Supporting Information for

Group 1 and group 2 metal complexes supported by bidentate bulky iminopyrrolyl ligand: synthesis, structural diversity, and ε-caprolactone polymerization study

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Table TS 1: Crystallographic details of details of ligand **1-H** and complexes **2-9**.

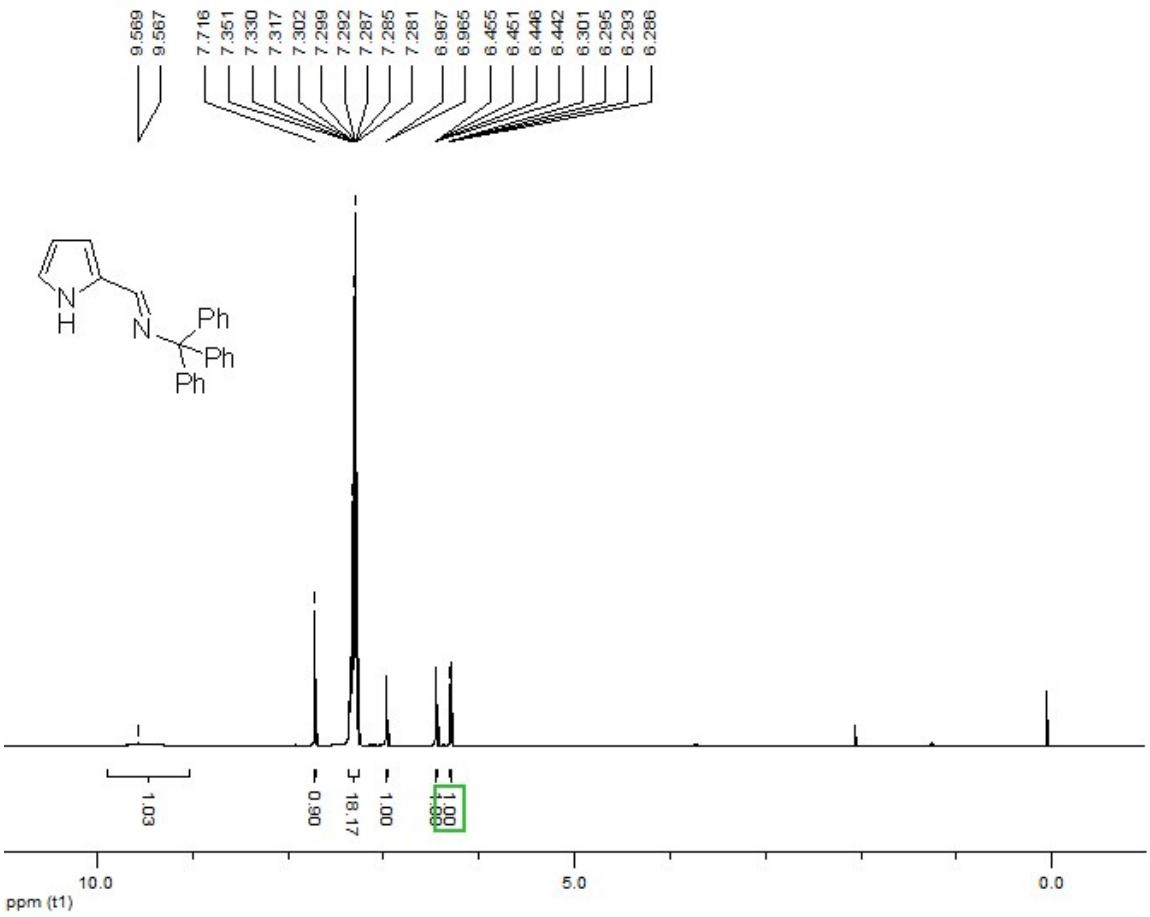
Crystal	**1-H**	**2**	**3**	**4**	**5**
CCDC No.	1418542	1418543	1418544	1418545	1418546
Empirical formula	$C_{24}H_{20}N_2$	$C_{32}H_{35}LiN_2O_2$	$C_{56}H_{54}N_4Na_2O_2$	$C_{104}H_{92}K_4N_8O_2$	$C_{39}H_{42}MgN_2O_2$
Formula weight	336.42	486.56	861.01	1642.26	595.06
T (K)	293(2)	150(2)	150(2)	150(2)	113(2)
λ (Å)	1.54184	1.54184	1.54184	1.54184	0.71075
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	$P\,2_1/c$	$P\,b\,c\,a$	$P\,2_1/c$	$P\,2_1/c$	P-1
a (Å)	11.7601(8)	16.6177(16)	9.3375(5)	16.7937(12)	9.530(3)
b (Å)	10.7213(9)	16.4089(8)	17.8616(9)	10.7713(6)	17.850(6)
c (Å)	29.0076(15)	39.7532(16)	15.0867(10)	24.1946(17)	20.350(7)
α (°)	90	90	90	90	109.890(4)
β (°)	98.480(7)	90	111.528(5)	90.543(8)	96.251(2)
γ (°)	90	90	90	90	93.303(3)
V (Å^3)	3617.4(4)	10839.8(12)	2340.7(2)	4376.4(5)	3219.3(18)
Z	8	16	2	2	4
D_{calc} g cm^{-3}	1.235	1.193	1.222	1.246	1.228
μ (mm^{-1})	0.557	0.570	1.54184	2.239	0.092
F (000)	1424.0	4160	912	1728	1272
Theta range for data collection	6.16 to 143.63 deg.	3.47 to 71.08 deg.	4.01 to 70.95 deg.	3.65 to 70.78 deg.	3.02 to 27.00 deg.
Limiting indices	-14<=h<=13 -11<=k<=13 -35<=l<=19	-17<=h<=19 -18<=k<=19 -48<=l<=47	-11<=h<=11, -16<=k<=21, -15<=l<=18	-16<=h<=20 -13<=k<=12 -29<=l<=29	-12<=h<=12 -21<=k<=22 -25<=l<=25
Reflections collected / unique	13546 / 6866 [R(int) = 0.0667]	24230 / 8741 [R(int) = 0.0562]	10068 / 4424 [R(int) = 0.0266]	21120 / 8234 [R(int) = 0.0891]	30518 / 13802 [R(int) = 0.0333]

Completeness to theta = 71.25	96.6 % (70.94)	83.3 % (71.08)	97.7 %	97.7 % (70.78)	98.2 % (27.00)
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	1.00000 and 0.25106	0.91 and 0.86	0.75 and 0.64	1.00000 and 0.62549	0.9746 and 0.9728
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6866/0/470	8741 / 0 / 679	4424 / 0 / 289	8234 / 0 / 532	13802 / 0 / 793
Goodness-of-fit on F^2	1.045	1.028	1.045	1.029	1.051
Final R indices [I>2sigma(I)]	R1 = 0.1059, wR2 = 0.2790	R1 = 0.0792, wR2 = 0.2056	R_1 = 0.0524, wR_2 = 0.1416	R1 = 0.0796, wR2 = 0.2067	R1 = 0.0651, wR2 = 0.1577
R indices (all data)	R1 = 0.1878, wR2 = 0.3599	R1 = 0.1315, wR2 = 0.2412	R_1 = 0.0597, wR_2 = 0.1492	R1 = 0.1102, wR2 = 0.2461	R1 = 0.0988, wR2 = 0.1893
Largest diff. peak and hole	0.42 and -0.38 $e.A^{-3}$	0.339 and -0.267 $e.A^{-3}$	0.456 and -0.548 $e.A^{-3}$	0.641 and -0.574 $e.A^{-3}$	0.906 and -0.526 $e.A^{-3}$

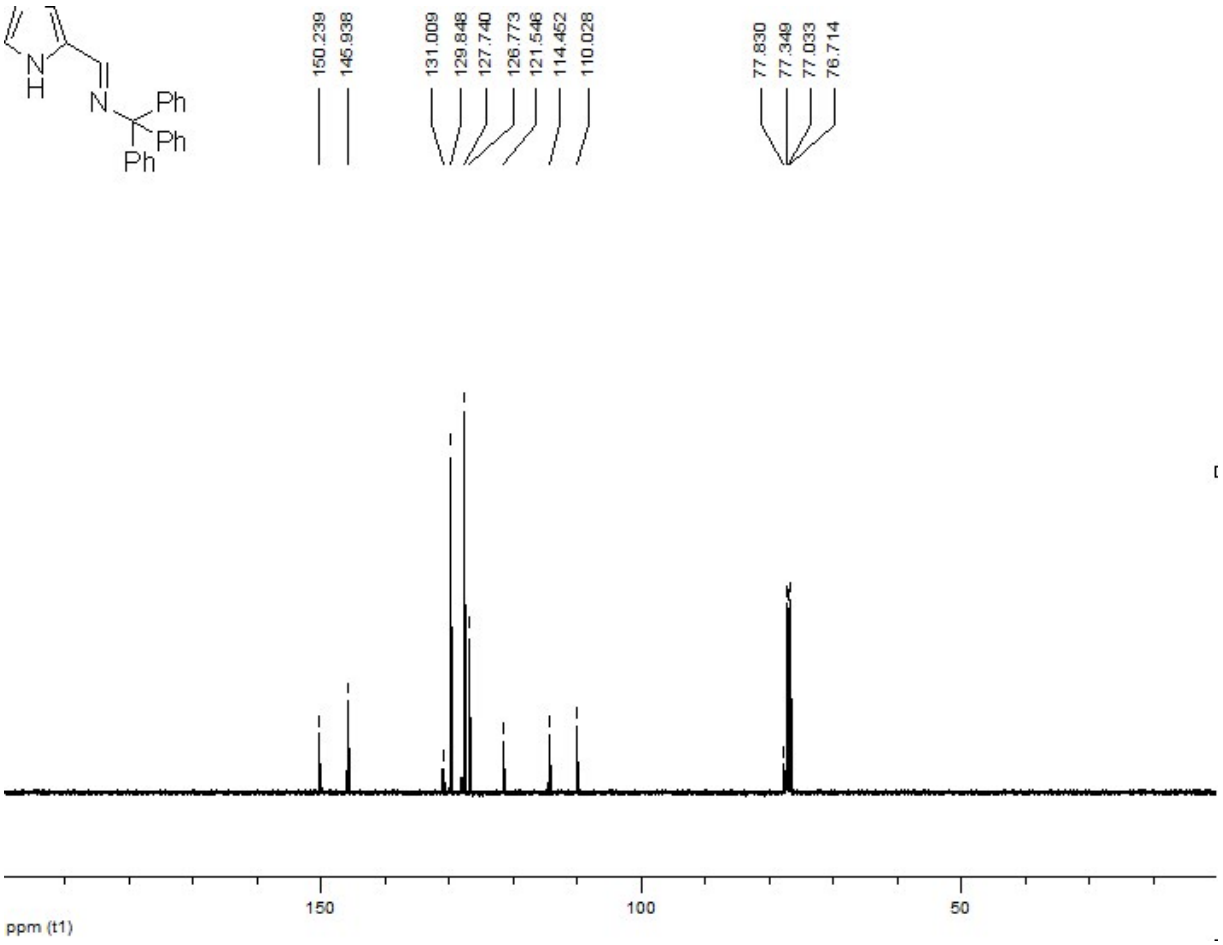
Table TS 1: Crystallographic details of details of ligand **1-H** and complexes **2-9** (contd).

