Electronic Supplementary Material (ESI) for Chemical Science.

Photolysis-Driven Bond Activation by Thorium and Uranium Tetraosmate Polyhydride Complexes

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Supporting Information

Experimental Procedures

General considerations: Unless otherwise noted, all reactions were performed using standard Schlenk line techniques under an atmosphere of nitrogen, or in an MBraun inert atmosphere glove box under an atmosphere of nitrogen. Glassware and Celite® were stored in an oven at ca. 150 °C for at least 3 h prior to use. Molecular sieves (4 Å) were activated by heating to 200 °C overnight under vacuum prior to storage in a glovebox. NMR spectra were recorded on Bruker AV-600, AV-700, and AV-500 spectrometers. ^{1}H chemical shifts are given relative to residual solvent peaks and are recorded in units of parts per million (ppm). FT-IR samples were prepared as Nujol mulls pressed between KBr plates, with data collected with a Nicolet iS10 FT-IR spectrometer. Melting points were determined using sealed capillaries prepared under nitrogen on an OptiMelt automated melting point system. Elemental analyses were determined at the Microanalytical Facility at the College of Chemistry, University of California, Berkeley.

Materials: Tetrahydrofuran (THF), toluene, benzene, *n*-hexane, and *n*-pentane were purified by passage through columns of activated alumina and degassed by sparging with dinitrogen. Deuterated solvents were degassed with three freeze-pump-thaw cycles and stored over molecular sieves. Benzylpotassium,[1] Cp^*OsH_5,[2,3] UCl_4,[4] and $ThCl_4(DME)_2$[5] were synthesized according to literature procedures. Mesitylene and fluorobenzene were purchased from commercial sources and stored on molecular sieves. All other chemicals were purchased from commercial sources and used as received.

In-situ generation of K[Cp*OsH$_5$] (1):

Cp^*OsH_5 (5.0 mg, 0.015 mmol, 1.0 equiv.) and benzyl potassium (2.0 mg, 0.015 mmol, 1.0 equiv.) were dissolved in 0.4 mL d_8-THF each, then added together in a J. Young NMR tube and sealed. The colorless and orange solutions immediately become very pale yellow (nearly colorless). Analysis of the solution revealed the quantitative formation of **1** along with toluene. ^{1}H NMR (500 MHz, THF-d_8): δ 2.16 (s, 15H, CH_{3Cp^*}), –17.15 (s, 4H, Os–H).

Synthesis of Th{(μ-H$_4$)OsCp*}$_4$ (2-Th):

Cp^*OsH_5 (160.4 mg, 0.485 mmol, 4.0 equiv.) and benzyl potassium (63.1 mg, 0.485 mmol, 4.0 equiv.) were added to a 20 mL scintillation vial with THF (4 mL) to generate a solution of $K[Cp^*OsH_4]$. $ThCl_4(DME)_2$ (67.2 mg, 0.121 mmol, 1.0 equiv.) was dissolved in THF (4 mL) and added to the $K[Cp^*OsH_4]$ solution. The colorless solution immediately turned pale yellow and opaque as KCl precipitated out of solution. After stirring at room temperature for 2 h, the solvent was removed *in vacuo*. The crude solid was then triturated with *n*-hexane and the product was extracted with *n*-hexane (8 mL), filtered through Celite, and concentrated (2 mL). This solution was cooled to –40 °C, affording cubic colorless crystals (104.4 mg). A second crop of crystals were grown after concentration of the mother liquor to 1 mL (124.3 mg total, 66% total yield). Mp ca. 190 °C (slow decomp. starting from 110 °C); ^{1}H NMR (600 MHz, C_6D_6): δ 2.13 (s, 60H, CH_{3Cp^*}), –11.01 (s, 16H, Th–H–Os); ^{13}C NMR (600 MHz, C_6D_6): δ 92.5 ($C_5(CH_3)_5$), 12.5

($C_5(CH_3)_5$); IR (Nujol mull on KBr): 1993 (s), 1073 (w), 1034 (m), 863 (m), 560 (m); Anal. Calcd (%) for $ThOs_4C_{40}H_{76}$: C, 31.00; H, 4.94. Found: C, 31.16; H, 4.93.

Synthesis of U{(μ-H$_4$)OsCp*}$_4$ (2-U):

Cp*OsH_5 (146.8 mg, 0.444 mmol, 4.0 equiv.) and benzyl potassium (59.8 mg, 0.459 mmol, 4.1 equiv.) were added to a 20 mL scintillation vial with THF (4 mL) to generate a solution of K[Cp*OsH_4]. UCl_4 (42.1 mg, 0.111 mmol, 1.0 equiv.) was dissolved in THF (4 mL) and added to the K[Cp*OsH_4] solution. The colorless solution immediately turned bright yellow and opaque as KCl precipitated out of solution. After stirring at room temperature for 2 h, the solvent was removed *in vacuo*. The crude solid was then triturated with *n*-hexane and the product was extracted with *n*-hexane (8 mL), filtered through Celite, and concentrated (2 mL). This solution was cooled to –40 °C, affording cubic yellow crystals (87.6 mg). A second crop of crystals were grown after concentration of the mother liquor to 1 mL (110.7 mg total, 64% total yield). Mp ca. 240 °C (decomp.); ^{1}H NMR (600 MHz, C_6D_6): δ 89.8 (s, 16H, U–H–Os), 3.65 (s, 60H, CH_{3Cp^*}); ^{13}C NMR (600 MHz, C_6D_6): δ 114.2 ($C_5(CH_3)_5$), 12.4 ($C_5(CH_3)_5$); IR (Nujol mull on KBr): 2091 (w), 1990 (s), 1072 (w), 1034 (m), 862 (m), 559 (m); Anal. Calcd (%) for $UOs_4C_{40}H_{76}$: C, 30.88; H, 4.92. Found: C, 31.21; H, 4.75.

Synthesis of 3-U *via* photolysis of 2-U:

2-U (38.5 mg, 0.025 mmol) was dissolved in 3 mL benzene and transferred to a Teflon-tap sealed quartz cuvette. The yellow solution was photolyzed for 6 hours, yielding a dark brown solution. After removing the solvent *in vacuo*, the crude solid was extracted with *n*-hexane, filtered, and concentrated to 0.5 mL. This solution was allowed to stand at RT overnight, yielding dark brown crystals (16.7 mg, 43% yield). Mp. 235 °C (slow decomp. starting from 208 °C); ^{1}H NMR (600 MHz, C_6D_6): δ 55.46 (s, 8H, Cp*Os_a(*μ-H*)$_4$), 9.84 (s, 6H, [(CH_2)*Me*$_4C_5$]Os_c), 1.43 (s, 30H, *Cp**Os_a), –2.44 (s, 15H, *Cp**Os_b), –4.82 (s, 6H, [(CH_2)*Me*$_4C_5$]Os_c), –89.11 (s, 2H, [(C*H$_2$*)Me_4C_5]Os_c); ^{13}C NMR (600 MHz, C_6D_6): δ 106.43, 74.34 (*C*H_2), 29.97, 12.75, 7.52, –4.46; IR (Nujol mull on KBr): 1990 (s), 1152 (w), 1072 (w), 1032 (m), 947 (w), 890 (w), 625 (w), 585 (w); Anal. Calcd (%) for $UOs_4C_{40}H_{73}$•C_6H_{14}: C, 33.71; H, 5.35. Found: Sample 1: C, 33.81; H, 4.97. Sample 2: C, 33.78; H, 5.04.

Synthesis of 3-Th and 4-Th *via* photolysis of 2-Th:

Complex **2-Th** (29.4 mg, 0.019 mmol) was dissolved in 3 mL benzene and transferred to a Teflon-tap sealed quartz cuvette. The colorless solution was photolyzed for 6 hours, yielding an orange solution. After removing the solvent *in vacuo*, the crude solid was extracted with *n*-hexane and minimal benzene, filtered, and concentrated to 0.5 mL. This solution was allowed to stand at RT overnight, yielding orange crystals composed of 22% **3-Th** and 78% **4-Th** (mol/mol %) by ^{1}H NMR (20.4 mg, 66% total yield by Th). Both products consistently co-crystallize in similar ratios across multiple syntheses, and show no evident differences in color. Mp. 215 °C (slow decomp. starting from 182 °C); IR (Nujol mull on KBr): 2009 (s), 1566 (w), 1549 (w), 1152 (w), 1071 (w), 1033 (m), 901 (w), 710 (w), 585 (w); Anal. Calcd (%) for 0.22 $ThOs_4C_{40}H_{70}$·C_6H_{14}/0.78 $ThOs_4C_{46}H_{74}$: C, 34.06; H, 4.73. Found: C, 34.29; H, 4.85.

Isolation of **3-Th**: A sample of **2-Th** (9.6 mg, 0.006 mmol) was dissolved in 0.75 mL benzene and photolyzed in a sealed J.Young NMR tube for 66.5 hours, then dried *in vacuo*, extracted with *n*-hexane, filtered, and concentrated to 0.5 mL. This solution was allowed to stand at –40 °C overnight, yielding orange crystals of **3-Th** (1.7 mg, 17% yield). The ^{1}H NMR and ^{13}C NMR spectra can be found in Figures S16 and S17.

3-Th: ^{1}H NMR (700 MHz, C_6D_6): δ 7.98 (d, 1H, H_d), 7.76 (d, 1H, H_c), 7.20 (td, 1H, H_e), 7.07 (m, 2H, H_f/$H_{f'}$), 2.87 (s, 3H, Cp*$_{activ}$), 2.79 (s, 3H, Cp*$_{activ}$), 2.15 (s, 15H, Cp*), 2.13 (s, 15H, Cp*), 1.87 (s, 15H, Cp*), 1.82 (s, 3H, Cp*$_{activ}$), 1.77 (s, 3H, Cp*$_{activ}$), 1.37 (d, 1H, H_a), 1.08 (d, 1H, H_b), –8.16 (t, 1H, H_h), –9.80 (s, 3H, $H_{hydride}$), –10.54 (d, 1H, H_g), –10.84 (s, 1H, H_i), –11.59 (s, 4H, Cp*Os(μ-*H*)$_4$Th); ^{13}C NMR (600 MHz, C_6D_6): δ 155.0 (C_d), 150.9 (C_c), 136.0 (C_c–*C*–C_d), 130.1 (C_e), 127.0 (C_f, $C_{f'}$), 100.4, 93.9, 92.0, 80.3, 79.7, 78.8, 77.4, 77.4, 61.0 (CH_aH_b), 14.0, 13.7, 12.6, 11.8, 11.4, 11.1, 11.1.

Isolation of **4-Th**: A single sample containing 16.1 mg **3-Th** and 13.7 mg **4-Th** was recrystallized from a 1:1 *n*-hexane/benzene solution at –40 °C, yielding 8.2 mg of crystals containing 88% **4-Th** (mol%). The ^{1}H and ^{13}C NMR spectra can be found in Figures S18 and S19.

4-Th: ^{1}H NMR (600 MHz, C_6D_6) δ 2.89 (s, 6H, Cp*$_{activ.}$), 2.16 (s, 15H, *Cp**Os(μ-H)$_3$OsCp*$_{activ.}$), 2.13 (s, 30H, [*Cp**Os(μ-H)$_4$]$_2$Th), 1.77 (s, 6H, Cp*$_{activ.}$), 1.34 (s, 2H, C*H*$_2$–Th), –9.76 (s, 3H, Cp*Os(μ-*H*)$_3$OsCp*$_{activ}$), –11.07 (s, 8H, [Cp*Os(μ-*H*)$_4$]$_2$Th); ^{13}C NMR (600 MHz, C_6D_6): δ 103.6 (Cp*$_{activ.}$, ring C), 92.9 ([*C*$_5$Me$_5$Os(μ-H)$_4$]$_2$Th), 80.9 (*C*$_5$Me$_5$Os(μ-H)$_3$OsCp*$_{active}$), 79.7 (Cp*$_{activ.}$, ring C), 77.2 (Cp*$_{activ.}$, ring C), 65.6 (Th–*C*H$_2$), 13.8 (Cp*$_{activ.}$, CH$_3$), 12.4 ([C$_5$*Me*$_5$Os(μ-H)$_4$]$_2$Th), 11.7 (C$_5$*Me*$_5$Os(μ-H)$_3$OsCp*$_{active}$), 10.9 (Cp*$_{activ.}$, CH$_3$).

UV-Vis Spectra

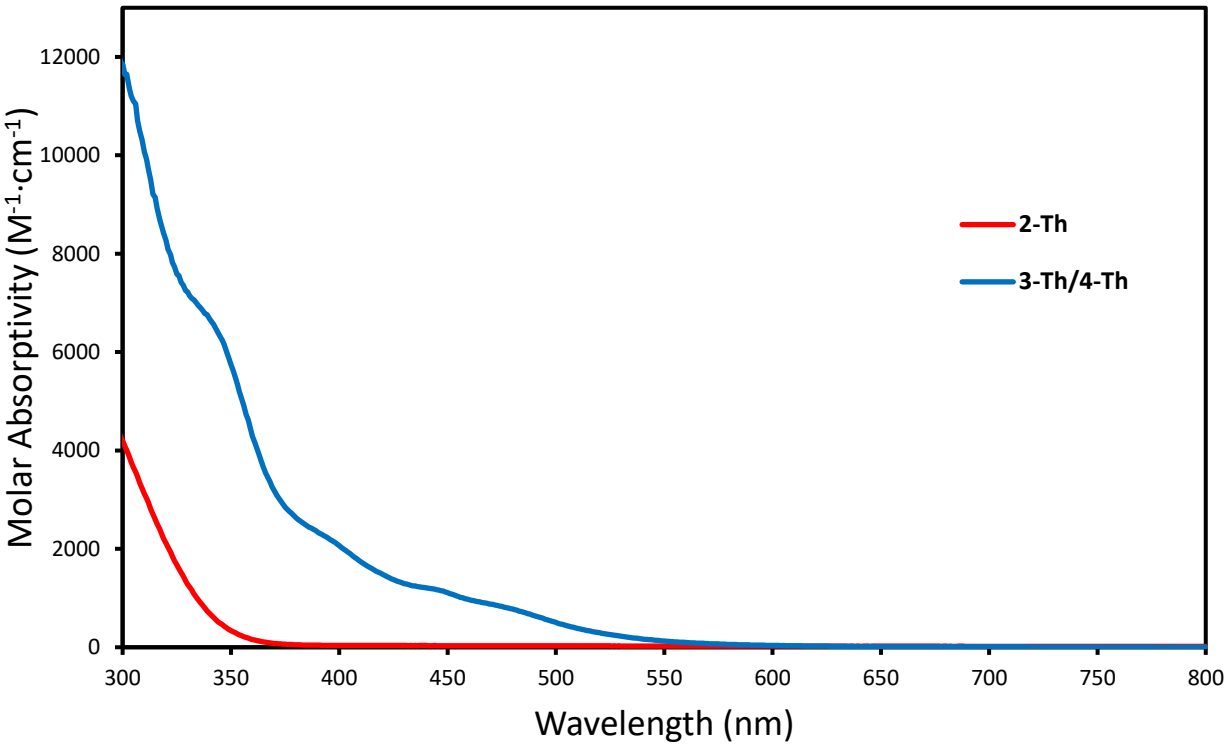


Figure S1. UV-vis spectra of colorless **2-Th** and crystallized 22:78 **3-Th/4-Th** in benzene.

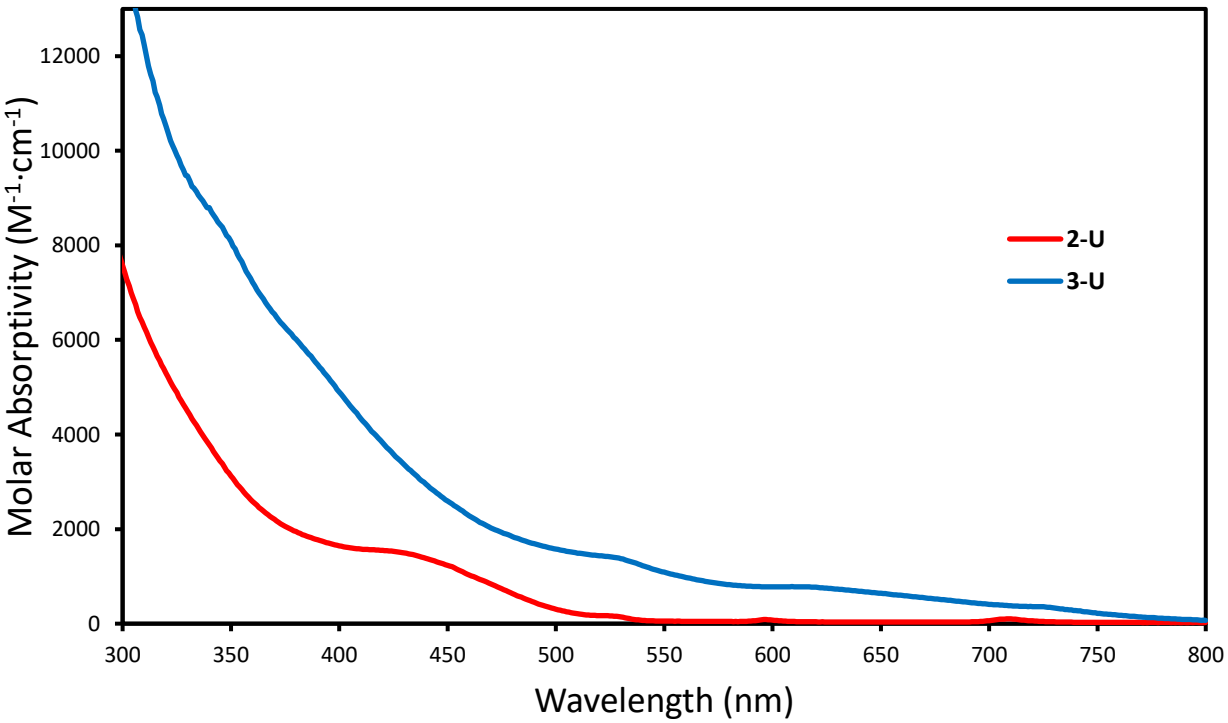


Figure S2. UV-vis spectra of yellow **2-U** and dark brown photolysis product **3-U** in benzene.

IR Spectra

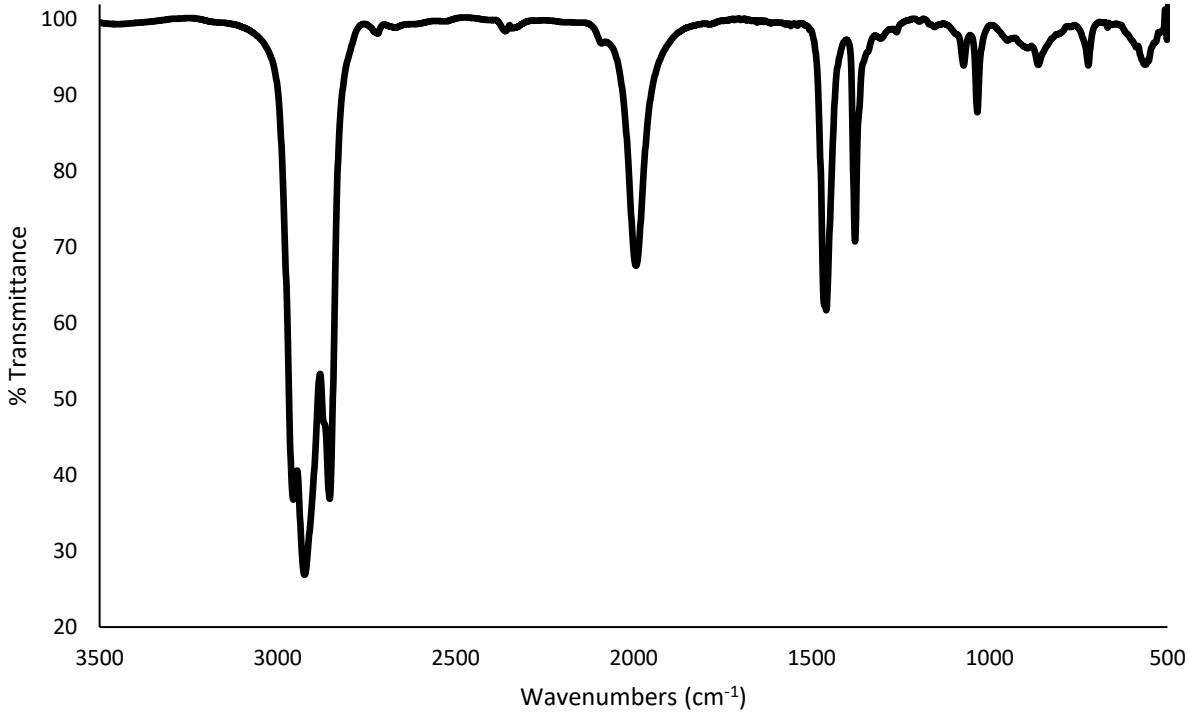


Figure S3. IR spectrum of **2-Th** (Nujol mull).

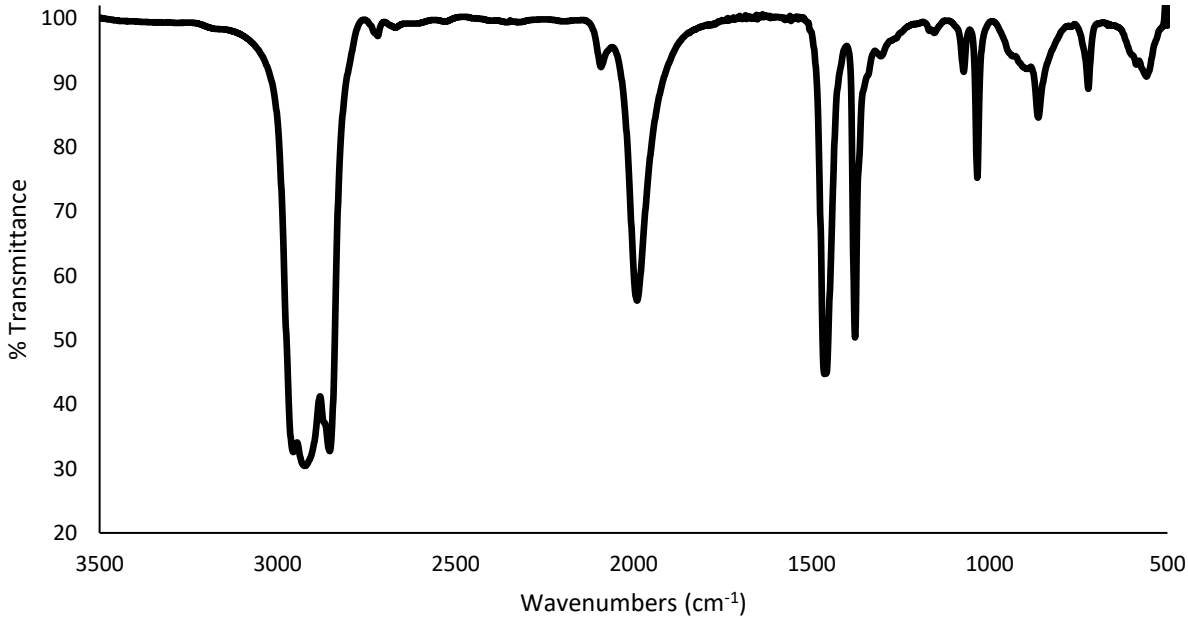


Figure S4. IR spectrum of **2-U** (Nujol mull).

