A mechanistic investigation of the Suzuki polycondensation reaction using MS/MS methods

SUPPORTING INFORMATION

Michelle Y. C. Ting, Lars P. E. Yunker, Ian C. Chagunda, Katherine Hatlelid, Meghan Vieweg, J. Scott McIndoe*

Department of Chemistry, University of Victoria,
PO Box 1700 STN CSC, Victoria, BC V8W 2Y2, Canada.
Fax: +1 (250) 721-7147; Tel: +1 (250) 721-7181; E-mail: mcindoe@uvic.ca

Mass Spectrometry Analysis

Full scan – MS Tuning parameters

The capillary voltage was held at 3 kV, cone voltage at 14 V, extraction cone voltage at 3 V, and RF lens at 0.3 V. The desolvation settings were optimized: desolvation gas flow rate 100 L/h, cone gas flow 200 L/h, source temperature 79°C, desolvation temperature 180°C. Mass range was set to *m/z* 50 –1800; scan duration was 1 second; LM and HM resolution were set to 12.0 and a total number 4497 scans were collected.

Selected ion recording – MS Tuning parameters

The capillary voltage was held at 3 kV, cone voltage at 14 V, and extraction cone voltage at 3 V and RF lens at 0.3 V. The desolvation settings were optimized: desolvation gas flow rate 300 L/h, cone gas flow 200 L/h, source temperature 79°C, desolvation temperature 175°C. LM and HM resolution were set to 12.0 and a total of 2553 scans were collected. Sixteen channels were set up with 0.1 second dwell time and 2 Da span on each channel.

Neutral loss scan - collision-induced dissociation tuning parameters

Two functions of the neutral loss scan were set up to detect precursor ions with a 262 Da neutral loss of the triphenylphosphine (PPh_3) at two collision-induced dissociation voltages. Function 1 was set up to detect aryl species at low mass range *m/z* 300-1000 with CID set to 35 V. Function 2 was set up to detect palladium-containing species at high mass range *m/z* 900-1800 with CID at 15 V. Both functions were set to have 1 second scan time and same collision gas flow 0.22 mL/min.

MS Tuning parameter

The capillary voltage was held at 3.1 kV, cone voltage at 14 V, and extraction cone voltage at 2 V and RF lens at 0.3 V. The desolvation settings were optimized: desolvation gas flow rate 300 L/h, cone gas flow 150 L/h, source temperature 79°C, desolvation temperature 150°C. LM and HM

resolution were set to 13 and a total of 1279 and 1278 scans were collected for Function 1 and Function 2.

Multiple reaction monitoring – MS Tuning parameters

The capillary voltage was held at 3.1 kV, cone voltage at 13 V, and extraction cone voltage at 3 V and RF lens at 0.3 V. The desolvation settings were optimized: desolvation gas flow rate 300 L/h, cone gas flow 200 L/h, source temperature 80℃, desolvation temperature 150℃. LM and HM resolution were set to 13 and a total of 2821 scans were collected. The MRM mass selection data is summarized in Table SI 1.

Product ion scan – CID tuning conditions

All MS/MS spectra were collected using PSI-ESI-MS and the SPC reactions were monitored in full using the same tuning parameters as full scan mode from above. $\mathbf{1}_{0\text{-}4}$, $\mathbf{3}_{0\text{-}4}$, and $\mathbf{4}_{0\text{-}4}$ were studied under CID at 30, 33, and 35 V; $\mathbf{2}_{0\text{-}4}$ were studied under CID at 5, 10, 15, 25, and 35 V.

Table SI 1: CID scan specifications for aryl iodide species $1_{0\text{-}4}$, intermediates $2_{0\text{-}4}$, and capped oligomer products $3_{0\text{-}4}$ and $4_{0\text{-}4}$.

Species	Precursor Ion *m/z*	Fragment *m/z*	Dwell Time (s)	Collision Energy (V)
1_0	479	217	0.05	35
1_1	555	293	0.05	35
1_2	631	369	0.05	35
1_3	707	445	0.05	35
1_4	783	521	0.07	35
2_0	1108	846	0.05	35
2_1	1185	922	0.05	15
2_2	1258	996	0.05	15
2_3	1339	1077	0.05	15
2_4	1413	1152	0.05	15
3_0	429	167		
3_1	506	244		
3_2	582	320		
3_3	658	396		
3_4	733	471		
4_0	459	197	0.06	35
4_1	535	173	0.07	35
4_2	611	349	0.06	35
4_3	687	425	0.06	35
4_4	763	501	0.08	35

