Electronic Supplementary Information for

Synthesis, Physicochemical Characterization and Aquatic Toxicity Studies of Anionic Surfactants Derived from Amino and α-Hydroxy Acids

Demian Kalebic[a], Koen Binnemans[a], Peter de Witte[b], Wim Dehaen*[a]

[a] KU Leuven, Department of Chemistry, Celestijnenlaan 200F, P.O. box 2404, B-3001 Leuven, Belgium.

[b] KU Leuven, Laboratory for Molecular Biodiscovery, Department of Pharmaceutical and Pharmacological Sciences, Herestraat 49 box 824, B-3000 Leuven, Belgium

Chemicals and Instrumentation

Decanoyl chloride (98%), myristoyl chloride (97%) and iminodiacetic acid (99%) were purchased from TCI Europe. Lauroyl chloride (98%), palmitoyl chloride (98%), L-methionine (98%), L-glutamic acid (99%), L-malic acid (99%), and citric acid (anhydrous, 99%) were purchased from Acros Organics. L-aspartic acid (98%) was purchased from J&K Scientific. Solvents were purchased from Fisher Scientific and were of analytical grade. NMR spectra were recorded on a Bruker 400 AV 400 MHz instrument (Bruker, Biospin), and chemical shifts (δ) were reported in ppm and referenced to the NMR solvent signal (DMSO-d_6 and acetone-d_6). High-resolution mass spectra (HRMS) were acquired on a quadrupole orthogonal acceleration time-of-flight (TOF) mass spectrometer. Samples were infused at a rate of 3 μL min^{-1} and the spectra were recorded in positive or negative ionization mode with a resolution of 15.000 full width at half maximum (FWHM) using leucine enkephalin as the lock mass. Ultra-pure water (Milli-Q, Merck) with an electrical resistivity of 18.2 MΩ cm was used for the preparation of aqueous solutions of surfactants. Danieau's solution (1.5 mM HEPES, pH 7.2, 17.4 mM NaCl, 0.21 mM KCl, 0.12 mM $MgSO_4$, 0.18 mM $Ca(NO_3)_2$ and 0.6 μM methylene blue) was used for toxicity studies with zebrafish larvae.[1]

Characterization data of the prepared compounds

N-Decanoyl L-methionine (**C_{10}Met**, **1a**) was prepared according to the general procedure using methionine (1.00 g, 6.70 mmol) and decanoyl chloride (1.53 mL, 7.37 mmol). The compound was isolated as a white solid (1.42 g, 4.7 mmol, 70%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm 12.54 (s, 1H), 8.05 (d, J = 7.8 Hz, 1H), 4.29 (ddd, J = 9.4, 7.8, 4.5 Hz, 1H), 2.50 – 2.38 (m, 2H), 2.10 (td, J = 7.3, 2.5 Hz, 2H), 2.03 (s, 3H), 2.00 – 1.88 (m, 1H), 1.87 – 1.75 (m, 1H), 1.56 – 1.36 (m, 2H),

1.41 – 1.15 (m, 12H), 0.98 – 0.78 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 173.5, 172.4, 50.8, 35.1, 31.3, 30.7, 29.7, 28.9, 28.8, 28.7, 28.5, 25.2, 22.1, 14.6, 14.0. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for $C_{15}H_{29}NO_3S$: 302.1795, found: 302.1785.

N-Lauroyl L-methionine (**C_{12}Met**, **1b**) was prepared according to the general procedure using methionine (1.00 g, 6.70 mmol) and lauroyl chloride (1.75 mL, 7.37 mmol). The compound was isolated as a white solid (1.98 g, 6.0 mmol, 89%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 12.55 (s, 1H), 8.05 (d, J = 7.9 Hz, 1H), 4.29 (ddd, J = 9.5, 7.8, 4.5 Hz, 1H), 2.50 – 2.34 (m, 2H), 2.10 (td, J = 7.2, 2.7 Hz, 2H), 2.03 (s, 3H), 2.00 – 1.87 (m, 1H), 1.89 – 1.75 (m, 1H), 1.57 – 1.39 (m, 2H), 1.35 – 1.11 (m, 16H), 0.94 – 0.77 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 173.5, 172.4, 50.7, 35.0, 31.3, 30.7, 29.7, 29.0, 29.0, 28.8, 28.7, 28.6, 25.2, 22.1, 14.6, 14.0. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for $C_{17}H_{33}NO_3S$: 330.2108, found: 330.2107.

N-Myristoyl L-methionine (**C_{14}Met**, **1c**) was prepared according to the general procedure using methionine (1.00 g, 6.70 mmol) and myristoyl chloride (2.00 mL, 7.37 mmol). The compound was isolated as a white solid (2.14 g, 6.0 mmol, 89%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 12.55 (s, 1H), 8.05 (d, J = 7.9 Hz, 1H), 4.29 (ddd, J = 9.4, 7.8, 4.5 Hz, 1H), 2.50 – 2.36 (m, 2H), 2.10 (td, J = 7.2, 2.8 Hz, 2H), 2.03 (s, 3H), 2.00 – 1.87 (m, 1H), 1.89 – 1.75 (m, 1H), 1.59 – 1.41 (m, 2H), 1.42 – 1.01 (m, 20H), 0.95 – 0.76 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 173.5, 172.4, 50.7, 35.1, 31.3, 30.7, 29.7, 29.1, 29.0, 29.0, 28.8, 28.7, 28.6, 25.2, 22.1, 14.6, 14.0. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for $C_{19}H_{37}NO_3S$: 358.2421, found: 358.2415.

N-Palmitoyl L-methionine (**C_{16}Met**, **1d**) was prepared according to the general procedure using methionine (1.00 g, 6.70 mmol) and palmitoyl chloride (2.24 mL, 7.37 mmol). The compound was isolated as a white solid (1.92 g, 4.96 mmol, 74%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 12.55

(s, 1H), 8.05 (d, J = 7.9 Hz, 1H), 4.29 (ddd, J = 9.4, 7.8, 4.5 Hz, 1H), 2.50 – 2.38 (m, 2H), 2.10 (td, J = 7.3, 2.9 Hz, 2H), 2.03 (s, 3H), 2.00 – 1.87 (m, 1H), 1.89 – 1.75 (m, 1H), 1.54 – 1.41 (m, 2H), 1.32 – 1.17 (m, 24H), 0.98 – 0.79 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 173.5, 172.4, 50.8, 35.1, 31.3, 30.7, 29.8, 29.1, 29.0, 29.0, 28.8, 28.7, 28.6, 25.3, 22.1, 14.6, 14.0. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for $C_{21}H_{41}NO_3S$: 386.2734, found: 386.2723.

N-Decanoyl L-aspartic acid (**C_{10}Asp**, **2a**) was prepared according to the general procedure using aspartic acid (1.00 g, 7.51 mmol) and decanoyl chloride (1.79 mL, 8.64 mmol). The compound was isolated as a white solid (1.69 g, 5.86 mmol, 78%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 12.50 (s, 2H), 8.09 (d, J = 8.0 Hz, 1H), 4.50 (td, J = 7.6, 5.7 Hz, 1H), 2.67 (dd, J = 16.4, 5.8 Hz, 1H), 2.59 – 2.49 (m, 3H), 2.08 (t, J = 7.4 Hz, 2H), 1.55 – 1.40 (m, 2H), 1.32 – 1.17 (m, 12H), 0.96 – 0.77 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 172.6, 172.1, 171.7, 48.5, 36.1, 35.0, 31.3, 28.9, 28.8, 28.7, 28.5, 25.2, 22.1, 14.0. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for $C_{14}H_{25}NO_5$: 286.1660, found: 286.1654.

N-Lauroyl L-aspartic acid (**C_{12}Asp**, **2b**) was prepared according to the general procedure using aspartic acid (1.00 g, 7.51 mmol) and lauroyl chloride (2.08 mL, 8.64 mmol). The compound was isolated as a white solid (1.94 g, 6.16 mmol, 82%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 12.49 (s, 2H), 8.09 (d, J = 8.0 Hz, 1H), 4.51 (td, J = 7.6, 5.7 Hz, 1H), 2.67 (dd, J = 16.4, 5.8 Hz, 1H), 2.59 – 2.50 (m, 2H), 2.08 (t, J = 7.4 Hz, 2H), 1.52 – 1.40 (m, 2H), 1.34 – 1.16 (m, 16H), 0.91 – 0.78 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 172.6, 172.1, 171.7, 48.5, 36.1, 35.0, 31.3, 29.1, 29.0, 29.0, 28.8, 28.7, 28.5, 25.2, 22.1, 14.0. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for $C_{16}H_{29}NO_5$: 314.1973, found: 314.1964.

N-Myristoyl L-aspartic acid (**C_{14}Asp**, **2c**) was prepared according to the general procedure using aspartic acid (1.00 g, 7.51 mmol) and myristoyl chloride (2.35 mL, 8.64 mmol). The compound was isolated as a white solid (2.00 g, 5.86 mmol, 78%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 13.71 (s, 1H), 7.92 (d, J = 7.6 Hz, 1H), 4.38 (td, J = 7.7, 5.5 Hz, 1H), 2.59 (dd, J = 16.2, 7.8 Hz, 1H), 2.48 – 2.40 (m, 1H), 2.08 (t, J = 7.4 Hz, 2H), 1.51 – 1.40 (m, 2H), 1.30 – 1.16 (m, 20H), 0.90 – 0.80 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 172.9, 172.1, 171.8, 48.5, 37.6, 35.1, 31.3, 29.1, 29.1, 29.0, 29.0, 28.8, 28.7, 28.6, 25.2, 22.1, 14.0. HRMS(ESI-Q-TOF)*m*/*z* $[M-H]^-$ calculated for $C_{18}H_{33}NO_5$: 342.2286, found: 342.2274.

N-Palmitoyl L-aspartic acid (**C_{16}Asp**, **2d**) was prepared according to the general procedure using aspartic acid (1.00 g, 7.51 mmol) and palmitoyl chloride (2.62 mL, 8.64 mmol). The compound was isolated as a white solid (1.68 g, 4.51 mmol, 60%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 12.48 (s, 2H), 8.09 (d, J = 8.1 Hz, 1H), 4.51 (td, J = 7.6, 5.7 Hz, 1H), 2.67 (dd, J = 16.5, 5.8 Hz, 1H), 2.58 – 2.51 (m, 1H), 2.07 (t, J = 7.4 Hz, 2H), 1.52 – 1.41 (m, 2H), 1.31 – 1.16 (m, 24H), 0.92 – 0.80 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 172.6, 172.1, 171.7, 48.5, 36.1, 35.0, 31.3, 29.1, 29.1, 29.0, 29.0, 28.8, 28.7, 28.6, 25.2, 22.1, 14.0. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for $C_{20}H_{37}NO_5$: 370.2599, found: 370.2598.

N-Decanoyl L-glutamic acid (**C_{10}Glu**, **3a**) was prepared according to the general procedure using glutamic acid (1.00 g, 6.80 mmol) and decanoyl chloride (1.62 mL, 7.8 mmol). The compound was isolated as a white solid (1.76 g, 5.85 mmol, 86 %). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 12.34 (s, 2H), 8.02 (d, J = 7.8 Hz, 1H), 4.26 – 4.10 (m, 1H), 2.31 – 2.21 (m, 2H), 2.15 – 2.05 (m, 2H), 2.00 – 1.89 (m, 1H), 1.80 – 1.68 (m, 1H), 1.53 – 1.40 (m, 2H), 1.33 – 1.16 (m, 12H), 0.93 – 0.79 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 173.7, 173.5, 172.4, 51.0, 35.1, 31.3,

30.1, 29.0, 28.8, 28.7, 28.6, 26.4, 25.3, 22.1, 14.0. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for $C_{15}H_{27}NO_5$: 300.1816, found: 300.1802.

N-Lauroyl L-glutamic acid (**C_{12}Glu**, **3b**) was prepared according to the general procedure using glutamic acid (1.00 g, 6.80 mmol) and lauroyl chloride (1.81 mL, 7.8 mmol). The compound was isolated as a white solid (1.96 g, 5.98 mmol, 88%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm 12.32 (s, 2H), 8.02 (d, J = 7.8 Hz, 1H), 4.27 – 4.12 (m, 1H), 2.37 – 2.19 (m, 2H), 2.16 – 2.04 (m, 2H), 2.01 – 1.85 (m, 1H), 1.83 – 1.66 (m, 1H), 1.55 – 1.40 (m, 2H), 1.36 – 1.10 (m, 16H), 0.95 – 0.72 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 173.7, 173.5, 172.4, 51.0, 35.0, 31.3, 30.1, 29.0, 29.0, 29.0, 28.8, 28.7, 28.6, 26.3, 25.2, 22.1, 14.0. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for: 328.2129, found: 328.2119.

N-Myristoyl L-glutamic acid (**C_{14}Glu**, **3c**) was prepared according to the general procedure using glutamic acid (1.00 g, 6.80 mmol) and myristoyl chloride (2.12 mL, 7.8 mmol). The compound was isolated as a white solid (1.46 g, 4.08 mmol, 60%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 12.32 (s, 2H), 8.02 (d, J = 7.9 Hz, 1H), 4.31 – 4.08 (m, 1H), 2.33 – 2.18 (m, 2H), 2.15 – 2.04 (m, 2H), 2.01 – 1.86 (m, 1H), 1.81 – 1.67 (m, 1H), 1.54 – 1.39 (m, 2H), 1.36 – 1.14 (m, 20H), 0.91 – 0.79 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 173.7, 173.5, 172.4, 51.0, 35.1, 31.3, 30.1, 29.1, 29.1, 29.0, 28.8, 28.8, 28.6, 26.3, 25.3, 22.1, 14.0. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for: 356.2442, found: 356.2430.

N-Palmitoyl L-glutamic acid (**C_{16}Glu**, **3d**) was prepared according to the general procedure using glutamic acid (1.00 g, 6.80 mmol) and palmitoyl chloride (2.37 mL, 7.8 mmol). The compound was isolated as a white solid (1.65 g, 4.28 mmol, 63%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 12.48 (s, 1H), 7.96 (d, J = 7.8 Hz, 1H), 4.27 – 4.11 (m, 1H), 2.34 – 2.20 (m, 2H), 2.19 – 2.06 (m,

2H), 2.03 – 1.84 (m, 1H), 1.84 – 1.62 (m, 1H), 1.54 – 1.39 (m, 2H), 1.39 – 1.01 (m, 24H), 0.95 – 0.74 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 173.8, 173.5, 172.2, 51.2, 35.1, 31.3, 30.4, 29.1, 29.0, 29.0, 29.0, 28.8, 28.7, 28.6, 26.6, 25.3, 22.1, 14.0. HRMS(ESI-Q-TOF)*m*/*z* $[M-H]^-$ calculated for: 384.2755, found: 384.2746.

N-Decanoyl iminodiacetic acid (**C_{10}IDA**, **4a**) was prepared according to the general procedure using iminodiacetic acid (1.00 g, 7.51 mmol) and decanoyl chloride (1.79 mL, 8.64 mmol). The compound was isolated as a white solid (1.77 g, 6.16 mmol, 82%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 12.68 (s, 2H), 4.14 (s, 2H), 3.95 (s, 2H), 2.21 (t, J = 7.4 Hz, 2H), 1.54 – 1.38 (m, 2H), 1.37 – 1.00 (m, 12H), 0.98 – 0.63 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 172.9, 171.1, 170.8, 49.9, 48.2, 31.7, 31.3, 28.9, 28.9, 28.7, 28.6, 24.5, 22.1, 14.0. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for $C_{14}H_{25}NO_5$: 286.1660, found: 286.1664.

N-Lauroyl iminodiacetic acid (**C_{12}IDA**, **4b**) was prepared according to the general procedure using iminodiacetic acid (1.00 g, 7.51 mmol) and lauroyl chloride (2.08 mL, 8.64 mmol). The compound was isolated as a white solid (2.22 g, 7.04 mmol, 94%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 3.89 (s, 2H), 3.80 (s, 2H), 2.12 (t, J = 7.4 Hz, 2H), 1.52 – 1.37 (m, 2H), 1.35 – 1.09 (m, 16H), 0.96 – 0.77 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 173.0, 172.8, 172.4, 54.9, 53.7, 31.9, 31.3, 29.0, 29.0, 29.0, 28.9, 28.7, 24.3, 22.1, 14.0. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for $C_{16}H_{29}NO_5$: 314.1973, found: 314.1980.

N-Myristoyl iminodiacetic acid (**C_{14}IDA**, **4c**) was prepared according to the general procedure using iminodiacetic acid (1.00 g, 7.51 mmol) and myristoyl chloride (2.35 mL,8.64 mmol). The compound was isolated as a white solid (2.01 g, 5.85 mmol, 78%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 14.22 (s, 2H), 4.03 (s, 2H), 3.88 (s, 2H), 2.17 (t, J = 7.3 Hz, 2H), 1.51 – 1.37 (m, 2H),

1.39 – 0.96 (m, 20H), 0.94 – 0.74 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 172.9, 171.8, 171.5, 52.1, 50.5, 31.8, 31.3, 29.1, 29.0, 29.0, 28.9, 28.7, 28.7, 24.4, 22.1, 14.0. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for $C_{18}H_{33}NO_5$: 342.2286, found: 342.2277.

N-Palmitoyl iminodiacetic acid (**C_{16}IDA**, **4d**) was prepared according to the general procedure using iminodiacetic acid (1.00 g, 7.51 mmol) and palmitoyl chloride (2.62 mL, 8.64 mmol). The compound was isolated as a white solid (1.84 g, 4.95 mmol, 66%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 12.63 (s, 1H), 4.14 (s, 2H), 3.95 (s, 2H), 2.21 (t, J = 7.4 Hz, 2H), 1.52 – 1.42 (m, 2H), 1.28 – 1.16 (m, 24H), 0.94 – 0.76 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 172.9, 171.1, 170.8, 50.0, 48.2, 31.7, 31.3, 29.1, 29.1, 29.0, 29.0, 28.9, 28.7, 28.6, 24.5, 22.1, 14.0. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for $C_{20}H_{37}NO_5$: 370.2599, found: 370.2599.

O-Decanoyl malic acid (**C_{10}Mal**, **5a**) was prepared according to the general procedure using malic acid (1.00 g, 7.46 mmol) and decanoyl chloride (3.10 mL, 14.9 mmol). The compound was isolated as a white solid (1.81 g, 6.28 mmol, 84%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 12.87 (s, 2H), 5.20 (dd, J = 8.6, 4.0 Hz, 1H), 2.81 (dd, J = 16.6, 4.0 Hz, 1H), 2.69 (dd, J = 16.7, 8.7 Hz, 1H), 2.31 (t, J = 7.3 Hz, 2H), 1.58 – 1.45 (m, 2H), 1.24 (s, 12H), 0.96 – 0.78 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 172.2, 170.6, 170.2, 68.3, 35.8, 33.2, 31.3, 28.9, 28.7, 28.7, 28.3, 24.4, 22.1, 14.0. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for: 287.1500, found $C_{14}H_{24}O_6$: 287.1492.

O-Lauroyl L-malic acid (**C_{12}Mal**, **5b**) was prepared according to the general procedure using malic acid (1.00 g, 7.46 mmol) and lauroyl chloride (3.45 mL, 14.9 mmol). The compound was isolated as a white solid (1.91 g, 6.08 mmol, 81%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 12.84 (s, 2H), 5.20 (dd, J = 8.6, 4.0 Hz, 1H), 2.81 (dd, J = 16.6, 4.0 Hz, 1H), 2.69 (dd, J = 16.6, 8.7 Hz, 1H), 2.31 (t, J = 7.3 Hz, 2H), 1.58 – 1.45 (m, 2H), 1.38 – 1.15 (m, 16H), 0.92 – 0.79 (m, 3H). ^{13}C-NMR

(101 MHz, DMSO-d_6): (δ) ppm, 172.2, 170.6, 170.2, 68.3, 35.7, 33.2, 31.3, 29.0, 28.9, 28.7, 28.7, 28.3, 24.4, 22.1, 14.0. HRMS (ESI-Q-TOF) *m*/*z* [M−H]$^-$ calculated for: 315.1813, found $C_{16}H_{28}O_6$: 315.1818.

O-Myristoyl L-malic acid (**C_{14}Mal**, **5c**) was prepared according to the general procedure using malic acid (1.00 g, 7.46 mmol) and myristoyl chloride (4.05 mL, 14.9 mmol). The compound was isolated as a white solid (1.82 g, 5.29 mmol, 71%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 12.87 (s, 2H), 5.20 (dd, J = 8.6, 4.0 Hz, 1H), 2.81 (dd, J = 16.6, 4.0 Hz, 1H), 2.69 (dd, J = 16.6, 8.7 Hz, 1H), 2.31 (t, J = 7.3 Hz, 2H), 1.60 – 1.45 (m, 2H), 1.36 – 1.10 (m, 20H), 0.94 – 0.77 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 172.2, 170.6, 170.2, 68.3, 35.7, 33.2, 31.3, 29.1, 29.1, 29.0, 29.0, 28.9, 28.7, 28.7, 28.3, 24.4, 22.1, 14.0. HRMS (ESI-Q-TOF) *m*/*z* [M−H]$^-$ calculated for $C_{18}H_{32}O_6$: 343.2126, found: 343.2112.

O-Palmitoyl L-malic acid (**C_{16}Mal**, **5d**) was prepared according to the general procedure using malic acid (1.00 g, 7.46 mmol) and palmitoyl chloride (4.53 mL, 14.9 mmol). The compound was isolated as a white solid (1.70 g, 4.56 mmol, 61%). ^{1}H-NMR (400 MHz, DMSO-d_6): (δ) ppm, 12.86 (s, 2H), 5.20 (dd, J = 8.7, 4.0 Hz, 1H), 2.81 (dd, J = 16.7, 4.0 Hz, 1H), 2.69 (dd, J = 16.7, 8.7 Hz, 1H), 2.31 (t, J = 7.3 Hz, 2H), 1.63 – 1.45 (m, 2H), 1.34 – 1.14 (m, 24H), 0.93 – 0.76 (m, 3H). ^{13}C-NMR (101 MHz, DMSO-d_6): (δ) ppm, 172.2, 170.6, 170.2, 68.3, 35.7, 33.2, 31.3, 29.1, 29.0, 29.0, 29.0, 28.9, 28.7, 28.7, 28.3, 24.4, 22.1, 14.0. HRMS (ESI-Q-TOF) *m*/*z* [M−H]$^-$ calculated for: 371.2439, found $C_{20}H_{36}O_6$: 371.2432.

O-Decanoyl citric acid (**C_{10}Cit**, **6a**) was prepared according to the general procedure using citric acid (1.00 g, 5.21 mmol) and decanoyl chloride (2.16 mL, 10.4 mmol). The compound was isolated as a white solid (1.13 g, 3.27 mmol, 71%). ^{1}H-NMR (400 MHz, acetone-d_6): (δ) ppm, 3.58 – 3.22

(m, 4H), 2.43 (t, J = 7.4 Hz, 2H), 1.66 – 1.56 (m, 2H), 1.36 – 1.26 (m, 12H), 0.97 – 0.83 (m, 3H). ^{13}C-NMR (101 MHz, acetone-d_6): (δ) ppm, 174.0, 172.1, 170.9, 168.8, 77.9, 40.8, 39.6, 33.9, 32.6, 30.1, 30.0, 29.9, 29.8, 29.5, 25.2, 23.3, 14.3. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for $C_{16}H_{26}O_8$: 345.1555, found: 345.1555.

O-Lauroyl citric acid (**C_{12}Cit**, **6b**) was prepared according to the general procedure using citric acid (1.00 g, 5.21 mmol) and lauroyl chloride (2.41 mL, 10.4 mmol). The compound was isolated as a white solid (1.32 g, 3.53 mmol, 68%).). ^{1}H-NMR (400 MHz, acetone-d_6): (δ) ppm, 3.59 – 3.21 (m, 4H), 2.43 (t, J = 7.4 Hz, 2H), 1.70 – 1.53 (m, 2H), 1.39 – 1.23 (m, 16H), 0.97 – 0.81 (m, 3H). ^{13}C-NMR (101 MHz, acetone-d_6): (δ) ppm, 174.0, 172.1, 170.9, 168.7, 77.9, 40.8, 39.6, 33.9, 32.6, 30.3, 30.3, 30.1, 30.1, 29.9, 29.5, 25.2, 23.3, 14.4. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for $C_{18}H_{30}O_8$: 373.1868, found: 373.1862.

O-Myristoyl citric acid (**C_{14}Cit**, **6c**) was prepared according to the general procedure using citric acid (1.00 g, 5.21 mmol) and myristoyl chloride (2.83 mL, 10.4 mmol). The compound was isolated as a white solid (1.67 g, 4.15 mmol, 80%). ^{1}H-NMR (400 MHz, acetone-d_6): (δ) ppm, 3.58 – 3.22 (m, 4H), 2.43 (t, J = 7.4 Hz, 2H), 1.67 – 1.56 (m, 2H), 1.36 – 1.23 (m, 20H), 0.94 – 0.80 (m, 3H). ^{13}C-NMR (101 MHz, acetone-d_6): (δ) ppm, 174.0, 172.1, 170.9, 168.7, 77.9, 40.8, 39.6, 33.9, 32.6, 30.4, 30.4, 30.3, 30.1, 30.1, 29.9, 29.5, 25.2, 23.3, 14.4. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for $C_{20}H_{34}O_8$: 401.2181, found: 401.2174.

O-Palmitoyl citric acid (**C_{16}Cit**, **6d**) was prepared according to the general procedure using citric acid (1.00 g, 5.21 mmol) and palmitoyl chloride (3.16 mL, 10.4 mmol). The compound was isolated as a white solid (1.79 g, 4.16 mmol, 80%). ^{1}H-NMR (400 MHz, acetone-d_6): (δ) ppm, 3.58 – 3.22 (m, 4H), 2.43 (t, J = 7.4 Hz, 2H), 1.61 (t, J = 7.2 Hz, 2H), 1.37 – 1.22 (m, 24H), 0.94 – 0.83 (m,

3H). ^{13}C-NMR (101 MHz, acetone-d_6): (δ) ppm, 174.0, 172.1, 170.9, 168.7, 77.9, 40.8, 39.6, 33.9, 32.6, 30.4, 30.4, 30.3, 30.2, 30.1, 29.9, 29.5, 25.2, 23.3, 14.4. HRMS (ESI-Q-TOF) *m*/*z* $[M-H]^-$ calculated for $C_{22}H_{38}O_8$: 429.2494, found: 429.2483.

