Supplementary information for:

Sequence-defined peptoids via iterative exponential growth

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Table of Contents

1. Materials and Methods

Unless otherwise stated, all starting materials were purchased from commercial sources and used without further purification. Reactions run at room temperature were performed at 25 ºC.

1.1 Ultra-high-performance liquid chromatography

UHPLC analyses were performed on a PerkinElmer AltusTM A-30 UPLC system (equivalent to a Waters Acquity H-Class UHPLC instrument) with a C18 50 × 2.1 mm i.d., 1.7 µm column and an ultra-violet (UV) detector. Peptoid samples were analyzed using a flow rate of 0.5 mL/min, UV detection at 214 nm, injection volume of 2.5 µL, and a concentration of 0.5 mg/mL. Solvent A: 95:5 (v/v) water:acetonitrile, solvent B: acetonitrile. Method: Linear gradient of 0%-100% B in 12 minutes followed by 100% B for 8 minutes. Data acquisition and processing were conducted using Waters Empower 3 software.

1.2 Mass spectrometry

MALDI-TOF analyses were performed on a Bruker AutoFlex Speed MALDI-TOF mass spectrometer. All samples were analyzed using the conventional dried droplet method with a ground steel target using a 1:1 (v/v) mixture of peptoid (5 mg/mL in 1:1 acetonitrile:water) and 2,5-dihydroxybenzoic acid (DHB) matrix dissolved in 1:1 acetonitrile:water at 10 mg/mL. Scan mode: linear; ionization mode: positive. Red phosphorous was used as the calibrant. DART-MS analyses were performed on a JEOL AccuTOF Plus 4G (JMS-T100LP-4G model) time-of-flight mass spectrometer equipped with a DART ion source with positive ion polarity. ESI-MS analyses were performed on an Agilent 6538 UHD in positive ion mode.

1.3 Nuclear magnetic resonance spectrometry

Nuclear magnetic resonance (NMR) spectra were acquired on a 400 MHz Bruker Avance III NMR Spectrometer or a 500 MHz Agilent DD2 NMR spectrometer. 1D ^{1}H spectra were acquired using a zg45 or s2pul pulse sequence at 25 °C, a 1-10 s recycle delay, and 16-32 transients. 1D ^{13}C spectra were acquired using a zgpg35 or s2pul pulse sequence at 25 °C, a 0.2-1 s recycle delay, and 512-2000 transients. NMR Processing was carried out using MestreNova software (v 14. 3.0-30573). All ^{1}H-NMR spectra were Fourier transformed with 0.2222 Hz exponential line broadening (0.5000 Hz for ^{13}C NMR), phased, and then baseline corrected (some ^{13}C NMR were not baseline corrected to maintain the signal). Chemical shifts were referenced relative to residual solvent peaks ($CDCl_3$, $\delta(^{1}H)$ = 7.26 ppm, $\delta(^{13}C)$ = 77.16 ppm; CD_2Cl_2, $\delta(^{1}H)$ = 5.32 ppm, $\delta(^{13}C)$ = 53.84 ppm). Structural assignments were made as needed with gCOSY, gHSQC, and gHMBC experiments.

1.4 Recycling preparative gel permeation chromatography

Purification of peptoids was performed using a JAI LaboACE LC-7080 recycling preparative gel permeation chromatography (GPC) system equipped with JAIGEL-2.5HR and JAIGEL-3HR columns (20 mm i.d., 600 mm length) and dual UV and RI detectors using ACS reagent grade chloroform (contains 0.5-1.0% ethanol as stabilizer).

1.5 Circular dichroism spectroscopy

Circular dichroism spectroscopy was performed using a Jasco J-1100 circular dichroism spectropolarimeter with a range of 190-290 nm and equipped with a Peltier temperature-controlled cell holder and a PM-539 detector. The spectra were collected with 0.1 nm data intervals, continuous scanning mode, D.I.T. of 1 s, 4 accumulations, at 24.99 °C. Peptoids were dissolved in acetonitrile at a concentration of 60 µmol/L and run in 10 mm cuvettes with baseline correction. Data acquisition and processing were conducted using Jasco software.

1.6 Gel permeation chromatography

Size exclusion chromatography (SEC) analysis was performed using a Tosoh EcoSEC Ambient (Room Temperature)-GPC equipped with two TSK gel GPC columns connected in series (G3000Hhr and

G4000Hhr; 7.8 mm I.D. x 30 cm) and calibrated with a conventional calibration curve using Sigma-Aldrich monodisperse polystyrene standards ranging from 1.0 MDa to 500 Da. Dimethylformamide (DMF) with 0.1 wt% of Lithium Bromide (40 °C) was used as a carrier solvent at the flow rate of 1.0 mL/min. Samples were prepared at a concentration of around 1 mg/mL in DMF with 0.1% LiBr with a sample injection volume of 50 µL. Instrument equipped RI detector was used as the main source of peak detection, and peak analysis was conducted using EcoSEC Elite GPC System Workstation Software.

1.7 Conditions for the self-assembly of peptoid nanosheets

Cbz-Ndc_8-Nte_8-tBu peptoids were dissolved in 2:2:1:1 v/v tetrahydrofuran (THF)/water/acetonitrile (MeCN)/isopropyl alcohol (IPA) at a concentration of 1.3 mg/mL. The organic solvents were evaporated at room temperature over a period of 4 days, leaving behind the aqueous peptoid solution at a concentration of 4 mg/mL. The solutions turned opaque and cloudy, which is expected upon formation of nanosheets.

1.8 Transmission electron microscopy

TEM micrographs were obtained used a Hitachi HT7700 TEM with Dual-Mode objective lens, tungsten filament, and acceleration voltage of 60 kV. The nanosheet solution was diluted to 0.4 mg/mL and 0.2 mg/mL (diluted condition to image single nanosheets), deposited on commercially available "Carbon Film only on 400 mesh, copper" TEM grids (01844-F, Ted Pella) and "Ultrathin Carbon Type A, 400 mesh, copper" TEM grids (01822-F, TED Pella), and allowed to dry before imaging.

2. Synthetic and self-assembly protocols

Table S1. Summary of IEG cycle efficiencies for synthesized peptoids

Peptoid	Deprotection of Cbz	Deprotection of tBu	Coupling	Cycle Total	Cumulative Yield
Cbz-Ndc_2-tBu	-	-	90%	90.0%	90.0%
Cbz-Npe_2-tBu	-	-	90%	90.0%	90.0%
Cbz-Nte_2-tBu	-	-	81%	81.0%	81.0%
Cbz-Nme_2-tBu	-	-	96%	96.0%	96.0%
Cbz-Ndc_4-tBu	100%	93%	77%	72.0%	64.8%
Cbz-Npe_4-tBu	91%	88%	93%	74.5%	67.0%
Cbz-Nte_4-tBu	94%	74%	75%	52.2%	42.3%
Cbz-Nme_4-tBu	100%	76%	100%	76.0%	73.0%
Cbz-Ndc_8-tBu	94%	95%	98%	87.5%	56.7%
Cbz-Npe_8-tBu	92%	76%	57%	39.9%	26.7%
Cbz-Nte_8-tBu	98%	64%	45%	28.2%	11.9%
Cbz-Nme_8-tBu	93%	94%	88%	76.9%	56.1%
Cbz-Nme_{16}-tBu	99%	87%	62%	53.4%	30.0%
Cbz-Nme_{32}-tBu	15%	95%	7%	1.0%	0.3%
Cbz-Nme_4-Npe_4-tBu	92%	94%	47%	40.6%	19.9%
Cbz-Nme_4-Npe_{12}-tBu	96%	89%	26%	22.2%	4.4%

Cbz-Ndc_8-Nte_8-tBu	45%	94%	16%	6.8%	0.5%
Cbz-Nhx-Npe-tBu	-	-	89%	89.0%	89.0%
Cbz-Ndc-Nme-tBu	-	-	89%	89.0%	89.0%
Cbz-Nhx-Npe-Ndc-Nme-tBu	97%	71%	88%	60.6%	48.0%
Cbz-(Nhx-Npe-Ndc-$Nme)_2$-tBu	78%	81%	88%	55.6%	26.7%
Cbz-(Nhx-Npe-Ndc-$Nme)_4$-tBu	91%	84%	67%	51.2%	13.7%
Cbz-Nme_4-Npe_4-(Nhx-Npe-Ndc-$Nme)_2$-tBu	91%	89%	67%	54.3%	2.9%
Cbz-Nme-Nrpe-tBu	-	-	74%	74.0%	74.0%
Cbz-Nme-Nspe-tBu	-	-	80%	80.0%	80.0%
Cbz-(Nme-$Nrpe)_2$-tBu	90%	98%	62%	54.7%	40.5%
Cbz-(Nme-$Nspe)_2$-tBu	93%	71%	51%	33.7%	26.9%
Cbz-(Nme-$Nrpe)_4$-tBu	95%	92%	47%	41.1%	16.6%
Cbz-(Nme-$Nspe)_4$-tBu	85%	70%	15%	8.9%	2.4%
Cbz-(Nme-$Nrpe)_4$-(Nme-$Nspe)_4$-tBu	95%	89%	30%	25.4%	0.1%
Cbz-Npe_4-Nall-tBu	-	76%	64%	48.6%	32.6%
Cbz-Npe_4-Nalk-tBu	-	76%	53%	40.3%	27.0%
Cbz-Npe_4-Nalk-Npe_2-tBu	91%	100%	59%	53.7%	14.5%

(Note: yield calculations do not include the steps to obtain the singly protected monomers).

2.1 General procedure for the synthesis of the *tert*-butyl ester protected peptoid monomers

A solution of the amine in tetrahydrofuran (THF; 0.6-0.7 M) was prepared in a round-bottomed flask and 1.9 equiv. of triethylamine was added. The reaction mixture was stirred on an ice bath. 1.0 equiv. of *tert*-butyl bromoacetate was added dropwise and the reaction was allowed to slowly warm to room temperature. Once TLC analysis indicated full consumption of the starting amine (4 hours to overnight), the reaction was filtered (if salt was present), concentrated, and purified by column chromatography.

2.2 General procedure for the Cbz protection of peptoid monomers

Under an atmosphere of N_2, a round-bottomed flask containing a solution of the tert-butyl ester peptoid in dry dichloromethane (DCM; 0.2-0.3 M) and 2 equiv. of triethylamine was placed in an ice bath. The benzyl chloroformate (1.2 equiv.) was added to the reaction vessel slowly. The ice bath was removed, and the mixture was stirred at room temperature overnight. Once TLC analysis indicated full consumption of the starting peptoid (ninhydrin stain for the secondary amine), the reaction mixture was quenched with water and extracted with DCM. The organic layer was separated, washed with 0.1M $NaHCO_3$ solution and brine, dried with $MgSO_4$, concentrated, and purified by column chromatography.

2.3 General procedure for the *tert*-butyl ester deprotection of peptoids

A solution of the *tert*-butyl ester protected peptoid in dichloromethane (DCM; 0.4-0.5M) was cooled in an ice bath and an equal volume of trifluoroacetic acid was added slowly. The reaction mixture was stirred in an ice bath until TLC analysis indicated full consumption of the starting material. The reaction mixture was quenched with a 0.1M $NaHCO_3$ solution and diluted with DCM. The organic layer was separated and washed with 0.1M $NaHCO_3$ and brine. The aqueous layers were extracted with DCM and the organic layers combined, dried with $MgSO_4$, concentrated, and purified by column chromatography.

2.3 General procedure for the Cbz deprotection of peptoids

A solution of the Cbz protected peptoid in ethanol (EtOH; 0.1-0.2M) and 10% Pd/C ((8-10% by weight) was prepared and triethylsilane (4 equiv.) was added dropwise under N_2 atmosphere. The reaction mixture was stirred at room temperature overnight. Once TLC analysis indicated full conversion of the starting peptoid (ninhydrin stain for the secondary amine), the reaction mixture was filtered through a celite plug, concentrated, and purified by a short silica plug to remove excess triethylsilane.

2.4 General procedure for the amide coupling of peptoids

To a solution of 1 equiv. of the Cbz protected peptoid and 1 equiv. of the tert-butyl ester protected peptoid in DCM or N,N-dimethylformamide (DMF) (0.08-0.1M) was added 1 equiv. of PyBop (benzotriazol-1-yloxytripyrrolidinophosphonium hexafluorophosphate) and 1 equiv. of DIEA (N,N-diisopropylethylamine). The reaction mixture was stirred at room temperature or at 45 °C until TLC analysis indicated completion (1-3 days). The reaction mixture was then quenched by the addition of water, extracted with DCM, dried with $MgSO_4$, concentrated, and purified by column chromatography or recycling preparative gel permeation chromatography.

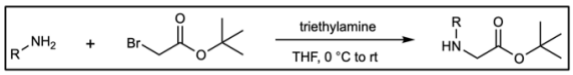
2.5 Self-assembly and TEM imaging of Cbz-Ndc_8-Nte_8-tBu

Cbz-Ndc_8-Nte_8-tBu peptoids were dissolved in 2:2:1:1 v/v tetrahydrofuran (THF) /water/acetonitrile (MeCN) /isopropyl alcohol (IPA) at a concentration of 1.3 mg/mL. The organic solvents were evaporated at room temperature, over a period of 4 days, leaving behind the aqueous peptoid solution at a concentration of 4 mg/mL. The solutions turned opaque and cloudy, which is expected upon formation of nanosheets. TEM micrographs were obtained used a Hitachi HT7700 TEM with Dual-Mode objective lens, tungsten filament, and acceleration voltage of 60 kV. The nanosheet solution was diluted to 0.4 mg/mL and 0.2 mg/mL (diluted condition to image single nanosheets), deposited on commercially available “Carbon Film only on 400 mesh, copper” TEM grids (01844-F, Ted Pella) and “Ultrathin Carbon Type A, 400 mesh, copper” TEM grids (01822-F, TED Pella), and allowed to dry before imaging.

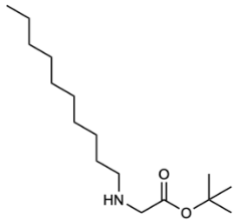
3. Characterization of the synthesized peptoids

3.1 Peptoid homopolymers

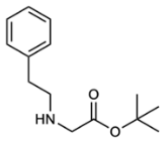
3.1.1 *tert*-butyl ester protection of peptoid monomers



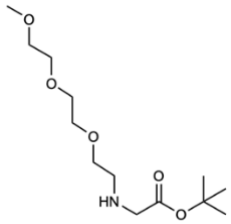
Scheme 1



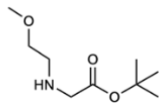
Ndc-tBu (1a): Synthesized from N-decylamine using the general procedure for the synthesis of *tert*-butyl ester protected peptoid monomers, purified by column chromatography (5% EtOAc in hexanes and then increased to 100% EtOAc), pale yellow oil, 11.265 g, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.26 (s, 2H), 2.59 – 2.51 (m, 2H), 1.57 (s, 1H), 1.44 (s, 11H), 1.34 – 1.19 (m, 14H), 0.90 – 0.80 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 81.1, 52.0, 49.7, 32.0, 30.3, 29.7 – 29.6 (m), 29.4, 28.2, 27.4, 22.8, 14.2. ESI-MS $[M+H]^+$ calculated m/z = 272.3; observed m/z = 272.3.



Npe-tBu (1b): Synthesized from phenethylamine using the general procedure for the synthesis of *tert*-butyl ester protected peptoid monomers, purified by column chromatography (5% EtOAc in hexanes and then increased to 100% EtOAc), yellow oil, 11.521 g, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.16 (m, 5H), 3.31 (s, 2H), 2.92 – 2.84 (m, 2H), 2.83 – 2.78 (m, 2H), 1.66 (s, 1H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 139.9, 126.3, 81.2, 51.9, 50.9, 36.7, 28.2. DART-MS $[M+H]^+$ calculated m/z = 236.2; observed m/z = 236.2.

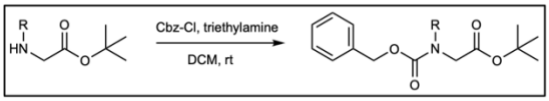


Nte-tBu (1c): Synthesized from 2-(2-(2-methoxyethoxy)ethoxy)ethanamine using the general procedure for the synthesis of *tert*-butyl ester protected peptoid monomers, purified by column chromatography (100% EtOAc and then increased to 10% MeOH in EtOAc), pale yellow oil, 2.205 g, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 – 3.48 (m, 10H), 3.34 (s, 3H), 3.29 (s, 2H), 2.76 (dd, J = 5.7, 4.9 Hz, 2H), 2.03 (s, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 81.3, 72.0, 70.7, 70.7, 70.6, 70.4, 59.1, 51.7, 48.8, 28.2. DART-MS $[M+H]^+$ calculated m/z = 278.2; observed m/z = 278.2.

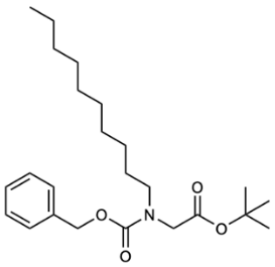


Nme-tBu (1d): Synthesized from 2-methoxyethylamine using the general procedure for the synthesis of *tert*-butyl ester protected peptoid monomers, purified by column chromatography (10% EtOAc in hexanes and then increased to 100% EtOAc), pale yellow oil, 4.257 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.44 – 3.37 (m, 2H), 3.28 (s, 3H), 3.24 (s, 2H), 2.74 – 2.66 (m, 2H), 1.83 (s, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 81.0, 72.1, 58.7, 51.7, 48.7, 28.1. DART-MS $[M+H]^+$ calculated m/z = 190.1; observed m/z = 190.1

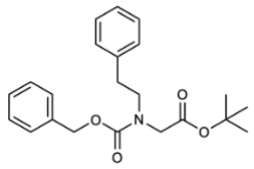
3.1.2 Cbz protection of peptoid monomers



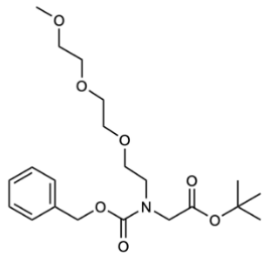
Scheme 2



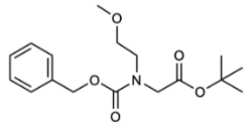
Cbz-Ndc-tBu (2a): Synthesized from Ndc-tBu (1a) using the general procedure for the Cbz protection of peptoid monomers, purified by column chromatography (100% hexanes and then increased to 10% EtOAc in hexanes), pale yellow oil, 11.5617 g, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 5H), 5.14 (d, *J* = 15.6 Hz, 2H), 3.87 (d, *J* = 26.9 Hz, 2H), 3.31 (dt, *J* = 12.4, 7.3 Hz, 2H), 1.59 – 1.48 (m, 2H), 1.42 (d, *J* = 27.0 Hz, 9H), 1.34 – 1.19 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.01, 156.63, 156.07, 136.90, 136.82, 128.51, 128.46, 127.97, 127.95, 127.86, 81.68, 67.34, 67.21, 49.92, 49.80, 49.13, 48.30, 31.98, 29.67, 29.64, 29.50, 29.41, 29.40, 28.47, 28.17, 28.15, 28.06, 26.88, 26.83, 22.77, 14.20. Note: unusual splitting patterns observed due to rotamers from the two end groups. DART-MS $[M+Na]^+$ calculated m/z = 428.3; observed m/z = 428.3



Cbz-Npe-tBu (2b): Synthesized from Npe-tBu (1b) using the general procedure for the Cbz protection of peptoid monomers, purified by column chromatography (100% hexanes and then increased to 10% EtOAc in hexanes), pale yellow oil, 13.6804 g, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.07 (m, 10H), 5.16 (d, *J* = 1.3 Hz, 2H), 3.80 (d, *J* = 29.9 Hz, 2H), 3.62 – 3.51 (m, 2H), 2.87 (dt, *J* = 23.2, 7.8 Hz, 2H), 1.43 (d, *J* = 27.5 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.92, 156.46, 155.94, 139.07, 138.94, 136.70, 128.92, 128.86, 128.63, 128.58, 128.50, 128.10, 128.03, 127.96, 127.87, 126.51, 126.45, 81.84, 67.53, 67.32, 51.11, 50.54, 50.47, 50.24, 35.21, 34.69, 28.17, 28.06. Note: unusual splitting patterns observed due to rotamers from the two end groups.

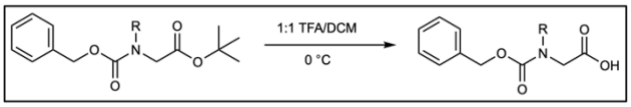


Cbz-Nte-tBu (2c): Synthesized from Nte-tBu (1c) using the general procedure for the Cbz protection of peptoid monomers, purified by column chromatography (100% hexanes and then increased to 100% EtOAc), pale yellow oil, 1.515 g, 88% yield. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.39 – 7.25 (m, 5H), 5.11 (d, *J* = 17.3 Hz, 2H), 3.98 (d, *J* = 4.8 Hz, 2H), 3.64 – 3.45 (m, 12H), 3.33 (d, *J* = 0.9 Hz, 3H), 1.42 (d, *J* = 19.2 Hz, 9H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.41, 169.36, 156.36, 137.37, 137.29, 128.81, 128.72, 128.29, 128.20, 128.11, 127.98, 81.68, 72.31, 70.92, 70.85, 70.81, 70.37, 70.33, 67.55, 67.41, 59.01, 51.11, 50.99, 48.81, 48.17, 28.20, 28.14. Note: unusual splitting patterns observed due to rotamers from the two end groups.

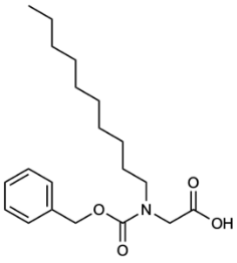


Cbz-Nme-tBu (2d): Synthesized from Nme-tBu (1d) using the general procedure for the Cbz protection of peptoid monomers, purified by column chromatography (100% hexanes and then increased to 20% EtOAc), pale yellow oil, 18.003 g, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H), 5.14 (d, J = 15.6 Hz, 2H), 3.99 (d, J = 20.7 Hz, 2H), 3.54 (s, 2H), 3.52 – 3.46 (m, 2H), 3.30 (d, J = 10.0 Hz, 3H), 1.43 (d, J = 24.2 Hz, 10H). ^{13}C NMR (101 MHz, $CDCl_3$-insert) δ 169.09, 128.60, 128.51, 128.02, 127.98, 127.88, 81.52, 71.94, 71.88, 67.55, 67.42, 58.95, 50.95, 48.76, 48.02, 28.23, 28.13. Note: unusual splitting patterns observed due to rotamers from the two end groups. DART-MS $[M+H]^+$ calculated m/z =324.2; observed m/z =324.2.

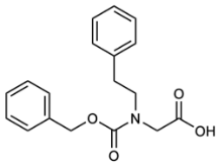
3.1.3 *tert*-butyl deprotection of peptoid monomers



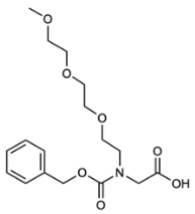
Scheme 3



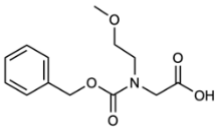
Cbz-Ndc (3a): Synthesized from Cbz-Ndc-tBu (2a) using the general procedure for *tert*-butyl ester deprotection of peptoids, pale yellow oil, 10.260 g, 84% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.69 – 7.50 (m, 2H), 7.42 – 7.27 (m, 5H), 5.16 (d, J = 19.8 Hz, 2H), 4.03 (d, J = 4.5 Hz, 2H), 3.38 – 3.31 (m, 2H), 1.55 (p, J = 7.1 Hz, 2H), 1.37 – 1.23 (m, 14H), 0.92 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 174.14, 173.83, 156.94, 156.05, 136.71, 136.60, 128.46, 128.43, 128.38, 128.34, 128.19, 127.97, 127.89, 127.86, 127.70, 127.65, 127.57, 67.56, 67.31, 48.99, 48.75, 48.40, 31.92, 29.63, 29.57, 29.41, 29.34, 29.31, 28.24, 27.85, 26.72, 26.68, 22.71, 13.92. Note: unusual splitting patterns observed due to rotamers from the two end groups. DART-MS $[M+H]^+$ calculated m/z =372.2; observed m/z =372.2.



Cbz-Npe (3b): Synthesized from Cbz-Npe-tBu (2b) using the general procedure for *tert*-butyl ester deprotection of peptoids, white solid, 10.170 g, 89% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.44 – 7.07 (m, 11H), 5.12 (s, 2H), 3.92 (d, J = 7.2 Hz, 2H), 3.55 (q, J = 7.6 Hz, 2H), 2.85 (dt, J = 14.9, 7.6 Hz, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 175.06, 174.76, 157.07, 156.10, 139.32, 139.15, 137.08, 136.92, 129.19, 129.16, 128.89, 128.86, 128.79, 128.42, 128.30, 128.16, 127.96, 126.80, 126.74, 68.02, 67.69, 51.05, 50.67, 49.99, 49.47, 35.31, 34.71. Note: unusual splitting patterns observed due to rotamers from the two end groups. DART-MS $[M+H]^+$ calculated m/z =314.1; observed m/z =314.1.

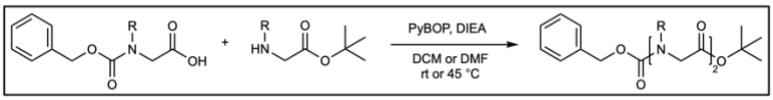


Cbz-Nte (3c): Synthesized from Cbz-Nte-tBu (2c) using the general procedure for *tert*-butyl ester deprotection of peptoids, clear oil, 0.935 g, 73% yield. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.44 – 7.25 (m, 5H), 5.14 (d, *J* = 13.5 Hz, 2H), 4.08 (d, *J* = 8.2 Hz, 2H), 3.64 – 3.49 (m, 12H), 3.38 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 171.83, 137.28, 128.84, 128.75, 128.36, 128.21, 128.16, 127.93, 72.58, 72.49, 70.81, 70.69, 70.59, 70.52, 70.13, 69.99, 67.79, 67.59, 58.84, 51.09, 50.94, 49.59, 49.03. Note: unusual splitting patterns observed due to rotamers from the two end groups.

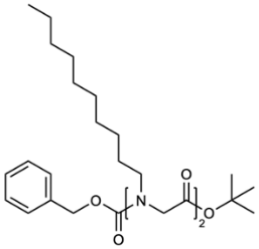


Cbz-Nme (3d): Synthesized from Cbz-Nme-tBu (2d) using the general procedure for *tert*-butyl ester deprotection of peptoids, pale yellow oil, 9.674 g, 92% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 11.02 (s, 1H), 7.43 – 7.28 (m, 5H), 5.18 (d, *J* = 19.3 Hz, 2H), 4.17 (d, *J* = 9.3 Hz, 2H), 3.61 – 3.51 (m, 4H), 3.32 (d, *J* = 9.3 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 174.39, 174.33, 156.89, 156.48, 136.88, 136.86, 129.21, 129.06, 128.86, 128.79, 128.58, 128.45, 128.35, 128.17, 127.98, 127.43, 72.44, 71.83, 71.74, 68.61, 68.08, 67.94, 67.28, 66.68, 58.84, 58.79, 54.24, 50.54, 50.45, 48.99, 48.42. Note: unusual splitting patterns observed due to rotamers from the two end groups. DART-MS $[M+H]^+$ calculated m/z =268.1; observed m/z =268.1.

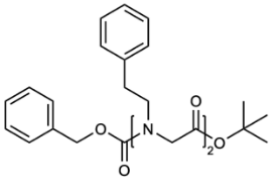
3.1.4 Synthesis of dimers



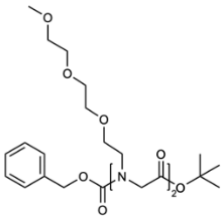
Scheme 4



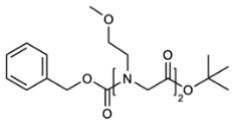
Cbz-Ndc$_2$-tBu (4a): Synthesized from Cbz-Ndc (3a) and Ndc-tBu (1a) using the general procedure for the amide coupling (DCM, rt, 8 hr), pale yellow oil, 1.415 g, 90% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.38 – 7.26 (m, 5H), 5.20 – 4.99 (m, 2H), 4.17 – 3.74 (m, 4H), 3.38 – 3.12 (m, 4H), 1.46 (d, *J* = 17.9 Hz, 13H), 1.36 – 1.18 (m, 27H), 0.89 (t, *J* = 6.8 Hz, 6H). ESI-MS $[M+H]^+$ calculated m/z =603.5; observed m/z =603.5.



Cbz-Npe$_2$-tBu (4b): Synthesized from Cbz-Npe (3b) and Npe-tBu (1b) using the general procedure for the amide coupling (DCM, rt, overnight), pale yellow oil, 1.415 g, 90% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.44 – 7.08 (m, 15H), 5.18 – 5.06 (m, 2H), 3.98 – 3.35 (m, 8H), 2.92 – 2.69 (m, 4H), 1.55 – 1.41 (m, 9H). ESI-MS $[M+H]^+$ calculated m/z =531.3; observed m/z =531.2.

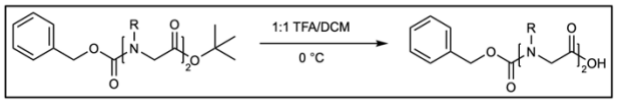


Cbz-Nte$_2$-tBu (4c): Synthesized from Cbz-Nte (3c) and Nte-tBu (1c) using the general procedure for the amide coupling (DMF, 45 °C, overnight), orange oil, 1.250 g, 81% yield. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.32 – 7.16 (m, 5H), 5.07 – 4.97 (m, 2H), 4.29 – 3.87 (m, 4H), 3.56 – 3.30 (m, 25H), 3.24 (d, *J* = 1.7 Hz, 6H), 1.43 – 1.33 (m, 9H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =637.3; observed m/z =637.4.

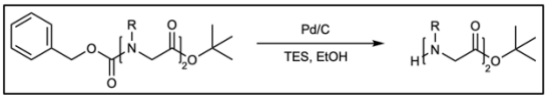


Cbz-Nme$_2$-tBu (4d): Synthesized from Cbz-Nme (3dc) and Nme-tBu (1d) using the general procedure for the amide coupling (DCM, rt, overnight), pale yellow oil, 15.160 g, 96% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.40 – 7.27 (m, 5H), 5.17 – 5.04 (m, 2H), 4.34 – 3.92 (m, 4H), 3.58 – 3.18 (m, 14H), 1.52 – 1.39 (m, 9H). DART-MS $[M+H]^+$ calculated m/z =439.2; observed m/z =439.3.

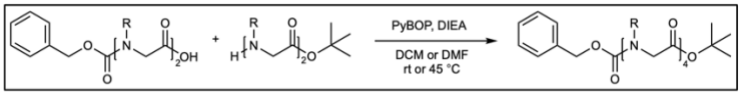
3.1.5 Synthesis of tetramers



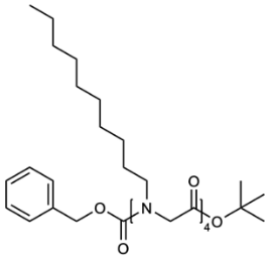
Scheme 5



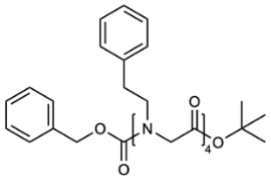
Scheme 6



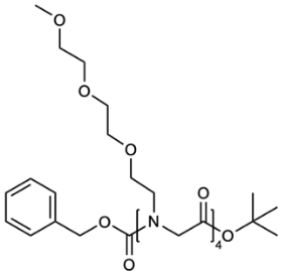
Scheme 7



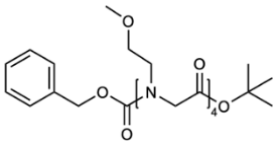
Cbz-Ndc$_4$-tBu (5a): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Ndc$_2$ (93% yield). The general procedure for the Cbz deprotection was used to obtain Ndc$_2$-tBu (quantitative yield). Synthesized using the general procedure for the amide coupling (DCM, rt, overnight), pale yellow oil, 8.879 g, 77% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.40 – 7.27 (m, 5H), 5.19 – 5.01 (m, 2H), 4.35 – 3.71 (m, 9H), 3.42 – 3.17 (m, 8H), 1.63 – 1.43 (m, 18H), 1.34 – 1.24 (m, 55H), 0.89 (td, J = 7.0, 1.7 Hz, 12H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =1019.8; observed m/z =1019.6.



Cbz-Npe$_4$-tBu (5b): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Npe$_2$ (88% yield). The general procedure for the Cbz deprotection was used to obtain Npe$_2$-tBu (91% yield). Synthesized using the general procedure for the amide coupling (DCM, rt, overnight), pale yellow oil, 5.077 g, 93% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.42 – 7.04 (m, 25H), 5.15 – 5.05 (m, 2H), 4.18 – 3.24 (m, 16H), 2.93 – 2.57 (m, 8H), 1.55 – 1.38 (m, 9H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =875.4; observed m/z =875.6.

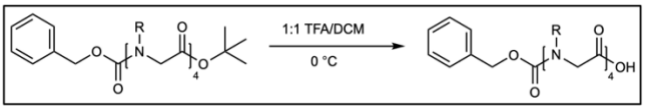


Cbz-Nte$_4$-tBu (5c): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Nte$_2$ (74% yield). The general procedure for the Cbz deprotection was used to obtain Nte$_2$-tBu (94% yield). Synthesized using the general procedure for the amide coupling (DMF, 45°C, overnight), yellow oil, 0.486 g, 75% yield. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.39 – 7.25 (m, 5H), 5.16 – 5.03 (m, 2H), 4.51 – 3.94 (m, 8H), 3.67 – 3.40 (m, 49H), 3.35 – 3.27 (m, 12H), 1.52 – 1.39 (m, 9H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =1043.6; observed m/z =1043.1.

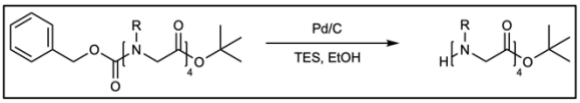


Cbz-Nme$_4$-tBu (5d): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Nme$_2$ (76% yield). The general procedure for the Cbz deprotection was used to obtain Nme$_2$-tBu (quantitative yield). Synthesized using the general procedure for the amide coupling (DMF, 45°C, overnight), yellow oil, 10.419 g, quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 6H), 5.14 – 5.02 (m, 2H), 4.47 – 3.93 (m, 8H), 3.58 – 3.05 (m, 30H), 1.50 – 1.37 (m, 9H). DART-MS $[M+H]^+$ calculated m/z =669.4; observed m/z =669.4.

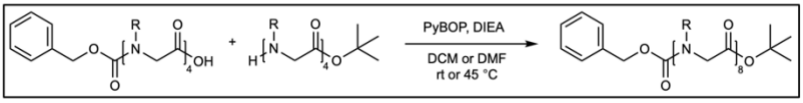
3.1.6 Synthesis of octamers



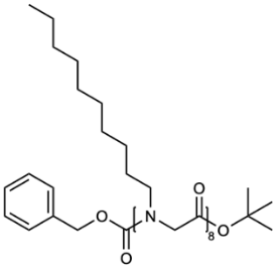
Scheme 8



Scheme 9

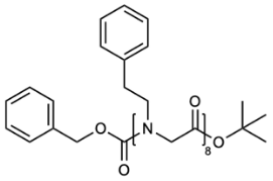


Scheme 10

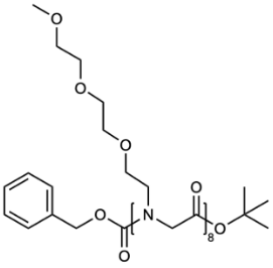


Cbz-Ndc$_8$-tBu (6a): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Ndc$_4$ (95% yield). The general procedure for the Cbz deprotection was used to obtain Ndc$_4$-tBu (94% yield). Synthesized using the general procedure for the amide coupling (DCM, rt, 1 day), yellow oil, 8.225 g, 98% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.43 – 7.25 (m, 5H), 5.18 – 5.01 (m, 2H), 4.35 – 3.82 (m, 17H), 3.43 – 3.20 (m, 16H), 1.65 – 1.41 (m, 32H), 1.38 –

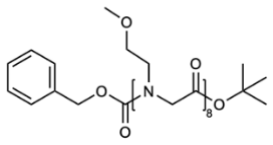
1.19 (m, 137H), 0.91 – 0.83 (m, 29H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =1808.5; observed m/z =1808.8.



Cbz-Npe$_8$-tBu (6b): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Npe$_4$ (76% yield). The general procedure for the Cbz deprotection was used to obtain Npe$_4$-tBu (92% yield). Synthesized using the general procedure for the amide coupling (DCM, rt, 1 day), off-white solid, 0.783 g, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 73H), 5.17 – 5.02 (m, 2H), 4.24 – 3.17 (m, 35H), 2.74 (d, J = 57.3 Hz, 17H), 1.56 – 1.33 (m, 10H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =1519.8; observed m/z =1518.9

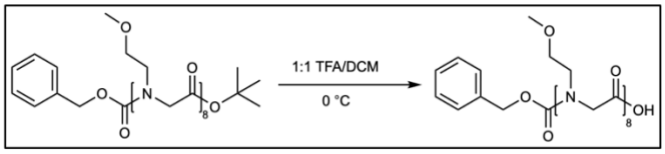


Cbz-Nte$_8$-tBu (6c): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Nte$_4$ (64% yield). The general procedure for the Cbz deprotection was used to obtain Nte$_4$-tBu (98% yield). Synthesized using the general procedure for the amide coupling (DMF, 45 °C, 2 days), pale yellow oil, 0.109 g, 45% yield. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.42 – 7.25 (m, 5H), 5.10 (d, J = 18.3 Hz, 2H), 4.54 – 3.94 (m, 16H), 3.64 – 3.42 (m, 98H), 3.32 (p, J = 1.3 Hz, 25H), 1.53 – 1.41 (m, 9H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =1856.0; observed m/z =1855.0.

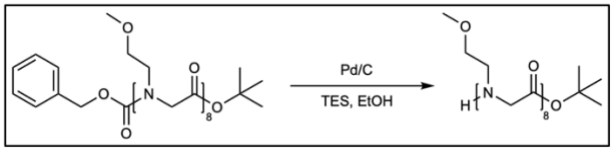


Cbz-Nme$_8$-tBu (6d): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Nme$_4$ (94% yield). The general procedure for the Cbz deprotection was used to obtain Nme$_4$-tBu (93% yield). Synthesized from Cbz-Nme$_4$ (8d) and Nme$_4$-tBu (9d) using the general procedure for the amide coupling (DMF, 45 °C, 1 day), pale yellow oil, 0.539 g, 88% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.43 – 7.23 (m, 6H), 5.19 – 5.02 (m, 2H), 4.47 – 3.91 (m, 15H), 3.60 – 3.03 (m, 61H), 1.49 – 1.41 (m, 10H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =1151.6; observed m/z =1151.8.

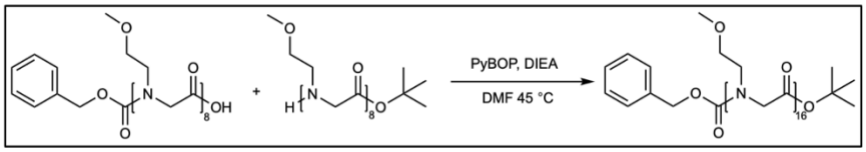
3.1.7 Synthesis of Cbz-Nme$_{16}$-tBu



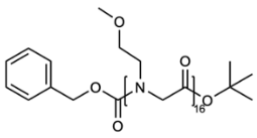
Scheme 11



Scheme 12

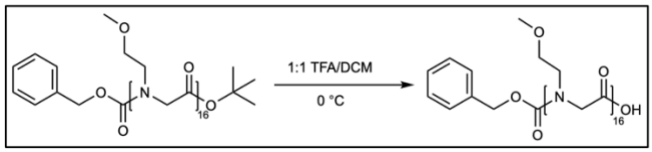


Scheme 13

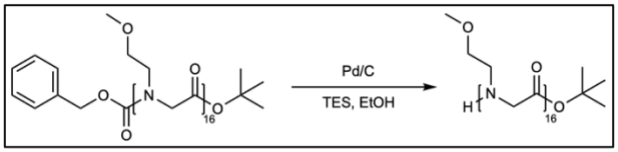


Cbz-Nme$_{16}$-tBu (7): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Nme$_8$ (87% yield). The general procedure for the Cbz deprotection was used to obtain Nme$_8$-tBu (99% yield). Synthesized using the general procedure for the amide coupling (DMF, 45 °C, 1 day), pale yellow solid, 1.582 g, 62% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.43 – 7.24 (m, 5H), 5.10 (m, 2H), 4.51 – 3.91 (m, 34H), 3.60 – 3.41 (m, 65H), 3.38 – 3.18 (m, 51H), 1.53 – 1.41 (m, 9H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =2072.1; observed m/z =2071.5.

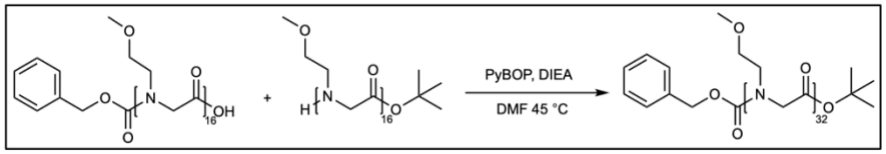
3.1.8 Synthesis of Cbz-Nme$_{32}$-tBu



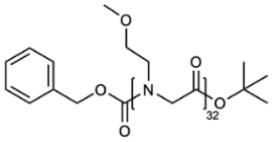
Scheme 14



Scheme 15



Scheme 16



Cbz-Nme$_{32}$-tBu (8): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Nme$_{16}$ (95% yield). The general procedure for the Cbz deprotection was used to obtain Nme$_{16}$-tBu (15% yield). Synthesized using the general procedure for the amide coupling (DMF, 45 °C, 3 days), pale yellow solid, 0.010 g, 7% yield. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.38 – 7.28 (m, 5H), 5.13 – 5.06 (m, 2H), 4.62 – 3.84

(m, 64H), 3.72 – 3.10 (m, 224H), 1.52 – 1.42 (m, 9H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =3913.1; observed m/z =3913.7.

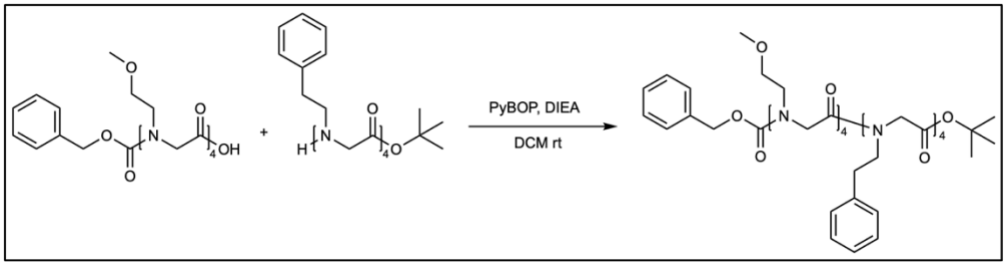
Table S2. Summary of GPC data for Nme peptoid series

Peptoid	Mn	Mw	Mw/Mn
Cbz-Nme$_4$-tBu	1.8 kDa	1.8 kDa	1.00
Cbz-Nme$_8$-tBu	2.0 kDa	2.0 kDa	1.01
Cbz-Nme$_{16}$-tBu	3.0 kDa	3.0 kDa	1.02
Cbz-Nme$_{32}$-tBu	5.6 kDa	5.7 kDa	1.03

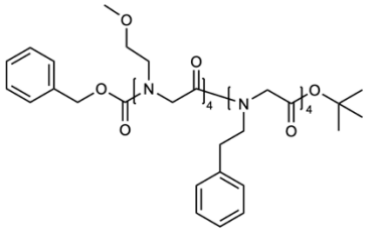
Note: Broader dispersities than 1.00 are due to differences in peak start and end selection. The higher molecular weight peptoids experience some peak fronting.

3.2 Diblock peptoids

3.2.1 Synthesis of Cbz-Nme$_4$-Npe$_4$-tBu

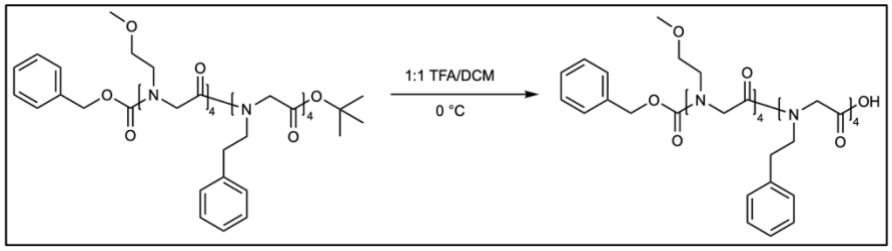


Scheme 17

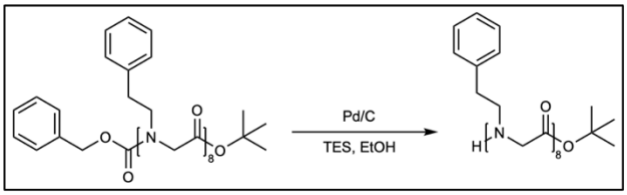


Cbz-Nme$_4$-Npe$_4$-tBu (9): Synthesized from Cbz-Nme$_4$ and Npe$_4$-tBu using the general procedure for the amide coupling (DCM, rt, 1 day), 0.6491 g, 47% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.35 – 7.15 (m, 28H), 5.22 – 4.88 (m, 2H), 4.48 – 3.06 (m, 62H), 2.89 – 2.60 (m, 10H), 1.53 – 1.36 (m, 12H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =1335.7; observed m/z =1335.3.

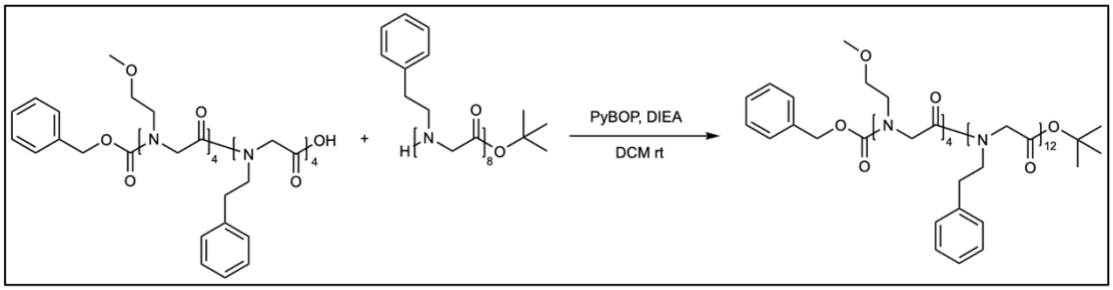
3.2.2 Synthesis of Cbz-Nme$_4$-Npe$_{12}$-tBu



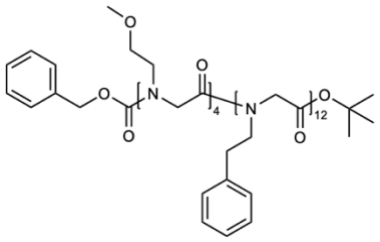
Scheme 18



Scheme 19

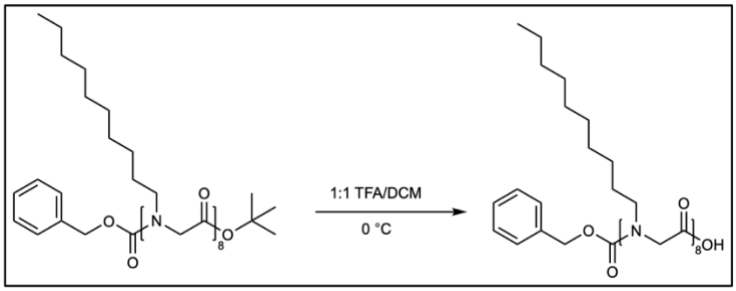


Scheme 20

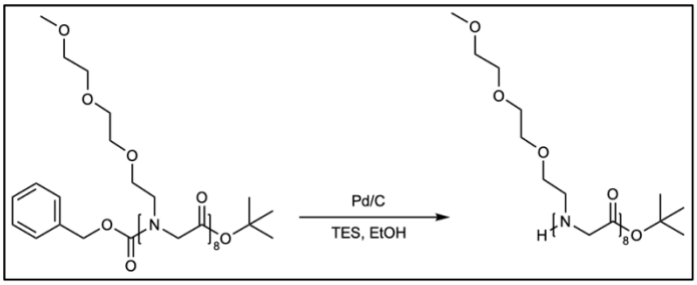


Cbz-Nme$_4$-Npe$_{12}$-tBu (10): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Nme$_4$-Npe$_4$ (89% yield). The general procedure for the Cbz deprotection was used to obtain Npe$_8$-tBu (96% yield). Synthesized using the general procedure for the amide coupling (DMF, 45 °C, 2 days), 0.249 g, 26% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 82H), 5.12 (d, J = 15.3 Hz, 2H), 4.55 – 3.13 (m, 96H), 2.71 (d, J = 61.2 Hz, 28H), 1.52 – 1.31 (m, 11H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =2624.3; observed m/z =2623.8.

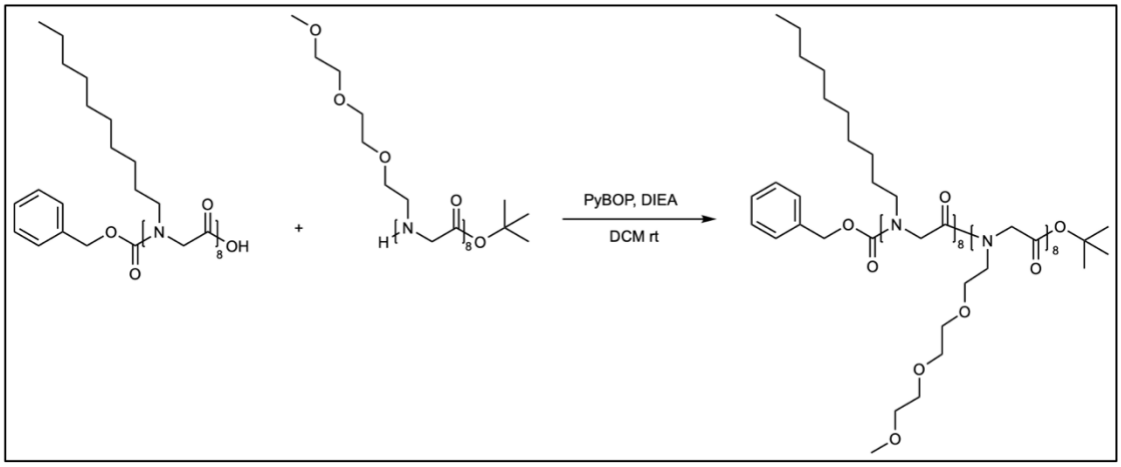
3.2.3 Synthesis of Cbz-Ndc$_8$-Nte$_8$-tBu



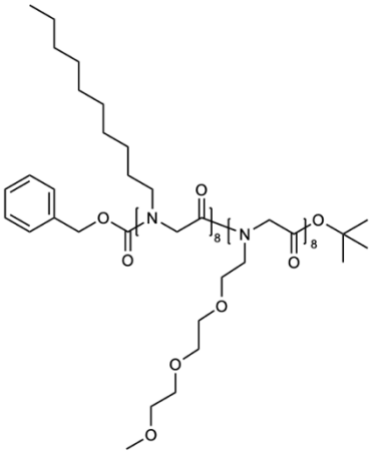
Scheme 21



Scheme 22



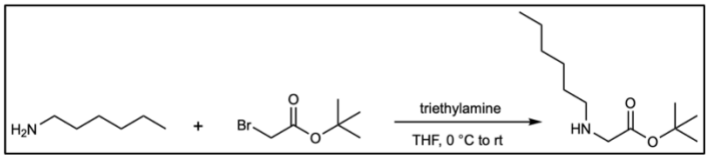
Scheme 23



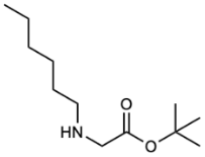
Cbz-Ndc$_8$-Nte$_8$-tBu (11): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Ndc$_8$ (94% yield). The general procedure for the Cbz deprotection was used to obtain Nte$_8$-tBu (45% yield). Synthesized using the general procedure for the amide coupling (DMF, 45 °C, 2 days), 0.016 g, 16% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, J = 13.0, 4.4 Hz, 5H), 5.19 – 5.03 (m, 2H), 4.68 – 3.73 (m, 32H), 3.78 – 3.38 (m, 89H), 3.41 – 3.14 (m, 40H), 1.74 – 1.39 (m, 25H), 1.24 (d, J = 6.6 Hz, 135H), 0.86 (h, J = 4.2 Hz, 26H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =3433.5; observed m/z =3433.9.

3.3 Sequence-defined periodic and aperiodic peptoids

3.3.1 *tert*-butyl ester protection of Nhx monomer

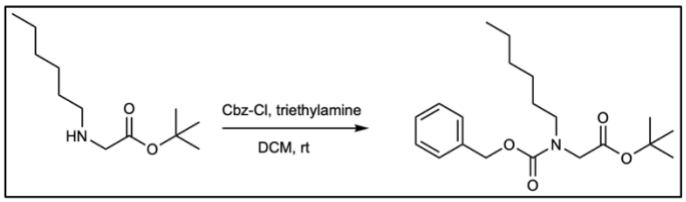


Scheme 24

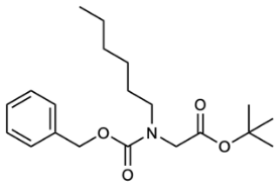


Nhx-tBu (12): Synthesized from hexylamine using the general procedure for the synthesis of *tert*-butyl ester protected peptoid monomers, purified by column chromatography (5% EtOAc in hexanes and then increased to 100% EtOAc), pale yellow oil, 5.296 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.25 (s, 2H), 2.58 – 2.49 (m, 2H), 1.53 (s, 1H), 1.43 (s, 11H), 1.35 – 1.18 (m, 6H), 0.91 – 0.79 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.97, 81.09, 77.48, 77.16, 76.84, 51.95, 49.72, 31.85, 30.20, 28.20, 27.04, 22.68, 14.11. DART-MS $[M+H]^+$ calculated m/z =216.2; observed m/z =216.2.

3.3.2 Cbz protection of Nhx-tBu

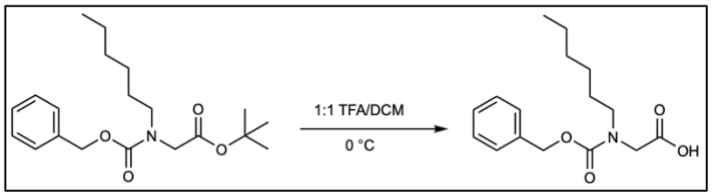


Scheme 25

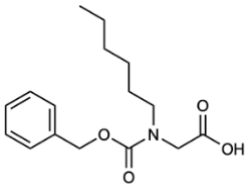


Cbz-Nhx-tBu (13): Synthesized from Nhx-tBu (12) using the general procedure for the Cbz protection of peptoid monomers, purified by column chromatography (100% hexanes and then increased to 20% EtOAc), pale yellow oil, 3.882 g, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 5H), 5.14 (d, J = 15.4 Hz, 2H), 3.87 (d, J = 26.7 Hz, 2H), 3.37 – 3.26 (m, 2H), 1.42 (d, J = 27.0 Hz, 11H), 1.35 – 1.21 (m, 6H), 0.92 – 0.82 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.02, 128.53, 128.48, 127.97, 127.87, 81.70, 77.48, 77.16, 76.84, 67.36, 67.22, 49.93, 49.80, 49.12, 48.31, 31.70, 31.60, 28.42, 28.18, 28.09, 28.07, 26.54, 26.49, 22.68, 22.63, 14.12, 14.10. DART-MS $[M+H]^+$ calculated m/z =350.2; observed m/z =350.2.

3.3.3 *tert*-butyl ester deprotection of Cbz-Nhx-tBu

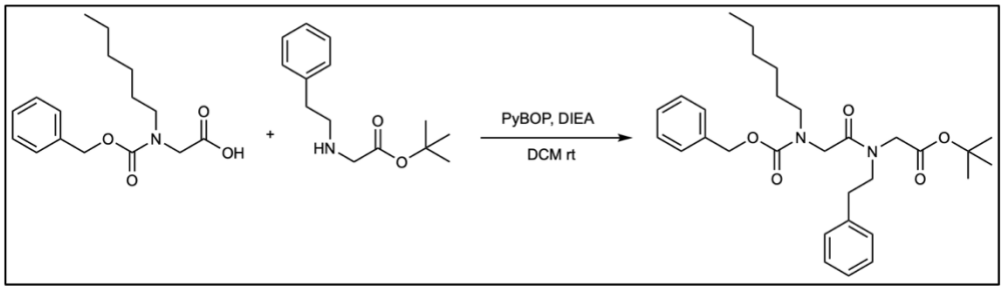


Scheme 26

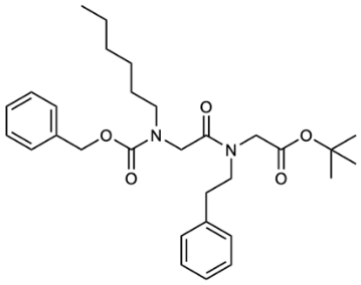


Cbz-Nhx (14): Synthesized from Cbz-Nhx-tBu (13) using the general procedure for *tert*-butyl ester deprotection of peptoids, yellow oil, 2.880 g, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 7.43 – 7.28 (m, 5H), 5.18 (d, *J* = 13.4 Hz, 2H), 4.05 (d, *J* = 15.2 Hz, 2H), 3.36 (dt, *J* = 11.0, 7.4 Hz, 2H), 1.55 (q, *J* = 6.9 Hz, 2H), 1.30 (d, *J* = 17.4 Hz, 6H), 0.89 (q, *J* = 5.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.04, 156.03, 128.60, 128.16, 128.07, 127.92, 127.85, 67.79, 67.55, 48.96, 48.50, 31.66, 31.56, 28.31, 27.94, 26.43, 22.64, 14.10. DART-MS $[M+H]^+$ calculated m/z =294.2; observed m/z =294.2.

3.3.4 Synthesis of Cbz-Nhx-Npe-tBu

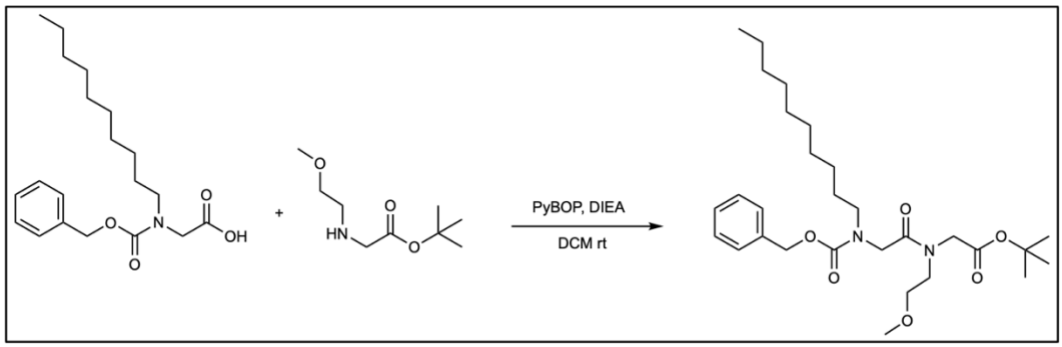


Scheme 27

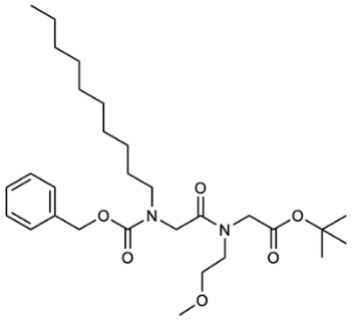


Cbz-Nhx-Npe-tBu (15): Synthesized from Cbz-Nhx (14) and Npe-tBu (1b) using the general procedure for the amide coupling (DCM, rt, overnight), yellow oil, 1.794 g, 89% yield. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.41 – 7.10 (m, 9H), 5.18 – 5.01 (m, 2H), 4.02 – 3.70 (m, 4H), 3.61 – 3.11 (m, 4H), 2.93 – 2.72 (m, 2H), 1.58 – 1.15 (m, 18H), 0.89 (ddt, *J* = 10.4, 7.2, 4.7 Hz, 3H). ESI-MS $[M+H]^+$ calculated m/z =511.3; observed m/z =511.3.

3.3.5 Synthesis of Cbz-Ndc-Nme-tBu

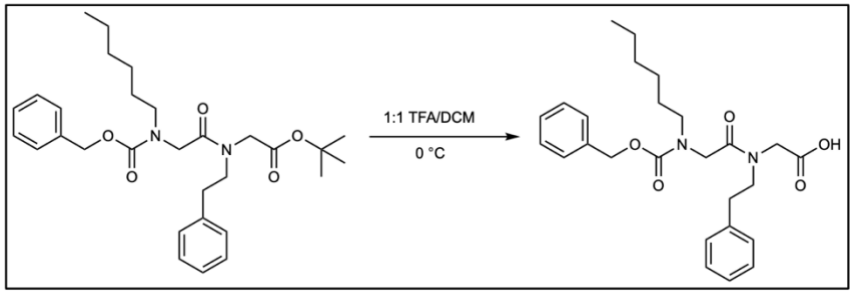


Scheme 28

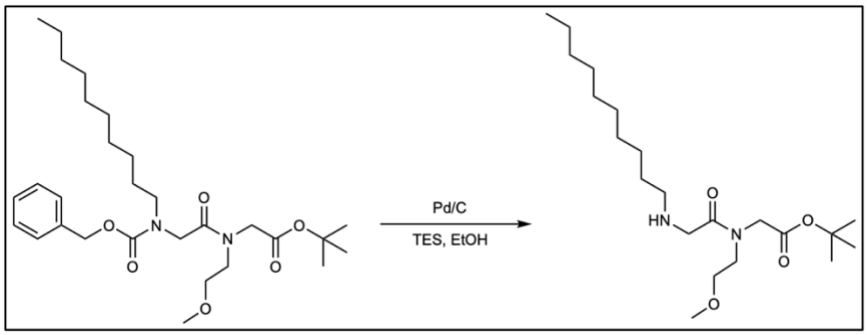


Cbz-Ndc-Nme-tBu (16): Synthesized from Cbz-Ndc (3a) and Nme-tBu (1d) using the general procedure for the amide coupling (DCM, rt, overnight), yellow oil, 1.684 g, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 5H), 5.10 (d, J = 19.0 Hz, 2H), 4.25 – 3.89 (m, 4H), 3.61 – 3.13 (m, 10H), 1.44 (d, J = 13.2 Hz, 11H), 1.24 (dd, J = 17.9, 6.9 Hz, 14H), 0.85 (t, J = 6.8 Hz, 3H). DART-MS $[M+H]^+$ calculated m/z =521.4; observed m/z =521.4.

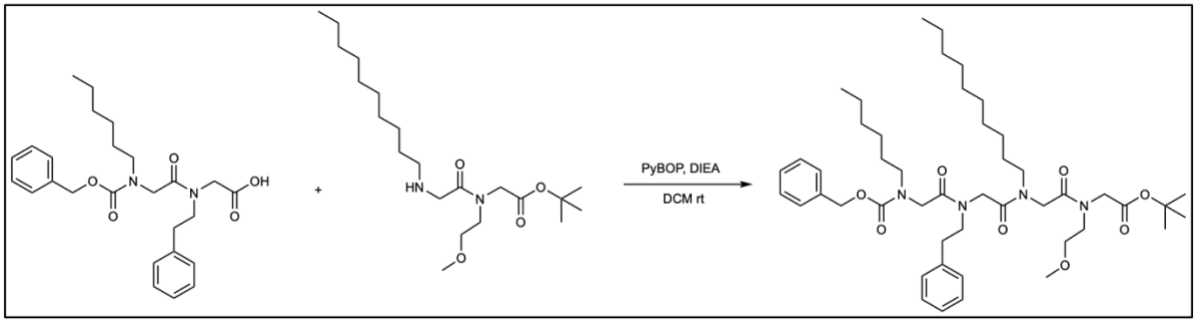
3.3.6 Synthesis of Cbz-Nhx-Npe-Ndc-Nme-tBu



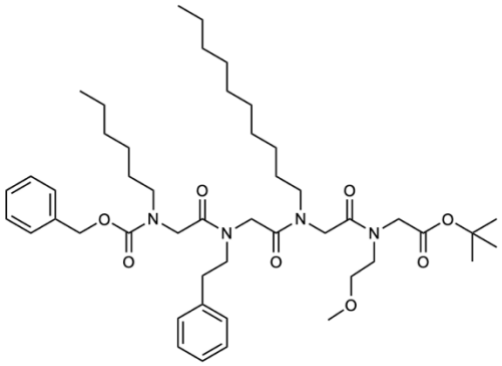
Scheme 29



Scheme 30

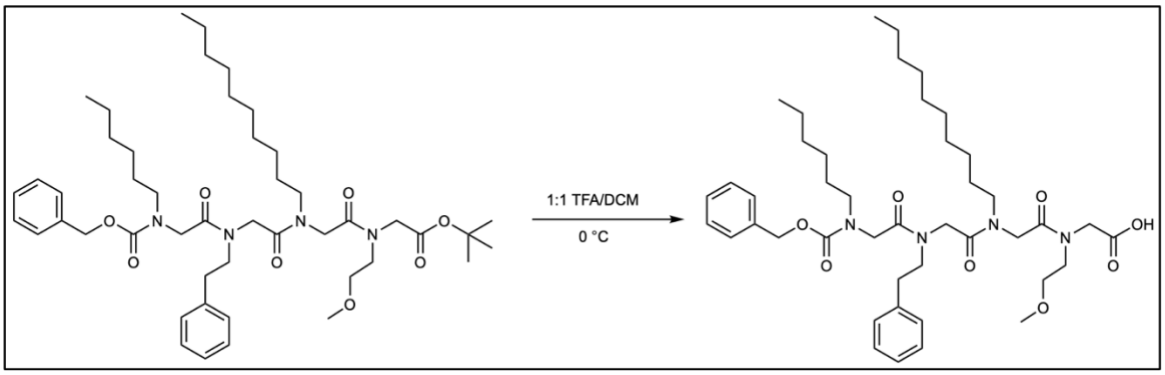


Scheme 31

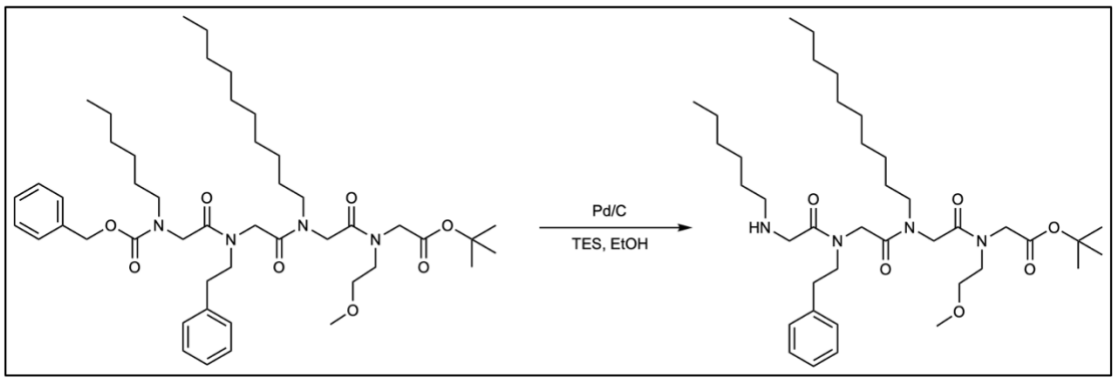


Cbz-Nhx-Npe-Ndc-Nme-tBu (17): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Nhx-Npe (71% yield). The general procedure for the Cbz deprotection was used to obtain Ndc-Nme-tBu (97% yield). Synthesized using the general procedure for the amide coupling (DCM, rt, overnight), yellow oil, 1.672 g, 88% yield. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.43 – 7.09 (m, 10H), 5.15 – 4.99 (m, 2H), 4.37 – 3.01 (m, 22H), 2.92 – 2.69 (m, 2H), 1.67 – 1.37 (m, 13H), 1.33 – 1.20 (m, 20H), 0.93 – 0.79 (m, 6H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =845.5; observed m/z =845.2.

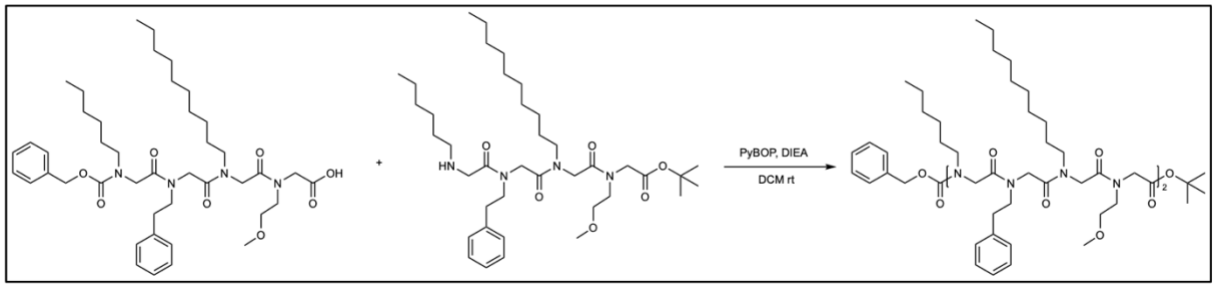
3.3.7 Synthesis of Cbz-(Nhx-Npe-Ndc-Nme)$_2$-tBu



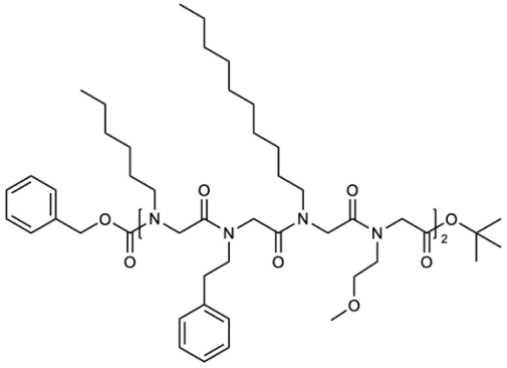
Scheme 32



Scheme 33

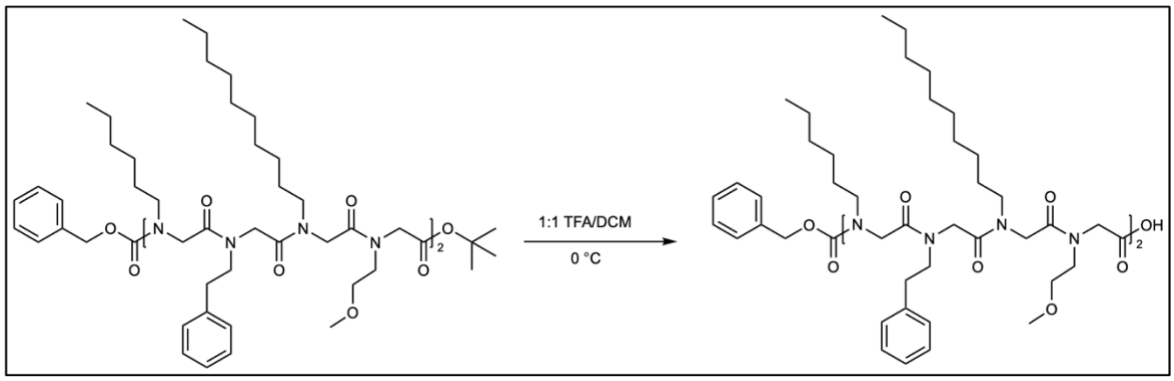


Scheme 34

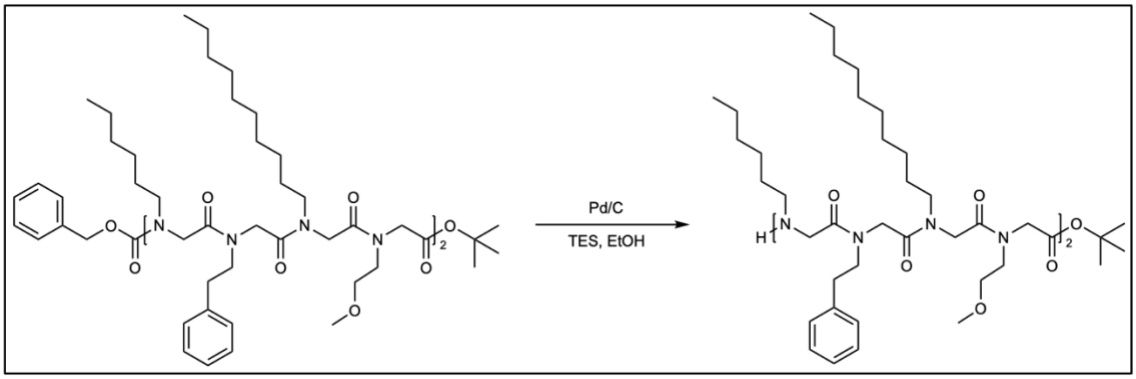


Cbz-(Nhx-Npe-Ndc-Nme)$_2$-tBu (18): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Nhx-Npe-Ndc-Nme (81% yield). The general procedure for the Cbz deprotection was used to obtain Nhx-Npe-Ndc-Nme-tBu (78% yield). Synthesized using the general procedure for the amide coupling (DCM, rt, overnight), yellow oil, 0.7523 g, 88% yield. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.40 – 7.08 (m, 16H), 5.17 – 5.00 (m, 2H), 4.42 – 2.99 (m, 43H), 2.96 – 2.70 (m, 4H), 1.66 – 1.40 (m, 16H), 1.35 – 1.18 (m, 41H), 0.97 – 0.80 (m, 12H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =1460.0; observed m/z =1460.0.

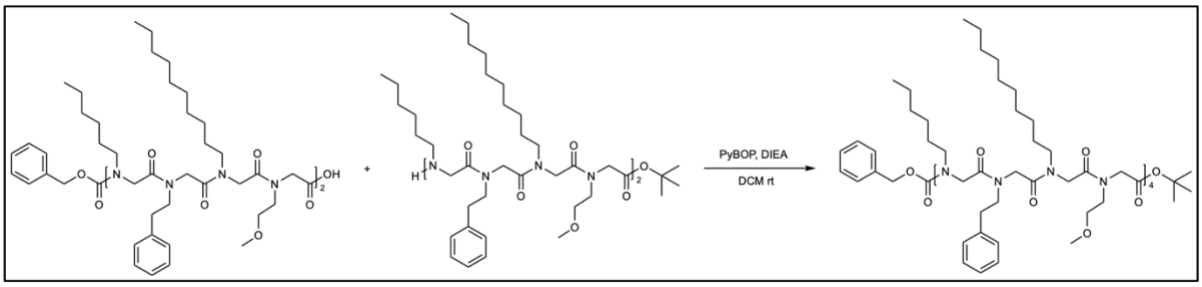
3.3.8 Synthesis of Cbz-(Nhx-Npe-Ndc-Nme)$_4$-tBu



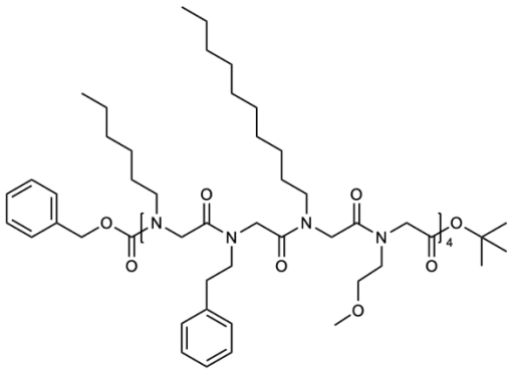
Scheme 35



Scheme 36

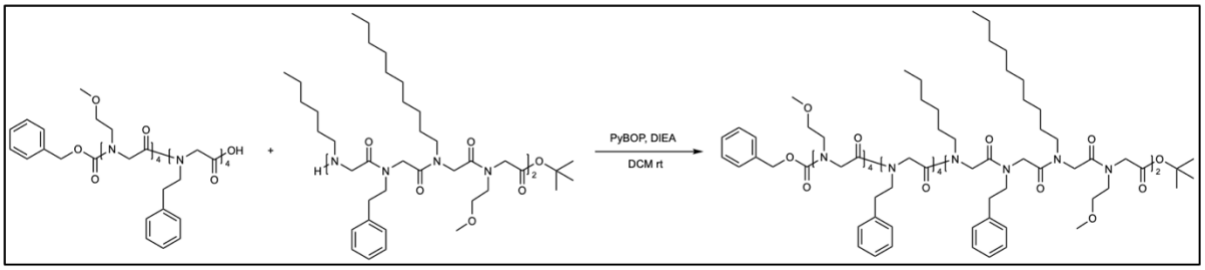


Scheme 37

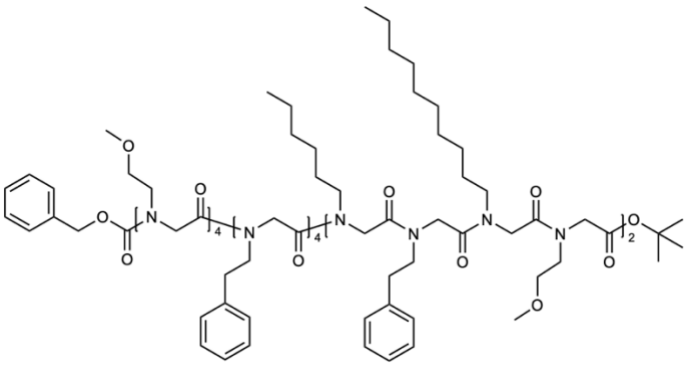


Cbz-(Nhx-Npe-Ndc-Nme)$_4$-tBu (19): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-(Nhx-Npe-Ndc-Nme)$_2$ (84% yield). The general procedure for the Cbz deprotection was used to obtain (Nhx-Npe-Ndc-Nme)$_2$-tBu (91% yield). Synthesized using the general procedure for the amide coupling (DMF, 45 °C, 1 day), yellow oil, 0.170 g, 65% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.36 – 7.14 (m, 27H), 5.16 – 4.99 (m, 2H), 4.33 – 3.22 (m, 88H), 2.89 – 2.71 (m, 8H), 1.57 – 1.19 (m, 116H), 0.92 – 0.82 (m, 26H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =2688.9; observed m/z =2688.5.

3.3.9 Synthesis of Cbz-Nme$_4$-Npe$_4$-(Nhx-Npe-Ndc-Nme)$_2$-tBu



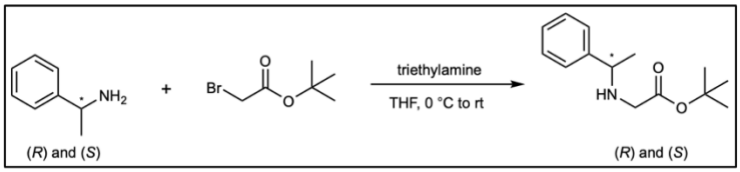
Scheme 38



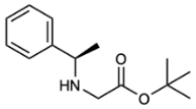
Cbz-Nme$_4$-Npe$_4$-(Nhx-Npe-Ndc-Nme)$_2$-tBu (20): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Nme$_4$-Npe$_4$ (89% yield). The general procedure for the Cbz deprotection was used to obtain (Nhx-Npe-Ndc-Nme)$_2$-tBu (91% yield). Synthesized using the general procedure for the amide coupling (DMF, 45 °C, 1 day), yellow oil, 0.141 g, 67% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.34 – 7.13 (m, 38H), 5.17 – 5.02 (m, 2H), 4.39 – 3.20 (m, 108H), 3.05 – 2.49 (m, 16H), 1.50 – 1.21 (m, 59H), 0.94 – 0.84 (m, 13H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =2564.6; observed m/z =2563.7.

3.4 Stereo-defined alternating peptoids

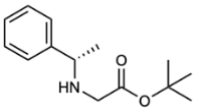
3.4.1. *tert*-butyl ester protection of N(r/s)pe



Scheme 39

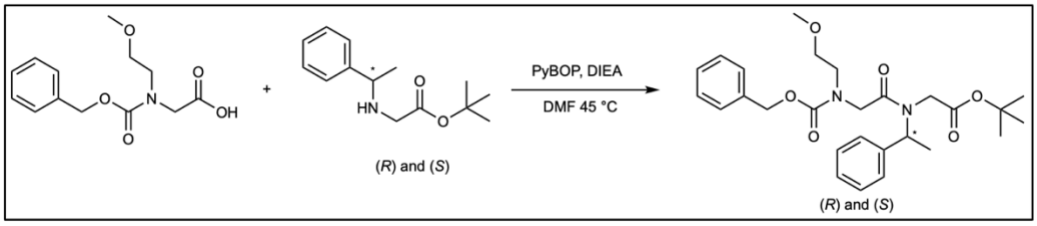


Nrpe-tBu (21): Synthesized from (*R*)-methylbenzylamine using the general procedure for the synthesis of *tert*-butyl ester protected peptoid monomers, purified by column chromatography (5% EtOAc in hexanes and then increased to 20% EtOAc), pale yellow oil, 5.013 g, 79% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.37 – 7.17 (m, 5H), 3.77 (q, *J* = 6.6 Hz, 1H), 3.16 (d, *J* = 17.2 Hz, 1H), 3.08 (d, *J* = 17.2 Hz, 1H), 1.85 (s, 1H), 1.44 (s, 9H), 1.34 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 172.18, 145.73, 128.78, 127.35, 127.19, 81.11, 58.07, 50.14, 28.24, 24.63. DART MS $[M+H]^+$ calculated m/z =236.2; observed m/z =236.2.

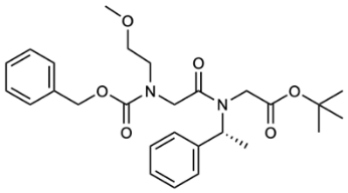


Nspe-tBu (22): Synthesized from (*S)*-methylbenzylamine using the general procedure for the synthesis of *tert*-butyl ester protected peptoid monomers, purified by column chromatography (5% EtOAc in hexanes and then increased to 20% EtOAc), pale yellow oil, 5.9147 g, 95% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.40 – 7.21 (m, 5H), 3.80 (q, *J* = 6.6 Hz, 1H), 3.19 (d, *J* = 17.3 Hz, 1H), 3.11 (d, *J* = 17.2 Hz, 1H), 1.89 (s, 1H), 1.47 (s, 8H), 1.37 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 172.19, 145.78, 128.82, 127.39, 127.22, 81.07, 58.11, 50.16, 28.29, 24.72. DART MS $[M+H]^+$ calculated m/z =236.2; observed m/z =236.2.

3.4.2 Synthesis of Cbz-Nme-N(r/s)pe-tBu

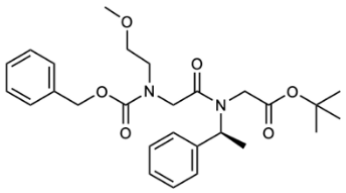


Scheme 40



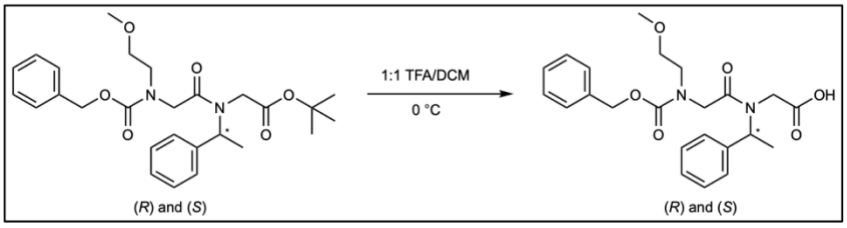
Cbz-Nme-Nrpe-tBu (23): Synthesized from Cbz-Nme (3d) and Nrpe-tBu (21) using the general procedure for the amide coupling (DMF, 45 °C, 2 days), yellow oil, 1.544 g, 74% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.44 – 7.18 (m, 10H), 5.21 – 5.12 (m, 2H), 4.51 – 3.26 (m, 11H), 1.70 – 1.34 (m, 12H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.17, 169.61, 169.54, 169.01, 168.89, 168.84, 168.59, 168.54, 156.85, 156.76, 156.72, 156.68, 140.52, 140.48, 140.44, 140.37, 137.45, 137.41, 129.05, 129.04, 128.82, 128.80, 128.77, 128.75, 128.24, 128.18, 128.13, 128.08, 128.04, 128.03,

128.02, 127.96, 127.85, 127.30, 127.10, 82.64, 81.38, 81.34, 71.92, 71.82, 71.80, 67.58, 67.55, 67.53, 67.40, 60.61, 58.92, 54.82, 54.67, 54.27, 54.24, 54.06, 53.84, 53.62, 53.41, 51.84, 50.08, 50.01, 49.99, 49.97, 48.78, 48.68, 48.05, 47.82, 45.63, 45.49, 28.08, 28.06, 28.04, 27.94, 27.93, 21.17, 18.33, 16.32, 16.20, 14.40. DART MS $[M+H]^+$ calculated m/z =485.3; observed m/z =485.3.

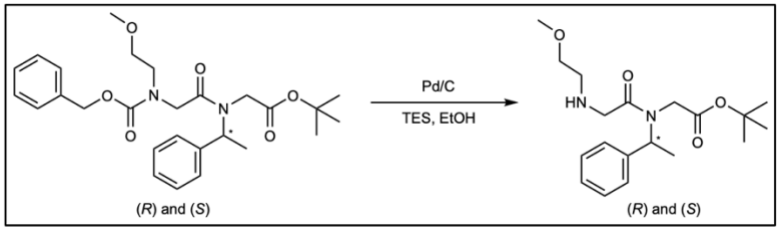


Cbz-Nme-Nspe-tBu (24): Synthesized from Cbz-Nme (3d) and Nrpe-tBu (21) using the general procedure for the amide coupling (DMF, 45 °C, 2 days), yellow oil, 2.708 g, 80% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.43 – 7.17 (m, 10H), 5.19 – 5.10 (m, 2H), 4.50 – 3.21 (m, 11H), 1.61 – 1.28 (m, 12H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.16, 169.61, 169.54, 169.01, 168.89, 168.84, 168.59, 168.54, 156.84, 156.75, 156.72, 156.68, 140.52, 140.48, 140.44, 140.37, 137.45, 137.42, 129.05, 129.03, 128.82, 128.80, 128.76, 128.75, 128.24, 128.18, 128.13, 128.08, 128.04, 128.03, 128.01, 127.96, 127.85, 127.30, 127.10, 82.63, 81.37, 81.33, 71.91, 71.82, 71.80, 67.58, 67.55, 67.52, 67.39, 60.60, 58.92, 54.81, 54.67, 54.27, 54.24, 54.06, 53.84, 53.62, 53.41, 51.84, 50.08, 50.01, 49.99, 49.97, 48.78, 48.68, 48.05, 47.82, 45.63, 45.49, 28.08, 28.06, 27.94, 27.93, 21.17, 18.32, 16.32, 16.20, 14.40. DART MS $[M+H]^+$ calculated m/z =485.3; observed m/z =485.3.

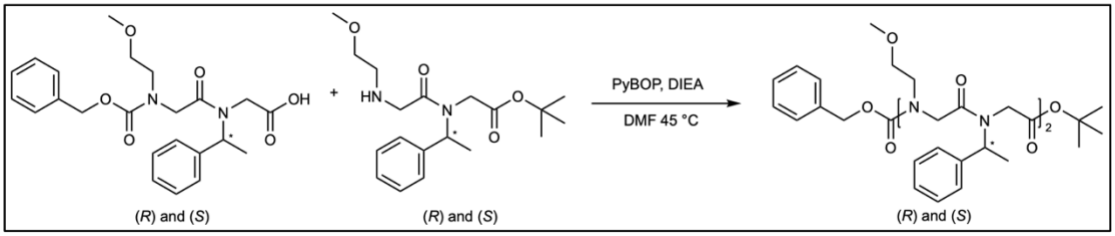
3.4.3 Synthesis of Cbz-(Nme-N(r/s)pe)$_2$-tBu



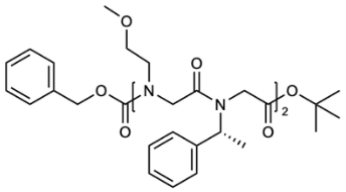
Scheme 41



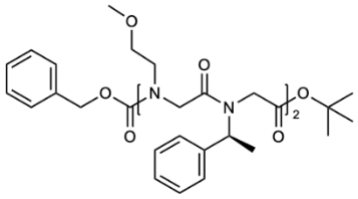
Scheme 42



Scheme 43

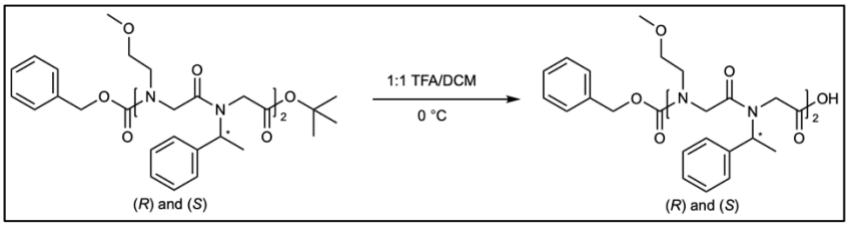


Cbz-(Nme-Nrpe)$_2$-tBu (25): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Nme-Nrpe (98% yield). The general procedure for the Cbz deprotection was used to obtain Nme-Nrpe-tBu (90% yield). Synthesized using the general procedure for the amide coupling (DMF, 45 °C, 2 days), yellow oil, 0.479 g, 62% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.44 – 7.23 (m, 15H), 5.19 – 5.07 (m, 2H), 4.57 – 3.19 (m, 20H), 1.67 – 1.25 (m, 16H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =783.4; observed m/z =783.2.

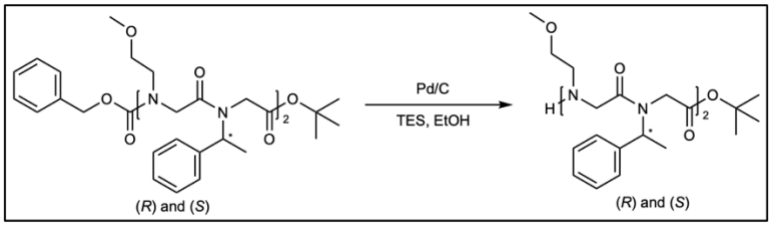


Cbz-(Nme-Nspe)$_2$-tBu (26): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Nme-Nspe (71% yield). The general procedure for the Cbz deprotection was used to obtain Nme-Nspe-tBu (93% yield). Synthesized using the general procedure for the amide coupling (DMF, 45 °C, 2 days), yellow oil, 0.780 g, 51% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.47 – 7.06 (m, 17H), 5.12 (tdd, J = 17.9, 14.1, 8.8 Hz, 2H), 4.68 – 3.16 (m, 19H), 1.65 – 1.25 (m, 14H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =783.4; observed m/z =783.5.

