Supporting Information for:

Trimethyltriazacyclohexane Coordination Chemistry of Simple Rare-Earth Metal Salts

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Experimental

All synthesis and manipulations were conducted with rigorous exclusion of air and water using standard vacuum line and glovebox techniques. Solvents were sparged with UHP argon and dried by passage through columns containing water and oxygen scavengers. Deuterated NMR solvents were dried over NaK alloy, degassed by three freeze-pump-thaw cycles, and vacuum transferred before use. ^{1}H and ^{13}C NMR spectra were recorded on a CRYO500 MHz spectrometer at 298 K. Infrared spectra were recorded as compressed solids on an Agilent Cary 630 ATR-FTIR. Elemental analyses were conducted at the Irvine Materials Research Institute on a ThermoFisher FlashSmart CHNS/O Elemental Analyzer.

Anhydrous $LnCl_3$,[1] $La(OTf)_3$,[1a,2] $SmI_2(THF)_2$,[2] and $LnI_3(THF)_x$,[3] were prepared as previously described. Anhydrous, base-free SmI_2 (Sigma) was used as received. Me_3tach and Me_3tacn (Fisher) were purchased under argon and kept over molecular sieves in the glovebox.

Synthesis of $(Me_3tach)_2LaI_3$, 1-La. $LaI_3(THF)_4$ (130 mg, 0.161 mmol) was dissolved in THF (5 mL) to form a colorless solution. Me_3tach (48 mg, 0.37 mmol) was dissolved in THF (1 mL) and was slowly added to the stirring solution by pipet. The solution was stirred for two hours and a small amount of precipitate formed. The solids were removed via filtration and the solvent was removed under vacuum to afford a white powder. The solids were redissolved in minimal THF and layered under hexane and placed at −35 °C. Colorless crystals of **1-La**, suitable for X-ray diffraction, were grown overnight (9 mg, 14%). The data provided connectivity of the molecule only. ^{1}H NMR (THF-d_8): δ 5.48 (s, 6H, CH_2), 3.13 (s, 6H, CH_2), 2.46 ppm (s, 18H, Me). ^{13}C NMR (THF-d_8): δ 80.1 (CH_2), 38.6 ppm (Me). IR (cm^{-1}): 2954w, 2903w, 2864w, 2801m, 2748w, 2687w, 1686w, 1640w, 1465m, 1384m, 1260s, 1165m, 1104s, 1009m, 935s, 889w, 801w. Anal. Calcd for $C_{12}H_{30}N_6LaI_3$: C, 18.53; H, 3.89; N, 10.80. Found: C, 19.940;

H, 4.193; N, 11.679. The values were consistently high and suggest incomplete combustion or decomposition of the sample. The observed ratio of $C_{12}H_{30.1}N_{6.0}$ is close to the expected values.

Synthesis of $(Me_3tach)_2CeI_3$, 1-Ce. As described above for **1-La**, $CeI_3(THF)_4$ (53 mg, 0.065 mmol) and Me_3tach (20 mg, 0.15 mmol) were reacted in THF (3 mL). Colorless crystals of **1-Ce** were grown from THF/hexane at −35 °C overnight (33 mg, 65%). The data provided connectivity of the molecule only. ^{1}H NMR (THF-d_8): δ 38.95 (br s, 6H, CH_2), 29.23 (br s, 6H, CH_2), 6.93 ppm (br s, 18H, Me). ^{13}C NMR (THF-d_8): δ 48.6 (CH_2), 30.4 ppm (Me). IR (cm^{-1}): 1984w, 1950w, 2908w, 2860w, 2801m, 2749m, 2686m, 1642m, 1464s, 1384s, 1361m, 1287m, 1259s, 1165m, 1106s, 1075m, 1042w, 1009m, 936s, 866m, 861w, 795w, 727w, 694w. Anal. Calcd for $C_{12}H_{30}N_6CeI_3$: C, 18.50; H, 3.88; N, 10.79. Found: C, 21.03; H, 3.782; N, 9.213. The values were consistently high and suggest incomplete combustion or decomposition of the sample. The observed ratio of $C_{12}H_{30.0}N_{6.0}$ matches the expected values.

Synthesis of $(Me_3tach)_2NdI_3$, 1-Nd and $[(Me_3tach)_2NdI_2][I]$, 2-Nd. As above, $NdI_3(THF)_{3.5}$ (102 mg, 0.131 mmol) was reacted with Me_3tach (34 mg, 0.26 mmol) in THF (5 mL). Pale blue needle-like crystals of **1-Nd** suitable for X-ray diffraction were grown from THF/hexane at −35 °C overnight (85 mg, 83%). The data provided connectivity of the molecule only. Pale blue parallelepiped crystals of **2-Nd** were grown by recrystallization of **1-Nd** from THF/hexane at −35 °C. No resonances in the ^{1}H NMR spectrum were observed between ± 400 ppm besides residual solvent. IR (cm^{-1}): 2919m, 2869m, 2804m, 2748m, 2684m, 1642s, 1449s, 1385s, 1288w, 1261s, 1169s, 1104s, 1078m, 1041m, 937s, 888m, 799w, 723w, 693w. Anal. Calcd for $C_{12}H_{30}N_6NdI_3$: C, 18.40; H, 3.86; N, 10.73. Found: C, 17.63; H, 4.261; N, 8.700.

Crystallization of $[(Me_3tach)_2SmI_2][I]$, 2-Sm. $SmI_2(THF)_2$ (67 mg, 0.12 mmol) was dissolved in THF (2 mL) to form a deep blue solution. Me_3tach was dissolved in THF and added

to the stirring solution via pipet. The solution became dark green. After a few hours, the solution became yellow. The solution was stirred overnight then dried under vacuum. The solids were redissolved in minimal THF and layered under hexane and placed at −35 °C. A few colorless crystals of **2-Sm**, suitable for X-ray diffraction, were grown overnight. The data provided connectivity of the molecule only.

Synthesis of $(Me_3tach)_2LaCl_3$, 3-La. $LaCl_3$ (44 mg, 0.18 mmol) was added to THF (5 mL). Me_3tach (46 mg, 0.36 mmol) was dissolved in THF and added to the stirring suspension by pipet. White solid immediately precipitated. The suspension was stirred for 90 minutes then the mixture was centrifuged. The colorless supernatant was collected and dried under vacuum to yield white solids of **3** (7 mg, 8%). Colorless hexagonal prism crystals of **3** were grown from THF/hexane at −35 °C overnight. ^{1}H NMR (THF-d_8): δ 2.20 ppm (s, 18H, Me). Only one resonance was observed, presumably due to the low solubility, and a ^{13}C spectrum could not be obtained. IR (thin film from THF-d_8, cm^{-1}): 2921s, 2853m, 2806m, 2749w, 2686w, 1644m, 1453s, 1385m, 1263s, 1171m, 1108s, 1079m, 1043m, 1013m, 938s, 889w, 825w.

Synthesis of $(Me_3tach)YCl_3(THF)_2$, 4-Y. YCl_3 (50 mg, 0.20 mmol) was stirred in THF (5 mL). Me_3tach was added by pipet to the stirring slurry to form a colorless solution. The solution was stirred for two hours then dried under vacuum. The white solids were redissolved in minimal THF and layered under hexane at −35 °C. Large, colorless crystals of **4**, suitable for X-ray diffraction, were grown overnight (97 mg, 92%). ^{1}H NMR (THF-d_8): δ 4.48 (d, J = 6.9 Hz, 6H, CH_2), 3.05 (d, J = 6.9 Hz, 6H, CH_2), 2.35 ppm (s, 18H, Me). ^{13}C NMR (THF-d_8): δ 77.8 (CH_2), 38.5 ppm (CH_3). Only unbound, free THF was observed in the NMR spectra. IR (cm^{-1}): 2966m, 2898m, 2879m, 2811m, 1648m, 1454s, 1384s, 1264s, 1175s, 1110s, 1015s, 939s, 865s, 666m.

Anal. Calcd for $C_{14}H_{36}N_3O_2YCl_3$: C, 35.88; H, 6.67; N, 8.97. Found: C, 15.70; H, 5.998; N, 8.432. Low C values suggest incomplete combustion or carbide formation.

Synthesis of {[(Me$_3$tach)La(μ–OH)(μ–OTf)]$_2$(μ–OTf)$_2$}$_2$, 5-La. La(OTf)$_3$ (66 mg, 0.11 mmol) was dissolved in THF. Me$_3$tach (29 mg, 0.22 mmol) was added to the stirring solution by pipet. The solution was dried, the solids were redissolved in minimal THF, layered under hexane, and placed at −35 °C. Overnight, colorless crystals of **5** suitable for X-ray diffraction deposited. The infrared spectrum of the La(OTf)$_3$ starting material showed two broad absorptions above 3000 cm^{-1}.

Synthesis of [(Me$_3$tach)$_2$La(OTf)$_4$][HMe$_3$tach], 6-La. La(OTf)$_3$ (52 mg, 0.089 mmol) was dissolved in THF to form a colorless solution. Me$_3$tach (23 mg, 0.18 mmol) was added by pipet and the solution was stirred overnight. The solvent was removed under vacuum and the product was extracted in toluene and placed at −35 °C. Overnight, large colorless plates of **6·toluene** deposited.

Synthesis of (Me$_3$tach)$_2$SmI$_2$(THF), 7-Sm. Me$_3$tach (24 mg, 0.19 mmol) was dissolved in THF. SmI$_2$ (50 mg, 0.12 mmol) was added to the stirring solution. The solution became green. The solution was stirred for 30 minutes then dried under vacuum to afford red solids. The solids were redissolved in minimal THF, layered under Et$_2$O, and placed at −35 °C for crystallization. Over two days, dark green crystals of **7** formed (50 mg, 55%). The crystal data was not of high enough quality to discuss metrical parameters but provided connectivity of the molecule. ^{1}H NMR (THF-d_8): δ −3.24 ppm. This was the only resonance observed between 600 and −300 ppm. No ^{13}C signals were observed in a reasonable scan time. IR (cm^{-1}): 2983w, 2951m, 1866m, 2798m, 2737m, 2687m, 2664w, 1643m, 1468s, 1446s, 1385s, 1267s, 1161s, 1110s, 1082m, 1042w, 1013s,

932s, 886w, 739m. Anal. Calcd for $C_{16}H_{38}N_6OsmI_2$: C, 26.16; H, 5.21; N, 11.44. Found: C, 24.98; H, 4.838; N, 11.02. The observed ratio of $C_{16}H_{36.9}N_{6.1}$ is close to the expected values.

Synthesis of (Me_3tacn)LaI_3(THF), 8-La. $LaI_3(THF)_4$ (56 mg, 0.069 mmol) was dissolved in THF. Me_3tacn (~50 mg, 0.292 mmol) was added to the stirring solution. The solution was stirred for 15 minutes then dried under vacuum. The white solids were redissolved in minimal THF, layered under hexane, and placed at −35 °C for crystallization. Overnight, colorless needles of **8** suitable for X-ray diffraction were formed (26 mg, 49%). ^{1}H NMR (THF-d_8): δ 3.68 (m, 6H, CH_2), 3.07 (s, 9H, Me), 2.89 ppm (m, 6H, CH_2). ^{13}C NMR (THF-d_8): δ 58.1 (CH_2), 50.5 ppm (Me). IR (cm^{-1}): 2921w, 2848w, 2822w, 2770w, 1635w, 1446s, 1368s, 1341m, 1302m, 1279m, 1220w, 1188m, 1065s, 1031m, 998s, 861m, 819w, 764m, 738s, 692m. Anal. Calcd for $C_{13}H_{29}N_3OlaI_3$: C, 20.46; H, 3.83; N, 5.51. Found: C, 19.91; H, 3.601; N, 4.990.

Synthesis of (Me_3tacn)YCl_3, 9-Y. YCl_3 (50 mg, 0.26 mmol) was added to THF (5 mL) to form a white slurry. Me_3tacn (44 mg, 0.26 mmol) was added and the mixture became a colorless solution. The solution was stirred for two hours then dried under vacuum. The mixture was redissolved in minimal THF and layered under hexane at −35 °C. Overnight, white crystals of **9** suitable for X-ray diffraction formed (13 mg, 14%). ^{1}H NMR (THF-d_8): δ 3.33 (m, 6H, CH_2), 2.85 (s, 9H, Me), 2.76 ppm (m, 6H, CH_2). ^{13}C NMR (THF-d_8): δ 56.7 (CH_2), 49.4 ppm (Me). IR (cm^{-1}): 2993w, 2966w, 2933w, 2903w, 2865w, 2824w, 1490m, 1462s, 1364m, 1298s, 1201m, 1153m, 1124w, 1060s, 998s, 884m, 773s, 741s. Anal. Calcd for $C_9H_{21}N_3YCl_3$: C, 29.49; H, 5.78; N, 11.46. Found: C, 30.92; H, 6.048; N, 10.77.

Synthesis of (Me_3tacn)SmI_2(THF), 10-Sm. SmI_2 (50 mg, 0.12 mmol) and Me_3tacn (16 mg, 0.93 mmol) were combined in THF (5 mL) to form a blue/green solution. The solution was stirred for 30 minutes the dried. The mixture was redissolved in minimal THF and layered under

hexane at −35 °C. Overnight, dark blue crystals of **10** suitable for X-ray diffraction formed (14 mg, 18%). ^{1}H NMR (THF-d_8): δ 17.56 (s, 9H, Me), −2.08 (s, 6H, CH_2), −6.34 ppm (s, 6H, CH_2). No ^{13}C resonances were observed in a reasonable scan time. IR (cm^{-1}): 2935m, 2882, 2810m, 1449s, 1366m, 1340w, 1294m, 1174m, 1148m, 1102m, 1066m, 1005s, 917w, 871s, 823s, 749s, 670w.

Crystallization of [HMe$_3$tach][Cl]. Colorless crystals of [HMe$_3$tach][Cl] were obtained from THF/hexane at −35 °C from the reaction of $ScCl_3$ with 2 equivalents of Me$_3$tach in THF. The crystal data were not of high enough quality to discuss metrical parameters but provided connectivity of the molecule.

Crystallization of [HMe$_3$tach][Br]. Colorless crystals of [HMe$_3$tach][Br] were obtained from a concentrated THF solution at −20 °C from the reaction of $ThBr_4(THF)_4$ with 2 equivalents of Me$_3$tach in THF.

Crystallization of [HMe$_3$tach][I]. Colorless crystals of [HMe$_3$tach][I] were obtained from a concentrated THF solution at −35 °C from the reaction of $TbI_3(THF)_{3.5}$ with 2 equivalents of Me$_3$tach in THF. The crystal data were not of high enough quality to discuss metrical parameters but provided connectivity of the molecule.

Crystallization of [HMe$_3$tacn][OTf]. Colorless rod-like crystals of [HMe$_3$tacn][OTf] were obtained from THF/hexane at −35 °C during the reaction of $La(OTf)_3$ with Me$_3$tacn. The crystal data were not of high enough quality to discuss metrical parameters but provided connectivity of the molecule.

Table S1: M–Cnt distances in rare-earth metal R_3tach complexes. Complexes containing chelating R substituents are omitted. [a] one distance due to symmetry

	M–Cnt (Å)	Eight-coordinate ionic radius (Å)[4]	M–Cnt distance – radius (Å)
$(Me_3tach)_2LaCl_3$, **3-La**	2.428[a]	1.16	1.268
$[(Me_3tach)La(O_2CCPh_3)](\mu$–$O_2CCPh_3)_3[La(O_2CCPh_3)_2]$[5]	2.395	1.16	1.235
$(^iPr_3tach)La[\eta^4$-$Me_3AlCH_2AlMe_2CH_2AlMe_3]$[6]	2.405	1.16	1.245
5-La	2.411, 2.419	1.16	1.251, 1.259
6-La	2.449, 2.454	1.16	2.289, 1.294
$(Me_3tach)La(AlMe_4)(Me_3AlCH_2AlMe_3)$[7]	2.465	1.16	1.305
$(Me_3tach)La(O_2CCPh_3)_4][MeNH_3]$[5]	2.488	1.16	1.328
$(^tBu_3tach)La[\eta^4$-$Me_3AlCH_2AlMe_2CH_2AlMe_3]$[6]	2.469	1.16	1.309
$(Me3tach)Ce(CF_3$-camphor$)_2$[8]	2.462	1.143	1.319
$[(Et_3tach)Pr(OTf)_2]_3(\mu$–$OTf)_3$[9]	2.282, 2.291	1.126	1.156, 1.165
$(Me_3tach)_2Pr(OTf)_3$[9]	2.305, 2.307	1.126	1.179, 1.181
$(Me_3tach)Pr[CH(AlMe_3)_3]$[6]	2.322, 2.398	1.126	1.196, 1.272
$(^tBu_3tach)Pr[\eta^4$-$Me_3AlCH_2AlMe_2CH_2AlMe_3]$[6]	2.411	1.126	1.285
$(Me_3tach)NdCl_2(C_5Ph_3H_2)$[10]	2.295	1.109	1.186
$(Me_3tach)Nd(O_2CCPh_3)_3$[5]	2.316	1.109	1.207
$(Me_3tach)Sm[\eta^4$-$Me_3AlCH_2AlMe_2CH_2AlMe_3]$[7]	2.262, 2.270	1.079	1.183, 1.191
$(^iPr_3tach)Sm[\eta^4$-$Me_3AlCH_2AlMe_2CH_2AlMe_3]$[11]	2.315	1.079	1.236
$(Cy_3tach)Sm[CH(AlMe_3)_3]$[12]	2.351	1.079	1.272
$(^iPr_3tach)_2Sm(AlMe_4)_2$[11]	2.409[a]	1.079	1.330
$(Et_3tach)_2Sm(AlMe_4)_2$[11]	2.416[a]	1.079	1.337
$(cyclohexyl_3tach)_2Sm(AlMe_4)_2$[12]	2.447, 2.455	1.079	1.368, 1.376
$(Me_3tach)TbCl_2[C_5Ph_2(OMePh)H_2]$[10]	2.177, 2.166	1.04	1.137, 1.126
$(Me_3tach)TbCl_2(C_5Ph_3H_2)$[10]	2.181	1.04	1.141
$(Me_3tach)TbCl_2[C_5Ph_2(OMePh)H_2]$[10]	2.170, 2.174, 2.180, 2.193	1.04	1.13, 1.134, 1.14, 1.153
$(Me_3tach)_2Y(C{\equiv}CPh)_2][AlMe_2(C{\equiv}CPh)_2]$[13]	2.160, 2.171	1.019	1.141, 1.152
4-Y	2.214	1.019	1.195
$(^iPr_3tach)Y(AlMe_4)(\eta^3$-$Me_3AlCH_2AlMe_3)$[14]	2.22	1.019	1.201
$(^iPr_3tach)Y(AlMe_4)(Me_3AlCH_2AlMe_3)$[14]	2.22	1.019	1.201
$[(Me_3tach)_2YMe_2][AlMe_4]$[14]	2.223, 2.229	1.019	1.204, 1.21
$[(cyclohexyl_3tach)_2YMe_2][AlMe_4]$[14]	2.281, 2.291	1.019	1.262, 1.272
$(Me_3tach)_2Y(1,8$-dialkynylanthracene$)_3$[13]	2.273, 2.298	1.019	1.254, 1.279
$(Me_3tach)_2Ho(C{\equiv}CPh)_3$[13]	2.283, 2.298	1.015	1.268, 1.283
$(Me_3tach)ScCl_3$[15]	1.912	0.87	1.042

Table S2: M–Cnt distances in rare-earth metal Me_3tacn complexes. Complexes containing chelating R substituents are omitted. [a] multiple independent molecules in the unit cell.

