Supporting Information for

Agile Synthesis and Automated, High-Throughput Evaluation of Diglycolamides for Liquid-Liquid Extraction of Rare-Earth Elements

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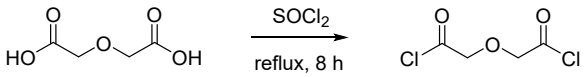
1. General Methods

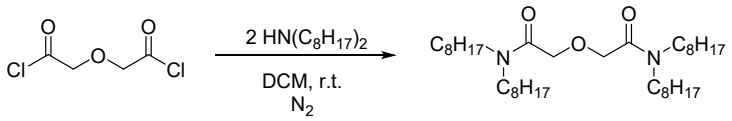
All reagents and solvents were purchased from commercial sources and used without further purification unless specified. Diglycolic acid was purchased from TCI America. The secondary amines used for DGA synthesis were purchased from Oakwood Chemicals, Combi Blocks, or Thermo Fisher Scientific. Commercial TODGA was purchased from Ambeed. Lanthanide chlorides (>99.9% purity) and nitrates (>99.9% purity) were purchased from Sigma-Aldrich or Thermo Fisher Scientific Inc. Deionized water was obtained from a Barnstead E-pure system. Trace-metal grade hydrochloric acid (HCl) and nitric acid (HNO_3) were purchased from Fisher Scientific. Isopar L and Tridecyl Alcohol Exxal 13 were purchased from Univar Solutions. Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AV-600 or NEO-400 instrument. The chemical shifts (δ) are given in parts per million (ppm) relative to $CDCl_3$ (7.26 ppm for ^1H) or TMS (0 ppm for ^1H) and $CDCl_3$ (77.0 ppm for ^{13}C) and coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Electrospray ionization high-resolution mass spectra (ESI-HRMS) were recorded using an LTQ FT-ICR mass spectrometer equipped with an electrospray ionization source (Finnigan LTQ FT, Thermo Fisher Scientific, Waltham, MA) operated in positive ion mode. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) spectra were obtained on an Agilent 5800 ICP-OES instrument.

2. Synthesis of Diglycolamides

2.1 TODGA Synthesis via Schotten-Baumann Method:



Step 1:[1] Under a nitrogen atmosphere, a mixture of diglycolic acid (1.35 g, 10 mmol) and thionyl chloride (23.80 g, 200 mmol, 20 equiv.) was refluxed (85 °C) in a 50 mL round bottom flask (RBF) for 8 hours. The reaction mixture was then cooled to room temperature, and the unreacted thionyl chloride was removed by vacuum evaporation. The crude diglycolyl chloride was used in step 2 without further purification.



Step 2:[2, 3] The crude diglycolic chloride (10 mmol, 1.0 equiv.) from Step 1 in anhydrous Et_2O (60 mL) was added dropwise to an aqueous solution (36 mL) of dioctyl amine (21 mmol, 2.1 eq) and NaOH (1.20 g, 30 mmol) in a 250 mL RBF at 0 °C over 30 min. The reaction mixture was stirred at 0 °C for 2 h. Subsequently, the two phases were separated and the aqueous layer was extracted with Et_2O (3 × 30 mL). The combined organic layers were washed sequentially with aqueous HCl (5 wt%, 50 mL), saturated aqueous $NaHCO_3$ solution (50 mL), water (50 mL), and brine (50 mL). The organic layer was collected and dried over anhydrous Na_2SO_4 (25 g). After filtration and evaporation under vacuum, the residue was purified by silica gel (200 g) column chromatography using hexanes/ethyl acetate as the eluent. The product 2,2'-oxybis(*N*,*N*′-dioctylacetamide) or TODGA was obtained as a colorless oil, 4.94 g, 85% yield.

2.2 General Procedure for the Two-Step Melt Amidation Synthesis of DGA

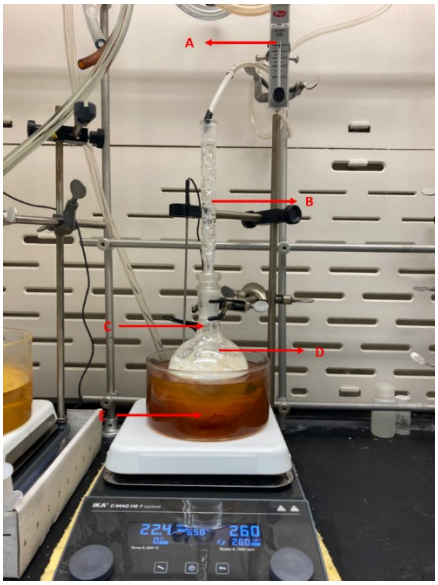
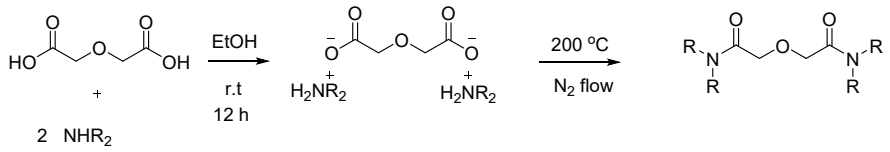


Figure S1. Details of the reaction setup. (A) N_2 flowmeter, (B) Air condenser (20 cm). (C) PTFE tubing for N_2 flow, (D) 500 mL RBF, and (E) high-temperature silicone oil bath.



Step 1: To an ethanolic solution of dialkyl amine (2.0 equiv., 5 M) in an RBF was added solid diglycolic acid (1.0 equiv.) portion-wise at room temperature. The resulting mixture was stirred at room temperature overnight. After which, ethanol was recovered, giving the ammonium salt as a white solid in quantitative yield.

Step 2: To an RBF, the ammonium salt from Step 1 and a magnetic stir bar were introduced. Nitrogen (N_2) was then purged into the RBF through a Teflon tube at a flow rate of 100 ccm. After purging with N_2 for 10 minutes, the RBF was equipped with an air condenser (20 cm). The reaction mixture was subsequently heated to 200 °C under stirring and maintained at this temperature for 24 hours under N_2 flow (100 ccm). After cooling down to room temperature, TODGA was obtained as a pale yellow oil. The purity of the produced DGA was determined by ^{1}H NMR in $CDCl_3$. Using *N,N,N′,N′*-tetra(n-hexyl)diglycolamide (THDGA) **4a** as an example, The main by-product detected by ^{1}H-NMR was the monosubstituted product, 2-(2-(dihexylamino)-2-oxoethoxy)acetic acid, which shows two asymmetric O-CH_2-CO signals at 4.20 ppm and 4.38 ppm.[4] The purity of the product was ascertained by comparing the integration of the O-CH_2-CO peak at 4.30 ppm, attributed to the main product, against the integration of the O-CH_2-CO peak at 4.20 and 4.38 ppm, associated with the side product (Figure S1.1). To further validate the purity, trimethoxybenzene was introduced as an internal standard, with the results detailed in Figure S19 of the supporting information.

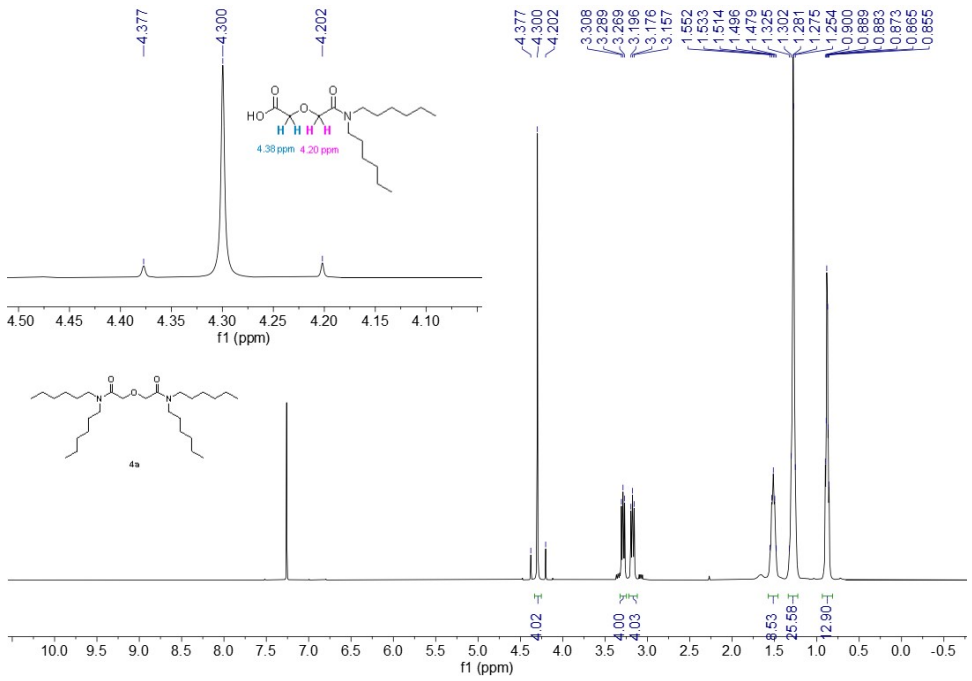
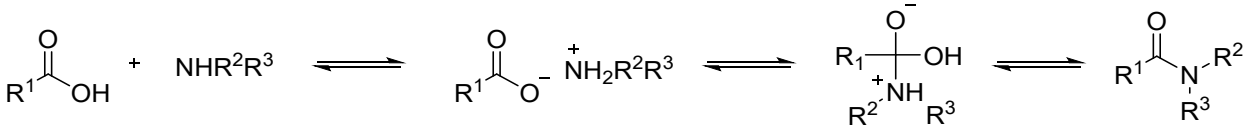
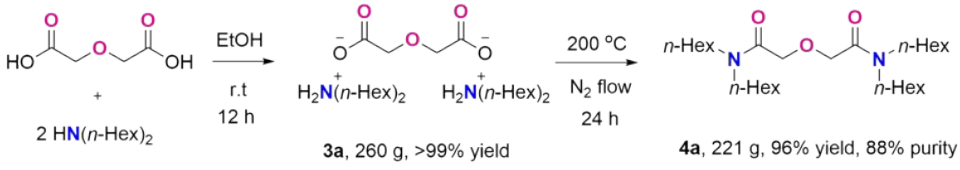


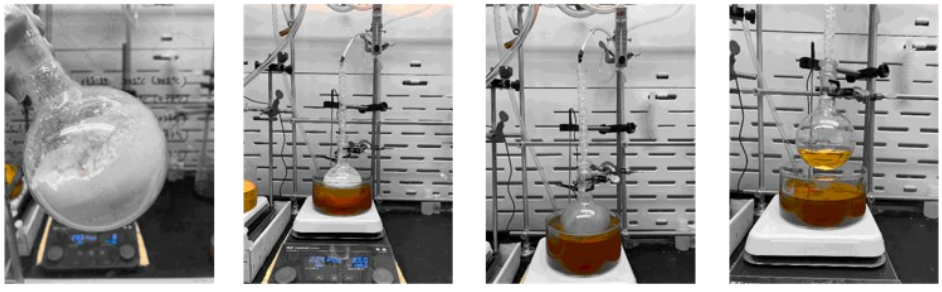
Figure S1.1. Determination of the purity of **4a** by ^{1}H-NMR.



Scheme S1. Proposed mechanism for the direct amidation of carboxylic acids.

2.3 One-pot synthesis of TEHDGA at 200 g scale





3a, 260 g

Reaction setup for melt amidation

THDGA, 221 g

Scheme S2. 200-gram scale one-pot synthesis of **4a**.

In a 500 mL RBF, to an ethanolic solution (200 mL) of dihexyl amine (186.0 g, 1 mol, 2.0 equiv.) was gradually added diglycolic acid (67.1 g, 0.5 mol, 1.0 equiv.) at room temperature. The reaction mixture was then stirred overnight at the same temperature. Subsequently, the RBF was placed in an oil bath over a hot plate, and the ethanol was distilled off and recovered at 85 °C. The flask was outfitted with an air condenser (20 cm) and flushed with industrial-grade N_2 for 10 minutes at 100 ccm. The temperature of the reaction was then raised to 200 °C, and the mixture was stirred for 24 hours under 100 ccm N_2 flow at the same temperature. Upon cooling to room temperature, TEHDGA (221 g in 88% purity) was obtained as a pale-yellow oil.

2.4 Substrate Scope Studies

2,2'-oxybis(N,N-dihexylacetamide) 4a. The reaction was carried out on the 50 mmol scale using the corresponding ammonium salt (25.30 g) at 200 °C for 24 hours. **4a** was obtained in 90% yield as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (s, 4H), 3.33 – 3.25 (m, 4H), 3.21 – 3.14 (m, 4H), 1.57 – 1.46 (m, 8H), 1.35 – 1.22 (m, 24H), 0.93 – 0.84 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 69.1, 46.9, 45.7, 31.6, 31.5, 28.9, 27.5, 26.7, 26.5, 22.57, 22.55, 14.0, 13.9. HRMS: Calculated for $C_{28}H_{57}N_2O_3$ ($M+H^+$): 469.4369; Found: 469.4361.

2,2'-oxybis(N,N-dibutylacetamide) (4b). The reaction was carried out on the 31 mmol scale using the corresponding ammonium salt (18.00 g) at 200 °C for 24 hours. To achieve complete conversion, additional dibutyl amine (15.5 mmol, 0.5 equiv.) was introduced and the reaction mixture was stirred at 200 °C for another 12 hours. **4b** was obtained in 89% yield as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.30 (s, 4H), 3.33 – 3.28 (m, 4H), 3.21 – 3.16 (m, 4H), 1.54 – 1.47 (m, 8H), 1.34 – 1.26 (m, 8H), 0.96 – 0.88 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.4, 69.0, 46.6, 45.4, 30.9, 29.6, 20.1, 19.9, 13.8, 13.7. HRMS: Calculated for $C_{20}H_{41}N_2O_3$ ($M+H^+$): 357.3117; Found: 357.3110.

2,2'-oxybis(N,N-dioctylacetamide) (4c). The reaction was carried out on the 300 mmol scale using the corresponding ammonium salt (185.0 g) and one-pot synthesis method at 200 °C for 24 hours. **4c** was obtained in 93% yield as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (s, 4H), 3.32 – 3.26 (m, 4H), 3.21 – 3.15 (m, 4H), 1.58 – 1.46 (m, 8H), 1.33 – 1.20 (m, 44H), 0.92 –

0.83 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.41, 69.03, 46.87, 45.72, 31.74, 31.69, 29.30, 29.25, 29.18, 29.14, 28.89, 27.53, 26.97, 26.77, 22.57, 22.55, 14.01, 14.00. HRMS: Calculated for $C_{36}H_{73}N_2O_3$ ($M+H^+$): 581.5621; Found: 581.5611.