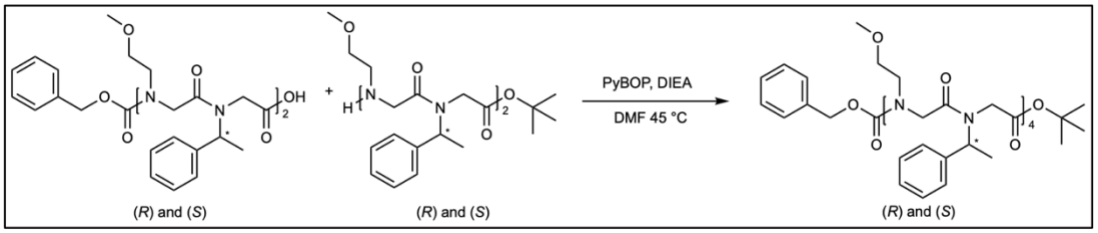
3.4.4 Synthesis of Cbz-(Nme-N(r/s)pe)$_4$-tBu



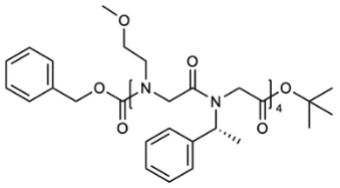
Scheme 44



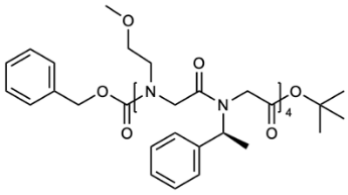
Scheme 45



Scheme 46

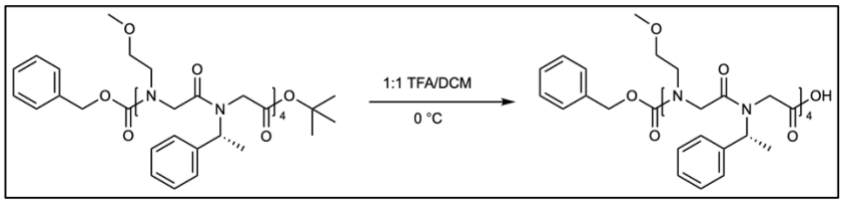


Cbz-(Nme-Nrpe)$_4$-tBu (27): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-(Nme-Nrpe)$_2$ (92% yield). The general procedure for the Cbz deprotection was used to obtain (Nme-Nrpe)$_2$-tBu (95% yield). Synthesized using the general procedure for the amide coupling (DMF, 45 °C, 2 days), yellow oil, 0.153 g, 47% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.34 – 7.18 (m, 26H), 6.03 – 5.89 (m, 4H), 5.20 – 5.10 (m, 2H), 4.64 – 3.09 (m, 50H), 1.63 – 1.32 (m, 24H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =1335.7; observed m/z =1335.9.

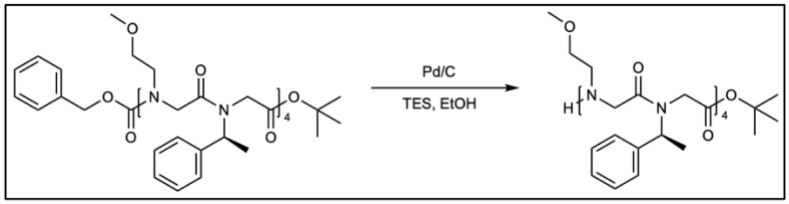


Cbz-(Nme-Nspe)$_4$-tBu (28): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-(Nme-Nspe)$_2$ (70% yield). The general procedure for the Cbz deprotection was used to obtain (Nme-Nspe)$_2$-tBu (85% yield). Synthesized using the general procedure for the amide coupling (DMF, 45 °C, 2 days), yellow oil, 0.074 g, 15% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.40 – 7.21 (m, 34H), 6.02 – 5.88 (m, 4H), 5.16 – 5.09 (m, 2H), 4.65 – 3.05 (m, 56H), 1.67 – 1.33 (m, 26H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =1335.7; observed m/z =1334.7.

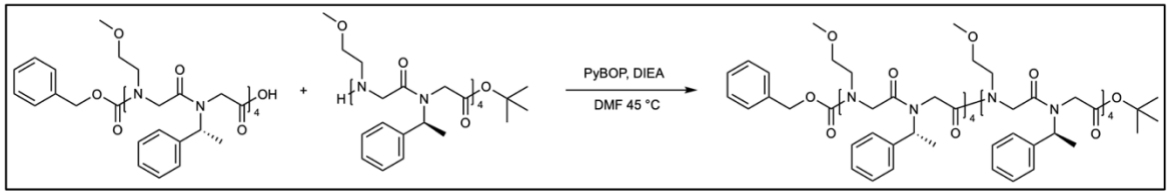
3.4.5 Synthesis of Cbz-(Nme-Nrpe)$_4$-(Nme-Nspe)$_4$-tBu



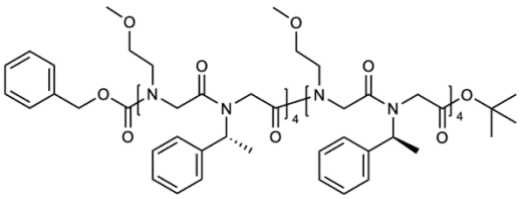
Scheme 47



Scheme 48



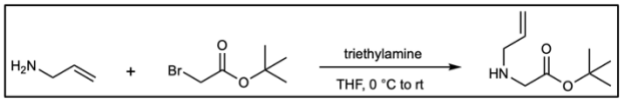
Scheme 49



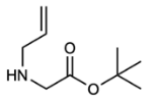
Cbz-(Nme-Nrpe)$_4$-(Nme-Nspe)$_4$-tBu (29): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-(Nme-Nrpe)$_4$ (89% yield). The general procedure for the Cbz deprotection was used to obtain (Nme-Nspe)$_4$-tBu (95% yield). Synthesized using the general procedure for the amide coupling (DMF, 45 °C, 2 days), white solid, 0.035 g, 30% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.45 – 7.03 (m, 46H), 6.00 – 5.89 (m, 6H), 5.18 – 5.06 (m, 2H), 4.68 – 3.08 (m, 87H), 1.63 – 1.26 (m, 37H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =2440.3; observed m/z =2439.7.

3.5 Post-IEG modifications with thiol-ene and CuAAC click reactions

3.5.1 *tert*-butyl ester protection of Nall

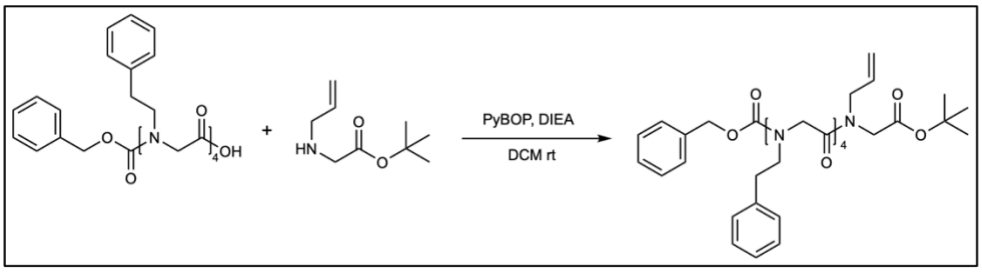


Scheme 50

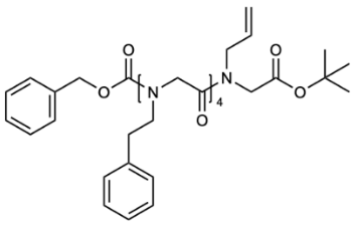


Nall-tBu (30): Synthesized from allylamine using the general procedure for the synthesis of *tert*-butyl ester protected peptoid monomers, purified by column chromatography (5% EtOAc in hexanes and then increased to 50% EtOAc), pale yellow oil, 2.292 g, 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 (ddt, *J* = 17.2, 10.2, 6.0 Hz, 1H), 5.15 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.10 – 5.04 (m, 1H), 3.26 (s, 2H), 3.22 (dt, *J* = 6.0, 1.4 Hz, 2H), 1.43 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.77, 136.33, 116.50, 116.49, 116.48, 81.21, 77.42, 77.16, 76.91, 51.90, 50.90, 28.19.

3.5.2 Synthesis of Cbz-Npe$_4$-Nall-tBu

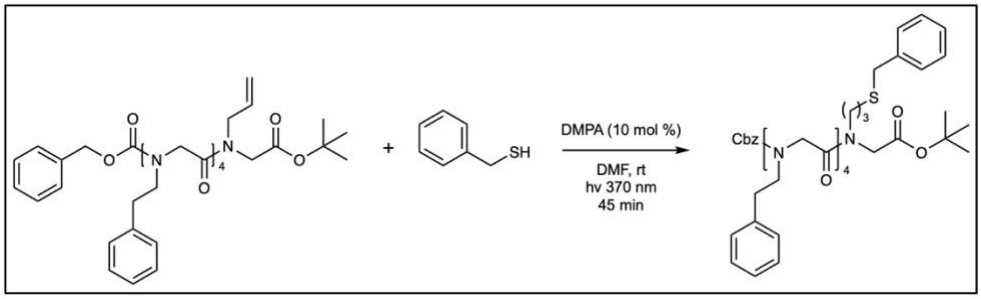


Scheme 51

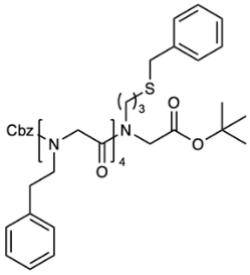


Cbz-Npe$_4$-Nall-tBu (31): Synthesized from Cbz-Npe$_4$ and Nall-tBu (30) using the general procedure for the amide coupling (DCM, rt, 1 day), yellow oil, 0.06 g, 64% yield. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.38 – 7.02 (m, 25H), 5.91 – 5.63 (m, 1H), 5.29 – 5.03 (m, 4H), 4.30 – 3.26 (m, 20H), 3.03 – 2.54 (m, 8H), 1.53 – 1.35 (m, 9H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =972.5; observed m/z =972.7.

3.5.3 Thiol-ene click reaction on Cbz-Npe$_4$-Nall-tBu

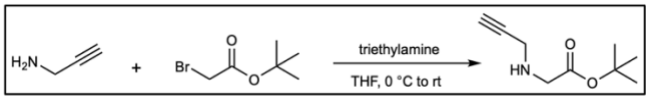


Scheme 52

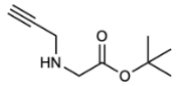


Cbz-Npe$_4$-Nthio-tBu (32): To a solution of Cbz-Npe$_4$-Nall-tBu (31) in DMF (0.5 mL) was added benzyl mercaptan (1.2 equiv) and 2,2,-dimethoxy-2-phenylacetophenone (DMPA) (0.1 equiv). The vial was sealed with a rubber septum and sparged for 15 minutes with N_2. The vial was irradiated at room temperature for 45 minutes with stirring using 370 nm light. The reaction mixture was quenched with water and diluted with DCM. The organic layer was separated and washed with water and brine, dried with $MgSO_4$, concentrated, and purified by recycling preparative GPC. Yellow oil, 0.012 g, 81% yield (90% conversion by UHPLC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.08 (m, 34H), 5.20 – 5.00 (m, 2H), 4.28 – 3.08 (m, 25H), 2.94 – 2.64 (m, 8H), 2.49 – 2.23 (m, 3H), 1.72 (ddp, J = 43.6, 21.3, 6.9 Hz, 3H), 1.53 – 1.37 (m, 10H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =1096.5; observed m/z =1096.7.

3.5.4 *tert*-butyl ester protection of Nalk

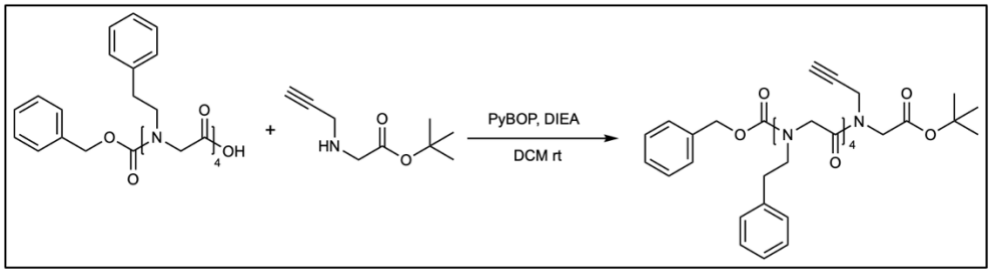


Scheme 53

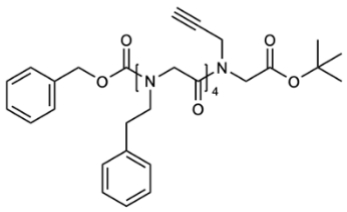


Nalk-tBu (33): Synthesized from allylamine using the general procedure for the synthesis of *tert*-butyl ester protected peptoid monomers, purified by column chromatography (5% EtOAc in hexanes and then increased to 50% EtOAc), pale yellow oil, 1.950 g, 74% yield. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.32 (d, J = 2.5 Hz, 2H), 3.23 (s, 2H), 2.15 (t, J = 2.4 Hz, 1H), 1.63 (s, 1H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 171.53, 82.06, 81.40, 71.69, 54.11, 53.84, 53.57, 50.47, 37.90, 28.21. DART MS $[M+H]^+$ calculated m/z =170.1; observed m/z =170.1.

3.5.5 Synthesis of Cbz-Npe$_4$-Nalk-tBu

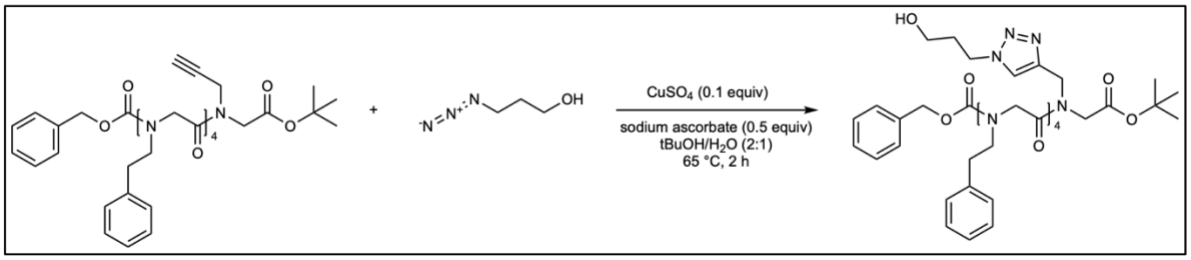


Scheme 54

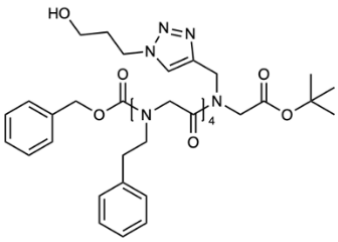


Cbz-Npe$_4$-Nalk-tBu (34): Synthesized from Cbz-Npe$_4$ and Nalk-tBu (33) using the general procedure for the amide coupling (DCM, rt, 1 day), yellow oil, 0.120 g, 53% yield. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.42 – 7.02 (m, 26H), 5.15 – 5.03 (m, 2H), 4.40 – 3.26 (m, 20H), 2.93 – 2.56 (m, 8H), 2.46 – 2.23 (m, 1H), 1.56 – 1.38 (m, 9H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =970.5; observed m/z =970.8.

3.5.6 CuAAC click reaction on Cbz-Npe$_4$-Nalk-tBu

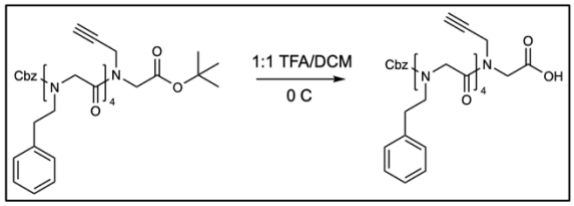


Scheme 55

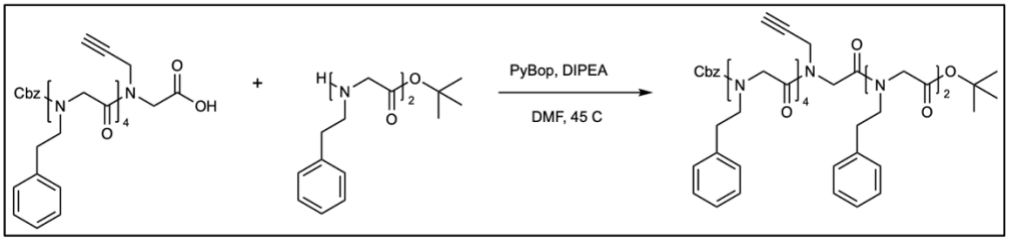


Cbz-Npe$_4$-Ntriazo-tBu (35): To a solution of Cbz-Npe$_4$-Nalk-tBu in tBuOH/H_2O (2:1) was added CuSO4 (0.1 equiv) and sodium ascorbate (0.5 equiv). The mixture was stirred for 2 hours at 65 °C. The reaction mixture was quenched with water and diluted with DCM. The organic layer was separated and washed with water and brine, dried with $MgSO_4$, concentrated, and purified by recycling preparative GPC. Yellow oil, 0.023 g, 99% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.91 – 7.49 (m, 1H), 7.43 – 7.01 (m, 27H), 5.08 (dtd, *J* = 14.9, 8.6, 4.6 Hz, 2H), 4.71 – 3.25 (m, 26H), 2.97 – 2.60 (m, 8H), 1.97 (dddd, *J* = 22.5, 9.7, 6.3, 3.6 Hz, 2H), 1.49 – 1.37 (m, 9H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =1071.5; observed m/z =1071.4.

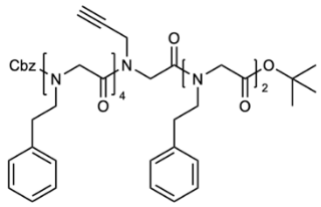
3.5.7 Synthesis of Cbz-Npe$_4$-Nalk-Npe$_2$-tBu



Scheme 56

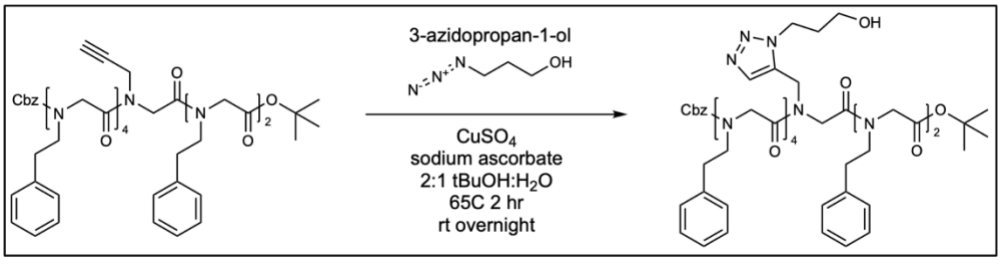


Scheme 57

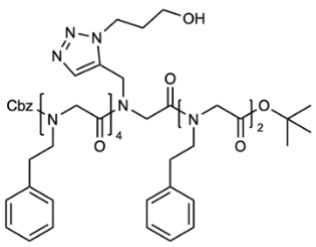


Cbz-Npe$_4$-Nalk-Npe$_2$-tBu (36): The general procedure for the *tert*-butyl ester deprotection was used to obtain Cbz-Npe$_4$-Nalk (quantitative yield). The general procedure for the Cbz deprotection was used to obtain Npe$_2$-tBu (91% yield). Synthesized using the general procedure for the amide coupling (DMF, 45 °C, 1 day), yellow oil, 0.120 g, 59% yield. ^{1}H NMR (500 MHz, CDCl3) δ 7.26 (s, 49H), 5.15 – 5.06 (m, 2H), 4.44 – 3.20 (m, 33H), 2.91 – 2.59 (m, 13H), 2.36 – 2.17 (m, 1H), 1.54 – 1.37 (m, 10H). MALDI-TOF MS [M+Na]$^+$ calculated m/z =1292.6; observed m/z =1292.3.

3.5.8 CuAAC click reaction on Cbz-Npe$_4$-Nalk-Npe$_2$-tBu



Scheme 58



Cbz-Npe$_4$-Ntriazo-Npe$_2$-tBu (37): To a solution of Cbz-Npe$_4$-Nalk-Npe$_2$-tBu in tBuOH/H$_2$O (2:1) was added CuSO4 (0.1 equiv) and sodium ascorbate (0.5 equiv). The mixture was stirred for 2 hours at 65 °C and overnight at room temperature. The reaction mixture was quenched with water and diluted with DCM. The organic layer was separated and washed with saturated ammonium chloride water and brine, dried with MgSO$_4$, and concentrated. Yellow oil, 0.019 g, 88% yield. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.26 (s, 49H), 5.15 – 5.06

(m, 2H), 4.44 – 3.20 (m, 33H), 2.91 – 2.59 (m, 13H), 2.36 – 2.17 (m, 1H), 1.54 – 1.37 (m, 10H). MALDI-TOF MS $[M+Na]^+$ calculated m/z =1393.7; observed m/z =1393.7.

4. TEM micrographs of peptoid nanosheets

4.1 Additional TEM images of peptoid nanosheets

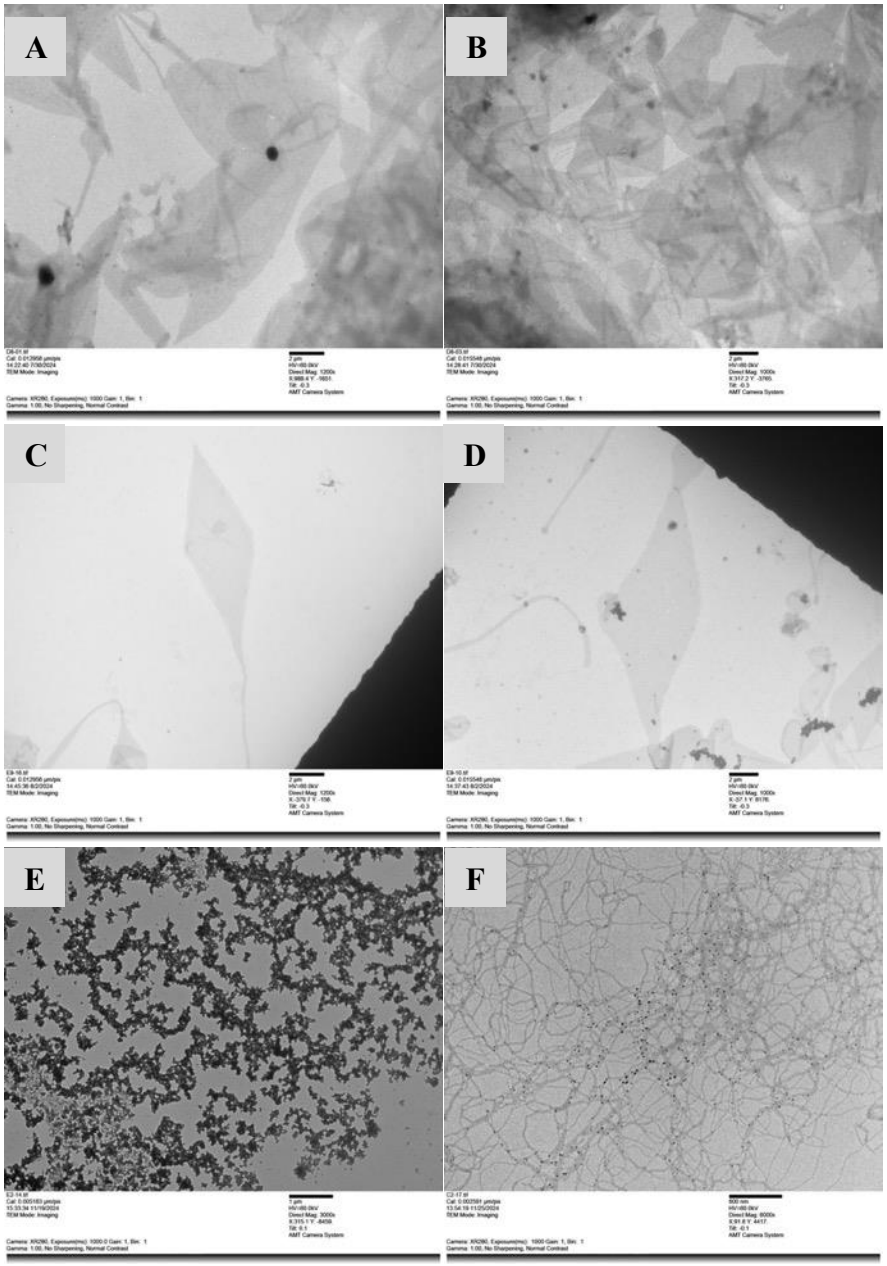


Fig. S1 TEM micrographs of (a-d) Cbz-Ndc_8-Nte_8-tBu nanosheets (scale bars are 2 μm), (e) Ndc_8-Nte_8-tBu aggregates (scale bar is 1 μm) and (f) Ndc_8-Nte_8 nanofibrils (scale bar is 600 nm).

5. UHPLC and MALDI/DART/ESI spectra

5.1 Peptoid homopolymers

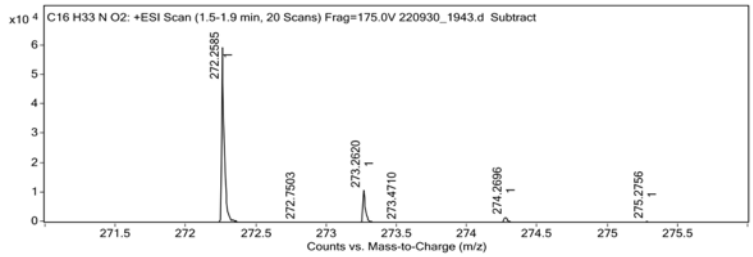


Fig. S2 HRMS of Ndc-tBu.

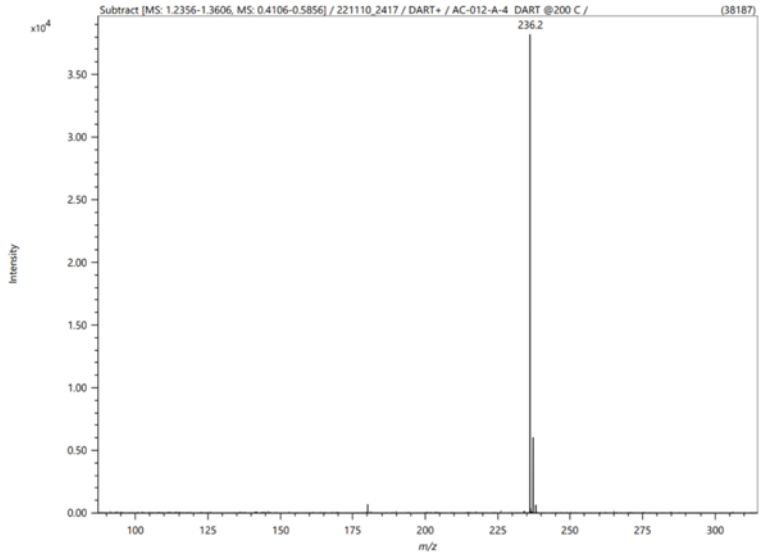


Fig. S3 DART-MS of Npe-tBu.

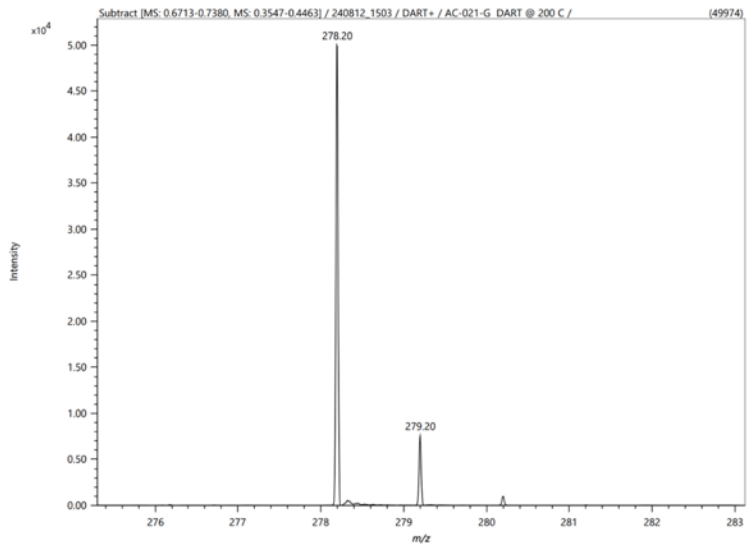


Fig. S4 DART-MS of Nte-tBu.

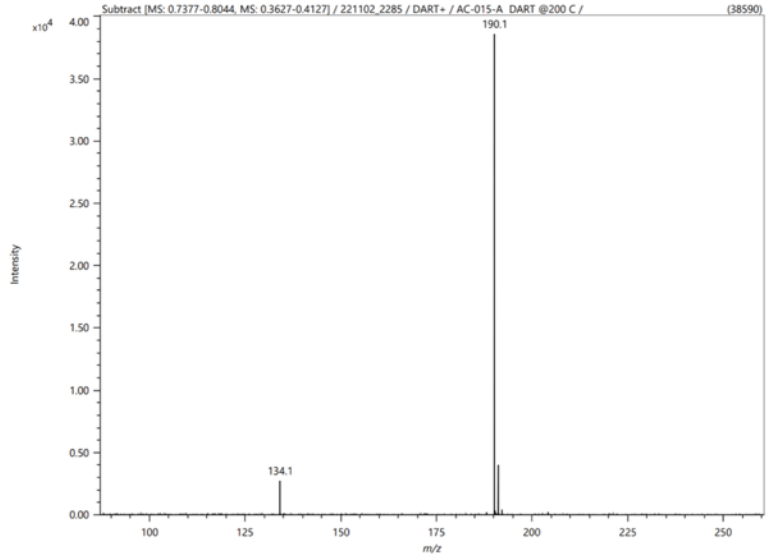


Fig. S5 DART-MS of Nme-tBu.

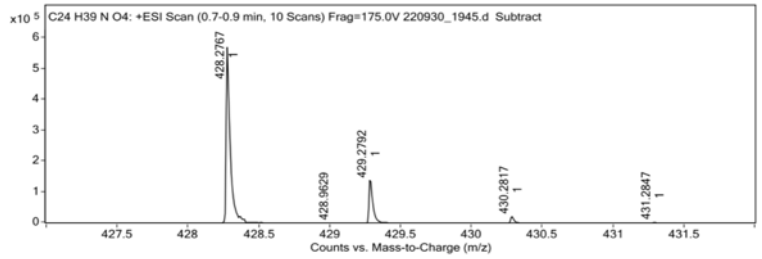


Fig. S6 HRMS of Cbz-Ndc-tBu.

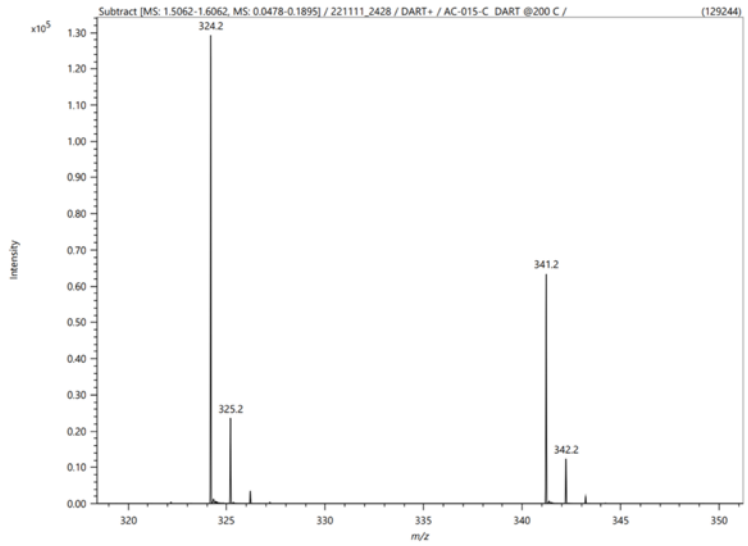


Fig. S7 DART-MS of Cbz-Nme-tBu.

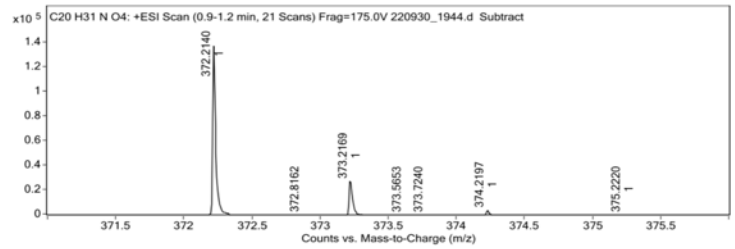


Fig. S8 HRMS of Cbz-Ndc.

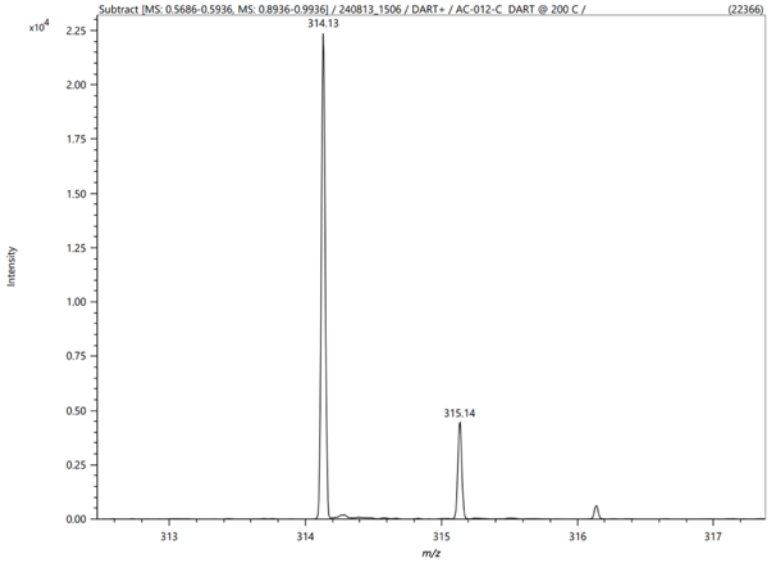


Fig. S9 DART-MS of Cbz-Npe.

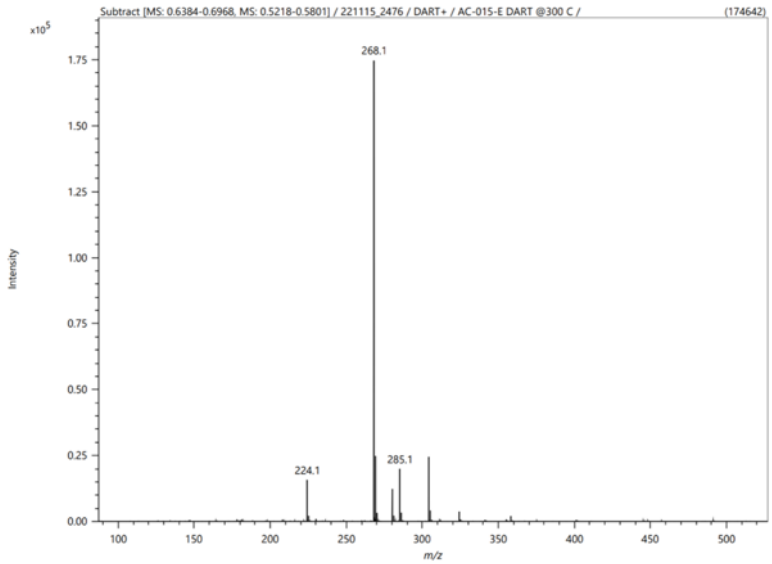


Fig. S10 DART-MS of Cbz-Nme.

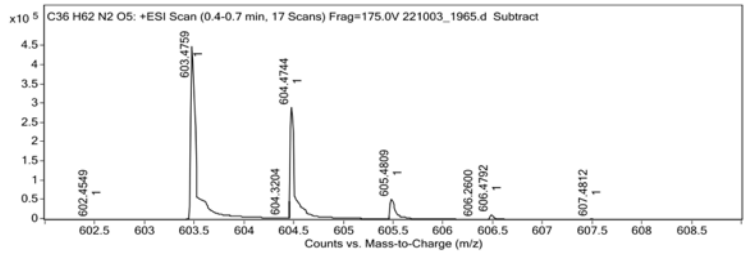


Fig. S11 HRMS of Cbz-Ndc$_2$-tBu.

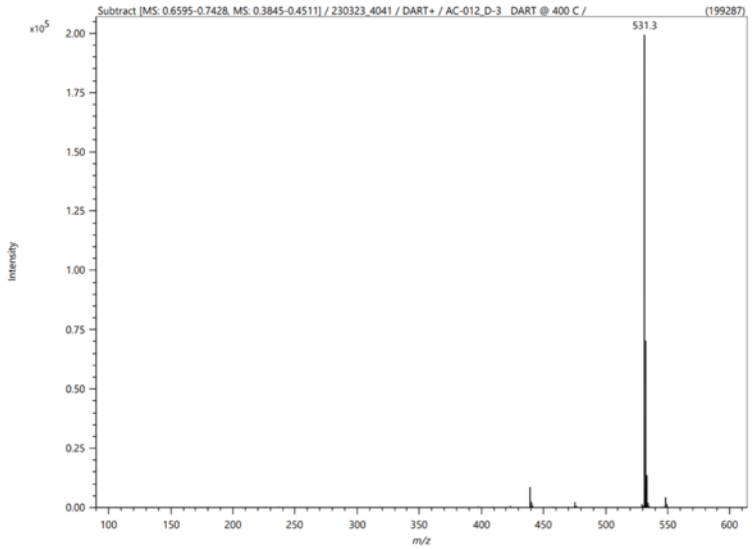


Fig. S12 DART-MS of Cbz-Npe$_2$-tBu.

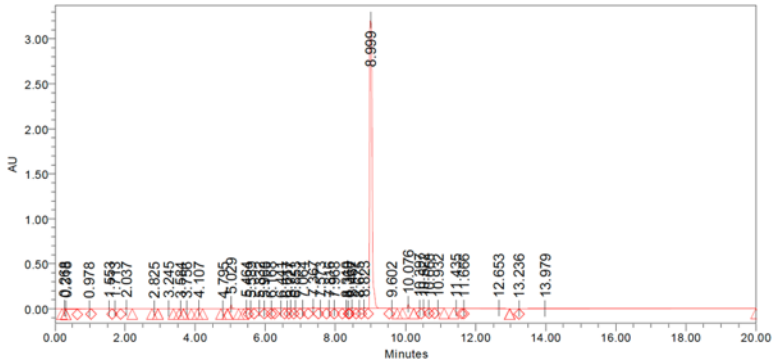


Fig. S13 UHPLC of Cbz-Npe$_2$-tBu.

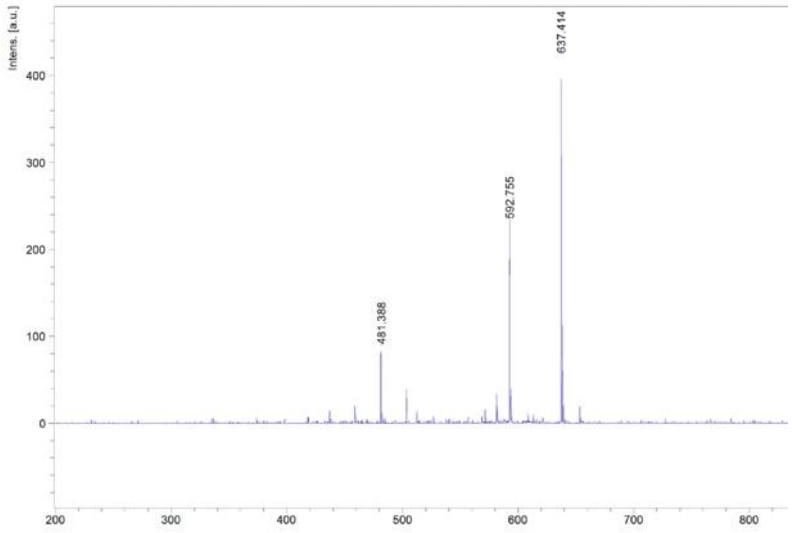


Fig. S14 MALDI-TOF MS of Cbz-Nte$_2$-tBu.

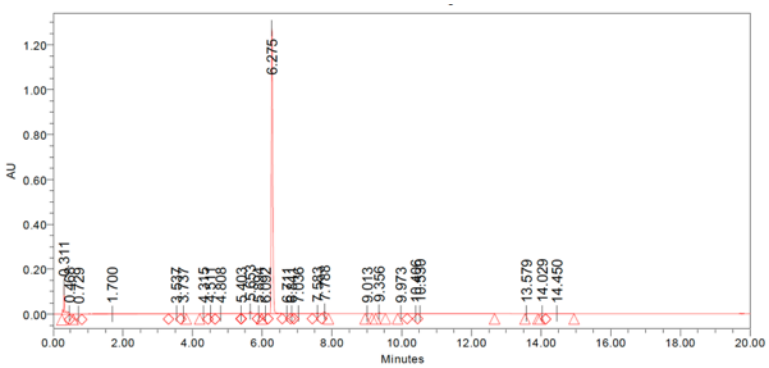


Fig. S15 UHPLC of Cbz-Nte$_2$-tBu.

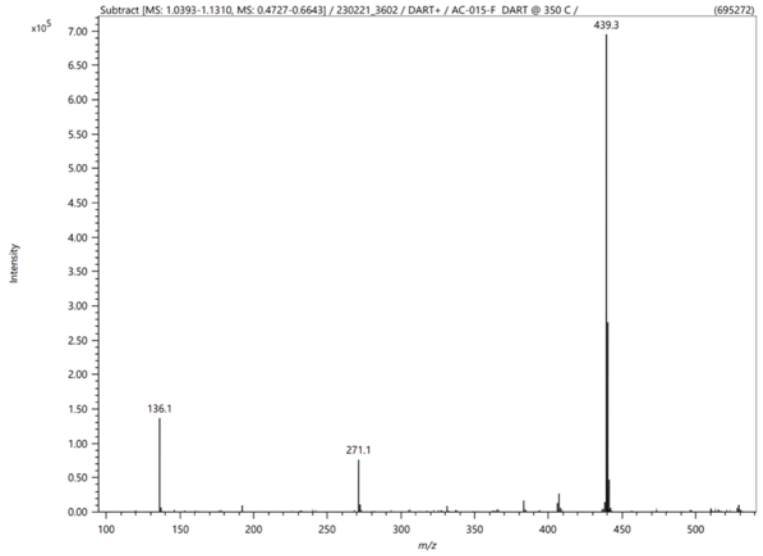


Fig. S16 DART-MS of Cbz-Nme$_2$-tBu.

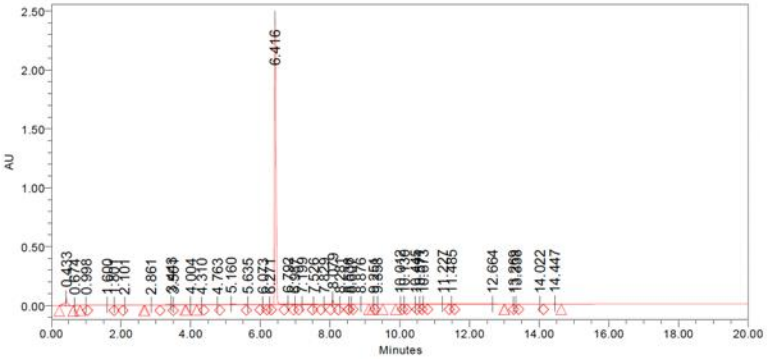


Fig. S17 UHPLC of Cbz-Nme$_2$-tBu.

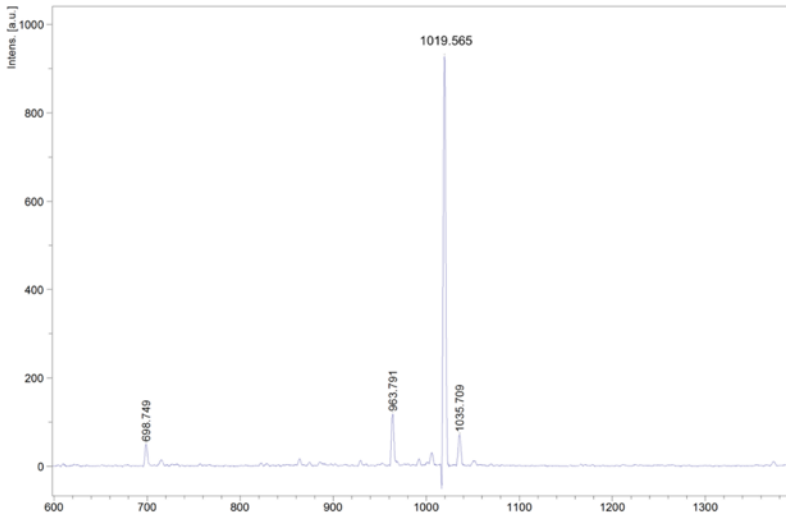


Fig. S18 MALDI-TOF MS of Cbz-Ndc$_4$-tBu.

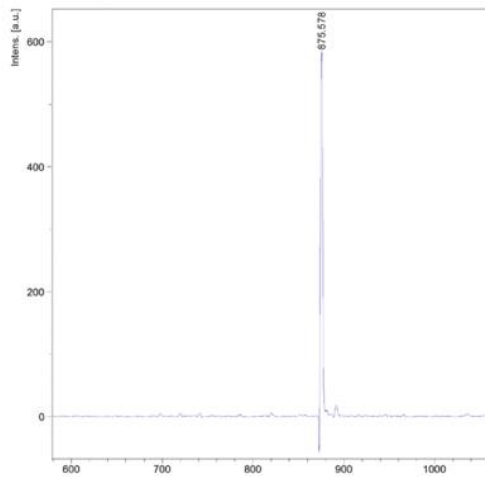


Fig. S19 MALDI-TOF MS of Cbz-Npe$_4$-tBu.

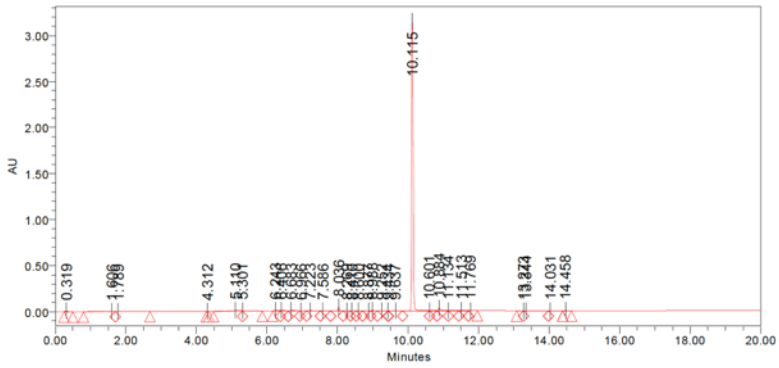


Fig. S20 UHPLC of Cbz-Npe$_4$-tBu.

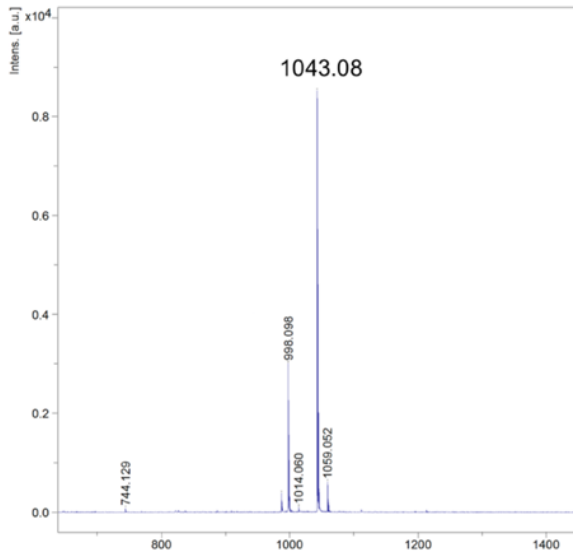


Fig. S21 MALDI-TOF MS of Cbz-Nte$_4$-tBu.

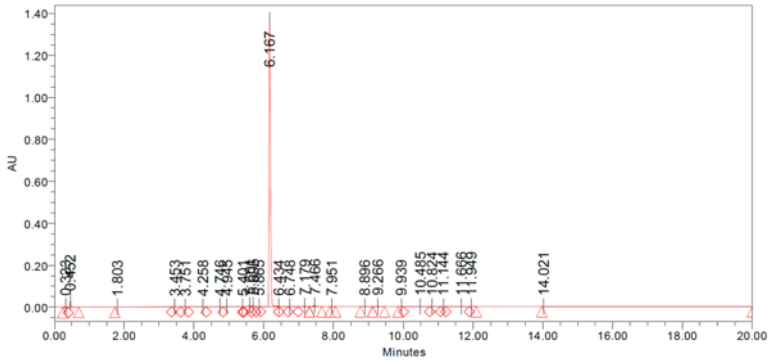


Fig. S22 UHPLC of Cbz-Nte$_4$-tBu.

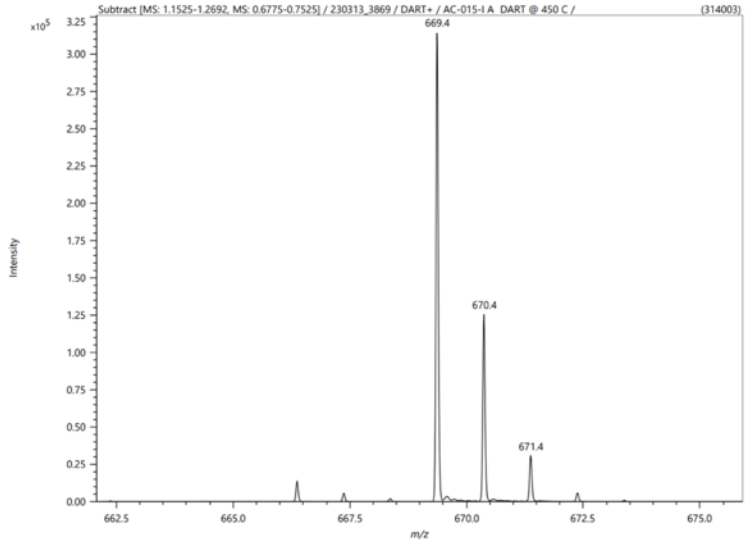


Fig. S23 DART-MS of Cbz-Nme$_4$-tBu.

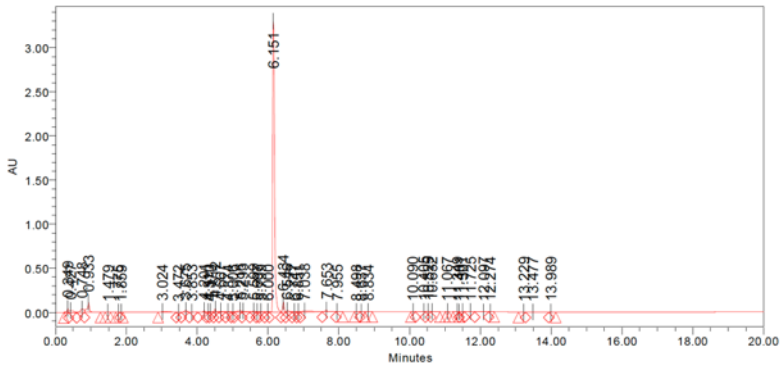


Fig. S24 UHPLC of Cbz-Nme$_4$-tBu.

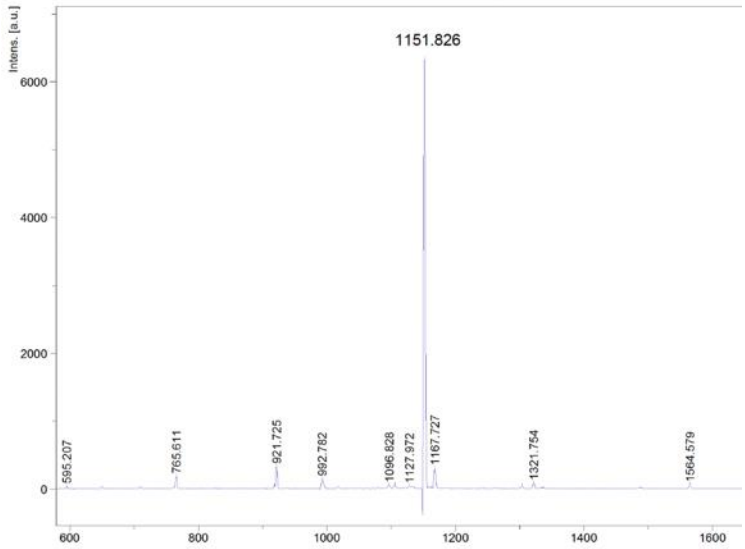


Fig. S25 MALDI-TOF MS of Cbz-Nme$_8$-tBu.

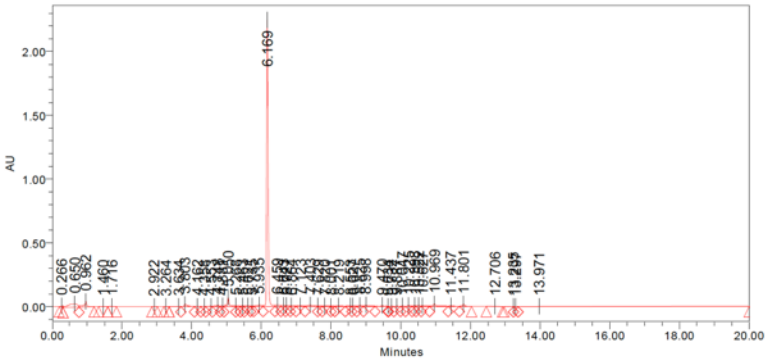


Fig. S26 UHPLC of Cbz-Nme$_8$-tBu.

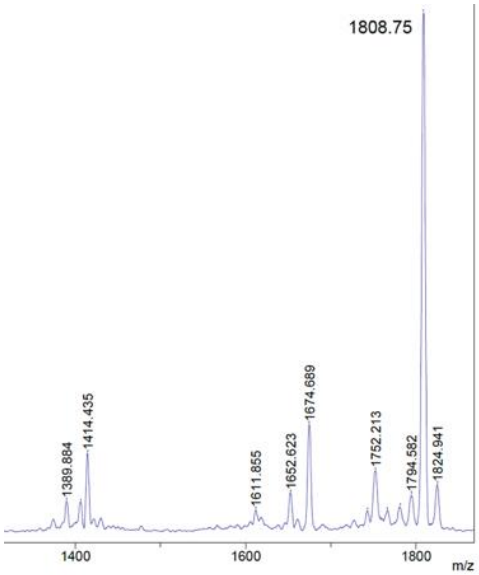


Fig. S27 MALDI-TOF MS of Cbz-Ndc$_8$-tBu.

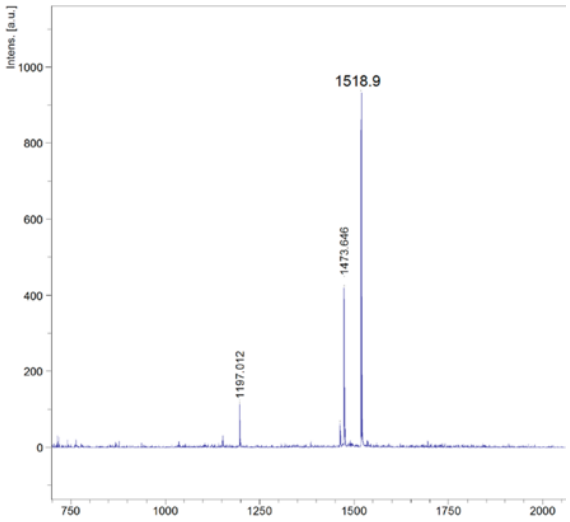


Fig. S28 MALDI-TOF MS of Cbz-Npe$_8$-tBu.

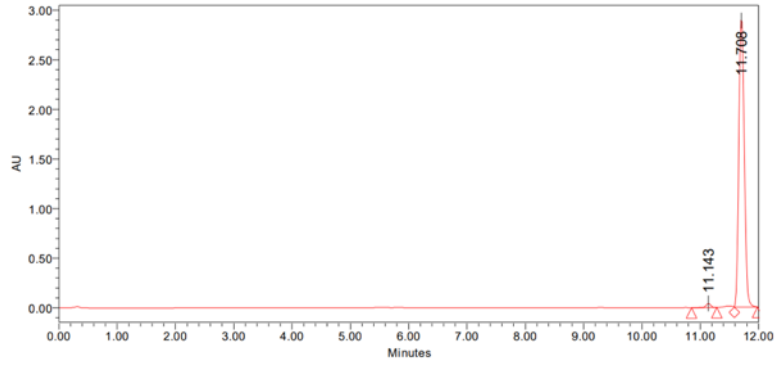


Fig. S29 UHPLC of Cbz-Npe$_8$-tBu.

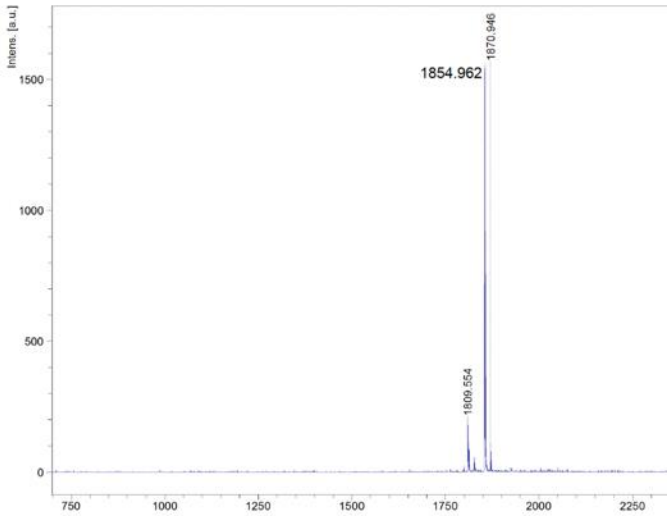


Fig. S30 MALDI-TOF MS of Cbz-Nte$_8$-tBu.

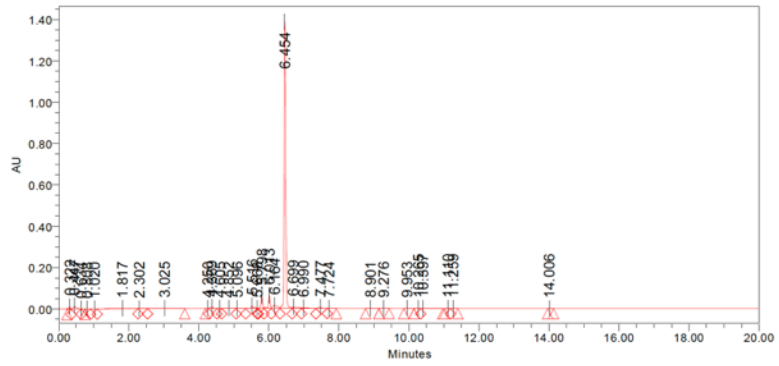


Fig. S31 UHPLC of Cbz-Nte$_8$-tBu.

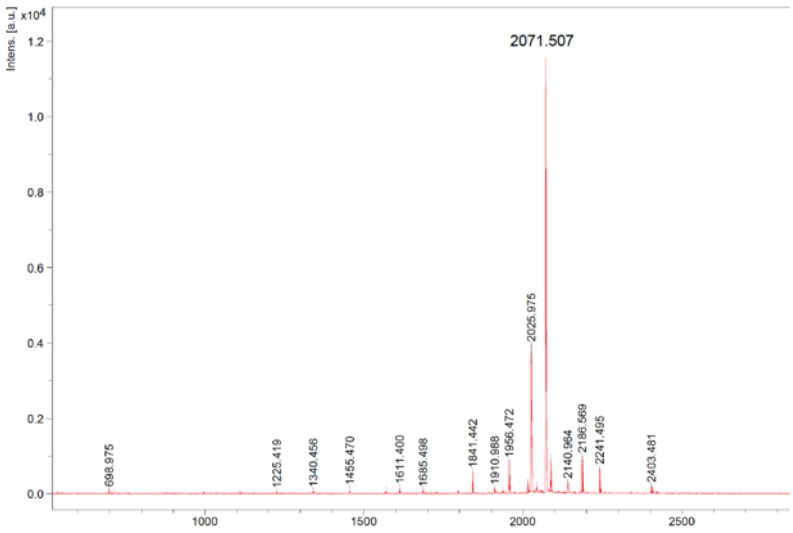


Fig. S32 MALDI-TOF MS of Cbz-Nme$_{16}$-tBu.

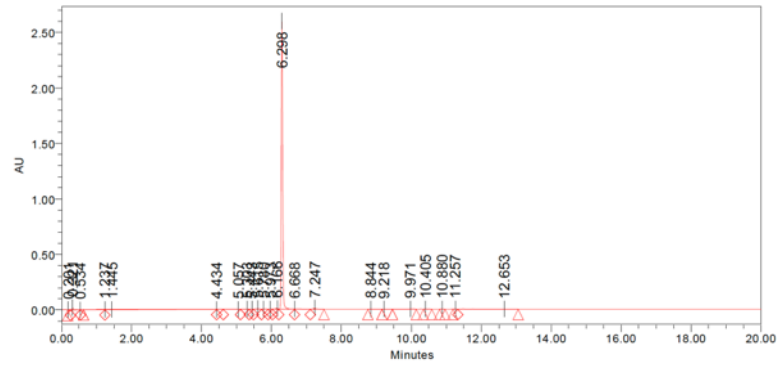


Fig. S33 UHPLC of Cbz-Nme$_{16}$-tBu.

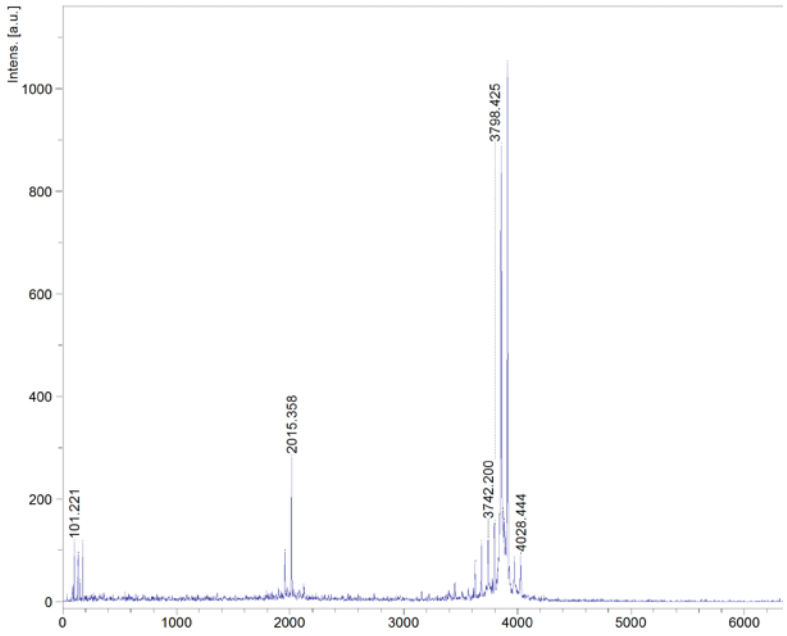


Fig. S34 MALDI-TOF MS of Cbz-Nme$_{32}$-tBu.

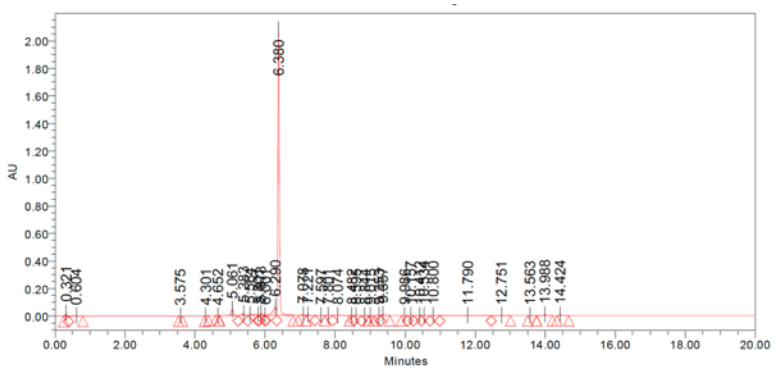


Fig. S35 UHPLC of Cbz-Nme$_{32}$-tBu.

5.2 Diblock peptoids

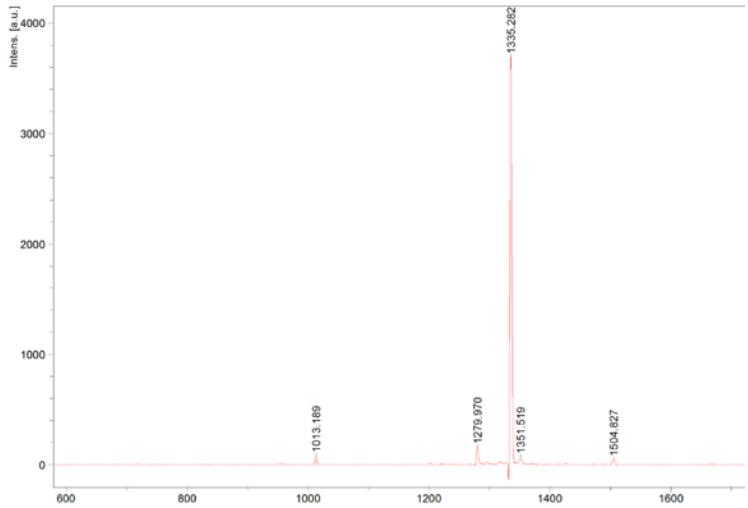


Fig. S36 MALDI-TOF MS of Cbz-Nme$_4$-Npe$_4$-tBu.

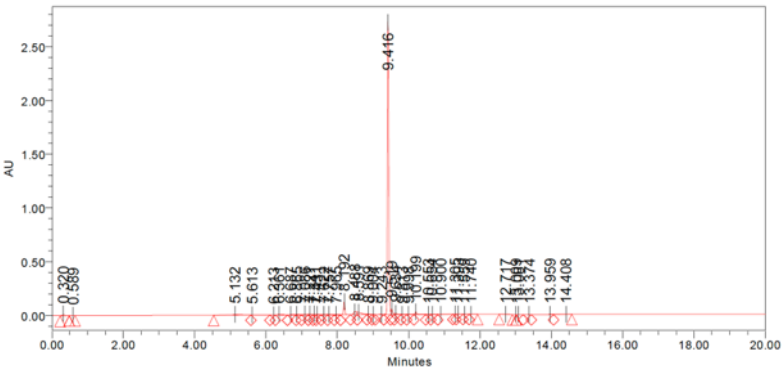


Fig. S37 UHPLC of Cbz-Nme$_4$-Npe$_4$-tBu.

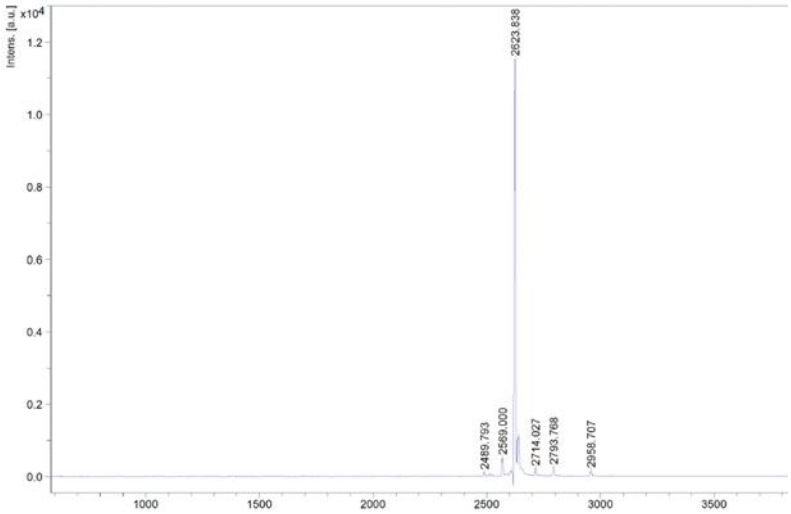


Fig. S38 MALDI-TOF MS of Cbz-Nme$_4$-Npe$_{12}$-tBu.

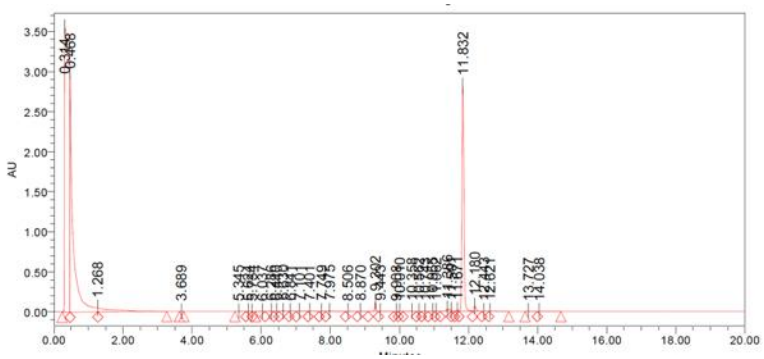


Fig. S39 UHPLC of Cbz-Nme$_4$-Npe$_{12}$-tBu.

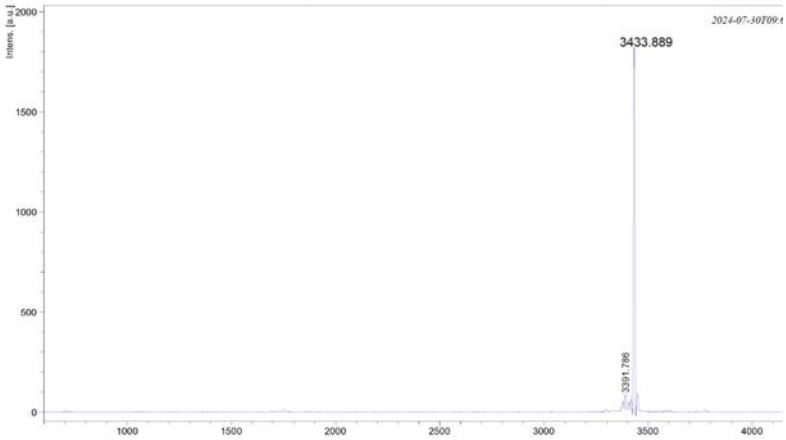


Fig. S40 MALDI-TOF MS of Cbz-Ndc$_8$-Nte$_8$-tBu.

5.3 Sequence-defined periodic and aperiodic peptoids

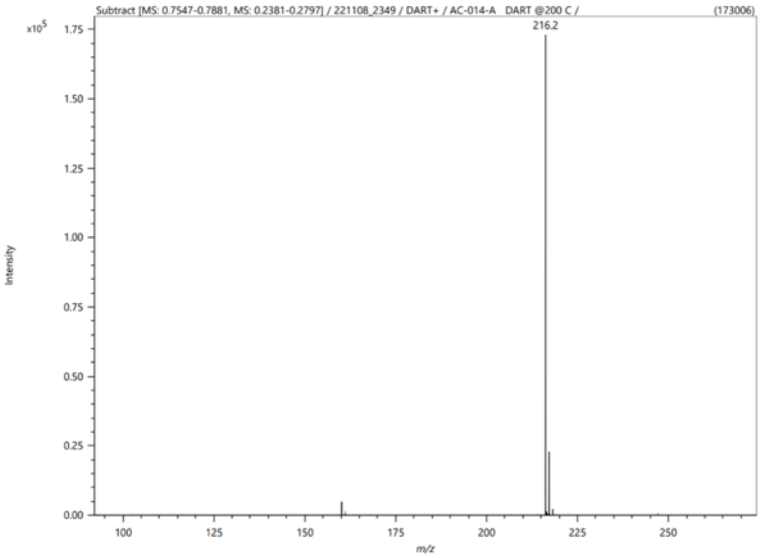


Fig. S41 MALDI-TOF MS of Nhx-tBu.

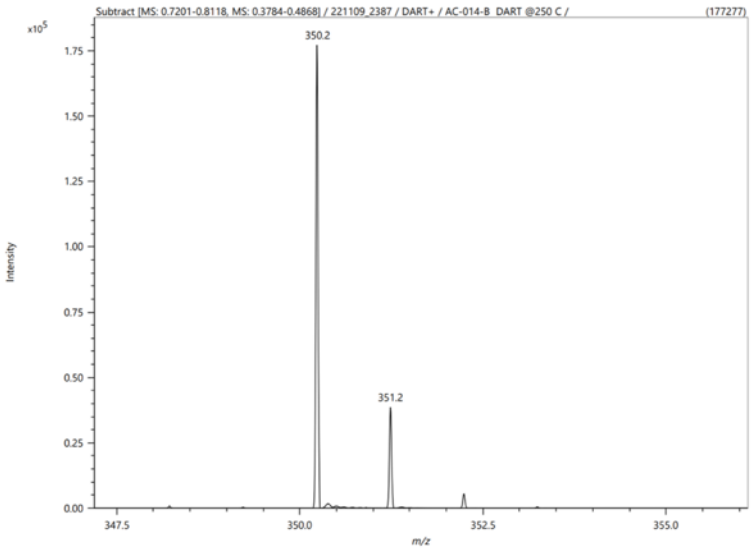


Fig. S42 DART-MS of Cbz-Nhx-tBu.

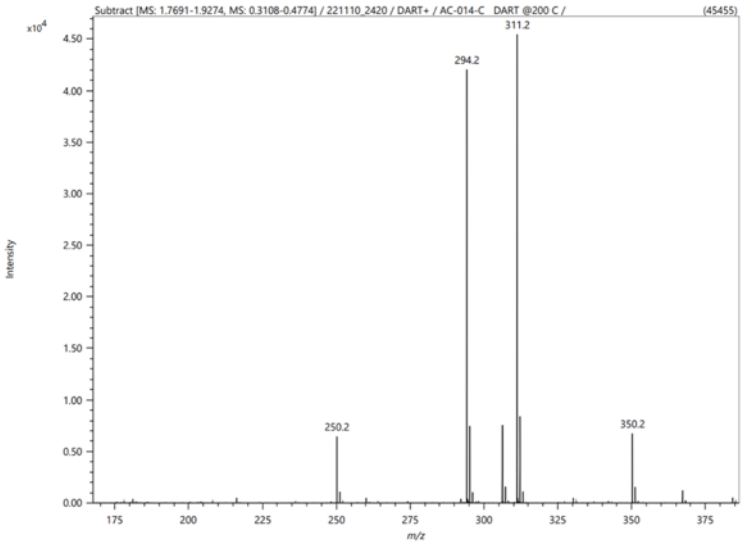


Fig. S43 DART-MS of Cbz-Nhx.

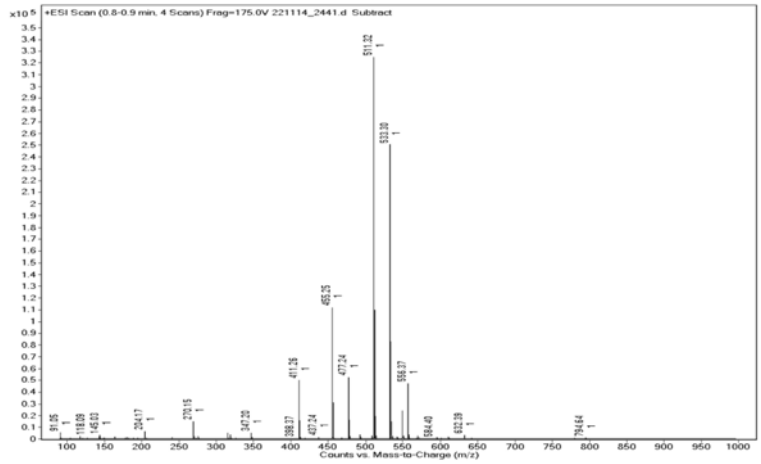


Fig. S44 HRMS of Cbz-Nhx-Npe-tBu.

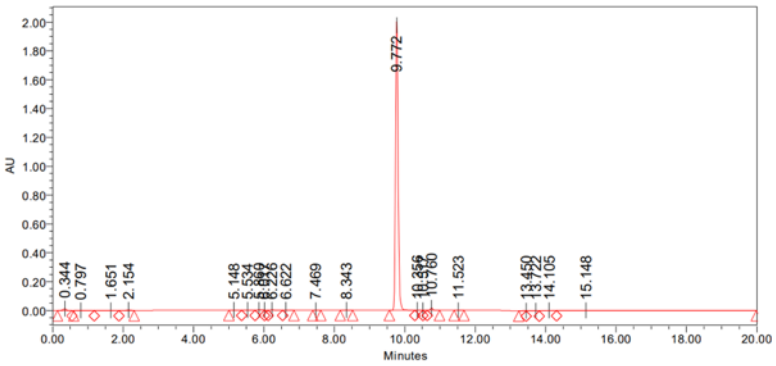


Fig. S45 UHPLC of Cbz-Nhx-Npe-tBu.

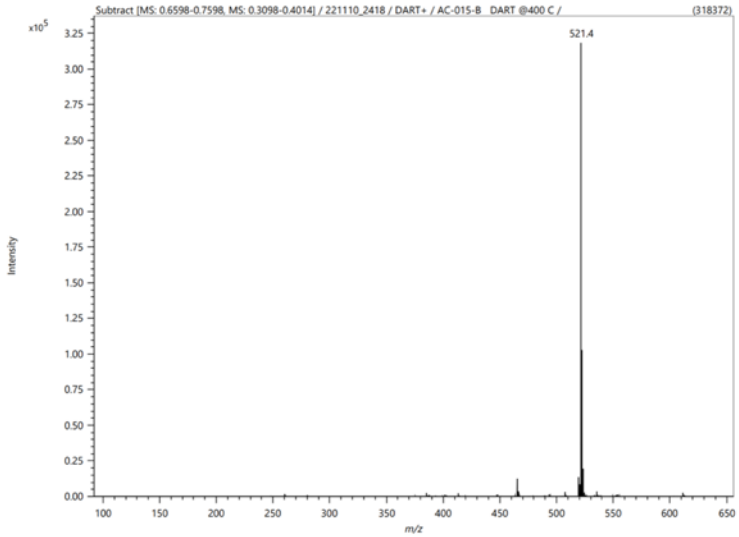


Fig. S46 DART-MS of Cbz-Ndc-Nme-tBu.

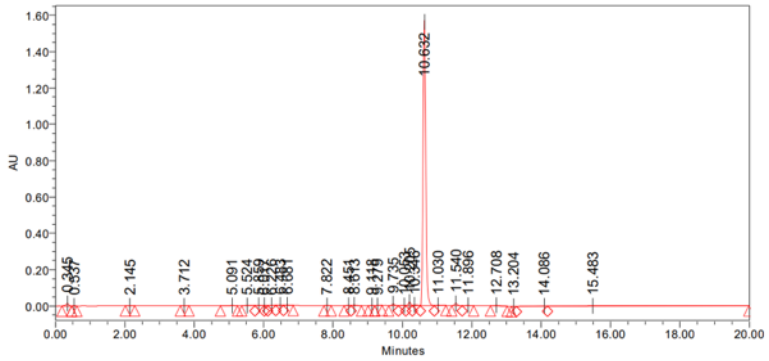


Fig. S47 UHPLC of Cbz-Ndc-Nme-tBu.

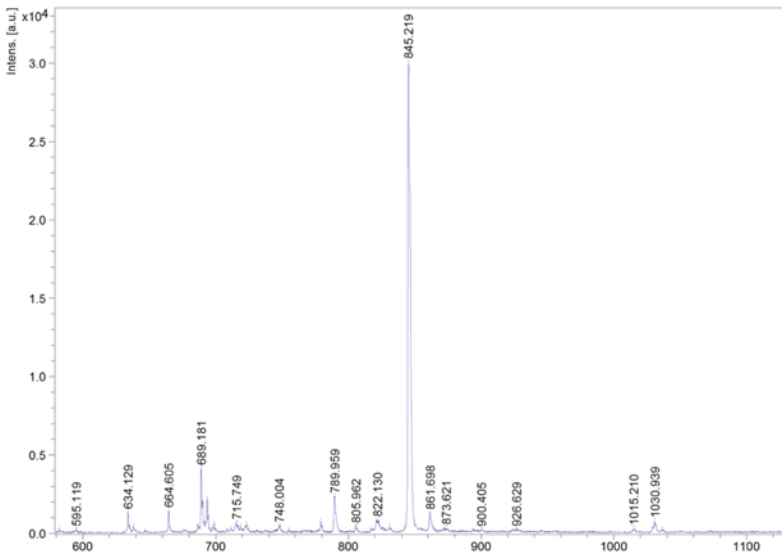


Fig. S48 MALDI-TOF MS of Cbz-Nhx-Npe-Ndc-Nme-tBu.

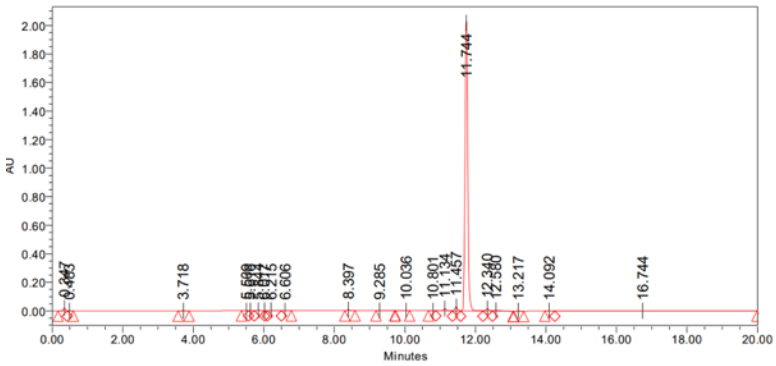


Fig. S49 UHPLC of Cbz-Nhx-Npe-Ndc-Nme-tBu.

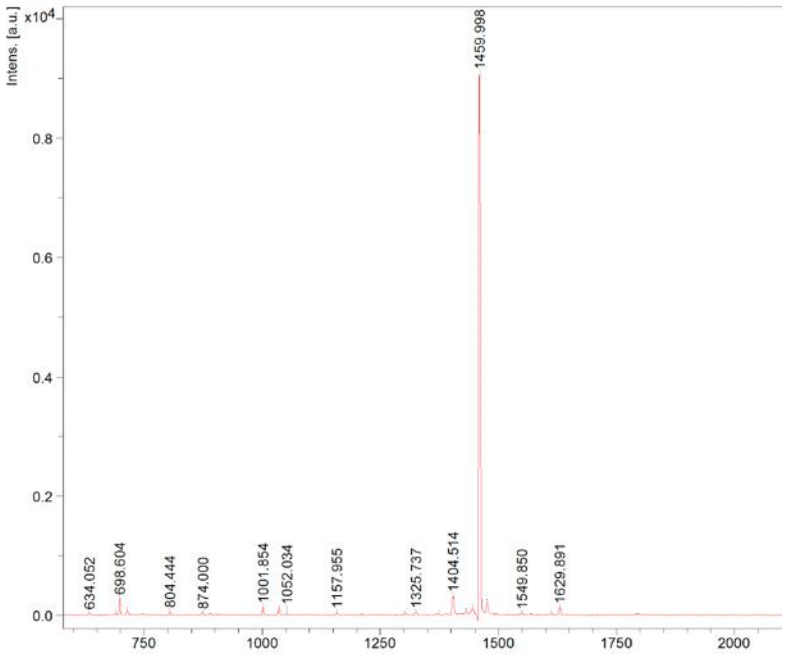


Fig. S50 MALDI-TOF MS of Cbz-(Nhx-Npe-Ndc-Nme)$_2$-tBu.

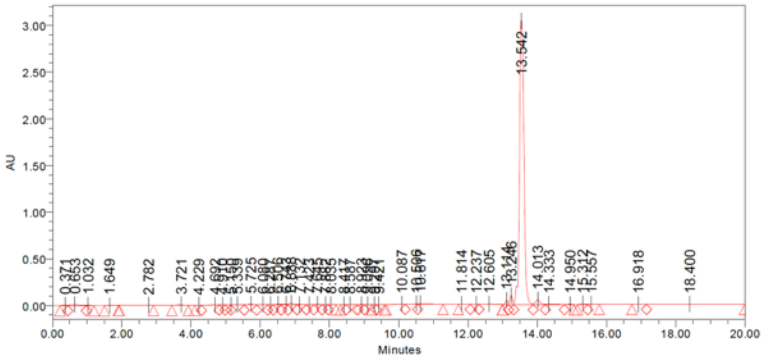


Fig. S51 UHPLC of Cbz-(Nhx-Npe-Ndc-Nme)$_2$-tBu.

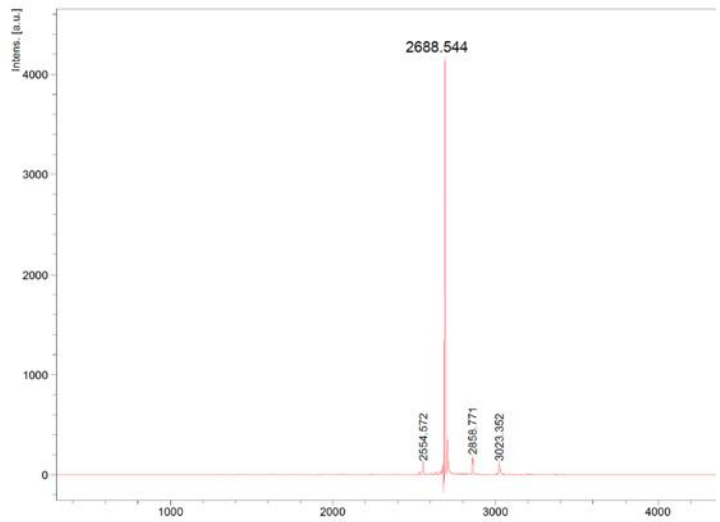


Fig. S52 MALDI-TOF MS of Cbz-(Nhx-Npe-Ndc-Nme)$_4$-tBu.

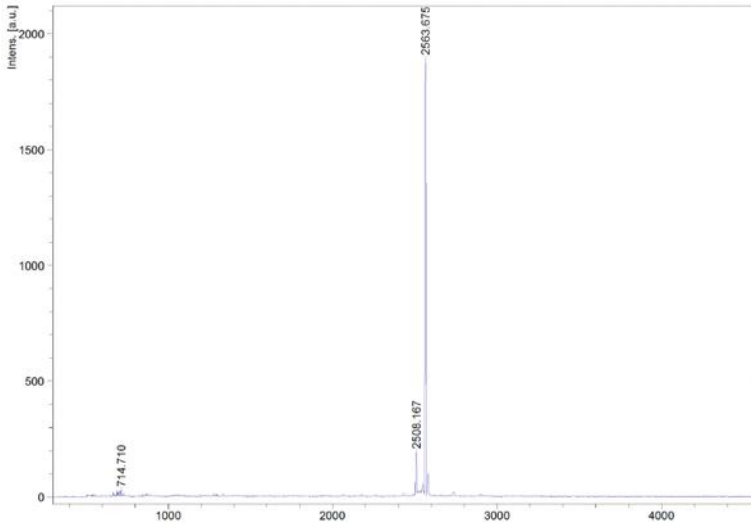


Fig. S53 MALDI-TOF MS of Cbz-Nme$_4$-Npe$_4$-(Nhx-Npe-Ndc-Nme)$_2$-tBu.

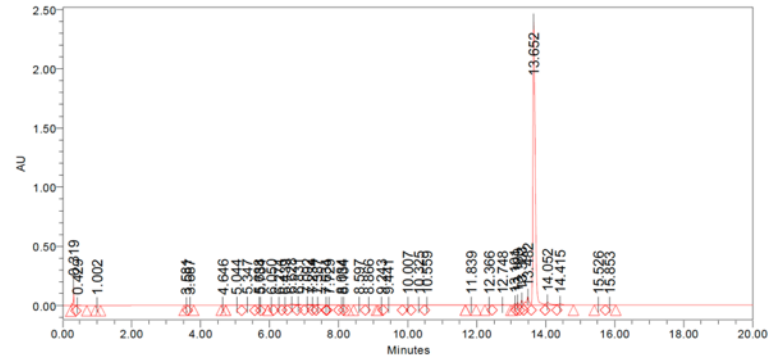


Fig. S54 UHPLC of Cbz-Nme$_4$-Npe$_4$-(Nhx-Npe-Ndc-Nme)$_2$-tBu.

5.4 Stereo-defined alternating peptoids

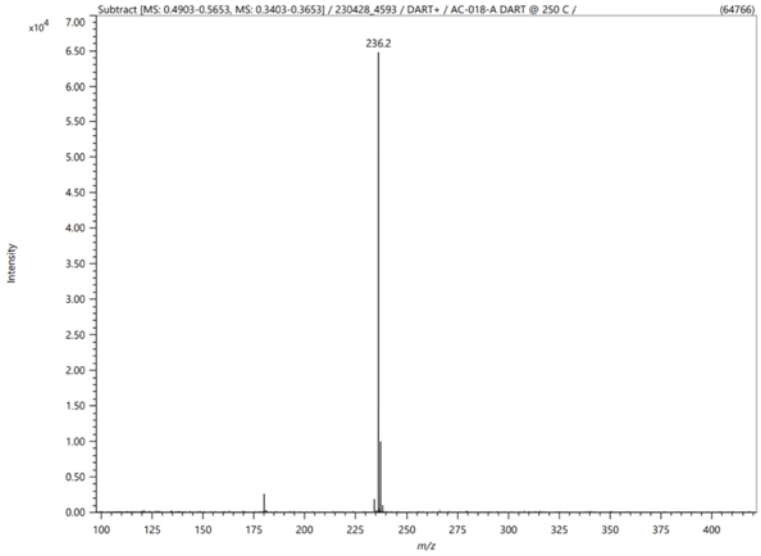


Fig. S55 DART-MS of Nrpe-tBu.

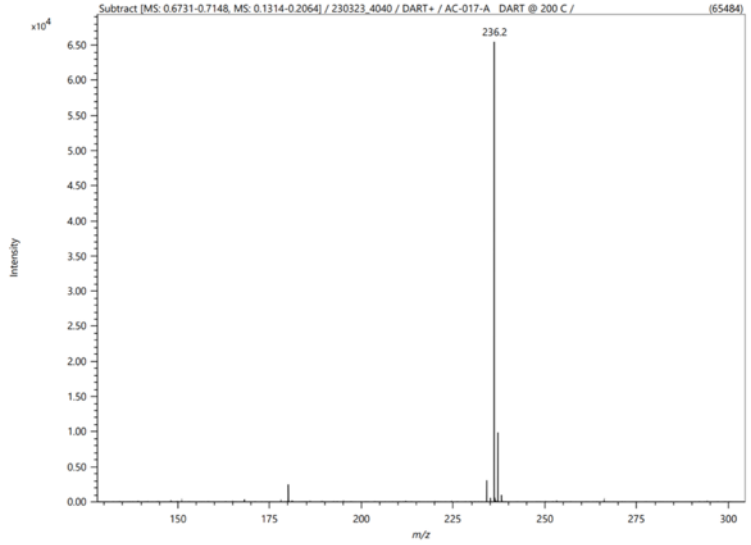


Fig. S56 DART-MS of Nspe-tBu.

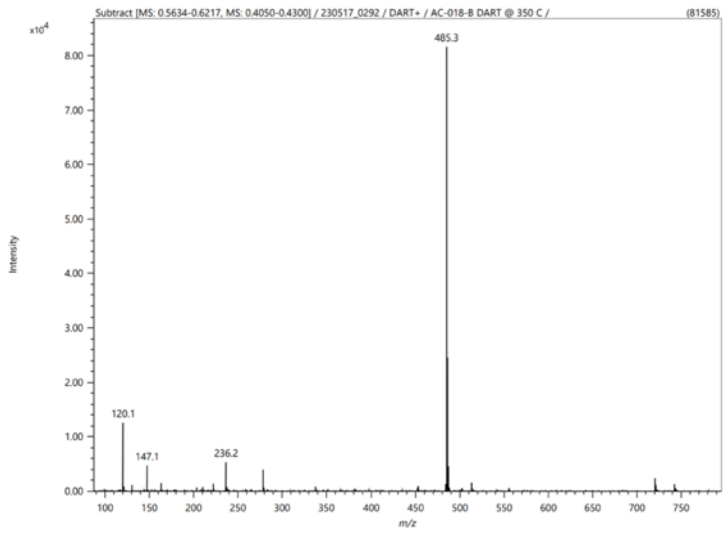


Fig. S57 DART-MS of Cbz-Nme-Nrpe-tBu.

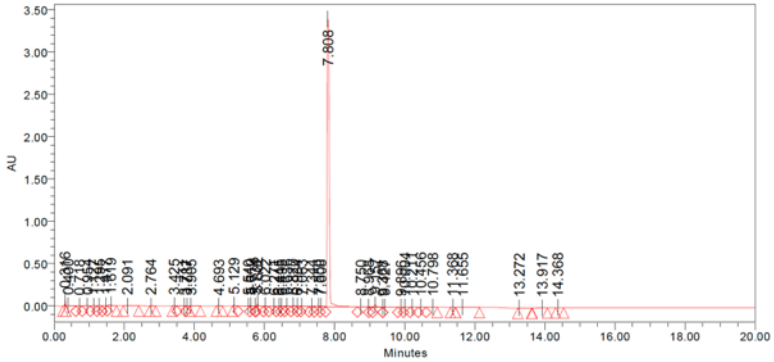


Fig. S58 UHPLC of Cbz-Nme-Nrpe-tBu.

