Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for:

A Molecular Basis to Rare Earth Separations for Recycling: Tuning TriNOx Ligand Properties for Improved Performance

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Supporting Information

Experimental Procedures

General Methods

Unless otherwise noted, all reactions and manipulations were performed under an inert atmosphere (N_2) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with equipped with a molecular sieves 13X/Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried for at least three hours at 150 °C prior to use. ^{1}H NMR spectra were obtained on a Bruker DMX-300 Fourier transform NMR spectrometer while operating at a ^{1}H frequency of 300 MHz. ^{13}C{^{1}H} NMR spectra were obtained on a UNI 400 instrument while operating at a ^{13}C frequency of 100.61 MHz. Chemical shifts were recorded in units of parts per million and referenced against residual proteo solvent peaks for ^{1}H NMR and characteristic solvent peaks for ^{13}C NMR. Elemental analyses were performed on a Costech ECS 4010 Analyzer. Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) analysis was performed at the University of Pennsylvania Earth & Environmental Science Dept. on a Spectro Genesis ICP-OES Spectrometer.

Materials

Tetrahydrofuran, diethyl ether, dimethoxyethane, benzene, toluene, dichloromethane, hexanes, and pentane were purchased from Fisher Scientific. All solvents were sparged with dry argon for 30 minutes and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina, respectively (benzene, toluene, DCM, hexanes, pentane), or two columns of neutral alumina (THF, Et_2O, and DME). $CDCl_3$, C_6D_6, and pyridine-d_5 were purchased from Cambridge Isotope Laboratories, Inc. and stored over 4A molecular sieves prior to use. Potassium bis(trimethylsilyl)amide was purchased from Sigma Aldrich and used as received. H_3TriNOx,[1] RE[N(Si(CH$_3$)$_3$)$_2$]$_3$,[2] were synthesized according to literature procedures.

X-Ray Crystallography

X-ray intensity data for all reported compounds were collected on a Bruker APEXIII[3] D8QUEST CMOS area detector employing graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 100(1) K. In all cases, rotation frames were integrated using SAINT[4], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS[5]. All structures were solved by direct methods (SHELXT[6]). Refinement was by full-matrix least squares based on F^2 using SHELXL-2014[7]. All reflections were used during refinements. Non-hydrogen atoms were refined anisotropically.

Thermogravimetric Analyses

Thermogravimetric analysis of Nd(TriNOx$^{\mathrm{OMe}}$)(THF) and Dy(TriNOx$^{\mathrm{OMe}}$)(THF) were performed with a TA Instruments SDT Q600 thermogravimetric analyzer from 25-450 °C at a heating rate of 10 °C/min in an N_2 flow with a rate of 100 mL/min.

Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

Inductively coupled plasma optical emission spectroscopy was conducted on a Spectro Genesis ICP-OES spectrometer (SPECTRO Analytical Instruments GmbH, Kleve, Germany) equipped with an integrated three channel peristaltic pump and a ASX-260 auto-sampler (CETAC Technologies, Omaha, NE, USA). Samples solutions were delivered to the nebulizer using a

Mod Lichte spray chamber and single-use PVC PT-2140PF tubing (Precision Glassblowing, Centennial, CO, USA). Each data acquisition was preceded by a 35 second rinse sequence at different pump speeds. Other relevant parameters were previously optimized to give the smallest RSD and are summarized in Table S1.

Table S1. Instrumental and operating conditions for ICP-OES measurements

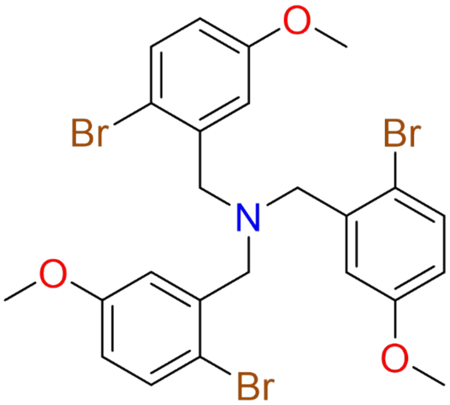
Instrument conditions	
Forward power (W)	1350
Plasma gas flow rate (L min^{-1})	13.50
Auxiliary gas flow rate (L min^{-1})	1.00
Nebulizer flow rate (L min^{-1})	0.90
Wavelengths (nm)	Nd 430.358 Dy 364.540

Nitric acid (Fisher, Certified ACS Plus grade), hydrogen peroxide (Fisher, 30% solution in water), and distilled-deionized water (Milli-Q, 18.2 MΩ.cm, Millipore) were used for sample preparation and dilution. Samples were prepared by digestion in a (4:1) HNO_3:H_2O_2 mixture at 100 °C for 1 hour, followed by dilution to a concentration of *ca.* 5% HNO_3 to limit matrix effects. Analytical plasma standard solutions were obtained from Alfa Aesar (Specpure®, 1000 ppm RE_2O_3 in 5% HNO_3).

Calibrations were performed before each set of measurements using a range of 7 standardized solutions (125–0.025 ppm). Calibration curves were confirmed to have $R^2 > 0.999$ for the selected elements. Potential instrumental drift was monitored by continuously measuring Ar lines at 430.010 and 404.442 nm; absence of drift was finally confirmed by measuring a standardized solution at the end of each measurement session. The following wavelengths (nm) were used for element quantifications and reviewed for the absence of interferences: 364.540 (Dy), 430.358 (Nd) and were consistent with literature recommendations. The wavelengths selected had the highest signal intensity, in agreement with the literature,[8] and were the most relevant for the studied range of concentrations.

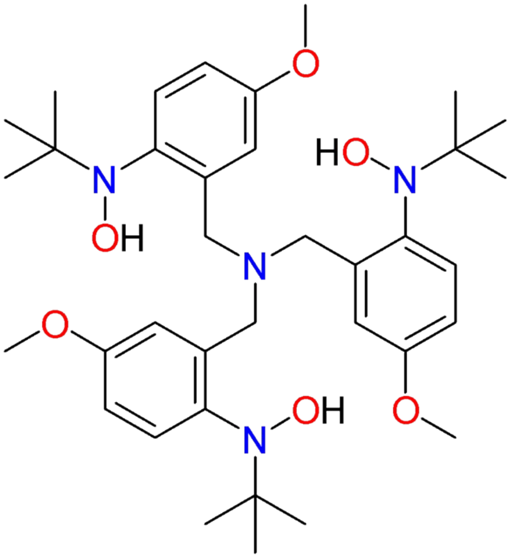
Synthetic Details

Synthesis of tris(2-bromo-5-methoxy)benzylamine



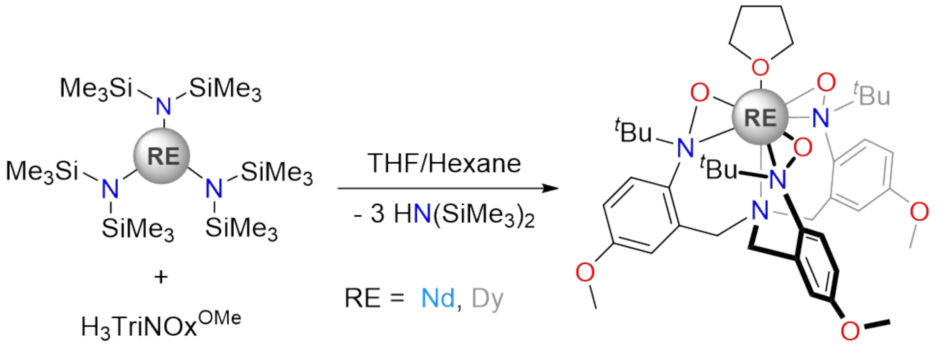
2-bromo-5-methoxybenzylbromide (10.0 g, 35.7 mmol, 3.0 equiv.) was stirred hot ethanol to dissolve all solids. Ammonium hydroxide (29%) (6.00 g, 102.3 mmol, 8.6 equiv.) was added to solution dropwise and the reaction mixture was stirred at room temperature for 2 days, producing a white solid. The precipitate was collected by filtration, washed with ethanol, and dried under reduced pressure overnight to yield a white solid (5.37 g, 74%). Mp = 96.2 – 98.4 °C. ^{1}H NMR (ppm, d_5-pyr, 300 MHz): δ = 7.51 (d, J = 8.7 Hz, 3H), 7.48 (s, 3H), 6.77 (dd, J = 8.7, 2.9 Hz, 3H), 3.98 (s, 6H), 3.68 (s, 9H). ^{13}C NMR (ppm, pyridine-d_5, 400 MHz): δ = 160.0, 140.0, 134.1, 116.9, 115.4, 115.2, 59.3, 55.8. IR: v = 3094, 3070, 3002, 2958, 2932, 2906, 2834, 2357, 1870, 1591, 1569, 1474, 1456, 1447, 1434, 1416, 1376, 1367, 1302, 1284, 1233, 1220, 1191, 1158, 1124, 1109, 1055, 1021, 993, 971, 938, 892, 874, 862, 801, 736, 696, 668, 646, 637, 616, 598, 590, 573, 521, 467, 441 cm^{-1}. HRMS: (ESI) m/z calc. for $C_{24}H_{25}Br_3NO_3$ (M+H): 611.9385, found: 611.9388.

