Supporting Information

Heterogeneous Supramolecular Catalysis through Immobilization of Anionic M_4L_6 Assemblies on Cationic Polymers.

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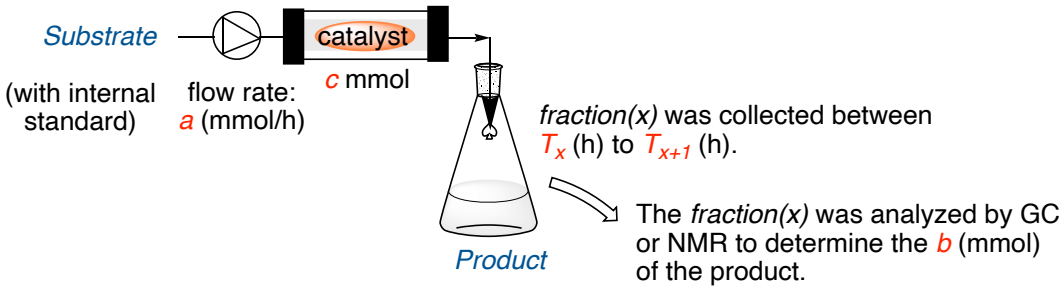
1 General remarks

- Unless otherwise noted, all reactions were carried out in oven-dried glassware sealed with a rubber septum
- Diethyl ether (Et_2O), benzene, and methylene chloride (DCM) were dried by passing the previously degassed solvents through activated alumina columns under argon.
- Unless otherwise noted, multi-deuterium (D_n) and deuterated solvents were purchased from Cambridge Isotope Laboratories, the solvents were sparged with N_2 for 30 minutes prior to storing in the glovebox
- $Ga(acac)_3$ (99.99% trace metals analysis) were purchased from Sigma Aldrich and used as received.
- Divinylbenzene was passed through a short basic-alumina pad before use.
- D_2O (pD 8, 100 mM PO_4^-) buffered solution was prepared from D_2O, K_3PO_4, and DCl (35 wt% in D_2O).
- All other reagents were purchased from Sigma Aldrich or Fischer Scientific and used as received without further purification.
- The racemic Ga_4**1**$_6$ assembly (**2**) and the resolved Ga_4**1**$_6$ assemblies (**16** and **17**) were prepared following previously reported procedures.[1]
- Proton nuclear magnetic resonance (^{1}H NMR) spectra were measured using AV-300 opperating at 300 MHz and AVB-400 or AVQ-400 Bruker spectrometers operating at 400MHz. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were measures using AVB-400 or AVQ-400 Bruker spectrometers operating at 100 MHz. Chemical shifts are reported in parts per million (ppm) with reference to the appropriate residual solvent signal
- GC analysis was performed on a Shimadzu GC-2014 Gas Chromatograph with FID equipped with Astec CHIRALDEX™ G-PN fused silica capillary column (30 m x 250 μm x 0.12 μm). The following run method was employed: injector temperature at 250 ºC with 35:1 split, 21.1 mL/min total flow rate, 0.5 mL/min column flow rate

(N_2 carrier gas), pressure 50.0 kPa, linear velocity 15.2 cm/sec, purge flow 3.0 mL/min, detector temperature 300 ºC, initial oven temperature 60 ºC for 5 minutes followed by a 2 ºC/min ramp to 100 ºC, then a 10 ºC/min ramp to 200 ºC, followed by a 10 minutes hold at 200 ºC. *o*-Xylene was used as internal standard for quantitative analysis.

- Inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis was performed on Shimadzu ICPS-7510 equipment.
- Monomers **3a**[2], **3b**[3] and **3c**[4] were prepared following previously reported procedures.
- Substrates **9**[5] and **13**[6] were prepared following previously reported procedures.
- Monomers containing cations derived from quinidine and cinchonidine, for preparation of polymer **18** and **19,** were prepared following previously reported procedures.[7]
- A peristaltic pump (MCRP204 by Minato Concept Inc.), 5 mm (diameter) x 5 or 10 cm (length) glass column with PTFE filter and PEEK joints on both ends (Custom-made by Tokyo Rika Kikai Co. Ltd (EYELA)), The Flexar Solvent Manager 5-Ch Vacuum Degasser # N2600580 (PerkinElmer) and PEEK or PTFE tube (external diameter 1/16 inch) were used for continuous-flow system.
- Yield of the continuous-flow experiments was determined using following scheme and was plotted to the charts.



Yield of the *fraction(x)* (T_x (h) to T_{x+1} (h)): $Y_x = b/\{a \times (T_{x+1} - T_x)\}$

Y_x is plotted at the time point of $(T_{x+1} + T_x)/2$

- STEM/EDS images were obtained using a JEOL JEM-2100F instrument operating at 200 kV. All STEM samples were prepared by placing a drop of the solution on

carbon-coated Cu grids and dried in air (without staining).

2 *Preparation of polymers and heterogeneous catalysts*

2.1 Typical procedure for the preparation of a linear polymer

Styrene (4.16 g, 40 mmol, 0.8 eq.), **3a** (2.1 g, 10 mmol, 0.2 eq.) and azobisisobutylnitrile (AIBN) (82 mg, 0.5 mmol) were dissolved in chloroform (25.0 mL). The mixture was degassed in a sonicator under reduced pressure and stirred for 48 h at 60 ºC under a nitrogen atmosphere. The resulting polymer-containing solution was diluted with chloroform (10 mL) and acetone was added until a precipitate formed. The precipitated polymer was dissolved in a minimum amount of chloroform and acetone was added to induce precipitation. This process was repeated an additional two times. The precipitated polymer was collected by filtration, washed with diethyl ether several times and dried *in vacuo* to afford the desired copolymer (**4b**, 3.50 g, 56% yield).

2.2 Typical procedure for the preparation of a cross-linked polymer

N-tert-Butyl acrylamide (4.80 g, 38 mmol, 0.76 eq.), **3a** (2.1 g, 10 mmol, 0.20 eq.), divinylbenzene (0.28 mL, 2 mmol. 0.04 eq.) and azobisisobutylnitrile (AIBN) (82 mg, 0.5 mmol) were combined in chloroform (25.0 mL). The mixture was degassed in a sonicator under reduced pressure and stirred for 48 h at 60 ºC under a nitrogen atmosphere. The resulting solid was collected by filtration and washed with chloroform, water, methanol and acetone several times. The collected solid was crushed into small particles using pestle and mortar, then dried *in vacuo* to afford the desired cross-linked copolymer (**6a**, 6.83 g, 89% yield).

2.3 Typical procedure for immobilization of 2 on a cationic polymer

To the cross-linked copolymer **6a** (1.39 g) suspended in degassed methanol (6.0 ml) and DMF (internal standard), in a Teflon-lined septum-capped 1-dram vials containing a Teflon coated magnetic stir bar, was added **2** (395.0 mg, 0.12 mmol) dissolved in pD 8 buffered D_2O (6.0 ml) at room temperature in an air-free glove box. The mixture was stirred for 48 h and the copolymer immobilized cluster **2** was collected by filtration in the

air-free glove box. The collected solid was washed with D_2O and methanol, then dried *in vacuo* to afford catalyst **8a** (1.589 g). To establish the amount of that **2** was immobilized in polymer phase, the filtrate was analyzed by ^1H NMR and amount of **2** remaining in the solution phase was calculated using an internal standard. Loading of cluster **2** on the polymer was further confirmed by determine the amount of Ga in the polymer using ICP analysis as described below.

2.3.1 **Detail of procedure for determining catalyst loading using ICP**

8.8 mg of the catalyst **8a** was placed in a test tube. 1 mL of sulfuric acid was added into this test tube. The test tube was heated at 200 ºC and nitric acid was added dropwise until all of the solid had dissolved and no additional brown fumes were observed. The mixture was cooled to room temperature and was brought to 50 mL with water in a volumetric flask (Sample A). Standard aqueous solutions of Ga^{3+} (10 ppm, 5 ppm, 1 ppm and 0.5 ppm) with 2% H_2SO_4 were prepared by dilution of 1000 ppm Ga standard solution (purchased from Kanto Chemical Co. Inc.). ICP measurements was conducted 5 times for each sample and average of 5 measurements is reported. A Calibration curve was prepared from Ga standard solutions and blank solution (2% H_2SO_4) with 0.99999 of coefficient of correlation and 0.01166 of standard deviation, and detection limit and quantitation limit were calculated as 0.022 ppm and 0.067 ppm, respectively, from parameters of calibration curve. Ga concentration of Sample A (50 mL) was calculated as 3.269 ppm and Ga concentration of catalyst **8a** was calculated as 0.265 mmol/g. Thus, concentration of cluster **2** in catalyst **8a** was calculated as 0.066 mmol/g.

3 Aza-Prins reaction

3.1 General procedure for the aza-Prins reaction under batch reactor conditions (Table 1)

Catalyst **8a** (128 mg), paraformaldehyde (31.4 mg), **9** (15.0 mg), methanol (1.5 mL) and D_2O (0.15 mL) were combined in a Teflon lined septum-capped 1-dram vial containing a Teflon coated magnetic stir bar. The mixture was stirred for 40 h at 50 ºC. The heterogeneous catalyst was removed by filtration and the filtrate was analyzed by ^1H NMR using DMF as an internal standard to determine yield of **10** as 86%.

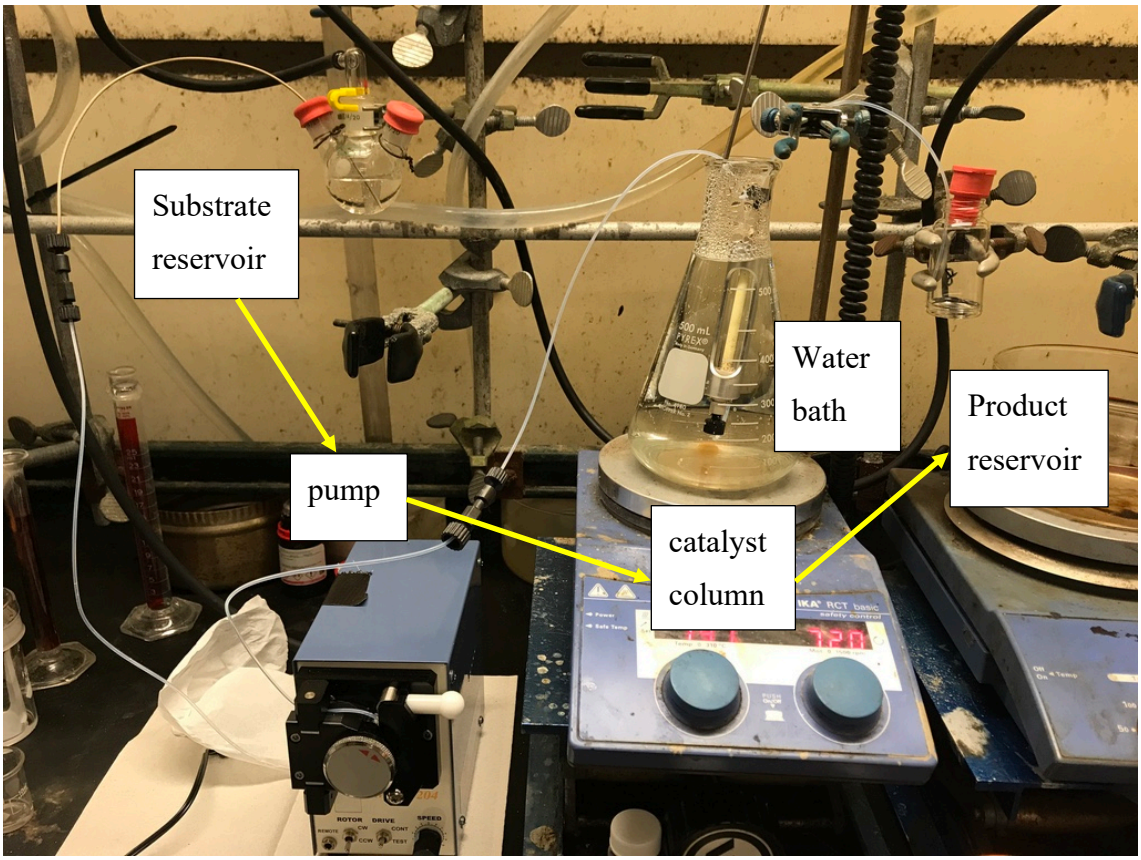
3.2 Typical procedure for the aza-Prins reaction under continuous-flow reactor conditions (Figure 2)

Polymer immobilized cluster catalyst **8a** (500 mg, 0.030 mmol **2**) was suspended in 2 mL of CH_3OH-D_2O (pD 8) (3:1). The suspended solution was introduced into the glass column (5ΦX100 mm) equipped with a PTFE filter and a PEEK column bottom-end which was connected to vacuumed chamber by a PTFE tube. Excess solvent was drained using a vacuumed chamber and the polymer catalyst, swelled with solvent, was packed into the column. The PTFE filter and PEEK column top-end were attached. The bottom-end part was connected to a peristaltic pump and top-end was connected to product fraction reservoir.

Paraformaldehyde (71 mg) was dissolved in 5 mL of D_2O and the resulting mixture was combined with **9** (32 mg) and DMF (9.9 mg; internal standard) in methanol to prepare the substrate solution. The substrate solution was stored in a 3-necked round bottom flask connected to a Schlenk line. The PEEK tube, which was connected to the peristaltic pump on the opposite end, was put into the substrate solution through a septa. When the substrate solution was close to being consumed, another portion of substrate solution, composed of the same components and concentrations, was added. The pump was run at the flow rate of 0.030 mL/min (time point 0 min.) and the solution was passed through the column, which was submersed in room temperature water bath, from bottom to top (up-flow). The eluted solution was collected in vials as fractions at given time intervals. Collected fractions were analyzed by ^{1}H NMR to determine yields of **10** using DMF as internal standard. The temperature of water bath was changed from room temperature to 50 ºC at the time point of 150 min and changed from 50 ºC to 60 ºC at the time point of 1455 min.

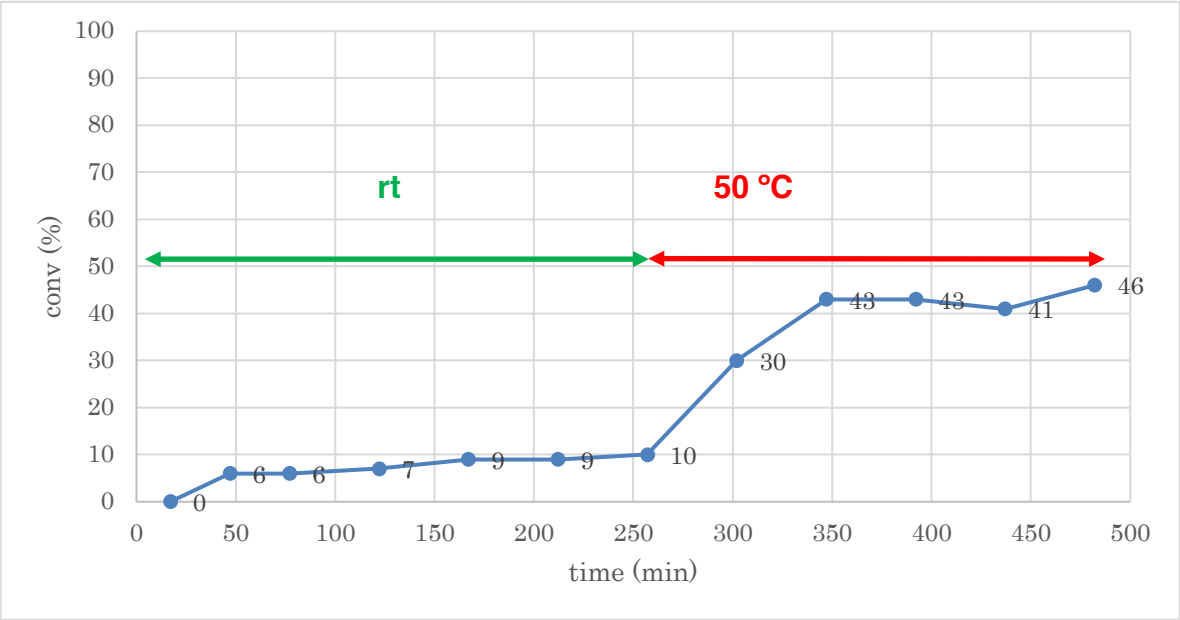
3.3 Photographic image of the continuous-flow system

Glass column with PTFE filter (left), glass column fixed in an aluminum column jacket equipped with PEEK column end (middle), and **8a** packed in the column (right).



