Electronic Supplementary Material (ESI) for Chemical Communications

Luminescence phenomena of biodegradable photoluminescent poly(diol citrates)

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Supplementary information

Methods

Synthesis and characterization of 5-oxo-2,3-dihydro-5*H*-[1,3]thiazolo[3,2-*a*]pyridine-3,7-dicarboxylic acid (TPA)

Citric acid 1.21 g (6.3 mmol) (Sigma-Alrich, Germany) was mixed with L-cysteine 0.79 g (6.3 mmol) (Sigma-Aldrich, Germany) and water (1 ml) until complete dissolution then the solvent was evaporated under vacuum (10 mbar) at r.t. Afterwards mixture was heated at 100°C for 40 minutes and purified by preparative high pressure liquid chromatography (Knauer HPLC set: degasser, pump K-500, detectors RI 2300 and UV/VIS A2500) at r.t. on Eurospher 100 C-18 column and eluted by 1.35×10^{-3} M trifluoroacetic acid in water at a flow rate 10 ml/min. The luminescent fraction of desired product was collected and freeze-dried. The chemical structure was confirmed by C^{13}, H^{1}, HSQC and COSY NMR experiments carried out in DMSO-d6 solution using a Varian Mercury-VX 300 MHz spectrometer. LC-ESI-MS measurements were performed on a Waters ACQUITY triple-quadrupole tandem mass spectrometric detector with an electrospray ionization (ESI) interface. The separation was accomplished at 40^{o}C, on Acquity UPLC BEH C18 1.7 μm, 2.1 x 100 mm column using 0,1 % water solution of formic acid as the eluent at flow 0,3 ml/min. UV/VIS absorption spectra and emission spectra (excitation at 365 nm) of water solutions of TPA were acquired on a PG Instruments Ltd P80+ spectrophotometer and an Ocean Optics MINI-D2 spectrofluorymeter, respectively.

Synthesis and hydrolysis of cys-BPLP, POC, POCTPA0.0001-1 films

Citric acid, 1,8-octanediol and L-cysteine were combined at molar ratio 1:1:0.5. After melting the mixture at 160°C for 20 minutes, the temperature was brought down to 140 °C stirring continuously for another 45 minutes to obtain the cys-BPLP prepolymer (pre-cys-BPLP). For comparison reaction without amino acid was also conducted as well as with different amounts of TPA (1, 0.1, 0.01, 0.001 and 0.0001 % w/w) added instead of L-cysteine to form pre-POC and pre-POCTPA0.0001-1, respectively. Afterwards 30% w/w 1,4-dioxane solutions of prepolymers (pre-cys-BPLP, POC and POCTPA-0.0001-1) were cast on Teflon molds, heated to 80°C and kept at this temperature for 5 days to produce cross-linked films of cys-BPLP, POC, POCTPA0.0001-1. For hydrolysis 1g of each sample was placed in 6ml of 2 M Na_2CO_3 and kept at 90°C for 24 hours. Next the hydrolyzate was neutralized with 1M HCl and luminescent fraction was collected using preparative HPLC and freeze-dried as described above.

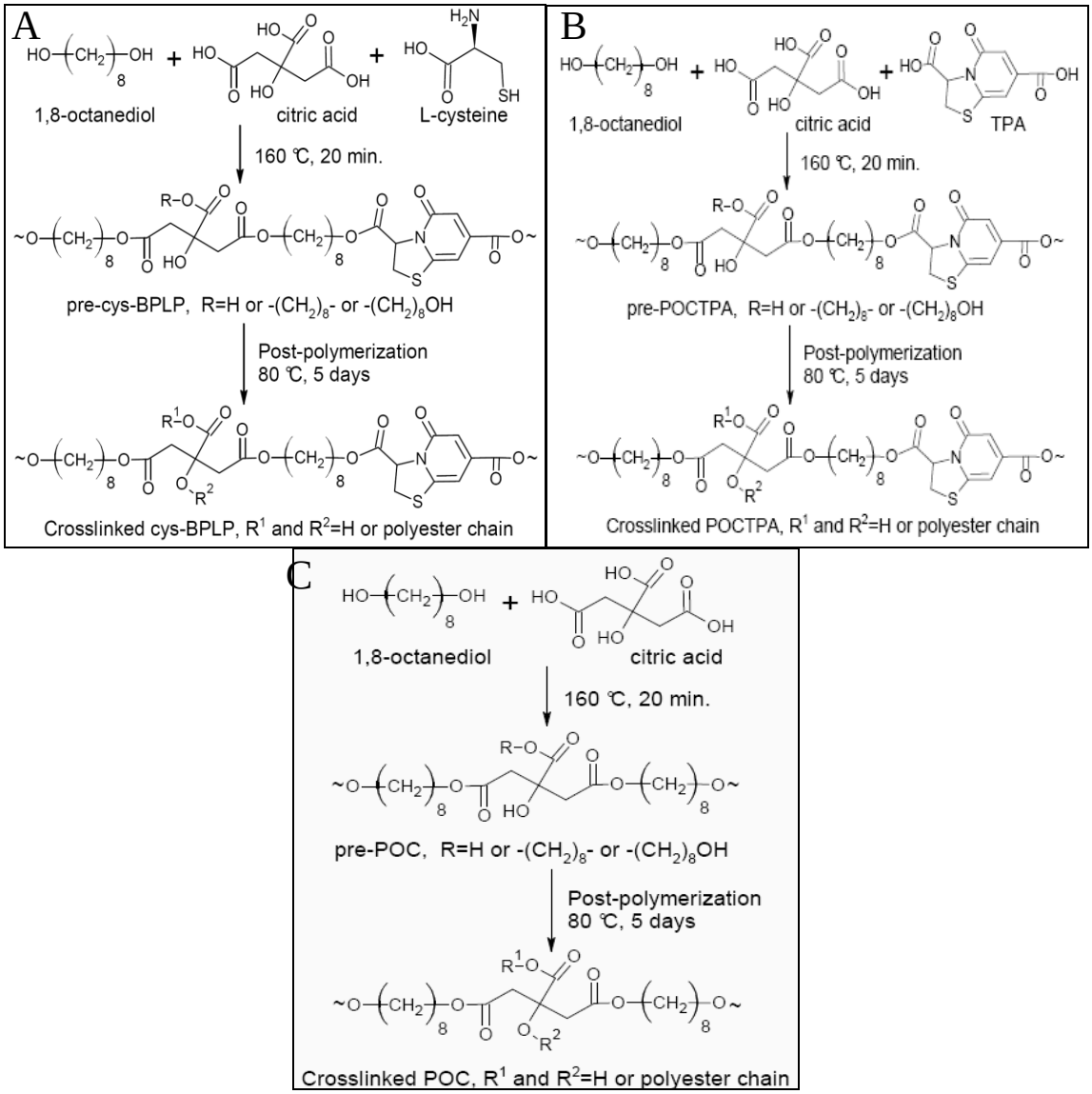

Figure S1 Synthesis of cys-BPLP (A), POCTPA0.0001-1 (B) and POC (C).

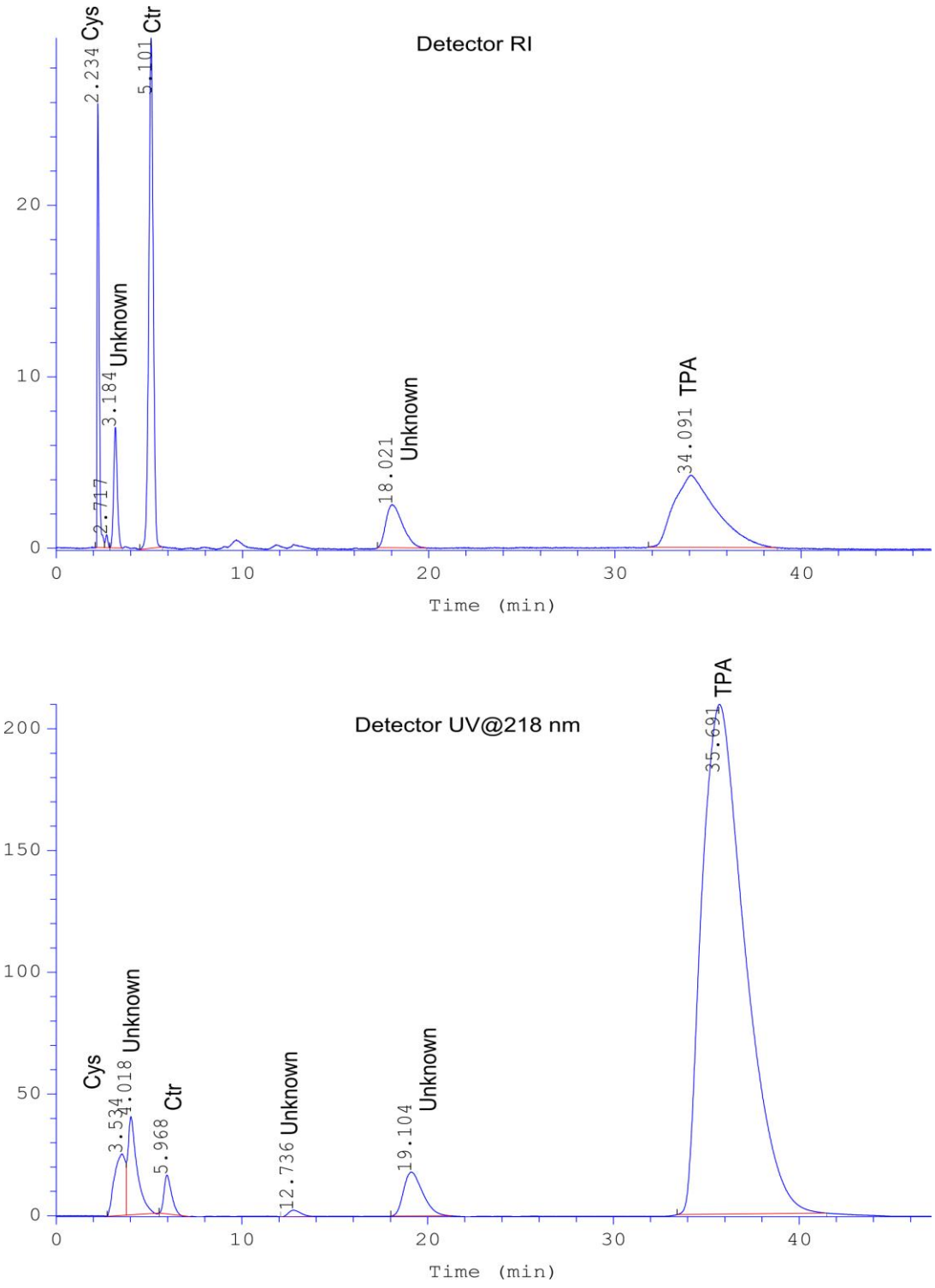

Figure S2. Chromatograms of reaction mixture containing TPA (6,3 mmol of citric acid and 6,3 mmol of L-cysteine heated for 40 minutes at 100°C).

