Electronic Supplementary Information

Systematic comparison of the structure of homoleptic tetradentate N_2O_2-type Schiff base complexes of tetravalent *f*-elements (M(IV) = Ce, Th, U, Np, and Pu) in solid state and in solution

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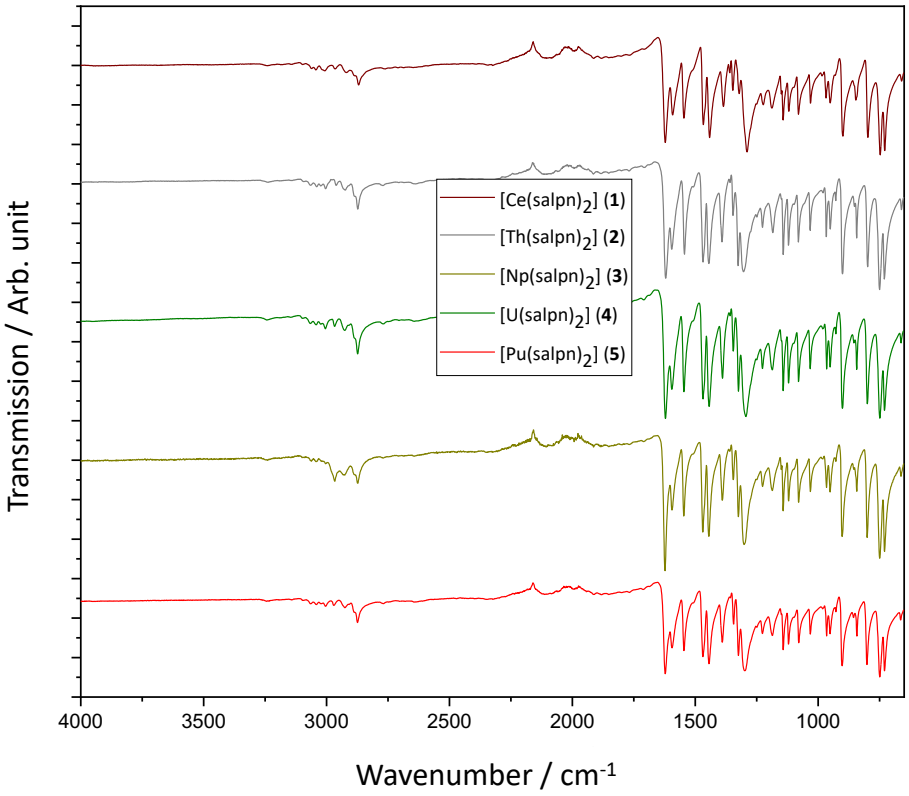

Figure S1 IR spectra of compounds **1-5**.

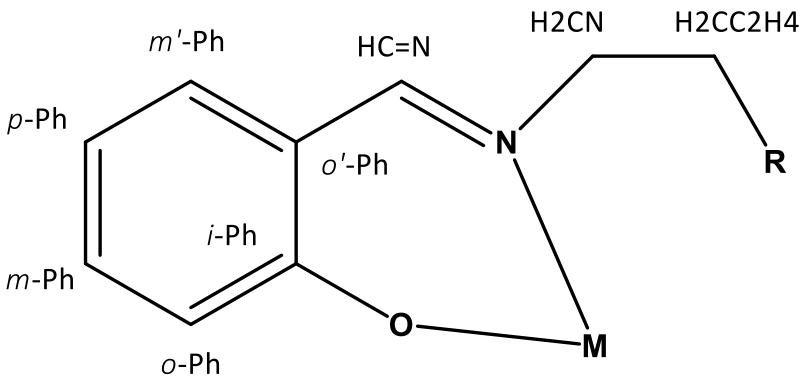

Figure S2 Notation of NMR signals associated with salpn.

