Supporting Information:

Experimental

ODCB was purchased from Fisher Scientific and used as received. Microcrystalline synthetic graphite (< 20 um) and Boc-Phe(4-NH_2)-OH and all other reagents were purchased from Sigma-Aldrich and used as received. Sonication was performed with an ultrasonic processor (Cole-Parmer) with probe attachment at 30% amplitude. Centrifugation was at 3300 rpm for 15 min. (Sorvall ST 16, RCF_{3300} = 2045) unless otherwise specified. All reactions are performed under an inert atmosphere.

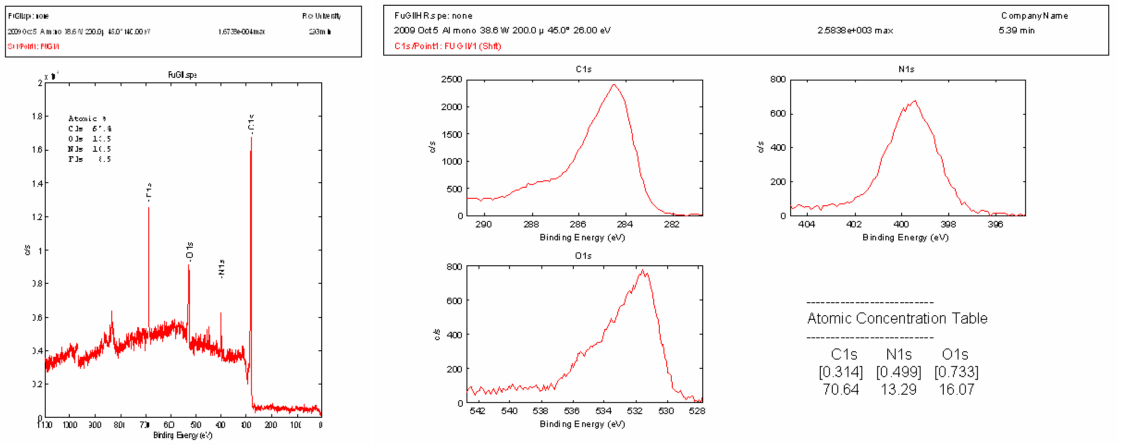
ODCB suspensions. Synthetic microcrystalline graphite (50 mg) was added to 20 mL ODCB. The mixture was probe sonicated for one hour. The slurry was centrifuged for 30 minutes at 4400 rpm. High shear mixing of the ODCB/μG suspension was not performed in an effort to maintain the large lateral dimensions of the μG starting material. Therefore, our dispersions may not be exfoliated to the same degree as previous examples using this method. Collection of the supernatant yielded ODCB dispersions of graphene. [7] The supernatant of the μG solution was used in the nitrene reaction (Scheme 1). Resuspension and filtration of the μG pellet yielded 41 mg of recovered μG.

Boc-Phe(4-N_3)-OH In a 500 mL Schlenk flask, imidizole-1-sulfonylazide.HCl (1.02 g, 6 mmol), Boc-Phe(4-NH_2)-OH (1.40 g, 5 mmol), and $ZnCl_2$ (27.3 mg, 0.20 mmol) was dissolved in MeOH:MeCN (3:2, 300 mL) to this was added NEt_3 (1.39 mL, 10.0 mmol). After stirring at room temperature for 12 hrs, it was diluted with Et_2O (200 mL) and washed with AcOH (10%, 3x) and brine (1x). Drying with $MgSO_4$ and concentration, followed by flash chromatography yielded the pure product. Yield = 1.2 g, 80%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 [2H, d, *J*(H–H) = 8.97 Hz, C*H*], 6.97 [2H, d, *J*(H–H) = 8.97 Hz, C*H*], 4.93 [1H, d, *J*(H–H) = 8.63 Hz, N*H*], 4.58 [1H, dd, *J*(H–H) = 6.64 Hz, *J*(H–H) = 14.92 Hz, C*H*], 3.12 [1H, dd, *J*(H–H) = 5.12 Hz, *J*(H–H) = 13.92 Hz, CH_2], 3.05 [1H, dd, *J*(H–H) = 6.41 Hz, *J*(H–H) = 13.64 Hz, CH_2], 1.42 [9H, s, ^{t}Bu]. IR (cm^{-1}): 2115 (ν_{N3}).

