Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Interplay of Chloride Levels and Palladium(II)-Catalyzed *O*-deallenylation Bioorthogonal Uncaging Reactions

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1. Experimental Procedures

1.1 General procedures

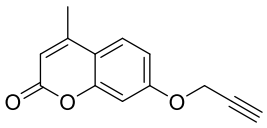
All reagents and solvents used were obtained from commercial suppliers and were used without further purification. Ultrapure water (resistivity of 18.2 Ωm), was used in all systems. Column chromatography was performed on silica gel (70–230 mesh). ^{1}H and ^{13}C spectroscopy was carried out with a Varian FT-NMR 200 MHz system at 25 °C, using $CDCl_3$ and D_2O as the solvent and tetramethylsilane (TMS) as the internal standard. The electrospray ionization-mass spectrometry (ESI-MS) experiments were performed in a Amazon X Ion Trap mass spectrometer (Bruker Daltonics). Aliquots of the reaction medium were periodically taken, diluted in water and eluted with a flow rate of 5.0 µL min^{-1}. The samples were analyzed in the postive and negative ion mode. ESI parameters were as follows: Trap Drive 48.7, Capillary Exit 140.0 V, Dry Temp 180 °C, Nebulizer 10.15 psi, Dry Gas 4.00 l/min, HV Capillary 4500 V, HV End Plate Offset -500 V. The mass spectra acquisition range was 50–2800 m/z

1.2 Quantum Mechanical Calculations

Full geometry optimizations were carried out with Gaussian 16[1] using the M06-2X[2] hybrid functional and 6-311+G(d,p) basis set for C, O, Cl, and H, and SDD[3,4] effective core potential for Pd atoms in combination with ultrafine integration grids. Bulk solvent effects in water were considered implicitly through the IEF-PCM polarizable continuum model.[5] The possibility of different conformations for all species was taken into account. Frequency analyses were carried out at the same level used in the geometry optimizations, and the nature of the stationary points was determined in each case according to the appropriate number of negative eigenvalues of the Hessian matrix. The quasiharmonic approximation reported by Truhlar et al. was used to replace the harmonic oscillator approximation for the calculation of the vibrational contribution to entropy.[6] Scaled frequencies were not considered. Mass-weighted intrinsic reaction coordinate (IRC) calculations were carried out by using the Hratchian and Schlegel algorithm[7,8] in order to ensure that the TSs indeed connected the appropriate reactants and products. Gibbs free energies (ΔG) were used for the discussion on the relative stabilities of the considered structures. The lowest energy conformer for each calculated stationary point was considered in the discussion; all the computed structures can be obtained from authors upon request. Electronic energies, entropies, enthalpies, Gibbs free energies, and lowest frequencies of the lowest energy calculated structures are summarized in Table S2. Cartesian coordinates of the lowest energy structures calculated with PCM(H_2O)/M06-2X/6-311+G(d,p)+SDD(Pd) are shown in Table S3.

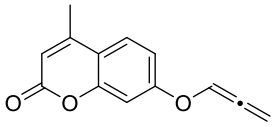
2. Synthetic procedures

4-Methyl-7-(propargyloxy)-*2H*-chromene-2-one (Prop-4-MU)



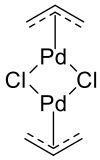
The substrate 4-Methyl-7-(propargyloxy)-*2H*-chromene-2-one was prepared using a modified version of a procedure reported in the literature[9] Potassium carbonate (7.0 g, 50.0 mmol) was added in into a 100 mL round bottom flask containing a magnetic stir bar and a solution of the 4-Methyl-7-hydroxy-*2H*-chromene-2-one (881 mg, 5.0 mmol) in CH_3CN (40 mL). Then, propargyl bromide (80% in toluene, 630 μL, 5.5 mmol) was added to the solution and system was closed with a rubber septum. The reaction was stirred for 24 h at 60 °C, after the completion of the reaction the solvent was evaporated under reduced pressure. The reaction was diluted with water (20 mL) and extracted with CH_2Cl_2 (3x 20 mL). The organic phase is washed with an NH_4Cl saturated aqueous solution (20 ml) and brine (20 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent evaporated under reduced pressure, obtaining a white solid (1.1 g, 94% yield) used without further purification. Melting point: 134-137 °C, Lit.[9] 130-134 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C) δ = 7.53 (d, *J* = 9.5 Hz, 1H), 6.96 – 6.91 (m, 2H), 6.15 (s, 1H), 4.76 (d, *J* = 2.4 Hz, 2H), 2.59 (t, *J* = 2.4 Hz, 1H), 2.40 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C) δ = 161.1, 160.4, 155.1, 152.5, 125.7, 114.3, 112.7, 112.5, 102.3, 77.5, 76.6, 56.3, 18.7. Agrees with data previously reported in the literature.[9]

4-Methyl-7-(propa-1,2-dien-1-yloxy)-*2H*-chromen-2-one (Alle-4-MU)



The substrate 4-methyl-7-(propa-1,2-dien-1-yloxy)-*2H*-chromen-2-one was prepared by adapting procedures described in the literature.[10,11] An oven-dried 25 mL round bottom flask, equipped with a rubber septum and a stirrer bar, was charged with the 4-methyl-7-(propargyloxy)-*2H*-chromene-2-one (10.0 mmol, 2,14 g). The system was evacuated and backfilled with nitrogen (operation performed three times), then DMSO (10 mL), *t*-BuOK (5.0 mmol, 0.56 g in 5 mL of DMSO) were added successively in a nitrogen atmosphere. The round bottom flask was sealed and the mixture was stirred at room temperature for 24 h. The crude reaction mixture was purified via column chromatography (without prior removal of the DMSO), by using 0-4% ethyl acetate in hexane solution as eluent, obtaining a white solid (311 mg, 14.5% yield). Melting point: 101-104 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C) δ = 7.54 (d, *J* = 9.5 Hz, 1H), 7.04 – 6.97 (m, 2H), 6.86 (t, *J* = 5.9 Hz, 1H), 6.19 (s, 1H), 5.52 (d, *J* = 5.9 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C) δ = 202.8, 161.1, 160.1, 155.1, 152.4, 125.8, 116.7, 115.3, 113.6, 113.0, 104.2, 90.3, 18.8. Agrees with data previously reported in the literature.[10]

Allylpalladium(II) chloride dimer ($Allyl_2Pd_2Cl_2$)



The allylpalladium(II) chloride dimer was prepared using a modified version of a procedure reported in the literature.[12] An oven-dried 25 mL round bottom flask, equipped with a stirrer bar, was charged with the $PdCl_2$ (430 mg, 2.5 mmol) and KCl (562 mg, 7.5 mmol) was dissolved in H_2O (15 mL) and stirred for 1 h at room temperature. Then allylchloride (0.62 mL, 7.5 mmol) was added and the mixture was stirred at 50°C for 18 h. The reaction was extracted with $CHCl_3$ (3x 15 mL) and the organic phase is washed with water (20 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent evaporated under reduced pressure obtaining a yellow solid (339 mg, 44% yield), stored under N_2 atmosphere at -25°C and used without further purification. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C) δ = 5.45 (tt, *J* = 12.1, 6.7 Hz, 1H), 4.10 (d, *J* = 6.7 Hz, 2H), 3.03 (d, *J* = 12.1 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C) δ = 111.3, 63.1. Agrees with data previously reported in the literature.[12,13]

3. Kinetic assays

3.1 Kinetic profiles

The catalytic activity of the Pd(II) complexes (Na_2PdCl_4 and $Allyl_2Pd_2Cl_2$) in the hydrolysis of 1,2-allenyl and propargyl protected coumarins was evaluated in a 95/5 (v:v) H_2O/DMSO phosphate buffered aqueous medium (pH 7.4) at 37 ºC, by monitoring the appearance of the phenolate (ε = 7.410 L mol^{-1} cm^{-1}) absorption band at 364 nm using a Varian Cary 50 UV-vis spectrophotometer equipped with a controlled temperature multicell holder. In a typical experiment, 3.04 mL of a phosphate-buffered aqueous solution at pH 7.4 ($[buffer]_{final}$ = 1.00 x 10^{-2} mol L^{-1}), DMSO solution of the Pd(II) complexes (0.1 – 0.5 eq.) and a volume of DMSO for final volume (3.20 mL) were added to a 1 cm path-length cell. The reaction was initiated by the addition of 80 µL of a DMSO substrate solution ($[substrate]_{final}$ = 1.0 x 10^{-4} mol L^{-1}). Fresh DMSO solution of the Pd(II) complexes were used in all experiments. Phosphate-buffered saline (PBS) was prepared by dissolving PBS tablets (Sigma-Aldrich) in deionized water. The total ion concentration of PBS solution was 0.15 mol L^{-1} (0.01 mol L^{-1} phosphate buffer, 0.0027 mol L^{-1} potassium chloride and 0.137 mol L^{-1} sodium chloride). For experiments with variation on chloride concentration, the phosphate buffered aqueous medium was prepared by dissolving sodium dihydrogen phosphate (0.01 mol L^{-1}), sodium chloride and the ionic strength was maintained constant by the addition of sodium perchlorate. The pH was adjusted by adding a solution of sodium hydroxide.

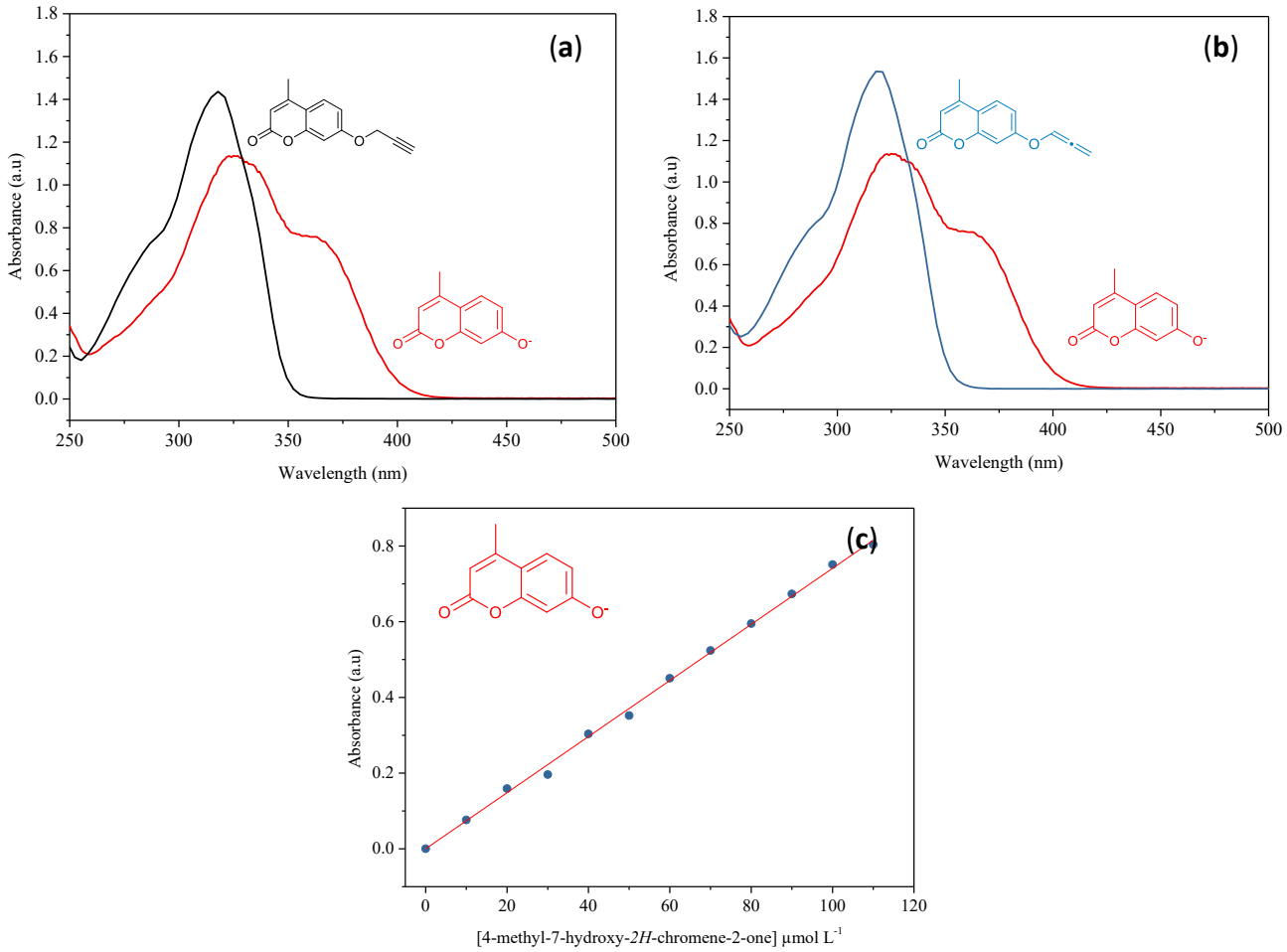


Figure S1 - **(a-b)** UV-vis spectra of the protected coumarins and their respective unprotected coumarins. Conditions: 100 µmol L^{-1} of coumarins, PBS buffer (0.01 mmol L^{-1}), pH: 7.4, 5% DMSO at 37°C. **(c)** calibration curve for *O*-Coumarin. Conditions: 0-100 µmol L^{-1} of coumarins, PBS buffer (0.01 mmol L^{-1}), pH: 7.4, 5% DMSO at 37°C.

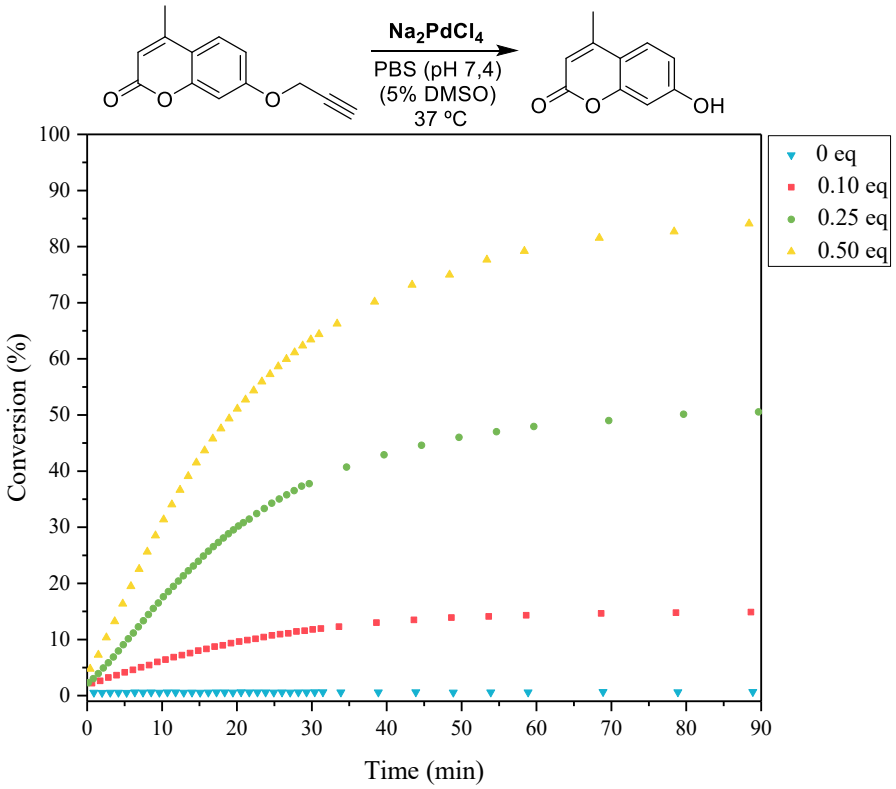


Figure S2 - Reaction kinetic profiles for the depropargylation reaction mediated by Na_2PdCl_4. Reaction conditions: [Prop-4-MU] = 100 µmol L^{-1}, [Na_2PdCl_4] = 0, 10, 25 and 50 µmol L^{-1}, PBS buffer, pH: 7.4, 5% DMSO at 37°C.

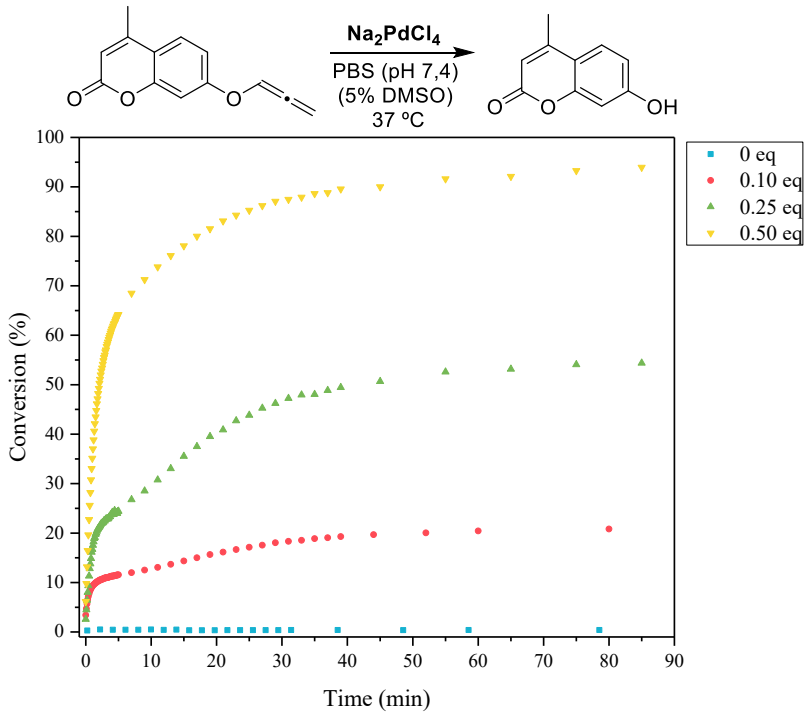


Figure S3 - Reaction kinetic profiles for the deallenylation reaction mediated by Na_2PdCl_4. Reaction conditions: [Alle-4-MU] = 100 µmol L^{-1}, [Na_2PdCl_4] = 0, 10, 25 and 50 µmol L^{-1}, PBS buffer, pH: 7.4, 5% DMSO at 37°C.

The exponential fit of the kinetic curves (eq 1) enabled the determination of observed macroscopic rate constants and the yield of each phase for the C-O cleavage reaction for both substrates (S4a-b). On the basis of these macroscopic rate constants, the cleavage reaction of Alle-4-MU was deconvoluted into two reaction kinetics profiles (S5, blue squares and green triangles for the fast and slow phases, respectively), namely, Rx1 and Rx2, respectively. For Prop-4-MU substrate a monophasic kinetic was observed (Rx1).

$$Abs = Abs_{inf} - (Abs_{inf} - Abs_0)e^{-kt} \quad \text{(eq 1)}$$

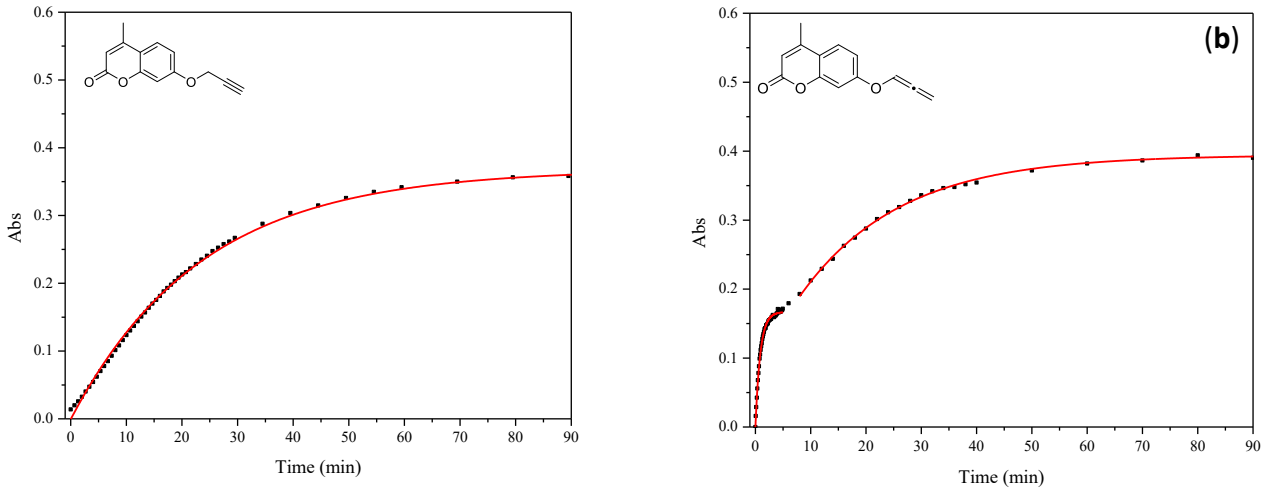


Figure S4 - Exponential adjustment for the deprotection reactions (a) Prop-4-MU and (b) Alle-4-MU. Reaction conditions: 100 µmol L^{-1} protected-coumarins, 25 µmol L^{-1} Na_2PdCl_4, PBS buffer (0.01 mmol L^{-1}), pH: 7.4, 5% DMSO at 37°C .

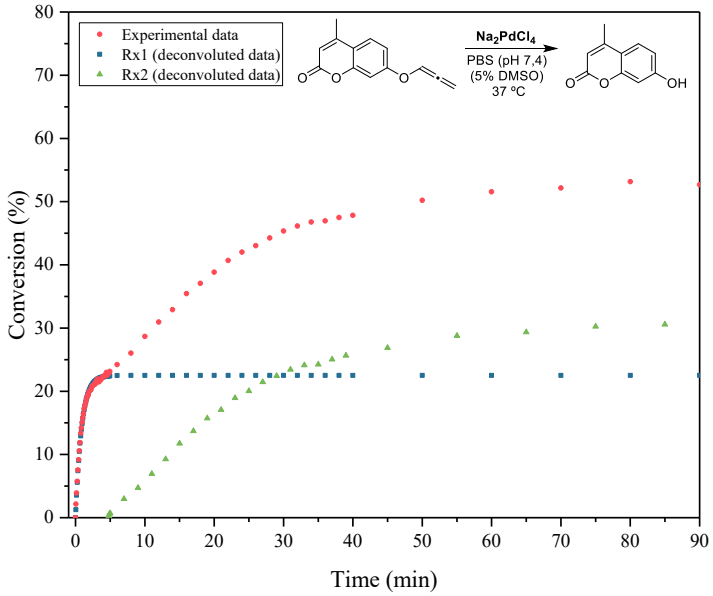


Figure S5 – Deconvoluted kinetics profiles for the deprotection reaction of Alle-4-UM substrate. Reaction conditions: 100 µmol L^{-1} Alle-4-MU, 25 µmol L^{-1} Na_2PdCl_4, PBS buffer (0.01 mmol L^{-1}), pH: 7.4, 5% DMSO at 37 °C.

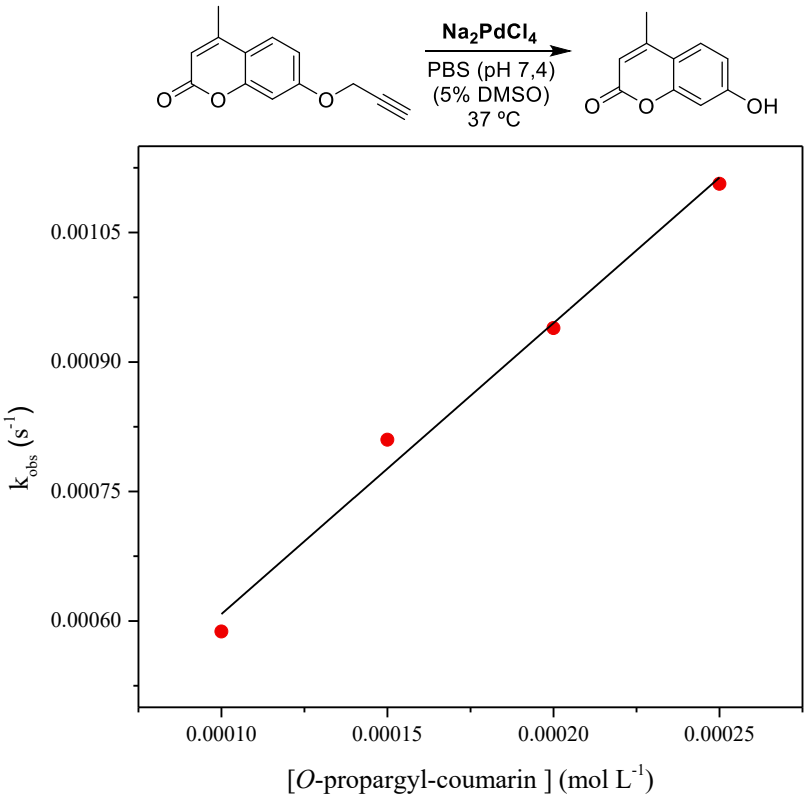


Figure S6 - Second-order rate constant (k_2) determination under *pseudo* first-order conditions for depropargylation reaction by Na_2PdCl_4. Reaction conditions: [Prop-4-MU] = 100-250 µmol L^{-1}, [Na_2PdCl_4] = 10 µmol L^{-1}, PBS buffer, pH: 7.4, 5% DMSO at 37°C.