2,2'-oxybis(N-methyl-N-octylacetamide) (4d). The reaction was carried out on the 15 mmol scale using the corresponding ammonium salt (6.4 g) at 200 °C for 24 hours. **4d** was obtained in 95% yield as a pale brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 (s, 2H), 4.29 (s, 2H), 3.38 – 3.30 (m, 2H), 3.27 – 3.18 (m, 2H), 2.96 (s, 3H), 2.92 (s, 3H), 1.59 – 1.46 (m, 4H), 1.34 – 1.20 (m, 20H), 0.92 – 0.84 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.69, 168.63, 168.47, 168.40, 69.47, 69.35, 69.11, 68.95, 48.93, 47.81, 34.09, 33.08, 31.71, 31.66, 29.28, 29.24, 29.14, 29.10, 28.26, 27.00, 26.75, 26.59, 22.55, 22.53, 14.00, 13.98. HRMS: Calculated for $C_{22}H_{45}N_2O_3$ ($M+H^+$): 385.3430; Found: 385.3413.

2,2'-oxybis(N,N-didecylacetamide) (4e). The reaction was carried out on the 8.8 mmol scale using the corresponding ammonium salt (6.50 g) at 200 °C for 24 hours. **4e** was obtained in 87% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (s, 4H), 3.32 – 3.24 (m, 4H), 3.22 – 3.12 (m, 4H), 1.56 – 1.46 (m, 8H), 1.32 – 1.20 (m, 56H), 0.91 – 0.84 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 69.1, 46.9, 45.8, 31.88, 31.86, 29.59, 29.55, 29.51, 29.41, 29.37, 29.30, 29.28, 28.9, 27.6, 27.0, 26.8, 22.7, 14.1. HRMS: Calculated for $C_{44}H_{89}N_2O_3$ ($M+H^+$): 693.6873; Found: 693.6848.

2,2'-oxybis(N,N-didodecylacetamide) (4f). The reaction was carried out on the 7.3 mmol scale using the corresponding ammonium salt (6.20 g) at 200 °C for 24 hours. **4f** was obtained in 88% yield as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.29 (s, 4H), 3.31 – 3.23 (m, 4H), 3.20 – 3.14 (m, 4H), 1.55 – 1.47 (m, 8H), 1.32 – 1.20 (m, 72H), 0.90 – 0.85 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.4, 69.1, 46.9, 45.8, 31.9, 29.63, 29.62, 29.60, 29.59, 29.58, 29.5, 29.40, 29.36, 29.3, 28.9, 27.6, 27.0, 26.8, 22.7, 14.1. HRMS: Calculated for $C_{52}H_{105}N_2O_3$ ($M+H^+$): 805.8125; Found: 805.8132.

2,2'-oxybis(1-(piperidin-1-yl)ethan-1-one) (4g). The reaction was carried out on the 39.4 mmol scale using the corresponding ammonium salt (12.00 g) at 200 °C for 24 hours. To achieve

complete conversion, additional piperidine (19.7 mmol, 0.5 equiv.) was introduced and the reaction mixture was stirred at 200 °C for another 12 hours. **4g** was obtained in 85% yield as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.26 – 4.24 (m, 4H), 3.54 – 3.48 (m, 4H), 3.39 – 3.34 (m, 4H). 1.64 – 1.58 (m, 4H), 1.56 – 1.50 (m, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.93, 69.71, 45.82, 42.75, 26.32, 25.46, 24.37. HRMS: Calculated for $C_{14}H_{25}N_2O_3$ ($M+H^+$): 269.1865; Found: 269.1857.

2,2'-oxybis(N,N-bis(2-ethylhexyl)acetamide) (4h). The reaction was carried out on the 200 mmol scale using the corresponding ammonium salt (123.60 g) at 200 °C for 24 hours. 1,3,5-Trimethoxybenzene was added as an internal standard to verify the NMR yield. **4h** was obtained in 96% yield as a pale brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 (s, 4H), 3.41 – 3.17 (m, 4H), 3.10 (s, 2H), 3.08 (s, 2H), 1.71 – 1.62 (m 4H), 1.60 – 1.50 (m, 4H), 1.32 – 1.16 (m, 32H), 0.93 – 0.81 (m, 24H).^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 69.14, 49.9, 47.8, 37.8, 36.6, 30.5, 30.4, 28.77, 28.76, 28.65, 28.64, 23.74, 23.70, 23.04, 22.96, 14.03, 13.98, 10.9, 10.6, 10.54. HRMS: Calculated for $C_{36}H_{73}N_2O_3$ ($M+H^+$): 581.5621; Found: 581.5610.

2-(2-(bis(2-methoxyethyl)amino)-2-oxoethoxy)-N-(2-methoxyethyl)-N-(3-methoxypropyl)acetamide (4i). The reaction was carried out on the 47 mmol scale using the corresponding ammonium salt (19.00 g) at 200 °C for 24 hours. **4i** was obtained in 90% yield as a pale ywllow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37 (s, 4H), 3.60 – 3.45 (m, 16H), 3.32 (s, 6H), 3.31 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 71.0, 70.7, 69.4, 59.0, 58.8, 47.9, 46.1. HRMS: Calculated for $C_{16}H_{33}N_2O_3$ ($M+H^+$): 365.2288; Found: 365.2278.

3. Life Cycle Analysis (LCA)

Table S1. Life cycle inventory for 1 kg Diglycolic Acid Production.

Material/ Energy	Value	Unit	Unit process
Diglycol	0.8071885	kg	Diethylene glycol, at plant/US- US-EI U
HNO3(56%)	2.8784648	kg	Nitric acid, in water (60% HNO3) (NPK 13.2-0-0), at plant {RNA} Economic, S
Natural Gas	0.2577909	MJ	Natural gas, burned in power plant/US US-EI U

Table S2. Life cycle inventory for 1 kg Furfural Production.

Material/ Energy	Value	Unit	Unit process
Cornchop	1.3623978	kg	Maize chop {RoW} | market for maize chop | APOS, S
Water	0.0928883	kg	Water, ultrapure {RoW}| market for water, ultrapure | APOS, S
Natural Gas	0.2102047	MJ	Natural gas, burned in power plant/US US-EI U

Table S3. Life cycle inventory for 1 kg 1-Octanol Production.

Material/ Energy	Value	Unit	Unit process
Furfural	0.0109793	kg	Furfural
Acetone	0.0439171	kg	Acetone, liquid {RoW}| market for acetone, liquid | APOS, S
Acetic acid	0.5764126	kg	Acetic anhydride {GLO}| market for acetic anhydride | APOS, S
Sodium hydroxide	0.3071316	kg	Sodium hydroxide, without water, in 50% solution state {GLO}| market for | APOS, S
Electricity	24.209328	kWh	Electricity, low voltage, at grid, Iowa/US US-EI U
Natural Gas	0.304095	MJ	Natural gas, burned in power plant/US US-EI U

Table S4. Life cycle inventory for 1 kg Dioctylamine Production.

Material/ Energy	Value	Unit	Unit process
1-Octanol	1.078688	kg	1-Octanol
Ammonia	0.0705334	kg	Ammonia, steam reforming, liquid, at plant/US- US-EI U
Natural Gas	0.3606187	MJ	Natural gas, burned in power plant/US US-EI U

Table S5. Life cycle inventory for 1 kg TODGA (New method) Production.

Material/ Energy	Value	Unit	Unit process
Diglycolic acid	0.2480307	kg	Diglycolic Acid
Dioctylamine	0.8938732	kg	Dioctylamine
Nitrogen	0.3333356	kg	Nitrogen, via cryogenic air separation, production mix, at plant, gaseous EU-27 S
Silicone oil	0.0035909	kg	Silicone product, at plant/US- US-EI U
Electricity	2.267264	kWh	Electricity, low voltage, at grid, Iowa/US US-EI U

Table S6. Life cycle inventory for 1 kg Diglycolyl Chloride Production.

Material/ Energy	Value	Unit	Unit process
Diglycolic acid	0.7837174	kg	Diglycolic acid
Thionyl chloride	1.3916248	kg	Thionyl chloride {RoW}| market for thionyl chloride | APOS, S
Silicone oil	0.060858	kg	Silicone product, at plant/US- US-EI U
Tap water (Condensing)	180.69165	kg	Tap water {GLO}| market group for | APOS, S
Electricity	8.0628952	kWh	Electricity, low voltage, at grid, Iowa/US US-EI U

Table S7. Life cycle inventory for 1 kg TODGA (Traditional method) Production.

Material/ Energy	Value	Unit	Unit process
Diglycolic chloride	0.3461134	kg	Diglycolyl chloride
Dioctylamine	1.0264494	kg	Dioctylamine
Diethyl ether	1.516336	kg	Diethyl ether, without water, in 99.95% solution state {RoW}| market for diethyl ether, without water, in 99.95% solution state | APOS, S
Sodium hydroxide	0.242915	kg	Sodium hydroxide, without water, in 50% solution state {GLO}| market for | APOS, S
Hydrogen chloride (HCl)	0.5060729	kg	Hydrogen chloride gas, production mix for PVC production, at plant RER
Sodium bicarbonate ($NaHCO_3$)	0.9716599	kg	Sodium bicarbonate {GLO}| market for sodium bicarbonate | APOS, S
Sodium chloride (Brine)	5.0607287	kg	Sodium chloride, brine solution {GLO}| market for | APOS, S
Water	80.97166	kg	Water, ultrapure {RoW}| market for water, ultrapure | APOS, S
Sodium sulfate (Na_2SO_4)	5.0607287	kg	Sodium sulfate, anhydrite {RoW}| market for | APOS, S
Silica	4.048583	kg	Silica sand {GLO}| market for | APOS, S
Hexane	8.0040486	kg	Hexane {GLO}| market for | APOS, S
Ethyl acetate	2.7388664	kg	Ethyl acetate {GLO}| market for | APOS, S
Electricity	4.3437247	KWh	Electricity, low voltage, at grid, Iowa/US US-EI U
Natural Gas	82.59871	MJ	Natural gas, burned in power plant/US US-EI U

Table S8. Assumptions for new DGA synthesis system.

Assumptions	Value	Unit
Insulation layer thickness	0.04	m
Outer surface temperature of the insulation layer	40	°C

Table S9. Assumptions for traditional DGA synthesis system.

Assumptions	Value	Unit
Diglycolyl chloride yield rate	1	
Brine mass fraction	50	wt%
Frequency of silica gel column use	10	times
Ethyl acetate consumption to regenerate silica gel column	4500	mL
Ethyl acetate (for silica gel column regeneration) recycle rate	1	
Diethyl ether recycle rate	0.93	
Electricity use (for vacuun evaporation) scale up rate for unit product	1	

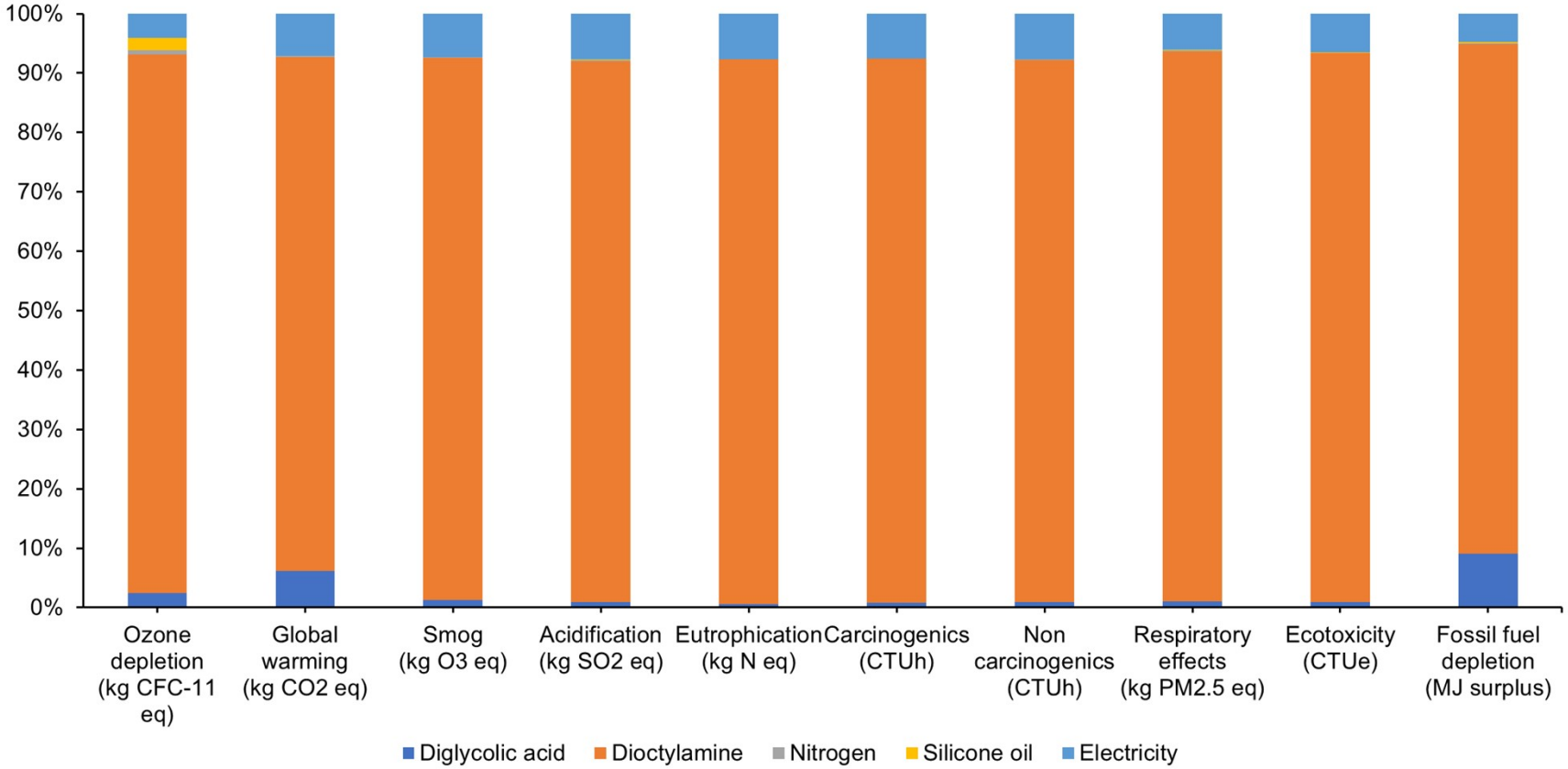


Figure S2. Contribution analysis on the TODGA synthesis via melt-amidation.

Table S10. Data for Figure S2.