Synthesis of tris(2-*tert*-butylhydroxylaminato-5-methoxy)benzylamine ([(2-^{t}BuNOH)(5-OCH$_3$)C$_6$H$_3$CH$_2$]$_3$N, H$_3$TriNOx^{OMe})



Tris(2-bromo-5-methoxy)benzylamine (2.00 g, 3.26 mmol, 1 equiv.) was dissolved in THF (20 mL) and added to a 200 mL Schlenk flask equipped with a magnetic stir bar. The flask was placed under atmosphere and cooled to -100 °C. A 1.6 M solution of *n*-butyllithium complex in hexanes (6.7 mL, 10.7 mmol, 3.3 equiv.) was added dropwise and reaction was stirred for 3 hours. A THF solution of 2-methyl-2-nitrosopropane dimer (1.14 g, 6.51 mmol, 2 equiv.) was added and the reaction was gradually warmed to room temperature and stirred for 3 hours. The reaction was quenched with a saturated aqueous ammonium chloride solution. The organic portion was extracted with 3 x 50 mL diethyl ether. The combined organics were dried over magnesium sulfate, gravity filtered, and volatiles removed under reduced pressure, yielding a tan solid. The crude solid was purified washing extensively with hexanes, followed by drying on high vacuum at room temperature overnight, yielding pure H_3TriNOx^{OMe} as an off-white solid (1.76 g, 85%). Single crystals were grown from a hot THF solution allowed to cool to room temperature, layered with hexanes. Mp = 135.7 – 137.8 °C. ^{1}H NMR (ppm, pyridine-d_5, 300 MHz): δ = 9.86 (s, 3H), 7.96 (d, J = 2.2 Hz, 3H), 7.88 (d, J = 8.8 Hz, 3H), 6.99 (dd, J = 8.8, 0.6 Hz, 3H), 4.20 (s, 6H), 3.81 (s, 9H), 1.17 (s, 27H). ^{13}C NMR (ppm, $CDCl_3$, 400 MHz): δ = 158.4, 143.7, 139.3, 128.6, 113.1, 112.5, 61.2, 55.6, 55.1, 26.5. IR: ν = 3253, 3085, 2982, 2832, 2068, 1915, 1735, 1605, 1492, 1465, 1442, 1391, 1369, 1301, 1289, 1276, 1236, 1196, 1160, 1138, 1092, 1083, 1040, 980, 948, 928, 913, 897, 869, 825, 802, 732, 697, 652, 628, 592, 536, 515, 504, 491, 450, 412 cm^{-1}. HRMS: (ESI) m/z calc. for $C_{36}H_{55}N_4O_6$ (M+H): 639.4122, found: 639.4114. Anal. calc. for $C_{36}H_{54}N_4O_6$: C, 67.68; H, 8.52; N, 8.77. Found: C, 67.85; H, 8.65; N, 8.42.

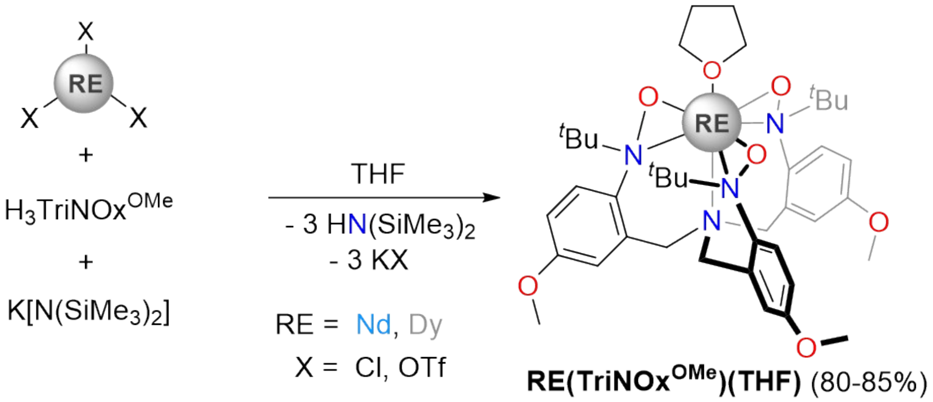
General Procedure A for the synthesis of RE(TriNOx^{OMe})(THF) complexes



RE(TriNOx^{OMe})(THF) (84-87%)

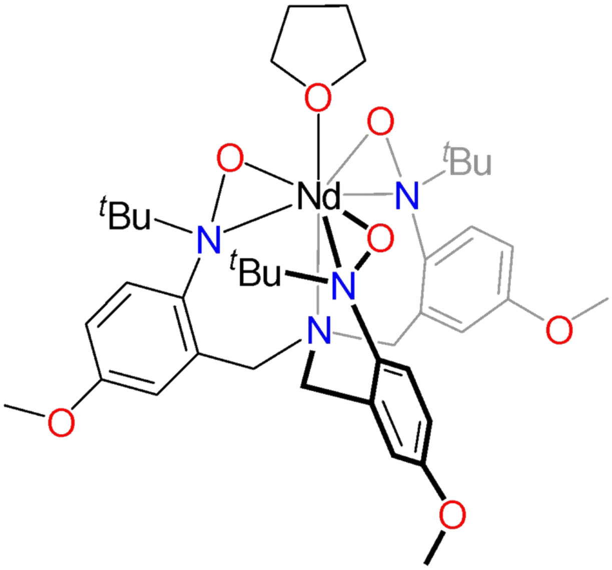
H_3TriNOx^{OMe} (1 equiv.) was dissolved in a boiling THF solution and set aside to cool to room temperature before it was added to a THF solution of RE[N$(SiMe_3)_2]_3$ (1 equiv.), RE = Nd, Dy. The reaction mixture was stirred for 2 hours, and volatiles were removed under reduced pressure. Sample was stirred in pentane and filtered, and the solid was dried under reduced pressure to yield pure solid (84-87%).

General Procedure B (Alternative Synthesis) for the synthesis of RE(TriNOx^{OMe})(THF) complexes



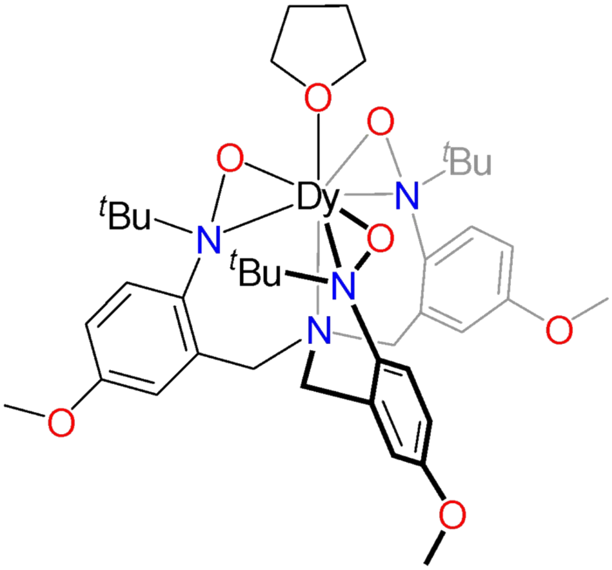
$H_3TriNOx^{OMe}$ (1 equiv.) was dissolved in a boiling THF solution and set aside to cool to room temperature before REX_3 (1 equiv.) RE = Nd, Dy; X = Cl, OTf; was added as a solid. A THF solution of $K[N(SiMe_3)_2]$ (3 equiv.) was added, and the suspension was stirred for 2 hours. After volatiles were removed under reduced pressure, the resulting mixture was stirred in dichloromethane and filtered. The filtrate was stirred in pentane and filtered, and the solids were collected. The solid portion was dissolved in THF, and volatiles were removed under reduced pressure to yield pure compounds (80-85%).

Synthesis of Nd(TriNOx^{OMe})(THF)



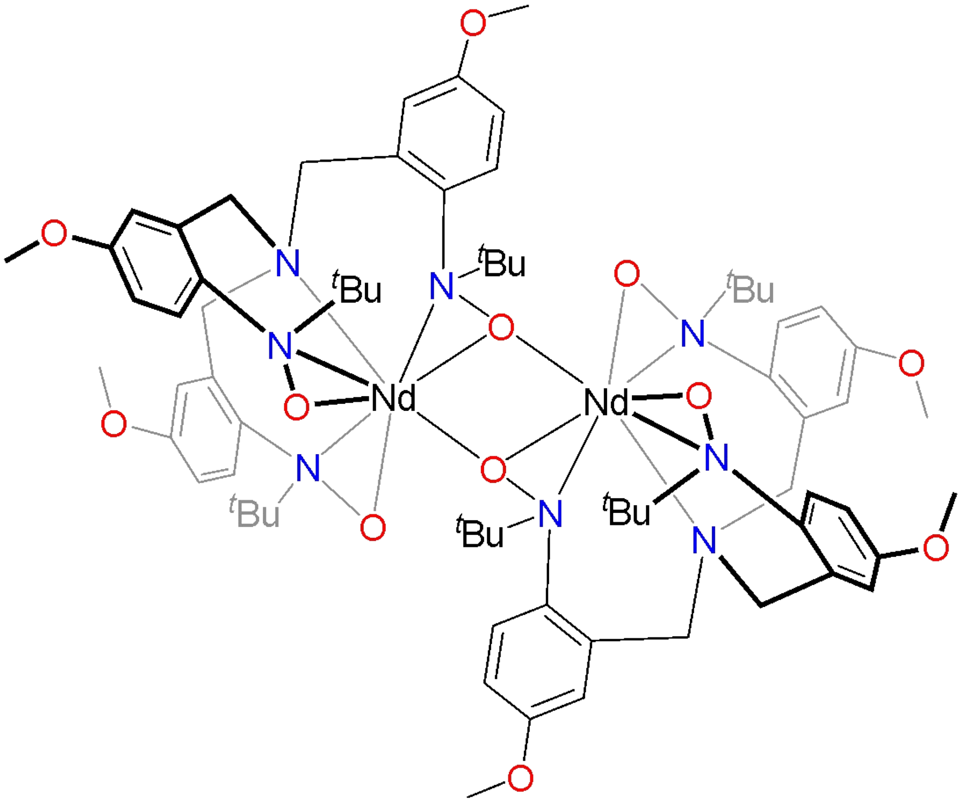
Single crystals of Nd(TriNOx^{OMe})(THF), as a blue crystalline solid, were grown from a THF solution layered with hexanes. ^1H NMR (ppm, pyridine-d_5, 300 MHz): δ = 17.86 (s, 3H), 9.53 (s, 3H), 6.65 (s, 27H), 3.68 (m, 4H), 3.44 (s, 9H), 1.64 (s, 3H), 1.64 (overlapping, 4H), -7.95 (s, 3H), -11.87 (s, 3H). Anal. Calc. for $C_{40}H_{59}N_4NdO_7$: C, 56.38; H, 6.98; N, 6.57. Found: C, 56.62; H, 6.73; N, 6.64.

