SUPPORTING INFORMATION

Secondary brown carbon formation *via* the dicarbonyl imine pathway: nitrogen heterocycle formation and synergistic effects

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Summary

Table S1. List of initial and final pH, as well as *m/z* values for targeted MS2 analyses of reaction systems studied in this work.

Reaction system	**initial pH**	**final pH**	***m/z* for targeted MS^2**
Gly/AS	3.2-3.4	2.4-2.5	69.1. 115.1
MGly/AS	3.0-3.1	2.3	125.1, 126.1, 83.2, 251.1, 215.1
BD/AS	3.4-3.5	2.8	221.1, 195.1
AcAc/AS	4.0-4.2	3.7-3.9	
HD/AS	3.9-4.2	3.6-3.7	201.2, 280.3, 265.3, 187.2, 217.2, 96.14
GA/AS	3.4-3.6	2.3-2.5	214.2, 296.3, 82.2, 314.3
AcA+AcAc/AS	3.7-3.8	2.5-2.6	230.2, 209.2, 208.2, 164.2
Gly+AcAc/AS	3.3	1.7	140.2, 164.2, 69.1
Gly+MGly/AS	2.9	2.1	125.1, 168.1, 111.2, 115.2, 69.1, 257.1, 83.2, 234.2
Gly+MGly+GA/AS	2.8	1.9	125.1, 115.2, 214.2, 296.3, 225.2, 235.2, 153.2, 207.2, 167.2
Gly/glycine	3.9	3.4	185.1, 199.1, 143.1
MGly/glycine	3.5	2.9	184.1, 156.1
BD/glycine	4.9	3.9	254.1, 238.1, 213.1
HD/glycine	4.3	3.4	317.2, 381.3, 166.1, 454.3, 248.2, 307.3, 315.2, 344.3, 154.1
GA/glycine	3.5	3.3	138.1, 238.2, 340.3, 220.2, 152.0

1. UV/Vis Spectrometry

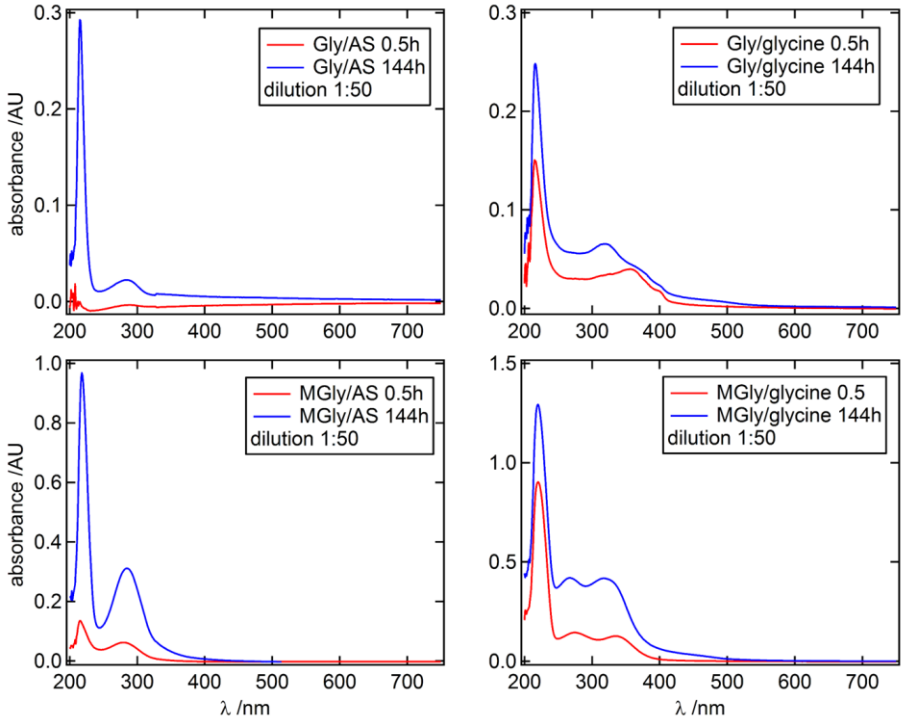


Figure S1. UV/Vis spectra of Gly/AS (top left), Gly/glycine (top right), MGly/AS (bottom left), and MGly/glycine (bottom right). Initial dicarbonyl concentrations were 1M, AS was 1M, and glycine was 0.5M.

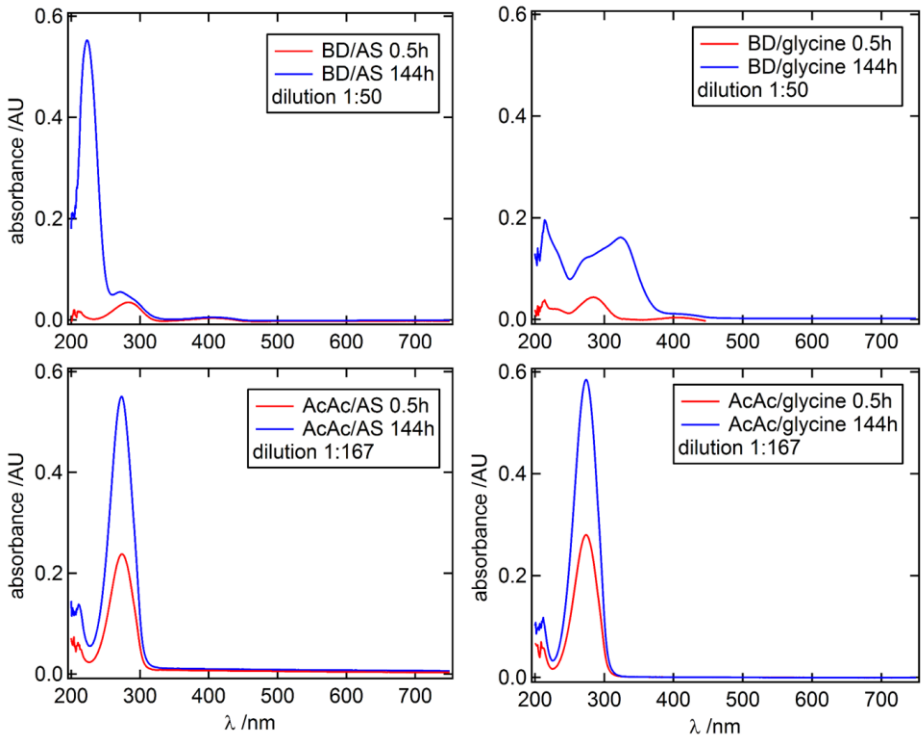


Figure S2. UV/Vis spectra of BD/AS (top left), BD/glycine (top right), AcAc/AS (bottom left), and AcAc/glycine (bottom right). Initial dicarbonyl concentrations were 1M, AS was 1M, and glycine was 0.5M.

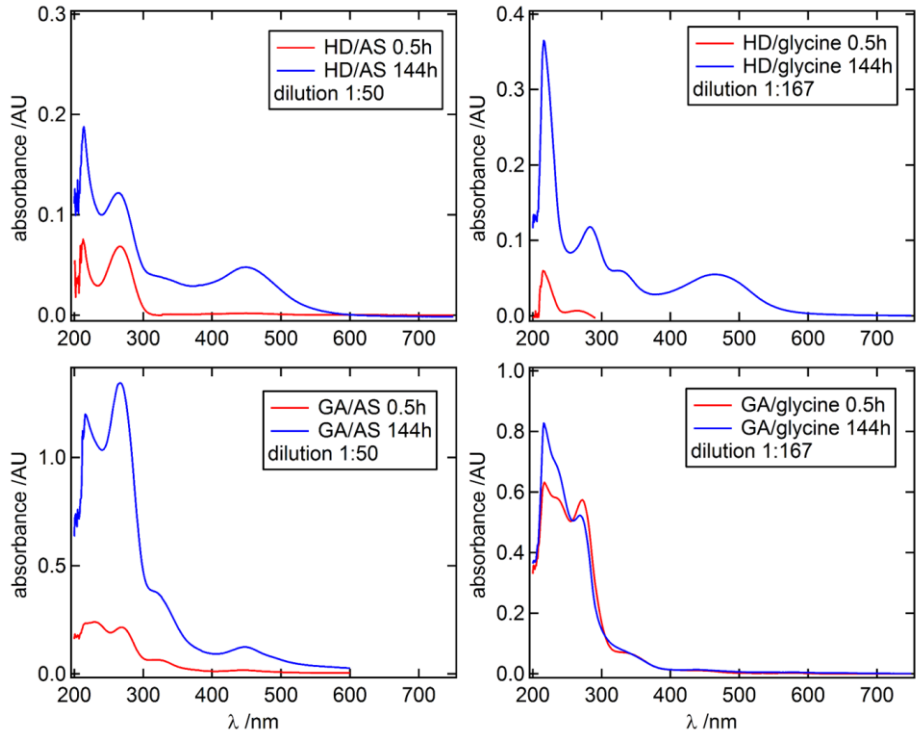


Figure S3. UV/Vis spectra of HD/AS (top left), HD/glycine (top right), GA/AS (bottom left), and GA/glycine (bottom right). Initial dicarbonyl concentrations were 1M, AS was 1M, and glycine was 0.5M.

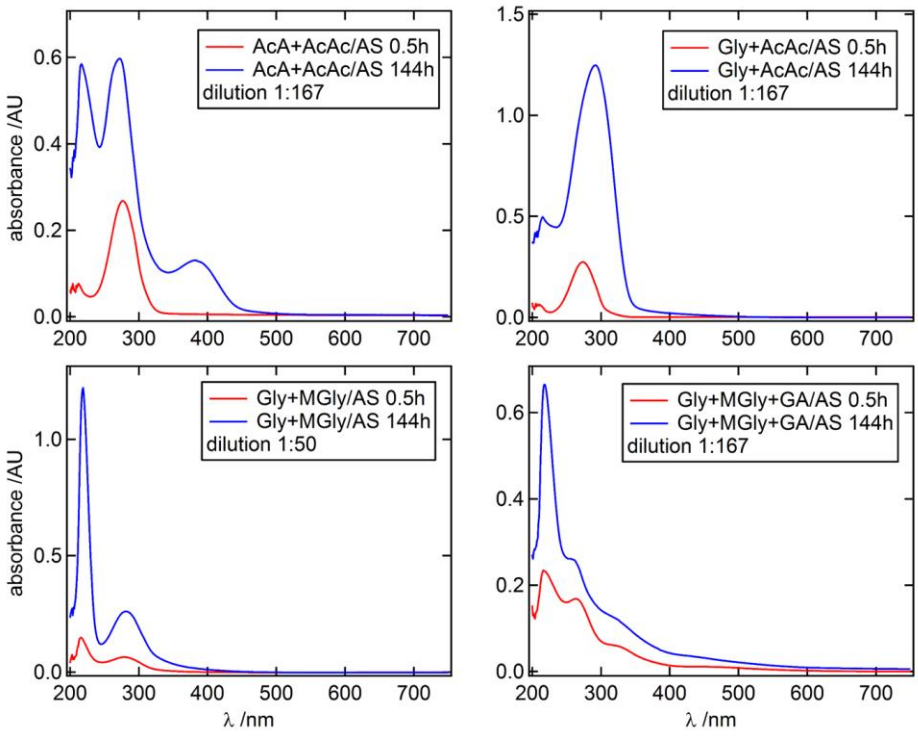


Figure S4. UV/Vis spectra of AcA+AcAc/AS (top left), Gly+AcAc/AS (top right), Gly+MGly/AS (bottom left), and Gly+MGly+GA/AS (bottom right). Initial dicarbonyl and AS concentrations were 1M.

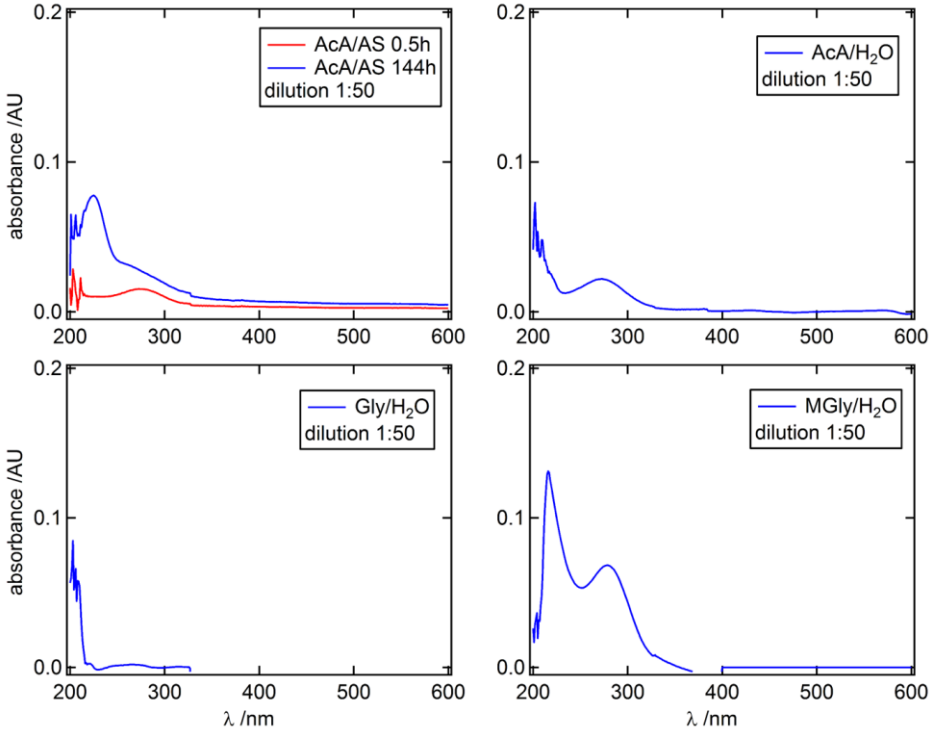


Figure S5. UV/Vis spectra of AcA/AS (top left), AcA/H_2O (top right), Gly/H_2O (bottom left), and MGly/H_2O (bottom right). Initial dicarbonyl and AS concentrations were 1M.