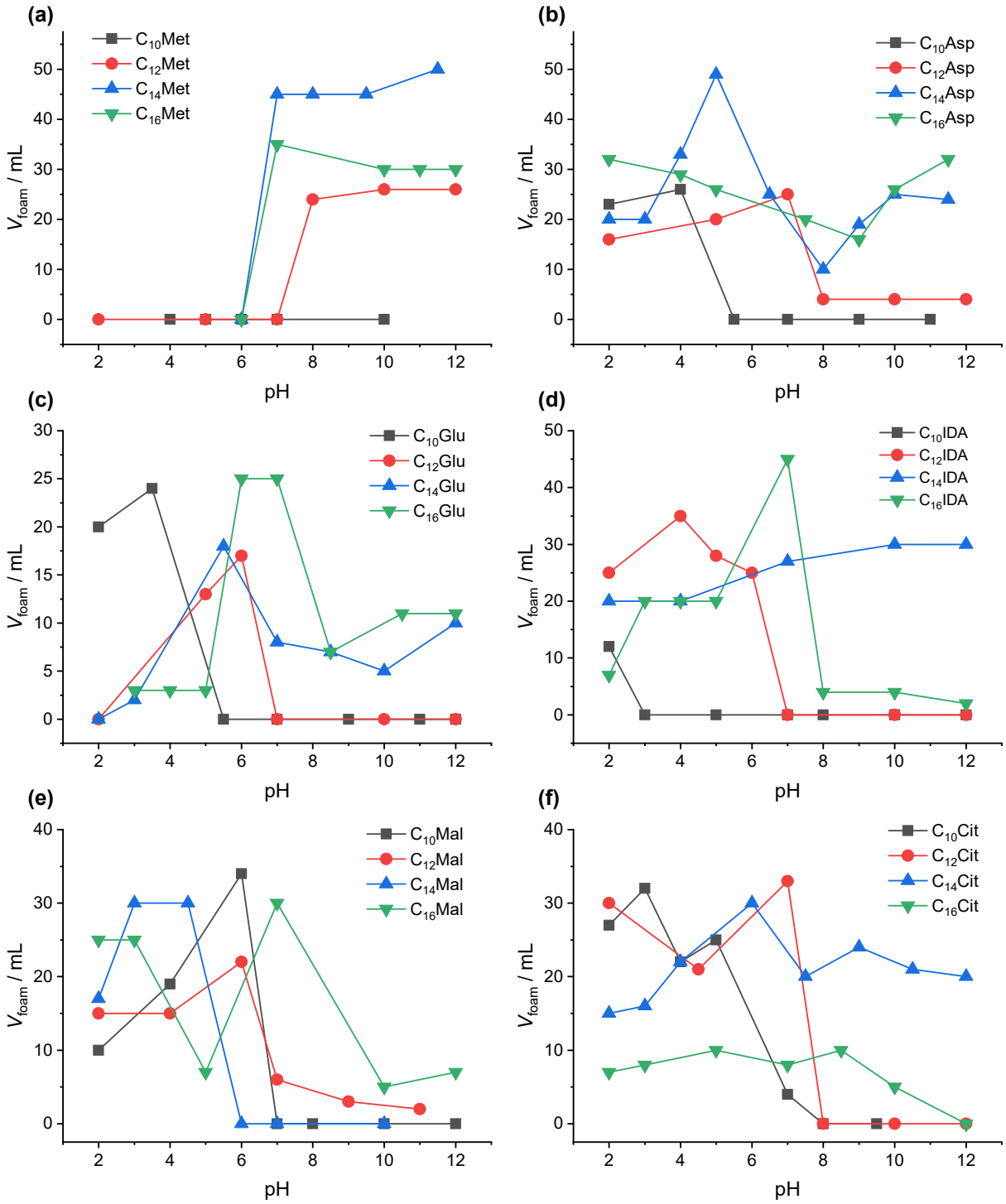


Figure S1. Volume of stable foam formed across the studied pH range for each surfactant (40 mL solutions, 0.1% w/v) as determined by the Bartsch method in a 100 mL volumetric cylinder at room temperature.

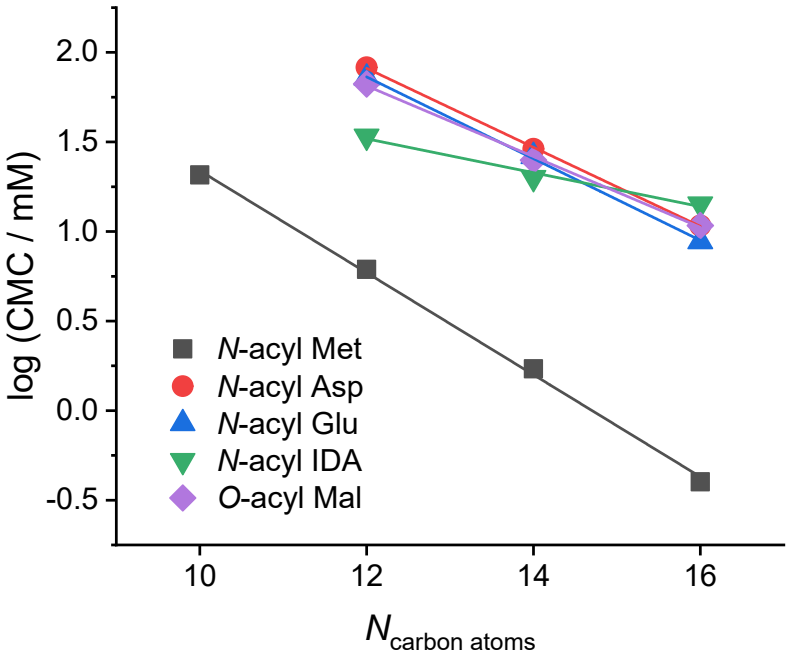


Figure S2. Logarithm of CMC values as a function of the number of carbon atoms in the hydrophobic moiety of the prepared surfactants. Symbols represent experimental data, while lines represent a linear fit.

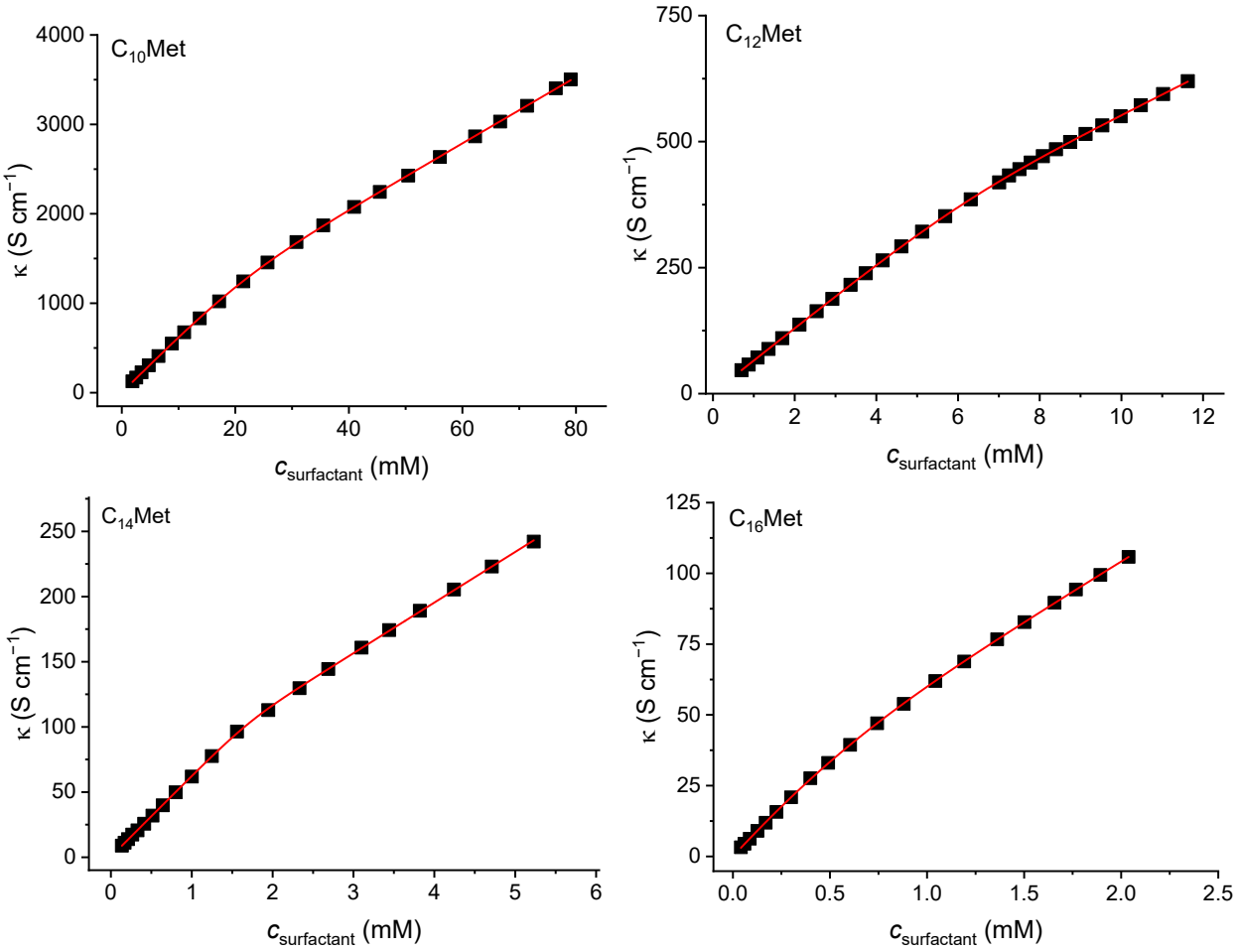


Figure S3. Electrical conductivity as a function of surfactant concentration for the determination of CMC value of the prepared methionine surfactants at room temperature. The compound abbreviation is annotated in the upper left corner and corresponds to the fully deprotonated form isolated as a sodium salt (e.g. C_{10}MetNa). See main text Figure 1 for the molecular structure. ■ experimental data, — curves of the best fit, determined by the method of Carpena and co-workers.[2]

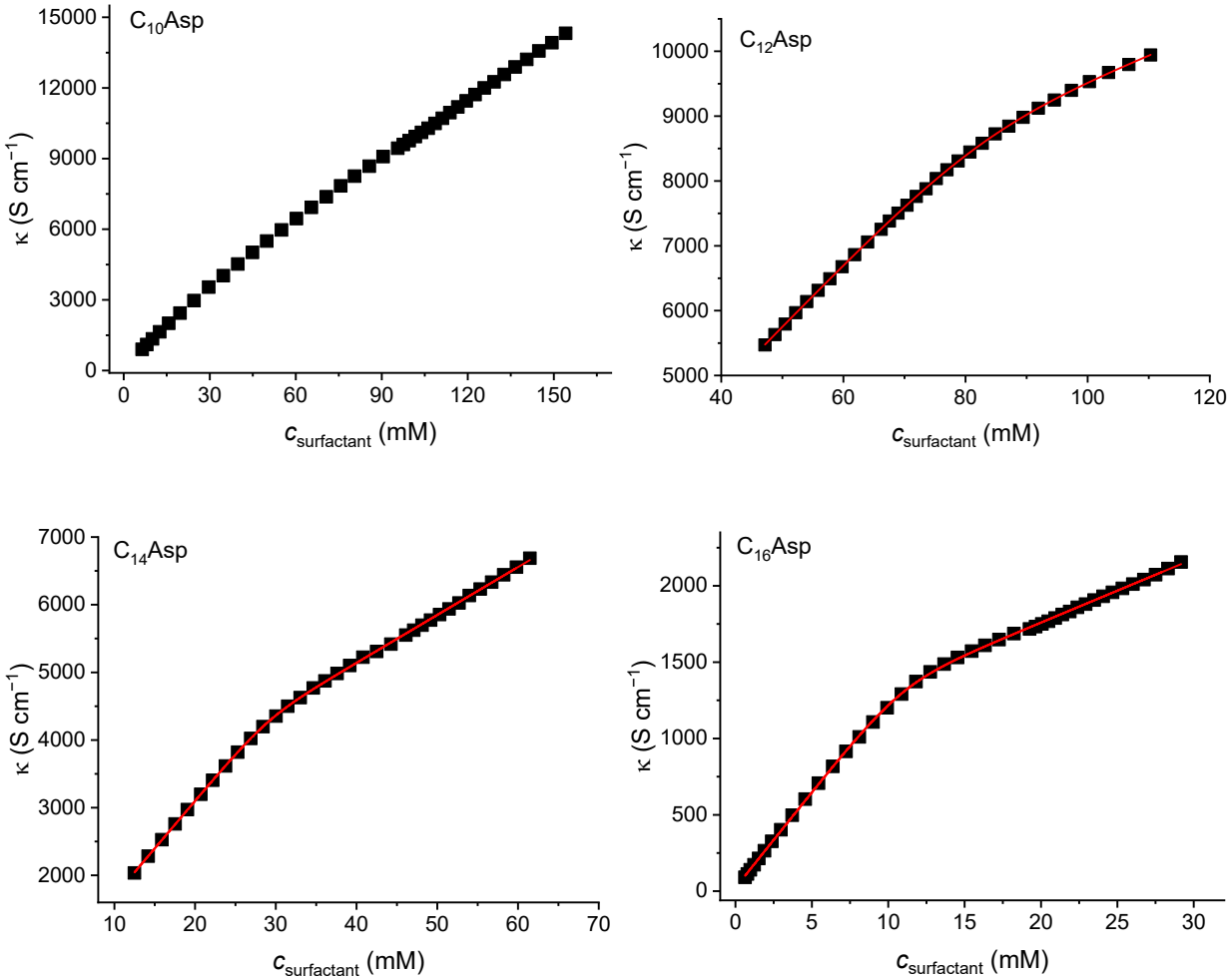


Figure S4. Electrical conductivity as a function of surfactant concentration for the determination of CMC value of the prepared aspartic acid surfactants at room temperature. The compound abbreviation is annotated in the upper left corner and corresponds to the fully deprotonated form isolated as a sodium salt (e.g. $C_{10}AspNa_2$). See main text Figure 1 for the molecular structure. ■ experimental data, — curves of the best fit, determined by the method of Carpena and co-workers.[2]

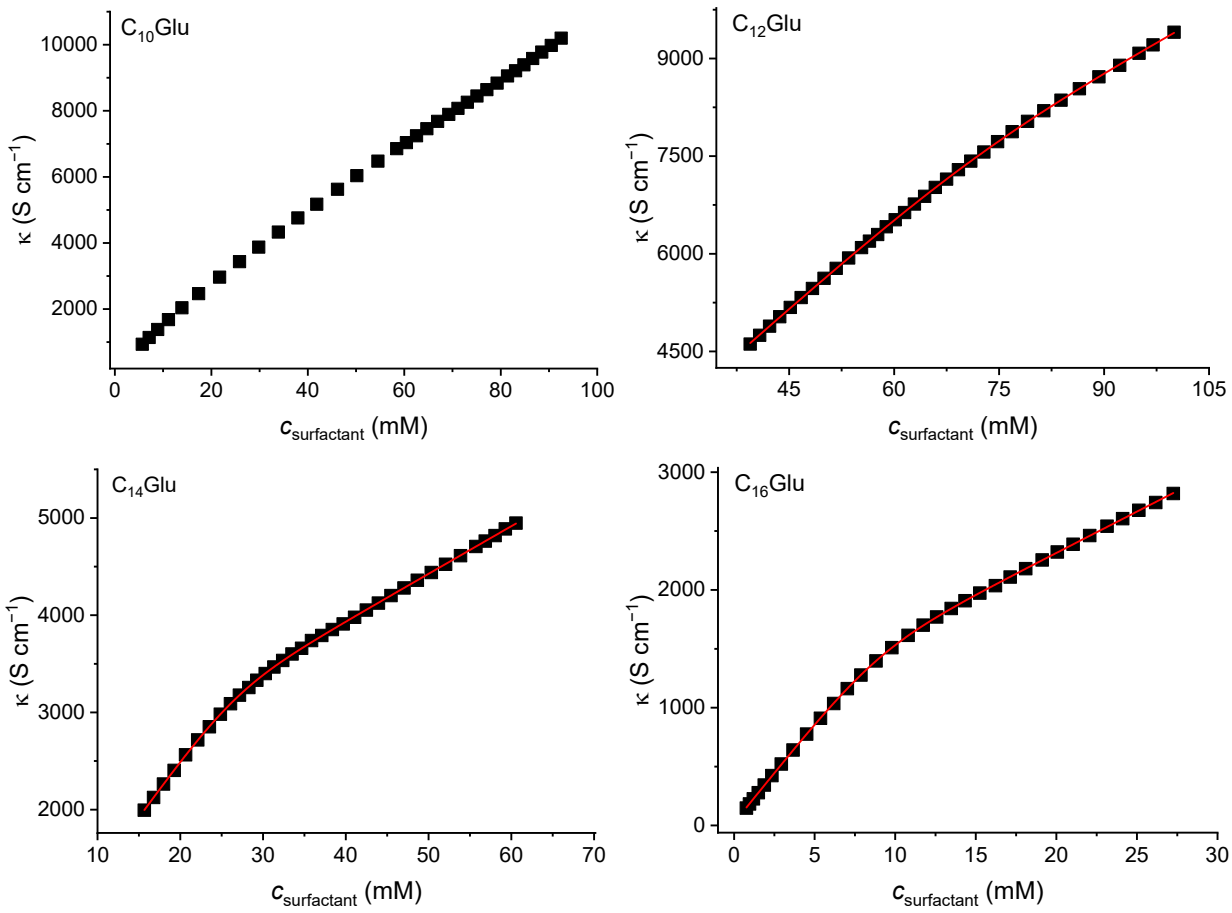


Figure S5. Electrical conductivity as a function of surfactant concentration for the determination of CMC value of the prepared glutamic acid surfactants at room temperature. The compound abbreviation is annotated in the upper left corner and corresponds to the fully deprotonated form isolated as a sodium salt (e.g. $C_{10}GluNa_2$). See main text Figure 1 for the molecular structure. ■ experimental data, — curves of the best fit, determined by the method of Carpena and co-workers.[2]

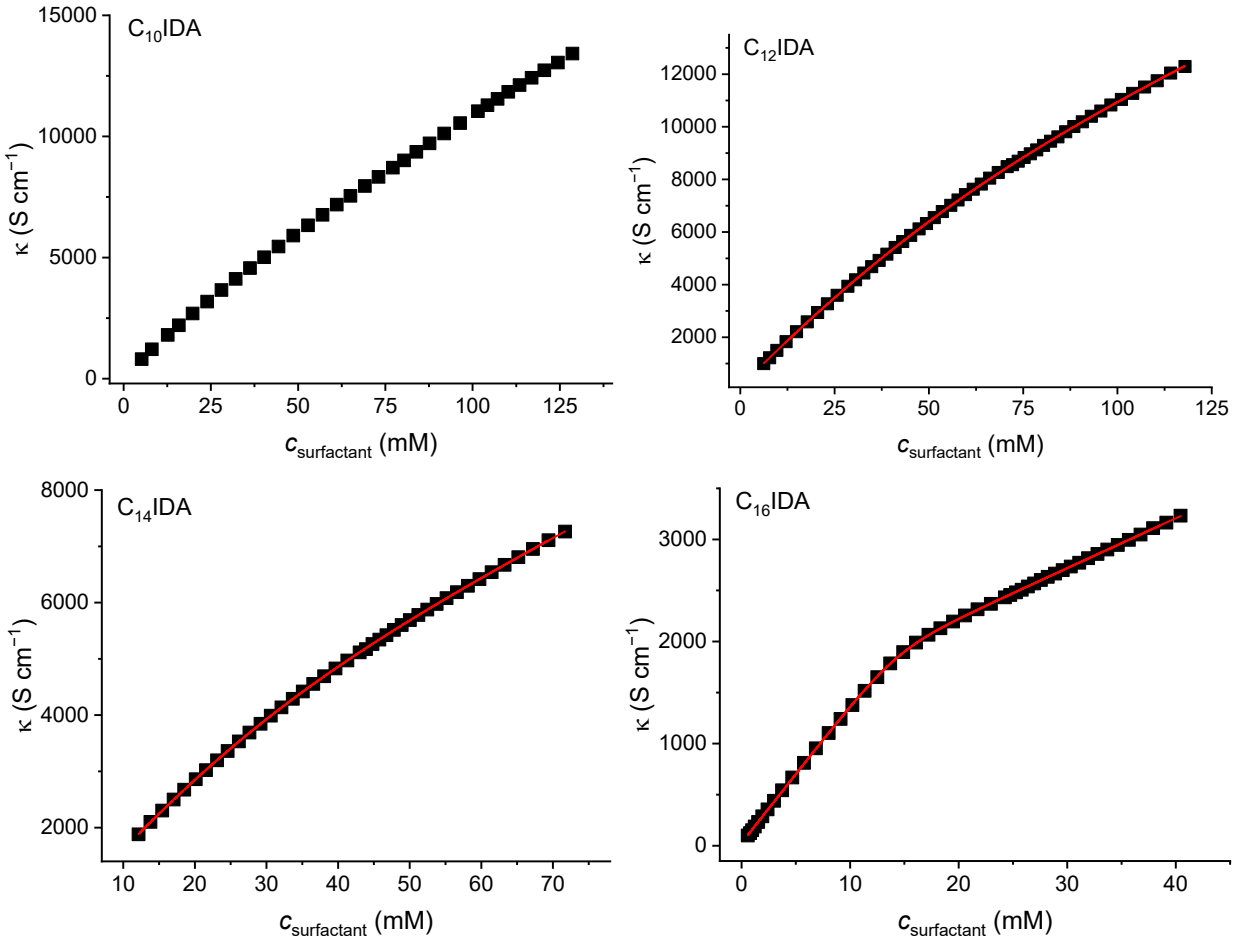


Figure S6. Electrical conductivity as a function of surfactant concentration for the determination of CMC value of the prepared iminodiacetic acid (IDA) surfactants at room temperature. The compound abbreviation is annotated in the upper left corner and corresponds to the fully deprotonated form isolated as a sodium salt (e.g. $C_{10}IDANa_2$). See main text Figure 1 for the molecular structure. ■ experimental data, — curves of the best fit, determined by the method of Carpena and co-workers.[2]

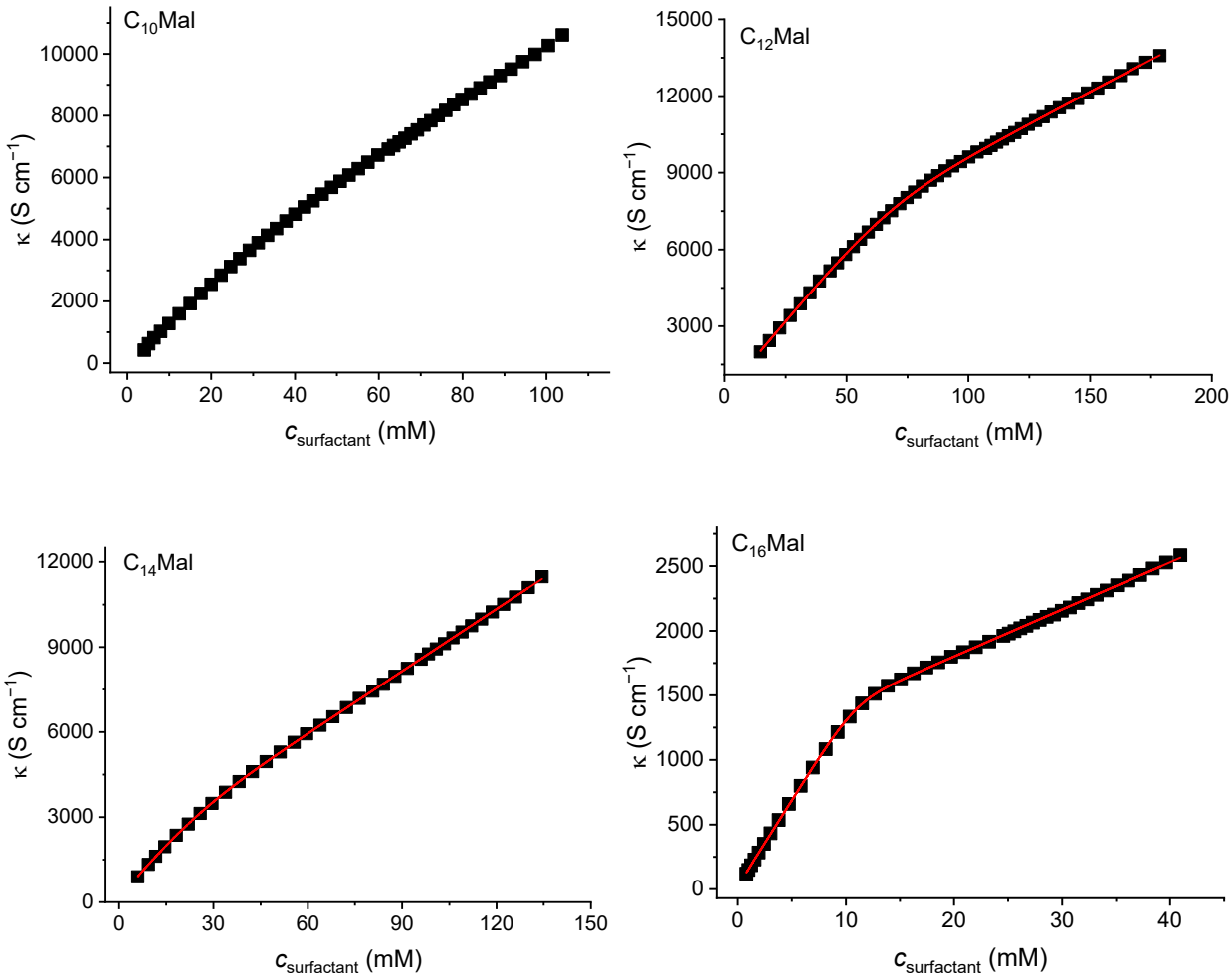


Figure S7. Electrical conductivity as a function of surfactant concentration for the determination of CMC value of the prepared malic acid surfactants at room temperature. The compound abbreviation is annotated in the upper left corner and corresponds to the fully deprotonated form isolated as a sodium salt (e.g. $C_{10}MalNa_2$). See main text Figure 1 for the molecular structure. ■ experimental data, — curves of the best fit, determined by the method of Carpena and co-workers.[2]

