Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

for

Synthesis and Reactivity of Uranium(IV) Complex Supported by Monoanionic Nitrogen-Phosphorus Ligand

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Table S1. Crystal data and structure refinements for **1** and **2**.

Complex	**1**	**2**
Formula	$C_{20}H_{48}Cl_2N_4P_2U$	$C_{20}H_{48}I_2N_4P_2U$
*M*r [g/mol]	715.49	898.39
Temp. [K]	296.15	193.00
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a[Å]	22.444(6)	8.9014(7)
b[Å]	8.321(2)	14.8611(12)
c[Å]	16.158(4)	11.4945(10)
α[°]	90	90
β[°]	98.132(8)	96.941(4)
γ[°]	90	90
Volume[Å^3]	2987.1(13)	1509.4(2)
Z/$D_{calcd.}$[g/cm^3]	4/1.591	2/1.977
μ[mm^{-1}]	5.733	23.141
F(000)	1408.0	848.0
θ range/deg	5.164 - 54.914	10.132 - 107.77
Index ranges	$-21 \le h \le 29$ $-10 \le k \le 10$ $-20 \le l \le 20$	$-10 \le h \le 9$ $-16 \le k \le 17$ $-13 \le l \le 13$
Collected data	26266	9293
Unique data	6741 [R_{int} = 0.0557, R_{sigma} = 0.0508]	2735 [R_{int} = 0.0469, R_{sigma} = 0.0376]
Completeness	99%	99%
Data/parameters	6741/0/274	2740/0/139
GOF on F^2	1.021	1.192
Final R indices [I>2σ(*I*)]	R_1 = 0.0320 wR_2 = 0.0633	R_1 = 0.0269 wR_2 = 0.0747
Final R indices [all data]	R_1 = 0.0499 wR_2 = 0.0715	R_1 = 0.0290 wR_2 = 0.0756
Largest diff. peak/hole (e·Å^{-3})	1.85/-1.52	1.09/-1.33

Table S2. Crystal data and structure refinements for **3** and **4**.

Complex	**3**	**4**
Formula	$C_{32}H_{56}N_4P_2U$	$C_{29}H_{59}N_5P_2U$
*M*r [g/mol]	796.77	777.78
Temp. [K]	193.00	296.15
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	P-1
a[Å]	11.1259(5)	10.0133(5)
b[Å]	26.0312(11)	12.6600(6)
c[Å]	12.8003(5)	14.4679(7)
α[°]	90	79.663(2)
β[°]	109.612(2)	71.870(2)
γ[°]	90	86.689(2)
Volume[Å^3]	3492.2(3)	1714.72(15)
Z/$D_{calcd.}$[g/cm^3]	4/1.515	2/1.506
μ[mm^{-1}]	10.517	4.851
F(000)	1592.0	780.0
θ range/deg	5.908-107.864	4.28-55.084
Index ranges	$-12 \le h \le 13$ $-31 \le k \le 29$ $-15 \le l \le 14$	$-9 \le h \le 13$ $-16 \le k \le 16$ $-17 \le l \le 18$
Collected data	39278	16048
Unique data	6363 [R_{int} = 0.0740, R_{sigma} = 0.0578]	7817 [R_{int} = 0.0528, R_{sigma} = 0.0693]
Completeness	100%	99%
Data/parameters	6363/1116/517	7817/0/347
GOF on F^2	1.114	1.032
Final R indices [I>2σ(*I*)]	R_1 = 0.0952 wR_2 = 0.1809	R_1 = 0.0366 wR_2 = 0.0939
Final R indices [all data]	R_1 = 0.1342 wR_2 = 0.1996	R_1 = 0.0397 wR_2 = 0.0963
Largest diff. peak/hole (e·Å^{-3})	5.43/-4.54	1.09/-1.32

Table S3. Crystal data and structure refinements for **5-7**.

Complex	**5·2C$_4$H$_8$O**	**6**	**7·CH$_2$Cl$_2$**
Formula	$C_{56}H_{128}Cl_8N_8O_4P_4Ru_2U_2$	$C_{40}H_{96}Cl_6N_8P_4Rh_2U_2$	$C_{42}H_{100}Cl_{10}N_8P_4Ir_2U_2$
*M*r [g/mol]	2063.34	1707.70	2056.13
Temp. [K]	296.15	193.00	193.00
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a[Å]	14.973(3)	10.7929(4)	11.5738(6)
b[Å]	12.2805(19)	26.3286(10)	16.9717(9)
c[Å]	22.594(4)	11.1451(4)	18.2716(9)
α[°]	90	90	90
β[°]	102.793(6)	110.635(2)	96.101(2)
γ[°]	90	90	90
Volume[Å^3]	4051.2(11)	2963.83(19)	3568.7(3)
Z/$D_{calcd.}$[g/cm^3]	2/1.691	2/1.914	2/1.913
μ[mm^{-1}]	4.737	16.493	8.738
F(000)	2040.0	1656.0	1952.0
θ range/deg	4.334-54.938	5.84-108.086	3.984-55
Index ranges	$-17 \le h \le 19$ $-15 \le k \le 15$ $-29 \le l \le 26$	$-13 \le h \le 13$ $-30 \le k \le 31$ $-13 \le l \le 13$	$-15 \le h \le 13$ $-21 \le k \le 22$ $-23 \le l \le 23$
Collected data	33633	29584	31309
Unique data	9177 [R_{int} = 0.0992, R_{sigma} = 0.0927]	5437 [R_{int} = 0.0685, R_{sigma} = 0.0523]	8174 [R_{int} = 0.0430, R_{sigma} = 0.0381]
Completeness	99%	99%	99%
Data/parameters	9177/131/411	5437/12/292	8174/54/338
GOF on F^2	0.987	1.025	1.030
Final R indices [I>2σ(*I*)]	R_1 = 0.0717 wR_2 = 0.1951	R_1 = 0.0485 wR_2 = 0.1316	R_1 = 0.0294 wR_2 = 0.0621

