ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Selective aliphatic/aromatic organogelation controlled by the side chain of serine amphiphiles

Jessica Ramos,[a] Santiago Arufe,[b] Ròisìn O'Flaherty,[a] Denise Rooney,[a] Ramon Moreira,[b] and Trinidad Velasco-Torrijos.[a]

Table of Contents

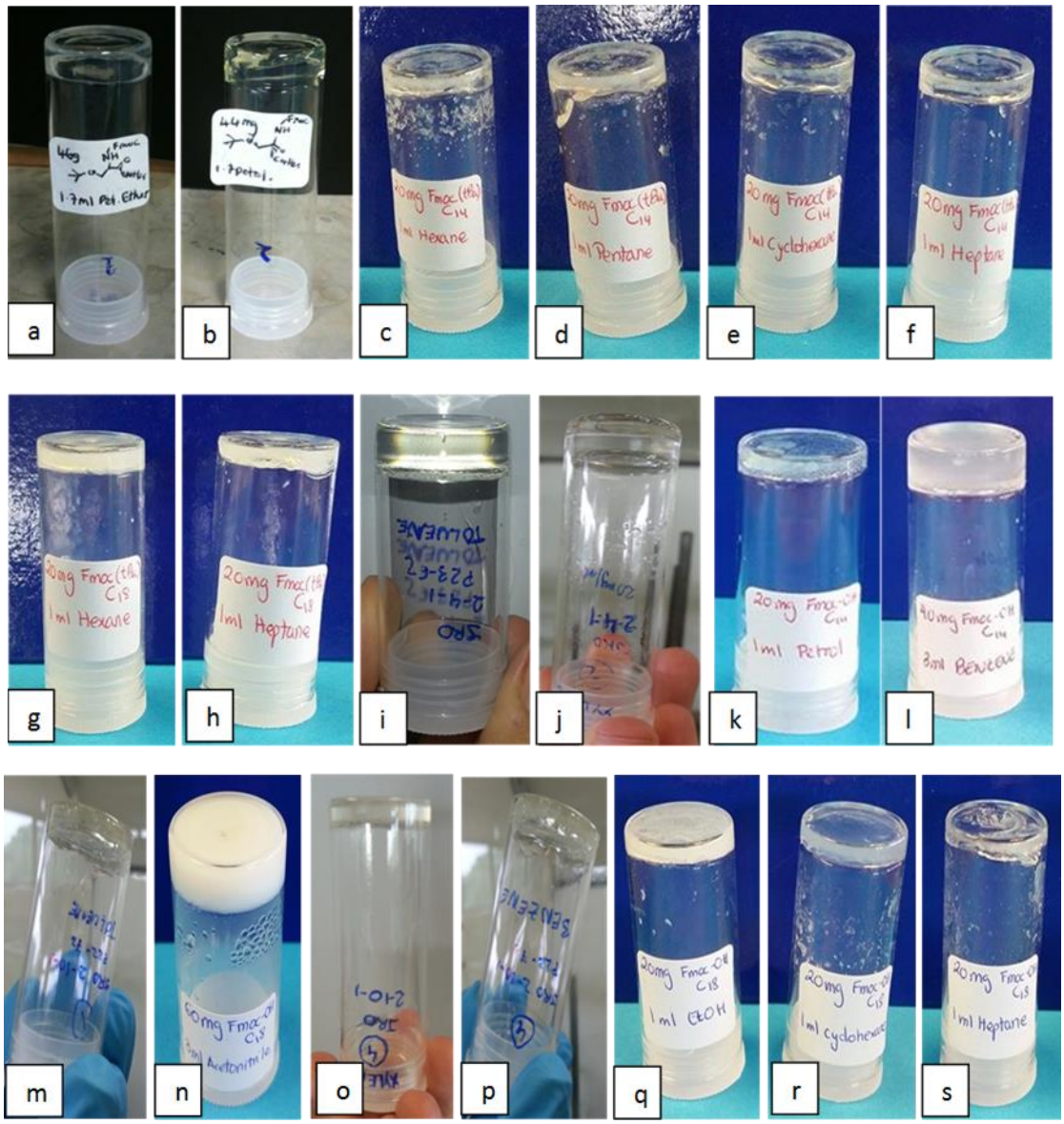


Figure S1. Physical appearance of the organogels: (**lipoamino acid gelator**) *solvent:* a) **1**, *petroleum ether*; b) **1**, *petrol*; c) **1**, *hexane*; d) **1**, *pentane*; e) **1**, *cyclohexane*; f) **1**, *heptane;* g) **2**, *hexane;* h) **2**, *heptane*; i) **3**, *toluene*; j) **3**, *xylene*; k) **3**, *benzene*; l) **3**, *petrol*; m) **4**, *toluene*; n) **4**, *acetonitrile*; o) **4**, *xylene;* p) **4**, *benzene*; q) **4**, *ethanol;* r) **4**, *cyclohexane*; s) **4**, *heptane*. (All gels were prepared at CGC).

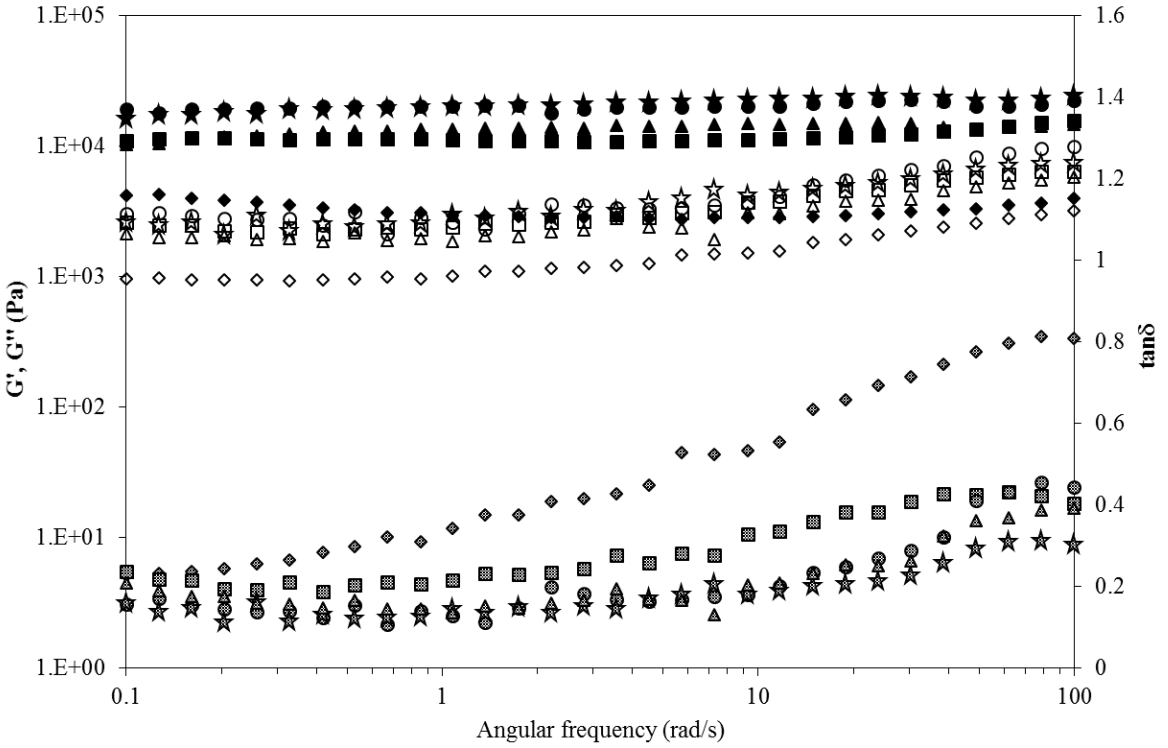


Figure S2. Frequency sweep at 25 °C at a strain of 0.1% of **3** in toluene 1.3w/v % at 24 (♦), 48 (■), 72 (▲), 96 (●) and 120 (★). (G' (filled markers), G'' (empty markers) and tand (dot filled markers).

