Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

for

Coordination Chemistry of Alkali Metal Dimesityl-thio- and Dimesityl-selenophosphinites $[(L)_2A\text{-}EPMes_2]_2$ (A = Li, Na, K; E = S, Se; L = THF, THP) and $[(18C6)K\text{-}SPMes_2]$

Richard C. C. Dorow, Phil Liebing, Helmar Görls, and Matthias Westerhausen

Dimesitylphosphane sulfide (**1a**)

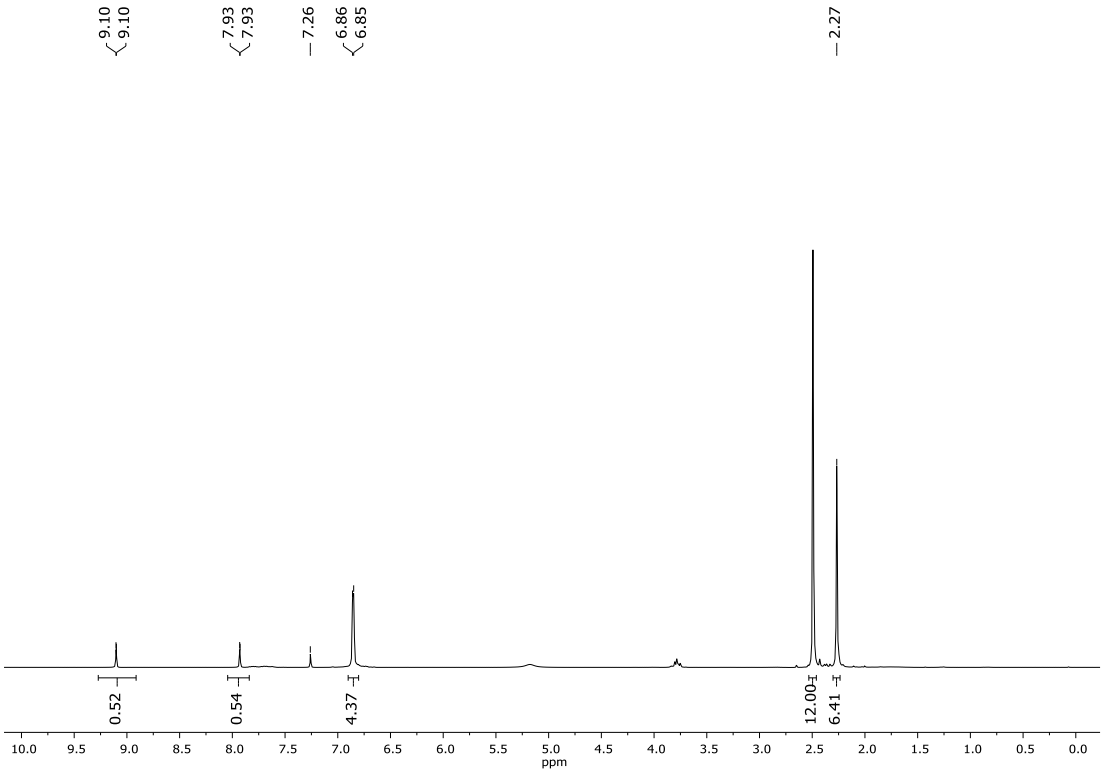

Figure S1. ^{1}H NMR spectrum (400.13 MHz, $CDCl_3$, 298 K).

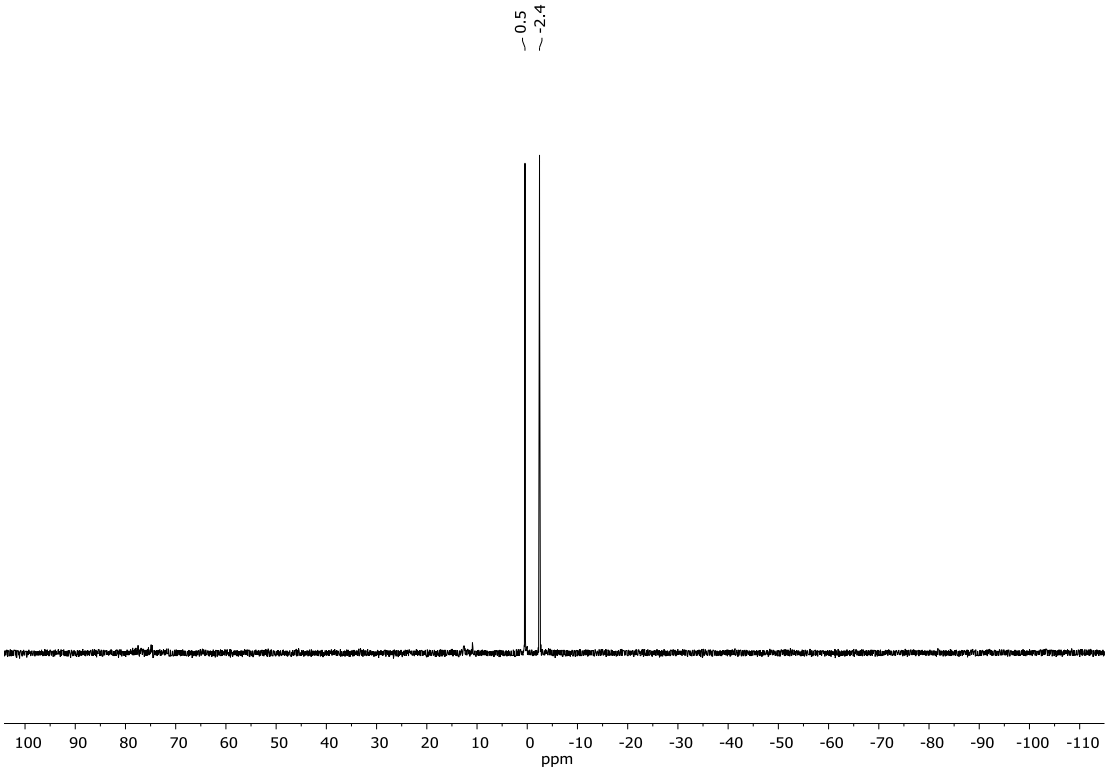

Figure S2. ^{31}P NMR spectrum (161.98 MHz, $CDCl_3$, 298 K).

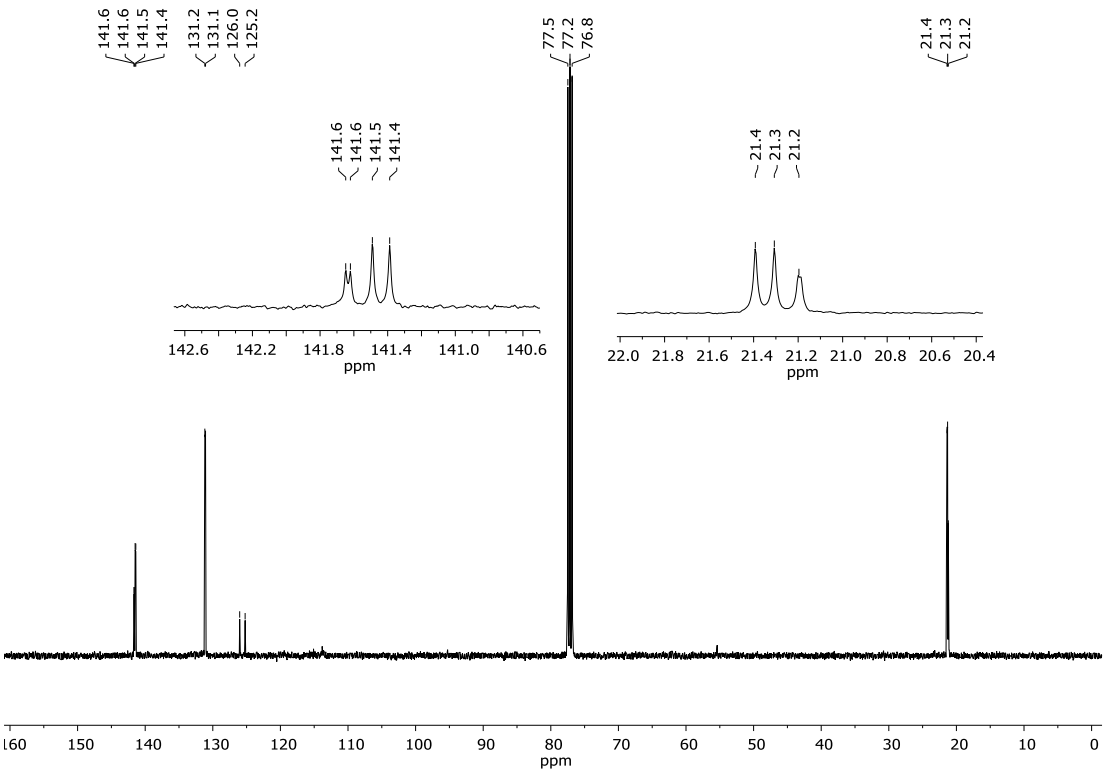

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, $CDCl_3$, 298 K).

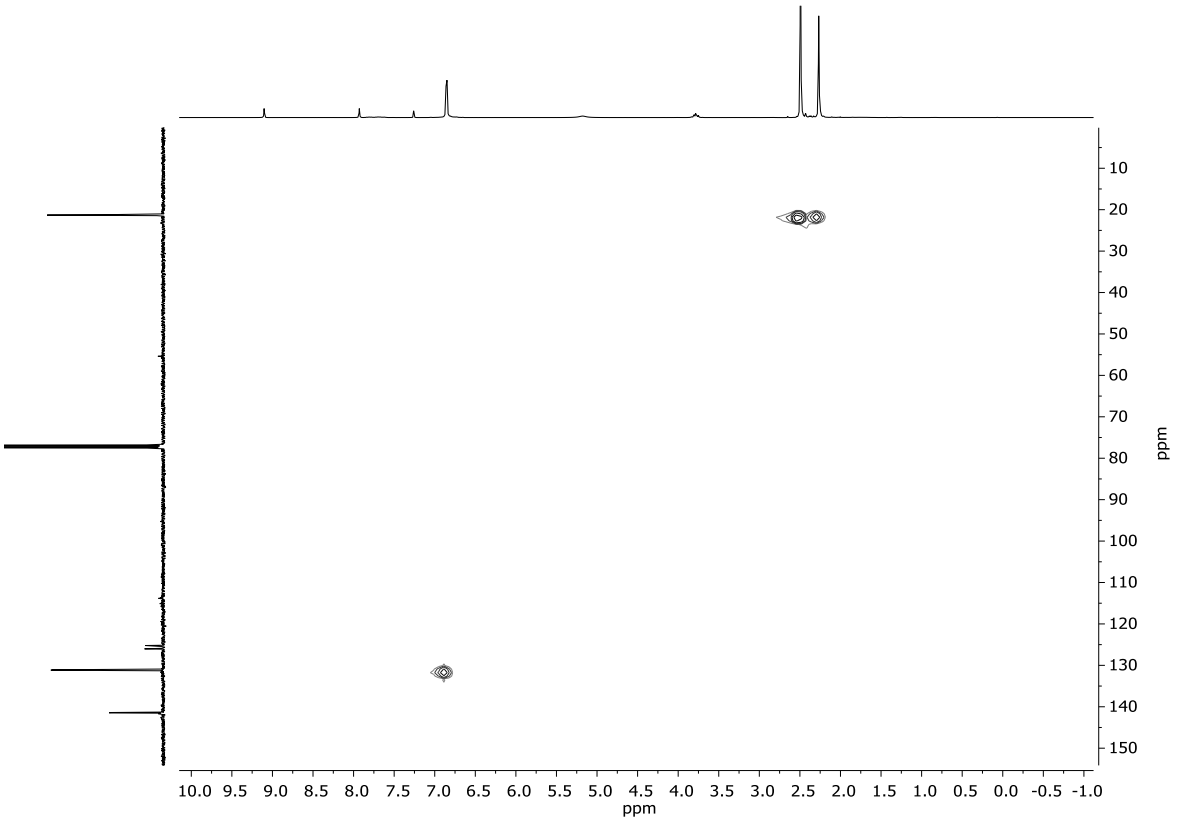

Figure S4. HSQC NMR spectrum (400.13/100.61 MHz, $CDCl_3$, 298 K).

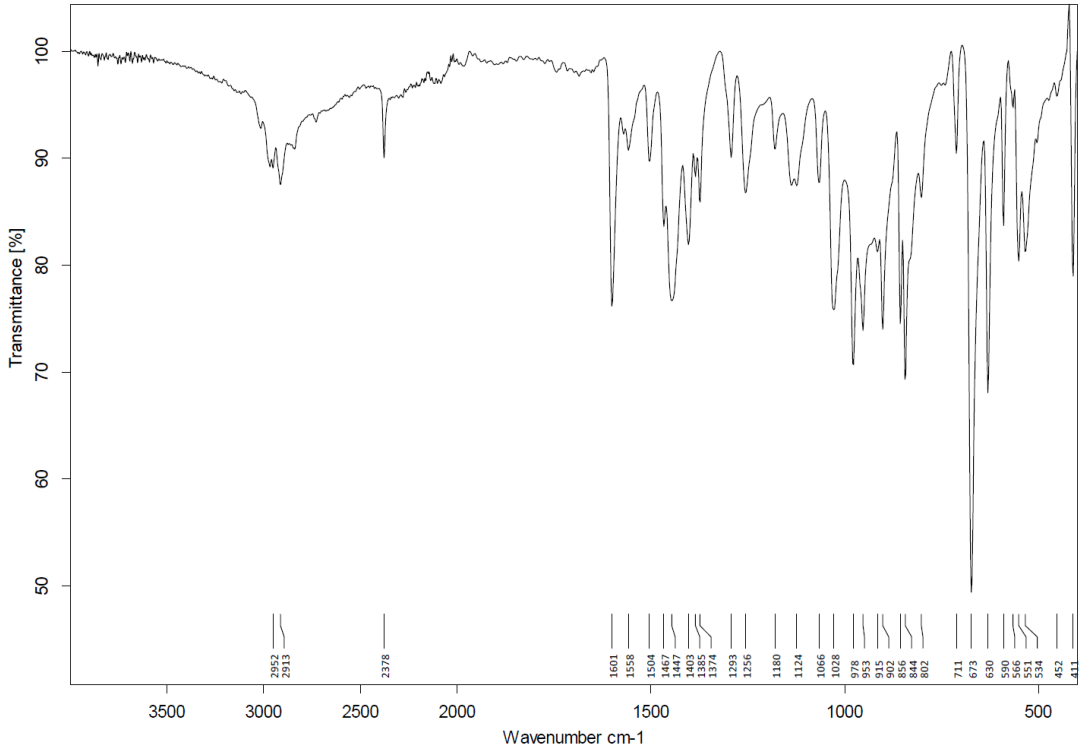

Figure S5. IR (ATR).

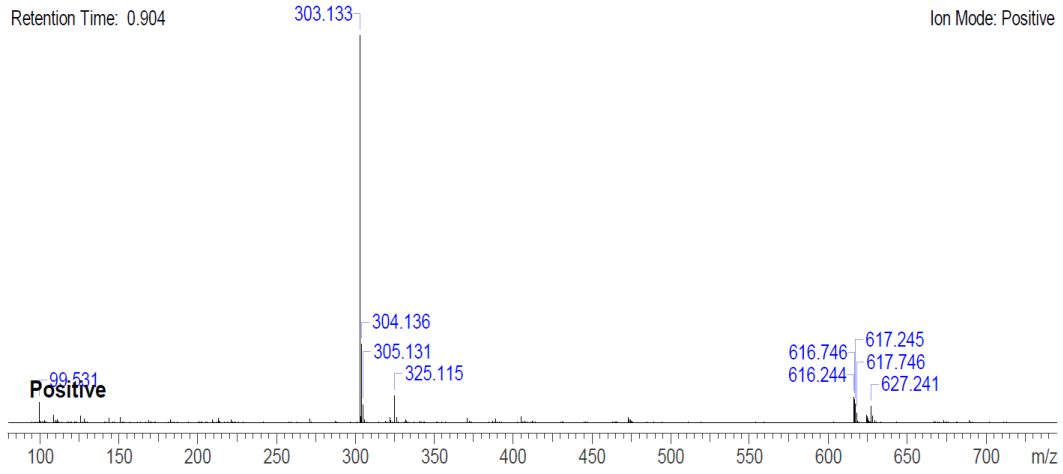

Figure S6. MS.

Dimesitylphosphane selenide (**1b**)

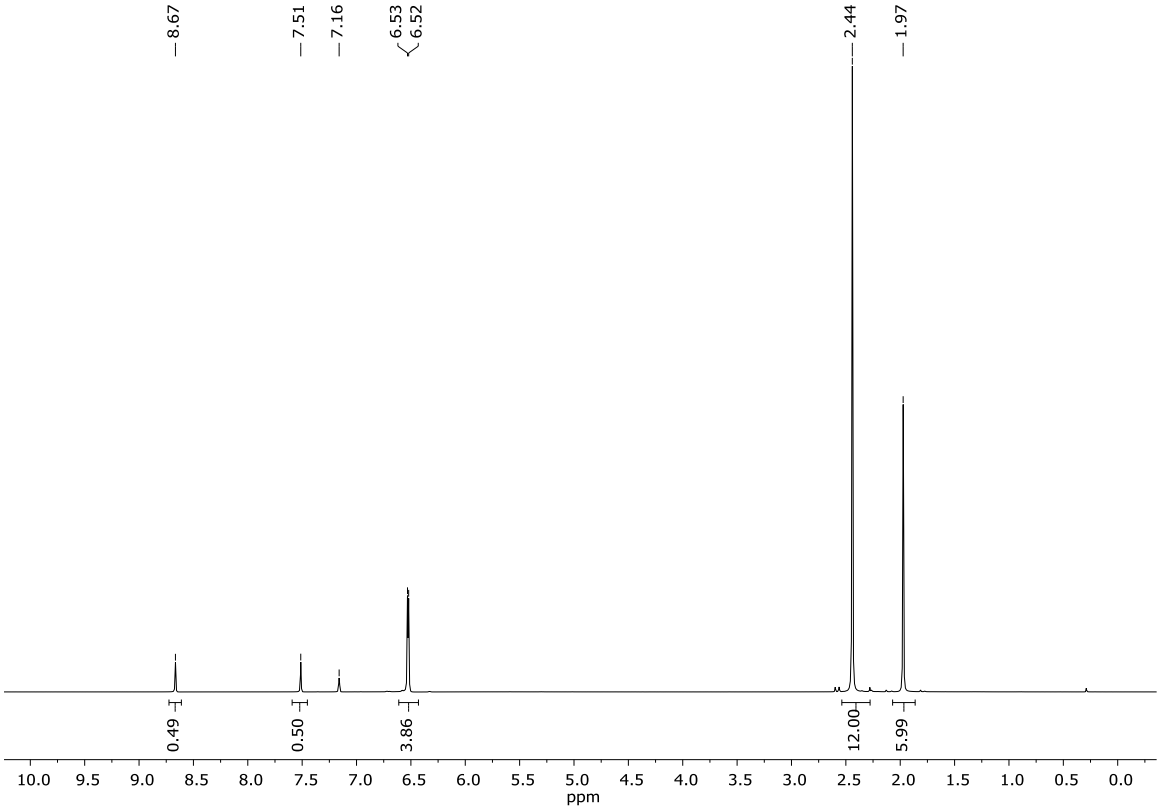

Figure S7. ^{1}H NMR spectrum (400.13 MHz, C_6D_6, 298 K).

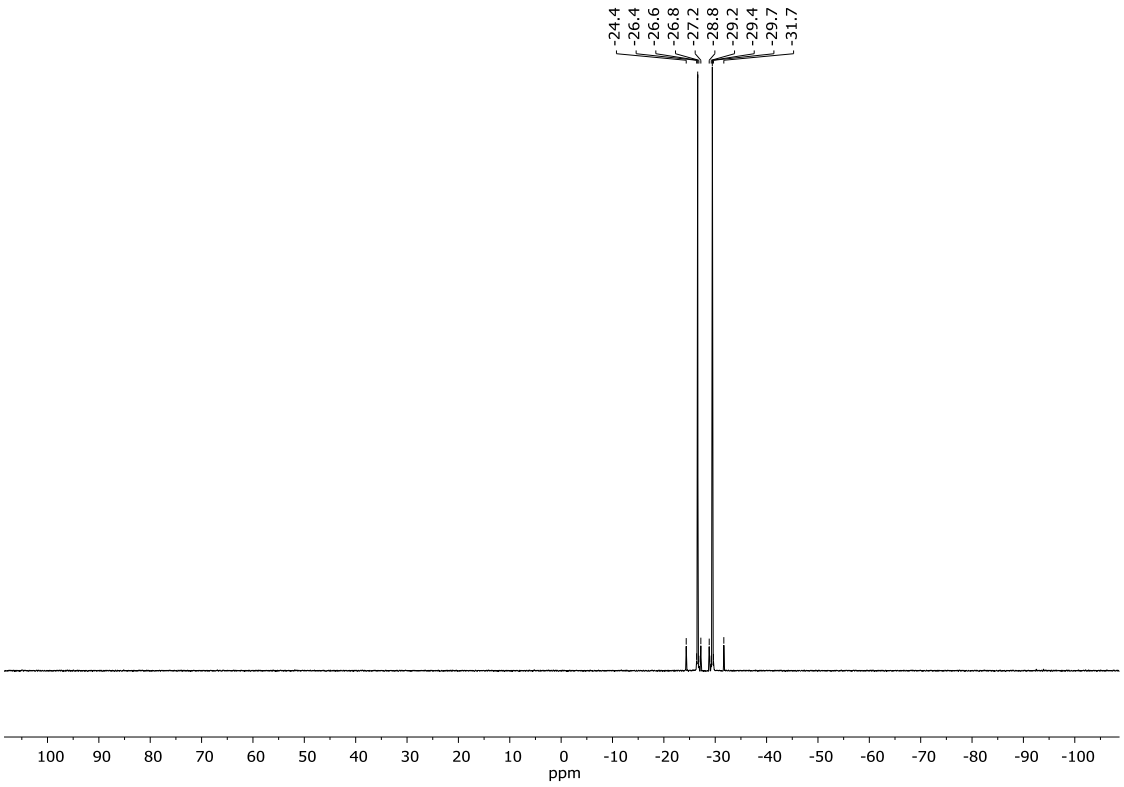

Figure S8. ^{31}P NMR spectrum (161.98 MHz, C_6D_6, 298 K).

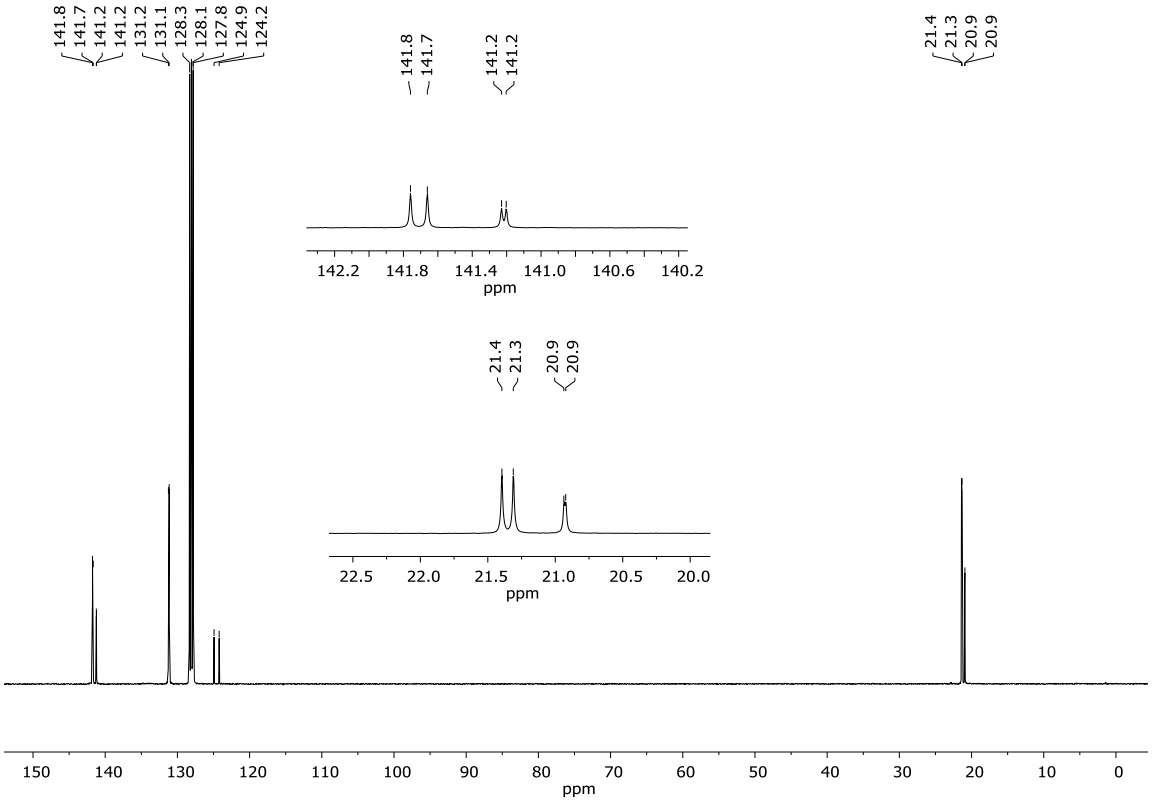

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, C_6D_6, 298 K).

