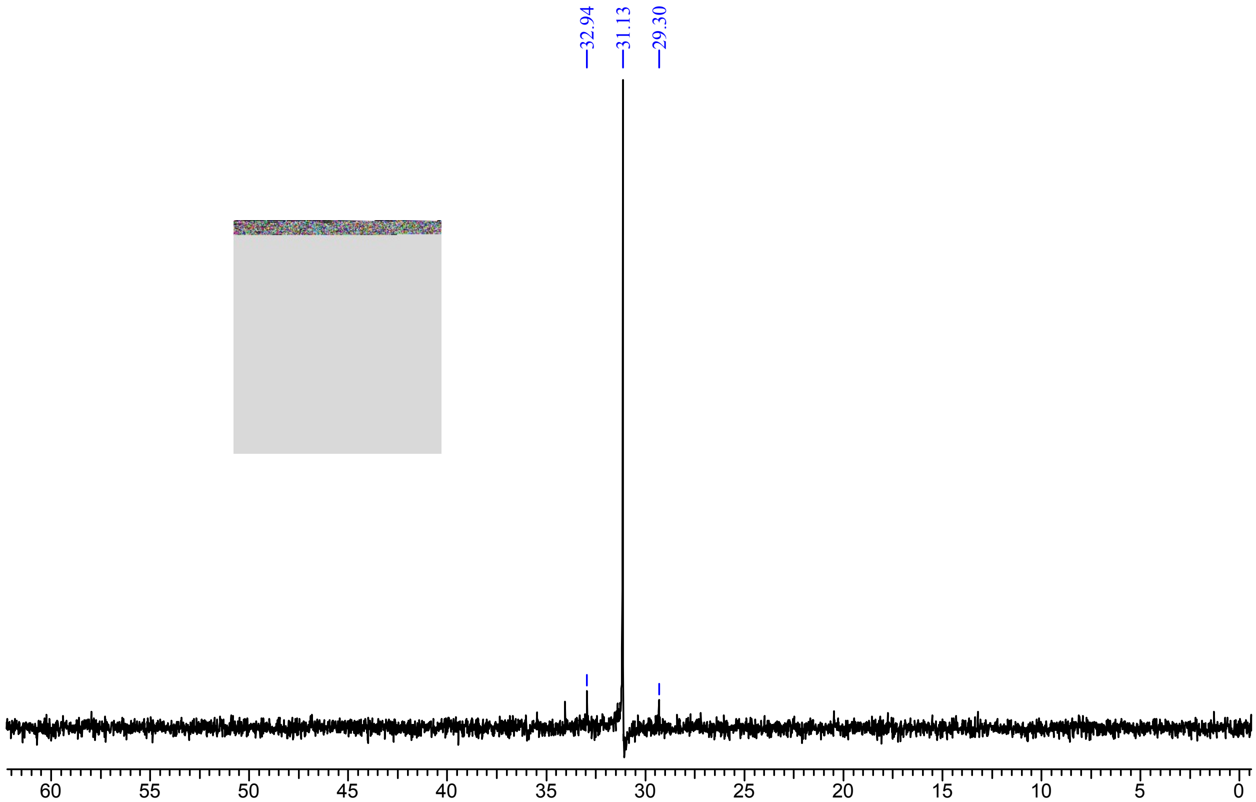
S18. $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 161.9 MHz, 298 K) of [{L^2}Ca{N($SiMe_3$)$_2$}(thf)] (**2**)



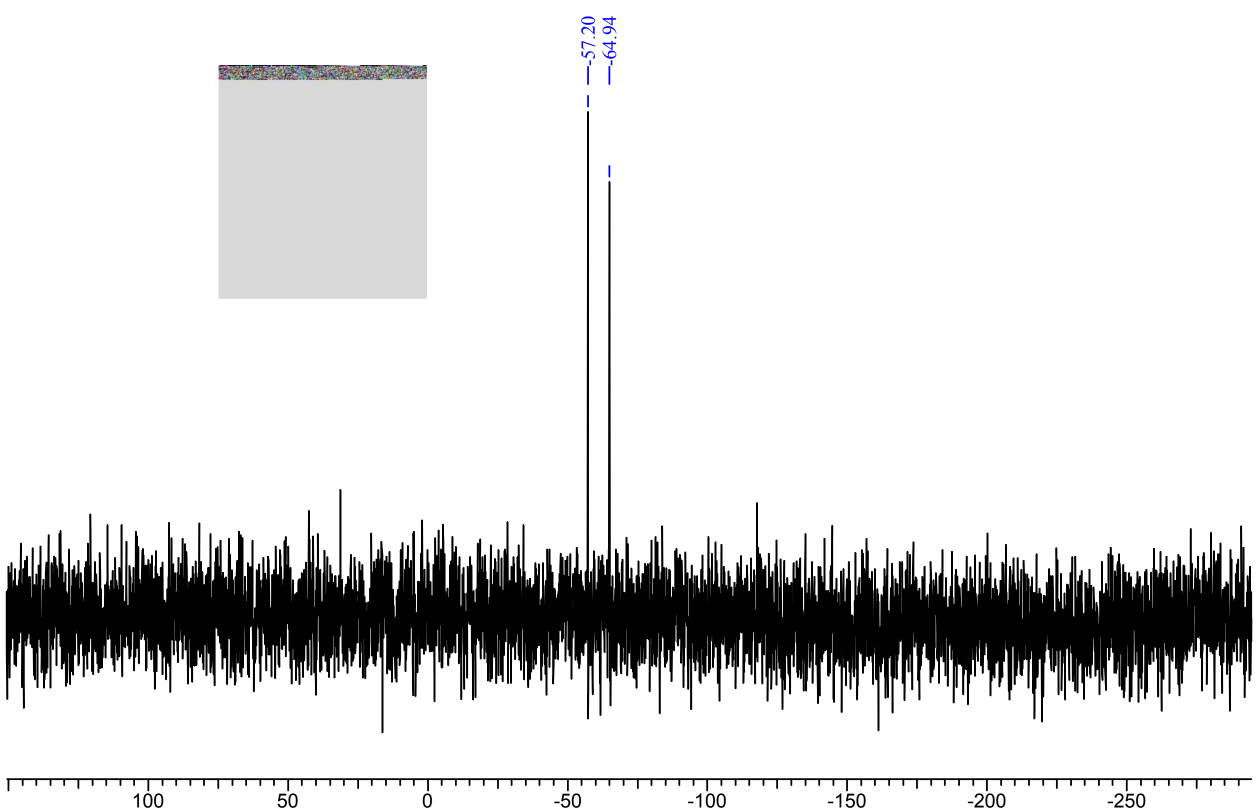
S19. $^{13}C\{^1H\}$ NMR spectrum (C_6D_6, 125.76 MHz, 298 K) of [{L^2}Ca{N($SiMe_3$)$_2$}(thf)] (**2**)