Crystal	**6**	**7**	**8**	**9**
CCDC No.	1418547	1418548	1418549	1418550
Empirical formula	$C_{56}H_{54}MgN_4O_2$	$C_{66}H_{70}CaN_4O_4$	$C_{60}H_{62}N_4O_3Sr$	$C_{68}H_{77}BaN_4O_5$
Formula weight	839.34	999.32	974.76	1167.68
T (K)	150(2)	113(2)	150(2)	150(2)
λ (Å)	1.54184	0.71075	1.54184	1.54184
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	*P*-1	$P\ 2_1/n$	*P*-1	*P*-1
a (Å)	9.9208(12)	11.185(18)	11.5131(13)	10.7818(11)
b (Å)	9.9609(15)	13.42(2)	13.2509(13)	14.4888(15)
c (Å)	12.4778(12)	18.43(3)	18.1457(15)	21.2076(19)
α (°)	108.752(11)	90	75.334(8)	109.626(9)
β (°)	92.798(9)	104.24(2)	78.968(9)	93.344(8)
γ (°)	106.729(12)	90	71.140(10)	106.825(9)
V (Å^3)	1104.5(3)	2681(7)	2516.1(4)	2942.1(5)
Z	1	2	2	2
D_{calc} g cm^{-3}	1.262	1.238	1.287	1.318
μ (mm^{-1})	0.722	0.170	1.871	5.668

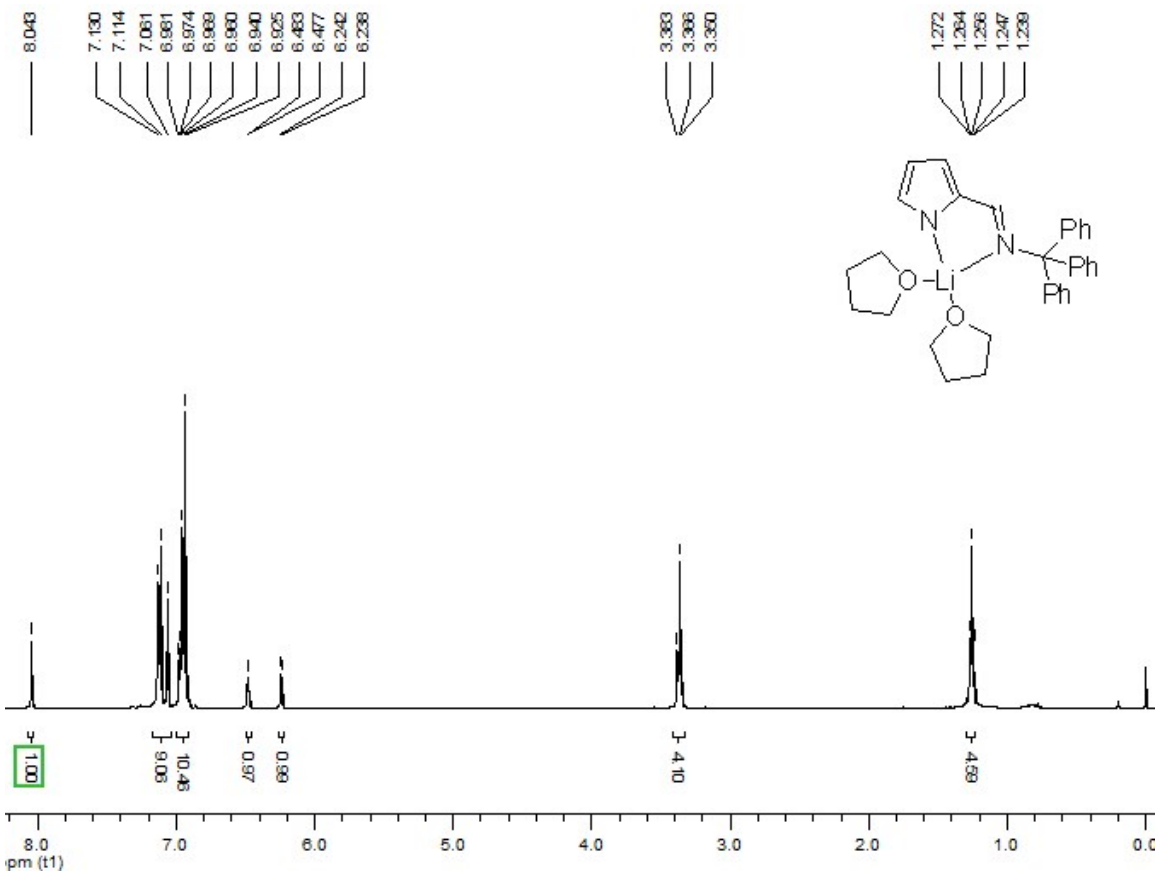
F (000)	446	1068	1024	1218
Theta range for data collection	3.787 to 70.588 deg.	3.04 to 26.00 deg.	3.60 to 71.27deg.	3.33 to 71.43 deg.
Limiting indices	-12<=h<=11, -9<=k<=12, -15<=l<=15	-13<=h<=12 -15<=k<=16 -22<=l<=18	-14<=h<=14 -11<=k<=16 -21<=l<=22	-12<=h<=13, -17<=k<=17, -17<=l<=25
Reflections collected / unique	7976 / 4126 [R(int) = 0.0321]	11436 / 5075 [R(int) = 0.1009]	19225 / 9452 [R(int) = 0.0559]	21652 / 11049 [R(int) = 0.0796]
Completeness to theta = 71.25	99.7 % (67.68)	96.3 % (26.00)	96.7 % (71.27)	96.5 %
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	1.00000 and 0.82260	0.9668 and 0.9668	1.00000 and 0.92842	1.000 and 0.51963
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4126 / 0 / 290	5075 / 0 / 331	9452 / 0 / 613	11049 / 0 / 703
Goodness-of-fit on F^2	1.039	0.999	1.094	1.009
Final R indices [I>2sigma(I)]	R_1 = 0.0417, wR_2 = 0.1019	R1 = 0.0766, wR2 = 0.1573	R1 = 0.0925, wR2 = 0.2361	R_1 = 0.0667, wR_2 = 0.1670
R indices (all data)	R_1 = 0.0539, wR_2 = 0.1114	R1 = 0.1713, wR2 = 0.2128	R1 = 0.0975, wR2 = 0.2480	R_1 = 0.0874, wR_2 = 0.2011
Largest diff. peak and hole	0.155 and -0.266 $e.A^{-3}$	0.393 and -0.361 $e.A^{-3}$	2.717 and -1.215 $e.A^{-3}$	1.832 and -2.737 $e.A^{-3}$



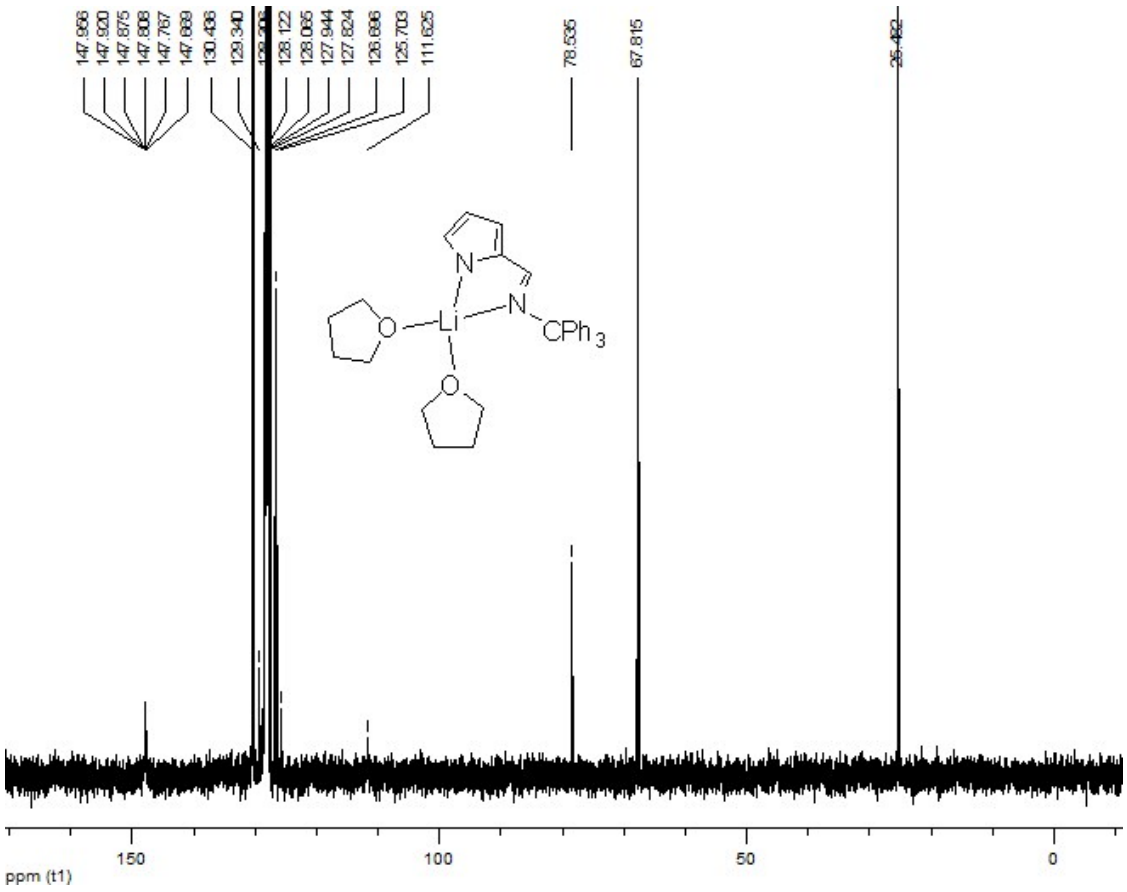
S1. ^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of [2-($Ph_3CN{=}CH)C_4H_3NH$] (**1-H**)