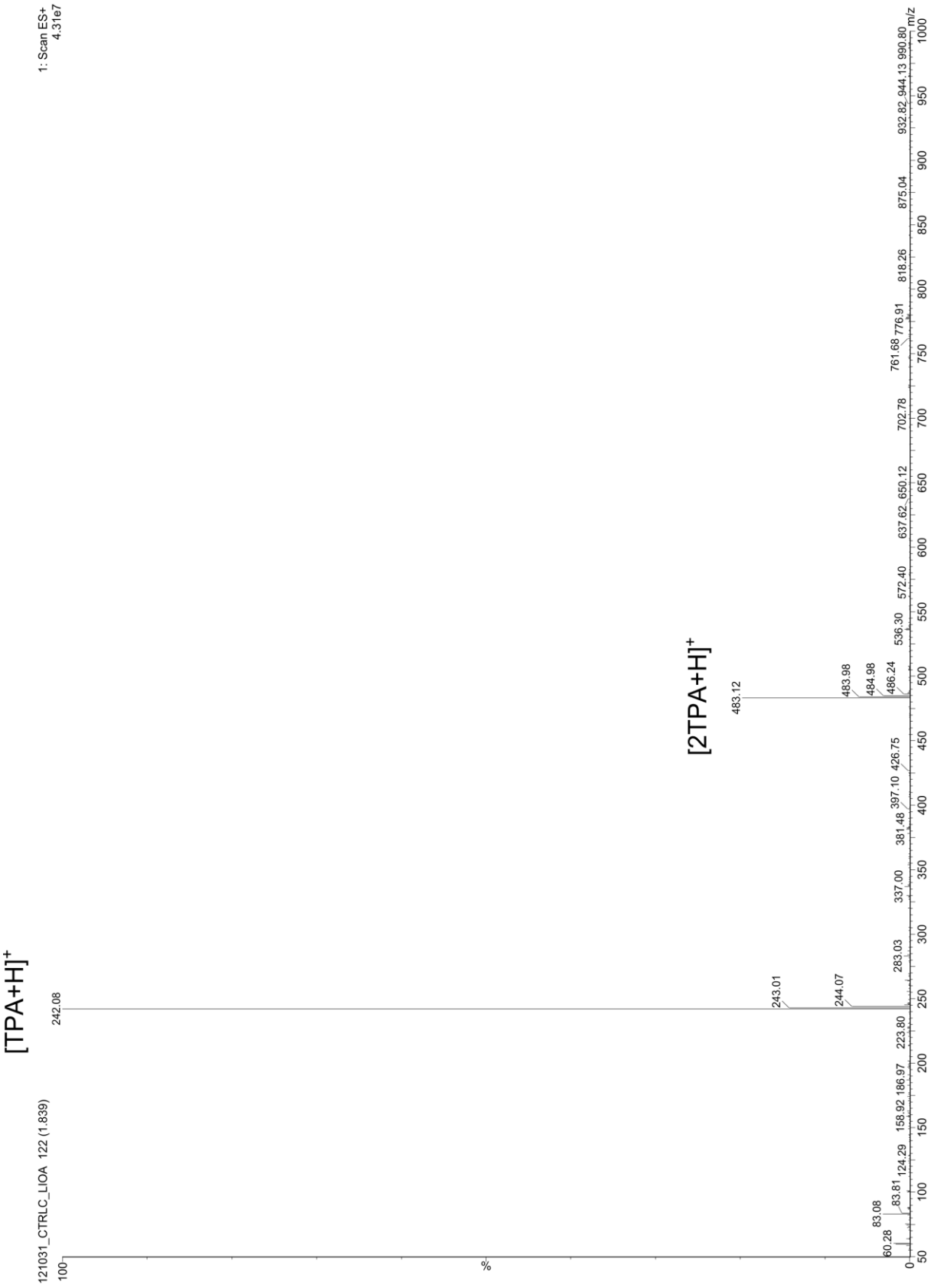

Figure S3. ESI-MS mass spectrum of 5-oxo-2,3-dihydro-5*H*-[1,3]thiazolo[3,2-*a*]pyridine-3,7-dicarboxylic acid (TPA).

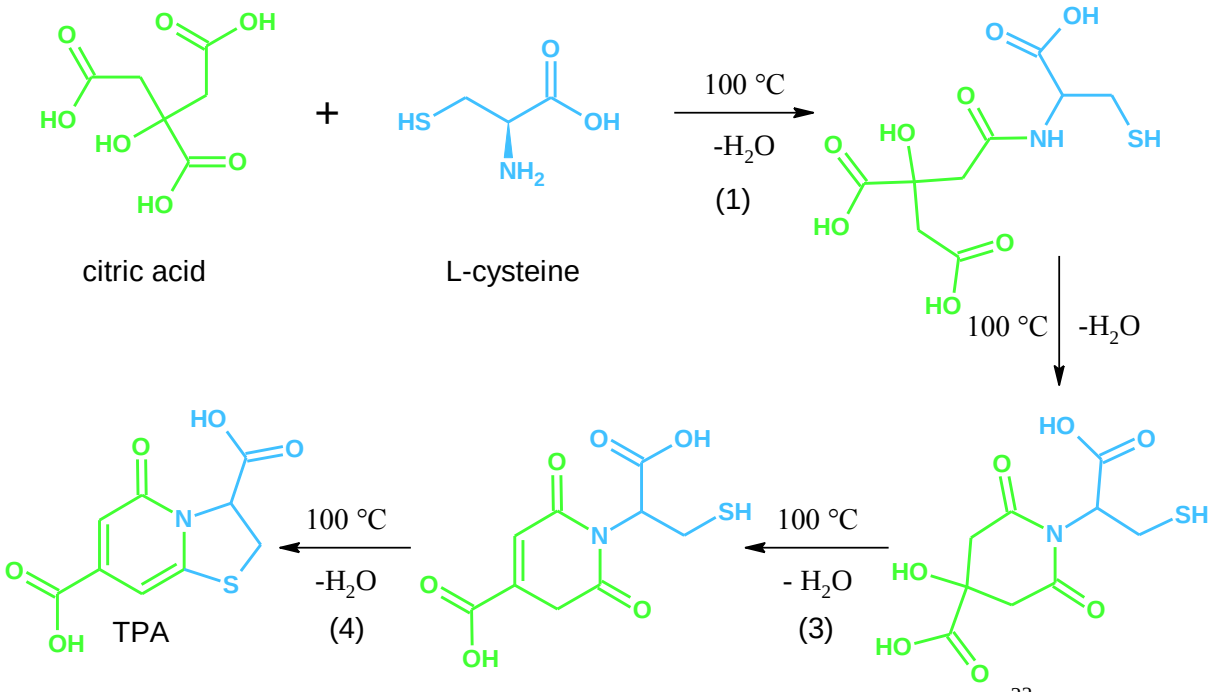

Figure S4. The proposed mechanism of TPA formation basing on Olthoff et al.[23]; amide formation (1), imide formation (2), dehydratation (3), intramolecular condensation (4)[23, 24].

