Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Rapid and Mild Synthesis of Au-NHC Complexes in a Simple Two-Phase Flow Reactor

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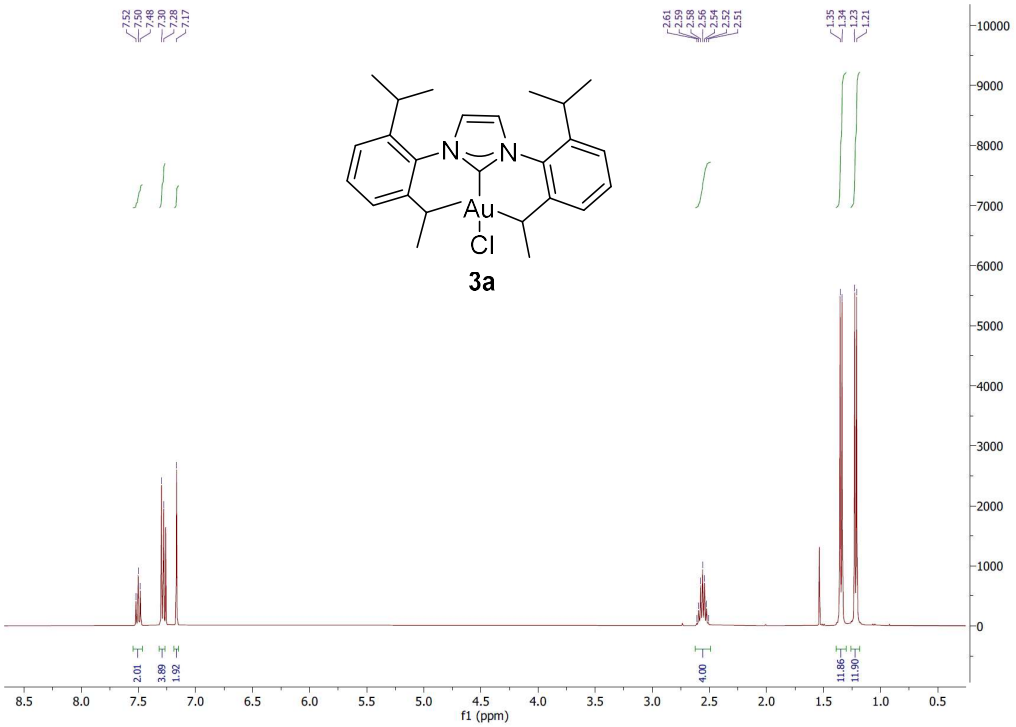
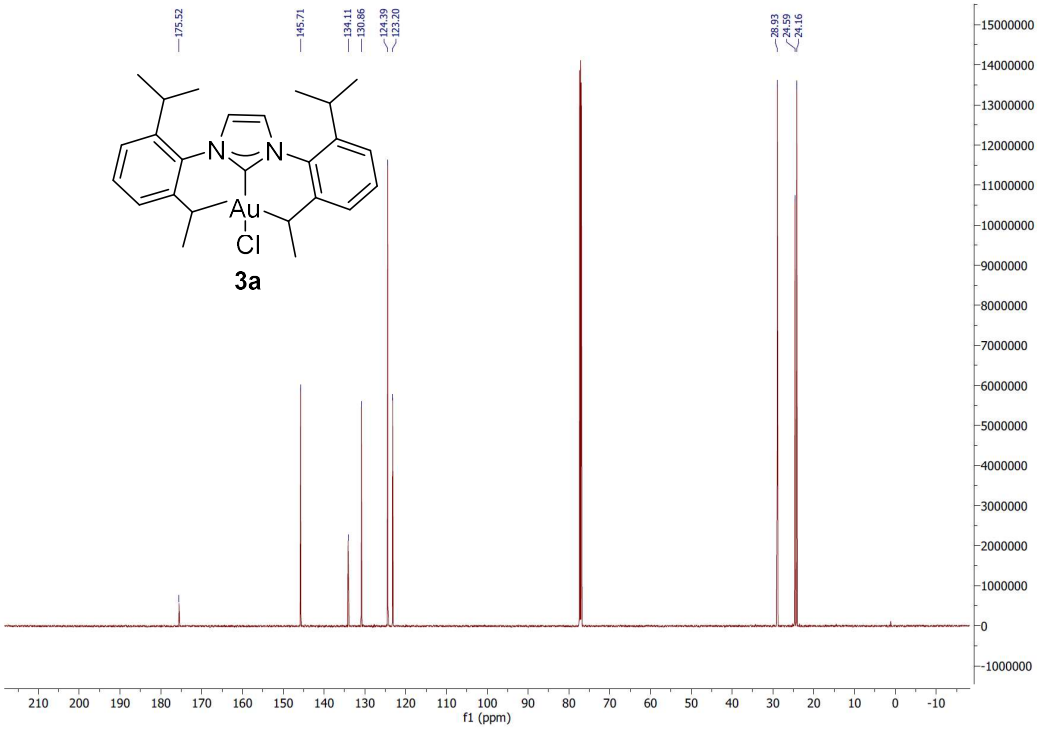
NMR Spectra