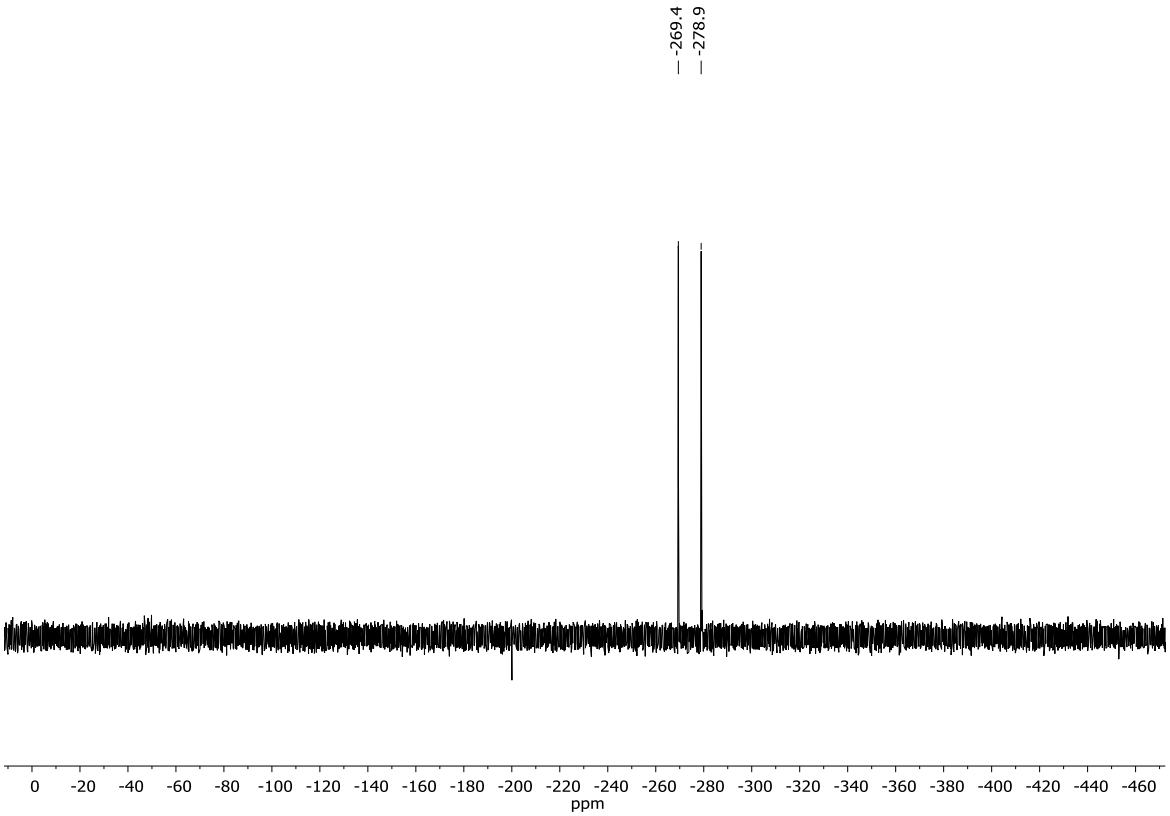

Figure S10. ^{77}Se NMR spectrum (76.31 MHz, C_6D_6, 298 K).

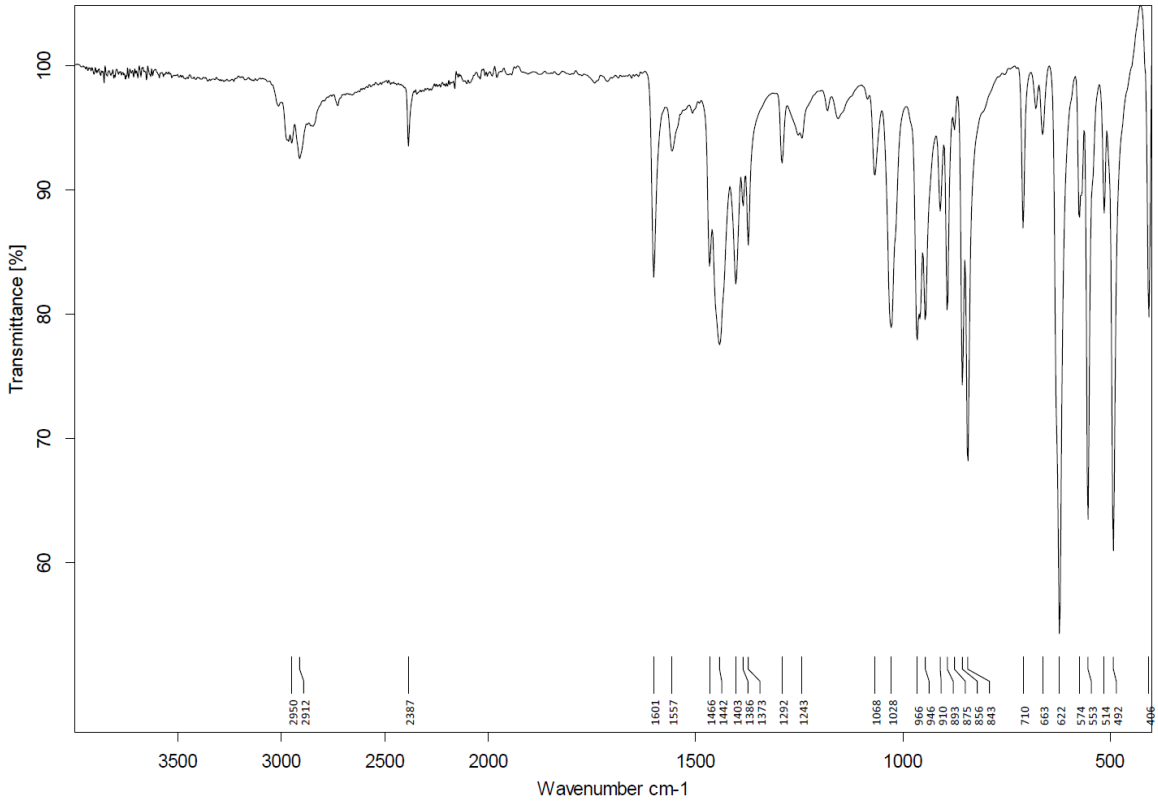

Figure S11. IR (ATR).

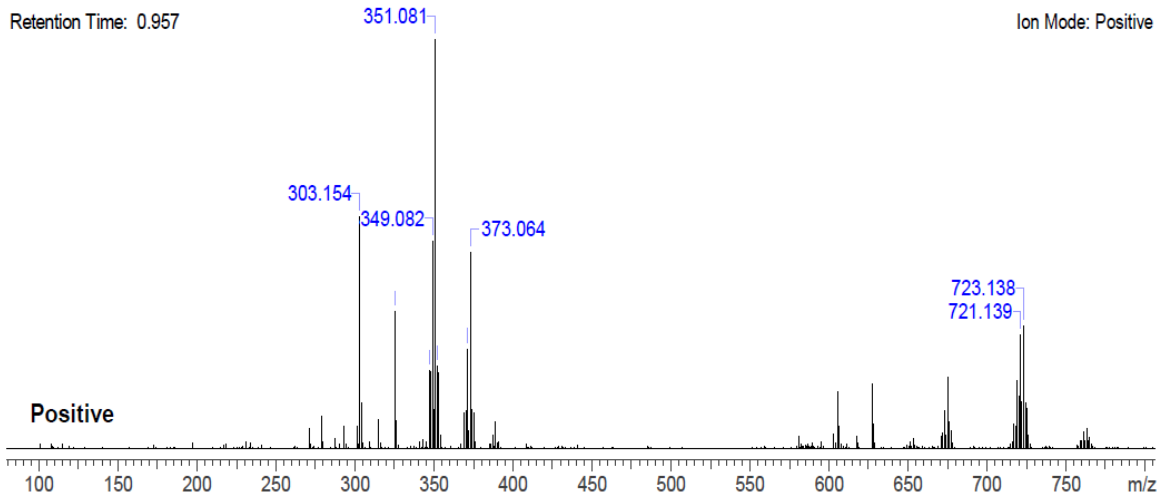

Figure S12. MS.

$[Mes_2PSK(thf)_2]_2$ (**2a)**

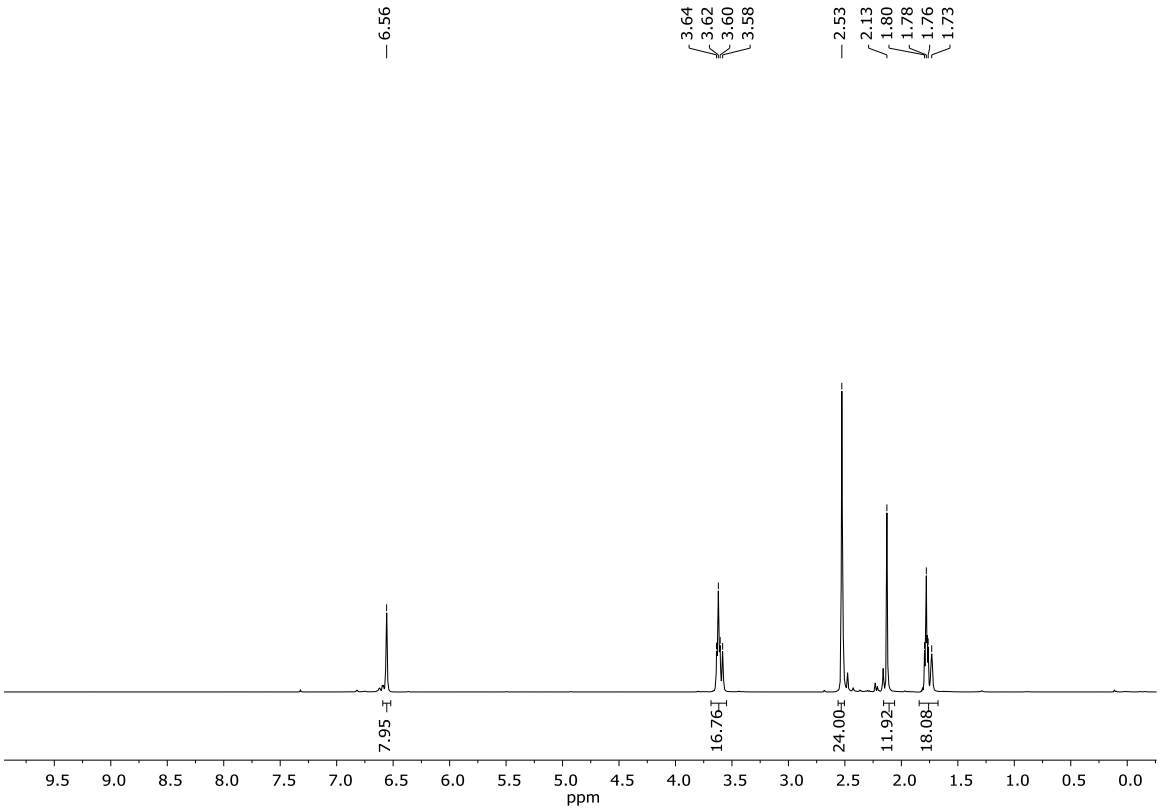

Figure S13. ^{1}H NMR spectrum (400.13 MHz, THF-d_8, 253 K).

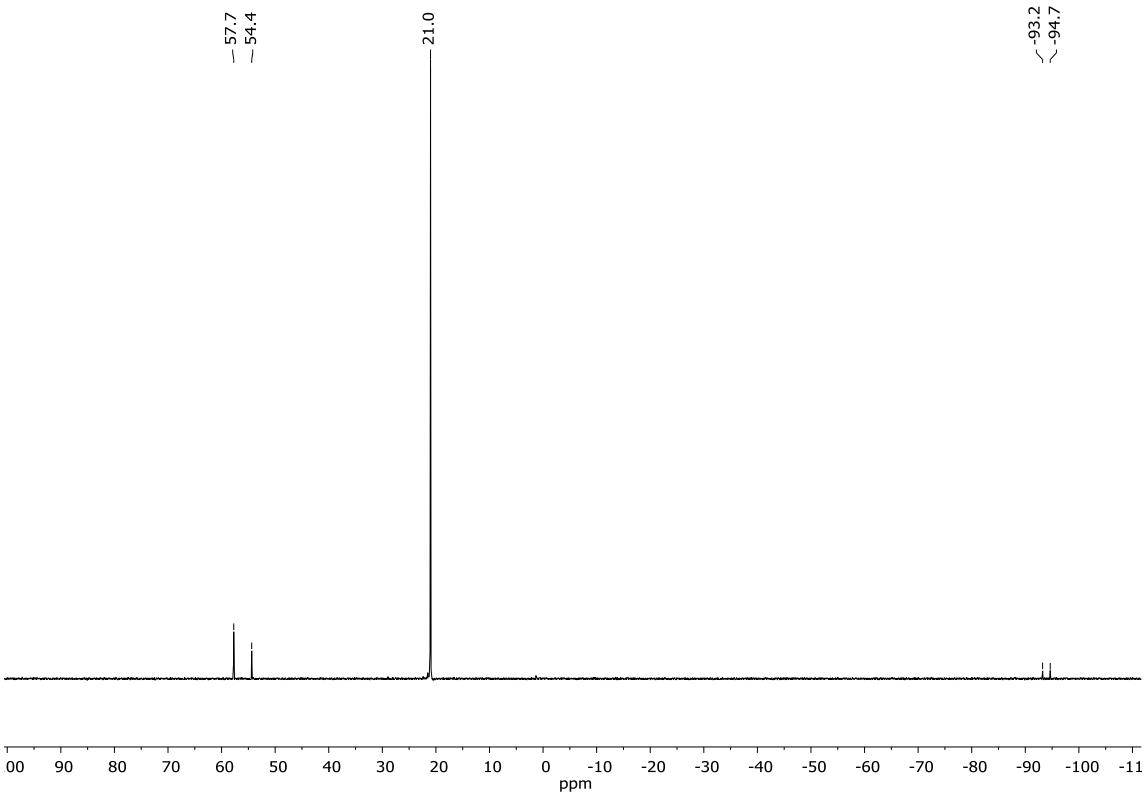

Figure S14. ^{31}P-NMR-spectrum (161.98 MHz, THF-d_8, 253 K) (57.7 and 54.4 ppm are probably $Mes_2P(=S)OK$ and Mes_2PS_2K, -94.0 pm = Mes_2PH).

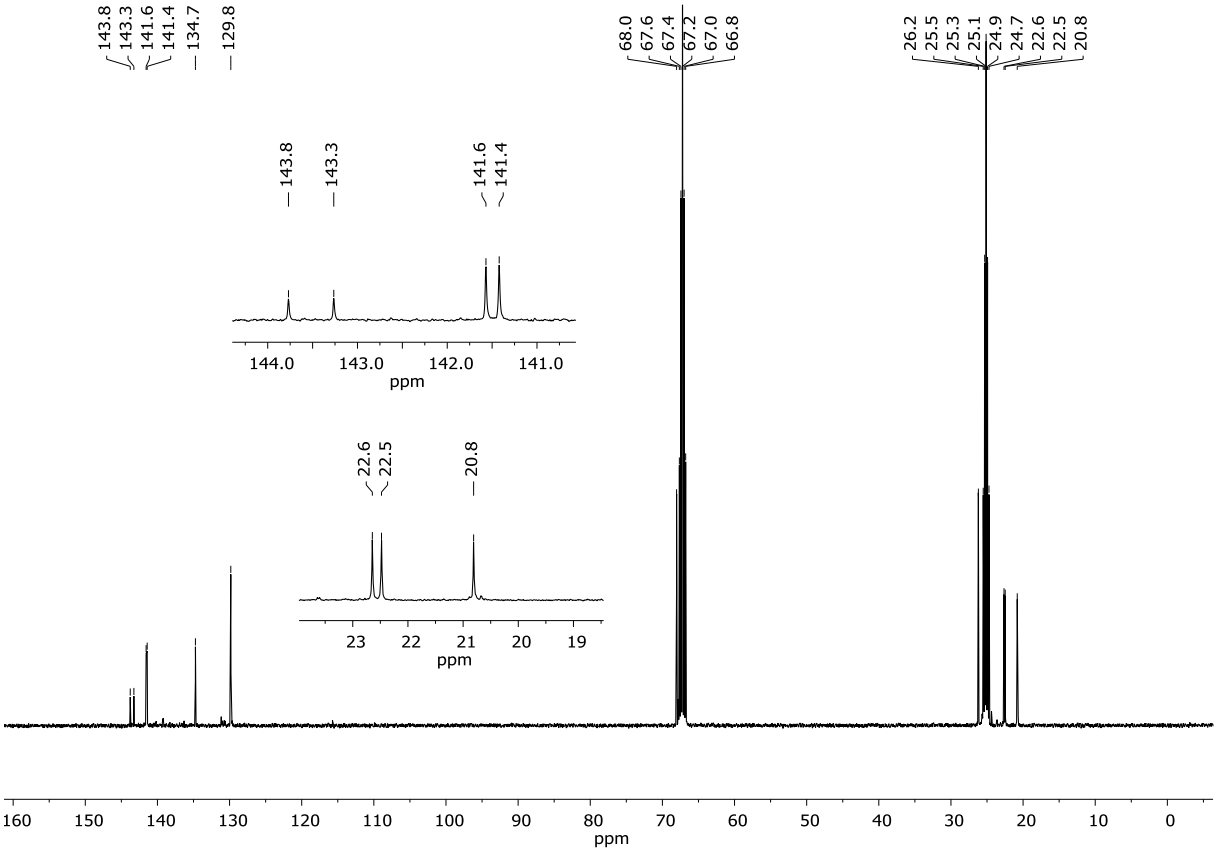

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, THF-d_8, 253 K).

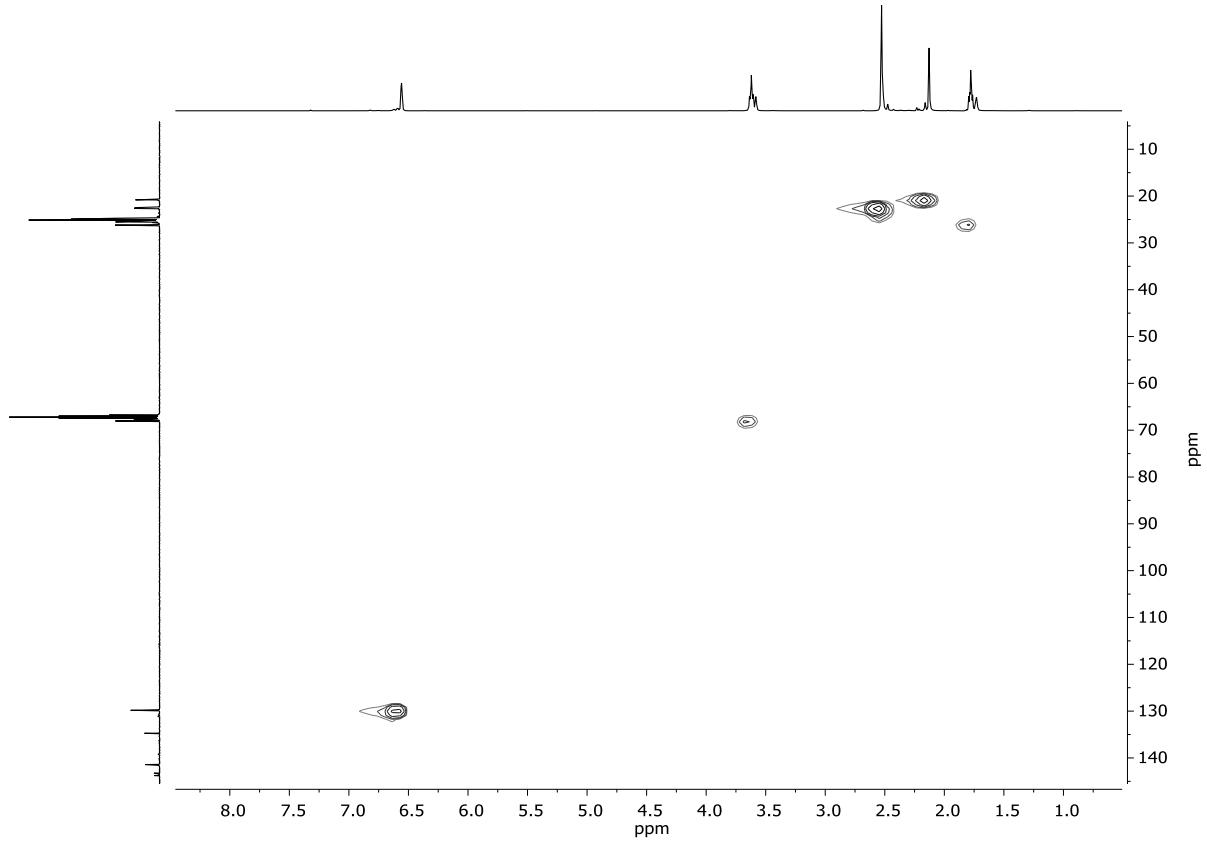

Figure S16. HSQC NMR spectrum (400.13/100.61 MHz, THF-d_8, 253 K).

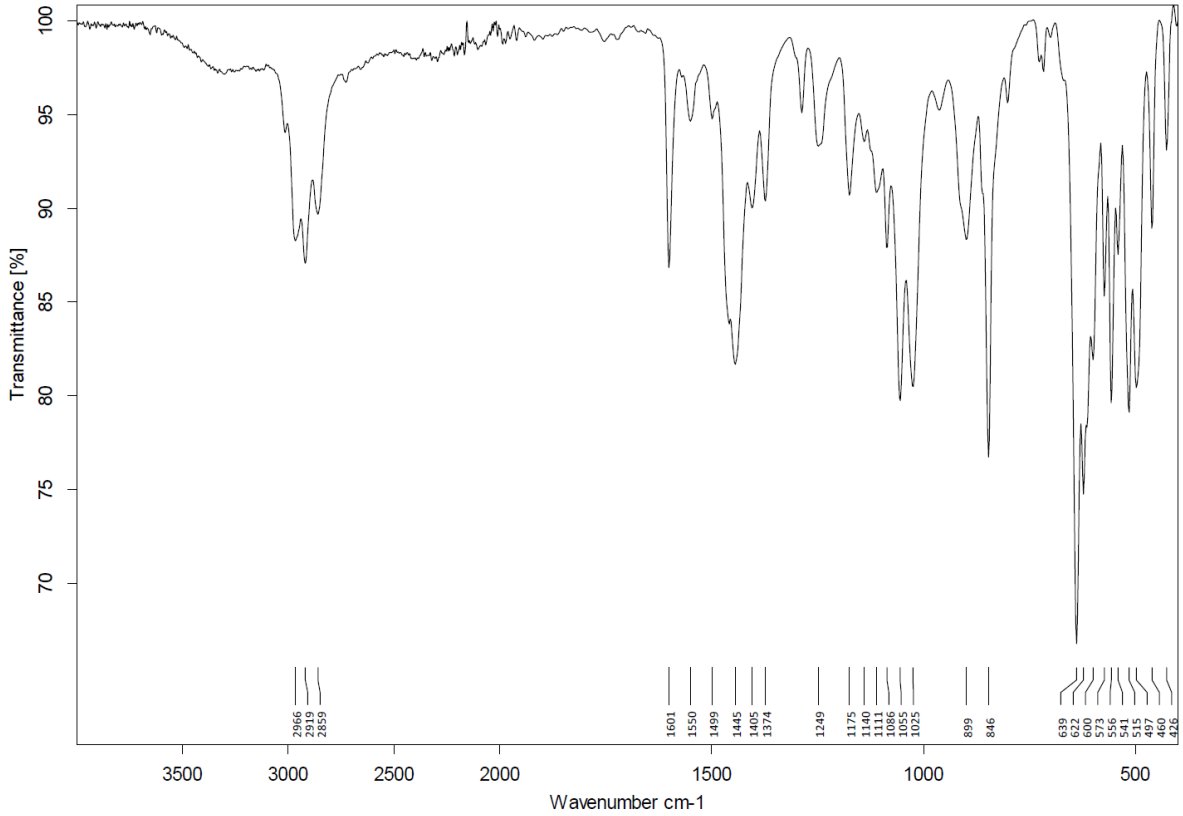

Figure S17. IR (ATR).

