Electronic Supplementary Information

From Ag_2S to luminescent Ag-In-S nanocrystals *via* ultrasonic method – in situ synthesis study in an NMR tube

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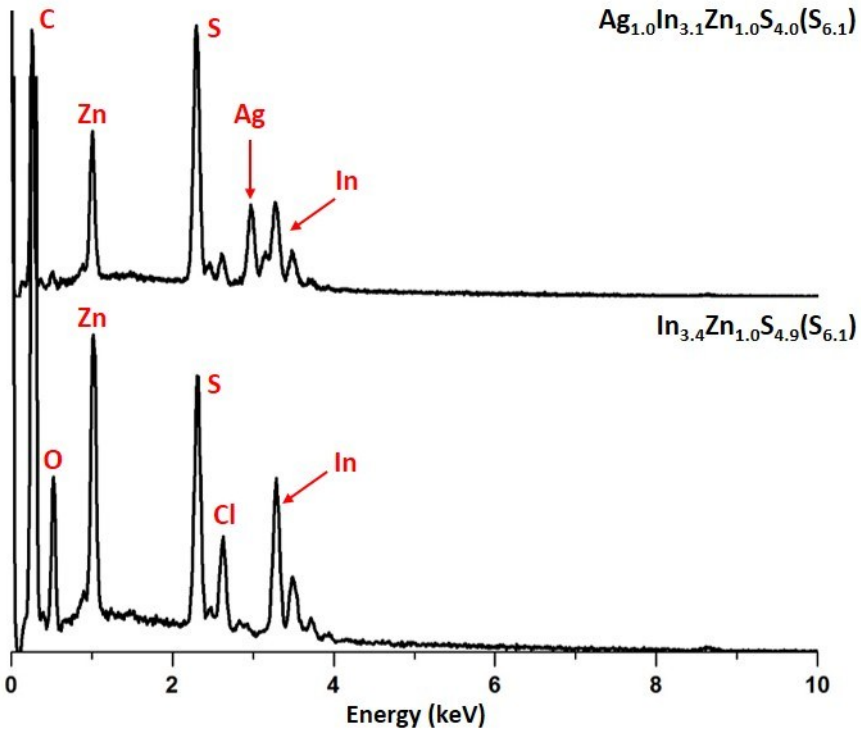


Fig. S1 Energy-dispersive spectra of nanocrystals obtained from reaction mixtures with $AgNO_3$ (**$Ag_{1.0}In_{3.1}Zn_{1.0}S_{4.0}(S_{6.1})$**) and without $AgNO_3$ (**$In_{3.4}Zn_{1.0}S_{4.9}(S_{6.1})$**).

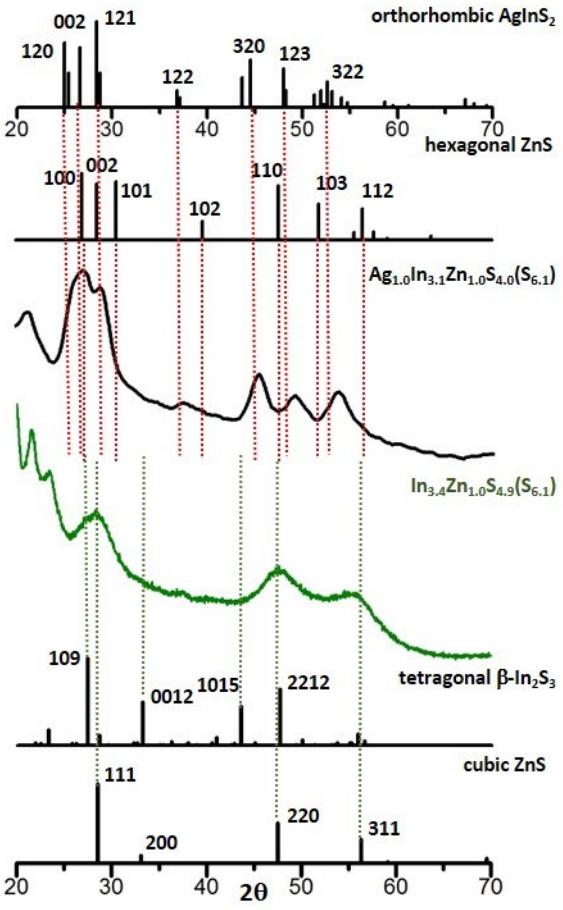


Fig. S2 X-ray powder diffractograms of nanocrystals obtained from reaction mixtures with $AgNO_3$ (**$Ag_{1.0}In_{3.1}Zn_{1.0}S_{4.0}(S_{6.1})$**) and without $AgNO_3$ (**$In_{3.4}Zn_{1.0}S_{4.9}(S_{6.1})$**), for comparison purposes XRD patterns of the orthorhombic $AgInS_2$ (JCPDS 00-025-1328), hexagonal ZnS (JCPDS 00-036-1450), tetragonal β-In_2S_3 (JCPDS 00-025-390) and cubic ZnS (JCPDS 00-005-0566).