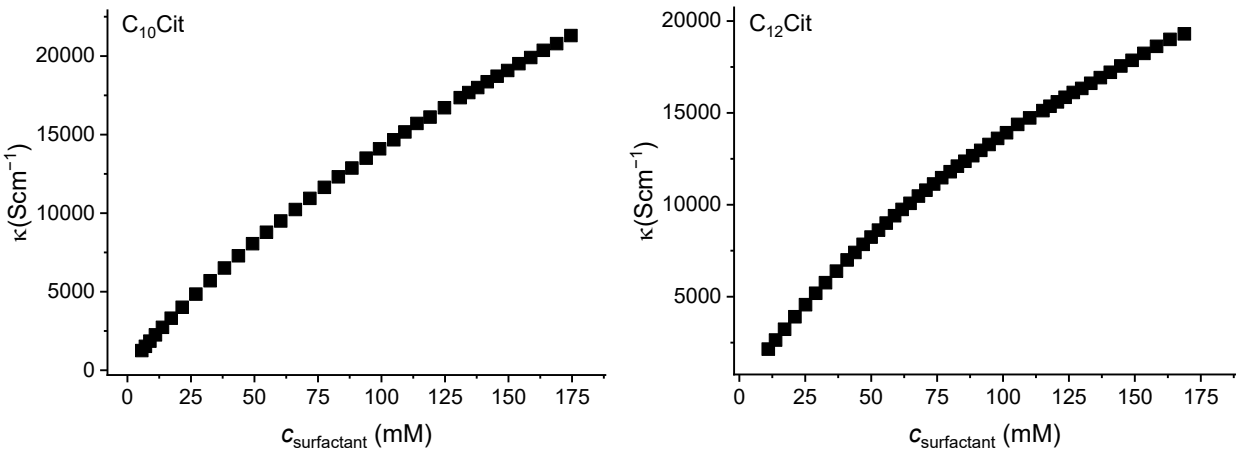


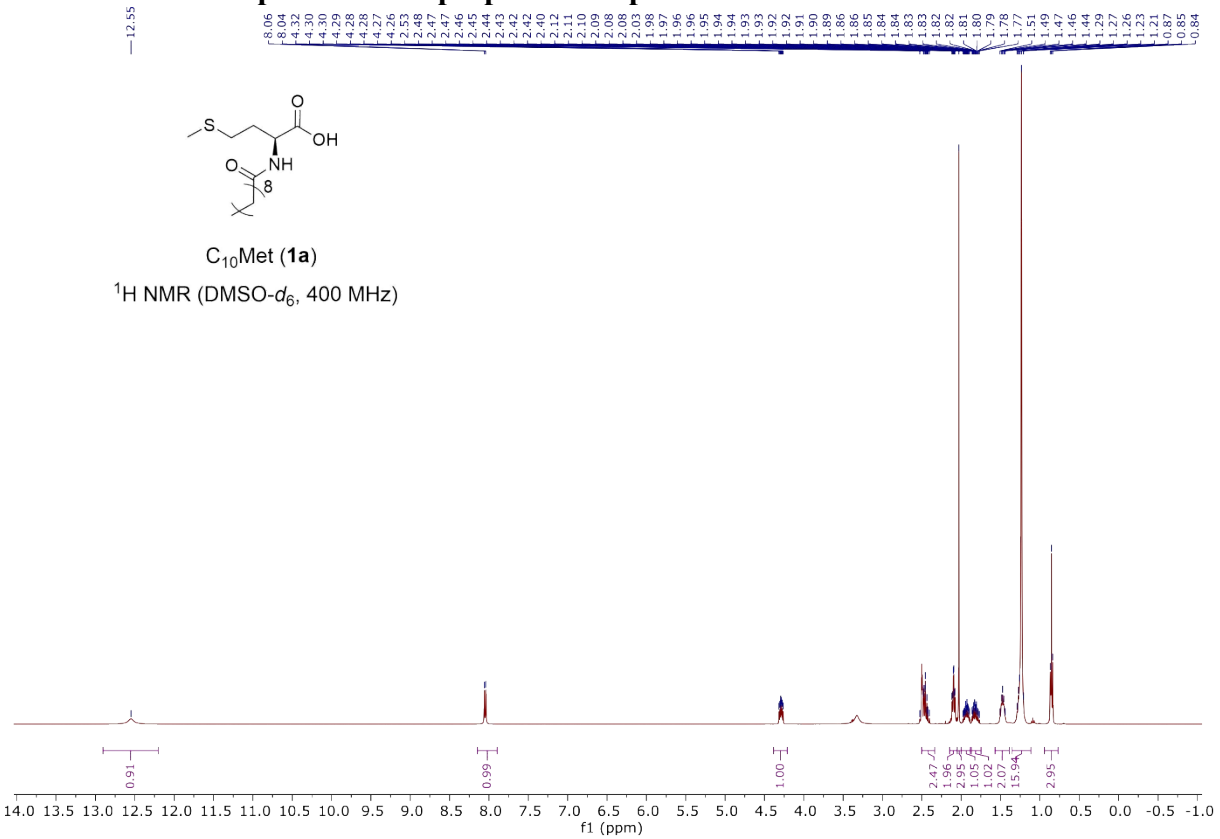
Figure S8. Electrical conductivity as a function of surfactant concentration for the determination of CMC value of the prepared citric acid surfactants at room temperature. The compound abbreviation is annotated in the upper left corner and corresponds to the fully deprotonated form isolated as a sodium salt (e.g. $C_{10}CitNa_3$). See main text Figure 1 for the molecular structure. ■ experimental data.

References

1 D.-H. Pham, B. De Roo, X.-B. Nguyen, M. Vervaele, A. Kecskés, A. Ny, D. Copmans, H. Vriens, J.-P. Locquet, P. Hoet and P. A. M. de Witte, *Sci Rep*, 2016, **6**, 37145.

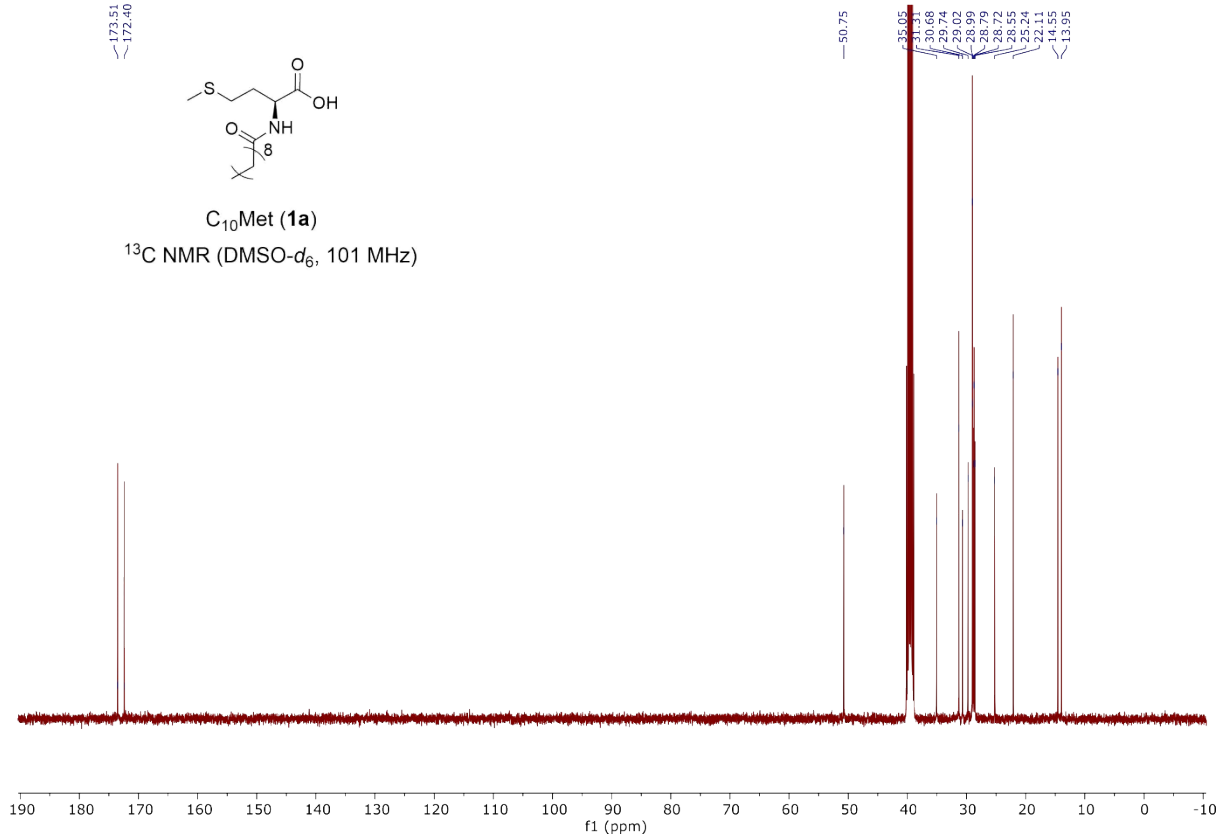
2 P. Carpena, J. Aguiar, P. Bernaola-Galván and C. Carnero Ruiz, *Langmuir*, 2002, **18**, 6054–6058.

^{1}H and ^{13}C NMR spectra of the prepared compounds



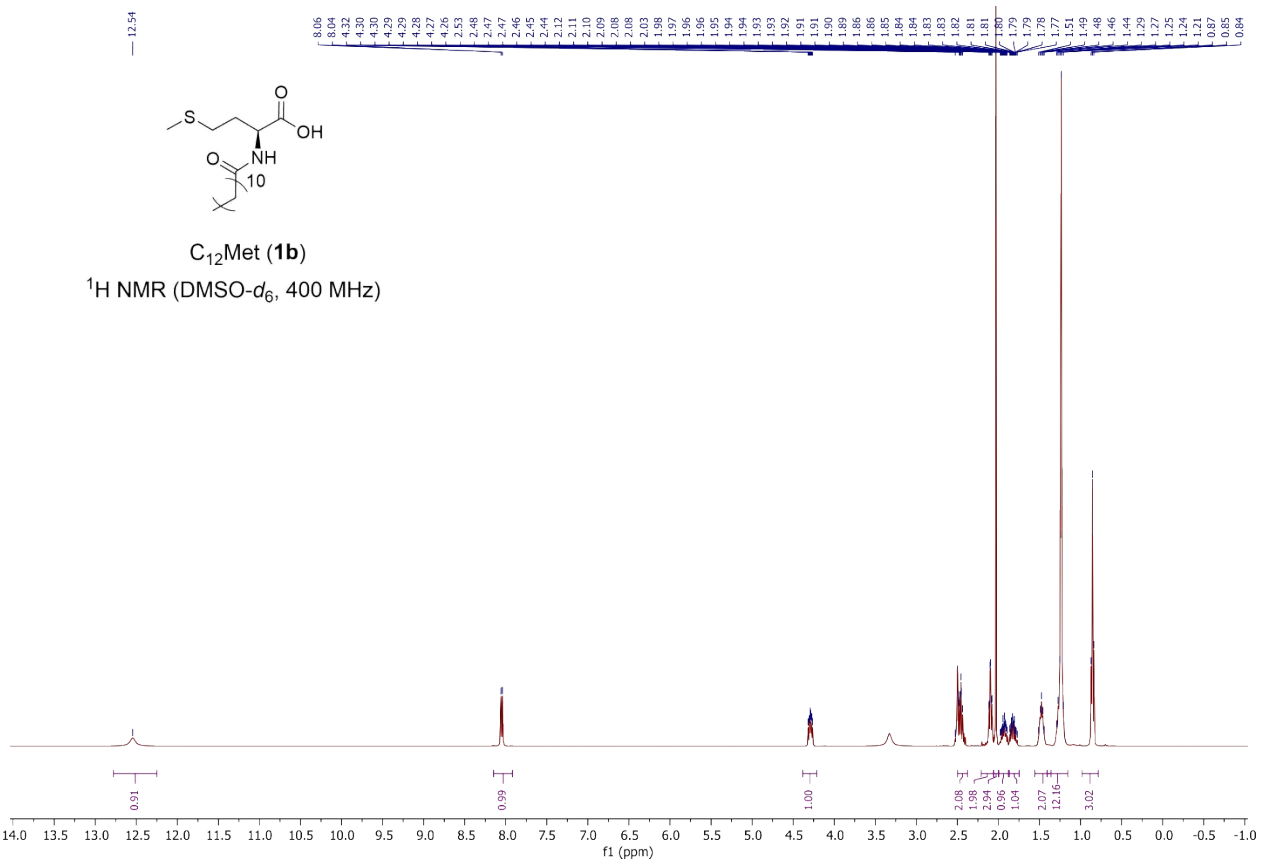
C_{10}Met (**1a**)

^{1}H NMR (DMSO-d_6, 400 MHz)



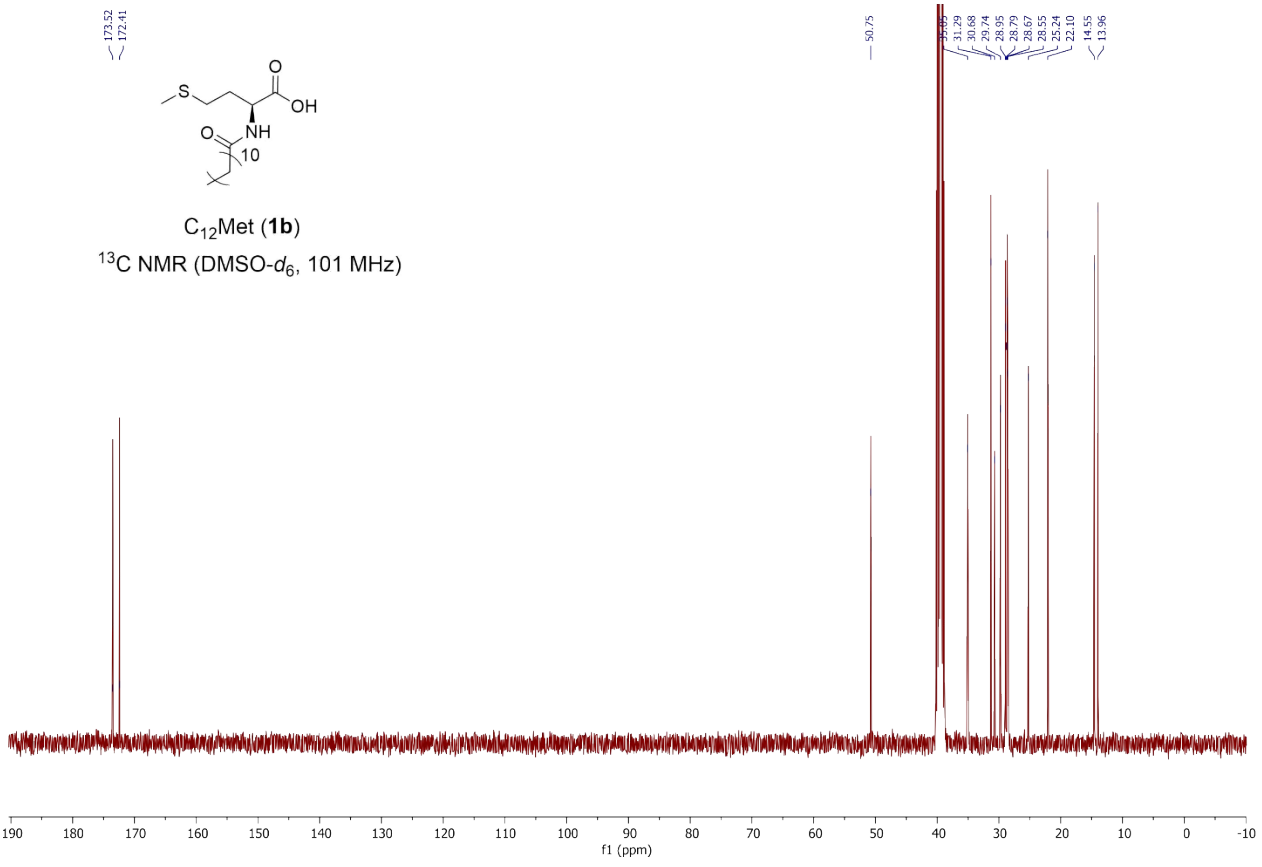
C_{10}Met (**1a**)

^{13}C NMR (DMSO-d_6, 101 MHz)



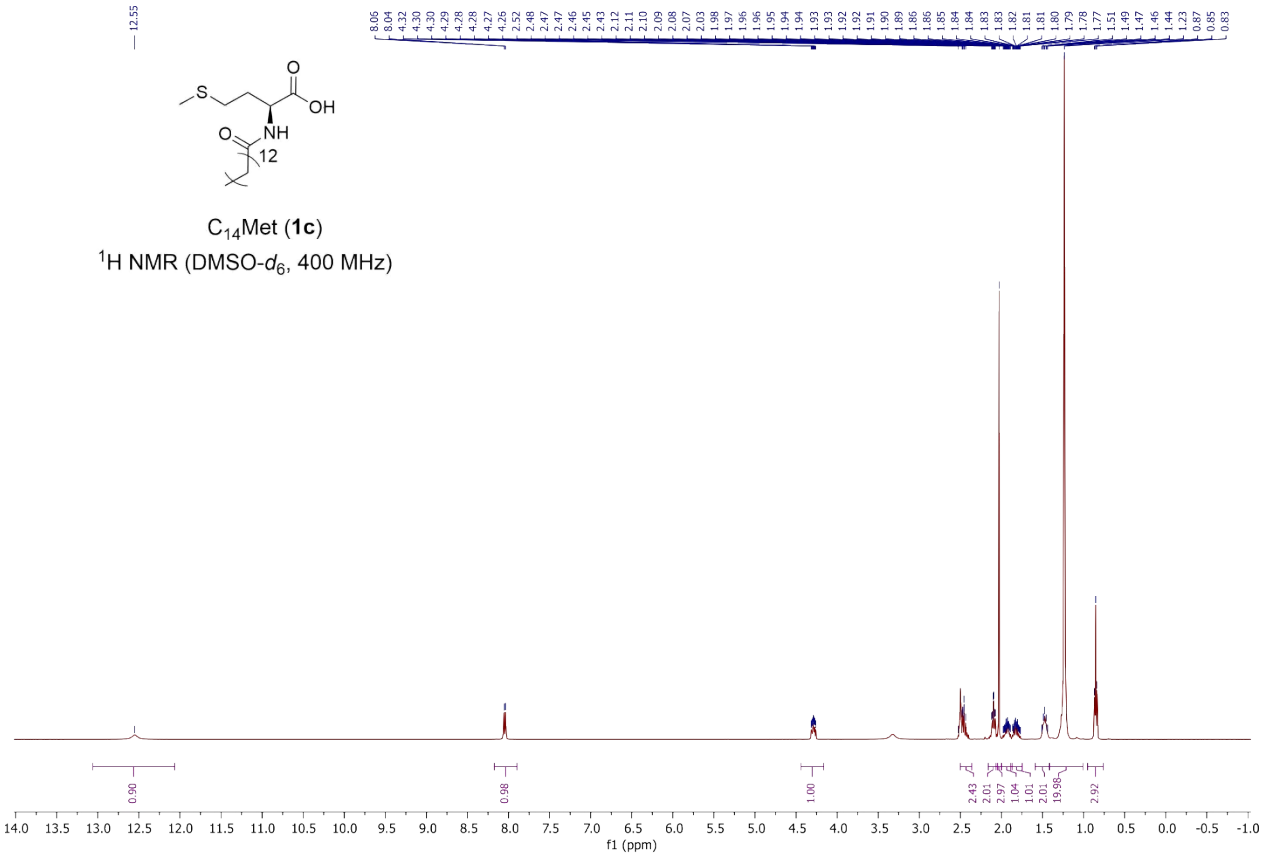
C_{12}Met (**1b**)

^{1}H NMR (DMSO-d_6, 400 MHz)



C_{12}Met (**1b**)

^{13}C NMR (DMSO-d_6, 101 MHz)



C_{14}Met (**1c**)

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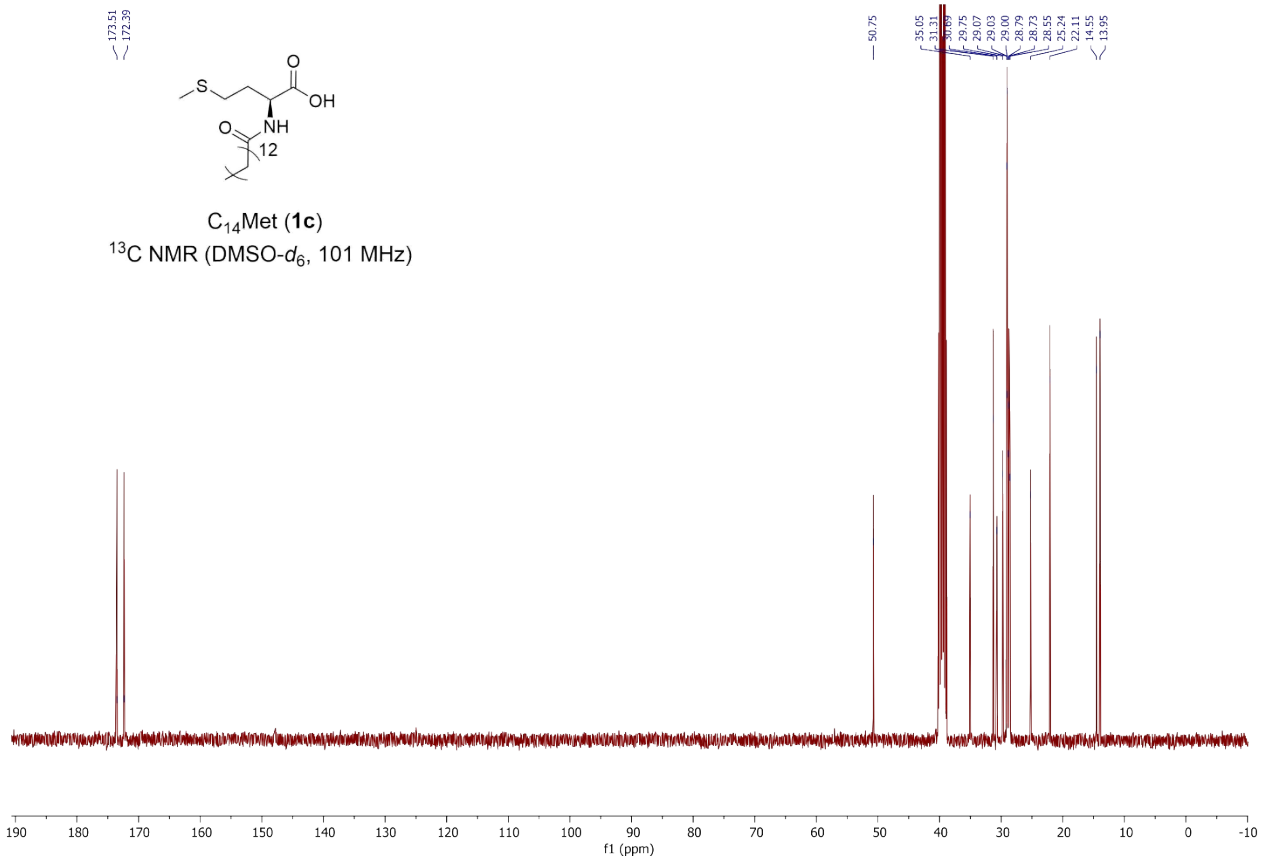
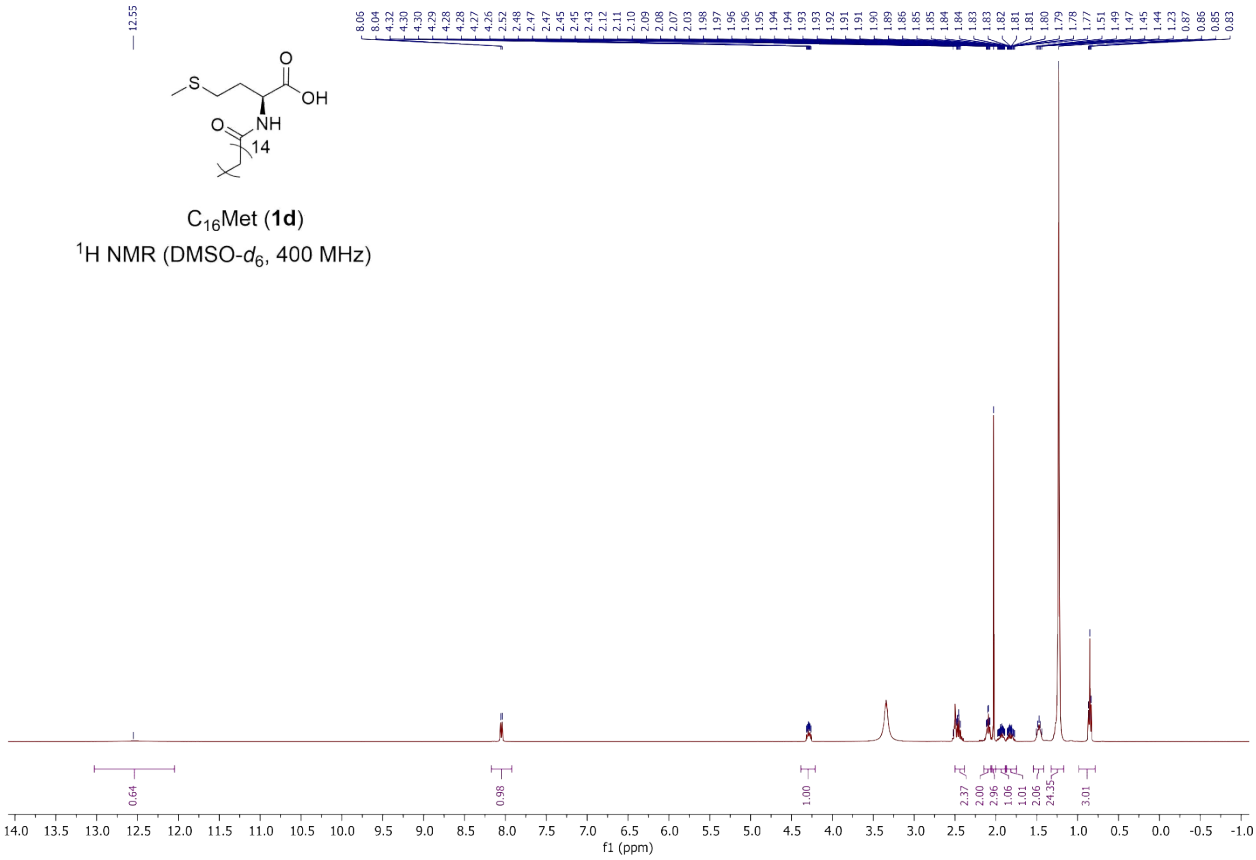