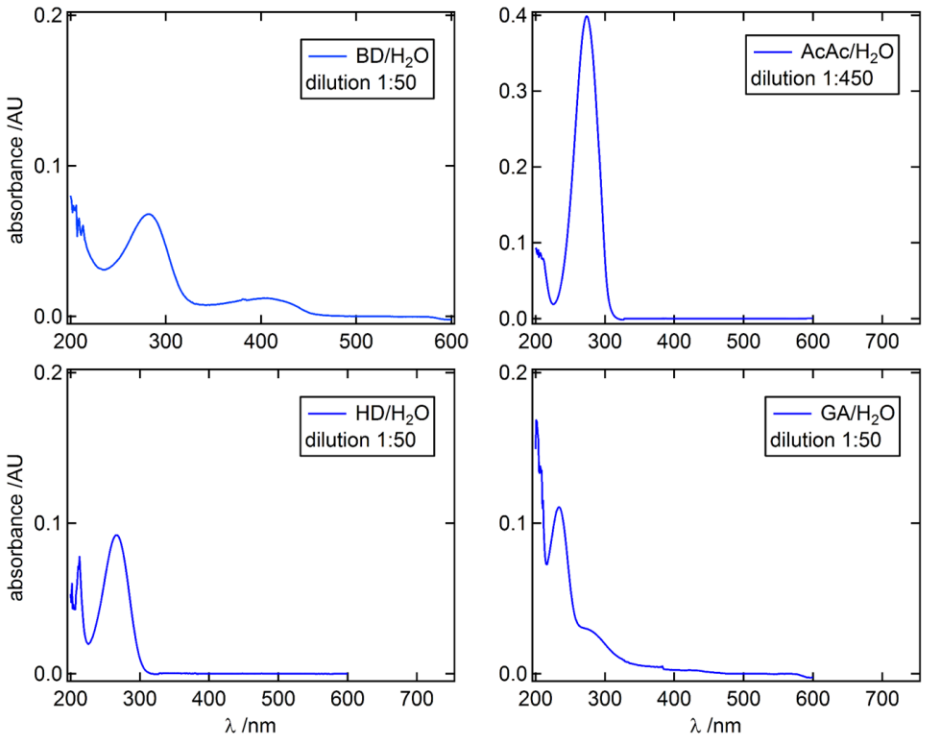


Figure S6. UV/Vis spectra of BD/H_2O (top left), AcAc/H_2O (top right), HD/H_2O (bottom left), and GA/H_2O (bottom right). Initial dicarbonyl concentrations were 1M.

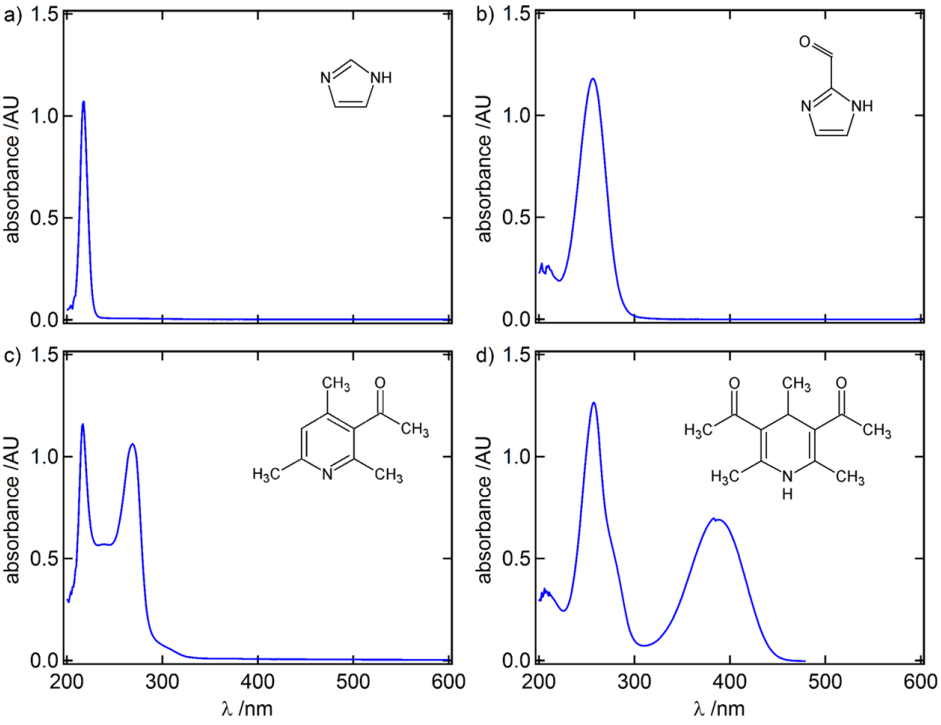


Figure S7. UV/Vis spectra of reference compounds in H_2O: a) 1*H*-Imidazole (IM), b) 1*H*-Imidazole-2-carbaldehyde (IC), c) 3-Acetyl-2,4,6-trimethylpyridine, d) 3,5-Diacetyl-2,4,6-trimethyl-1,4-dihydropyridine.

2. HPLC-DAD analysis

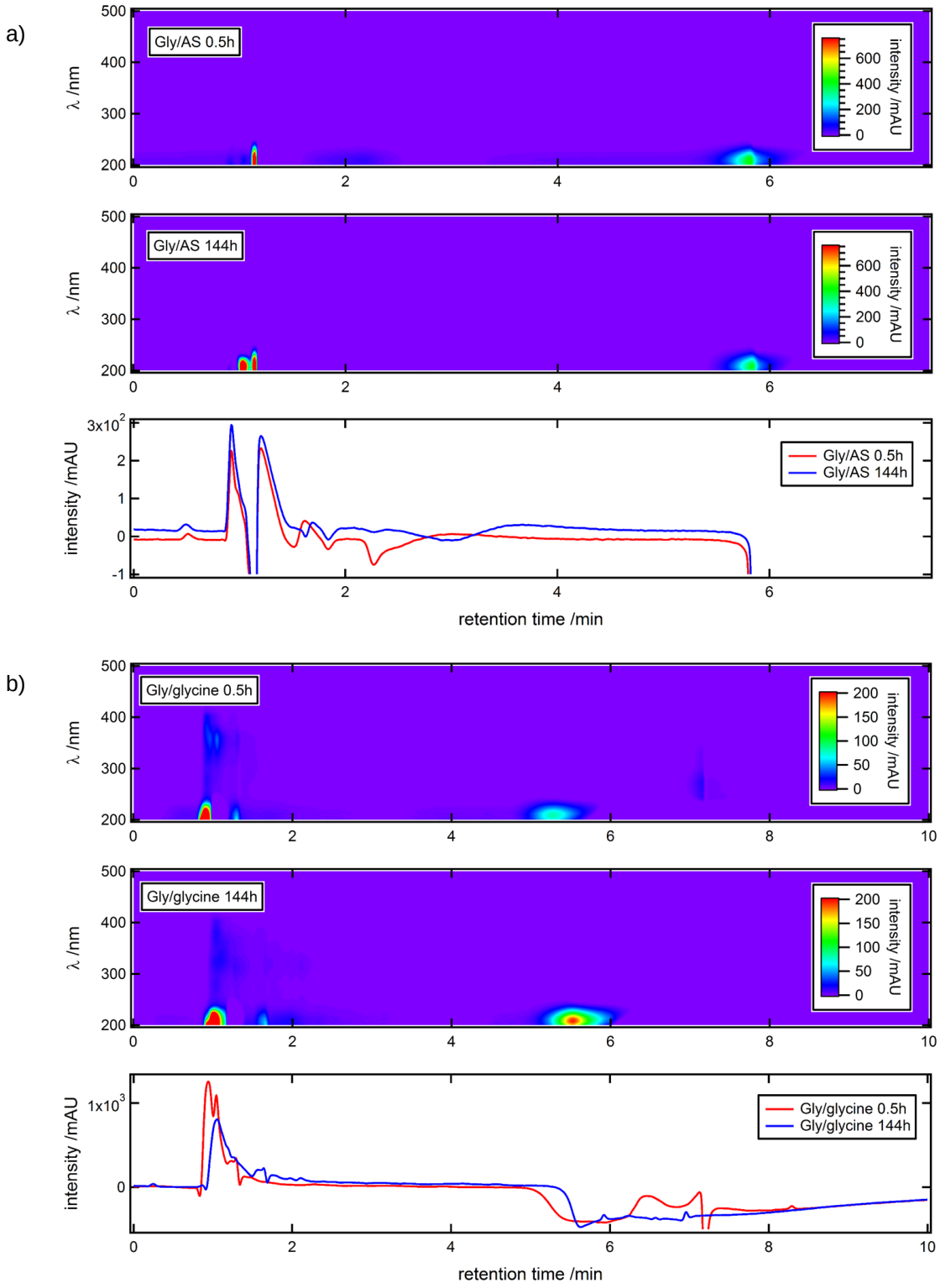


Figure S8 a) HPLC-DAD image plot for Gly/AS: 0.5 (top) and 144 h (middle) reaction time; UV/Vis chromatogram (sum of λ = 300 - 500 nm) for Gly/AS (bottom); b) HPLC-DAD image plot for Gly/glycine: 0.5 (top) and 144 h (middle) reaction time; UV/Vis chromatogram (sum of λ = 300 - 500 nm) for Gly/glycine (bottom).

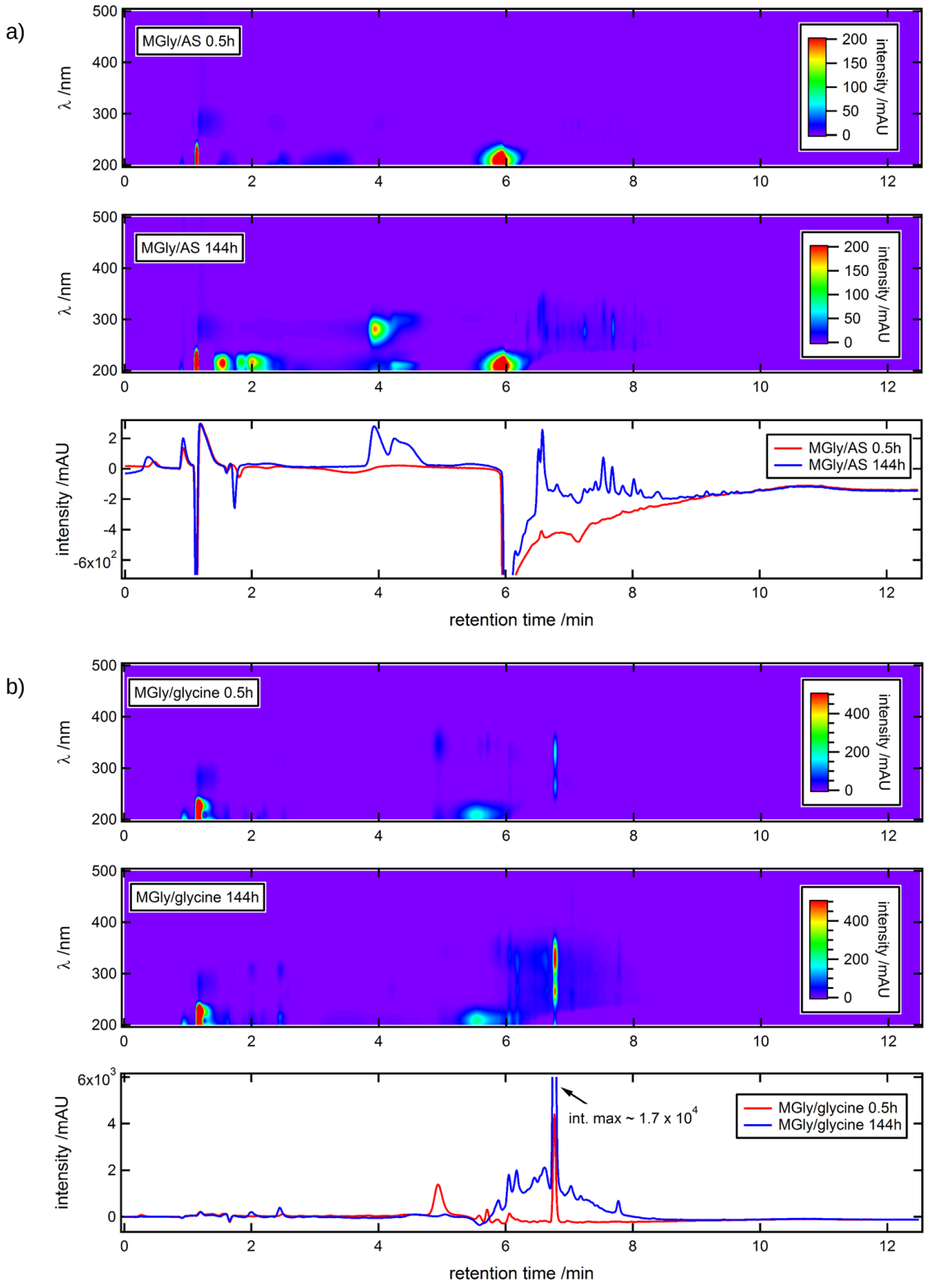


Figure S9 a) HPLC-DAD image plot for MGly/AS: 0.5 (top) and 144 h (middle) reaction time; UV/Vis chromatogram (sum of λ = 300 - 500 nm) for MGly/AS (bottom); b) HPLC-DAD image plot for MGly/glycine: 0.5 (top) and 144 h (middle) reaction time; UV/Vis chromatogram (sum of λ = 300 - 500 nm) for MGly/glycine (bottom).