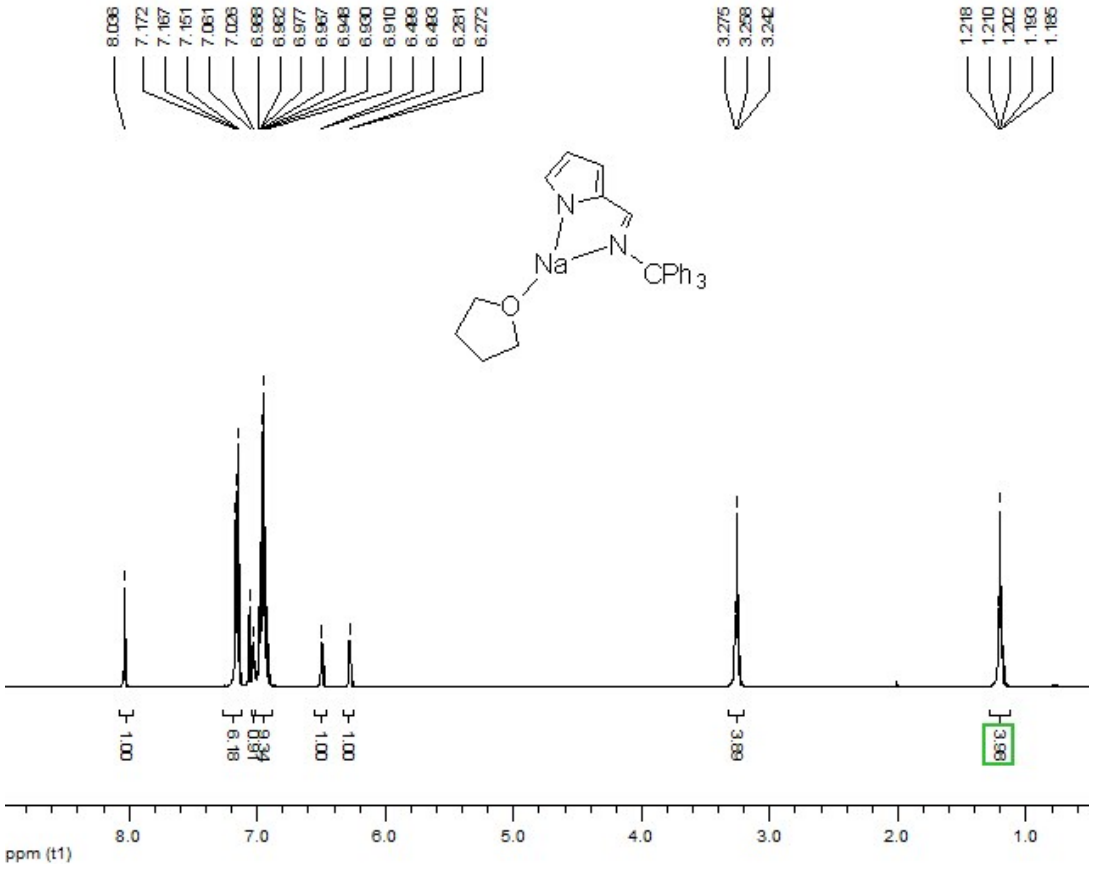
S2. ^{13}C NMR spectrum (100 MHz, 25°C, $CDCl_3$) of [2-($Ph_3CN{=}CH)C_4H_3NH$] (**1-H**)



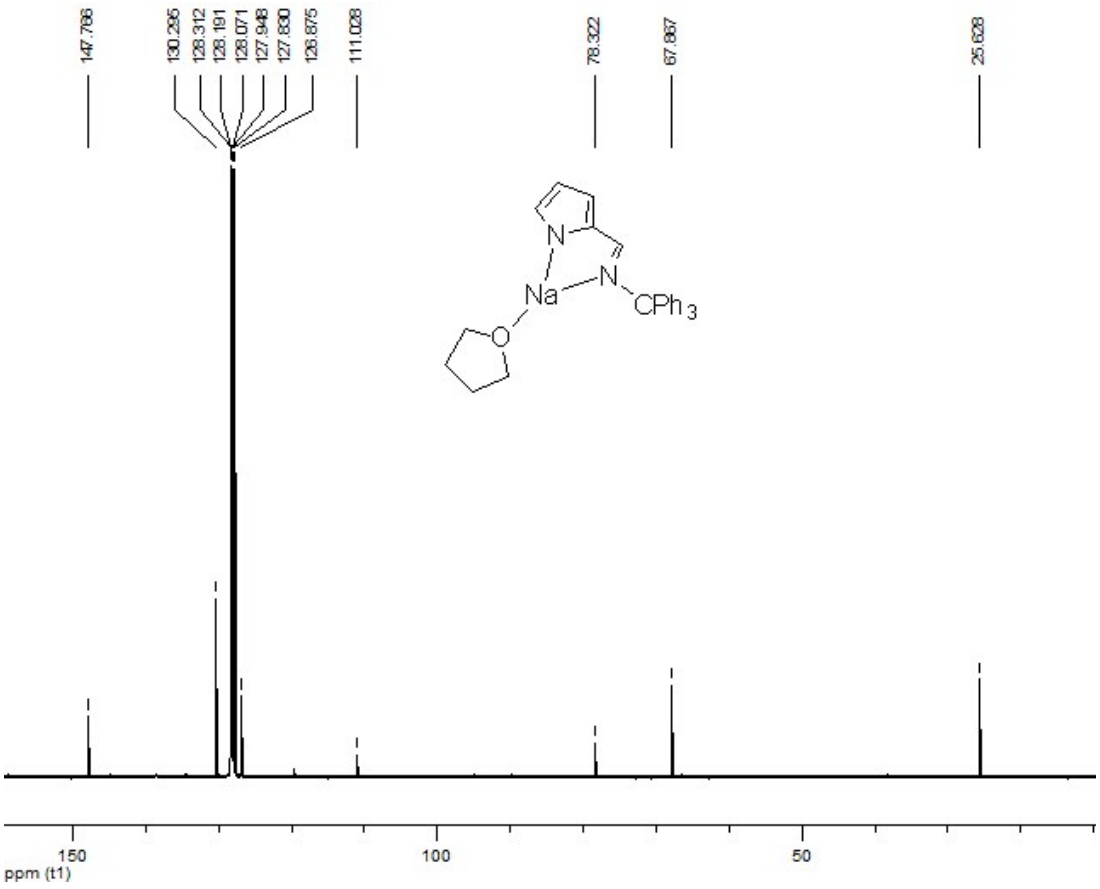
S3. ^{1}H NMR spectrum (400 MHz, 25°C, C_6D_6) of $[(THF)_2Li(2\text{-}(Ph_3CN{=}CH)C_4H_3N)]$ (**2**)