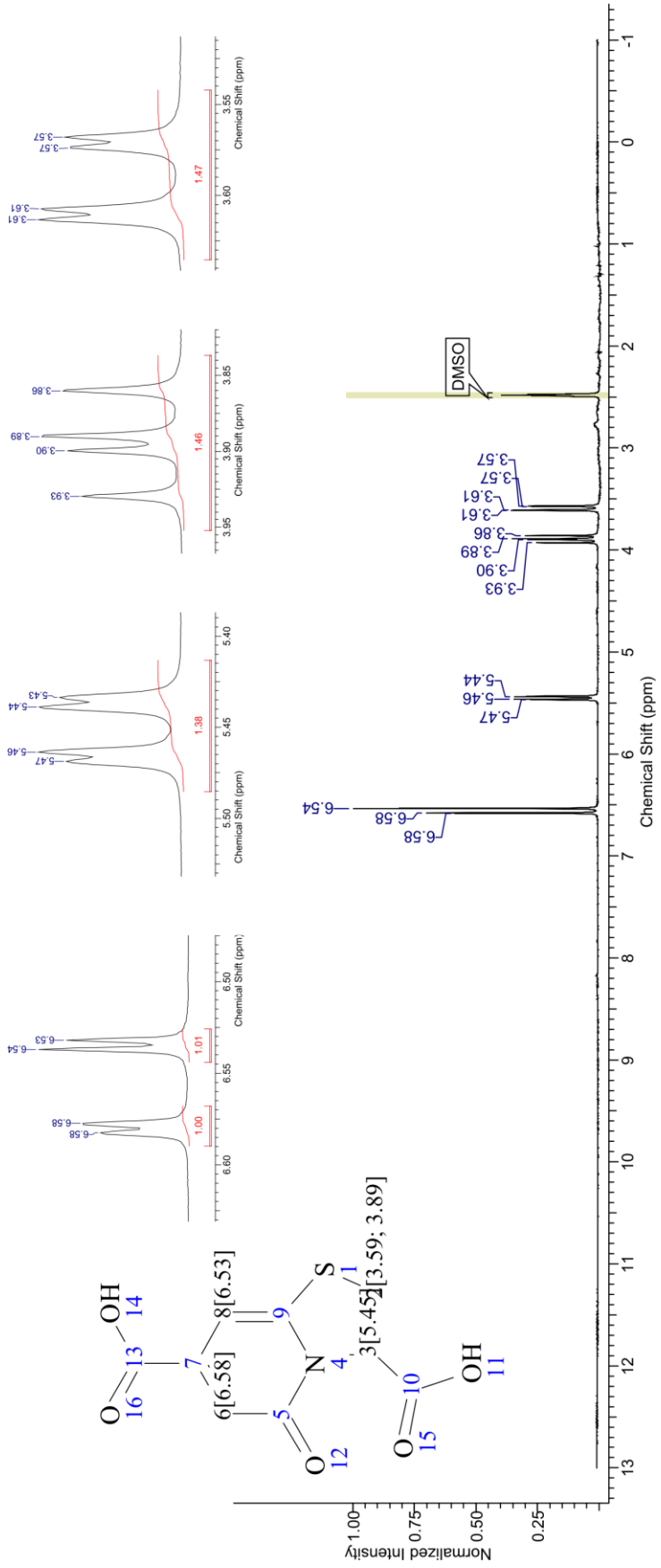

Figure S5. H[1] NMR spectrum of 5-oxo-2,3-dihydro-5*H*-[1,3]thiazolo[3,2-*a*]pyridine-3,7-dicarboxylic acid (TPA).

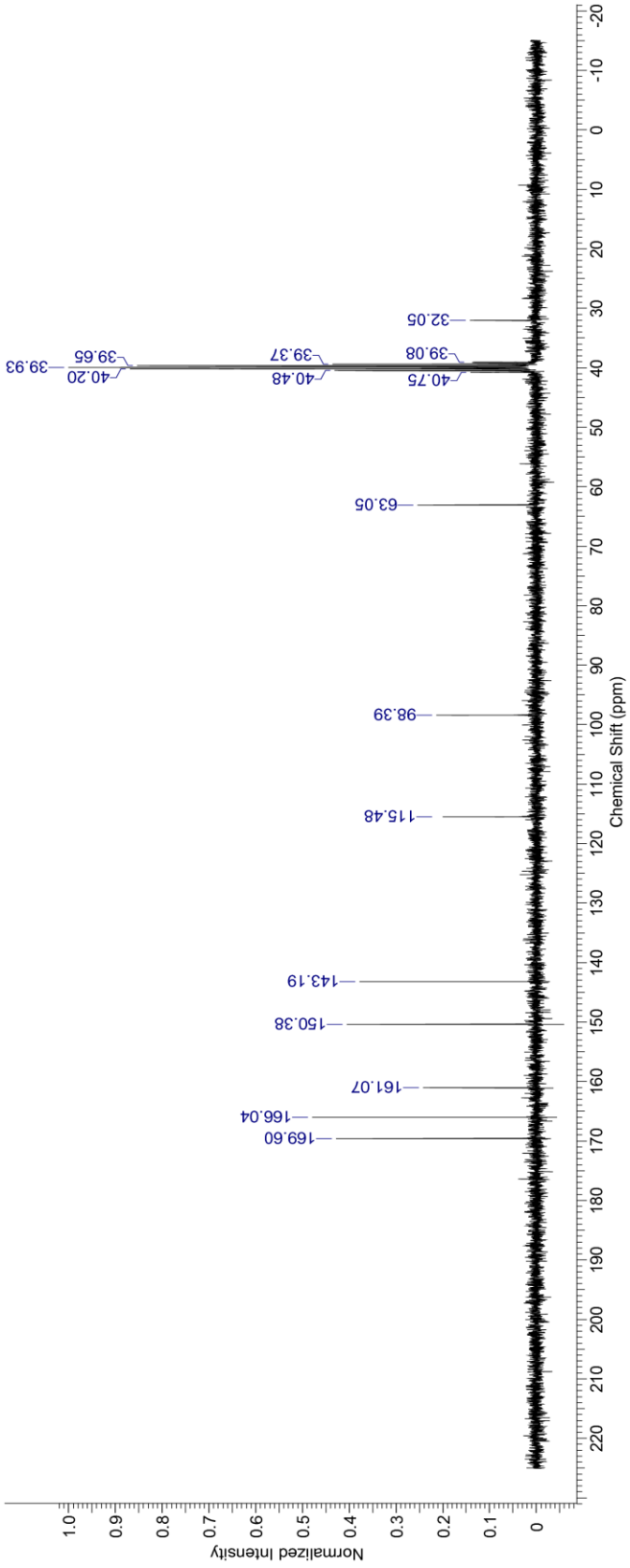

Figure S6. C^{13} NMR spectrum of 5-oxo-2,3-dihydro-5*H*-[1,3]thiazolo[3,2-*a*]pyridine-3,7-dicarboxylic acid (TPA).

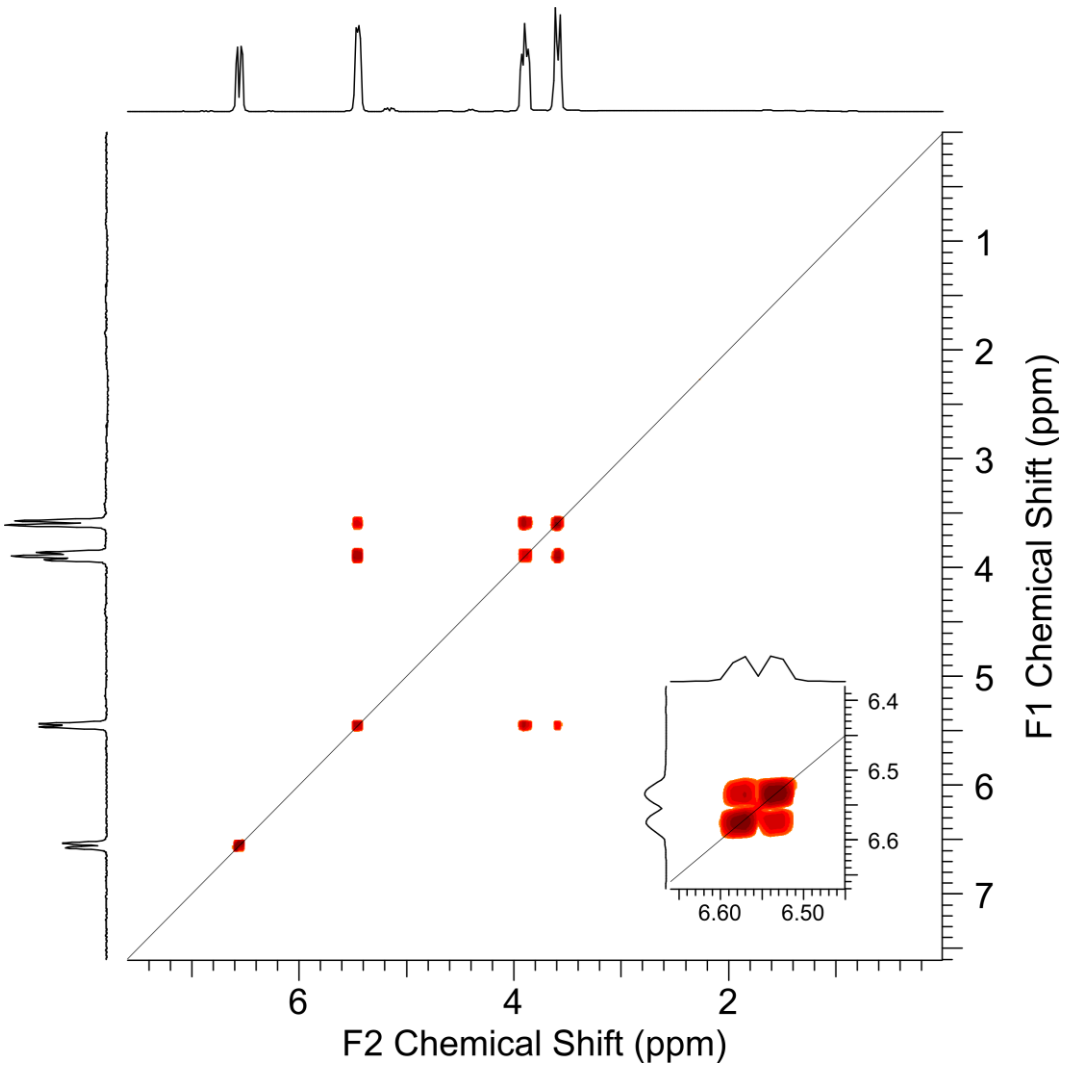

Figure S7. COSY NMR spectrum of 5-oxo-2,3-dihydro-5*H*-[1,3]thiazolo[3,2-*a*]pyridine-3,7-dicarboxylic acid (TPA).