Because of the possible loss of the Boc protecting group at 180 °C (refluxing temperature of ODCB), we needed to confirm that polymerization of phenylalanine on the surface of the graphene sheet was not occuring and leading to our conclusion of high density functionalization. Thusly, we protected both the carboxy (methyl ester) and amino ends (Boc) of our amino acid and performed the reaction at slightly lower temperatures (~165-170 °C). The product formed is **2**.

Boc-Phe(4-N_3)-OMe In a 250 mL Shlenk flask, Boc-Phe(4-N_3)-OH (153.6 mg, 0.5 mmol) was dissolved in MeOH (200 mL, seived) under an inert atmosphere. Two equivalents of chlorotrimethylsilane (TMS-Cl, 126.5 μL, 1.0 mmol) were added to the stirring solution. After stirring at room temperature for 5 hours, the reaction mixture was dried on a rotary evaporator. The residue was dissolved in DCM and filtered to remove white precipitate. The filtrate was applied to an SiO_2 plug and eluted with ethyl acetate:hexanes (1:1; R_f 0.85) followed by rotary evaporation. Yield = 43 mg, 0.14 mmol, 27 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 [2H, d, *J*(H–H) = 8.35 Hz, C*H*], 6.96 [2H, d, *J*(H–H) = 8.47 Hz, C*H*], 4.98 [1H, d, *J*(H–H) = 7.76 Hz, N*H*], 4.57 [1H, dd, *J*(H–H) = 5.91 Hz, *J*(H–H) = 14.07 Hz, C*H*], 3.10 [1H, dd, *J*(H–H) = 5.78 Hz, *J*(H–H) = 13.75 Hz, CH_2], 3.01 [1H, dd, *J*(H–H) = 5.94 Hz, *J*(H–H) = 13.75 Hz, CH_2], 1.42 [9H, s, ^{t}Bu], 1.25 [3H, s, CH_3]. IR (cm^{-1}): 2115 (ν_{N3}).

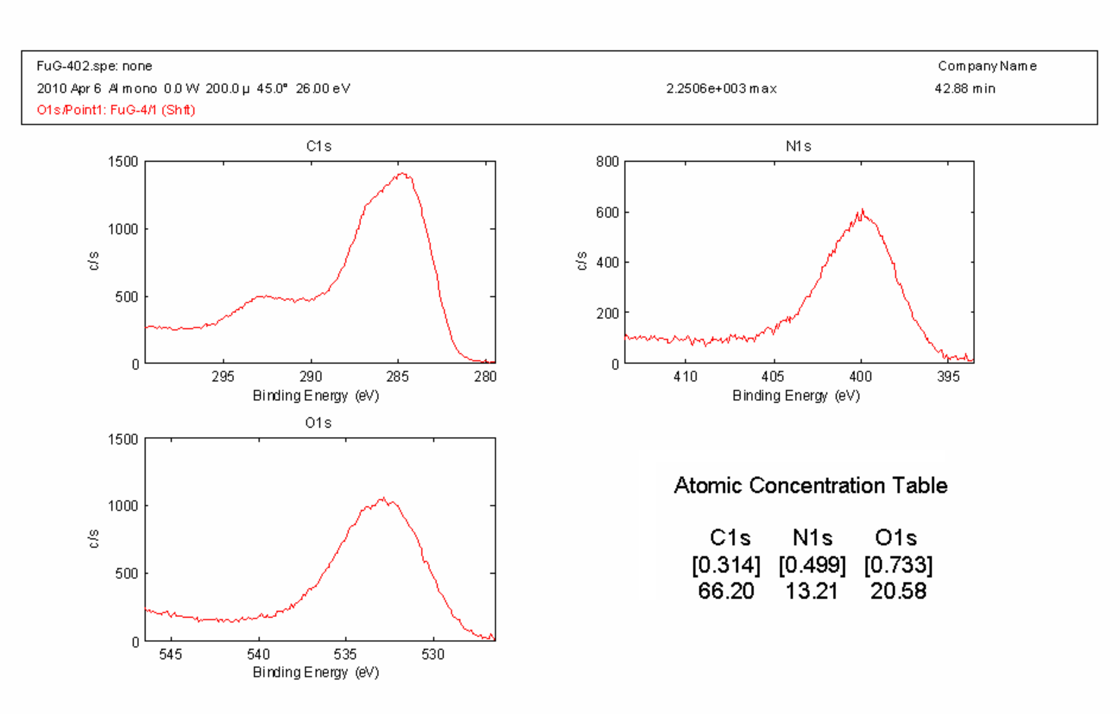
Boc-Phe-OMe-(N)-μG (**2**) Boc-Phe(4-N_3)-OMe (35 mg in ODCB, 2-3 mL) was added to the exfoliated μG solution (~ 5 mL) in a 50 mL 3-neck flask fitted with a condenser, a thermometer, a stopper and a stir bar. The reaction was diluted to 25 mL with ODCB and the temperature was maintained at 165 °C for 4 days under Ar after which the brown suspension was filtered over a 0.2 um PTFE filter paper. The filter cake was washed copiously with MeOH, $CHCl_3$, and DMF to remove any unreacted Boc-Phe(N_3)-OMe. The fine brown powder was dried in an oven overnight at 125 °C. Final yield: 14 mg.