Synthesis of Dy(TriNOx^{OMe})(THF)



Single crystals of Dy(TriNOx^{OMe})(THF), as a white crystalline solid, were grown from a THF solution layered with hexanes. ^{1}H NMR (ppm, pyridine-d_5, 300 MHz): δ = 209.89 (s, 3H), 131.31 (s, 27H), 57.82 (s, 3H), -3.34 (s, 9H), -103.36 (s, 3H), -302.05 (s, 3H), -355.47 (s, 3H). Anal. Calc. for $C_{36}H_{51}DyN_4O_6$: C, 54.16; H, 6.44; N, 7.02. Found: C, 53.76; H, 6.44; N, 6.64.

Synthesis of [Nd(TriNOx^{OMe})]$_2$



Dissolved Nd(TriNOx^{OMe})(THF) (0.200 g, mmol) in 3 mL toluene and removed volatiles under reduced pressure to yield a blue solid (0.152 g, 83%). Single crystals were grown from a toluene solution layered with hexanes. ^{1}H NMR (ppm, C_6D_6, 300 MHz): δ = 37.54 (s, 2H), 15.33 (s, 2H), 13.93 (s, 2H), 12.17 (s, 2H), 9.51 (s, 2H), 8.53 (overlapping, 18H), 6.65 (s, 2H), 3.60 (s, 6H) 2.91 (s, 6H), 2.12 (overlapping, 6H), 0.81 (s, 18H), 0.71 (s, 18H), 0.56 (s, 2H), -1.32 (s, 2H), -5.78 (s, 2H), -12.37 (s, 2H), -13.22 (s, 2H), -13.79 (s, 2H), -15.70 (s, 2H), -21.04 (s, 2H), -23.54 (s, 2H). Anal. Calc. for $C_{72}H_{102}N_8Nd_2O_{12}$·1.5tol: C, 58.35; H, 6.77; N, 6.60. Found: C, 57.89; H, 6.80; N, 6.45.

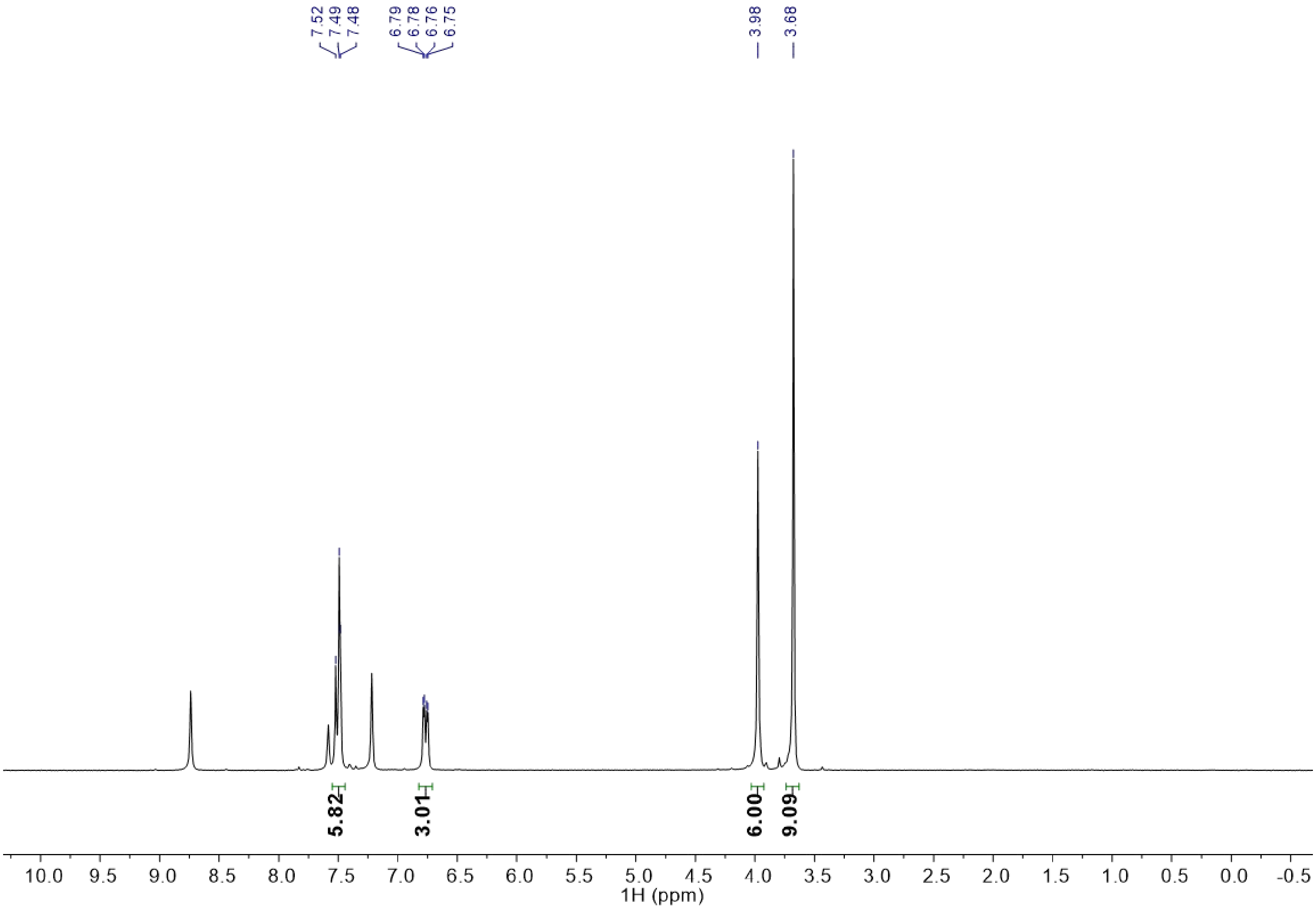


Figure S1. ^{1}H NMR spectrum of tris(2-bromo-5-methoxy)benzylamine in pyr-d_5

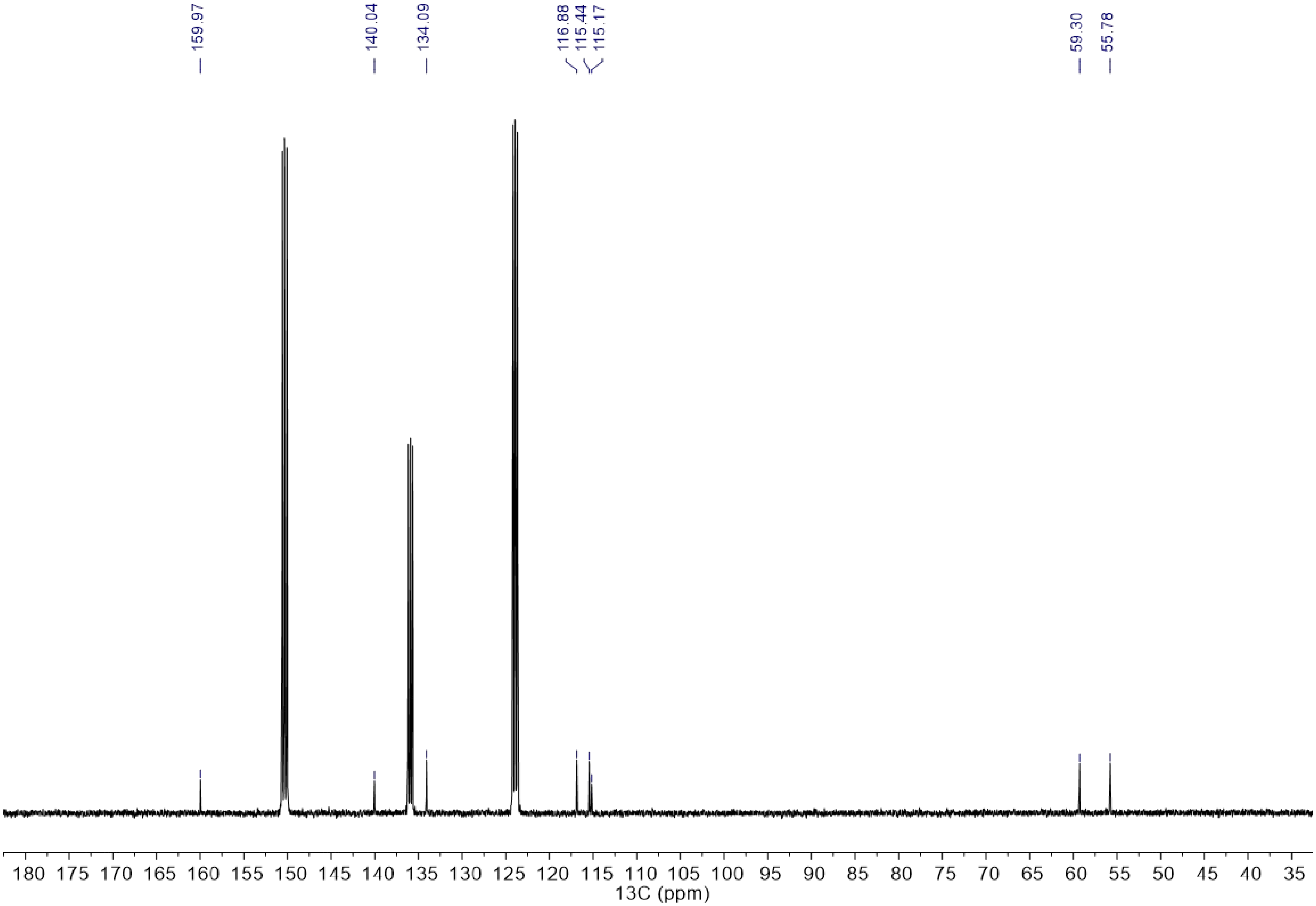


Figure S2. ^{13}C NMR spectrum of tris(2-bromo-5-methoxy)benzylamine in pyr-*d*$_5$