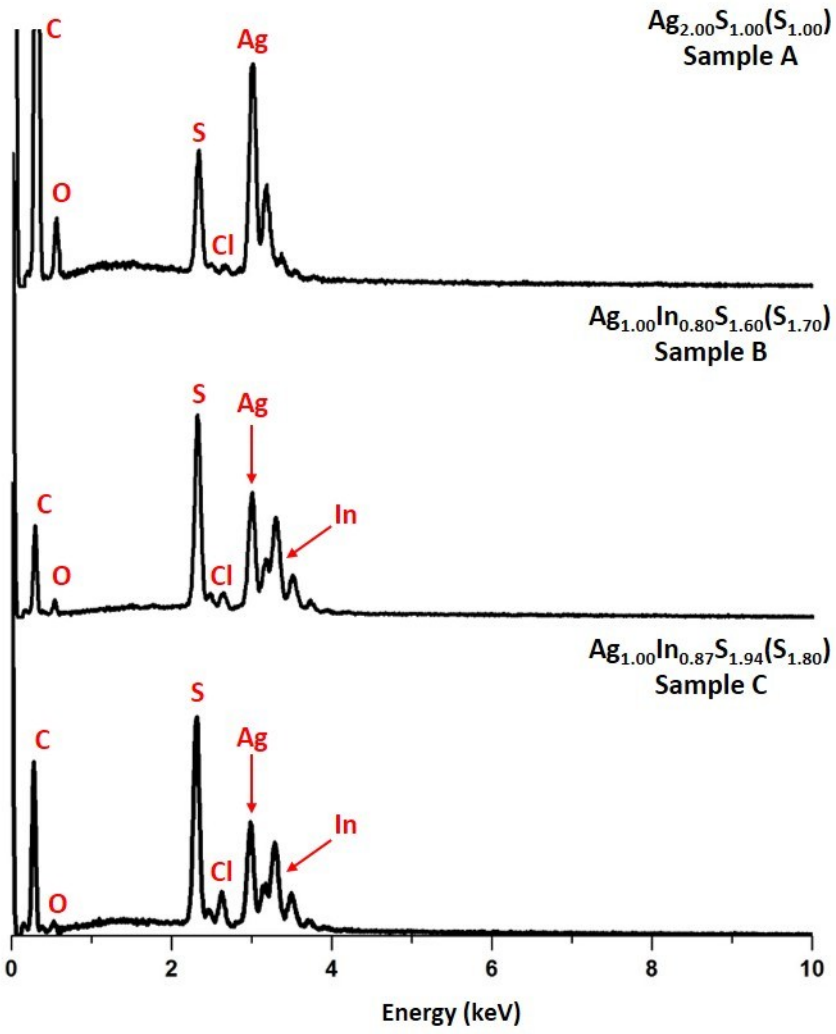


Fig. S3 Energy-dispersive spectra of $\mathbf{Ag_{2.00}S_{1.00}(S_{1.00})}$ (**sample A**), $\mathbf{Ag_{1.00}In_{0.80}S_{1.60}(S_{1.70})}$ (**sample B**) and $\mathbf{Ag_{1.00}In_{0.87}S_{1.94}(S_{1.80})}$ (**sample C**) nanocrystals.

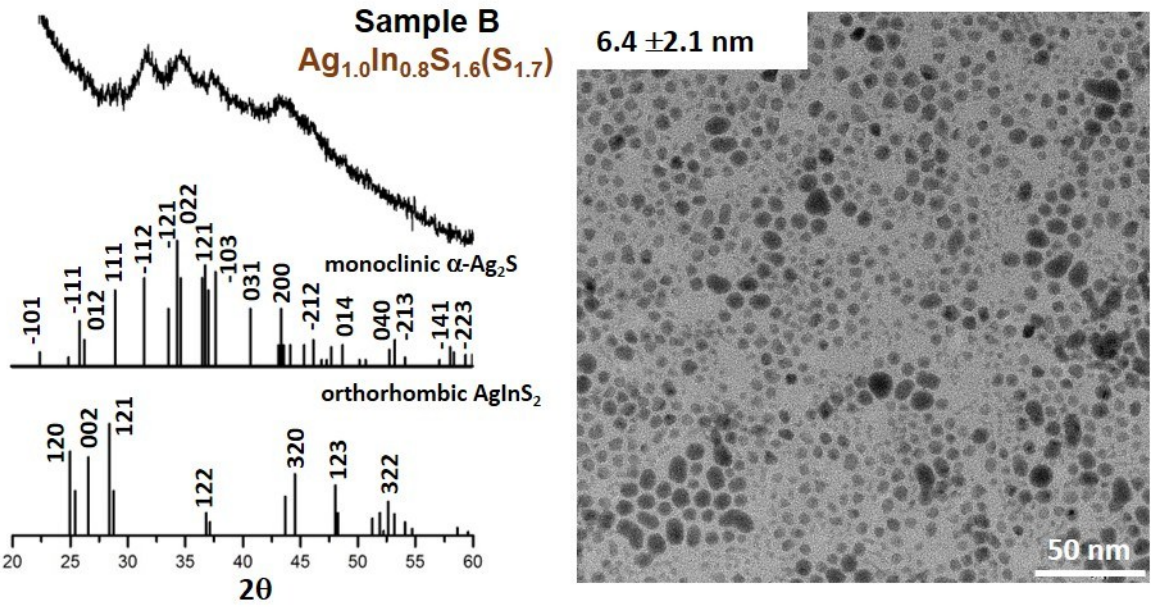
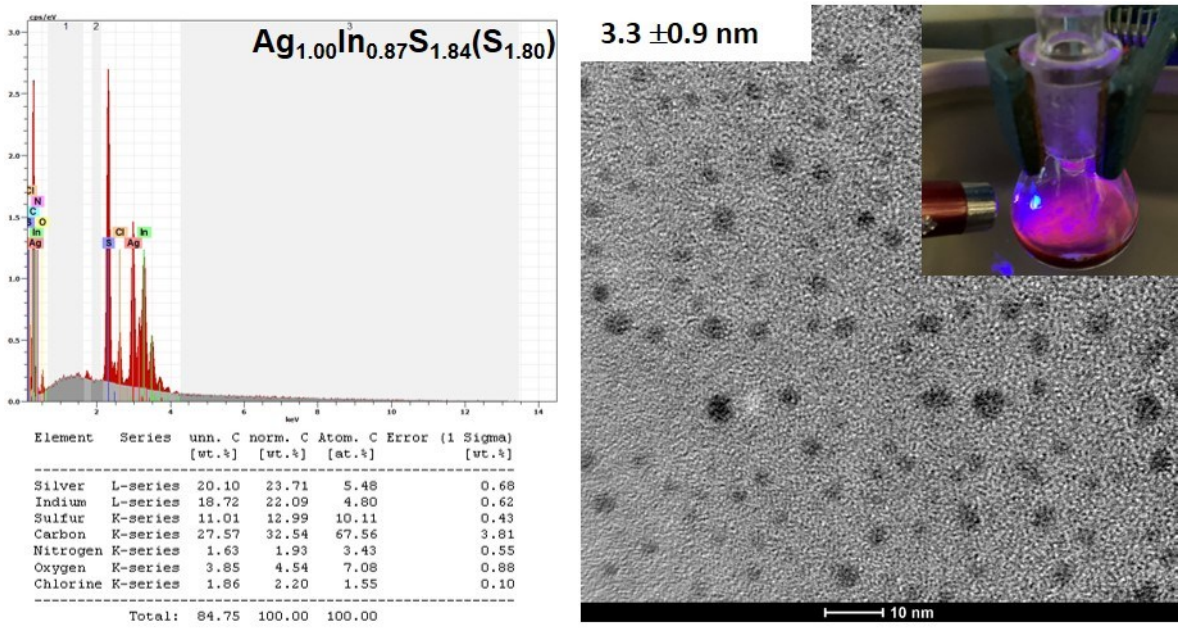


Fig. S4 X-ray powder diffractogram and TEM image of $\mathbf{Ag_{1.0}In_{0.8}S_{1.6}(S_{1.7})}$ (**sample B**) nanocrystals.



Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Silver	L-series	20.10	23.71	5.48	0.68
Indium	L-series	18.72	22.09	4.80	0.62
Sulfur	K-series	11.01	12.99	10.11	0.43
Carbon	K-series	27.57	32.54	67.56	3.81
Nitrogen	K-series	1.63	1.93	3.43	0.55
Oxygen	K-series	3.85	4.54	7.08	0.88
Chlorine	K-series	1.86	2.20	1.55	0.10
Total:		84.75	100.00	100.00	

Fig. S5 Energy-dispersive spectra and TEM image of $\mathbf{Ag_{1.00}In_{0.87}S_{1.84}(S_{1.80})}$ nanocrystals (d = 3.3 ±0.9 nm) obtained using hexane as solvent.

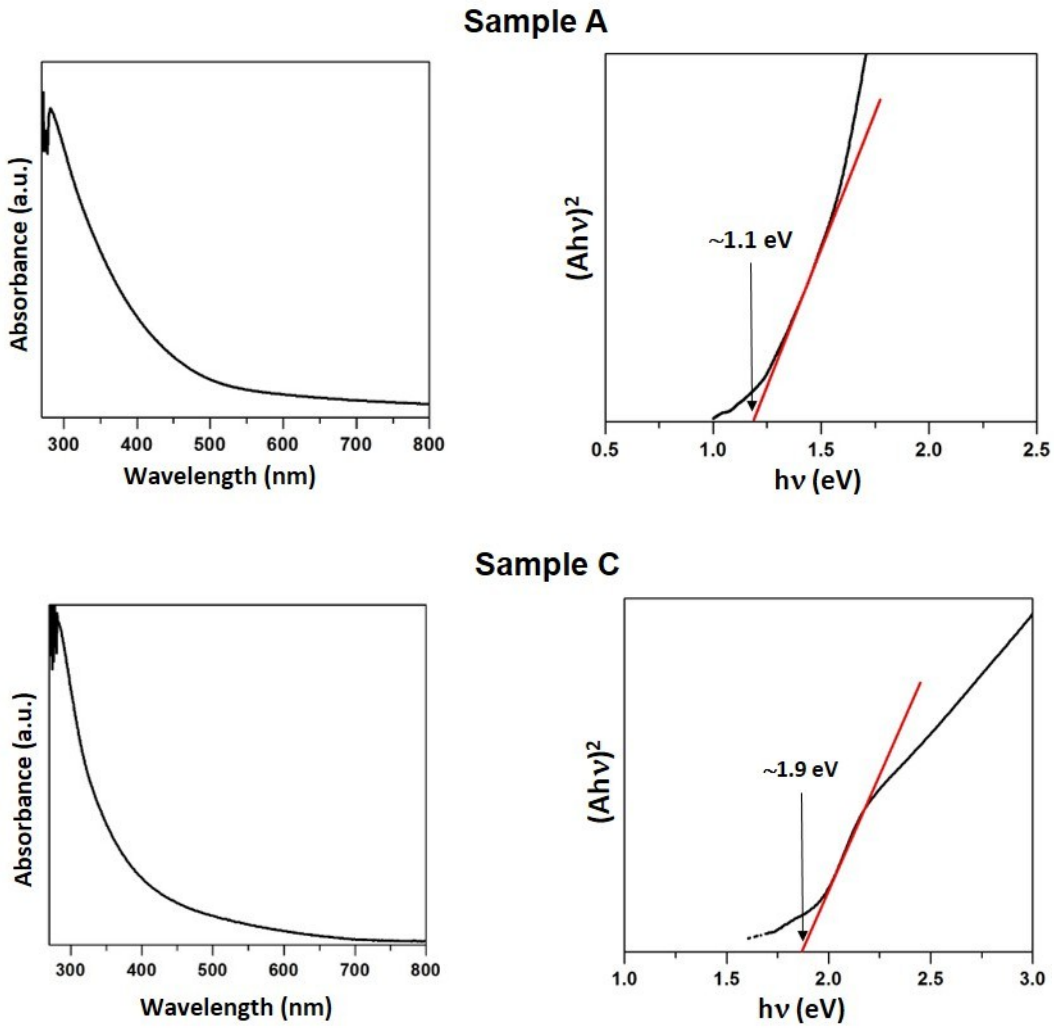


Fig. S6 Room temperature UV-vis-NIR spectra of toluene dispersion of **Ag_2S** (**sample A**) and **$Ag_{1.00}In_{0.87}S_{1.94}(S_{1.80})$** (**sample C**) nanocrystals and the corresponding $(Ah\nu)^2$ *vs* $h\nu$ curves (where A = absorbance, h = Planck's constant and ν = frequency).

