

Sustainable Itaconamide Monomers from Amino Acids for Vat Photopolymerization 3D Printing

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SUPPORTING INFORMATION

Table S1. Summary of experimental conditions for the synthesis of MEIA derivatives.

Compound	i)	ii)
Oct-MEIA	-	Solvent: DCM --- Base: none
Ala-MEIA	24 h	Solvent: ethyl acetate --- Base: Na ₂ CO ₃
Phe-MEIA	24 h	Solvent: 2-MeTHF --- Base: NaHCO ₃
Ile-MEIA	72 h	Solvent: 2-MeTHF --- Base: NaHCO ₃
Val-MEIA	48 h	Solvent: 2-MeTHF --- Base: NaHCO ₃

Step i) Esterification of the amino acid, the table reports reaction time under reflux conditions.

Step ii) Synthesis of the itaconamide intermediate (IA), the table reports selected solvent(s)

Table S2. Composition (wt.%) of the prepared MEIA-based photocurable resins. In brackets, the molar concentration of photocurable groups coming from each monomer in the final resin.

Resin ID	MEIA	IBOMA	EGPEA	HDDA
Blank	-	45 wt.% (38.6 mol.%)	45 wt.% (44.6 mol.%)	10 wt.% (16.8 mol.%)
Oct-MEIA 10	13.1 wt.% (10 mol.%)	38.6 wt.% (33.9 mol.%)	38.6 wt.% (39.2 mol.%)	9.7 wt.% (16.8 mol.%)
Oct-MEIA 25	31.5 wt.% (25 mol.%)	29.6 wt.% (27 mol.%)	29.6 wt.% (31.2 mol.%)	9.4 wt.% (16.8 mol.%)
Oct-MEIA 40	48.6 wt.% (40 mol.%)	21.2 wt.% (20 mol.%)	21.2 wt.% (23.1 mol.%)	9.1 wt.% (16.8 mol.%)
Ala-MEIA 10	11.2 wt.% (10 mol.%)	39.4 wt.% (33.9 mol.%)	39.4 wt.% (39.2 mol.%)	10.0 wt.% (16.8 mol.%)
Ala-MEIA 25	27.9 wt.% (25 mol.%)	31.1 wt.% (27 mol.%)	31.1 wt.% (31.2 mol.%)	9.9 wt.% (16.8 mol.%)
Ala-MEIA 40	44.3 wt.% (40 mol.%)	22.9 wt.% (20 mol.%)	22.9 wt.% (23.1 mol.%)	9.8 wt.% (16.8 mol.%)
Phe-MEIA 10	14.6 wt.% (10 mol.%)	37.9 wt.% (33.9 mol.%)	37.9 wt.% (39.2 mol.%)	9.6 wt.% (16.8 mol.%)
Phe-MEIA 25	34.4 wt.% (25 mol.%)	28.3 wt.% (27 mol.%)	28.3 wt.% (31.2 mol.%)	9.0 wt.% (16.8 mol.%)
Phe-MEIA 40	51.9 wt.% (40 mol.%)	19.8 wt.% (20 mol.%)	19.8 wt.% (23.1 mol.%)	8.5 wt.% (16.8 mol.%)
Ile-MEIA 10	13.6 wt.% (10 mol.%)	40.0 wt.% (33.9 mol.%)	40.0 wt.% (39.2 mol.%)	10.1 wt.% (16.8 mol.%)
Ile-MEIA 25	31.8 wt.% (25 mol.%)	29.6 wt.% (27 mol.%)	29.6 wt.% (31.2 mol.%)	9.4 wt.% (16.8 mol.%)
Ile-MEIA 40	47.6 wt.% (40 mol.%)	20.6 wt.% (20 mol.%)	20.6 wt.% (23.1 mol.%)	8.8 wt.% (16.8 mol.%)
Val-MEIA 10	13.1 wt.% (10 mol.%)	38.6 wt.% (33.9 mol.%)	38.6 wt.% (39.2 mol.%)	9.7 wt.% (16.8 mol.%)
Val-MEIA 25	31.6 wt.% (25 mol.%)	29.5 wt.% (27 mol.%)	29.5 wt.% (31.2 mol.%)	9.4 wt.% (16.8 mol.%)
Val-MEIA 40	48.8 wt.% (40 mol.%)	21.1 wt.% (20 mol.%)	21.1 wt.% (23.1 mol.%)	9.0 wt.% (16.8 mol.%)