Atomic Concentration Table

C1s	N1s	O1s
[0.314]	[0.499]	[0.733]
70.64	13.29	16.07

Figure S1. XPS spectra of **1**, (a) survey scan showing the presence of C, O, N, and F (attributed to fluro-grease), (b) High-resolution XPS C1s, N1s and O1s spectra (y-axis arb units) showing the presence of C (70.3 %), O (16.1 %) and N (13.3 %). The XPS data of **1** indicates 13:1 carbon to phenylalanine ratio. Data were acquired on a Physical Electronics, Inc. Phi Quantera instrument with monochromated Al Kα. Y-axis arb units.



FuG-402.spe: none
2010 Apr 6 Al mono 0.0 W 200.0 µ 45.0° 26.00 eV
O1s/Point1: FuG-4/1 (Shft)
Company Name
2.2506e+003 max
42.88 min

Atomic Concentration Table

C1s	N1s	O1s
[0.314]	[0.499]	[0.733]
66.20	13.21	20.58

Figure S2. High-resolution XPS spectra of **2**, C1s, N1s and O1s spectra (y-axis arb units) showing the presence of C (66.20 %), O (20.58 %) and N (13.21 %). The data corresponds to 12:1 carbon to phenylalanine ratio for the product **2**. Data were acquired on a Physical Electronics, Inc. Phi Quantera instrument with monochromated Al Kα. Y-axis arb units.