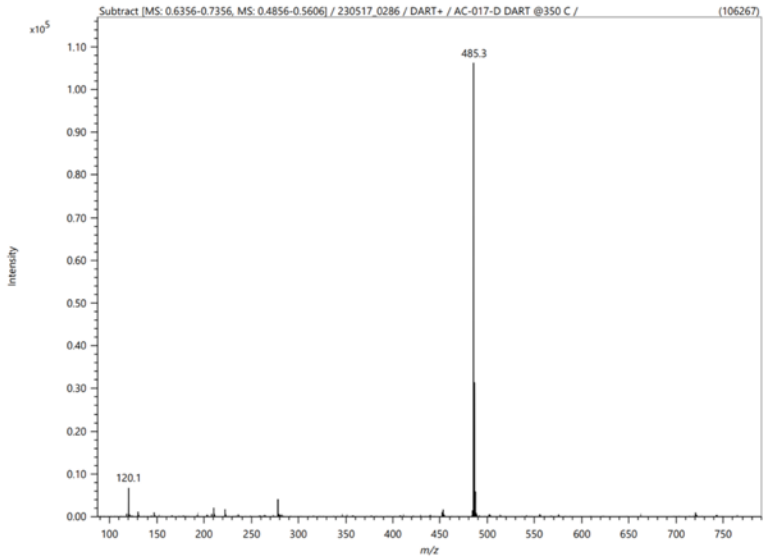


Fig. S59 DART-MS of Cbz-Nme-Nspe-tBu.

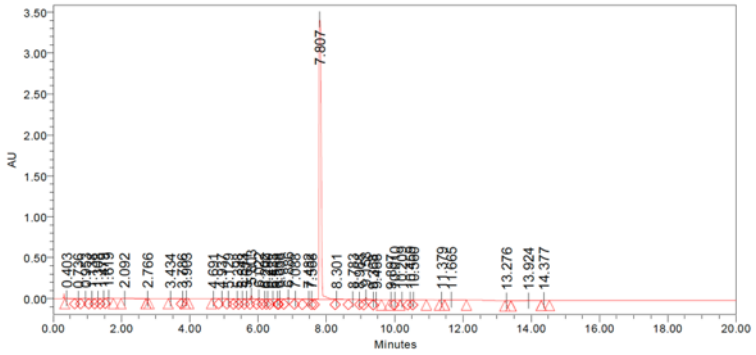


Fig. S60 UHPLC of Cbz-Nme-Nspe-tBu.

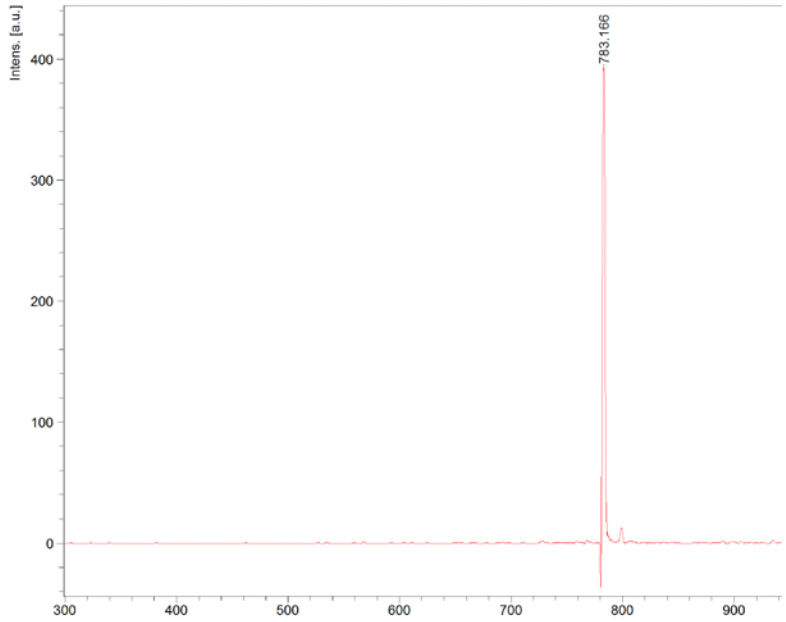


Fig. S61 MALDI-TOF MS of Cbz-(Nme-Nrpe)$_2$-tBu.

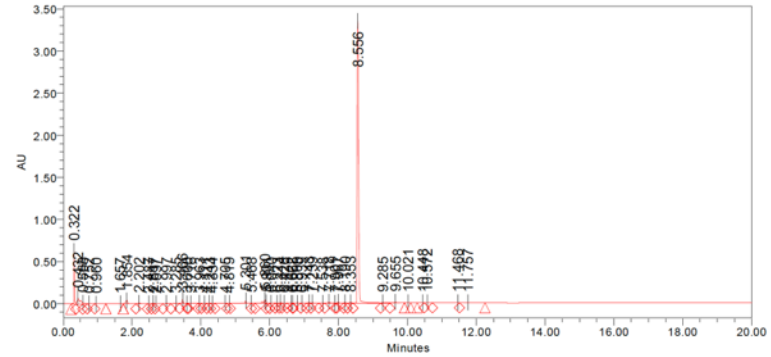


Fig. S62 UHPLC of Cbz-(Nme-Nrpe)$_2$-tBu.

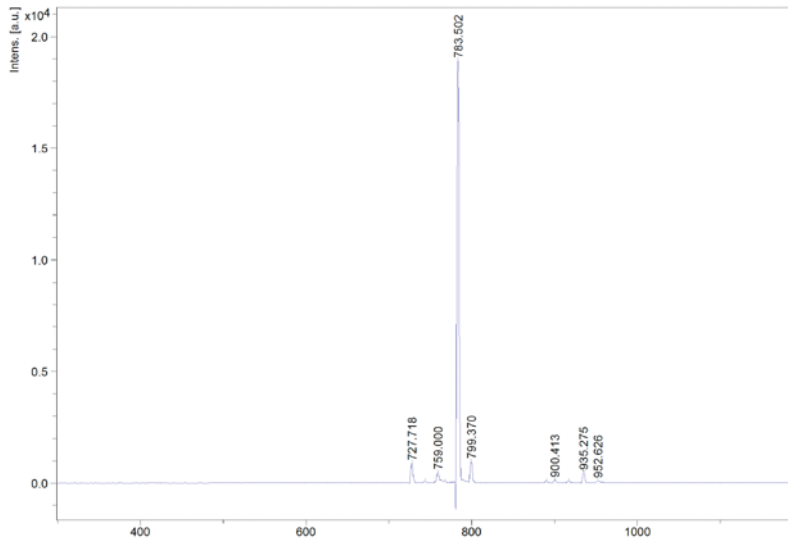


Fig. S63 MALDI-TOF MS of Cbz-(Nme-Nspe)$_2$-tBu.

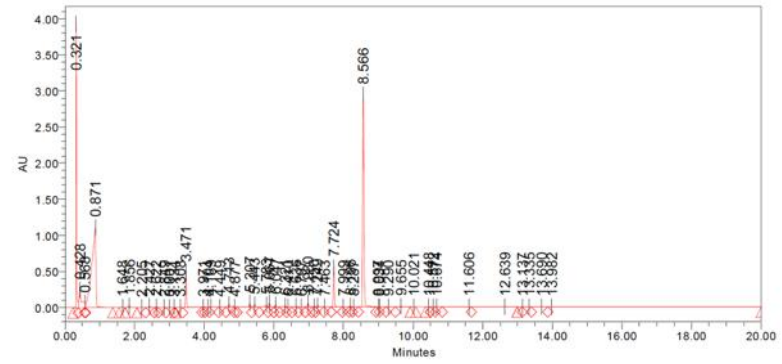


Fig. S64 UHPLC of Cbz-(Nme-Nspe)$_2$-tBu.

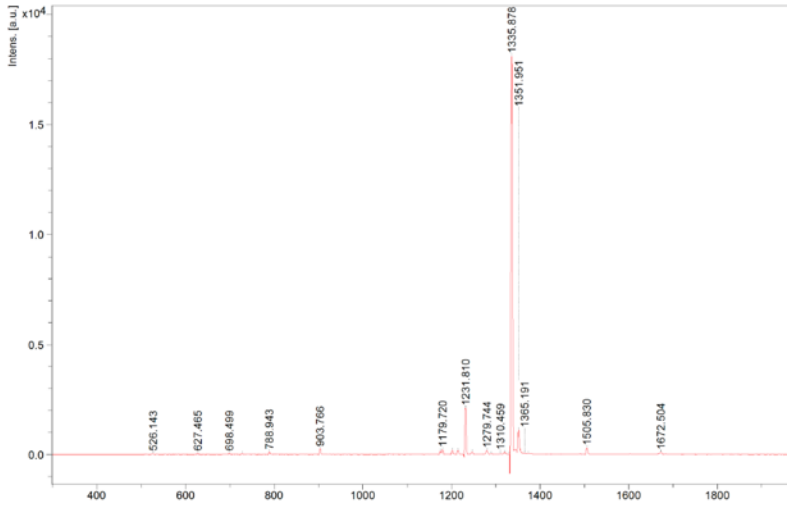


Fig. S65 MALDI-TOF MS of Cbz-(Nme-Nrpe)$_4$-tBu.

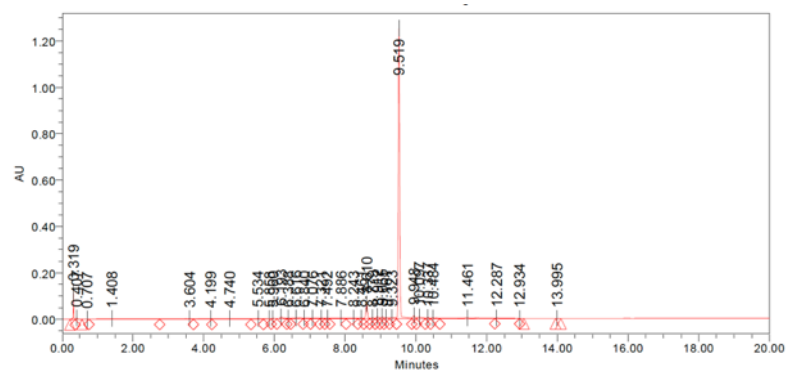


Fig. S66 UHPLC of Cbz-(Nme-Nrpe)$_4$-tBu.

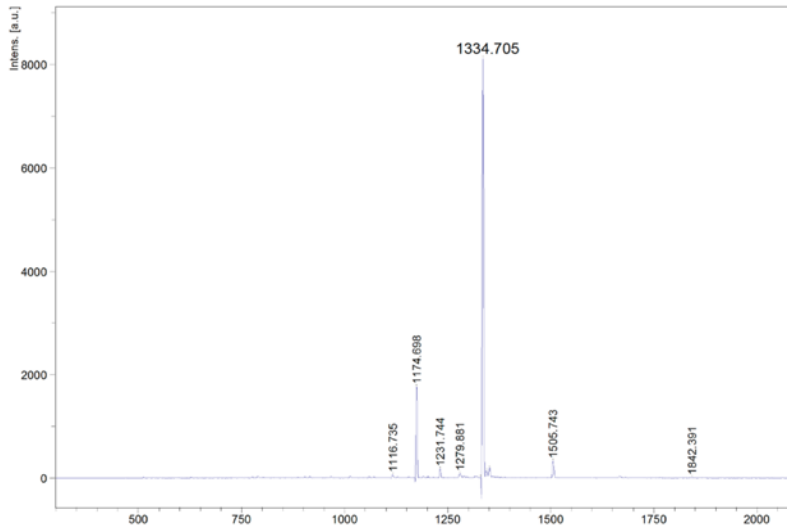


Fig. S67 MALDI-TOF MS of Cbz-(Nme-Nspe)$_4$-tBu.

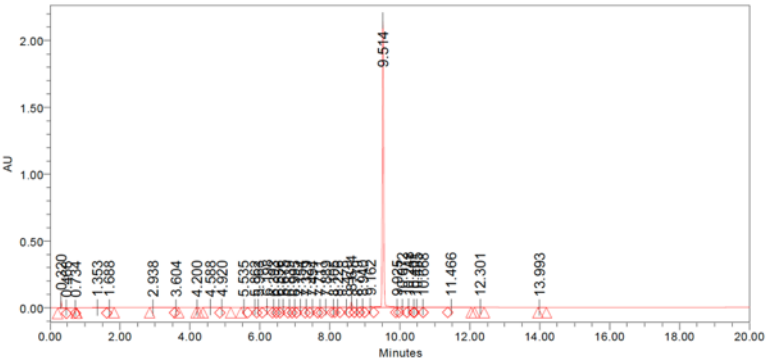


Fig. S68 UHPLC of Cbz-(Nme-Nspe)$_4$-tBu.

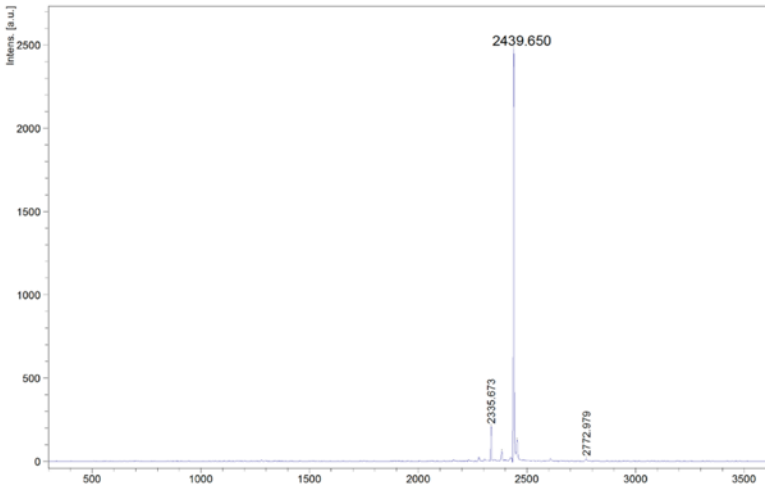


Fig. S69 MALDI-TOF MS of Cbz-(Nme-Nrpe)$_4$-(Nme-Nspe)$_4$-tBu.

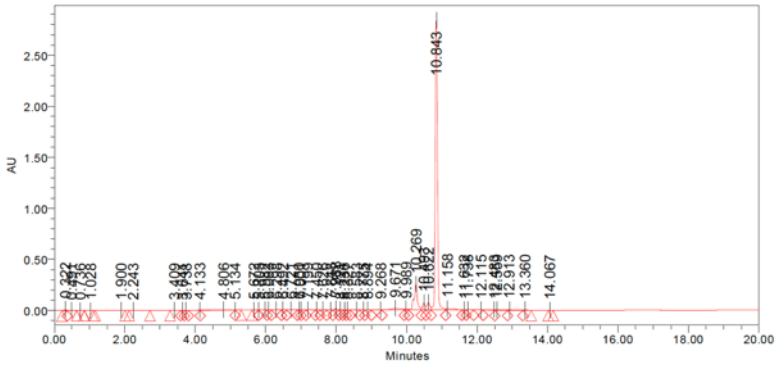


Fig. S70 UHPLC of Cbz-(Nme-Nrpe)$_4$-(Nme-Nspe)$_4$-tBu.

5.5 Post-IEG modifications with thiol-ene and CuAAC click reactions

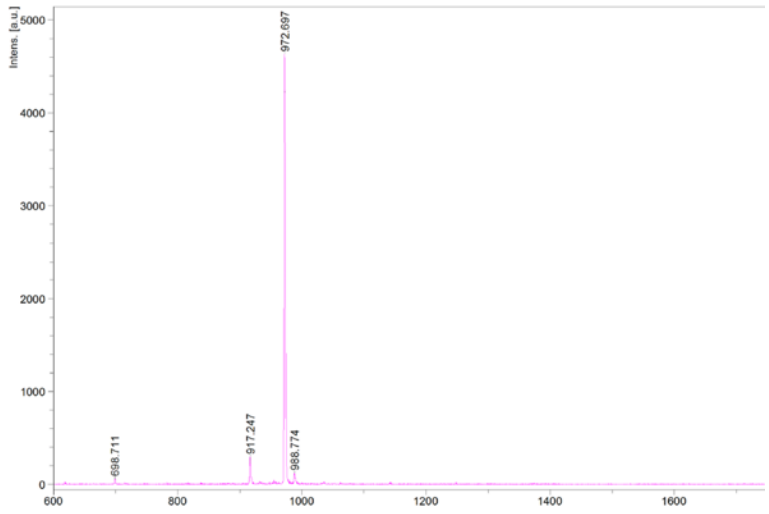


Fig. S71 MALDI-TOF MS of Cbz-Npe$_4$-Nall-tBu.

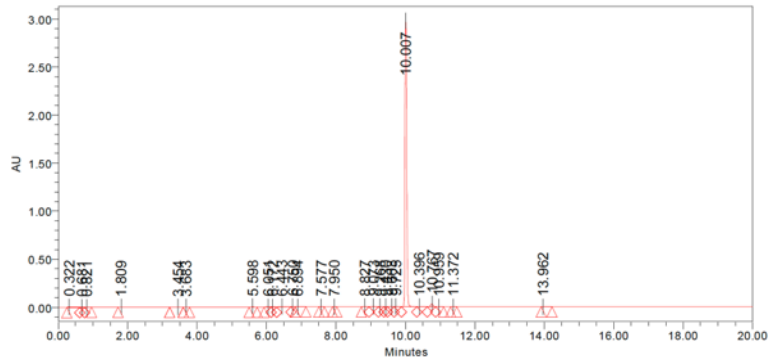


Fig. S72 UHPLC of Cbz-Npe4-Nall-tBu.

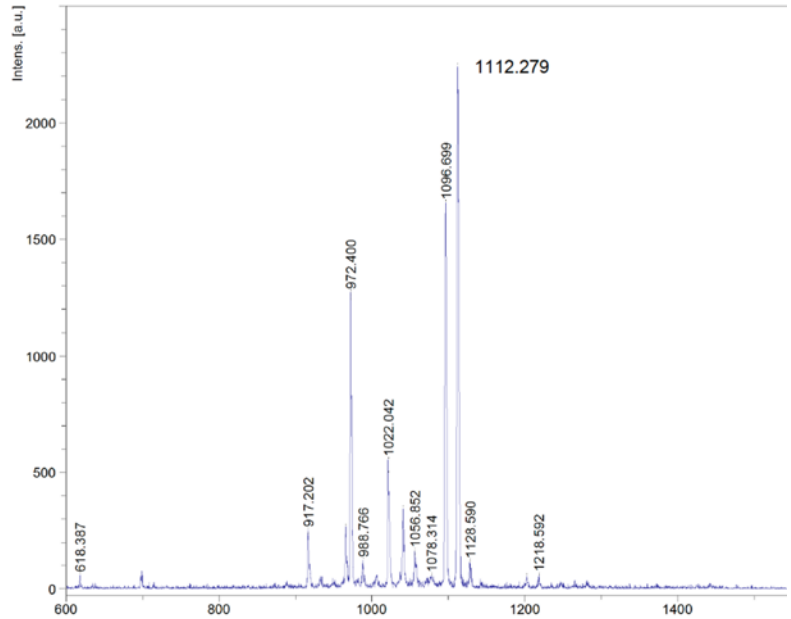


Fig. S73 MALDI-TOF MS of Cbz-Npe4-Nthio-tBu.

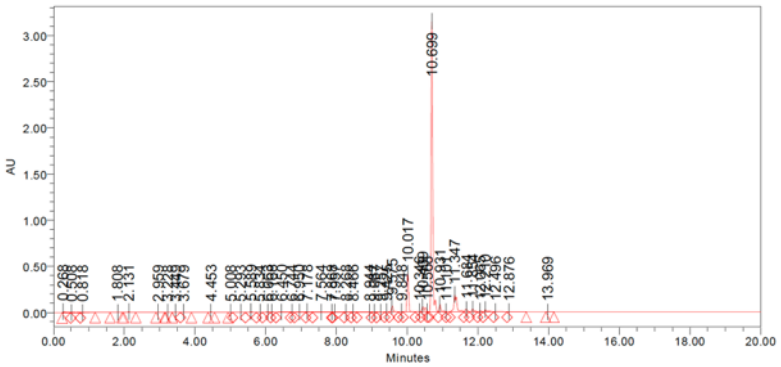


Fig. S74 UHPLC of Cbz-Npe4-Nthio-tBu.

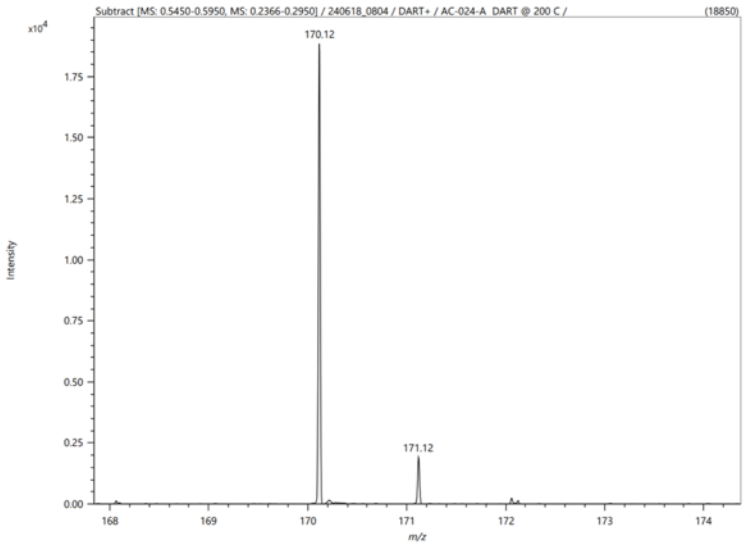


Fig. S75 DART-MS of Nalk-tBu.

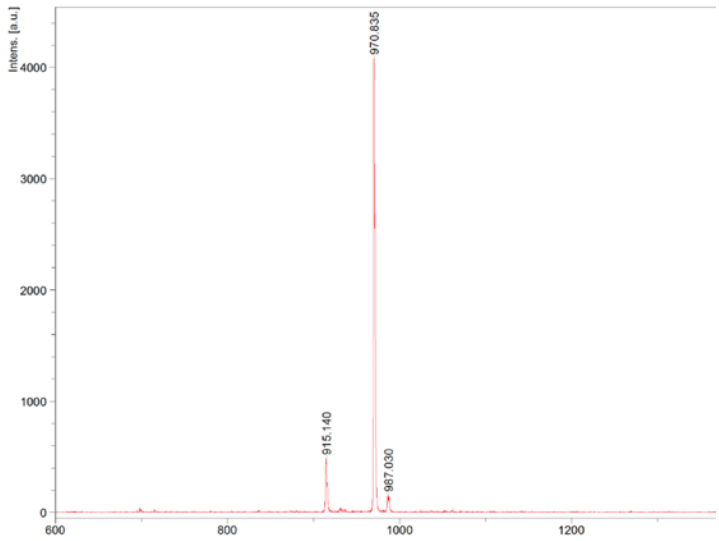


Fig. S76 MALDI-TOF MS of Cbz-Npe$_4$-Nalk-tBu.

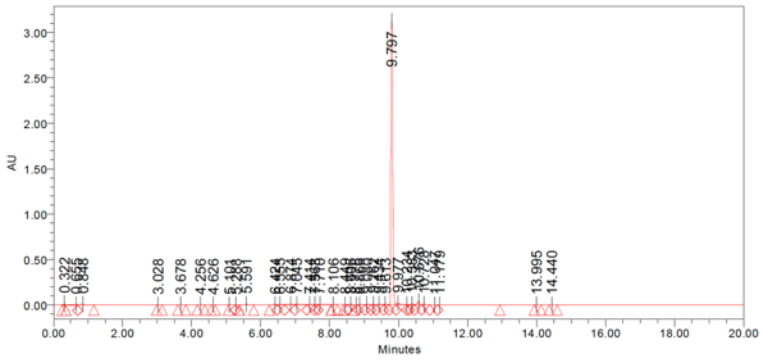


Fig. S77 UHPLC of Cbz-Npe$_4$-Nalk-tBu.

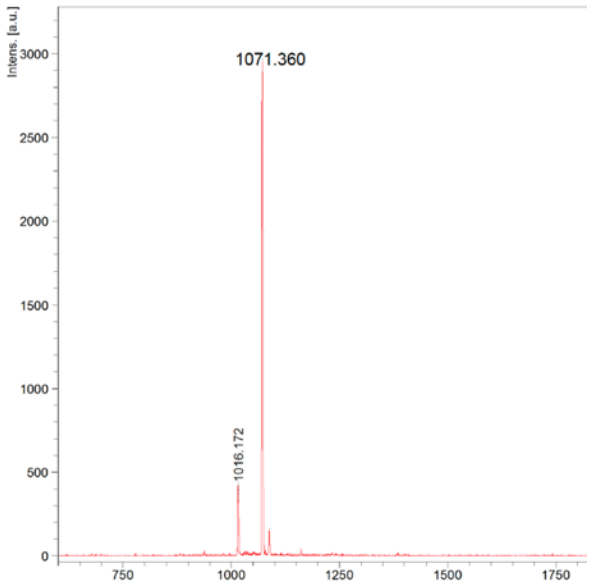


Fig. S78 MALDI-TOF MS of Cbz-Npe$_4$-Ntriazo-tBu.

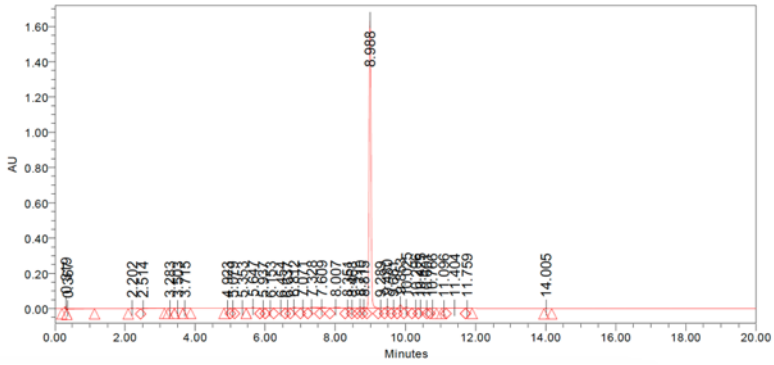


Fig. S79 UHPLC of Cbz-Npe$_4$-Ntriazo-tBu.

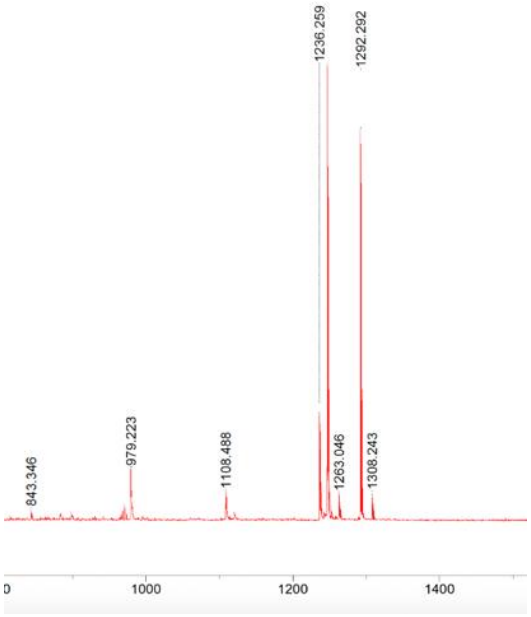


Fig. S80 MALDI-TOF MS of Cbz-Npe$_4$-Nalk-Npe$_2$-tBu.

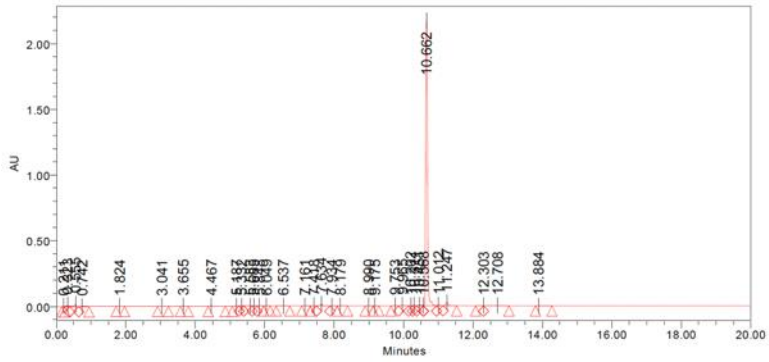


Fig. S81 UHPLC of Cbz-Npe$_4$-Nalk-Npe$_2$-tBu.

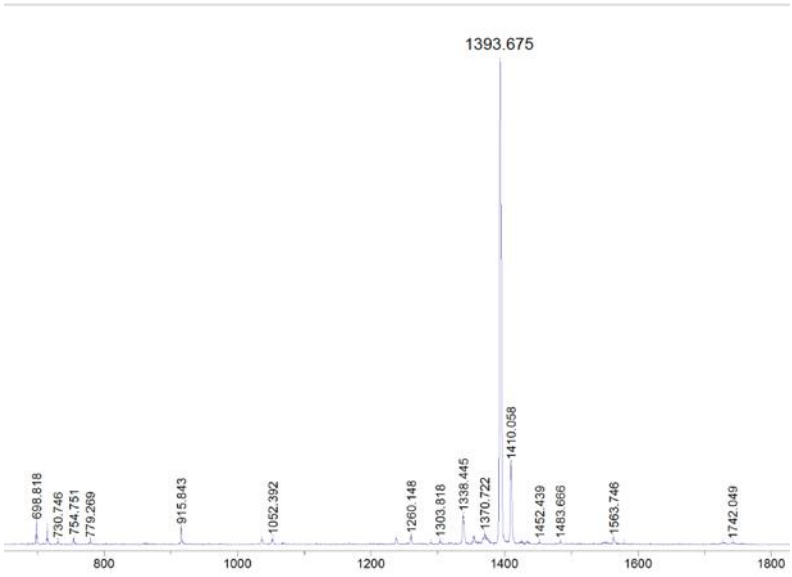


Fig. S82 MALDI-TOF MS of Cbz-Npe$_4$-Ntriazo-Npe$_2$-tBu.

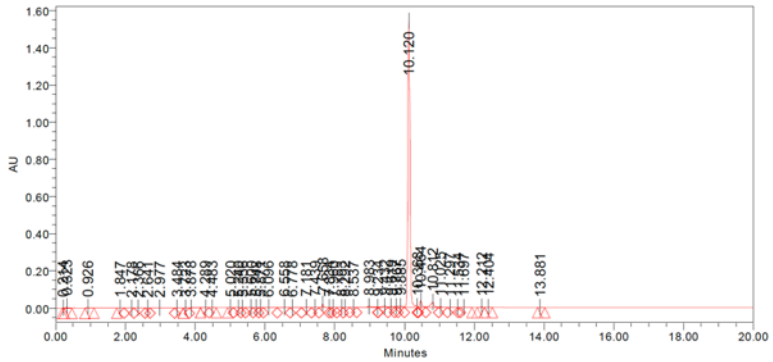


Fig. S83 UHPLC of Cbz-Npe$_4$-Ntriazo-Npe$_2$-tBu.

6. NMR spectra

6.1 Peptoid homopolymers

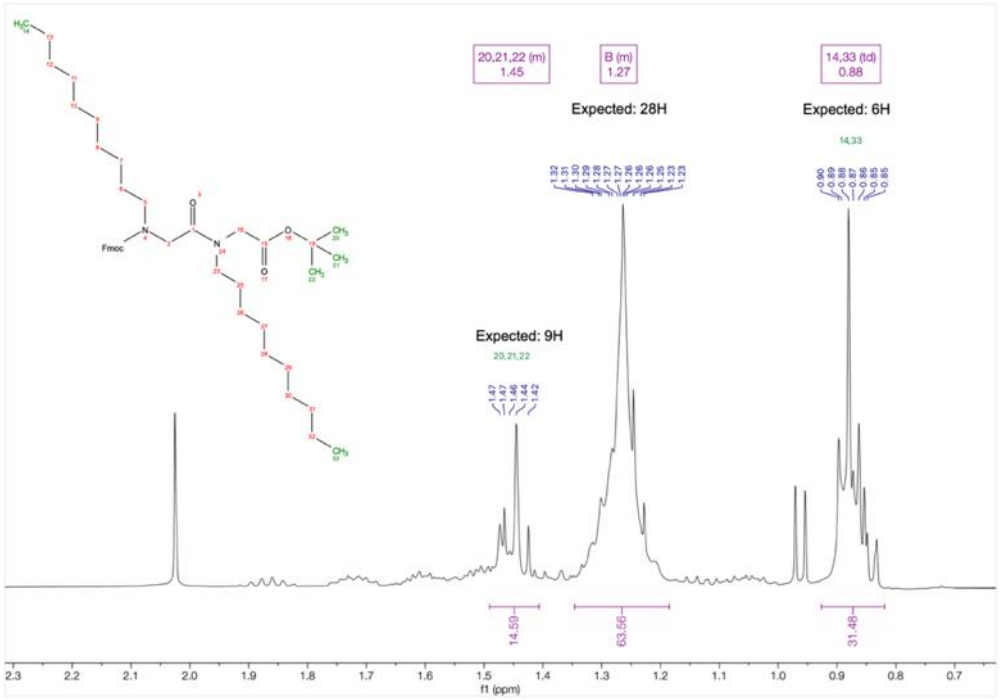


Fig. S84 [1]H-NMR of Ndc dimer with Fmoc protecting group showing uncontrolled reaction after coupling.

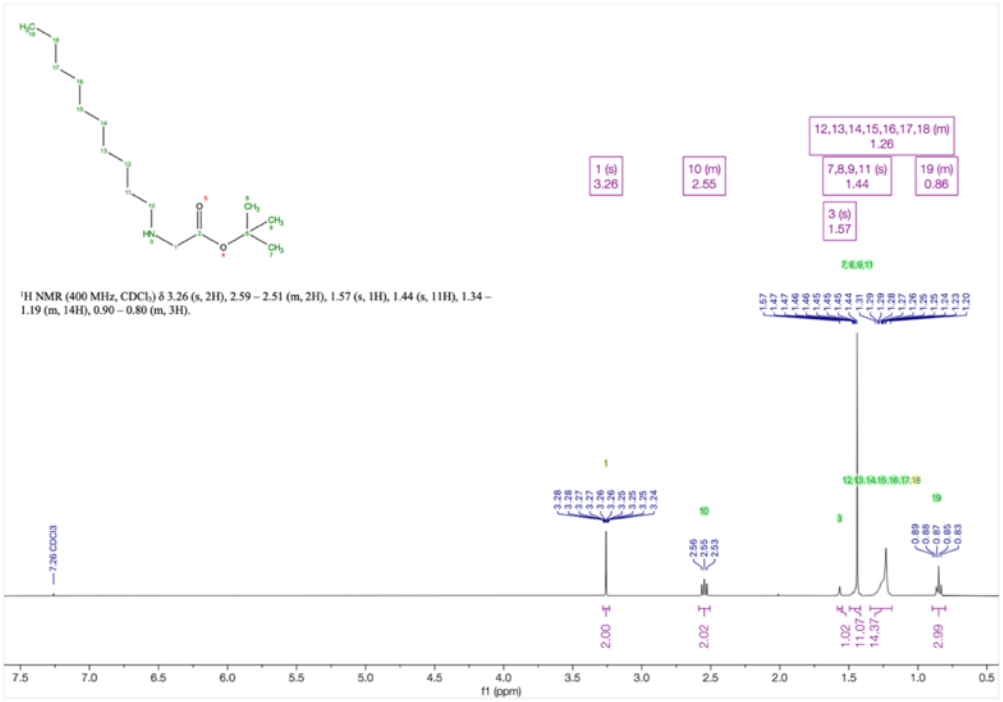


Fig. S85 [1]H NMR of Ndc-tBu.

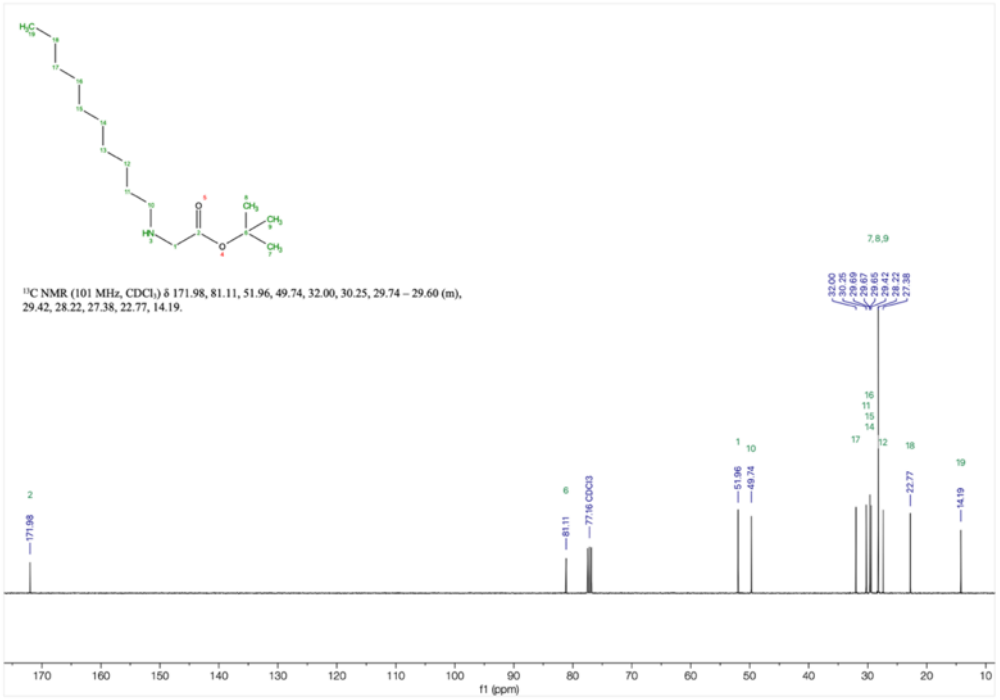


Fig. S86 ^{13}C NMR of Ndc-tBu.

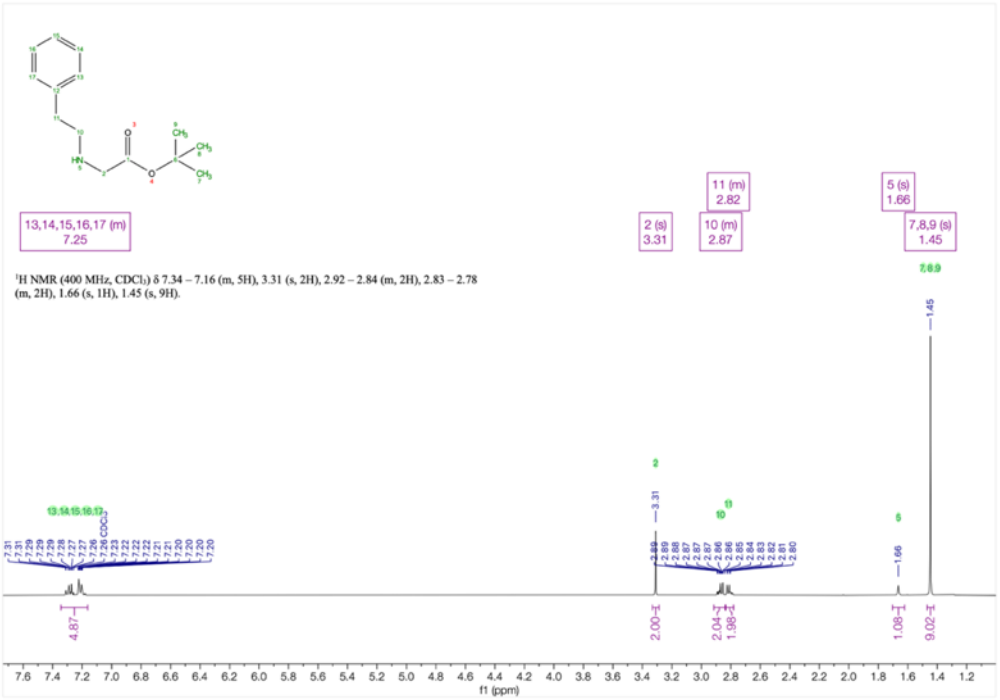


Fig. S87 ^{1}H NMR of Npe-tBu.

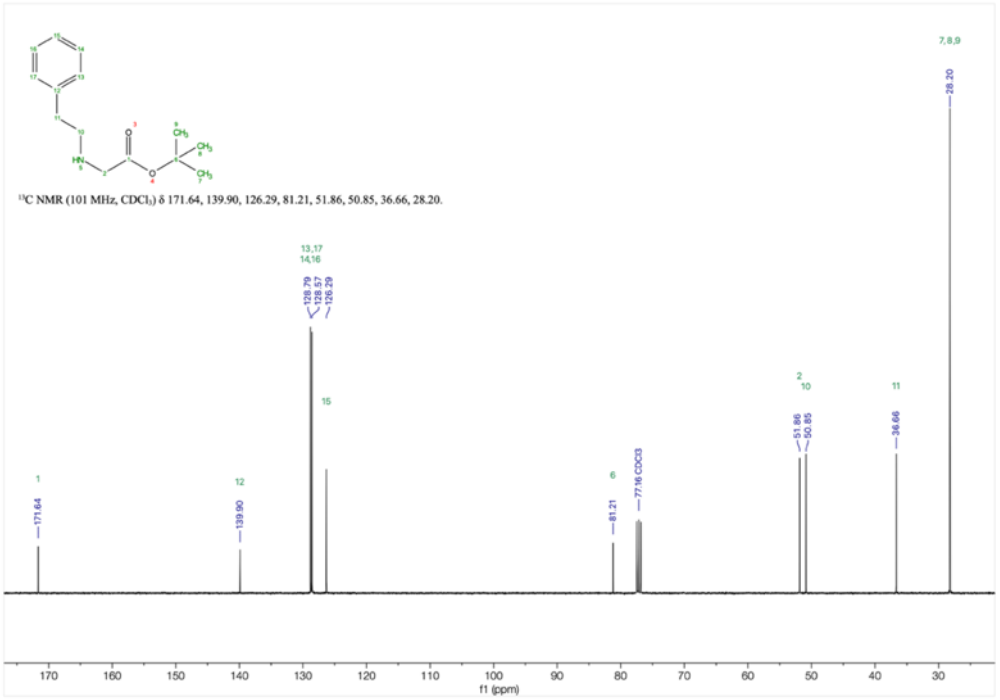


Fig. S88 ^{13}C NMR of Npe-tBu.

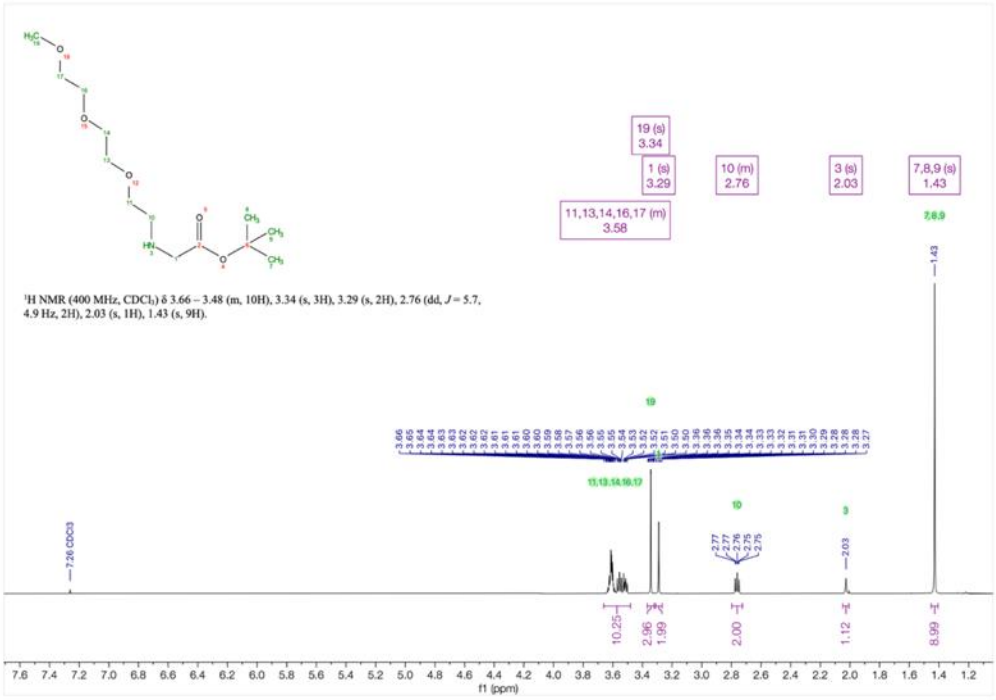


Fig. S89 ^{1}H NMR of Nte-tBu.

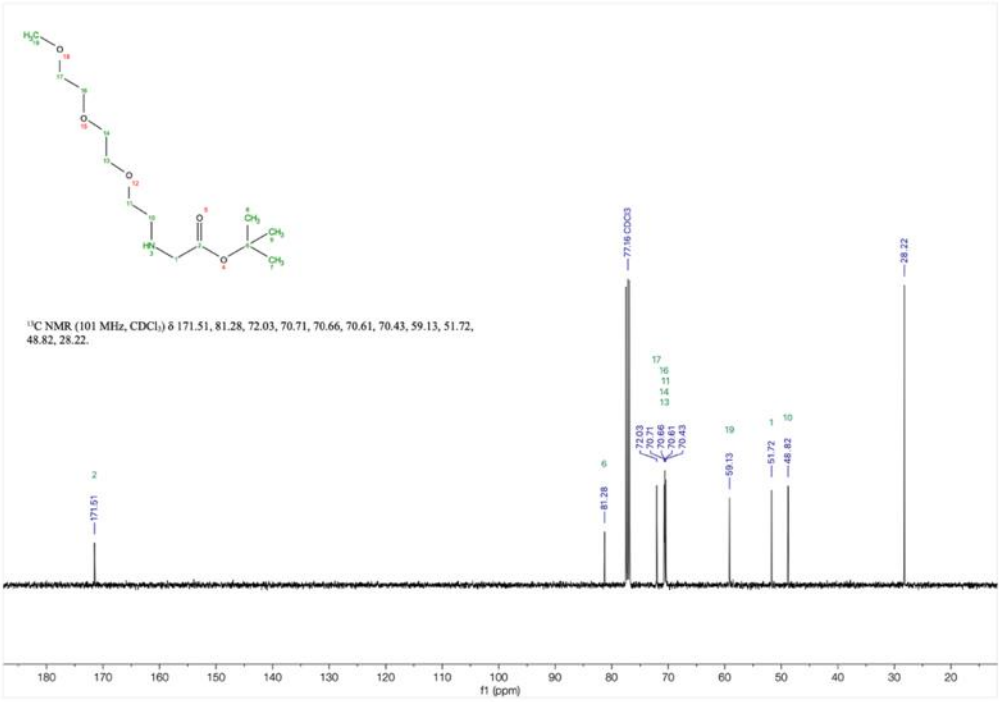


Fig. S90 ^{13}C NMR of Nte-tBu.

Fig. S91 ^{1}H NMR of Nme-tBu.

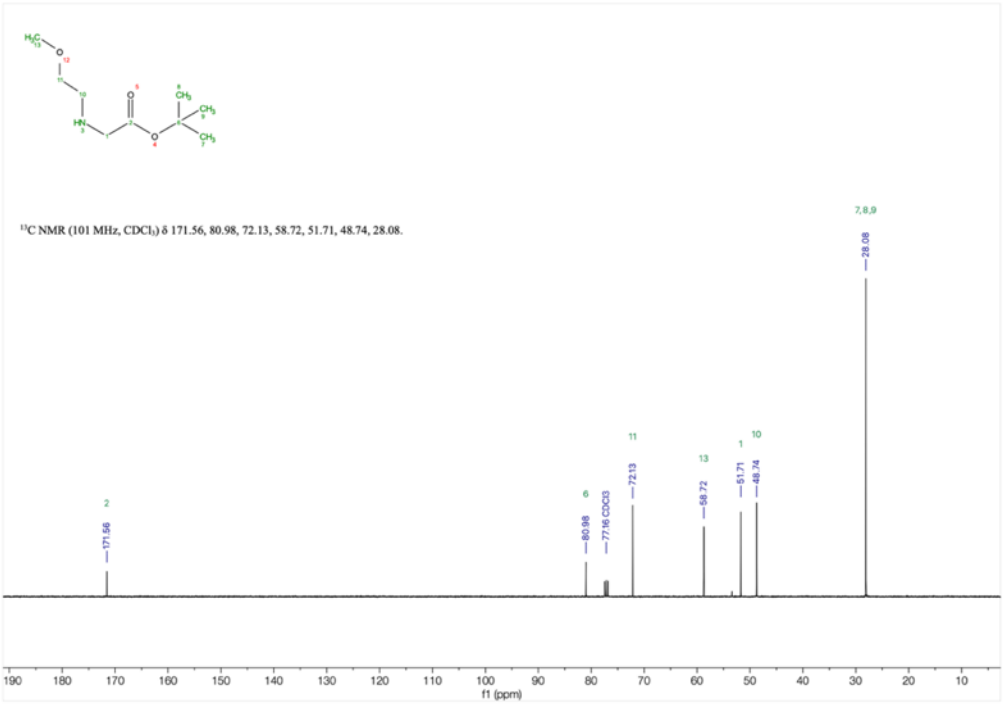


Fig. S92 ^{13}C NMR of Nme-tBu.

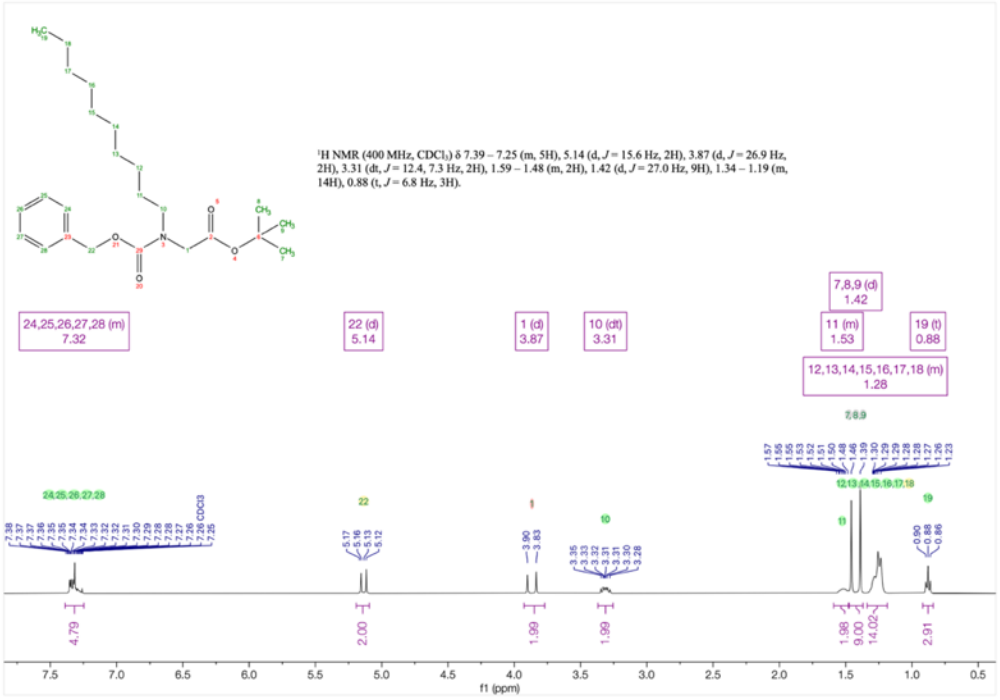


Fig. S93 ^{1}H NMR of Cbz-Ndc-tBu.

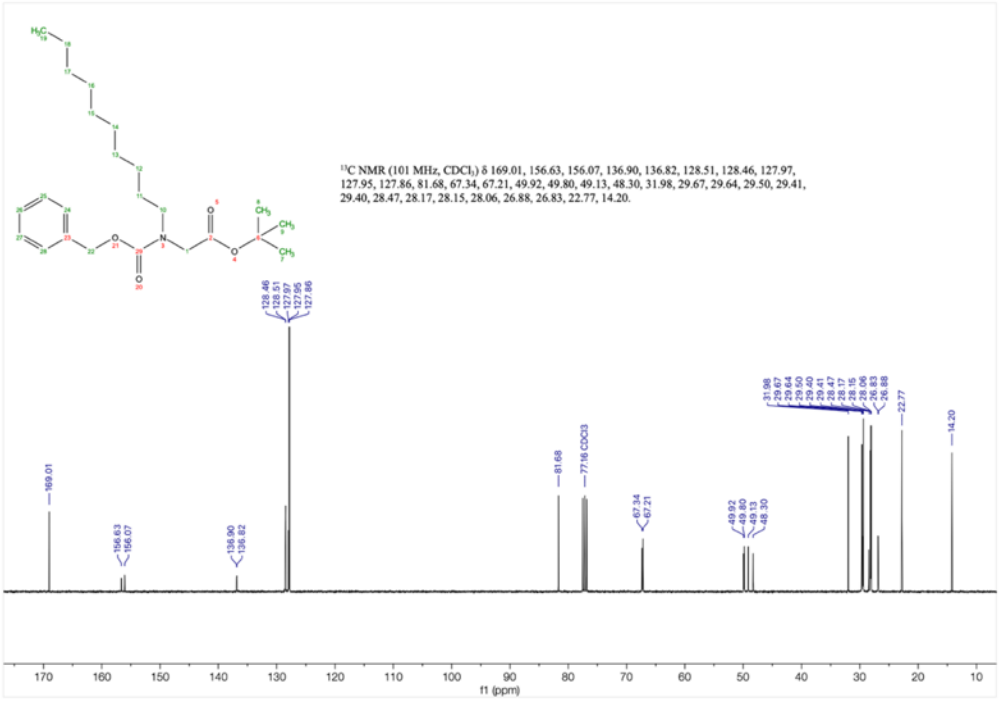


Fig. S94 ^{13}C NMR of Cbz-Ndc-tBu.

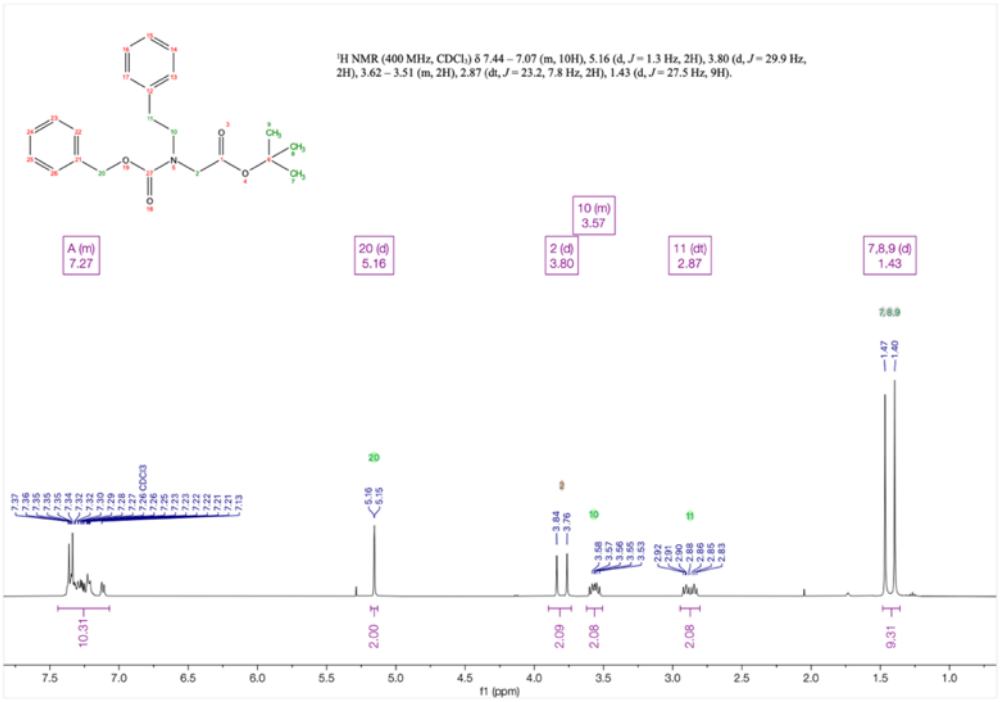


Fig. S95 ^{1}H NMR of Cbz-Npe-tBu.

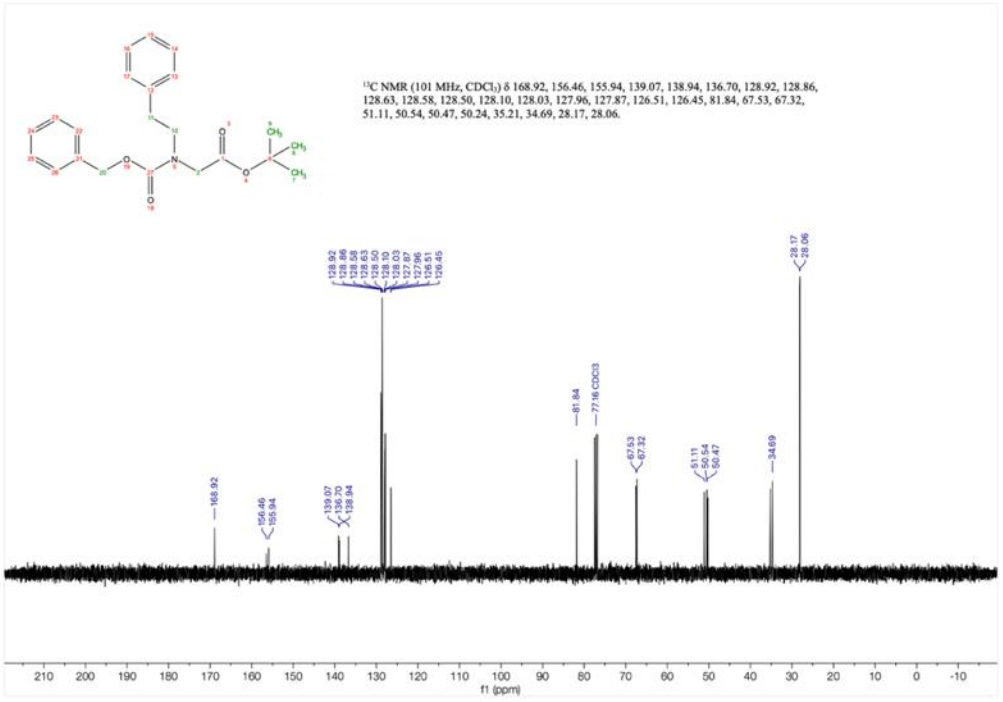


Fig. S96 ^{13}C NMR of Cbz-Npe-tBu.

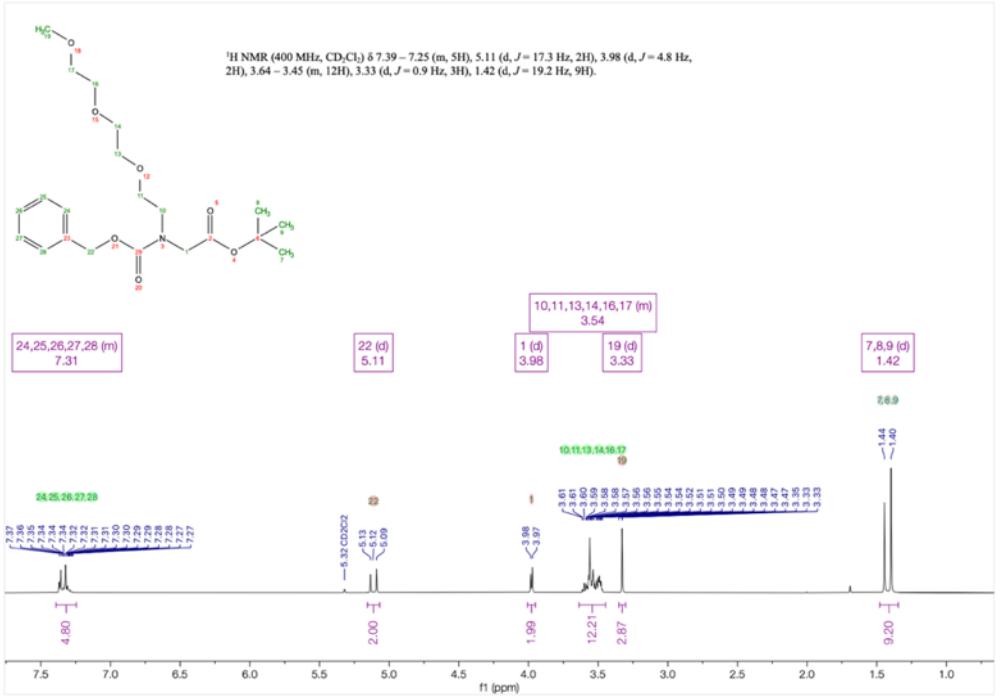


Fig. S97 ^{1}H NMR of Cbz-Nte-tBu.

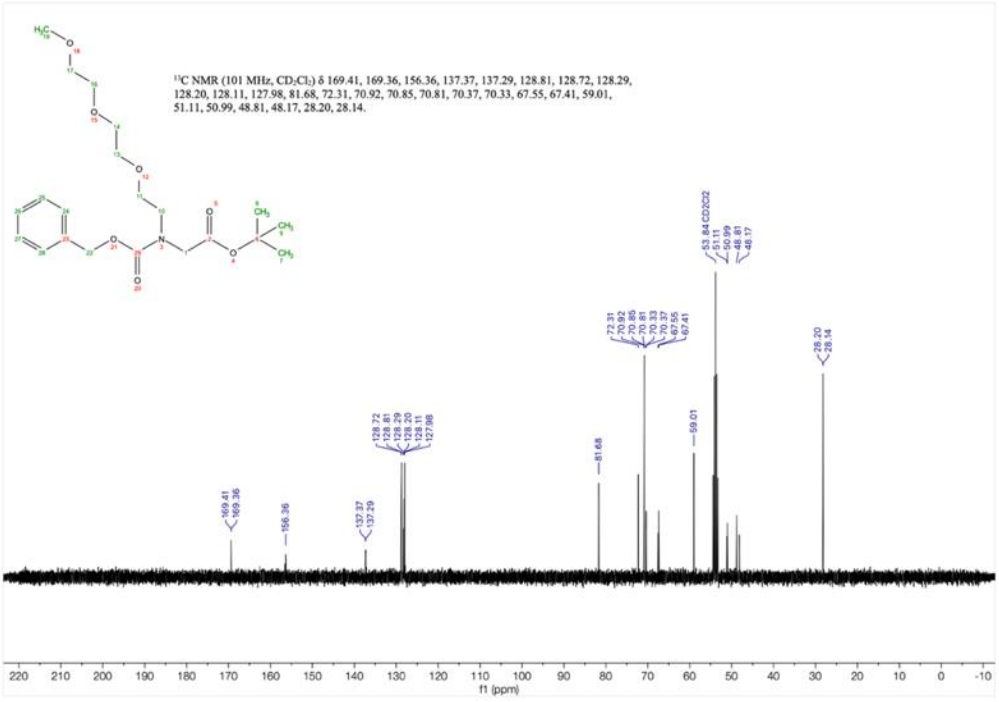


Fig. S98 ^{13}C NMR of Cbz-Nte-tBu.

Fig. S99 ^{1}H NMR of Cbz-Nme-tBu.

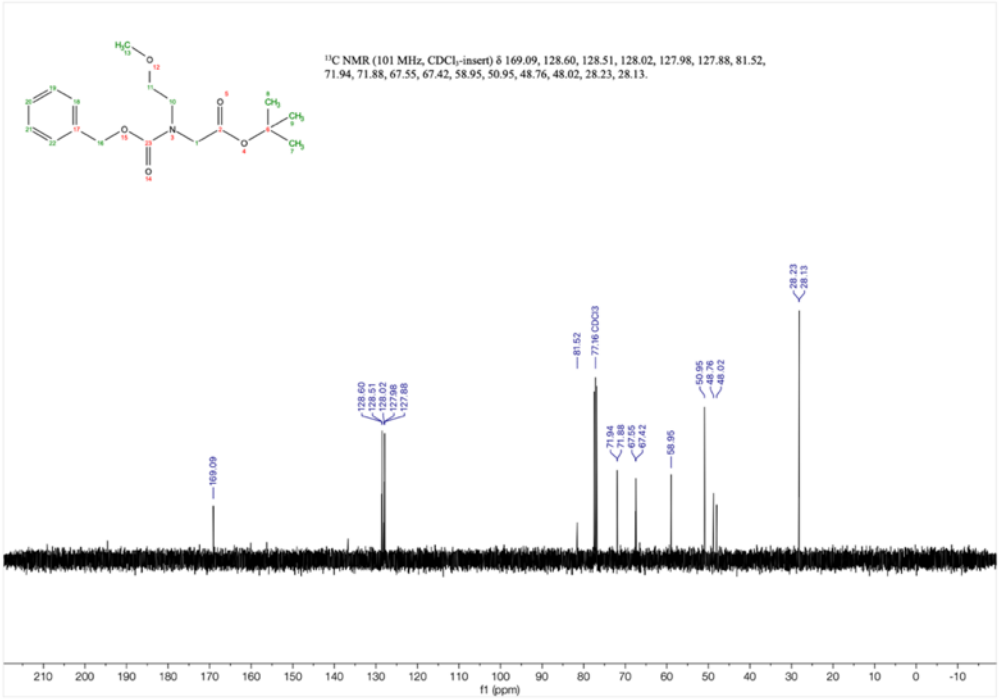


Fig. S100 ^{13}C NMR of Cbz-Nme-tBu.

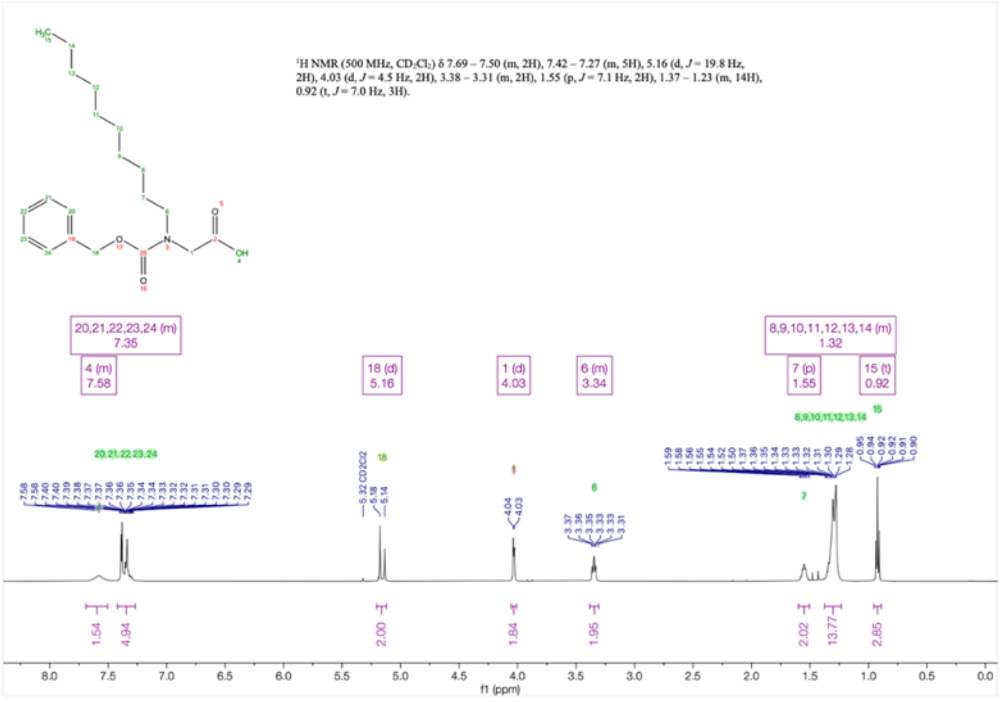


Fig. S101 ^{1}H NMR of Cbz-Ndc.

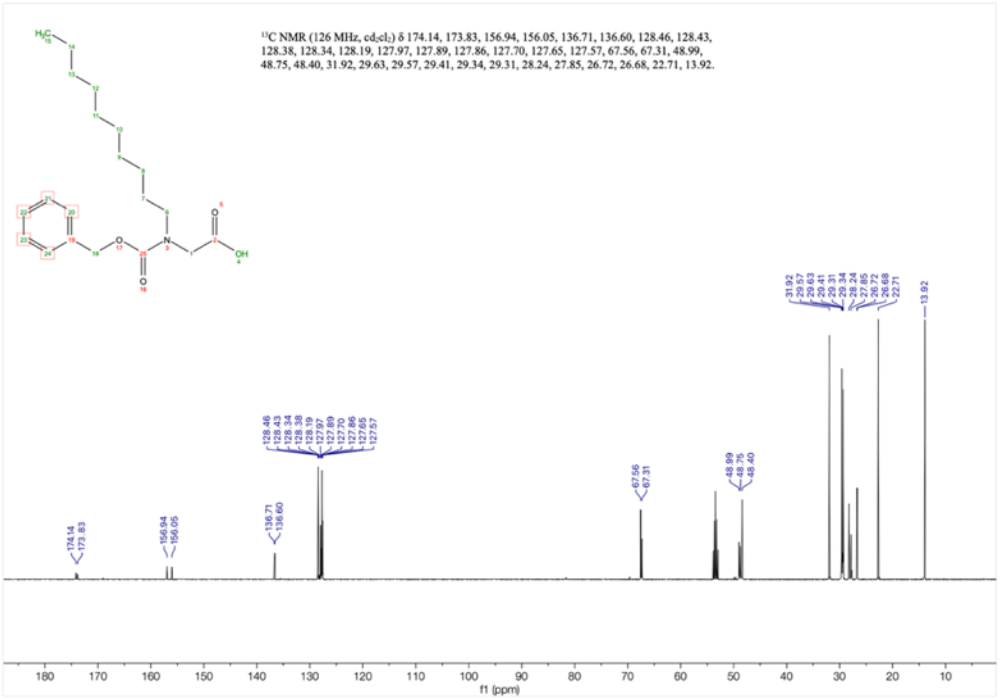


Fig. S102 ^{13}C NMR of Cbz-Ndc.

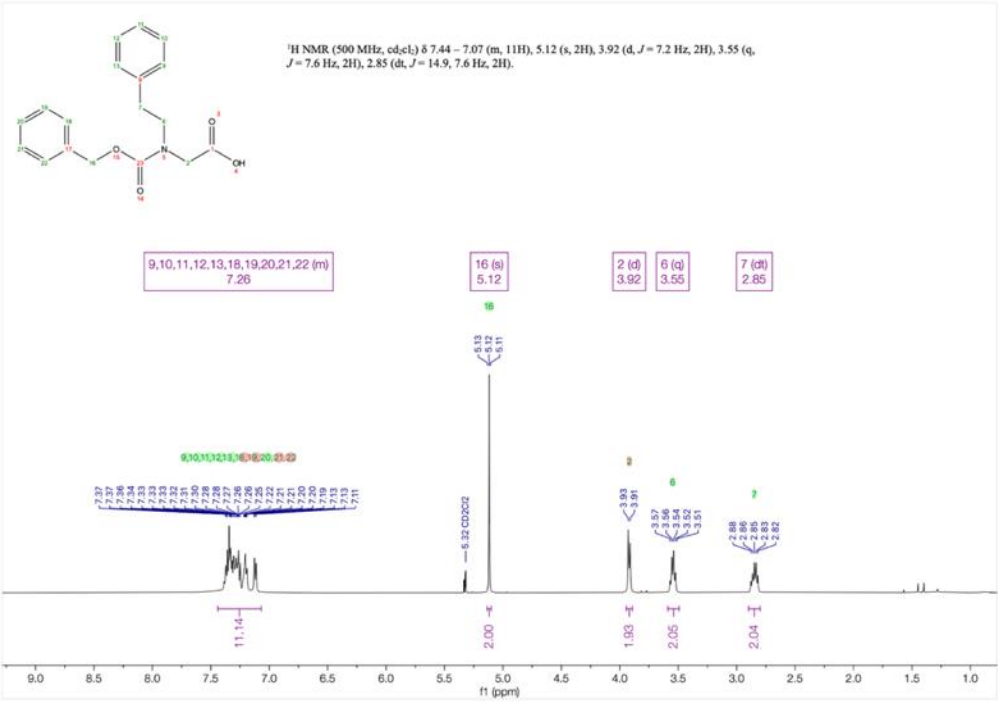


Fig. S103 ^{1}H NMR of Cbz-Npe.

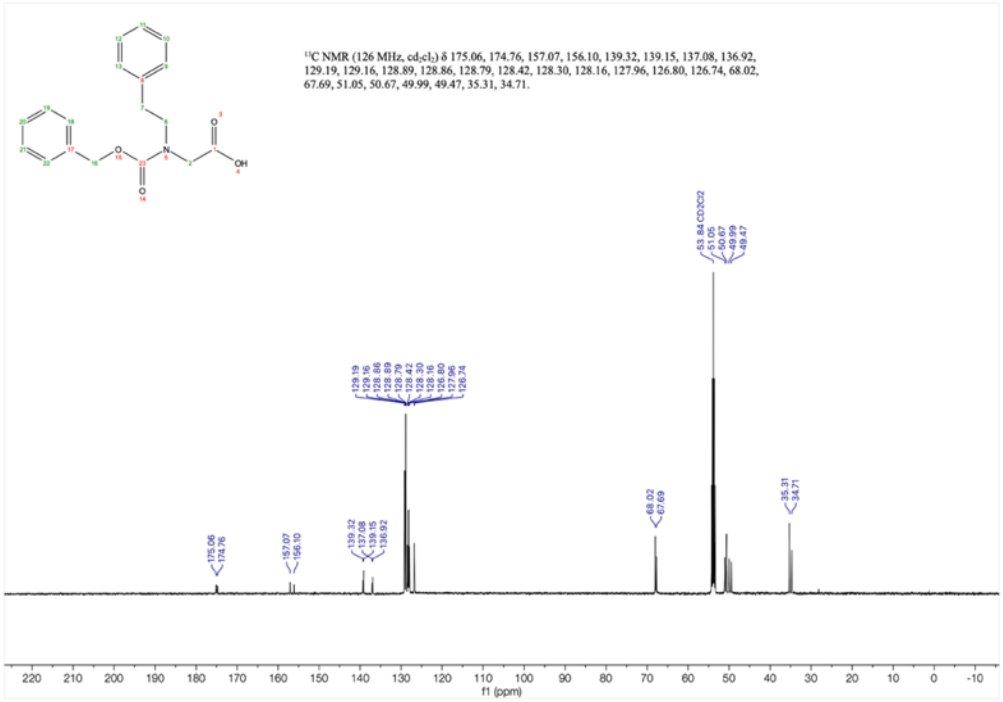


Fig. S104 ^{13}C NMR of Cbz-Npe.

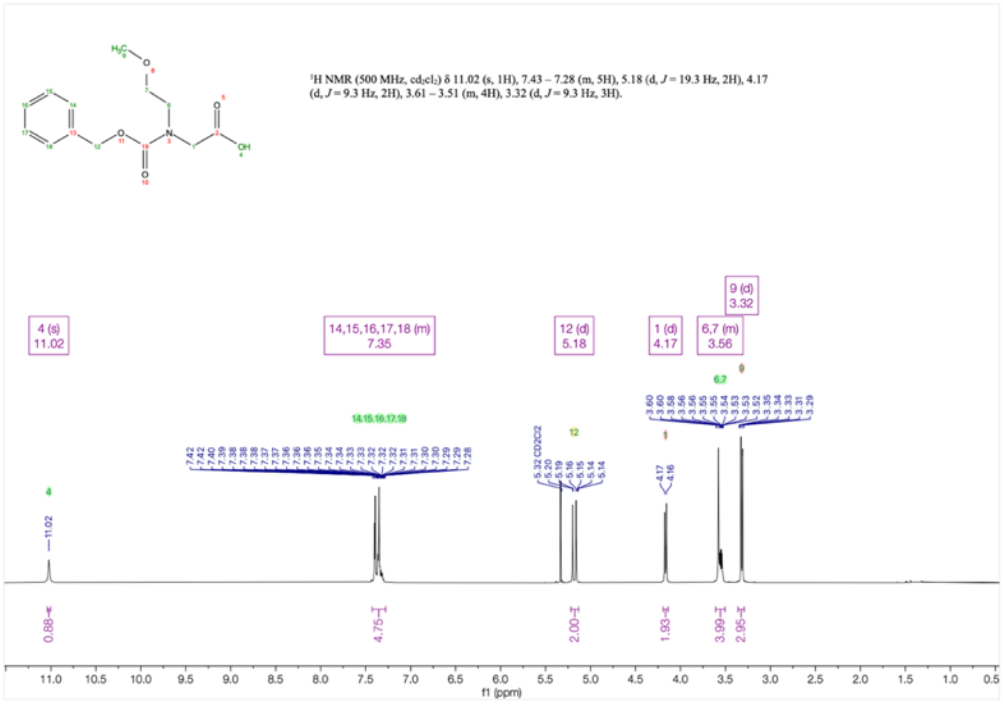


Fig. S105 ^{1}H NMR of Cbz-Nme.

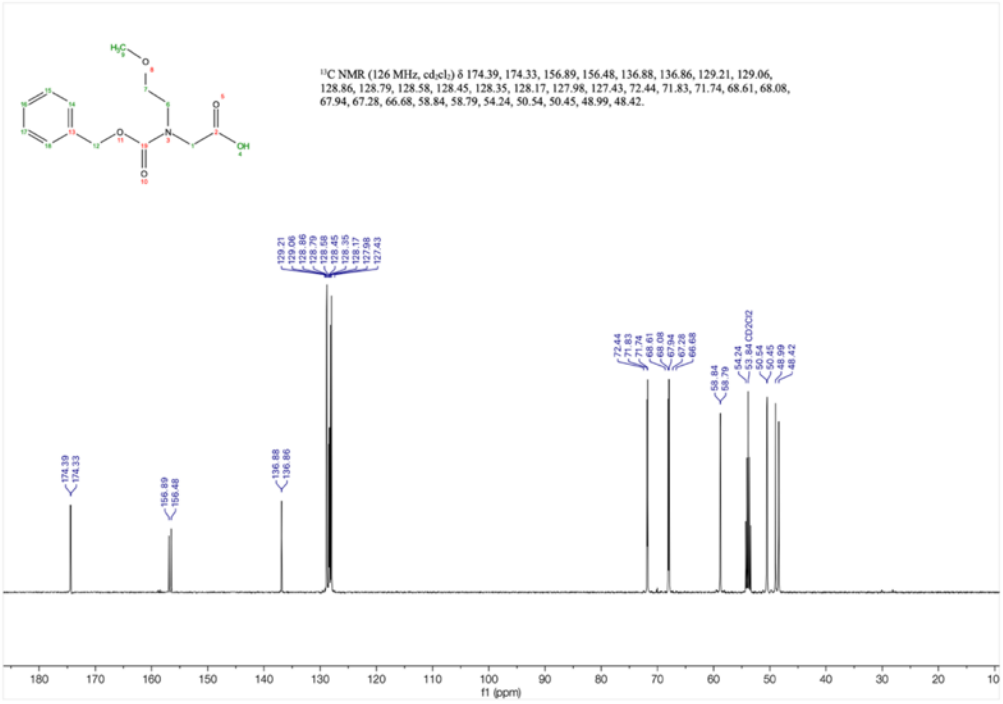


Fig. S106 ^{13}C NMR of Cbz-Nme.

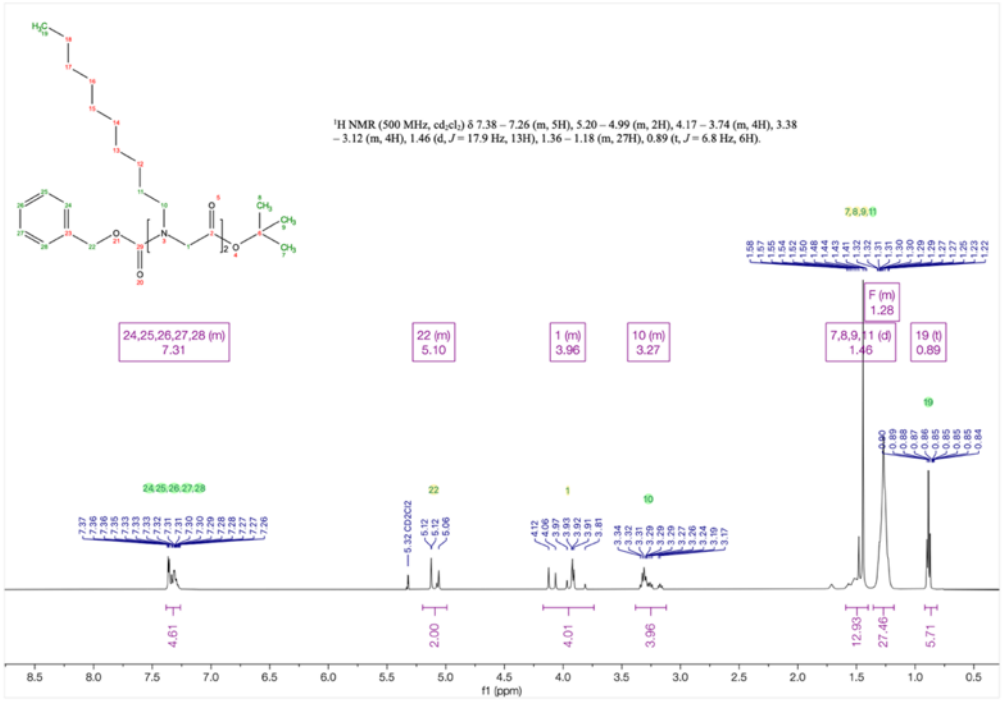


Fig. S107 ^{1}H NMR of Cbz-Ndc$_2$-tBu.

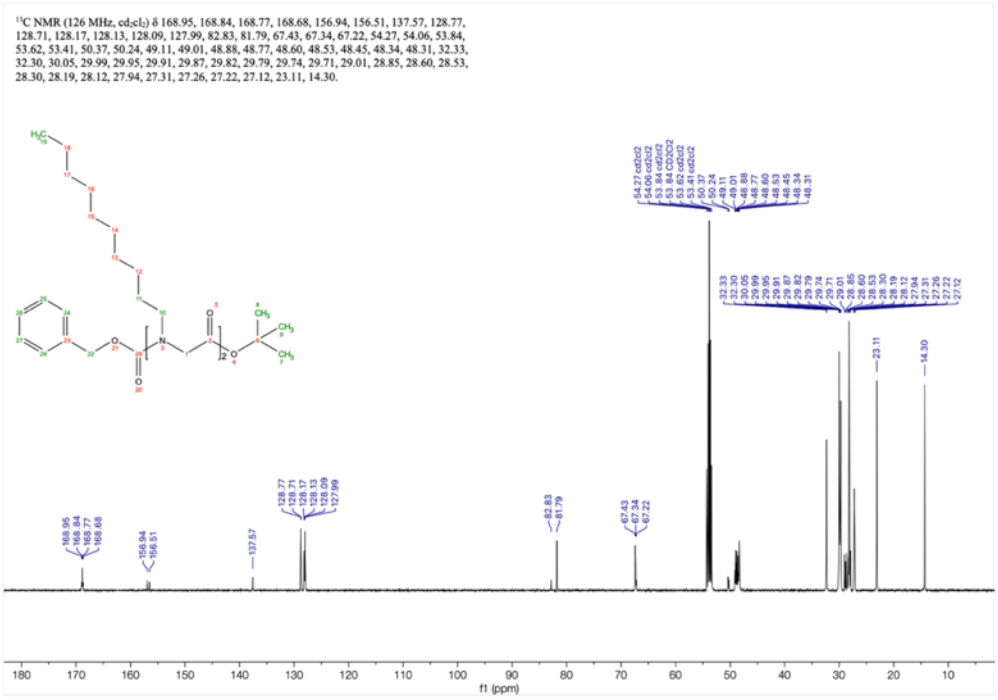


Fig. S108 ^{13}C NMR of Cbz-Ndc$_2$-tBu.

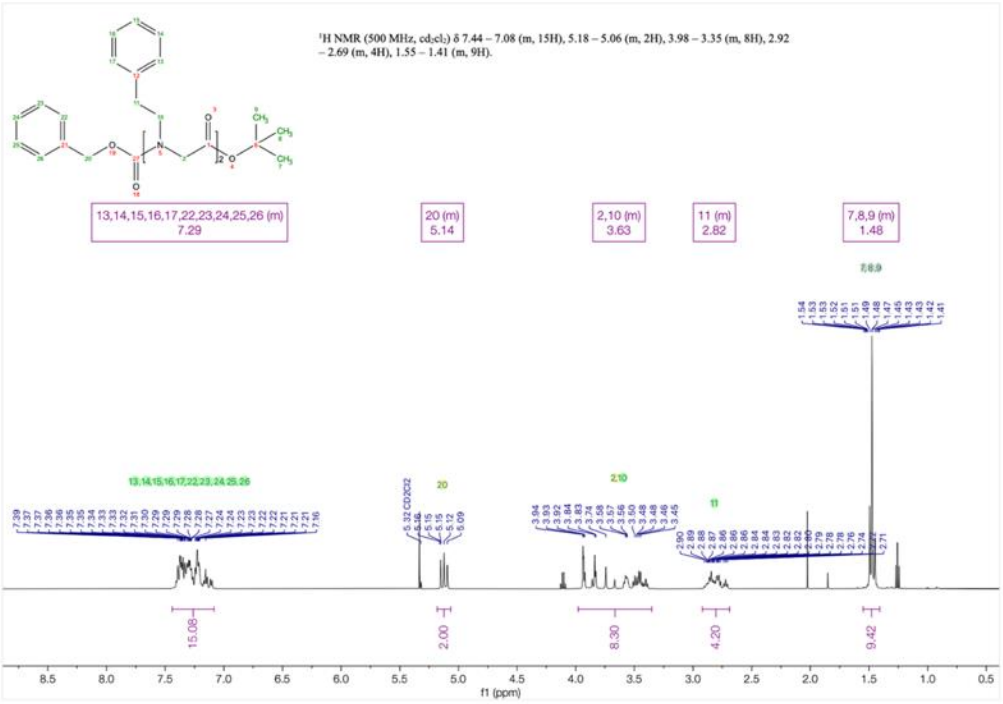


Fig. S109 ^{1}H NMR of Cbz-Npe$_2$-tBu.

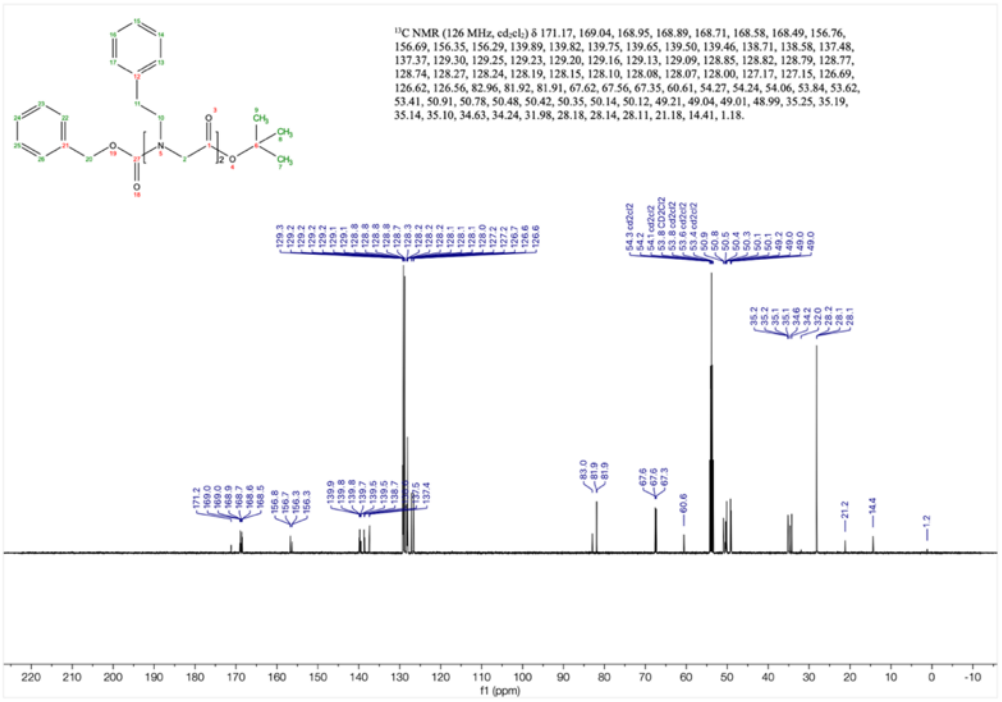


Fig. S110 ^{13}C NMR of Cbz-Npe$_2$-tBu.

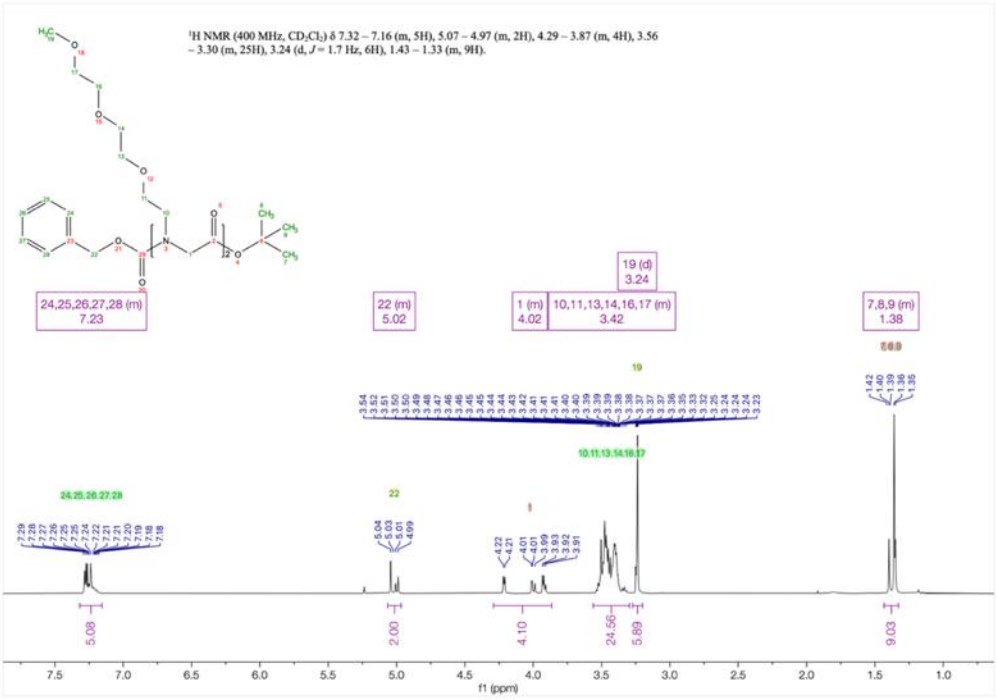


Fig. S111 ^{1}H NMR of Cbz-Nte$_2$-tBu.

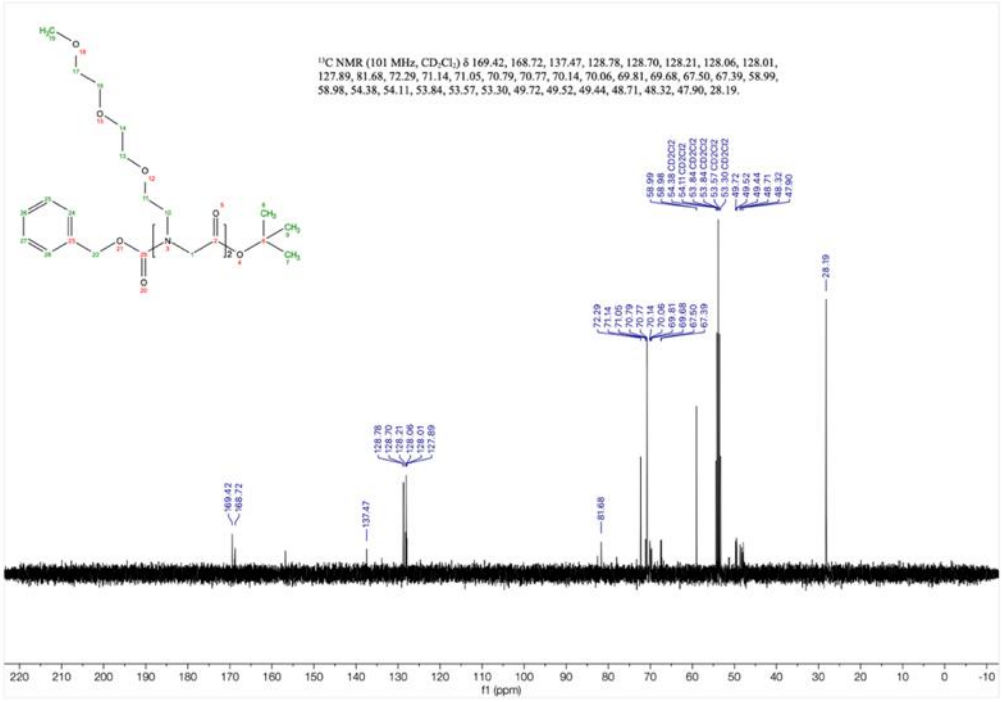


Fig. S112 ^{13}C NMR of Cbz-Nte$_2$-tBu.