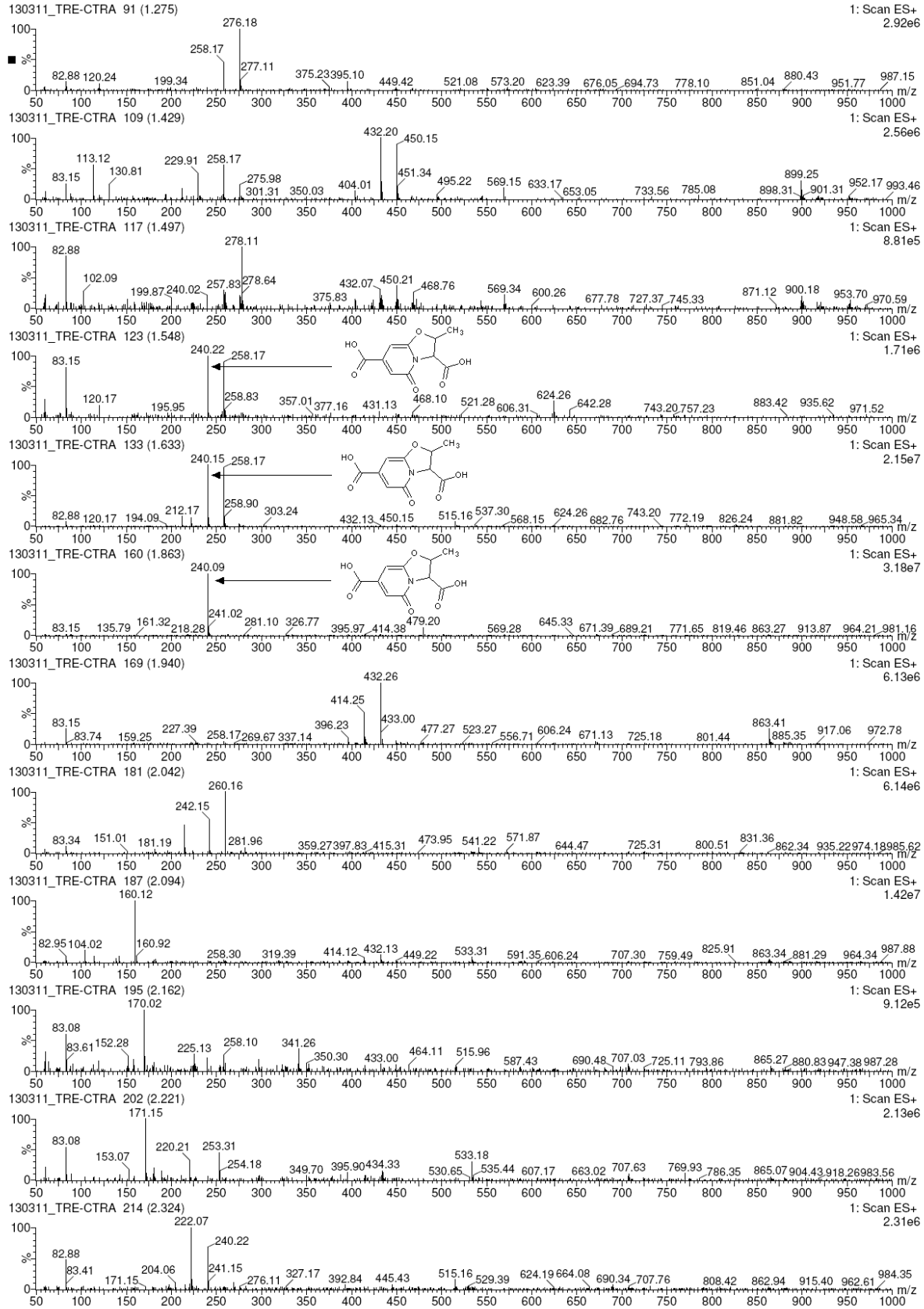

Figure S8. ESI-MS spectrum of nonpurified reaction mixture of L-treonine and citric acid (1:1 mol/mol) after heating at 100°C for 40 minutes. Peaks at m/z=~240 indicate formation of 2-methyl-5-oxo-2,3-dihydro-5*H*-[1,3]oxazolo[3,2-*a*]pyridine-3,7-dicarboxylic acid.

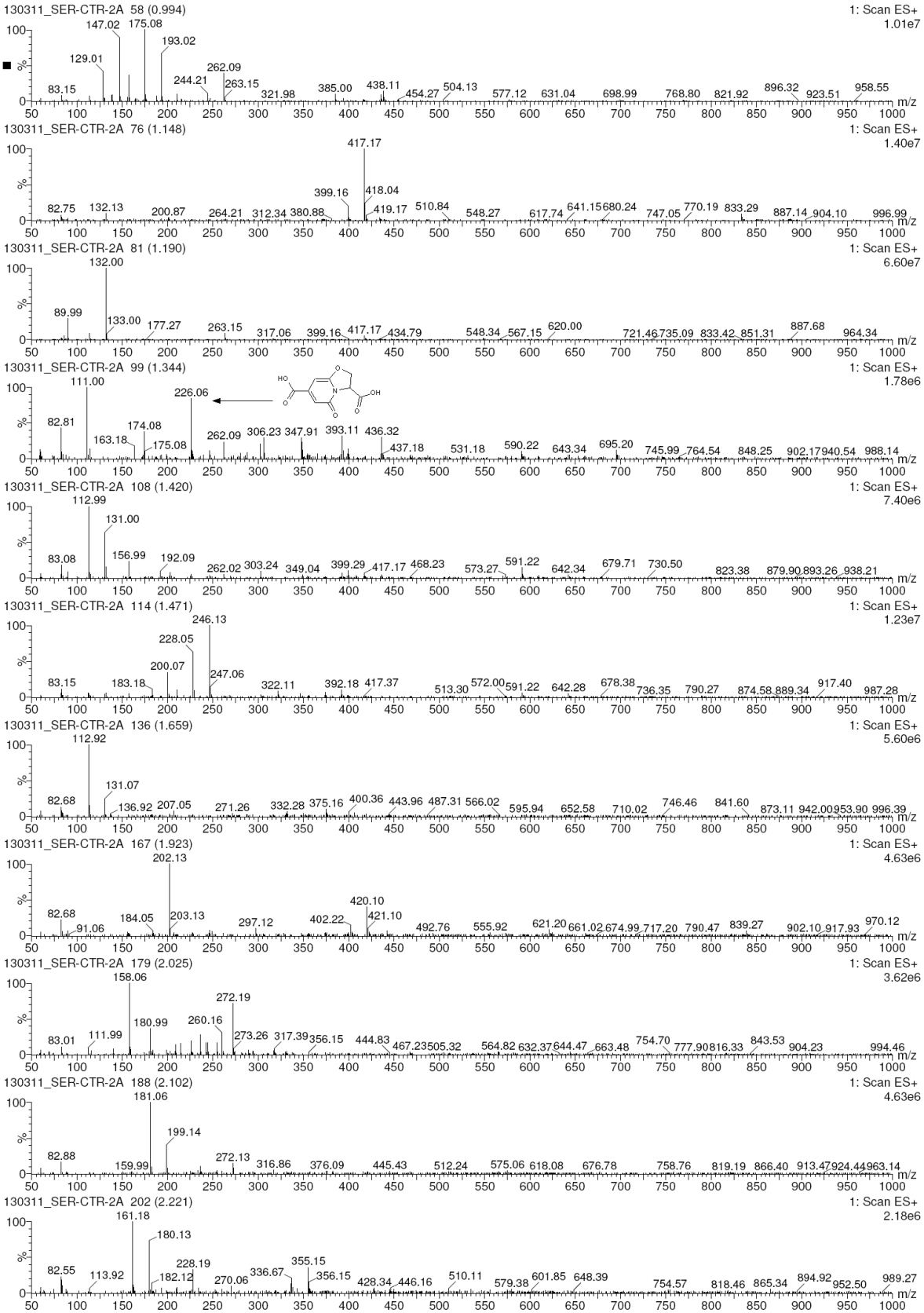

Figure S9. ESI-MS spectrum of nonpurified reaction mixture of L-serine and citric acid (1:1 mol/mol) after heating at 100°C for 40 minutes. Peak at m/z=~226 indicates formation of 5-oxo-2,3-dihydro-5*H*-[1,3]oxazolo[3,2-*a*]pyridine-3,7-dicarboxylic acid.

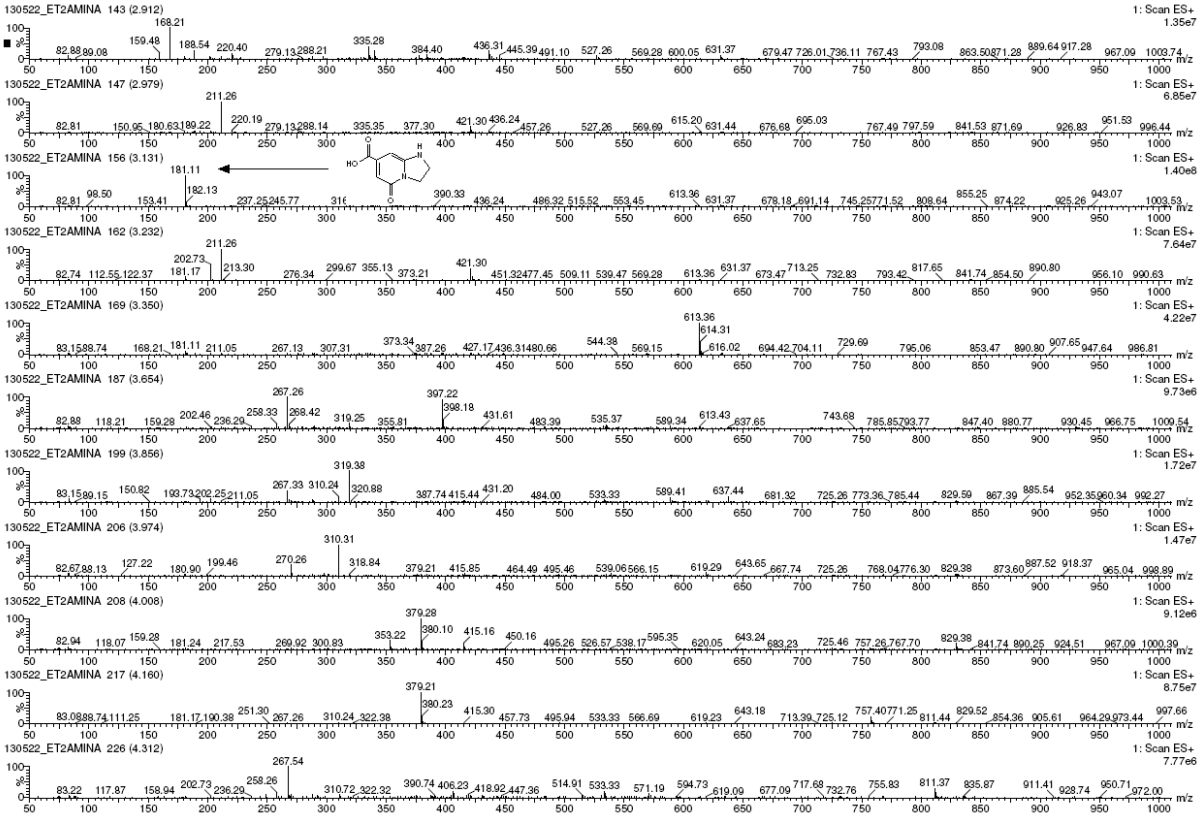

Figure S10. ESI-MS spectrum of nonpurified reaction mixture of ethylenediamine and citric acid (1:1 mol/mol) after heating at 100°C for 40 minutes. Peak at m/z=~181 indicates formation of 5-oxo-1,2,3,5-tetrahydroimidazo[1,2-*a*]pyridine-7-carboxylic acid.

