New supporting ligands in actinide chemistry: Tetramethyltetraazaannulene complexes with thorium and uranium

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Supporting Information

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Synthesis of H_2TMTAA (H_2L):

Ligand synthesis was adapted from literature procedures.[1]

o-phenylenediamine (2 eq, 201 mmol, 21.32 g), 2,4-pentadione (2 eq, 201 mmol, 19.7 g, 20.2 ml) and $Ni(OAc)_2 \cdot 4H_2O$ (1 eq, 105 mmol, 24.5 g) were mixed in n-butanol (250 ml) and heated to reflux for 3 days without any precautions to exclude oxygen or moisture to give a very dark green to black solution with a fine purple precipitate. The solution was then cooled to room temperature and filtered through a medium porosity frit. The purple solid was extensively washed with methanol to give the nickel template molecule **LNi (**29 %, 30 mmol, 12.34 g) ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C): 6.71 – 6.69 (m, 4H, Aryl-*H*); 6.59 – 6.57 (m, 4H, Aryl-*H*); 4.88 (s, 2H, C*H*); 2.10 (s, 12H, C*H*$_3$); ^{13}C-NMR (100 MHz, $CDCl_3$, 25°C): 155.5 (C=N), 147.4, 121.9; 120.9 (all Aryl-*C*), 111.2 (central *C*H), 22.1 (*C*H_3); HR-MS calcd for 400.1192 [$C_{22}H_{22}Ni$] found 400.1184.

LNi (1 eq, 15mmol, 6 g) was dissolved in absolute methanol (200 ml) in a three-necked flask. The flask was connected to an HCl lecture bottle (a second flask was connected between the lecture bottle and the flask containing the compound was used to prevent backflow of the solution into the gas cylinder). A moderate stream of HCl was bubbled through the dark green solution until a turquoise precipitate formed and heat was generated. After the precipitate was formed, the flask was closed and the solution was cooled to -40 °C for 2 h. The cold solution was filtered to give a white/turquoise powder that was then washed with small amounts of ethanol and diethyl ether to give **H_4L^1[$NiCl_4$]** (91 %, 13.8 mmol, 7.43 g).

Anion exchange was immediately performed on **H_4L^1[$NiCl_4$]** to synthesize **H_4L^1[PF_6]$_2$**. **H_4L^1[$NiCl_4$]** (1 eq, 13.8 mmol, 7.43 g) was dissolved in water (100 ml) and stirred for 1 h until all solids dissolved. Then NH_4PF_6 (excess, 5 g) dissolved in water (10 ml) was added dropwise and the resulting slurry was stirred at room temperature for another 30 min after the addition of

the last drop of the NH_4PF_6 solution. The white precipitate was filtered, washed with water (50 ml) and dried in air to give **$H_4L^1[PF_6]_2$** (85 %, 11.7 mmol, 7.44 g).

$H_4L^1[PF_6]_2$ (7.44g, 11.7 mmol) was suspended in MeOH (50 ml) to give a white slurry. NEt_3 (excess, 4 ml) was added to the slurry to give a fine yellow precipitate. The solution was allowed to stirr for another 30 minutes. The solution was then extracted with DCM (150 ml) and the organic phase was washed with concentrated aqueous NH_4Cl (2 x 100 ml), concentrated aqueous $KHCO_3$ (2 x 100 ml) and brine (100 ml). The organic layer was then dried over $MgSO_4$, filtered and evaporated to dryness to give **H_2L^1 (TMTAA)** as an orange powder in an overall yield of 51 % (7.6 mmol, 2.6 g) from **L^1Ni**. ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C): 12.6 (s, broad, 2H, N*H*); 7.04 (s, 8H, Aryl-*H*); 4.92 (s. 2H, C*H*); 2.18 (s, 12H, CH_3) ^{13}C-NMR (100 MHz, $CDCl_3$, 25°C): 159.0 (C=N), 138.5, 123.2, 122.9 (all Aryl-*C*), 98.0 (central *C*H), 21.0 (*C*H_3); HR-MS calcd for 345:2074 [$C_{22}H_{24}N_4 + H^+$] found 345.2066.

