Supporting information for:

Ring-opening of a Thorium Cyclopropenyl Complex Generates a Transient Thorium-bound Carbene

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Experimental

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions under an atmosphere of dinitrogen. Diethyl ether (Et_2O), pentane, and hexanes were dried using a Vacuum Atmospheres DRI-SOLV Solvent Purification system and stored over 3Å sieves for 24 h prior to use. Tetrahydrofuran (THF) was distilled over calcium hydride then distilled over sodium benzophenone, collected, and stored over 3Å sieves for 24 h prior to use. Isooctane was distilled over sodium benzophenone, collected, and stored over 3Å sieves for 24 h prior to use. THF-d_8 and C_6D_6 were stored over 3Å sieves for 24 h prior to use. [Cp_3ThCl], lithium diisopropylamide (LDA), and 3,3-diphenylcyclopropene were synthesized according to previously reported literature procedures.[1-3] All other reagents were purchased from commercial vendors and used as received.

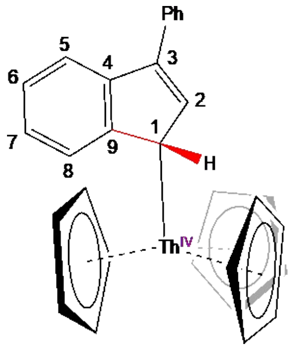
^1H, $^{13}C\{^1H\}$, and 2D NMR spectra were recorded on a Varian UNITY INOVA 500 MHz or a Varian Unity Inova AS600 600 MHz spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to external $SiMe_4$ using the residual protio solvent peaks as internal standards.[4, 5] IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer with a NXR FT Raman Module. Electronic absorption spectra were recorded on a Shimadzu UV3600 UV-NIR Spectrometer. Elemental analyses were performed by the Microanalytical Laboratory at University of California (Berkeley, CA).

X-ray Crystallography: Data for complexes **1**-**3** were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromater with a Mo Kα X-ray source ($\alpha = 0.71073$ Å). The crystals were mounted on a cryoloop under Paratone-N oil. Data for complexes **1** and **3** were collected at 110(2) K, whereas data for **2** were collected at 100(2) K using an Oxford nitrogen gas cryostream system. X-ray data for **1**, **2**, and **3** were collected utilizing frame exposures of 30, 15, and 40 s, respectively. Data collection and cell parameter determination were conducted using the SMART program.[6] Integration of the data frames and final cell parameter refinement were performed using SAINT software.[7] Absorption corrections of the data were carried out using the multi-scan method SADABS.[8] Subsequent calculations were carried out using SHELXTL.[9] Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[9] Further crystallographic details can be found in Tables S4. Complexes **1-3** have been deposited in the Cambridge Structural Database (**1**: CCDC 2155766; **2**: CCDC 2155767; **3**: CCDC 2155768).

Synthesis of [Cp$_3$Th(3,3-diphenylcyclopropenyl)] (1). To a cold (-25 °C), colorless Et$_2$O solution (0.5 mL) of 3,3-diphenylcyclopropene (69.0 mg, 0.358 mmol) was added quickly a cold (–25 °C), colorless Et$_2$O solution (0.5 mL) of LDA (36.6 mg, 0.342 mmol). The solution immediately turned pale yellow. This solution was then added drop wise to a cold (–25 °C) stirring white slurry of [Cp$_3$ThCl] (158.3 mg, 0.342 mmol) in Et$_2$O (3 mL). The stirring solution immediately turned pale yellow concomitant with the deposition of a pale grey precipitate. After stirring for 25 min the volatiles were removed *in vacuo* and the resulting grey solid was triturated with pentane (3 × 1 mL). The grey solid was then extracted into toluene (6 mL), and the resulting pale yellow solution was filtered through a Celite column supported on glass wool (0.5 cm × 2 cm) and the filtrate was layered with hexanes (6 mL). Storage of this solution at -25 ºC for 24 h resulted in the deposition of colorless plates. Decanting the supernatant, rinsing the crystals with cold (–25 °C) pentane (2 mL), and drying *in vacuo* afforded **1** as white plates (158.7 mg, 75 % yield). Anal. Calcd for ThC$_{30}$H$_{26}$: C, 58.25; H, 4.25. Found: C, 58.25; H, 4.35. ^{1}H NMR (500 MHz, 25 ºC, THF-*d*$_8$): δ 7.62 (s, 1H, α-C*H*), 7.39 (d, *J* = 6.8 Hz, 4H, *o*-CH), 7.27 (t, *J* = 7.6 Hz, 4H, *m*-CH), 7.06 (t, *J* = 7.3 Hz, 2H, *p*-CH), 6.17 (s, 15H, Cp). ^{13}C NMR (126 MHz, 25 ºC, THF-*d*$_8$): δ 177.37 (C$_\alpha$), 152.04 (C$_{ipso}$), 129.59 (*o*-C), 128.46 (*m*-C), 127.23 (C$_\beta$), 124.86 (*p*-C), 117.58 (Cp), 39.49 (C$_q$). IR (KBr pellet, cm^{-1}): 3095 (w), 3076 (w), 3024 (w), 1603 (w), 1593 (w), 1574 (w), 1489 (m), 1439 (m), 1284 (w), 1196 (w), 1173 (w), 1120 (w), 1095 (w), 1076 (w), 1012 (m), 991 (w), 895 (m), 808 (s), 783 (s), 731 (s), 698 (s), 669 (s), 561 (m), 544 (w).

Synthesis of [Cp$_3$Th(C(H)=CH$_2$)] (2). To a stirring colorless slurry of [Cp$_3$ThCl] (114.5 mg, 0.247 mmol) in cold (–25 ºC) Et$_2$O (3 mL) was added vinyl magnesium chloride dropwise as a cold (–25 ºC) 1.6 M THF solution (155 µL, 0.247 mmol). The stirring solution immediately turned pale yellow, concomitant with the deposition of a dark-grey precipitate. After stirring for 25 min the volatiles were removed *in vacuo* and the resulting grey solid was triturated with pentane (3 × 1 mL). The grey solid was then extracted into toluene (1.5 mL), and the resulting pale yellow solution was filtered through a Celite column supported on glass wool (0.5 cm × 2 cm) and the filtrate was layered with hexanes (6 mL). Storage of this solution at -25 ºC for 24 h resulted in the deposition of colorless needles. Decanting the supernatant, rinsing the crystals with cold (–25 °C) pentane (2 mL), and drying *in vacuo* afforded **2** as white needles (90.1 mg, 80 % yield). Anal. Calcd for $ThC_{17}H_{18}$: C, 44.94; H, 3.99. Found: C, 44.88; H, 3.97. ^{1}H NMR (500 MHz, 25 ºC, Benzene-d_6): δ 8.19 (dd, *J* = 21.1, 16.4 Hz, 1H, C$_{\alpha}$H), 7.00 (dd, *J* = 16.4, 5.2 Hz, 1H, C$_{\beta}$H), 6.21 (dd, *J* = 21.1, 5.2 Hz, 1H, C$_{\beta}$H), 5.96 (s, 15H, Cp). ^{13}C NMR (126 MHz, 25 ºC, Benzene-d_6): δ 199.55 (C$_{\alpha}$), 134.34 (C$_{\beta}$), 116.73 (Cp). IR (KBr pellet, cm^{-1}): 3088 (w), 2983 (w), 2929 (w), 2891 (w), 2830 (w), 2810 (w), 2713 (w), 1547 (w, C=C$_{vinyl}$), 1439 (m), 1383 (w), 1240 (w), 1122 (w), 1063 (w), 1011 (s), 922 (m), 787 (s), 640 (m), 609 (w).

Synthesis of [Cp$_3$Th(3-phenyl-1H-inden-1-yl)] (3). A 25 mL Schlenk flask equipped with the teflon rotoflow valve was charged with a magnetic stir bar, **1** (100.1 mg, 0.162 mmol), and toluene (5 mL). The flask was removed from the glovebox and heated to 70 ºC with stirring, which resulted in a colour change to yellow-orange. After 36 h, the solution was cooled to room temperature, which resulted in the deposition of yellow-orange crystals on the walls of the reaction vessel. The reaction mixture was brought inside the glovebox and the solution and crystals were transferred to a 20 mL scintillation vial. Decanting the supernatant, rinsing the crystals with cold (–25 °C) pentane (2 × 1 mL), and drying *in vacuo* afforded **3** as yellow-orange blocks (45 mg, 45 % yield). The supernatant was concentrated in vacuo to 3 mL and layered with hexane (5 mL). Storage of this solution at −25 °C for 48 h led to the deposition of more crystals (15 mg), which were isolated by decanting off the supernatant, rinsing the crystals with cold (–25 °C) pentane (2 × 1 mL), and drying *in vacuo* (combined yield: 60 mg, 60%). Anal. Calcd for $ThC_{30}H_{26}$: C, 58.25; H, 4.25. Found: C, 57.89; H, 4.27. ^{1}H NMR (500 MHz, 25 ºC, THF-d_8): δ 8.00 (d, *J* = 8.1 Hz, 1H, **5**/**8**), 7.85 (d, *J* = 8.0 Hz, 1H, **5**/**8**), 7.81 (d, *J* = 8.2 Hz, 2H, *o*-H), 7.57 (d, *J* = 2.1 Hz, 1H, **2**), 7.41 (t, *J* = 7.7 Hz, 2H, *m*-H), 7.15 (t, *J* = 7.4 Hz, 1H, *p*-H), 7.11 (t, *J* = 7.5 Hz, 1H, **6**/**7**), 7.04 (t, *J* = 7.5 Hz, 1H, **6**/**7**), 6.20 (s, 15H, Cp), 5.35 (d, *J* = 2.1 Hz, 1H, **1**). ^{13}C NMR (126 MHz, 25 ºC, THF-d_8): δ 142.26 (**4**/**3**/C$_{ipso}$), 140.23 (**4**/**3**/C$_{ipso}$), 136.99 (**4**/**3**/C$_{ipso}$), 130.28 (**2**), 129.39 (*m*-C), 128.37 (*o*-C), 126.19 (**9**), 125.51 (*p*-C), 122.36 (**5**/**8**), 121.1 (**5**/**8**), 121.03 (**6**/**7**), 120.64 (**6**/**7**), 119.97 (**Cp**), 88.90 (**1**). UV-Vis/NIR (C_6H_6, 0.60 mM, 25 °C, L·mol^{-1}·cm^{-1}): 369 nm (ε = 2200). IR (KBr pellet, cm^{-1}): 3082 (vw), 3024 (vw), 1595 (w), 1514 (w), 1439 (w), 1333 (w), 1306 (w), 1227 (vw), 1186 (w), 1142 (w), 1072 (vw), 1072 (m), 1009 (s), 941 (w), 910 (vw), 816 (s), 793 (s), 789 (s), 773 (s), 741 (s), 700 (s), 683 (m), 650 (m), 638 (m), 611 (w), 577 (w), 513 (w).



