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Alkali Metal Complexes Having Sterically Bulky Bis-Iminopyrrolyl Ligands – Control of Dimeric to Monomeric Complex

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Table TS1. Crystallographic details and refinement parameters of compounds **1-H, 2-H, 3-H, 1-Li, 1-Na, 1-K**.

Crystal	**1-H**	**2-H**	**3-H**	**1-Li**	**1-Na**	**1-K**
CCDC Nos.	**1476165**	**1476169**	**1476170**	**1476168**	**1476166**	**1476167**
Empirical formula	$C_{38}H_{39}N_3O_{1.5}$	$C_{26}H_{35}N_3$	$C_{52}H_{51}N_3O_2$	$C_{72}H_{68}Li_2N_6O_2$	$C_{68}H_{60}N_6Na_2O$	$C_{40}H_{42}KN_3O_2$
Formula weight	561.72	389.57	749.95	1063.20	1022.20	635.87
T (K)	150(2)	298(2)	298 (2)	150(2)	150(2)	150(2)
λ (Å)	1.54184	1.54184	1.54184	1.54184	1.54184	1.54184
Crystal system	monoclinic	Monoclinic	orthorhombic	Triclinic	Triclinic	monoclinic
Space group	$P2_1/n$	$C2/c$	Pbcm	P-1	P-1	$C2/c$
a (Å)	14.5185(6)	25.4797(19)	7.3665(4)	13.8108(5)	13.7972(6)	13.6800(5)
b (Å)	9.4875(3)	6.8484(4)	17.5179(5)	21.2028(8)	14.1023(8)	16.1870(3)
c (Å)	25.1680(12)	27.753(2)	32.0143(14)	21.5594(7)	17.3629(8)	16.4227(6)
α (°)	90	90	90	98.470(3)	66.499(5)	90
β (°)	115.815(4)	112.294(8)	90	92.153(3)	88.058(4)	108.696(4)
γ (°)	90	90	90	107.438(3)	64.994(5)	90
V (Å^3)	3120.8(2)	4480.8(6)	4131.3(3)	5935.0(4)	2770.6(3)	3444.72(19)

Z	4	8	4	4	2	4
D_{calc} g cm^{-3}	1.196	1.155	1.206	1.190	1.226	1.226
μ (mm^{-1})	0.073	0.514	0.565	0.551	0.706	1.643
F (000)	1200	1696	1600	2256	1080	1352.0
Theta range for data collection	1.558 to 25.791	3.442 to 71.464	5.049 to 69.955	3.282 to 70.920	3.582 to 71.262	4.371 to 71.054
Limiting indices	-17 ≤ h ≤ 10, -11 ≤ k ≤ 10, -30≤ l ≤ 30	-27<=h<=31, -8<=k<=8, -31<=l<=33	-7 ≤ h ≤ 8, -15 ≤ k ≤ 21, -38 ≤ l ≤ 23	-16 ≤ h ≤ 16, -25 ≤ k ≤ 25, -26 ≤ l ≤ 16	-16 ≤ h ≤ 15, -16 ≤ k ≤ 17, -21 ≤ l ≤ 19	-14 ≤ h ≤ 16, -19 ≤ k ≤ 17, -19 ≤ l ≤ 20
Reflections collected / unique	12874 / 5903 [R(int) = 0.0305]	8805/4286 [R(int) = 0.0207]	10185/3932 [R(int) = 0.0303]	46701/22370 [R(int) = 0.0281]	18989/10535 [R(int) = 0.0320]	7159/3263 [R(int) = 0.0179]
Completeness to theta = 71.25	99.9%	99.9	98%	99.9%	99.9%	98%
Absorption correction	Multi-scan	Multi-scan	Multi-scan	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	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5903/335/435	4286 / 0 / 263	3932/262/288	22370/1608/1475	10535/0/695	3263/0/210
Goodness-of-fit on F^2	1.015	0.936	1.096	1.046	1.058	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0610, wR2 = 0.1577	R1 = 0.0855, wR2 = 0.2789	R1 = 0.0727, wR2 = 0.2078	R1 = 0.0598, wR2 = 0.1638	R1 = 0.0498, wR2 = 0.1310	R1 = 0.0405, wR2 = 0.1123
R indices (all data)	R1 = 0.0829, wR2 = 0.1796	R1 = 0.1128, wR2 = 0.3061	R1 = 0.0975, wR2 = 0.2194	R1 = 0.0745, wR2 = 0.1796	R1 = 0.0645, wR2 = 0.1411	R1 = 0.0436, wR2 = 0.1162

Table TS1 (contd). Crystallographic details and refinement parameters of compounds **3-Li, 3-Na, 3-K**.

Crystal	**3-Li**	**3-Na**	**3-K**
CCDC Nos.	**1476171**	**1476172**	**1476173**
Empirical formula	$C_{52}H_{50}LiN_3O_2$	$C_{56}H_{58}N_3NaO_3$	$C_{56}H_{58}KN_3O_3$
Formula weight	755.89	844.04	860.15
T (K)	150(2)	150(2)	150(2)
λ (Å)	1.54184	1.54184	1.54184
Crystal system	triclinic	Triclinic	Triclinic
Space group	*P-1*	*P-1*	*P-1*
a (Å)	9.0800(8)	8.8522(3)	9.7401(3)
b (Å)	12.8271(10)	9.4272(3)	17.9994(6)
c (Å)	18.6899(14)	29.1528(8)	28.4384(9)
α (°)	92.384(6)	81.636(3)	97.723(3)
β (°)	95.649(7)	88.161(2)	95.643(2)
γ (°)	106.228(7)	74.457(3)	104.922(3)
V (Å^3)	2074.5(3)	2318.88(13)	4727.6(3
Z	2	2	4
D_{calc} g cm^{-3}	1.210	1.209	1.208

μ (mm^{-1})	0.563	0.659	1.346
F (000)	804.0	900.0	1832.0
Theta range for data collection	3.598 to 71.379	4.599 to 70.703	3.2381 to 70.7245
Limiting indices	$-11 \leq h \leq 10$, $-15 \leq k \leq 11$, $-22 \leq l \leq 19$	$-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-35 \leq l \leq 28$	$-11 \leq h \leq 9$, $-21 \leq k \leq 20$, $-33 \leq l \leq 34$
Reflections collected / unique	15211 / 7804 [R(int) = 0.0342]	17860 / 8688 [R(int) = 0.0172]	36317/17729 [R(int) = 0.0317]
Completeness to theta = 71.25	99.8 %	99 %	99%
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / restraints / parameters	7804/2/527	8688/0/568	17729/1/1158
Goodness-of-fit on F^2	1.036	1.047	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0501, wR2 = 0.1251	R1 = 0.0484, wR2 = 0.1251	R1 = 0.0804, wR2 = 0.2327
R indices (all data)	R1 = 0.0636, wR2 = 0.1370	R1 = 0.0507, wR2 = 0.1268	R1 = 0.0870, wR2 = 0.2401