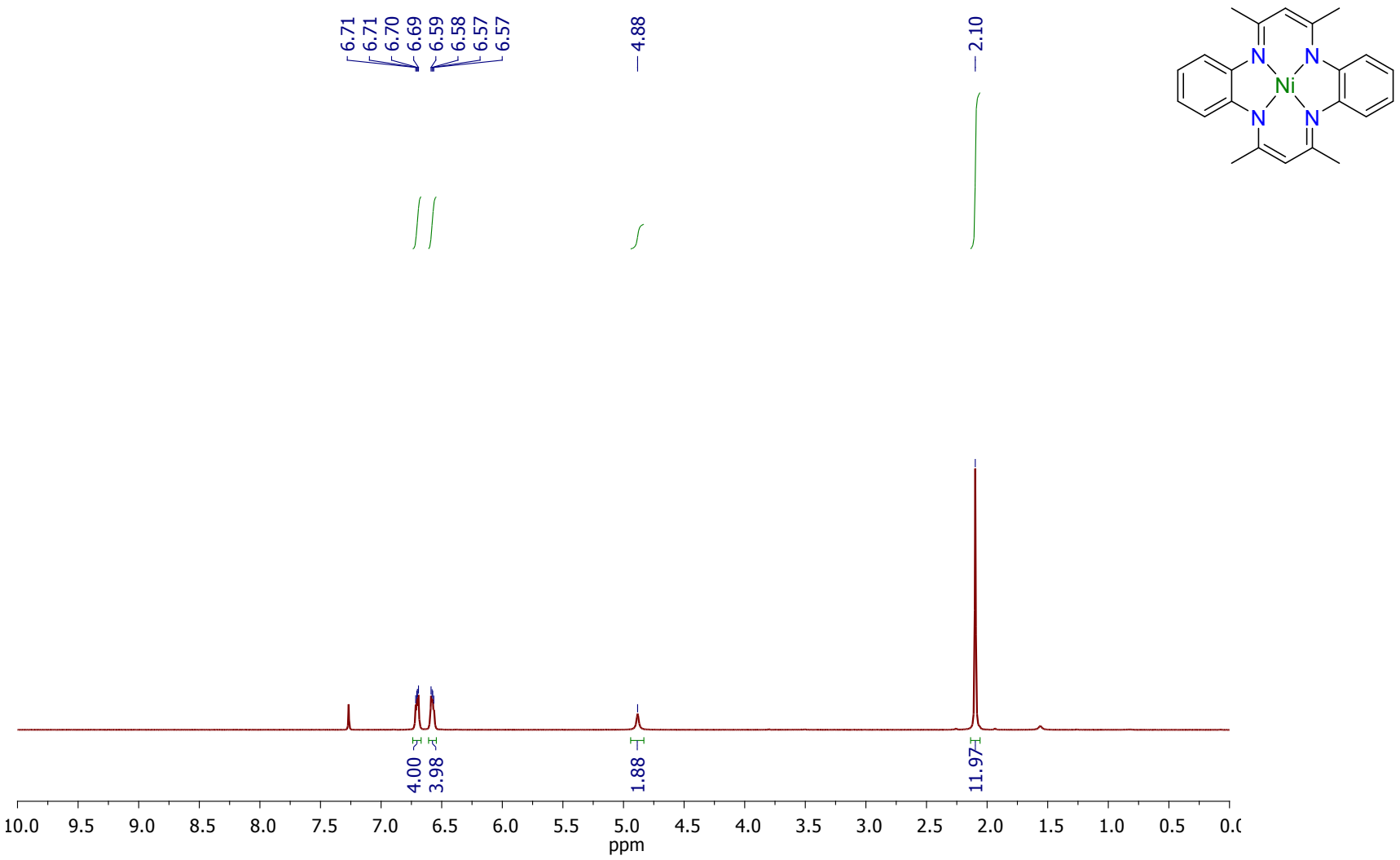

Figure S1: ^{1}H-NMR of **NiL^{1}** in $CDCl_3$

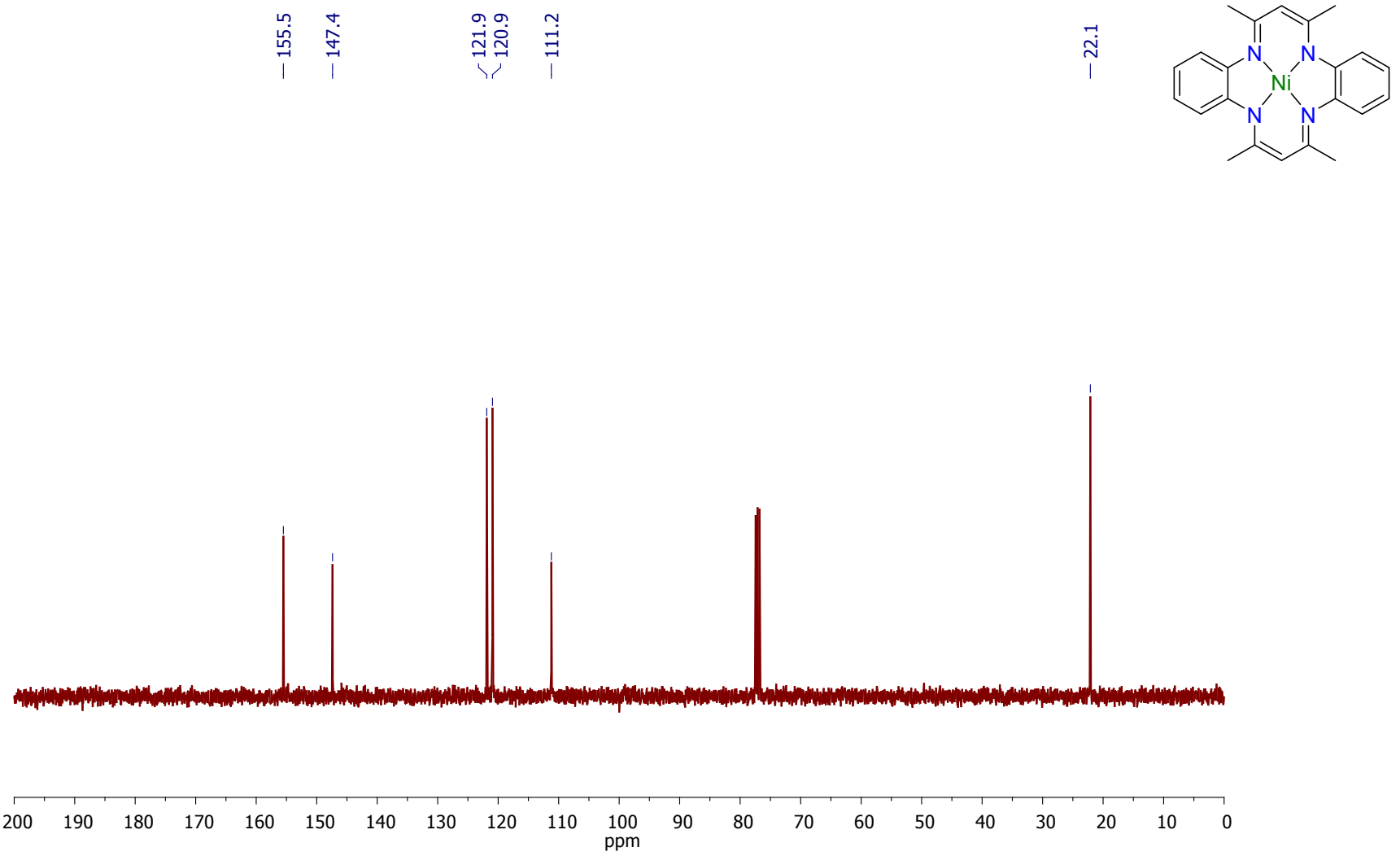

Figure S2: ^{13}C-NMR of **NiL^{1}** in $CDCl_3$

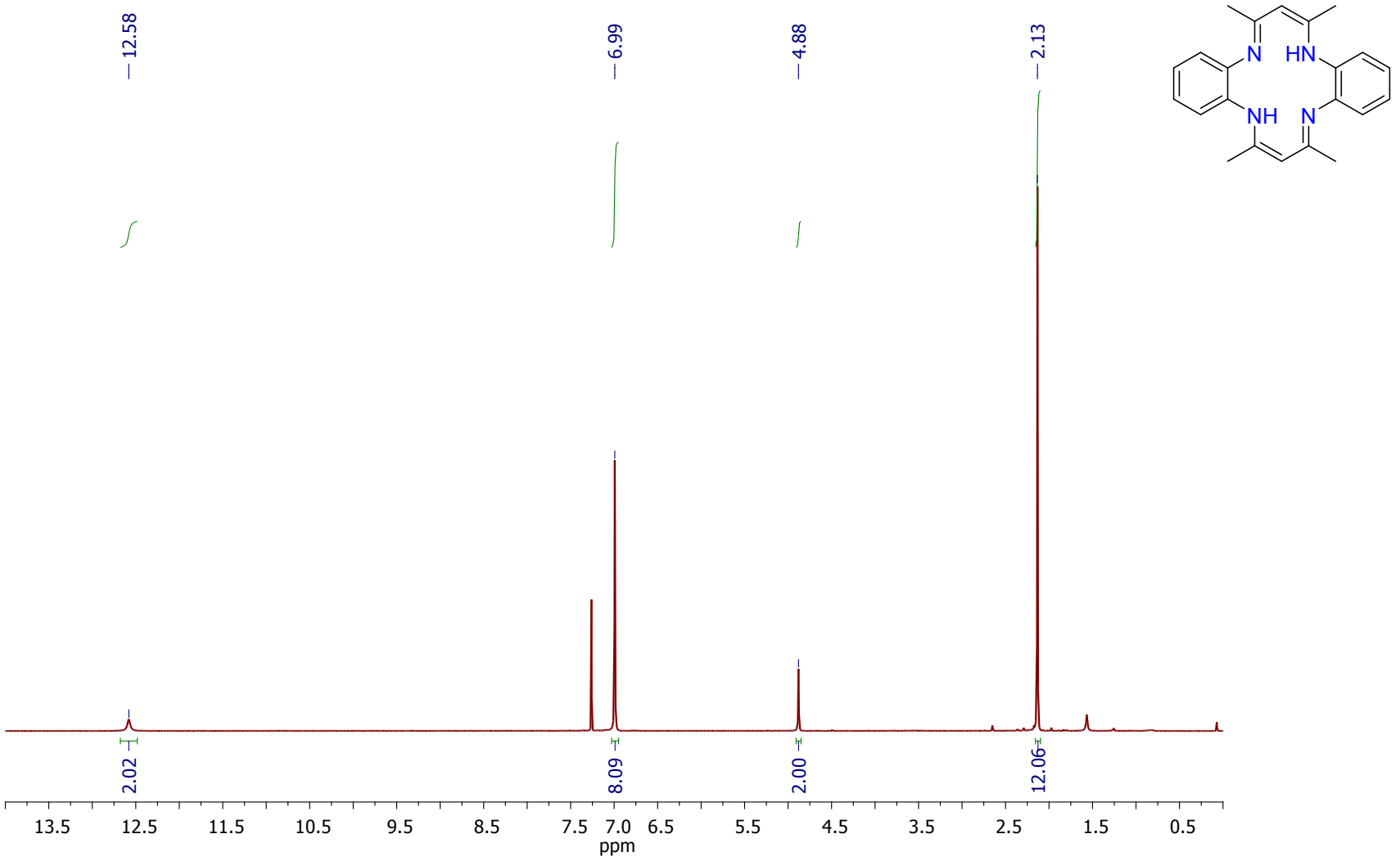

Figure S3: ^{1}H-NMR of $\mathbf{H_2L^1}$ in $CDCl_3$

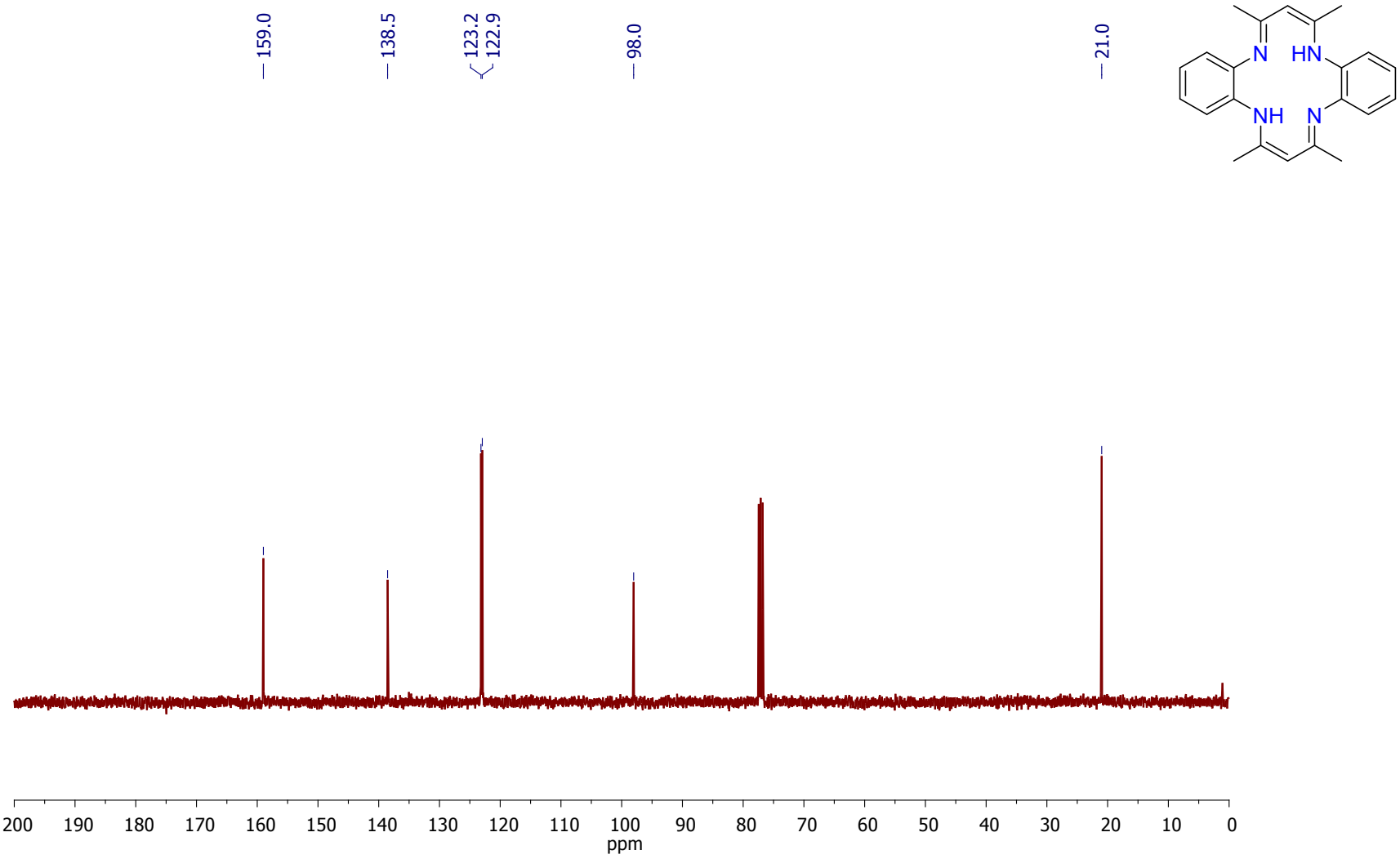

Figure S4: ^{13}C-NMR of $\mathbf{H_2L^1}$ in $CDCl_3$

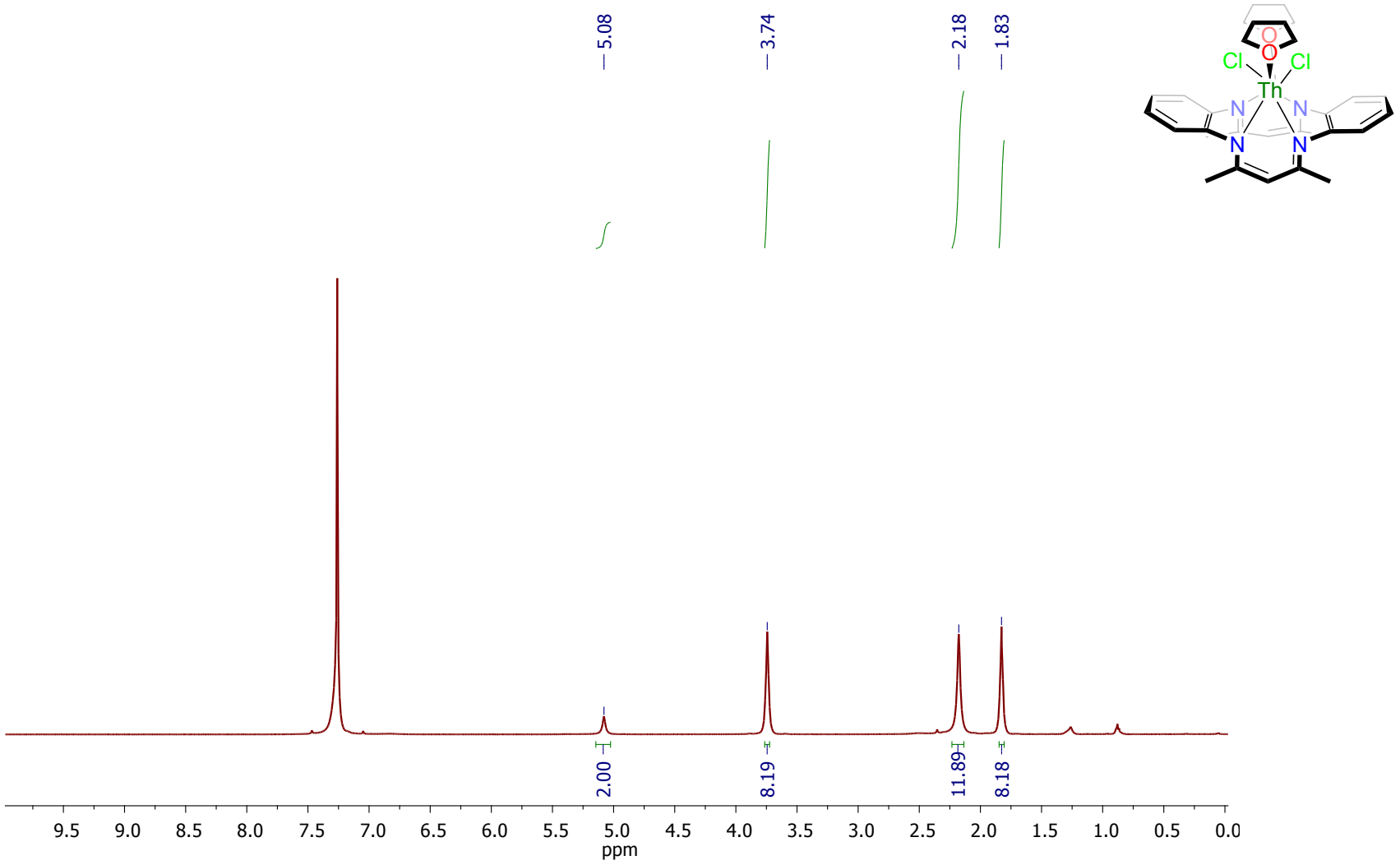

Figure S5: ^{1}H-NMR of **1** in $CDCl_3$

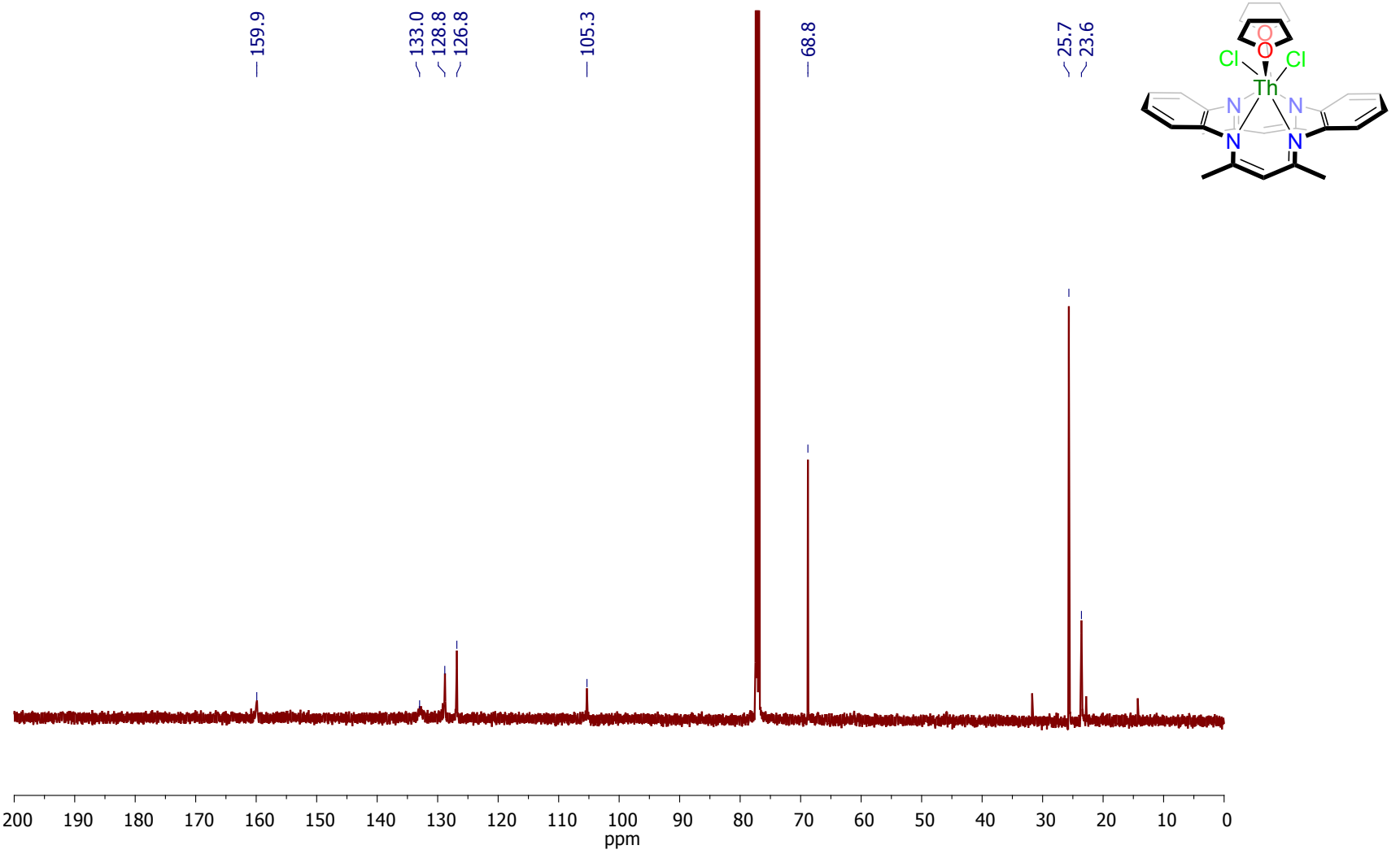

Figure S6: ^{13}C-NMR of **1** in $CDCl_3$