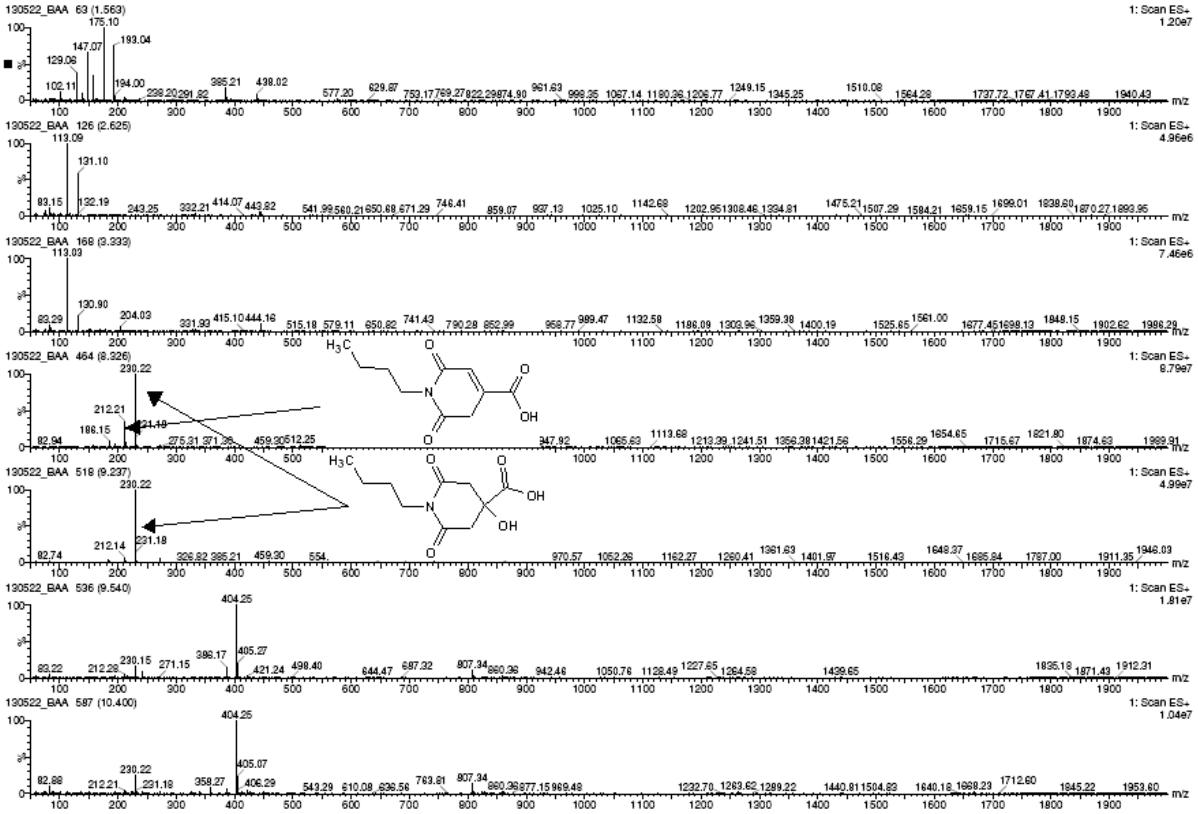

Figure S11. ESI-MS spectrum of nonpurified reaction mixture of ethylenediamine and citric acid (1:1 mol/mol) after heating at 100°C for 40 minutes. Peak at m/z=~212 indicates formation of 1-butyl-2,6-dioxo-1,2,3,6-tetrahydropyridine-4-carboxylic acid.

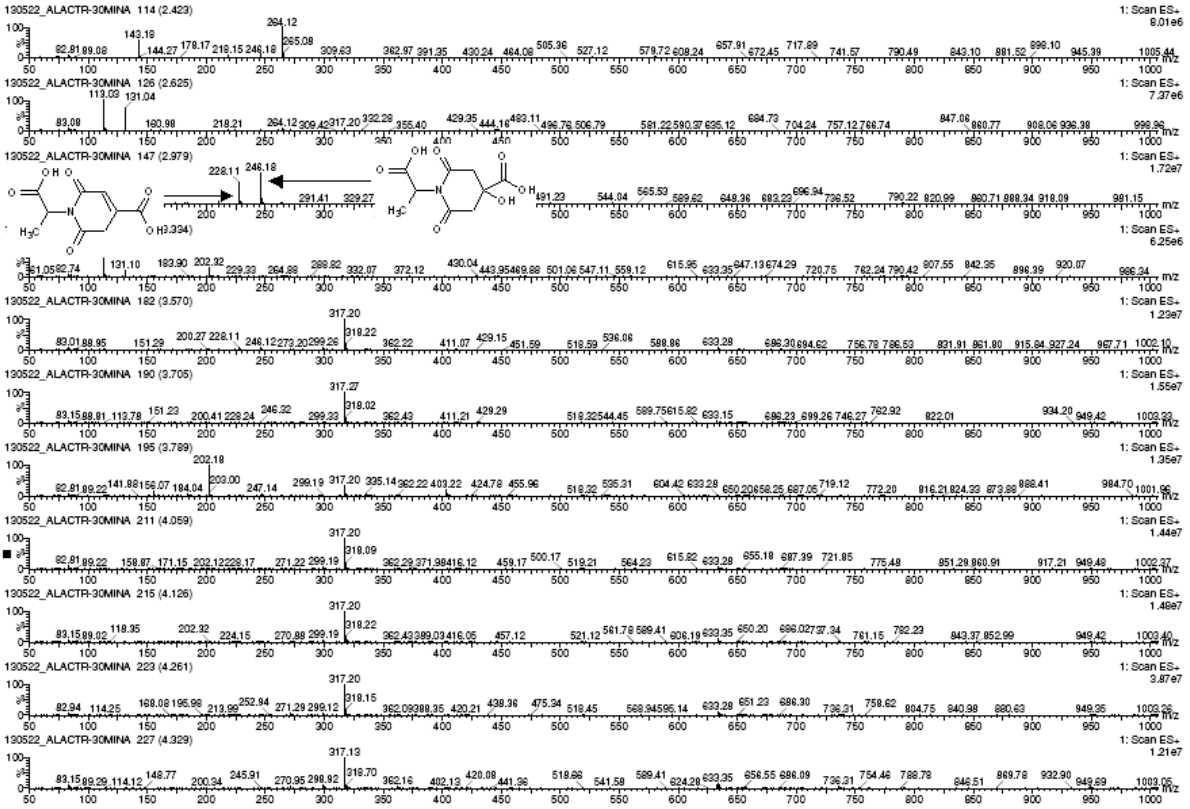

Figure S12. ESI-MS spectrum of nonpurified reaction mixture of ethylenediamine and citric acid (1:1 mol/mol) after heating at 100°C for 40 minutes. Peak at m/z=~228 indicates formation of 1-(1-carboxyethyl)-2,6-dioxo-1,2,3,6-tetrahydropyridine-4-carboxylic acid.

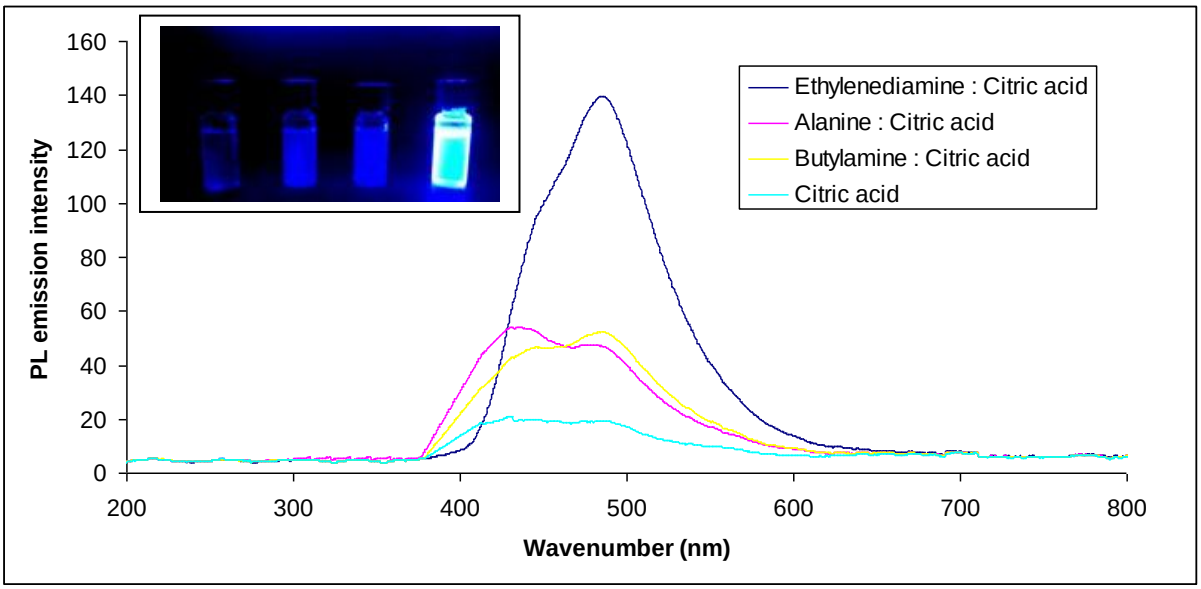

Figure S13. Photoluminescence emission spectrum of 2,5 mg/ml aqueous solutions of nonpurified reaction mixtures of various amines and citric acid (1:1 mol/mol) after heating at 100°C for 40 minutes. For comparison a spectra of a solution of citric acid heated at that same conditions is provided. All samples were excited with 365 nm light.

