Supplementary information

Cryogels with Noble Metal Nanoparticles as Catalyst for "Green" Decomposition of Chlorophenols

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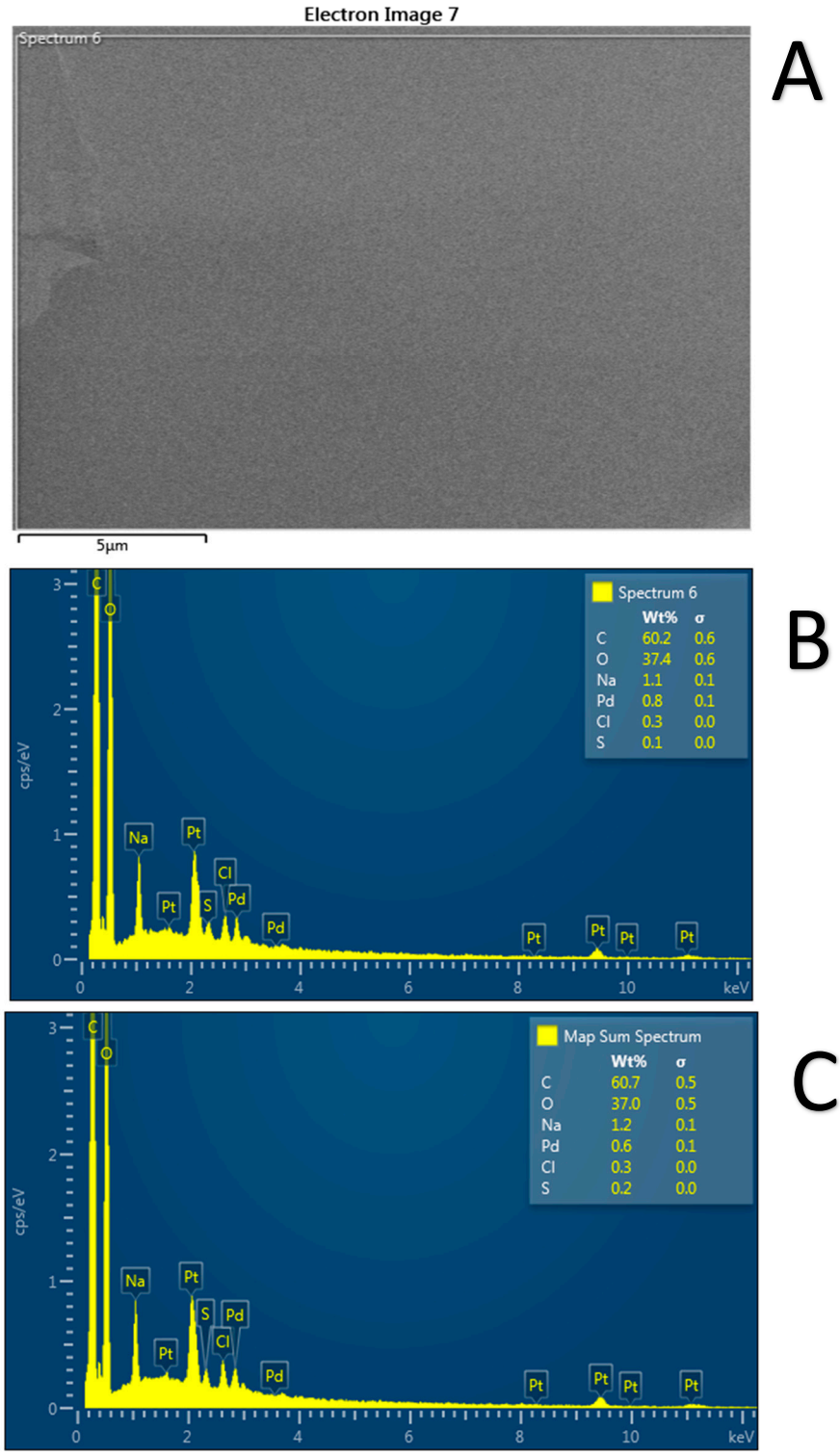


Figure S1. A) SEM image of CHI-GA-PdNPs cryogel containing 0.6mM PdNPs ; B) Energy-dispersive X-ray spectra of CHI-GA-PdNPs cryogels containing 0.6mM PdNPs C) Energy-dispersive X-ray spectra of CHI-GA-PdNPs 0.4mM.

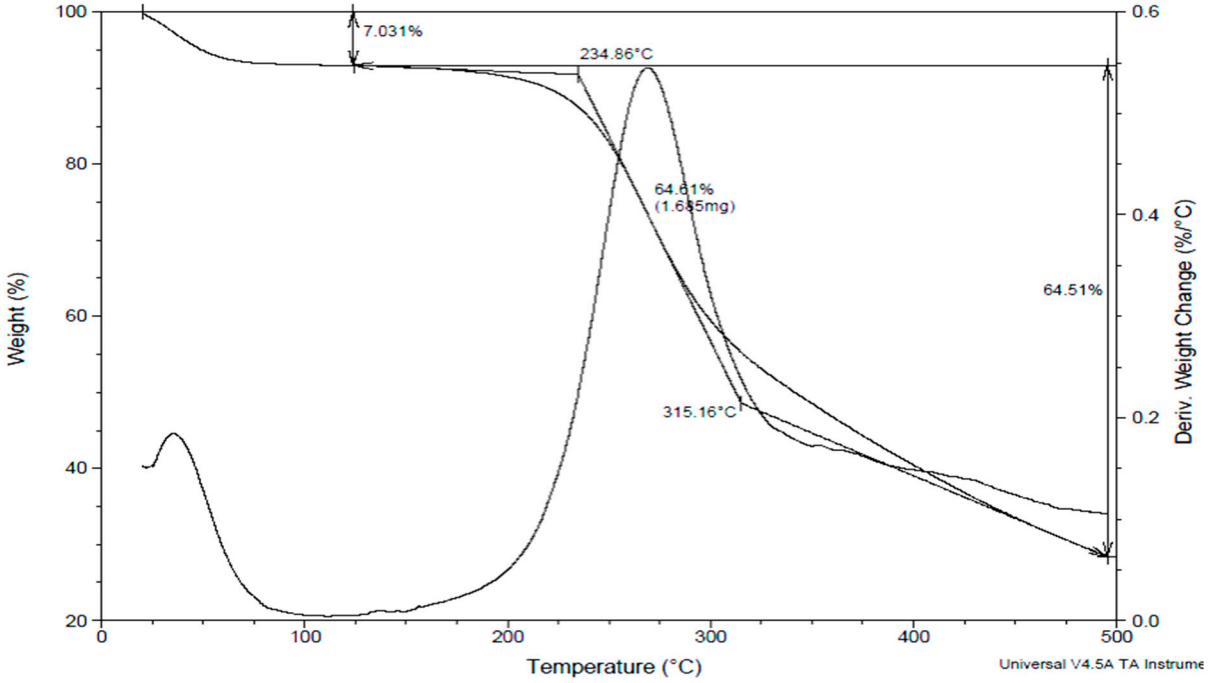


Figure S2. TGA of freeze dried cryogel CHI-GA-PdNPs 0.05 mM in air and derivative gravimetric analysis.

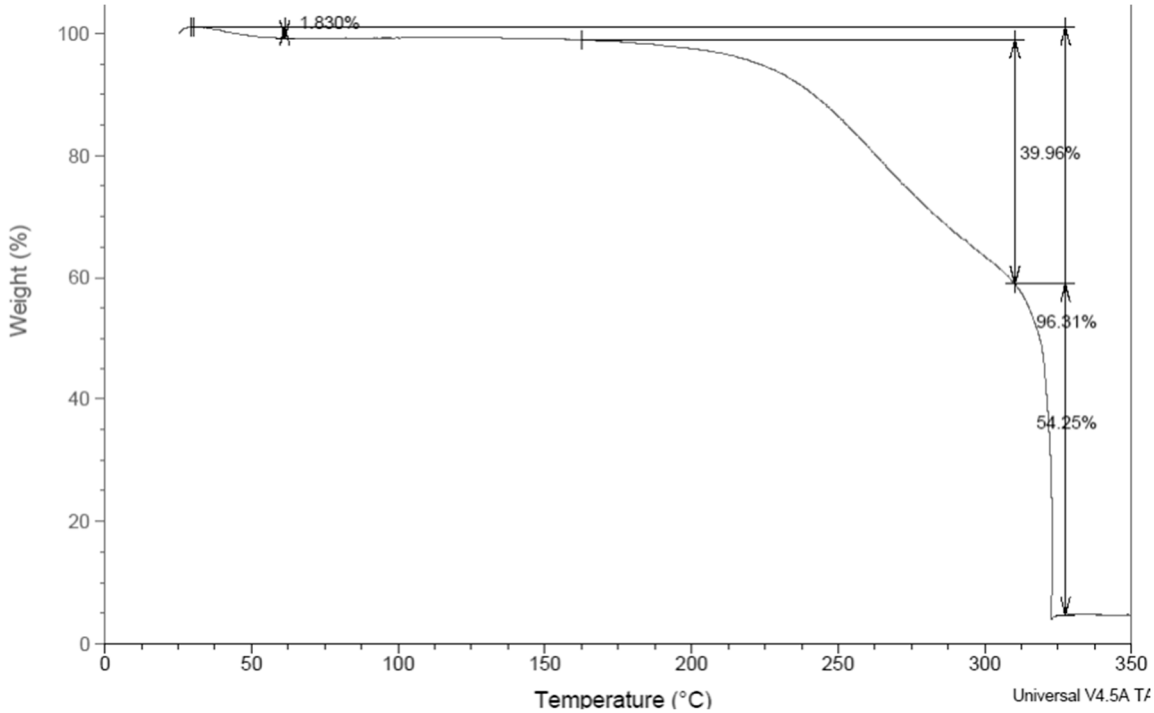


Figure S3. TGA of freeze dried CHI-GA-PdNPs 0.2mM cryogel in air.