$[Mes_2PSeK(thf)_2]_2$ (**2b**)

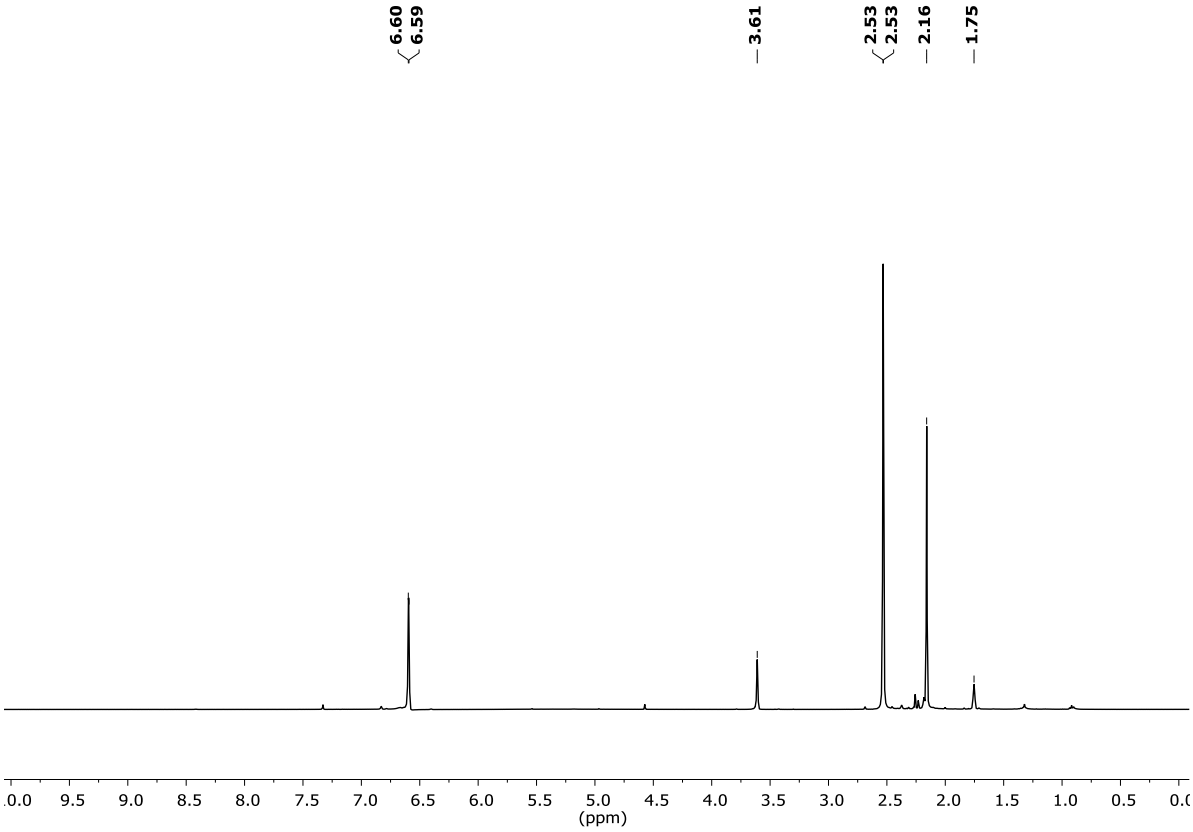

Figure S18. ^{1}H NMR spectrum (400.13 MHz, THF-d_8, 253 K).

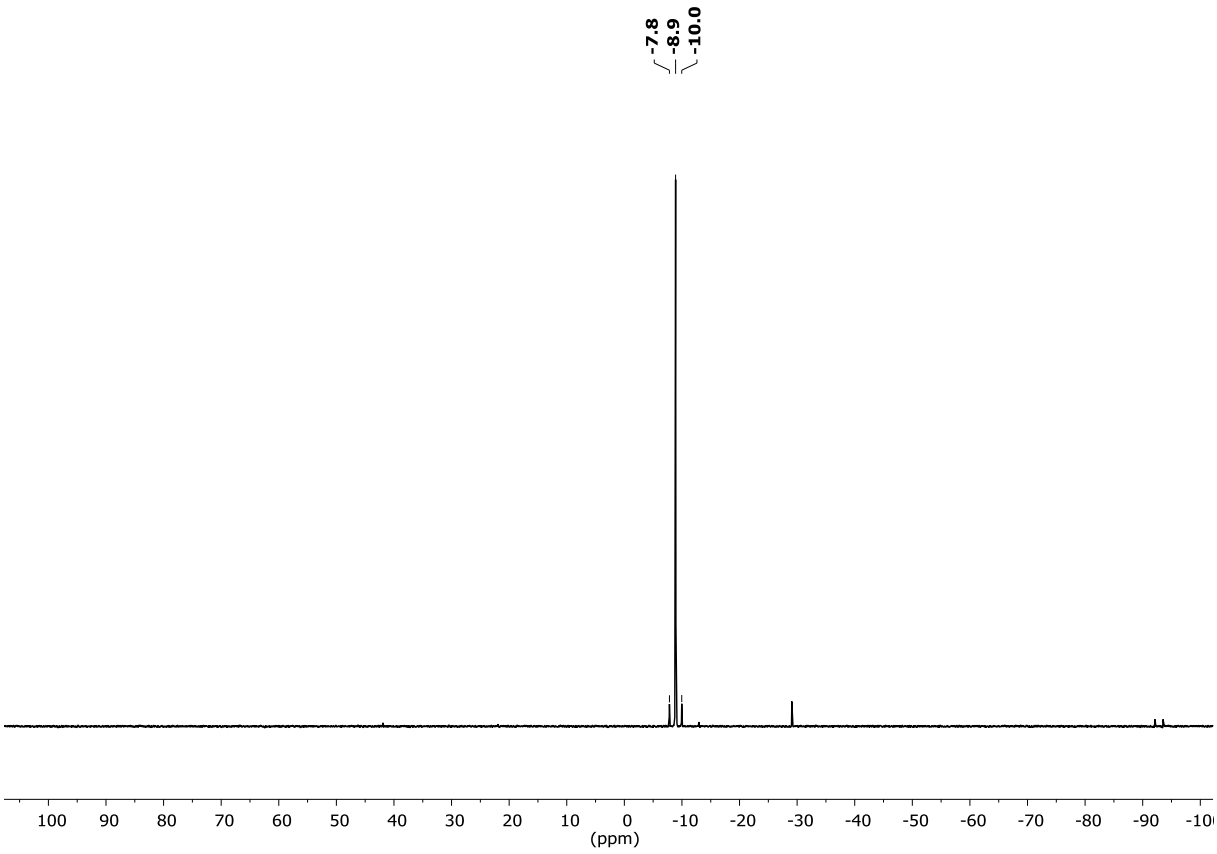

Figure S19. ^{31}P NMR spectrum (161.98 MHz, THF-d_8, 253 K).

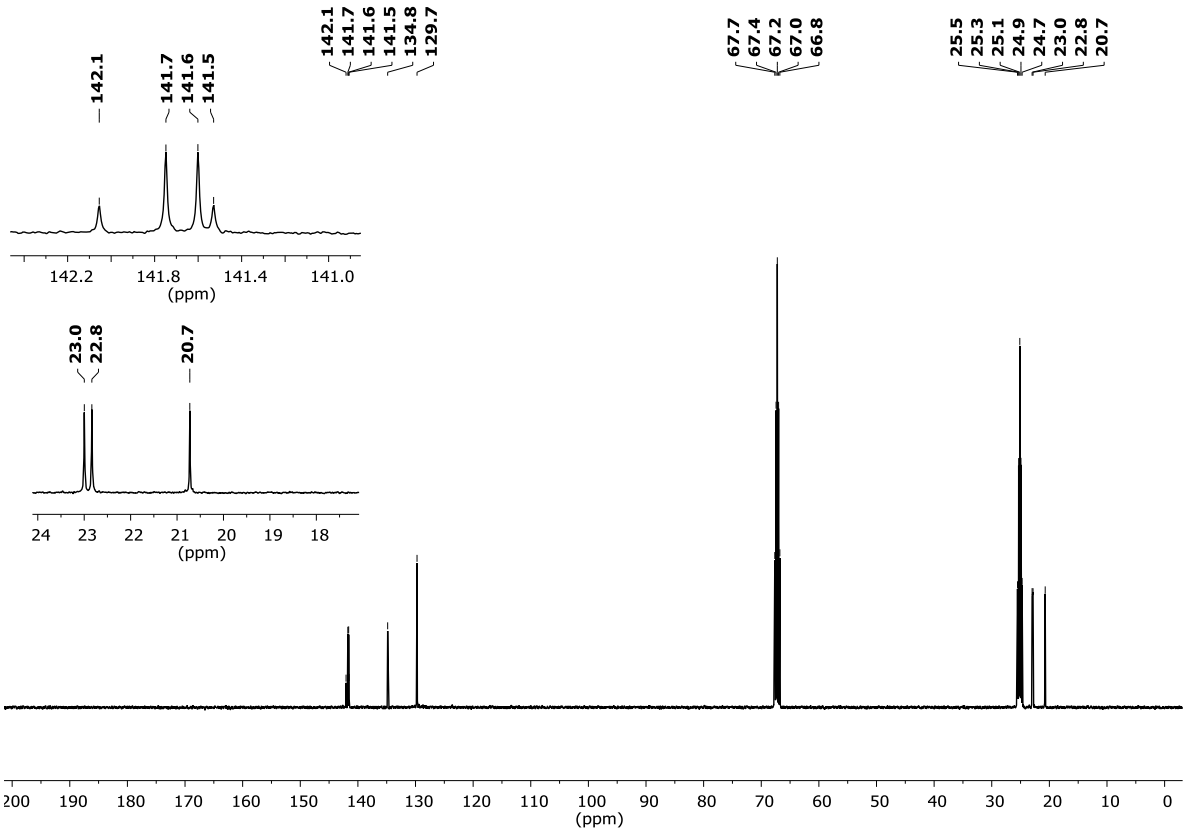

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, THF-d_8, 253 K).

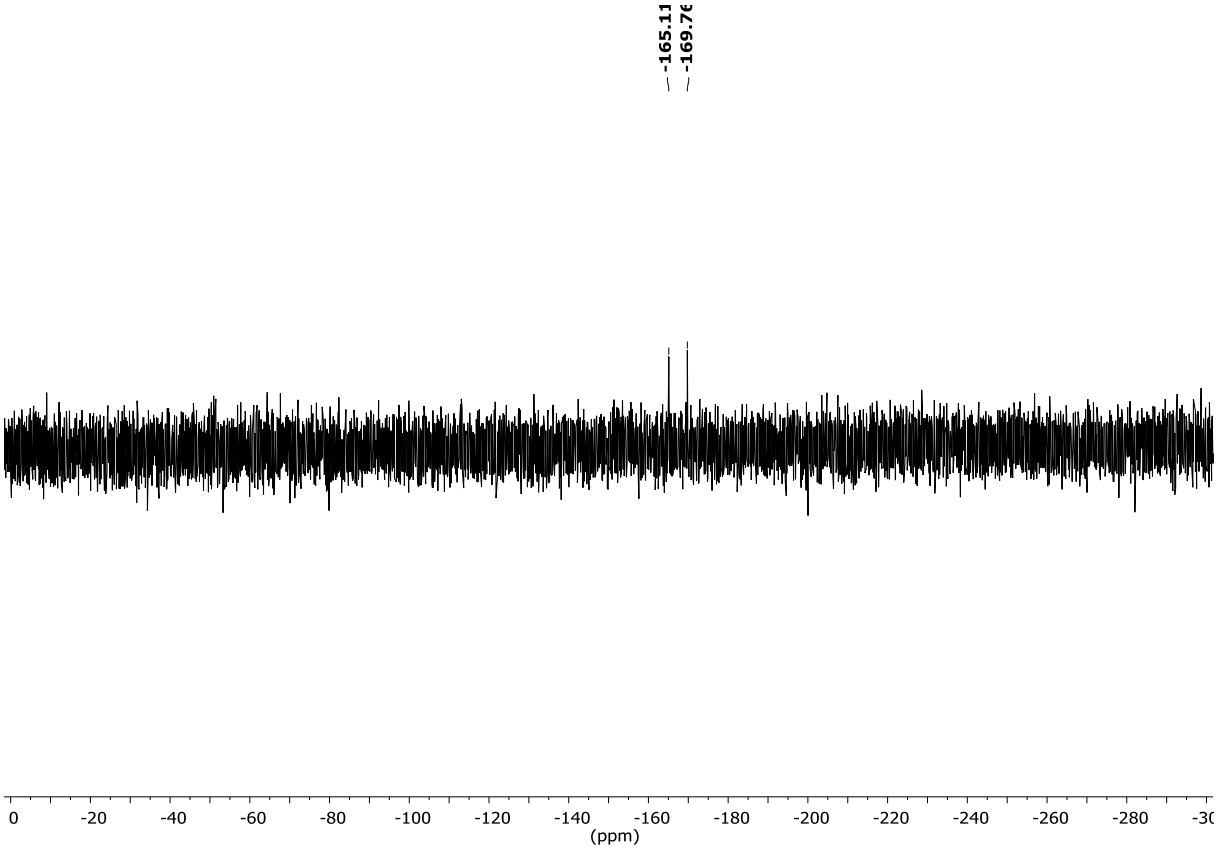

Figure S21. ^{77}Se NMR spectrum (76.31 MHz, THF-d_8, 253 K).

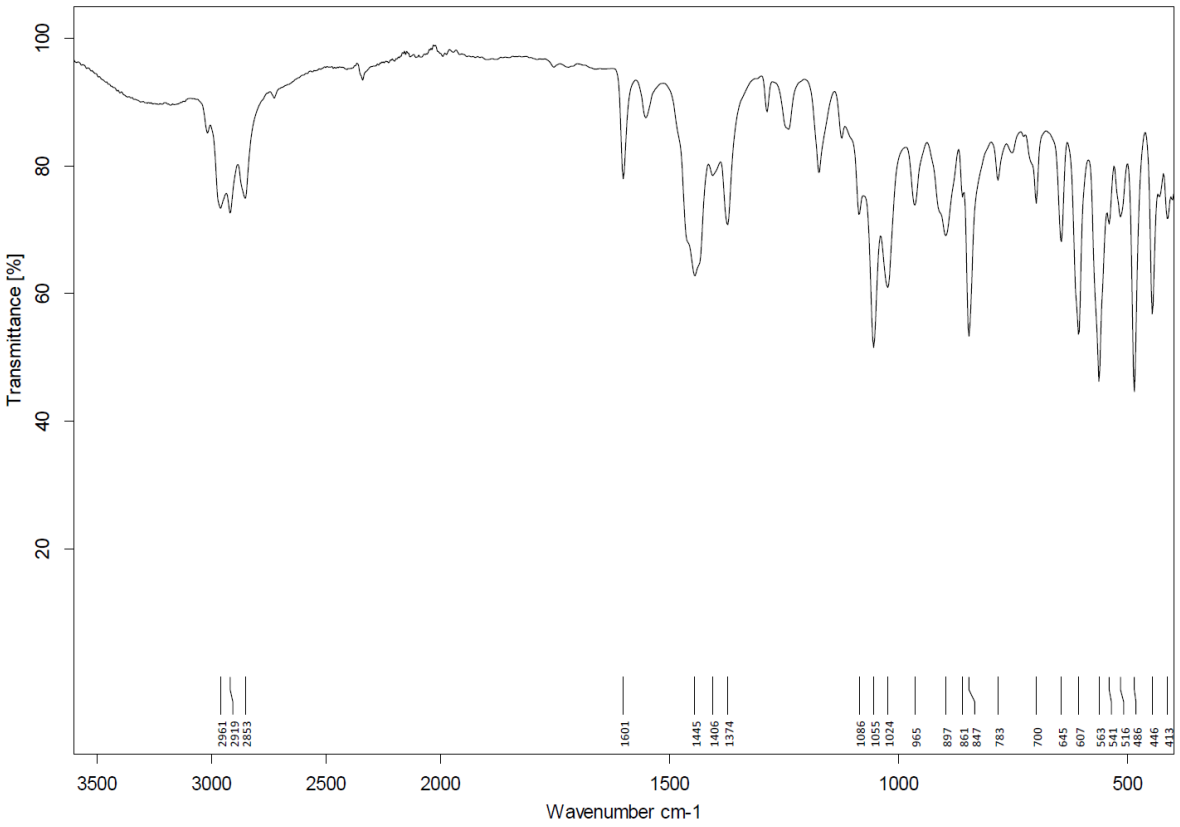

Figure S22. IR (ATR).

$[Mes_2PSK(thp)_2]_2$ (**3a**)

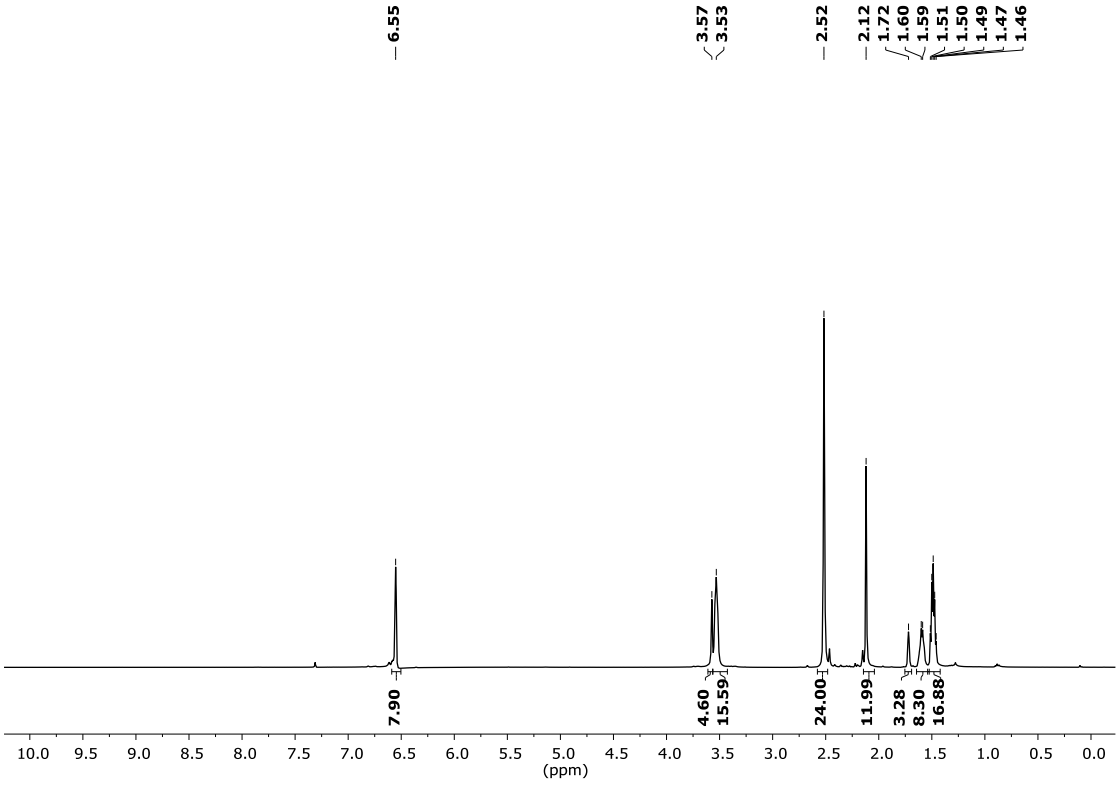

Figure S23. ^{1}H NMR spectrum (400.13 MHz, THF-d_8, 253 K).

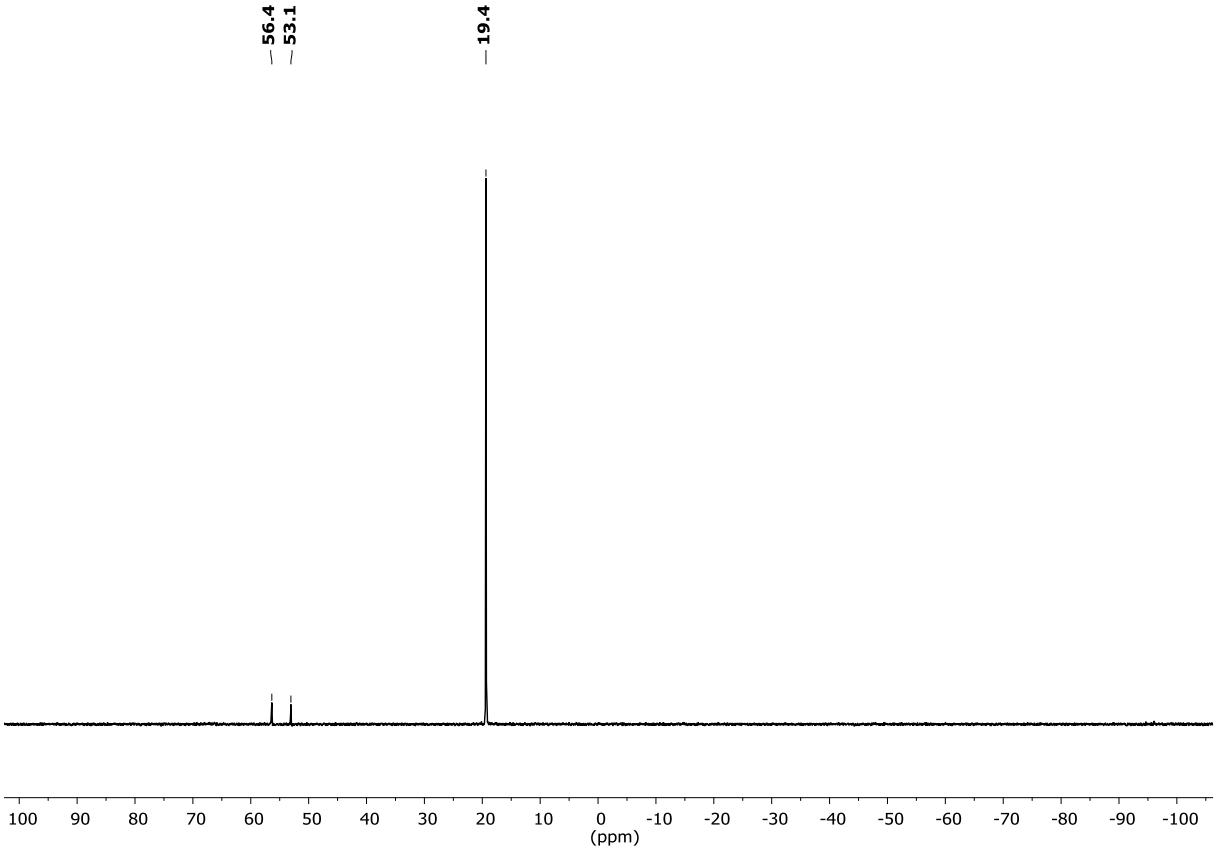

Figure S24. ^{31}P NMR spectrum (161.98 MHz, THF-d_8, 253 K) (56.4 ppm and 53.1 ppm probably $Mes_2P(=S)OK$ and Mes_2PS_2K).

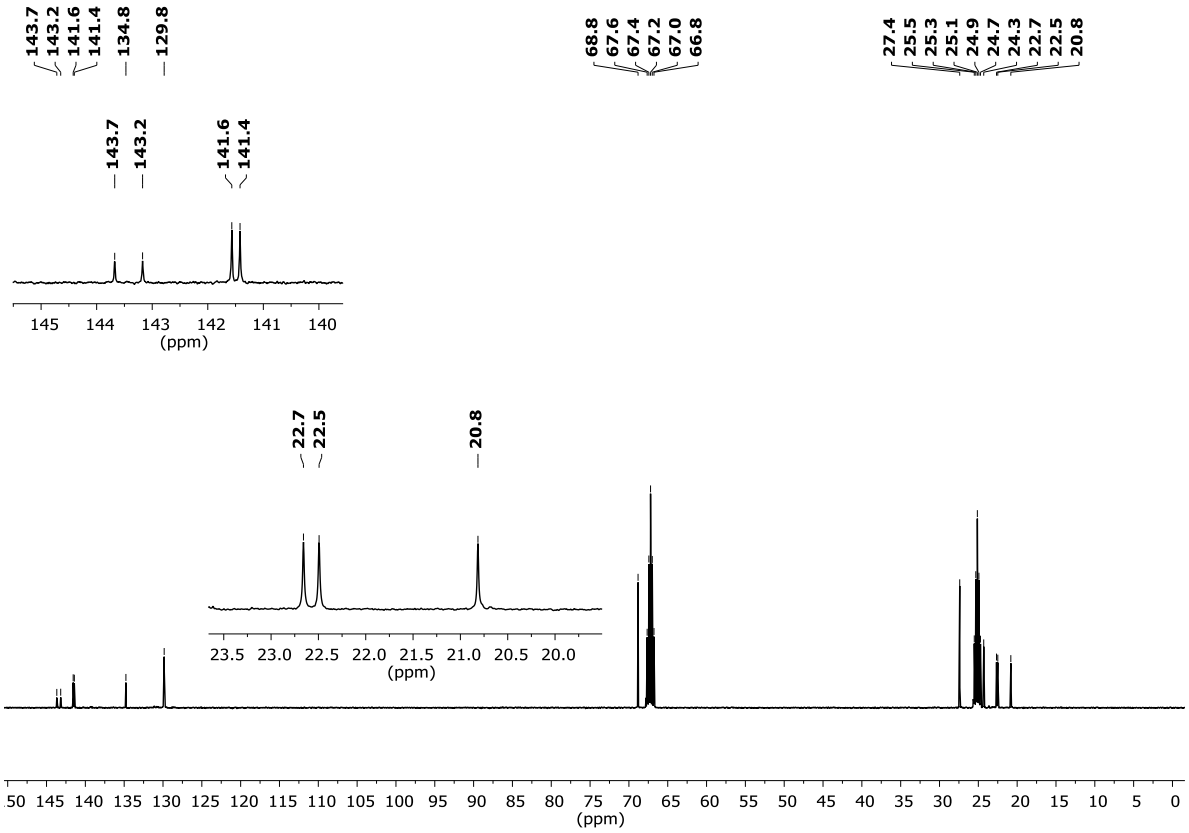

Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, THF-d_8, 253 K).