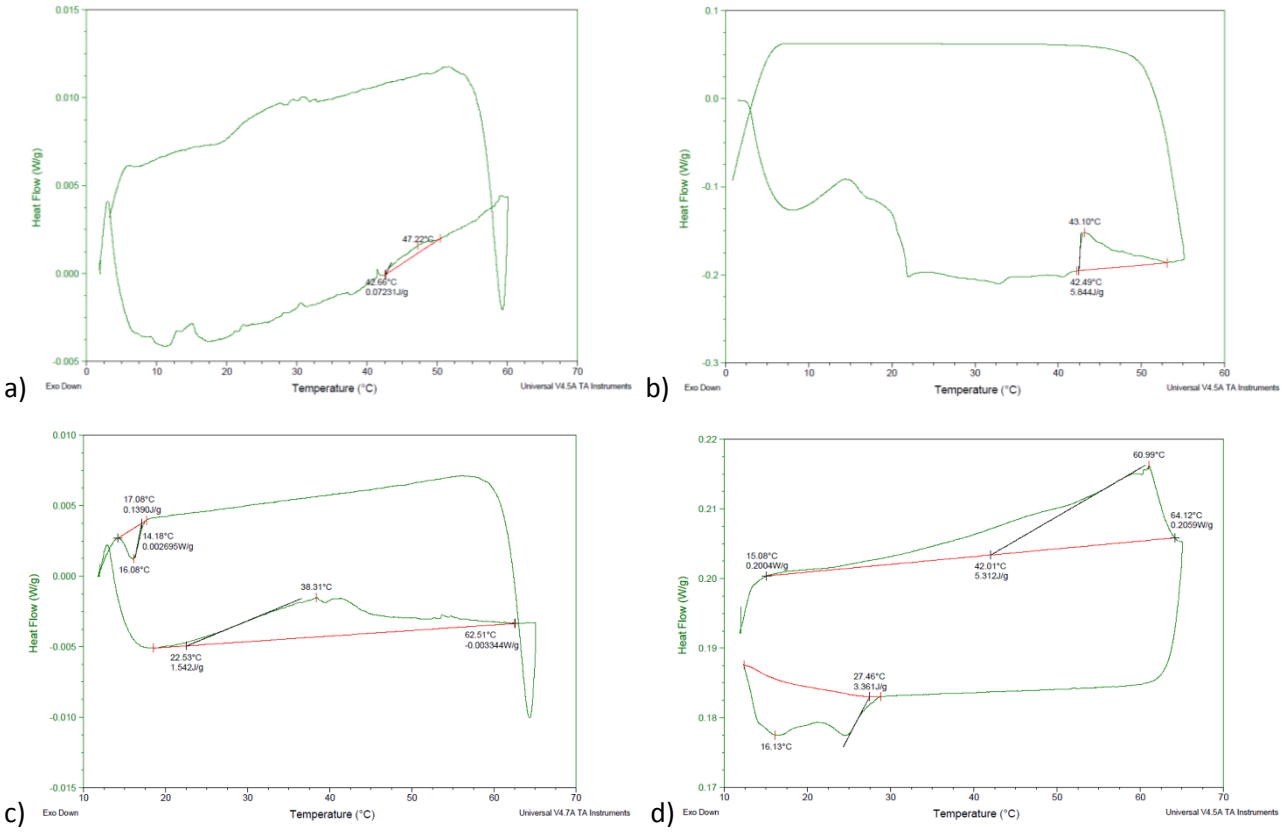


Figure S3. Differential scanning calorimetry scans of the gel formed by a) **1** in hexane (0.7 w/v %) and b) **2** in hexane (1.3 w/v %) during the heating/cooling cycles. The sample was heating from 2°C to 60°C at 2°C/min and cooling the same range of temperature; c) **3** in toluene (1.3 w/v %) and d) **4** in toluene (1.4 w/v %) during the heating/cooling cycles. The sample was heating from 11°C to 65°C at 2°C/min and cooling the same range of temperature. Reproducible/duplicated cycles for the four samples.

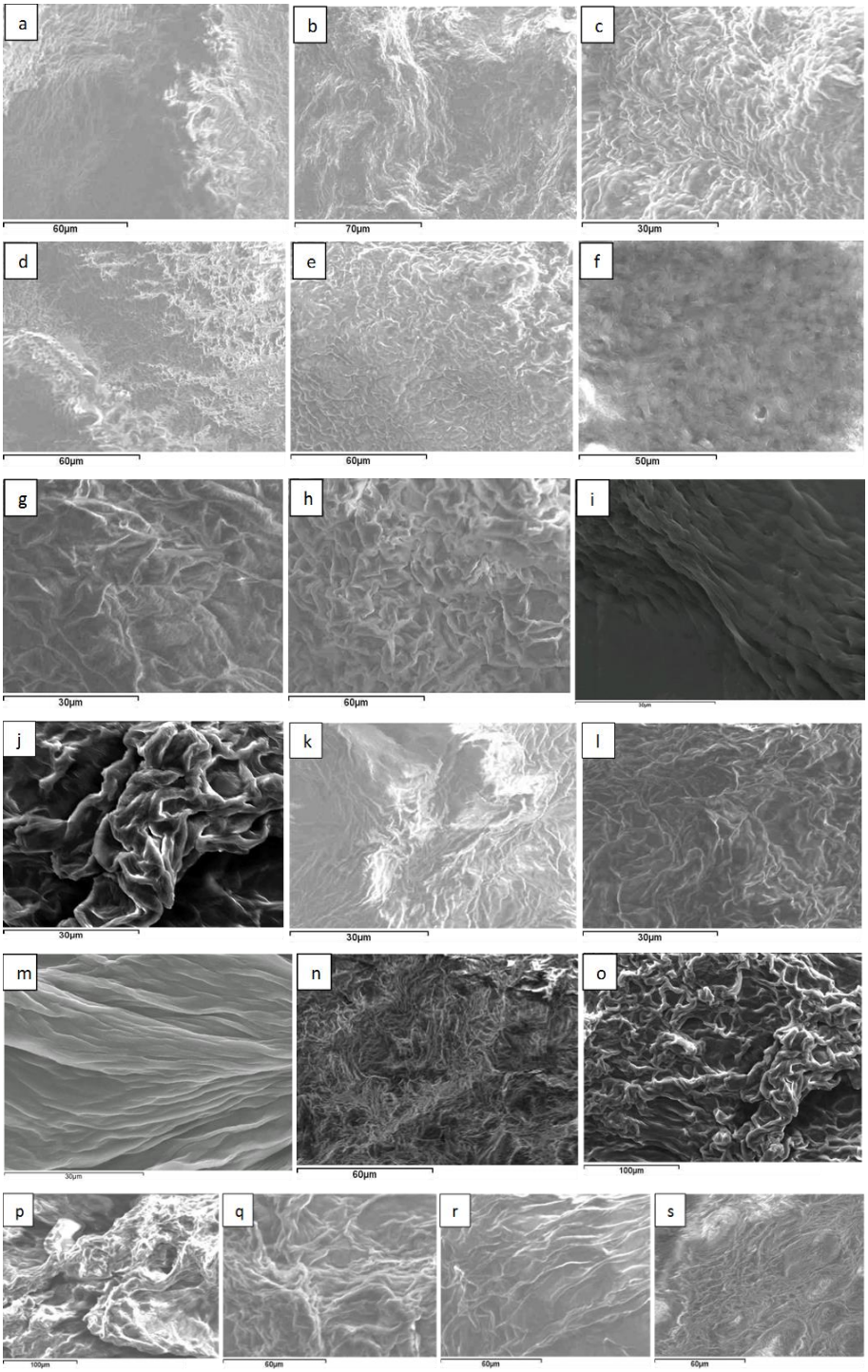


Figure S4. SEM images of xerogels formed by lipoamino acids **1**-**4**. **lipoamino acid gelator**, *solvent:* a) **1**, *petroleum ether*; b) **1**, *petrol*; c) **1**, *hexane*; d) **1**, *pentane*; e) **1**, *cyclohexane*; f) **1**, *heptane*; g) **2**, *hexane*; h) **2**, *heptane*; i) **3**, *toluene;* j) **3**, *xylene*; k) **3**, *benzene*; l) **3**, *petrol*; m) **4**, *toluene*; n) **4**, *acetonitrile*; o) **4**, *xylene;* p) **4**, *benzene*; q) **4**, *ethanol;* r) **4**, *cyclohexane*; s) **4**, *heptane*; (All gels were prepared at CGC).