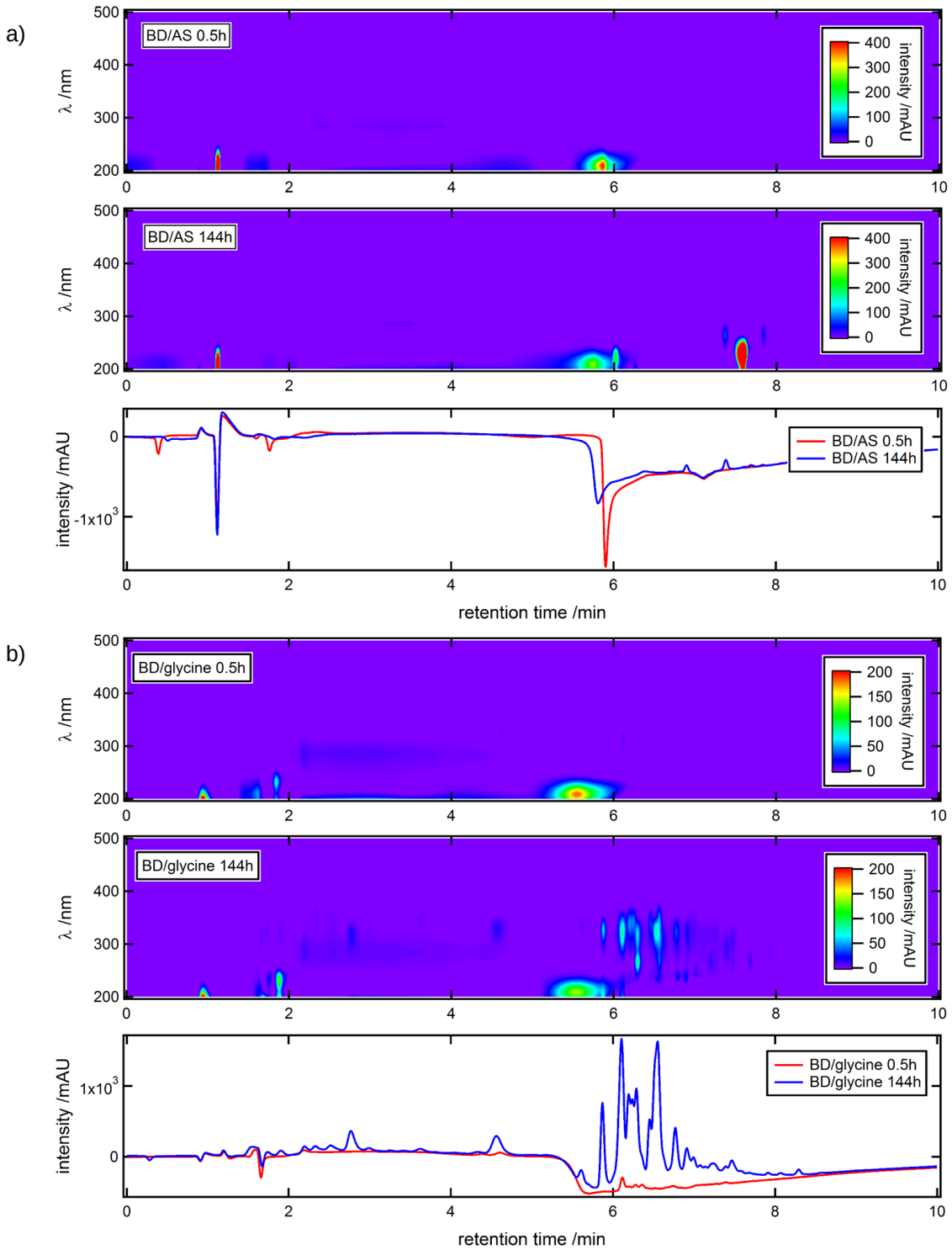


Figure S10 a) HPLC-DAD image plot for BD/AS: 0.5 (top) and 144 h (middle) reaction time; UV/Vis chromatogram (sum of λ = 300 - 500 nm) for BD/AS (bottom); b) HPLC-DAD image plot for BD/glycine: 0.5 (top) and 144 h (middle) reaction time; UV/Vis chromatogram (sum of λ = 300 - 500 nm) for BD/glycine (bottom).

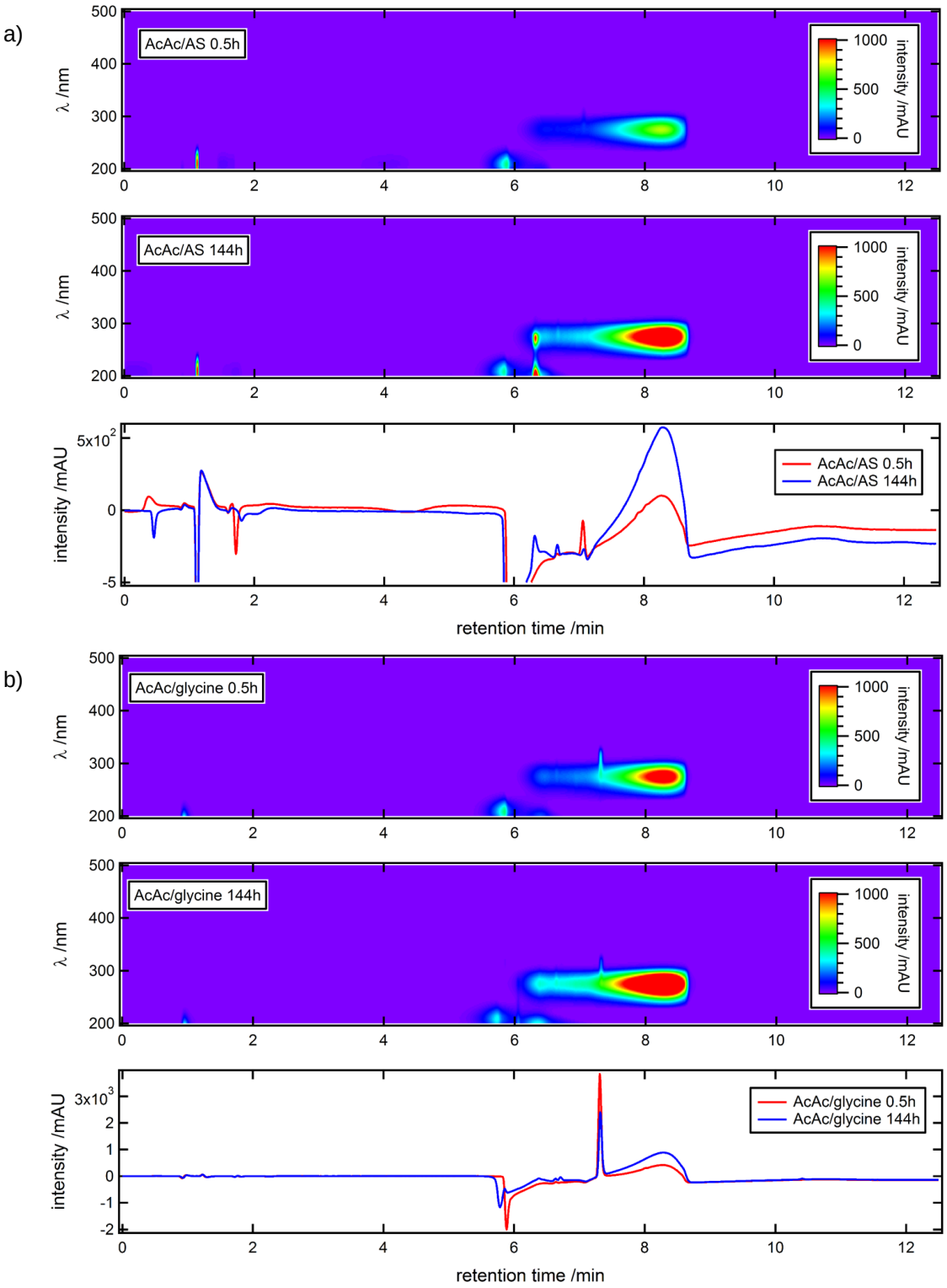


Figure S11 a) HPLC-DAD image plot for AcAc/AS: 0.5 (top) and 144 h (middle) reaction time; UV/Vis chromatogram (sum of λ = 300 - 500 nm) for AcAc/AS (bottom); b) HPLC-DAD image plot for AcAc/glycine: 0.5 (top) and 144 h (middle) reaction time; UV/Vis chromatogram (sum of λ = 300 - 500 nm) for AcAc/glycine (bottom).

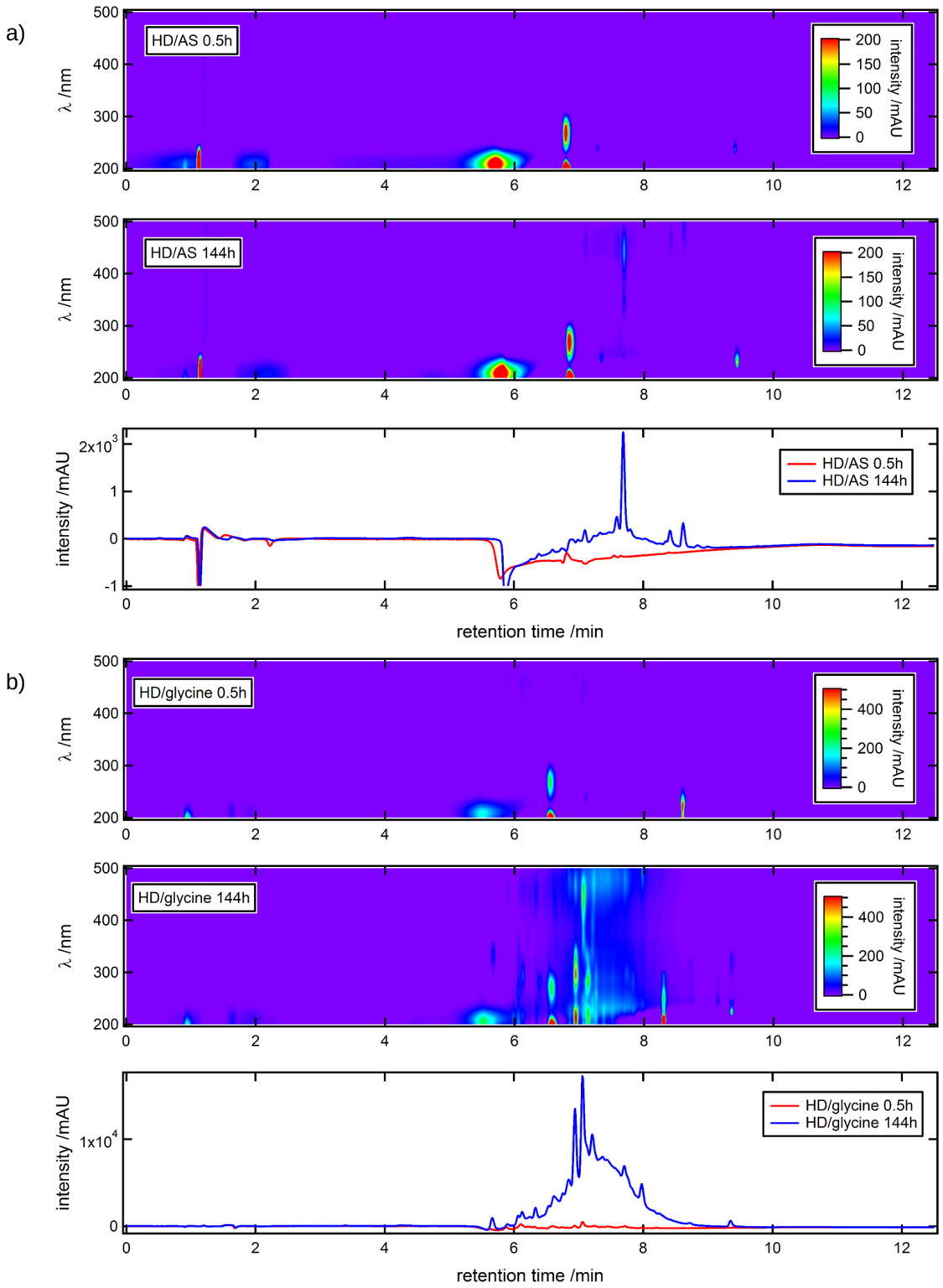


Figure S12 a) HPLC-DAD image plot for HD/AS: 0.5 (top) and 144 h (middle) reaction time; UV/Vis chromatogram (sum of λ = 300 - 500 nm) for HD/AS (bottom); b) HPLC-DAD image plot for HD/glycine: 0.5 (top) and 144 h (middle) reaction time; UV/Vis chromatogram (sum of λ = 300 - 500 nm) for HD/glycine (bottom).