Computational Details. Kohn-Sham density functional calculations were performed for **1**-**3** with the 2017 release of the Amsterdam Density Functional (ADF) suite.[10] The crystal structure coordinates were optimized for hydrogen positions using the Perdew-Burke-Ernzerhof[11] (PBE) exchange-correlation functional, the all-electron scalar-relativistic Zeroth-Order Regular Approximation[12] (ZORA) Hamiltonian, and Slater-type atomic orbital (STO) basis sets of triple-ζ doubly polarized (TZ2P)[13] quality for all atoms. An atom-pairwise correction for dispersion forces were considered via Grimme's D3 model augmented with the Becke-Johnson (BJ) damping.[14] The conductor-like screening model (COSMO) was used to describe solvent effect.[15] To quantify the compositions of the chemical bonds, natural localized molecular orbital (NLMO) analyses were carried out with the NBO program, version 6.0, as interfaced with ADF.[16]

The computations of the NMR shielding tensors (σ, ppm) for **1**-**3** were performed with the NMR module of ADF 2017, using both the scalar relativistic and spin-orbit all electron ZORA Hamiltonian.[17] Functionals used for the NMR calculations were BP86, PBE, PBE0 (25% exact exchange), and PBE0 (40% exact exchange). The ^{13}C chemical shifts (δ, ppm) were obtained by subtracting the α-carbon nuclear magnetic shielding of interest from the reference compound (Tetramethylsilane, TMS), with the latter calculated at the same level of theory.

To obtain the Gibbs free energy profile for a ring-opening reaction of the thorium cyclopropenyl complex, we performed additional calculation for complexes **1**, **3** and intermediate **A** using the Gaussian (G16) package.[18] The structures were fully optimized using the hybrid PBE0 exchange-correlation functional. Small-core Stuttgart energy-consistent relativistic pseudopotentials, ECP60MBW for Th, were used with matching valence basis set.[19] The 6-31G(d) basis set was used for C and H atoms.[20] Atom-pairwise corrections for dispersion forces were also considered, which were the same as in the aforementioned ADF calculations.[14] For carbene intermediate **A**, we carried out the spin singlet calculations with an unrestricted "broken-symmetry" approach. The spin triplet calculations likewise used an unrestricted approach. The <S^2> values for triplet and singlet before annihilation of spin contaminants were 2.02 and 1.03, respectively, and therefore well within the expected ranges. To understand the electronic structure of intermediate **A**, an NLMO analysis was performed with the NBO 6.0 program.[16]

Cartesian Coordinates (unit: angstrom) for optimized structures

Compound **1**

Th	0.02764212	-0.02911351	-0.01690708
C	-0.12970136	-0.04327352	2.48014145
C	-0.47135736	0.41614850	3.65751535
C	0.42169932	-0.75654544	3.77851641
C	-0.19134671	-2.06669619	4.18020280
C	1.87873286	-0.55675591	4.06812977
C	-0.33391283	-3.99331929	5.66286986
C	0.56028891	2.63432973	0.62490646
C	1.63940317	1.88912069	-1.24960337
C	-1.91588213	-3.76081361	3.86911223
C	2.35881757	0.68892037	4.49003587
C	2.81680851	-1.57641651	3.84808045
C	-2.59982734	-1.04612747	0.04136248
C	4.64003548	-0.10488498	4.44454652
C	-1.43354597	-4.48260720	4.95975133
C	0.51130815	2.61010952	-0.78676011
C	0.27914925	-2.80376062	5.27709371
C	-1.30610020	-2.56789688	3.49298623
C	2.39523152	1.49042799	-0.12023573
C	2.07402440	-1.62378909	-1.07565477
C	1.01425148	-2.55964870	0.72581603
C	1.72918613	1.94631890	1.03603233
C	0.88661143	-2.24018840	-1.53725215
C	3.72048934	0.91649783	4.67613516
C	-2.67784204	0.15386131	0.78768365
C	0.23257316	-2.81802821	-0.42204213
C	-2.27922295	0.70326331	-1.39737669
C	4.17917456	-1.35434936	4.03044253
C	-2.35972440	-0.70697838	-1.31033692
C	-2.47717151	1.23397677	-0.09961224
C	2.14877667	-1.81445122	0.32480234
H	0.05017170	-4.53990191	6.52089700
H	-0.16760361	3.09497497	1.28305965
H	1.89192298	1.69663097	-2.28711400
H	-1.04491812	1.12133293	4.24688730
H	-2.77381517	-4.12592614	3.30913818
H	1.64708434	1.49392324	4.66259825

H	2.47227225	-2.55635263	3.52698769
H	-2.71460911	-2.04947903	0.43497958
H	5.70324301	0.06921725	4.58694626
H	-1.90991797	-5.41221510	5.25969136
H	-0.25473926	3.05978534	-1.40785777
H	1.13662150	-2.43859771	5.83615362
H	-1.69303811	-2.00238097	2.64925311
H	3.32212718	0.93029919	-0.13923403
H	2.79870230	-1.10150365	-1.68969519
H	0.77302222	-2.85949066	1.73801982
H	2.04909818	1.78600320	2.05804824
H	0.54227329	-2.27146832	-2.56563582
H	4.06333577	1.89426345	5.00590421
H	-2.85263213	0.22855068	1.85293899
H	-0.70040174	-3.36839585	-0.44670589
H	-2.11252794	1.27629643	-2.30326407
H	4.88422900	-2.16126266	3.84554807
H	-2.25755221	-1.40383513	-2.13487468
H	-2.47829499	2.28470139	0.16521439
H	2.93171138	-1.45673376	0.98428674

Compound **3**

Th	-0.00135963	0.01586147	0.06939407
C	0.07023253	-0.12732861	2.78636802
C	0.67092229	1.13265043	3.13877534
C	-0.26741913	1.99775645	3.68332806
C	-1.52179912	1.28809488	3.73931344
C	-2.81460105	1.70349489	4.09989896
C	-3.86374078	0.79857108	4.04826978
C	-3.64057452	-0.53105713	3.64558650
C	-2.38091989	-0.94976338	3.24188091
C	-1.30975872	-0.03925498	3.23966433
C	-0.71304754	-2.62362760	0.77465486
C	-1.80366576	-2.11521492	0.03174505
C	-1.40279713	2.38401423	0.62973022
C	-0.83139438	2.60190340	-0.63938156
C	2.31832214	1.57625977	0.09185977
C	-0.67146548	3.98851575	5.15397261
C	-0.03073635	-2.38826356	-1.39498270
C	2.02944088	1.40207934	-1.28064318
C	-0.44827218	5.32207652	5.48241352
C	-2.45207473	0.99974639	-0.85632235
C	-1.46474848	1.73197748	-1.56084408
C	-0.03501169	3.39616553	4.04922535
C	2.25740391	0.04618393	-1.61072645
C	0.84187258	4.19667848	3.29672043
C	-1.38050133	-1.97640718	-1.31294155
C	2.74898529	0.32719113	0.60737700
C	0.42508513	6.10044158	4.72360681
C	1.07454140	5.52658486	3.63131704
C	0.38076127	-2.78583164	-0.10166777

C	2.71520527	-0.61268203	-0.44386799
C	-2.40647292	1.39036817	0.49868669
H	-0.70836198	-2.86691594	1.82889795
H	-2.78467958	-1.87392099	0.42403239
H	-2.24026740	-1.97865867	2.92595580
H	0.64124685	-1.05851241	2.80792229
H	-1.12917075	2.89013306	1.54560910
H	-0.05015294	3.31609697	-0.86690168
H	2.24060034	2.50400440	0.64646062
H	-1.32838569	3.38532459	5.77418056
H	0.57611507	-2.40806531	-2.29245140
H	1.69821945	2.17062969	-1.96781568
H	1.72434391	1.36870958	3.03201443
H	-2.99634891	2.72992943	4.40787402
H	-4.46690261	-1.23783374	3.64318660
H	-0.95409269	5.75408472	6.34247022
H	-3.13001507	0.27241973	-1.28470432
H	-1.25148732	1.65903286	-2.62234691
H	-4.86540552	1.11499787	4.32853499
H	2.13386329	-0.39993582	-2.59072951
H	1.32874541	3.76496787	2.42558726
H	-1.98561861	-1.63087653	-2.14259120
H	3.06460896	0.12743252	1.62470558
H	0.59679760	7.14237261	4.97997712
H	1.75549242	6.12179011	3.02780491
H	1.35457795	-3.17221847	0.17158617
H	3.00397865	-1.65318912	-0.37319948
H	-3.02924158	1.01007671	1.30024670

Intermediate **A** (Triplet)

Th	4.49259231	13.24173253	10.62465413
C	3.88266824	10.91335553	10.63781275
C	3.59637395	9.63594738	10.24984194
C	4.52457492	8.64016937	9.85076195
C	4.07054711	7.44453692	9.14298543
C	5.95951888	8.80949850	10.13652009
C	4.35053057	5.09209067	8.56149500
C	4.31619727	13.33644029	13.44735114
C	6.26043304	14.17622472	12.58315535
C	2.45552420	6.30918410	7.71033345
C	6.39580298	9.23482615	11.40183465
C	6.93223950	8.55209293	9.15530972
C	2.11878633	13.53929391	9.14797440
C	8.70124338	9.15912074	10.68479127
C	3.17949230	5.12016542	7.80352094
C	4.98105773	14.52840435	13.07615790
C	4.79032073	6.23389895	9.21913926
C	2.89384070	7.45318170	8.36546420
C	6.38327275	12.76801381	12.64580997
C	6.95671097	13.61571032	9.31591589
C	5.67302536	11.95408335	8.40685288