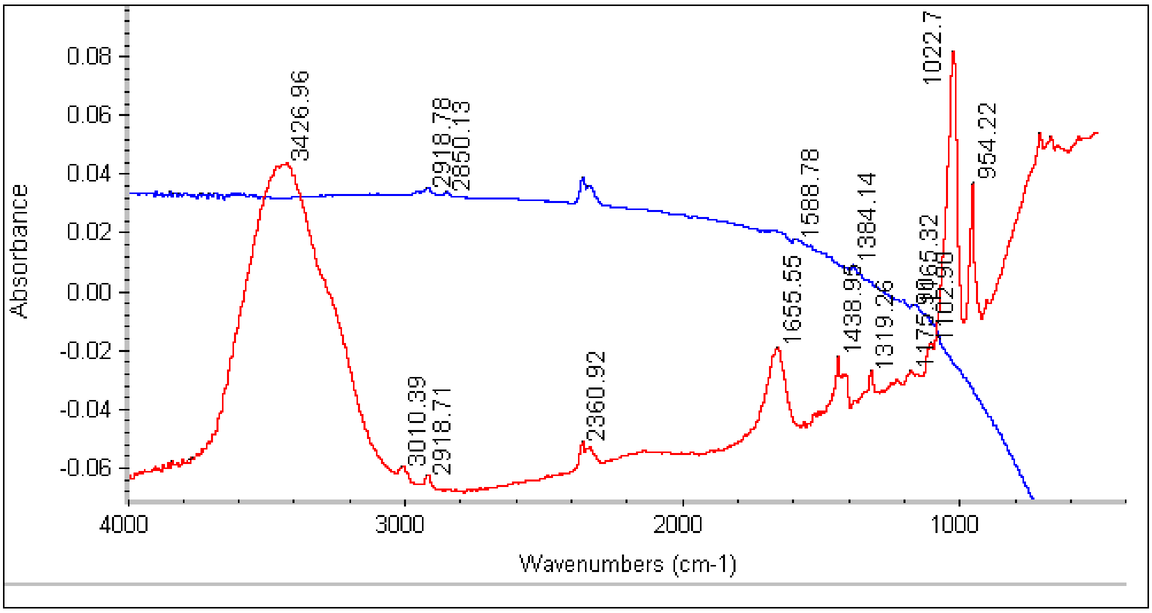


Figure S3. Thin film IR spectra of **1** showing absorption at ~3200 and 1438 (COOH), 3426 (NH), 1655 (C=O), 1319 (C-N, carbamate), and 1022 (C-N, aziridino amines) cm^{-1} taken on a KBr salt plate.