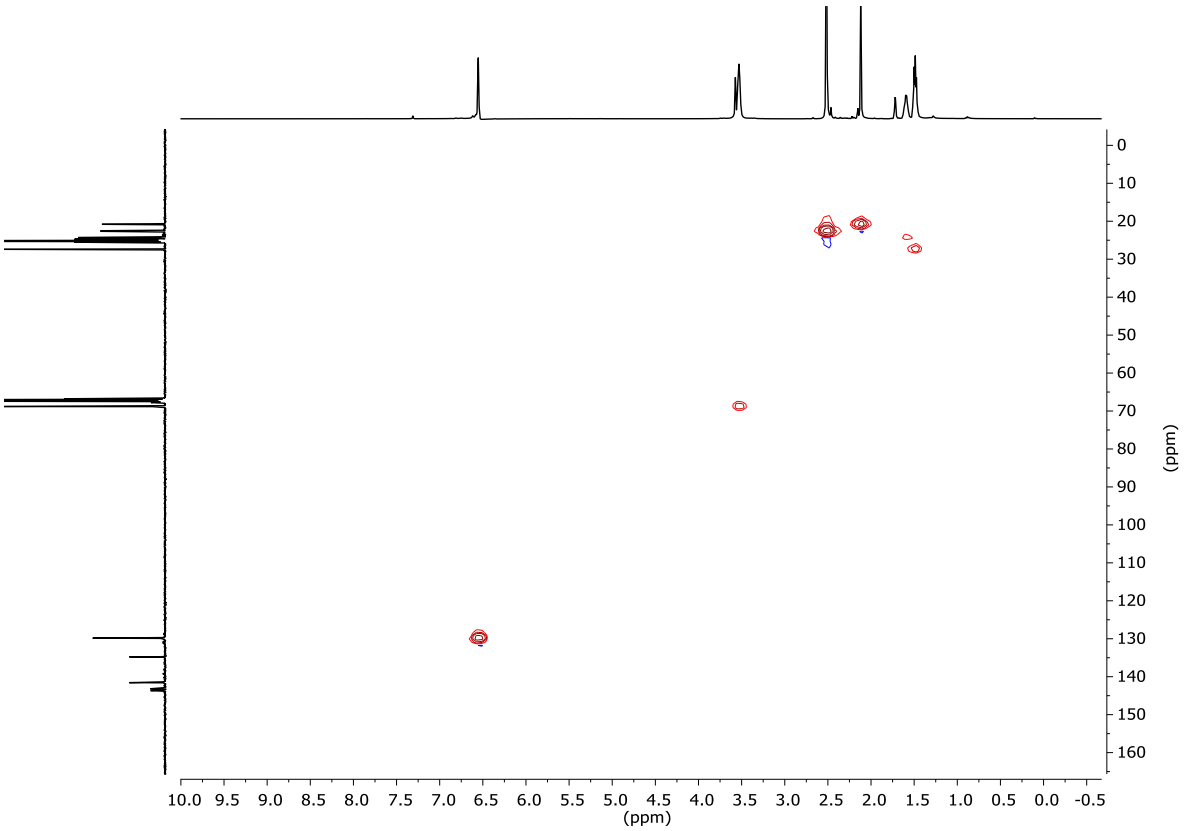

Figure S26. HSQC NMR spectrum (400.13/100.61 MHz, THF-d_8, 253 K).

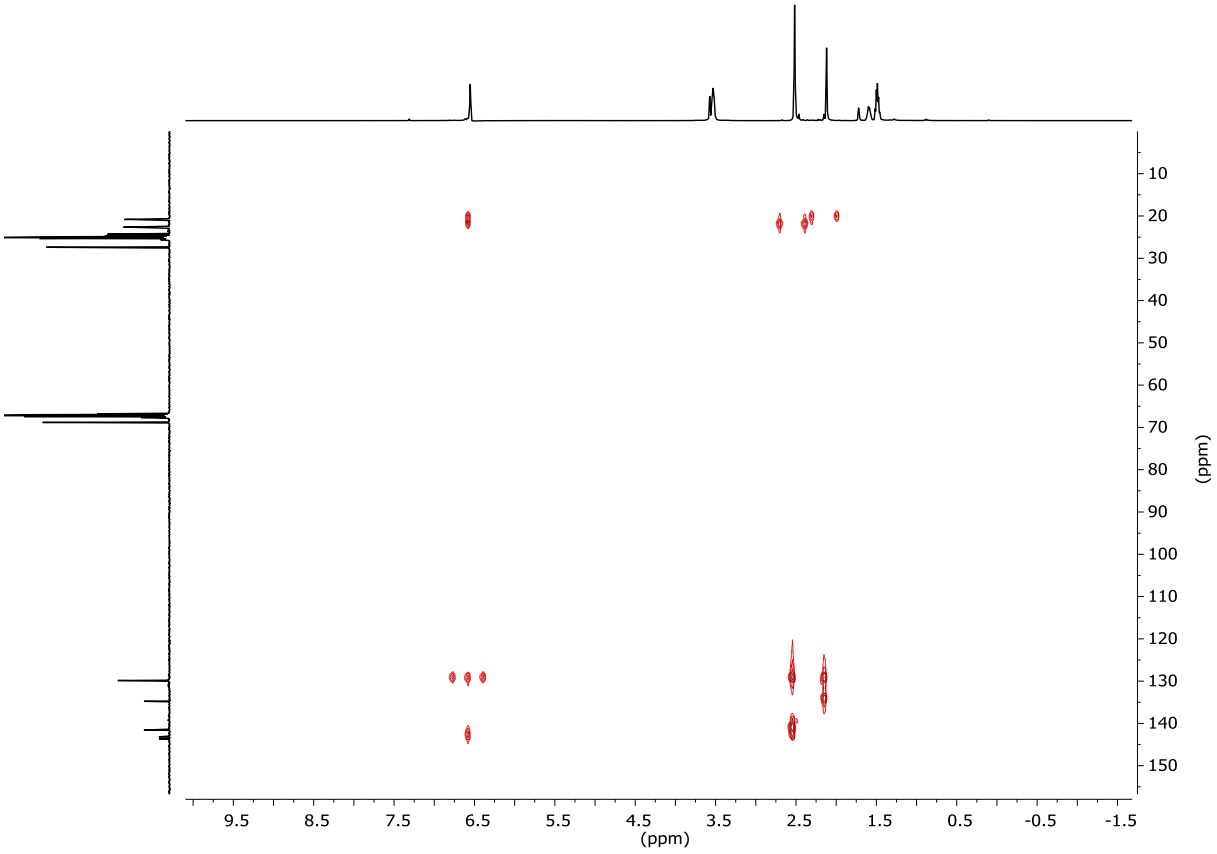

Figure S27. HMBC NMR spectrum (400.13/100.61 MHz, THF-d_8, 253 K).

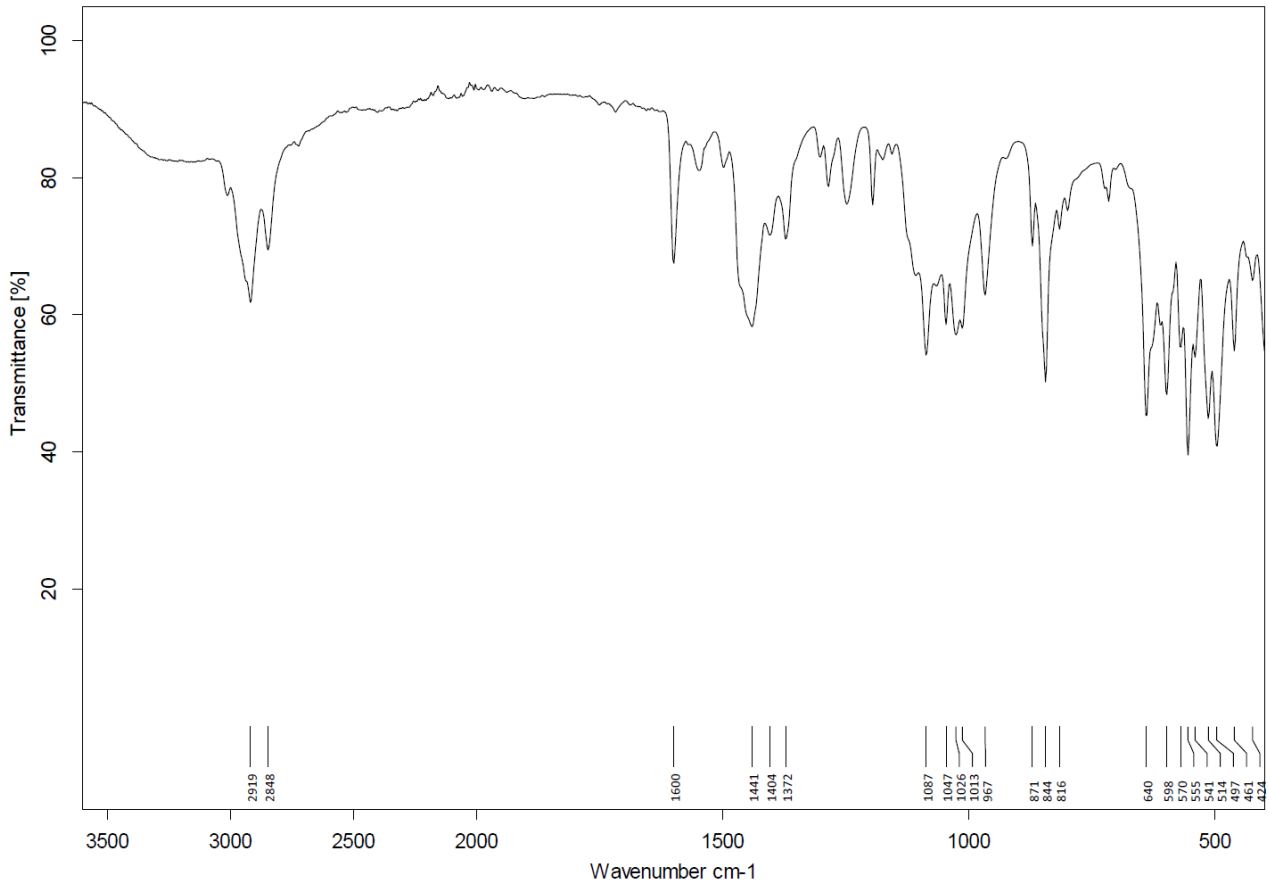

Figure S28. IR (ATR).

$[Mes_2PSeK(thp)_2]_2$ (**3b**)

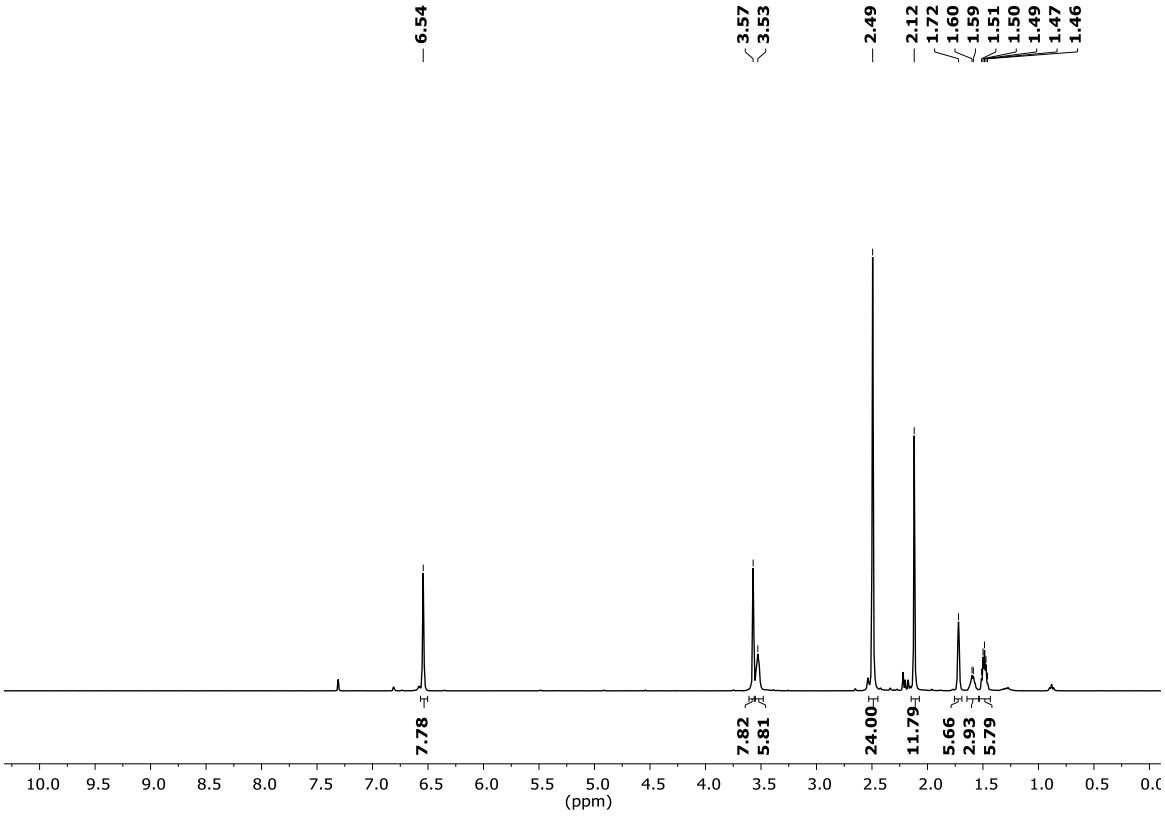

Figure S29. ^{1}H NMR spectrum (400.13 MHz, THF-d_8, 253 K).

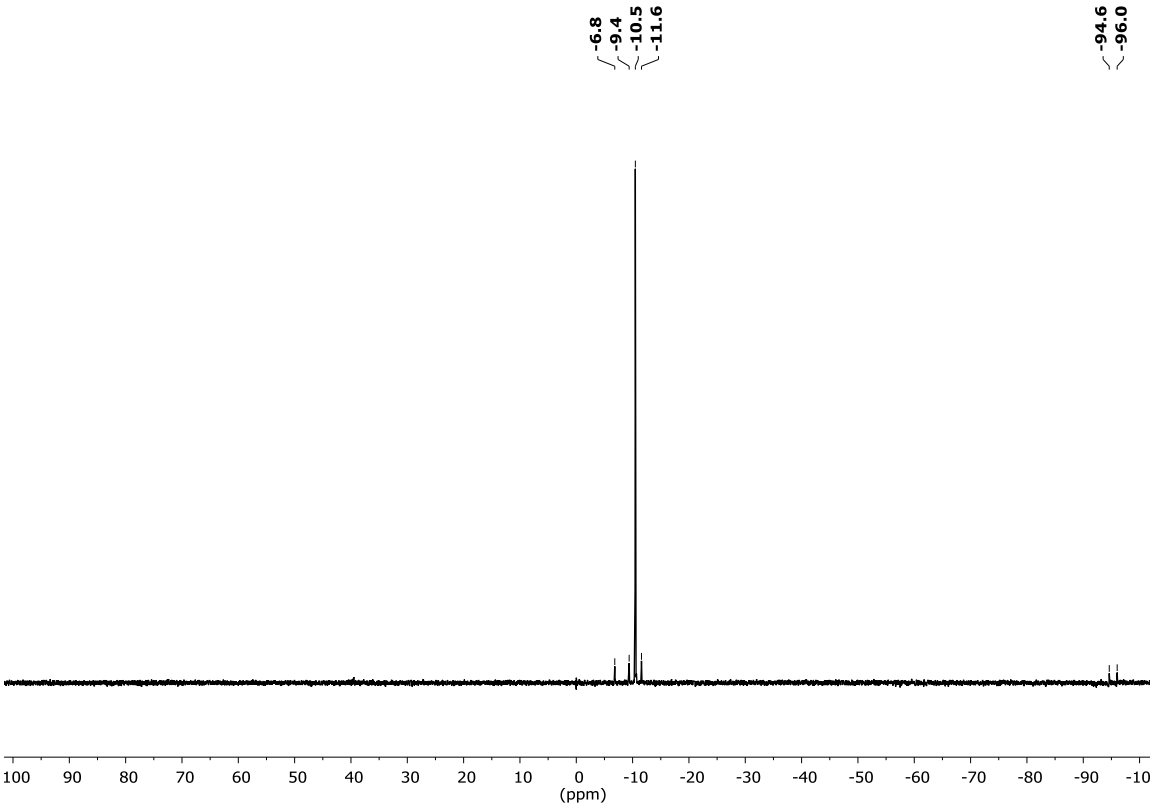

Figure S30. ^{31}P NMR spectrum (161.98 MHz, THF-d_8, 253 K) (-6.8 ppm = Mes_2PSe_2K, -95.3 ppm = Mes_2PH).

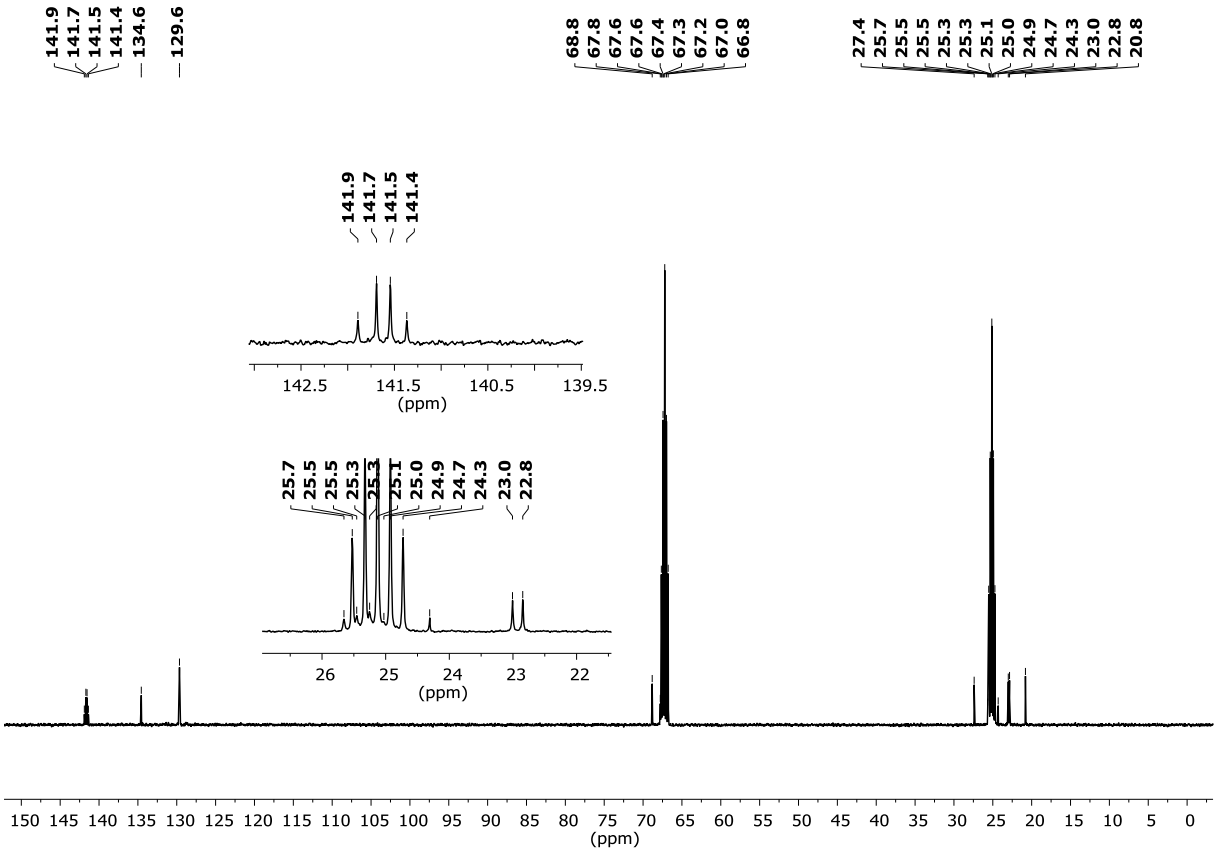

Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, THF-d_8, 253 K).

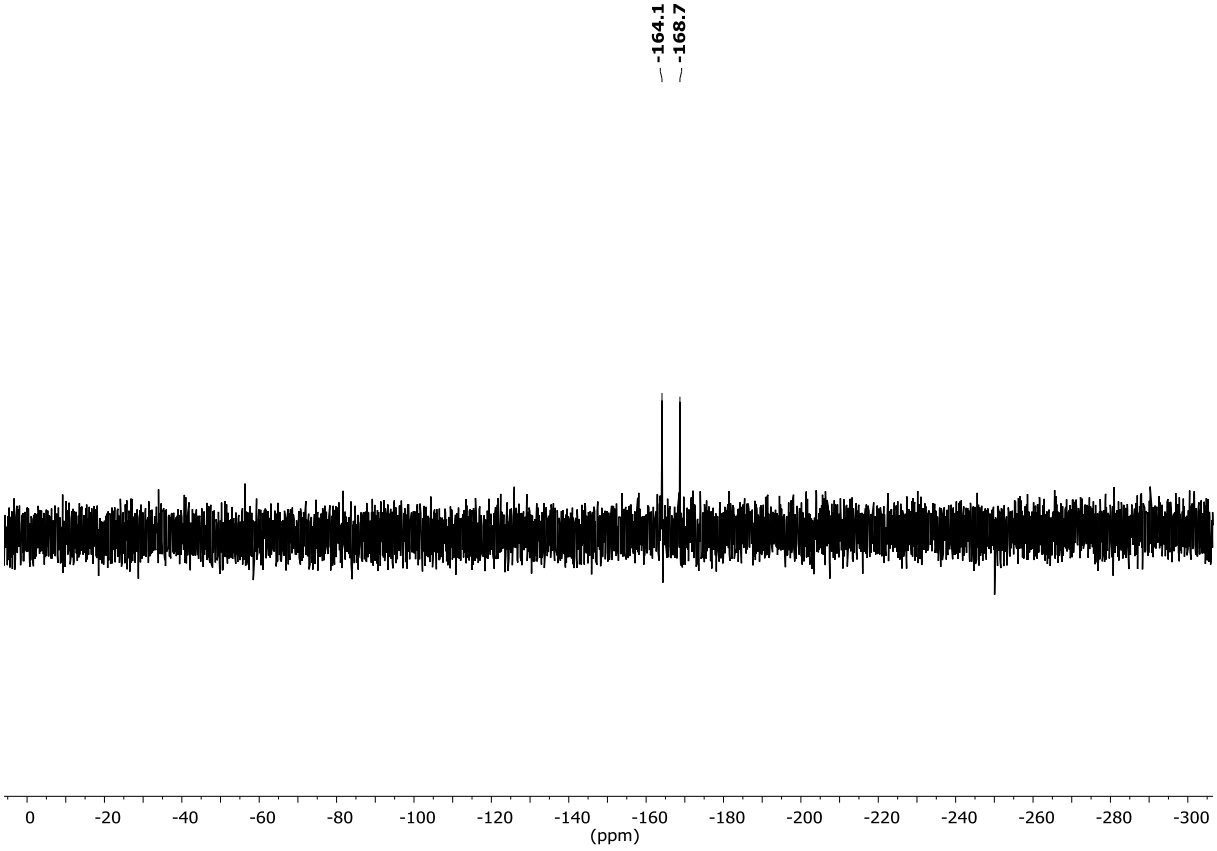

Figure S32. ^{77}Se NMR spectrum (76.31 MHz, THF-d_8, 253 K).