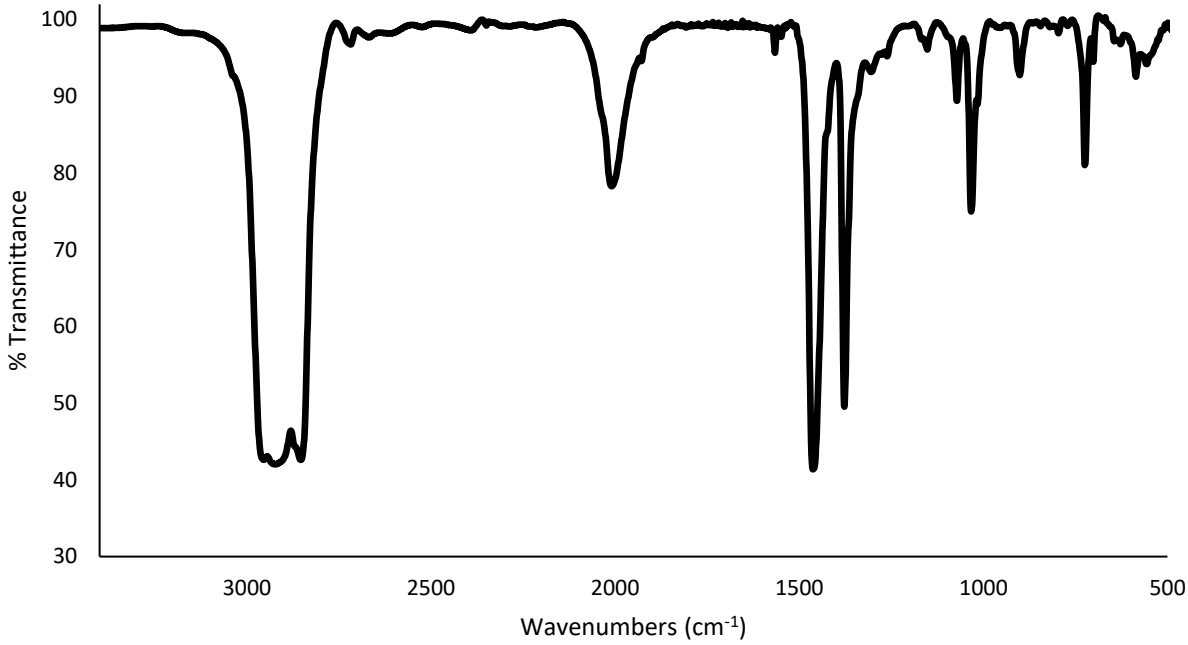


Figure S5. IR spectrum of crystallized 22:78 **3-Th/4-Th** (Nujol mull).

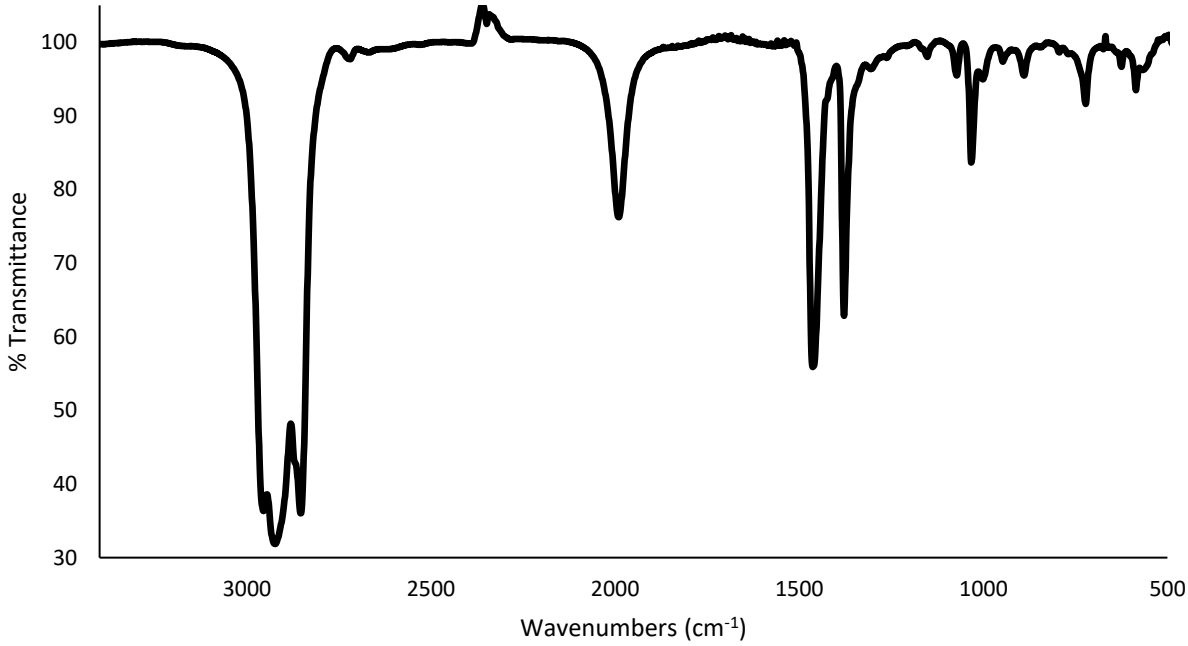


Figure S6. IR spectrum of **3-U** (Nujol mull) .

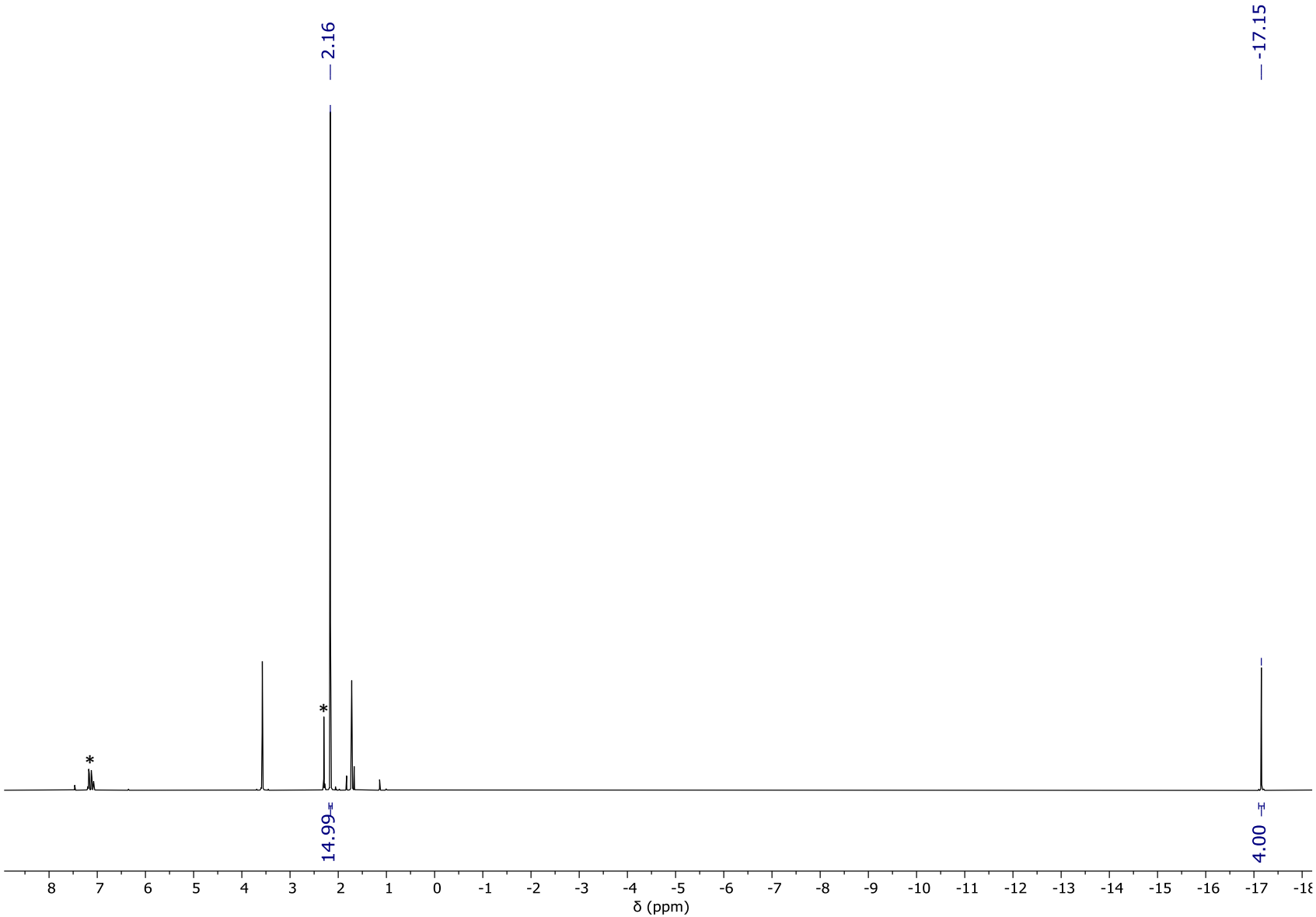


Figure S7. ^{1}H NMR spectrum of *in-situ* generated **1** at 298 K in THF-d_8, * = toluene.

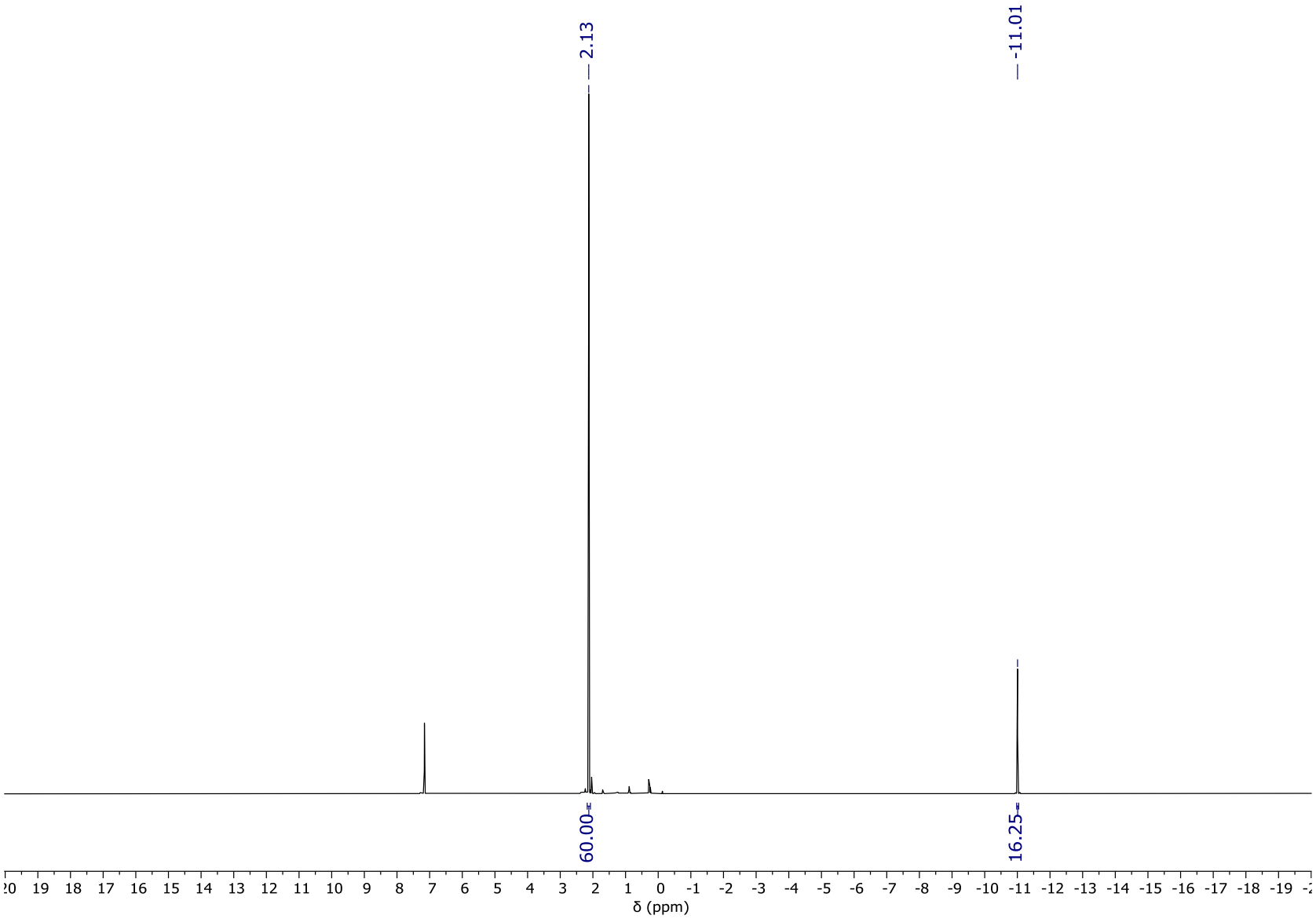


Figure S8. ^{1}H NMR spectrum of **2-Th** at 298 K in C_6D_6.

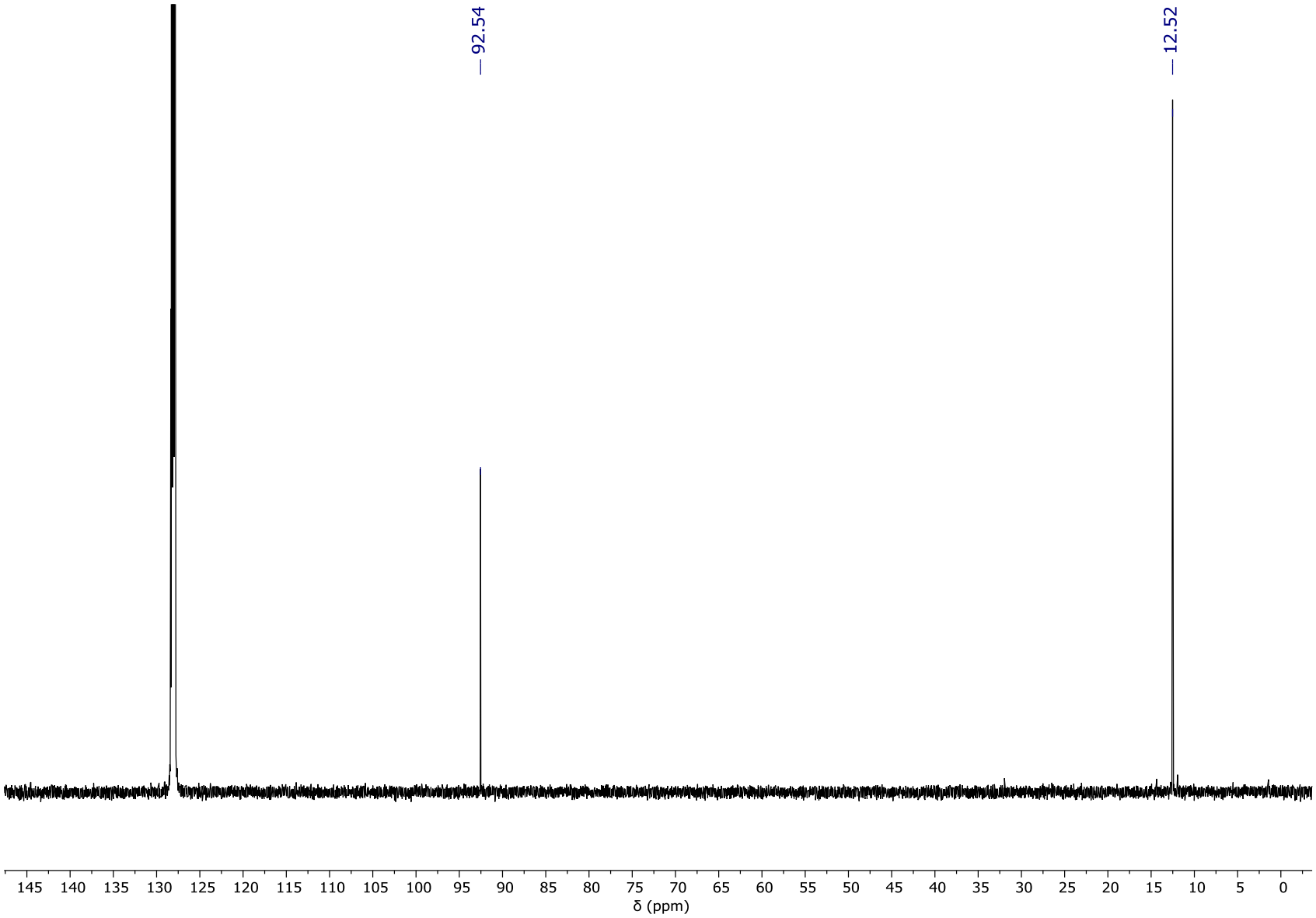


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **2-Th** at 298 K in C_6D_6.

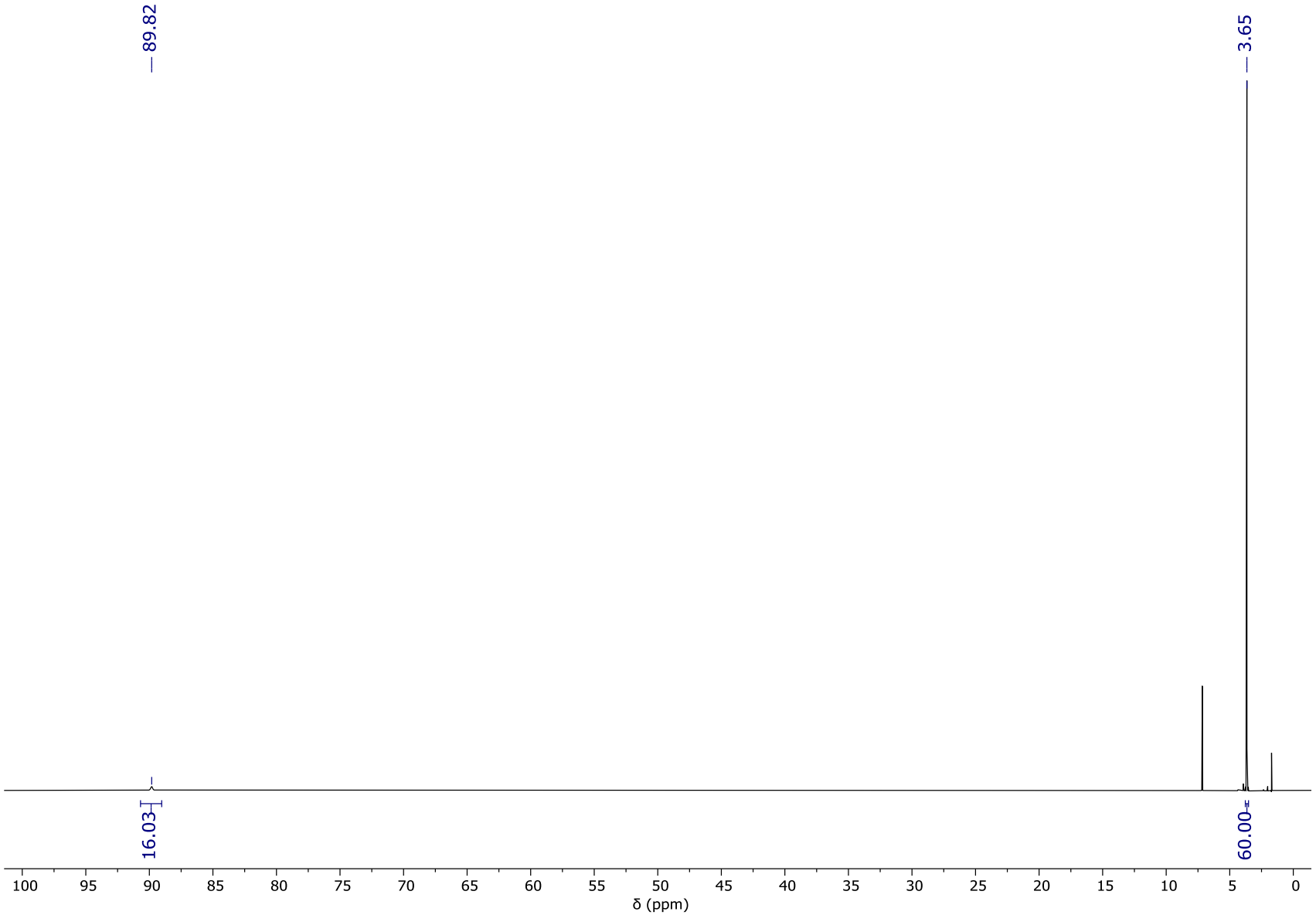


Figure S10. ^{1}H NMR spectrum of **2-U** at 298 K in C_6D_6.

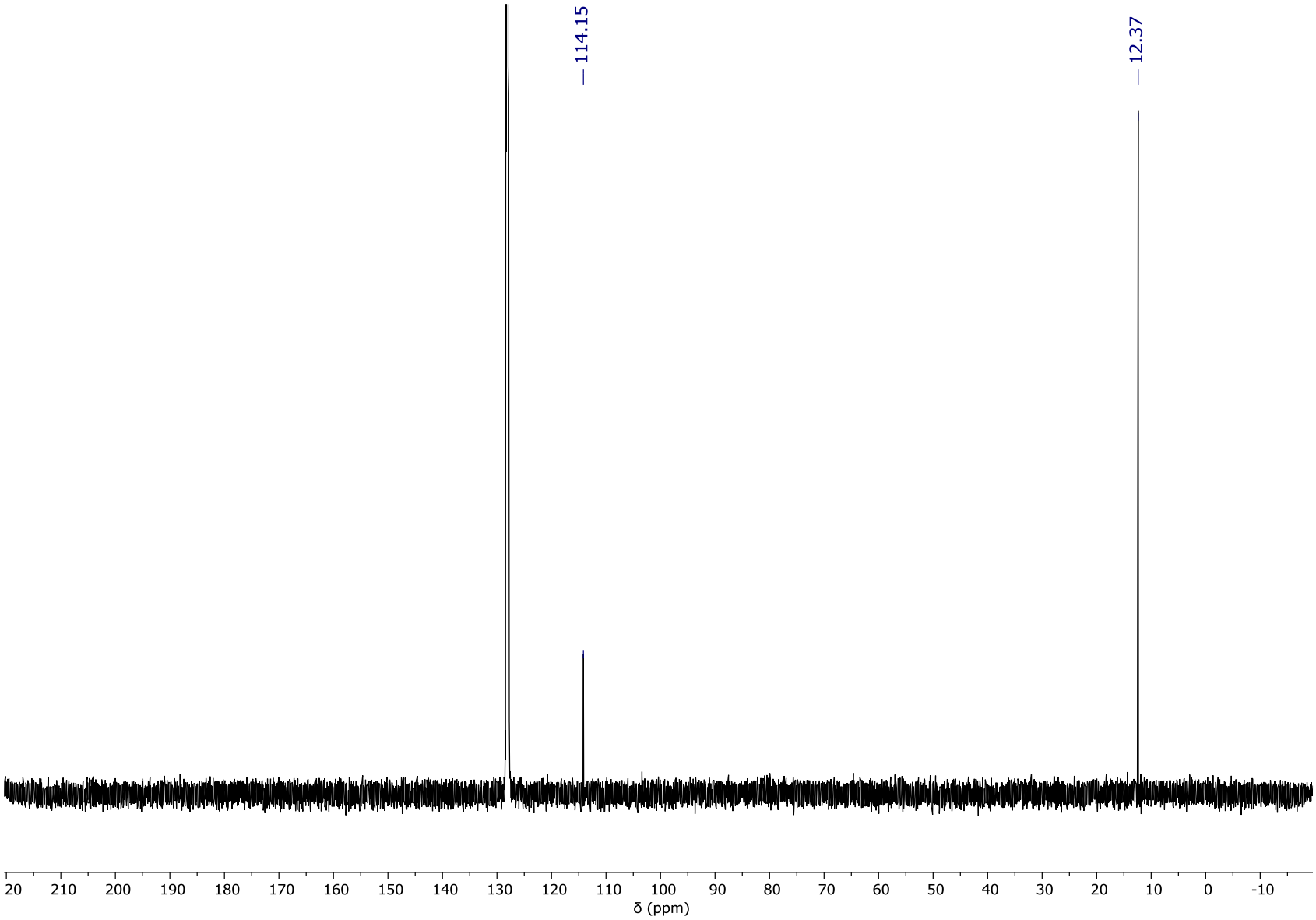


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **2-U** at 298 K in C_6D_6.