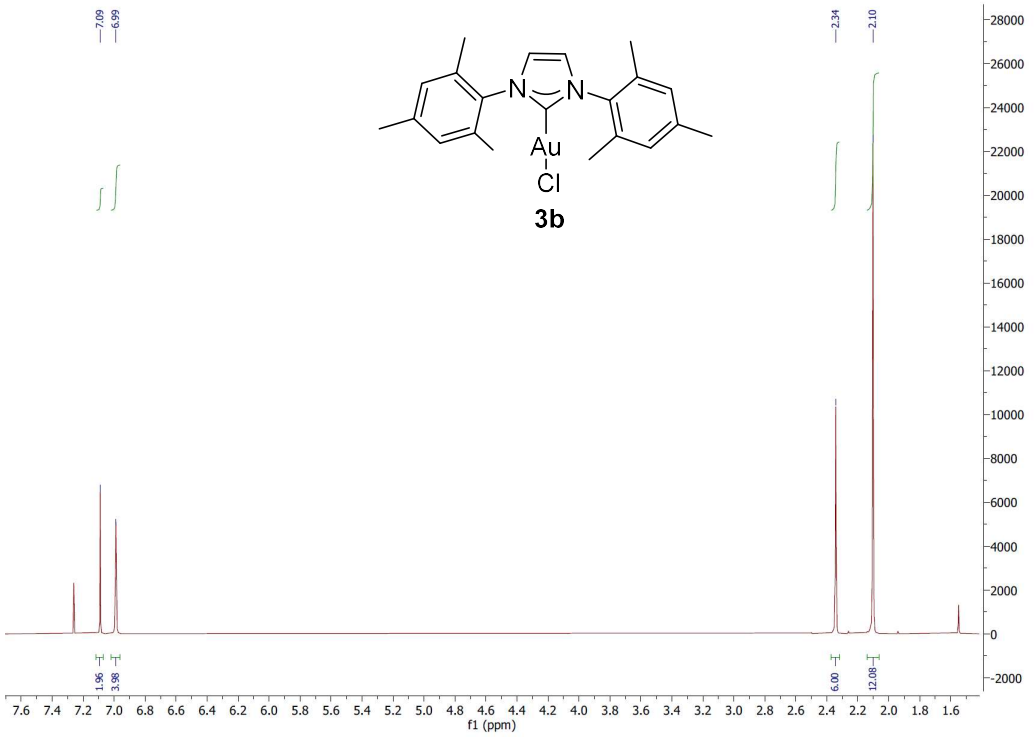
^{1}H NMR spectrum of Au(I)-NHC complex **3a**



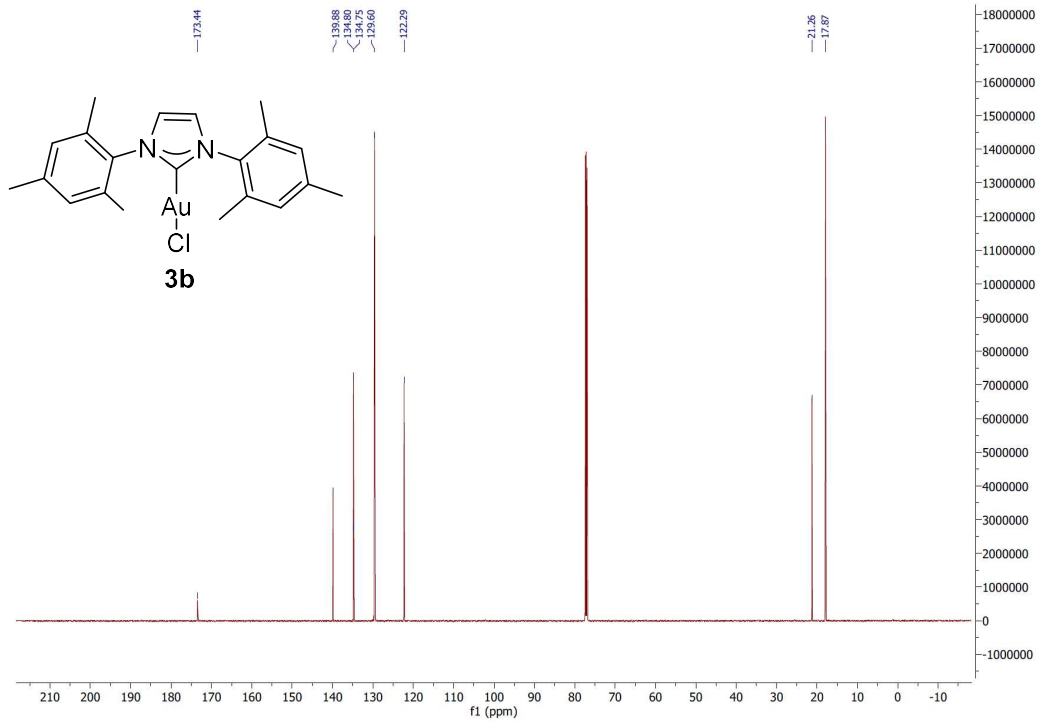
^{13}C NMR spectrum of Au(I)-NHC complex **3a**



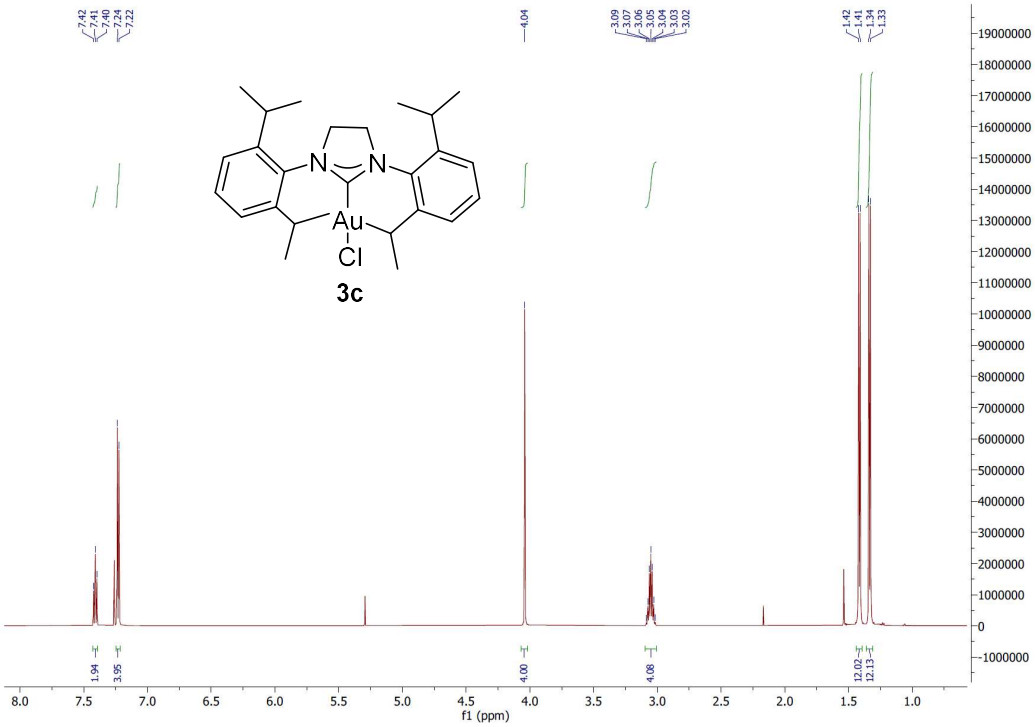
^{1}H NMR spectrum of Au(I)-NHC complex **3b**