	M–Cnt (Å)	Eight-coordinate ionic radius (Å)[4]	M–Cnt distance – radius (Å)
(Me_3tacn)La(*p*-Me-benzyl)$_3$[16]	2.185	1.16	1.025
8-La	2.129	1.16	0.969
(Me_3tacn)$NdCl_2(C_5Ph_3H_2)$[10]	2.072	1.109	0.963
(Me_3tacn)Gd[(Mes_2(*p*-OMePh)corrole][17]	2.056	1.053	1.003
10-Sm	2.065	1.27	0.795
(Me_3tacn)$TbCl_2(C_5Ph_3H_2)$[10]	1.990	1.04	0.95
(Me_3tacn)YI_3[18]	1.820	1.019	0.801
9-Y	1.848	1.019	0.829
[(Me_3tacn)YI_2]$_2$(μ–O)[18]	1.889, 1.892 [a]	1.019	0.87, 0.873
(Me_3tacn)Y[OSi(O^{t}Bu)$_3$]$_3$[19]	1.966	1.019	0.947
(Me_3tacn)Y(CH_2SiMe_3)$_3$[20]	1.981, 1.983, 1.995 [a]	1.019	0.962, 0.964, 0.976
(Me_3tacn)$ScCl_3$[21]	1.655	0.87	0.785
[(Me_3tacn)ScF_2](μ–F)($SnMe_3Cl$)[18]	1.667	0.87	0.797
(Me_3tacn)ScF_2Cl[18]	1.677	0.87	0.807
(Me_3tacn)$ScMe_3$[22]	1.752	0.87	0.882
(Me_3tacn)Sc(CH_2SiMe_3)$_3$[15]	1.812, 1.825 [a]	0.87	0.942, 0.955

Crystallographic Details

Table S3: Crystal data and structure refinement for **1-Ln**. The data were not high enough quality to discuss metrical parameters, hence only the unrefined cell data are given.

	1-La	**1-Ce**	**1-Nd**
Identification code	jcw87	jcw90	jcw96
Empirical Formula	$C_{12}H_{30}N_6I_3La$	$C_{12}H_{30}N_6I_3Ce$	$C_{12}H_{30}N_6I_3Nd$
Formula weight	778.09	779.30	783.42
Temperature (K)	93(2)	133(2)	133(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*
a (Å)	23.664	23.499	23.556
b (Å)	10.680	10.642	10.557
c (Å)	12.365	12.427	12.203
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
Volume ($Å^3$)	3125	3107.4	3034.5
Z	4	4	4
Color	colorless	colorless	pale blue
Crystal size (mm^3)	0.166x0.215x0.289	0.133x0.199x0.240	0.200x0.265x0.329

Table S4: Crystal data and structure refinement for **2-Ln** and **3-La**. The data of **2-Ln** were not high enough quality to discuss metrical parameters, hence only the unrefined cell data are given.

	2-Nd	**2-Sm**	**3-La**
CCDC Deposition Number			2236571
Identification code	jcw83	jcw100	jcw84
Empirical Formula	$C_{12}H_{30}N_6I_3Nd$	$C_{12}H_{30}N_6I_3Sm$	$C_{12}H_{30}N_6Cl_3La$
Formula weight	783.42	789.54	503.67
Temperature (K)	133(2)	92(2)	133(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Hexagonal
Space group	$P2_1/c$	$P2_1/m$	$P6_3/m$
a (Å)	11.504	9.073	11.9427(7)
b (Å)	12.661	11.911	11.9427(7)
c (Å)	21.998	12.804	10.5184(6)
α (°)	90	90	90
β (°)	92.384	92.110	90

γ (°)	90	90	120
Volume (Å^3)	3201.1	1382.8	1299.23(17)
Z	4	4	2
Density (mg/m^3)			1.288
Absorption coefficient			1.956
F(000)			504
Color	pale blue	colorless	colorless
Crystal size (mm^3)	0.208x0.210x0.276	0.117x0.131x0.201	0.381x0.186x0.156
θ range for collection (°)			2.762 to 30.502
Index ranges			$-17 \leq h \leq 17$, $-17 \leq k \leq 16$, $-14 \leq l \leq 14$
independent reflections collected			1382
completeness			98.9
Absorption correction			semi-empirical from equivalents
refinement method			Full-matrix least-squares on F^2
data / restraints / parameters			1382 / 0 / 37
Goodness-of-fit on F^2			1.111
Final R indices [I>2σ(I)]			R1 = 0.0118, wR2 = 0.0315
R indices (all data)			R1 = 0.0124, wR2 = 0.0317
Data cutoff (Å)			0.70
Largest diff. peak and hole (e·Å^3)			0.390 and −0.263

Table S5: Crystal data and structure refinement for **4-Y**, **5-La**, **6-La**, and **7-Sm**. The data of **7-Sm** were not high enough quality to discuss metrical parameters, hence only unrefined cell data are given.

	4-Y	**5-La**	**6-La**	**7-Sm**
CCDC Deposition Number	2236569	2244010	2236568	
Identification code	jcw107	jcw89	jcw115	jcw118
Empirical Formula	$C_{14}H_{31}N_3O_2Cl_3Y$	$C_{32}H_{64}F_{24}La_4N_{12}O_{28}S_8$•2($C_4H_8O$)	$C_{16}H_{30}N_6O_{12}F_{12}S_4La$•$C_7H_8$	$C_{16}H_{38}N_6OI_2Sm$
Formula weight	468.68	2477.28	1215.96	734.76
Temperature (K)	133(2)	133(2)	93(2)	93(2)

Wavelength (Å)	0.71073	0.71073	0.71073	1.54178
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$	*Pnma*
a (Å)	7.5589(5)	15.371(5)	10.4880(9)	14.328
b (Å)	13.5752(9)	15.387(5)	23.4369(19)	11.238
c (Å)	20.0150(13)	18.158(6)	19.8069(16)	16.435
α (°)	90	90	90	90
β (°)	90	93.231(5)	92.0552(14)	90
γ (°)	90	90	90	90
Volume (Å^3)	2053.8(2)	4288(2)	4865.5(7)	2646.2
Z	4	2	4	4
Density (mg/m^3)	1.516	1.919	1.660	
Absorption coefficient	3.240	2.277	1.157	
F(000)	968	2432	2464	
Color	colorless	colorless	colorless	red
Crystal size (mm^3)	0.377x0.271x0.230	0.257x0.151x0.087	0.242x0.199x0.176	0.092x0.093x0.139
θ range for collection (°)	1.813 to 30.549	1.690 to 28.334	1.738 to 25.682	
Index ranges	$-10 \le h \le 10$, $-19 \le k \le 18$, $-27 \le l \le 28$	$-20 \le h \le 20$, $-20 \le k \le 20$, $-24 \le l \le 24$	$-12 \le h \le 12$, $-28 \le k \le 28$, $-24 \le l \le 24$	
independent reflections collected	6104	10679	9139	
completeness	100.0	100.	99.0	
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents	Semi-empirical from equivalents	
refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	
data / restraints / parameters	6104 / 0 / 211	10679 / 2 / 519	9139 / 0 / 618	
Goodness-of-fit on F^2	0.958	1.062	1.009	
Final R indices [I>2σ(I)]	R1 = 0.0188, wR2 = 0.0372	R1 = 0.0394, wR2 = 0.0999	R1 = 0.0390, wR2 = 0.0705	
R indices (all data)	R1 = 0.0224, wR2 = 0.0377	R1 = 0.0594, wR2 = 0.1122	R1 = 0.0649, wR2 = 0.0771	
Absolute structure parameter	−0.0062(17)	N/A	N/A	
Data cutoff (Å)	0.70	0.75	0.82	
Largest diff. peak and hole (e·Å^3)	0.470 and −0.252	1.935 and −1.211	0.640 and −0.599	

Table S6: Crystal data and structure refinement for **8-La**, **9-Y**, and **10-Sm**.

	8-La	**9-Y**	**10-Sm**
CCDC Deposition Number	2236570	2236566	2236567
Identification code	jcw114	jcw116	jcw95
Empirical Formula	$C_{13}H_{29}N_3OI_3La$	$C_9H_{21}Cl_3N_3Y$	$C_{13}H_{29}N_3OI_2Sm$
Formula weight	763.00	366.55	647.54
Temperature (K)	93(2)	93(2)	93(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	*Pna*2$_1$	*P*2$_1$/*c*	*Pna*2$_1$
a (Å)	16.0712(13)	12.6519(18)	17.308(4)
b (Å)	10.0909(8)	7.6180(11)	8.404(2)
c (Å)	13.2624(10)	15.904(2)	13.853(3)
α (°)	90	90	90
β (°)	90	90.870(3)	90
γ (°)	90	90	90
Volume (Å^3)	2150.8(3)	1532.7(4)	2015.0(8)
Z	4	4	4
Density (mg/m^3)	2.356	1.588	2.135
Absorption coefficient	6.295	4.309	5.979
F(000)	1408	744	1216
Color	colorless	colorless	Green
crystal size (mm^3)	0.184x0.165x0.082	0.236x0.208x0.177	0.226x0.166x0.120
θ range for collection	2.383 to 30.510	1.280 to 26.372	2.353 to 30.602
Index ranges	$-22 \le h \le 22$, $-14 \le k \le 14$, $-18 \le l \le 18$	$-15 \le h \le 15$, $-9 \le k \le 9$, $-19 \le l \le 19$	$-22 \le h \le 22$, $-11 \le k \le 11$, $-18 \le l \le 18$
independent reflections collected	6364	3137	4718
completeness	100.0	100.0	100.0
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.4330 and 0.3064	0.4330 and 0.3449	0.7461 and 0.6191
refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
data / restraints / parameters	6364 / 1 / 193	3137 / 0 / 149	4178 / 1 / 179
Goodness-of-fit on F^2	1.021	1.098	0.985
Final R indices [I>2σ(I)]	R1 = 0.0397, wR2 = 0.0837	R1 = 0.0521, wR2 = 0.1279	R1 = 0.0506, wR2 = 0.0489
R indices (all data)	R1 = 0.0493, wR2 = 0.0872	R1 = 0.0738, wR2 = 0.1458	R1 = 0.1029, wR2 = 0.0563
Data cutoff	0.70	0.80	0.76
Largest diff. peak and hole (e·Å^3)	3.879 and −1.764	1.166 and −0.739	1.252 and −1.120

Table S7: Crystal data and structure refinement for [HMe_3tach][Br], [HMe_3tach][I], and [HMe_3tacn][OTf].

	[HMe_3tach][Br]	[HMe_3tach][I]	[HMe_3tacn][OTf]
CCDC Deposition Number	2236565		
Identification code	jcw119	jcw91	jcw97
Empirical Formula	$C_6H_{16}N_3Br$	$C_6H_{16}N_3I$	$C_{10}H_{22}F_3N_3O_3S$
Formula weight	210.13	257.12	321.37
Temperature (K)	93(2)	93(2)	93(2)
Wavelength (Å)	1.54178	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
a (Å)	6.6133(5)	6.6726(14)	9.096(7)
b (Å)	11.0336(9)	11.590(2)	12.377(11)
c (Å)	12.9024(11)	13.362(3)	13.351(9)
α (°)	90	90	90
β (°)	97.338(5)	96.205(4)	90
γ (°)	90	90	90
Volume (Å^3)	933.76(13)	1027.3(4)	1503(2)
Z	4	4	4
Density (mg/m^3)	1.495		
Absorption coefficient	5.513		
F(000)	432		
Color	colorless	colorless	colorless
Crystal size (mm^3)	0.150x0.114x0.083	0.257x0.192x0.164	0.360x0.256x0.173
θ range for collection	5.293 to 68.825		
Index ranges	$-7 \leq h \leq 7$, $-13 \leq k \leq 13$, $-15 \leq l \leq 15$		
Independent reflections collected	1723		
Completeness	100.0		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.4675 and 0.2187		
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	1723 / 0 / 155		
Goodness-of-fit on F^2	1.033		
Final R indices [I>2σ(I)]	R1 = 0.0290, wR2 = 0.0657		
R indices (all data)	R1 = 0.0385, wR2 =		

	0.0700		
Data cutoff	0.83		
Largest diff. peak and hole (e·Å^3)	0.613 and −0.445		

X-ray Data Collection, Structure Solution and Refinement for **3-La**.

A colorless crystal of approximate dimensions 0.156 x 0.186 x 0.381 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[23] program package was used to determine the unit-cell parameters and for data collection (10 sec/frame scan). The raw frame data was processed using SAINT[24] and SADABS[25] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[26] program package. The systematic absences were consistent with the hexagonal space groups $P6_3$, $P6_3/m$ and $P6_322$. The centrosymmetric space group $P6_3/m$ was assigned and later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[27] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

Least-squares analysis yielded wR2 = 0.0317 and Goof = 1.111 for 37 variables refined against 1382 data (0.70 Å), R1 = 0.0118 for those 1329 data with $I > 2.0\sigma(I)$.

There were several high residuals present in the final difference-Fourier map. It was not possible to determine the nature of the residuals. The crystals were obtained from a mixture of THF and hexane, however, a suitable model for the solvent(s) could not be established. The SQUEEZE[28] routine in the PLATON[29] program package was used to account for the electrons in the solvent accessible voids. The empirical formula reported does not contain contributions from the unidentified solvent(s).

Table S8: Bond lengths [Å] and angles [°] for **3-La**.

La(1)-N(1)#1	2.7759(8)	N(1)#1-La(1)-Cl(1)#4	75.556(17)
La(1)-N(1)#2	2.7759(8)	N(1)#2-La(1)-Cl(1)#4	75.556(17)
La(1)-N(1)#3	2.7759(8)	N(1)#3-La(1)-Cl(1)#4	76.379(17)
La(1)-N(1)#4	2.7759(8)	N(1)#4-La(1)-Cl(1)#4	76.379(17)
La(1)-N(1)	2.7759(8)	N(1)-La(1)-Cl(1)#4	119.009(17)
La(1)-N(1)#5	2.7759(8)	N(1)#5-La(1)-Cl(1)#4	119.010(17)
La(1)-Cl(1)#4	2.7878(4)	N(1)#1-La(1)-Cl(1)#1	76.379(17)
La(1)-Cl(1)#1	2.7878(4)	N(1)#2-La(1)-Cl(1)#1	76.379(17)
La(1)-Cl(1)	2.7878(4)	N(1)#3-La(1)-Cl(1)#1	119.010(17)
N(1)-C(2)	1.4663(12)	N(1)#4-La(1)-Cl(1)#1	119.010(17)
N(1)-C(1)	1.4662(12)	N(1)-La(1)-Cl(1)#1	75.555(17)
N(1)-C(1)#4	1.4669(12)	N(1)#5-La(1)-Cl(1)#1	75.556(17)
C(1)-N(1)#1	1.4669(12)	Cl(1)#4-La(1)-Cl(1)#1	120.0
		N(1)#1-La(1)-Cl(1)	119.009(17)
N(1)#1-La(1)-N(1)#2	121.97(3)	N(1)#2-La(1)-Cl(1)	119.009(17)
N(1)#1-La(1)-N(1)#3	151.932(15)	N(1)#3-La(1)-Cl(1)	75.554(17)
N(1)#2-La(1)-N(1)#3	49.67(3)	N(1)#4-La(1)-Cl(1)	75.554(17)
N(1)#1-La(1)-N(1)#4	49.67(3)	N(1)-La(1)-Cl(1)	76.379(17)
N(1)#2-La(1)-N(1)#4	151.932(15)	N(1)#5-La(1)-Cl(1)	76.377(17)
N(1)#3-La(1)-N(1)#4	121.97(3)	Cl(1)#4-La(1)-Cl(1)	120.0
N(1)#1-La(1)-N(1)	49.67(3)	Cl(1)#1-La(1)-Cl(1)	120.0
N(1)#2-La(1)-N(1)	151.931(15)	C(2)-N(1)-C(1)	111.84(8)
N(1)#3-La(1)-N(1)	151.930(15)	C(2)-N(1)-C(1)#4	112.02(8)
N(1)#4-La(1)-N(1)	49.67(3)	C(1)-N(1)-C(1)#4	108.95(9)
N(1)#1-La(1)-N(1)#5	151.931(15)	C(2)-N(1)-La(1)	129.49(7)
N(1)#2-La(1)-N(1)#5	49.67(3)	C(1)-N(1)-La(1)	96.10(5)
N(1)#3-La(1)-N(1)#5	49.67(3)	C(1)#4-N(1)-La(1)	96.08(5)
N(1)#4-La(1)-N(1)#5	151.928(15)	N(1)-C(1)-N(1)#1	105.32(8)
N(1)-La(1)-N(1)#5	121.97(3)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+y+1,-x+1,z #2 -x+y+1,-x+1,-z+1/2 #3 -y+1,x-y,-z+1/2
#4 -y+1,x-y,z #5 x,y,-z+1/2

X-ray Data Collection, Structure Solution and Refinement for **4-Y**.

A colorless crystal of approximate dimensions 0.230 x 0.271 x 0.377 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[23] program

package was used to determine the unit-cell parameters. Data was collected using a 40 sec/frame scan time. The raw frame data was processed using SAINT[24] and SADABS[25] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[26] program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group $P2_12_12_1$ that was later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[27] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

Least-squares analysis yielded wR2 = 0.0377 and Goof = 0.958 for 211 variables refined against 6104 data (0.70 Å), R1 = 0.0188 for those 5625 with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack[30] parameter.

Table S9: Bond lengths [Å] and angles [°] for **4-Y**.