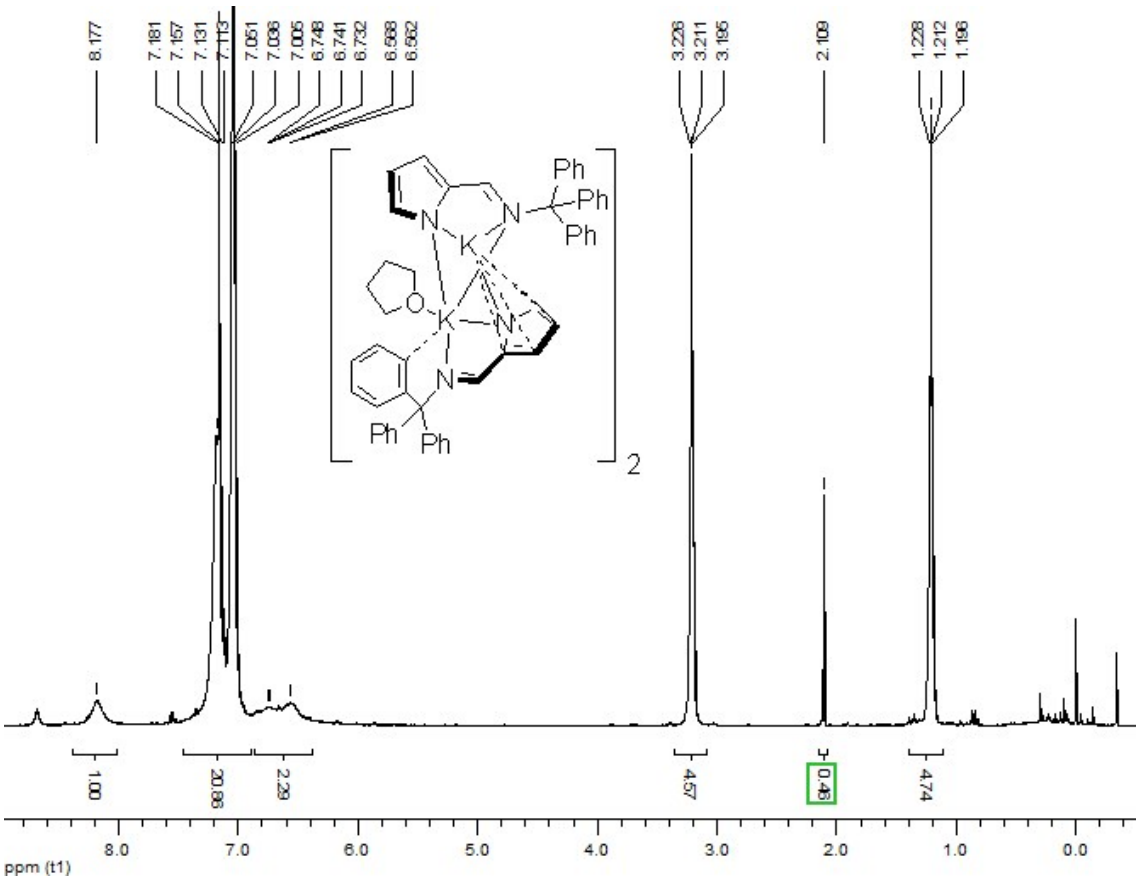
S4. ^{13}C NMR spectrum (100 MHz, 25°C, C_6D_6) of [(2-(Ph_3CN=CH)C_4H_3N)Li($THF)_2$] (**2**)



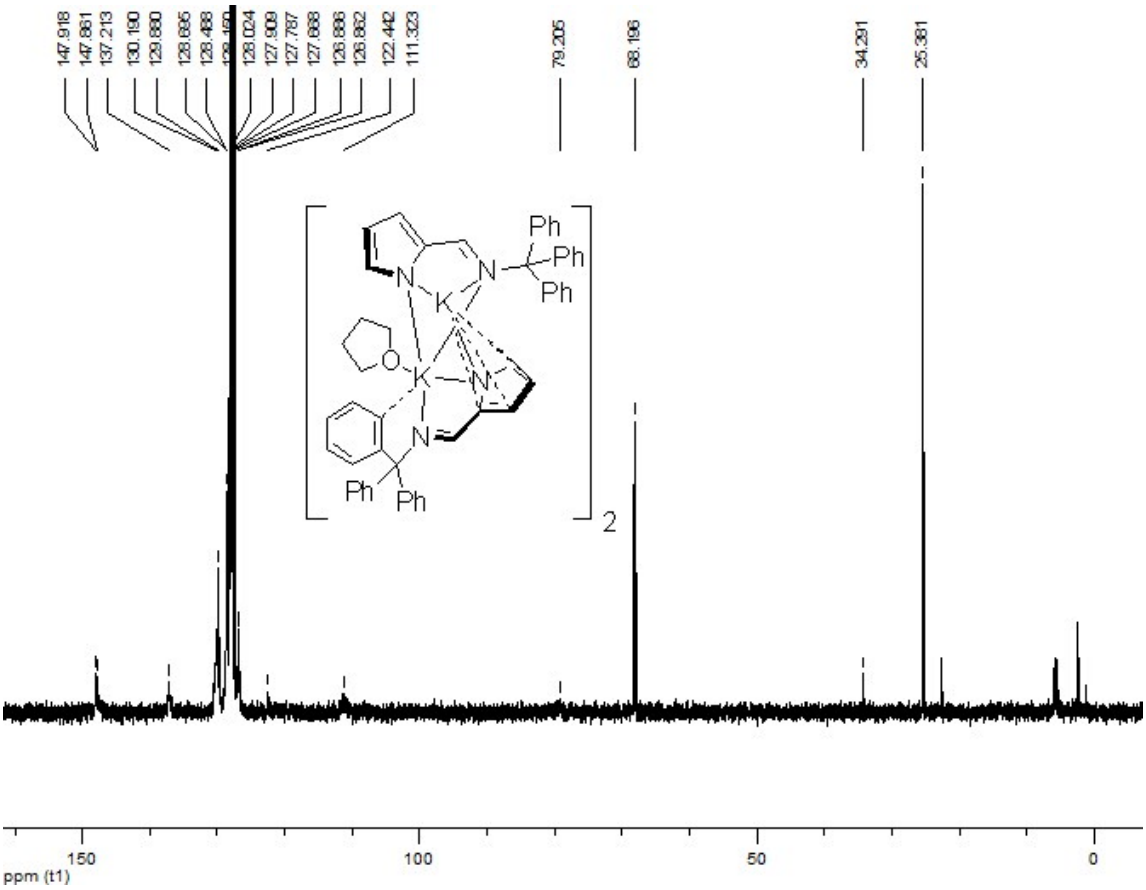
S5. ^{1}H NMR spectrum (400 MHz, 25°C, C_6D_6) of [{2-(Ph_3CN=CH)C_4H_3N}Na(THF)]$_2$ (**3**)



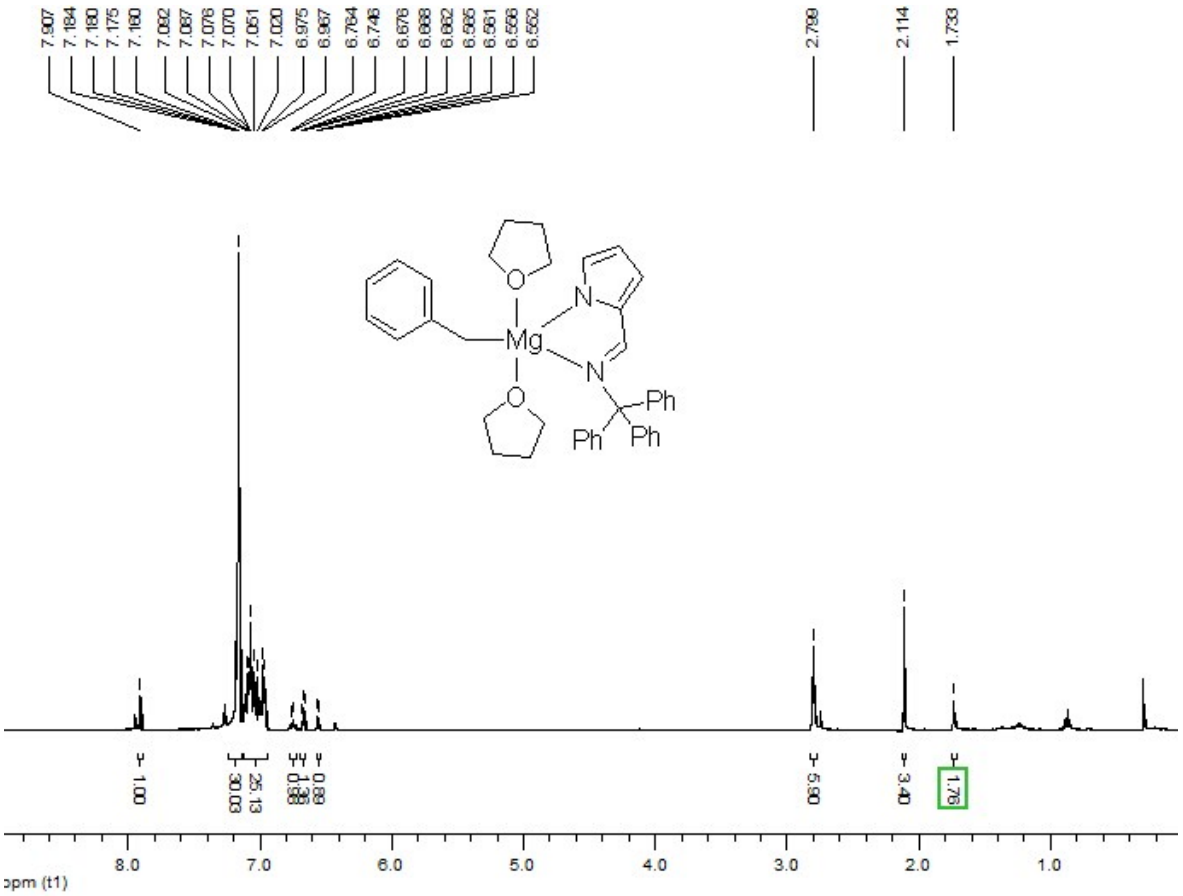
S6. ^{13}C NMR spectrum (100 MHz, 25°C, C_6D_6) of [{2-($Ph_3CN{=}CH)C_4H_3N$}Na(THF)]$_2$ (**3**)