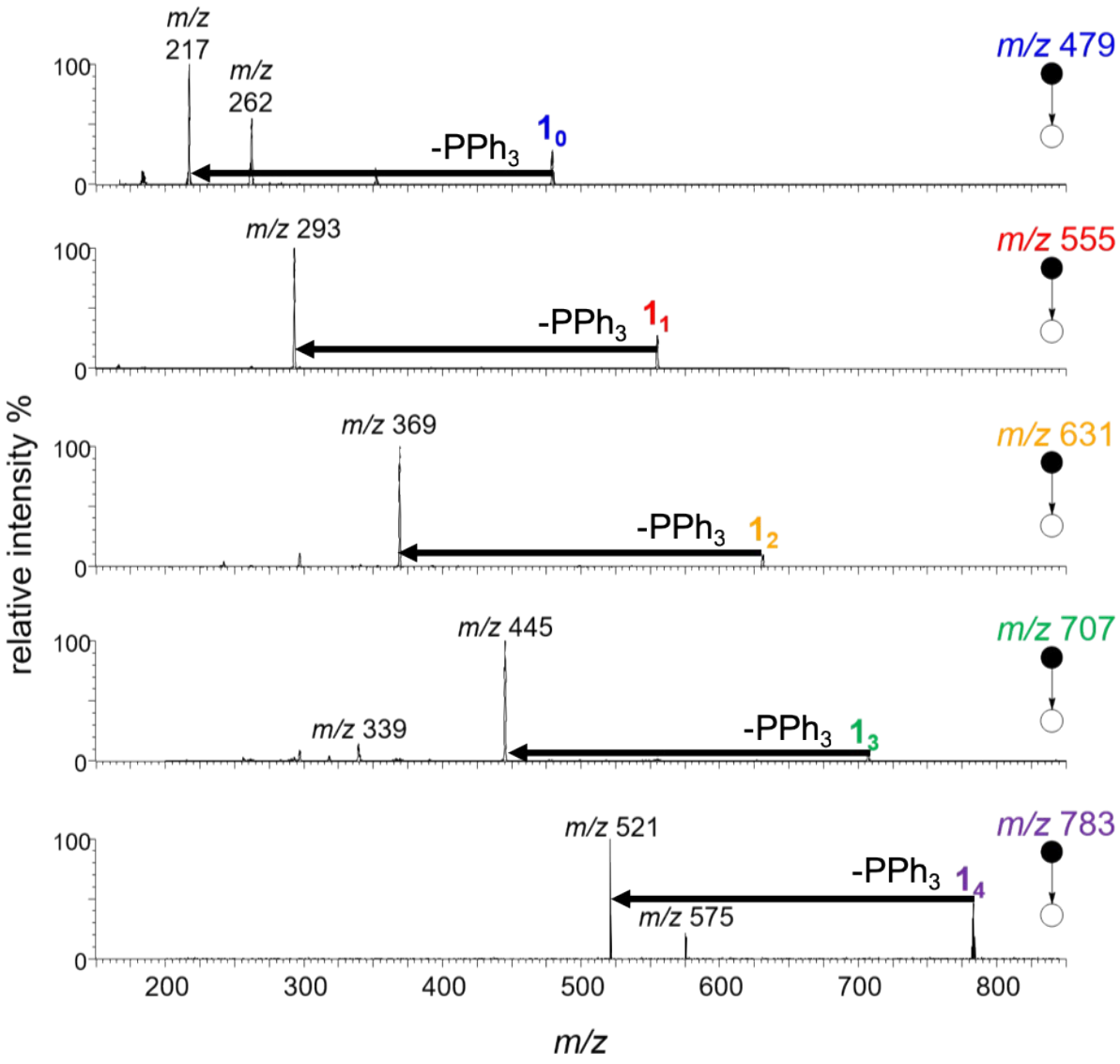

Figure SI 1: CID spectra of the aryl iodide species $1_{0\text{-}4}$ labelled as the precursor ion. The major fragmented ions were shown in the form of $[H_2CC_6H_4Ar_nI]^+$ and were indicated with an arrow showing the fragment as triphenylphosphine (PPh_3).