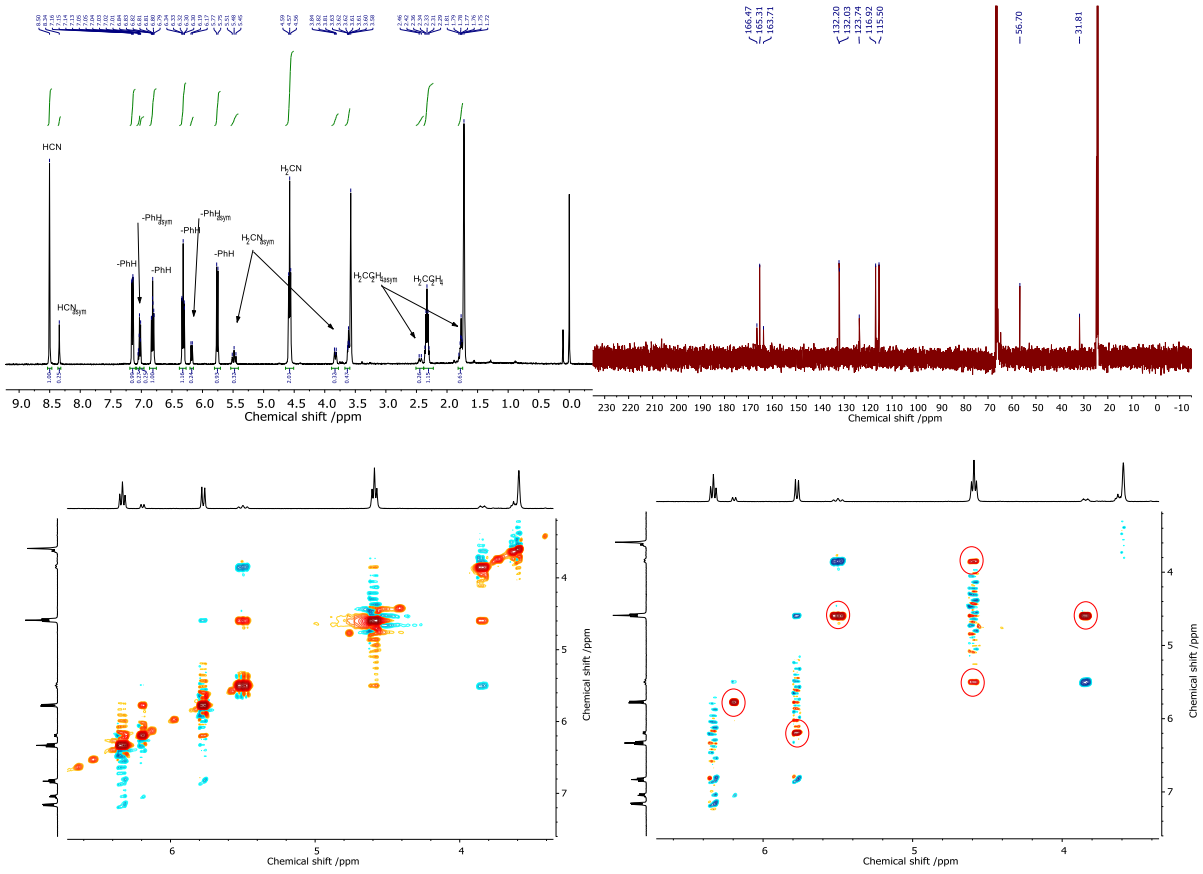

Figure S3 ^{1}H- (top left), ^{13}C- (top right), and ^{1}H-NOESY NMR spectra (bottom left) of [Ce(salpn)$_2$] (**1**) in thf-d_8. Diagonal signals are given on the bottom right to enhance the visibility of off-diagonal correlation peaks.