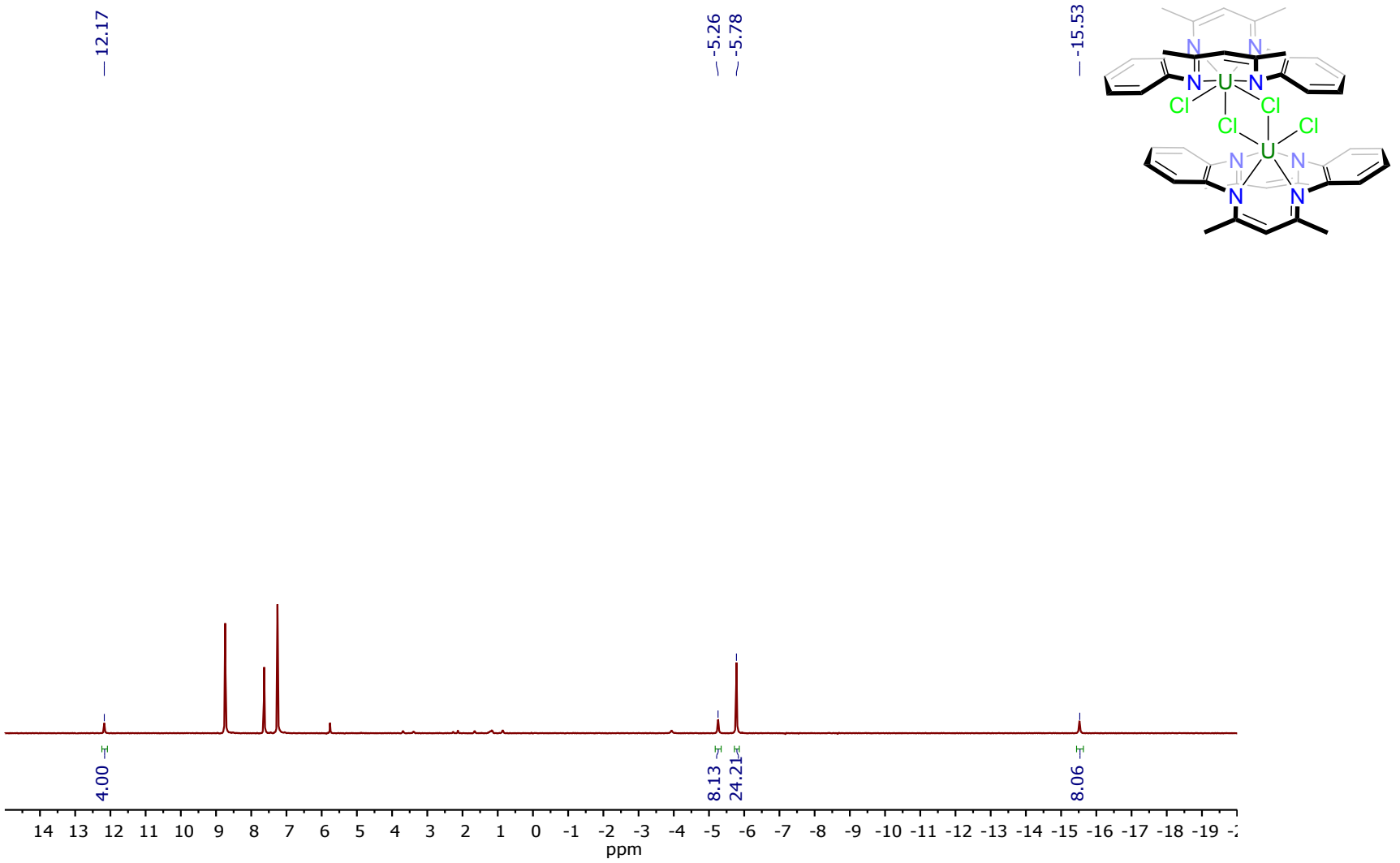

Figure S7: ^{1}H-NMR of **2** in pyr-d_5

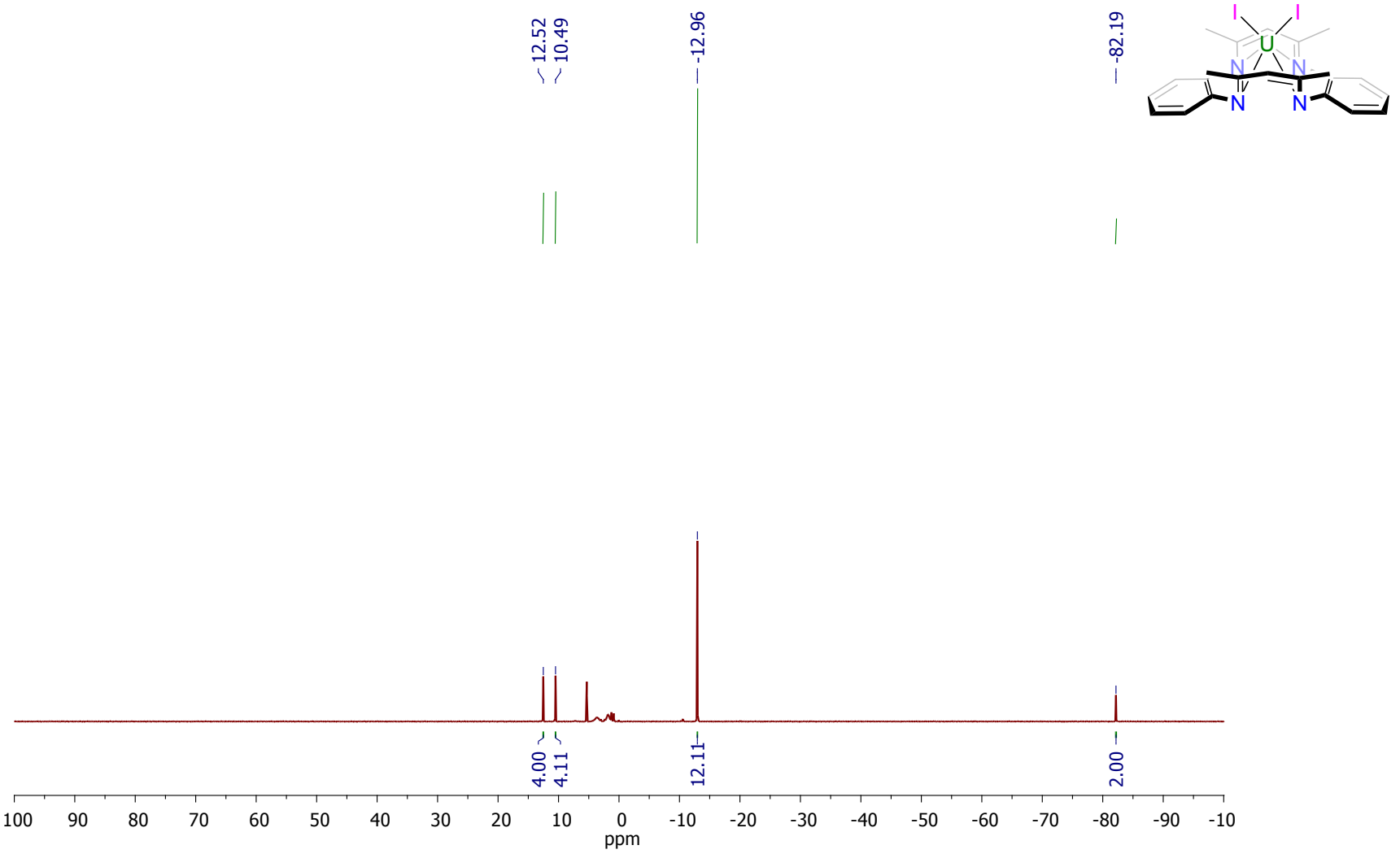

Figure S8: ^{1}H-NMR of **3** in CD_2Cl_2

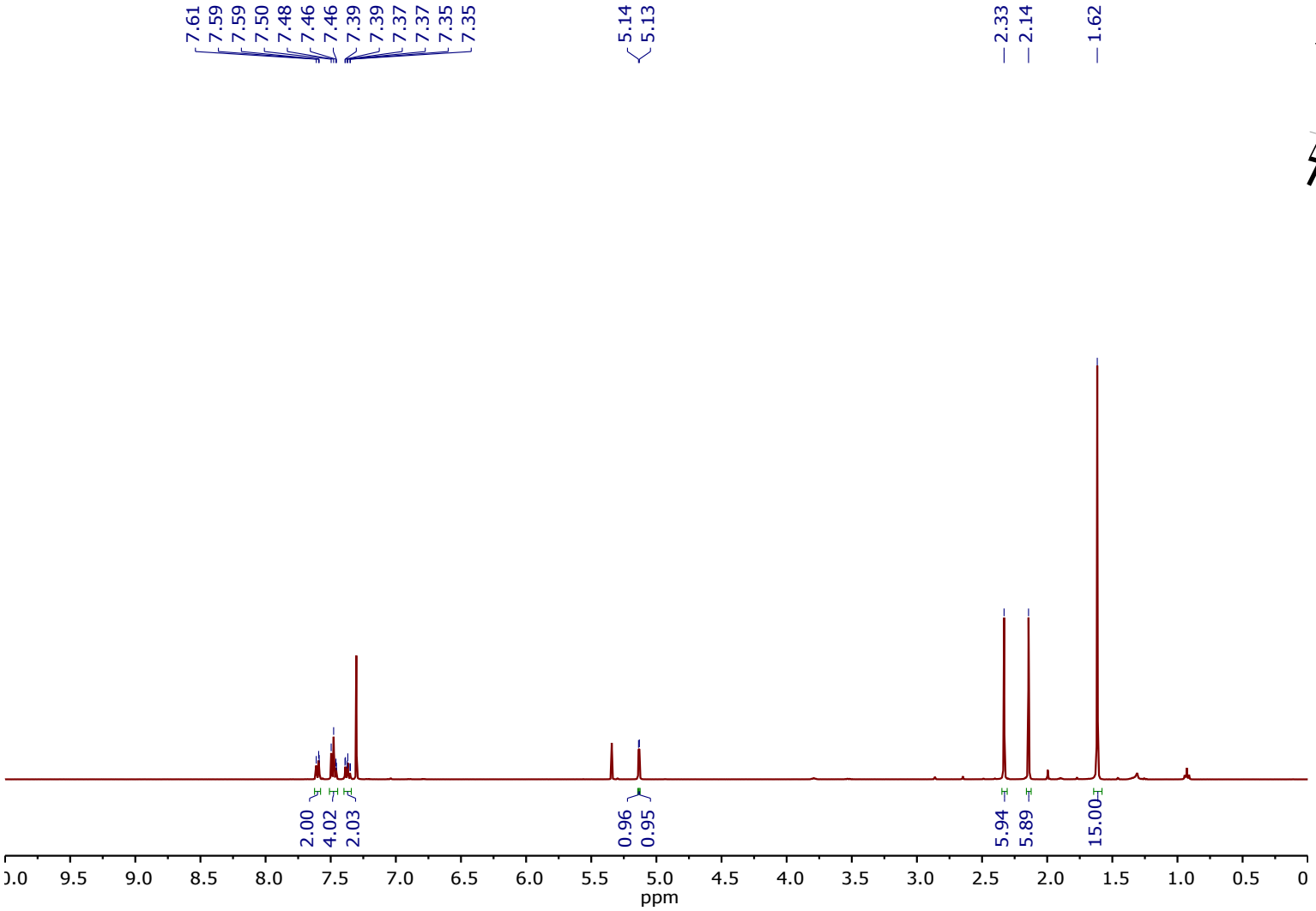

Figure S9: ^{1}H-NMR of **4** in $CDCl_3$

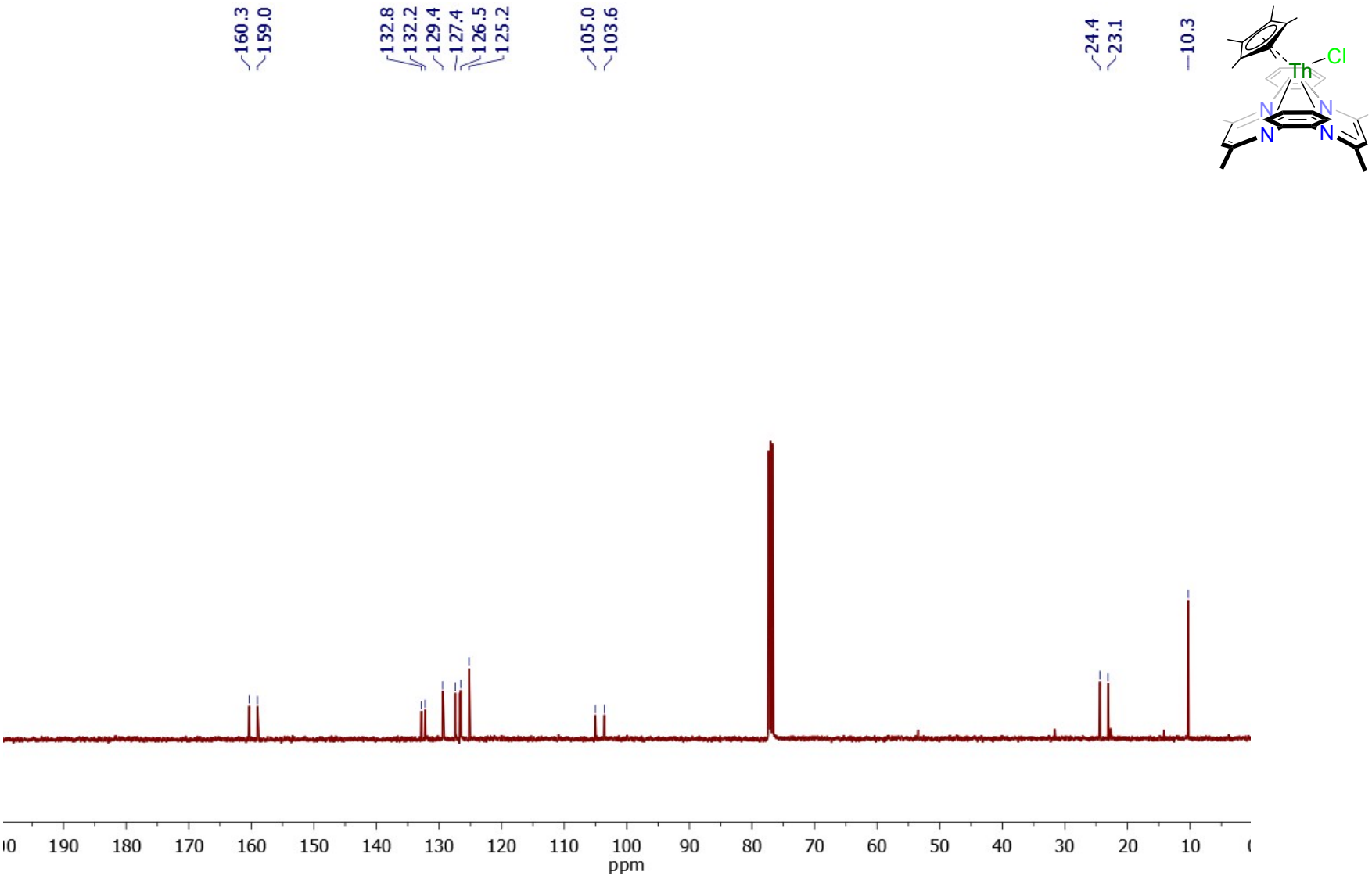

Figure S10: ^{13}C-NMR of **4** in $CDCl_3$

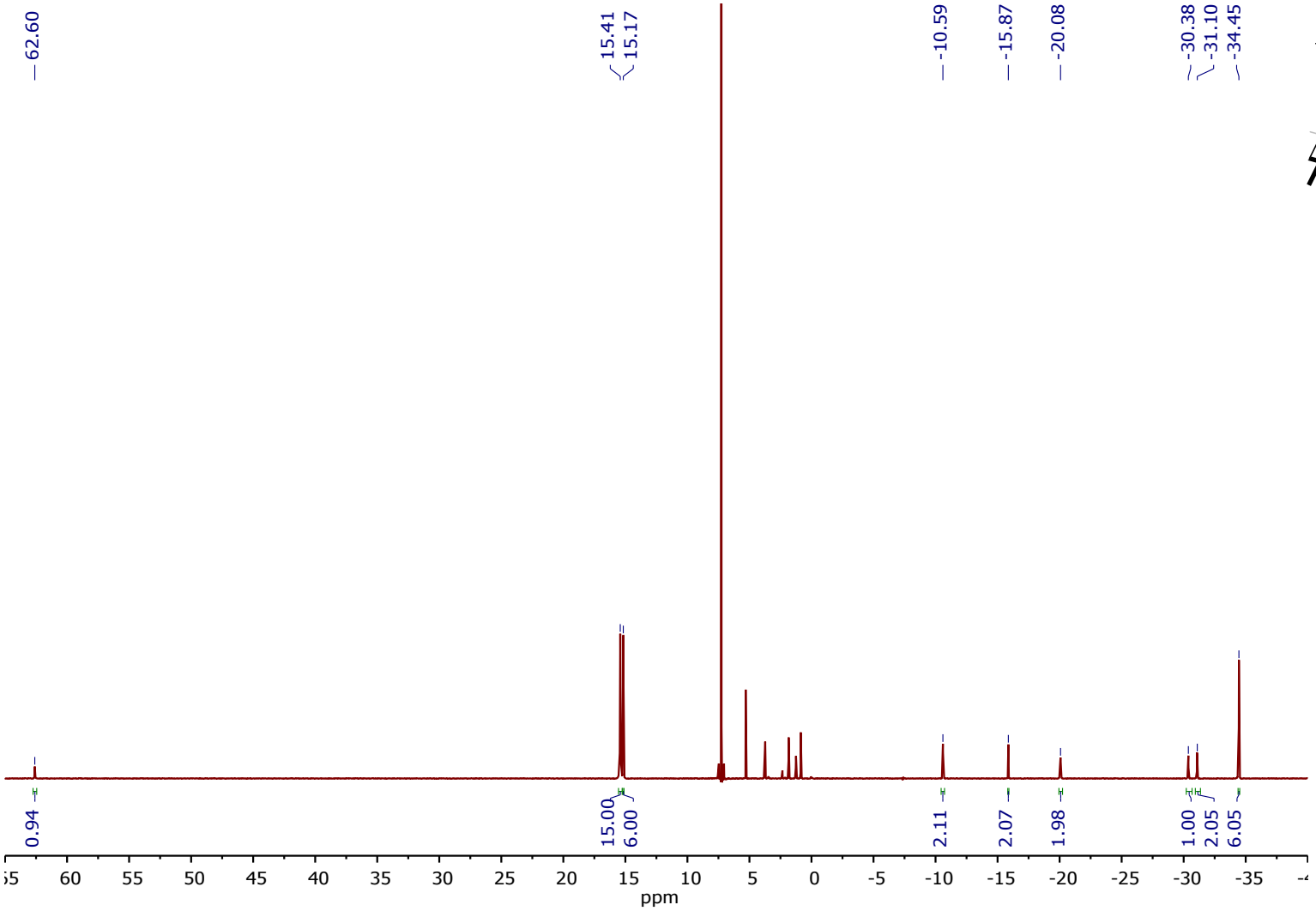

Figure S11: ^{1}H-NMR of **5** in $CDCl_3$ (signals in the diamagnetic region are solvent impurities from DCM, THF, and hexane)