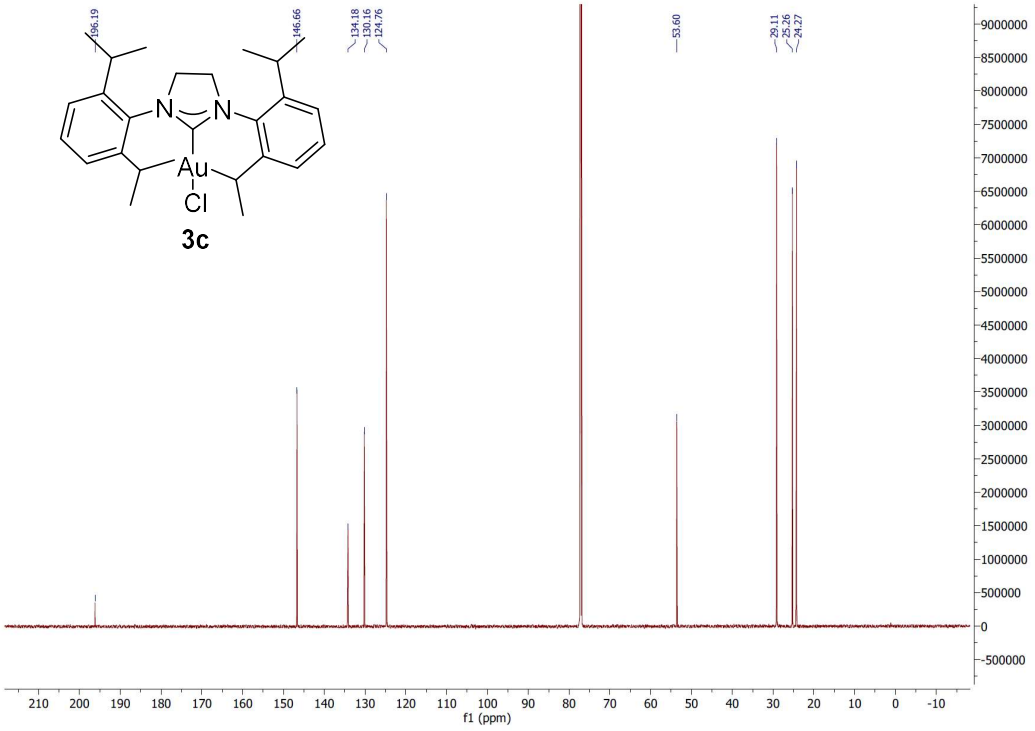
^{13}C NMR spectrum of Au(I)-NHC complex **3b**



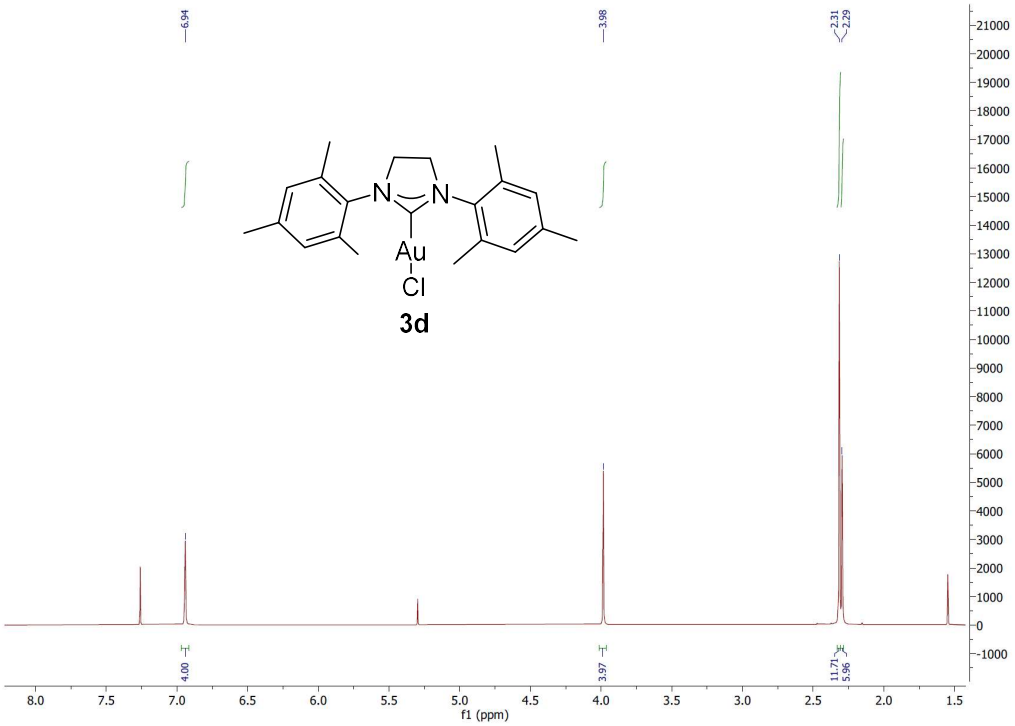
^{1}H NMR spectrum of Au(I)-NHC complex **3c**