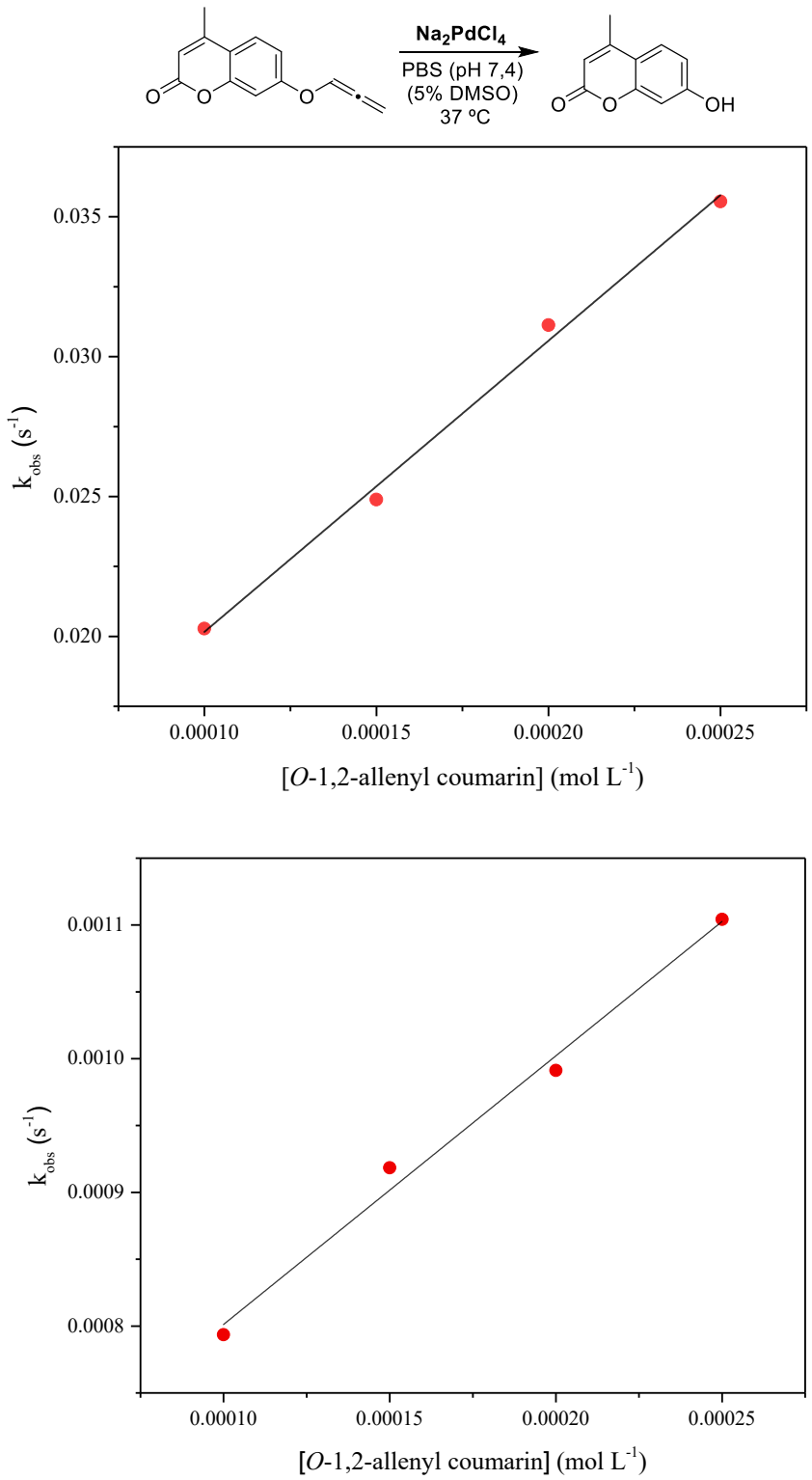


Figure S7 - Second-order rate constants (k_2) determination under *pseudo* first-order conditions for the two phases **(a-b)** of deallenylation reaction by Na_2PdCl_4. Reaction conditions: [Alle-4-MU] = 100-250 µmol L^{-1}, [Na_2PdCl_4] = 10 µmol L^{-1}, PBS buffer, pH: 7.4, 5% DMSO at 37°C.

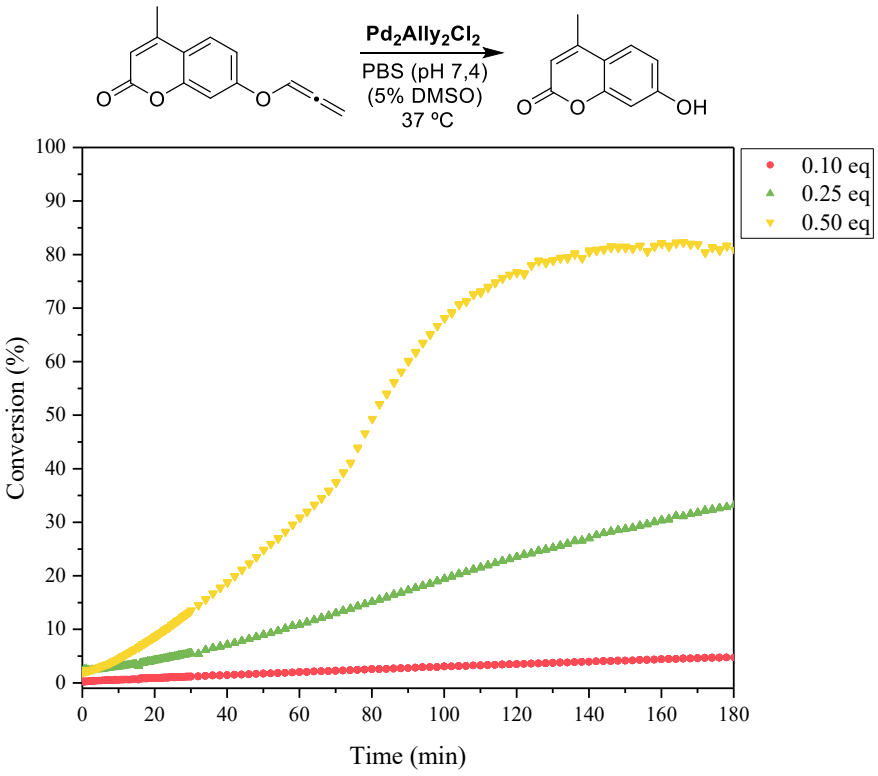


Figure S8 - Reaction kinetic profiles of deallenylation mediated by $Allyl_2Pd_2Cl_2$. Reaction conditions: [Alle-4-MU] = 100 µmol L^{-1}, [AllylPdCl] = 10, 25 and 50 µmol L^{-1}, PBS buffer, pH: 7.4, 5% DMSO at 37°C.

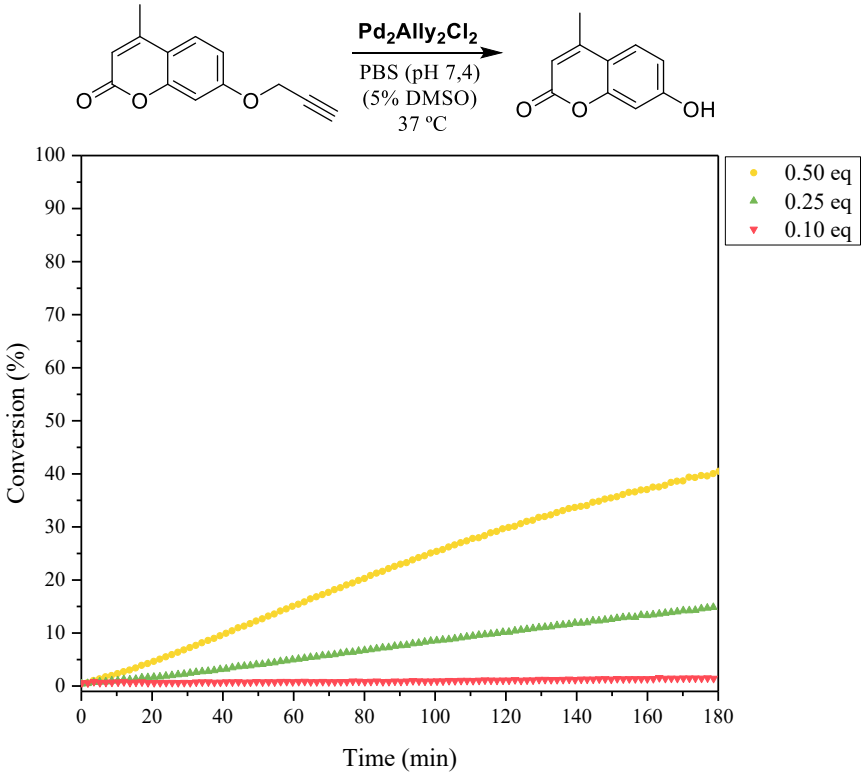


Figure S9 - Reaction kinetic profiles of depropargylation mediated by $Allyl_2Pd_2Cl_2$. Reaction conditions: [Prop-4-MU] = 100 µmol L^{-1}, [AllylPdCl] = 10, 25 and 50 µmol L^{-1}, PBS buffer, pH: 7.4, 5% DMSO at 37°C.

3.2 Effect of buffer on reaction kinetic profiles

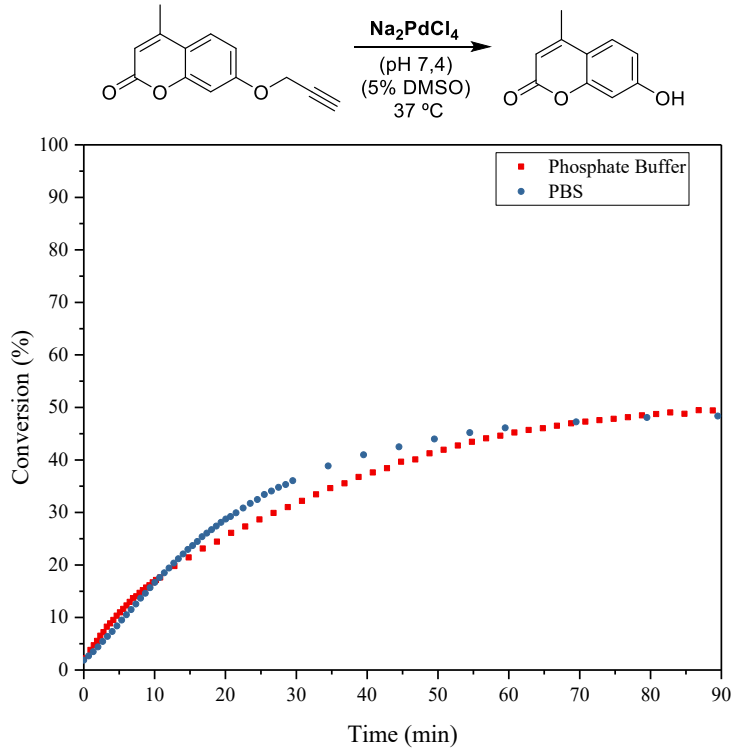


Figure S10 – Effect of buffer composition on the kinetic profiles of depropargylation mediated by Na_2PdCl_4. Reaction conditions: [Prop-4-MU] = 100 µmol L^{-1}, [Na_2PdCl_4] = 25 µmol L^{-1}, pH: 7.4, 5% DMSO at 37°C.

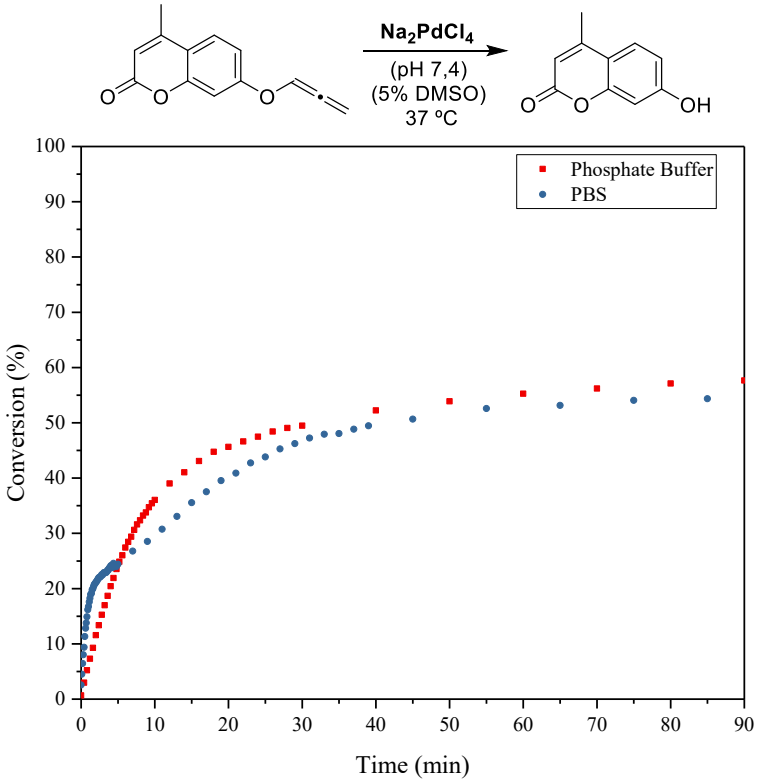


Figure S11 – Effect of buffer composition on the kinetic profiles of deallenylation mediated by Na_2PdCl_4. Reaction conditions: [Alle-4-MU] = 100 µmol L^{-1}, [Na_2PdCl_4] = 25 µmol L^{-1}, pH: 7.4, 5% DMSO at 37°C.

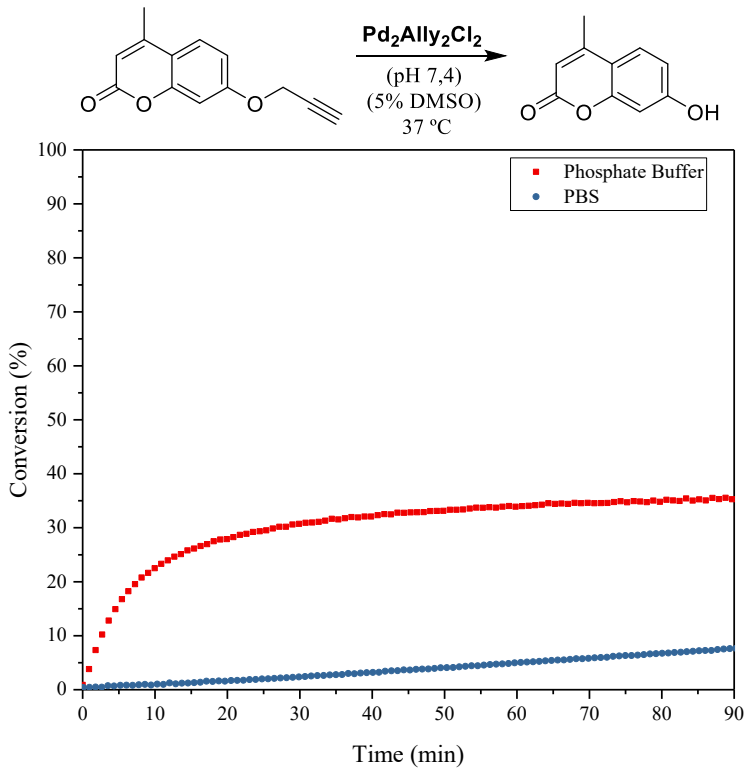


Figure S12 – Effect of buffer composition on the kinetic profiles of depropargylation mediated by $Allyl_2Pd_2Cl_2$. Reaction conditions: [Prop-4-MU] = 100 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1}, pH: 7.4, 5% DMSO at 37°C.

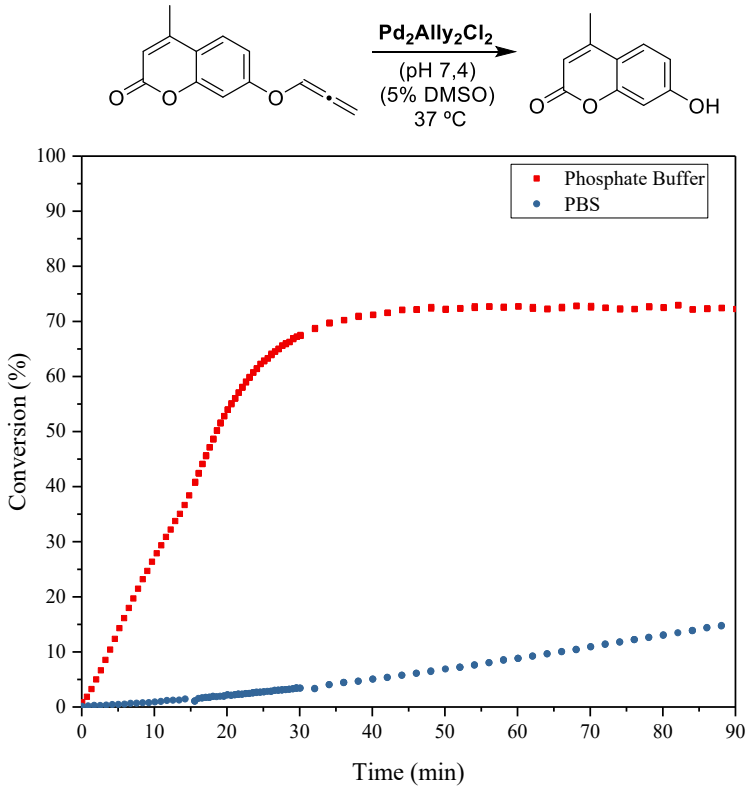


Figure S13 – Effect of buffer composition on the kinetic profiles of deallenylation mediated by $Pd_2Ally_2Cl_2$. Reaction conditions: [Alle-4-MU] = 100 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1}, pH: 7.4, 5% DMSO at 37°C.

3.3. Effect of NaCl concentration on reaction rate mediated by $Allyl_2Pd_2Cl_2$

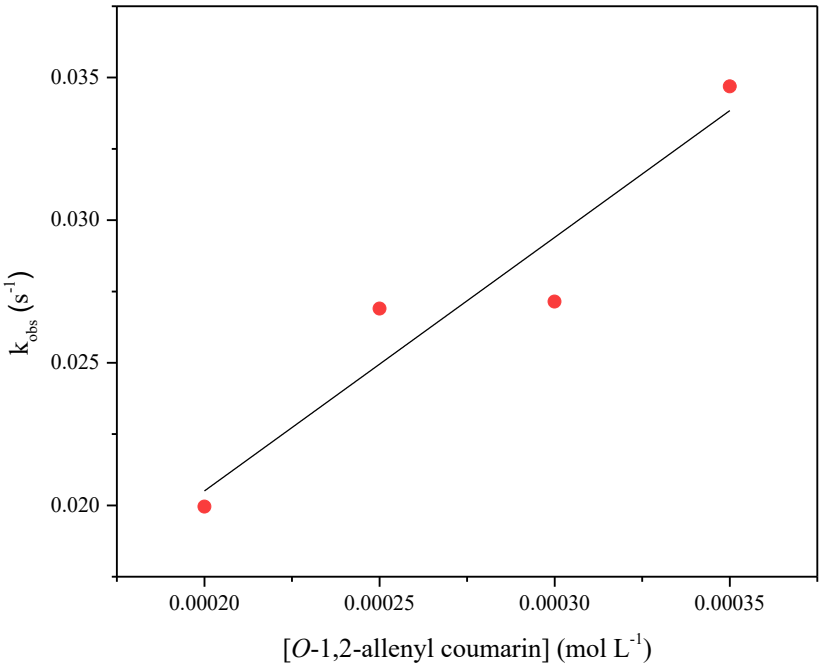


Figure S14 - Second-order rate constant (k_2) determination under *pseudo* first-order conditions for deallenylation reaction mediated by $Allyl_2Pd_2Cl_2$ in phosphate buffer (no salt). Reaction conditions: [Alle-4-MU] = 200-350 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1}, phosphate buffer (I = 140 mmol L^{-1} ($NaClO_4$)), pH: 7.4, 5% DMSO at 37°C.

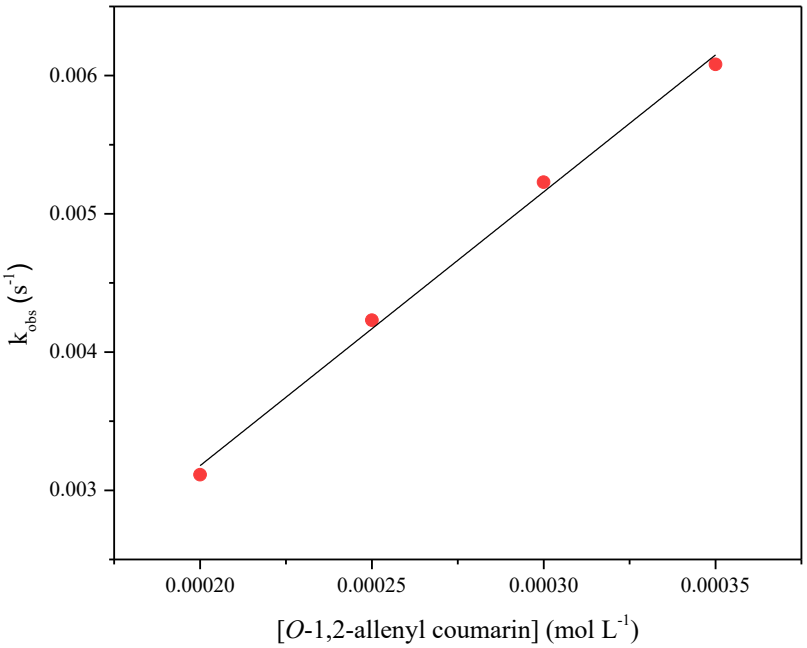


Figure S15 - Second-order rate constant (k_2) determination under *pseudo* first-order conditions for deallenylation reaction mediated by $Allyl_2Pd_2Cl_2$ in phosphate buffer with 15 mmol L^{-1} of NaCl. Reaction conditions: [Alle-4-MU] = 200-350 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1}, phosphate buffer (I = 140 mmol L^{-1} ($NaClO_4$)), pH: 7.4, 5% DMSO at 37°C.

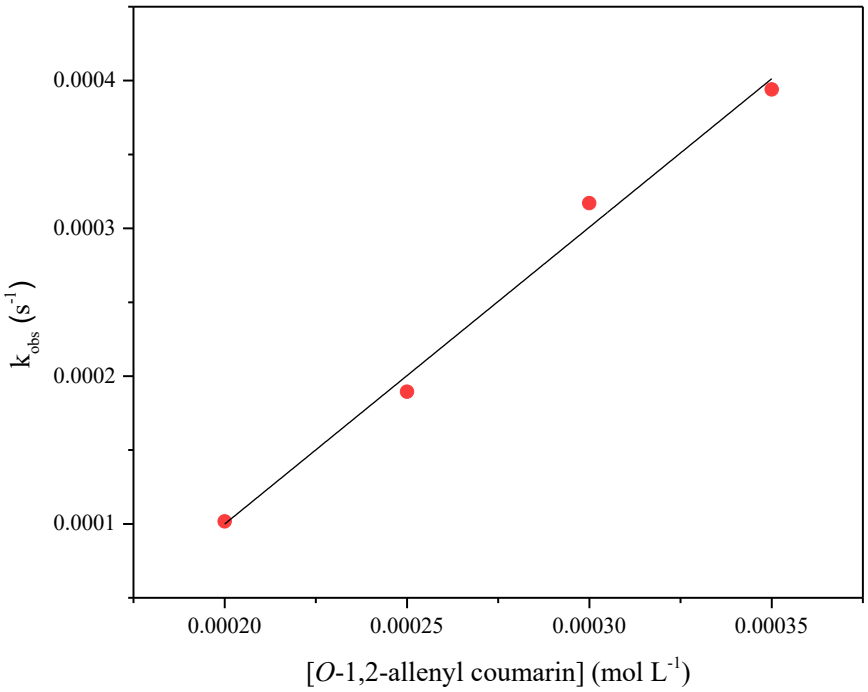


Figure S16 - Second-order rate constant (k_2) determination under *pseudo* first-order conditions for deallenylation reaction mediated by $Allyl_2Pd_2Cl_2$ in PBS. Reaction conditions: [Alle-4-MU] = 200-350 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1}, phosphate buffer (I = 140 mmol L^{-1}), pH: 7.4, 5% DMSO at 37°C.

