Thorium Amidates Function as Single-Source Molecular Precursors for Thorium Dioxide

Supplementary Information

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A. Experimental Section

General Considerations

Unless otherwise noted, all syntheses were performed using standard Schlenk techniques under an atmosphere of nitrogen or in an MBraun glovebox under an atmosphere of nitrogen. Glassware, cannulae, and Celite were stored in an oven at 160 °C for at least 12 hours prior to use. 3 Å and 4 Å molecular sieves were activated by heating under vacuum at 300 °C for 24 hours. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at room temperature using Bruker AV-600, AV-500, AVB-400, AVQ-400, and AV-300 spectrometers. ^{1}H chemical shifts were referenced to C_6D_5H ($\delta = 7.16$ ppm), C_5D_4HN ($\delta_1 = 8.74$ ppm), and $CHCl_3$ ($\delta = 7.26$ ppm). ^{13}C chemical shifts were referenced to C_6D_6 ($\delta = 128.39$ ppm) and C_5D_5N ($\delta_1 = 150.35$ ppm). ^{19}F chemical shifts were referenced to an external standard of C_6H_5F ($\delta = -113.11$ ppm). Samples for IR spectroscopy were prepared as Nujol mulls, and spectra were taken in KBr plates using a Nicolet iS10 spectrometer. Melting points were determined in sealed tubes under an atmosphere of nitrogen using a Stanford Research Systems OptiMelt instrument and are reported uncorrected.

Materials

Hexane, pentane, toluene, benzene, diethyl ether, and tetrahydrofuran (THF) were purified by passage through a column of activated alumina and degassed by sparging with nitrogen. C_6D_6 was purchased from Cambridge Isotope Labs, degassed with two freeze-pump-thaw cycles, and stored over 4 Å molecular sieves. C_5D_5N was purchased from Cambridge Isotope Labs and stored over 3 Å molecular sieves. d_{18}-Decalin was purchased from Sigma-Aldrich and stored over 4 Å molecular sieves. $CDCl_3$ was purchased from Cambridge Isotope Labs and used as received. The amide proligands N-*tert*-butylisobutyramide (H(ITA)), N-*tert*-butyl-(4-*tert*-butyl)benzamide (H(TPTA)), N-(3-pentyl)pivalamide (H(TEPA)), and N-*tert*-butyl-(3,5-bis(trifluoromethyl))benzamide (H(Ar^{F}TA)) were synthesized according to literature methods[1–4] and purified by sublimation. $ThCl_4(DME)_2$ was synthesized according to literature procedures.[5] Unless otherwise specified, all other chemicals were purchased from Sigma-Aldrich or Acros Organics and used as received.

Synthesis of Ligand Precursors

K(ITA): A THF solution (20 mL) of $KN(SiMe_3)_2$ (2.22 g, 11.1 mmol) was added via cannula to a stirred THF solution (40 mL) of H(ITA) (1.52 g, 10.6 mmol) maintained at -78 ^{o}C. After stirring at room temperature for 16 h, the solvent was removed *in vacuo* to give an off-white powder. This powder was washed with toluene (15 mL), then hexane (30 mL) to remove impurities, and then triturated with hexane and dried *in vacuo* to give the product as a colorless powder. (1.66 g, 86% yield)

^{1}H NMR (C_5D_5N, 500 MHz): δ 2.89 (m, 1H, $CH(CH_3)_2$), 1.82 (s, 9H, $C(CH_3)_3$), 1.46 (d, 6H, $CH(CH_3)_2$).

^{13}C NMR (C_5D_5N, 101 MHz): δ 176.61 (NCO), 51.69 ($C(CH_3)_3$), 39.82 ($CH(CH_3)_2$), 32.39 ($C(CH_3)_3$), 23.10 ($CH(CH_3)_2$).

IR (cm^{-1}): 1575 (m), 1557 (m), 1544 (m), 1336 (m), 1306 (w), 1282 (w), 1070 (m), 949 (w), 907 (w), 891 (w), 774 (w), 654 (w), 501 (w).

K(TEPA): A THF solution (50 mL) of $KN(SiMe_3)_2$ (4.90 g, 24.6 mmol) was added via cannula to a stirred THF solution (60 mL) of H(TEPA) (4.11 g, 23.9 mmol) maintained at -78 ^{o}C. The resulting solution was slowly warmed to room temperature and stirred for 16 h, then the solvent was removed *in vacuo* to give an off-white powder. This powder was washed with hexane (30 mL) to remove impurities, then dried *in vacuo* to give the product as a colorless powder. (4.91 g, 98% yield)

^{1}H NMR (C_5D_5N, 400 MHz): δ 4.15 (m, 1H, $CH(CH_2CH_3)_2$), 1.81 (m, 4H, $CH(CH_2CH_3)_2$), 1.64 (s, 9H, $C(CH_3)_3$), 1.18 (t, 6H, $CH(CH_2CH_3)_2$).

^{13}C NMR (C_5D_5N, 151 MHz): δ 177.31 (NCO), 56.88 ($C(CH_3)_3$), 39.89 ($CHCH_2CH_3$), 31.42 ($C(CH_3)_3$), 31.13 ($CHCH_2CH_3$), 12.49 ($CHCH_2CH_3$).

IR (cm^{-1}): 1534 (s), 1486 (m), 1387 (m), 1341 (m), 1327 (m), 1313 (m), 1213 (m), 1154 (w), 1122 (w), 1029 (w), 910 (w), 860 (w), 776 (w), 577 (w), 554 (w), 529 (w).

K(TPTA): A THF solution (100 mL) of $KN(SiMe_3)_2$ (7.52 g, 37.7 mmol) was added via cannula to a stirred THF solution (150 mL) of H(TPTA) (8.00 g, 34.3 mmol) maintained at -78 ^oC. The resulting solution was slowly warmed to room temperature and stirred for 16 h, then the solvent was removed *in vacuo* to give an off-white powder. This powder was washed twice with Et_2O (30 mL) to remove impurities, then dried *in vacuo* to give the product as a colorless powder. (8.62 g, 93% yield)

^1H NMR (C_5D_5N, 400 MHz): δ 8.66 (d, 2H, Ph-*H*), 7.36 (d, 2H, Ph-*H*), 1.88 (s, 9H, $C(CH_3)_3$), 1.25 (s, 9H, $C(CH_3)_3$).

^{13}C NMR (C_5D_5N, 151 MHz): δ 150.35 (NCO), 129.51 (*Ph*), 124.44 (*Ph*), 52.03 ($NC(CH_3)_3$), 34.48 ($PhC(CH_3)_3$), 32.73 ($NC(CH_3)_3$), 29.61 ($PhC(CH_3)_3$). Two additional resonances corresponding to the phenyl carbons are obscured by the resonances from residual pyridine.

IR (cm^{-1}): 1577 (m), 1544 (m), 1336 (m), 1267 (w), 1230 (w), 1211 (w), 1139 (w), 1105 (w), 1013 (w), 881 (w), 855 (w), 725 (w), 712 (w).

K(Ar^{F}TA): A THF solution (30 mL) of $KN(SiMe_3)_2$ (0.86 g, 4.37 mmol) was added via cannula to a stirred THF solution (50 mL) of H(Ar^{F}TA) (1.31 g, 4.17 mmol) maintained at -78 ^oC. The resulting solution was slowly warmed to room temperature and stirred for 16 h, then the solvent was removed *in vacuo* to give an off-white powder. This powder was washed with hexane (50 mL) to remove impurities, then dried *in vacuo* to give the product as a colorless powder. (1.28 g, 87% yield)

^1H NMR (C_5D_5N, 600 MHz): δ 9.33 (s, 2H, Ph-*H*), 7.85 (s, 1H, Ph-*H*), 1.88 (s, 9H, $C(CH_3)_3$).

^{13}C NMR (C_5D_5N, 151 MHz): δ 162.78 (NCO), 150.84 (*Ph*), 129.76 (q, *Ph*-CF_3), 129.38 (*Ph*), 126.22 (q, Ph-CF_3), 120.21 (*Ph*), 52.52 ($C(CH_3)_3$), 32.02 ($C(CH_3)_3$).

^{19}F NMR (C_5D_5N, 565 MHz): δ -63.60 (CF_3).

IR (cm^{-1}): 1622 (w), 1560 (m), 1353 (w), 1308 (m), 1282 (s), 1247 (w), 1170 (m), 1122 (m), 936 (w), 905 (w), 889 (w), 844 (w), 795 (w), 774 (w), 710 (w), 695 (w), 682 (m).

Synthesis of Thorium Complexes

$Th(ITA)_4$ (1): A THF solution (2 mL) of $ThCl_4(DME)_2$ (138 mg, 0.250 mmol) was added dropwise to a THF solution (6 mL) of K(ITA) (181 mg, 0.999 mmol). The colorless solution turned cloudy over the course of the reaction. The solution was stirred for 3 d, then the solvent was removed *in vacuo* and the product was extracted into Et_2O (3 mL). The resulting colorless solution was filtered to remove insoluble KCl, concentrated to 1 mL, and cooled to -40 ^oC, yielding colorless crystals (113 mg, 57% yield).

^1H NMR (C_6D_6, 600 MHz): δ 2.70 (m, 4H, $C\mathit{H}(CH_3)_2$), 1.35 (s, 36H, $C(C\mathit{H}_3)_3$), 1.21 (d, 24H, $CH(C\mathit{H}_3)_2$).

^{13}C NMR (C_6D_6, 151 MHz): δ 186.84 ($N\mathit{C}O$), 51.74 ($N\mathit{C}(CH_3)_3$), 34.39 ($C\mathit{C}(CH_3)_3$), 31.69 ($NC(\mathit{C}H_3)_3$), 19.76 ($CC(\mathit{C}H_3)_3$).

IR (cm^{-1}): 1544 (m), 1491 (w), 1389 (m), 1365 (m), 1345 (m), 1301 (m), 1210 (m), 1070 (m), 1036 (w), 1012 (m), 919 (w), 894 (w), 815 (w), 746 (w), 644 (w), 586 (w).

EA calcd for $C_{32}H_{64}N_4O_4Th$: C: 47.99%, H: 8.05%, N: 7.00%. Found: C: 47.83%, H: 8.06%, N: 6.81%.

Sublimation point: 261 ^oC.

$Th(TEPA)_4$ (2): A THF solution (3 mL) of $ThCl_4(DME)_2$ (303 mg, 0.548 mmol) was added dropwise to a THF solution (10 mL) of K(TEPA) (459 mg, 2.19 mmol). The colorless solution turned cloudy over the course of the reaction. The solution was stirred for 3 d, then the solvent was removed *in vacuo* and the resulting solids were triturated with hexane (3 mL). The product was extracted into Et_2O (10 mL) then the resulting colorless solution was filtered to remove insoluble KCl, concentrated to 5 mL, and cooled to -40 ^oC, yielding colorless crystals (399 mg, 80% yield).

^1H NMR (C_6D_6, 400 MHz): δ 3.80 (m, 4H, $C\mathit{H}(CH_2CH_3)_2$), 1.85 and 1.76 (dm, 16H, $CH(C\mathit{H}_2CH_3)_2$), 1.30 (s, 36H, $C(C\mathit{H}_3)_3$), 1.05 (t, 24H, $CH(CH_2CH_3)_2$).

^{13}C NMR (C_6D_6, 151 MHz): δ 185.64 (NCO), 60.21 (*C*(CH_3)$_3$), 41.27 (*C*HCH_2CH_3), 29.87 (CH*C*H_2CH_3), 29.07 (C(*C*H_3)$_3$), 12.55 (CHCH_2*C*H_3).

IR (cm^{-1}): 1588 (w), 1524 (s), 1491 (w), 1476 (m), 1403 (m), 1363 (m), 1336 (s), 1310 (w), 1208 (m), 1162 (w), 1141 (m), 1051 (m), 1017 (w), 922 (w), 872 (w), 852 (w) 802 (w), 746 (w), 606 (m), 587 (m).

EA calcd for $C_{40}H_{80}N_4O_4Th$: C: 52.61%, H: 8.83%, N: 6.14%. Found: 52.33%, H: 8.99%, N: 6.05%.

Sublimation point: 190 °C.

Th(Ar^{F}TA)$_4$ (3): A THF solution (1 mL) of $ThCl_4(DME)_2$ (57 mg, 0.103 mmol) was added dropwise to a THF solution (3 mL) of K(Ar^{F}TA) (145 mg, 0.413 mmol). The colorless solution turned cloudy over the course of the reaction. The solution was stirred for 3 d, then the solvent was removed *in vacuo* and the product was extracted into hexane (10 mL). The resulting colorless solution was filtered to remove insoluble KCl, concentrated to 5 mL, and cooled to -40 °C, yielding colorless crystals (81 mg, 56% yield).

^{1}H NMR (C_6D_6, 600 MHz): δ 7.95 (s, 8H, Ph-*H*), 7.66 (s, 4H, Ph-*H*), 1.16 (s, 36H, C(C*H*$_3$)$_3$).

^{13}C NMR (C_6D_6, 151 MHz): δ 175.97 (N*C*O), 142.49 (*Ph*), 132.50 (q, *Ph*-CF_3), 127.13 (*Ph*), 124.64 (q, Ph-*C*F_3), 123.23 (*Ph*), 54.28 (*C*(CH_3)$_3$), 32.41 (C(*C*H_3)$_3$).

^{19}F NMR (C_6D_6, 565 MHz): δ -63.36 (C*F*$_3$).

IR (cm^{-1}): 1621 (w), 1544 (w), 1328 (m), 1279 (m), 1217 (w), 1183 (m), 1146 (m), 903 (w), 845 (w), 794 (w), 682 (w), 599 (w).

EA calcd for $C_{52}H_{48}F_{24}N_4O_4Th$: C: 42.17%, H: 3.27%, N: 3.78%. Found: C: 42.07%, H: 3.04%, N: 3.73%.

Melting point: 148-150 °C; vaporizes slowly above 150 °C.

$Th(TPTA)_4$ (4): A THF solution (1 mL) of $ThCl_4(DME)_2$ (48 mg, 0.086 mmol) was added dropwise to a THF solution (3 mL) of K(TPTA) (93 mg, 0.344 mmol). The colorless solution turned cloudy over the course of the reaction. The solution was stirred for 3 d, then the solvent was removed *in vacuo* and the product was extracted into hexane (5 mL). The resulting colorless solution was filtered to remove insoluble KCl, concentrated to 1 mL, and cooled to -40 °C, yielding colorless crystals (85 mg, 85% yield).

^1H NMR (C_6D_6, 400 MHz): δ 7.61 (d, 8H, Ph-*H*), 7.27 (d, 8H, Ph-*H*), 1.53 (s, 36H, $C(CH_3)_3$), 1.18 (s, 36H, $C(CH_3)_3$).

^{13}C NMR (C_6D_6, 151 MHz): δ 179.76 (N*C*O), 151.36 (*Ph*CO), 138.84 (*Ph*), 126.68 (*Ph*), 125.19 (*Ph*CC), 53.49 ($NC(CH_3)_3$), 34.67 ($PhC(CH_3)_3$), 32.74 ($NC(CH_3)_3$), 31.36 ($PhC(CH_3)_3$).

IR (cm^{-1}): 1682 (w), 1643 (w), 1611 (w), 1548 (m), 1525 (w), 1364 (m), 1269 (w), 1223 (w), 1148 (w), 1117 (w), 1105 (w), 1036 (w), 985 (m), 920 (w), 845 (m), 812 (w), 767 (w), 752 (w), 652 (w), 577 (w), 540 (w).

EA calcd for $C_{60}H_{88}N_4O_4Th$: C: 62.05%, H: 7.64%, N: 4.82%. Found: C: 61.97%, H: 7.59%, N: 4.78%.

Sublimation point: 220 °C; minor decomposition is also observed.

NMR Decomposition Studies: Compounds **1-4** (10 mg each) were added to separate J. Young NMR tubes inside a nitrogen glovebox. The tubes were sealed and brought out of the glovebox and heated to 300 °C in an aluminum heating block for 16 h. After cooling down to room temperature, the tubes were brought back into the glovebox and placed into a liquid nitrogen-cooled cold well for 15 minutes to condense volatile decomposition products. A solution of hexamethylbenzene (1.0 mg) in C_6D_6 (0.50 mL) was quickly added to each tube, then the tubes were capped and allowed to warm to room temperature before collecting NMR spectra.

As compound **2** was observed to sublime completely when heated as a solid, decomposition was achieved by heating a solution of **2** (10 mg) in d_{18}-decalin (mixture of cis and trans isomers) at 240 °C for 2 weeks. Although only partial decomposition was observed over this timeframe, the decomposition products were detectable by ^{1}H NMR, and their identities were confirmed by spiking the solution with H(TEPA), pivalonitrile, and 2-pentene.

Pyrolysis to ThO_2: Compounds **1-4** (20-40 mg each) were added to quartz tubes and cycled onto the Schlenk line using a Cajun adapter. The samples were heated under a nitrogen atmosphere using a butane torch until full decomposition of the precursors was observed, then the tubes were evacuated to remove volatile organic byproducts and heated in direct flame under vacuum for an additional 60 seconds. After cooling to room temperature, the tubes were brought into the glovebox. The pyrolyzed solids were then sealed in capillaries under a nitrogen atmosphere and analyzed using powder X-ray diffraction.

Elemental analysis of pyrolyzed products:

ThO_2 from **1**: C: 6.43%, H: 0.32%, N: 0.35%.

ThO_2 from **2**: C: 6.56%, H: 0.26%, N: 0.64%.

ThO_2 from **3**: C: 12.89%, H: 0.49%, N: 0.47%.

ThO_2 from **4**: C:19.23%, H: 0.82%, N: 0.27%.

Powder X-ray Diffraction (PXRD): Powder X-ray diffraction patterns of the products formed via pyrolysis of **1-4** were collected on a Bruker AXS D8 Advance spectrometer with a LynxEye strip detector. All patterns were collected at the wavelength of Cu Kα (λ=1.5418 Å). Prior to measurement the samples were packed into a quartz or borosilicate glass capillaries under inert atmosphere, and flame sealed. Comparison with powder patterns from the literature reveals that all patterns are consistent with the presence of ThO_2 which has a fluorite structure in the *Fm*-3*m* space group.[6] The broad feature present in all patterns at around 20^{o} 2θ is attributed to the presence of amorphous material.

Soft X-ray Spectromicroscopy (STXM-XAS): Sample preparation methodology for the potentially oxygen and moisture-sensitive analytes was similar to that described previously.[7,8] Samples were prepared in an argon-filled glovebox by grinding the analyte into a fine powder with a mortar and pestle, and brushing the powder onto a Si_3N_4 membrane (100 nm, Silson) with a fiber. This method arranged a large number of micron-scale particles in a relatively compact area that were suitable for O K-edge as well as Th N-edge measurements. A second membrane was placed over the sample, and the edges were sealed together using Hardman Double/Bubble® 5 minute epoxy.

Data acquisition methodology was similar to that discussed previously.[7,8] Single-energy images and spectra were acquired using the Advanced Light Source beamline 5.3.2.2. The ALS operated in topoff mode (500 mA) and measurements were conducted at approximately 0.6 Torr. For these measurements, the X-ray beam was focused with a zone plate with 25 nm outer zones onto the sample, and the transmitted light was detected. Images at a single energy were obtained by raster-scanning the sample and collecting transmitted monochromatic light as a function of sample position. Spectra at particular regions of interest on the sample image were extracted from the "stack", which is a collection of images recorded at multiple, closely spaced photon energies across the absorption edge. Dwell times used to acquire an image at a single photon energy were typically 2 ms per pixel. To evaluate the absorbance signal, the measured transmitted intensity (I) was converted to optical density (OD) using Beer−Lambert's law: $OD = \ln(I/I_0) = \mu\rho d$, where I_0 is the incident photon flux intensity, d is the sample thickness, and μ and ρ are the mass absorption coefficient and density of the sample material, respectively. Incident photon intensity was measured through the sample-free region of the Si_3N_4 windows. O K-edge data were background-subtracted and normalized in *MATLAB* using the *MBACK* algorithm.[9]

B. X-Ray Crystallography

In a dry nitrogen glovebox, samples of single crystals of **1**, **3**, and **4** were coated in Paratone-N oil for transport to diffraction facilities. Crystals were mounted on either a Kapton loop (for **3**) or on a MiTeGen 10 μm aperture Dual-Thickness MicroMount (for **1** and **4**). X-ray diffraction data for **1** and **4** were collected at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, Berkeley, CA, beamline 12.2.1 using a silicon double crystal monochromator to provide a beam of 17 keV (λ = 0.7288 Å). X-ray diffraction data for **3** was 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, 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. For **1** and **4**, Bruker APEX3 software was used for the data collections, Bruker SAINT V8.38A software was used to conduct the cell refinement and data reduction procedures, and absorption corrections were carried out by a multi-scan method utilizing the SADABS program.[10] For **3**, CrysAlisPro was used for the data collections and data processing, including a multi-scan absorption correction applied using the SCALE3 ABSPACK scaling algorithm within CrysAlisPro.[11] Initial structure solutions were found using direct methods (SHELXT),[12] and refinements were carried out using SHELXL-2014,[13] as implemented by Olex2.[14] Thermal parameters for all non-hydrogen atoms were refined anisotropically. Thermal ellipsoid plots were made using Mercury.[15] Structure **1** displayed full molecule disorder and all components were modeled completely. While it does not cause any relevant crystallographic alerts, the model for structure **3** included a hexane molecule with unrealistic structural metrics in the asymmetric unit, likely a result of solvent disorder not being fully resolved. Attempts to solve the solid state structure of **2** were unsuccessful despite the screening of numerous single crystals grown from various solvents. These crystals produced strong and highly resolved spots in the diffraction pattern. However, these spots likely result from strong diffraction of the thorium metal center, while presumed full molecule disorder (perhaps similar to that seen in **1**) leads to weak or unobservable ligand diffraction peaks. As a result, workup of the data continually led to unsolvable or unreasonable structures. All structures have been deposited to the Cambridge Crystallographic Data Centre (CCDC), with deposition numbers listed in Table S1.

