Supporting information

Rapid Phosphine-Free Synthesis of CdSe Quantum Dots: Promoting the Generation of Se Precursors using a Radical Initiator

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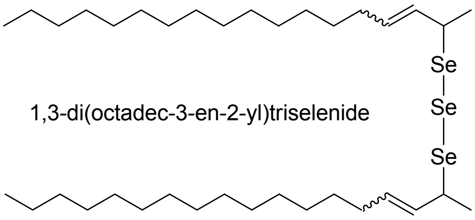
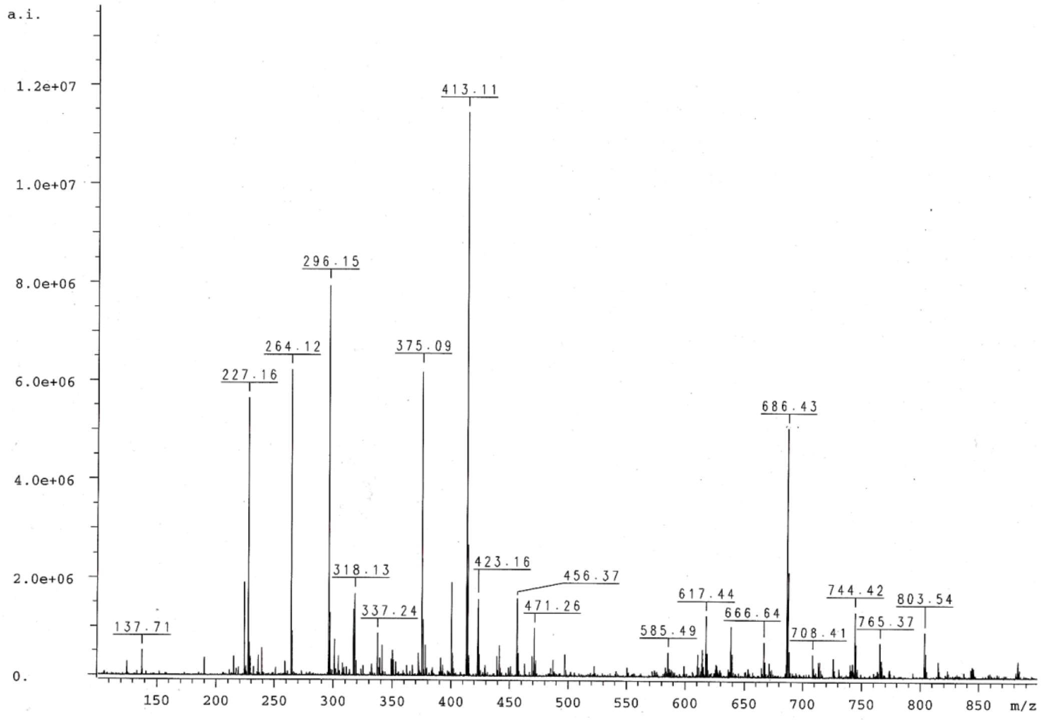
S1. Electrospray ionization (ESI) mass spectrometry analysis of Se-containing product.

The Se containing products were isolated by chromatography using hexane. The isolated product is dried in vacuum and re-dissolved into dichloromethane for ESI$^+$ analysis as shown in Figure S1. The mass spectrometry signal at $[M+Na]^+=765.29$ is consistent with the intermediate 1,3-di(octadec-3-en-2-yl)triselenide, identified by ^{77}Se NMR.

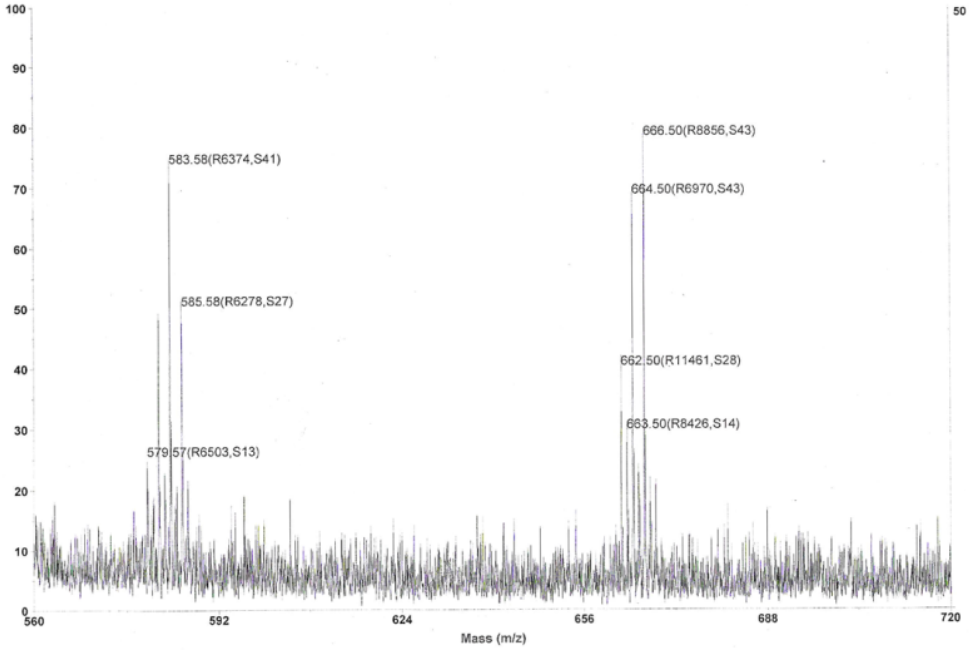


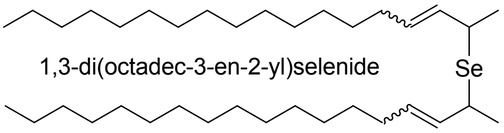


FigureS1. ESI$^+$ mass spectrometry analysis of Se containing species.