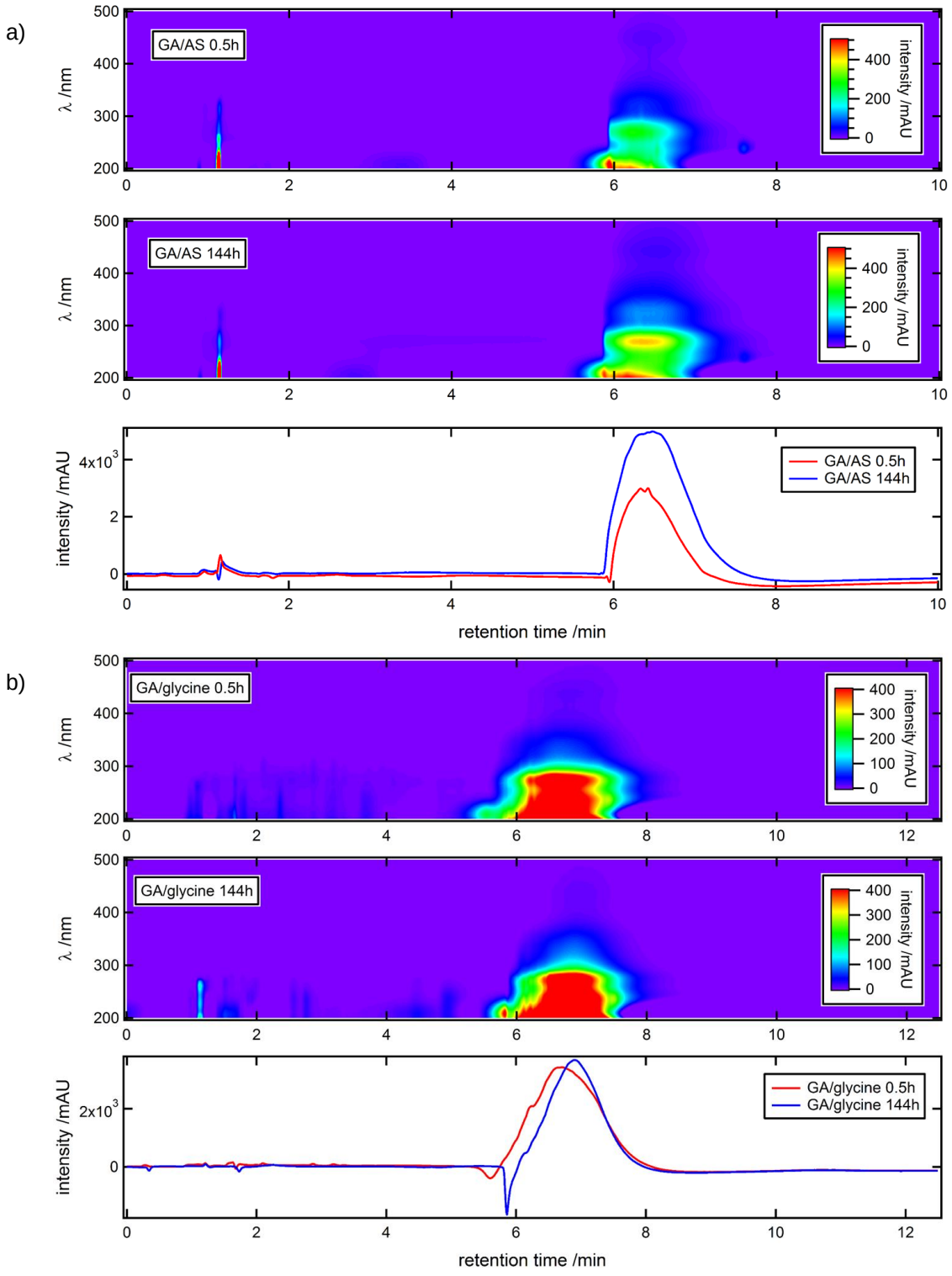


Figure S13 a) HPLC-DAD image plot for GA/AS: 0.5 (top) and 144 h (middle) reaction time; UV/Vis chromatogram (sum of λ = 300 - 500 nm) for GA/AS (bottom); b) HPLC-DAD image plot for GA/glycine: 0.5 (top) and 144 h (middle) reaction time; UV/Vis chromatogram (sum of λ = 300 - 500 nm) for GA/glycine (bottom).

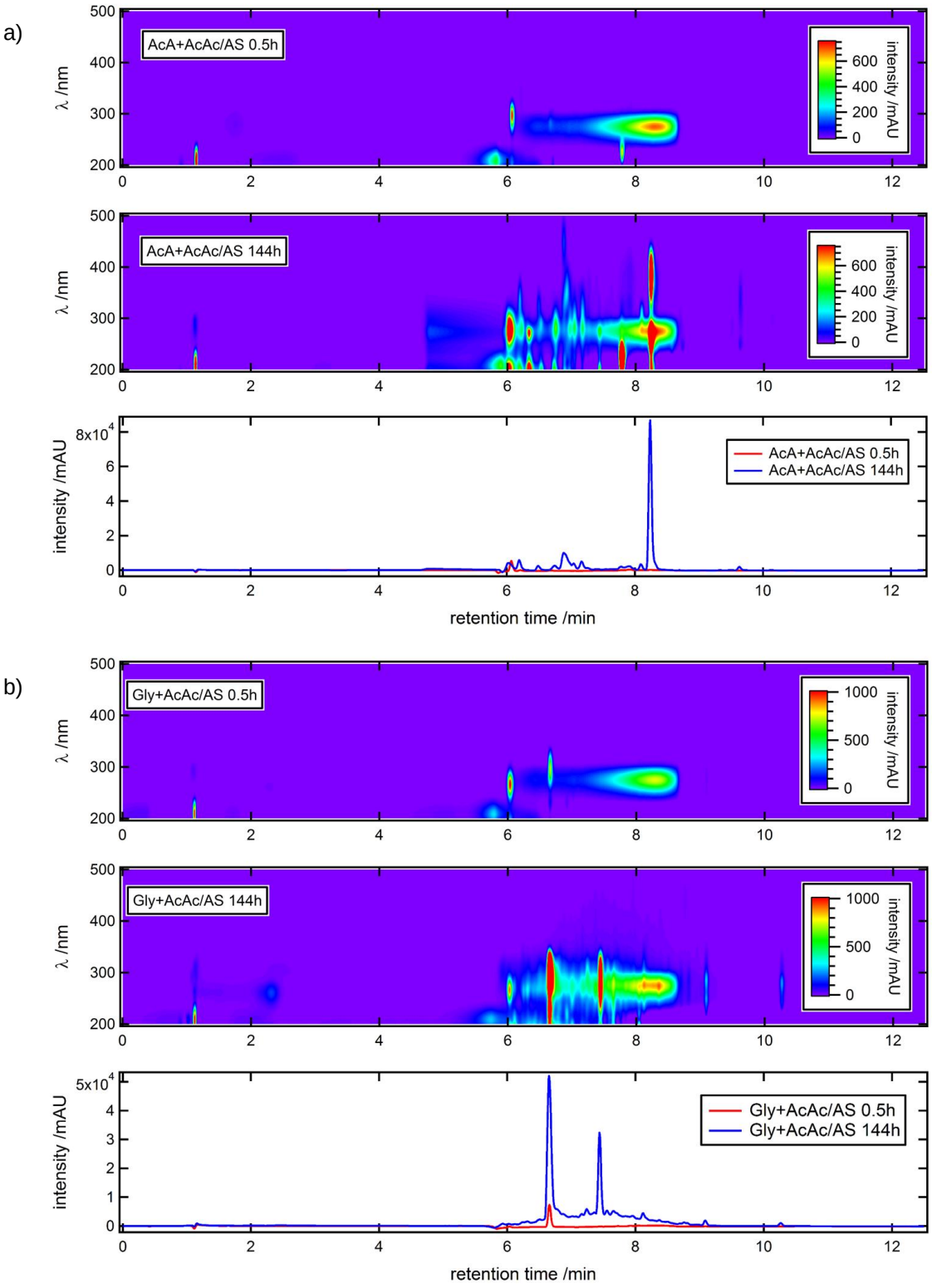


Figure S14 a) HPLC-DAD image plot for AcA+AcAc/AS: 0.5 (top) and 144 h (middle) reaction time; UV/Vis chromatogram (sum of λ = 300 - 500 nm) for AcA+AcAc/AS (bottom); b) HPLC-DAD image plot for Gly+AcAc/AS: 0.5 (top) and 144 h (middle) reaction time; UV/Vis chromatogram (sum of λ = 300 - 500 nm) for Gly+AcAc/AS (bottom).

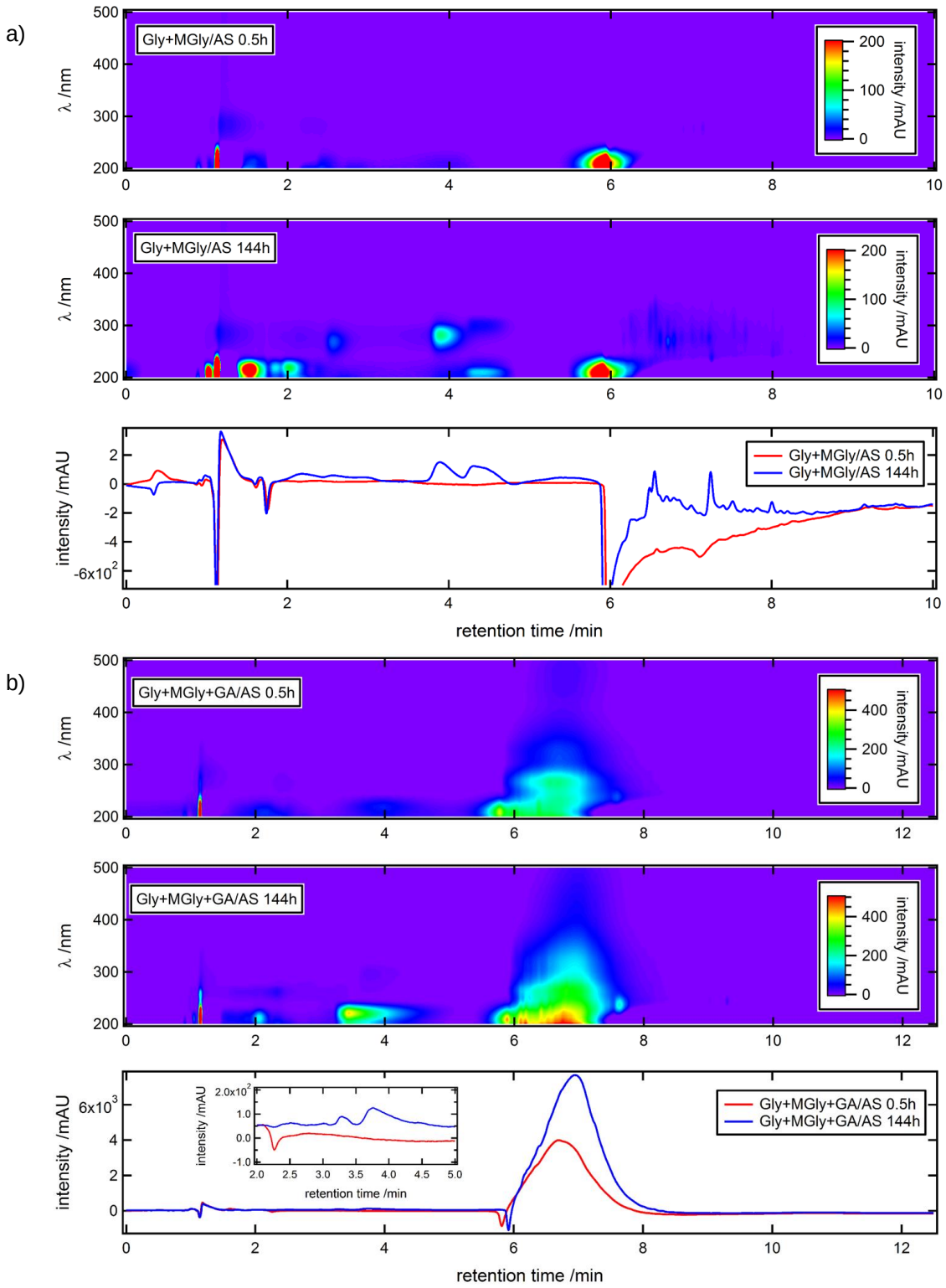


Figure S15 a) HPLC-DAD image plot for Gly+MGly/AS: 0.5 (top) and 144 h (middle) reaction time; UV/Vis chromatogram (sum of λ = 300 - 500 nm) for Gly+MGly/AS (bottom); b) HPLC-DAD image plot for Gly+MGly+GA/AS: 0.5 (top) and 144 h (middle) reaction time; UV/Vis chromatogram (sum of λ = 300 - 500 nm) for Gly+MGly+GA/AS (bottom).