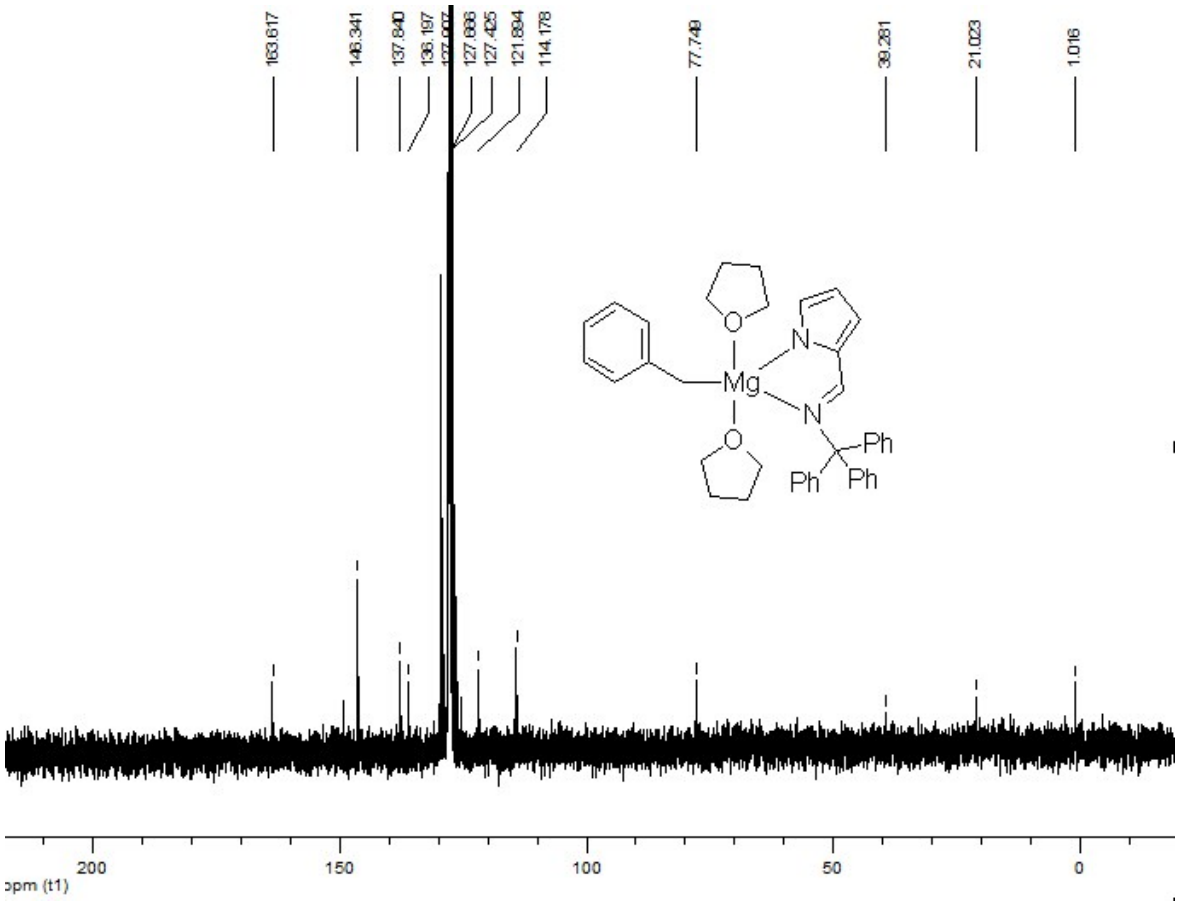
S7. ^{1}H NMR spectrum (400 MHz, 25°C, C_6D_6) of $[\{2\text{-}(Ph_3CN{=}CH)C_4H_3N\}K(THF)_{0.5}]_4$ (**4**)



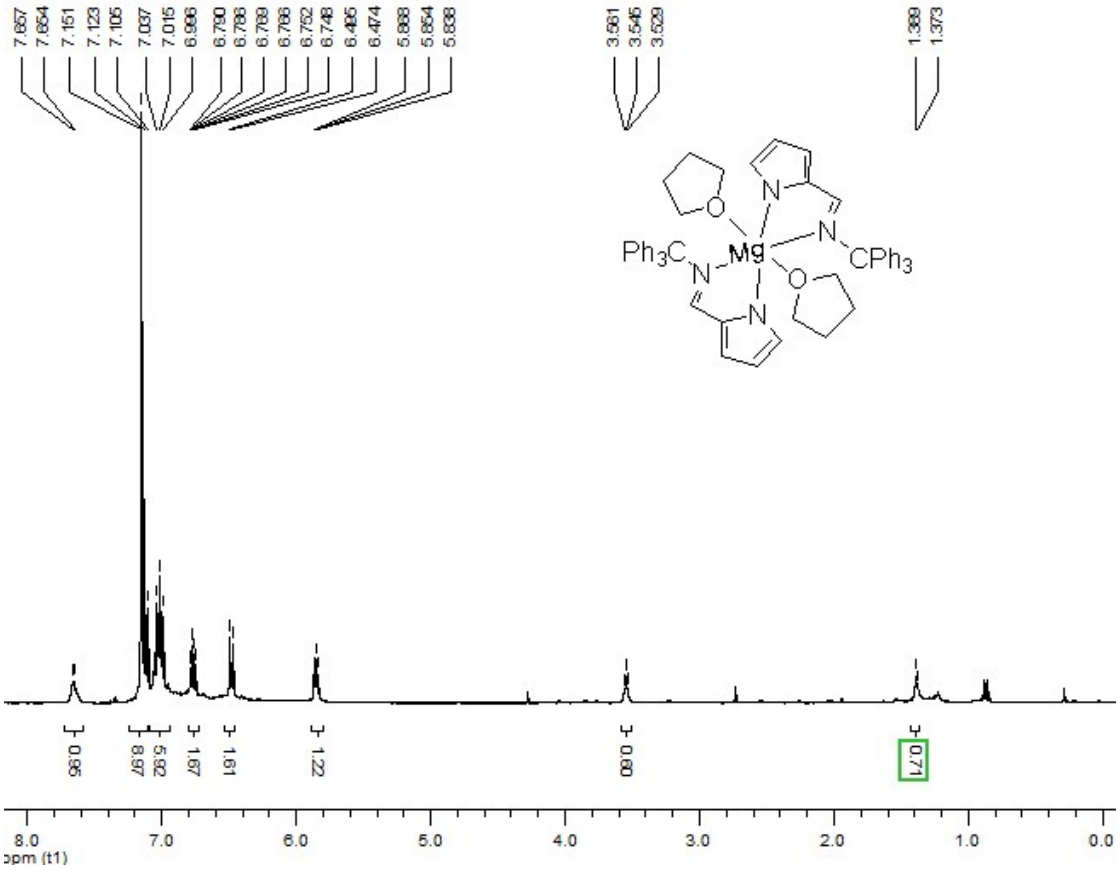
S8. ^{13}C NMR spectrum (100 MHz, 25°C, C_6D_6) of $[\{2\text{-}(Ph_3CN{=}CH)C_4H_3N\}K(THF)_{0.5}]_4$ (**4**)



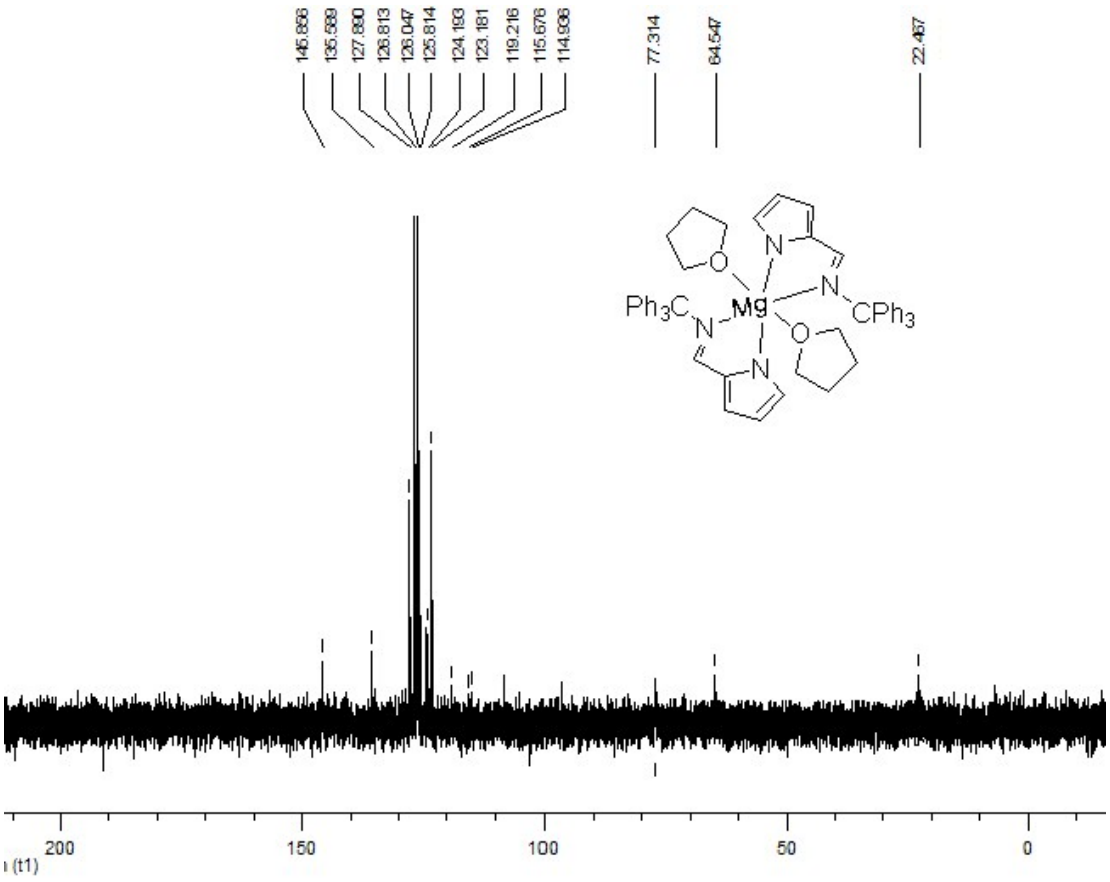
S9. ^{1}H NMR spectrum (400 MHz, 25°C, C_6D_6) of [{2-(Ph_3CN=CH)C_4H_3N}{$PhCH_2$}Mg($THF)_2$] (**5**)