S2. Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry analysis of Se-containing product.

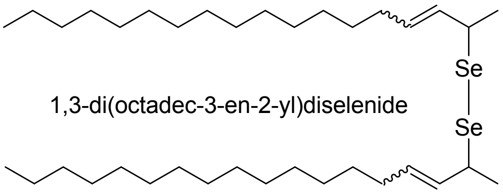
Negative ion matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra, figure S2, were recorded using a HP MALDI instrument (Applied Biosystems 4700 Proteomics Analyzer) with a gentisic acid matrix. The ions masses observed by mass spectrometry with m/z=582.46 and m/z=662.38 are closed to the proposed plausible structure of 1,3-di(octadec-3-en-2-yl)selenide, 1,3-di(octadec-3-en-2-yl)diselenide which attributed to the singlet in the ^{77}Se NMR and structure fragment of dialkyl polyselenides with m/z=331.19.





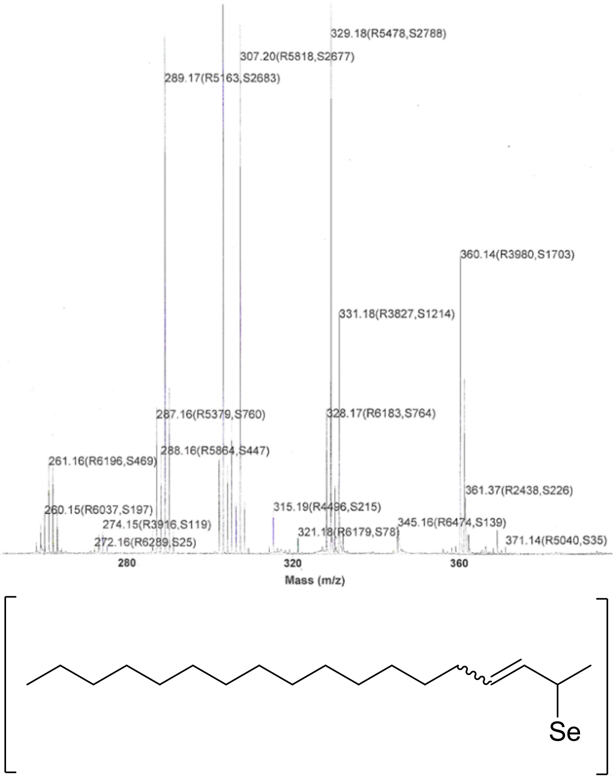
1,3-di(octadec-3-en-2-yl)selenide

Chemical Formula: $C_{36}H_{70}Se$
m/z=582.46



1,3-di(octadec-3-en-2-yl)diselenide

Chemical Formula: $C_{36}H_{70}Se_2$
m/z=662.38



Chemical Formula: $C_{18}H_{35}Se$
m/z=331.19

FigureS2. MALDI mass spectrometry analysis of Se containing species.

S3. 2D proton correlation spectroscopy (COSY) and Heteronuclear single quantum correlation spectroscopy (HSQC) analysis of sample V from Figure 1.

Figure S3 shows the 2D COSY spectrum of sample V from Figure 1. As indicated in the spectrum the olefin proton is correlated with protons which chemical shift are δ = 1.63 and 1.94 ppm. Combining with the HSQC spectrum shown in Figure S4 allows concluding that the ^{1}H signals at δ = 1.63 and 1.94 ppm are bonded with ^{13}C δ = 17.99 and 32.73 ppm which are attributed to CH_2 and CH_3 moiety. Therefore, as indicated in the manuscript, the 2-ODE was formed as the main reaction product.

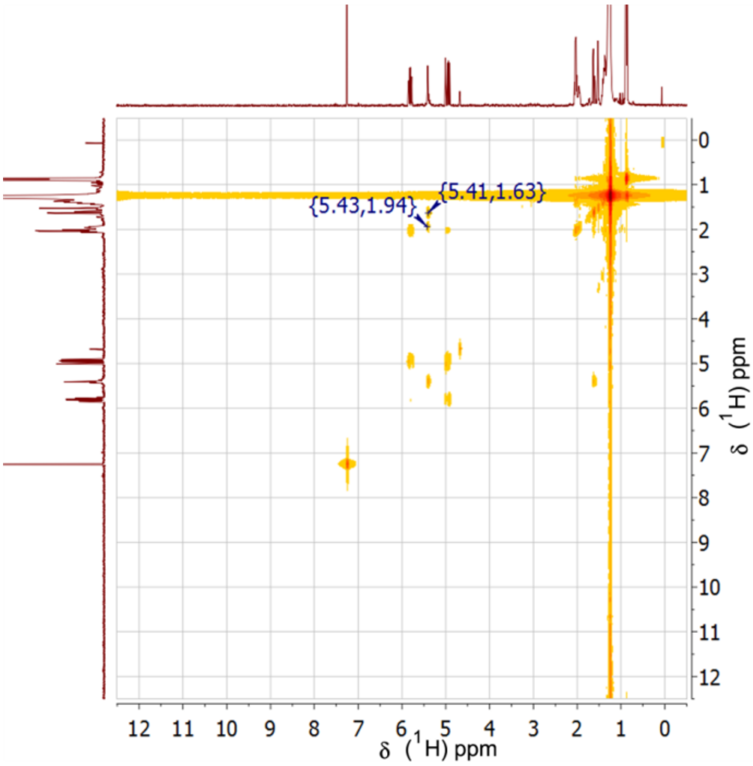


Figure S3. ^{1}H COSY analysis of sample V from figure 1d.