Final R indices [all data]	R_1 = 0.0965 wR_2 = 0.2244	R_1 = 0.0613 wR_2 = 0.1402	R_1 = 0.0394 wR_2 = 0.0660
Largest diff. peak/hole ($e \cdot Å^{-3}$)	1.36/-1.70	3.09/-2.24	1.55/-0.93

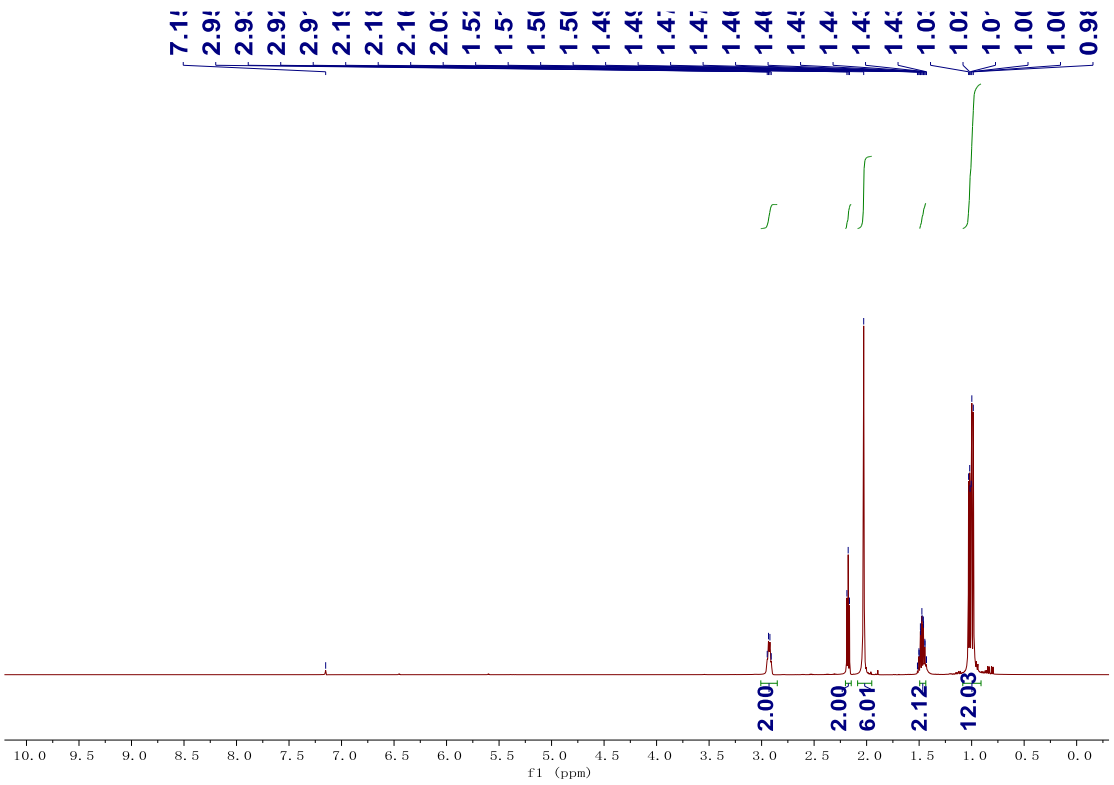

Figure S1. ^{1}H NMR spectrum of ligand **L3** in benzene-d_6.