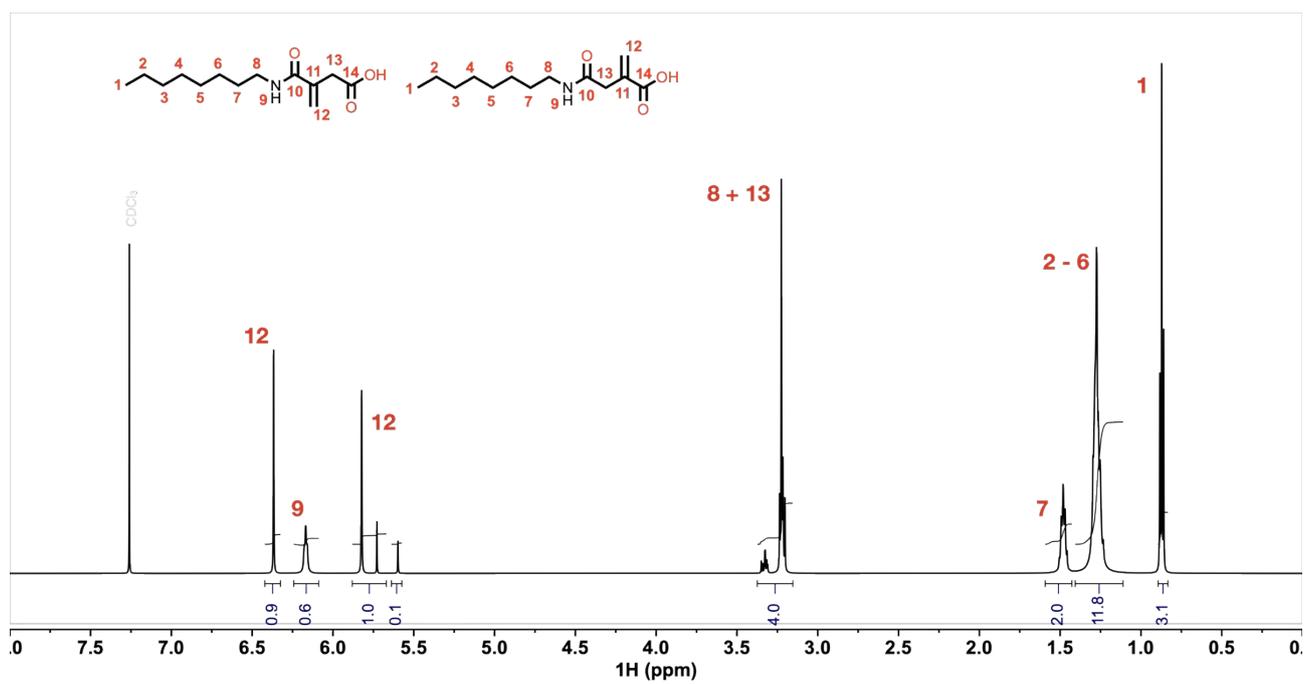


Figure S1. $^1\text{H-NMR}$ (600 MHz, CDCl_3) of Oct-IA

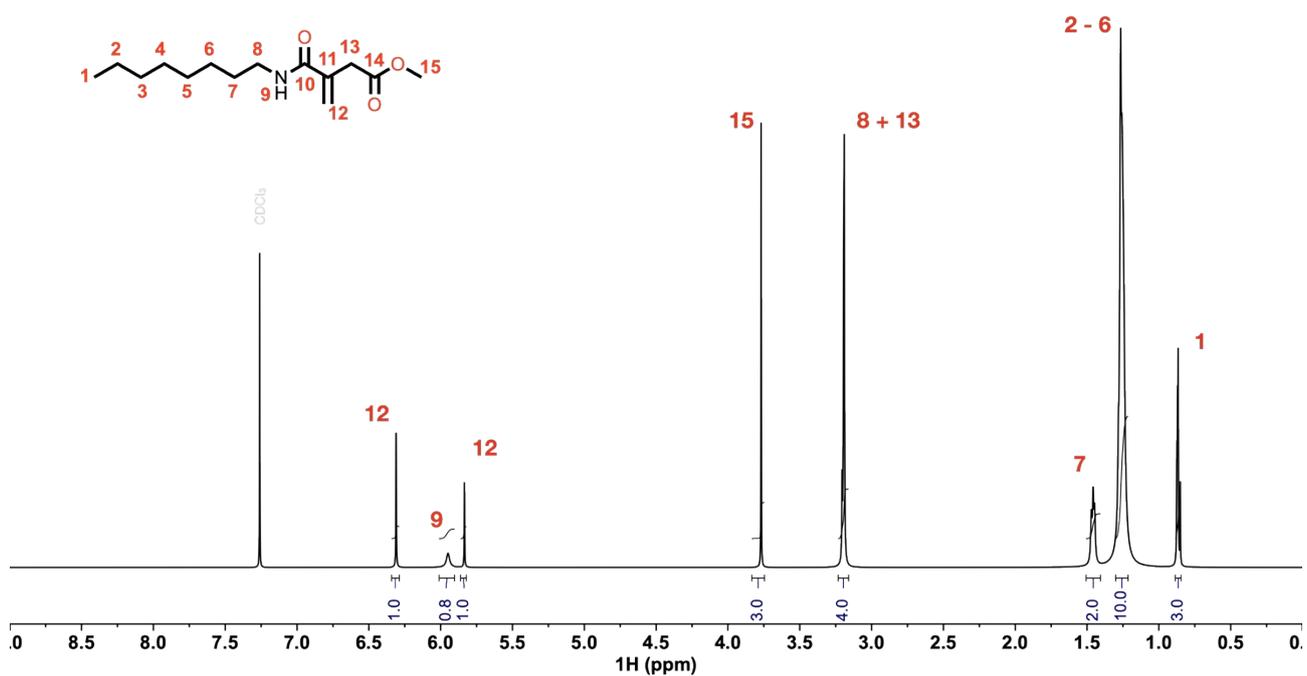


Figure S2. $^1\text{H-NMR}$ (600 MHz, CDCl_3) of Oct-MEIA

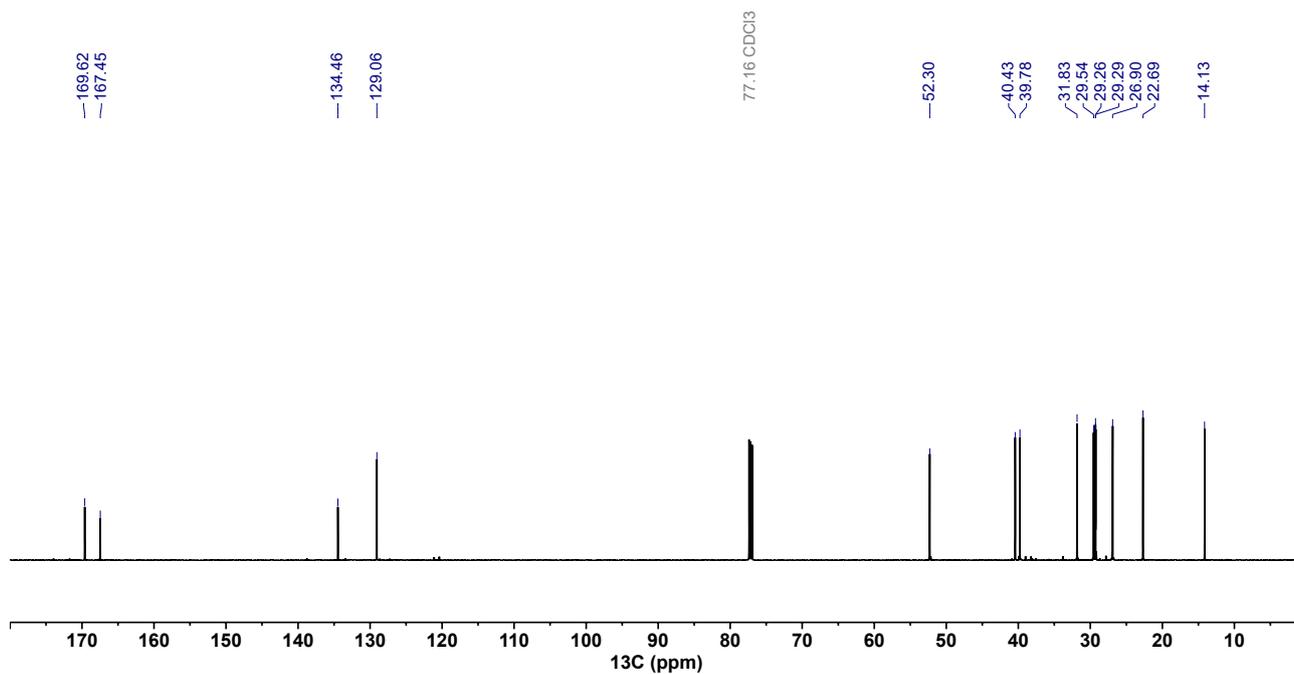


Figure S3. ¹³C-NMR (600 MHz, CDCl₃) of Oct-MEIA

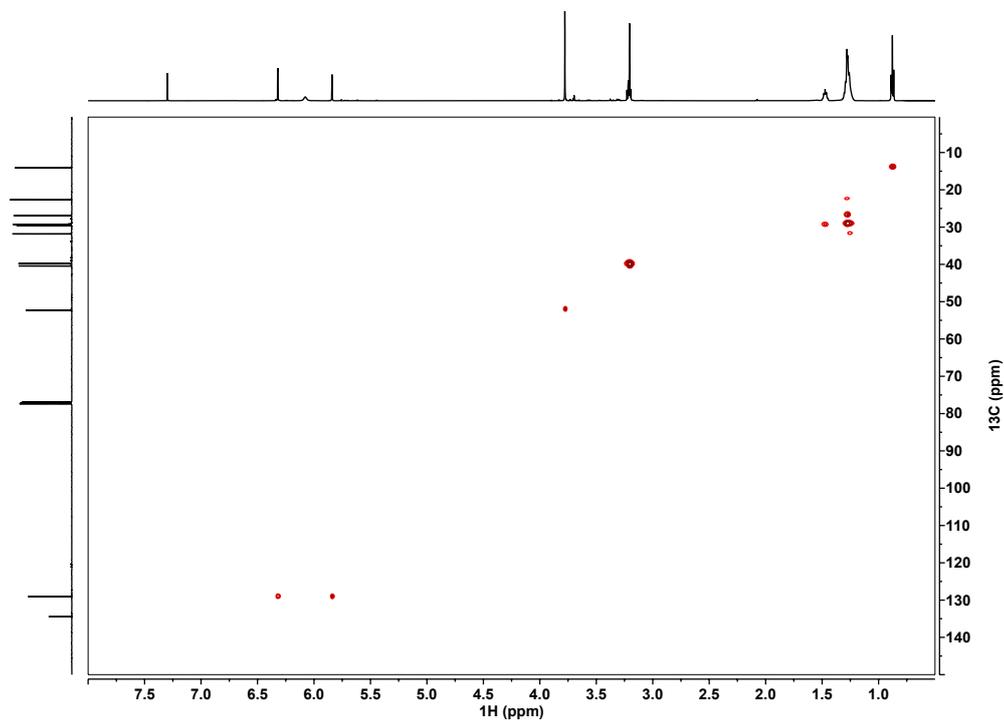
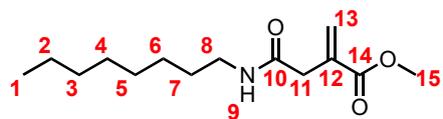


Figure S4. ¹H-¹³C HSQC (600 MHz, CDCl₃) NMR analysis of Oct-MEIA. Positive peaks are coloured in red and are related to CH and CH₃ groups, while negative peaks are coloured in blue and are related to CH₂ groups.

Table S3. NMR peak assignments for Oct-MEIA.



	^1H (ppm)	^{13}C (ppm)
1	0.87	14.13
2	1.27	22.69
3	1.27	26.90
4	1.27	29.26
5	1.27	29.54
6	1.27	31.83
7	1.47	29.29
8	3.21	39.78
9	5.94	\
10	\	169.62
11	3.21	40.43
12	\	134.46
13	6.32 and 5.84	129.06
14	\	167.45
15	3.77	52.30