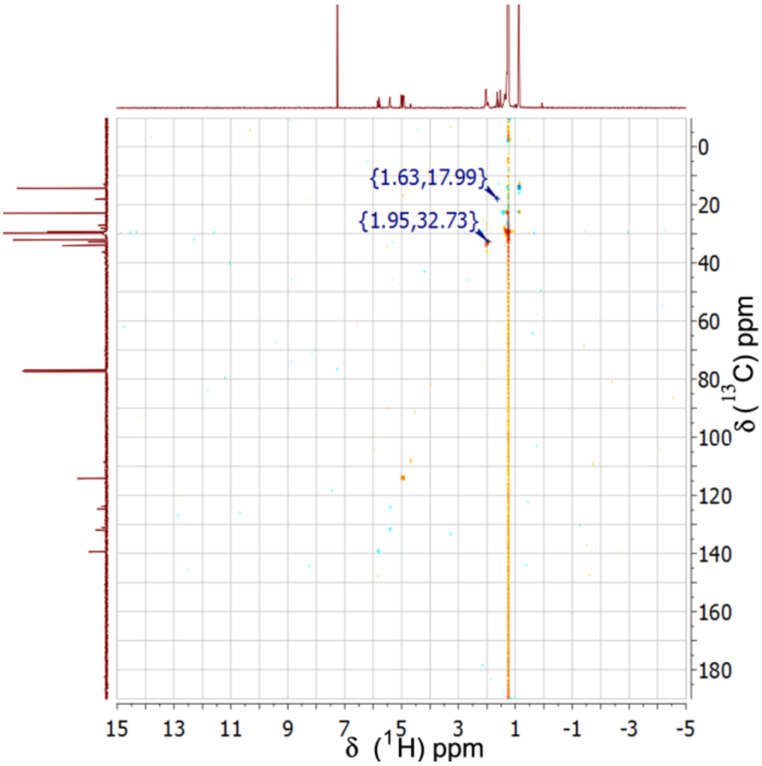


Figure S4. Full HSQC analysis of sample V in Figure 1d.

S4. 2D proton carbon HSQC and 2D HMBC analysis of selenium containing species during Se dissolution in 1-ODE.

The 2D ^1H and ^{13}C HMBC NMR spectra in figures S5 and S6 suggest the secondary carbon bonding with selenium is next to an olefin moiety carbon and a saturated carbon as described in the main text. The 2D ^1H and ^{13}C HSQC NMR spectrum in figure S7 further confirm that the olefinic moiety is vicinal to the C-Se bond.

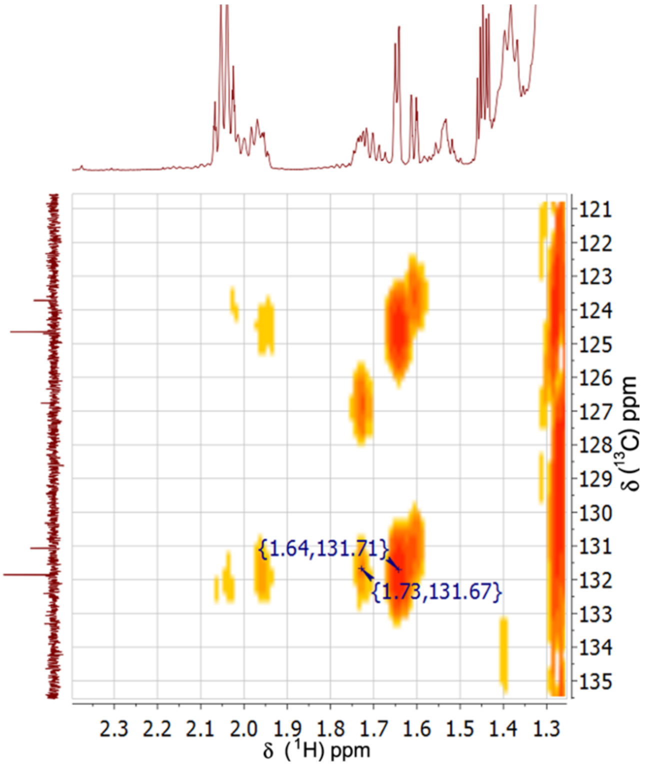


Figure S5. ^1H and ^{13}C HMBC NMR spectrum of Se precursor. As indicated in the image, ^{13}C (singlet, δ=131.67 ppm) correlates with a carbon containing ^1H NMR multiplet δ =1.73 and 1.64ppm.