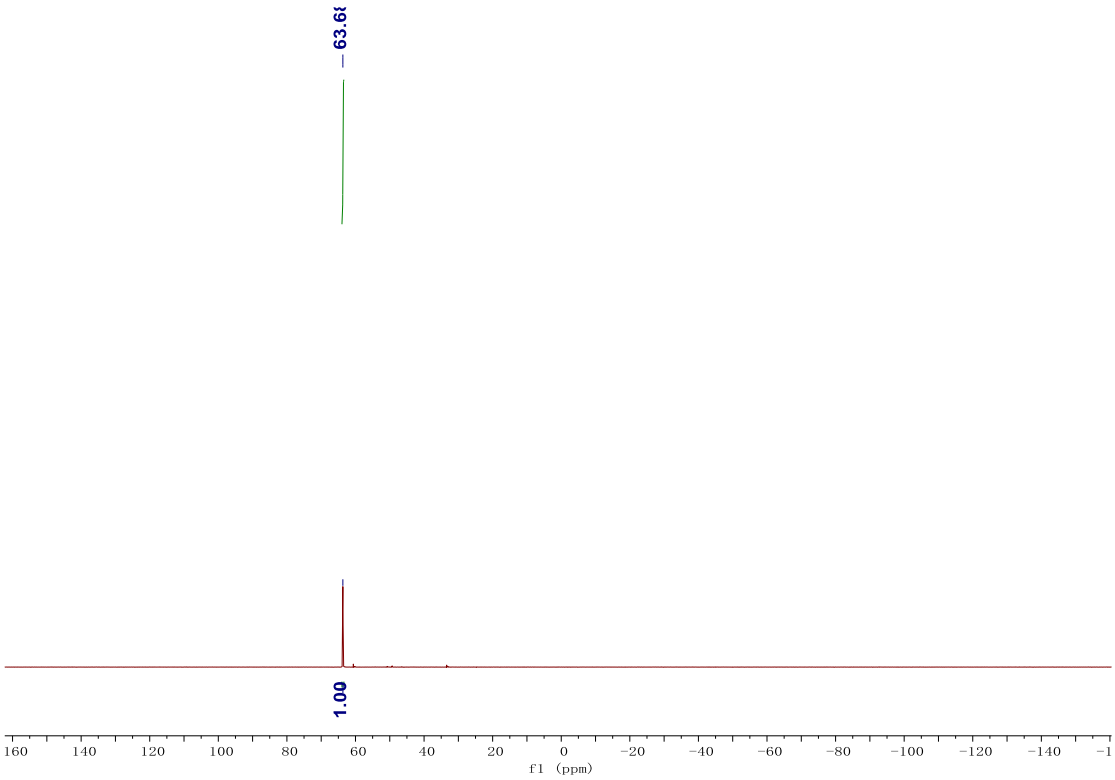

Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum of ligand **L3** in benzene-d_6.

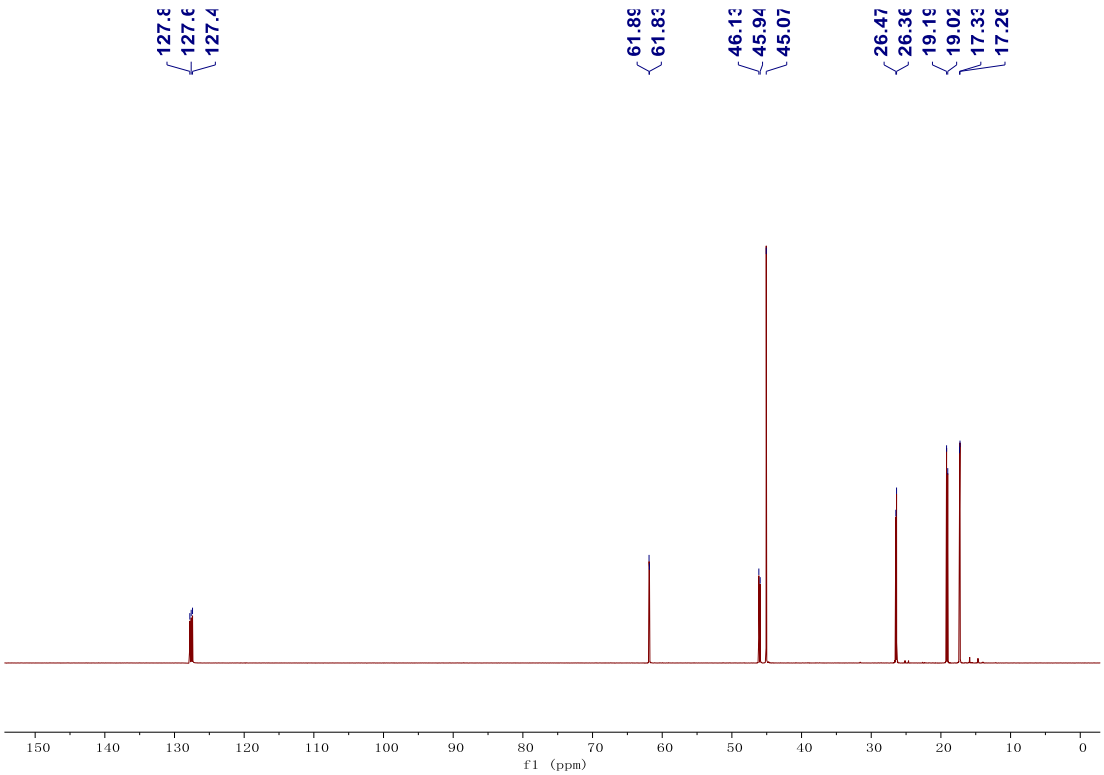

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of ligand **L3** in benzene-d_6.