3. UHPLC-HESI-HRMS^2 analysis

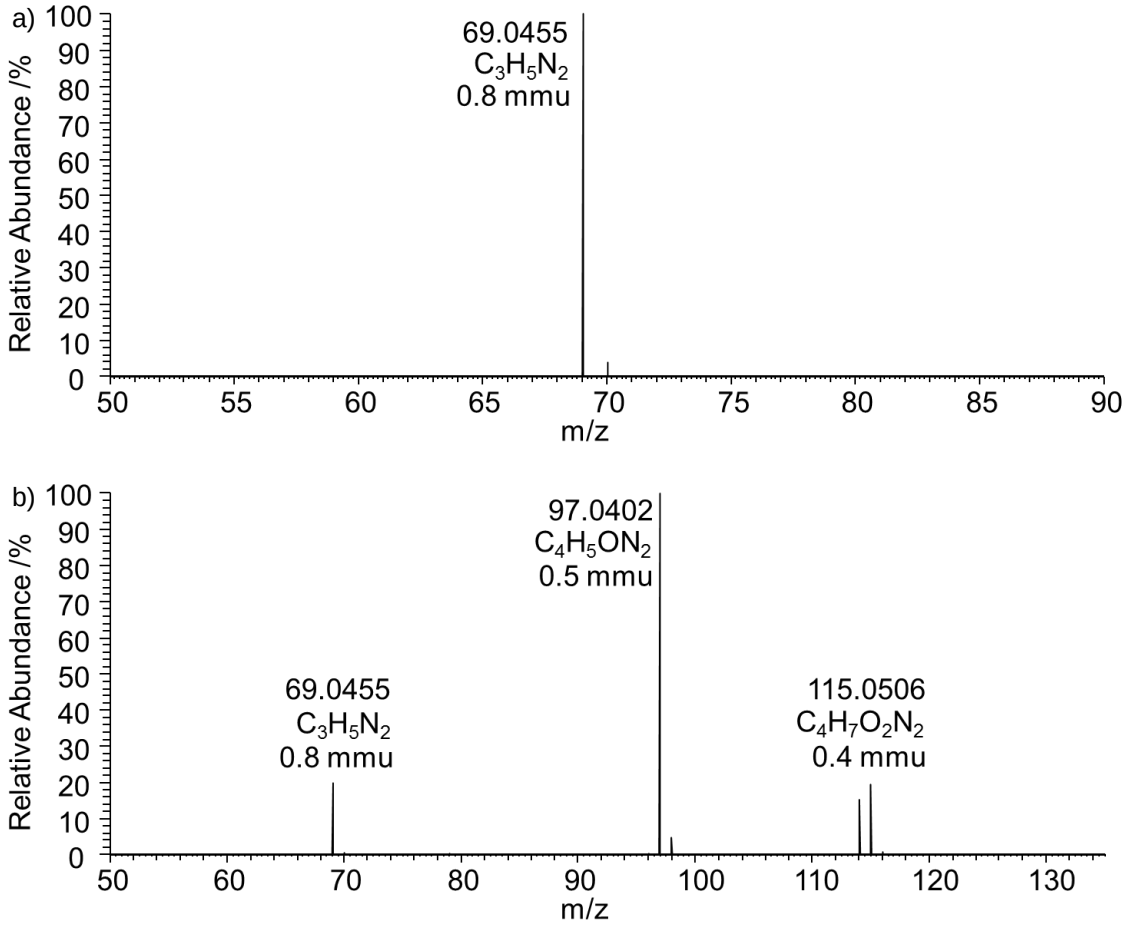


Figure S16 MS^2 spectra of products observed in Gly/AS: a) *m/z* 69.05 (HPLC RT = 1.2 min, UHPLC RT = 0.32 min), b) *m/z* 115.05 (HPLC RT = 1.1 min, UHPLC RT = 0.33 min). Spectra were acquired using a fragmentation energy of 70 NCE (instrument specific parameter).

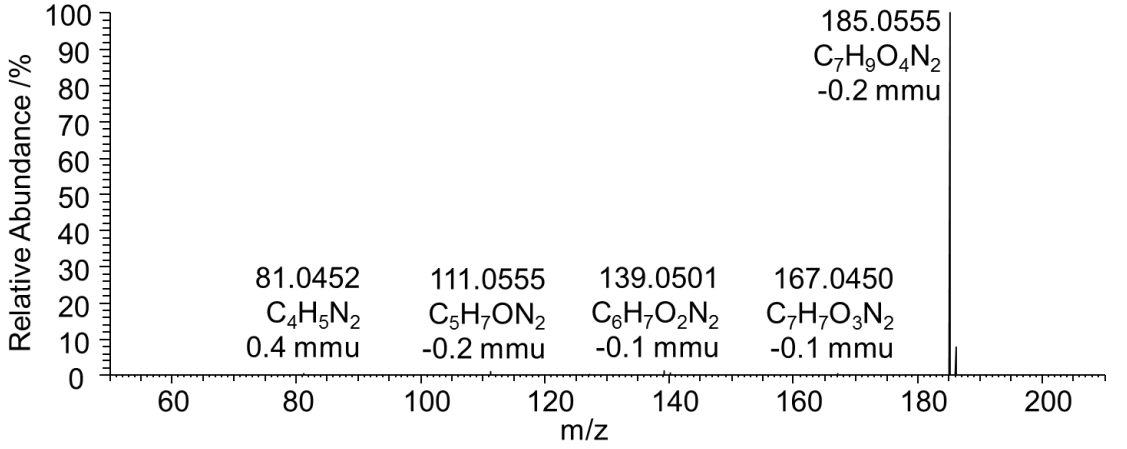


Figure S17 MS^2 spectrum of product observed in Gly/glycine: *m/z* 185.06 (HPLC RT = 1.1 min, UHPLC RT = 0.34 min). Spectra were acquired using a fragmentation energy of 70 NCE (instrument specific parameter).

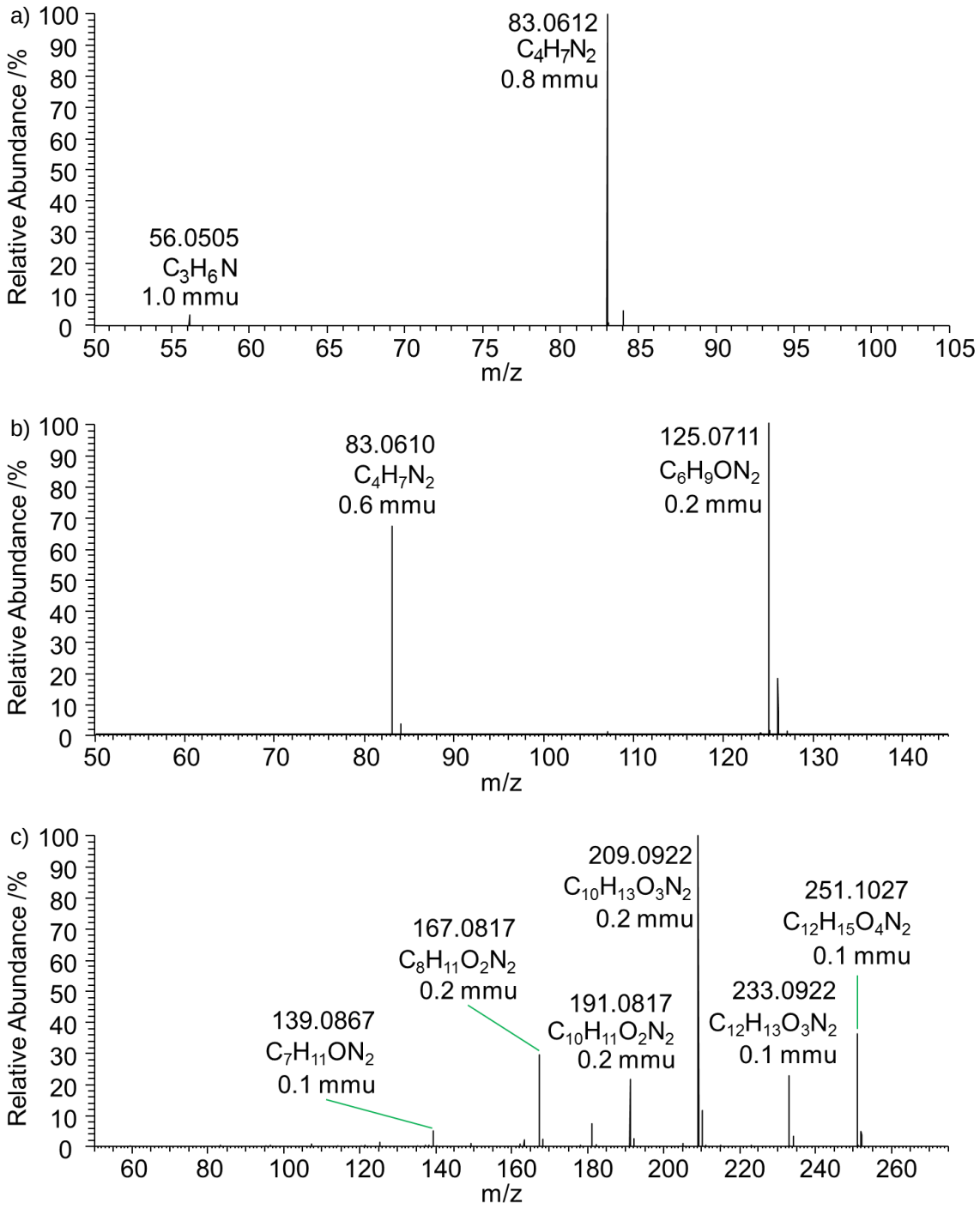


Figure S18 MS^2 spectra of products observed in MGly/AS: a) *m/z* 83.06 (HPLC RT = 1.2 min, UHPLC RT = 0.35 min) acquired using 70 NCE fragmentation energy (instrument specific parameter), b) *m/z* 125.07 (HPLC RT = 3.9 min, UHPLC RT = 0.64 min), c) *m/z* 251.10 (HPLC RT = 7.7 min, UHPLC RT = 1.75 min).

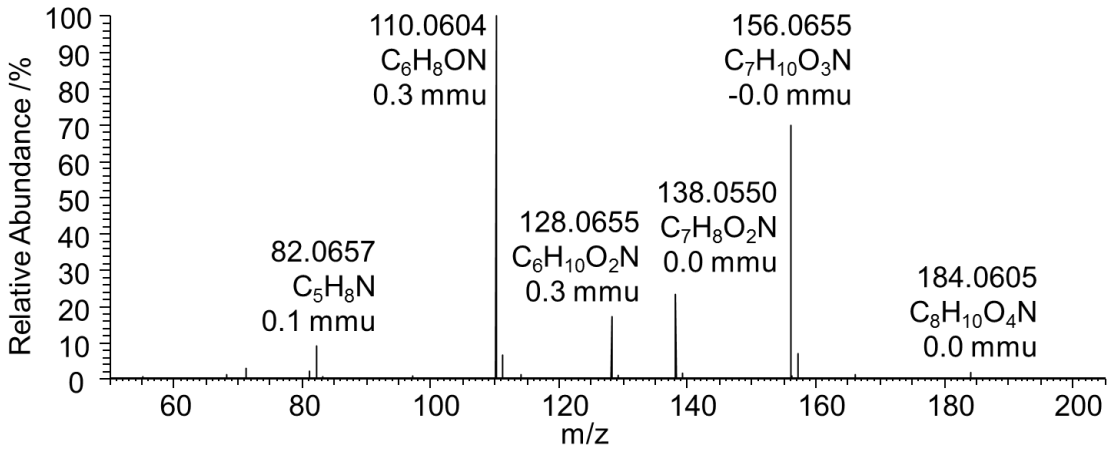


Figure S19 MS^2 spectrum of product observed in MGly/glycine: *m/z* 184.06 (HPLC RT = 6.8 min, UHPLC RT = 1.56 min).

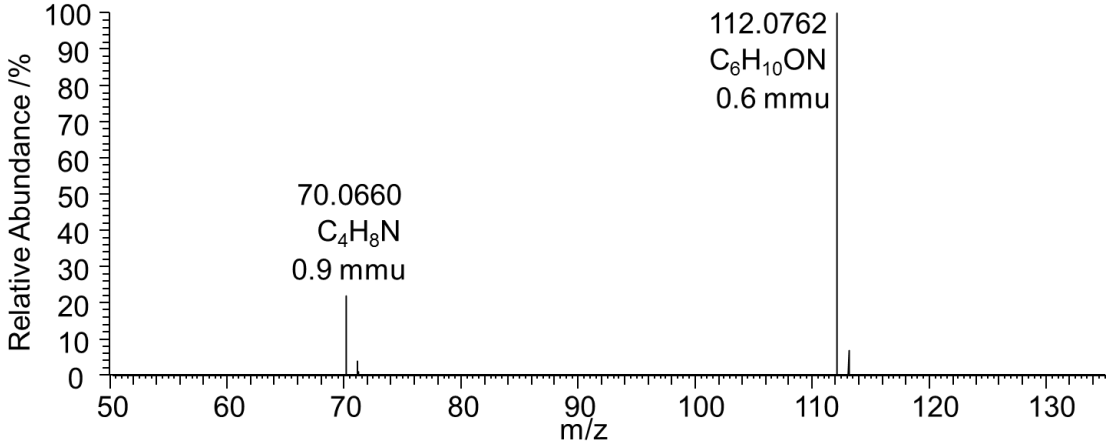


Figure S20 MS^2 spectrum of product observed in BD/AS: *m/z* 112.08 (HPLC RT = 7.8 min, UHPLC RT = 1.8 min).