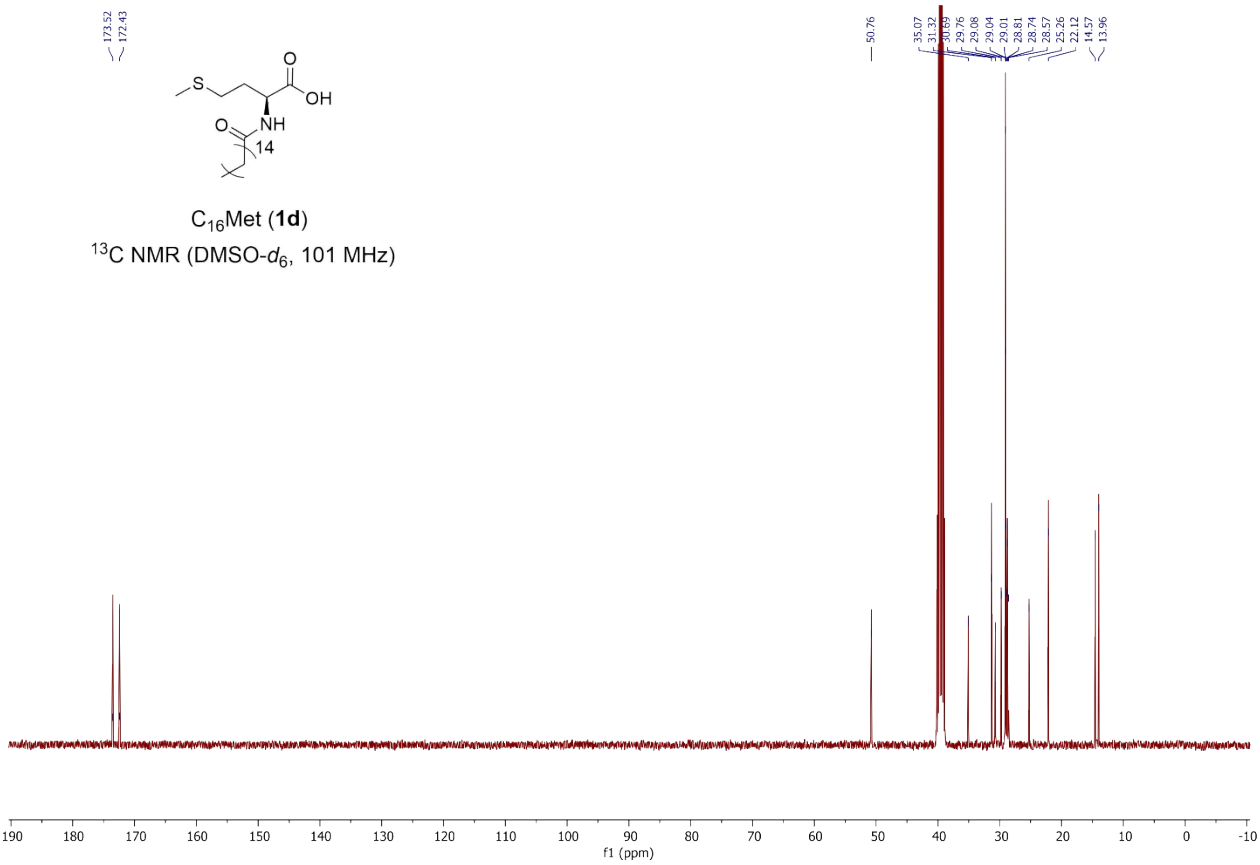
C_{14}Met (**1c**)

^{13}C NMR (DMSO-d_6, 101 MHz)



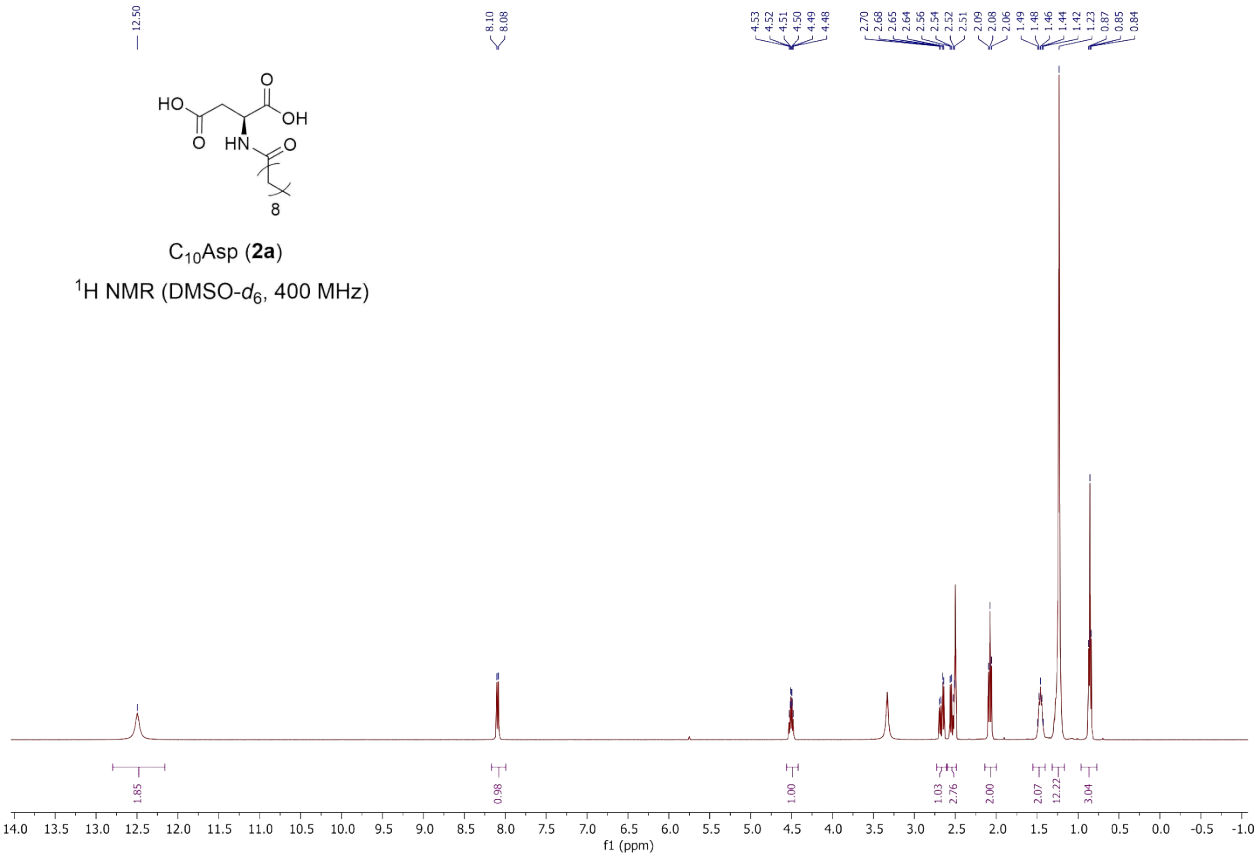
C_{16}Met (**1d**)

^{1}H NMR (DMSO-d_6, 400 MHz)



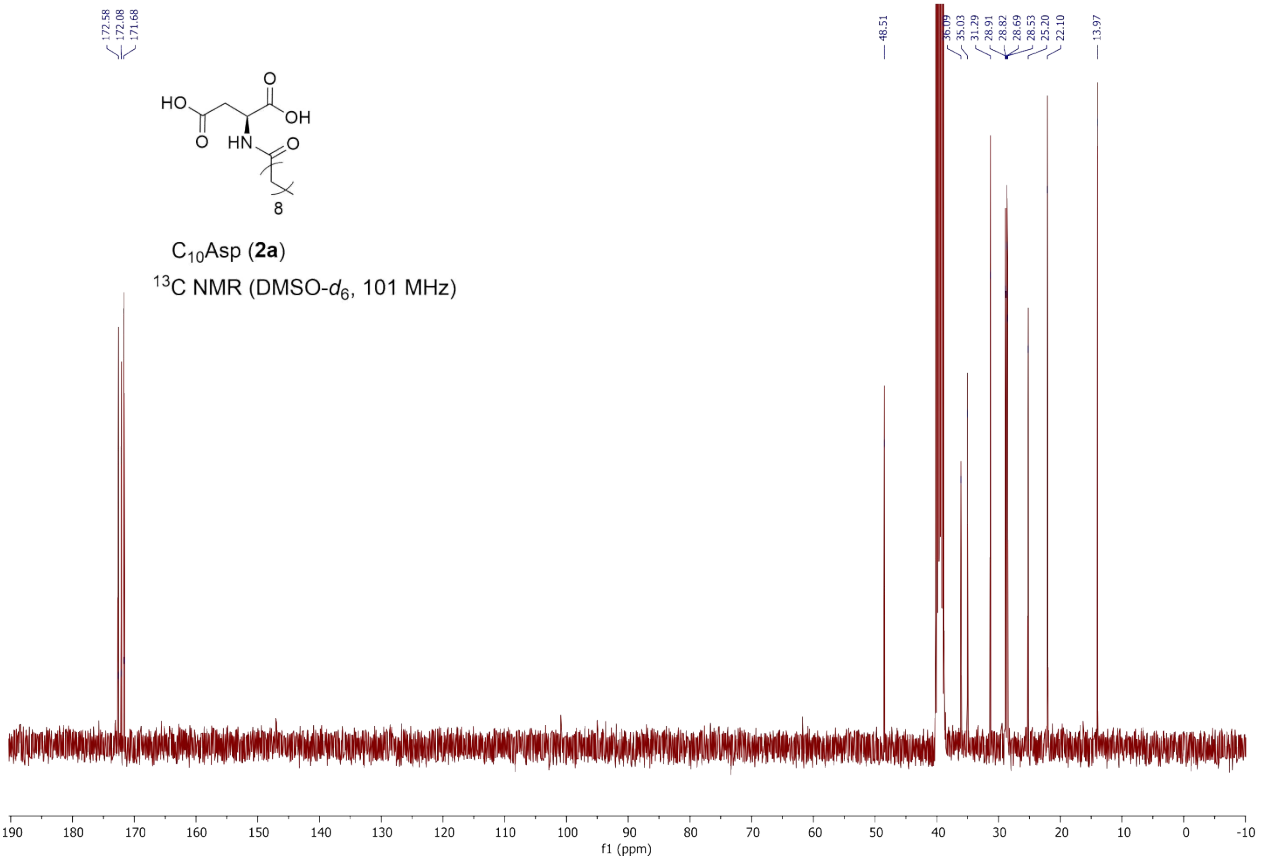
C_{16}Met (**1d**)

^{13}C NMR (DMSO-d_6, 101 MHz)



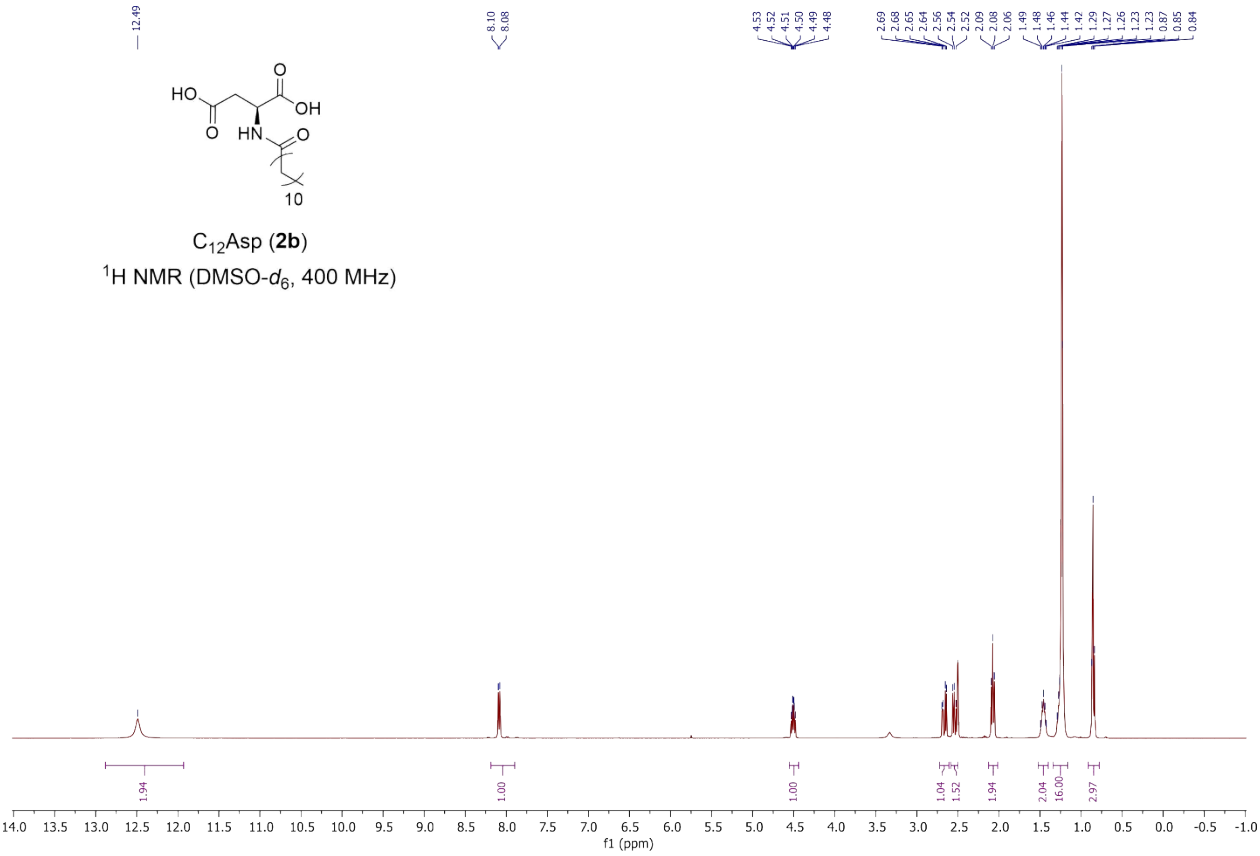
C_{10}Asp (**2a**)

^{1}H NMR (DMSO-d_6, 400 MHz)



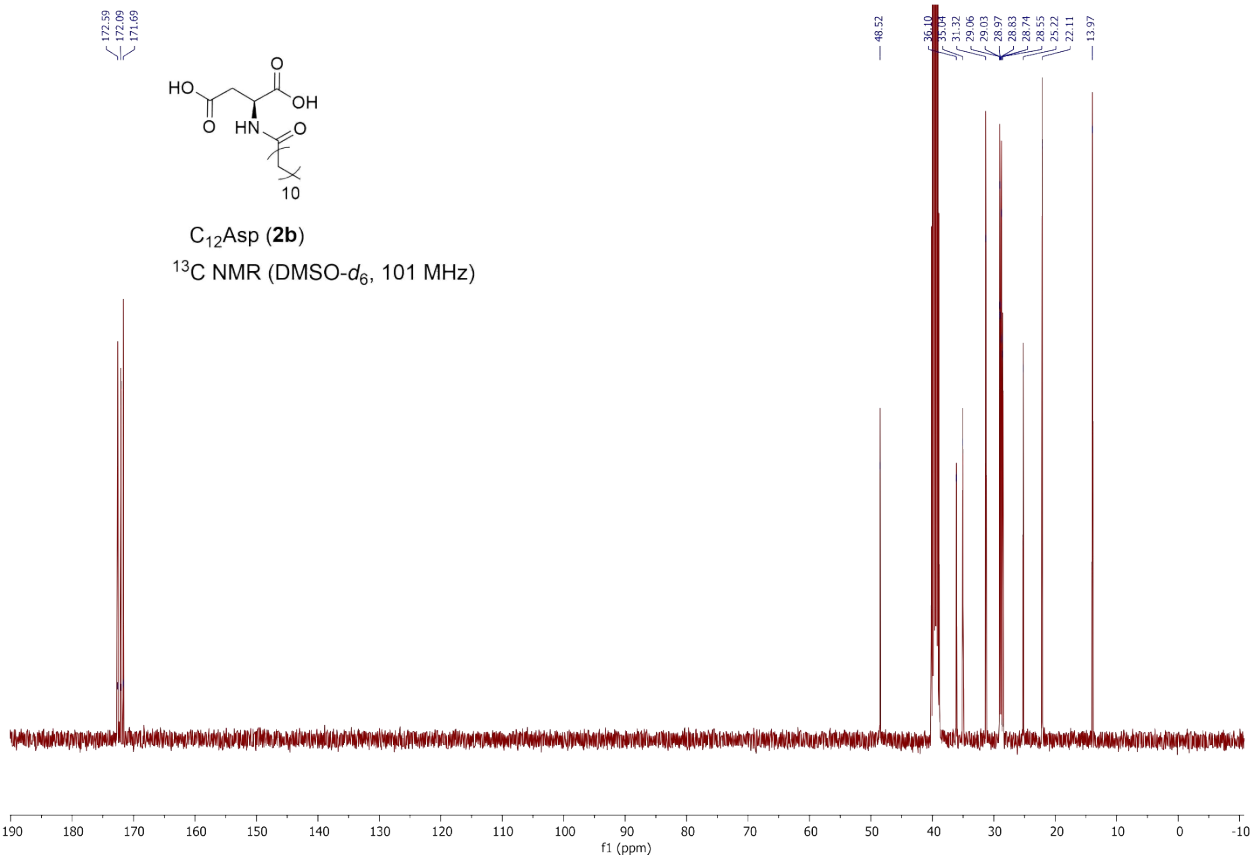
C_{10}Asp (**2a**)

^{13}C NMR (DMSO-d_6, 101 MHz)



C_{12}Asp (**2b**)

^{1}H NMR (DMSO-d_6, 400 MHz)



C_{12}Asp (**2b**)

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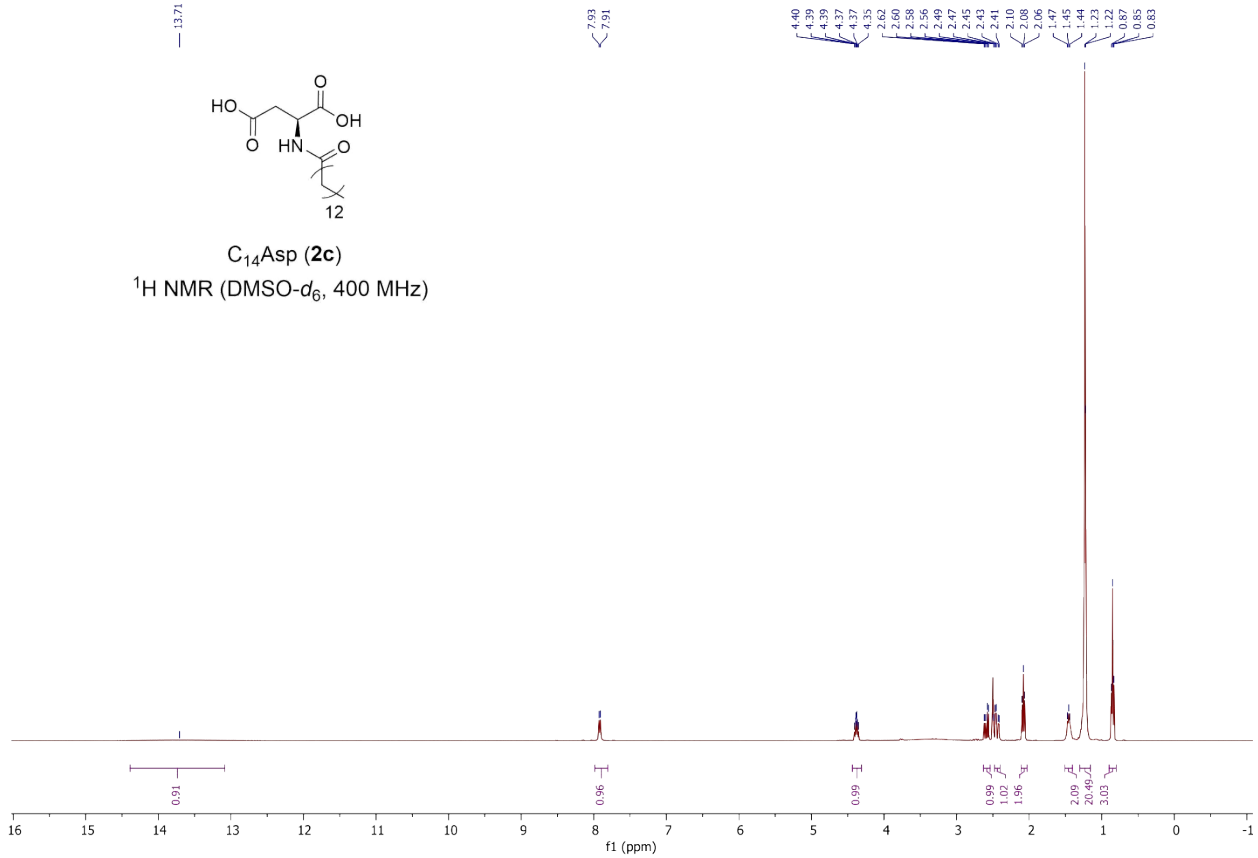

C_{14}Asp (**2c**)

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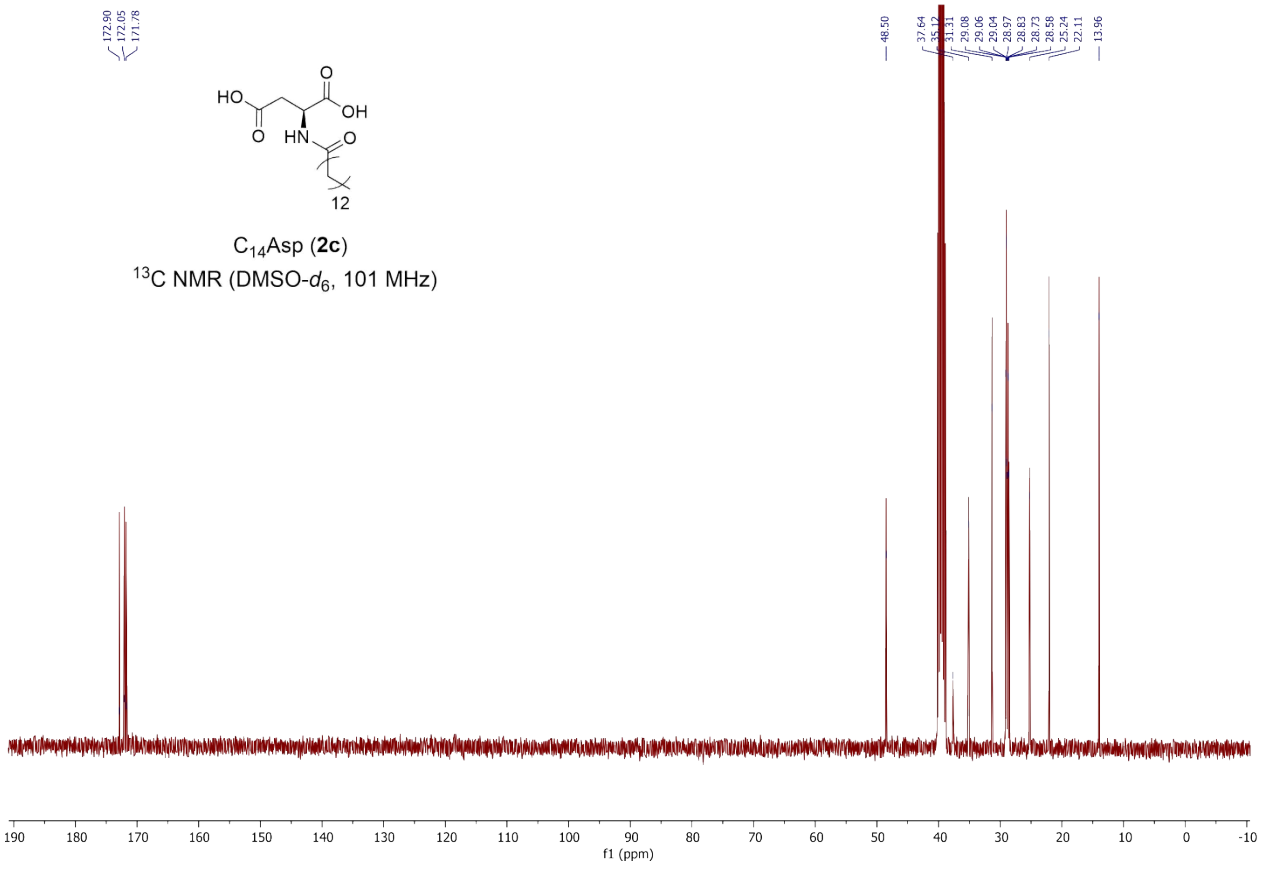
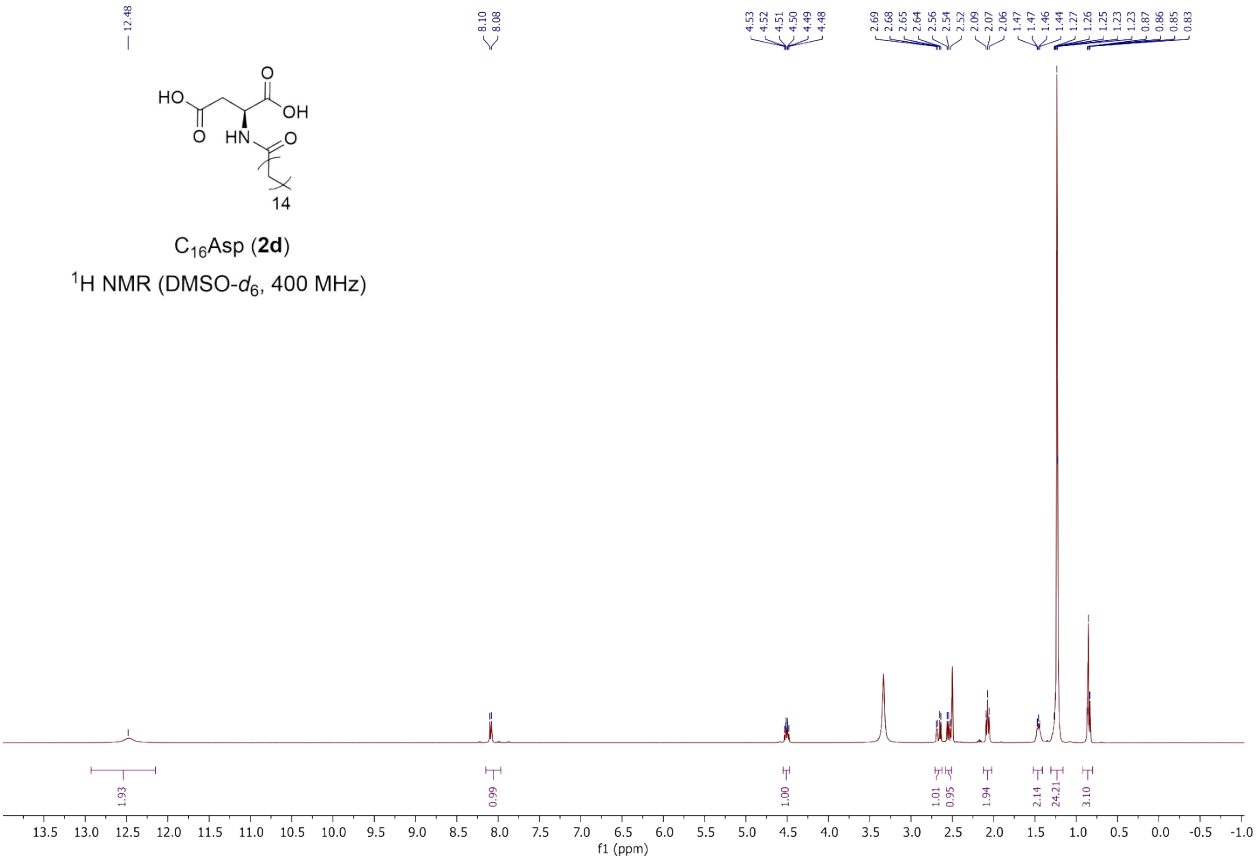