C	5.18270473	12.25101268	13.18425352
C	6.00385260	14.21767551	8.45809266
C	7.74942921	9.40050683	11.67595642
C	1.66599056	13.22193361	10.45132569
C	5.21356481	13.18602671	7.89443054
C	2.58864110	15.31606262	10.51098409
C	8.28515315	8.73441135	9.42280081
C	2.67949791	14.83705517	9.18349299
C	1.95968602	14.31641712	11.29375310
C	6.74634952	12.21864970	9.29183005
H	4.92240456	4.17154294	8.64596611
H	3.31951362	13.26327640	13.86600534
H	7.01685311	14.86783042	12.22925397
H	2.53785148	9.35125411	10.18524793
H	1.55017542	6.34929955	7.11007629
H	5.65630512	9.41335583	12.17516653
H	6.61467258	8.22385008	8.16910952
H	2.04270007	12.89878897	8.27668343
H	9.75841772	9.29562018	10.89546766
H	2.83833851	4.22762937	7.28630733
H	4.58460562	15.53413056	13.16228191
H	5.69562945	6.19286796	9.81783848
H	2.33757563	8.37911335	8.24927867
H	7.24031105	12.18508175	12.33058638
H	7.71625216	14.13652218	9.88760803
H	5.27819402	10.97357908	8.17314146
H	4.96216747	11.20821711	13.36968534
H	5.90679143	15.27923109	8.25626291
H	8.06273319	9.71463340	12.66845795
H	1.18379925	12.29890861	10.74897585
H	4.40257667	13.32023534	7.18871453
H	2.92598950	16.28426422	10.86536695
H	9.01760544	8.54726099	8.64206162
H	3.10514054	15.37141172	8.34219020
H	1.73248206	14.38672558	12.35044657
H	7.30291550	11.47145025	9.84480784

Intermediate **A** (Singlet)

Th	4.48722374	13.23369315	10.61864819
C	3.89777727	10.90235002	10.65065145
C	3.61249915	9.62584446	10.31212535
C	4.55005511	8.62761439	9.88217468
C	4.08407703	7.46100218	9.14741998
C	5.98071383	8.79784939	10.16375993
C	4.34893612	5.12856849	8.47761730
C	4.30726751	13.35215016	13.44085660
C	6.25721768	14.17357668	12.57171609
C	2.42396303	6.36768704	7.73028784
C	6.41803826	9.24557981	11.42310430
C	6.95658187	8.52644713	9.18733703
C	2.11238411	13.50826963	9.13963687

C	8.72466069	9.15351483	10.71025355
C	3.15342485	5.17840169	7.75851912
C	4.97925225	14.53714515	13.06057491
C	4.80780963	6.24752278	9.15898206
C	2.87976108	7.48993479	8.40962064
C	6.37202682	12.76549120	12.64619014
C	6.95022975	13.60888203	9.30963943
C	5.67529840	11.93556786	8.40994758
C	5.16771507	12.25965088	13.18734469
C	5.99453539	14.20117543	8.44786536
C	7.77100513	9.41174491	11.69620001
C	1.66179231	13.20204744	10.44650339
C	5.21000689	13.16215847	7.88975317
C	2.57458018	15.30109688	10.48417358
C	8.30906282	8.71117953	9.45411077
C	2.66695914	14.80894799	9.16166562
C	1.95084176	14.30650356	11.27752267
C	6.74738499	12.21079768	9.29336696
H	4.92389390	4.20677076	8.51408940
H	3.30990565	13.28818269	13.85930323
H	7.01804154	14.85803253	12.21345918
H	2.55747278	9.31947818	10.30660556
H	1.49888967	6.42479720	7.16233187
H	5.67855406	9.43962873	12.19243674
H	6.64068239	8.18900340	8.20383332
H	2.03879729	12.85851856	8.27499236
H	9.78164899	9.29218031	10.92026010
H	2.79713146	4.30250725	7.22347873
H	4.58844759	15.54583160	13.13786598
H	5.72919214	6.18623688	9.73059793
H	2.31692093	8.41664240	8.34306326
H	7.22604633	12.17526421	12.33656941
H	7.70710818	14.13695470	9.87813193
H	5.28644759	10.95154206	8.18097334
H	4.94120671	11.21982419	13.38189743
H	5.89237714	15.26099289	8.23954315
H	8.08350605	9.74023061	12.68433469
H	1.18331152	12.28016937	10.75356105
H	4.39875220	13.28787648	7.18279236
H	2.90787136	16.27434544	10.82844284
H	9.04183824	8.51343246	8.67627474
H	3.08975434	15.33662806	8.31472576
H	1.72345076	14.38680834	12.33345264
H	7.30729331	11.46952911	9.85100474

Table S1. % compositions of the Th-C bonding NLMOs in complexes **1-3**.

Complex	**Orbital**	**Total C_α**	**2s**	**2p**	**Total C_β**	**2s**	**2p**	**Total An**	**7s**	**7p**	**6d**	**5f**
1	σ(Th-C)	77	47	53	/	/	/	22	8	0	76	16
	π(Th-C)	45	0	100	49	0	100	2	0	0	38	62
2	σ(Th-C)	74	33	67	/	/	/	23	7	0	79	14
	π(Th-C)	47	0	100	51	0	100	3	0	0	42	58
3	σ(Th-C)	56	6	94	/	/	/	10	5	0	80	15

Table S2. The Wiberg Bond Orders for the selected bonds in complexes **1-3**.

Complex	**Th-C_α**	**C_α-C_β**
1	0.678	1.873
2	0.721	1.995
3	0.392	/

Table S3. Calculated carbon shielding (σ) and chemical shift (δ) for TMS and the C_α, C_β, C_q nuclei of **1**-**3** using various functionals.

Complex	Method	σ_{calc}(ppm)	δ_{calc}(ppm)	Δ_{SO} (ppm)	δ_{expt}(ppm)
TMS	BP86/SO-BP86	186.9 / 187.8	/	/	
	PBE/SO-PBE	187.5 / 188.4	/	/	
	PBE0/SO-PBE0 (25%) [a]	192.2 / 193.0	/	/	
	PBE0/SO-PBE0 (40%)	194.7 / 195.5	/	/	
1	BP86/SO-BP86	26.6, 59.7, 132.8/ 8.0, 58.9, 133.4	160.3, 127.2, 54.1/ 179.8, 128.9, 54.4	19.5, 1.7, 0.3	177.4, 127.2, 39.5
	PBE/SO-PBE	26.7, 60.3, 133.4/ 8.2, 59.4, 134.0	160.8, 127.2, 54.1/ 180.2, 129.0, 54.4	19.4, 1.8, 0.3	
	PBE0/SO-PBE0 (25%)	33.1, 61.9, 145.3/ 13.1, 61.2, 145.7	159.1, 130.3, 46.9/ 179.9, 131.8, 47.3	20.8, 1.5, 0.4	
	PBE0/SO-PBE0 (40%)	36.9, 63.5, 151.6/ 16.3, 62.9, 151.9	157.8, 131.2, 43.1/ 179.2, 132.6, 43.6	21.4, 1.4, 0.5	
2	BP86/SO-BP86	3.7, 59.4/ -12.6, 56.4	183.2, 127.5 / 200.4, 131.4	17.2, 3.9	199.6, 134.3
	PBE/SO-PBE	3.3, 59.9/ -13.0, 57.0	184.2, 127.6/ 201.4, 131.0	17.2, 3.8	
	PBE0/SO-PBE0 (25%)	10.1, 62.2/ -7.8, 59.8	182.1, 130.1/ 200.8, 133.2	18.7, 3.2	
	PBE0/SO-PBE0 (40%)	14.4, 64.0/ -4.4, 62.0	180.3, 130.7/ 199.9, 133.5	19.6, 2.8	
3	BP86/SO-BP86	90.6 / 88.1	96.3 / 99.7	3.4	88.9
	PBE/SO-PBE	91.3 / 88.8	96.2 / 99.6	3.4	
	PBE0/SO-PBE0 (25%)	101.9 / 98.0	90.3 / 95.0	4.7	
	PBE0/SO-PBE0 (40%)	107.8 / 103.0	86.9 / 92.5	5.6	

[a] Fraction of exact exchange in the functional in parentheses.

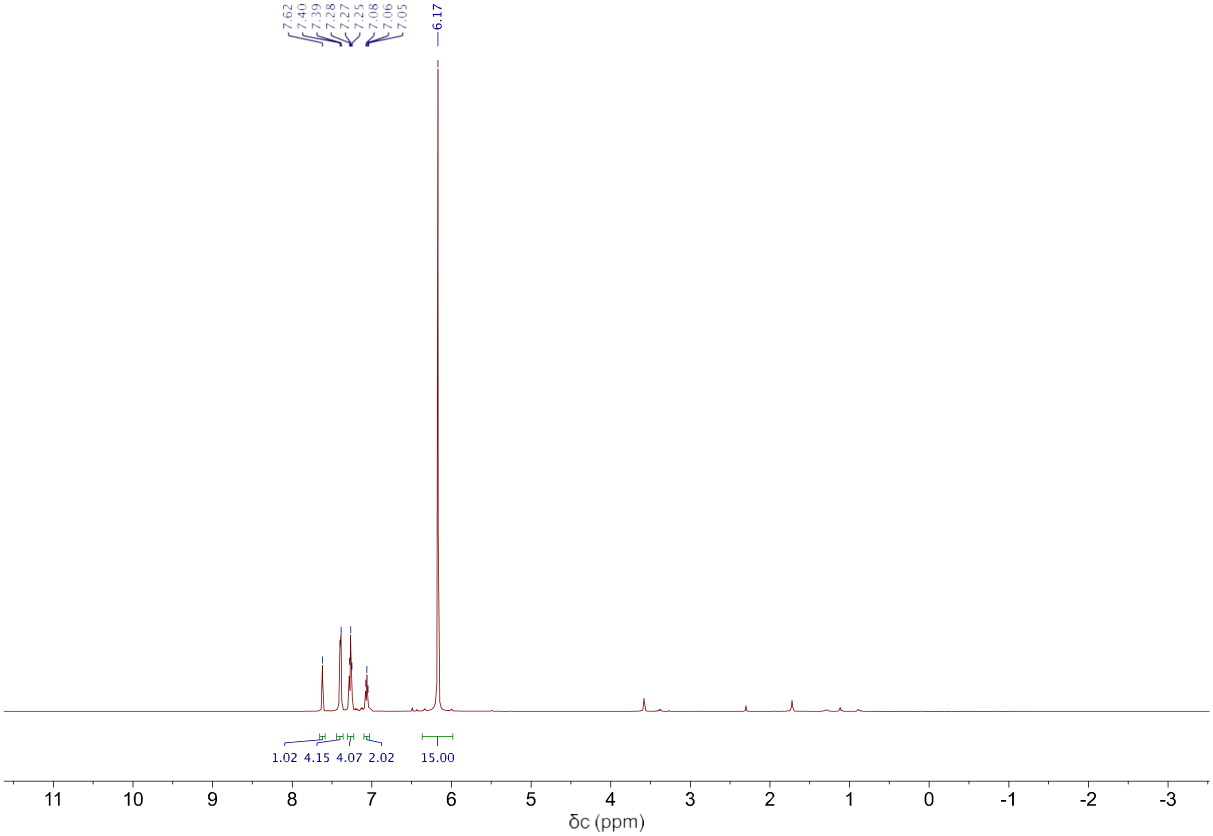


Figure S1. ^{1}H NMR spectrum of [Cp$_3$Th(3,3-diphenylcyclopropenyl)] (**1**) in THF-d_8 at room temperature.