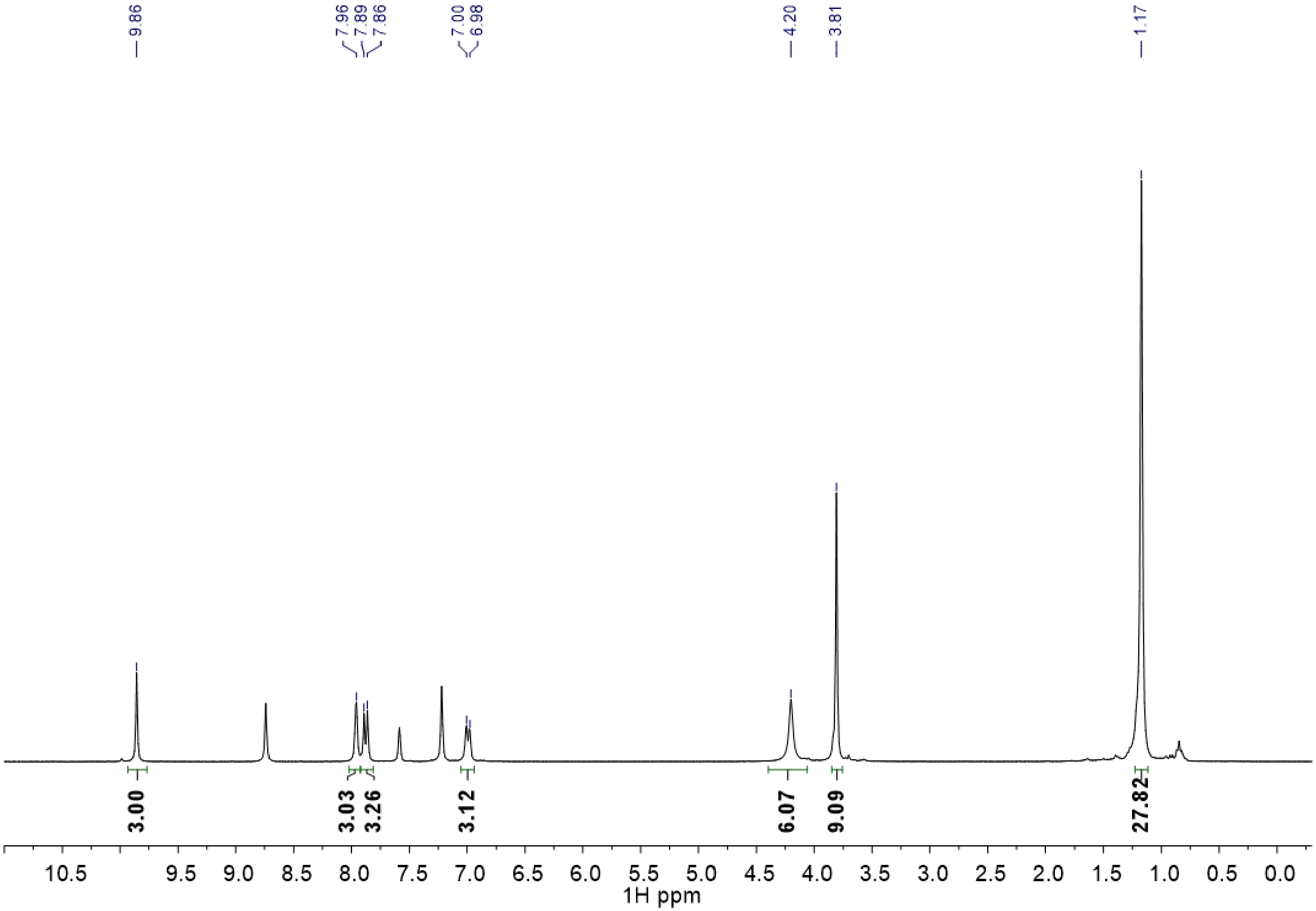


Figure S3. ^{1}H NMR spectrum of $H_3TriNOx^{OMe}$ in pyr-d_5

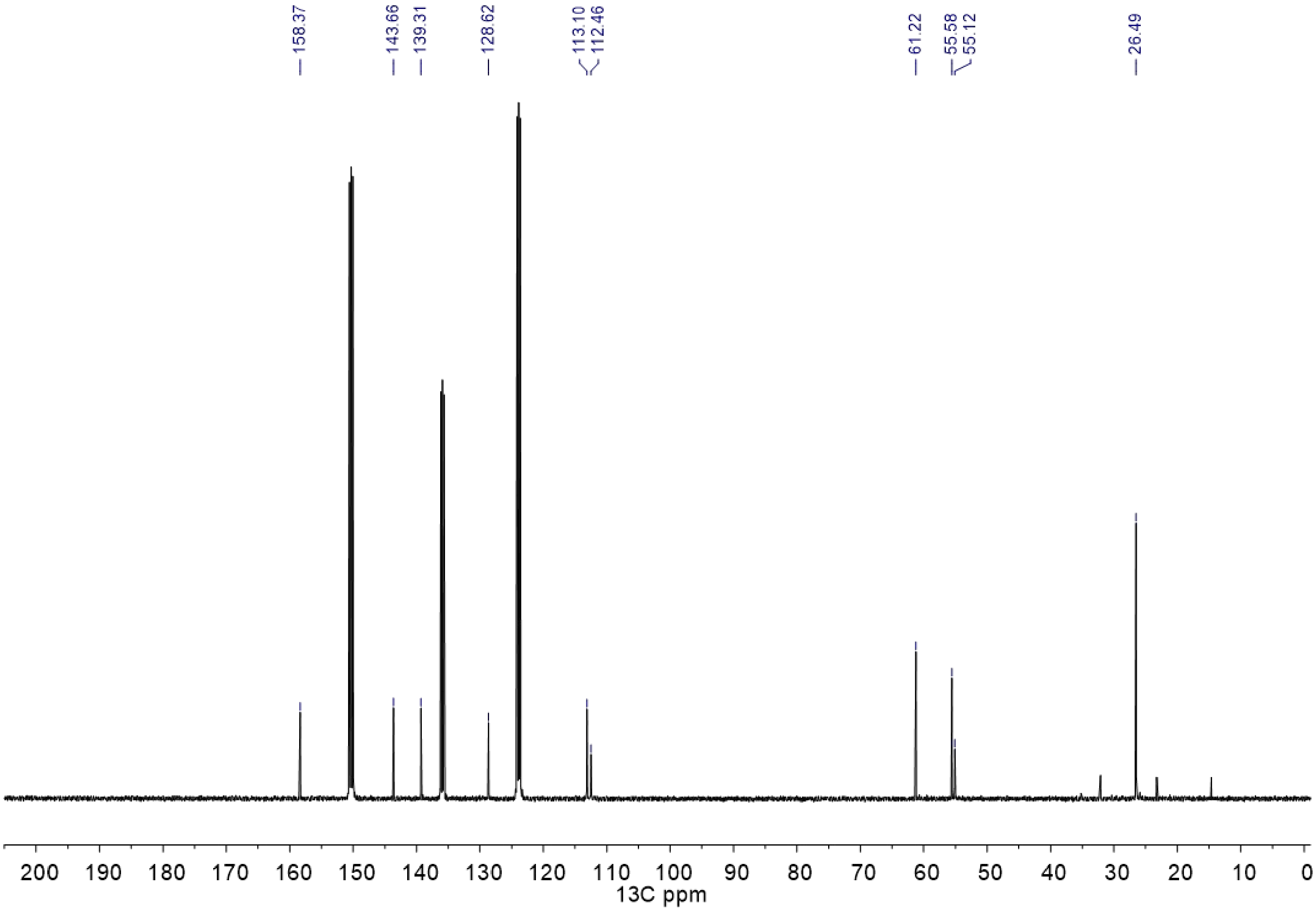


Figure S4. ^{13}C NMR spectrum of H_3TriNOx^{OMe} in pyr-d_5

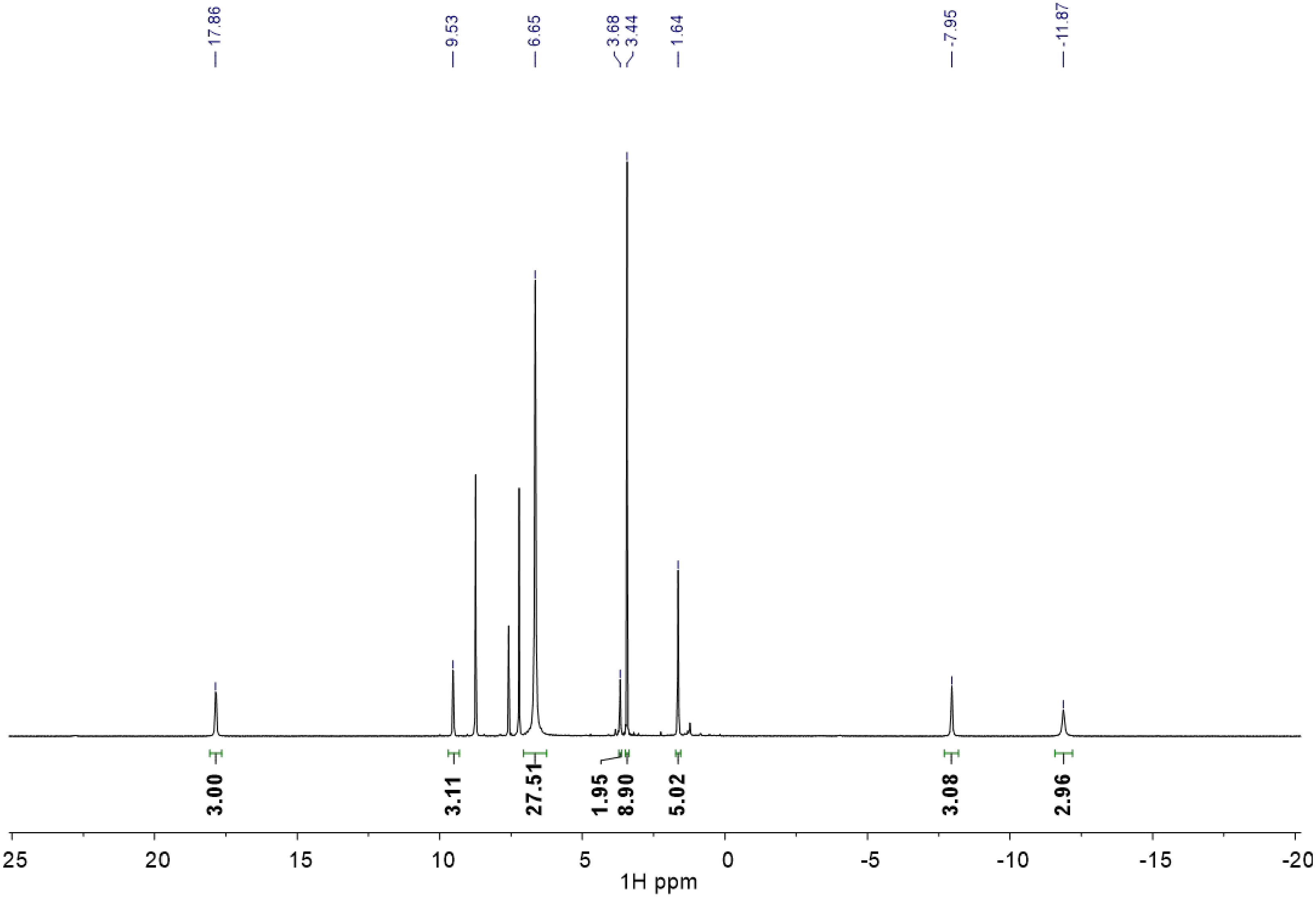


Figure S5. ^{1}H NMR spectrum of Nd(TriNOx^{OMe})(THF) in pyr-*d*$_5$

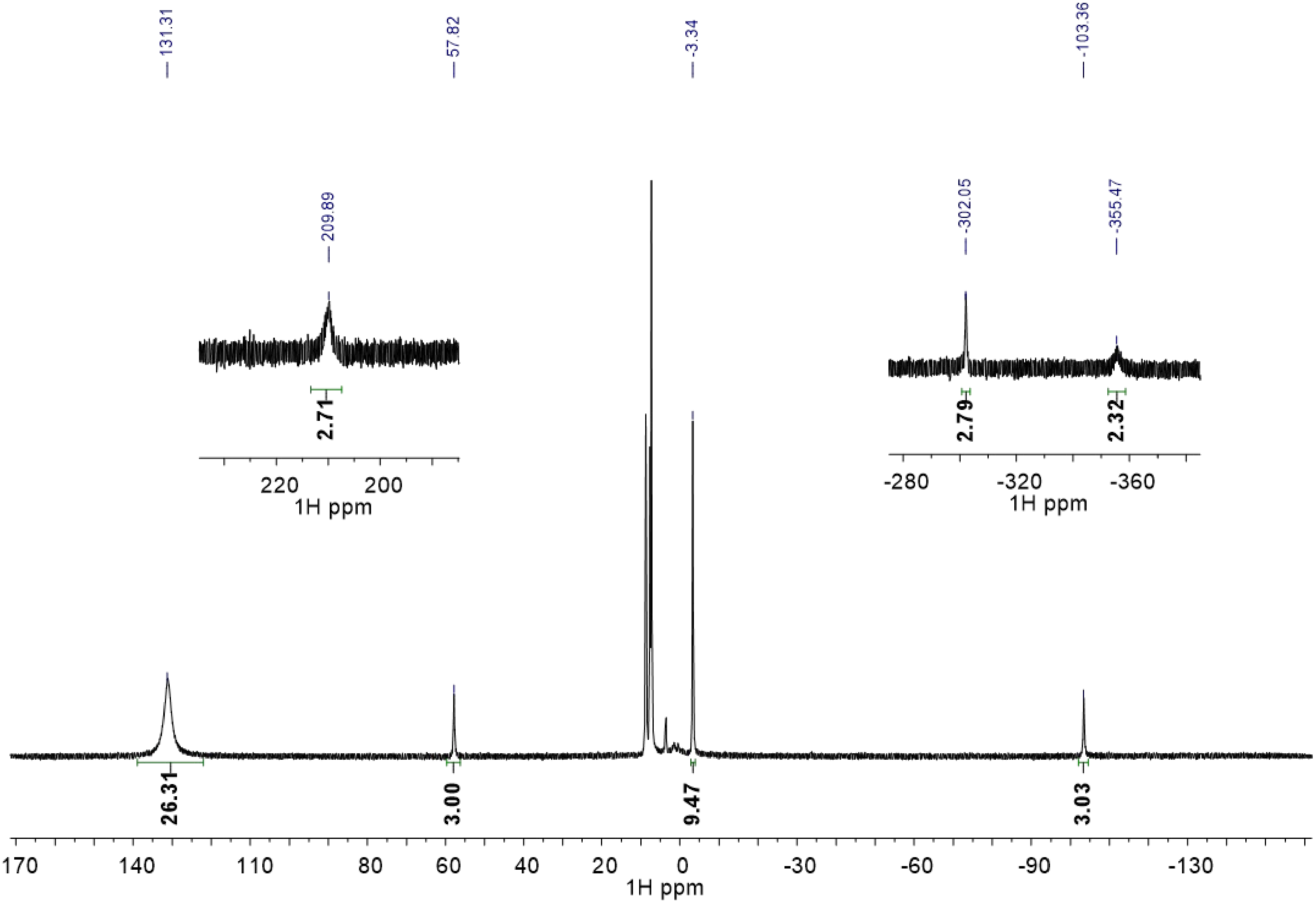


Figure S6. ^{1}H NMR spectrum of Dy(TriNOx^{OMe}) in pyr-d_5

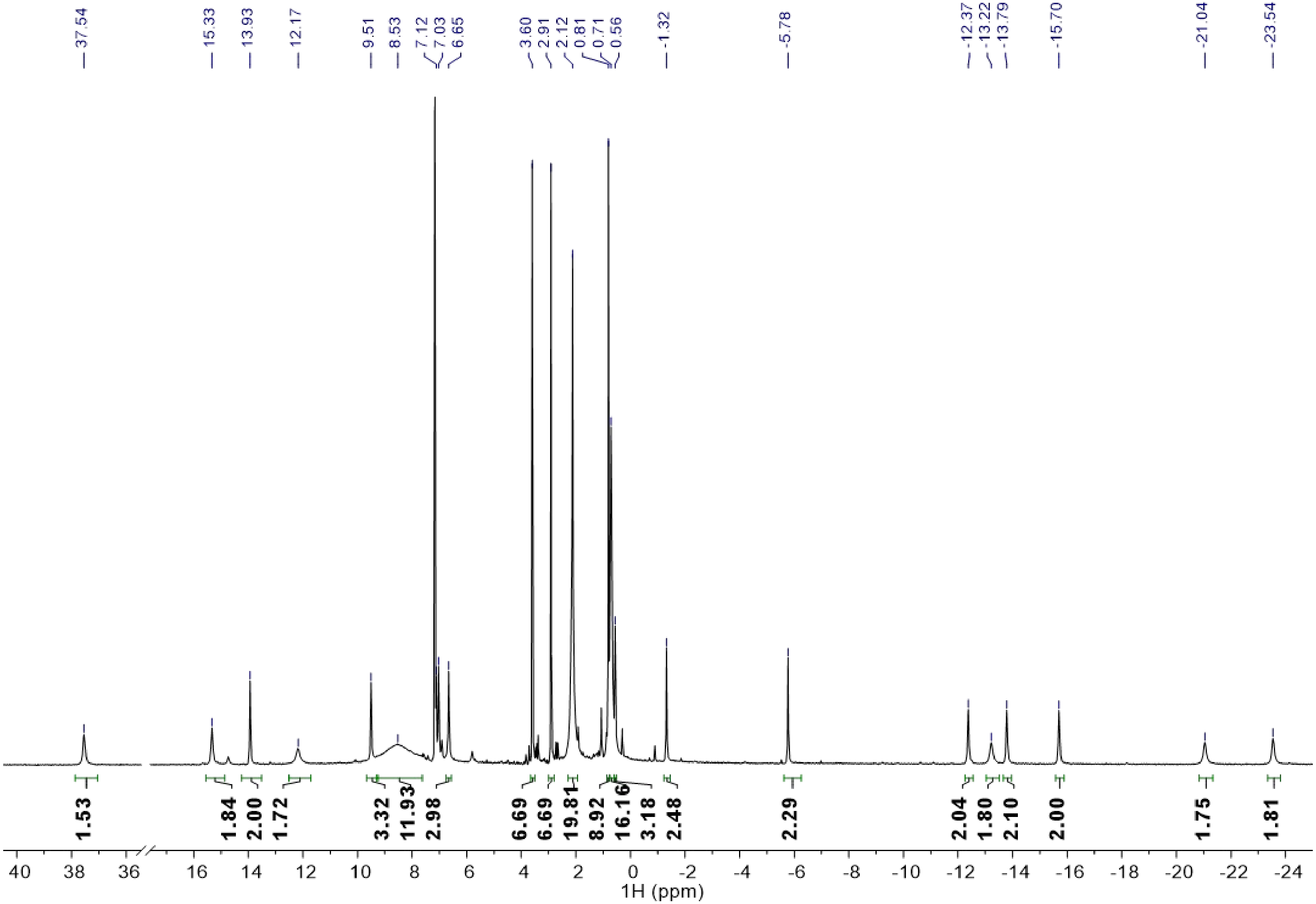


Figure S7. ^{1}H NMR spectrum of [Nd(TriNOx^{OMe})]$_2$ in C_6D_6

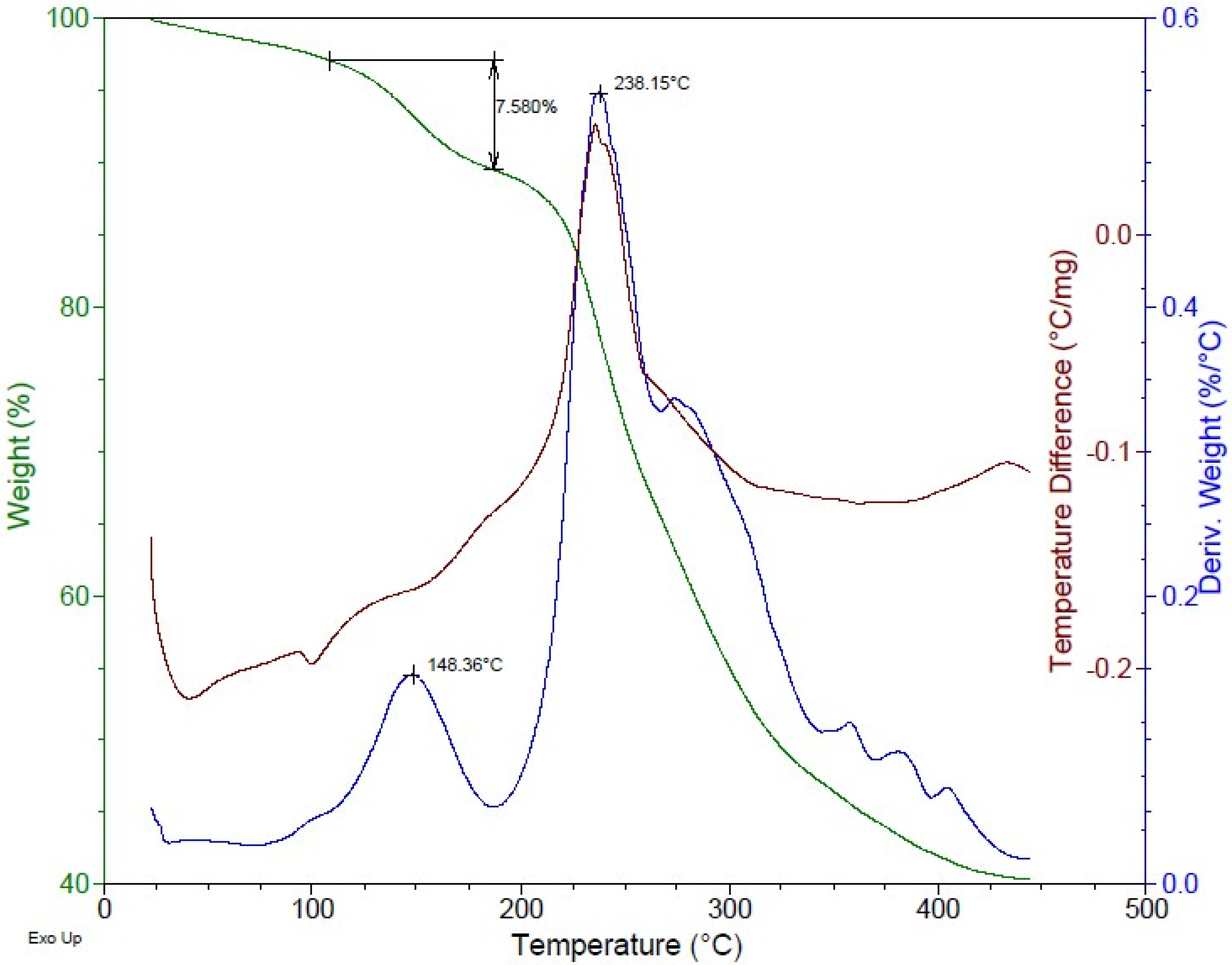