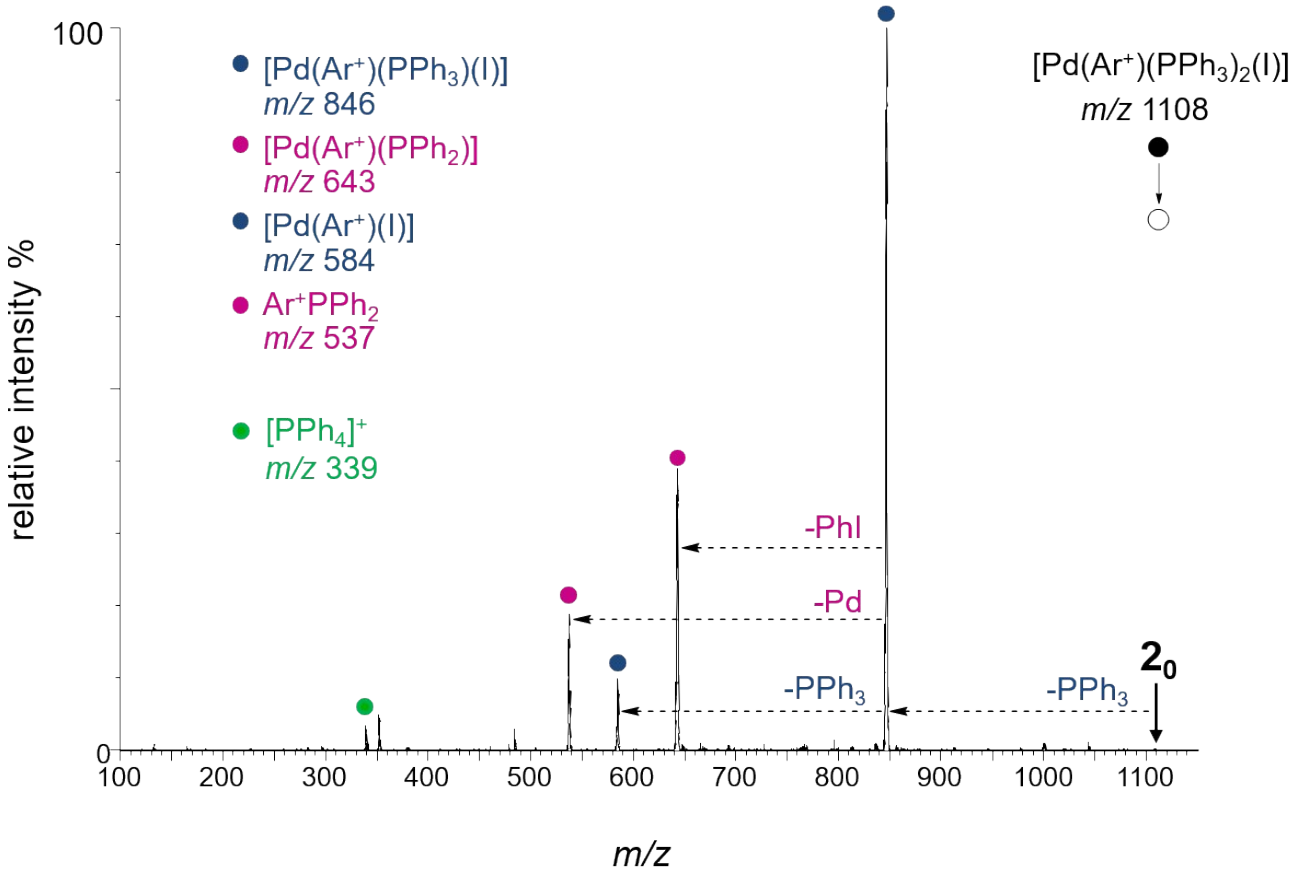

Figure SI 2: The CID spectrum of $\mathbf{2_0}$ showing the fragmentation pattern and $Ar^+ = Ph_3P^+CH_2C_6H_4$.

In Figure SI 2, the CID spectrum of the product ion scan of $\mathbf{2_0}$ displayed multiple fragments upon CID at 15 V. The most prominent peak at *m/z* 846 corresponded to the loss of one PPh_3 and was assigned as $[Pd(Ar^+)(PPh_3)(I)]^+$. A weaker signal at *m/z* 584 was shown to have lost two PPh_3. Product ions involving 262 Da loss are labelled with blue dots. We also observed species that are highlighted with pink dots to indicate that $\mathbf{2_0}$ has undergone phosphine scrambling pathway. Ions at *m/z* 643 and *m/z* 537 were assigned as $[Pd(Ar^+)(PPh_2)]$ and Ar^+PPh_2, having lost an iodobenzene and a palladium from $[Pd(Ar^+)(PPh_3)(I)]$. We found products that may have arisen from phosphine scrambling and further investigated this phenomenon with $\mathbf{2_{1\text{-}3}}$.