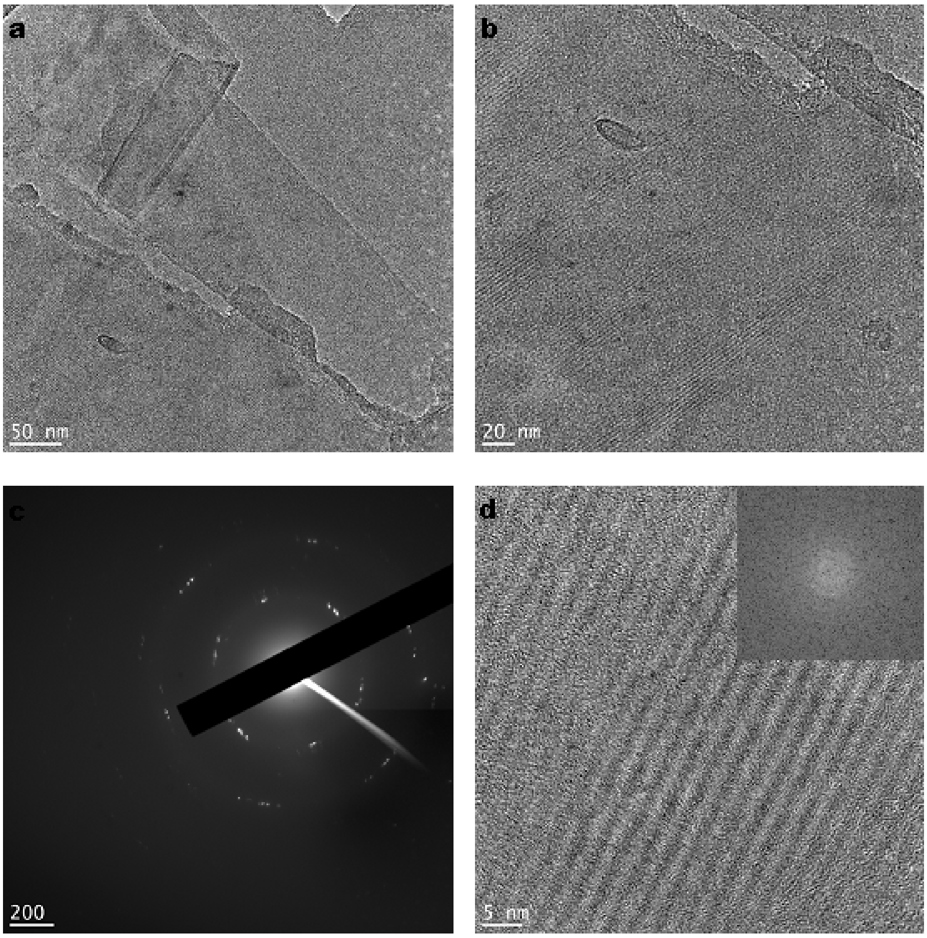
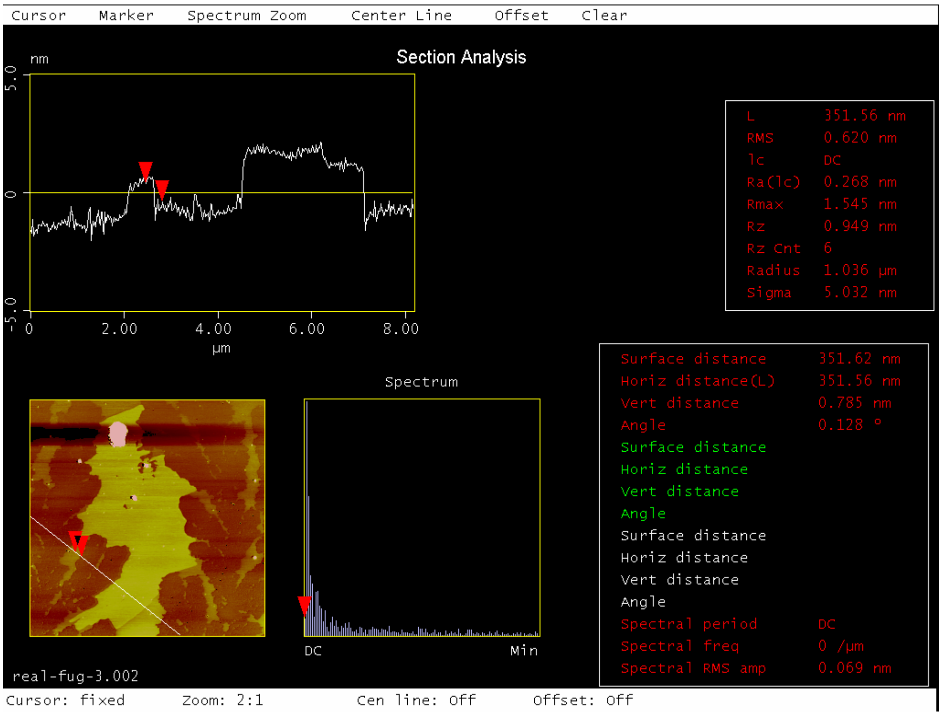
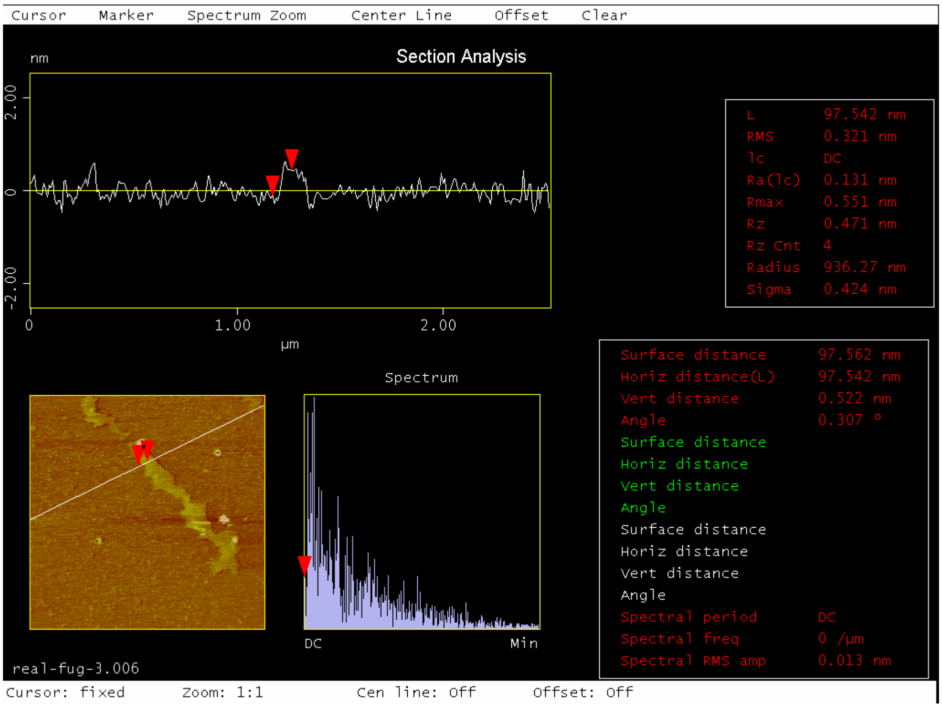


Figure S4. Additional TEM images of graphene from HOPG, collected with a Jeol JEM-2100F advanced field emission electron microscope with an accelerating voltage of 120 - 200 kV. TEM image of **1** showing (a) 50000x and (b) 80000x stacked, few- or multi-layer sheets of **1**; (c) SAED confirming few- or multi- layer graphene sheets; (d) selected area from (b) with FFT inset. Note: The stiping effect observed in Figs. b and d are caused by Moiré fringes, interference patterns occuring when two grid-like structures are overlaid at an angle.