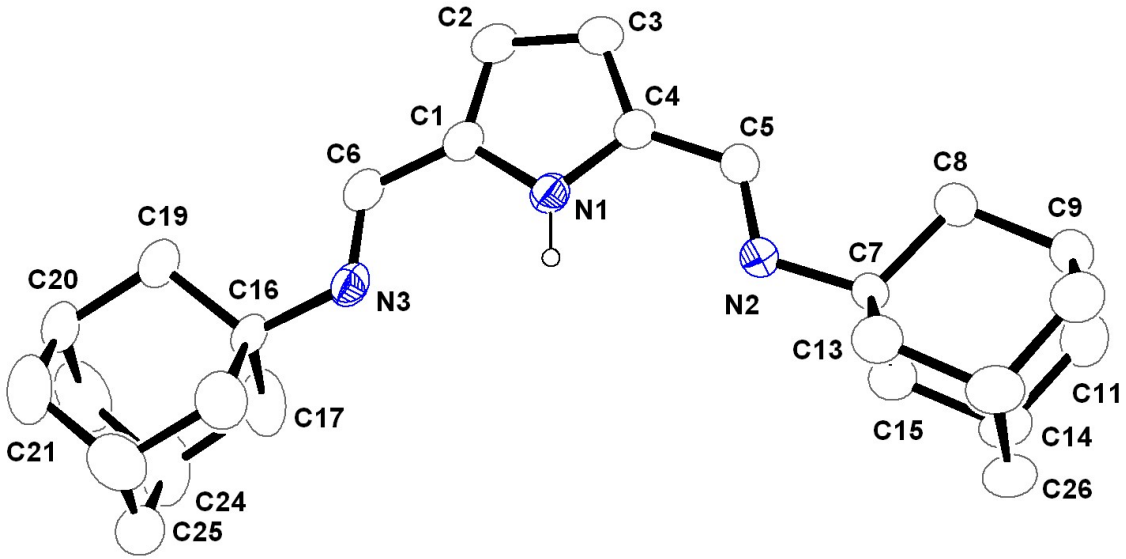
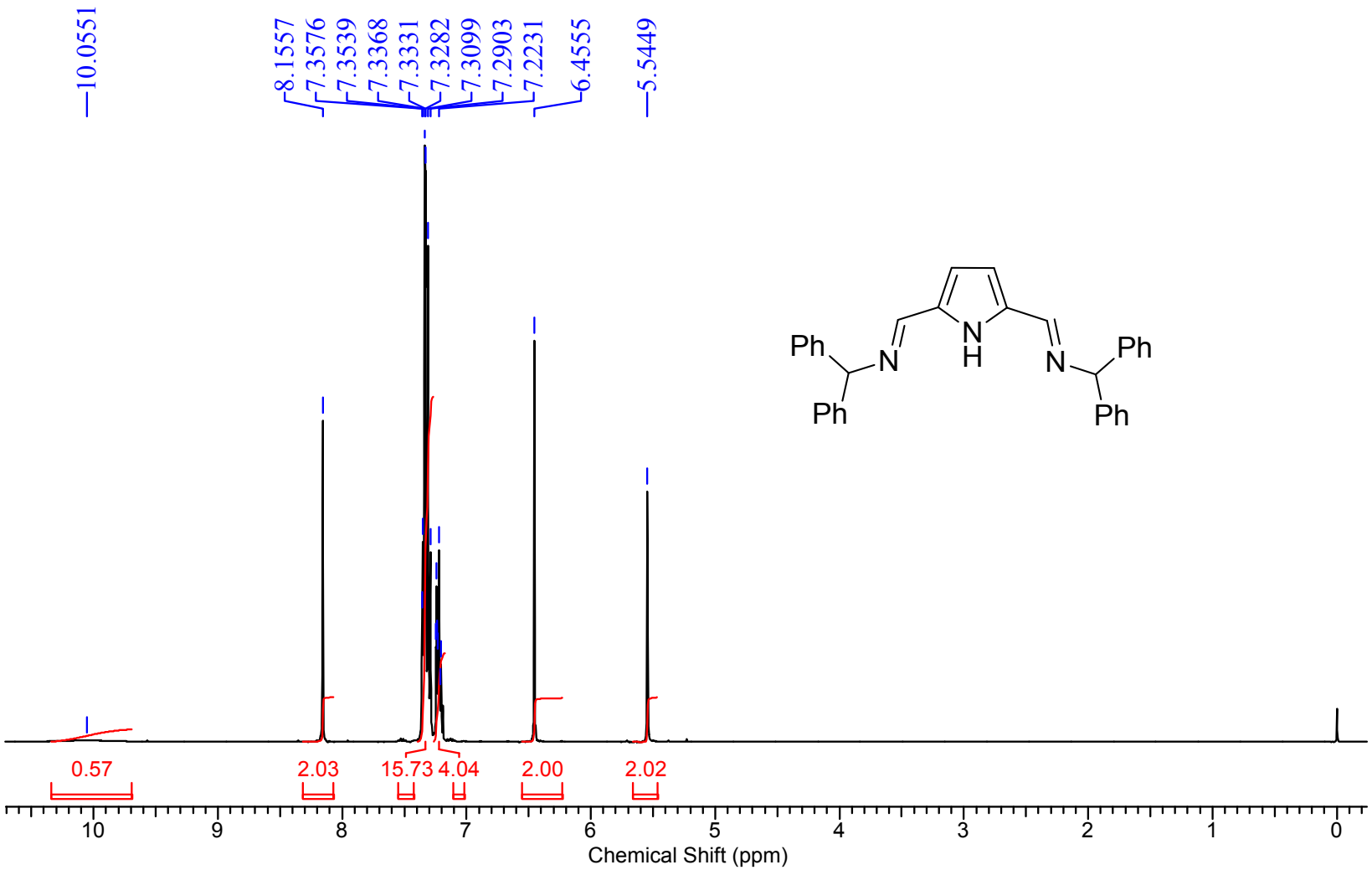
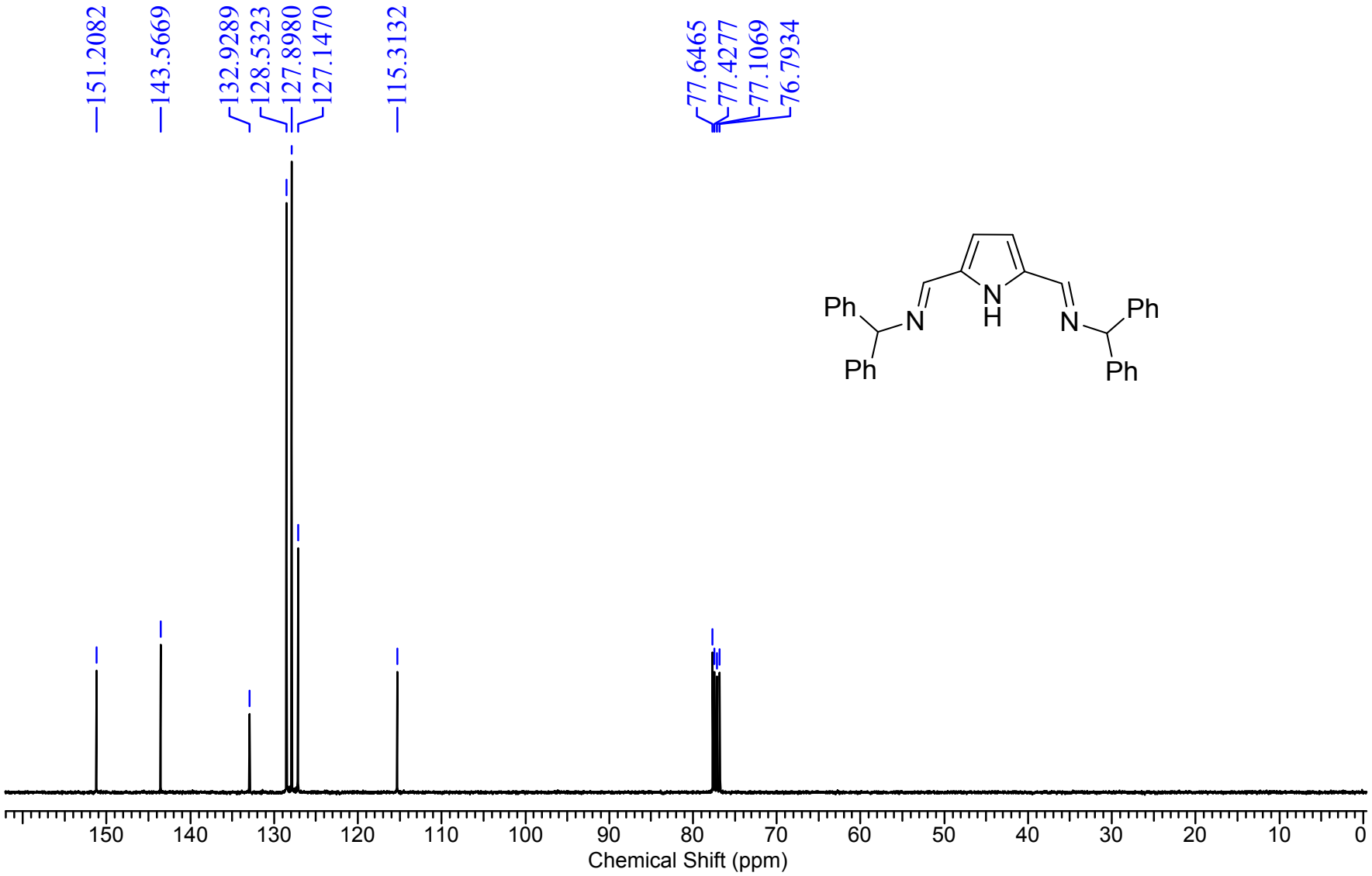


Figure FS1. Molecular structure of compound **2-H** in their solid state. **2-H**: N1-C1 1.366(4), N1-C4 1.361(4), C1-C2 1.371(5), C2-C3 1.399(5), C3-C4 1.370(5), N3-C6 1.258(4), N2-C5 1.259(4), C1-N1-C4 110.1(3), N1-C1-C6 122.3(3), C1-C6-N3 121.7(3), N1-C4-C5 122.4(3), C4-C5-N2 122.0(3).

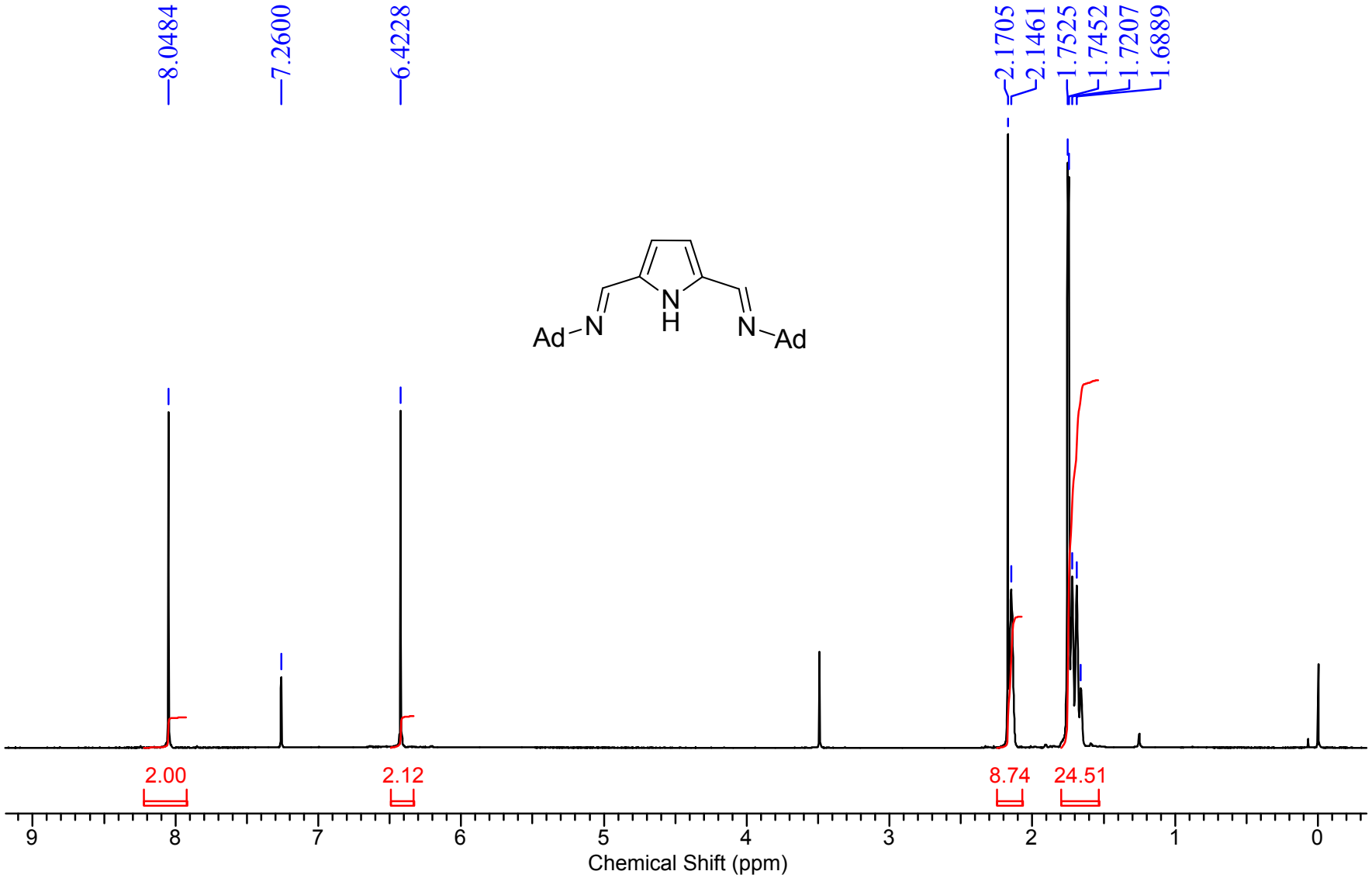
NMR soft copies of the all compounds.