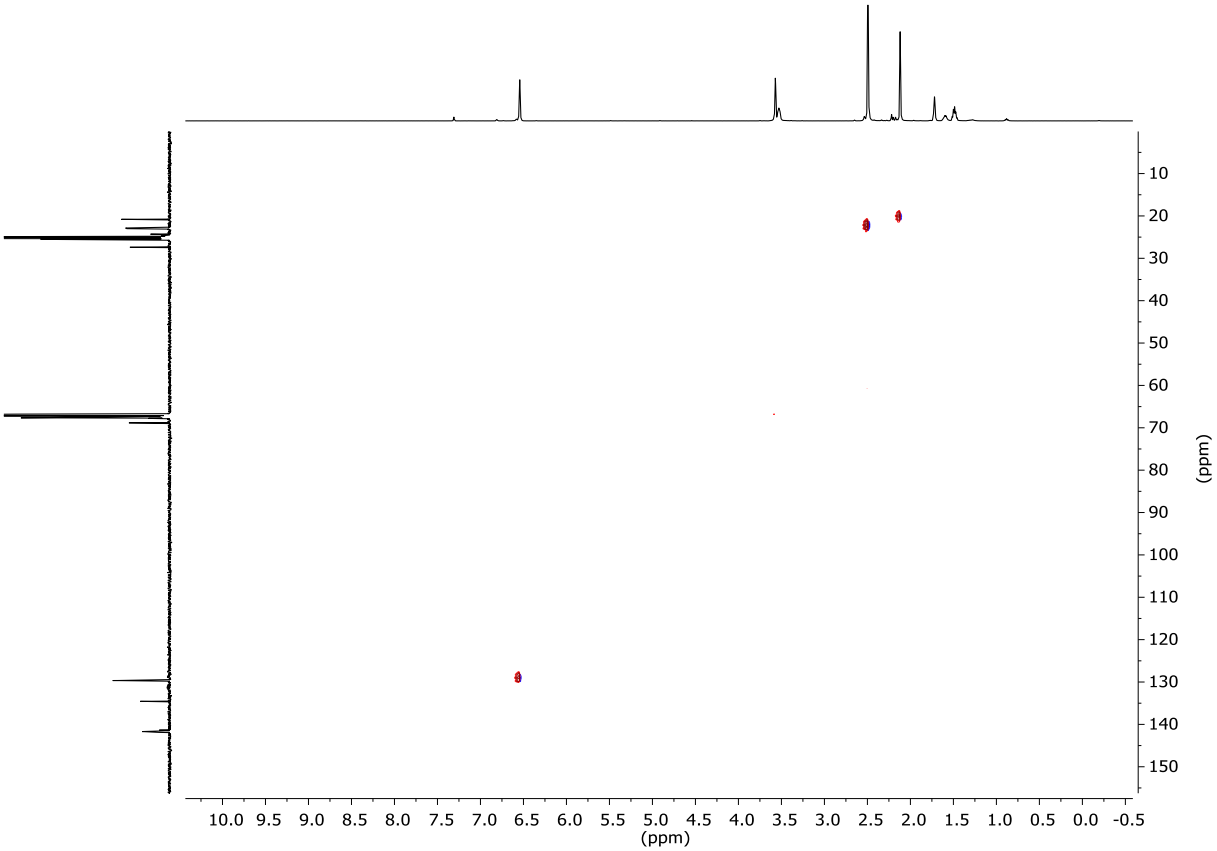

Figure S33. HSQC NMR spectrum (400.13/100.61 MHz, THF-d_8, 253 K).

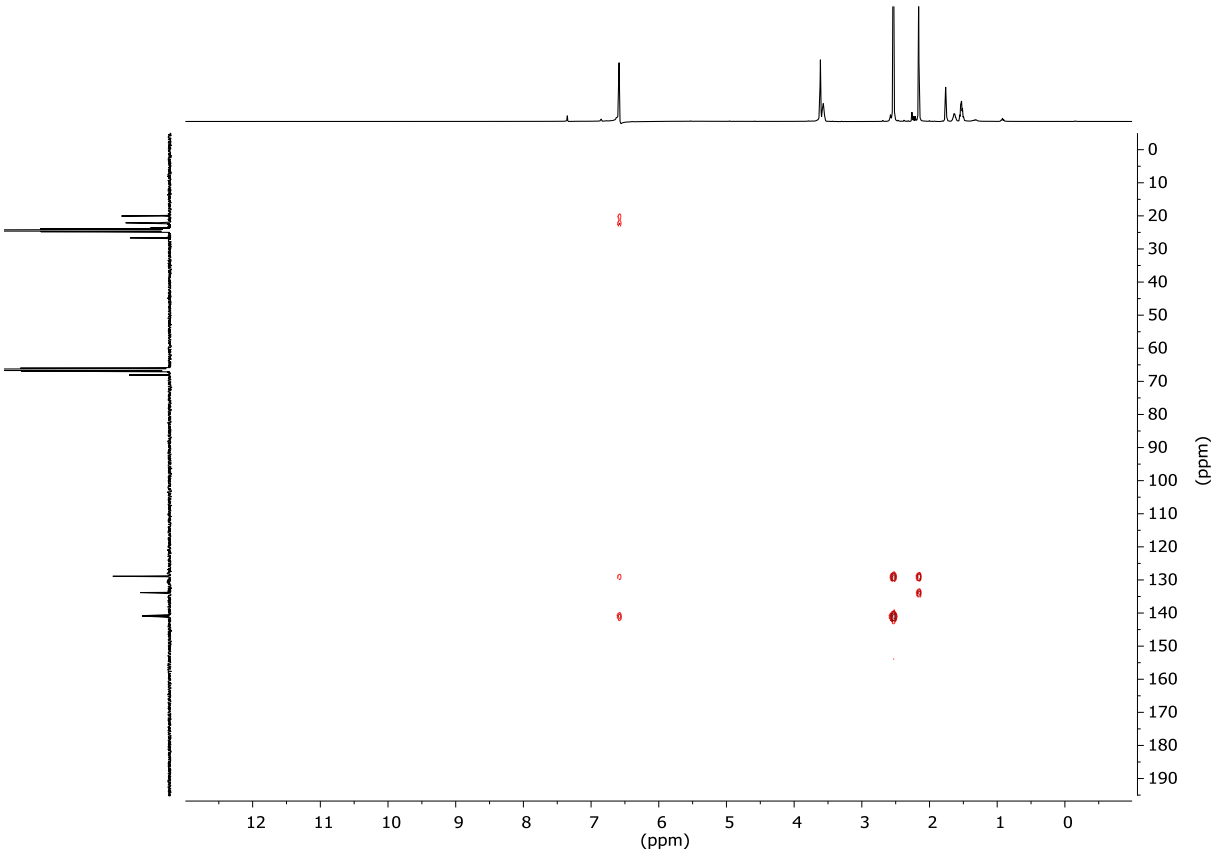

Figure S34. HMBC NMR spectrum (400.13/100.61 MHz, THF-d_8, 253 K).

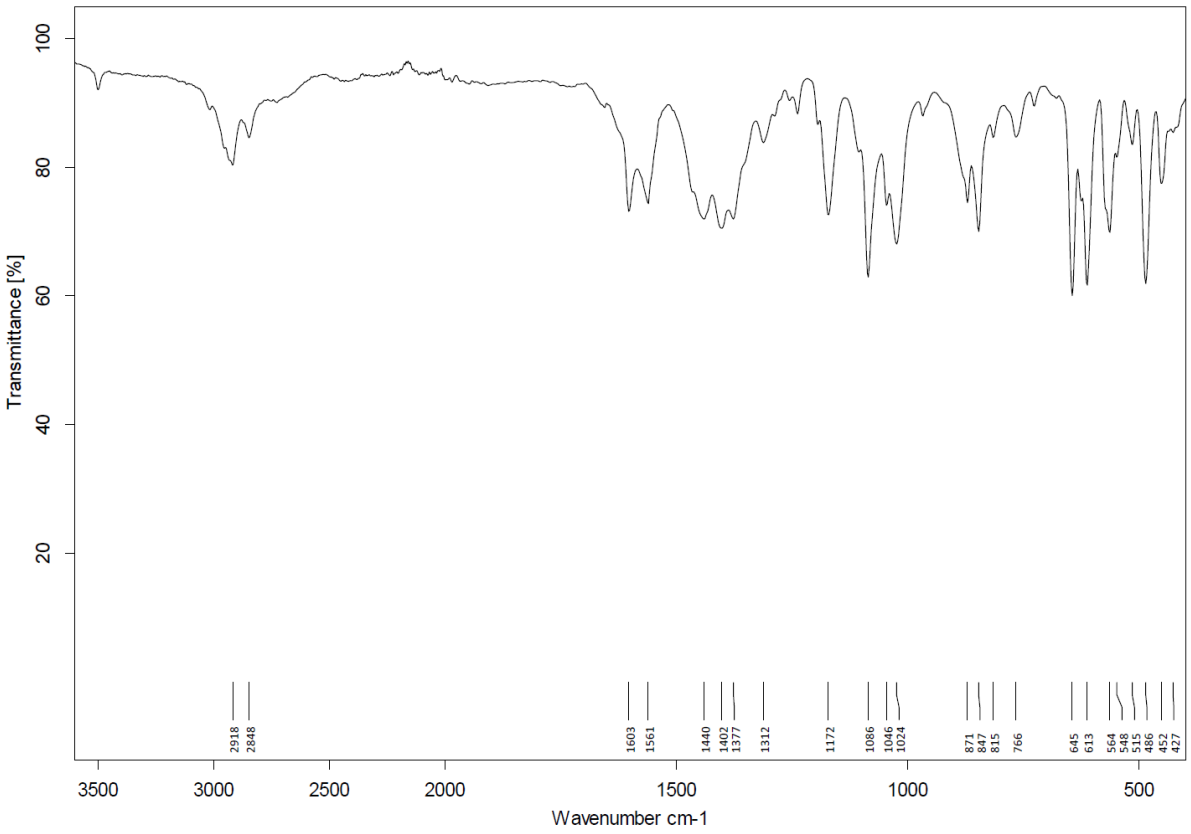

Figure S35. IR (ATR).

[$Mes_2PSLi(thf)_2$] (**4**)

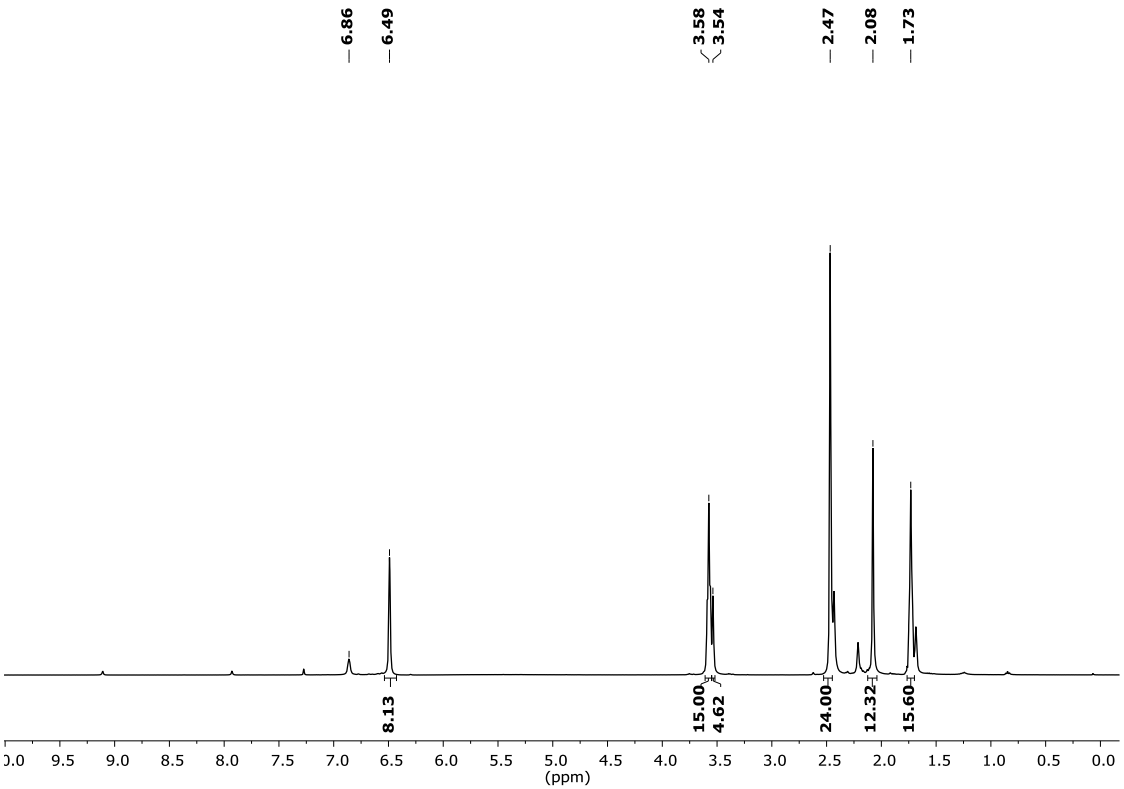

Figure S36. ^{1}H NMR spectrum (400.13 MHz, THF-d_8, 253 K).

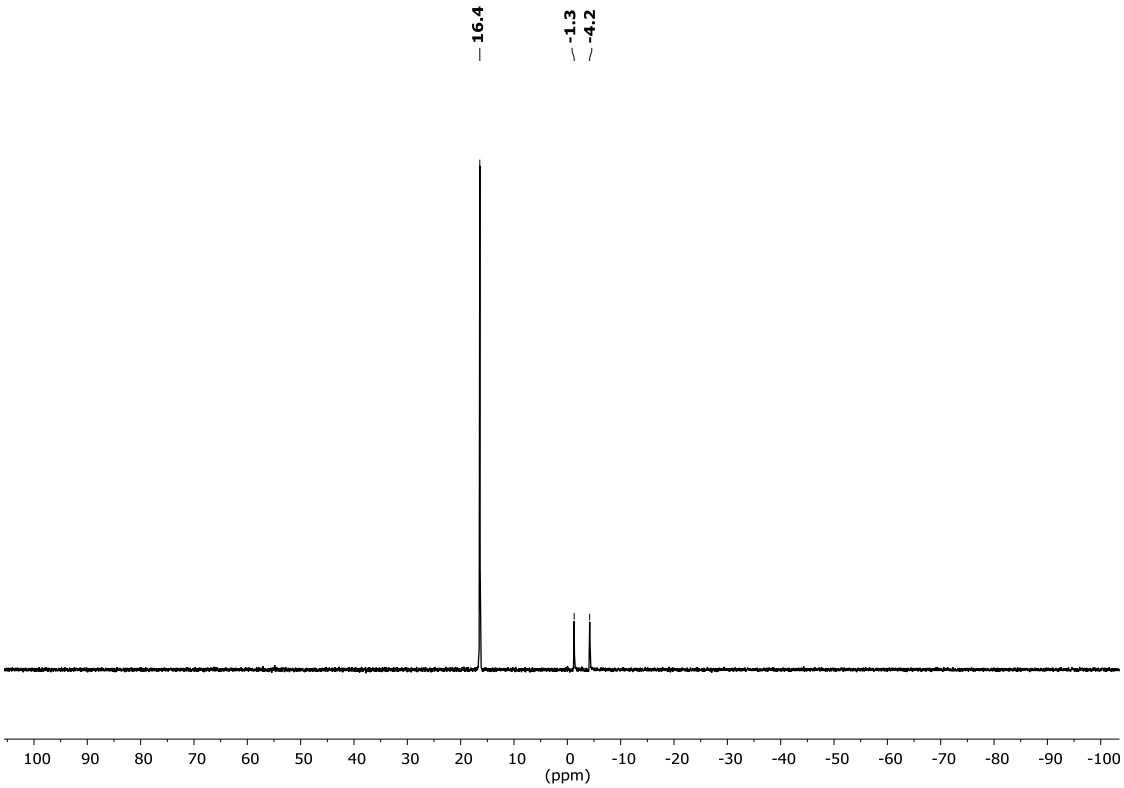

Figure S37. ^{31}P NMR spectrum (161.98 MHz, THF-d_8, 253 K) (doublet – $Mes_2P(=S)H$ by hydrolysis).

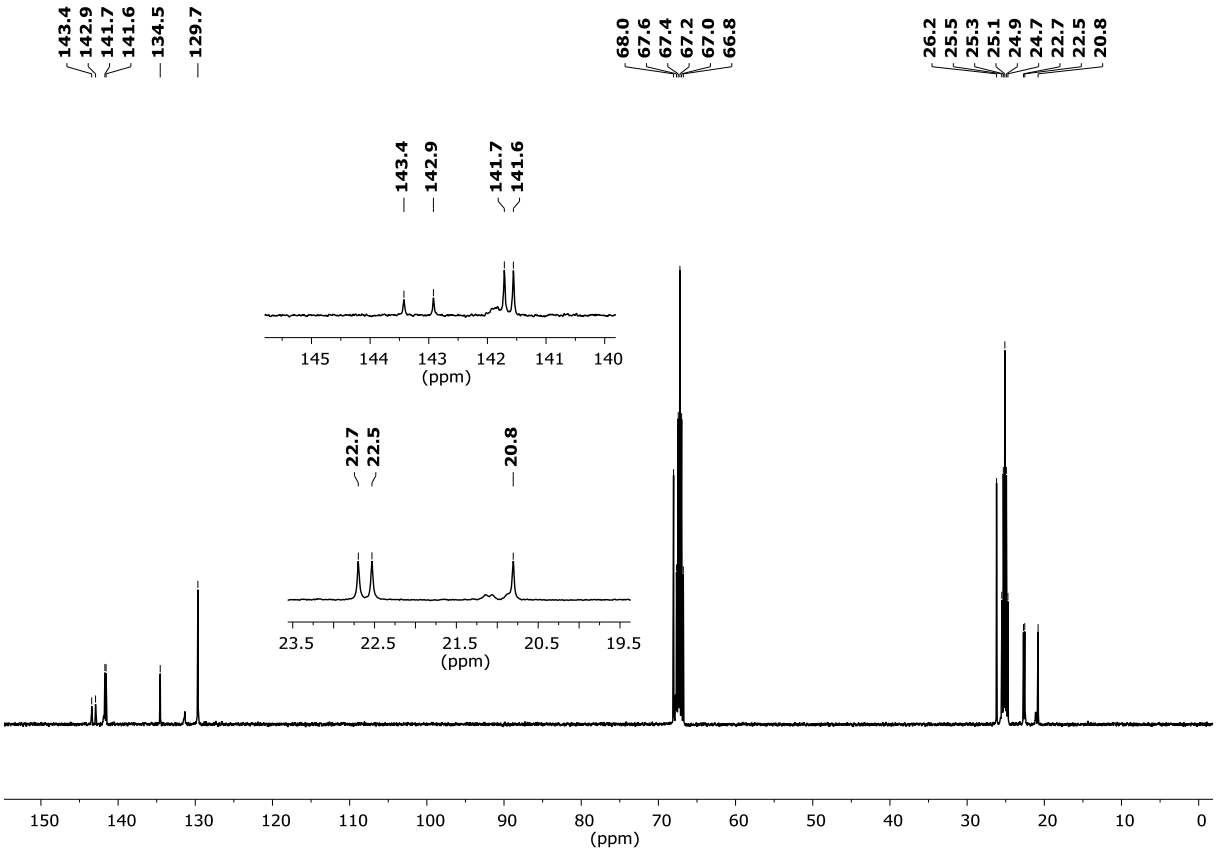

Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, THF-d_8, 253 K).

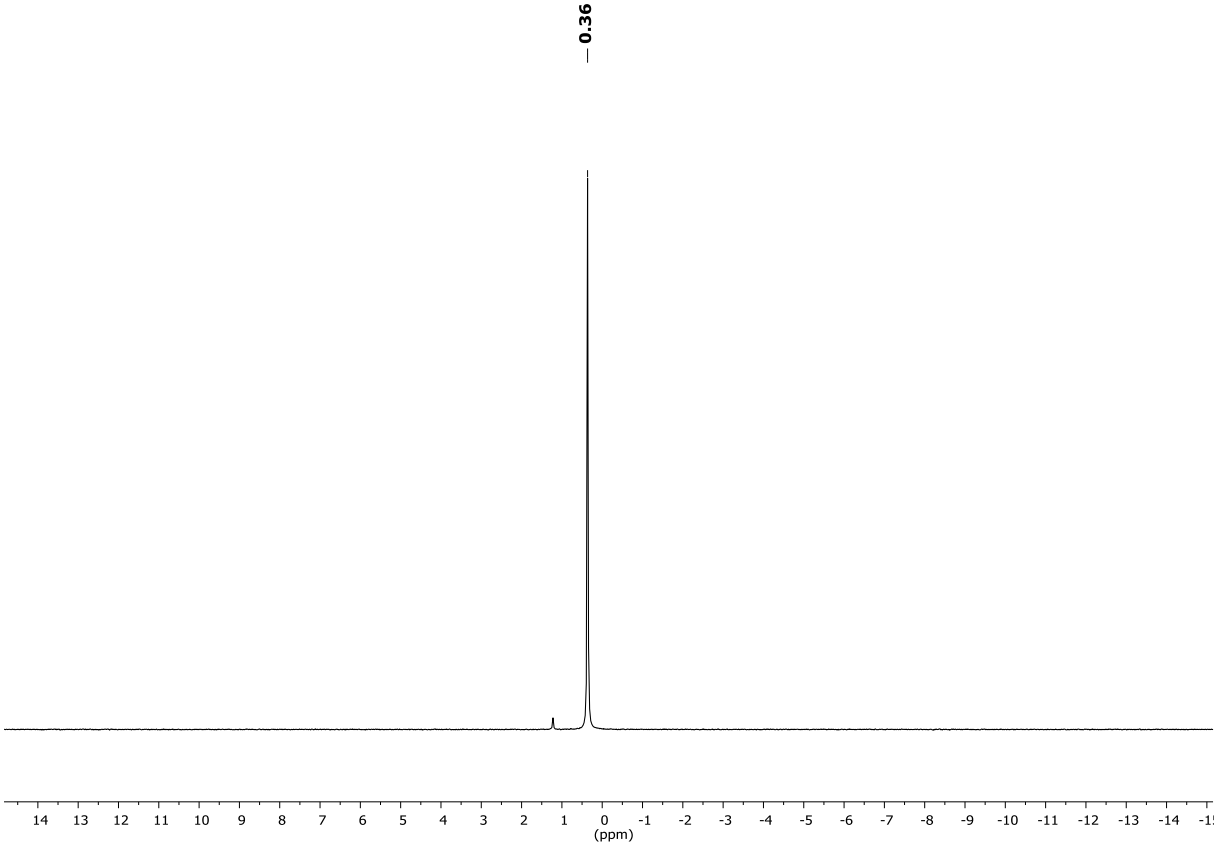

Figure S39. ^{7}Li NMR spectrum (155.51 MHz, THF-d_8, 253 K).

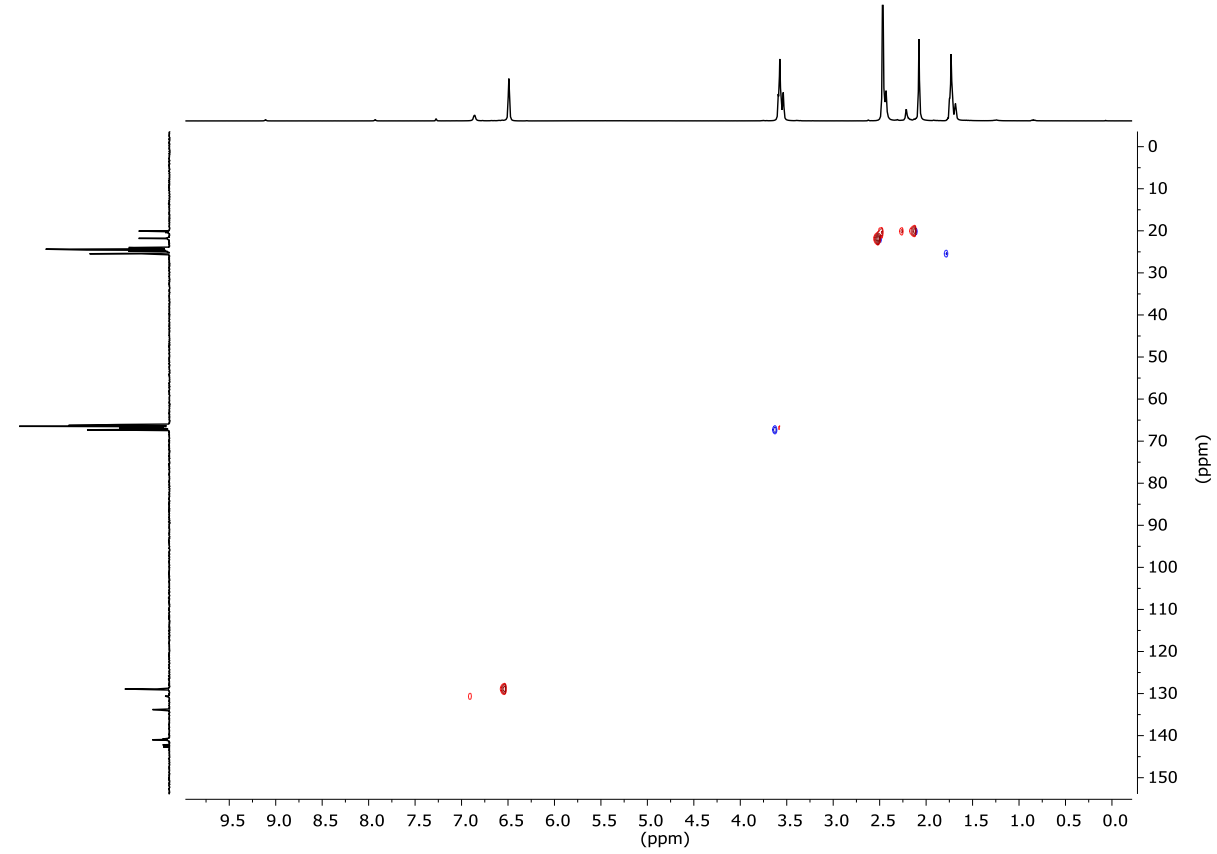

Figure S40. HSQC NMR spectrum (400.13/100.61 MHz, THF-d_8, 253 K).