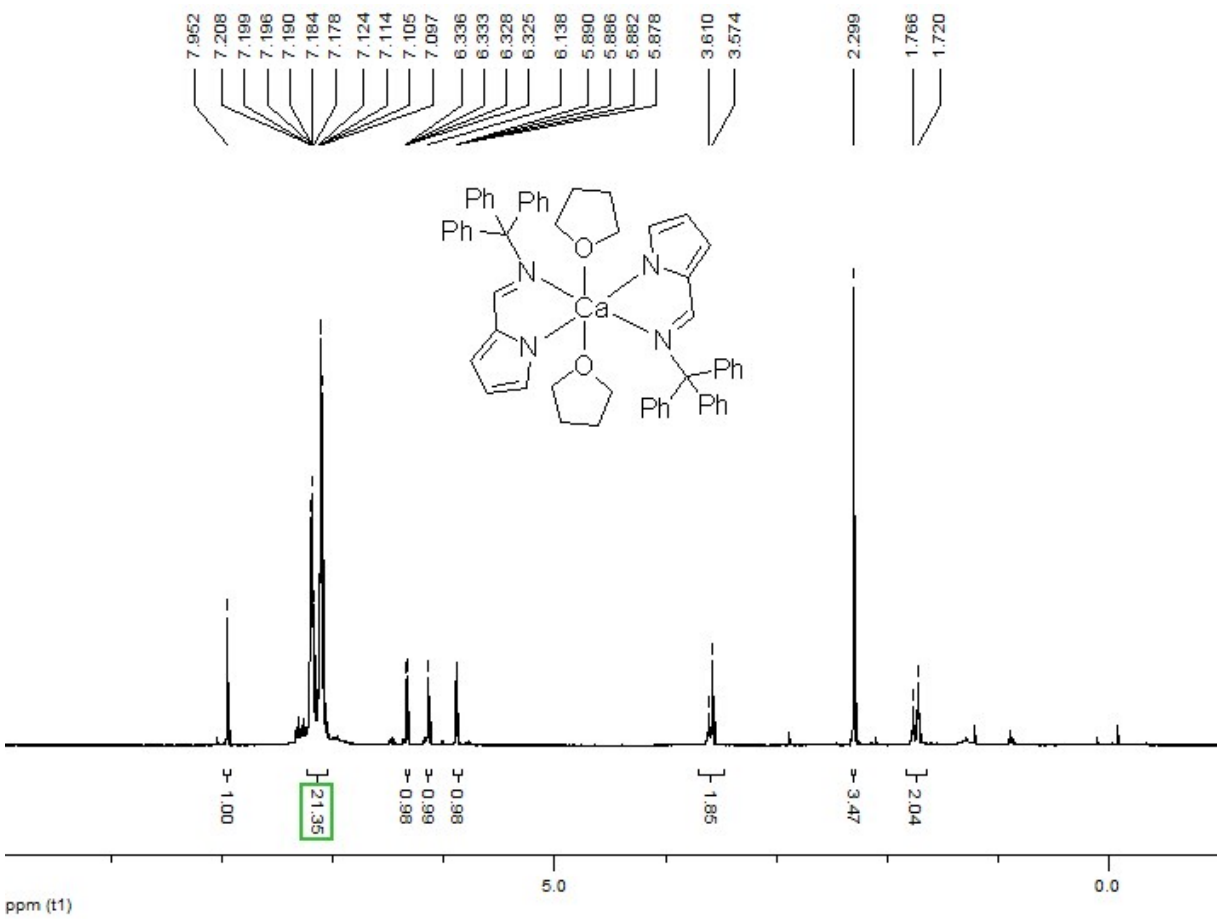
S10. ^{13}C NMR spectrum (100 MHz, 25°C, C_6D_6) of [{2-$(Ph_3CN{=}CH)C_4H_3N$}{$PhCH_2$}$Mg(THF)_2$] (**5**)



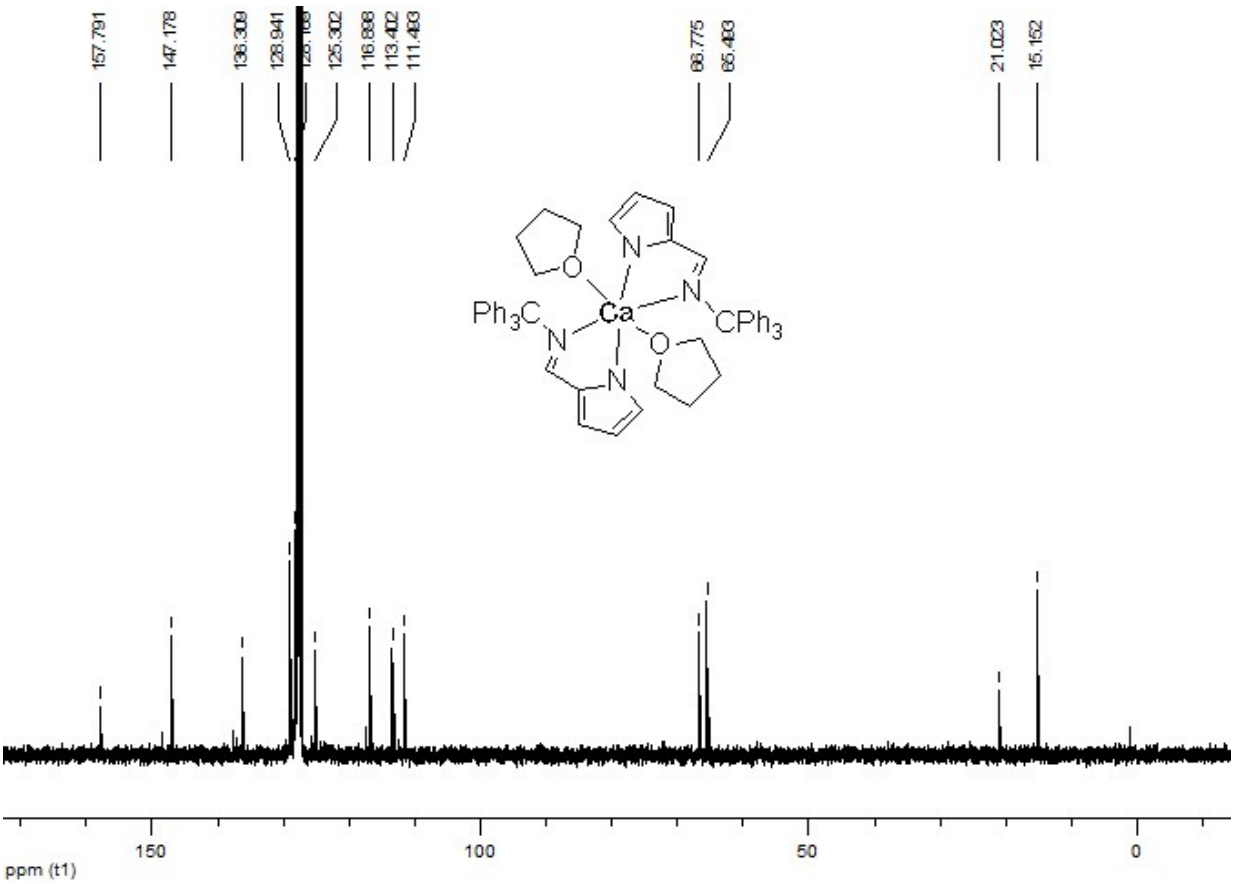
S11. ^{1}H NMR spectrum (400 MHz, 25°C, C_6D_6) of [{2-($Ph_3CN{=}CH)C_4H_3N$}$_2$Mg(THF)$_2$] (**6**)



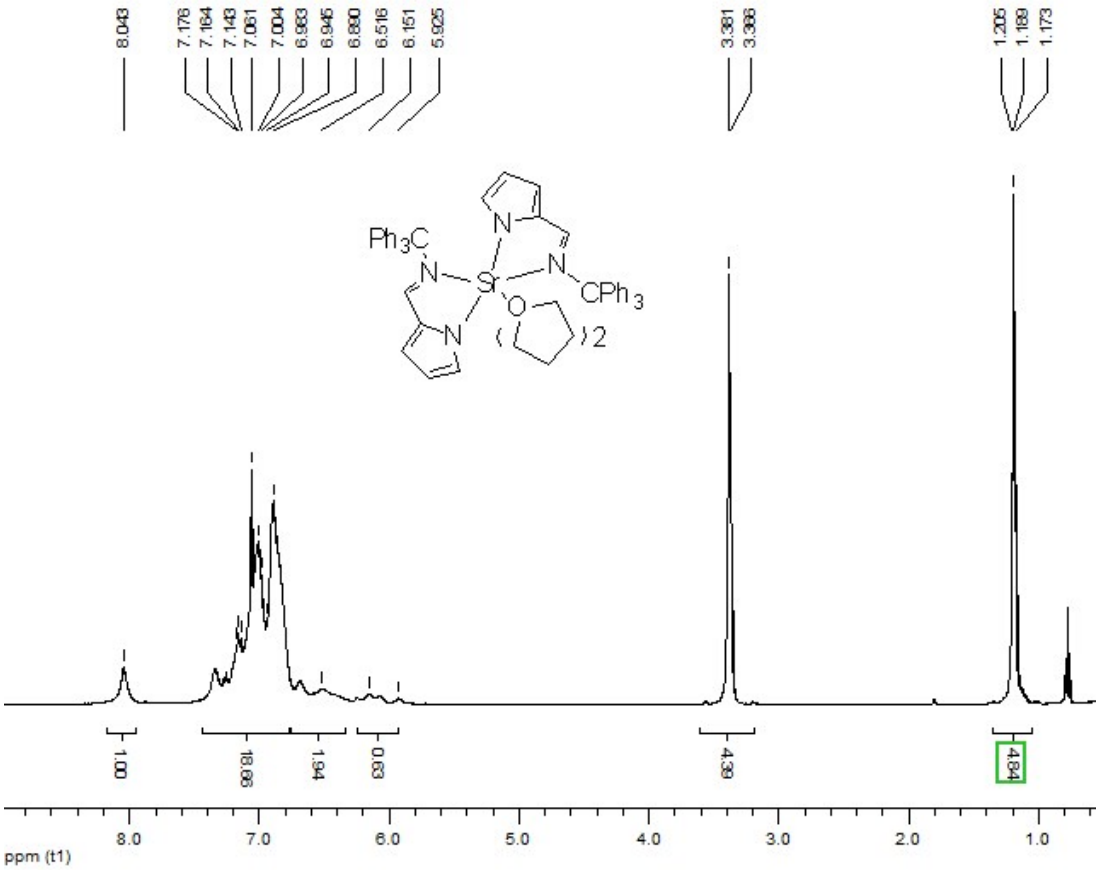
S12. ^{13}C NMR spectrum (100 MHz, 25°C, C_6D_6) of [{2-$(Ph_3CN{=}CH)C_4H_3N$}$_2$Mg$(THF)_2$] (**6**)