Y(1)-O(2)	2.4208(13)	C(9)-C(10)	1.506(3)
Y(1)-O(1)	2.4440(12)	C(11)-C(12)	1.513(3)
Y(1)-N(1)	2.5661(15)	C(12)-C(13)	1.524(3)
Y(1)-N(2)	2.5881(16)	C(13)-C(14)	1.532(3)
Y(1)-N(3)	2.6138(15)		
Y(1)-Cl(2)	2.6232(5)	O(2)-Y(1)-O(1)	73.82(4)
Y(1)-Cl(3)	2.6356(5)	O(2)-Y(1)-N(1)	144.77(5)
Y(1)-Cl(1)	2.6558(5)	O(1)-Y(1)-N(1)	124.22(5)
O(1)-C(10)	1.459(2)	O(2)-Y(1)-N(2)	146.78(5)
O(1)-C(7)	1.461(2)	O(1)-Y(1)-N(2)	74.90(5)
O(2)-C(11)	1.441(2)	N(1)-Y(1)-N(2)	53.75(5)
O(2)-C(14)	1.441(2)	O(2)-Y(1)-N(3)	154.18(5)
N(1)-C(3)	1.462(2)	O(1)-Y(1)-N(3)	113.37(5)
N(1)-C(1)	1.467(2)	N(1)-Y(1)-N(3)	53.08(5)
N(1)-C(2)	1.469(2)	N(2)-Y(1)-N(3)	53.30(5)
N(2)-C(6)	1.467(2)	O(2)-Y(1)-Cl(2)	83.98(3)
N(2)-C(5)	1.468(2)	O(1)-Y(1)-Cl(2)	156.37(3)
N(2)-C(1)	1.476(2)	N(1)-Y(1)-Cl(2)	78.91(4)
N(3)-C(4)	1.463(2)	N(2)-Y(1)-Cl(2)	128.36(4)
N(3)-C(5)	1.464(2)	N(3)-Y(1)-Cl(2)	83.51(4)
N(3)-C(3)	1.466(2)	O(2)-Y(1)-Cl(3)	80.53(3)
C(7)-C(8)	1.513(3)	O(1)-Y(1)-Cl(3)	78.25(3)
C(8)-C(9)	1.527(3)	N(1)-Y(1)-Cl(3)	129.69(4)

N(2)-Y(1)-Cl(3)	103.75(4)	C(6)-N(2)-C(1)	110.67(15)
N(3)-Y(1)-Cl(3)	77.06(4)	C(5)-N(2)-C(1)	108.48(14)
Cl(2)-Y(1)-Cl(3)	90.371(16)	C(6)-N(2)-Y(1)	134.19(12)
O(2)-Y(1)-Cl(1)	76.81(3)	C(5)-N(2)-Y(1)	95.35(10)
O(1)-Y(1)-Cl(1)	82.77(3)	C(1)-N(2)-Y(1)	94.22(10)
N(1)-Y(1)-Cl(1)	76.26(4)	C(4)-N(3)-C(5)	111.63(15)
N(2)-Y(1)-Cl(1)	88.47(4)	C(4)-N(3)-C(3)	111.76(16)
N(3)-Y(1)-Cl(1)	127.71(4)	C(5)-N(3)-C(3)	109.23(15)
Cl(2)-Y(1)-Cl(1)	100.232(17)	C(4)-N(3)-Y(1)	132.58(13)
Cl(3)-Y(1)-Cl(1)	153.725(16)	C(5)-N(3)-Y(1)	94.40(10)
C(10)-O(1)-C(7)	108.42(13)	C(3)-N(3)-Y(1)	94.57(10)
C(10)-O(1)-Y(1)	125.47(10)	N(1)-C(1)-N(2)	104.70(14)
C(7)-O(1)-Y(1)	126.11(10)	N(1)-C(3)-N(3)	104.45(14)
C(11)-O(2)-C(14)	104.89(15)	N(3)-C(5)-N(2)	105.44(14)
C(11)-O(2)-Y(1)	123.51(11)	O(1)-C(7)-C(8)	105.53(15)
C(14)-O(2)-Y(1)	127.81(11)	C(7)-C(8)-C(9)	101.42(15)
C(3)-N(1)-C(1)	108.73(14)	C(10)-C(9)-C(8)	101.53(15)
C(3)-N(1)-C(2)	112.62(15)	O(1)-C(10)-C(9)	105.58(15)
C(1)-N(1)-C(2)	112.25(15)	O(2)-C(11)-C(12)	102.67(16)
C(3)-N(1)-Y(1)	96.66(11)	C(11)-C(12)-C(13)	103.76(17)
C(1)-N(1)-Y(1)	95.36(10)	C(12)-C(13)-C(14)	104.09(16)
C(2)-N(1)-Y(1)	128.72(11)	O(2)-C(14)-C(13)	105.30(16)
C(6)-N(2)-C(5)	111.11(15)		

X-ray Data Collection, Structure Solution and Refinement for **5-La**.

A colorless crystal of approximate dimensions 0.087 x 0.151 x 0.257 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2[23] program package was used to determine the unit-cell parameters and for data collection (120 sec/frame scan time). The raw frame data was processed using SAINT[24] and SADABS[25] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[26] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[27] for neutral atoms were used throughout the analysis. The molecule was located about an inversion center. Hydrogen atoms H(1) and H(2) were located

from a difference-Fourier map and refined (x,y,z, riding U_{iso}) with d(O-H) = 0.80Å. The remaining hydrogen atoms were included using a riding model. There were two molecules of tetrahydrofuran solvent present per tetrameric formula-unit. The solvent molecule exhibited high thermal motion and was refined using isotropic displacement parameters.

Least-squares analysis yielded wR2 = 0.1122 and Goof = 1.062 for 519 variables refined against 10679 data (0.75 Å), R1 = 0.0394 for those 8252 data with I > 2.0σ(I).

Table S10. Bond lengths [Å] and angles [°] for **5-La**.

La(1)-O(1)	2.362(3)	S(4)-O(13)	1.448(3)
La(1)-O(2)	2.387(3)	S(4)-C(16)	1.834(5)
La(1)-O(9)	2.510(3)	F(1)-C(13)	1.315(6)
La(1)-O(12)	2.530(3)	F(2)-C(13)	1.334(6)
La(1)-O(3)	2.594(3)	F(3)-C(13)	1.332(6)
La(1)-O(6)	2.620(3)	F(4)-C(14)	1.312(6)
La(1)-N(2)	2.752(4)	F(5)-C(14)	1.318(6)
La(1)-N(3)	2.761(4)	F(6)-C(14)	1.339(6)
La(1)-N(1)	2.777(4)	F(7)-C(15)	1.317(6)
La(1)-La(2)	3.8289(9)	F(8)-C(15)	1.315(6)
La(2)-O(2)	2.367(3)	F(9)-C(15)	1.334(6)
La(2)-O(1)	2.369(3)	F(10)-C(16)	1.328(6)
La(2)-O(13)#1	2.537(3)	F(11)-C(16)	1.336(5)
La(2)-O(11)#1	2.551(3)	F(12)-C(16)	1.318(6)
La(2)-O(4)	2.588(3)	O(11)-La(2)#1	2.551(3)
La(2)-O(7)	2.592(3)	O(13)-La(2)#1	2.537(3)
La(2)-N(5)	2.761(4)	N(1)-C(3)	1.459(6)
La(2)-N(4)	2.771(4)	N(1)-C(4)	1.460(7)
La(2)-N(6)	2.783(4)	N(1)-C(1)	1.462(7)
S(1)-O(5)	1.424(4)	N(2)-C(2)	1.461(7)
S(1)-O(3)	1.443(3)	N(2)-C(1)	1.465(7)
S(1)-O(4)	1.446(3)	N(2)-C(5)	1.471(7)
S(1)-C(13)	1.813(5)	N(3)-C(3)	1.445(6)
S(2)-O(8)	1.426(4)	N(3)-C(2)	1.454(6)
S(2)-O(6)	1.451(3)	N(3)-C(6)	1.460(6)
S(2)-O(7)	1.452(3)	N(4)-C(7)	1.448(7)
S(2)-C(14)	1.826(5)	N(4)-C(10)	1.464(6)
S(3)-O(10)	1.410(4)	N(4)-C(9)	1.471(6)
S(3)-O(11)	1.437(4)	N(5)-C(7)	1.462(7)
S(3)-O(9)	1.444(3)	N(5)-C(11)	1.462(7)
S(3)-C(15)	1.817(5)	N(5)-C(8)	1.471(7)
S(4)-O(14)	1.423(3)	N(6)-C(12)	1.458(6)
S(4)-O(12)	1.446(3)	N(6)-C(8)	1.460(7)

N(6)-C(9)	1.467(6)
O(15)-C(20)	1.382(11)
O(15)-C(17)	1.399(14)
C(17)-C(18)	1.425(16)
C(18)-C(19)	1.541(14)
C(19)-C(20)	1.456(13)

O(1)-La(1)-O(2)	72.11(10)
O(1)-La(1)-O(9)	135.66(11)
O(2)-La(1)-O(9)	81.47(11)
O(1)-La(1)-O(12)	139.10(11)
O(2)-La(1)-O(12)	90.72(10)
O(9)-La(1)-O(12)	74.14(11)
O(1)-La(1)-O(3)	69.79(10)
O(2)-La(1)-O(3)	79.15(11)
O(9)-La(1)-O(3)	139.26(11)
O(12)-La(1)-O(3)	70.65(10)
O(1)-La(1)-O(6)	70.08(11)
O(2)-La(1)-O(6)	82.32(11)
O(9)-La(1)-O(6)	71.64(11)
O(12)-La(1)-O(6)	145.71(10)
O(3)-La(1)-O(6)	139.27(10)
O(1)-La(1)-N(2)	76.13(12)
O(2)-La(1)-N(2)	146.55(11)
O(9)-La(1)-N(2)	115.87(13)
O(12)-La(1)-N(2)	120.74(12)
O(3)-La(1)-N(2)	99.61(13)
O(6)-La(1)-N(2)	77.23(12)
O(1)-La(1)-N(3)	104.75(11)
O(2)-La(1)-N(3)	150.25(11)
O(9)-La(1)-N(3)	115.33(12)
O(12)-La(1)-N(3)	72.26(11)
O(3)-La(1)-N(3)	72.30(12)
O(6)-La(1)-N(3)	125.32(11)
N(2)-La(1)-N(3)	50.04(12)
O(1)-La(1)-N(1)	125.61(11)
O(2)-La(1)-N(1)	154.90(11)
O(9)-La(1)-N(1)	73.53(12)
O(12)-La(1)-N(1)	84.67(12)
O(3)-La(1)-N(1)	121.85(12)
O(6)-La(1)-N(1)	87.67(11)
N(2)-La(1)-N(1)	50.28(13)
N(3)-La(1)-N(1)	49.93(12)
O(1)-La(1)-La(2)	36.03(7)
O(2)-La(1)-La(2)	36.17(7)
O(9)-La(1)-La(2)	111.84(8)
O(12)-La(1)-La(2)	116.99(8)
O(3)-La(1)-La(2)	68.70(8)
O(6)-La(1)-La(2)	74.94(8)
N(2)-La(1)-La(2)	111.89(9)
N(3)-La(1)-La(2)	132.50(9)
N(1)-La(1)-La(2)	158.31(9)
O(2)-La(2)-O(1)	72.34(10)
O(2)-La(2)-O(13)#1	86.70(10)
O(1)-La(2)-O(13)#1	144.92(11)
O(2)-La(2)-O(11)#1	82.37(12)
O(1)-La(2)-O(11)#1	129.70(11)
O(13)#1-La(2)-O(11)#1	72.28(11)
O(2)-La(2)-O(4)	93.95(10)
O(1)-La(2)-O(4)	70.02(10)
O(13)#1-La(2)-O(4)	141.03(11)
O(11)#1-La(2)-O(4)	69.22(11)
O(2)-La(2)-O(7)	79.40(11)
O(1)-La(2)-O(7)	71.82(10)
O(13)#1-La(2)-O(7)	76.97(11)
O(11)#1-La(2)-O(7)	144.93(11)
O(4)-La(2)-O(7)	141.46(10)
O(2)-La(2)-N(5)	158.64(12)
O(1)-La(2)-N(5)	116.87(12)
O(13)#1-La(2)-N(5)	92.82(12)
O(11)#1-La(2)-N(5)	77.17(13)
O(4)-La(2)-N(5)	73.16(12)
O(7)-La(2)-N(5)	121.31(12)
O(2)-La(2)-N(4)	146.34(11)
O(1)-La(2)-N(4)	115.25(10)
O(13)#1-La(2)-N(4)	68.80(11)
O(11)#1-La(2)-N(4)	109.93(12)
O(4)-La(2)-N(4)	119.65(11)
O(7)-La(2)-N(4)	72.99(11)
N(5)-La(2)-N(4)	50.11(12)
O(2)-La(2)-N(6)	146.00(11)
O(1)-La(2)-N(6)	74.23(11)
O(13)#1-La(2)-N(6)	118.63(11)
O(11)#1-La(2)-N(6)	125.03(12)
O(4)-La(2)-N(6)	80.28(12)
O(7)-La(2)-N(6)	84.56(12)
N(5)-La(2)-N(6)	50.14(12)
N(4)-La(2)-N(6)	49.84(12)
O(2)-La(2)-La(1)	36.53(7)
O(1)-La(2)-La(1)	35.91(7)
O(13)#1-La(2)-La(1)	119.47(8)
O(11)#1-La(2)-La(1)	106.98(9)

O(4)-La(2)-La(1)	78.24(7)	C(2)-N(2)-C(5)	112.2(5)
O(7)-La(2)-La(1)	74.11(8)	C(1)-N(2)-C(5)	110.7(5)
N(5)-La(2)-La(1)	147.42(10)	C(2)-N(2)-La(1)	95.0(3)
N(4)-La(2)-La(1)	142.76(8)	C(1)-N(2)-La(1)	95.8(3)
N(6)-La(2)-La(1)	110.10(9)	C(5)-N(2)-La(1)	131.7(4)
O(5)-S(1)-O(3)	115.0(2)	C(3)-N(3)-C(2)	109.8(4)
O(5)-S(1)-O(4)	116.3(2)	C(3)-N(3)-C(6)	112.3(4)
O(3)-S(1)-O(4)	114.0(2)	C(2)-N(3)-C(6)	112.3(4)
O(5)-S(1)-C(13)	104.8(2)	C(3)-N(3)-La(1)	95.7(3)
O(3)-S(1)-C(13)	101.8(2)	C(2)-N(3)-La(1)	94.9(3)
O(4)-S(1)-C(13)	102.3(2)	C(6)-N(3)-La(1)	129.5(3)
O(8)-S(2)-O(6)	115.5(2)	C(7)-N(4)-C(10)	112.9(4)
O(8)-S(2)-O(7)	115.2(2)	C(7)-N(4)-C(9)	109.8(4)
O(6)-S(2)-O(7)	114.8(2)	C(10)-N(4)-C(9)	110.7(4)
O(8)-S(2)-C(14)	104.2(2)	C(7)-N(4)-La(2)	94.4(3)
O(6)-S(2)-C(14)	102.2(2)	C(10)-N(4)-La(2)	130.6(3)
O(7)-S(2)-C(14)	102.4(2)	C(9)-N(4)-La(2)	96.1(3)
O(10)-S(3)-O(11)	114.9(2)	C(7)-N(5)-C(11)	113.6(5)
O(10)-S(3)-O(9)	115.6(2)	C(7)-N(5)-C(8)	108.8(4)
O(11)-S(3)-O(9)	113.7(2)	C(11)-N(5)-C(8)	111.5(4)
O(10)-S(3)-C(15)	105.8(2)	C(7)-N(5)-La(2)	94.6(3)
O(11)-S(3)-C(15)	103.1(2)	C(11)-N(5)-La(2)	130.0(3)
O(9)-S(3)-C(15)	101.5(2)	C(8)-N(5)-La(2)	95.7(3)
O(14)-S(4)-O(12)	114.8(2)	C(12)-N(6)-C(8)	111.9(4)
O(14)-S(4)-O(13)	114.8(2)	C(12)-N(6)-C(9)	111.3(4)
O(12)-S(4)-O(13)	113.18(19)	C(8)-N(6)-C(9)	109.2(4)
O(14)-S(4)-C(16)	105.8(2)	C(12)-N(6)-La(2)	131.3(3)
O(12)-S(4)-C(16)	103.7(2)	C(8)-N(6)-La(2)	95.0(3)
O(13)-S(4)-C(16)	102.7(2)	C(9)-N(6)-La(2)	95.7(2)
La(1)-O(1)-La(2)	108.06(11)	N(1)-C(1)-N(2)	106.7(4)
La(2)-O(2)-La(1)	107.29(11)	N(3)-C(2)-N(2)	106.3(4)
S(1)-O(3)-La(1)	130.78(19)	N(3)-C(3)-N(1)	107.2(4)
S(1)-O(4)-La(2)	125.73(18)	N(4)-C(7)-N(5)	107.3(4)
S(2)-O(6)-La(1)	129.67(19)	N(6)-C(8)-N(5)	106.5(4)
S(2)-O(7)-La(2)	129.39(18)	N(6)-C(9)-N(4)	105.6(4)
S(3)-O(9)-La(1)	155.0(2)	F(1)-C(13)-F(3)	108.3(4)
S(3)-O(11)-La(2)#1	150.1(2)	F(1)-C(13)-F(2)	108.2(4)
S(4)-O(12)-La(1)	162.5(2)	F(3)-C(13)-F(2)	106.5(4)
S(4)-O(13)-La(2)#1	166.2(2)	F(1)-C(13)-S(1)	111.6(3)
C(3)-N(1)-C(4)	112.1(4)	F(3)-C(13)-S(1)	110.7(3)
C(3)-N(1)-C(1)	108.1(4)	F(2)-C(13)-S(1)	111.3(4)
C(4)-N(1)-C(1)	112.1(4)	F(4)-C(14)-F(5)	108.4(4)
C(3)-N(1)-La(1)	94.7(3)	F(4)-C(14)-F(6)	107.7(4)
C(4)-N(1)-La(1)	131.9(3)	F(5)-C(14)-F(6)	108.6(4)
C(1)-N(1)-La(1)	94.9(3)	F(4)-C(14)-S(2)	112.2(3)
C(2)-N(2)-C(1)	109.0(4)	F(5)-C(14)-S(2)	110.2(4)

F(6)-C(14)-S(2)	109.6(3)	F(10)-C(16)-F(11)	108.1(4)
F(8)-C(15)-F(7)	108.5(4)	F(12)-C(16)-S(4)	110.7(3)
F(8)-C(15)-F(9)	107.5(4)	F(10)-C(16)-S(4)	110.1(3)
F(7)-C(15)-F(9)	107.9(4)	F(11)-C(16)-S(4)	109.1(3)
F(8)-C(15)-S(3)	111.5(4)	C(20)-O(15)-C(17)	103.2(9)
F(7)-C(15)-S(3)	110.7(3)	O(15)-C(17)-C(18)	112.2(12)
F(9)-C(15)-S(3)	110.5(3)	C(17)-C(18)-C(19)	102.8(11)
F(12)-C(16)-F(10)	109.5(4)	C(20)-C(19)-C(18)	97.8(9)
F(12)-C(16)-F(11)	109.3(4)	O(15)-C(20)-C(19)	110.7(9)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

X-ray Data Collection, Structure Solution and Refinement for **6-La**.

A colorless crystal of approximate dimensions 0.242 x 0.199 x 0.176 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2[23] program package was used to determine the unit-cell parameters. Data collection used a 120 sec/frame scan time. The raw frame data was processed using SAINT[24] and SADABS[25] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[26] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[27] for neutral atoms were used throughout the analysis. Hydrogen atom H(7) was located from a difference-Fourier map refined (x,y,z and U_{iso}). The remaining hydrogen atoms were included using a riding model. There was one molecule of toluene present and one molecule of HMe_3tach present which is involved in hydrogen bonding to triflate oxygen atoms.

Least-squares analysis yielded wR2 = 0.0771 and Goof = 1.009 for 618 variables refined against 9139 data (0.82 Å), R1 = 0.0390 for those 6919 data with $I > 2.0\sigma(I)$.

Table S11: Bond lengths [Å] and angles [°] for **6-La**.