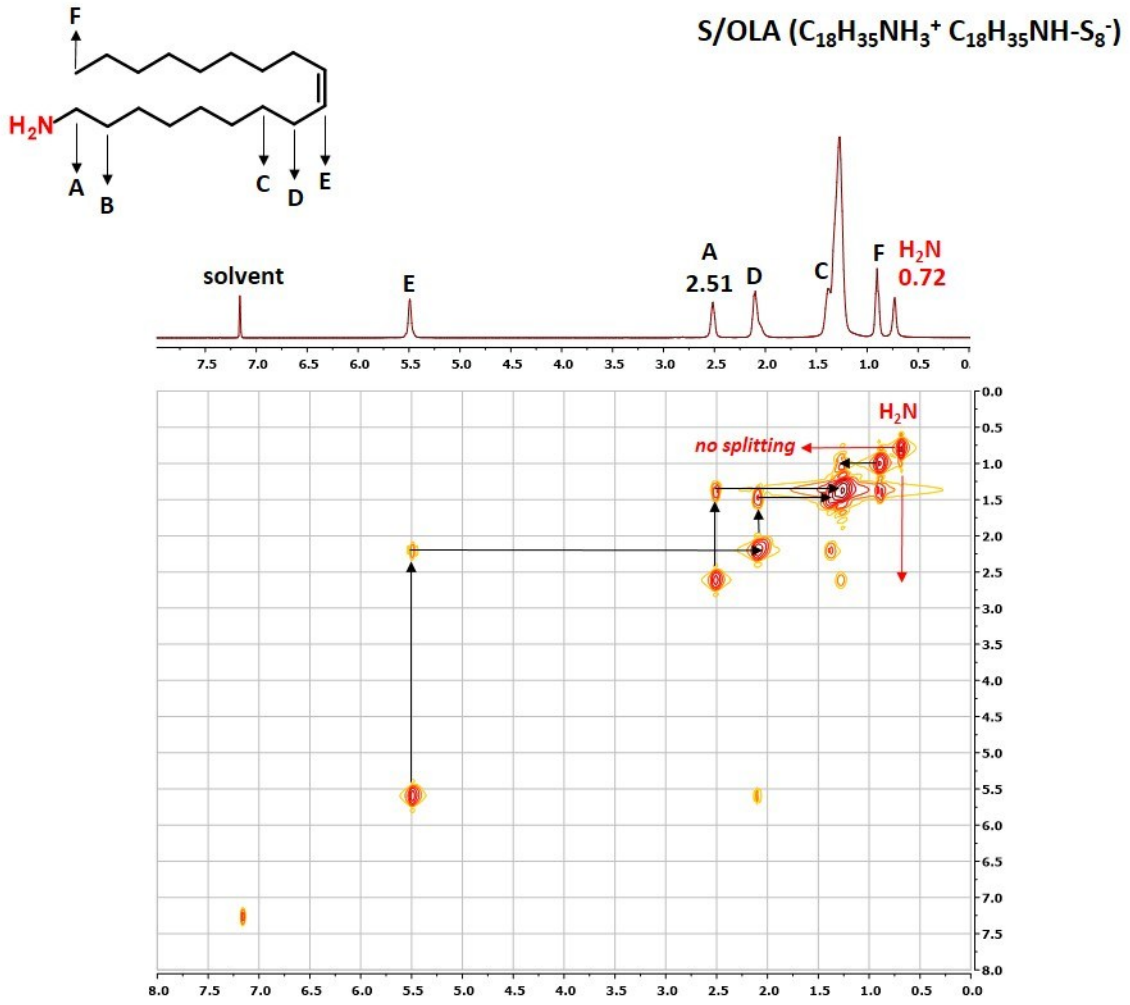


Fig. S7 ^{1}H and ^{1}H-^{1}H COSY NMR spectra of S/OLA ($C_{18}H_{35}NH_3^+C_{18}H_{35}NH$-$S_8^-$) in benzene-$d_6$ at 298 K.

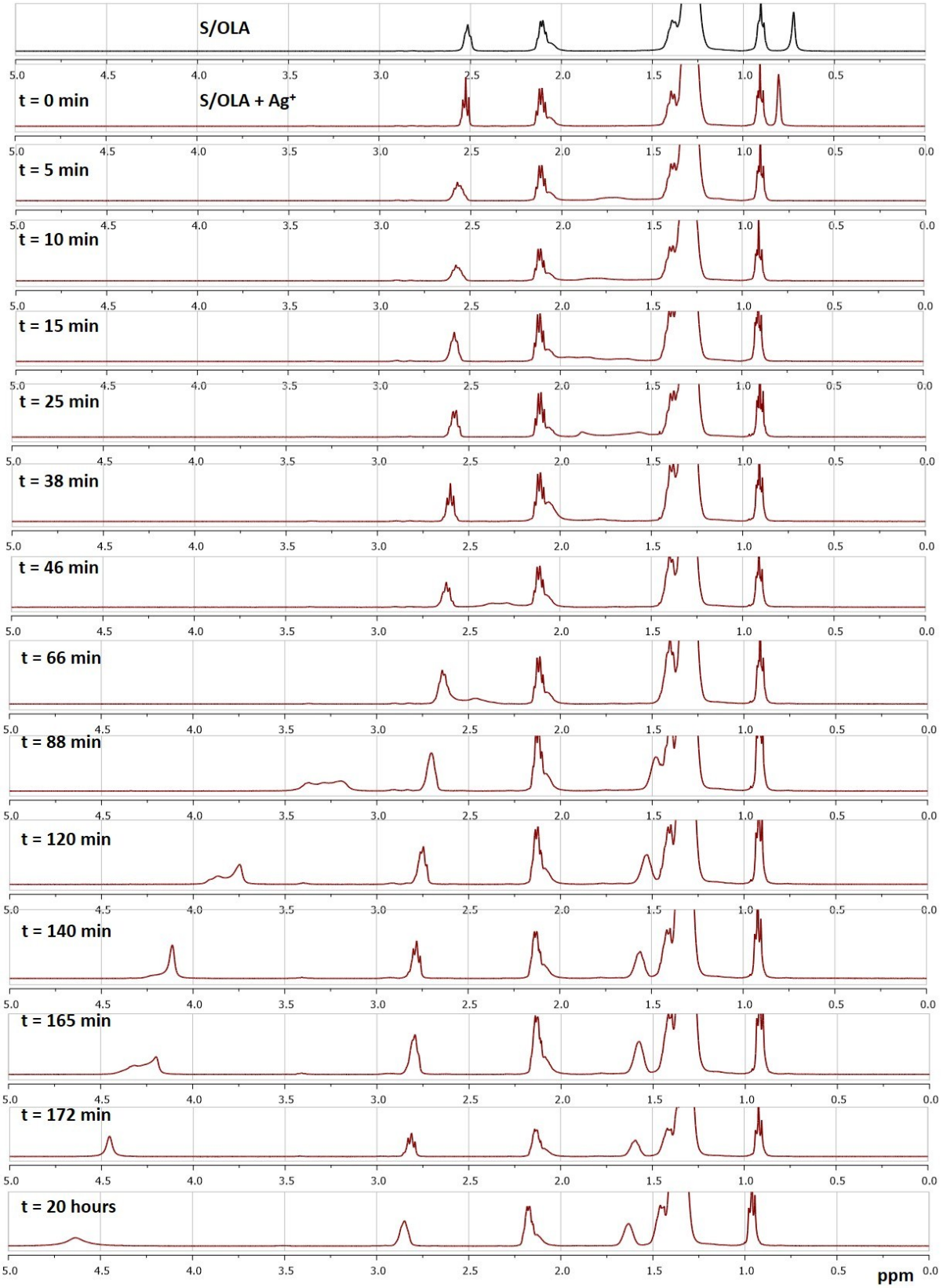


Fig. S8 ^{1}H NMR spectrum of S/OLA (a) and time evolution of the ^{1}H NMR spectrum of the reaction between S/OLA and $AgNO_3$ in benzene-d_6 at 298 K.