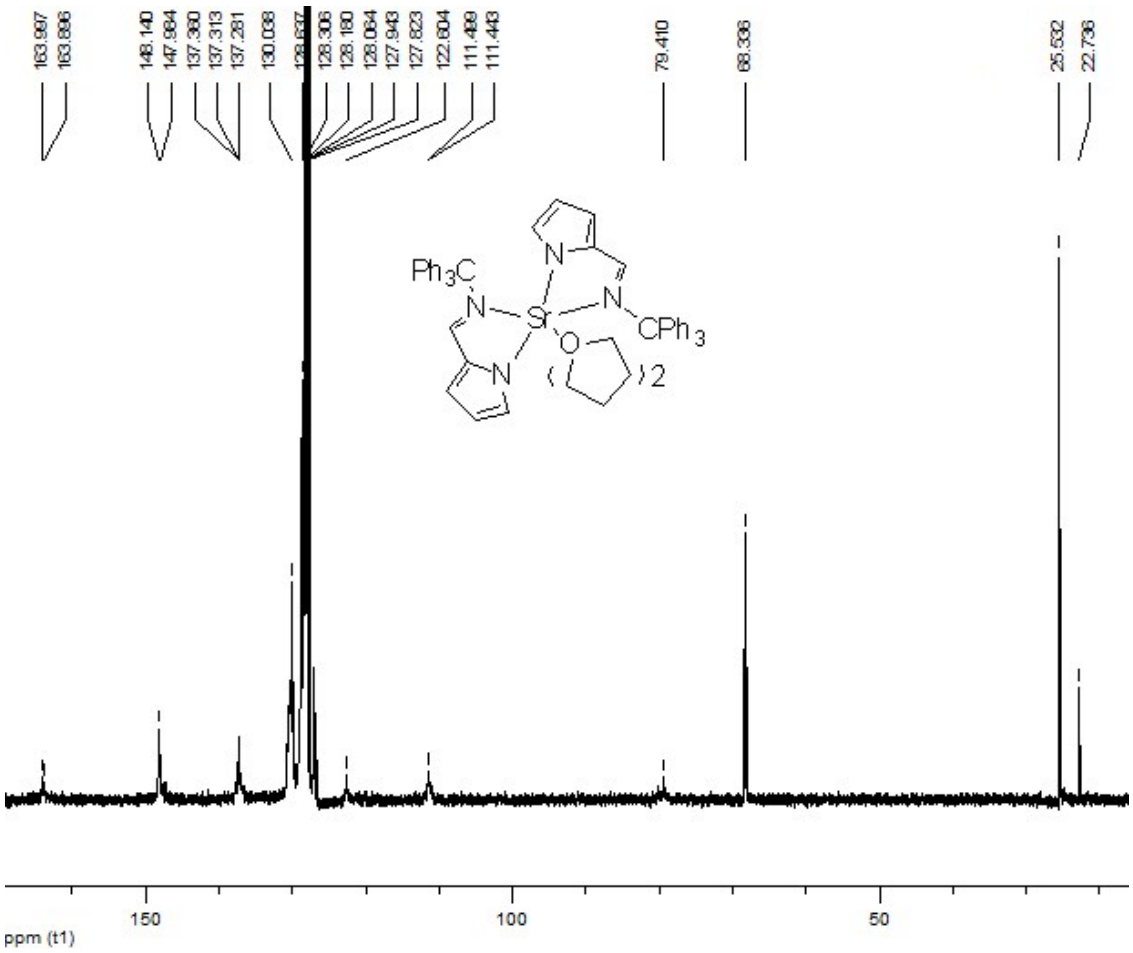
S13. ^{1}H NMR spectrum (400 MHz, 25°C, C_6D_6) of [{2-(Ph_3CN=CH)C_4H_3N}$_2$Ca(THF)$_2$] (**7**)



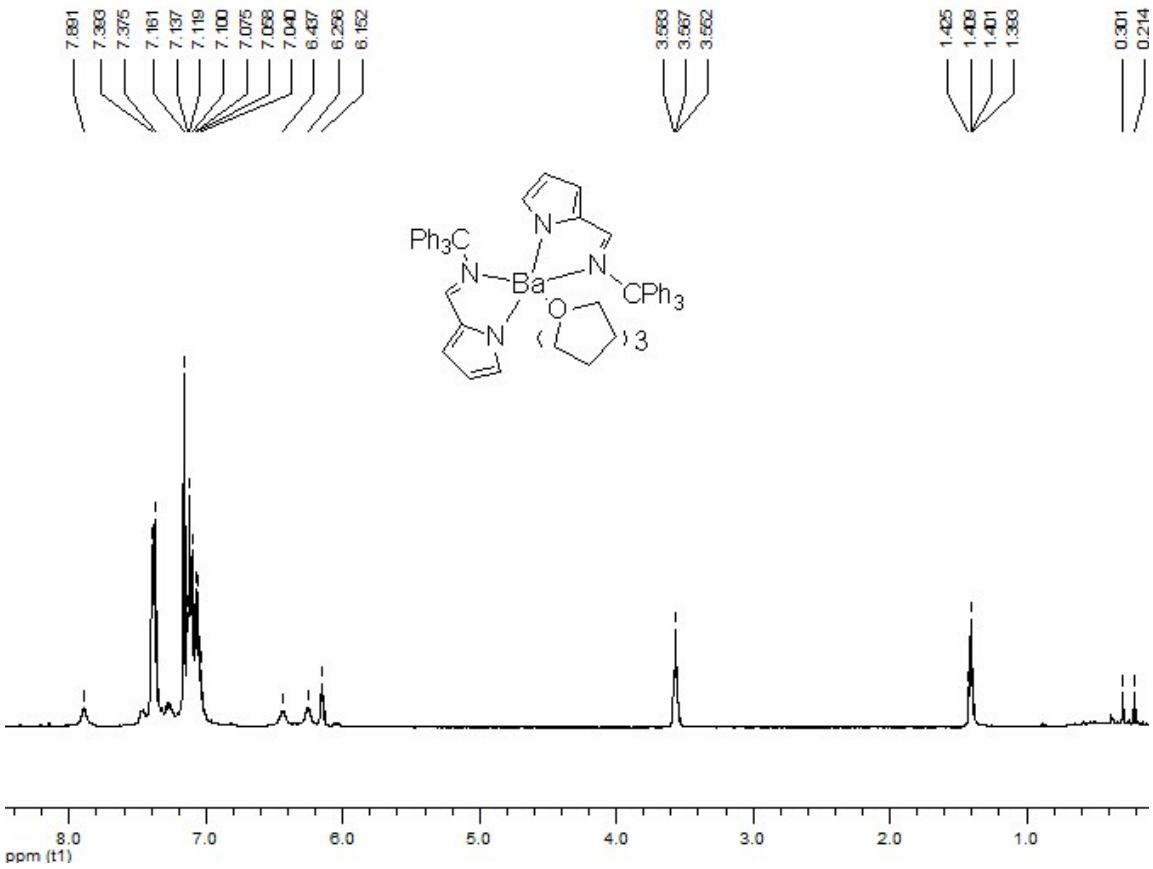
S14. ^{13}C NMR spectrum (100 MHz, 25°C, C_6D_6) of [{2-(Ph_3CN=CH)C_4H_3N}$_2$Ca(THF)$_2$] (**7**)