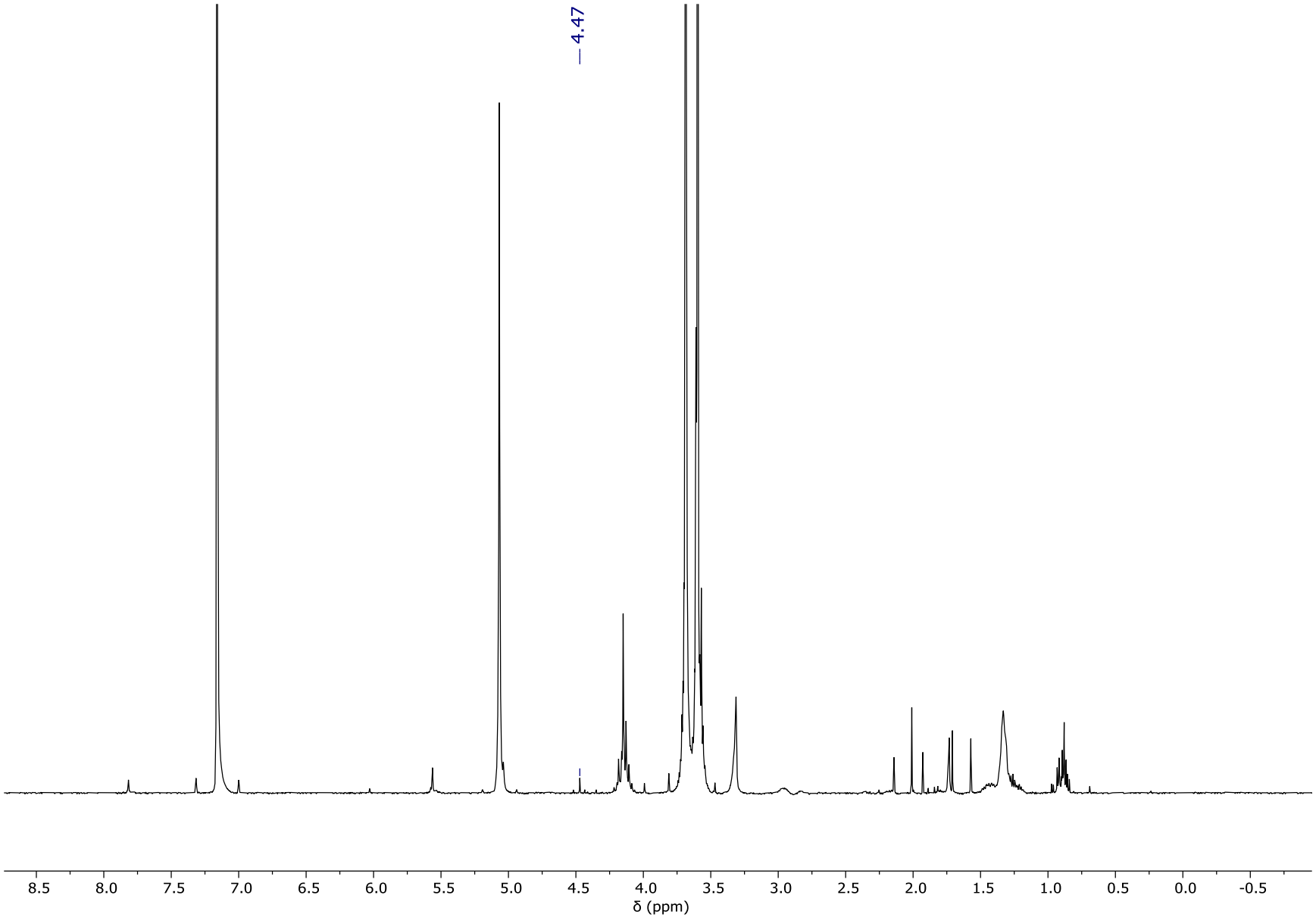


Figure S12. Crude ^{1}H NMR spectrum of the photolysis of **2-U** in C_6D_6, evidencing production of H_2 (4.47 ppm in C_6D_6).

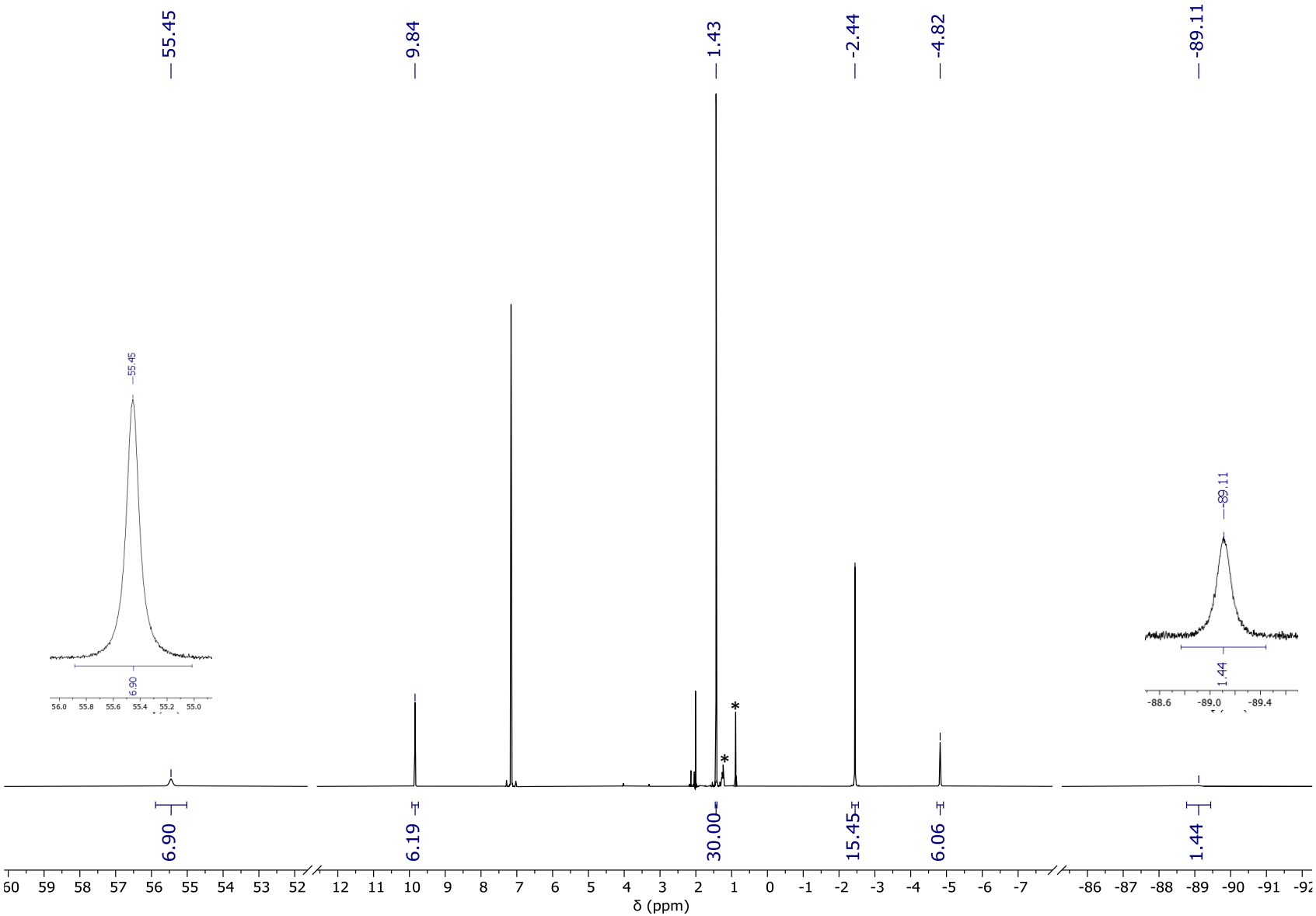


Figure S13. ^{1}H NMR spectrum of **3-U** at 298 K in C_6D_6, * = *n*-hexane. Insets: zoomed in view of upfield and downfield peaks.

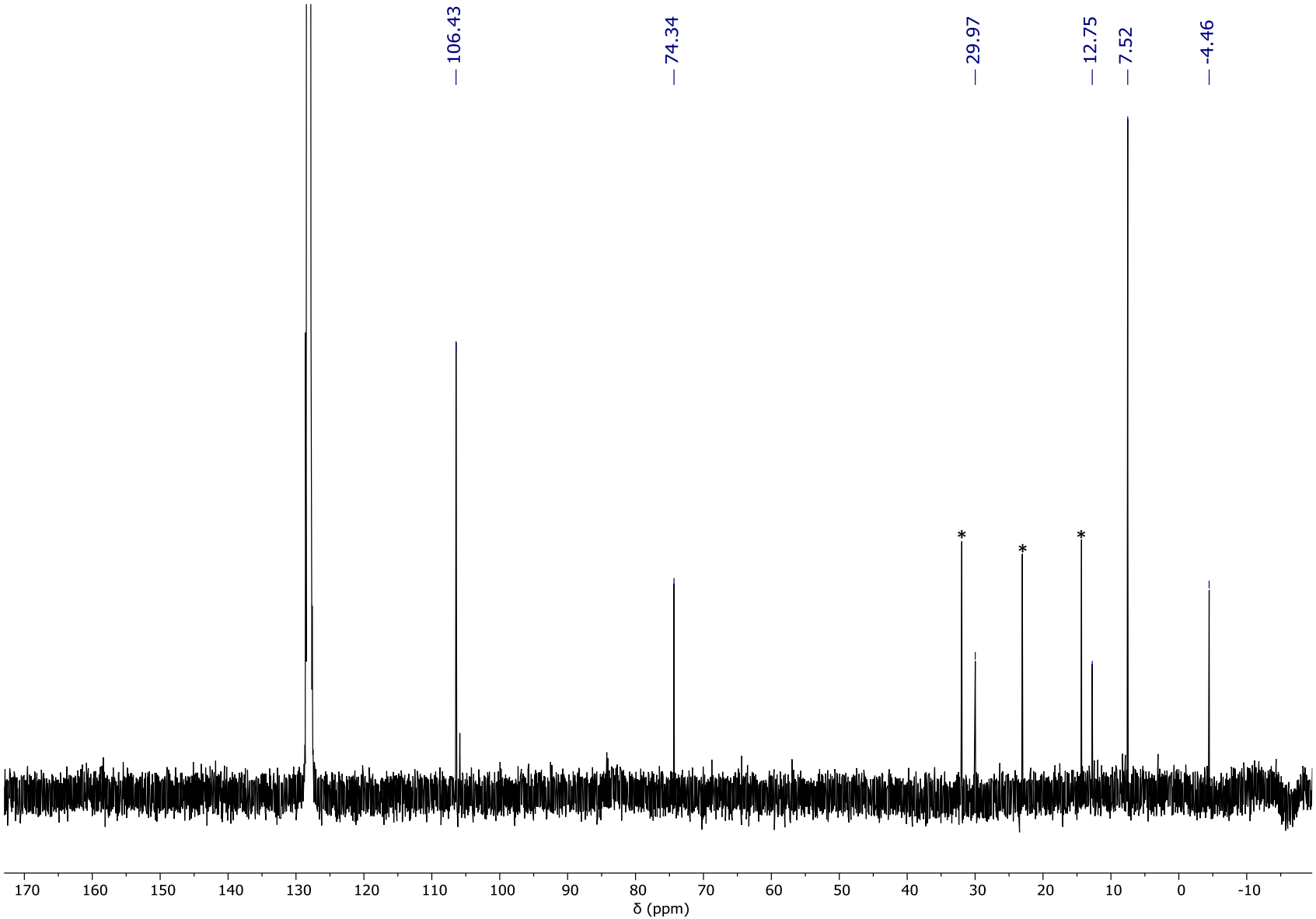


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **3-U** at 298 K in C_6D_6, * = *n*-hexane.

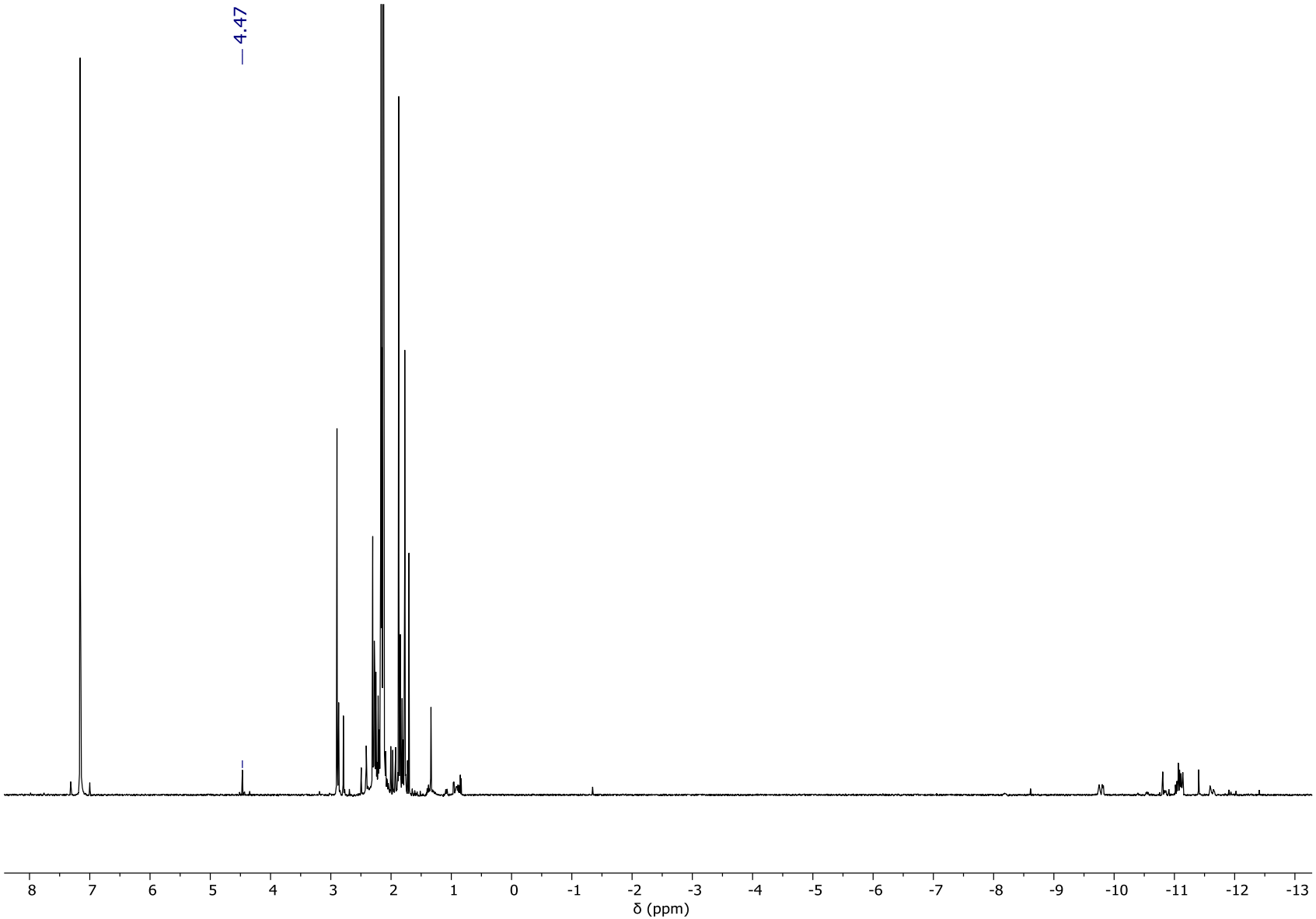


Figure S15. Crude ^{1}H NMR spectrum of the photolysis of **2-Th** in C_6D_6, evidencing production of H_2 (4.47 ppm in C_6D_6).

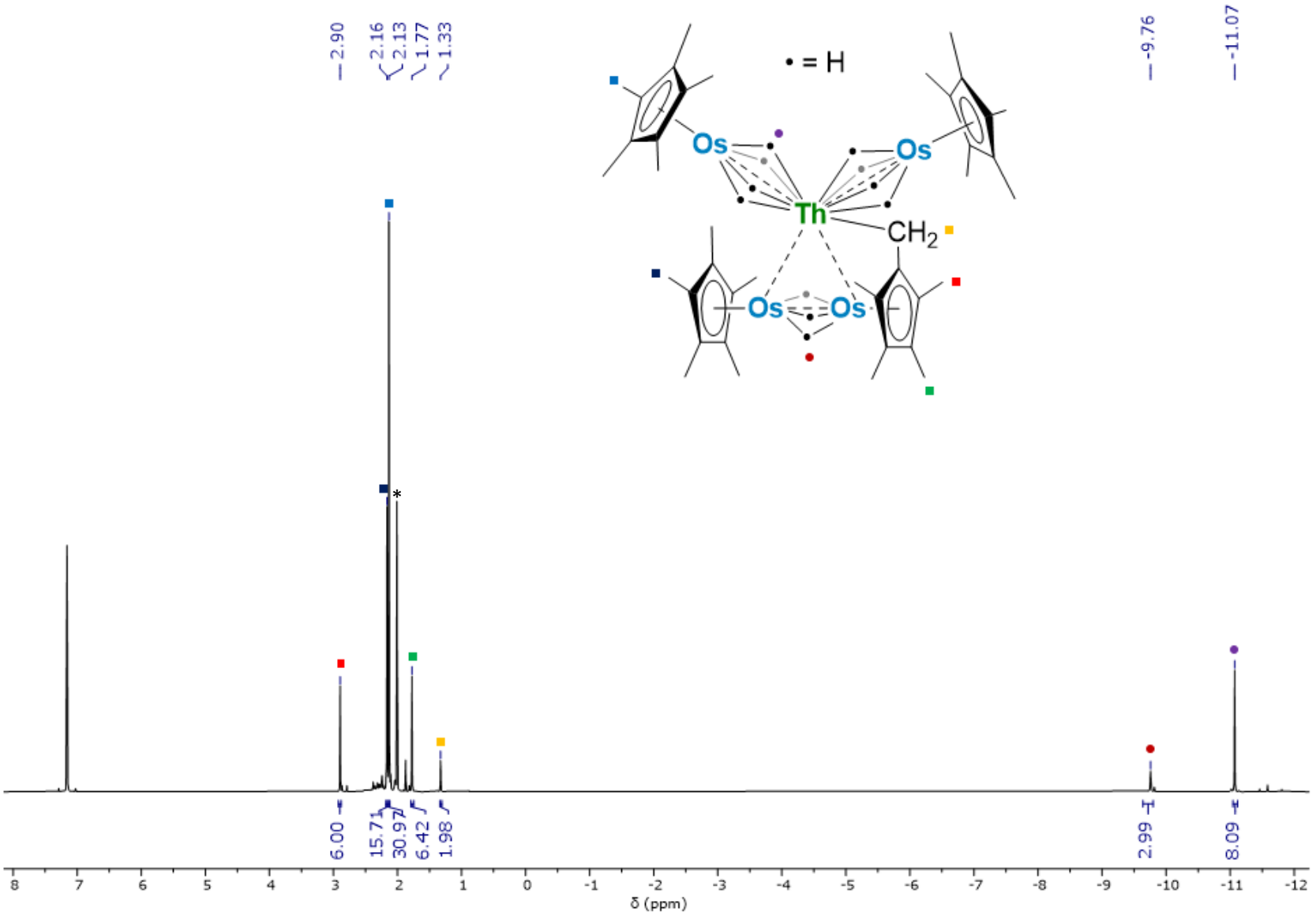


Figure S16. ^{1}H NMR of isolated **3-Th** at 298 K in C_6D_6, * = $[Cp^*OsH_2]_2$ decomp. product.