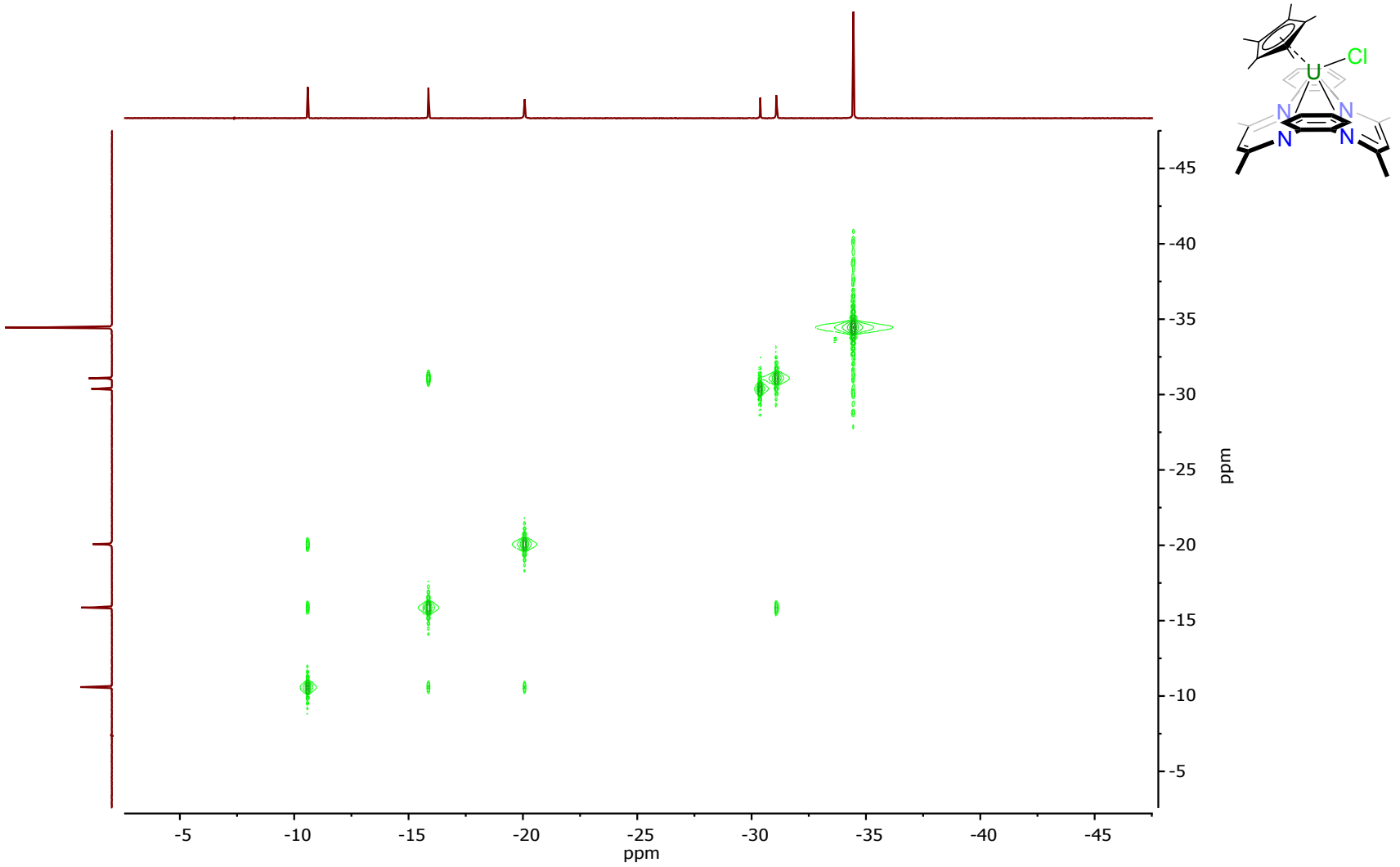

Figure S12: ^{1}H COSY of **5** in $CDCl_3$. Not all signals are present in this spectrum

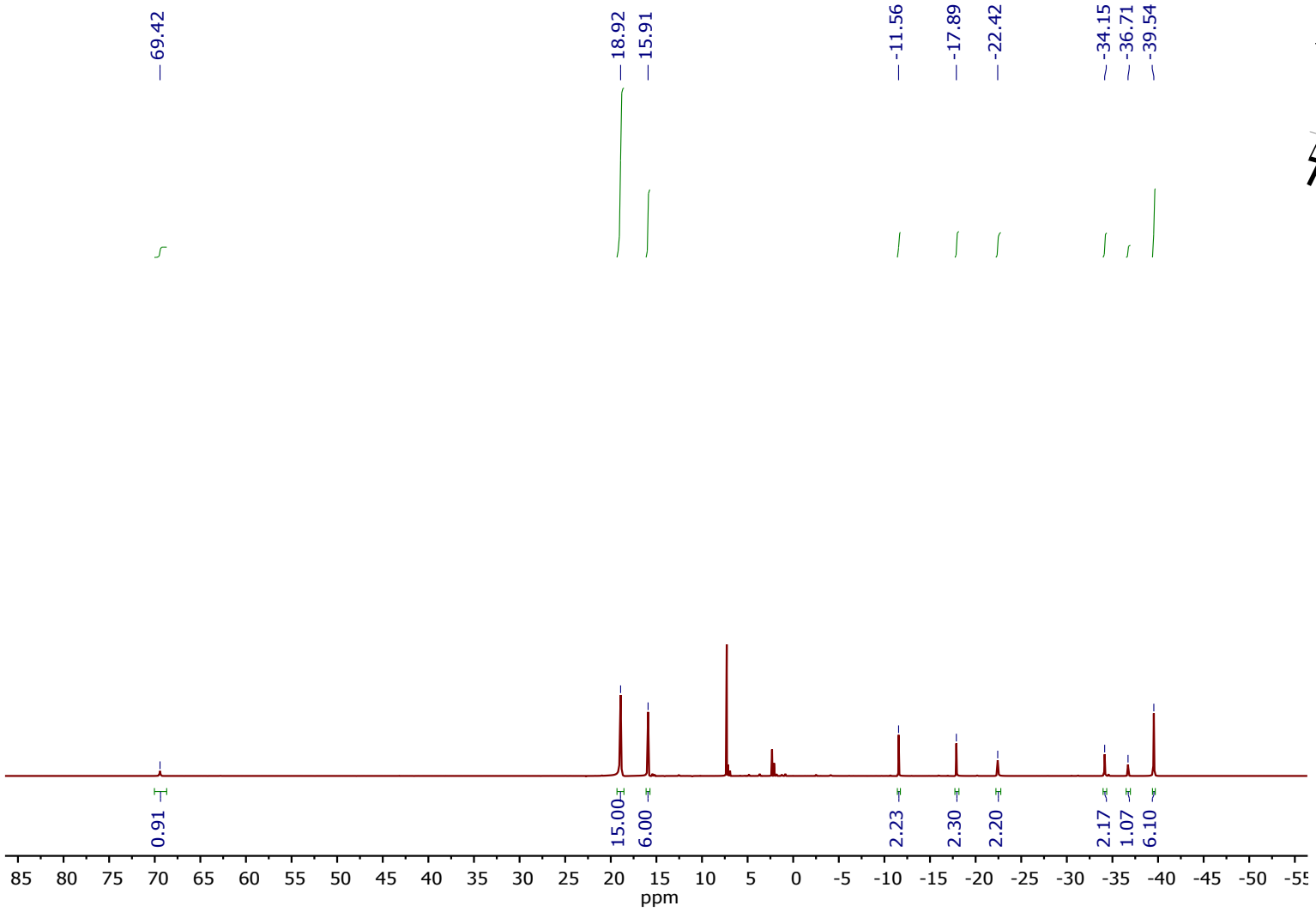

Figure S13: ^{1}H-NMR of **6** in $CDCl_3$.

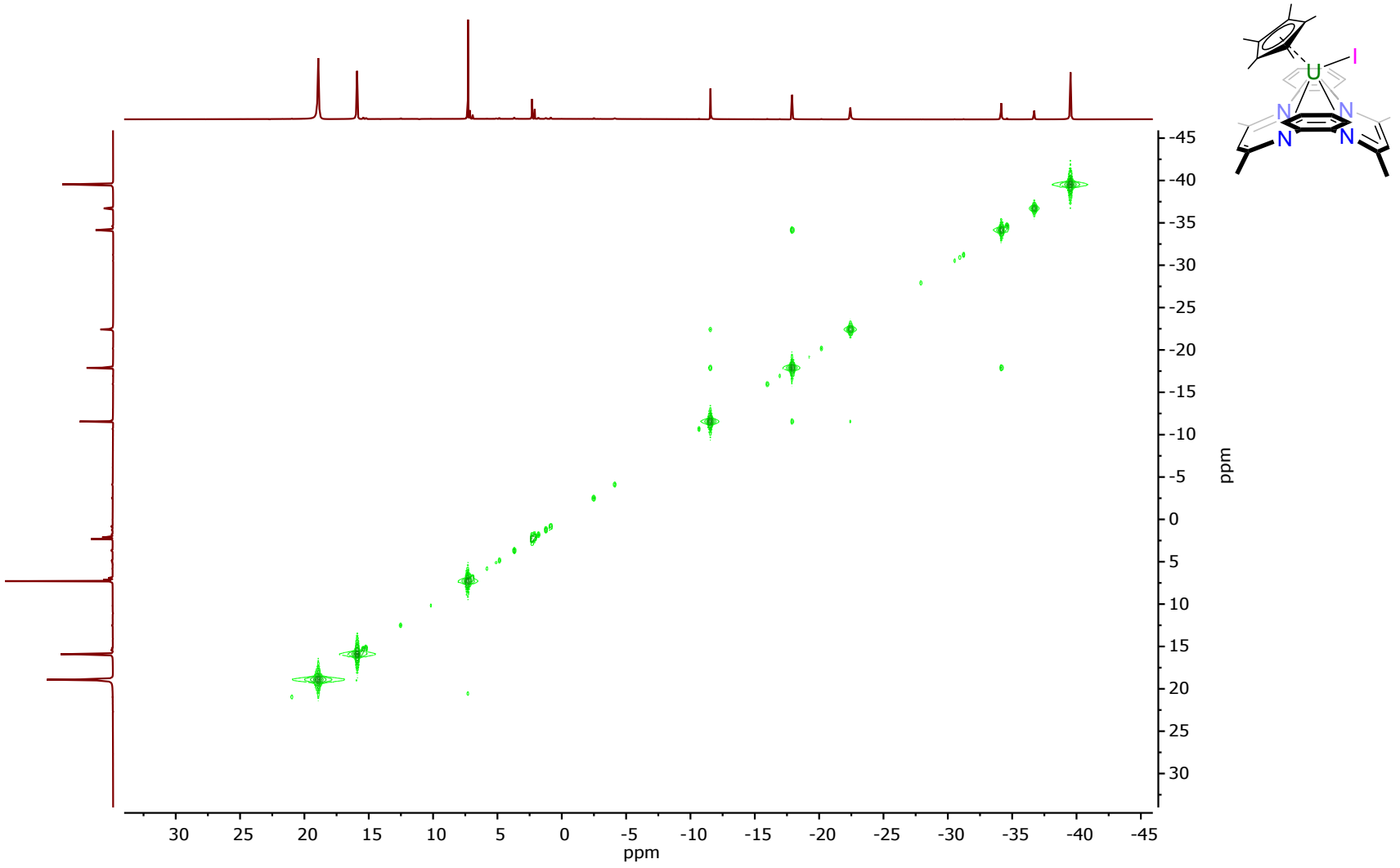

Figure S14: ^{1}H COSY of **6** in $CDCl_3$. Not all signals are present in this spectrum.

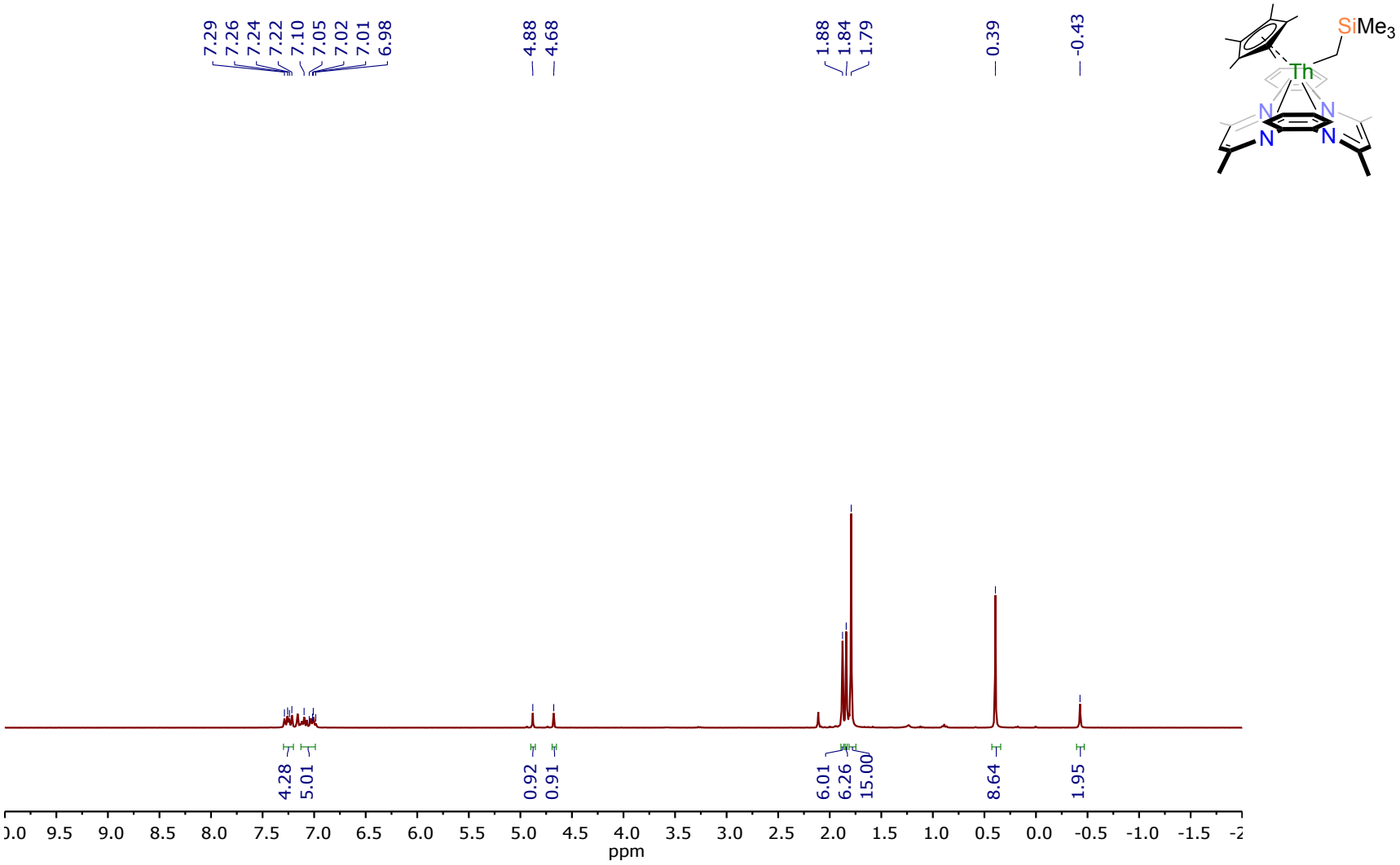

Figure S15: ^{1}H-NMR of **7** in C_6D_6 (small toluene impurity, 300 MHz)

