We demonstrate how it is possible to design a modular programmable inert-atmosphere Schlenkputer (Schlenk-line-computer) for the synthesis and manipulation of the most highly reactive compounds including those which are air- and moisture sensitive or pyrophoric. To do this we have designed and built a programmable Schlenk Line using the Chemputer architecture for the inertization of glassware which can achieve a vacuum line pressure of $1.5 \times 10^{-3}$ mbar and integrated a range of automated Schlenk glassware for the handling, storage, and isolation of reactive compounds at sub ppm levels of O$_2$ and H$_2$O. Utilising this hardware in conjunction with our platform has allowed the automation of a range of common organometallic reaction types for the synthesis of four highly reactive compounds from across the periodic table: [Cp$_2$Ti$^{III}$(MeCN)$_2$]$^+$ [1], Ce$^{III}$(N(SiMe$_3$)$_2$)$_3$ [2], B(C$_6$F$_5$)$_3$ [3] and {DippNacNacMg}$^1$ [4] which are variously sensitive to temperature, pressure, water and oxygen. Automated purification by crystallisation, filtration and sublimation are each demonstrated along with analysis using inline NMR or reaction sampling for UV/Vis. Finally, we demonstrate automated ultra-low temperature reactivity, down to $-90$ °C as well as safe handling and quenching of alkali metal reagents, using dynamic feedback from an *in-situ* temperature probe.

**Keywords:** Schlenk, air-sensitive, inert-atmosphere, automation, digital chemistry.

Automated systems for chemical synthesis, discovery and prediction have potential to revolutionise the chemical sciences. Bespoke equipment such as peptide synthesisers and preparative HPLC reduce the
level of training, time and discipline specific skill required for routine tasks and increasing safety by minimizing human contact with toxic reagents. Building on these advances recently there has been a drive towards more ‘universal’ synthesis machines which can undertake more of the operations automatically with minimal labour costs.  

Current chemical automation technologies focus strongly on aerobic transformations, often using liquid handling (LH) systems for low to medium scale synthesis. Whilst some of these systems incorporate basic inert atmosphere conditions control, these are normally rudimentary, are not programmable since they only can purge or blanket the system with inert gas. As such these approaches are inadequate for the majority of robust organometallic or air-sensitive chemistries which must be conducted at sub ppm levels of O₂ and H₂O. Similarly, reactions under controlled gas environments (e.g. CO, X₂ etc) are not remotely operable despite the safety concerns for manual handling. This means the use of automation at the forefront of highly reactive chemistry is severely underdeveloped.

Manual inert and controlled atmosphere chemistry has, on the other hand, developed hugely in the past 50 years due to the increasing availability of technologies such as positive-pressure gloveboxes, Schlenk lines and solvent purification systems. In tandem our ability to investigate and exploit species which hydrolyse or oxidise readily under atmospheric conditions has expanded rapidly. However, the manipulation of reactions under inert conditions still requires significant specialist training and many procedures fail due to poor technique. In addition, with manual handling it is significantly more challenging to carry out multiple inert reactions at one time limiting the number of new compounds which can be made, or the chemical space explored, meaning organometallic chemistry currently moves at a slower pace than its aerobic counterparts. Several key features delineate inert-atmosphere chemistry from traditional bench techniques. Firstly, removal of air from the flasks and system in question by
application of vacuum is required.\textsuperscript{17,18} This is typically achieved using Schlenk glassware which has a manually sealable gas handling side arm. Reduced pressure of at least <0.1 mbar is required for the most sensitive chemistry to reduce the levels of \( \text{O}_2 \) and \( \text{H}_2\text{O} \) to sub ppm quantities. This effect is carried out using a Schlenk line or Inert Manifold which has two distinct lines, one for vacuum and one for inert gas, and several sets of taps which allow connection to the reactors or glassware in question. After evacuation and refill in triplicate (often known as cycling or inertization), to reduce remaining air to adequate levels the flasks can be maintained under positive pressure throughout a reaction by retaining connection to the inert gas line on the manifold.

Herein, we report the design, development, and deployment of the first fully automated controlled-atmosphere synthesis robot known as the Schlenkputer, which can reach reduced pressures of \( 1.5 \times 10^{-3} \) mbar and allows for automated inertization of reactor flasks; a range of key glassware allowing for the gas tight sealing of the flask for the duration of our experiments; and the coupling of this inert-gas handling system with a liquid handling backbone Chemputer,\textsuperscript{2,5} see Fig. 1. Using this new system we demonstrate the complete automated synthesis of a range of sensitive compounds from across the periodic table including: the colorimetric indicator \( \text{Cp}_2\text{Ti}^{\text{III}}(\text{MeCN})_2 \) \textsuperscript{[1]}, readily oxidisable \( \text{Ce}^{\text{III}}\{\text{N(SiMe}_3\}_2\}_3 \) \textsuperscript{[2]}, highly moisture sensitive \( \text{B(C}_6\text{F}_5\}_3 \) \textsuperscript{[3]} and the alkali metal-reduced \{DippNacNacMgI\}_2 \textsuperscript{[4]}. Through the use of our Chemical Programming language (XDL)\textsuperscript{19} we are able to remotely program and conduct the synthesis, sampling and analysis of an entire reaction process whilst maintaining inert conditions. In addition, we demonstrate the incorporation of in-line NMR spectroscopy, temperature sensing for safe quenching of alkali metal reagents, and reaction sampling for UV/vis analysis.
**Fig. 1 Overview of the Schlenkputer.** The Schlenkputer combines automated liquid handling and gas handling systems in one platform. Route map shows the liquid handling connections (thin lines) between the Chemputer backbone and reactors as well as gas/vacuum handling connections (thicker lines) between the inert manifold and the bespoke glassware designed in this work (left to right: Schlenk filter flask, green; Schlenk collection ampoule, teal; sealable UV/vis cuvette, orange; J Young NMR tube adaptor, yellow; 3-necked RBF appended with remotely operable tap, blue; Solvent storage ampoules with inert gas flow splitter, red). (G: Inert gas inlet; V: vacuum inlet; W: waste outlet).

**Schlenkputer Hardware.** An inert manifold (Schlenk line) consists of an array of taps connecting two gas/vacuum lines to tubing for connection to various flasks and reactors. To allow for flexibility in conducting manipulations each tap must be independently operable. Two common Schlenk line tap designs exist: double oblique taps which are rotated to provide a connection between the reactor and the respective manifold lines; or a pair of greaseless stopcocks (J Young®, Rotaflo® etc) which individually open the reactor to either the vacuum or gas line (or potentially even both if improperly used). In our work we elected to design a manifold based on the latter style with 5 reactor lines thus using 10 vacuum
taps (i.e., 5 pairs). These vacuum taps can be linearly actuated by application of a weak positive or negative pressure (ca 50 mbar) to the hollow of the glass barrel, see Fig. 2A. Three FFKM O-rings provide a tight seal within the barrel towards the atmosphere with the terminal O-ring acting to open or close the system to the reactor depending upon the linear position of the barrel.

Control over the actuation of these taps was provided by utilising a programmable solenoid manifold consisting of 12 electromagnetic valves connected to a diaphragm pump and gas lines which when engaged were able to affect the opening and closing of each of these taps individually, see SI Section 3.2. Our Schlenkputer line, when coupled to a rotary vane pump can achieve ca $1.5 \times 10^{-3}$ mbar pressures and withstand at least 1 bar positive pressure of inert gas, see Fig. 2B. Using the combination of this technology the taps can be controlled using direct XDL commands such as “SchlenkLineOpenVacuum” (Fig. 2C) or these commands can be integrated to allow the use of high-level unit operations within the XDL file such as “EvacuateAndRefill” whereby the line is cycled automatically between opening the flask to the vacuum line and the gas line. In each case the length of time, cycle repeats and specific flask can be input as parameters with 3 mins vacuum, 2 mins gas and 3 repeats found to be optimal for inertization in our hands.

**Development of Automated Sealable Glassware for Inert Atmosphere Chemistry.** In classical Schlenk chemistry, flasks are commonly opened under a flow of inert gas to allow the insertion of a cannula, usually through septa, for liquid transfer. However, the Chemputer liquid handling backbone does not require opening and closing during a reaction and as such, our inert atmosphere syntheses can in large part be carried out using commercial Quickfit® glassware such as round bottomed flasks. Despite this there is still a need to utilise automated Schlenk-type flasks in key places where sensitive reagents
or reactants must be retrieved from a glovebox, where reactive products must be isolated as solids, or where the reactive species must be stored for long periods e.g., during crystallisation. In addition, there are some operations for which direct opening and closing of connections between one reactor and another may be required.

**Fig. 2 AutoSchlenk hardware.** (A) Remotely operable vacuum taps open and close by application of a negative pressure to the hollow of the glass tap. (B) Using these taps a remotely-operable, automated Schlenk line has been constructed which allows for the application of high vacuum (ca. $1.5 \times 10^{-3}$ mbar) and high pressure N$_2$/Argon (ca 1 bar) to reaction flasks. (C) Chemical programming language commands have been developed to operate these taps.

For these reasons we developed a set of key pieces of glassware to facilitate the full automation of our reactions, see Fig. 1, Fig. 3A. Each flask utilises the same remotely operable taps as the Schlenk line and is automatically controlled in a similar way. Chemically inert FFKM O-rings provide minimal swelling upon chemical or solvent exposure resisting at least 48 h submersion in solvent without loss of function.

Firstly, an isolation flask was developed for collection of pure material, see Fig. 3A left. A 250 mL RBF with a single automated tap was designed and built. Solutions of product materials may be transferred into this flask through the liquid handling system and the solvent removed *in vacuo* allowing the solid
material to be extracted in an inert atmosphere glovebox. Next a filtration flask, see Fig. 3A right, was produced, allowing separate inlet and outlet ports for isolation of solid material. The large volume allows crystallisation of the product in the flask or alternatively filtration through celite to remove particulate material. Finally, a single tap was appended to a Quickfit® joint for flexible use of a remotely operable tap connected to a standard RBF, see Fig.7E. This tap can be used to control the evaporation of solvent/reagents into an external cryogenic trap (for example in the Cerium(III) silylamide synthesis, below). The XDL commands SchlenkFlaskTapOpen and SchlenkFlaskTapClose were designed for use with any of this glassware. Up to two taps can be used in conjunction with the Schlenk line based on our current design.

Integration of the automated Schlenk line with liquid handling. Two different methods have been utilised for the integration of the gas handling system with the liquid handling backbone of the Chemputer. The simplest involves the use of multi-necked glassware fitted with both a liquid handling adaptor (B19 to GL14 adaptor for 1/8” LH tubing) and a gas/vacuum adaptor (B24 to 1/4 in. glass hose barb). However, this option does not allow for the facile, automated sealing of the vessel for transport to a glovebox or storage. The Schlenkputer glassware set we have described above (Fig. 3A) has been designed with only one inlet/outlet per tap (neck). For integration with these flasks a tube-in-tube strategy was designed to allow both inertization and liquid handling through a single port (Fig. 3B & S43).

A route-map style depiction of the integration of the hardware described herein with the previously reported liquid handling system of the Chemputer is shown in Fig. 1. Here, the solvent storage flasks, Fig. 1 pink, are connected to the Schlenkputer through a gas line splitter (Fig. S42) which means one manifold line can provide all the required solvents with a gas blanket. The Schlenk Filter Flask (Fig. 1
green, Fig. 3A right) described above is connected through a Tube-in-Tube adaptor on the top port but directly to liquid handling on the bottom while the Schlenk collection Flask (Fig. 1 teal, Fig. 3A left) only requires a single inlet position to transfer liquids in and to remove the solvents, allowing for collection of the solid reaction product. We have also designed a UV/vis cuvette (Fig. 1 orange, Fig. 6C) and J Young® tap NMR tube adaptor (Fig. 1 yellow) for our system to facilitate sampling during and after reactions. Finally, the alternate method of using a standard QuickFit® RBF allows for different necks to be connected to the liquid and gas handling manifolds respectively (Fig. 1 blue). The outlet port of the inert gas line on the Schlenkputer runs through the waste collection bottle and to a bubbler (Fig. S34). This line can also be split to allow an inert gas flow over subasealed reagent bottles such as nBuLi.