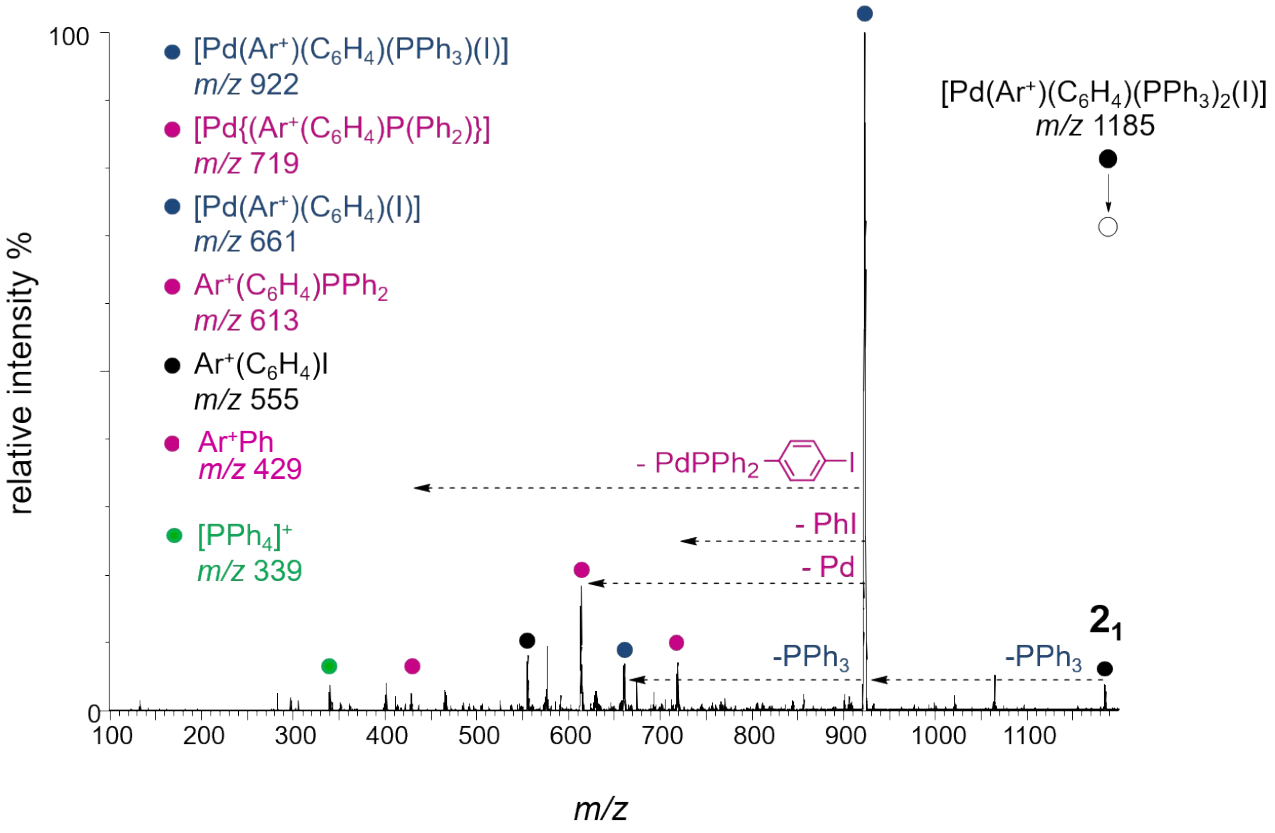

Figure SI 3: The CID spectrum of $\mathbf{2_1}$ showing the fragmentation pattern and (Ar $^+$) = $Ph_3P^+CH_2C_6H_4$.

In Figure SI 3, the product ion scan of $\mathbf{2_1}$ showed a prominent peak at *m/z* 922 and was assigned to $[Pd(Ar^+)(C_6H_4)(PPh_3)I]$ as it lost a PPh_3 fragment. This signal could either come from the oxidative addition species or transmetallation species as it is isomers of each other (See Scheme SI 1). A weaker signal at *m/z* 719 was assigned to $[Pd\{(Ar^+C_6H_4)P(Ph_2)\}]$ as it showed a loss of iodobenzene and a further loss of palladium (106 Da) at *m/z* 613 as $Ar^+(C_6H_4)I$. This observation suggests that *m/z* 1185 is most likely the oxidative addition species and is consistent with the MS/MS results of $\mathbf{2_0}$.

