Supporting Information

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Characterisation of **2**

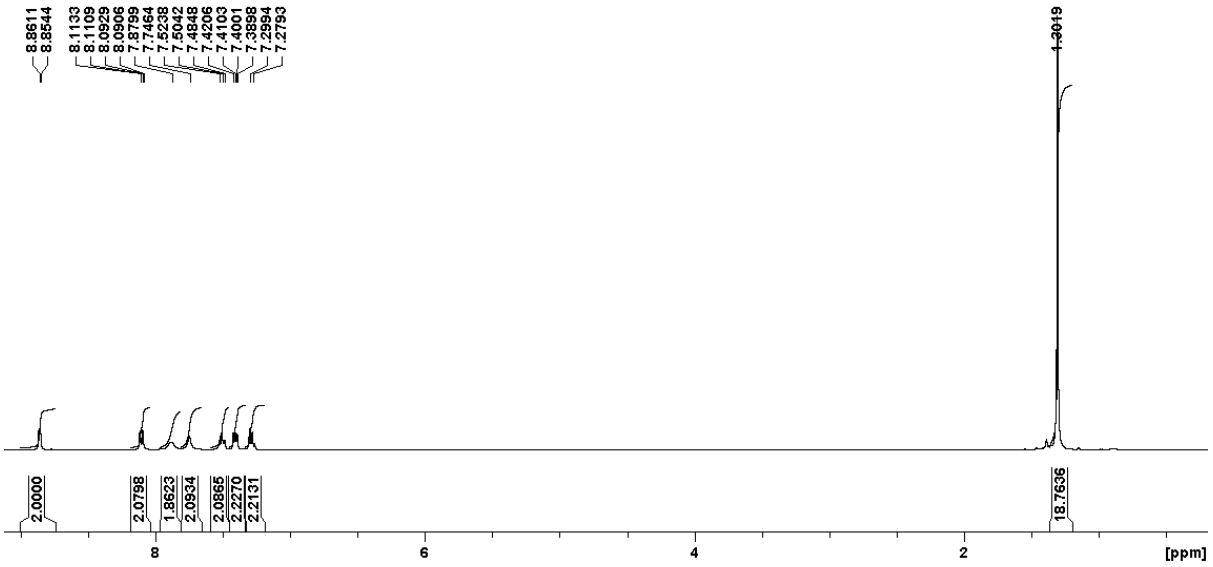


Figure S 1: ^{1}H NMR spectrum (25°C, $CDCl_3$, 500 MHz) of 2

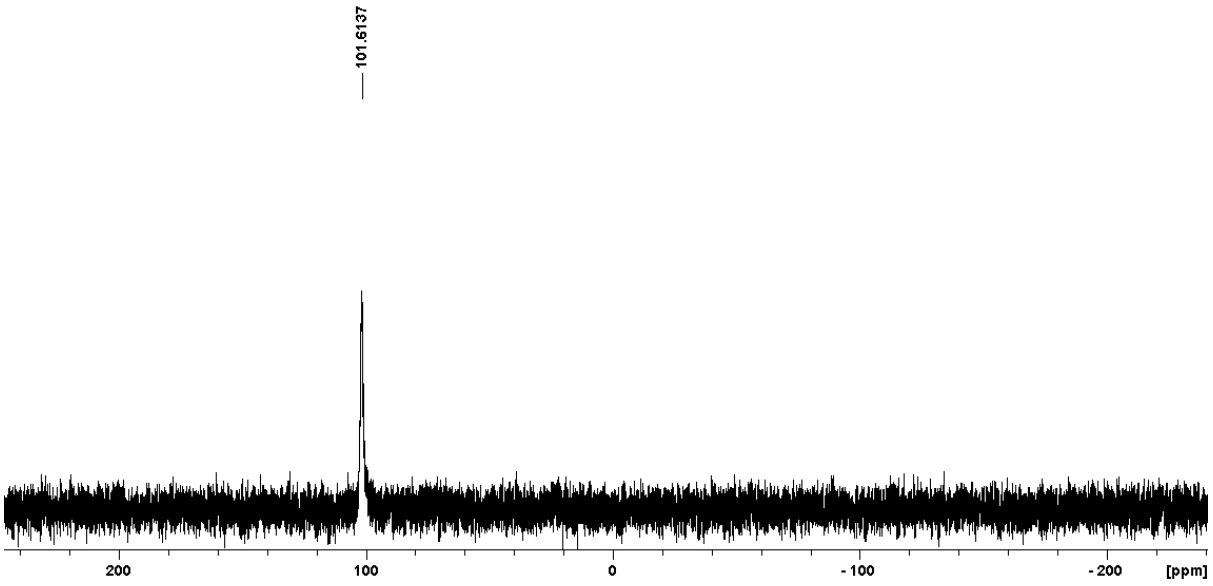


Figure S 2: ^{31}P NMR spectrum (25°C, $CDCl_3$, 202 MHz) of 2

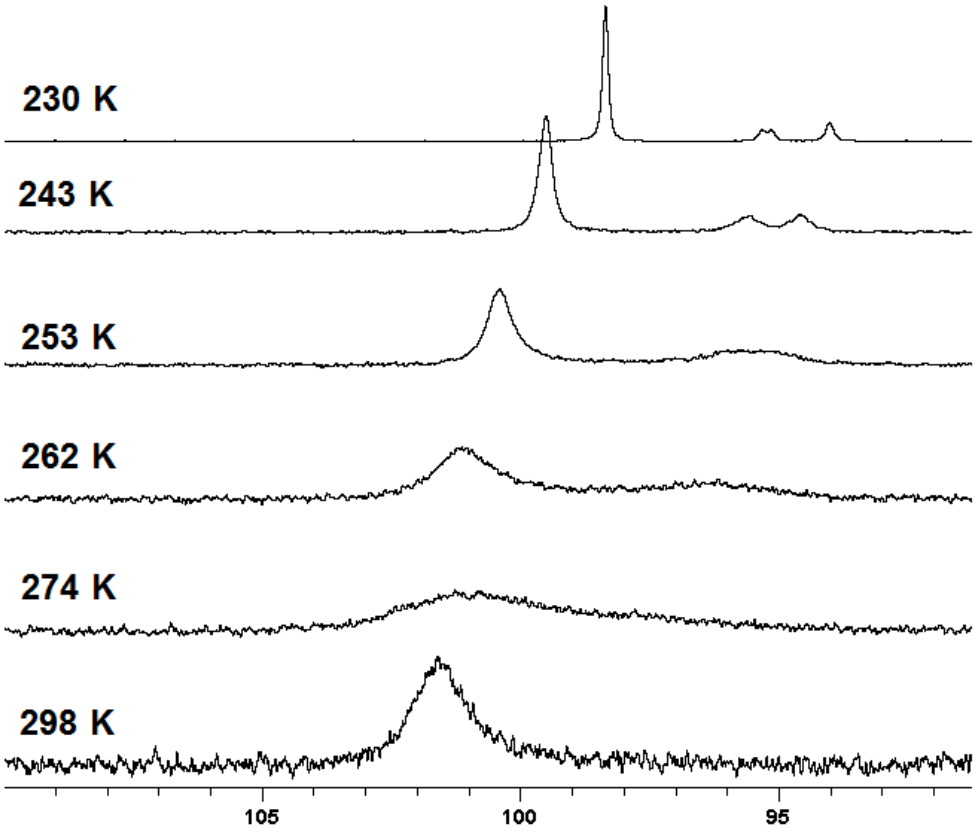


Figure S 3: ^{31}P VT NMR spectrum ($CDCl_3$, 202 MHz) of 2

Characterisation of **3** and **4**

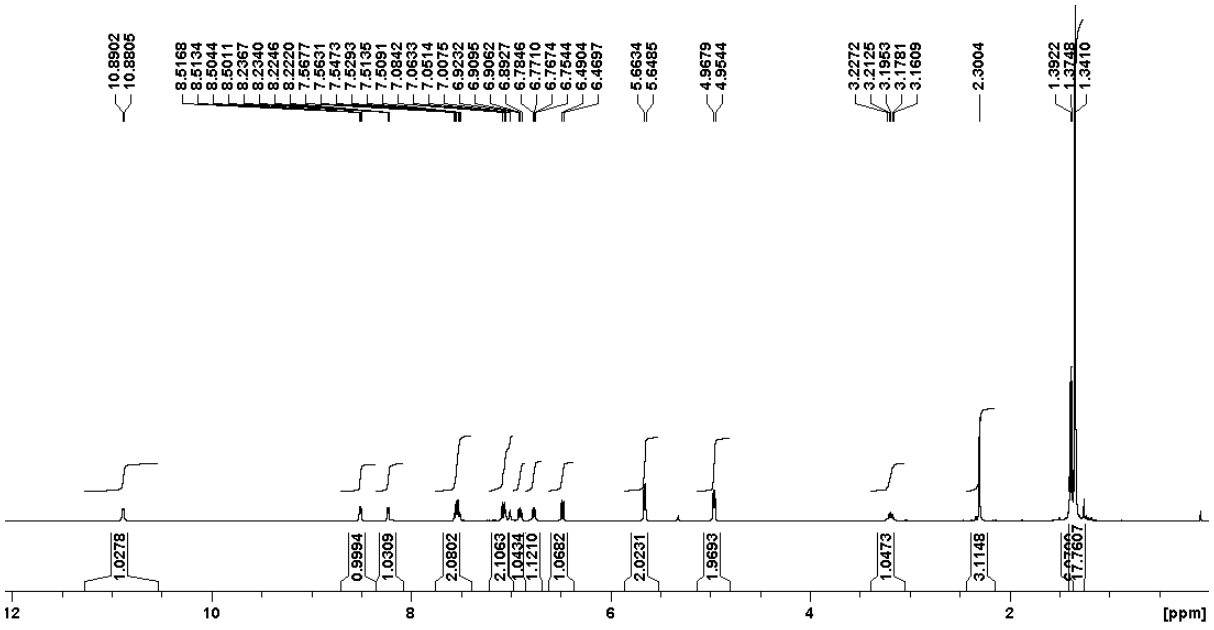


Figure S 4: ^{1}H NMR spectrum (25°C, CD_2Cl_2, 500MHz) of 3

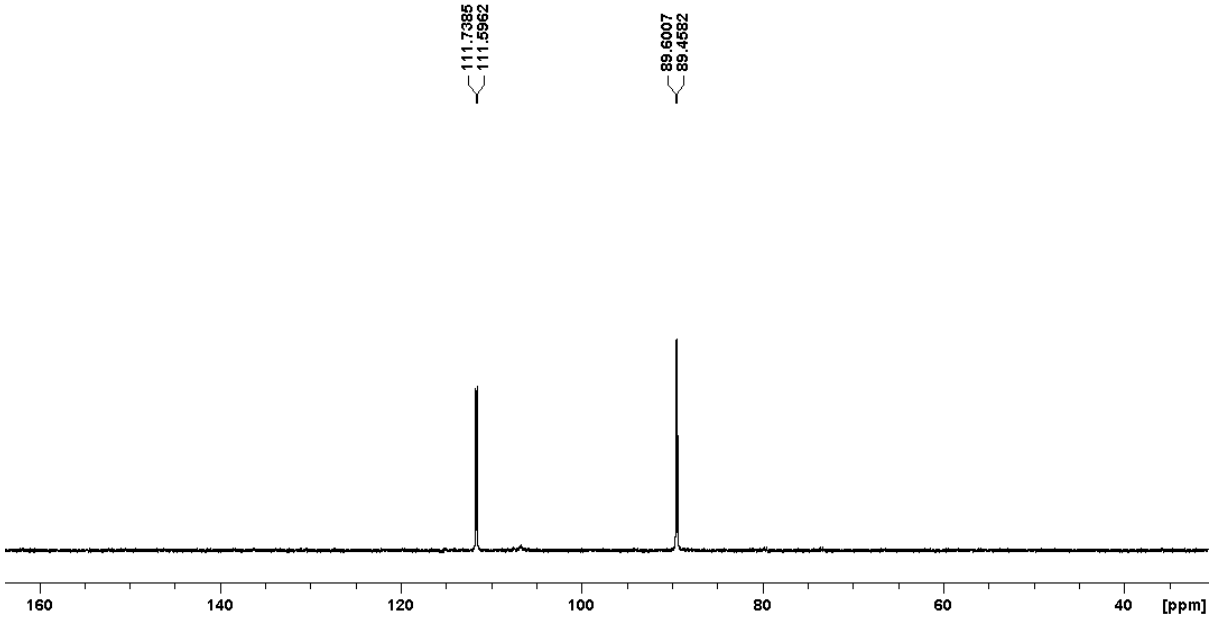


Figure S 5: ^{31}P NMR spectrum (25°C, CD_2Cl_2, 202MHz) of 3

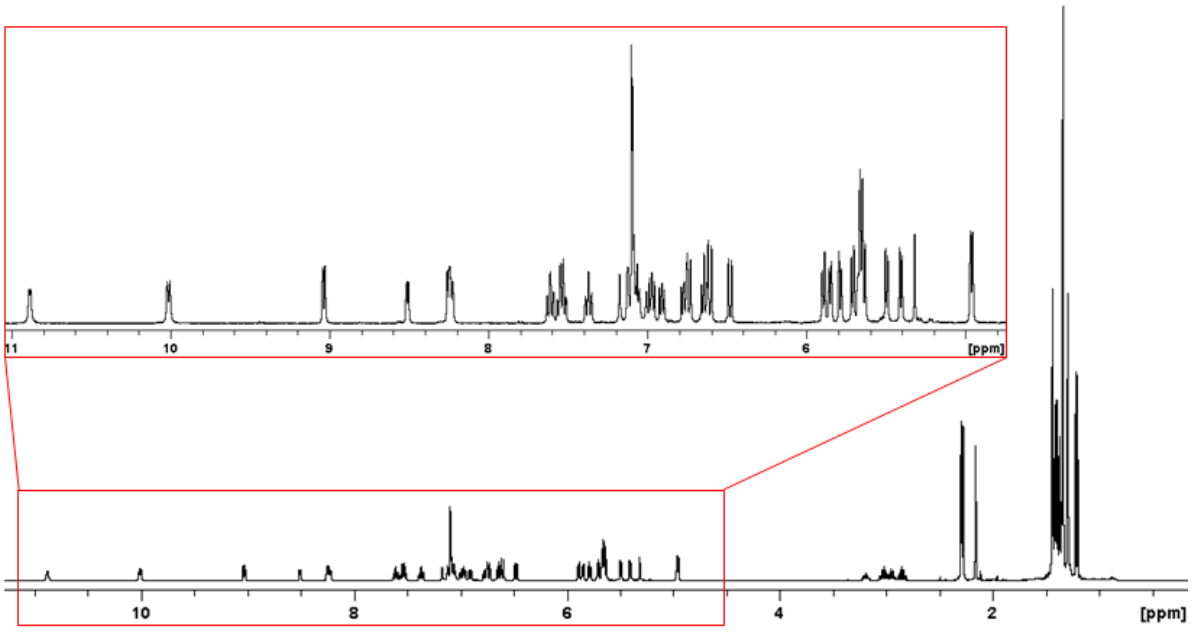


Figure S 6: ^{1}H NMR spectrum (25°C, CD_2Cl_2, 500 MHz) of a 1:1 mix of 3 and 4

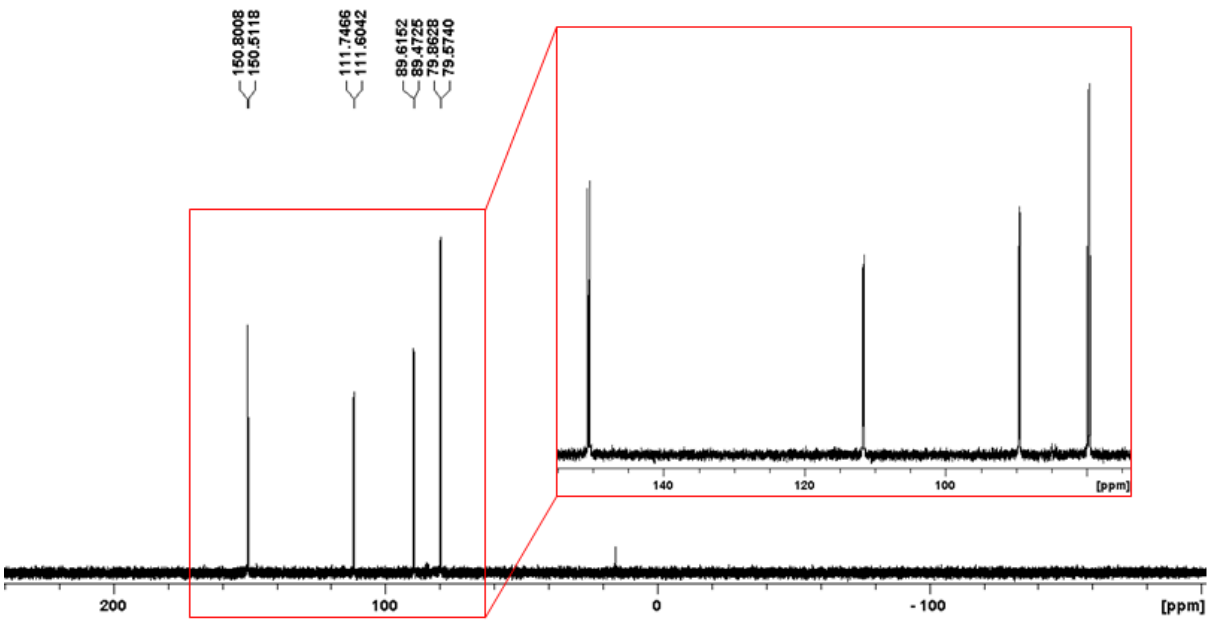


Figure S 7: ^{31}P NMR spectrum (25°C, CD_2Cl_2, 202MHz) of 1:1 mix of 3 and 4

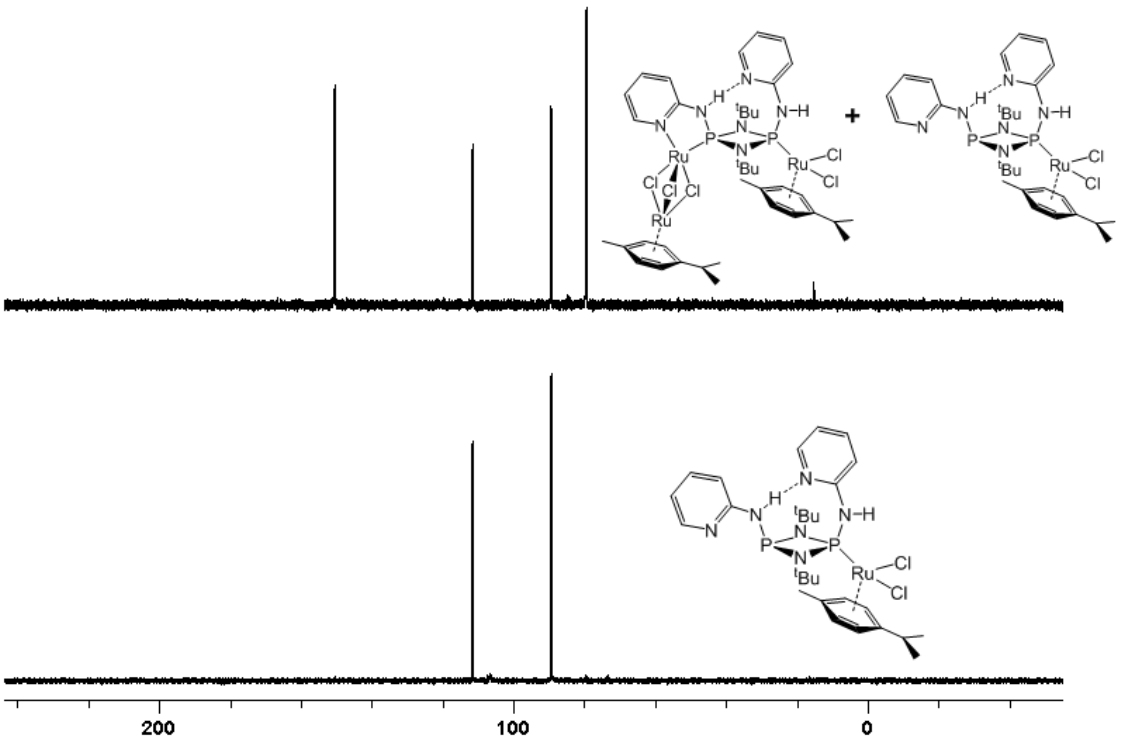


Figure S 8: overlaid ^{31}P NMR spectrum (25°C, CD_2Cl_2, 202MHz) of the mixture obtained above with the in situ NMR obtainted from the 1:1 reaction of 1 and Dichloro(p-cymene)ruthenium(II)dimer

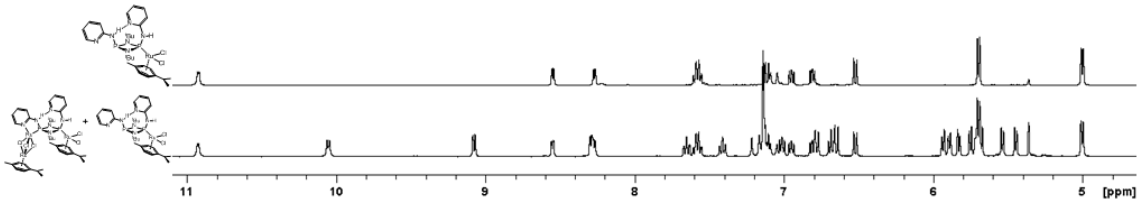


Figure S 9: overlaid ^{1}H NMR spectrum (25°C, CD_2Cl_2, 202MHz) of the mixture obtained above with the *in situ* NMR obtained from the 1:1 reaction of 1 and Dichloro(p-cymene)ruthenium(II)dimer