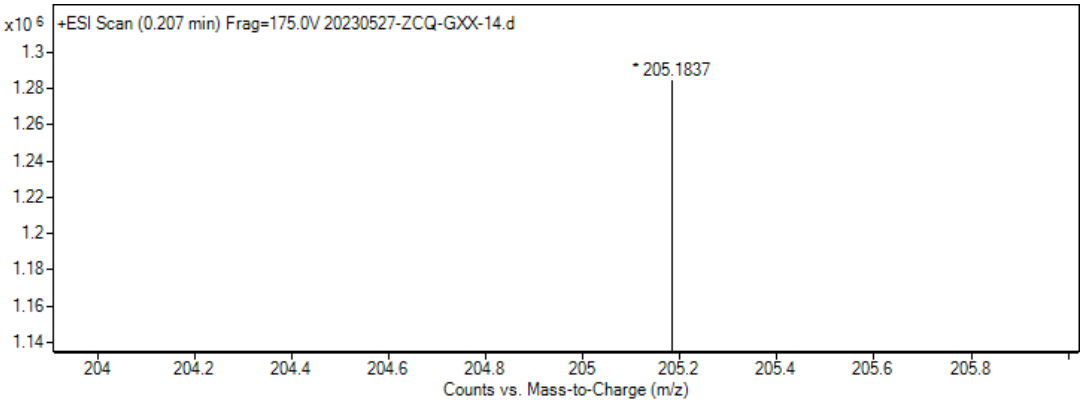

Figure S4. High resolution mass spectrum of **L3** in acetonitrile.

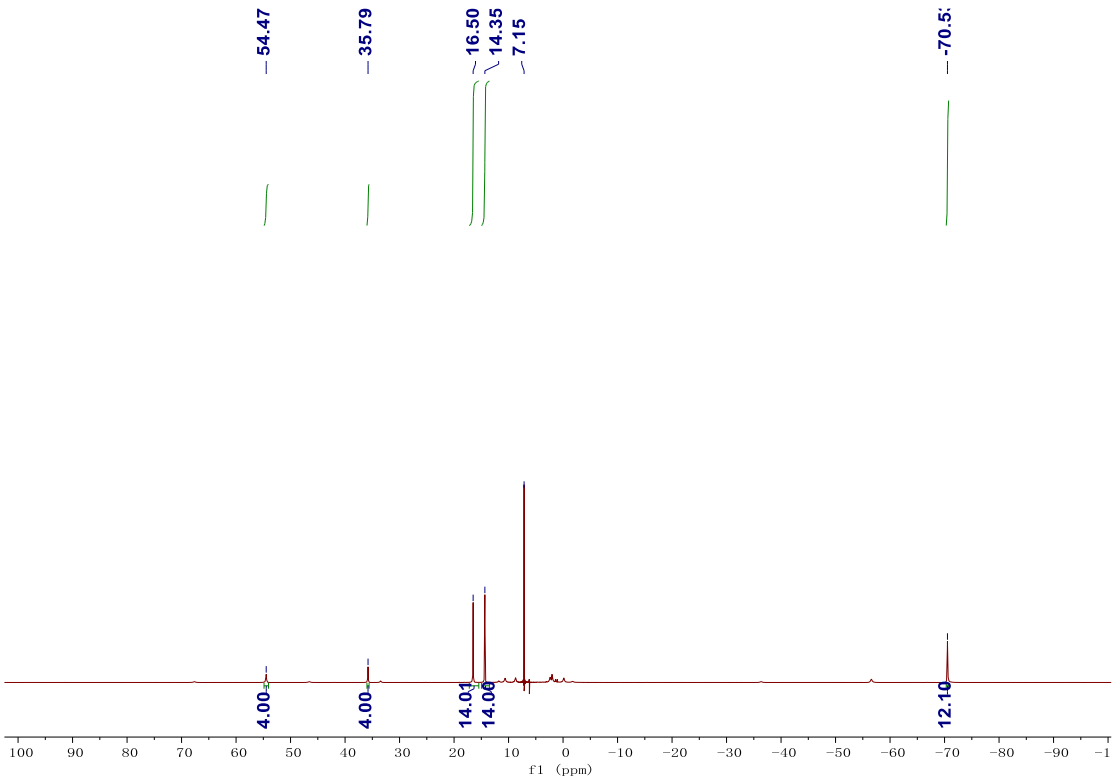

Figure S5. ^{1}H NMR spectrum of complex **1** in benzene- d_6.