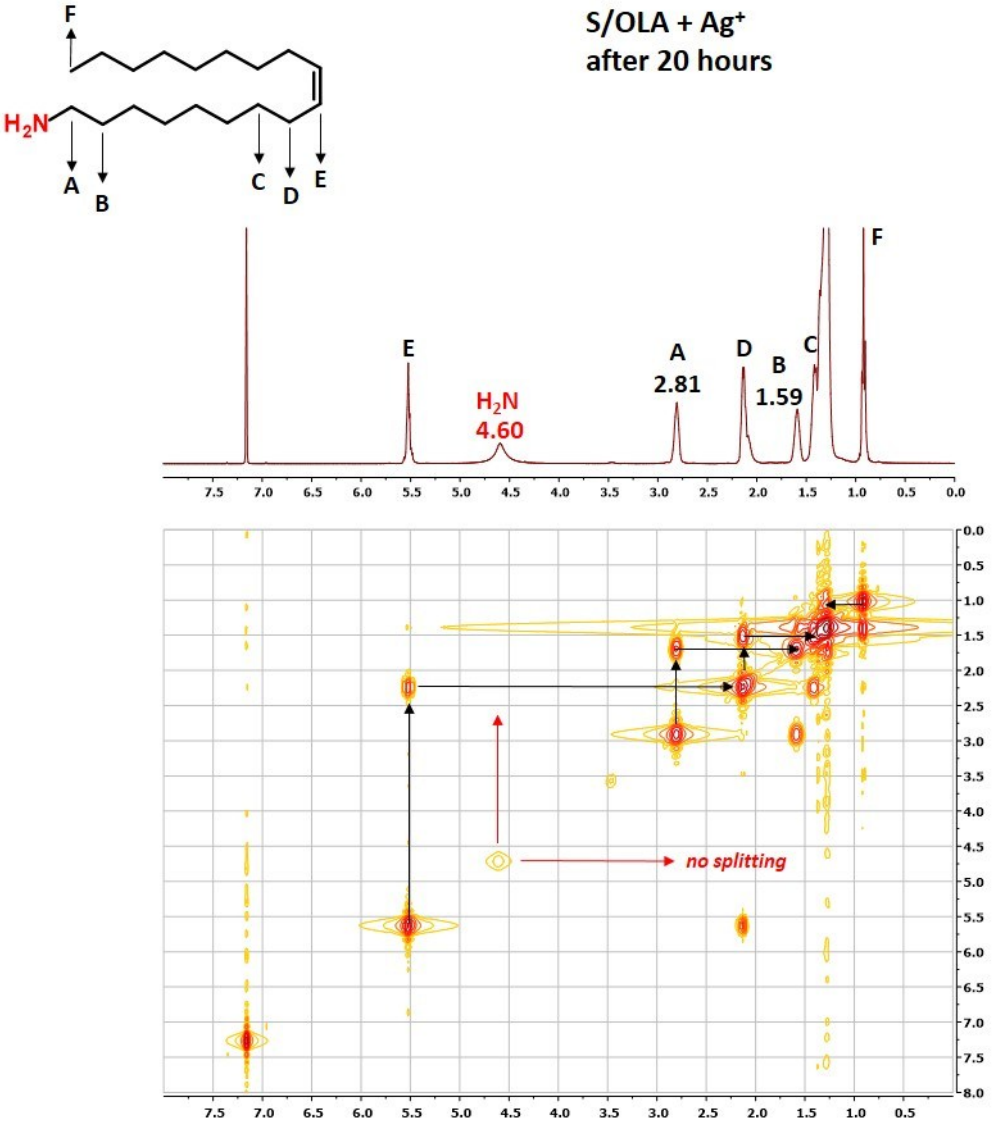


Fig. S9 ^{1}H and ^{1}H-^{1}H COSY NMR spectra of the reaction mixture (S/OLA + $AgNO_3$) after 20 hours in benzene-d_6 at 298 K.

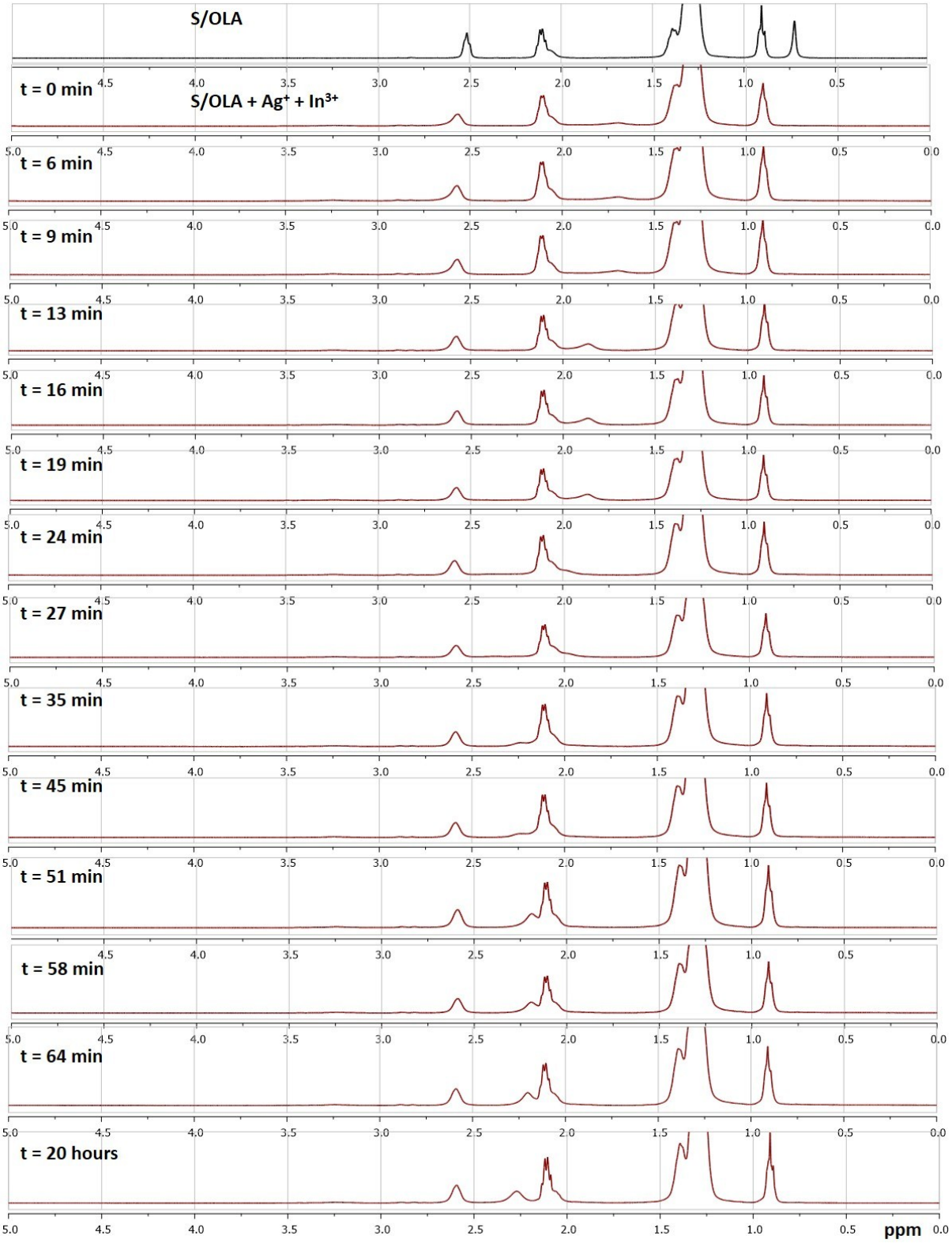


Fig. S10 ^{1}H NMR spectrum of S/OLA (a) and time evolution of the ^{1}H NMR spectrum of the reaction between S/OLA and $AgNO_3$ and $InCl_3$ in benzene-d_6 at 298 K.