La(1)-O(1)	2.468(2)	N(3)-C(5)	1.464(4)
La(1)-O(7)	2.525(2)	N(3)-C(4)	1.471(5)
La(1)-O(4)	2.525(2)	N(4)-C(7)	1.465(4)
La(1)-O(10)	2.579(2)	N(4)-C(11)	1.466(4)
La(1)-N(6)	2.774(3)	N(4)-C(12)	1.473(4)
La(1)-N(2)	2.778(3)	N(5)-C(9)	1.461(4)
La(1)-N(3)	2.782(3)	N(5)-C(7)	1.463(4)
La(1)-N(5)	2.795(3)	N(5)-C(8)	1.475(4)
La(1)-N(4)	2.824(3)	N(6)-C(9)	1.462(4)
La(1)-N(1)	2.842(3)	N(6)-C(10)	1.465(4)
S(1)-O(3)	1.427(3)	N(6)-C(11)	1.469(4)
S(1)-O(2)	1.436(3)	N(7)-C(22)	1.484(5)
S(1)-O(1)	1.447(2)	N(7)-C(17)	1.497(5)
S(1)-C(13)	1.819(4)	N(7)-C(21)	1.535(5)
S(2)-O(6)	1.434(3)	N(8)-C(17)	1.447(5)
S(2)-O(5)	1.444(2)	N(8)-C(18)	1.457(5)
S(2)-O(4)	1.453(2)	N(8)-C(19)	1.460(5)
S(2)-C(14)	1.818(4)	N(9)-C(21)	1.428(5)
S(3)-O(9)	1.417(3)	N(9)-C(19)	1.449(5)
S(3)-O(8)	1.430(3)	N(9)-C(20)	1.466(5)
S(3)-O(7)	1.470(2)	C(23)-C(28)	1.388(6)
S(3)-C(15)	1.818(5)	C(23)-C(24)	1.400(6)
S(4)-O(12)	1.429(3)	C(23)-C(29)	1.479(6)
S(4)-O(11)	1.429(3)	C(24)-C(25)	1.374(6)
S(4)-O(10)	1.463(2)	C(25)-C(26)	1.399(6)
S(4)-C(16)	1.818(4)	C(26)-C(27)	1.373(6)
F(1)-C(13)	1.347(4)	C(27)-C(28)	1.375(6)
F(2)-C(13)	1.320(4)		
F(3)-C(13)	1.327(4)	O(1)-La(1)-O(7)	155.93(8)
F(4)-C(14)	1.336(4)	O(1)-La(1)-O(4)	77.06(8)
F(5)-C(14)	1.334(4)	O(7)-La(1)-O(4)	79.21(7)
F(6)-C(14)	1.328(4)	O(1)-La(1)-O(10)	87.05(8)
F(7)-C(15)	1.322(5)	O(7)-La(1)-O(10)	116.69(7)
F(8)-C(15)	1.332(5)	O(4)-La(1)-O(10)	164.10(7)
F(9)-C(15)	1.316(5)	O(1)-La(1)-N(6)	123.11(8)
F(10)-C(16)	1.326(5)	O(7)-La(1)-N(6)	71.71(8)
F(11)-C(16)	1.324(4)	O(4)-La(1)-N(6)	116.07(7)
F(12)-C(16)	1.340(4)	O(10)-La(1)-N(6)	72.12(7)
N(1)-C(5)	1.459(4)	O(1)-La(1)-N(2)	93.64(8)
N(1)-C(1)	1.464(4)	O(7)-La(1)-N(2)	74.30(8)
N(1)-C(6)	1.474(4)	O(4)-La(1)-N(2)	69.91(8)
N(2)-C(1)	1.459(4)	O(10)-La(1)-N(2)	112.45(8)
N(2)-C(3)	1.459(4)	N(6)-La(1)-N(2)	143.23(8)
N(2)-C(2)	1.473(4)	O(1)-La(1)-N(3)	116.38(8)
N(3)-C(3)	1.464(4)	O(7)-La(1)-N(3)	71.76(8)

O(4)-La(1)-N(3)	117.59(8)	O(12)-S(4)-O(11)	116.27(17)
O(10)-La(1)-N(3)	70.18(8)	O(12)-S(4)-O(10)	114.10(15)
N(6)-La(1)-N(3)	105.33(8)	O(11)-S(4)-O(10)	114.94(15)
N(2)-La(1)-N(3)	49.67(8)	O(12)-S(4)-C(16)	103.01(19)
O(1)-La(1)-N(5)	100.09(8)	O(11)-S(4)-C(16)	103.55(18)
O(7)-La(1)-N(5)	74.64(8)	O(10)-S(4)-C(16)	102.37(17)
O(4)-La(1)-N(5)	68.43(8)	S(1)-O(1)-La(1)	156.03(15)
O(10)-La(1)-N(5)	114.46(8)	S(2)-O(4)-La(1)	153.13(14)
N(6)-La(1)-N(5)	49.61(8)	S(3)-O(7)-La(1)	154.51(14)
N(2)-La(1)-N(5)	131.55(8)	S(4)-O(10)-La(1)	159.30(14)
N(3)-La(1)-N(5)	143.54(8)	C(5)-N(1)-C(1)	109.2(3)
O(1)-La(1)-N(4)	73.85(8)	C(5)-N(1)-C(6)	111.3(3)
O(7)-La(1)-N(4)	115.68(7)	C(1)-N(1)-C(6)	110.4(3)
O(4)-La(1)-N(4)	102.49(7)	C(5)-N(1)-La(1)	95.88(18)
O(10)-La(1)-N(4)	71.83(7)	C(1)-N(1)-La(1)	93.16(18)
N(6)-La(1)-N(4)	49.55(8)	C(6)-N(1)-La(1)	134.2(2)
N(2)-La(1)-N(4)	166.80(8)	C(1)-N(2)-C(3)	109.3(3)
N(3)-La(1)-N(4)	139.80(8)	C(1)-N(2)-C(2)	110.0(3)
N(5)-La(1)-N(4)	49.49(8)	C(3)-N(2)-C(2)	110.9(3)
O(1)-La(1)-N(1)	67.44(8)	C(1)-N(2)-La(1)	95.91(19)
O(7)-La(1)-N(1)	115.10(8)	C(3)-N(2)-La(1)	95.98(19)
O(4)-La(1)-N(1)	103.89(8)	C(2)-N(2)-La(1)	132.6(2)
O(10)-La(1)-N(1)	69.98(8)	C(3)-N(3)-C(5)	106.5(3)
N(6)-La(1)-N(1)	139.91(8)	C(3)-N(3)-C(4)	111.6(3)
N(2)-La(1)-N(1)	49.32(8)	C(5)-N(3)-C(4)	111.6(3)
N(3)-La(1)-N(1)	49.04(8)	C(3)-N(3)-La(1)	95.68(19)
N(5)-La(1)-N(1)	166.99(8)	C(5)-N(3)-La(1)	98.26(19)
N(4)-La(1)-N(1)	125.94(8)	C(4)-N(3)-La(1)	130.3(2)
O(3)-S(1)-O(2)	117.01(16)	C(7)-N(4)-C(11)	108.9(3)
O(3)-S(1)-O(1)	113.60(15)	C(7)-N(4)-C(12)	109.8(3)
O(2)-S(1)-O(1)	113.60(15)	C(11)-N(4)-C(12)	110.6(3)
O(3)-S(1)-C(13)	104.14(17)	C(7)-N(4)-La(1)	94.19(18)
O(2)-S(1)-C(13)	103.60(17)	C(11)-N(4)-La(1)	95.30(18)
O(1)-S(1)-C(13)	102.66(17)	C(12)-N(4)-La(1)	135.4(2)
O(6)-S(2)-O(5)	115.72(16)	C(9)-N(5)-C(7)	109.5(3)
O(6)-S(2)-O(4)	114.63(15)	C(9)-N(5)-C(8)	110.9(3)
O(5)-S(2)-O(4)	113.72(15)	C(7)-N(5)-C(8)	110.7(3)
O(6)-S(2)-C(14)	104.16(18)	C(9)-N(5)-La(1)	95.36(18)
O(5)-S(2)-C(14)	103.14(16)	C(7)-N(5)-La(1)	95.46(18)
O(4)-S(2)-C(14)	103.31(16)	C(8)-N(5)-La(1)	132.6(2)
O(9)-S(3)-O(8)	117.35(19)	C(9)-N(6)-C(10)	111.0(3)
O(9)-S(3)-O(7)	114.02(15)	C(9)-N(6)-C(11)	107.4(3)
O(8)-S(3)-O(7)	113.27(16)	C(10)-N(6)-C(11)	112.3(3)
O(9)-S(3)-C(15)	103.62(19)	C(9)-N(6)-La(1)	96.18(18)
O(8)-S(3)-C(15)	104.5(2)	C(10)-N(6)-La(1)	130.0(2)
O(7)-S(3)-C(15)	101.70(17)	C(11)-N(6)-La(1)	97.29(18)

N(2)-C(1)-N(1)	106.8(3)	F(11)-C(16)-F(12)	107.5(3)
N(2)-C(3)-N(3)	106.1(3)	F(10)-C(16)-F(12)	107.3(3)
N(1)-C(5)-N(3)	106.1(3)	F(11)-C(16)-S(4)	111.8(3)
N(5)-C(7)-N(4)	106.9(3)	F(10)-C(16)-S(4)	112.0(3)
N(5)-C(9)-N(6)	106.2(3)	F(12)-C(16)-S(4)	109.9(3)
N(4)-C(11)-N(6)	106.2(3)	C(22)-N(7)-C(17)	110.7(3)
F(2)-C(13)-F(3)	107.4(3)	C(22)-N(7)-C(21)	111.5(3)
F(2)-C(13)-F(1)	107.2(3)	C(17)-N(7)-C(21)	109.1(3)
F(3)-C(13)-F(1)	107.4(3)	C(17)-N(8)-C(18)	110.0(3)
F(2)-C(13)-S(1)	110.6(3)	C(17)-N(8)-C(19)	110.1(3)
F(3)-C(13)-S(1)	112.6(3)	C(18)-N(8)-C(19)	111.8(3)
F(1)-C(13)-S(1)	111.3(3)	C(21)-N(9)-C(19)	110.5(3)
F(6)-C(14)-F(5)	107.8(3)	C(21)-N(9)-C(20)	114.7(3)
F(6)-C(14)-F(4)	107.8(3)	C(19)-N(9)-C(20)	113.6(3)
F(5)-C(14)-F(4)	106.7(3)	N(8)-C(17)-N(7)	109.3(3)
F(6)-C(14)-S(2)	111.6(3)	N(9)-C(19)-N(8)	111.2(3)
F(5)-C(14)-S(2)	112.4(3)	N(9)-C(21)-N(7)	111.7(3)
F(4)-C(14)-S(2)	110.3(3)	C(28)-C(23)-C(24)	117.1(4)
F(9)-C(15)-F(7)	108.1(4)	C(28)-C(23)-C(29)	121.2(4)
F(9)-C(15)-F(8)	108.1(4)	C(24)-C(23)-C(29)	121.7(4)
F(7)-C(15)-F(8)	106.9(4)	C(25)-C(24)-C(23)	122.1(4)
F(9)-C(15)-S(3)	111.1(3)	C(24)-C(25)-C(26)	119.5(4)
F(7)-C(15)-S(3)	111.2(4)	C(27)-C(26)-C(25)	118.8(4)
F(8)-C(15)-S(3)	111.3(3)	C(26)-C(27)-C(28)	121.3(4)
F(11)-C(16)-F(10)	108.2(4)	C(27)-C(28)-C(23)	121.2(4)

X-ray Data Collection, Structure Solution and Refinement for **8-La**.

A colorless crystal of approximate dimensions 0.184 x 0.165 x 0.082 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2[23] program package was used to determine the unit-cell parameters and for data collection (90 sec/frame scan time). The raw frame data was processed using SAINT[24] and SADABS[25] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[26] program package. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space groups *Pnma* and $Pna2_1$. It was later determined that space group $Pna2_1$ was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[27] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The structure was refined as an inversion twin.

Least-squares analysis yielded wR2 = 0.0873 and Goof = 1.021 for 193 variables refined against 6364 data (0.70 Å), R1 = 0.0397 for those 5660 data with $I > 2.0\sigma(I)$.

Table S12: Bond lengths [Å] and angles [°] for **8-La**.

La(1)-O(1)	2.628(6)	C(4)-H(4B)	0.9900
La(1)-N(2)	2.668(9)	C(5)-H(5A)	0.9900
La(1)-N(3)	2.744(8)	C(5)-H(5B)	0.9900
La(1)-N(1)	2.752(9)	C(6)-H(6A)	0.9800
La(1)-I(3)	3.1337(9)	C(6)-H(6B)	0.9800
La(1)-I(2)	3.1738(9)	C(6)-H(6C)	0.9800
La(1)-I(1)	3.1749(9)	C(7)-C(8)	1.493(17)
O(1)-C(13)	1.438(12)	C(7)-H(7A)	0.9900
O(1)-C(10)	1.455(13)	C(7)-H(7B)	0.9900
N(1)-C(9)	1.484(14)	C(8)-H(8A)	0.9900
N(1)-C(1)	1.493(13)	C(8)-H(8B)	0.9900
N(1)-C(8)	1.501(14)	C(9)-H(9A)	0.9800
N(2)-C(2)	1.478(13)	C(9)-H(9B)	0.9800
N(2)-C(3)	1.488(14)	C(9)-H(9C)	0.9800
N(2)-C(4)	1.509(14)	C(10)-C(11)	1.510(16)
N(3)-C(6)	1.478(12)	C(10)-H(10A)	0.9900
N(3)-C(7)	1.484(14)	C(10)-H(10B)	0.9900
N(3)-C(5)	1.515(14)	C(11)-C(12)	1.524(14)
C(1)-C(2)	1.491(15)	C(11)-H(11A)	0.9900
C(1)-H(1A)	0.9900	C(11)-H(11B)	0.9900
C(1)-H(1B)	0.9900	C(12)-C(13)	1.513(15)
C(2)-H(2A)	0.9900	C(12)-H(12A)	0.9900
C(2)-H(2B)	0.9900	C(12)-H(12B)	0.9900
C(3)-H(3A)	0.9800	C(13)-H(13A)	0.9900
C(3)-H(3B)	0.9800	C(13)-H(13B)	0.9900
C(3)-H(3C)	0.9800		
C(4)-C(5)	1.509(15)	O(1)-La(1)-N(2)	132.3(3)
C(4)-H(4A)	0.9900	O(1)-La(1)-N(3)	145.4(2)

N(2)-La(1)-N(3)	65.1(3)	C(2)-C(1)-N(1)	115.0(8)
O(1)-La(1)-N(1)	145.4(2)	C(2)-C(1)-H(1A)	108.5
N(2)-La(1)-N(1)	65.9(3)	N(1)-C(1)-H(1A)	108.5
N(3)-La(1)-N(1)	64.8(3)	C(2)-C(1)-H(1B)	108.5
O(1)-La(1)-I(3)	81.46(17)	N(1)-C(1)-H(1B)	108.5
N(2)-La(1)-I(3)	146.2(2)	H(1A)-C(1)-H(1B)	107.5
N(3)-La(1)-I(3)	86.90(17)	N(2)-C(2)-C(1)	114.6(9)
N(1)-La(1)-I(3)	85.72(19)	N(2)-C(2)-H(2A)	108.6
O(1)-La(1)-I(2)	72.39(16)	C(1)-C(2)-H(2A)	108.6
N(2)-La(1)-I(2)	86.13(19)	N(2)-C(2)-H(2B)	108.6
N(3)-La(1)-I(2)	80.92(18)	C(1)-C(2)-H(2B)	108.6
N(1)-La(1)-I(2)	142.19(19)	H(2A)-C(2)-H(2B)	107.6
I(3)-La(1)-I(2)	108.76(2)	N(2)-C(3)-H(3A)	109.5
O(1)-La(1)-I(1)	71.62(15)	N(2)-C(3)-H(3B)	109.5
N(2)-La(1)-I(1)	87.85(18)	H(3A)-C(3)-H(3B)	109.5
N(3)-La(1)-I(1)	142.91(18)	N(2)-C(3)-H(3C)	109.5
N(1)-La(1)-I(1)	81.55(19)	H(3A)-C(3)-H(3C)	109.5
I(3)-La(1)-I(1)	106.44(3)	H(3B)-C(3)-H(3C)	109.5
I(2)-La(1)-I(1)	124.13(3)	N(2)-C(4)-C(5)	114.7(9)
C(13)-O(1)-C(10)	108.9(7)	N(2)-C(4)-H(4A)	108.6
C(13)-O(1)-La(1)	126.8(6)	C(5)-C(4)-H(4A)	108.6
C(10)-O(1)-La(1)	120.0(6)	N(2)-C(4)-H(4B)	108.6
C(9)-N(1)-C(1)	109.1(8)	C(5)-C(4)-H(4B)	108.6
C(9)-N(1)-C(8)	106.9(9)	H(4A)-C(4)-H(4B)	107.6
C(1)-N(1)-C(8)	110.1(8)	C(4)-C(5)-N(3)	111.7(8)
C(9)-N(1)-La(1)	112.6(6)	C(4)-C(5)-H(5A)	109.3
C(1)-N(1)-La(1)	111.9(6)	N(3)-C(5)-H(5A)	109.3
C(8)-N(1)-La(1)	106.0(7)	C(4)-C(5)-H(5B)	109.3
C(2)-N(2)-C(3)	108.5(8)	N(3)-C(5)-H(5B)	109.3
C(2)-N(2)-C(4)	111.0(9)	H(5A)-C(5)-H(5B)	107.9
C(3)-N(2)-C(4)	110.2(9)	N(3)-C(6)-H(6A)	109.5
C(2)-N(2)-La(1)	105.9(6)	N(3)-C(6)-H(6B)	109.5
C(3)-N(2)-La(1)	104.8(6)	H(6A)-C(6)-H(6B)	109.5
C(4)-N(2)-La(1)	116.0(6)	N(3)-C(6)-H(6C)	109.5
C(6)-N(3)-C(7)	109.5(8)	H(6A)-C(6)-H(6C)	109.5
C(6)-N(3)-C(5)	107.0(8)	H(6B)-C(6)-H(6C)	109.5
C(7)-N(3)-C(5)	109.8(9)	N(3)-C(7)-C(8)	113.5(9)
C(6)-N(3)-La(1)	108.8(6)	N(3)-C(7)-H(7A)	108.9
C(7)-N(3)-La(1)	115.7(6)	C(8)-C(7)-H(7A)	108.9
C(5)-N(3)-La(1)	105.6(6)	N(3)-C(7)-H(7B)	108.9

C(8)-C(7)-H(7B)	108.9	H(10A)-C(10)-H(10B)	108.6
H(7A)-C(7)-H(7B)	107.7	C(10)-C(11)-C(12)	104.2(9)
C(7)-C(8)-N(1)	114.7(9)	C(10)-C(11)-H(11A)	110.9
C(7)-C(8)-H(8A)	108.6	C(12)-C(11)-H(11A)	110.9
N(1)-C(8)-H(8A)	108.6	C(10)-C(11)-H(11B)	110.9
C(7)-C(8)-H(8B)	108.6	C(12)-C(11)-H(11B)	110.9
N(1)-C(8)-H(8B)	108.6	H(11A)-C(11)-H(11B)	108.9
H(8A)-C(8)-H(8B)	107.6	C(13)-C(12)-C(11)	102.0(9)
N(1)-C(9)-H(9A)	109.5	C(13)-C(12)-H(12A)	111.4
N(1)-C(9)-H(9B)	109.5	C(11)-C(12)-H(12A)	111.4
H(9A)-C(9)-H(9B)	109.5	C(13)-C(12)-H(12B)	111.4
N(1)-C(9)-H(9C)	109.5	C(11)-C(12)-H(12B)	111.4
H(9A)-C(9)-H(9C)	109.5	H(12A)-C(12)-H(12B)	109.2
H(9B)-C(9)-H(9C)	109.5	O(1)-C(13)-C(12)	105.7(8)
O(1)-C(10)-C(11)	106.8(9)	O(1)-C(13)-H(13A)	110.6
O(1)-C(10)-H(10A)	110.4	C(12)-C(13)-H(13A)	110.6
C(11)-C(10)-H(10A)	110.4	O(1)-C(13)-H(13B)	110.6
O(1)-C(10)-H(10B)	110.4	C(12)-C(13)-H(13B)	110.6
C(11)-C(10)-H(10B)	110.4	H(13A)-C(13)-H(13B)	108.7

X-ray Data Collection, Structure Solution and Refinement for **9-Y**.