C_{14}Asp (**2c**)

^{13}C NMR (DMSO-d_6, 101 MHz)



C_{16}Asp (**2d**)

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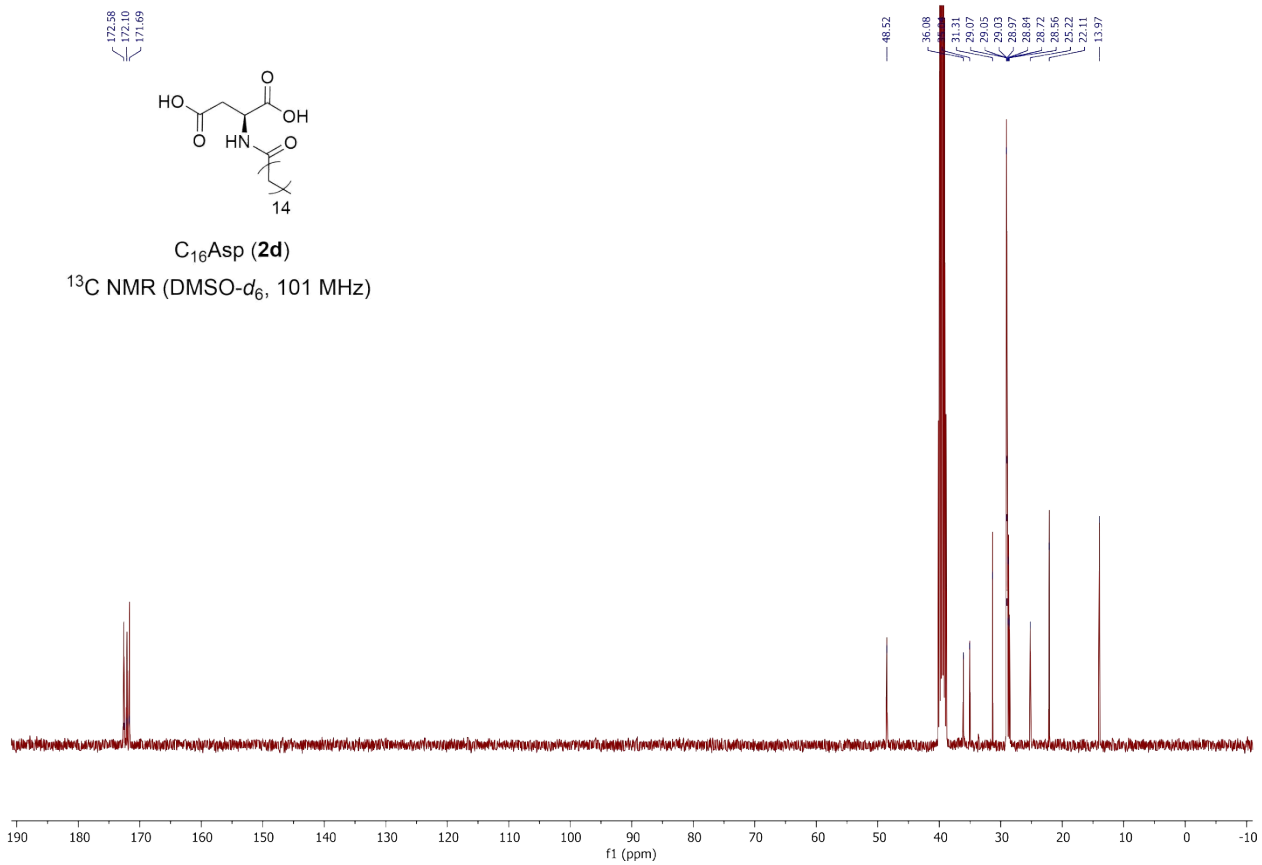

C_{16}Asp (**2d**)

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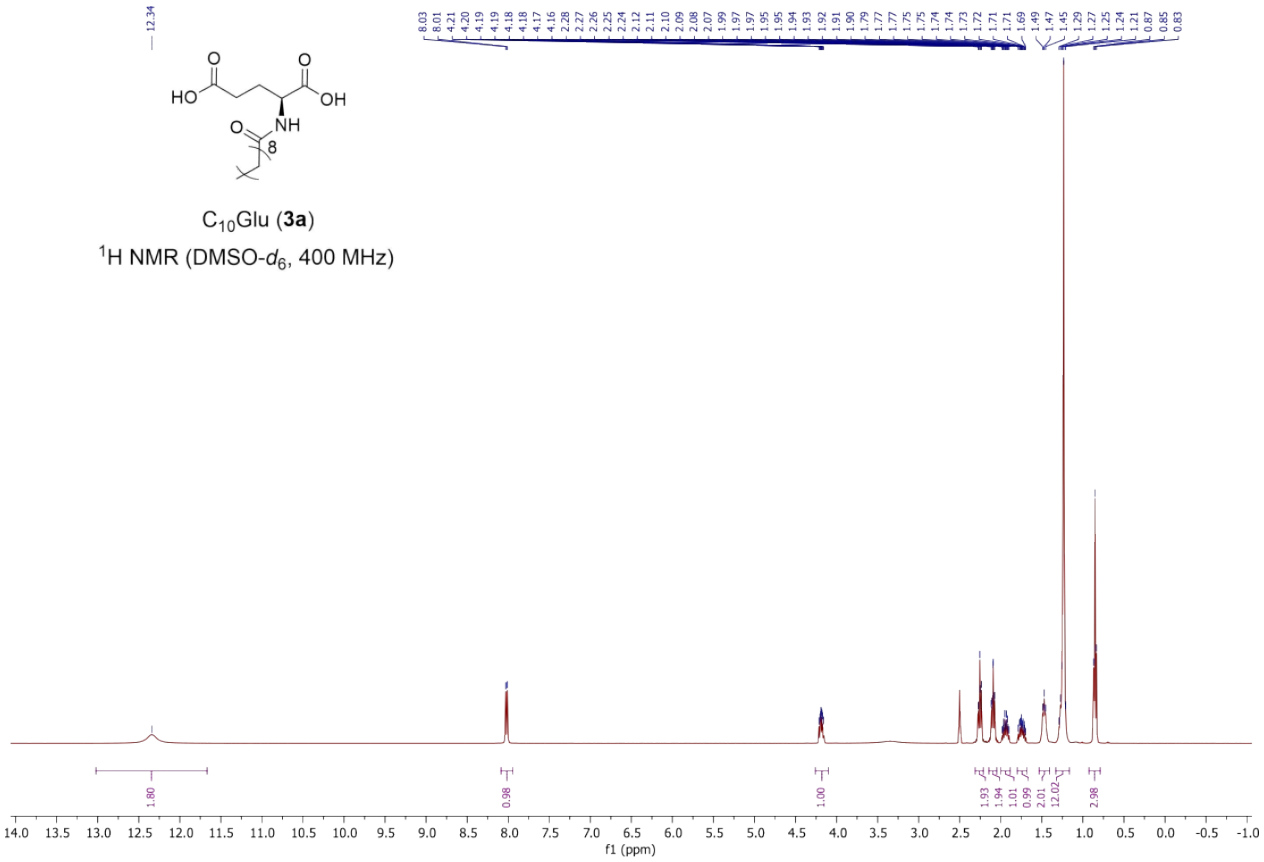

C_{10}Glu (**3a**)

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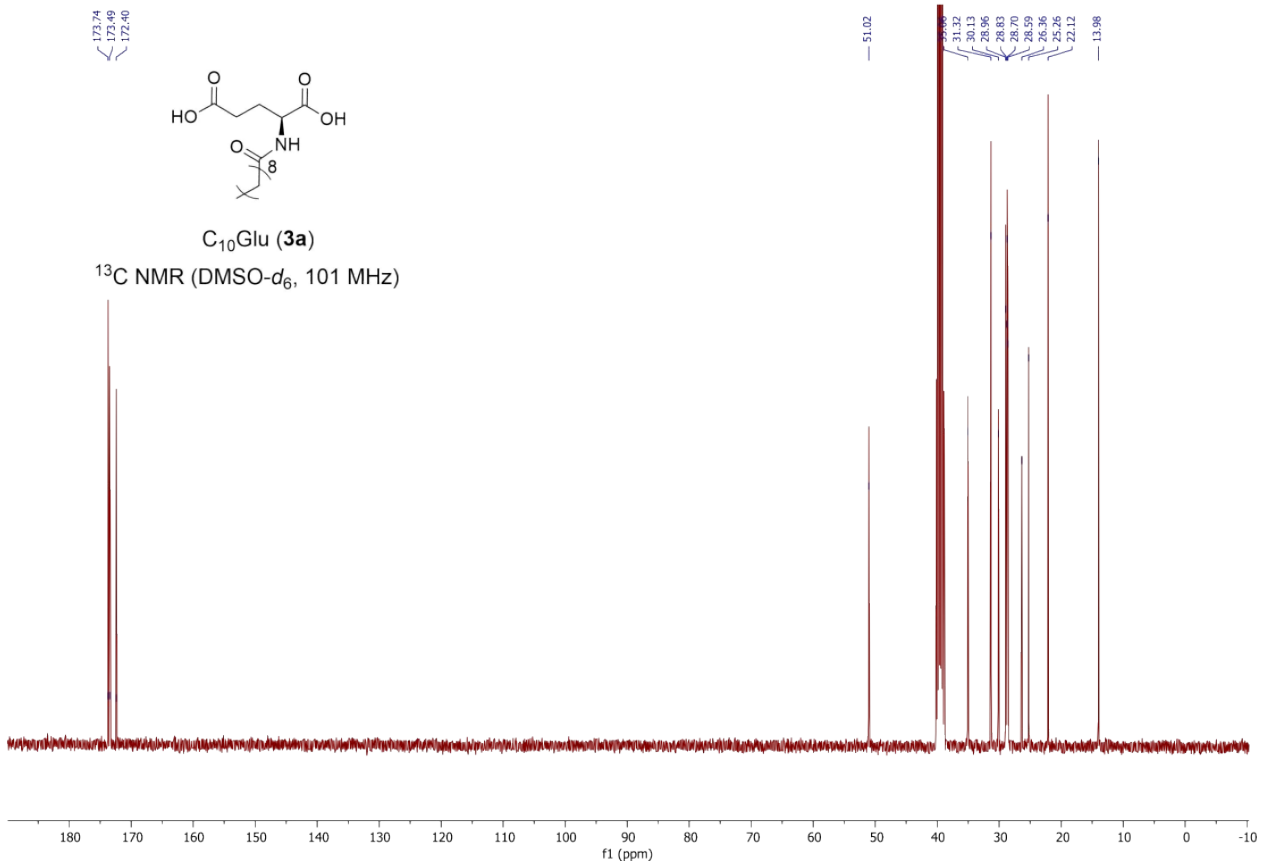

C_{10}Glu (**3a**)

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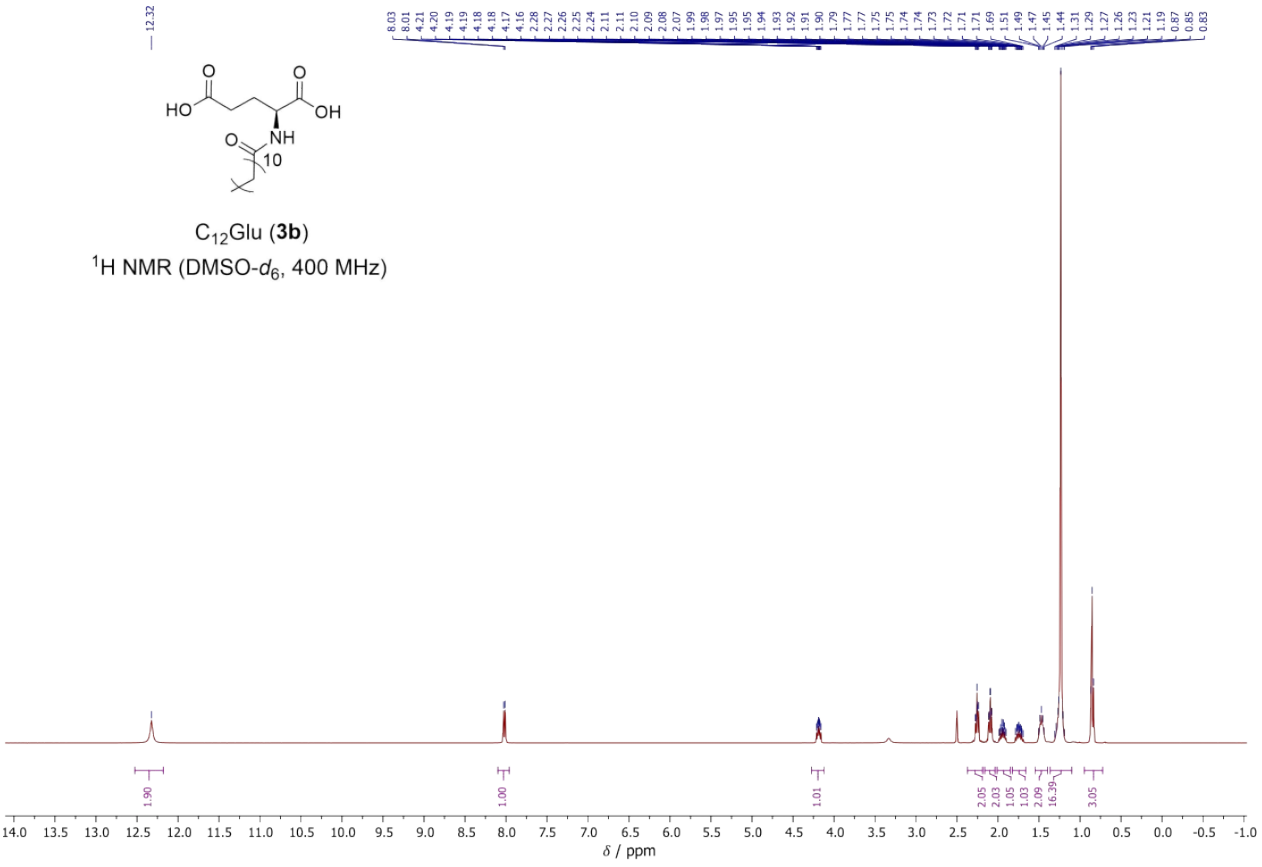

C_{12}Glu (**3b**)

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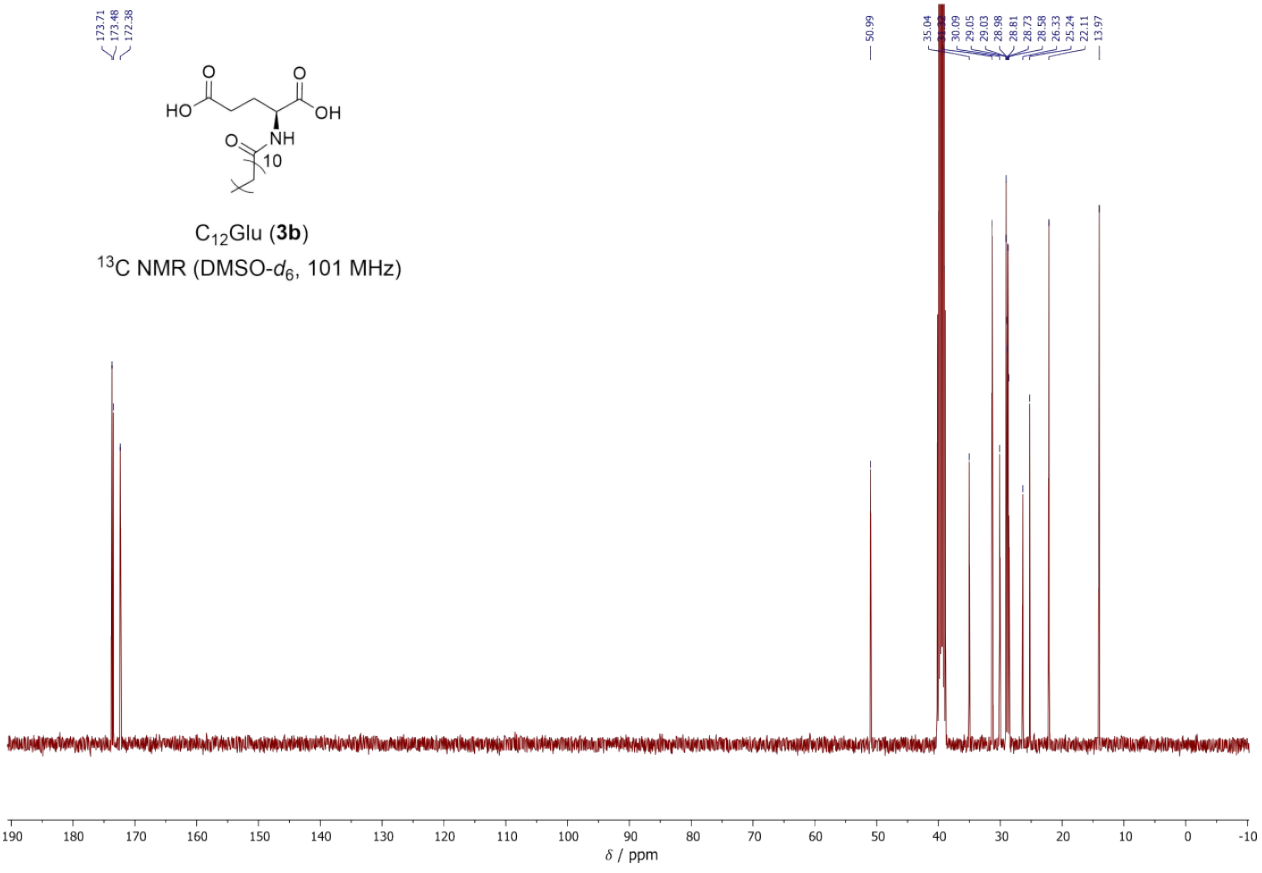
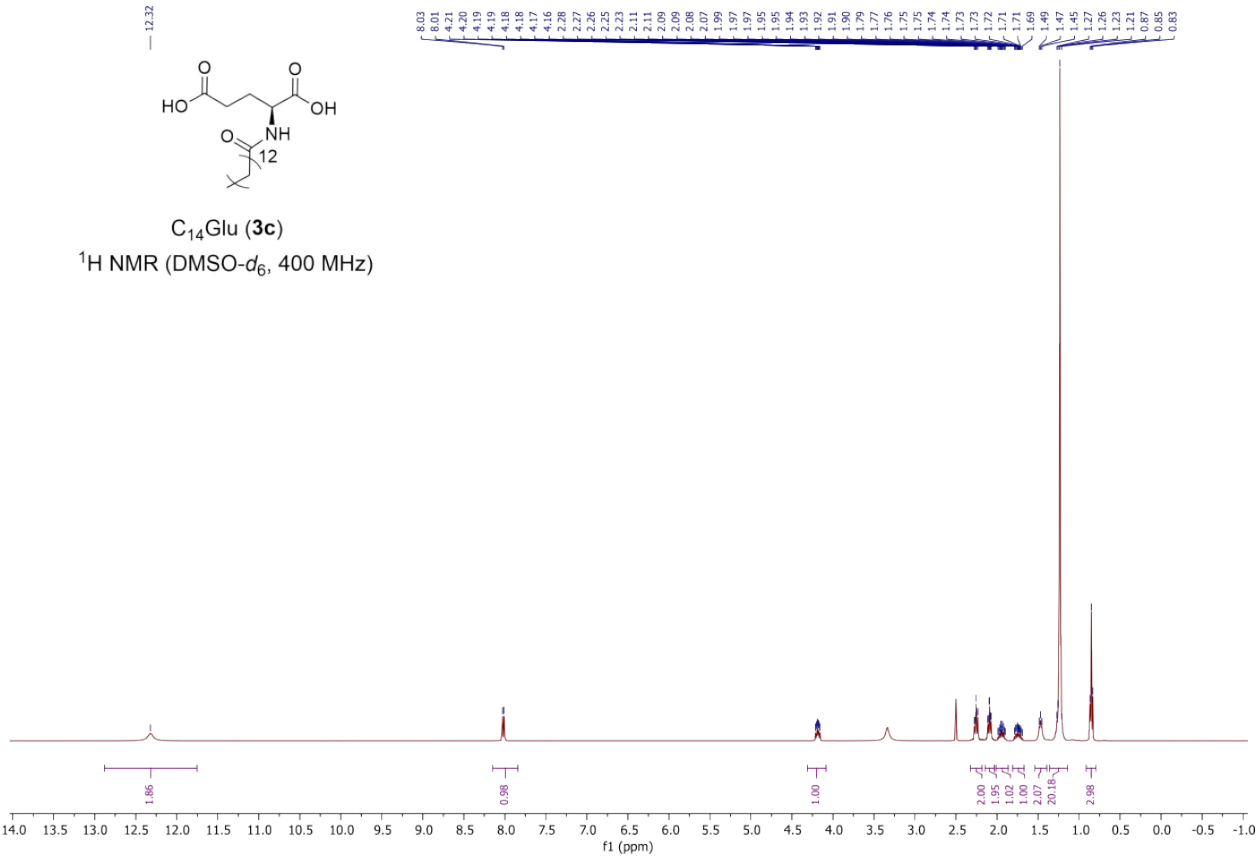


C_{12}Glu (**3b**)

^{13}C NMR (DMSO-d_6, 101 MHz)



C_{14}Glu (**3c**)

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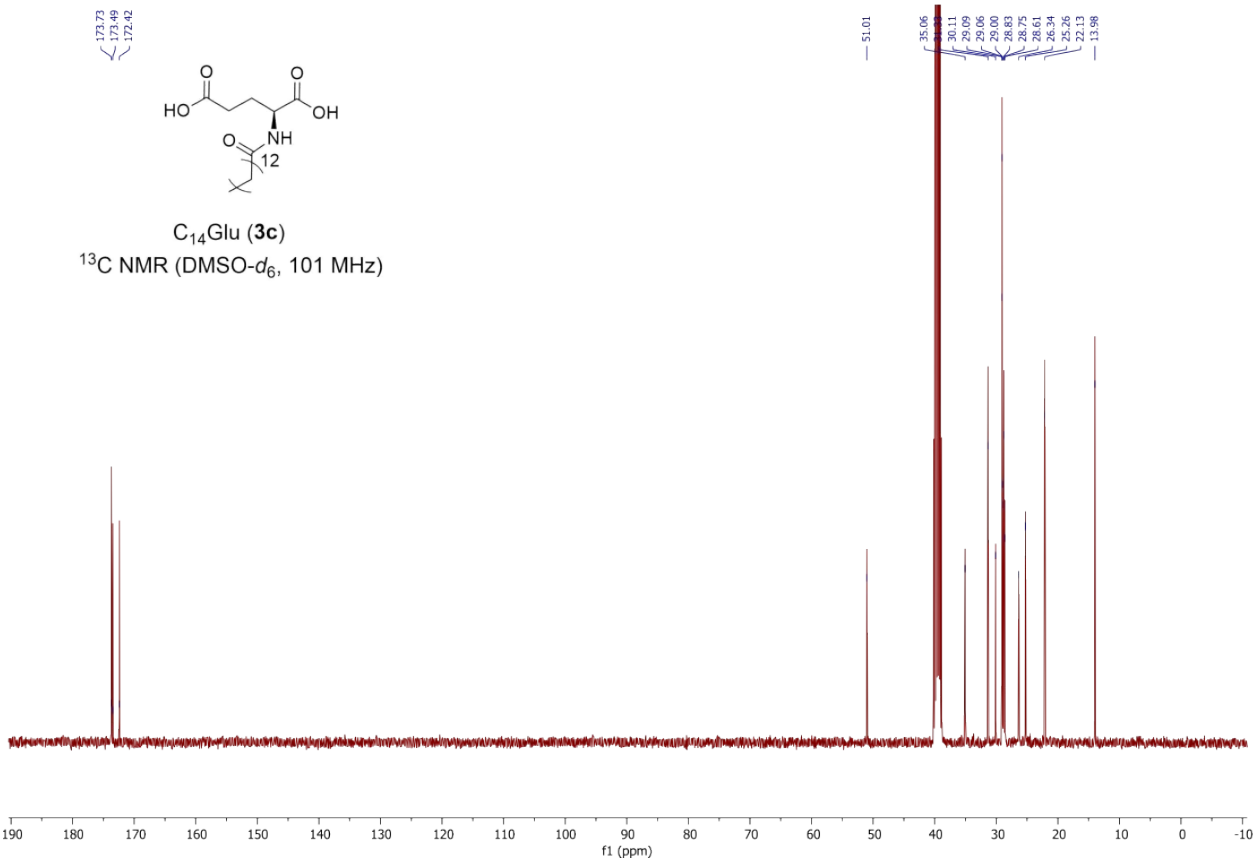