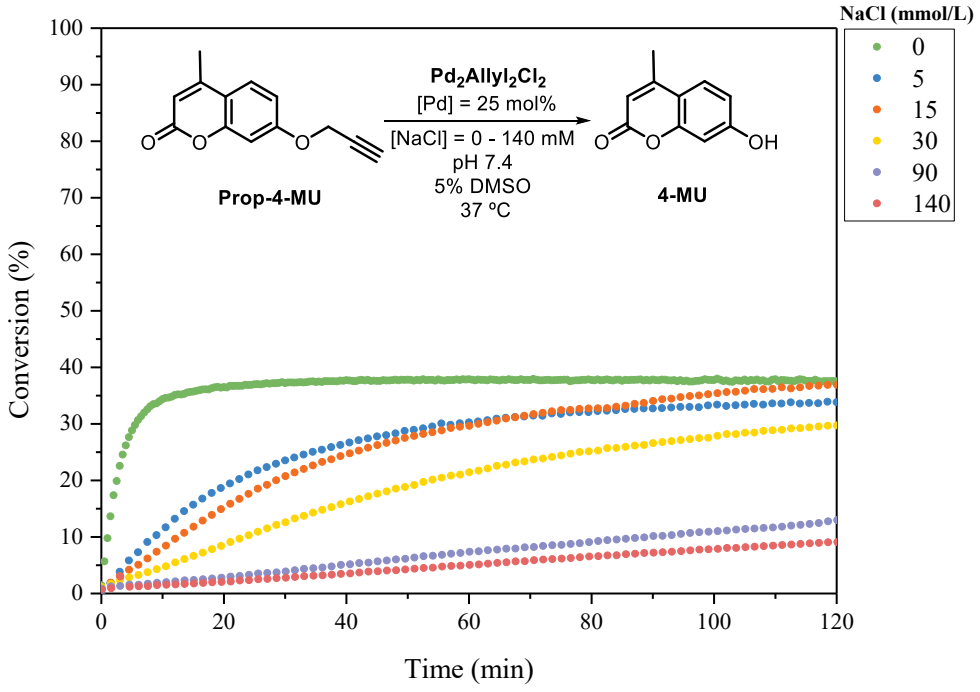


Figure S17 - Uncaging reaction of Prop-4-MU promoted by $Allyl_2Pd_2Cl_2$ in phosphate buffer with different NaCl concentrations. [Prop-4-MU] = 100 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1}, pH: 7.4, 5% DMSO at 37°C, ionic strength (I = 140 mmol L^{-1} ($NaClO_4$)).

3.4 Effect of additives SA and EDTA

3.4.1 Sodium ascorbate (SA) reducing agent of Pd(II) to Pd(0)

To investigate the effect Pd oxidation state [Pd(II) vs. Pd(0)] on the rate of C-O cleavage reactions, we added sodium ascorbate in the reaction medium, a common palladium reducing agent (Pd(II)→Pd(0)) for preparation of Pd(0)-NPs. For such, a solution of sodium ascorbate (SA, 1 mmol L^{-1}, 10 eq) in water was added to the cuvette after the addition of the palladium solution (Na_2PdCl_4 or $Allyl_2Pd_2Cl_2$, 25 µmol L^{-1}, 0.25 eq) and before adding the substrate. The substrates were added after 10 min and the reactions were followed for the next 90 min.

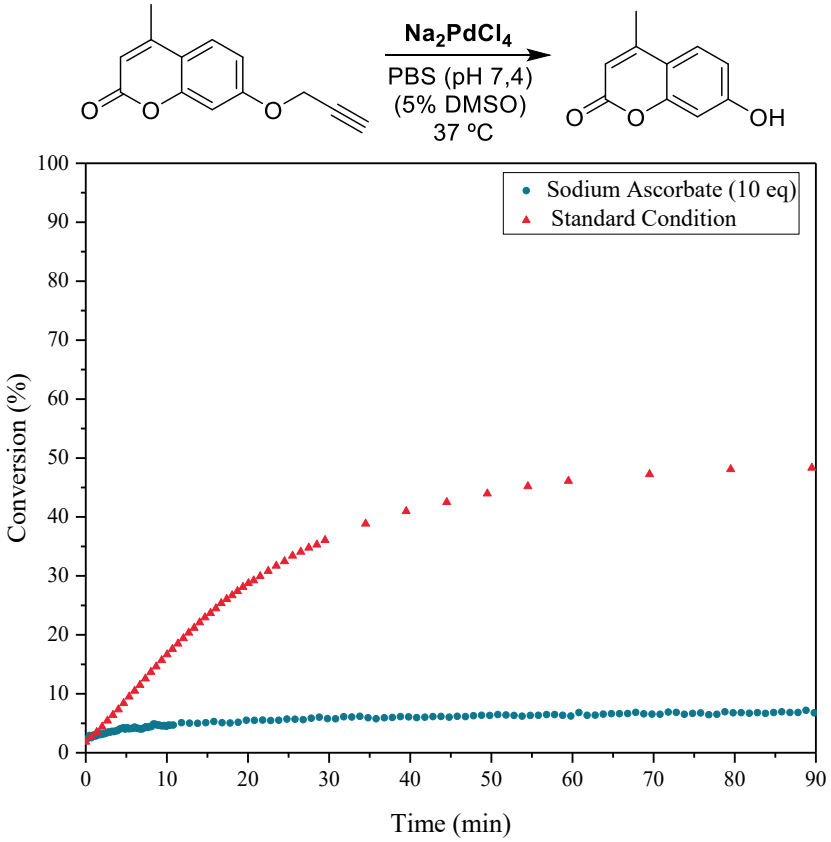


Figure S18 – Effect of SA addition on the kinetic profiles for the depropargylation reaction mediated by Na_2PdCl_4. Reaction conditions: [Prop-4-MU] = 100 µmol L^{-1}, [Na_2PdCl_4] = 25 µmol L^{-1}, [SA] = 1000 µmol L^{-1}, PBS buffer, pH: 7.4, 5% DMSO at 37°C.

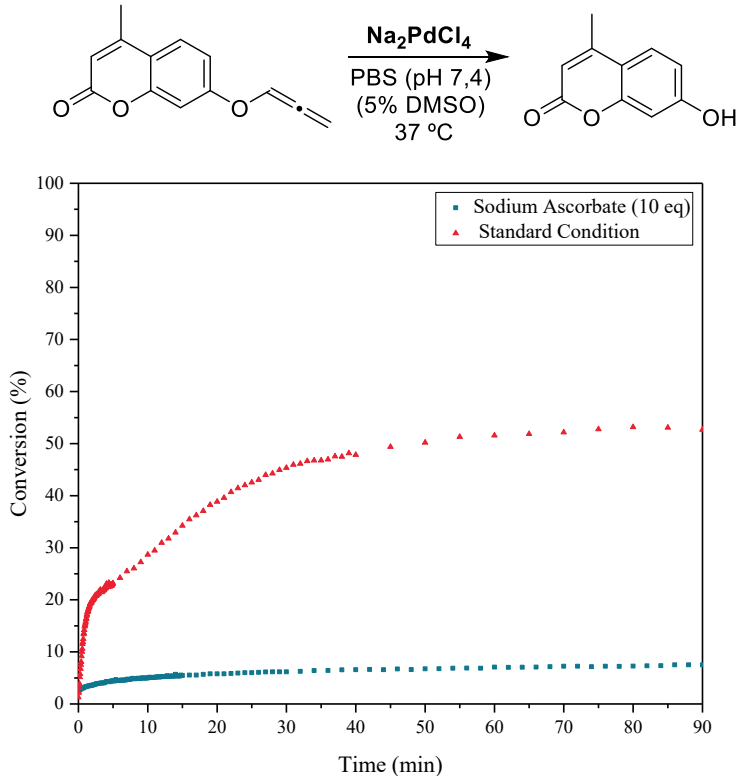


Figure S19 – Effect of SA addition on the kinetic profiles for the deallenylation recation mediated by Na_2PdCl_4. Reaction conditions: [Prop-4-MU] = 100 µmol L^{-1}, [Na_2PdCl_4] = 25 µmol L^{-1}, [SA] = 1000 µmol L^{-1}, PBS buffer, pH: 7.4, 5% DMSO at 37°C.

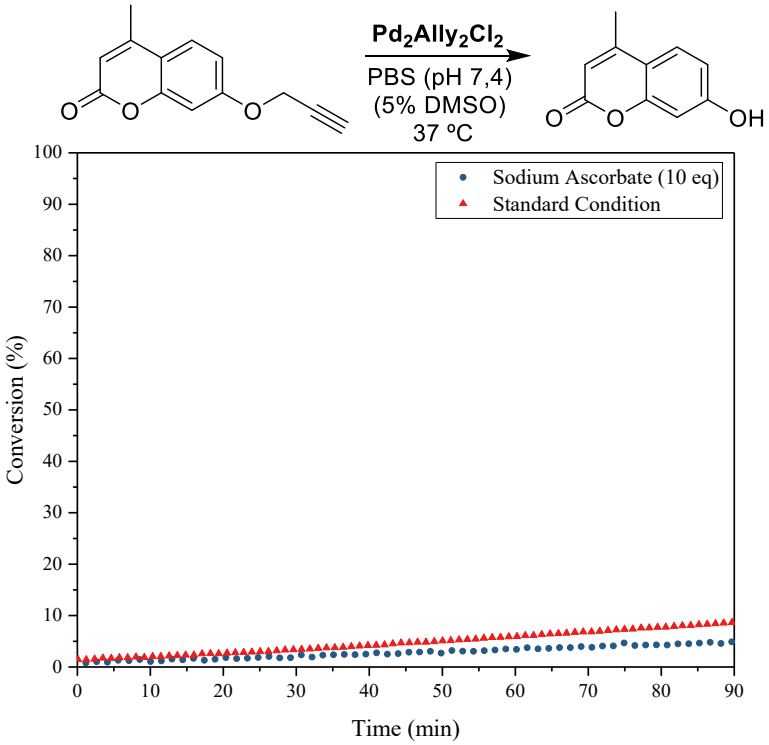


Figure S20 – Effect of SA adittion on the kinetic profiles for the depropargylation reaction mediated by $Allyl_2Pd_2Cl_2$. Reaction conditions: [Prop-4-MU] = 100 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1}, [SA] = 1000 µmol L^{-1}, PBS buffer, pH: 7.4, 5% DMSO at 37°C.

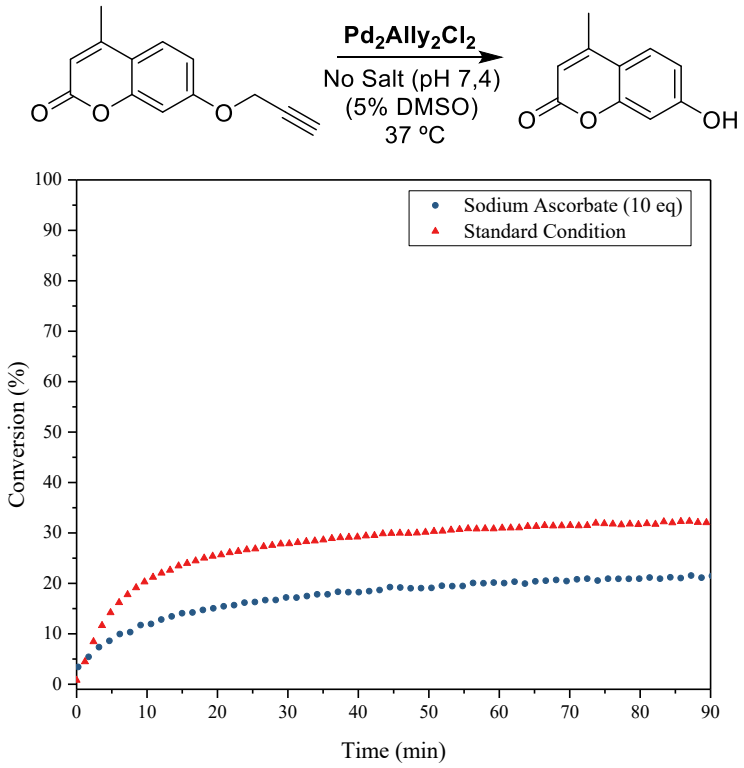


Figure S21 – Effect of SA addition on the kinetic profiles for the depropargylation reaction mediated by $Pd_2Ally_2Cl_2$. Reaction conditions: [Prop-4-MU] = 100 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1}, [SA] = 1000 µmol L^{-1}, phosphate buffer, pH: 7.4, 5% DMSO at 37°C.

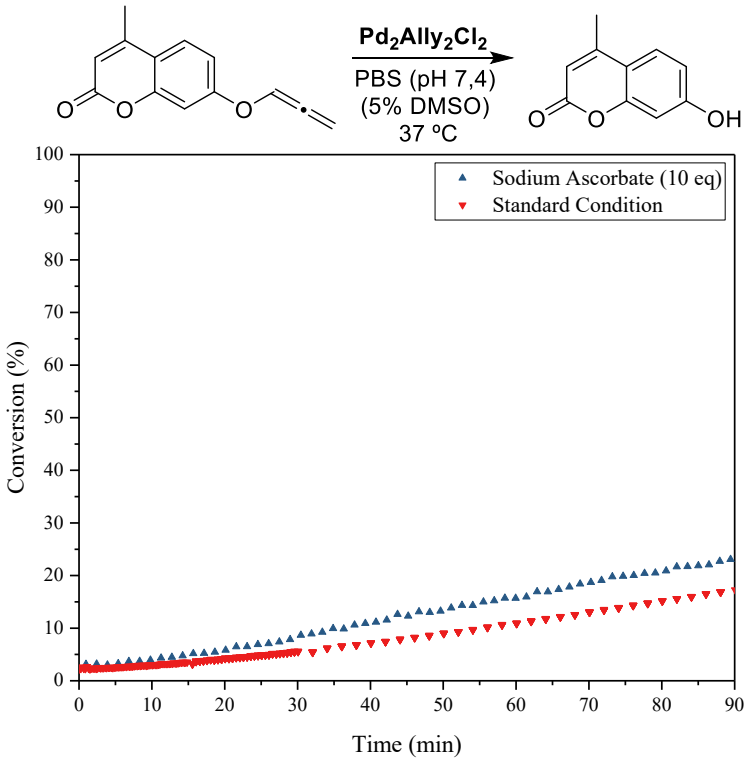


Figure S22 – Effect of SA addition on the kinetic profiles for the deallenylation recation mediated by $Pd_2Ally_2Cl_2$. Reaction conditions: [Prop-4-MU] = 100 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1}, [SA] = 1000 µmol L^{-1}, PBS buffer, pH: 7.4, 5% DMSO at 37°C.

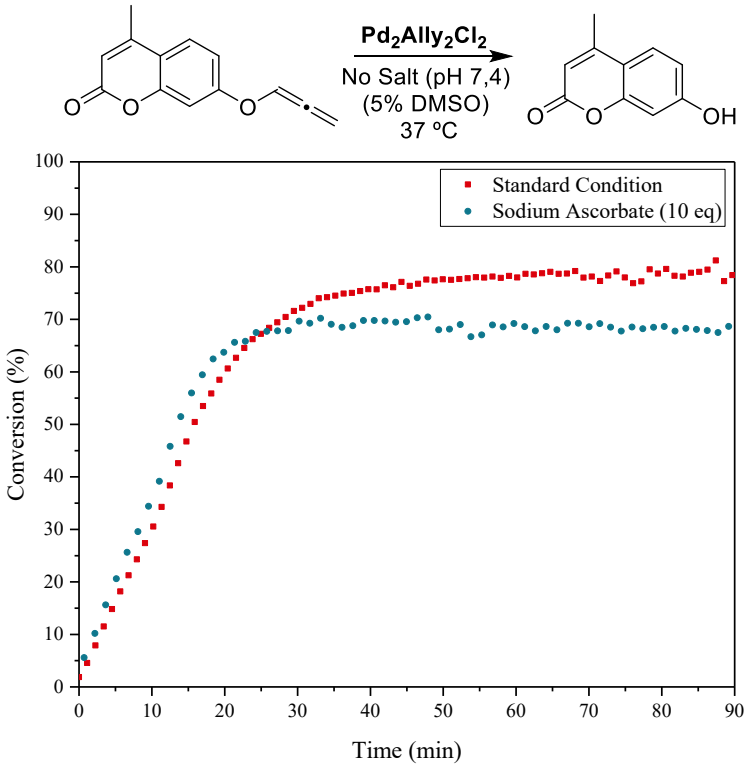


Figure S23 – Effect of SA addition on the kinetic profiles for the deallenylation reaction mediated by $Pd_2Ally_2Cl_2$. Reaction conditions: [Prop-4-MU] = 100 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1}, [SA] = 1000 µmol L^{-1}, phosphate buffer, pH: 7.4, 5% DMSO at 37°C.

3.4.2 Ethylenediamine tetraacetic acid (EDTA) complexation with Pd(II)

Palladium (II) and ethylenedinitrilotetracetic acid (EDTA) have an extremely strong affinity. For this reason, the addition of EDTA to the reaction medium will result in the unavailability of Pd(II), which is strongly bound to the chelating ligand, and will, inhibit the C–O bond-cleavage mediated by Pd(II). For such, a solution of ethylenedinitrilotetracetic acid (EDTA, 250 µmol L^{-1}, 2.5 eq) in water was added to the cuvette after the addition of the palladium solution (Na_2PdCl_4 or $Allyl_2Pd_2Cl_2$, 25 µmol L^{-1}, 0.25 eq) and before adding the substrate. The substrates were added after 30 min and the reactions were followed for the next 90 min.

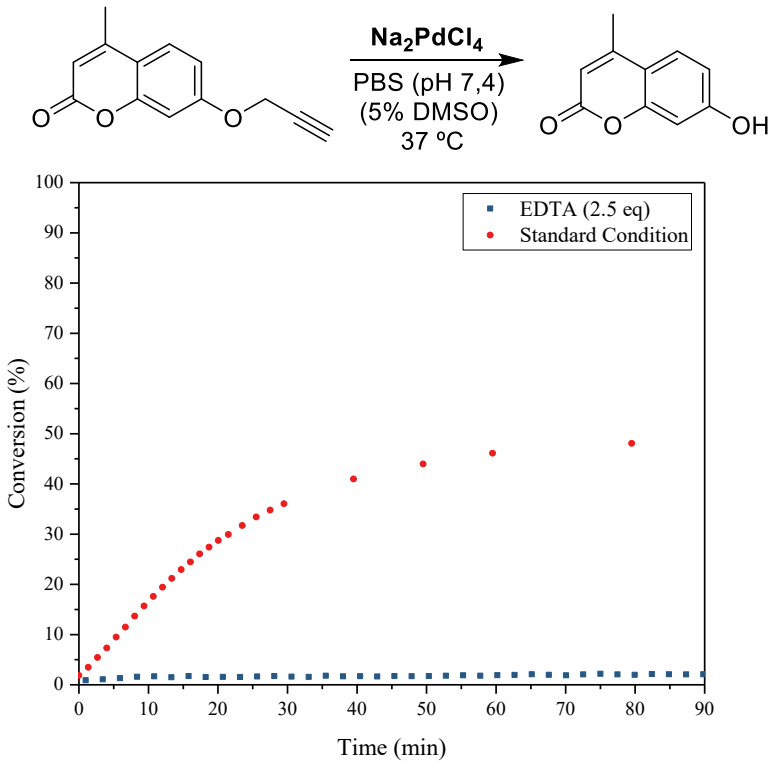


Figure S24 – Effect of EDTA addition on the kinetic profiles for the depropargylation reaction mediated by Na_2PdCl_4. Reaction conditions: [Prop-4-MU] = 100 µmol L^{-1}, [Na_2PdCl_4] = 25 µmol L^{-1}, [EDTA] = 250 µmol L^{-1}, PBS buffer, pH: 7.4, 5% DMSO at 37°C.

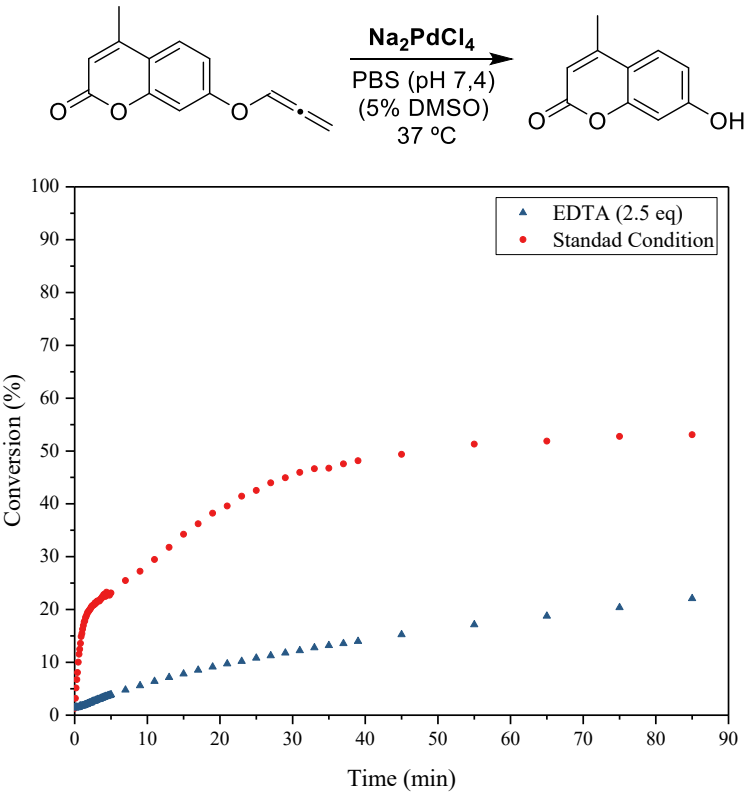


Figure S25 – Effect of EDTA addition on the kinetic profiles for the deallenylation reaction mediated by Na_2PdCl_4. Reaction conditions: [Prop-4-MU] = 100 µmol L^{-1}, [Na_2PdCl_4] = 25 µmol L^{-1}, [EDTA] = 250 µmol L^{-1}, PBS buffer, pH: 7.4, 5% DMSO at 37°C.

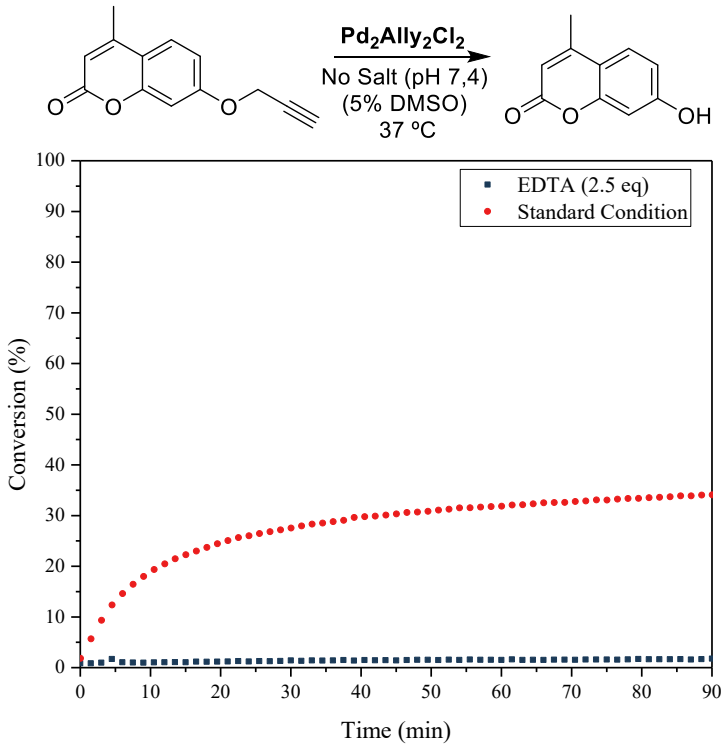


Figure S26 – Effect of EDTA addition on the kinetic profiles for the depropargylation reaction mediated by $Pd_2Ally_2Cl_2$. Reaction conditions: [Prop-4-MU] = 100 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1}, [EDTA] = 250 µmol L^{-1}, PBS buffer, pH: 7.4, 5% DMSO at 37°C

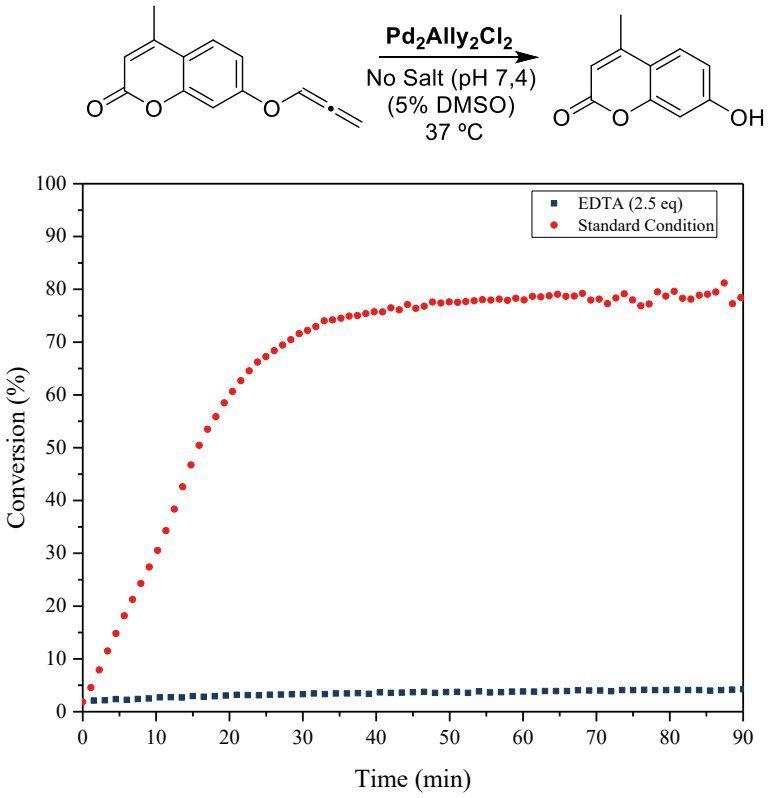


Figure S27 – Effect of EDTA addition on the kinetic profiles for the deallenylation reaction mediated by $Pd_2Ally_2Cl_2$. Reaction conditions: [Prop-4-MU] = 100 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1}, [EDTA] = 250 µmol L^{-1}, PBS buffer, pH: 7.4, 5% DMSO at 37°C.