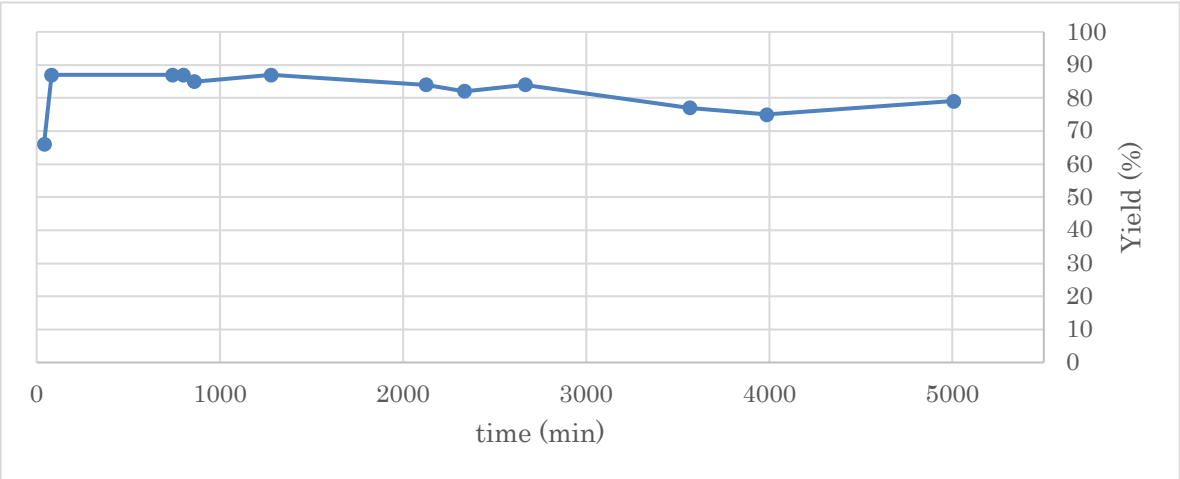
Photographic image of the continuous-flow reactor system.

3.4 Results of continuous-flow reaction at rt to 50 °C



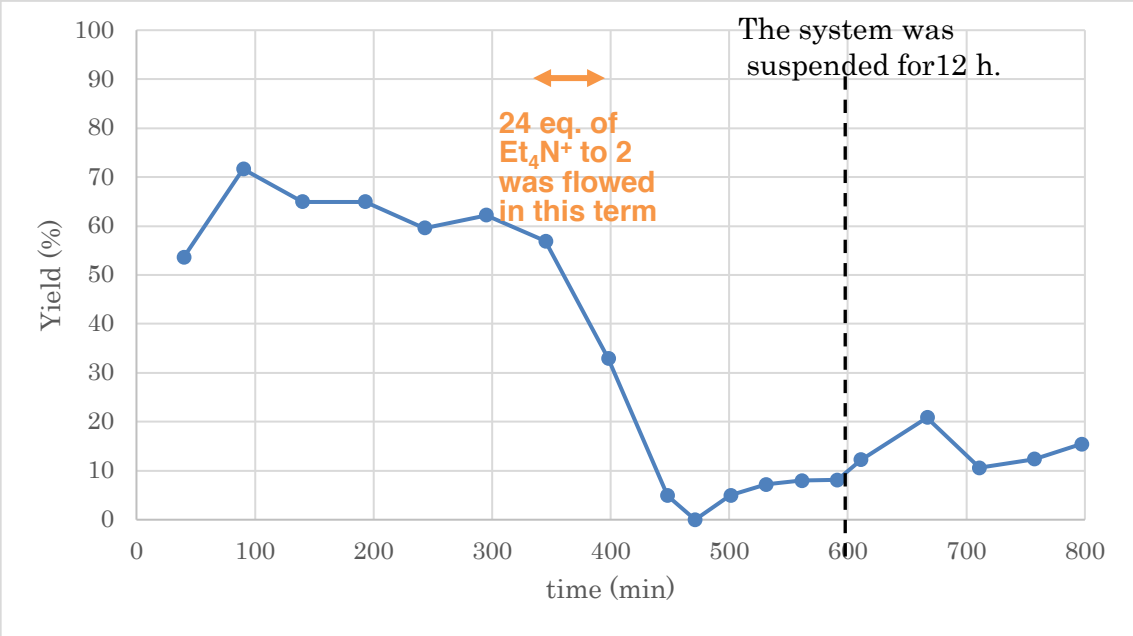
SI_Figure 1. 0.019 mmol of **2** in the column packed with **8a**, 0.030 mmol/min flow rat

3.5 Results of continuous-flow reaction at 50 ºC with 0.023 mL/min flow rate



SI_Figure 2. 0.038 mmol of 2 in a **column packed with 8a, water bath temperature: 50 ºC, 0.023 mmol/min flow rate.**

3.6 Results of continuous-flow reaction at 65 ºC including experiments of blocking cavity with tetraethylammonium cation



SI_Figure 3. 0.013 mmol of **2** in column packed with **8a**, water bath temperature: 65 ºC, 0.030 mmol/min flow rate.

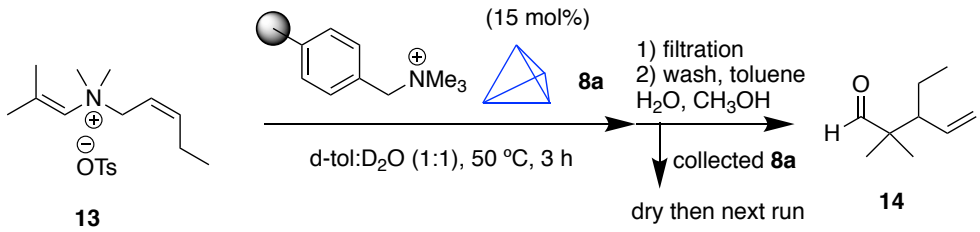
4 *Aza-Cope reaction*

4.1 General procedure for the aza-Cope reaction in the batch reactor system and method for recovery and reuse of the catalyst (SI_Table 1 conditions)

Catalyst **8a** (75 mg), **13** (10.0 mg), *d*-toluene (0.25 mL) and D_2O (0.25 mL) were combined in a Teflon lined septum-capped 1-dram vial containing a Teflon coated magnetic stir bar. The mixture was stirred for 3 h at 50 ºC. The heterogeneous catalyst was removed by filtration and the *d*-toluene layer of filtrate was analyzed by ^{1}H NMR using *o*-xylene as internal standard to determine yield of **14** as 92%. The filtered catalyst was washed with 1 mL of water-methanol (3:1) on the funnel. The solid catalyst was collected and dried *in vacuo* at room temperature for more than 2 h, then used in the next run.

4.2 Results of the recovery and reuse experiments in aza-Cope reaction.

SI_Table 1. Recovery and reuse of catalyst **8a**



run	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
yield (%)	92	99	99	97	99	96	99	99	99	99	99	89	93	95	99	99	96	99

4.3 The Aza-Cope reaction under continuous-flow conditions: Typical procedure for the aza-Cope reaction under continuous-flow conditions (Figure 4)

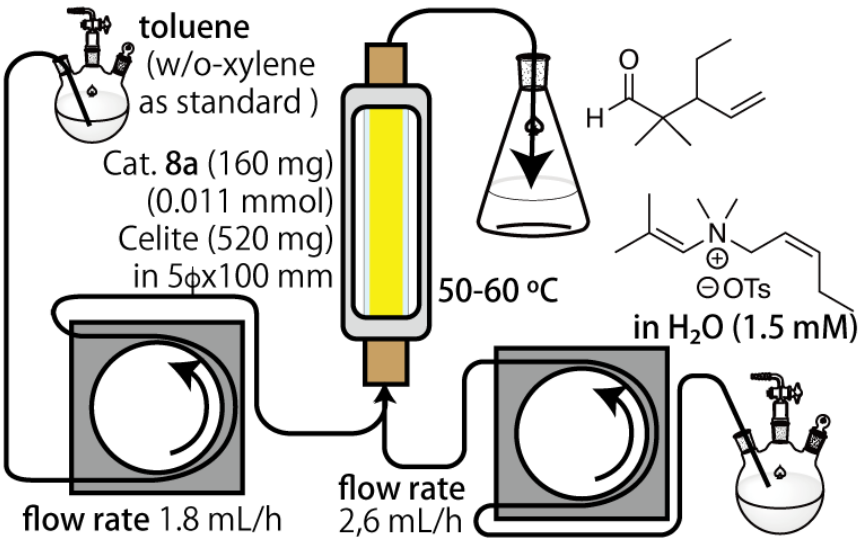
The polymer immobilized cluster catalyst **8a** (80 mg, 0.0055 mmol **2**) and Celite (300 mg) were added to small vial and mixed well under dried conditions. The mixture of catalyst and celite was introduced into the glass column (5ΦX50 mm) equipped with PTFE filter and T-shaped PEEK column bottom-end under dried conditions. The PTFE

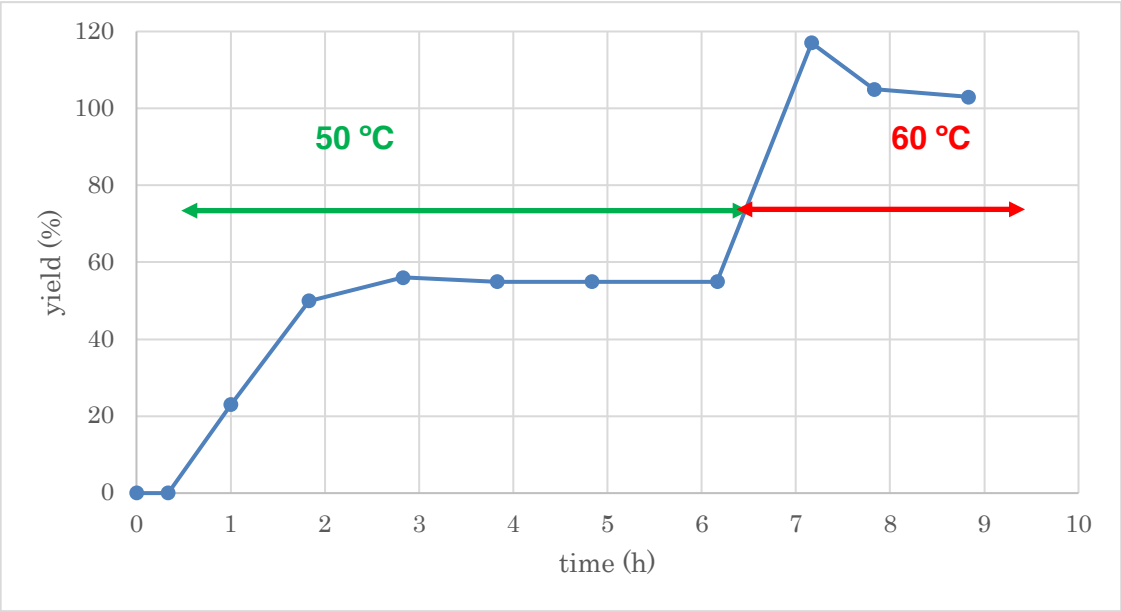
filter and PEEK column top-end were equipped. The two inlets of the T-shaped bottom-end part were connected to the two peristaltic pumps and top-end was connected to the product fraction reservoir.

Substrate **13** (25 mg) was dissolved in 25 mL of H_2O in a volumetric flask and the PTFE, tube which was connected to a peristaltic pump, was inserted and fixed by Parafilm.

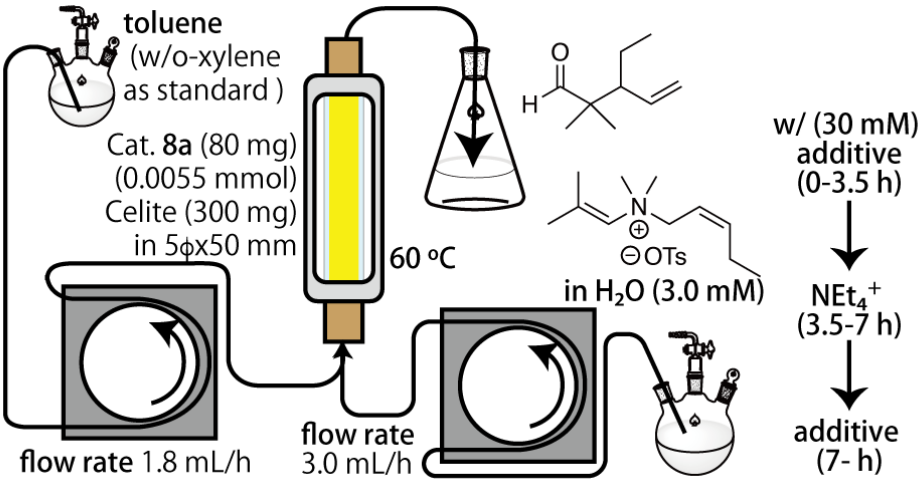
O-xylene (internal standard) (32 mg) was dissolved in 44 g of MeCN in an Erlenmeyer flask and the PTFE tube, which was connected to another peristaltic pump, was inserted into the flask and fixed by Parafilm.

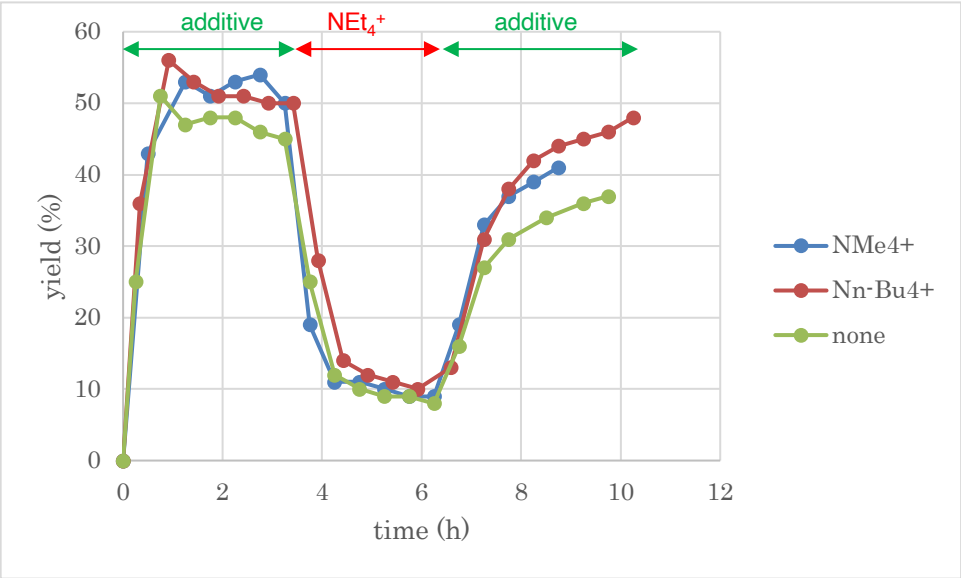
The substrate was pumped at a flow rate of 3.0 mL/h and the MeCN solution was pumped at the flow rate of 1.2 mL/h. The solutions were combined at a T-shape mixer at the bottom-end of the PEEK column and passed through the column, which was dipped in 50 ºC water bath, from bottom to top (up-flow). Then eluted solution was collected in test tubes as fractions at given time intervals. Toluene was added to the fractions and the biphasic solution separated. The toluene layer was collected and analyzed by GC to determine yields of **14** using *o*-xylene as an internal standard.