Table S1. Crystallographic details and refinement metrics.

	1	**3**	**4**
Chemical formula	$C_{32}H_{64}N_4O_4Th$	$C_{58}H_{62}F_{24}N_4O_4Th$	$C_{60}H_{88}N_4O_4Th$
Formula weight	800.91	1567.15	1161.38
Color, habit	Colorless, block	Colorless, block	Colorless, plate
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/m	P2/n	C2/c
a (Å)	18.676(1)	10.7799(2)	26.527(2)
b (Å)	12.397(1)	14.0321(3)	11.0968(1)
c (Å)	8.8081(4)	22.2223(5)	21.060(2)
α (°)	90	90	90
β (°)	113.055(1)	102.024(2)	107.646(4)
γ (°)	90	90	90
V ($Å^3$)	1876.4(2)	3287.7(1)	5907.6(7)
Z	2	2	4
Density (g/cm^3)	1.418	1.583	1.306
F(000)	812	1552	2392
Radiation Type	Synchrotron (λ = 0.7288 Å)	Mo K_α (λ = 0.71073 Å)	Synchrotron (λ = 0.7288 Å)
μ (mm^{-1})	4.274	2.382	2.739
Crystal size (mm)	0.18 x 0.10 x 0.09	0.40 x 0.18 x 0.18	0.085 x 0.058 x 0.026
Meas. Refl.	16912	48997	25021
Indep. Refl.	2994	6726	5433
Obsvd. [I>2σ(I)] Refl.	2994	6324	5433
R_{int}	0.0314	0.0487	0.0730
Final [I>=2σ (I)] R indices	R_1 = 0.0187 wR_2 = 0.0477	R_1 = 0.0219 wR_2 = 0.0543	R_1 = 0.0646 wR_2 = 0.1532
Goodness-of-fit	1.042	1.045	1.489
CCDC	1991580	1991582	1991581

Table S2. Selected atomic distances (Å) and angles (°) for **1**, **3**, and **4**.

Atoms	1	3	4
Th1–O1	2.331(3)	2.384(2)	2.401(9)
Th1–O2	2.337(4)	2.396(2)	2.379(5)
Th1–O3	2.444(2)	-	-
Th1–O4	-	-	-
Th1–N1	2.54(1)	2.565(2)	2.533(8)
Th1–N2	2.58(1)	2.551(2)	2.522(7)
Th1–N3	2.557(4)	-	-
Th1–N4	-	-	-
C1–O1	1.30(2)	1.301(3)	1.31(2)
C2–O2	1.315(7)	1.305(3)	1.31(2)
C3–O3	1.307(5)	-	-
C4–O4	-	-	-
C1–N1	1.30(2)	1.293(3)	1.31(1)
C2–N2	1.28(2)	1.297(3)	1.255(9)
C3–N3	1.303(6)	-	-
C4–N4	-	-	-
O1–C1–N1	114.9(7)	117.7(2)	115.5(9)
O2–C2–N2	118.0(9)	116.6(2)	116.5(7)
O3–C3–N3	117.0(4)	-	-
O4–C4–N4	-	-	-

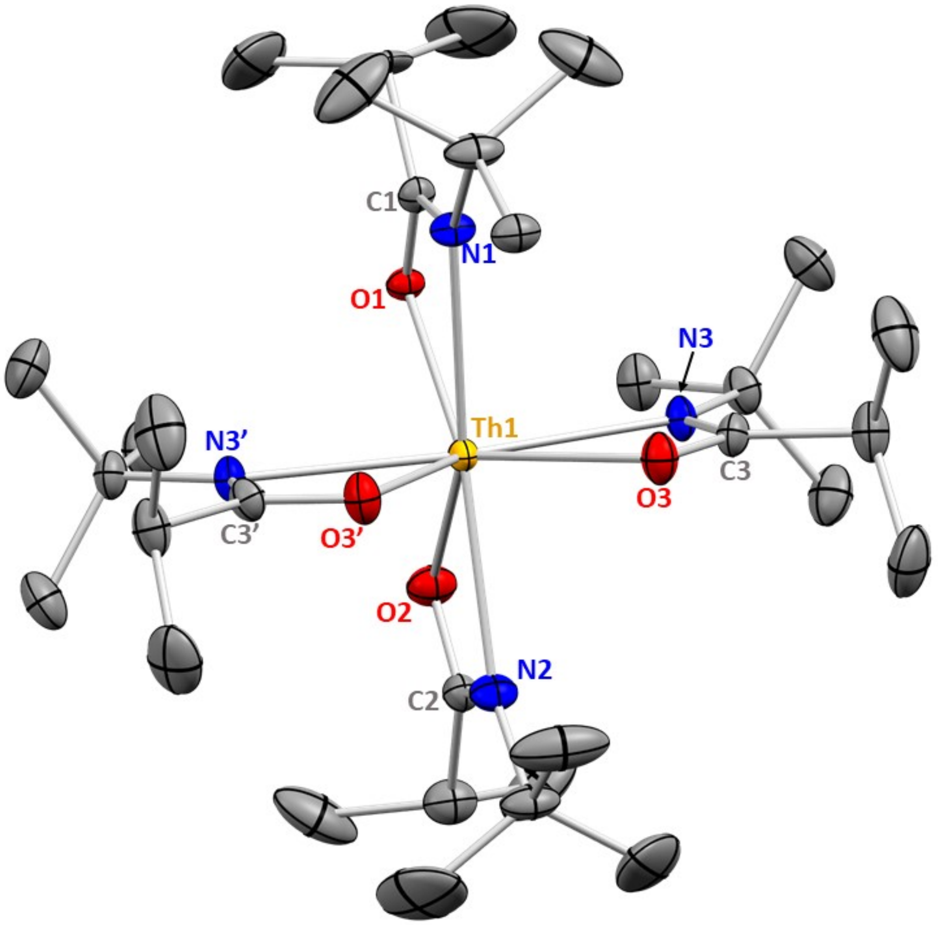

Figure S1. X-ray crystal structure of **1** with 50% probability ellipsoids. Hydrogen atoms and structural disorder are omitted for clarity. Selected structural metrics are shown in Table S2.

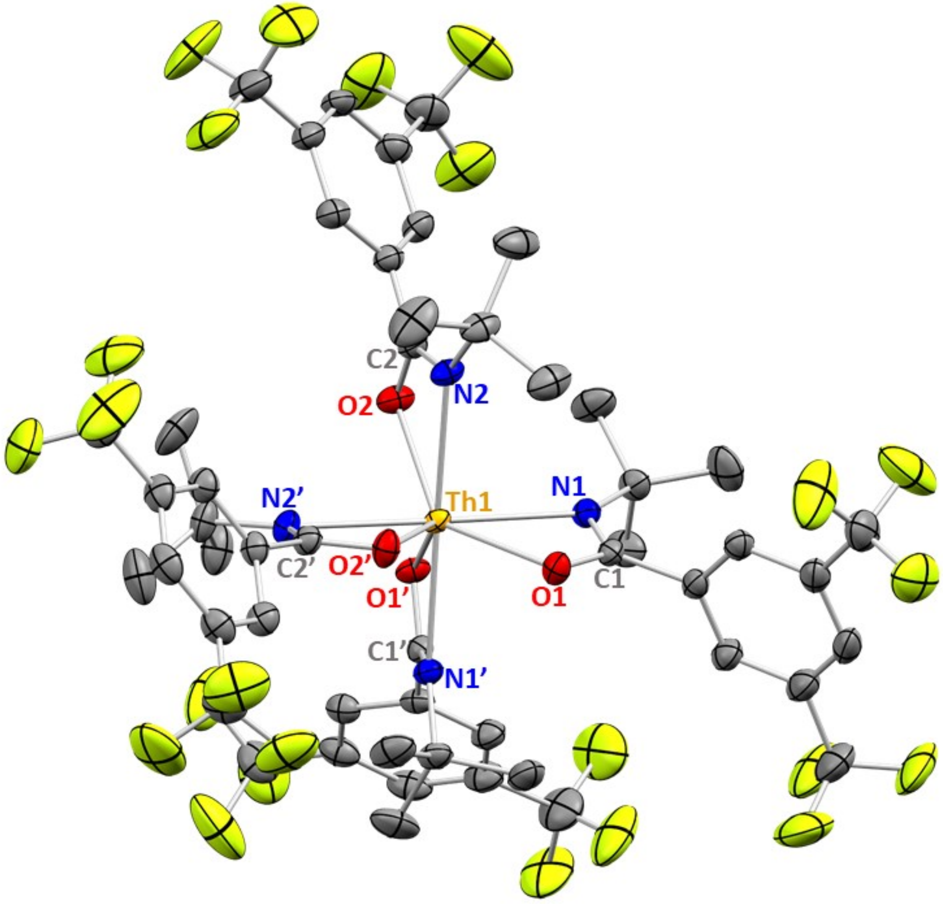

Figure S2. X-ray crystal structure of **3** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected structural metrics are shown in Table S2.

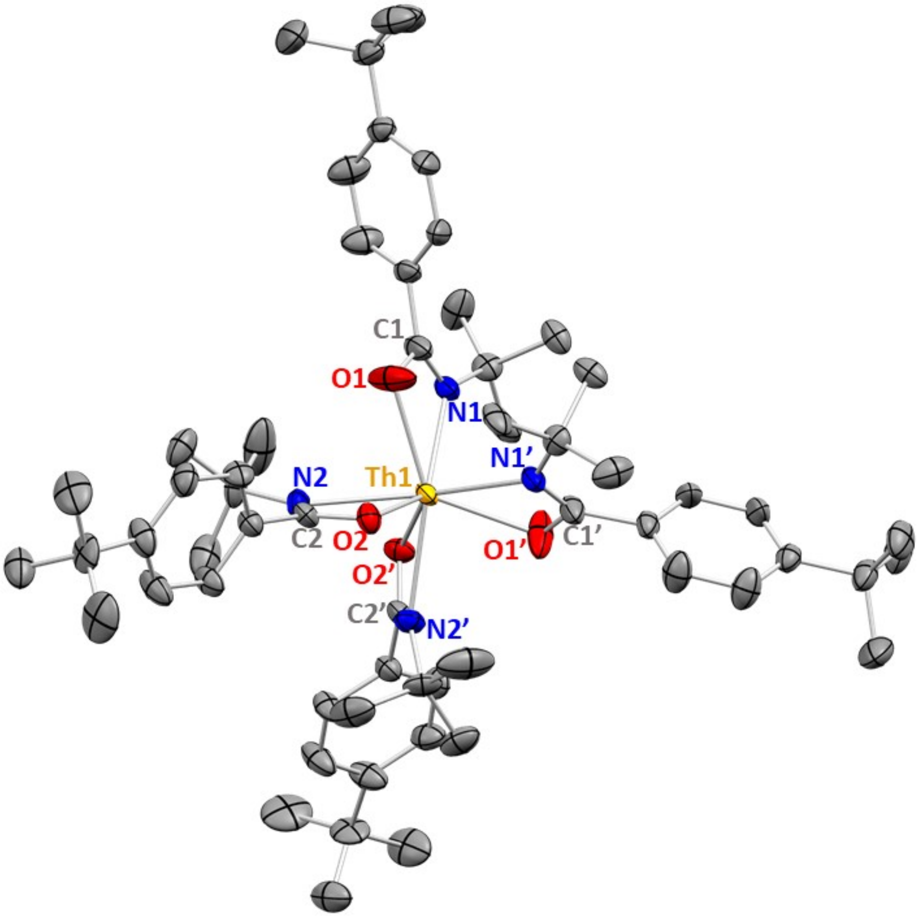

Figure S3. X-ray crystal structure of **4** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected structural metrics are shown in Table S2.

C. NMR Spectra

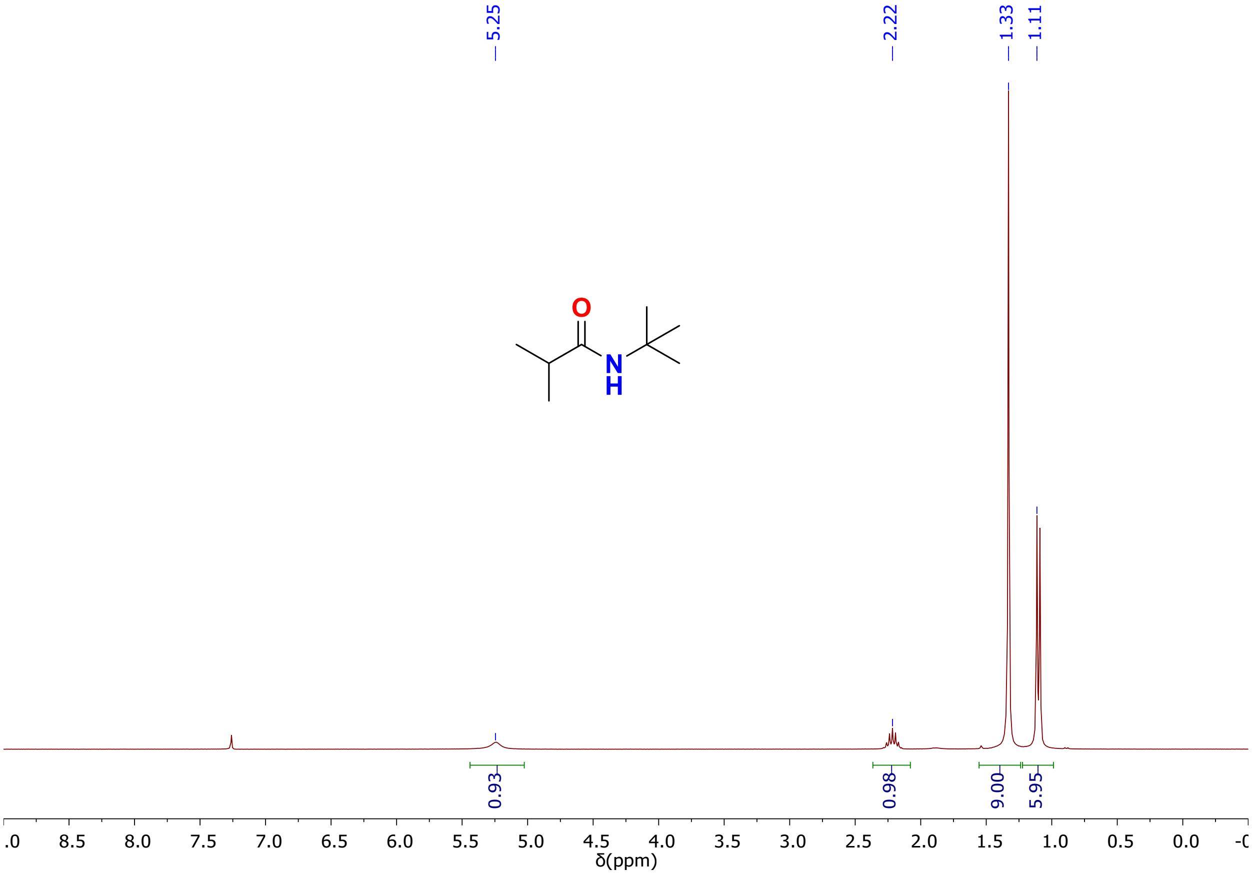

Figure S4. ^{1}H NMR spectrum of H(ITA) in $CDCl_3$.

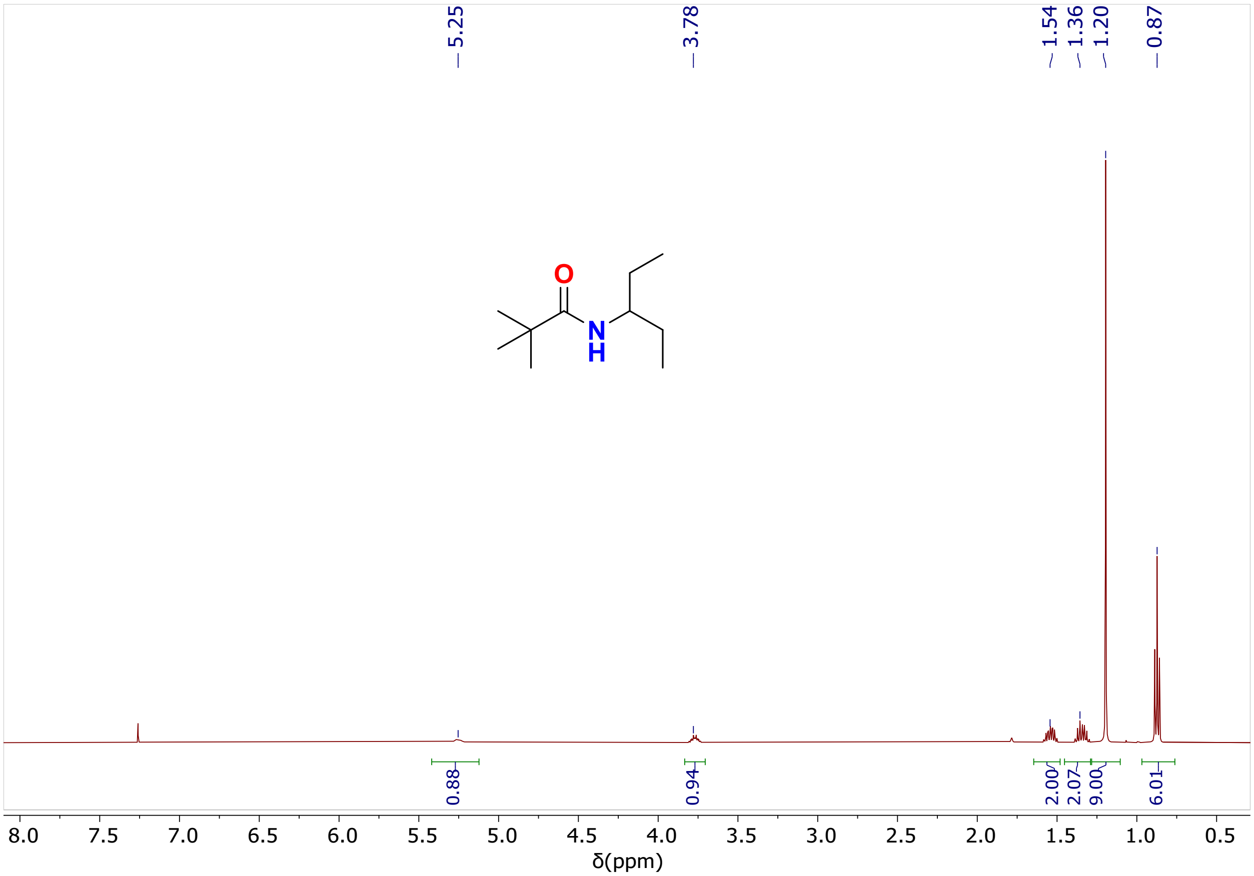

Figure S5. ^{1}H NMR spectrum of H(TEPA) in $CDCl_3$.

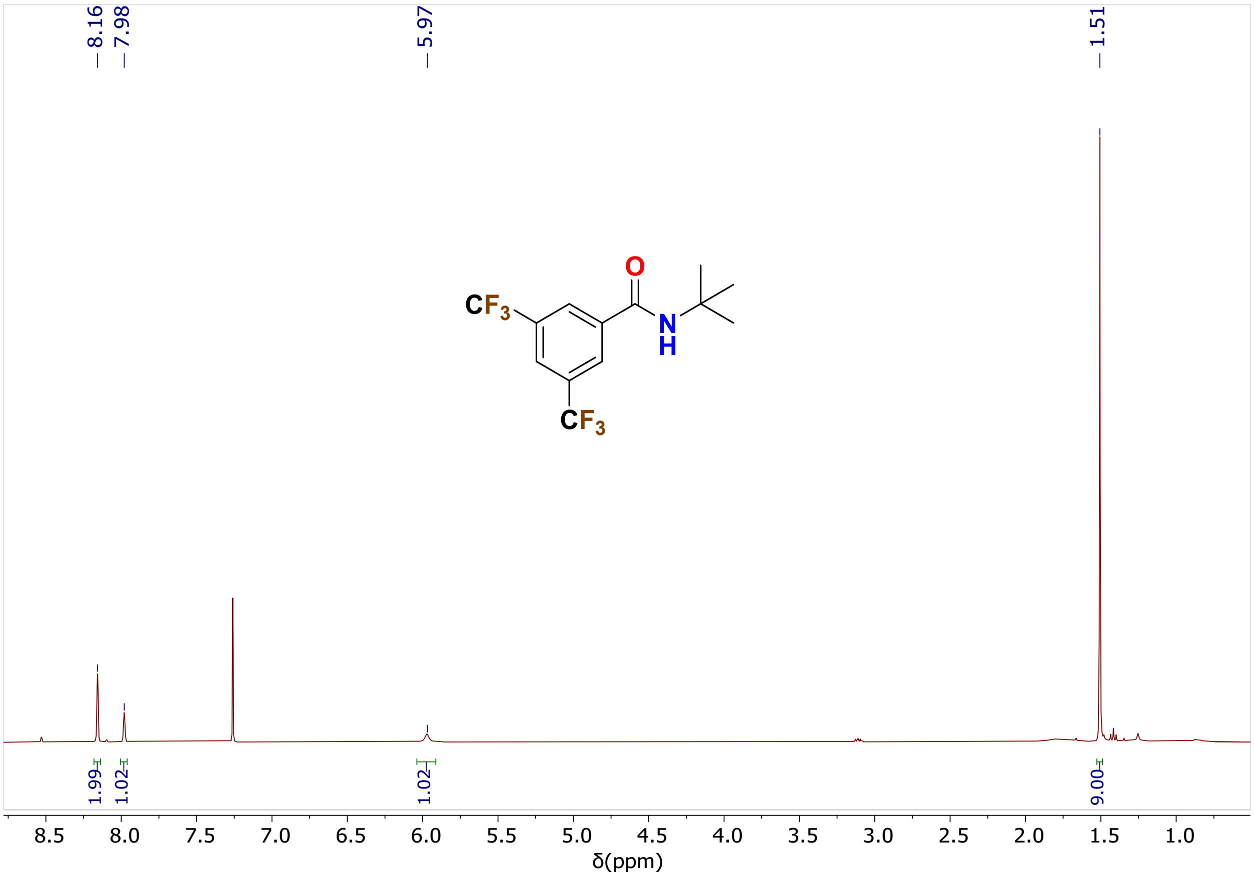

Figure S6. ^{1}H NMR spectrum of H(Ar^{F}TA) in $CDCl_3$.