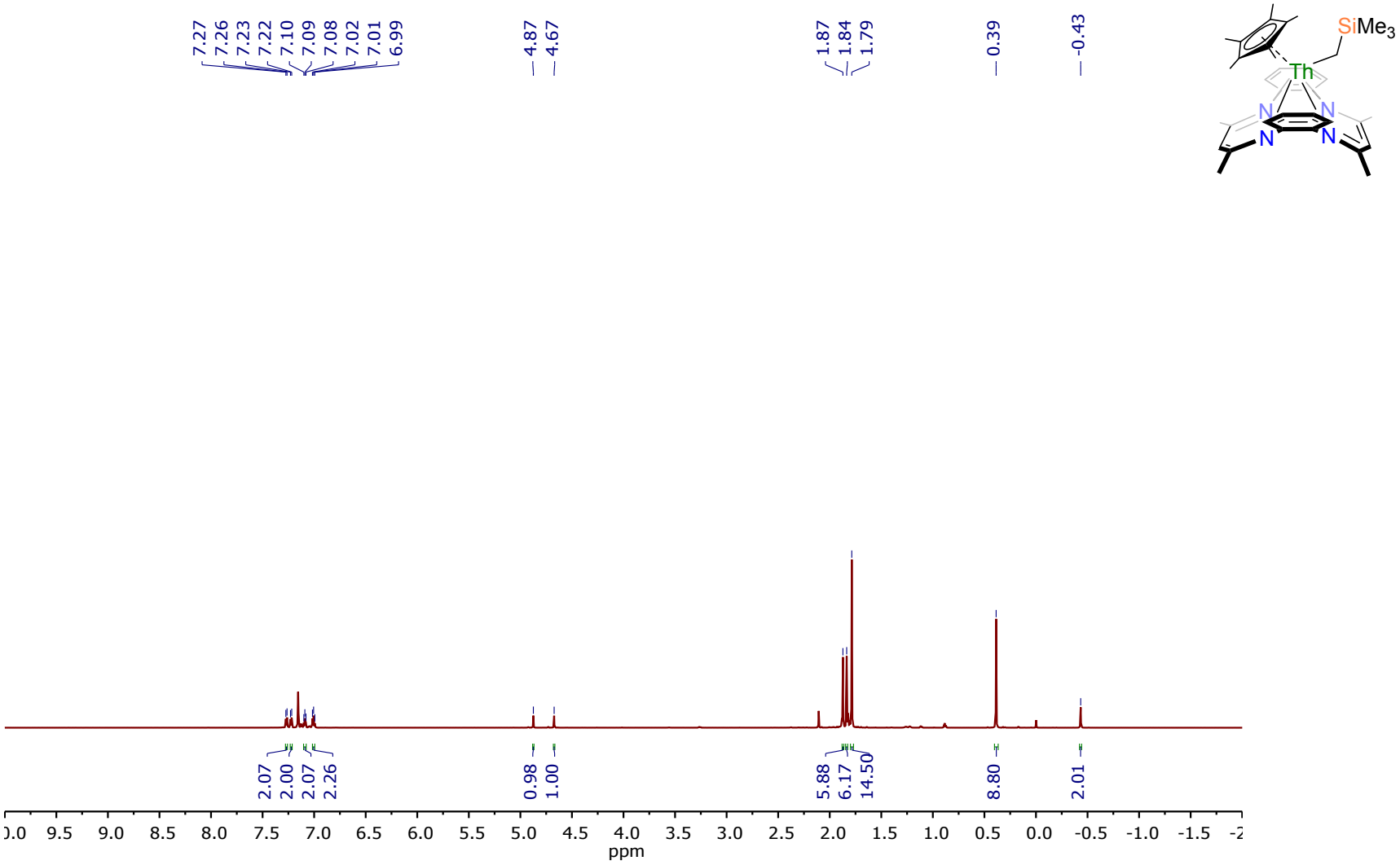

Figure S16: ^{1}H-NMR of **7** in C_6D_6 (small toluene impurity, 700 MHz)

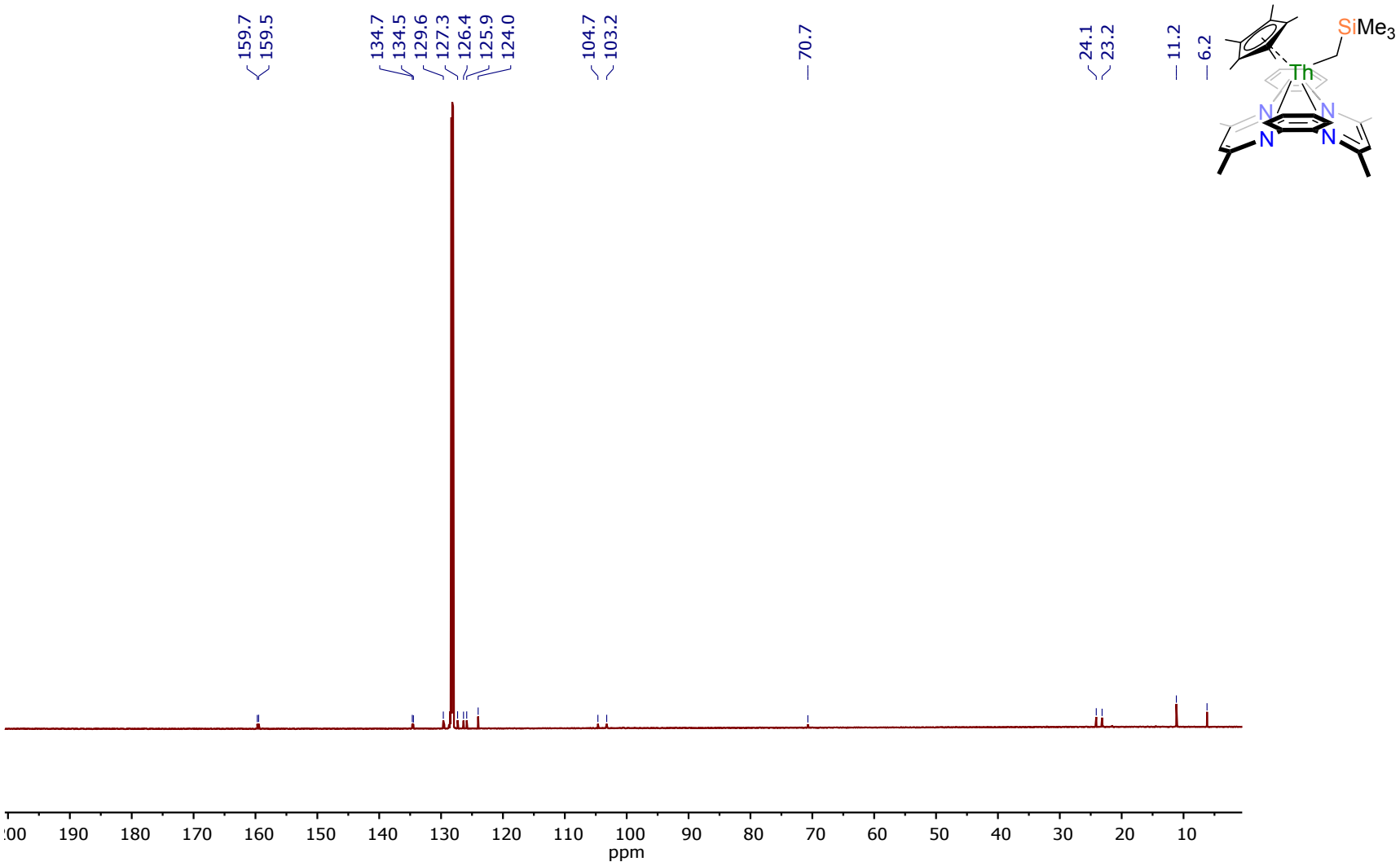

Figure S17: ^{13}C-NMR of **7** in C_6D_6

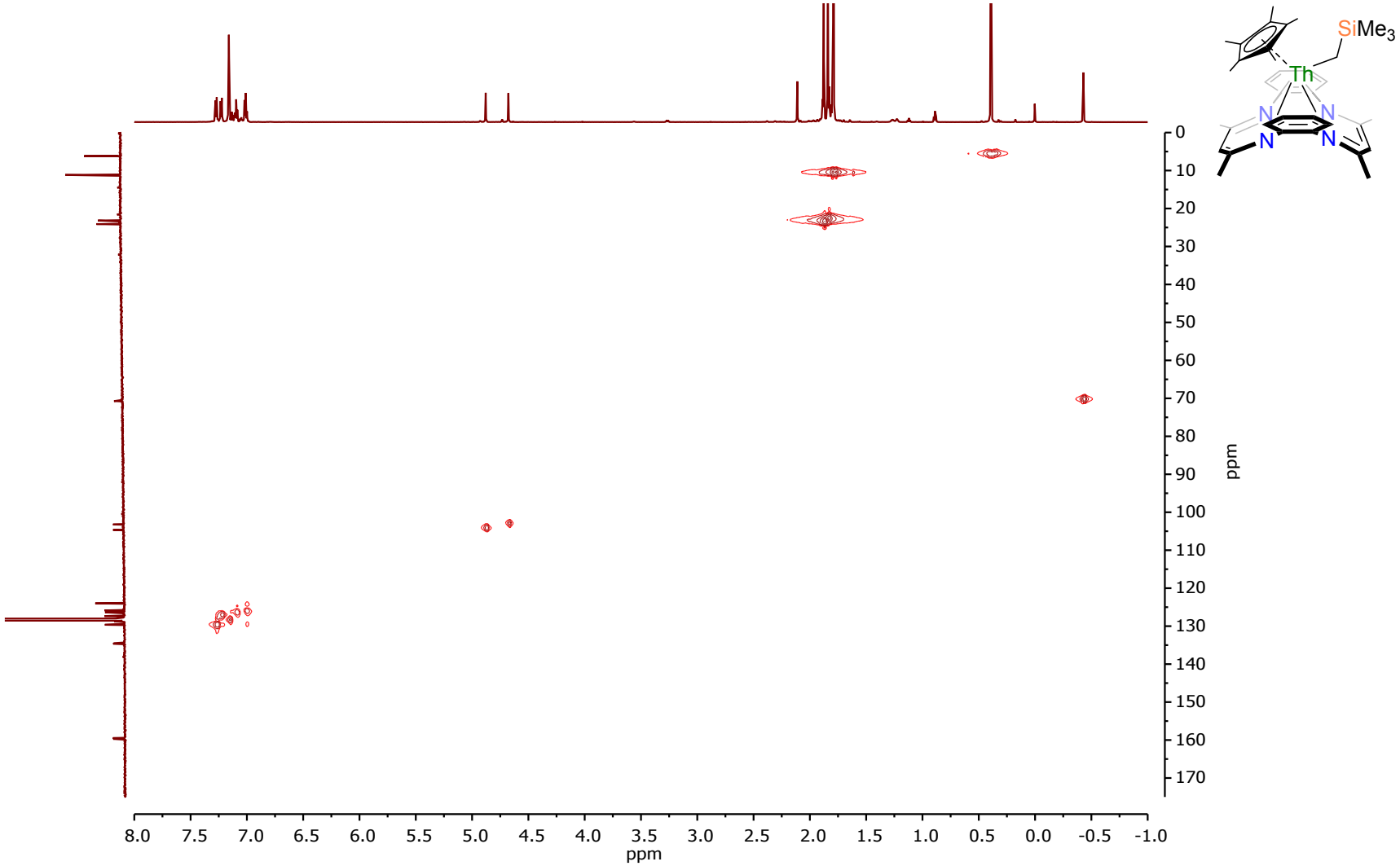

Figure S18: ^{1}H-^{13}C HSQC of **7** in C_6D_6

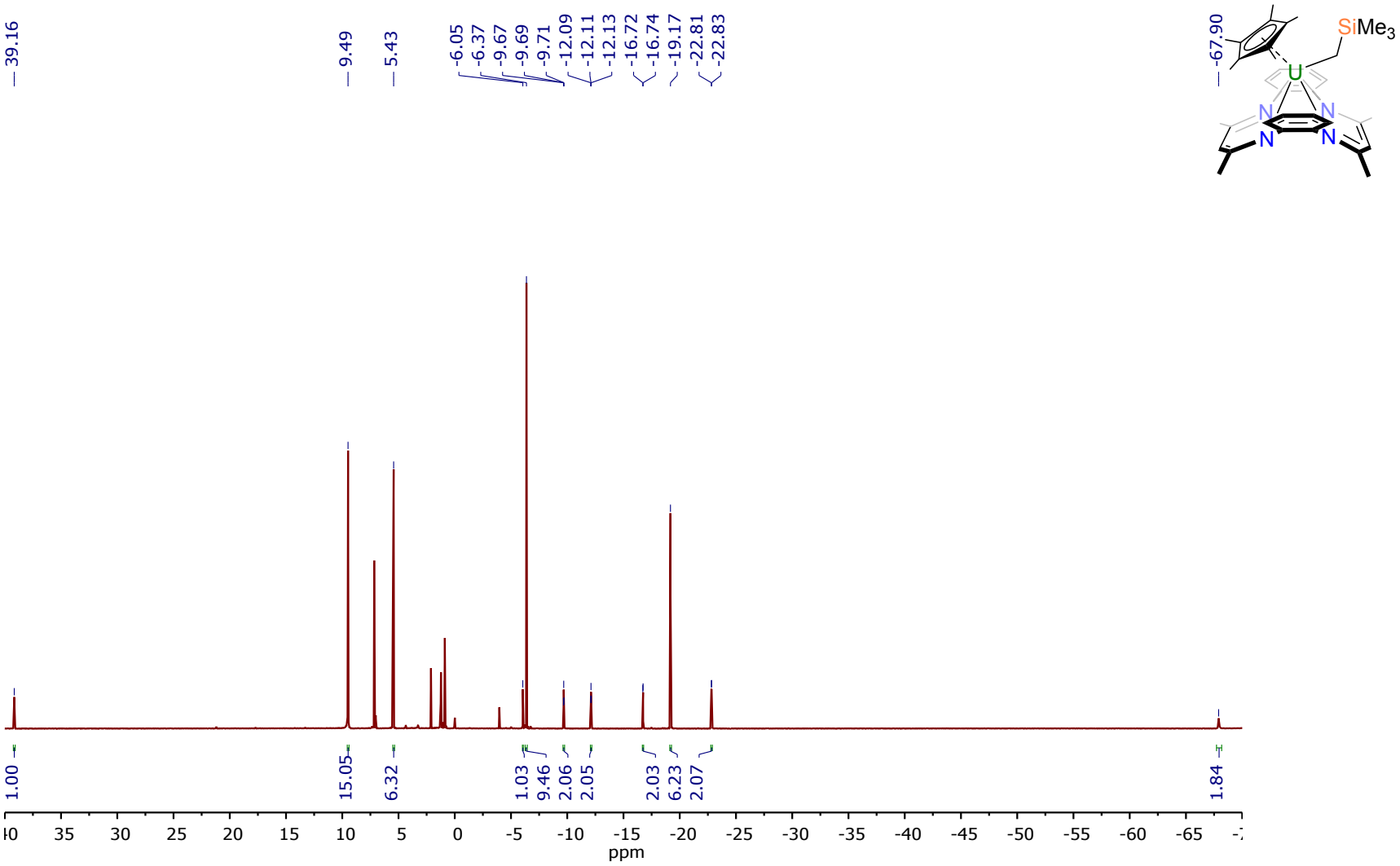

Figure S19: ^{1}H-NMR of **8** in C_6D_6 (impurities at 0.88, 1.25 and 2.1 ppm are hexane and toluene, unknown impurity at -3.96 ppm)