Characterisation of **5**

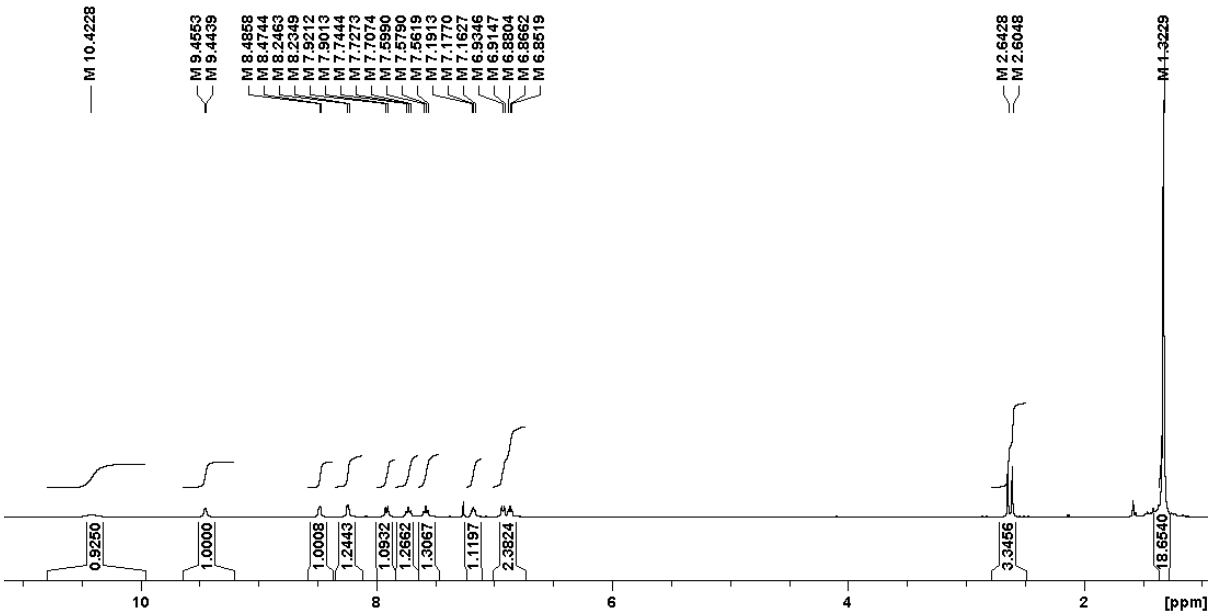


Figure S 10: ^{1}H NMR spectrum (25°C, $CDCl_3$, 500 MHz) of 5

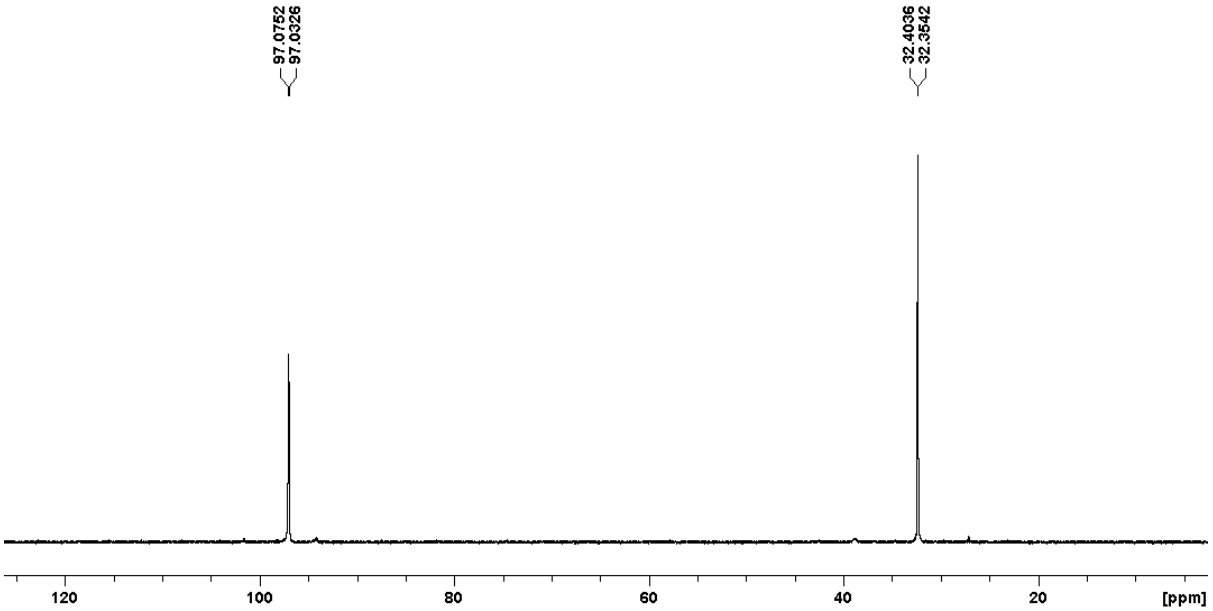


Figure S 11: ^{31}P NMR spectrum (25°C, $CDCl_3$, 202MHz) of 5

Characterisation of **6**

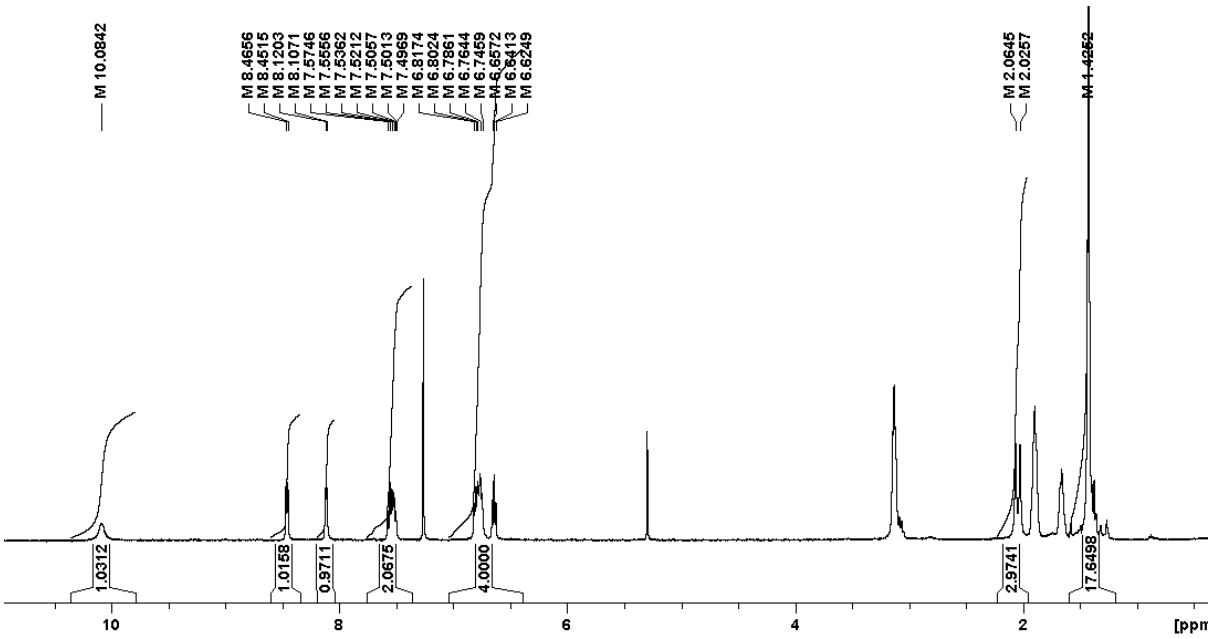


Figure S 12: ^{1}H NMR spectrum (25°C, $CDCl_3$, 500 MHz) of 6

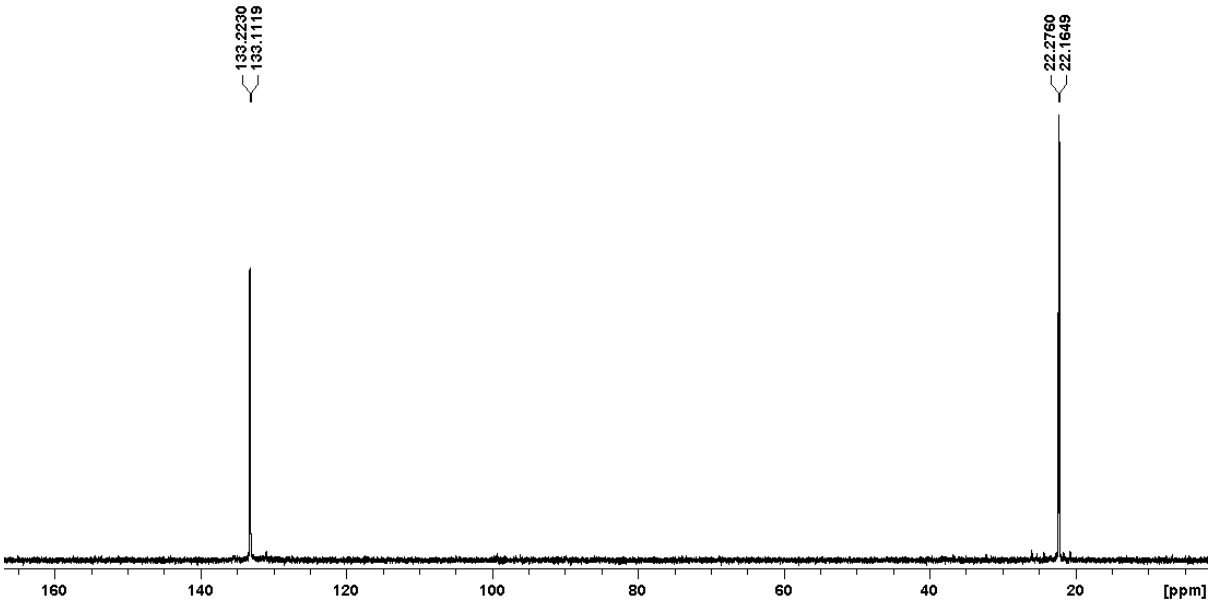


Figure S 13: ^{31}P NMR spectrum (25°C, $CDCl_3$, 202MHz) of 6

Characterisation of **7**

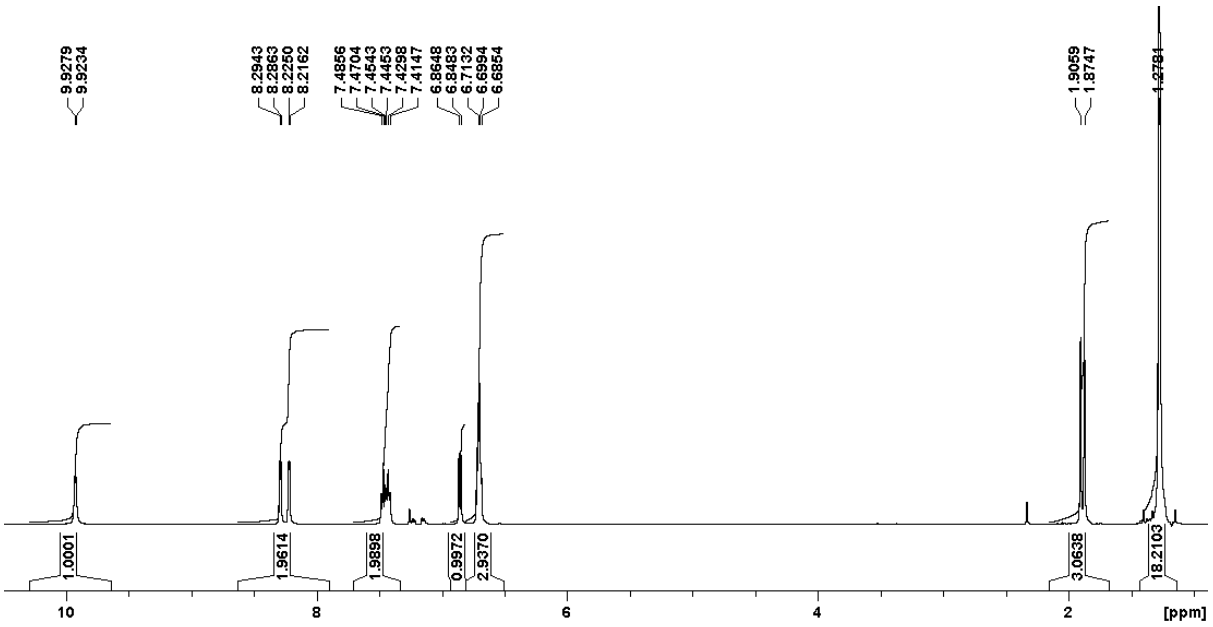


Figure S 14: ^{1}H NMR spectrum (25°C, $CDCl_3$, 500 MHz) of 7

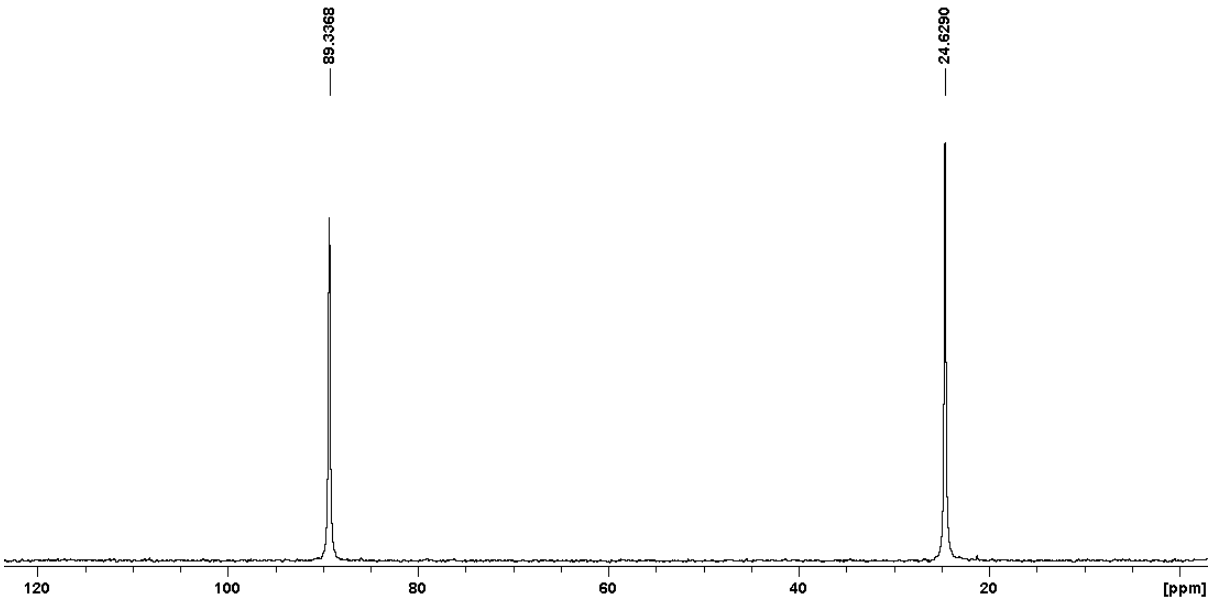


Figure S 15: ^{31}P NMR spectrum (25°C, $CDCl_3$, 202MHz) of 7

Characterisation of **8**

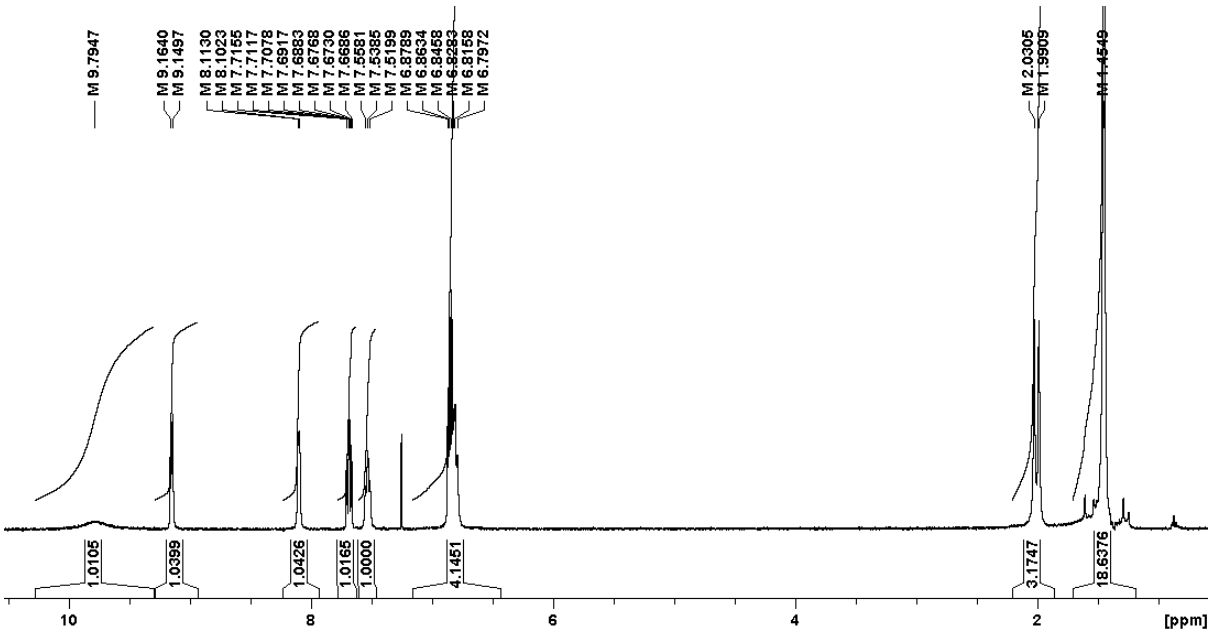


Figure S 16: ^{1}H NMR spectrum (25°C, $CDCl_3$, 500 MHz) of 8