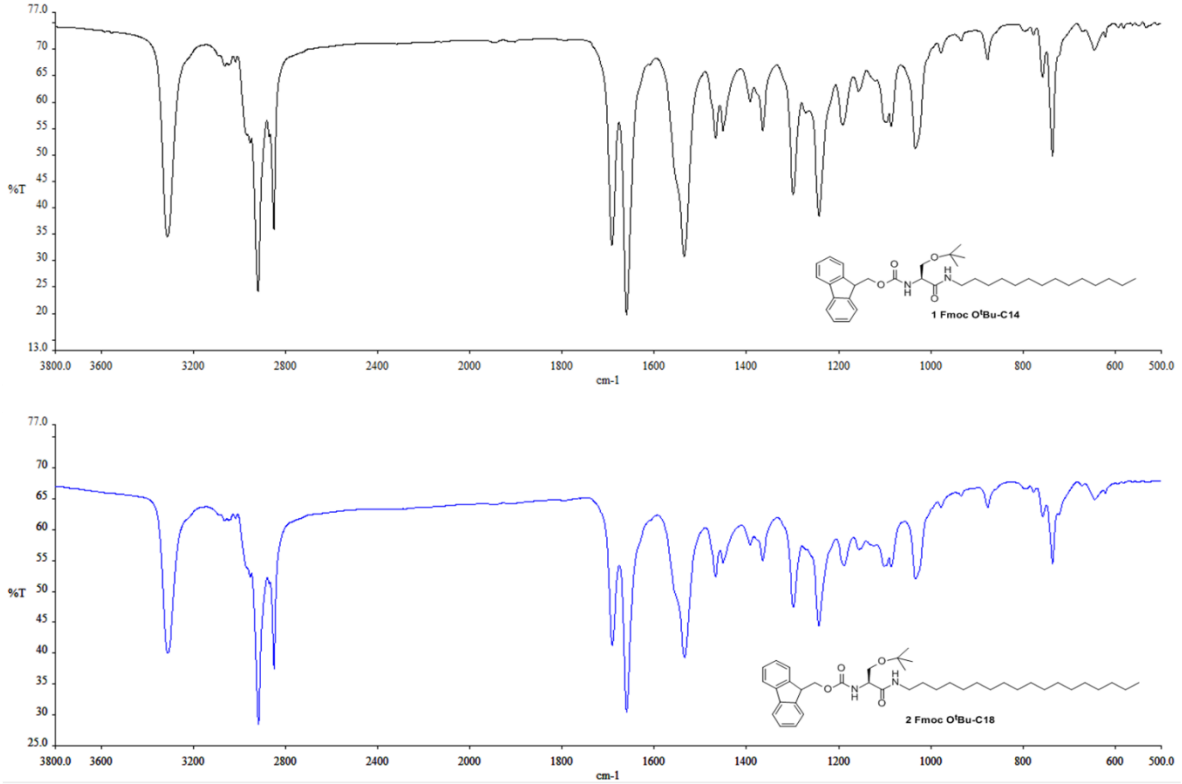


Figure S5. FTIR spectra of lipoamino acids **1** and **2** (solid state, from NaCl film).

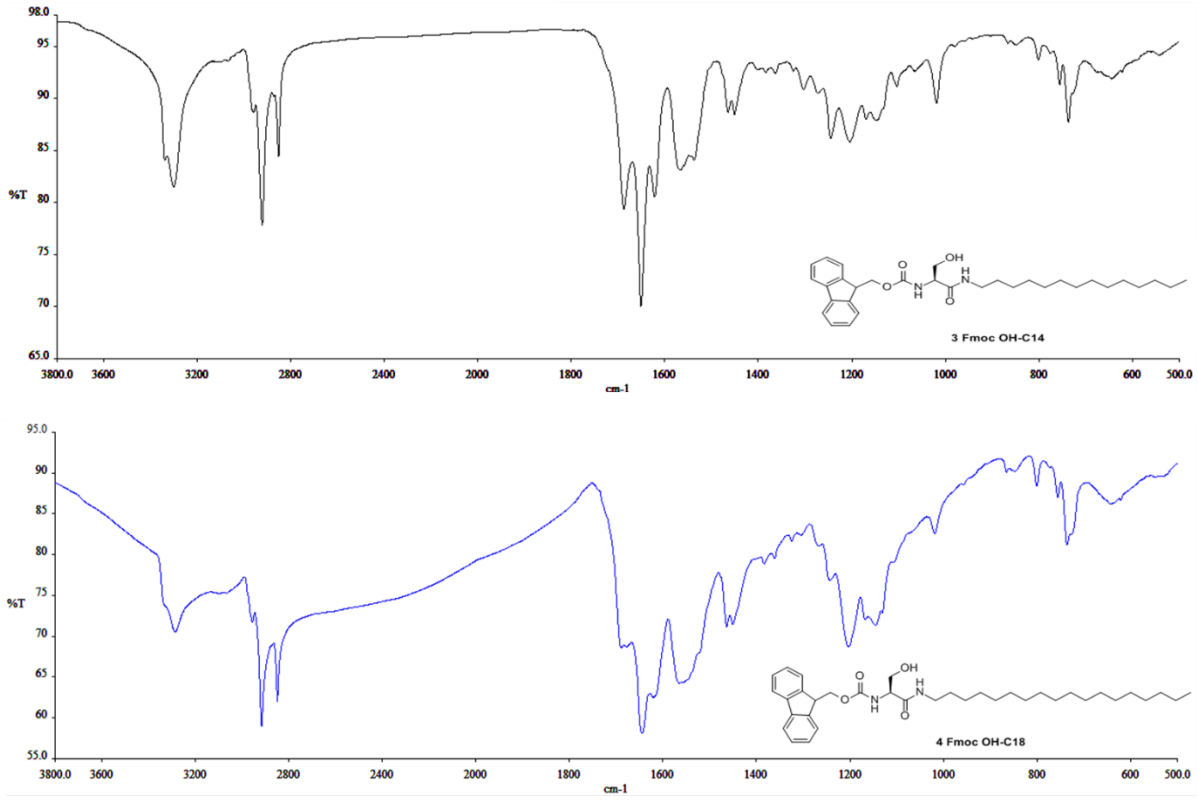


Figure S6. FTIR spectra of lipoamino acids **3** and **4** (solid state, from NaCl film).

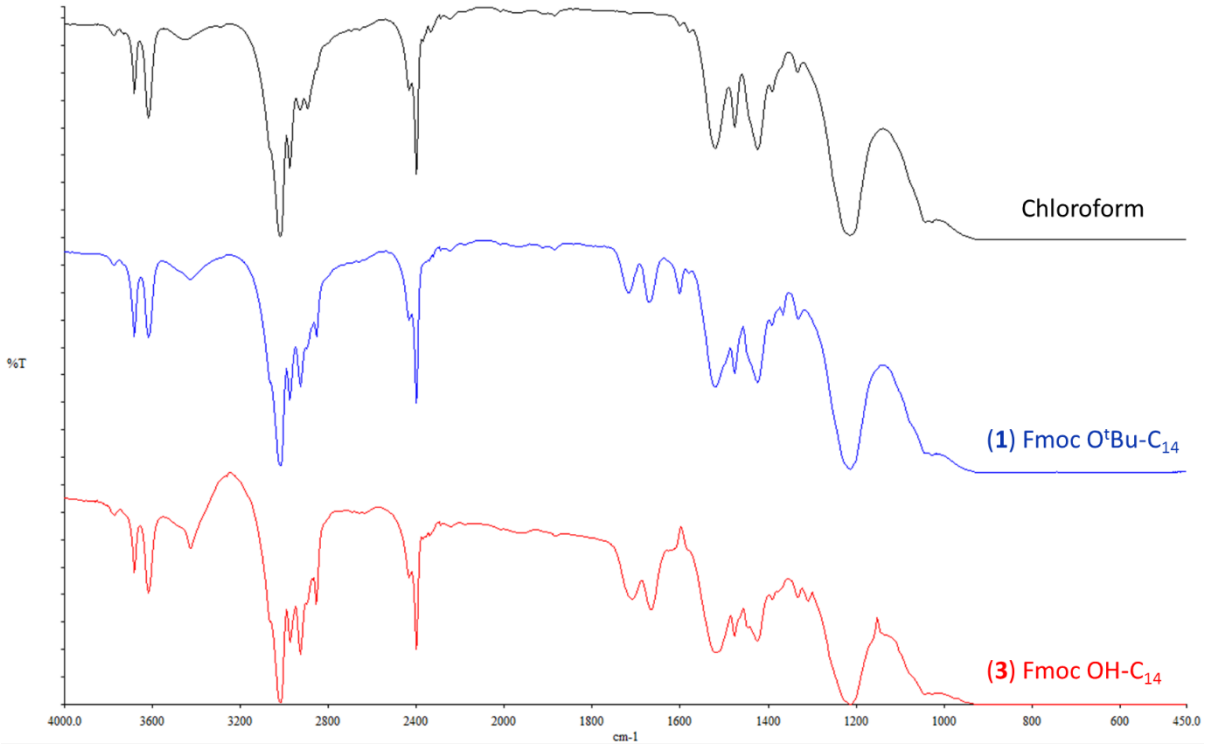


Figure S7. FTIR spectra of chloroform (black), lipoamino acids **1** (Blue) and **3** (Red) in chloroform solution. (transmission cell).