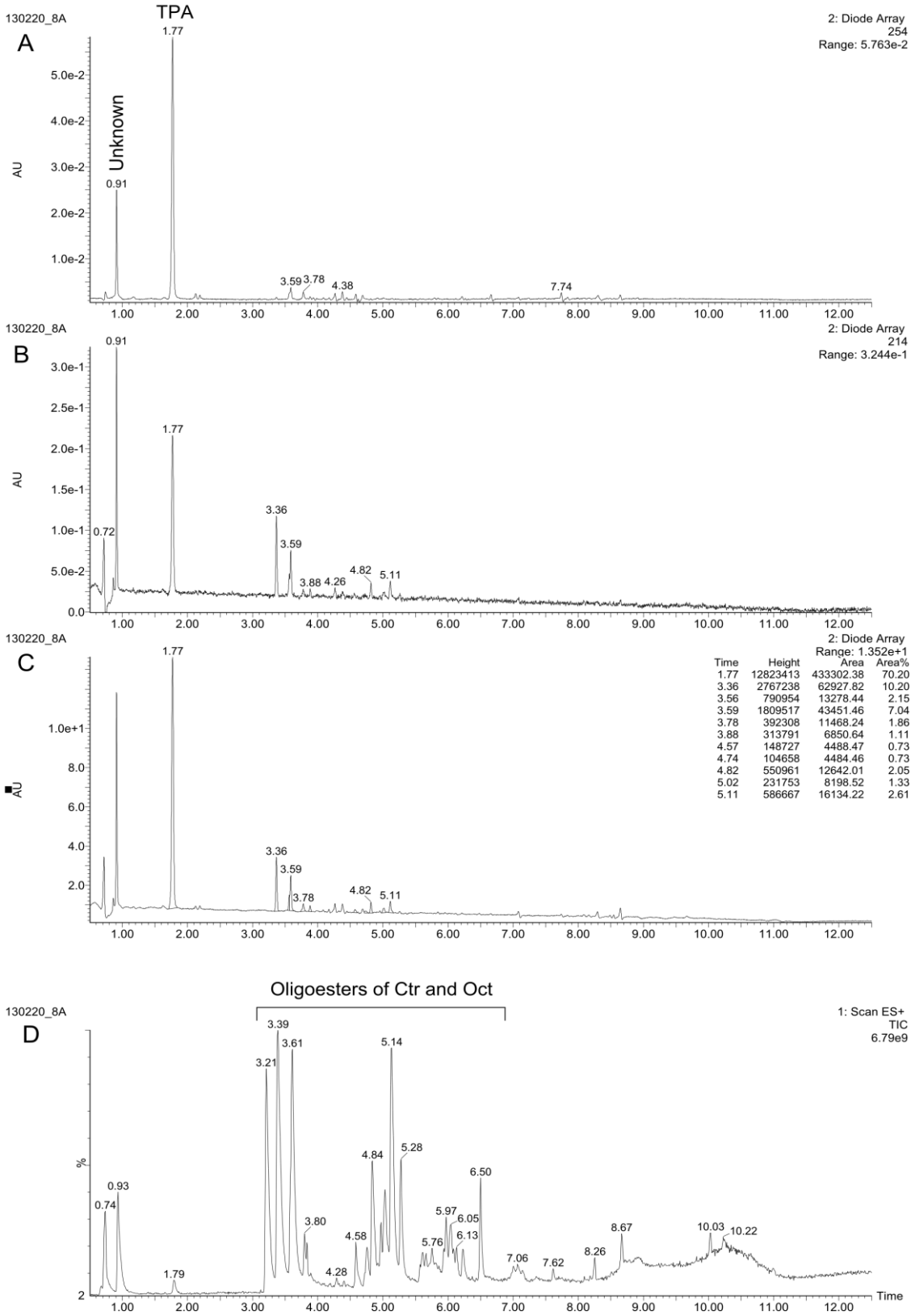

Figure S14a. HPLC elution profile of POCTPA1 hydrolyzate: diode array detector chromatograms at different wavelength (A,B,C) and total ion current chromatogram of the ESI-MS detector (D).

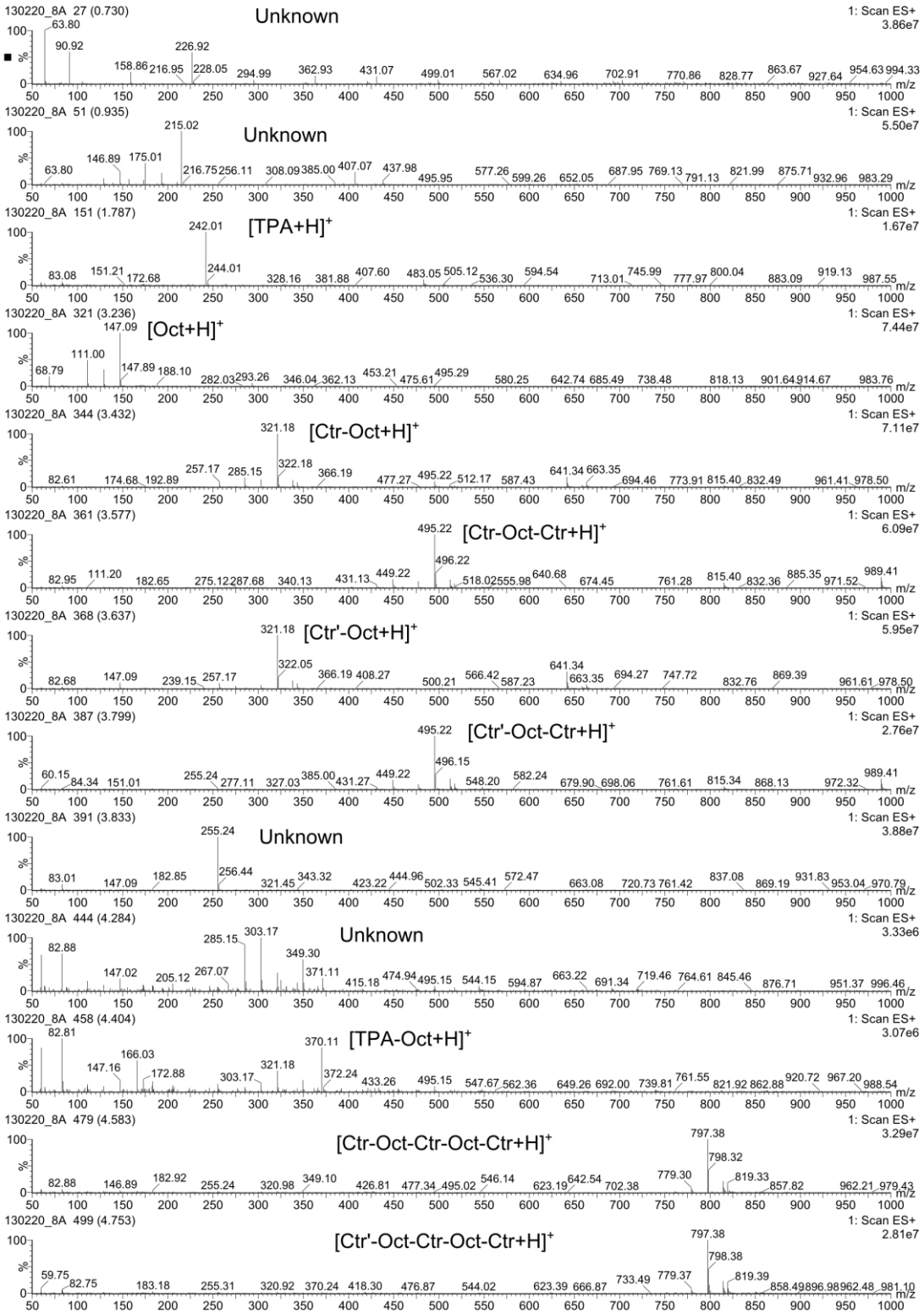

Figure S14b. ESI-MS spectrum of compounds separated from hydrolyzate of POCTPA1 (retention time ≤ 4.75 min.).