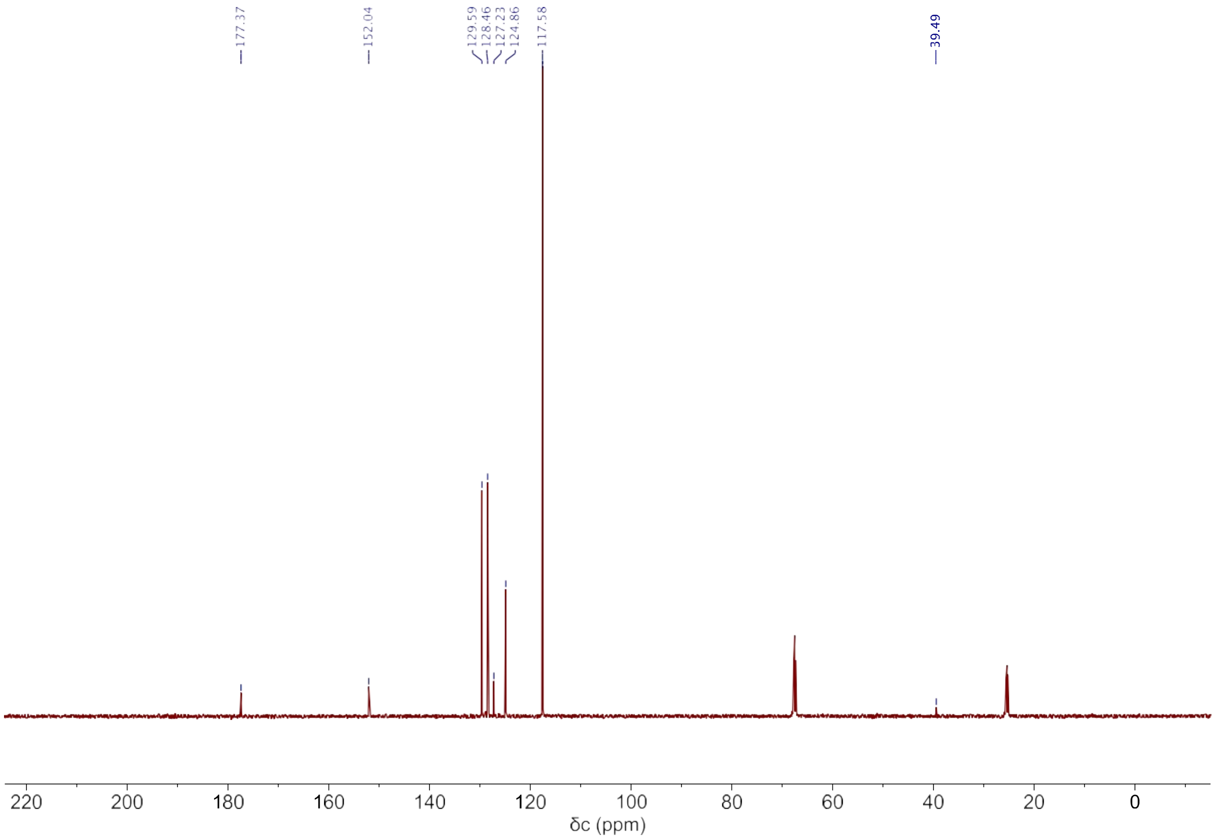


Figure S2. $^{13}C\{^1H\}$ NMR spectrum of [Cp_3Th(3,3-diphenylcyclopropenyl)] (**1**) in THF-d_8 at room temperature.

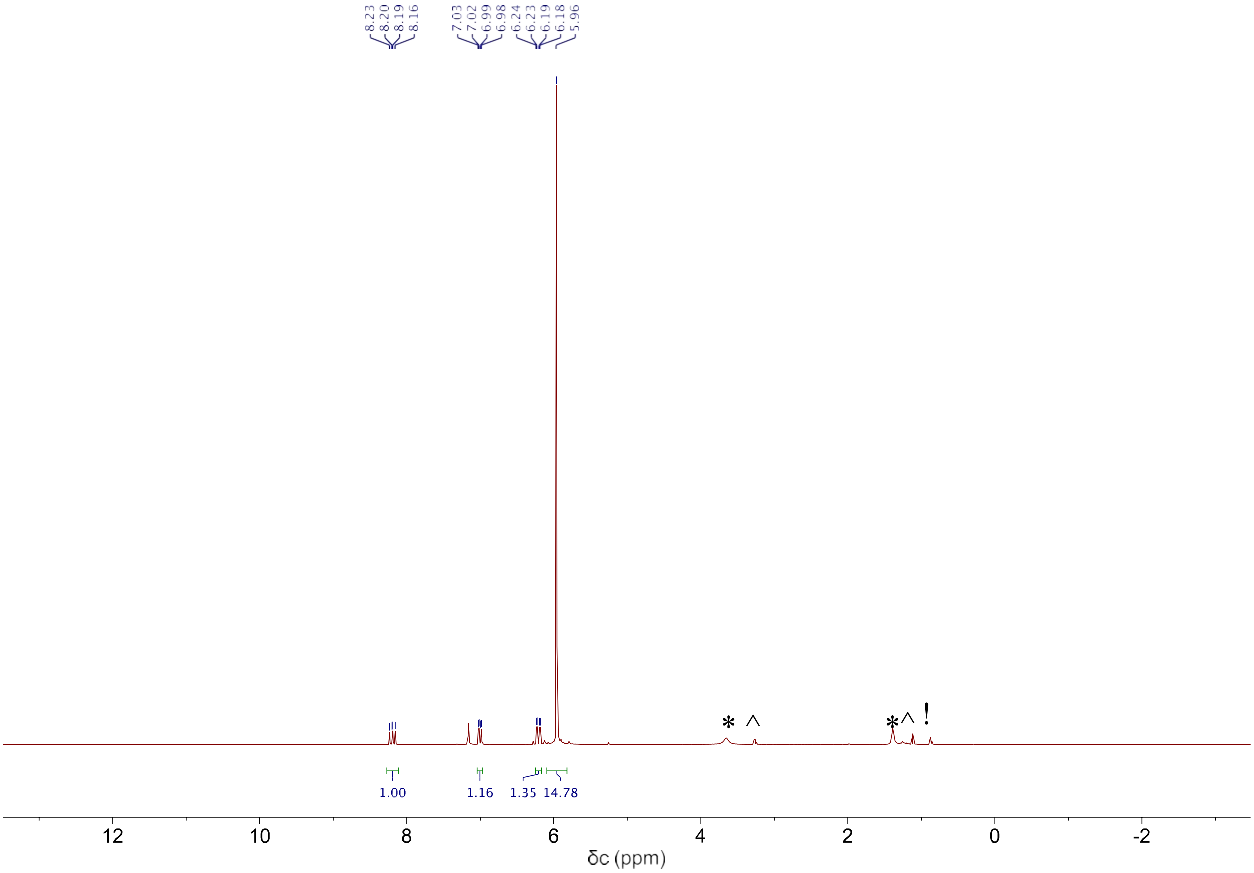


Figure S3. ^{1}H NMR spectrum of [$Cp_3Th(C(H)=CH_2)$] (**2**) in C_6D_6 at room temperature, (*) denotes THF, (^) denotes Et_2O, and (!) denotes pentane.