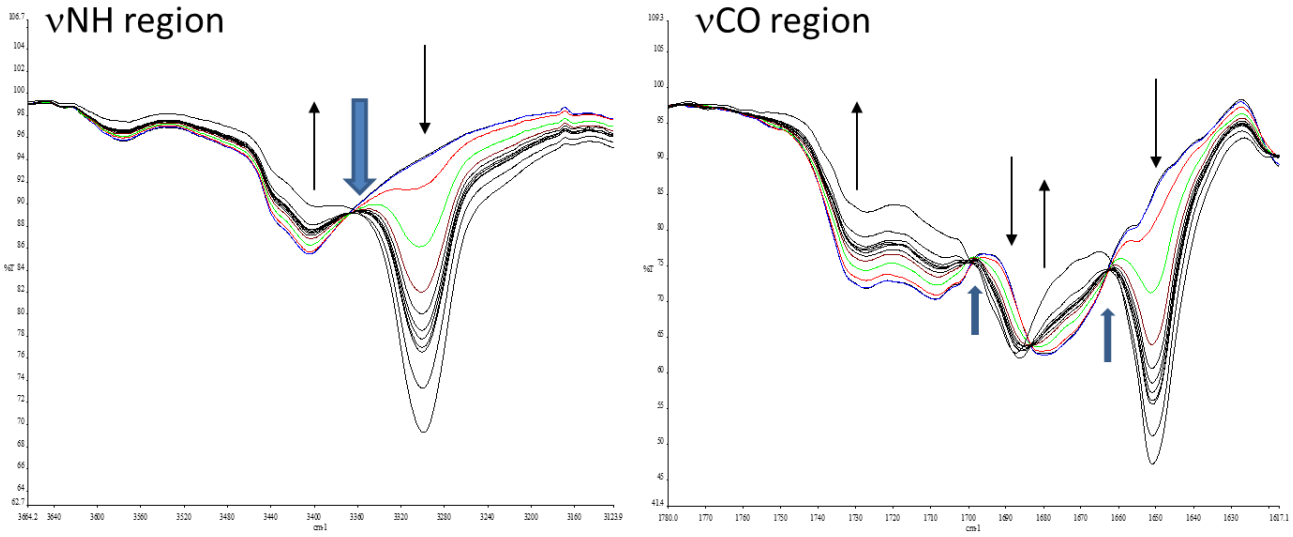


Figure S8. FTIR spectra of lipoamino acid **3** in 1.3 w/v% in toluene from 0 – 135 min. The solution injected into the cell was held at 50°C and was then was allowed to cool to room temperature. The νNH region and the νCO region are shown.

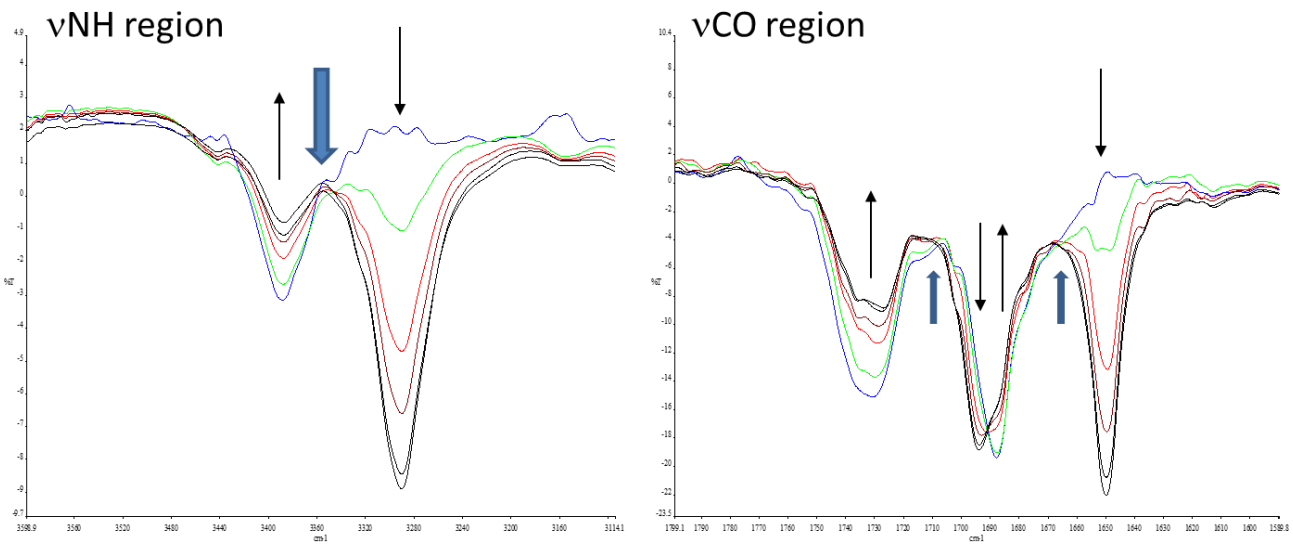


Figure S9. FTIR spectra of lipoamino acid **1** 0.7w/v% in cyclohexane from 0 – 135 min. The solution injected into the cell was held at 50°C and was then was allowed to cool to room temperature. The νNH region and the νCO region are shown.

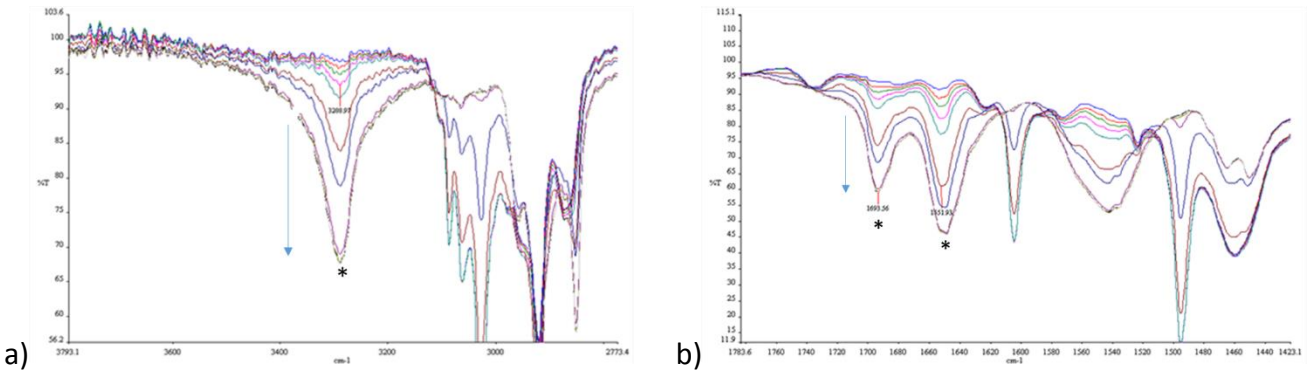


Figure S10. FTIR-ATR spectra of lipoamino acid **3** in 2.6 w/v% in toluene solution (ATR) recorded from 0 to 1 h at room temperature. The νNH region (a) and the νCO region (b) are shown.

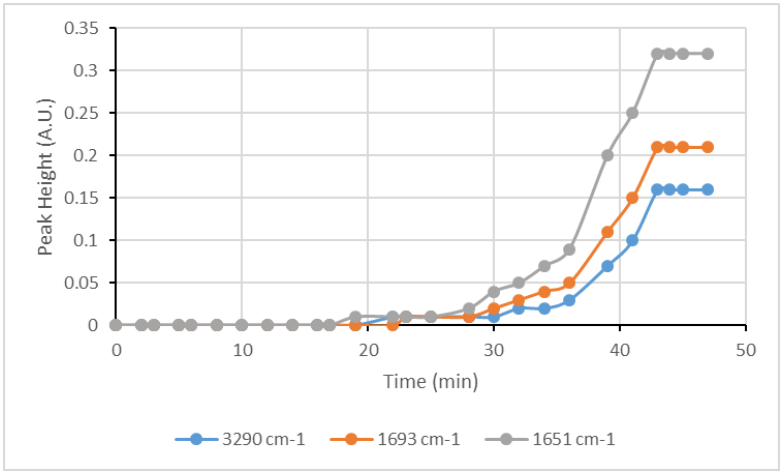


Figure S11. Increase in intensity of characteristic IR bands associated with the gel formation at (3290 (orange), 1693 (grey) and 1651 (yellow) cm^{-1} as a function of time. 2.6 w/v% **3** in toluene held at room temperature.

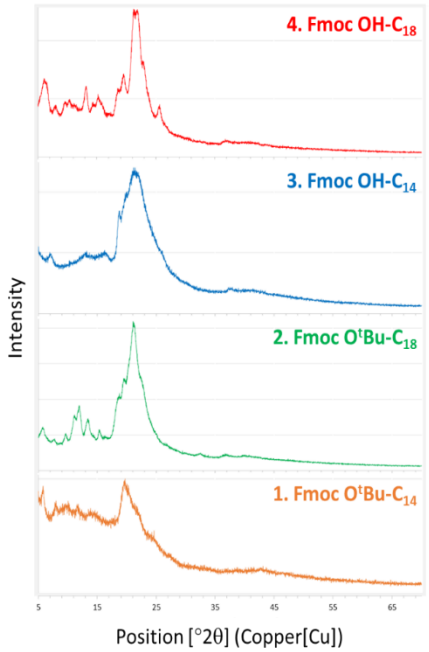


Figure S12. XRD diffractograms of xerogels from lipoamino acids: **1** and **2** from hexane gels; **3** and **4** from toluene gels. (All gels were prepared at CGC).