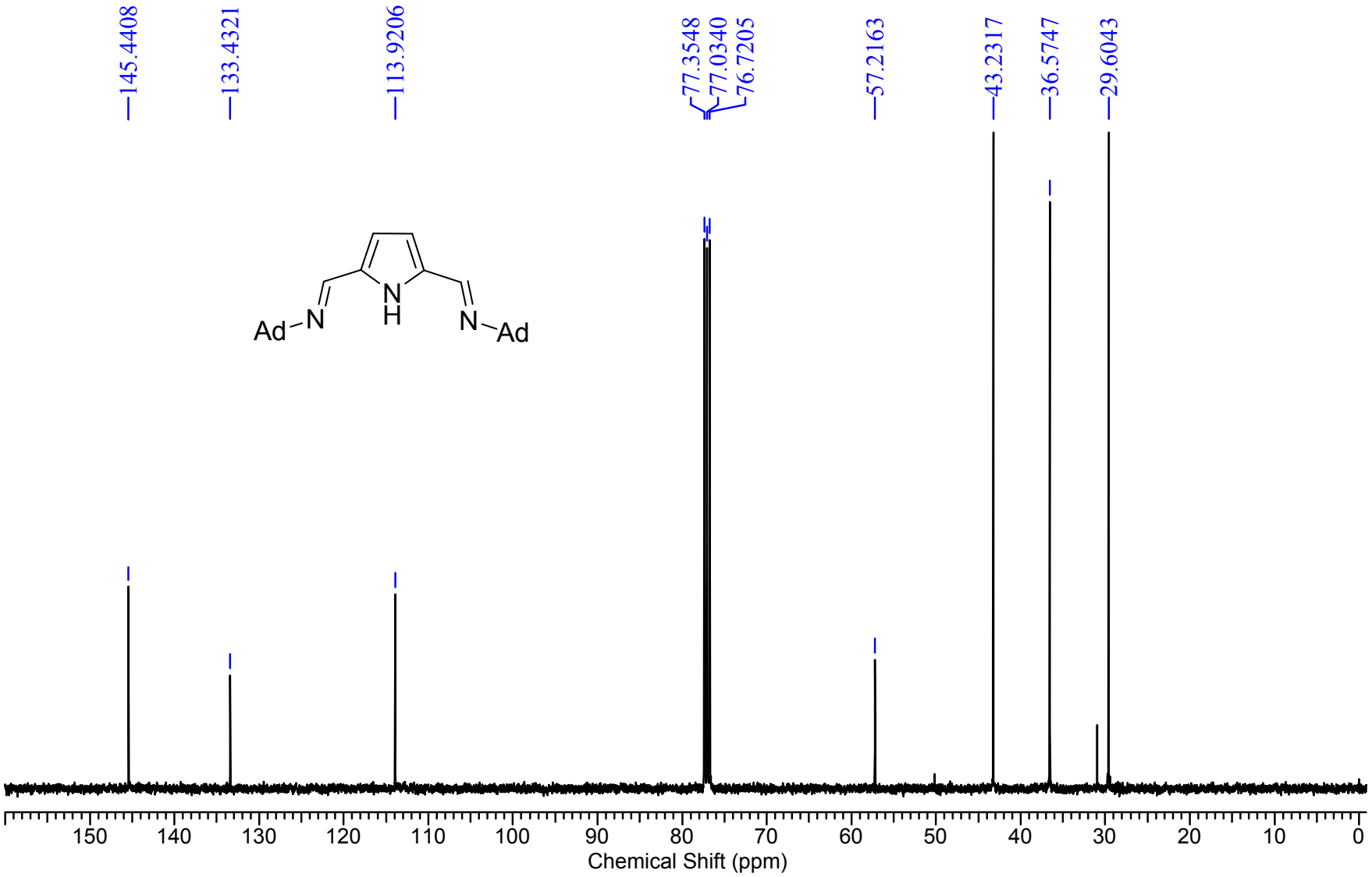
S1. ^{1}H NMR spectrum ($CDCl_3$, 400.13 MHz, 298 K) of $[(Ph_2CHN{=}CH)_2C_4H_2NH]$ (**1-H**)



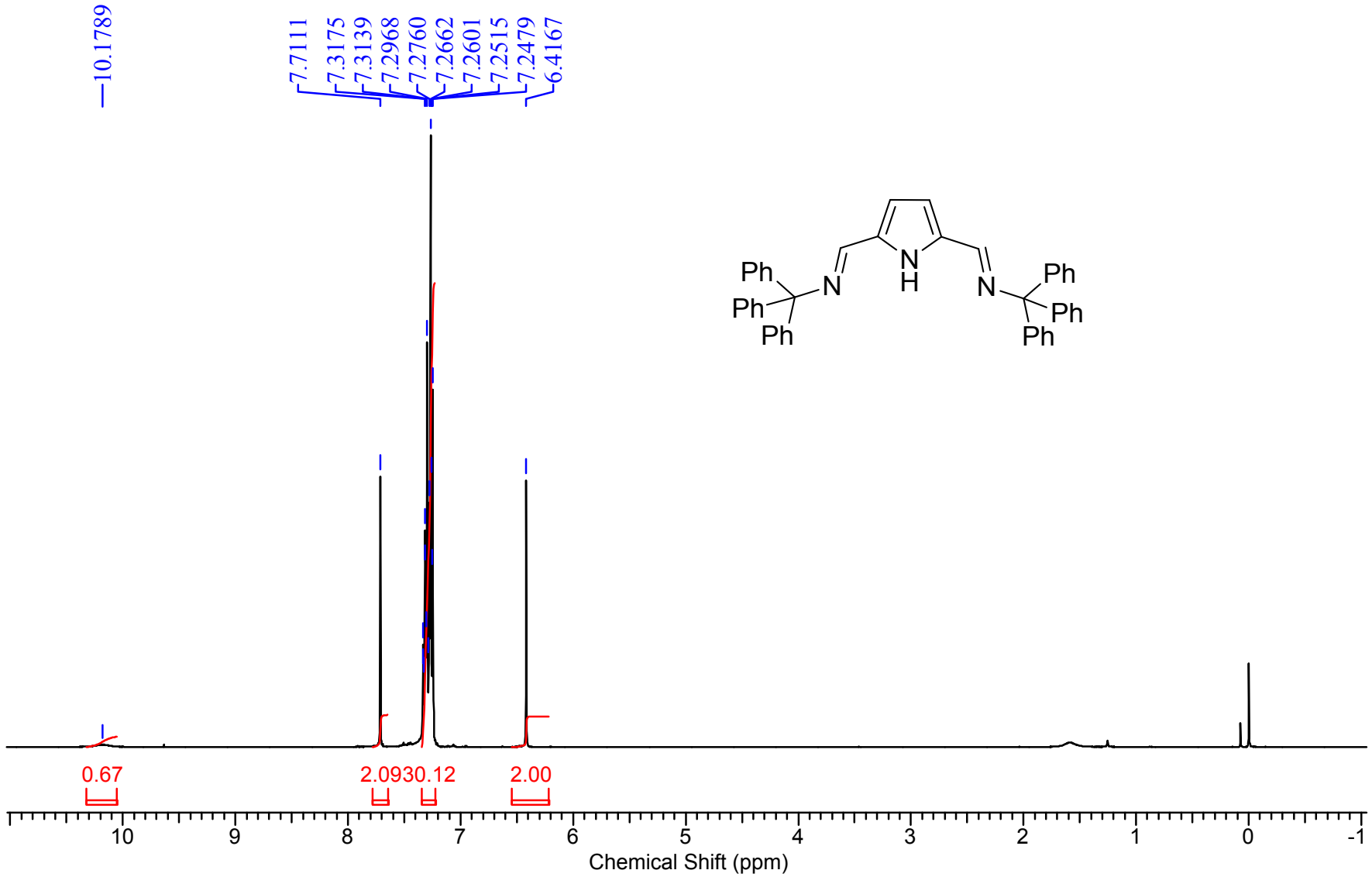
S2. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of $[(Ph_2CHN{=}CH)_2C_4H_2NH]$ (**1-H**)



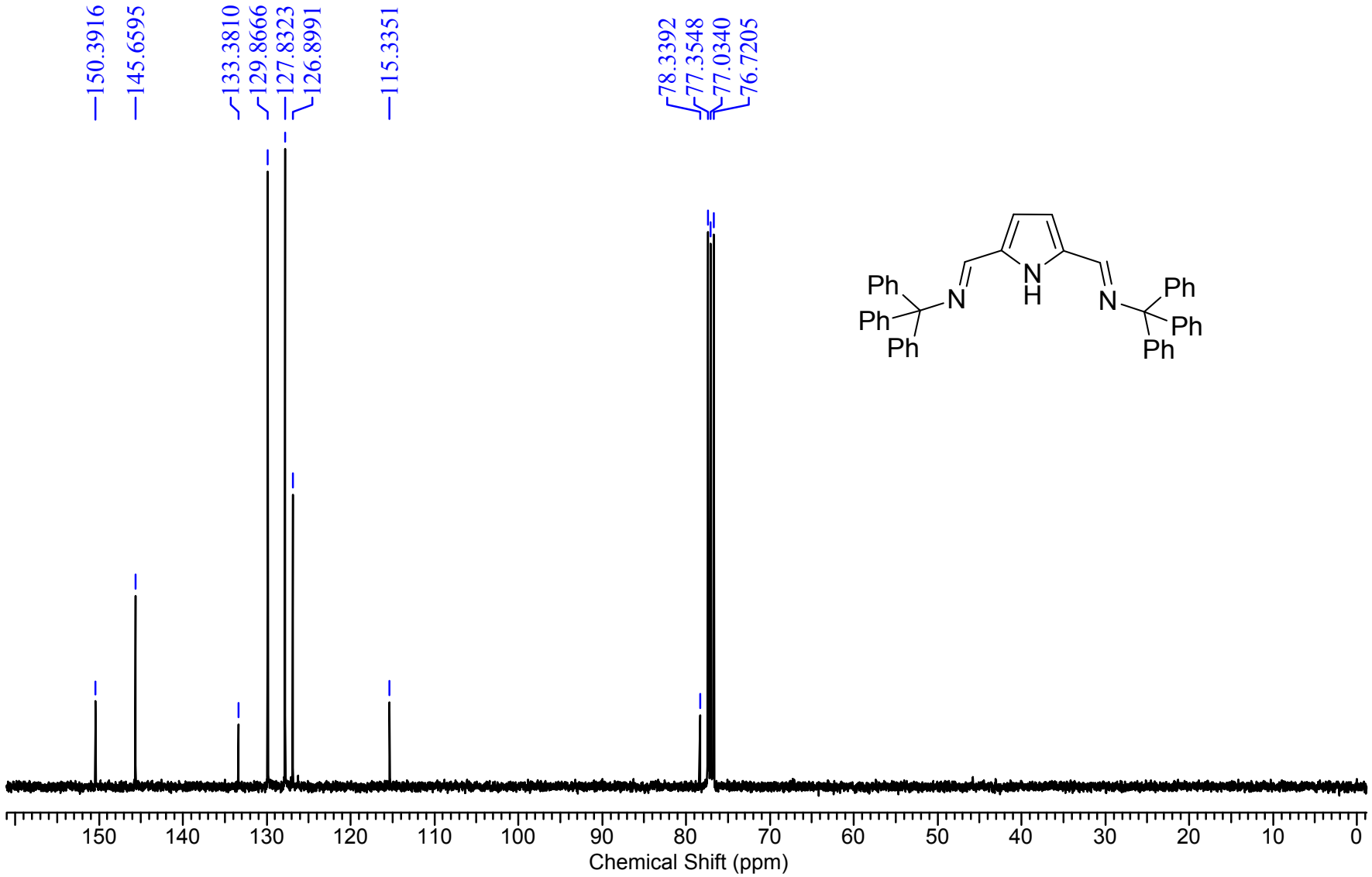
S3. ^{1}H NMR spectrum ($CDCl_3$, 400.13 MHz, 298 K) of $[(AdN{=}CH)_2C_4H_2NH]$ (**2-H**)