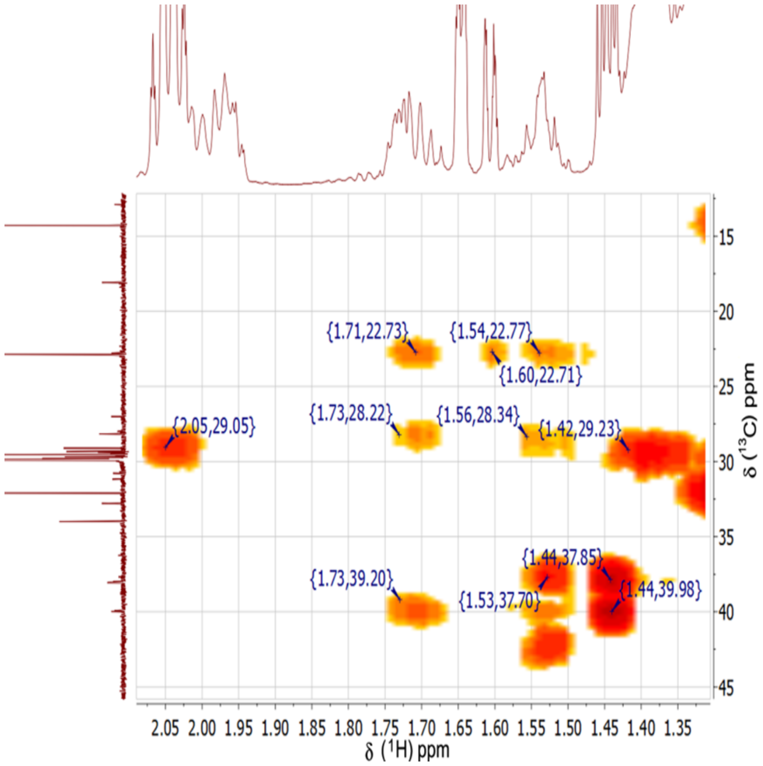


Figure S6. ^{1}H and ^{13}C HMBC NMR spectrum of Se precursor. As indicated in the image, ^{1}H (multiplet) δ=1.73 ppm bonding with a carbon with another carbon next to it with ^{13}C (singlet) δ=22.73, 28.22 and 39.20 ppm.

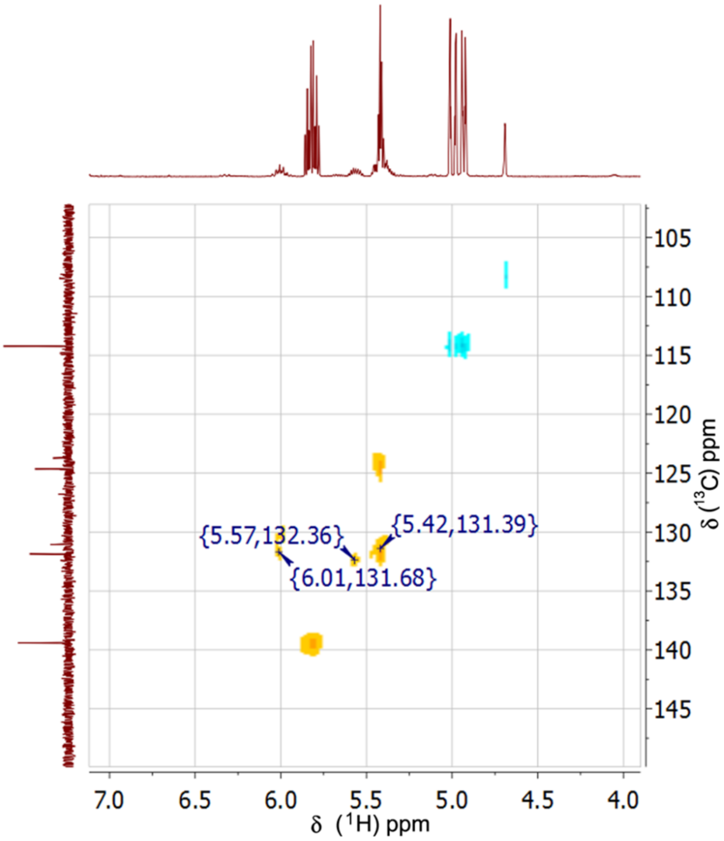


Figure S7. ^{1}H and ^{13}C HSQC spectrum of Se precursor showing the carbons δ = 131.68, 131.39 and 132.36 ppm are olefinic.

S5. FTIR analysis of 1-ODE at various temperatures

Figure S8 shows the FTIR spectra of 1-ODE during the following heating programme: room temperature (I), 60°C under vacuum for 30 minutes (II), 130 °C under vacuum for 30 minutes (III), 200°C for 30 minutes (IV) and 20 hours (V) under Ar. No changes in the IR bands are observed at any stage, confirming that the migration of the olefin group observed in the presence of Se is induced by thermally generated Se radicals. The IR spectra feature bands at:

A: 3078 cm^{-1} - olefin C-H stretching

B: 2956, 2921 and 2852 cm^{-1} - saturated C-H stretching

C: 1641 cm^{-1} - C=C stretching

D: 1466 and 1377 cm^{-1} - saturated C-H deformation

E: 991 and 908 cm^{-1} - terminal olefin $RCH=CH_2$ C-H out of plane deformation

F: 720 cm^{-1} - CH_2 single bond to hydrogen rocking

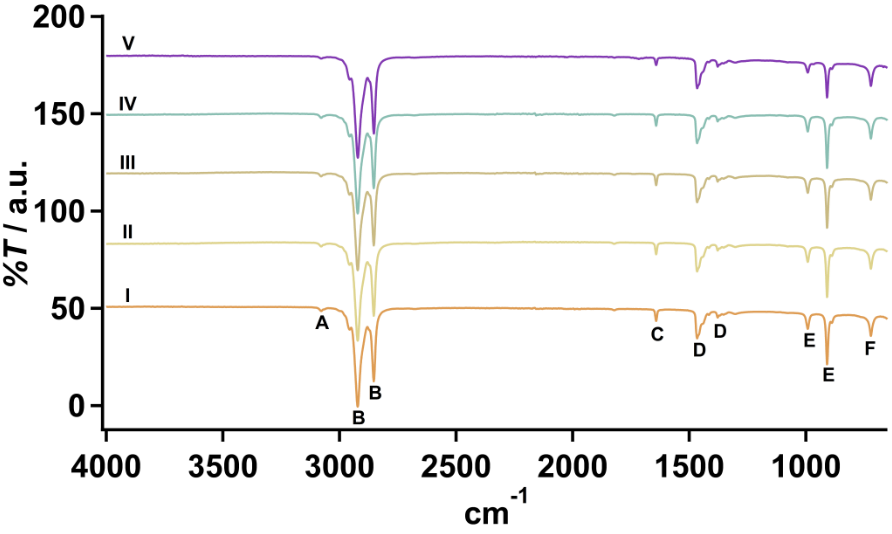


Figure S8. FTIR spectra of 1-ODE during the following heating programme: room temperature (I), 60 °C under vacuum for 30 minutes (II), 130 °C under vacuum for 30 minutes (III), 200 °C for 30 minutes (IV) and 20 hours (V) under Ar.