COMPOUND	Pos. [°2θ]	Height [cts]	d-spacing [Å]
1. Fmoc-O^{t}Bu-C$_{14}$ in hexane	5.7921	276.37	15.2
	7.9787	235.35	11.1
	9.8863	217.03	8.9
	11.7469	203.09	7.5
	19.6256	859.11	4.5
	22.0194	454.30	4.0
	24.8500	143.42	3.5
2. Fmoc-O^{t}Bu-C$_{18}$ in hexane	5.8640	564.19	15.0
	7.6652	160.33	11.5
	9.6154	449.27	9.2
	11.0213	1342.51	8.0
	11.8769	1887.84	7.4
	13.4607	1055.18	6.5
	15.4309	457.12	5.7
	18.1315	1604.68	4.8
	18.4252	2145.43	4.8
	19.4491	3222.15	4.5
	21.1840	6405.38	4.2
	22.7050	3118.04	3.9
	32.4392	134.80	2.7
	36.8439	118.76	2.4
3. Fmoc-OH-C$_{14}$ in toluene	7.1011	250.78	12.4
	16.4940	240.28	5.3
	18.6558	1581.75	4.7
	19.7234	2119.41	4.5
	22.0602	2902.67	4.0
	25.8604	649.17	3.4
	37.2761	95.71	2.4
4. Fmoc-OH-C$_{18}$ in toluene	6.0324	967.71	14.6
	6.6278	751.25	13.3
	8.0820	202.15	10.9
	9.5361	324.25	9.2
	10.3283	376.78	8.5
	13.1938	845.99	6.7

	14.2830	270.24	6.2
	15.3025	537.51	5.7
	18.5337	835.77	4.7
	19.5468	1426.98	4.5
	21.2237	3626.88	4.1
	22.1244	3390.39	4.0
	23.1675	1703.51	3.8
	25.5548	676.16	3.4
	36.8617	76.55	2.4

Table S1. X-Ray powder diffraction data for xerogels of compunds **1**-**2** from hexane gels and **3**-**4** from toluene gels.

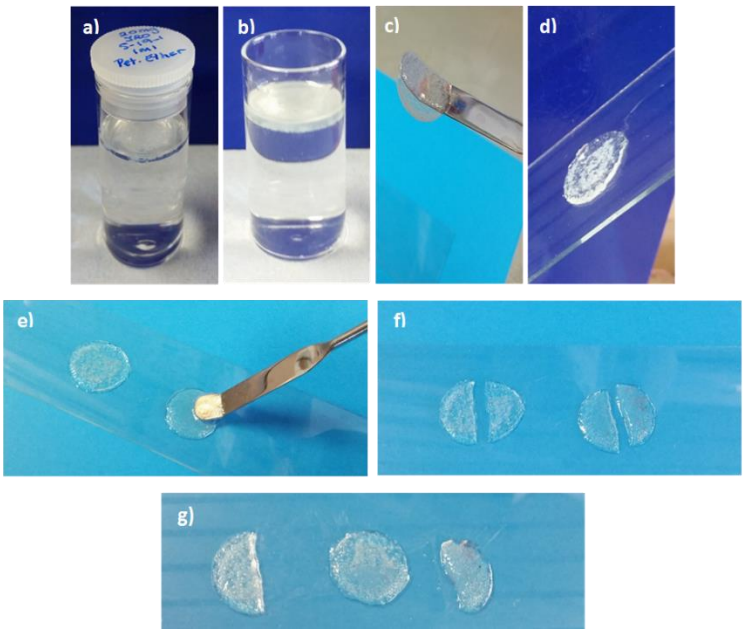


Figure S13. Phase selective gelation and self-healing capability of petroleum ether gel formed by lipoamino acid **1**: a solution of the gelator in the organic solvent of choice and an aqueous phase were stirred in a water bath at 45°C for 1 minute and then allowed to cool to room temperature. The phases separated and an organogel formed at the top; a, b) gelation of petroleum ether by gelator **1** (0.4 w/v%) in a biphasic aqueous mixture; c, d) Removal of the cyclohexane gel; e-g) Self-healing of petroleum ether gel formed from lipoamino acid **1**.

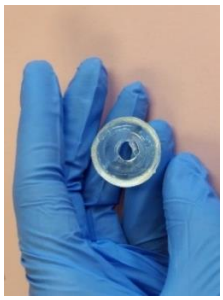


Figure S14. Gels malleability: gel in toluene formed by lipoamino acid **3** (1.3 w/v%) moulded into a "doughnut" shape.

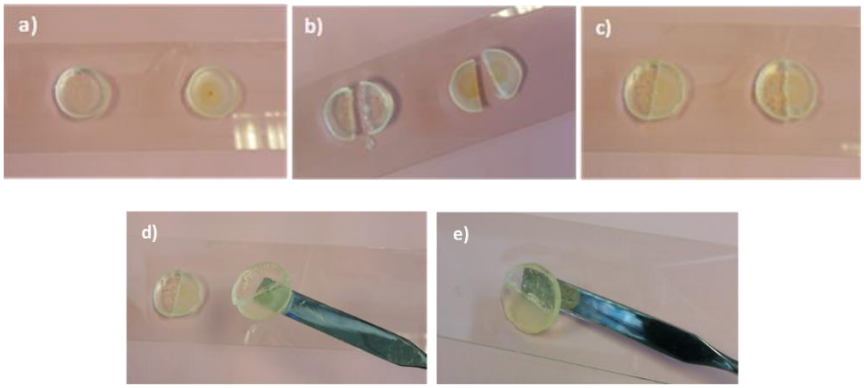
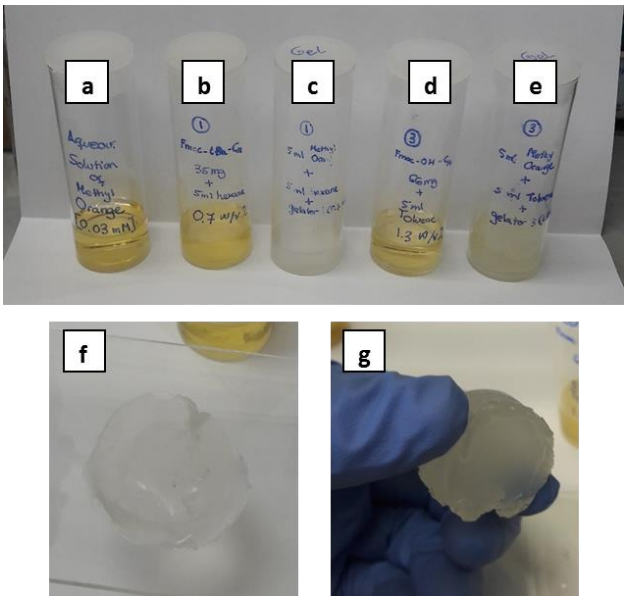


Figure S15. Self-healing capability of toluene gel formed by lipoamino acid **3** (1.3 w/v%); an orange dye was added to one of the gels in order to distinguish them during the self-healing process



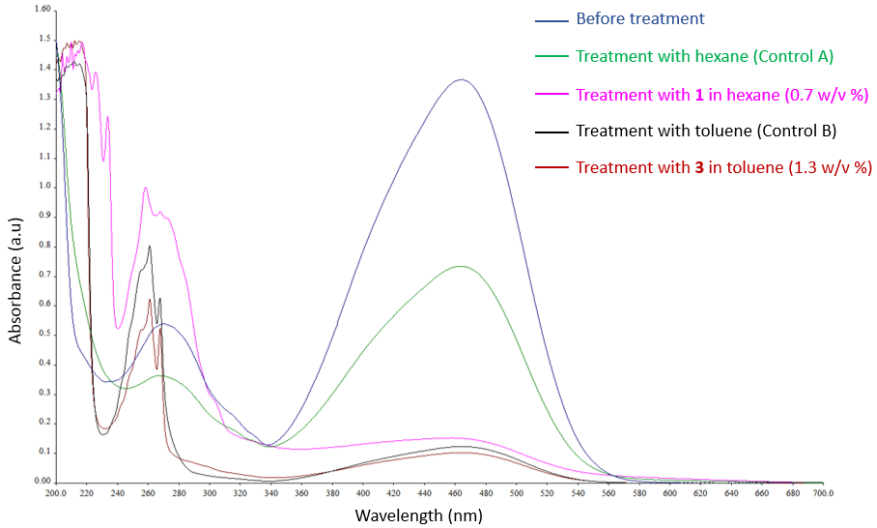


Fig. S16 Removal of aromatic dye methyl orange from aqueous solution by phase selective gelation: *Top:* aqueous solution of methyl orange [0.03 mM] (a); aqueous solution of methyl orange after treatment with compound **1** in hexane (b); after hexane extraction (c); after treatment with compound **3** in toluene (d); after toluene extraction (e); isolated gels: **1** in hexane (f), **3** in toluene (g) after treatment. *Bottom*: UV-Vis absorption spectra of methyl orange aqueous solution before and after dye removal by phase selective gelation. Solutions of compounds **1** and **3** were prepared at CGC.

Table S2 Determination of purification efficiency: UV-Vis absorbance (at 465 nm) of aqueous phase and [methyl orange] before and after treatment.