C_{14}Glu (**3c**)

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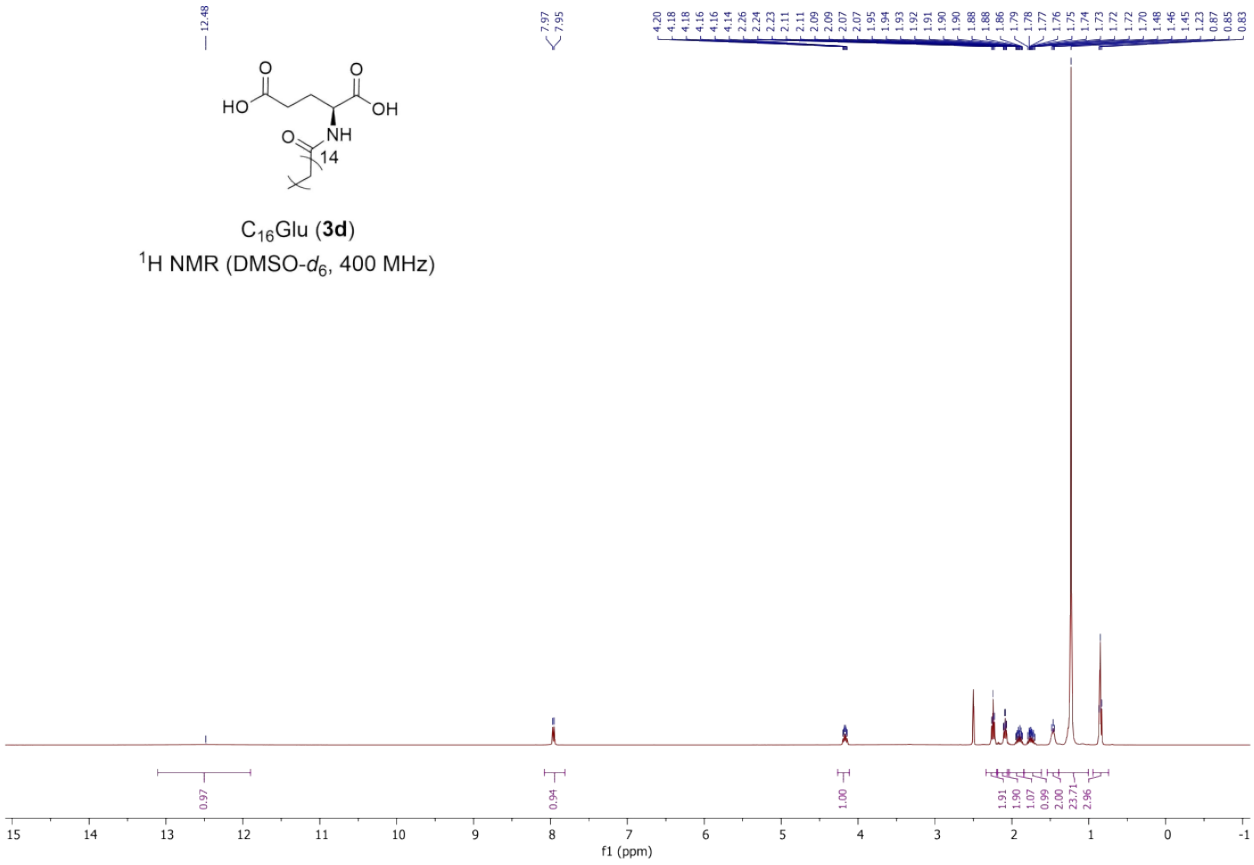
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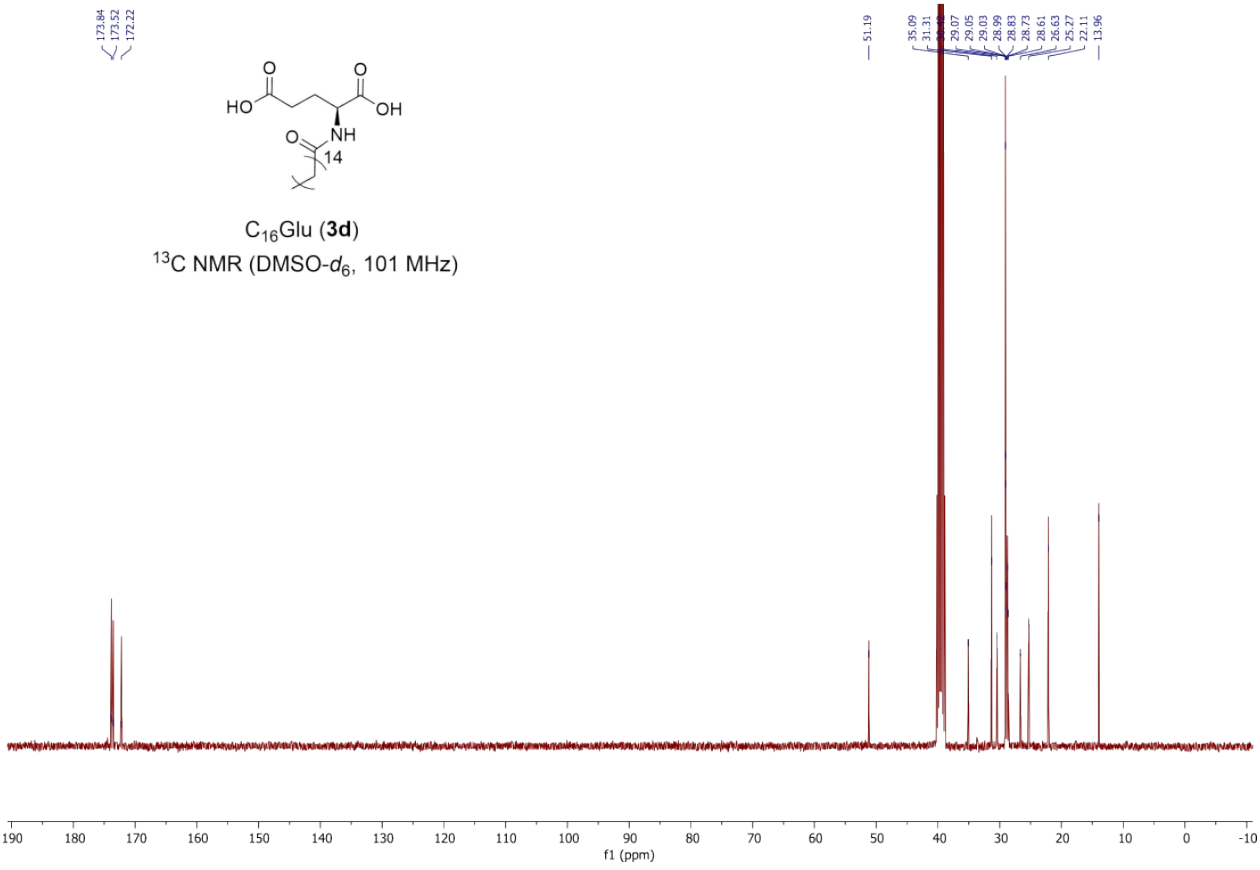
O
O
OH
NH
O
14
C16Glu (3d)
1H NMR (DMSO-d6, 400 MHz)
f1 (ppm)


HO
O
O
OH
NH
O
14
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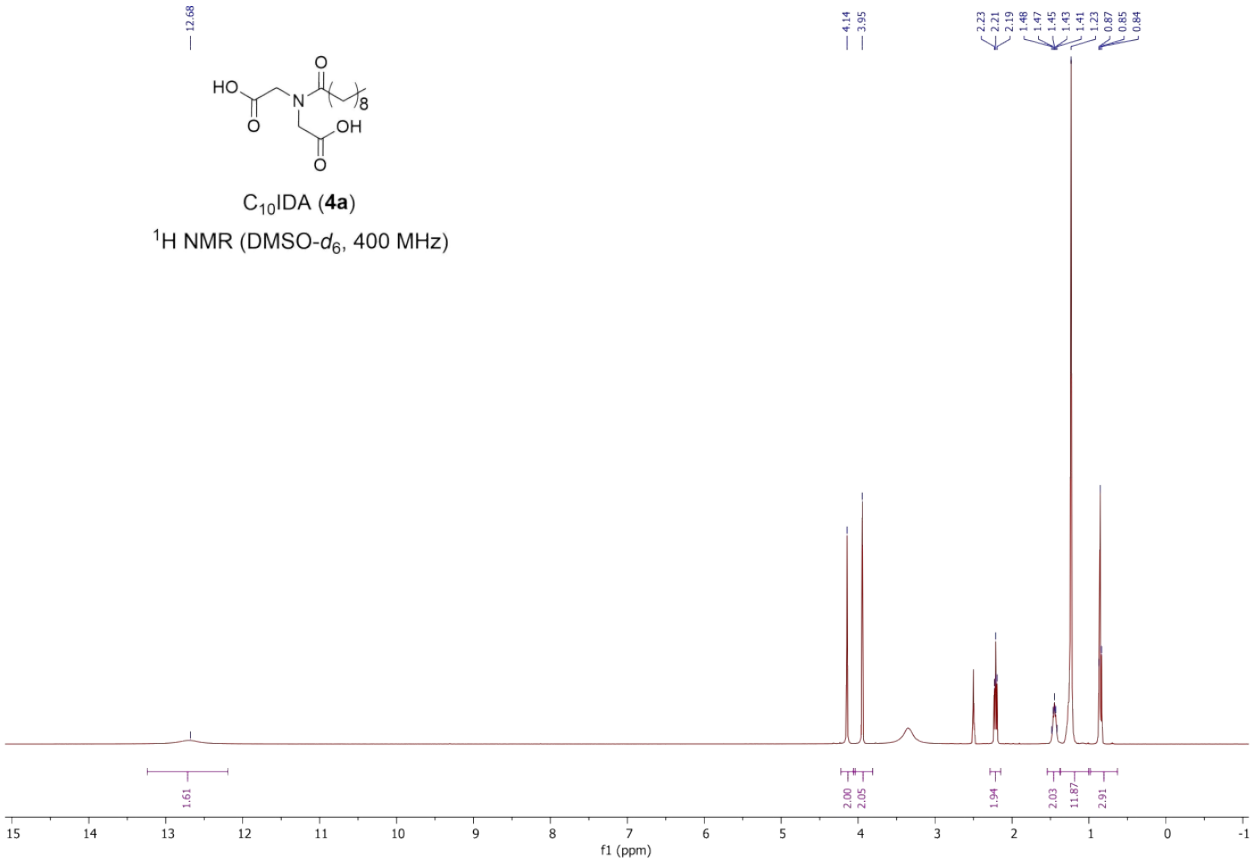
13C NMR (DMSO-d6, 101 MHz)
f1 (ppm)



C_{10}IDA (**4a**)

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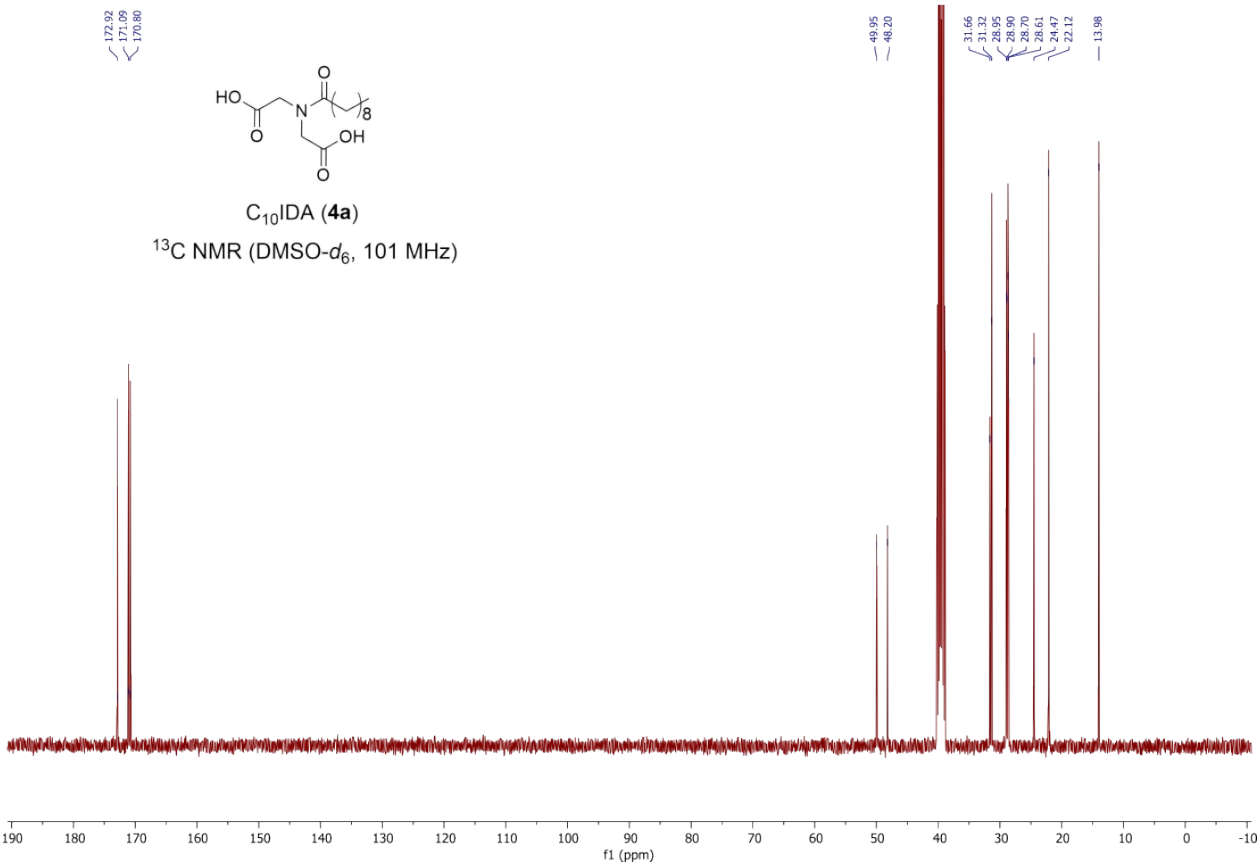
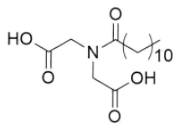


C_{10}IDA (**4a**)

^{13}C NMR (DMSO-d_6, 101 MHz)



C_{12}IDA (**4b**)

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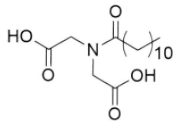
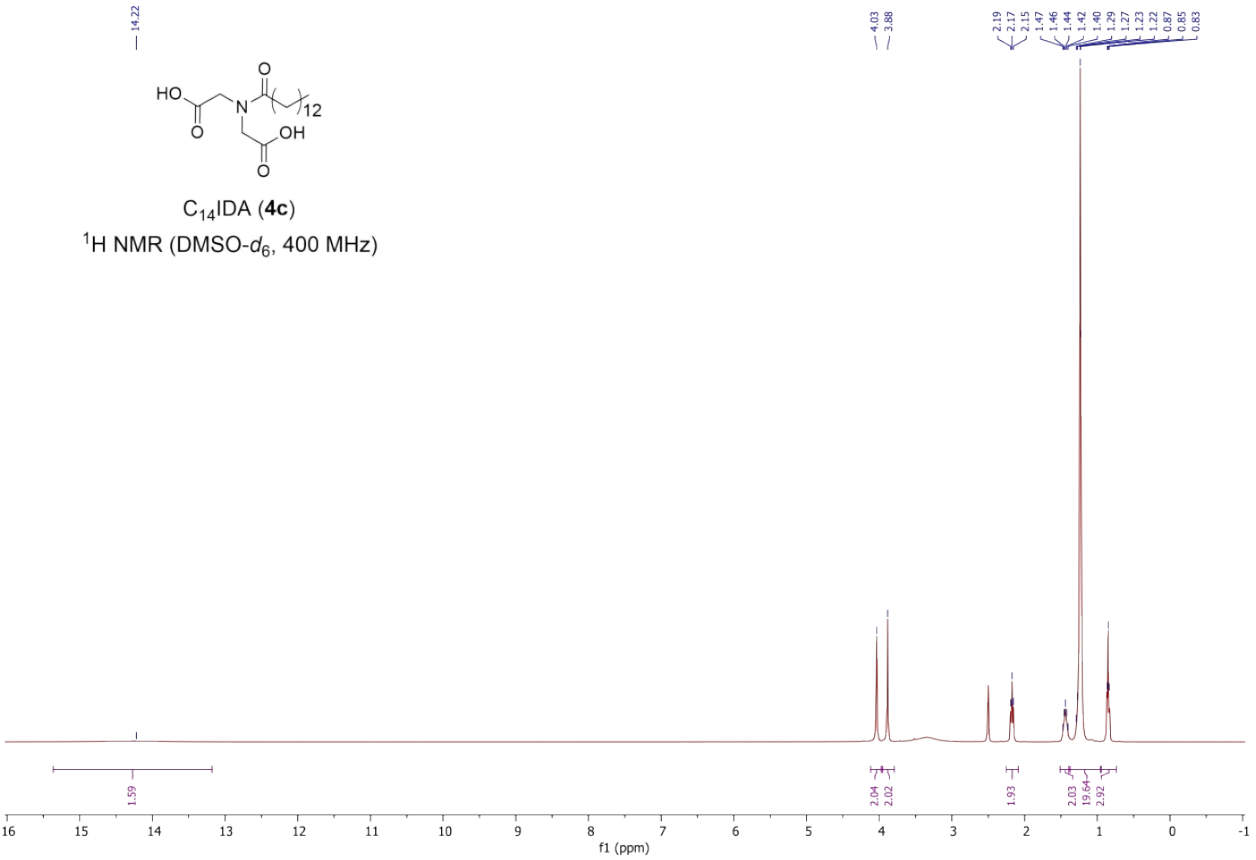


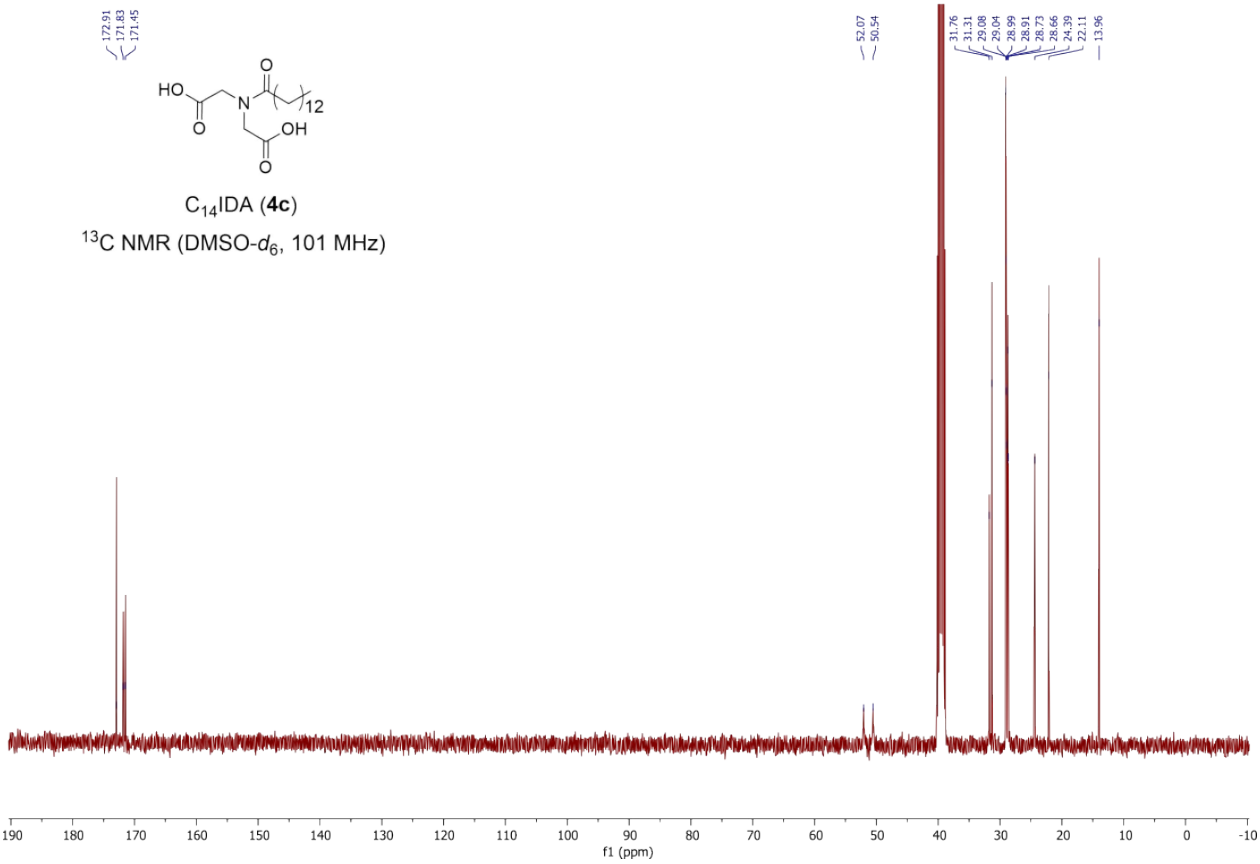
C_{12}IDA (**4b**)

^{13}C NMR (DMSO-d_6, 101 MHz)



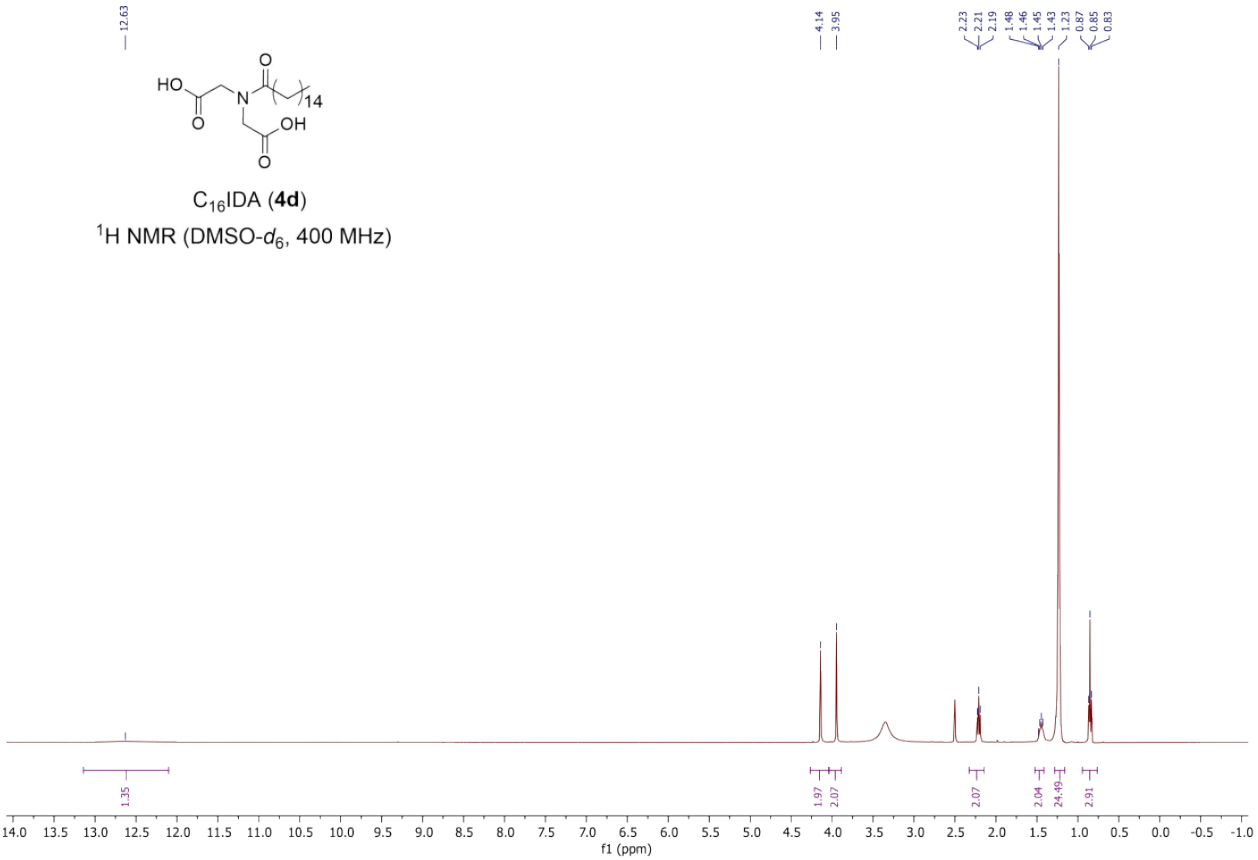
C_{14}IDA (**4c**)

^{1}H NMR (DMSO-d_6, 400 MHz)