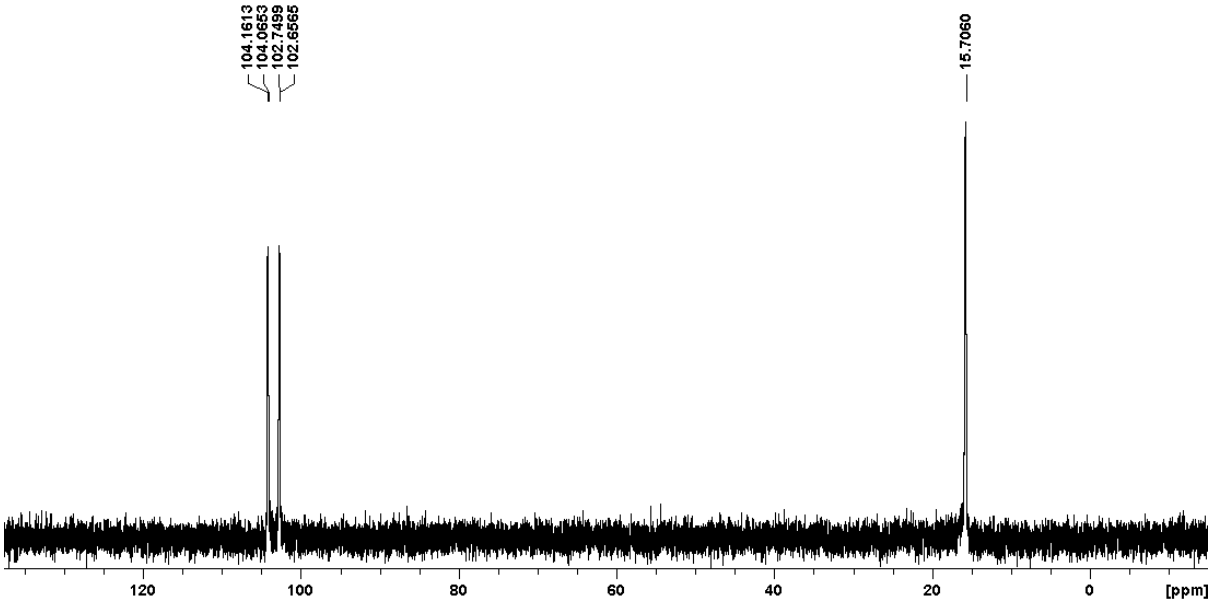


Figure S 17: ^{31}P NMR spectrum (25°C, $CDCl_3$, 202MHz) of 8

Characterisation of **9**

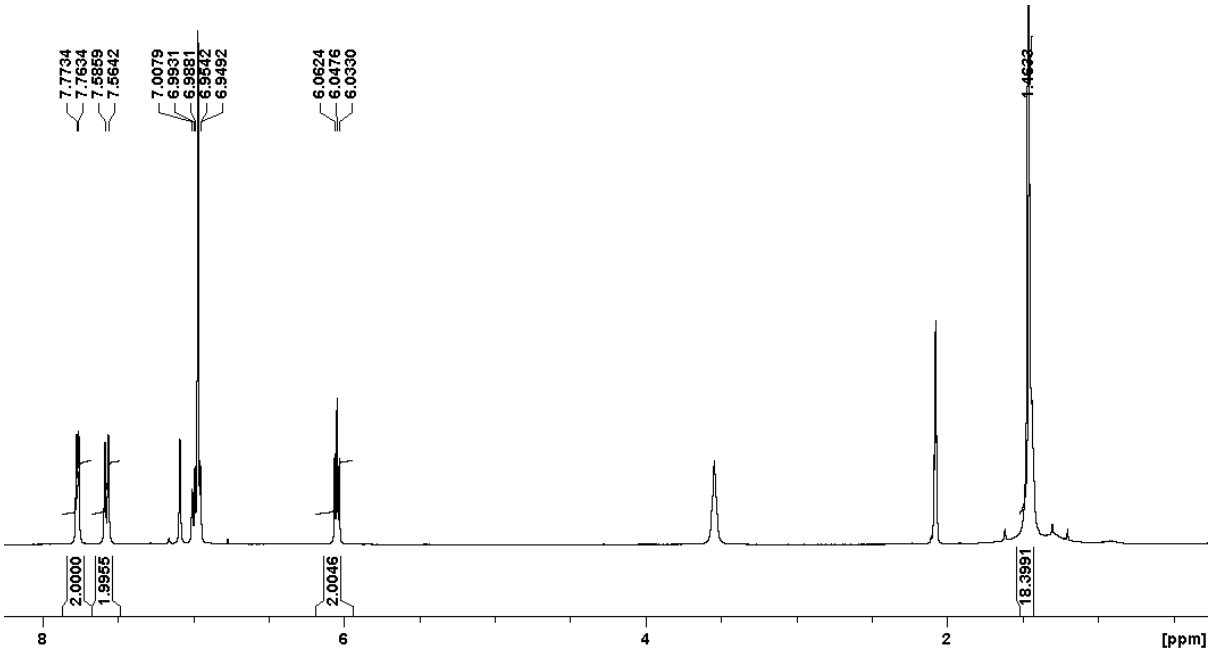


Figure S 18: ^{1}H NMR spectrum (25°C, d_8-toluene, 500 MHz) of 9

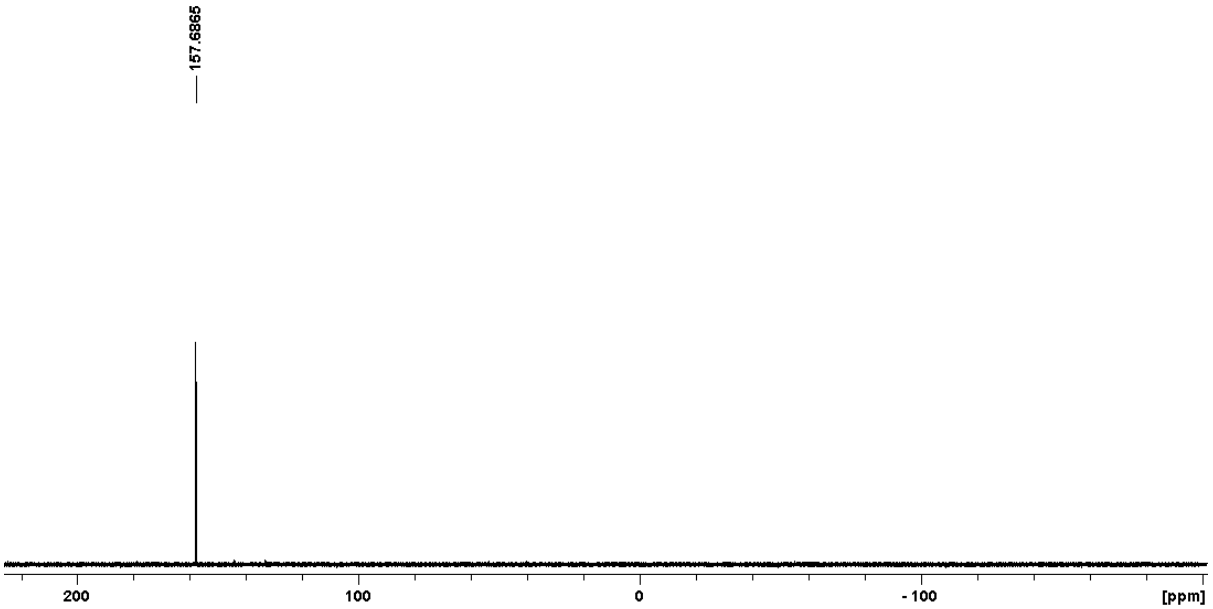


Figure S 19: ^{31}P NMR spectrum (25°C, d_8-toluene, 202MHz) of 9

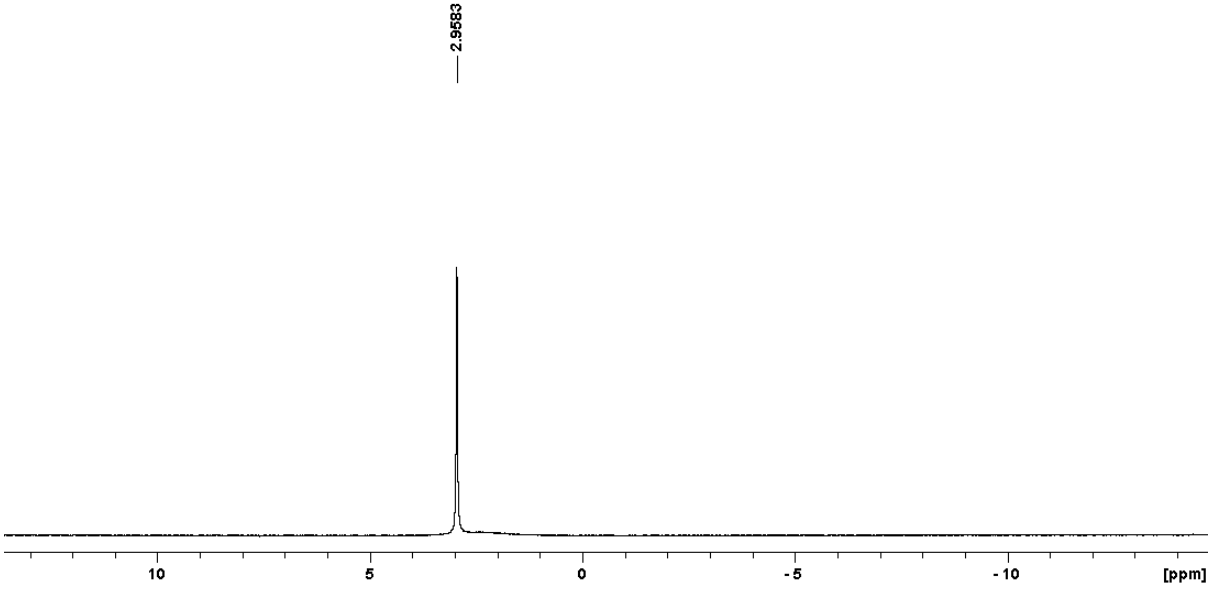


Figure S 20: ^{7}Li NMR spectrum (25°C, d_8-toluene, 194MHz) of 9

Characterisation of **10**

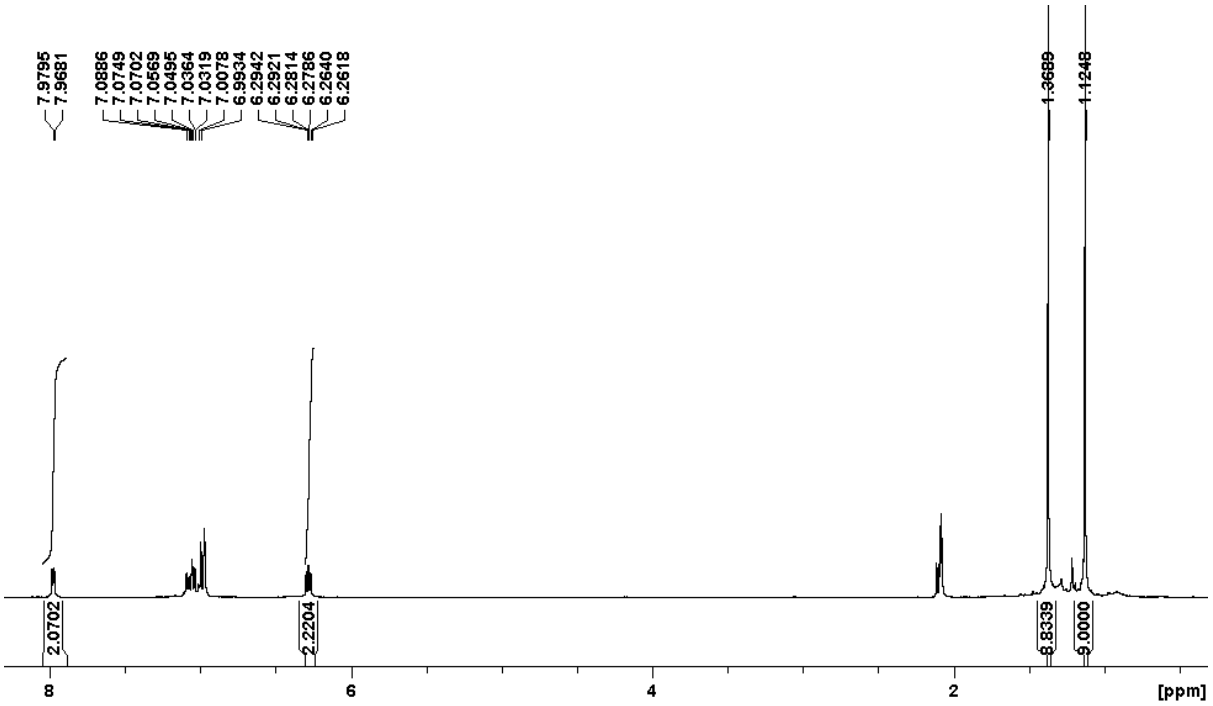


Figure S 21: ^{1}H NMR spectrum (25°C, d_8-toluene, 500 MHz) of 10

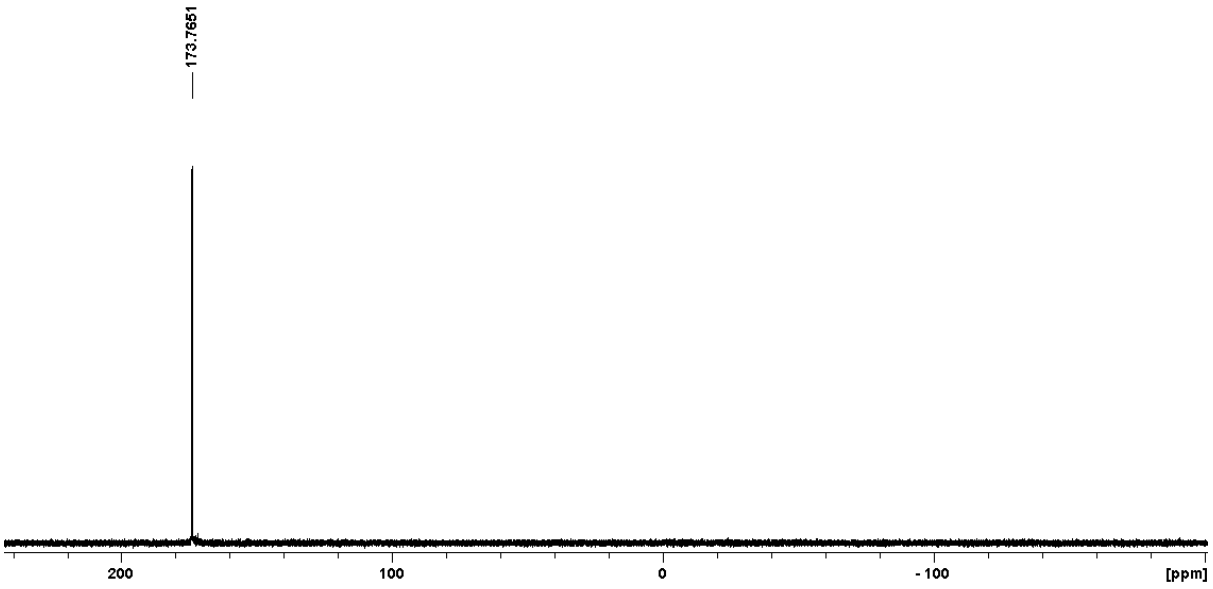


Figure S 22: ^{31}P NMR spectrum (25°C, d_8-toluene, 202MHz) of 10

Characterisation of **11**

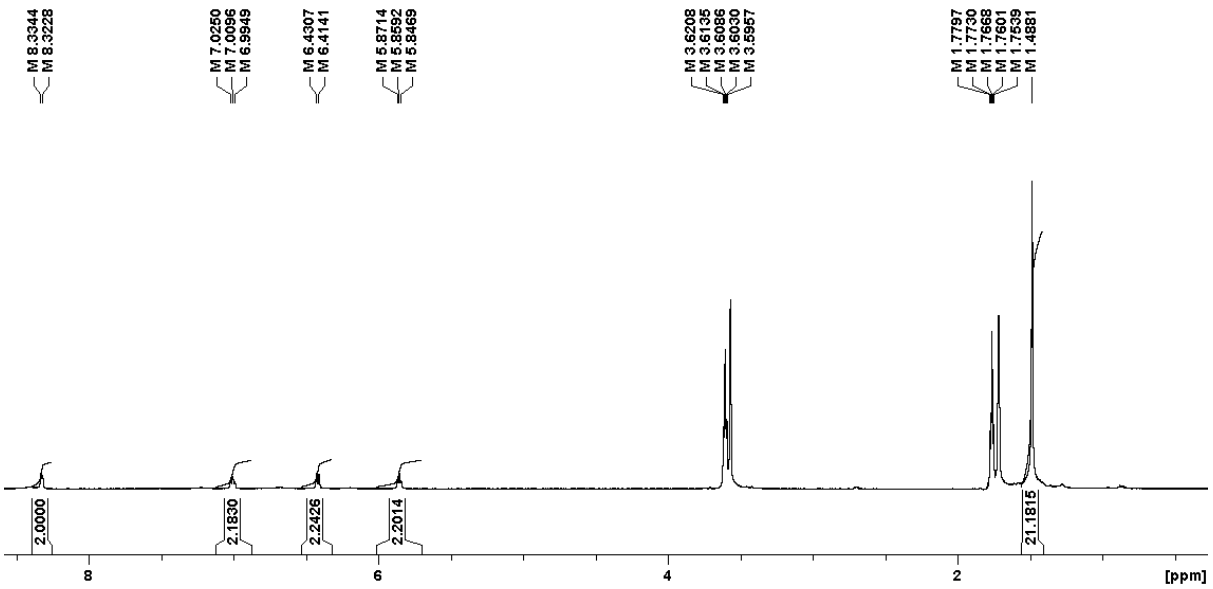


Figure S 23: ^{1}H NMR spectrum (25°C, d_8-THF, 500 MHz) of 11