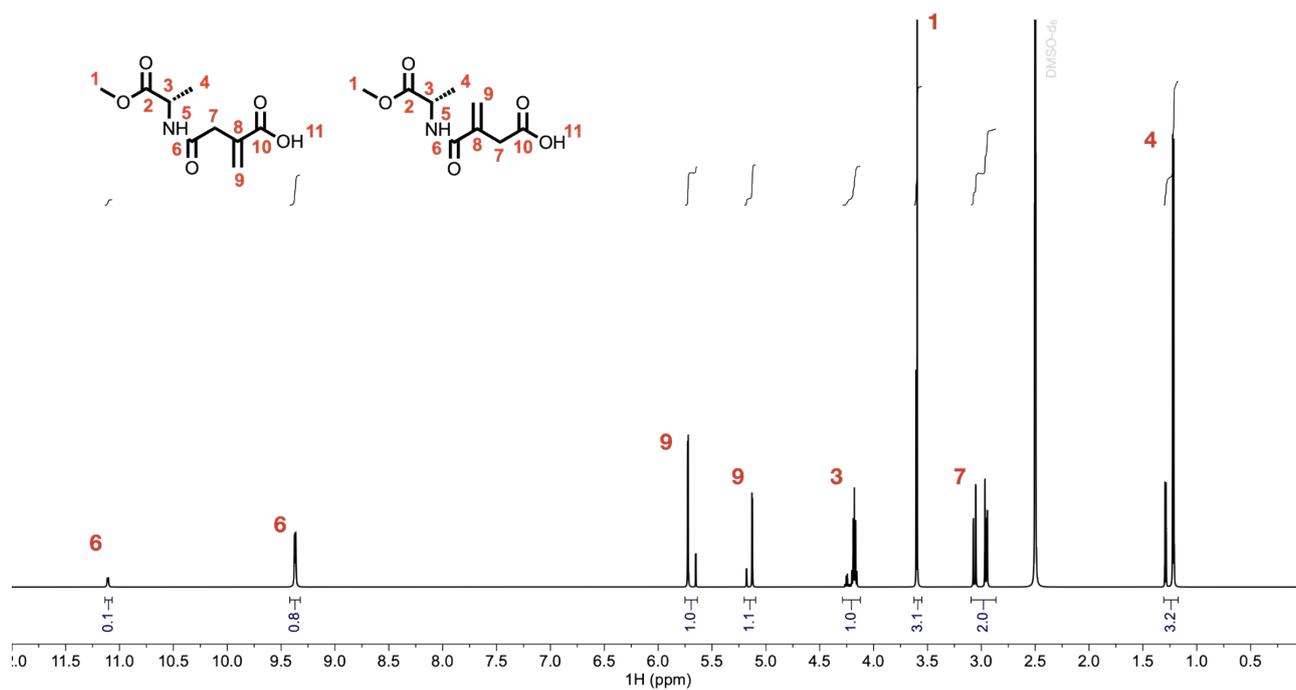


Figure S5. $^1\text{H-NMR}$ (600 MHz, DMSO-d_6) of Ala-IA

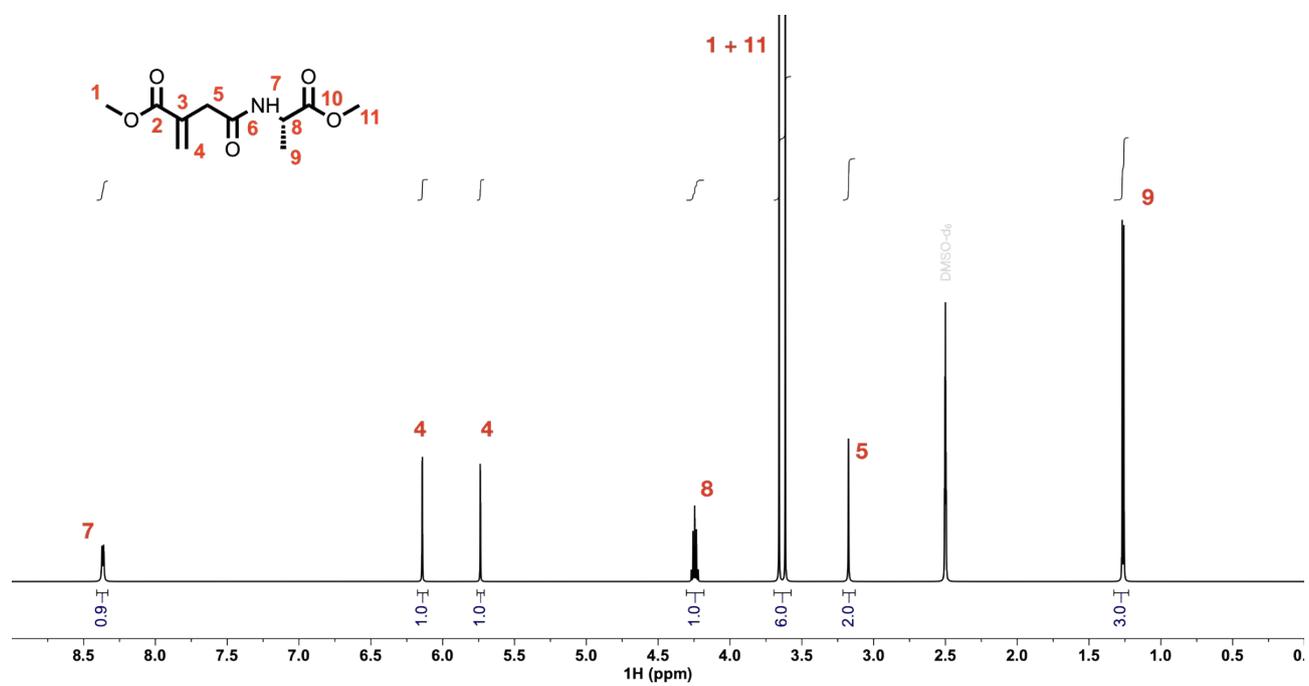


Figure S6. $^1\text{H-NMR}$ (600 MHz, DMSO-d_6) of Ala-MEIA

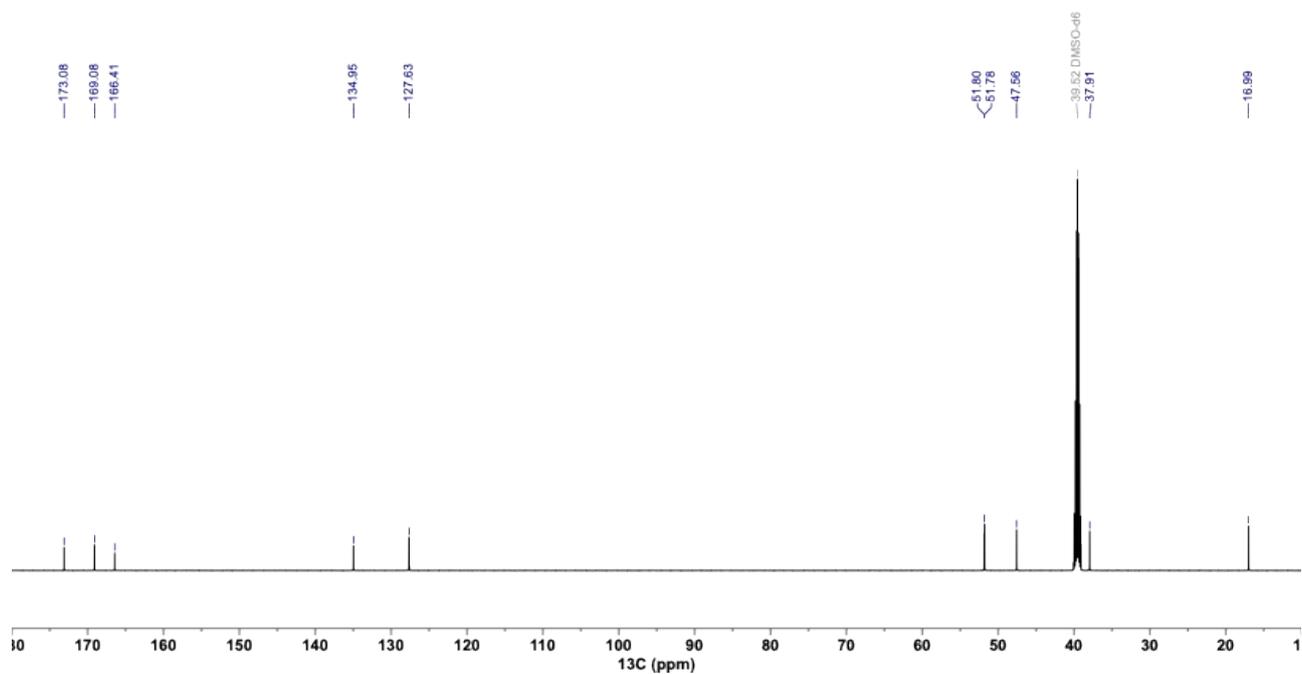


Figure S7. ^{13}C -NMR (600 MHz, DMSO-d_6) of Ala-MEIA

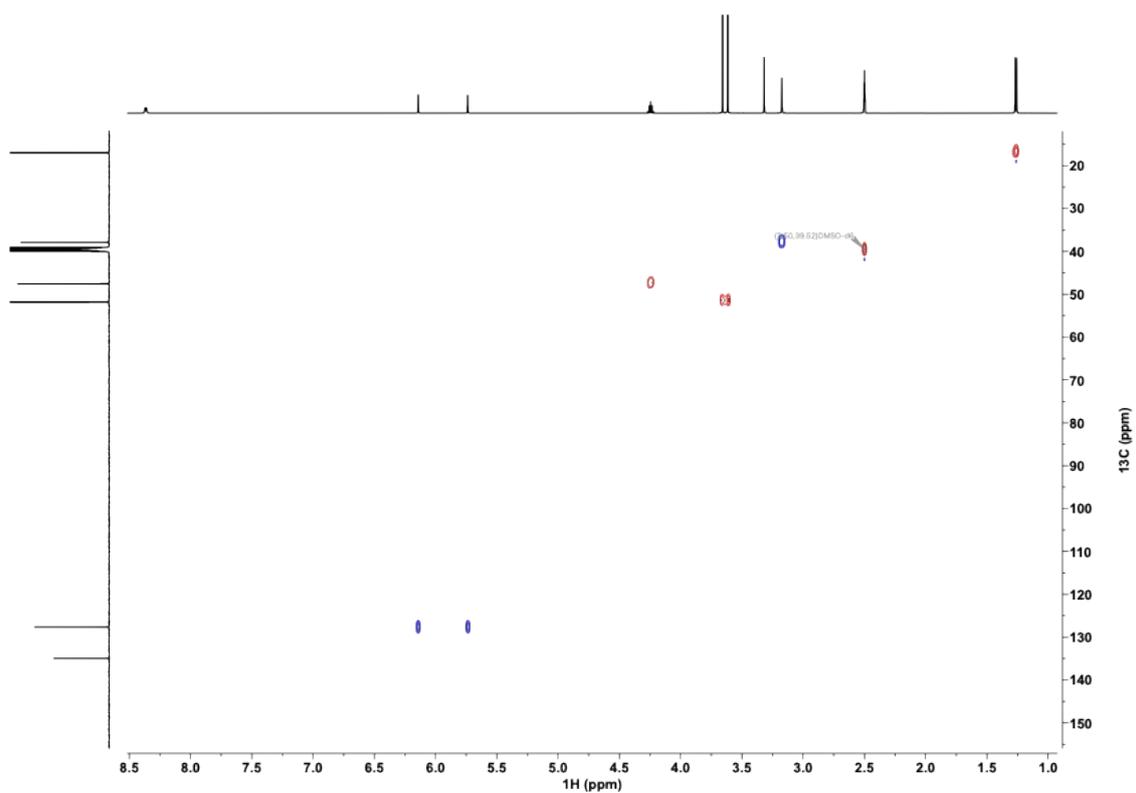
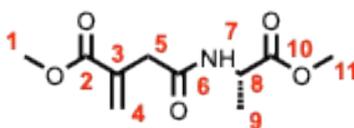


Figure S8. ^1H - ^{13}C HSQC (600 MHz, DMSO-d_6) NMR analysis of Ala-MEIA. Positive peaks are coloured in red and are related to CH and CH_3 groups, while negative peaks are coloured in blue and are related to CH_2 groups.

Table S4. NMR peak assignments for Ala-MEIA.



	^1H (ppm)	^{13}C (ppm)
1	3.66	51.80
2	\	169.08
3	\	134.95
4	8.36	\
5	3.17	37.91
6	\	173.08
7	6.14 – 5.74	127.63
8	4.25	47.56
9	1.25	16.99
10	\	166.41
11	3.61	51.78