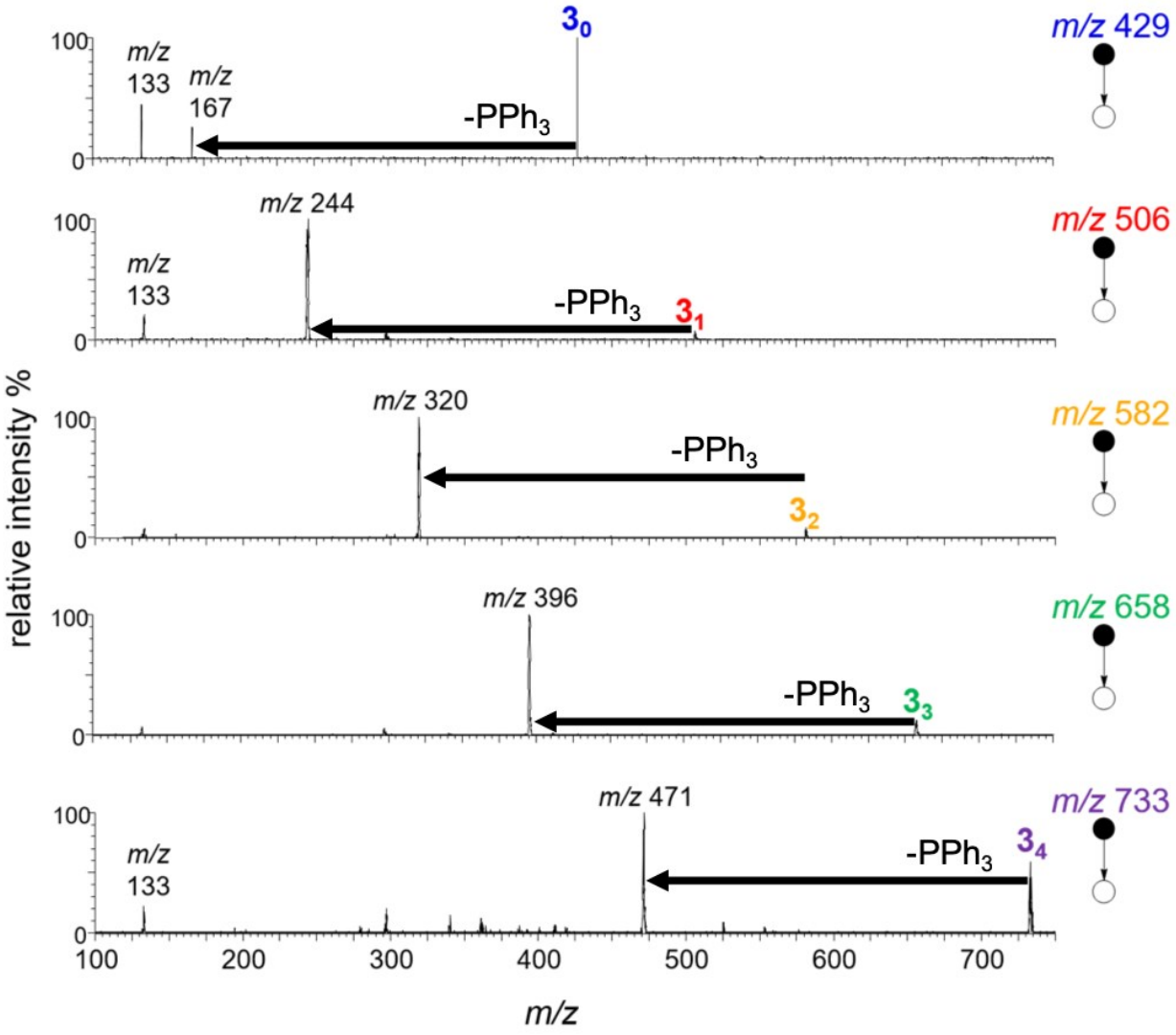

Figure SI 4: The CID spectra of the capped oligomer products $\mathbf{3_{0\text{-}4}}$ labelled as the precursor ion. The major fragmented ions were shown in the form of $[H_2CAr_nC_6H_5]^+$ and were indicated with an arrow showing the fragment as triphenylphosphine (PPh_3).