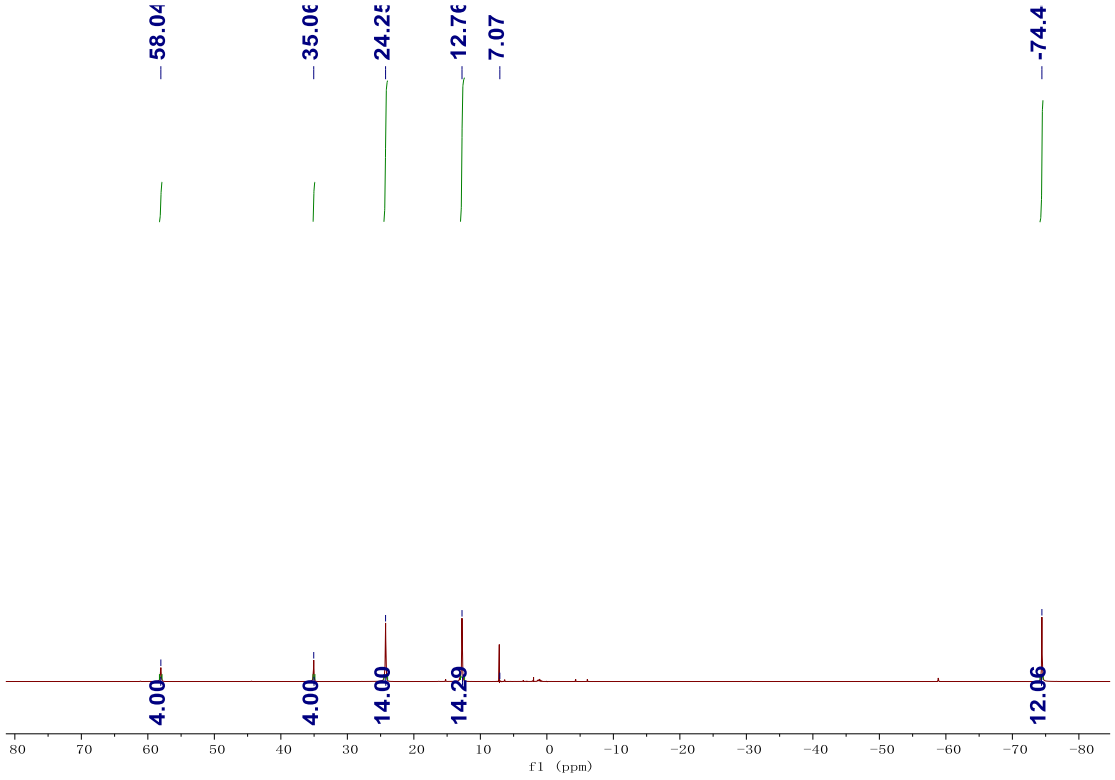

Figure S6. ^{1}H NMR spectrum of complex **2** in benzene- d_6.

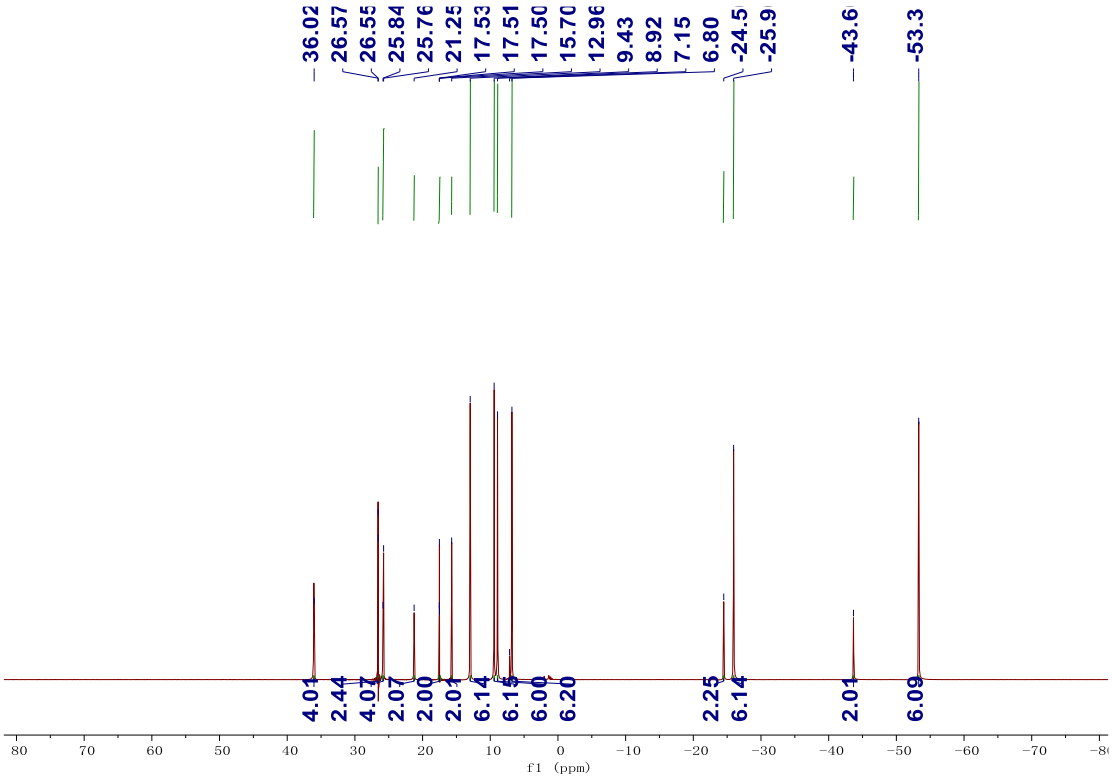

Figure S7. ^{1}H NMR spectrum of complex **3** in benzene- d_6.