**Fig. 3 Schlenkputer hardware for product isolation.** (A) Glassware for the Schlenkputer system including an inert atmosphere isolation flask and inert atmosphere filter flask; (B) The tube-in-tube adaptor system which allows liquid and gas handling through one flask port.

This method has several advantages: first, these tube-in-tube adaptors can allow for connection of the inert manifold to liquid handling systems which are not designed with inertization in mind or allow the
use of non-bespoke glassware; secondly, the adaptors can be connected in a daisy chain fashion thus making optimal use of the five manifold lines of the Schlenkputer; this setup also provides an additional safety feature for the handling of pyrophorics since any potential leaks in the LH tubing will only expose the system to inert gas rather than air.

**Periodic Table Flight** Having designed a programmable hardware and software system for inert atmosphere synthesis four sensitive compounds from across the periodic table were chosen to develop the Schlenkputer implementation focussing on control, reliability, safety, and interoperability. Each has a different sensitivity profile with some sensitive to oxygen, others moisture, as well as temperature and vacuum, see Fig. 4.

![Fig. 4 Periodic table flight](image)

Highly sensitive compounds can be found from around the periodic table. For our purposes a single compound from each block was chosen to demonstrate the versatility of the Schlenkputer. S-block: [(DippNacNac)Mg]₂, yellow, d-block: [Cp₂Ti³⁺(MeCN)₂]₂[ZnCl₄], blue; p-block: B(C₆F₅)₃, pink; f-block: Ce³⁺(N(SiMe₃)₂)_3, green.
d-block complex – Titanocene. All known automated chemical systems exploit liquid handling (LH) pumps and valves in concert with reactors or flow loops to undertake the operations required for synthesis. For reactions involving highly sensitive reagents it is key that not only the reactor is inertized but that the entire system is free from oxygen and moisture thus strategies to fully inertize the LH system were investigated using \([\text{Cp}_2\text{Ti}^\text{III}(\text{MeCN})_2]^+\). The titanocene species \([\text{Cp}_2\text{Ti}^\text{III}(\text{MeCN})_2]^+\) is one of the most widely used colorimetric indicators,\(^{21,22}\) turning from blue to yellow readily upon exposure to oxygen. In the first instance this reaction afforded us the opportunity to gain rapid feedback on our ability to exclude air from the pump-valve liquid handling system of the Chemputer. By transferring the blue solution through the sets of valves and pumps we could identify areas where simple cycling of the reactor flask was insufficient for an entire synthetic procedure.

We immediately identified the connections between the valves and pumps as well as the connections between individual valves as being ‘dead’ areas where our Schlenkputer line was unable to purge, see Fig. 5A. As such when transferring the blue titanocene solution between valves rapid decolourisation was observed. To address this, we adopted two complementary approaches which can both be used to inertize liquid handling systems: 1) When inertizing a reactor flask the liquid handling tubing connecting the glassware and the valve was naturally evacuated since it was open to the flask. By also turning the valve to the appropriate reactor position to open the connection between the pump and the flask before inertization we were able to remove air from these lines (Fig. 5A, yellow). 2) Removing air from the connection between valves (Fig. 5A, green) was more challenging since, in our system, these could not be directly connected to the flask and thus to the Schlenk line. Instead, these short tubes were purged by transferring dry solvent through the full liquid handling backbone in triplicate. With these measures in
place both the flasks and liquid handling system were demonstrated to be free from oxygen by repeated
transfer of the colorimetric indicator throughout the system (Fig. 5C).

The synthetic protocol for the synthesis of \([\text{Cp}_2\text{Ti}^\text{III}(\text{MeCN})_2]^+\) involves the suspension of the air stable
bis(cyclopentadienyl)titanium(IV)chloride in acetonitrile followed by reduction over solid Zinc dust
(Fig. 5B). During the reduction the red solution turns first green, then deep royal blue in the absence of
air however oxygen exposure results in rapid decolourisation. In order to achieve the automated synthesis
and isolation of the product in this case the reaction was setup to involve two RBFs and one crystallisation
(Schlenk) flask (Fig. 3A). Each RBF was charged with one of the solid reagents (\(\text{Cp}_2\text{TiCl}_2\) or \(\text{Zn}\) dust).
The automated procedure prompts the user to charge the flask at the appropriate time (i.e., once the flask
has cooled) and when addition has been confirmed the automated run continues. This ‘cobotic’ or
cooperative robotic strategy means the reaction setup is guided and assisted by automation, but the
reaction process is fully automated after run setup which takes approx. 15-20 mins (Fig’s 5E-F). Remote
notification steps which send a Slack message to the users phone or desktop can also be added for
hazardous processes or where the user would like to observe a portion of the reaction.

The \(\text{Cp}_2\text{TiCl}_2\) is then dissolved in acetonitrile before the red solution is transferred to the \(\text{Zn}\) containing
flask with stirring for 30 mins. The resultant blue solution is transferred through the liquid handling
backbone to the Schlenk Flask whereupon the upper tap has been automatically opened. Next the Schlenk
Flask is charged with dry Ethanol and the flask sealed for 48-72 h during which time the solution remained
deep blue. Finally, the bottom tap on the Schlenk flask is opened to pump out the mother liquor and yield
the crystalline product on the Schlenk Flask filter frit. These crystals can be isolated for XRD analysis
by pumping Fomblin Y oil automatically into the Schlenk Flask, thus providing some protection from
air upon retrieval of the crystals. In our case XRD analysis demonstrated the formation of the target compound by comparison with published structures (Fig. 5D).

**Fig. 5 | Synthesis of colorimetric indicator titanocene(III).** (A) Photograph of part of the Schlenkputer liquid handling backbone with Valve-Pump and Valve-Valve “dead” areas highlighted (yellow & green respectively). (B) Scheme showing Ti(IV) reduction with indicative solutions colours for different stages. (C) Colour of the product solution after passing through the fully inertized LH backbone. (D) XRD Crystal structure of isolated product from automated reaction. (E) Section of a XDL procedure showing the process of connecting and inertizing a flask and the liquid handling system. (F) Overview of the guided (semi-automated) reaction/platform setup process.

**f-block complex – Luminescent Cerium silylamide.** Lanthanide coordination chemistry is another field which relies upon inert-atmosphere techniques.\(^{23,24}\) Whilst most lanthanides exist almost exclusively in the 3+ oxidation state Cerium is one of the few which, in addition to undergoing rapid ligand hydrolysis, is readily oxidised in air to Ce(IV) owing to its position within the 4f block. In our next experiment we
targeted a widely used cerium amide which has been previously shown to exhibit luminescent properties, but which can also act as a precursor for a wide range of novel lanthanide species.\textsuperscript{25} For inert and anhydrous chemistry on salts to succeed it is vital that the precursors reagents are free from water coordination, as in the titanium example above. However, electropositive metals such as those of the f-block are highly hygroscopic yielding very stable hydrated species rapidly in air. The reagents required to dehydrate metal salts (e.g. HX acids, SOCl\textsubscript{2}, TMSCl and Tf\textsubscript{2}O) are often highly corrosive, and could be detrimental to our automated systems, therefore, our ability to automate the handling of these compounds was investigated.

Addition of excess neat triflic acid to an aqueous suspension of Ce\textsubscript{3}(CO\textsubscript{3})\textsubscript{2} was undertaken using the liquid handling backbone of the Schlenkputer under air (Fig. 6A). The resulting acid suspension was first refluxed (100 °C) in an RBF connected through a Findenser\textsuperscript{TM} to the Schlenkputer bubbler. This allowed us to investigate the effect of the acid on both the liquid handling hardware and the Schlenkputer O-rings. Visual inspection showed no impact of either the liquid transfer or refluxing of the acid solution. After automated workup, IR Analysis demonstrated that the resulting CeOTf\textsubscript{3} was free of hydration by the absence of the key -OH band at ca 1650 cm\textsuperscript{-1} (cf. 1657 cm\textsuperscript{-1} in CeOTf\textsubscript{3}.xH\textsubscript{2}O, See SI Fig. S10).\textsuperscript{26}

Our adapted literature procedure\textsuperscript{27} for the synthesis of Ce(N(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{3} consisted of the salt metathesis reaction of anhydrous Ce(OTf)\textsubscript{3} with KN(SiMe\textsubscript{3})\textsubscript{2} (KN") in THF, yielding highly soluble CeN"\textsubscript{3} as a yellow solid. Replacement of the THF solvent with hexane, by evaporation under reduced pressure is a key step in the isolation the highly soluble product from solvated side products. In organic chemistry a rotary evaporator may be automated to allow for removal of solvent,\textsuperscript{2,5} however, the pressure obtainable in these systems is usually insufficient to obtain a robustly inert system meaning an alternate solvent
removal route is required for the Schlenkputer. After mixing of THF solutions of the cerium salt and silylamide base the solvent was removed by connection of our automatically controllable side arm to a cryogenic trap which was maintained under dynamic vacuum, using the Schlenkputer, for 16 h (Fig. 6B). This external cryogenic trap is akin to the inline trap of the Schlenkputer however the ability to remotely isolate this trap from the reactor by means of the automated side arm is vital to allowing subsequent manipulations without manual intervention. In this case, after automated THF removal the residue was extracted with hexanes and transferred (through a filter-tipped tube) to a collection flask whereby the solvent was removed under reduced pressure to yield pure Ce(N(SiMe$_3$)$_2$)$_3$ (compound 2).

Since this cerium complex also exhibits a characteristic yellow colour, indicative of the Ce(III) oxidation state, the product has been characterised by UV-vis spectroscopy. While we have previously demonstrated inline UV/vis analysis, offline sampling may be desirable for some techniques. Thus, a quartz cuvette was designed which allowed facile connection to both the liquid and gas handling systems of our Schlenkputer whilst also being sealable for transport to the relevant spectrometer (Fig. 6c). UV/Vis analysis of the yellow solution was in keeping with published spectra.$^{25}$ Subsequent exposure of the sample to air for a brief period (ca. 3 secs) resulted in immediate darkening of the solution to deep orange/brown (See Fig. S12) demonstrating this compounds high reactivity towards air. NMR sampling was also developed and explored for both CeOTf$_3$ and CeN”$_3$. In each case a capillary of deuterated solvent was placed in the NMR tube before it was appended to the Schlenkputer followed by semi-automated transfer of the analyte solution (semi-automated since J Young® tap NMR tubes themselves have not been automated herein). Analytically sampled NMR spectra were in keeping with those collected within an inert atmosphere glovebox.
**Fig. 6** Synthesis of cerium(III)tris(bis(trimethylsilyl)amine) (2) in two stages. (A) Moving from an aerobic to anaerobic and anhydrous synthetic space in the Schlenkputer. (B) Setup for removal of solvent using an isolable cryogenic trap. (C) Automated UV/vis solution sampling allowed for the spectroscopic analysis of the Ce(III) product.