Aqueous Phase	Absorbance (a.u)	[Methyl Orange] (mM)	E (%)
Before treatment	1.36	0.030	-
Treatment with hexane (control A)	0.73	0.0161	36
Treatment with **1** in hexane (0.7 w/v %)	0.15	0.0033	89
Treatment with toluene (control B)	0.12	0.0026	91
Treatment with **3** in toluene (1.3 w/v%)	0.10	0.0022	93

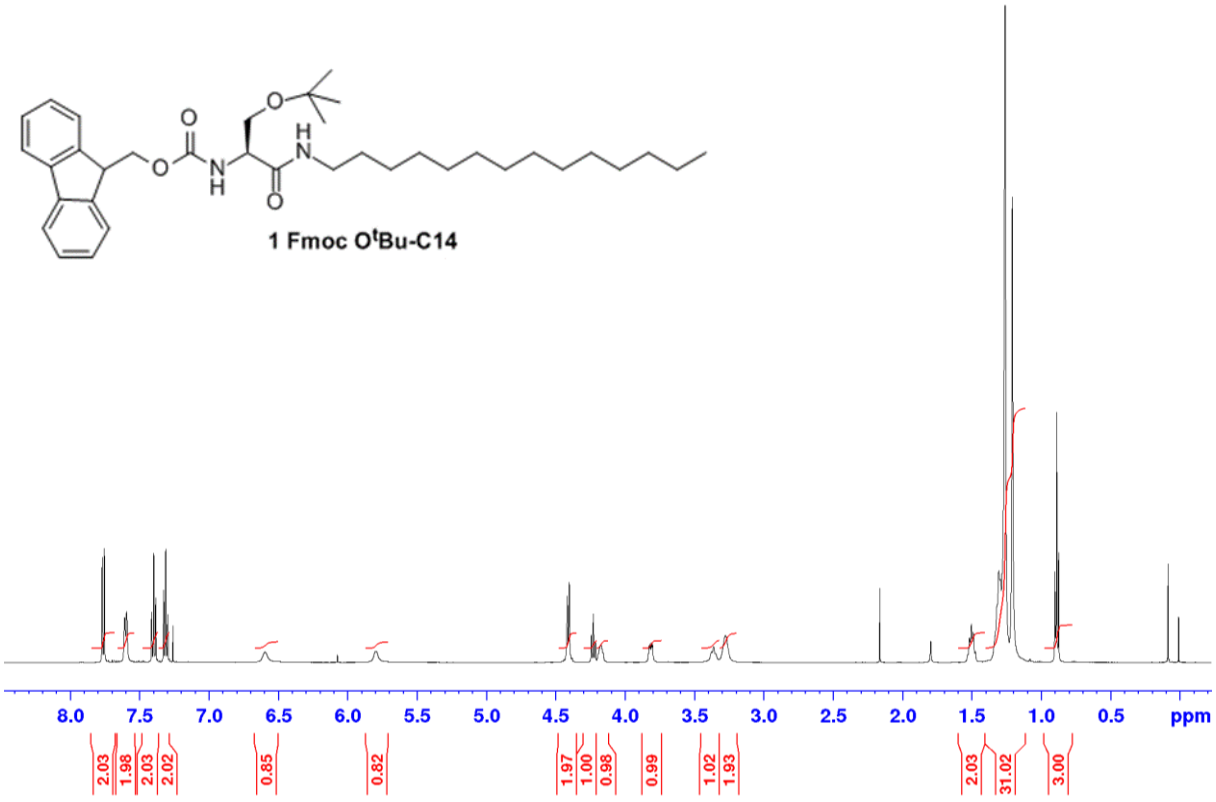


Figure S17. ^{1}H NMR spectrum of lipoamino acid **1** (500 MHz, $CDCl_3$).

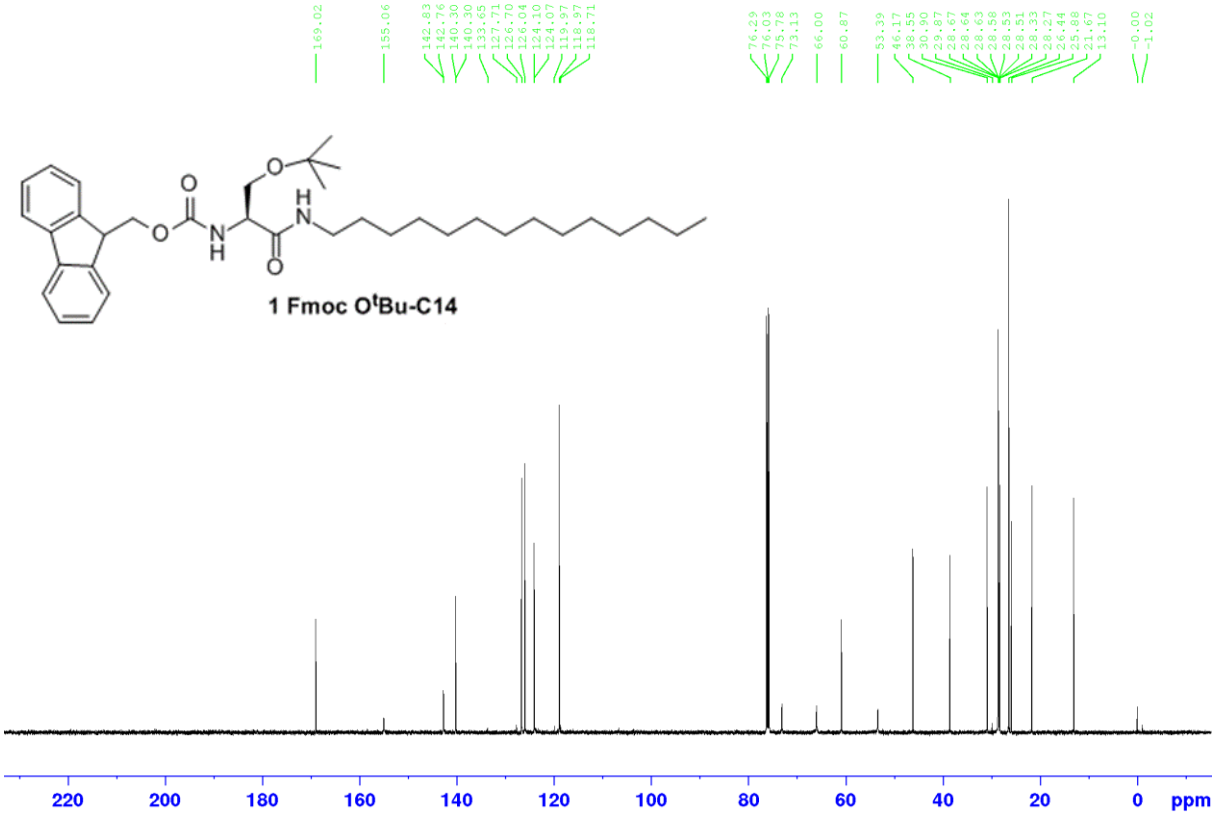


Figure S18. ^{13}C NMR spectrum of lipoamino acid **1** (125 MHz, $CDCl_3$).