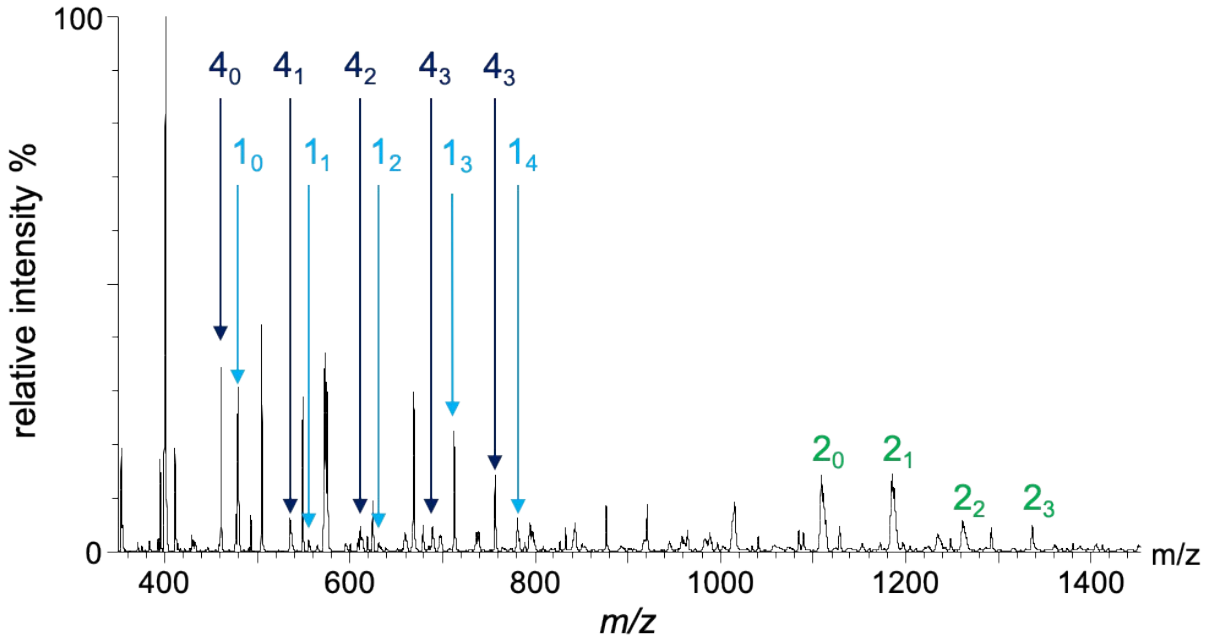

Figure SI 5: The summed ESI mass spectrum for the SPC species 1_n, 2_n, and 4_n (n = 0 – 4) in methanol in the presence of $Pd(PPh_3)_4$ with the new end-capping reagent $MeOC_6H_4B(OH)_2$ was added late in the reaction.

To confirm that the $\mathbf{4_n}$ species would undergo the same CID fragmentation pathway as the $\mathbf{1_n}$ and $\mathbf{3_n}$ species losing a PPh_3 ligand from the charged-tag, product ion MS/MS analysis was performed on $\mathbf{4_{0\text{-}4}}$ and shown in Figure SI 6.