**p-block compound - tris(pentafluorophenyl)borane.** Tris(pentafluorophenyl)borane (BCF) is a highly moisture sensitive Lewis acid.\textsuperscript{28} Accessed through the formation of an aryllithium intermediate, BCF, like many organometallics or other highly-reactive species, is commonly synthesised at very low temperatures (\(<−70\, ^\circ\text{C}\)). In addition the final product is often purified by double sublimation or sublimation followed by crystallisation to separate the organic product from LiCl and other impurities, a process which has not previously been automated. This borane also has several valuable NMR handles which can be used to accurately determine the degree of water coordination should the system be exposed to moisture due to dramatically different resonance shifts in the 3- and 4-coordinate examples (Fig. 7A). In order to achieve this synthesis in an automated fashion we therefore required the incorporation of an automated chilling system which was able to reach temperatures as low as \(<−90\, ^\circ\text{C}\), a sublimation protocol...
for purification of the product under inert conditions and we elected to include inline NMR analysis to provide rapid feedback on the formation of the anhydrous product. Two key reagents for this procedure, n-BuLi and BCl$_3$ were purchased as solutions and connected directly to the nitrogen and liquid handling systems using needles to minimise the requirement for bespoke equipment. Lithiation and coupling were carried out in a single flask which was cooled to $-80\,^\circ\text{C}$ automatically (Fig. 7B) before the temperature was autonomously raised to ambient over a period of 120 mins. A portion of the reaction mixture was then transferred to the flow NMR cell appended to the Schlenkputer and subject to $^{19}\text{F}$ NMR which demonstrated formation of the desired product, distinct from the unwanted aquo adduct ($-135, -155, -163\,\text{ppm}$) which was not observed (Fig. 7C).$^{30,31}$

Pure, colourless tris(pentafluorophenyl)borane is most commonly obtained through inert-atmosphere sublimation to separate the product from LiCl and other impurities.$^{32}$ For manual sublimation it is common to charge a sublimation tube with a solid crude product which can then be heated under vacuum and condenses on either a second room temperature tube or on a cold finger. In order to eliminate this manual step we transferred the product solution into a flask and removed the solvent in situ. The reaction mixture was thus transferred into a 3-necked RBF appended with an external cryogenic trap for automated solvent removal (Fig. 7 D/E). As for CeN”$_3$ above, this strategy meant that the solvent could be removed and then isolated in the trap allowing a vacuum pressure sufficient for sublimation to be achieved within the RBF.

**s-block complex – Mg(I) dimer.** Accessing usual or relatively unstable oxidation states is one common theme in modern organometallic and inert-atmosphere chemistry and is often achieved by exploiting the
reducing power of alkali metals. However, their use in organic solvents can present hazards which makes their automation challenging and a high level of expertise required for their manual handling.

Fig. 7 Synthesis & Isolation of tris(pentafluorophenyl)borane, a highly hygroscopic Lewis acid. (A) Reaction scheme for the synthesis of B(C₆F₅)₃. (B) Incorporation of an ultra-low temperature chiller unit allowed for automated reactivity at temperatures as low as −100 °C. (C) Inline low-field NMR analysis can detect formation of the desired product with no evidence of hydration. (D) schematic showing the setup and function of the automated evaporation & sublimation apparatus. (E) photograph of the setup and glassware used for automated sublimation of B(C₆F₅)₃.
We sought to undertake an alkali metal reduction reaction to yield Stasch & Jones’ Mg(I) dimer\textsuperscript{36} utilising our Schlenkputer system (Fig. 8A) providing a safe method for reacting with, and quenching Na(0) in automation. Herein we demonstrate mitigation of this risk by use of a temperature probe for real-time feedback upon automated quenching of the alkali metal. For our purposes we can consider the synthesis of Mg(I) as consisting of sets of operations running alongside each other: the Mg(II) reduction and the Na(0) handling. The first step in the magnesium reduction requires the metalation of the DippNacNac ligand (L) to yield moisture and vacuum sensitive LMgI(OEt\textsubscript{2})\textsubscript{n} (Fig. 8A). Limit the temperature to 50 °C total such that a runaway reaction with evaporation of solvent does not occur.

As for other solid reagents, during setup an RBF was manually charged with the solid ligand (L) while another was similarly charged with a dispersion of Na(0) in oil before cycling of the entire system. This commercially available dispersion exhibits significantly lower sensitivity to air and moisture with the oil acting as a barrier such that handling by non-experts in Schlenk technique can be conducted safely. Automated washing of the sodium metal using hexane removed the oil and provides the highly reactive metal in situ with the filtrate transferred to the waste flask which was maintained under a stream of N\textsubscript{2} for safety (Fig. 8B). Automated addition of MeMgI in toluene (3 M) to the ligand flask at −30 °C yielded a pale yellow solution. Due to the small volume of MeMgI solution added (680 µL) the liquid handling tubing (between valve and reactor) was flushed with additional toluene solvent (7 mL) to ensure stoichiometric reaction. The toluene solution of LMgI(OEt\textsubscript{2})\textsubscript{n} was transferred onto a suspension of Na(0) in toluene and the mixture stirred overnight. The solution was then automatically filtered and extracted into hexane to yield the product dimer [(DippNacNac)Mg]\textsubscript{2}, which was confirmed by NMR and XRD analysis.
Before the automated reaction run was completed however, the pyrophoric sodium metal was quenched while maintaining the solution temperature below 50 °C to reduce risk. In order to determine the safest addition rate, we carried out the Na quenching at various aliquot addition volumes and monitored the resulting solution temperature (Fig. 8C). In our work aliquot volume is a proxy for addition rate since an aliquot is added between each temperature measurement. Our analysis found that an aliquot volume of 0.5 mL produced a rather sharp increase in temperature whereas 0.25 mL was deemed to be more appropriate. Importantly, the key XDL command used in this procedure “AddDynamic” incorporates feedback to limit the temperature to 50 °C total such that a runaway reaction with evaporation of solvent does not occur.

**Fig. 8 Alkali metal reduction to generate Mg(I).** (A) Reduction of (NacNac)MgI with Na(0). (B) Risk mitigation steps for automated handling of pyrophoric and flammable species. (C) Temperature change with different rates of quenching (rate determined by aliquot size) of Na(0) with iPrOH (15% in Toluene). Monitoring stopped upon observation of no further temperature increase.
The automation of the most highly sensitive inert atmosphere synthesis has been demonstrated for the first time. We have described how to design an automatable and remotely operable gas/vacuum handling manifold, Schlenkputer, which can reduce system oxygen and water levels below 1 ppm and demonstrate how to integrate this with a liquid handling robotic platform (Chemputer) to create the Schlenkputer. We have designed a basic set of glassware which can be utilised alongside classical Quickfit® glassware for the undertaking of highly reactive synthesis. In demonstration of the abilities of our system we have synthesised four highly sensitive exemplar compounds from across the periodic table, Cp₂TiIII(MeCN)₂ [1], CeIII{N(SiMe₃)₂}₃ [2], B(C₆F₅)₃ [3] and {DippNacNacMgI}₂ [4], each with different synthetic challenges and sensitivity profiles. In this manner we have demonstrated inert atmosphere synthesis, crystallisation, solvent distillation/evaporation and sublimation; as well as analytical sampling, inline analysis, low temperature reactivity, and handling of pyrophoric alkali metals. In all this work demonstrates a comprehensive system for automation of inert atmosphere manipulations, potentially dramatically increasing the safety and throughput of handling highly reactive chemical species.

**Resource Availability**

The lead contact for this work is Prof. Leroy Cronin. The Supplementary Information file attached includes all materials required to reproduce this work. This includes a .xdl and a .json file for each synthesis and full analytical data as well as details on and photographs of the bespoke hardware described herein to allow reproduction. The software and the code to run the synthesis is attached as a .zip file and will be made available on GitHub upon publication. Supplementary movies show examples of the procedures underway in the Schlenkputer system.

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The authors would like to sincerely thank Dr Joy Farnaby and her student Tajrian Chowdhury for access to their Glovebox facilities and for sharing of anhydrous CeOTf₃ prepared manually by them in their lab. We would also like to thank Daniel Gahler for implementing the remote notification system. We gratefully acknowledge financial support from the EPSRC (Grant Nos. EP/L023652/1, EP/R020914/1, EP/S030603/1, EP/R01308X/1, EP/S017046/1, and EP/S019472/1), the ERC (Project No. 670467 SMART-POM), the EC (Project No. 766975 MADONNA), and DARPA (Project Nos. W911NF-18-2-0036, W911NF-17-1-0316, and HR001119S0003).

Author Contributions:
The concept was conceived by LC who also managed the team, raised the funding, and designed the programming language. NLB and LC designed the programable manifold, and NLB devised the experiments. Lab work and data analysis was carried out by NLB, FB, AB and DRW. Integration of the low temperature chiller was achieved by VSL. The manuscript and associated materials were prepared by NLB with help from LC.

References
1. RSC. Digital Futures; 2020.

7. We have previously reported the in situ formation of Grignard reagents in the Chemputer which was only possible by use of excess Mg(0) where the metal acted as both an in situ drying agent and reactant. Cronin, L.; Emmerling, F. et al., *Angew. Chem. Int. Ed.* 60, 23202 (2021)


A SciFinder Survey of papers published in JOC and Organometallics in 2020 showed an average of 25 and 16 compounds reported respectively per research article in each. Thus organometallic chemistry produces at 2/3rds the rate of organic.


Supplementary Information for:

Autonomous Execution of Highly Reactive Chemical Transformations in the Schlenkputer

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# Chemistry

1.1 General Experimental.................................................................4

1.2 Synthesis of \([\text{Cp}_2\text{Ti(CH}_3\text{CN})_2][\text{ZnCl}_2]\) (1) .................................................5

1.2.1 Hardware Graph..........................................................................6

1.2.2 Schlenkputer Hardware Setup ..................................................7

1.2.3 XDL............................................................................................8

1.3 Synthesis of \(\text{Ce(N(SiMe}_3)_2}_3\) (2) ....................................................13

1.3.1 Hardware Graph..........................................................................14

1.3.2 XDL – \(\text{Ce[N(SiMe}_3)_2}_3\) synthesis ........................................15

1.3.3 XDL – Analytical Sampling .........................................................19

1.3.4 Analytical Data ...........................................................................23

1.3.5 Synthesis of \(\text{CeOTf}_3 – \text{testing handling of corrosives in system} \) 26

1.3.6 Hardware Graph for \(\text{CeOTf}_3\) synthesis ..................................27

1.3.7 XDL – \(\text{CeOTf}_3\) synthesis ..........................................................28

1.3.8 Analytical Data for \(\text{CeOTf}_3\) .......................................................33

1.4 Synthesis of \(\text{B(C}_6\text{F}_3)_3\) (3) .................................................................35

1.4.1 Hardware Graph..........................................................................36

1.4.2 Schlenkputer Hardware Setup ..................................................37

1.4.3 XDL............................................................................................39

1.4.4 NMR Spectra of \(\text{B(C}_6\text{F}_3)_3\).........................................................45

1.5 Synthesis of \([(\text{DippNacNac})\text{Mg}]_2\) (4) ..............................................47

1.5.1 Hardware Graph..........................................................................49

1.5.2 NMR Data for \([(\text{DippNacNac})\text{Mg}]_2\)........................................50

# Hardware .......................................................................................58

2.1 AutoSchlenk Line...........................................................................58

2.2 Solenoid manifold Build .................................................................61

2.2.1 Programmable solenoid manifold...............................................61

2.2.2 Build differences from published design.....................................63

2.3 Glassware Build ............................................................................66

2.3.1 Isolation Flask ...........................................................................66

2.3.2 Schlenk (Filter) Flask .................................................................66

2.4 Other Hardware .............................................................................67

2.4.1 Pneumatic Splitter .....................................................................67

2.4.2 Tube-in-Tube splitter .................................................................67

2.4.3 Inline Filters for liquid handling system .....................................68
2.5 Benchtop NMR ................................................................. 68
2.6 Temperature Sensor Setup ................................................ 69
  2.6.1 SensorHub ................................................................... 69
  2.6.2 Reaction temperature sensor (RTD) ............................... 70
2.7 Ultra Low Temperature Chiller Setup .................................... 71
3 Software ............................................................................. 72
  3.1 XDL General ................................................................. 72
  3.2 XDL Steps Description .................................................... 72
  3.3 New/Custom Graph Nodes ............................................... 73
    3.3.1 NMR Machine .......................................................... 73
    3.3.2 Pneumatic Splitter ....................................................... 73
4 References ........................................................................ 74
1 Chemistry