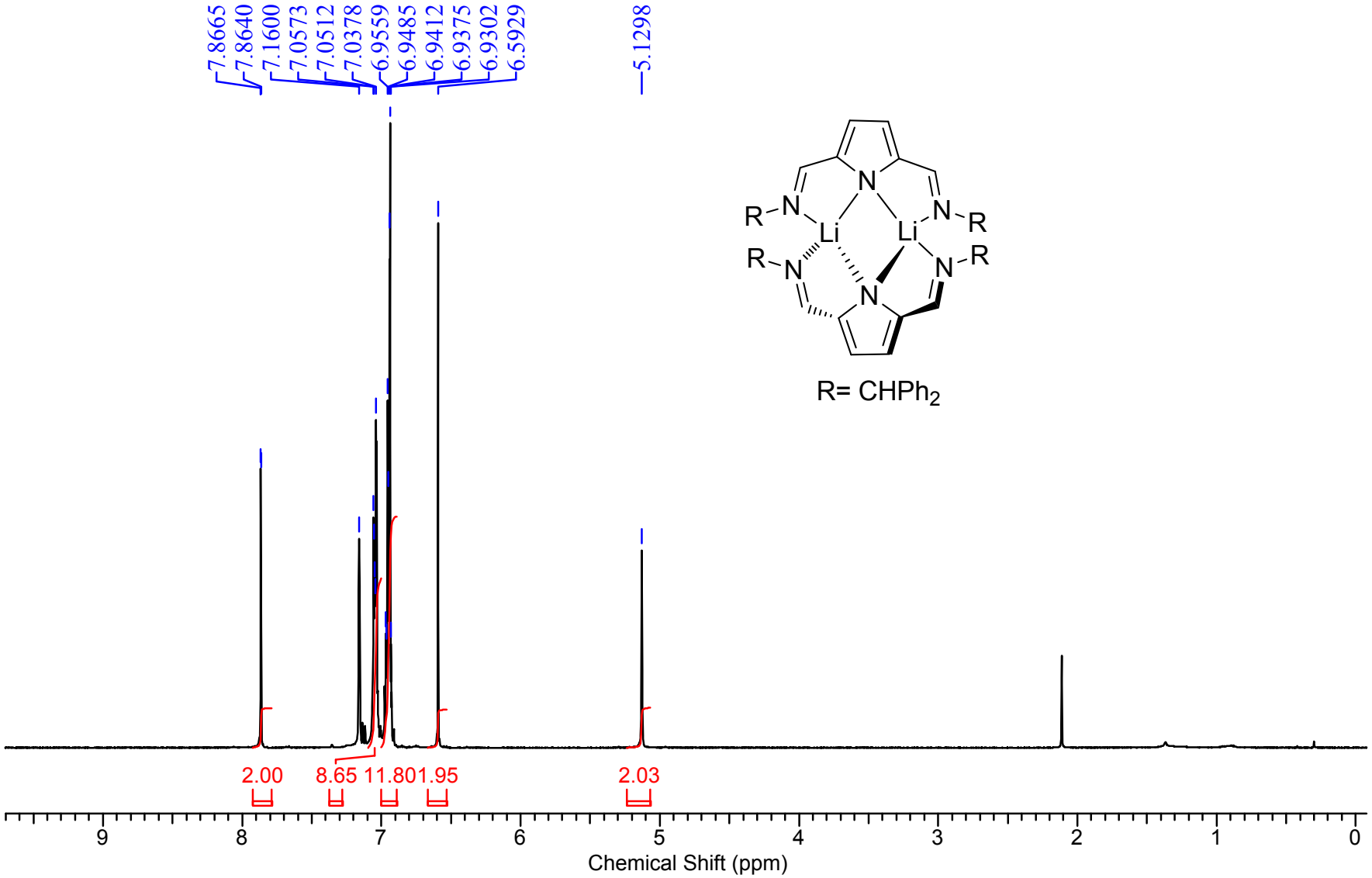
S4. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of $[(AdN{=}CH)_2C_4H_2NH]$ (**2-H**)



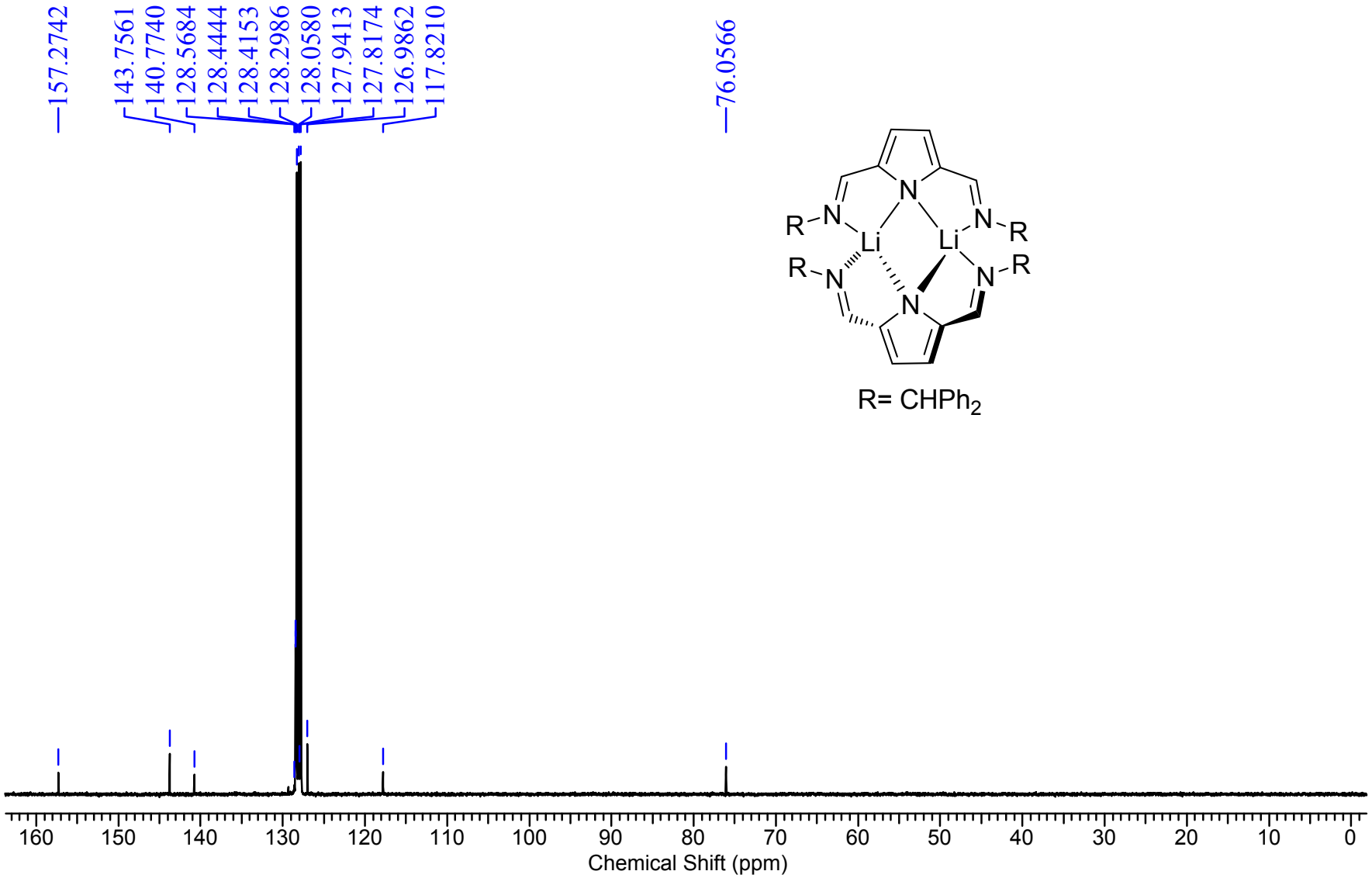
S5. ^{1}H NMR spectrum ($CDCl_3$, 400.13 MHz, 298 K) of $[(Ph_3CN{=}CH)_2C_4H_2NH]$ (**3-H**)



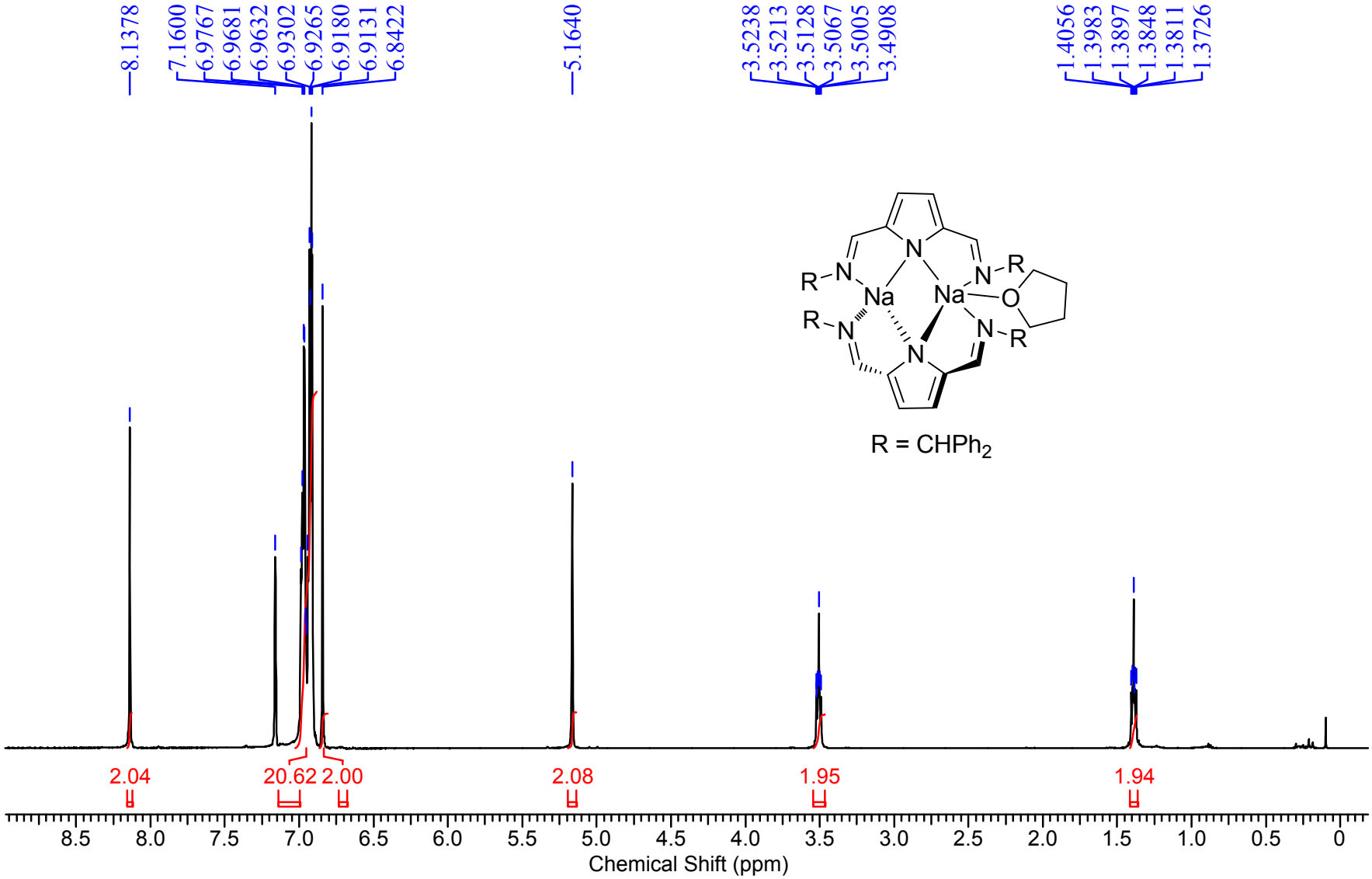
S6. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of $[(Ph_3CN{=}CH)_2C_4H_2NH]$ (**3-H**)