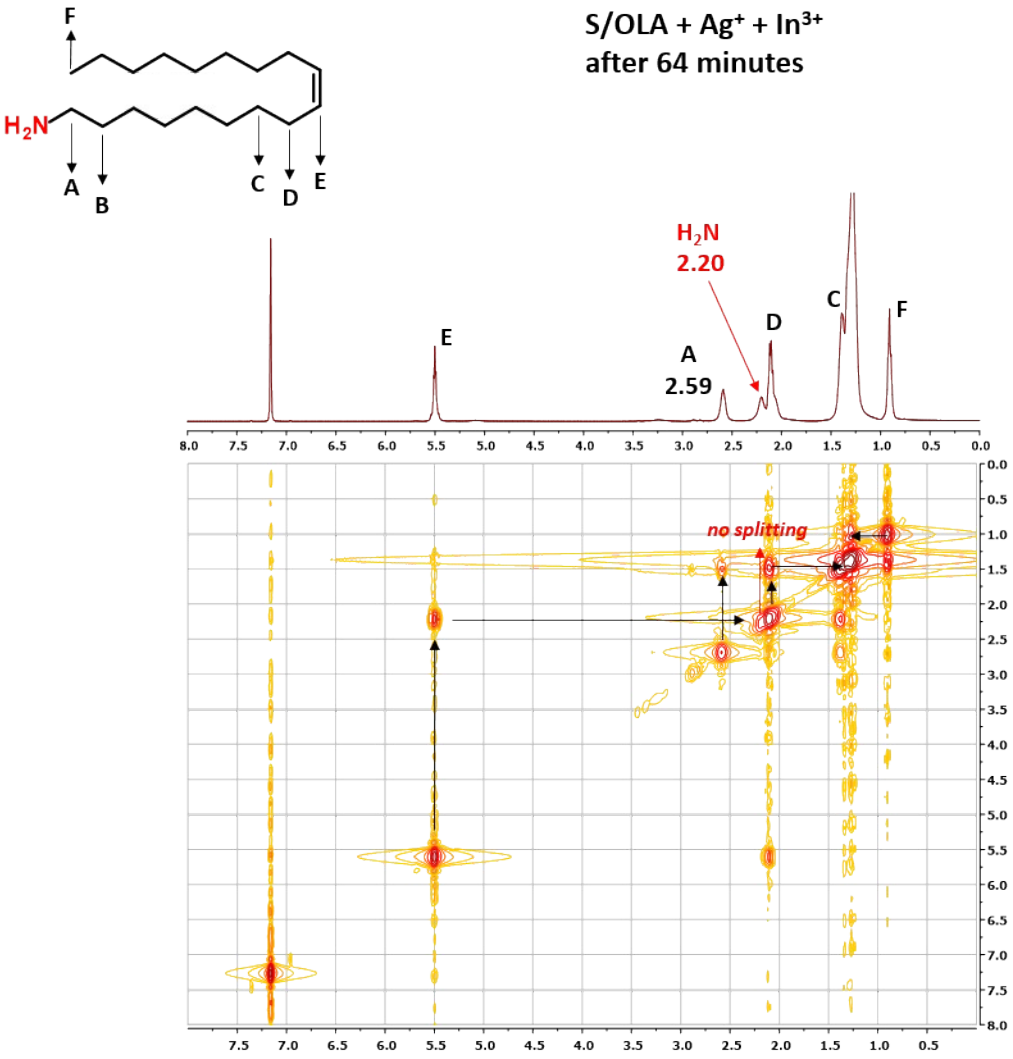


Fig. S11 ^{1}H and ^{1}H-^{1}H COSY NMR spectra of the reaction mixture (S/OLA + $AgNO_3$ + $InCl_3$) after 64 minutes in benzene-d_6 at 298 K.