Percentage	Ozone depletion (kg CFC-11 eq)	Global warming (kg CO_2 eq)	Smog (kg O_3 eq)	Acidification (kg SO_2 eq)	Eutrophication (kg N eq)	Carcinogenics (CTUh)	Non carcinogenics (CTUh)	Respiratory effects (kg PM2.5 eq)	Ecotoxicity (CTUe)	Fossil fuel depletion (MJ surplus)
Diglycolic acid	2.48%	6.22%	1.27%	0.96%	0.52%	0.85%	0.91%	1.07%	0.89%	9.11%
Dioctylamine	90.93%	87.08%	91.87%	91.64%	92.44%	92.19%	91.96%	93.01%	93.05%	86.19%
Nitrogen	0.71%	0.16%	0.11%	0.22%	0.00%	0.00%	0.02%	0.22%	0.00%	0.001262
Silicone oil	2.17%	0.06%	0.07%	0.10%	0.03%	0.03%	0.04%	0.11%	0.03%	0.17%
Electricity	3.71%	6.48%	6.68%	7.07%	7.01%	6.92%	7.07%	5.59%	6.02%	4.40%

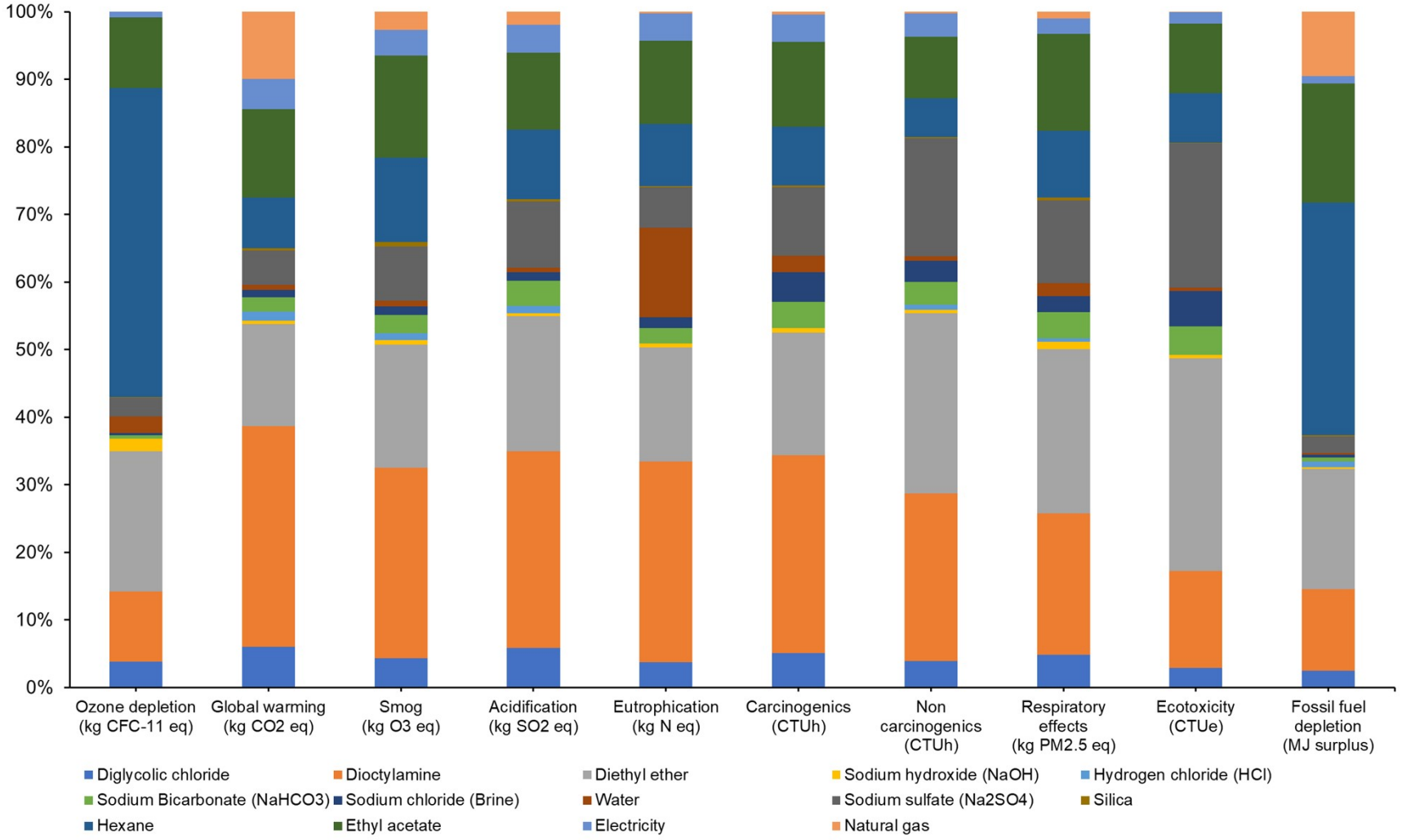


Figure S3. Contribution analysis on traditional TODGA synthesis method.

Table S11. Data for Figure S3.

Percentage	Ozone depletion (kg CFC-11 eq)	Global warming (kg CO_2 eq)	Smog (kg O_3 eq)	Acidification (kg SO_2 eq)	Eutrophication (kg N eq)	Carcinogenics (CTUh)	Non carcinogenics (CTUh)	Respiratory effects (kg PM2.5 eq)	Ecotoxicity (CTUe)	Fossil fuel depletion (MJ surplus)
Diglycolic chloride	3.87%	6.04%	4.32%	5.87%	3.73%	5.14%	3.96%	4.87%	2.89%	2.47%
Dioctylamine	10.33%	32.62%	28.16%	29.08%	29.68%	29.28%	24.75%	20.90%	14.34%	12.03%
Diethyl ether	20.81%	15.12%	18.27%	19.97%	16.92%	18.12%	26.68%	24.26%	31.48%	17.88%
Sodium hydroxide (NaOH)	1.78%	0.53%	0.64%	0.46%	0.54%	0.65%	0.53%	1.18%	0.54%	0.19%
Hydrogen chloride (HCl)	0.00%	1.30%	1.02%	1.08%	0.05%	0.03%	0.75%	0.44%	0.00%	0.90%
Sodium Bicarbonate ($NaHCO_3$)	0.54%	2.10%	2.74%	3.72%	2.31%	3.86%	3.36%	3.91%	4.20%	0.56%
Sodium chloride (Brine)	0.37%	1.09%	1.27%	1.31%	1.58%	4.39%	3.15%	2.37%	5.23%	0.41%
Water	2.42%	0.84%	0.84%	0.61%	13.23%	2.44%	0.65%	1.97%	0.53%	0.27%
Sodium sulfate (Na_2SO_4)	2.76%	5.05%	8.00%	9.79%	6.02%	10.14%	17.41%	12.20%	21.28%	2.44%
Silica	0.14%	0.30%	0.66%	0.36%	0.14%	0.20%	0.18%	0.42%	0.10%	0.15%
Hexane	45.70%	7.52%	12.53%	10.25%	9.15%	8.70%	5.78%	9.88%	7.37%	34.41%
Ethyl acetate	10.48%	13.12%	15.09%	11.44%	12.31%	12.58%	9.08%	14.33%	10.29%	17.65%
Electricity	0.77%	4.44%	3.75%	4.11%	4.12%	4.02%	3.48%	2.30%	1.70%	1.12%
Natural gas	0.03%	9.94%	2.73%	1.94%	0.22%	0.46%	0.24%	0.98%	0.06%	9.51%

Table S12. Data for Figure 1.

Impact category	Melt-amidation	Traditional Method
Ozone depletion	9.89%	100%
Global warming	32.62%	100%
Smog	26.69%	100%
Acidification	27.64%	100%
Eutrophication	27.96%	100%
Carcinogenics	27.65%	100%
Non carcinogenics	23.44%	100%
Respiratory effects	19.57%	100%
Ecotoxicity	13.42%	100%
Fossil fuel depletion	12.16%	100%

Table S13 Data for Figure 2.

	kg CO_2 eq	Melt-amidation	Traditional Method
Reactants	Diglycolic acid	1.161502418	0
	Diglycolic chloride	0	3.459949704
	Dioctylamine	16.26356219	18.67571777
Supporting materials	Silicone oil	0.012029999	0
	Nitrogen	0.029436981	0
	Diethyl ether	0	8.654488878
	Sodium hydroxide (NaOH)	0	0.305663808
	Hydrogen chloride (HCl)	0	0.741660071
	Sodium Bicarbonate ($NaHCO_3$)	0	1.201324626
	Sodium chloride (Brine)	0	0.623543009
	Water	0	0.480496943
	Sodium sulfate (Na_2SO_4)	0	2.889868337
	Silica	0	0.169357154
	Hexane	0	4.303921456
	Ethyl acetate	0	7.510408922
Energy	Electricity	1.210332287	2.543027477
	Natural gas	0	5.690642962

4. Liquid-liquid Extraction Studies

Manual Extraction: A 0.75 mL of 7.0 mM Ln(III) (0.5 mM of each Ln(III)) in 3.0 M HCl was contacted with 0.75 mL organic phase containing 0.10 M DGA ligands in Isopar L/Exxal 13 that were pre-equilibrated with the 3.0 M HCl. The two phases were contacted by end-over-end rotation in individual 2 mL centrifuge tubes using a rotating wheel (Fisher Scientific) at 36 rpm at 22.0 ± 0.5 °C for 1 hour. Following liquid-liquid contacting, the samples were subjected to centrifugation at 3500 rpm for 5 minutes to allow phase separation. All extraction experiments were triplicated independently and experimental uncertainties were calculated with error propagation from the ICP analysis. Each sample was then sampled, with 0.5 mL aliquots of the aqueous phases transferred to individual polypropylene tubes (15 mL) containing 2.5 mL of 4% HNO_3 for the elemental analysis using ICP-OES. Two samples of the initial lanthanide solution were also prepared for the elemental analysis.

High-throughput Automated Extraction: The automated extraction experiments were conducted using a Chemspeed SWING robotic system equipped with a four-needle dispense head (Figure S4, **B**) and four 10 ml syringe pumps (**G**). Each pump was individually calibrated for precise liquid transfer. Solid dispensing was facilitated by the dispensing unit (**C**), with the 14 lanthanide salts stored in separate storage units (**D**). To prepare the lanthanide stock solution, the 13 Ln salts were first dispensed into the 20 mL vial using unit **C**, followed by the addition of 3.0 M HCl (prepared manually) to prepare the 7.0 mM Ln(III) (0.5 mM of each Ln(III)). This solution was thoroughly mixed using a shaker unit (**J**) at 100 rpm for 5 minutes. Due to the high viscosity of neat DGA, the organic phase containing 0.10 M DGA ligand in the Isopar L/Exxal 13 mixture was prepared manually and pre-mixed with 3.0 M HCl. After preparing the stock solutions, 2.0 mL of Ln(III) stock solution and 2.0 mL of organic phase were transferred to a 15 mL centrifuge tube using unit **B**. The centrifuge tube was capped, and the two-phase solution was contacted by end-over-end rotation using a rotating wheel at 36 rpm at 22.0 ± 0.5 °C for 1 hour. All extraction experiments (except for **4g** and **4i**) were triplicated independently and experimental uncertainties were calculated with error propagation from the ICP analysis. Subsequently, the samples were subjected to centrifugation at 3500 rpm for 5 minutes to separate the two phases. Each triplicate was then subsampled, with the upper layer organic phase (~2 mL) first removed, followed by transferring 1

mL aliquots of the aqueous phase into a new 15 mL centrifuge tube. 5 mL of 4% HNO_3 was transferred to the above centrifuge tube to dilute the sample for ICP analysis. Two samples of the initial lanthanide solution were also prepared in the same way for the elemental analysis.

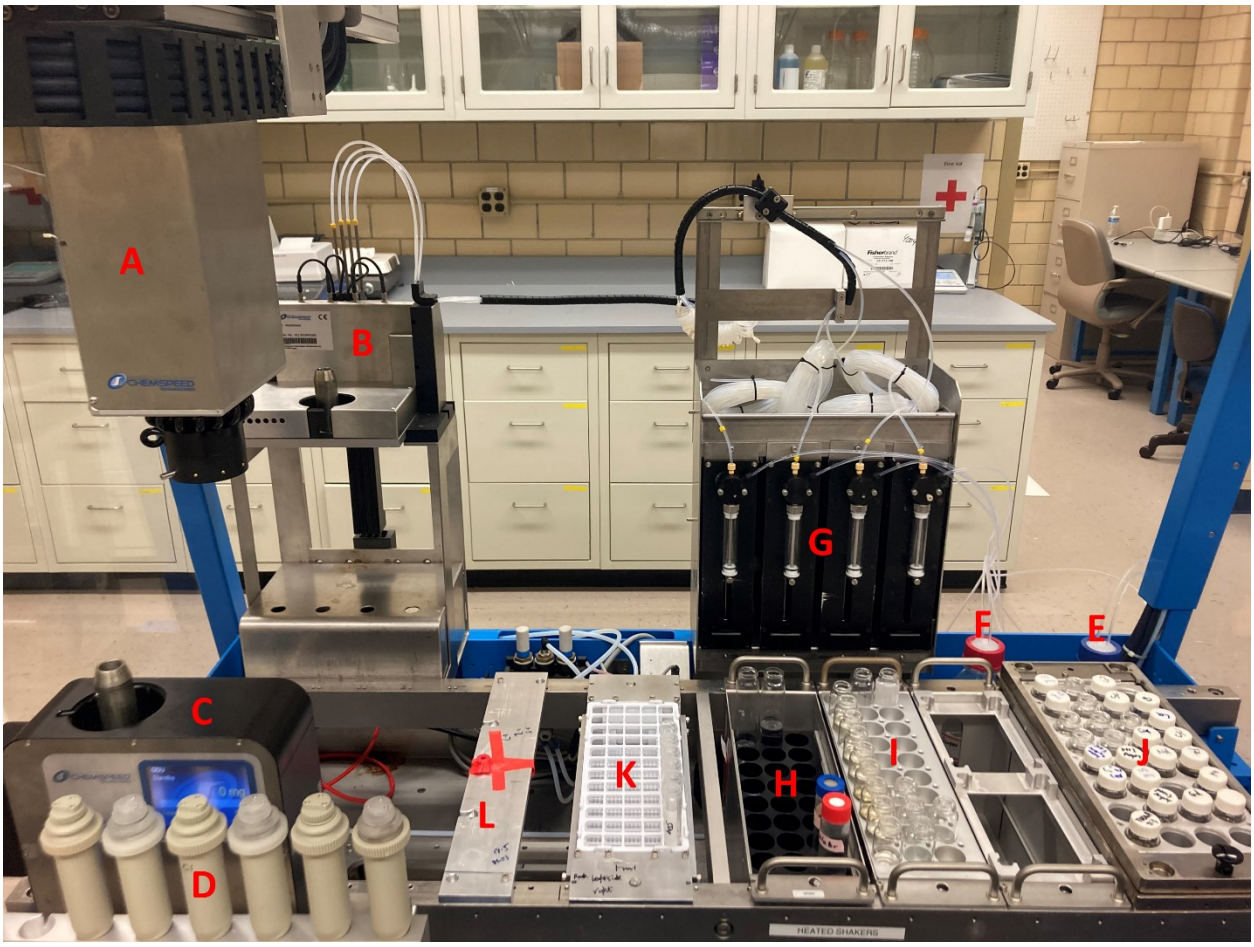


Figure S4. Details of the high-throughput extraction system. (A) Robotic arm. (B) Needlehead for dispensing and transferring liquids, equipped with four needles. (C) Solid dispensing unit. (D) Lanthanide metal salts storage units. (E) DI water storge bottle. (F) Isopar L and Exxal 13 storage bottle. (G) Syringe pumps (10 mL). (H) 50 mL vial rack. (I) 20 mL vial rack. (J) Shaker with heating unit. (K) ICP sampling rack. (L) Injection port.