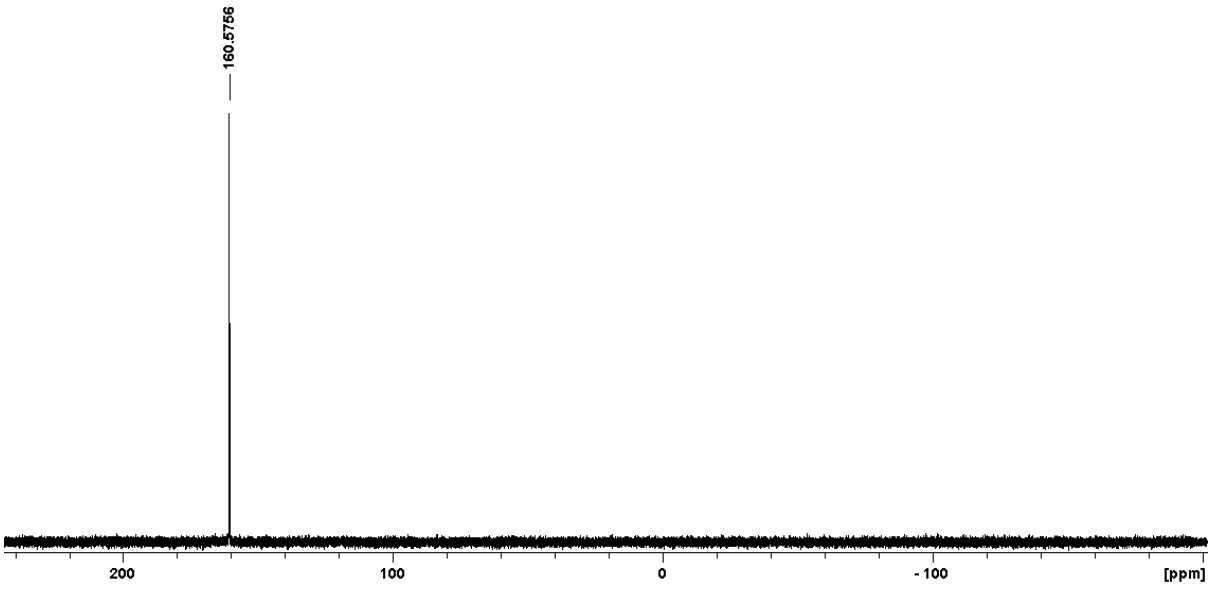


Figure S 24: ^{31}P NMR spectrum (25°C, d_8-THF, 202 MHz) of 11

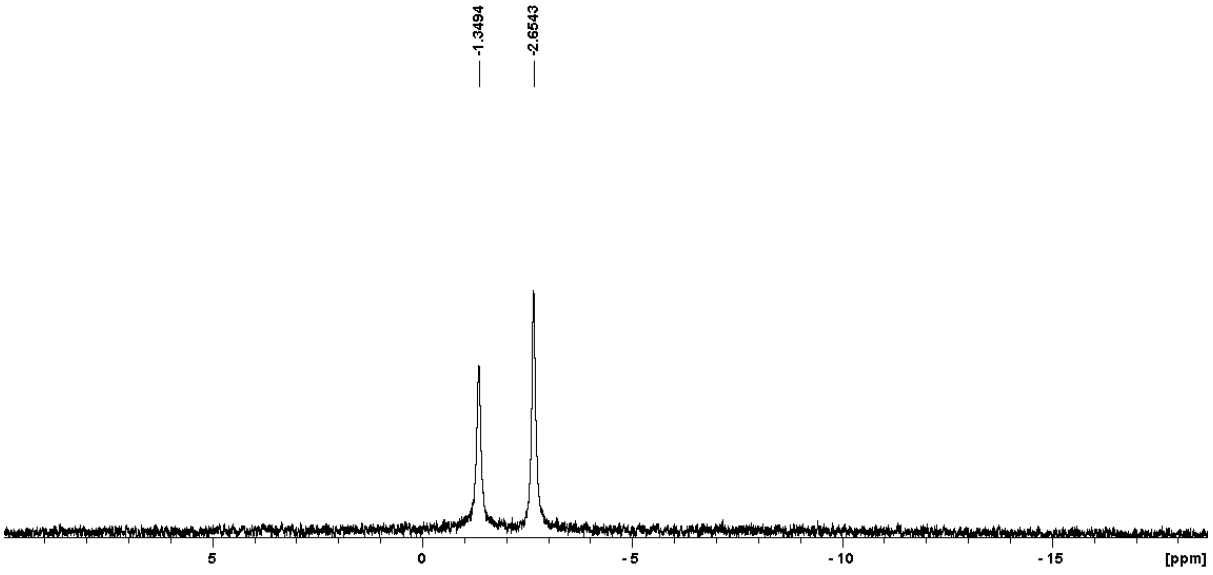


Figure S 25: ^{7}Li NMR spectrum (25°C, d_8-THF, 194MHz) of 11

Characterisation of **12**

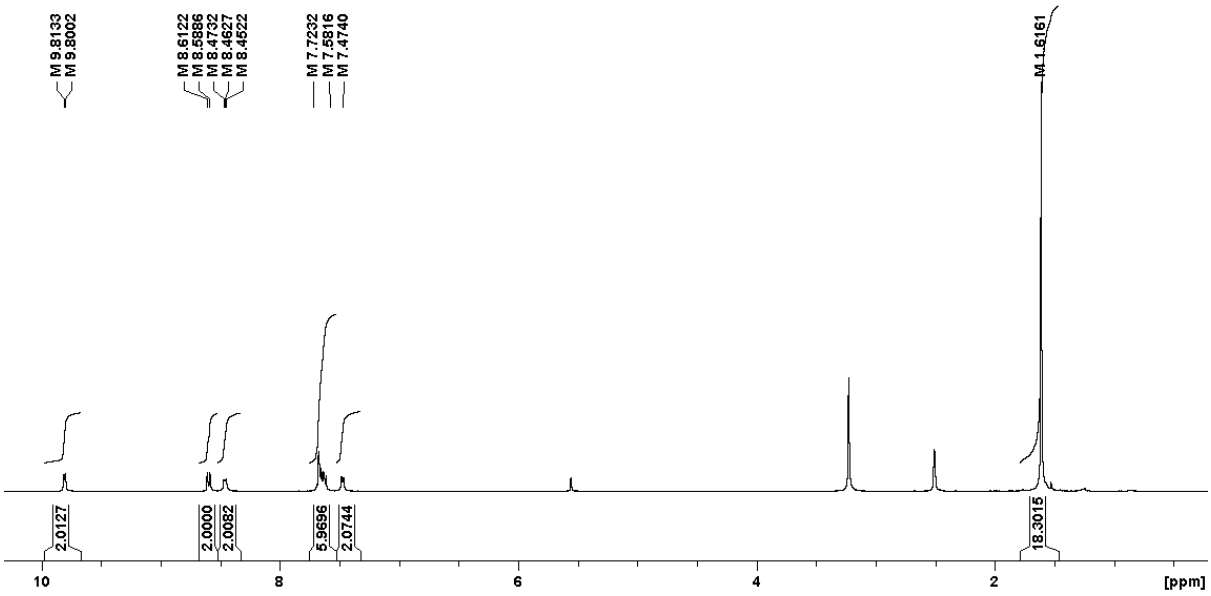


Figure S 26: ^{1}H NMR spectrum (25°C, d_6-DMSO, 500 MHz) of 12

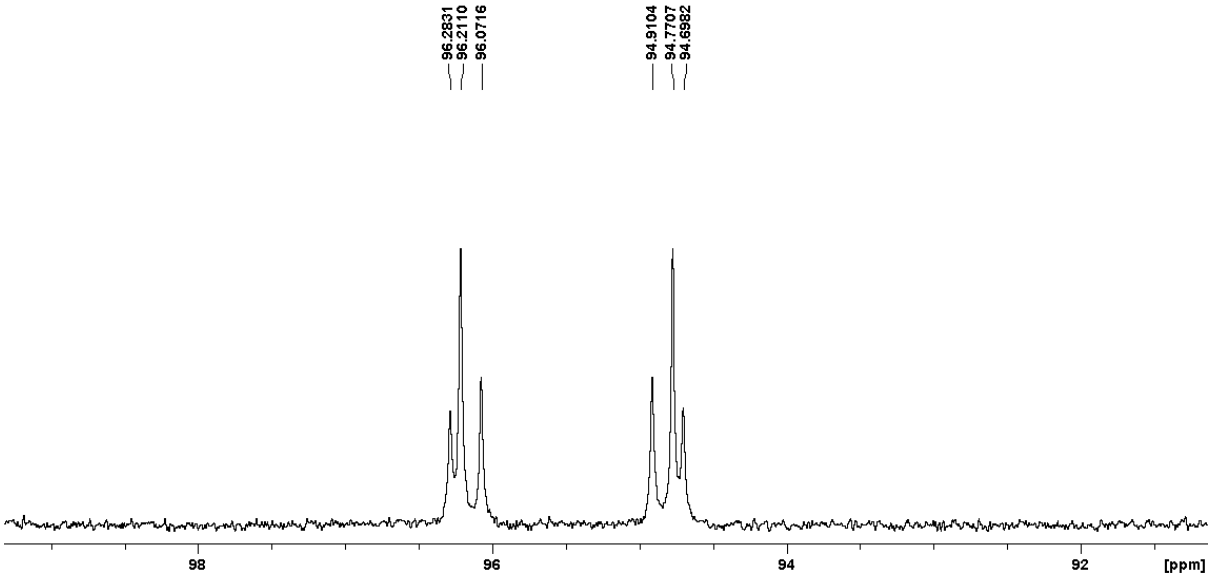


Figure S 27: ^{31}P NMR spectrum (25°C, d_6-DMSO, 202MHz) of 12

NMR Titration of **12** with TBACl and fitting

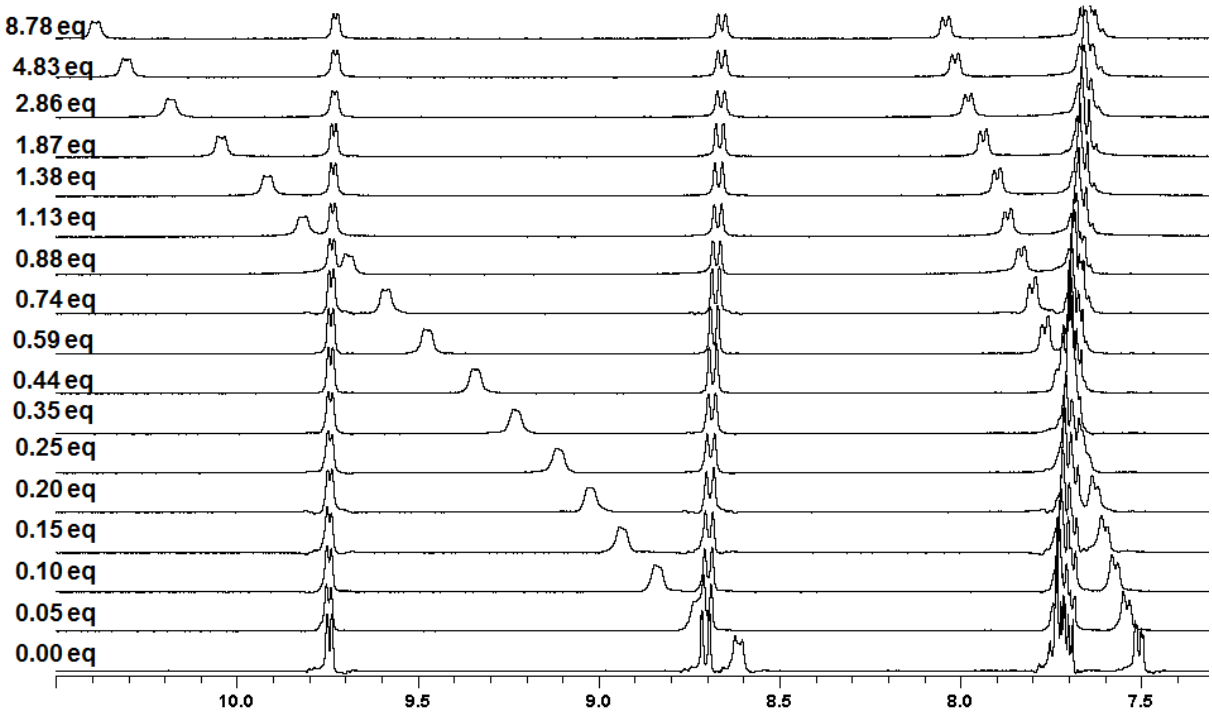


Figure S 28: ^{1}H NMR titration (25°C, d_6-DMSO, 400 MHz) of 12 with increasing amounts of tetrabutylammoniumchloride.

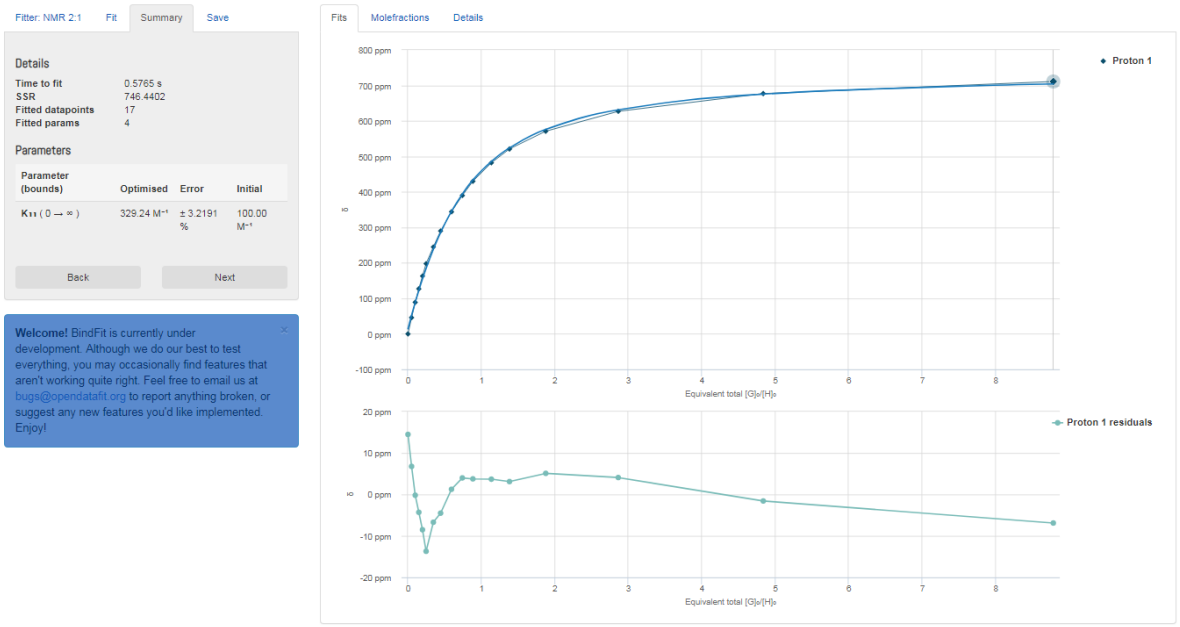


Figure S 29: Fit to a 2:1 non-cooperative binding model using the Bindfit program suite; fit to a cooperative model failed; y-axis in Hz not ppm.[1]