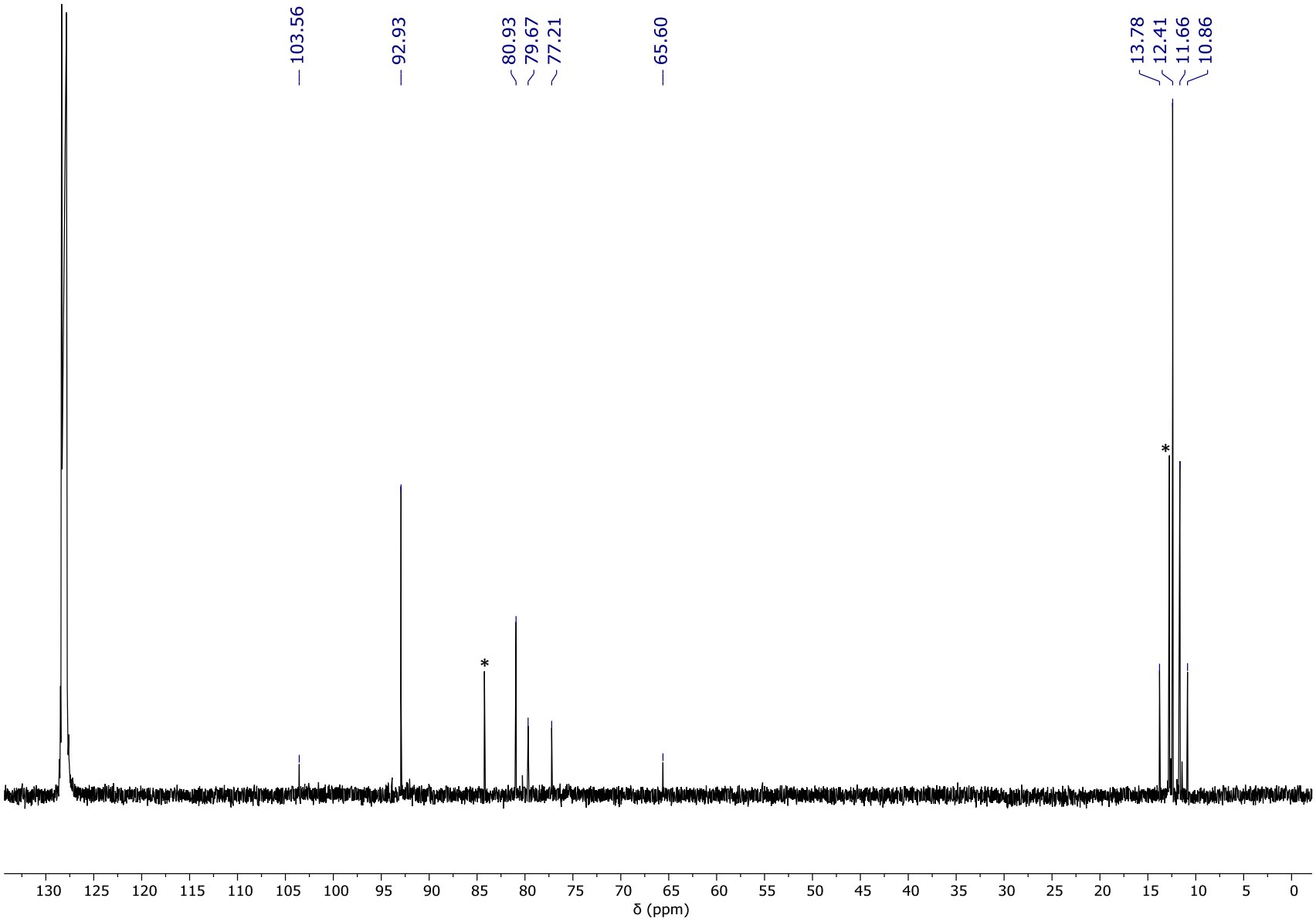


Figure S17. $^{13}C\{^{1}H\}$ NMR of isolated **3-Th** at 298 K in C_6D_6, * = $[Cp^*OsH_2]_2$ decomp. product.

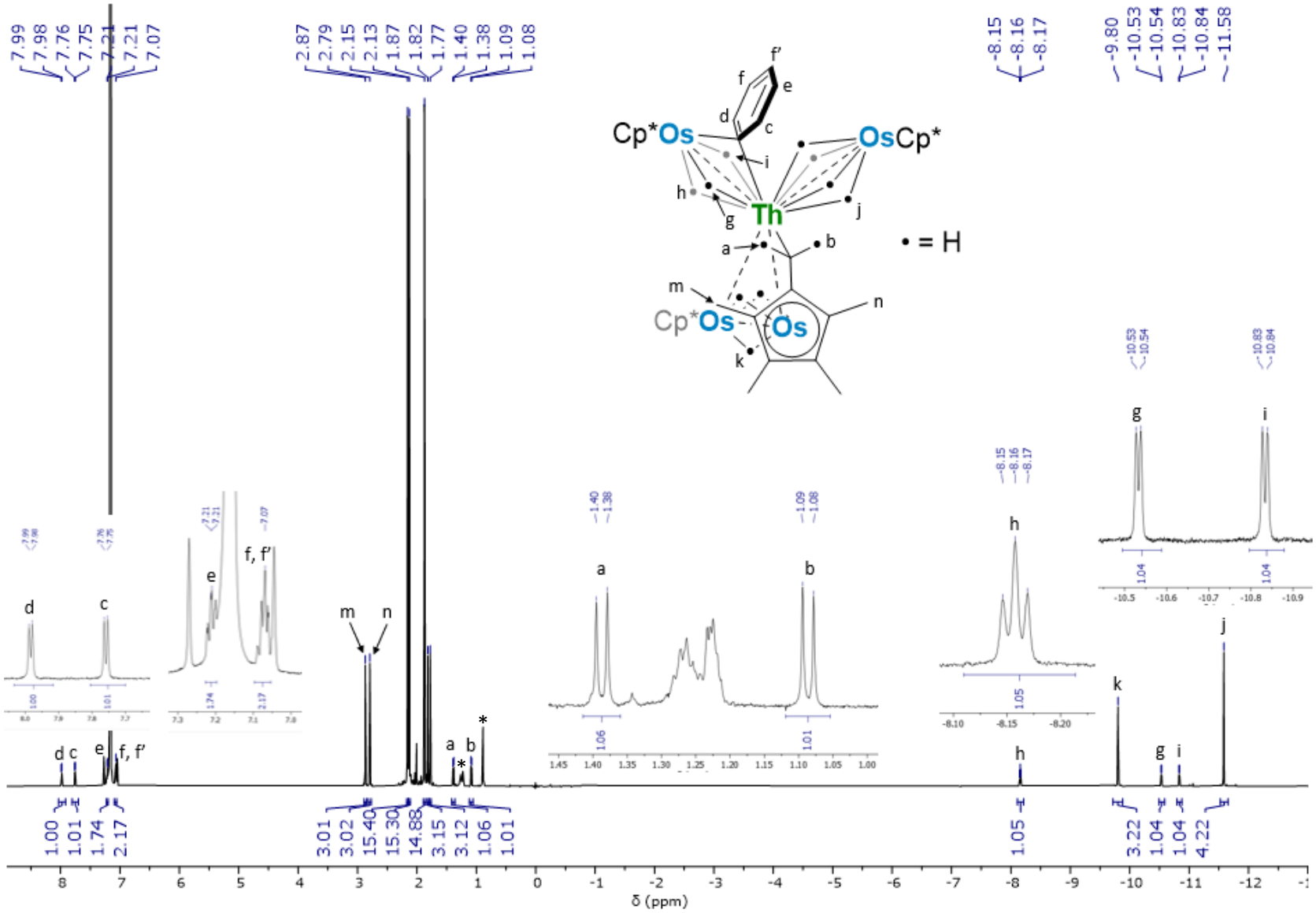


Figure S18. ^{1}H NMR spectrum of isolated **4-Th** at 298 K in C_6D_6, * = *n*-hexane. Insets: zoomed in view of peak splitting.

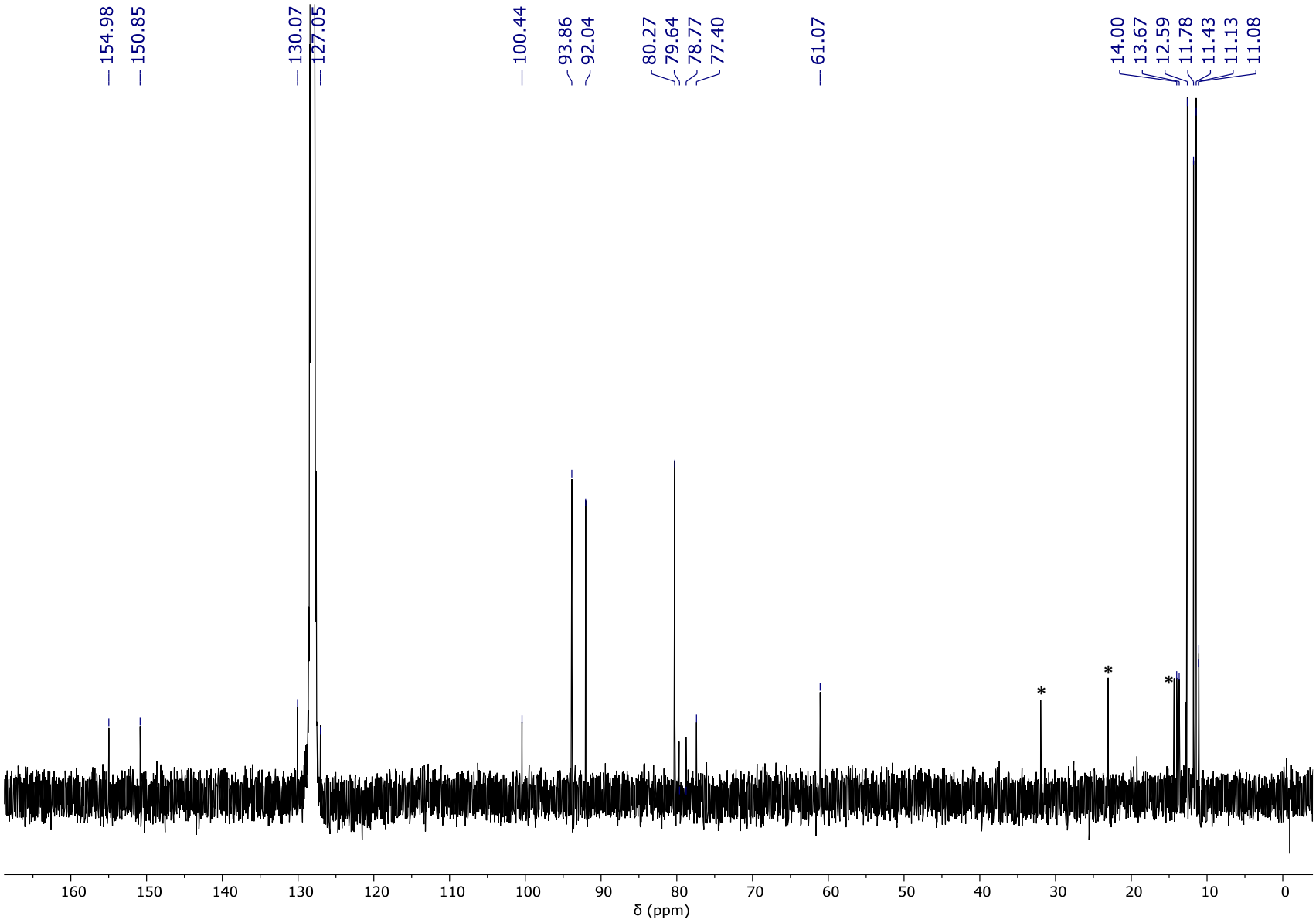


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of isolated **4-Th** at 298 K in C_6D_6, * = *n*-hexane.

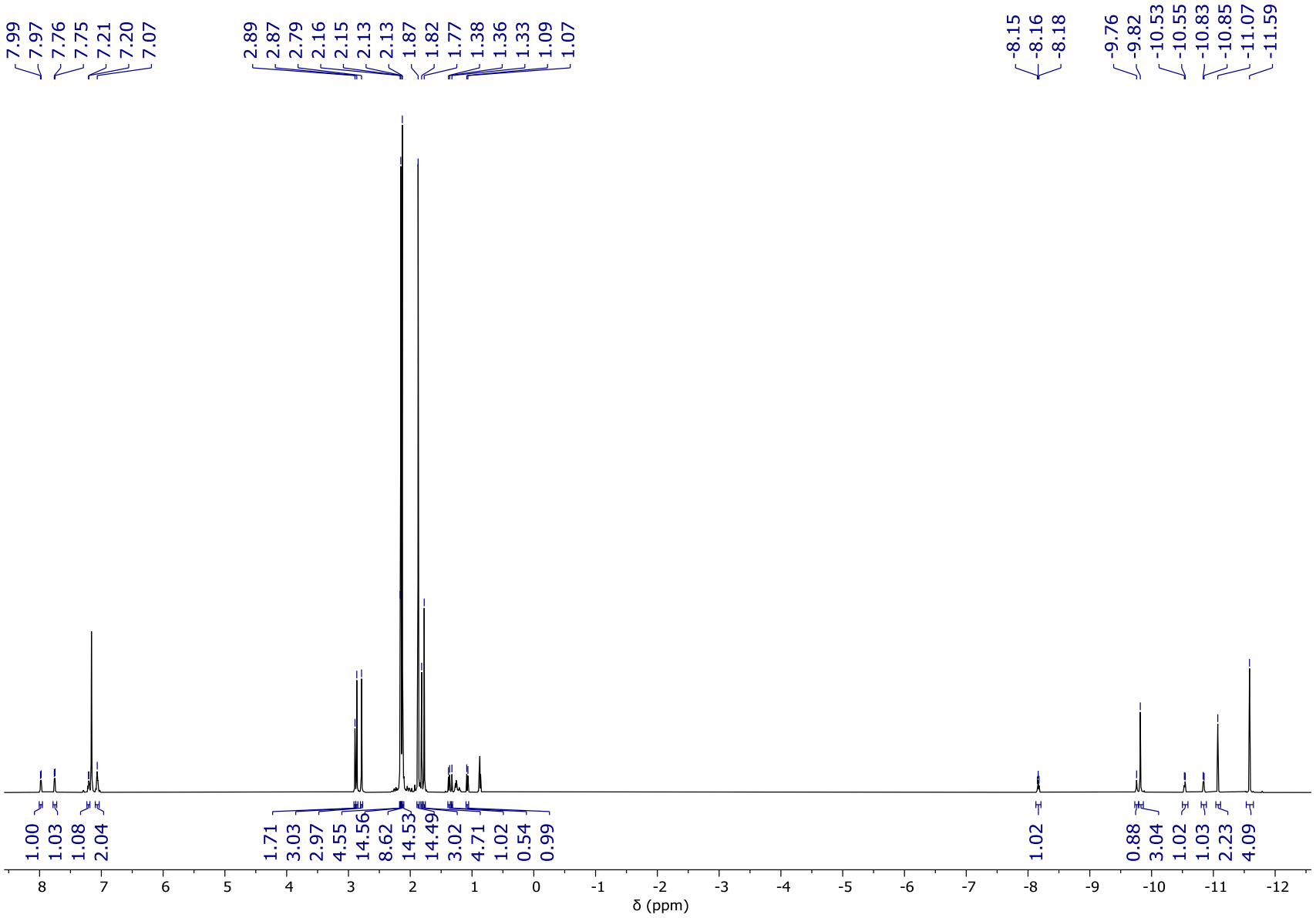


Figure S20. ^{1}H NMR spectrum of crystallized 22:78 **3-Th/4-Th** at 298 K in C_6D_6.

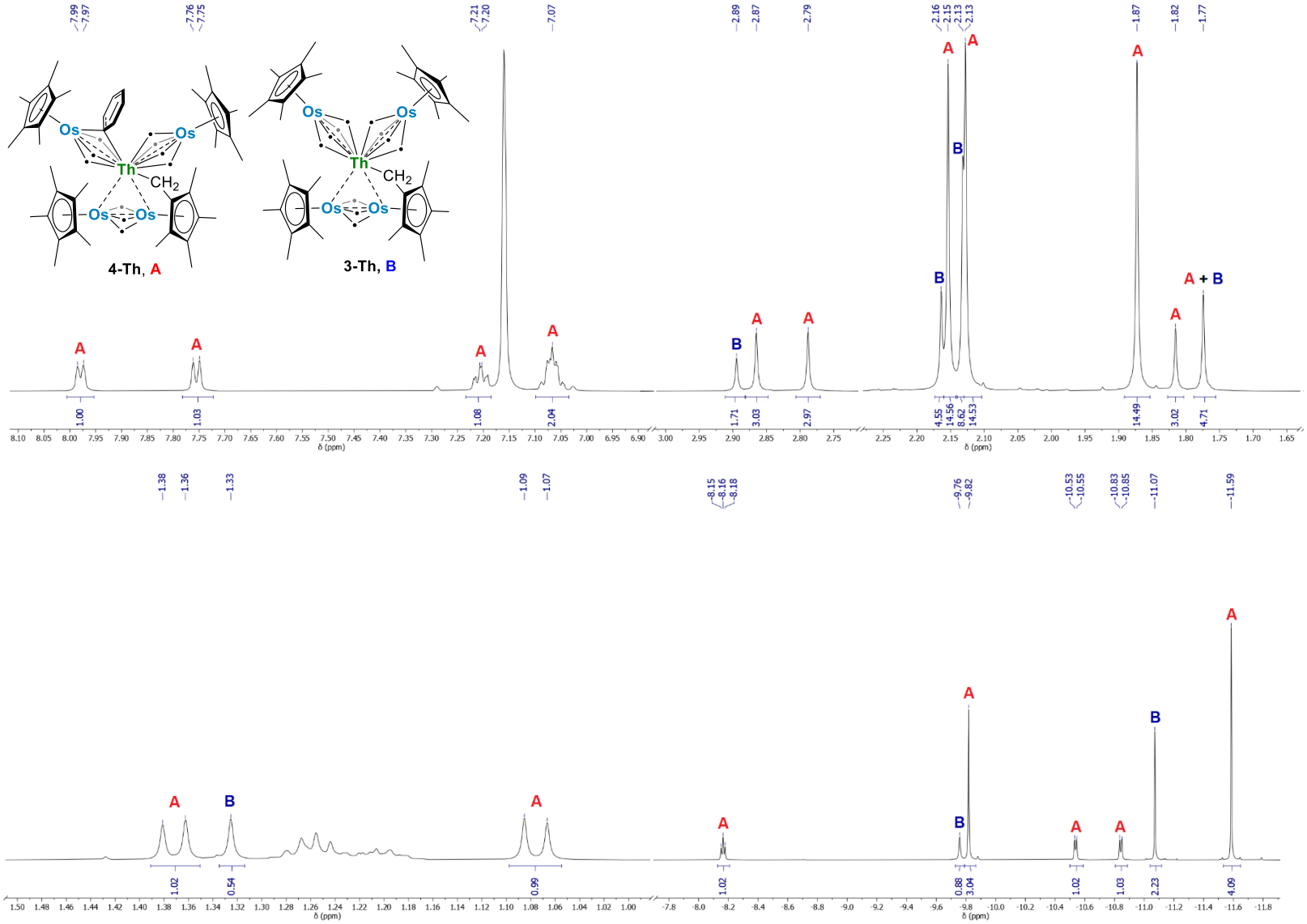


Figure S21. ^{1}H NMR spectrum of crystallized 22:78 **3-Th/4-Th** at 298 K in C_6D_6, zoomed in and labeled.

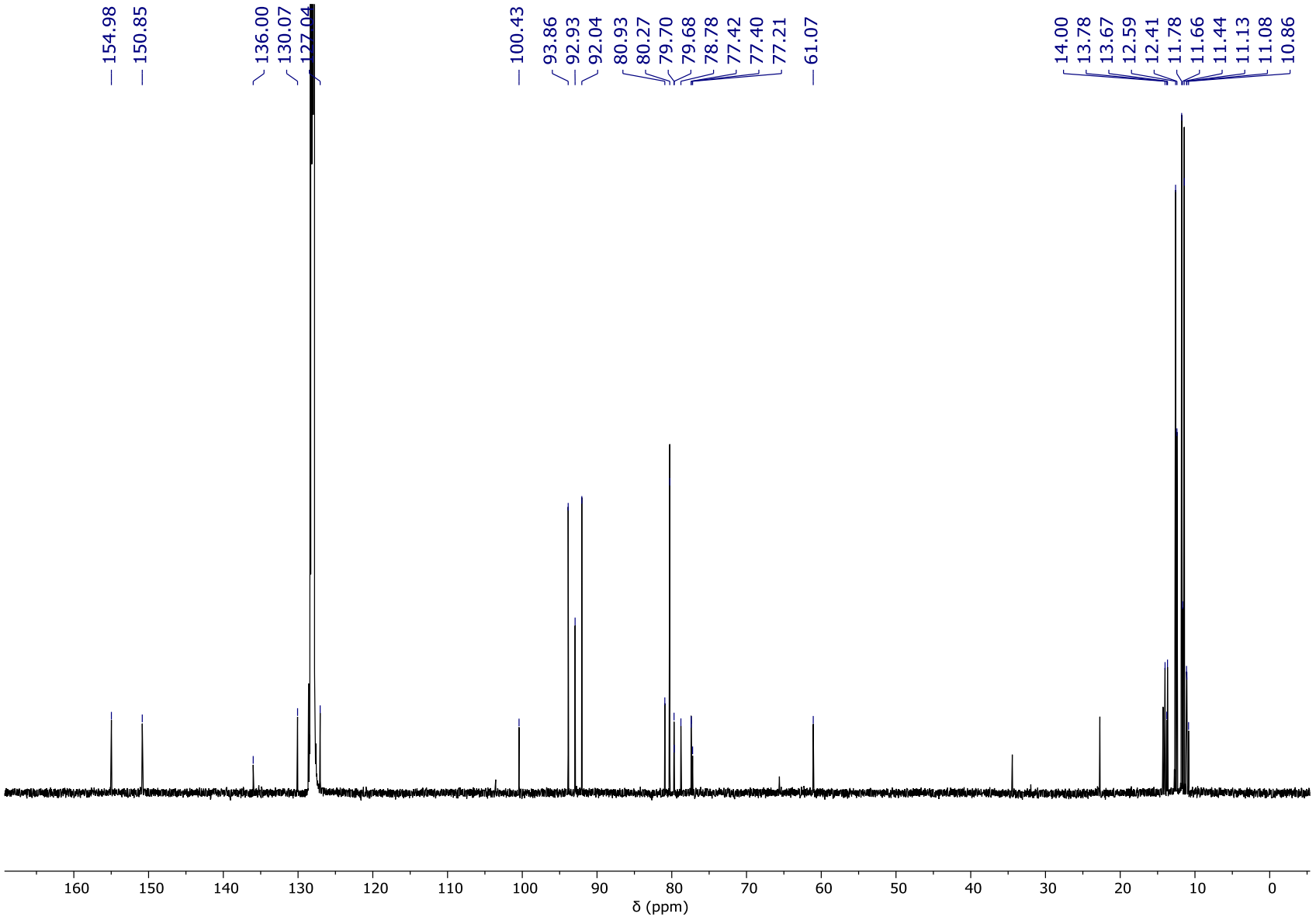


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of crystallized 22:78 **3-Th/4-Th** at 298 K in C_6D_6, * = *n*-pentane.