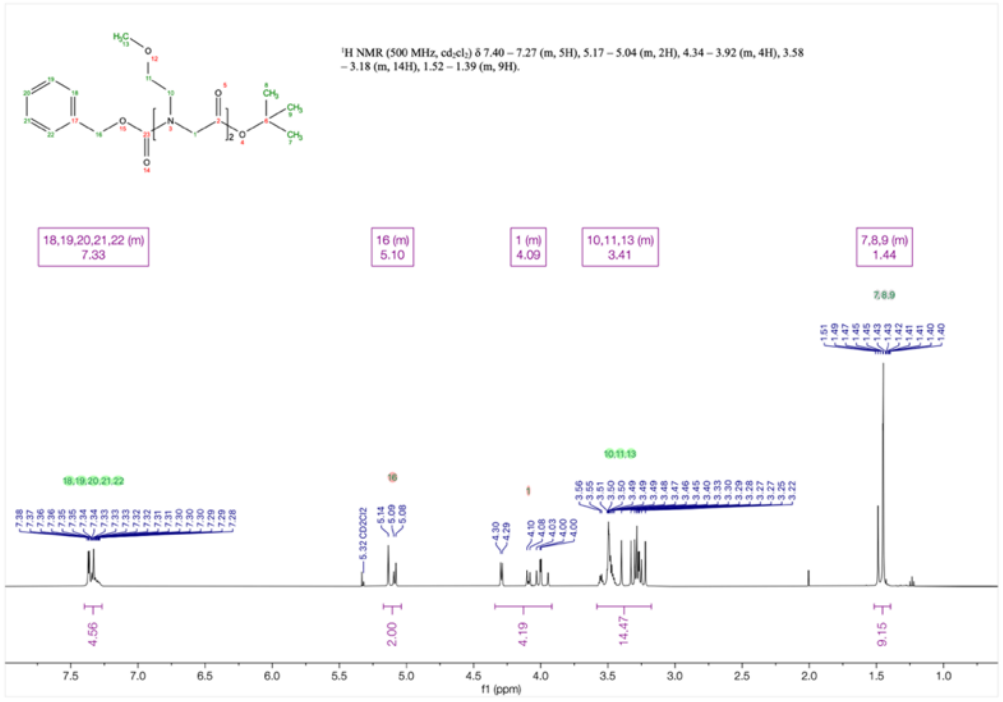


Fig. S113 ^{1}H NMR of Cbz-Nme$_2$-tBu.

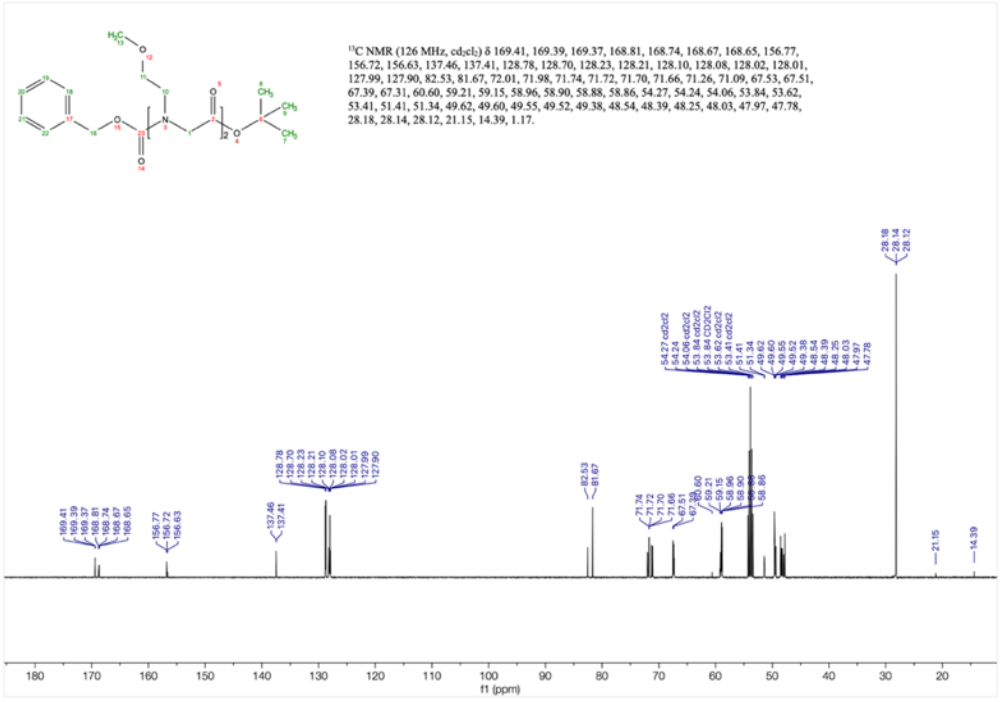


Fig. S114 ^{13}C NMR of Cbz-Nme$_2$-tBu.

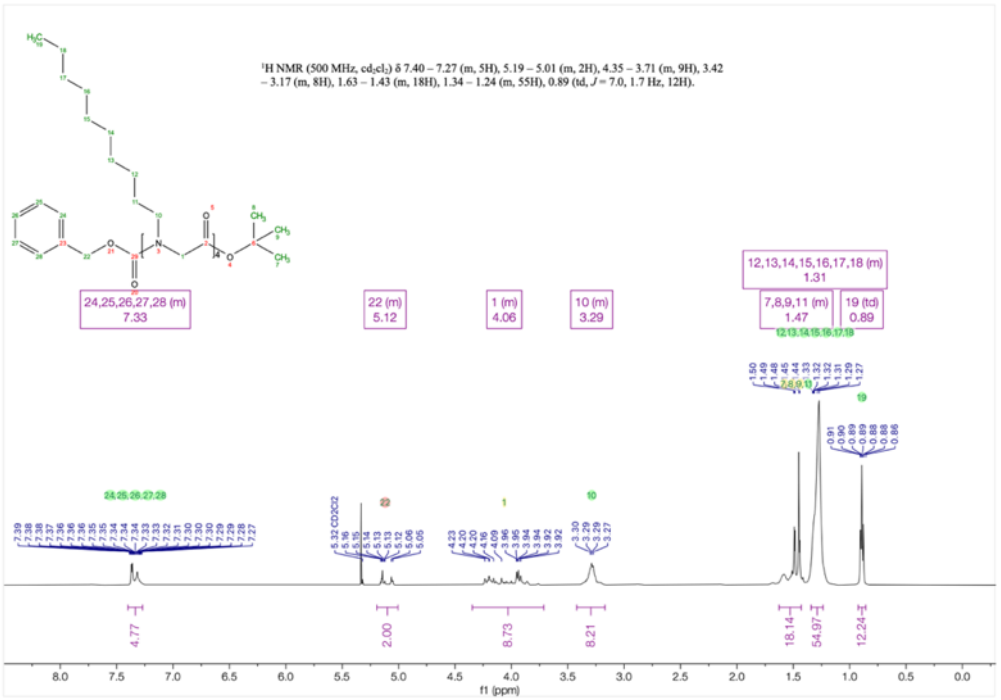


Fig. S115 ^{1}H NMR of Cbz-Ndc$_4$-tBu.

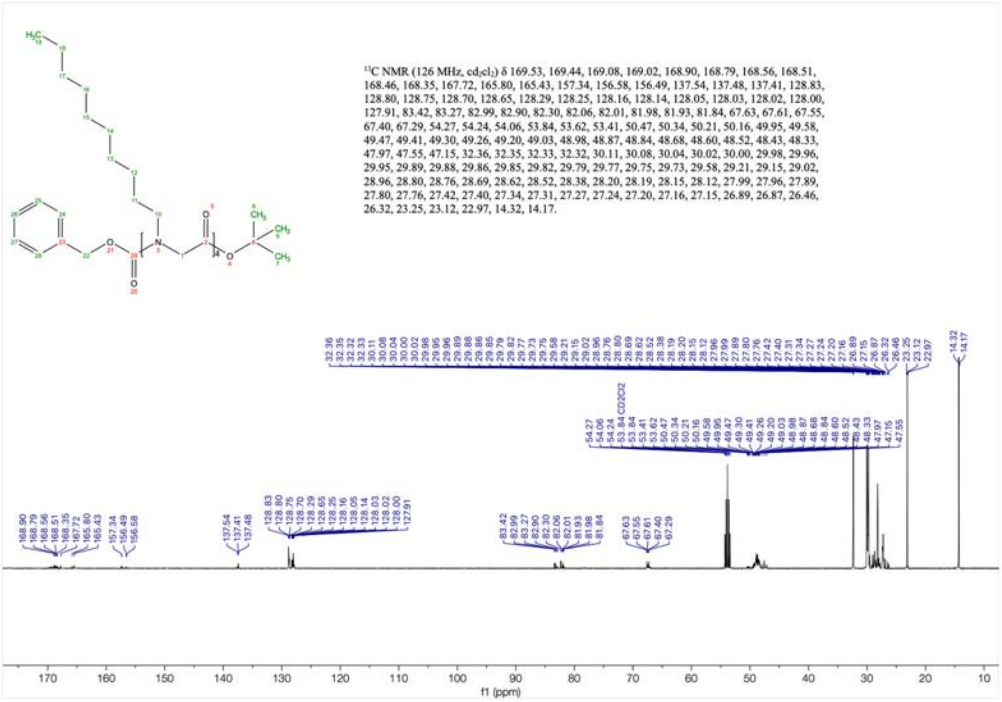


Fig. S116 ^{13}C NMR of Cbz-Ndc$_4$-tBu.

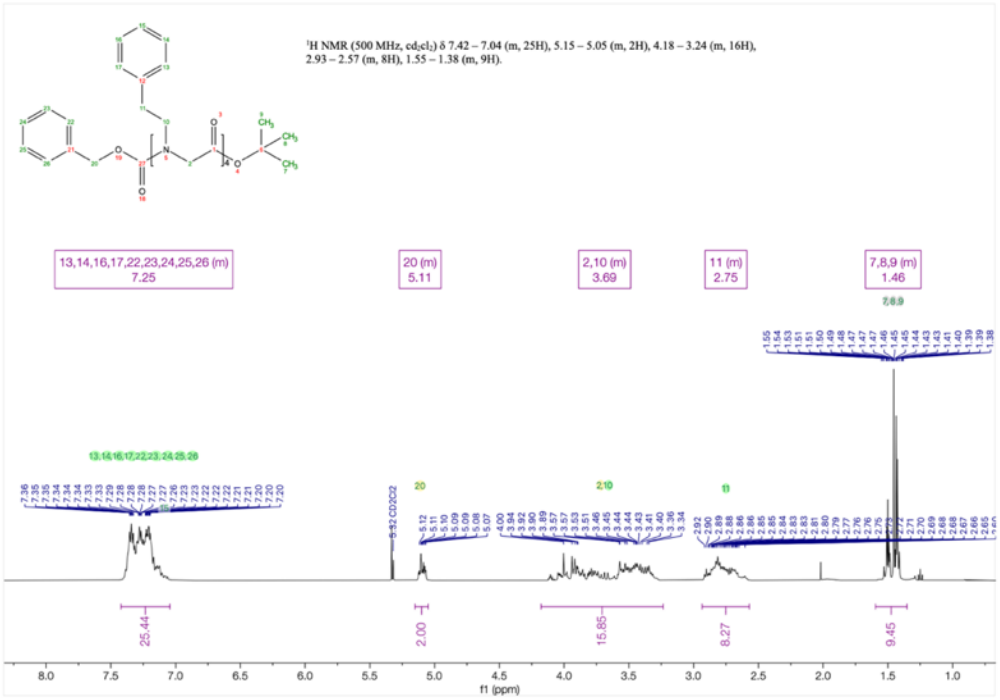


Fig. S117 ^{1}H NMR of Cbz-Npe$_4$-tBu.

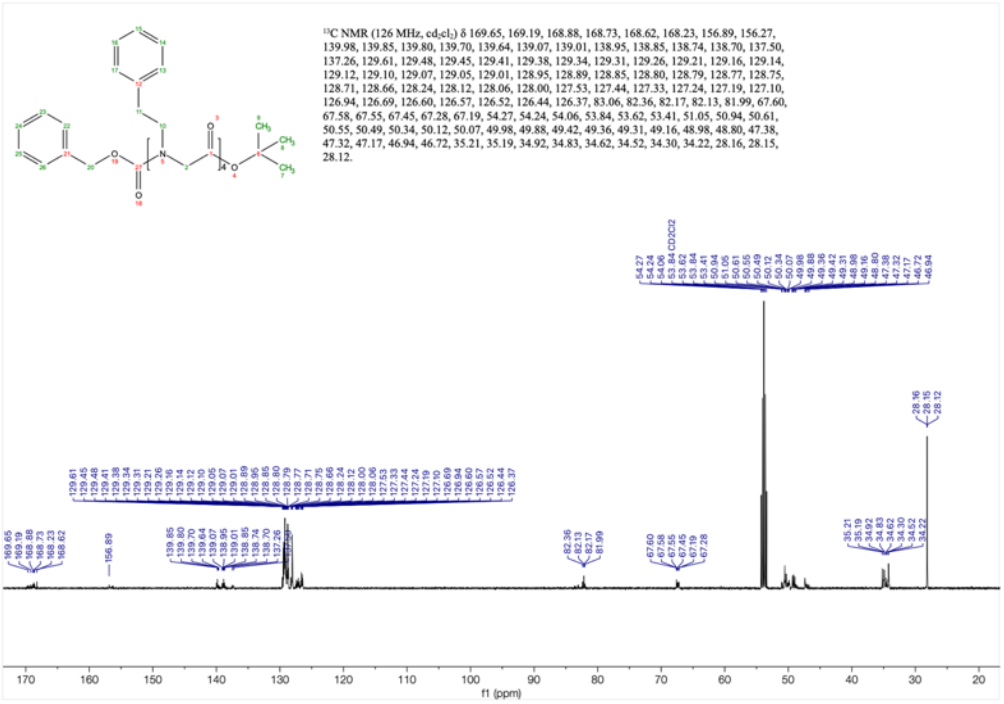


Fig. S118 ^{13}C NMR of Cbz-Npe$_4$-tBu.

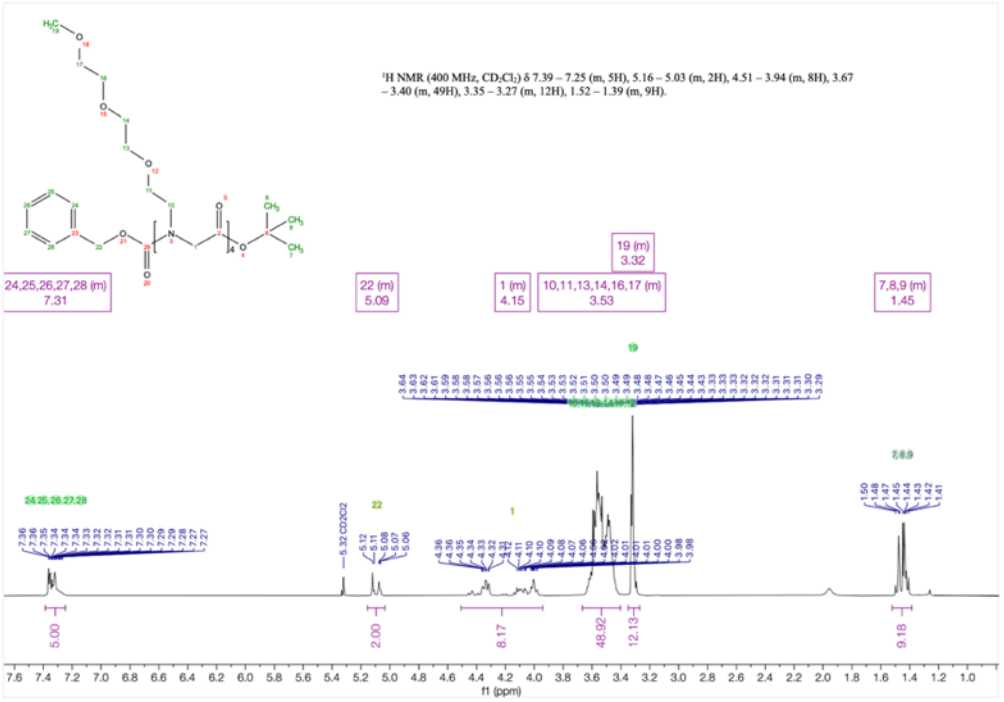


Fig. S119 ^{1}H NMR of Cbz-Nte$_4$-tBu.

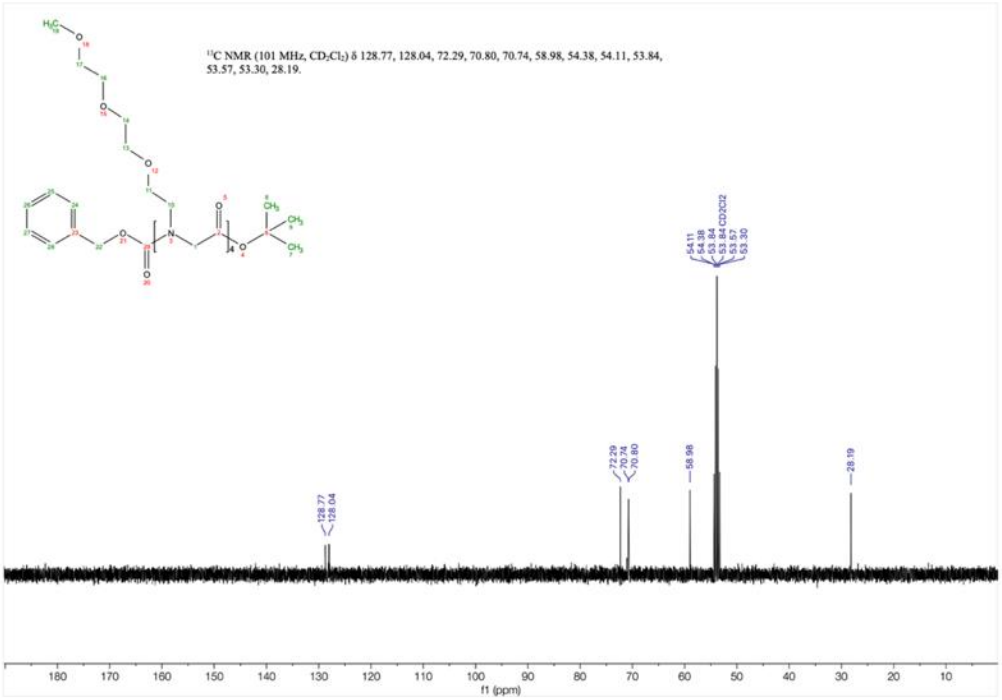


Fig. S120 ^{13}C NMR of Cbz-Nte$_4$-tBu.

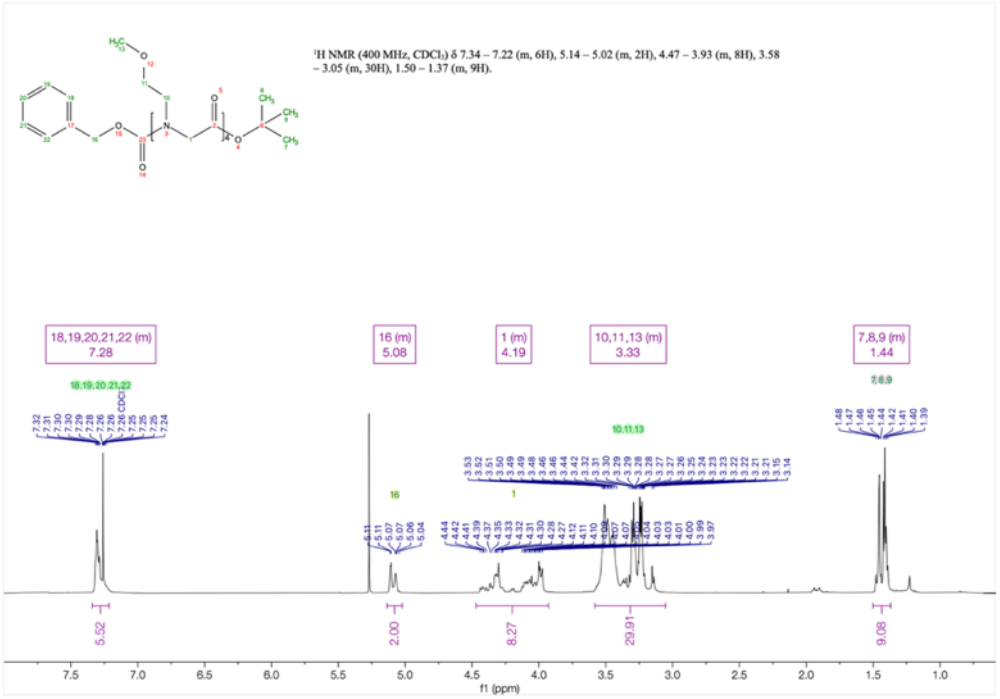


Fig. S121 ^{1}H-NMR of Cbz-Nme$_4$-tBu.

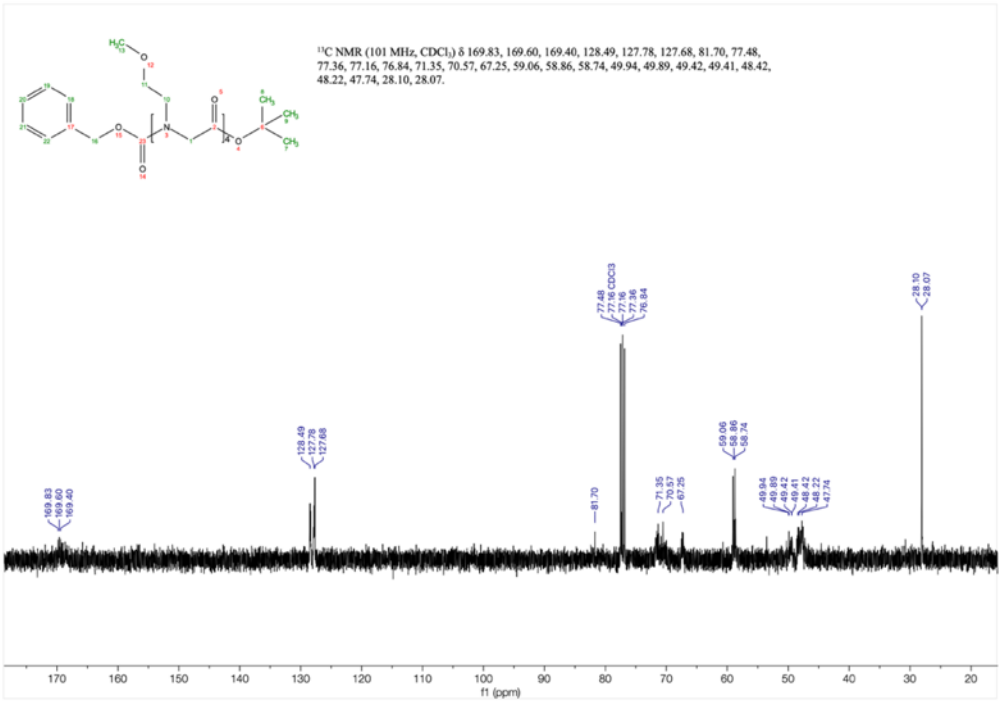


Fig. S122 ^{13}C-NMR of Cbz-Nme$_4$-tBu.

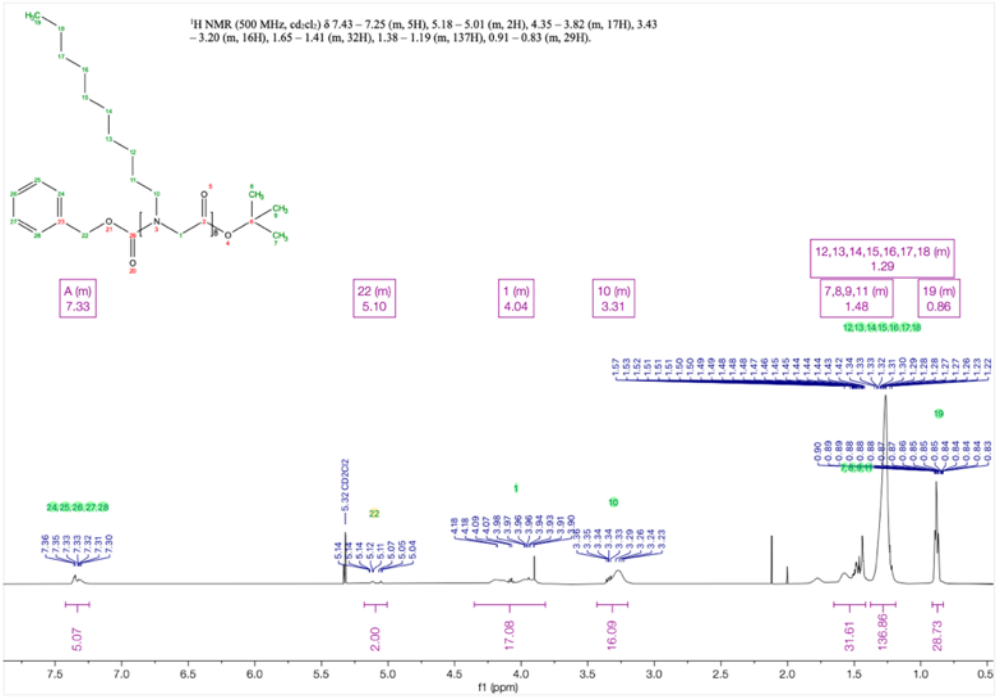


Fig. S123 ^{1}H NMR of Cbz-Ndc$_8$-tBu.

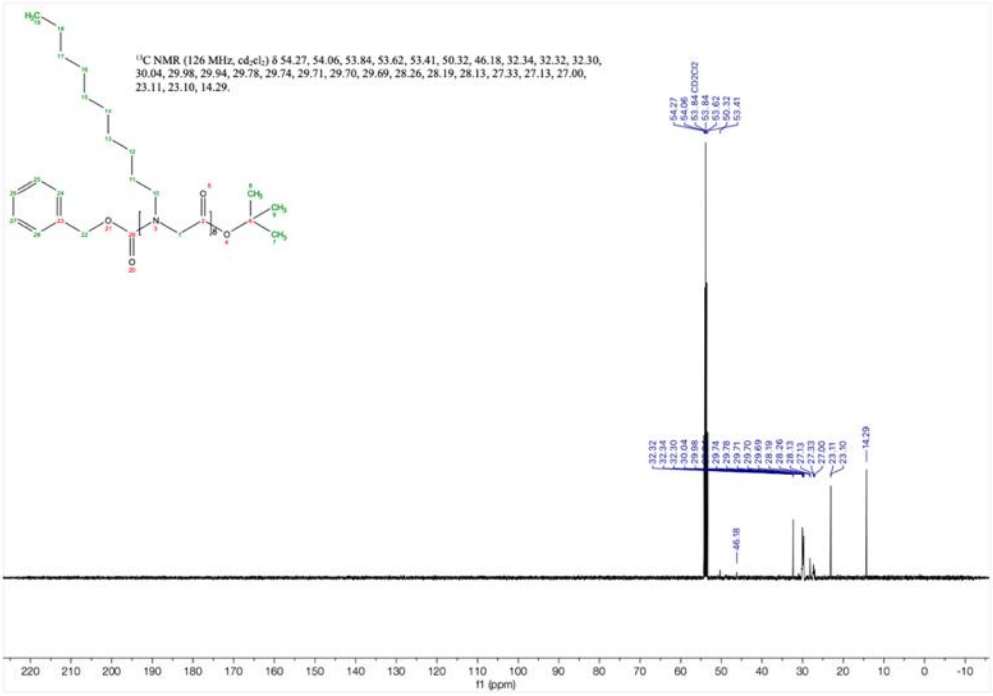


Fig. S124 ^{13}C NMR of Cbz-Ndc$_8$-tBu.

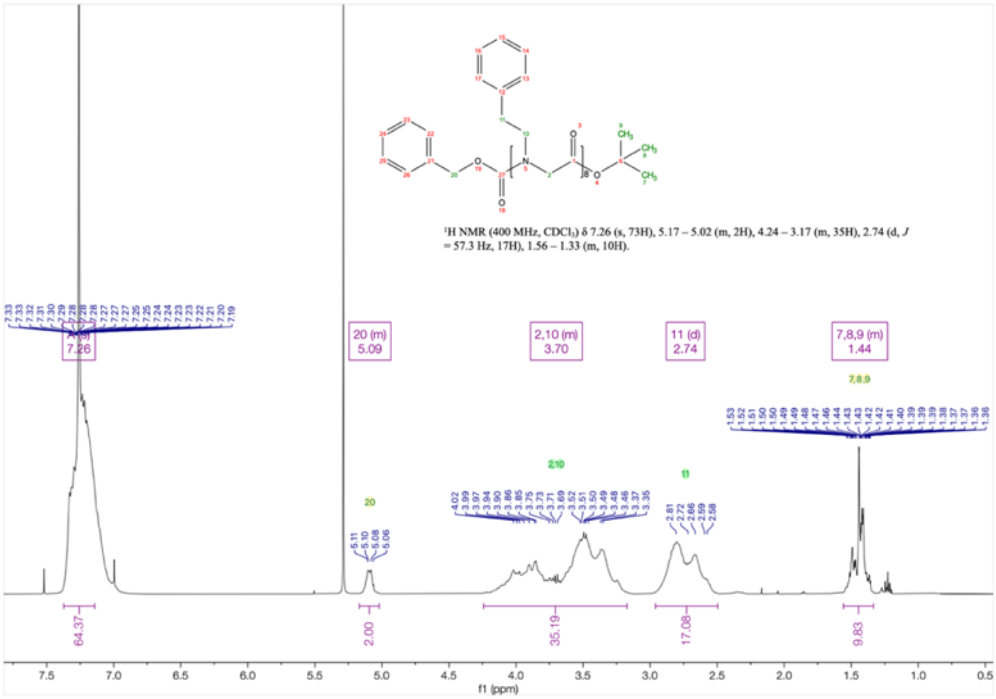


Fig. S125 ^{1}H NMR of Cbz-Npe$_8$-tBu.

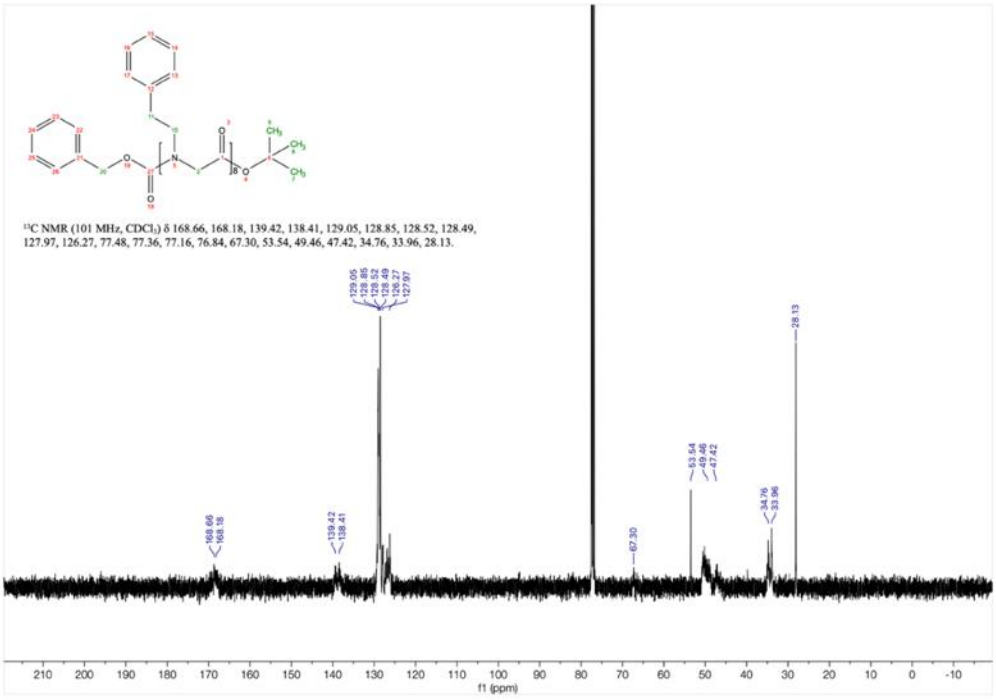


Fig. S126 ^{13}C NMR of Cbz-Npe$_8$-tBu.

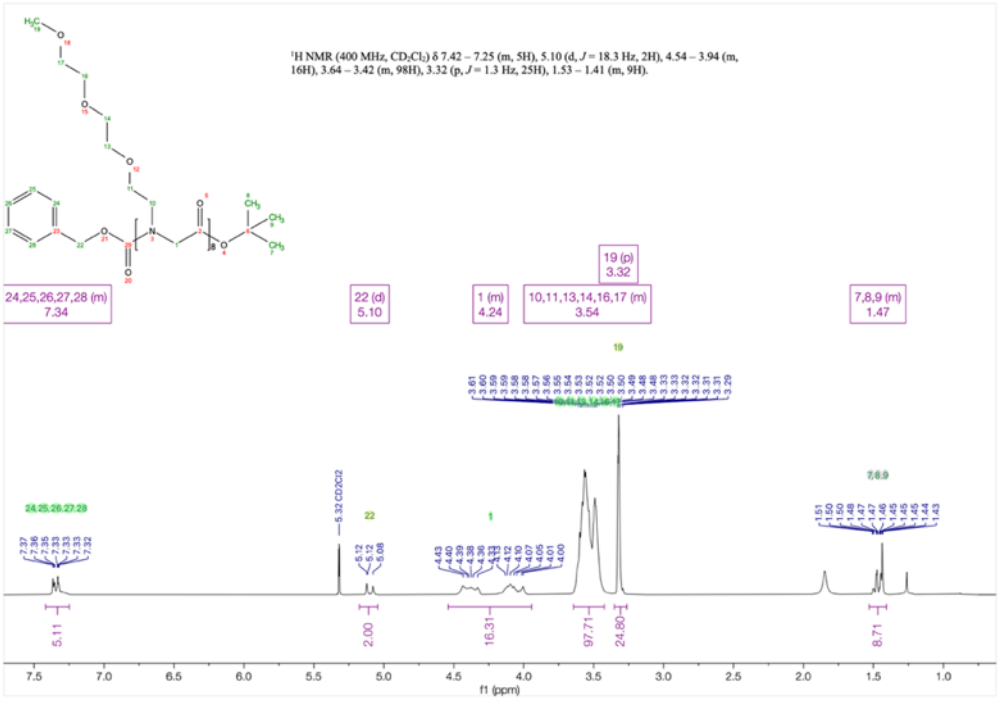


Fig. S127 ^{1}H NMR of Cbz-Nte$_8$-tBu.

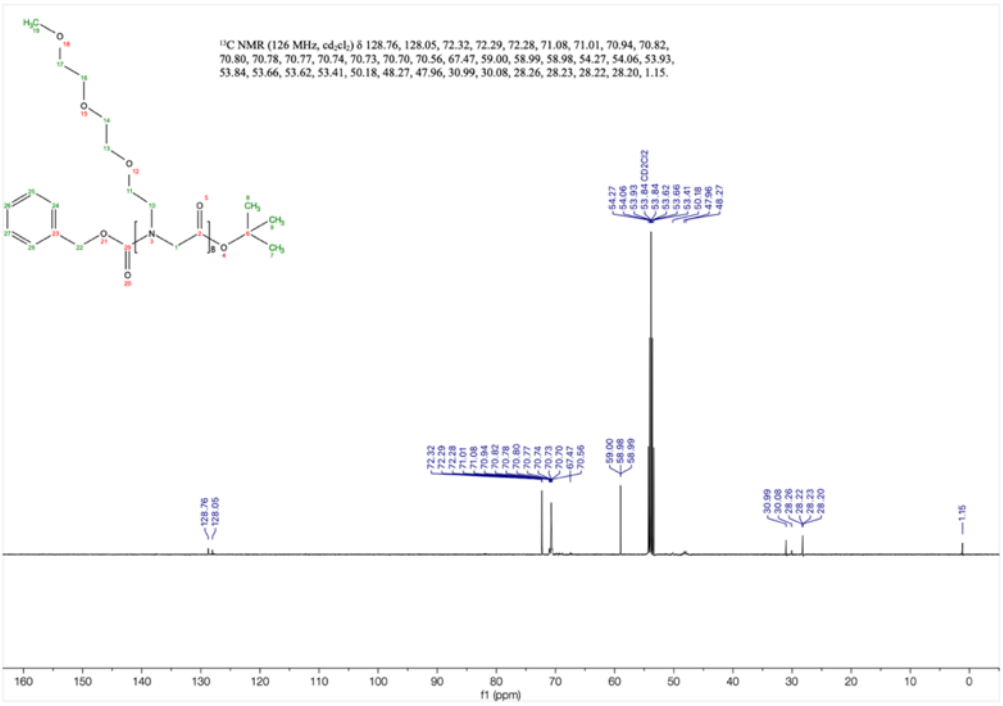


Fig. S128 ^{13}C NMR of Cbz-Nte$_8$-tBu.

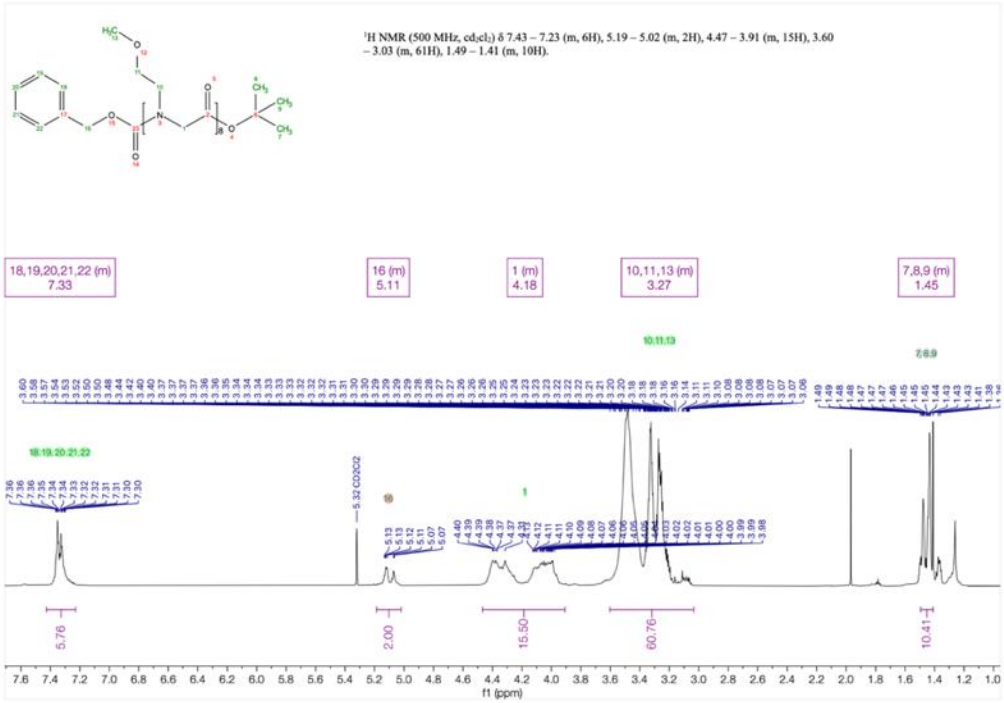


Fig. S129 ^{1}H NMR of Cbz-Nme$_8$-tBu.

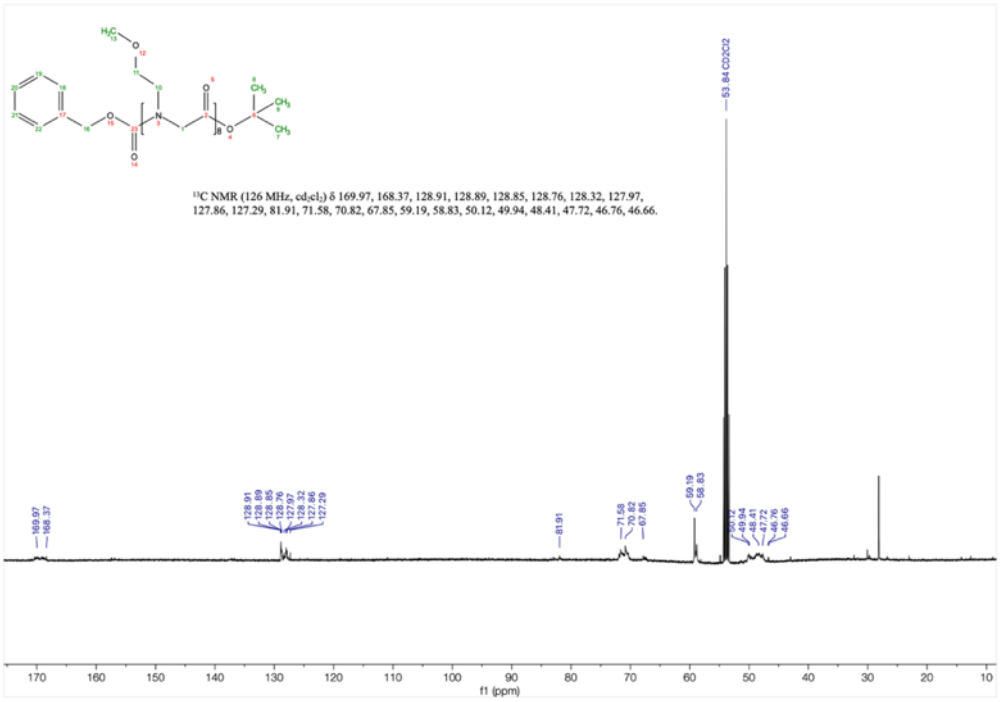


Fig. S130 ^{13}C NMR of Cbz-Nme$_8$-tBu.

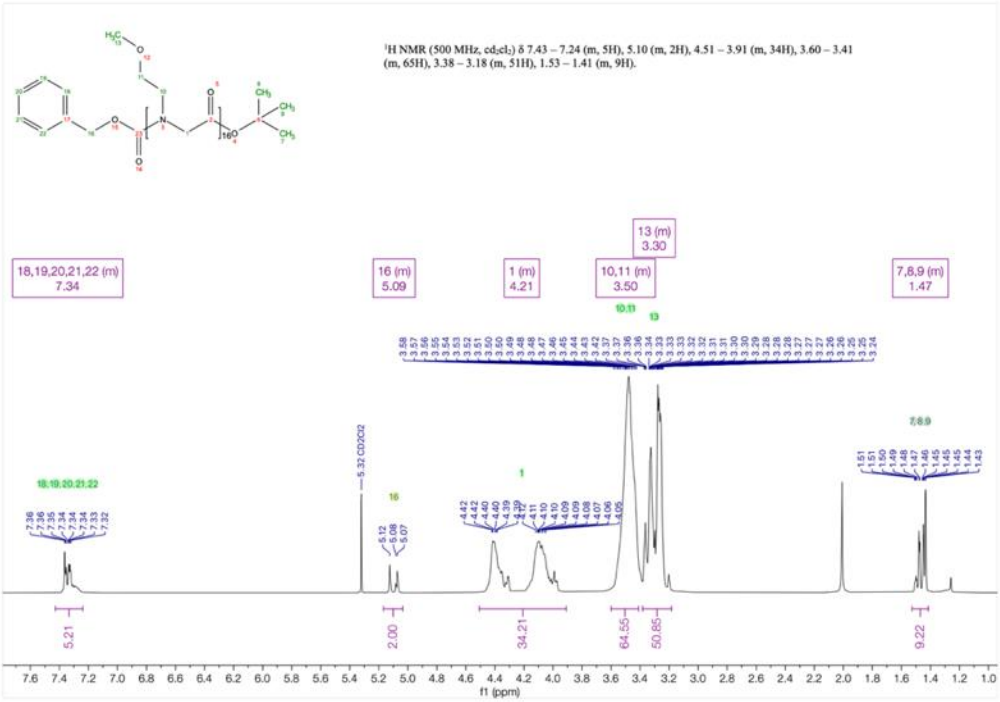


Fig. S131 ^{1}H NMR of Cbz-Nme$_{16}$-tBu.

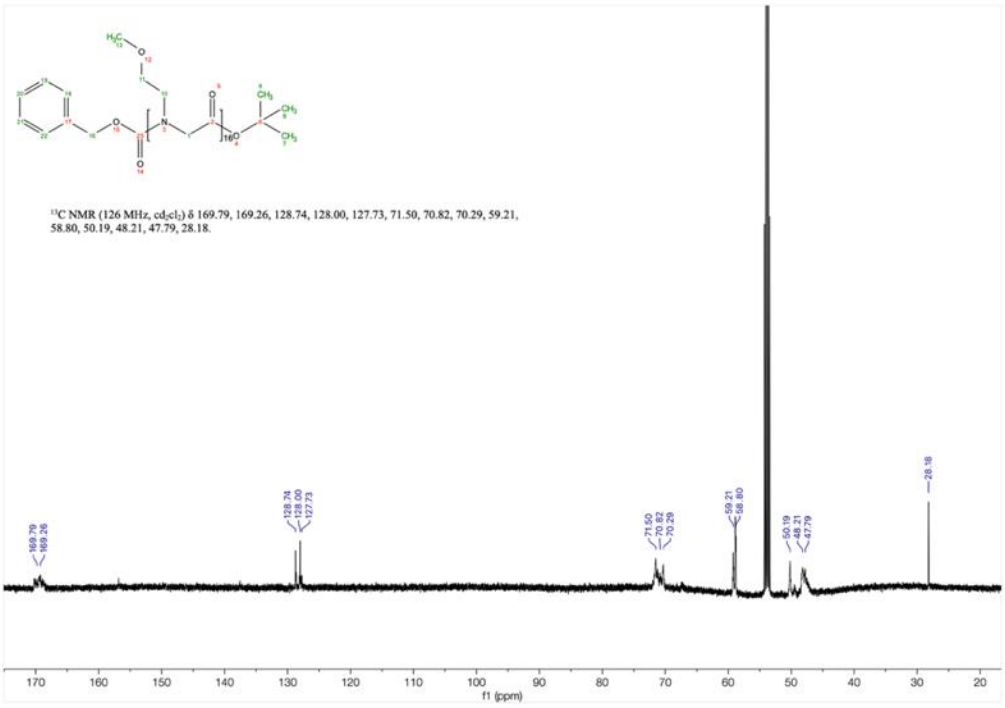


Fig. S132 ^{13}C NMR of Cbz-Nme$_{16}$-tBu. Note: baseline not corrected to maintain signal.

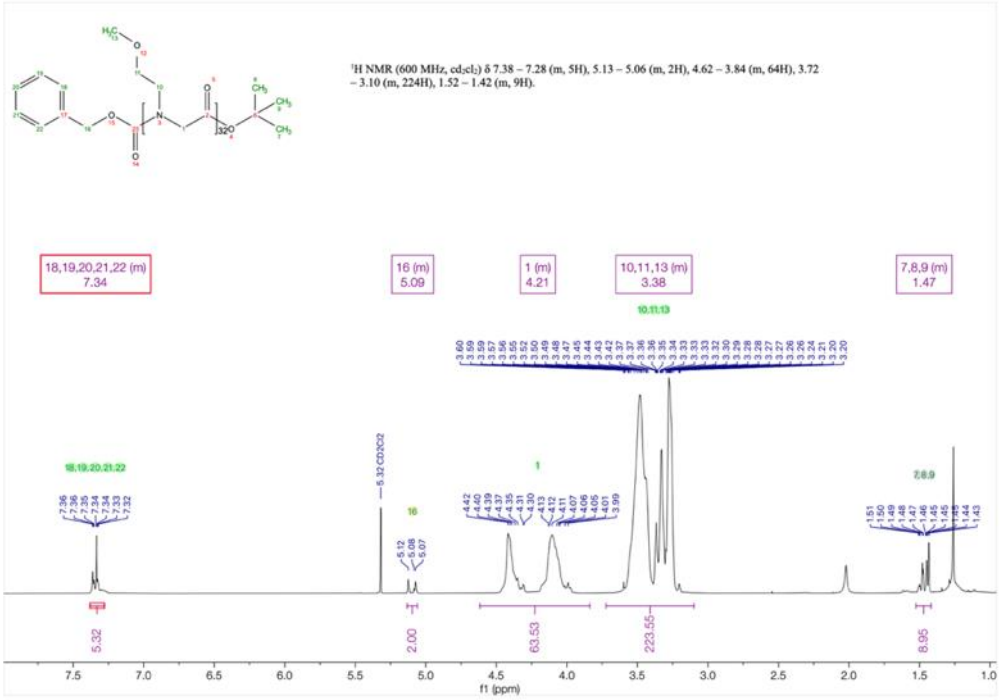


Fig. S133 ^{1}H NMR of Cbz-Nme$_{32}$-tBu.

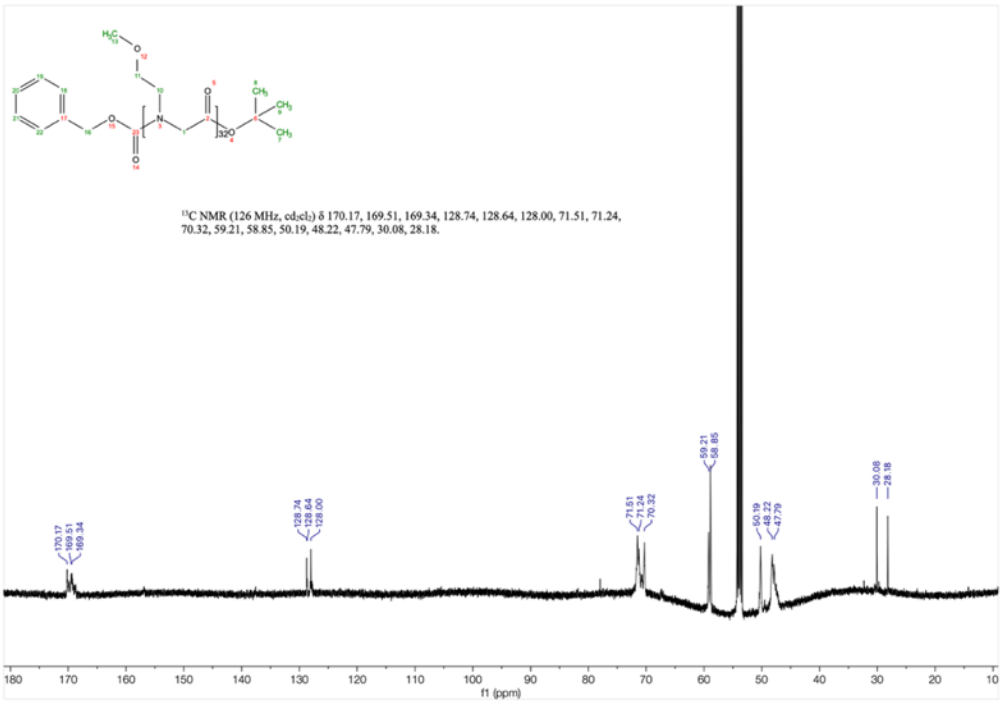


Fig. S134 ^{13}C NMR of Cbz-Nme$_{32}$-tBu. Note: baseline not corrected to maintain signal.

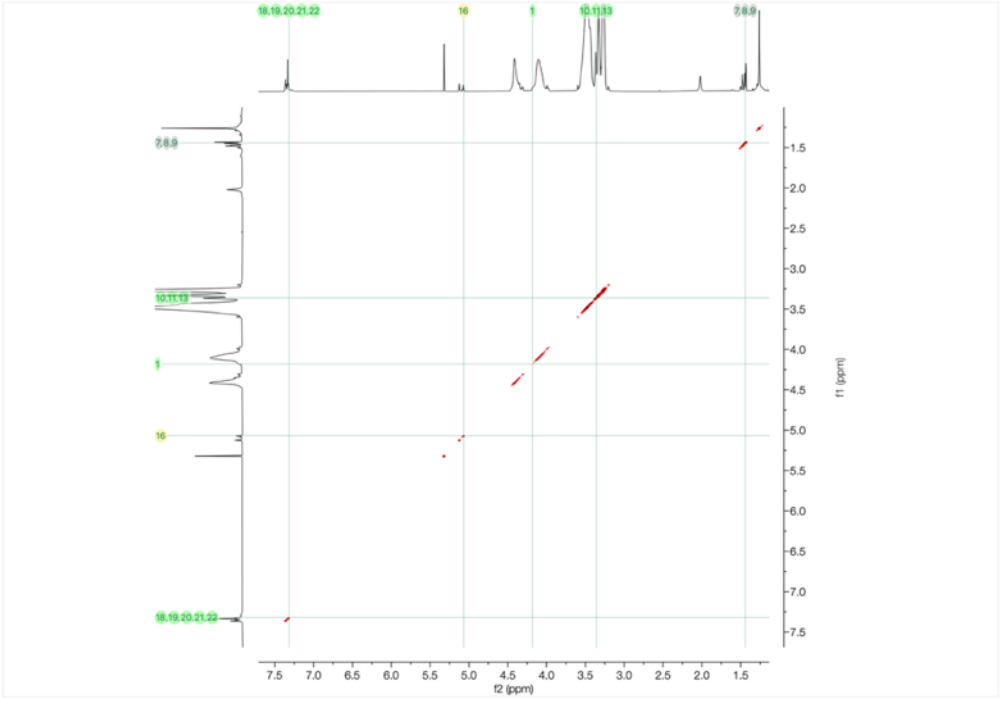


Fig. S135 COSY of Cbz-Nme$_{32}$-tBu.

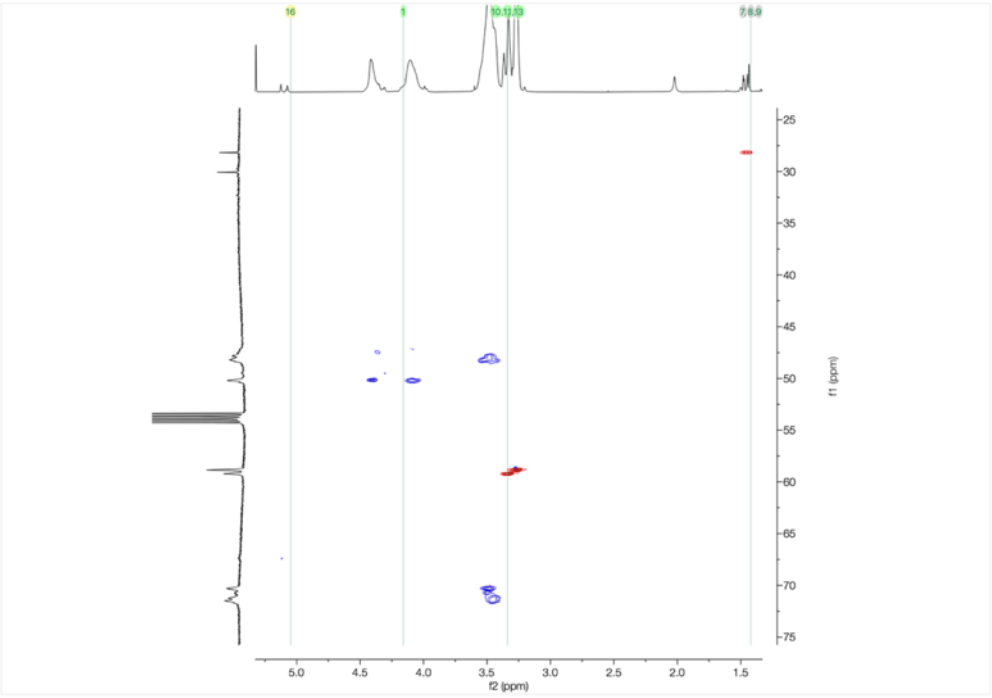


Fig. S136 HSQC of Cbz-Nme$_{32}$-tBu.

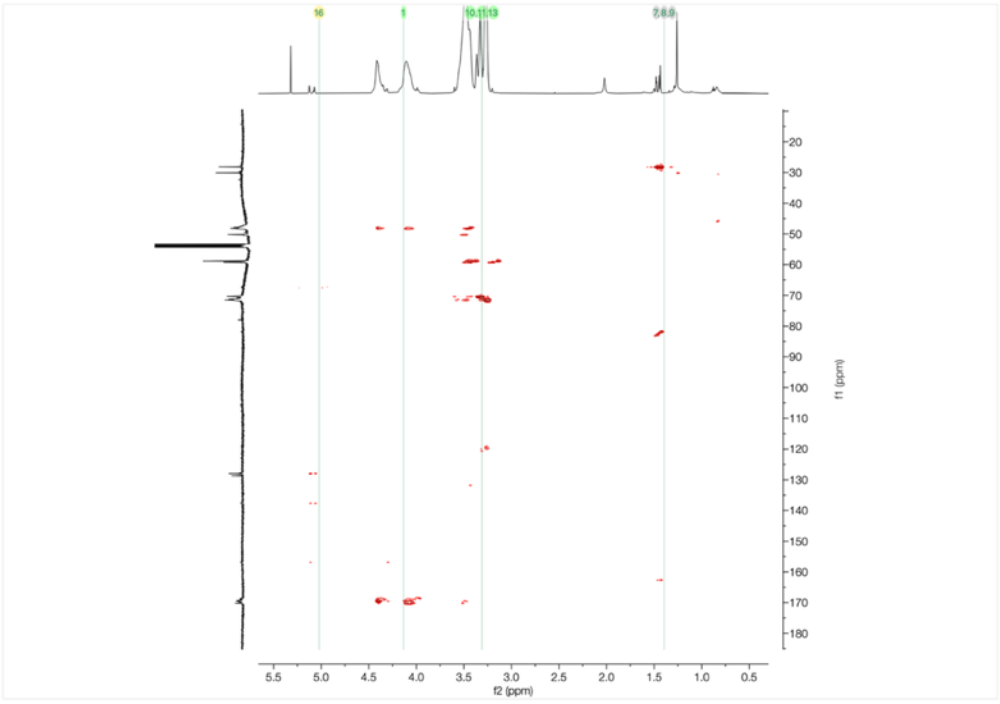


Fig. S137 HMBC of Cbz-Nme$_{32}$-tBu.

6.2 Diblock peptoids

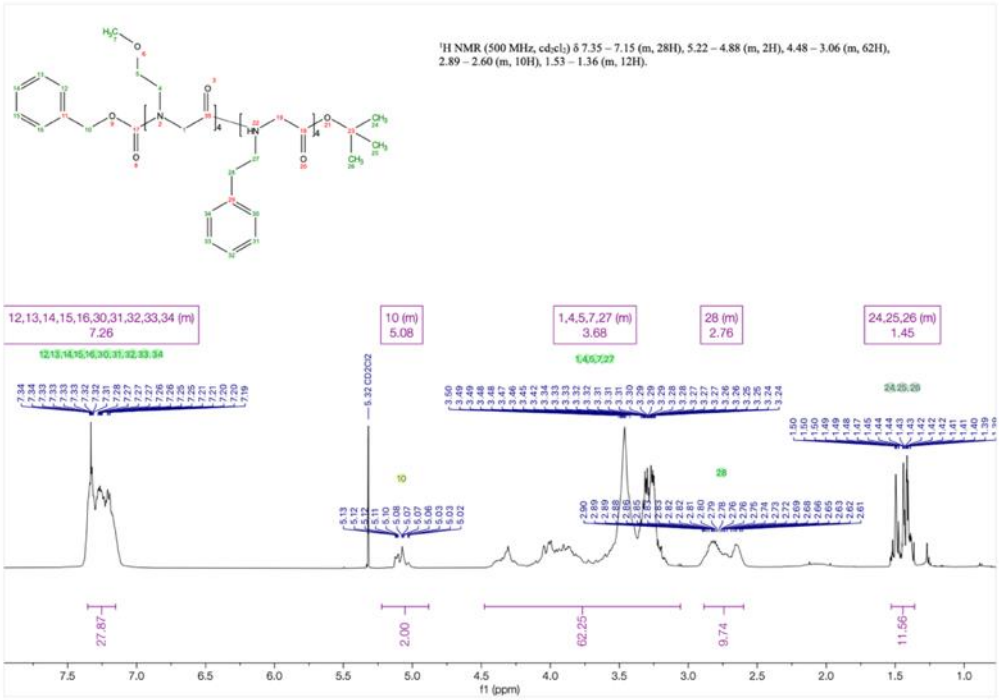


Fig. S138 [1]H-NMR of Cbz-Nme4-Npe4-tBu.

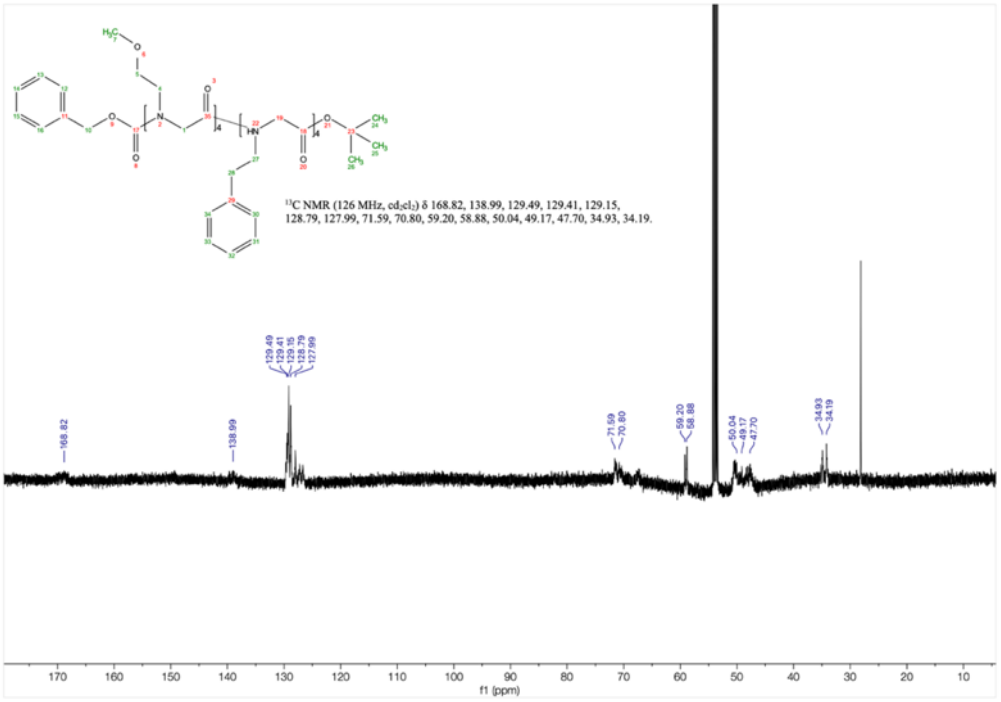


Fig. S139 [13]C-NMR of Cbz-Nme4-Npe4-tBu. Note: baseline not corrected to maintain signal.

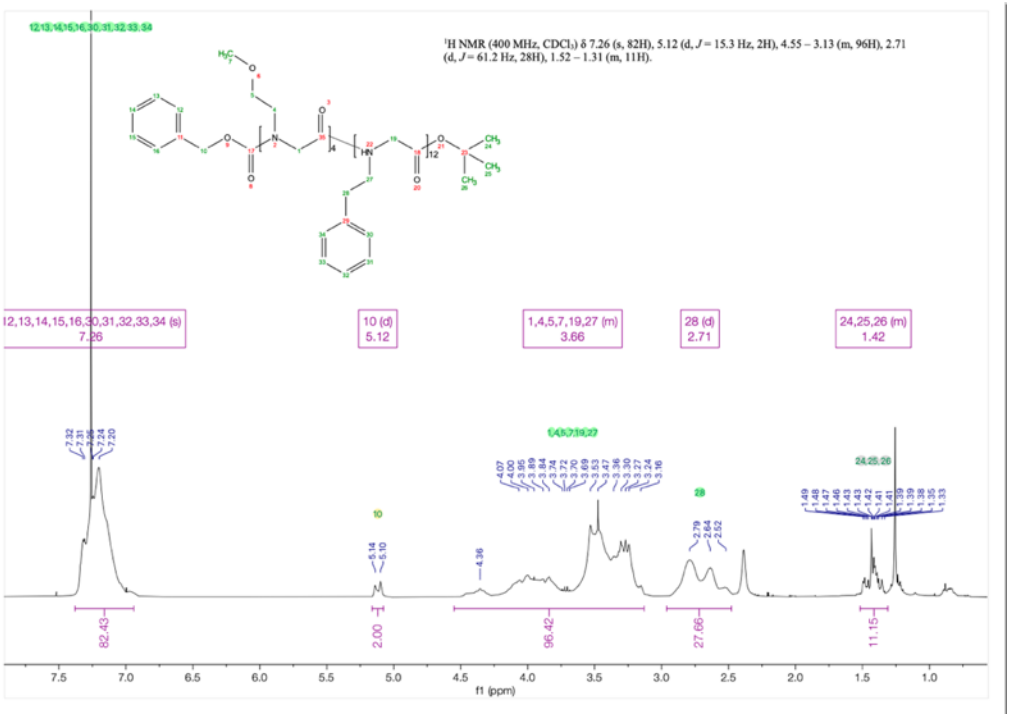


Fig. S140 ^{1}H NMR of Cbz-Nme$_4$-Npe$_{12}$-tBu.

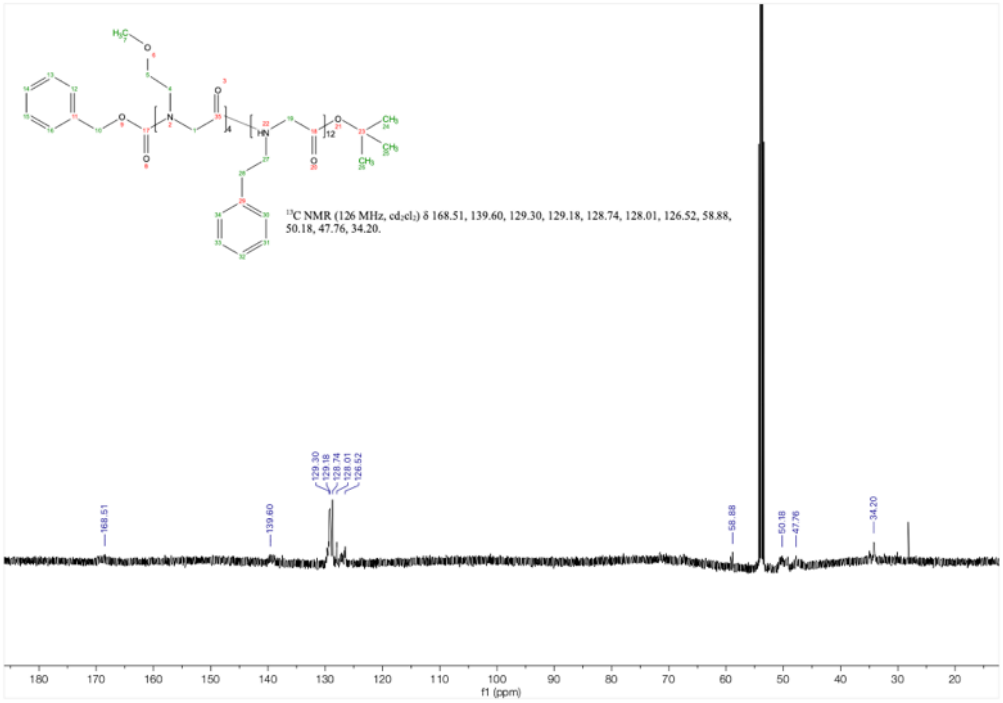


Fig. S141 ^{13}C NMR of Cbz-Nme$_4$-Npe$_{12}$-tBu. Note: baseline not corrected to maintain signal.

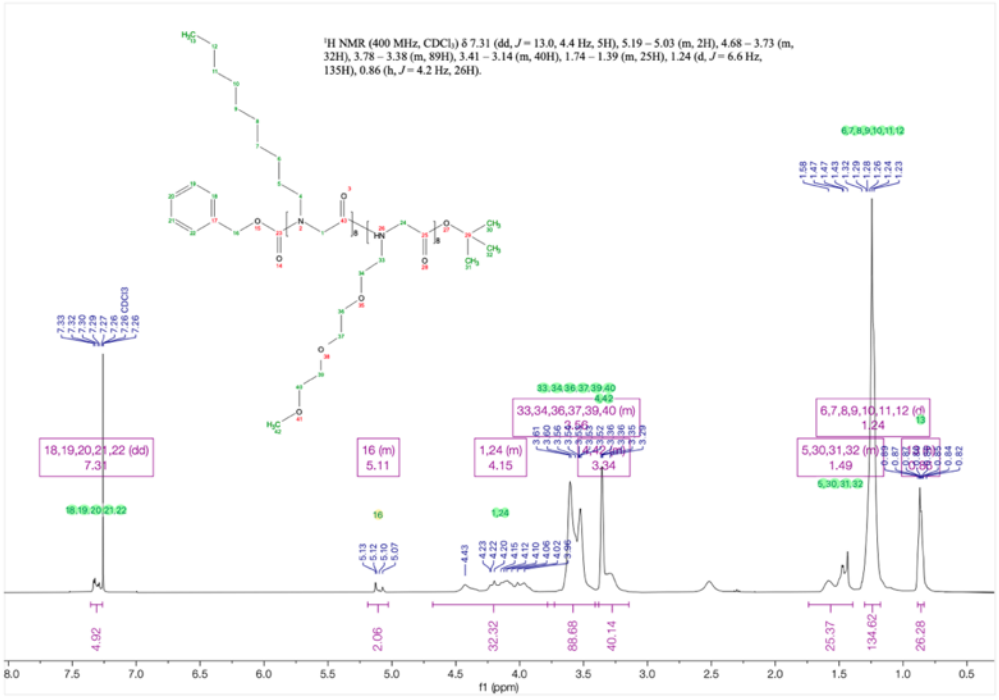


Fig. S142 ^{1}H NMR of Cbz-Ndc$_{8}$-Nte$_{8}$-tBu.

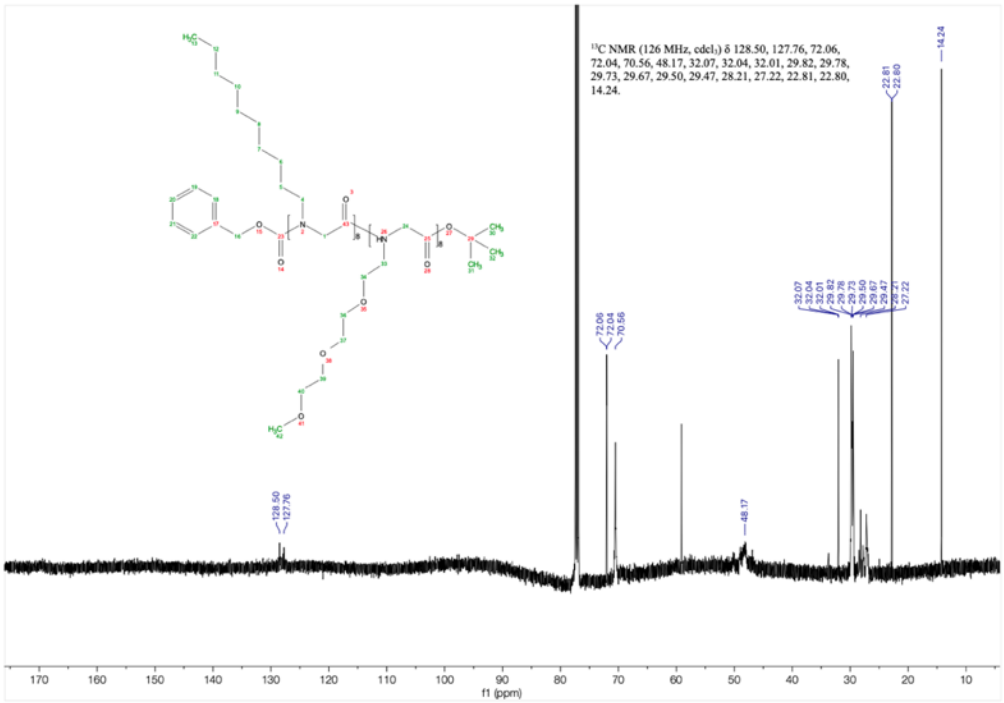


Fig. S143 ^{13}C NMR of Cbz-Ndc$_{8}$-Nte$_{8}$-tBu. Note: baseline not corrected to maintain signal.

6.3 Sequence-defined periodic and aperiodic peptoids

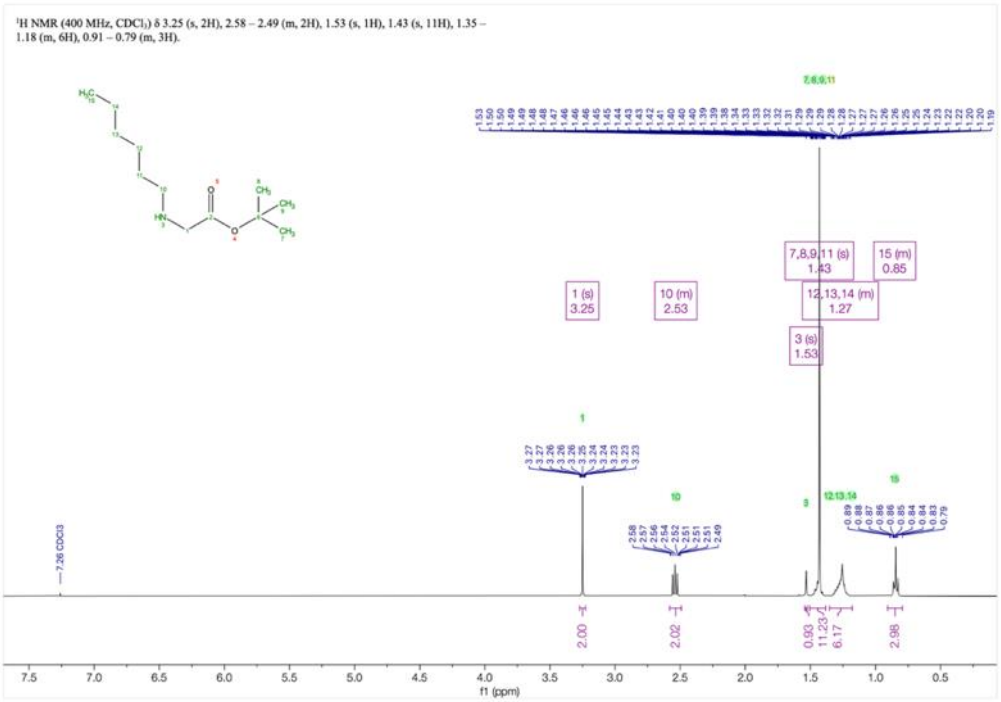


Fig. S144 [1]H NMR of Nhx-tBu.

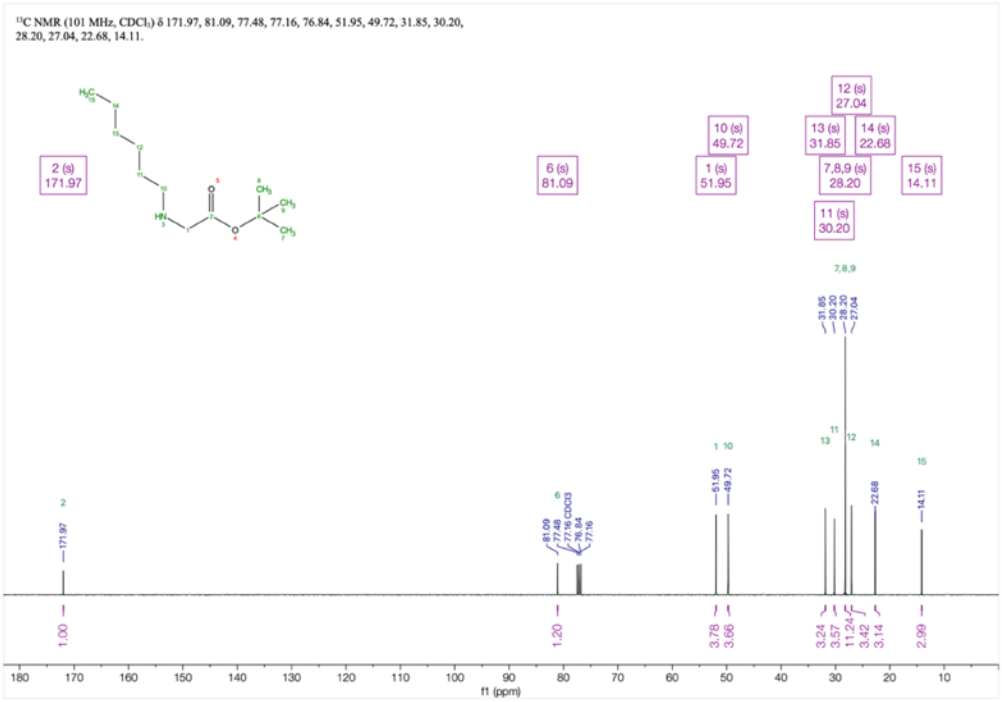


Fig. S145 [13]C NMR of Nhx-tBu.

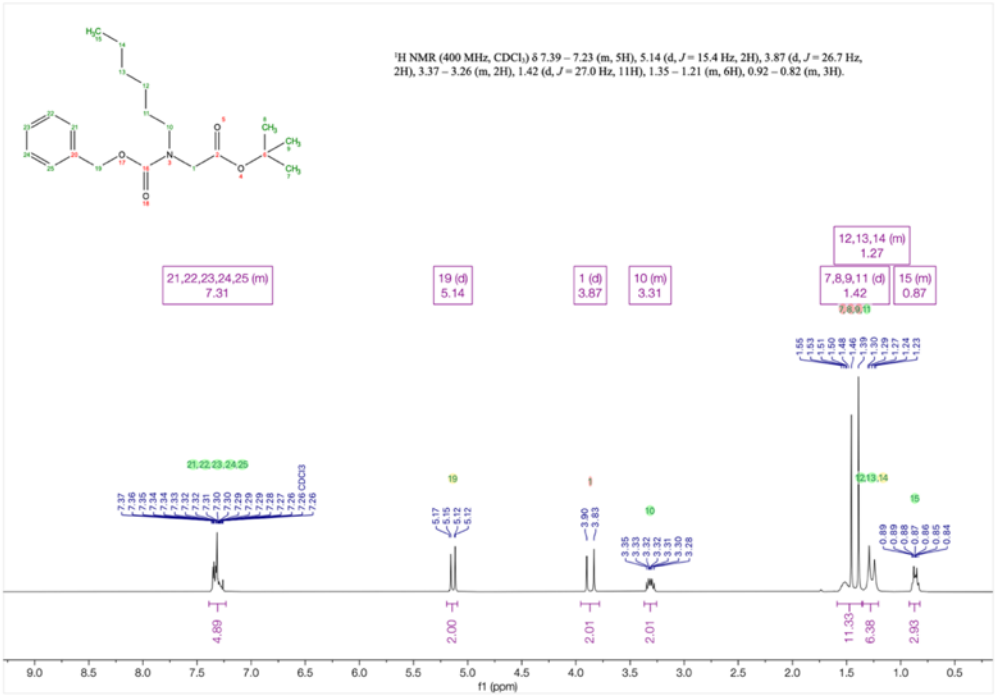


Fig. S146 ^{1}H NMR of Cbz-Nhx-tBu.

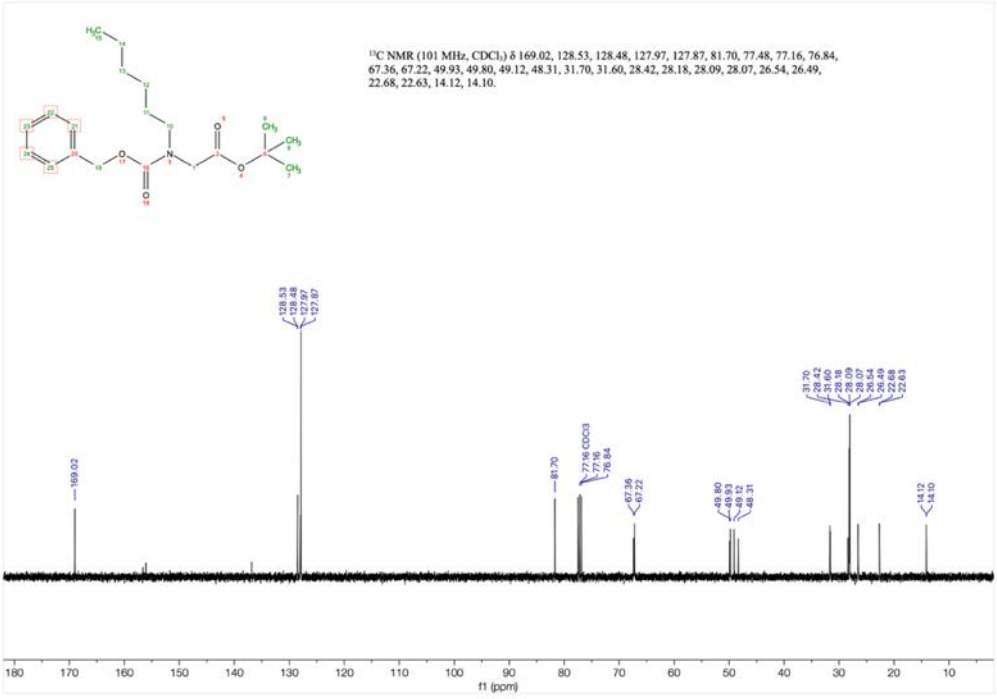


Fig. S147 ^{13}C NMR of Cbz-Nhx-tBu.

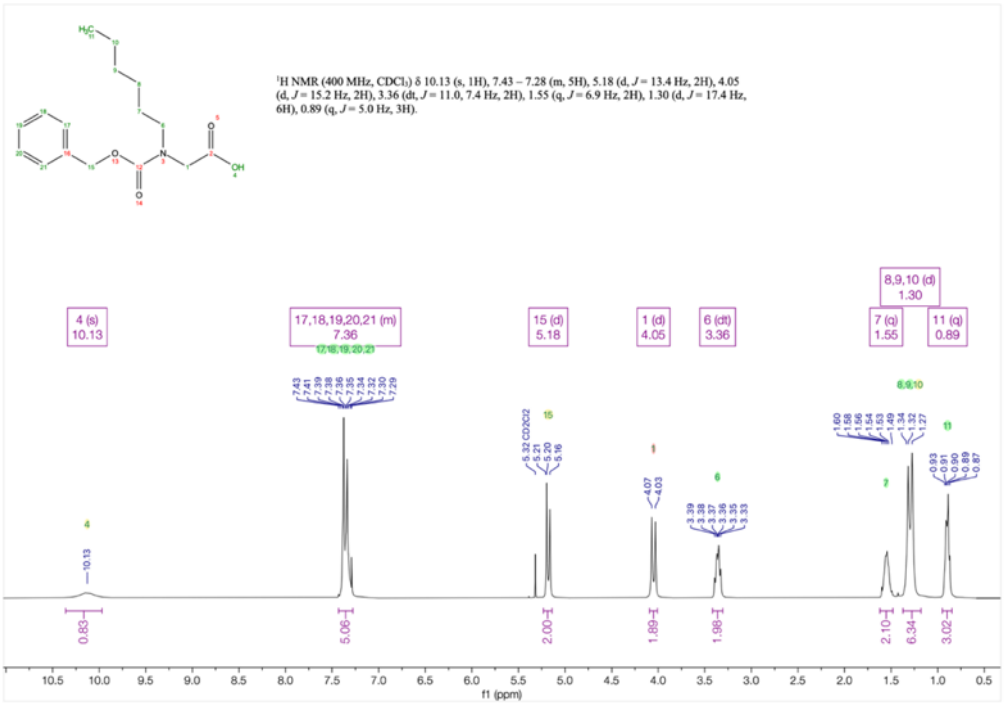


Fig. S148 ^{1}H NMR of Cbz-Nhx.

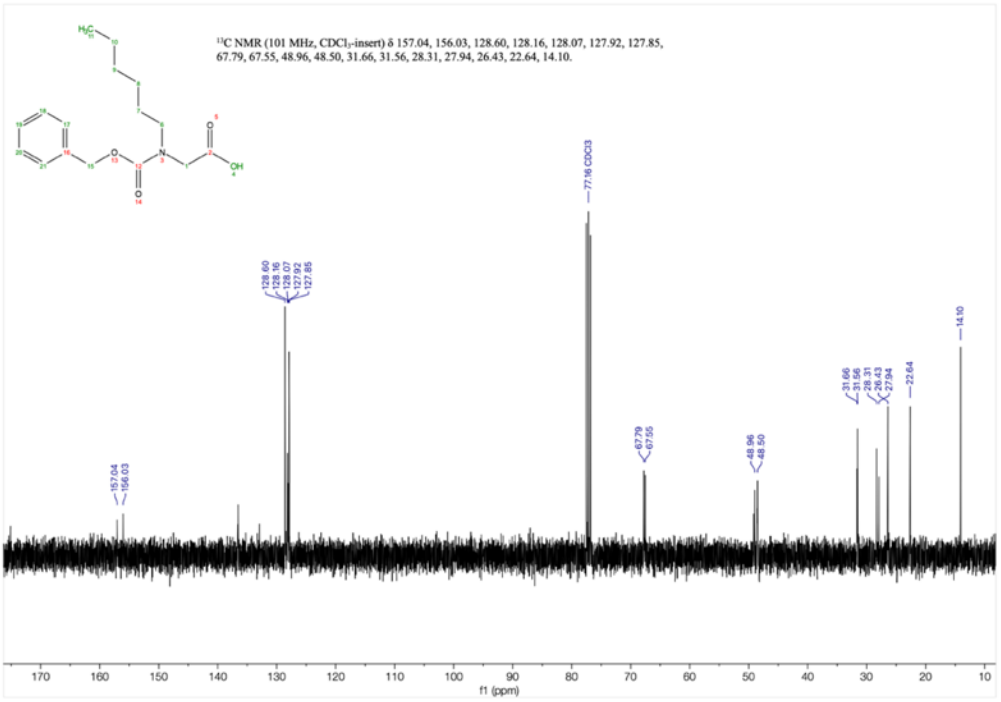


Fig. S149 ^{13}C NMR of Cbz-Nhx.

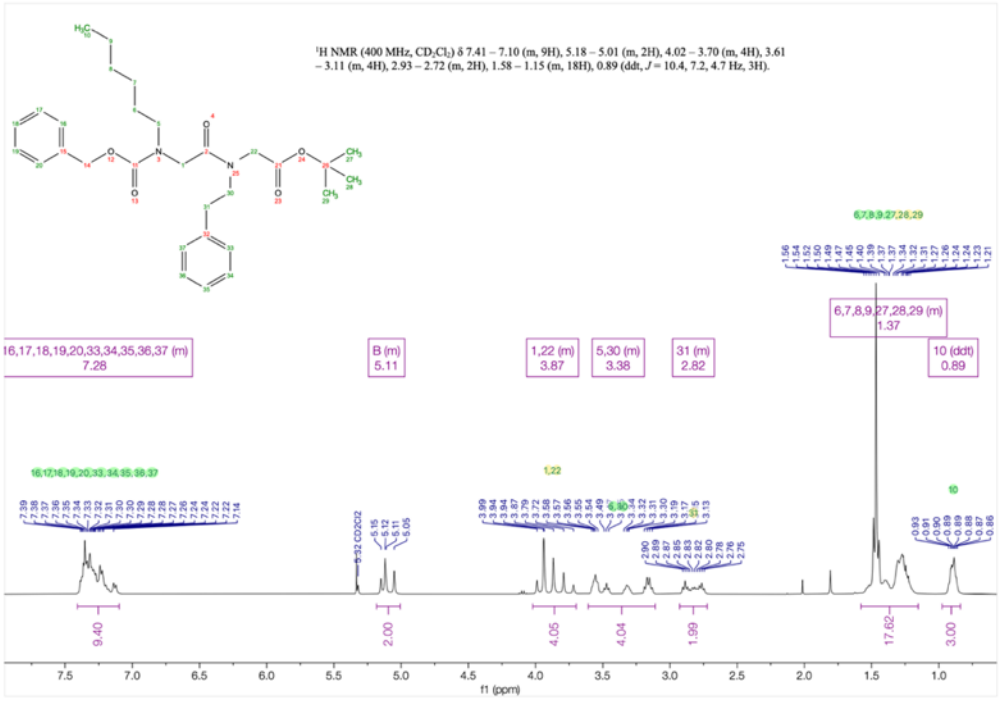


Fig. S150 ^{1}H NMR of Cbz-Nhx-Npe-tBu.

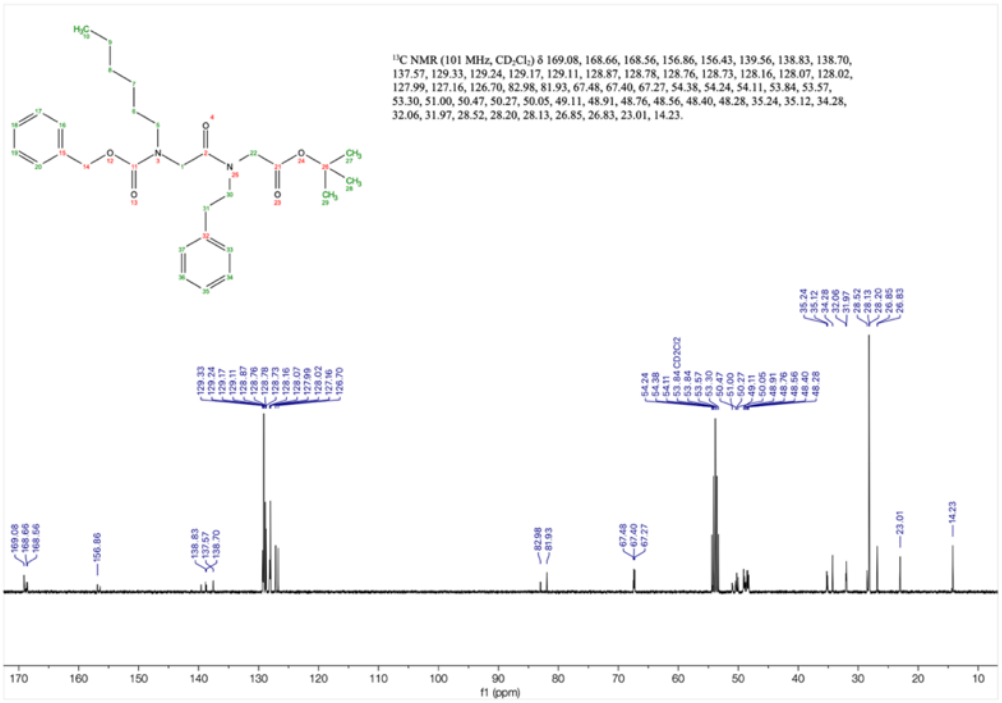


Fig. S151 ^{13}C NMR of Cbz-Nhx-Npe-tBu.