4. Allypalladium chloride dimer in aqueous solutions

4.1 UV-vis studies

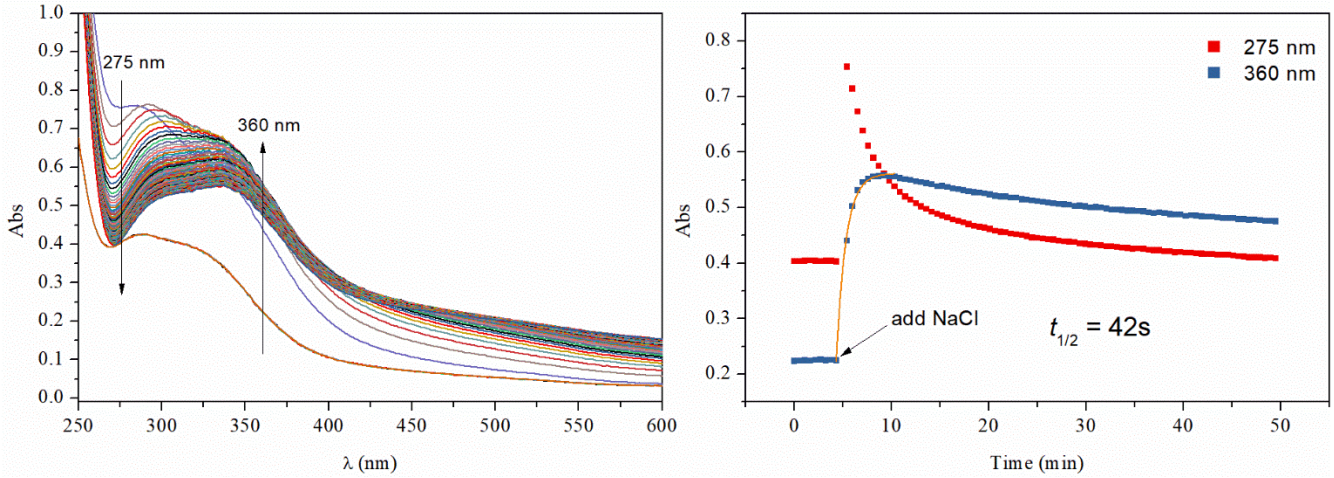


Figure S28 - UV-vis spectra scanning kinetic of pre-formed PdAlly$(H_2O)_2$ in PB buffer, with addition of $NaCl_{aq}$ (140 mmol L^{-1}) after 5 min. [AllylPd$(H_2O)_2$] = 1.0 mmol L^{-1}, pH 7.4, at 37°C. The pre-formed diaquo was prepared by mixing $Allyl_2Pd_2Cl_2$ with a aqueous solution of $AgNO_3$ for 24h, resulting in the formation of AllylPd$(H_2O)_2$ and the precitipation of chloride as AgCl.

4.2 ^{1}H NMR studies

In order to determine the nature of the diferent active species of $Allyl_2Pd_2Cl_2$ on the C-O cleavage reactions, ^{1}H NMR spectroscopy was used to follow the signals of the η_3-allylic protons (5.95 ppm (m, 1H), 4.49 ppm (d, *J* = 6,7, 2H) 3.51 ppm (d, *J*= 12,4, 2H)) of the complex in deutered oxide solution (10% DMSO-*d6*). The effect of chloride concentration on the signals was also evaluated. For this, a solution of $Allyl_2Pd_2Cl_2$ (10 mmol L^{-1}) in D_2O was followed for 140 min in the absence and presence of NaCl (140 mmol L^{-1}). No change in the spectra was observed in the time of analysis, indicating that the (η_3-allylic)Pd is stable in water, and the observed difference in reactivity of C-O cleavage reactions occurs due to the change of the groups (L = H_2O or Cl) bonded directly to the metal atom. However, in the presence of sodium chloride a decrease in coupling constants was observed, probably due to the change in the electronic charge of the solution. Water residual peak (4.79 ppm) has been removed for clarity.

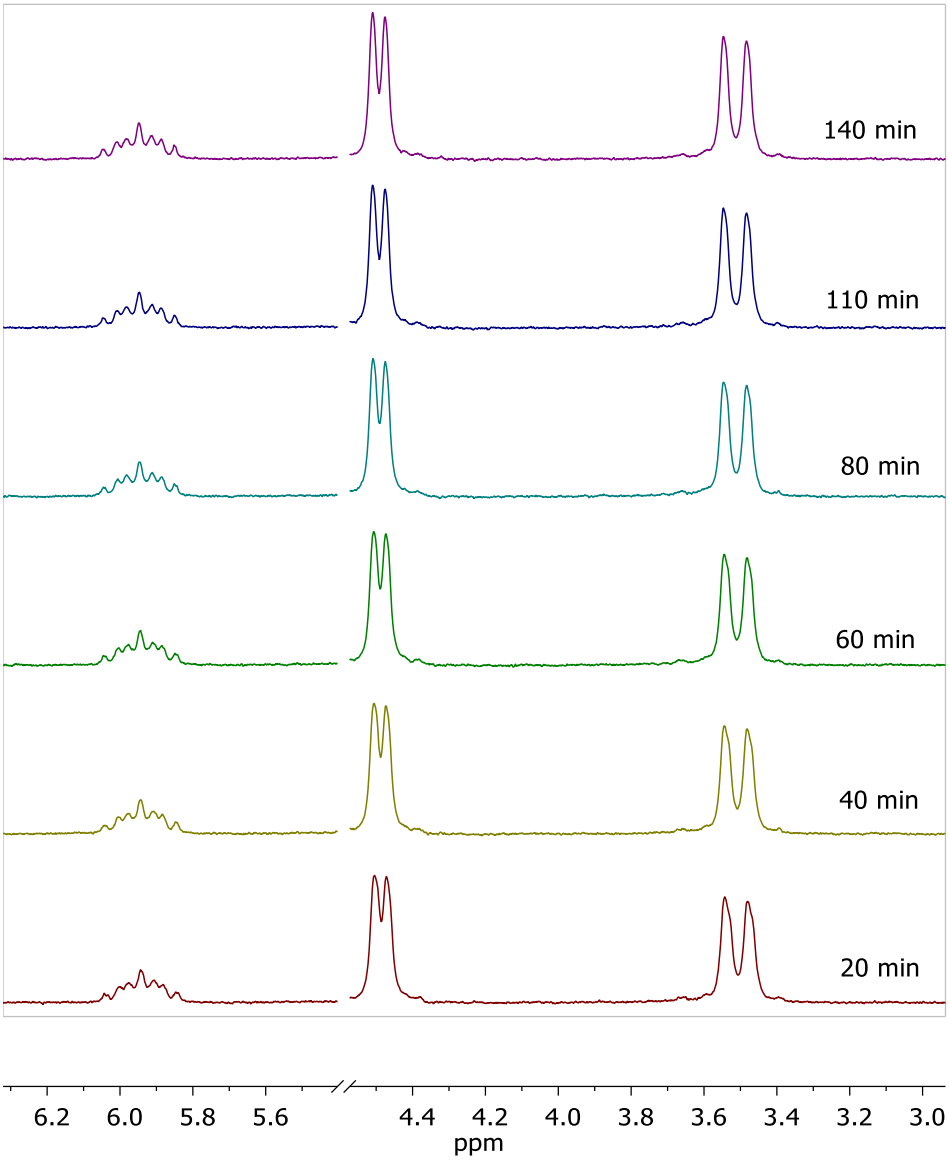


Figure S29 - Temporal analysis of $Pd_2Ally_2Cl_2$ (10 mmol L^{-1}) in D_2O (10% DMSO-*d6*) monitored by ^{1}H NMR (200 MHz).

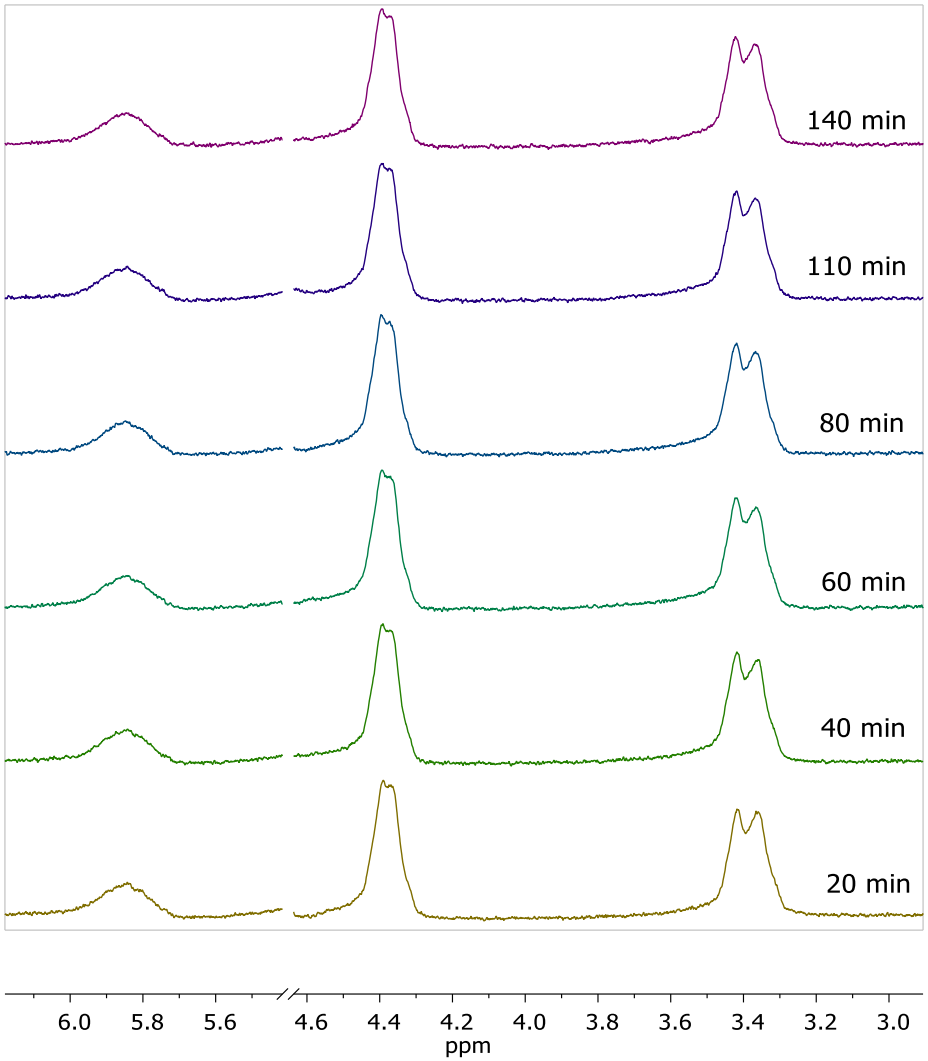


Figure S30 - Temporal analysis of $Pd_2Ally_2Cl_2$ (10 mmol L^{-1}) in D_2O (10% DMSO-*d6*) with NaCl (140 mmol L^{-1}) monitored by ^1H NMR (200 MHz).

4.3 XAS studies

X-Ray Absorption Spectroscopy (XAS) data was acquired at EMA beamline at Sirius, the fourth-generation light source at the Brazilian Synchrotron Light Laboratory (LNLS/CNPEM) in Campinas-SP.[14] The spectra were acquired at room temperature in transmission mode. A standard Pd foil (metallic Pd) was used to perform energy calibration in all scans. Four spectra were collected to improve the signal-to-noise ratio. The Palladium K-edge was chosen at 24.350 keV and the data acquired in transmission using solid and liquid samples in a 3D printed sample holder. The XAS spectra was analyzed using Demeter package (Athena/Artemis)[15] by fitting in R space using a Hanning window (dk = 1 in k space and dk = 0 in R space), using different k-ranges and a k^2 weighing factor. The structural parameters derived from fitting EXAFS using single-crystal data as reference standards (CCDC 1102405 for $Allyl_2Pd_2Cl_2$ and ICSD 41431 for OH_n parameters). In order to have a better signal-to-noise ratio, we increased the concentration of the Pd in solution to 5 mmol L^{-1} ($Allyl_2Pd_2Cl_2$ = 2,5 mmol L^{-1}). The X-ray absorption near edge structure (XANES) spectra of the $AllylPdX_n$ compounds shows very similar features, with the $AllylPdX_n$-PB having a more prominent first peak, but in comparison with the standard compound, $Allyl_2Pd_2Cl_2$, it is shifted downwards by some eV's.

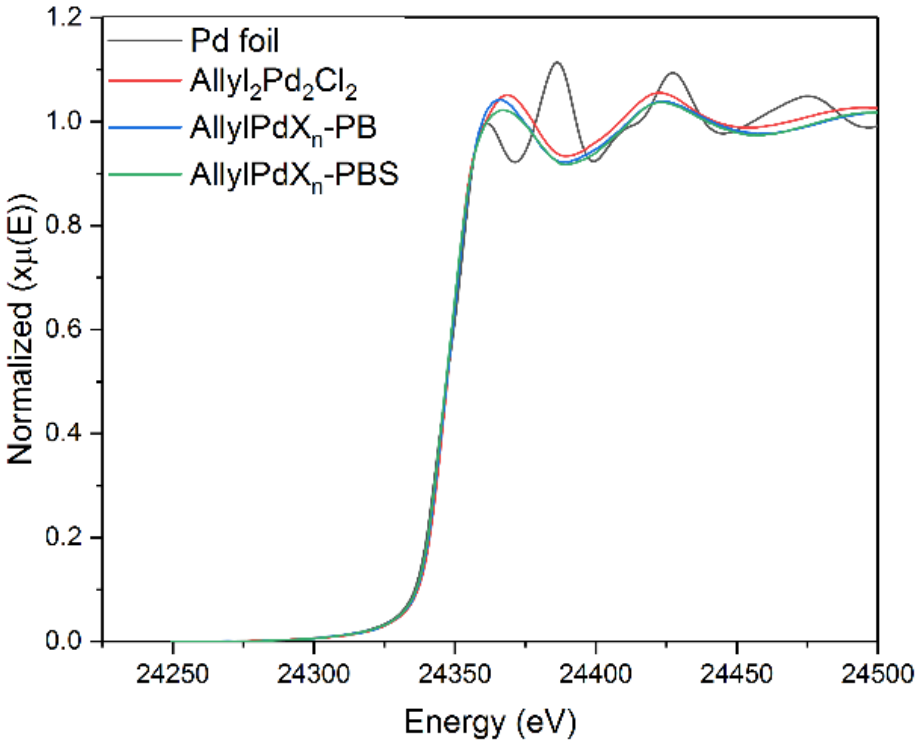


Figure S31 - Normalized XANES spectra of the samples analyzed in this work.The Pd foil standard was included as a reference

For the Extended X-ray absorption fine structure (EXAFS) experiments, the amplitude and E_0 parameters were obtained from the fitting of the solid sample $Allyl_2Pd_2Cl_2$ and used throughout the analysis. The measured structural parameters agree with the single crystal data, although we only considered one type of carbon with a coordination number of 3 for this analysis, with a n_3-Allyl coordination to the palladium. As a result, the Debye-Waller factor may be higher than expected due to the different bond distances between Pd and the C_1, C_2, and C_3 atoms of the Allyl moiety. All the structural parameters for the EXAFS analysis presented in Figure S31 are depicted in Table S1 below.

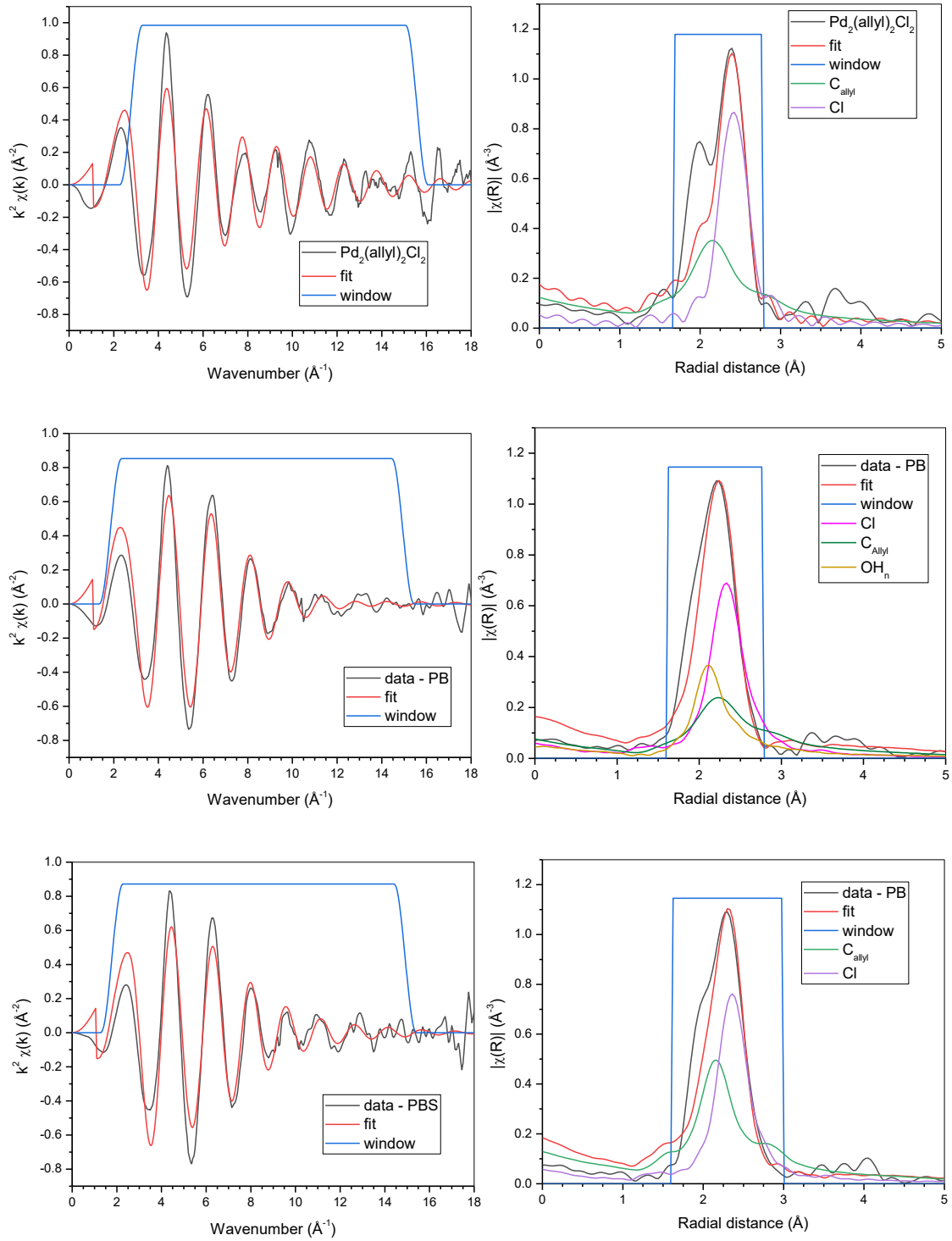


Figure S32 - k^2-weighted EXAFS spectra and respective Fourier Transforms showing the radial distance of the samples analyzed in this word. (a) $Allyl_2Pd_2Cl_2$, (b) $AllylPdX_n$-PB and (c) $AllylPdX_n$-PBS.

Table S1. Structural parameters obtained from EXAFS analysis of the catalyst systems employed in this work.

Sample	$Allyl_2Pd_2Cl_2$	$Allyl_2PdX_n$-PB	$Allyl_2PdX_n$-PBS
Amp	0.83 ± 0.02	0.83[a]	0.83[a]
E_0 (eV)	4.51 ± 0.35	4.51[a]	4.51[a]
R_{Pd-C} (Å)	2.14 ± 0.01	2.21 ± 0.01	2.18 ± 0.01
R_{Pd-Cl} (Å)	2.38 ± 0.01	2.31 ± 0.01	2.34 ± 0.01
R_{Pd-OHn} (Å)	-	2.07 ± 0.01	-
N_C	3.0[a]	2.53 ± 0.26	2.96 ± 0.26
N_{Cl}	2.0[a]	2.02 ± 0.06	2.04 ± 0.08
N_{OHn}	-	1.09 ± 0.10	-
σ^2_C ($x10^{-3}$)	12.3 ± 2.7	12.4 ± 2.7	8.1 ± 1.2
σ^2_{Cl} ($x10^{-3}$)	3.6 ± 0.3	6.9 ± 0.3	5.7 ± 0.4
σ^2_{OHn} ($x10^{-3}$)	-	4.3 ± 0.9	-
χ_v^2	90.20	114.52	220.15
R-factor ($x10^{-3}$)	8.6	5.2	10.0

[a] fixed values. Rx bond distance between Pd and the respective atom, σ^2 = Debye-Waller factor, N_X mean coordination number, χ_v^2 goodness of fit and R-factor is the agreement between the data and the reference crystal structure.