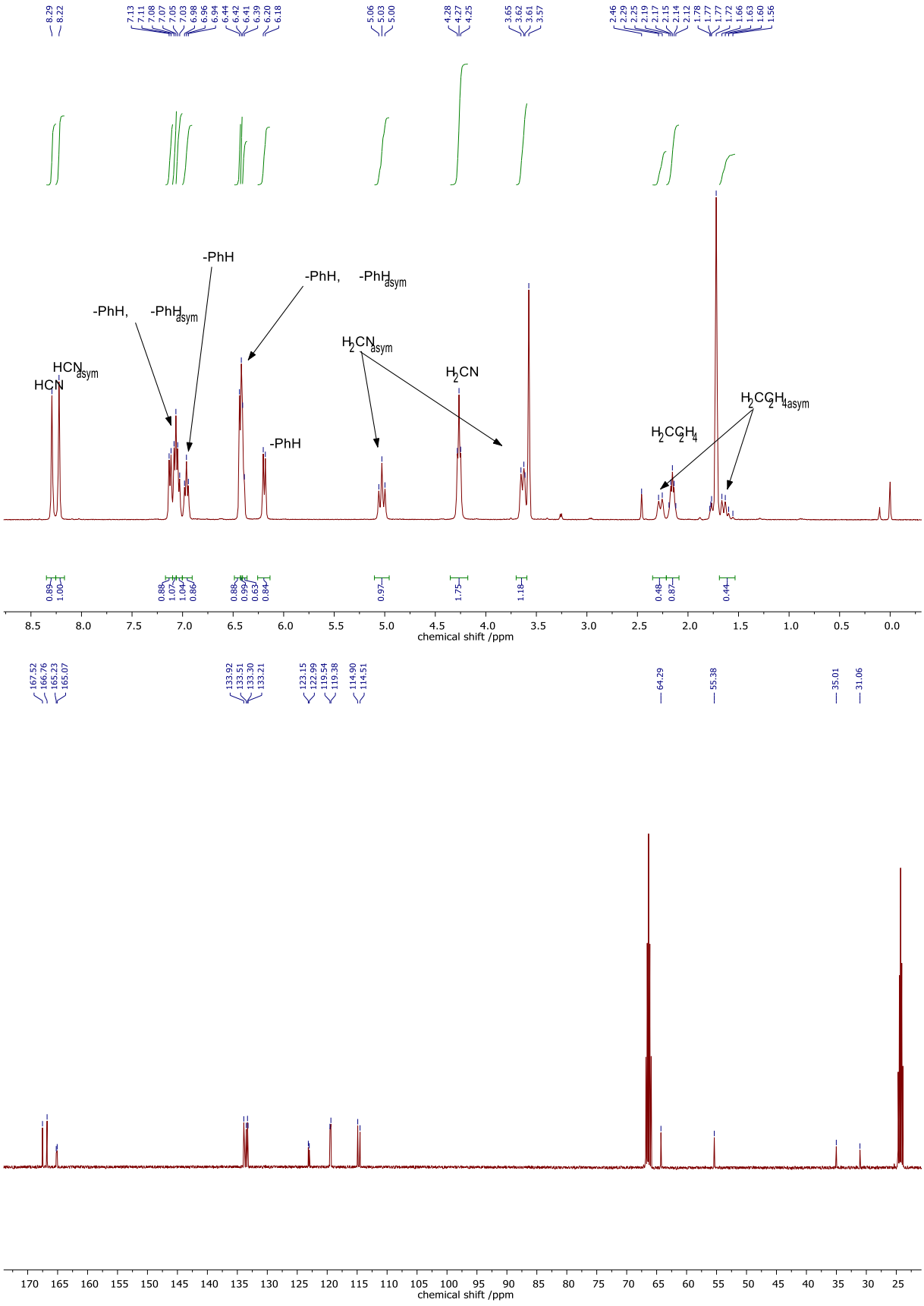

Figure S4 ^{1}H-(top) and ^{13}C-NMR spectra (bottom) of [Th(salpn)$_2$] (**2**) in thf-d_8.