Figure S8. Thermogravimetric analysis of Nd(TriNOx^{OMe})(THF)

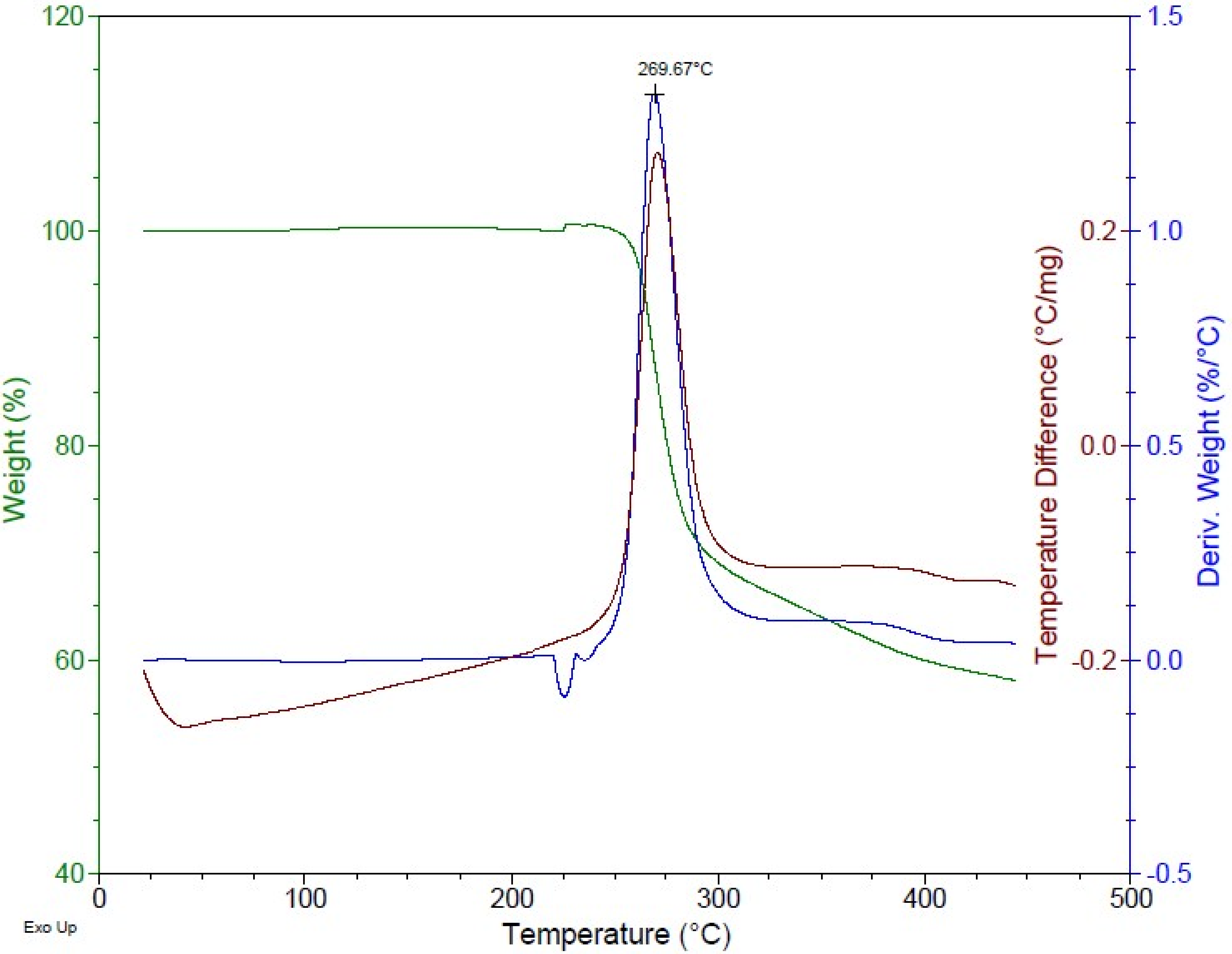


Figure S9. Thermogravimetric analysis of Dy(TriNOx^{OMe})

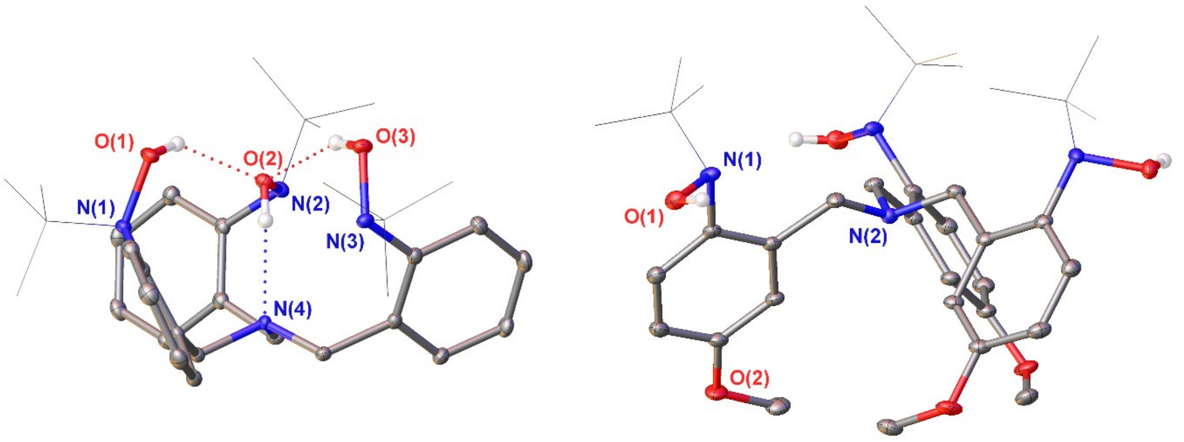


Figure S10. Thermal ellipsoid plots of H$_3$TriNOx[1] and H$_3$TriNOx$^{\mathrm{OMe}}$ at the 30% probability level. ^{t}Bu groups depicted in wireframe and hydrogen atoms omitted for clarity.

While the parent H$_3$TriNOx was air-stable in the solid and solution states for weeks, H$_3$TriNOx$^{\mathrm{OMe}}$ was stable in air for several days as a solid, but oxidized in THF solution over several hours. The solid-state structure of H$_3$TriNOx$^{\mathrm{OMe}}$ lacked the intramolecular hydrogen bonding network found in the parent H$_3$TriNOx (Figure S10). X-ray diffraction studies showed that the average N-O bond lengths were similar in H$_3$TriNOx (1.458(16) Å) and H$_3$TriNOx$^{\mathrm{OMe}}$ (1.458(3) Å). A decrease in the sum of the angles surrounding the hydroxylaminato nitrogen (Σ Y-N$^{t}_{\mathrm{BuNO}}$-Z) was noted for H$_3$TriNOx$^{\mathrm{OMe}}$ (328.45 °) compared to H$_3$TriNOx (332.17 °), indicating pyramidalization at the nitrogen atom in each hydroxylamine arm.