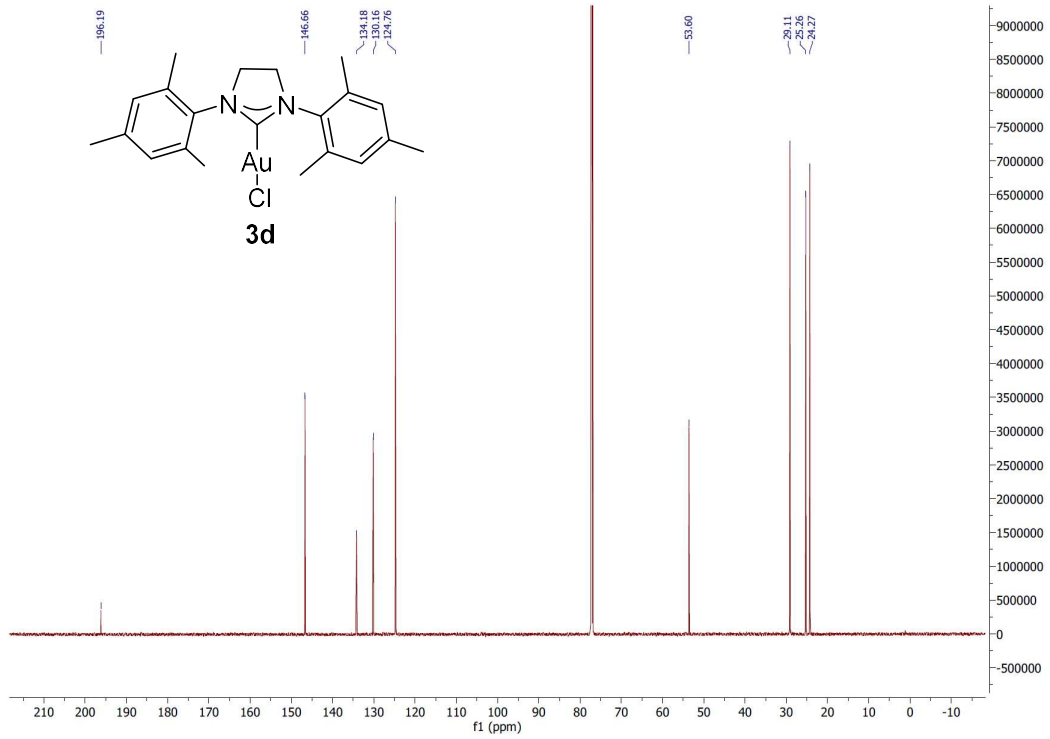
^{13}C NMR spectrum of Au(I)-NHC complex **3**



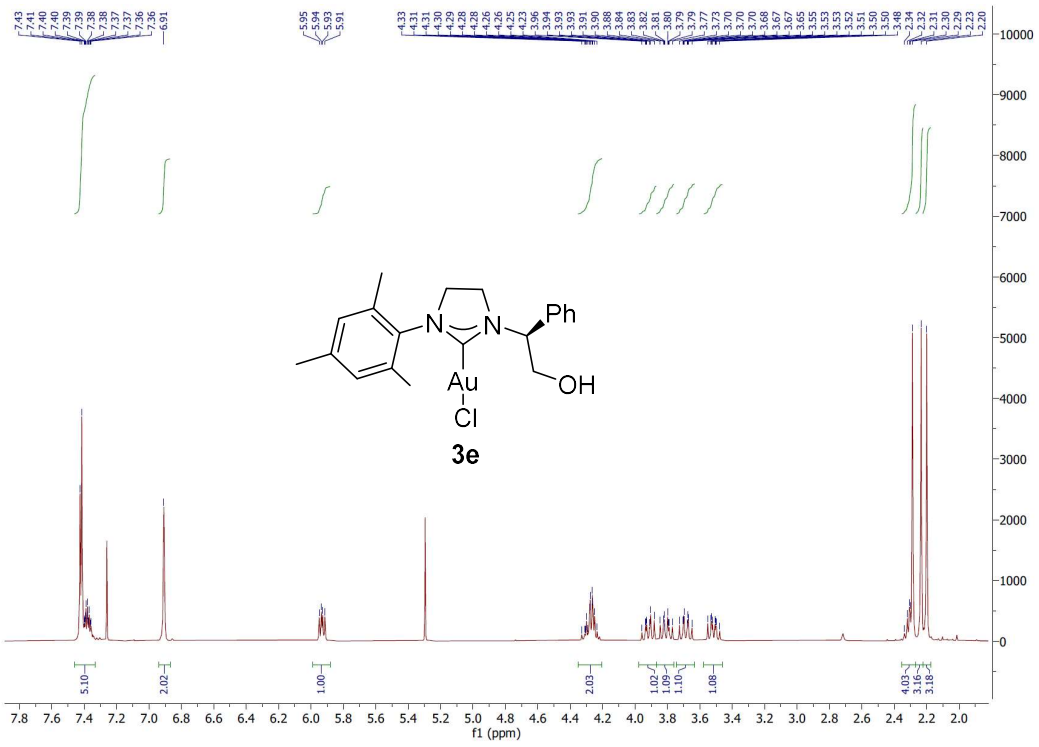
^{1}H NMR spectrum of Au(I)-NHC complex **3d**



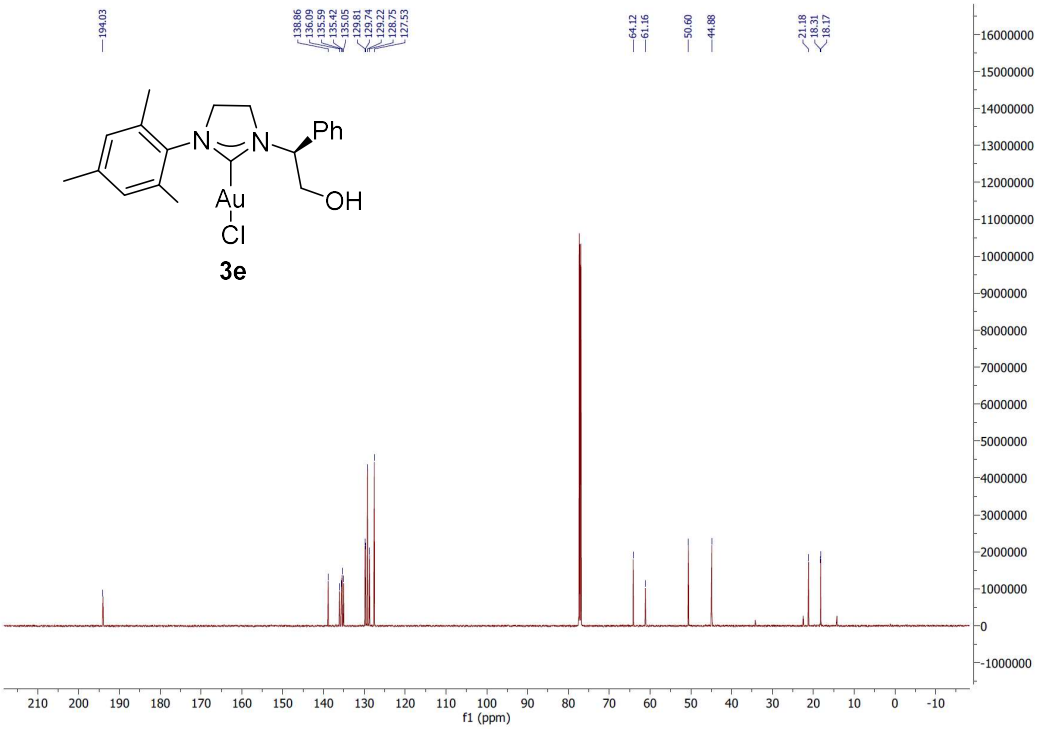
^{13}C NMR spectrum of Au(I)-NHC complex **3**