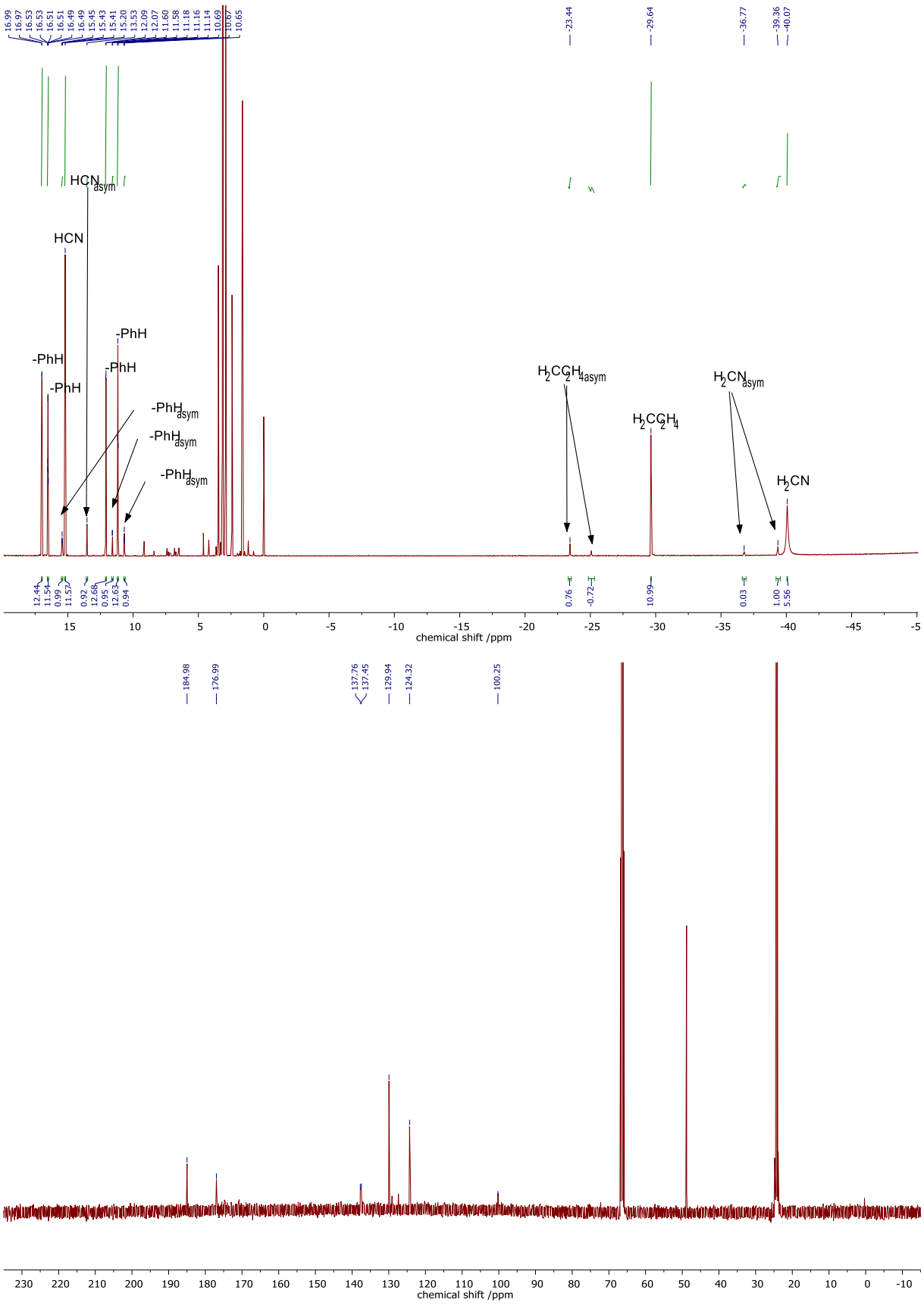

Figure S5 ^{1}H-(top) and ^{13}C-NMR spectra (bottom) of [U(salpn)$_2$] (**3**) in thf-d_8.