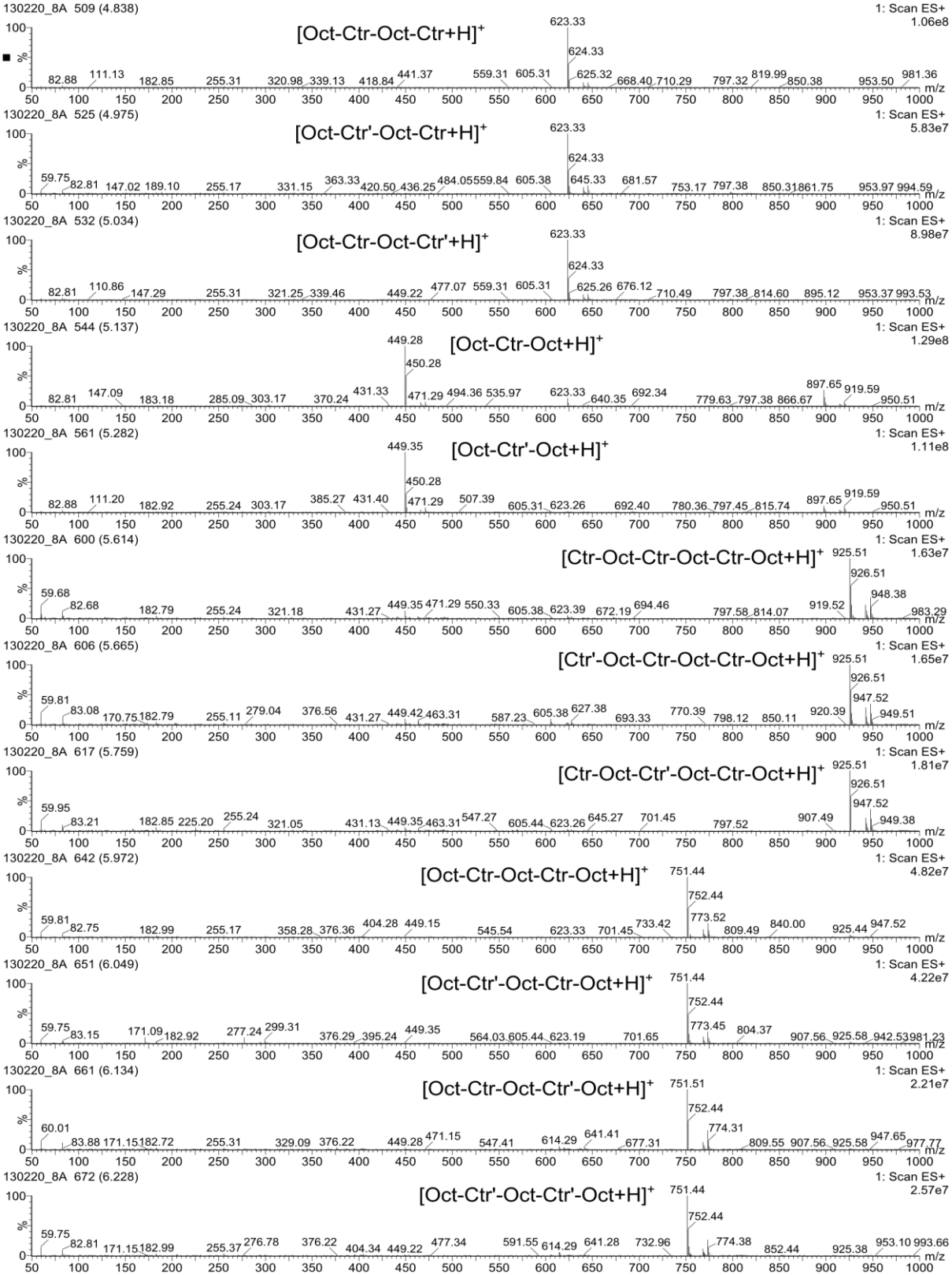

Figure S14c. ESI-MS spectrum of compounds separated from hydrolyzate of POCTPA1 (retention time > 4.75 min.).

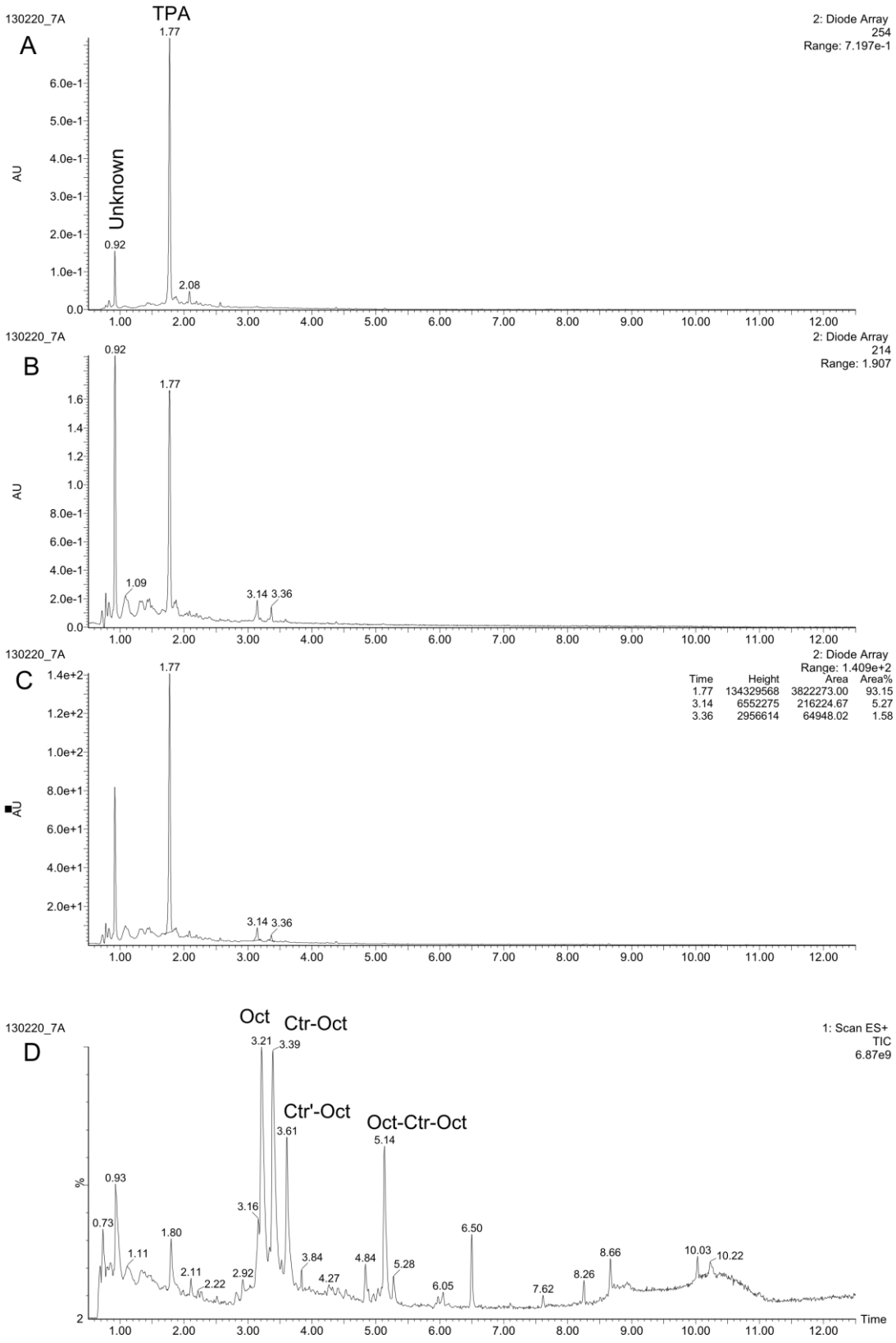

Figure S14d. HPLC elution profile of cys-BPLP hydrolyzate: diode array detector chromatograms at different wavelength (A,B,C) and total ion current chromatogram of the ESI-MS detector (D).

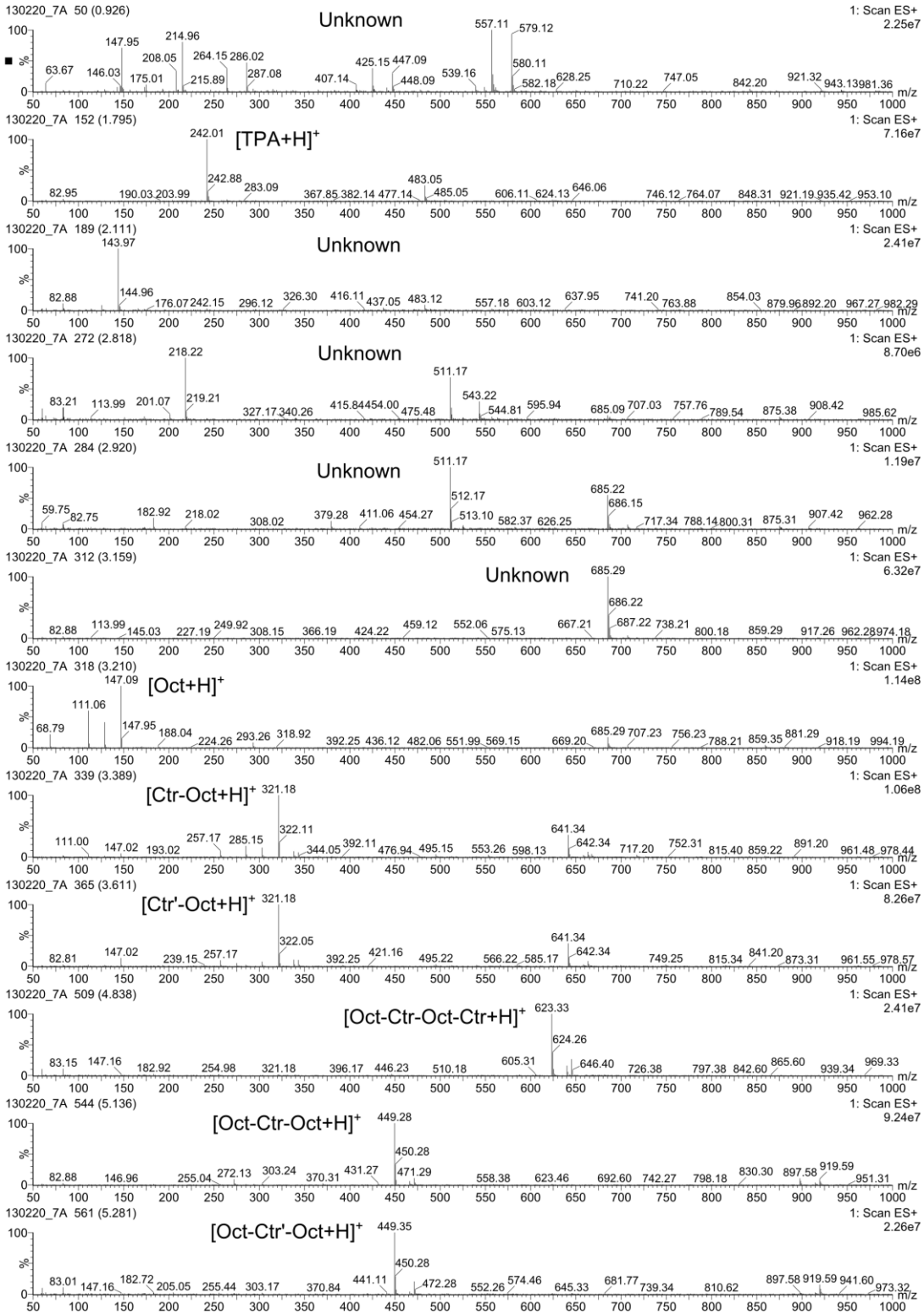

Figure S14e. ESI-MS spectrum of compounds separated from hydrolyzate of cys-BPLP.