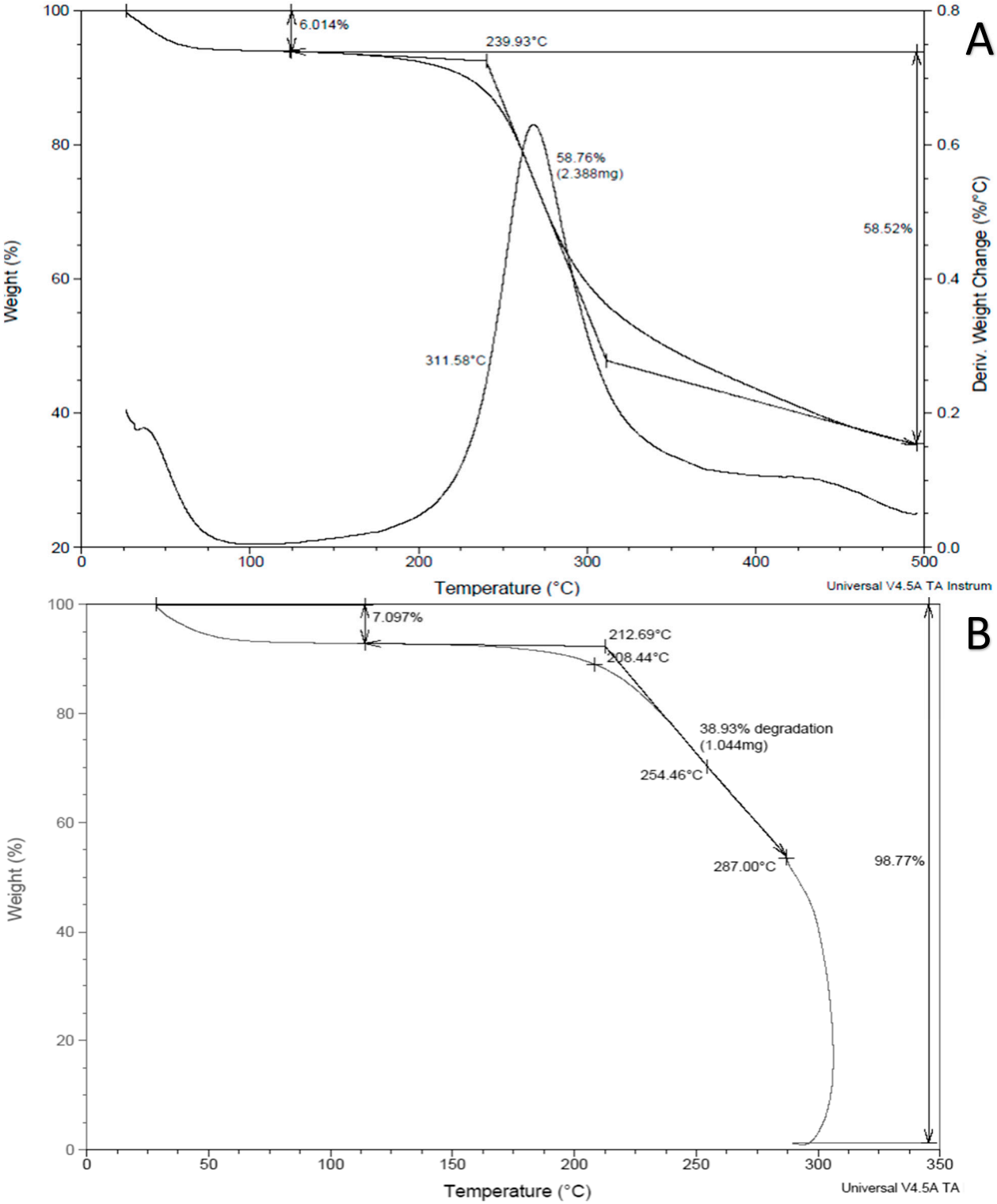


Figure S4. TGA of freeze dried: A) cryogel CHI-GA-PdNPs 4 mM in atmosphere of nitrogen and derivative gravimetric analysis. B) hydrogel CHI-GA-PdNPs 4 mM in air.

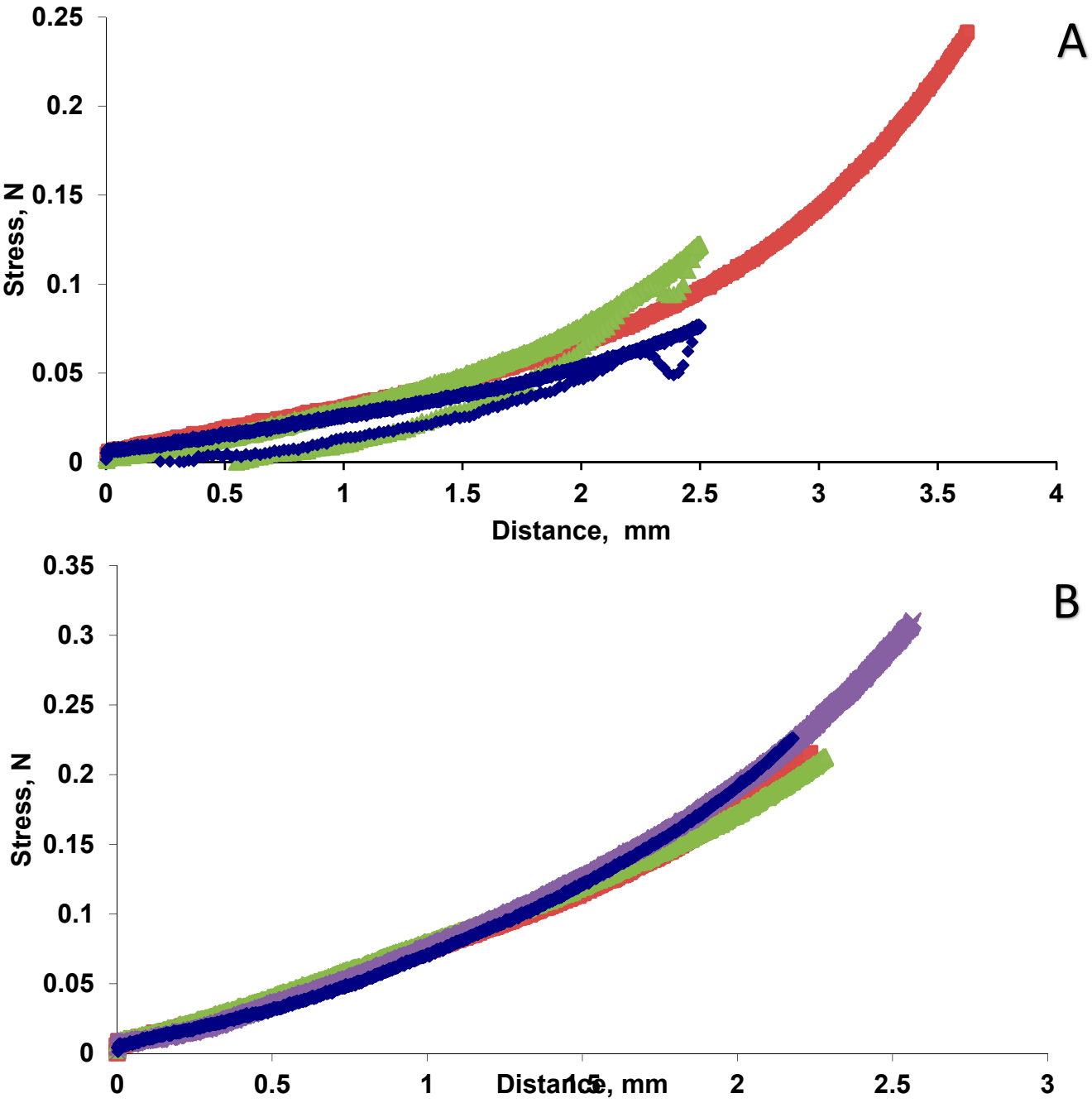
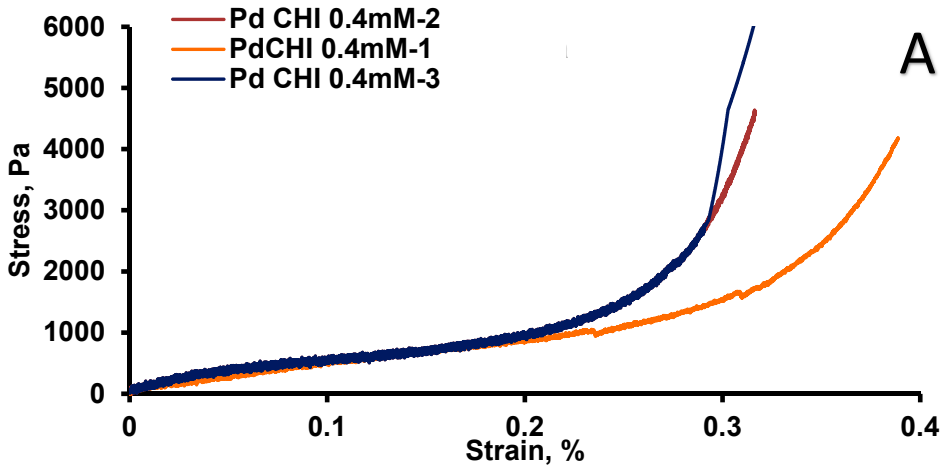