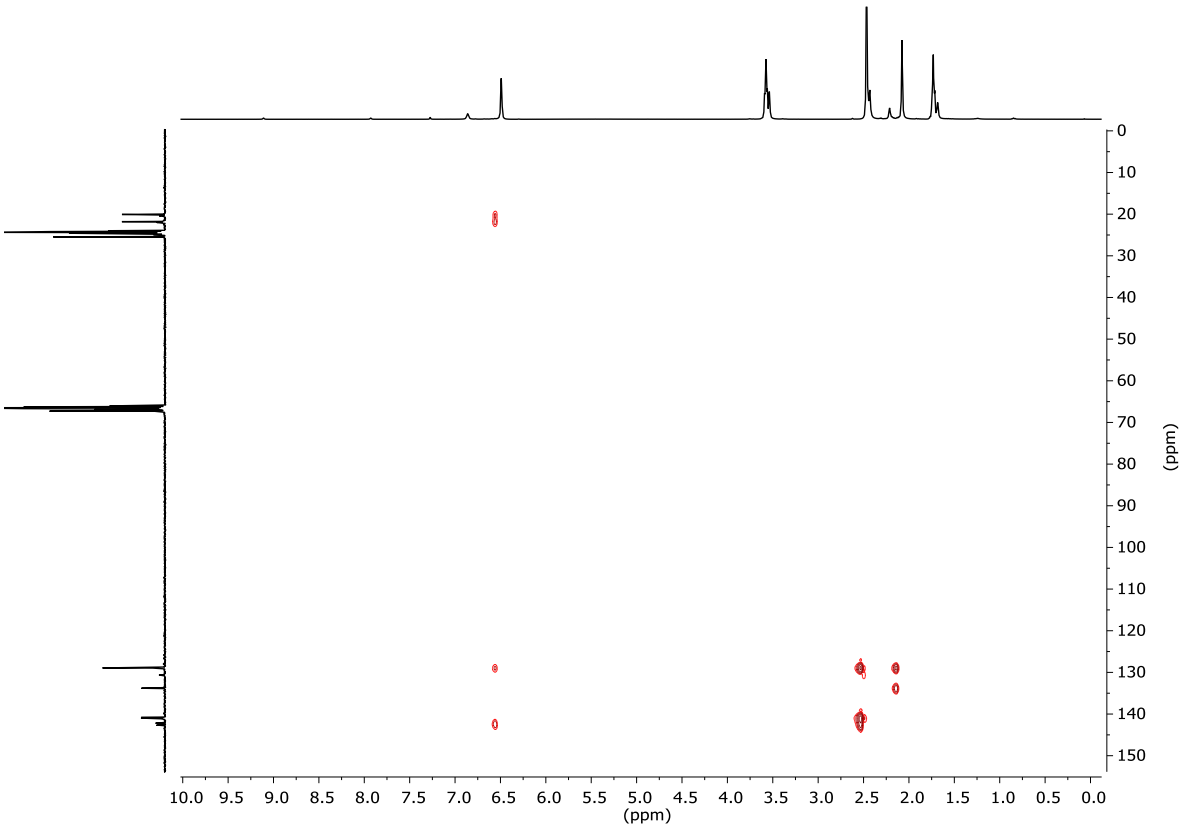

Figure S41. HMBC NMR spectrum (400.13/100.61 MHz, THF-d_8, 253 K).

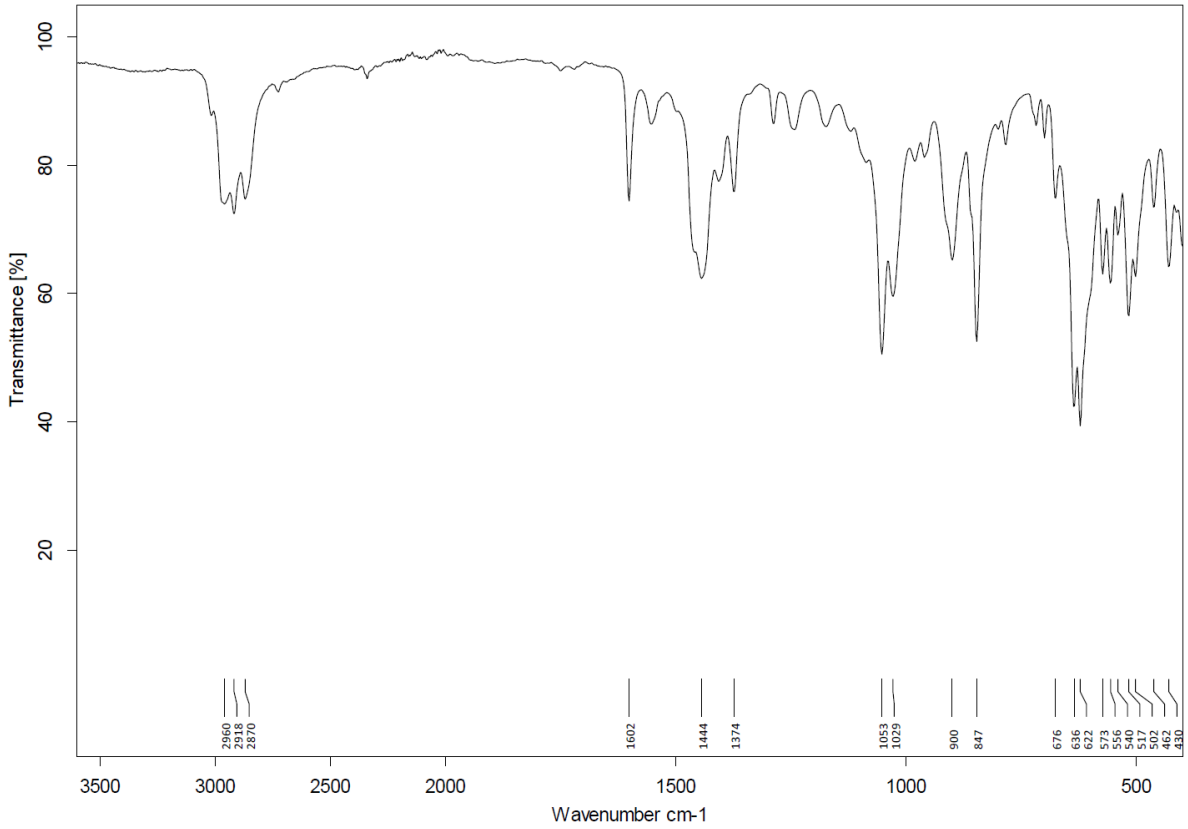

Figure S42. IR (ATR).

$[Mes_2PSNa(thf)_2]_2$ (**5**)

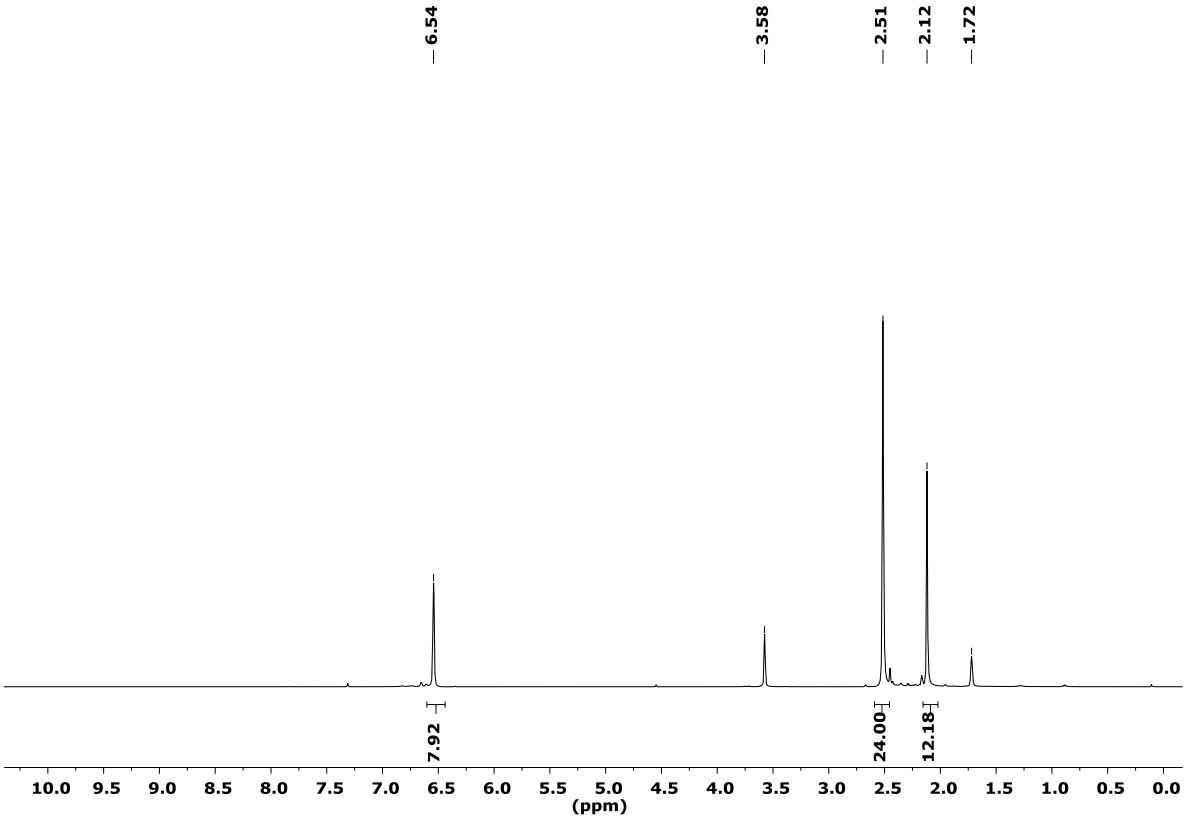

Figure S43. ^{1}H NMR spectrum (400.13 MHz, THF-d_8, 253 K).

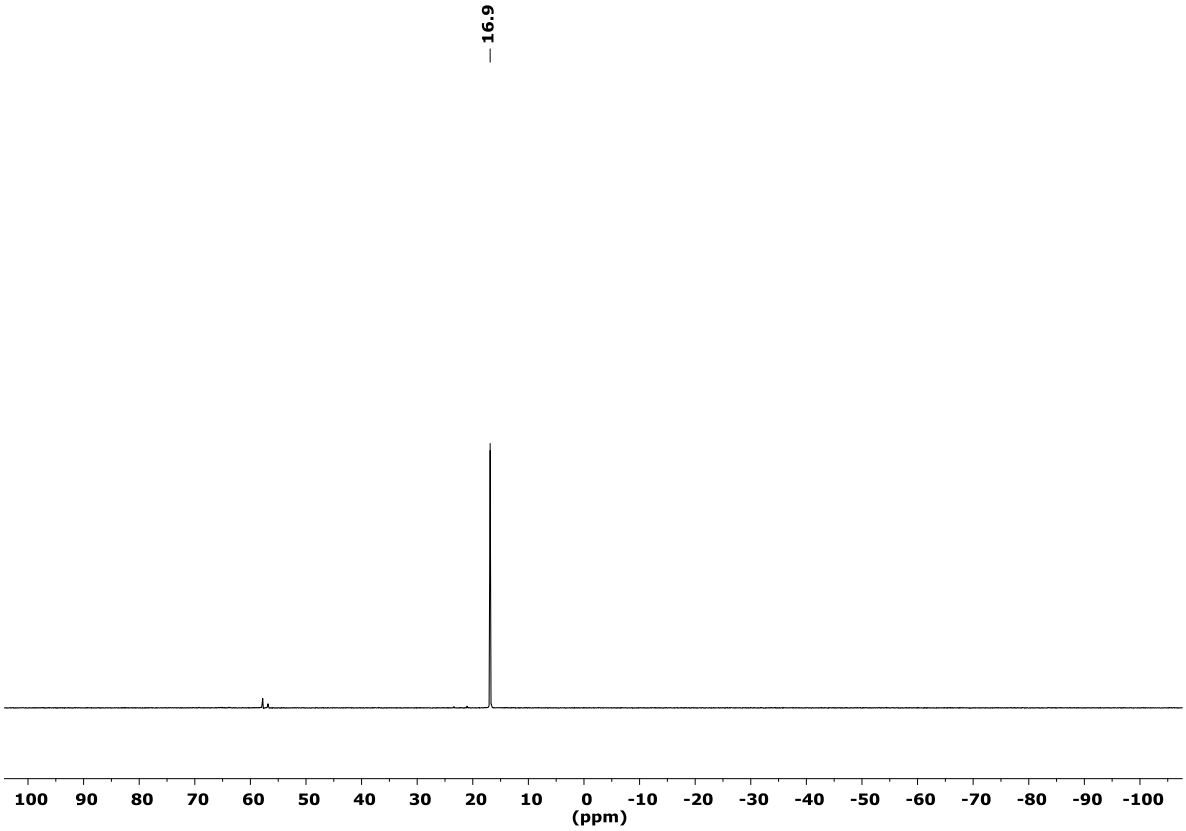

Figure S44. ^{31}P NMR spectrum (161.98 MHz, THF-d_8, 253 K).

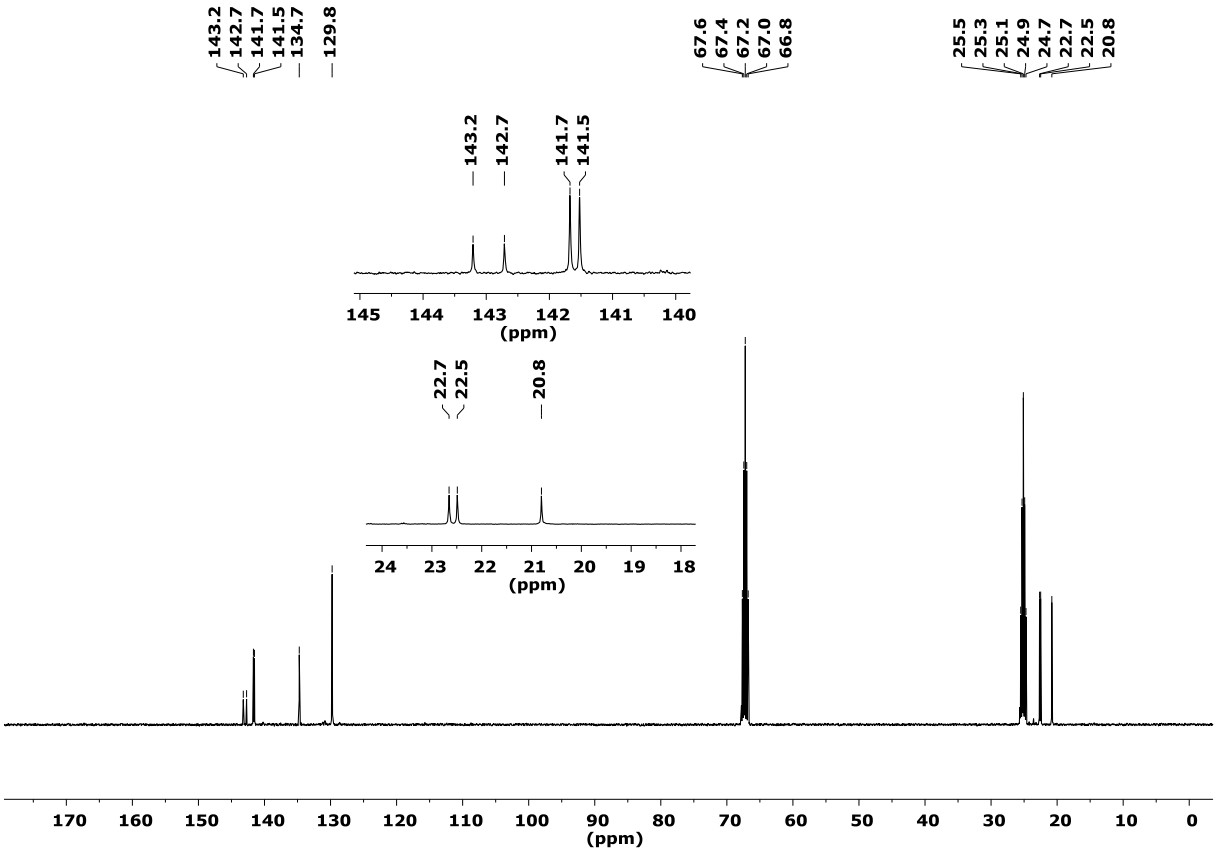

Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, THF-d_8, 253 K).

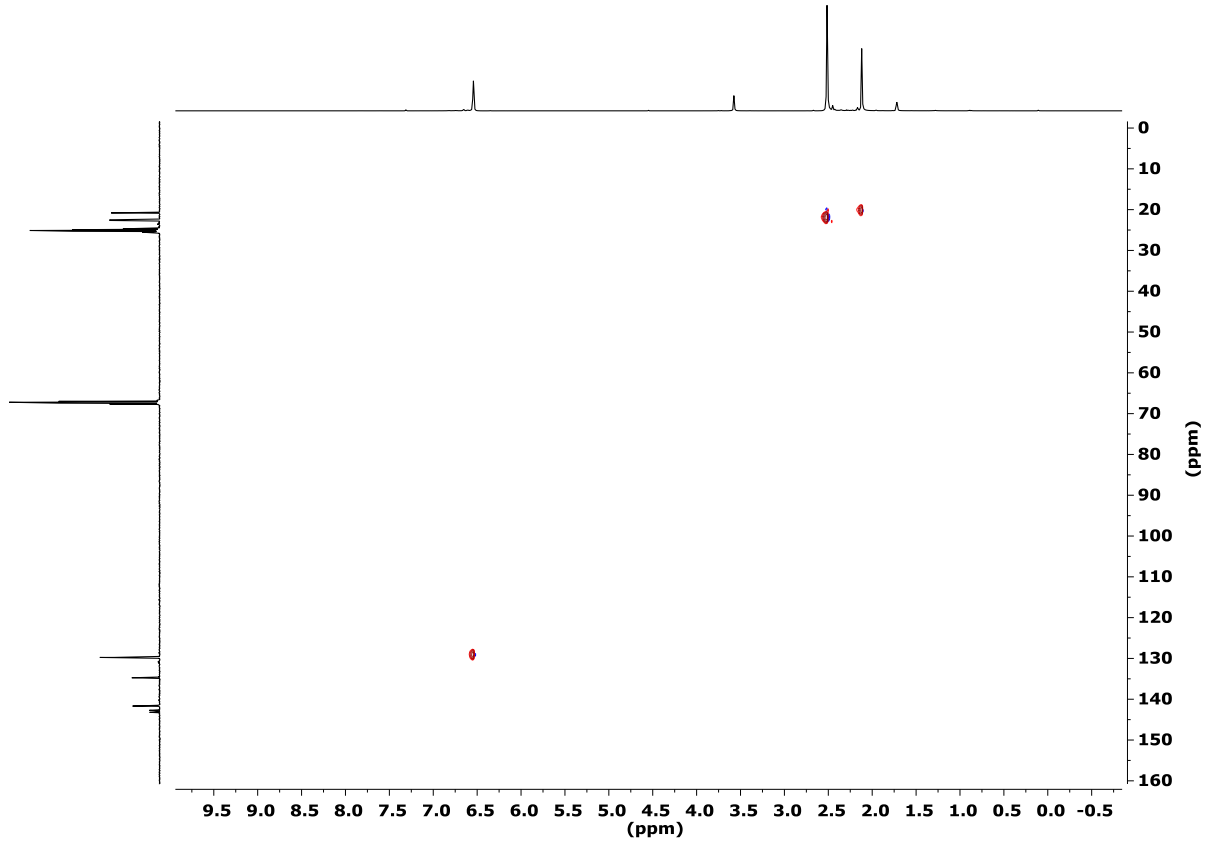

Figure S46. HSQC NMR spectrum (400.13/100.61 MHz, THF-d_8, 253 K).

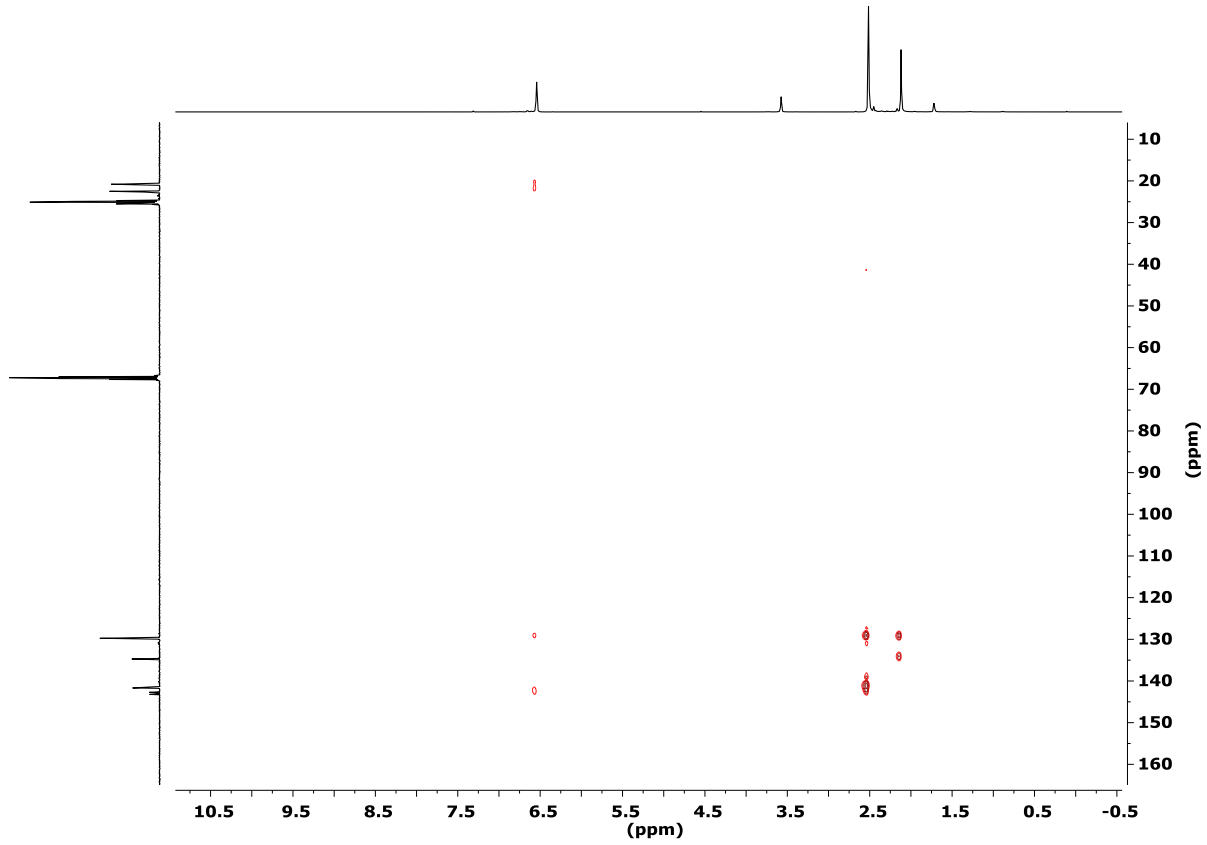

Figure S47. HMBC NMR spectrum (400.13/100.61 MHz, THF-d_8, 253 K).