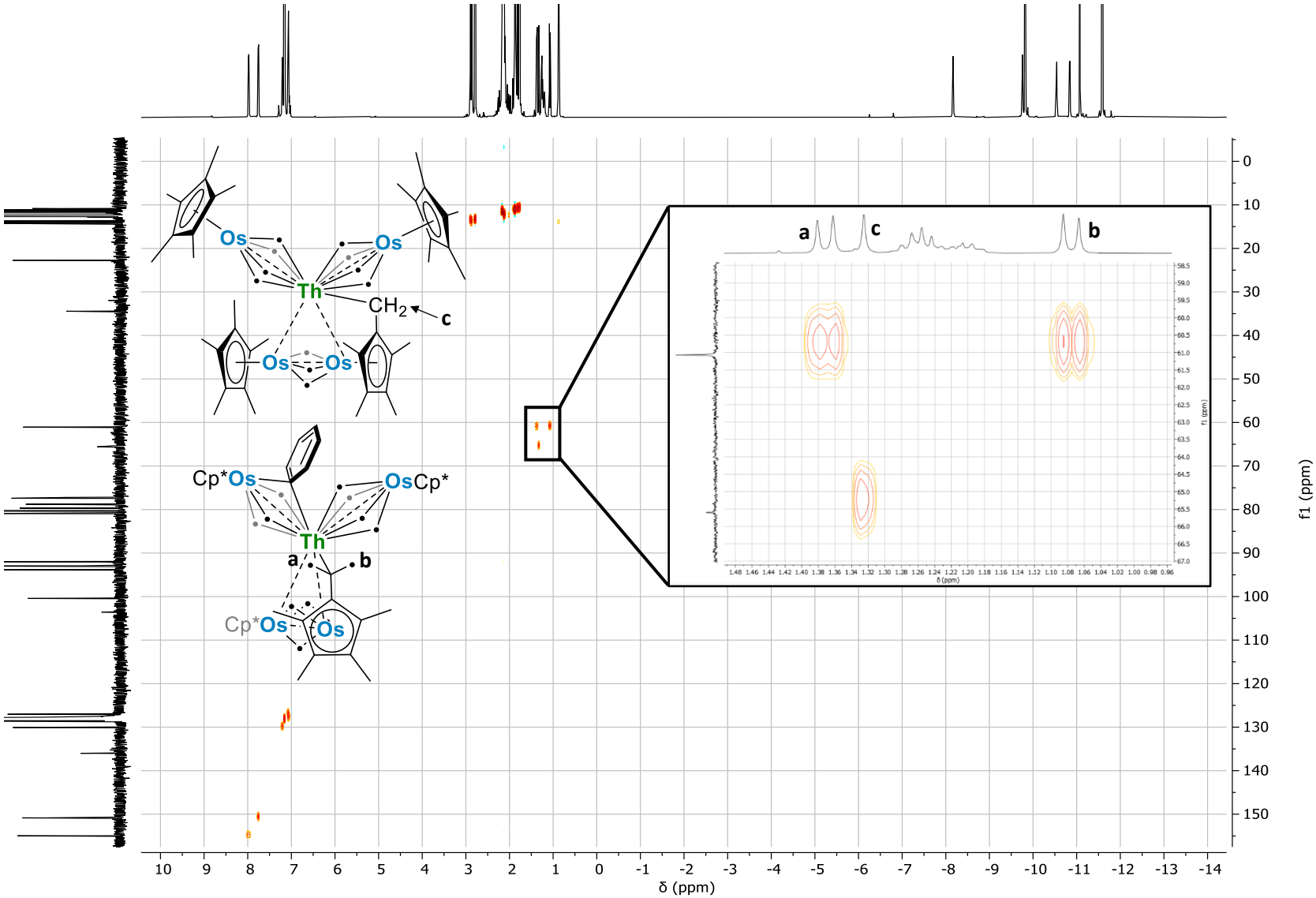


Figure S23. ^{1}H-^{13}C HSQC NMR spectrum of crystallized 22:78 **3-Th/4-Th** at 298 K in C_6D_6. Inset: zoomed in view of methylene H-C interactions.

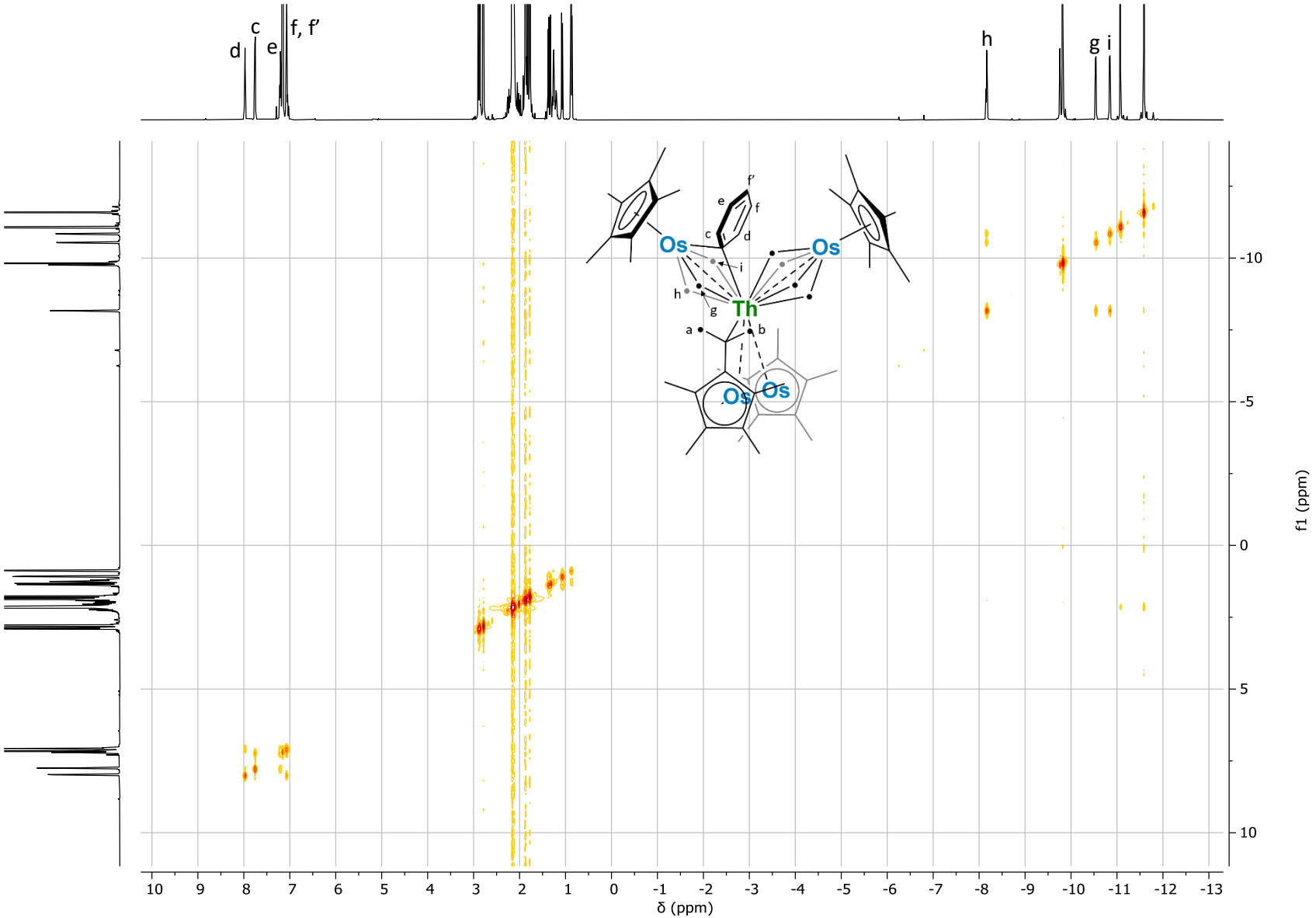


Figure S24. ^{1}H-^{1}H COSY NMR spectrum of crystallized 22:78 **3-Th/4-Th** at 298 K in C_6D_6.

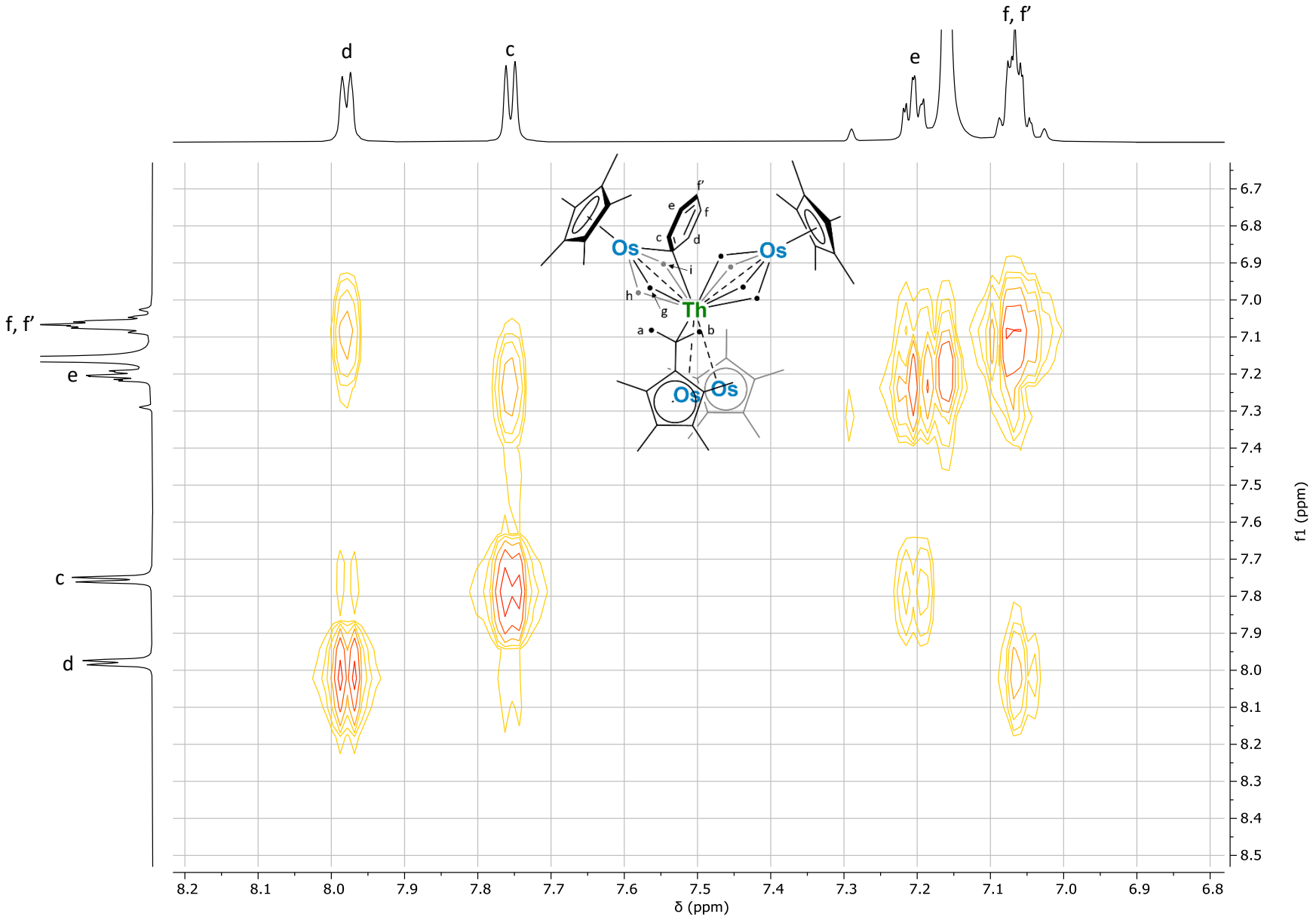


Figure S25. ^{1}H-^{1}H COSY NMR spectrum of crystallized 22:78 **3-Th/4-Th** at 298 K in C_6D_6, aromatic interactions.

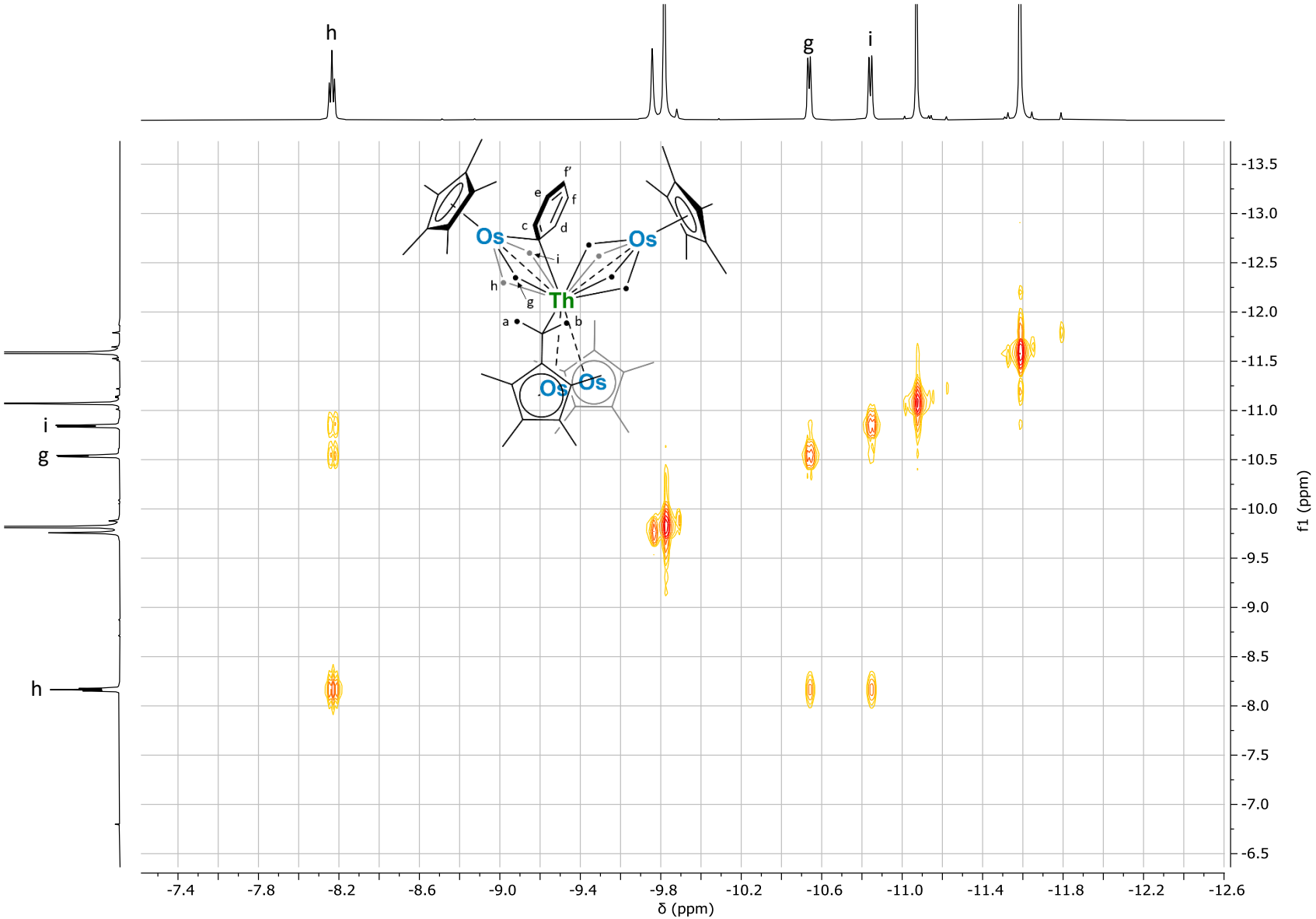


Figure S26. ^{1}H-^{1}H COSY NMR spectrum NMR of crystallized 22:78 **3-Th/4-Th** at 298 K in C_6D_6, hydride interactions.

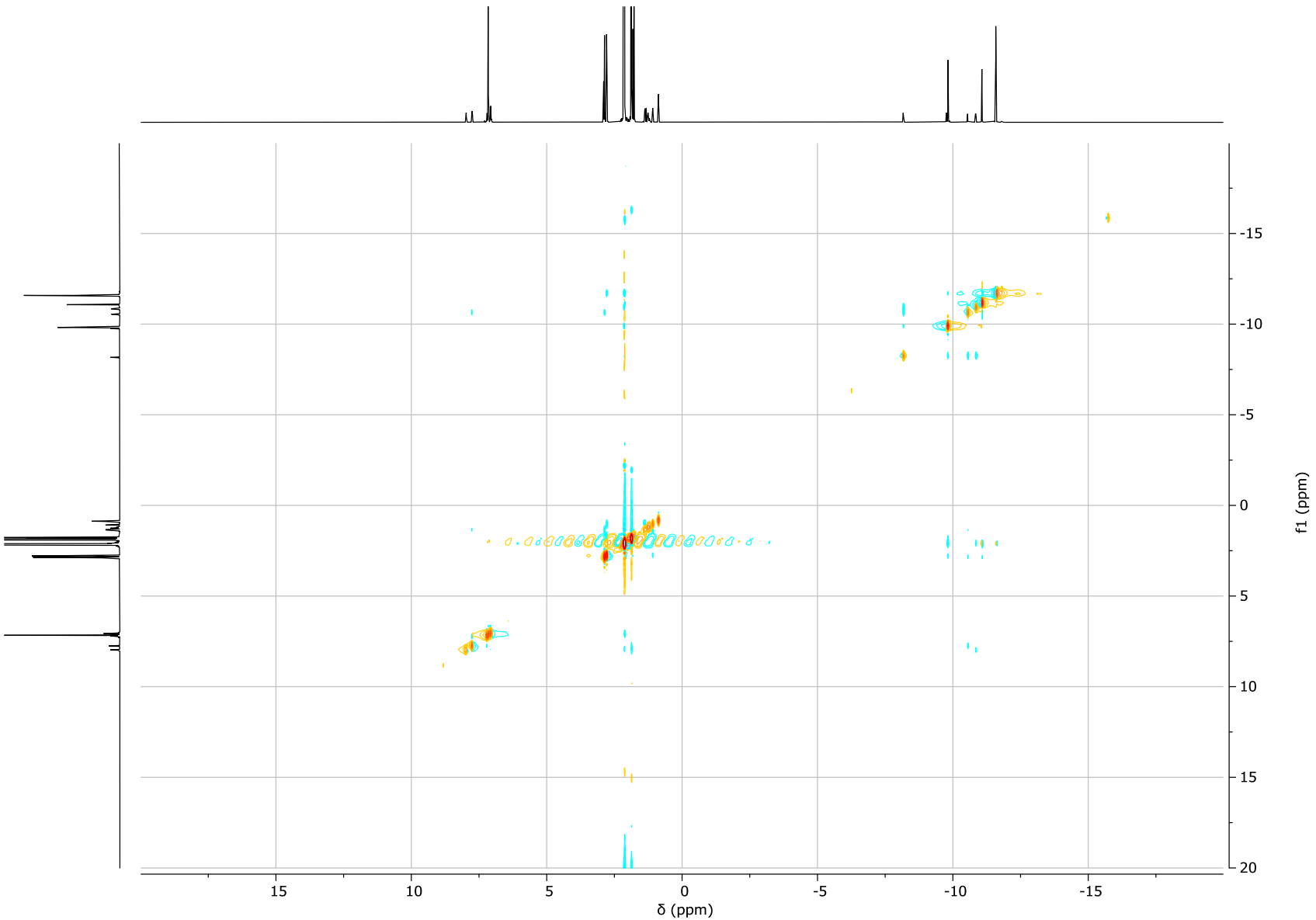


Figure S27. NOESY NMR spectrum of crystallized 22:78 **3-Th/4-Th** at 298 K in C_6D_6.

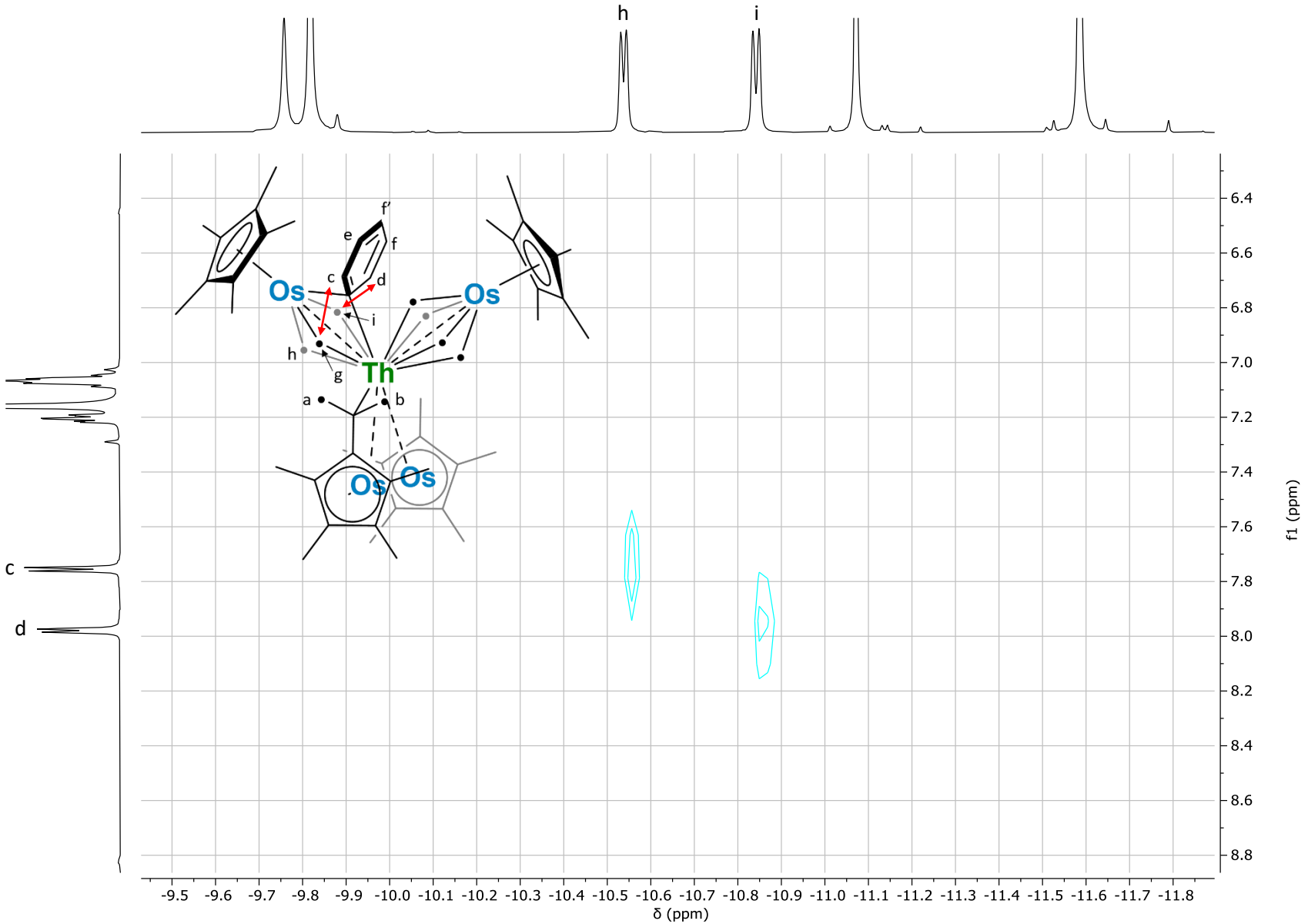


Figure S28. NOESY NMR spectrum of crystallized 22:78 **3-Th/4-Th** at 298 K in C_6D_6, aromatic proton/hydride interactions.