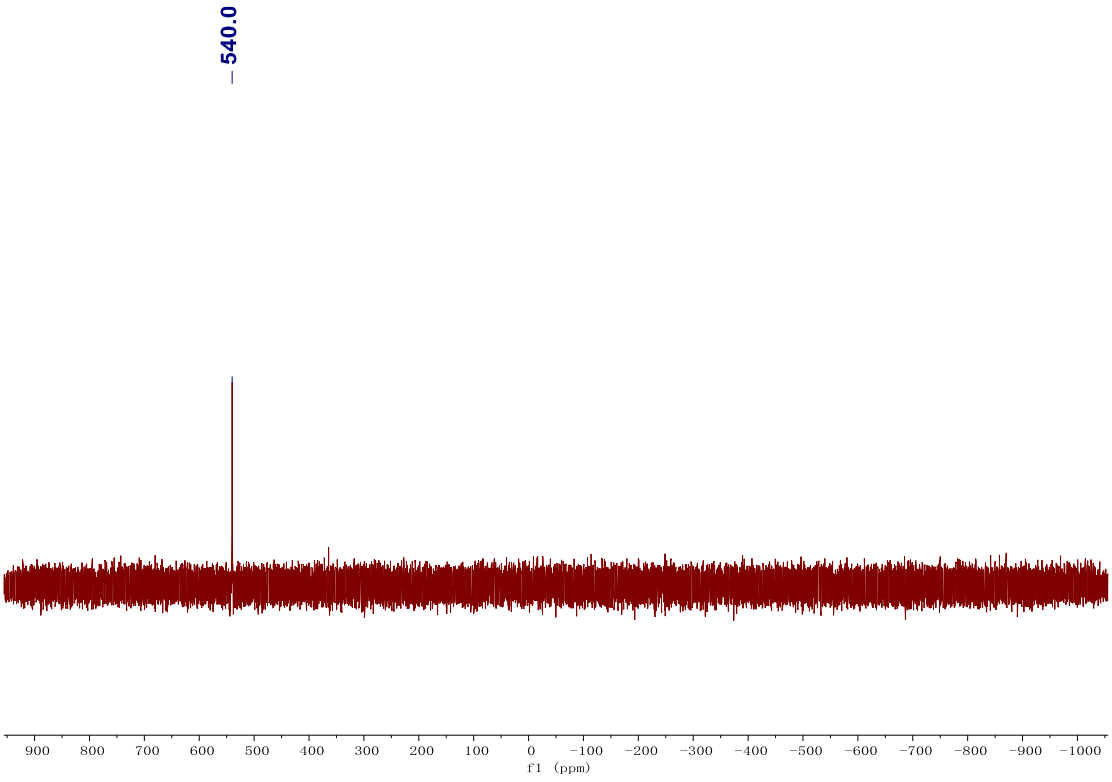

Figure S8. ^{31}P{^{1}H} NMR spectrum of complex **3** in benzene- d_6.