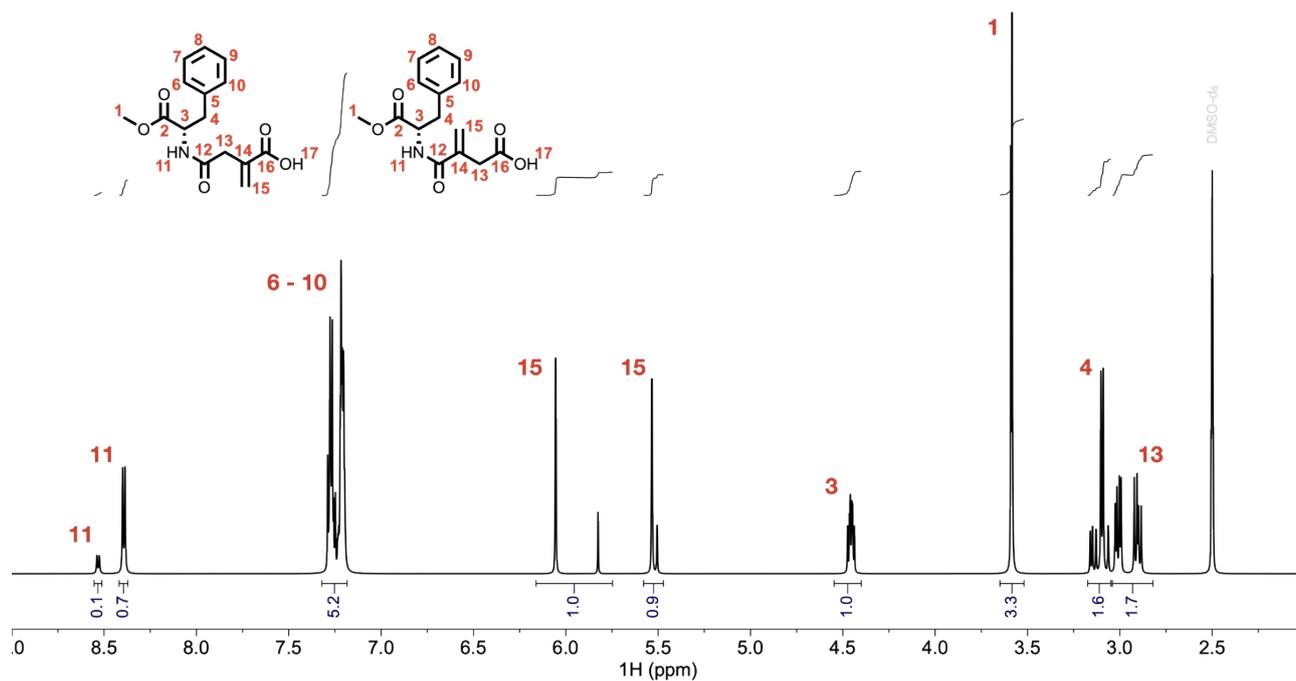


Figure S9. $^1\text{H-NMR}$ (600 MHz, DMSO-d_6) of Phe-IA

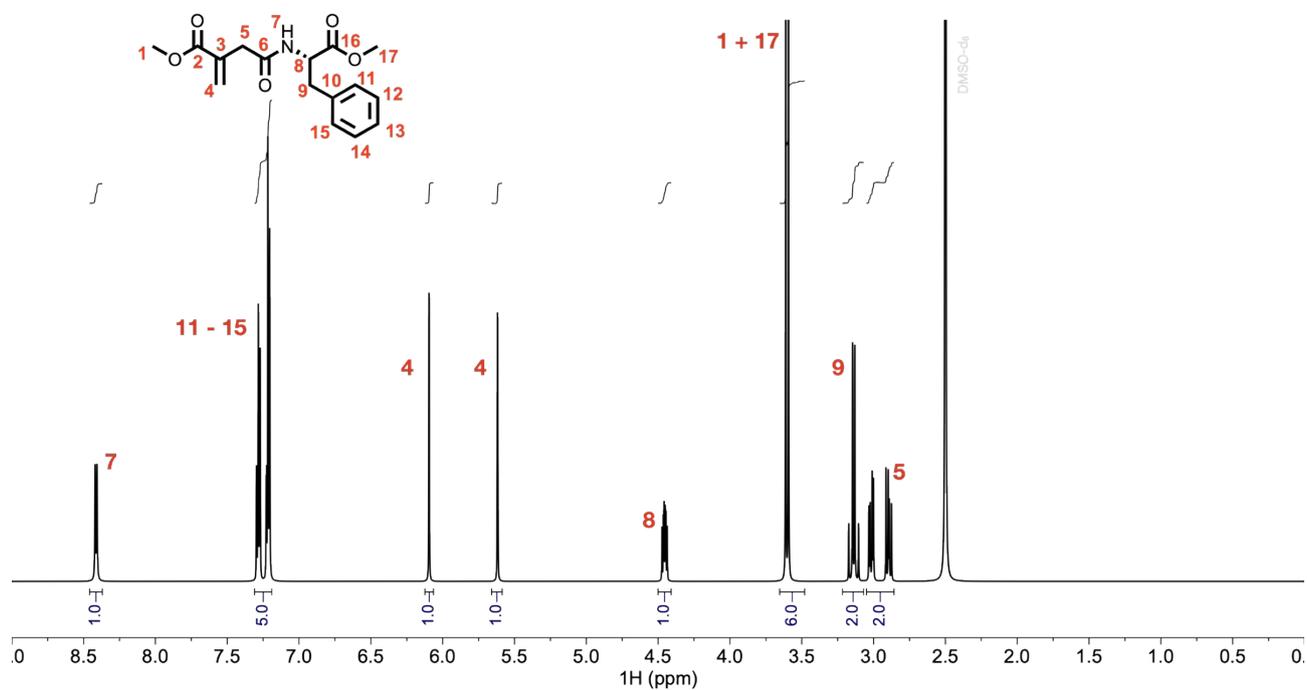


Figure S10. $^1\text{H-NMR}$ (600 MHz, DMSO-d_6) of Phe-MEIA

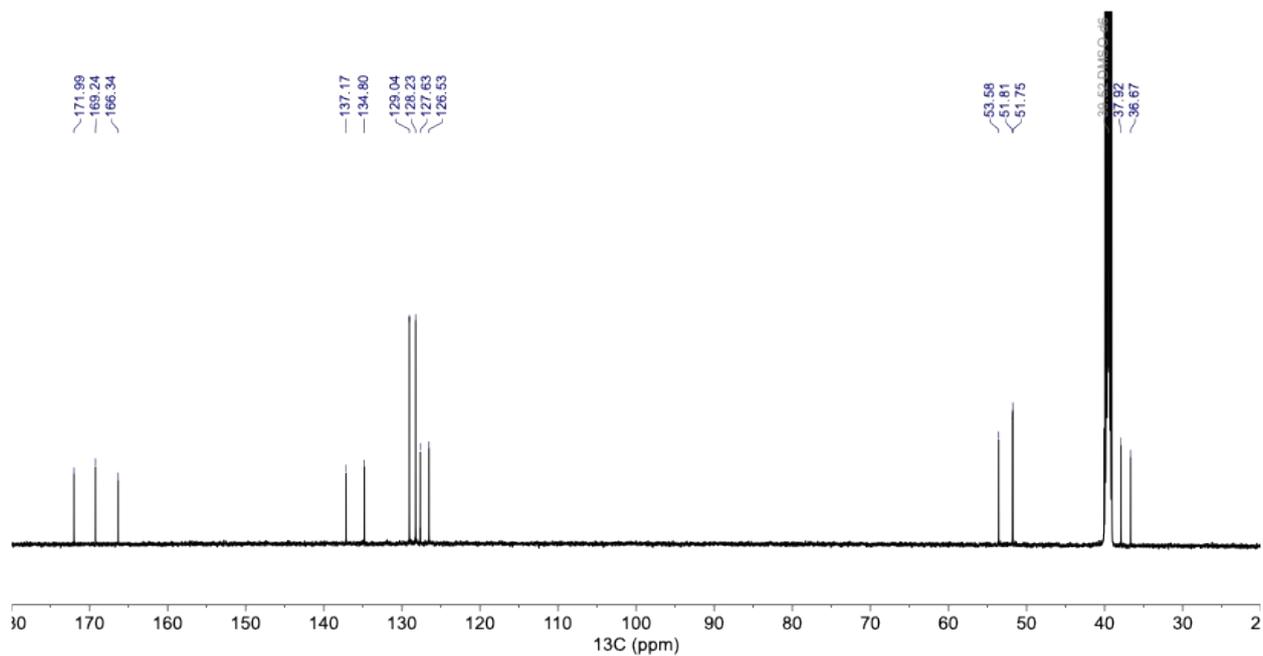


Figure S11. ^{13}C -NMR (600 MHz, DMSO-d_6) of Phe-MEIA

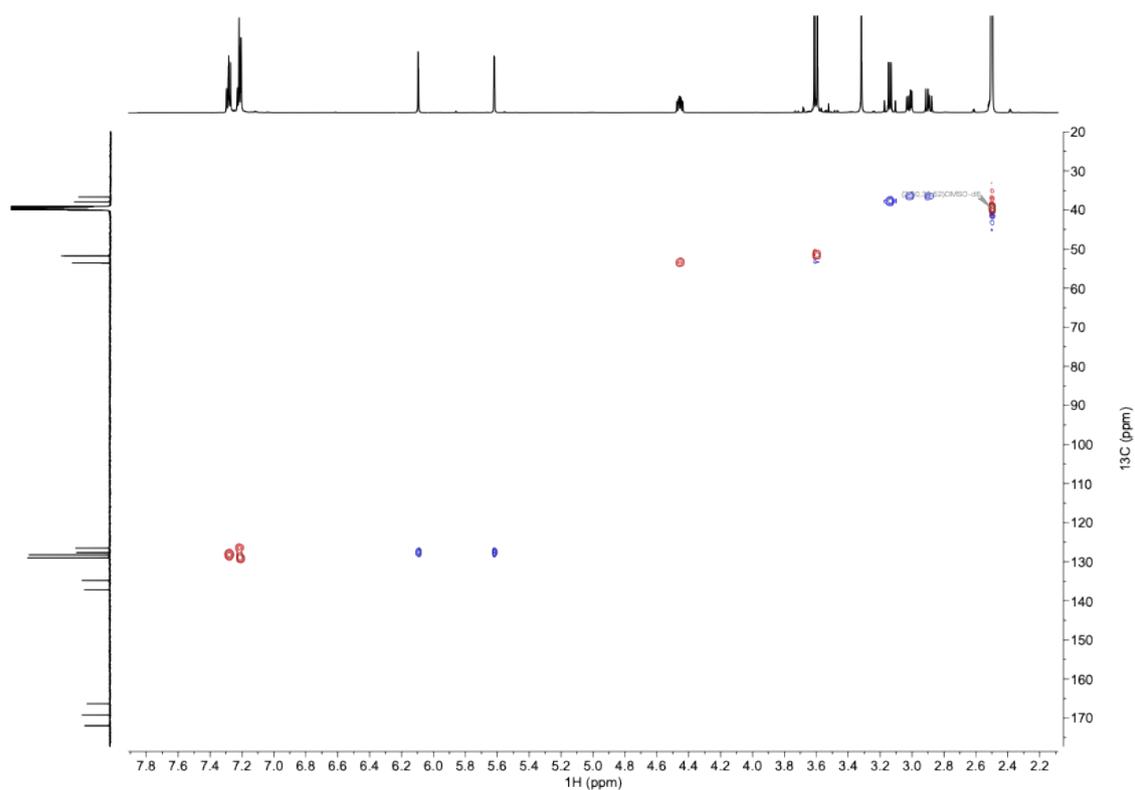
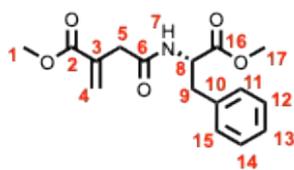


Figure S12. ^1H - ^{13}C HSQC (600 MHz, DMSO-d_6) NMR analysis of Phe-MEIA. Positive peaks are coloured in red and are related to CH and CH_3 groups, while negative peaks are coloured in blue and are related to CH_2 groups.

Table S5. NMR peak assignments for Phe-MEIA.



	^1H (ppm)	^{13}C (ppm)
1	3.58	51.75
2	\	169.24
3	\	134.80
4	5.62 – 6.10	127.63
5	3.03 – 2.88	36.67
6	\	171.99
7	8.41	\
8	4.46	53.58f
9	3.13	37.92
10	\	137.17
11-15	7.30 – 7.20	126.53
12-14	7.30 – 7.20	128.23
13	7.30 – 7.20	129.04
16	\	166.34
17	3.60	51.81