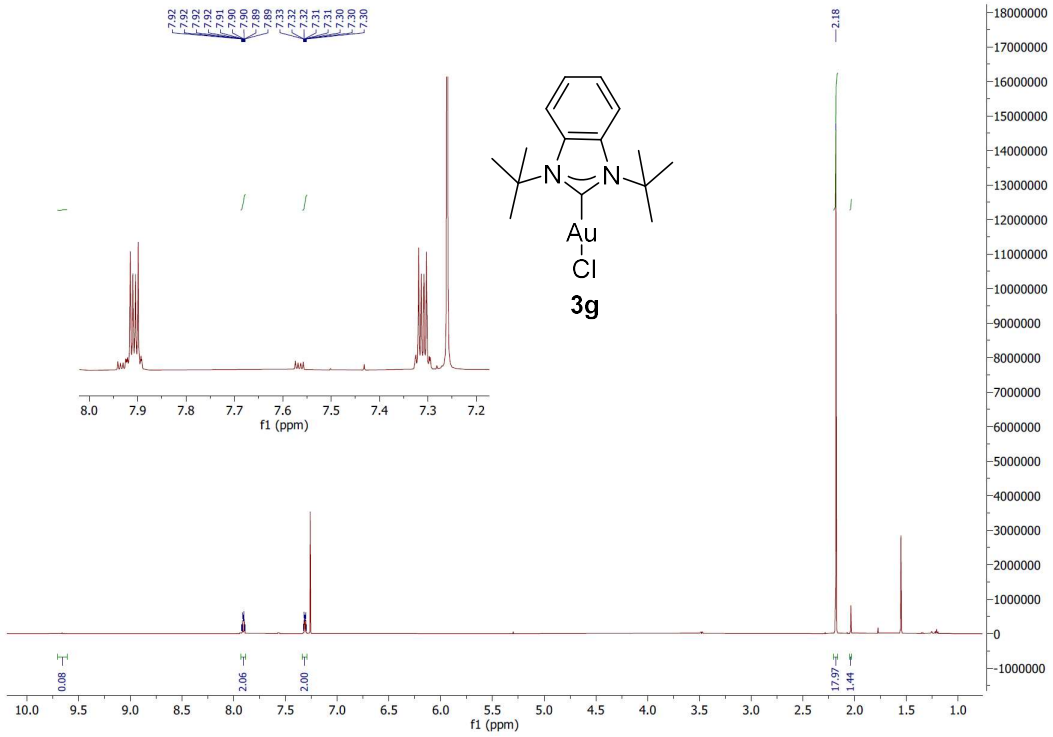
^{1}H NMR spectrum of Au(I)-NHC complex **3e**



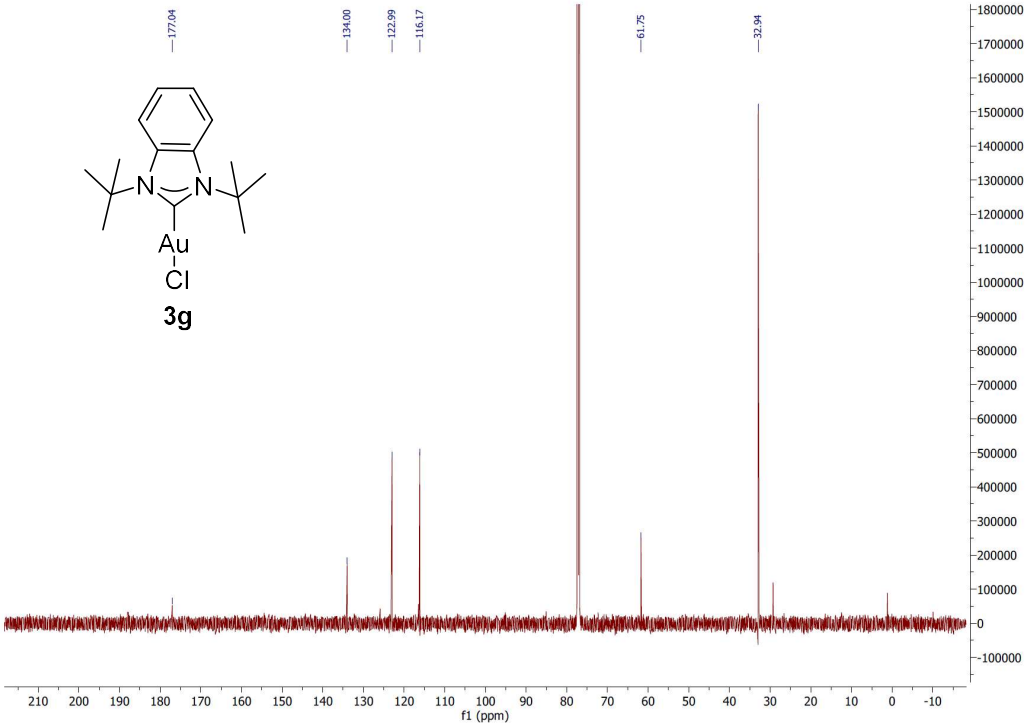
^{13}C NMR spectrum of Au(I)-NHC complex **3e**