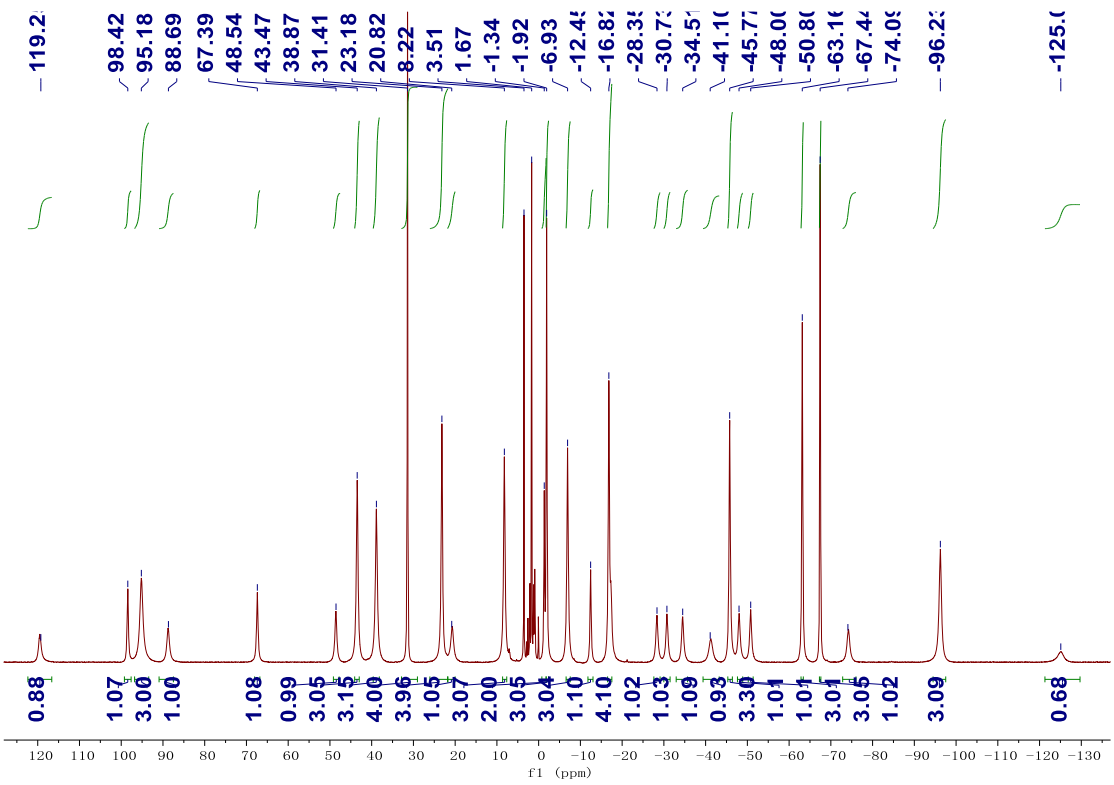

Figure S9. ^{1}H NMR spectrum of complex **4** in tetrahydrofuran-d_8.

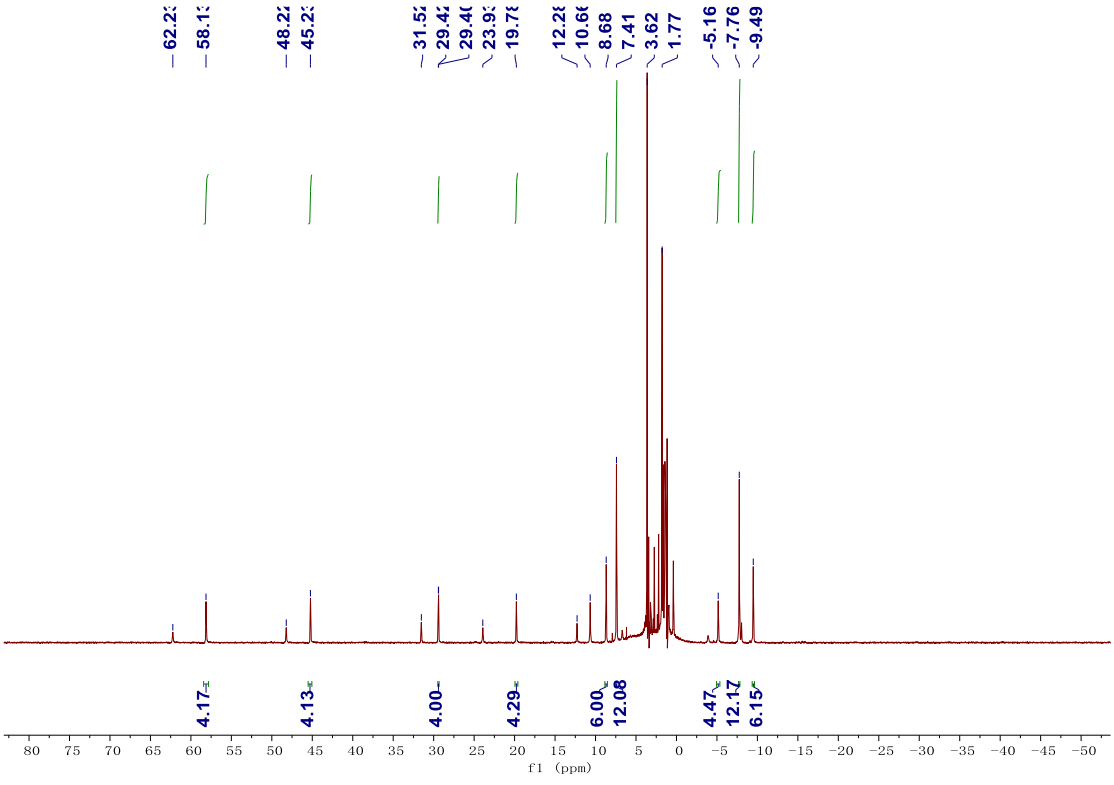

Figure S10. The *in-situ* ^{1}H NMR spectrum for the synthesis of complex **5** in tetrahydrofuran-d_8.