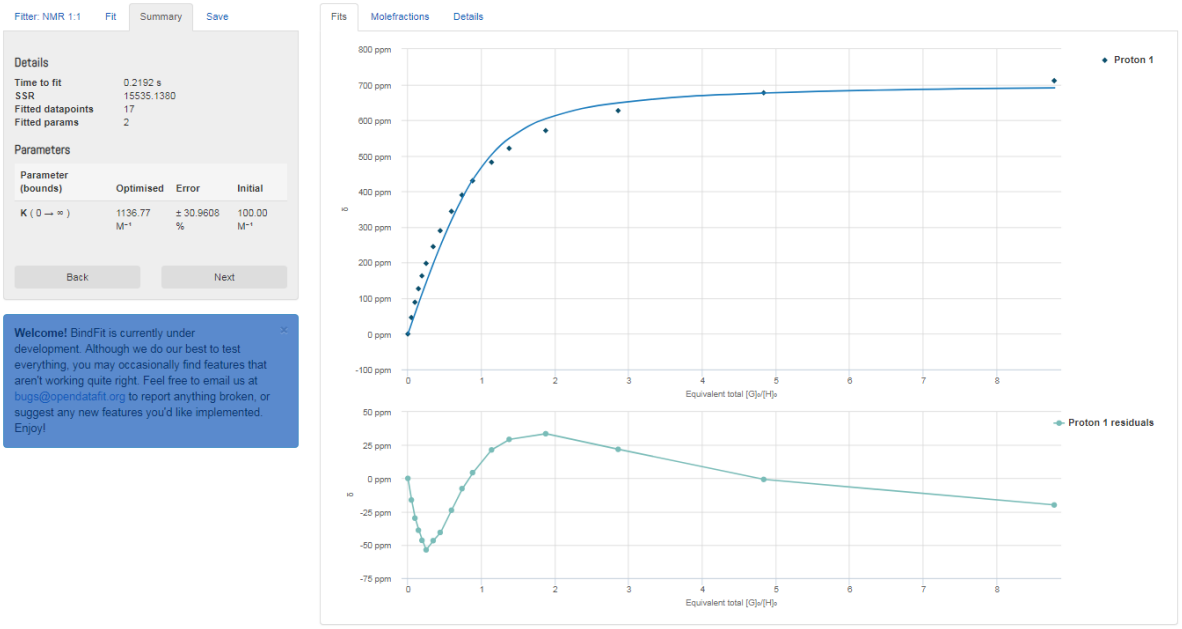


Figure S 30: Fit to a 1:1 binding model using the Bindfit program suite; fit to a cooperative model failed; y-axis in Hz not ppm.[1]