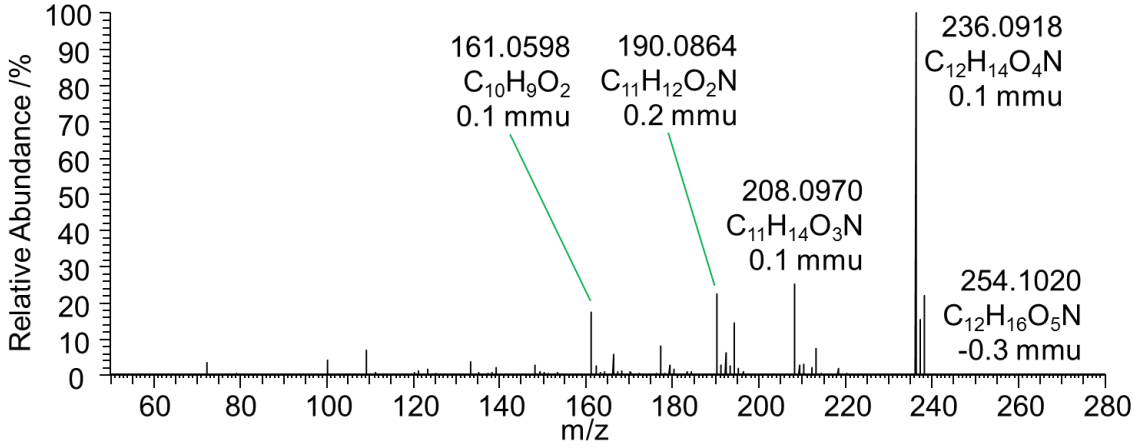


Figure S21 MS^2 spectrum of product observed in BD/glycine: *m/z* 254.10 (HPLC RT = 6.8 min, UHPLC RT = 1.48 min).

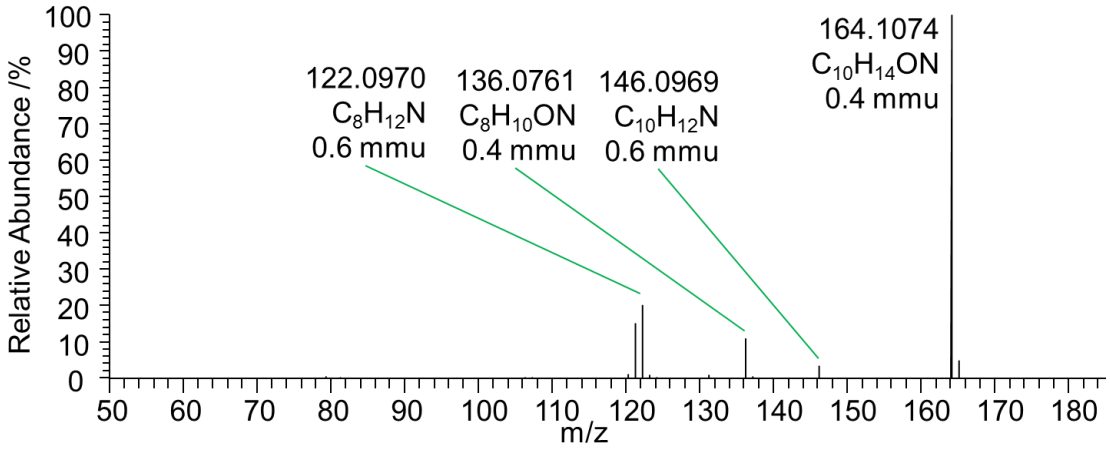


Figure S22 MS^2 spectrum of product observed in AcAc/AS: *m/z* 164.10 (HPLC RT = 6.3 min, UHPLC RT = 0.64 min). Spectra were acquired using a fragmentation energy of 70 NCE (instrument specific parameter).

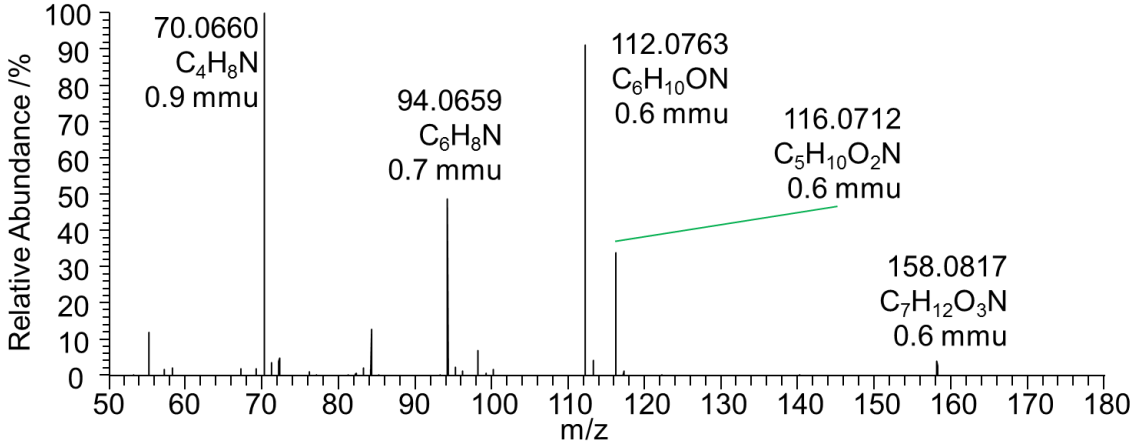


Figure S23 MS^2 spectrum of product observed in AcAc/glycine: *m/z* 158.0817 (HPLC RT = 7.3 min, UHPLC RT = 1.34 min). Spectra were acquired using a fragmentation energy of 70 NCE (instrument specific parameter).

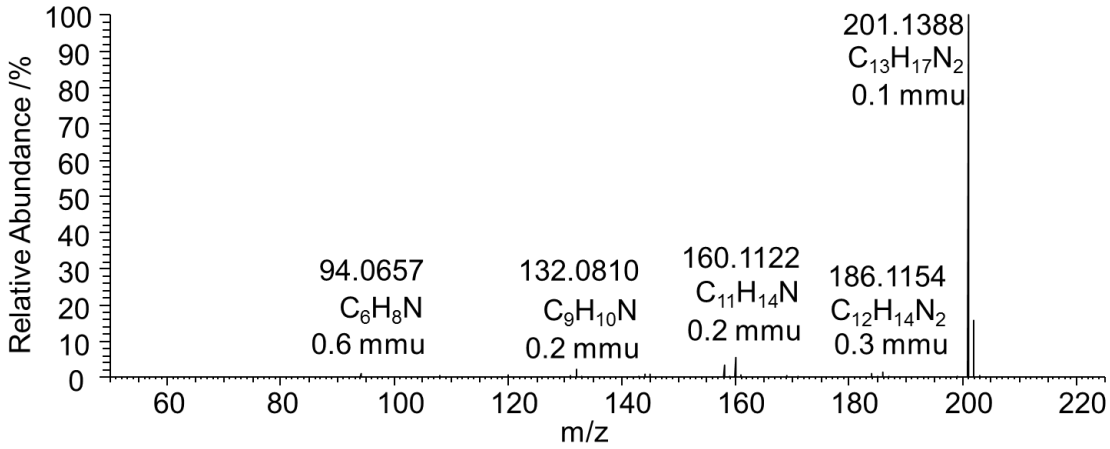


Figure S24 MS^2 spectrum of product observed in HD/AS: *m/z* 201.14 (HPLC RT = 7.7 min, UHPLC RT = 1.83 min).

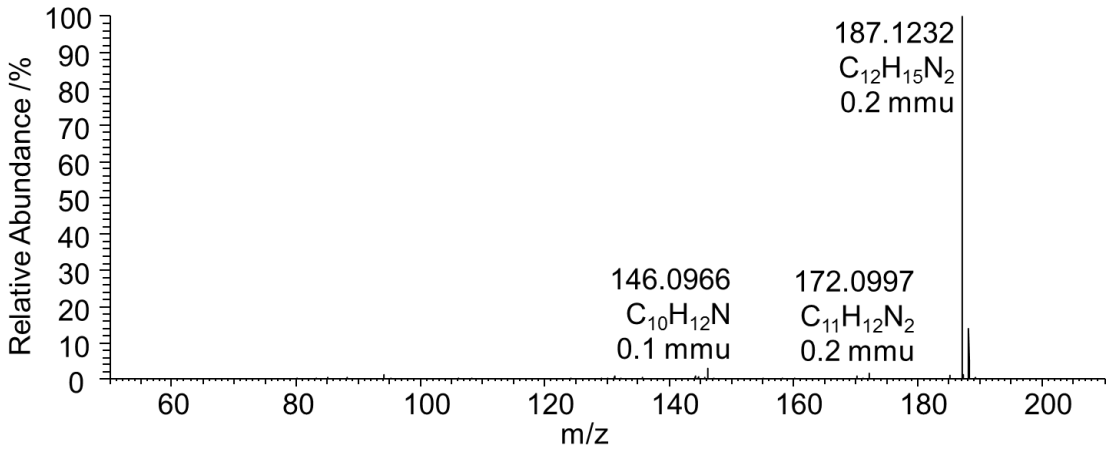


Figure S25 MS^2 spectra of products observed in HD/AS: *m/z* 187.12 (HPLC RT = 7.6 min, UHPLC RT = 1.76 min)

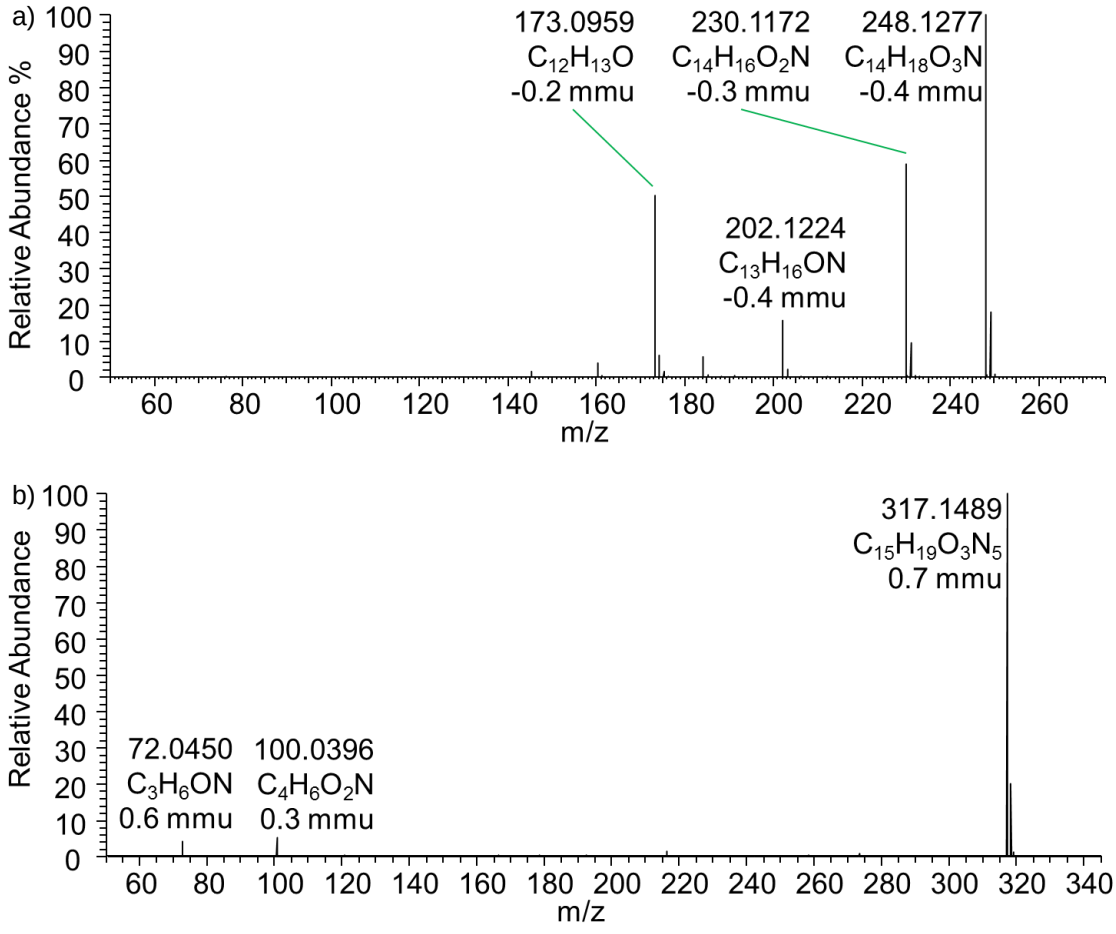


Figure S26 MS^2 spectrum of product observed in HD/glycine: a) *m/z* 248.13 (HPLC RT = 6.9 min, UHPLC RT = 1.55 min); b) *m/z* 317.15 (HPLC RT = 7.1 min, UHPLC RT = 1.57 min).

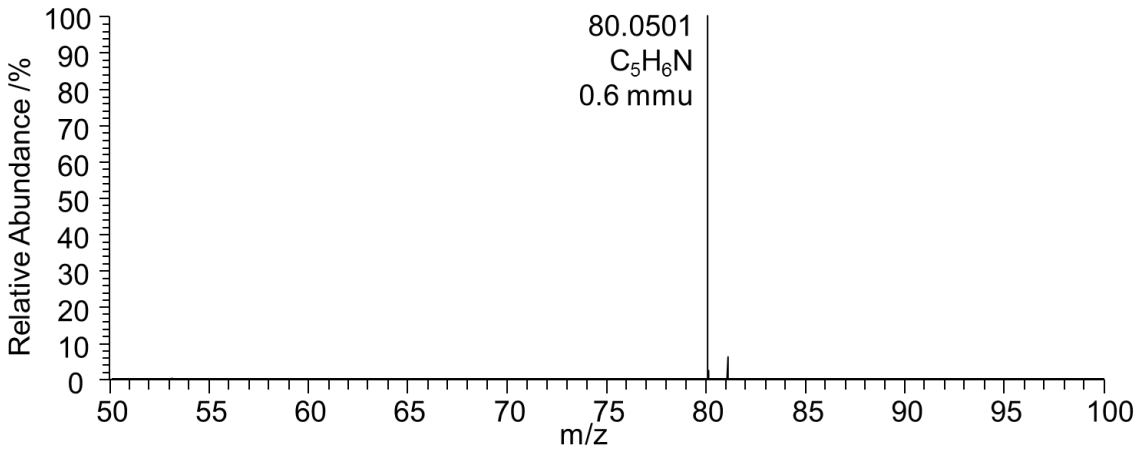


Figure S27 MS^2 spectrum of product observed in GA/AS: a) *m/z* 80.05 (HPLC RT = 0.9 min, UHPLC RT = 0.36 min).