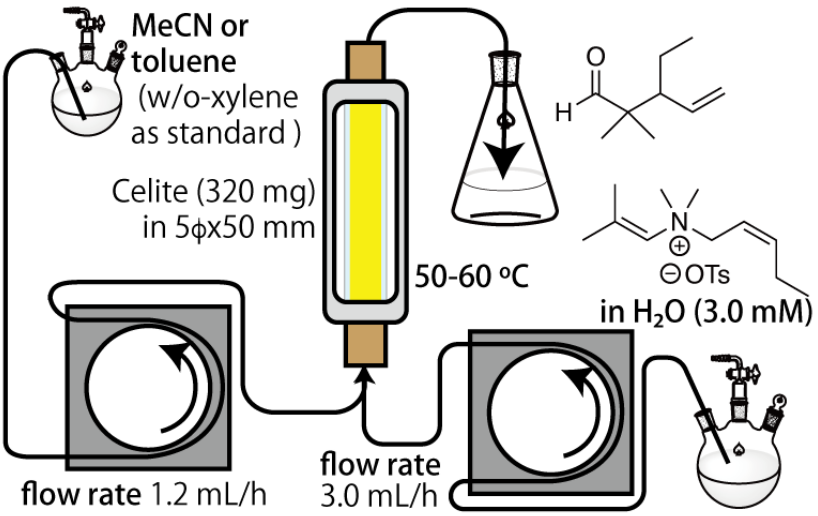


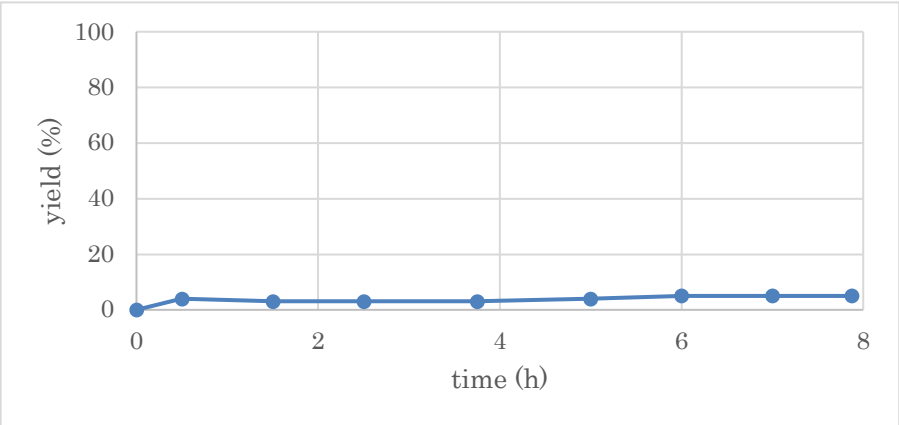
SI_Figure 4. Schematic image of continuous the flow system (upper). Time course of the aza-Prins reaction under continuous-flow conditions (lower) at two temperatures.



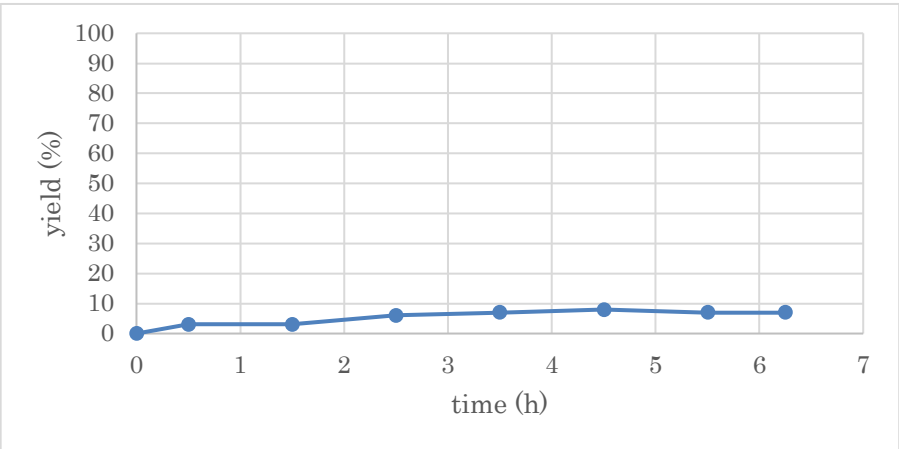


SI_Figure 5. Schematic image of continuous-flow system (upper). Time course of the aza-Cope reaction under continuous-flow conditions (lower) with varying ammonium additives. NMe_4^+ as additive (blue); N*n*-Bu_4^+ as additive (red); no additive (green).





SI_Figure 6. Schematic image of the continuous-flow system (upper). Time course of the background aza-Cope reaction in H_2O-MeCN under continuous-flow conditions (lower) with changing temperatures (50 ºC 0-4.5 h; 60 ºC 4.5 h-).

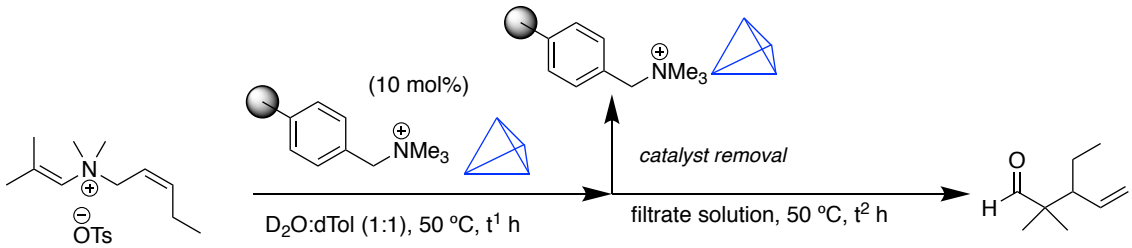


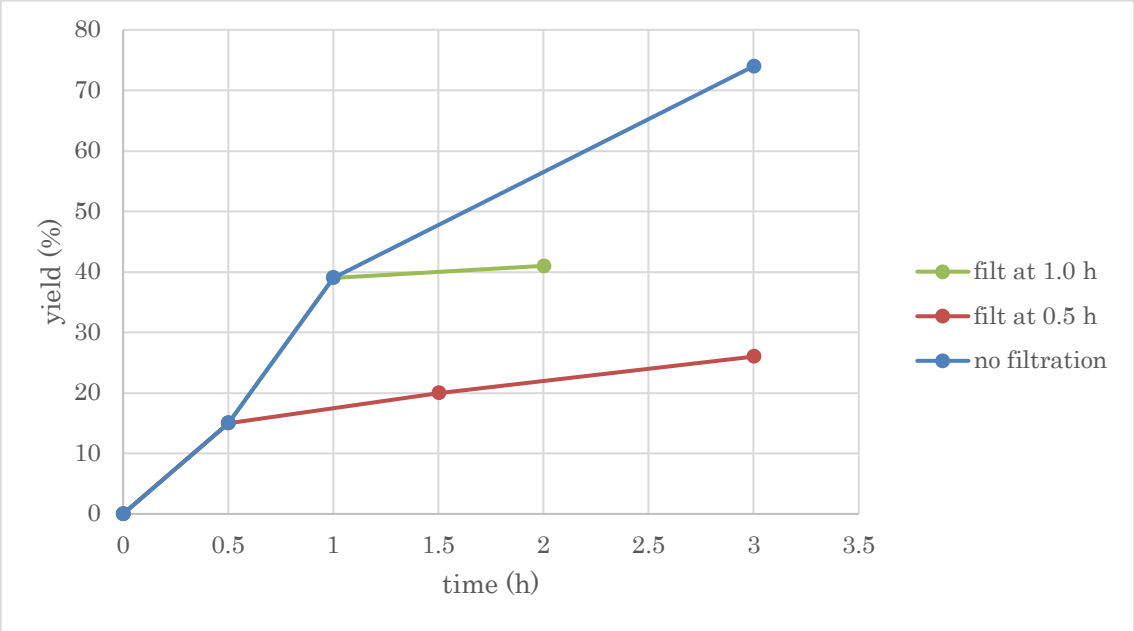
SI_Figure 7. Time course of background the aza-Cope reaction in H_2O-toluene under continuous-flow conditions (lower) with changing temperatures (50 ºC 0-3 h; 60 ºC 3 h-).

4.4 Hot filtration experiments in the aza-Cope reaction.

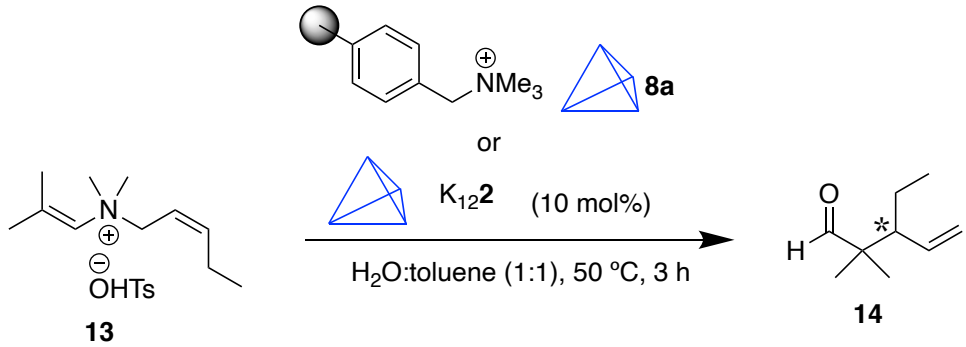
Catalyst **8a** (50 mg), **13** (10.0 mg), *d*-toluene (0.25 mL), *o*-xylene (internal standard) and D_2O (0.25 mL) were combined in a Teflon-lined septum-capped 1-dram vial containing a Teflon coated magnetic stir bar. The mixture was stirred for 0.5 h or 1 h at 50 ºC. The heterogeneous catalyst was removed by syringe filtration without allowing the mixture to cool. An aliquot of the filtrate was analyzed by ^{1}H NMR using *o*-xylene as internal standard to determine yields. The remaining solution was placed in a Teflon-lined septum-capped 1-dram vial containing a Teflon coated magnetic stir bar and stirred for 1 h. The *d*-toluene layer was analyzed by ^{1}H NMR using *o*-xylene as internal standard to determine yields.

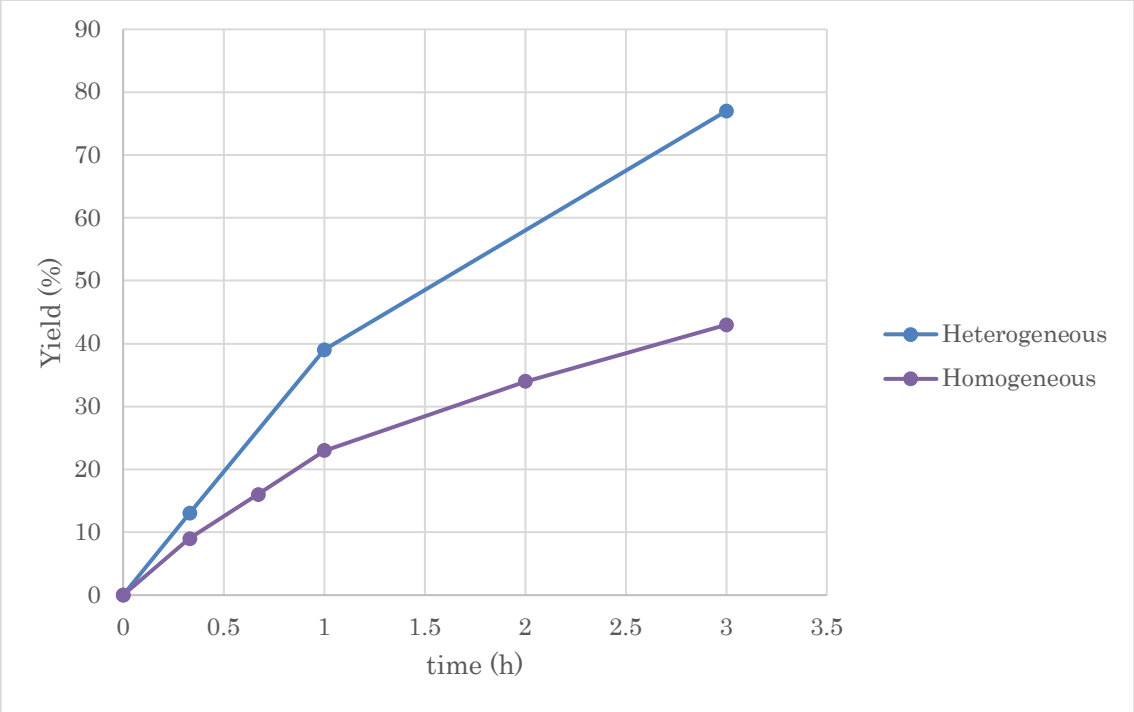
SI_Scheme 1. Hot filtration procedure





SI_Figure 8. Reaction profiles of the aza-Cope reaction w/o filtration (blue), w/ filtration at 0.5 h (red), and w/ filtration at 1 h (green).



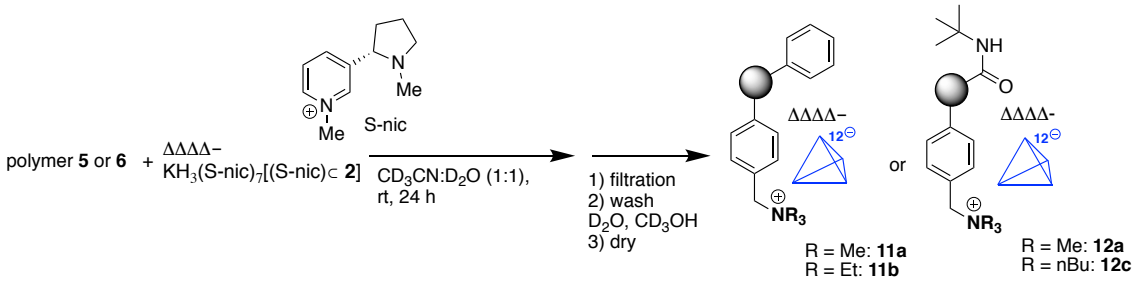


SI_Figure 9. Reaction profiles under homogeneous (K_{12}**2** as catalyst) and heterogeneous conditions (**8a** as catalyst).

4.5 Typical preparation procedure of the polymer-immobilized resolved cluster.

Copolymer **6a** (55.3 mg), resolved cluster **17** (19.0 mg), CD_3CN (0.5 mL) and D_2O (0.5 mL) were combined in a Teflon-lined septum-capped 1-dram vial with a Teflon-coated magnetic stir bar. The resulting mixture was stirred for 24 h at room temperature. The heterogeneous catalyst was separated by filtration from solution and was washed with 1 mL of water-methanol (3:1) on the funnel. The solid catalyst **12a** was collected and dried *in vacuo* at room temperature for more than 2 h.

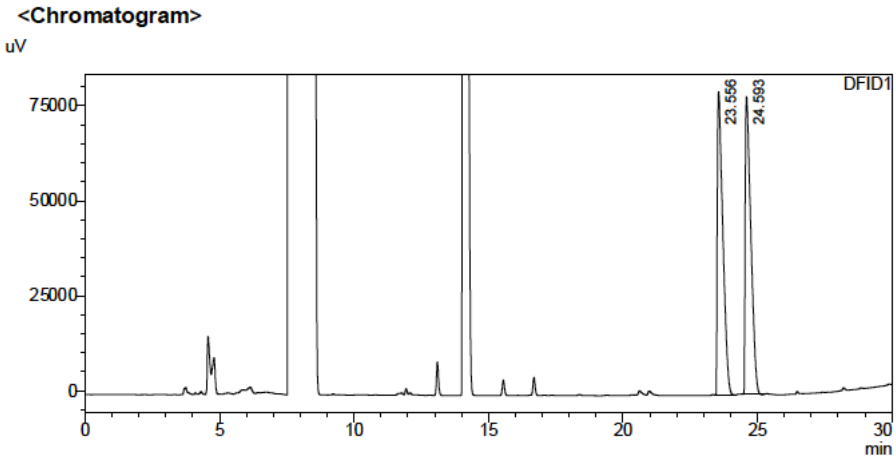
SI_Scheme 2. Immobilization of resolved cluster.



4.6 General procedure for the asymmetric aza-Cope reaction in the batch reactor system (Recovery and reuse procedures).

Catalyst **12a**, **13** (7.0 mg), toluene (0.25 mL) and H_2O (0.25 mL) were combined in a Teflon-lined septum-capped 1-dram vial with a Teflon-coated magnetic stir bar. The mixture was stirred for 3 h at 50 ºC. Toluene (2 mL), containing *o*-xylene (5.0-10 mg) as an internal standard, was added to the reaction mixture and the heterogeneous catalyst was removed by filtration. The toluene layer of the filtrate was analyzed by chiral GC to determine the enantioselectivity and yield of **14**. The filtered catalyst was washed with 1 mL of water-methanol (3:1) on the funnel. The solid catalyst was collected and dried *in vacuo* at room temperature for more than 2 h and then used in the next run.