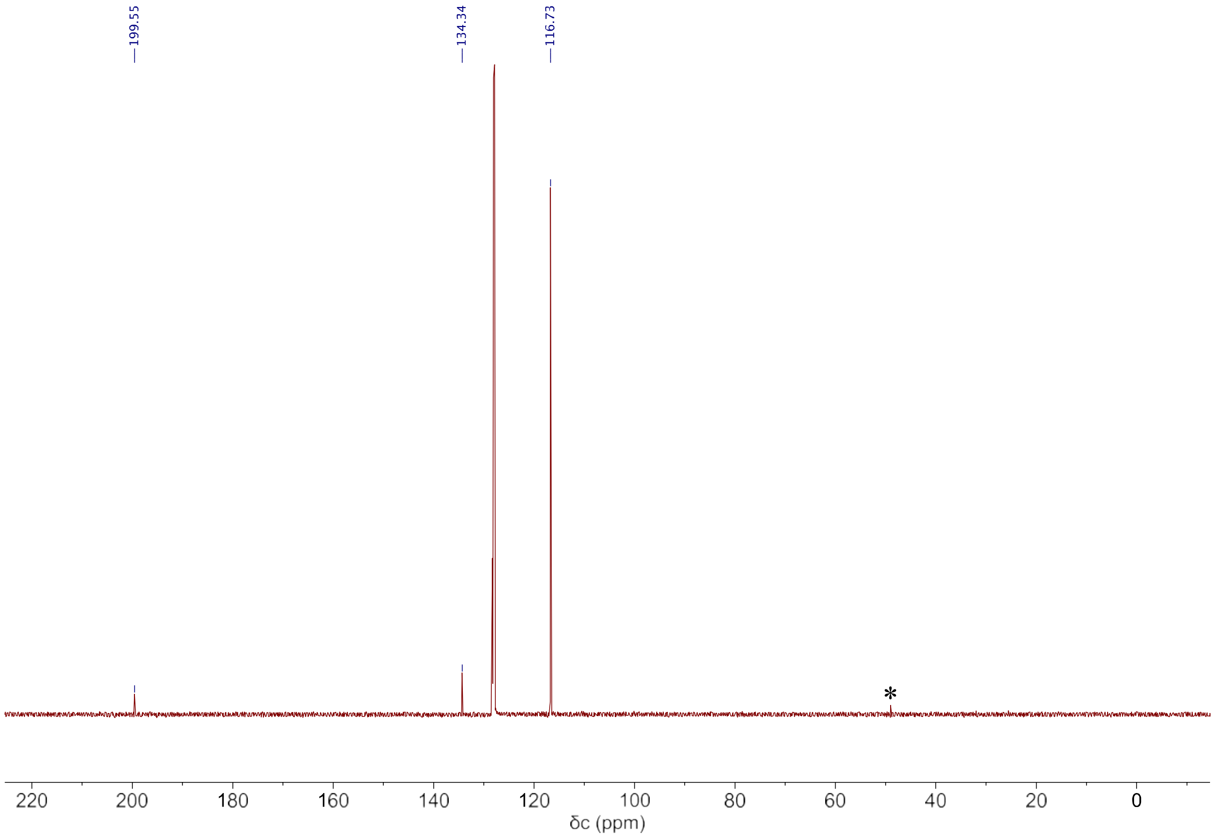


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of [$Cp_3Th(C(H)=CH_2)$] (**2**) in C_6D_6 at room temperature, (*) denotes a spectrometer artifact.

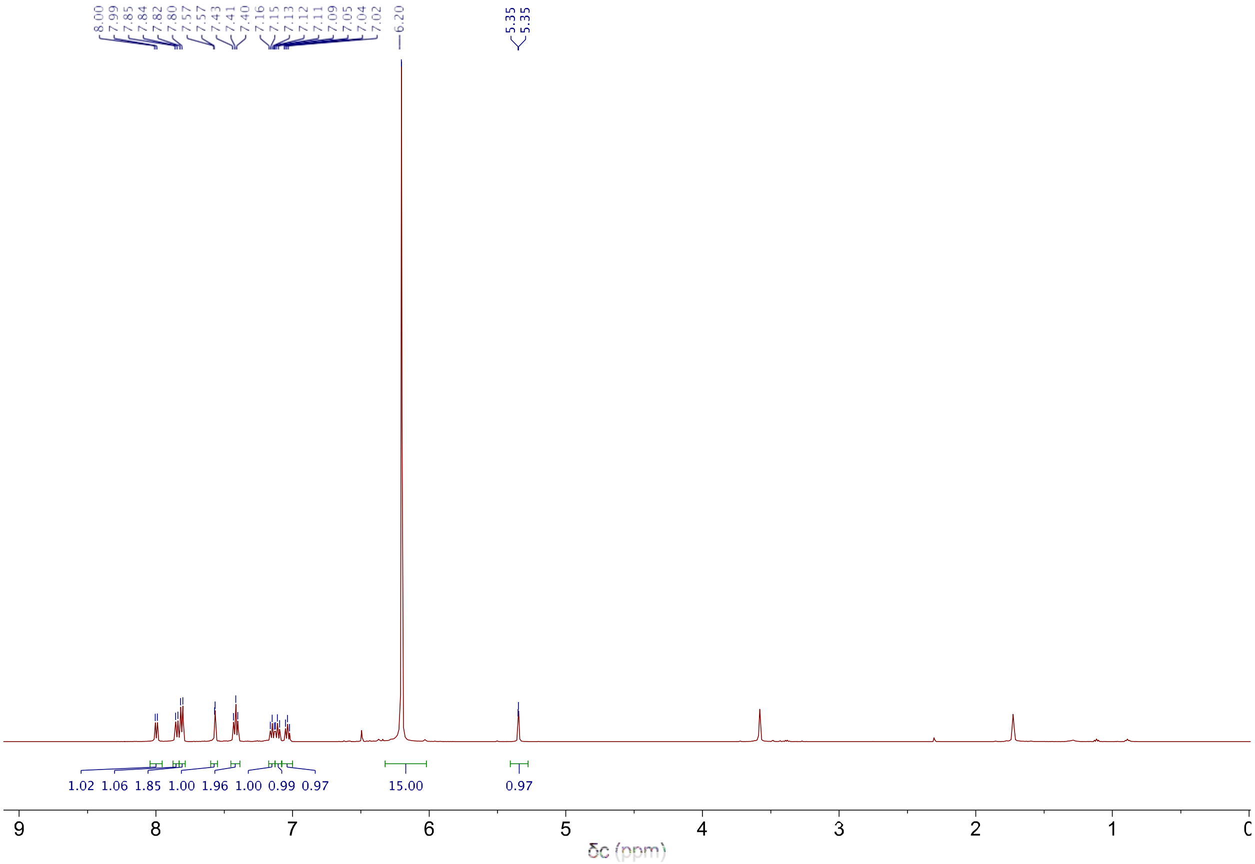


Figure S5. ^{1}H NMR spectrum of [Cp_3Th(3-phenyl-1H-inden-1-yl)] (**3**) in THF-d_8 at room temperature.

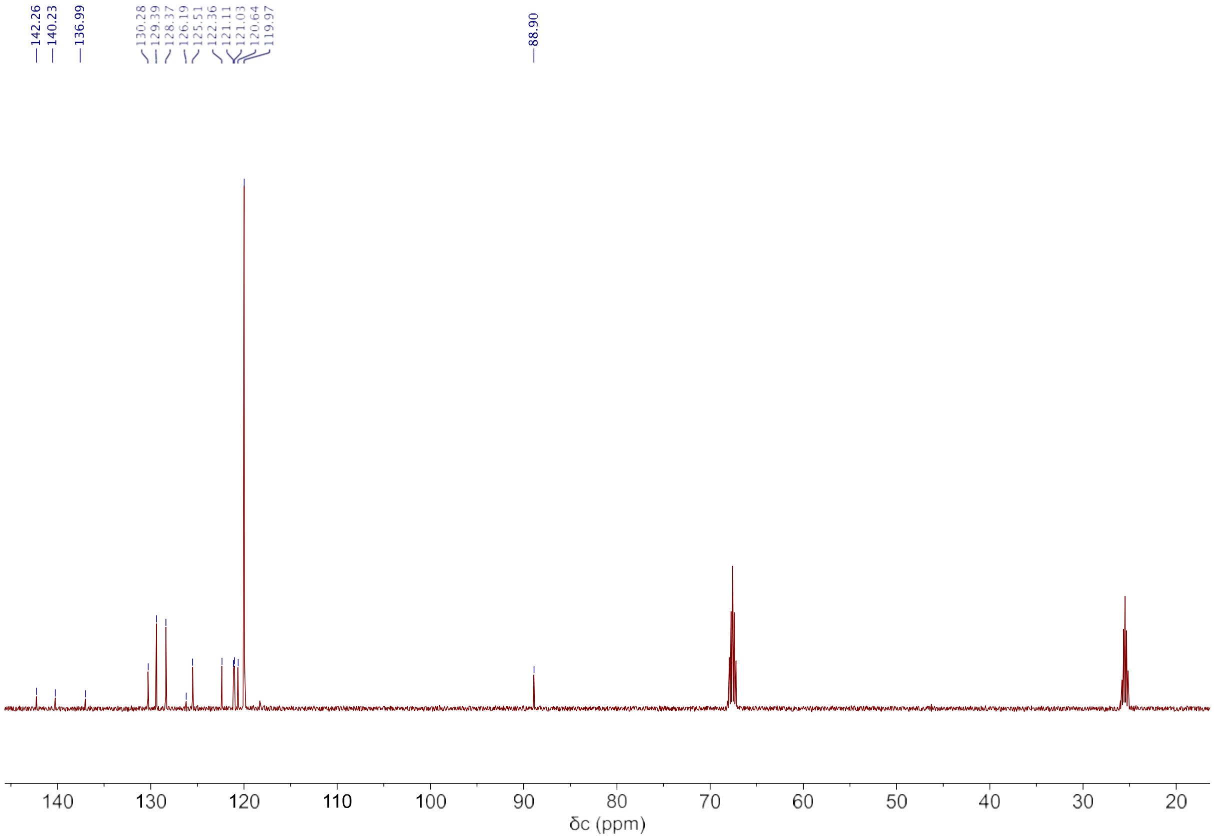


Figure S6. $^{13}C\{^1H\}$ NMR spectrum of [Cp_3Th(3-phenyl-1H-inden-1-yl)] (**3**) in THF-d_8 at room temperature.