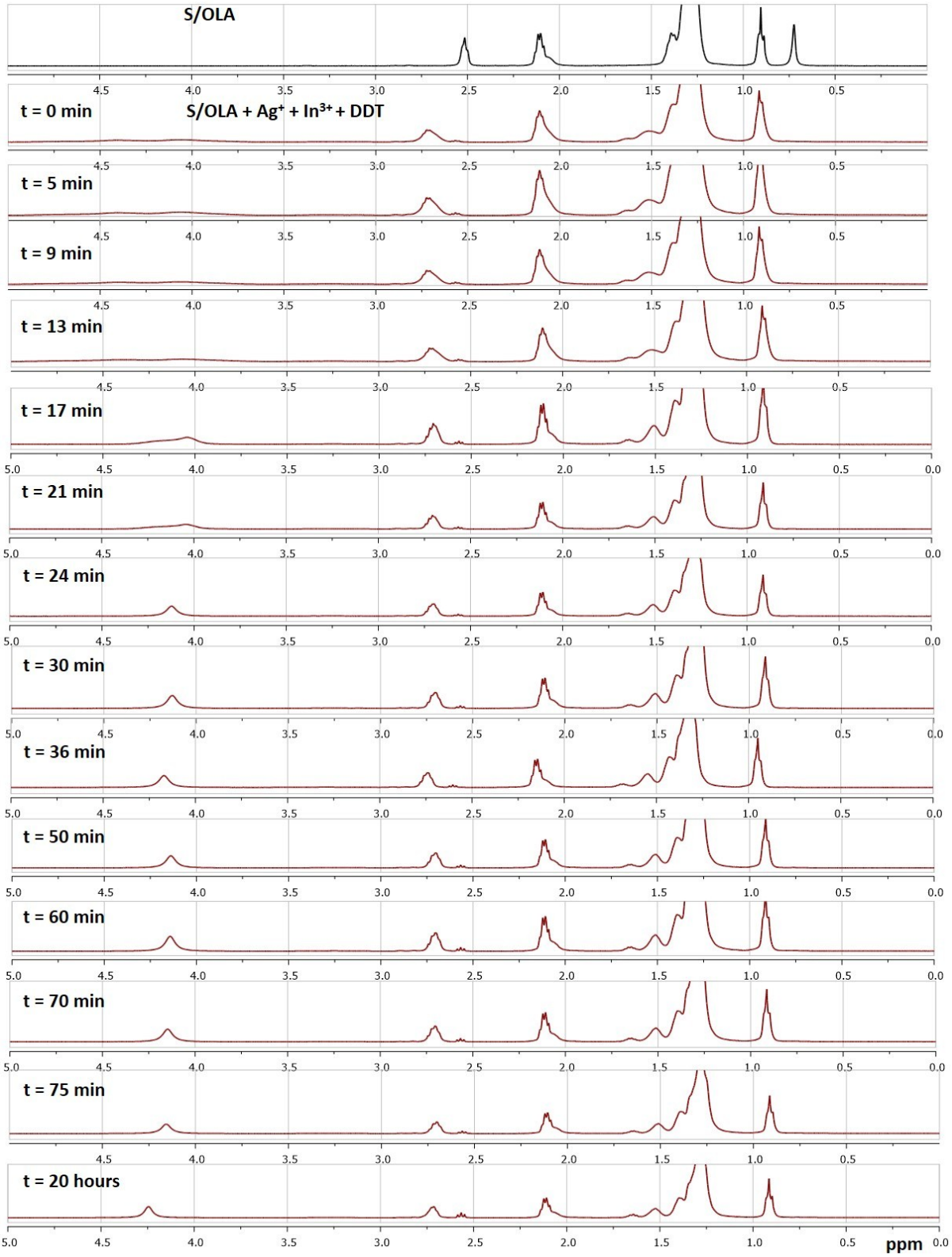


Fig. S12 ^{1}H NMR spectrum of S/OLA (a) and time evolution of the ^{1}H NMR spectrum of the reaction between S/OLA and $AgNO_3$ and $InCl_3$ and DDT in benzene-d_6 at 298 K.

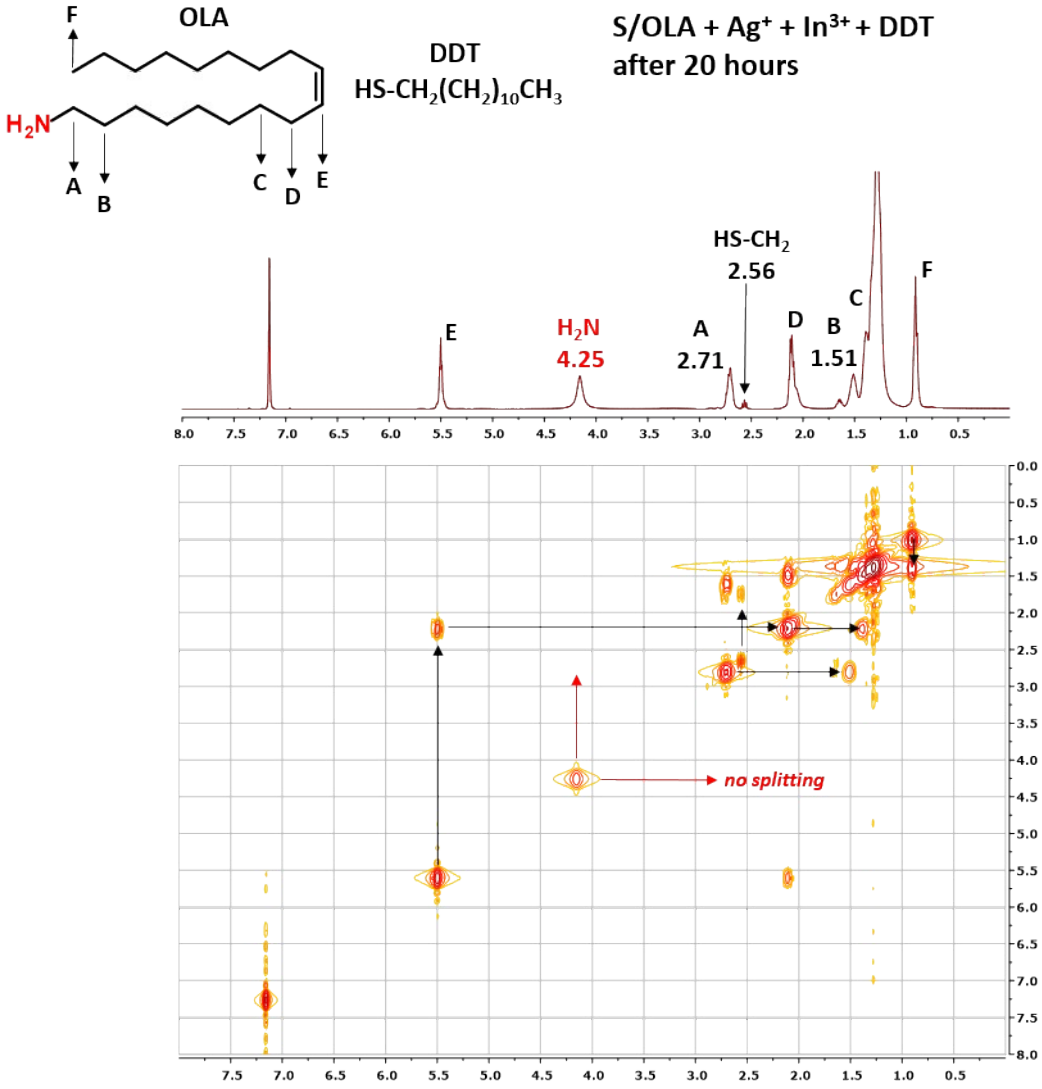


Fig. S13 ^{1}H and ^{1}H-^{1}H COSY NMR spectra of the reaction mixture (S/OLA + $AgNO_3$ + $InCl_3$ + DDT) after 20 hours in benzene-d_6 at 298 K.