Figure S5. Compression test of ionic cryogels: A) freshly synthesized CHI-$[PdCl_4]^{2-}$ 0.8mM; B) CHI-$[PdCl_4]^{2-}$ 0.8mM swollen for 72h in 0.1M HAc.



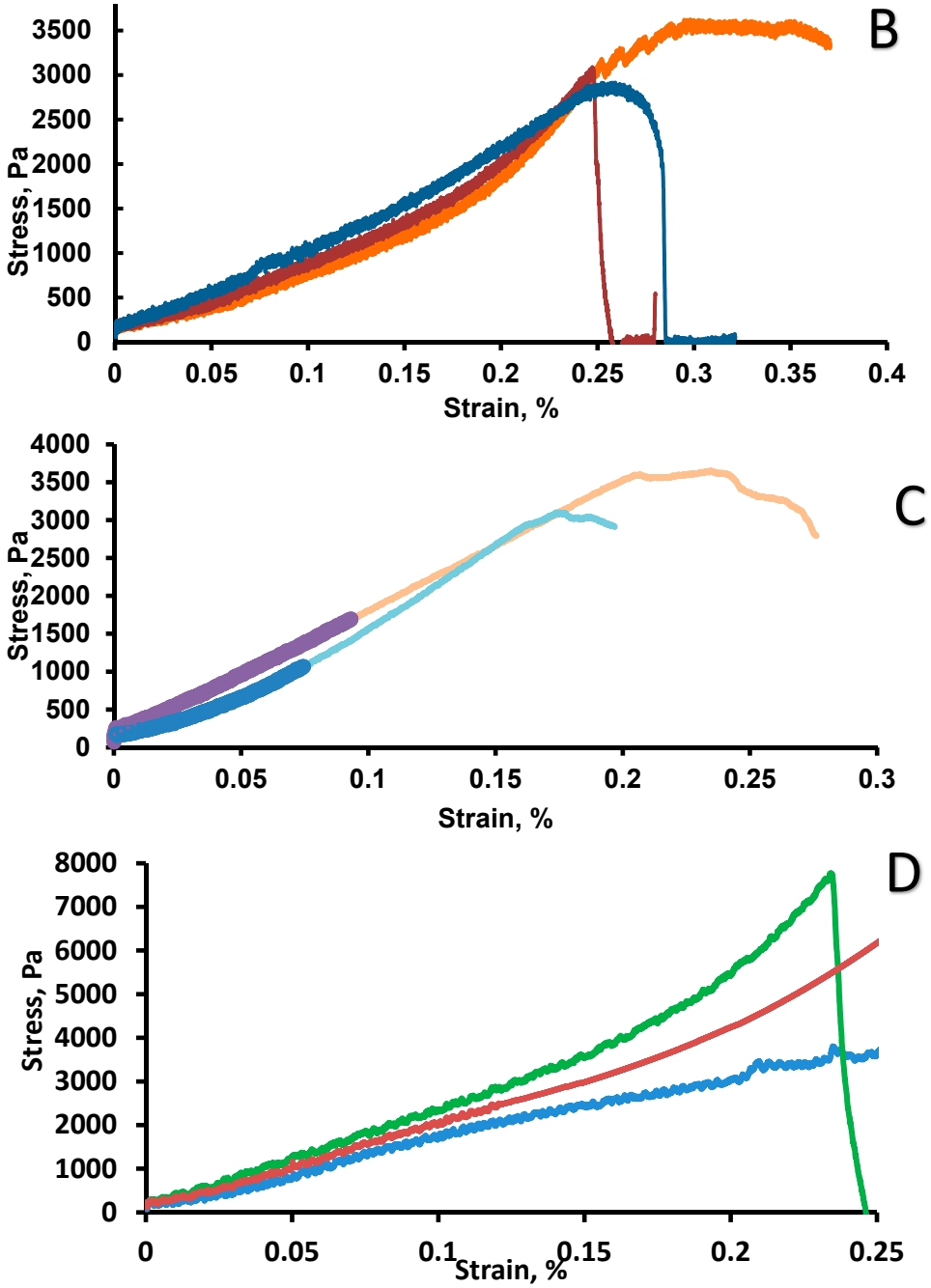


Figure S6 Rrepresentative stress–strain curves of ionic cryogels: A) freshly synthesized CHI-$[PdCl_4]^{2-}$ 0.4 mM; B) equilibrium-swollen ionic cryogels CHI-$[PdCl_4]^{-2}$ 0.4 mM in water; C) freshly synthesized CHI-$[PdCl_4]^{-2}$ 0.2 mM pH 4.7; D) freshly synthesized CHI-$[PdCl_4]^{2-}$ 0.6 mM.

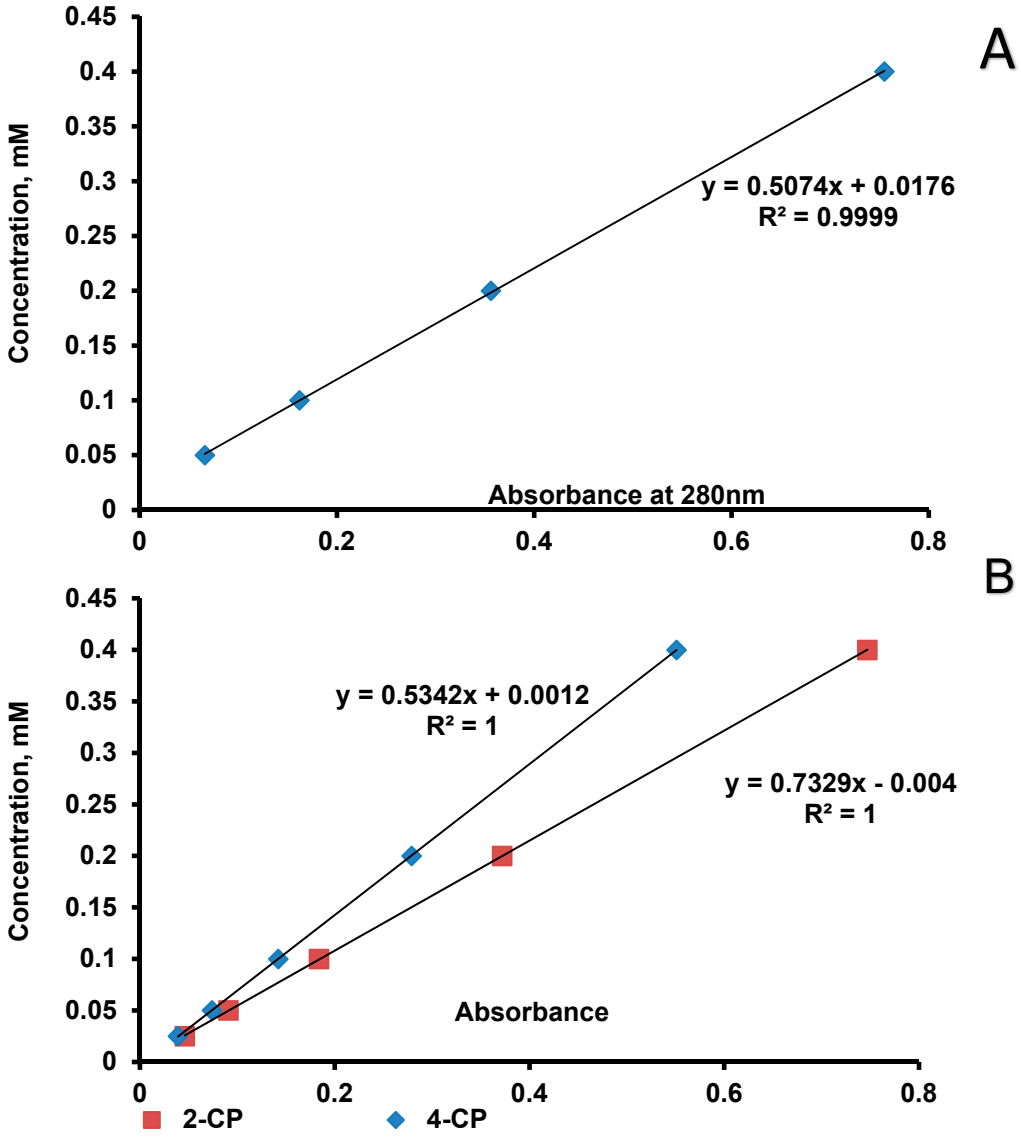


Figure S7 Calibration curves for chlorophenols using UV spectroscopy at 280nm: A) 2-CP in 20mM HCOOH at pH3; B) 4CP and 2CP in water.