4.7 GC charts for compound 14

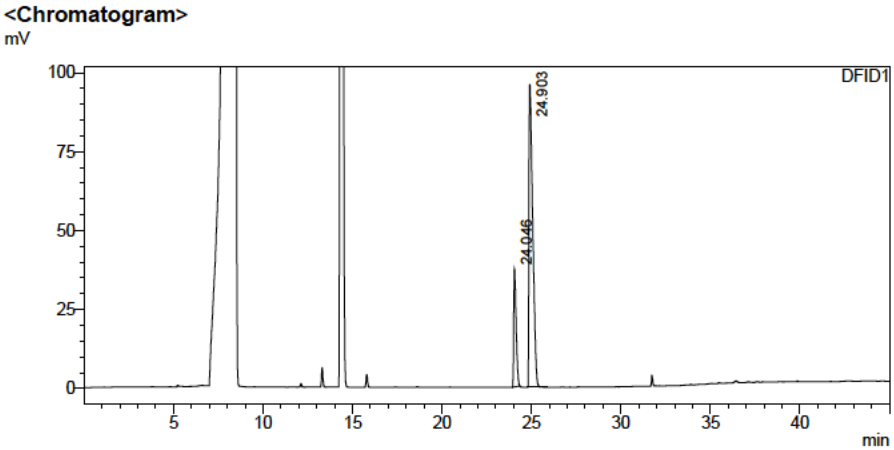


<Peak Table>

DFID1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.556	1140879	79745	50.074		M	
2	24.593	1137500	78211	49.926		M	
Total		2278378	157956				

GC chart of racemic **14**

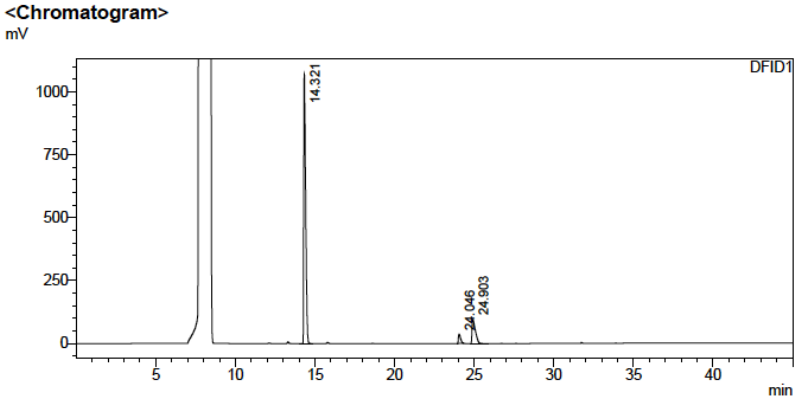


<Peak Table>

DFID1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	24.046	351085	37302	20.056		M	
2	24.903	1399481	95931	79.944		M	
Total		1750566	133233				

GC chart of **14** from asymmetric catalysis (Table 4, entry 3)

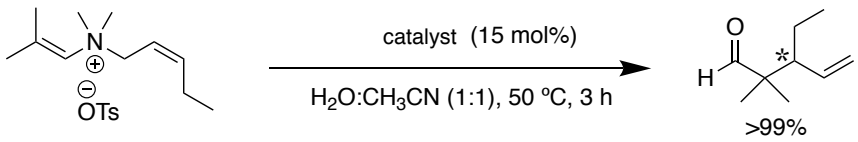


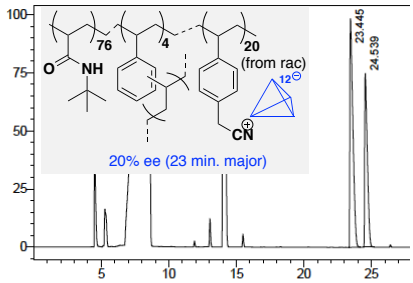
<Peak Table>

DFID1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.321	8983312	1068898	83.691		M	
2	24.046	351085	37302	3.271		M	
3	24.903	1399481	95931	13.038		M	
Total		10733878	1202131				

GC chart with integration of internal standard (*o*-xylene; 14.321 min) (Table 4, entry 3)

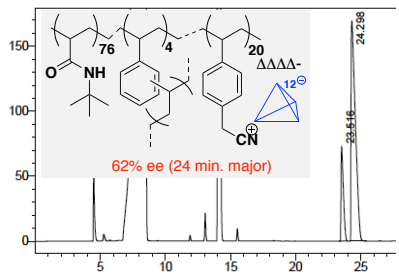




<Peak Table>

DFID1

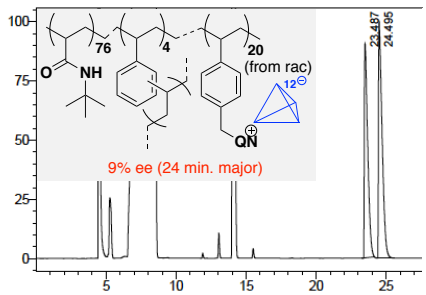
Peak#	Ret. Time	Area	Height	Conc.	Unit	M
1	23.445	1532861	98295	59.945		
2	24.539	1024233	74654	40.055		
Total		2557094	172949			



<Peak Table>

DFID1

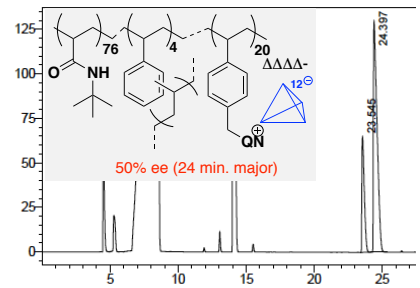
Peak#	Ret. Time	Area	Height	Conc.	Unit	M
1	23.516	910250	72756	19.021		
2	24.298	3875155	169390	80.979		
Total		4785405	242145			



<Peak Table>

DFID1

Peak#	Ret. Time	Area	Height	Conc.	Unit	M
1	23.487	1510143	90331	45.696		
2	24.495	1794644	99703	54.304		
Total		3304786	190034			



<Peak Table>

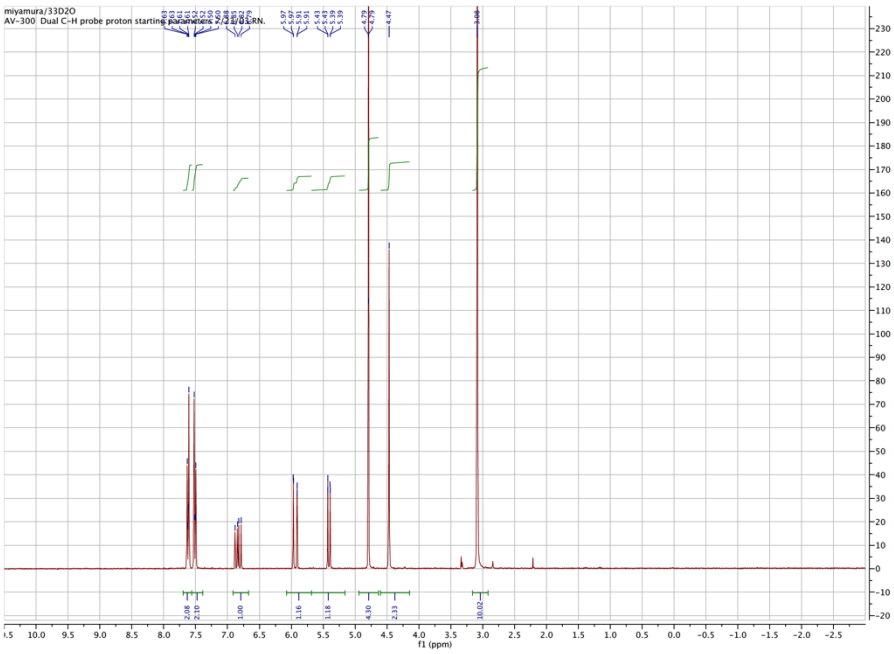
DFID1

Peak#	Ret. Time	Area	Height	Conc.	Unit	M
1	23.545	812103	65157	25.000		
2	24.397	2436357	129910	75.000		
Total		3248460	195067			

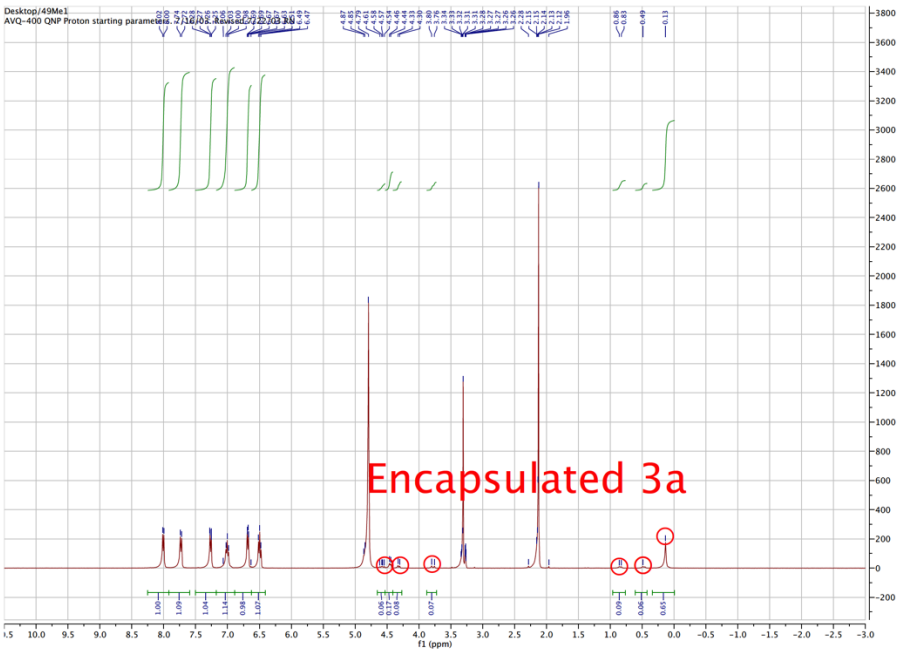
5 *Preparation of samples for ICP analysis (Metal leaching check)*

The solvent and volatile materials of the fractions collected from continuous-flow reactions were removed by evaporation. The residues ~~The comparison of reaction profiles of homogeneous and heterogeneous systems under the same reaction conditions showed faster reaction rate under heterogeneous conditions than homogeneous conditions (SI_Figure 9 for detail of reaction profiles of entries 15 and 16).~~ were transferred into a test tube and 1 mL of sulfuric acid was added. The test tube was heated at 200 ºC and nitric acid was added dropwise until all the solid had dissolved and no additional brown fumes were observed. The mixture was cooled to room temperature and aqua regia (1 mL) was added slowly. The resulting mixture was made up to 50 mL with water in a volumetric flask and the resulting solution was subjected to ICP analysis (Detail of analysis is same as 2.3.1). Detection limit was calculated as 7.02×10^{-5} mmol and observed results were under detection limit (<0.12% Ga leaching).

6 ^{1}H NMR observations for interaction between 2 and monomers or linear polymers.

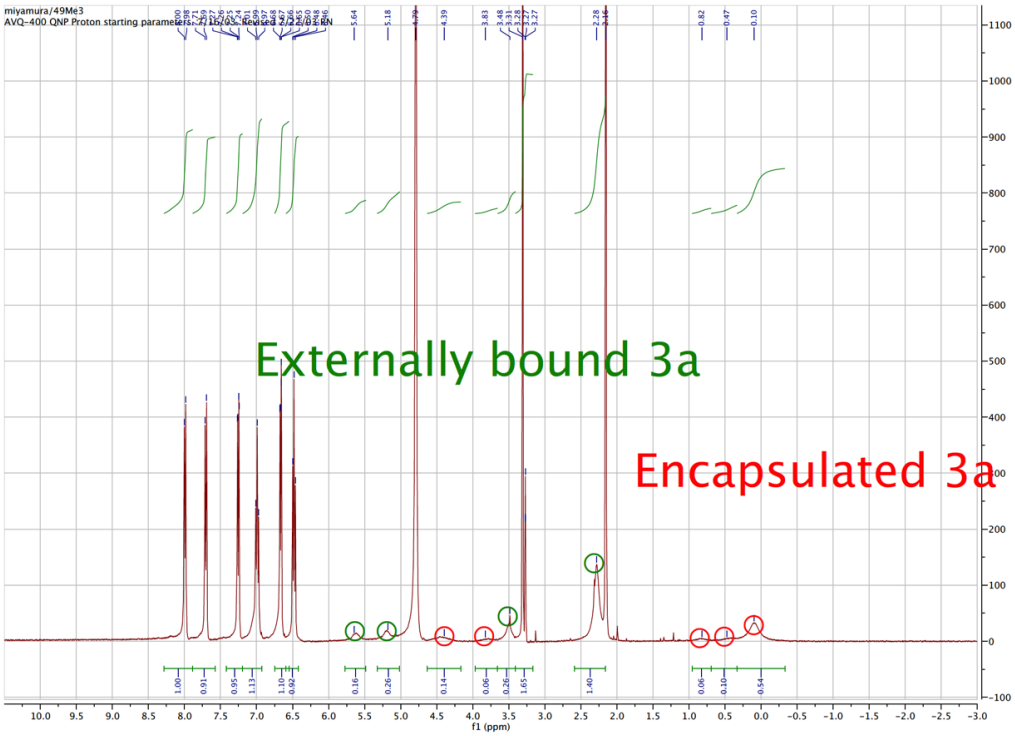


SI_Figure 10. ^{1}H NMR (in D_2O) of **3a**



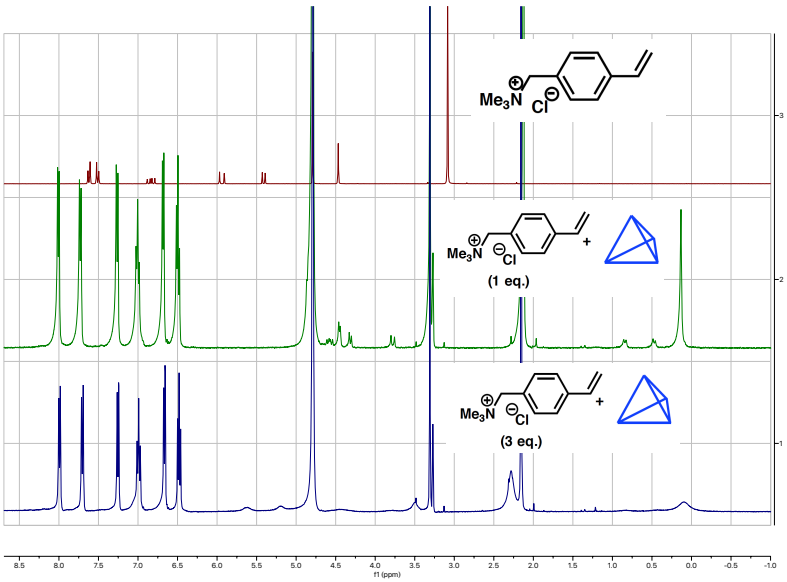
SI_Figure 11. ^{1}H NMR (in D_2O-CD_3OD) of **3a** : **2 = 1:1 (mol)**

3a is fully encapsulated by **2**.