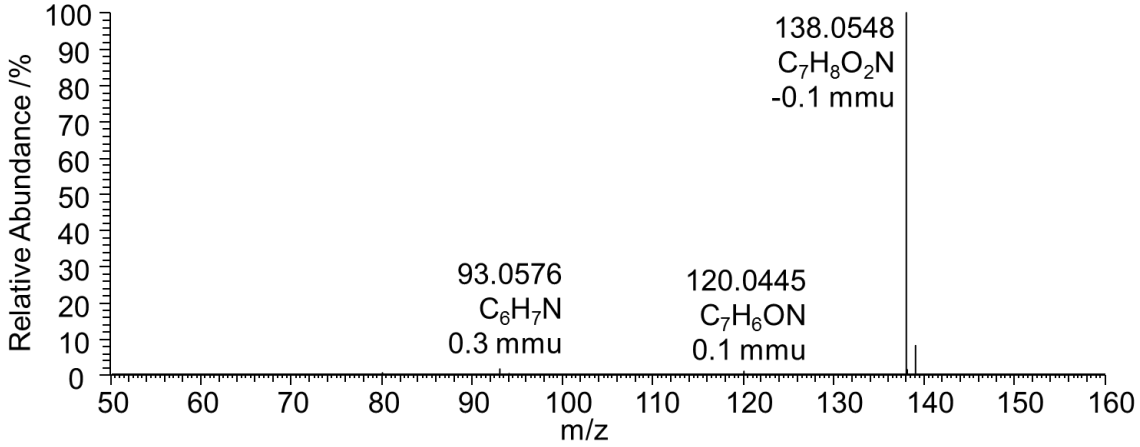


Figure S28 MS^2 spectrum of product observed in GA/glycine: *m/z* 138.05 (HPLC RT = 1.1 min, UHPLC RT = 0.36 min).

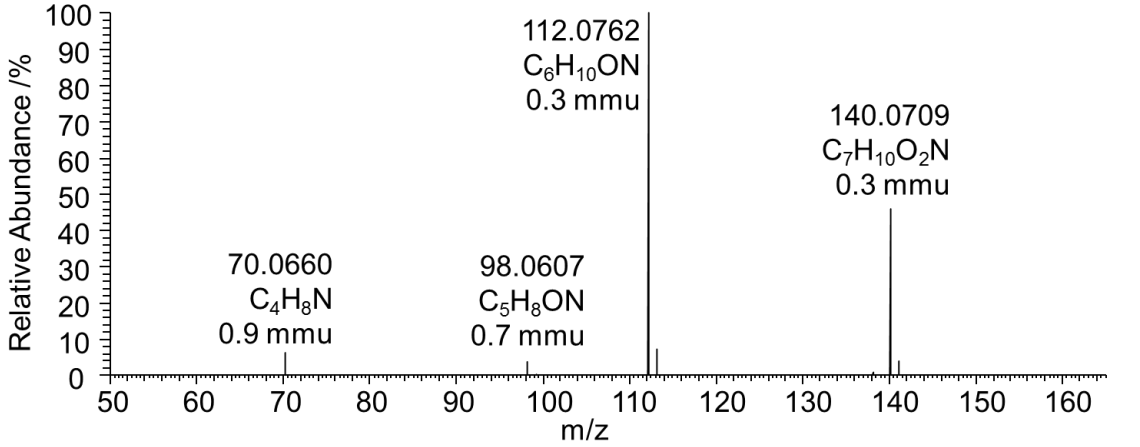


Figure S29 MS^2 spectrum of product observed in AcAc+Gly/AS: *m/z* 140.07 (HPLC RT = 6.7 min, UHPLC RT = 1.51 min).

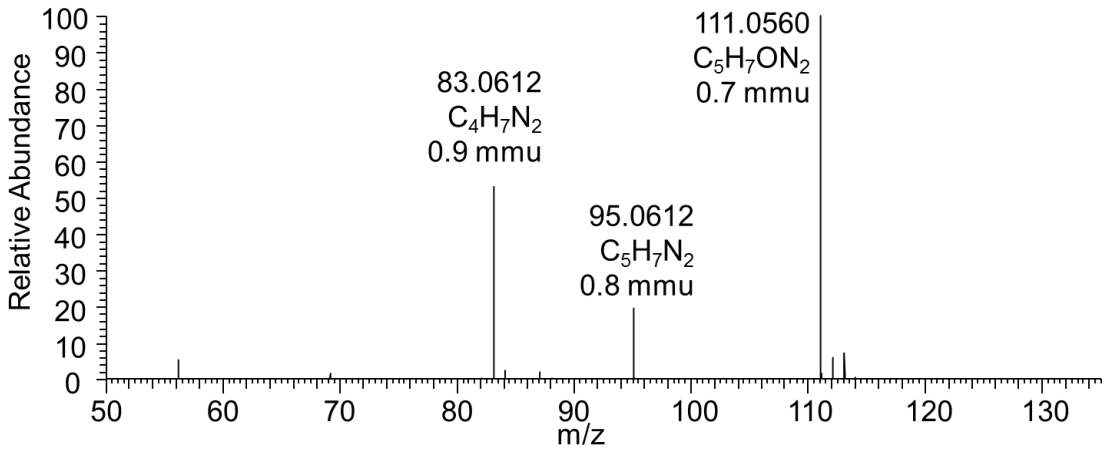


Figure S30 MS^2 spectrum of product observed in Gly+MGly/AS: *m/z* 111.06 (HPLC RT = 1.4 min, UHPLC RT = 0.37 min).

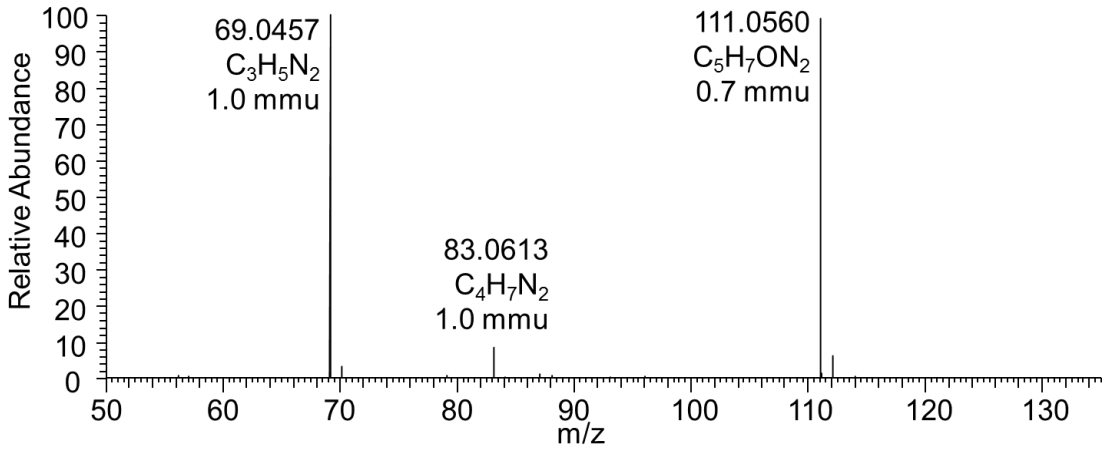


Figure S31 MS^2 spectrum of product observed in Gly+MGly/AS: *m/z* 111.06 (HPLC RT = 2.5 min, UHPLC RT = 0.56 min).

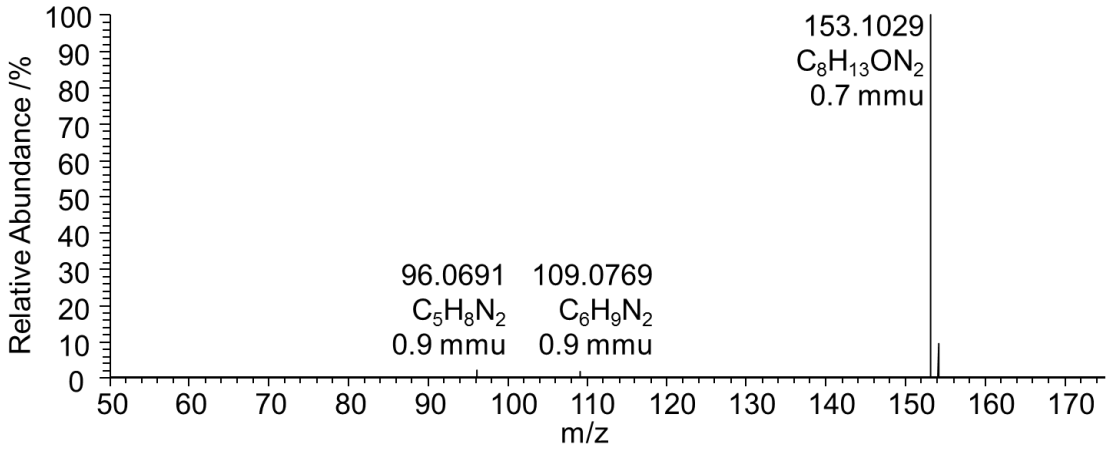


Figure S32 MS^2 spectrum of product observed in Gly+MGly+GA/AS: *m/z* 153.10 (HPLC RT = 3.5 min, UHPLC RT = 0.61 min).

4. Reference compound analysis

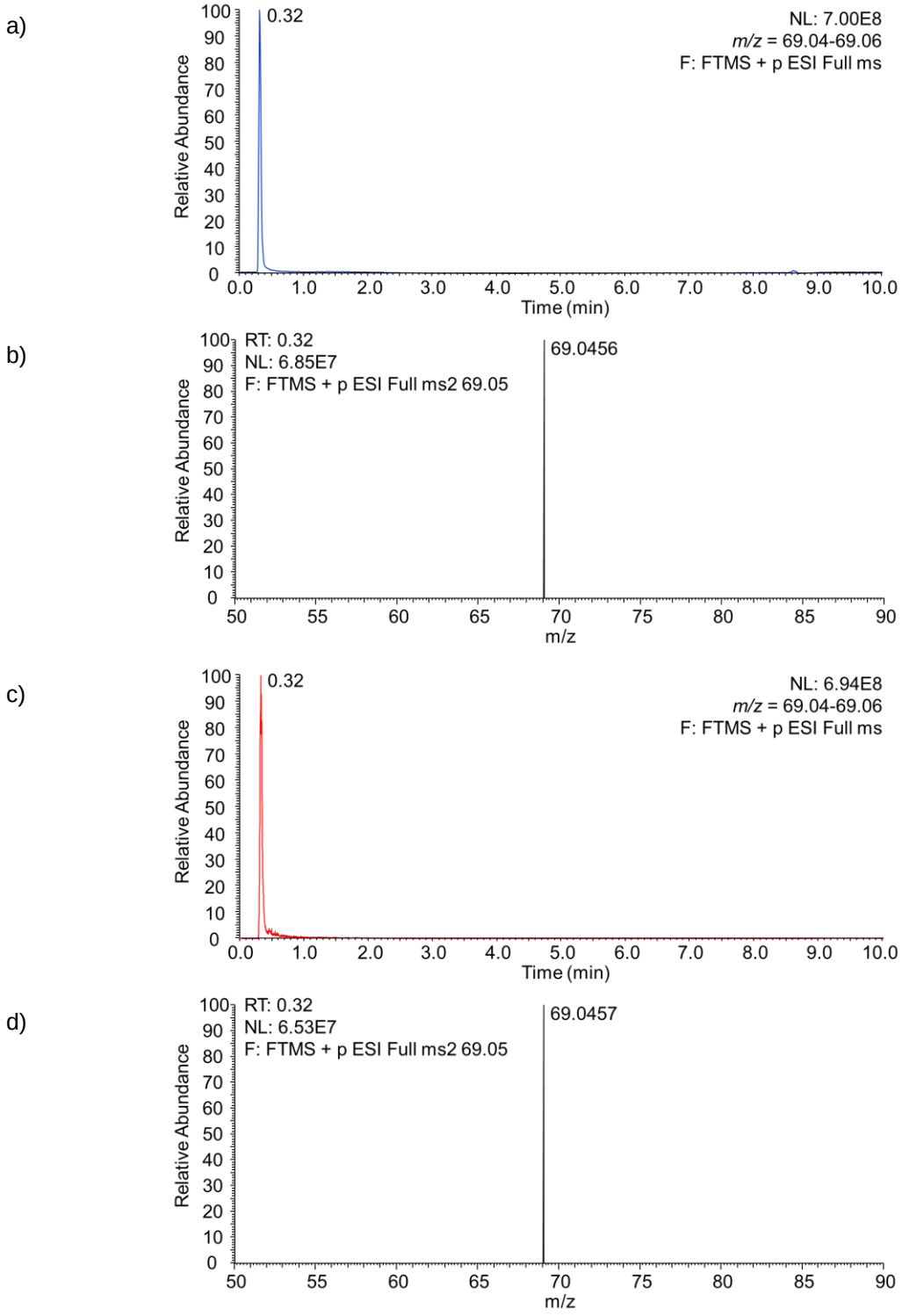
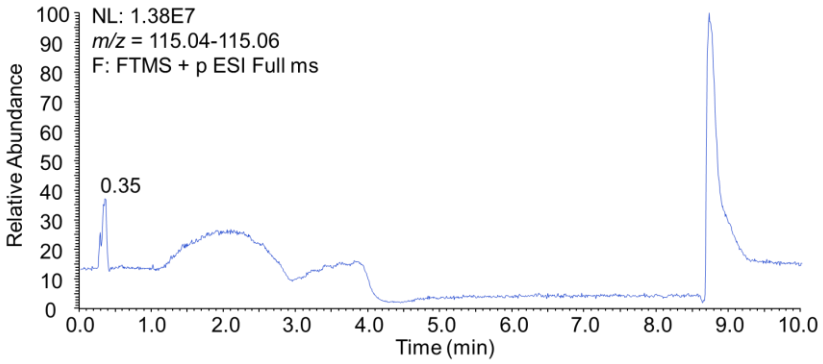
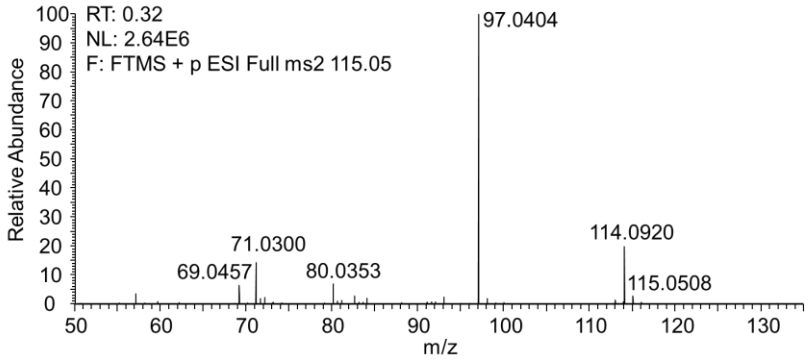