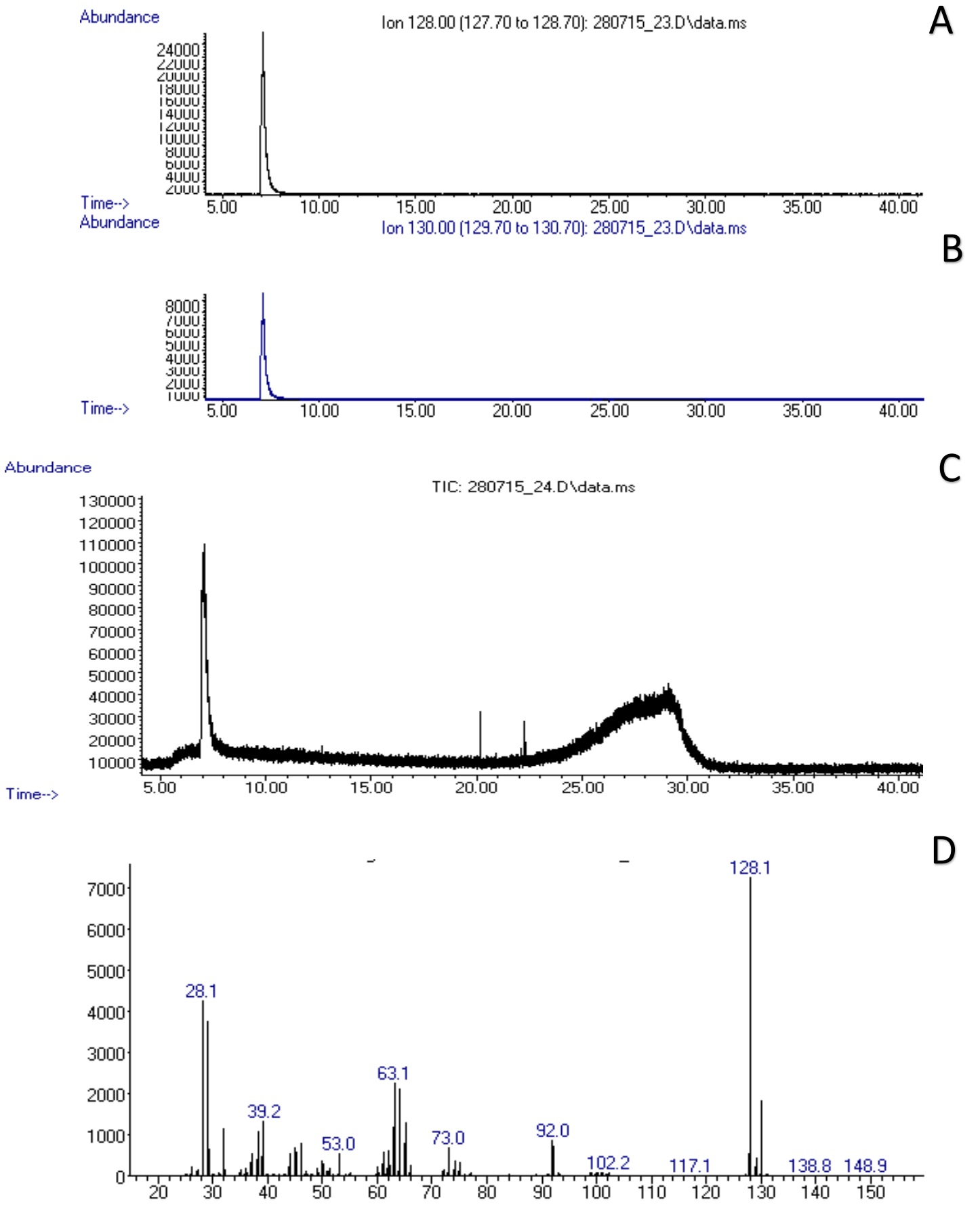


Figure S8 GC analysis of the initial 2CP solution. A and B) GC chromatogram 2CP standard in water. C) GC chromatogram of the reference solution (diluted 1/3 in water) containing 40 mM formic acid; D) GC-MS/MS analysis of the 2CP peak with retention time of 7min.

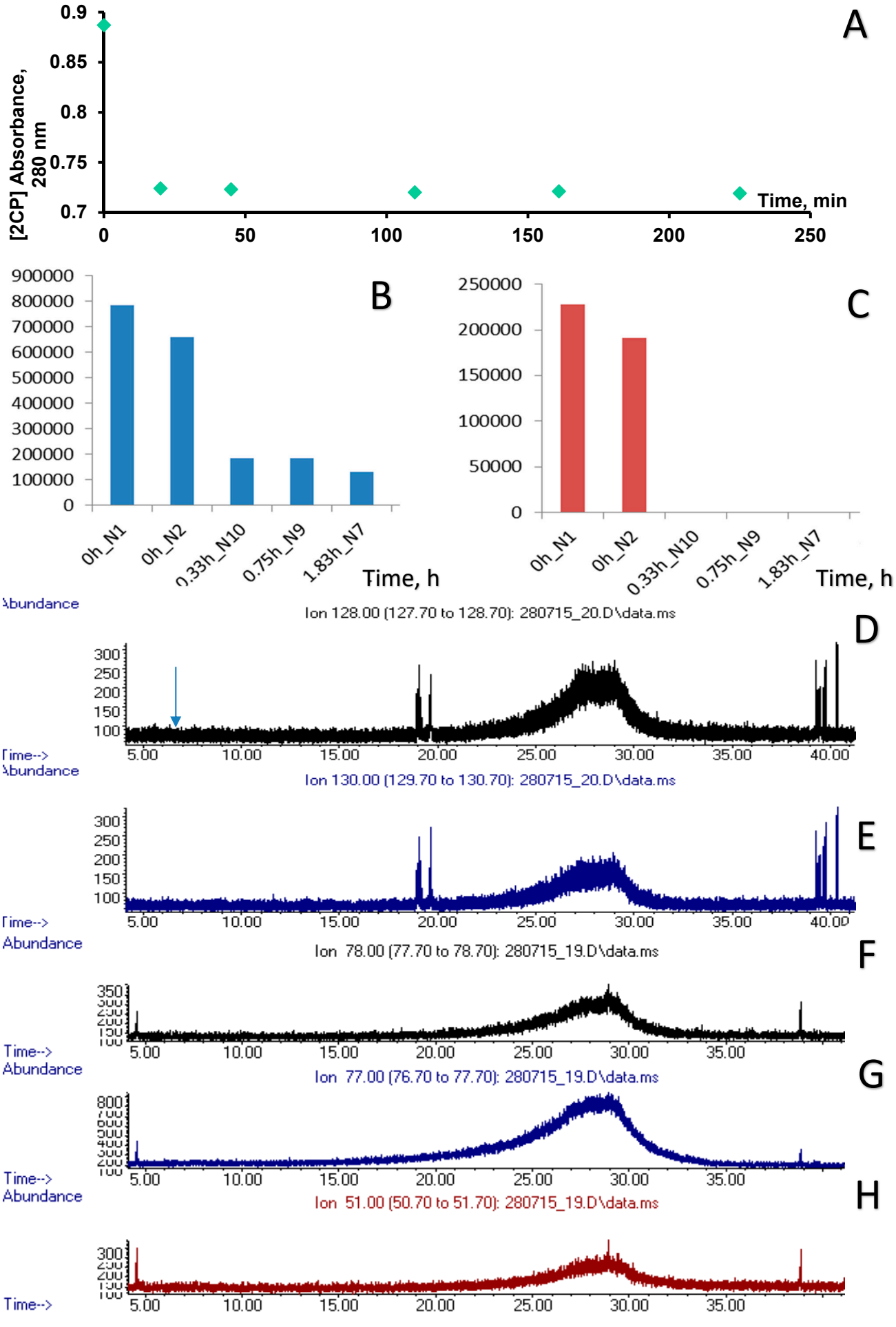

A
[2CP] Absorbance, 280 nm
0.9
0.85
0.8
0.75
0.7
0
50
100
150
200
250
Time, min
B
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
0h_N1
0h_N2
0.33h_N10
0.75h_N9
1.83h_N7
Time, h
C
250000
200000
150000
100000
50000
0
0h_N1
0h_N2
0.33h_N10
0.75h_N9
1.83h_N7
Time, h
Abundance
Ion 128.00 (127.70 to 128.70): 280715_20.D\data.ms
D
300
250
200
150
100
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
Time-->
Abundance
Ion 130.00 (129.70 to 130.70): 280715_20.D\data.ms
E
Time-->
Abundance
Ion 78.00 (77.70 to 78.70): 280715_19.D\data.ms
F
Time-->
Abundance
Ion 77.00 (76.70 to 77.70): 280715_19.D\data.ms
G
Time-->
Abundance
Ion 51.00 (50.70 to 51.70): 280715_19.D\data.ms
H
Time-->