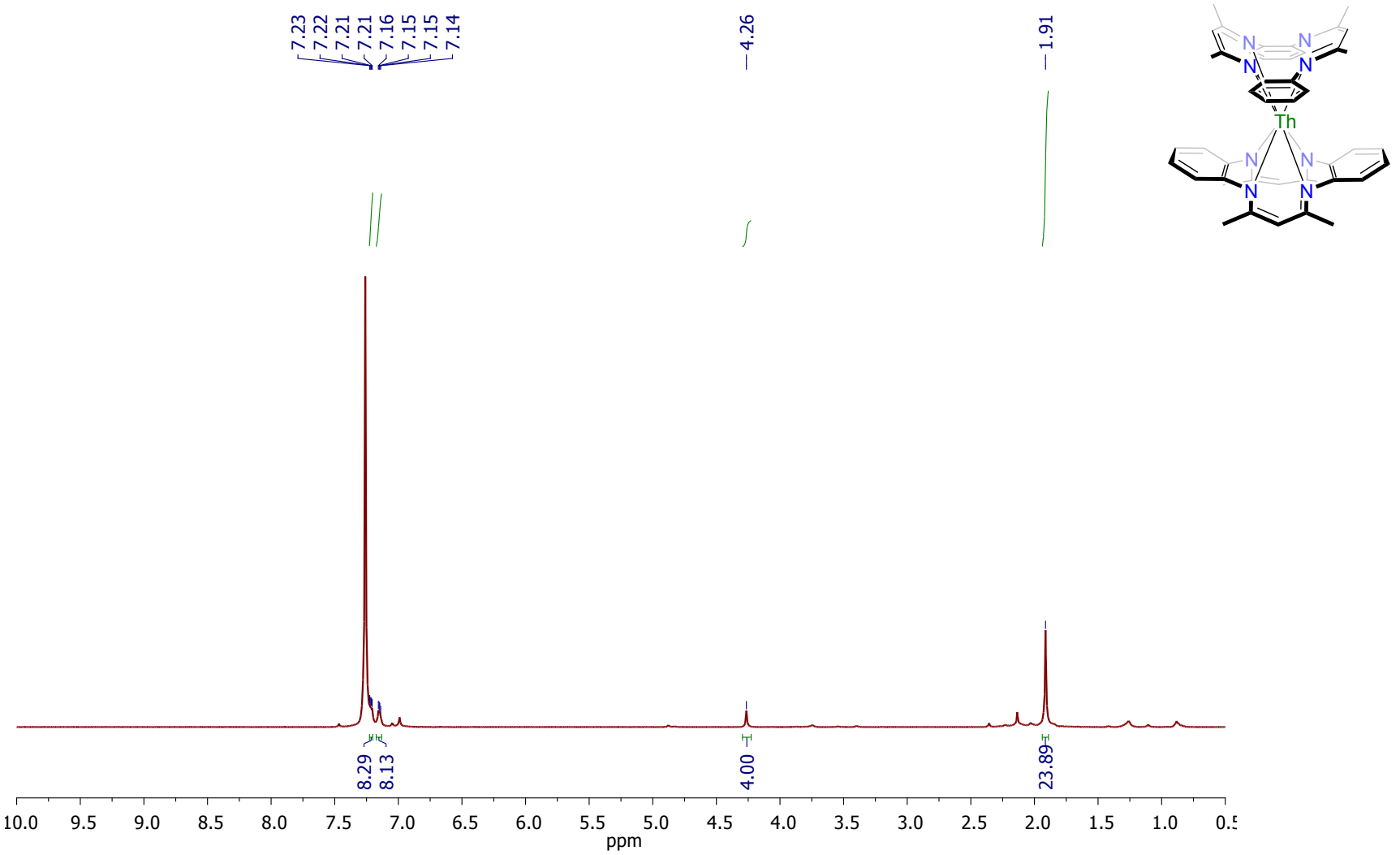

Figure S20: ^{1}H-NMR of **9** in $CDCl_3$

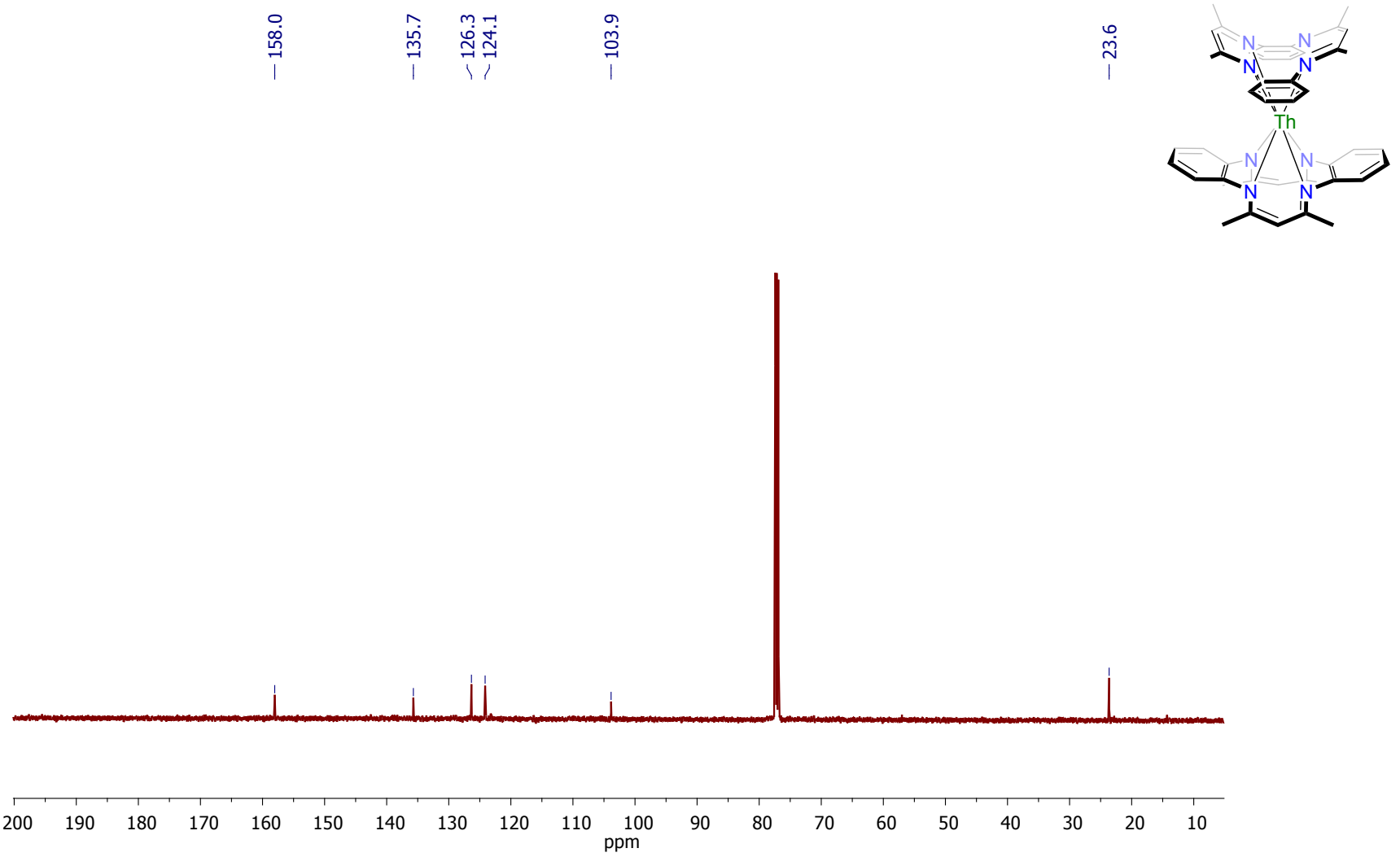

Figure S21: ^{13}C-NMR of **9** in $CDCl_3$

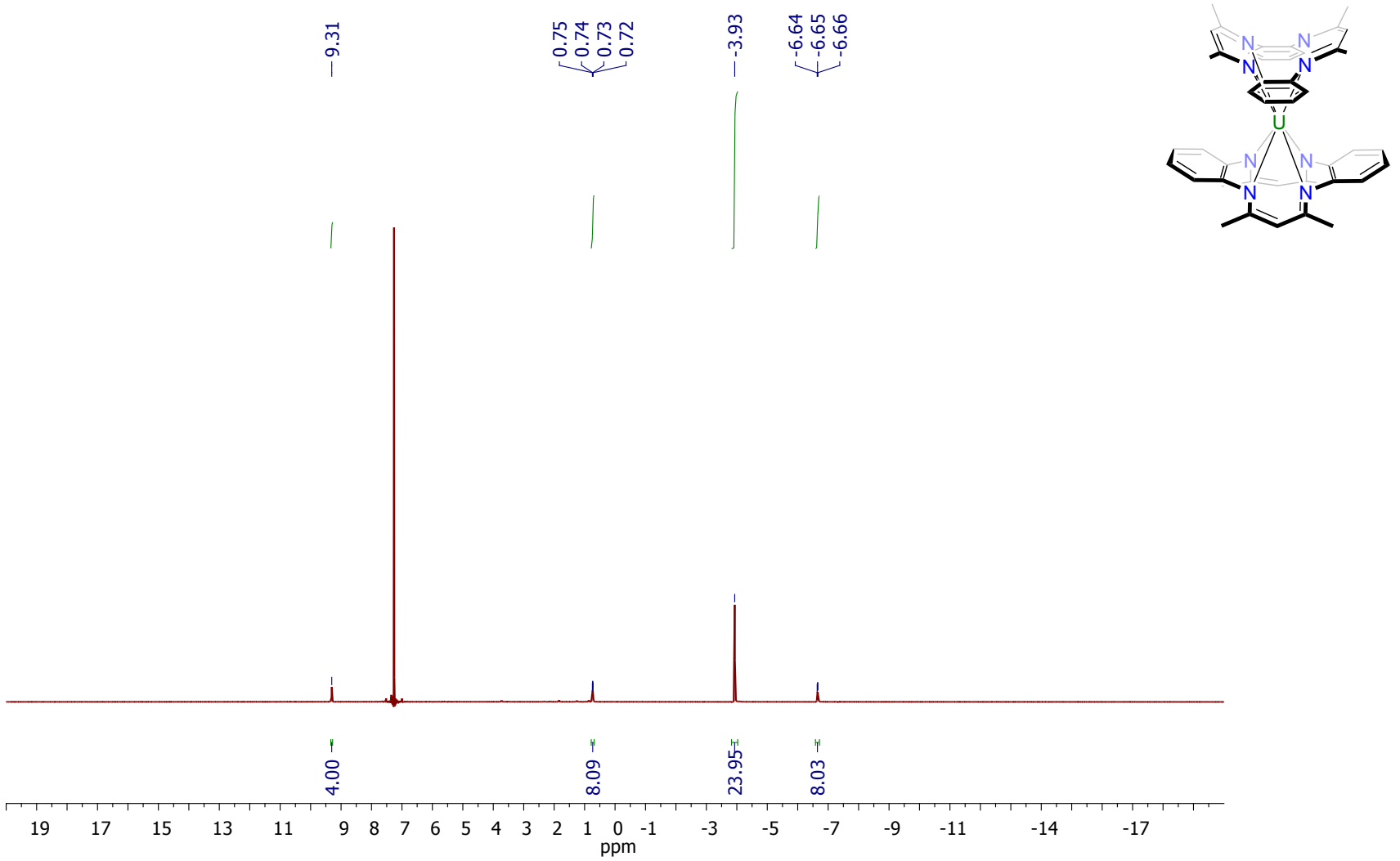

Figure S22: ^{1}H-NMR of **10** in $CDCl_3$

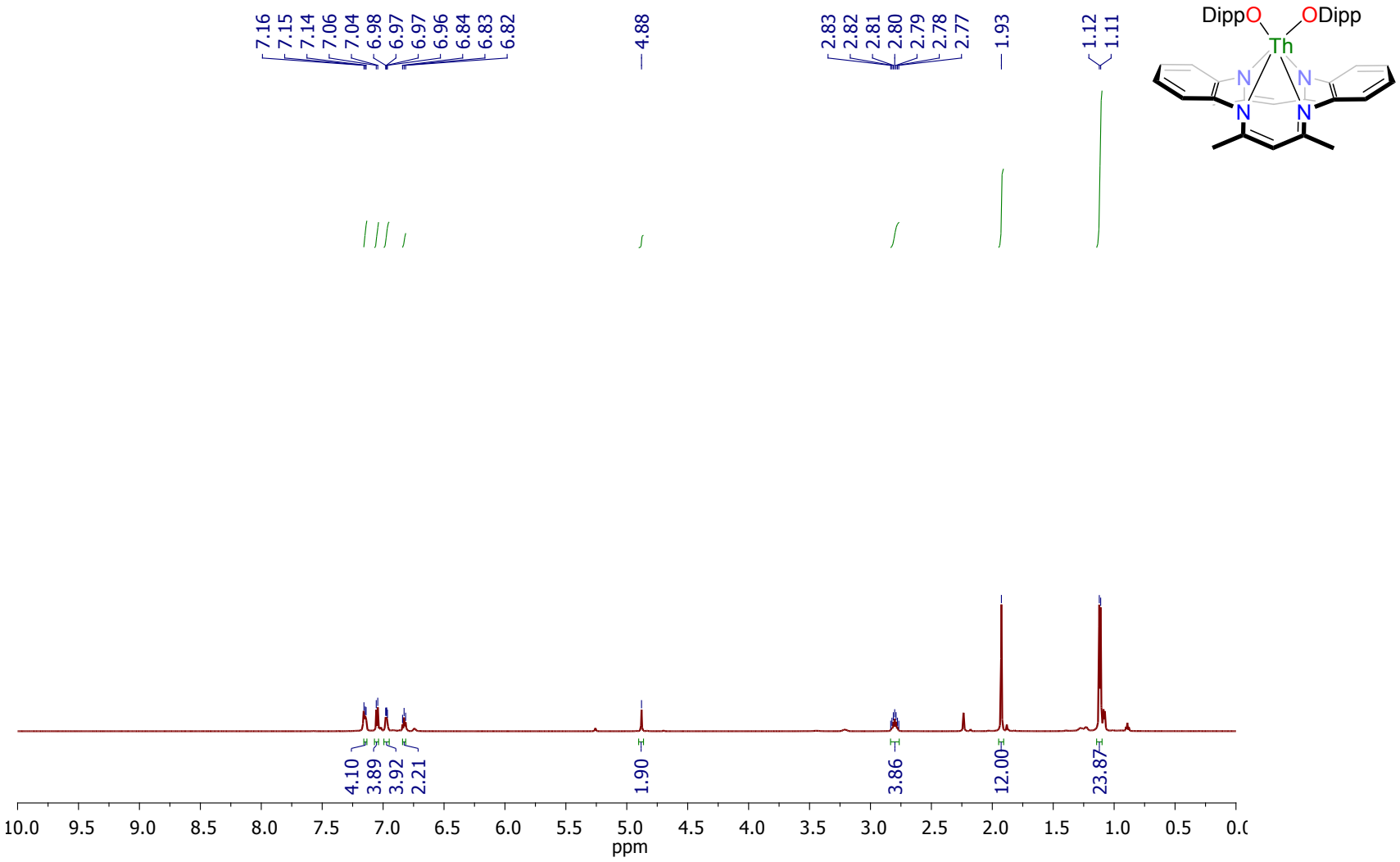

Figure S23: ^{1}H-NMR of **11** in C_6D_6 (signals at 6.71, 5.26, 3.18, 2.20 and 1.05 ppm are from an unknown impurity)