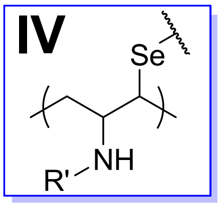
Table S1. ^{77}Se NMR Chemical Shifts and ESI, MALDI Masses of the Selenium-Containing Species.

Plausible Structure	$\delta_{(^{77}Se)}$ (ppm)	Mass (m/z)
A	307.4, 373.1 and 373.3	662.28
B	416.4	765.29[a]
C	416.4	582.4
D[b]	–	331.19

a: $[M+Na]^+$; b: Fragment arising from ionization process.

S6. 2D proton carbon HSQC and HMBC analysis of selenium containing species during Se solubilisation in oleylamine

The 2D ^{1}H and ^{13}C HMBC NMR spectrum in figure S9a suggests the secondary carbon bound to selenium is next to carbons with chemical shifts at δ = 26.79 ppm and 47.24ppm. The HSQC result in Figure S9b shows these carbons are CH and CH_2 moieties. The analysis also indicates that CH is attached to a nitrogen due to its ^{1}H at = 2.76 ppm and ^{13}C at = 26.78 ppm. Therefore, as described in the main text, structure IV is proposed to be the core structures after the consuming of double bonds.



polyalkyl polyaminoselenides

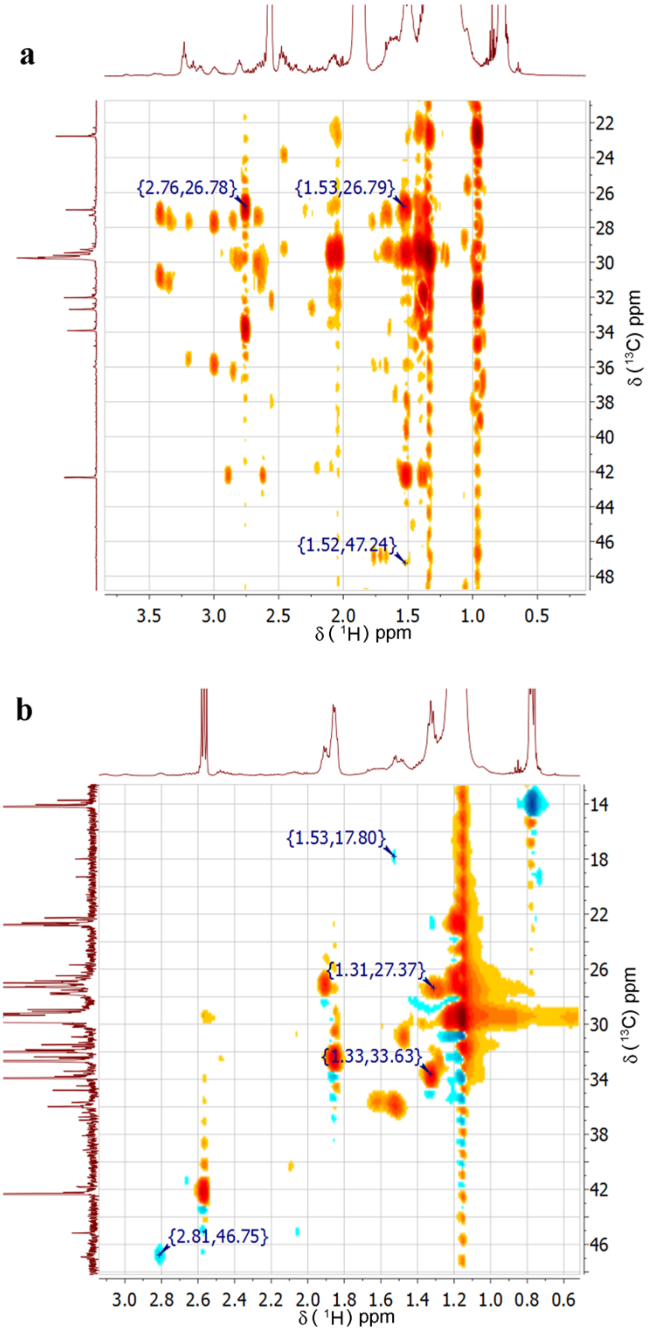


Figure S9. a) ^{1}H and ^{13}C HMBC NMR spectra of selenium containing species after solubilisation of Se in oleylamine. b) ^{1}H and ^{13}C HSQC NMR analysis of the same sample.

S7. Full ^{1}H, ^{13}C and 2D HSQC NMR spectra shown in Figures 1 and 8.