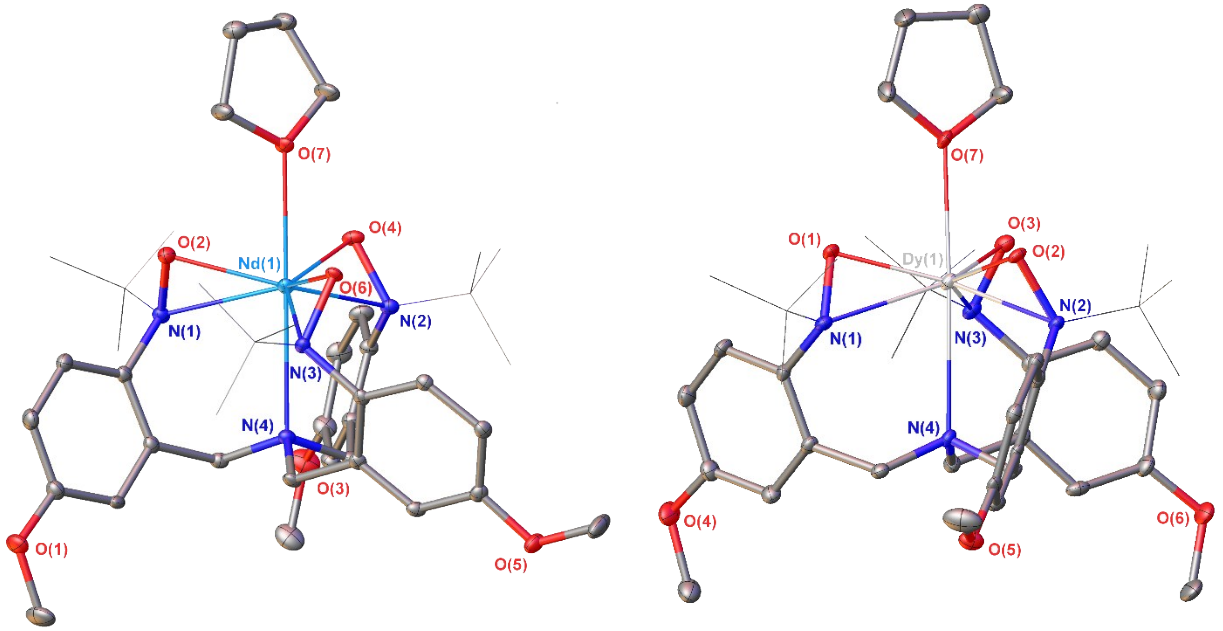


Figure S11. Thermal ellipsoid plots of Nd(TriNOx$^{\mathrm{OMe}}$)(THF) and Dy(TriNOx$^{\mathrm{OMe}}$)(THF) at the 30% probability. ^{t}Bu groups depicted in wireframe and hydrogen atoms omitted for clarity.

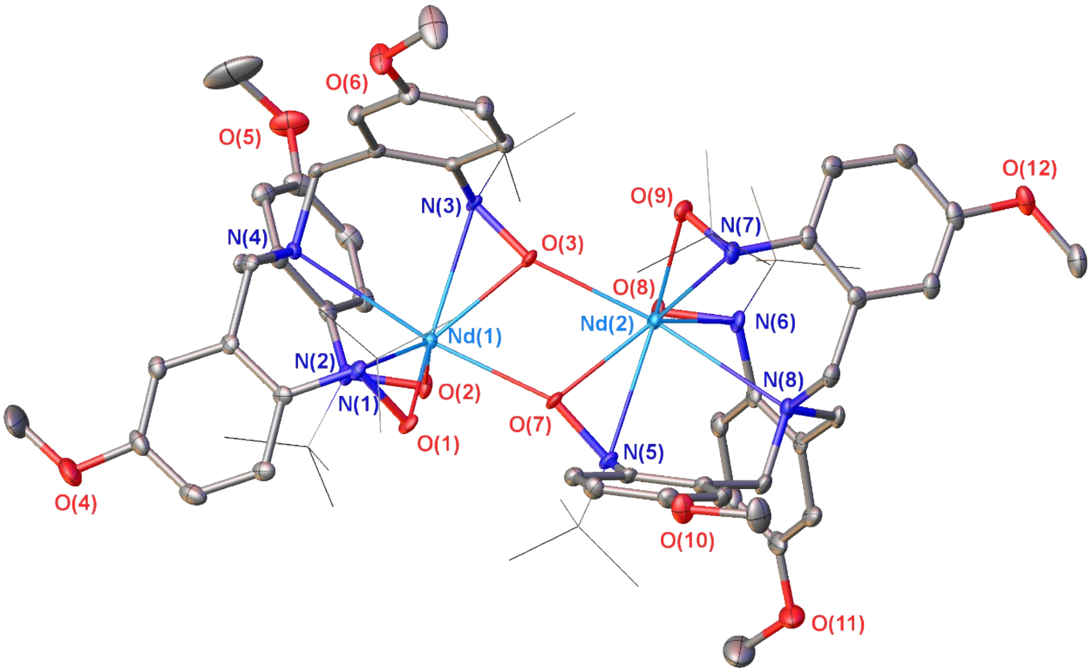
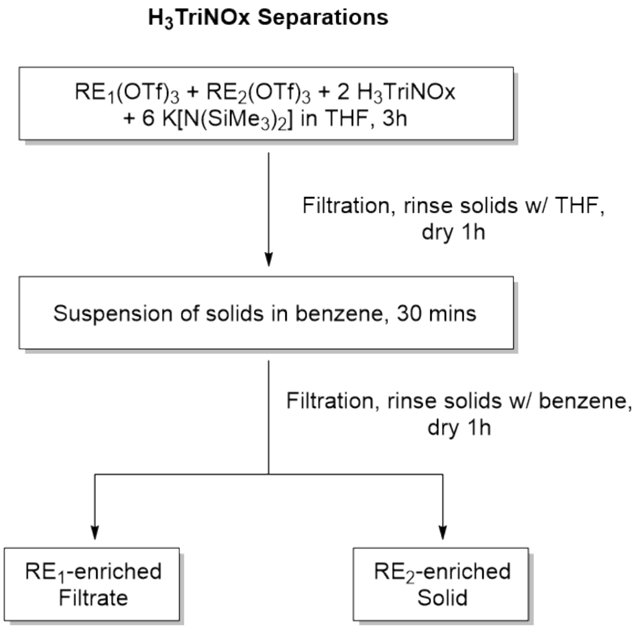


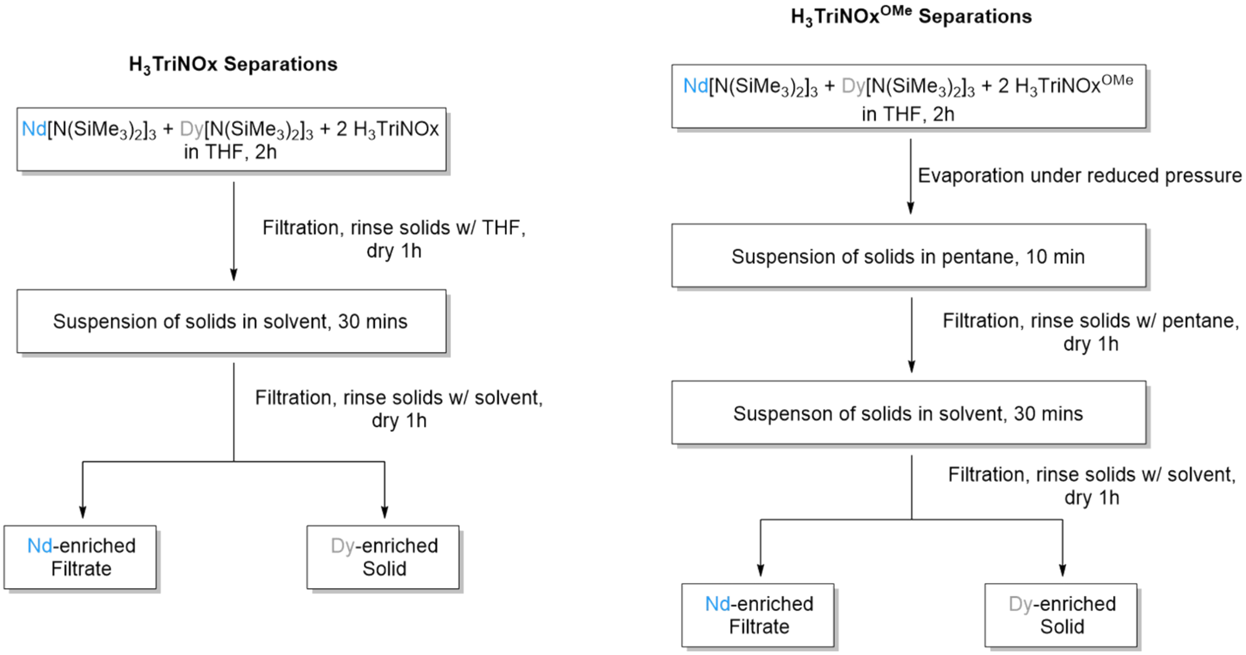
Figure S12. Thermal ellipsoid plot of [Nd(TriNOx$^{\text{OMe}}$)]$_2$ at the 30% probability. tBu groups depicted in wireframe. Interstitial toluene molecules and hydrogen atoms omitted for clarity.

Table S2. Bond metrics (Å), %V_{bur} and temperature of THF dissociation (°C) for selected compounds.

Compounds	N-O	RE-O$_{\text{NO}}$	RE-N$_{\text{NO}}$	RE-O$_{\text{axial}}$	RE-N$_{\text{bridgehead}}$	%V_{bur}	THF Diss. (°C)
Nd(TriNOx)(THF)[1]	1.420(4)	2.260(3)	2.554(4)	2.546(9)	2.819(9)	79.9	153
Nd(TriNOx$^{\text{OMe}}$)(THF)	1.441(3)	2.270(2)	2.553(3)	2.625(2)	2.826(3)	80.1	149
Dy(TriNOx)(THF)[1]	1.424(4)	2.180(3)	2.508(3)	2.487(10)	2.810(9)	81.3	85
Dy(TriNOx$^{\text{OMe}}$)(THF)	1.445(5)	2.192(3)	2.496(4)	2.551(3)	2.816(4)	81.7	-
[Nd(TriNOx)]$_2$[1]	1.446(2)	2.2781(16)	2.6102(18)	2.5413(17)	2.923(2)	77.2	-
[Nd(TriNOx$^{\text{OMe}}$)]$_2$	1.450(3)	2.2784(18)	2.620(2)	2.5037(17)	2.940(2)	76.5	-



Scheme S1. Parent separations procedure for RE(TriNOx) mixtures (RE_1 = La, Ce, Pr, Nd, Sm, Eu; RE_2 = Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu).