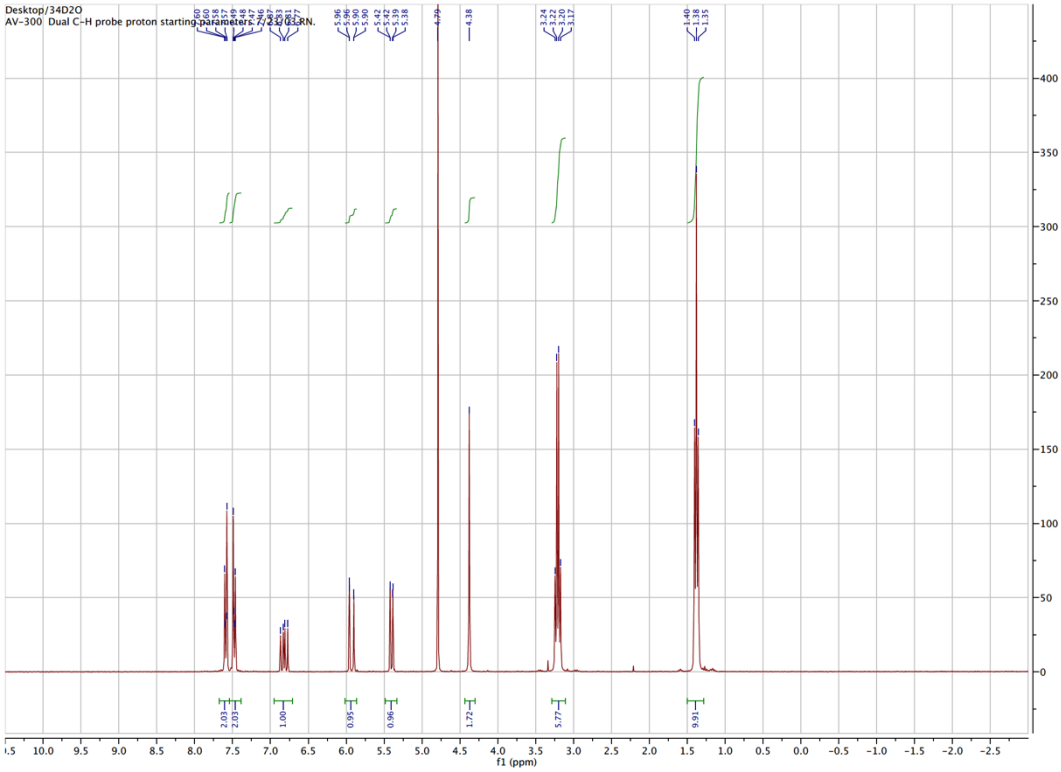


SI_Figure 12. ^{1}H NMR (in D_2O-CD_3OD) of **3a** : **2 = 3:1 (mol)**

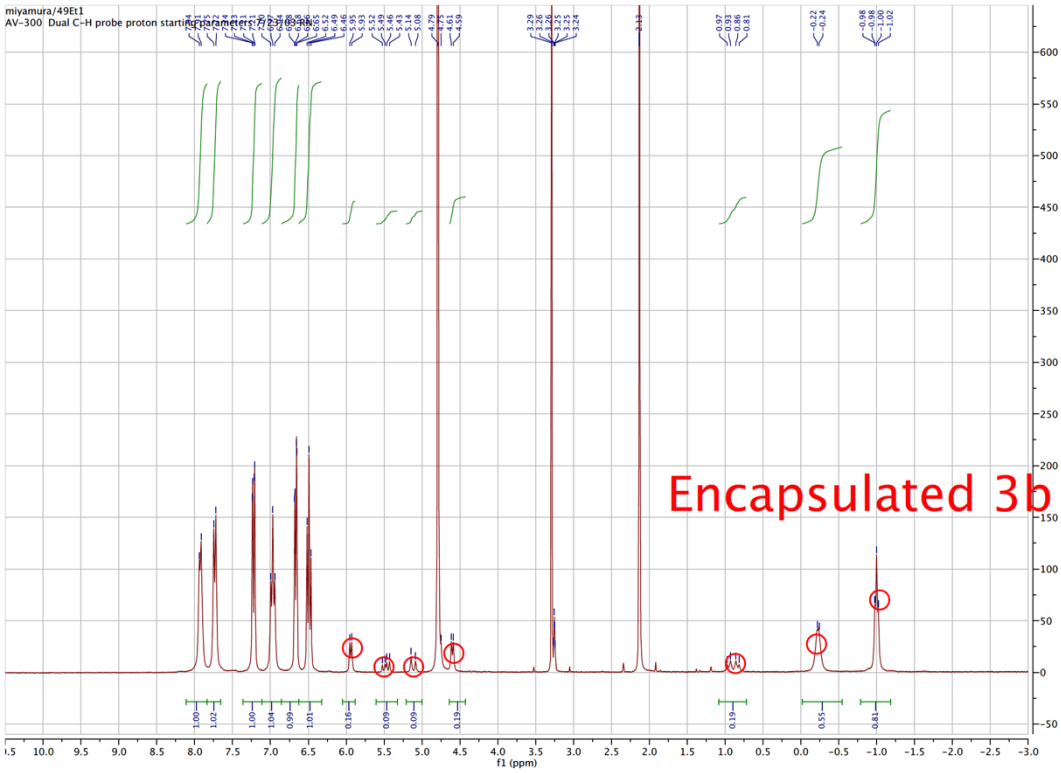
1 equivalent of **3a** is encapsulated by **2** and 2 equivalents of **3a** interacts with **2** externally. There is quick exchange between encapsulated **3a** and external **3a,** resulting in peak broading.



SI_Figure 13. Stack of SI_Figures 10-12 **3a+2**

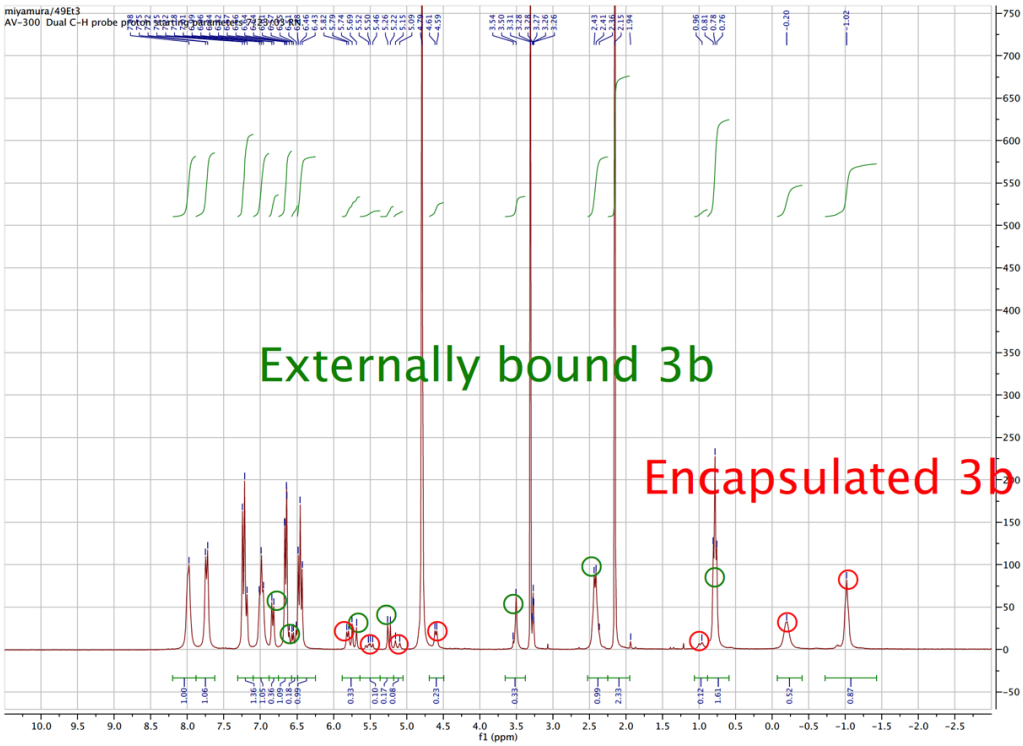


SI_Figure 14. ^{1}H NMR (in D_2O) of **3b**



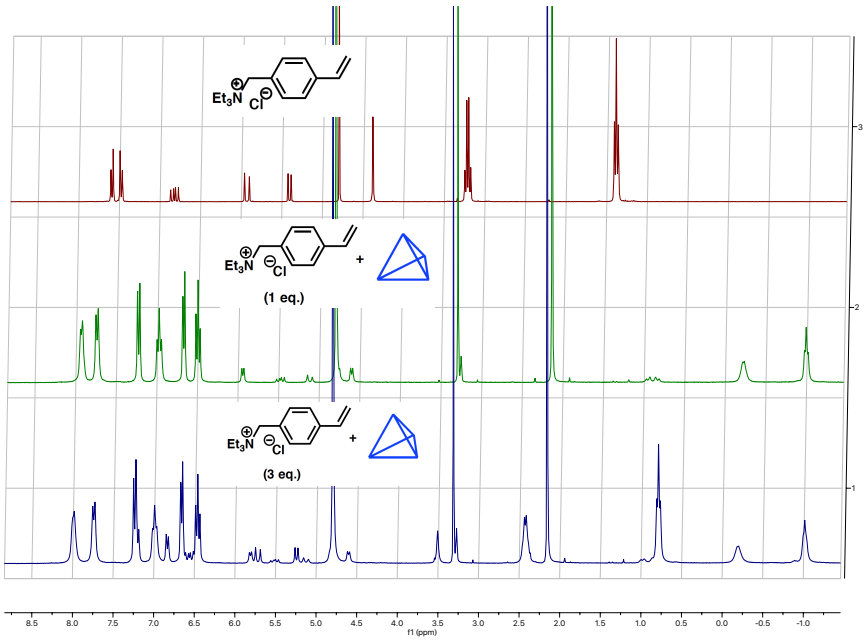
SI_Figure 15. ^{1}H NMR (in D_2O-CD_3OD) of **3b** : **2 = 1:1 (mol)**

3b is fully encapsulated by **2**.

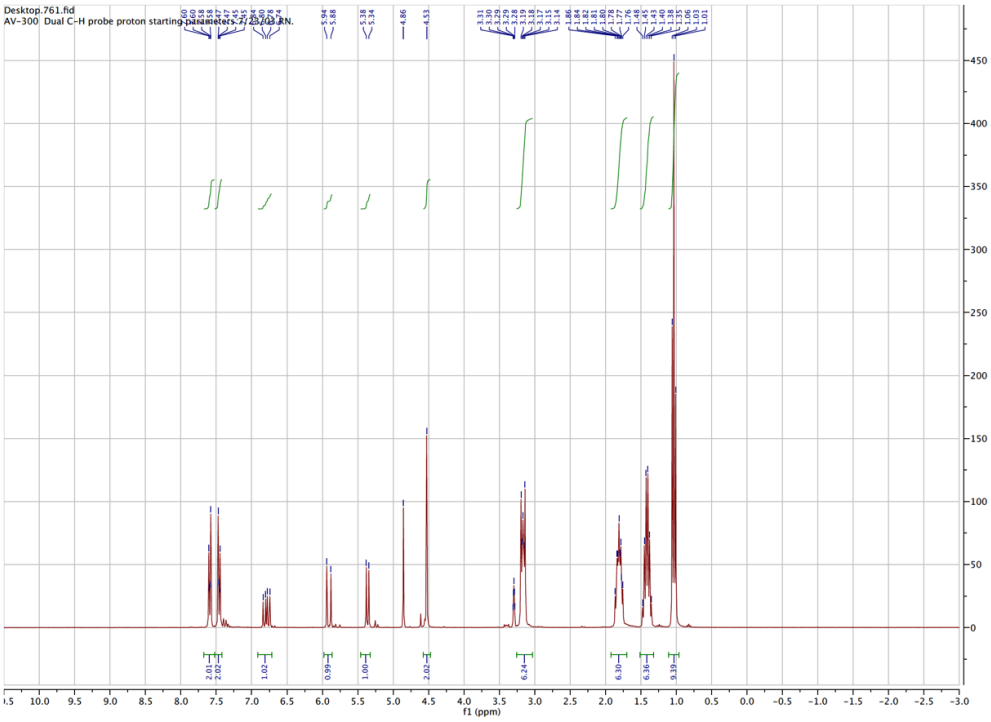


SI_Figure 16. ^{1}H NMR (in D_2O-CD_3OD) of **3b** : **2 = 3:1 (mol)**

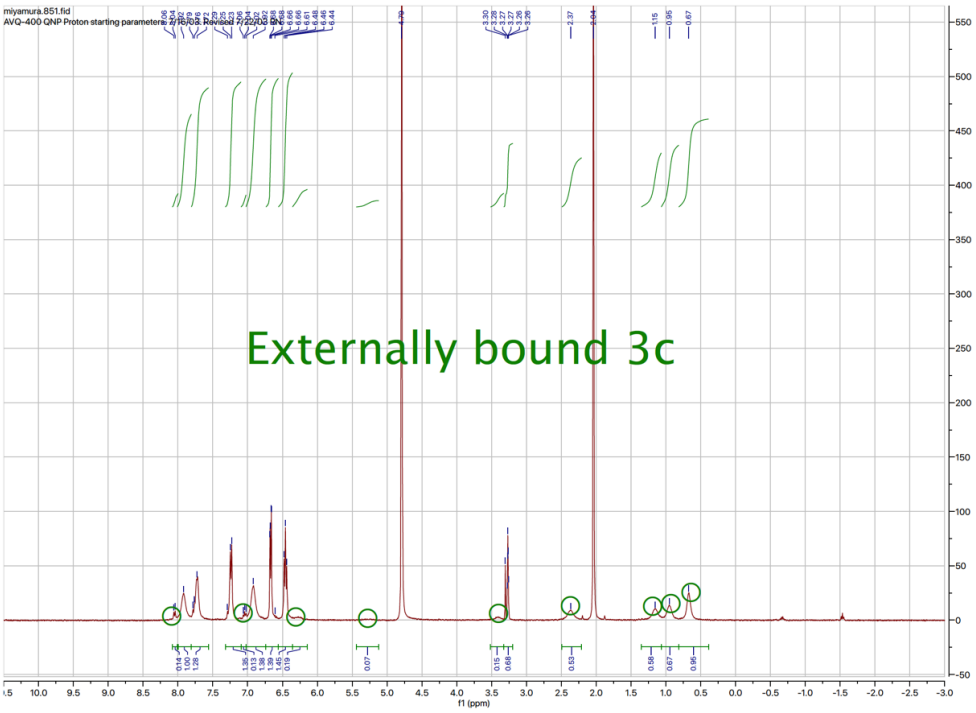
1 equivalent of **3b** is encapsulated by **2** and 2 equivalents of **3b** interacts with **2** externally. Speed of exchange of encapsulated **3b** and external **3b** is relatively slow, thus peaks are sharp.