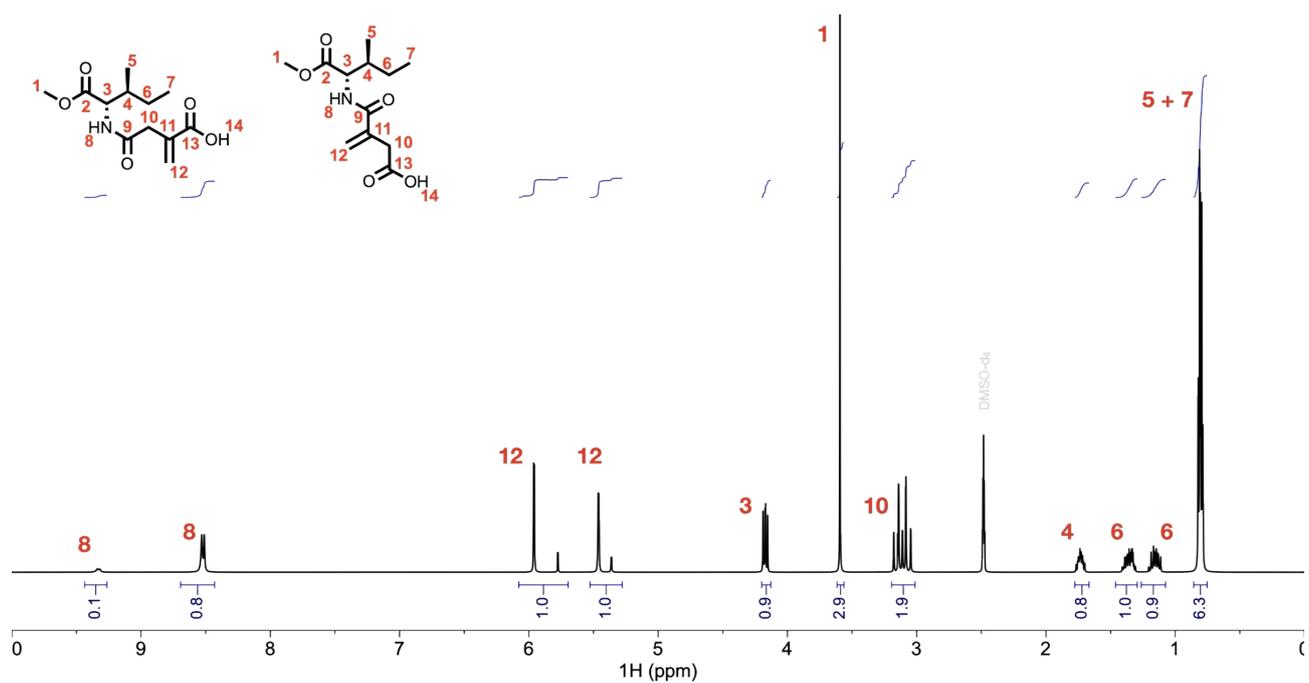


Figure S13. $^1\text{H-NMR}$ (600 MHz, DMSO-d_6) of Ile-IA

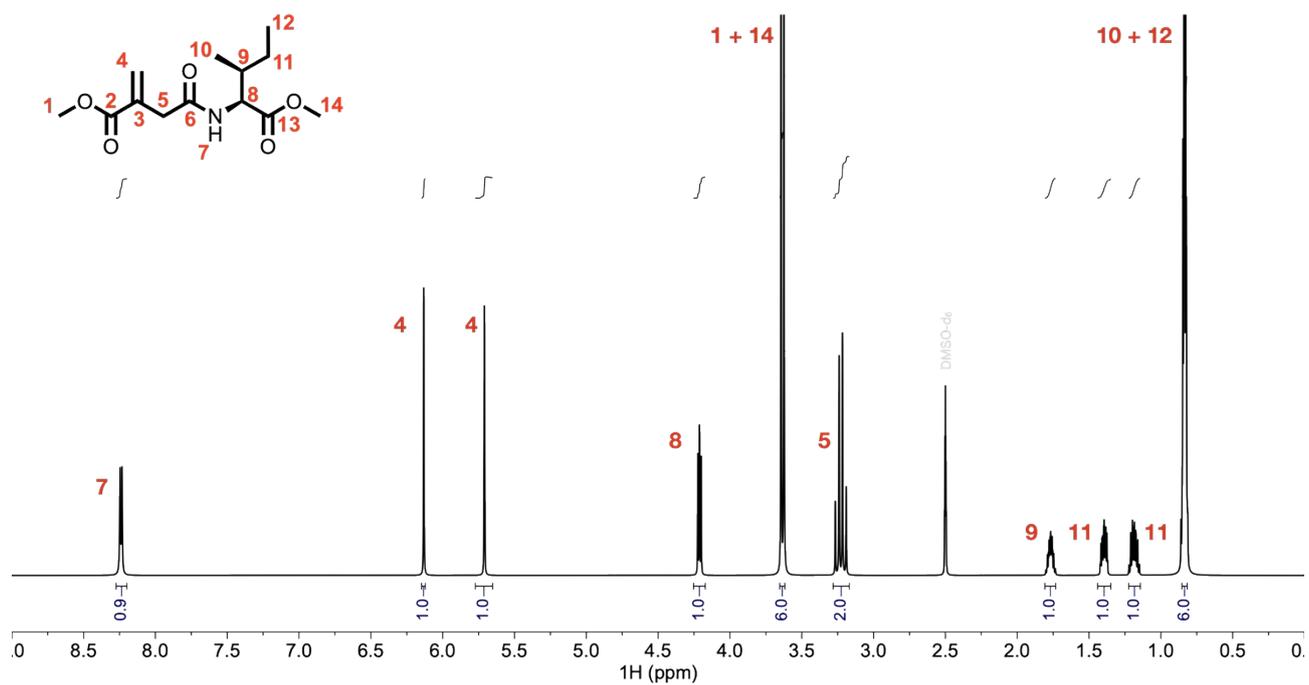


Figure S14. $^1\text{H-NMR}$ (600 MHz, DMSO-d_6) of Ile-MEIA

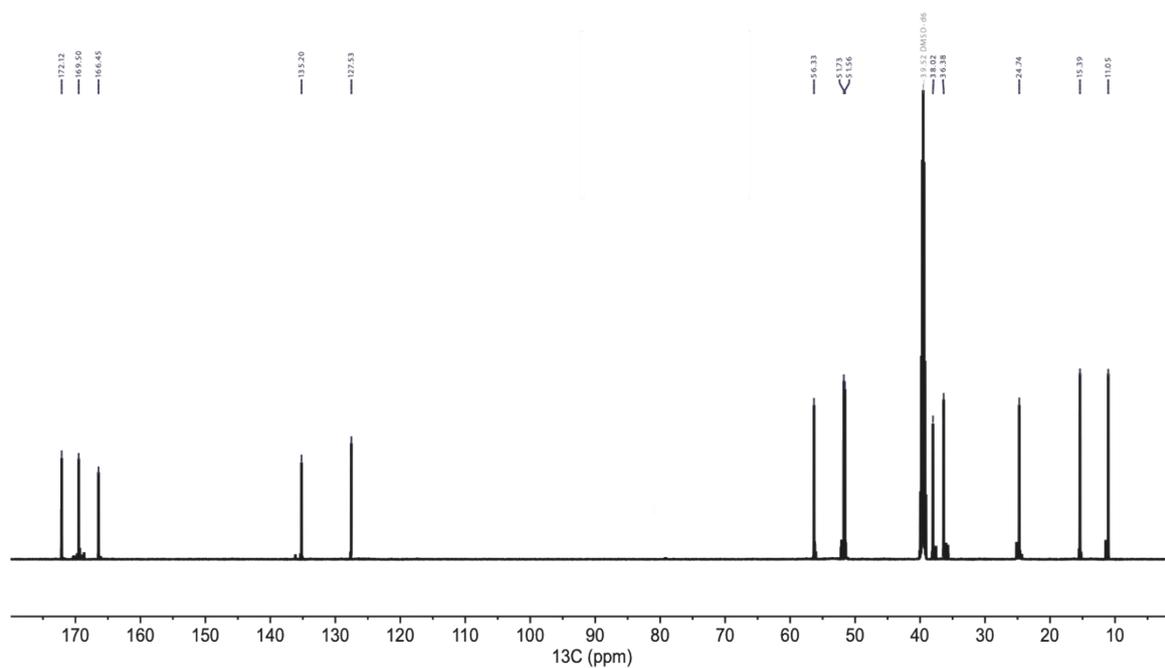


Figure S15. ^{13}C -NMR (600 MHz, DMSO-d_6) of Ile-MEIA

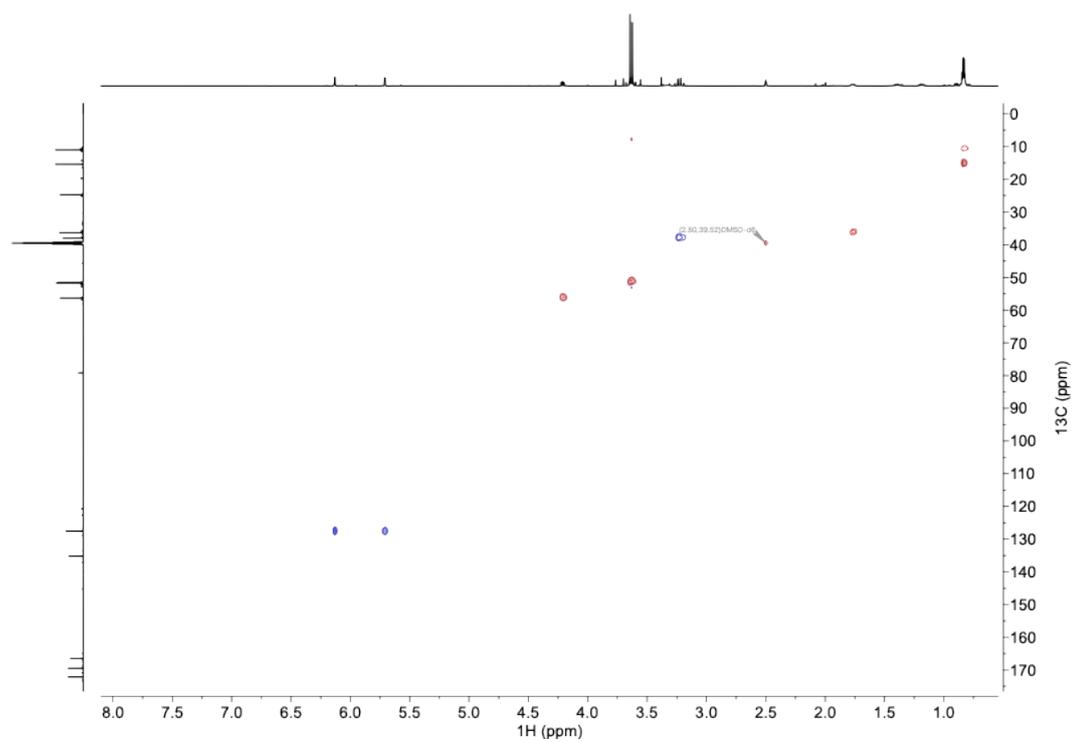
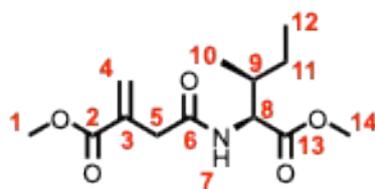


Figure S16. ^1H - ^{13}C HSQC (600 MHz, DMSO-d_6) NMR analysis of Phe-MEIA. Positive peaks are coloured in red and are related to CH and CH_3 groups, while negative peaks are coloured in blue and are related to CH_2 groups.

Table S6. NMR peak assignments for Ile-MEIA.