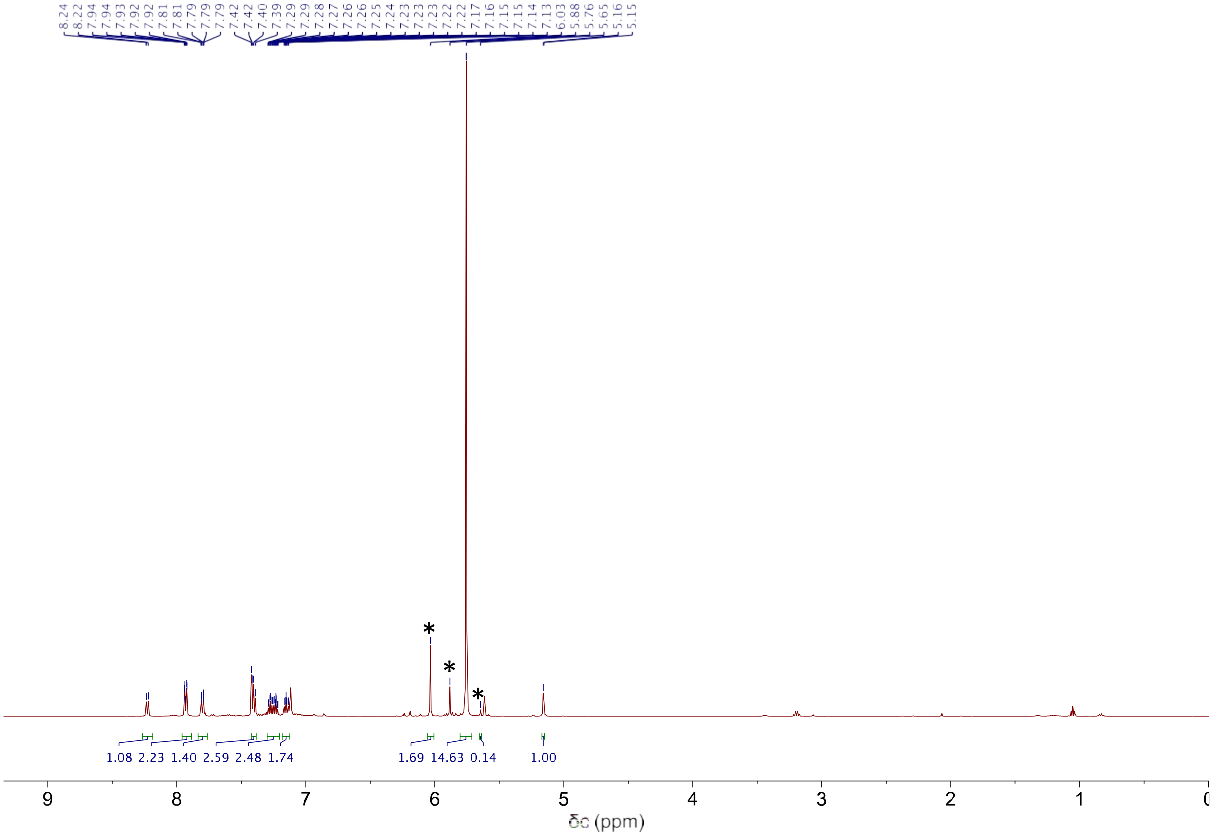


Figure S7. ^{1}H NMR spectrum of the crude reaction mixture of **1** in benzene-d_6 at room temperature. (*) denotes unidentified Cp containing compounds at 6.03, 5.88, and 5.65 ppm.

Table S4. X-ray Crystallographic Data for Complexes **1**, **2**, and **3**.

	1	**2**	**3**
empirical formula	$C_{30}H_{26}Th$	$C_{17}H_{18}Th$	$C_{30}H_{26}Th$
Crystal habit, color	Plate, Colorless	Needle, Colorless	Block, Yellow-Orange
crystal size (mm)	0.20 × 0.15 × 0.10	0.25 × 0.15 × 0.10	0.25 × 0.15 × 0.10
crystal system	Orthorhombic	Orthorhombic	Monoclinic
space group	Pbca	Pna2_1	P2_1/n
vol (Å^3)	4577.5(8)	2948.8(9)	2265.8(11)
a (Å)	8.4047(8)	24.971(6)	11.148(3)
b (Å)	20.089(2)	8.4506(11)	11.719(3)
c (Å)	27.111(2)	13.974(3)	18.069(5)
α (deg)	90.00	90.00	90.00
β (deg)	90.00	90.00	106.281(6)
γ (deg)	90.00	90.00	90.00
Z	8	8	4
fw (g/mol)	618.55	454.35	618.55
density (calcd) (Mg/m^3)	1.795	2.047	1.813
abs coeff (mm^{-1})	6.530	10.094	6.596
F_{000}	2368	1680	1184
Total no. reflections	17950	17268	13039
Unique reflections	4686	6206	4792
R_{int}	0.1436	0.0985	0.0652
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0504$ $wR_2 = 0.0868$	$R_1 = 0.0539$, $wR_2 = 0.0742$	$R_1 = 0.0416$ $wR_2 = 0.0680$
largest diff peak and hole (e$^-$Å^{-3})	1.360 and -1.790	1.748 and -1.401	1.524 and -1.248
GOF	0.982	1.063	0.977

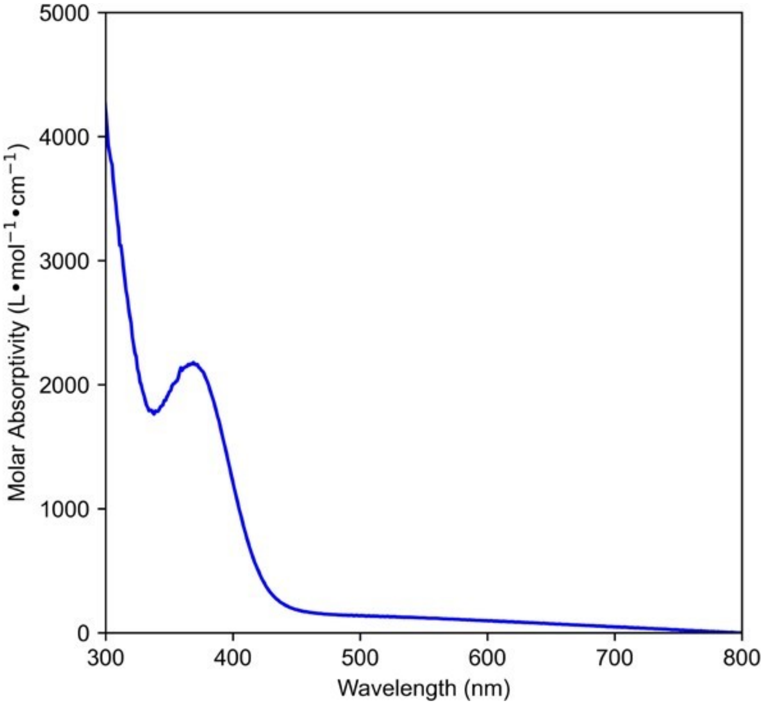


Figure S8. UV–Vis spectra of **3** (0.60 mM) in C_6H_6. The absorption centered at 369 nm is likely a result of a LMCT from the indenyl anion to the Th^{4+} center.

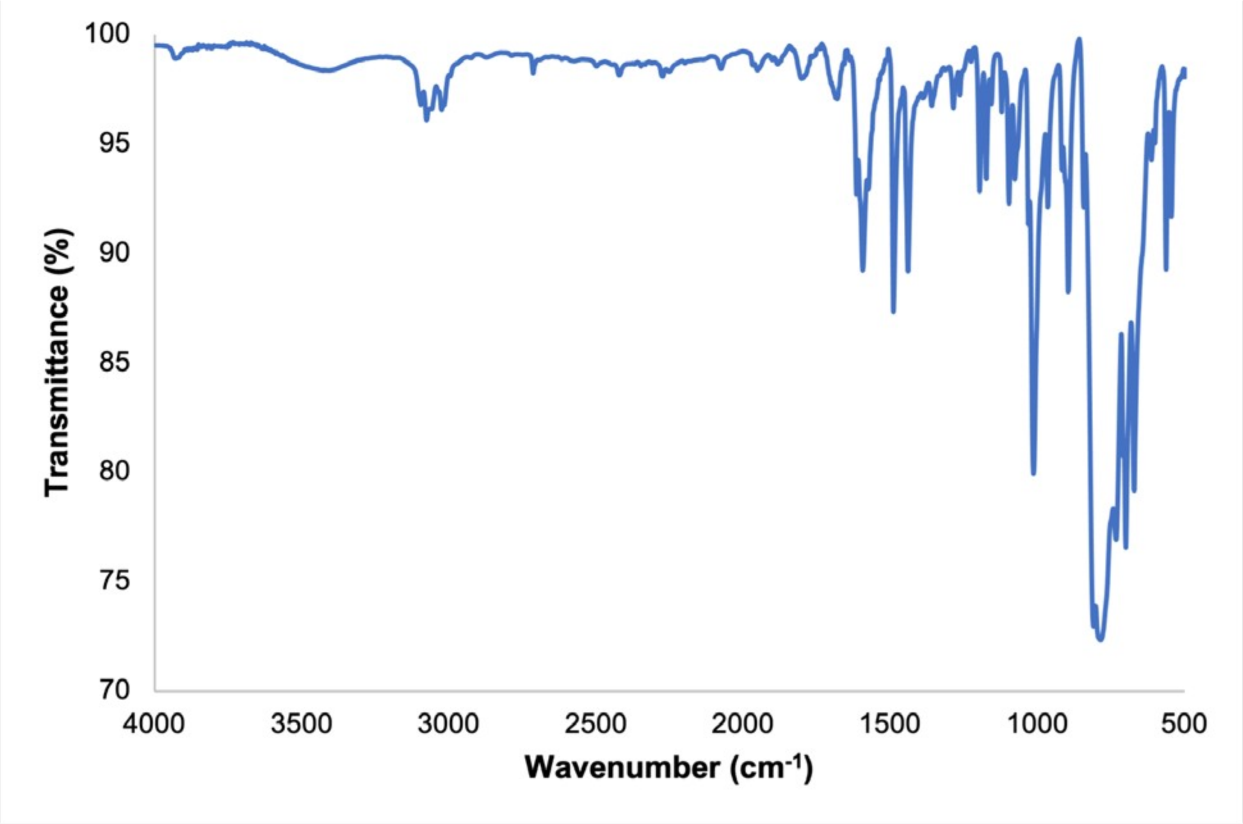


Figure S9. IR spectrum of **1** (KBr Pellet).