A colorless crystal of approximate dimensions 0.177 x 0.208 x 0.236 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2[23] program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time). The raw frame data was processed using SAINT[24] and SADABS[25] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[26] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[27] for neutral atoms were used throughout the analysis.

Hydrogen atoms were included using a riding model. The structure was refined as a two-component twin.

Least-squares analysis yielded wR2 = 0.1458 and Goof = 1.098 for 149 variables refined against 3137 data (0.80 Å), R1 = 0.0521 for those 2475 data with I > 2.0σ(I).

Table S13: Bond lengths [Å] and angles [°] for **9-Y**.

Y(1)-N(3)	2.483(5)	N(3)-Y(1)-Cl(2)	94.02(13)
Y(1)-N(2)	2.499(5)	N(2)-Y(1)-Cl(2)	91.78(14)
Y(1)-N(1)	2.508(5)	N(1)-Y(1)-Cl(2)	159.82(13)
Y(1)-Cl(1)	2.5555(17)	Cl(1)-Y(1)-Cl(2)	101.28(6)
Y(1)-Cl(3)	2.5592(18)	Cl(3)-Y(1)-Cl(2)	101.92(6)
Y(1)-Cl(2)	2.5610(17)	C(9)-N(1)-C(1)	108.4(5)
N(1)-C(9)	1.485(9)	C(9)-N(1)-C(8)	110.3(5)
N(1)-C(1)	1.492(9)	C(1)-N(1)-C(8)	111.0(5)
N(1)-C(8)	1.495(8)	C(9)-N(1)-Y(1)	109.4(4)
N(2)-C(2)	1.490(9)	C(1)-N(1)-Y(1)	104.2(4)
N(2)-C(4)	1.491(8)	C(8)-N(1)-Y(1)	113.4(4)
N(2)-C(3)	1.505(9)	C(2)-N(2)-C(4)	112.8(5)
N(3)-C(6)	1.488(8)	C(2)-N(2)-C(3)	110.4(5)
N(3)-C(5)	1.498(8)	C(4)-N(2)-C(3)	108.2(5)
N(3)-C(7)	1.506(9)	C(2)-N(2)-Y(1)	112.5(4)
C(1)-C(2)	1.504(10)	C(4)-N(2)-Y(1)	103.2(4)
C(4)-C(5)	1.509(9)	C(3)-N(2)-Y(1)	109.3(4)
C(7)-C(8)	1.513(9)	C(6)-N(3)-C(5)	110.0(5)
		C(6)-N(3)-C(7)	107.8(5)
N(3)-Y(1)-N(2)	71.74(18)	C(5)-N(3)-C(7)	111.3(5)
N(3)-Y(1)-N(1)	70.84(17)	C(6)-N(3)-Y(1)	110.0(4)
N(2)-Y(1)-N(1)	71.15(19)	C(5)-N(3)-Y(1)	112.2(4)
N(3)-Y(1)-Cl(1)	156.86(13)	C(7)-N(3)-Y(1)	105.5(4)
N(2)-Y(1)-Cl(1)	90.37(13)	N(1)-C(1)-C(2)	112.9(5)
N(1)-Y(1)-Cl(1)	89.82(13)	N(2)-C(2)-C(1)	113.7(5)
N(3)-Y(1)-Cl(3)	92.35(14)	N(2)-C(4)-C(5)	112.9(5)
N(2)-Y(1)-Cl(3)	159.81(13)	N(3)-C(5)-C(4)	113.1(5)
N(1)-Y(1)-Cl(3)	92.22(14)	N(3)-C(7)-C(8)	112.1(5)
Cl(1)-Y(1)-Cl(3)	101.23(6)	N(1)-C(8)-C(7)	112.2(5)

X-ray Data Collection, Structure Solution and Refinement for **10-Sm**.

A green crystal of approximate dimensions 0.226 x 0.166 x 0.120 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2[23]

program package was used to determine the unit-cell parameters and for data collection (120 sec/frame scan time). The raw frame data was processed using SAINT[24] and SADABS[25] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[26] program package. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space groups *Pnma* and $Pna2_1$. It was later determined that space group $Pna2_1$ was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[27] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Disordered carbon atoms were included using multiple components, partial site-occupancy-factors and equivalent isotropic displacement parameters.

Least-squares analysis yielded wR2 = 0.0563 and Goof = 0.985 for 179 variables refined against 4718 data (0.76 Å), R1 = 0.0506 for those 3222 data with $I > 2.0\sigma(I)$. The structure was refined as a two-component inversion twin.

Table S14: Bond lengths [Å] and angles [°] for **10-Sm**.

Sm(1)-O(1)	2.534(9)	N(3)-C(8A)	1.42(3)
Sm(1)-N(3)	2.636(9)	N(3)-C(6B)	1.44(3)
Sm(1)-N(1)	2.653(10)	N(3)-C(7)	1.447(16)
Sm(1)-N(2)	2.699(10)	N(3)-C(8B)	1.56(3)
Sm(1)-I(2)	3.1804(12)	N(3)-C(6A)	1.59(3)
Sm(1)-I(1)	3.2030(11)	C(1)-H(1A)	0.9800
O(1)-C(10)	1.394(16)	C(1)-H(1B)	0.9800
O(1)-C(13)	1.469(17)	C(1)-H(1C)	0.9800
N(1)-C(2)	1.466(18)	C(2)-C(3B)	1.37(3)
N(1)-C(1)	1.468(17)	C(2)-C(3A)	1.43(4)
N(1)-C(9)	1.481(18)	C(2)-H(2A)	0.9900
N(2)-C(5)	1.440(17)	C(2)-H(2B)	0.9900
N(2)-C(3B)	1.46(3)	C(3A)-H(3AA)	0.9900
N(2)-C(4)	1.465(16)	C(3A)-H(3AB)	0.9900
N(2)-C(3A)	1.55(4)	C(3B)-H(3BA)	0.9900

C(3B)-H(3BB)	0.9900	N(1)-Sm(1)-N(2)	65.8(3)
C(4)-H(4A)	0.9800	O(1)-Sm(1)-I(2)	94.5(2)
C(4)-H(4B)	0.9800	N(3)-Sm(1)-I(2)	101.9(2)
C(4)-H(4C)	0.9800	N(1)-Sm(1)-I(2)	157.4(2)
C(5)-C(6A)	1.31(3)	N(2)-Sm(1)-I(2)	91.9(2)
C(5)-C(6B)	1.53(3)	O(1)-Sm(1)-I(1)	93.0(2)
C(5)-H(5A)	0.9900	N(3)-Sm(1)-I(1)	94.6(2)
C(5)-H(5B)	0.9900	N(1)-Sm(1)-I(1)	93.8(2)
C(6A)-H(6AA)	0.9900	N(2)-Sm(1)-I(1)	156.3(2)
C(6A)-H(6AB)	0.9900	I(2)-Sm(1)-I(1)	106.95(3)
C(6B)-H(6BA)	0.9900	C(10)-O(1)-C(13)	109.4(10)
C(6B)-H(6BB)	0.9900	C(10)-O(1)-Sm(1)	132.5(8)
C(7)-H(7A)	0.9800	C(13)-O(1)-Sm(1)	113.2(8)
C(7)-H(7B)	0.9800	C(2)-N(1)-C(1)	110.2(12)
C(7)-H(7C)	0.9800	C(2)-N(1)-C(9)	112.9(13)
C(8A)-C(9)	1.53(3)	C(1)-N(1)-C(9)	110.1(11)
C(8A)-H(8AA)	0.9900	C(2)-N(1)-Sm(1)	110.6(8)
C(8A)-H(8AB)	0.9900	C(1)-N(1)-Sm(1)	104.2(8)
C(8B)-C(9)	1.33(3)	C(9)-N(1)-Sm(1)	108.6(9)
C(8B)-H(8BA)	0.9900	C(5)-N(2)-C(3B)	126.8(15)
C(8B)-H(8BB)	0.9900	C(5)-N(2)-C(4)	109.2(11)
C(9)-H(9A)	0.9900	C(3B)-N(2)-C(4)	101.8(13)
C(9)-H(9B)	0.9900	C(5)-N(2)-C(3A)	95.4(17)
C(10)-C(11)	1.477(19)	C(4)-N(2)-C(3A)	120.7(17)
C(10)-H(10A)	0.9900	C(5)-N(2)-Sm(1)	106.8(8)
C(10)-H(10B)	0.9900	C(3B)-N(2)-Sm(1)	103.4(11)
C(11)-C(12)	1.54(2)	C(4)-N(2)-Sm(1)	107.5(8)
C(11)-H(11A)	0.9900	C(3A)-N(2)-Sm(1)	115.6(14)
C(11)-H(11B)	0.9900	C(8A)-N(3)-C(7)	119.0(15)
C(12)-C(13)	1.45(2)	C(6B)-N(3)-C(7)	117.9(14)
C(12)-H(12A)	0.9900	C(6B)-N(3)-C(8B)	110.4(17)
C(12)-H(12B)	0.9900	C(7)-N(3)-C(8B)	102.7(13)
C(13)-H(13A)	0.9900	C(8A)-N(3)-C(6A)	109.1(17)
C(13)-H(13B)	0.9900	C(7)-N(3)-C(6A)	102.8(12)
		C(8A)-N(3)-Sm(1)	118.1(13)
O(1)-Sm(1)-N(3)	159.0(3)	C(6B)-N(3)-Sm(1)	117.5(12)
O(1)-Sm(1)-N(1)	93.1(3)	C(7)-N(3)-Sm(1)	105.0(7)
N(3)-Sm(1)-N(1)	66.9(3)	C(8B)-N(3)-Sm(1)	101.1(12)
O(1)-Sm(1)-N(2)	99.8(3)	C(6A)-N(3)-Sm(1)	100.2(11)
N(3)-Sm(1)-N(2)	66.9(3)	N(1)-C(1)-H(1A)	109.5

N(1)-C(1)-H(1B)	109.5	C(5)-C(6A)-H(6AB)	107.8
H(1A)-C(1)-H(1B)	109.5	N(3)-C(6A)-H(6AB)	107.8
N(1)-C(1)-H(1C)	109.5	H(6AA)-C(6A)-H(6AB)	107.1
H(1A)-C(1)-H(1C)	109.5	N(3)-C(6B)-C(5)	113.5(19)
H(1B)-C(1)-H(1C)	109.5	N(3)-C(6B)-H(6BA)	108.9
C(3B)-C(2)-N(1)	119.8(16)	C(5)-C(6B)-H(6BA)	108.9
C(3A)-C(2)-N(1)	120(2)	N(3)-C(6B)-H(6BB)	108.9
C(3B)-C(2)-H(2A)	107.4	C(5)-C(6B)-H(6BB)	108.9
N(1)-C(2)-H(2A)	107.4	H(6BA)-C(6B)-H(6BB)	107.7
C(3B)-C(2)-H(2B)	107.4	N(3)-C(7)-H(7A)	109.5
N(1)-C(2)-H(2B)	107.4	N(3)-C(7)-H(7B)	109.5
H(2A)-C(2)-H(2B)	106.9	H(7A)-C(7)-H(7B)	109.5
C(2)-C(3A)-N(2)	111(2)	N(3)-C(7)-H(7C)	109.5
C(2)-C(3A)-H(3AA)	109.5	H(7A)-C(7)-H(7C)	109.5
N(2)-C(3A)-H(3AA)	109.5	H(7B)-C(7)-H(7C)	109.5
C(2)-C(3A)-H(3AB)	109.5	N(3)-C(8A)-C(9)	114(2)
N(2)-C(3A)-H(3AB)	109.5	N(3)-C(8A)-H(8AA)	108.8
H(3AA)-C(3A)-H(3AB)	108.1	C(9)-C(8A)-H(8AA)	108.8
C(2)-C(3B)-N(2)	120.4(19)	N(3)-C(8A)-H(8AB)	108.8
C(2)-C(3B)-H(3BA)	107.2	C(9)-C(8A)-H(8AB)	108.8
N(2)-C(3B)-H(3BA)	107.2	H(8AA)-C(8A)-H(8AB)	107.7
C(2)-C(3B)-H(3BB)	107.2	C(9)-C(8B)-N(3)	117(2)
N(2)-C(3B)-H(3BB)	107.2	C(9)-C(8B)-H(8BA)	108.0
H(3BA)-C(3B)-H(3BB)	106.9	N(3)-C(8B)-H(8BA)	108.0
N(2)-C(4)-H(4A)	109.5	C(9)-C(8B)-H(8BB)	108.0
N(2)-C(4)-H(4B)	109.5	N(3)-C(8B)-H(8BB)	108.0
H(4A)-C(4)-H(4B)	109.5	H(8BA)-C(8B)-H(8BB)	107.2
N(2)-C(4)-H(4C)	109.5	C(8B)-C(9)-N(1)	120.7(18)
H(4A)-C(4)-H(4C)	109.5	N(1)-C(9)-C(8A)	117.4(15)
H(4B)-C(4)-H(4C)	109.5	C(8B)-C(9)-H(9A)	107.2
C(6A)-C(5)-N(2)	123.3(17)	N(1)-C(9)-H(9A)	107.2
N(2)-C(5)-C(6B)	119.2(15)	C(8B)-C(9)-H(9B)	107.2
C(6A)-C(5)-H(5A)	106.5	N(1)-C(9)-H(9B)	107.2
N(2)-C(5)-H(5A)	106.5	H(9A)-C(9)-H(9B)	106.8
C(6A)-C(5)-H(5B)	106.5	O(1)-C(10)-C(11)	109.9(12)
N(2)-C(5)-H(5B)	106.5	O(1)-C(10)-H(10A)	109.7
H(5A)-C(5)-H(5B)	106.5	C(11)-C(10)-H(10A)	109.7
C(5)-C(6A)-N(3)	118(2)	O(1)-C(10)-H(10B)	109.7
C(5)-C(6A)-H(6AA)	107.8	C(11)-C(10)-H(10B)	109.7
N(3)-C(6A)-H(6AA)	107.8	H(10A)-C(10)-H(10B)	108.2

C(10)-C(11)-C(12)	102.1(12)	C(13)-C(12)-H(12B)	110.5
C(10)-C(11)-H(11A)	111.3	C(11)-C(12)-H(12B)	110.5
C(12)-C(11)-H(11A)	111.3	H(12A)-C(12)-H(12B)	108.7
C(10)-C(11)-H(11B)	111.3	C(12)-C(13)-O(1)	105.4(13)
C(12)-C(11)-H(11B)	111.3	C(12)-C(13)-H(13A)	110.7
H(11A)-C(11)-H(11B)	109.2	O(1)-C(13)-H(13A)	110.7
C(13)-C(12)-C(11)	106.0(13)	C(12)-C(13)-H(13B)	110.7
C(13)-C(12)-H(12A)	110.5	O(1)-C(13)-H(13B)	110.7
C(11)-C(12)-H(12A)	110.5	H(13A)-C(13)-H(13B)	108.8

X-ray Data Collection, Structure Solution and Refinement for [HMe_3tach][Br].

A colorless crystal of approximate dimensions 0.150 x 0.114 x 0.083 mm was mounted in a cryoloop and transferred to a Bruker X8 Prospector diffractometer system. The APEX3[31] program package was used to determine the unit-cell parameters and for data collection (10 sec/frame scan time). The raw frame data was processed using SAINT[24] and SADABS[25] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[26] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[27] for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}).

Least-squares analysis yielded wR2 = 0.0700 and Goof = 1.033 for 155 variables refined against 1723 data (0.83 Å), R1 = 0.0290 for those 1453 data with $I > 2.0\sigma(I)$.

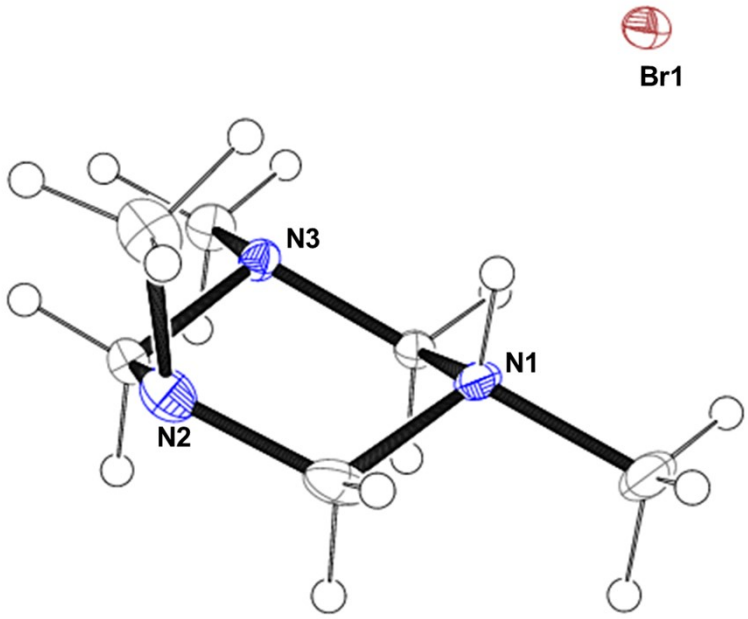

Figure S1: Molecular structure of [HMe_3tach][Br] with selective atom labelling. Ellipsoids are drawn at the 35% probability level.

Table S15: Bond lengths [Å] and angles [°] for [HMe_3tach][Br].