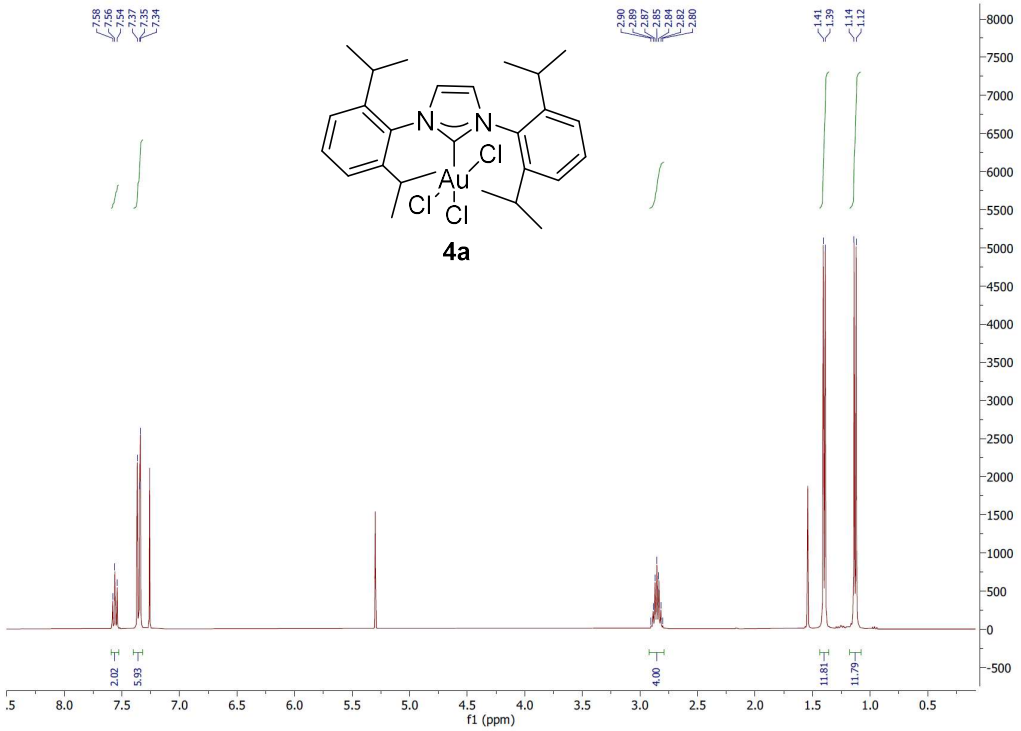
^{1}H NMR spectrum of Au(I)-NHC complex **3g** (93% purity)



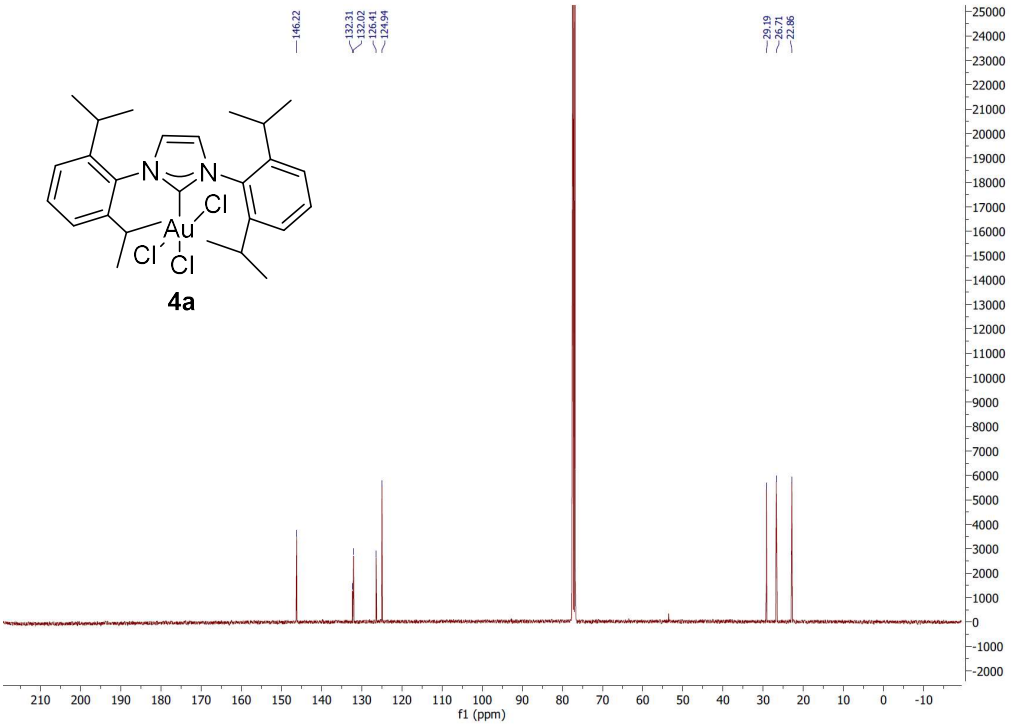
^{13}C NMR spectrum of Au(I)-NHC complex **3g** (93% purity)