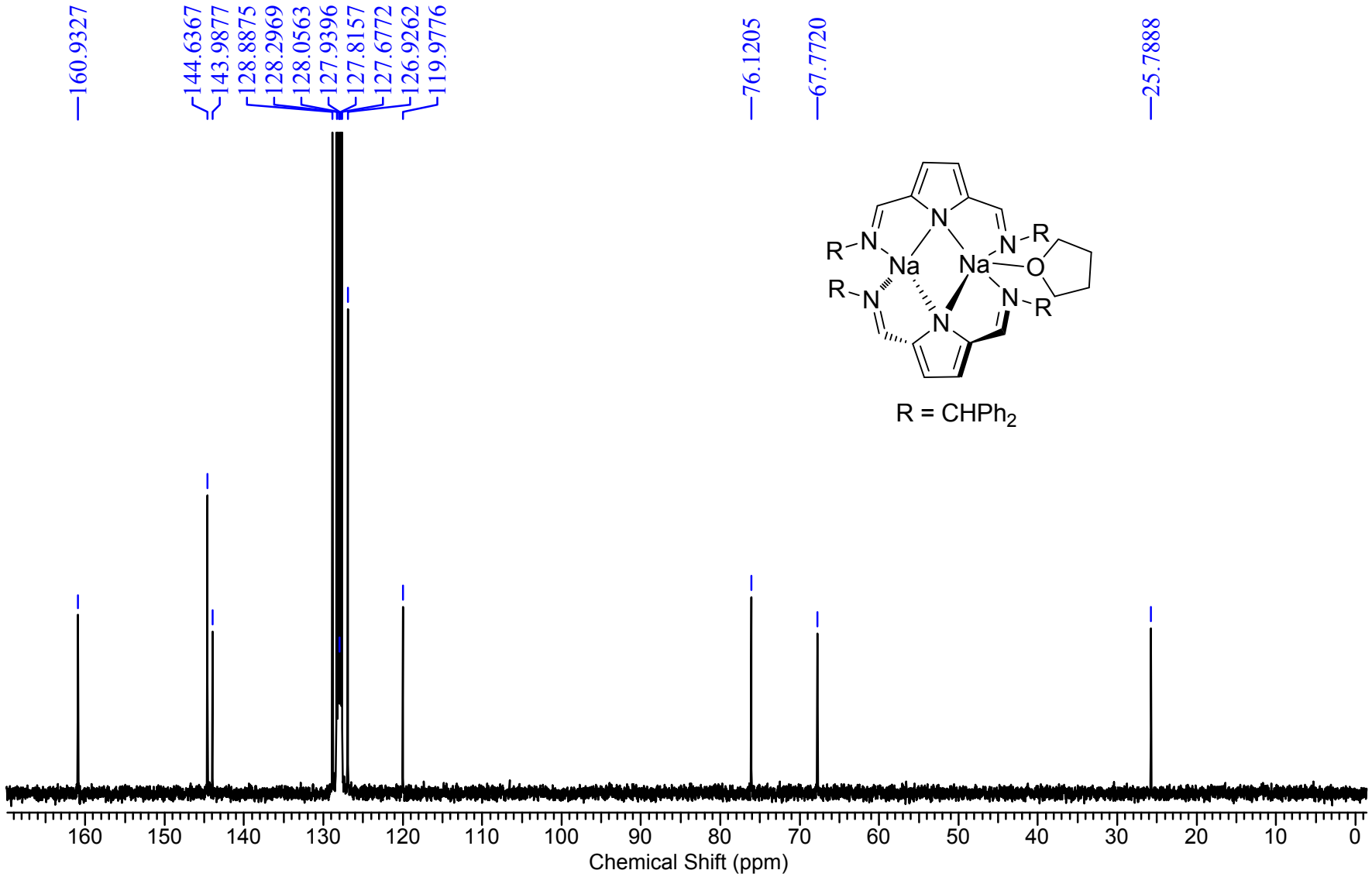
S7. ^{1}H NMR spectrum (C_6D_6, 400.13 MHz, 298 K) of [{$(Ph_2CHN{=}CH)_2C_4H_2NLi\}_2$] (**1-Li**)



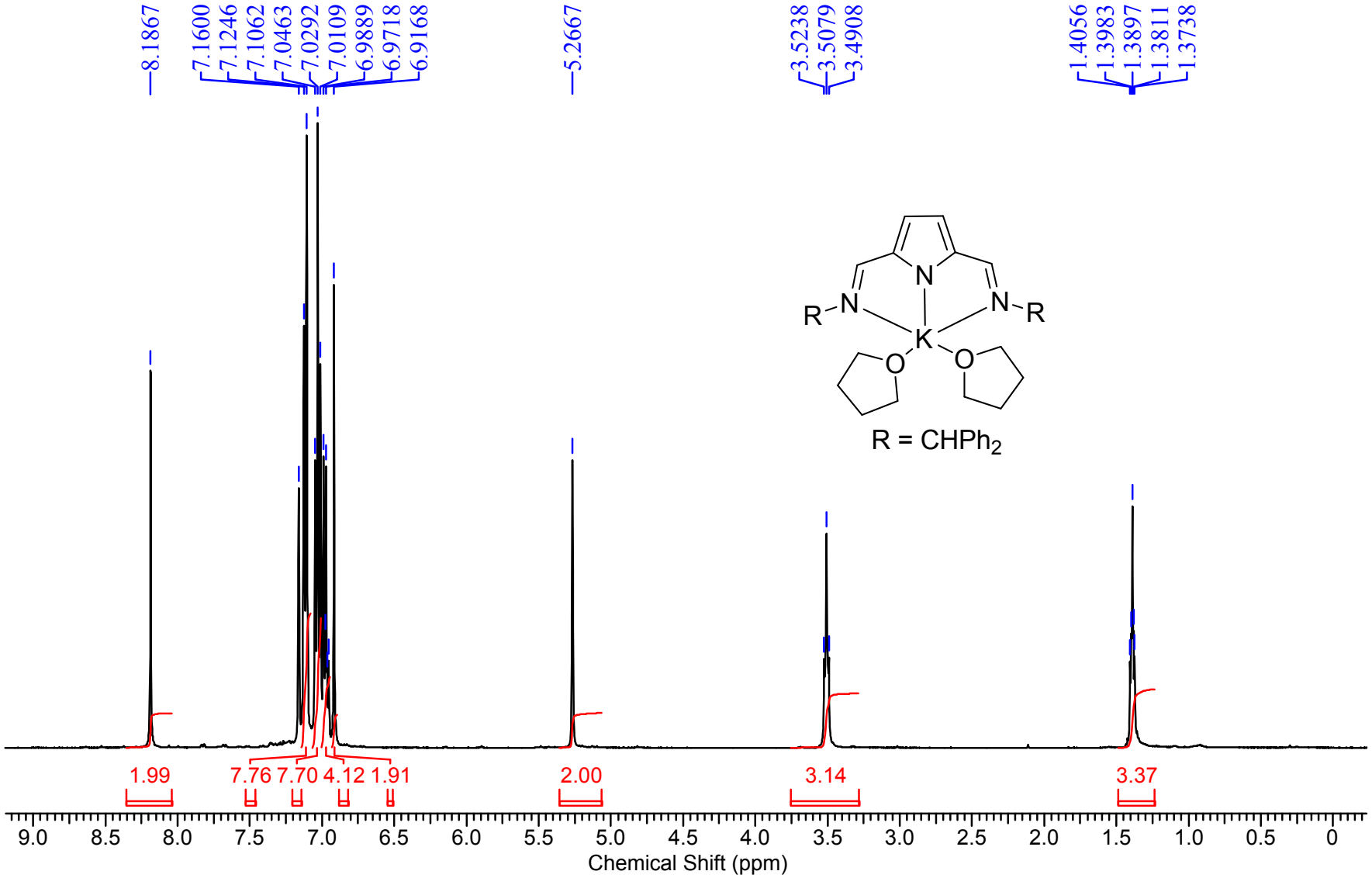
S8. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 100 MHz, 298 K) of [{$(Ph_2CHN{=}CH)_2C_4H_2NLi\}_2$] (**1-Li**)



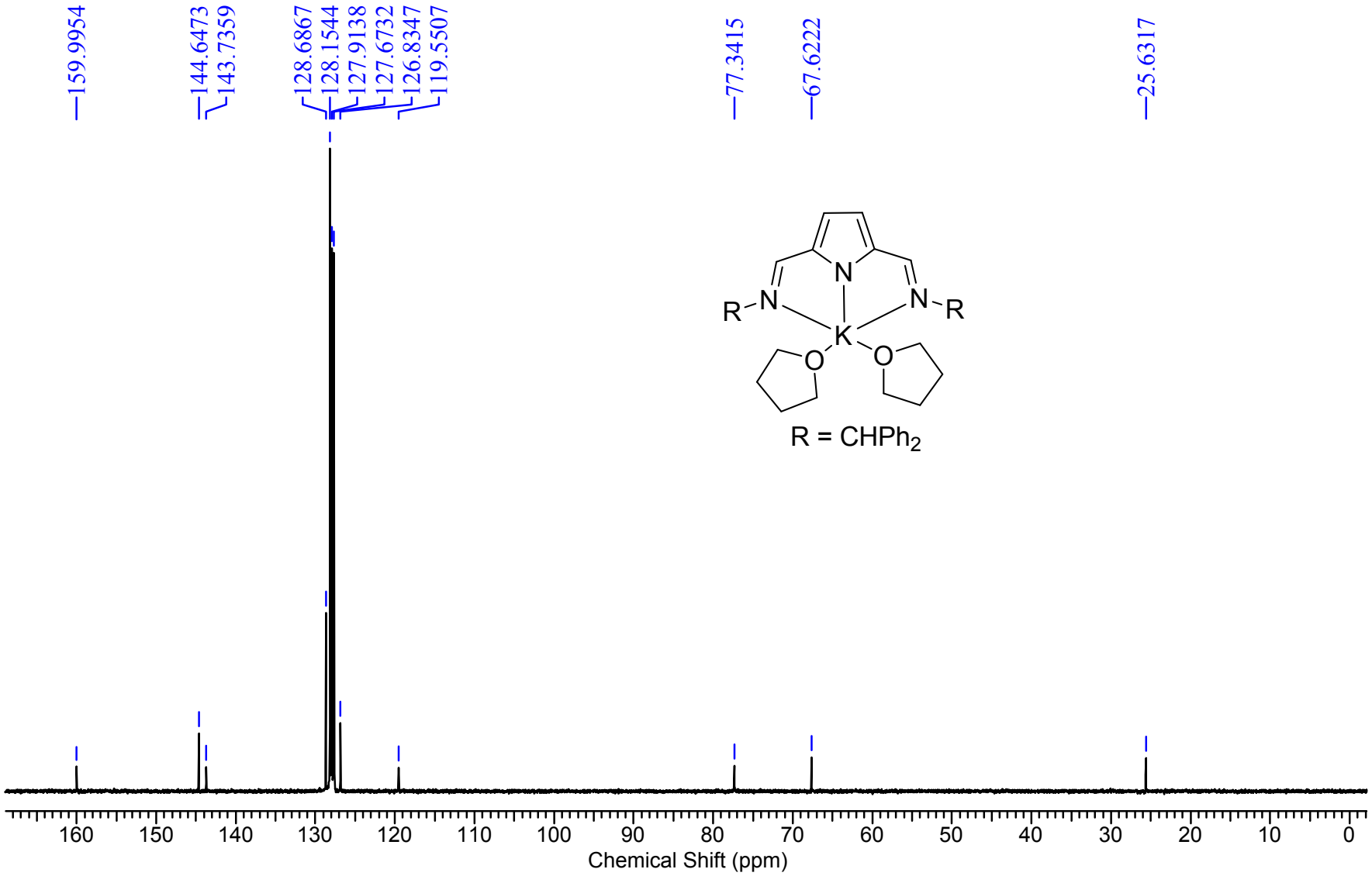
S9. ^{1}H NMR spectrum (C_6D_6, 400.13 MHz, 298 K) of [{Na(Ph$_2$CHN=CH)$_2$C$_4$H$_2$N}$_2$(THF)] (**1-Na**)