1.1 General Experimental

All reactions were carried out under inert atmosphere using the technology described herein to evacuate and refill glassware with N₂ gas cylinder purging throughout the reaction. Unless otherwise stated isolated sensitive materials were stored and prepared for offline NMR & XRD analysis in a nitrogen atmosphere MBraun Labstar Glovebox with O₂ levels < 1 ppm and H₂O levels < 2 ppm. Solvents (excepting hexane) were obtained from an SPS system and dried over activated 3Å molecular sieves for 48h after collection. Anhydrous hexane solvent was purchased from Sigma Aldrich and stored over activated 3Å molecular sieves under nitrogen. Deuterated solvents for NMR analysis were dried over activated 3Å molecular sieves. NacNacDipp ligand was prepared manually by a published method.¹ Anhydrous Cerium Triflate for the synthesis of Ce(N{SiMe₃}₂)₃ was kindly provided by Tajrian Chowdhury from the group of Dr Joy Farnaby and prepared manually by their method, prior to our automated synthesis of CeOTf₃ described below. Unless otherwise stated all other reagents were purchased from Sigma, Acros, Alfa Aesar, Fisher or Fluorochem and used as received. Inline NMR spectra were collected on Spinsolve 43 Carbon from Magritek at a frequency of 43 MHz while full offline spectra were collected on a Bruker Avance III HD 600 MHz or Bruker Avance II 400 MHz spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane and for offline samples are referenced to residual protium in the NMR solvent (C₆D₆, δ = 7.16; THF-d₈, δ = 3.58). X-ray crystal structures of compounds 1 & 4 were collected on a Bruker Apex-II diffractometer and confirmed to match CCDC 1167669 (1) and CCDC 661566 (4) in the CSD. Chilling was provided by a Huber TC100E cooling system.
1.2 Synthesis of \([\text{Cp}_2\text{Ti(CH}_3\text{CN)}_2][\text{ZnCl}_4]\) (1)

![Reaction scheme showing synthesis of compound 1.](image)

**Figure S1:** Reaction scheme showing synthesis of compound 1.

*The following procedure was carried out without the use of an inert atmosphere glovebox at any point.*

Following an adapted literature procedure, 8.3 g (29.7 mmol, 1 eq.) of \(\text{Cp}_2\text{TiCl}_2\) was suspended in a mixture of 75 mL THF and 35 mL MeCN under nitrogen. The red solution was then rapidly added to a flask containing Zn dust (2.3 g, 35.2 mmol) and the resulting suspension was stirred for 30 minutes. During this time, the initial red solution turned dark blue. The filtered solution was transferred to a filter flask, and the solution layered with diethyl ether (170 mL). The flask was sealed and allowed to stand for 48h leading to the precipitation of compound 1 as dark blue crystals (5 g, >43 %). In order to extract crystals for X-ray diffraction, Fomblin Y Oil was added to the flask to allow their handling in air. Screening experiments determined the unit cell parameters to be \(a = 28.4\ \text{Å}, b = 15.2\ \text{Å}, c = 15.4\ \text{Å}\) for an Orthorhombic cell with \(V = 6,648\ \text{Å}^3\) matching CSD entry 1167669. Crystal Data for Compound 1: \(a = 28.4\ \text{Å}, b = 15.2\ \text{Å}, c = 15.4\ \text{Å}, \alpha = \beta = \gamma = 90^\circ\), orthorhombic, \(Pbca\).
1.2.1 Hardware Graph

Figure S2: Visual Representation of the hardware graph for the synthesis of \([\text{Cp}_2\text{Ti(CH}_3\text{CN})_2]_2[\text{ZnCl}_4]\). Full graph file as .json available on https://github.com/croningp and visualisable through https://croningroup.gitlab.io/chemputer/xdlapp/.
1.2.2 Schlenkputer Hardware Setup

Figure S3: Photograph showing how glassware maps onto Hardware Graph above.

Figure S4: Photograph of synthesis platform during crystallisation.
1.2.3 XDL

The following is the XDL file executed by the platform in concert with the graph shown above (Figure S2). The XDL file has three sections: Hardware, Reagents and Procedure. Comments are added in black for clarity of the reader.

```xml
<Synthesis>
  <Hardware>
    <Component id="Pump1" type='Pump'/>
    <Component id="Pump2" type='Pump'/>
    <Component id="Line" type="pneumatic_controller"/>
    <Component id="Waste" type='waste'/>
    <Component id="PneumaticSplitter" type="custom"/>
    <Component id="Schlenk Flask" type="filter"/>
    <Component id="Round Bottomed Flask" type="reactor"/>
    <Component id="Two Necked Flask" type="reactor"/>
    <Component id="Valve 1" type='Valve'/>
    <Component id="Valve 2" type='Valve'/>
  </Hardware>
  <Reagents>
    <Reagent name='Cp2TiCl2' type='solvent'/>
    <Reagent name='Zinc Dust' type='solvent'/>
    <Reagent name='MeCN' type='solvent'/>
    <Reagent name='THF'/>
  </Reagents>
</Synthesis>
```
<Reagents>
<Reagent
  name="Ether"
  type='solvent'
/>  
<Reagent
  name="Oil"
  type='solvent'
/>  
</Reagents>

<Procedure>
<!-- Connecting Schlenk Flask hot out of the oven and pulling vaccum -->

<Confirm
  msg = 'Is Schlenk Flask Connected?' />
<SchlenkFlaskTapOpen
  pneumatic_controller='Line'
  position='top'
/>  
<CConnect
  from_vessel = 'Schlenk Flask'
  to_vessel = 'Pump1'
/>  <!-- CConnect allows us to vac out the tubing up to the pump-->  
<SchlenkLineTapOpenVacuum
  pneumatic_controller='Line'
  port='1'
/>  

<!-- Connecting Round Bottomed Flask hot out of the oven and pulling vaccum -->

<Confirm
  msg = 'Is Round Bottomed Flask Connected?' />
<CConnect
  from_vessel = 'Round Bottomed Flask'
  to_vessel = 'Pump1'
/>  
<SchlenkLineTapOpenVacuum
  pneumatic_controller='Line'
  port='2'
/>  

<!-- Connecting Two Necked Flask Flask hot out of the oven and pulling vaccum -->

<Confirm
  msg = 'Is Two Necked Flask Connected?' />
<CConnect
  from_vessel = 'Two Necked Flask'
  to_vessel = 'Pump2'
/>  
<SchlenkLineTapOpenVacuum
  pneumatic_controller='Line'
  port='3'
/>  

<Wait
time = '5 minutes'
/>  <!-- Lets the flasks cool to room temp-->  

<!-- Starting to purge Two Necked Flask with N2, manually charging it with Cp2TiCl2, then pulling vaccum -->

<StartPurge
  vessel = 'Two Necked Flask'
/>  
/AddSolid
vessel = 'Two Necked Flask'
reagent = 'Cp2TiCl2'
mass = '8.3 g'
confirm_solid = 'True'

<SchlenkLineTapOpenVacuum
pneumatic_controller='Line'
port='3'/>

<!-- Starting to purge Round Bottomed Flask and manually charging it with Zinc metal dust, then pulling vacuum -->

<StartPurge
vessel = 'Round Bottomed Flask'/>

<AddSolid
vessel = 'Round Bottomed Flask'
reagent = 'Zinc Dust'
mass = '2.3 g'
confirm_solid = 'True'/>

<SchlenkLineTapOpenVacuum
pneumatic_controller='Line'
port='2'/>

 <!-- Alternately pulling vacuum and purging on the three flasks, three times. The Async command allows all of these flasks to be evacuated and refilled at the same time-->

<Async> <!-- this splits the gas line to connect to all three solvent flasks -->

<EvacuateAndRefill
vessel='PneumaticSplitter'
after_vacuum_wait_time='3 minutes'
repeats='3'
gas='low'/>
</Async>

<Async>

<EvacuateAndRefill
vessel='Two Necked Flask'
after_vacuum_wait_time='3 minutes'
repeats='3'
gas='low'/>
</Async>

<Async>

<Wait
time = '5 seconds'/>
</Async>

<EvacuateAndRefill
vessel='Round Bottomed Flask'
after_vacuum_wait_time='3 minutes'
repeats='3'
gas='high'/>
</Async>

<Async>

<Wait
time = '10 seconds'/>
</Async>

<EvacuateAndRefill
vessel='Schlenk Flask'
after_vacuum_wait_time='3 minutes'
repeats='3'
gas='high'/>
</Async>

<Async>

<Wait
time = '13 mins'/>
</Async>
<StartPurge
vessel = 'Schlenk Flask'
/>
<StartPurge
vessel = 'Round Bottomed Flask'
/>
<StartPurge
vessel = 'Two Necked Flask'
/>
<StartPurge
vessel = 'PneumaticSplitter'
/>
<Confirm
msg = 'Are the three solvents connected?'
/>

<ResetHandling
solvent='THF'
repeats='3'
volume='5mL'
/>
<Add
reagent='THF'
vessel='Two Necked Flask'
volume = '75 mL'
/>
<ResetHandling
solvent='MeCN'
repeats='3'
volume='5mL'
/>
<Add
reagent='MeCN'
vessel='Two Necked Flask'
volume = '25 mL'
/>
<Stir
vessel='Two Necked Flask'
time = '40 mins'
stir_speed = '200'
/>
<StartStir
vessel='Round Bottomed Flask'
stir_speed = '200'
/>
<Transfer
from_vessel='Two Necked Flask'
to_vessel='Round Bottomed Flask'
volume = '100 mL'
rinsing_solvent = 'MeCN'
rinsing_volume = '5 mL'
rinsing_repeats = '2'
aspiration_speed = '100'
move_speed = '50'
dispense_speed = '200'
/>
<StopStir
vessel = 'Two Necked Flask'
/>
<Wait

<StartPurge
vessel = 'Schlenk Flask'
/>
<StartPurge
vessel = 'Round Bottomed Flask'
/>
<StartPurge
vessel = 'Two Necked Flask'
/>
<StartPurge
vessel = 'PneumaticSplitter'
/>
<Confirm
msg = 'Are the three solvents connected?'
/>

<ResetHandling
solvent='THF'
repeats='3'
volume='5mL'
/>
<Add
reagent='THF'
vessel='Two Necked Flask'
volume = '75 mL'
/>
<ResetHandling
solvent='MeCN'
repeats='3'
volume='5mL'
/>
<Add
reagent='MeCN'
vessel='Two Necked Flask'
volume = '25 mL'
/>
<Stir
vessel='Two Necked Flask'
time = '40 mins'
stir_speed = '200'
/>
<StartStir
vessel='Round Bottomed Flask'
stir_speed = '200'
/>
<Transfer
from_vessel='Two Necked Flask'
to_vessel='Round Bottomed Flask'
volume = '100 mL'
rinsing_solvent = 'MeCN'
rinsing_volume = '5 mL'
rinsing_repeats = '2'
aspiration_speed = '100'
move_speed = '50'
dispense_speed = '200'
/>
<StopStir
vessel = 'Two Necked Flask'
/>
<Wait

<StartPurge
vessel = 'Schlenk Flask'
/>
<StartPurge
vessel = 'Round Bottomed Flask'
/>
<StartPurge
vessel = 'Two Necked Flask'
/>
<StartPurge
vessel = 'PneumaticSplitter'
/>
<Confirm
msg = 'Are the three solvents connected?'
/>

<ResetHandling
solvent='THF'
repeats='3'
volume='5mL'
/>
<Add
reagent='THF'
vessel='Two Necked Flask'
volume = '75 mL'
/>
<ResetHandling
solvent='MeCN'
repeats='3'
volume='5mL'
/>
<Add
reagent='MeCN'
vessel='Two Necked Flask'
volume = '25 mL'
/>
<Stir
vessel='Two Necked Flask'
time = '40 mins'
stir_speed = '200'
/>
<StartStir
vessel='Round Bottomed Flask'
stir_speed = '200'
/>
<Transfer
from_vessel='Two Necked Flask'
to_vessel='Round Bottomed Flask'
volume = '100 mL'
rinsing_solvent = 'MeCN'
rinsing_volume = '5 mL'
rinsing_repeats = '2'
aspiration_speed = '100'
move_speed = '50'
dispense_speed = '200'
/>
<StopStir
vessel = 'Two Necked Flask'
/>
<Wait

<StartPurge
vessel = 'Schlenk Flask'
/>
<StartPurge
vessel = 'Round Bottomed Flask'
/>
<StartPurge
vessel = 'Two Necked Flask'
/>
<StartPurge
vessel = 'PneumaticSplitter'
/>
<Confirm
msg = 'Are the three solvents connected?'
/>