5. ESI-MS(+) analysis of the deallenylation reaction mediated by $Pd_2Ally_2Cl_2$ in water

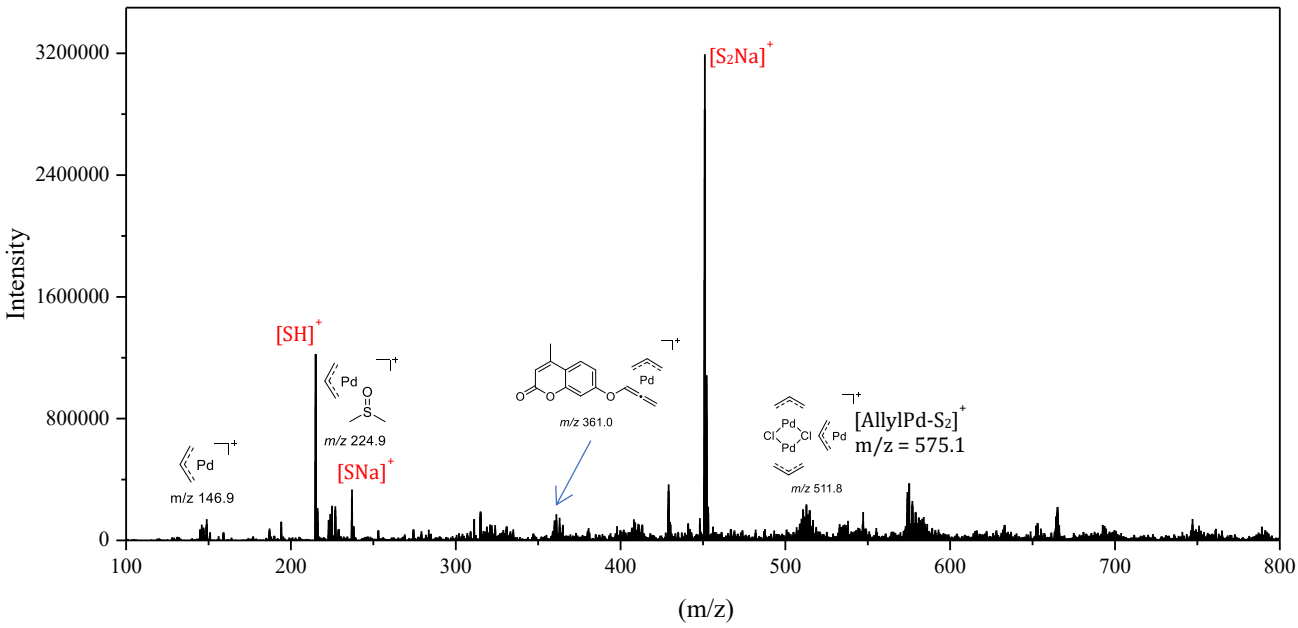


Figure S33 - ESI-MS(+) of the reaction medium after the start of deallenylation reaction mediated by $Allyl_2Pd_2Cl_2$ in water. Reaction conditions: [Alle-4-MU] = 100 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1} at 37°C. S = Alle-4-MU. (100 µL of reaction diluted in 100 µL of ACN)

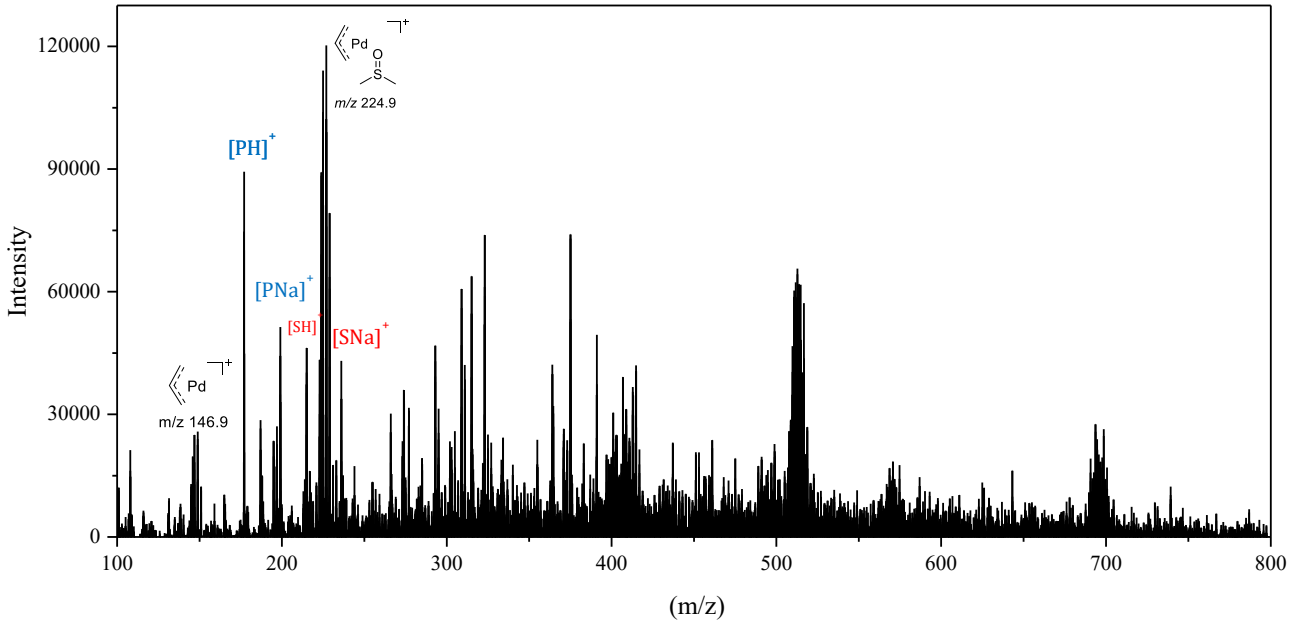


Figure S34 - ESI-MS(+) of the reaction medium after 15 min of deallenylation reaction mediated by $Allyl_2Pd_2Cl_2$ in water. Reaction conditions: [Alle-4-MU] = 100 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1} at 37°C. S = Alle-4-MU. (100 µL of reaction diluted in 100 µL of ACN)

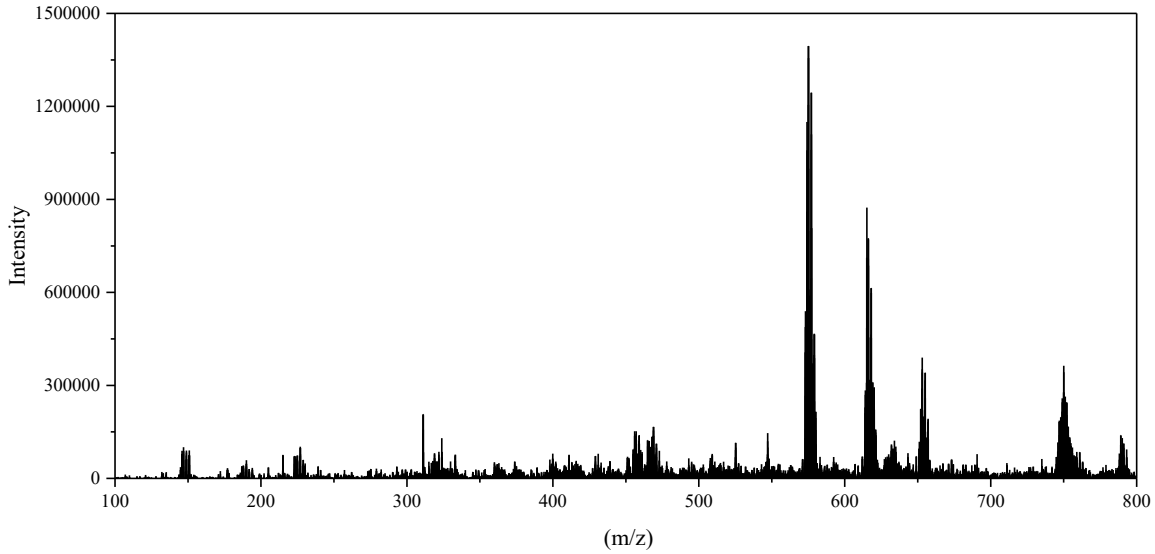


Figure S35 - ESI-MS(+) of the reaction medium after 15 min of deallenylation mediated by $Pd_2Ally_2Cl_2$ in water. Reaction conditions: [Alle-4-MU] = 100 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1} at 37°C. S = Alle-4-MU. (100 µL of reaction diluted in 100 µL of ACN)

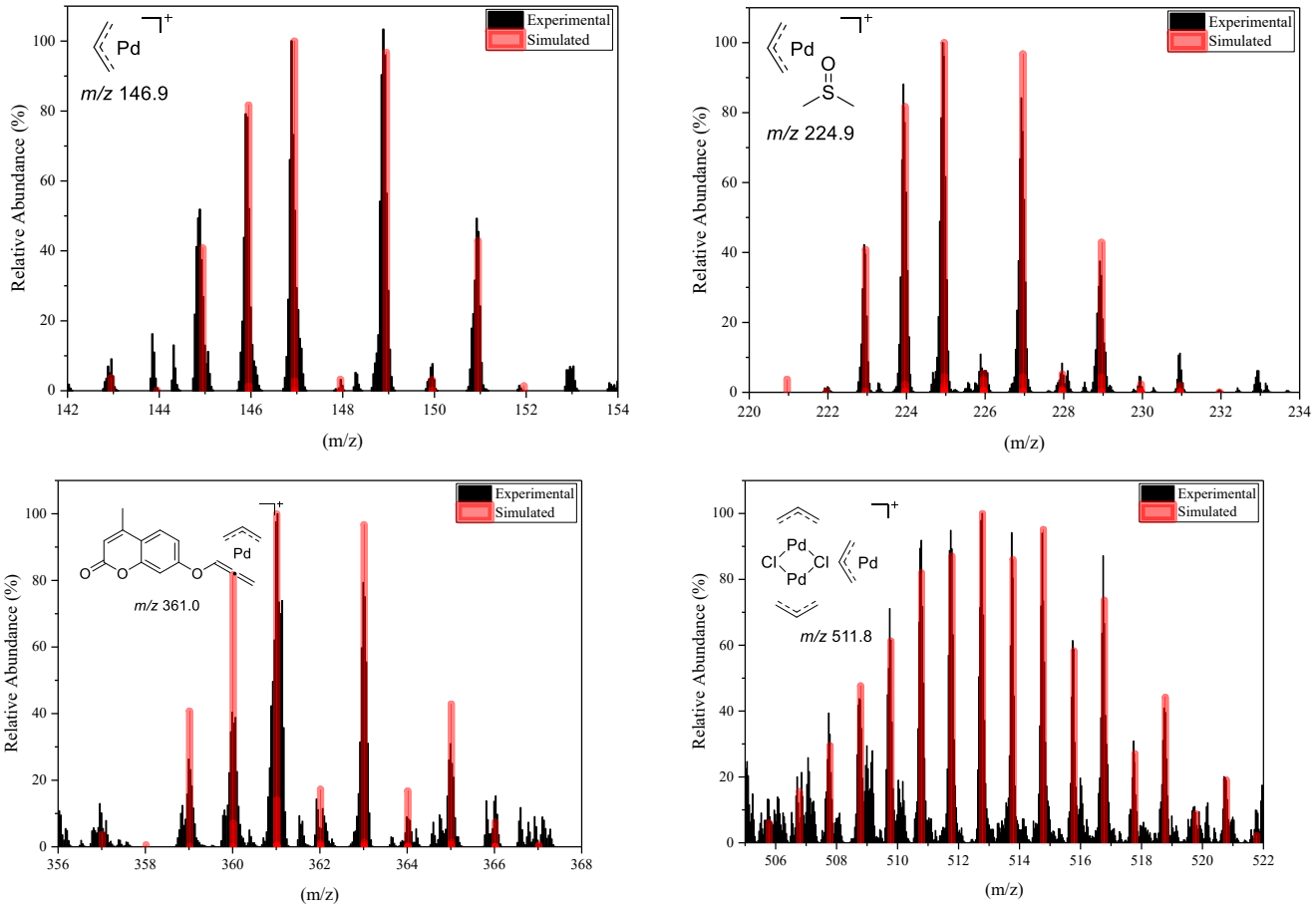


Figure S36 - ESI-MS simulated isotopologue patterns and exact masses of the Pd species presented at Figure S32-S33.

6. Mechanistic pathways calculated for deallenylation and depropargylation reactions

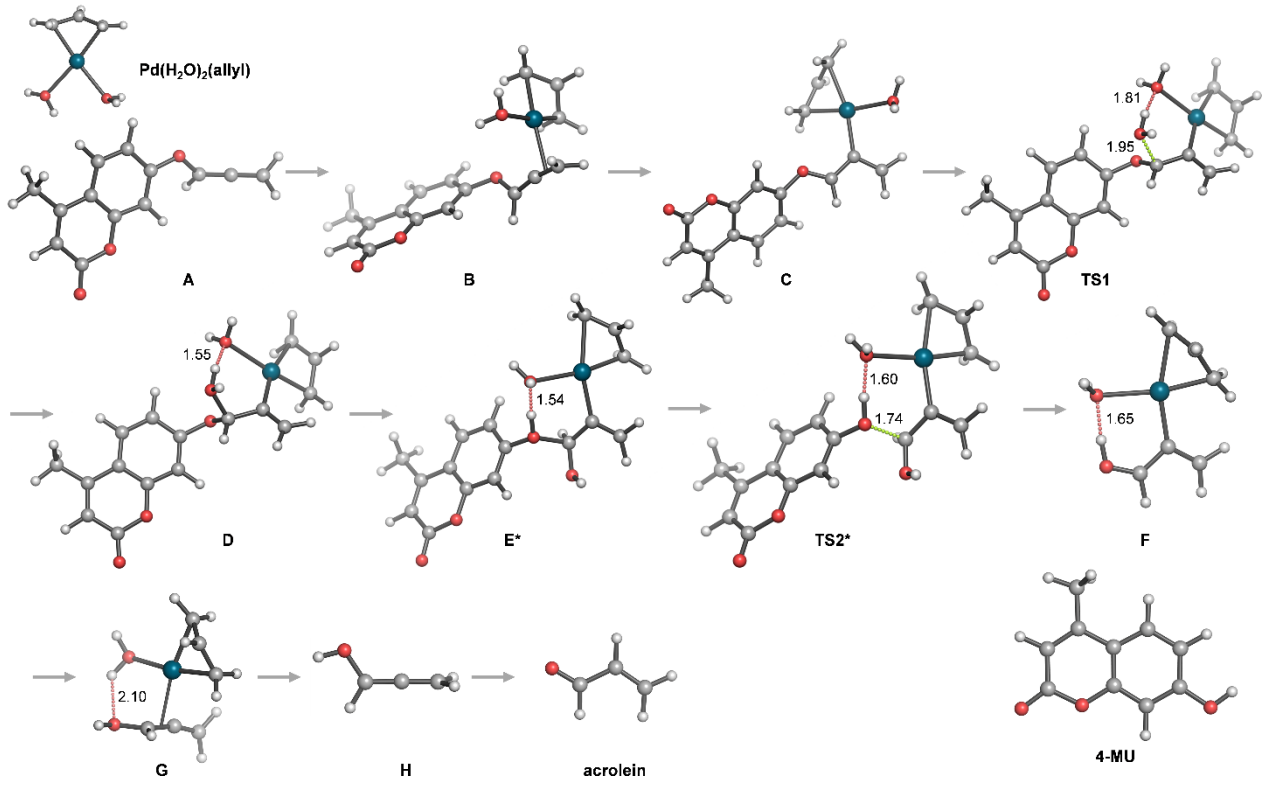


Figure S37 - Lowest-energy structures calculated with PCM(H_2O)/M06-2X/6-311+G(d,p)+SDD(Pd) level for the deallenylation reaction of Alle-4-MU (**A**) catalyzed by AllylPd(H_2O)$_2$ in water. Breaking/forming bonds are represented with green dotted lines. Hydrogen bonds are represented with red dotted lines. Distances are given in angstrom. Asterisks in stationary points **E** and **TS2** denote high-energy geometries.

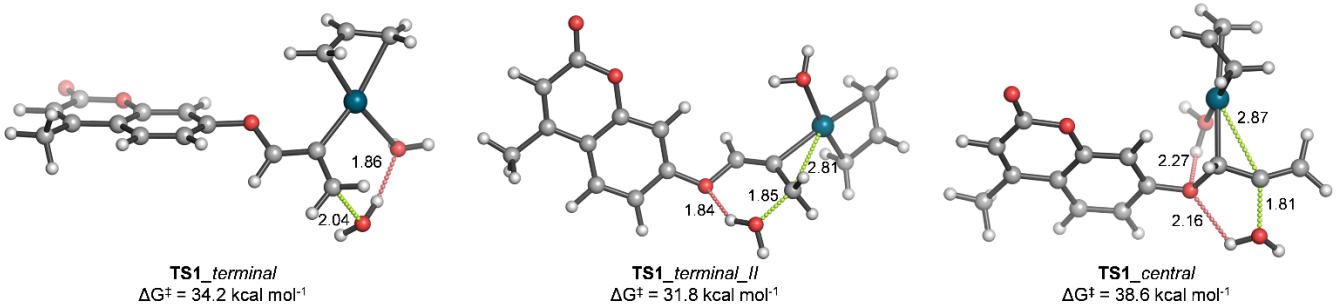


Figure S38 - Lowest-energy transition structures calculated with PCM(H_2O)/M06-2X/6-311+G(d,p)+SDD(Pd) for the attack of one water molecule to the terminal carbon atom of σ-complex **C** (**TS1**_*terminal*), of π-complex **B** (**TS1**_*terminal_II*), or to the central carbon atom of π-complex **B** (**TS1**_*central*). Breaking/forming bonds are represented with green dotted lines. Hydrogen bonds are represented with red dotted lines. Distances are given in angstrom.

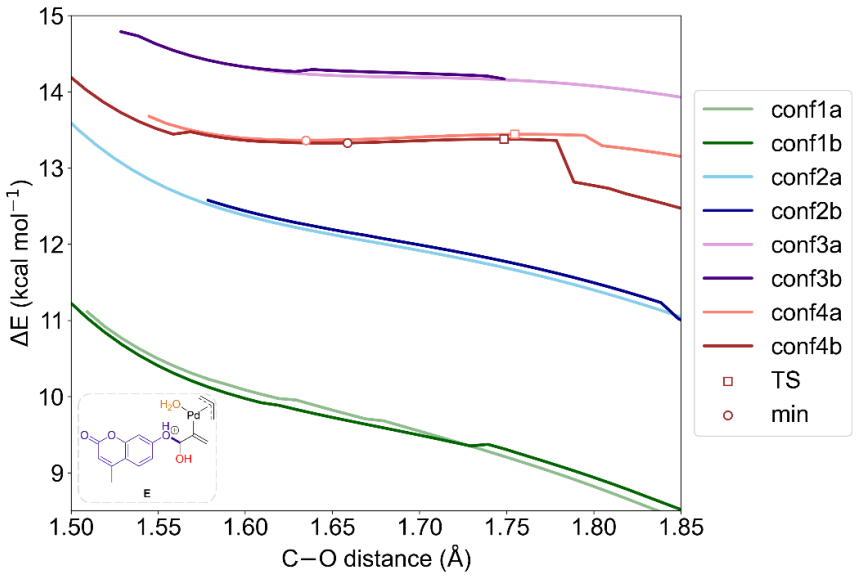


Figure S39 - Relaxed scans along the breaking C-O bond (in blue in the inset) from different conformers of intermediate **E** calculated with PCM(H_2O)/M06-2X/6-311+G(d,p)+SDD(Pd). Electronic energy is referred to that calculated for the separate reactants ($\Delta E = E_E - E_A - E_{Pd(H_2O)_2(allyl)}$). Only the scans for *conf4a* and *conf4b* (salmon and red lines, respectively) showed a minimum and a maximum (circle and square points, respectively) whose geometries could be fully optimized at the same theory level (labeled as **E*** and **TS2*** from *conf4b*).

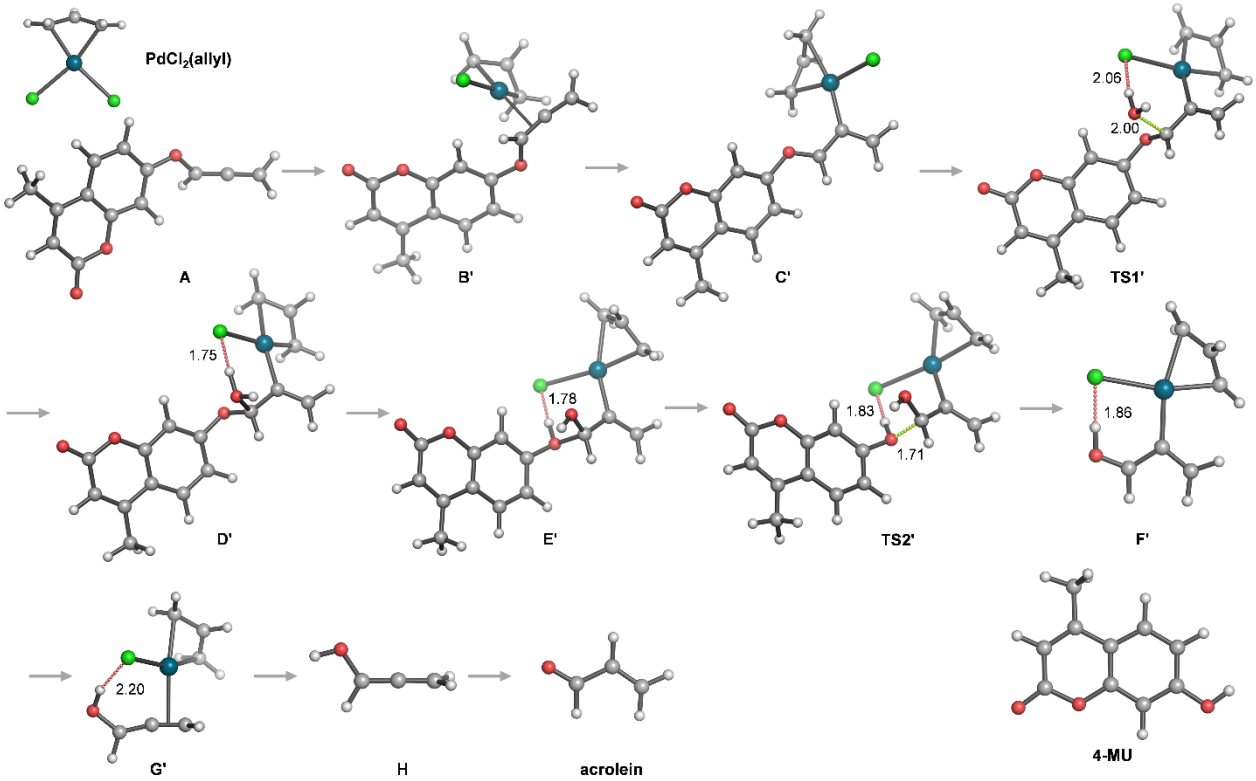


Figure S40 - Lowest-energy structures calculated with PCM(H_2O)/M06-2X/6-311+G(d,p)+SDD(Pd) for the deallenylation reaction of Alle-4-MU (**A**) catalyzed by Allyl$PdCl_2$ in water. Breaking/forming bonds are represented with green dotted lines. Non-covalent interactions are represented with red dotted lines. Distances are given in angstrom.

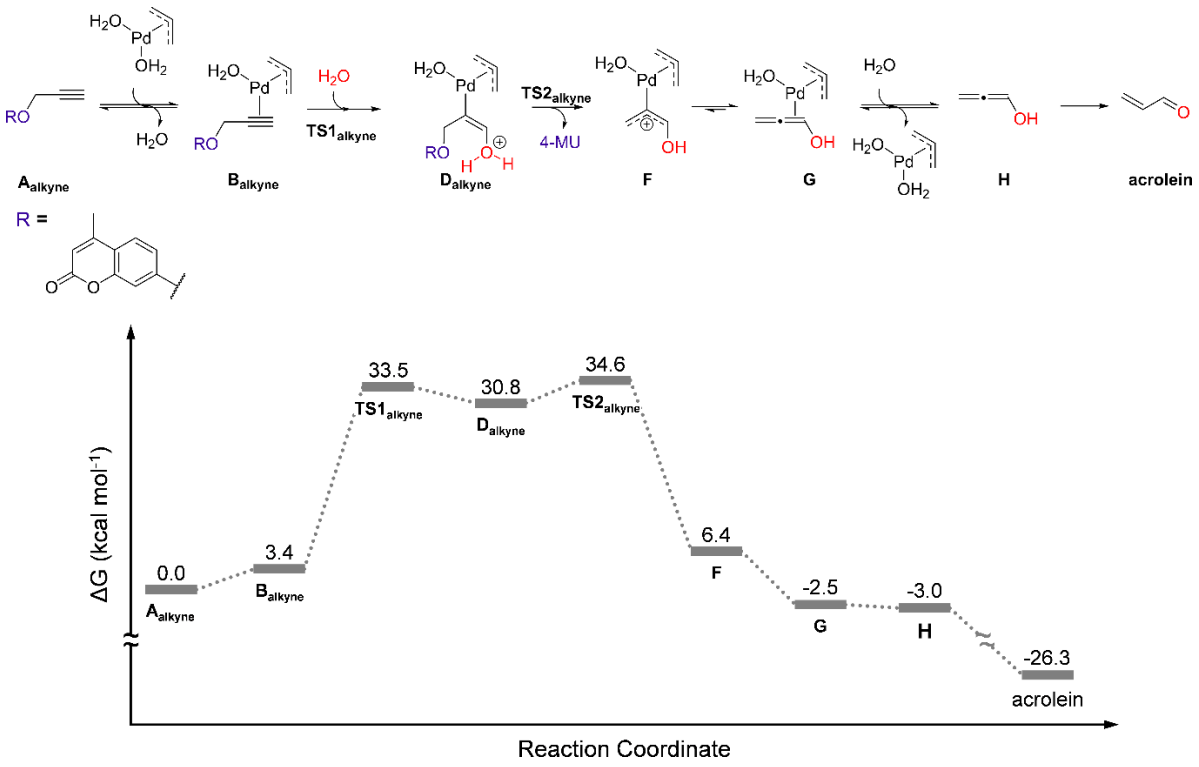


Figure S41 - Proposed mechanism and minimum energy pathway calculated with PCM(H_2O)/M06-2X/6-311+G(d,p)+SDD(Pd) for the first turnover of the depropargylation reaction of Prop-4-MU (**A_{alkyne}**) catalyzed by AllylPd(H_2O)$_2$ in water.