Figure S9. Kinetic of 2CP reduction in presence of CHI-GA-PdNPs 0.4 mM (21ug PdNPs) and 40mM formic acid using: A) UV monitoring of the reaction mixture; B) using GC-MS monitoring surface area of the peak for phenol; C) surface area of the peak for 2CP using GC-MS monitoring 2CP LOD estimated 10 ppb; D) and E) 0.75h; C), D and E) 1.83 h at different scanning mode.

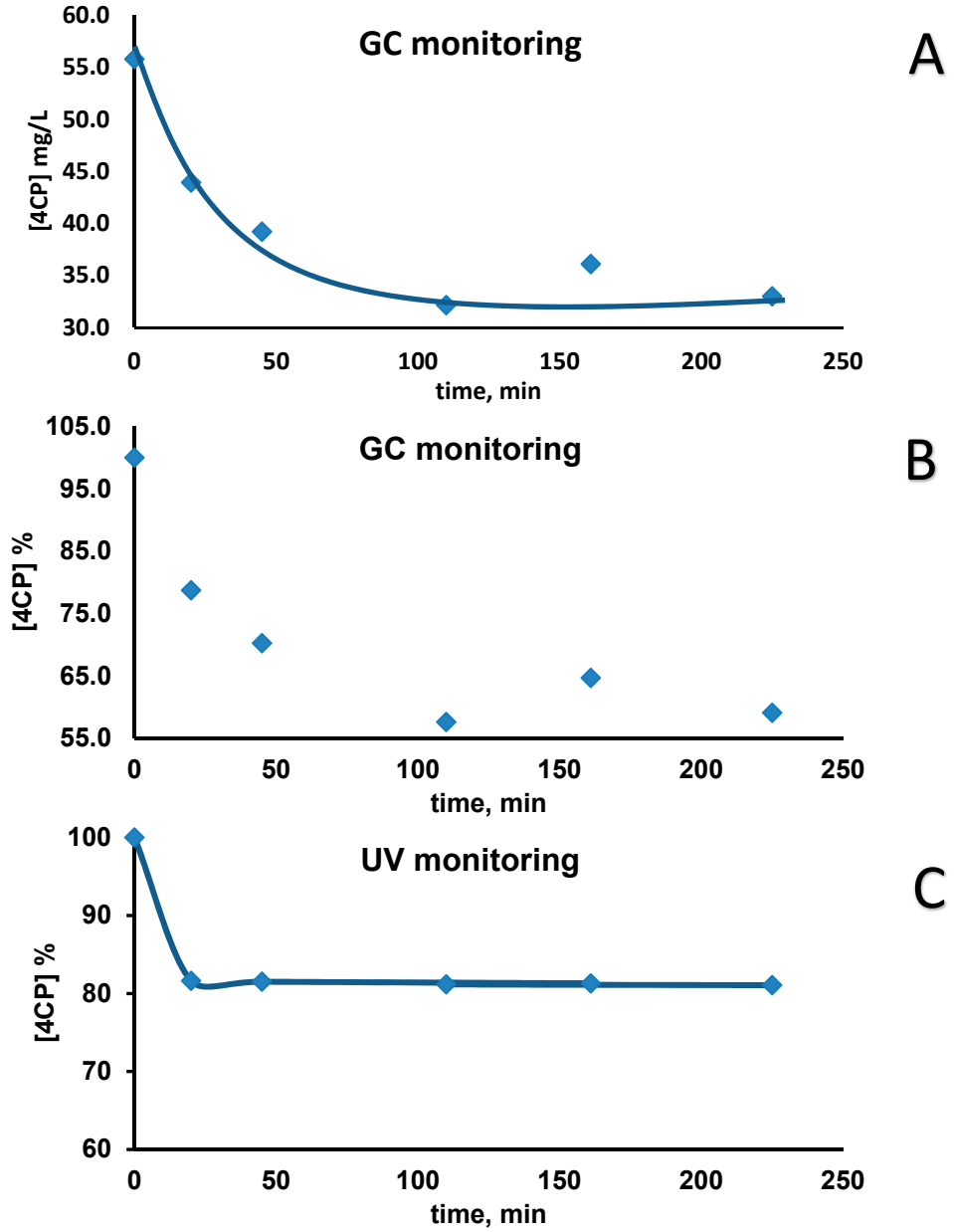


Figure S10. Kinetic curve of 4-CP decomposition for 1st cycle catalysed by CHI-GA-PdNPs 0.2 mM (5ug PdNPs): A) concentration GC-MS vs time; B) GC-MS monitoring of concentration; C) UV monitoring at 280 nm.