	¹ H (ppm)	¹³ C (ppm)
1	3.62	51.56
2	\	169.50
3	\	135.20
4	6.13 - 5.71	127.53
5	3.27 – 3.19	38.02
6	\	172.12
7	8.24	\
8	4.21	56.33
9	1.80 – 1.73	36.38
10	0.86 – 0.81	15.39
11	1.42 – 1.37	24.74
12	0.86 – 0.81	11.05
13	\	166.45
14	3.64	51.73

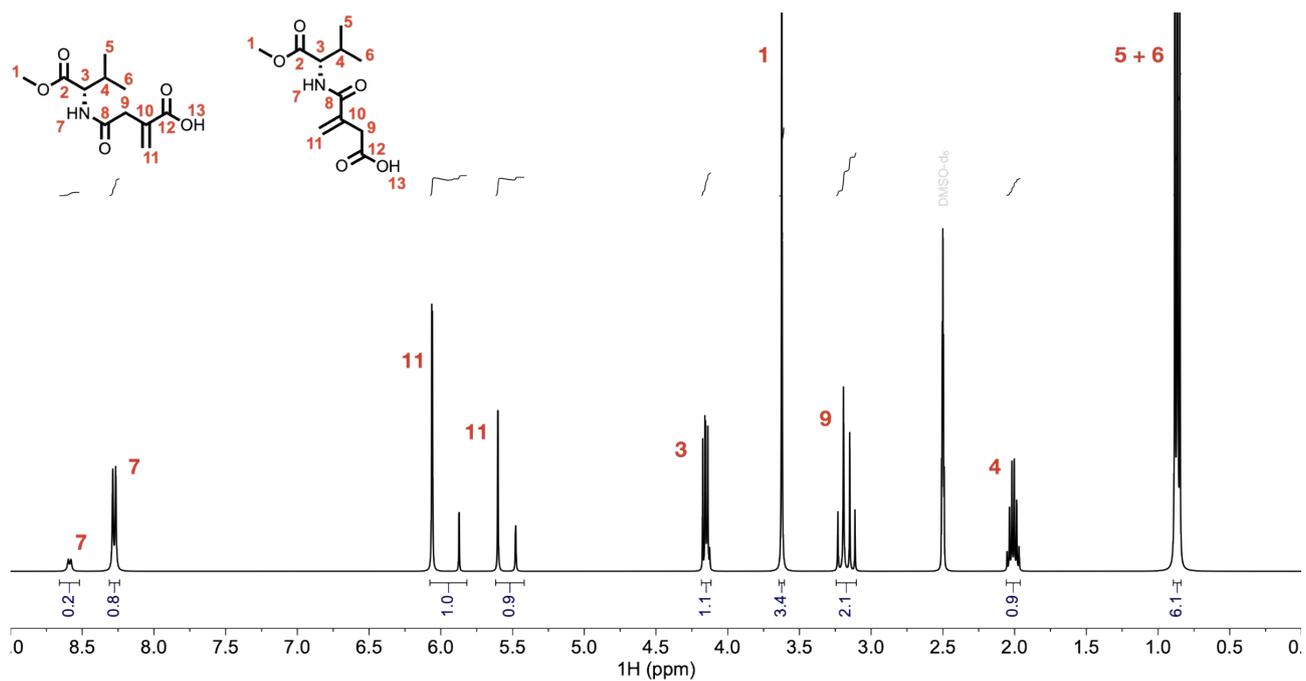


Figure S17. $^1\text{H-NMR}$ (600 MHz, DMSO-d_6) of Val-IA

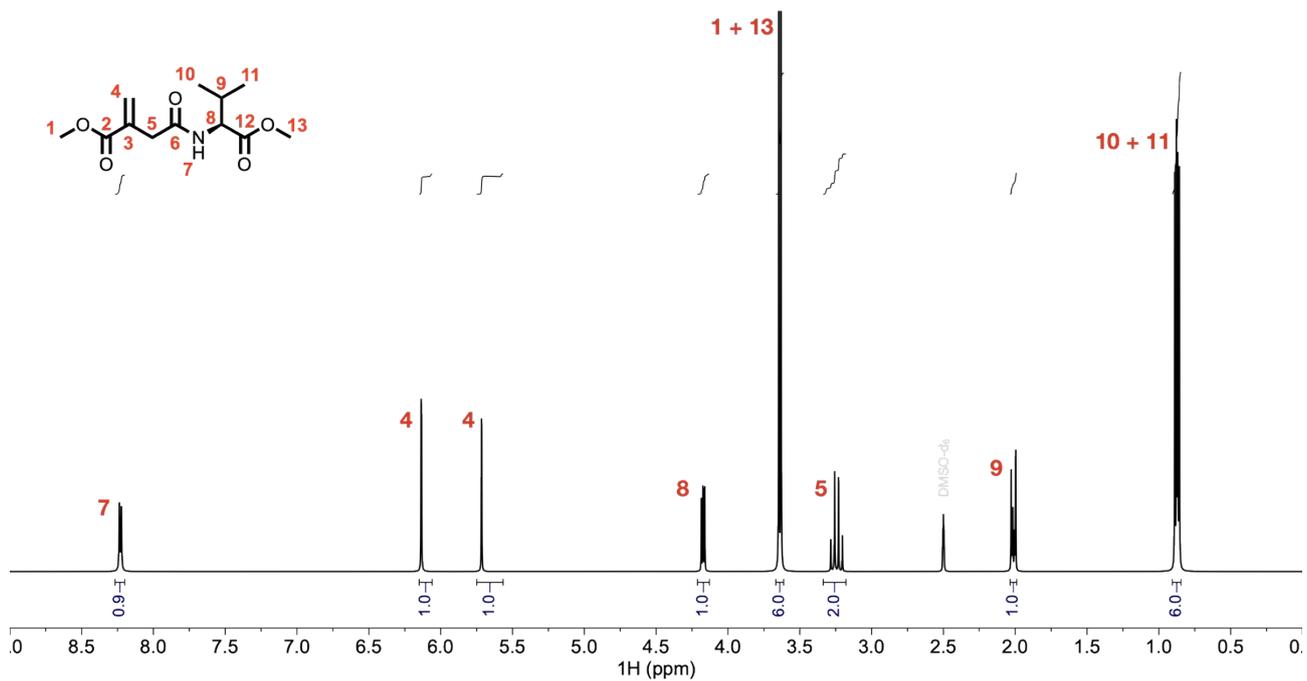


Figure S18. $^1\text{H-NMR}$ (600 MHz, DMSO-d_6) of Val-MEIA

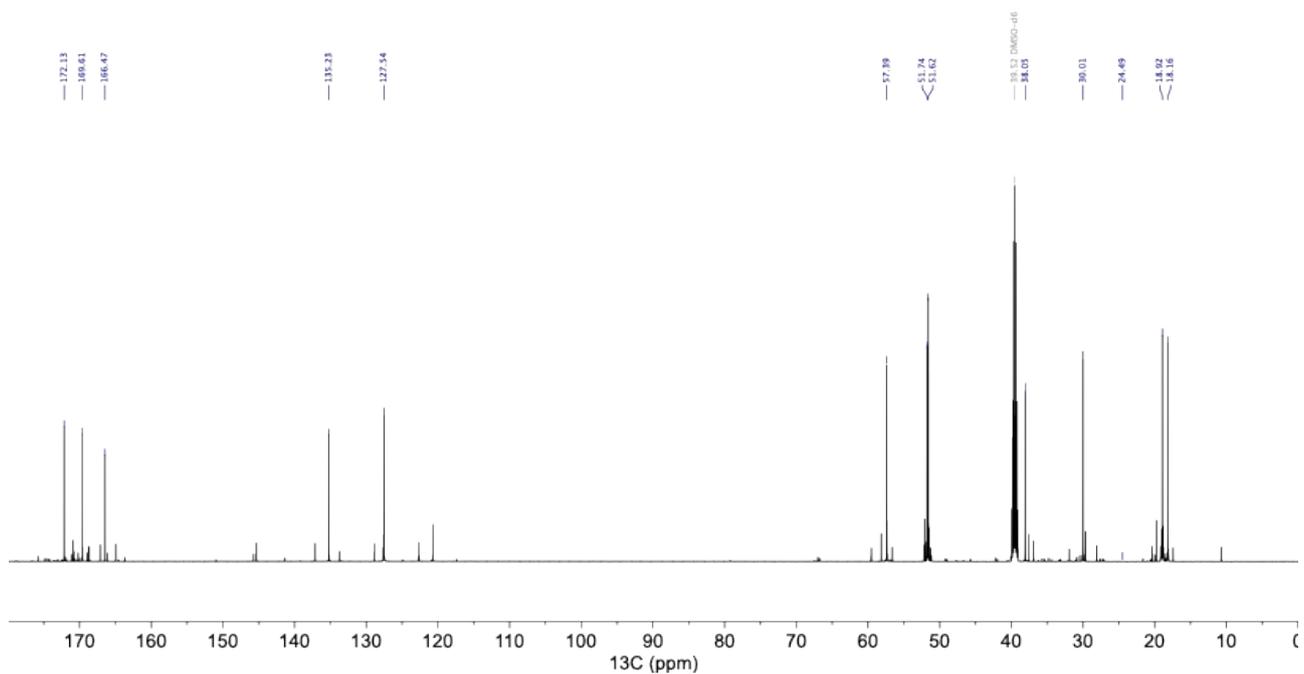


Figure S19. ^{13}C -NMR (600 MHz, DMSO-d_6) of Val-MEIA

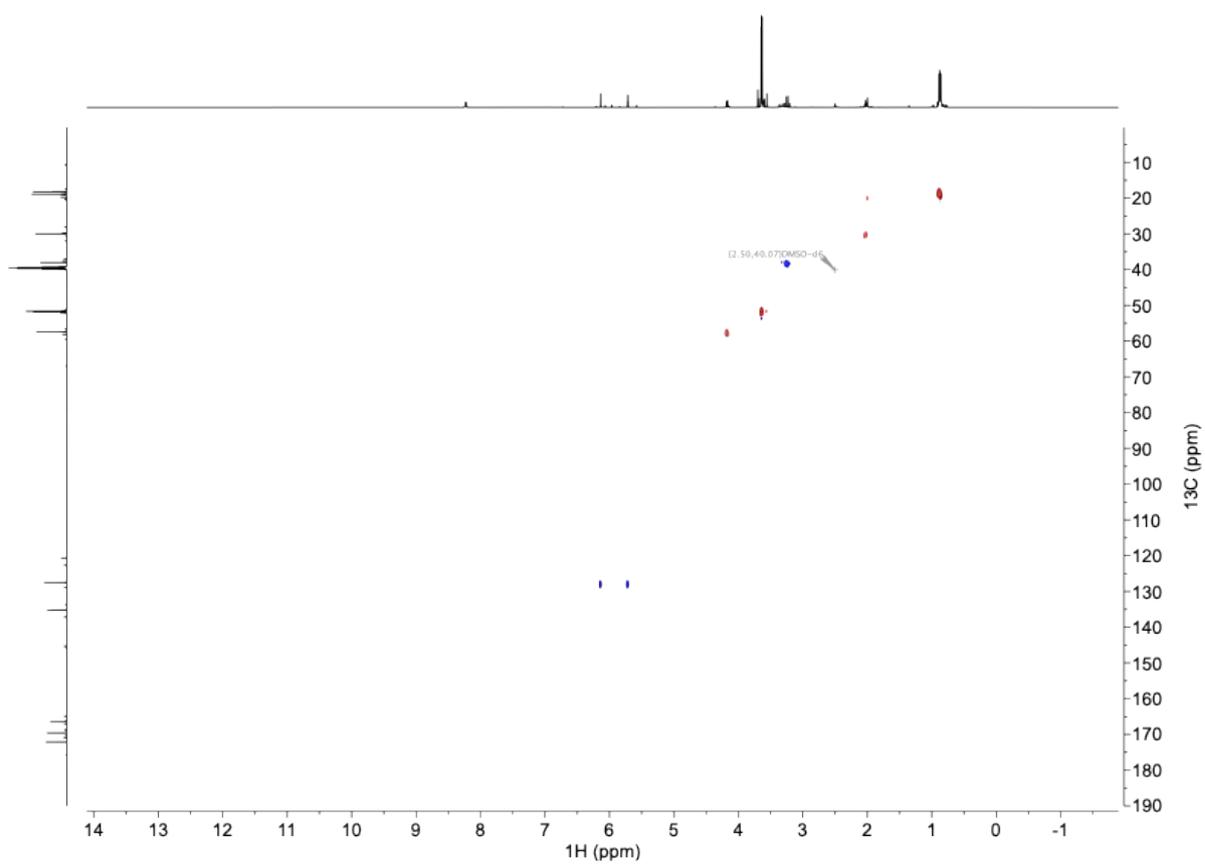
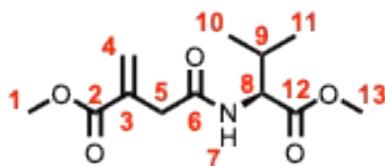


Figure S20. ^1H - ^{13}C HSQC (600 MHz, DMSO-d_6) NMR analysis of Phe-MEIA. Positive peaks are coloured in red and are related to CH and CH_3 groups, while negative peaks are coloured in blue and are related to CH_2 groups.