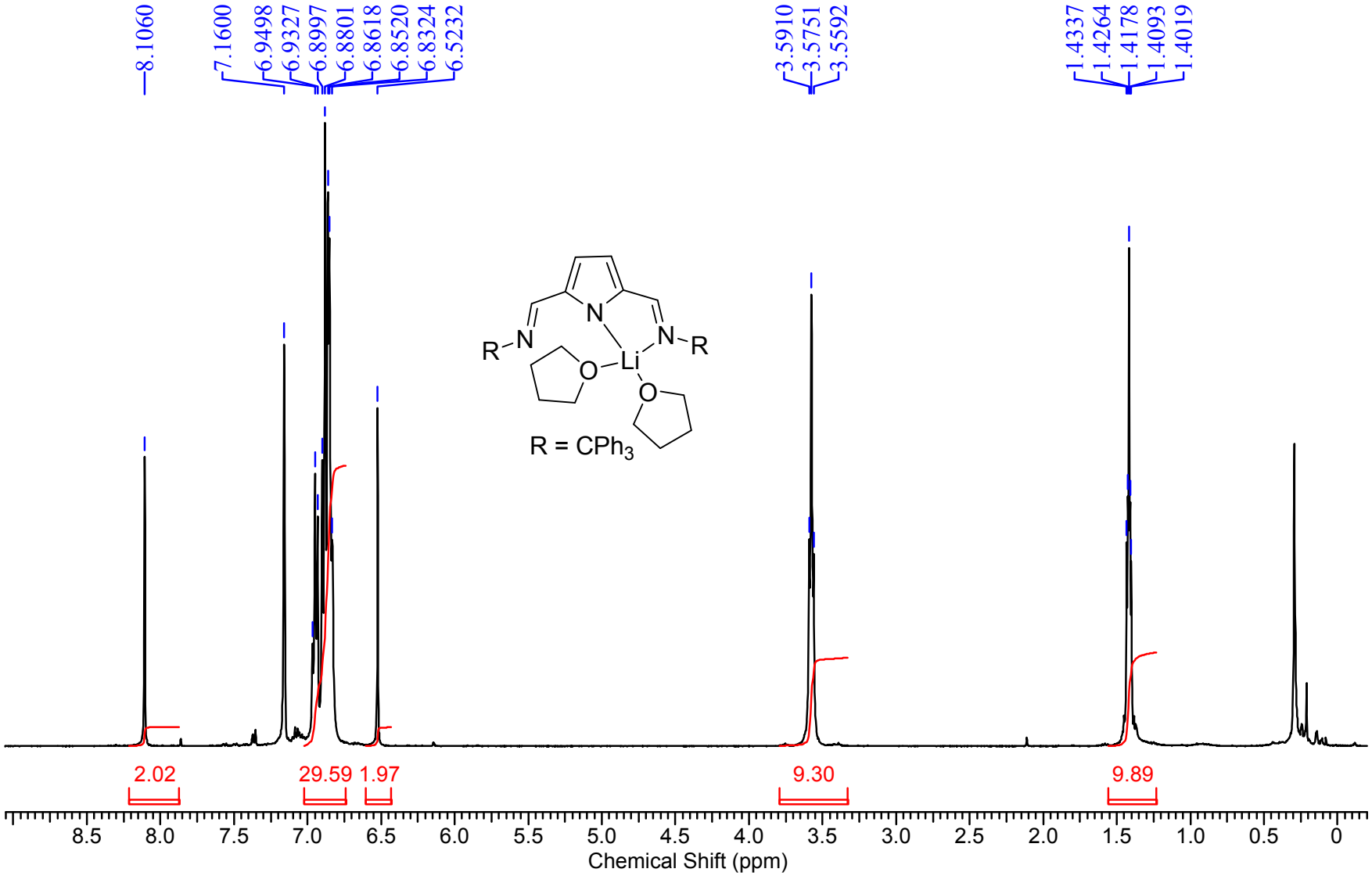
S10. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 100 MHz, 298 K) of [{Na($Ph_2CHN{=}CH)_2C_4H_2N$}$_2$(THF)] (**1-Na**)



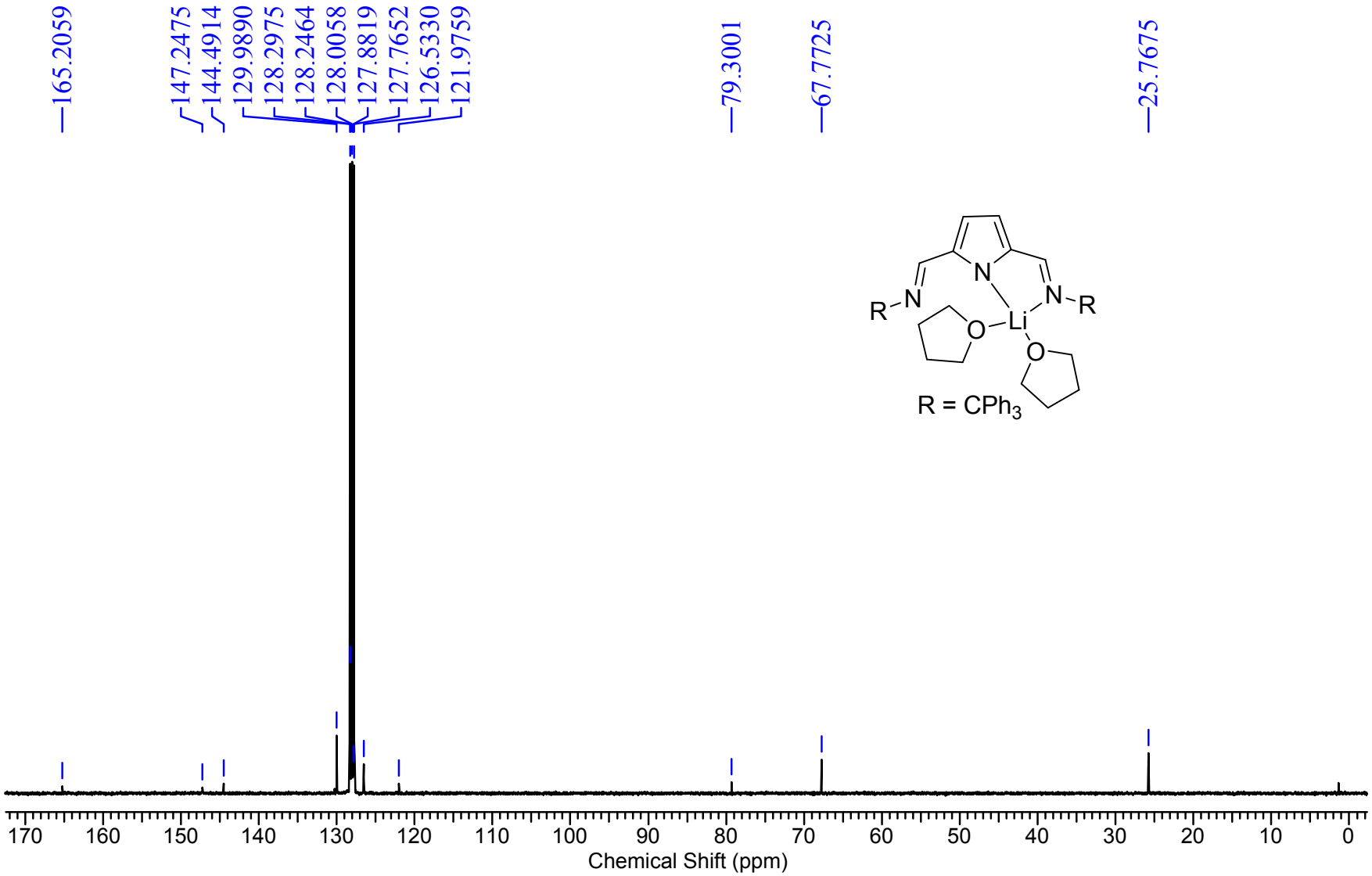
S11. ^{1}H NMR spectrum (C_6D_6, 400.13 MHz, 298 K) of $[(Ph_2CHN{=}CH)_2C_4H_2NK(THF)_2]$ (**1-K**)