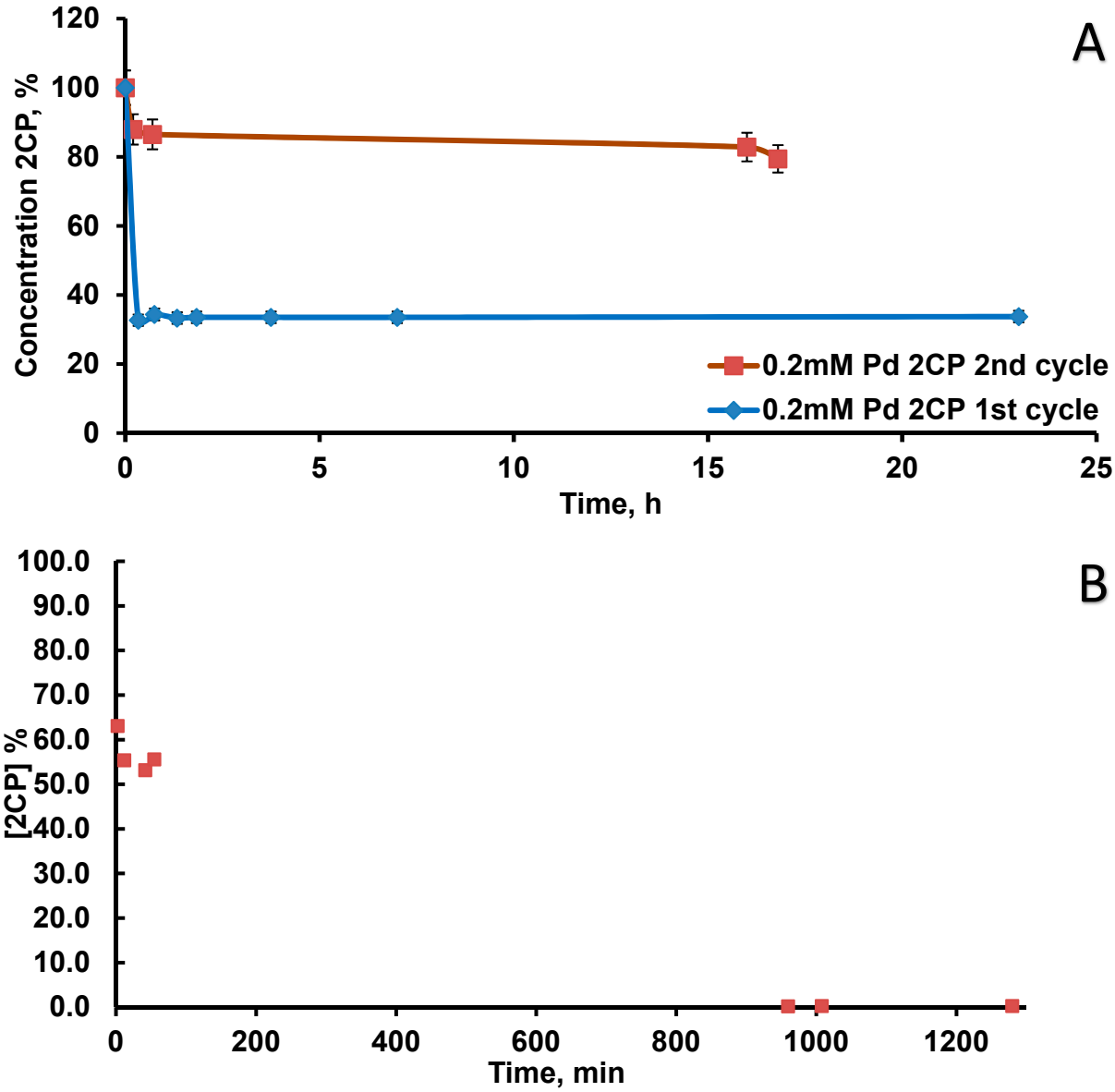
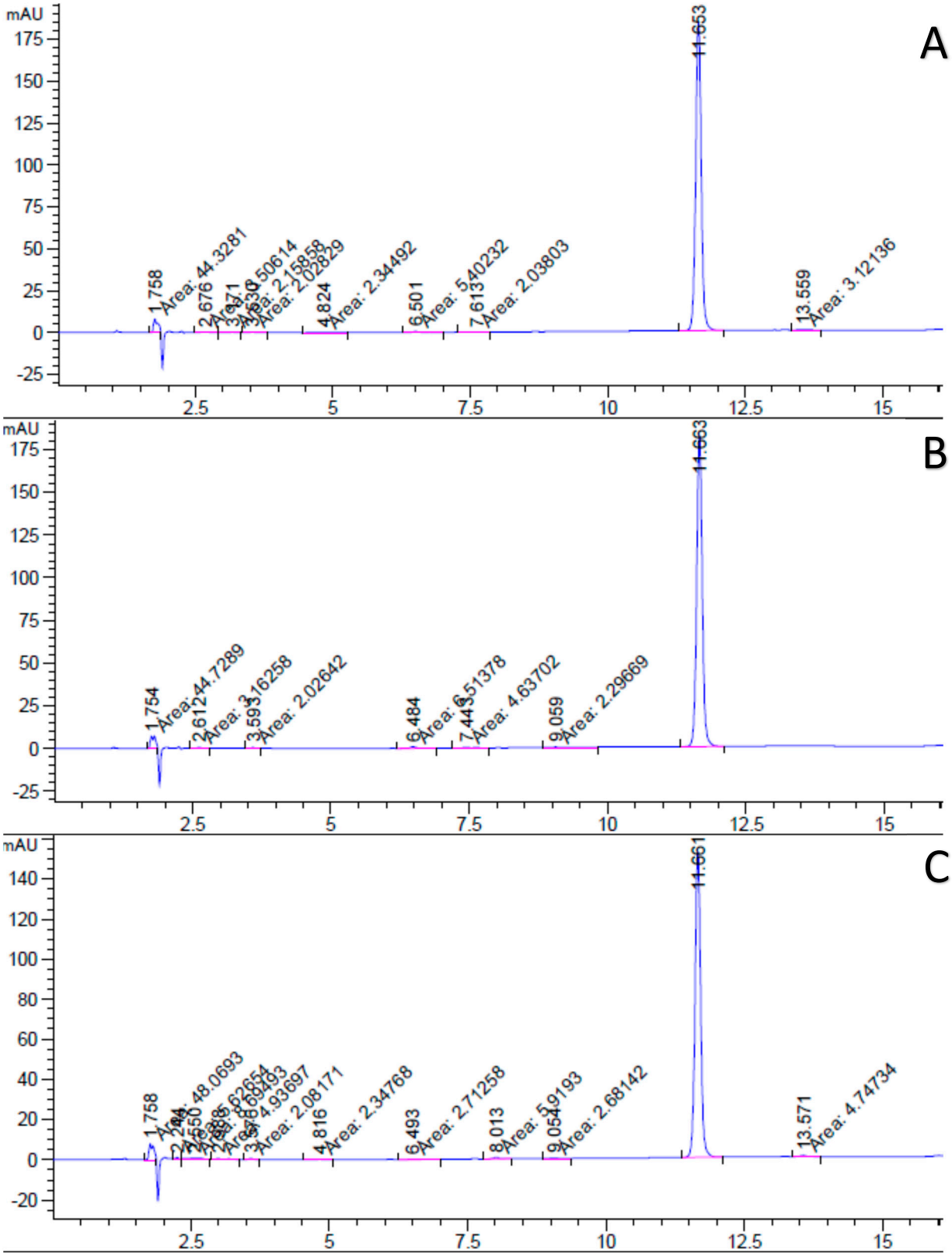


Figure S11 Kinetic curves of 2-chlorophenol decomposition in presence of cryogels CHI-GA-PdNPs 0.2 mM (5ug PdNPs). B) GC-MS analysis monitoring 2CP; additional degassing performed at 960 min.


A
mAU
1.758
Area: 44.3281
2.676
3.471
3.630
Area: 2.02829
4.824
Area: 2.34492
6.501
Area: 5.40232
7.613
Area: 2.03803
11.653
13.559
Area: 3.12136
B
mAU
1.754
Area: 44.7289
2.612
Area: 3.16258
3.593
Area: 2.02642
6.484
Area: 4.63702
9.059
Area: 2.29669
11.663
C
mAU
1.758
Area: 48.0693
4.816
Area: 2.34768
6.493
Area: 2.71258
8.013
Area: 2.68142
11.661
13.571
Area: 4.74734