Table S7. NMR peak assignments for Val-MEIA.



	¹ H (ppm)	¹³ C (ppm)
1	3.63	51.62
2	\	169.61
3	\	135.20
4	6.13 and 5.71	127.54
5	3.26-3.23	38.05
6	\	172.13
7	8.23	\
8	4.19-4.15	57.39
9	2.02 - 2.00	30.01
10-11	0.89 – 0.86	18.92 and 18.16
12	\	166.47
13	3.64	51.74

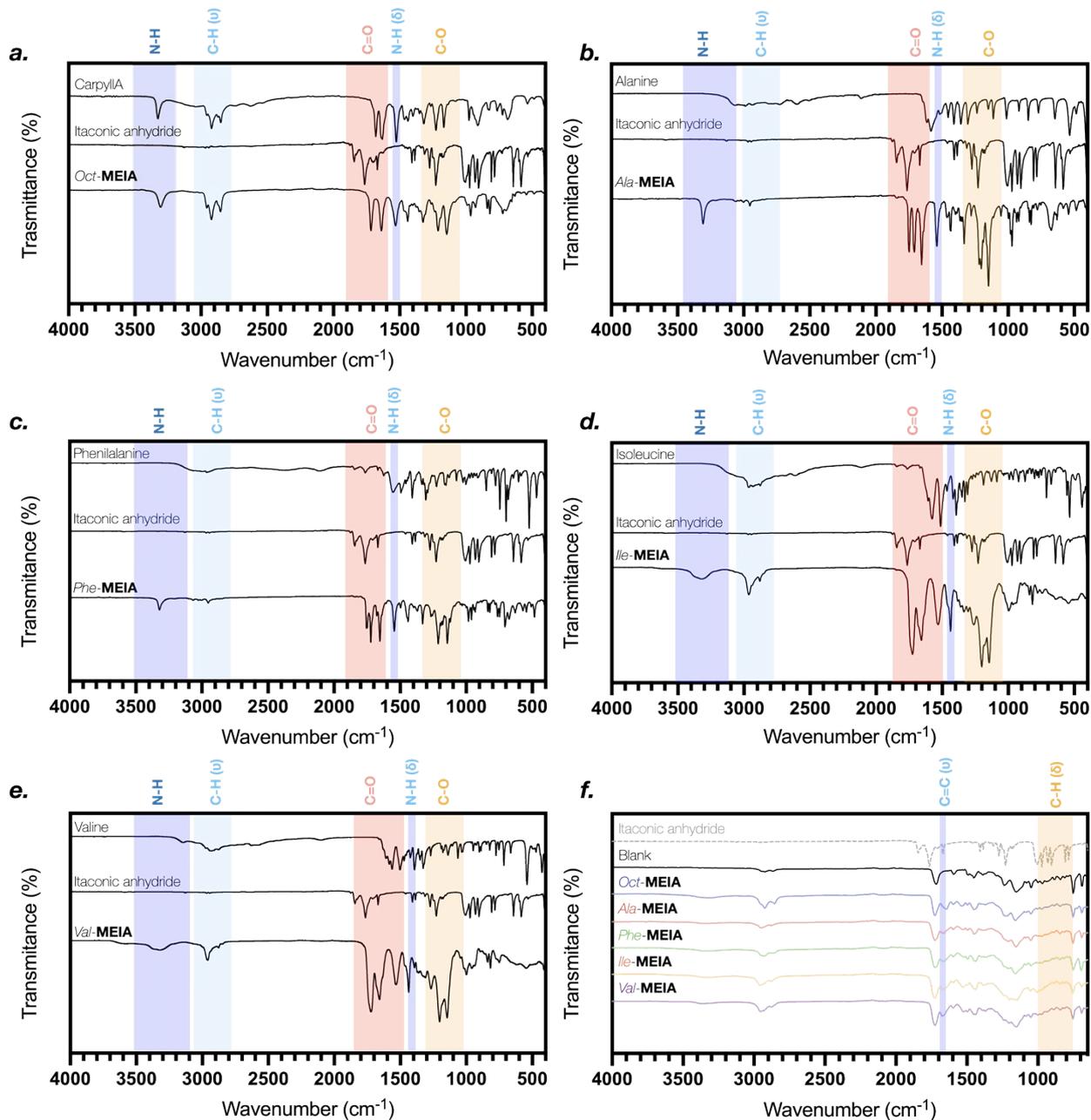


Figure S21. a. – e.) ATR-FTIR of the itaconamide monomers, showing the regions of characteristic stretching and bending modes. f.) ATR-FTIR of the post-cured 3D-Printed samples with the specific vinylic highlighted regions.

Table S8. Tensile properties and Shore hardness of MEIA-based formulations. Data are expressed as mean \pm SD of a minimum of 5 independent measurements

Resin	Tensile Modulus (GPa)	Elongation (%)	Tensile strength (MPa)	Hardness (Shore D)
Blank	1.16 \pm 0.13	3.5 \pm 0.2	33.4 \pm 0.9	76 \pm 1
Oct-MEIA10	0.92 \pm 0.16	6.0 \pm 1.0	34.0 \pm 2.0	80 \pm 1
Oct-MEIA25	0.69 \pm 0.09	16 \pm 7	29.8 \pm 3.2	76 \pm 1
Oct-MEIA40	0.48 \pm 0.09	17 \pm 9	24.1 \pm 2.3	77 \pm 1
Ala-MEIA10	0.68 \pm 0.12	7.3 \pm 2.4	35.6 \pm 1.2	84 \pm 1
Ala-MEIA25	0.54 \pm 0.03	6.8 \pm 1.0	27.0 \pm 0.5	79 \pm 1
Ala-MEIA40	0.37 \pm 0.03	13 \pm 9	17.2 \pm 1.5	77 \pm 1
Phe-MEIA10	0.89 \pm 0.11	4.5 \pm 1.0	40.2 \pm 6.3	83 \pm 1
Phe-MEIA25	0.81 \pm 0.06	3.9 \pm 2.0	31.2 \pm 12.2	77 \pm 1
Phe-MEIA40	0.98 \pm 0.11	2.8 \pm 0.6	28.0 \pm 5.7	40 \pm 1
Ile-MEIA10	0.89 \pm 0.05	7.0 \pm 3.3	35.3 \pm 2.8	77 \pm 1
Ile-MEIA25	0.72 \pm 0.03	11 \pm 3	31.0 \pm 0.5	78 \pm 1
Ile-MEIA40	0.48 \pm 0.04	14 \pm 8	23.4 \pm 1.7	77 \pm 1
Val-MEIA10	1.19 \pm 0.11	3.2 \pm 0.6	34.7 \pm 4.4	80 \pm 1
Val-MEIA25	0.58 \pm 0.15	5.6 \pm 0.4	35.3 \pm 1.9	76 \pm 1
Val-MEIA40	0.59 \pm 0.11	10 \pm 2	26.0 \pm 1.7	70 \pm 1

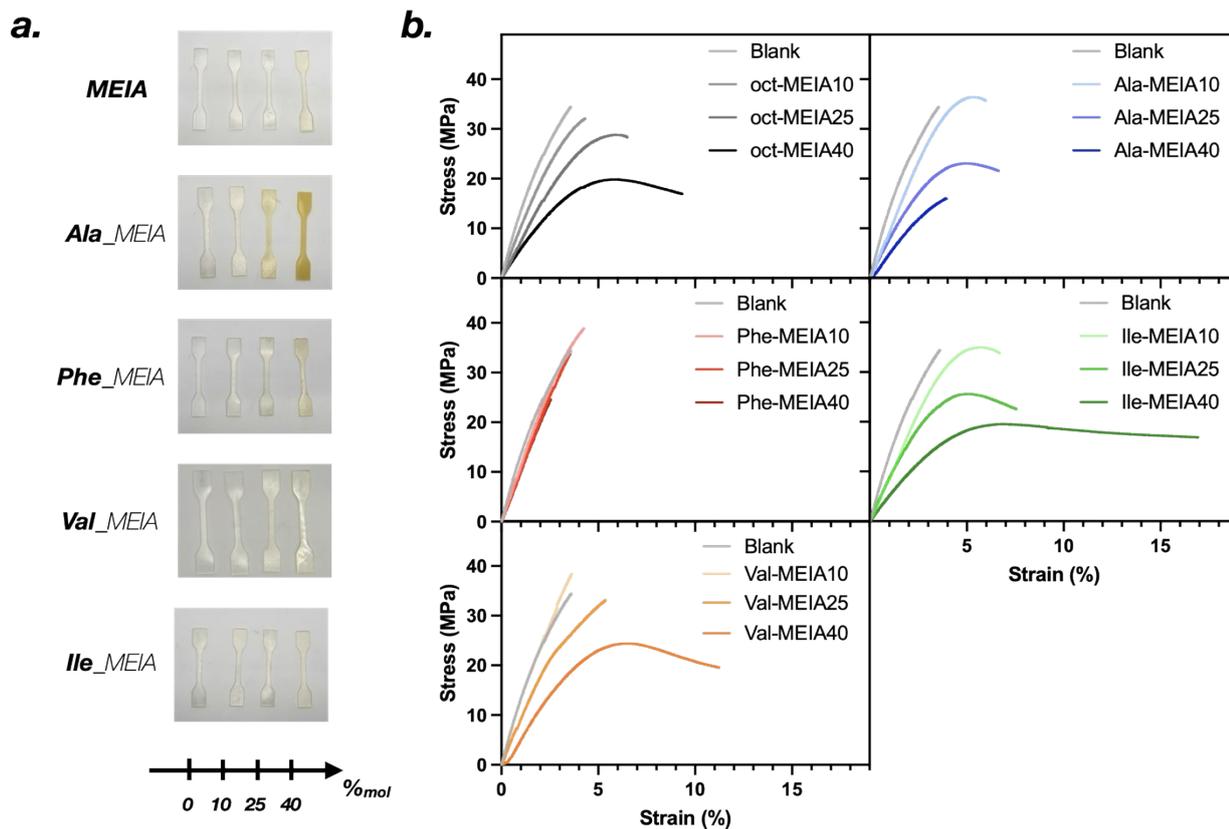


Figure S22. a) Picture of the tensile test specimens and b) mechanical tensile test curves of all the MEIA's based resin sets and 3D-printed dogbones, increasing the synthetic monomer.