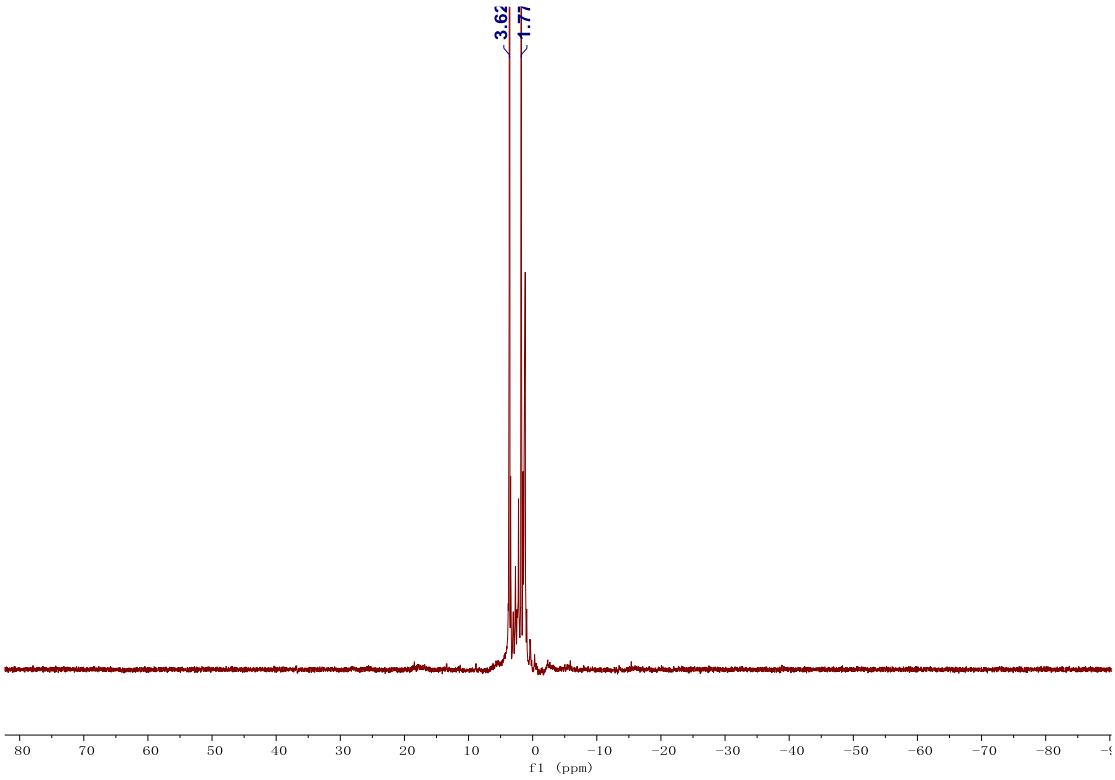

Figure S11. The *in-situ* ^{1}H NMR spectrum for the synthesis of complex **6** in tetrahydrofuran-d_8.

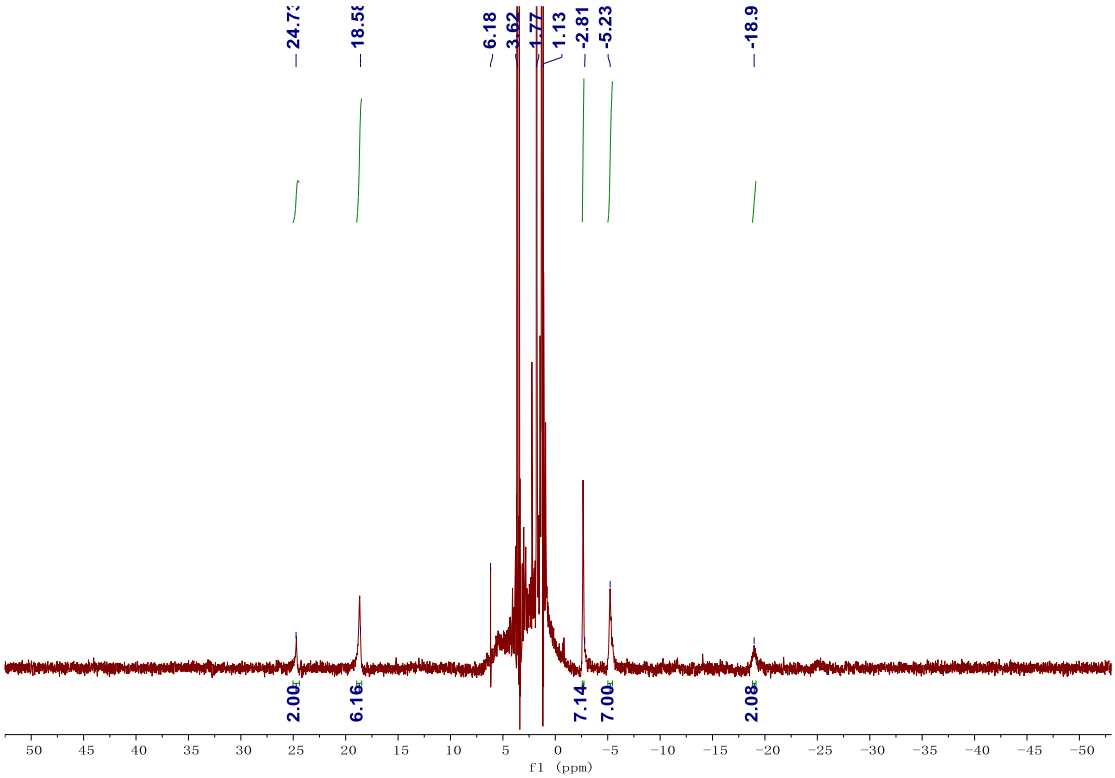

Figure S12. The *in-situ* ^{1}H NMR spectrum for the synthesis of complex **7** in tetrahydrofuran-d_8.