N(1)-C(3)	1.489(4)	C(6)-H(6A)	1.02(4)
N(1)-C(4)	1.498(4)	C(6)-H(6B)	1.03(4)
N(1)-C(1)	1.523(4)	C(6)-H(6C)	0.91(4)
N(1)-H(1)	0.93(3)		
N(2)-C(1)	1.430(4)	C(3)-N(1)-C(4)	110.9(3)
N(2)-C(2)	1.455(4)	C(3)-N(1)-C(1)	109.2(2)
N(2)-C(5)	1.467(5)	C(4)-N(1)-C(1)	111.9(3)
N(3)-C(3)	1.446(4)	C(3)-N(1)-H(1)	109(2)
N(3)-C(2)	1.471(4)	C(4)-N(1)-H(1)	108(2)
N(3)-C(6)	1.474(4)	C(1)-N(1)-H(1)	108(2)
C(1)-H(1A)	0.97(4)	C(1)-N(2)-C(2)	109.5(3)
C(1)-H(1B)	1.00(4)	C(1)-N(2)-C(5)	114.6(3)
C(2)-H(2A)	0.95(3)	C(2)-N(2)-C(5)	113.5(3)
C(2)-H(2B)	0.99(3)	C(3)-N(3)-C(2)	109.4(2)
C(3)-H(3A)	0.92(4)	C(3)-N(3)-C(6)	109.7(2)
C(3)-H(3B)	0.99(3)	C(2)-N(3)-C(6)	110.1(2)
C(4)-H(4A)	1.02(4)	N(2)-C(1)-N(1)	112.7(3)
C(4)-H(4B)	1.01(4)	N(2)-C(1)-H(1A)	110(2)
C(4)-H(4C)	0.96(4)	N(1)-C(1)-H(1A)	107(2)
C(5)-H(5A)	0.99(4)	N(2)-C(1)-H(1B)	107(2)
C(5)-H(5B)	1.02(4)	N(1)-C(1)-H(1B)	107(2)
C(5)-H(5C)	0.87(4)	H(1A)-C(1)-H(1B)	113(3)

N(2)-C(2)-N(3)	111.0(2)	N(1)-C(4)-H(4C)	111(2)
N(2)-C(2)-H(2A)	108(2)	H(4A)-C(4)-H(4C)	111(3)
N(3)-C(2)-H(2A)	108(2)	H(4B)-C(4)-H(4C)	112(3)
N(2)-C(2)-H(2B)	109.2(19)	N(2)-C(5)-H(5A)	109(2)
N(3)-C(2)-H(2B)	110.7(19)	N(2)-C(5)-H(5B)	113(2)
H(2A)-C(2)-H(2B)	110(3)	H(5A)-C(5)-H(5B)	109(3)
N(3)-C(3)-N(1)	108.8(2)	N(2)-C(5)-H(5C)	108(3)
N(3)-C(3)-H(3A)	113(2)	H(5A)-C(5)-H(5C)	110(3)
N(1)-C(3)-H(3A)	107(2)	H(5B)-C(5)-H(5C)	108(3)
N(3)-C(3)-H(3B)	114.4(19)	N(3)-C(6)-H(6A)	109(2)
N(1)-C(3)-H(3B)	106.0(19)	N(3)-C(6)-H(6B)	111.8(19)
H(3A)-C(3)-H(3B)	107(3)	H(6A)-C(6)-H(6B)	108(3)
N(1)-C(4)-H(4A)	108(2)	N(3)-C(6)-H(6C)	108(2)
N(1)-C(4)-H(4B)	105(2)	H(6A)-C(6)-H(6C)	110(3)
H(4A)-C(4)-H(4B)	110(3)	H(6B)-C(6)-H(6C)	111(3)

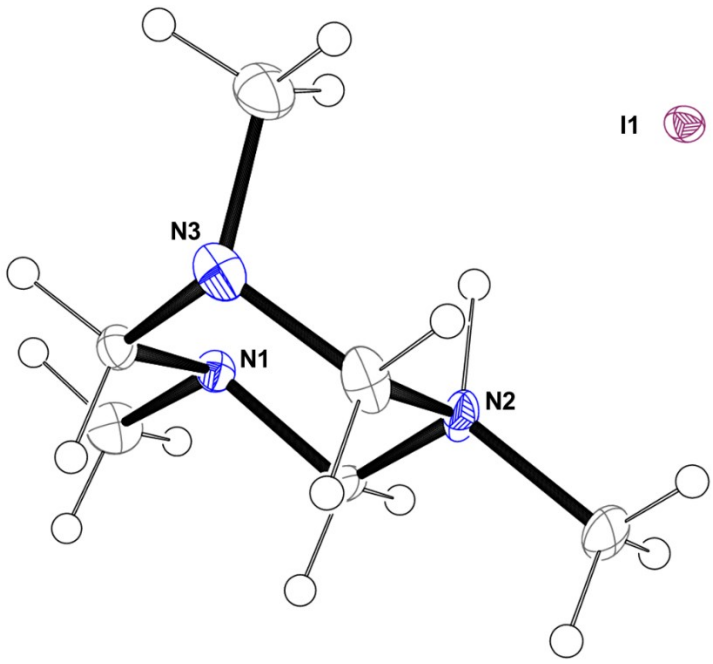

Figure S2: Connectivity plot of [HMe$_3$tach][I] with selective atom labelling.

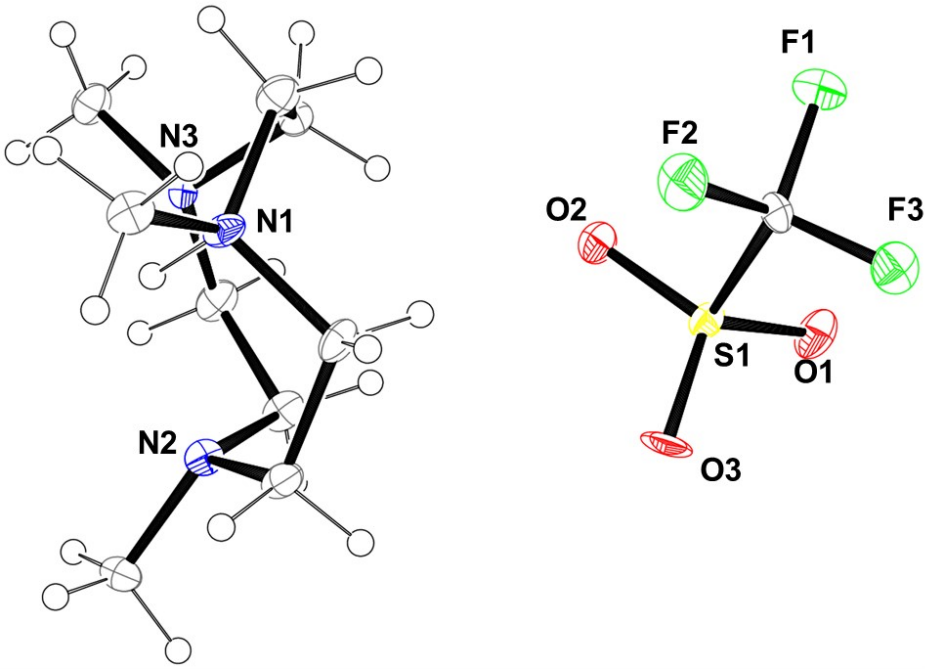

Figure S3: Connectivity plot of [HMe$_3$tacn][OTf] with selective atom labelling.

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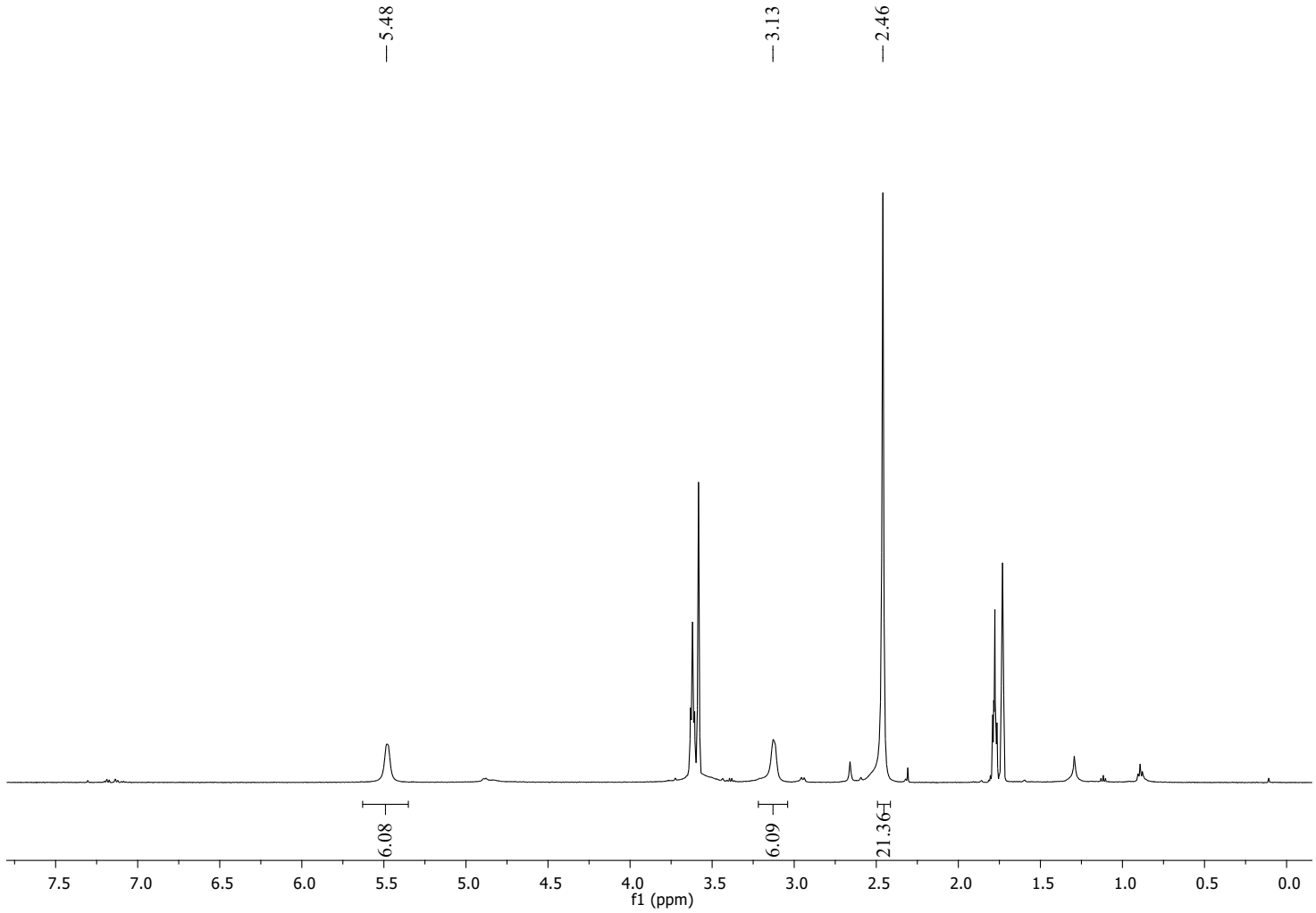

Figure S4: ^{1}H NMR spectrum of **1-La** in THF-d_8. Unlabeled peaks are due to residual THF and hexane.

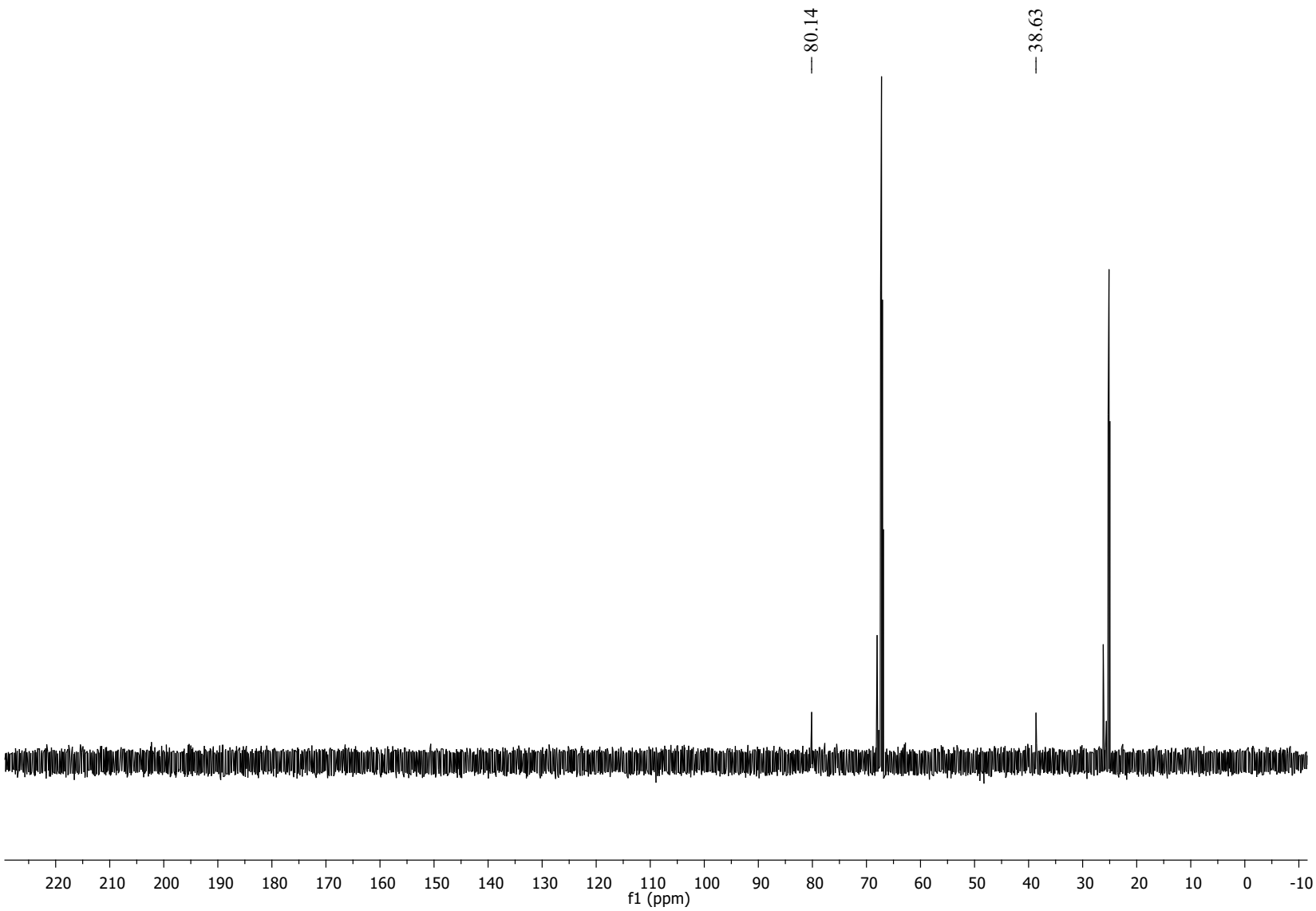

Figure S5: ^{13}C NMR spectrum of **1-La** in THF-d_8.

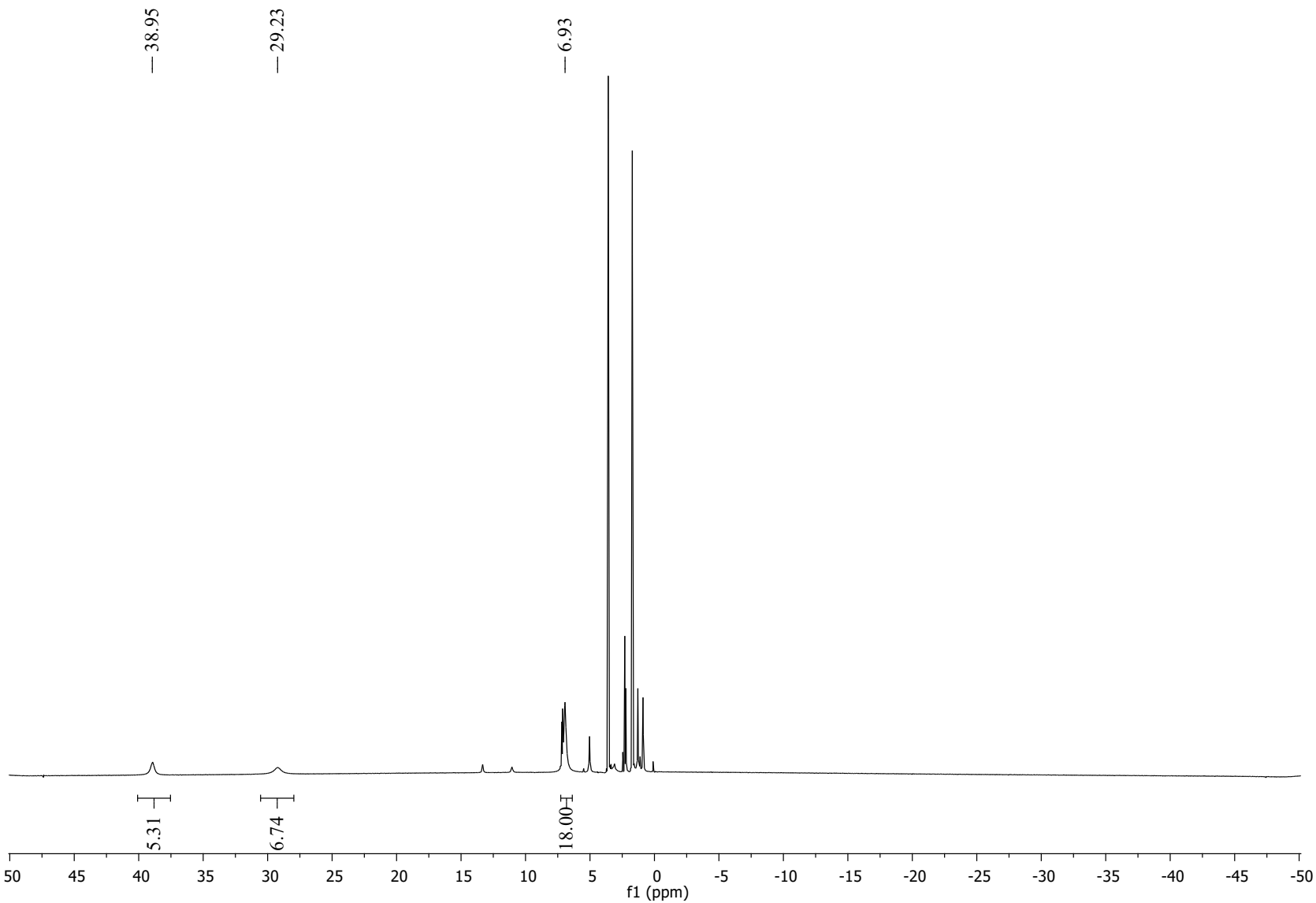

Figure S6: ^{1}H NMR spectrum of **1-Ce** in THF-d_8. Unlabeled peaks are due to residual THF, hexane, and toluene.