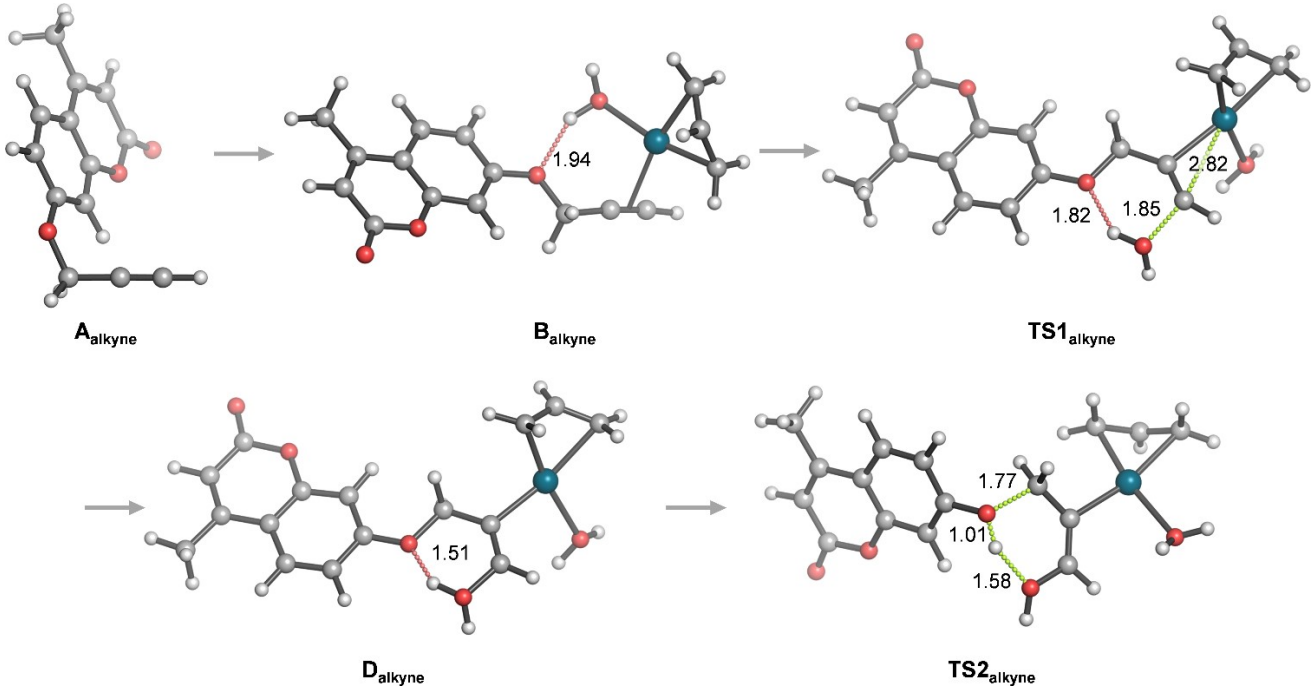


Figure S42 - Lowest-energy structures calculated with PCM(H_2O)/M06-2X/6-311+G(d,p)+SDD(Pd) for the depropargylation reaction of Prop-4-MU (**A_{alkyne}**) catalyzed by AllylPd(H_2O)$_2$ in water. Breaking/forming bonds are represented with green dotted lines. Hydrogen bonds are represented with red dotted lines. Distances are given in angstrom.

Table S2. Energies, entropies, and lowest frequencies of the lowest energy calculated structures.[a]

Structure	E_{elec} (Hartree)	E_{elec} + ZPE (Hartree)	H (Hartree)	S (cal mol^{-1} K^{-1})	G (Hartree)	Lowest freq. (cm^{-1})	# imag. freq.
H_2O	–76.428909	–76.407410	–76.403630	45.1	–76.425052	1604.0	0
PhOH	–611.506519	–611.346296	–611.334859	99.6	–611.382101	91.9	0
$Pd(H_2O)_2$(allyl)	–397.808562	–397.687094	–397.675734	98.6	–397.722367	84.7	0
A	–726.925605	–726.728099	–726.713409	118.2	–726.767575	27.9	0
B	–1048.305756	–1048.010476	–1047.986669	164.8	–1048.059672	18.2	0
C	–1048.279628	–1047.983957	–1047.960414	162.9	–1048.032945	13.8	0
TS1	–1124.714010	–1124.391330	–1124.366767	166.4	–1124.440965	–230.7	1
D	–1124.717183	–1124.392687	–1124.368478	166.6	–1124.441963	6.2	0
E	–1124.712934	–1124.388901	–1124.364542	164.9	–1124.438342	19.4	0
TS2	–1124.712848	–1124.389289	–1124.365337	163.7	–1124.438331	–102.0	1
F	–513.220846	–513.059615	–513.046415	109.6	–513.097291	30.1	0
G	–513.233006	–513.073061	–513.059115	112.0	–513.111465	42.8	0
H	–191.848697	–191.787891	–191.781908	69.8	–191.815023	93.8	0
acrolein	–191.887839	–191.825881	–191.820591	66.5	–191.852165	166.5	0
TS1_*terminal_II*	–1124.710068	–1124.388399	–1124.362978	172.5	–1124.439241	–365.1	1
TS1_*terminal*	–1124.707839	–1124.385469	–1124.360582	170.5	–1124.435398	–317.5	1
TS1_*central*	–1124.699073	–1124.378098	–1124.353024	166.7	–1124.428417	–445.2	1
A_{alkyne}	–726.926542	–726.727955	–726.713390	116.5	–726.767280	36.4	0
B_{alkyne}	–1048.306960	–1048.010424	–1047.987064	161.5	–1048.059233	16.0	0
$TS1_{alkyne}$	–1124.707058	–1124.385425	–1124.359921	173.2	–1124.436260	–391.1	1
D_{alkyne}	–1124.713561	–1124.390151	–1124.365066	173.1	–1124.440572	6.6	0
$TS2_{alkyne}$	–1124.706233	–1124.384395	–1124.359372	171.4	–1124.434546	–313.4	0
$PdCl_2$(allyl)	–1165.731179	–1165.658458	–1165.648954	94.6	–1165.693676	81.5	1
Cl^-	–460.380113	–460.380113	–460.377752	36.6	–460.395136		0
B'	–1432.272368	–1432.001215	–1431.978581	158.5	–1432.049729	25.7	0
C'	–1432.240860	–1431.969415	–1431.946920	159.5	–1432.017923	16.6	0
TS1'	–1508.678447	–1508.381491	–1508.357508	165.4	–1508.431117	–255.8	0
D'	–1508.685021	–1508.387389	–1508.363781	165.8	–1508.436519	10.0	1
E'	–1508.683493	–1508.386335	–1508.362335	166.5	–1508.436006	18.2	0
TS2'	–1508.683426	–1508.386227	–1508.362776	163.7	–1508.435510	–129.2	0
F'	–897.186338	–897.051088	–897.038619	108.3	–897.088773	27.2	1
G'	–897.199845	–897.064301	–897.051306	109.9	–897.102521	44.4	0

[a]Energy values calculated at the PCM(H_2O)/M06-2X/6-311+G(d,p)+SDD(Pd) level of theory.

1 Hartree = 627.51 kcal mol^{-1}. Thermal corrections at 298.15 K.

Table S3. Cartesian coordinates of the lowest energy structures calculated with PCM(H_2O)/M06-2X/6-311+G(d,p)+SDD(Pd).

Structure **H_2O**

O	-0.000000	0.000000	0.117644
H	0.000000	0.760078	-0.470577
H	-0.000000	-0.760078	-0.470577

Structure **4-MU**

C	-1.461658	-1.202733	-0.000153
C	-2.546910	-0.336927	0.000031
C	-2.353508	1.051788	0.000264
C	-1.070328	1.560825	0.000257
C	0.049567	0.715397	0.000018
H	-1.606235	-2.275202	-0.000280
H	-3.209995	1.716084	0.000473
H	-0.928137	2.634371	0.000490
C	-0.183290	-0.665253	-0.000121
O	0.847615	-1.557247	-0.000190
C	2.160204	-1.160825	0.000040
C	2.418644	0.265517	-0.000138
O	2.997337	-2.031844	0.000390
C	1.423744	1.180706	-0.000120
H	3.461883	0.552022	-0.000297
C	1.712143	2.650443	-0.000169
H	1.272250	3.125177	-0.880557
H	1.274159	3.124765	0.881407
H	2.785008	2.833726	-0.001255
O	-3.780343	-0.893050	-0.000148
H	-4.457452	-0.207449	0.000147

Structure **Pd(H_2O)$_2$(allyl)**

Pd	-0.086288	0.006834	0.011007
C	1.999913	-0.028478	-0.447995
C	1.624426	-1.211846	0.212074
H	1.692379	-1.276701	1.294385
C	1.660667	1.170788	0.204601
H	1.691226	2.105618	-0.342125
H	1.733550	1.240064	1.286352
H	1.624610	-2.150291	-0.329289
H	-1.838908	-2.038197	-0.782687
H	-1.648968	2.335048	-0.428534
O	-1.749009	1.505935	0.050610
O	-1.836448	-1.411998	-0.050358
H	-2.571641	1.108203	-0.258052
H	-1.970362	-1.936764	0.746861
H	2.230987	-0.035638	-1.507342

Structure **A**

C	3.511830	0.198661	0.582029
C	4.602070	0.568317	-0.030683
C	5.709095	0.943186	-0.603548
H	6.662138	0.506395	-0.322254
H	3.139265	0.687934	1.476372
H	5.710086	1.700586	-1.380819
O	2.797797	-0.910770	0.160754
C	1.440693	-0.807311	0.110661
C	0.737460	-2.017855	0.025237
C	0.773686	0.407994	0.116876
C	-0.637539	-2.000488	-0.044394
H	1.292650	-2.946789	0.019379
H	1.293677	1.355957	0.152065
C	-1.352855	-0.789681	-0.028748
H	-1.176606	-2.937543	-0.107858
C	-0.616750	0.393980	0.052242
O	-1.227515	1.611252	0.063756
C	-2.591134	1.747771	0.001871
C	-3.371393	0.528692	-0.078308
O	-3.032443	2.871795	0.019098
C	-2.799910	-0.695918	-0.095191
H	-4.443987	0.662152	-0.125592
C	-3.622550	-1.944282	-0.182338
H	-3.355561	-2.514263	-1.075678
H	-3.436759	-2.584818	0.683224
H	-4.683838	-1.706217	-0.221938

Structure **B**

Pd	3.265650	-0.151462	0.292982
C	4.541644	1.621840	0.216904
C	3.869957	1.631385	1.435273
H	2.868208	2.046727	1.508221
C	3.748172	1.458628	-0.944330
H	4.227648	1.223965	-1.887399
H	2.777168	1.944560	-1.007853
H	4.414043	1.495642	2.361567
H	3.183293	-1.579108	2.725348
O	2.710346	-1.655194	1.889454
H	1.773763	-1.671687	2.117285
H	5.607203	1.423772	0.181515
C	3.170418	-1.951808	-1.249507
H	3.301625	-2.783377	-0.563270
H	3.978155	-1.730432	-1.941059
C	2.012951	-1.307571	-1.324021
C	0.831955	-0.816027	-1.594695
H	0.170243	-1.296715	-2.309351
O	0.396130	0.366232	-1.051689
C	-0.930519	0.471573	-0.733337
C	-1.427775	1.774284	-0.607378
C	-1.737409	-0.632893	-0.516496
C	-2.751569	1.961293	-0.274152
H	-0.763281	2.610517	-0.781257
H	-1.365625	-1.647379	-0.574712
C	-3.610460	0.869037	-0.061318
H	-3.137323	2.968751	-0.181287
C	-3.072556	-0.412946	-0.189571
O	-3.830050	-1.526229	0.008828
C	-5.160662	-1.457791	0.337523
C	-5.738219	-0.133975	0.469360
O	-5.743545	-2.503637	0.490344
C	-5.015974	0.992663	0.284327
H	-6.788549	-0.106104	0.727472
C	-5.629180	2.351065	0.428323
H	-5.118138	2.918390	1.210051
H	-5.531680	2.914283	-0.502939
H	-6.684319	2.273535	0.683565

Structure **C**

Pd	3.521623	-0.221354	0.011639
C	3.646229	-1.527367	1.773782
C	4.359144	-2.210289	0.809706
H	3.847740	-2.795316	0.050632
C	2.325459	-1.069500	1.466820
H	1.828122	-0.411978	2.169889
H	1.662425	-1.722450	0.904512
H	5.421177	-2.382048	0.931947
H	5.836767	-0.107295	-1.611777
O	5.030875	0.417469	-1.558194
H	4.675076	0.444316	-2.453458
H	4.173299	-1.100865	2.621618
C	2.859108	2.608454	-0.896828
H	3.930865	2.756287	-0.992703

H	2.235750	3.469232	-1.140829
C	2.345831	1.415671	-0.485703
C	0.937386	1.484530	-0.453130
H	0.374936	2.363165	-0.781893
O	0.237173	0.485001	-0.042632
C	-1.158060	0.577416	0.058292
C	-1.757854	1.690249	0.636619
C	-1.863792	-0.517184	-0.392549
C	-3.138115	1.703790	0.734716
H	-1.165261	2.509349	1.023221
H	-1.365890	-1.373904	-0.826744
C	-3.909331	0.627080	0.278746
H	-3.624643	2.559174	1.185378
C	-3.247672	-0.473520	-0.278250
O	-3.924088	-1.558267	-0.736658
C	-5.293621	-1.642115	-0.679974
C	-5.999938	-0.510680	-0.102280
O	-5.802315	-2.644576	-1.111805
C	-5.363771	0.583486	0.362492
H	-7.077365	-0.604438	-0.069243
C	-6.108548	1.738409	0.954978
H	-5.795708	1.903299	1.988899
H	-5.898956	2.654031	0.396794
H	-7.180870	1.554108	0.938018

Structure **TS1**

Pd	3.423409	0.078603	-0.153839
C	5.262096	-0.463243	-1.257416
C	4.964946	0.771782	-1.784751
H	4.178996	0.887532	-2.525538
C	4.244029	-1.475517	-1.211899
H	4.453436	-2.393035	-0.674320
H	3.591688	-1.592387	-2.074161
H	5.640765	1.606274	-1.646496
H	3.366689	2.547592	1.208726
O	2.643622	2.054064	0.801152
H	2.269879	2.641553	0.131752
H	6.149299	-0.577099	-0.642046
C	2.353707	-2.210339	1.630364
C	2.110571	-1.081109	0.941293
C	0.717099	-0.681743	1.022988
O	0.740944	0.772699	2.318856
H	1.583031	-2.723992	2.206603
H	-0.001636	-1.232380	1.631210
H	1.433337	1.365228	1.957868
H	1.057479	0.462626	3.178110
O	0.224269	-0.010378	0.009149
H	3.334859	-2.673750	1.636973
C	-1.153230	0.223956	-0.030784
C	-2.025345	-0.842718	-0.097736
C	-1.574421	1.548362	-0.055899
H	-1.683477	-1.869991	-0.110089
C	-2.930591	1.804353	-0.136083
H	-0.844545	2.345720	-0.007507
C	-3.862980	0.758070	-0.195554
H	-3.276542	2.829940	-0.151806
C	-3.384218	-0.555416	-0.174846
O	-4.221566	-1.624077	-0.241152
C	-5.583718	-1.480090	-0.329976
C	-6.102446	-0.123305	-0.348370
O	-6.241829	-2.488130	-0.384663
C	-5.302801	0.961228	-0.285470
H	-7.178882	-0.038533	-0.416901
C	-5.856651	2.351638	-0.305943
H	-5.567829	2.889968	0.600085
H	-5.460442	2.907046	-1.159473
H	-6.942738	2.333055	-0.372620

Structure **D**

Pd	3.440040	0.095568	-0.100886
C	5.314460	-0.301666	-1.225190
C	5.038007	0.986780	-1.611599
H	4.261058	1.196675	-2.341121
C	4.291922	-1.308842	-1.322484
H	4.489931	-2.285609	-0.896736
H	3.662579	-1.320315	-2.209438
H	5.714575	1.794510	-1.362626
H	3.257743	2.332018	1.685089
O	2.585682	1.943365	1.108116
H	2.272316	2.653210	0.530323
H	6.187984	-0.494052	-0.609711
C	2.310920	-2.437023	1.244605
C	2.101128	-1.194560	0.795714
C	0.717877	-0.688872	1.020097
O	0.774957	0.442126	2.098677
H	1.529478	-3.022976	1.730507
H	0.009722	-1.382281	1.480249
H	1.481249	1.120176	1.812156
H	1.000577	0.087617	2.975971
O	0.211355	-0.045780	-0.076267
H	3.273832	-2.926661	1.144571
C	-1.153354	0.210146	-0.083118
C	-2.051190	-0.839407	-0.145071
C	-1.568579	1.539620	-0.083617
H	-1.727065	-1.872377	-0.172118
C	-2.922032	1.817284	-0.137982
H	-0.828274	2.328505	-0.043106
C	-3.870509	0.785315	-0.188829
H	-3.253477	2.847971	-0.137518
C	-3.406461	-0.534038	-0.190865
O	-4.260773	-1.591927	-0.249399
C	-5.621446	-1.430103	-0.305436
C	-6.123812	-0.067538	-0.298683
O	-6.294097	-2.429871	-0.355038
C	-5.308487	1.006349	-0.244410
H	-7.200368	0.031404	-0.341313
C	-5.845954	2.403517	-0.239646
H	-5.532278	2.928988	0.665672
H	-5.459991	2.963011	-1.095203
H	-6.933371	2.398978	-0.284522

Structure **E**

Pd	-3.351425	-0.252662	0.196764
C	-5.423752	-0.889042	-0.234062
C	-4.825985	-2.072725	0.131720
H	-4.183162	-2.609448	-0.560159
C	-4.804933	-0.068326	-1.237553
H	-5.205760	0.922859	-1.414037
H	-4.382852	-0.552428	-2.115233
H	-5.151331	-2.603231	1.017653
H	-1.970707	-0.506618	2.691444
O	-1.760109	-0.842007	1.808974
H	-1.618439	-1.794389	1.896848
H	-6.180867	-0.455157	0.411799
C	-2.911527	2.684315	-0.481864
C	-2.335738	1.483655	-0.345407
C	-0.908912	1.395469	-0.769852
O	-0.161865	0.654394	0.496187
H	-2.398316	3.565247	-0.868448
H	-0.703355	0.676740	-1.561898
H	-0.765063	0.022749	1.013126
O	-0.166232	2.494659	-0.964281
H	-3.957715	2.835250	-0.238547
H	-0.450197	3.194542	-0.358438
C	1.115081	0.124489	0.254307
C	2.194481	0.941561	0.510718

C	1.239414	-1.168546	-0.243292
H	2.067973	1.943566	0.897692
C	2.511800	-1.660723	-0.471949
H	0.360887	-1.769407	-0.444909
C	3.645893	-0.874648	-0.225208
H	2.629879	-2.667566	-0.850906
C	3.460750	0.424122	0.260464
O	4.510084	1.246969	0.522568
C	5.811143	0.854710	0.330324
C	6.025766	-0.492119	-0.172514
O	6.672804	1.654764	0.592075
C	5.010800	-1.336588	-0.445851
H	7.060488	-0.775106	-0.313874
C	5.252214	-2.720457	-0.962361
H	4.832471	-3.461338	-0.277547
H	4.766989	-2.855693	-1.932014
H	6.318170	-2.909235	-1.073604

Structure **TS2**

Pd	-3.356163	-0.254057	0.170207
C	-5.422768	-0.857674	-0.313508
C	-4.836403	-2.052465	0.037616
H	-4.190760	-2.581161	-0.657830
C	-4.780793	-0.022701	-1.288711
H	-5.169417	0.975487	-1.452187
H	-4.343364	-0.492055	-2.166900
H	-5.178055	-2.598646	0.907780
H	-2.071618	-0.599547	2.694675
O	-1.839076	-0.922607	1.813719
H	-1.731856	-1.879986	1.888872
H	-6.187381	-0.431647	0.328641
C	-2.909451	2.705403	-0.407938
C	-2.330990	1.500740	-0.305301
C	-0.918350	1.436834	-0.742724
O	-0.143200	0.618191	0.588262
H	-2.401676	3.596677	-0.778426
H	-0.672887	0.708209	-1.512860
H	-0.750963	-0.032792	1.047407
O	-0.159723	2.516818	-0.871627
H	-3.954862	2.848515	-0.156668
H	-0.461917	3.211716	-0.267203
C	1.123372	0.092850	0.332515
C	2.203340	0.925266	0.540416
C	1.254787	-1.209309	-0.144174
H	2.076480	1.933402	0.911097
C	2.526011	-1.691967	-0.395934
H	0.378492	-1.822718	-0.315913
C	3.657546	-0.888261	-0.196982
H	2.645934	-2.704759	-0.758375
C	3.468256	0.418393	0.264976
O	4.514232	1.260257	0.478480
C	5.813881	0.881902	0.253698
C	6.032535	-0.473355	-0.222775
O	6.671643	1.700369	0.469280
C	5.021197	-1.337489	-0.445230
H	7.066398	-0.746331	-0.387835
C	5.267008	-2.730917	-0.933433
H	4.874200	-3.459152	-0.219685
H	4.758626	-2.896504	-1.886358
H	6.332072	-2.909791	-1.067702

Structure **F**

Pd	-0.416715	-0.132103	-0.044633
C	-2.453626	0.451704	0.579928
C	-2.671150	-0.656088	-0.208095
H	-2.644901	-0.584000	-1.291739
C	-1.635161	1.512593	0.069237
H	-1.338288	2.304922	0.746784
H	-1.760642	1.815048	-0.968524
H	-3.091097	-1.558874	0.217221
H	0.275392	-2.852492	0.452157
O	0.621016	-2.209629	-0.180604
H	0.564299	-2.621445	-1.052842
H	-2.647213	0.395048	1.646331
C	2.655956	0.337761	0.199878
C	1.386655	0.935826	-0.053380
C	1.553774	2.256227	-0.318838
H	0.720012	2.904418	-0.569372
H	3.563757	0.933652	0.315664
O	2.870432	-0.911501	0.315263
H	2.533478	2.735109	-0.311818
H	2.043834	-1.453741	0.179615

Structure **G**

Pd	-0.368329	-0.135068	-0.055269
C	-2.341429	0.340013	0.723131
C	-2.500901	-0.512779	-0.367692
H	-2.544271	-0.111517	-1.376560
C	-1.547420	1.493287	0.517685
H	-1.211463	2.066943	1.373377
H	-1.615755	2.033942	-0.423175
H	-2.876295	-1.518200	-0.223913
H	0.168962	-2.799208	-0.852746
O	0.645759	-1.963436	-0.883474
H	1.475100	-2.095933	-0.402954
H	-2.536534	-0.016236	1.728638
C	1.833219	0.355510	0.920956
C	1.656345	1.030391	-0.214760
C	1.777547	1.821212	-1.247741
H	1.012357	1.899742	-2.011598
H	1.524694	0.762731	1.878772
O	2.496796	-0.835369	0.933827
H	2.470472	-1.213349	1.820674
H	2.671239	2.428831	-1.360447

Structure **H**

C	-0.623366	0.475113	-0.000011
C	0.639104	0.137606	-0.000002
C	1.908524	-0.161889	0.000003
H	2.459749	-0.292453	0.926871
H	-0.920617	1.518651	-0.000160
H	2.459658	-0.292875	-0.926860
O	-1.633084	-0.454882	0.000030
H	-2.479693	0.000760	-0.000029

Structure **acrolein**

C	0.669587	0.349298	-0.000098
C	-0.561660	-0.456290	-0.000069
C	-1.749864	0.146127	0.000062
H	-2.676664	-0.414112	0.000091
H	0.518443	1.444579	-0.000210
H	-1.824107	1.229572	0.000137
O	1.785551	-0.119918	0.000095
H	-0.450453	-1.535511	-0.000146

Structure **TS1_*terminal_II***

Pd	-3.516892	-0.499355	-0.024038
C	-5.523383	-0.366630	-0.877884
C	-5.224983	-1.718212	-0.871552
H	-4.625397	-2.156786	-1.664038
C	-4.581824	0.527359	-1.468094
H	-4.717796	1.593873	-1.333231
H	-4.076777	0.234440	-2.385429
H	-5.786575	-2.399581	-0.244914
H	-2.650966	-2.832209	1.349364
O	-2.514231	-1.884653	1.455789

H	-1.559522	-1.751334	1.477602
H	-6.281868	0.020176	-0.205319
C	-2.393830	1.776055	1.184751
H	-2.542196	1.414356	2.197232
C	-1.890681	0.871510	0.233399
C	-0.743372	0.756811	-0.403960
H	-0.506163	0.003525	-1.145694
O	0.282820	1.701386	-0.217360
H	-3.140075	2.489897	0.847300
O	-1.119891	3.018566	1.672885
H	-0.395461	2.875998	1.032953
H	-1.429688	3.929315	1.569472
C	1.578828	1.262518	-0.235676
C	1.921481	-0.056697	0.011964
C	2.556435	2.231718	-0.493787
H	1.185313	-0.815128	0.242369
C	3.884711	1.865247	-0.508741
H	2.249275	3.252484	-0.681221
C	4.275335	0.535472	-0.275524
H	4.639111	2.615366	-0.710385
C	3.270183	-0.399005	-0.018004
O	3.560358	-1.706129	0.229198
C	4.847305	-2.181956	0.237778
C	5.903870	-1.226555	-0.034537
O	4.997523	-3.356995	0.470160
C	5.653907	0.077654	-0.283066
H	6.909038	-1.626714	-0.026257
C	6.757973	1.049789	-0.562718
H	6.621773	1.507892	-1.545378
H	6.754538	1.853687	0.177406
H	7.726086	0.553208	-0.537532