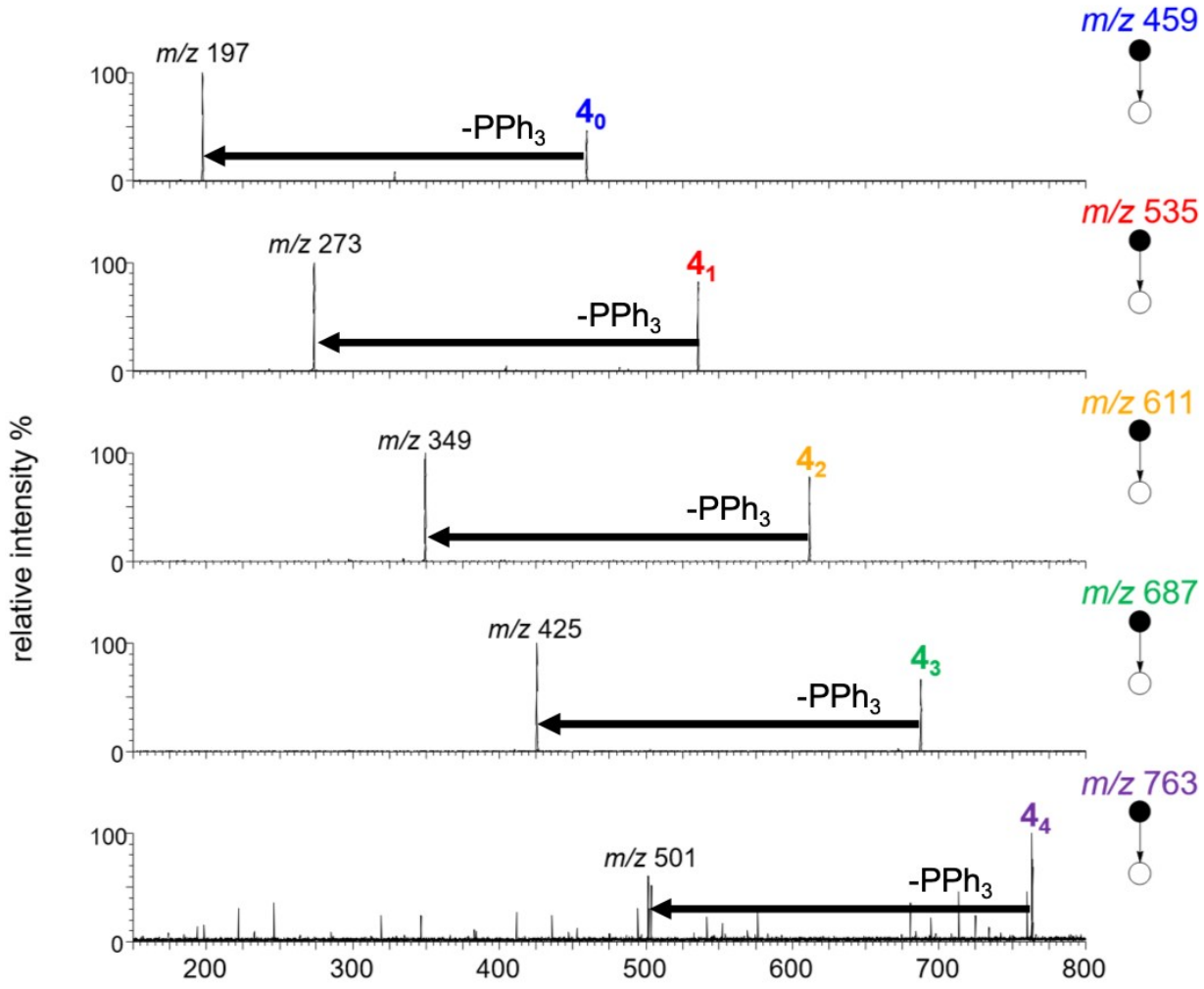

Figure SI 6: CID spectra of the capped oligomer products $\mathbf{4_{0\text{-}4}}$ labelled as the precursor ion. The major fragmented ions were shown in the form of $[H_2CAr_nC_6H_5]^+$ and indicated with a dotted arrow showing the fragment as triphenylphosphine (PPh_3).