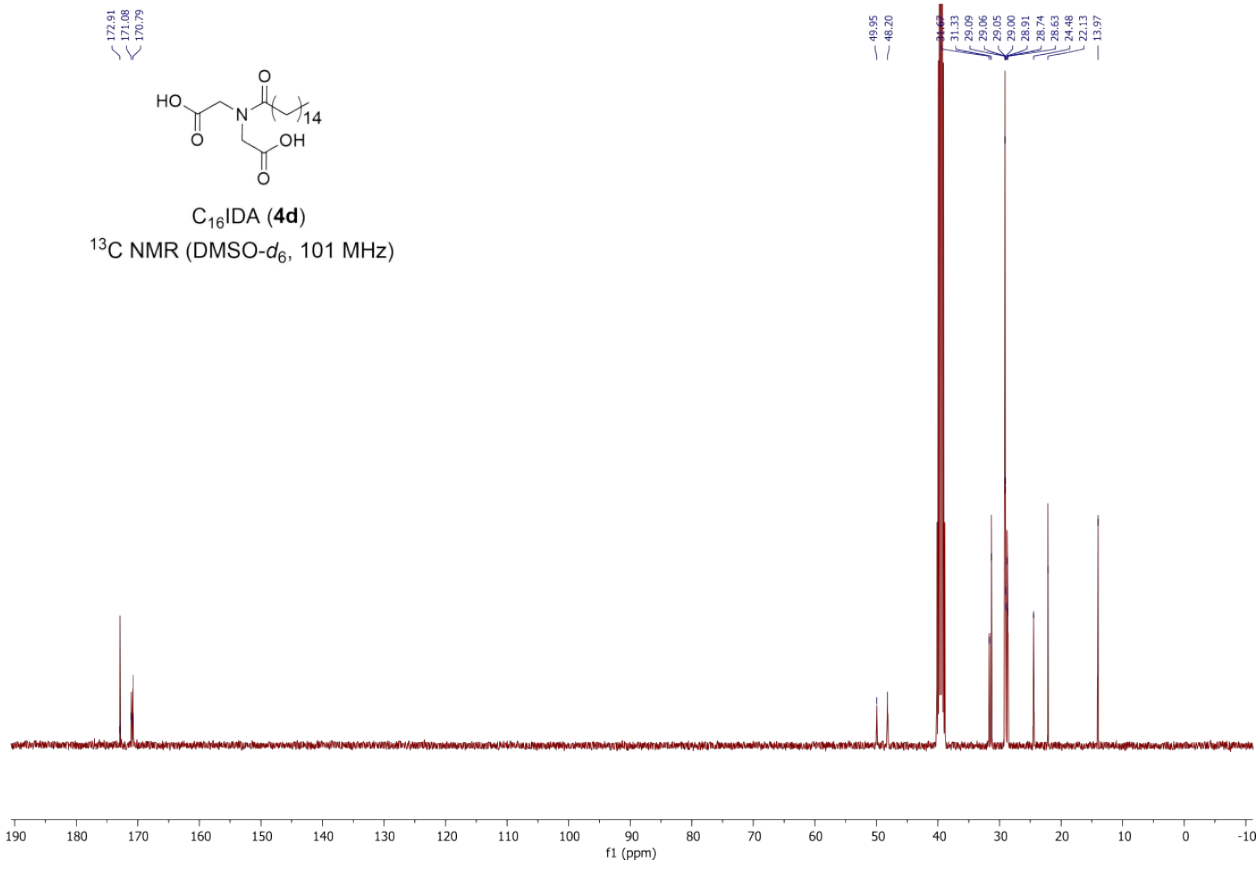
C_{14}IDA (**4c**)

^{13}C NMR (DMSO-d_6, 101 MHz)



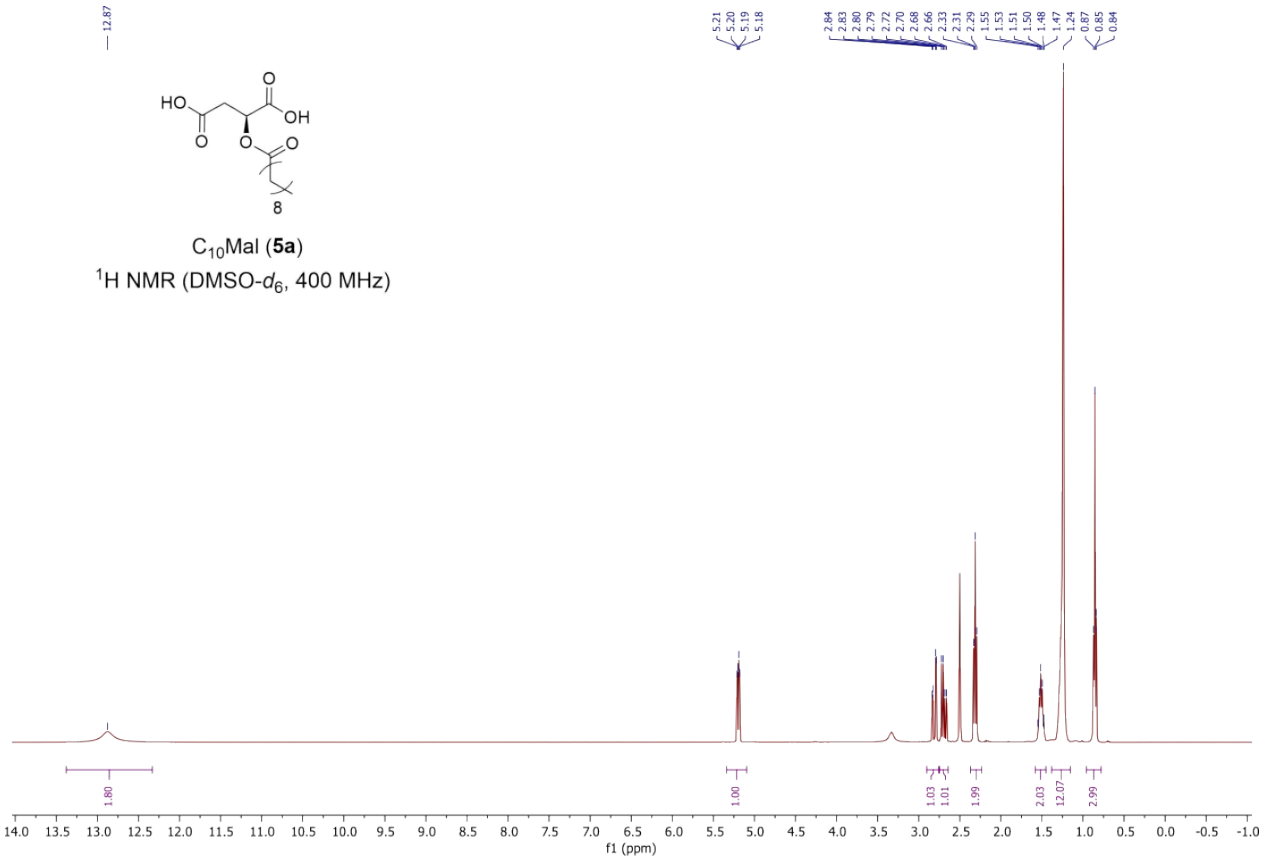
C_{16}IDA (**4d**)

^{1}H NMR (DMSO-d_6, 400 MHz)



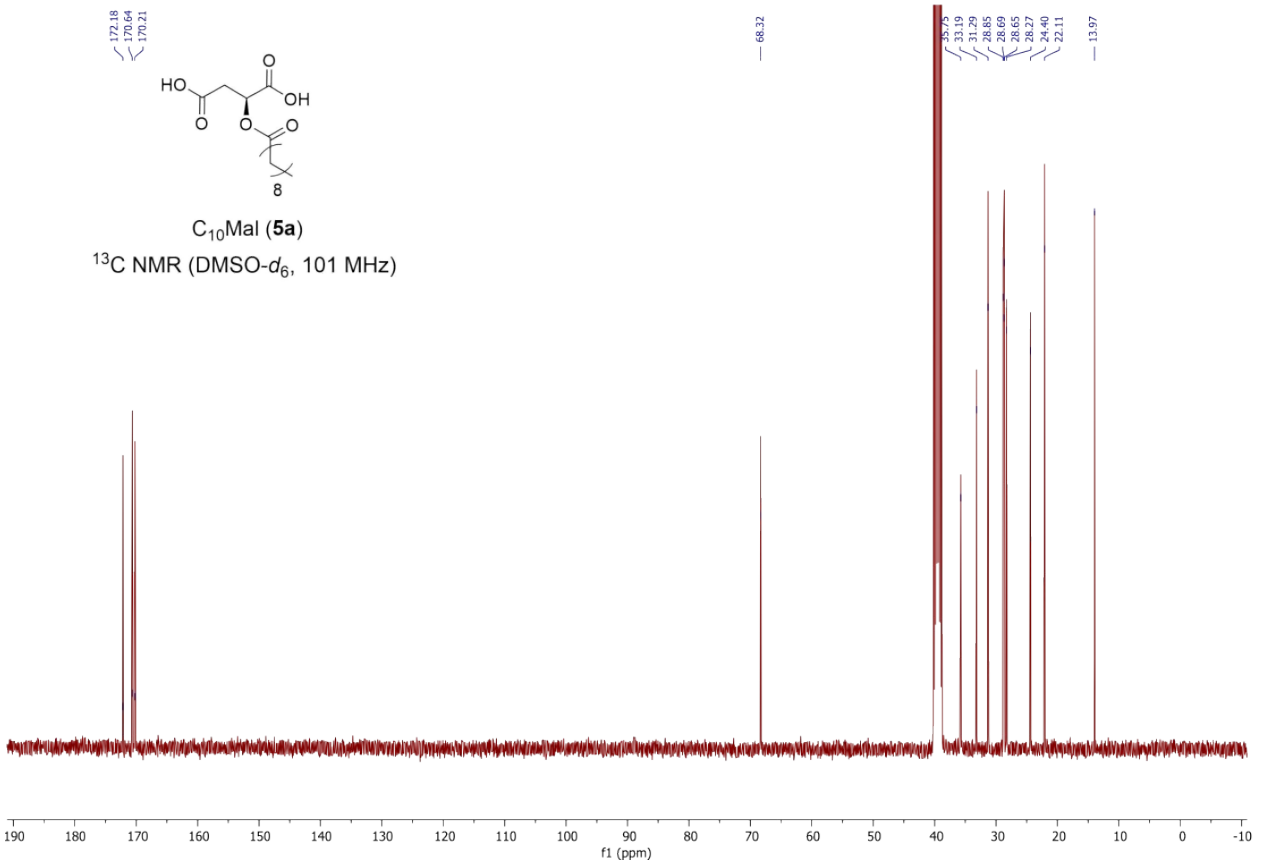
C_{16}IDA (**4d**)

^{13}C NMR (DMSO-d_6, 101 MHz)



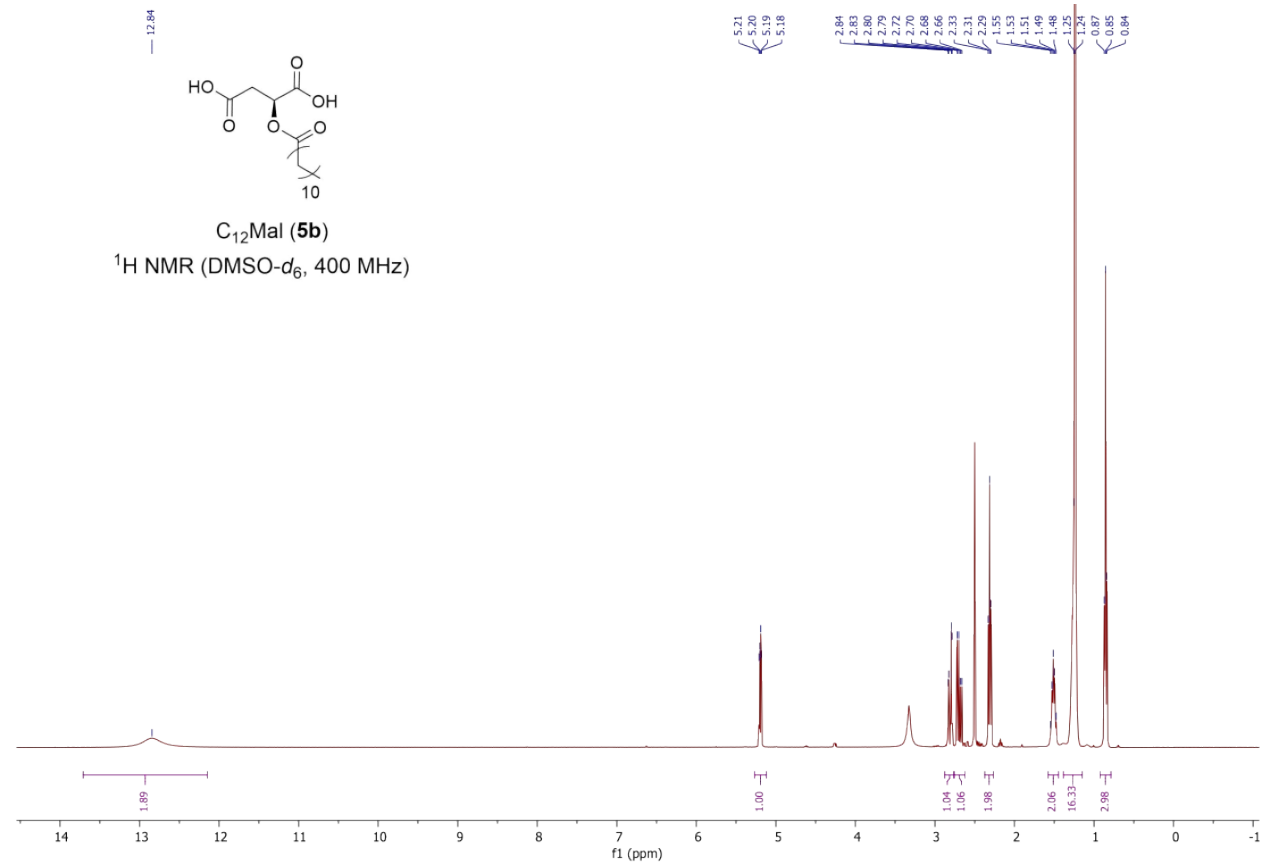
C_{10}Mal (**5a**)

^{1}H NMR (DMSO-d_6, 400 MHz)



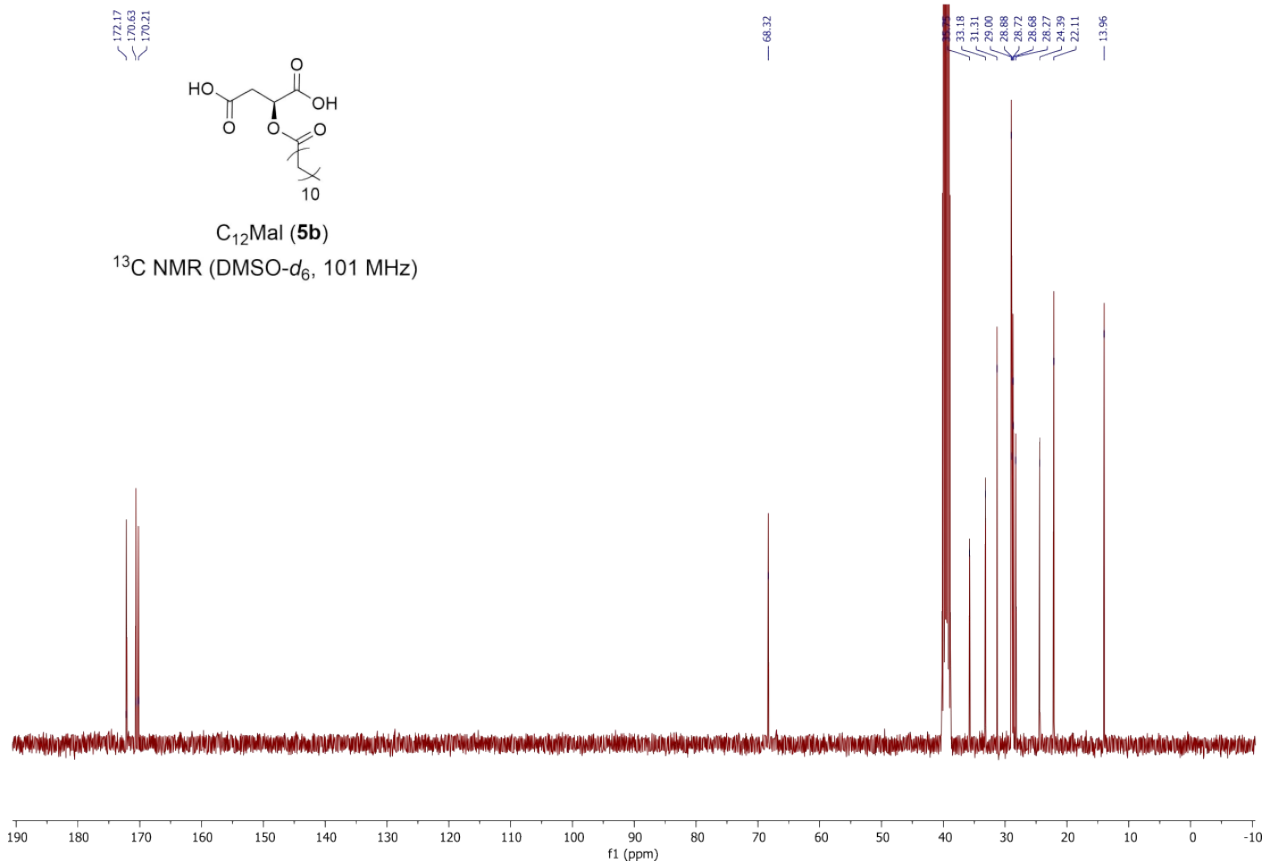
C_{10}Mal (**5a**)

^{13}C NMR (DMSO-d_6, 101 MHz)



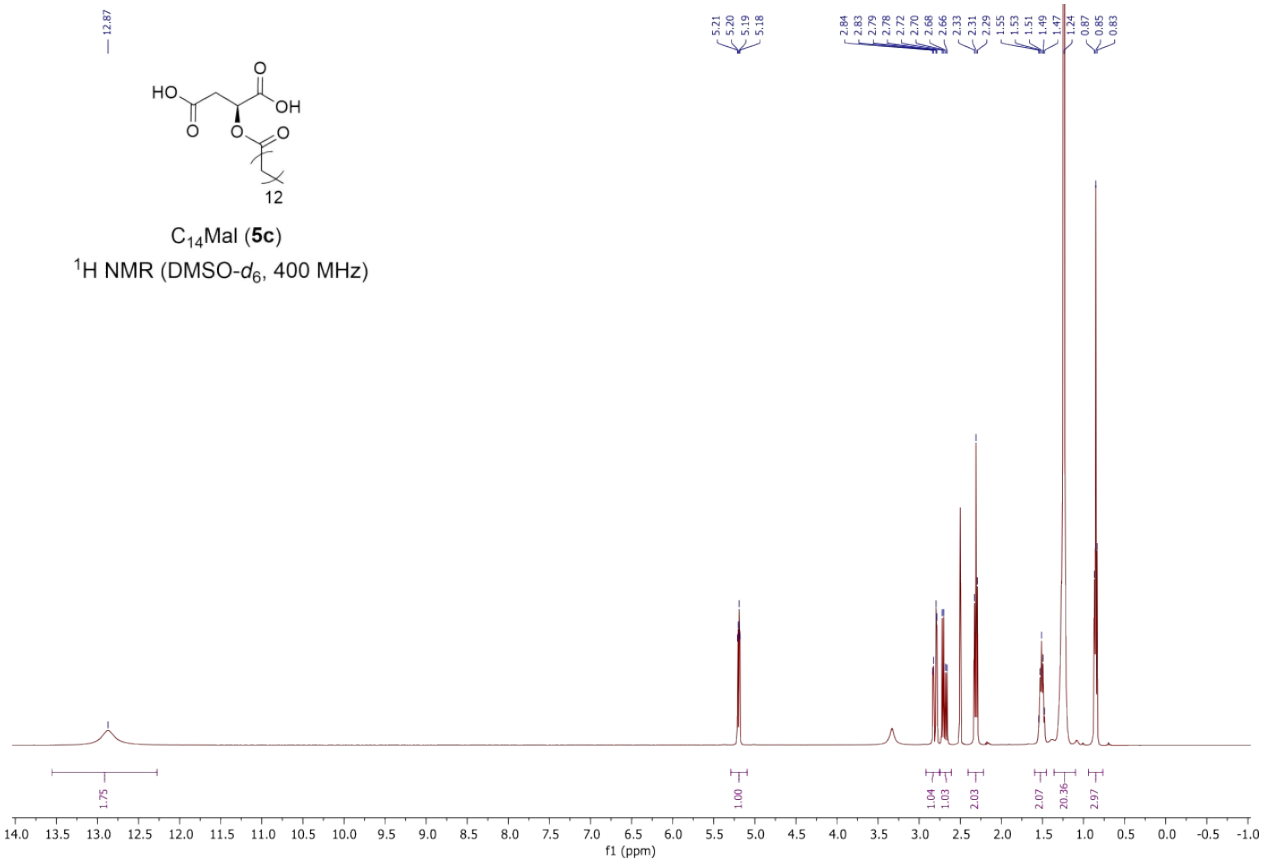
C_{12}Mal (**5b**)

^{1}H NMR (DMSO-d_6, 400 MHz)



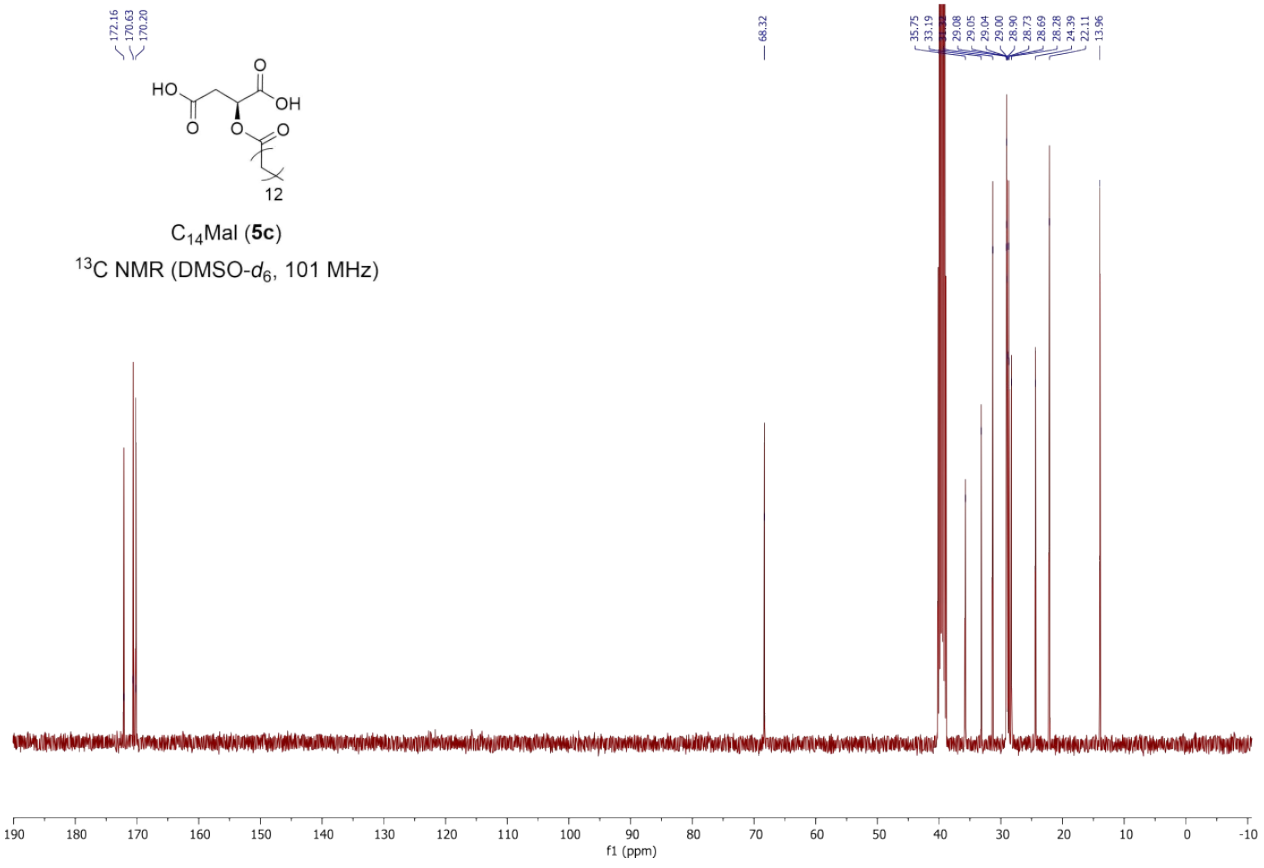
C_{12}Mal (**5b**)

^{13}C NMR (DMSO-d_6, 101 MHz)



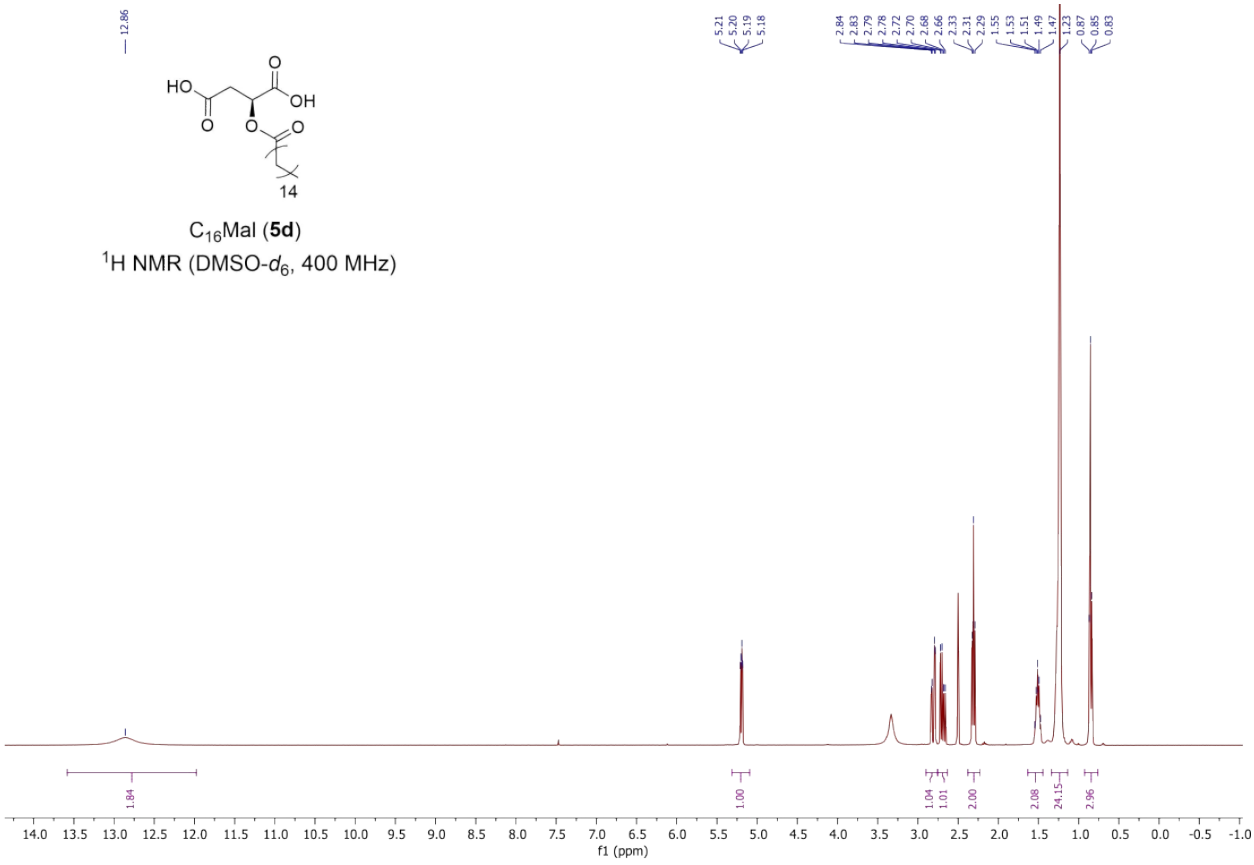
C_{14}Mal (**5c**)