<ResetHandling
solvent='THF'
repeats='3'
volume='5mL'
/>
<Add
reagent='THF'
vessel='Two Necked Flask'
volume = '75 mL'
/>
<ResetHandling
solvent='MeCN'
repeats='3'
volume='5mL'
/>
<Add
reagent='MeCN'
vessel='Two Necked Flask'
volume = '25 mL'
/>
<Stir
vessel='Two Necked Flask'
time = '40 mins'
stir_speed = '200'
/>
<StartStir
vessel='Round Bottomed Flask'
stir_speed = '200'
/>
<Transfer
from_vessel='Two Necked Flask'
to_vessel='Round Bottomed Flask'
volume = '100 mL'
rinsing_solvent = 'MeCN'
rinsing_volume = '5 mL'
rinsing_repeats = '2'
aspiration_speed = '100'
move_speed = '50'
dispense_speed = '200'
/>
<StopStir
vessel = 'Two Necked Flask'
/>
<Wait

<StartPurge
vessel = 'Schlenk Flask'
/>
<StartPurge
vessel = 'Round Bottomed Flask'
/>
<StartPurge
vessel = 'Two Necked Flask'
/>
<StartPurge
vessel = 'PneumaticSplitter'
/>
<Confirm
msg = 'Are the three solvents connected?'
/>

<ResetHandling
solvent='THF'
repeats='3'
volume='5mL'
/>
<Add
reagent='THF'
vessel='Two Necked Flask'
volume = '75 mL'
/>
time = '30 mins'

<!-- Opening bottom tap of Schlenk Flask and addition of Diethyl Ether from the bottom -->
<SchlenkFlaskTapOpen
    pneumatic_controller='Line'
    position='bottom'
/>

/AddFilterDeadVolume
    filter_vessel = 'Schlenk Flask'
    solvent = 'Ether'
    volume = '20 mL'
/>

<SchlenkFlaskTapClose
    pneumatic_controller='Line'
    position='bottom'
/>

<!-- Transferring reaction mixture from Round Bottomed Flask through filter into Schlenk Flask -->
<SchlenkFlaskTapOpen
    pneumatic_controller='Line'
    position='top'
/>

/Transfer
    from_vessel = 'Round Bottomed Flask'
    to_vessel = 'Schlenk Flask'
    to_port = 'top'
    volume = '130 mL'
/>

<!-- Layering of diethyl ether on top of solution and waiting 48h for crystallisation to occur -->
/Add
    reagent = 'Ether'
    vessel = 'Schlenk Flask'
    volume = '150 mL'
/>

<Wait
    time = '72 h'
/>

<!-- Removing liquid from the bottom of Schlenk Flask with filter, leaving solid product in Schlenk Flask -->
<SchlenkFlaskTapOpen
    pneumatic_controller='Line'
    position='bottom'
/>

/Transfer
    from_vessel = 'Schlenk Flask'
    from_port = 'bottom'
    to_vessel = 'Waste'
    volume = '350 mL'
/>

<SchlenkFlaskTapClose
    pneumatic_controller='Line'
    position='bottom'
/>

<!-- Addition of Oil prepares and protects obtained blue crystals for x-ray crystallography, closing of taps at Schlenk Flask stores product under nitrogen, to transport it conveniently to x-ray machine -->
<SchlenkFlaskTapOpen
    pneumatic_controller='Line'
    position='top'
/>

/Add
    reagent = 'Oil'
    vessel = 'Schlenk Flask'
    port = 'top'
    volume = '20 mL'
/>

<SchlenkFlaskTapClose
    pneumatic_controller='Line'
    position='top'
>
Figure S5: Photographs showing the solution of Ti(III) after filtration (left) and the crystals formed (right).
1.3 Synthesis of Ce(N(SiMe$_3$)$_2$)$_3$ (2)

\[
\text{Ce(OTf)$_3$} \xrightarrow{\text{KN(SiMe$_3$)$_2$}} \text{THF, rt, 2h} \xrightarrow{} \text{Ce(N(SiMe$_3$)$_2$)$_3$}
\]

**Figure S6:** Reaction scheme for the synthesis of CeN"$_3$" (compound 2).

Following an adapted literature procedure$^3$ the white powders Ce(OTf)$_3$ (0.5 g, 0.867 mmol, 1.0 equivalent) and KN(SiMe$_3$)$_2$ (KN"$, 540$ mg, 2.707 mmol, 3.1 equiv.) were weighed into a J-Youngs tapped ampoule in the glovebox. THF (10 mL) was added to suspend the reagents and a slow colour change from colourless to pale yellow was observed. The mixture was stirred at room temperature for 2 hours before being transferred into a second flask with washing with THF (10 mL). Subsequently, the THF was distilled into a cryogenic trap for 16 h before the orange residue was extracted into hexane (3 x 10 mL) and transferred through a filter tipped tube into a collection flask. The extractions in hexane were pumped down yielding a yellow powder CeN"$_3$" (187 mg, 35%).

Analytical data was consistent with literature reported values for [Ce(N(SiMe$_3$)$_2$)$_3$]$^{3,4}$

$^1$H NMR (C$_6$D$_6$): $\delta$ −3.36 (54H, s, Ce(N(SiMe$_3$)$_2$)$_3$) ppm. A small amount of HN" impurity ($\delta$ 0.10, ~3.8%) was also present.
1.3.1 Hardware Graph

Figure S7: Visual Representation of the hardware graph for the synthesis of CeN\textsuperscript{3}. Full graph file as .json available on https://github.com/croningp and visualisable through https://croningroup.gitlab.io/chemputer/xdlapp/.
1.3.2 XDL – Ce{N(SiMe$_3$)$_2$)$_3$ synthesis

The following is the XDL file executed by the platform in concert with the graph shown above (Figure S7). The XDL file has three sections: Hardware, Reagents and Procedure. Comments are added in black for clarity of the reader.

```xml
<Synthesis>
  <Hardware>
    <Component id="PneumaticSplitter" type="custom"/>
    <Component id="Trap" type="reactor"/>
    <Component id="ReactionFlask" type="reactor"/>
    <Component id="IsolationFlask" type="reactor"/>
    <Component id="CeOTf" type="reactor"/>
    <Component id="Cuvette" type="reactor"/>
    <Component id="NMRTube" type="reactor"/>
    <Component id="Line" type="pneumatic_controller"/>
    <Component id="Valve1" type='Valve'/>
    <Component id="Valve2" type='Valve'/>
    <Component id="Valve3" type='Valve'/>
    <Component id="Pump1" type='Pump'/>
    <Component id="Pump2" type='Pump'/>
    <Component id="Waste3" type='Waste'/>
    <Component id="Waste1" type='Waste'/>
  </Hardware>
</Synthesis>
```
<Hardware>

<Reagents>
    <Reagent name='Toluene'>
        type='solvent'
    </Reagent>
    <Reagent name='Hexane'>
        type='solvent'
    </Reagent>
    <Reagent name='THF'>
        type='reagent'
    </Reagent>
    <Reagent name='CeOTf3'>
        type='solid'
    </Reagent>
    <Reagent name='KN'>
        type='solid'
    </Reagent>
</Reagents>

</Procedure>

<!-- -- Reaction Setup -->

<!-- -- Connect Reaction Flasks -->

<Confirm>
    msg = 'Is CeOTf Connected?'
</Confirm>

<SchlenkLineTapOpenVacuum pneumatic_controller='Line' port='1'>
    <CConnect from_vessel = 'CeOTf' to_vessel = 'Pump1' />
    <Confirm msg = 'Is ReactionFlask Connected?' />
    <SchlenkLineTapOpenVacuum pneumatic_controller='Line' port='2'>
        <CConnect from_vessel = 'ReactionFlask' to_vessel = 'Pump2' />
        <Wait time = '2 min' />
        <Confirm msg = 'Are flasks cool to rt?' />
    </SchlenkLineTapOpenVacuum>
</SchlenkLineTapOpenVacuum>

<!-- EvacuateAndRefill Steps for Flasks -->

<Async>
    <EvacuateAndRefill vessel='CeOTf' after_vacuum_wait_time='3 minutes'
                          after_inert_gas_wait_time = '2 mins'
                          repeats='3'
                          gas='high' />
</Async>

<Async>
    <EvacuateAndRefill vessel='ReactionFlask' after_vacuum_wait_time='3 minutes'/>
</Async>
after_inert_gas_wait_time = '2 mins'
repeats = 3

gas = 'high'

</Async>
<Async>
<EvacuateAndRefill
  vessel = 'PneumaticSplitter'
  after_vacuum_wait_time = '3 minutes'
  after_inert_gas_wait_time = '2 mins'
  repeats = 3
  gas = 'high'
  /></Async>

<Wait
time = '16 mins'
/>
<Confirm
msg = 'Are the solvents connected to the liquid handling backbone?'
/>
<ResetHandling
  solvent = 'THF'
  repeats = 4
  volume = '5mL'
/>

<!-- Step 1 – Begin Reaction -->
/Add
  reagent = 'THF'
  vessel = 'CeOTf'
  volume = '10 mL'
  stir = 'true'
  stir_speed = '500'
  aspiration_speed = '5'
/>
<Stir
  vessel = 'CeOTf'
  stir_speed = '500'
  time = '2h'
/>
<Transfer
  from_vessel = 'CeOTf'
  to_vessel = 'ReactionFlask'
  aspiration_speed = '5'
  volume = '20 mL'
  rinsing_solvent = 'THF'
  rinsing_volume = '10 mL'
  rinsing_repeats = '1'
/>

<!-- Step 3 -->
<Confirm
  msg = 'Is the cryo trap filled with liquid N2?'
/>
<StartStir
  vessel = 'ReactionFlask'
  stir_speed = '500'
/>
<SchlenkLineTapClose
  pneumatic_controller = 'Line'
  port = '2'
/>
<SchlenkLineTapOpenVacuum
  pneumatic_controller = 'Line'
  port = '3'
/>
<SchlenkFlaskTapOpen
  pneumatic_controller = 'Line'
  position = 'bottom'
/>
<Wait
time = '30 mins'
/>
position = 'bottom'

<SchlenkLineTapClose
  pneumatic_controller = 'Line'
  port = '3'
/>

<SchlenkLineTapOpenArgon
  pneumatic_controller = 'Line'
  port = '2'
/>

<!-- Insert Analytical Sampling steps here if required (see below) -->

<SchlenkLineTapOpenVacuum
  pneumatic_controller = 'Line'
  port = '2'
/>

<!-- Evacuate flask directly overnight -->
<SchlenkLineTapOpenVacuum
  pneumatic_controller = 'Line'
  port = '2'
/>

<Wait
time = '16 h'
/>

<SchlenkLineTapOpenArgon
  pneumatic_controller = 'Line'
  port = '2'
/>

<!-- Day 2: Setup Isolation Flask and reinertise the system for completeness/robustness -->
<Confirm
  msg = 'Is IsolationFlask Connected?'
/>

<SchlenkFlaskTapOpen
  pneumatic_controller = 'Line'
  position = 'top'
/>

<SchlenkLineTapOpenVacuum
  pneumatic_controller = 'Line'
  port = '4'
/>

<CConnect
  from_vessel = 'IsolationFlask'
to_vessel = 'Pump2'
/>

<Wait
time = '2 min'
/>

<Confirm
  msg = 'Is IsolationFlask cool to rt?'
/>

<SchlenkFlaskTapOpen
  pneumatic_controller = 'Line'
  position = 'top'
/>

<Async>
<EvacuateAndRefill
  vessel = 'PneumaticSplitter'
after_vacuum_wait_time = '3 minutes'
after_inert_gas_wait_time = '2 mins'
repeats = '3'
gas = 'high'
/>
</Async>
<Async>
<EvacuateAndRefill
  vessel = 'IsolationFlask'
after_vacuum_wait_time = '3 minutes'
after_inert_gas_wait_time = '2 mins'
repeats = '3'
gas = 'high'
/>
1.3.3 XDL – Analytical Sampling