Stripping Studies: After high-throughput extraction experiments, 1.5 mL of DGA-Ln enriched organic phase (upper layer) was transferred to a 15 mL centrifuge tube using unit B. Then 1.5 mL of a certain concentration of aqueous HCl solution was added to the above mixture and the two phases were contacted by end-over-end rotation using a rotating wheel (Fisher Scientific) at 36 rpm at 22.0 ± 0.5 °C for 1 hour. Following liquid-liquid contacting, the samples were subjected to centrifugation at 3500 rpm for 5 minutes to allow phase separation. All extraction experiments

were triplicated independently and experimental uncertainties were calculated with error propagation from the ICP analysis. Each sample was then sampled, with 1.0 mL aliquots of the aqueous phases transferred to individual centrifuge tubes (15 mL) containing 5.0 mL of 4% HNO_3 for the elemental analysis using ICP-OES.

D values are calculated according to

$$[Ln]_{org} = [Ln]_{sample} - [Ln]_{aq}$$

$$D = \frac{[Ln]_{org}}{[Ln]_{aq}}$$

Extraction efficiencies (EE) are calculated according to

$$EE = \frac{[Ln]_{org}}{[Ln]_{sample}} \times 100$$

Stripping efficiencies (E_s) are calculated according to

$$Es = \frac{[Ln]_{aq}^{Stripping}}{[Ln]_{org}} \times 100$$

5. Supplementary Data

Table S14. Plotting data for Figure 5a.

		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
TODGA-1	E	13.04	30.74	51.06	53.33	--	90.78	95.03	96.45	98.04	98.76	99.19	99.34	99.31	99.41	99.38
	uncertainty	0.46	0.06	0.31	0.58	--	0.27	0.20	0.15	0.10	0.08	0.07	0.06	0.06	0.06	0.06
TODGA-3	E	11.18	28.89	49.81	52.12	--	90.58	94.96	96.42	98.05	98.80	99.23	99.37	99.35	99.45	99.42
	uncertainty	0.75	1.14	1.29	1.65	--	0.62	0.40	0.33	0.23	0.19	0.15	0.14	0.14	0.13	0.12
TODGA-2	E	13.82	33.64	50.73	52.90	--	90.86	96.26	97.26	98.51	99.07	99.40	99.50	99.48	99.57	99.52
	uncertainty	1.54	1.29	1.06	1.04	--	0.23	0.11	0.10	0.06	0.04	0.03	0.02	0.02	0.02	0.02

Table S15. Plotting data for Figure 5b.

		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
TODGA-Manual	Log D	-0.82	-0.35	0.02	0.06	--	0.99	1.28	1.43	1.70	1.90	2.09	2.18	2.16	2.23	2.20
	uncertainty	0.02	0.00	0.01	0.01	--	0.01	0.02	0.02	0.02	0.03	0.04	0.04	0.04	0.04	0.04
TODGA-Automatic	Log D	-0.82	-0.33	0.06	0.12	--	1.07	1.36	1.50	1.77	1.97	2.16	2.24	2.23	2.31	2.27
	uncertainty	0.03	0.01	0.01	0.01	--	0.01	0.01	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.00
DMDODGA-Manual	Log D	0.28	0.60	0.93	1.06	--	2.00	2.27	2.38	2.68	2.90	3.16	3.16	3.17	3.35	3.17
	uncertainty	0.02	0.02	0.02	0.02	--	0.05	0.03	0.03	0.05	0.06	0.11	0.10	0.10	0.06	0.09
DMDODGA-Automatic	Log D	0.36	0.67	1.00	1.13	--	2.01	2.29	2.41	2.71	2.93	3.14	3.16	3.17	3.29	3.16
	uncertainty	0.01	0.01	0.01	0.01	--	0.02	0.01	0.01	0.01	0.02	0.05	0.07	0.07	0.09	0.04

Table S16. Plotting data for Figure 5c.

Log D	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Sequential	-0.45	-0.13	0.13	0.17	--	0.99	1.26	1.38	1.64	1.82	1.98	2.07	2.05	2.11	2.10
Direct	-0.74	-0.34	-0.05	-0.04	--	0.83	1.11	1.26	1.52	1.73	1.89	2.00	1.99	2.05	2.05

Table S17. Plotting data for Figure 5d.

Ratio of Isopar L: Exxal 13		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
9:1	Log D	-1.07	-0.62	-0.28	-0.40	--	0.53	0.83	0.99	1.26	1.48	1.66	1.76	1.74	1.79	1.81
	error	0.01	0.00	0.01	0.01	--	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
7:3	Log D	-0.82	-0.33	0.06	0.12	--	1.07	1.36	1.50	1.77	1.97	2.16	2.24	2.23	2.31	2.27
	error	0.03	0.01	0.01	0.01	--	0.01	0.01	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.00
5:5	Log D	-0.65	-0.21	0.15	0.21	--	1.12	1.43	1.56	1.84	2.06	2.25	2.33	2.32	2.39	2.35
	error	0.01	0.00	0.00	0.00	--	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.00

Table S18. Plotting data for Figure 5e.

		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
0.1 M HCl	LogD	-0.95	-0.94	-0.98	-0.95	--	-0.96	-0.91	-0.92	-0.91	-0.90	-0.87	-0.84	-0.85	-0.84	-0.80
	uncertainty	0.10	0.11	0.15	0.13	--	0.13	0.11	0.10	0.11	0.12	0.11	0.11	0.10	0.09	0.08
1.5 M HCl	LogD	-0.89	-0.67	-0.66	-0.82	--	-0.29	-0.05	0.07	0.31	0.50	0.65	0.74	0.73	0.76	0.82
	uncertainty	0.11	0.07	0.06	0.09	--	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00
3.0 M HCl	LogD	-0.82	-0.33	0.06	0.12	--	1.07	1.36	1.50	1.77	1.97	2.16	2.24	2.23	2.31	2.27
	uncertainty	0.03	0.01	0.01	0.01	--	0.01	0.01	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.00

Table S19. Plotting data for Figure 5f.

		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
TODGA HCl	E	18.2	37.9	58.5	62.0	--	93.0	96.4	97.3	98.6	99.1	99.4	99.5	99.5	99.6	99.6
	uncertainty	0.2	0.2	0.2	0.3	--	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TODGA HNO_3	E	85.6	95.9	98.6	99.0	--	99.8	99.9	99.9	99.9	100.0	100.0	100.0	100.0	100.0	100.0
	uncertainty	1.4	0.4	0.2	0.1	--	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TEHDGA HCl	E	5.0	8.5	10.1	8.8	--	14.8	18.7	18.2	23.3	26.9	28.9	29.3	25.7	24.5	24.0
	uncertainty	0.4	0.5	0.4	0.5	--	1.2	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
TEHDGA HNO_3	E	52.5	70.4	75.3	73.3	--	84.1	88.6	90.9	94.9	96.7	97.5	97.8	97.6	97.5	97.4
	uncertainty	2.0	1.4	1.2	1.3	--	0.9	0.7	0.6	0.3	0.2	0.2	0.1	0.1	0.2	0.2

Table S20. Plotting data for Figure 6.

		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
4c	LogD	-0.82	-0.33	0.06	0.12	--	1.07	1.36	1.50	1.77	1.97	2.16	2.24	2.23	2.31	2.27
	uncertainty	0.03	0.01	0.01	0.01	--	0.01	0.01	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.00
4h	LogD	-1.47	-1.25	-1.21	-1.29	--	-0.99	-0.88	-0.85	-0.72	-0.64	-0.58	-0.58	-0.63	-0.66	-0.66
	uncertainty	0.09	0.07	0.07	0.07	--	0.05	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.02	0.02
4d	LogD	0.36	0.67	1.00	1.13	--	2.01	2.29	2.41	2.71	2.93	3.14	3.16	3.17	3.29	3.16
	uncertainty	0.01	0.01	0.01	0.01	--	0.02	0.01	0.01	0.01	0.02	0.05	0.07	0.07	0.09	0.04
4g	LogD	-0.67	-0.69	-0.74	-0.71	--	-0.73	-0.68	-0.69	-0.74	-0.76	-0.75	-0.77	-0.74	-0.71	-0.66
		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
4i	LogD	-0.65	-0.67	-0.72	-0.69	--	-0.70	-0.65	-0.65	-0.71	-0.73	-0.72	-0.74	-0.71	-0.67	-0.62
		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

6. NMR and HRMS Spectra of Synthesized Diglycolamides

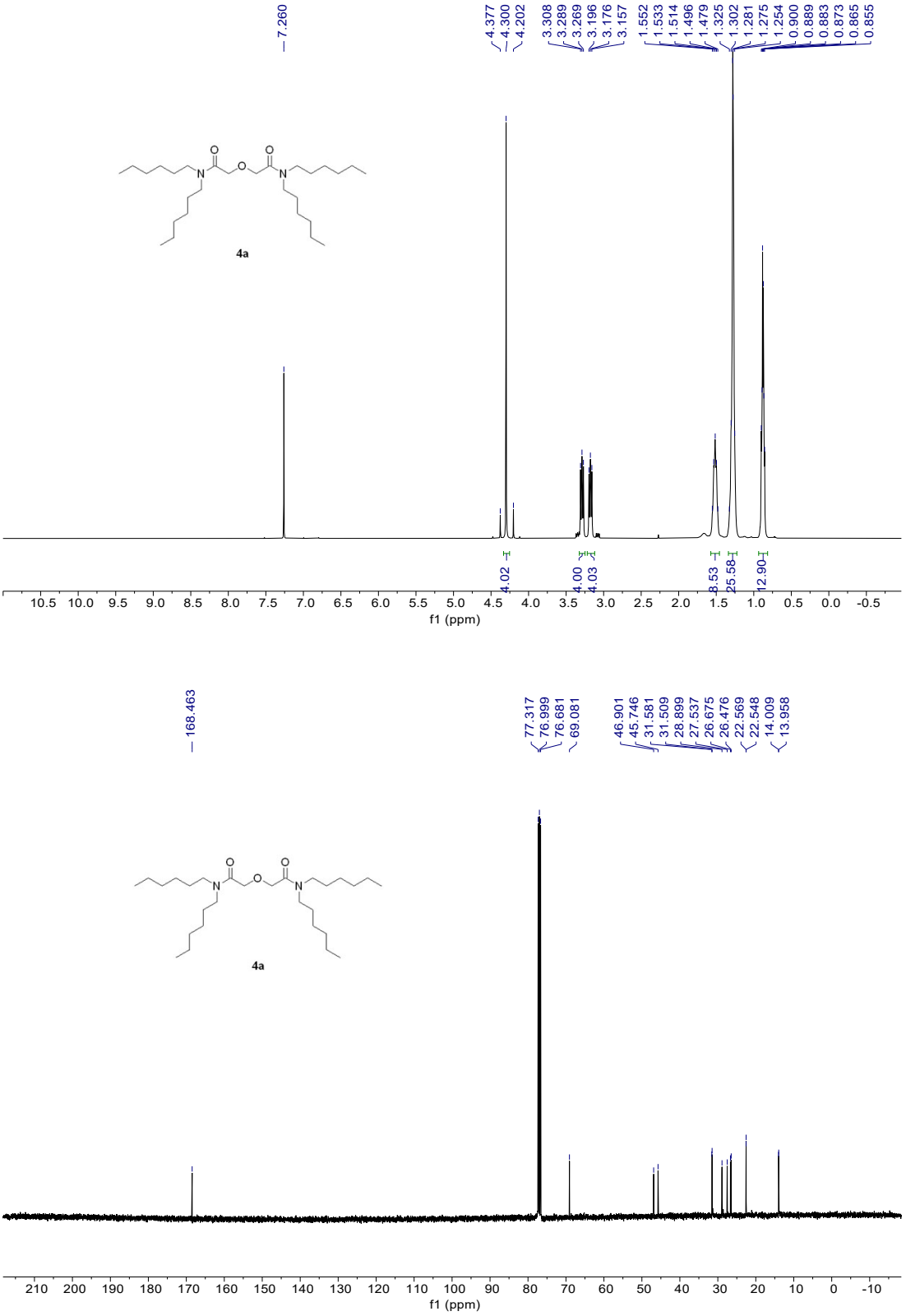


Figure S5. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **4a**.