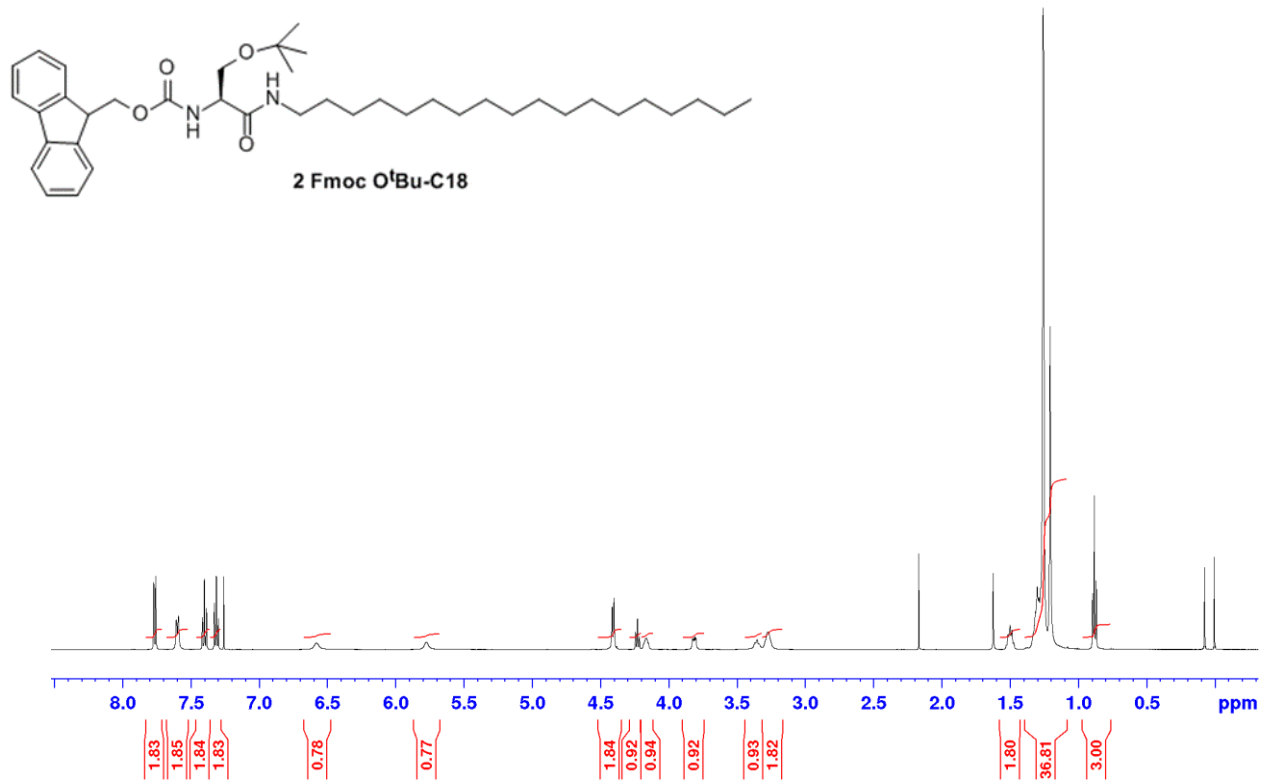


Figure S19. ^{1}H NMR spectrum of lipoamino acid **2** (500 MHz, $CDCl_3$).

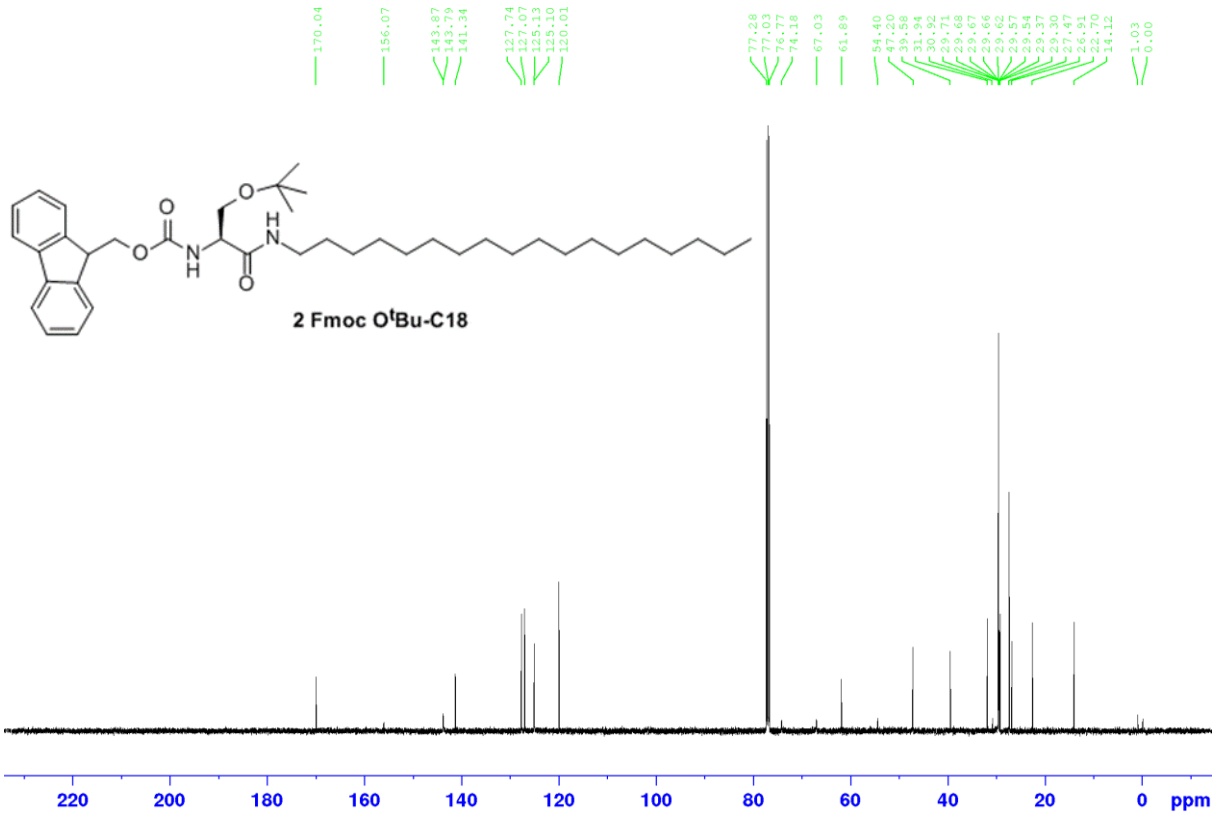


Figure S20. ^{13}C NMR spectrum of lipoamino acid **2** (125 MHz, $CDCl_3$).

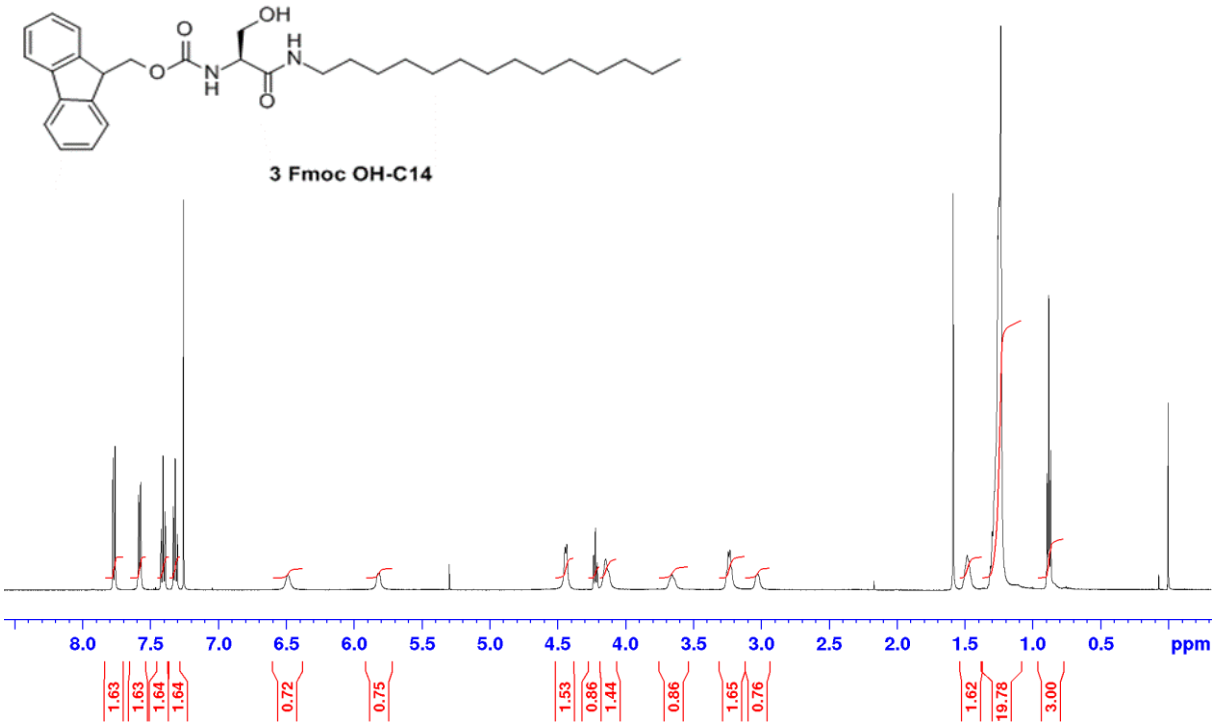


Figure S21. ^{1}H NMR spectrum of lipoamino acid **3** (500 MHz, $CDCl_3$).