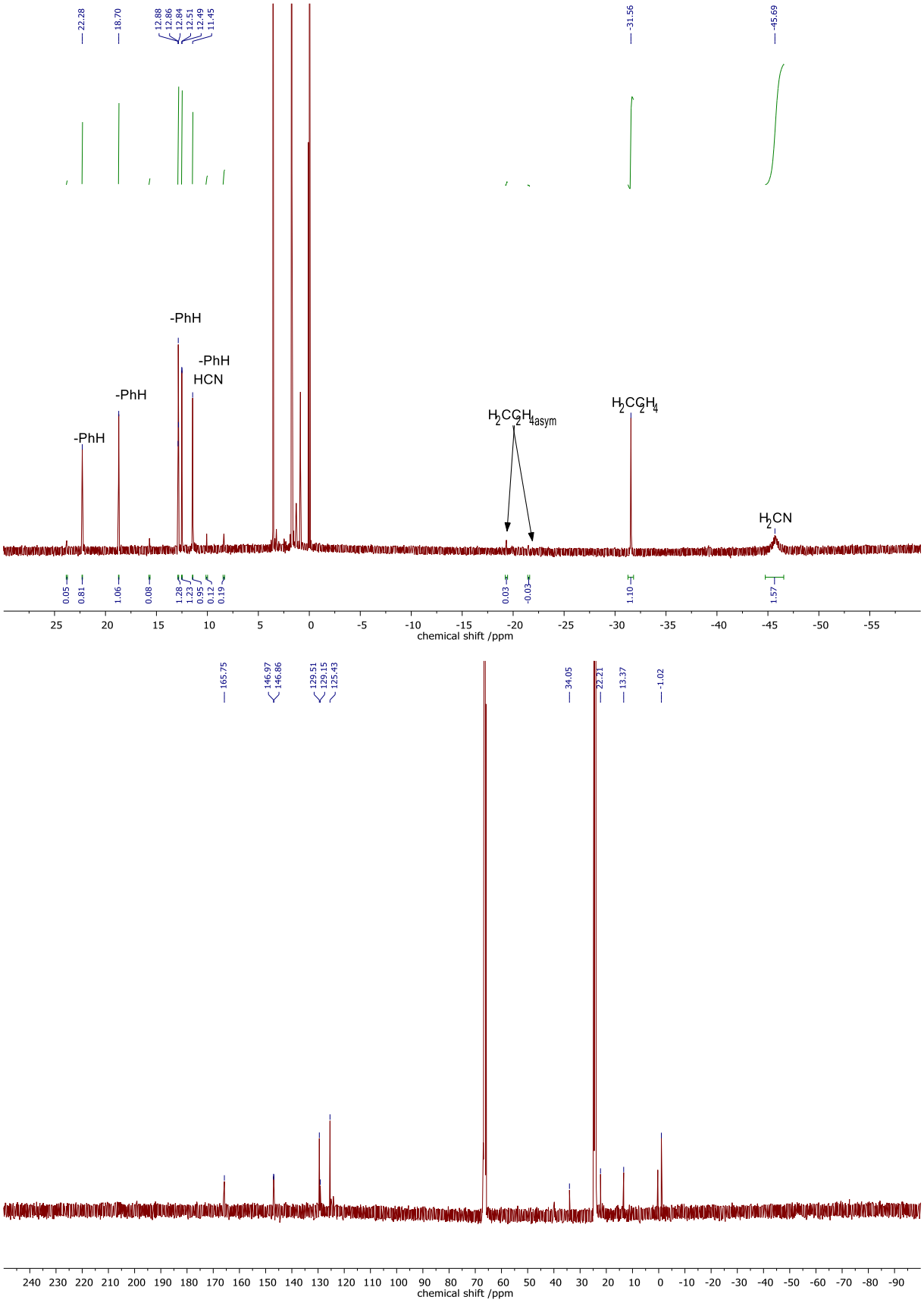

Figure S6 ^{1}H-(top) and ^{13}C-NMR spectra (bottom) of [Np(salpn)$_2$] (**4**) in thf-d_8.