SI_Figure 17. Stack plots of 1H-NMR spectra from SI_Figures 14-16 **3b+2.**

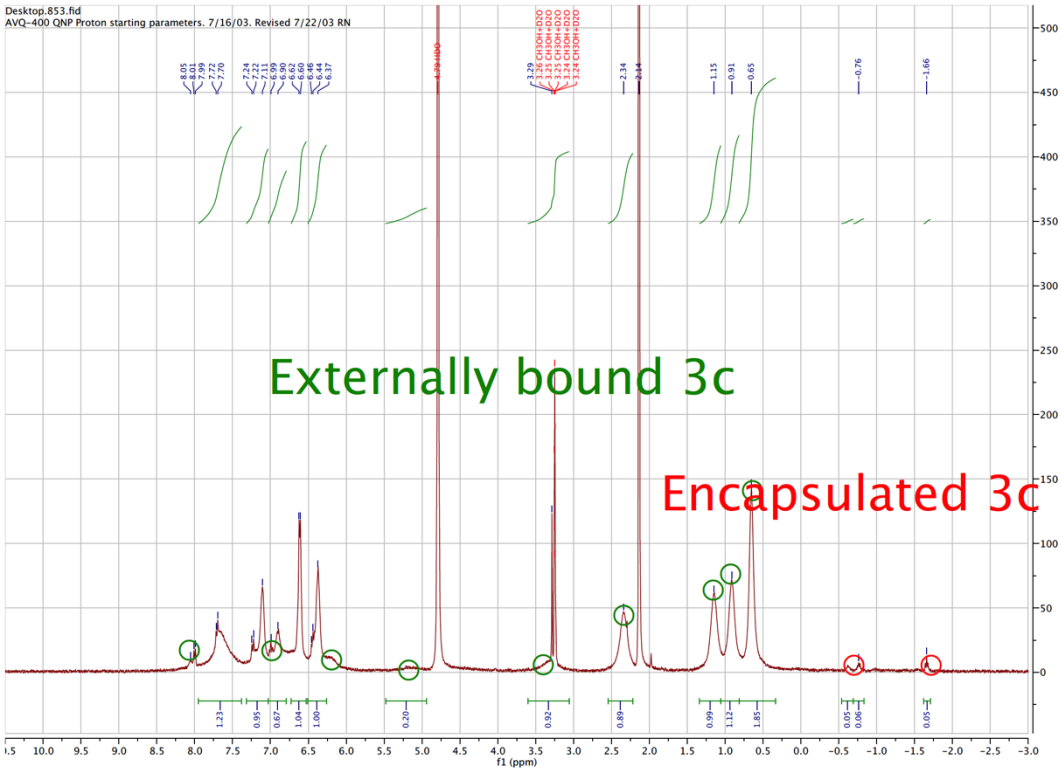


SI_Figure 18. ^{1}H NMR (in CD_3OD) of **3c**



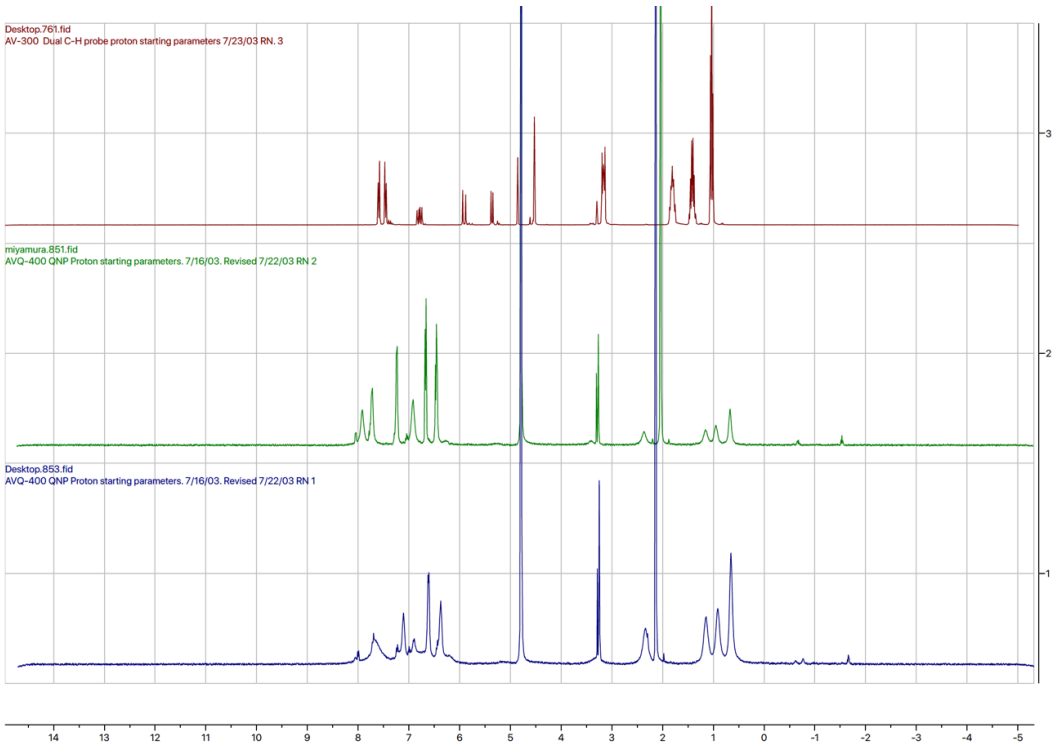
SI_Figure 19. ^{1}H NMR (in D_2O-CD_3OD) of **3c** : **2 = 1:1 (mol)**

Most of **3c** interacts with **2** externally.

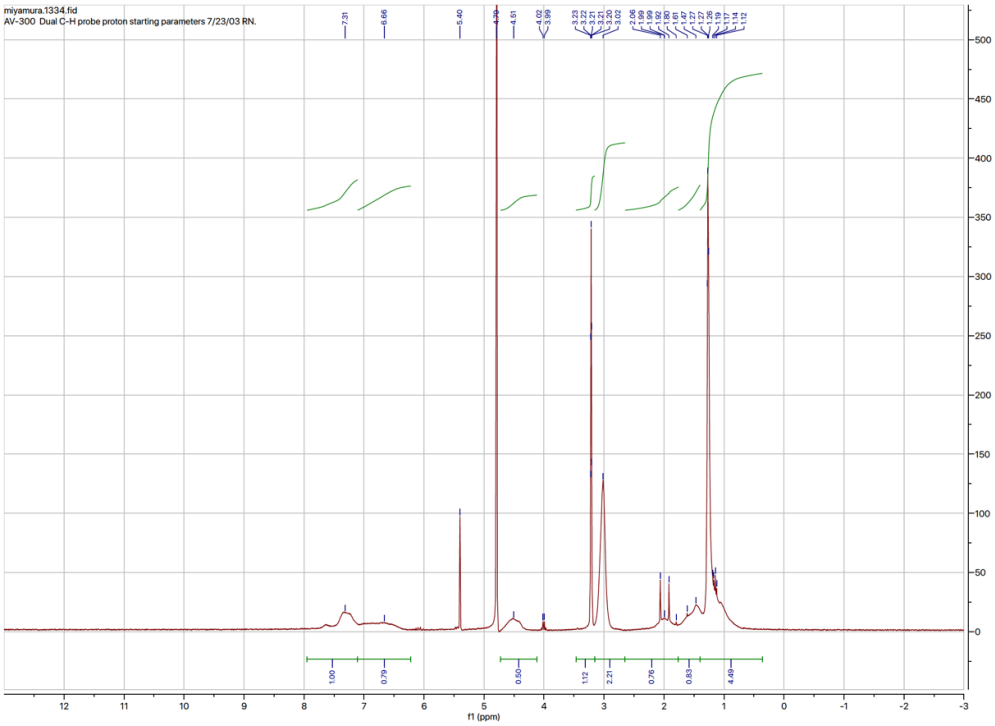


SI_Figure 20. ^{1}H NMR (in D_2O-CD_3OD) of **3c** : **2 = 3:1 (mol)**

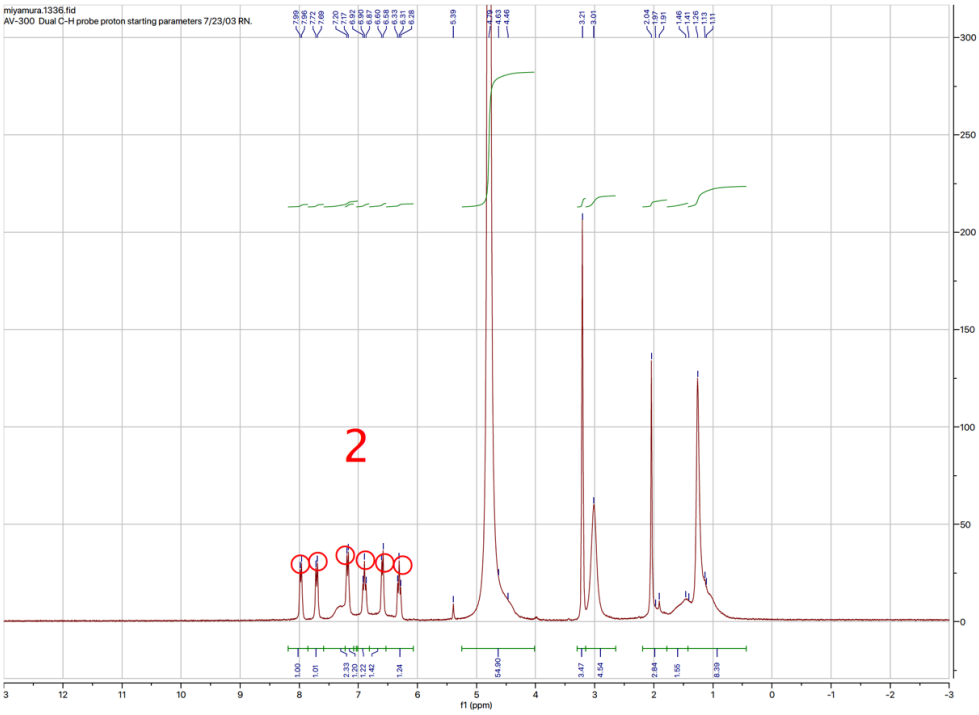
Most of **3c** interacts with **2** externally and trace amount of **3c** is encapsulated.



SI_Figure 21. Stack plots of ^{1}H-NMR spectra from from SI_Figures 18-20 **3c+2**

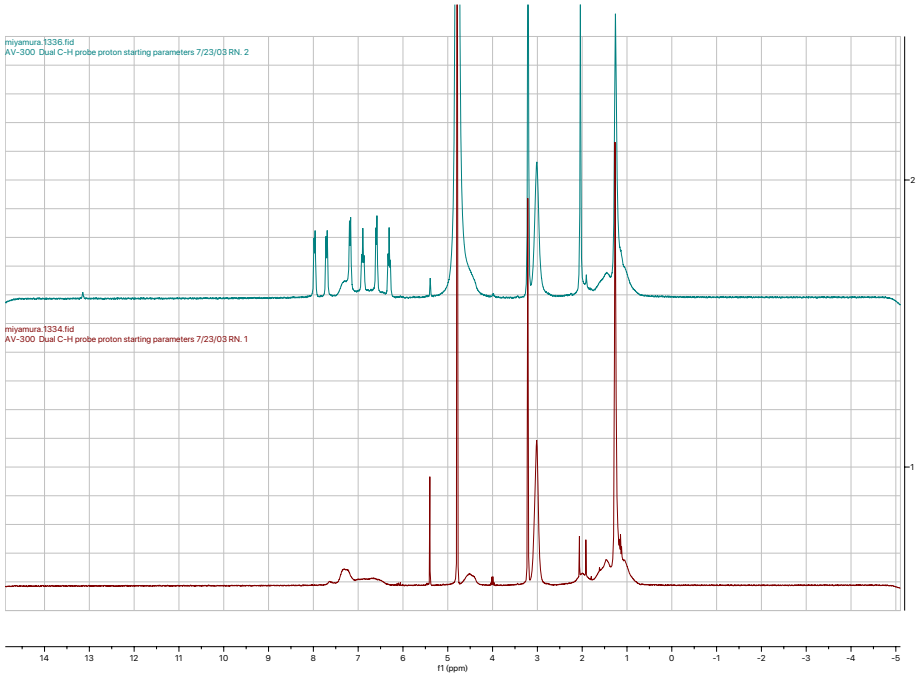


SI_Figure 22. ^{1}H NMR (in D_2O-CD_3OD) of **4a**

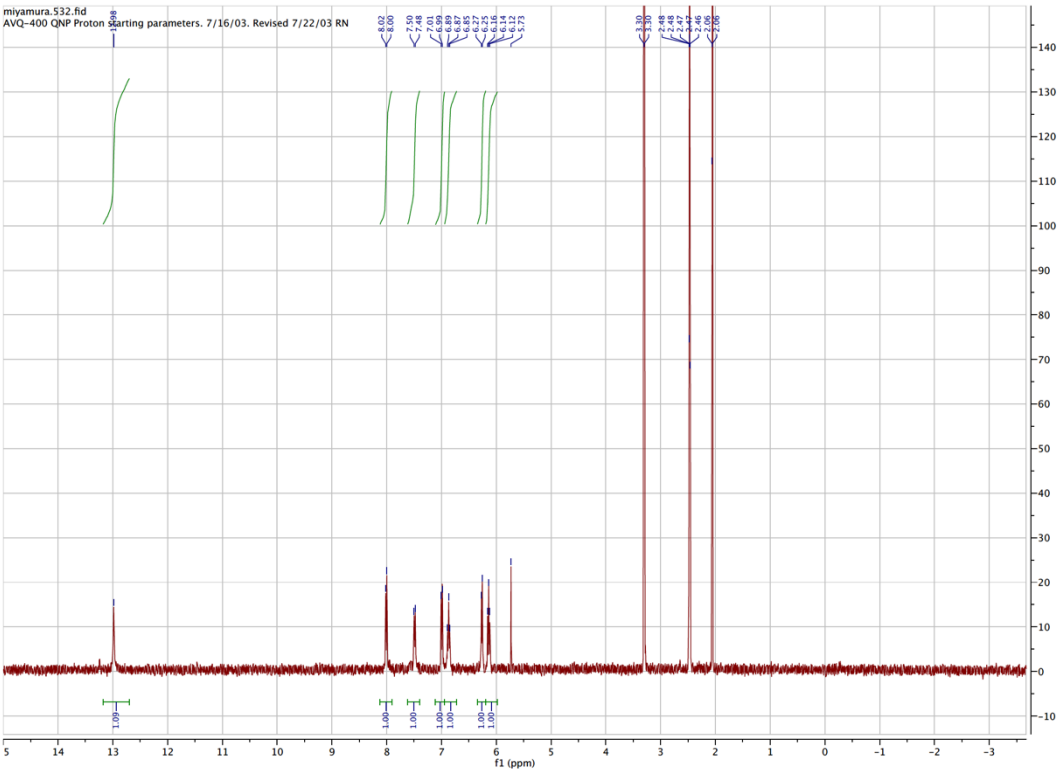


SI_Figure 23. ^{1}H NMR (in D_2O-CD_3OD) of **4a** + **2**

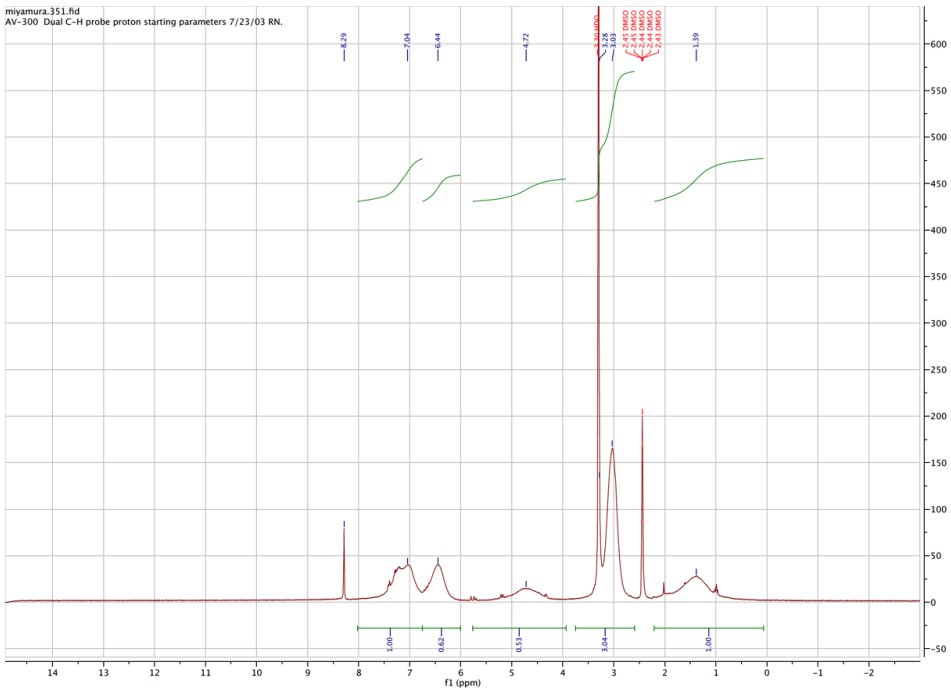
The absence of changes in the chemical shifts of polymer residues indicates they are not encapsulated by **2**.