^{1}H NMR spectrum of Au(III)-NHC complex **4a**



^{13}C NMR spectrum of Au(III)-NHC complex **4a**



Supporting Figures

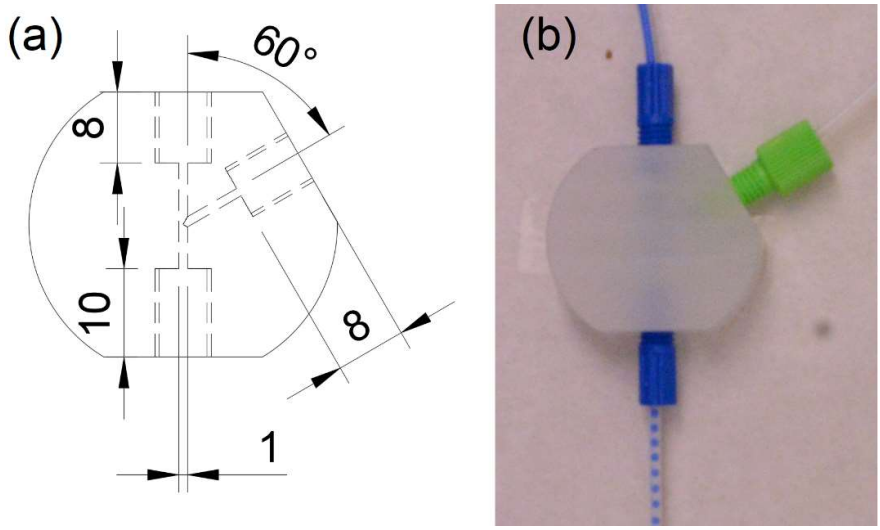


Figure S1. Detail of y-shaped mixers. (a) Technical drawing of y-shaped mixer. Dimensions are in millimetres, and all threads are ¼" UNF. The mixer is formed from a drilled-out block of PTFE cut from 35 mm diameter bar stock. **(b)** Photograph of y-mixer in use, using DCM and (dyed) water for visualisation of droplet formation. Fluidic connections are made using standard nut-and-ferrule type connectors.

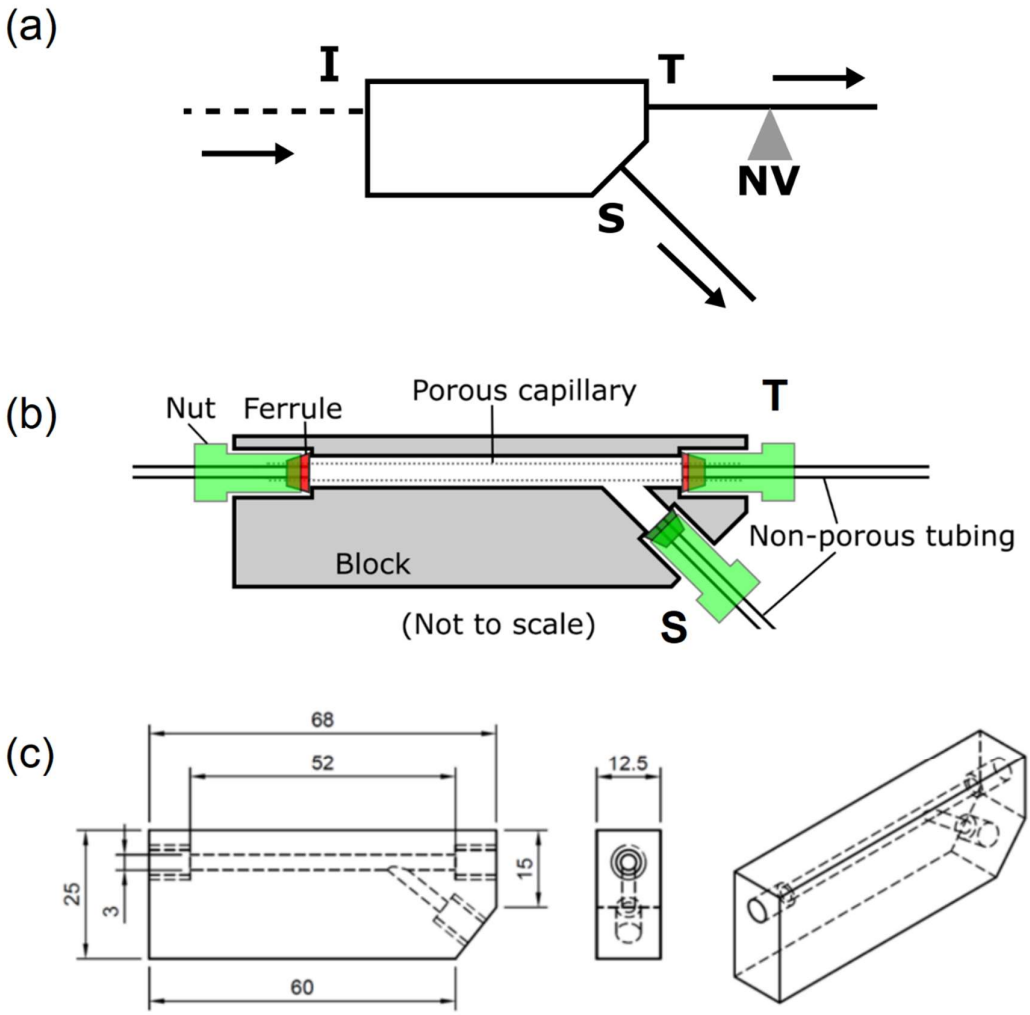


Figure S2. Detail of separator block. (a) Schematic of fluidic configuration of separator, with labels for the inlet **I**, through-outlet **T**, side outlet **S** and micro-metering needle valve **NV**. The dashed line represents a segmented flow entering the inlet **I**, with solid lines representing continuous flow from each outlet **S** and **T**. **(b)** Details of fluidic connections within separator block. The porous capillary tube is threaded over the non-porous tubing at the inlet and through outlet **T** and secured with a ferrule and nut. Another nut-and-ferrule type connector is used to secure non-porous tubing to the side outlet **S**. **(c)** Technical drawing of separator block, with dimensions in millimetres. All threads are ¼" UNF. The block is formed from drilled and tapped aluminium stock. Partially adapted from reference.[1]

DCM wets the porous capillary more readily than water and can therefore be forced through the microscopic pores in the capillary wall, where it is coerced into a continuous flow stream which exits the block at the side outlet (**S**). The aqueous phase travels straight through the porous capillary and exits the separator at **T**. Error-free operation of the separator requires control of the relative back-pressures at **S** and **T**. If the back-pressure is too high at **T** relative to **S**, then a portion of the aqueous phase will be forced through the capillary walls and exit at **S**. Conversely, if the pressure is too low at **T**, some of the DCM phase will pass straight through the separator and exit the block at **T**. To control the relative back-pressures, the micro-metering needle valve **NV** is set such that continuous streams of the organic and aqueous solutions are seen to emerge from **S** and **T** respectively.

[1] A. J. Harvie, J. O. Herrington and J. C. deMello, *React. Chem. Eng.*, 2019, **4**, 1579–1588.