Scheme S2. Standardized separations procedures for RE(TriNOx) and RE(TriNOx^{OMe}) (RE = Nd, Dy) mixtures.

Table S3. Comparison of Enrichment (D) and Separation Factors (S) for ^{1}H NMR estimations and ICP-OES analysis. (Separations performed in triplicate, reported with standard errors).

Ligand	Solvent	^{1}H NMR Estimations			ICP-OES Results		
		$D_{Filtrate}$	D_{Solid}	$S_{Nd/Dy}$	$D_{Filtrate}$	D_{Solid}	$S_{Nd/Dy}$
TriNOx	C_6H_6	28 ± 3	16 ± 2	430 ± 15	17 ± 2	18 ± 2	303 ± 19
TriNOx	Toluene	23.6 ± 0.9	1.79 ± 0.08	42 ± 4	15.4 ± 0.7	1.94 ± 0.06	30 ± 2
TriNOx^{OMe}	C_6H_6	16 ± 1	24 ± 3	363 ± 65	9.8 ± 0.4	29 ± 3	299 ± 35
TriNOx^{OMe}	Toluene	23 ± 3	20 ± 3	440 ± 32	12 ± 2	22 ± 4	254 ± 10
TriNOx^{OMe}	DME	4.3 ± 0.2	10.4 ± 0.2	44 ± 3	3.5 ± 0.2	11.6 ± 0.5	41 ± 4
TriNOx^{OMe}	Et_2O	19 ± 3	1.01 ± 0.06	20 ± 4	7.2 ± 0.3	1.16 ± 0.07	8.4 ± 0.6

The ^{1}H NMR estimations of the enrichment and separation factors vary somewhat from the results found by ICP-OES. Several factors, including the degree of solubility of the complexes in deuterated solvents used, broadening of NMR peaks into the baseline interfering with accurate integration of the peaks, and the general error of NMR integrations (~5%) may all contribute to the differences observed between the data sets.

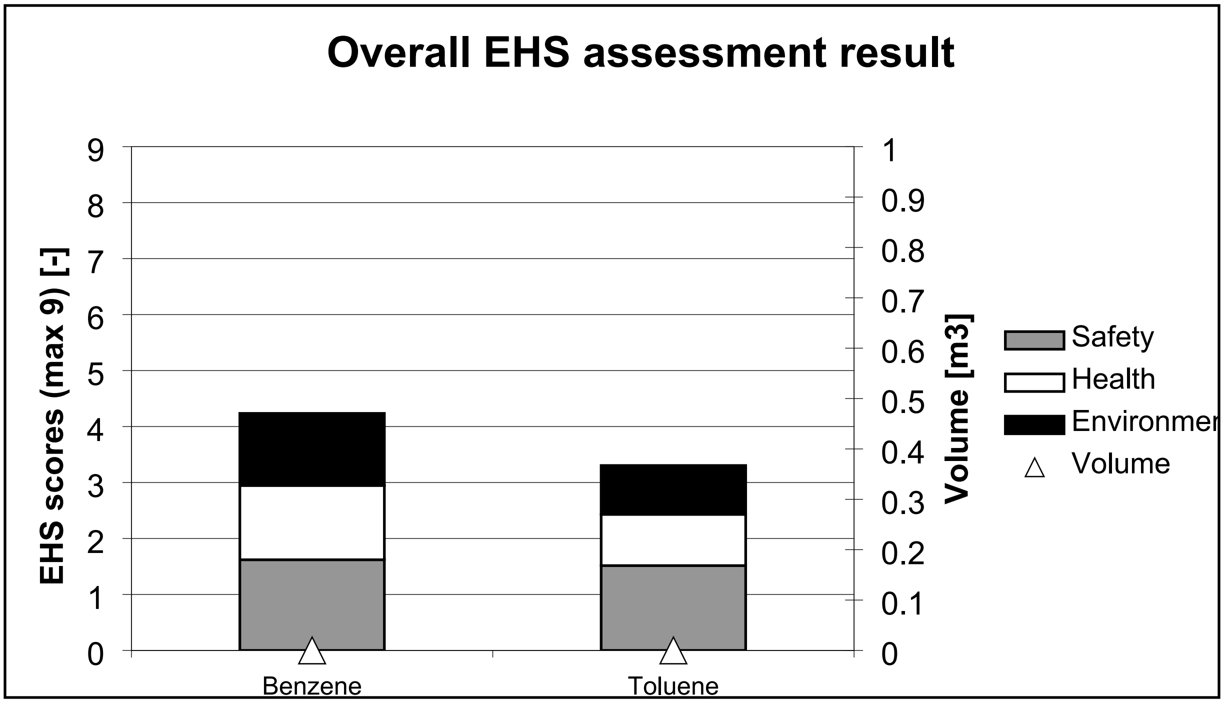
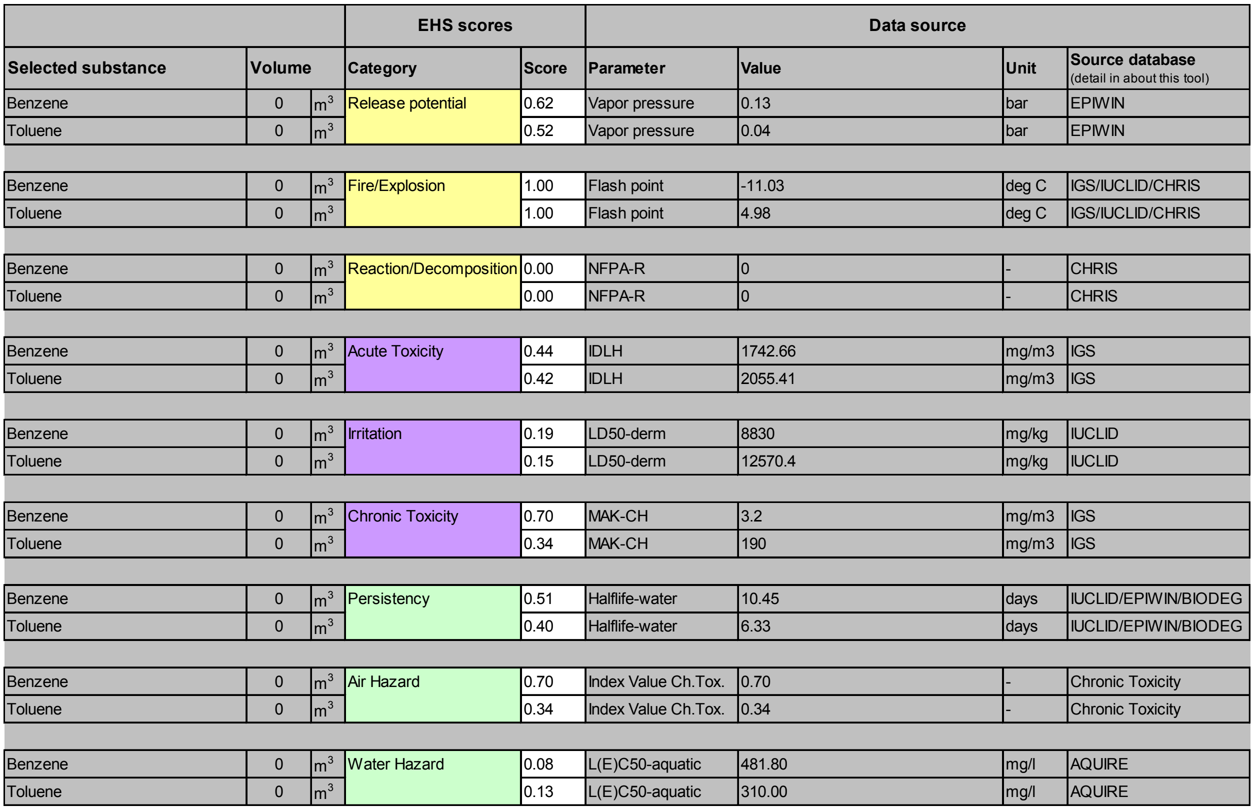


Figure S13. EHS Assessment of benzene (left) and toluene (right) as determined by the EHS Excel Tool.[9]



			EHS scores		Data source			
Selected substance	**Volume**		**Category**	**Score**	**Parameter**	**Value**	**Unit**	**Source database** (detail in about this tool)
Benzene	0	m^3	Release potential	0.62	Vapor pressure	0.13	bar	EPIWIN
Toluene	0	m^3		0.52	Vapor pressure	0.04	bar	EPIWIN
Benzene	0	m^3	Fire/Explosion	1.00	Flash point	-11.03	deg C	IGS/IUCLID/CHRIS
Toluene	0	m^3		1.00	Flash point	4.98	deg C	IGS/IUCLID/CHRIS
Benzene	0	m^3	Reaction/Decomposition	0.00	NFPA-R	0	-	CHRIS
Toluene	0	m^3		0.00	NFPA-R	0	-	CHRIS
Benzene	0	m^3	Acute Toxicity	0.44	IDLH	1742.66	mg/m3	IGS
Toluene	0	m^3		0.42	IDLH	2055.41	mg/m3	IGS
Benzene	0	m^3	Irritation	0.19	LD50-derm	8830	mg/kg	IUCLID
Toluene	0	m^3		0.15	LD50-derm	12570.4	mg/kg	IUCLID
Benzene	0	m^3	Chronic Toxicity	0.70	MAK-CH	3.2	mg/m3	IGS
Toluene	0	m^3		0.34	MAK-CH	190	mg/m3	IGS
Benzene	0	m^3	Persistency	0.51	Halflife-water	10.45	days	IUCLID/EPIWIN/BIODEG
Toluene	0	m^3		0.40	Halflife-water	6.33	days	IUCLID/EPIWIN/BIODEG
Benzene	0	m^3	Air Hazard	0.70	Index Value Ch.Tox.	0.70	-	Chronic Toxicity
Toluene	0	m^3		0.34	Index Value Ch.Tox.	0.34	-	Chronic Toxicity
Benzene	0	m^3	Water Hazard	0.08	L(E)C50-aquatic	481.80	mg/l	AQUIRE
Toluene	0	m^3		0.13	L(E)C50-aquatic	310.00	mg/l	AQUIRE

Figure S14. EHS assessment score determination and data sources for benzene and toluene from the EHS Excel Tool.[9]

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