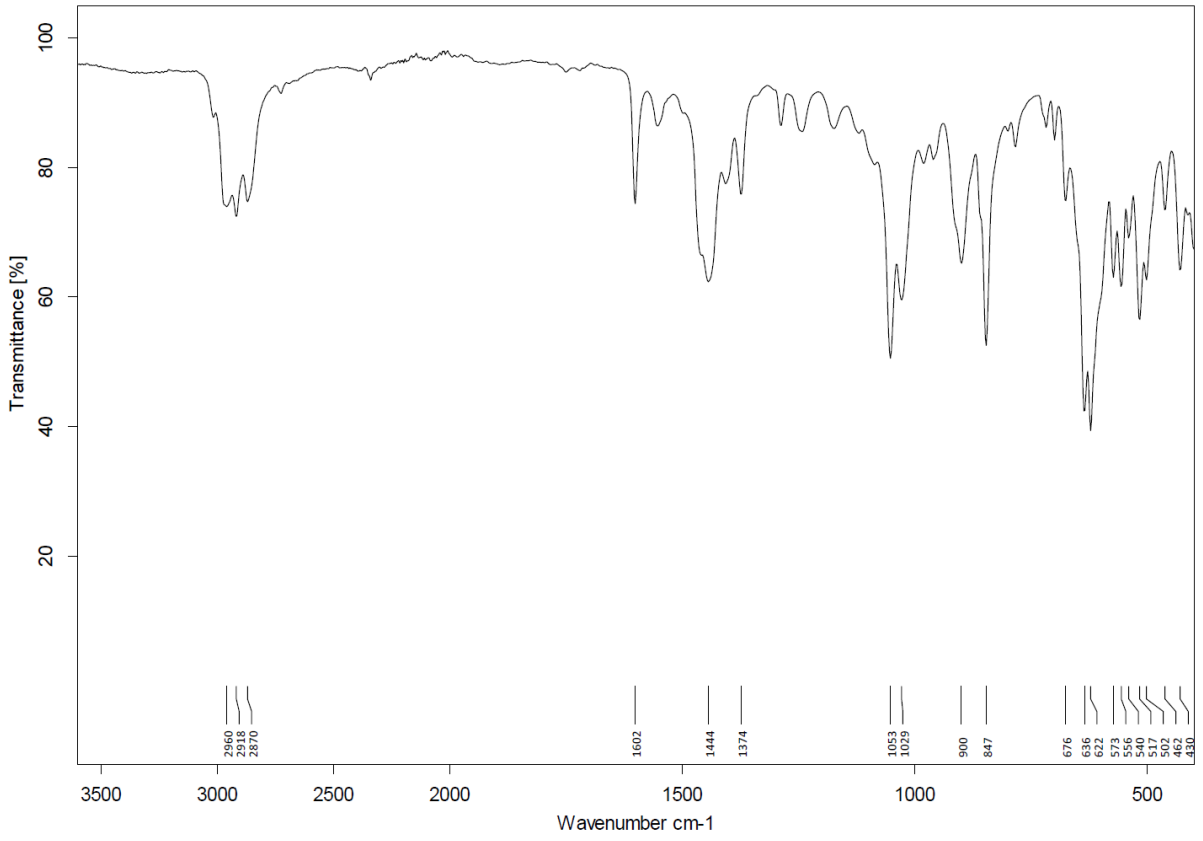

Figure S48. IR (ATR).

Mes_2PSK-[18]crown-6 (**6**)

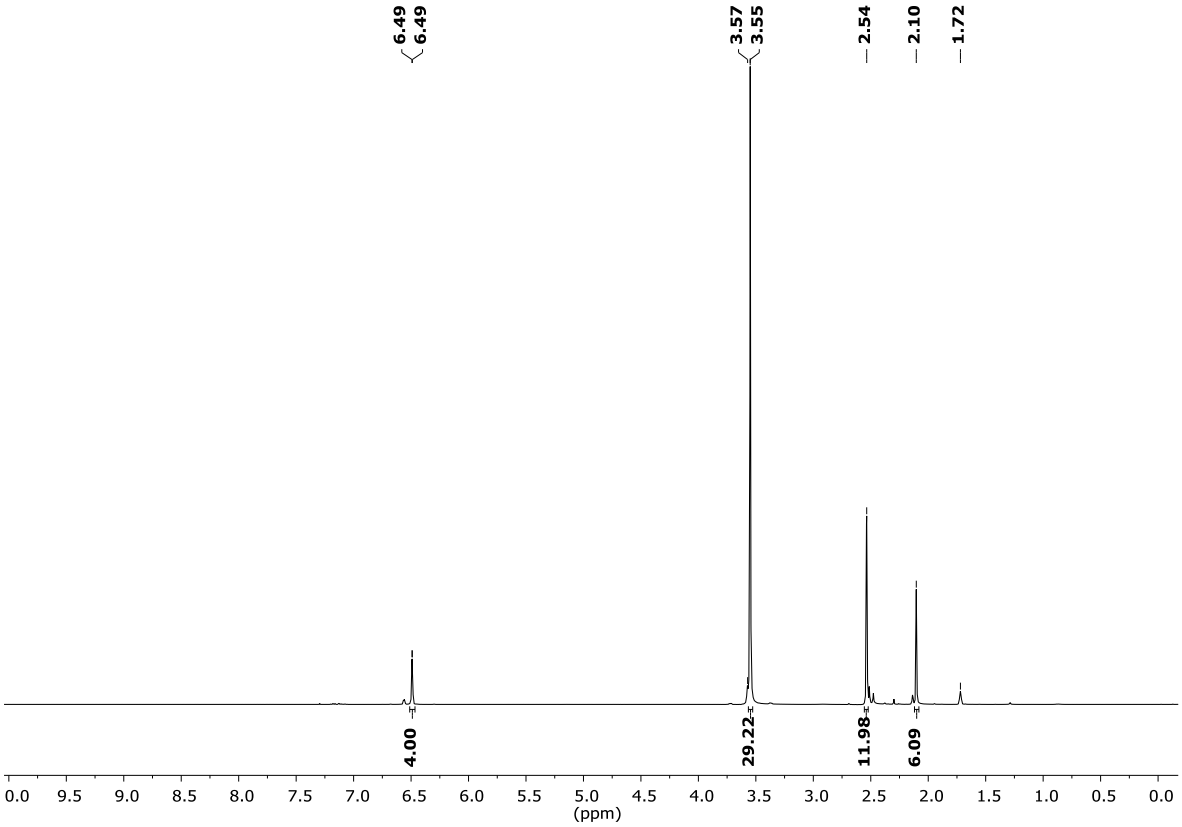

Figure S49. ^{1}H NMR spectrum (400.13 MHz, THF-d_8, 298 K).

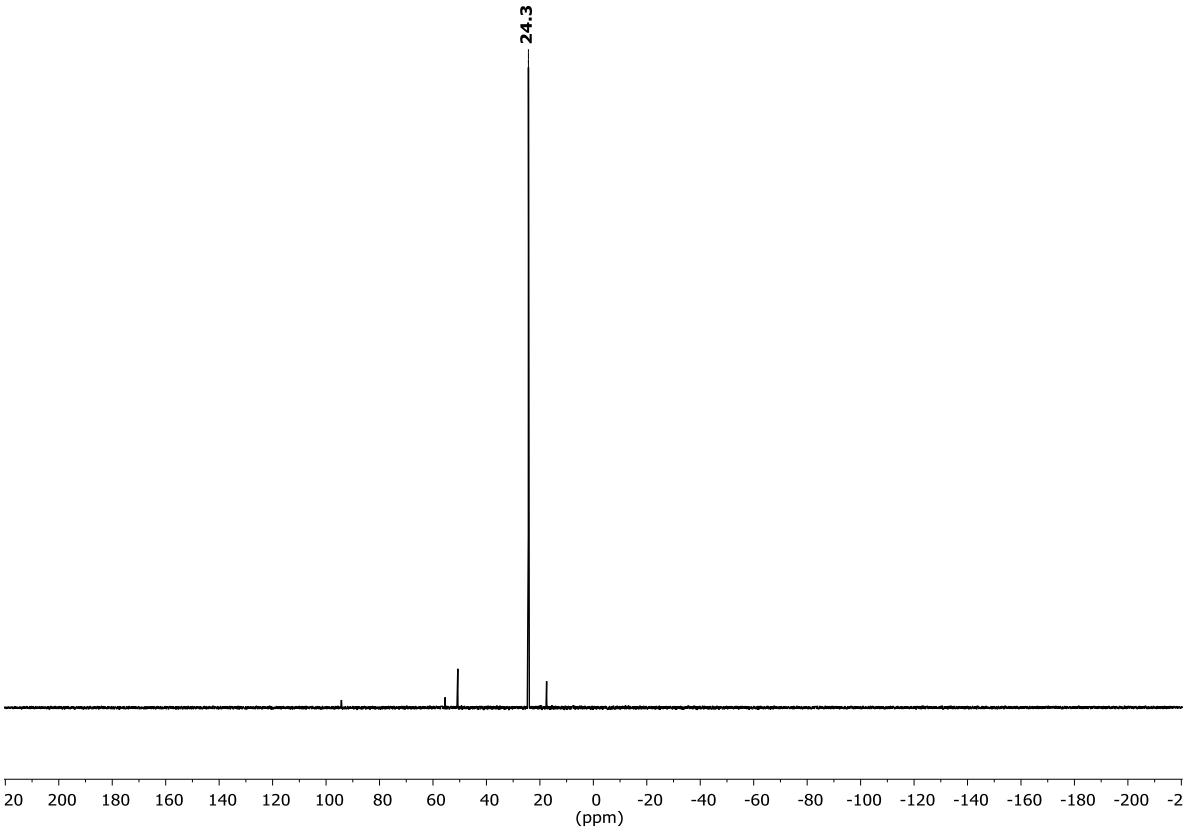

Figure S50. ^{31}P NMR spectrum (161.98 MHz, THF-d_8, 253 K).

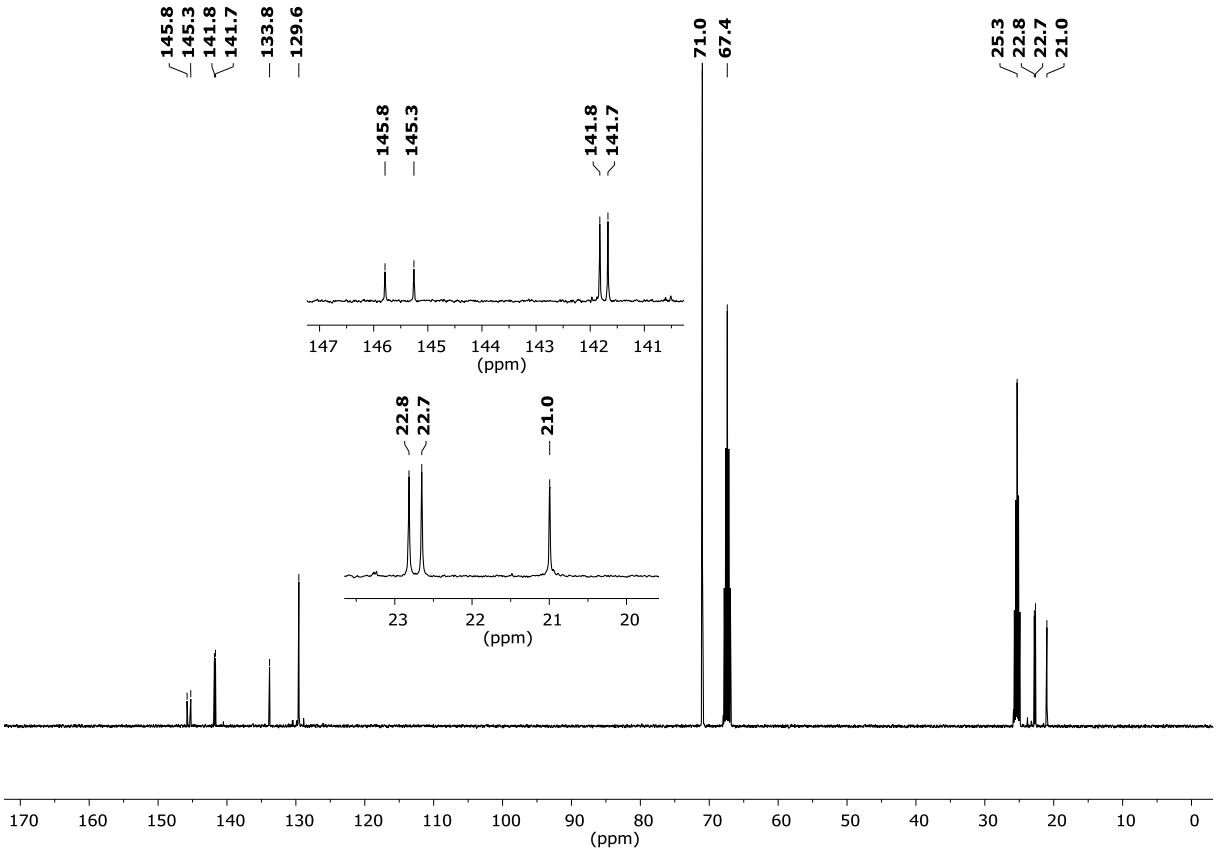

Figure S51. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, THF-d_8, 253 K).

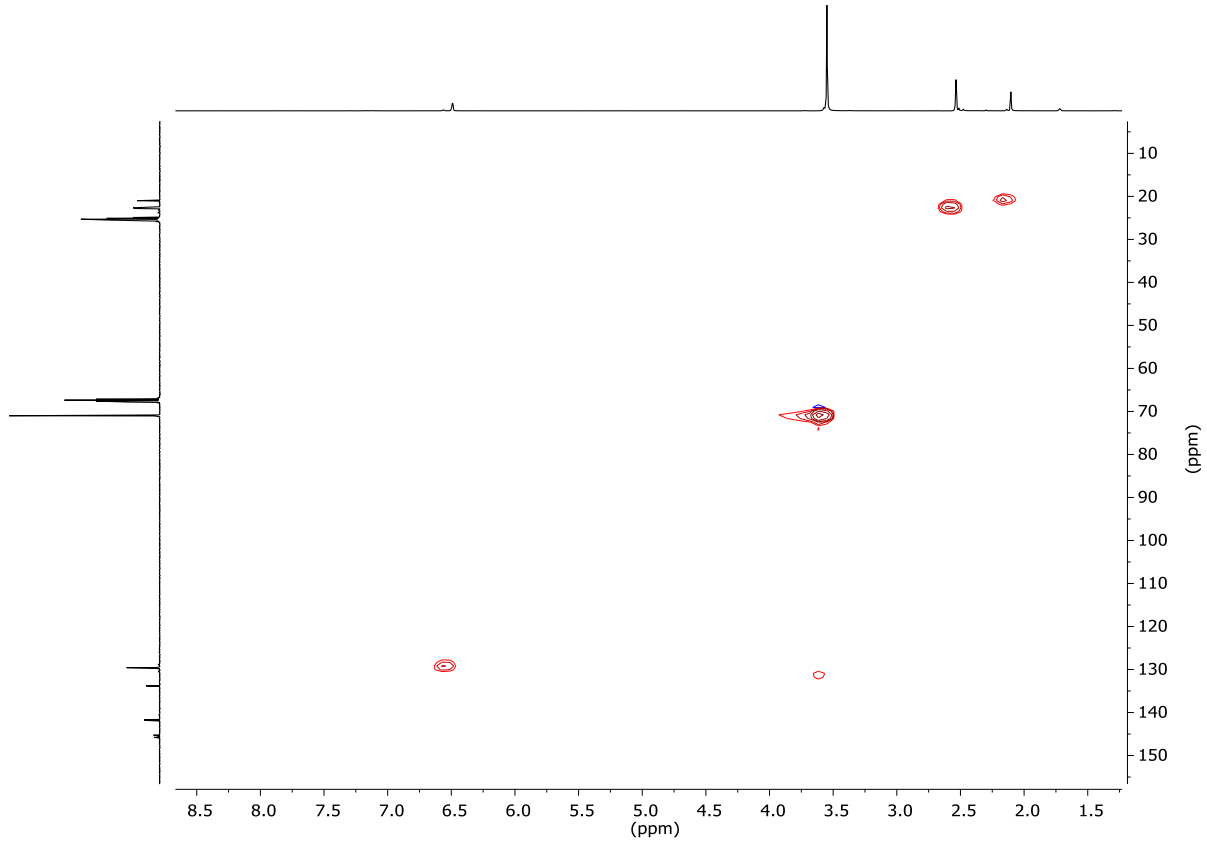

Figure S52. HSQC NMR spectrum (400.13/100.61 MHz, THF-d_8, 253 K).

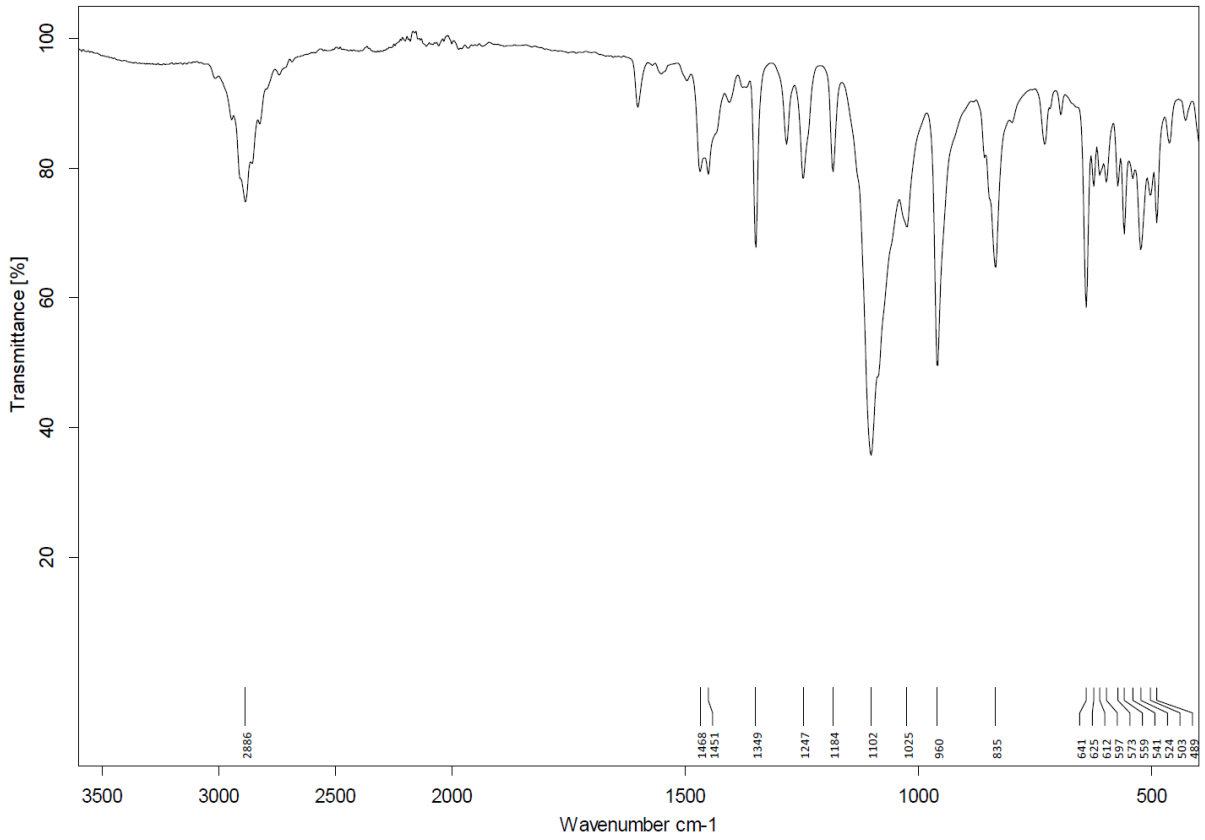

Figure S53. IR (ATR).

Reaction mixture of Ph_2PH with KH and grey Se

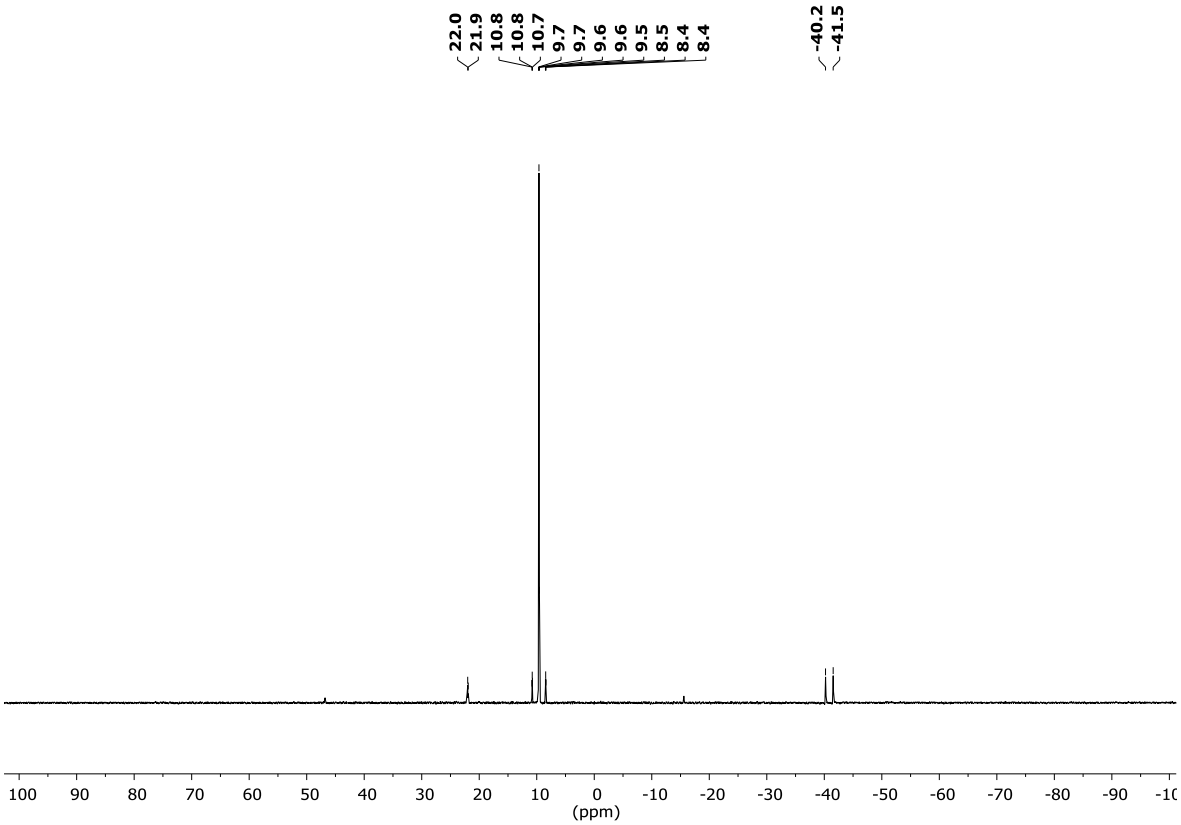

Figure S54. ^{31}P NMR spectrum (161.98 MHz, THF-d_8, 298 K), -40.2 = Ph_2PH.

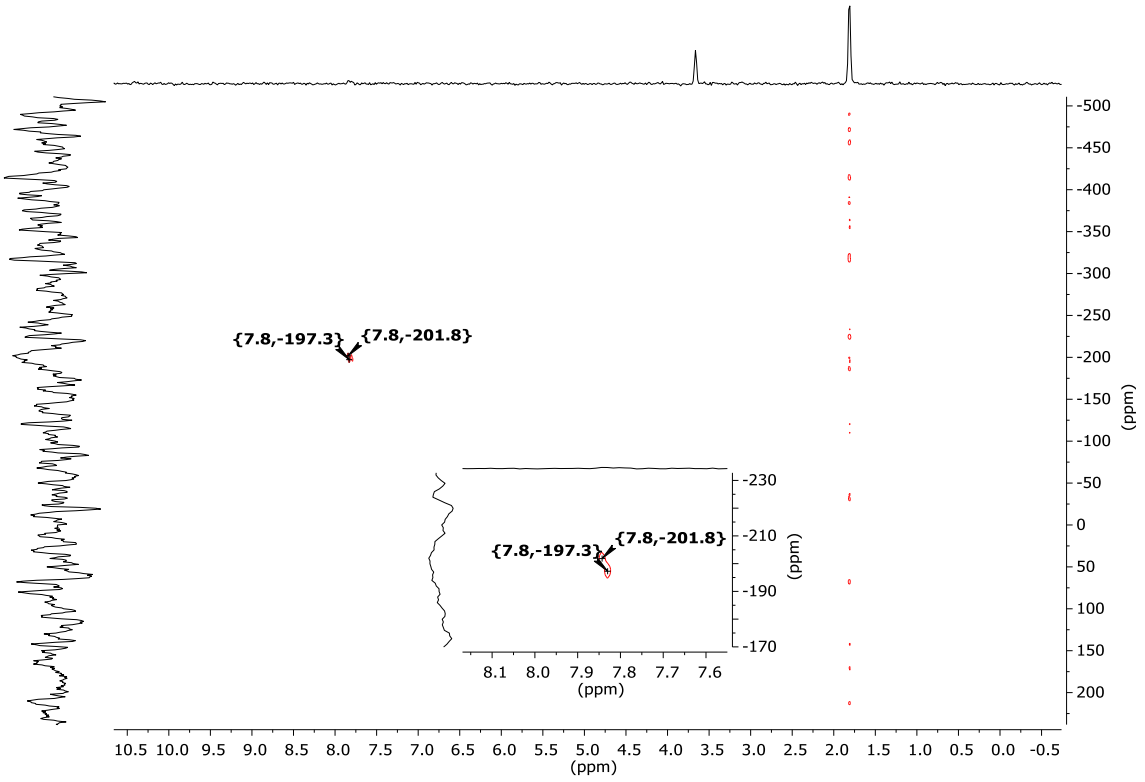

Figure S55. ^{1}H-^{77}Se-HMBC NMR spectrum (161.98 MHz/400.13 MHz, THF-d_8, 298 K).