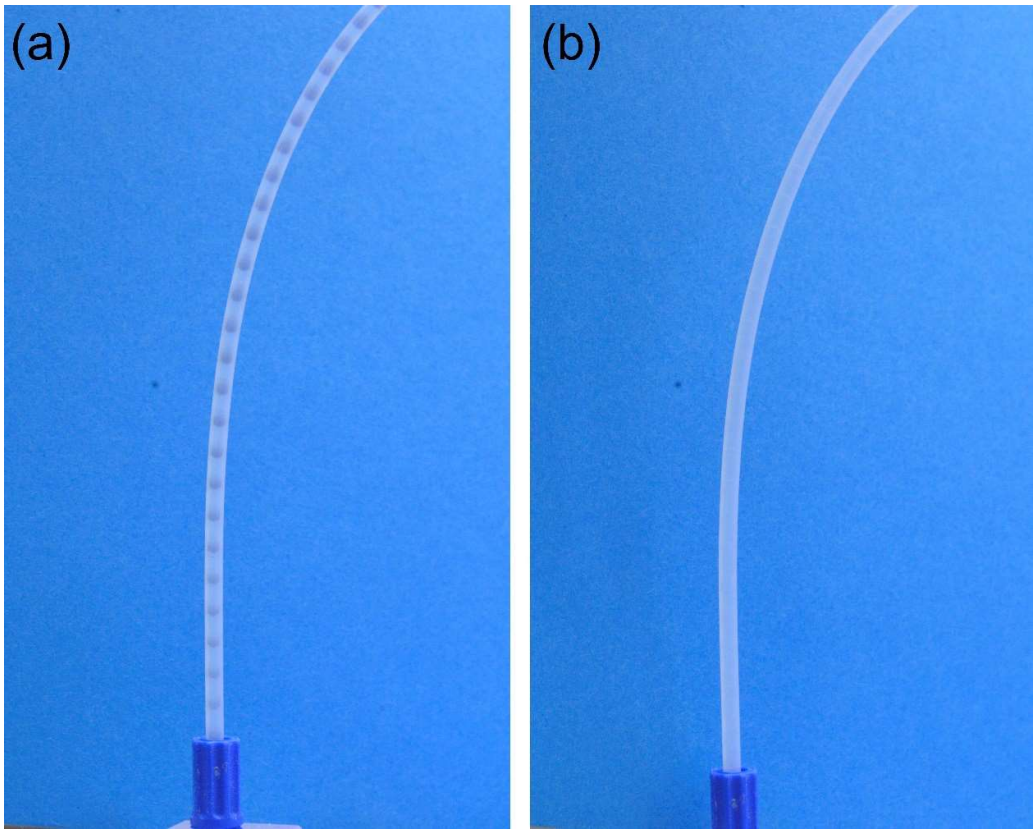


Figure S3. Formation of Au(0) during attempted synthesis of compound 3f. (a) Photograph of tubing immediately downstream of mixer Y1. Au(0) is seen forming rapidly as a dark grey solid within the DCM phase. **(b)** For comparison, an image of the same tubing supporting a segmented flow where no Au(0) is observed.

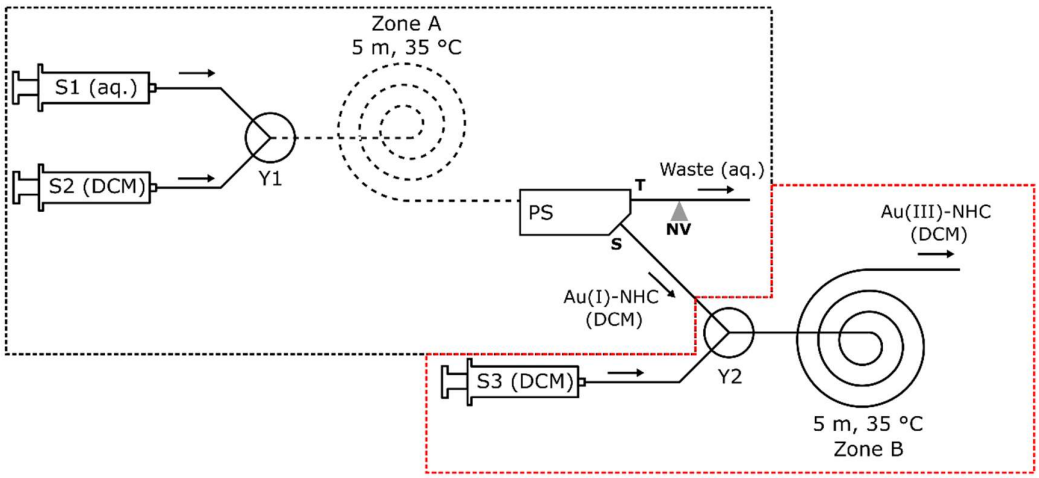


Figure S4. Full schematic of two-stage reactor for synthesis of Au(III)-NHC complex **4a**. The full reactor is constructed by adding a second reaction stage (red dashed box) to the single-stage reactor used to synthesise the Au(I) complexes (black dashed box). An aqueous base solution and a solution of an imidazolium aurate salt in DCM are injected at equal flow rates into a y-shaped mixer (Y1) using a matched pair of syringes (S1 and S2) mounted within a dual-channel syringe pump. The mixer generates a 1:1 segmented flow of the aqueous and DCM solutions, which enters a 5 m length of coiled tubing (Zone A) where the aurate intermediate in the DCM reacts with the aqueous base, forming the corresponding Au(I)-NHC complex. The tubing that comprises Zone A is kept at 35 °C by submersion in a temperature-controlled water bath. The segmented flow then enters a liquid-liquid phase separator (PS). The aqueous phase containing partially depleted base exits the separator at the through-port T, then passes through a micro-metering needle valve NV, before being discarded as waste. The DCM phase containing the Au(I)-NHC complex is directed to one inlet of a second y-mixer Y2, where it mixes with a solution of the organic oxidant $PhICl_2$, which is supplied to the other inlet port of Y2 from a third syringe S3. This single-phase reaction mixture then passes through a second 5 m length of coiled tubing (Zone B) - which is also held at 35 °C within the same water bath as Zone A - before it is collected for analysis.