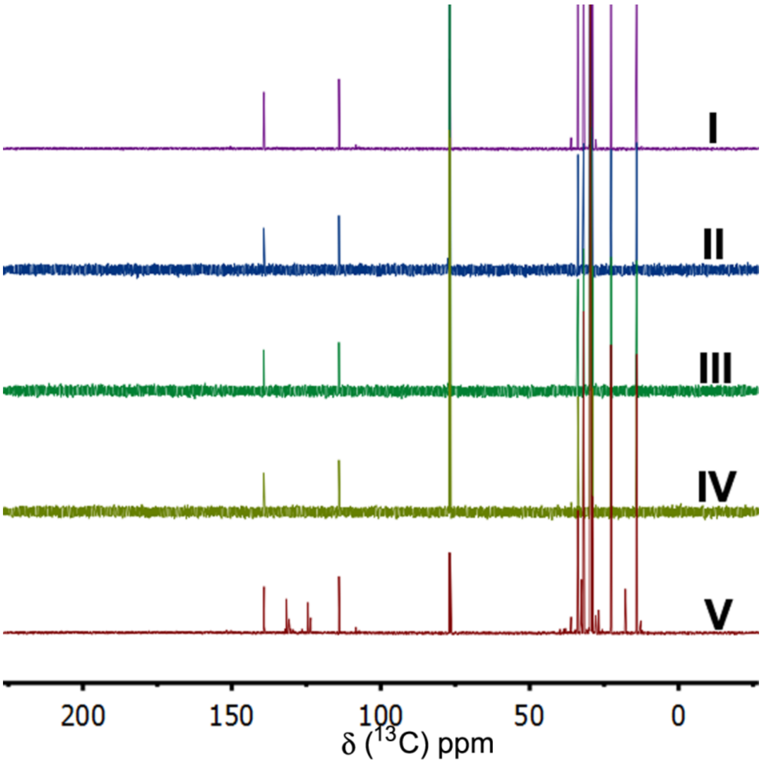


Figure S10 Full ^{13}C NMR spectra of Figure 1a.

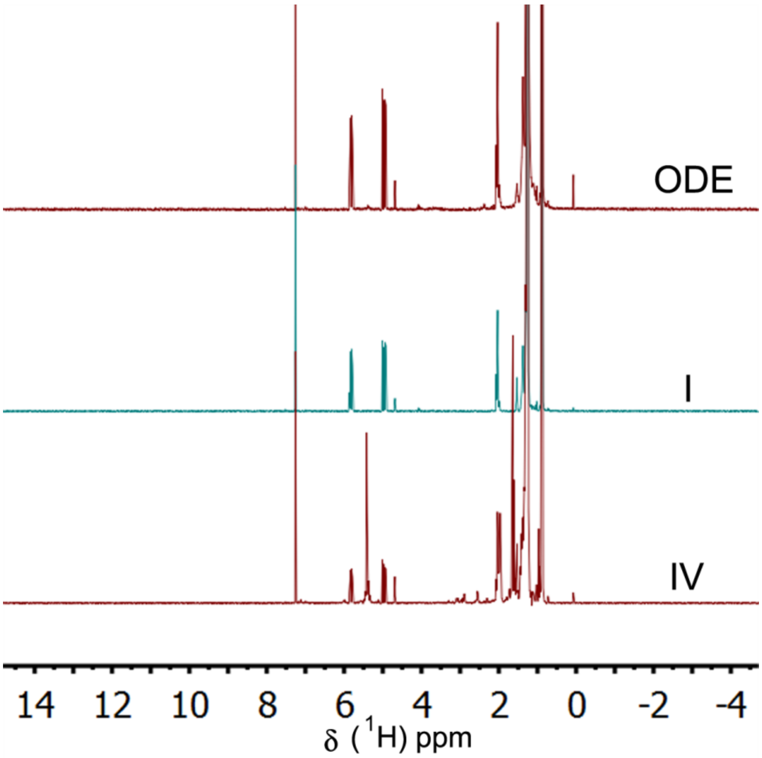


Figure S11 Full ^{1}H NMR spectra of Figure 1b.

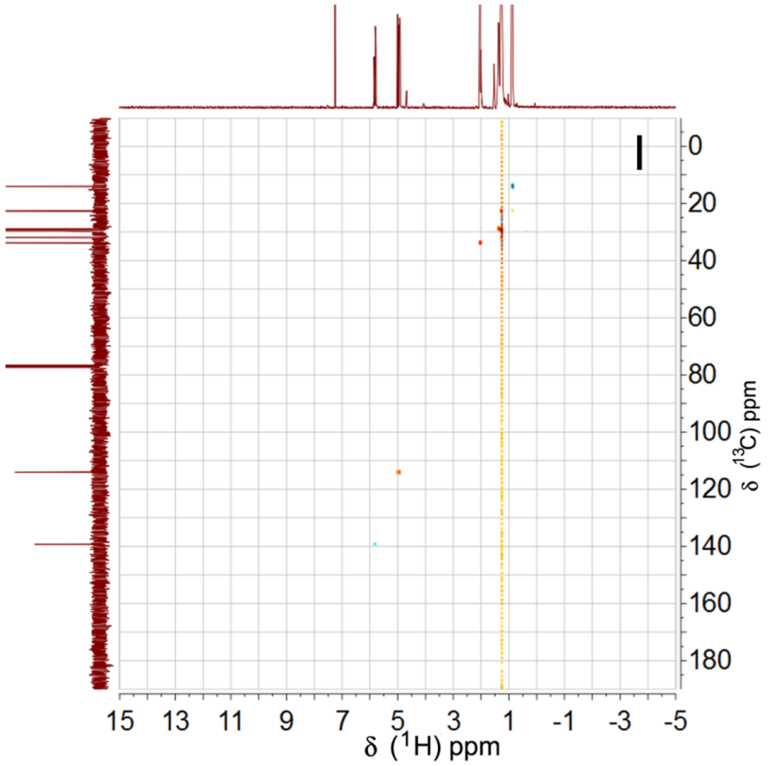


Figure S12 Full 2D HSQC NMR spectra of Figure 1c.