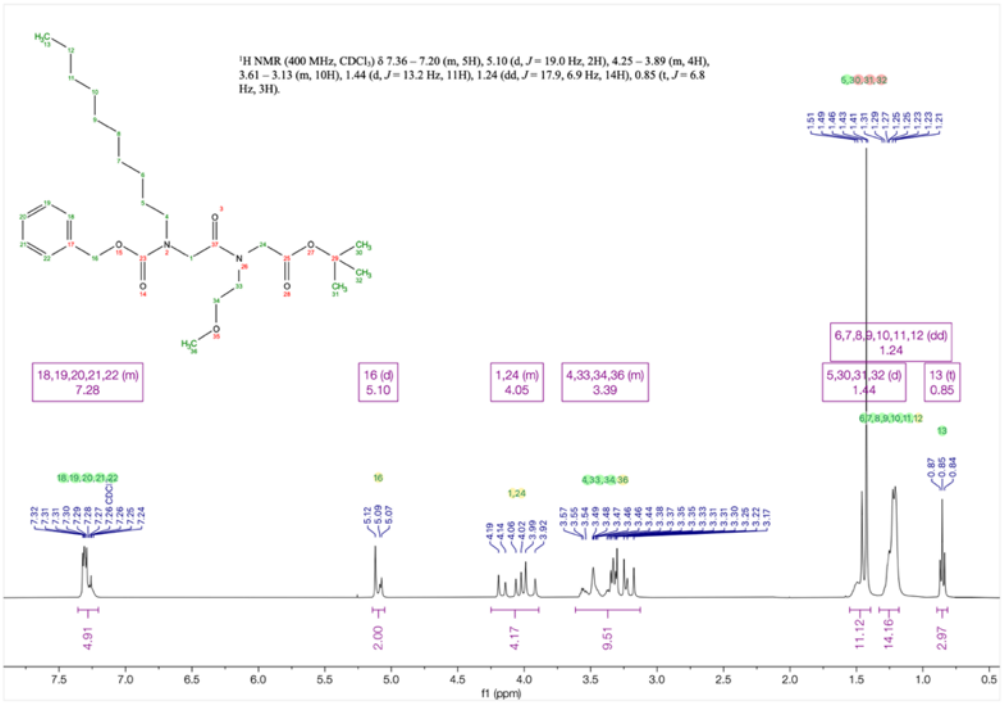


Fig. S152 ^{1}H NMR of Cbz-Ndc-Nme-tBu.

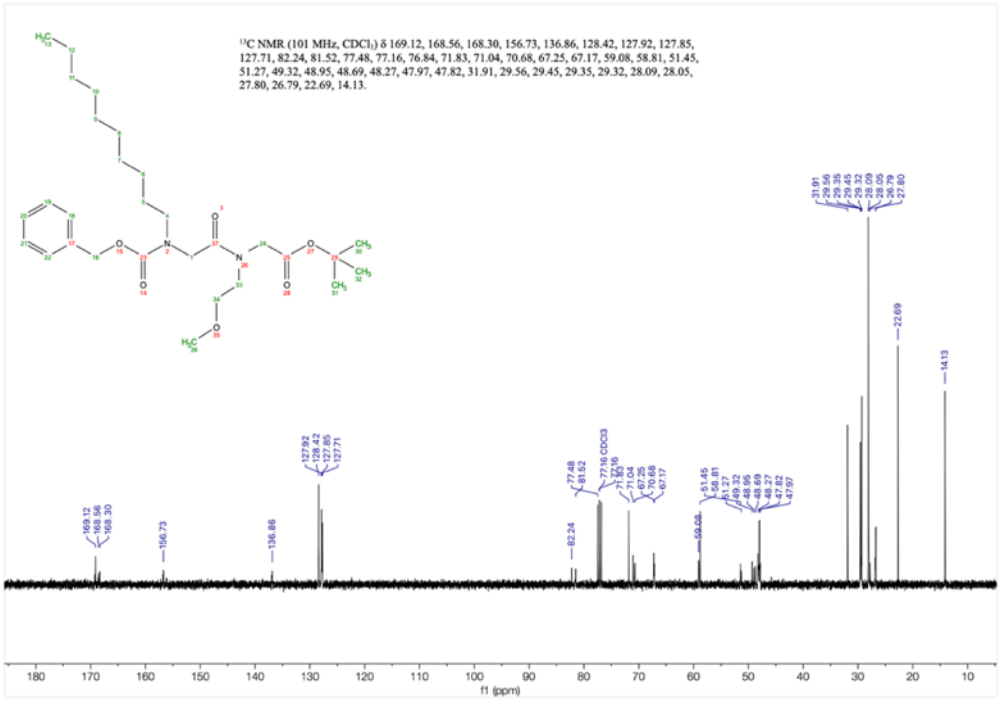


Fig. S153 ^{13}C NMR of Cbz-Ndc-Nme-tBu.

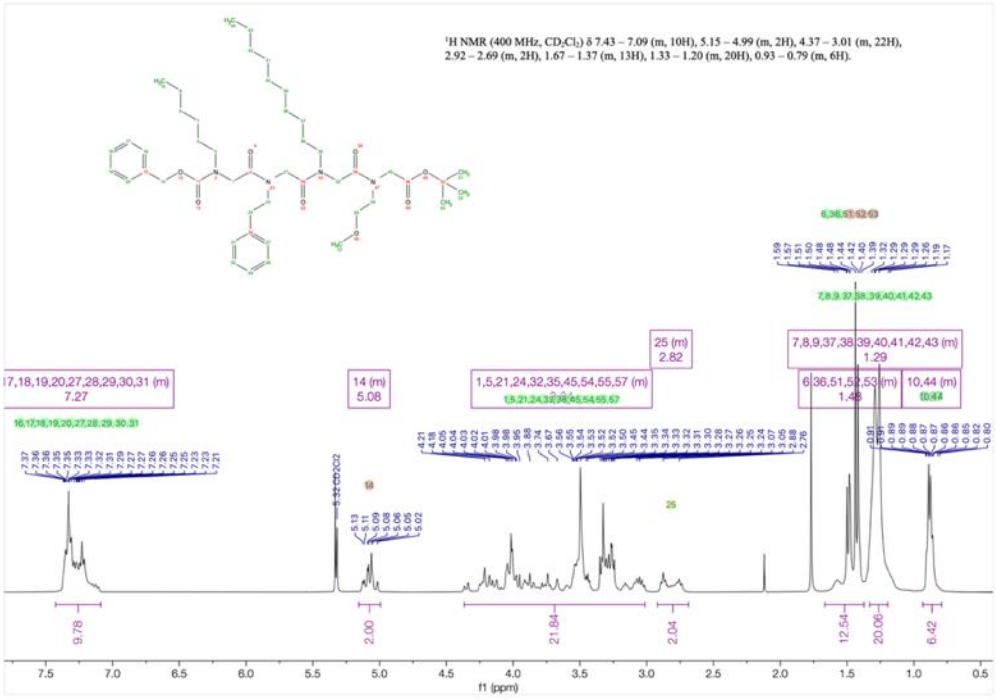


Fig. S154 ^{1}H NMR of Cbz-Nhx-Npe-Ndc-Nme-tBu.

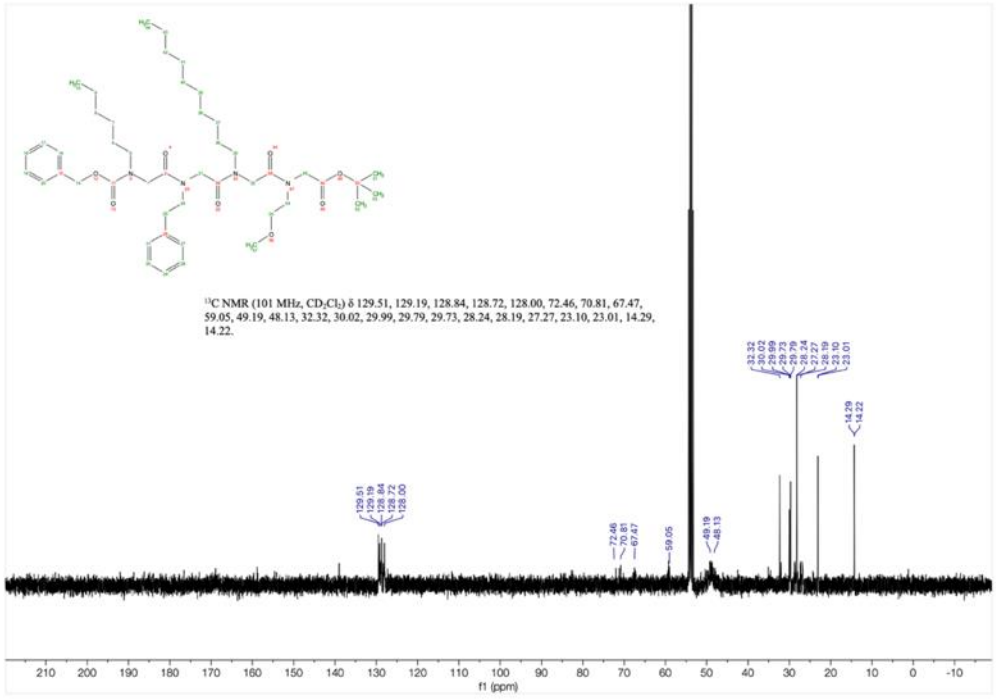


Fig. S155 ^{13}C NMR of Cbz-Nhx-Npe-Ndc-Nme-tBu.

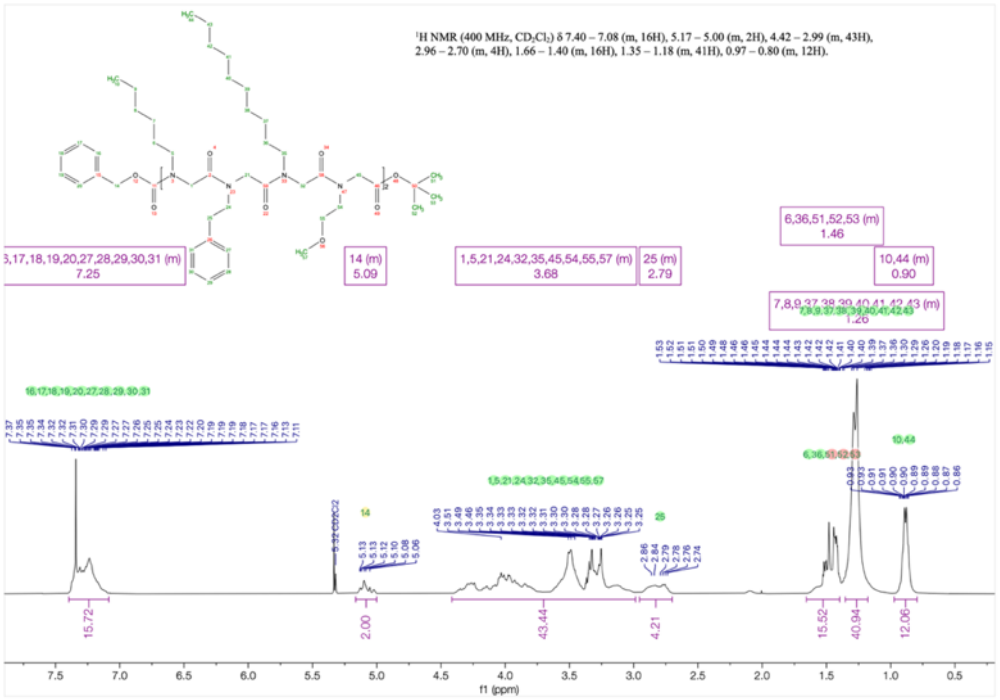


Fig. S156 ^{1}H NMR of Cbz-(Nhx-Npe-Ndc-Nme)$_2$-tBu.

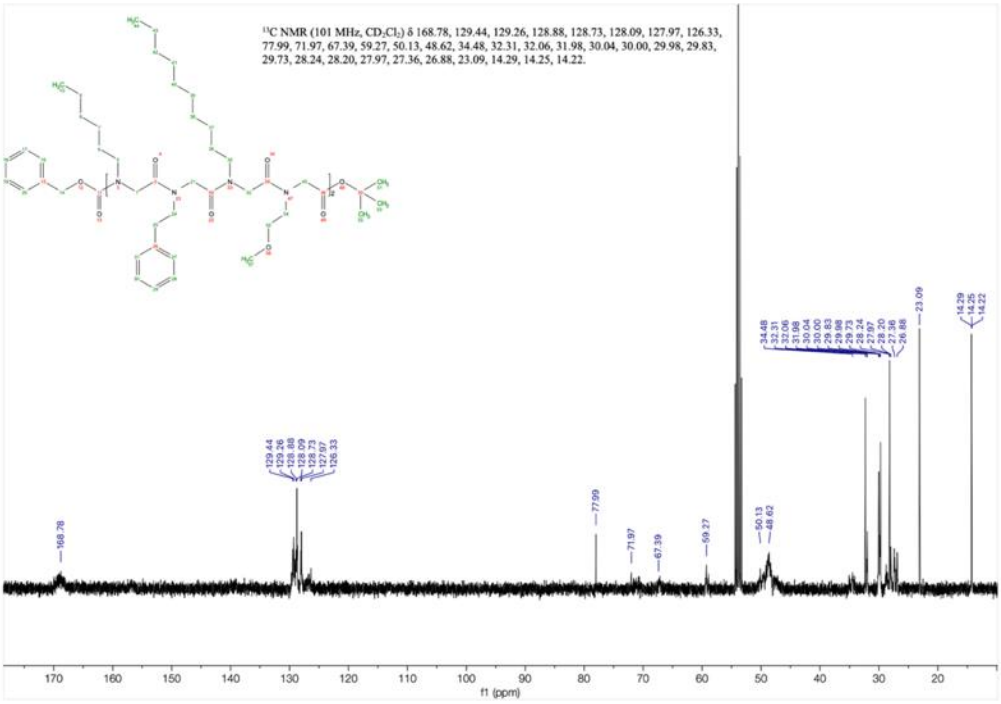


Fig. S157 ^{13}C NMR of Cbz-(Nhx-Npe-Ndc-Nme)$_2$-tBu.

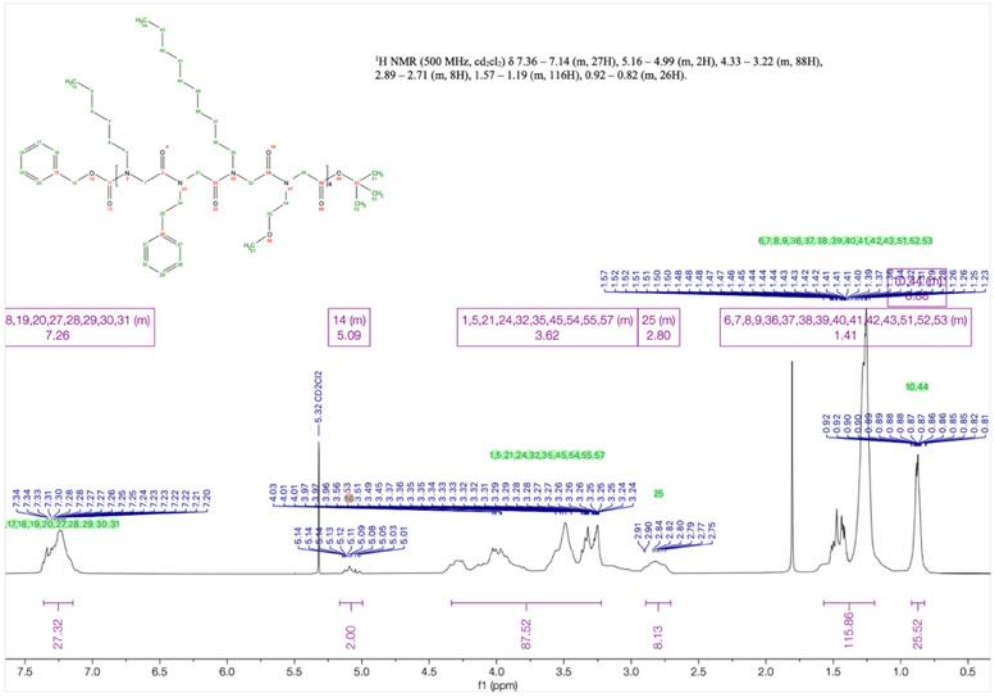


Fig. S158 ^{1}H NMR of Cbz-(Nhx-Npe-Ndc-Nme)$_4$-tBu.

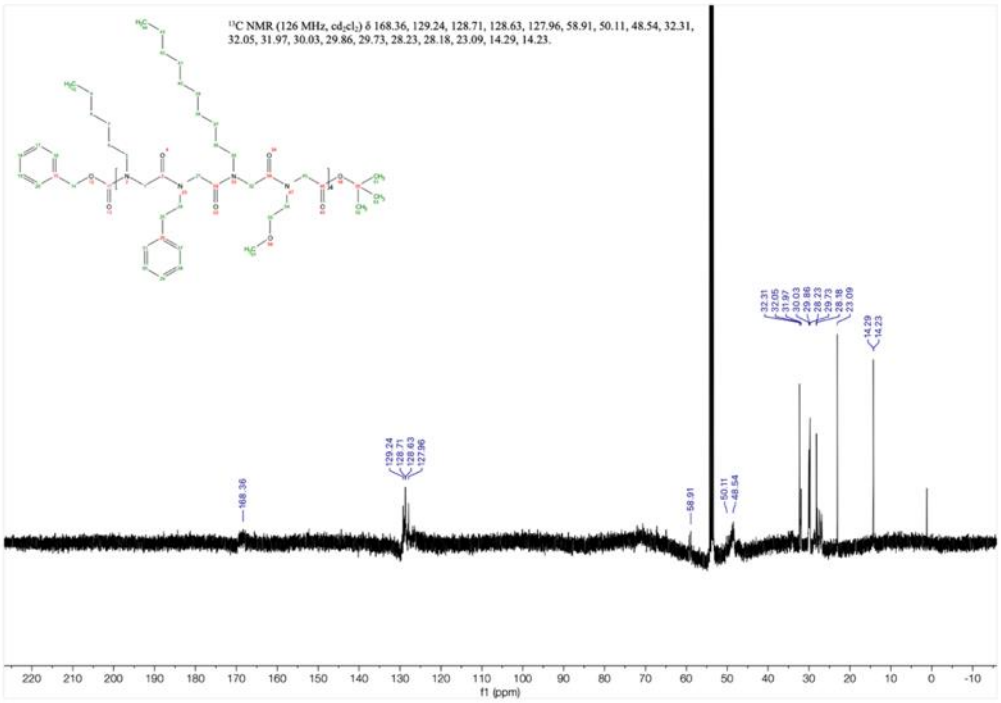


Fig. S159 ^{13}C NMR of Cbz-(Nhx-Npe-Ndc-Nme)$_4$-tBu. Note: baseline not corrected to maintain signal.

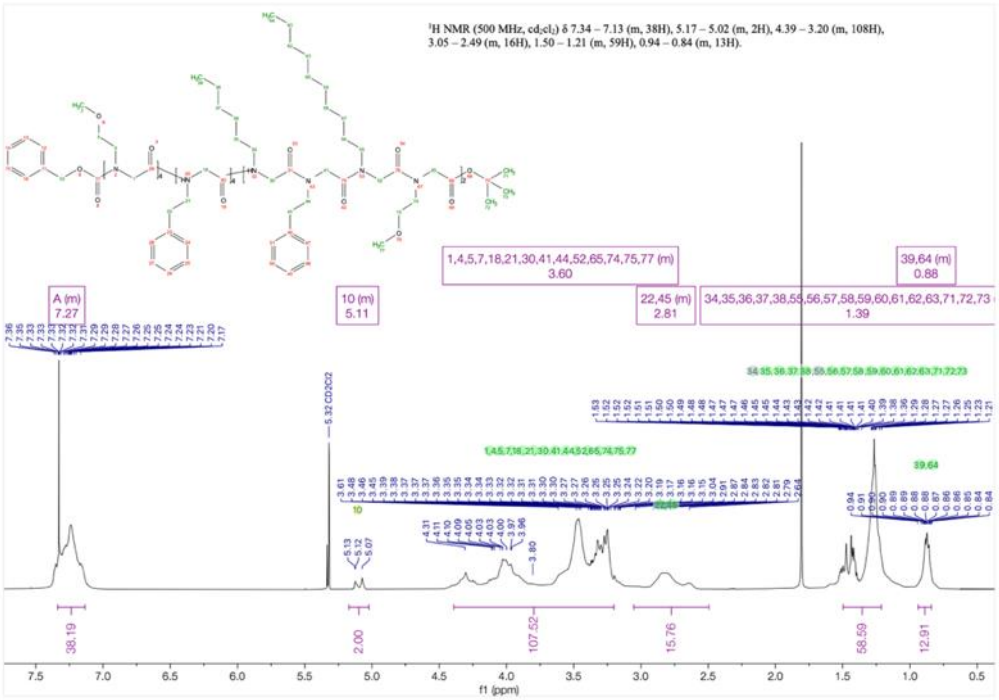


Fig. S160 [1]H-NMR of Cbz-Nme$_4$-Npe$_4$-(Nhx-Npe-Ndc-Nme)$_2$-tBu.

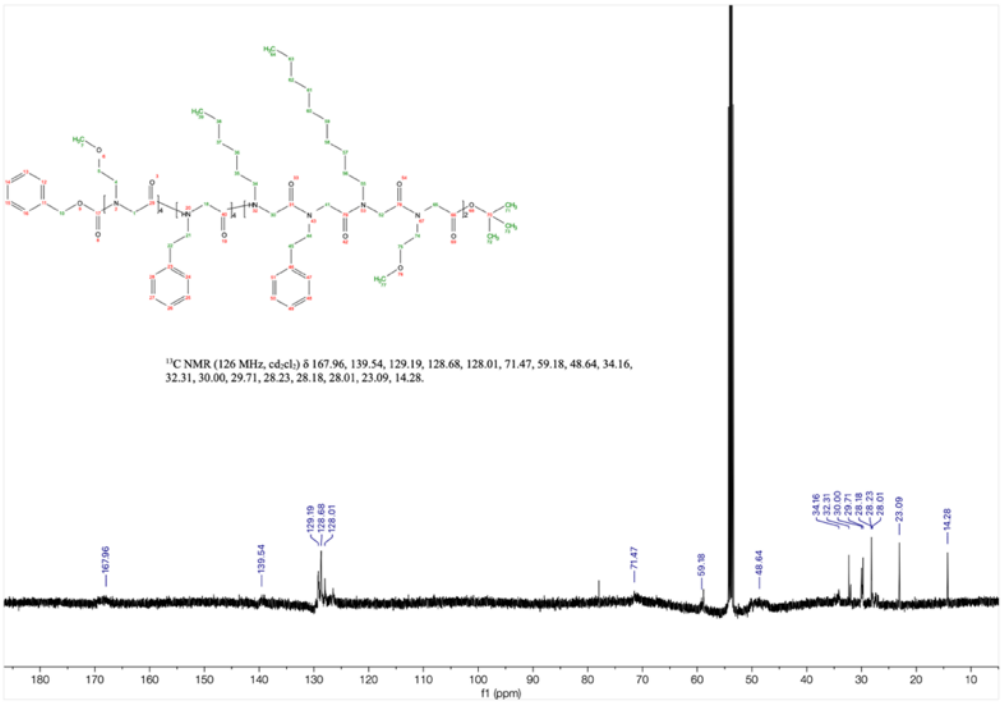


Fig. S161 [13]C-NMR of Cbz-Nme$_4$-Npe$_4$-(Nhx-Npe-Ndc-Nme)$_2$-tBu. Note: baseline not corrected to maintain signal.

6.4 Stereo-defined alternating peptoids

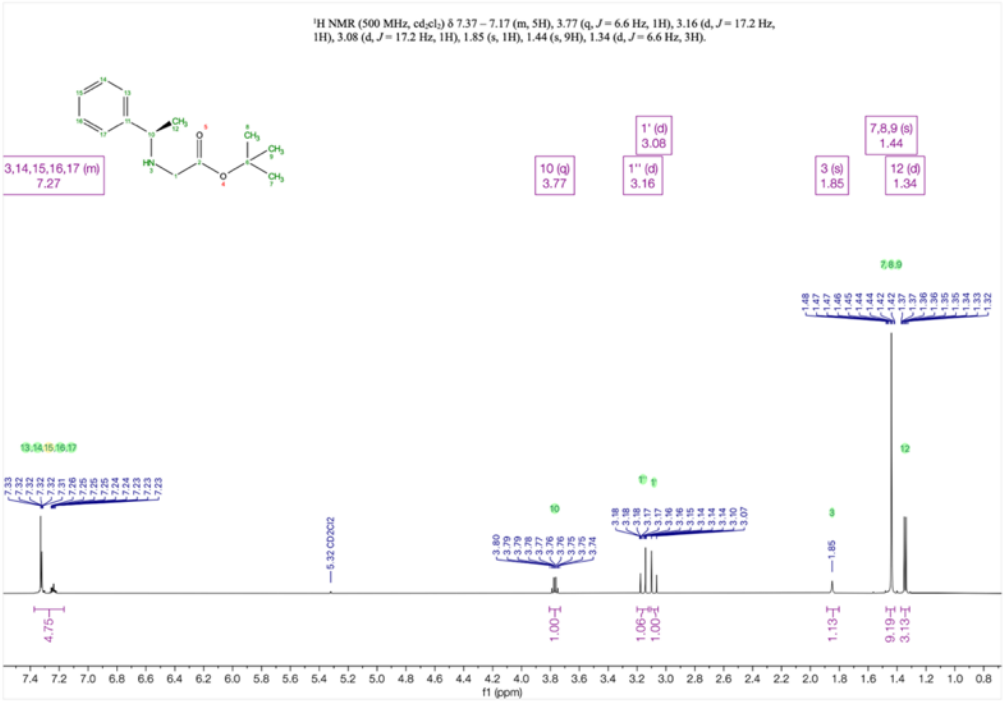


Fig. S162 [1]H-NMR of Nrpe-tBu.

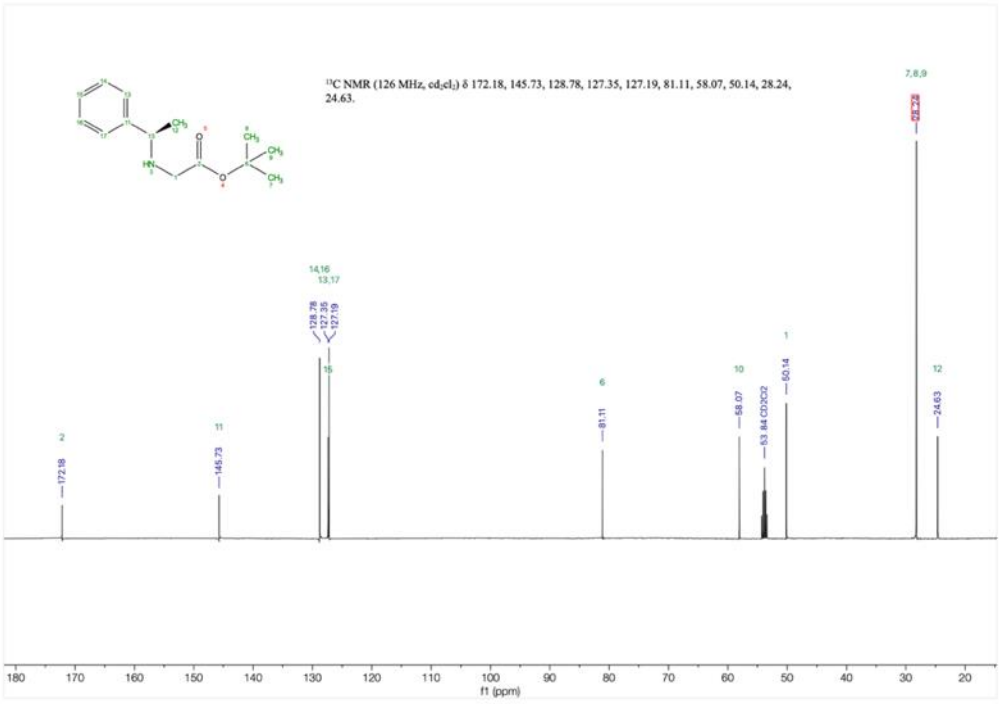


Fig. S163 [13]C-NMR of Nrpe-tBu.

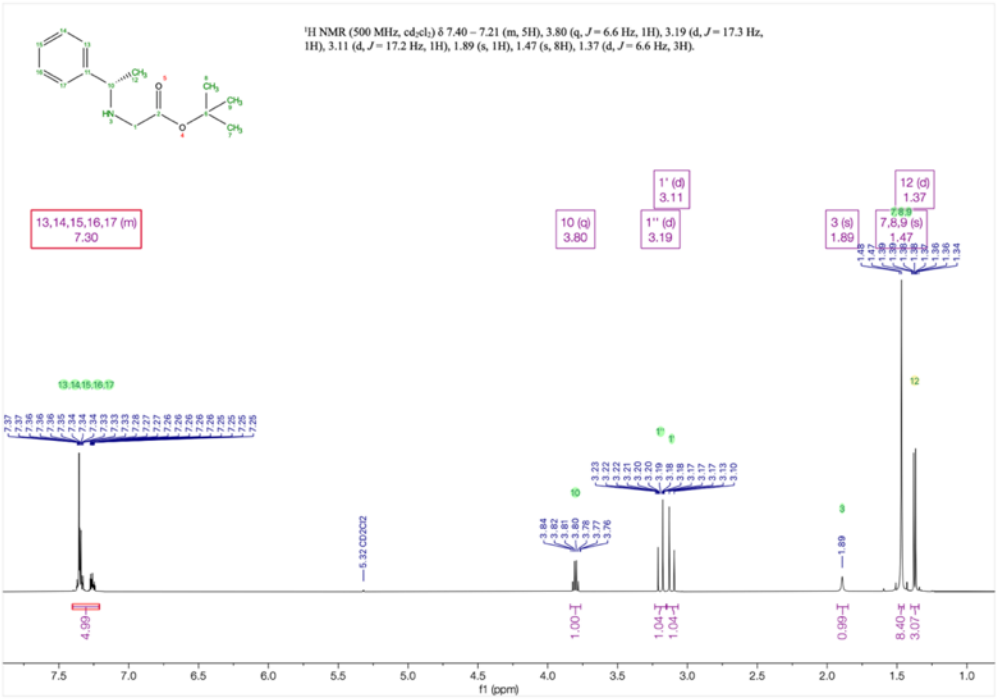


Fig. S164 [1]H-NMR of Nspe-tBu.

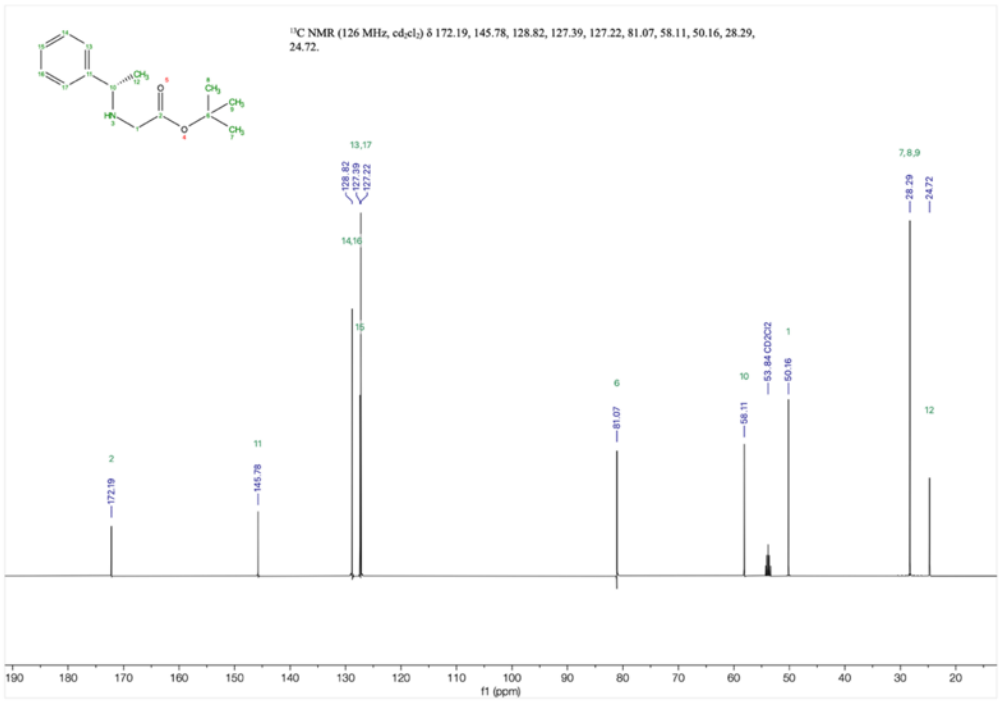


Fig. S165 [13]C-NMR of Nspe-tBu.

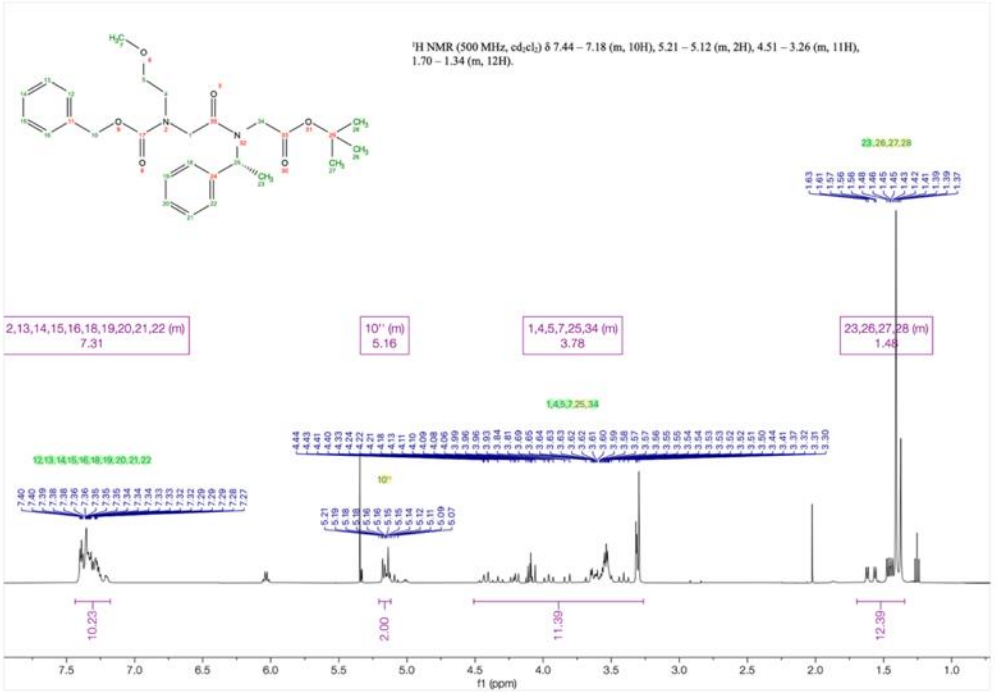


Fig. S166 ^{1}H NMR of Cbz-Nme-Nrpe-tBu.

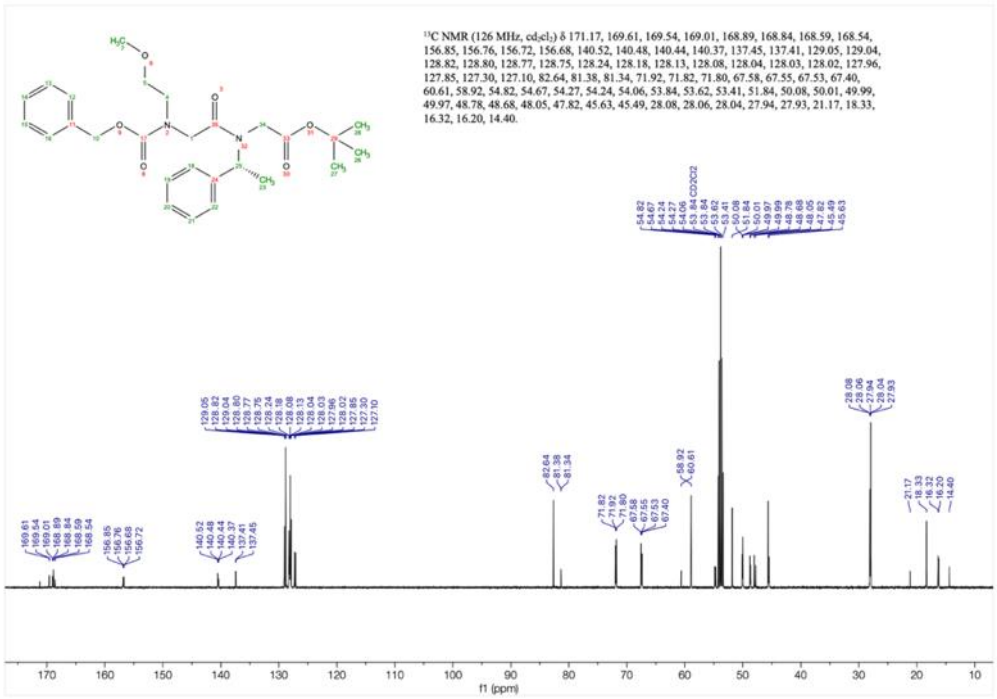


Fig. S167 ^{13}C NMR of Cbz-Nme-Nrpe-tBu.

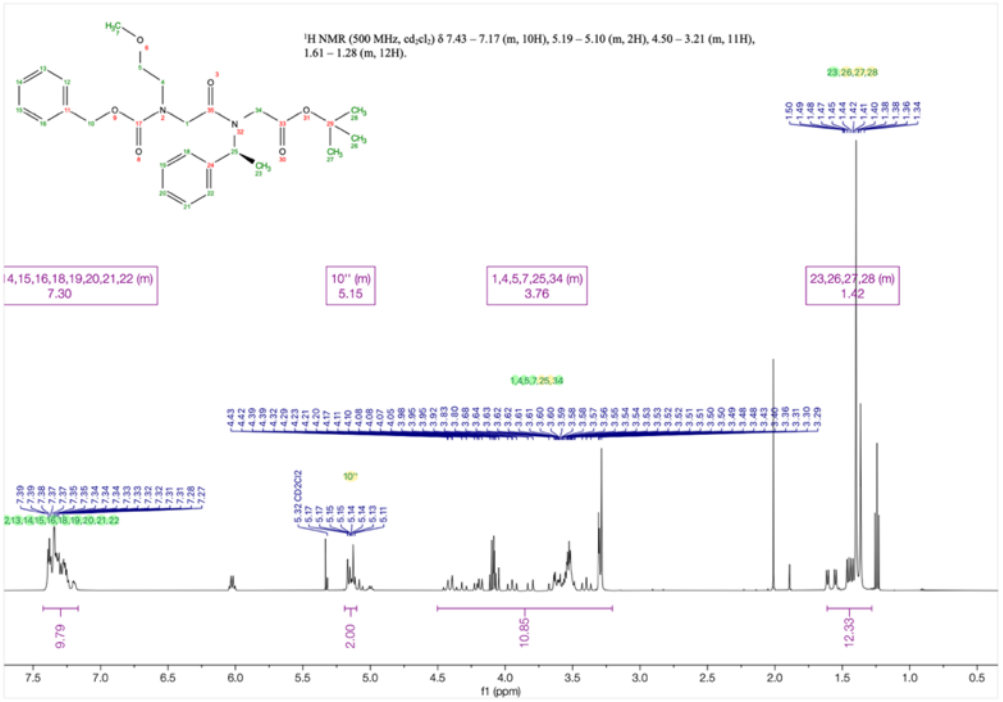


Fig. S168 ^{1}H NMR of Cbz-Nme-Nspe-tBu.

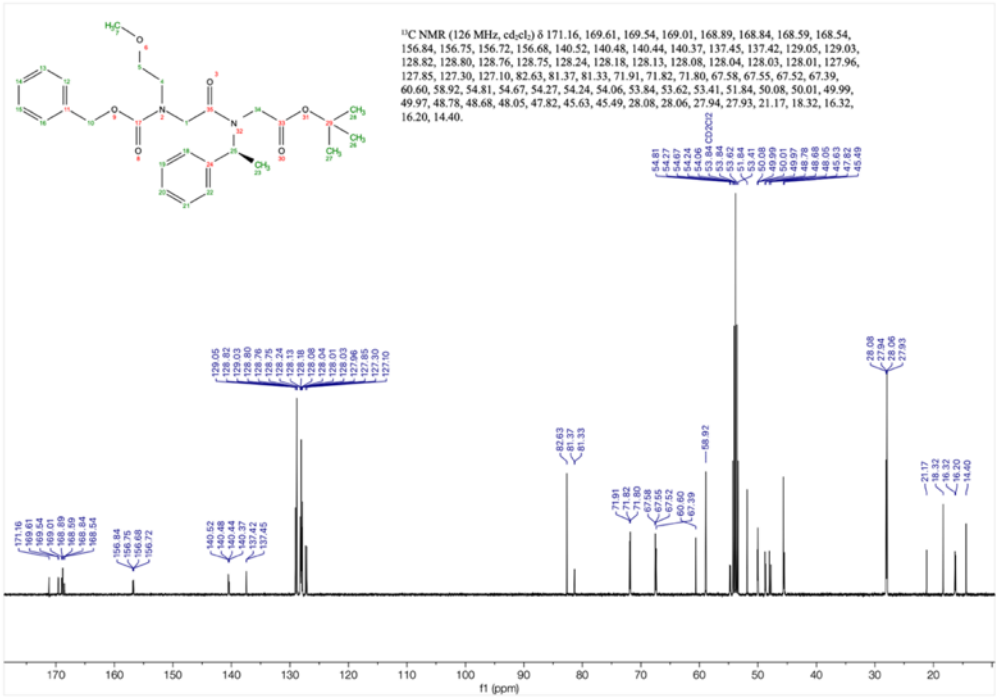


Fig. S169 ^{13}C NMR of Cbz-Nme-Nspe-tBu.

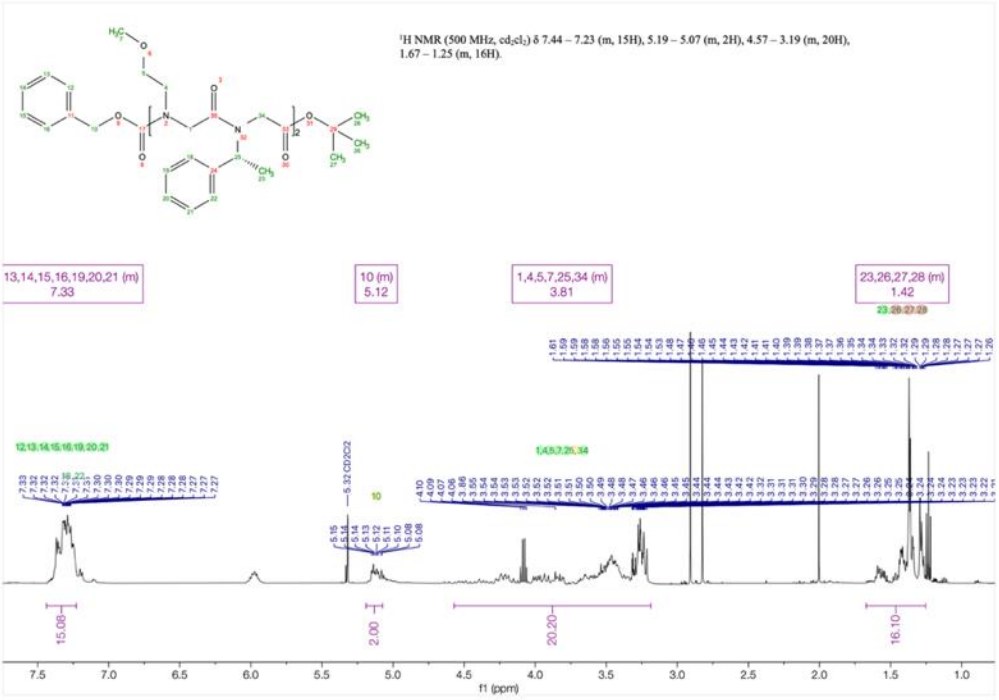


Fig. S170 ^{1}H NMR of Cbz-(Nme-Nrpe)$_2$-tBu.

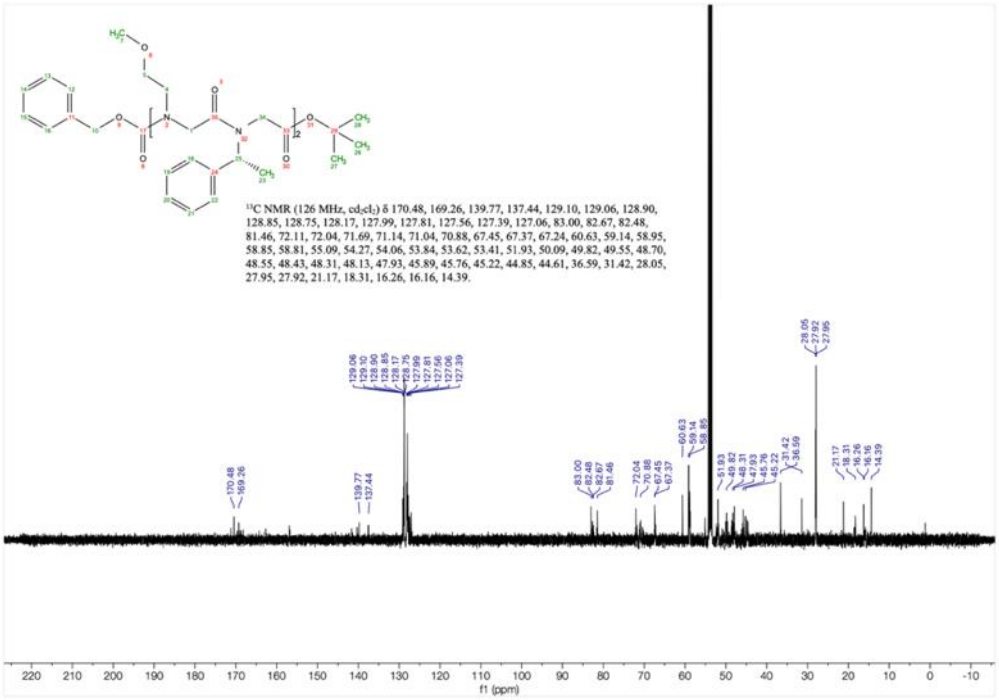


Fig. S171 ^{13}C NMR of Cbz-(Nme-Nrpe)$_2$-tBu.

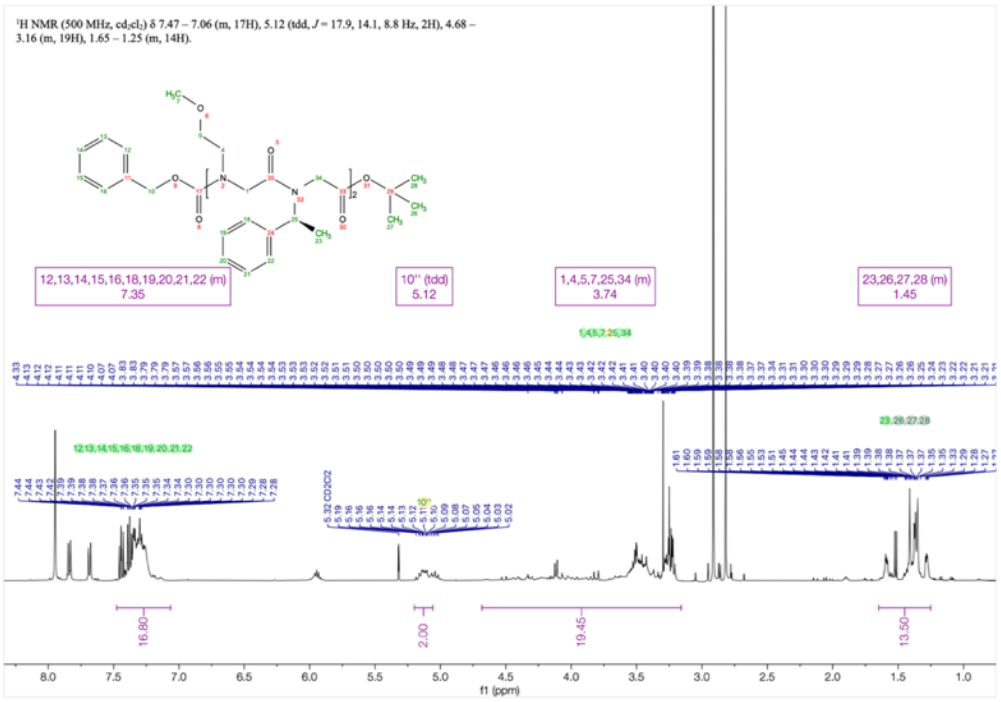


Fig. S172 ^{1}H NMR of Cbz-(Nme-Nspe)$_2$-tBu.

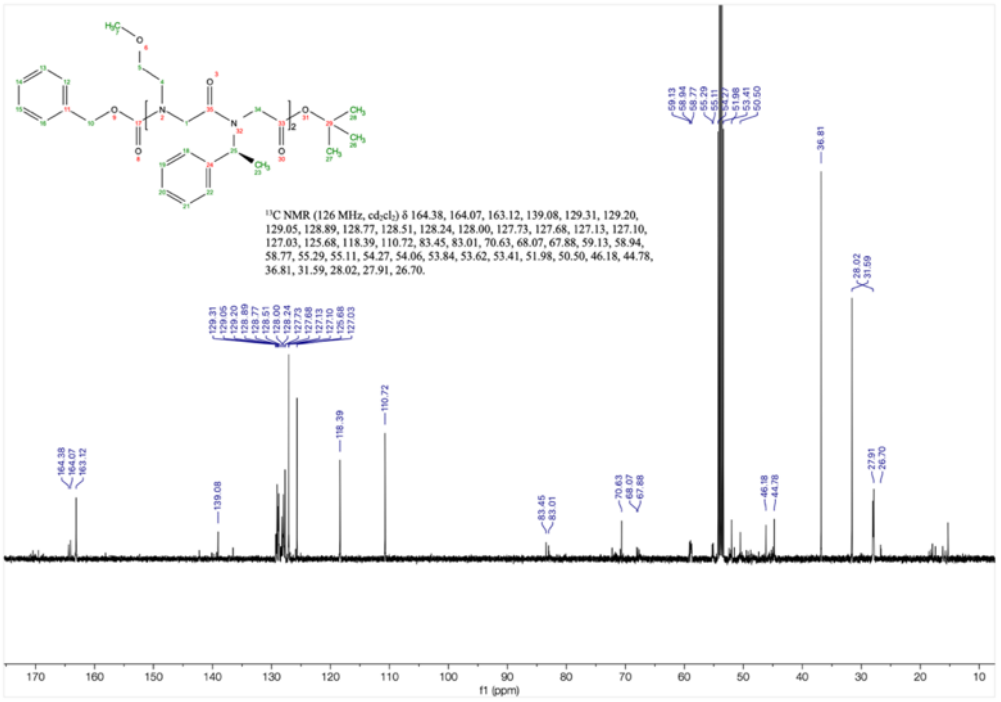


Fig. S173 ^{13}C NMR of Cbz-(Nme-Nspe)$_2$-tBu.

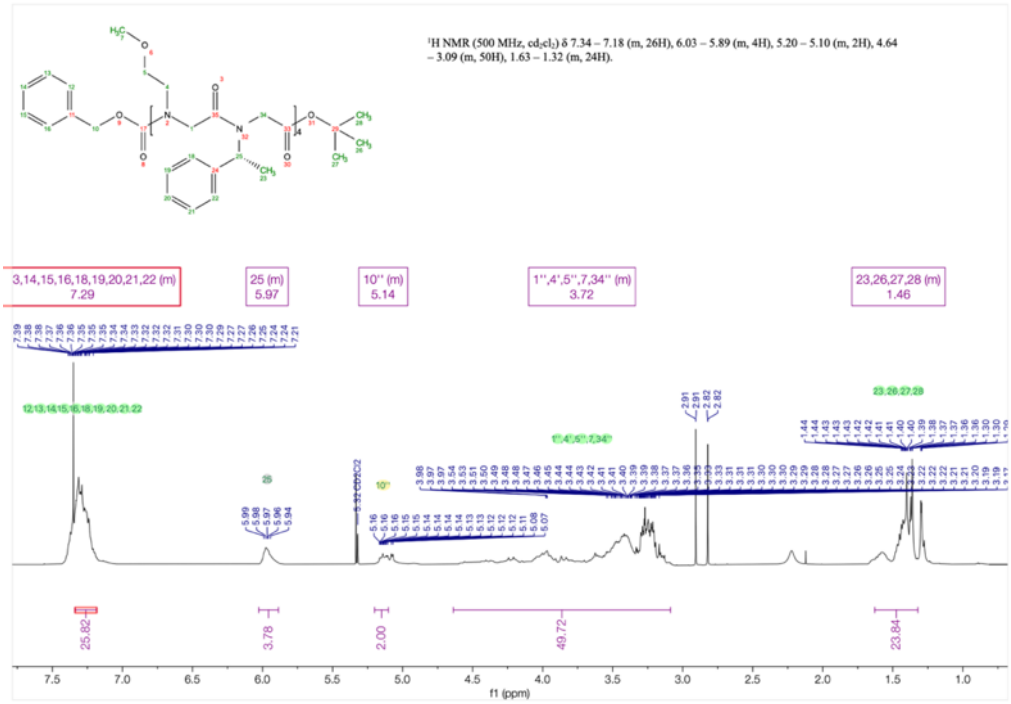


Fig. S174 [1]H NMR of Cbz-(Nme-Nrpe)4-tBu.

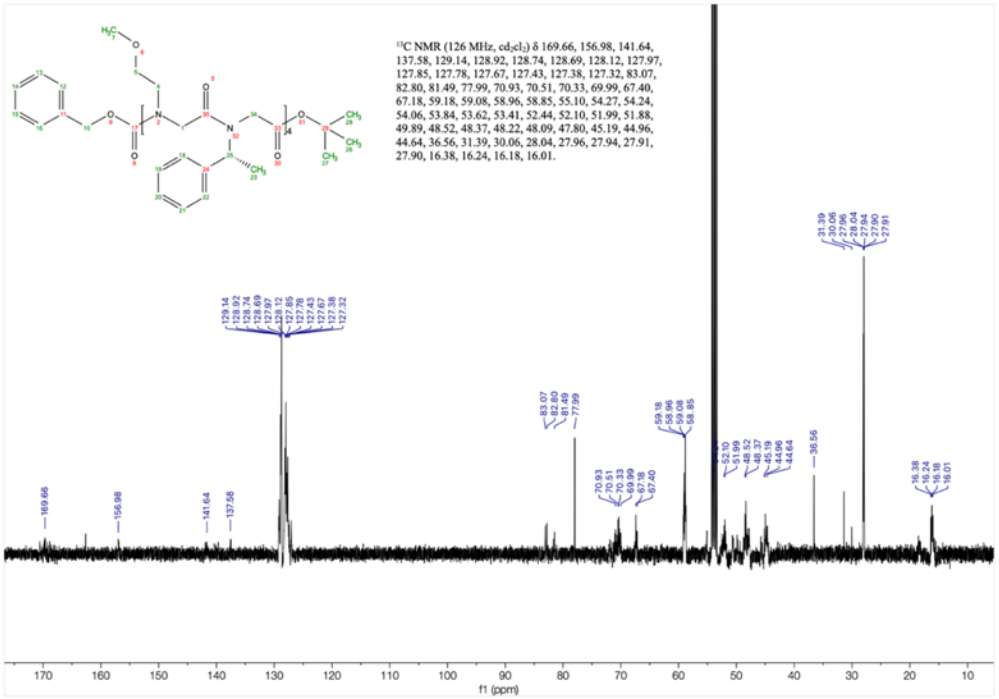


Fig. S175 [13]C NMR of Cbz-(Nme-Nrpe)4-tBu.

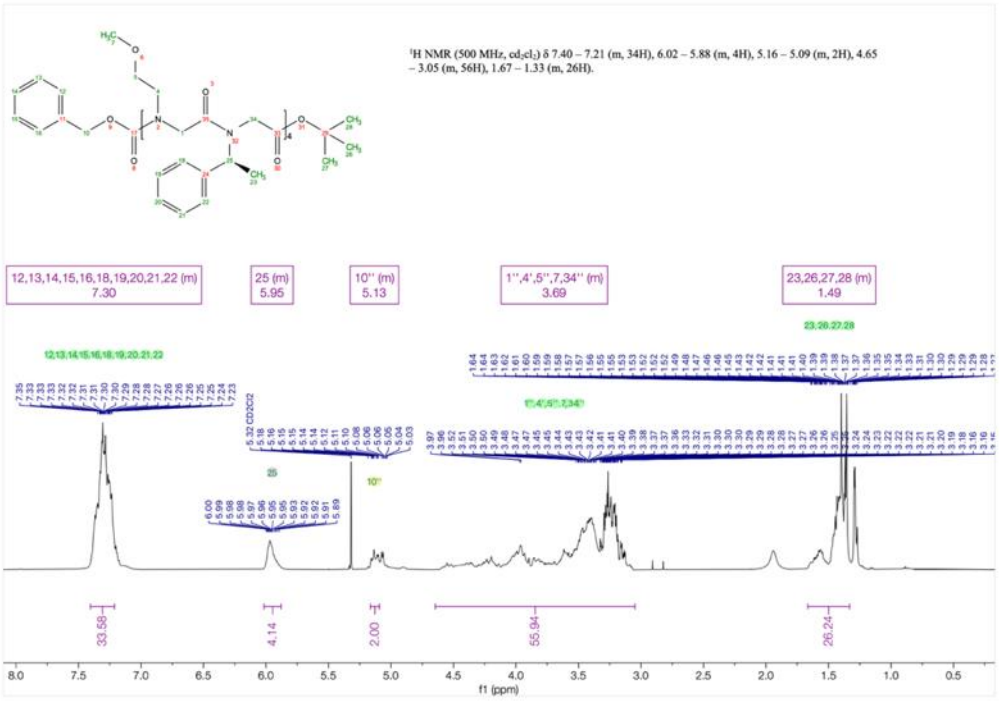


Fig. S176 ^{1}H NMR of Cbz-(Nme-Nspe)$_4$-tBu.

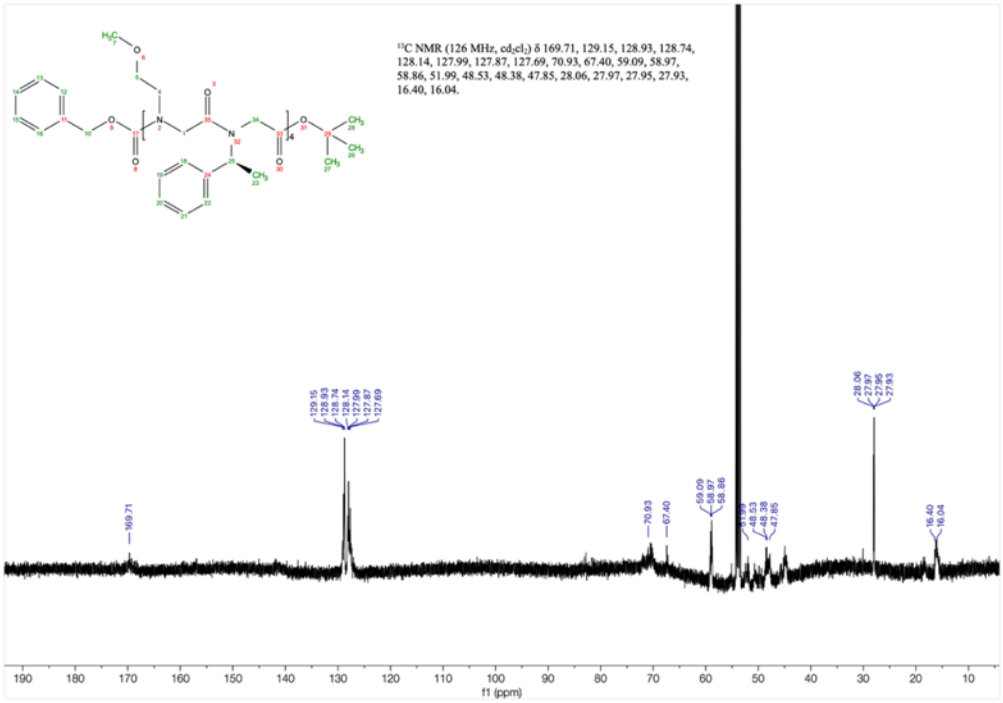


Fig. S177 ^{13}C NMR of Cbz-(Nme-Nspe)$_4$-tBu. Note: baseline not corrected to maintain signal.

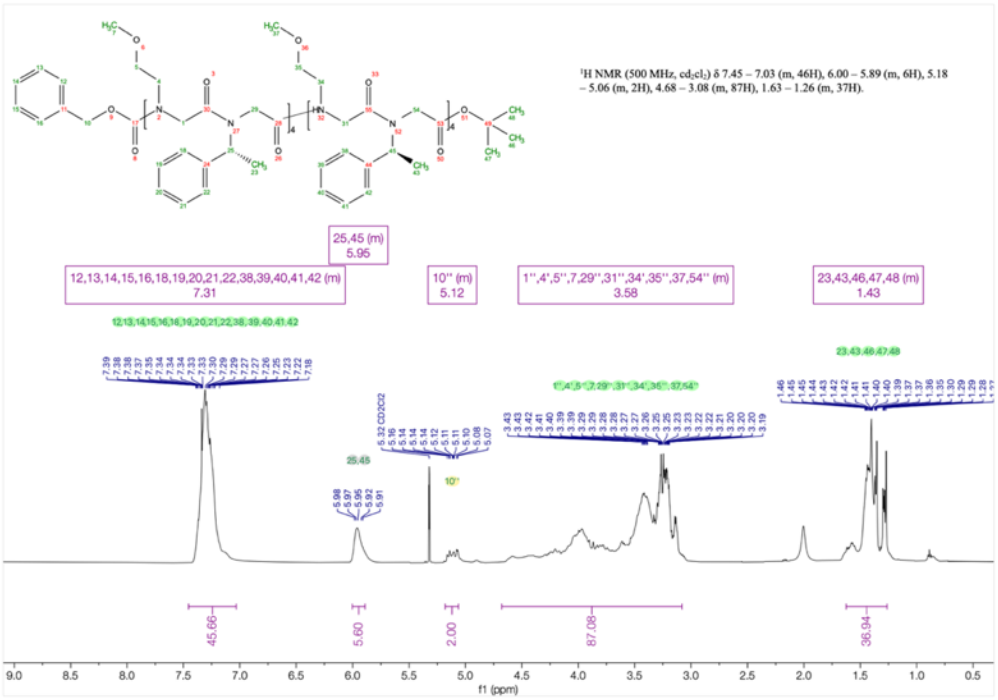


Fig. S178 ^{1}H NMR of Cbz-(Nme-Nrpe)$_4$-(Nme-Nspe)$_4$-tBu.

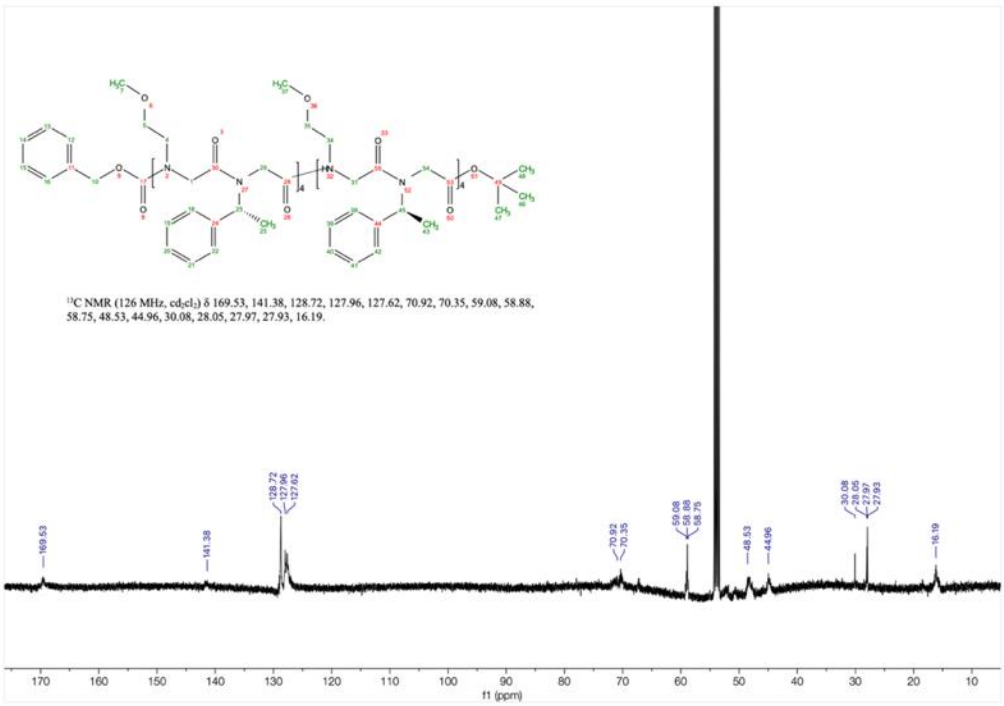


Fig. S179 ^{13}C NMR of Cbz-(Nme-Nrpe)$_4$-(Nme-Nspe)$_4$-tBu. Note: baseline not corrected to maintain signal.

6.5 Post-IEG modifications with thiol-ene and CuAAC click reactions

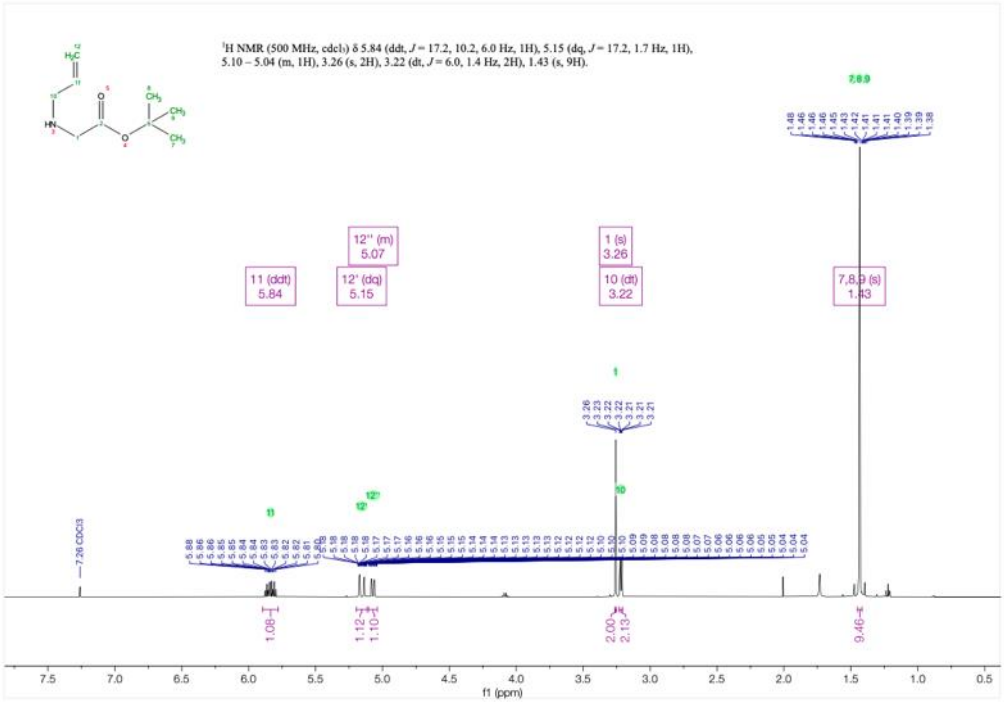


Fig. S180 ^{1}H NMR of Nall-tBu.

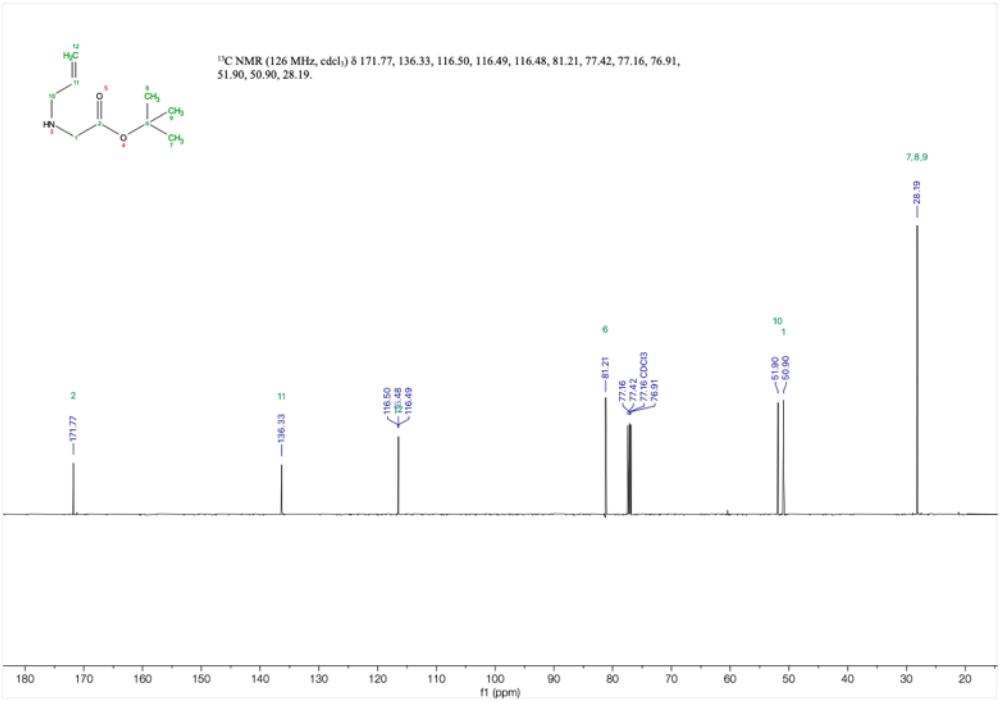


Fig. S181 ^{13}C NMR of Nall-tBu.

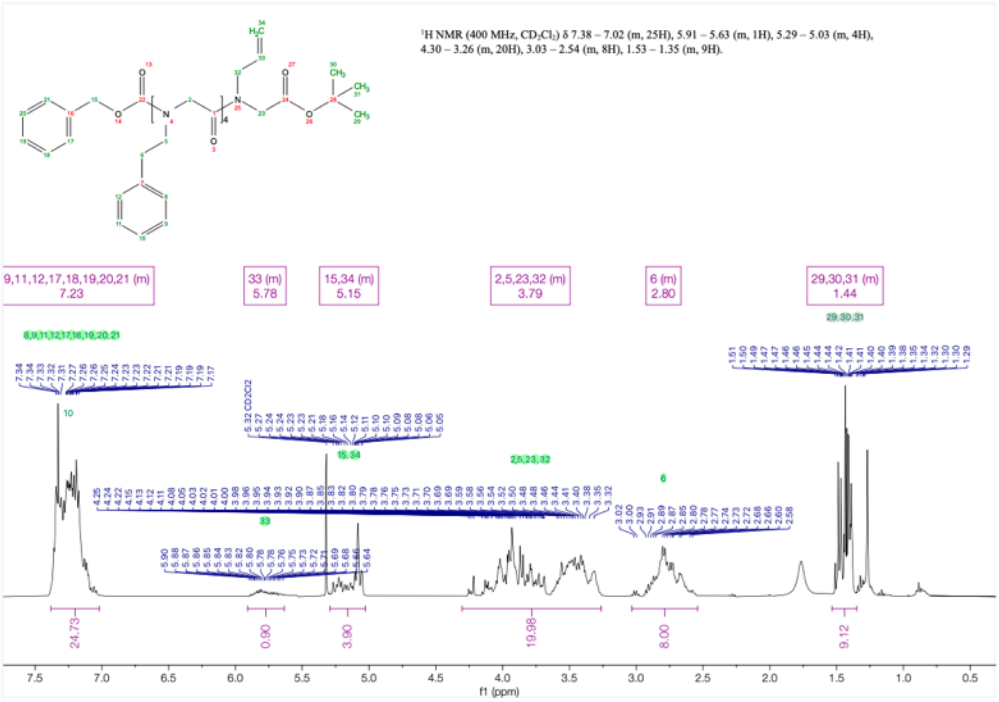


Fig. S182 [1]H NMR of Cbz-Npe4-Nall-tBu.

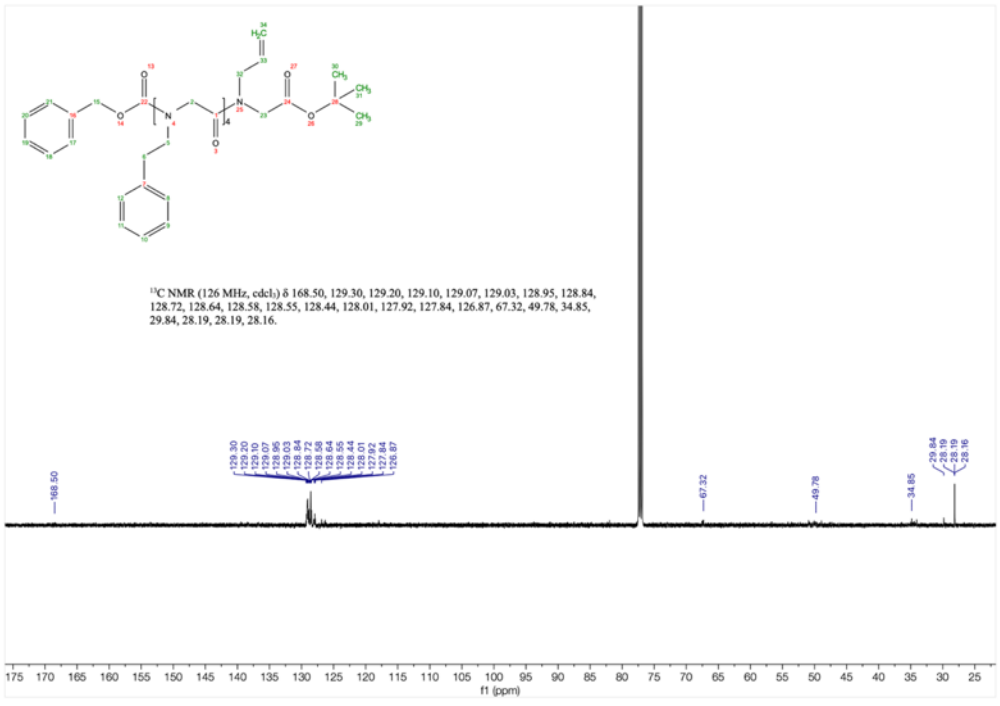


Fig. S183 [13]C NMR of Cbz-Npe4-Nall-tBu.

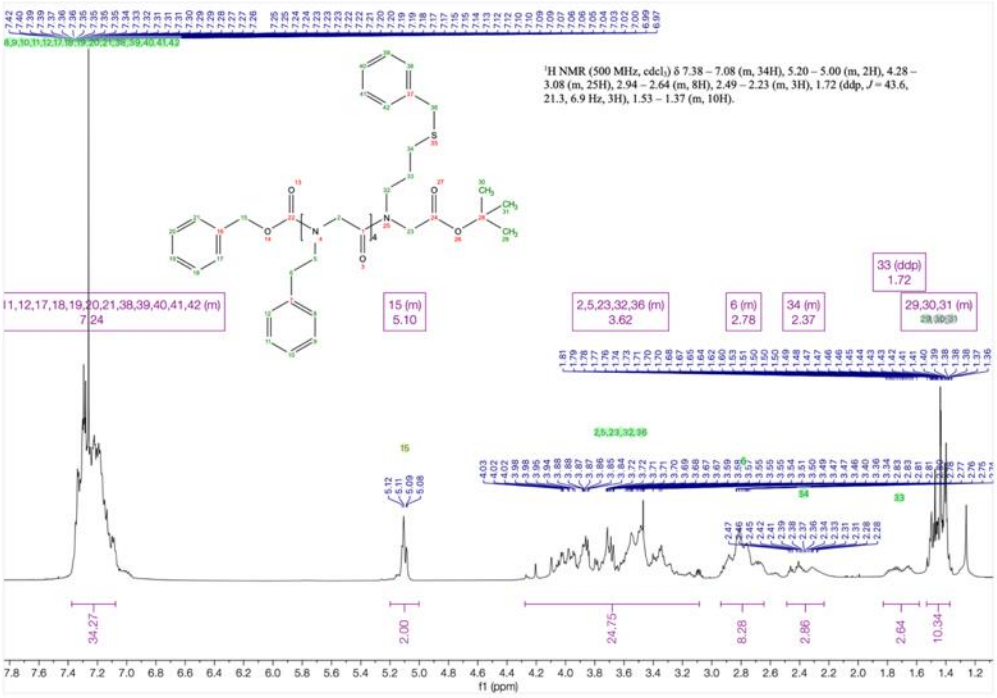


Fig. S184 ^{1}H NMR of Cbz-Npe$_4$-Nthio-tBu.

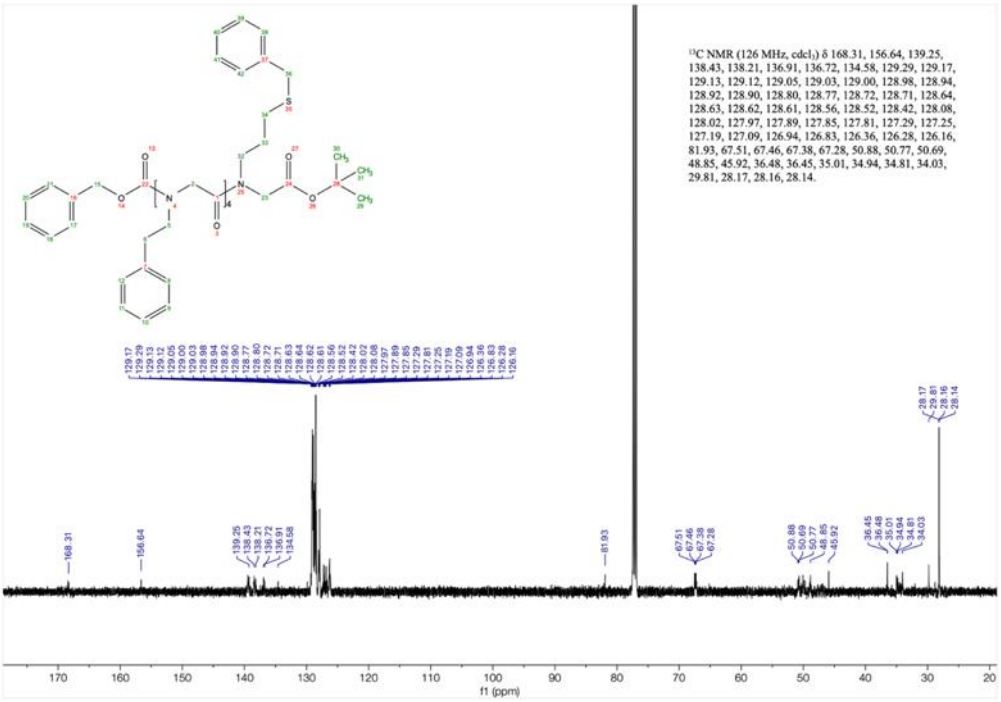


Fig. S185 ^{13}C NMR of Cbz-Npe$_4$-Nthio-tBu.

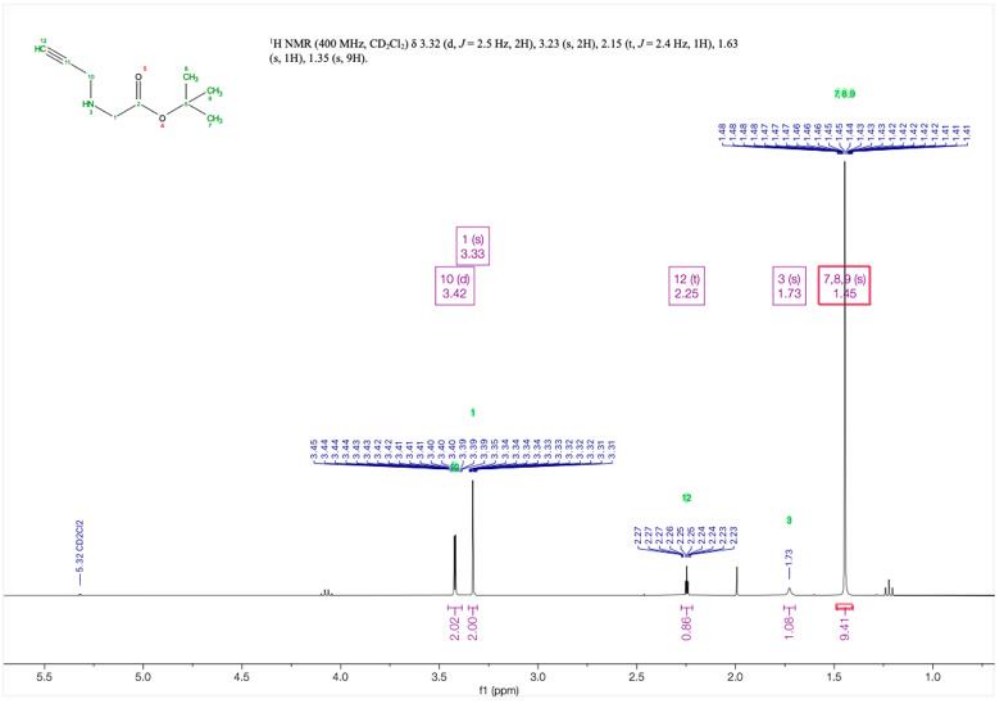


Fig. S186 ^{1}H NMR of Nalk-tBu.

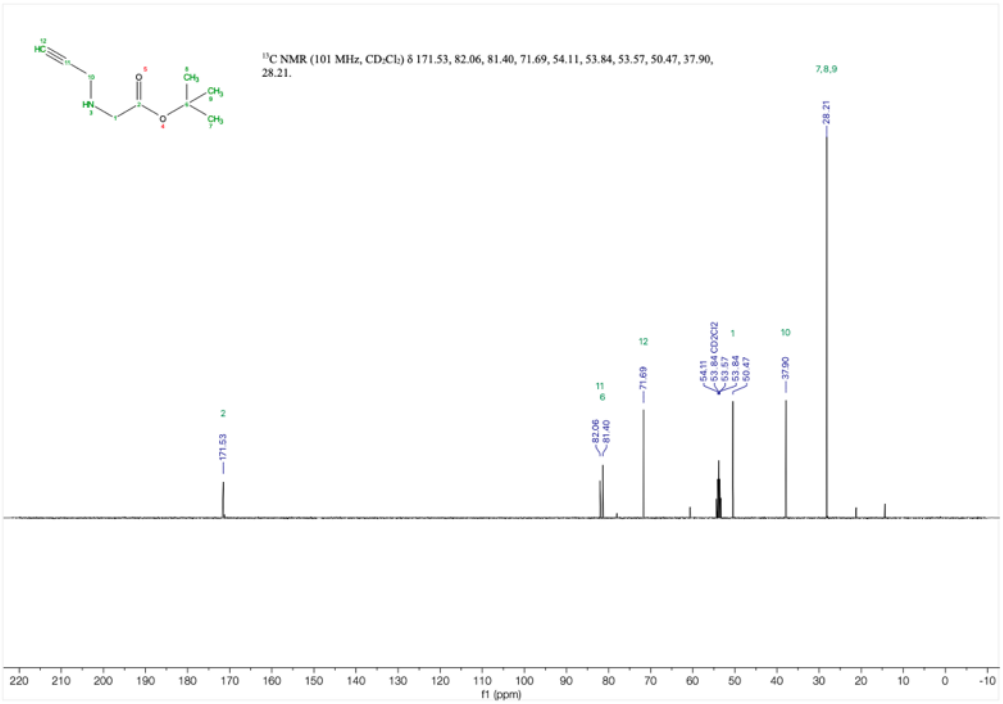


Fig. S187 ^{13}C NMR of Nalk-tBu.

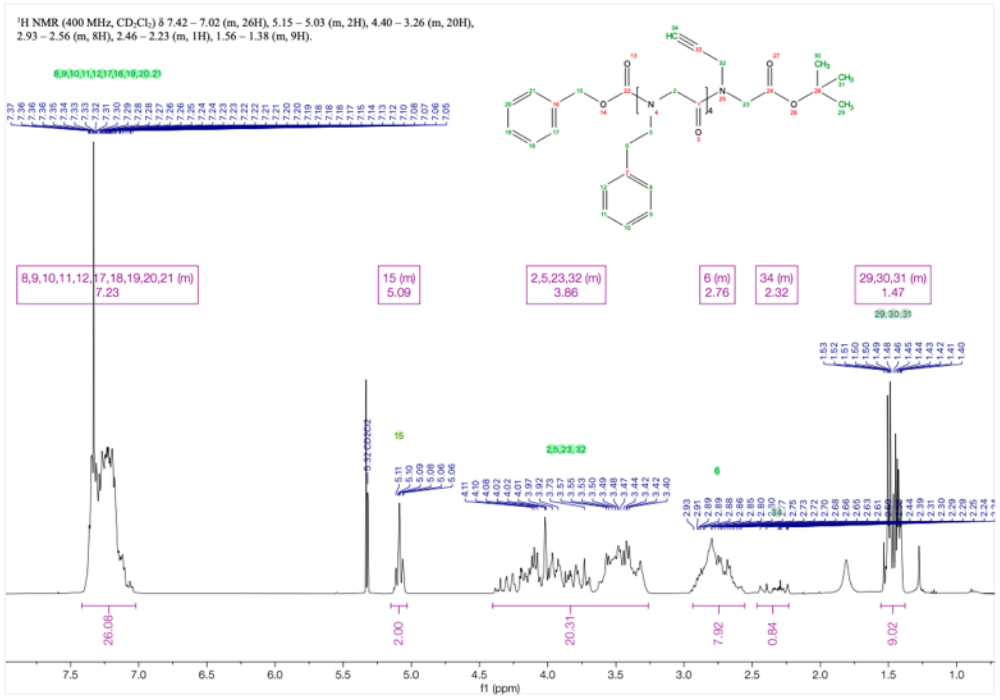


Fig. S188 ^{1}H NMR of Cbz-Npe$_4$-Nalk-tBu.

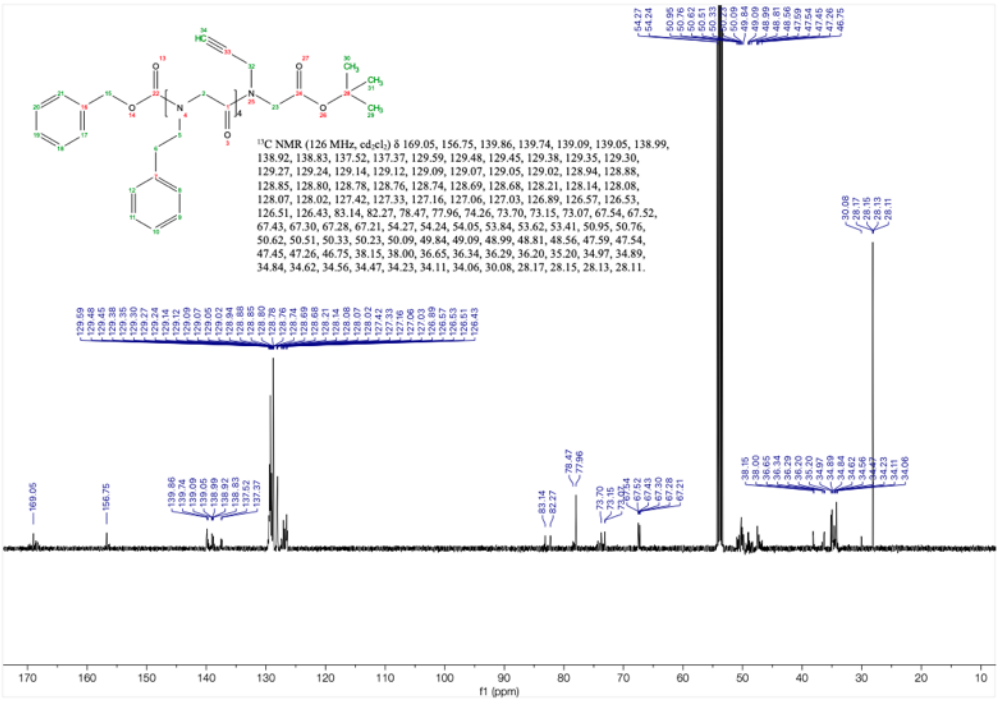


Fig. S189 ^{13}C NMR of Cbz-Npe$_4$-Nalk-tBu.

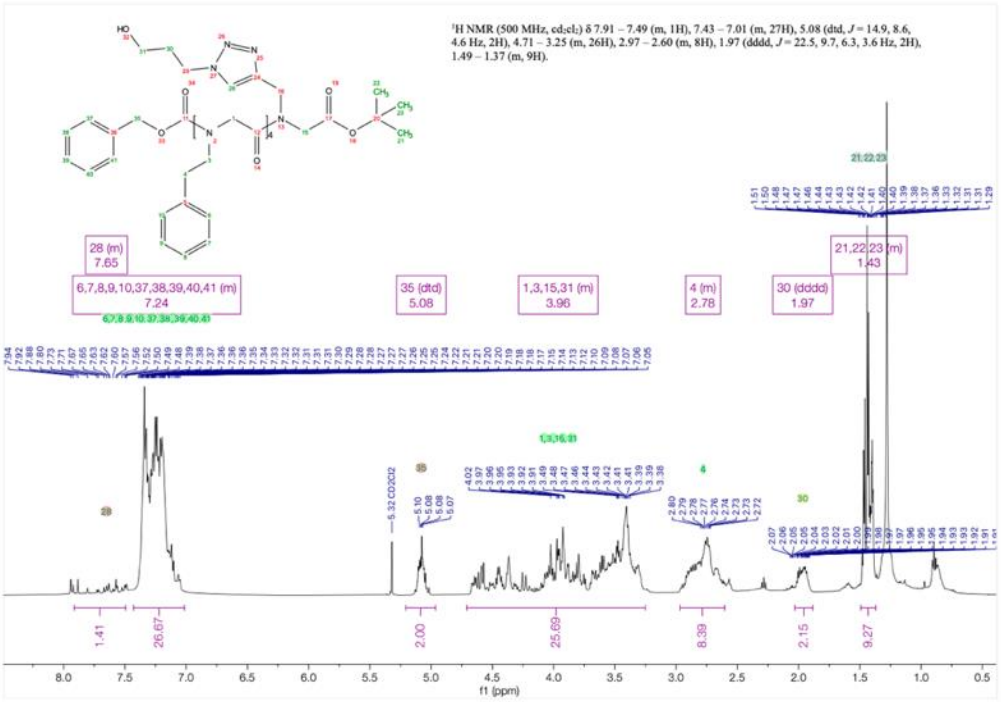


Fig. S190 ^{1}H NMR of Cbz-Npe$_4$-Ntriazo-tBu.

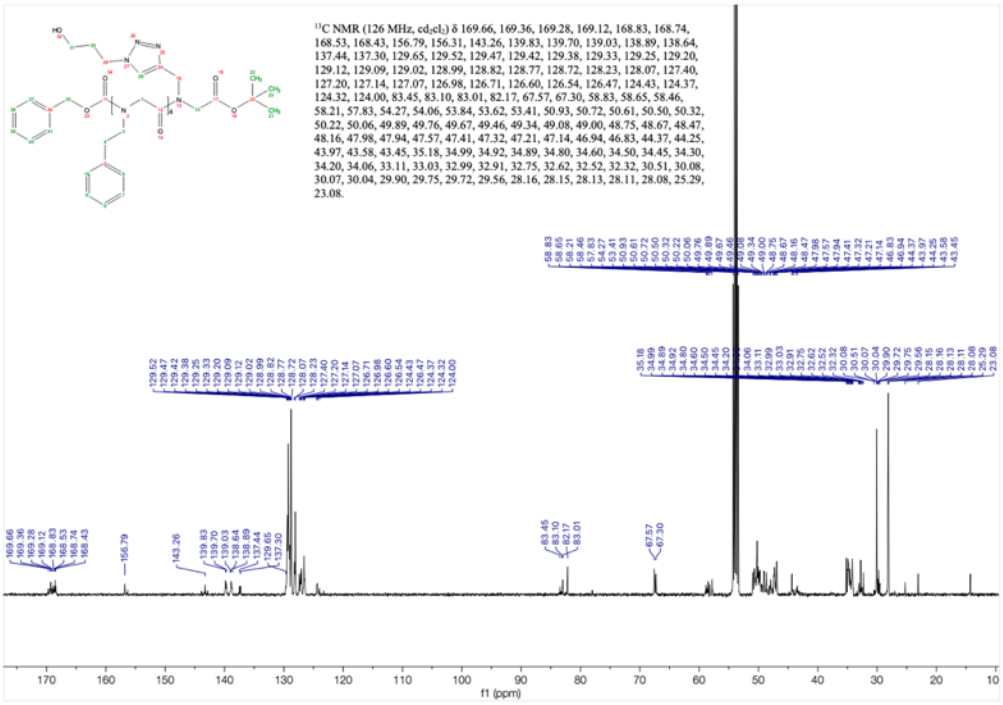


Fig. S191 ^{13}C NMR of Cbz-Npe$_4$-Ntriazo-tBu.