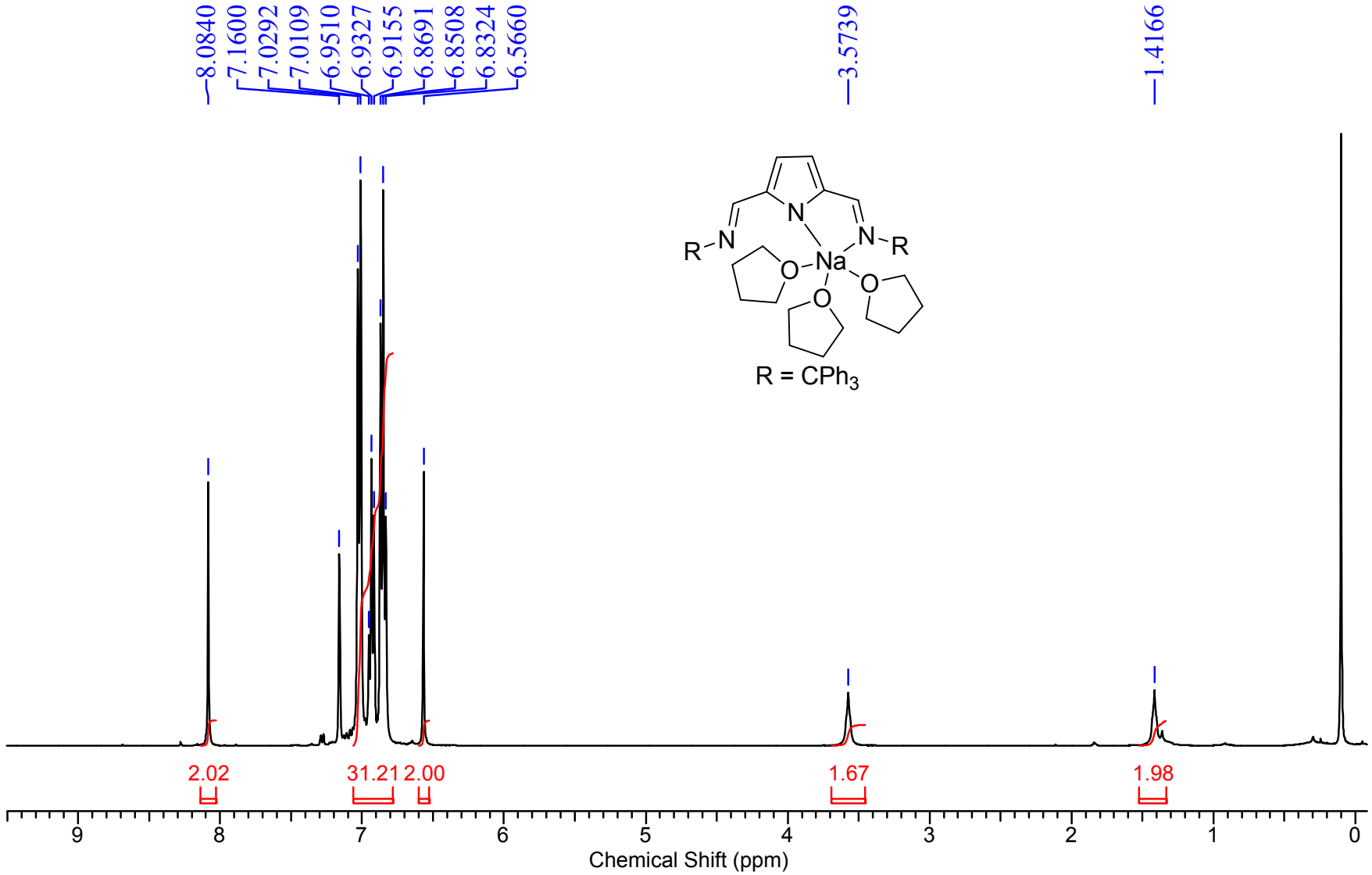
S12. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 100 MHz, 298 K) of $[(Ph_2CHN{=}CH)_2C_4H_2NK(THF)_2]$ (**1-K**)]



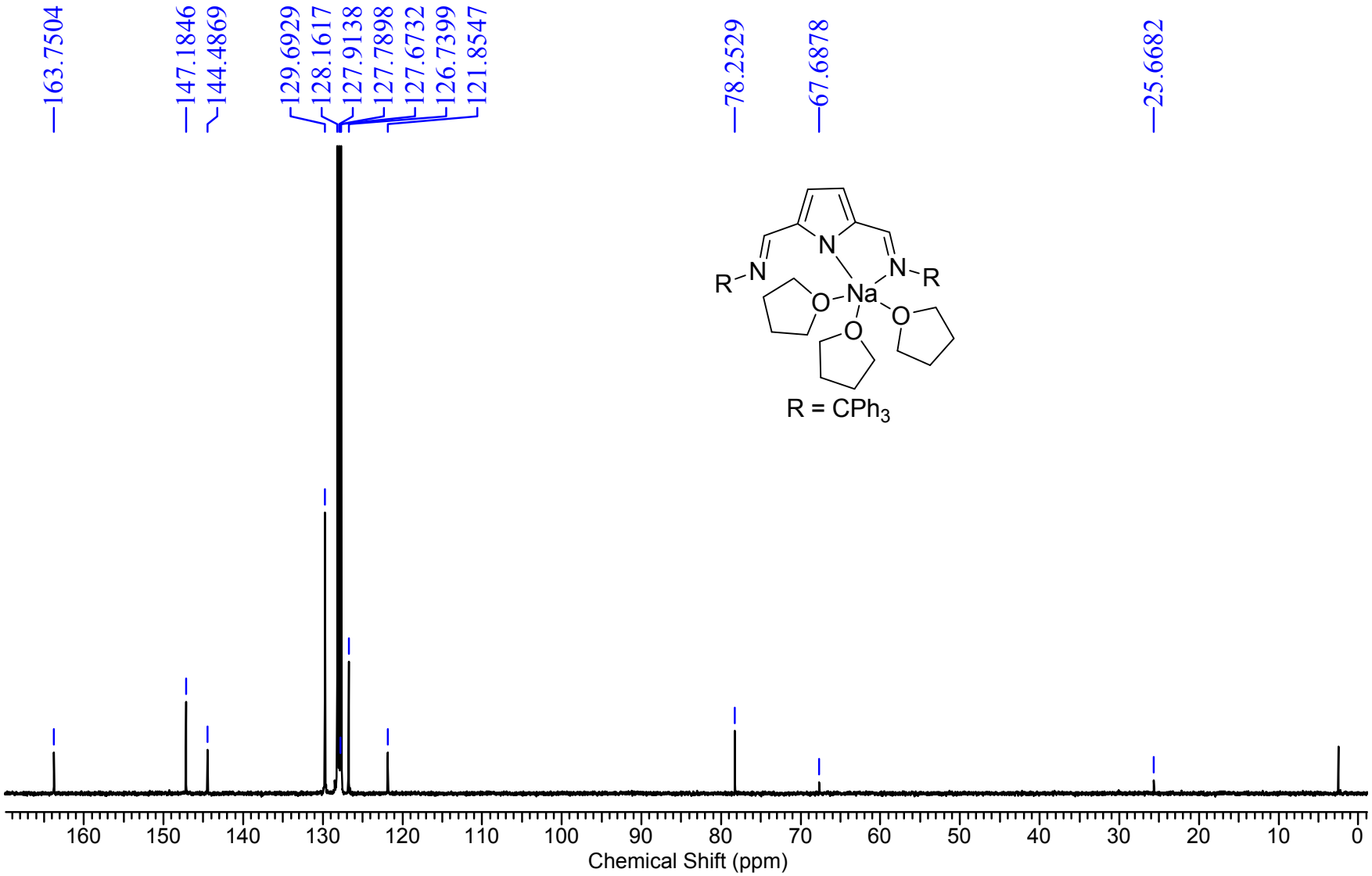
S13. ^{1}H NMR spectrum (C_6D_6, 400.13 MHz, 298 K) of $[(Ph_3CN{=}CH)_2C_4H_2NLi(THF)_2]$ (**3-Li**)



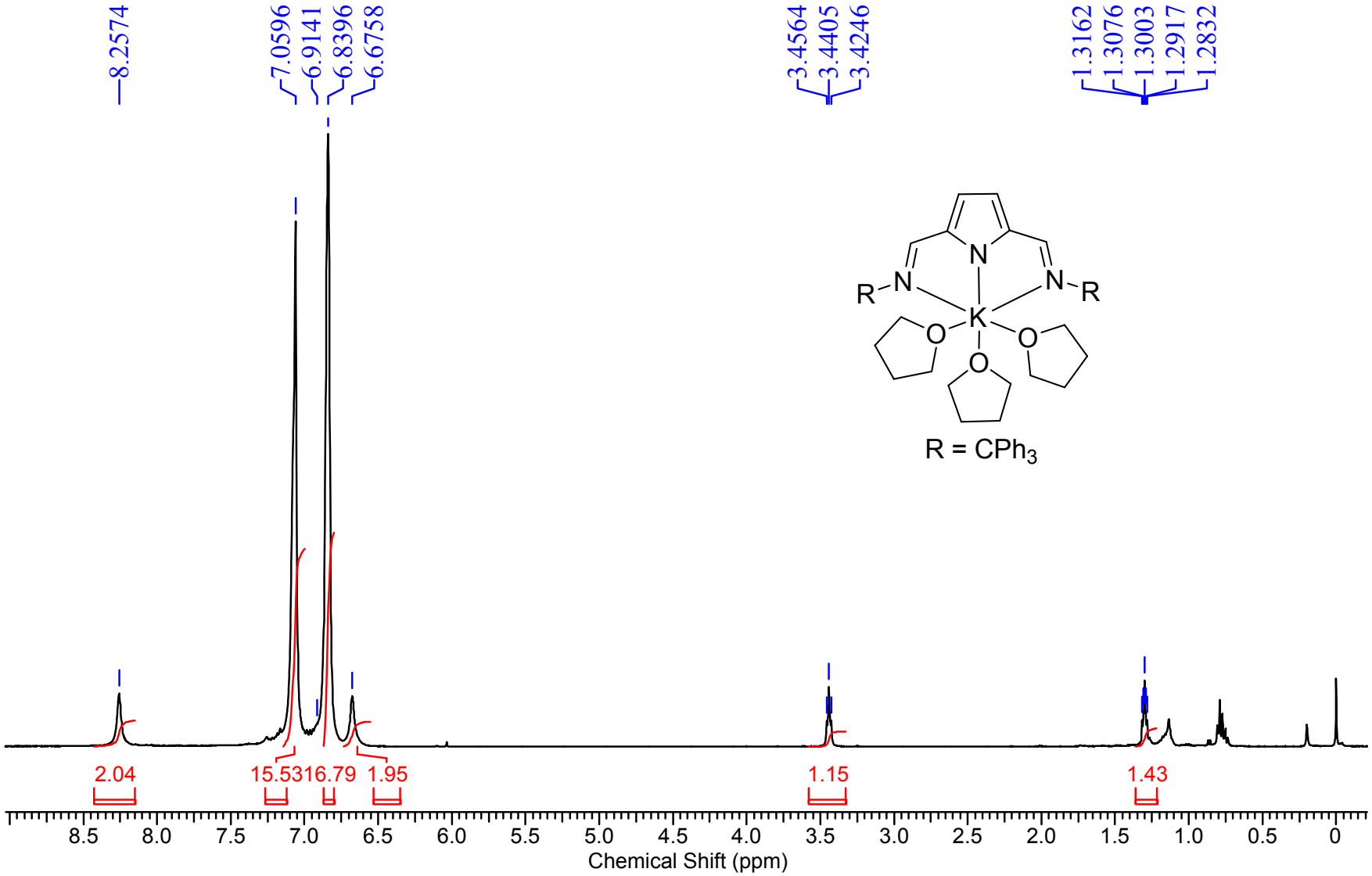
S14. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 100 MHz, 298 K) of $[(Ph_3CN{=}CH)_2C_4H_2NLi(THF)_2]$ (**3-Li**)