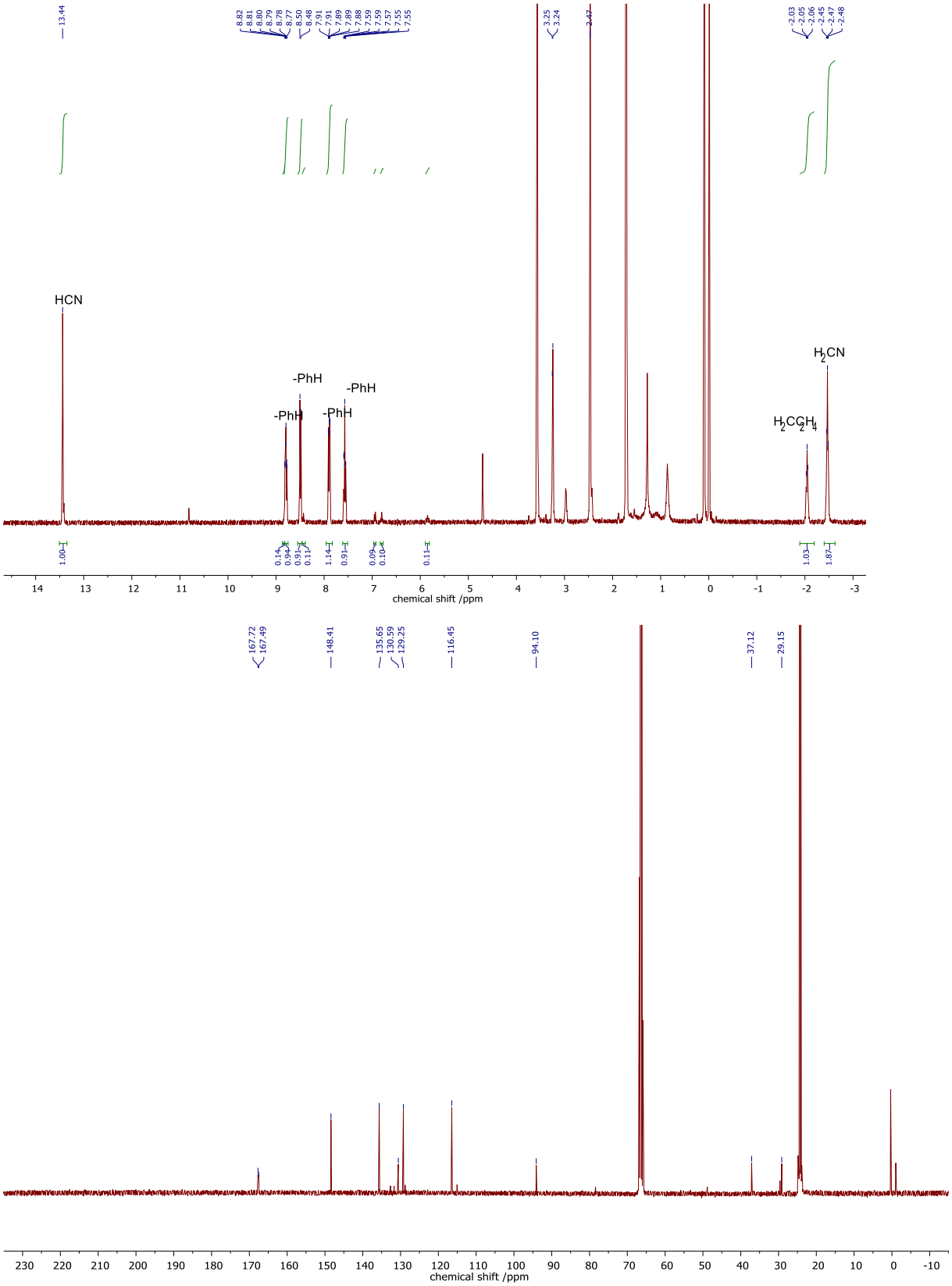

Figure S7 ^{1}H-(top) and ^{13}C-NMR spectra (bottom) of [Pu(salpn)$_2$] (**5**) in thf-d_8.

Table S1 Summary of crystallographic data for compounds **1-5**

Compound	$[Ce(salpn)_2]$ (**1a**)	$[Ce(salpn)_2]$ (**1b**)	$[Th(salpn)_2]$ (**2**)	$[U(salpn)_2]$ (**3**)
CCDC#	1970780	1970781	1970782	1970778
Empirical formula	$C_{34}H_{32}CeN_4O_4$	$C_{34}H_{32}CeN_4O_4$	$C_{34}H_{32}N_4O_4Th$	$C_{34}H_{32}N_4O_4U$
Formula weight	700.75	700.75	792.67	797.94
Temperature/K	100.0	100	100	100
Crystal system	triclinic	monoclinic	orthorhombic	orthorhombic
Space group	*P*-1	*P*21/n	*P*ban	*P*ban
a/Å	8.5959(7)	14.6108(14)	14.7012(7)	14.6015(7)
b/Å	13.3829(10)	13.4604(13)	14.7004(7)	14.6038(8)
c/Å	13.4915(10)	14.9187(15)	13.9369(7)	13.9168(7)
α/°	103.250(2)	90	90	90
β/°	100.909(2)	91.480(3)	90	90
γ/°	97.822(2)	90	90	90
Volume/$Å^3$	1457.03(19)	2933.0(5)	3012.0(3)	2967.6(3)
Z	2	4	4	4
$\rho_{calc}g/cm^3$	1.597	1.587	1.748	1.786
μ/mm^{-1}	1.609	1.598	4.996	5.515
F(000)	708.0	1416.0	1544.0	1551.0
Crystal size/mm^3	0.125 × 0.061 × 0.057	0.233 × 0.079 × 0.068	0.143 × 0.142 × 0.119	0.55 × 0.55 × 0.55
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.914 to 52.802	4.9 to 50.052	6.196 to 56.674	6.302 to 56.684
Index ranges	-10 ≤ h ≤ 10, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16	-17 ≤ h ≤ 17, -16 ≤ k ≤ 14, -17 ≤ l ≤ 17	-19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -18 ≤ l ≤ 18	-19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -18 ≤ l ≤ 18
Reflections collected	65425	146349	95957	172988
Independent reflections	5963 [R_{int} = 0.0459, R_{sigma} = 0.0243]	5168 [R_{int} = 0.0530, R_{sigma} = 0.0137]	3725 [R_{int} = 0.0247, R_{sigma} = 0.0077]	3709 [R_{int} = 0.0471, R_{sigma} = 0.0115]
Data/restraints/parameters	5963/0/388	5168/438/388	3725/162/241	3709/0/238
Goodness-of-fit on F^2	1.068	1.065	1.195	1.243
Final R indexes [I>=2σ (I)]	R_1 = 0.0256, wR_2 = 0.0587	R_1 = 0.0622, wR_2 = 0.1389	R_1 = 0.0295, wR_2 = 0.0618	R_1 = 0.0251, wR_2 = 0.0480
Final R indexes [all data]	R_1 = 0.0326, wR_2 = 0.0613	R_1 = 0.0760, wR_2 = 0.1557	R_1 = 0.0400, wR_2 = 0.0669	R_1 = 0.0337, wR_2 = 0.0547
Largest diff. peak/hole / e $Å^{-3}$	1.73/-0.73	9.15/-2.88	3.23/-1.35	0.81/-0.55