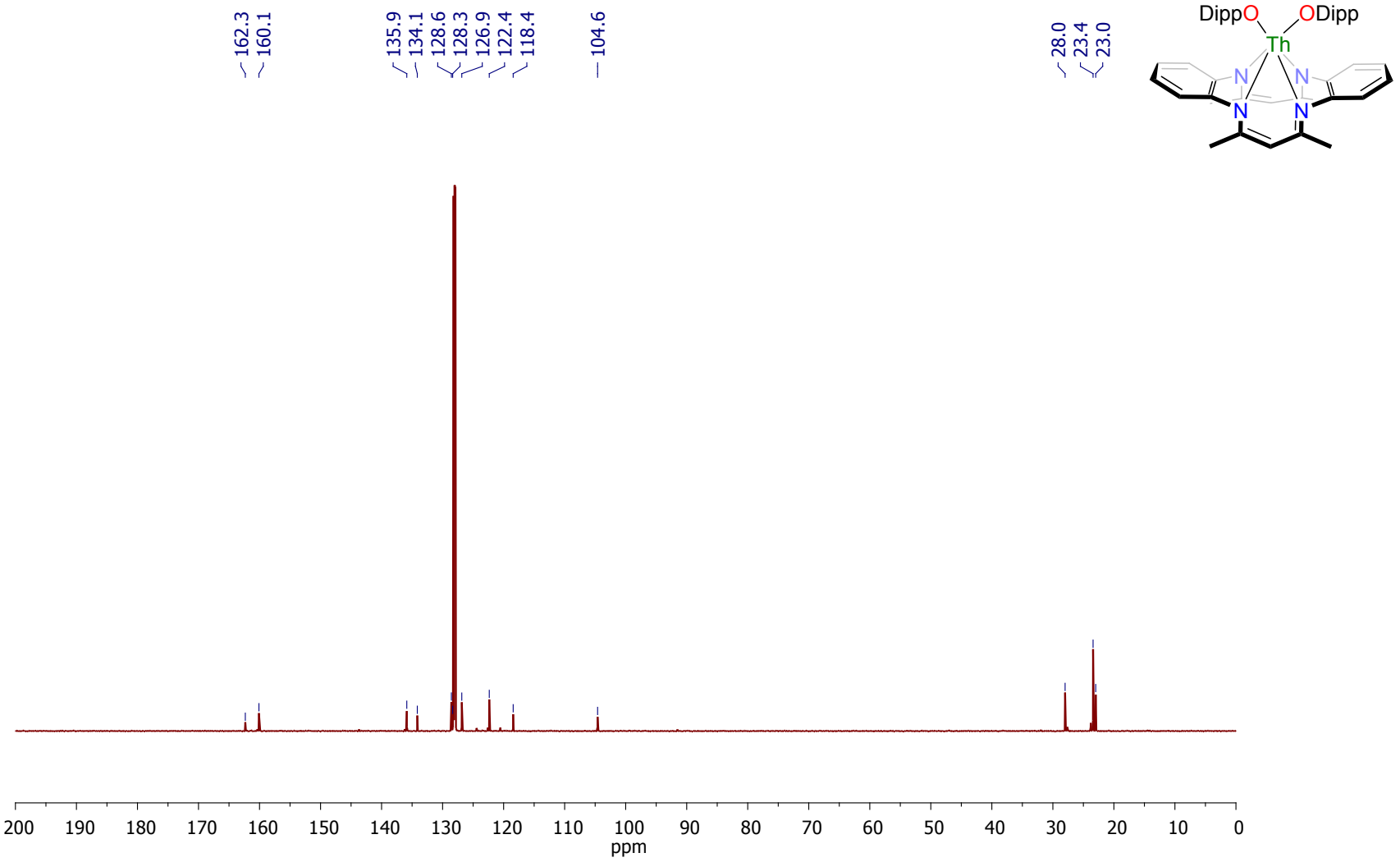

Figure S24: ^{13}C-NMR of **11** in C_6D_6

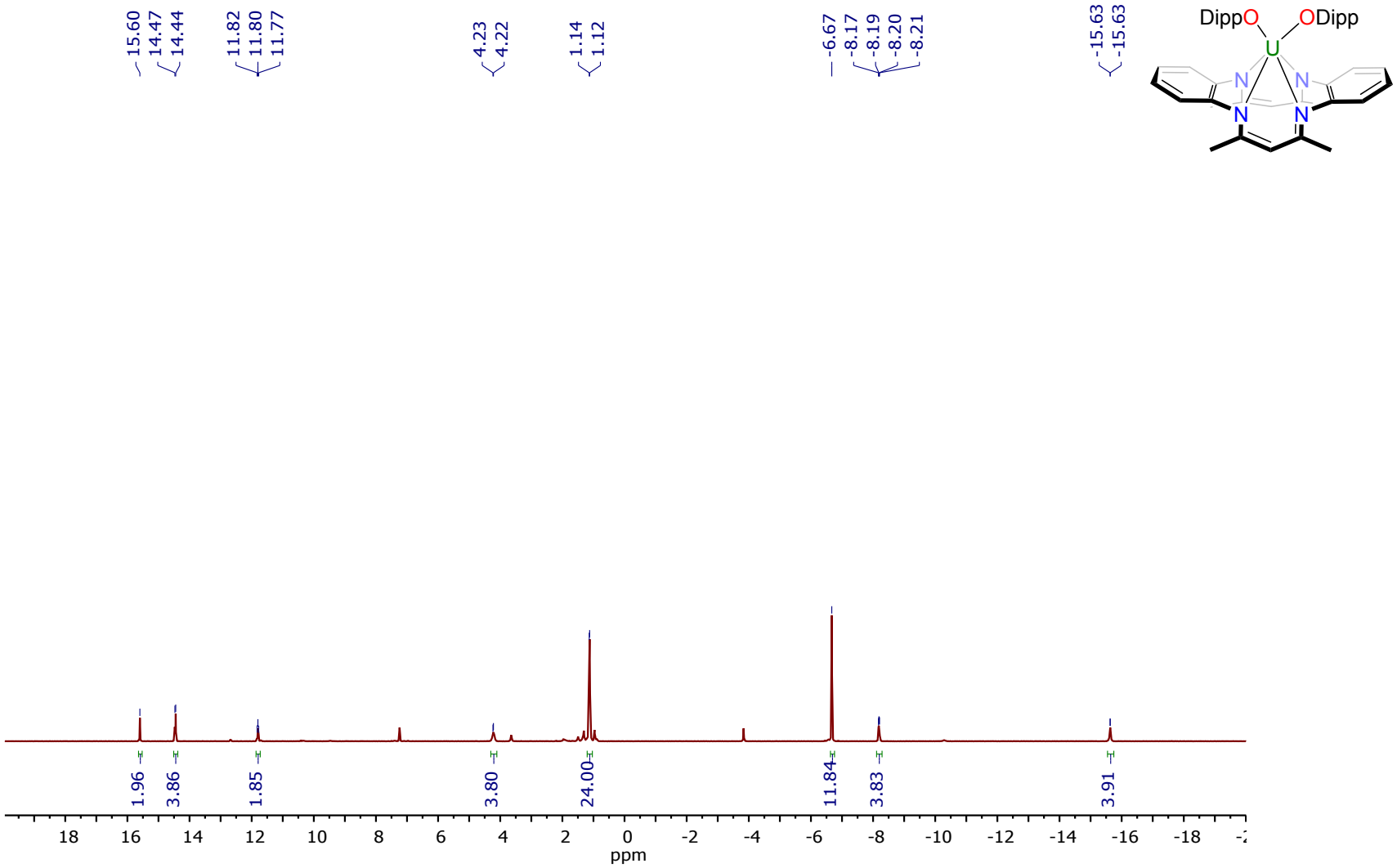

Figure S25: ^{1}H-NMR of **12** in C_6D_6 (signals in the diamagnetic region are solvent impurities from hexane, small impurity of **10** at -3.97 ppm)