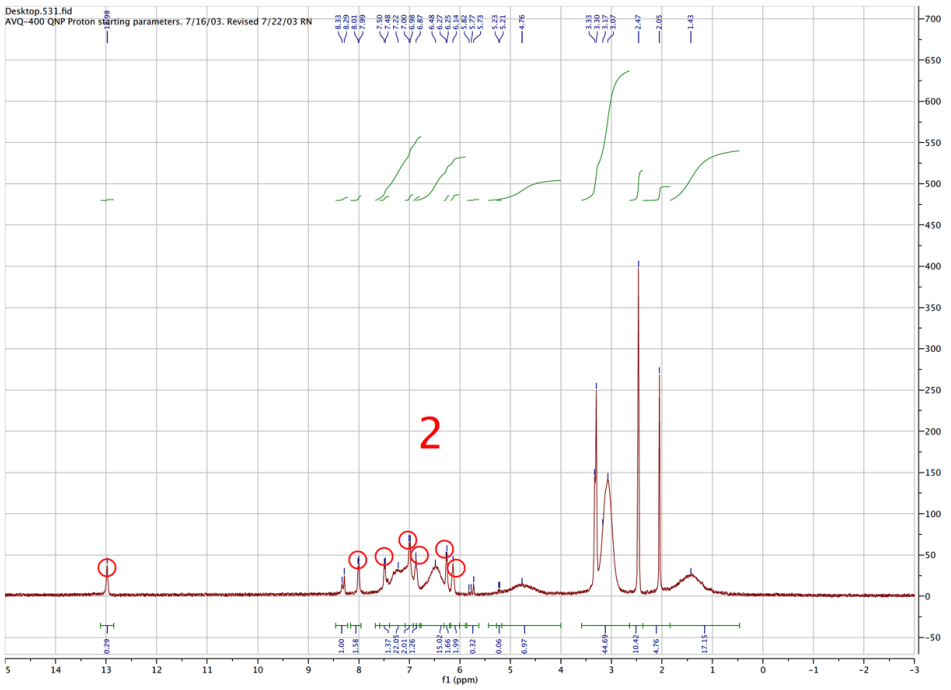
SI_Figure 24. Stack plots of ^{1}H-NMR spectra from SI_Figures 22-23 **4a+2**



SI_Figure 25. ^{1}H NMR (in *d*-DMSO) of **2**

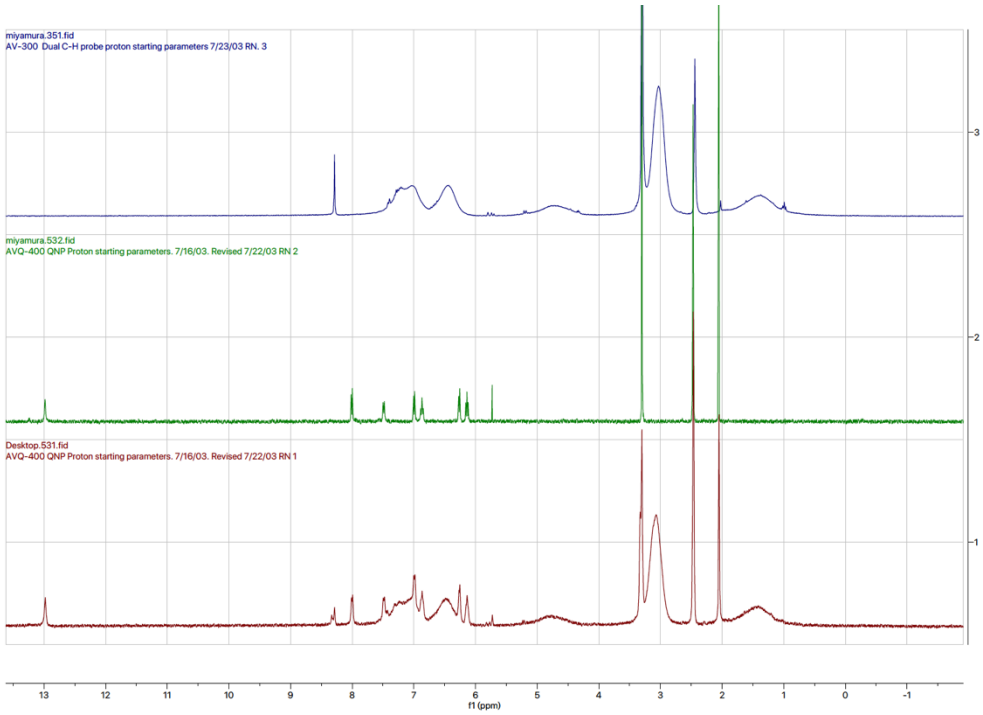


SI_Figure 26. ^{1}H NMR (in *d*-DMSO) of **4b**

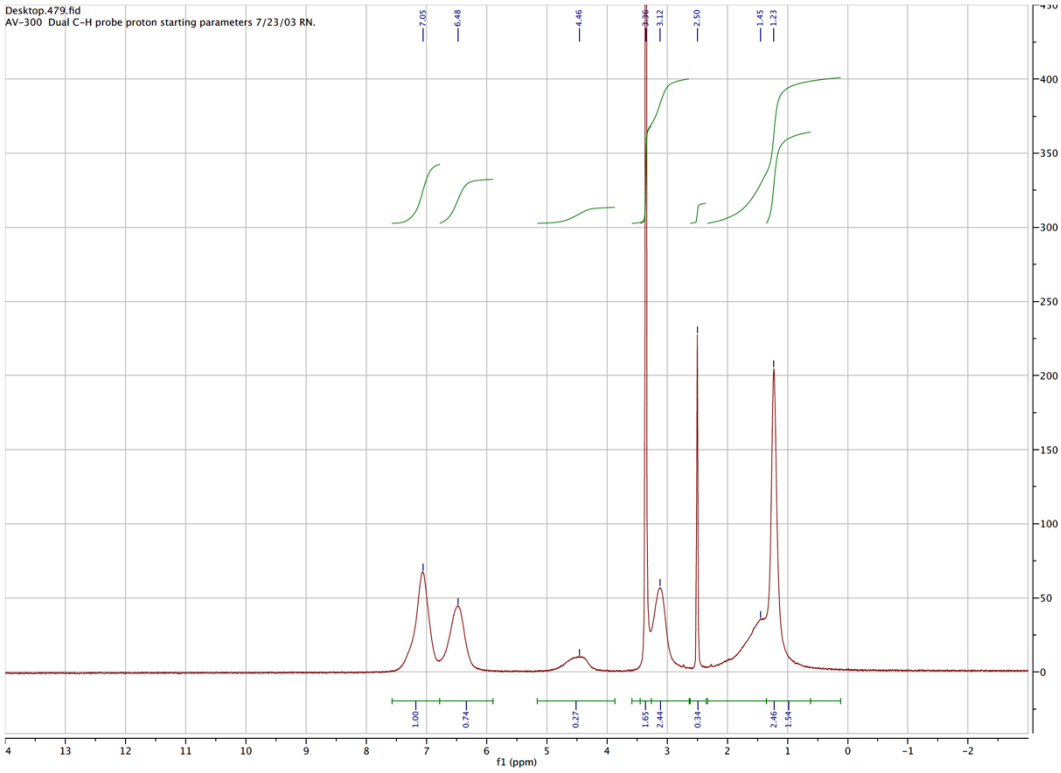


SI_Figure 27. ^{1}H NMR (in *d*-DMSO) of **4b+2**

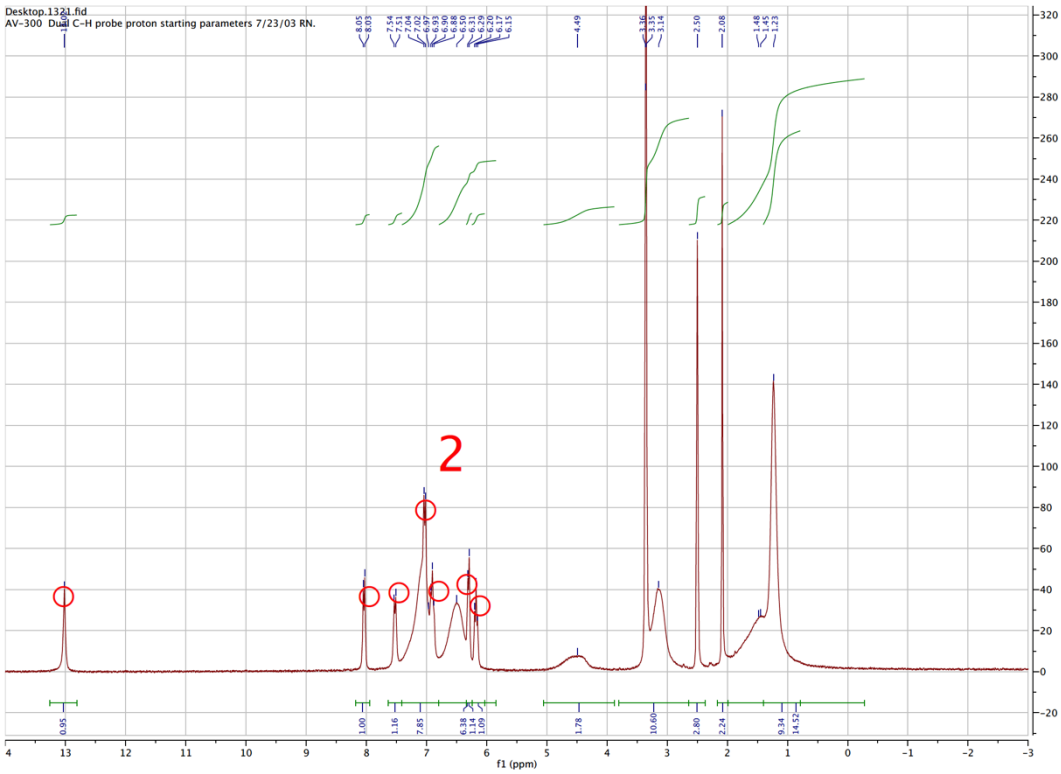
The absence of changes in the chemical shifts of polymer residues indicates they are not encapsulated by **2**.



SI_Figure 28. Stack of SI_Figures 25-27 **4b+2**

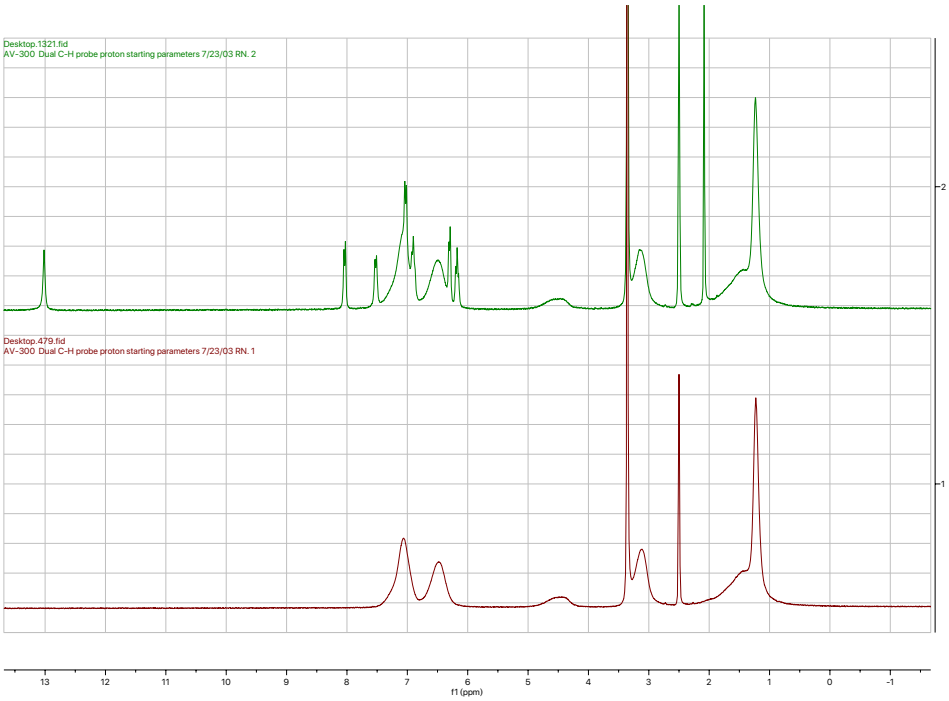


SI_Figure 29. ^{1}H NMR (in *d*-DMSO) of **4c**



SI_Figure 30. ^{1}H NMR (in *d*-DMSO) of **4c+2**

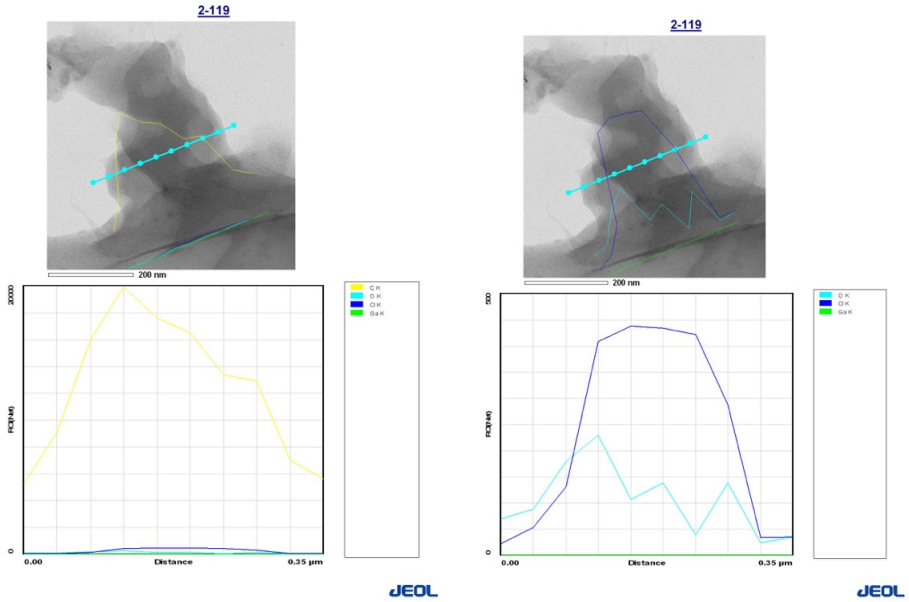
The absence of changes in the chemical shifts of polymer residues indicates they are not encapsulated by **2**.



SI_Figure 31. Stack of SI_Figures 29-30 **4c+2**

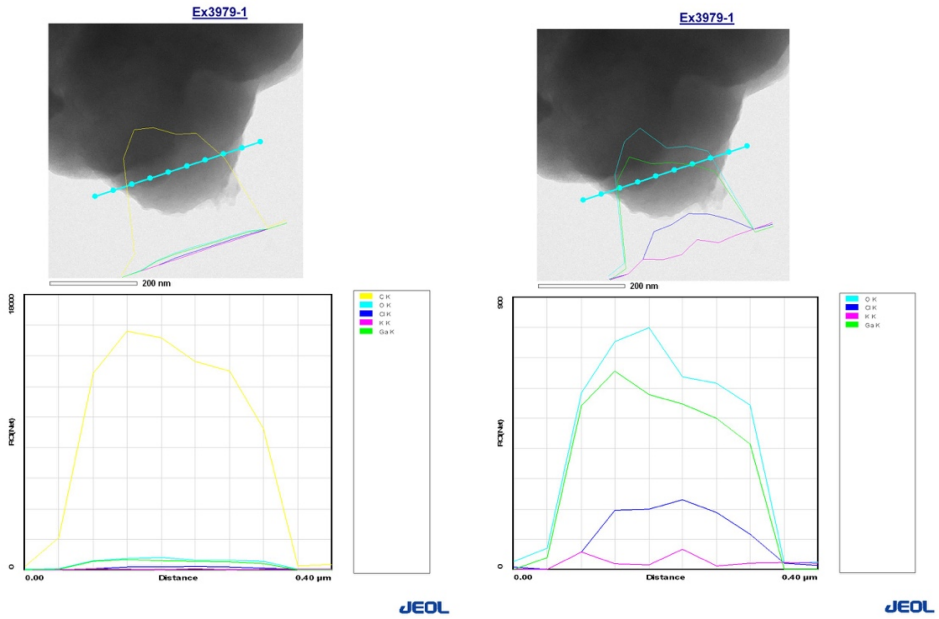
7 *STEM and EDS analysis*

Polymer 6a

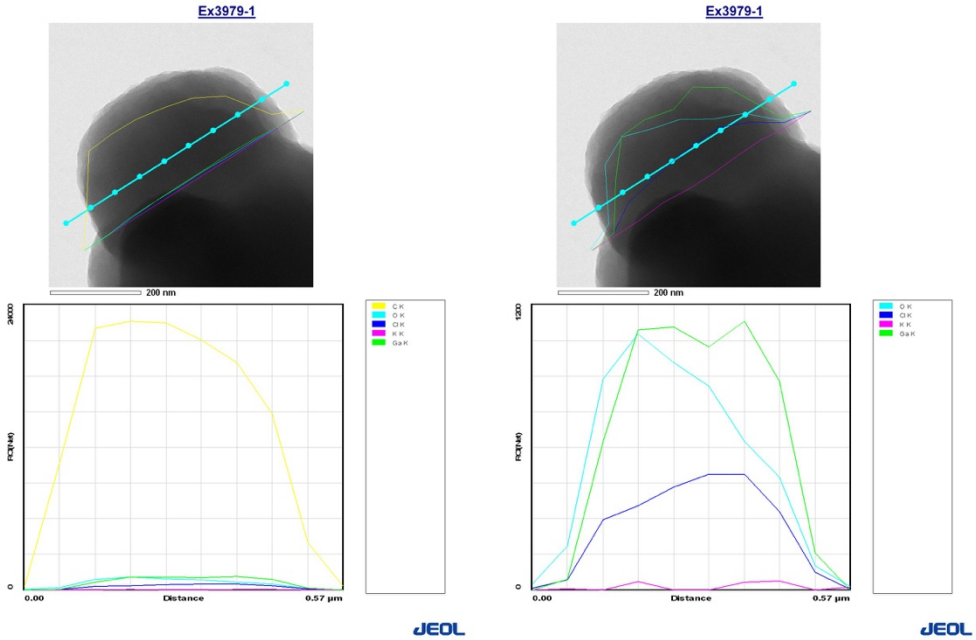


SI_Figure 32. STEM-EDS line analysis of polymer **6a** (Elements: C, O, Cl, Ga [Left]; O, Cl, Ga [Right])