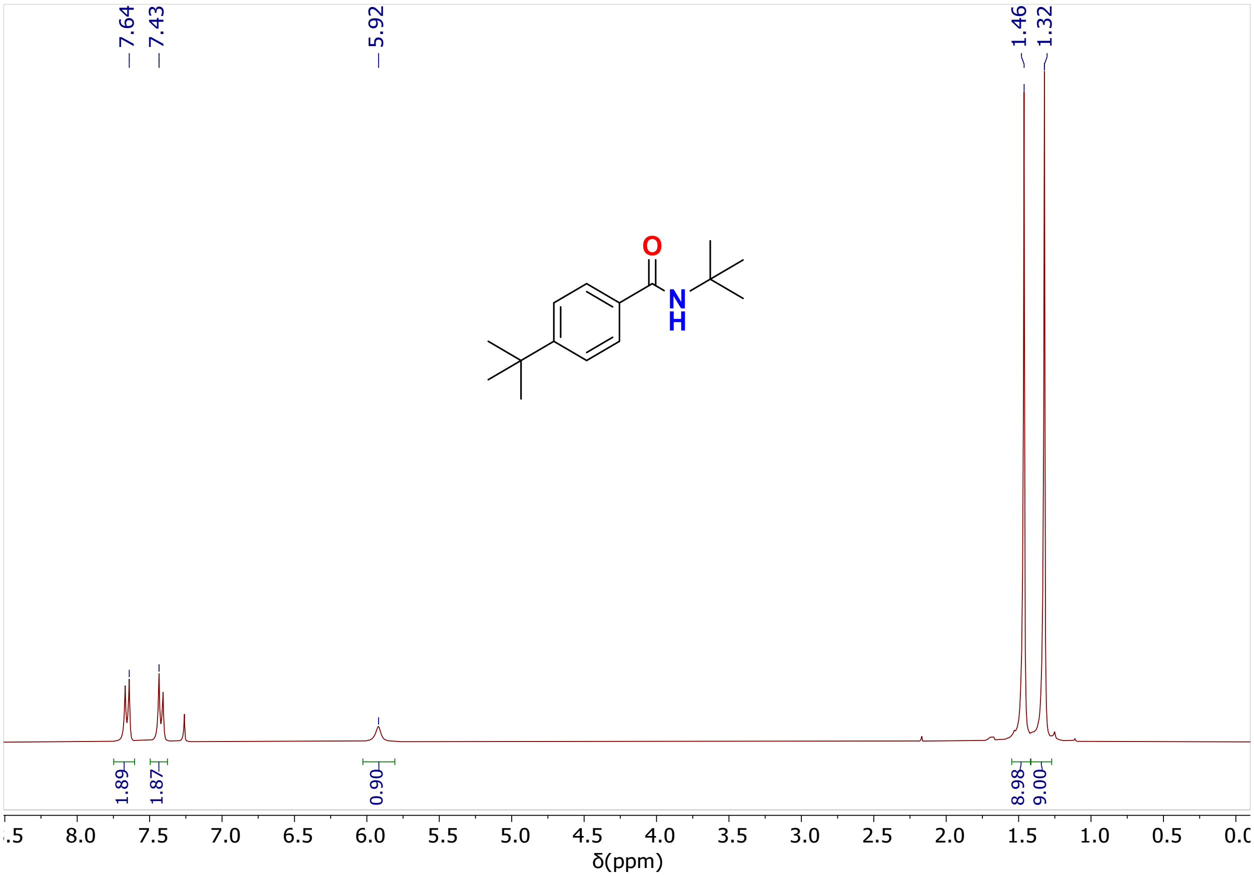

Figure S7. ^{1}H NMR spectrum of H(TPTA) in $CDCl_3$.

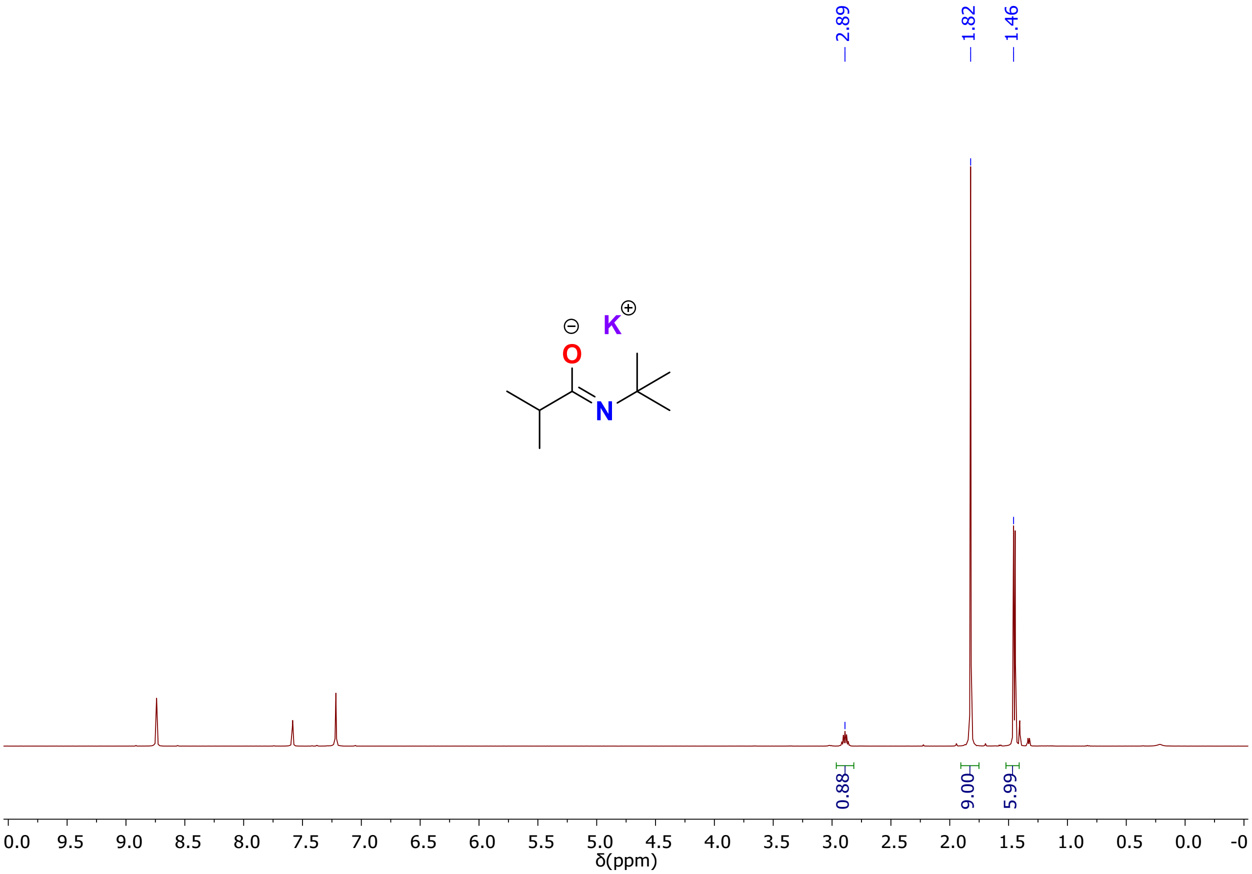

Figure S8. ^{1}H NMR spectrum of K(ITA) in C_5D_5N.

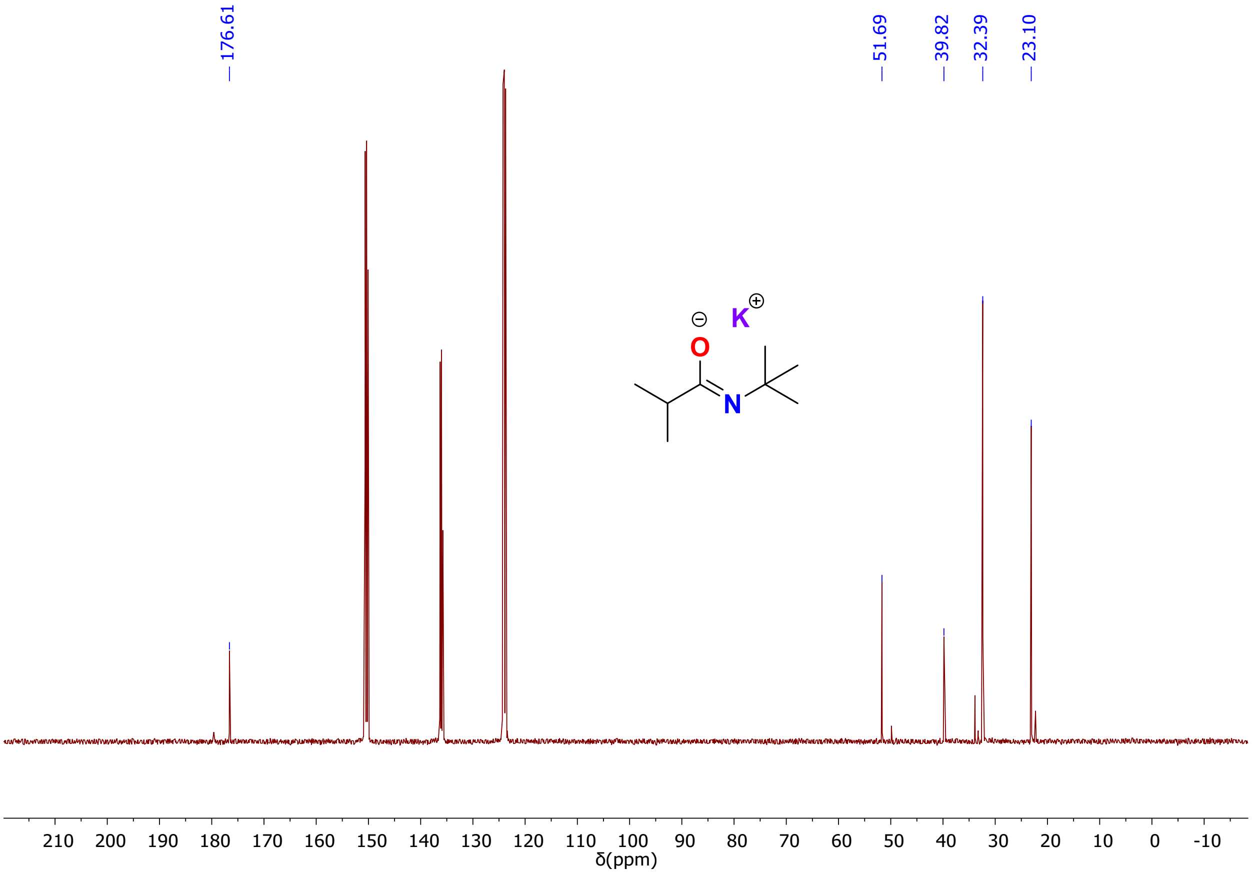

Figure S9. ^{13}C NMR spectrum of K(ITA) in C_5D_5N. The small peaks at 49.88, 33.88, and 22.88 ppm are from a trace amount of H(ITA).

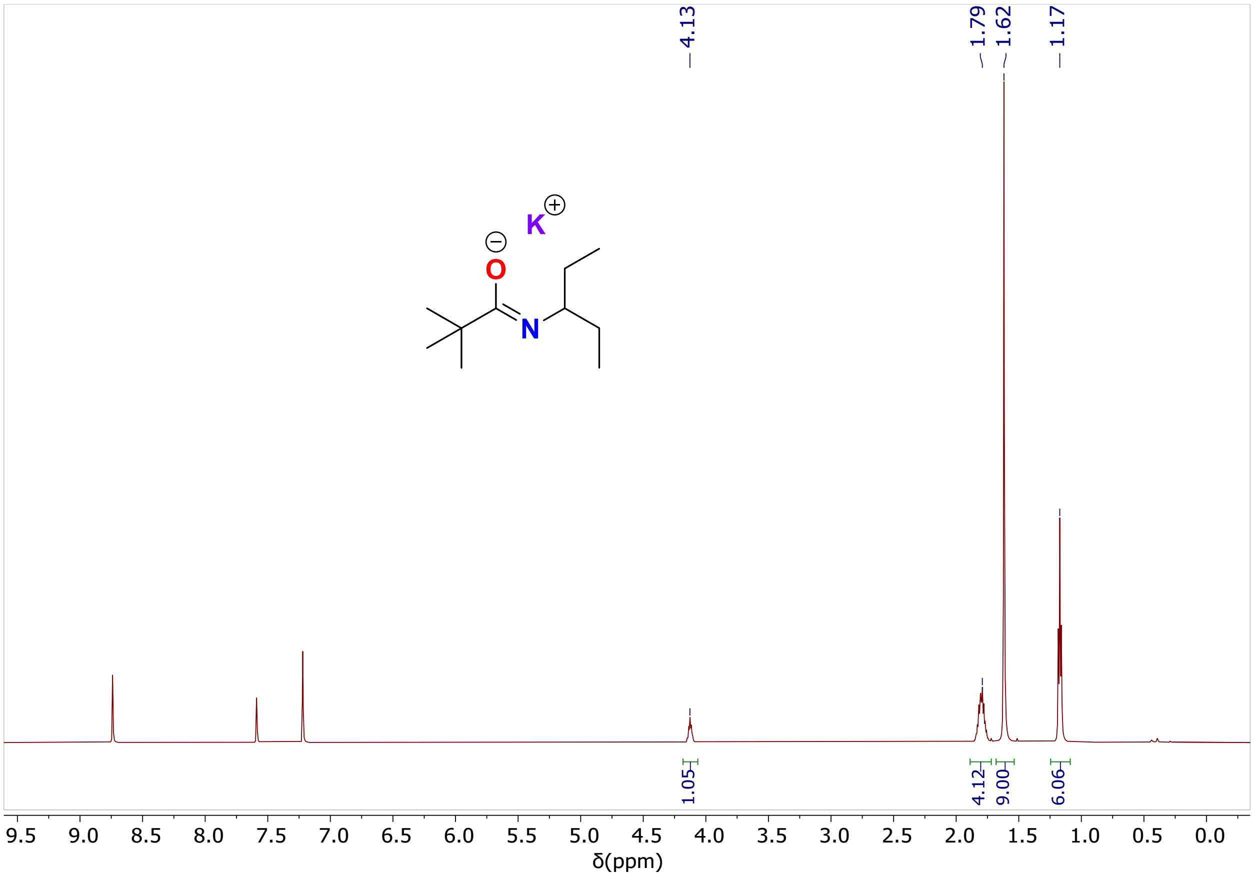

Figure S10. ^{1}H NMR spectrum of K(TEPA) in C_5D_5N.

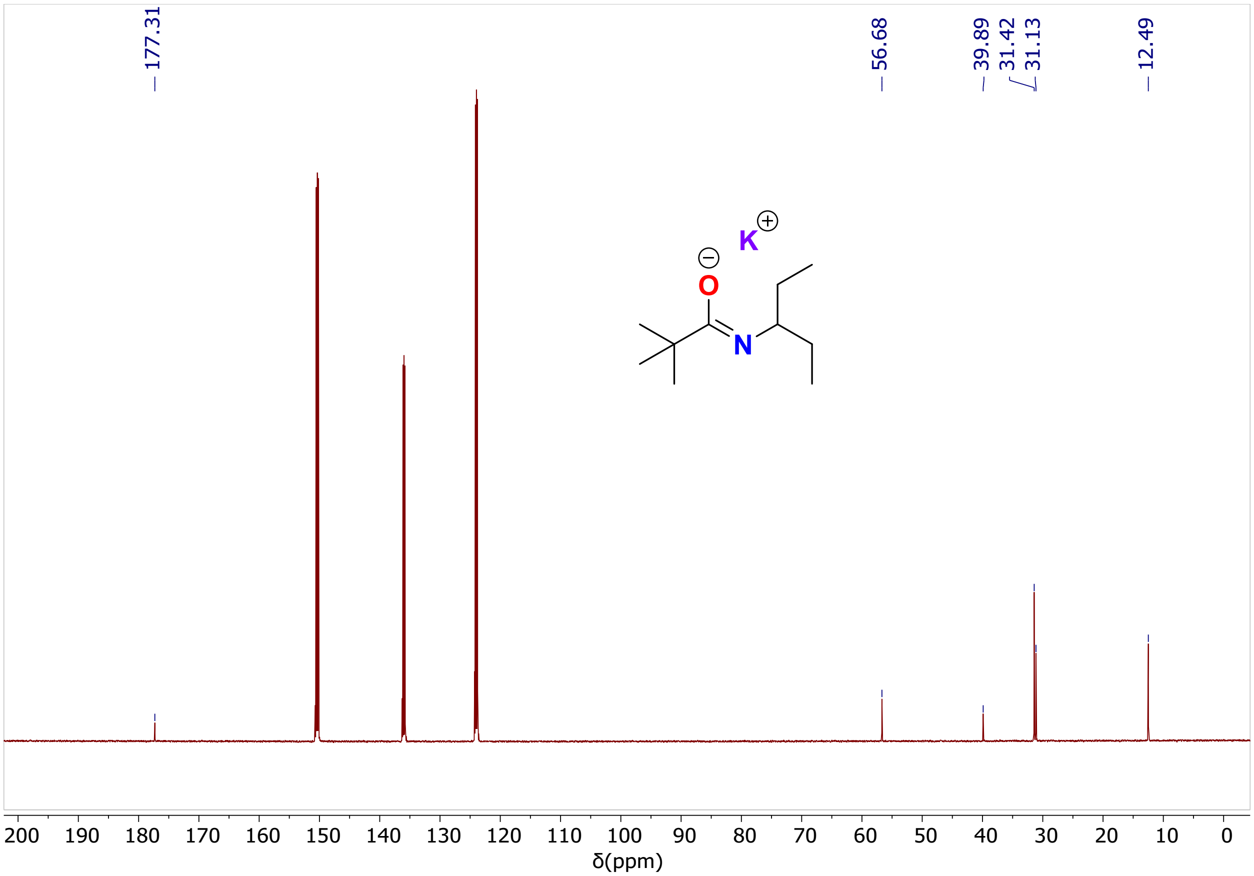

Figure S11. ^{13}C NMR spectrum of K(TEPA) in C_5D_5N.