Coloured components of the XDL file below can be added to the above XDL (CeN₃ synthesis) where indicated above (i.e. before Day 2: Isolation steps) for integrated synthesis and analysis. The following XDL was run as a stand alone method for our testing.

```xml
<Procedure>

<Step 4: Hexane extraction -->>

/Add
  reagent='Hexane'
  vessel='ReactionFlask'
  volume='20 mL'
  stir = 'true'
  stir_speed = '300'
/>;

/Stir
  stir_speed = '300'
  vessel='ReactionFlask'
  time='10 min'
/>;

/Transfer
  from_vessel='ReactionFlask'
  to_vessel='IsolationFlask'
  aspiration_speed = '10'
  volume = '60 mL'
/>;

/StartStir
  stir_speed = '1000'
  vessel='IsolationFlask'
/>;

/Wait
  time = '1 min'
/>;

/SchlenkLineTapOpenVacuum
  pneumatic_controller='Line'
  port = '4'
/>;

/SchlenkFlaskTapClose
  pneumatic_controller = 'Line'
  position = 'top'
/>;

</Procedure>
</Synthesis>
```
id="ReactionFlask"
type="reactor"
/>  
<Component 
id="Cuvette"
type="reactor"
/>  
<Component 
id="NMRTube"
type="reactor"
/>  
<Component 
id="Line"
type="pneumatic_controller"
/>  
<Component 
id="Valve1"
type='Valve'
/>  
<Component 
id="Valve2"
type='Valve'
/>  
<Component 
id="Valve3"
type='Valve'
/>  
<Component 
id="Pump1"
type='Pump'
/>  
<Component 
id="Pump2"
type='Pump'
/>  
<Component 
id="Waste3"
type='Waste'
/>  
<Component 
id="Waste1"
type='Waste'
/>  
<Component 
id="Waste2"
type='Waste'
/>  
</Hardware>

<Reagents>
 <Reagent 
    name='Toluene'
type='solvent'
/>  
 <Reagent 
    name='Hexane'
type='solvent'
/>  
 <Reagent 
    name='THF'
type='reagent'
/>  
</Reagents>

<Procedure>
 <!-- Analytical Sampling Steps-->  
<Confirm
    msg = 'Is Cuvette connected?'
/>  
<!-- Evacuating air from cuvette tubing (path Cuvette-Valve3-Valve2-Pump2) -->  
<CValveMoveToPosition
    valve_name = 'Valve3'
    position = '3'
/>
<SchlenkLineTapOpenVacuum
    pneumatic_controller='Line'
    port='1'/>
<Confirm
    msg='Is JY NMR Tube connected?'/>
<SchlenkLineTapOpenVacuum
    pneumatic_controller='Line'
    port='3'/>
<Wait
    time='2 mins'/>
<Confirm
    msg='Is ReactionFlask connected?'/>
<CConnect
    from_vessel='ReactionFlask'
    to_vessel='Pump2'/>
<Async>
    <EvacuateAndRefill
        vessel='PneumaticSplitter'
        after_vacuum_wait_time='2 minutes'
        after_inert_gas_wait_time='2 mins'
        repeats='3'
        gas='high'/>
</Async>
<Async>
    <EvacuateAndRefill
        vessel='ReactionFlask'
        after_vacuum_wait_time='2 minutes'
        after_inert_gas_wait_time='2 mins'
        repeats='3'
        gas='high'/>
</Async>
<Async>
    <EvacuateAndRefill
        vessel='Cuvette'
        after_vacuum_wait_time='2 minutes'
        after_inert_gas_wait_time='2 mins'
        repeats='3'
        gas='high'/>
</Async>
<Async>
    <EvacuateAndRefill
        vessel='NMRTube'
        after_vacuum_wait_time='2 minutes'
        after_inert_gas_wait_time='2 mins'
        repeats='3'
        gas='high'/>
</Async>
<Wait
    time='15 mins'/>
<Confirm
    msg='Are ReactionFlask and Solvents connected to liquid backbone?'/>
<ResetHandling
    solvent='Toluene'
    repeats='3'
    volume='5mL'/>
<Add
    reagent='Toluene'
    vessel='ReactionFlask'
    volume='15 mL'
    stir='true'
stir_speed = '900'
aspiration_speed = '5'

<StartStir
  stir_speed = '400'
vessel='ReactionFlask'
/>

<Wait
time = '10 mins'
/>

<!-- Transfer UV/vis/NIR/Luminescence sample to cuvette and seal up -->
<Transfer
  from_vessel='ReactionFlask'
to_vessel='Cuvette'
aspiration_speed = '5'
volume = '5 mL'
/>

<SchlenkLineTapOpenVacuum
  pneumatic_controller = 'Line'
port = '3'
/>

<!-- Transfer NMR sample to J-Youngs tapped NMR tube and seal up -->
<Confirm
  msg = 'Is NMR tube sealed under vacuum?'
/>

<Transfer
  from_vessel='ReactionFlask'
to_vessel='NMRTube'
aspiration_speed = '5'
volume = '3 mL'
/>

<Confirm
  msg = 'Is NMR tube opened to pull through solution?'
/>

<SchlenkLineTapOpenArgon
  pneumatic_controller = 'Line'
port = '3'
/>

<Confirm
  msg = 'Are cuvette, NMR tube and solvents sealed?'
/>

<SchlenkLineTapClose
  pneumatic_controller='Line'
port = '1'
/>

<SchlenkLineTapClose
  pneumatic_controller='Line'
port = '3'
/>
1.3.4 Analytical Data

**Figure S8:** $^1$H NMR spectrum of CeN$_3$ (-3.40 ppm). >97% pure by NMR.

**Figure S9:** $^{29}$Si NMR spectrum of CeN$_3$.
Figure S10: Semi-Automatically sampled $^1$H NMR spectrum of CeN$^3_3$ solution in H$_2$-toluene (with C$_6$D$_6$ capillary in tube for locking).

Figure S11: Automatically sampled UV/vis spectrum of CeN$^3_3$ in toluene (ca. 4 mM).
**Figure S12:** Cerium(III) tris(bis(trimethylsilylamide)) before and after exposure to air for 3s.
1.3.5 Synthesis of CeOTf₃ – testing handling of corrosives in system

Following a literature procedure an RBF was charged with Ce₂(CO₃)₃.xH₂O (1.5 g, 3.26 mmol, 1 equiv.) and suspended in 20 mL of deionised water. Neat HOTf (2 mL, 22.6 mmol, 6.9 equiv.) was added to the suspension, with stirring, resulting in an immediate vigorous fuming of the solution. The reaction mixture was refluxed at 101°C for 18 hours under a flow of N₂. After 18 hours all solids had dissolved, leaving a colourless solution. Water was removed and the white solids were washed with Et₂O (4 × 10 mL) and hexanes (2 × 10 mL), and dried at 220°C for 36 hours; yielding a whitish free flowing powder. The complete removal of water was confirmed by the absence of the key -OH band at 1657 cm⁻¹ which is present in the hydrated salt (Figure S16) upon rapid IR analysis of the solid material by ATR-IR in air. Semi-automated NMR sampling of the white solids in dry MeCN into a J-Youngs NMR tube containing a capillary of d₃-MeCN (Figure S13B) showed only solvent in the ¹H spectrum (Figure S17) and a single ¹⁹F resonance at −74.1 ppm (Figure S16, CeOTf₃).

Figure S13: (A) Setup of CeOTf₃ synthesis (taken after reaction); (B) Semi-Automated NMR Sampling Analysis.
1.3.6 Hardware Graph for CeOTf₃ synthesis

Figure S14: Visual Representation of the hardware graph for the synthesis of CeOTf₃. Full graph file as .json available on https://github.com/croningp and visualisable through https://croningroup.gitlab.io/chemputer/xdlapp/.
1.3.7 XDL – CeOTf₃ synthesis

The following is the XDL file executed by the platform in concert with the graph shown above (Figure S14). The XDL file has three sections: Hardware, Reagents and Procedure. Comments are added in black for clarity of the reader.

```xml
<Synthesis>
  <Hardware>
    <Component id="PneumaticSplitter" type="reactor"/>
    <Component id="Trap" type="reactor"/>
    <Component id="ReactorFlask" type="reactor"/>
    <Component id="NMRTube" type="reactor"/>
    <Component id="HOTf" type="Flask"/>
    <Component id="DI_H2O" type="Flask"/>
    <Component id="Et2O" type="Flask"/>
    <Component id="ACN" type="Flask"/>
    <Component id="Hexane" type="Flask"/>
    <Component id="Line" type="pneumatic_controller"/>
    <Component id="Valve1" type="Valve"/>
    <Component id="Valve2" type="Valve"/>
    <Component id="Valve3" type="Valve"/>
    <Component id="Pump1" type="Pump"/>
    <Component id="Pump2" type="Pump"
```
<Component id="Waste3" type="Waste"/>
<Component id="Waste1" type="Waste"/>
<Component id="Waste2" type="Waste"/>
</Hardware>

<Reagents>
  <Reagent name='Et2O' type='solvent'/>
  <Reagent name='Hexane' type='solvent'/>
  <Reagent name='ACN' type='solvent'/>
  <Reagent name='DI_H2O' type='solvent'/>
  <Reagent name='HOTf' type='solution'/>
  <Reagent name='Ce2CO33' type='solid'/>
</Reagents>

<Procedure>
  <!-- Setup Flasks & Solvents -->
  <Confirm
    msg='Is Ce2(CO3)3 (1.5 g) loaded into ReactorFlask?'/>
  <Connect
    from_vessel='ReactorFlask'
    to_vessel='Pump1'/>
  <SchlenkLineTapOpenVacuum
    pneumatic_controller='Line'
    port='1'/>
  <Wait
    time='2 mins'/>
  <!-- EvacuateAndRefill Steps for ReactorFlask and Trap-->
  <Async
    <EvacuateAndRefill
      vessel='ReactorFlask'
      after_vacuum_wait_time='2 min'
      after_inert_gas_wait_time='3 min'
      repeats='3'
      gas='high'/>
  </Async>
  <Async
    <EvacuateAndRefill
      vessel='PneumaticSplitter'
      after_vacuum_wait_time='2 min'/>
  </Async>
</Procedure>
after_inert_gas_wait_time = '3 min'
repeats='3'
gas='high'

</Async>
<Wait
time = '16 mins'
/>
</-- Begin Reaction -->
<SchlenkLineTapOpenArgon
  pneumatic_controller = 'Line'
  port = '1'
/>
<StartStir
  vessel = 'ReactorFlask'
  stir_speed = '500'
/>
<Transfer
  from_vessel='DI_H2O'
  to_vessel='ReactorFlask'
  aspiration_speed = '15'
  volume = '20 mL'
  from_port = '0'
  to_port = '1'
/>
<Wait
time = '1 min'
/>
<Confirm
  msg = 'Is HOTf connected to the liquid backbone?'
/>
<Transfer
  from_vessel='HOTf'
  to_vessel='ReactorFlask'
  aspiration_speed = '1'
  volume = '2 mL'
  to_port = '1'
  dispense_speed = '1'
/>
<HeatChillToTemp
  vessel = 'ReactorFlask'
  temp = '100'
  active = 'True'
  continue_heatchill = 'True'
  stir = 'True'
  stir_speed = '500'
/>
<Wait
time = '18 h'
/>
<HeatChillReturnToRT
  vessel = 'ReactorFlask'
  stir = 'True'
  stir_speed = '250'
/>
</-- Day 2. Evaporation -->
<Confirm
  msg= 'Is external trap filled with liquid N2?'
/>
<StartStir
  vessel = 'ReactorFlask'
  stir_speed = '500'
/>
<SchlenkLineTapClose
  pneumatic_controller = 'Line'
  port = '1'
/>
<SchlenkLineTapOpenVacuum
  pneumatic_controller = 'Line'
  port = '2'
/>
<SchlenkFlaskTapOpen
  pneumatic_controller = 'Line'
  position = 'top'
<Wait
time = '1h'/>
<SchlenkFlaskTapClose
pneumatic_controller = 'Line'
position = 'top'/>
<SchlenkLineTapClose
pneumatic_controller = 'Line'
port = '2'/>
/
<!-- Wash solids -->
<SchlenkLineTapOpenArgon
pneumatic_controller = 'Line'
port = '1'/>
<EvacuateAndRefill
vessel = 'PneumaticSplitter'
after_vacuum_wait_time = '3 minutes'
after_inert_gas_wait_time = '1 mins'
repeats = '3'
gas = 'high'/>
<Confirm
msg = 'Are the solvents connected to the LH backbone'/>
/<ResetHandling
solvent = 'Et2O'
volume = '10 ml'
repeats = '2'/>
<WashSolid
vessel = 'ReactorFlask'
solvent = 'Et2O'
aspiration_speed = '10'
volume = '10 mL'
stir = 'True'
stir_speed = '500'
time = '5 min'
vacuum_attached = 'False'
repeats = '4'/>
/
<!-- Wash two times with hexanes -->
<ResetHandling
solvent = 'Hexane'
volume = '3mL'
repeats = '3'/>
<WashSolid
vessel = 'ReactorFlask'
solvent = 'Hexane'
aspiration_speed = '10'
volume = '10 mL'
stir = 'True'
stir_speed = '500'
time = '5 min'
vacuum_attached = 'False'
repeats = '2'/>
/SchlenkLineTapOpenVacuum
pneumatic_controller = 'Line'
port = '1'/>
<HeatChill
vessel = 'ReactorFlask'
temp = '220'
time = '36 h'
stir = 'True'
stir_speed = '400'/>
<HeatChillReturnToRT
vessel = 'ReactorFlask'
stir = 'True'/>
stir_speed = '250'