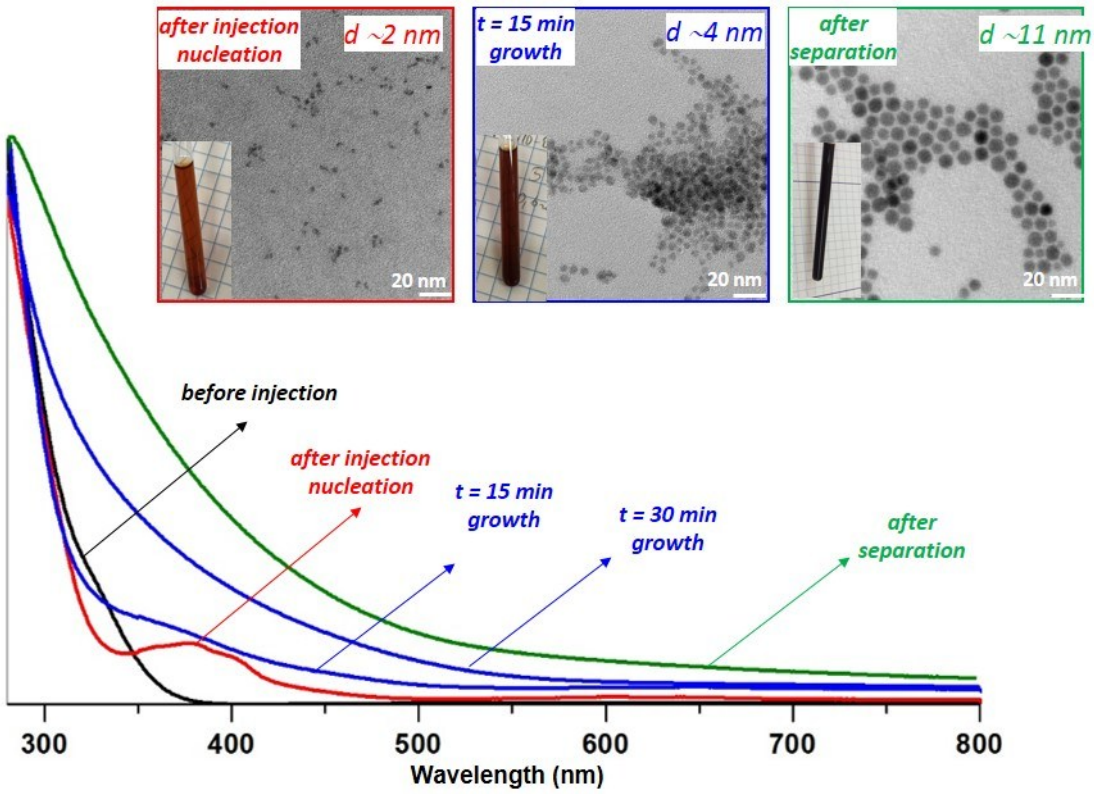


Fig. S14 Evolution of UV-vis spectra of the Ag_2S nanocrystals obtained in an NMR tube. Inset: TEM images of nanocrystals Ag_2S isolated from reaction mixture after injection nucleation; after 15 min of the reaction and after separation of the final fraction (180 min of the reaction).

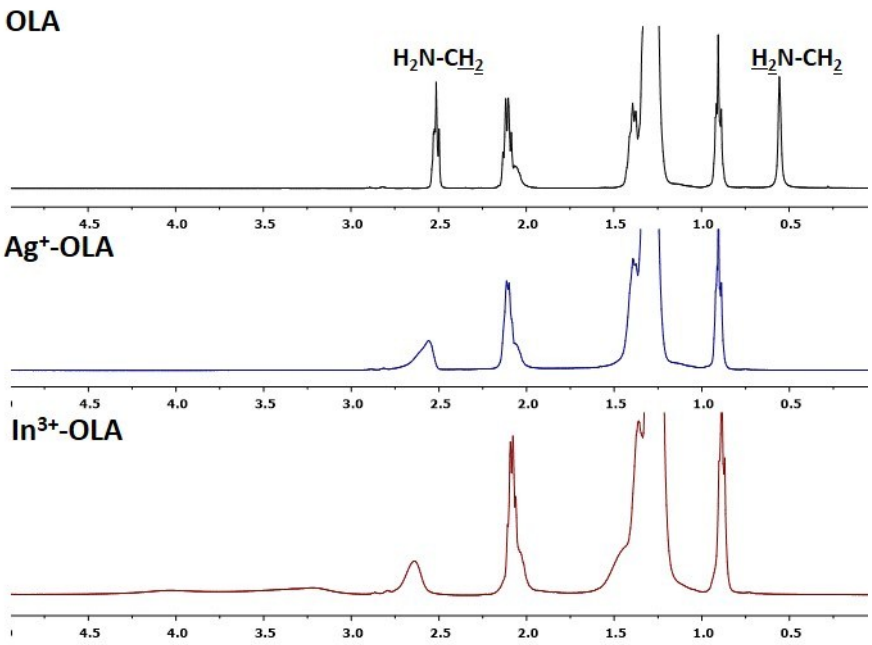


Fig. S15 ^{1}H NMR spectra of OLA and Ag^{+}-OLA (5 mg of $AgNO_3$ + 60 μL of OLA) and In^{3+}-OLA (10 mg of $InCl_3$ + 60 μL of OLA) in benzene-d_6 at 298 K.

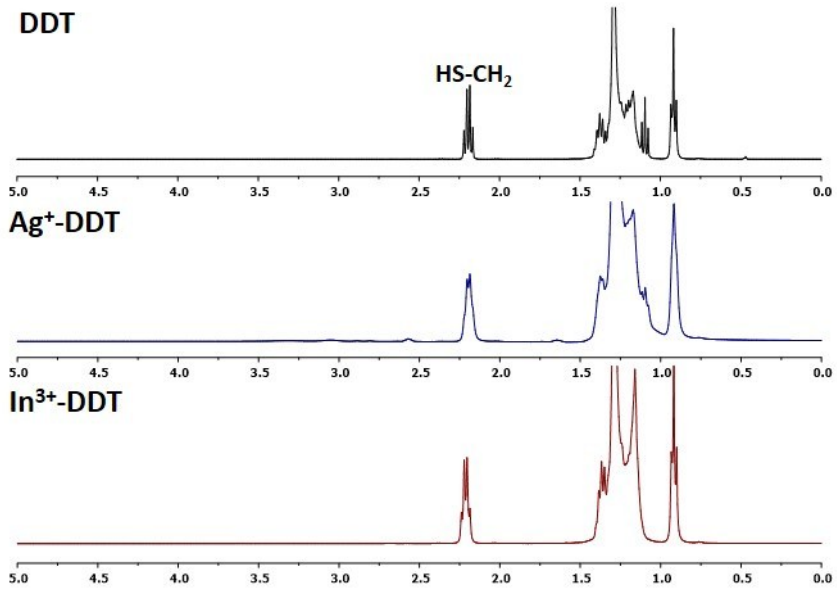


Fig. S16 ^{1}H NMR spectra of DDT and Ag^{+}-DDT (5 mg of $AgNO_3$ + 40 μL of DDT) and In^{3+}-DDT (10 mg of $InCl_3$ + 40 μL of DDT) in benzene-d_6 at 298 K.