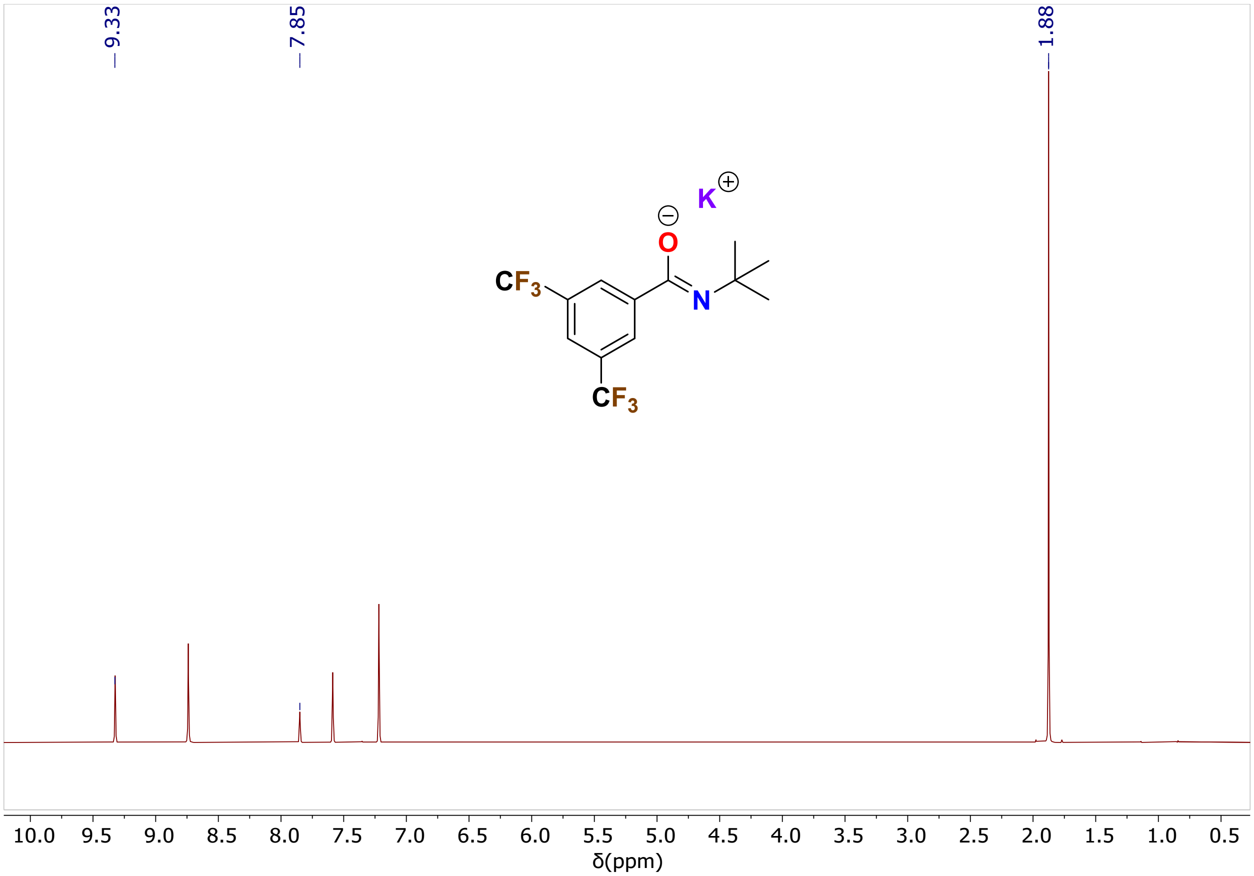

Figure S12. ^{1}H NMR spectrum of K(Ar^{F}TA) in C_5D_5N.

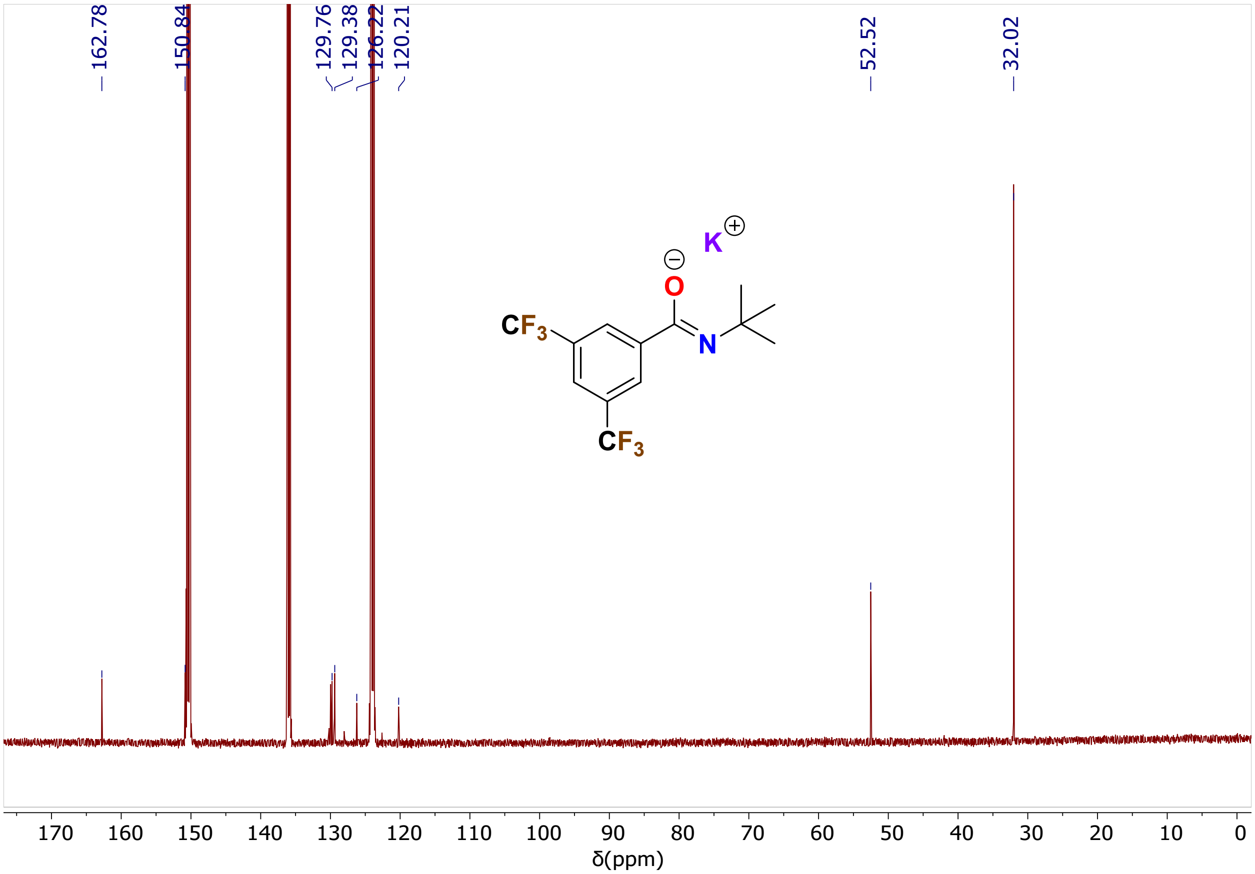

Figure S13. ^{13}C NMR spectrum of K(Ar^{F}TA) in C_5D_5N.

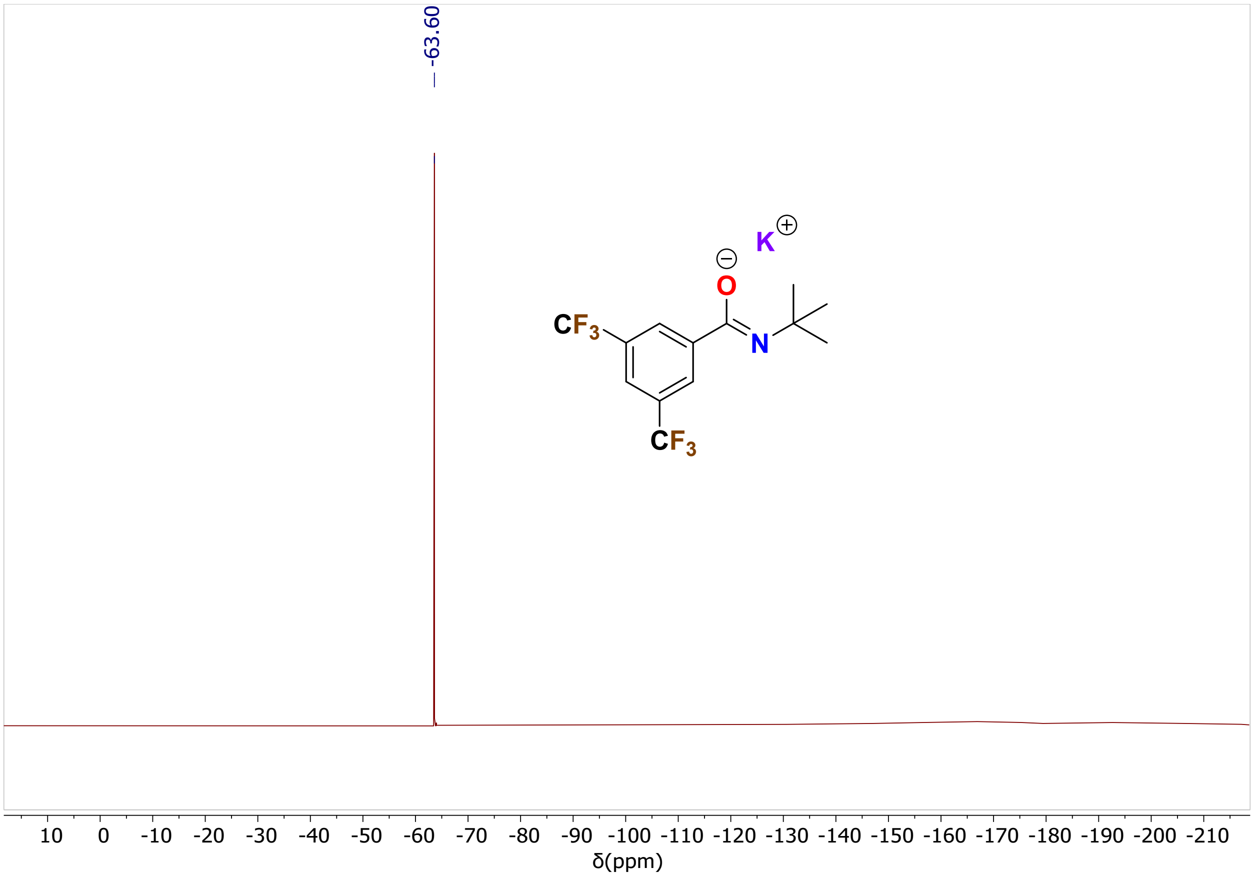

Figure S14. ^{19}F NMR spectrum of K(Ar^{F}TA) in C_5D_5N.

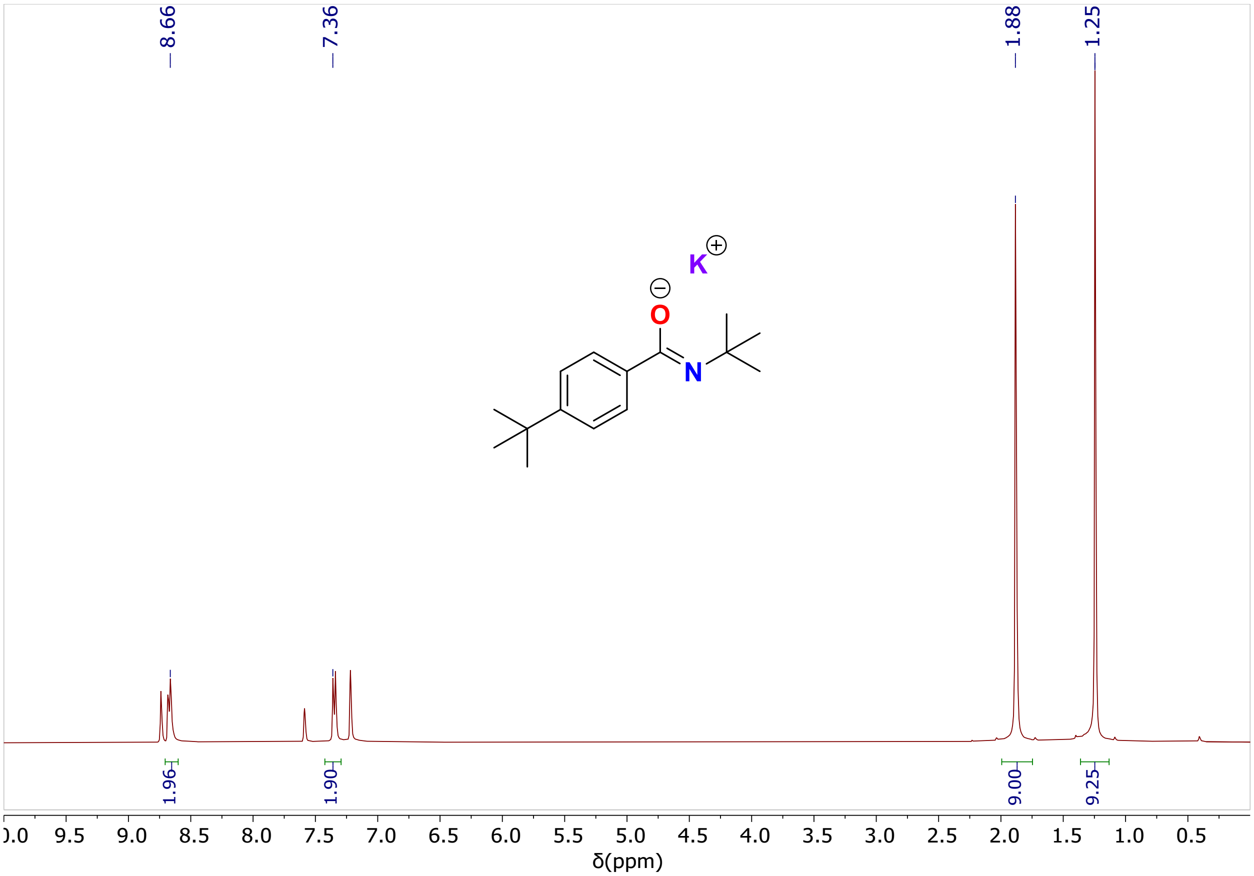

Figure S15. ^{1}H NMR spectrum of K(TPTA) in C_5D_5N.

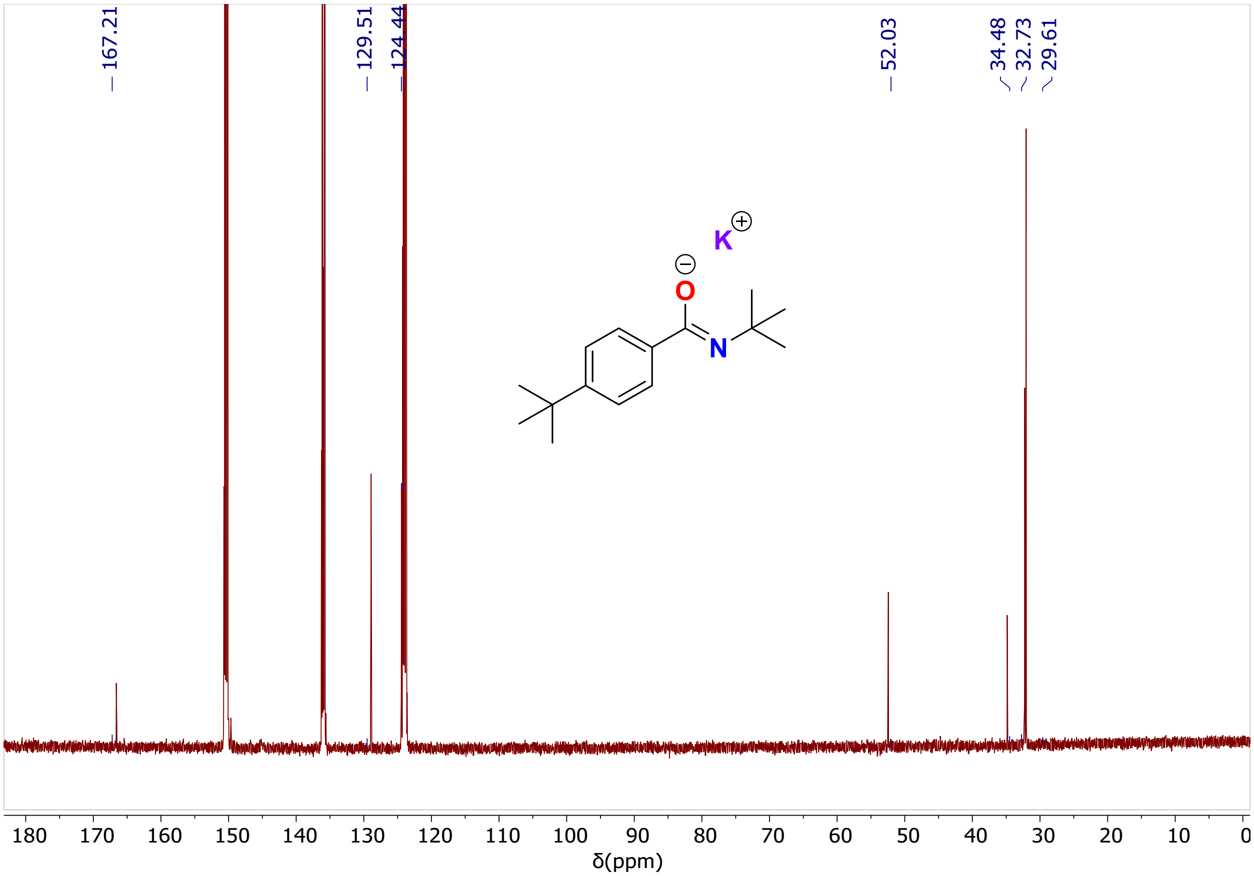

Figure S16. ^{13}C NMR spectrum of K(TPTA) in C_5D_5N.

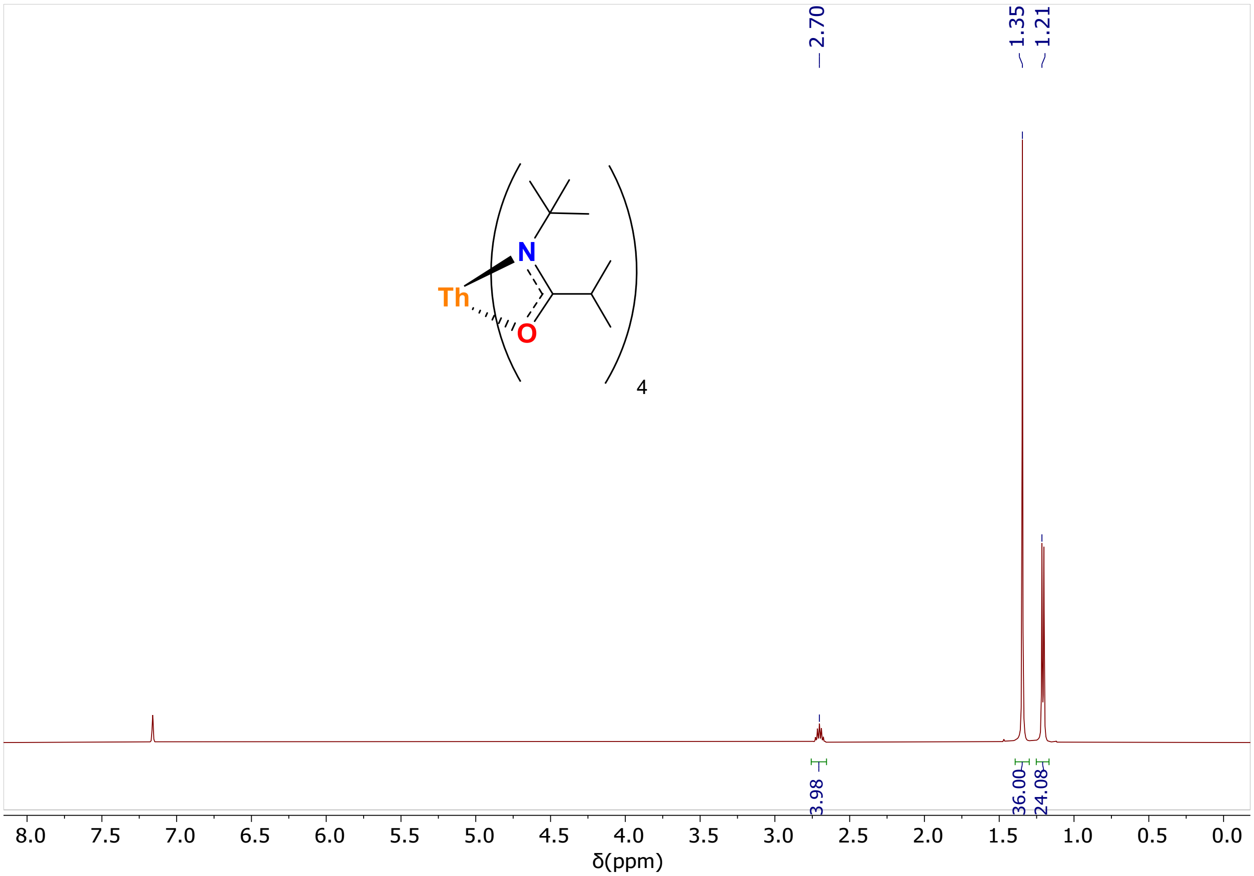

Figure S17. ^{1}H NMR spectrum of Th(ITA)$_4$ **(1)** in C_6D_6.