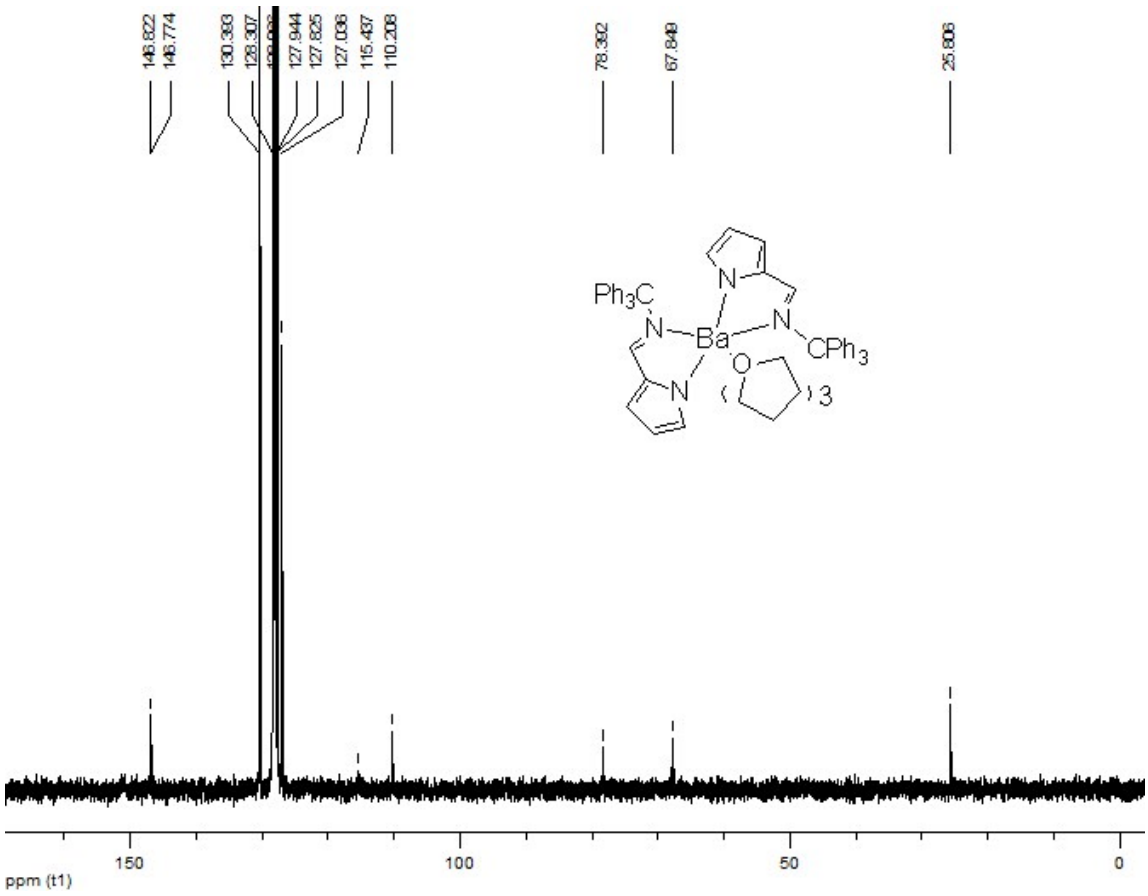
S15. ^{1}H NMR spectrum (400 MHz, 25°C, C_6D_6) of [{2-$(Ph_3CN{=}CH)C_4H_3N$}$_2$Sr$(THF)_2$] (**8**)



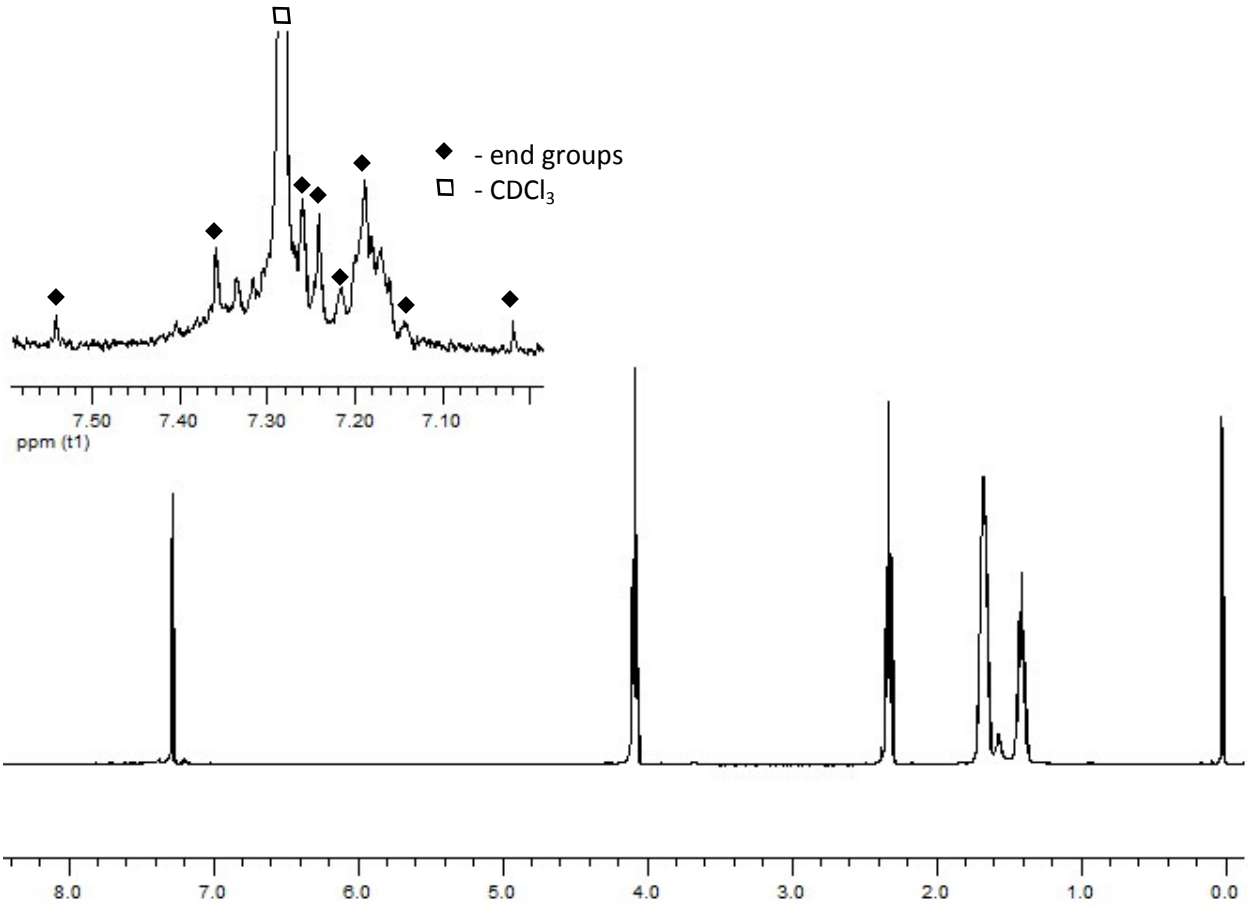
S16. ^{13}C NMR spectrum (100 MHz, 25°C, C_6D_6) of [{2-($Ph_3CN{=}CH)C_4H_3N$}$_2$Sr(THF)$_2$] (**8**)



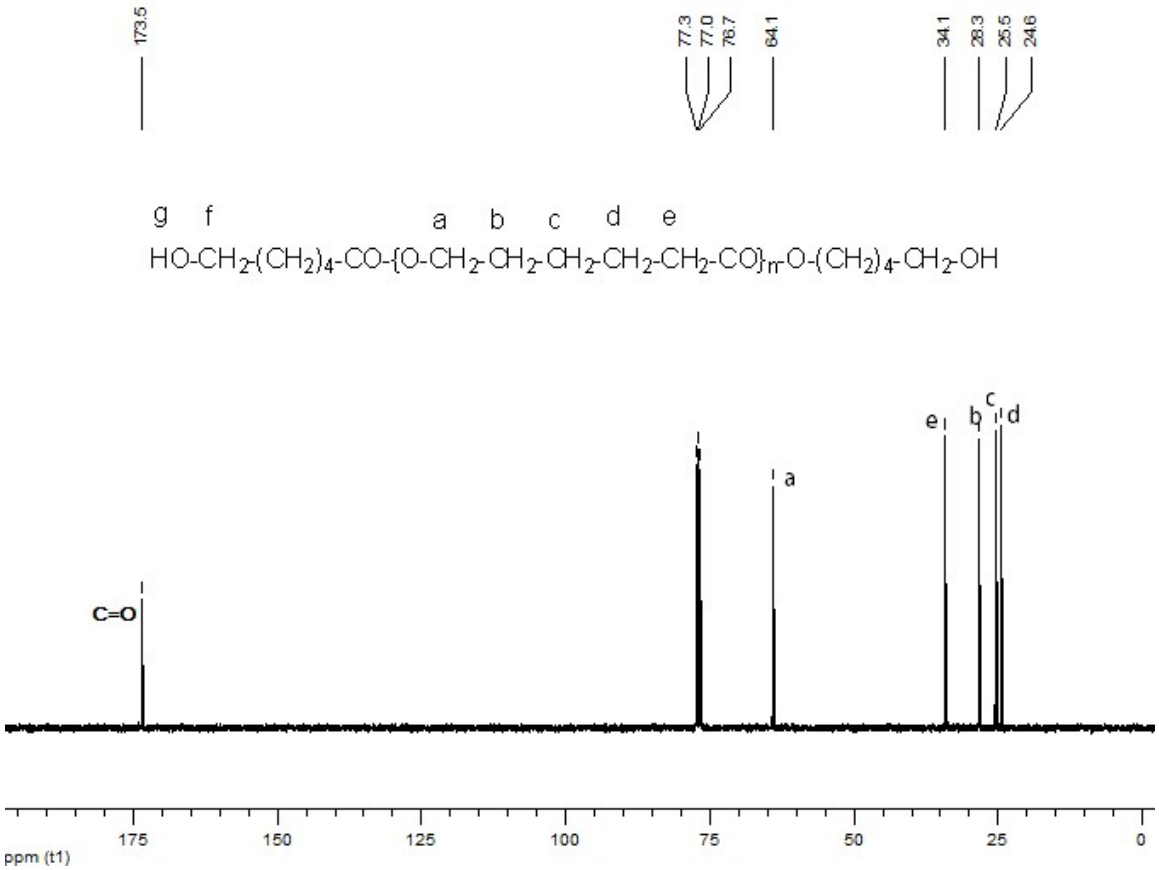
S17. ^{1}H NMR spectrum (400 MHz, 25°C, C_6D_6) of [{2-(Ph_3CN=CH)C_4H_3N}$_2$Ba(THF)$_3$] (**9**)



S18. ^{13}C NMR spectrum (100 MHz, 25°C, C_6D_6) of [{2-(Ph_3CN=CH)C_4H_3N}$_2$Ba(THF)$_3$] (**9**)



S19. ^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of Poly(ε-Caprolactone) initiated by complex (**9**)



S20. ^{13}C NMR spectrum (100 MHz, 25°C, $CDCl_3$) of Poly(ε-Caprolactone)