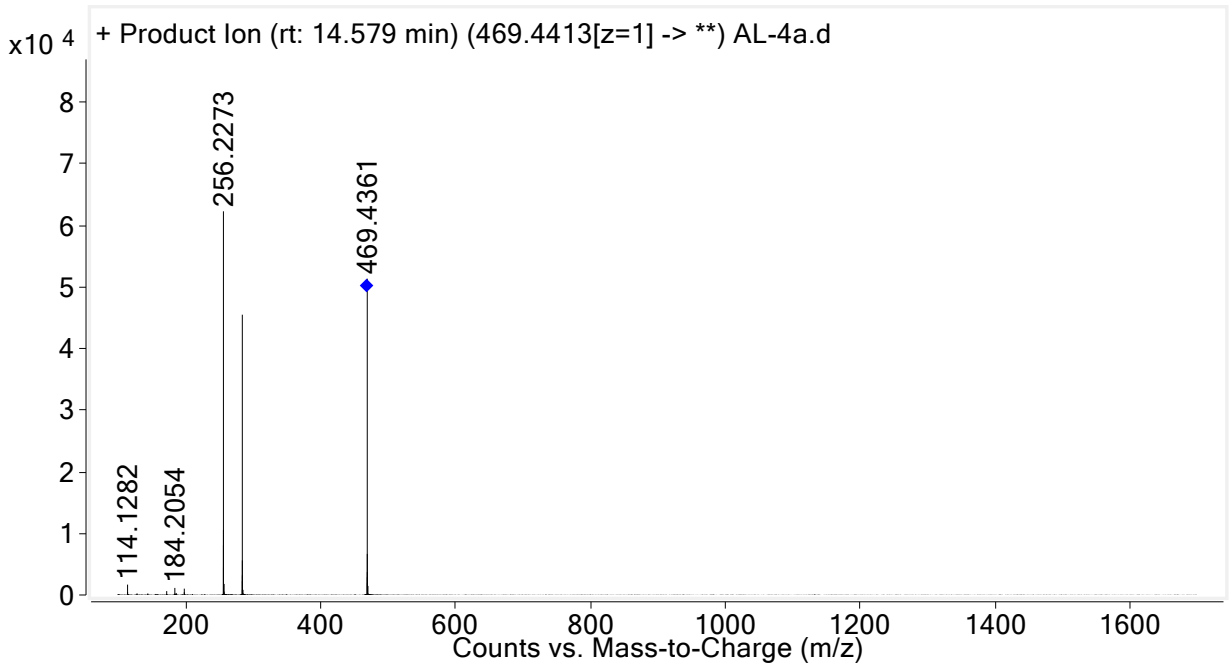
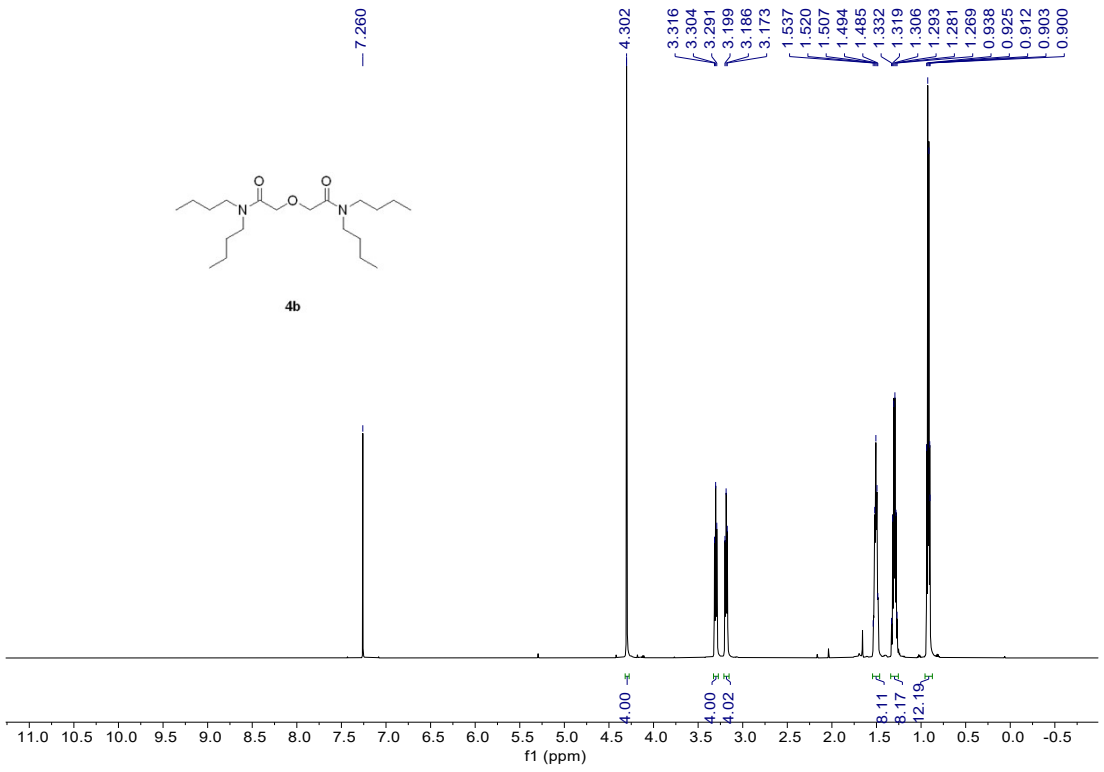


Figure S6. HRMS spectrum of compound **4a**.



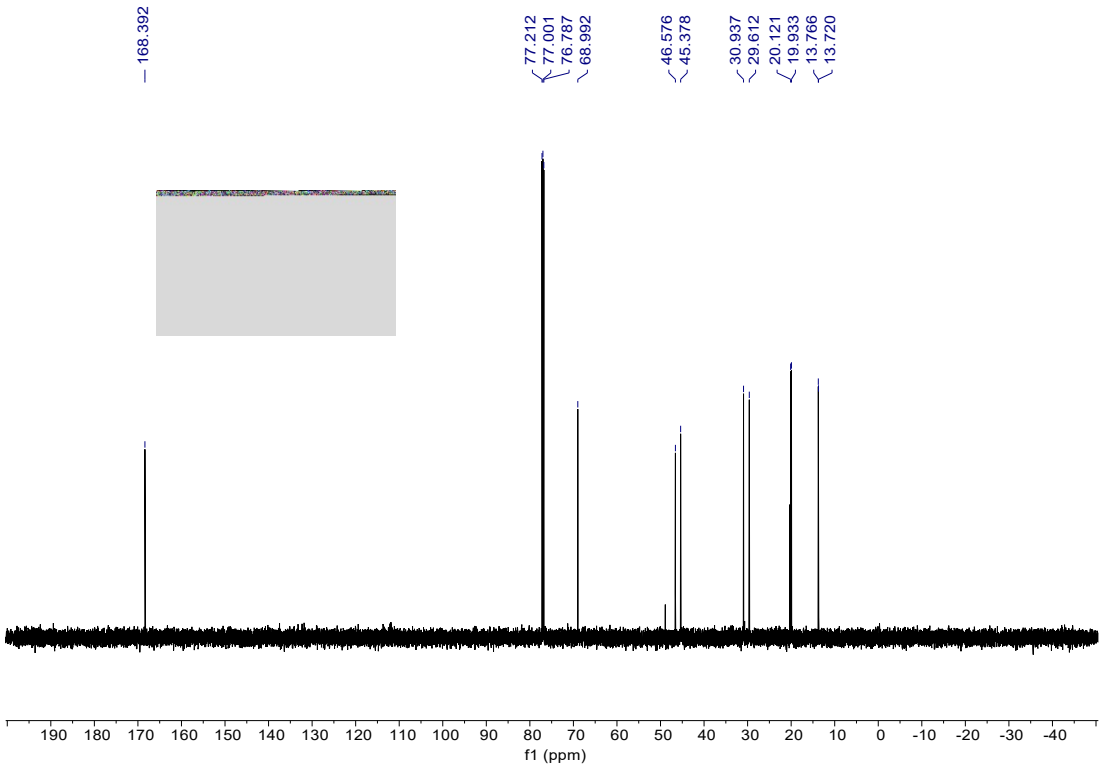


Figure S7. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **4b**.

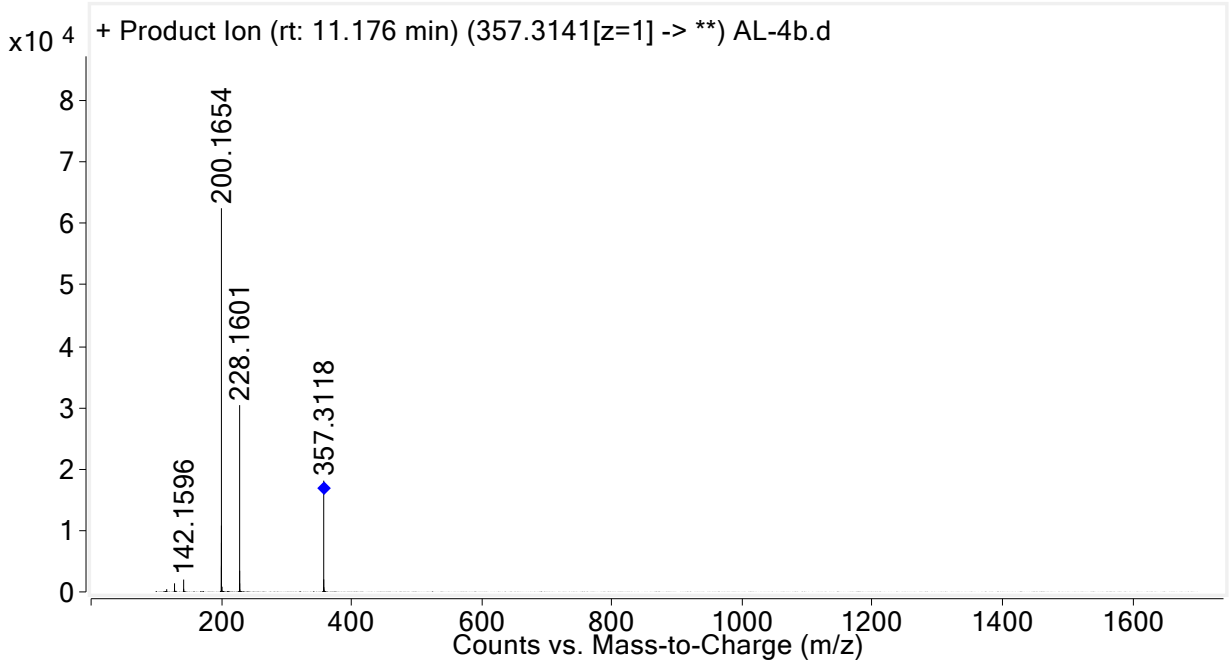


Figure S8. HRMS spectrum of compound **4b**.

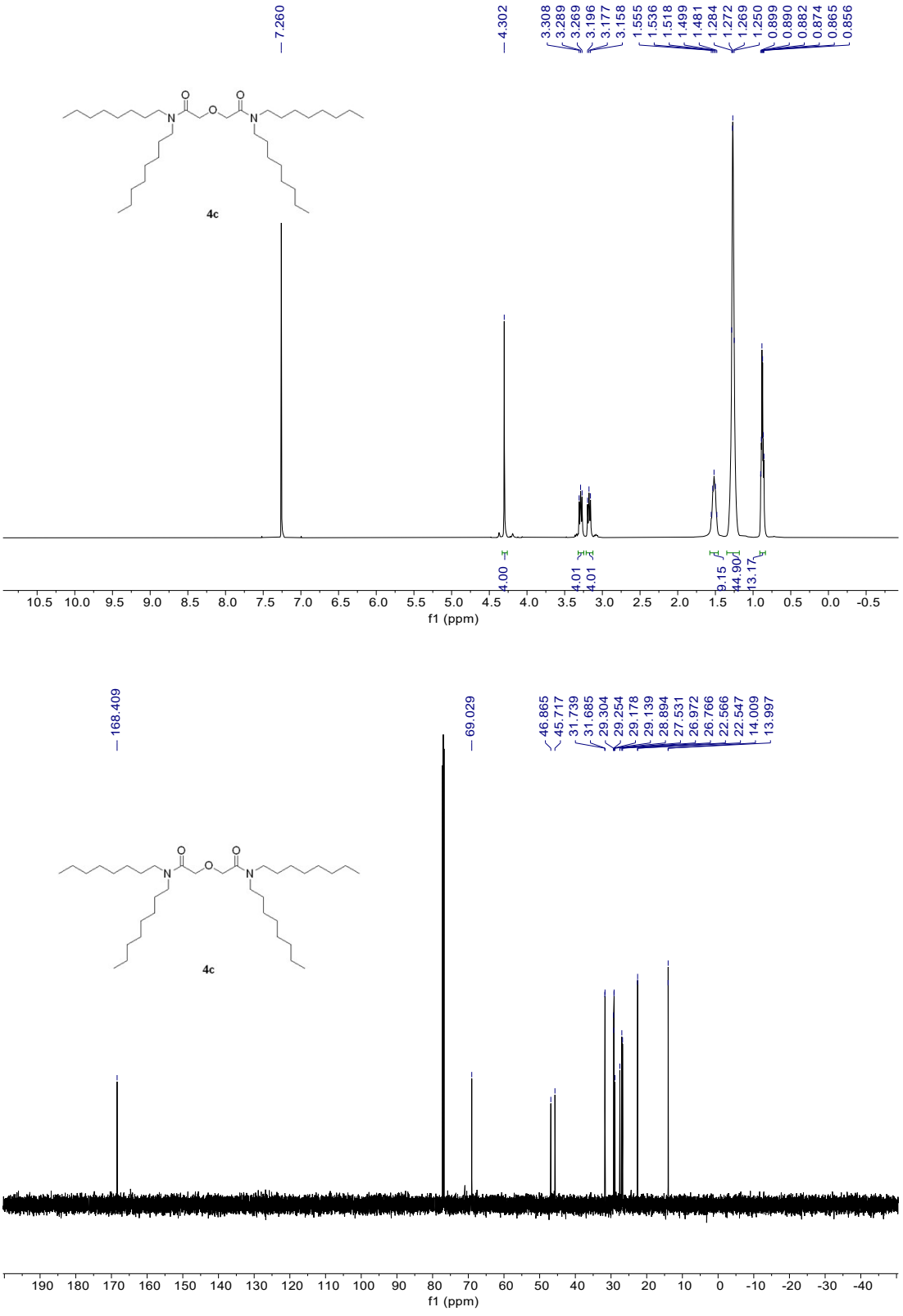


Figure S9. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **4c**.