L	351.56 nm
RMS	0.620 nm
lc	DC
Ra(lc)	0.268 nm
Rmax	1.545 nm
Rz	0.949 nm
Rz Cnt	6
Radius	1.036 µm
Sigma	5.032 nm

Surface distance	351.62 nm
Horiz distance(L)	351.56 nm
Vert distance	0.785 nm
Angle	0.128 °
Surface distance	
Horiz distance	
Vert distance	
Angle	
Surface distance	
Horiz distance	
Vert distance	
Angle	
Spectral period	DC
Spectral freq	0 /µm
Spectral RMS amp	0.069 nm



L	97.542 nm
RMS	0.321 nm
lc	DC
Ra(lc)	0.131 nm
Rmax	0.551 nm
Rz	0.471 nm
Rz Cnt	4
Radius	936.27 nm
Sigma	0.424 nm

Surface distance	97.562 nm
Horiz distance(L)	97.542 nm
Vert distance	0.522 nm
Angle	0.307 °
Surface distance	
Horiz distance	
Vert distance	
Angle	
Surface distance	
Horiz distance	
Vert distance	
Angle	
Spectral period	DC
Spectral freq	0 /µm
Spectral RMS amp	0.013 nm

Figure S5. Additional AFM images. Measurements were obtained using a Digital Instruments NanoScope IIIa scanning probe microscope in tapping mode. AFM samples were spin coated from $CHCl_3$ (pH 9) onto cleaved mica substrates.

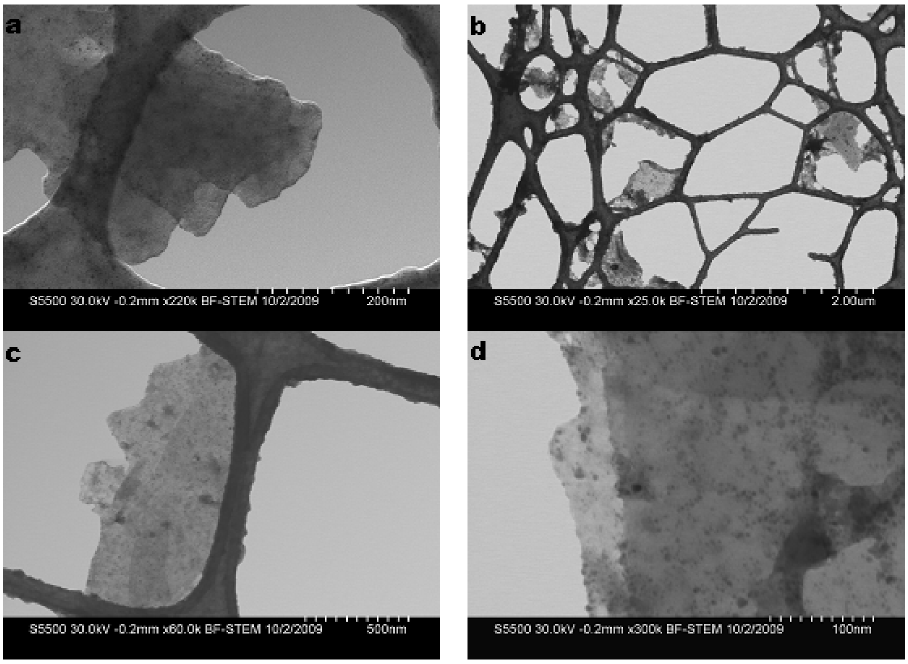


Figure S6. BF-STEM images of **1** deposited from DMSO showing (a) few layer graphene sheets of width measuring 150, 200, and 275 nm; (b) several large groups of >1 µm single and few layer sheets along with smaller aggregates of flakes; (c) 375 nm x 1.2 µm sheet on top of 1.3 x 0.5 µm sheet; (d) sheet with dark spots covering the basal plane. EDX analysis of the dark spots showed the presence of O in the spots but not N, therefore, we were unable to definitively confirm that the spots are phenylalaine substituents. Data was collected with a Hitachi S5500 scanning transmission electron microscope.