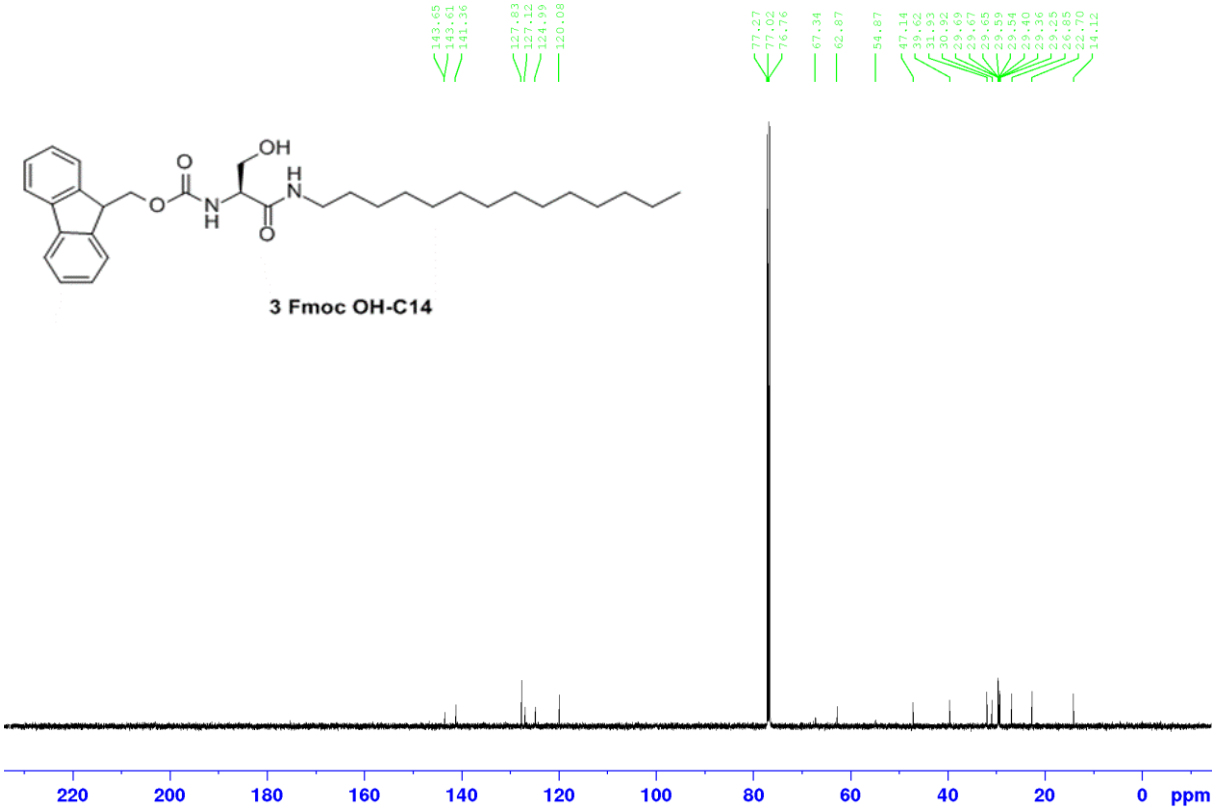


Figure S22. ^{13}C NMR spectrum of lipoamino acid **3** (125 MHz, $CDCl_3$).

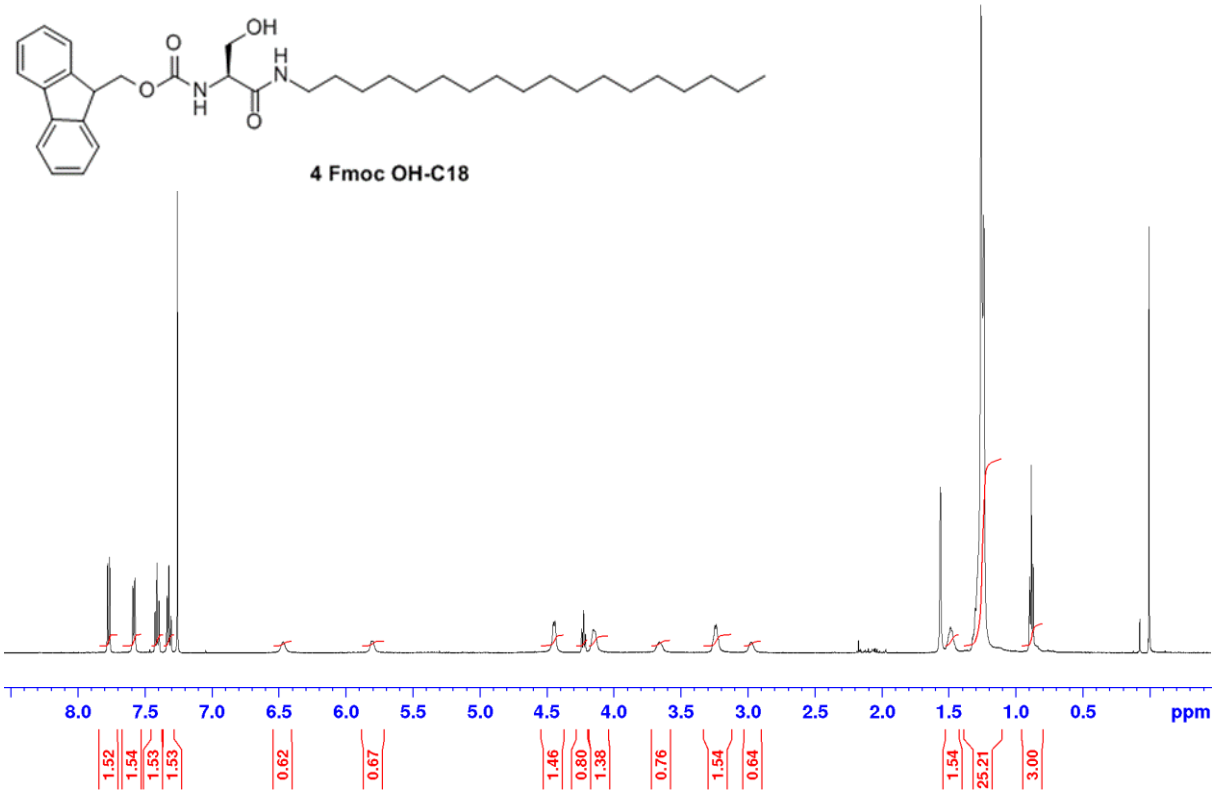


Figure S23. ^{1}H NMR spectrum of lipoamino acid **4** (500 MHz, $CDCl_3$).

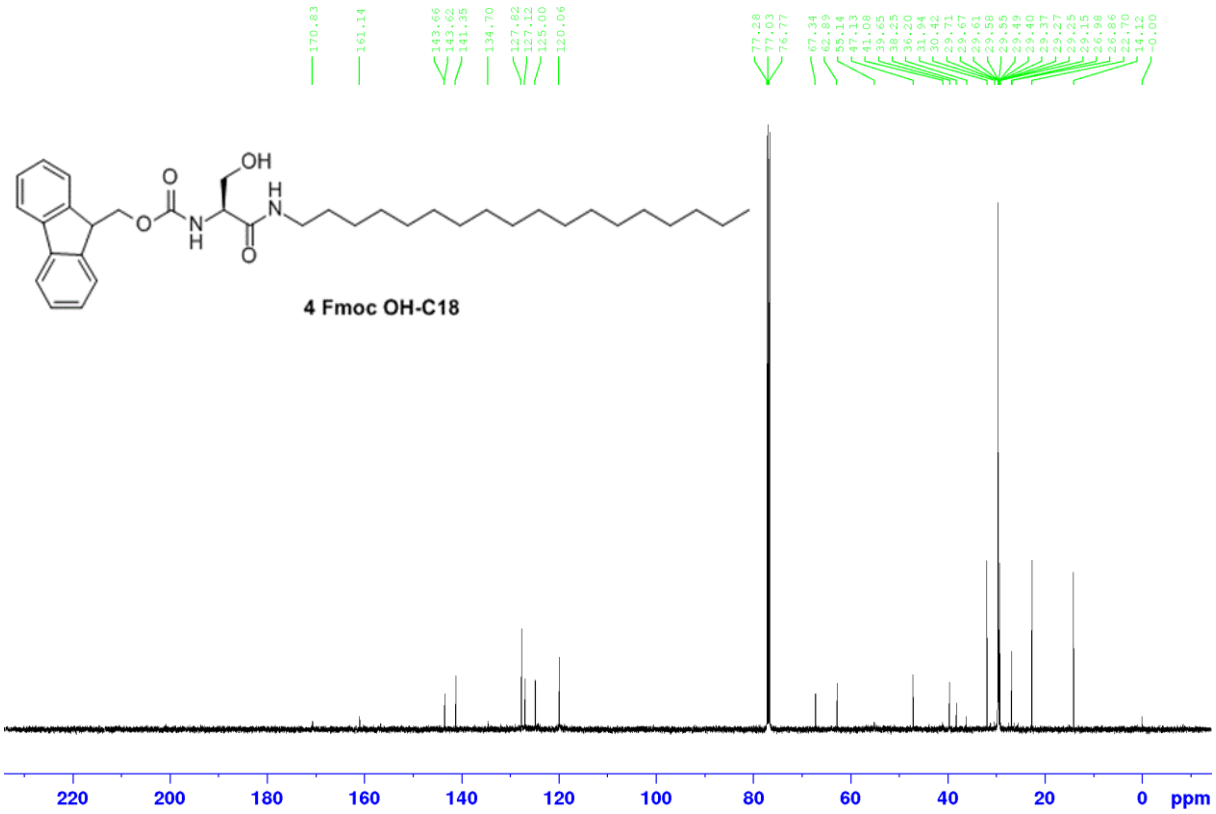


Figure S24. ^{13}C NMR spectrum of lipoamino acid **4** (125 MHz, $CDCl_3$).