Structure **TS1_*terminal***

Pd	3.322310	-0.469291	-0.133249
C	3.038098	-2.391640	-1.175086
C	4.373444	-2.430964	-0.842137
H	5.108207	-1.876223	-1.418622
C	2.513131	-1.243260	-1.857888
H	1.440493	-1.166239	-1.987562
H	3.105752	-0.798771	-2.654032
H	4.747400	-3.182650	-0.158511
H	4.269899	-0.397772	2.511817
O	4.496961	0.174149	1.767689
H	5.450843	0.080853	1.650504
H	2.350951	-3.077723	-0.689207
C	0.836844	1.341702	-0.033811
C	2.198648	1.263000	-0.086193
C	2.780162	2.540977	-0.053136
H	3.794399	2.697505	-0.400027
O	3.523217	2.804697	1.831223
H	0.287013	2.281777	0.045074
O	0.079321	0.249748	-0.076348
H	2.172085	3.442946	0.001631
H	3.909295	1.922215	1.990332
H	2.773450	2.878936	2.435080
C	-1.292127	0.377278	-0.211777
C	-1.852304	1.284632	-1.110891
C	-2.064921	-0.480304	0.547516
C	-3.229720	1.340300	-1.222607
H	-1.222569	1.916340	-1.724319
H	-1.612846	-1.182741	1.235061
C	-4.055530	0.499326	-0.464805
H	-3.674629	2.039248	-1.919257
C	-3.444642	-0.406287	0.409929
O	-4.174832	-1.259667	1.177746
C	-5.546114	-1.284532	1.140482
C	-6.198503	-0.353992	0.236195
O	-6.102463	-2.075931	1.860179
C	-5.509020	0.507433	-0.540578
H	-7.279596	-0.395881	0.225669
C	-6.200096	1.460039	-1.465841
H	-5.941704	2.491533	-1.213977
H	-5.886177	1.284845	-2.497787
H	-7.280238	1.342963	-1.402537

Structure **TS1_*central***

Pd	2.128309	-0.792408	0.393170
C	2.142407	-2.922766	-0.058696
C	2.706191	-2.818292	1.202987
H	3.757737	-2.573200	1.320711
C	2.673944	-2.116364	-1.106688
H	2.136919	-2.060291	-2.046353
H	3.750522	-1.978730	-1.174359
H	2.198659	-3.235223	2.063655
H	1.267466	0.090988	2.950457
O	1.761215	0.479575	2.220790
H	1.311128	1.302816	1.992863
H	1.158109	-3.366099	-0.171183
C	1.716111	0.984823	-0.808423
C	2.955676	1.654071	-0.860489
C	4.251617	1.595409	-0.696572
H	4.678038	0.730030	-0.205936
H	1.356435	0.696098	-1.798269
O	0.768889	1.835772	-0.145553
H	4.915269	2.375292	-1.046058
O	2.584220	3.293089	-1.536325
H	1.673531	3.466267	-1.243693
H	3.132858	3.999568	-1.162691
C	-0.527757	1.436774	-0.061511
C	-1.005788	0.239676	-0.574957
C	-1.386622	2.329687	0.600755
H	-0.378963	-0.477002	-1.086856
C	-2.718627	2.016112	0.745463
H	-0.979644	3.255262	0.987786
C	-3.242042	0.812317	0.239901
H	-3.373604	2.709982	1.257462
C	-2.359038	-0.049113	-0.412320
O	-2.778683	-1.236165	-0.931588
C	-4.082971	-1.654220	-0.845910
C	-5.013697	-0.770469	-0.172481
O	-4.350475	-2.724104	-1.338103
C	-4.632985	0.414532	0.354644
H	-6.035821	-1.120852	-0.118018
C	-5.609033	1.314387	1.047808
H	-5.297912	1.490898	2.080347
H	-5.653763	2.285167	0.548159
H	-6.604815	0.875095	1.051331

Structure **A_{alkyne}**

C	-4.000785	1.651410	1.407816
H	-4.107422	2.290364	2.254673
C	-3.875731	0.932745	0.454934
C	-3.740667	0.050472	-0.709626
H	-4.716644	-0.343235	-0.988962
H	-3.338045	0.601502	-1.564284
O	-2.941091	-1.093057	-0.434945
C	-1.604554	-0.928621	-0.278838
C	-0.882232	-2.105388	-0.016390
C	-0.952578	0.293271	-0.371741
C	0.482771	-2.051036	0.144987
H	-1.421561	-3.041309	0.051111
H	-1.464325	1.227415	-0.556138
C	1.178986	-0.831684	0.053810
H	1.029655	-2.964171	0.344851
C	0.430164	0.316653	-0.205887
O	1.019755	1.540528	-0.308685

C	2.372853	1.716956	-0.167364
C	3.165315	0.534418	0.103511
O	2.794788	2.843418	-0.278725
C	2.614528	-0.695360	0.213207
H	4.229099	0.698603	0.212201
C	3.450439	-1.906109	0.493350
H	3.129621	-2.384148	1.422153
H	3.339134	-2.639934	-0.308596
H	4.501817	-1.638564	0.581229

Structure **B_{alkyne}**

Pd	-3.497991	0.093279	-0.151475
C	-4.360464	-0.861204	-1.884290
C	-4.507799	0.526421	-1.997668
H	-5.383100	1.018850	-1.583017
C	-4.836877	-1.440443	-0.690816
H	-4.547889	-2.452455	-0.433910
H	-5.751431	-1.068745	-0.236070
H	-3.953117	1.070885	-2.752024
H	-2.161713	2.542715	-0.569732
O	-2.295318	1.965387	0.189321
H	-1.414191	1.700643	0.496355
H	-3.652124	-1.392749	-2.509768
C	-0.733775	-0.926561	1.362466
C	-2.135722	-0.743427	1.746121
C	-3.267256	-0.643797	2.159513
H	-4.230413	-0.590805	2.620486
H	-0.206424	-1.433287	2.176077
O	-0.166757	0.361331	1.135198
C	1.147804	0.415318	0.768220
C	1.678463	1.705123	0.620084
C	1.926559	-0.708154	0.544040
C	2.990985	1.859998	0.235687
H	1.047026	2.562462	0.816010
C	3.252033	-0.519046	0.156765
H	1.562692	-1.720436	0.649905
H	-0.674469	-1.536394	0.456890
C	3.814032	0.746696	-0.008809
C	5.204073	0.833795	-0.420764
C	5.890221	-0.311513	-0.627552
C	5.289367	-1.619325	-0.451265
H	6.926950	-0.311265	-0.936839
O	3.974542	-1.651839	-0.057075
O	5.838822	-2.680789	-0.618499
C	5.840583	2.176043	-0.608184
H	5.303954	2.749318	-1.368133
H	5.803760	2.748513	0.321848
H	6.879367	2.071483	-0.915588
H	3.395052	2.858144	0.122507

Structure **$TS1_{alkyne}$**

Pd	3.718211	-0.379060	0.105409
C	4.307111	-2.120154	-1.050630
C	5.393278	-1.806297	-0.244602
H	6.108891	-1.048949	-0.551593
C	3.751421	-1.080781	-1.846334
H	2.799363	-1.246070	-2.336605
H	4.414800	-0.372184	-2.335758
H	5.702569	-2.484212	0.541029
H	4.340758	-0.361605	2.873837
O	4.088727	0.302459	2.223462
H	3.353444	0.792004	2.608789
H	3.728307	-3.015996	-0.851803
C	0.673818	0.400548	-0.021961
C	2.025907	0.990453	-0.063412
C	2.514084	2.154835	-0.144389
H	0.553392	-0.308527	-0.845857
O	-0.326617	1.430598	-0.137021
C	-1.636489	1.063316	-0.110544
C	-2.057586	-0.250639	0.030888
C	-2.568730	2.106221	-0.235180
H	-1.379099	-1.086142	0.127001
C	-3.915482	1.824659	-0.213118
H	-2.213758	3.122611	-0.348463
C	-4.382076	0.506143	-0.068385
H	-4.627280	2.634981	-0.309343
H	0.533144	-0.134419	0.921762
H	3.396076	2.762174	-0.207923
O	1.309775	3.546652	-0.295589
H	0.458206	3.072554	-0.233976
H	1.368055	4.131927	0.472469
C	-3.427487	-0.504049	0.049522
O	-3.787956	-1.809188	0.191234
C	-5.101014	-2.207393	0.226504
C	-6.106284	-1.169780	0.106663
O	-5.313230	-3.388991	0.355183
C	-5.785074	0.135195	-0.034853
H	-7.133547	-1.507577	0.138798
C	-6.836841	1.194328	-0.155167
H	-6.736685	1.923792	0.652280
H	-6.728688	1.733523	-1.099385
H	-7.832574	0.756995	-0.112223

Structure **D_{alkyne}**

Pd	3.709155	-0.358731	0.087789
C	4.115767	-2.367936	-0.685455
C	5.355242	-1.910963	-0.282874
H	5.933122	-1.242273	-0.914259
C	3.323283	-1.553729	-1.554510
H	2.301041	-1.854699	-1.750947
H	3.812812	-1.029944	-2.371912
H	5.880082	-2.397434	0.529616
H	4.947015	0.419430	2.528866
O	4.505084	0.874479	1.804282
H	3.813050	1.412930	2.204577
H	3.641391	-3.173630	-0.133911
C	0.727823	0.387724	-0.017116
C	2.097478	0.965066	-0.101048
C	2.376216	2.241127	-0.246472
H	0.572849	-0.329192	-0.827029
O	-0.299114	1.417940	-0.129009
C	-1.620247	1.071546	-0.100102
C	-2.042564	-0.236203	0.070774
C	-2.540191	2.118221	-0.251247
H	-1.364475	-1.068984	0.190647
C	-3.889152	1.842640	-0.230271
H	-2.180046	3.130558	-0.383049
C	-4.361688	0.530373	-0.058913
H	-4.596409	2.653869	-0.348542
H	0.593003	-0.122881	0.939989
H	3.320196	2.755345	-0.337741
O	1.286523	3.260586	-0.394370
H	0.414424	2.742677	-0.292048
H	1.351410	3.971631	0.265347
C	-3.413649	-0.482570	0.088689
O	-3.781308	-1.781310	0.260480
C	-5.097012	-2.171538	0.298165
C	-6.096085	-1.131650	0.144311
O	-5.316686	-3.347619	0.456353
C	-5.767773	0.167405	-0.027299
H	-7.125192	-1.463785	0.176670
C	-6.812648	1.228458	-0.183764
H	-6.715974	1.977905	0.605606
H	-6.693313	1.742417	-1.140650
H	-7.810909	0.797237	-0.138597

Structure **TS2$_{alkyne}$**

Pd	3.576813	-0.306176	0.257260
C	3.819719	-2.170121	1.360546
C	5.047066	-1.959014	0.757573
H	5.212530	-2.240521	-0.278168
C	2.646799	-2.138136	0.547268
H	1.678772	-2.142690	1.034838
H	2.676121	-2.603830	-0.435072
H	5.924139	-1.759713	1.360354
H	4.607901	2.063280	-0.724666
O	4.907195	1.498676	-0.002757
H	5.847229	1.347672	-0.149097
H	3.727332	-2.070021	2.437106
C	1.115898	0.152486	-1.256043
C	1.934729	0.896975	-0.355333
C	1.809447	2.156015	0.029641
H	1.503413	-0.014661	-2.257739
O	-0.313435	1.078349	-1.733239
C	-1.537383	0.555876	-1.334041
C	-2.173697	1.059377	-0.216165
C	-2.059499	-0.492856	-2.086606
H	-1.754227	1.865753	0.372979
C	-3.267444	-1.042890	-1.702427
H	-1.523180	-0.851638	-2.955629
C	-3.962366	-0.558862	-0.584060
H	-3.686538	-1.856446	-2.280542
H	0.588857	-0.707024	-0.846354
H	2.473479	2.667676	0.715482
O	0.778173	2.962590	-0.476611
H	-0.122944	1.970049	-1.309167
H	0.579031	3.700803	0.109688
C	-3.393628	0.494078	0.139255
O	-4.001157	1.019009	1.235840
C	-5.206063	0.550609	1.698252
C	-5.815189	-0.540940	0.958977
O	-5.663114	1.081411	2.679089
C	-5.241913	-1.087447	-0.133371
H	-6.764692	-0.889857	1.342741
C	-5.887154	-2.211581	-0.882221
H	-6.073372	-1.921283	-1.919098
H	-5.231907	-3.085906	-0.897533
H	-6.832553	-2.489251	-0.420134

Structure **PdCl$_2$(allyl)**

Pd	0.135868	-0.006598	0.003028
C	2.235211	-0.037464	-0.431414
C	1.866441	-1.232850	0.209736
H	1.919243	-1.308575	1.292108
C	1.897682	1.162957	0.218533
H	1.947717	2.099357	-0.323315
H	1.953072	1.230245	1.301401
H	1.894265	-2.166327	-0.338717
H	2.475740	-0.036404	-1.489068
Cl	-1.493863	1.895990	-0.017663
Cl	-1.590606	-1.829559	-0.015445

Structure **Cl$^-$**

Cl	0.000000	0.000000	0.000000

Structure **B'**

Pd	-2.278939	0.365677	0.277613
C	-3.021149	0.380523	2.319916
C	-2.305959	1.560715	2.072406
H	-1.233509	1.595041	2.244621
C	-2.368759	-0.833576	2.041076
H	-2.940629	-1.752737	1.996605
H	-1.303476	-0.935512	2.232447
H	-2.822929	2.511352	2.037214
H	-4.101810	0.407547	2.409543
C	-1.568385	-1.260648	-1.376504
C	-2.866268	-1.442028	-1.148889
C	-4.123261	-1.790208	-1.143970
H	-4.839969	-1.354373	-0.457303
H	-1.208825	-0.564261	-2.128219
O	-0.648373	-2.098700	-0.801437
H	-4.477357	-2.539814	-1.846002
C	0.609898	-1.624900	-0.542021
C	1.529775	-2.591529	-0.115265
C	2.819095	-2.213456	0.187211
H	1.207397	-3.621113	-0.031438
C	3.229958	-0.873938	0.073266
H	3.527383	-2.962922	0.517438
Cl	-1.925773	2.139713	-1.421004
C	0.969748	-0.291816	-0.663376
H	0.286572	0.488911	-0.974952
C	2.282892	0.057073	-0.355465
O	2.592890	1.375803	-0.491885
C	3.845481	1.865658	-0.221703
C	4.841897	0.912301	0.227652
O	4.018744	3.050102	-0.378051
C	4.570025	-0.402698	0.376060
H	5.820739	1.322920	0.436966
C	5.611013	-1.372640	0.842515
H	5.286618	-1.866863	1.761559
H	5.771674	-2.149777	0.091280
H	6.555330	-0.865296	1.030653

Structure **C'**

Pd	3.320951	-0.245286	0.148976
C	3.415316	-1.564319	1.903285
C	4.096043	-2.258824	0.919410
H	3.556660	-2.833277	0.171894
C	2.103110	-1.074580	1.636162
H	1.635846	-0.414941	2.357559
H	1.415348	-1.693756	1.066099
H	5.154449	-2.461006	1.024227
H	3.971147	-1.157157	2.742563
C	2.702398	2.637057	-0.645991
H	3.775820	2.779651	-0.723166
H	2.084463	3.513182	-0.846540
C	2.178454	1.426678	-0.301589
C	0.772691	1.498125	-0.308781
H	0.222372	2.376286	-0.658301
O	0.053824	0.496064	0.072765
C	-1.342163	0.589652	0.119672
C	-1.967680	1.709674	0.656444
C	-2.029664	-0.512961	-0.341025
C	-3.350653	1.721614	0.700737
H	-1.392871	2.536725	1.052746
H	-1.513709	-1.374908	-0.742635
C	-4.101923	0.635801	0.233112
H	-3.855894	2.582931	1.118267
Cl	5.015897	0.275886	-1.632272
C	-3.416848	-0.471514	-0.280346
O	-4.073298	-1.565565	-0.746582
C	-5.443540	-1.652671	-0.739941
C	-6.173915	-0.514458	-0.207453
O	-5.933341	-2.663566	-1.174485
C	-5.558097	0.589130	0.262739
H	-7.251621	-0.610897	-0.213194
C	-6.327353	1.751351	0.807900
H	-6.051331	1.936284	1.848882
H	-6.101473	2.657688	0.240940
H	-7.397760	1.562310	0.756804

Structure **TS1'**

Pd	3.271278	0.195024	-0.170417
C	5.188497	0.186004	-1.258827
C	4.644111	1.404238	-1.609542
H	3.875458	1.470758	-2.373992
C	4.416302	-1.008652	-1.414203
H	4.807970	-1.934372	-1.008962
H	3.803946	-1.121728	-2.305534
H	5.128780	2.327057	-1.316956
H	6.067628	0.165512	-0.621652
C	2.754689	-2.465713	1.304070
C	2.246652	-1.362793	0.721659
C	0.799228	-1.349143	0.778589
O	0.407691	-0.121109	2.311548
H	2.129022	-3.215909	1.789965
H	0.233671	-2.130425	1.286888
H	0.907931	0.685975	2.037473
H	0.839705	-0.448110	3.111364
O	0.162252	-0.678565	-0.145223
H	3.821177	-2.666562	1.310385
C	-1.232861	-0.736265	-0.174980
C	-1.887845	-1.954694	-0.321707
C	-1.896611	0.469700	-0.102297
C	-3.270012	-1.951162	-0.377920
H	-1.327419	-2.877014	-0.407085
H	-1.357888	1.401907	0.009602
C	-3.995901	-0.754782	-0.299251
H	-3.796251	-2.889795	-0.494445
Cl	2.049482	2.081543	1.035672
C	-3.284728	0.442849	-0.165106
O	-3.916631	1.644161	-0.084793
C	-5.283412	1.754824	-0.131479
C	-6.040416	0.522830	-0.272823
O	-5.749719	2.863404	-0.052195
C	-5.449945	-0.687058	-0.355784
H	-7.115513	0.639832	-0.308032
C	-6.247043	-1.945601	-0.502237
H	-5.974104	-2.464156	-1.424601
H	-6.044320	-2.624552	0.329577
H	-7.312726	-1.726358	-0.524915

Structure **D'**

Pd	3.281548	0.204393	-0.134633
C	5.206433	0.264786	-1.223630
C	4.663846	1.492759	-1.531513
H	3.886156	1.585373	-2.283997
C	4.436831	-0.927749	-1.424608
H	4.834309	-1.866920	-1.058095
H	3.830895	-1.009067	-2.323885
H	5.147467	2.405307	-1.206695
H	6.086421	0.222121	-0.588670
C	2.754250	-2.579724	1.057301
C	2.255134	-1.403745	0.659682
C	0.783862	-1.259591	0.880702
O	0.539309	-0.239139	1.992447
H	2.131760	-3.360566	1.497566
H	0.271903	-2.147107	1.263214
H	1.055707	0.660490	1.750189
H	0.864200	-0.574476	2.845055
O	0.148436	-0.713694	-0.212377
H	3.808793	-2.816427	0.961578
C	-1.236467	-0.744195	-0.200812
C	-1.916068	-1.959248	-0.301005
C	-1.904672	0.463373	-0.142481
C	-3.297680	-1.951330	-0.331351
H	-1.362736	-2.887686	-0.367724
H	-1.363883	1.398226	-0.066326
C	-4.017165	-0.748281	-0.272185
H	-3.831927	-2.889501	-0.412288
Cl	1.995375	2.020312	1.165795
C	-3.294343	0.445364	-0.182329
O	-3.917777	1.654304	-0.122407
C	-5.283298	1.774110	-0.146137
C	-6.051668	0.545781	-0.241759
O	-5.740474	2.888946	-0.086265
C	-5.470065	-0.670517	-0.304122
H	-7.126430	0.669303	-0.260792
C	-6.279542	-1.925968	-0.404649
H	-6.026189	-2.469991	-1.317919
H	-6.067378	-2.585517	0.440309
H	-7.343925	-1.699228	-0.414721

Structure **E'**

Pd	3.240149	-0.254589	0.070851
C	4.918029	-1.260958	-0.973211
C	4.912853	-1.901760	0.245555
H	5.333046	-1.426524	1.127226
C	4.935497	0.171615	-1.032310
H	4.813484	0.649920	-1.996405
H	5.563755	0.713993	-0.328663
H	4.704055	-2.962235	0.308669
H	4.637907	-1.819098	-1.861752
C	2.863286	2.769934	-0.215451
C	2.316808	1.551964	-0.303812
C	0.888298	1.553298	-0.718485
O	0.592784	0.622569	-1.651030
H	2.294051	3.681825	-0.402461
H	0.428655	2.527467	-0.899451
H	-0.237299	0.831966	-2.098139
O	0.083108	1.141707	0.627601
H	3.908442	2.908596	0.042507
C	-1.294717	0.948053	0.475458
C	-1.776468	-0.309922	0.171270
C	-2.117307	2.061185	0.615104
H	-1.119245	-1.162838	0.058066
C	-3.478970	1.896414	0.443468
H	-1.687588	3.023514	0.860873
C	-4.023539	0.639447	0.142308
H	-4.134424	2.750974	0.550790
Cl	1.414733	-1.131734	1.654429
H	0.556323	0.300752	1.049780
C	-3.152411	-0.446726	0.015205
O	-3.602766	-1.695116	-0.278226
C	-4.934827	-1.964516	-0.469101
C	-5.857794	-0.849731	-0.338118
O	-5.235760	-3.101860	-0.729239
C	-5.448846	0.401805	-0.046223
H	-6.901531	-1.090708	-0.490641
C	-6.414829	1.537557	0.085154
H	-6.354240	1.975911	1.084334
H	-6.177885	2.324704	-0.634750
H	-7.434123	1.198015	-0.088162

Structure **TS2'**

Pd	-3.236860	0.260470	0.053632
C	-4.893305	1.260949	-1.024048
C	-4.887475	1.924167	0.183451
H	-5.324160	1.472887	1.069659
C	-4.928586	-0.171385	-1.056535
H	-4.804594	-0.669418	-2.010317
H	-5.566797	-0.693493	-0.346627
H	-4.664279	2.982652	0.228086
H	-4.598774	1.798615	-1.920506
C	-2.868657	-2.777397	-0.127681
C	-2.325419	-1.561875	-0.273774
C	-0.916325	-1.593403	-0.717445
O	-0.584848	-0.662814	-1.614865

H	-2.302155	-3.695770	-0.289142
H	-0.441268	-2.565502	-0.862507
H	0.252447	-0.874267	-2.049374
O	-0.058295	-1.180570	0.708496
H	-3.909281	-2.906367	0.152557
C	1.305751	-0.969504	0.529646
C	1.777655	0.297849	0.242896
C	2.140679	-2.081547	0.610967
H	1.115500	1.151693	0.172550
C	3.495574	-1.906685	0.403903
H	1.722565	-3.052570	0.842481
C	4.027400	-0.639412	0.122472
H	4.156654	-2.761353	0.467504
Cl	-1.431837	1.150743	1.644640
H	-0.528253	-0.344080	1.095931
C	3.147820	0.444897	0.050330
O	3.584802	1.703136	-0.222619
C	4.909583	1.984332	-0.443995
C	5.840766	0.871750	-0.368381
O	5.197761	3.130068	-0.682422
C	5.445219	-0.389358	-0.098669
H	6.878916	1.121849	-0.542792
C	6.420205	-1.522638	-0.022795
H	6.388762	-1.986411	0.966214
H	6.168071	-2.292762	-0.755778
H	7.432764	-1.172982	-0.214649

Structure **F'**

Pd	0.450680	-0.012360	-0.011401
C	2.591545	0.436170	-0.287362
C	2.585579	-0.801576	0.324397
H	2.445991	-0.891179	1.397793
C	1.842755	1.504128	0.294381
H	1.742267	2.425092	-0.267468
H	1.847757	1.621195	1.375343
H	2.957349	-1.673851	-0.198169
H	2.909157	0.515325	-1.322438
C	-2.577591	0.758407	0.178738
C	-1.242764	1.223129	-0.052815
C	-1.280581	2.555928	-0.303316
H	-0.389798	3.127825	-0.538284
H	-3.409744	1.459288	0.287359
O	-2.935593	-0.452172	0.278392
H	-2.211182	3.125203	-0.299495
Cl	-0.734797	-2.263049	-0.188657
H	-2.160440	-1.108224	0.145686

Structure **G'**

Pd	-0.461514	-0.027986	-0.099552
C	-2.633308	-0.140533	0.128256
C	-2.157500	1.081891	0.620540
H	-1.843457	1.167014	1.657336
C	-2.032469	-1.304865	0.632578
H	-2.209831	-2.253174	0.140837
H	-1.719049	-1.349762	1.672068
H	-2.399713	2.005013	0.109240
H	-3.192137	-0.175095	-0.800500
C	0.657604	-1.921348	-1.070739
H	0.627851	-1.690773	-2.132547
H	0.019947	-2.726417	-0.720404
C	1.545641	-1.343201	-0.269022
C	2.608199	-0.982323	0.413096
H	3.481837	-1.626501	0.390258
O	2.773712	0.116368	1.188727
Cl	0.952192	1.991586	-0.521470
H	2.158217	0.811388	0.890015

7. Activation parameters determination: Eyring plot

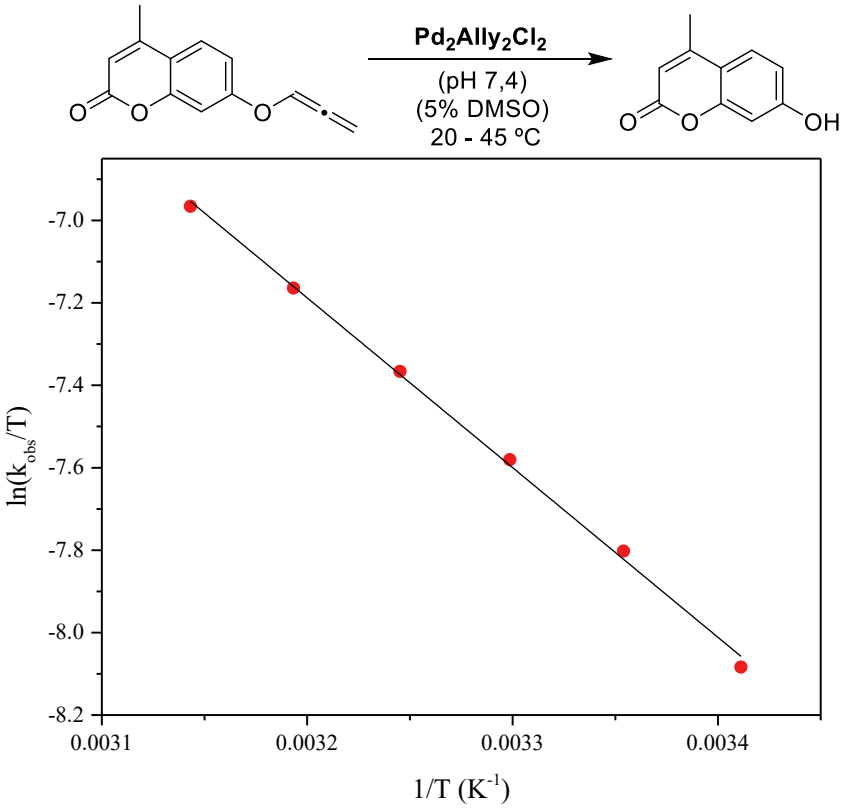


Figure S43 - The temperature dependence of the rate constant in the form of Eyring plot for deallenylation reaction mediated by $Allyl_2Pd_2Cl_2$. Reaction conditions: [Alle-4-MU] = 100 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1}, phosphate buffer ([Cl^-] = 0 mol L^{-1}, *I* = 140 mmol L^{-1} ($NaClO_4$)), pH: 7.4, 5% DMSO.