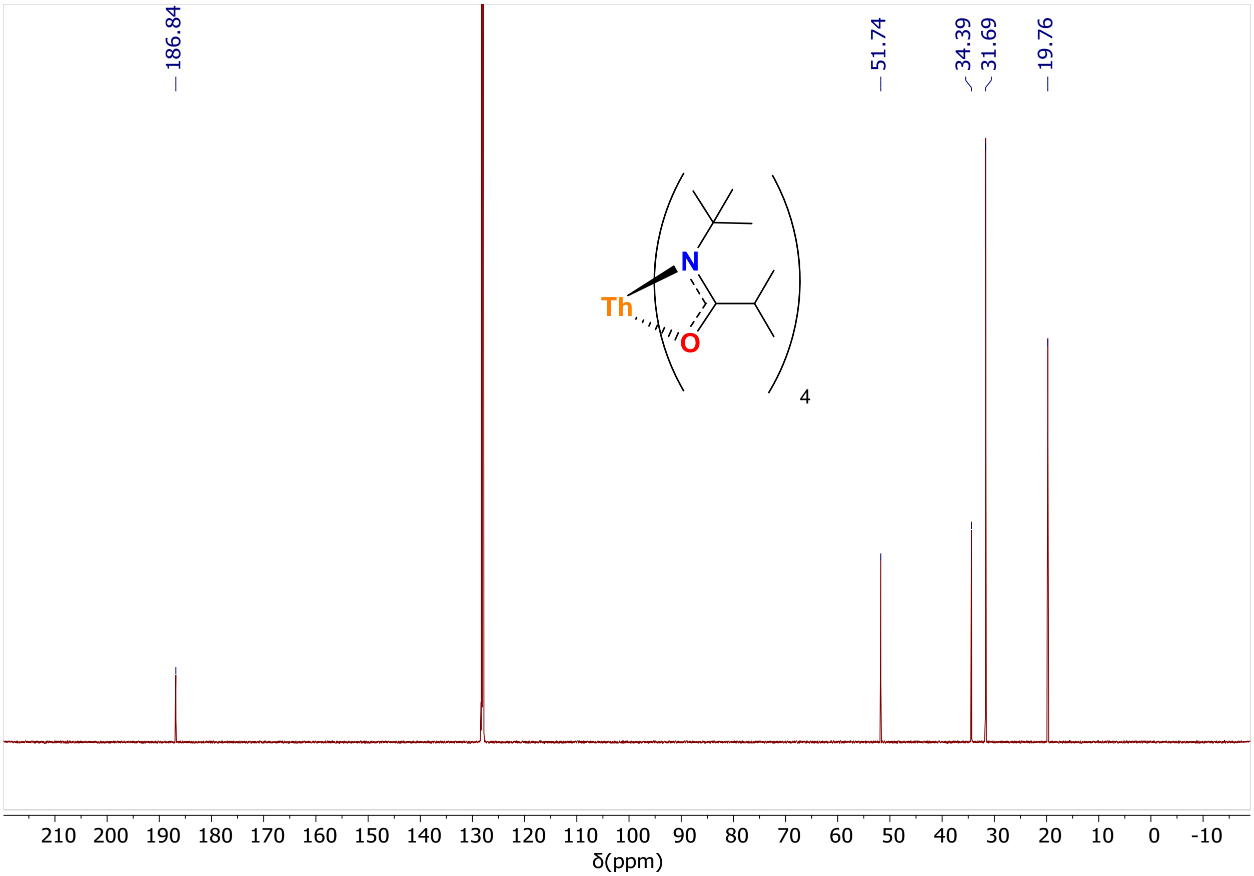

Figure S18. ^{13}C NMR spectrum of Th(ITA)$_4$ **(1)** in C_6D_6.

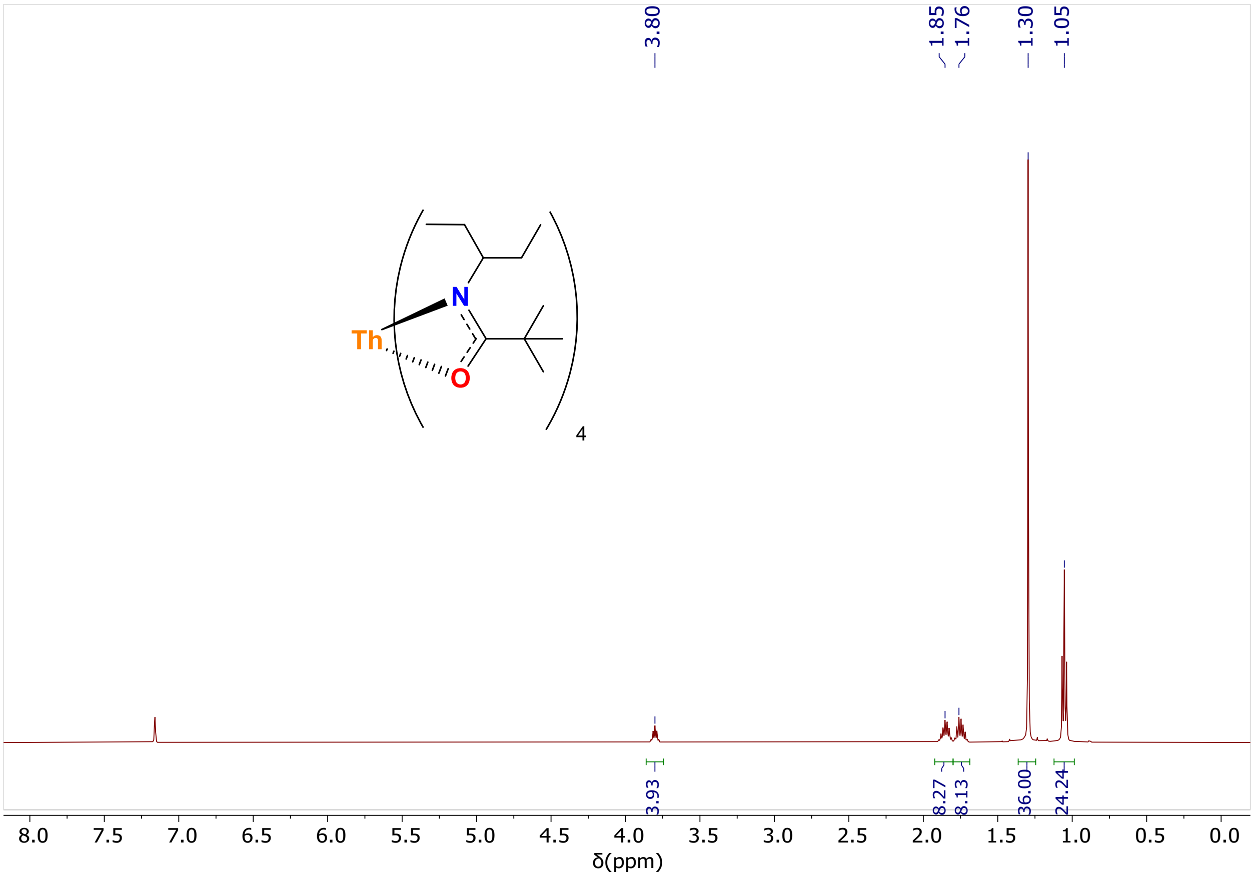

Figure S19. ^{1}H NMR spectrum of Th(TEPA)$_4$ **(2)** in C_6D_6.

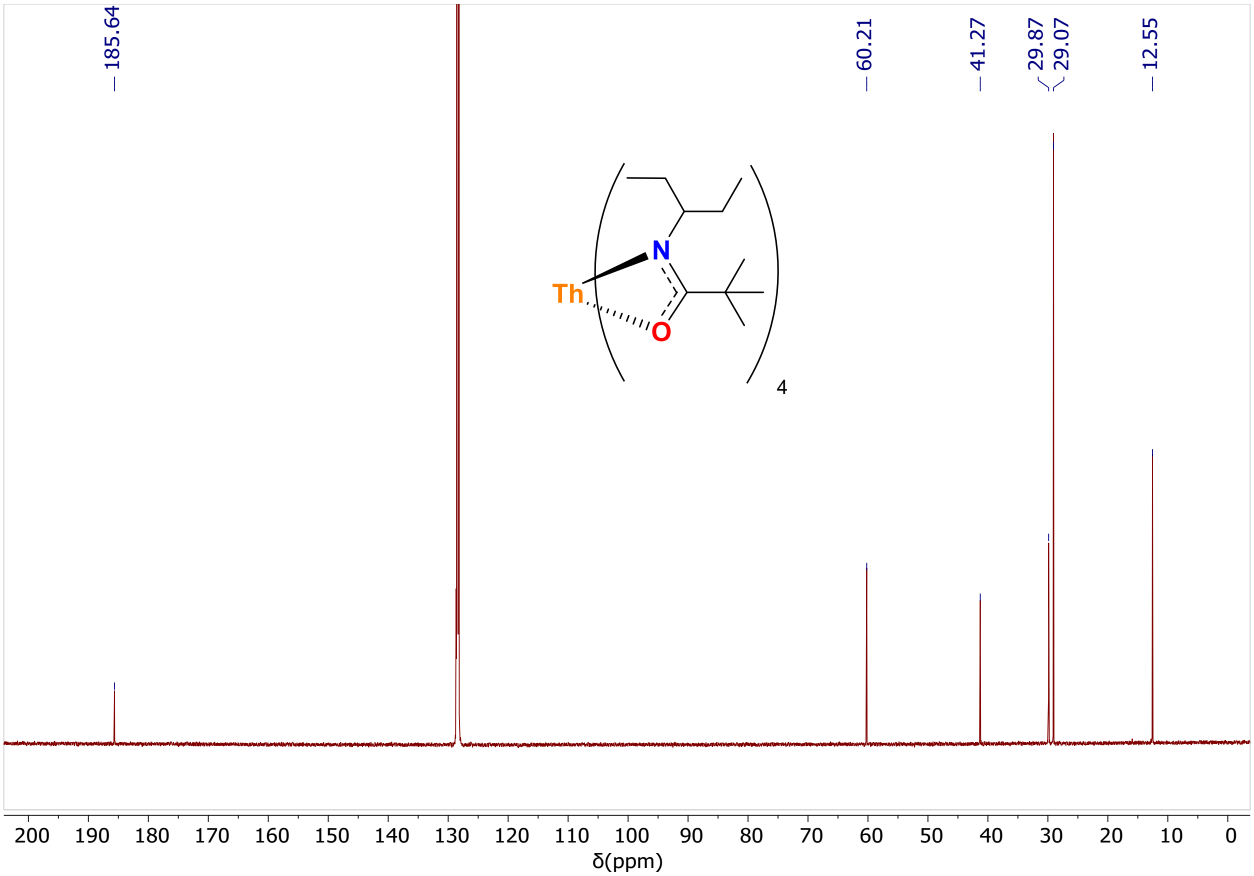

Figure S20. ^{13}C NMR spectrum of Th(TEPA)$_4$ **(2)** in C_6D_6.

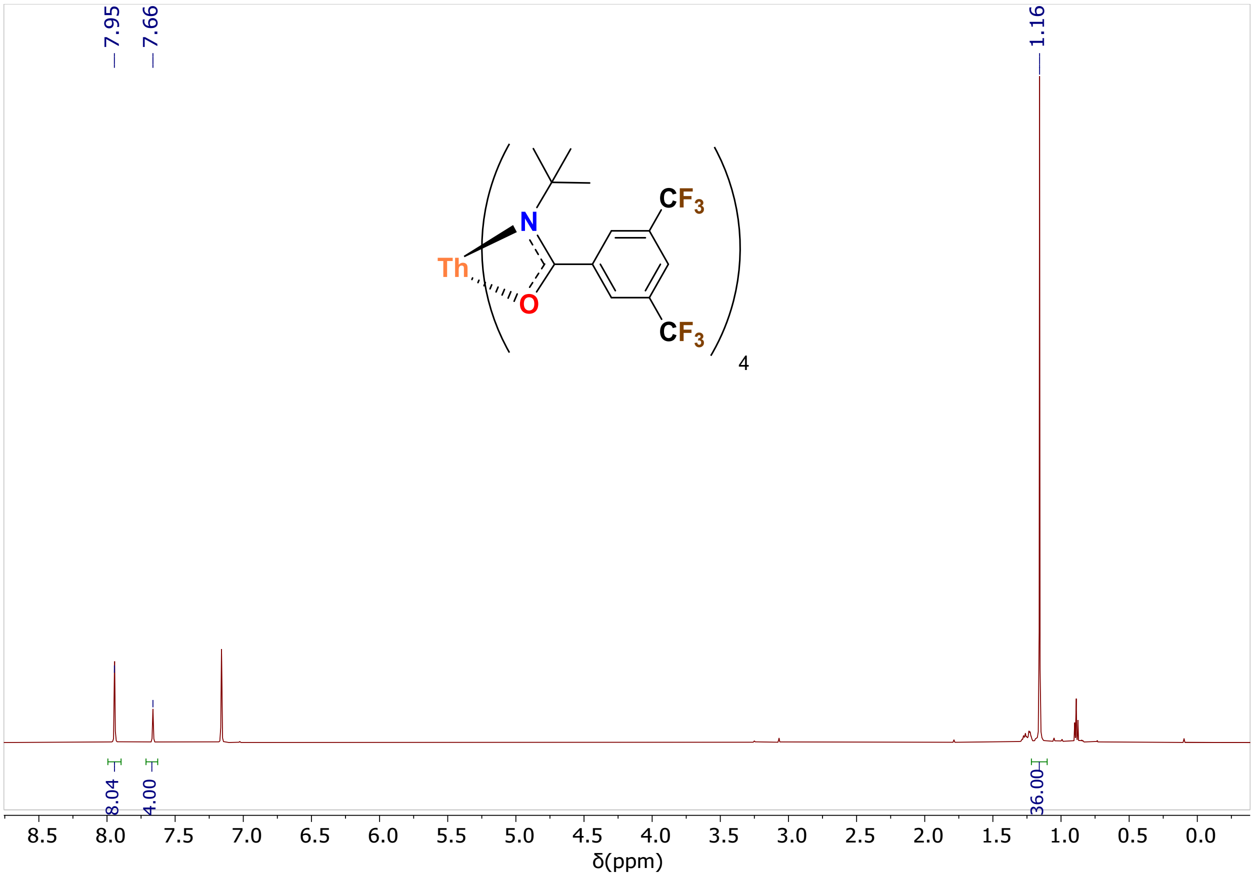

Figure S21. ^{1}H NMR spectrum of Th(Ar^{F}TA)$_4$ **(3)** in C_6D_6.

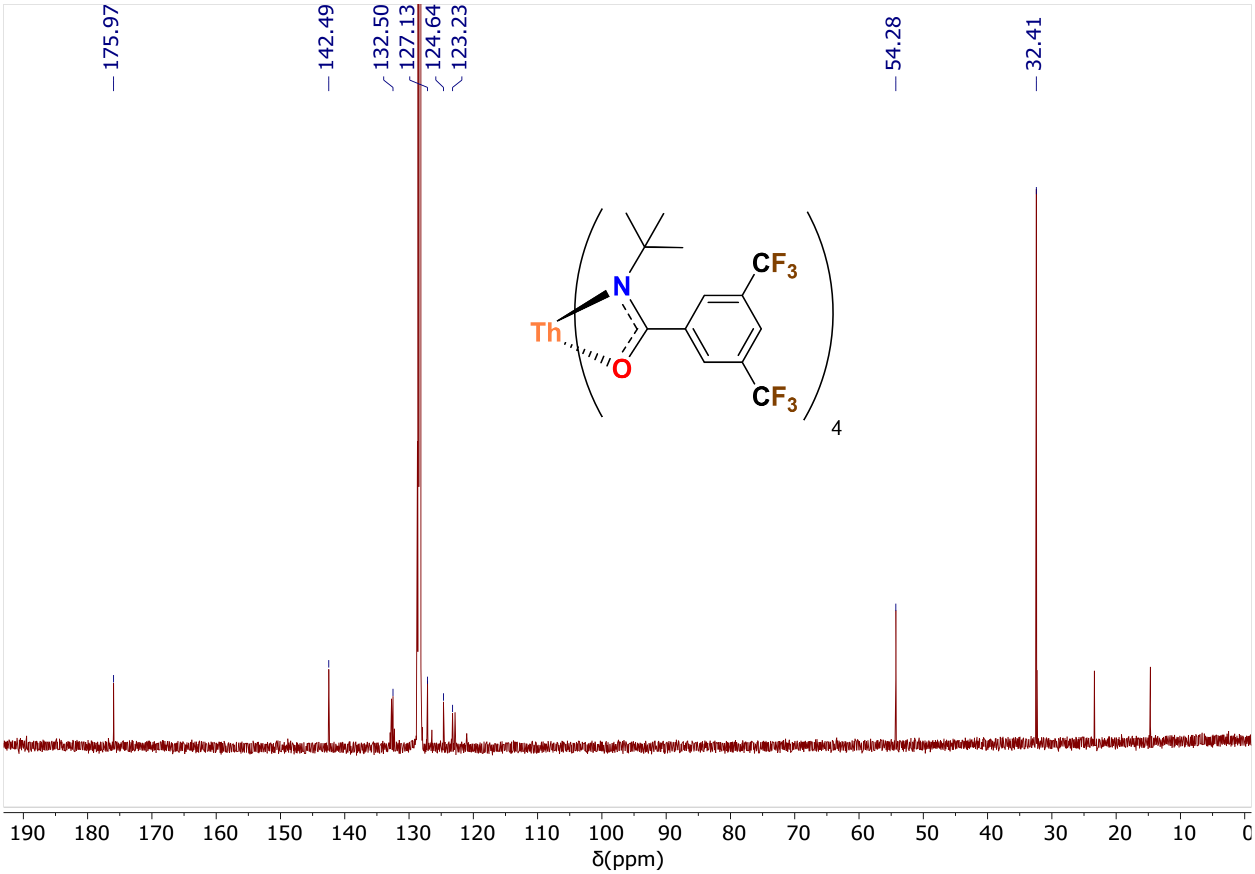

Figure S22. ^{13}C NMR spectrum of Th(Ar^{F}TA)$_4$ **(3)** in C_6D_6. The peaks at 14.67 and 23.38 ppm are from residual n-hexane.

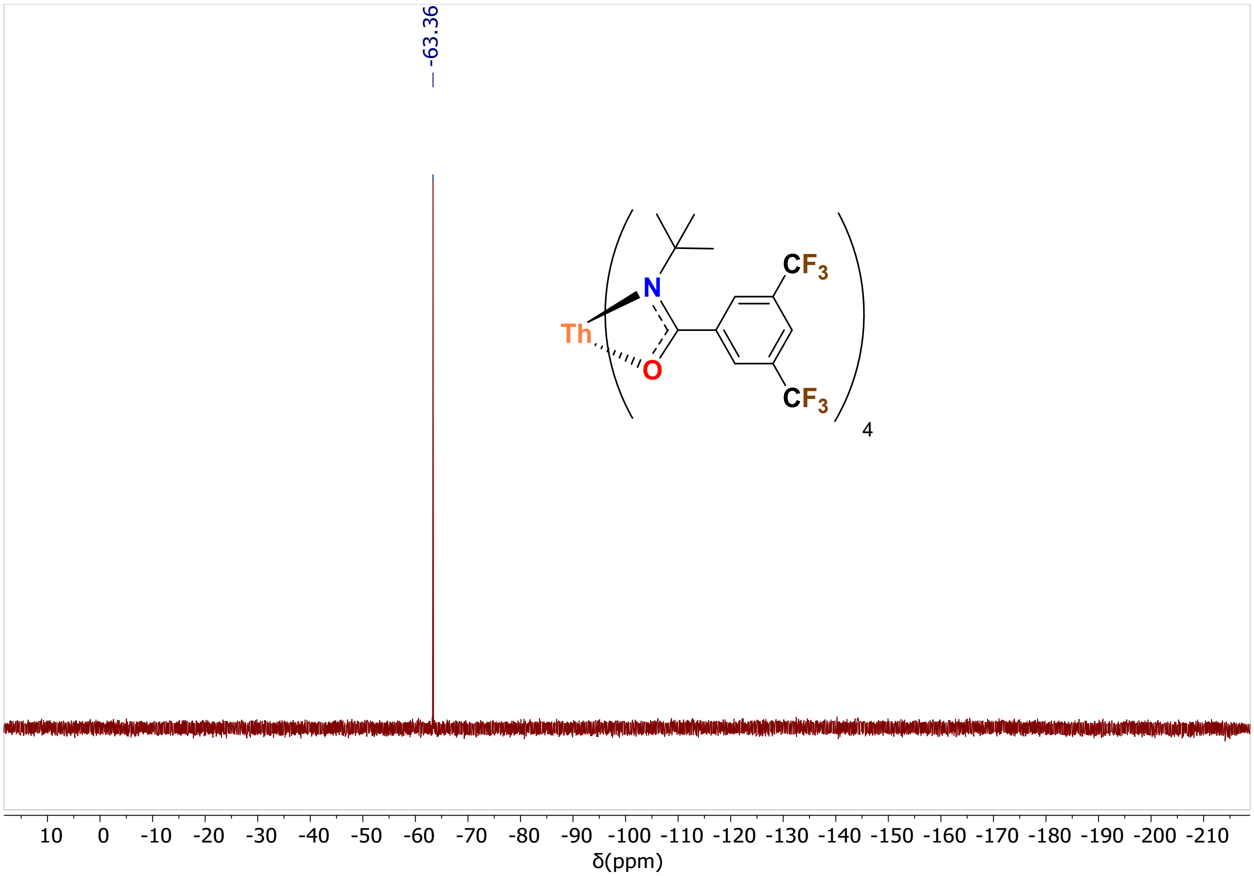

Figure S23. ^{19}F NMR spectrum of Th(Ar^{F}TA)$_4$ **(3)** in C_6D_6.