Reaction mixture of Ph_2PH with NaHMDS and Se:

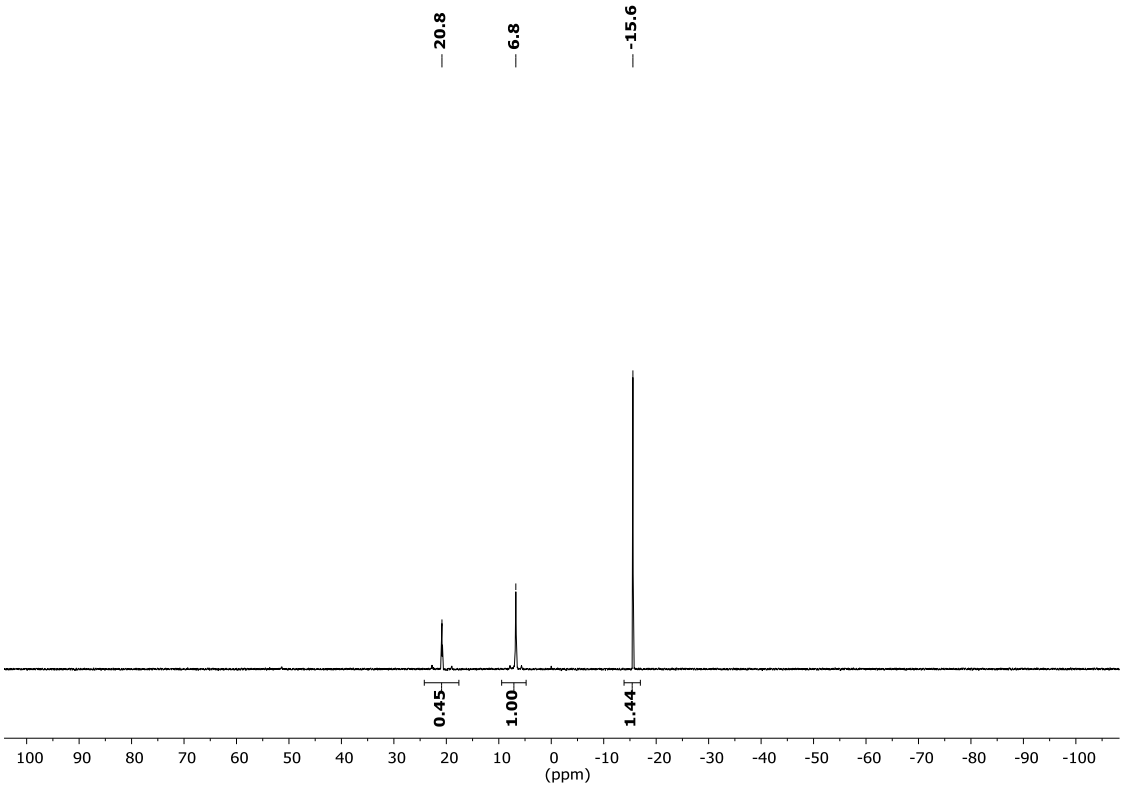

Figure S56. ^{31}P NMR spectrum (161.98 MHz, THF-d_8, 298 K), 20.8 ppm = Ph_2PSe_2Na, 6.8 ppm = Ph_2PSeNa, -15.6 ppm = Ph_2PNa

Reaction mixture of Mes_2PSeH with *n*BuLi:

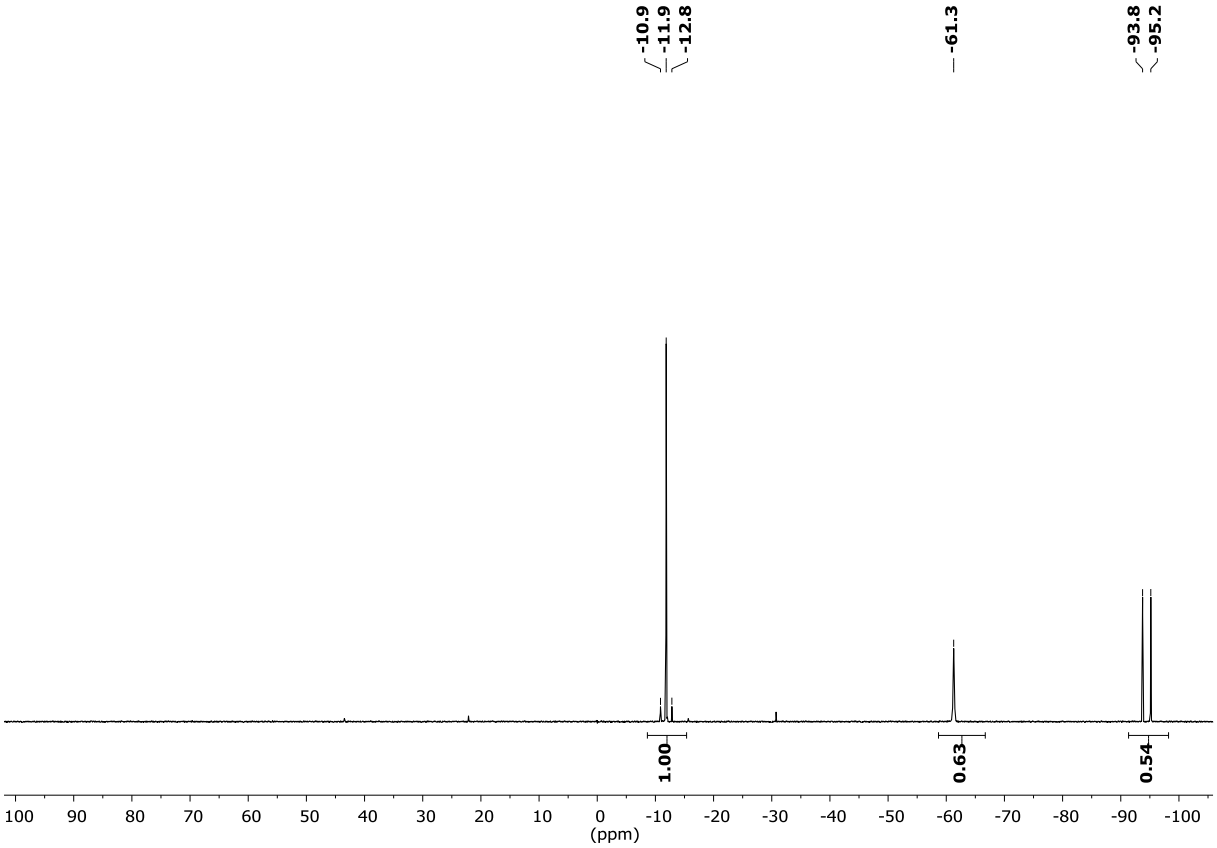

Figure S57. ^{31}P NMR spectrum (161.98 MHz, THF-d_8, 298 K).

Reaction mixture of Mes_2PSeH with NaHMDS:

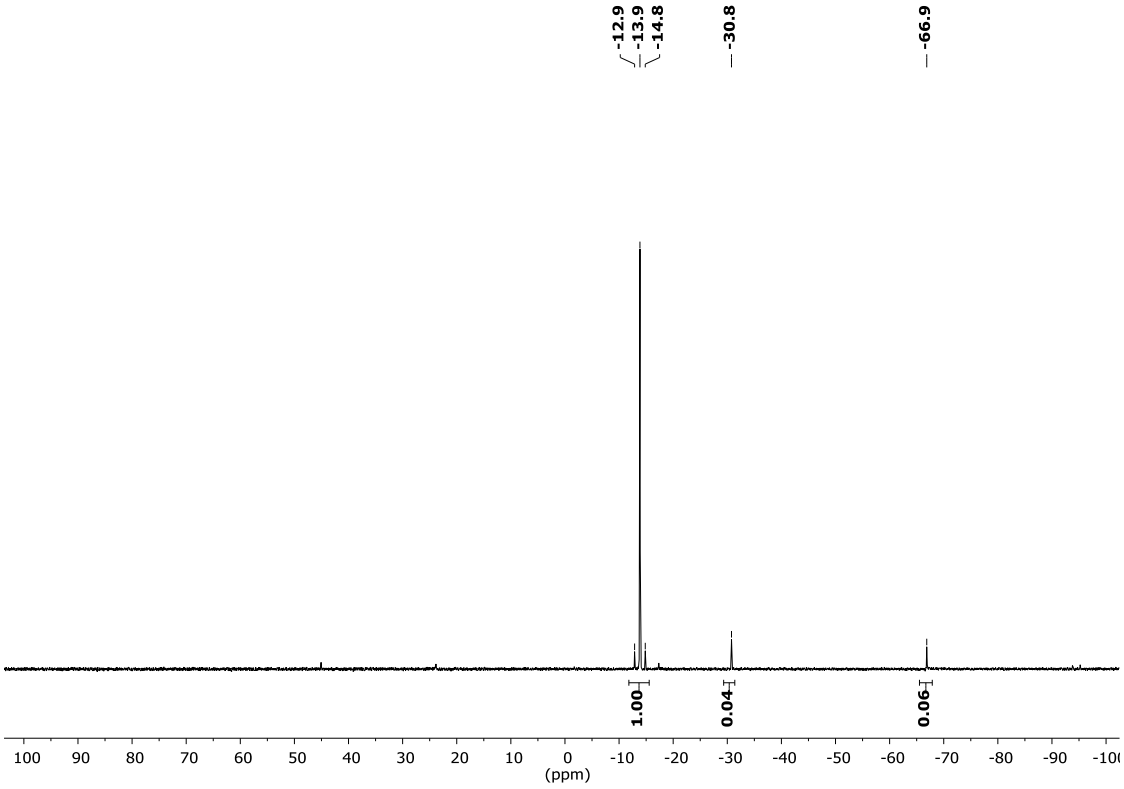

Figure S58. ^{31}P NMR spectrum (161.98 MHz, THF-d_8, 298 K).

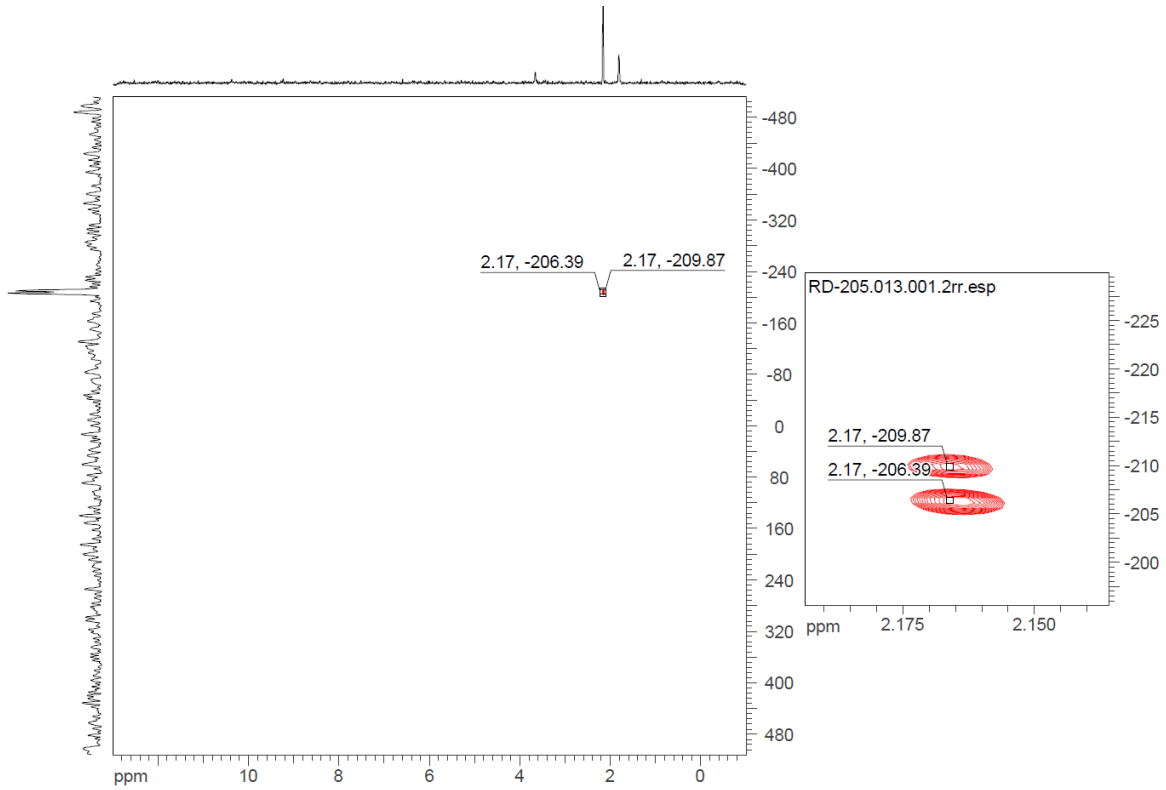

Figure S59. ^{1}H-^{77}Se-HMBC NMR spectrum (161.98 MHz/400.13 MHz, THF-d_8, 298 K).

Crystallographic Studies

Table S1: Crystal data and refinement details for the X-ray structure determinations.

Compound	**1a**	**1b**	**2a**	**2b**	**3a**
formula	$C_{18}H_{23}PS$	$C_{18}H_{23}PSe$	$C_{52}H_{76}K_2O4P_2S_2$	$C_{52}H_{76}K_2O_4P_2Se_2$	$C_{56}H_{84}K_2O_4P_2S_2$
fw ($g \cdot mol^{-1}$)	302.39	349.29	969.38	1063.18	1025.49
T/°C	-140(2)	-140(2)	-140(2)	-140(2)	-156(2)
crystal system	triclinic	triclinic	monoclinic	monoclinic	triclinic
space group	P $\bar{1}$	P $\bar{1}$	P 2_1/n	P 2_1/n	P $\bar{1}$
a/ Å	8.0974(3)	8.1648(17)	11.9719(2)	11.9075(3)	13.4390(15)
b/ Å	8.5354(3)	8.5743(16)	16.8153(3)	16.8014(4)	13.7423(14)
c/ Å	12.0938(4)	12.161(2)	13.0896(2)	13.2648(2)	17.2067(19)
α/°	83.001(2)	82.479(5)	90	90	92.241(3)
β/°	77.127(2)	77.391(5)	93.338(1)	92.043(1)	108.058(3)
γ/°	89.041(2)	89.456(5)	90	90	108.624(3)
V/Å^3	808.73(5)	823.5(3)	2630.61(8)	2652.1(1)	2829.2(5)
Z	2	2	2	2	2
ρ ($g \cdot cm^{-3}$)	1.242	1.409	1.224	1.331	1.204
μ (cm^{-1})	2.88	23.66	3.62	16.53	3.4
measured data	6301	11315	21077	19978	41447
data with I > 2σ(I)	3376	4313	5475	5113	9512
unique data (R_{int})	3602/0.0185	4881/0.0191	6005/0.0215	6057/0.0428	16704/0.0613
wR_2 (all data, on F^2)[a)]	0.1090	0.0590	0.1334	0.0985	0.1974
R_1 ($I > 2\sigma(I)$) [a)]	0.0427	0.0235	0.0478	0.0434	0.0741
s [b)]	1.089	1.020	1.033	1.059	1.025
Res. dens./$e \cdot Å^{-3}$	1.173/-0.346	0.429/-0.371	1.275/-0.355	1.517/-0.551	1.043/-0.936
absorpt method	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
absorpt corr $T_{min}/_{max}$	0.6985/0.7456	0.6075/0.7456	0.7014/0.7456	0.6794/0.7456	0.6574/0.7456
CCDC No.	2184155	2184156	2184157	2184158	2184159

Table S1: Crystal data and refinement details for the X-ray structure determinations.

Compound	**3b**	**4**	**5**	**(tmeda)NaOPMes$_2$**	**6**
formula	$C_{56}H_{84}K_2O_4P_2Se_2$	$C_{52}H_{76}Li_2O_4P_2S_2$	$C_{60}H_{92}Na_2O_6P_2S_2$	$C_{48}H_{76}N_4Na_2O_2P_2$	$C_{30}H_{46}KO_6PS$
fw (g·mol^{-1})	1119.29	905.06	1081.37	849.04	604.80
°C	-140(2)	-140(2)	-140(2)	-140(2)	-153(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	P 2_1/n	P 2_1/c	P 2_1/c	P 2_1/n	P 2_1/n
a/ Å	12.344(3)	8.7520(10)	11.5510(17)	12.5768(3)	11.4806(14)
b/ Å	17.315(4)	13.3652(17)	10.5196(14)	15.2815(4)	14.5572(16)
c/ Å	13.494(4)	22.037(3)	25.647(4)	13.3242(3)	19.572(2)
α/°	90	90	90	90	90
β/°	92.518(10)	95.393(4)	101.101(4)	92.363(2)	97.148(3)
γ/°	90	90	90	90	90
V/Å^3	2881.4(13)	2566.3(5)	3058.2(8)	2558.63(11)	3245.6(6)
Z	2	2	2	2	4
ρ (g·cm^{-3})	1.290	1.171	1.174	1.102	1.238
μ (cm^{-1})	15.25	2.08	2	1.4	3.16
measured data	49625	35232	30199	17389	40013
data with I > 2σ(I)	6972	6202	5694	4881	7145
unique data (R_{int})	8945/0.0270	7834/0.0340	7528/0.0453	5815/0.0332	9674/0.0304
wR_2 (all data, on F^2)[a)]	0.0800	0.1010	0.1649	0.1683	0.1342
R_1 ($I > 2\sigma(I)$) [a)]	0.0310	0.0385	0.0640	0.0589	0.0508
s [b)]	1.041	1.041	1.085	1.054	1.036
Res. dens./e·Å^{-3}	0.512/-0.413	0.527/-0.307	1.567/-0.357	0.729/-0.364	1.043/-0.492
absorpt method	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
absorpt corr $T_{min}/_{max}$	0.6139/0.7456	0.6928/0.7456	0.6642/0.7456	0.6779/0.7456	0.8068/0.8623
CCDC No.	2184160	2184161	2184162	2184163	2254279

[a)] Definition of the *R* indices: $R_1 = (\Sigma \left|\left| F_o \right| - \left| F_c \right|\right|)/\Sigma \left| F_o \right|$;

$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2+bP$; $P = [2F_c^2 + Max(F_O^2]/3$;

[b)] $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

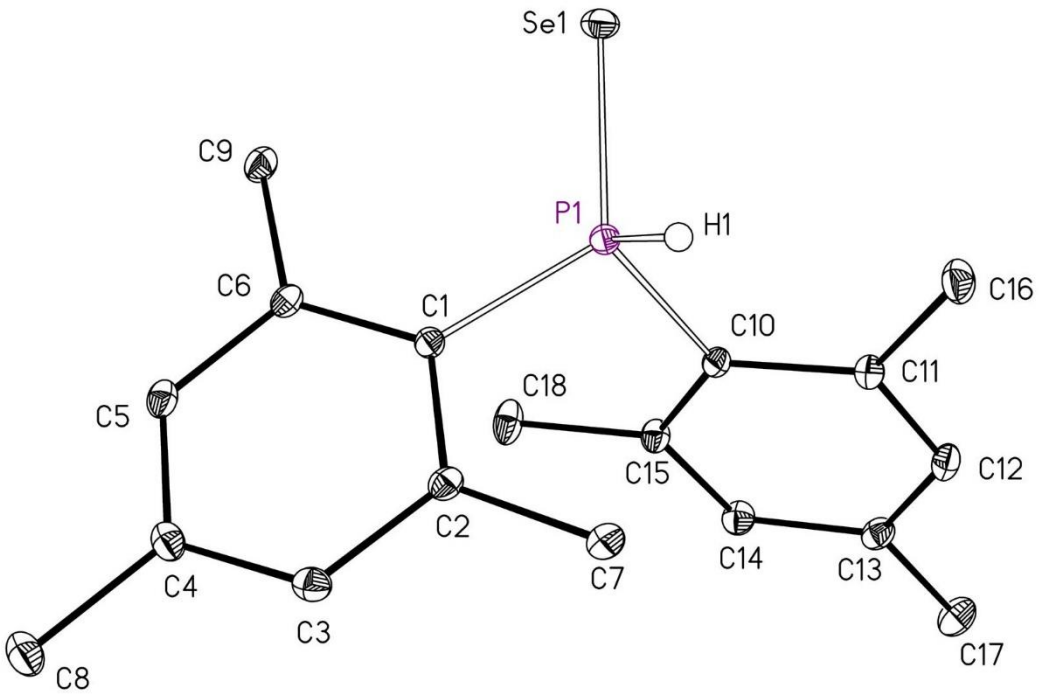

Figure S60. Solid state molecular structure and atom labelling scheme of $Mes_2P(Se)H$ (**1b**). The ellipsoids represent a probability of 30 %, H atoms bound to C atoms are neglected for the sake of clarity. Selected bonding parameters are listed in Table 2.

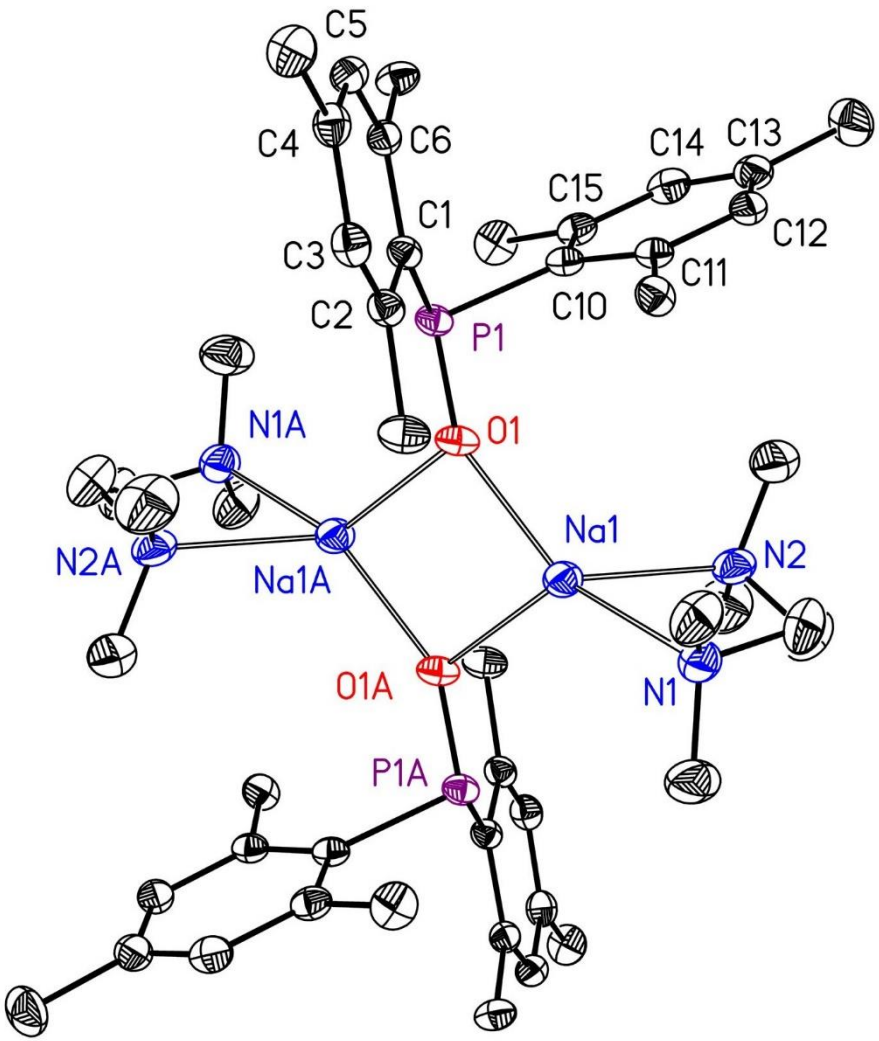

Figure S61. Solid state molecular structure and atom labelling scheme of $[(tmeda)Na\text{-}OPMes_2]_2$. The ellipsoids represent a probability of 30 %, H atoms are omitted for clarity reasons. Selected bond lengths (pm): P-O 156.4(2), P-C 186.9(2) and 187.2(2), av. Na-O 224.2; bond angle (°): C-P-C 100.32(8)°.