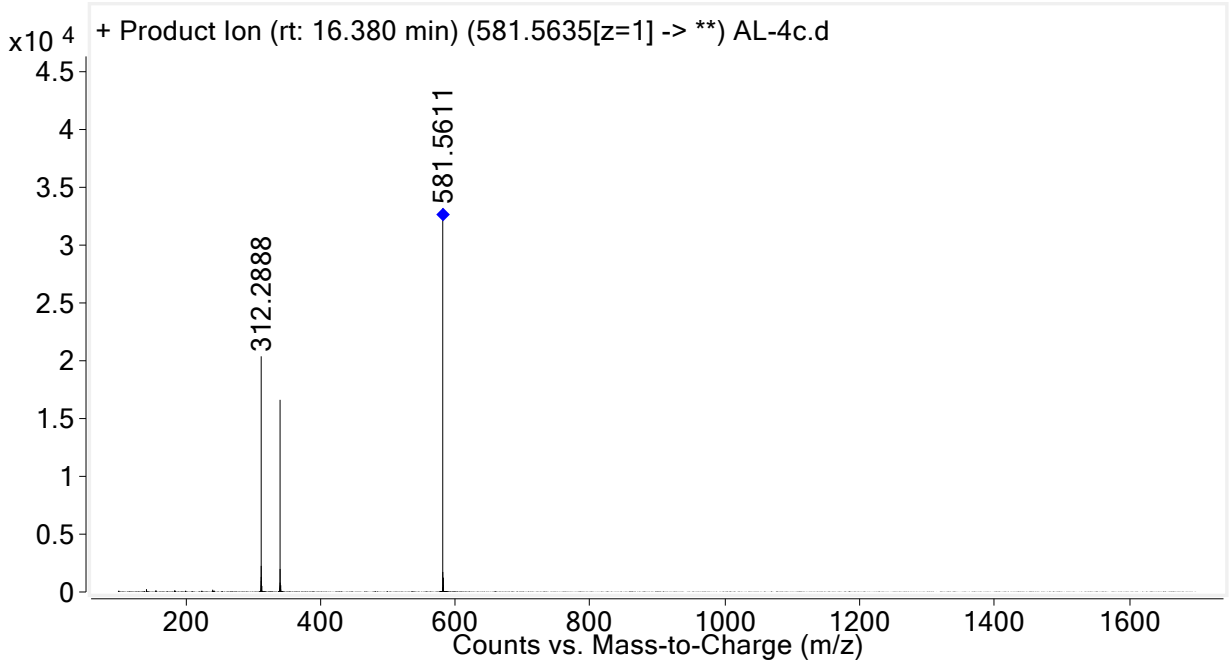
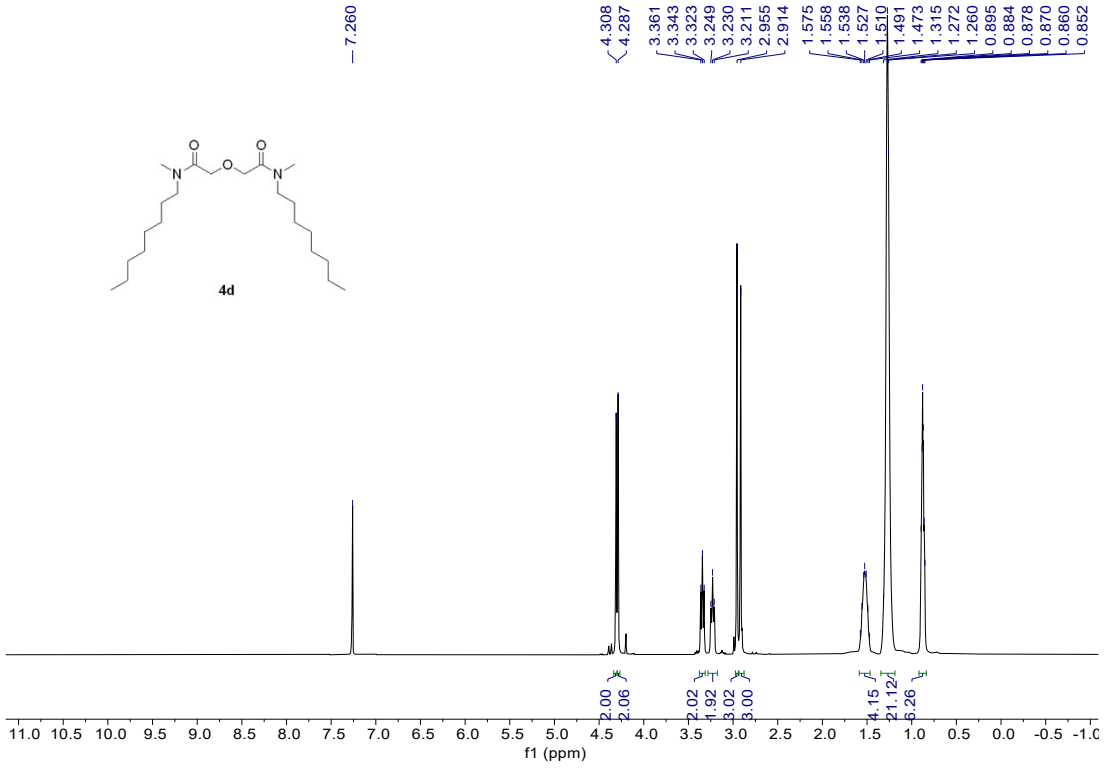


Figure S10. HRMS spectrum of compound **4c**.



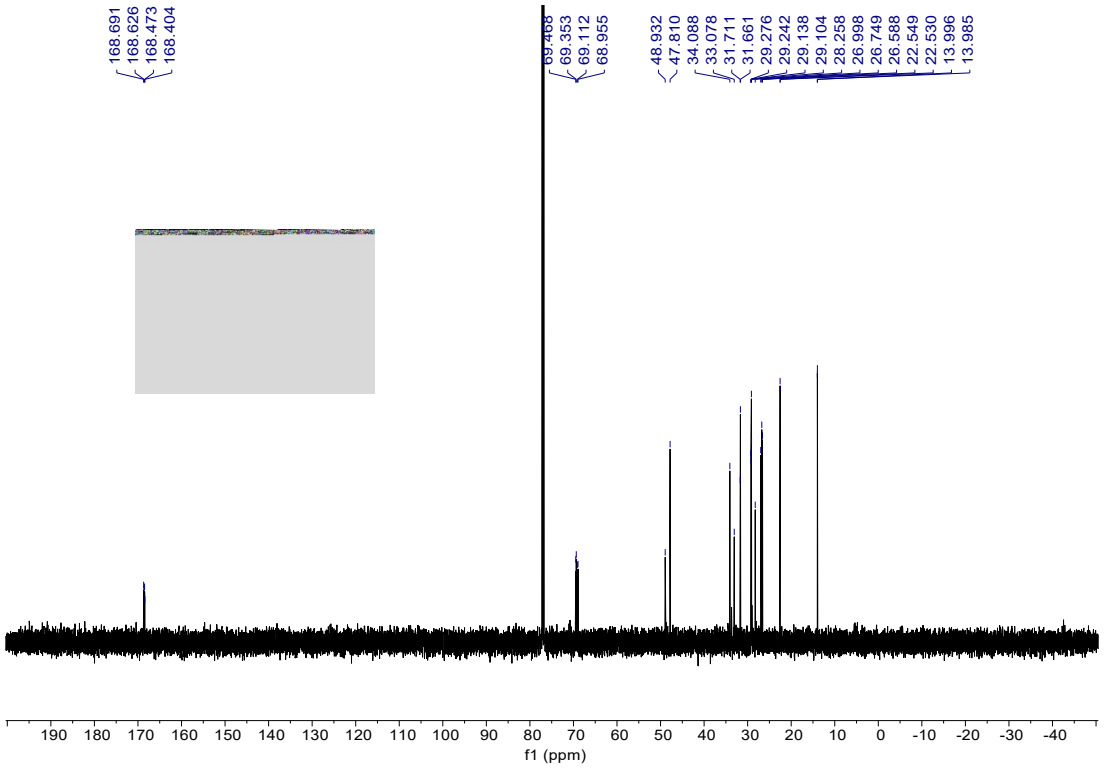


Figure S11. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **4d**.

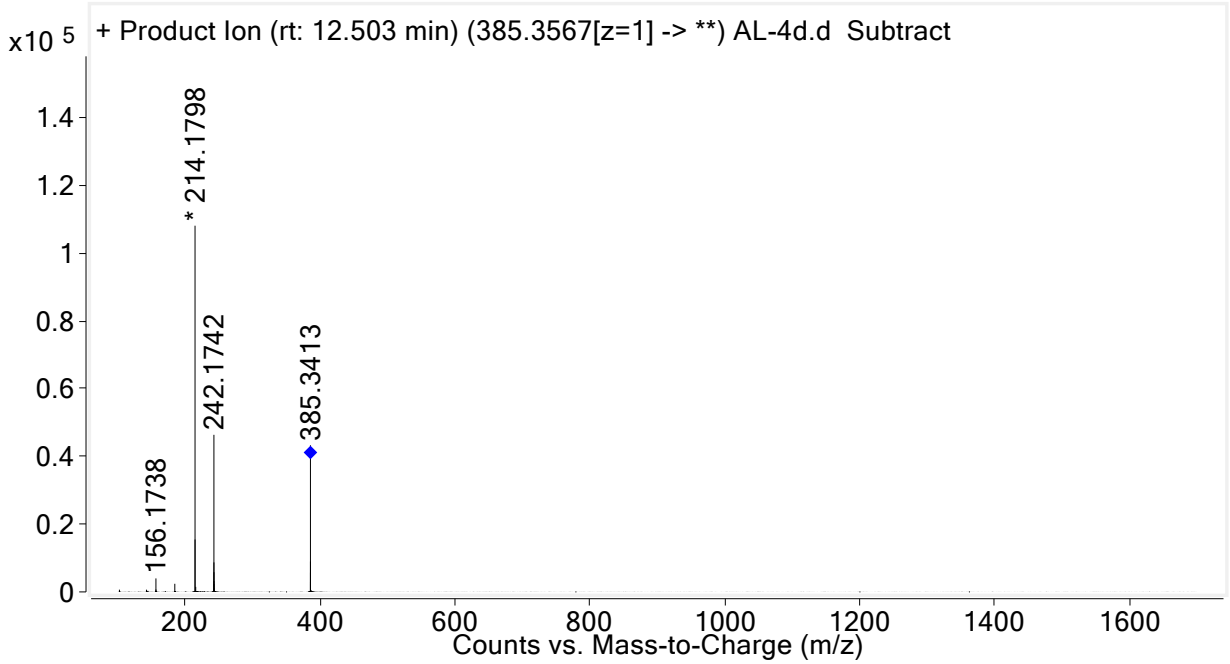


Figure S12. HRMS spectrum of compound **4d**.

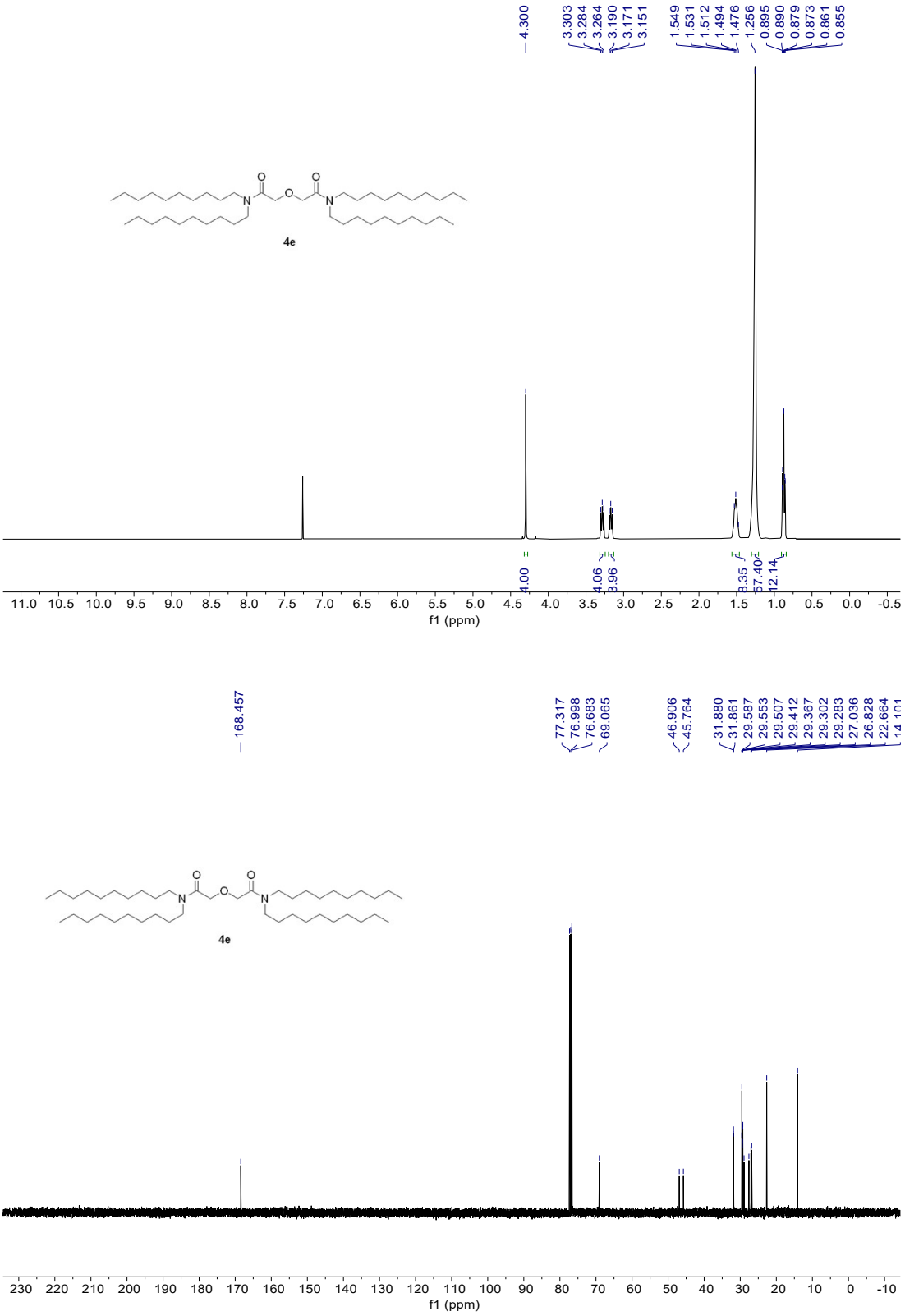


Figure S13. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **4e**.