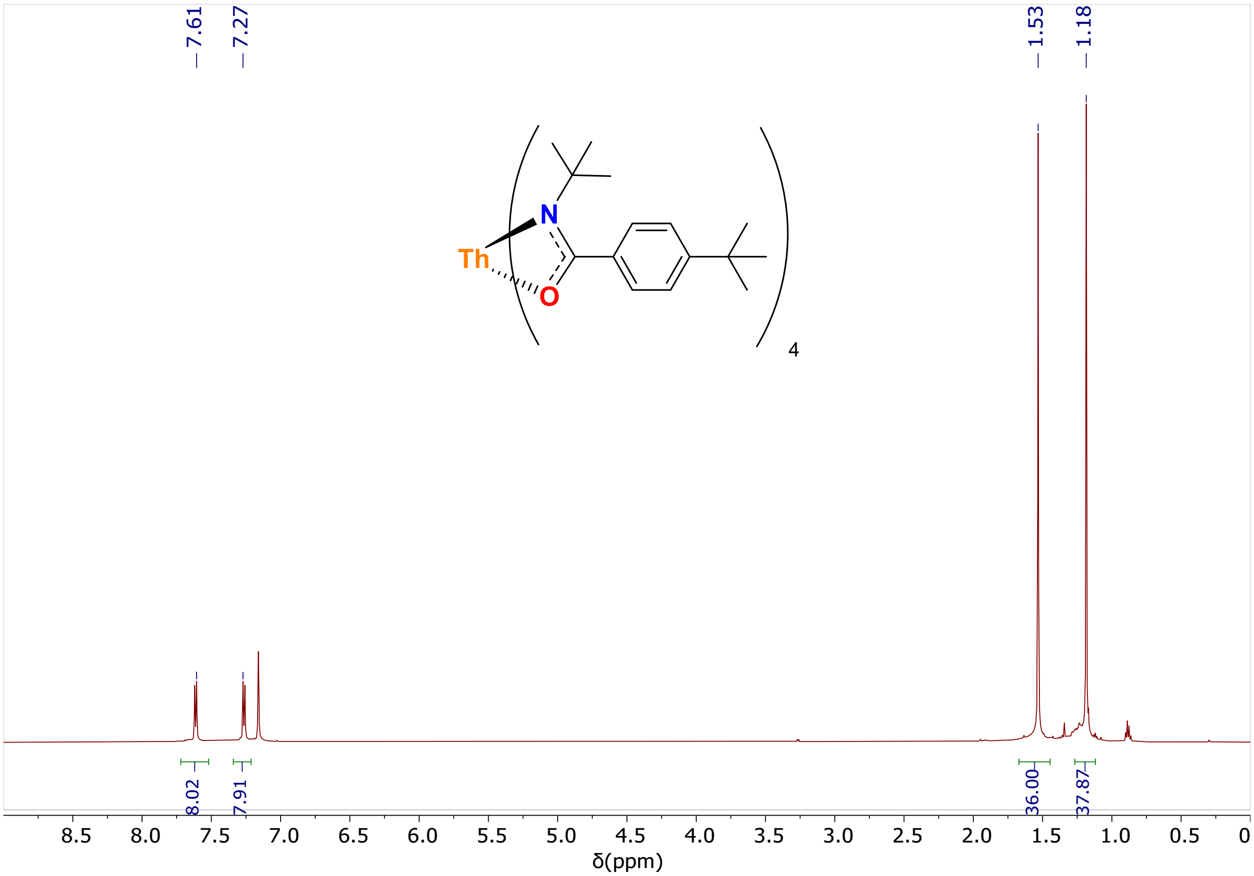

Figure S24. ^{1}H NMR spectrum of Th(TPTA)$_4$ **(4)** in C_6D_6.

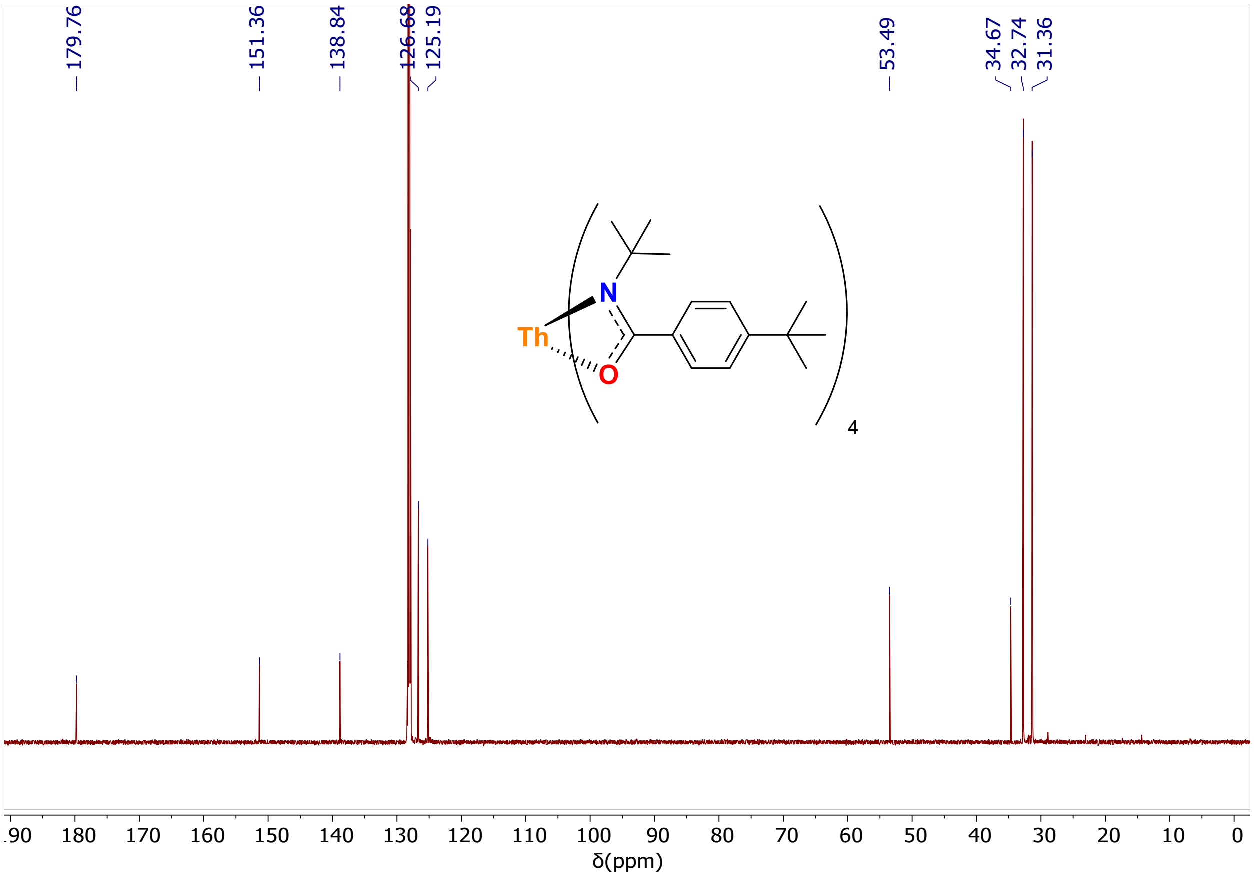

Figure S25. ^{13}C NMR spectrum of Th(TPTA)$_4$ **(4)** in C_6D_6.

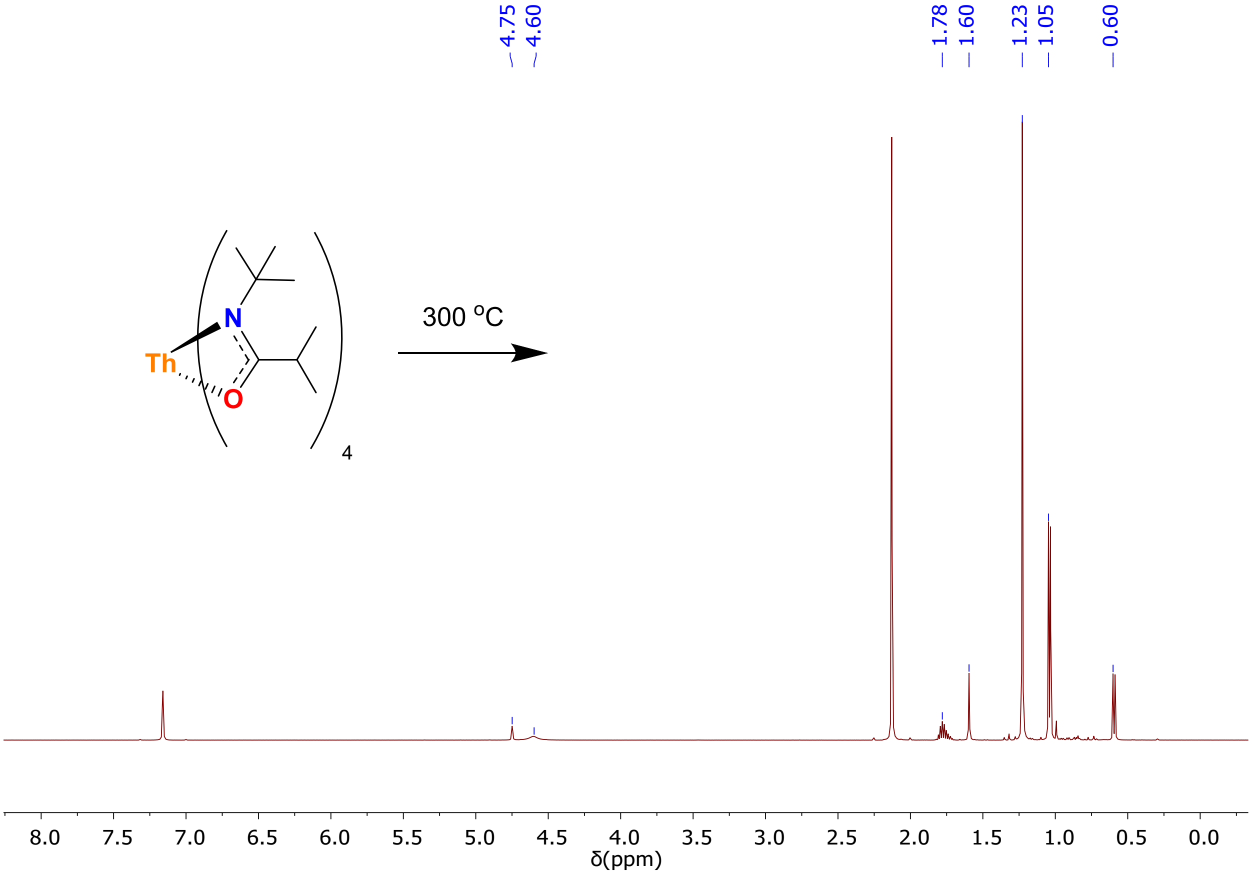

Figure S26. ^{1}H NMR spectrum in C_6D_6 of the products formed by heating a solid sample of **1** to 300 °C for 16 h. The isobutylene resonances are present at 4.75 and 1.60 ppm, the isobutyronitrile resonances are present at 1.78 and 0.60 ppm, and the H(ITA) resonances are present at 4.60, 1.78, 1.23, and 1.05 ppm. The peak at 2.13 ppm is from C_6Me_6 (internal standard).

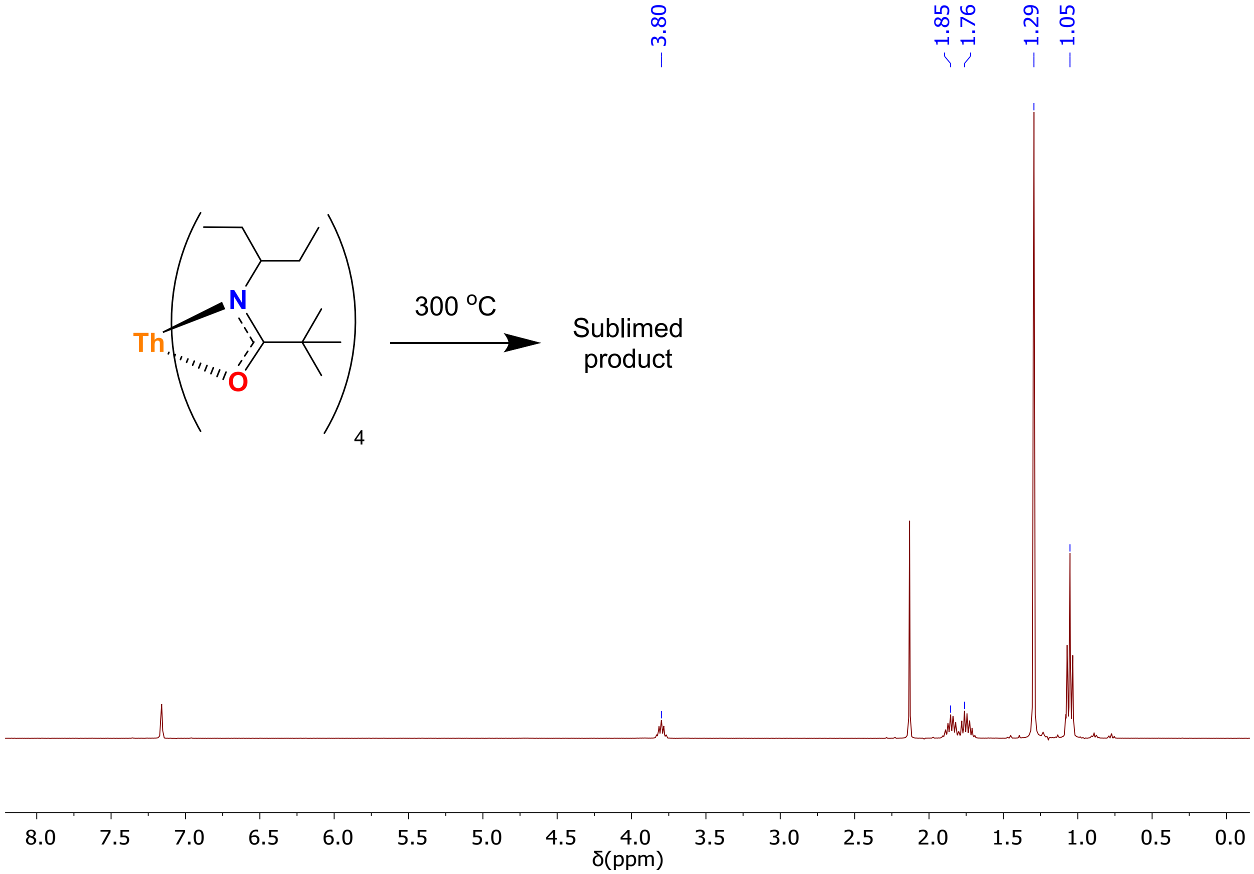

Figure S27. ^{1}H NMR spectrum in C_6D_6 of **2** after heating a solid sample to 300 °C for 16 h. Under these conditions, **2** sublimed completely; no decomposition was observed. The peak at 2.13 ppm is from C_6Me_6 (internal standard).

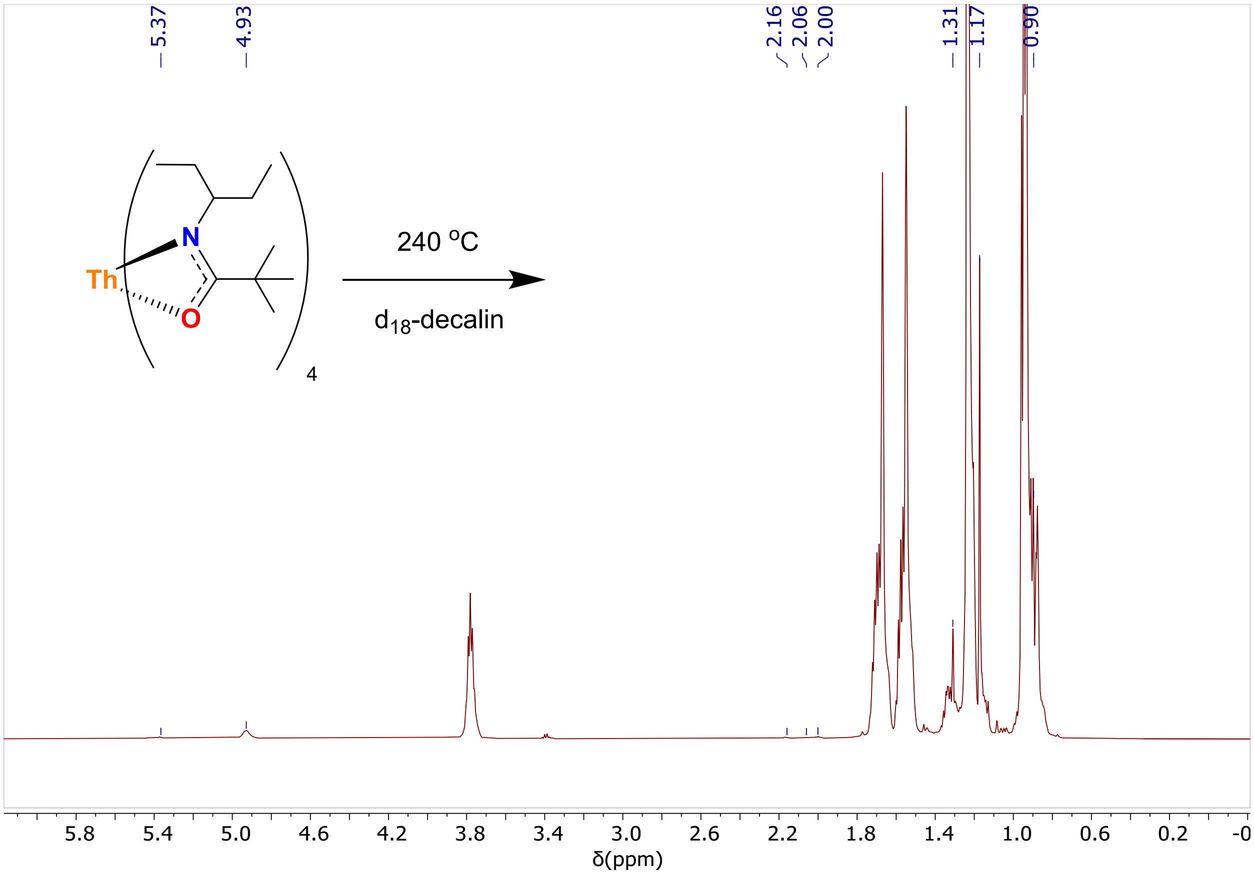

Figure S28. ^{1}H NMR spectrum in C_6D_6 of the products formed by heating a sample of **2** to 240 °C for 2 weeks in d_{18}-decalin. Although most of the starting material was still present after this time, decomposition products were present in sufficient quantities to facilitate identification and their presence was confirmed by spiking. The pivalonitrile resonance is present at 1.31 ppm, the H(TEPA) resonances are present at 4.93, 1.17, and 0.90 ppm, and the 2-pentene resonances are present at 5.37, 2.16, 2.06, and 2.00 ppm. Resonances that overlap with starting material or decalin have been excluded from this list for clarity.

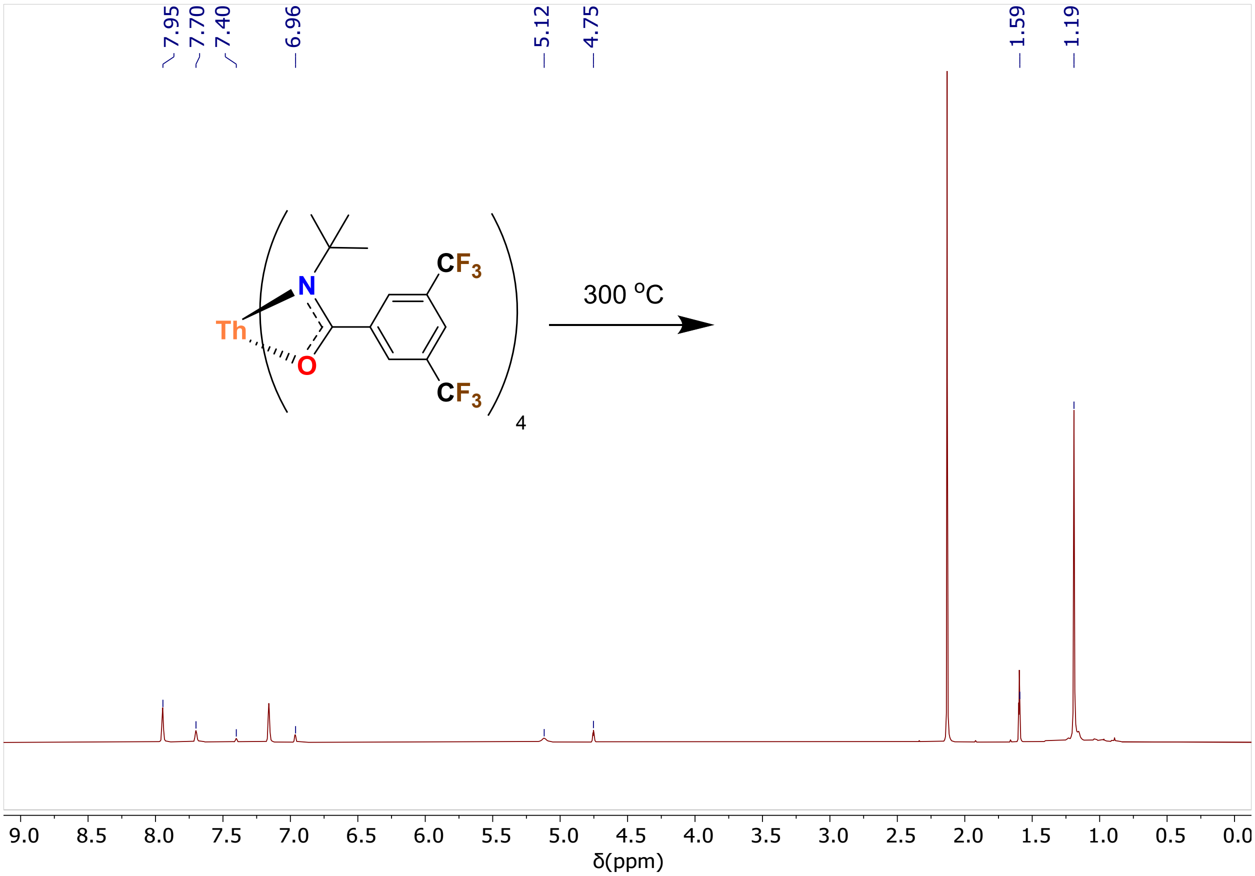

Figure S29. ^{1}H NMR spectrum in C_6D_6 of the products formed by heating a solid sample of **3** to 300 °C for 16 h. The isobutylene resonances are present at 4.75 and 1.59 ppm, the (3,5-bis(trifluoromethyl))benzonitrile resonances are present at 7.40 and 6.96 ppm, and the H(Ar^{F}TA) resonances are present at 7.95, 7.70, 5.12, and 1.19 ppm. The peak at 2.13 ppm is from C_6Me_6 (internal standard).