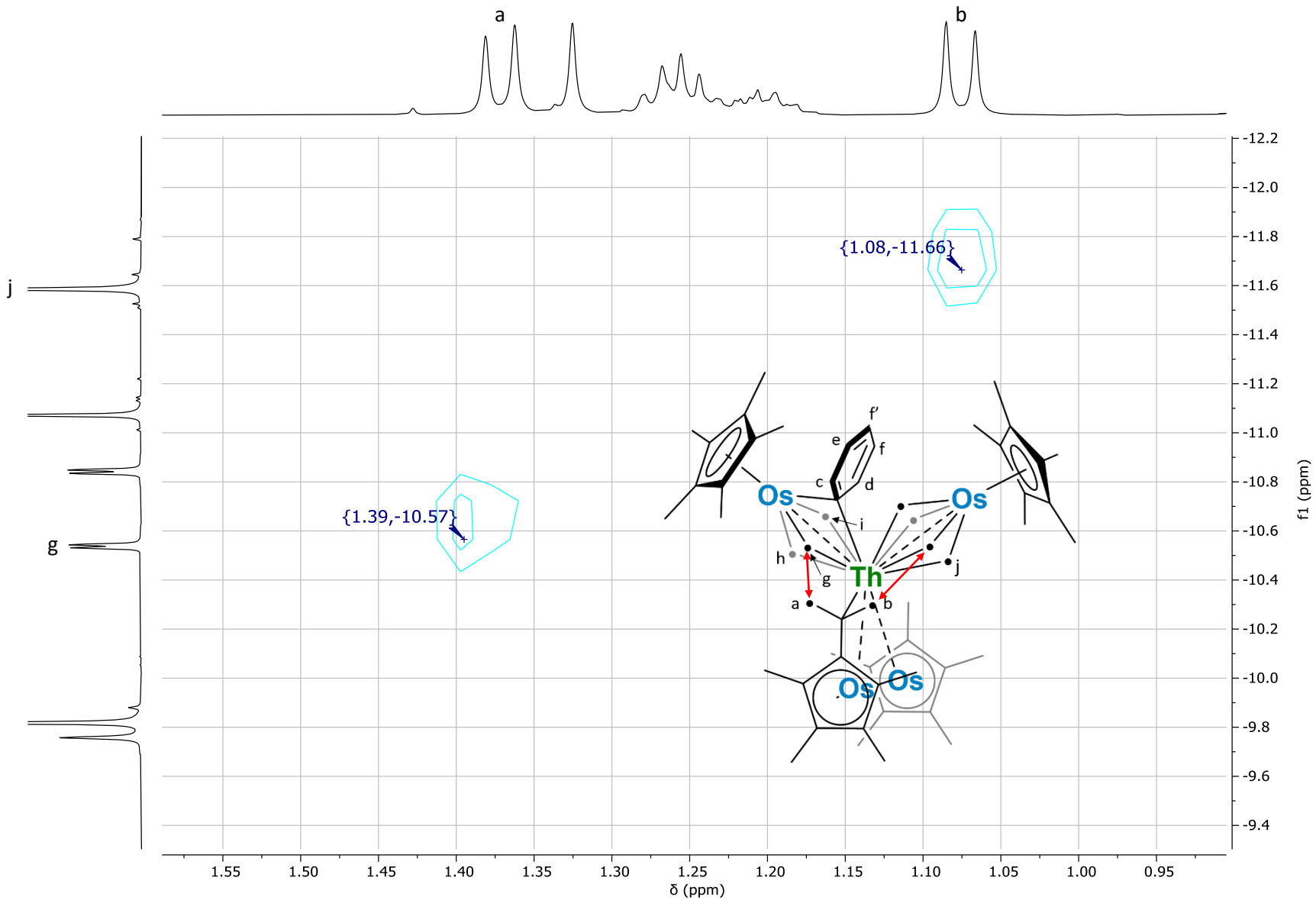


Figure S29. NOESY NMR spectrum of crystallized 22:78 **3-Th/4-Th** at 298 K in C_6D_6, methylene/hydride interactions.

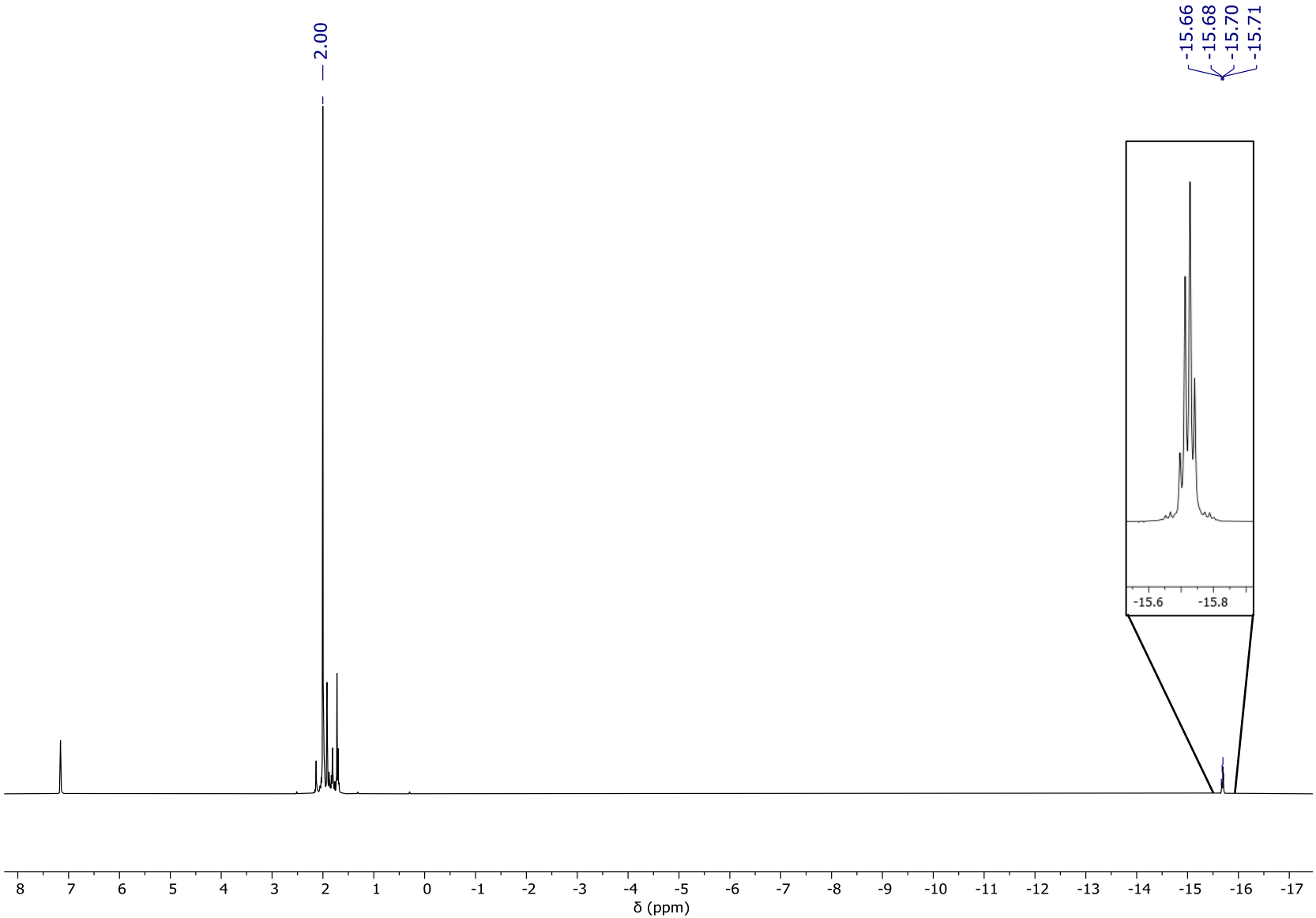


Figure S30. Crude ^{1}H NMR spectrum of the photolysis of Cp^*OsH_5 to form $[Cp^*OsX_2]_2$ (X = H, D) in C_6D_6, showing evidence of H/D exchange at the hydrides. Inset: zoomed in view of hydride signals.

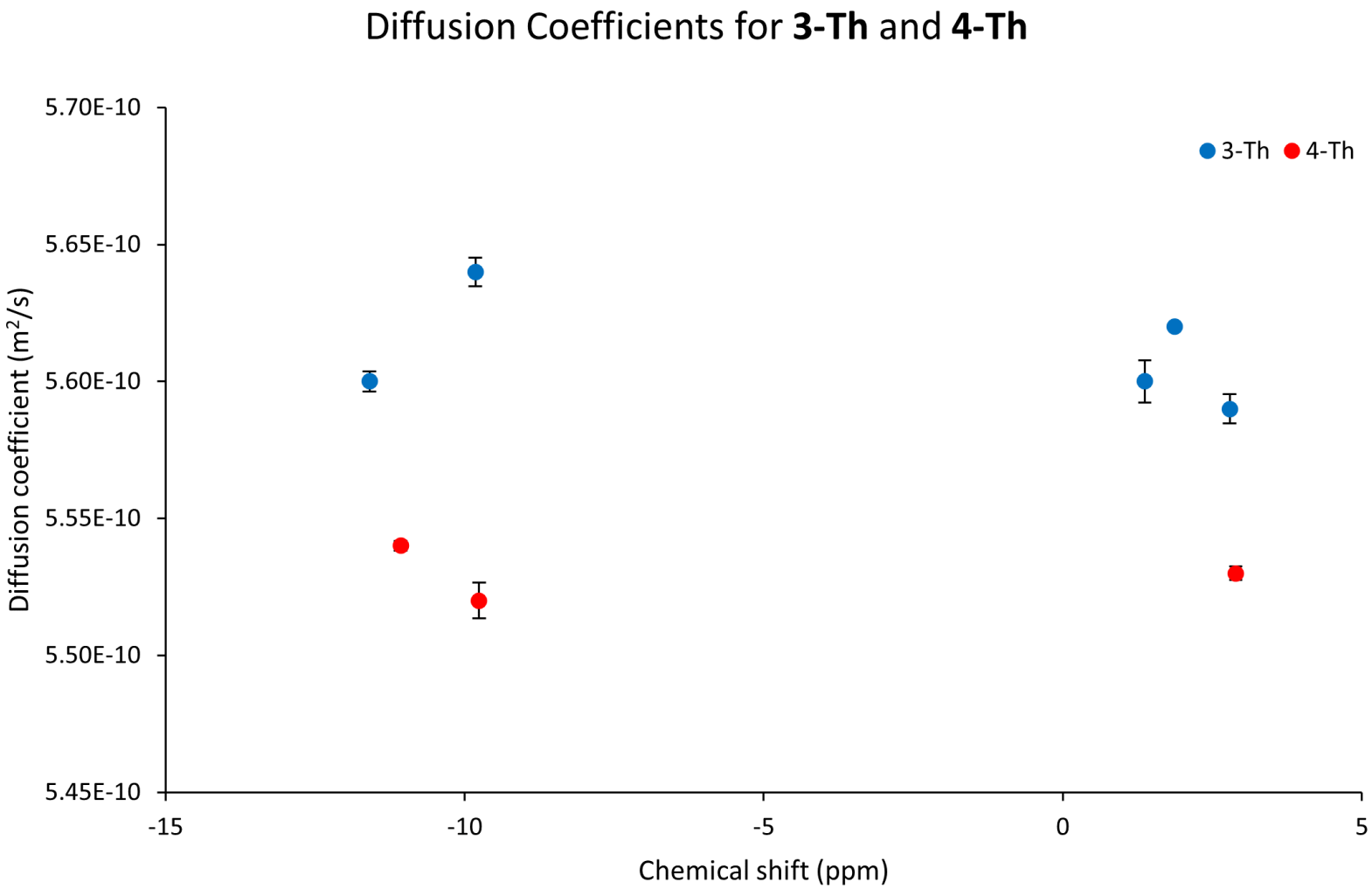


Figure S31. Diffusion coefficients calculated for ^{1}H NMR peaks from DOSY of a ~1:1 sample of **3-Th**/**4-Th**.

X-ray crystallography details

In a dry nitrogen glovebox, samples of single crystals were coated in Paratone-N oil for transport to the Advanced Light Source (ALS) or CheXray. Crystals were mounted on a MiTeGen 10 μm aperture Dual-Thickness MicroMount loop (ALS) or Kaptan loop (CheXray). X-ray diffraction data for **2-Th**, **2-U**, **3-U**, and **4-Th** were collected at the ALS, Lawrence Berkeley National Lab, Berkeley, CA, station 12.2.1 using a silicon monochromated beam of 17 keV (λ = 0.7288 Å) synchrotron radiation. Data was collected at 100 K, with the crystals cooled by a stream of dry nitrogen. Bruker APEX3 software was used for the data collections, Bruker SAINT v8.37A or V8.38A software was used to conduct the cell refinement and data reduction procedures,[6] and absorption corrections were carried out by a multi-scan method utilizing the SADABS program.[6] X-ray diffraction data for **3-Th** were collected at CheXray, Berkeley, CA, using a Rigaku XtaLAB P200 equipped with a MicroMax-007 HF microfocus rotating anode and a Pilatus 200K hybrid pixel array detector. Data was collected using Mo Kα radiation (λ = 0.71073 Å). All data collections were conducted at 100 K, with the crystals cooled by a stream of dry nitrogen. CrysAlis Pro was used for the data collections and data processing, including a multi-scan absorption correction applied using the SCALE3 ABSPACK scaling algorithm within CrysAlis Pro. Initial structure solutions were found using direct methods (SHELXT),[7] and refinements were carried out using SHELXL-2014,[8] as implemented by Olex2.[9] Thermal parameters for all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined isotropically. Thermal ellipsoid plots were made using Mercury.[10] The structures have been deposited to the Cambridge Crystallographic Data Centre (CCDC) with deposition numbers 2346841 (**2-Th**), 2346842 (**2-U**), 2346843 (**3-U**), 2346844 (**3-Th**), and 2346845 (**4-Th**).

Compound	**2-Th**	**2-U**	**3-U**	**3-Th**	**4-Th**
Empirical formula*	$C_{40}H_{60}Os_4Th$	$C_{40}H_{60}Os_4U$	$C_{40}H_{59}Os_4U$	$C_{40}H_{59}Os_4Th \cdot C_6H_{14}$	$C_{46}H_{64}Os_4Th$
Formula weight	1533.72	1539.71	1538.70	1618.88	1609.81
Temperature/K	100	100	100	100.00	100
Crystal system	monoclinic	cubic	monoclinic	orthorhombic	tetragonal
Space group	$P2_1/c$	Pa-3	C2/c	$Pmn2_1$	$P4_2/ncm$
a/Å	23.163(2)	21.395(2)	40.875(4)	18.6052(5)	13.7391(15)
b/Å	12.6413(11)	21.395(2)	10.0269(10)	9.9998(3)	13.7391(15)
c/Å	15.7810(13)	21.395(2)	23.315(2)	13.3830(4)	25.158(3)
α/°	90	90	90	90	90
β/°	91.796(3)	90	113.731(4)	90	90
γ/°	90	90	90	90	90
Volume/$Å^3$	4618.6(7)	9793(3)	8747.7(15)	2489.88(12)	4748.8(12)
Z	4	8	8	2	4
$\rho_{calc}g/cm^3$	2.206	2.089	2.337	2.159	2.252
μ/mm^{-1}	15.063	12.483	13.975	13.171	14.656
F(000)	2776.0	5568.0	5560.0	1486.0	2936.0
Crystal size/mm^3	0.05 × 0.05 × 0.01	0.1 × 0.1 × 0.05	0.03 × 0.02 × 0.02	0.2 × 0.1 × 0.05	0.3 × 0.02 × 0.02
Radiation	synchrotron (λ = 0.7288)	synchrotron (λ = 0.7288)	synchrotron (λ = 0.7288)	Mo Kα (λ = 0.71073)	synchrotron (λ = 0.7288)
2Θ range for data collection/°	1.882 to 29.119	3.904 to 55.608	3.642 to 52.084	5.982 to 61.012	4.608 to 52.084
Index ranges	$-30 \le h \le 30, 0 \le k \le 16, 0 \le l \le 21$	$-27 \le h \le 27, -27 \le k \le 27, -27 \le l \le 27$	$-49 \le h \le 49, -12 \le k \le 11, -28 \le l \le 28$	$-25 \le h \le 26, -14 \le k \le 13, -19 \le l \le 18$	$-16 \le h \le 16, -16 \le k \le 16, -30 \le l \le 30$
Reflections collected	11258	125415	52702	27906	53451
Independent reflections	11258	3605 [R_{int} = 0.1087, R_{sigma} = 0.0356]	7991 [R_{int} = 0.0502, R_{sigma} = 0.0335]	7260 [R_{int} = 0.0340, R_{sigma} = 0.0322]	2317 [R_{int} = 0.1416, R_{sigma} = 0.0530]
Data/restraints/parameters	11258/206/427	3605/75/206	7991/186/532	7260/31/279	2317/51/177
Goodness-of-fit on F^2	1.041	1.109	1.069	1.045	1.214
Final R indexes [I>=2σ (I)]	R1 = 0.0387, wR2 = 0.0801	R_1 = 0.0342, wR_2 = 0.0965	R_1 = 0.0314, wR_2 = 0.0670	R_1 = 0.0216, wR_2 = 0.0463	R_1 = 0.0445, wR_2 = 0.1071
Final R indexes [all data]	R1 = 0.0521, wR2 = 0.0862	R_1 = 0.0372, wR_2 = 0.0986	R_1 = 0.0397, wR_2 = 0.0701	R_1 = 0.0247, wR_2 = 0.0470	R_1 = 0.0510, wR_2 = 0.1101
Largest diff. peak/hole / e $Å^{-3}$	2.77/-2.36	1.35/-1.91	1.90/-2.54	2.13/-1.14	1.08/-1.37
CSD entry	2346841	2346842	2346843	2346844	2346845

Table S1. Crystal data for complexes **2-Th**, **2-U**, **3-U**, **3-Th**, and **4-Th**. *Hydrides are not observed, and are therefore not included in the empirical formulas.

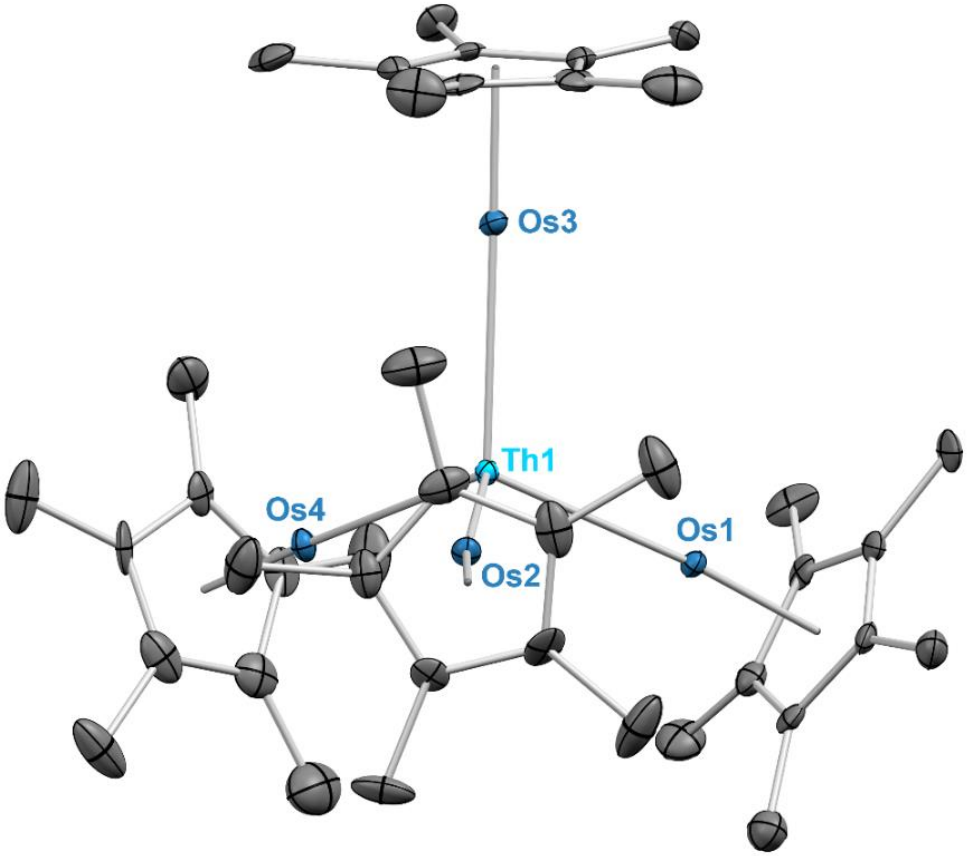


Figure S32. ORTEP diagram for **2-Th**, with ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Th1–Os1 3.0215(7), Th1–Os2 3.0379(6), Th1–Os3 3.0183(6), Th1–Os4 3.0288(7), Th1–Os1–$Cp^*_{centroid}$ 175.81(2), Th1–Os2–$Cp^*_{centroid}$ 171.10(2), Th1–Os3–$Cp^*_{centroid}$ 176.92(3), Th1–Os4–$Cp^*_{centroid}$ 171.88(3), Os1–Th1–Os4 103.291(17), Os2–Th1–Os4 115.805(16).