<!-- Prep NMR sample -->

 resets:
 solvent = 'ACN'
 volume = '3 mL'
 repeats = '3'

 transfer:
 to_vessel = 'ReactorFlask'
 to_port = '1'
 from_vessel = 'ACN'
 from_port = '0'
 volume = '30 mL'

 startstir:
 vessel = 'ReactorFlask'
 stir_speed = '500'

 wait:
 time = '10 min'

 take NMR sample:

 confirm:
 msg = 'NMR tube connected?'

 connect:
 from_vessel = 'ReactorFlask'
 to_vessel = 'Pump2'

 evacuate and refill:
 vessel = 'NMRTube'
 after_vacuum_wait_time = '3 minutes'
 after_inert_gas_wait_time = '1 mins'
 repeats = '3'
 gas = 'high'

 schlenk line tap open vacuum:
 pneumatic_controller = 'Line'
 port = '3'

 confirm:
 msg = 'Is NMR tube closed under vacuum?'

 schlenk line tap open argon:
 pneumatic_controller = 'Line'
 port = '3'

 transfer:
 from_vessel = 'ReactorFlask'
 from_port = '1'
 to_vessel = 'Waste1'
 to_port = '0'
 volume = '2 mL'
 aspiration_speed = '2'

 startstir:
 vessel = 'ReactorFlask'
 stir_speed = '400'

 transfer:
 from_vessel = 'ReactorFlask'
 from_port = '1'
 to_vessel = 'NMRTube'
 to_port = '0'
 volume = '2 mL'
 aspiration_speed = '2'

 confirm:
 msg = 'Is NMR tube filled?'

 -->

</Procedure>
</Synthesis>
1.3.8 Analytical Data for CeOTf₃

**Figure S15:** IR Spectrum of synthesised CeOTf₃ (green) compared with hydrated CeOTf₃ (blue) showing absence of key OH band at 1657 cm⁻¹.

**Figure S16:** ¹⁹F NMR of anhydrous CeOTf₃ in H₃-MeCN (w/d₃-MeCN capillary).
Figure S17: $^1$H NMR of CeOTf$_3$ in H$_3$-MeCN (1.96 ppm, w/ $d_3$-MeCN capillary) showing absence of H$_2$O (2.13 ppm) and HOTf resonances (br., variable).
1.4 Synthesis of B(C₆F₅)₃ (3)

![Reaction scheme showing synthesis of compound 3.](image)

Figure S18: Reaction scheme showing synthesis of compound 3.

Following an adapted literature procedure,⁶ to a stirred solution of bromopentafluorobenzene C₆F₅Br (1.6 mL, 12.8 mmol) in toluene (5 mL), n-BuLi (1.6 M in hexanes, 7.8 mL, 0.162 mol) was added dropwise at −80 °C over a period of 7.8 minutes followed by further addition of toluene (5 mL) to ensure complete washing of the n-BuLi from the liquid handling tubing. The resulting colourless suspension was stirred for one hour at this temperature. A boron trichloride/n-hexane solution (4.2 mL, 1 M, 4.2 mmol) was then added within 50 seconds before further washing of the liquid handling tubing with toluene (5 mL) and the resulting colourless suspension was then slowly warmed to ambient temperature over a period of 90 mins. In situ ¹⁹F NMR analysis was conducted by transferring 10 mL of the reaction mixture to the NMR machine’s flow cell to confirm conversion. The whole solution was then transferred through a frit to a 3-necked round bottomed flask appended on one neck with an inverted Schlenk tube and on a second attached to an independent solvent trap through a remotely operable Lowers Hanique tap (See Fig.s 7 and S22). The solvent was distilled into the cryogenic solvent trap under reduced pressure, resulting in a yellowish residue. The solid residue was sublimed into the inverted Schlenk Flask at 100°C yielding B(C₆F₅)₃ (840 mg, 38%) as a colourless, needle-like solid.

Analytical data was consistent with literature values for anhydrous B(C₆F₅)₃.⁶,⁷

¹⁹F NMR (C₇H₈, 43 MHz) δ −128.8 (m, 6F), −142.5 (m, 3F), −160.5 (m, 6F) ppm; (C₆D₆, 376 MHz) δ −128.8 (m, 6F), −141.6 (m, 3F), −160.0 (m, 6F) ppm;

¹¹B NMR (C₆D₆, 160 MHz) δ −58.6 (br. s) ppm.
1.4.1 Hardware Graph

Figure S19: Visual Representation of the hardware graph for the Synthesis of B(C₆F₅)₃. Full graph file as .json available on https://github.com/croningp and visualisable through https://croningroup.gitlab.io/chemputer/xdlapp/.
1.4.2 Schlenkputer Hardware Setup

**Figure S20:** Full setup showing Coupling Flask (LHS) and the Evaporating Flask (RHS), above a paraffin oil bath, which is shown in more detail below.

**Figure S21:** Coupling flask with chiller setup to cool a dewar of acetone.
**Figure S22:** Photograph showing the sublimation setup of the evaporation flask with annotation.

**Figure S23:** Top down photographs of the sublimate (compound 3) condensing in the inverted Schlenk tube.
1.4.3 XDL

The following is the XDL file executed by the platform in concert with the graph shown above (Figure S19). The XDL file has three sections: Hardware, Reagents and Procedure. Comments are added in black for clarity of the reader.

```xml
<Synthesis>
  <Hardware>
    <Component id="CouplingFlask" type="reactor"/>
    <Component id="PneumaticSplitter" type="custom"/>
    <Component id="Toluene" type="reagent"/>
    <Component id="EvaporatingFlask" type="reactor"/>
    <Component id="ExternalTrap" type='reactor' />
    <Component id="SchlenkFlask" type="reactor"/>
    <Component id="nmr" type="custom"/>
    <Component id="Line" type="pneumatic_controller"/>
    <Component id="HuberChiller" type="chiller"/>
    <Component id="Dewar" type='reactor' />
    <Component id="Valve1" type='Valve' />
    <Component id="Valve2" type='Valve' />
    <Component id="Valve3" type='Valve' />
    <Component id="Valve4" type='Valve' />
    <Component id="Pump1" type='Pump'
```
<Component id="Pump2" type='Pump' />
<Component id="Pump3" type='Pump' />
<Component id="Waste3" type='Waste' />
<Component id="Waste4" type='Waste' />
<Component id="Waste1" type='Waste' />
<Component id="Waste2" type='Waste' />
</Hardware>

<Reagents>
  <Reagent name='Hexane' type='solvent' />
  <Reagent name='Acetone' type='solvent' />
  <Reagent name='Toluene' type='solvent' />
  <Reagent name='Arylbromide' type='reagent' />
  <Reagent name='Borontrichloride' type='reagent' />
  <Reagent name='BuLi' type='reagent' />
</Reagents>

<Procedure>
  <!-- Setup Flasks & Solvents -->
  <Confirm msg='Is CouplingFlask Connected?' />

  <SchlenkLineTapOpenVacuum
    pneumatic_controller='Line'
    port='2' />

  <CConnect
    from_vessel='CouplingFlask'
    to_vessel='Pump1' />

  <Confirm msg='Is EvaporatingFlask Connected?' />
  <!-- Setup Flasks & Solvents -->
</Procedure>

- When setting up open tap on inverted Schlenk flask so that tubing up to the line is also evacuated. Make sure N2 does not slightly pop the tap out during the run. This is where elastic bands are best. -->

<SchlenkLineTapOpenVacuum
  pneumatic_controller='Line'
port='4'

<!--CConnect
    from_vessel = 'EvaporatingFlask'
    to_vessel = 'Pump2'
-->  
<Wait
    time = '2 min'
/>

<!--Async
    <EvacuateAndRefill
        vessel='CouplingFlask'
        after_vacuum_wait_time='3 minutes'
        repeats='3'
        gas='high'
    >
    <Wait
        time = '13 mins'
    />

    <!--This steps allows us to replace the rotoflow tap on the solvent ampoule with a SubaSeal and liquid Handling Tubing-->
    <Confirm
        msg = 'Are the solvents connected to the liquid handling backbone?'
    />

    <ResetHandling
        solvent='Toluene'
        repeats='3'
        volume='5mL'
    />

    <!--Begin Reaction -->
    <Add
        reagent='Toluene'
        vessel='CouplingFlask'
        port = '0'
        volume = '13 mL'
        stir = 'true'
        stir_speed = '200'
    />

    <Add
        reagent='Arylbromide'
        vessel='CouplingFlask'
        volume = '1.6 mL'
        dispense_speed='20'
        stir = 'true'
        stir_speed='200'
        port = '0'
    />

    <Add
        reagent='Toluene'
        vessel='CouplingFlask'
        port = '0'
        volume = '5 mL'
        dispense_speed='20'
        stir = 'true'
    -->
<stir_speed>'200'</stir_speed>

<HeatChillToTemp
  vessel='CouplingFlask'
  temp=-80'
  active='True'
  continue_heatchill='True'
/>

<StartStir
  vessel='CouplingFlask'
  stir_speed='400'
/>

/Add
  reagent='BuLi'
  vessel='CouplingFlask'
  dispense_speed='1'
  stir_speed='200'
  port='0'
  volume='7.8 mL'
  stir='true'
/>

/Add
  reagent='Toluene'
  vessel='CouplingFlask'
  dispense_speed='1'
  stir_speed='200'
  port='0'
  volume='5 mL'
  stir='true'
/>

/<Wait
time='1h'/>

<!-- Slow Addition at -80 °C -->

<Confirm
  msg='BCl3 connected to SchlenkLine?'/>

/Add
  reagent='Borontrichloride'
  vessel='CouplingFlask'
  dispense_speed='1'
  stir_speed='200'
  port='0'
  aspiration_speed='1'
  volume='4.2 mL'
  stir='true'
/>

/Add
  reagent='Toluene'
  vessel='CouplingFlask'
  dispense_speed='5'
  stir_speed='200'
  port='0'
  volume='5 mL'
  stir='true'
/>

/<Wait
time='60 min'/>

<!-- Warm flask to RT by siphoning off cold bath-->

<Async>
  <Transfer
    from_vessel='Dewar'
    to_vessel='Waste4'
    volume='2000'
    aspiration_speed='100'
    dispense_speed='100'
  />
</Async>

<HeatChillToTemp
  vessel='CouplingFlask'
  temp='10'
  active='True'
  continue_heatchill='True'
/>