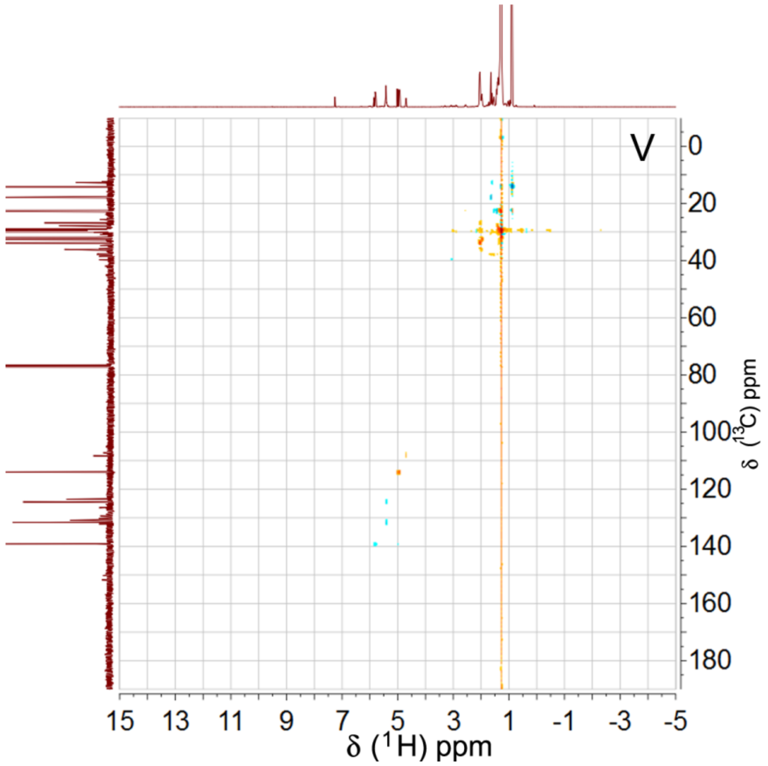


Figure S13 Full 2D HSQC NMR spectra of Figure 1d.

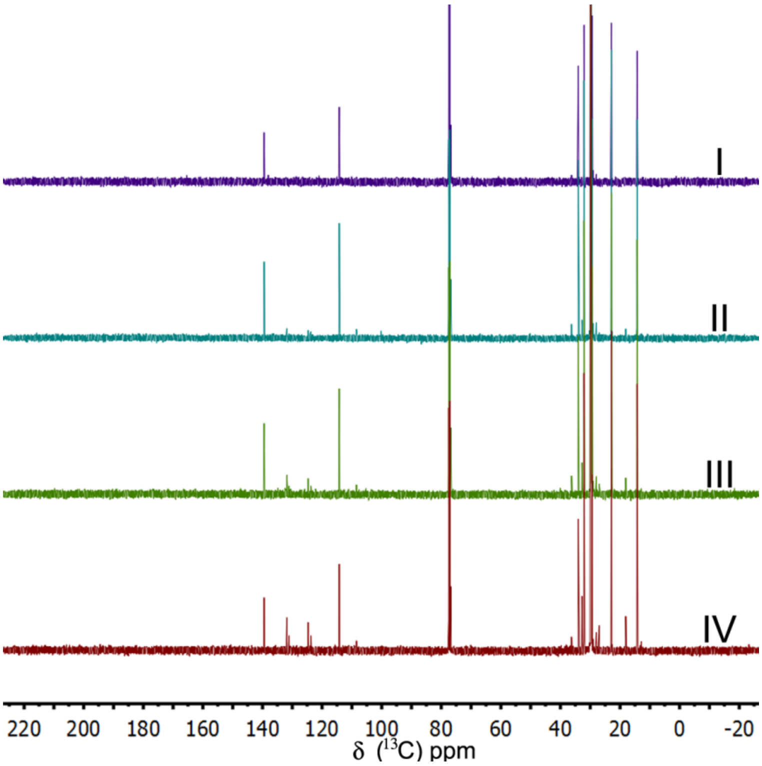


Figure S14 Full ^{13}C NMR spectra of Figure 8a.

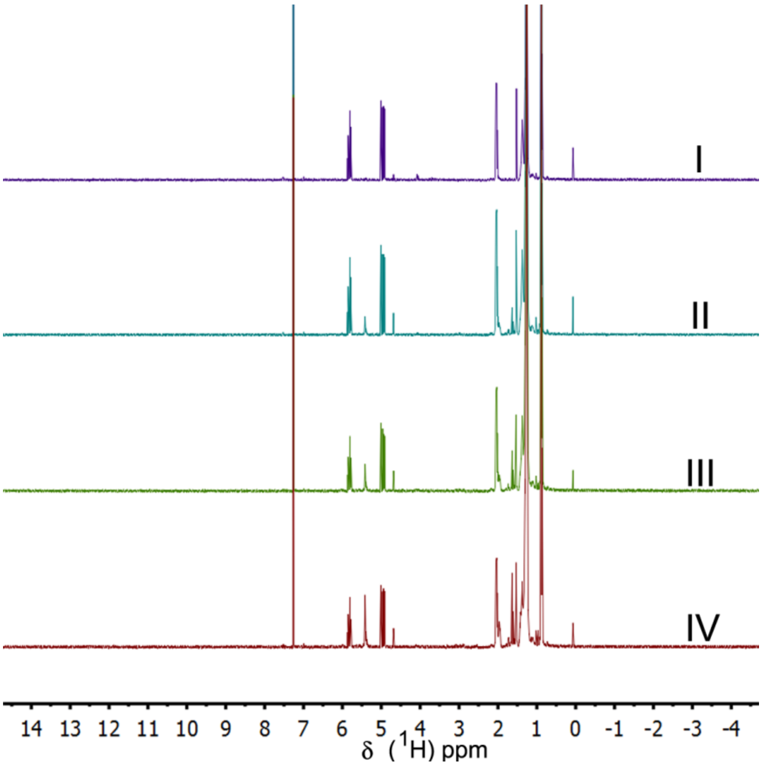


Figure S15 Full ^{1}H NMR spectra of Figure 8b.