Characterisation of **13**

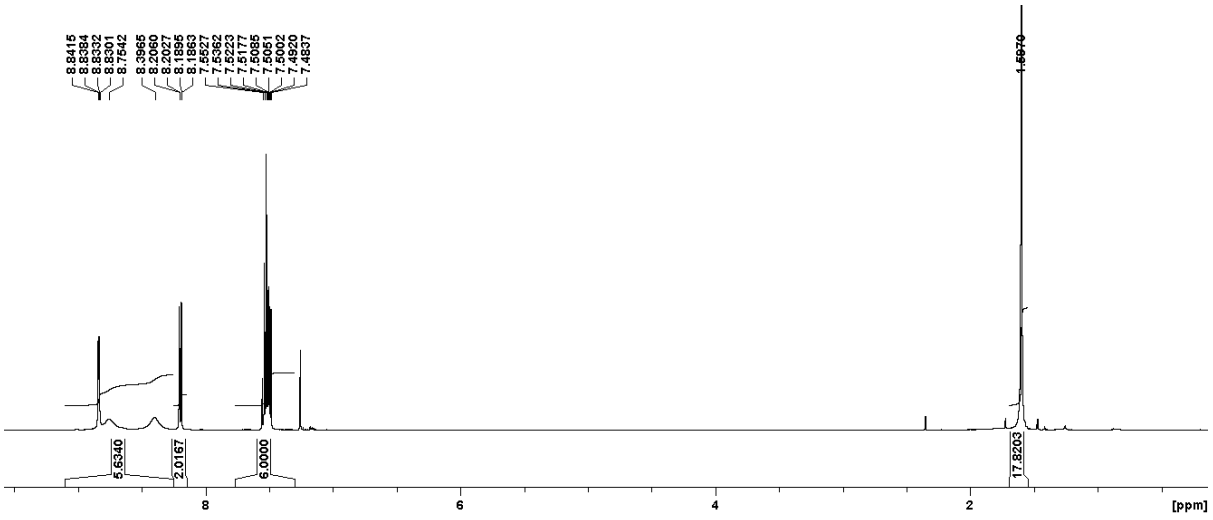


Figure S 31: ^{1}H NMR spectrum (25°C, CDCl, 500 MHz) of 13

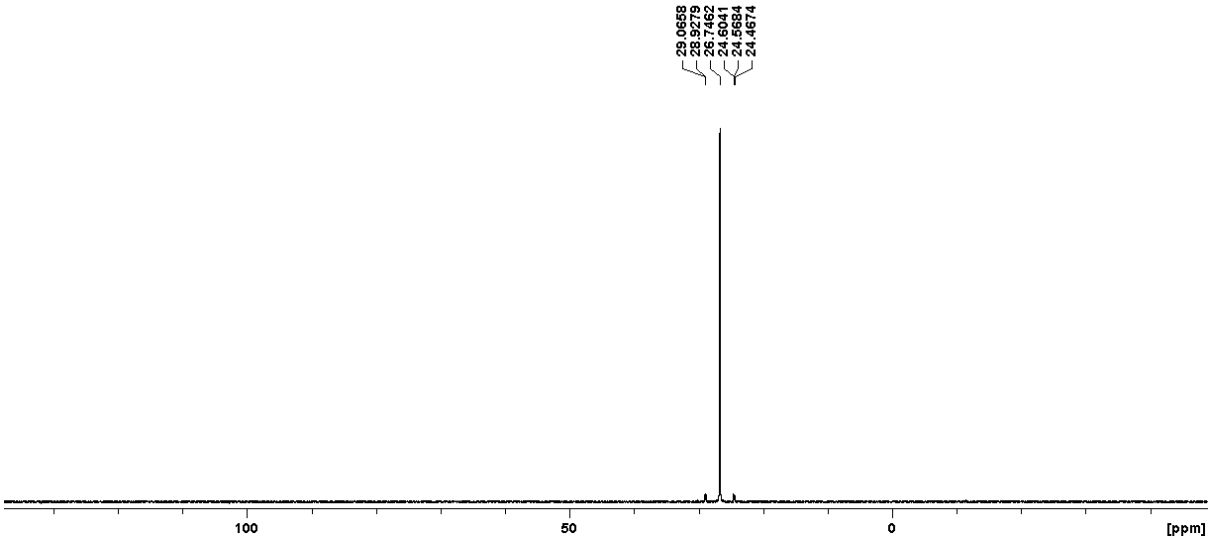


Figure S 32: ^{31}P NMR spectrum (25°C, $CDCl_3$, 202 MHz) of 13

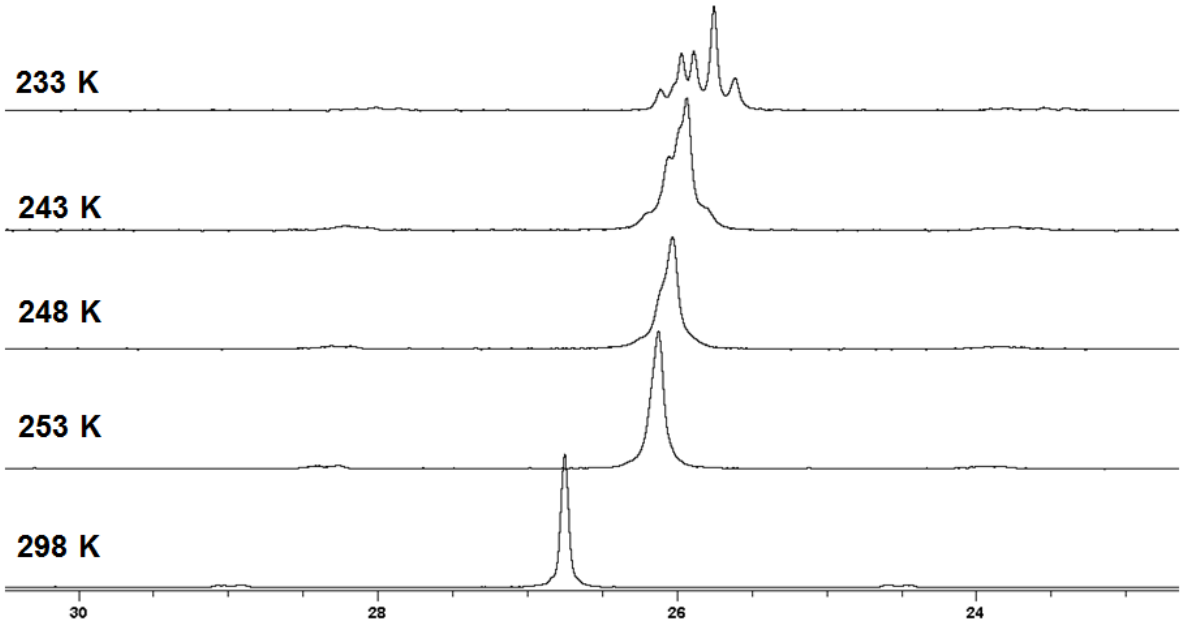


Figure S 33: ^{31}P VT NMR spectrum ($CDCl_3$, 202 MHz) of 13

Characterisation of **14**

14

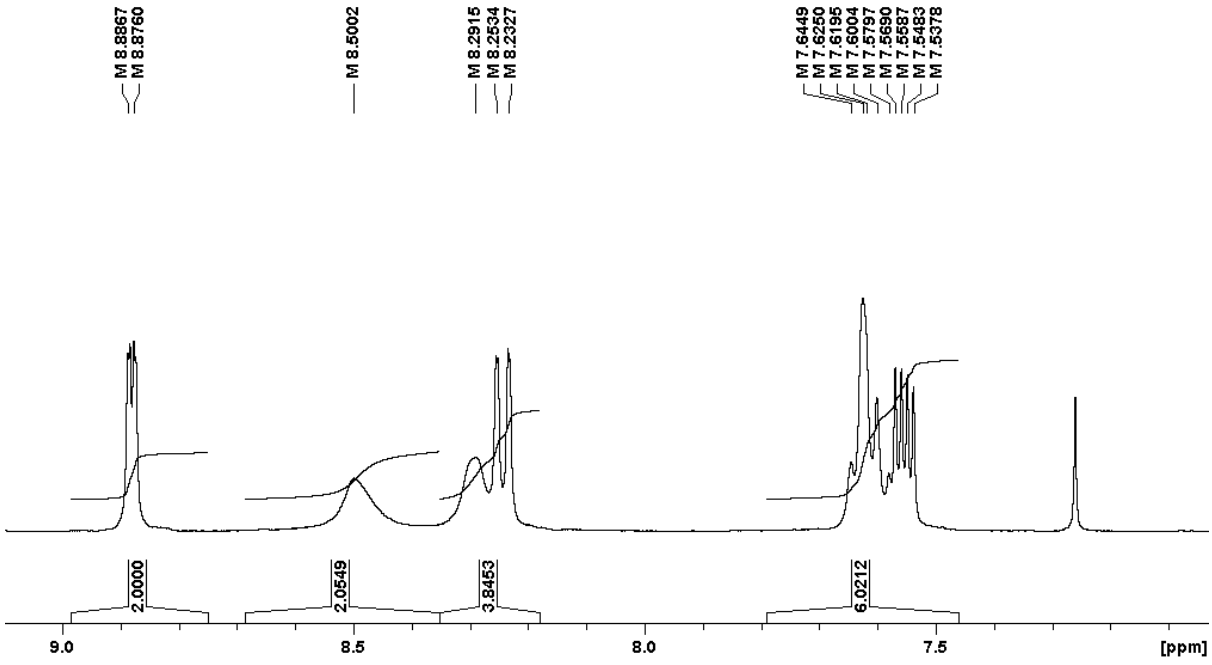


Figure S 34: ^{1}H NMR spectrum (25°C, CDCl, 500 MHz) of 14

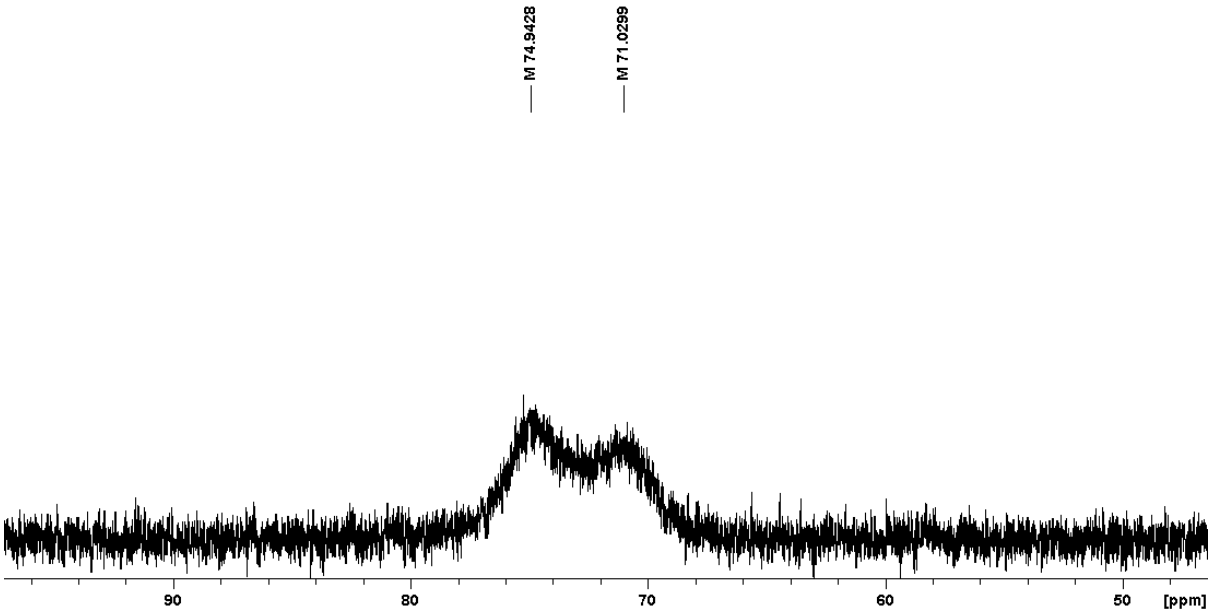


Figure S 35: ^{31}P NMR spectrum (25°C, $CDCl_3$, 202 MHz) of 14

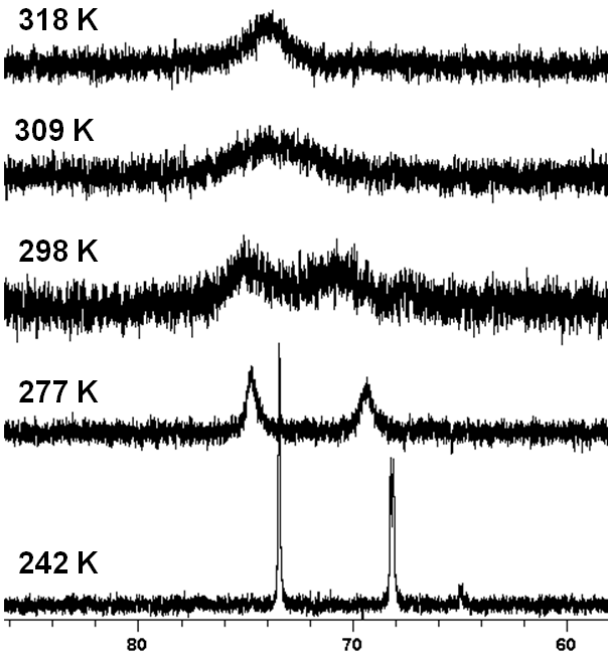


Figure S 36: ^{31}P VT NMR spectrum ($CDCl_3$, 202 MHz) of 14

Characterisation of **15**

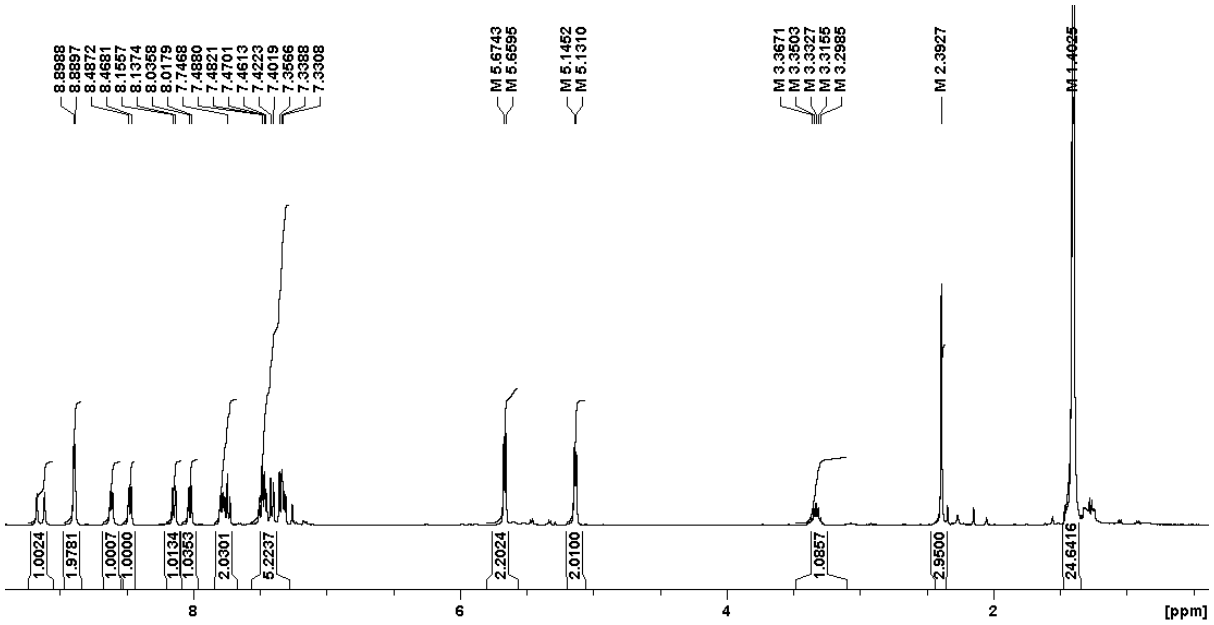


Figure S 37: ^{1}H NMR spectrum (25°C, CD_3Cl, 500 MHz) of 15

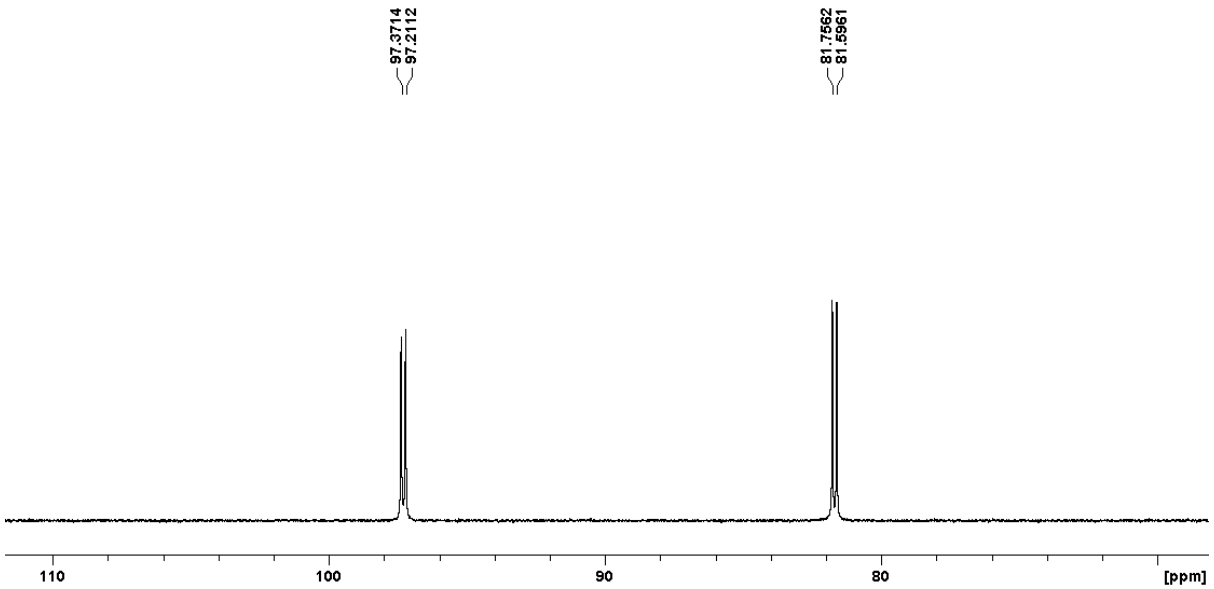


Figure S 38: ^{31}P NMR spectrum (25°C, $CDCl_3$, 202 MHz) of 15

Characterisation of **16**

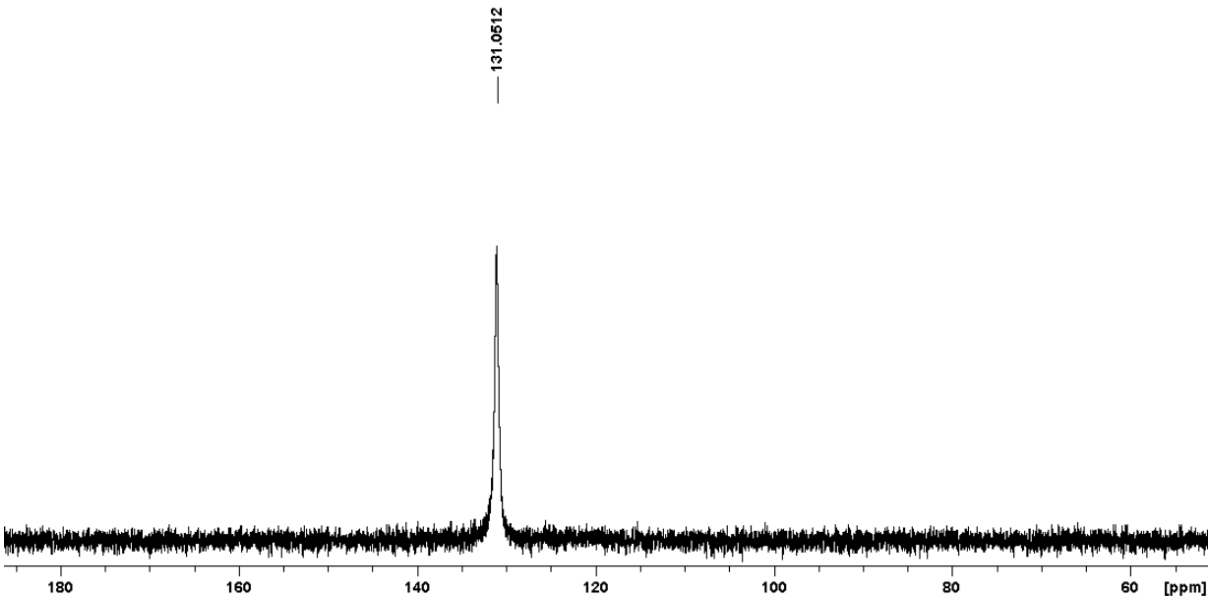


Figure S 39: ^{31}P NMR spectrum (25°C, d_8-toluene, 202 MHz) of 16