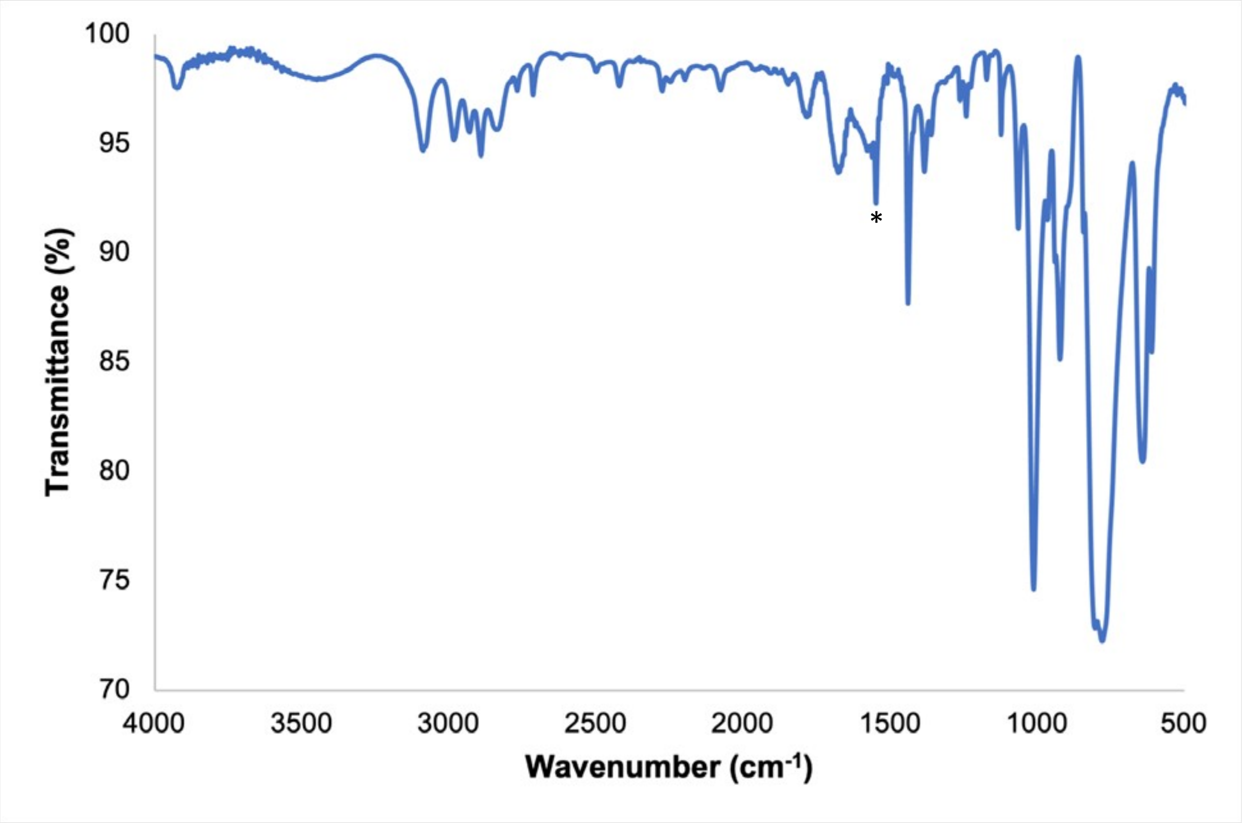


Figure S10. IR spectrum of **2** (KBr Pellet). (*) indicates C=C stretch.

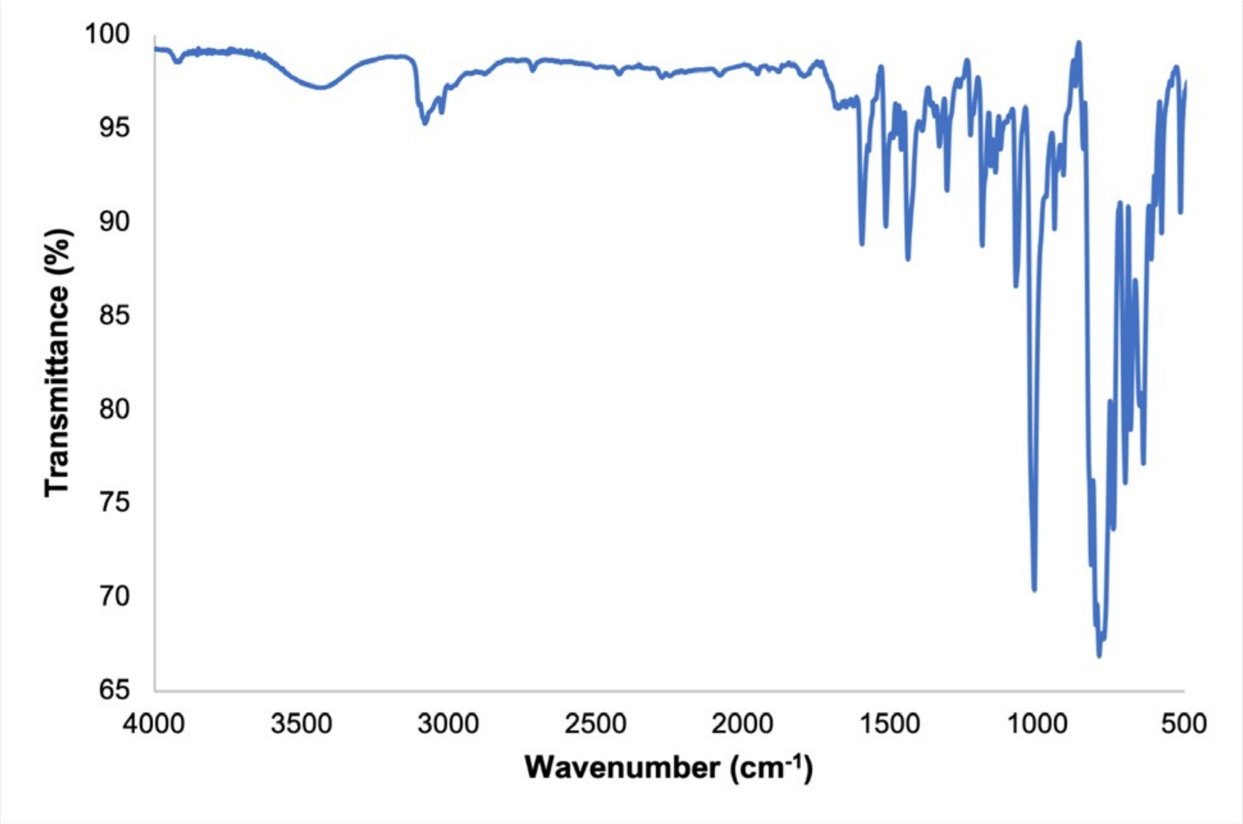


Figure S11. IR spectrum of **3** (KBr Pellet).

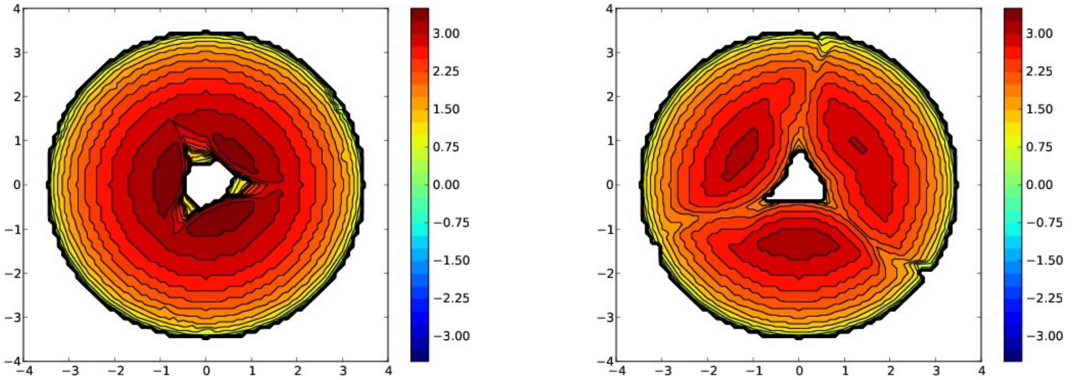


Figure S12. Steric profile maps of [Th(N(SiMe$_3$)$_2$)$_3$]$^+$ (left) and [ThCp$_3$]$^+$ (right).[21]

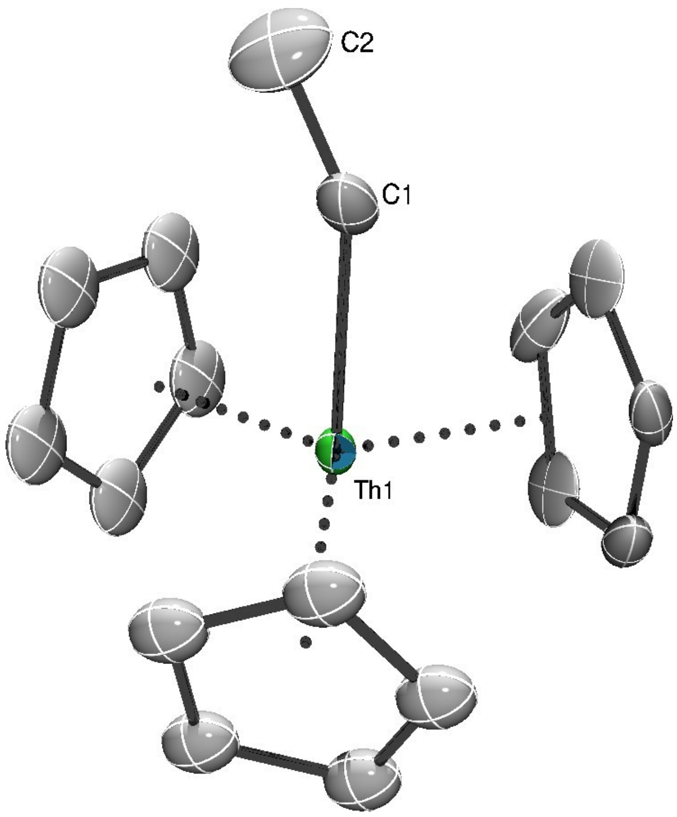


Figure S13. Solid state molecular structure of **2**, shown with thermal ellipsoids set at 50% probability. A second molecule in the asymmetric unit and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Th1–C1= 2.52(3), Th2–C33 = 2.52(2), C1–C2 = 1.32(3), C33–C34 = 1.24(3), Th1–C1–C2 = 139.1(19), Th2–C33–C34 = 134(2).