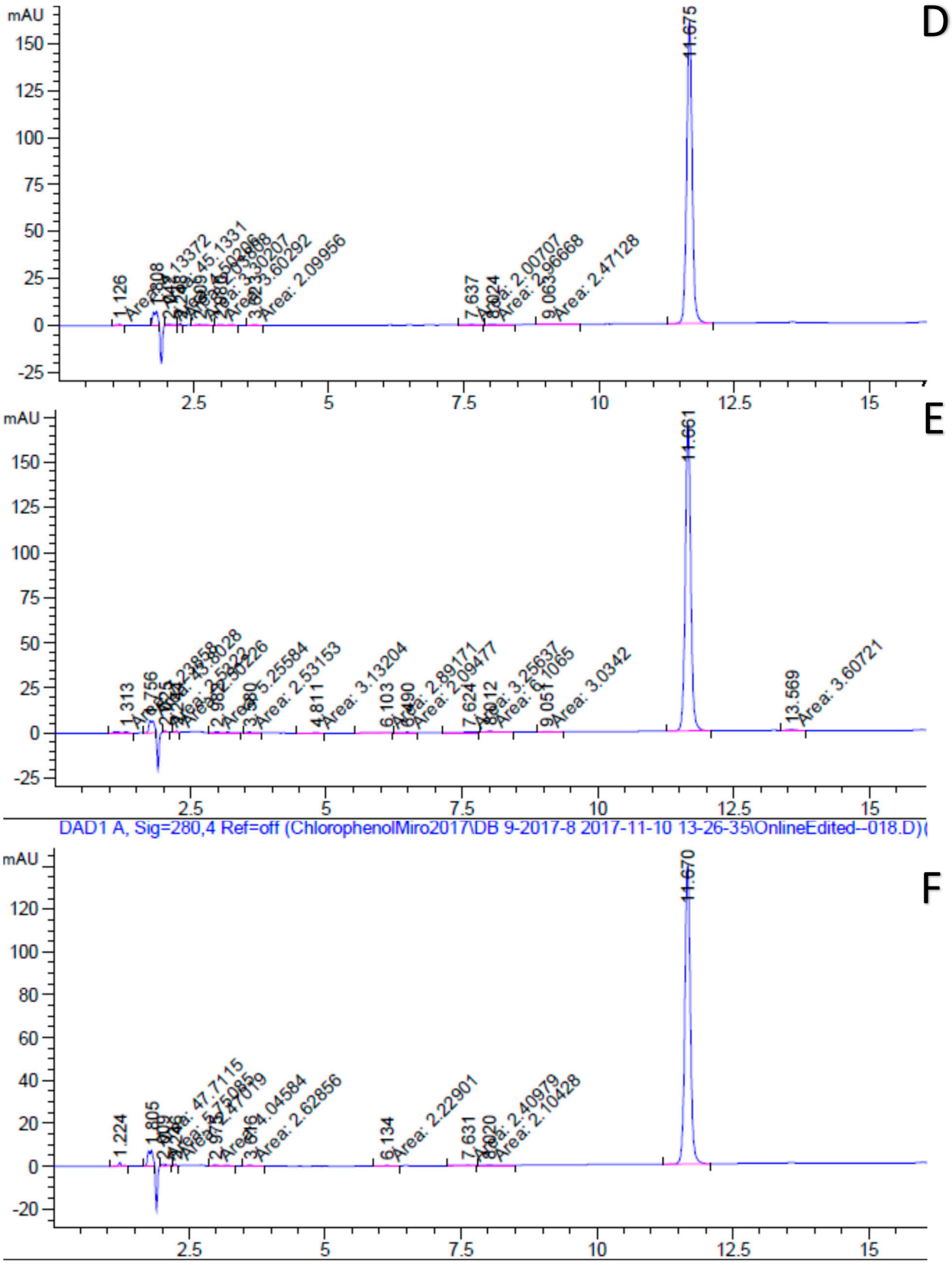
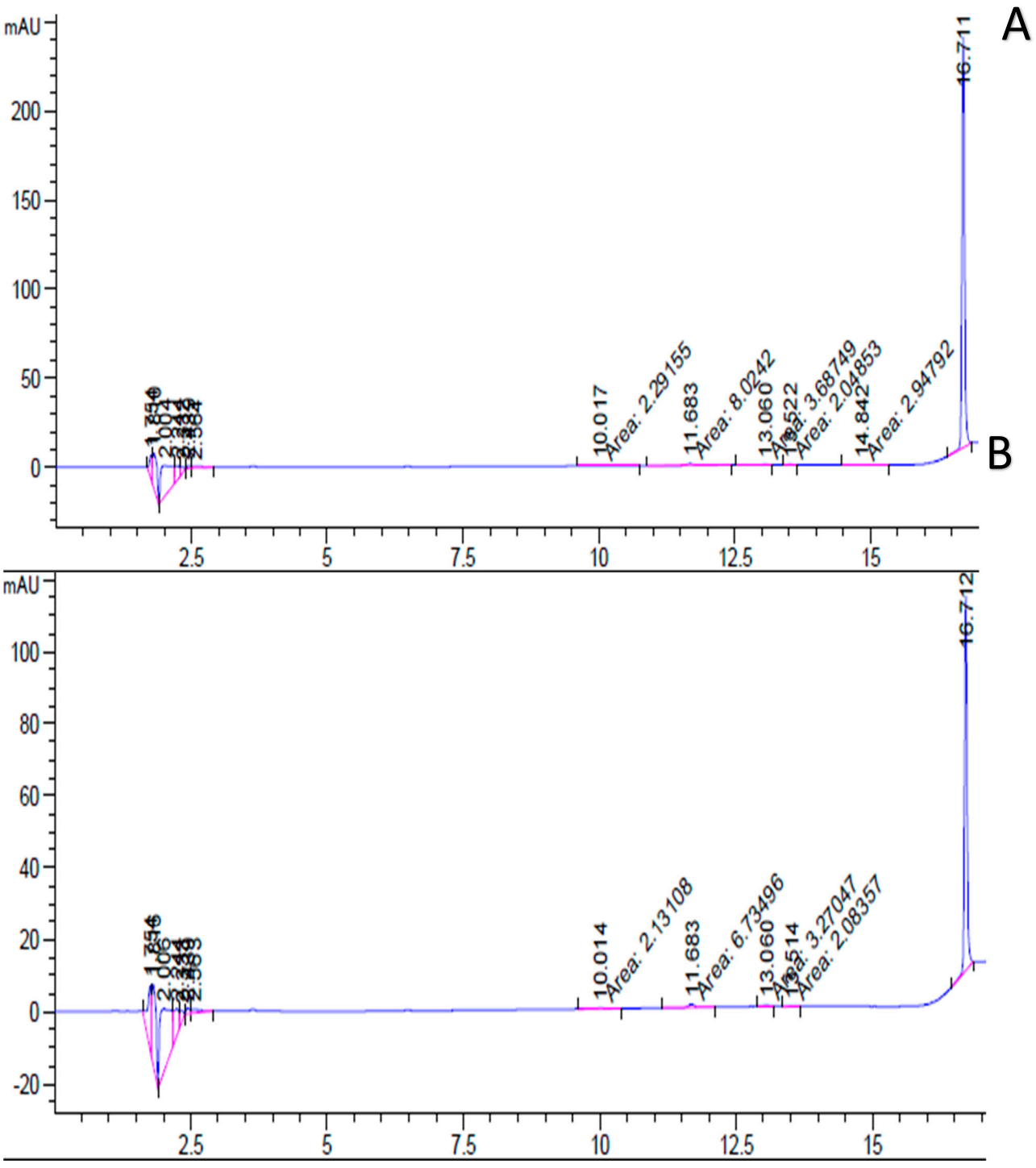


Figure S12 HPLC chromatograms of the reaction mixtures of 2-chlorophenol (2-CP) 50 ppm and 20 mM formic acid at pH 3 and CHI-GA-PdNPs (reduced by $NaBH_4$) : A) 1h ; B)1h (0.1 mM Ag^+); C) 28 h ; D) 28 h (0.1mM Ag^+); E) 96h, f) 96 h (0.1 mM Ag^+).


A
mAU
200
150
100
50
0
16.711
10.017
Area: 2.29155
11.683
Area: 8.0242
13.060
Area: 3.68749
14.842
Area: 2.04853
Area: 2.94792
2.5
5
7.5
10
12.5
15
B
mAU
100
80
60
40
20
0
-20
16.712
10.014
Area: 2.13108
11.683
Area: 6.73496
13.060
Area: 3.27047
Area: 2.08357
2.5
5
7.5
10
12.5
15

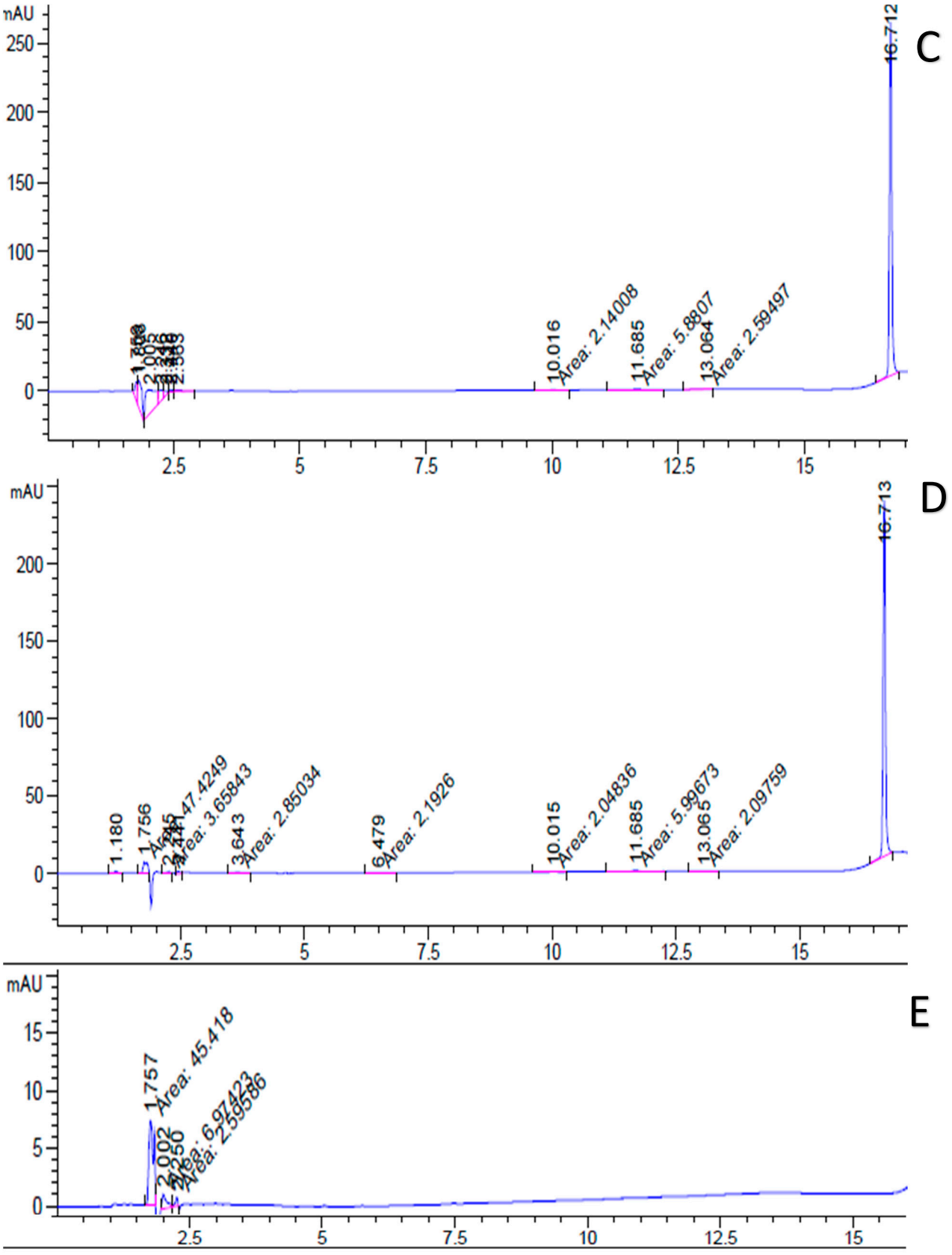


Figure S13. HPLC chromatograms of the reaction mixtures of 2,4-dichlorophenol and 20 mM formic acid at pH3 and CHI-GA-PtNPs 1mM (reduced by $NaBH_4$): A) 10 min; B) 30 min; C) 1 h; D) 24 h; E) control CHI-GA-PdNPs leaking of other compounds from the scaffold.