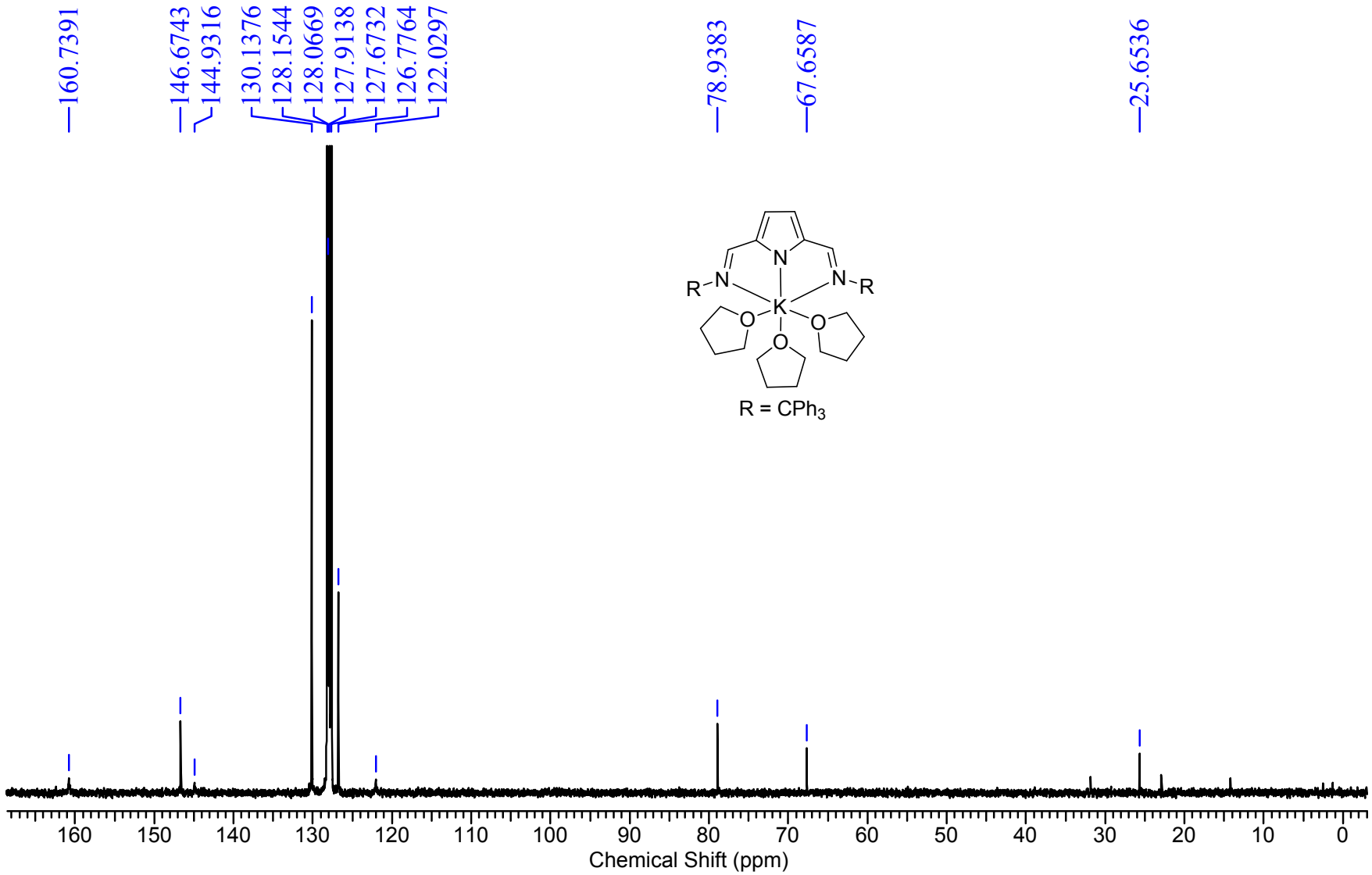
S15. ^{1}H NMR spectrum (C_6D_6, 400.13 MHz, 298 K) of $[(Ph_3CN{=}CH)_2C_4H_2NNa(THF)_3]$ (**3-Na**)



S16. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 100 MHz, 298 K) of $[(Ph_3CN{=}CH)_2C_4H_2NNa(THF)_3]$ (**3-Na**)

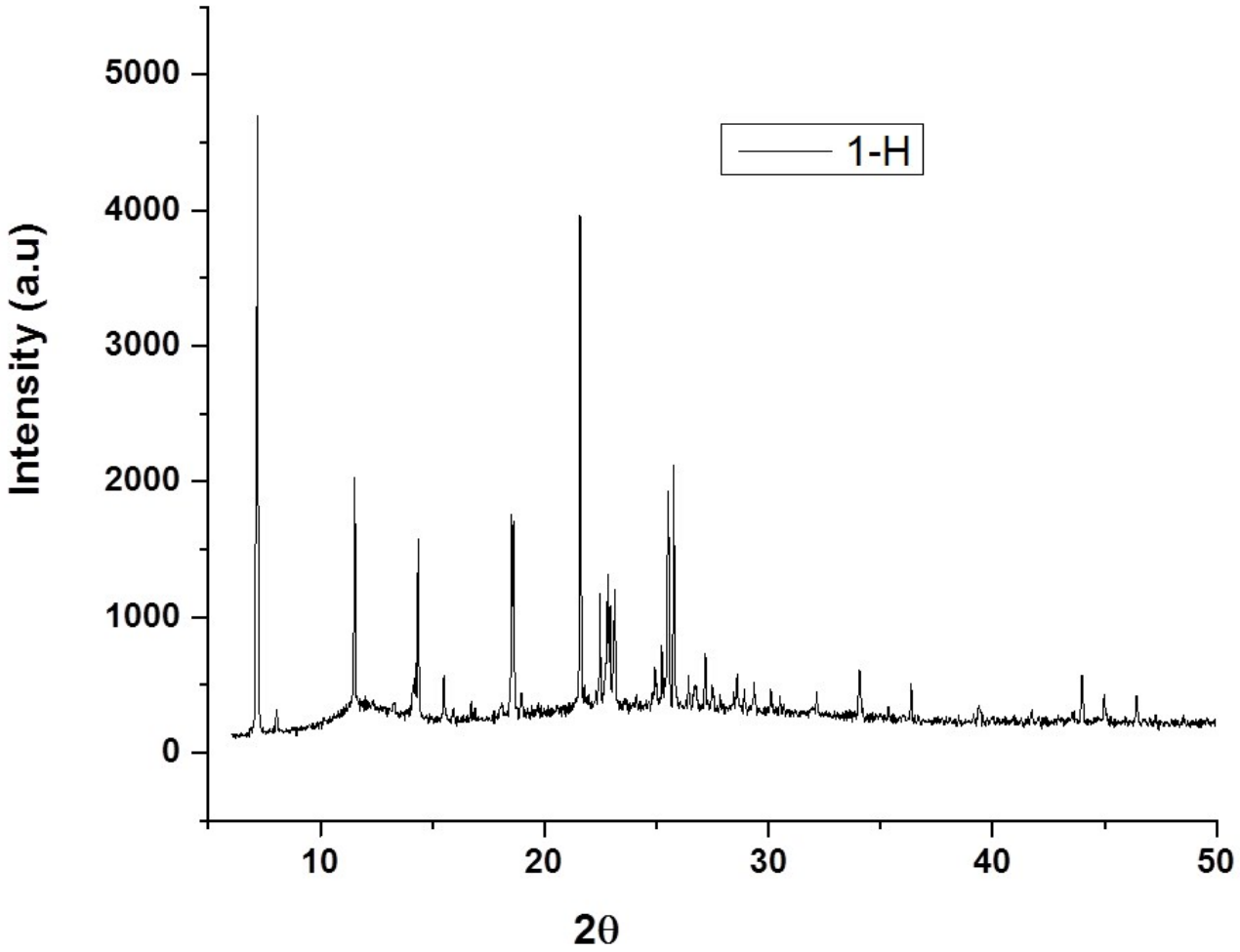


S17. ^{1}H NMR spectrum (C_6D_6, 400.13 MHz, 298 K) of $[(Ph_3CN{=}CH)_2C_4H_2NK(THF)_3]$ (**3-K**)

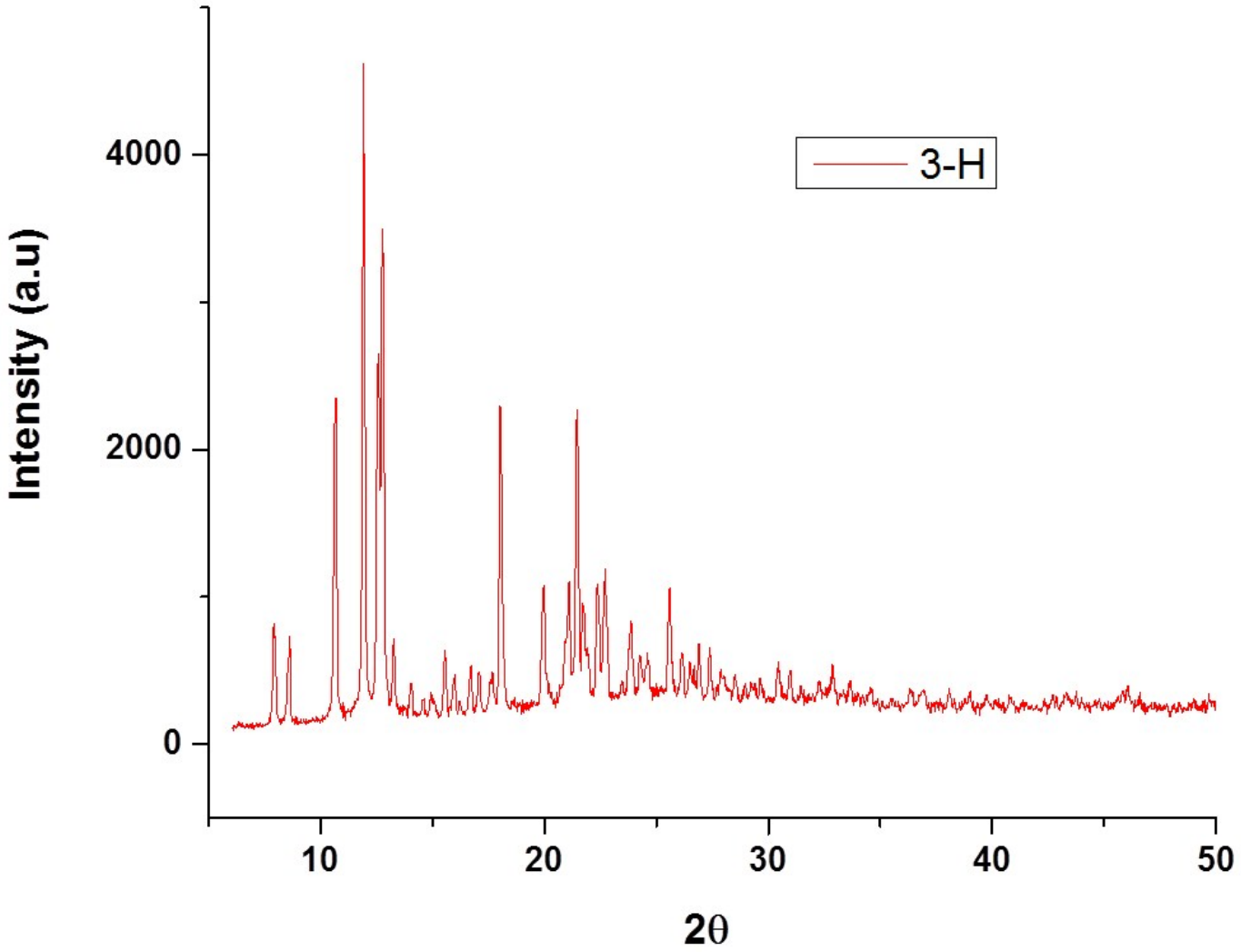


S18. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 100 MHz, 298 K) of $[(Ph_3CN{=}CH)_2C_4H_2NK(THF)_3]$ (**3-K**)

Powder XRD:



S19. Powder XRD pattern for compound **1-H**.



S20. Powder XRD pattern for compound **3-H**.