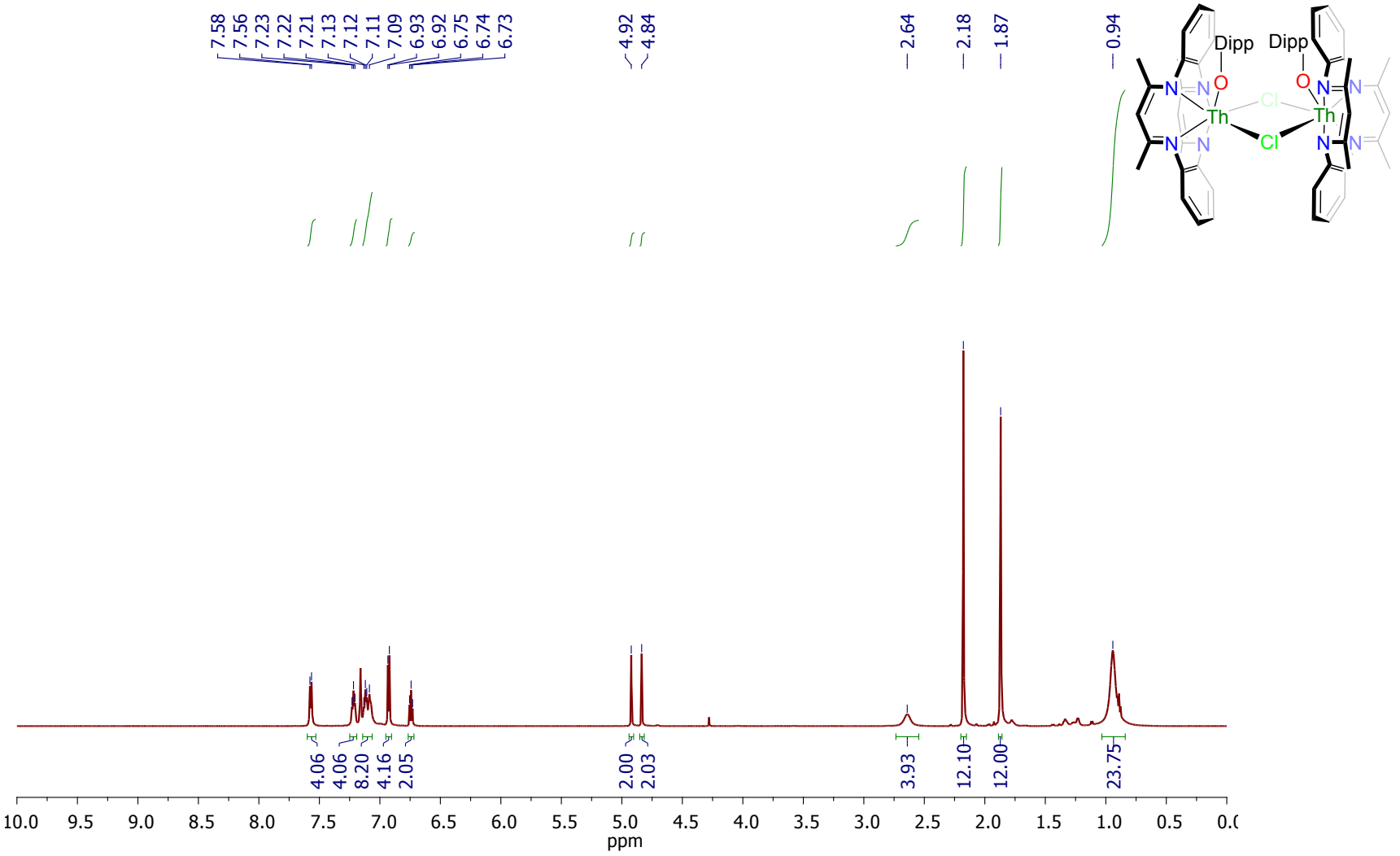

Figure S26: ^{1}H-NMR of **13** in C_6D_6

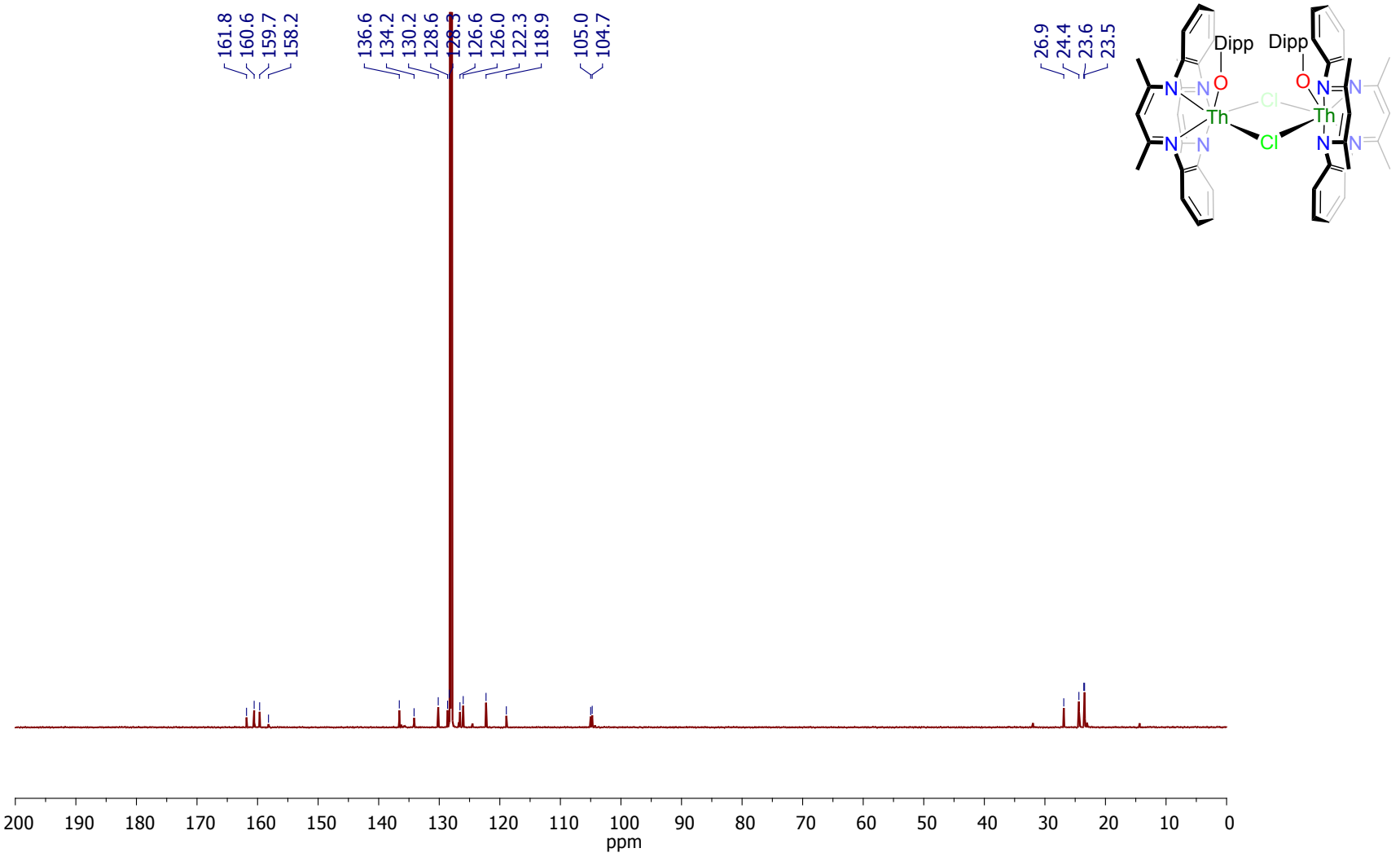

Figure S27: ^{13}C-NMR of **13** in C_6D_6

Crystallographic details

Tables S1: Crystallographic details

	K_2L^1	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Chemical formula	$C_{30}H_{42}N_4O_4K_2$	$C_{30}H_{38}N_4O_2Cl_2Th$	$C_{44}H_{44}N_8Cl_4U_2$	$C_{22}H_{22}N_4I_2U$	$C_{32}H_{37}N_4Cl_1Th$	$C_{32}H_{37}N_4Cl_1U$	$C_{32}H_{37}N_4I_1U$	$C_{36}H_{48}N_4Si_1Th$	$C_{36}H_{48}N_4Si_1U$ $0.5(C_6H_{14})$
M_r	600.87	789.58	1302.73	834.26	745.14	751.13	842.58	796.91	845.99
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	C2/c	P2(1)2(1)2(1)	P2(1)/c	P2(1)/m	P-1	P-1	P2(1)/n	P-1	P-1
a (Å)	20.775(2)	9.1064(3)	11.9519(5)	20.991(1)	10.4328(5)	10.321(2)	13.7325(6)	10.4299(3)	10.3468(7)
b (Å)	34.796(4)	12.5806(4)	16.7752(7)	10.687(1)	11.7779(6)	11.792(2)	14.3766(6)	11.9194(4)	11.7713(9)
c (Å)	19.435(3)	26.4577(9)	11.8899(5)	23.293(1)	14.0722(7)	14.111(2)	17.8153(9)	15.9610(5)	15.4024(11)
α (°)	90	90	90	90	112.907(2)	113.173(7)	90	111.716(2)	74.430(3)
β (°)	119.070(2)	90	117.261(2)	115.619(2)	90.535(3)	90.878(8)	98.805(2)	96.787(2)	81.235(3)
γ (°)	90	90	90	90	92.754(2)	92.274(9)	90	94.947(2)	87.926(3)
V (Å^3)	12268(3)	3031.1(2)	2119.1(1)	4711.8(5)	1590.2(1)	1576.7(5)	3475.8(3)	1812.2(1)	1789.0(2)
Z	16	4	2	8	2	2	4	2	2
Densitiy (g cm^{-3})	1.301	1.730	2.042	2.352	1.556	1.582	1.610	1.460	1.573
F(000)	5120	1544	1232	3040	728	732	1608	792	846
Radiation Type	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α
μ (mm^{-1})	0.349	5.129	7.928	9.526	4.798	5.257	5.581	4.175	4.611
Crystal size	0.16	0.4	0.12	0.10	0.12	0.22	0.15	0.12	0.08
	0.12	0.02	0.10	0.10	0.11	0.18	0.14	0.08	0.07
	0.12	0.02	0.09	0.10	0.09	0.17	0.10	0.08	0.05
Meas. Refl.	99919	51711	32877	116475	45069	21079	19741	66817	20197
Indep. Refl.	11304	5579	3914	8771	6518	5745	6349	8328	6575
Obsvd. [$I > 2\sigma(I)$]	7335	5493	3221	8333	6212	5514	4520	7419	5249
R_{int}	0.0929	0.0669	0.0373	0.1304	0.0367	0.0246	0.0920	0.0626	0.0685
R [$F^2 > 2\sigma(F^2)$]	0.0563	0.0198	0.0218	0.0652	0.0230	0.0184	0.0635	0.0327	0.0663
wR(F^2)	0.1485	0.0476	0.0519	0.1755	0.0437	0.0403	0.1542	0.0661	0.1732
S	1.016	1.080	1.062	1.154	1.086	1.062	1.016	1.093	1.014
$\Delta\rho_{max}$	0.963	1.086	2.353	12.344[#]	1.105	1.213	4.426	2.589	9.565
$\Delta\rho_{min}$	-0.655	-0.751	-0.747	-3.220	-0.516	-0.951	-1.139	-0.708	-1.722
CCDC	1488210	1412406	1554547	1488211	1554548	1554550	1516431	1554551	1554549

[#]The high peak is close to one of iodine atoms and results from unresolvable twinning in the crystals. Crystallization using other methods was attempted but did not improve crystal quality.

Tables S2: Crystallographic details

	11	**12**	**13**
Chemical formula	$C_{46}H_{56}N_4O_2Th$	$C_{46}H_{56}N_4O_2U$	$C_{68}H_{78}N_8O_2Cl_2Th_2$ C_6H_{14} C_6H_6
M_r	928.98	934.97	1738.64
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c	P2(1)/n
a (Å)	11.203(3)	11.2024(8)	14.5644(6)
b (Å)	17.832(4)	17.7114(12)	25.0430(11)
c (Å)	20.941(5)	20.8161(15)	20.6741(8)
α (°)	90	90	90
β (°)	110.962(5)	102.734(2)	96.878(2)
γ (°)	90	90	90
V (Å^3)	4092.7(16)	4028.5(5)	7486.3(5)
Z	4	4	4
Densitiy (g cm^{-3})	1.508	1.542	1.543
F(000)	1864	1872	3456
Radiation Type	MoK_α	MoK_α	MoK_α
μ (mm^{-1})	3.685	4.072	4.901
Crystal size	0.10	0.12	0.20
	0.10	0.08	0.20
	0.06	0.08	0.20
Meas. Refl.	74389	100057	108644
Indep. Refl.	7532	8290	13747
Obsvd. [$I > 2\sigma(I)$]	6218	6317	11533
R_{int}	0.0814	0.0884	0.0339
R [$F^2 > 2\sigma(F^2)$]	0.0320	0.0405	0.0370
wR(F^2)	0.0744	0.0964	0.0838
S	1.067	1.056	1.035
$\Delta\rho_{max}$	1.744	3.627	3.410
$\Delta\rho_{min}$	-0.753	-1.006	-1.334
CCDC	1554554	1554553	1554552

Table S3: Selected bond lengths and angles.

Atoms	K_2L^1	1	2	3[#]	4	5	6	7
M1 /M2 – N10	2.705(2) / 2.816(2)	2.478(4)	2.363(3)	2.33(1)	2.424(2)	2.380(2)	2.38(1)	2.468(3)
M1 / M2 – N11	2.653(3) / 2.863(3)	2.469(4)	2.350(3)	-	2.444(2)	2.395(2)	2.38(1)	2.437(3)
M1 / M2 – N20	-	2.474(5)	2.358(3)	2.32(1)	2.435(2)	2.372(2)	2.35(1)	2.461(3)
M1 / M2 – N21	-	2.466(4)	2.365(3)	-	2.448(2)	2.402(2)	2.39(1)	2.513(2)
M1 – X1*	-	2.755(1)	2.767(1)	3.08(1)	2.737(1)	2.696(1)	3.16(1)	2.598(3)
M1 – X2*	-	2.758(1)	2.660(1)	3.06(1)	-	-	-	-
M1 – O100	-	2.606(4)	-	-	-	-	-	-
M1 – O200	-	2.575(4)	-	-	-	-	-	-
C10 – N10	1.401(4)	1.426(6)	1.424(5)	1.40(1)	1.411(4)	1.417(4)	1.42(1)	1.401(4)
C11 – N11	1.397(4)	1.423(7)	1.416(5)	-	1.417(4)	1.422(4)	1.44(1)	1.422(4)
C10 – C11	1.436(4)	1.421(7)	1.405(5)	1.43(3)**	1.422(4)	1.423(4)	1.41(1)	1.418(5)
C11 – C12	1.395(4)	1.391(8)	1.407(5)	-	1.407(4)	1.405(4)	1.40(1)	1.397(5)
C12 – C13	1.383(4)	1.369(8)	1.368(5)	-	1.380(4)	1.385(4)	1.41(1)	1.383(5)
C13 – C14	1.384(4)	1.394(8)	1.385(6)	1.37(4)[##]	1.388(5)	1.387(4)	1.35(2)	1.380(6)
C14 – C15	1.390(4)	1.374(8)	1.385(6)	1.40(3)	1.377(5)	1.383(4)	1.39(1)	1.369(5)
C15 – C10	1.400(4)	1.394(8)	1.397(5)	1.39(2)	1.402(4)	1.404(4)	1.40(1)	1.406(5)
N10 – C29	1.318(4)	1.339(7)	1.323(5)	1.32(2)	1.333(4)	1.334(3)	1.32(1)	1.326(4)
C30 – C29	1.513(4)	1.506(7)	1.507(6)	1.50(2)	1.515(4)	1.514(4)	1.50(1)	1.518(5)
C29 – C28	1.410(4)	1.406(8)	1.402(5)	1.42(2)	1.394(4)	1.402(4)	1.41(1)	1.397(5)
C28 – C27	-	1.393(8)	1.382(5)	1.40(2)	1.397(4)	1.398(4)	1.36(2)	1.393(5)
C27 – C26	-	1.492(8)	1.507(5)	1.50(2)	1.509(4)	1.514(4)	1.52(1)	1.517(5)
C27 – N20	-	1.331(7)	1.344(5)	1.34(2)	1.336(4)	1.332(3)	1.35(1)	1.338(4)
M1 – $N4_{plane}$	1.806(1)/2.036(1)	1.506(3)	1.390(1)	1.36(1)	1.490(1)	1.426(1)	1.42(1)	1.530(1)
M1 – Cp_{cent}	-	-	-	-	2.578(1)	2.513(1)	2.51(1)	2.603(1)
Ph vs $N4_{plane}$	21.4(1) / 24.4(1)	13.0(1) / 14.0(1)	22.8(1) / 24.7(1)	33.9(1) / 31.4(1)	22.2(1) / 18.1(1)	22.6(1) / 18.4(1)	20.9(2) / 18.8(2)	15.5(1) / 19.3(1)
NacNac vs $N4_{Plane}$	37.2(1) / 37.2(1)	32.5(2) / 37.1(2)°	46.3(2) / 38.8(2)	33.6(1) / 32.1(1)	48.9(1) / 41.4(1)	47.5(1) / 41.2(1)	35.8(3) / 39.5(2)	46.0(2) / 16.6(2)
Upper vs lower	-	44.7(1)	-	-	-		-	-
Cp_{cent} – U1 – $N4_{cent}$	-	-	-	-	144.03(1)	144.92(2)	145.0(1)	141.7(1)

[#]Due to poor quality of the crystals these values are just given for orientation.

*X = Cl. I C or O

**C10 – C10

[##] C14 – C14

Table S4: Selected bond lengths and angles.

Atoms	8	11	12	13
M1 /M2 – N10	2.42(1)	2.467(3)	2.418(4)	2.438(4)
M1 / M2 – N11	2.41(1)	2.390(4)	2.358(4)	2.484(4)
M1 / M2 – N20	2.40(1)	2.417(3)	2.342(4)	2.454(4)
M1 / M2 – N21	2.42(1)	2.482(3)	2.398(4)	2.447(4)
M1 – X1*	2.48(1)	2.194(3)	2.151(4)	2.184(3) O1
M1 – X2*	-	2.192(3)	2.142(3)	2.872(1) Cl1 / Cl2
M1 – O100	-	-	-	-
M1 – O200	-	-	-	-
C10 – N10	1.40(1)	1.415(5)	1.411(7)	1.421(6)
C11 – N11	1.42(1)	1.429(5)	1.420(6)	1.414(6)
C10 – C11	1.43(2)	1.428(6)	1.420(7)	1.417(7)
C11 – C12	1.38(2)	1.398(6)	1.394(7)	1.408(7)
C12 – C13	1.36(2)	1.383(7)	1.380(8)	1.379(8)
C13 – C14	1.36(2)	1.387(7)	1.383(8)	1.380(9)
C14 – C15	1.41(2)	1.370(6)	1.362(8)	1.386(8)
C15 – C10	1.38(2)	1.404(6)	1.406(8)	1.395(7)
N10 – C29	1.32(1)	1.323(5)	1.329(6)	1.339(6)
C30 – C29	1.54(2)	1.508(6)	1.519(7)	1.515(7)
C29 – C28	1.36(2)	1.407(6)	1.400(7)	1.384(7)
C28 – C27	1.42(2)	1.384(6)	1.389(7)	1.413(8)
C27 – C26	1.49(2)	1.508(6)	1.515(7)	1.516(7)
C27 – N20	1.34(1)	1.344(5)	1.333(6)	1.319(7)
M1 – $N4_{plane}$	1.46(1)	1.475(1)	1.380(1)	1.518(1)
M1 – Cp_{cent}	2.53(1)	-	-	-
Ph vs $N4_{plane}$	16.9(1) / 18.3(1)	22.0(1) / 19.7(1)	21.9(2) / 20.8(1)	18.9(1) / 21.2(1)
NacNac vs $N4_{Plane}$	44.6(1) / 46.1(1)	41.7(1) / 41.7(1)	41.3(3) / 40.5(3)	48.2(1) / 48.9(1)
Upper vs lower	-	-	-	-
-Cp_{cent} – U1 – $N4_{cent}$	143.3(2)	-	-	-

*X = Cl. I C or O

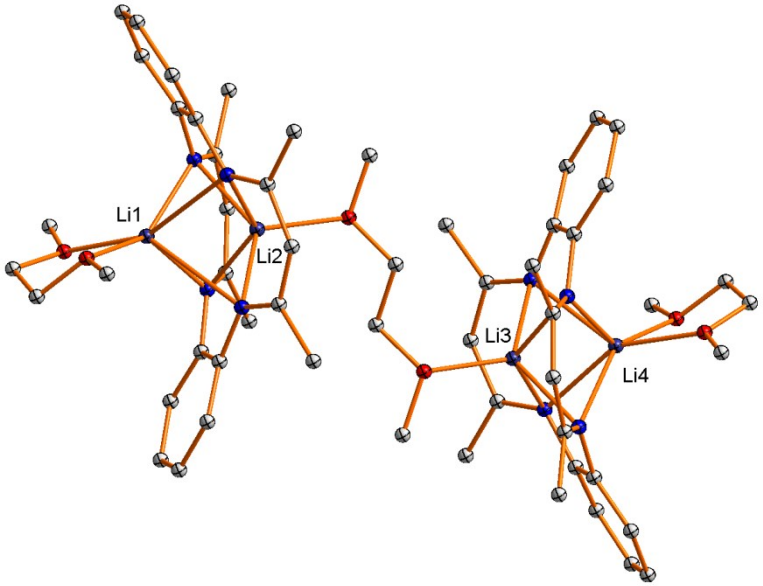

Figure S28: Ball and stick model of **Li_2TMTAA** characterized by Floriani *et. al.*[2]

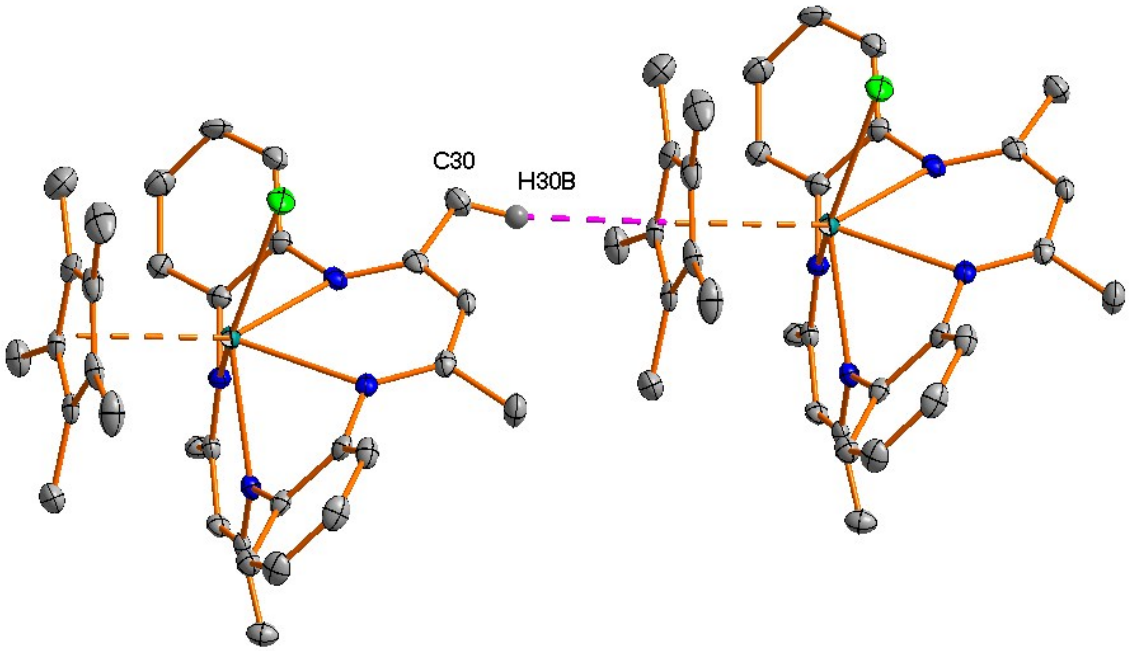

Figure S29: Crystal packing of **4** in the solid state. The pink bond indicates the CH…π-interaction in the structure. A similar short interaction can be seen in **5**.

Literature

1 J.H. Niewahner, K.A. Walters and A. Wagner, *J. Chem. Educ.*, 2007, **84**, 477.

2 S. De Angelis, E. Solari, E. Gallo, C. Floriani, A.Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1992, **31**, 2520.