^{1}H NMR (DMSO-d_6, 400 MHz)



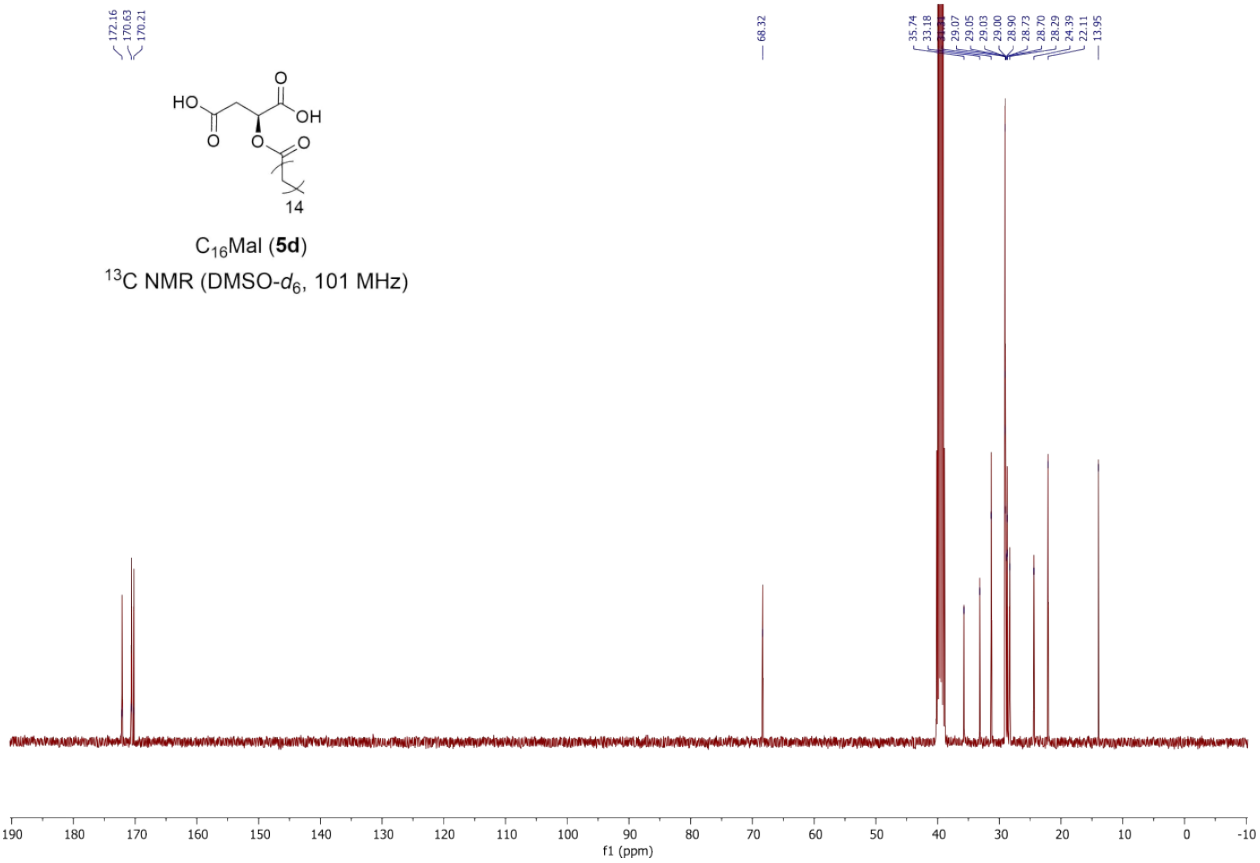
C_{14}Mal (**5c**)

^{13}C NMR (DMSO-d_6, 101 MHz)



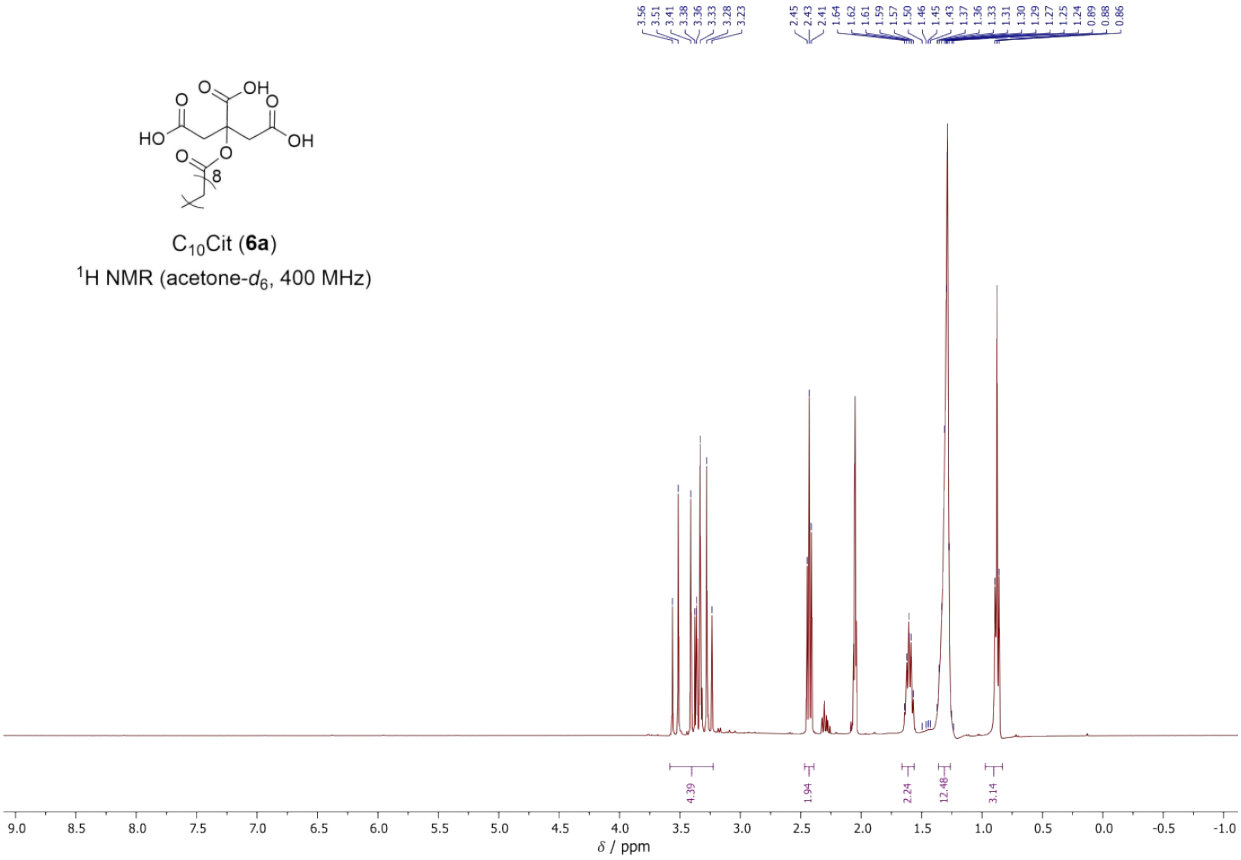
C_{16}Mal (**5d**)

^{1}H NMR (DMSO-d_6, 400 MHz)



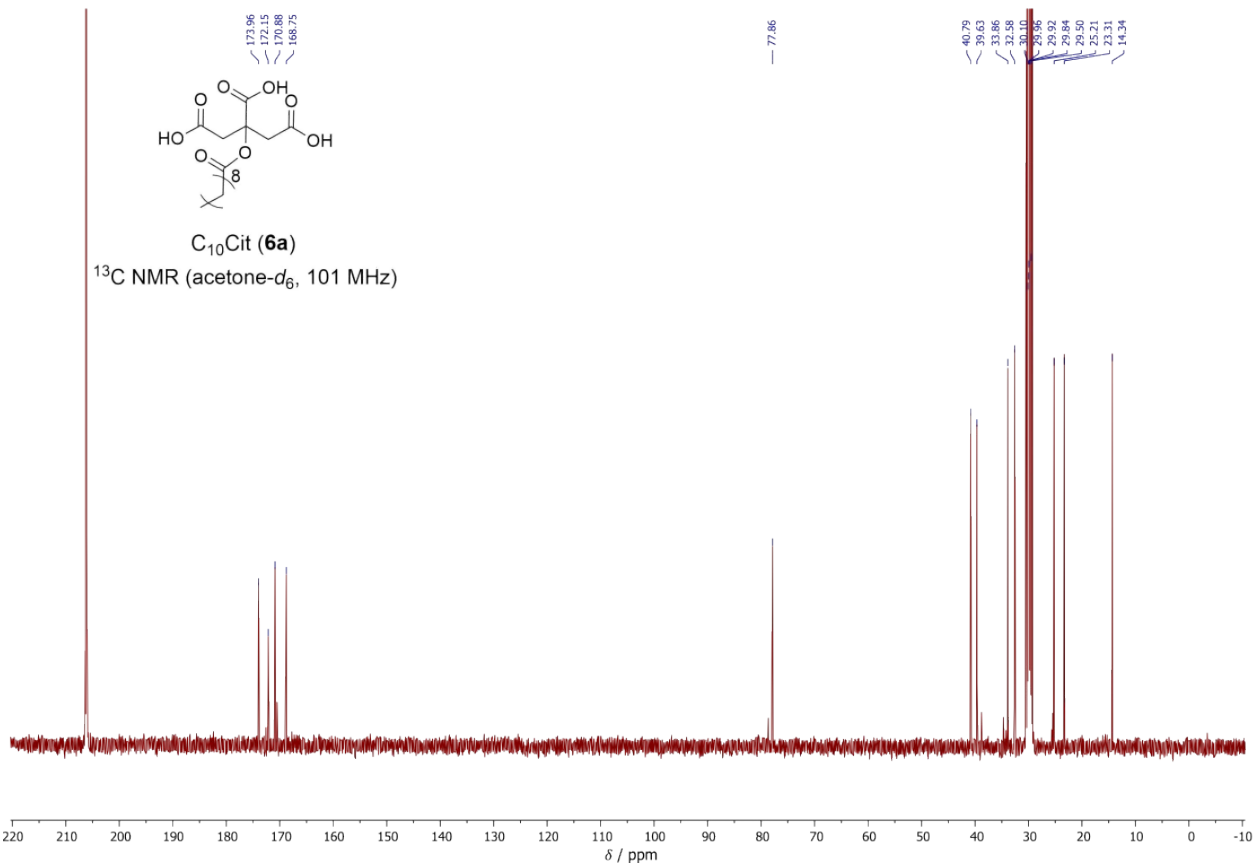
C_{16}Mal (**5d**)

^{13}C NMR (DMSO-d_6, 101 MHz)



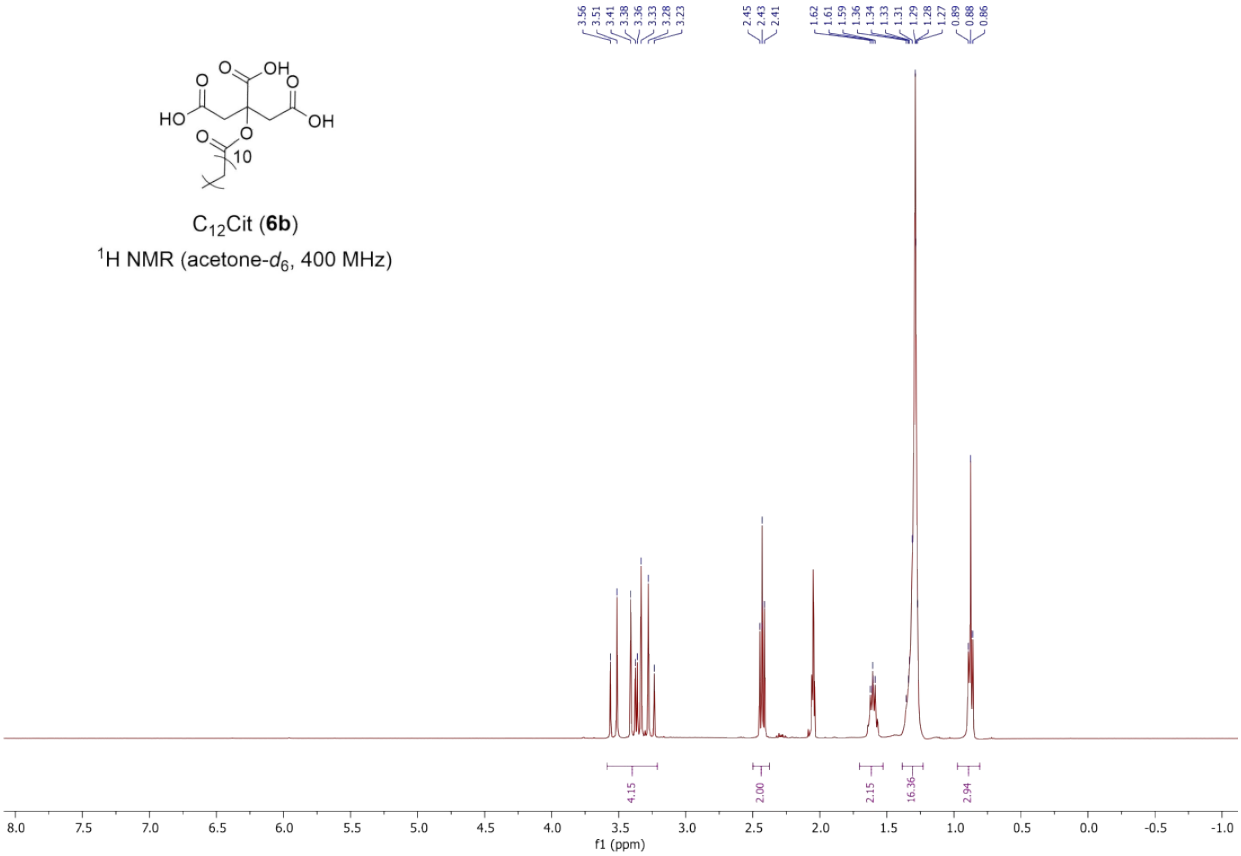
C_{10}Cit (**6a**)

^{1}H NMR (acetone-d_6, 400 MHz)



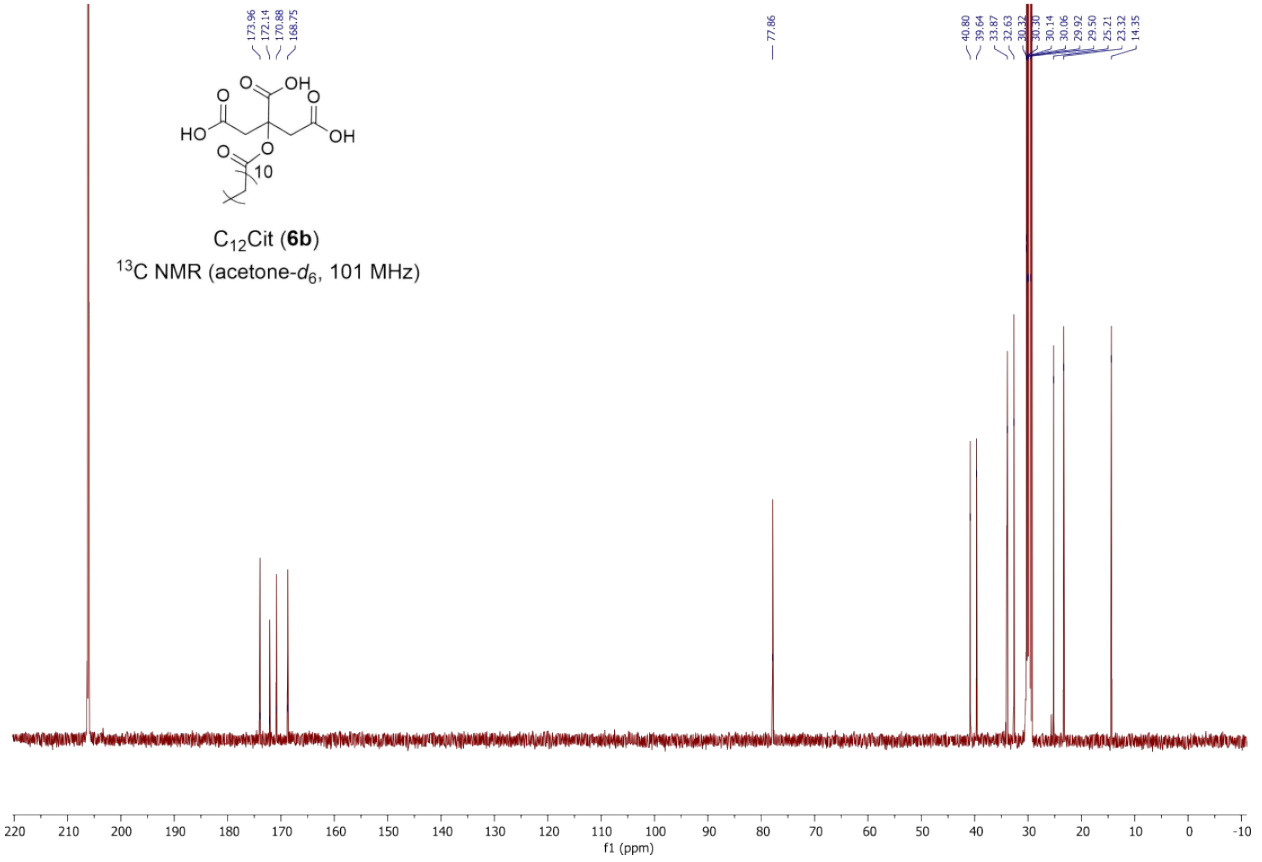
C_{10}Cit (**6a**)

^{13}C NMR (acetone-d_6, 101 MHz)



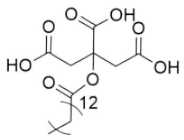
C_{12}Cit (**6b**)

^{1}H NMR (acetone-d_6, 400 MHz)



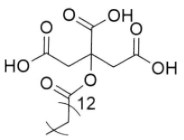
C_{12}Cit (**6b**)

^{13}C NMR (acetone-d_6, 101 MHz)



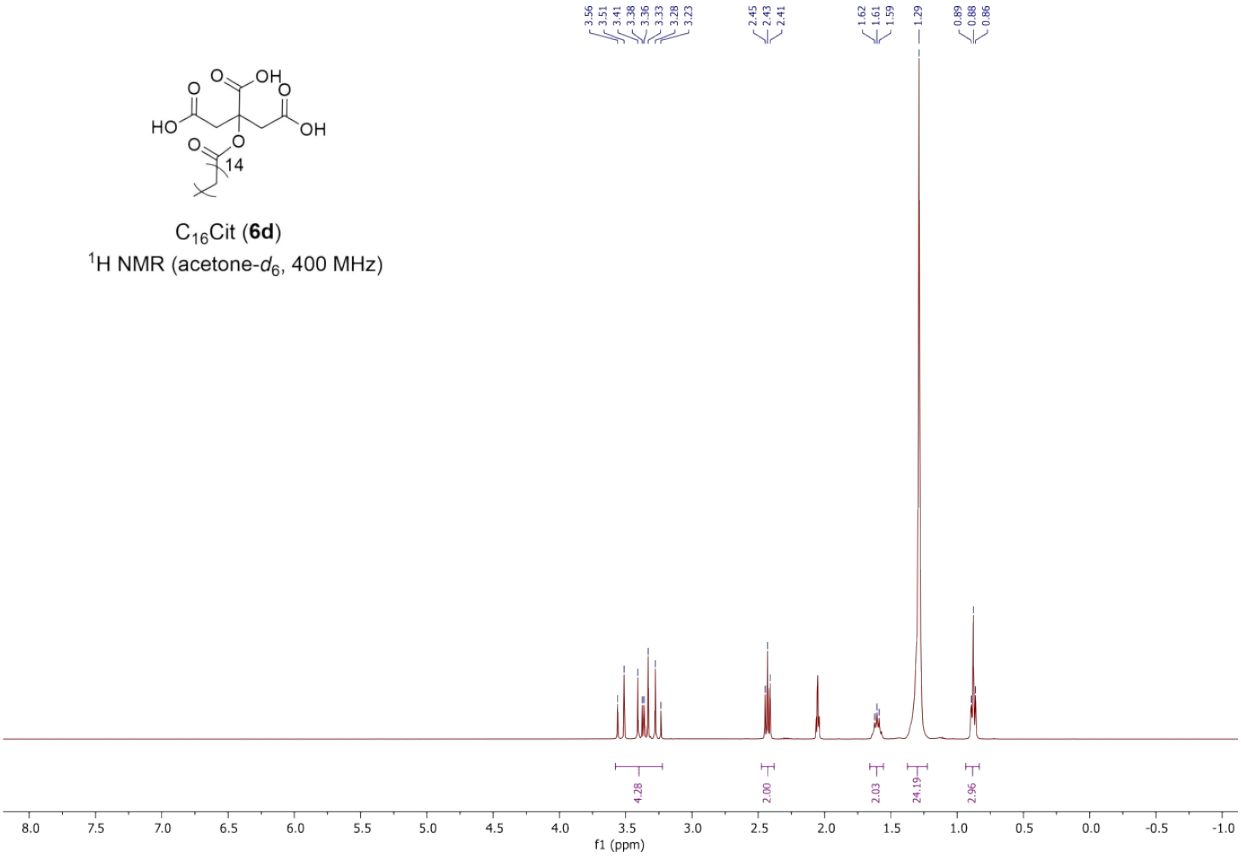
C_{14}Cit (**6c**)

^{1}H NMR (acetone-d_6, 400 MHz)

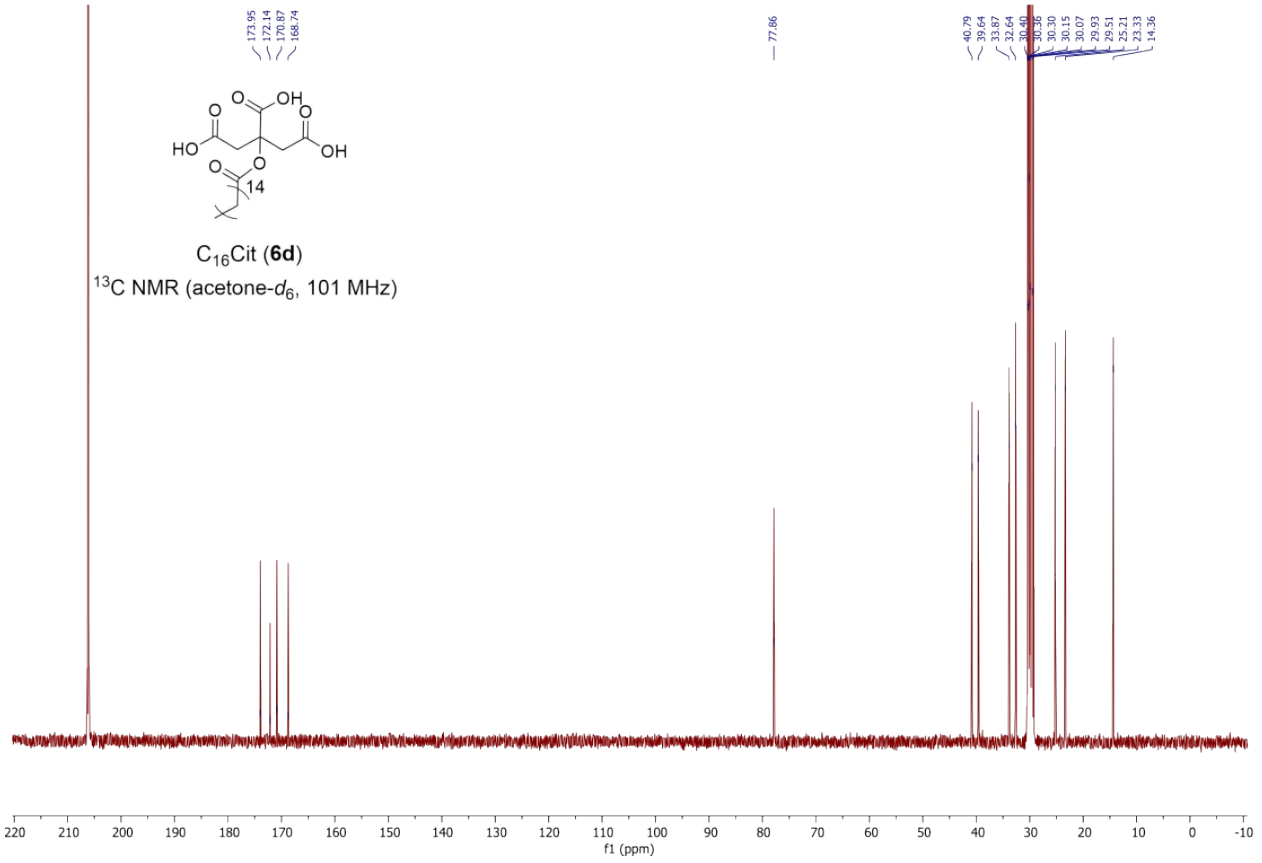


C_{14}Cit (**6c**)

^{13}C NMR (acetone-d_6, 101 MHz)



C_{16}Cit (**6d**)
^{1}H NMR (acetone-d_6, 400 MHz)



C_{16}Cit (**6d**)
^{13}C NMR (acetone-d_6, 101 MHz)