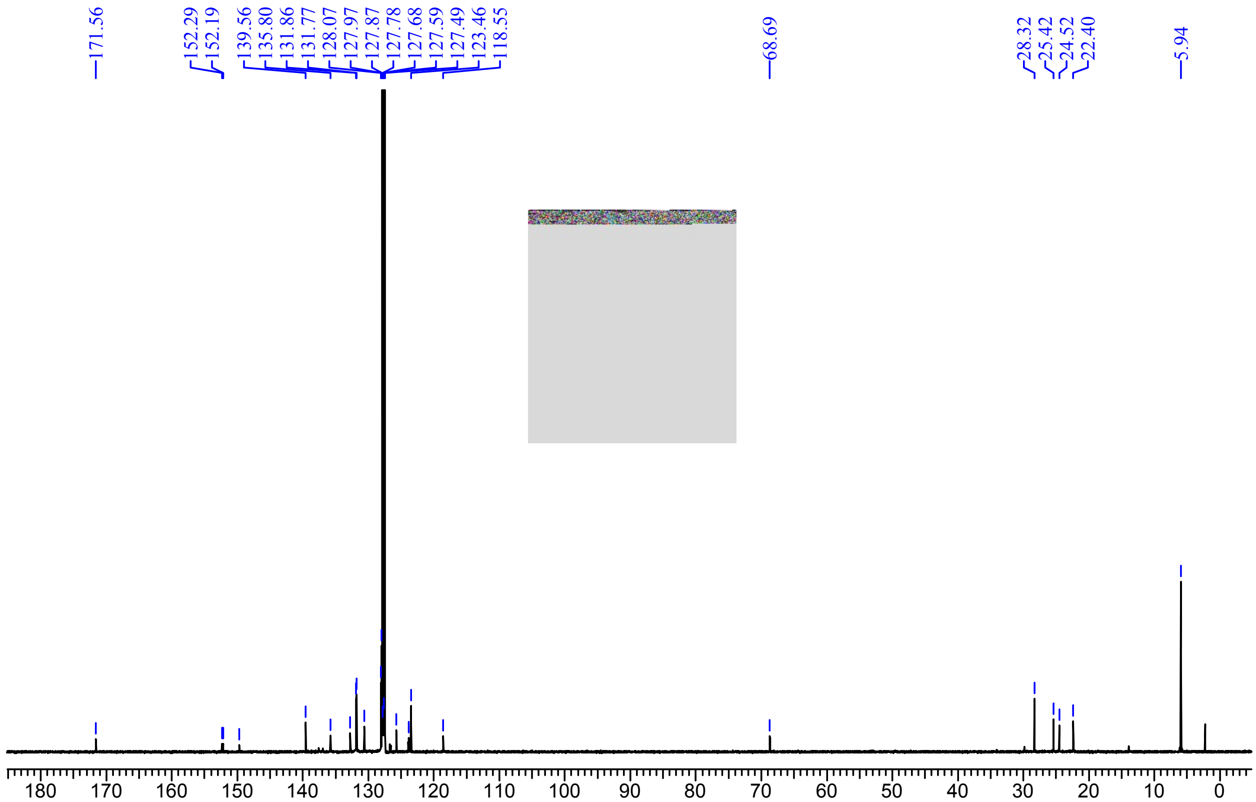
S20. ^1H NMR spectrum (C_6D_6, 500.13 MHz, 298 K) of [{L^3}Ca{N($SiMe_3$)$_2$}(thf)] (**3**)



S21. $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 161.9 MHz, 298 K) of [{L^3}Ca{$N(SiMe_3)_2$}(thf)] (**3**)



S22. $^{77}Se\{^{1}H\}$ NMR spectrum (C_6D_6, 76.31 MHz, 298 K) of [{L^3}Ca{$N(SiMe_3)_2$}(thf)] (**3**)



S23. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 125.76 MHz, 298 K) of [{L³}Ca{$N(SiMe_3)_2$}(thf)] (**3**)