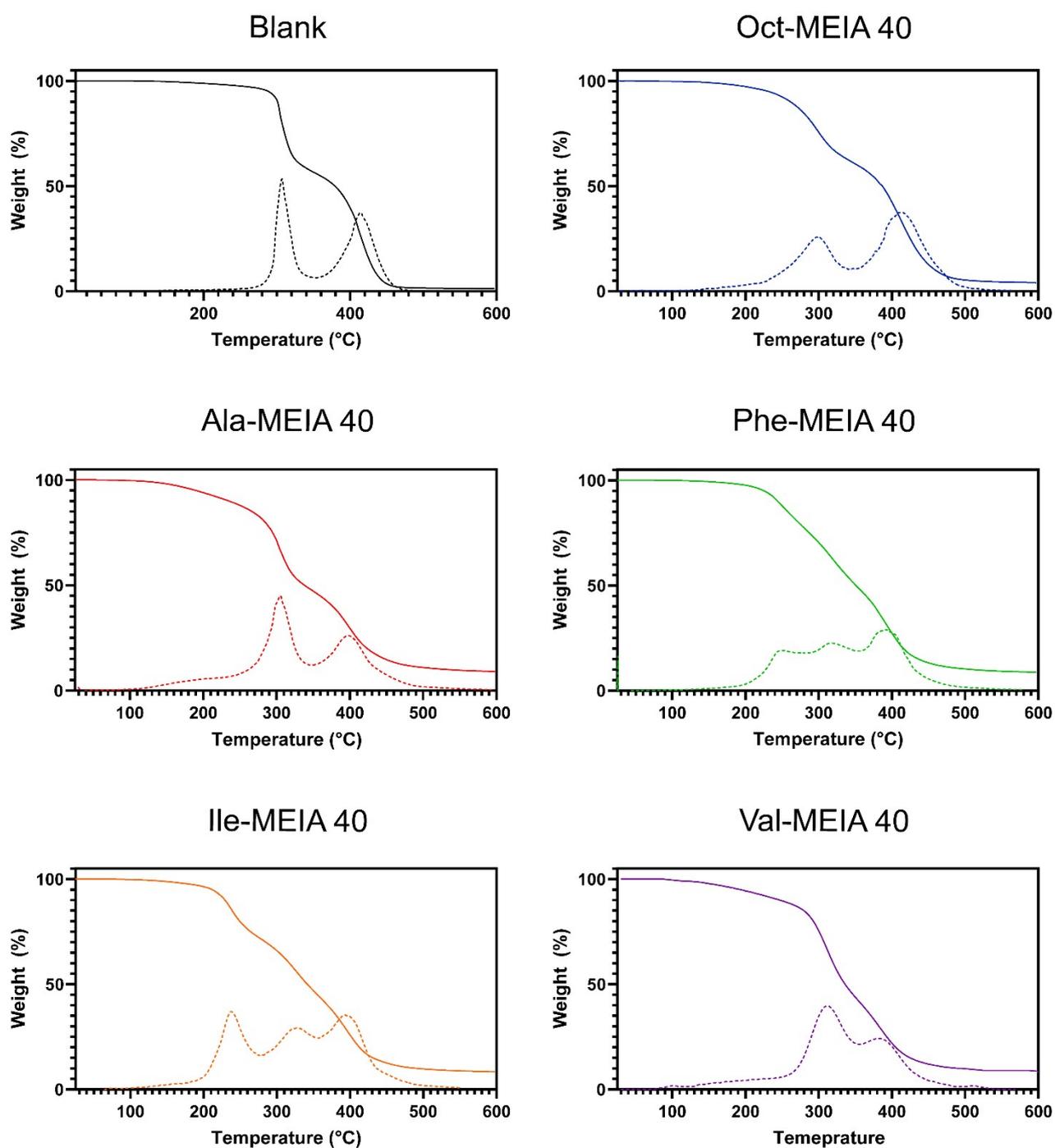


Figure S23. Thermogravimetric analysis (TGA) of the 3D printed materials containing the highest loading (40 mol.%) of the different itaconamide monomers. In all plots, solid line corresponds to the actual weight loss curve while dashed lines correspond to their first derivative.

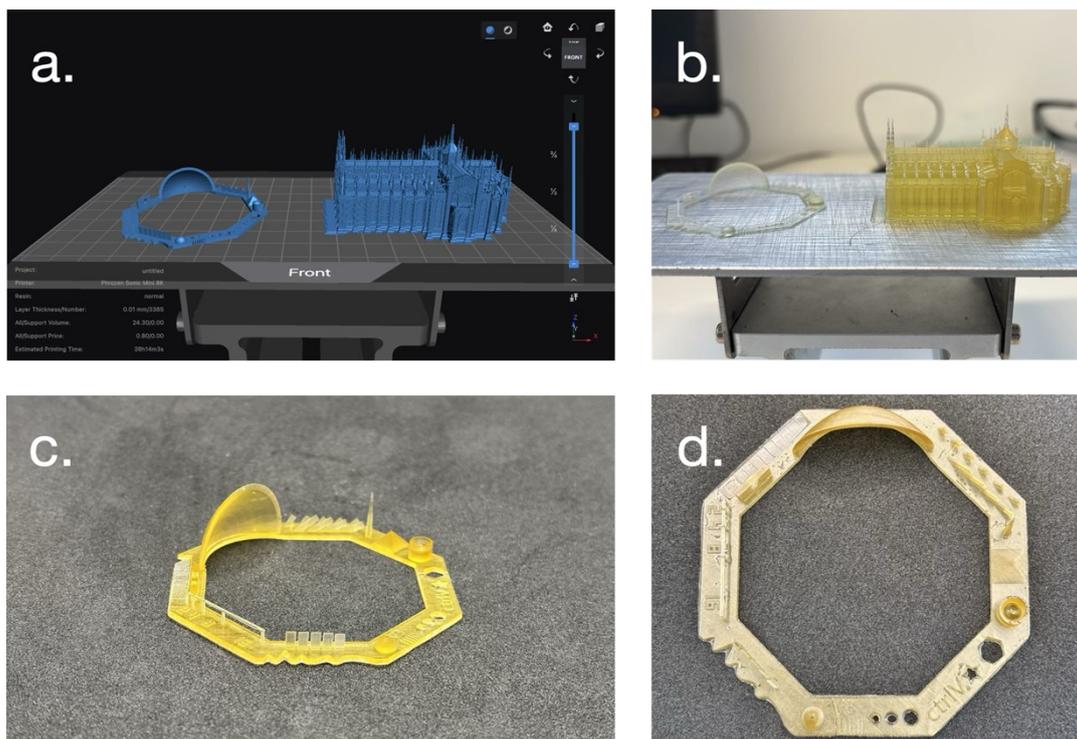


Figure S24. a.) Slicing process and b.) evaluation of the printing performances of the Ile-MEIA 40 mol.% content resin before the post-curing process. For Milano's dome b.): the spires present are less than 0.5 mm in size. On c.) and d.) Vertical hole in wall and bridge print with bridge length up to 16 mm; spike and overhanging walls up to 70° inclination, and walls of decreasing thickness up to 0.1 mm.

Resin	T _{max} (1)	T _{max} (2)	T _{max} (3)	Residue at 600°C
Blank	-	306°C	414°C	1.2%
Oct-MEIA 40	-	299°C	410°C	4.0%
Ala-MEIA 40	-	305°C	398°C	8.9%
Phe-MEIA 40	250°C	319°C	393°C	8.6%
Ile-MEIA 40	238°C	327°C	394°C	8.2%
Val-MEIA 40	-	311°C	384°C	8.0%

Table S9. Maximum degradation temperatures obtained as maxima of the DTG curves, together with the residual mass at 600°C.

Component	BCC _i %	f _{haz}	f _{solv}	f _T	f _t	f _{T+t}	AE	F _{syn}	F _{EoL}	Synthesis conditions
IBOMA	71%	0.70	1.20	0.90	0.8	0.88	0.78	0.574	0.8	Methacrylic acid 1.2 eq. Isoborneol 1 eq. 50°C 24 h
EGPEA	18%	0.7	1.2	0.8	1	0.8	0.69	0.46	0.8	Acrylic acid 1 eq, 2-phenoxyethanol 1.5 eq 100°C 5 h
HDDA	50%	0.7	1.2	0.8	1	0.8	0.68	0.46	0.8	Acrylic acid 1 eq, 1,6-hexanediol 0.75 eq 100°C 5 h
Ala-MEIA	100%	1.00	1.20	0.90	1	0.90	1.00	1.08	0.8	i) MeOH, H ₂ SO ₄ , 65 °C, 24 h; ii) Itaconic anhydride, Ethyl acetate, Na ₂ CO ₃ 24 h. iii) MeOH, H ₂ SO ₄ , 65 °C, 1 h.
Ile-MEIA	100%	1.00	1.20	0.90	1	0.90	1.00	1.08	0.8	i) MeOH, H ₂ SO ₄ , 65 °C, 72 h; ii) Itaconic anhydride, 2-MeTHF, NaHCO ₃ 24 h. iii) MeOH, H ₂ SO ₄ , 65 °C, 1 h.
Phe-MEIA	100%	1.00	1.20	0.90	1	0.90	1.00	1.08	0.8	i) MeOH, H ₂ SO ₄ , 65 °C, 24 h; ii) Itaconic anhydride, 2-MeTHF, Na ₂ CO ₃ 24 h. iii) MeOH, H ₂ SO ₄ , 65 °C, 1 h.
Val-MEIA	100%	1.00	1.20	0.90	1	0.90	1.00	1.08	0.8	i) MeOH, H ₂ SO ₄ , 65 °C, 48 h; ii) Itaconic anhydride, 2-MeTHF, Na ₂ CO ₃ 24 h. iii) MeOH, H ₂ SO ₄ , 65 °C, 1 h.
Oct-MEIA	43%	1.00	1.20	0.90	1	0.90	1.00	1.08	0.8	ii) Itaconic anhydride, DCM, 2 h. iii) MeOH, H ₂ SO ₄ , 65 °C, 1 h.

Table S10. Synthetic factors assigned to each component of the photocurable formulations for the calculation of the Sustainable Formulation Score (SFS). Such values were determined according to their original definition (see ref. 5)