Supporting information for Chemical Communication

Expanding diversity in dynamic combinatorial libraries: simultaneous exchange of disulfide and thioester linkages

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NMR ANALYSIS AFTER THE FIRST EQUILIBRIUM

NMR Methods and Parameters

NMR was performed using an Advance 500 Bruker instrument and a standard TCI Cryoprobe ^{1}H (presaturation).

NMR Spectrum (Figure 4)

1D NOESY with water presaturation during relaxation delay and mixing time (NOESYPR1D).

Solvent: H_2O/CD_3OD (90/10)
Exact field: 500.13 MHz
Exponential line broadening: 0.30 Hz
Relaxation time (D1): 8.00 seconds
Acquisition time (AQ): 3.172 seconds
Mixing time: 300 milliseconds
Number of points (TD): 65536

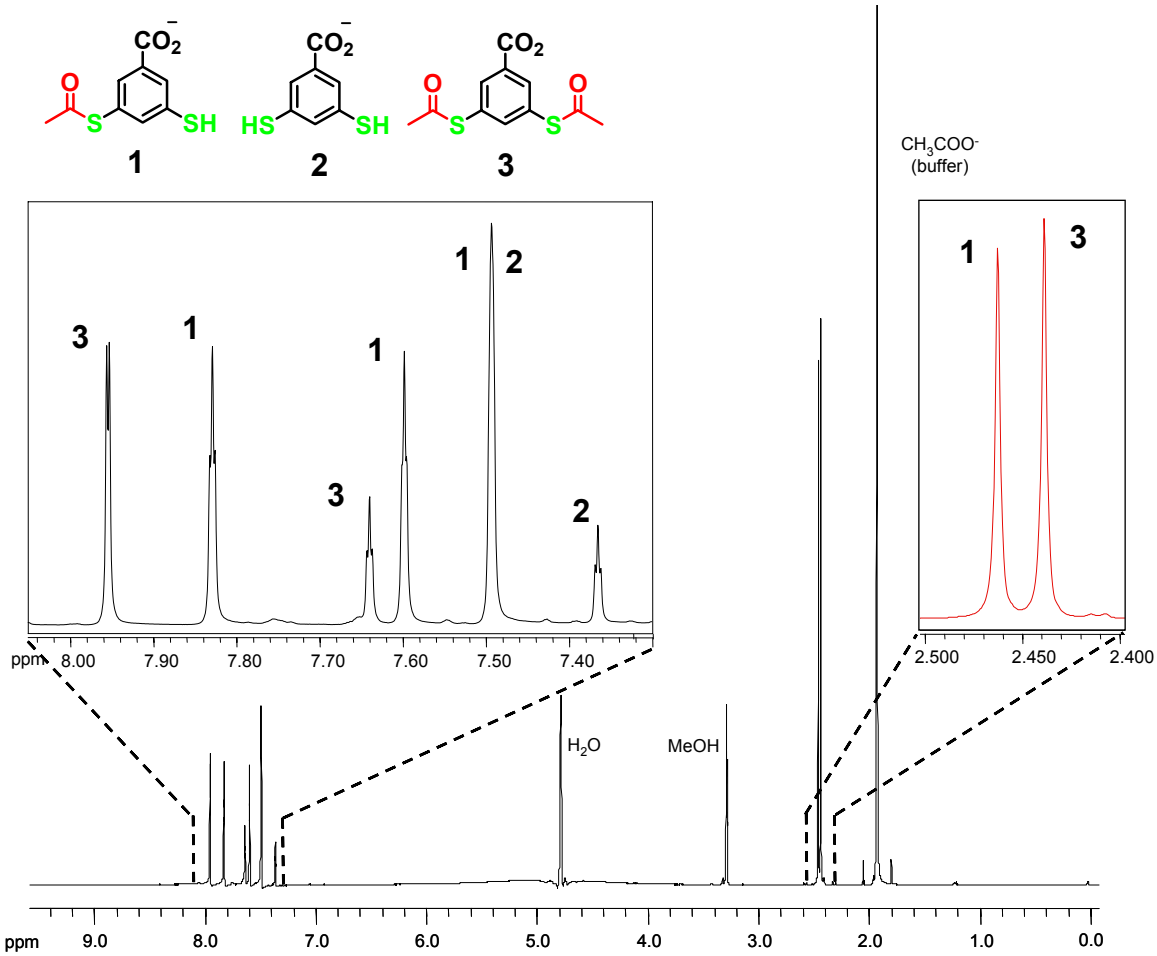

Fig. 4

HPLC/ESI-MS ANALYSIS OF THE LIBRARIES

LC-MS Methods and Parameters
LC-MS was performed using an Agilent 1100 series HPLC and Agilent XCT iontrap mass spectrometer. Solvents and formic acid were acquired from Romil.

HPLC Parameters
Injection volume 5µl
Flow rate 1.000 ml/min
Column: Waters symmetry C18 2.1 x 150mm (WAT106005)
Mobile phase: water with 0.1% formic acid (solvent A) and acetonitrile with 0.1% formic acid (solvent B)

Gradient elution

Time (mins)	Solvent B(%)
0	5
26	83
40	95
45	95
50	5
70	5

MS Parameters
Mass range mode: Ultra Scan
Ion polarity: Negative mode
Ion Source: ESI
Dry temperature: 350°C
Nebuliser pressure: 55.00 psi
Dry gas flow: 12 l/min
HV capillary: 4000V

Time (mins)		Target mass:
0	20.3	250
20.3	22.7	450
22.7	24.6	600
24.6	25.5	800
25.5	26.2	1000
26.2	27.9	600
27.9	29.0	1000
29.0	50.9	1100

ICC target: 200000

Base peak chromatogramme (Fig. 5) and extracted ion traces (Fig. 6) of the final library made from 1 after exposure to oxygen.
Structures can be identified and correlated to UV peaks by analysis of the base peak chromatogram. Structures often detected as singly charged species accompanied by the corresponding dimer chelating a sodium ion.