Table S1 Summary of crystallographic data for compounds **1-5** (contd.)

Compound	$[Np(salpn)_2]$ (**4**)	$[Pu(salpn)_2]$ (**5**)
CCDC#	1970784	1970783
Empirical formula	$C_{34}H_{32}N_4NpO_4$	$C_{34}H_{32}N_4O_4Pu$
Formula weight	797.63	802.63
Temperature/K	100	100
Crystal system	orthorhombic	orthorhombic
Space group	*P*ban	*P*ban
a/Å	14.5915(11)	14.5910(8)
b/Å	14.5923(11)	14.5959(8)
c/Å	13.8426(11)	13.8205(7)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/$Å^3$	2947.4(4)	2943.3(3)
Z	4	4
$\rho_{calc}g/cm^3$	1.798	1.811
μ/mm^{-1}	3.572	2.286
F(000)	1556.0	1560.0
Crystal size/mm^3	0.284 × 0.196 × 0.188	0.067 × 0.054 × 0.051
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.312 to 56.686	5.896 to 56.64
Index ranges	-19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -18 ≤ l ≤ 18	-19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -18 ≤ l ≤ 18
Reflections collected	229472	69587
Independent reflections	3683 [R_{int} = 0.0226, R_{sigma} = 0.0042]	3664 [R_{int} = 0.0335, R_{sigma} = 0.0110]
Data/restraints/parameters	3683/0/263	3664/162/224
Goodness-of-fit on F^2	1.183	1.285
Final R indexes [I>=2σ (I)]	R_1 = 0.0294, wR_2 = 0.0521	R_1 = 0.0328, wR_2 = 0.0581
Final R indexes [all data]	R_1 = 0.0364, wR_2 = 0.0554	R_1 = 0.0538, wR_2 = 0.0653
Largest diff. peak/hole / e $Å^{-3}$	1.53/-0.59	1.54/-0.48

Table S2 Summary of An-N and An-O bond lengths in the primary coordination sphere around the metal centre for a series of DFT-optimized [M(salpn)$_2$] complexes

Complex	An – N / pm	An – O / pm
[Ce(salpn)$_2$]	264/264/268/268	225/225/226/226
[Th(salpn)$_2$]	267/267/269/270	229/230/230/230
[Th(salpn)$_2$] w/o disp.*	270/270/273/273	228/228/231/231
[Pa(salpn)$_2$]	256/256/264/264	221/221/222/222
[U(salpn)$_2$]	260/260/263/264	221/222/223/223
[Np(salpn)$_2$]	259/263/263/266	222/223/224/224
[Pu(salpn)$_2$]	262/264/267/274	219/222/223/225
[Am(salpn)$_2$] w/o disp.*	267/267/277/279	220/221/223/223

* The complex structures optimised without dispersion correction are denoted as "w/o disp.".