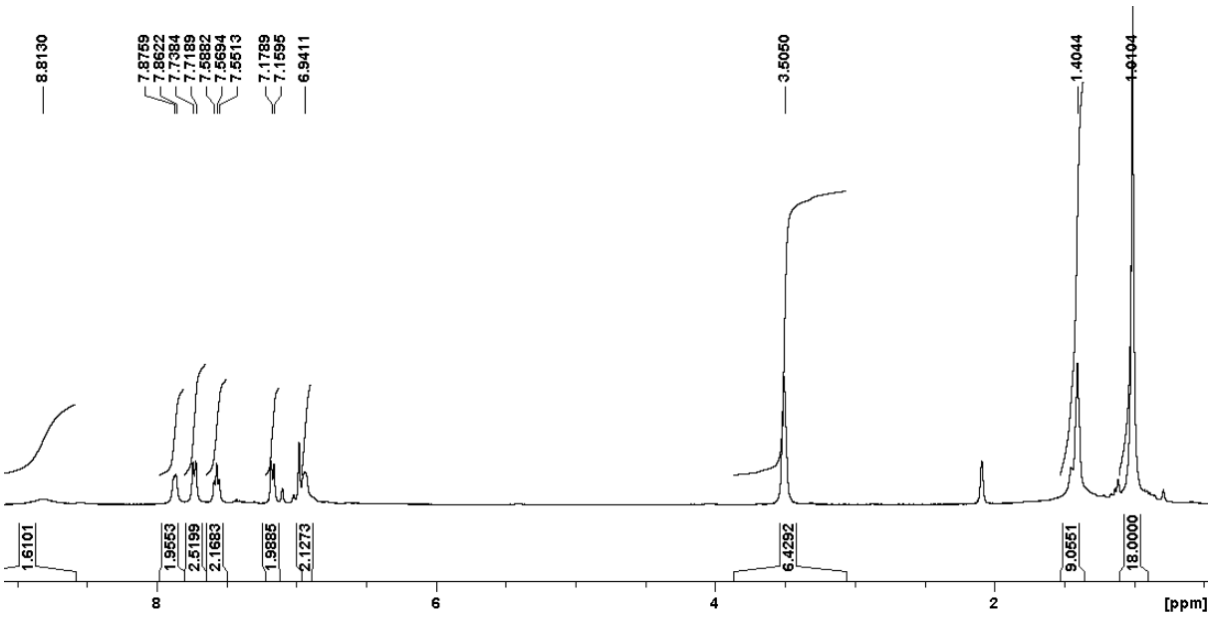


Figure S 40: ^{1}H NMR spectrum (25°C, d_8-toluene, 500 MHz) of 16

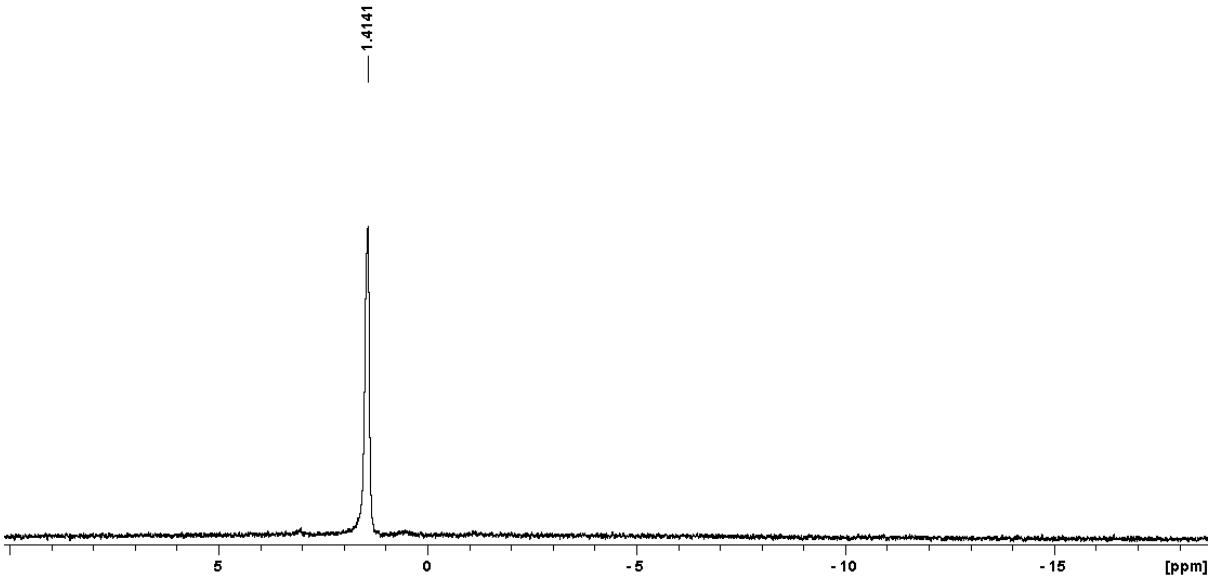


Figure S 41: ^{7}Li NMR spectrum (25°C, d_8-toluene, 194MHz) of 16

X-ray Crystallography

X-ray crystallographic data were collected using a D8-QUEST PHOTON-100 diffractometer equipped with an Incoatec IμS Cu microsource. The temperature was held at 180(2) K using an Oxford Cryosystems N_2 cryostat. Data integration and reduction were carried out with *SAINT* in the *APEX3* software suite. Multi-scan corrections were applied using SADABS. Structures were solved using *SHELXT*[1] and refined using *SHELXL*.[2]

Unless otherwise mentioned, the refinements were straightforward. For compounds **3**, **5**, **6**, **8**, **13**, **14** and **15**, H atoms attached to N atoms were located in difference Fourier maps and refined with an isotropic displacement parameter, and with the N–H distance restrained to 0.88(1) Å. For **4** and **12**, H atoms attached to N were placed geometrically (N–H = 0.88 Å) and refined as riding.