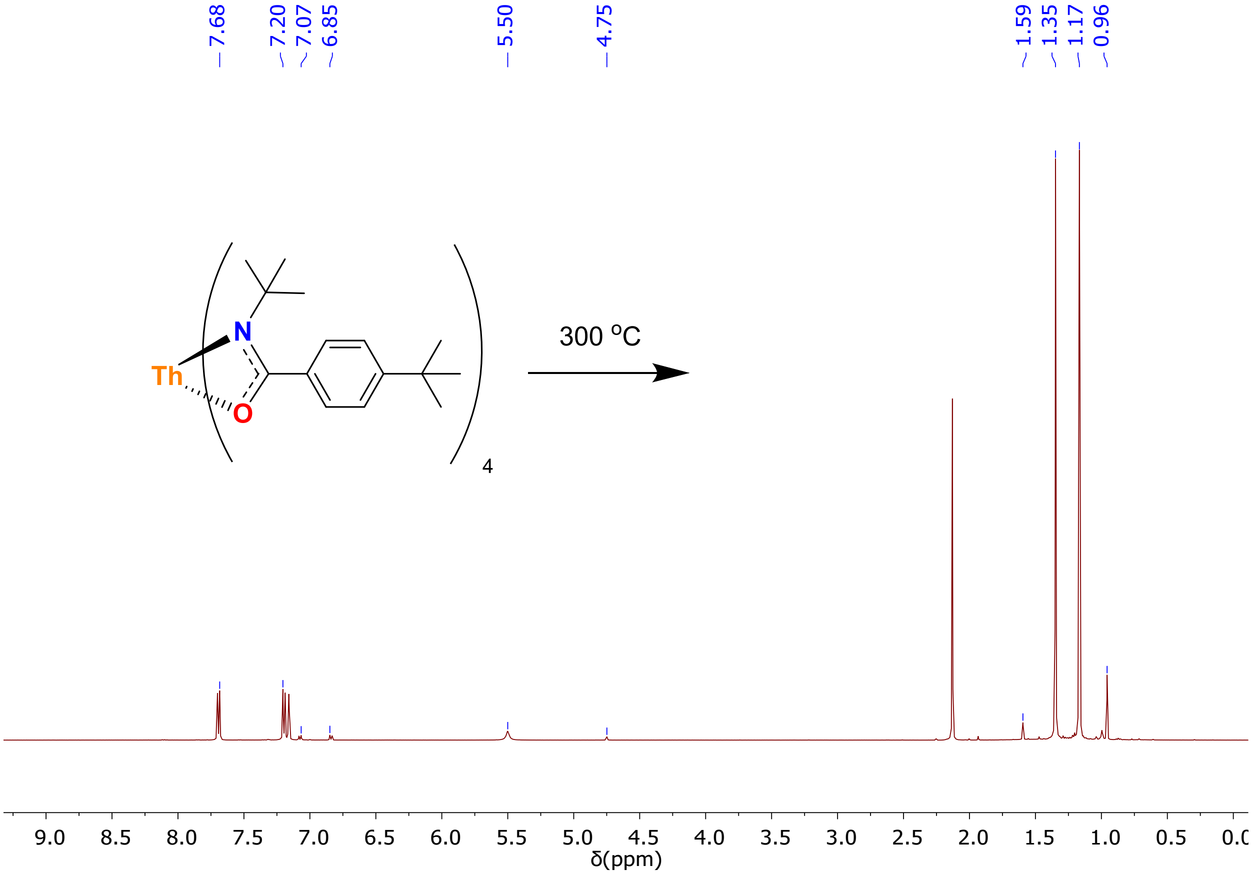

Figure S30. ^{1}H NMR spectrum in C_6D_6 of the products formed by heating a solid sample of **4** to 300 ^{o}C for 16 h. The isobutylene resonances are present at 4.75 and 1.59 ppm, the (4-tert-butyl)benzonitrile resonances are present at 7.07, 6.85, and 0.96 ppm, and the H(TPTA) resonances are present at 7.68, 7.20, 5.05, 1.35, and 1.17 ppm. The peak at 2.13 ppm is from C_6Me_6 (internal standard).

D. IR Spectra

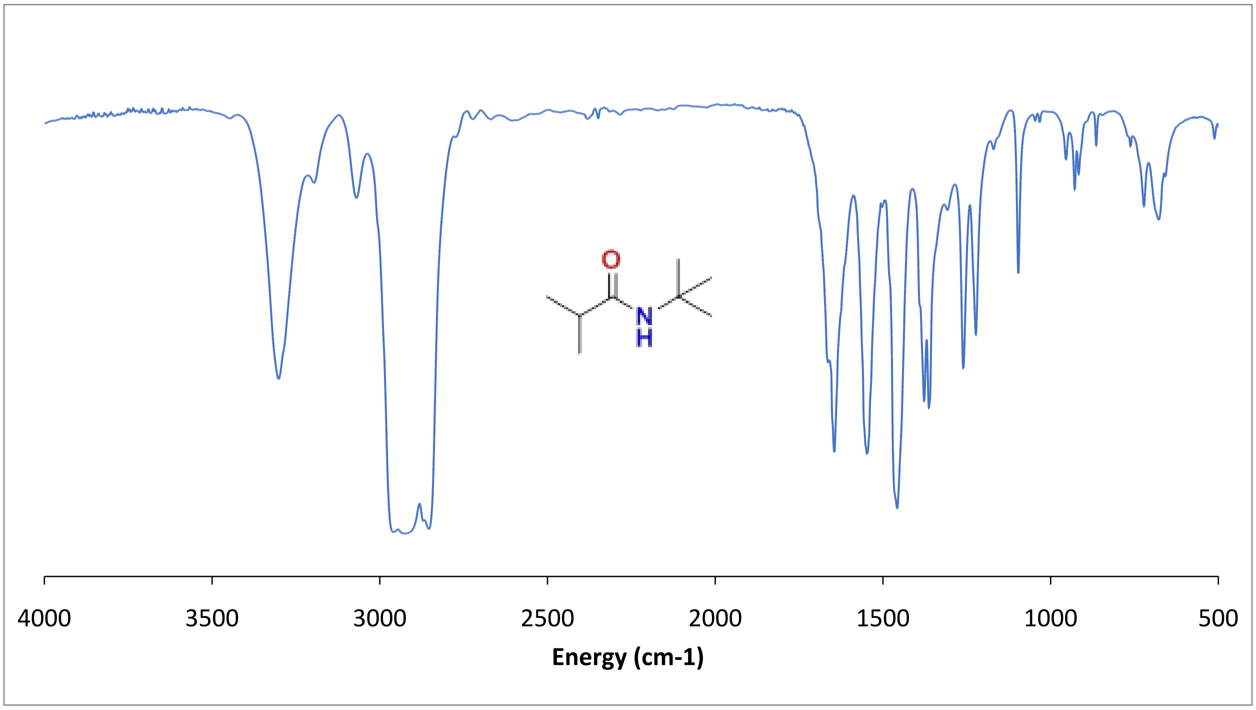

Figure S31. IR spectrum of H(ITA) prepared as a Nujol mull.

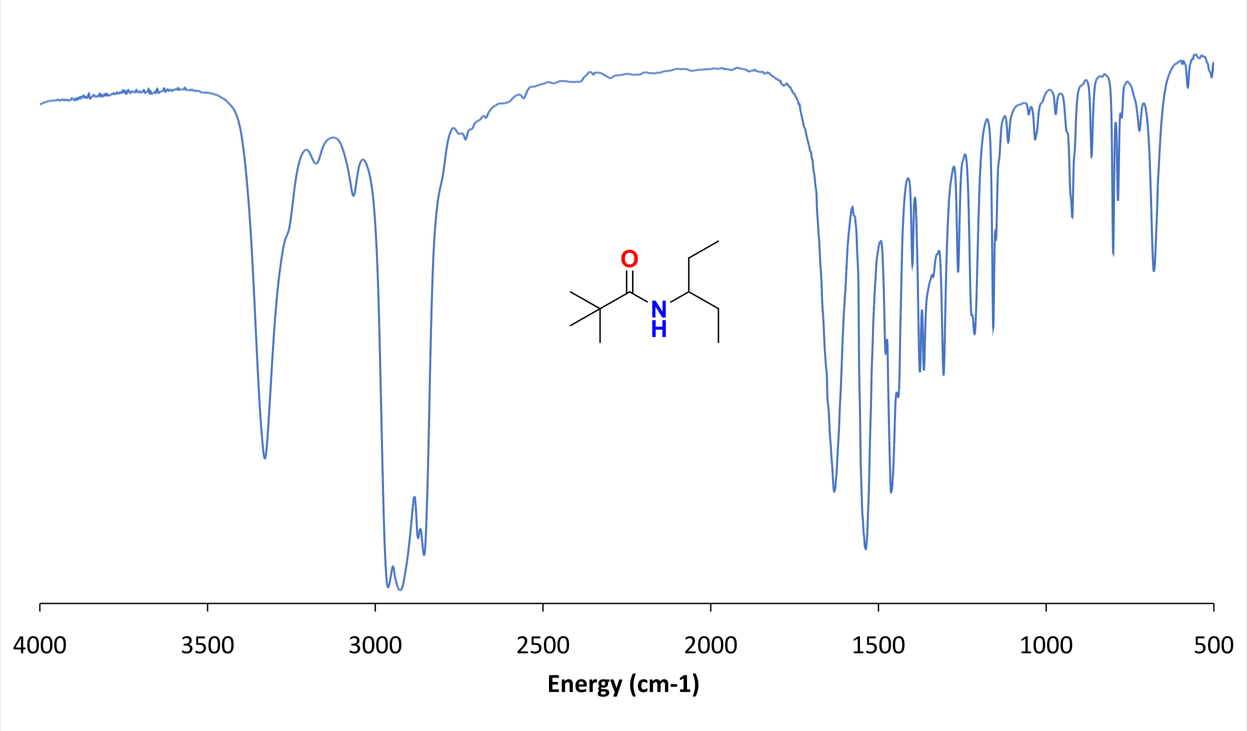

Figure S32. IR spectrum of H(TEPA) prepared as a Nujol mull.

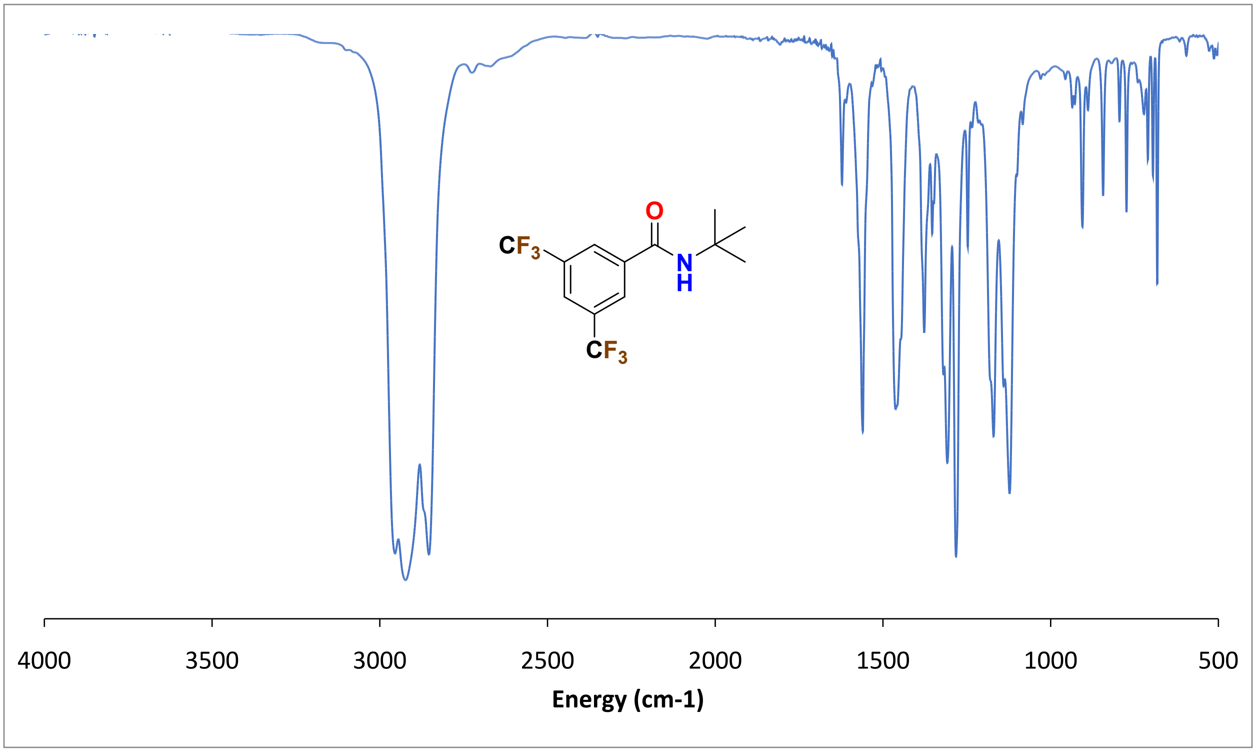

Figure S33. IR spectrum of H(Ar^{F}TA) prepared as a Nujol mull.

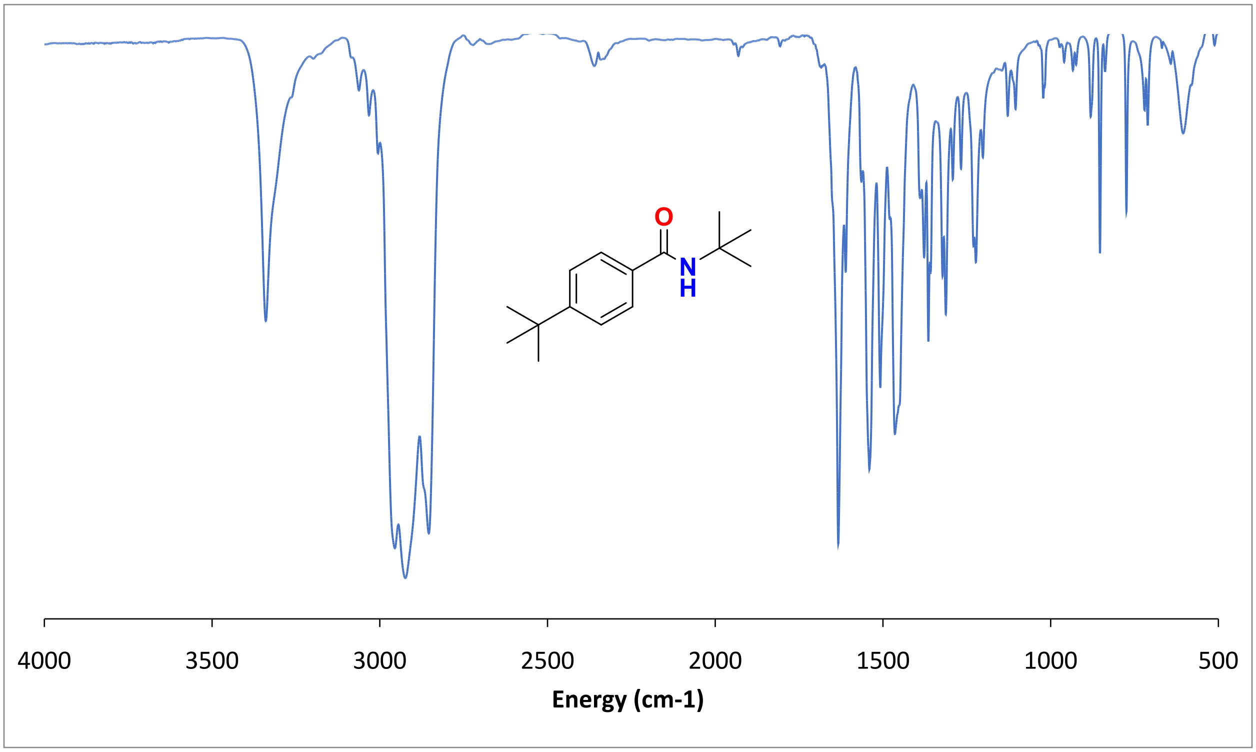

Figure S34. IR spectrum of H(TPTA) prepared as a Nujol mull.

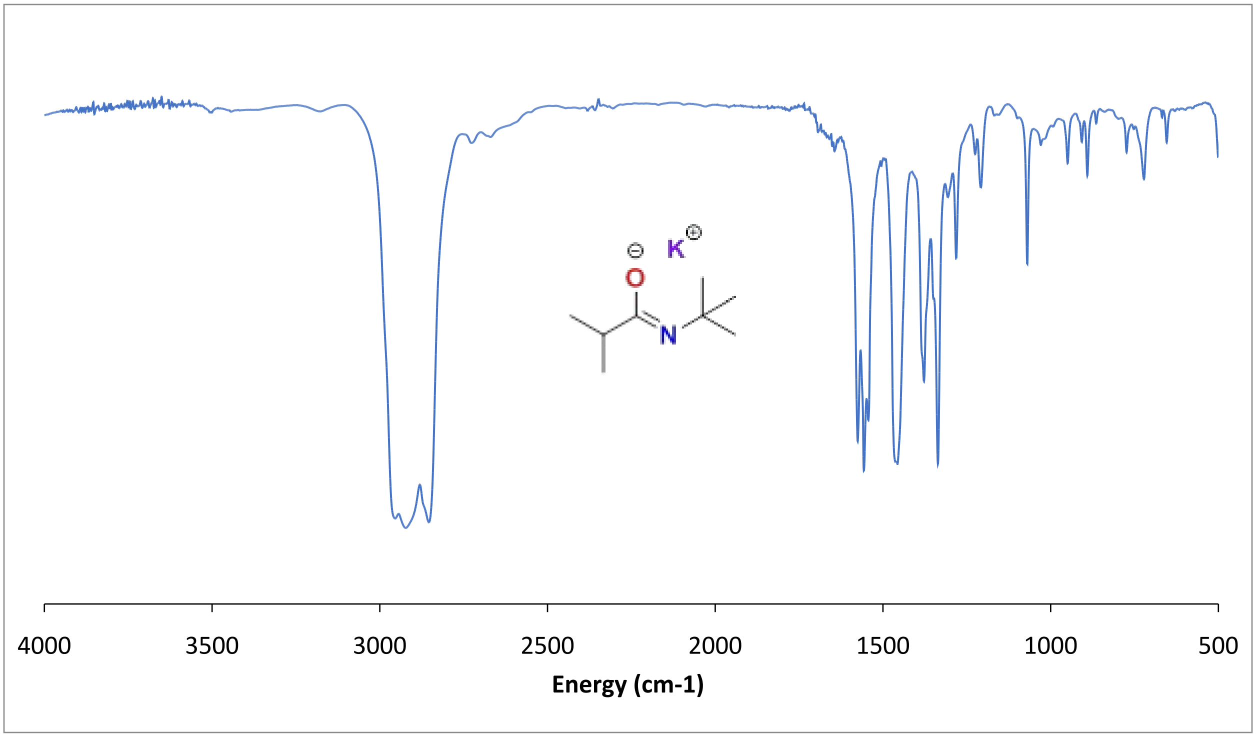

Figure S35. IR spectrum of K(ITA) prepared as a Nujol mull.