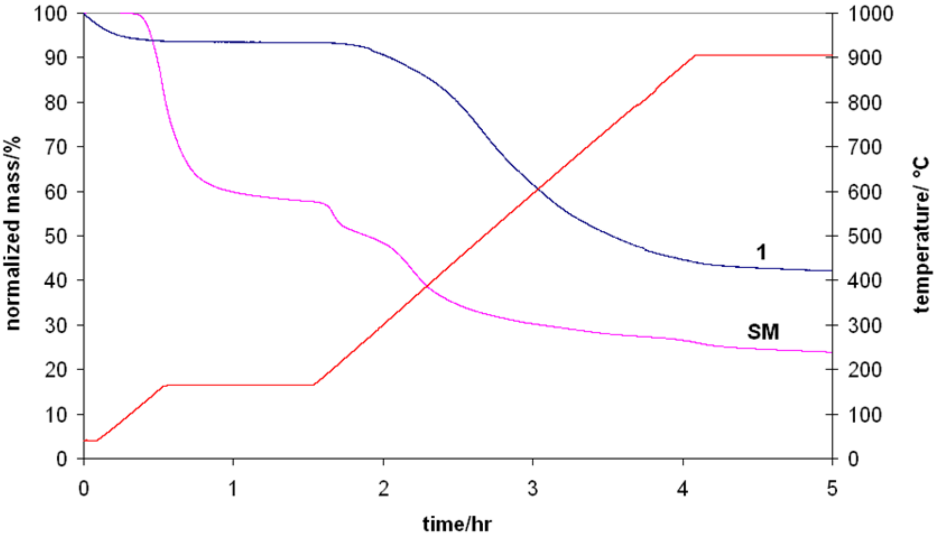


Figure S7. TGA of **1** showing 69 % normalized mass loss corresponding to a 10:1 C to Boc-Phe ratio. Note: 27 % of Boc-Phe(N_3)-OH (SM), remains after heating to 850 °C under Ar with a one hour hold time. The carbonaceous material remaining from phenylalanine was taken into account when calculating the mass loss. We assume no mass loss due to µG under the conditions specified above. XPS of **1** indicates 13:1 carbon to Boc-Phe-OH ratio confirming our assertion.

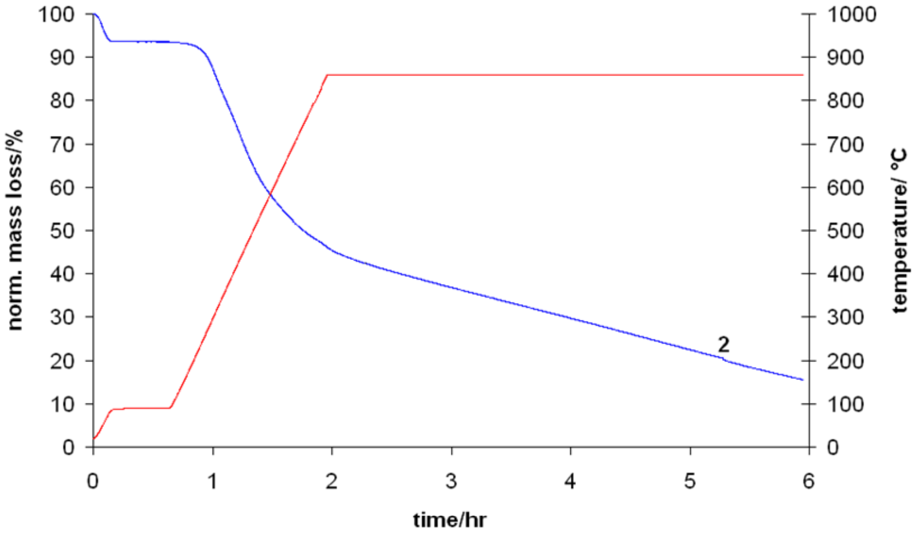


Figure S8. TGA of **2** showing 78 % normalized mass loss corresponding to a 5:1 C to Boc-Phe-OMe ratio. Note: We left a long hold time (4 hrs.) at 850 °C to ensure all of the phenylalanine is thermally decomposed. XPS data indicates 12:1 C to Boc-Phe-OMe ratio, therefore we must assume some mass loss due to µG under the above stated conditions.