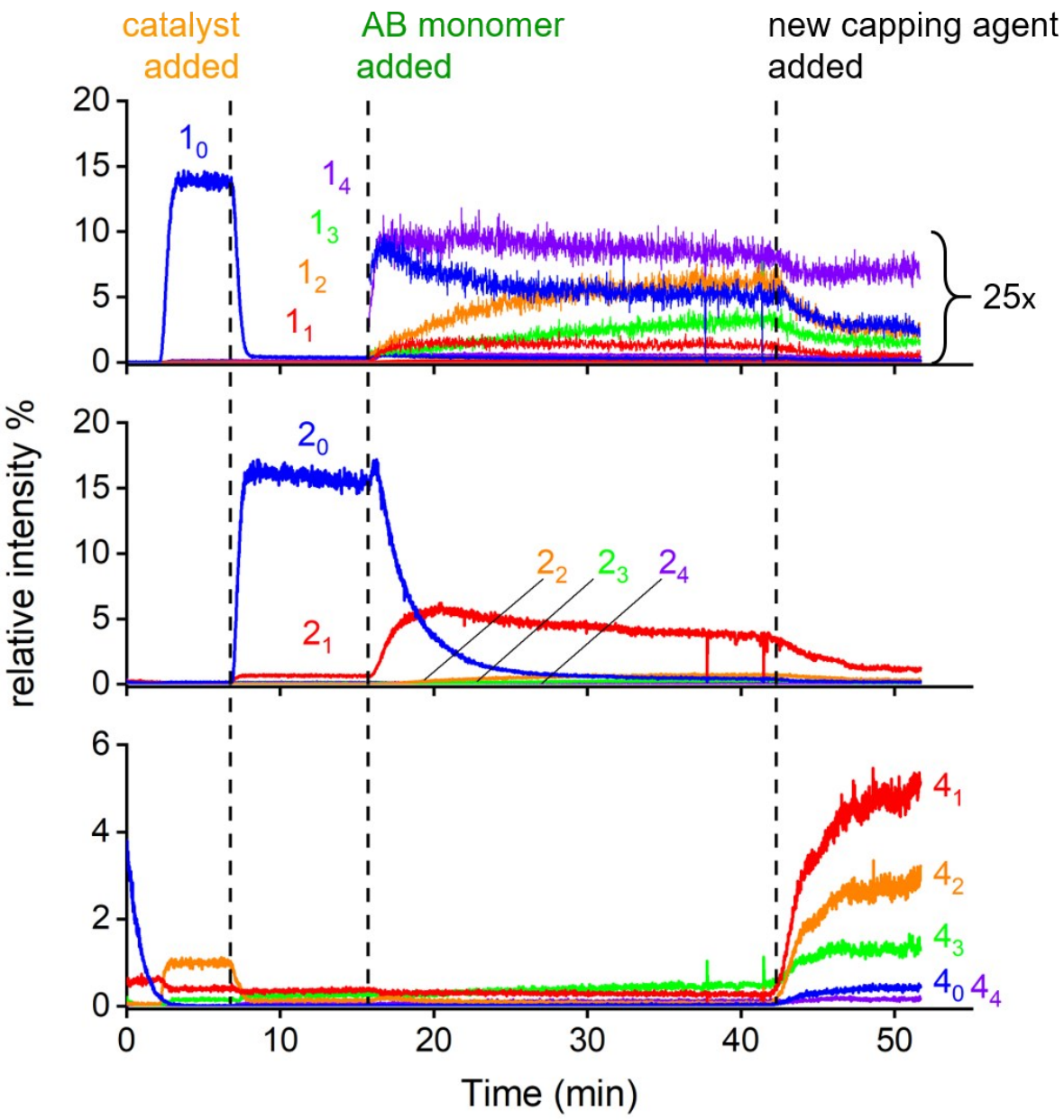

Figure SI 7: The normalized ESI-MS full scan chronogram of the SPC showing the relative intensity of aryl iodide species label as 1_n, intermediates as 2_n, and the new end-capped oligomer products as 4_n (n = 0 – 4).The aryl charge tag 1_0, $Pd(PPh_3)_4$ catalyst, AB monomer *p*-$(OH)_2BC_6H_4I$ and the end-capping agent $MeOC_6H_4B(OH)_2$ was added to the reaction solution at 2 minutes, 6 minutes, 16 minutes, and 43 minutes indicated in dotted lines.

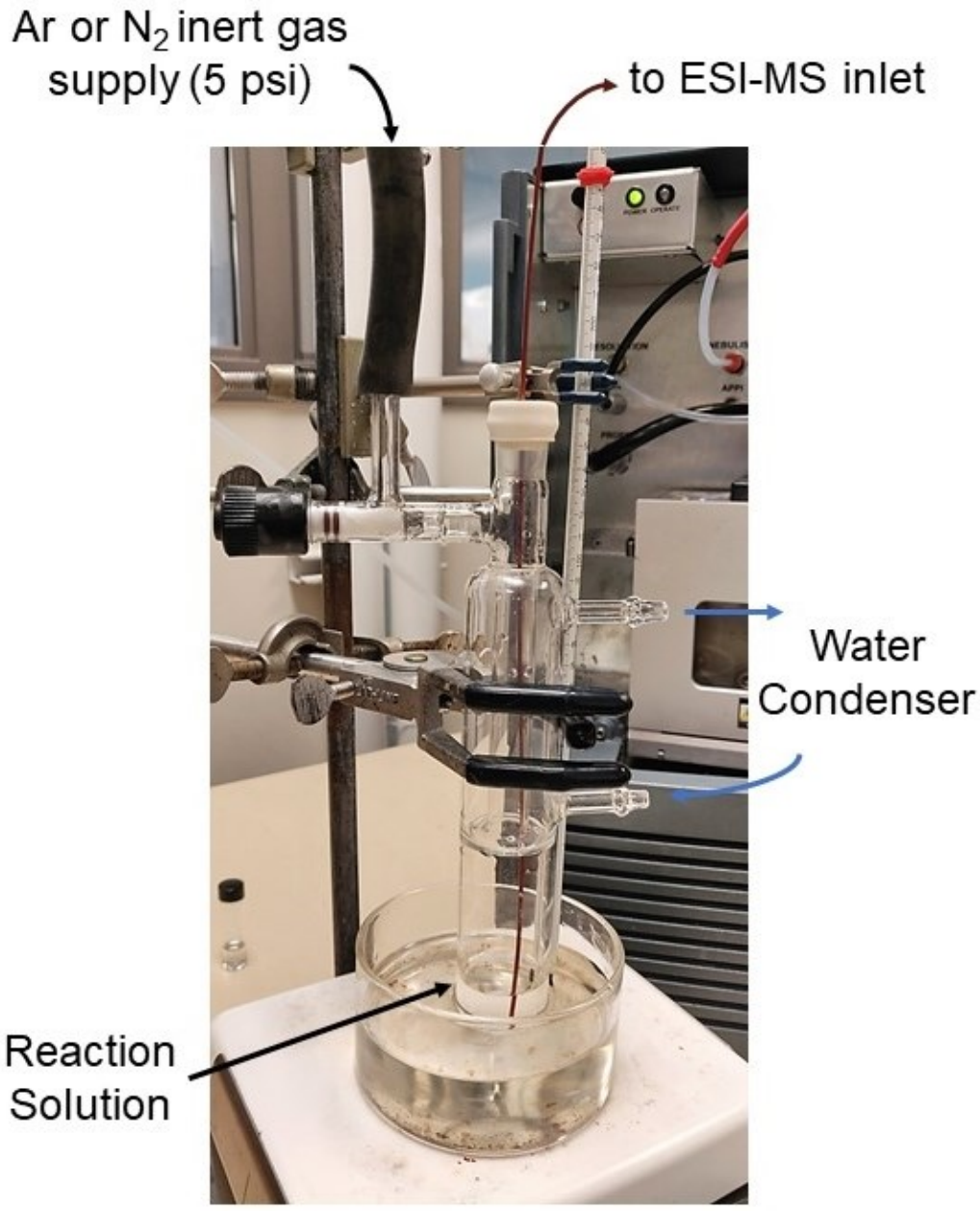

Figure SI 8: Photo of pressure sample infusion ESI-MS set-up