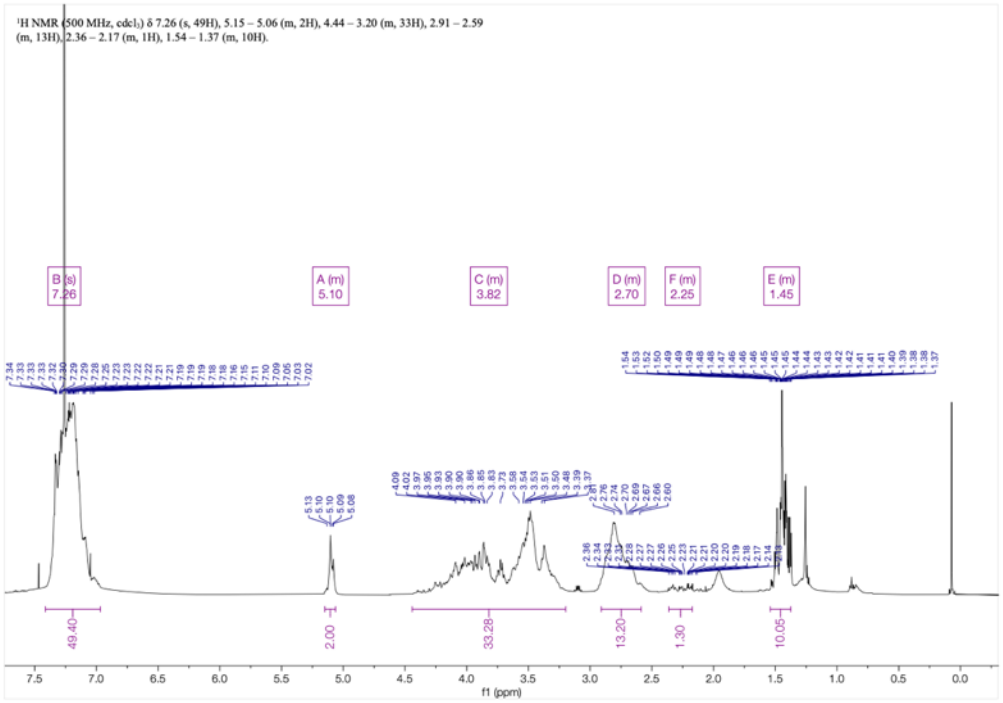


Fig. S192 ^{1}H NMR of Cbz-Npe$_4$-Nalk-Npe$_2$-tBu.

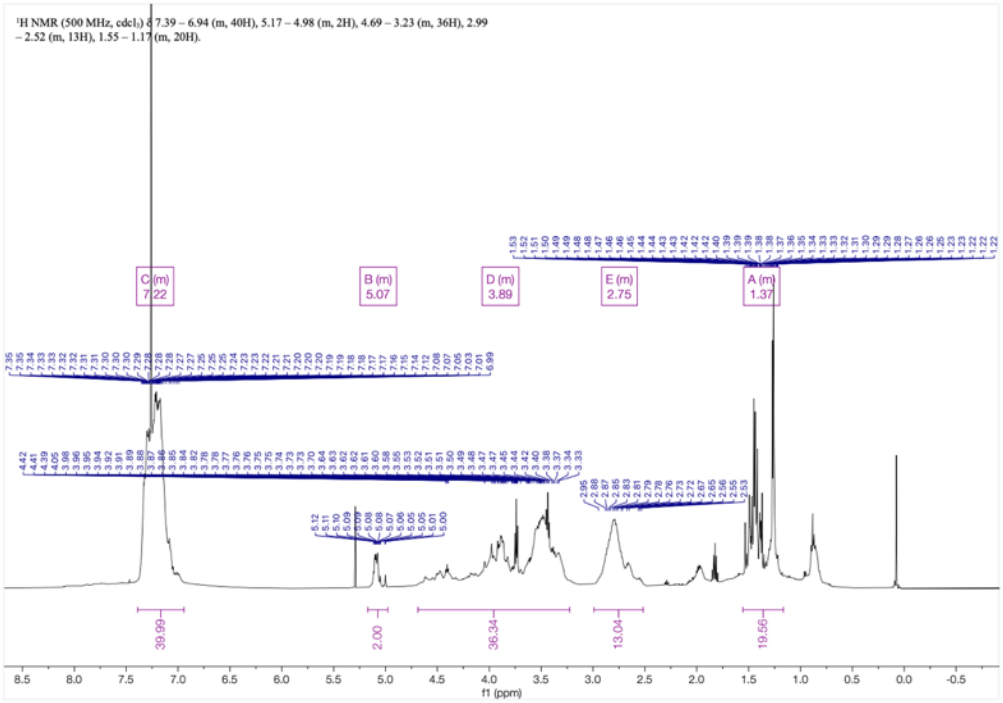


Fig. S193 ^{1}H NMR of Cbz-Npe$_4$-Ntriazo-Npe$_2$-tBu.

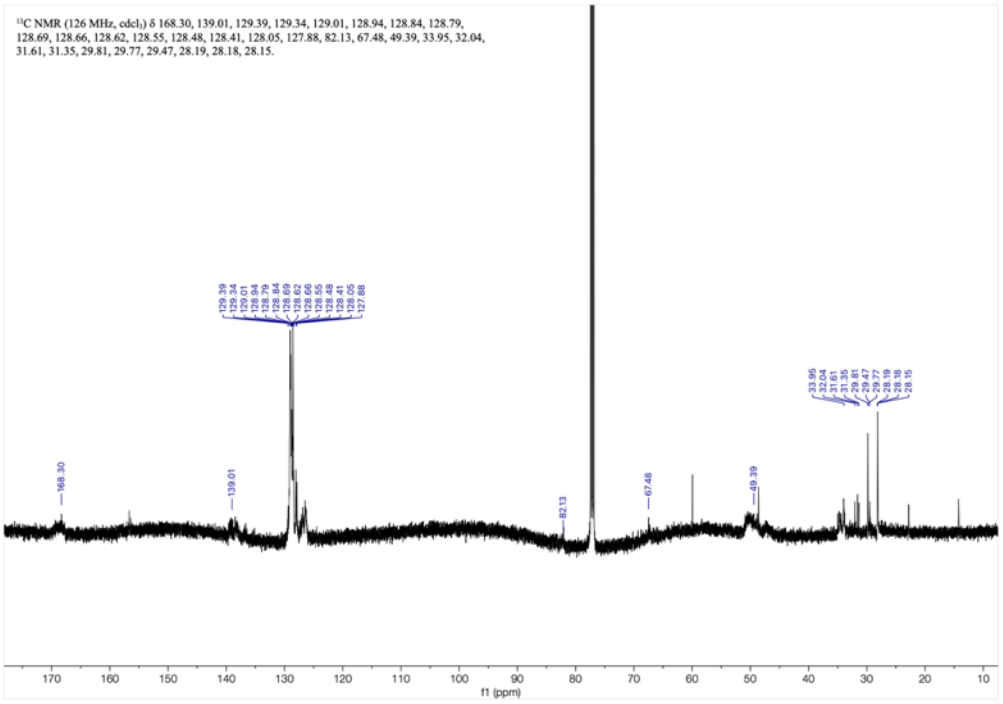


Fig. S194 ^{13}C NMR of Cbz-Npe$_4$-Ntriazo-Npe$_2$-tBu. Note: baseline not corrected to maintain signal.

7. Characterization of IEG intermediates (NMR and MALDI-MS)

7.1 Peptoid homopolymers

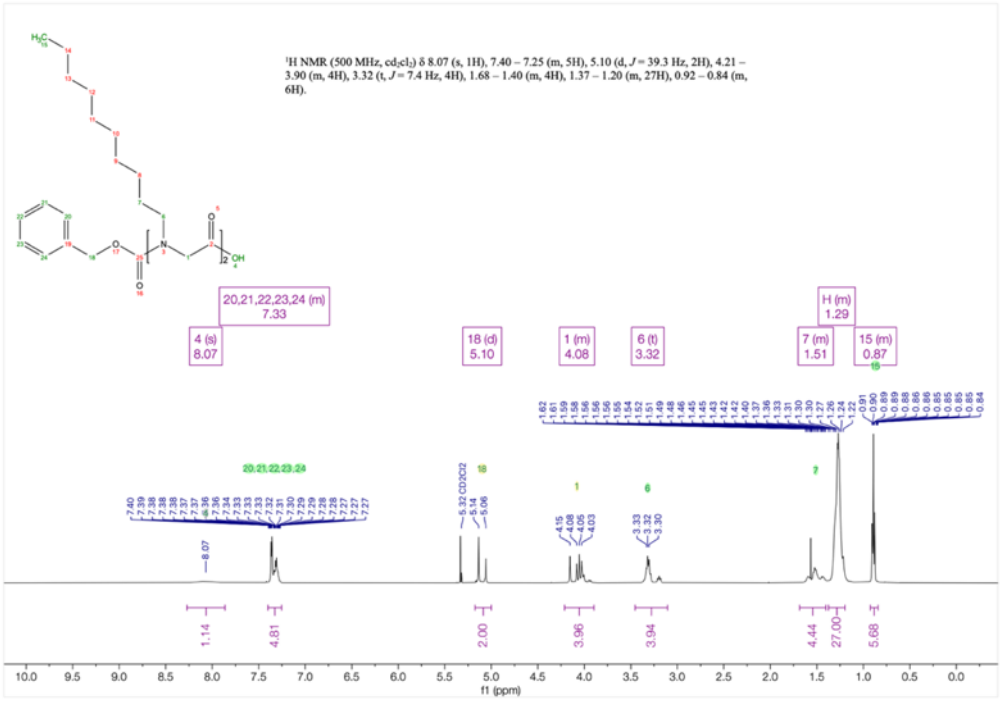


Fig. S195 ^{1}H NMR of Cbz-Ndc$_2$.

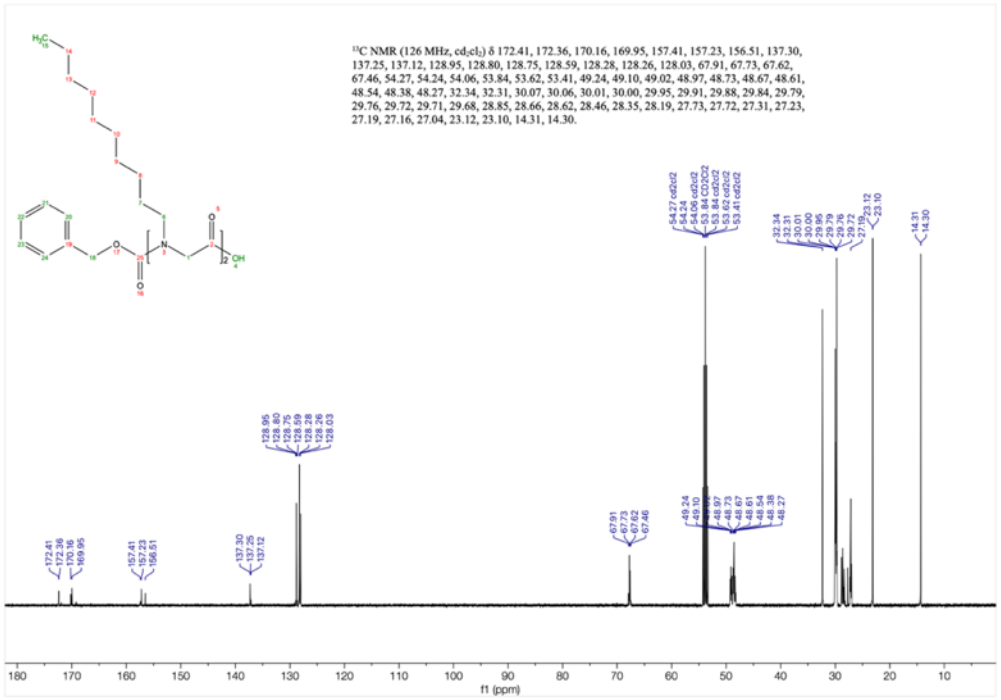


Fig. S196 ^{13}C NMR of Cbz-Ndc$_2$.

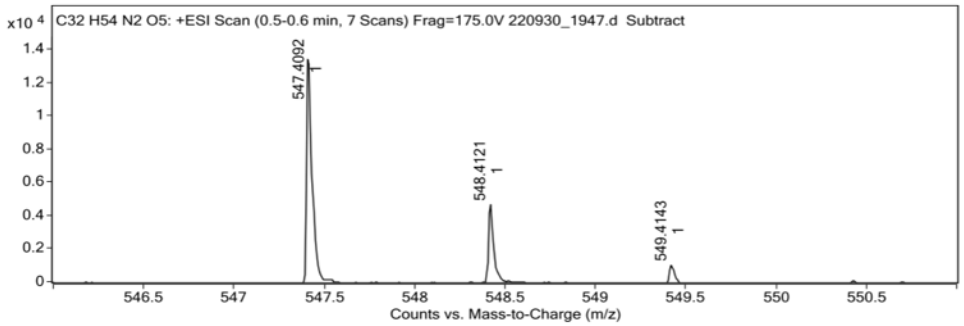


Fig. S197 HRMS of Cbz-Ndc2.

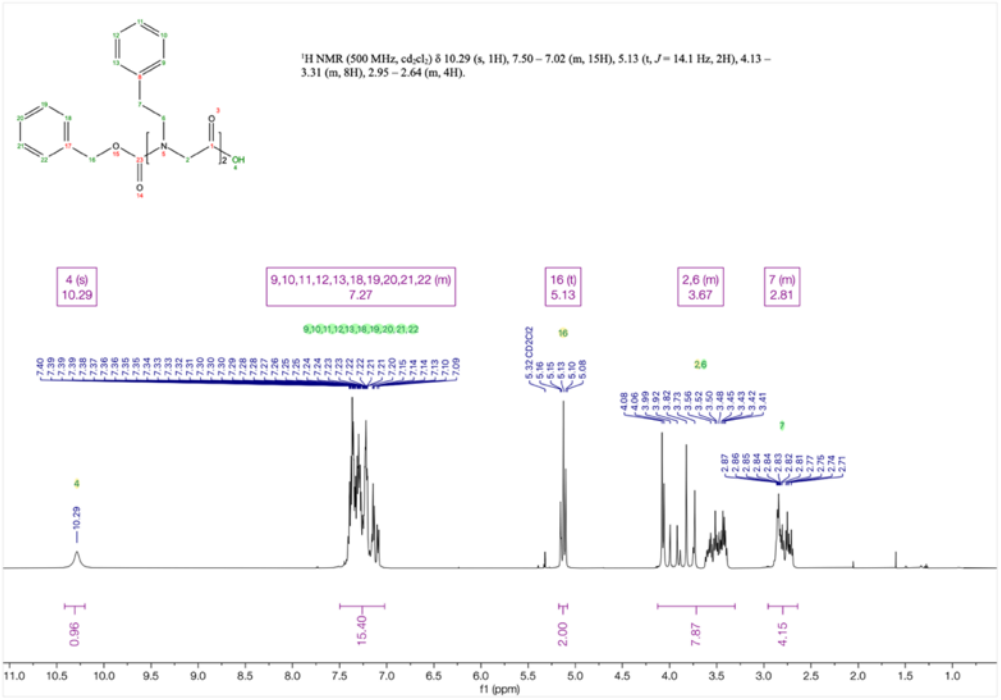


Fig. S198 [1]H NMR of Cbz-Npe2.

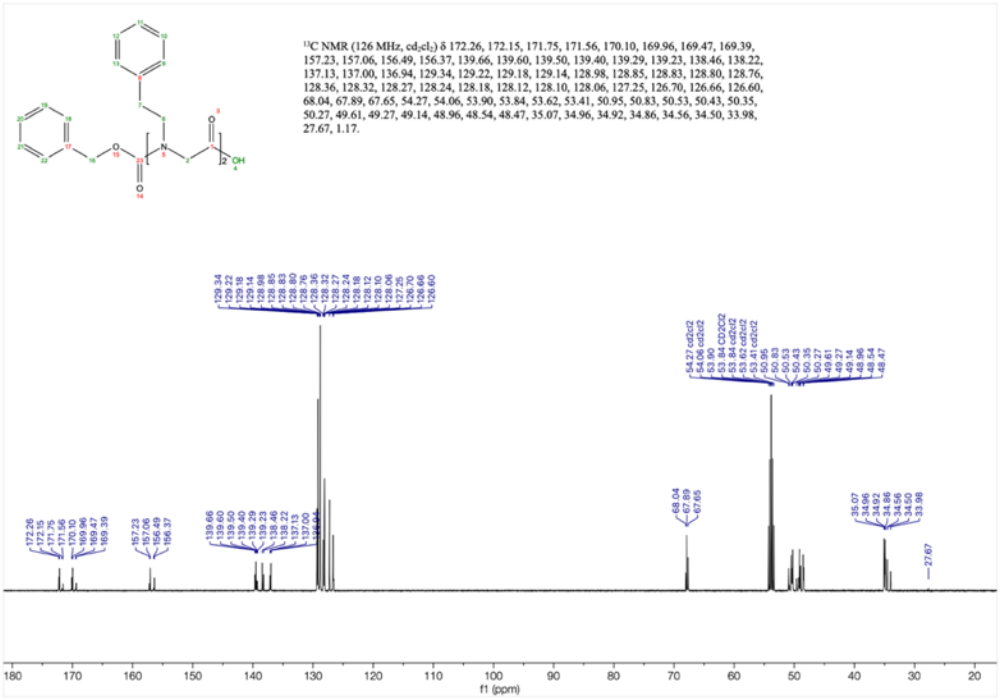


Fig. S199 ^{13}C NMR of Cbz-Npe$_2$.

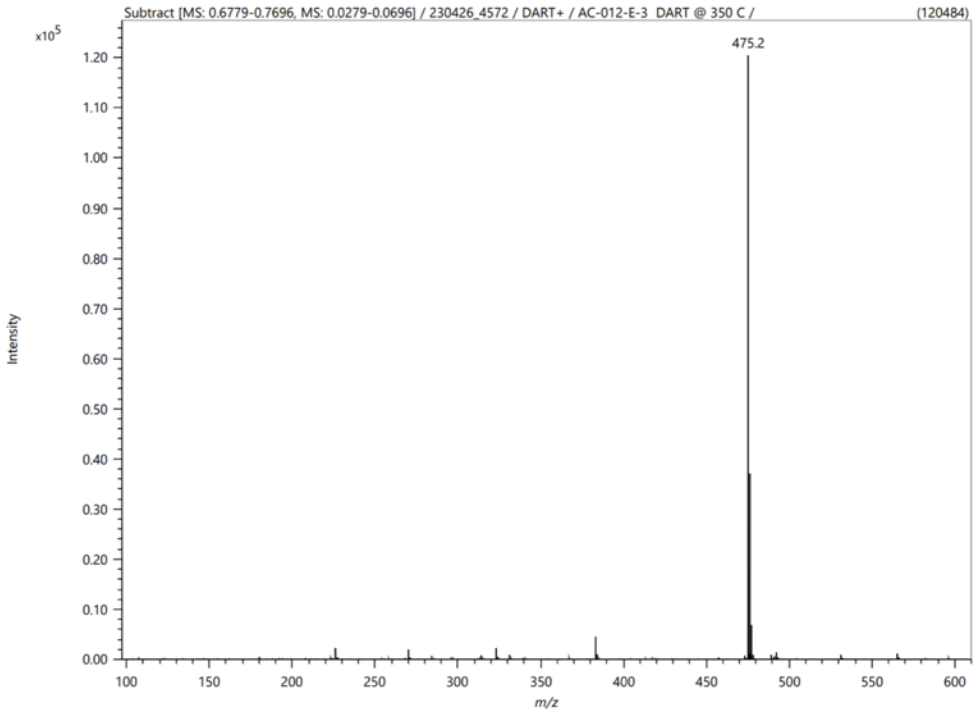


Fig. S200 DART-MS of Cbz-Npe$_2$.

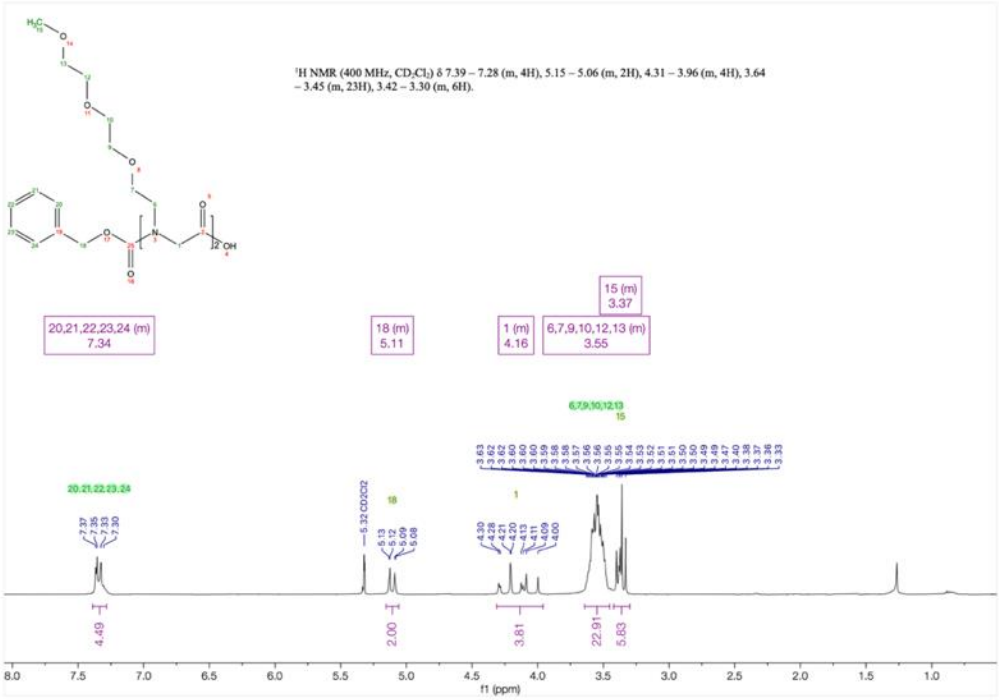


Fig. S201 ^{1}H NMR of Cbz-Nte$_2$.

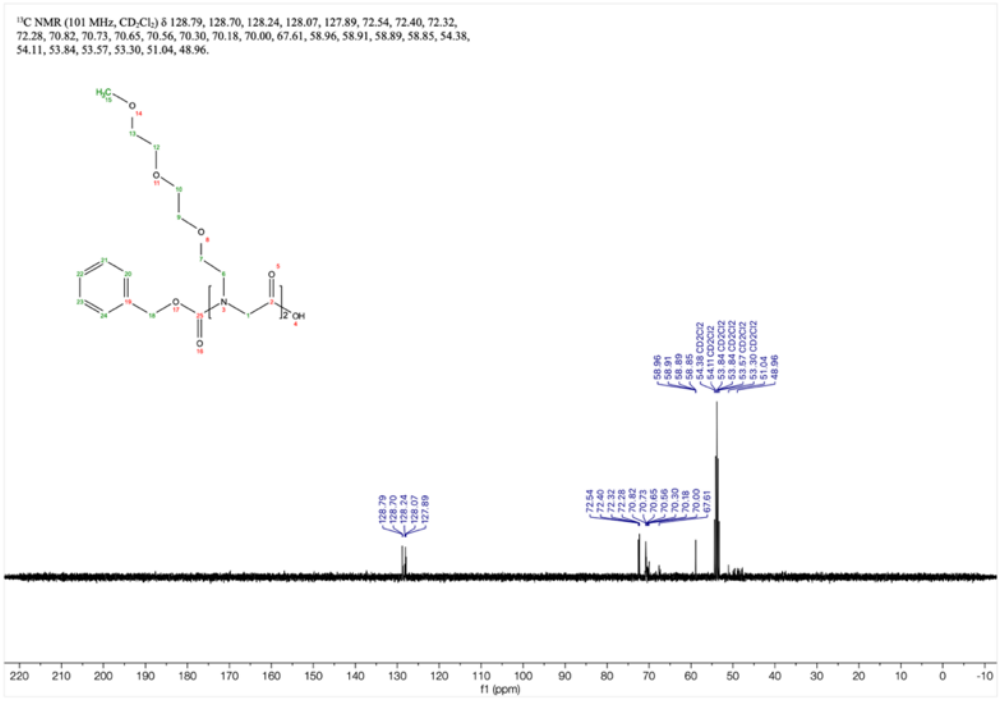


Fig. S202 ^{13}C NMR of Cbz-Nte$_2$.

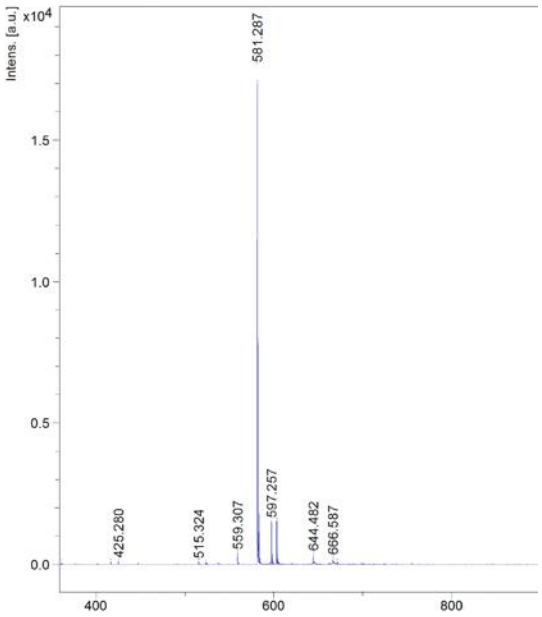


Fig. S203 MALDI-TOF MS of Cbz-Nte2.

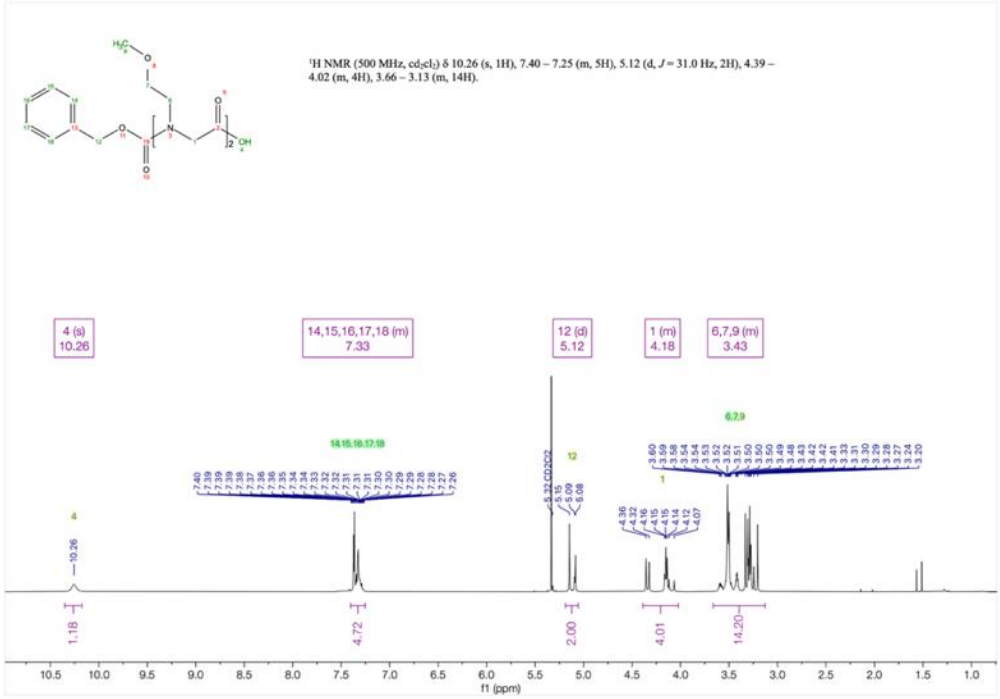


Fig. S204 ^{1}H NMR of Cbz-Nme2.

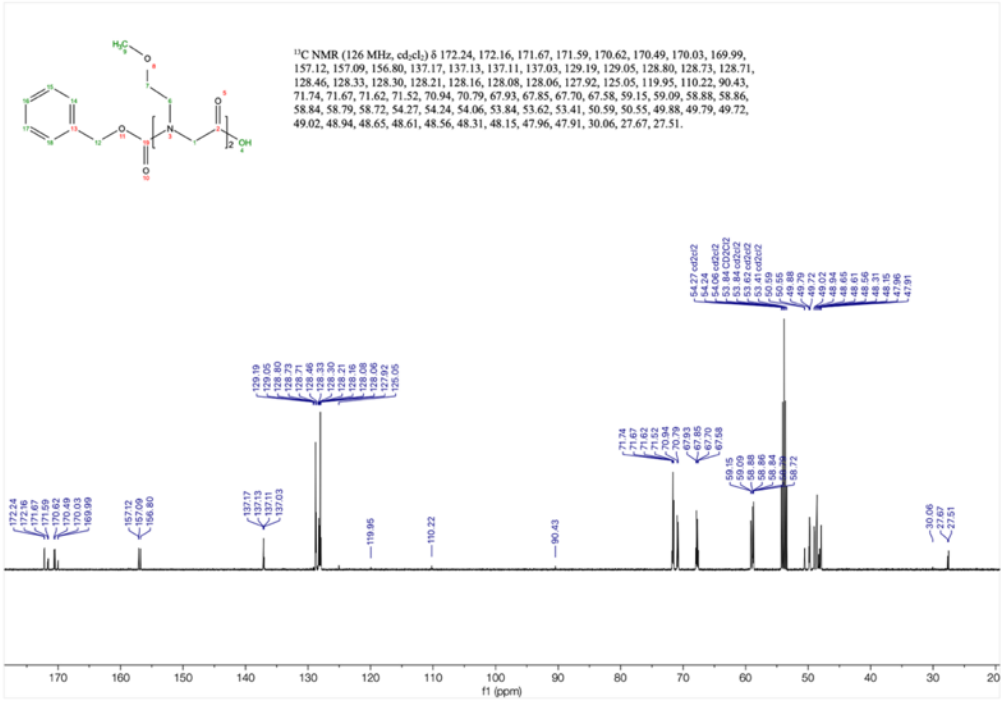


Fig. S205 ^{13}C NMR of Cbz-Nme$_2$.

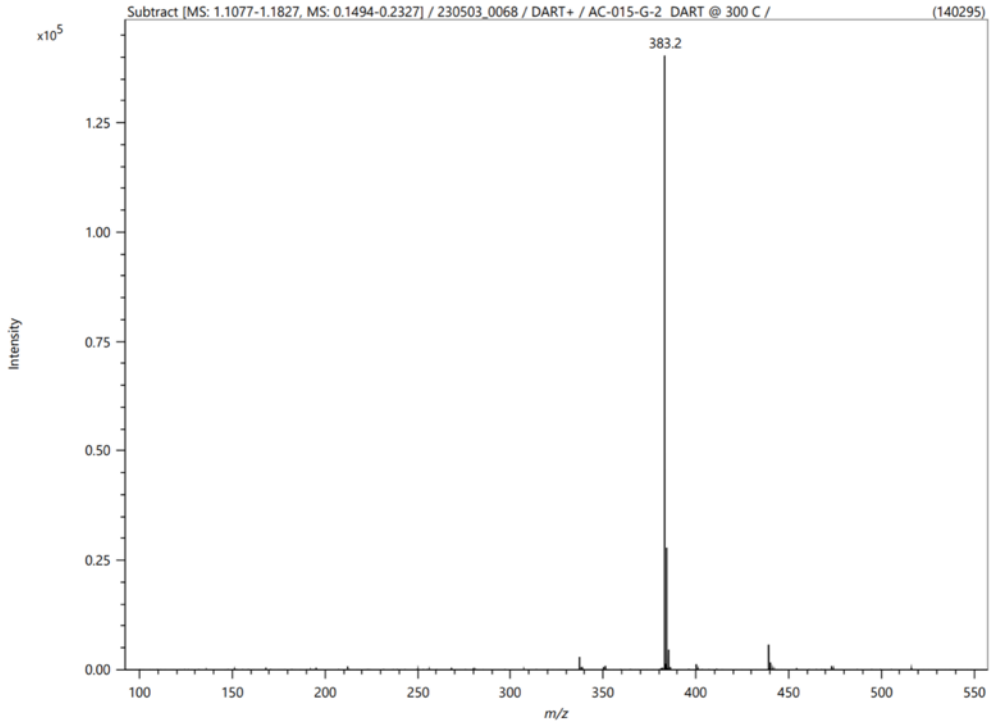


Fig. S206 DART-MS of Cbz-Nme$_2$.

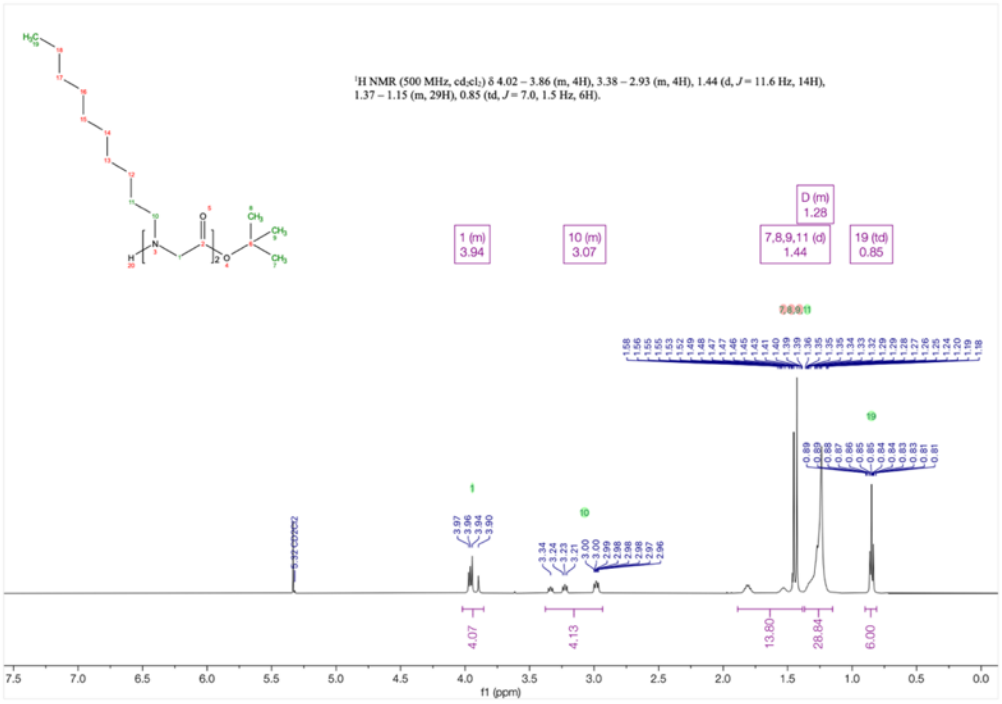


Fig. S207 ^{1}H NMR of Ndc$_2$-tBu.

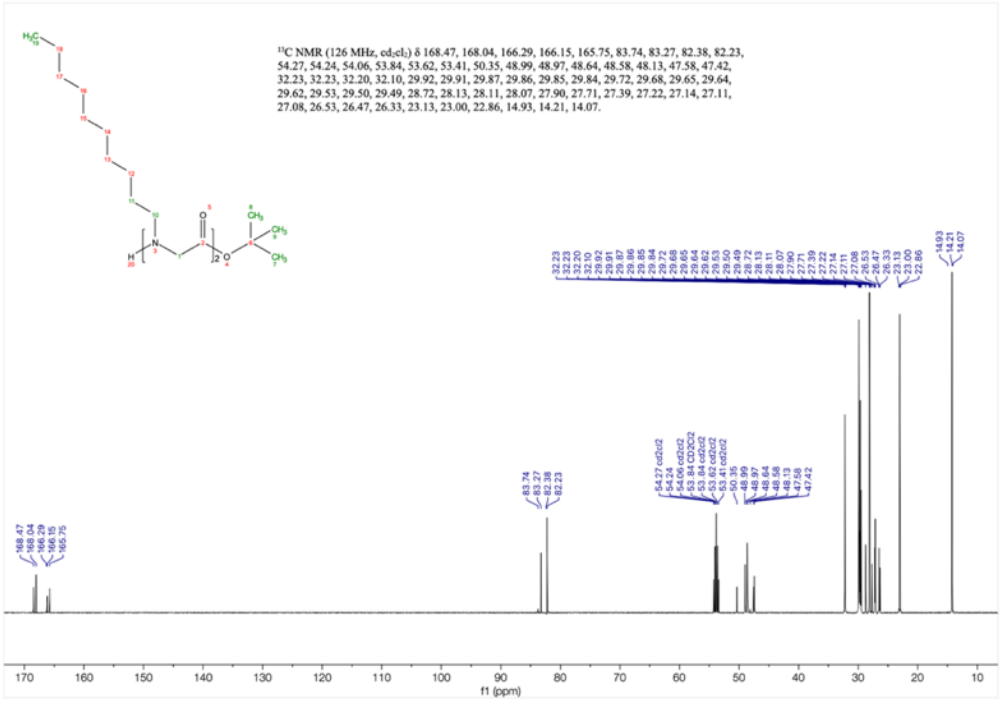


Fig. S208 ^{13}C NMR of Ndc$_2$-tBu.

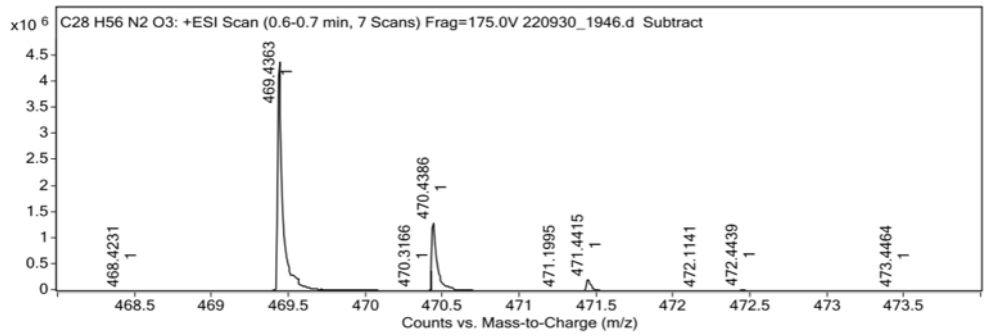


Fig. S209 HRMS of Ndc_2-tBu.

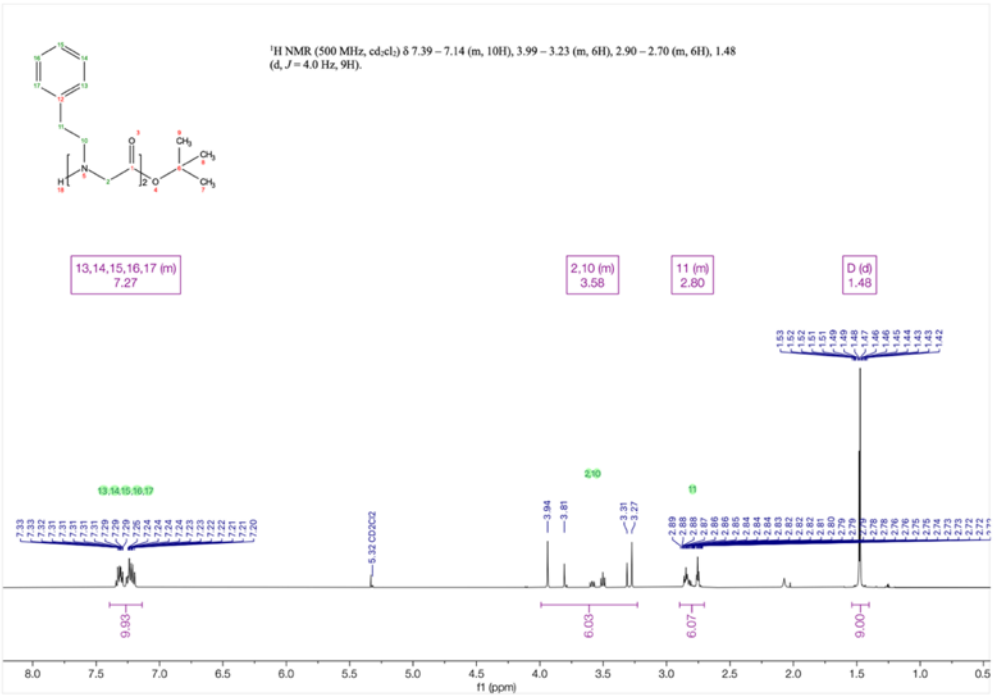


Fig. S210 ^{1}H NMR of Npe_2-tBu.

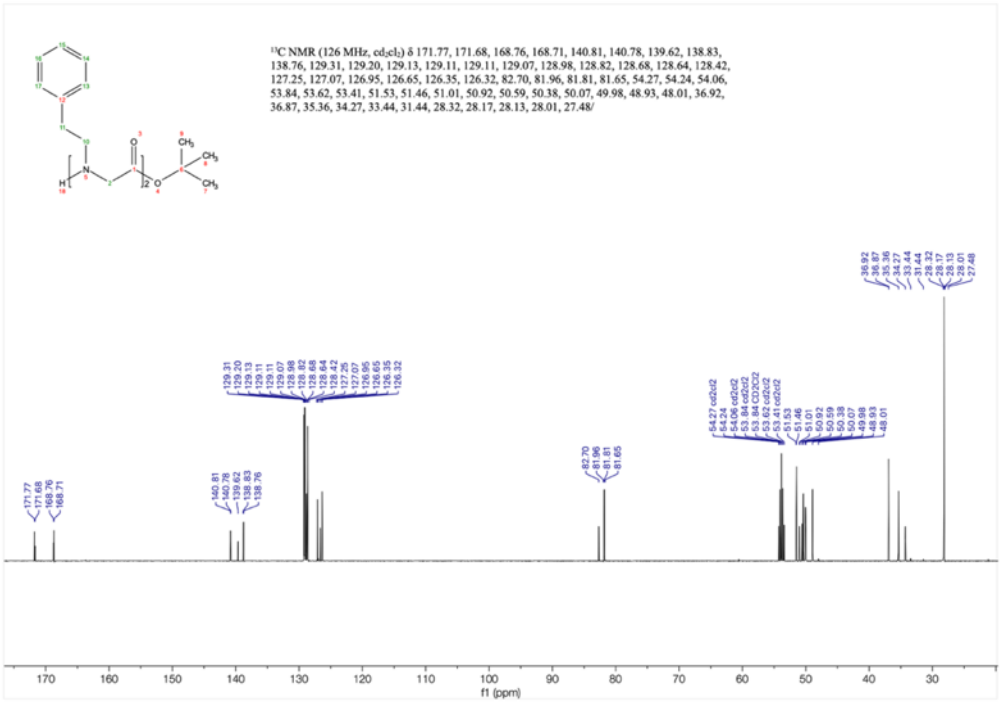


Fig. S211 ^{13}C NMR of Npe$_2$-tBu.

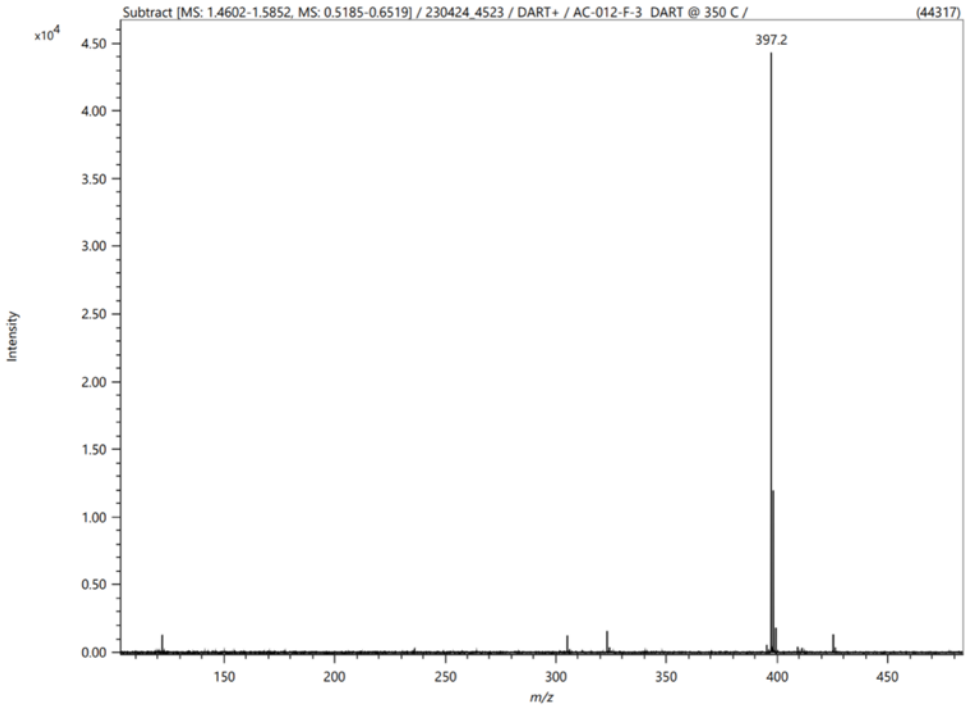


Fig. S212 DART-MS of Npe$_2$-tBu.

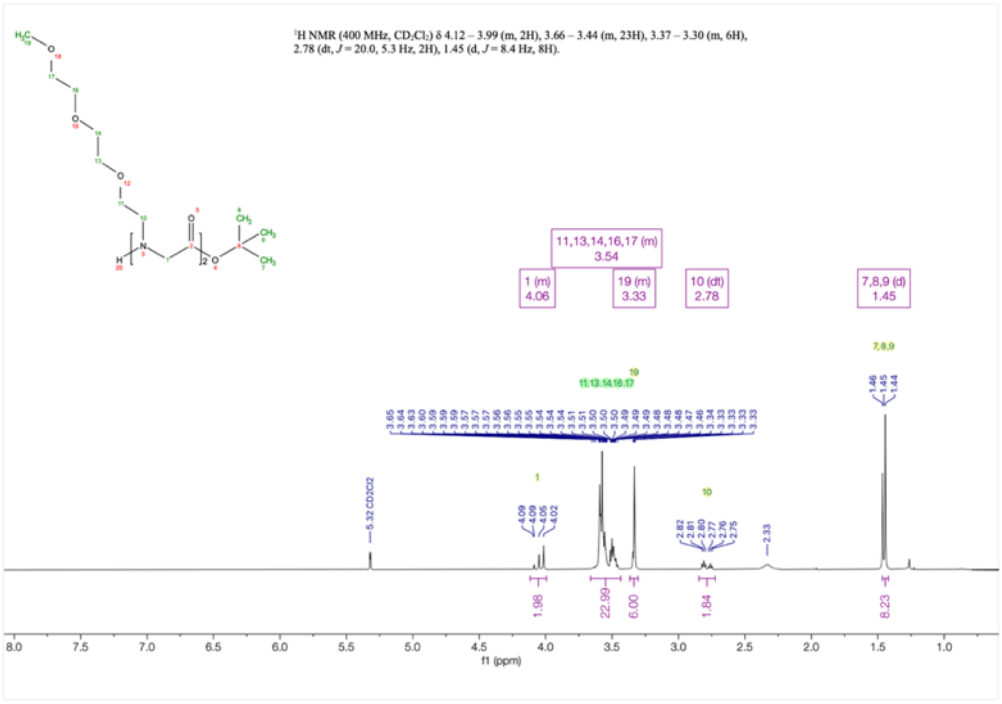


Fig. S213 ^{1}H NMR of Nte$_2$-tBu.

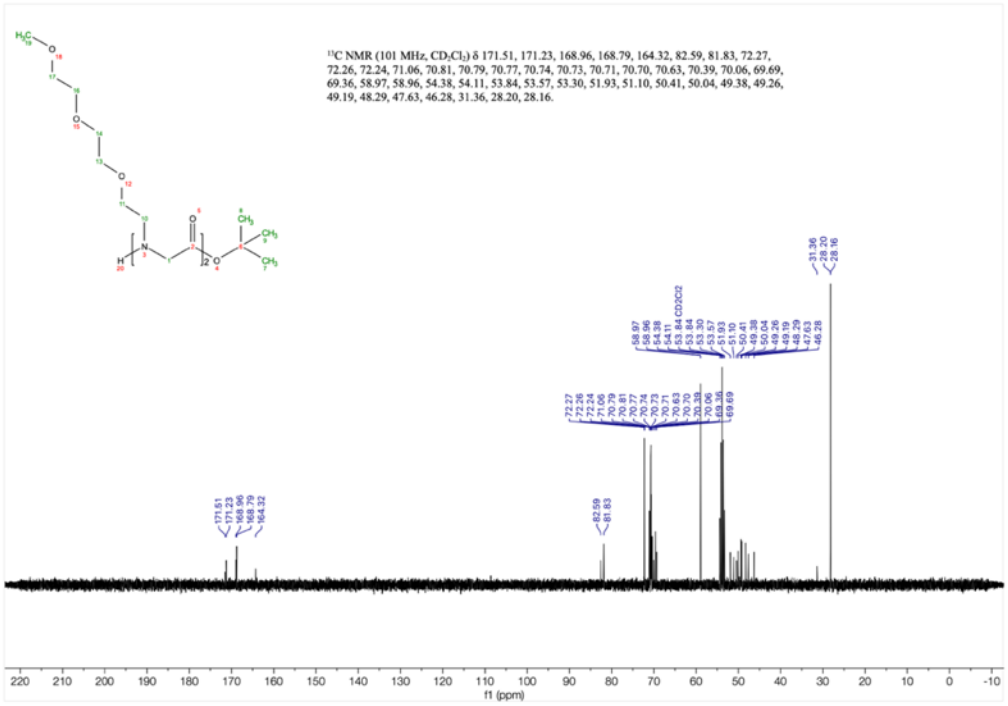


Fig. S214 ^{13}C NMR of Nte$_2$-tBu.

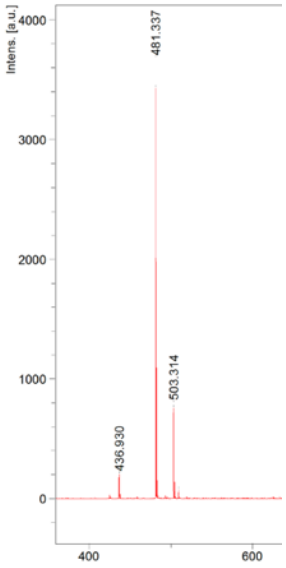


Fig. S215 MALDI-TOF MS of Nte_2-tBu.

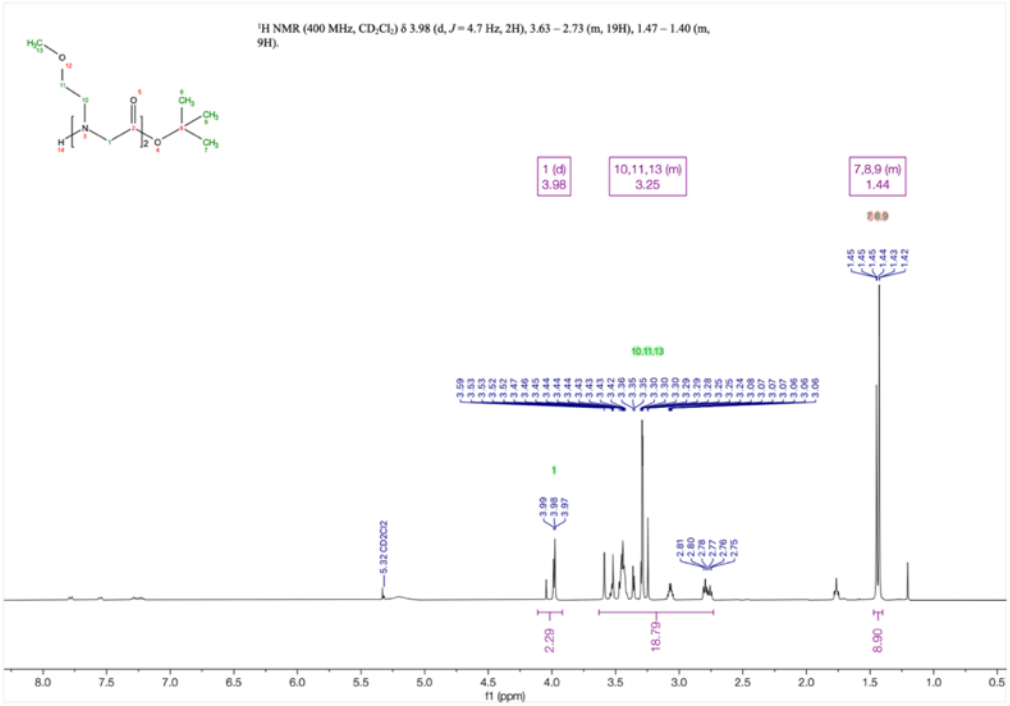


Fig. S216 ^{1}H NMR of Nme_2-tBu.

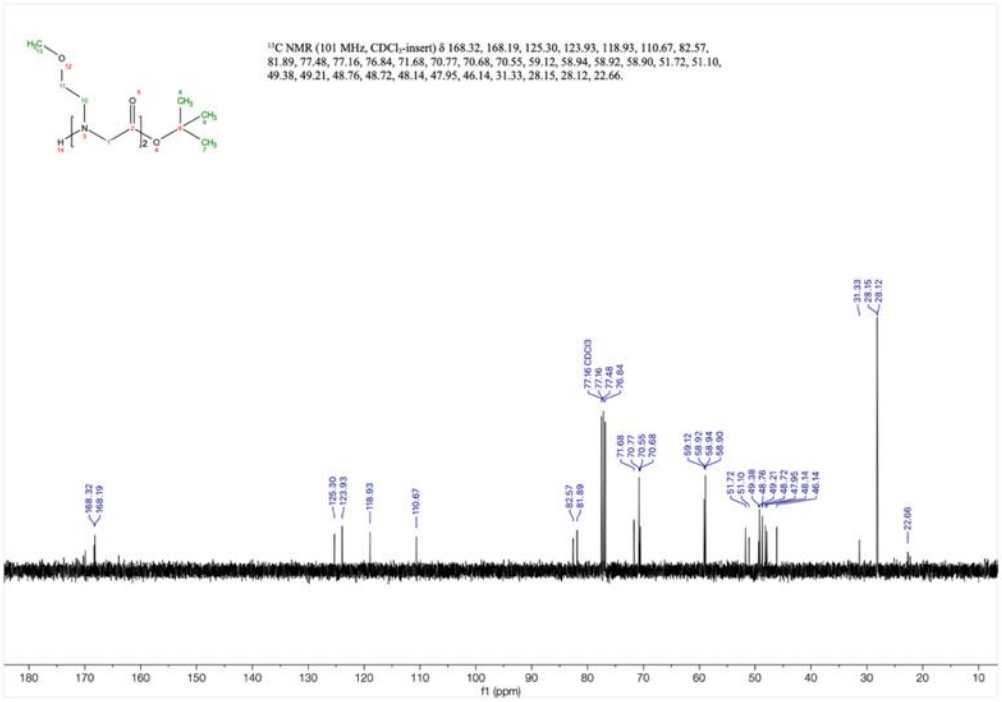


Fig. S217 ^{13}C NMR of Nme$_2$-tBu.

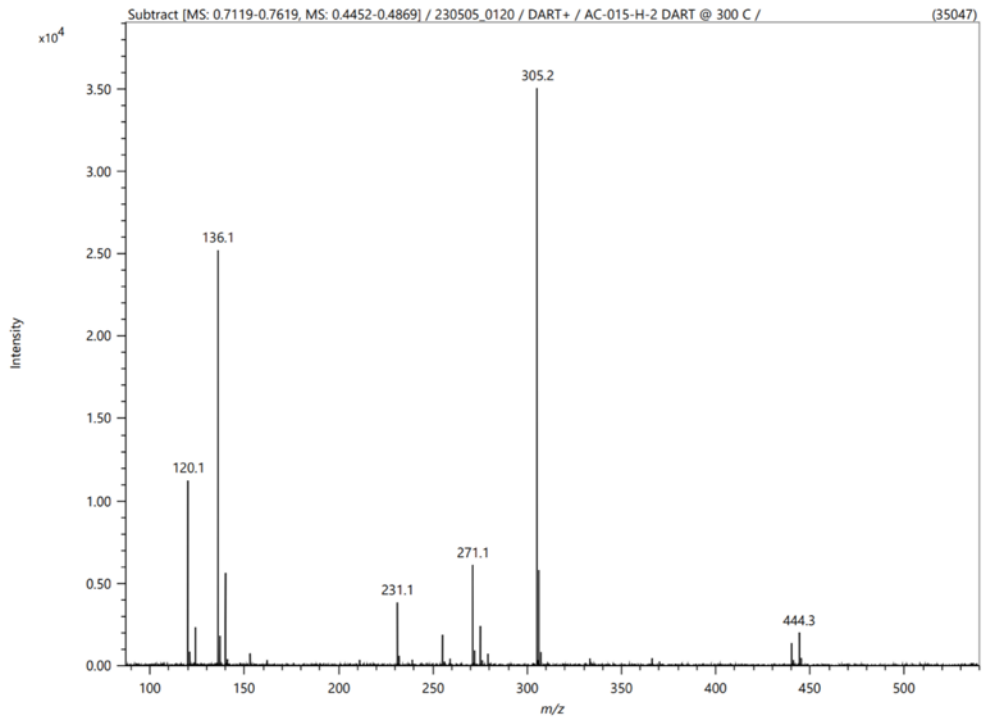


Fig. S218 DART-MS of Nme$_2$-tBu.

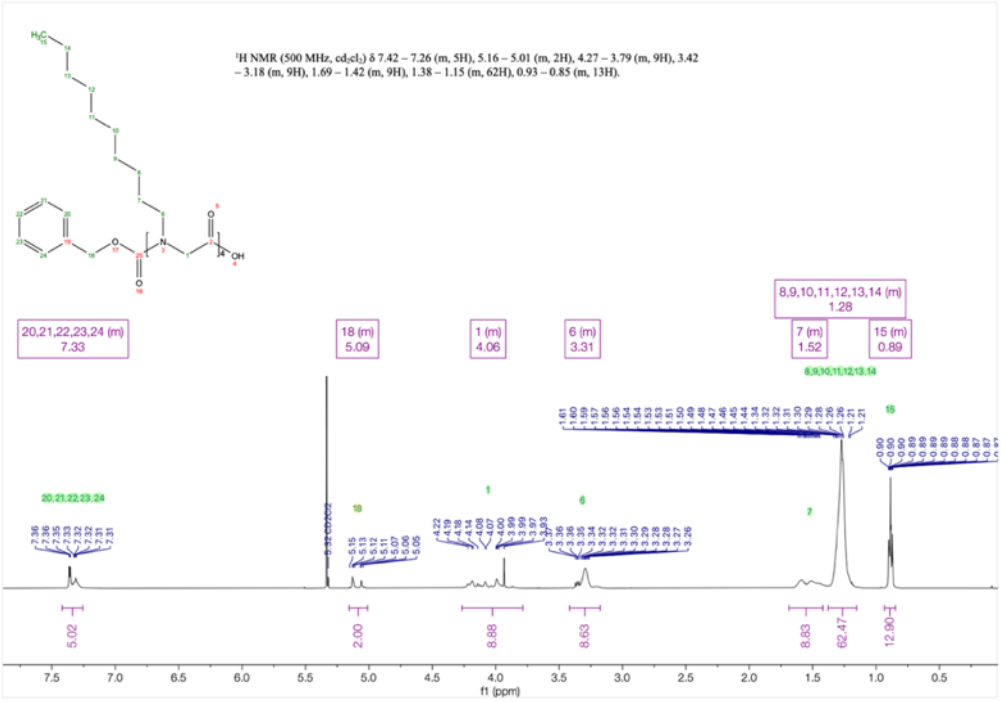


Fig. S219 ^{1}H NMR of Cbz-Ndc$_4$.

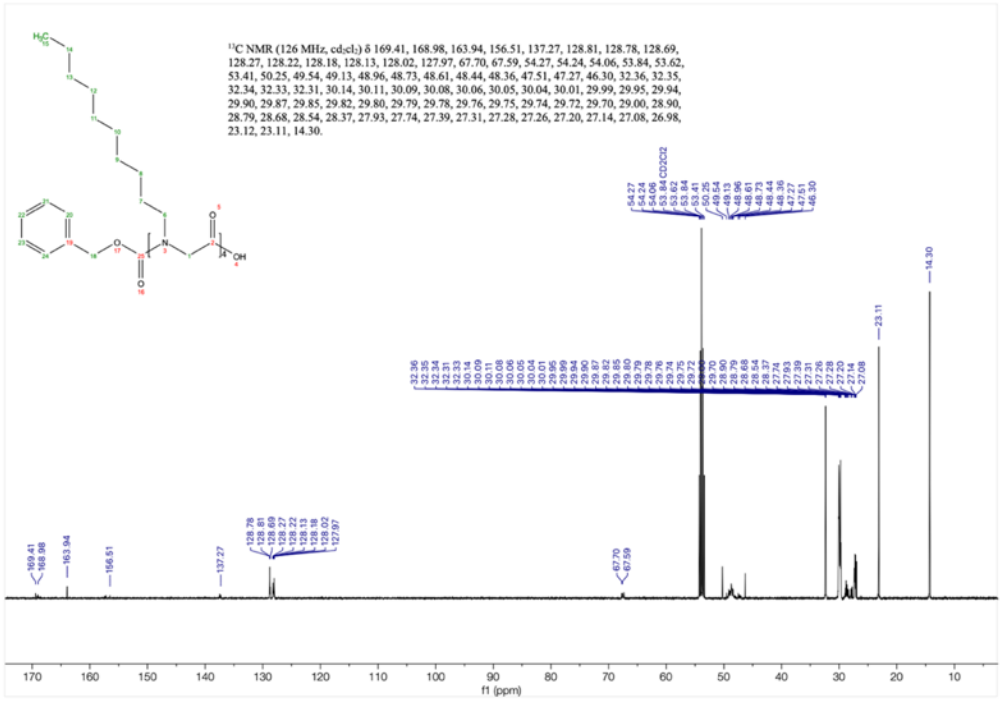


Fig. S220 ^{13}C NMR of Cbz-Ndc$_4$.

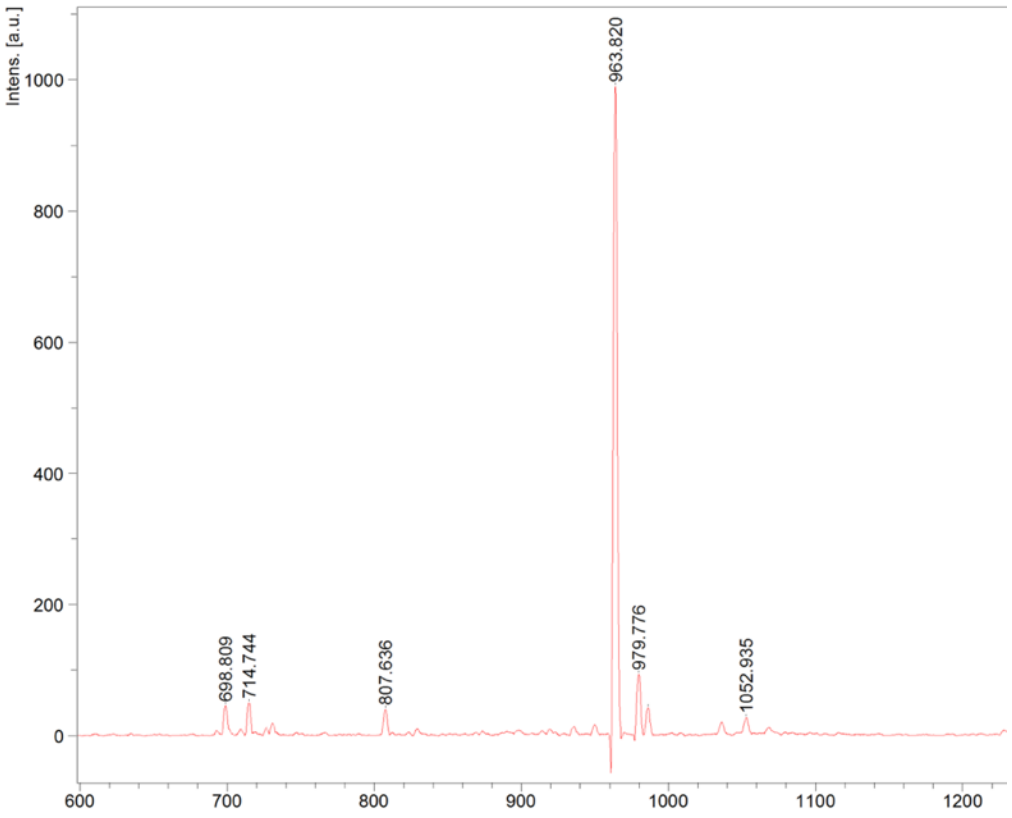


Fig. S221 MALDI-TOF MS of Cbz-Ndc4.

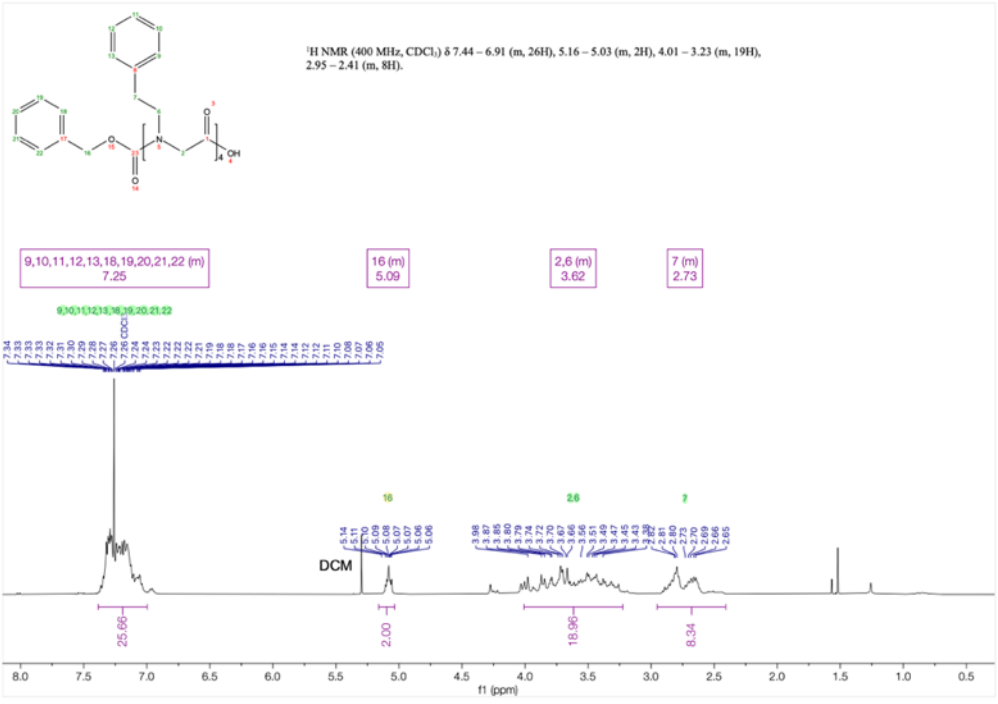


Fig. S222 [1]H NMR of Cbz-Npe4.

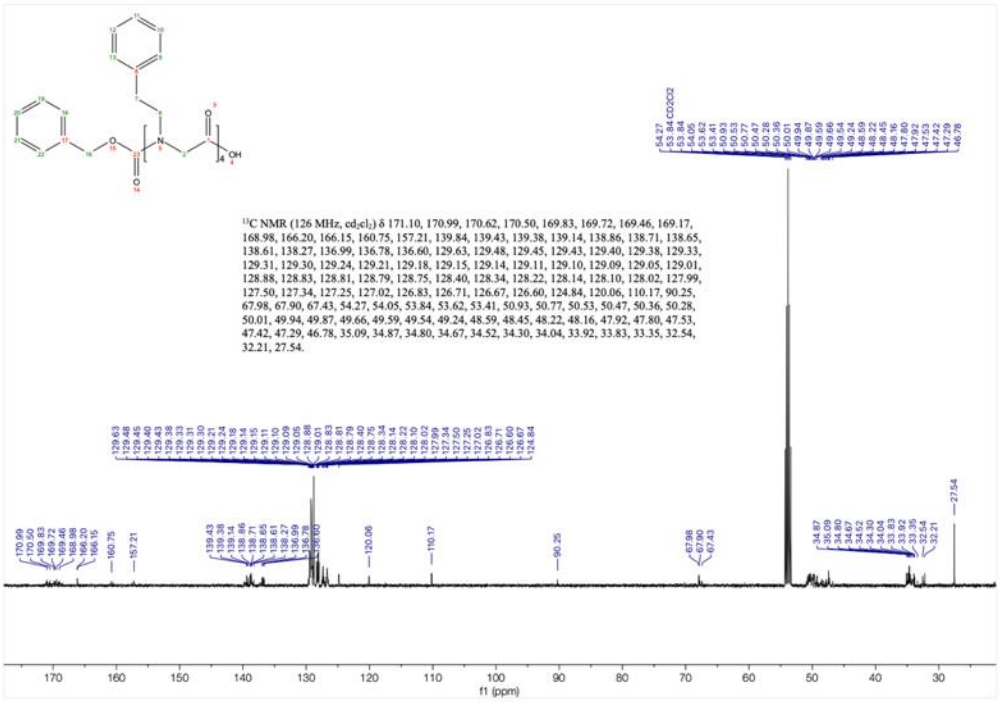


Fig. S223 ^{13}C NMR of Cbz-Npe$_4$.

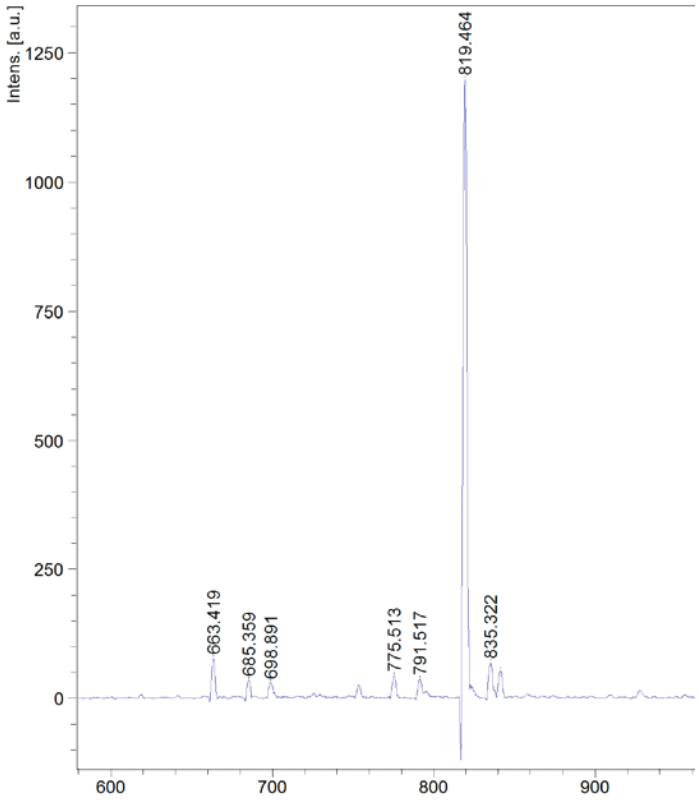


Fig. S224 MALDI-TOF MS of Cbz-Npe$_4$.

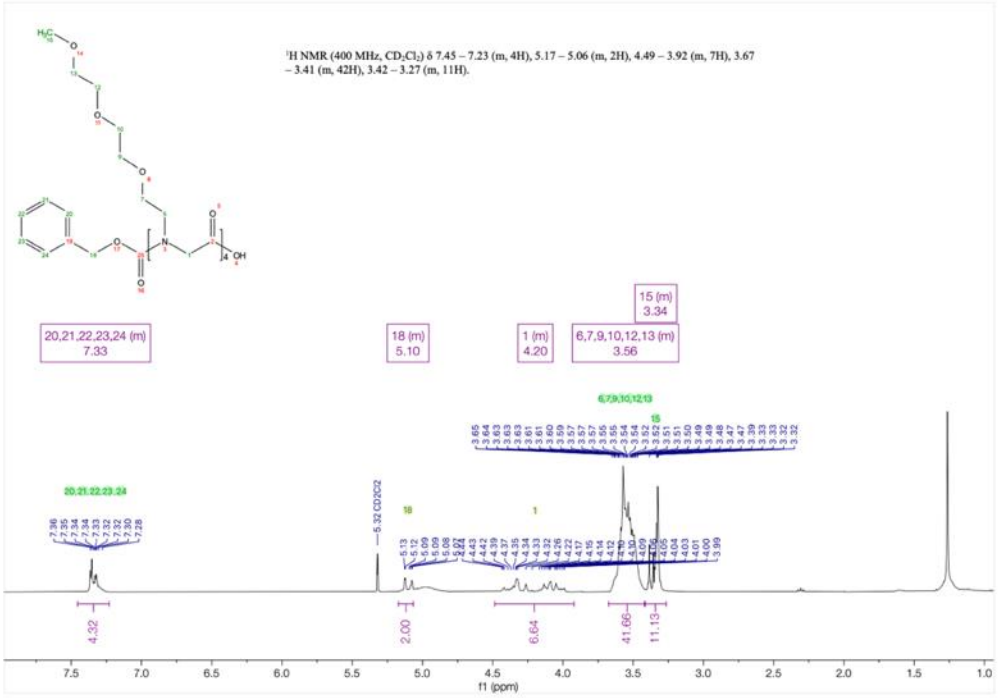


Fig. S225 ^{1}H NMR of Cbz-Nte$_4$.

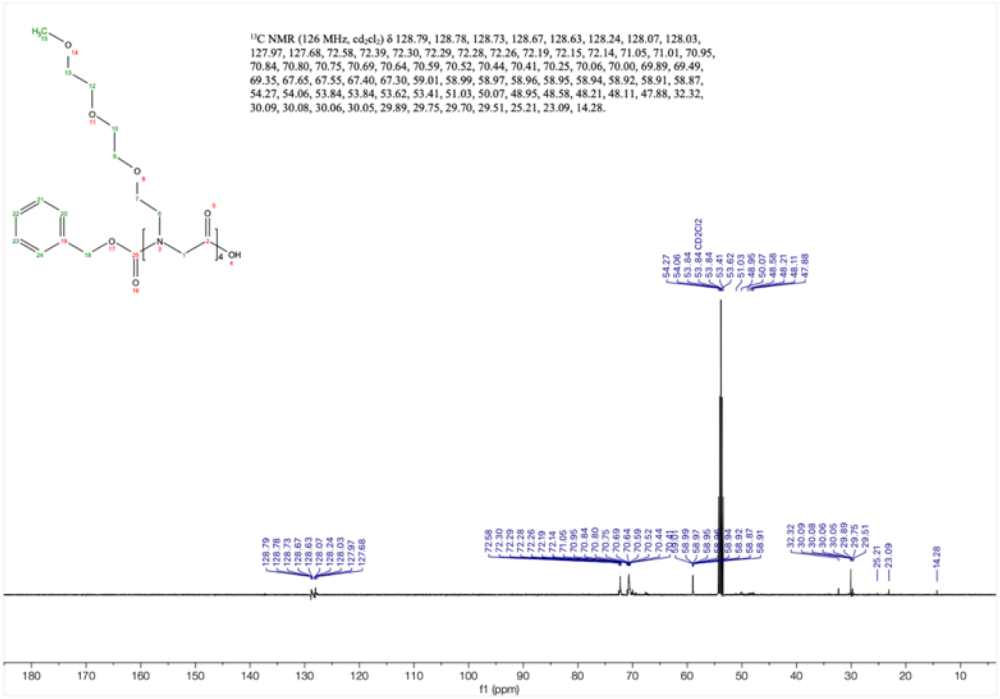


Fig. S226 ^{13}C NMR of Cbz-Nte$_4$.

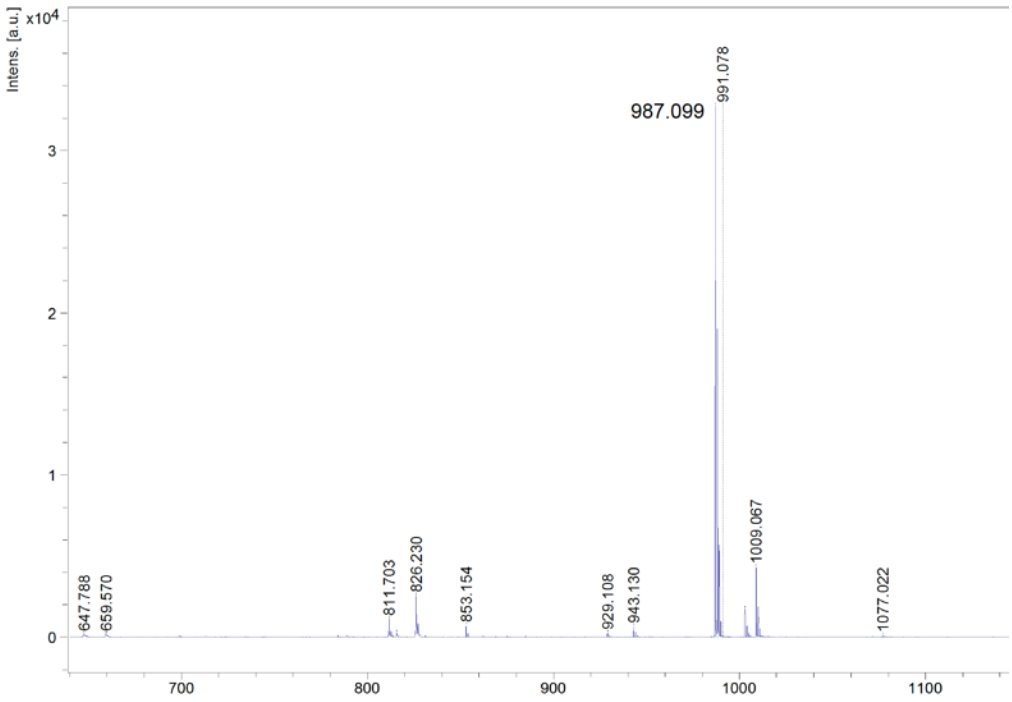


Fig. S227 MALDI-TOF MS of Cbz-Nte4.

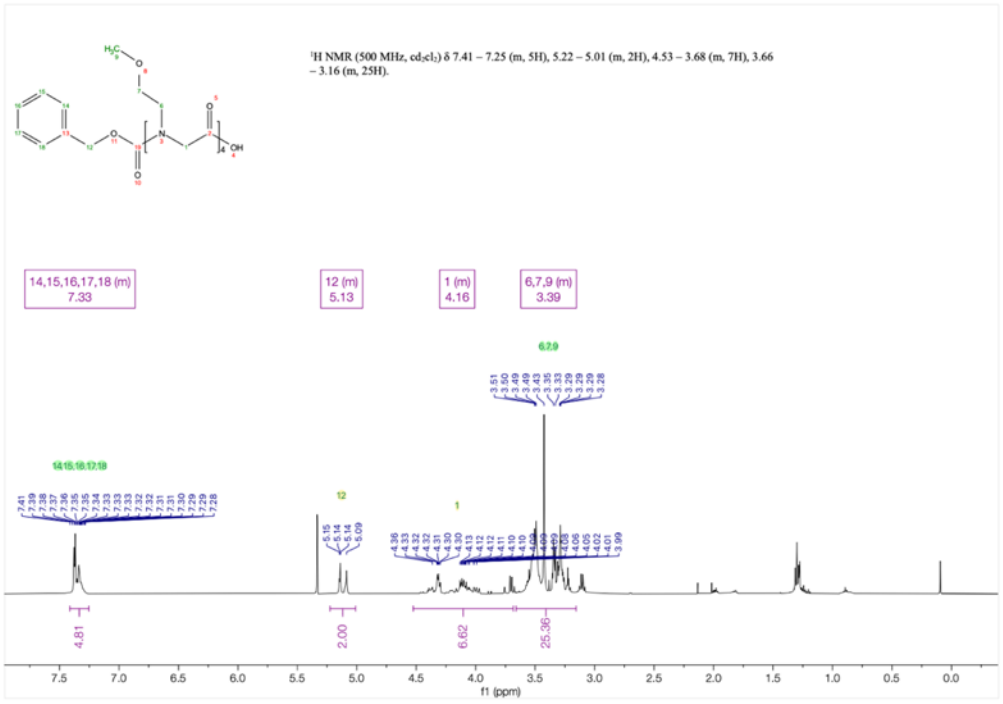


Fig. S228 [1]H NMR of Cbz-Nme4.

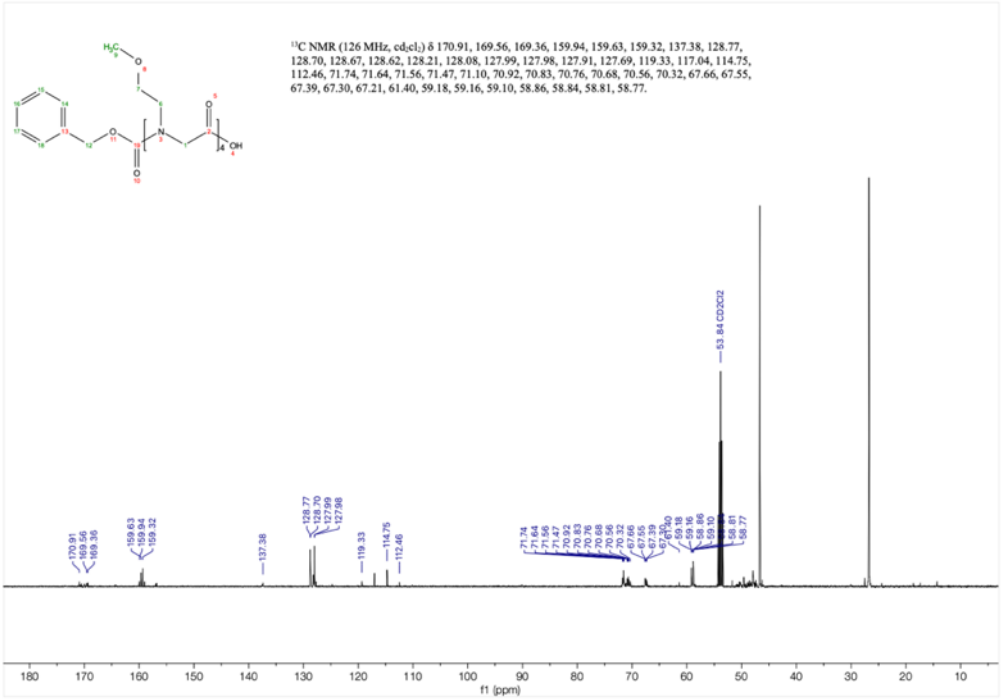


Fig. S229 ^{13}C NMR of Cbz-Nme$_4$.

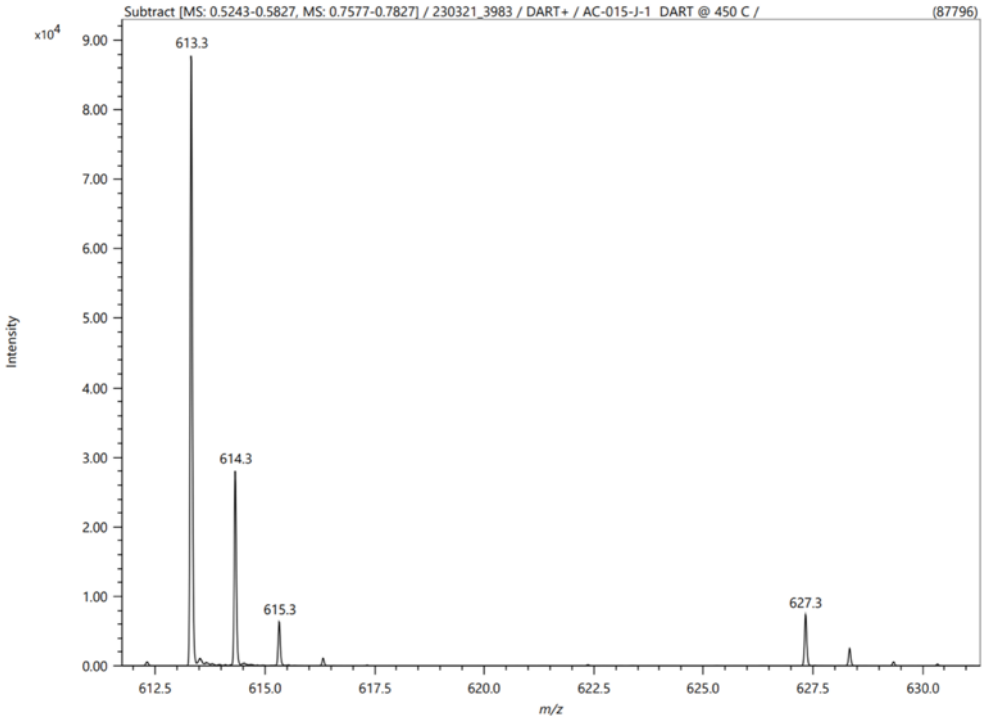


Fig. S230 DART-MS of Cbz-Nme$_4$.

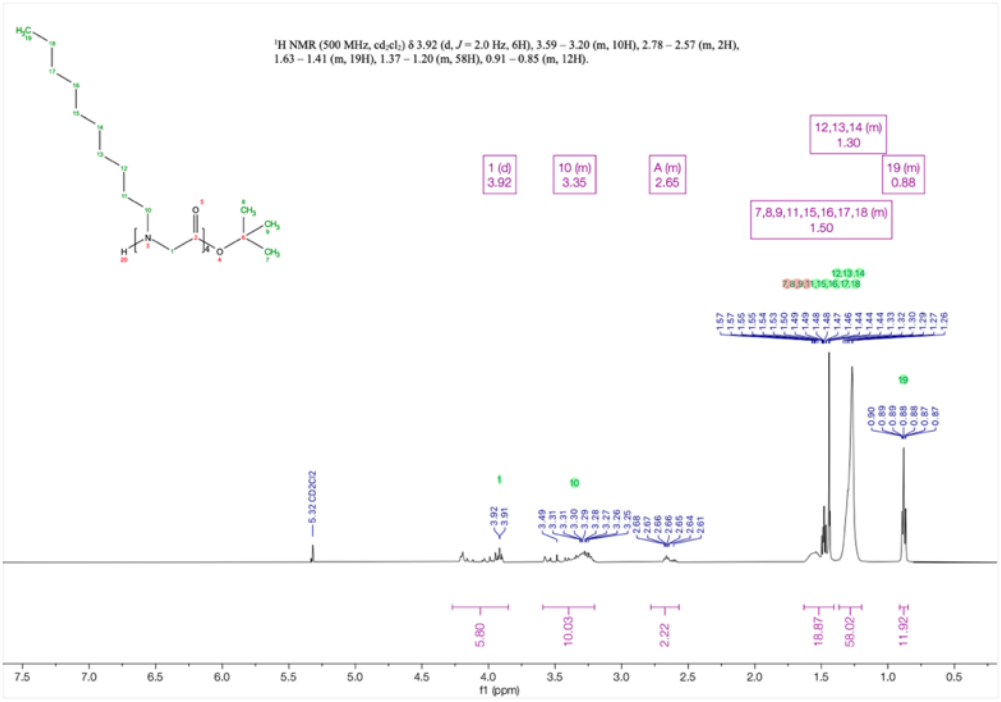


Fig. S231 ^{1}H NMR of Ndc4-tBu.

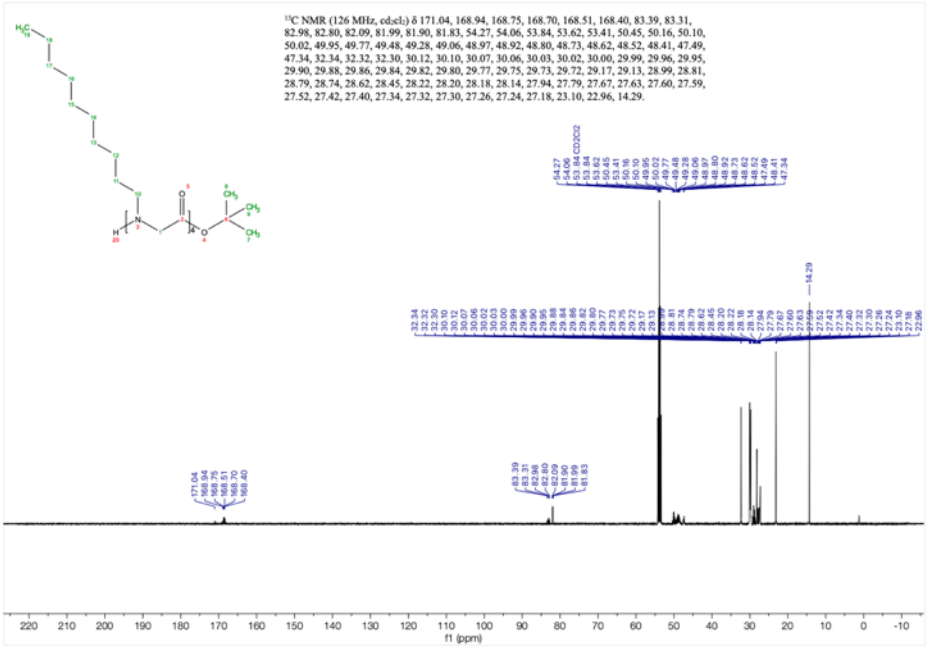


Fig. S232 ^{13}C NMR of Ndc4-tBu.

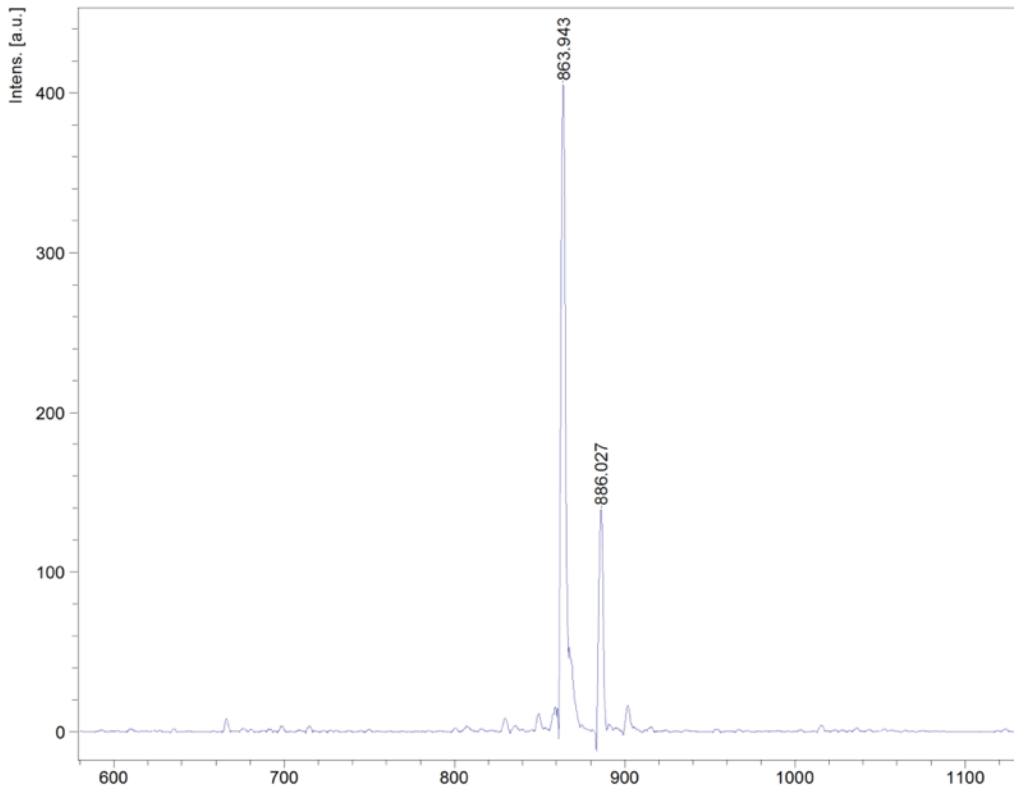


Fig. S233 MALDI-TOF MS of Ndc_4-tBu.