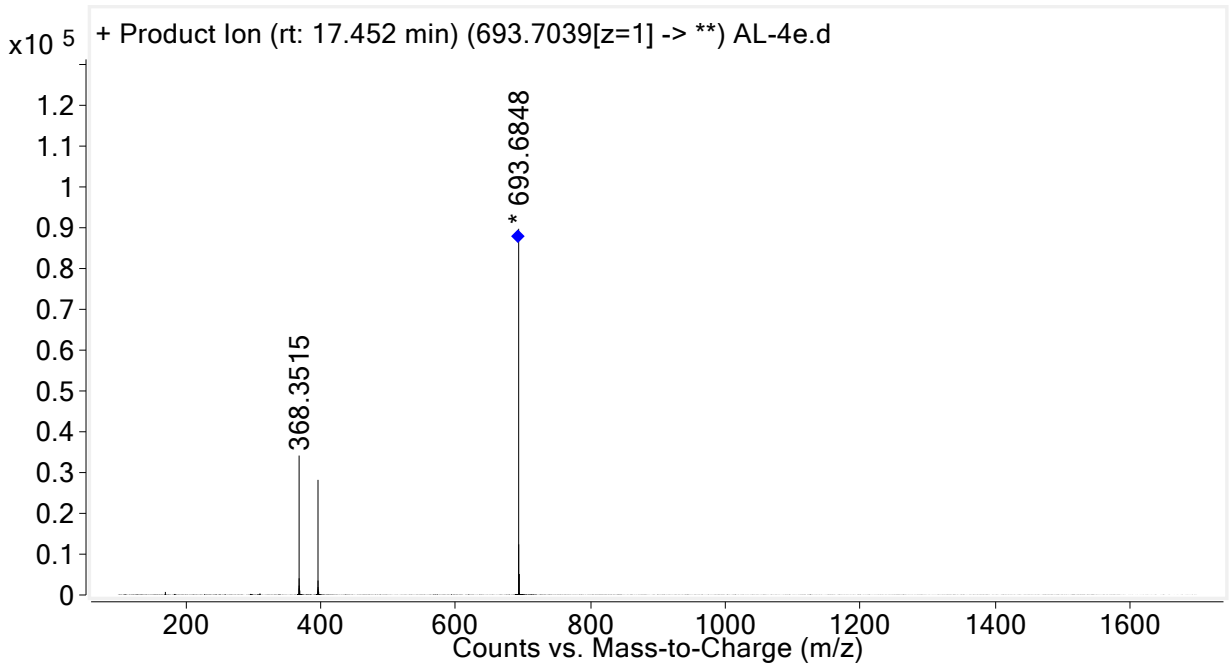
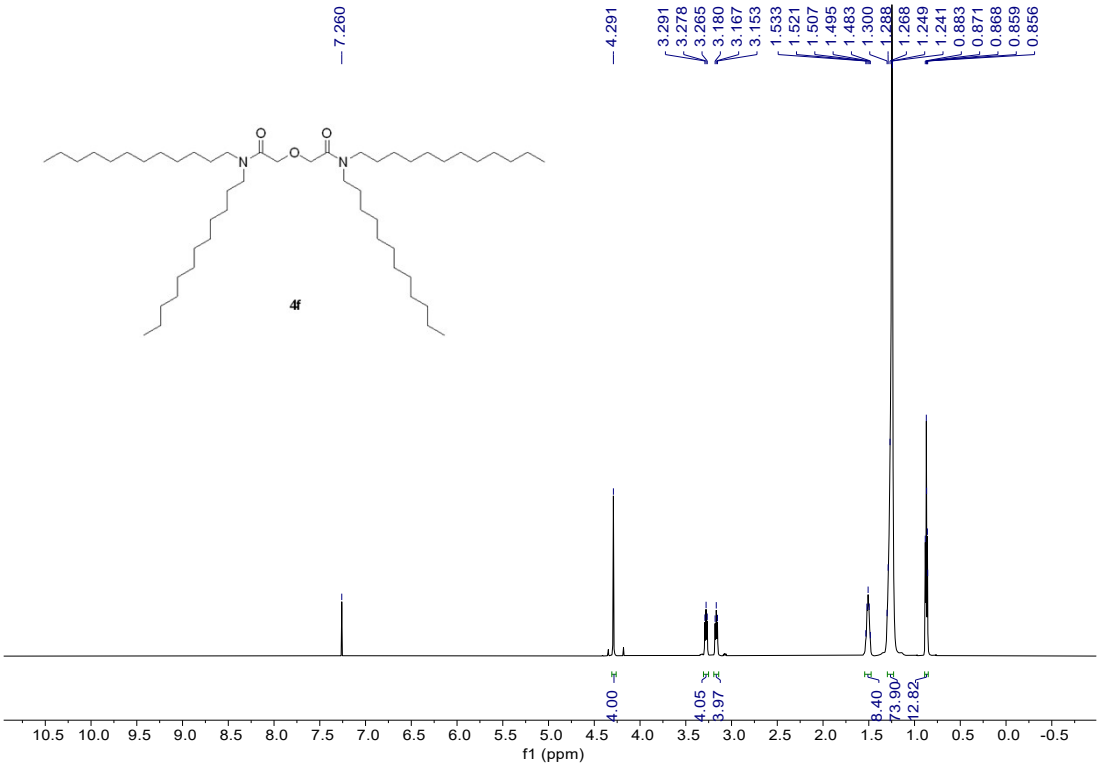


Figure S14. HRMS spectrum of compound **4e**.



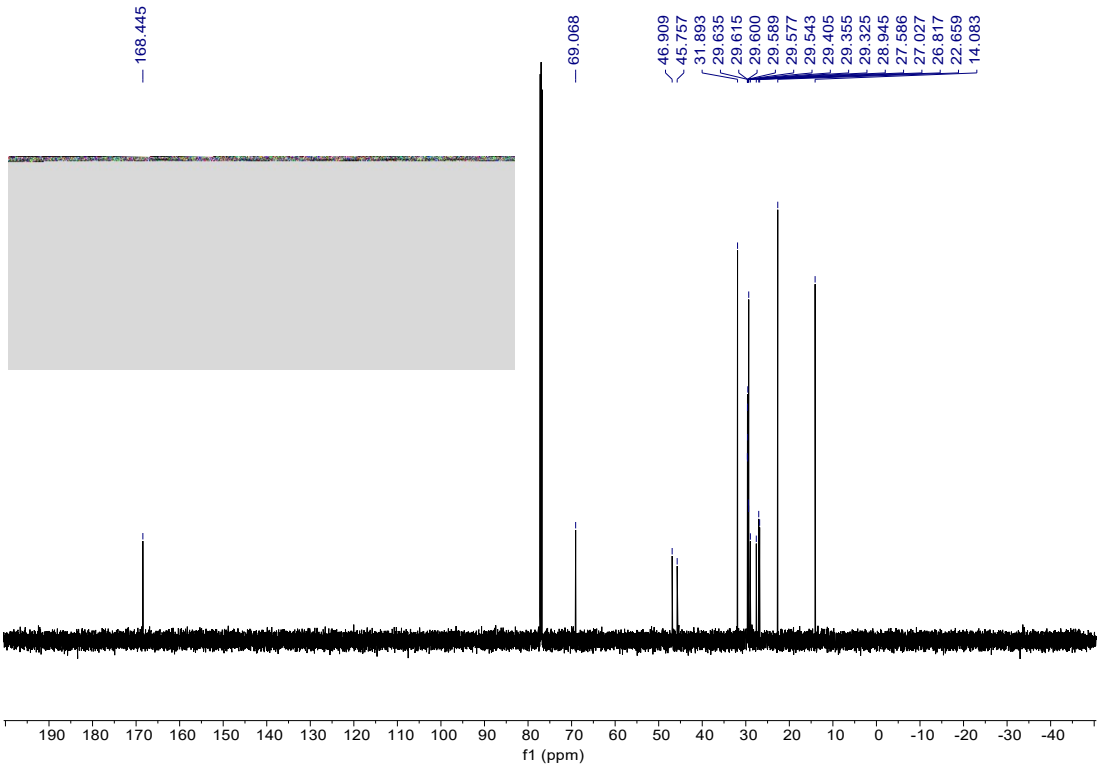


Figure S15. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **4f**.

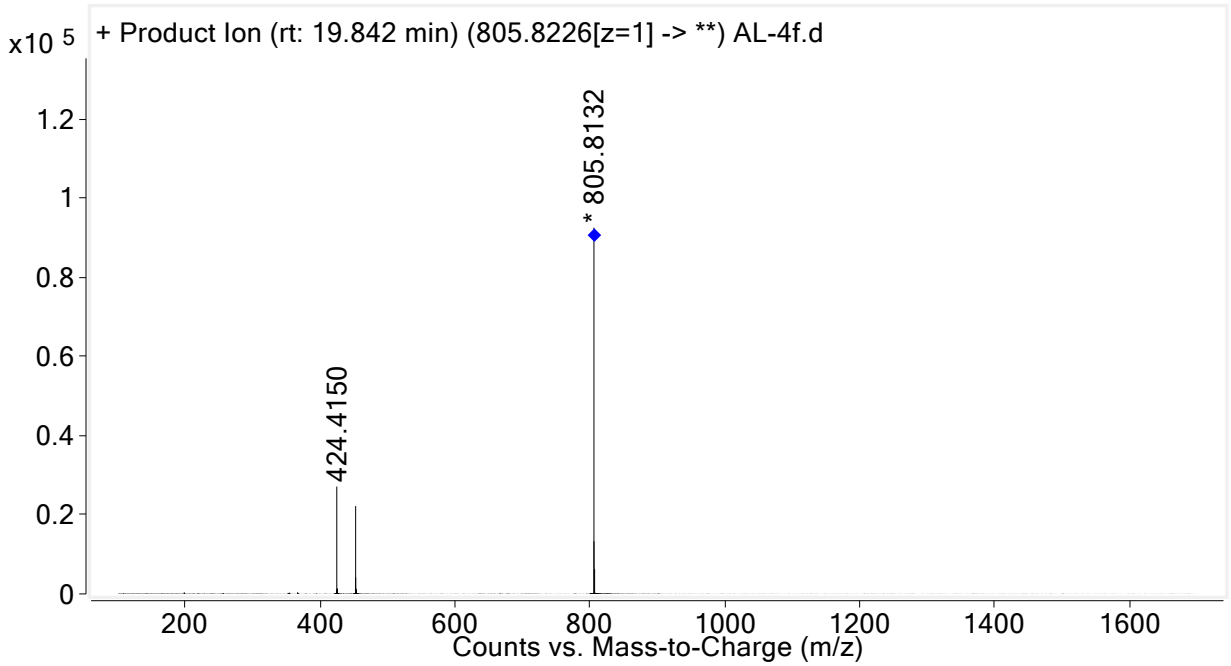


Figure S16. HRMS spectrum of compound **4f**.

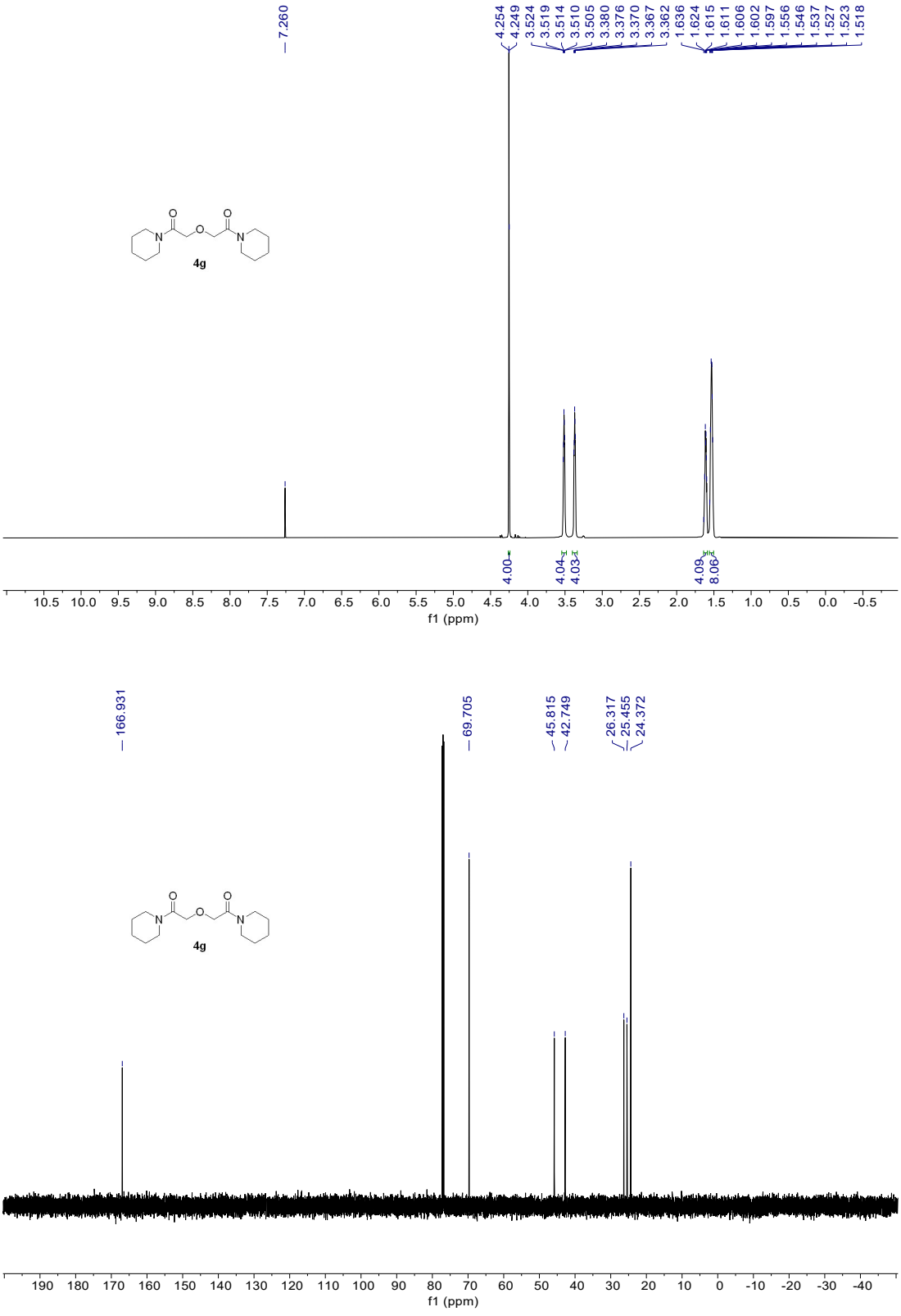


Figure S17. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **4f**.