Table S3 Summary of metal and donor charges (q), electron densities at the bond critical point (ρ_{BCP}), localization indices (λ), and delocalization indices (δ) obtained from QTAIM calculations for a series of DFT-optimised [M(salpn)$_2$] complexes

	q			**ρ_{BCP} / 0.01**	
Complex	M	N	O	An-N	An-O
[Ce(salpn)$_2$]	+2.57	-1.19/-1.19/-1.20/-1.20	-1.21/-1.20/-1.21/-1.20	4.34/4.31/3.97/3.93	8.63/8.61/8.35/8.32
[Th(salpn)$_2$]	+2.88	-1.20/-1.20/-1.21/-1.21	-1.26/-1.25/-1.26/-1.25	4.53/4.48/4.32/4.25	8.41/8.35/8.22/8.19
[Th(salpn)$_2$] w/o disp.*	+2.88	-1.20/-1.21/-1.20/-1.21	-1.25/-1.26/-1.25/-1.26	3.99/4.29/4.29/3.99	8.46/8.05/8.05/8.46
[Pa(salpn)$_2$]	+2.86	-1.18/-1.18/-1.18/-1.18	-1.22/-1.22/-1.22/-1.22	4.69/5.52/4.64/5.46	9.72/9.71/9.73/9.68
[U(salpn)$_2$]	+2.72	-1.18/-1.18/-1.18/-1.18	-1.22/-1.22/-1.23/-1.21	4.50/4.84/4.62/4.86	9.77/9.35/9.39/9.66
[Np(salpn)$_2$]	+2.66	-1.18/-1.19/-1.19/-1.19	-1.22/-1.22/-1.21/-1.21	5.00/4.59/4.52/4.29	9.34/9.34/9.07/9.00
[Pu(salpn)$_2$]	+2.60	-1.18/-1.19/-1.19/-1.18	-1.21/-1.22/-1.22/-1.20	4.11/4.30/4.56/3.60	9.37/9.02/8.69/9.99
[Am(salpn)$_2$] w/o disp.*	+2.51	-1.17/-1.19/-1.18/-1.19	-1.19/-1.19/-1.19/-1.20	3.06/4.00/3.95/3.20	9.32/8.72/8.80/9.28
	λ			***δ***	
	An	N	O	An–N	An–O
[Ce(salpn)$_2$]	53.64	6.48/6.48/6.49/6.49	8.11/8.10/8.11/8.10	0.23/0.23/0.25/0.25	0.53/0.53/0.53/0.53
[Th(salpn)$_2$]	85.51	6.49/6.50/6.51/6.51	8.17/8.19/8.19/8.17	0.24/0.24/0.26/0.26	0.48/0.48/0.48/0.48
[Th(salpn)$_2$] w/o disp.*	85.52	6.50/6.51/6.50/6.51	8.18/8.19/8.18/8.19	0.23/0.25/0.23/0.25	0.48/0.50/0.48/0.50
[Pa(salpn)$_2$]	86.15	6.45/6.45/6.45/6.45	8.11/8.11/8.11/8.11	0.27/0.34/0.33/0.26	0.56/0.57/0.57/0.56
[U(salpn)$_2$]	87.40	6.45/6.46/6.46/6.45	8.10/8.12/8.12/8.10	0.27/0.29/0.29/0.27	0.57/0.55/0.55/0.56
[Np(salpn)$_2$]	88.48	6.46/6.46/6.48/6.47	8.10/8.11/8.11/8.10	0.26/0.26/0.28/0.28	0.58/0.56/0.56/0.58
[Pu(salpn)$_2$]	89.55	6.46/6.48/6.48/6.47	8.08/8.11/8.11/8.08	0.25/0.27/0.27/0.21	0.58/0.61/0.53/0.62
[Am(salpn)$_2$] w/o disp.*	90.65	6.48/6.48/6.49/6.48	8.07/8.07/8.08/8.08	0.19/0.19/0.24/0.24	0.62/0.58/0.57/0.62

* The complex structures optimised without dispersion correction are denoted as "w/o disp.".

Table S4 Summary of Laplacian of the electron density for a series of DFT-optimised [M(salpn)$_2$] complexes

Complex	**Laplacian**	
	An-N	An-O
Ce_SalenP2	0.11/0.10	0.26/0.27
Th_SalenP2	0.11/0.10	0.26/0.27
Th_SalenP2 w.o. Disp	0.10/0.10	0.28/0.26/0.26/0.27
Pa_SalenP2	0.12/0.14	0.31/0.33
U_SalenP2	0.13	0.32
Np_SalenP2	0.12/0.13	0.31/0.33
Pu_SalenP2	0.12/0.12/0.13/0.10	0.35/0.34/0.32/0.38
Am_SalenP2_w.o.Disp	0.09/0.12/0.12/0.10	0.36/0.33/0.33/0.35