Compound 4 was refined as a 2-component inversion twin. The solvent used for crystallisation was CH_2Cl_2, but disorder produces atomic sites resembling $CHCl_3$. Two complete DCM molecules were defined, with one Cl atom common to both orientations. Site occupancies were refined for each component, constrained to sum to 1.0, and with geometrical restraints applied.

Compounds 8 and **12:** exhibit disorder of *tert*-butyl groups. The C–C and C…C distances were restrained to maintain regular tetrahedral geometry for the disorder components. Anisotropic ADPs are applied to all disordered C atoms, with ISOR restraints applied. Remaining elongation of the displacement ellipsoids is indicative of further rotational disorder.

Compound 9: conventional refinement clearly identified five molecules of THF in the asymmetric unit (20 per unit cell), but they are relatively poorly defined, with large displacement ellipsoids. This refinement gave a relatively large *wR*2 value (= 0.250). An additional refinement is reported with the

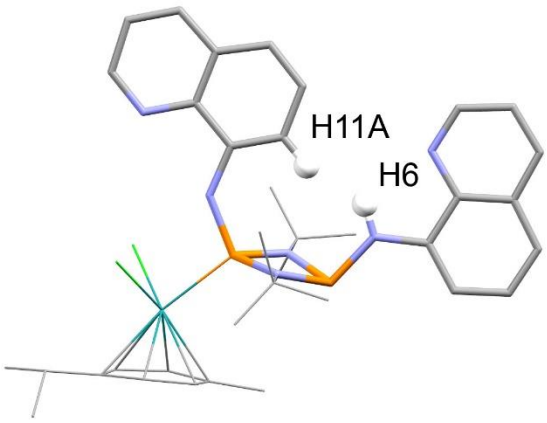
THF molecules omitted and *SQUEEZE* applied.[3] *SQUEEZE* corrects for a total of 788 electrons per unit cell, in good agreement with the expected total of 800 for 20 THF molecules. The result has a significantly smaller *wR*2 (= 0.159) and improved precision for the bond distances and angles of the main complex.

Compound 11: the carbonyl ligands on one Mo atom display significantly elongated displacement ellipsoids when refined anisotropically. These were modelled instead as two components with isotropic ADPs. Two of the coordinated THF molecules also display some disorder, and split C atoms in the disorder components were also refined with isotropic ADPs.

Compound 14: in addition to a well-ordered $CHCl_3$ molecule, the structure contains two apparent *n*-pentane molecules per unit cell, disordered across the inversion centres at (0.5,0,0) and (0,0.5,0.5). It is difficult to pick out well-defined molecules, so these molecules were eventually omitted and *SQUEEZE* was applied. The assumed *n*-pentane content is included in the empirical formula and in *F*(000).

Compound 15: the electron density indicates a DCM molecule occupying a site on the 4-fold axis, centred around 0.50,0.75,0.12. This was difficult to model as a single molecule, so *SQUEEZE* has been applied. *SQUEEZE* corrects exactly for 42 electrons per site, as expected for DCM. The solvent content amounts to four DCM per unit cell, which is 0.25 DCM per complex. This has been included in the empirical formula and in *F*(000).

This structure contains an apparent forced short H...H contact between quinolyl groups. Both H6 and H11A are evident in difference Fourier maps. The position of H6 is refined (with N–H restrained to 0.88(1) angstrom), and produces a sensible isotropic displacement parameter. The P–N(H) distance is consistent with all other similar structures and significantly different from the established P=N bonds in some of the other compounds. The displacement ellipsoids of the quinolyl group are moderately elongated perpendicular to the ring plane, which may indicate some out-of-plane displacement of this ring to mitigate this H...H contact.



Compound 16: contains a non-coordinated THF molecule showing conformational disorder. Two components were defined, with isotropic ADPs for all C atoms (anisotropic ADPs for the O atoms).

References

1. G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2015, **71**, 3–8.
2 G. M. Sheldrick, *Acta Crystallogr. Sect. C*, 2015, **71**, 3–8
3. A. L. Spek, *Acta Crystallogr. Sect. C*, 2015, C**71**, 9-18.

	3	**4**	**5**	**6**	**8**
CCDC number	1997071	1997075	1997070	1997072	1997074
Cambridge data number	DW_B2_0296	DW_B1_0295	DW_B1_0318	DW_B1_0317	DW_B1_0342
Chemical formula	$C_{28}H_{42}Cl_2N_6P_2Ru$	$C_{39}H_{58}Cl_8N_6P_2Ru_3$	$C_{19}H_{31}IN_6P_2$	$C_{23}H_{30}MoN_6O_4P_2$	$C_{22}H_{34}Cl_5N_6OP_2Rh$
Moiety formula	$C_{28}H_{42}Cl_2N_6P_2Ru$	$C_{38}H_{56}Cl_6N_6P_2Ru_3,CH_2Cl_2$	$C_{19}H_{31}N_6P_2^+,I^-$	$C_{23}H_{30}MoN_6O_4P_2$	$C_{20}H_{30}ClN_6OP_2Rh,2(CH_2Cl_2)$
Formula weight	696.58	1259.66	532.34	612.41	740.65
Temperature / K	180(2)	180(2)	180(2)	180(2)	180(2)
Crystal system	triclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	P–1	$P2_1$	$P2_1/c$	P–1	$P2_1/c$
a / Å	9.1453(3)	10.2519(3)	14.9210(6)	9.0018(3)	11.0171(3)
b / Å	10.1120(4)	15.5160(5)	12.1904(4)	10.1396(3)	20.0078(5)
c / Å	18.4952(6)	15.4618(5)	14.3360(5)	16.0932(5)	14.5787(4)
alpha / °	84.586(2)	90	90	92.700(2)	90
beta / °	76.586(2)	102.107(2)	106.730(2)	105.0885(14)	101.8831(8)
gamma / °	68.635(2)	90	90	91.079(2)	90
Unit-cell volume / $Å^3$	1549.30(10)	2404.78(13)	2497.24(16)	1415.95(8)	3144.69(15)
Z	2	2	4	2	4
Calc. density / g cm^{-3}	1.493	1.740	1.416	1.436	1.564
F(000)	720	1264	1080	628	1504
Radiation type	CuKα	CuKα	CuKα	CuKα	CuKα
Absorption coefficient / mm^{-1}	6.883	12.539	11.409	5.184	9.489
Crystal size / mm^3	0.15 x 0.13 x 0.07	0.07 x 0.05 x 0.05	0.22 x 0.08 x 0.08	0.14 x 0.08 x 0.03	0.35 x 0.30 x 0.25
2-Theta range / °	4.91-133.52	5.85-133.37	6.19-133.54	5.70-133.20	7.61-133.40
Completeness to max 2θ	0.969	0.990	0.994	0.991	0.991
No. of reflections measured	11868	23627	14477	13982	16849
No. of independent reflections	5298	8347	4401	4953	5522
R_{int}	0.0311	0.0599	0.0708	0.0340	0.0368
No. parameters / restraints	369 / 2	547 / 7	268 / 2	336 / 1	376 / 49
Final R1 values (I > 2σ(I))	0.0259	0.0396	0.0423	0.0271	0.0353
Final wR(F^2) values (all data)	0.0311	0.0476	0.0684	0.0344	0.0361
Goodness-of-fit on F^2	1.063	1.074	1.026	1.069	1.092
Largest difference peak & hole / e $Å^{-3}$	0.351, -0.518	0.865, -1.012	0.545, -0.477	0.299, -0.436	0.650, -0.899
Flack parameter		0.405(17)[a]			

[a] Refined as an inversion twin.

	9[b]	**9_squeeze**[b]	**10**	**11**	**12**
CCDC number	1997069	1997073	1997078	1997081	1997080
Cambridge data number	DW_B1_0321	DW_B1_0321	DW_B1_0348	DW_B1_0350	DW_B1_0307
Chemical formula	$C_{56}H_{92}Li_4N_{12}O_5P_4$	$C_{56}H_{92}Li_4N_{12}O_5P_4$	$C_{18}H_{26}ClN_6P_2Sb$	$C_{50}H_{74}Li_2Mo_2N_6O_{14}P_2$	$C_{68}H_{91}Cl_4N_{15}O_7P_4Ru_4S_3$
Moiety formula	$C_{36}H_{52}Li_4N_{12}P_4$,5($C_4H_8O$)	$C_{36}H_{52}Li_4N_{12}P_4$ [+solvent]	$C_{18}H_{26}ClN_6P_2Sb$	$C_{34}H_{42}LiMo_2N_6O_{10}P_2^-$, $C_{16}H_{32}LiO_4^+$	2($C_{28}H_{32}Cl_2N_6O_2P_2Ru_2$, 3($C_2H_6OS$),3($C_2H_3N$)
Formula weight	1165.05	1165.05	545.59	1250.85	1996.69
Temperature / K	180(2)	180(2)	180(2)	180(2)	180(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	P–1
a / Å	17.2715(4)	17.2715(4)	11.9663(4)	11.1962(3)	12.9507(3)
b / Å	14.0512(4)	14.0512(4)	9.7503(3)	26.7635(7)	13.6610(3)
c / Å	27.0601(8)	27.0601(8)	20.4587(7)	20.1316(5)	24.9545(6)
alpha / °	90	90	90	90	77.7605(11)
beta / °	99.968(2)	99.968(2)	106.1366(12)	103.217(2)	75.9773(11)
gamma / °	90	90	90	90	88.6159(12)
Unit-cell volume / $Å^3$	6468.0(3)	6468.0(3)	2292.97(13)	5872.6(3)	4184.27(17)
Z	4	4	4	4	2
Calc. density / g cm^{-3}	1.196	1.196	1.580	1.415	1.585
F(000)	2496	2496	1096	2592	2024
Radiation type	CuKα	CuKα	CuKα	CuKα	CuKα
Absorption coefficient / mm^{-1}	1.499	1.499	12.067	4.551	8.808
Crystal size / mm^3	0.18 x 0.18 x 0.05	0.18 x 0.18 x 0.05	0.14 x 0.14 x 0.04	0.14 x 0.14 x 0.10	0.32 x 0.17 x 0.08
2-Theta range / °	5.66-133.58	5.66-133.58	7.76-133.63	5.59-134.21	6.62-133.52
Completeness to max 2θ	0.991	0.991	0.999	0.994	0.991
No. of reflections measured	34370	34354	27354	76668	49117
No. of independent reflections	11395	11389	4075	10439	14716
R_{int}	0.0599	0.0599	0.0422	0.1069	0.0609
No. parameters / restraints	742 / 195	517 / 0	259 / 0	687 / 63	1018 / 132
Final R1 values (I > 2σ(I))	0.0885	0.0598	0.0215	0.0487	0.0428
Final wR(F^2) values (all data)	0.1200	0.0825	0.0251	0.0709	0.0524
Goodness-of-fit on F^2	1.038	1.021	1.092	1.026	1.087
Largest difference peak & hole / e $Å^{-3}$	0.680, -0.649	0.283, -0.291	0.263, -0.586	0.924, -1.172	1.749, -1.166

[b] Both a conventional refinement and *SQUEEZE* refinement are reported – see supplementary note.

	13	**14_squeeze**[c]	**15_squeeze**[c]	**16**
CCDC number	1997076	1997079	1997082	1997077
Cambridge data number	DW_B1_0352	DW_B1_0347	DW_B1_0351	DW_B1_0353
Chemical formula	$C_{26}H_{32}N_6P_2Se_2$	$C_{29.5}H_{39}Au_2Cl_5N_6P_2$	$C_{36.25}H_{46.5}Cl_{2.5}N_6P_2Ru$	$C_{38}H_{54}Li_2N_6O_3P_2$
Moiety formula	$C_{26}H_{32}N_6P_2Se_2$	$C_{26}H_{32}Au_2Cl_2N_6P_2$ [+solvent]	$C_{36}H_{46}Cl_2N_6P_2Ru$,0.25(CH_2Cl_2)	$C_{34}H_{46}Li_2N_6O_2P_2$,$C_4H_8O$
Formula weight	648.43	1110.79	817.93	718.69
Temperature / K	180(2)	180(2)	180(2)	180(2)
Crystal system	orthorhombic	monoclinic	tetragonal	triclinic
Space group	$P2_12_12_1$	$P2_1/n$	$I4_1/a$	P–1
a / Å	8.6388(3)	13.1448(4)	31.3989(10)	11.7548(3)
b / Å	16.4585(5)	19.8365(6)	31.3989(10)	11.8272(4)
c / Å	20.2269(6)	14.9792(5)	14.7265(5)	15.8891(5)
alpha / °	90	90	90	71.8345(13)
beta / °	90	97.116(2)	90	71.0760(14)
gamma / °	90	90	90	88.0370(14)
Unit-cell volume / $Å^3$	2875.90(16)	3875.7(2)	14518.7(10)	1979.97(11)
Z	4	4	16	2
Calc. density / g cm^{-3}	1.498	1.904	1.497	1.205
F(000)	1312	2124	6760	768
Radiation type	CuKα	CuKα	CuKα	CuKα
Absorption coefficient / mm^{-1}	4.473	18.214	6.302	1.331
Crystal size / mm^3	0.08 x 0.08 x 0.06	0.10 x 0.10 x 0.10	0.14 x 0.14 x 0.10	0.20 x 0.20 x 0.10
2-Theta range / °	6.92-133.65	7.43-140.76	5.63-133.74	6.20-134.05
Completeness to max 2θ	0.999	0.997	0.999	0.993
No. of reflections measured	17875	33480	71539	22266
No. of independent reflections	5085	7374	6451	6996
R_{int}	0.0374	0.0451	0.0777	0.0428
No. parameters / restraints	339 / 0	393 / 2	504 / 98	462 / 10
Final R1 values (I > 2σ(I))	0.0227	0.0245	0.0309	0.0486
Final wR(F^2) values (all data)	0.0260	0.0321	0.0438	0.0615
Goodness-of-fit on F^2	1.067	1.029	1.036	1.042
Largest difference peak & hole / e $Å^{-3}$	0.217, -0.269	0.982, -1.016	0.602, -0.364	0.700, -0.714
Flack parameter	-0.019(11)			

[c] Disordered solvent molecules handled with *SQUEEZE* – see supplementary note.