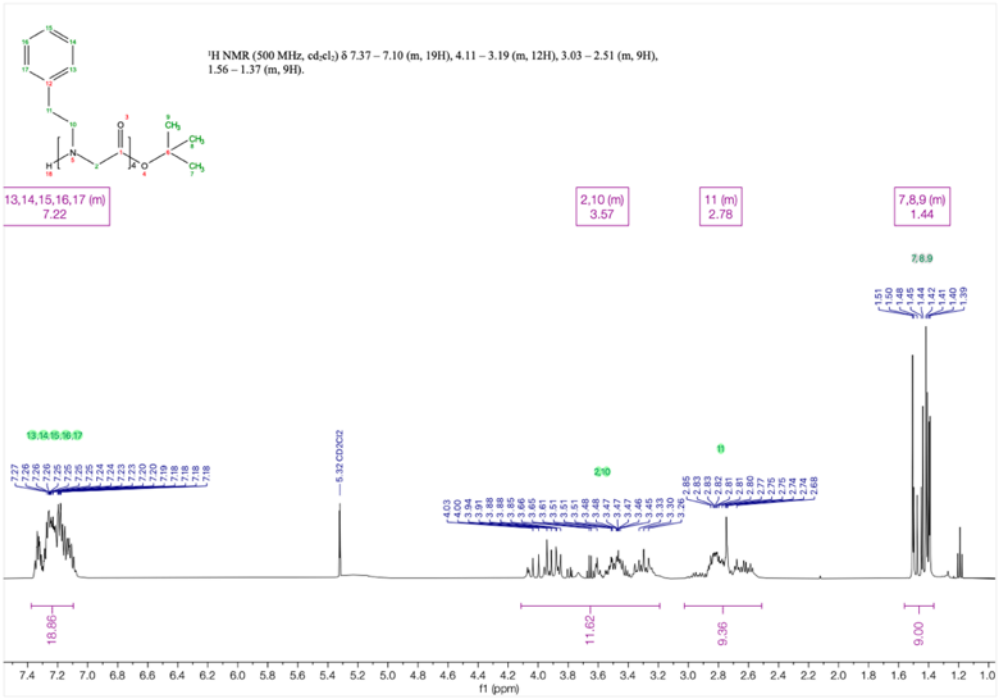


Fig. S234 ^{1}H NMR of Npe_4-tBu.

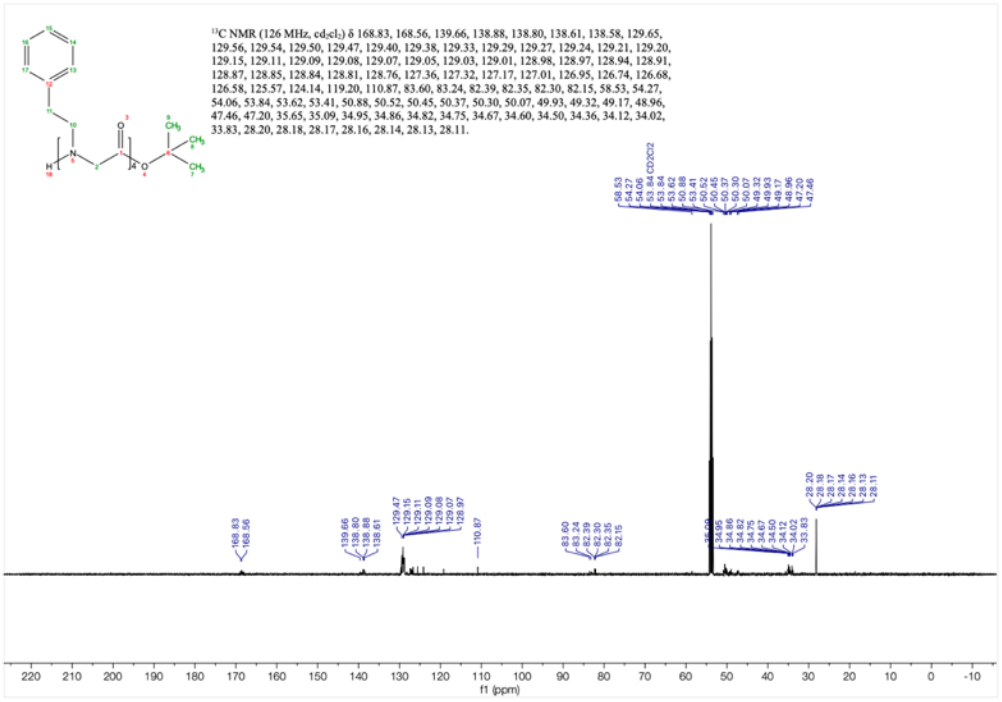


Fig. S235 ^{13}C NMR of Npe4-tBu.

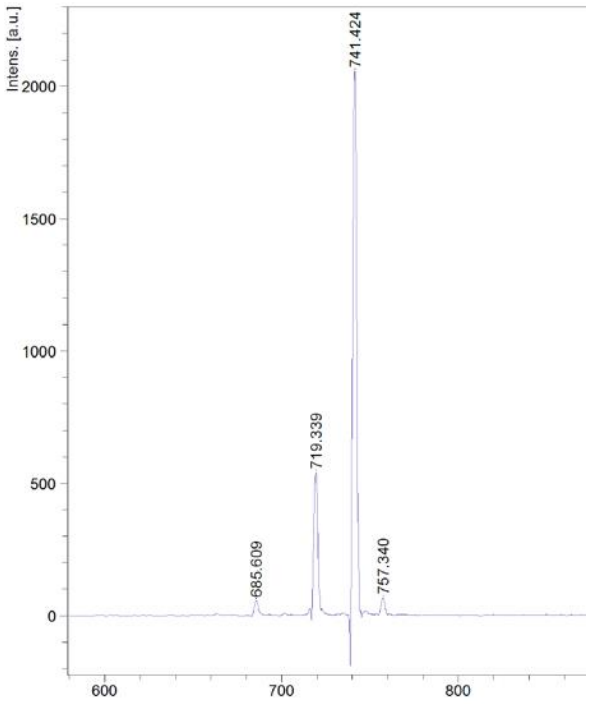


Fig. S236 MALDI-TOF MS of Npe4-tBu.

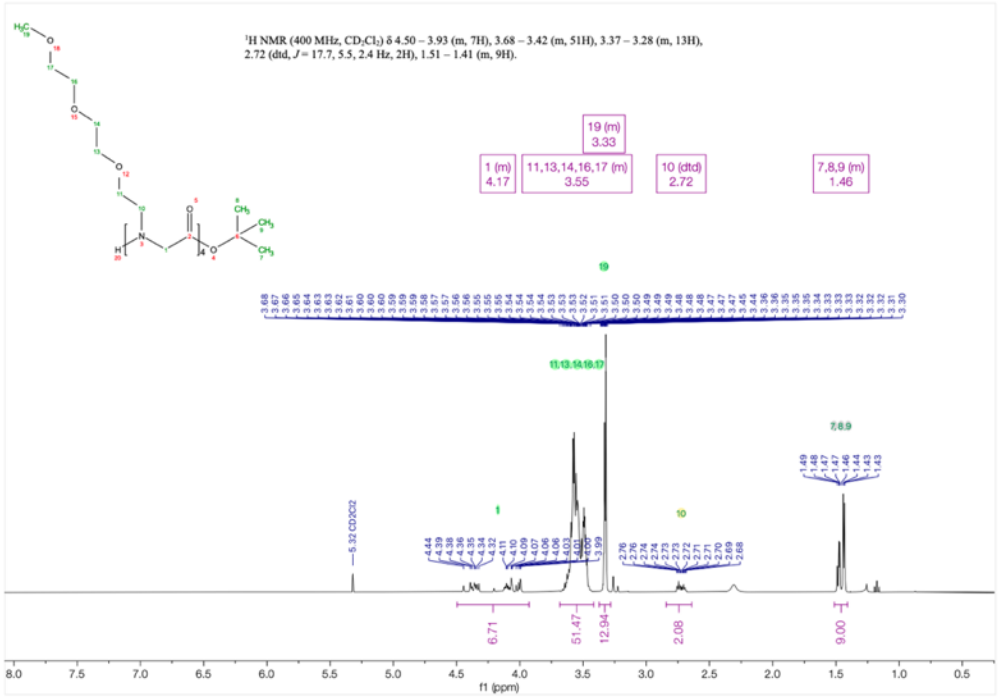


Fig. S237 ^{1}H NMR of Nte$_4$-tBu.

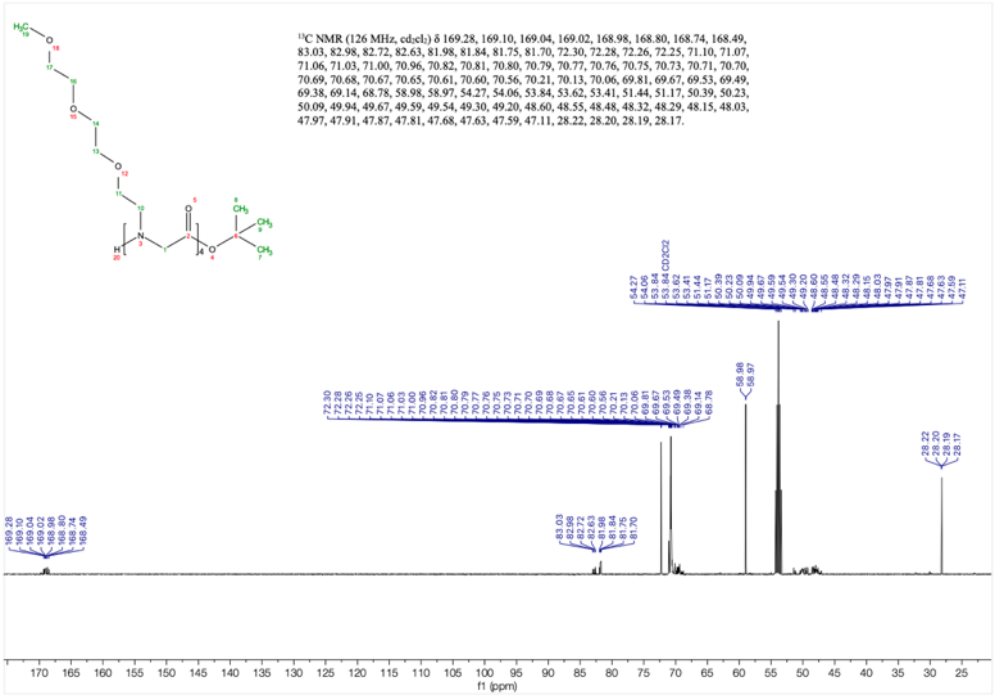


Fig. S238 ^{13}C NMR of Nte$_4$-tBu.

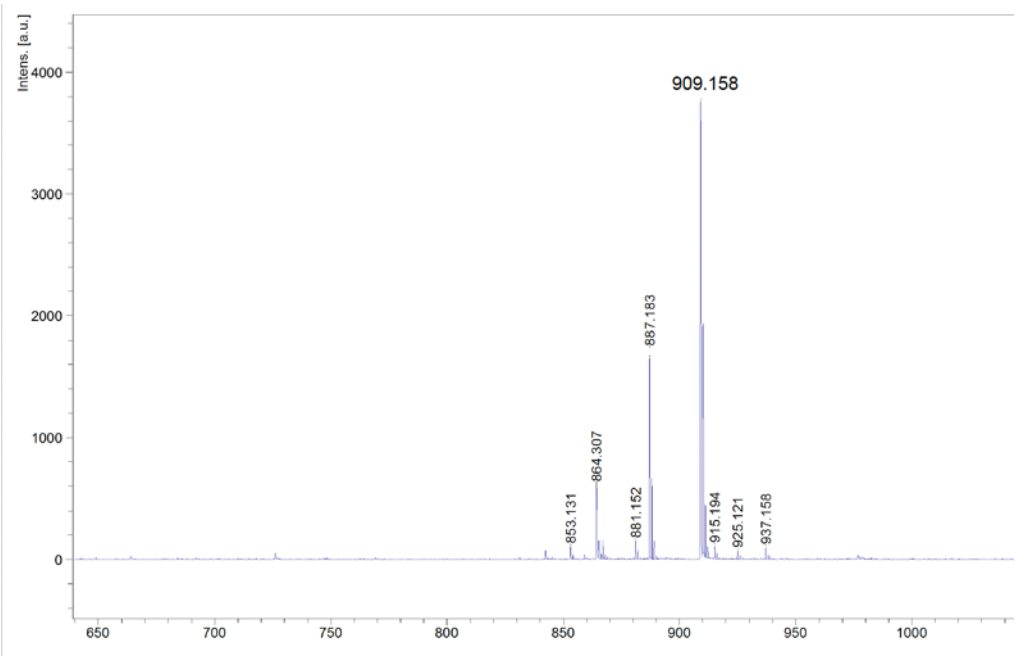


Fig. S239 MALDI-TOF MS of Nte$_4$-tBu.

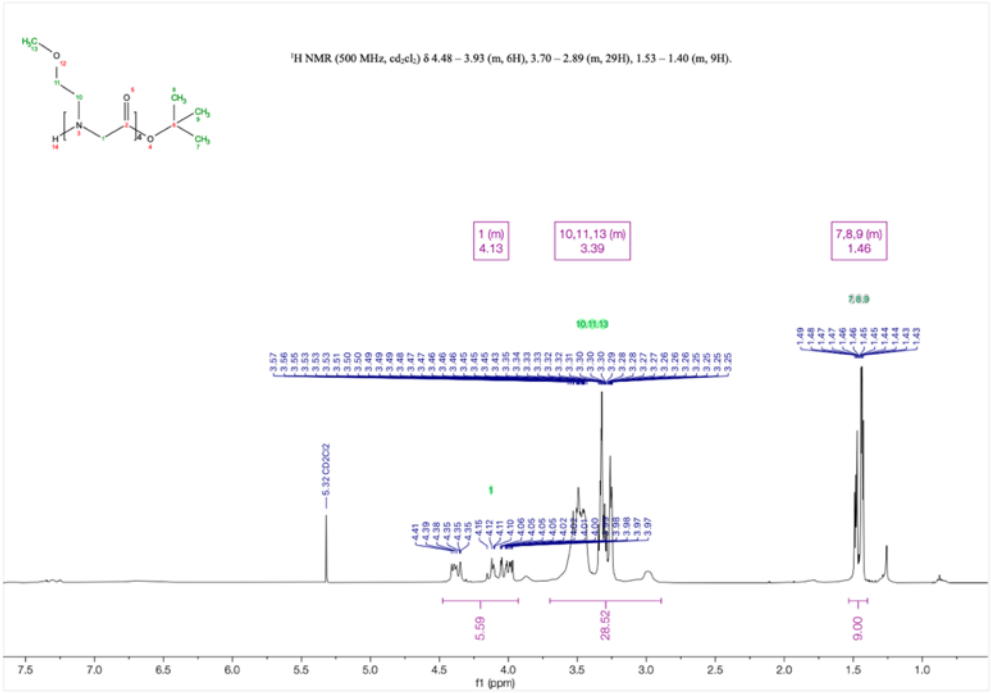


Fig. S240 ^{1}H NMR of Nme$_4$-tBu.

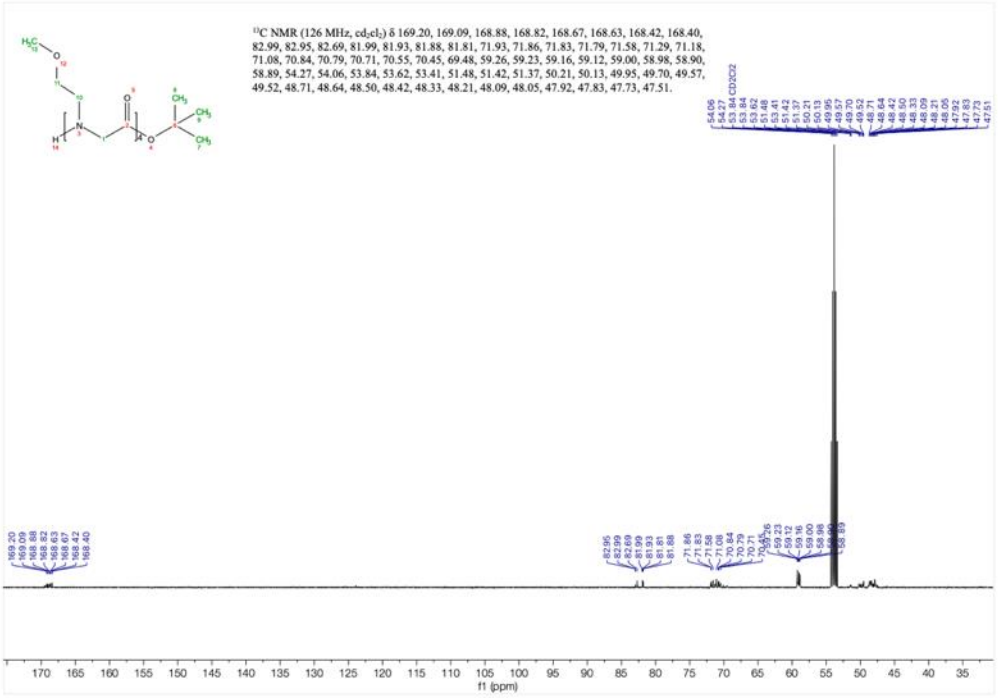


Fig. S241 ^{13}C NMR of Nme$_4$-tBu.

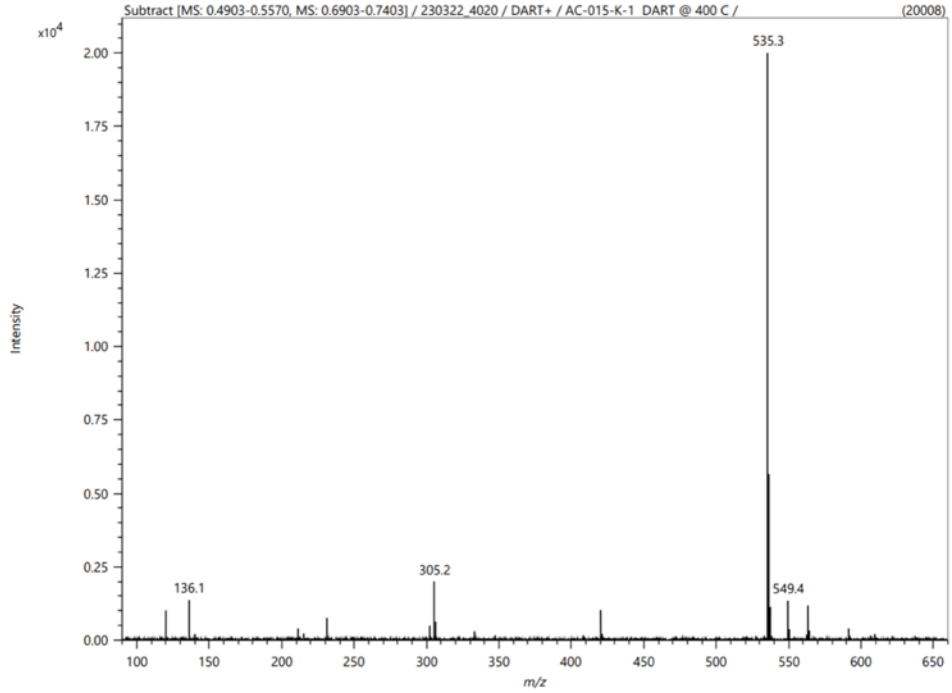


Fig. S242 DART-MS of Nme$_4$-tBu.

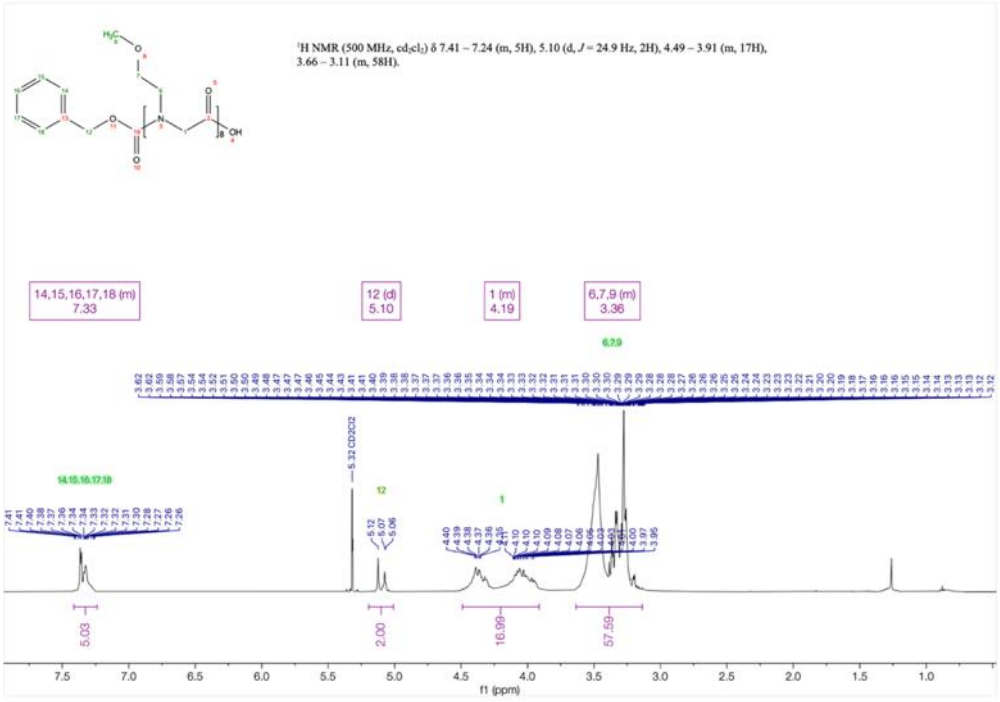


Fig. S243 ^{1}H NMR of Cbz-Nme$_8$.

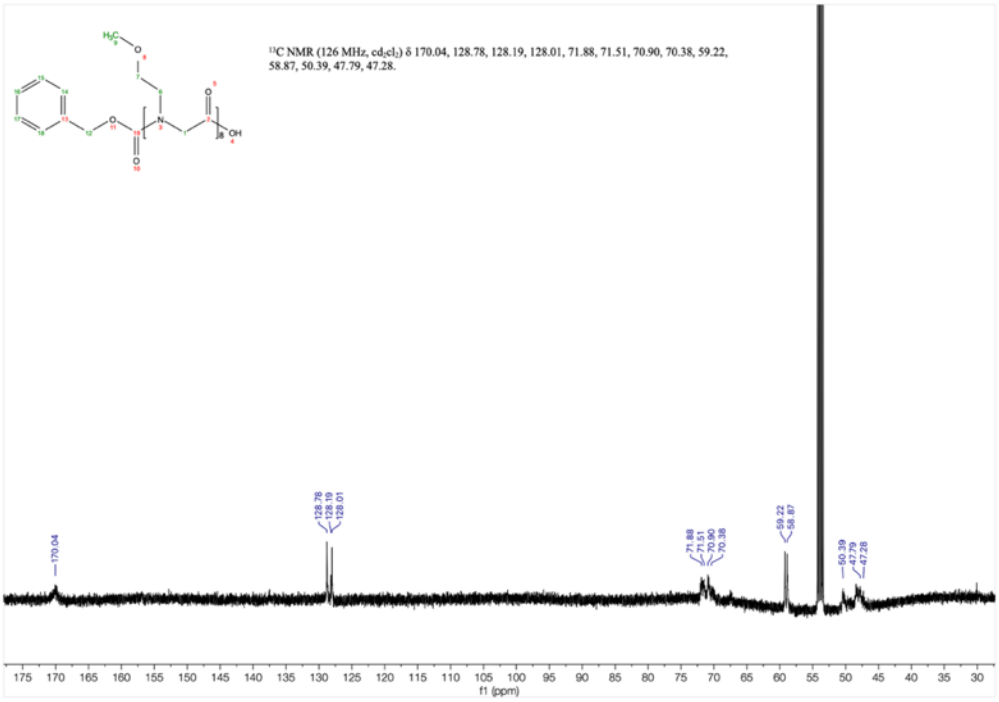


Fig. S244 ^{13}C NMR of Cbz-Nme$_8$.

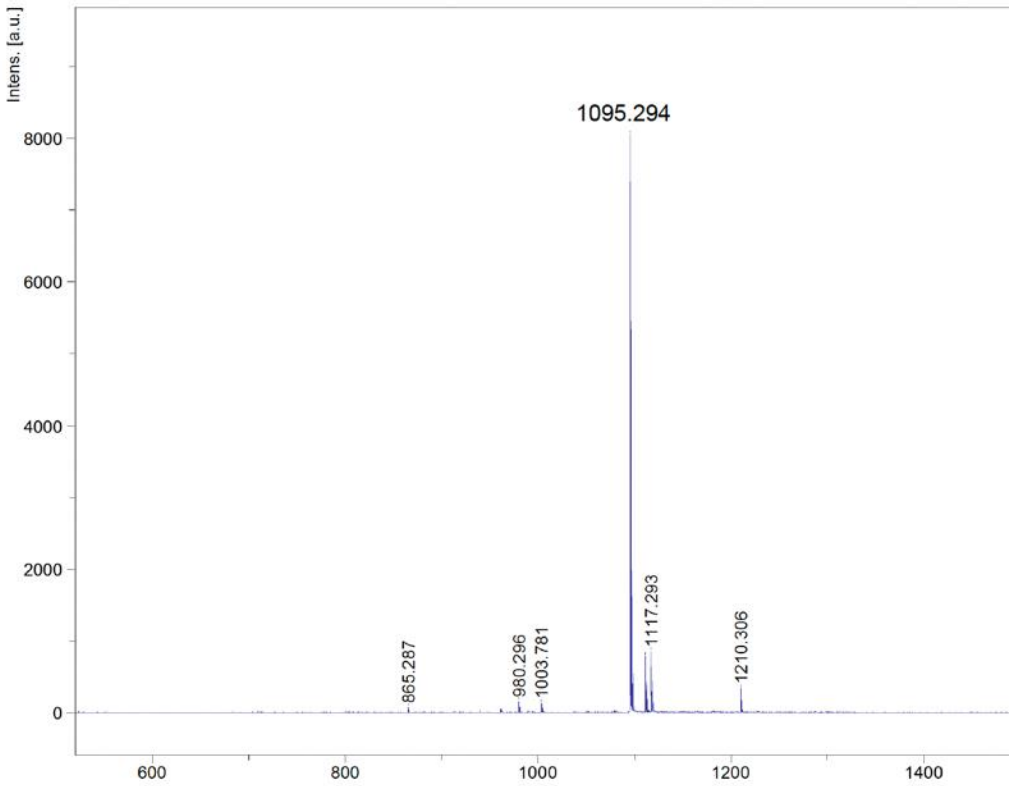


Fig. S245 MALDI-TOF MS of Cbz-Nme$_8$.

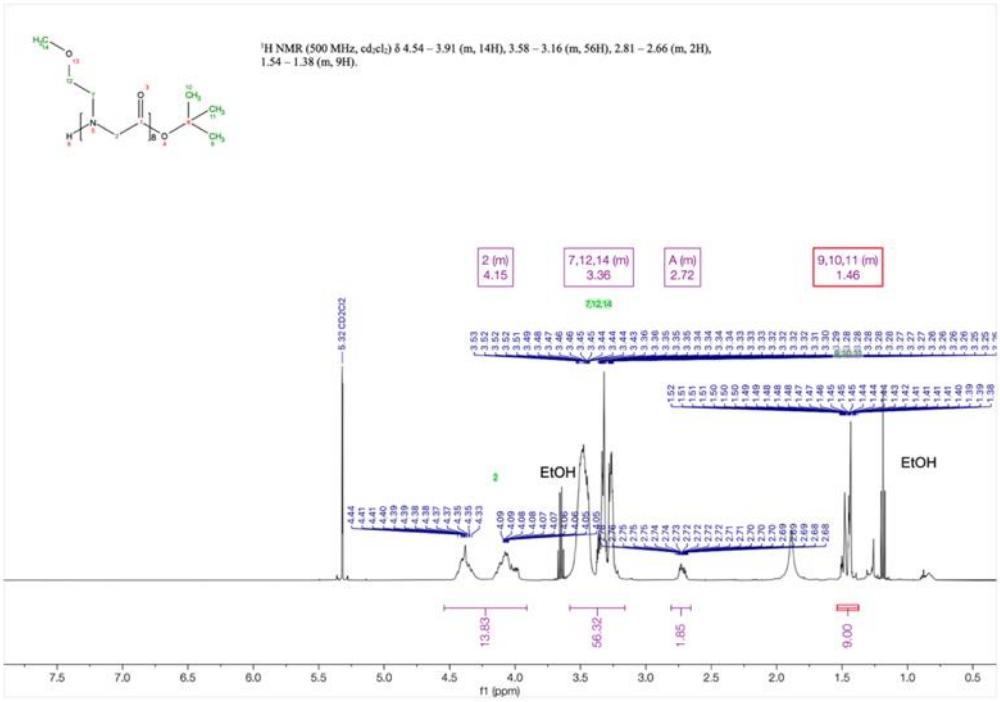


Fig. S246 ^{1}H NMR of Nme$_8$-tBu.

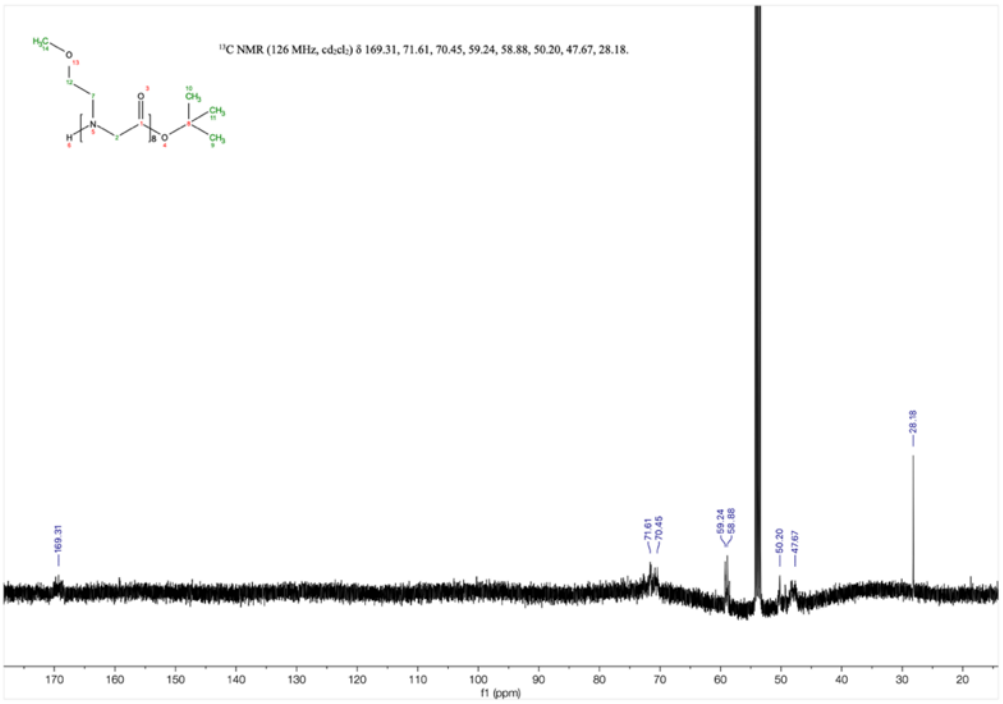


Fig. S247 ^{13}C NMR of Nme$_8$-tBu.

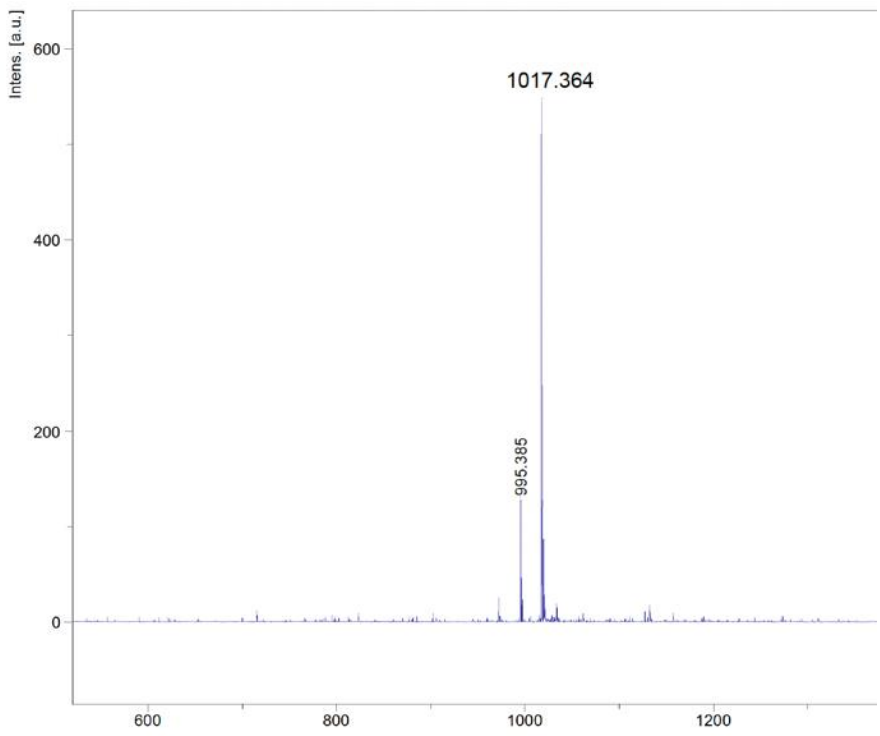


Fig. S248 MALDI-TOF MS of Nme$_8$-tBu.

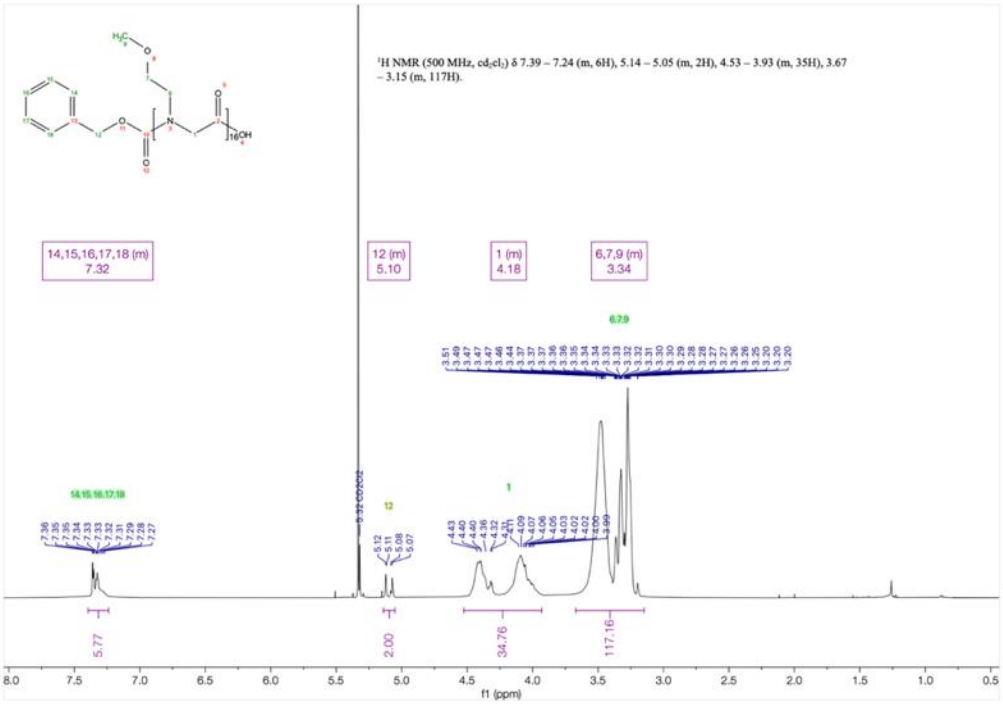


Fig. S249 ^{1}H NMR of Cbz-Nme$_{16}$.

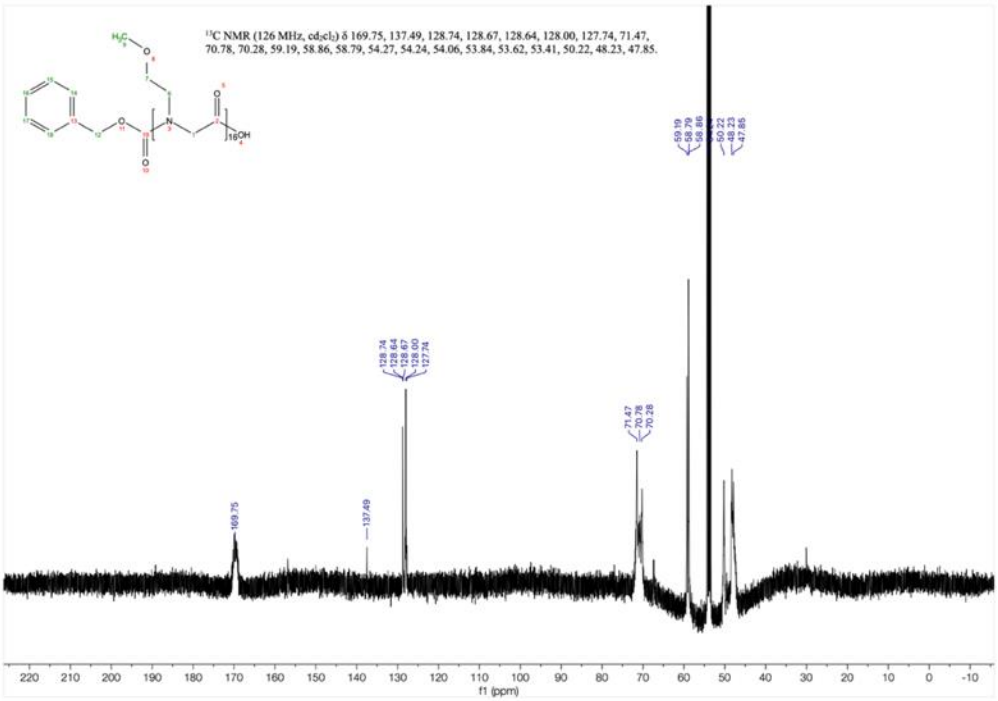


Fig. S250 ^{13}C NMR of Cbz-Nme$_{16}$.

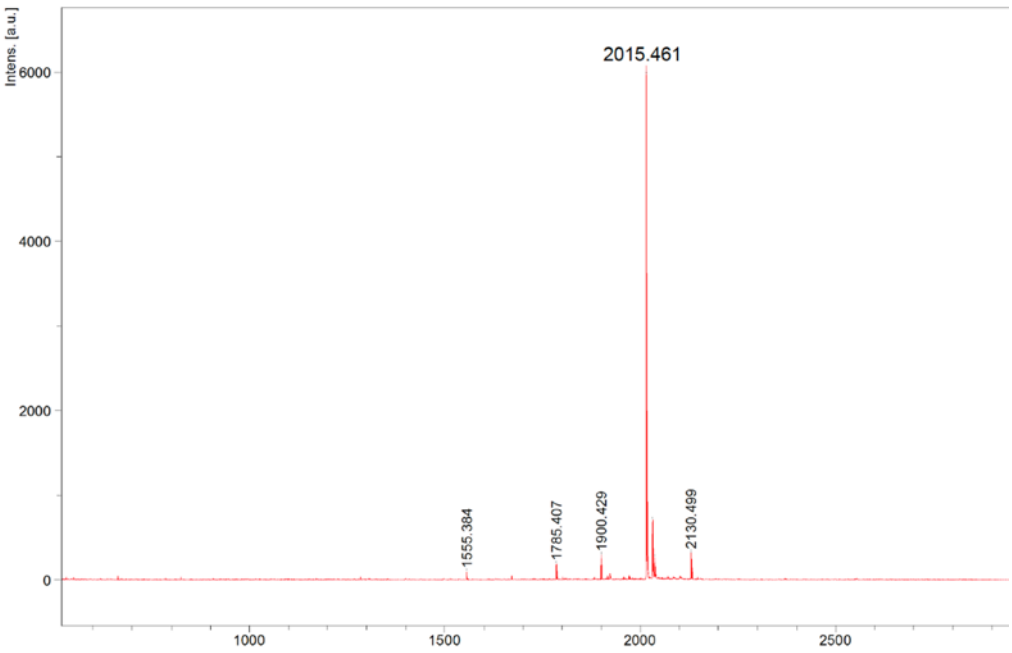


Fig. S251 MALDI-TOF MS of Cbz-Nme$_{16}$.

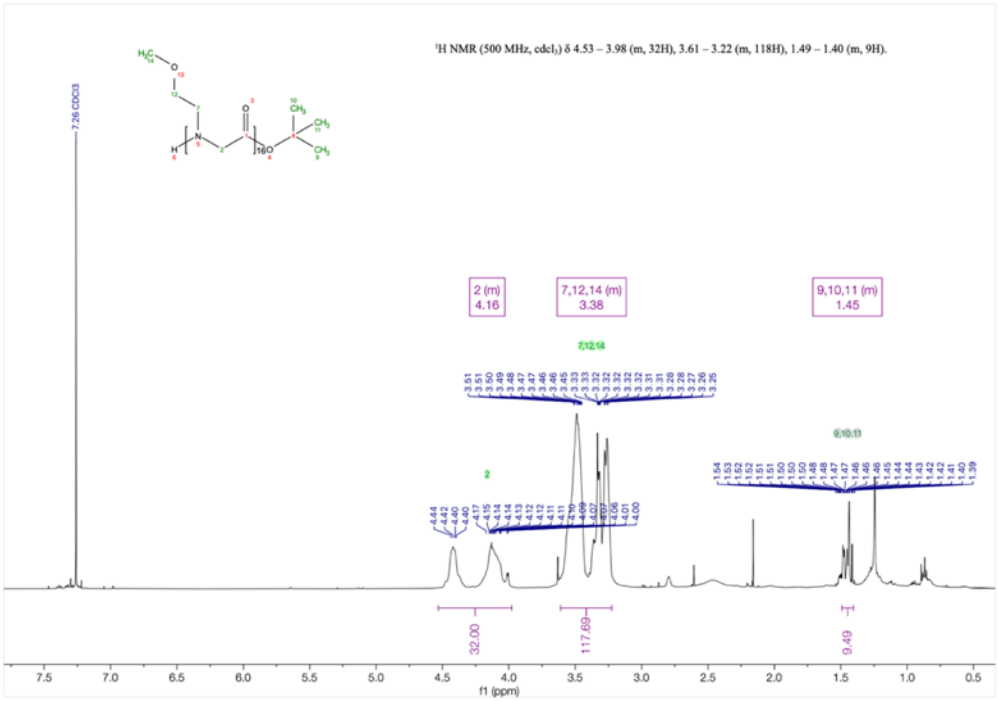


Fig. S252 ^{1}H NMR of Nme$_{16}$-tBu.

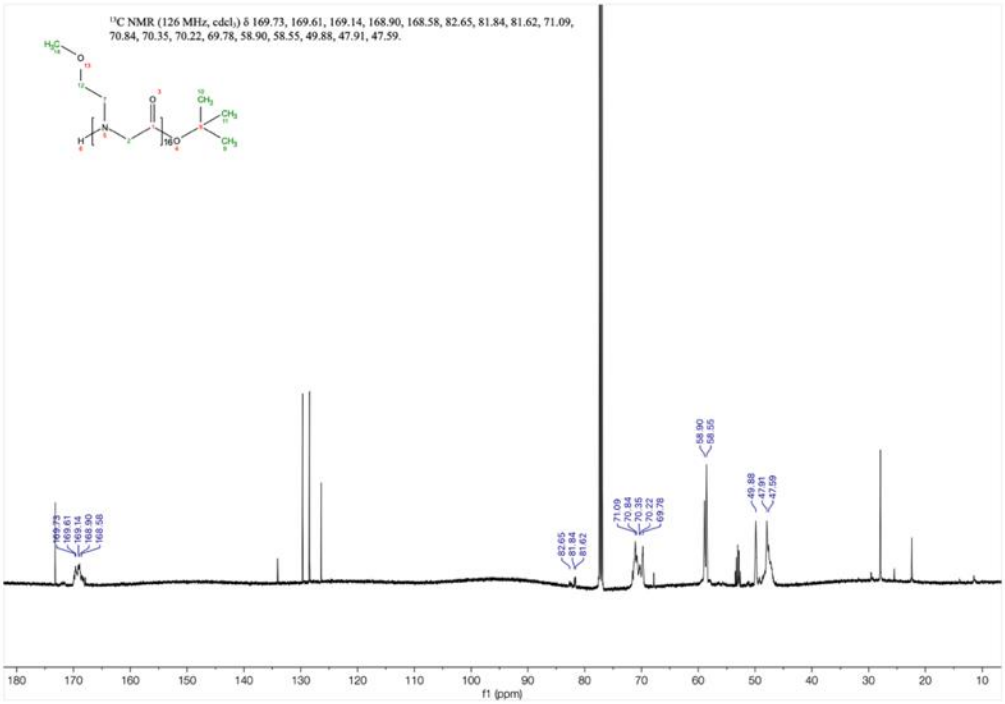


Fig. S253 ^{13}C NMR of Nme$_{16}$-tBu.

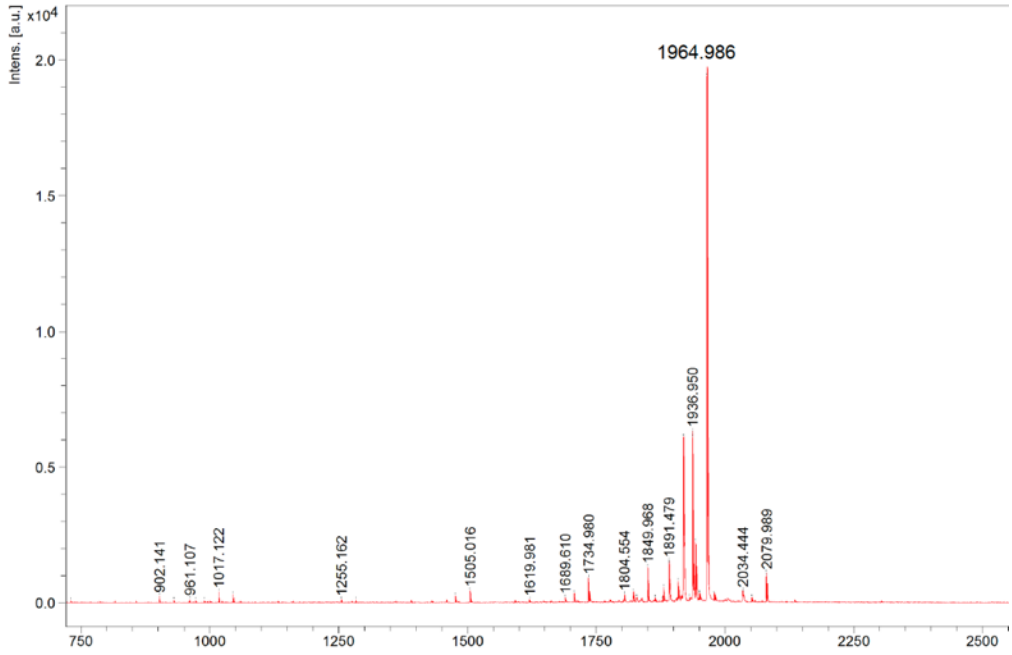


Fig. S254 MALDI-TOF MS of Nme$_{16}$-tBu.

7.2 Diblock peptoids

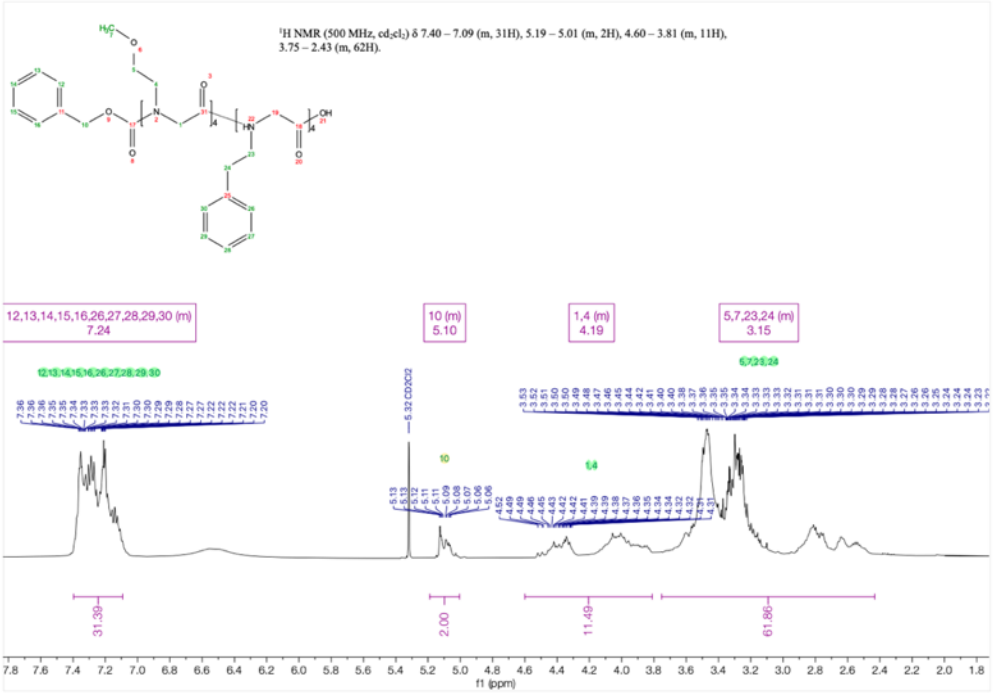


Fig. S255 ^{1}H NMR of Cbz-Nme$_4$-Npe$_4$.

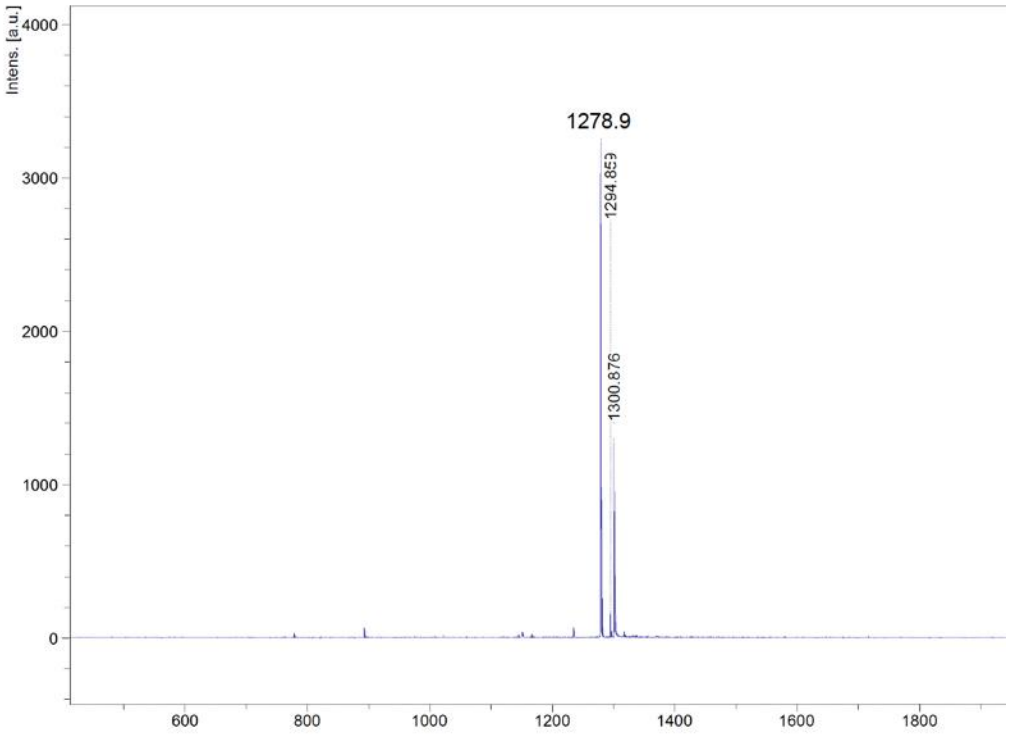


Fig. S256 MALDI-TOF MS of Cbz-Nme$_4$-Npe$_4$.

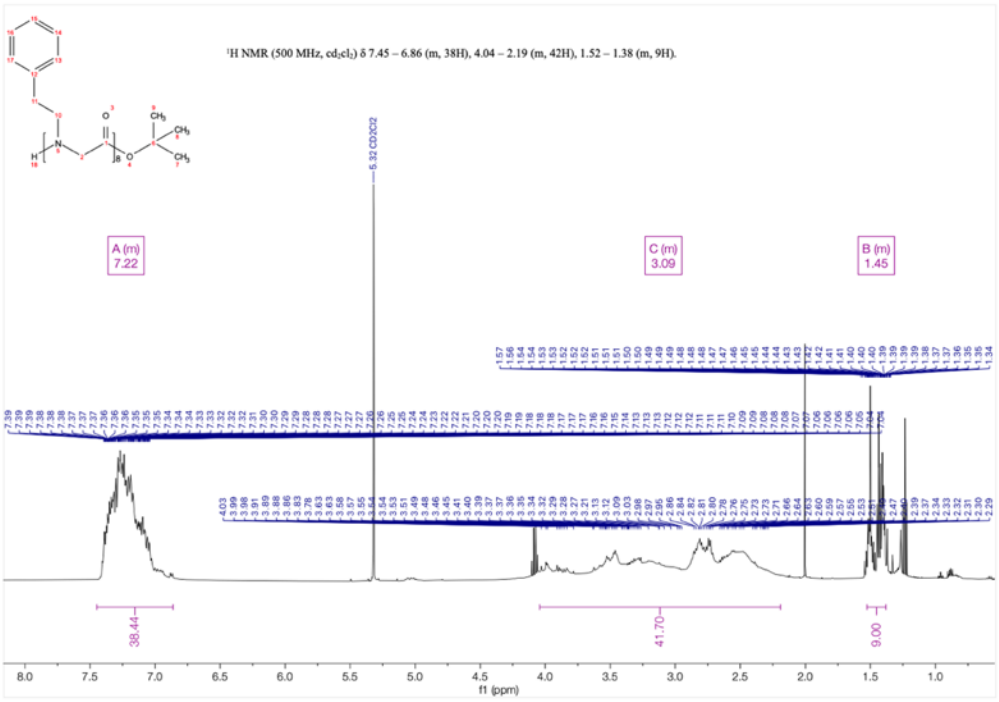


Fig. S257 ^{1}H NMR of Npe$_8$-tBu.

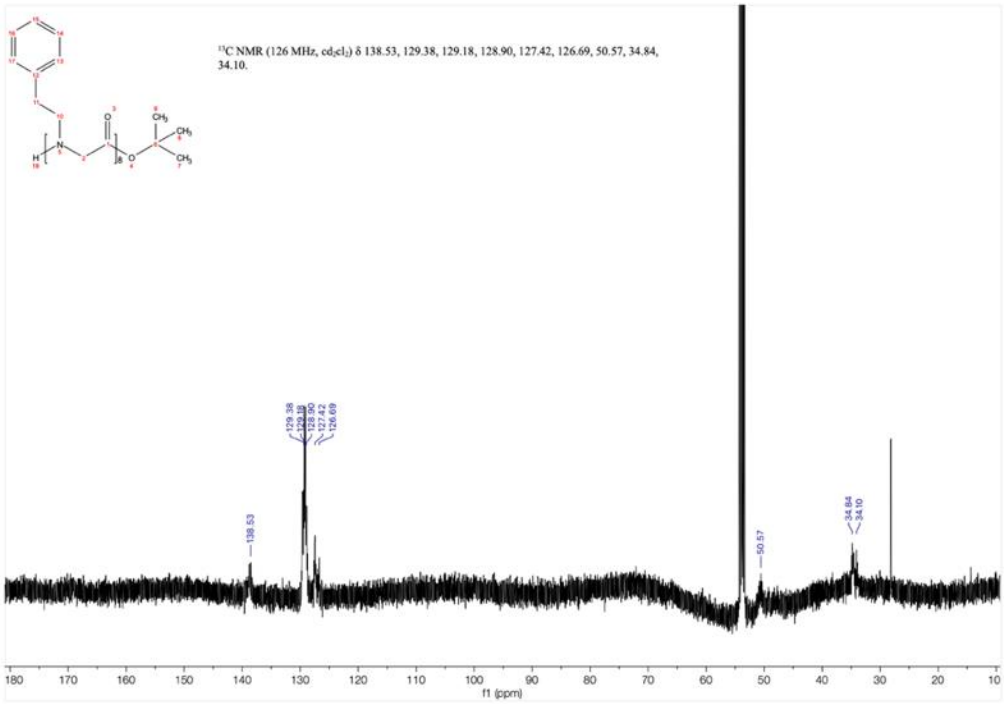


Fig. S258 ^{13}C NMR of Npe$_8$-tBu.

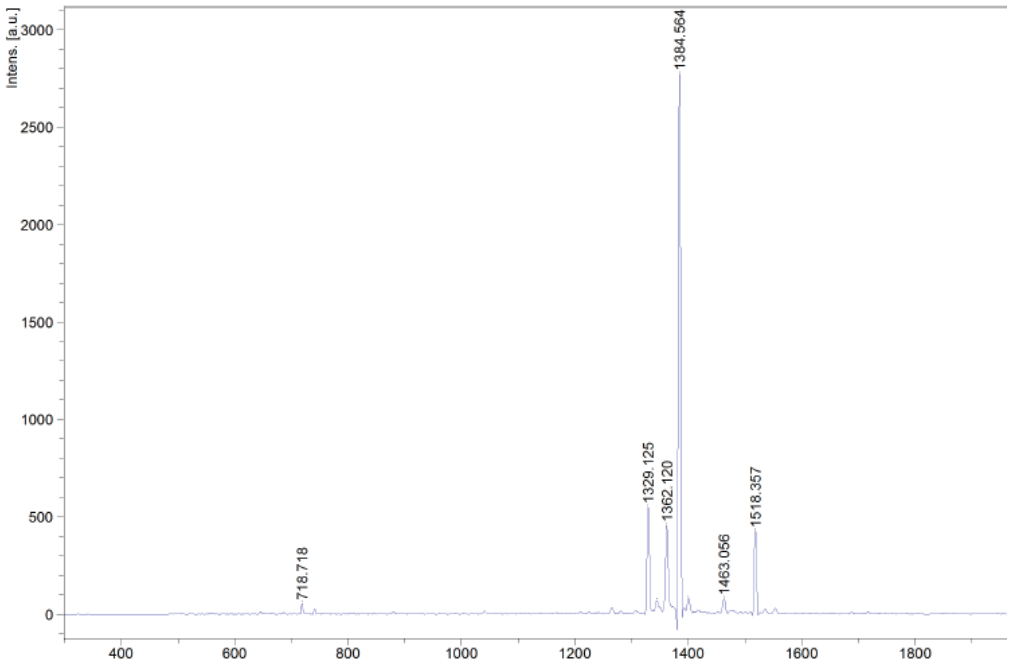


Fig. S259 MALDI-TOF MS of Npe$_8$-tBu.

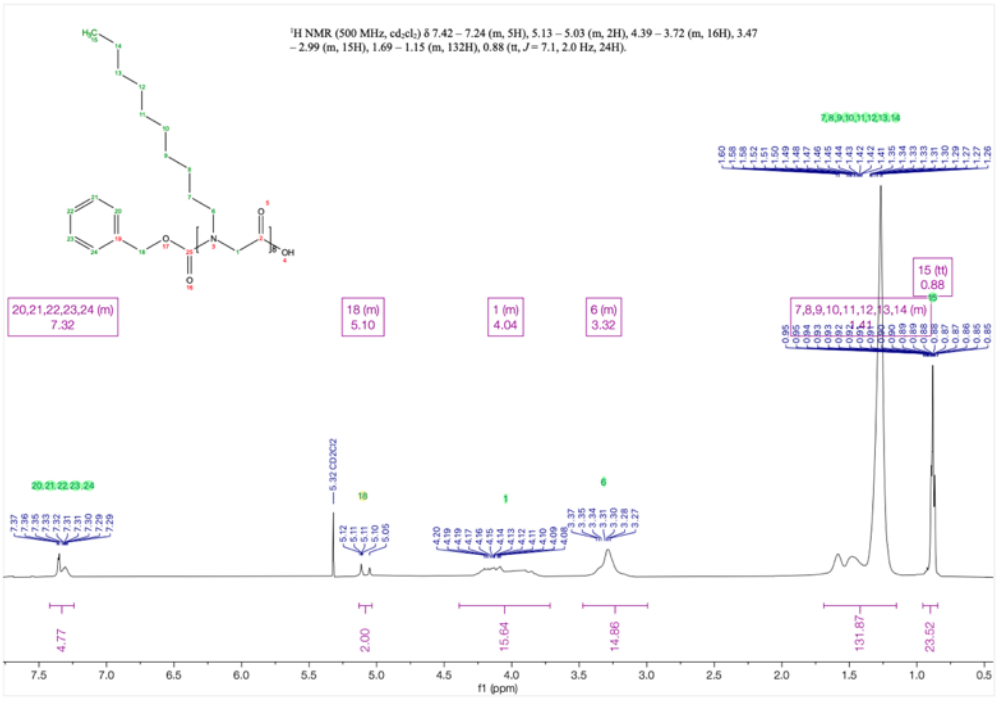


Fig. S260 ^{1}H NMR of Cbz-Ndc$_8$.

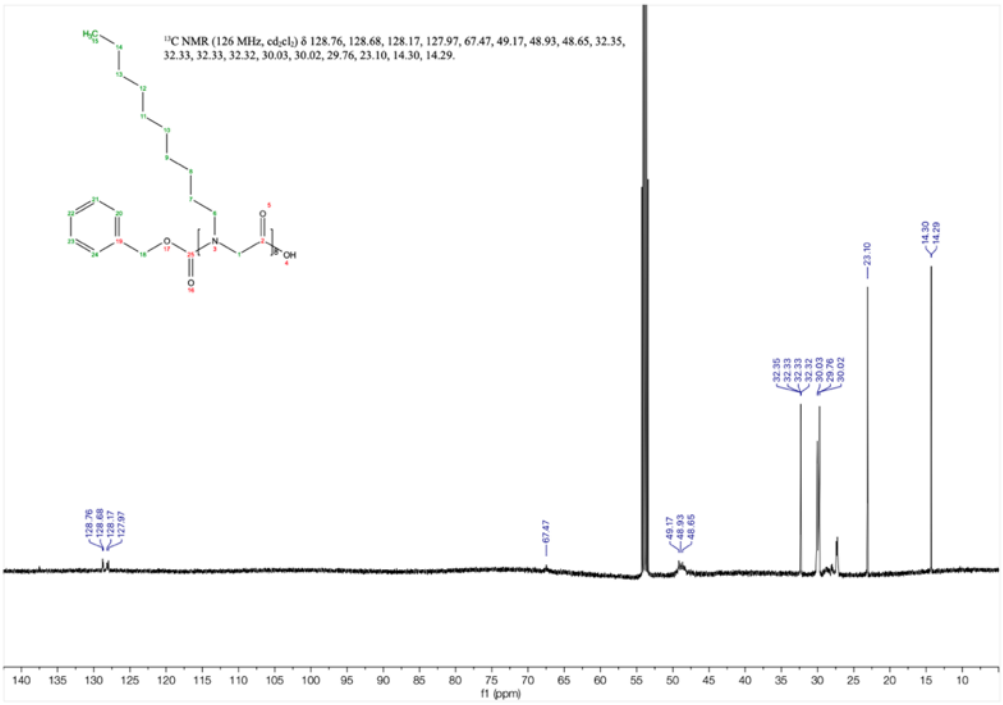


Fig. S261 ^{13}C NMR of Cbz-Ndc$_8$.

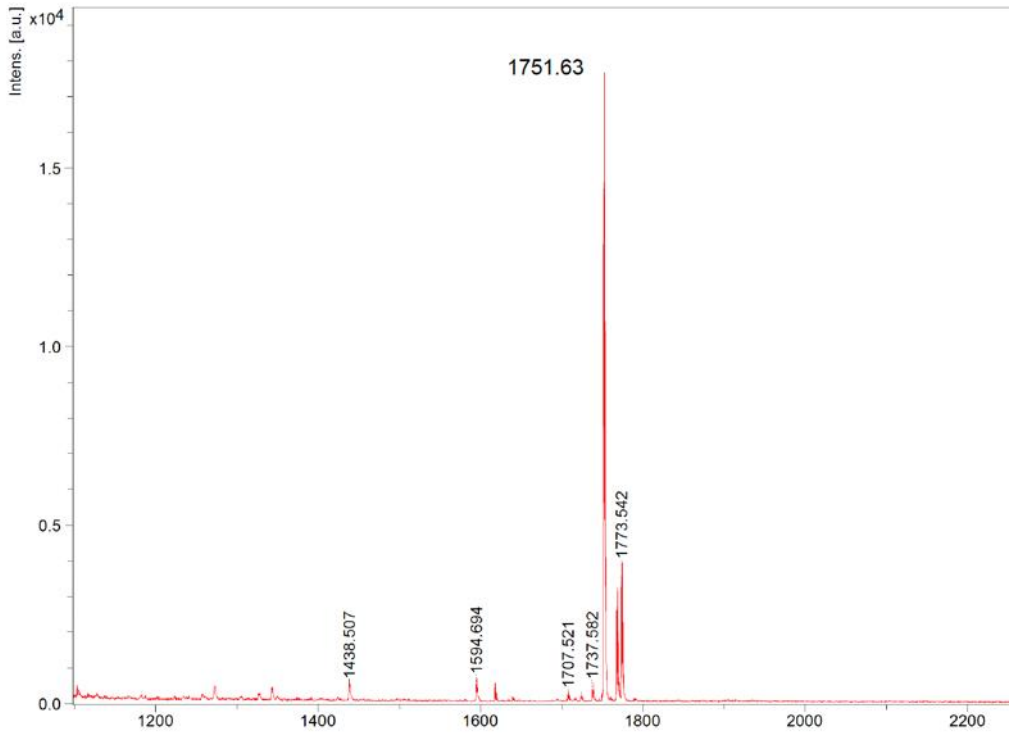


Fig. S262 MALDI-TOF MS of Cbz-Ndc$_8$.

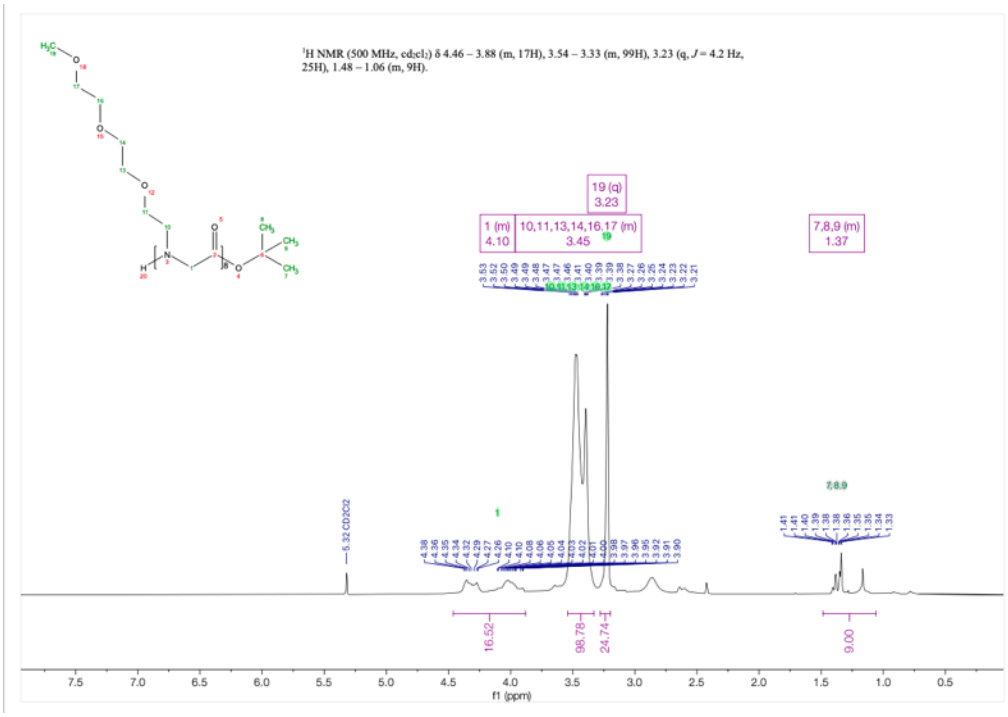


Fig. S263 ^{1}H NMR of Nte$_{8}$-tBu.

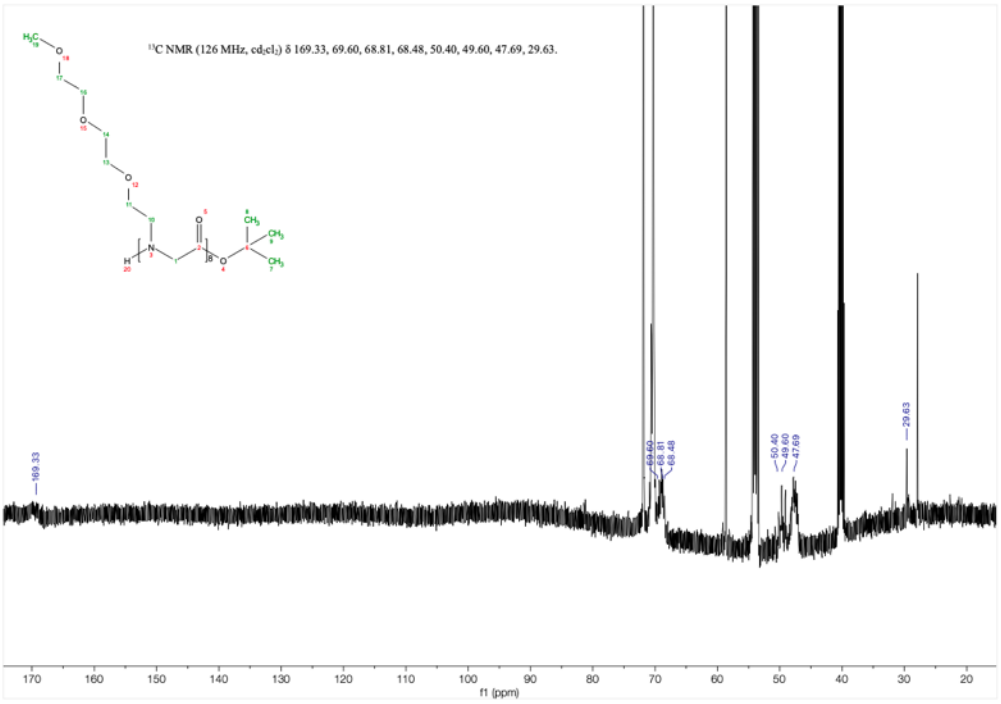


Fig. S264 ^{13}C NMR of Nte$_{8}$-tBu.

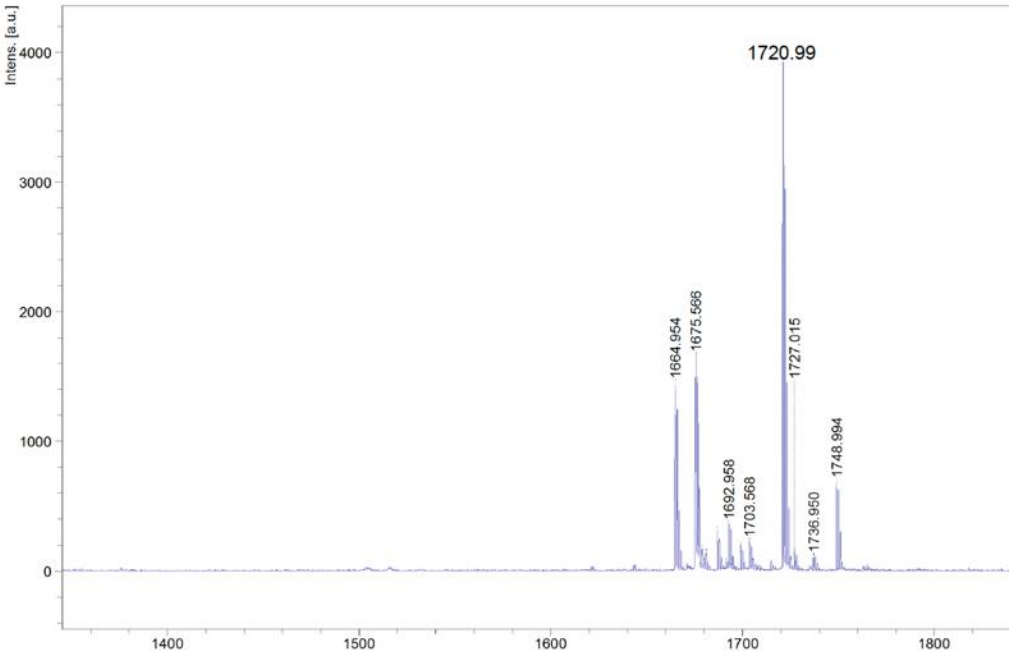


Fig. S265 MALDI-TOF MS of Nte$_8$-tBu.

7.3 Sequence-defined periodic and aperiodic peptoids

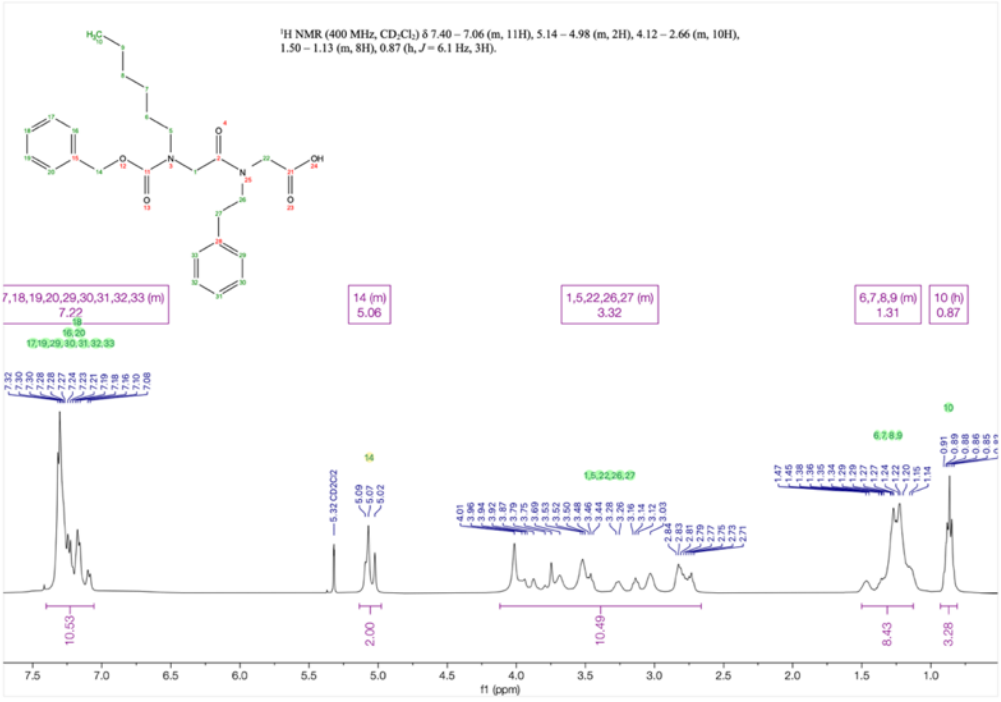


Fig. S266 ^{1}H NMR of Cbz-Nhx-Npe.

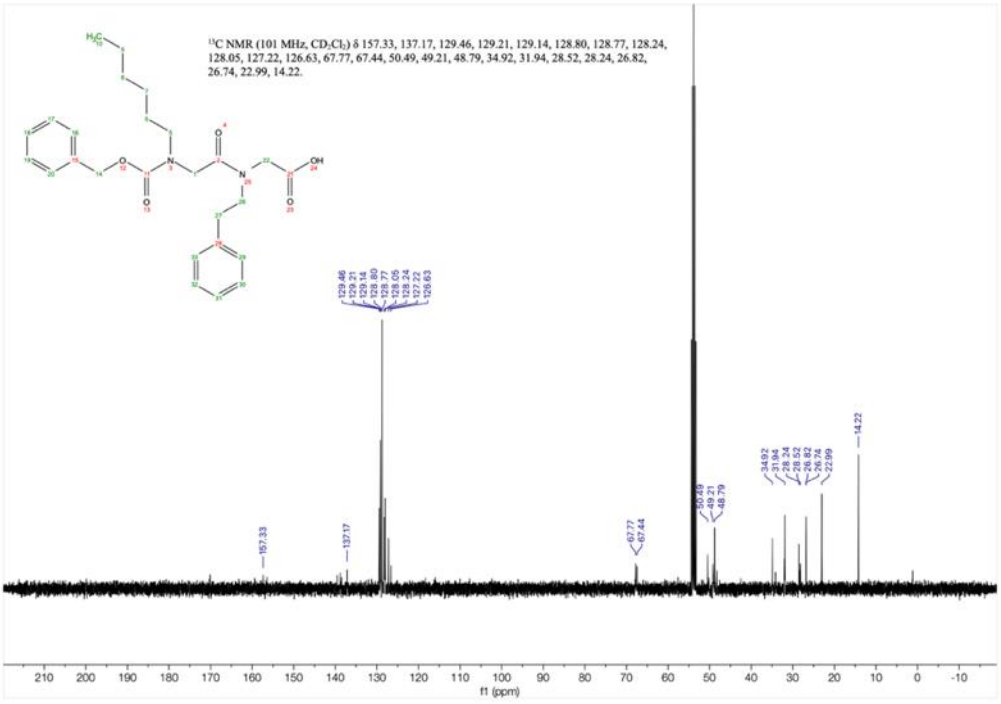


Fig. S267 ^{13}C NMR of Cbz-Nhx-Npe.

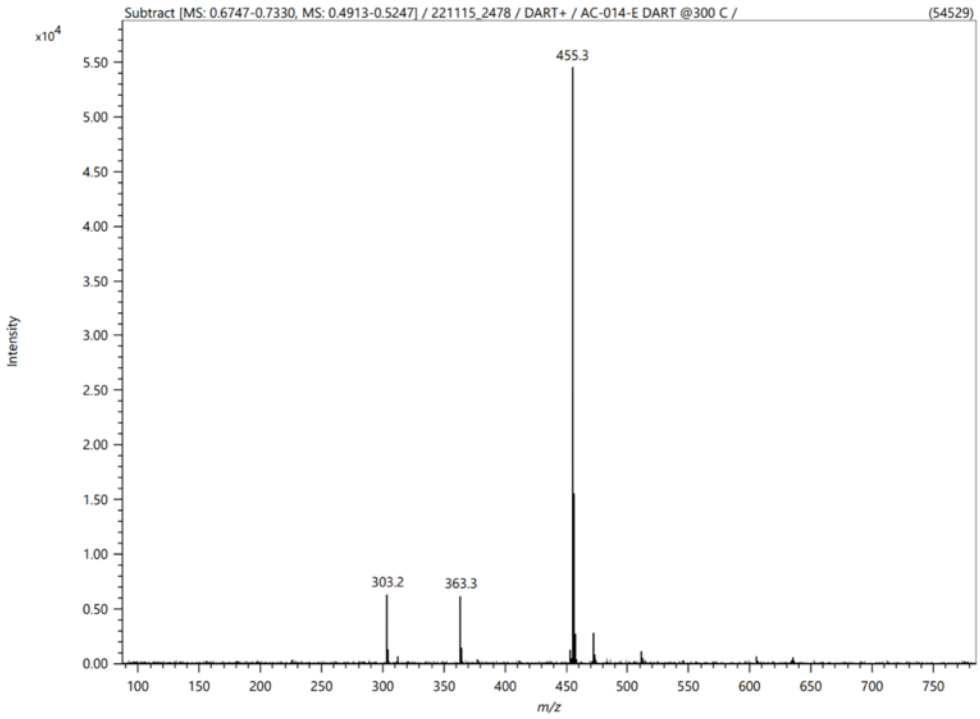


Fig. S268 DART-MS of Cbz-Nhx-Npe.

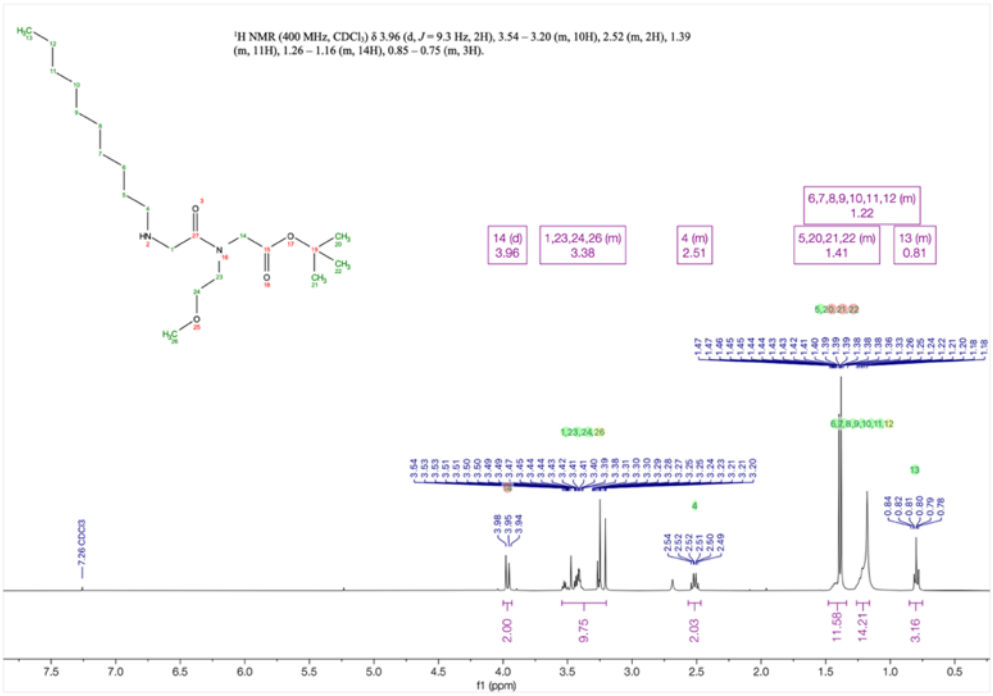


Fig. S269 [1]H NMR of Ndc-Nme-tBu.

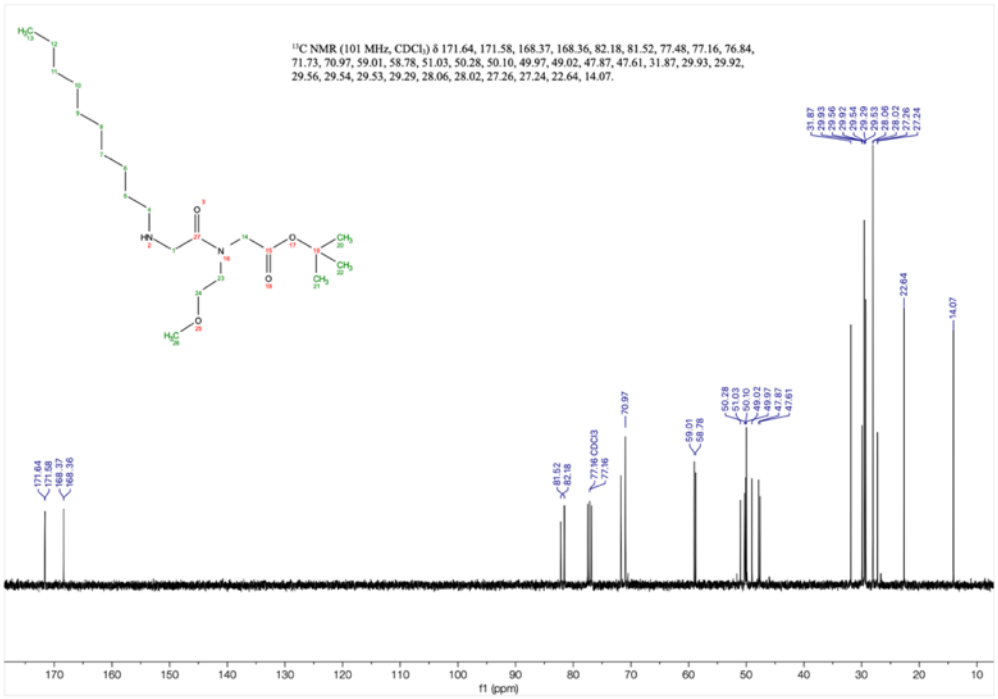


Fig. S270 [13]C NMR of Ndc-Nme-tBu.

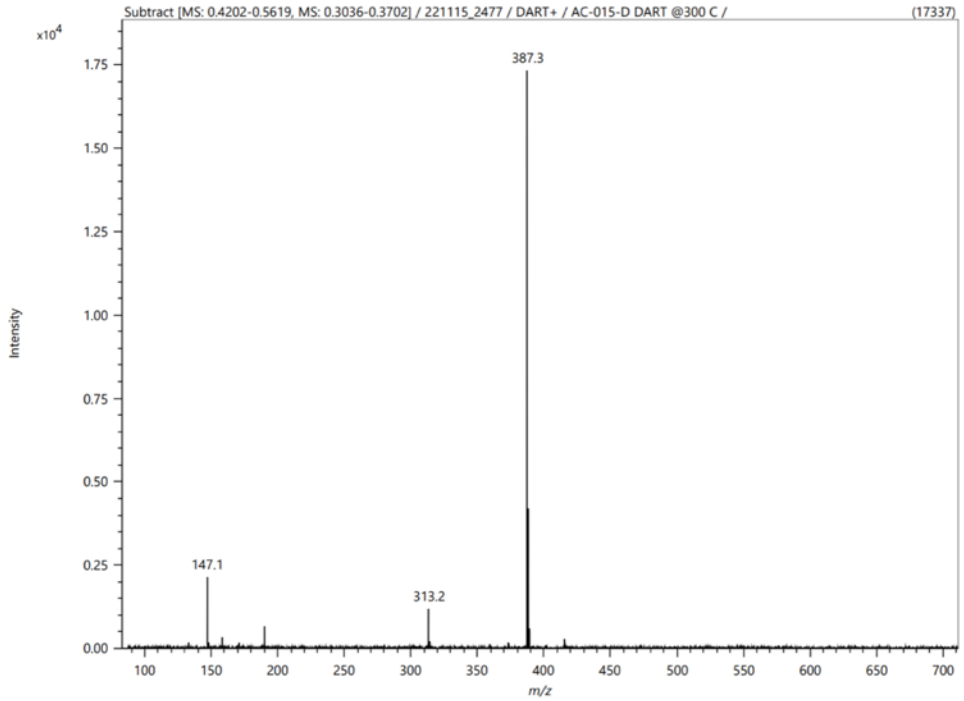


Fig. S271 DART-MS of Ndc-Nme-tBu.

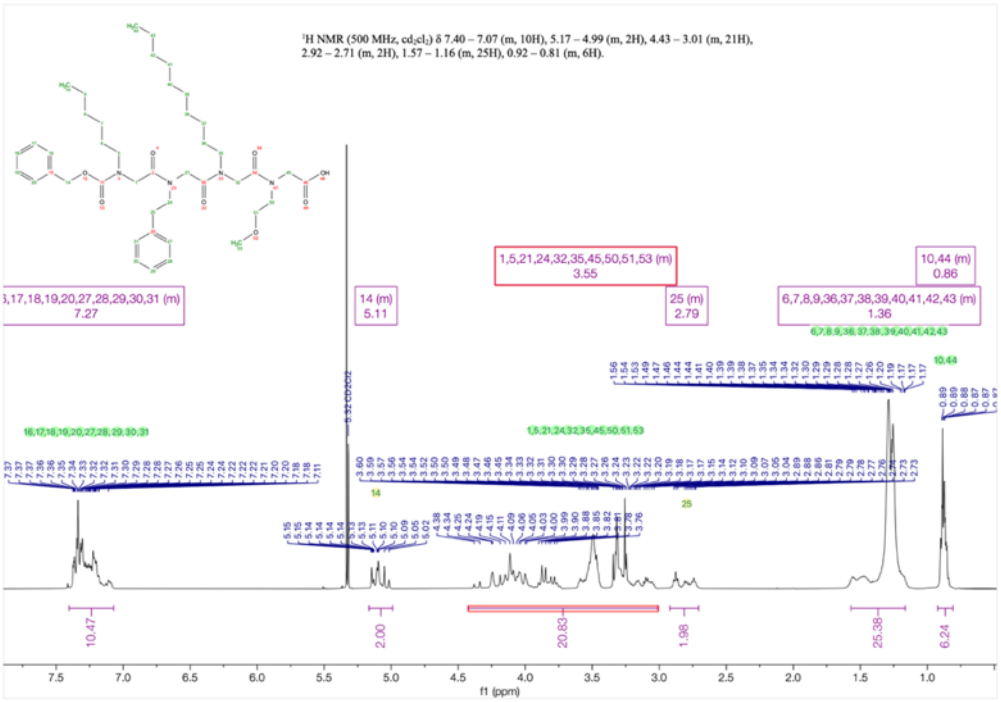


Fig. S272 ^{1}H NMR of Cbz-Nhx-Npe-Ndc-Nme.

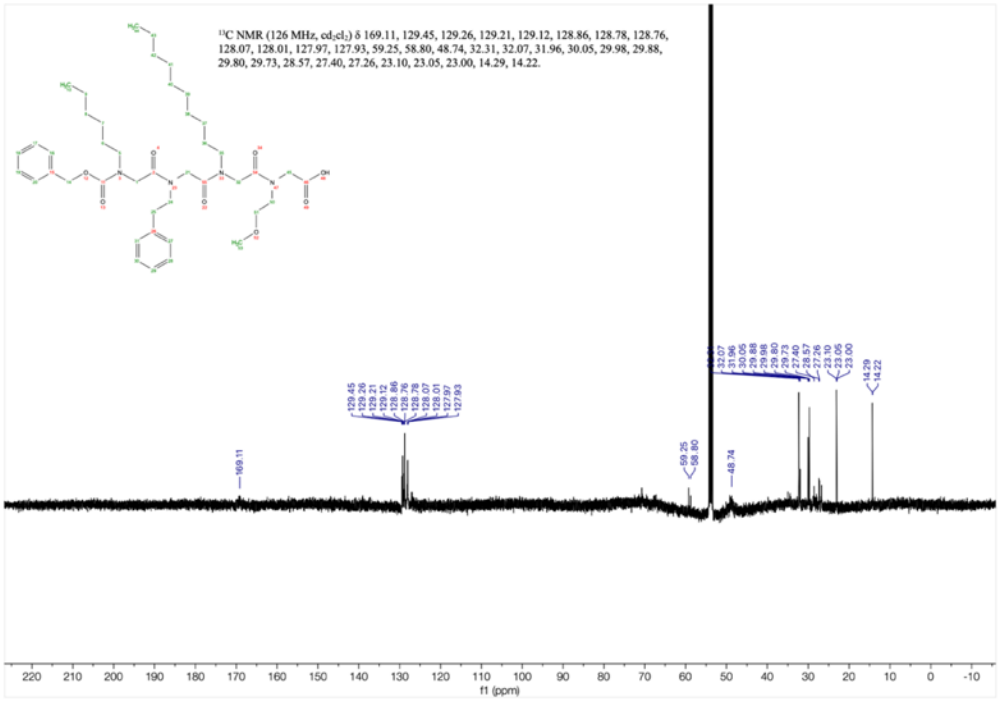


Fig. S273 ^{13}C NMR of Cbz-Nhx-Npe-Ndc-Nme.