Figure S33 1*H*-imidazole (IM): reference compound a) UHPLC-MS EIC *m/z* 69.04-69.06, b) MS^2 of *m/z* 69.05; product in Gly/AS c) UHPLC-MS EIC *m/z* 69.04-69.06, d) MS^2 of *m/z* 69.05. MS^2 spectra were acquired using 70 NCE fragmentation energy (instrument specific parameter).

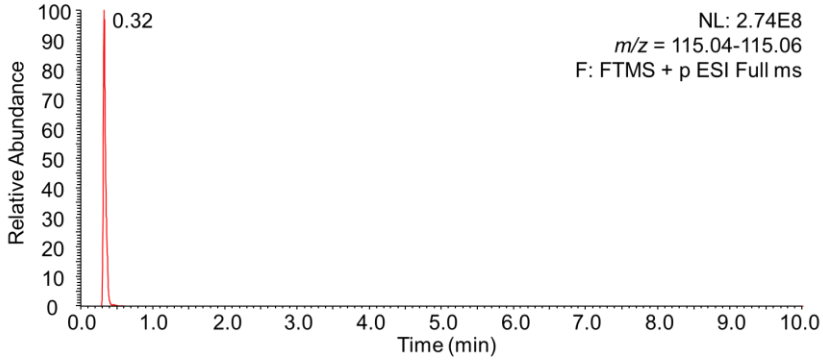
a)



b)



c)



d)

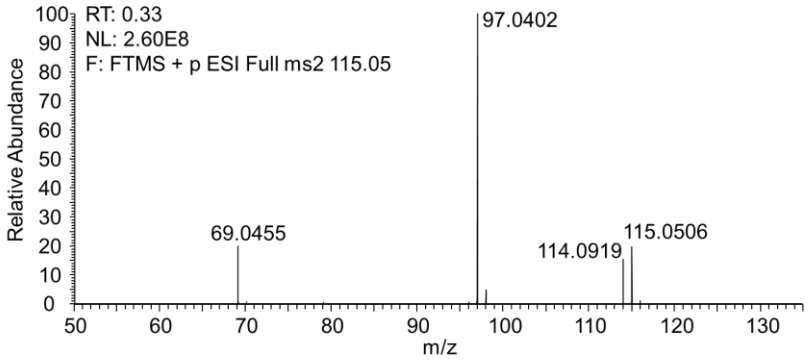
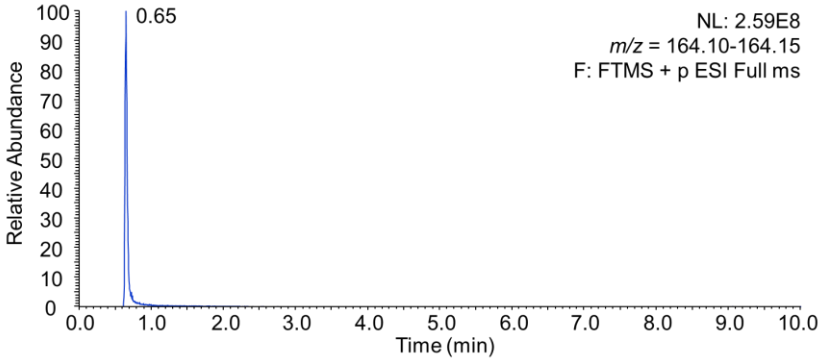
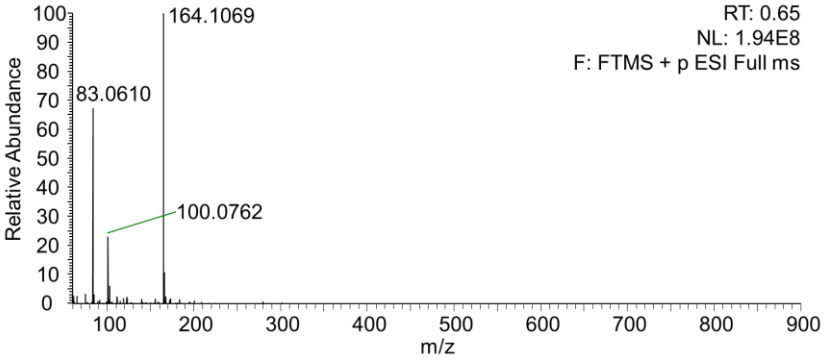


Figure S34 1*H*-imidazole-2-carbaldehyde (IC): reference compound a) UHPLC-MS EIC *m/z* 115.04-115.06, b) MS^2 of *m/z* 115.05; product in Gly/AS c) UHPLC-MS EIC *m/z* 115.04-115.06, d) MS^2 of *m/z* 115.05. MS^2 spectra were acquired using 70 NCE fragmentation energy (instrument specific parameter).

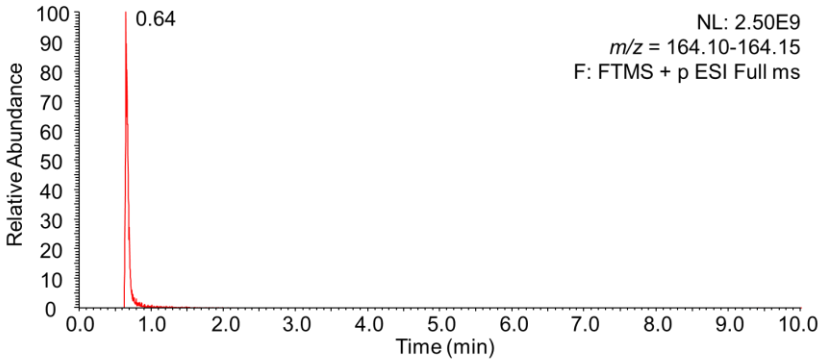
a)



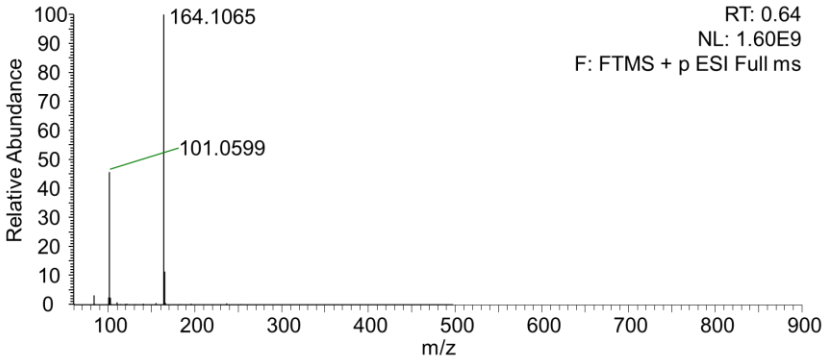
b)



c)



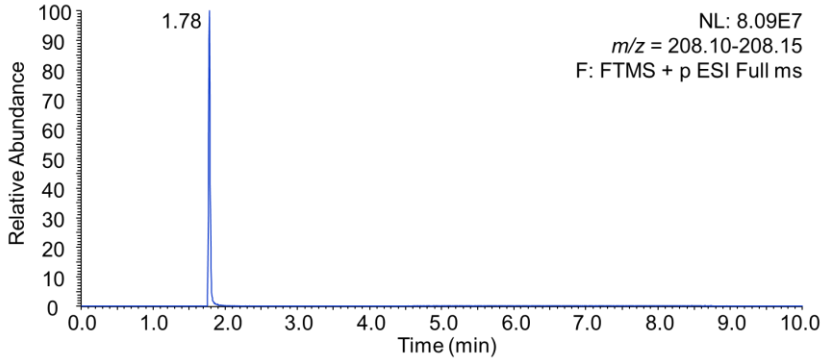
d)



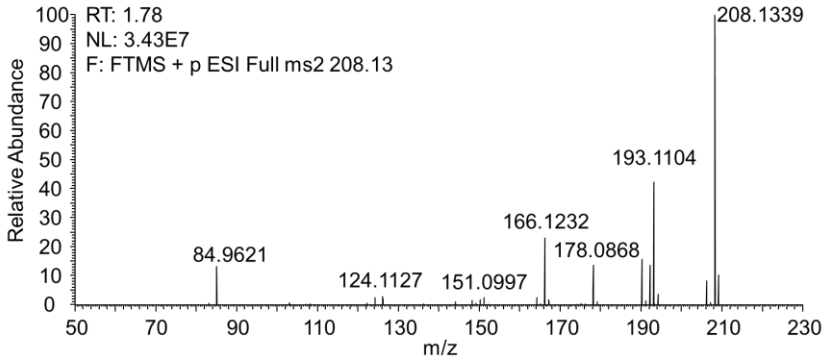
164,1-

Figure S35 3-acetyl-2,4,6-trimethylpyridin (Pyr): reference compound a) UHPLC-MS EIC *m/z* 164.10-164.15, b) MS 0.65 min RT; product in AcAc/AS c) UHPLC-MS EIC *m/z* 164.10-164.15, d) MS at 0.64 min RT. No MS^2 spectra of *m/z* 164.1 were recorded.

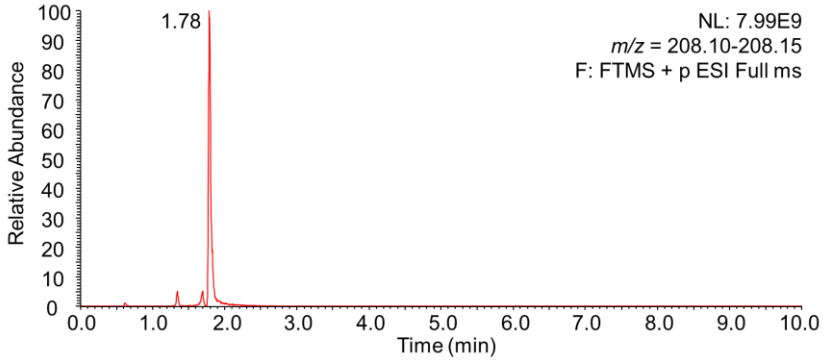
a)



b)



c)



d)

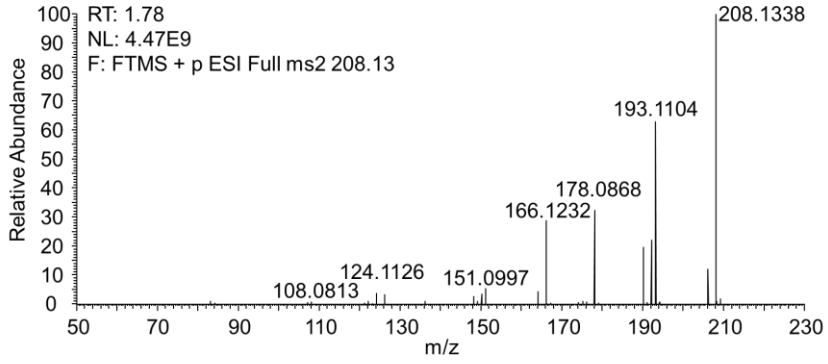


Figure S36 3,5-diacetyl-2,4,6-trimethyl-1,4-dihydropyridin (DHP): reference compound a) UHPLC-MS EIC *m/z* 208.10-208.15, b) MS^2 of *m/z* 208.13; product in AA+AcAc/AS c) UHPLC-MS EIC *m/z* 208.10-208.15, d) MS^2 of *m/z* 208.13. MS^2 spectra were acquired using 70 NCE fragmentation energy (instrument specific parameter).