8. Ionic strength effect

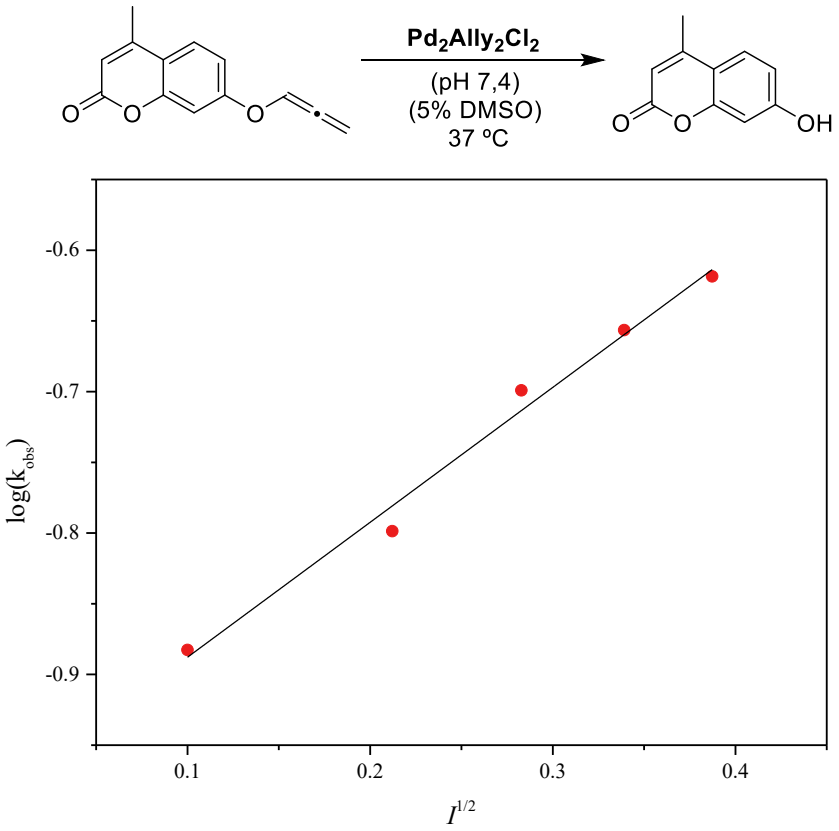
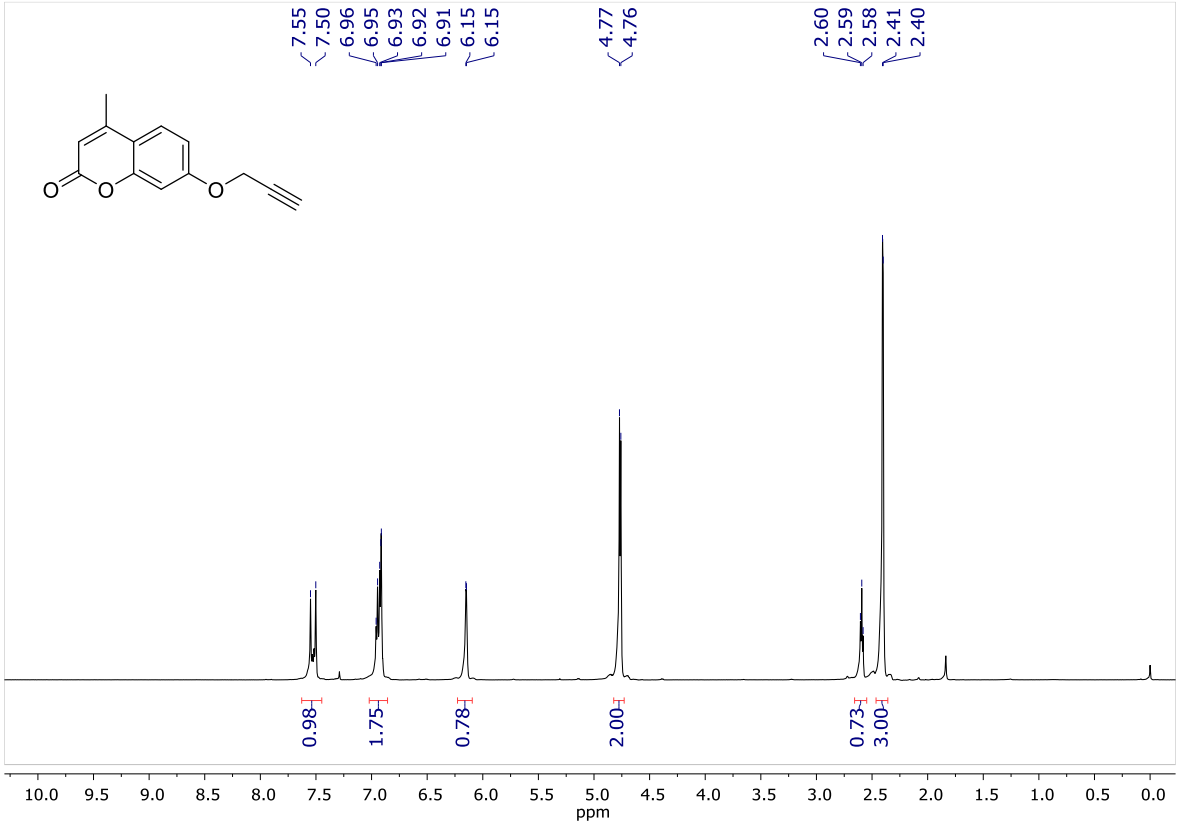
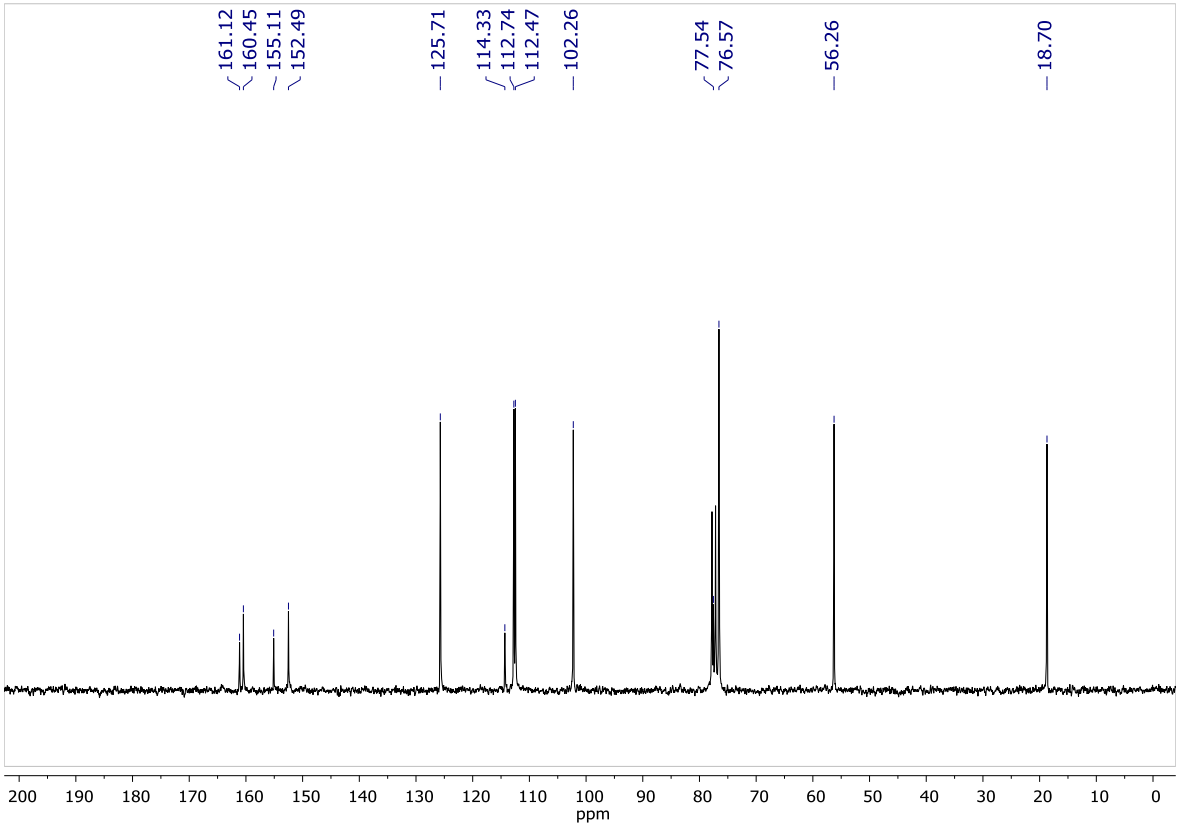
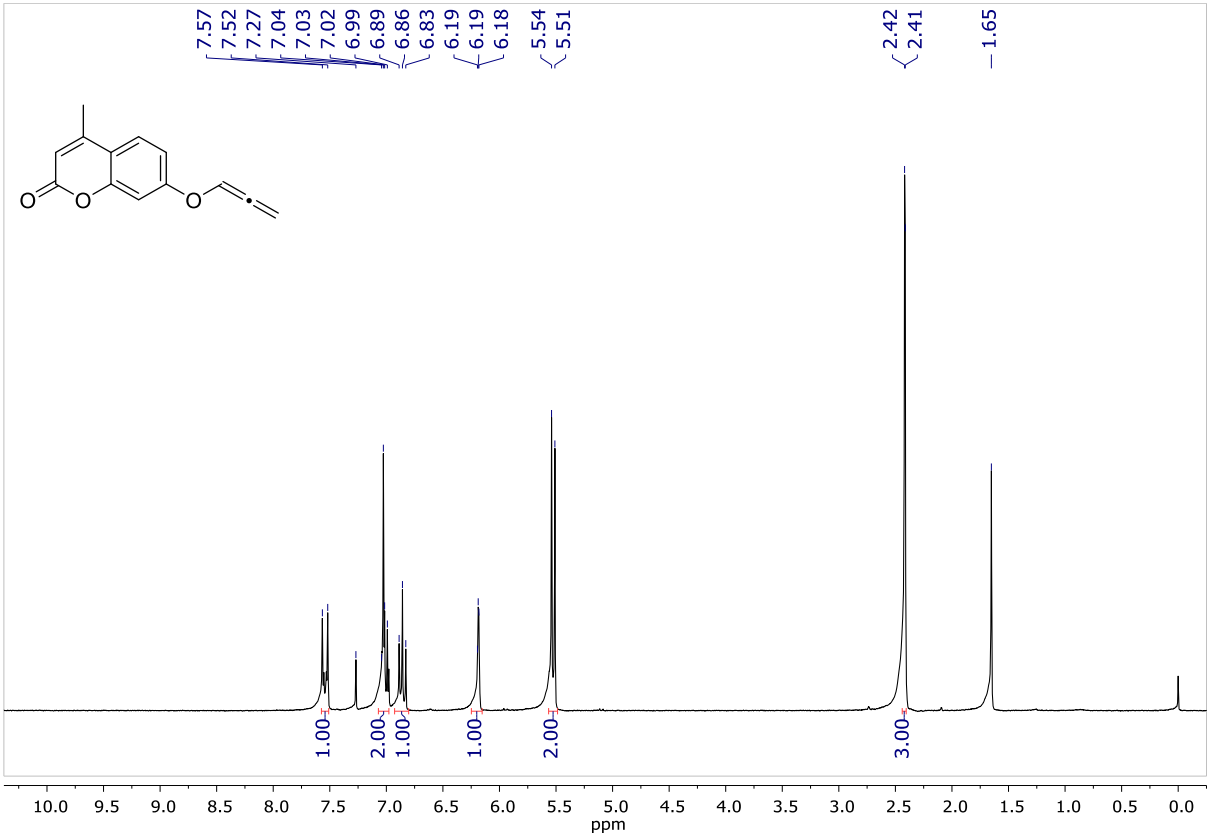


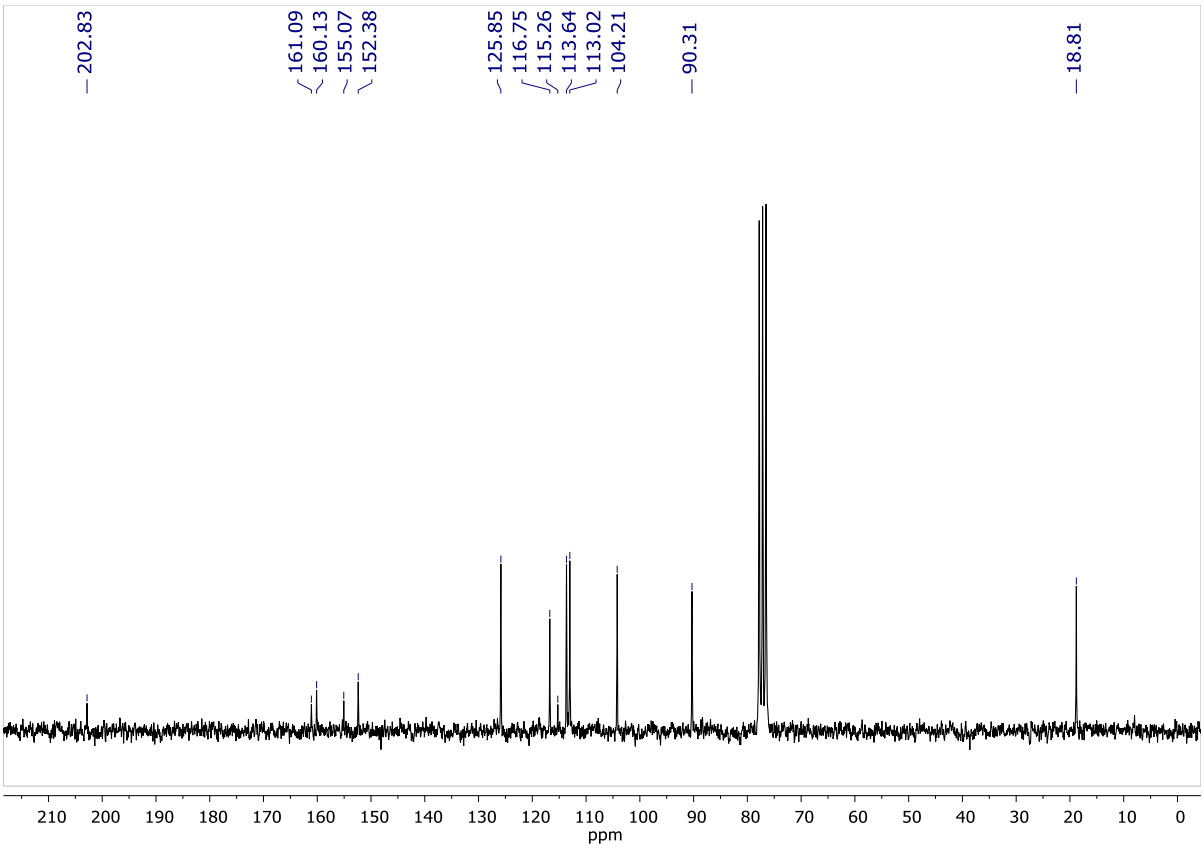
Figure S44 - Logarithm of rate constants against square root of ionic strength for the deallenylation reaction mediated by $Allyl_2Pd_2Cl_2$. Reaction conditions: [Alle-4-MU] = 100 µmol L^{-1}, [AllylPdCl] = 25 µmol L^{-1}, phosphate buffer, pH: 7.4, 5% DMSO at 37°C.

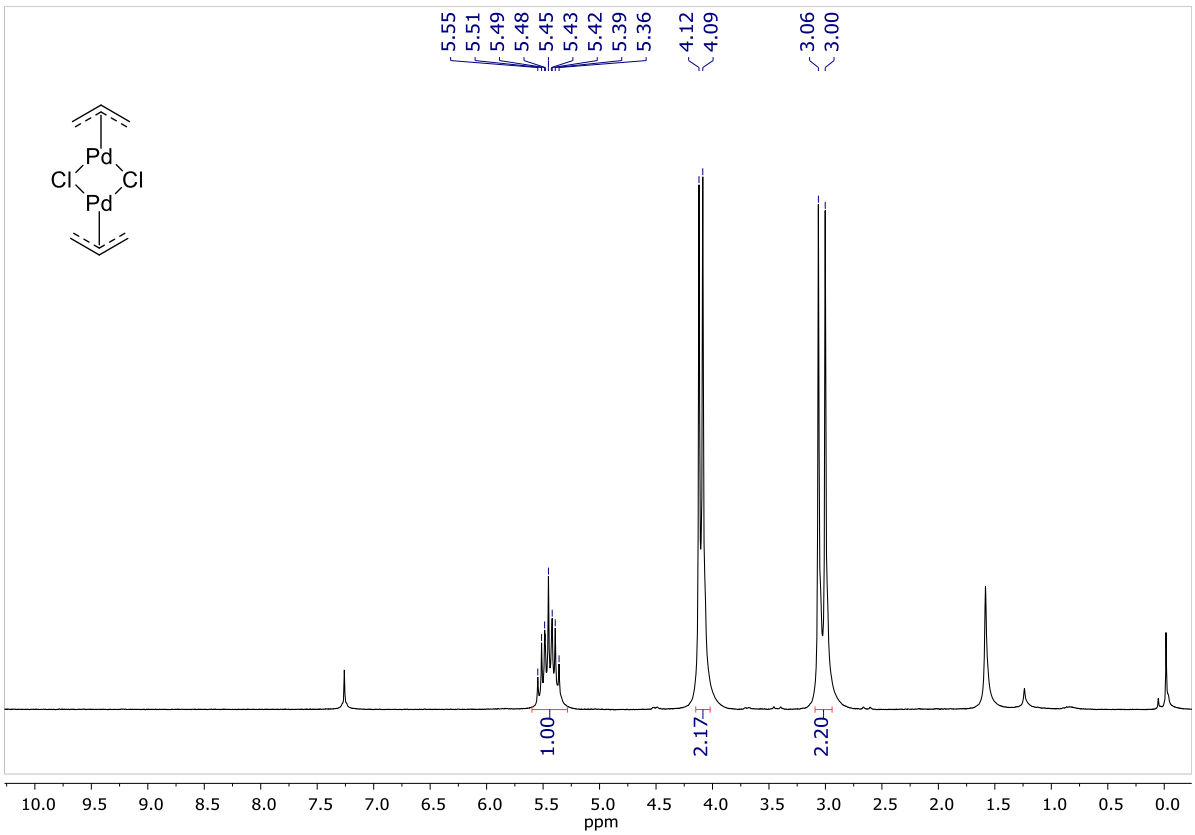
9. NMR Spectra

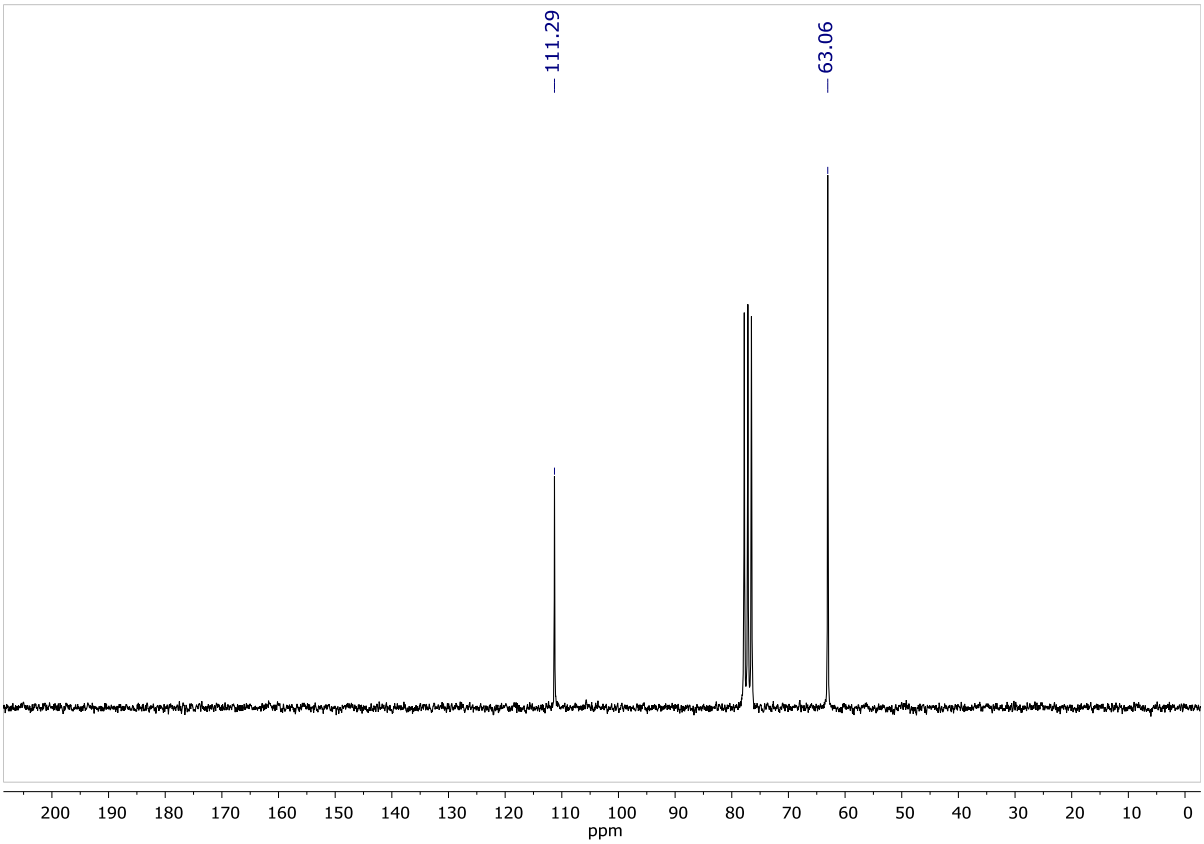





7.57
7.52
7.27
7.04
7.03
7.02
6.99
6.89
6.86
6.83
6.19
6.19
6.18
5.54
5.51
2.42
2.41
1.65
1.00
2.00
1.00
1.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


202.83
161.09
160.13
155.07
152.38
125.85
116.75
115.26
113.64
113.02
104.21
90.31
18.81
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


5.55
5.51
5.49
5.48
5.45
5.43
5.42
5.39
5.36
4.12
4.09
3.06
3.00
Pd
Cl
Cl
Pd
1.00
2.17
2.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


111.29
63.06
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

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