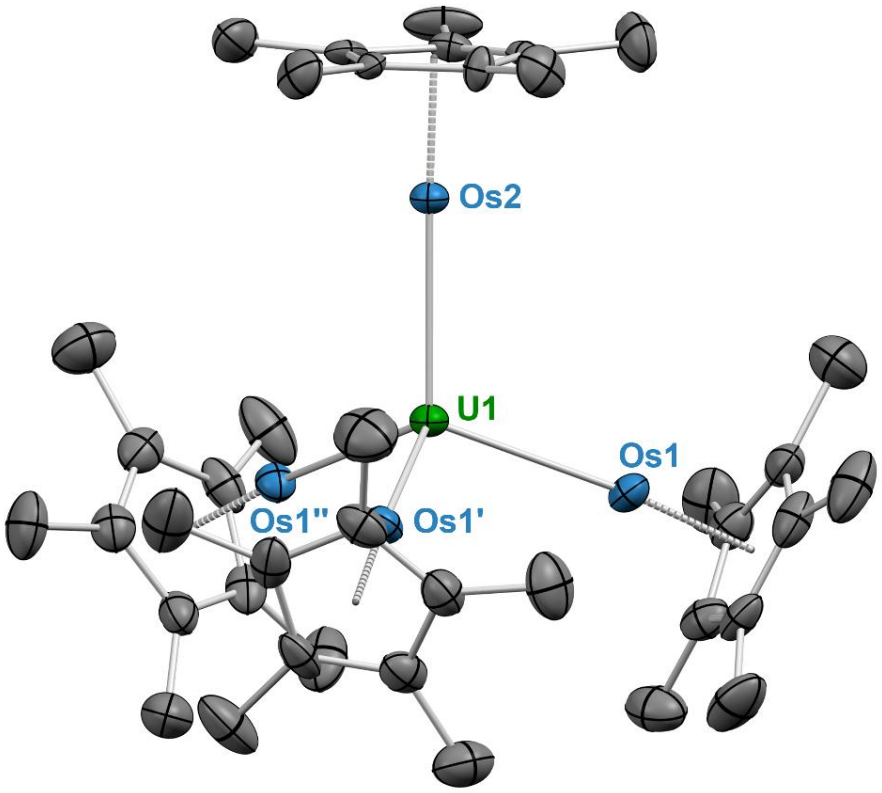
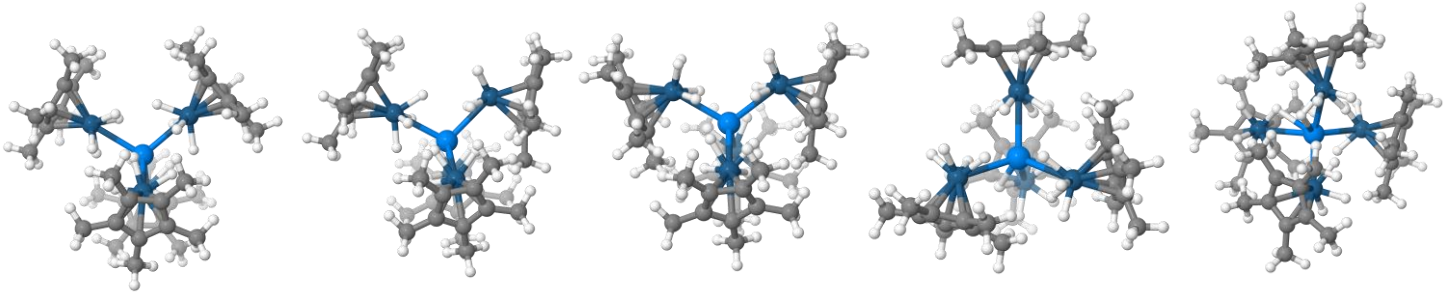


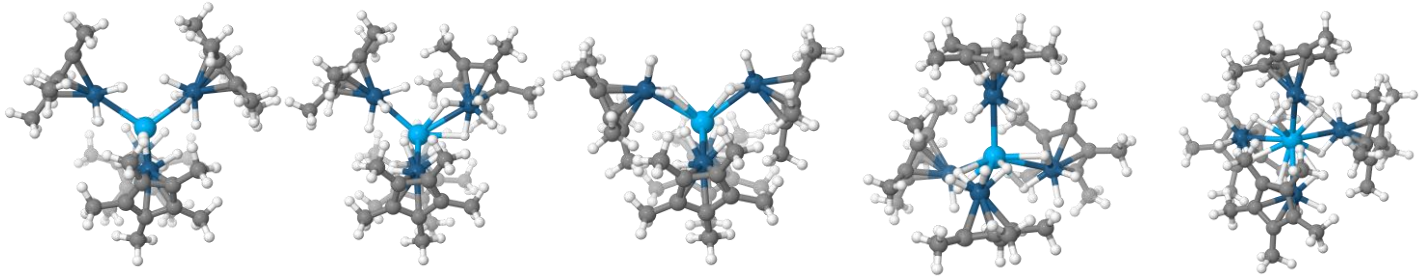
Figure S33. ORTEP diagram for **2-U**, with ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): U1–Os1 2.9501(7), U1–Os2 2.9490(6), U1–Os1–Cp*$_{centroid}$ 175.30(2), U1–Os2–Cp*$_{centroid}$ 176.40(2), Os1–U1–Os1' 107.900(9), Os1–U1–Os2 110.998(9).

Computational details

All DFT calculations were carried out with the Gaussian 09 suite of programs.[11] Geometries were fully optimized in gas phase without symmetry constraints, employing the B3PW91 functional.[12,13] The nature of the extrema was verified by analytical frequency calculations. The calculation of electronic energies and enthalpies of the extrema of the potential energy surface (minima and transition states) were performed at the same level of theory as the geometry optimizations. IRC calculations were performed to confirm the connections of the optimized transition states. Uranium, thorium and osmium atoms were treated with a small core effective core potential (60 MWB), associated with its adapted basis set[14–16] augmented, for osmium atoms, with a polarization function (ζ_f = 0.886).[17] For the other elements (H and C), Pople's double-ζ basis set 6-31G(d,p) was used.[18–20] Dispersion corrections were treated with the D3 version of Grimme's dispersion with Becke-Johnson damping.[21] The electronic charges (at the DFT level) were computed using the natural population analysis (NPA) technique.[22]



2-U	Linear			1 - Bent			2 - Bent			3 - Bent			4 - Bent		
Spin Multiplicity	singlet	triplet	quintet	singlet	triplet	quintet	singlet	triplet	quintet	singlet	triplet	quintet	singlet	triplet	quintet
ΔrH (kcal/mol)	25.0	0.0	–	26.1	1.5	35.7	30.7	4.1	39.0	–	9.9	–	58.6	17.5	–
ΔrG (kcal/mol)	26.7	0.0	–	32.5	5.9	40.4	39.7	12.7	44.5	–	17.9	–	66.8	27.3	–



2-Th	Linear		1 - Bent		2 - Bent		3 - Bent		4 - Bent	
Spin Multiplicity	singlet	triplet	singlet	triplet	singlet	triplet	singlet	triplet	singlet	triplet
ΔrH (kcal/mol)	0.0	269.7	1.4	57.7	5.8	58.4	11.7	63.6	18.7	–
ΔrG (kcal/mol)	0.0	273.7	6.3	61.0	15.5	65.9	20.5	73.43	30.5	–

Table S2. Relative energies, for **2-U** and **2-Th**, as a function of the number of bent Cp^* groups and spin multiplicity

	2-U	2-Th
	Linear (triplet)	Linear (singlet)
Os–H distance (Å)	[1.628 – 1.652] (μ-H)	[1.630 – 1.648] (μ-H)
U/Th–H distance (Å)	[2.444 – 2.595]	[2.536 – 2.601]
U/Th–Os distance (Å)	2.911, 2.912, 2.913, 2.913	2.977, 2.977, 2.977, 2.978
U/Th–C(Cp*) distance (Å)	[4.858 – 5.037]	[4.945 – 5.089]
U/Th–C(Me-Cp*) distance (Å)	[5.476 – 5.708]	[5.564 – 5.749]
Os–C(Cp*) distance (Å)	[2.187 – 2.300]	[2.187 – 2.306]
Os–U/Th–Os angle (º)	[107.1 – 111.3]	[108.3 – 110.1]
Os–U/Th–Cp (centroid) angle (º)	177.1 ; 177.8 ; 179.1 ; 179.2	178.9 ; 179.8 ; 179.2, 179.3
Os–H (cm^{-1})	[2056 – 1947], [939 – 818], [675 – 653]	[2051 – 1963], [947 – 838], [678 – 667]

Table S3. Tabulated calculated bond distances/angles and Os-H frequencies for **2-U** and **2-Th**.

	2-U (triplet)	2-Th (singlet)
	Wiberg Bond Indexes (WBI)	
Os – H	[0.57 – 0.60]	[0.60]
U/Th – (μ-H)	[0.18 – 0.24]	[0.19 – 0.21]
U/Th – Os	[0.81 - 0.83]	[0.72 - 0.73]
U/Th – C (Cp*)	[0.02 - 0.03]	[0.02 - 0.03]
2nd Order NBO Analysis	LP C (Cp*) → LP* U: [4 – 5] kcal/mol	BD C (Cp*) – C (Cp*) → LP*: 3 kcal/mol BD C (Me-Cp*) – H → LP* U: [8 - 12] kcal/mol LP C (Cp*) → LP* U: [42 – 48] kcal/mol
	Natural Charges	
Os Natural Charges	-0.95 - -0.96	-0.98
U/Th Natural Charges	-0.36	0.04

Table S4. Wiberg Bond Indexes and Natural Charges for **2-U** and **2-Th**.

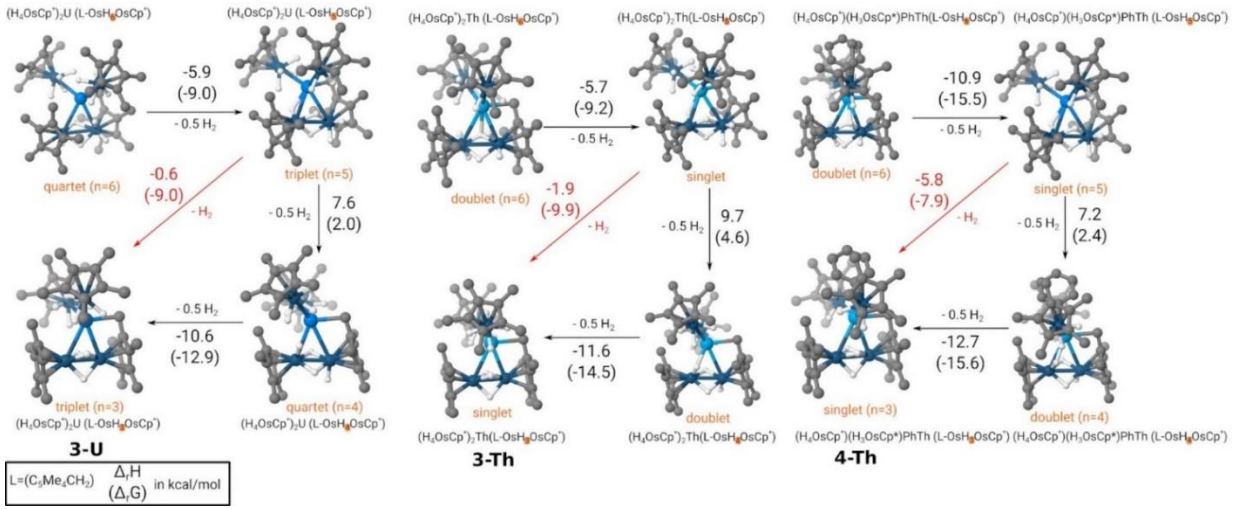


Figure S34. Determination of the number of hydrogen atoms on complexes **3-U**, **3-Th** and **4-Th**.

$(H_4OsCp^*)_2U((C_5Me_4CH_2)OsH_nOsCp^*)$	n = 2			n = 3			n = 4			n = 5			n = 6		
Spin Multiplicity	doublet	quartet	sextet	singlet	triplet	quintet	doublet	quartet	sextet	singlet	triplet	quintet	doublet	quartet	sextet
ΔrH (kcal/mol)	1.1	0.0	34.3	25.6	0.0	23.3	2.7	0.0	29.3	32.6	0.0	11.1	1.2	0.0	30.3
ΔrG (kcal/mol)	0.6	0.0	32.6	26.8	0.0	22.9	3.6	0.0	27.8	32.0	0.0	9.6	1.6	0.0	26.8

$(PhH_3OsCp^*)(H_4OsCp^*)Th((C_5Me_4CH_2)OsH_nOsCp^*)$	n = 0		n = 1		n = 2		n = 3		n = 4		n = 5		n = 6	
Spin Multiplicity	doublet	quartet	singlet	triplet	doublet	quartet	singlet	triplet	doublet	quartet	singlet	triplet	doublet	quartet
ΔrH (kcal/mol)	0.0	44.4	0.0	36.5	0.0	46.8	0.0	42.4	0.0	-	0.0	-	0.0	-
ΔrG (kcal/mol)	0.0	40.8	0.0	34.6	0.0	45.2	0.0	36.6	0.0	-	0.0	-	0.0	-

Table S5. Relative energies, for **3-U** and **4-Th**, as a function of the number of hydrogens atoms and of the spin multiplicity.

	3-U (triplet)	3-Th (singlet)	4-Th (singlet)
Os – H distance (Å)	[1.630 – 1.649] $(H_4OsCp^*)_2$ [1.794 – 1.838] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[1.632 – 1.647] $(H_4OsCp^*)_2$ [1.798 – 1.834] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[1.625 – 1.642] $(H_4OsCp^*)_2$ [1.797 – 1.834] $((C_5Me_4CH_2)OsH_3OsCp^*)$
Os–C(Ph) distance (Å)	-	-	2.113
U/Th–H distance (Å)	[2.464 – 2.543] $(H_4OsCp^*)_2$ [2.662, 2.667, 4.065] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[2.542 – 2.630] $(H_4OsCp^*)_2$ [2.738, 2.734, 4.127] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[2.518 – 2.644] $(H_4OsCp^*)_2$ [2.737, 2.742, 4.132] $((C_5Me_4CH_2)OsH_3OsCp^*)$
U/Th–C(Ph) distance (Å)	-	-	2.856
U/Th–Os distance (Å)	[2.918, 2.922] $(H_4OsCp^*)_2$ [2.856, 3.150] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[2.984, 2.987] $(H_4OsCp^*)_2$ [2.941, 3.178] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[3.040, 2.988] $(H_4OsCp^*)_2$ [2.948, 3.179] $((C_5Me_4CH_2)OsH_3OsCp^*)$
Os–Os distance (Å) $((C_5Me_4CH_2)OsH_3OsCp^*)$	2.474	2.475	2.472
Os–C(Cp*) distance (Å)	[2.188 – 2.301] $(H_4OsCp^*)_2$ [2.175 – 2.241] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[2.193 – 2.309] $(H_4OsCp^*)_2$ [2.175 – 2.248] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[2.183 – 2.318] $(H_4OsCp^*)_2$ [2.178 – 2.243] $((C_5Me_4CH_2)OsH_3OsCp^*)$
Os–C(Me-Cp*) distance (Å)	[3.306 – 3.412] $(H_4OsCp^*)_2$ [3.280 – 3.446] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[3.313 – 3.421] $(H_4OsCp^*)_2$ [3.281 – 3.437] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[3.305 – 3.431] $(H_4OsCp^*)_2$ [3.284 – 3.405] $((C_5Me_4CH_2)OsH_3OsCp^*)$
U/Th–C(CH_2) distance (Å)	2.438	2.504	2.518
Os–U/Th–Os angle (º) (H_4OsCp^*)	116.3	120.7	135.6
Os–U/Th–Os angle (º) $((C_5Me_4CH_2)OsH_3OsCp^*)$	48.3	47.5	47.4
U/Th–Os–Os angle (º) $((C_5Me_4CH_2)OsH_3OsCp^*)$	72.0, 59.6	71.3, 61.2	71.2, 61.4
U/Th–Os–Cp(centroid) angle (º)	179.1, 179.1 $(H_4OsCp^*)_2$ 103.0, 121.7 $((C_5Me_4CH_2)OsH_3OsCp^*)$	178.1, 179.6 $(H_4OsCp^*)_2$ 103.6, 120.0 $((C_5Me_4CH_2)OsH_3OsCp^*)$	177.9, 177.6 $(H_4OsCp^*)_2$ 104.2, 119.3 $((C_5Me_4CH_2)OsH_3OsCp^*)$
Os–Os–Cp (centroid) angle (º)	175.0, 178.5	174.8, 178.7	175.3, 179.3
Os–H (cm^{-1})	[2050 – 1953] $(H_4OsCp^*)_2$ [1619 – 1561] $((C_5Me_4CH_2)OsH_3OsCp^*)$ [1061 – 1057, 1036, 947, 900, 776, 644] $((C_5Me_4CH_2)OsH_3OsCp^*)$ [930 – 918, 856 – 837, 644 – 642, 585 – 564] $(H_4OsCp^*)_2$	[2037 – 1964] $(H_4OsCp^*)_2$ [1608 – 1561] $((C_5Me_4CH_2)OsH_3OsCp^*)$ [1032 – 1019, 958, 907, 788, 648] $((C_5Me_4CH_2)OsH_3OsCp^*)$ [949 – 916, 887 – 846, 667 – 660, 588 – 570] $(H_4OsCp^*)_2$	[2072 – 1999] $(H_4OsCp^*)_2$ [1620 – 1565] $((C_5Me_4CH_2)OsH_3OsCp^*)$ [1061 – 1060, 1034, 958, 908, 790 – 787, 651] $((C_5Me_4CH_2)OsH_3OsCp^*)$ [955 – 923, 902, 875 – 825, 759, 674, 576 – 569] $(H_4OsCp^*)_2$

Table S6. Tabulated calculated bond distances/angles and Os-H frequencies for **3-U, 3-Th** and **4-Th**.

	3-U (triplet)	3-Th (singlet)	4-Th (singlet)
	Wiberg Bond Indexes (WBI)		
Os – H	[0.60 – 0.62] $(H_4OsCp^*)_2$ [0.32 – 0.41] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[0.61 – 0.63] $(H_4OsCp^*)_2$ [0.32 – 0.41] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[0.60 – 0.61] (PhH_3OsCp^*) [0.60 – 0.62] (H_4OsCp^*) [0.31 – 0.40] $((C_5Me_4CH_2)OsH_3OsCp^*)$
Os – Os $((C_5Me_4CH_2)OsH_3OsCp^*)$	0.74	0.73	0.73
U/Th – H	[0.18 – 0.21] $H_4OsCp^*)_2$ [0.14, 0.15, 0.01] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[0.18 – 0.21] $H_4OsCp^*)_2$ [0.15, 0.16, 0.02] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[0.16 – 0.21] (PhH_3OsCp^*) [0.18 – 0.20] (H_4OsCp^*) [0.16, 0.16, 0.03] $((C_5Me_4CH_2)OsH_3OsCp^*)$
U/Th – Os	[0.72, 0.72] $H_4OsCp^*)_2$ [0.79, 0.53] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[0.69, 0.70] $H_4OsCp^*)_2$ [0.68, 0.53] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[0.61 (Ph), 0.71] $(H_4OsCp^*)_2$ [0.70, 0.55] $((C_5Me_4CH_2)OsH_3OsCp^*)$
U/Th – CH2	0.72	0.64	0.65
C (Cp*) – Os, C (Cp*) – Th	-	-	0.70, 0.27
Os – C (Cp*)	[0.31 – 0.42] $H_4OsCp^*)_2$ [0.35 – 0.43] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[0.30 – 0.41] $H_4OsCp^*)_2$ [0.36 – 0.43] $((C_5Me_4CH_2)OsH_3OsCp^*)$	[0.30 – 0.41] (PhH_3OsCp^*) [0.29 – 0.41] (H_4OsCp^*) [0.36 – 0.42] $((C_5Me_4CH_2)OsH_3OsCp^*)$
	Natural Charges		
Os Natural Charges $(H_4OsCp^*)_2$	[-1.02, -1.03]	[-1.02, -1.03]	[-0.82 (Ph), -1.00]
Os Natural Charges $((C_5Me_4CH_2)OsH_3OsCp^*)$	[-0.57, -0.60]	[-0.60, -0.61]	[-0.58, -0.58]
U/Th Natural Charges	0.52	0.68	0.44

Table S7. Wiberg Bond Indexes and Natural Charges for **3-U, 3-Th** and **4-Th**.

3-U	3-Th	4-Th
Alpha Spin Orbitals (0.75325) BD (1)Os 15 -Os 16 (50.26%) Os 15 s(0.08%)p48.18(3.80%)d99.99(96.10%) (49.74%) Os 16 s(0.06%)p81.37(4.50%)d99.99(95.41%) (0.72128) BD (2)Os 15 -Os 16 (48.78%) Os 15 s(0.00%)p 1.00(3.14%)d30.83(96.84%) (51.22%) Os 16 s(0.00%)p1.00(3.44%)d28.04(96.54%) **Beta Spin Orbitals** (0.75552) BD (1)Os 15 -Os 16 (50.54%) Os 15 s(0.09%)p42.07(3.66%)d99.99(96.23%) (49.46%) Os 16 s(0.07%)p63.21(4.31%)d99.99(95.59%) (0.72156) BD (2)Os 15 -Os 16 (48.87%) Os 15 s(0.00%)p 1.00(3.12%)d31.01(96.86%) (51.13%) Os 16 s(0.00%)p 1.00(3.44%)d28.09(96.55%)	(1.83739) BD (1)Os 25 -Os 36 (55.70%) Os 25 s(0.24%)p 7.41(1.81%)d99.99(97.94%) (44.30%) Os 36 s(0.20%)p 8.17(1.65%)d99.99(98.14%) (1.59753) BD*(1)Os 25 -Os 36 (44.30%) Os 25 s(0.24%)p 7.41(1.81%)d99.99(97.94%) (55.70%) Os 36 s(0.20%)p 8.17(1.65%)d99.99(98.14%)	
Alpha Spin Orbitals CR Os 15 → LP* Os 16 ~190 LP Os 15 → LP* Os 16 ~140 CR Os 16 → LP* Os 15 ~150 LP Os 16 → LP*Os 15 ~70 **Beta Spin Orbitals** CR Os 15 → LP* Os 16 ~210 LP Os 15 → LP* Os 16 ~140 CR Os 16 → LP* Os 15 ~140 LP Os 16 → LP*Os 15 ~70	CR Os 25 → LP* Os 36 ~430 LP Os 25 → LP* Os 36 ~205 CR Os 36 → LP* Os 25 ~303 LP Os 36 → LP*Os 25 ~130	CR Os 30 → LP* Os 4 ~440 LP Os 30 → LP* Os 41 ~320 CR Os 41 → LP* Os 30 ~370 LP Os 41 → LP* Os 30 ~240

Table S8. NBO Analysis of the Os–Os bonding in **3-U, 3-Th** and **4-Th**.

	4-Th
NBO bonding	(1.82905) BD C - Os (55.49%) C s(33.22%) p 2.01(66.78%) d 0.00(0.01%) (44.51%) Os s(15.23%) p 0.80(12.15%) d 4.77(72.59%) f 0.00(0.03%)
Second order perturbation analysis	7. BD (1) C2-Os7/208. LP*(1)Th 18 337.24 kcal/mol 7. BD (1) C2-Os7/209. LP*(2)Th 18 56.60 kcal/mol 7. BD (1) C2-Os7/210. LP*(3)Th 18 294.98 kcal/mol 7. BD (1)C2-Os7/211. LP*(4)Th 18 550.91 kcal/mol 7. BD (1) C2-Os7/213. LP*(6)Th 18 37.08 kcal/mol 7. BD (1) C2-Os7/214. LP*(7)Th 18 400.92 kcal/mol 7. BD (1) C2-Os7/215. LP*(8)Th 18 253.85 kcal/mol 7. BD (1) C2-Os7/216. LP*(9)Th 18 230.39 kcal/mol 7. BD (1) C2-Os7/217. LP*(10)Th 18 119.21 kcal/mol 7. BD (1) C2-Os7/218. LP*(11)Th 18 276.41 kcal/mol 7. BD (1) C2-Os7/219. LP*(12)Th 18 32.30 kcal/mol 7. BD (1) C2-Os7/220. LP*(13)Th 18 40.26 kcal/mol 7. BD (1) C2-Os7/221. LP*(14)Th 18 2.06 kcal/mol 7. BD (1) C2-Os7/222. LP*(15)Th 18 147.04 kcal/mol 7. BD (1) C2-Os7/***. BD*(1)Th 18-C 38 192.37 kcal/mol

Table S9. NBO Analysis of the Th–C_{phenyl}–Os bonding in **4-Th**.