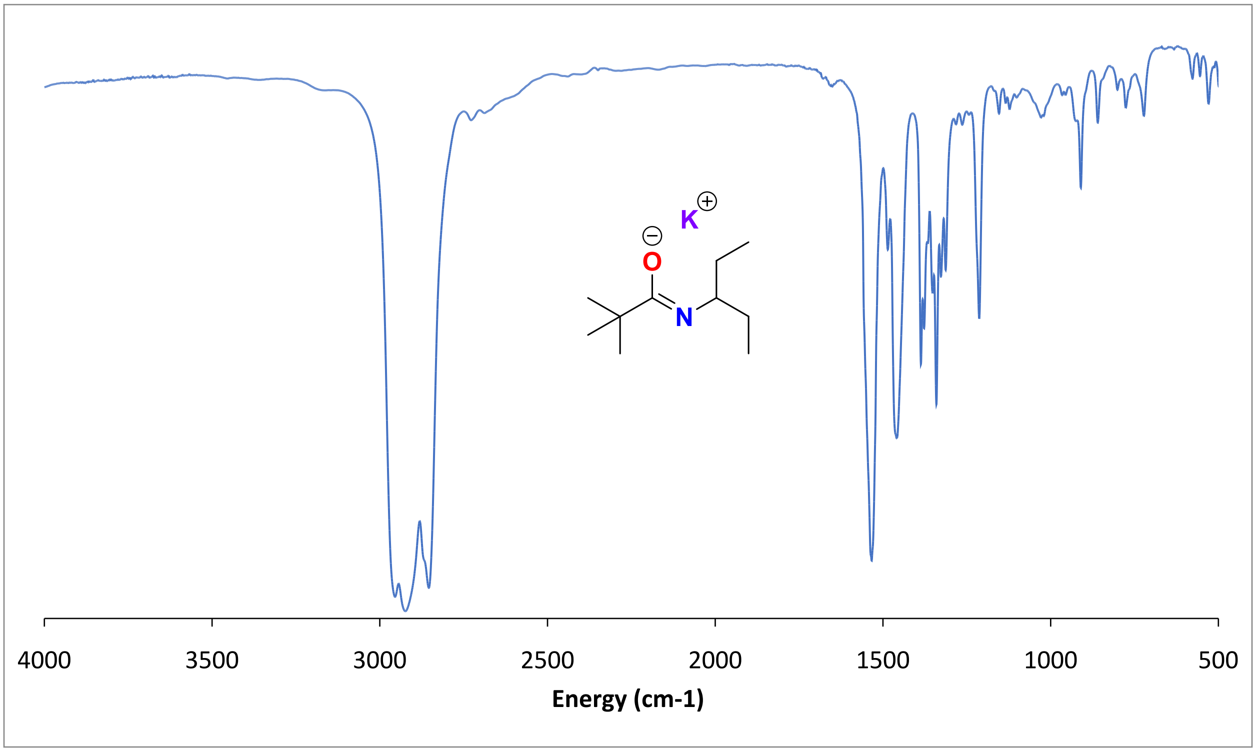

Figure S36. IR spectrum of K(TEPA) prepared as a Nujol mull.

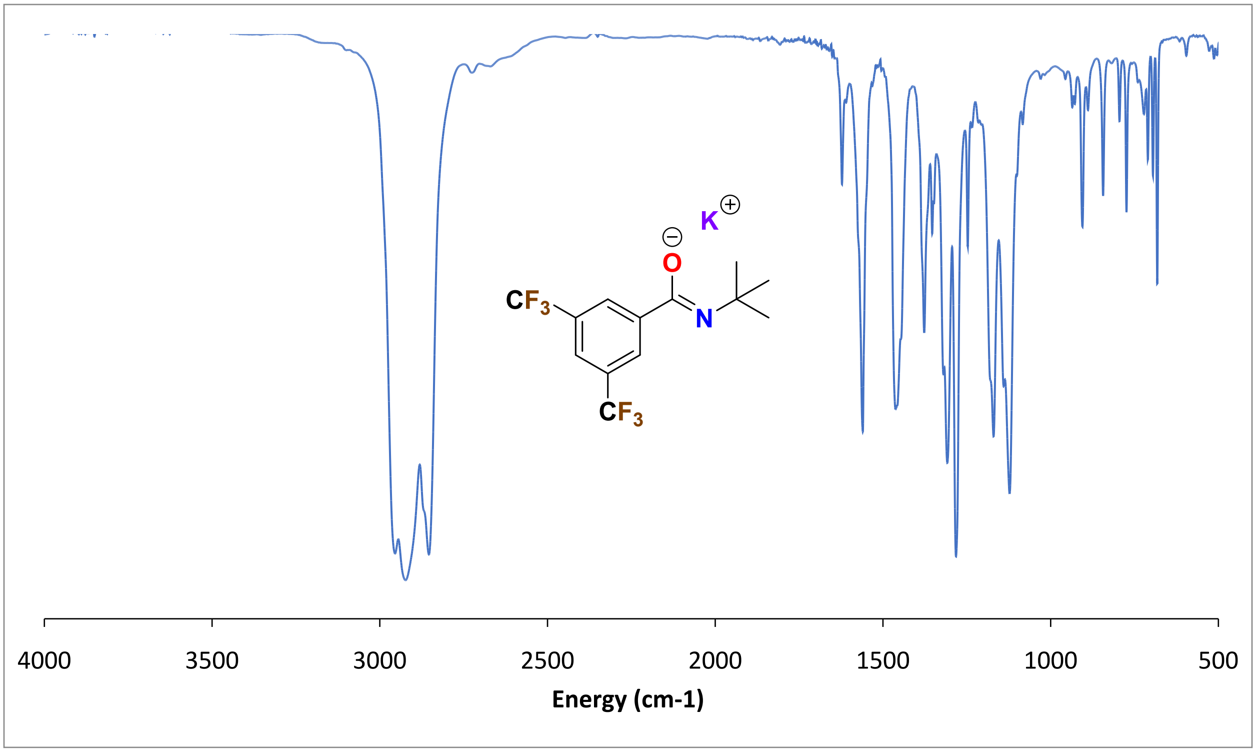

Figure S37. IR spectrum of K(Ar^{F}TA) prepared as a Nujol mull.

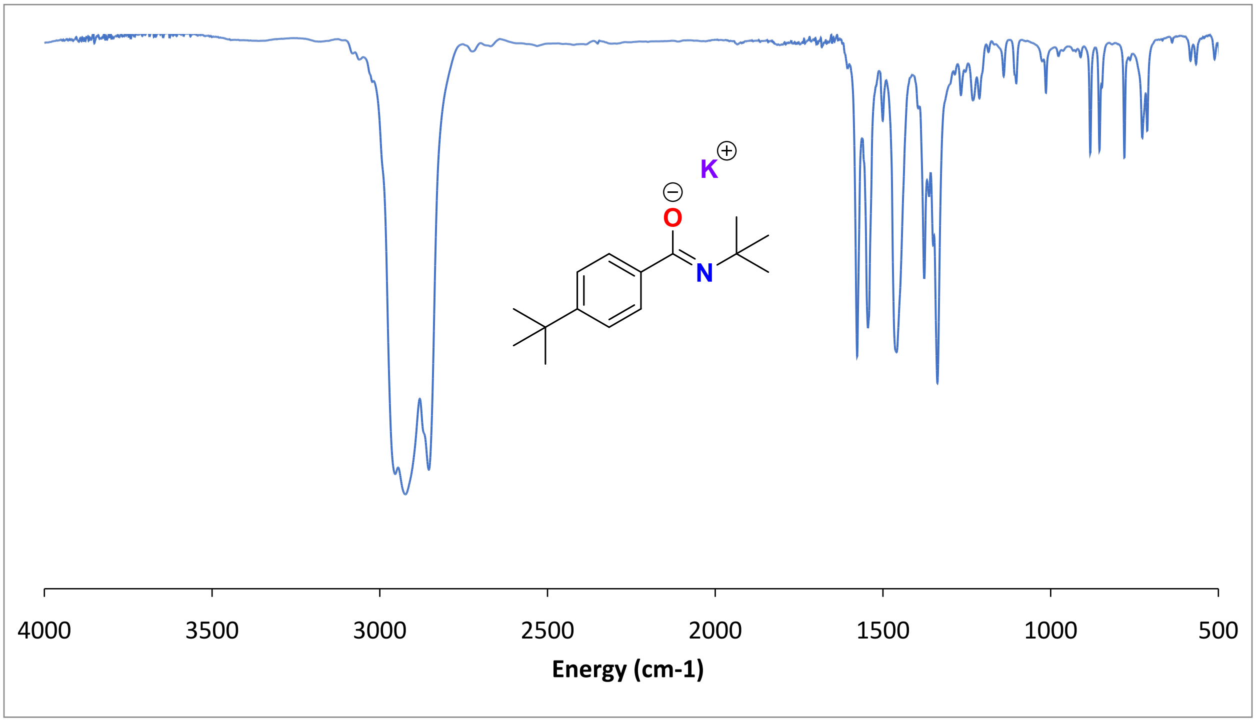

Figure S38. IR spectrum of K(TPTA) prepared as a Nujol mull.

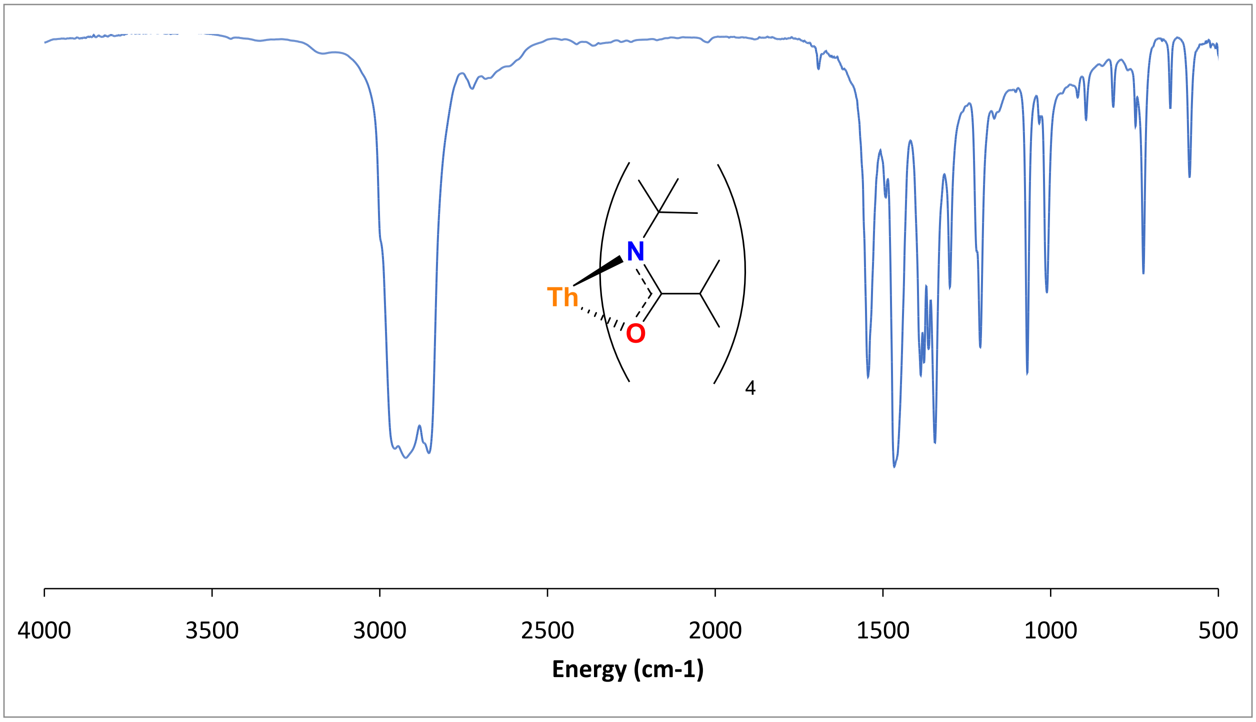

Figure S39. IR spectrum of Th(ITA)$_4$ **(1)** prepared as a Nujol mull.

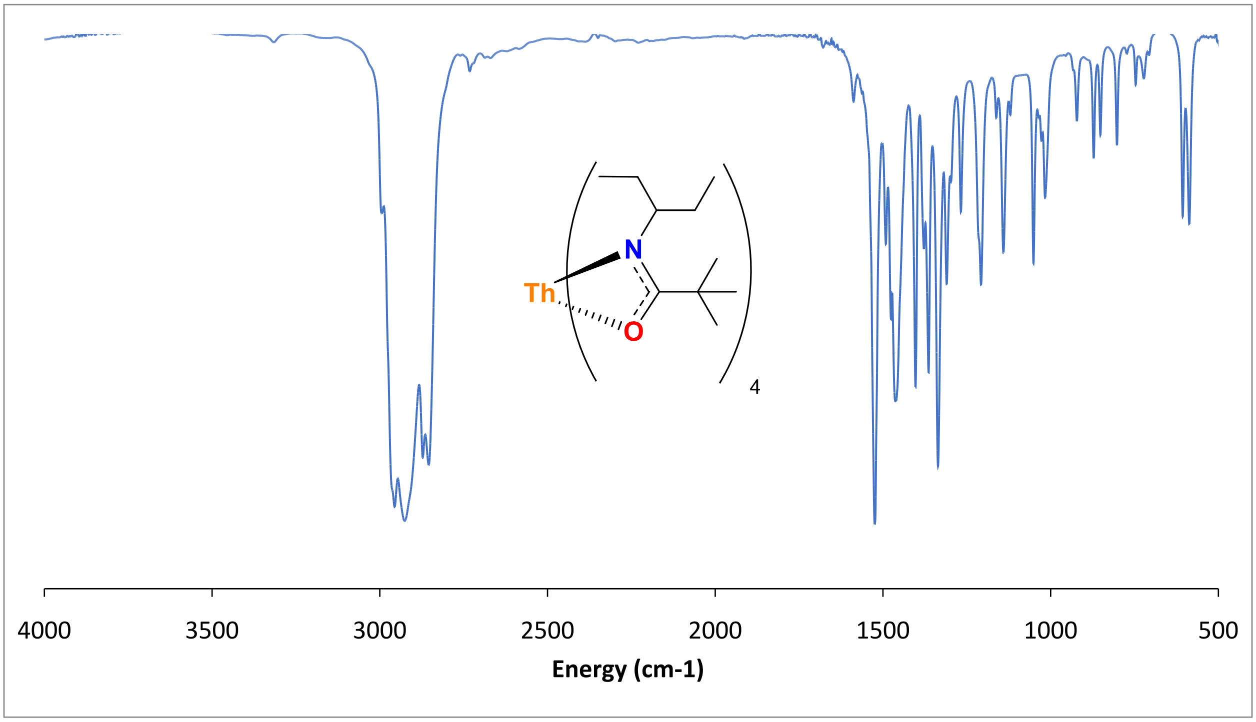

Figure S40. IR spectrum of Th(TEPA)$_4$ **(2)** prepared as a Nujol mull.

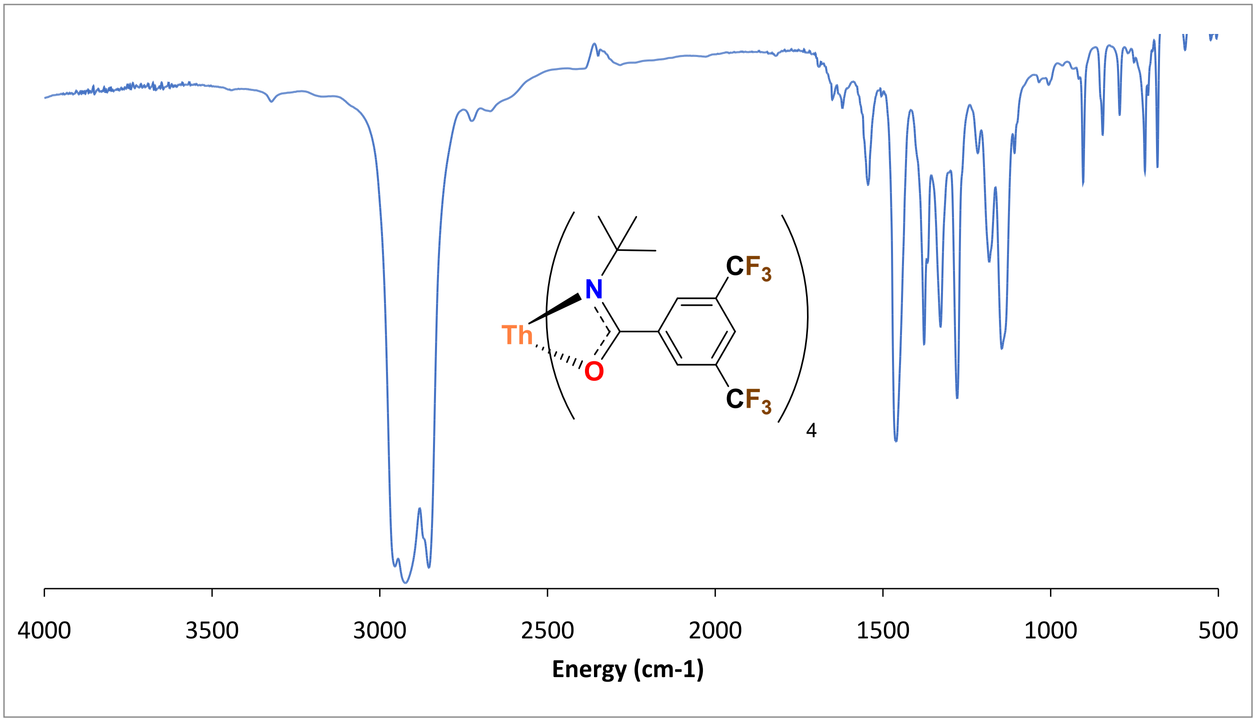

Figure S41. IR spectrum of Th(Ar^{F}TA)$_4$ **(3)** prepared as a Nujol mull.

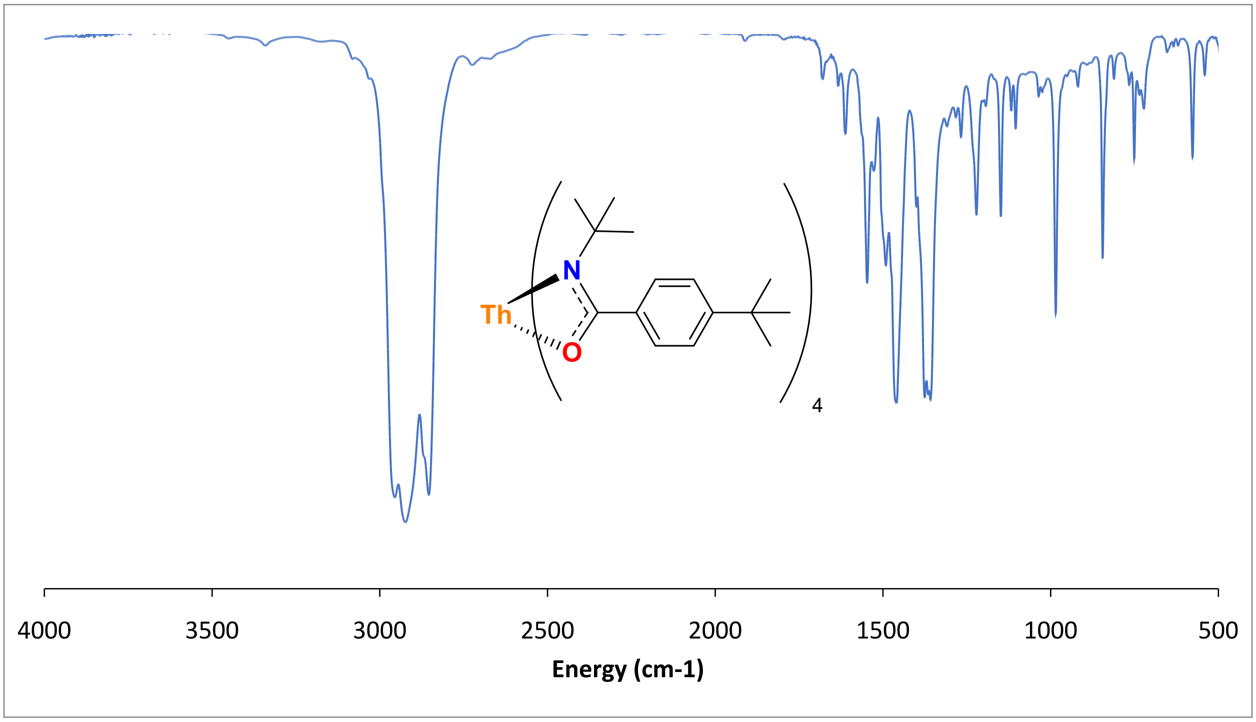

Figure S42. IR spectrum of Th(TPTA)$_4$ **(4)** prepared as a Nujol mull.

E. References

1 M. D. Straub, J. Leduc, M. Frank, A. Raauf, T. D. Lohrey, S. G. Minasian, S. Mathur and J. Arnold, *Angew. Chem. Int. Ed.*, 2019, **58**, 5749–5753.

2 B.-H. Huang, T.-L. Yu, Y.-L. Huang, B.-T. Ko and C.-C. Lin, *Inorg. Chem.*, 2002, **41**, 2987–2994.

3 C. Li, R. K. Thomson, B. Gillon, B. O. Patrick and L. L. Schafer, *Chem. Commun.*, 2003, **98**, 2462.

4 R. Zhao and W. Lu, *Org. Lett.*, 2017, **19**, 1768–1771.

5 T. Cantat, B. L. Scott, and J. L. Kiplinger, *Chem. Commun.*, 2010, **46**, 919.

6 H. J. Whitfield, D. Roman and A. R. Palmer, *J. Inorg. Nucl. Chem.*, 1966, **28**, 2817–2825.

7 L. M. Moreau, A. Herve, M. D. Straub, D. R. Russo, R. J. Abergel, S. Alayoglu, J. Arnold, A. Braun, G. J. P. Deblonde, Y. Liu, T. D. Lohrey, D. T. Olive, Y. Qiao, J. A. Rees, D. K. Shuh, S. J. Teat, H. Booth and S. G. Minasian, *Chem. Sci.*, 2020, **11**, 4648–4668.

8 A. B. Altman, J. I. Pacold, J. Wang, W. W. Lukens and S. G. Minasian, *Dalton Trans.*, 2016, **45**, 9948–9961.

9 T.-C. Weng, G. S. Waldo and J. E. Penner-Hahn, *J. Synchrotron Radiat.*, 2004, **12**, 506–510.

10 APEX3, SADABS, and SAINT. Bruker AXS. Madison, WI, USA.

11 CrysAlisPro 1.171.39.45f (Rigaku Oxford Diffraction, 2018).

12 G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.

13 G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3–8.

14 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

15 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. Van De Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466–470.