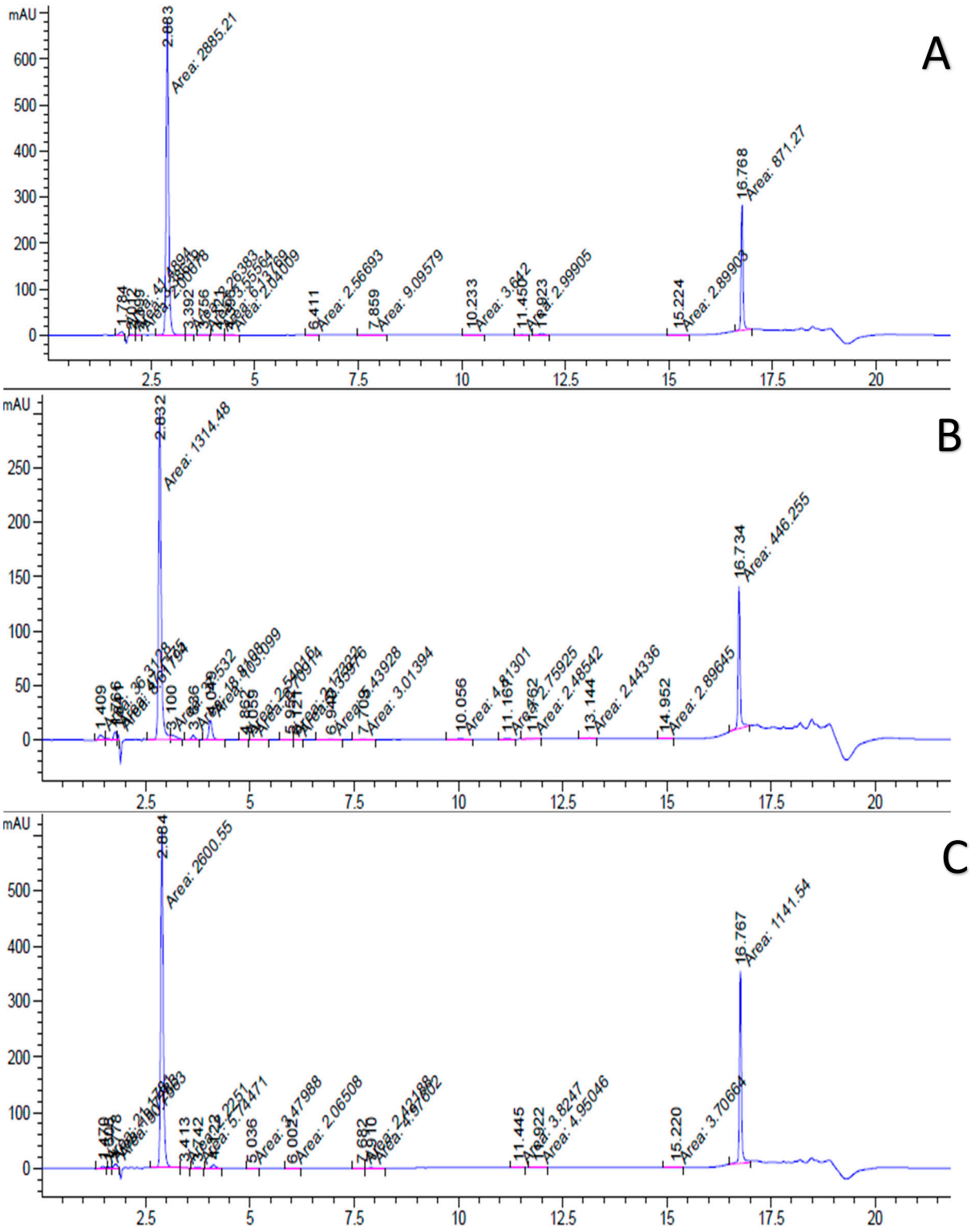


Figure S14 HPLC chromatograms of the reaction mixtures of 2,4-dichlorophenol and formic acid at pH 6.2 and CHI-GA-PdNPs (reduced by NaBH4): A) 15 days, RT, (pH3, $AgNO_3$); B) 99.5h, RT, pH 6.2; C) 141h, RT, pH 6.2. 50mg/L of hydroquinone (retention time 2.88 min) was used as internal standard to eliminate effect of adsorption during sample preparation.

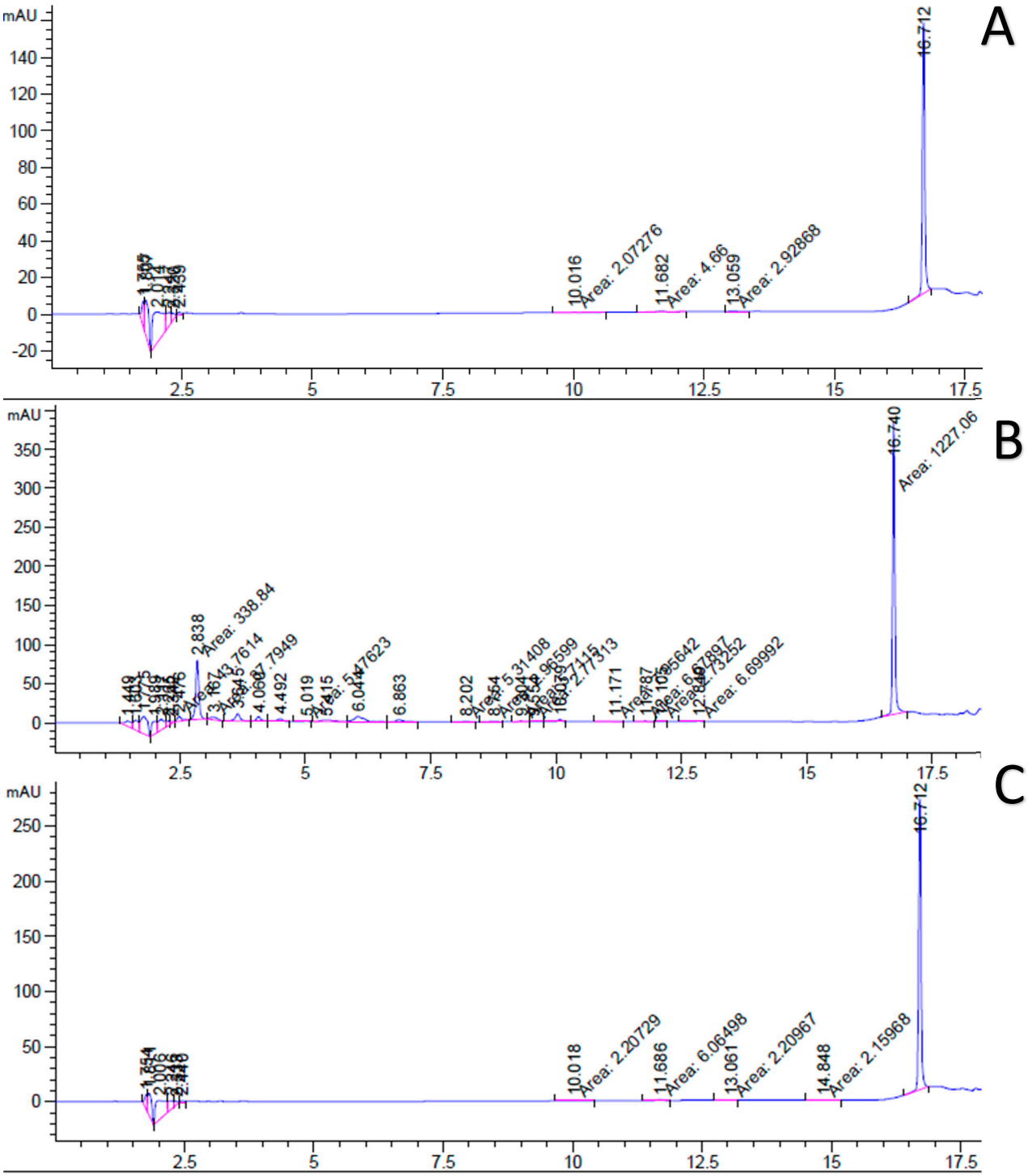


Figure S15 HPLC chromatograms of the reaction mixtures of 2,4-dichlorophenol and formic acid 20 mM: A) 24h, RT; B) 27h, RT, pH 6.2; C) 96h , RT, pH 3, 0.1mM $AgNO_3$; Retention time (min) for compounds were identified as phenol (5.58-6.6), p-hydroxybenzoic acid (3.4), hydroquinone (1.97), protocatechuate (2.39), 2-chlorophenol (9.44), 4-chlorophenol (10.75).