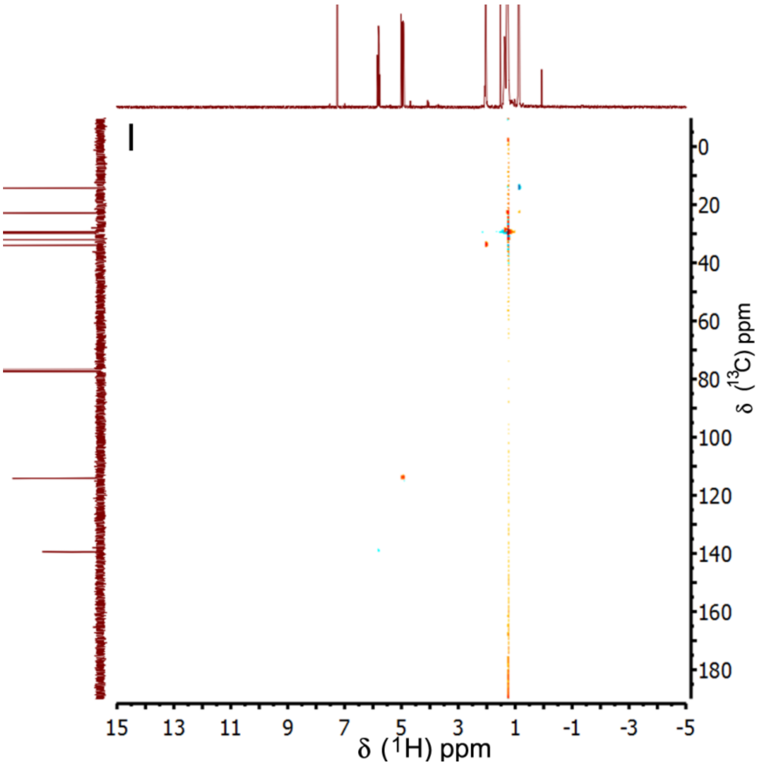


Figure S16 Full 2D HSQC NMR spectra of Figure 8c.

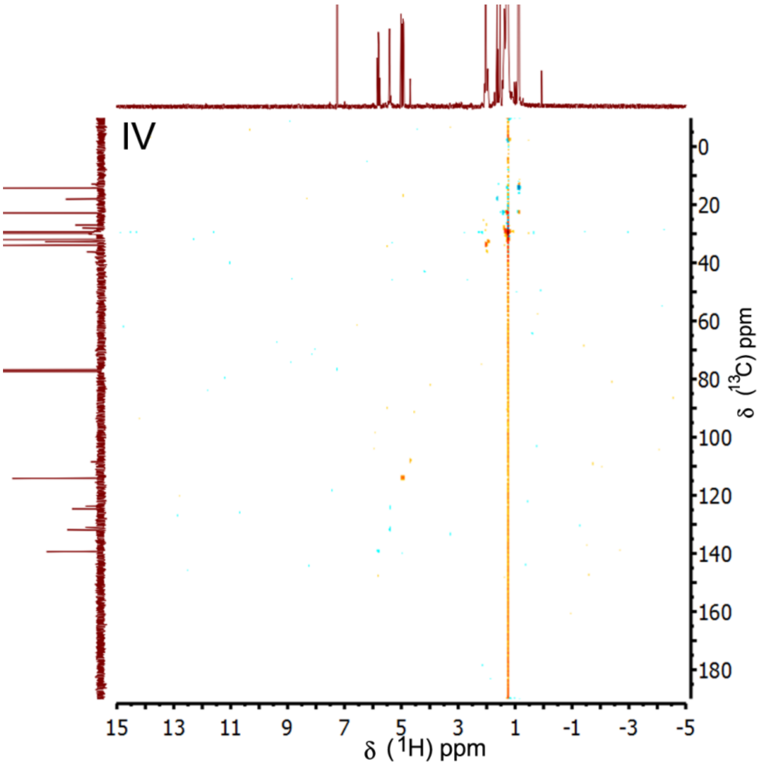


Figure S17 Full 2D HSQC NMR spectra of Figure 8d.

Table S2. Reported Se solubilisation times in 1-ODE as a function of concentration and temperature

Concentration (mol×dm^{-3})	*Temperature (^{o}C)*	*Time (hour)*	*AIBN (mg)*
0.10	150	48	0[a]
0.10	180	5	0[a]
0.10	200	2	0[b]
0.10	200	1	0[a]
0.10	210	0.6	0[a]
0.06	220	0.08	0[c]
0.13	220	3	0[d]
0.06	280	0.5	0[e]
0.10	190	4	0[f]
0.10	200	2	0[f]
1.04	200	20	0[f]
0.10	100	-	1[f]
0.10	130	-	1[f]
0.10	150	45	1[f]
0.10	170	6	1[f]
0.10	180	3.5	1[f]
0.10	190	2.5	1[f]
0.10	200	1	1[f]
1.04	200	3	1[f]

a- Reference 17a
b- Reference 8
c- Reference 9b
d- Reference 9a
e- Reference 9c
f- This work