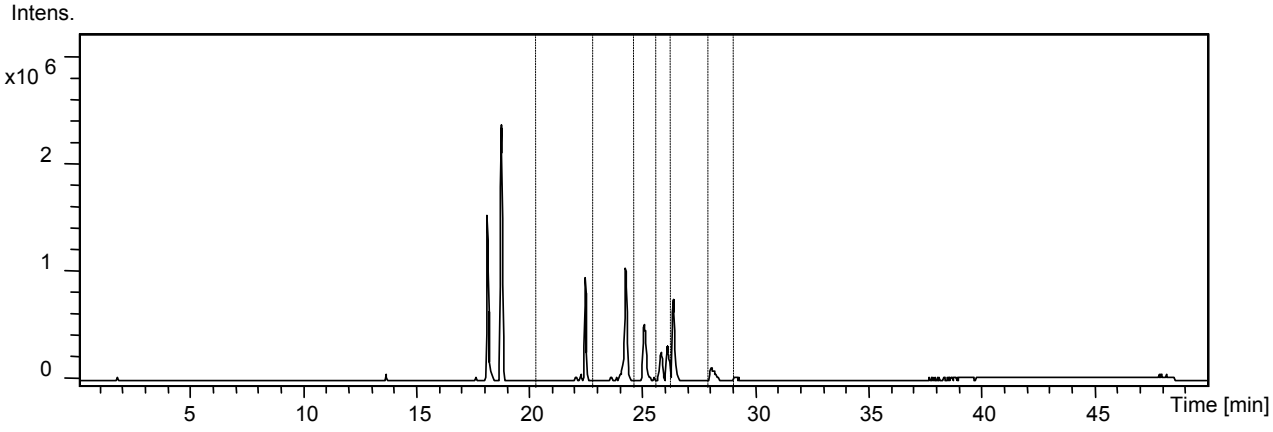

Fig. 5

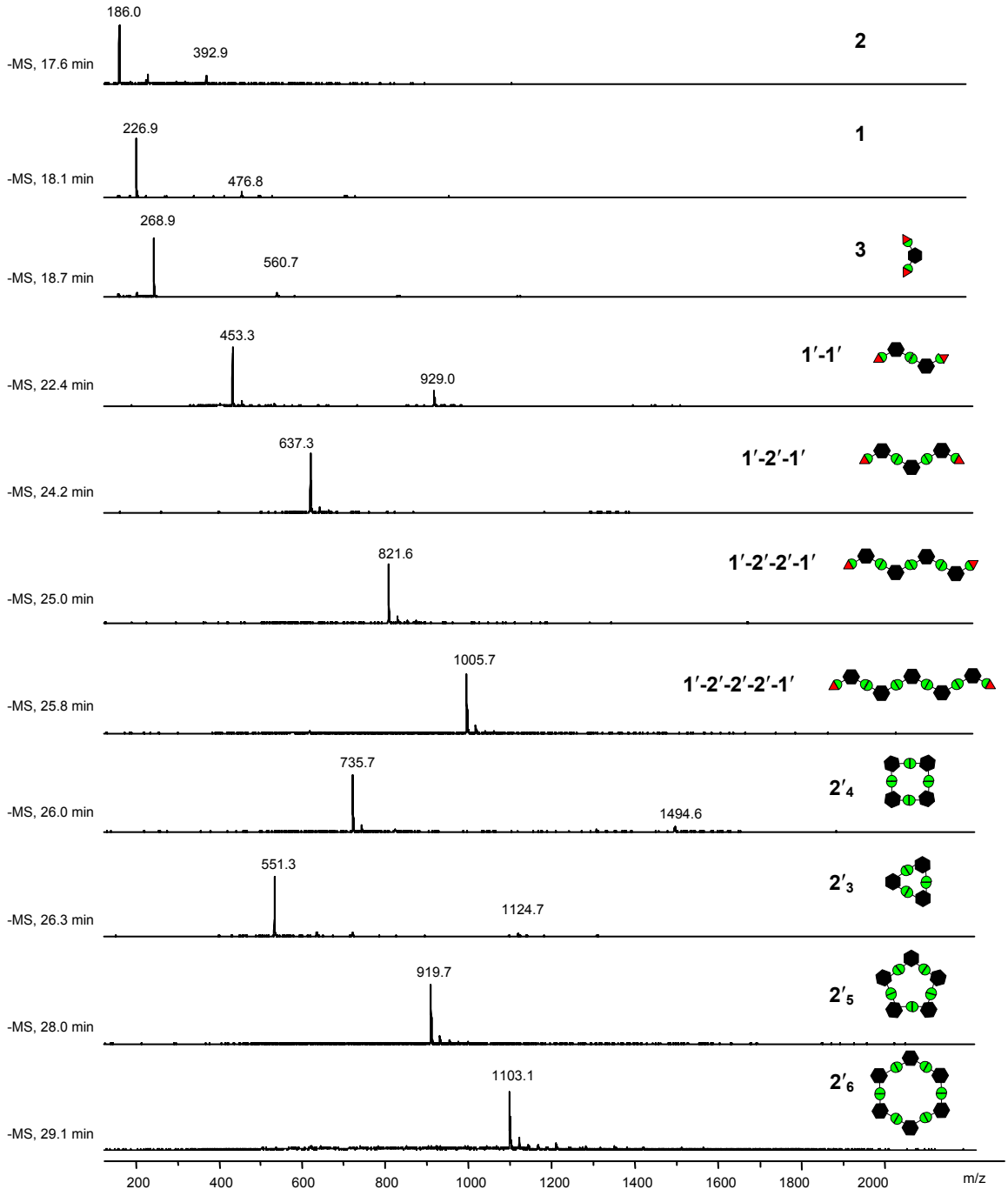

Fig. 6