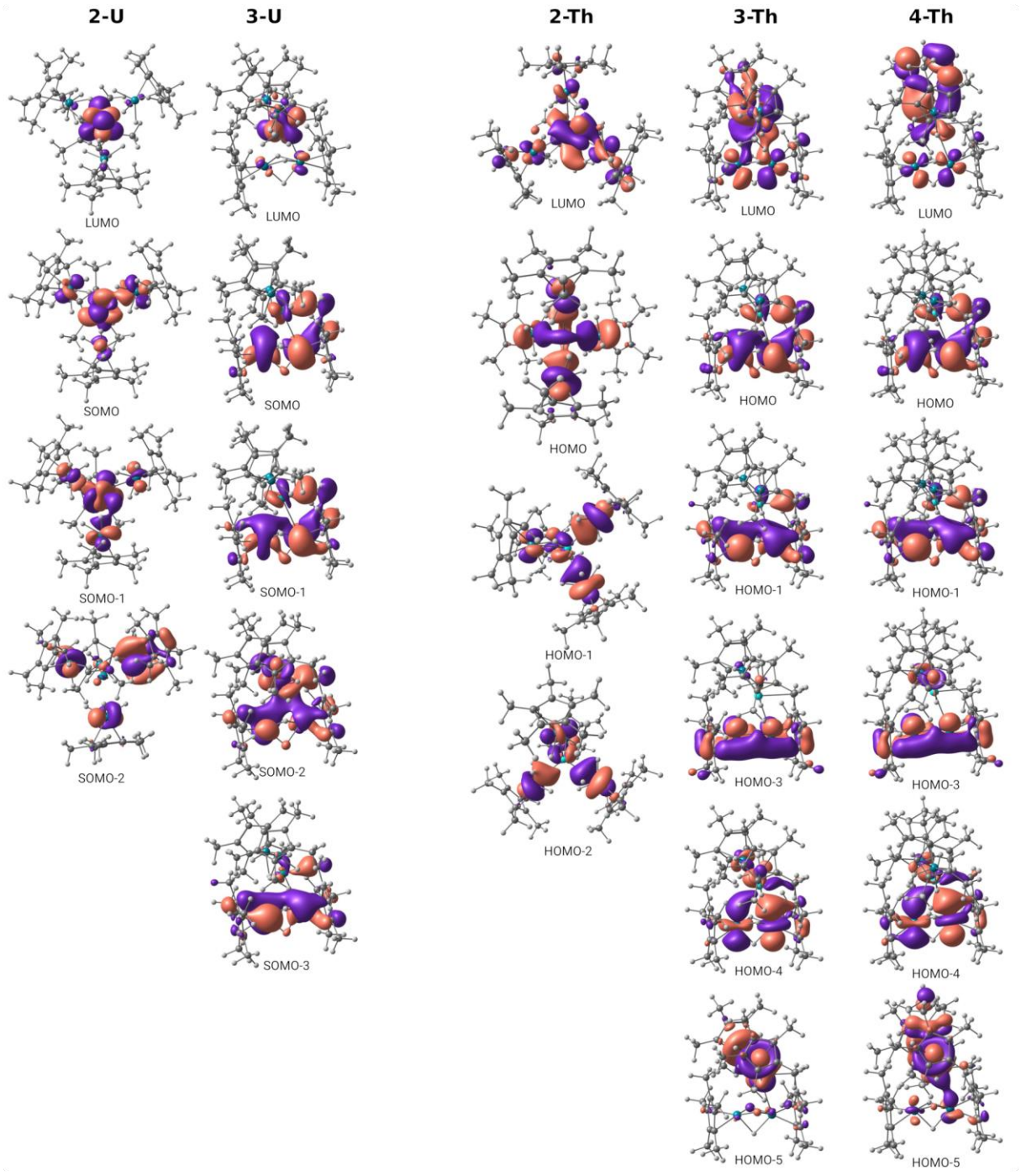


Figure S35. Lowest unoccupied molecular orbital and highest occupied molecular orbitals of complexes **2-U, 3-U, 2-Th, 3-Th** and **4-Th**.

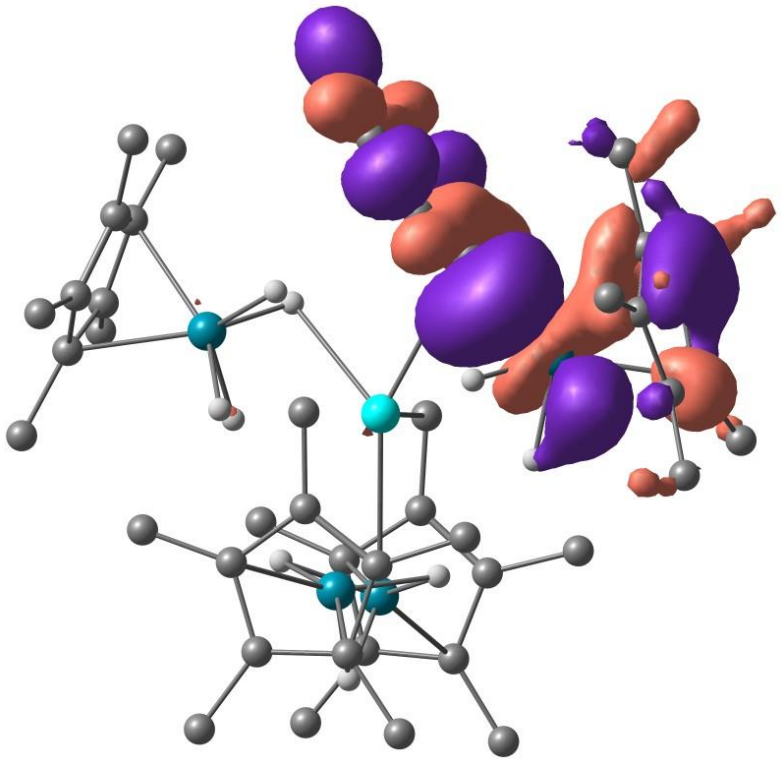


Figure S36. Depiction of the molecular orbital corresponding to the Th–C_{phenyl}–Os three-center-two-electron bond in **4-Th**.

Table S10. Coordinates of the most stable computed structures.

2-U linear triplet

C	10.573605	3.349826	3.096335
C	9.825026	2.862014	1.954930
C	9.162305	1.644839	2.358364
C	9.494247	1.383429	3.723800
C	10.355368	2.430506	4.187288
Os	8.426980	3.425191	3.558105
U	6.142816	5.123644	4.173205
Os	5.736045	6.866361	1.878492
C	4.876264	8.838468	1.033365
C	6.299635	8.837429	0.905388
C	6.679489	7.713958	0.081259
C	5.465339	7.018884	-0.295506
C	4.355586	7.719657	0.306314
C	8.056907	7.416864	-0.420446
C	5.366976	5.879579	-1.259467
C	7.230453	9.863896	1.467170
C	2.908310	7.392975	0.120410
C	4.066385	9.846981	1.782039
C	9.857314	3.429895	0.571507
C	8.328969	0.770596	1.476989
C	10.996424	2.503011	5.536207
C	9.041897	0.205341	4.524459
C	11.522756	4.505667	3.096977
Os	3.786012	3.484628	4.669917
C	1.507388	3.358194	4.613733
C	2.011529	2.298249	3.799570
C	2.835869	1.453207	4.614484
C	2.834760	1.989128	5.957093
C	2.009917	3.180452	5.951996
C	1.710833	2.089591	2.350444
C	3.486028	0.179002	4.178651
C	3.437634	1.341355	7.162906
C	1.629219	3.992858	7.148717
C	0.573165	4.436534	4.167271
Os	6.649233	6.761661	6.528311
C	7.246678	8.748177	7.338408
C	5.928342	8.381551	7.809253
C	6.072405	7.198844	8.633006
C	7.468147	6.858390	8.672310
C	8.186248	7.804817	7.880033
C	4.983856	6.530908	9.411366
C	8.068899	5.726962	9.442585
C	4.673592	9.172807	7.618073
C	9.667332	7.835334	7.680601
C	7.588215	9.966185	6.540594
H	4.680328	9.688507	6.655154
H	4.553644	9.925394	8.407941
H	3.796386	8.522043	7.632471
H	10.090826	6.828942	7.709155
H	10.152993	8.429958	8.464514
H	9.924688	8.275664	6.714960
H	4.020549	6.643180	8.909297
H	4.895341	6.959432	10.417921
H	5.175460	5.460252	9.514605

H	8.449311	9.783821	5.893474
H	7.827130	10.814001	7.195299
H	6.753556	10.258223	5.899681
H	2.423936	3.978792	7.897711
H	0.713476	3.608156	7.615758
H	1.457808	5.036658	6.875325
H	0.709222	5.343308	4.760353
H	-0.470957	4.115831	4.272310
H	0.743203	4.698279	3.120556
H	3.802325	0.235241	3.134463
H	2.797691	-0.669671	4.280455
H	4.373371	-0.031313	4.779512
H	1.538304	3.040773	1.842195
H	0.813385	1.470810	2.225589
H	2.539086	1.588666	1.844749
H	4.350550	0.801359	6.901525
H	2.739674	0.629888	7.622626
H	3.704735	2.088428	7.913646
H	7.364304	4.898010	9.536953
H	8.348827	6.050631	10.452947
H	8.965492	5.344761	8.949688
H	6.859918	10.255568	2.417090
H	7.347883	10.706484	0.774044
H	8.218612	9.437037	1.650800
H	2.768288	6.323941	-0.052942
H	2.491230	7.933778	-0.738529
H	2.326308	7.661985	1.004878
H	8.811099	7.694111	0.319849
H	8.270990	7.964751	-1.347123
H	8.175580	6.349984	-0.621639
H	3.149723	9.402910	2.176047
H	3.784510	10.680917	1.127126
H	4.626843	10.255549	2.625654
H	11.199737	5.274961	2.392141
H	12.534821	4.188002	2.815259
H	11.574538	4.969534	4.084628
H	8.963310	0.456202	5.584493
H	9.750249	-0.626617	4.424890
H	8.062041	-0.144527	4.192474
H	11.214964	3.537235	5.810127
H	11.938711	1.940930	5.552798
H	10.341897	2.089464	6.306877
H	7.549076	0.262186	2.048262
H	8.947025	0.006095	0.989486
H	7.837559	1.355870	0.697003
H	8.912502	3.249902	0.053159
H	10.663919	2.984552	-0.025023
H	10.012076	4.510714	0.598951
H	6.265681	5.259961	-1.222251
H	5.243588	6.240094	-2.288703
H	4.517181	5.236099	-1.020350
H	7.268959	2.911486	4.609054
H	7.033652	3.414560	2.679689
H	8.306586	4.958462	3.011951
H	8.524350	4.385818	4.873273
H	5.262472	2.789684	4.657641
H	4.604988	4.144471	5.913016

H	3.704471	5.111989	4.418149
H	4.393847	3.700973	3.150524
H	6.560710	5.470975	1.731737
H	4.663302	5.662986	2.133376
H	5.035428	7.170746	3.341738
H	7.012374	7.025873	2.905678
H	7.826683	6.465561	5.413627
H	6.164742	7.466731	5.143029
H	5.152559	6.188599	6.228393
H	6.817694	5.118549	6.530237

2-Th linear singlet

C	10.669209	3.319280	3.229976
C	10.033419	2.830677	2.023215
C	9.338824	1.616355	2.352996
C	9.527350	1.351908	3.743844
C	10.343172	2.397616	4.297172
Os	8.505183	3.397635	3.534559
Th	6.158504	5.131700	4.131589
Os	5.685561	6.919480	1.799929
C	4.770583	8.869524	0.971631
C	6.187449	8.889430	0.784232
C	6.550536	7.763450	-0.041229
C	5.333263	7.044277	-0.361284
C	4.237523	7.734906	0.277856
C	7.911257	7.481998	-0.594752
C	5.213529	5.896262	-1.312416
C	7.123378	9.936831	1.296437
C	2.788924	7.386182	0.151964
C	3.975799	9.876205	1.738805
C	10.184586	3.411231	0.653157
C	8.581933	0.755267	1.393902
C	10.871030	2.449935	5.695447
C	9.001606	0.167526	4.488900
C	11.623892	4.467266	3.318030
Os	3.742571	3.469985	4.647148
C	1.475709	3.357179	4.603870
C	1.957402	2.272045	3.807568
C	2.774373	1.432618	4.632214
C	2.794077	1.992742	5.962990
C	1.986176	3.196274	5.943920
C	1.641116	2.038486	2.365673
C	3.412277	0.146707	4.213321
C	3.401225	1.359078	7.174130
C	1.619472	4.029737	7.130584
C	0.543699	4.432940	4.146162
Os	6.700985	6.775954	6.554062
C	7.258995	8.769770	7.399685
C	5.960022	8.351094	7.878690
C	6.151994	7.149675	8.666349
C	7.559935	6.850715	8.673158
C	8.235032	7.843277	7.899225
C	5.098433	6.433320	9.449930
C	8.209677	5.722693	9.408011
C	4.680472	9.111013	7.729251
C	9.710692	7.924306	7.676187
C	7.549521	10.015500	6.624999

H	4.652246	9.644841	6.776653
H	4.557198	9.844761	8.536139
H	3.821948	8.436045	7.749578
H	10.164660	6.930976	7.673051
H	10.190734	8.513943	8.467216
H	9.938444	8.396163	6.718082
H	4.122485	6.531100	8.969719
H	5.019152	6.834563	10.468399
H	5.321008	5.366136	9.521965
H	8.405518	9.875711	5.960852
H	7.772634	10.854244	7.296640
H	6.695905	10.296361	6.004558
H	2.418972	4.020294	7.874572
H	0.703364	3.660214	7.609000
H	1.455797	5.070660	6.842093
H	0.688652	5.348057	4.724001
H	-0.501547	4.119735	4.262296
H	0.709267	4.677767	3.094648
H	3.717848	0.181127	3.165093
H	2.718511	-0.694345	4.338001
H	4.303899	-0.059000	4.809240
H	1.473489	2.981389	1.840816
H	0.735849	1.427285	2.262050
H	2.458794	1.518687	1.861870
H	4.308430	0.808582	6.914777
H	2.701369	0.659827	7.649370
H	3.678570	2.115658	7.911392
H	7.530402	4.872966	9.502345
H	8.504439	6.035231	10.417669
H	9.104172	5.374511	8.886934
H	6.784983	10.333577	2.256174
H	7.198538	10.772968	0.589821
H	8.125045	9.527980	1.444281
H	2.657993	6.313219	-0.003129
H	2.330983	7.910713	-0.696218
H	2.238071	7.657386	1.055489
H	8.690256	7.785831	0.108360
H	8.075659	8.017869	-1.538405
H	8.041714	6.414164	-0.783015
H	3.081008	9.424629	2.172435
H	3.658023	10.698002	1.084996
H	4.561949	10.302441	2.555762
H	11.364491	5.245853	2.597143
H	12.653539	4.144773	3.116816
H	11.597591	4.921541	4.311064
H	8.836121	0.407537	5.541278
H	9.710145	-0.668772	4.439159
H	8.050128	-0.170508	4.072555
H	11.074474	3.479771	5.996416
H	11.803135	1.877939	5.787087
H	10.148933	2.038282	6.404370
H	7.755665	0.242229	1.890763
H	9.238938	-0.005504	0.954054
H	8.161240	1.349544	0.580137
H	9.291896	3.230849	0.049752
H	11.043830	2.972963	0.129547
H	10.332407	4.492093	0.702258

H	6.122317	5.290458	-1.307404
H	5.042830	6.246929	-2.338349
H	4.384131	5.241971	-1.034277
H	7.370725	2.916235	4.624651
H	7.109885	3.291871	2.663694
H	8.354126	4.865582	2.835945
H	8.588732	4.469126	4.760694
H	5.206300	2.747778	4.555265
H	4.606327	4.083827	5.885220
H	3.643307	5.098696	4.447554
H	4.271431	3.728275	3.107391
H	6.563189	5.556998	1.630161
H	4.646858	5.692824	2.095971
H	5.013813	7.250742	3.268258
H	6.974649	7.130695	2.797972
H	7.894662	6.475148	5.459756
H	6.232619	7.511118	5.175468
H	5.199936	6.214530	6.251452
H	6.866545	5.137303	6.569450

3-U n=3 triplet

C	1.897157	8.430945	8.584890
C	3.022094	7.820931	9.265304
C	4.130236	8.744194	9.185604
C	3.691600	9.906908	8.473322
C	2.326047	9.715926	8.095165
Os	3.524849	8.038222	7.135741
U	4.337943	6.704833	4.667056
C	6.741742	7.103095	4.776259
C	7.099160	5.677000	4.702133
C	7.240460	4.757654	5.813175
C	7.489198	3.443294	5.293298
C	7.464858	3.522588	3.851504
C	7.206376	4.890281	3.492813
C	5.469795	8.561208	9.824509
Os	5.505906	4.101839	4.637072
Os	3.049643	3.824453	4.666810
C	1.034962	4.778342	4.766336
C	1.177822	4.039918	3.540104
C	1.394177	2.658562	3.865964
C	1.405487	2.542946	5.308460
C	1.198478	3.850468	5.856153
C	1.048977	4.617652	2.169701
C	1.509836	1.529334	2.894069
C	1.098359	4.200248	7.303501
C	1.551796	1.273702	6.083631
C	7.236971	5.147931	7.254645
C	7.162280	5.443562	2.106085
C	7.754816	2.404955	2.903726
C	7.790007	2.222218	6.099759
C	0.555227	6.187201	4.891512
C	4.512645	11.125381	8.200359
C	2.992458	6.554852	10.061078
C	1.466264	10.712293	7.386050
C	0.493730	7.915912	8.561495
Os	3.670277	8.013579	2.139833
C	2.065252	8.651675	0.612491

C	2.997263	7.740245	0.015408
C	4.310750	8.342961	0.070551
C	4.171035	9.632057	0.714331
C	2.781735	9.810647	1.044904
C	5.546361	7.808038	-0.580320
C	5.249438	10.656006	0.873183
C	2.659194	6.458570	-0.676393
C	2.182287	11.028376	1.671471
C	0.590003	8.441009	0.729486
H	2.185704	0.559129	5.553237
H	0.575296	0.801146	6.250113
H	2.009789	1.458920	7.057910
H	6.815434	4.691051	1.394215
H	8.161321	5.775128	1.794933
H	6.482495	6.296241	2.040126
H	6.555336	5.982856	7.434723
H	8.242500	5.453356	7.571060
H	6.916422	4.317137	7.887135
H	1.942892	1.868215	1.950115
H	0.526717	1.090372	2.680090
H	2.154536	0.738090	3.284200
H	0.859729	6.797084	4.037455
H	0.940641	6.668945	5.791908
H	-0.542225	6.202505	4.937030
H	1.633951	3.476316	7.921715
H	0.051525	4.224527	7.632387
H	1.543636	5.181903	7.482517
H	1.503266	5.610999	2.130225
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H	1.561964	3.994663	1.433783
H	5.572198	10.876267	8.113308
H	4.401968	11.853811	9.013010
H	4.206853	11.608423	7.270064
H	7.288013	2.257940	7.069398
H	8.868708	2.126474	6.278802
H	7.452961	1.318346	5.586763
H	7.420352	1.446695	3.308572
H	8.831272	2.329361	2.702190
H	7.242462	2.556521	1.950849
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H	0.347618	7.381166	0.829897
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H	5.721891	7.502018	9.907576
H	5.484429	8.992600	10.833130
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H	2.902716	11.530941	2.319902
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H	7.009066	7.561489	5.731259
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H	4.612166	8.720959	6.101919
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H	2.957097	6.557467	6.742677
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H	5.185525	8.036766	2.745828
H	2.529828	7.284921	3.072862
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3-Th n=3 singlet

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Os	8.354274	8.520901	8.572232
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C	8.269561	6.333061	7.851352
C	7.275882	6.575603	8.855634
C	6.380967	7.600672	8.363792
C	7.113304	5.816885	10.133713
C	9.366170	5.321027	7.931647
C	8.780309	7.231404	5.462168
C	5.113358	8.046459	9.020156
C	6.151535	8.925580	6.111243
Th	9.885332	10.721711	9.886566
Os	12.082748	12.173622	8.476154
C	13.502992	12.261582	6.676963
C	12.723918	13.458599	6.686859
C	12.960715	14.141170	7.929085
C	13.909811	13.358635	8.693767
C	14.239765	12.187375	7.908544
C	14.559531	13.774104	9.975346
C	12.428675	15.487492	8.304108
C	11.850660	13.944366	5.575623
C	15.277716	11.163549	8.239942
C	13.583536	11.278373	5.554157
Os	9.268727	11.322151	12.696088
C	7.182528	11.744811	12.171484
C	8.005409	12.604026	11.350400
C	8.788658	13.415967	12.255667
C	8.408515	13.106001	13.607125
C	7.408226	12.064434	13.555876
C	8.895260	13.798466	14.838060
C	9.755552	14.474428	11.837120
C	8.148324	12.527928	9.886270

C	6.670177	11.492012	14.721650
C	6.190067	10.759757	11.645677
Os	11.052261	9.607703	12.623421
C	13.186740	9.187744	12.298627
C	12.430588	8.372934	11.381751
C	11.567356	7.524155	12.161319
C	11.807518	7.789831	13.552640
C	12.817214	8.824523	13.635502
C	11.188392	7.073180	14.708532
C	10.645393	6.488676	11.607278
C	12.678509	8.256986	9.912693
C	13.409380	9.369865	14.894521
C	14.229068	10.180737	11.905344
H	8.263545	14.663371	15.079593
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H	9.664489	5.141212	8.966363
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H	9.839767	6.268453	12.311357
H	11.184929	5.554665	11.402063
H	10.183204	6.839601	10.681015
H	5.769625	12.078719	14.946164
H	6.361873	10.462699	14.523053
H	7.296122	11.480900	15.617441
H	14.990052	10.174571	7.874982
H	16.242408	11.423864	7.786815
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H	14.370175	11.565260	4.845312
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H	6.049212	9.931894	12.344782
H	5.217427	11.242452	11.484687
H	6.520367	10.333990	10.694816
H	7.212565	12.271046	9.383634
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 H    15.457666    14.375690     9.786795
 H    14.852372    12.904936    10.567719
 H    10.205836    10.428636    13.987916
 H     9.288713     9.539715    12.273698
 H    11.052794    11.372141    12.269405

4-Th n=3 singlet
 C    10.588108     9.036032     6.661809
 C     9.304495     9.451252     7.082956
 C     8.746826    10.544883     6.373744
 C     9.351129    11.068221     5.230185
 C    10.565609    10.554809     4.780410
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Os     8.240961     8.379386     8.563722
 C     6.475831     7.811535     7.314124
 C     7.569383     7.031393     6.804495
 C     8.063502     6.202020     7.854254
 C     7.268773     6.441756     9.027111
 C     6.272287     7.435914     8.691739
 C     7.308150     5.639724    10.287877
 C     9.173553     5.206667     7.732172
 C     8.069510     7.047142     5.399257
 C     5.130194     7.862051     9.558391
 C     5.625710     8.737995     6.507748
Th     9.994644    10.631468     9.616857
Os    12.226153    12.271438     8.612884
 C    13.861151    12.618785     6.998912
 C    12.878594    13.664370     7.009573
 C    12.916403    14.295813     8.318998
 C    13.917124    13.592664     9.108448
 C    14.494280    12.567358     8.275341
 C    14.376762    13.970328    10.481493
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 C    12.090666    14.121074     5.824855
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 C    14.177417    11.738466     5.833705
Os     9.374080    11.329878    12.382259
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C	7.555709	12.192259	13.232268
C	9.123321	13.955582	14.369929
C	9.921526	14.427579	11.323519
C	8.229967	12.422147	9.522449
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C	6.254435	10.805800	11.439488
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C	13.375192	9.309295	14.744723
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