Synthesis of esters of TPA and 1,8-octanediol

TPA 50 mg (0,2 mmol) and 1,8-octanediol 90 mg (0,6 mmol) were combined and heated at 140°C for 1 hour. Products of this reaction were characterized by LC-ESI-MS (Figure S10a and S10b).

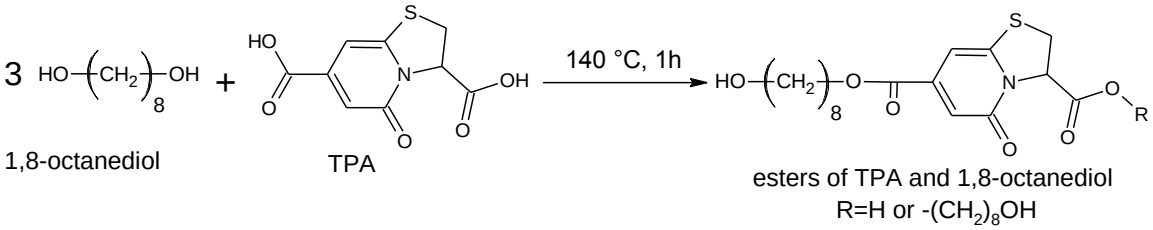

Figure S15 Synthesis of esters of TPA and 1,8-octanediol.

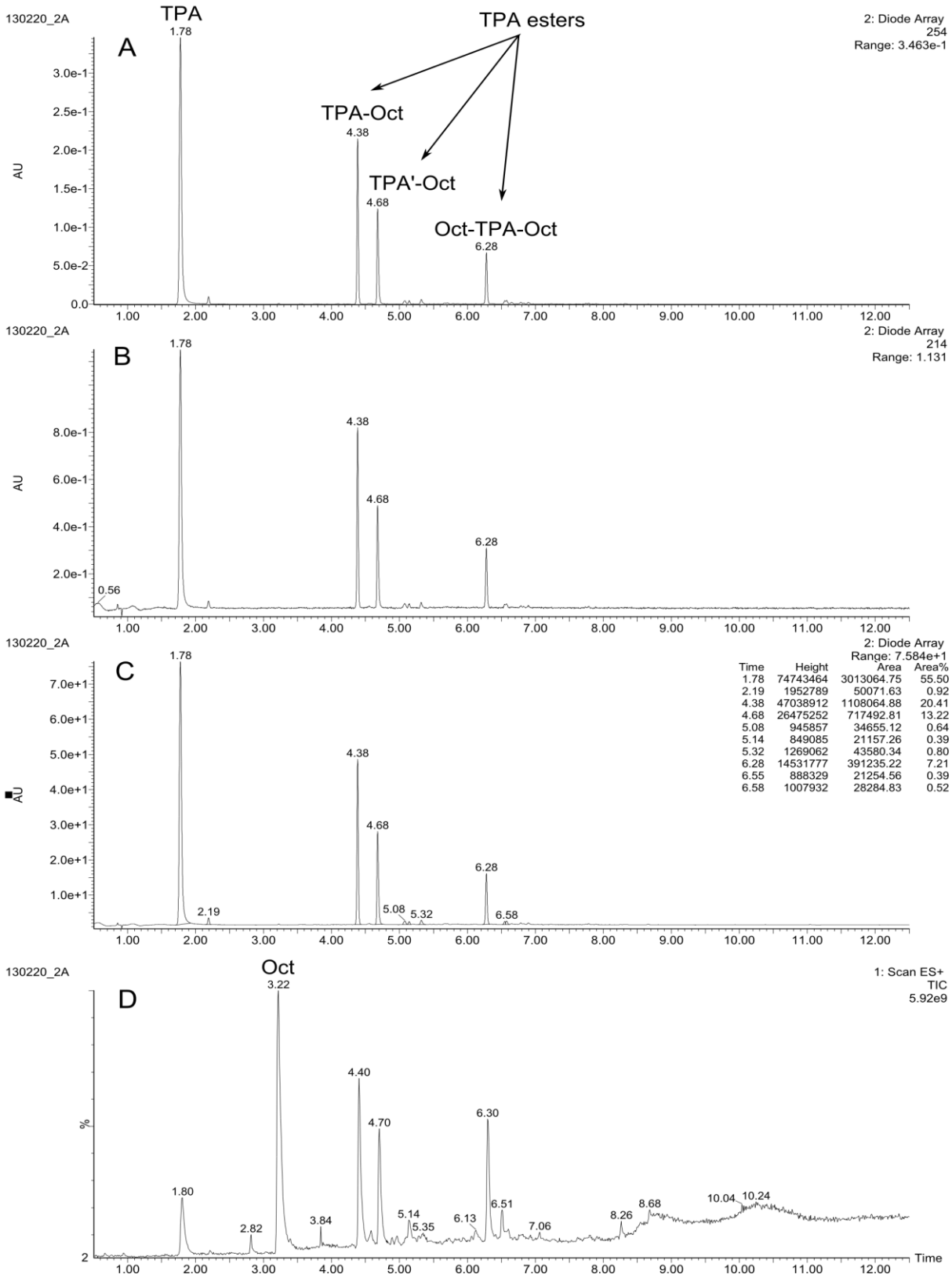

Figure S16a. HPLC elution profile of esters of TPA and 1,8-octanediol: diode array detector chromatograms at different wavelength (A,B,C) and total ion current chromatogram of the ESI-MS detector (D).

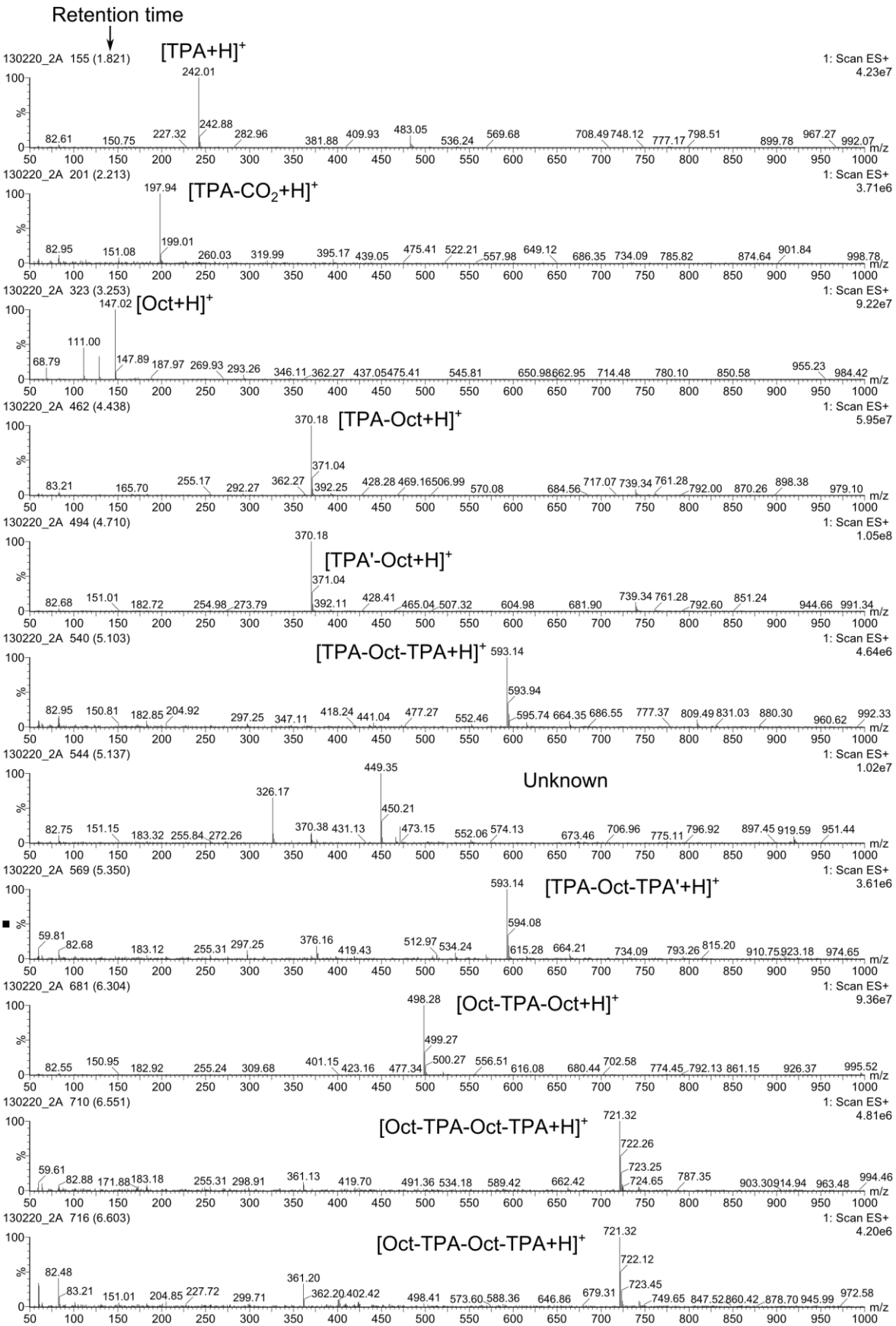

Figure S16b. ESI-MS spectrum of esters of TPA and 1,8-octanediol.