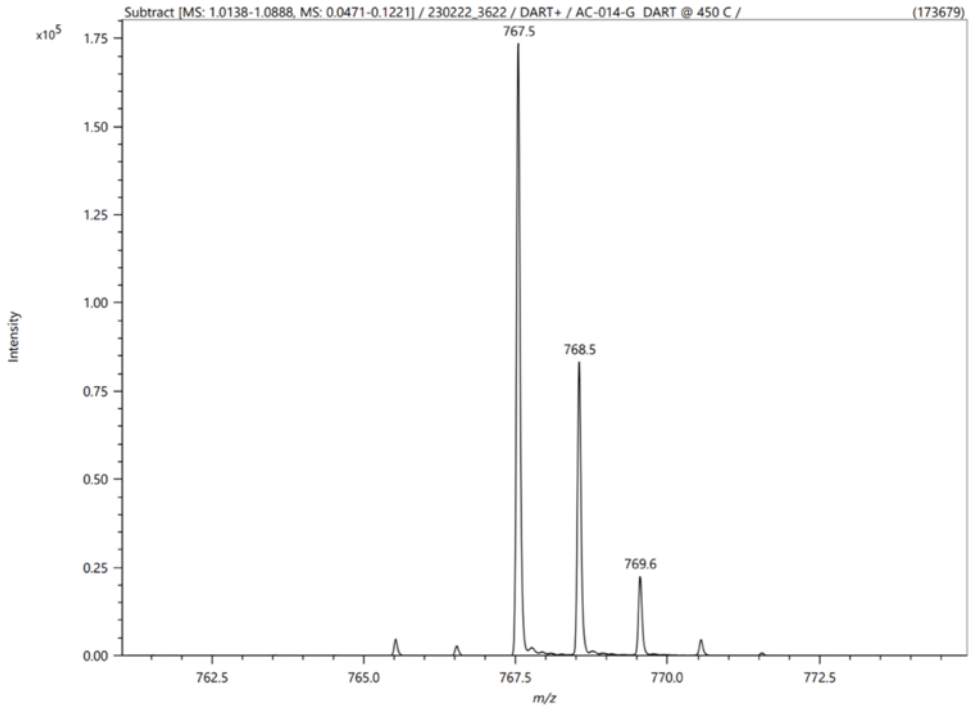


Fig. S274 DART-MS of Cbz-Nhx-Npe-Ndc-Nme.

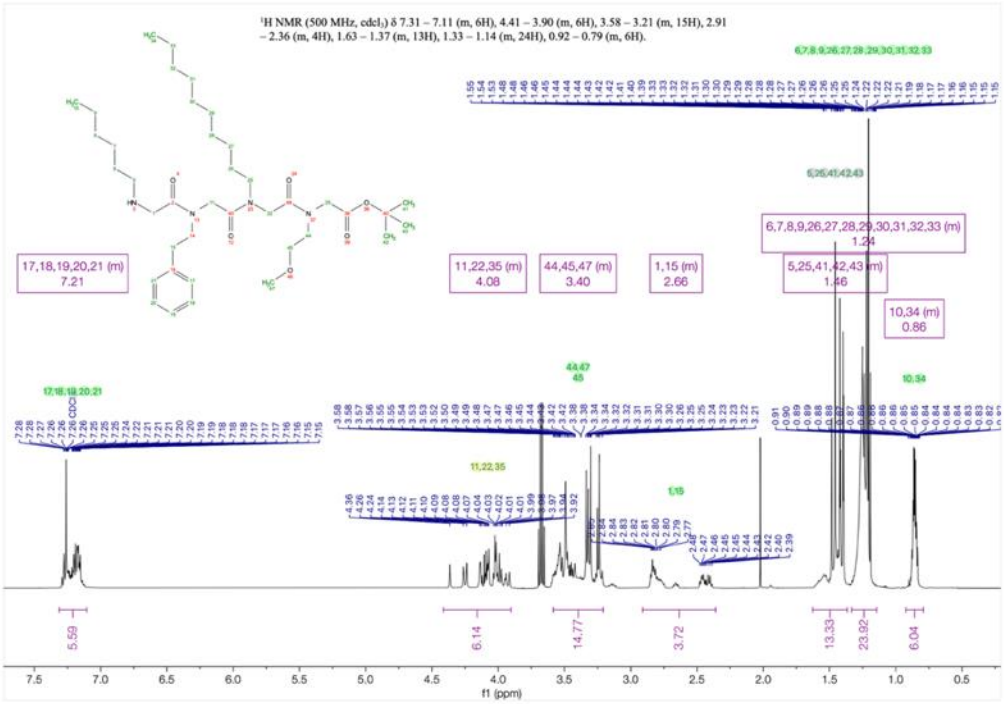


Fig. S275 [1]H NMR of Nhx-Npe-Ndc-Nme-tBu.

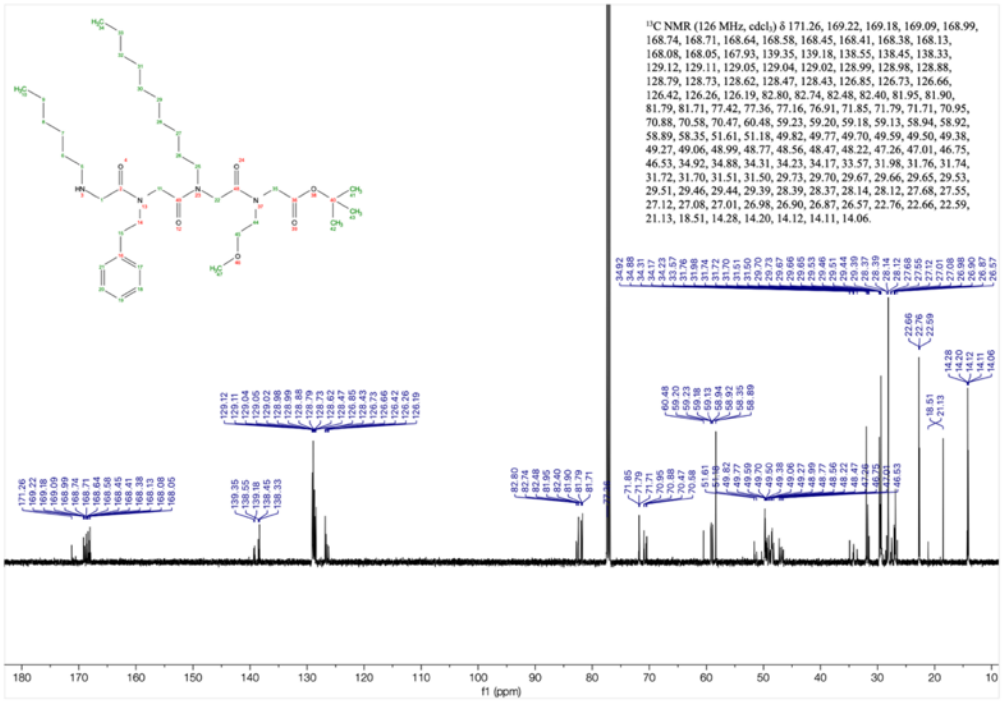


Fig. S276 [13]C NMR of Nhx-Npe-Ndc-Nme-tBu.

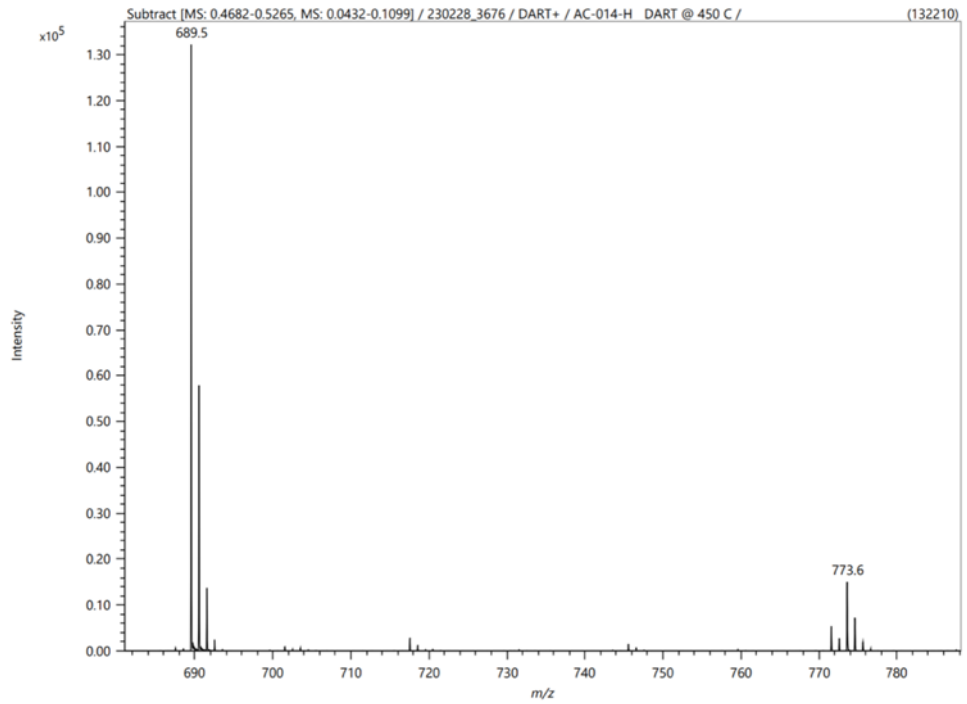


Fig. S277 DART-MS of Nhx-Npe-Ndc-Nme-tBu.

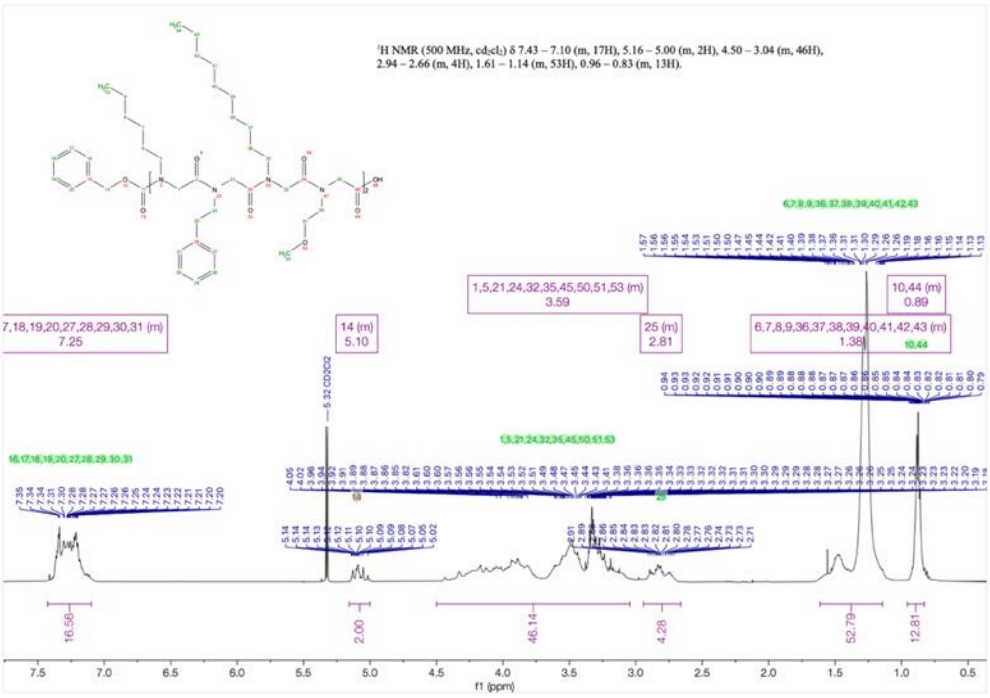


Fig. S278 ^{1}H NMR of Cbz-(Nhx-Npe-Ndc-Nme)$_2$.

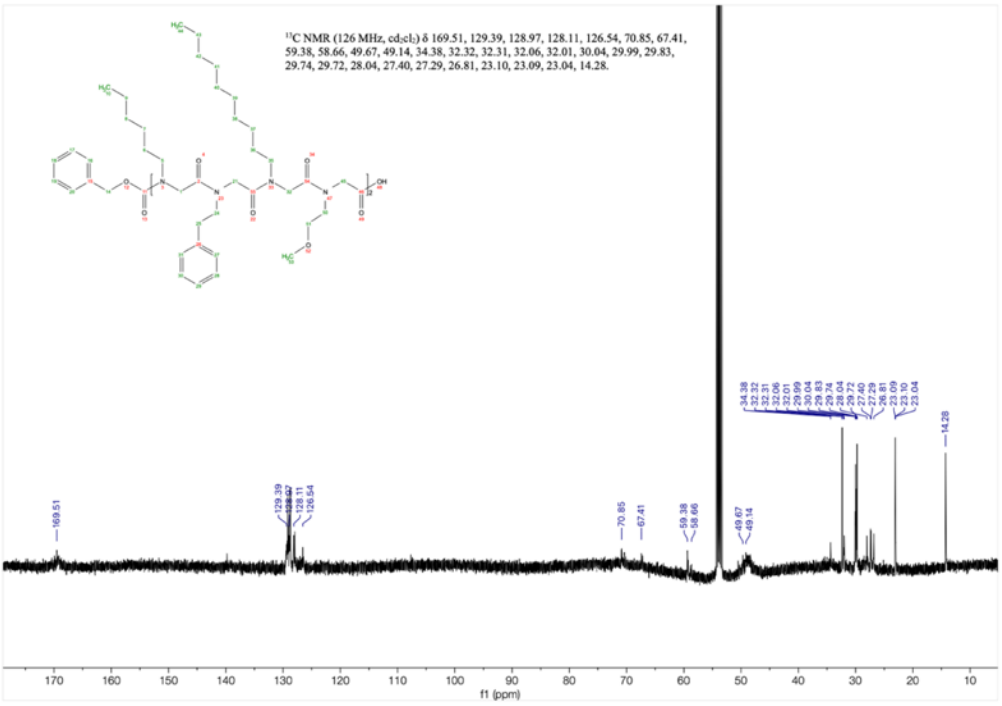


Fig. S279 ^{13}C NMR of Cbz-(Nhx-Npe-Ndc-Nme)$_2$.

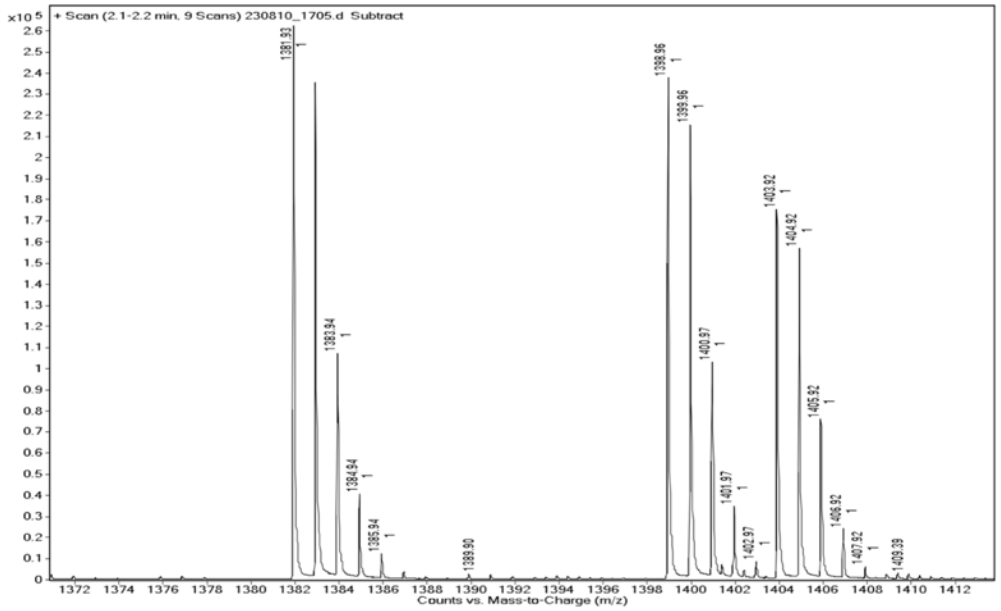


Fig. S280 HRMS of Cbz-(Nhx-Npe-Ndc-Nme)$_2$.

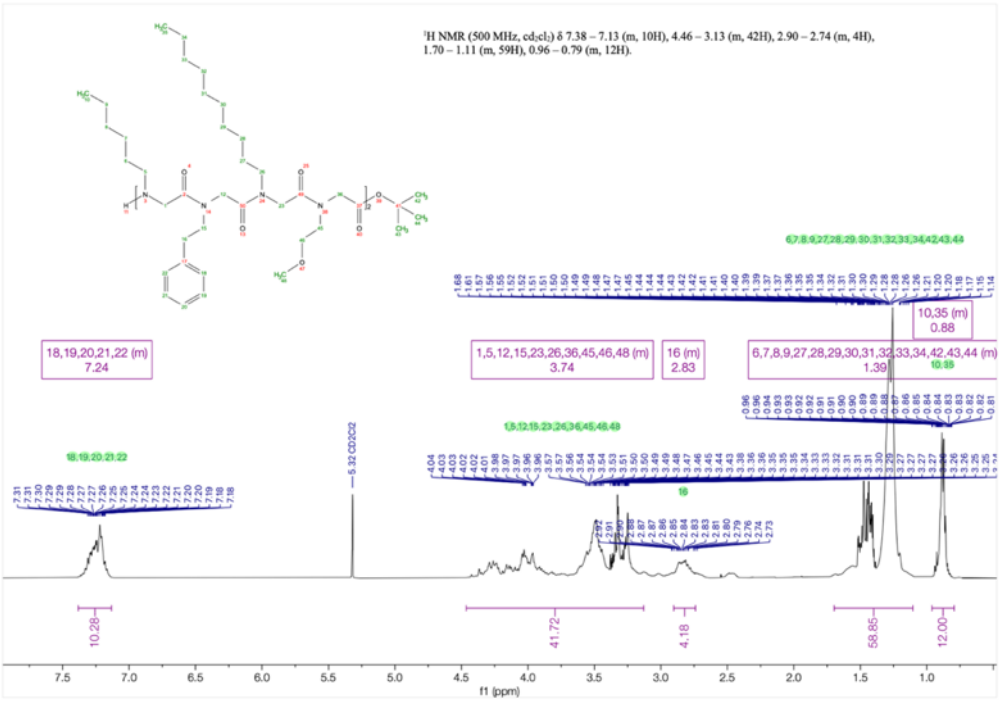


Fig. S281 ^{1}H NMR of (Nhx-Npe-Ndc-Nme)$_2$-tBu.

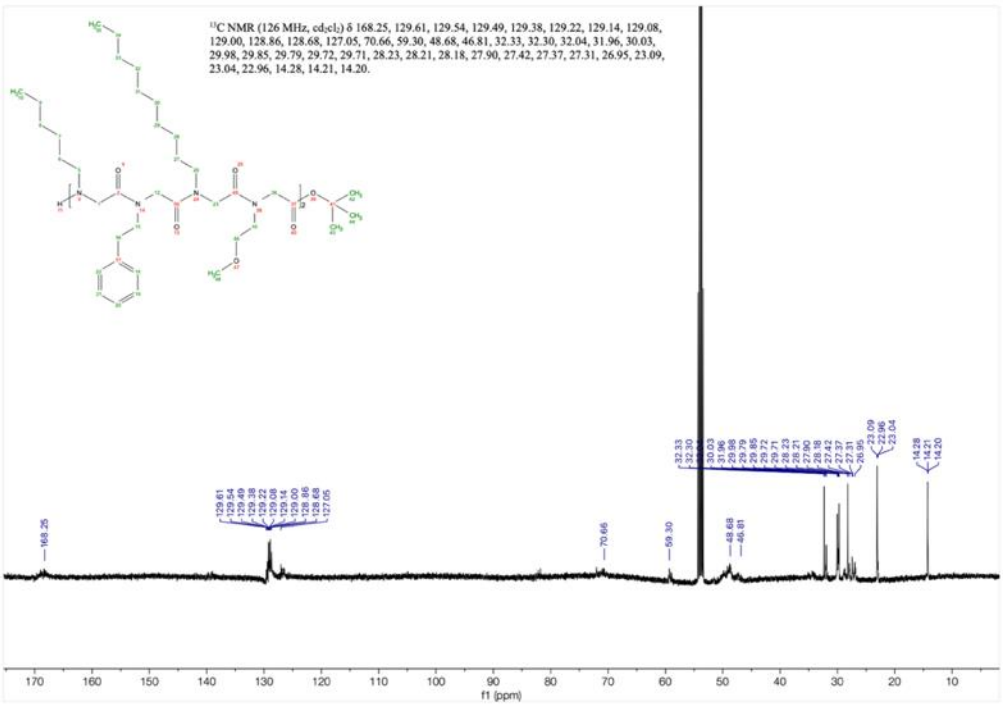


Fig. S282 ^{13}C NMR of (Nhx-Npe-Ndc-Nme)$_2$-tBu.

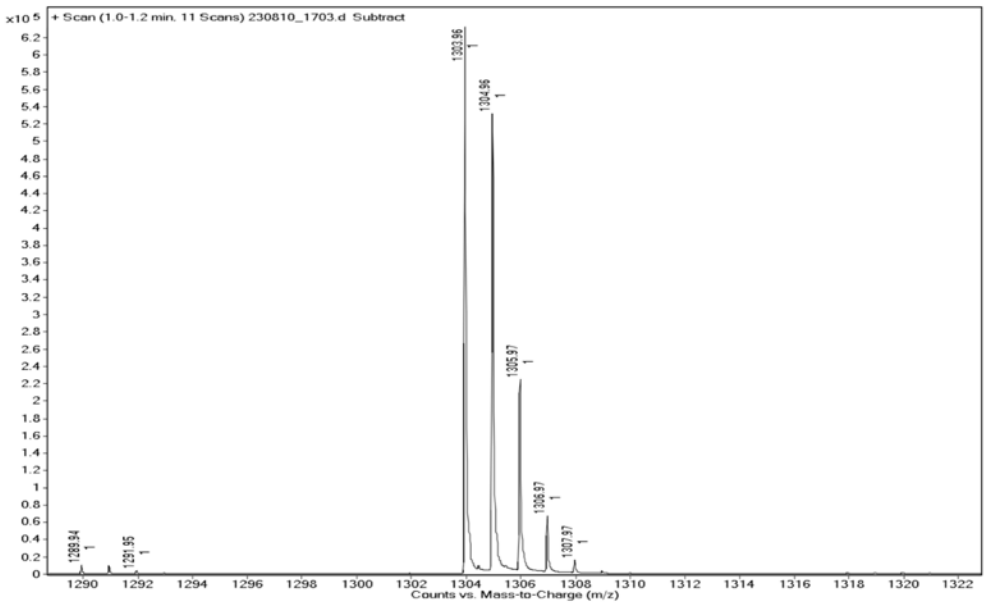


Fig. S283 HRMS of (Nhx-Npe-Ndc-Nme)$_2$-tBu.

7.4 Stereo-defined alternating peptoids

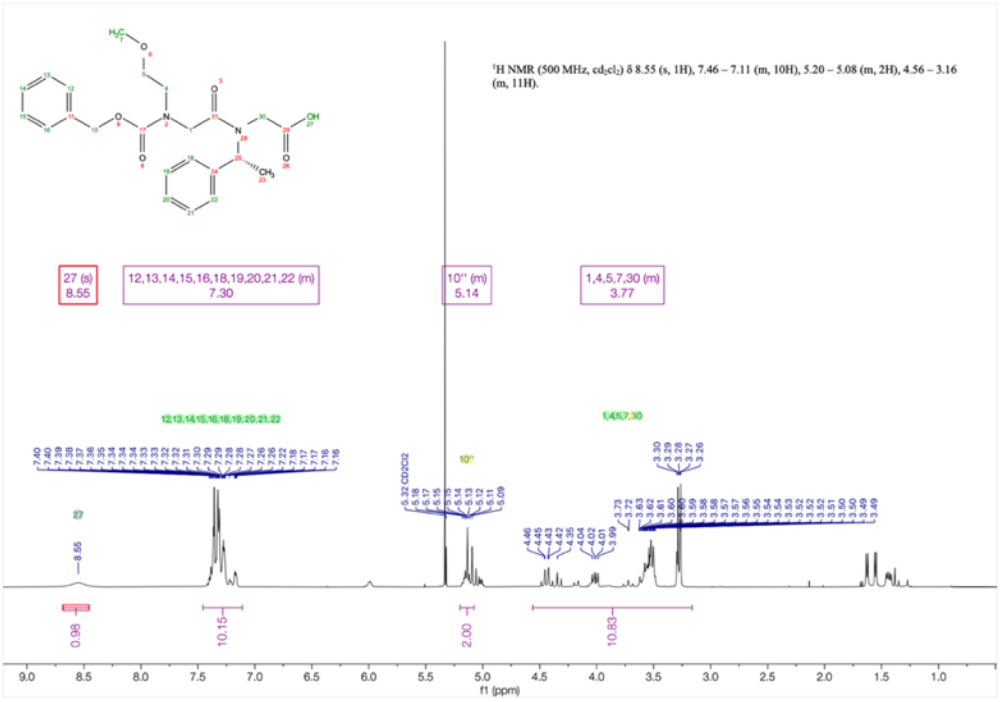


Fig. S284 ^{1}H NMR of Cbz-Nme-Nrpe.

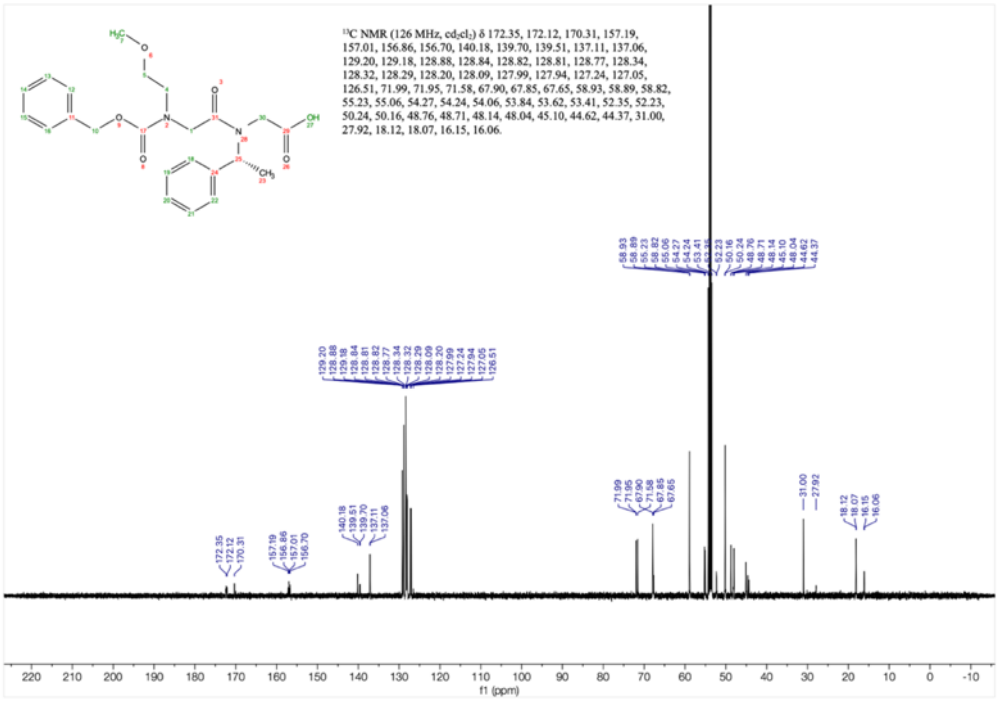


Fig. S285 ^{13}C NMR of Cbz-Nme-Nrpe.

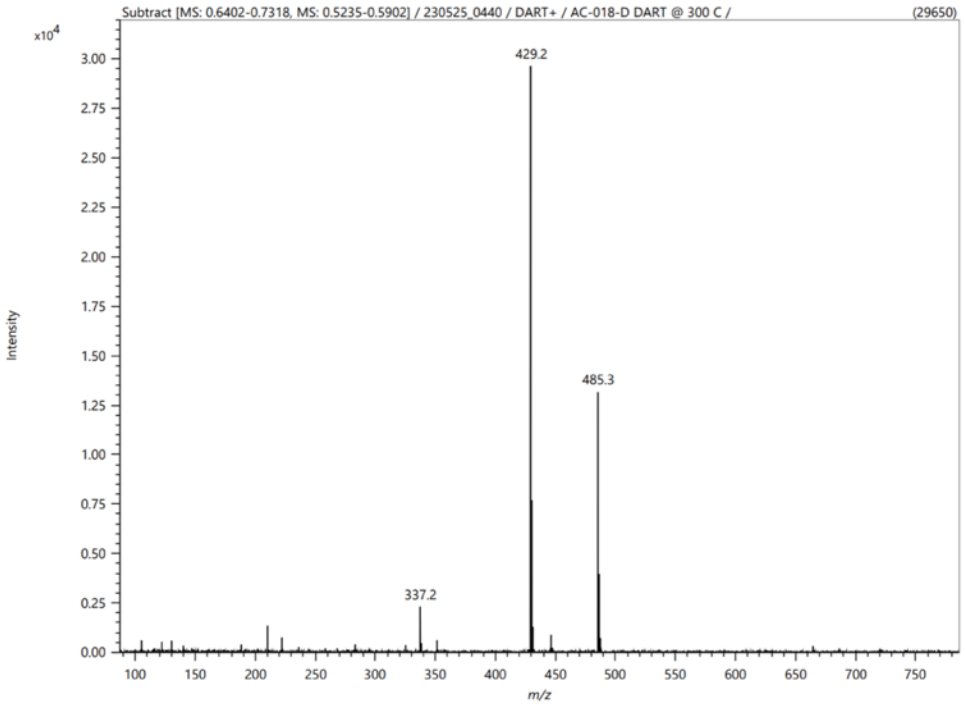


Fig. S286 DART-MS of Cbz-Nme-Nrpe.

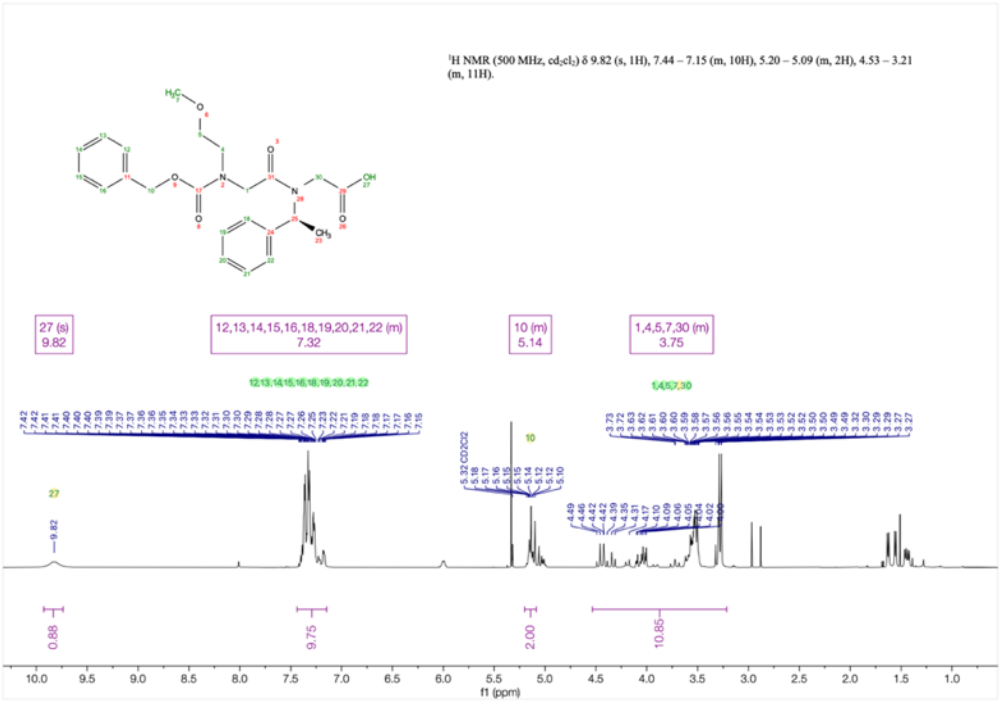


Fig. S287 [1]H NMR of Cbz-Nme-Nspe.

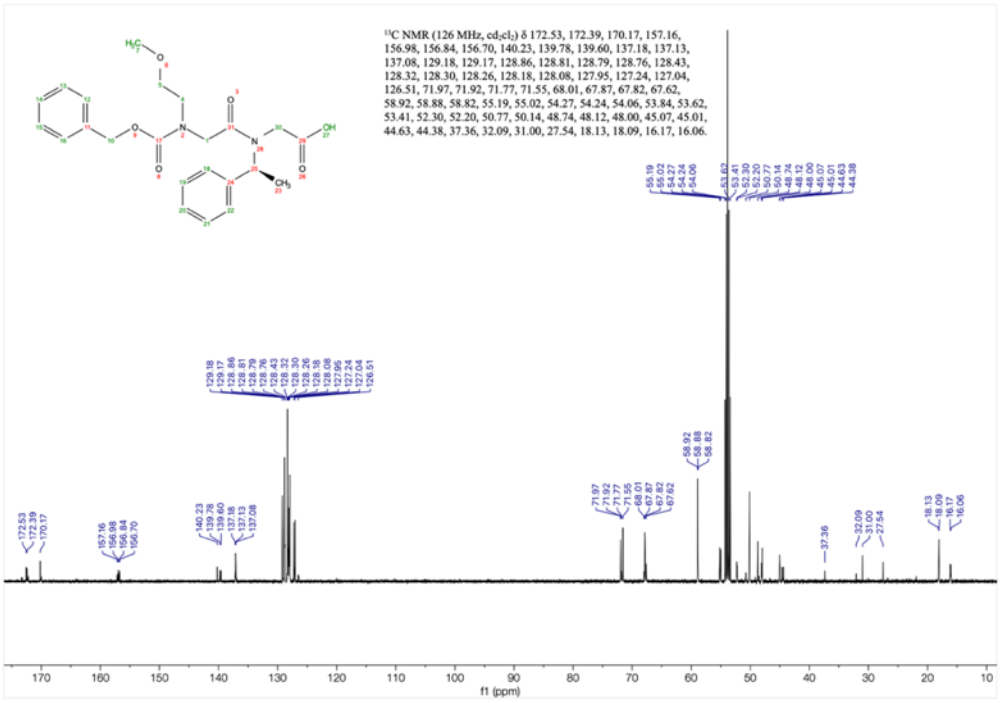


Fig. S288 [13]C NMR of Cbz-Nme-Nspe.

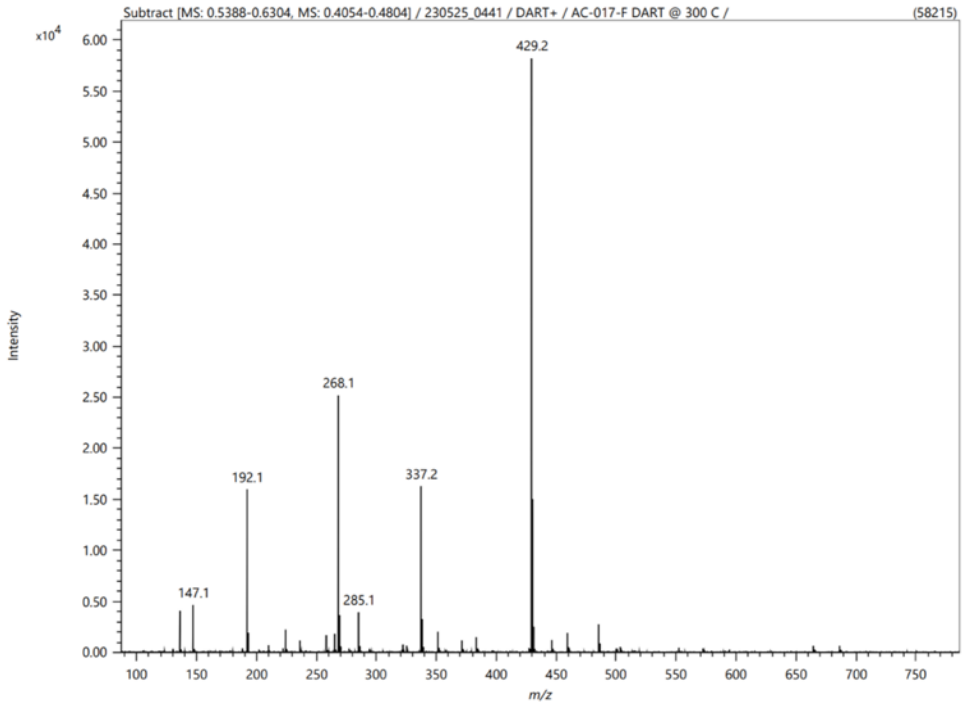


Fig. S289 DART-MS of Cbz-Nme-Nspe.

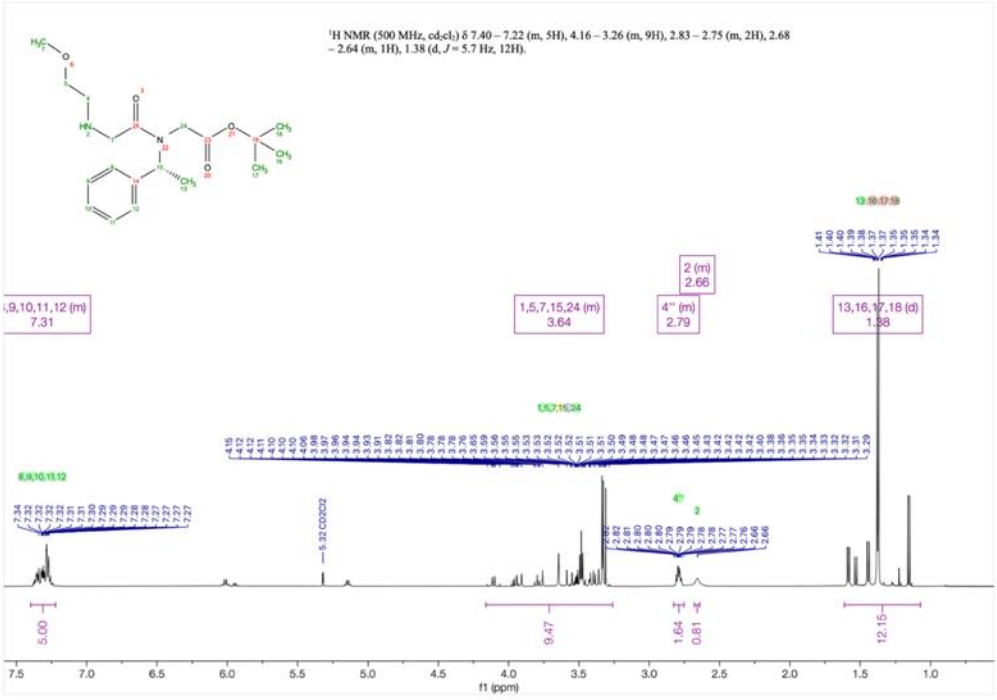


Fig. S290 ^{1}H NMR of Nme-Nrpe-tBu.

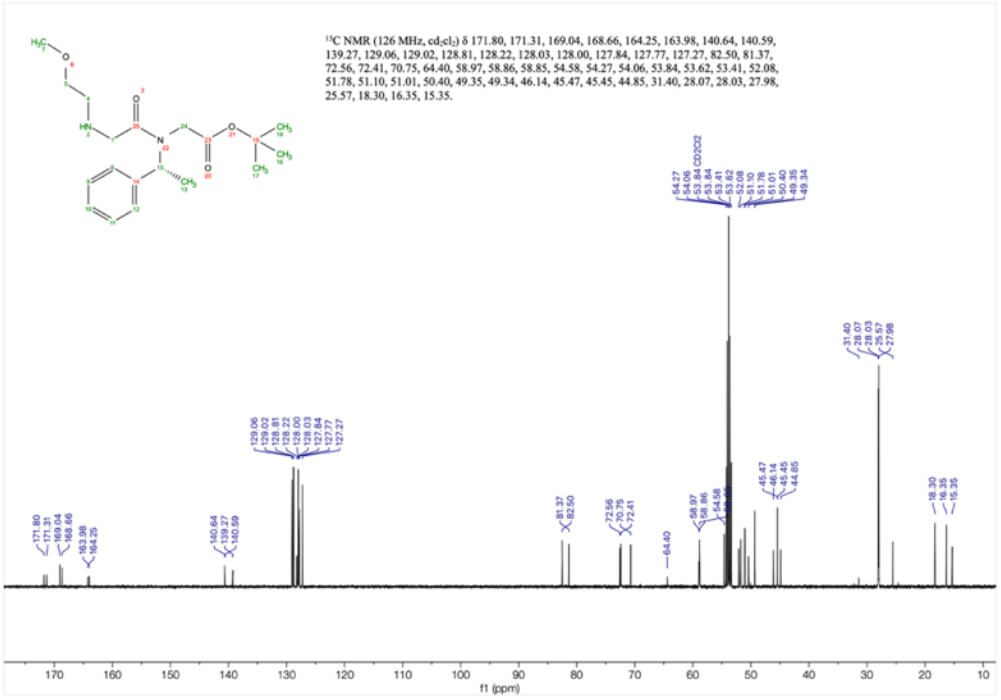


Fig. S291 ^{13}C NMR of Nme-Nrpe-tBu.

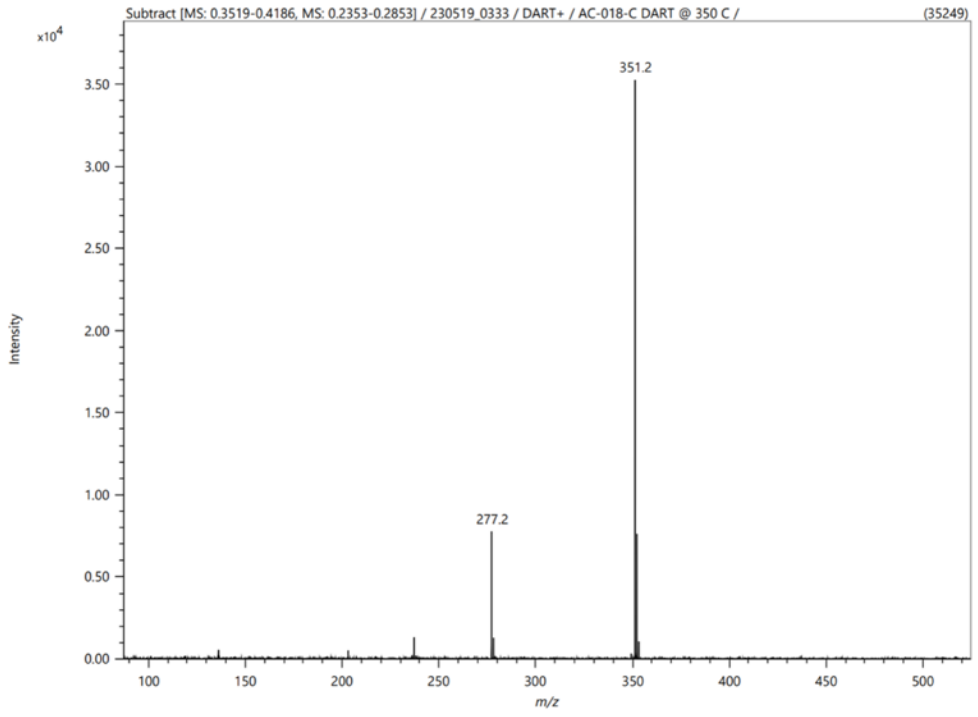


Fig. S292 DART-MS of Nme-Nrpe-tBu.

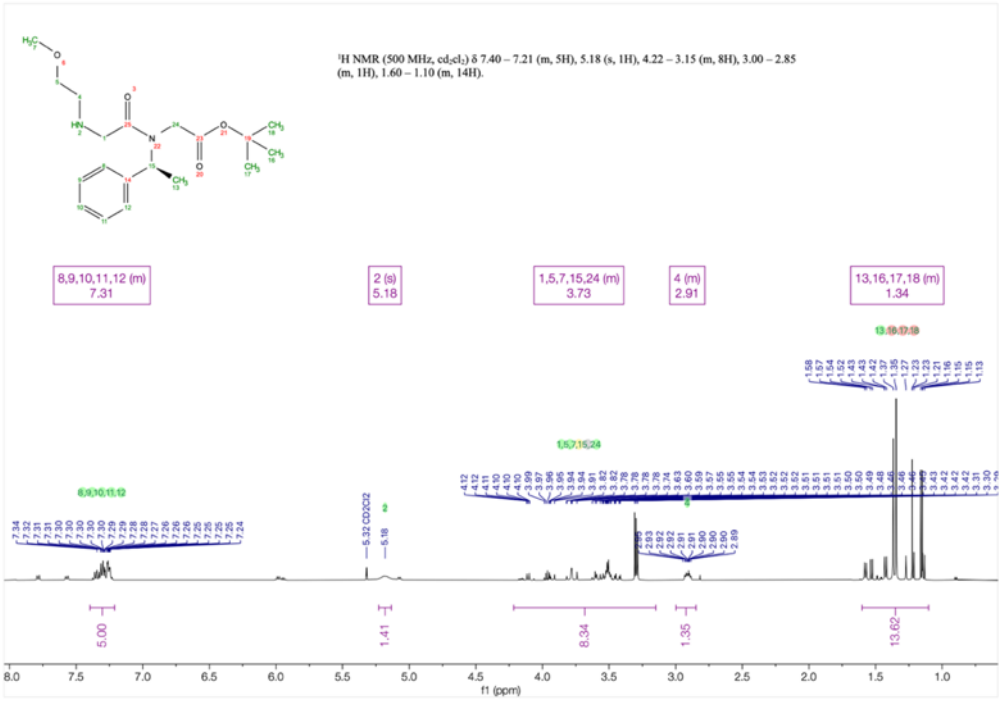


Fig. S293 [1]H NMR of Nme-Nspe-tBu.

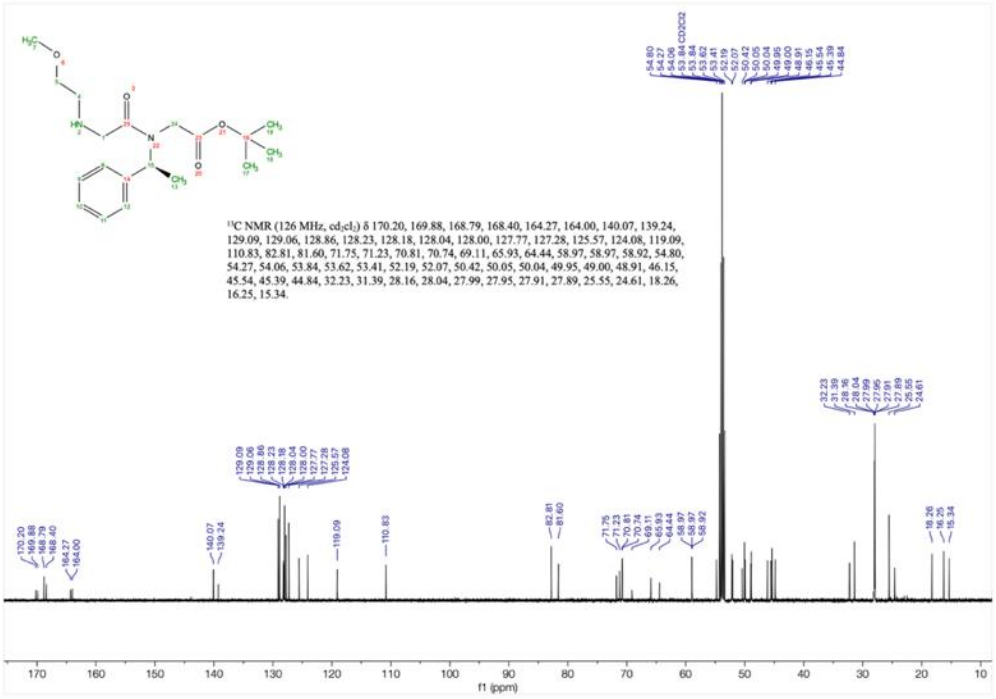


Fig. S294 [13]C NMR of Nme-Nspe-tBu.

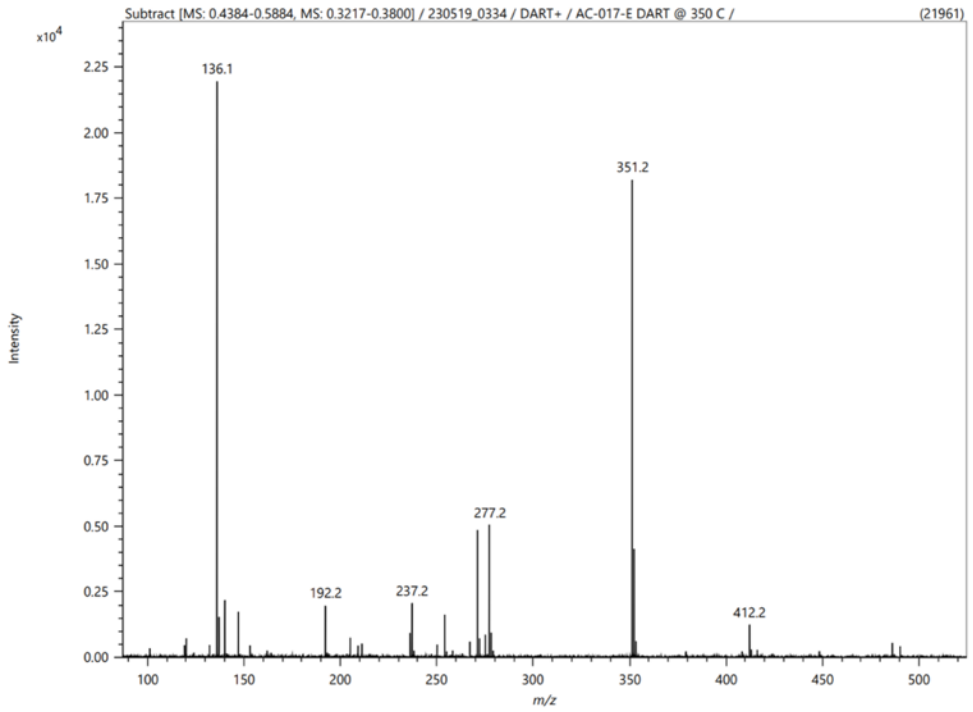


Fig. S295 DART-MS of Nme-Nspe-tBu.

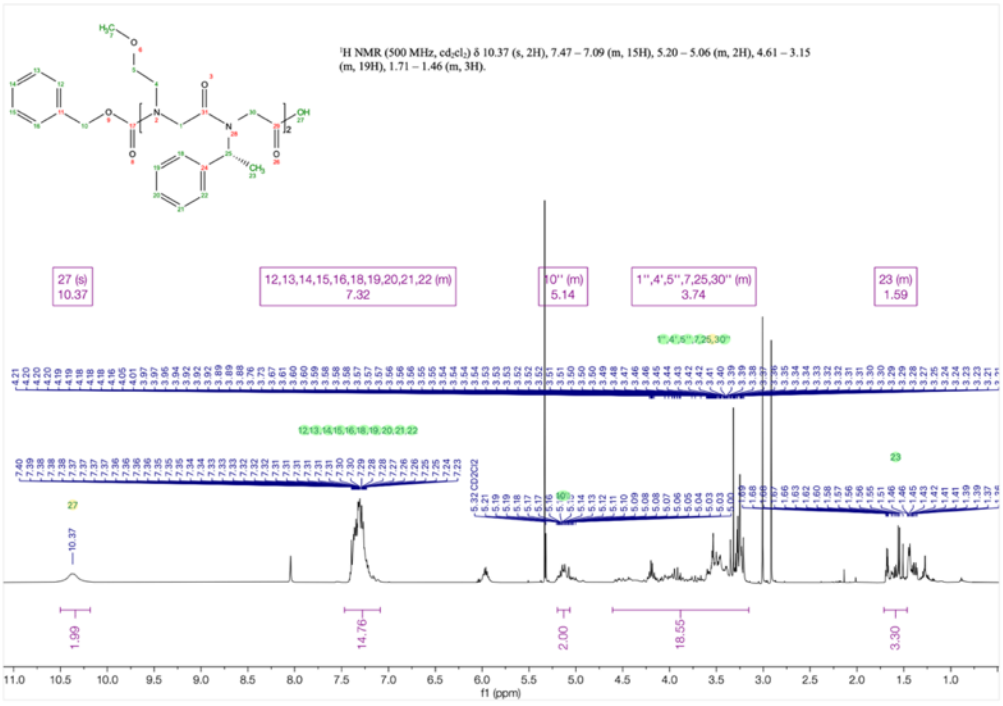


Fig. S296 ^{1}H NMR of Cbz-(Nme-Nrpe)$_2$.

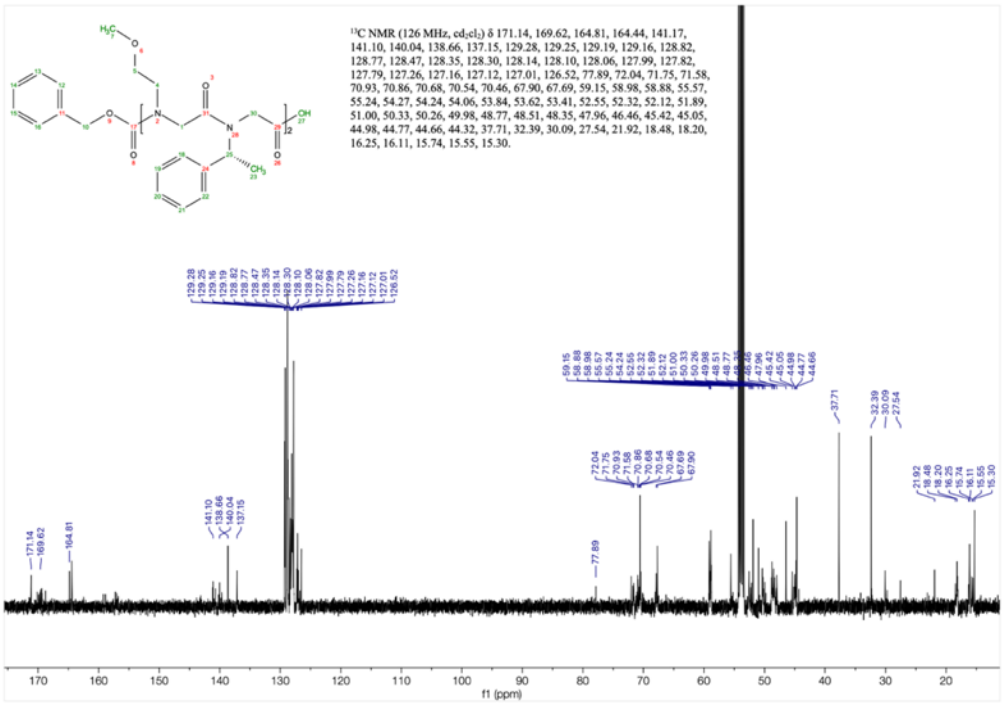


Fig. S297 ^{13}C NMR of Cbz-(Nme-Nrpe)$_2$.

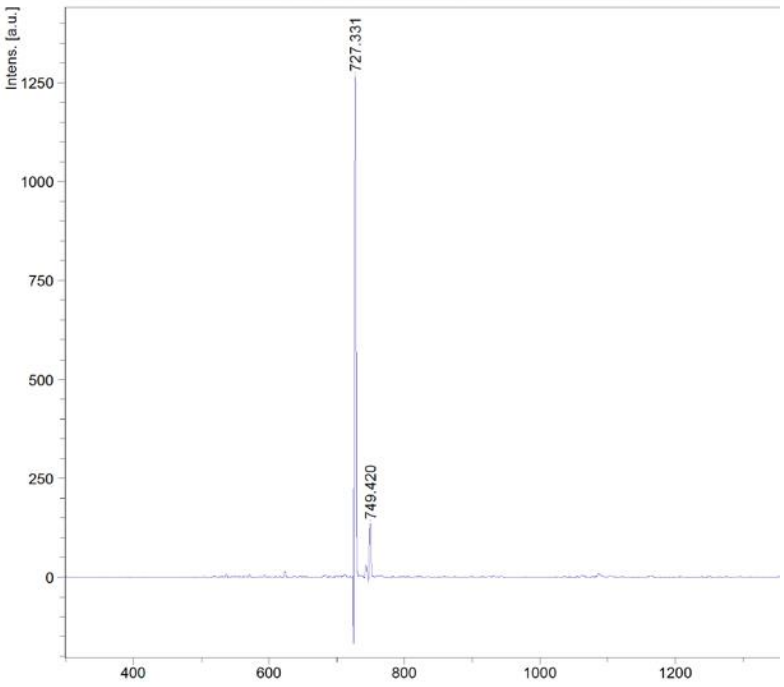


Fig. S298 MALDI-TOF MS of Cbz-(Nme-Nrpe)$_2$.

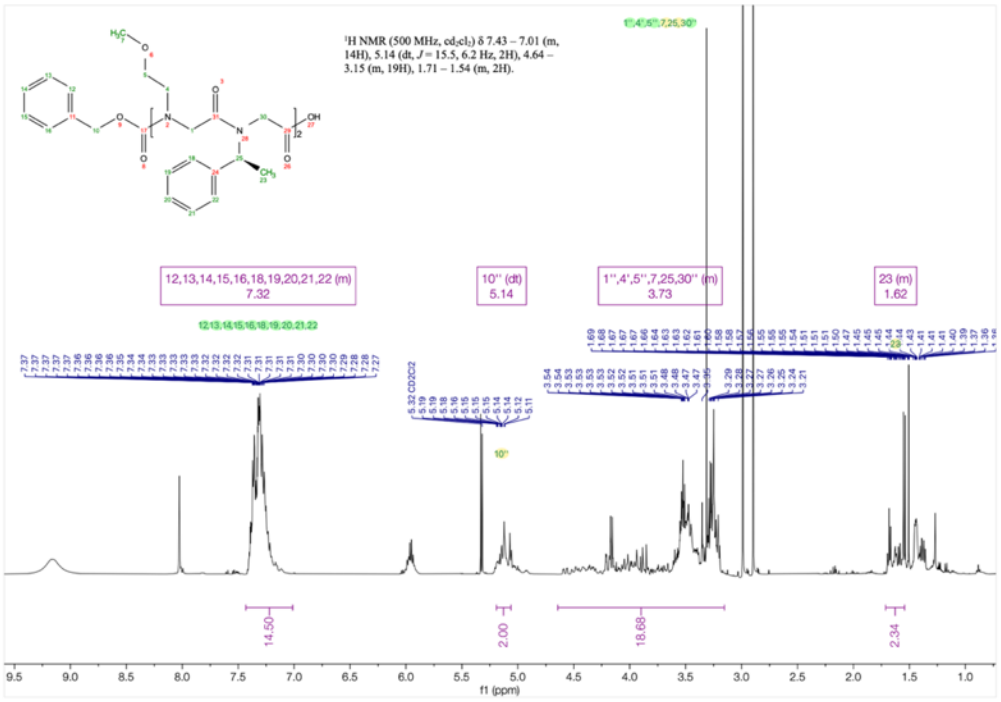


Fig. S299 ^{1}H NMR of Cbz-(Nme-Nspe)$_2$.

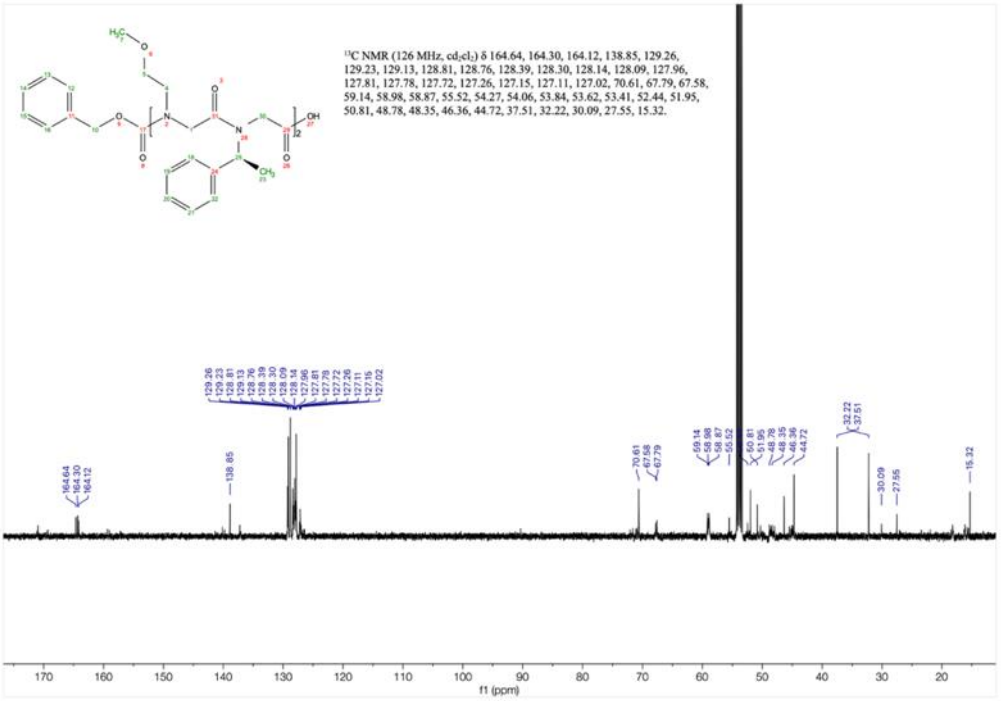


Fig. S300 ^{13}C NMR of Cbz-(Nme-Nspe)$_2$.

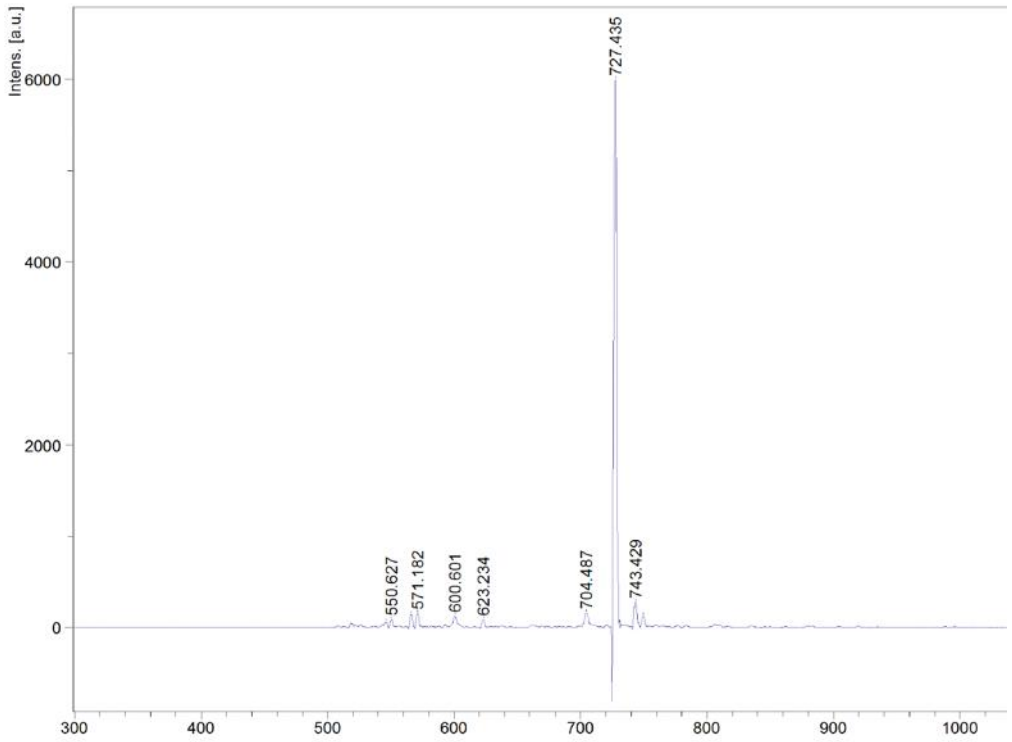


Fig. S301 MALDI-TOF MS of Cbz-(Nme-Nspe)$_2$.

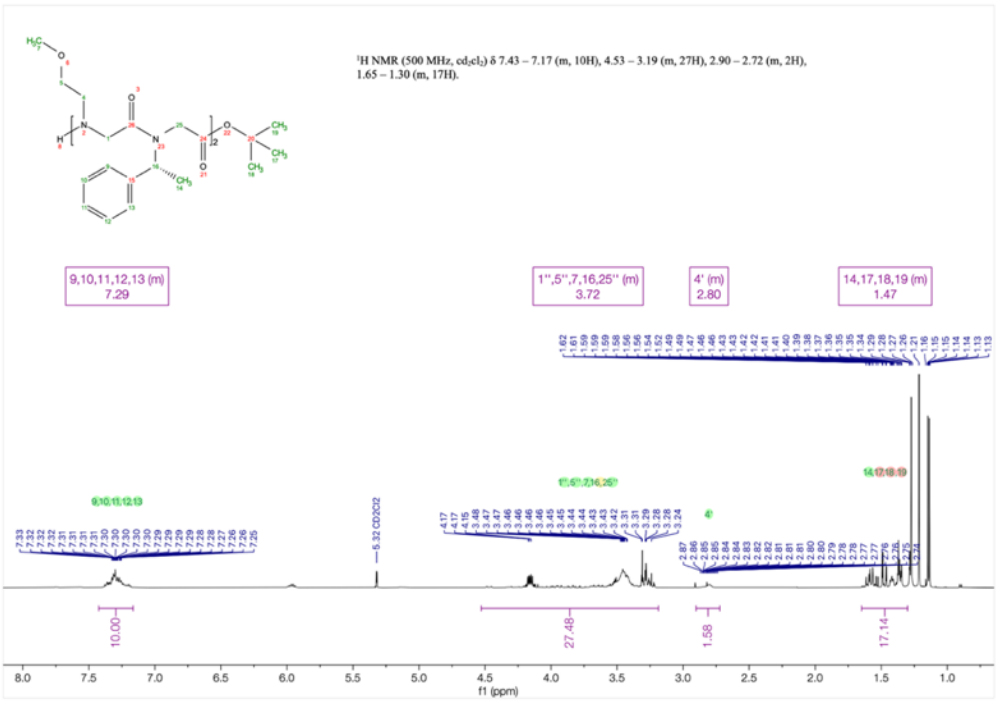


Fig. S302 ^{1}H NMR of (Nme-Nrpe)$_2$-tBu.

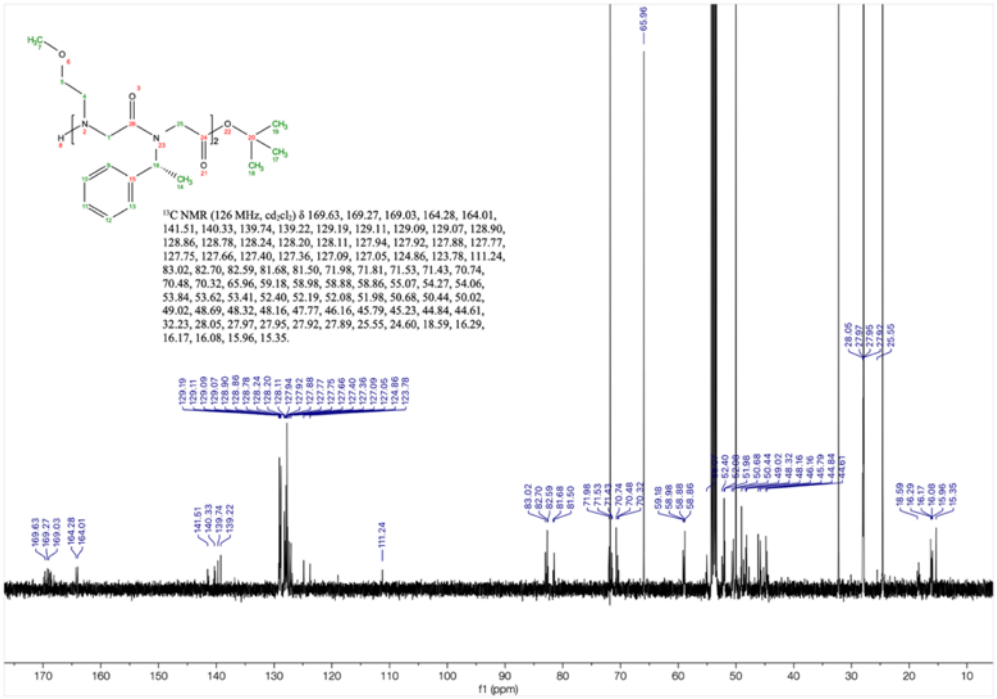


Fig. S303 ^{13}C NMR of (Nme-Nrpe)$_2$-tBu.

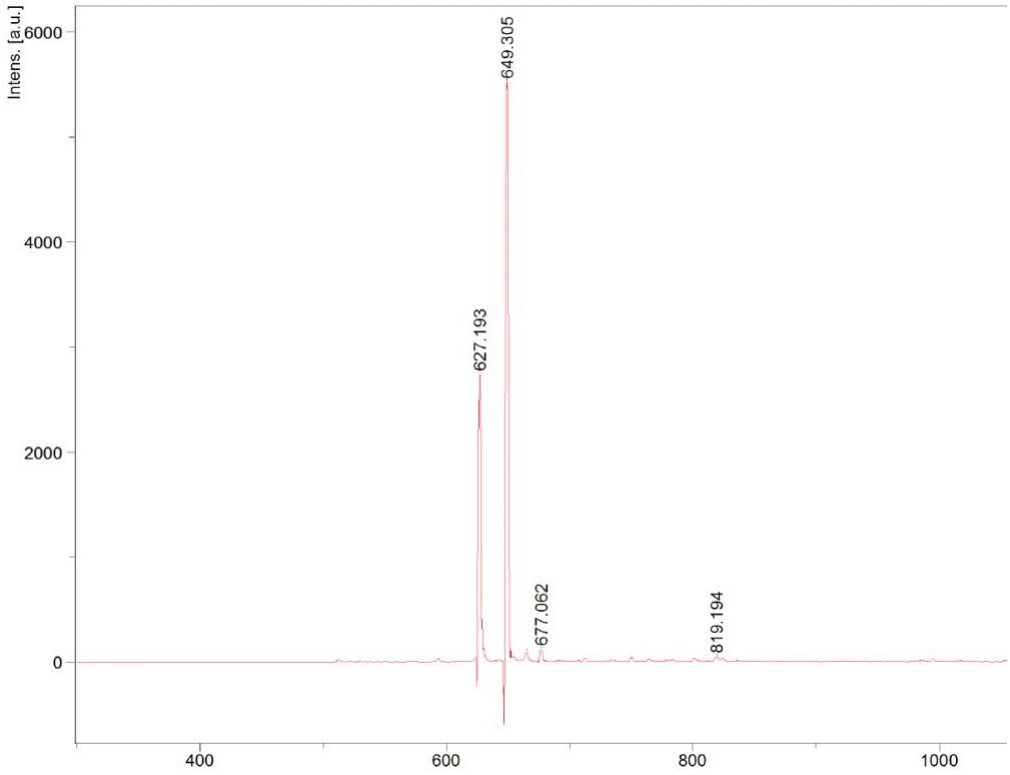


Fig. S304 MALDI-TOF MS of (Nme-Nrpe)$_2$-tBu.

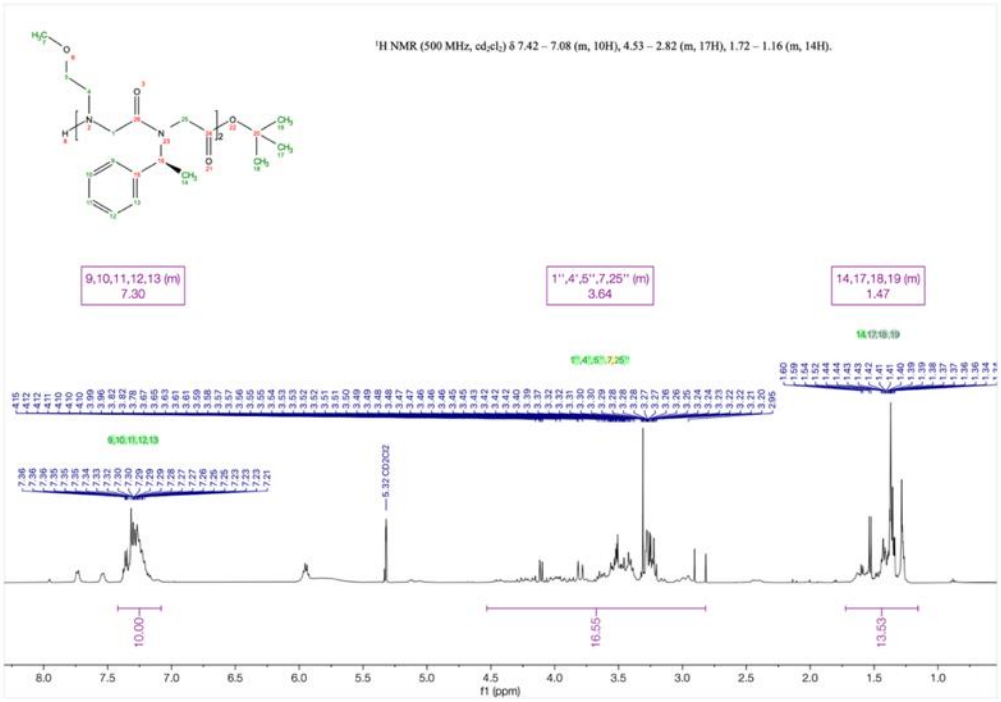


Fig. S305 ^{1}H NMR of (Nme-Nspe)$_2$-tBu.

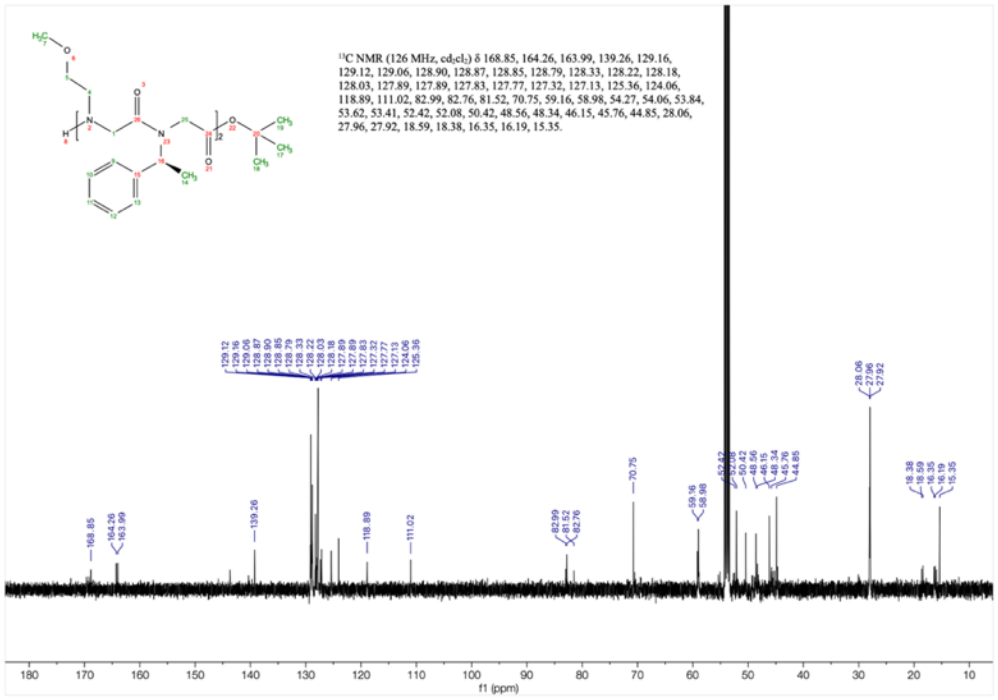


Fig. S306 ^{13}C NMR of (Nme-Nspe)$_2$-tBu.

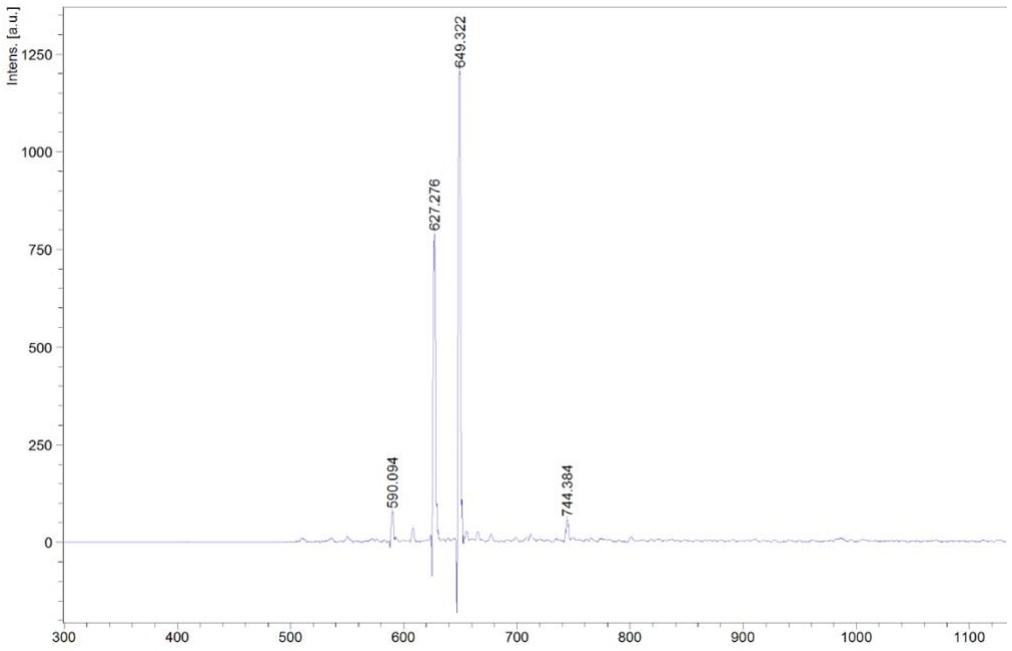


Fig. S307 MALDI-TOF MS of (Nme-Nspe)$_2$-tBu.

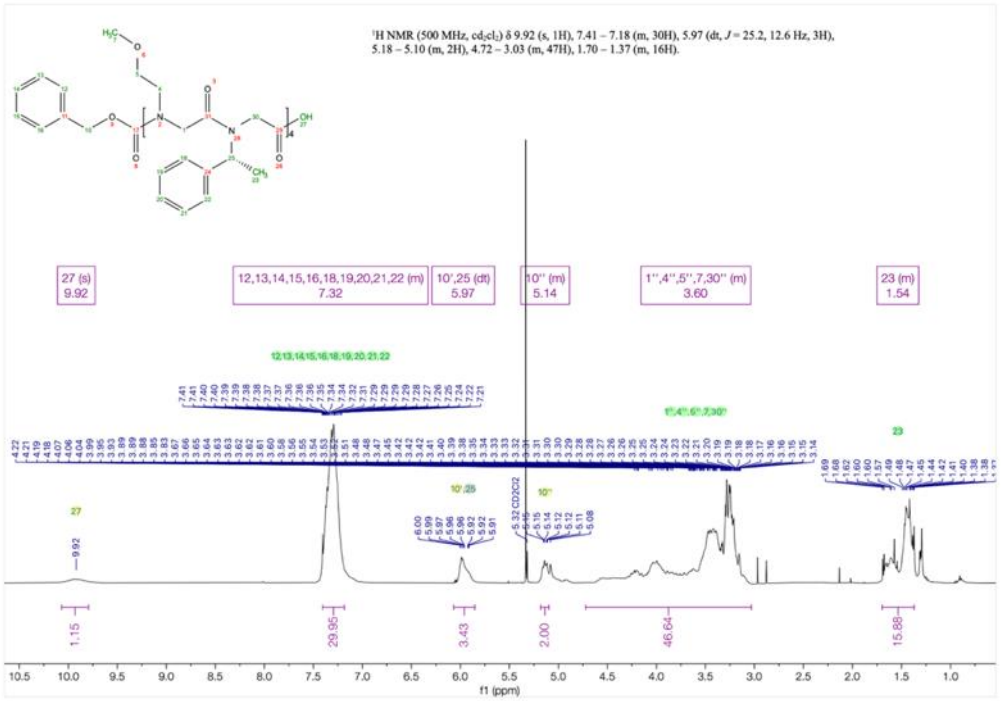


Fig. S308 ^{1}H NMR of Cbz-(Nme-Nrpe)$_4$.

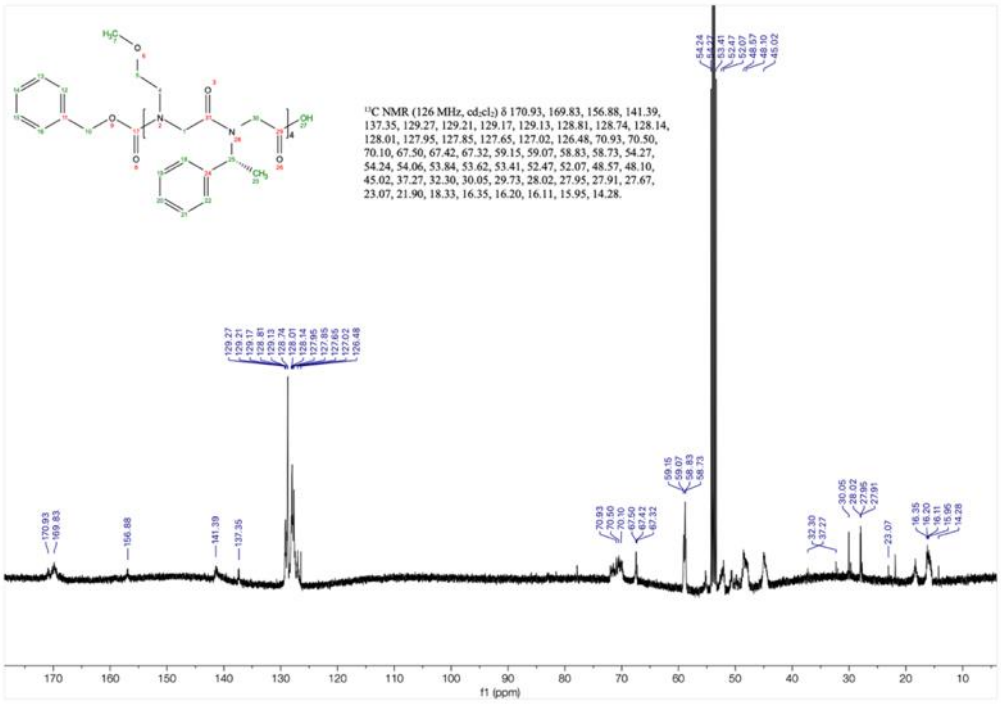


Fig. S309 ^{13}C NMR of Cbz-(Nme-Nrpe)$_4$.

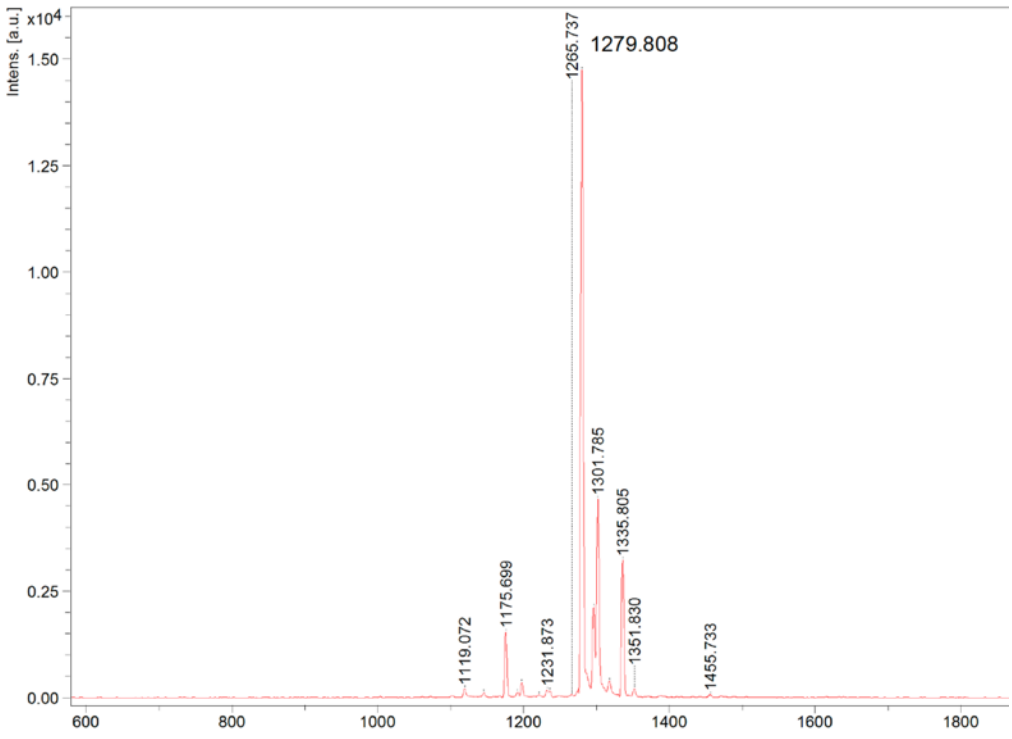


Fig. S310 MALDI-TOF MS of Cbz-(Nme-Nrpe)$_4$.

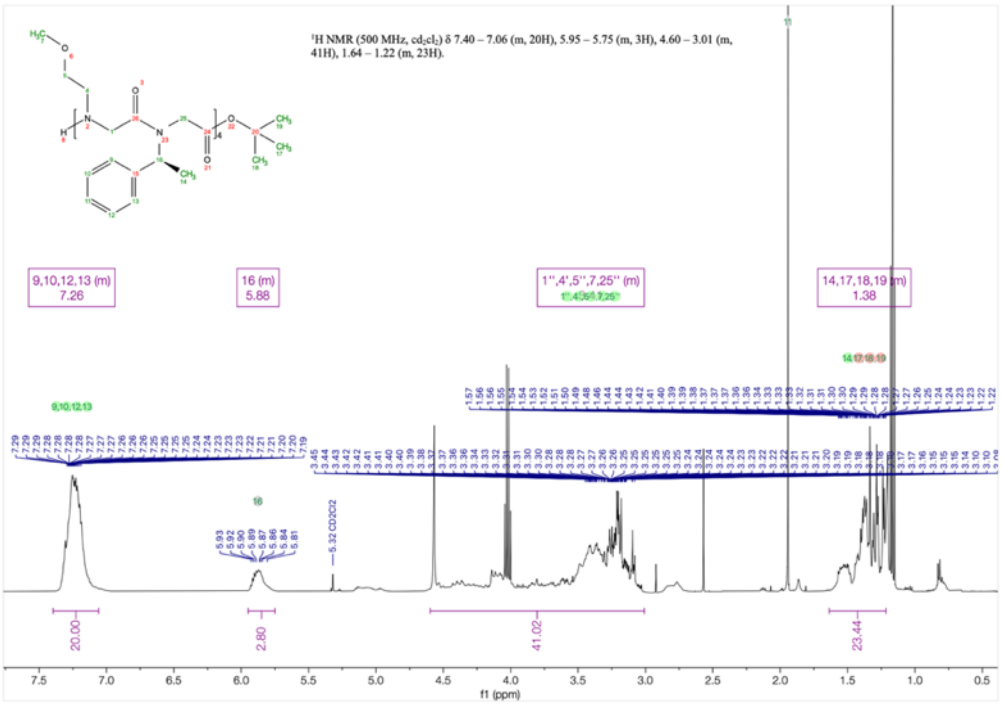


Fig. S311 ^{1}H NMR of (Nme-Nspe)$_4$-tBu.

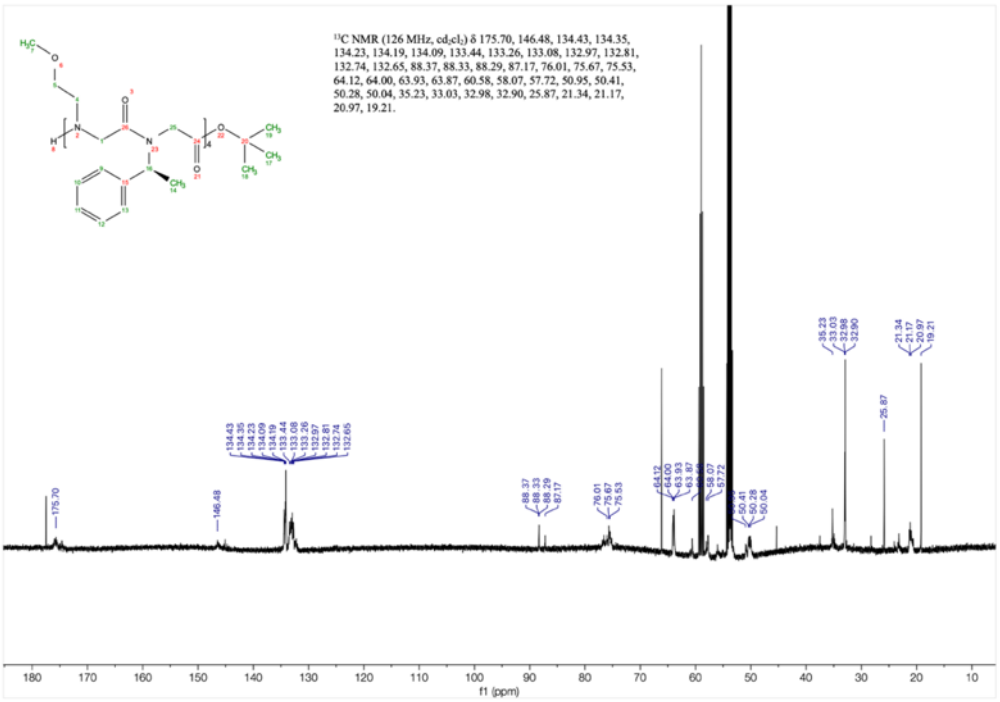


Fig. S312 ^{13}C NMR of (Nme-Nspe)$_4$-tBu.

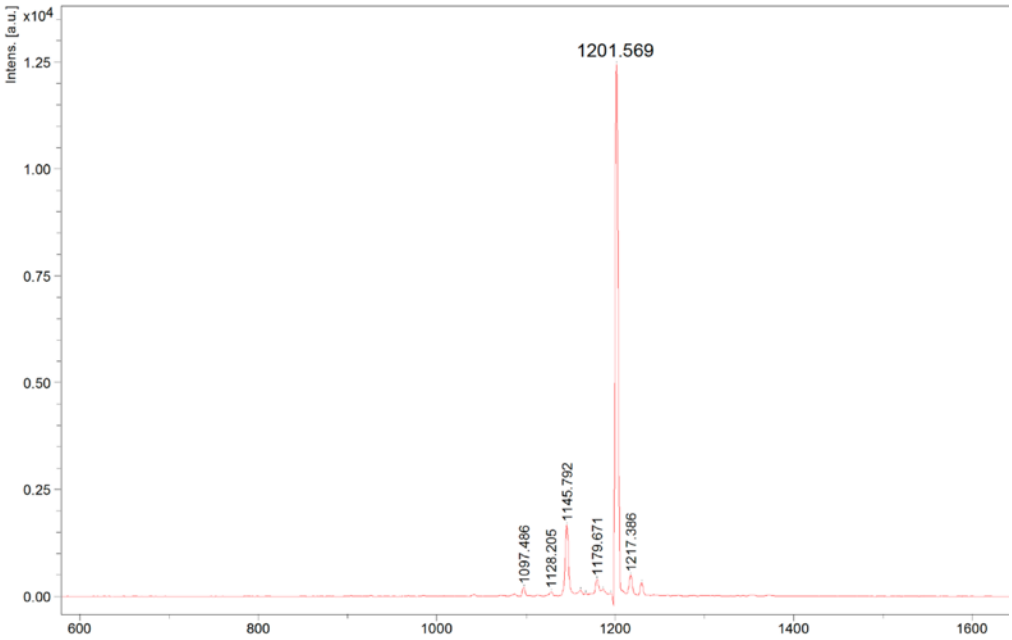


Fig. S313 MALDI-TOF MS of (Nme-Nspe)$_4$-tBu.