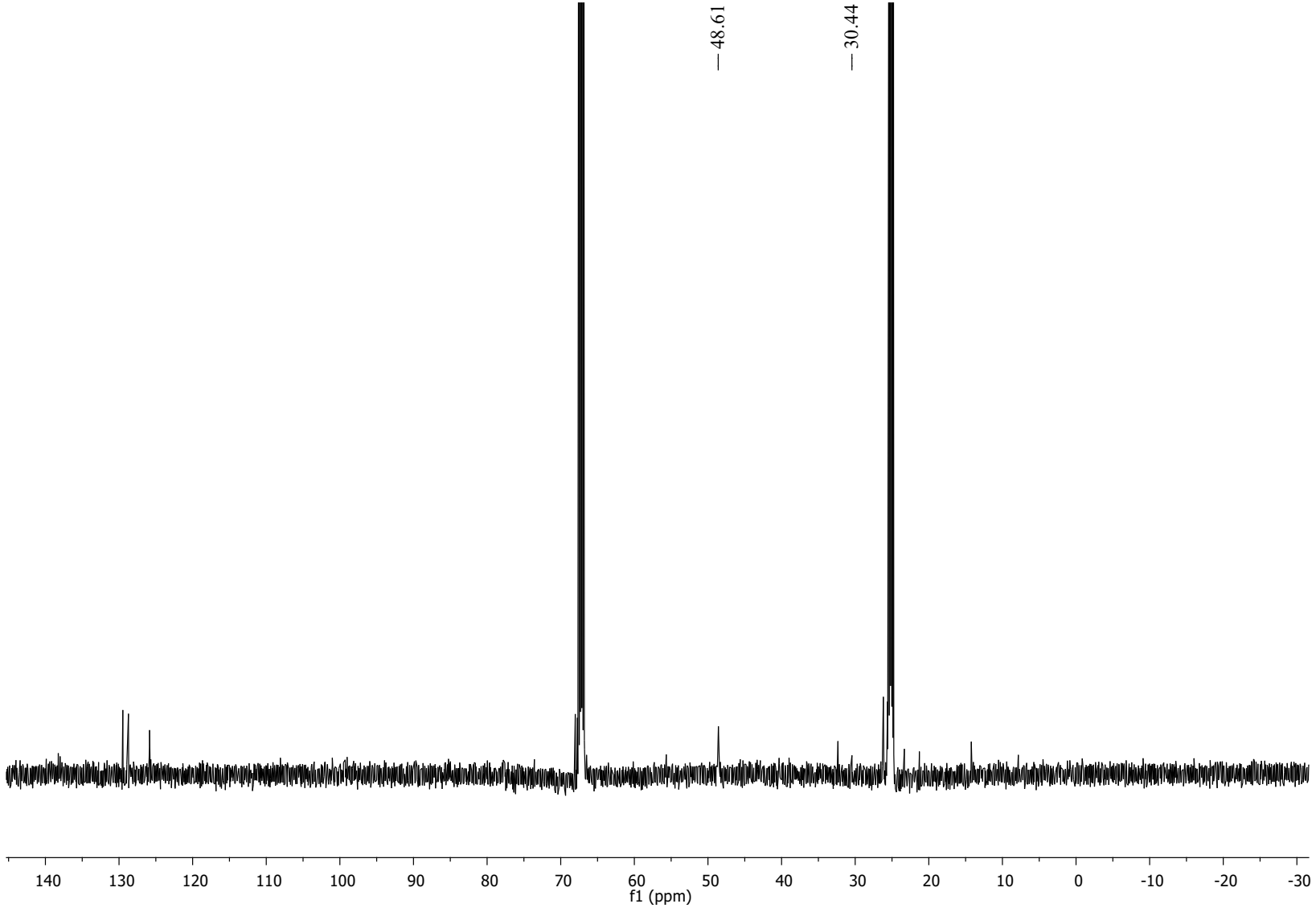

Figure S7: ^{13}C NMR spectrum of **1-Ce** in THF-d_8. Unlabeled peaks are due to residual THF, hexane, and toluene.

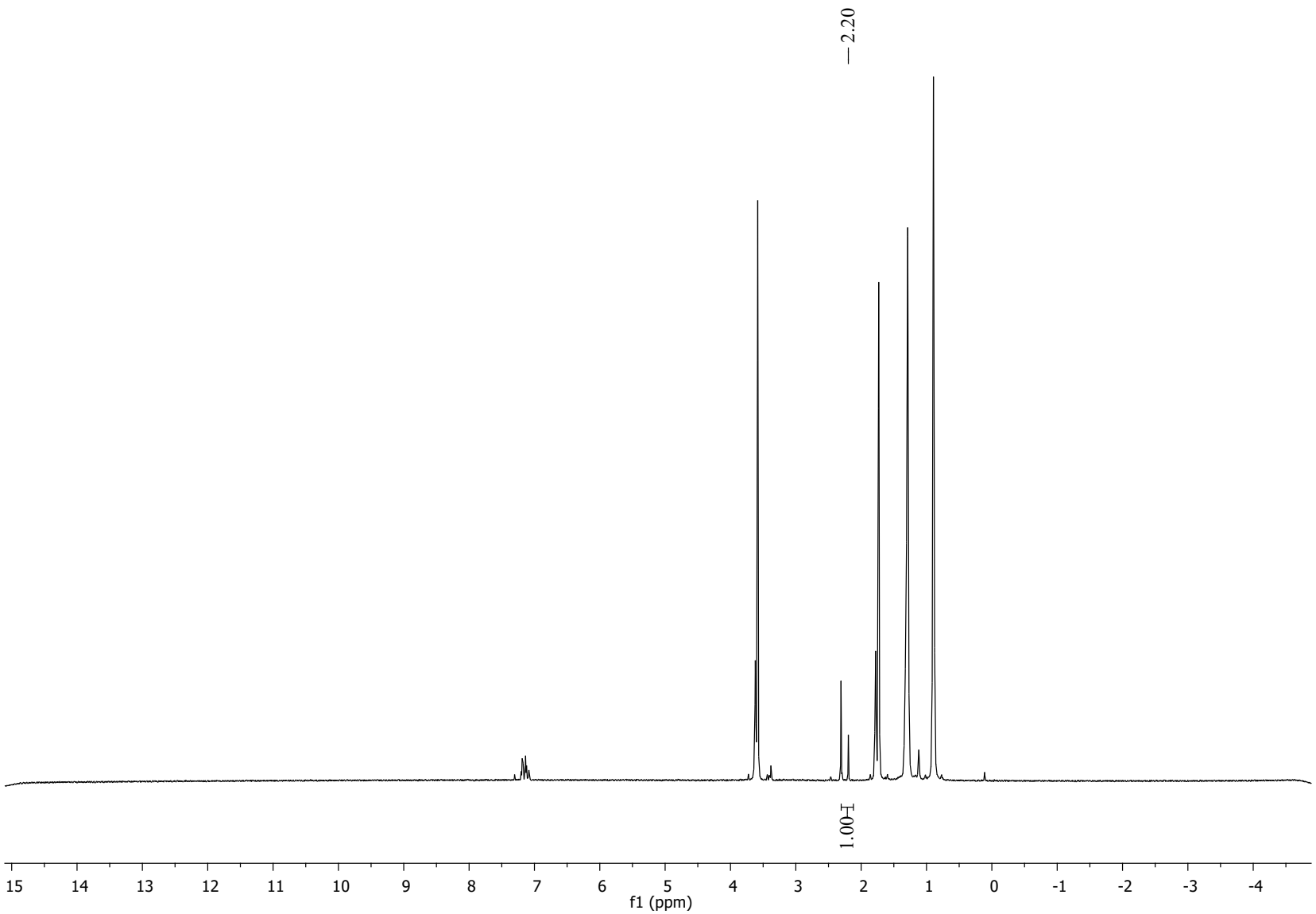

Figure S8: ^{1}H NMR spectrum of **3-La** in THF-d_8. All other unlabeled peaks are due to residual THF, hexane, and toluene.

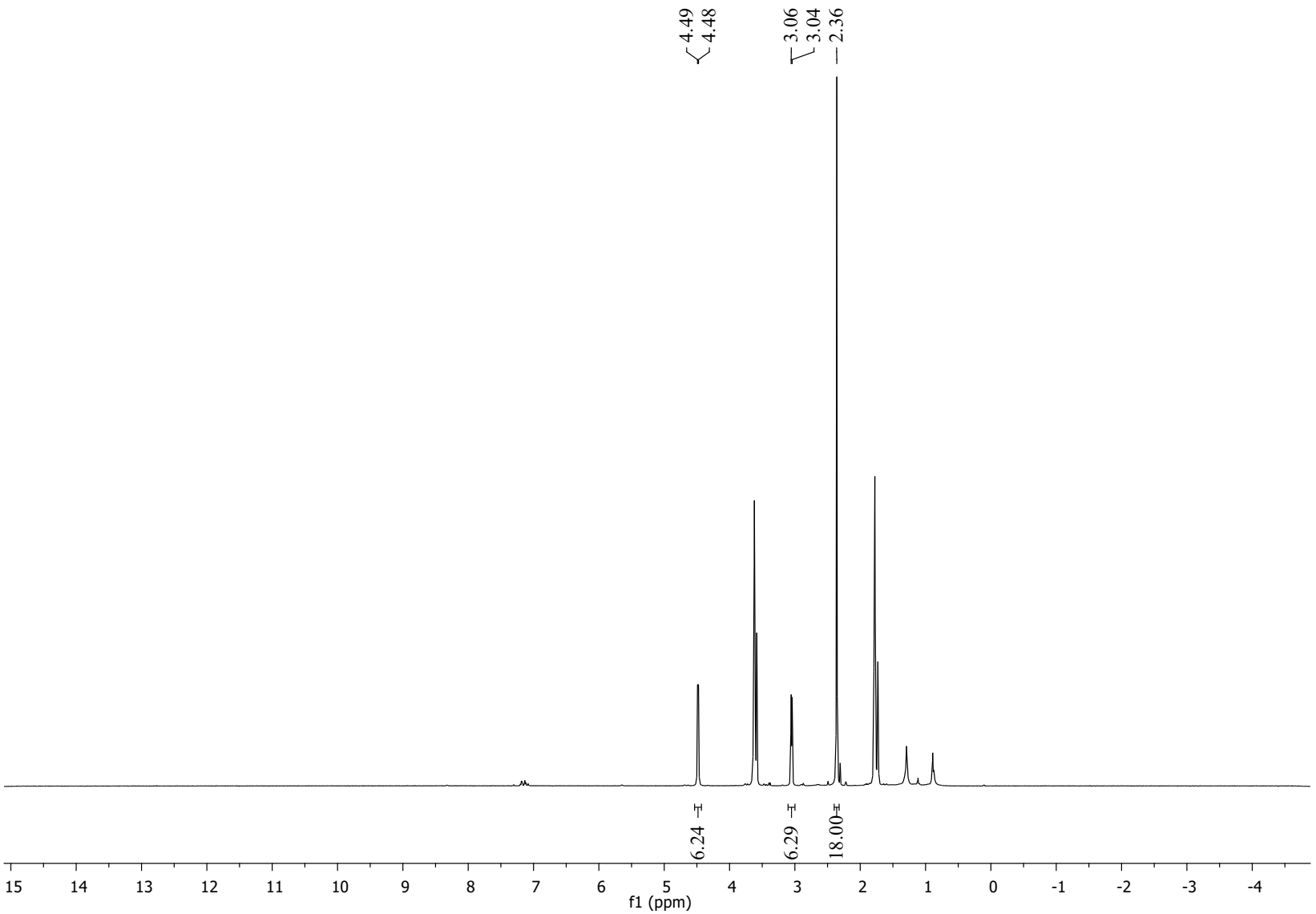

Figure S9: ^{1}H NMR spectrum of **4-Y** in THF-d_8. Unlabeled peaks are due to residual THF, hexane, and toluene.

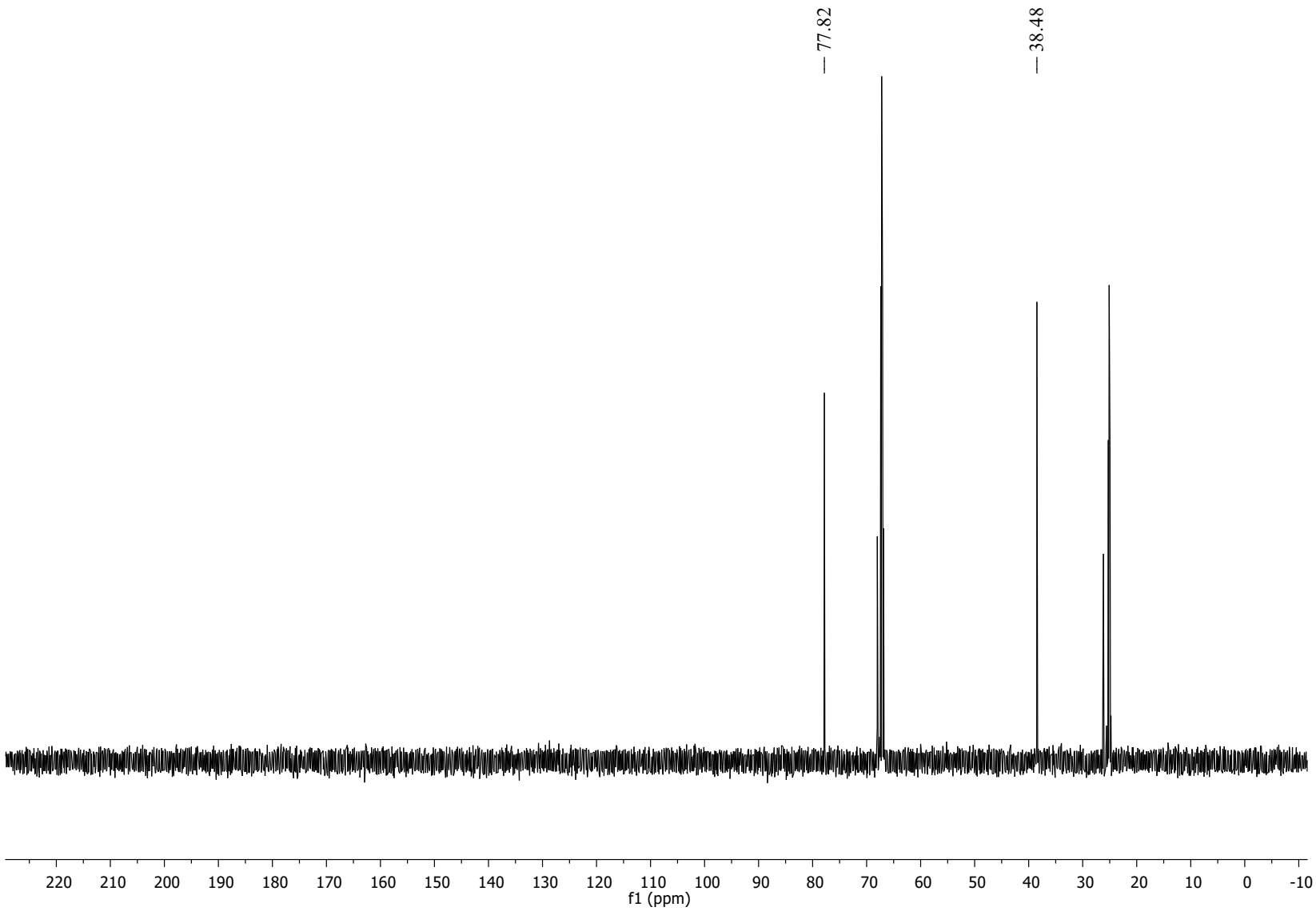

Figure S10: ^{13}C NMR spectrum of **4-Y** in THF-d_8.

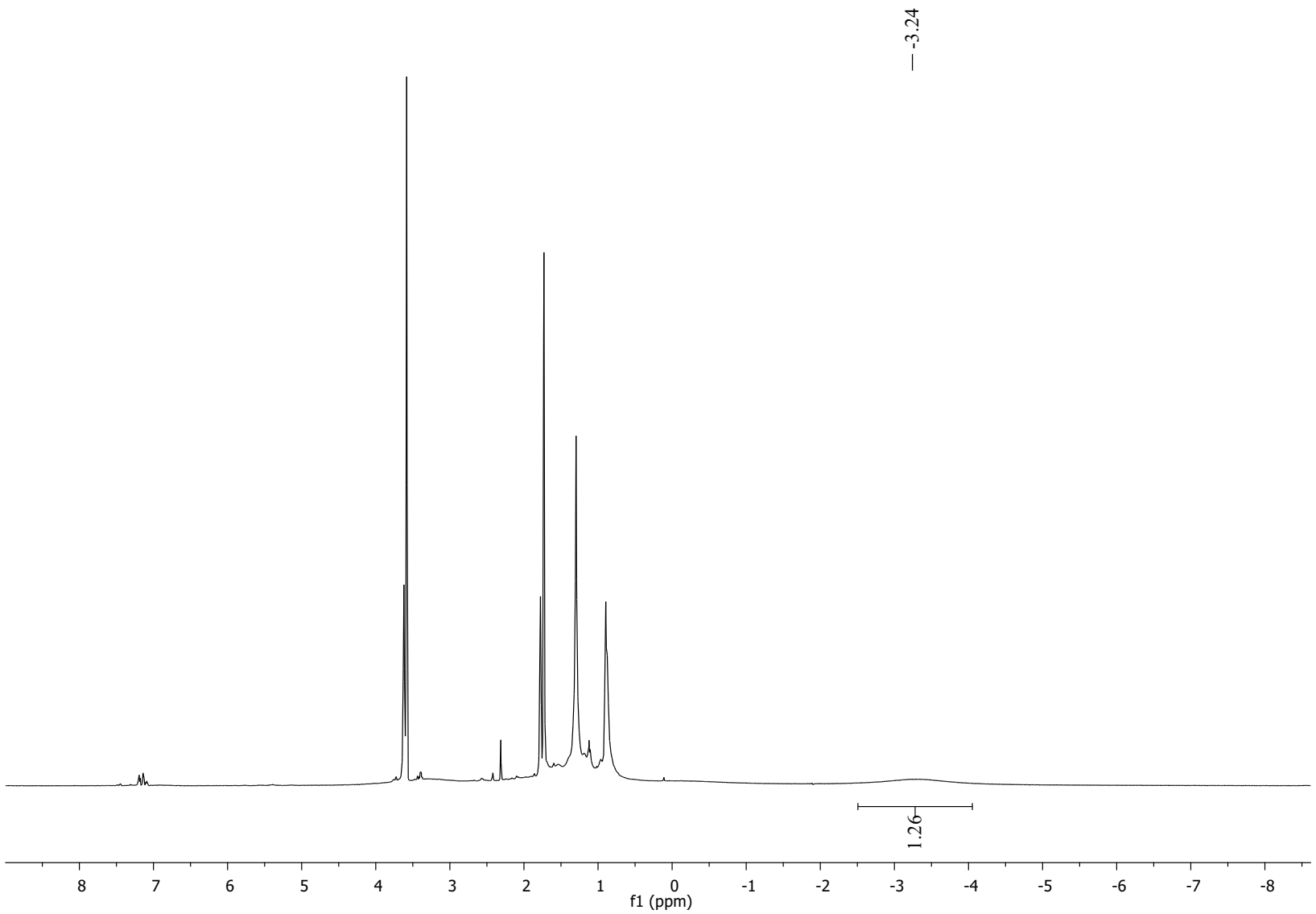

Figure S11: ^{1}H NMR spectrum of **7-Sm** in THF-d_8. Unlabeled peaks are due to residual THF, hexane, and toluene.