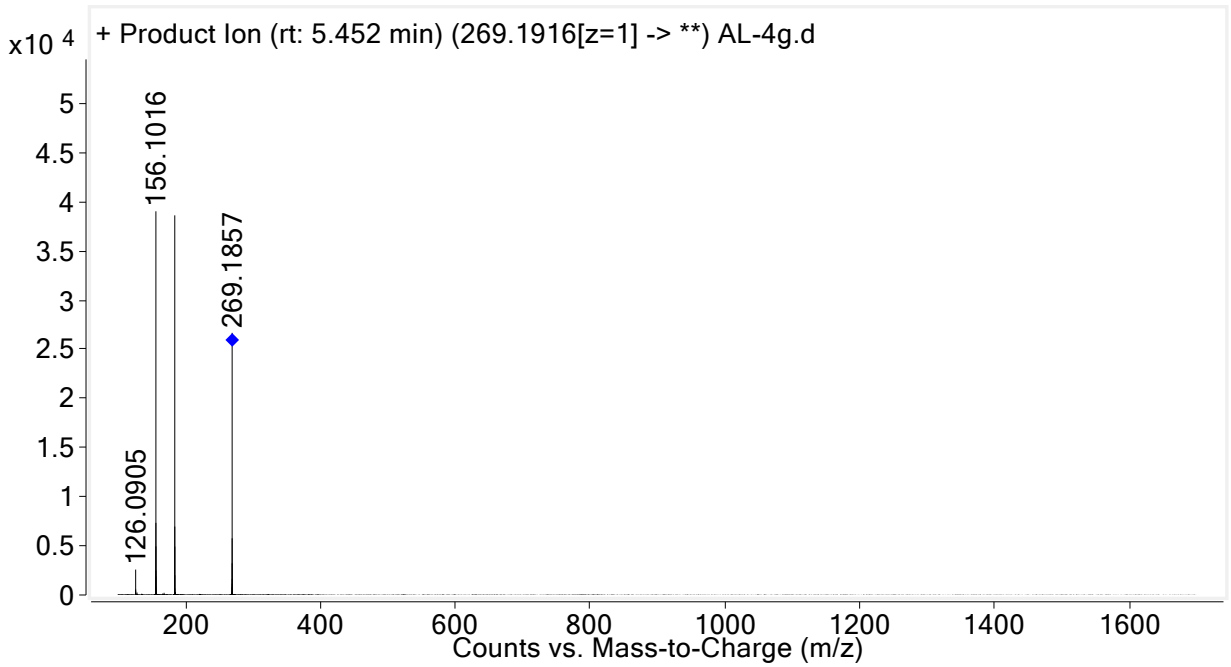
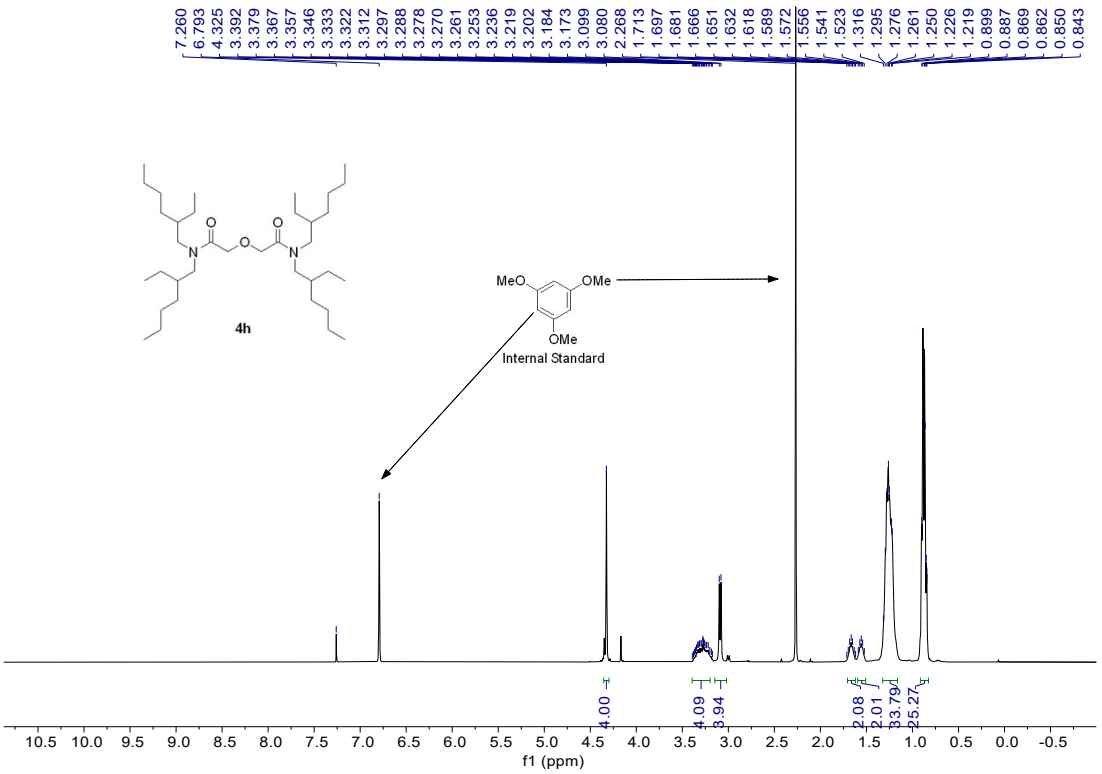


Figure S18. HRMS spectrum of compound **4g**.



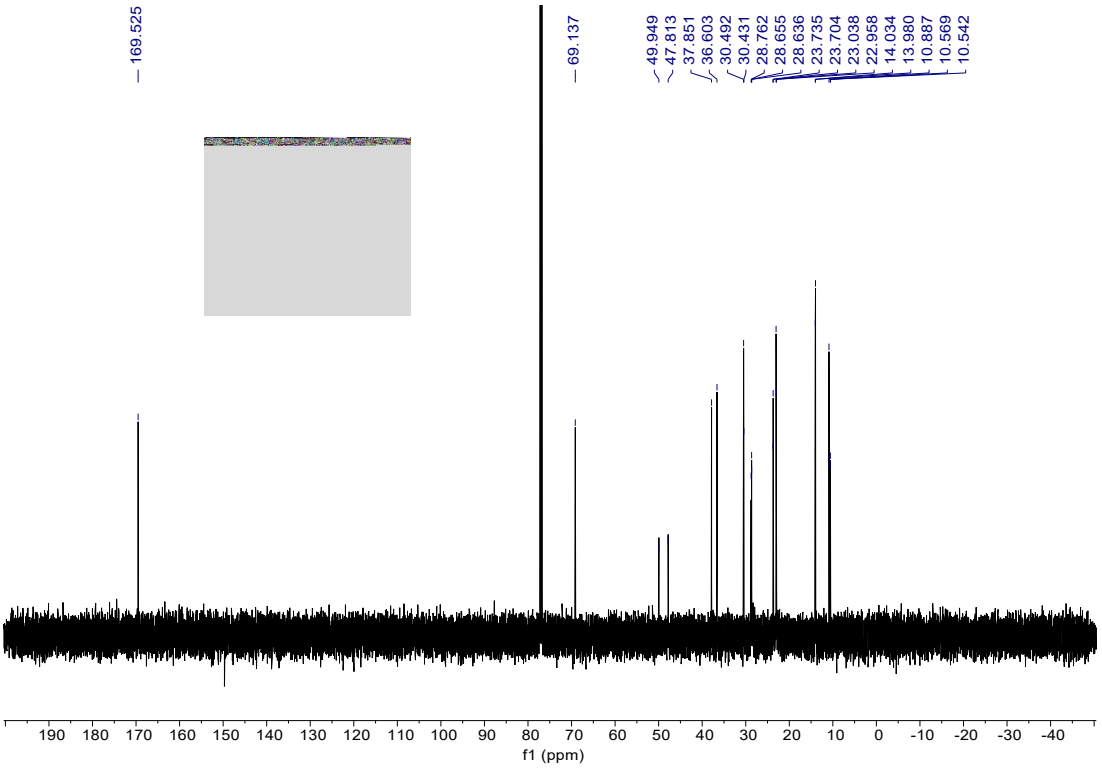


Figure S19. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **4h**.

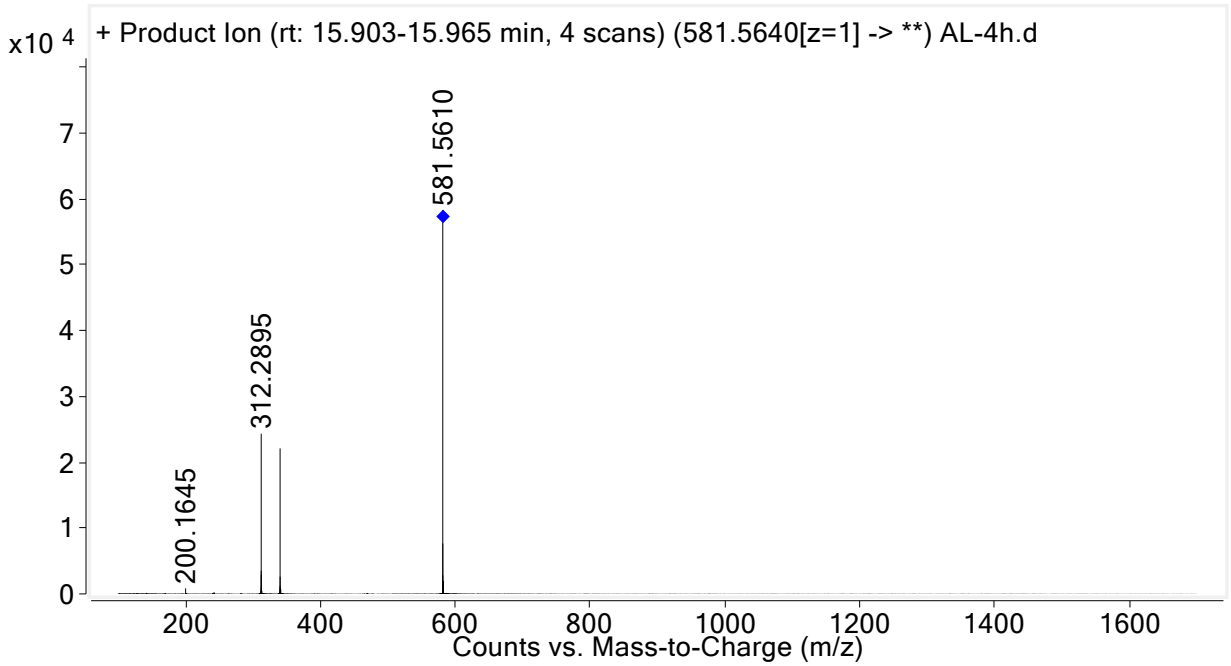


Figure S20. HRMS spectrum of compound **4h**.

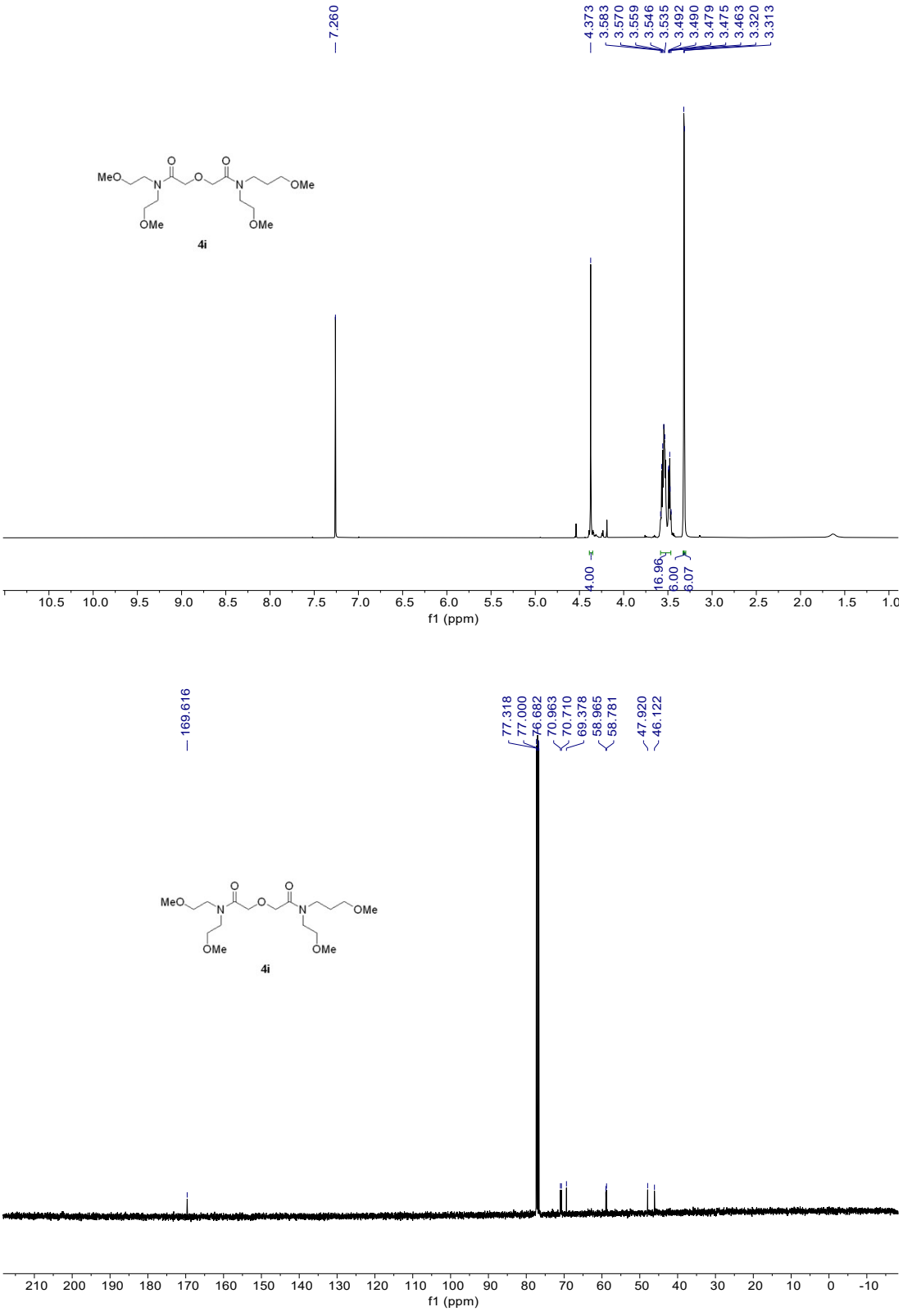


Figure S21. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **4i**.

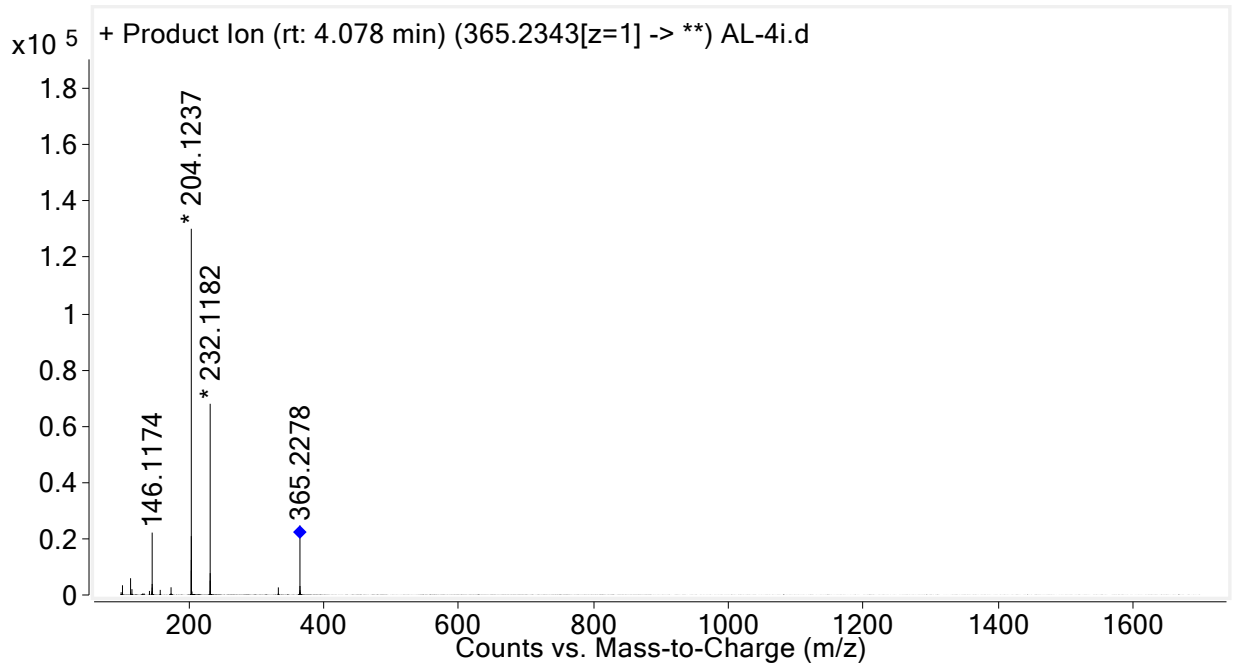


Figure S22. HRMS spectrum of compound **4i**.

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