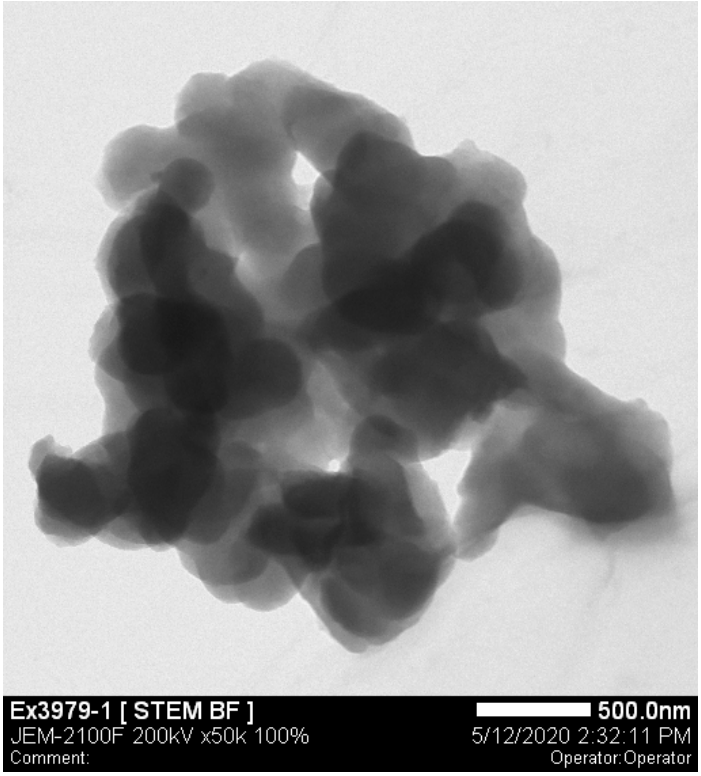
Catalyst 8a before use



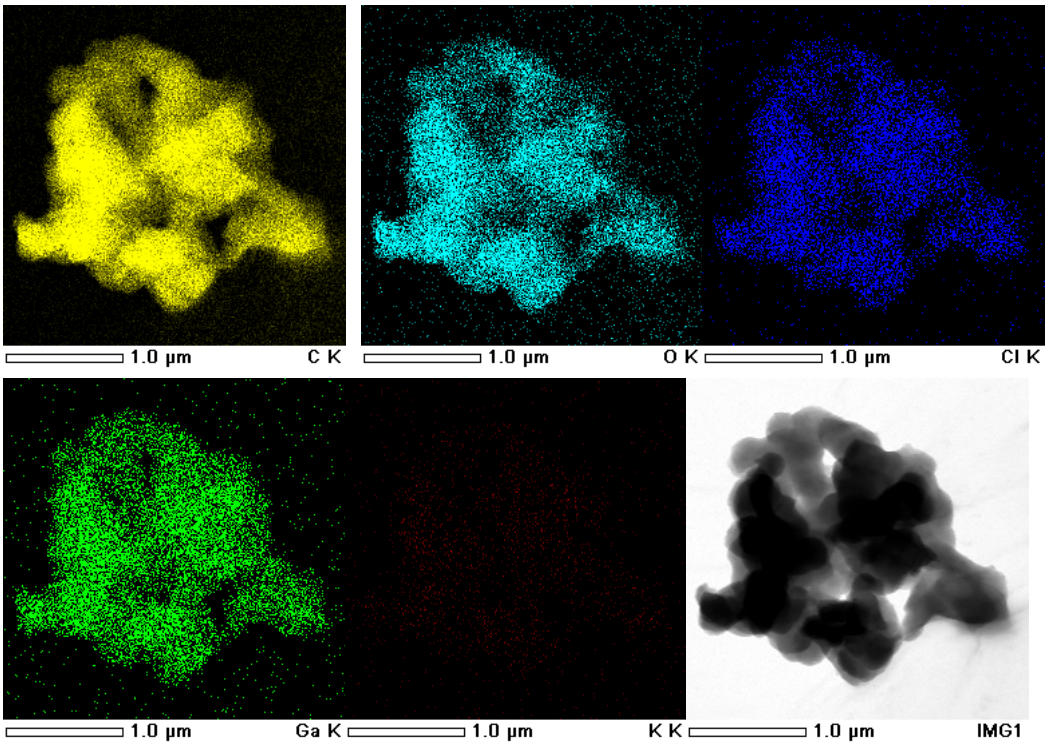
SI_Figure 33. STEM-EDS line analysis of catalyst **8a** (Elements: C, O, Cl, K, Ga [Left]; O, Cl, K, Ga [Right])



SI_Figure 34. STEM-EDS line analysis of catalyst **8a** (Elements: C, O, Cl, K, Ga [Left]; O, Cl, K, Ga [Right])

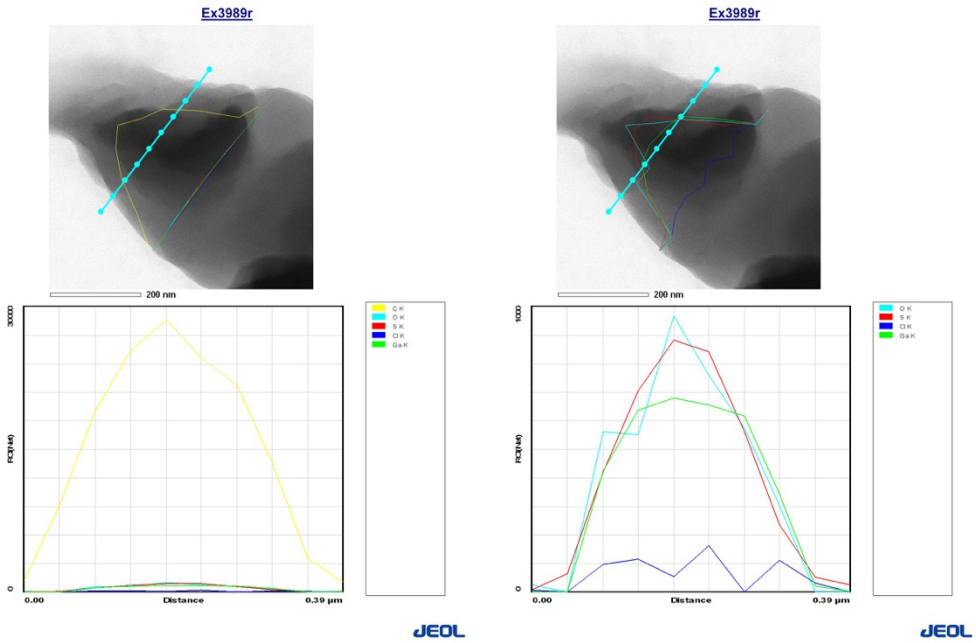


SI_Figure 35. STEM analysis of catalyst **8a**

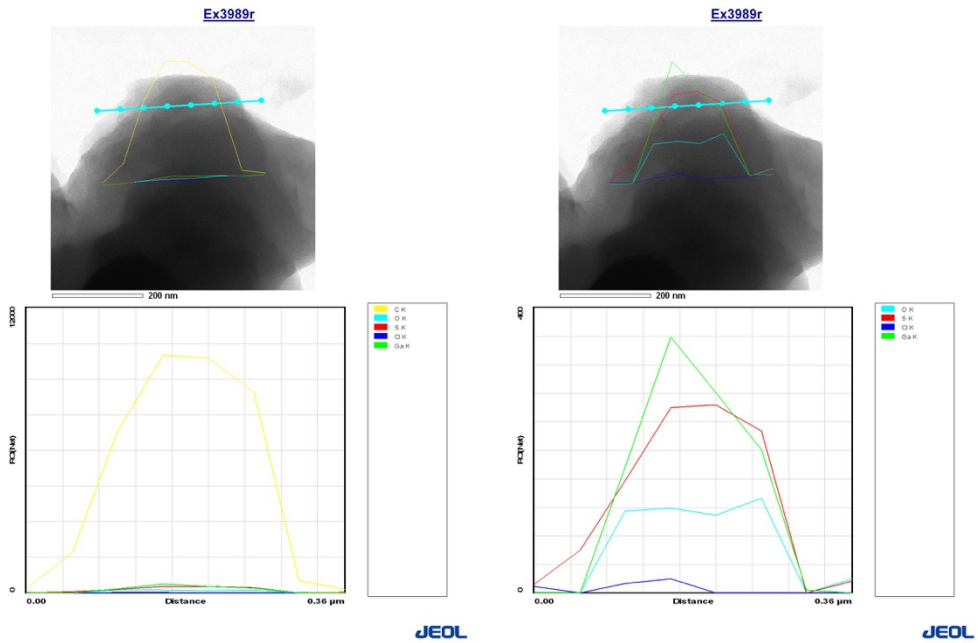


SI_Figure 36. STEM-EDS mapping analysis of catalyst **8a** (Elements: C, O, Cl, Ga, K)

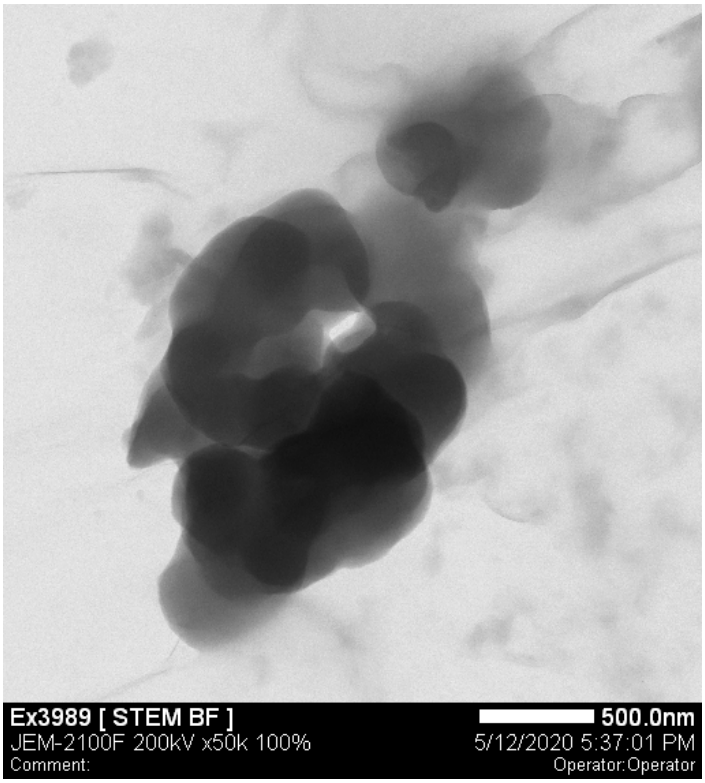
Catalyst 8a after use



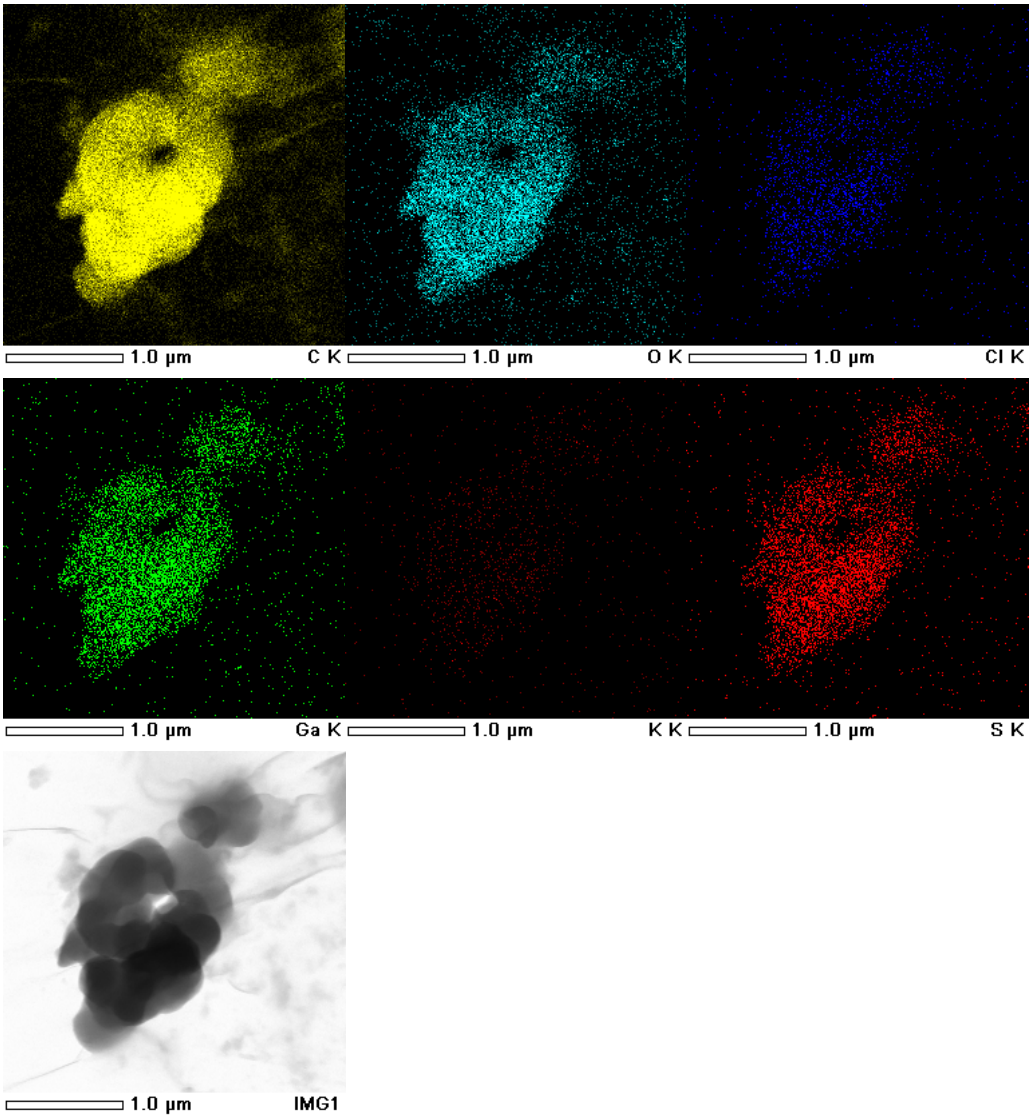
SI_Figure 37. STEM-EDS line analysis of catalyst **8a** after use (Elements: C, O, Cl, Ga, S [Left]; O, Cl, Ga, S [Right])



SI_Figure 38. STEM-EDS line analysis of catalyst **8a** after use (Elements: C, O, Cl, Ga, S [Left]; O, Cl, Ga, S [Right])



SI_Figure 39. STEM analysis of catalyst **8a** after use



SI_Figure 40. STEM-EDS mapping analysis of catalyst **8a** after use (Elements: C, O, Cl, Ga, K, S)

8 References

(1) (a) Hong, C. M.; Morimoto, M.; Kapustin, E. A.; Alzakhem, N.; Bergman, R. G.; Raymond, K. N.; Toste, F. D., Deconvoluting the role of charge in a supramolecular catalyst. *J. Am. Chem. Soc.* **2018,** *140*, 6591-6595; (b) Davis, A. V.; Fiedler, D.; Ziegler, M.; Terpin, A.; Raymond, K. N., Resolution of chiral, tetrahedral m4l6 metal–ligand hosts1. *J. Am. Chem. Soc.* **2007,** *129*, 15354-15363.

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