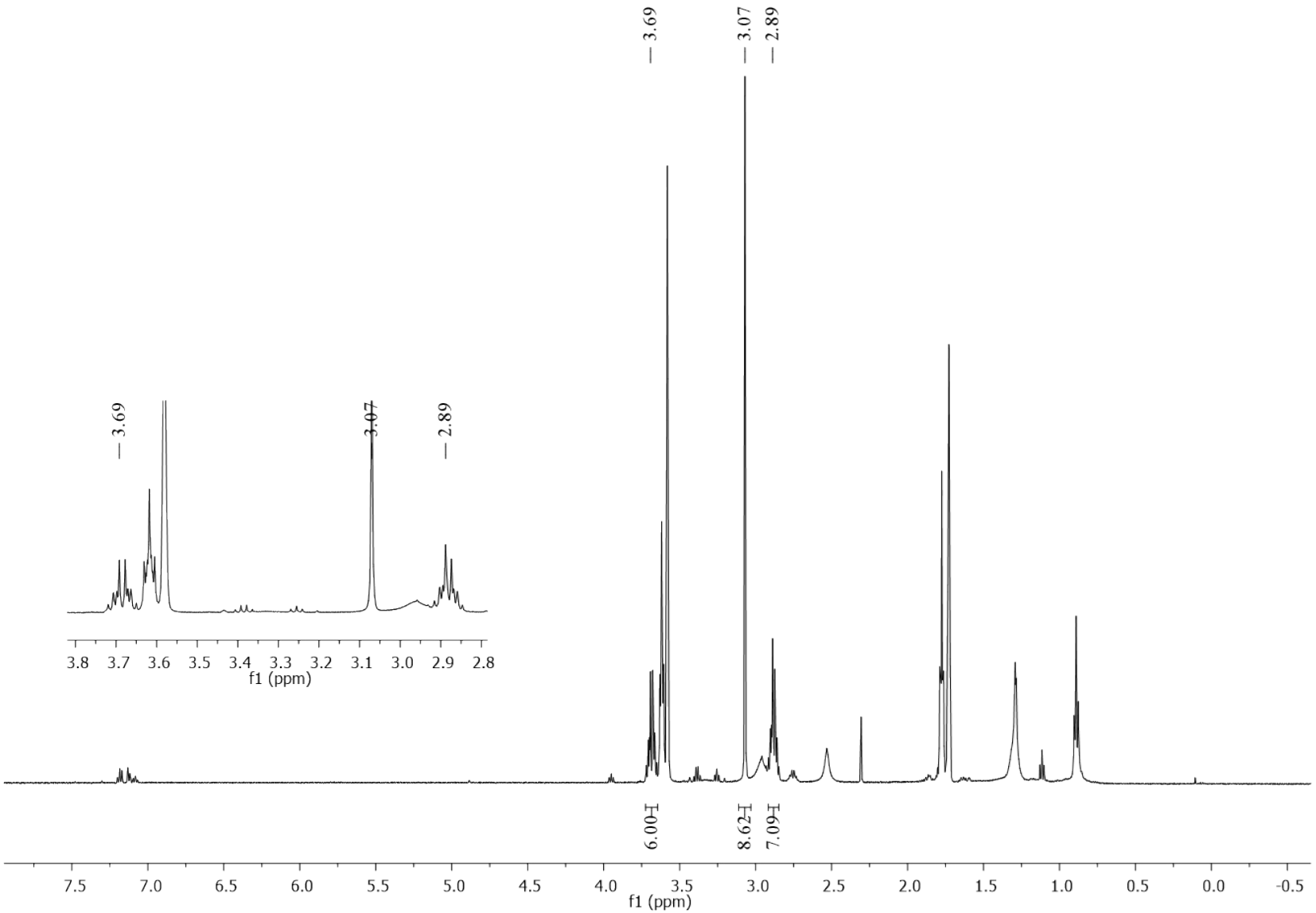

Figure S12: ^{1}H NMR spectrum of **8-La** in THF-d_8. Unlabeled peaks are due to residual THF, hexane, and toluene.

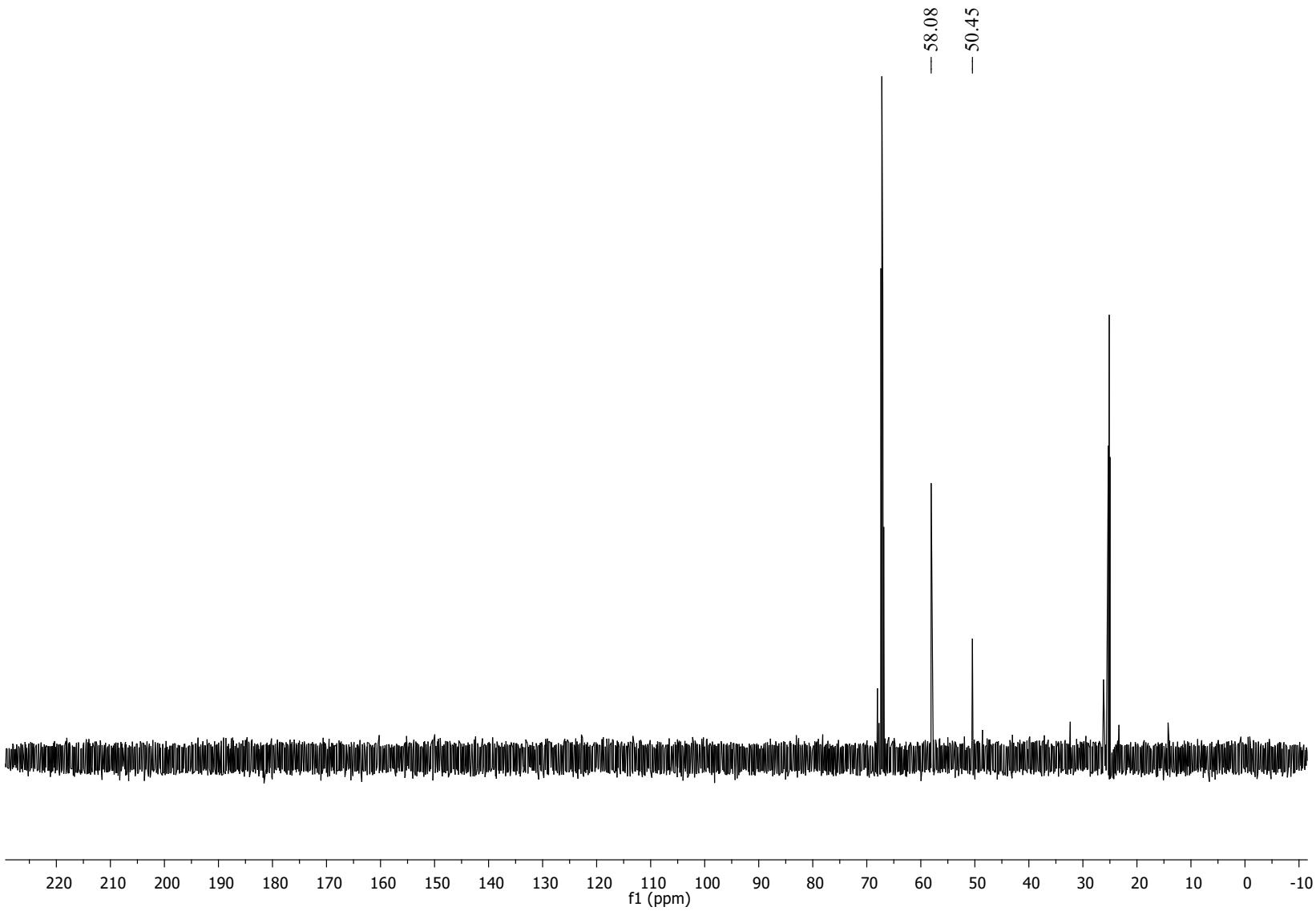

Figure S13: ^{13}C NMR spectrum of **8-La** in THF-d_8.

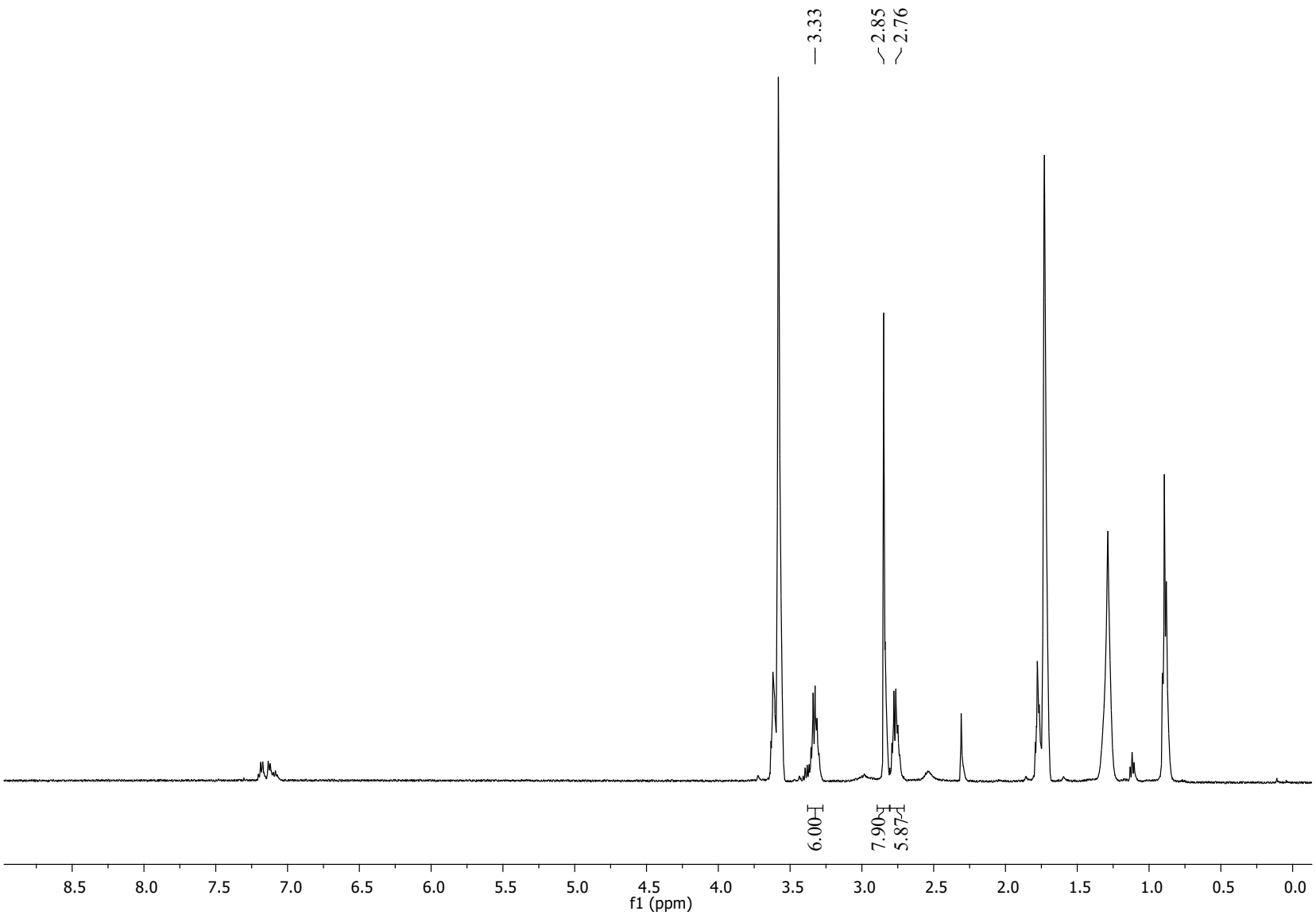

Figure S14: ^{1}H NMR spectrum of **9-Y** in THF-d_8. Unlabeled peaks are due to residual THF, hexane, and toluene.

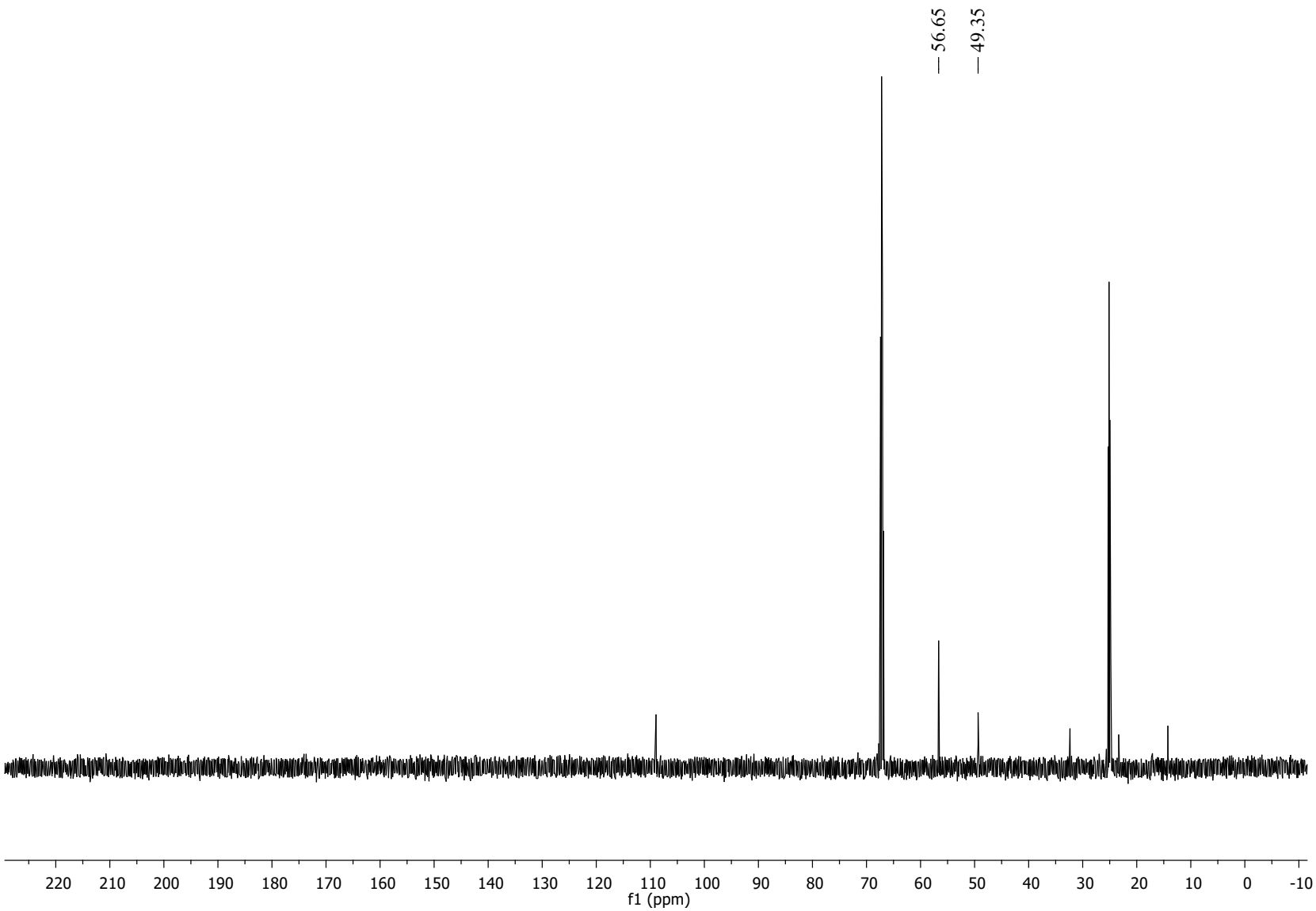

Figure S15: ^{13}C NMR spectrum of **9-Y** in THF-d_8. Unlabeled peaks are due to residual THF and hexane.

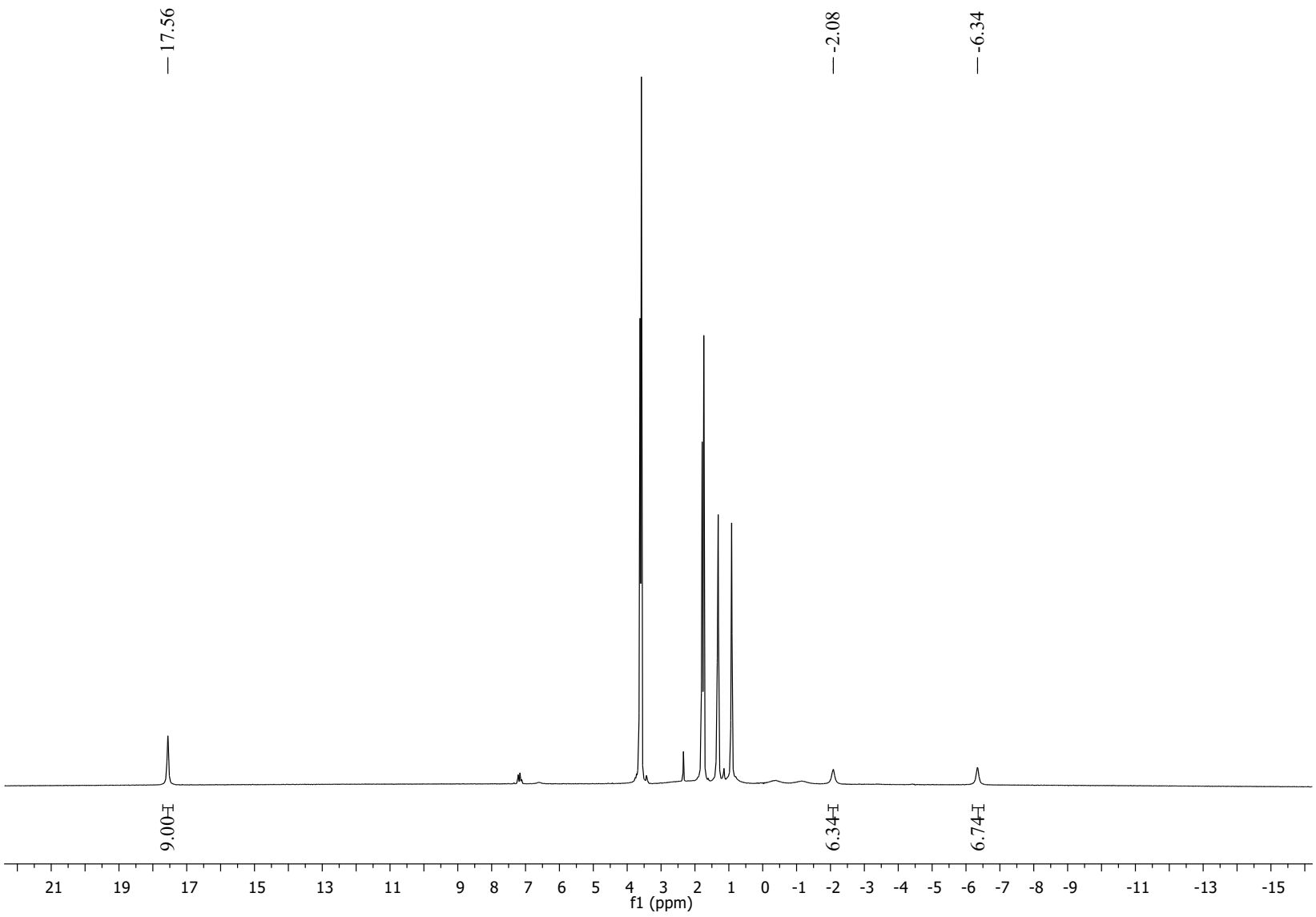

Figure S16: ^{1}H NMR spectrum of **10-Sm** in THF-d_8. Unlabeled peaks are due to residual THF, hexane, and toluene.