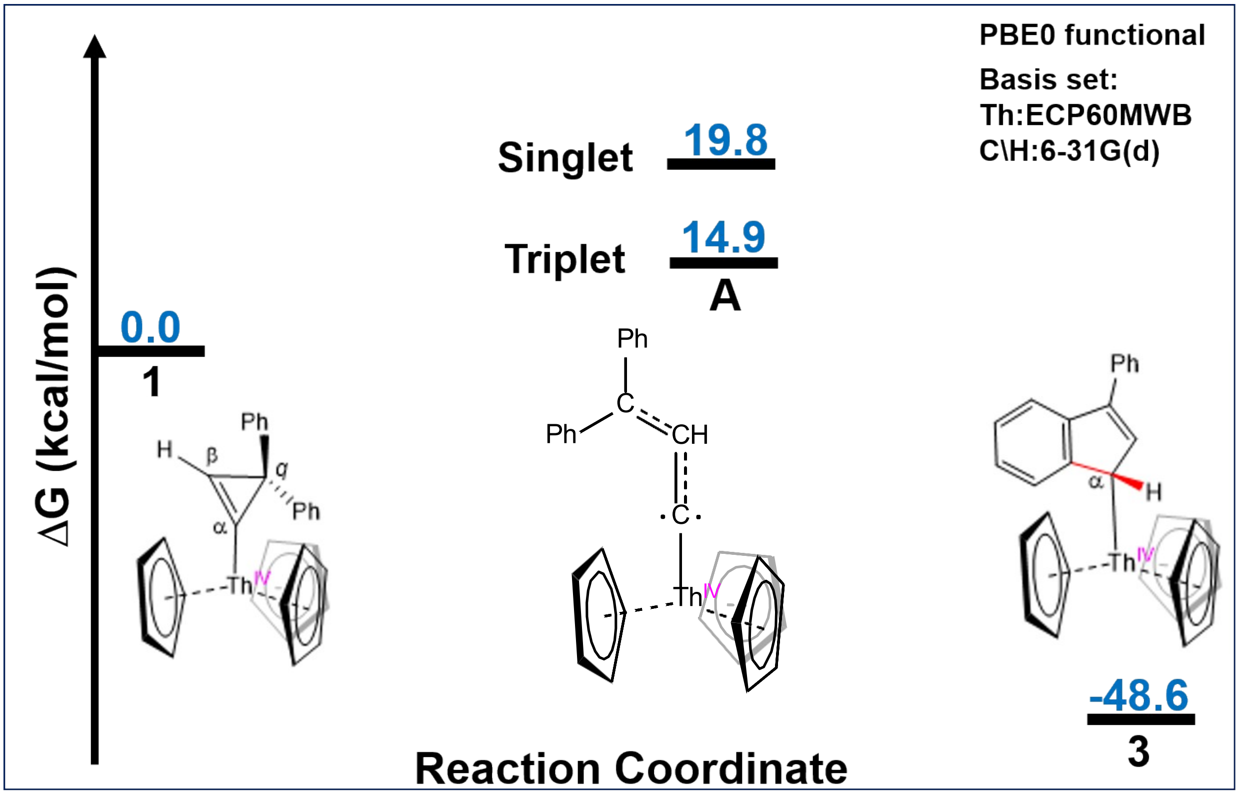


Figure S14. Gibbs energy (kcal/mol) profile for complex **1** and **3**, and intermediate **A**.

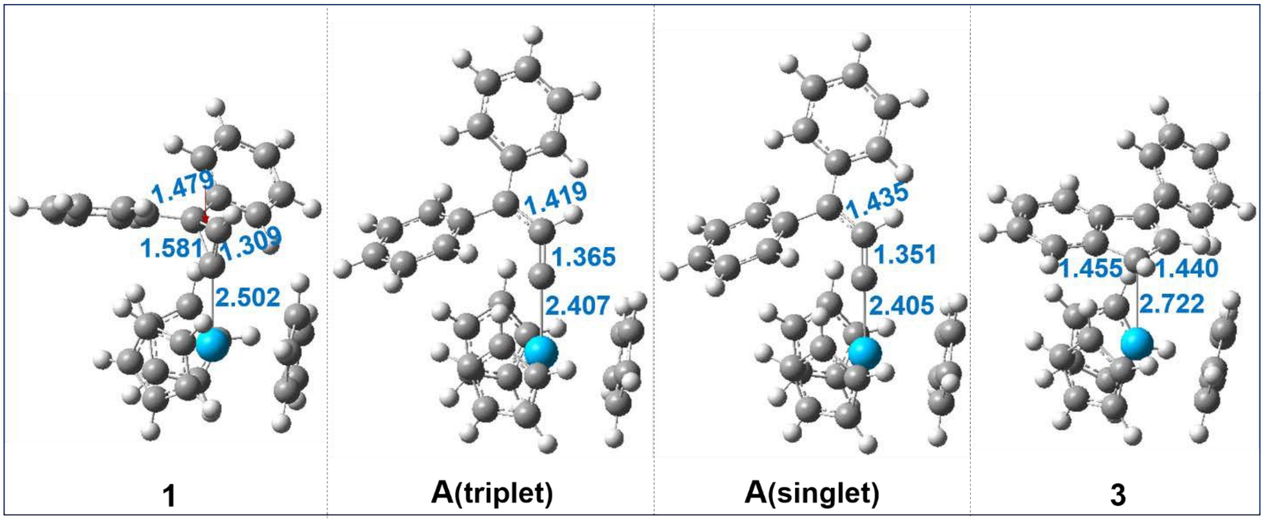
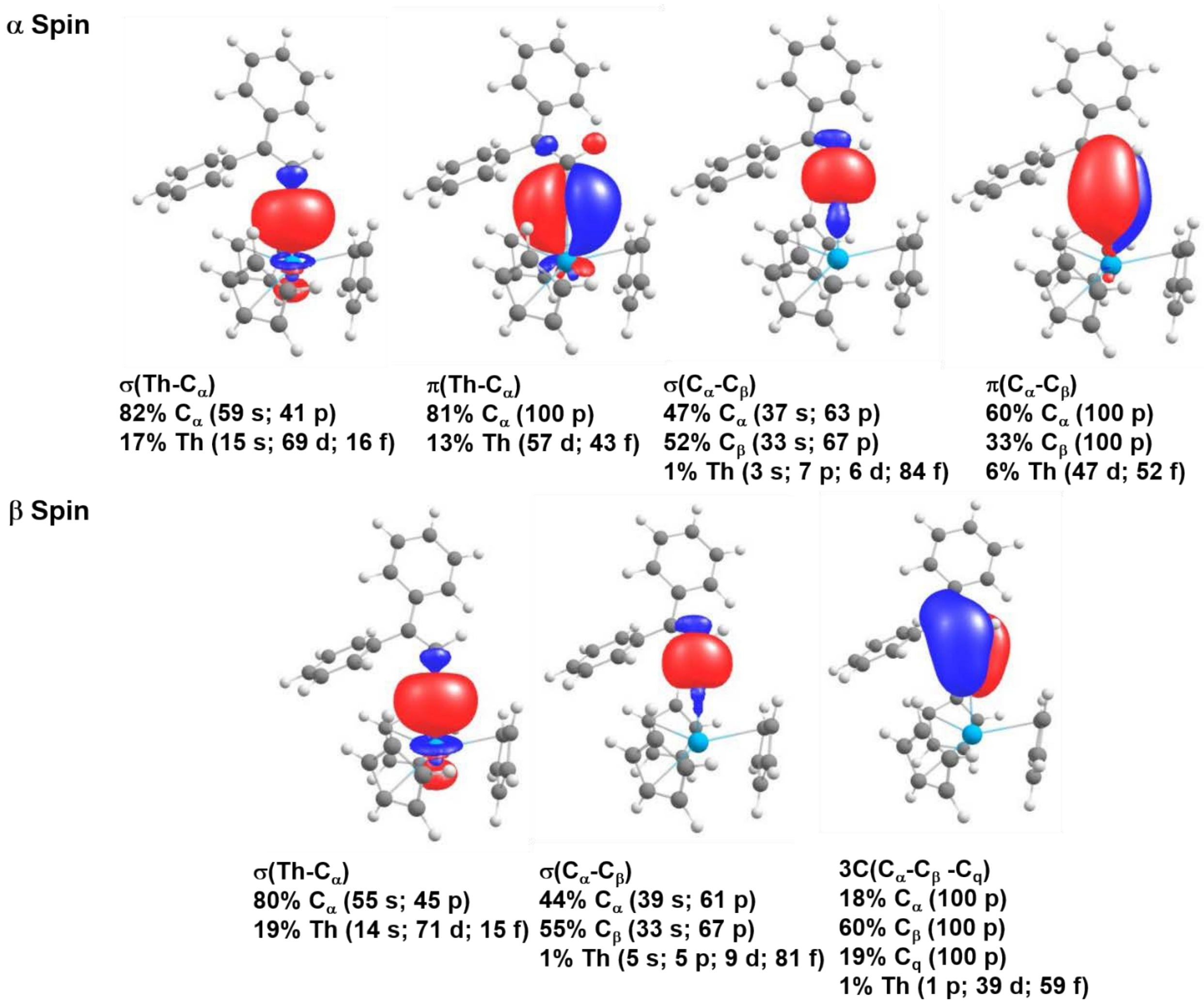


Figure S15. Optimized structure for complexes **1**, **3**, and intermediate **A**, and selected bond lengths (Å).



α Spin

σ(Th-C_α)
82% C_α (59 s; 41 p)
17% Th (15 s; 69 d; 16 f)

π(Th-C_α)
81% C_α (100 p)
13% Th (57 d; 43 f)

σ(C_α-C_β)
47% C_α (37 s; 63 p)
52% C_β (33 s; 67 p)
1% Th (3 s; 7 p; 6 d; 84 f)

π(C_α-C_β)
60% C_α (100 p)
33% C_β (100 p)
6% Th (47 d; 52 f)

β Spin

σ(Th-C_α)
80% C_α (55 s; 45 p)
19% Th (14 s; 71 d; 15 f)

σ(C_α-C_β)
44% C_α (39 s; 61 p)
55% C_β (33 s; 67 p)
1% Th (5 s; 5 p; 9 d; 81 f)

3C(C_α-C_β -C_q)
18% C_α (100 p)
60% C_β (100 p)
19% C_q (100 p)
1% Th (1 p; 39 d; 59 f)

Figure S16. Isosurfaces (±0.03 au) of the Th–Cα and Cα-Cβ bonding NLMOs in intermediate **A** (α spin in upper row and β spin in lower row), along with total weight-% metal character and 7s vs 6d vs 5f contributions at the metal, and ligand character.

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