<!-- -->
vessel = 'Dewar'
reagent = 'Acetone'
volume = '500'

<!--Cleaning Benchtop NMR-->

<CleanVessel
    vessel = 'nmr'
    solvent = 'Toluene'
    volume = '10 mL'
    repeats = '3'
/>

<!-- First NMR measurement-->

<Transfer
    from_vessel = 'CouplingFlask'
    to_vessel = 'nmr'
    volume = '9 mL'
    aspiration_speed = '10'
/>

<RunNMR
    nmr = 'nmr'
    protocol="1D FLUORINE+
    protocol_options=[{"Number": 64, 'RepetitionTime': 5, 'AcquisitionTime': 3.2, 'PulseAngle': 90}]
    comment="First Measurement" />

<Transfer
    from_vessel = 'nmr'
    to_vessel = 'CouplingFlask'
    volume = '10 mL'
/>

<!-- Evaporation & Sublimation Steps -->

<Confirm
    msg = 'Ready for evaporation and sublimation?'
/>

<SchlenkLineTapOpenVacuum
    pneumatic_controller='Line'
    port='1'
/>

<StartStir
    vessel = 'EvaporatingFlask'
    stir_speed = '200'
/>

<Transfer
    from_vessel = 'CouplingFlask'
    to_vessel = 'EvaporatingFlask'
    from_port = '1'
    aspiration_speed = '1'
    volume = '100 mL'
/>

<StartStir
    vessel = 'EvaporatingFlask'
    stir_speed = '500'
/>

<SchlenkLineTapClose
    pneumatic_controller = 'Line'
    port = '4'
/>

<SchlenkFlaskTapOpen
    pneumatic_controller = 'Line'
    position = 'top'
/>

<HeatChill
    vessel = 'EvaporatingFlask'
    temp = '40'
    stir = 'true'
    stir_speed = '420'
    time = '30 mins'
/>

<SchlenkFlaskTapClose
    pneumatic_controller = 'Line'
/>
position = 'top'

<SchlenkLineTapClose
   pneumatic_controller = 'Line'
   port = '1'
/>

<SchlenkLineTapOpenVacuum
   pneumatic_controller='Line'
   port = '4'
/>

<Wait
   time = '10 mins'
/>

<HeatChill
   vessel='EvaporatingFlask'
   temp='120'
   stir='true'
   stir_speed='320'
   time = '3 h'
/>

<Confirm
   msg = 'Sublimation complete?'
/>

<SchlenkLineTapOpenArgon
   pneumatic_controller='Line'
   port='4'
/>

<Confirm
   msg = 'Disconnect Flask and analyse product'
/>
</Procedure>
</Synthesis>
1.4.4 NMR Spectra of B(C₆F₅)₃.

**Figure S24**: $^{19}$F NMR spectrum (43 MHz $^1$H) of B(C₆F₅)₃ before sublimation. Sample prepared in PhMe and transferred to NMR flow cell through Schlenkputer liquid handling system.

**Figure S25**: $^{19}$F NMR spectrum (376 MHz) of the automatically sublimed product (~98% pure by NMR). Sample prepared in C₆D₆ in Argon filled plastic glovebag.
Figure S26: $^{11}$B NMR (160 MHz) of automatically sublimed B(C$_6$F$_5$)$_3$.

Figure S27: $^{19}$F NMR spectrum (C$_6$D$_6$) of automatically sublimed B(C$_6$F$_5$)$_3$ recrystallised from toluene at $-30^\circ$C ($>99.9\%$ pure by NMR). Prepared in a nitrogen filled glovebox.
1.5 Synthesis of [(Dipp)NacNac]Mg$_2$ (4)

![Reaction scheme of compound 4.](image)

Starting material DippNacnacH was prepared according to a method reported in literature. Under nitrogen, MeMgI (0.68 mL, 3.0 M in Et$_2$O, 2.05 mmol) was added to a stirred solution of DippNacnacH (715 mg, 1.71 mmol) in toluene (37 mL) at -30°C. Followed by addition of a further aliquot of toluene (7 mL). The \{DippNacnacMgI(OEt$_2$)\} solution was allowed to reach room temperature yielding a colourless precipitate. Meanwhile a separate 3-neck round bottom flask, appended with a temperature probe, was charged with a sodium in oil dispersion (ca 9 mL, 40% w/w Na(0)) and washed with hexane (3 x 20 mL) with stirring before addition of the toluene suspension to this flask. This suspension was stirred for 20 h at RT after which time the solution was filtered and the solvent removed yielding a dark residue which was redissolved in hexane, filtered and the solvent removed under reduced pressure to give \{(DippNacNac)Mg\}$_2$ (328 mg, 43%) as a dark yellow solid. A solution of isopropanol (15% in toluene) was added slowly to the flask containing Na(0), maintaining the temperature below 50°C in 0.25 mL aliquots. The temperature change with different aliquot addition volumes (0.1-0.5 mL between temperature readings) was recorded for different experiments and is shown in Fig. 8 in the MS. NMR data was consistent with literature values for compound 4.

$^1$H NMR (C$_6$D$_6$, 400 MHz) δ 7.07 (m, 12H, m-CH$_{Ar}$ & p-CH$_{Ar}$), 4.82 (s, 2H, NC(CH)CN), 3.07 (sept., 8H, CH(CH$_3$)$_2$), 1.54 (s, 12H, NC(CH$_3$)), 1.16 (d, 24H, (CH$_3$)CH(CH$_3$)), 0.98 (d, 24H, (CH$_3$)CH(CH$_3$)); (d$_8$-THF, 400 MHz, recrystallised) δ 7.00 (m, 12H, m-CH$_{Ar}$ & p-CH$_{Ar}$), 4.70 (s, 2H, NC(CH)CN), 3.19 (sept., 8H, CH(CH$_3$)$_2$), 1.55 (s, 12H, NC(CH$_3$)), 1.05 (dd, 48H, CH(CH$_3$)$_2$).
Analytically pure crystals for XRD analysis and $d_8$-THF NMR were grown from slow cooling of a hexane solution to $-30^\circ$C in a glovebox freezer and the unit cell was confirmed to match the previously reported species $\left[(\text{DippNacNac})\text{Mg}\right]_2$.\textsuperscript{9}
1.5.1 Hardware Graph

Figure S29: Visual Representation of the hardware graph for synthesis of [(Dipp)NacNac]Mg\(_2\). Full graph file as .json available on https://github.com/croningp and visualisable through https://croninggroup.gitlab.io/chemputer/xdlapp/.
1.5.1 XDL

The following is the XDL file executed by the platform in concert with the graph shown above (Figure S29). The XDL file has three sections: Hardware, Reagents and Procedure. Comments are added in black for clarity of the reader.

```xml
<Synthesis>
  <Hardware>
    <Component id="LigandFlask" type="reactor"/>
    <Component id="PneumaticSplitter" type="reactor"/>
    <Component id="NaFlask" type="reactor"/>
    <Component id="IsolationFlask" type="reactor"/>
    <Component id="PrecipitationFlask" type="reactor"/>
    <Component id="HuberChiller" type="chiller"/>
    <Component id="Dewar" type="reactor"/>
    <Component id="Line" type="pneumatic_controller"/>
    <Component id="Valve1" type="Valve"/>
    <Component id="Valve2" type="Valve"/>
    <Component id="Valve3" type="Valve"/>
    <Component id="Valve4" type="Valve"/>
    <Component id="Pump1" type="Pump"/>
    <Component id="Pump2" type="Pump"/>
    <Component id="Pump3" type="Pump"/>
  </Hardware>
```
<Component id="Waste4" type='Waste'/>
<Component id="Waste3" type='Waste'/>
<Component id="Waste1" type='Waste'/>
<Component id="Waste2" type='Waste'/>
</Hardware>

<Reagents>
  <Reagent name='Toluene' type='solvent'/>
  <Reagent name='Acetone' type='solvent'/>
  <Reagent name='Hexane' type='solvent'/>
  <Reagent name='Killing Solution' type='reagent'/>
  <Reagent name='MeMgI' type='reagent'/>
  <Reagent name='Na dispersion in oil' type='reagent'/>
  <Reagent name='NacNac' type='reagent'/>
</Reagents>

<Procedure>
<!--Reaction Setup-->  
<Confirm msg = 'Ligand Flask Setup'/>
<CConnect>
  from_vessel = 'LigandFlask'
to_vessel = 'Pump1'
</CConnect>
<SchlenkLineTapOpenVacuum pneumatic_controller = 'Line'
  port = '2'/>
<Confirm msg = 'Na Flask Setup'/>
<CConnect>
  from_vessel = 'NaFlask'
to_vessel = 'Pump1'
</CConnect>
<SchlenkLineTapOpenVacuum pneumatic_controller = 'Line'
  port = '4'/>
</Procedure>
<Wait
time = '2 mins'
/>
<StartPurge
vessel = 'LigandFlask'
/>
/AddSolid
vessel = 'LigandFlask'
reagent = 'NaCl
mass = '715 mg'
confirm_solid = 'True'
/>
<StartPurge
vessel = 'NaFlask'
/>
/AddSolid
vessel = 'NaFlask'
reagent = 'Na dispersion in oil'
mass = '3 g'
stir = 'True'
confirm_solid = 'True'
/>
<Async>
<EvacuateAndRefill
vessel='LigandFlask'
after_vacuum_wait_time='3 minutes'
repeats='3'
gas='high'
 />
</Async>
<Async>
<EvacuateAndRefill
vessel='NaFlask'
after_vacuum_wait_time='3 minutes'
repeats='3'
gas='high'
 />
</Async>
<Async>
<EvacuateAndRefill
vessel='PneumaticSplitter'
after_vacuum_wait_time='3 minutes'
repeats='3'
gas='high'
 />
</Async>
<Wait
time = '13 mins'
/>
<Confirm
msg = 'Are the solvents and MeMgI connected to the liquid handling backbone?' />
<ResetHandling
solvent='Toluene'
repeats='3'
volume='5mL'
/>
/<!-- Step 1: Magnesiation of the ligand-->
/Add
reagent='Toluene'
vessel='LigandFlask'
port = '1'
volume = '30 mL'
stir = 'true'
stir_speed = '220'
/>
<HeatChillToTemp
vessel = 'LigandFlask'
temp = '-30'
active = 'True'
continue_heatchill = 'True'
stir = 'True'
stir_speed = '200'

/Add
reagent='MeMgI'
vessel='LigandFlask'
port = '1'
volume = '0.7 mL'
stir = 'true'
stir_speed = '220'
dispense_speed = '1'
apiration_speed = '1'
prime_n_times = '1'
priming_volume = '3 ml'

/Add
reagent='Toluene'
vessel='LigandFlask'
port = '1'
volume = '7 mL'
stir = 'true'
stir_speed = '220'
dispense_speed = '1'

/-- Step 2: Washing oil from Na dispersion --/
<ResetHandling
solvent='Hexane'
repeats = '3'
volume = '5 mL'
/>
<WashSolid
vessel = 'NaFlask'
solvent = 'Hexane'
volume = '20 mL'
stir = 'true'
stir_speed = '80'
time = '4 min'
repeats = '3'
vacuum_attached = 'False'
apiration_speed = '5'
/>
/-- Warm flask to RT by siphoning off cold bath--/
<Async
<Transfer
from_vessel = 'Dewar'
to_vessel = 'NaFlask'
volume = '2000'
apiration_speed = '100'
dispense_speed = '100'
/>
</Async>
<HeatChillToTemp
vessel = 'LigandFlask'
temp = '10'
active = 'True'
continue_heatchill = 'True'
/> -->
/Add
vessel = 'Dewar'
reagent = 'Acetone'
volume = '500'
/>

/-- Step 3: Reduction of NacNacMgI --/
<Add
reagent = 'Toluene'
vessel = 'NaFlask'
port = '1'
volume = '10 mL'
stir = 'true'
stir_speed = '80'

/\StartStir
vessel = 'NaFlask'
stir_speed = '80'

/\Transfer
from_vessel = 'LigandFlask'
to_vessel = 'NaFlask'
aspiration_speed = '5'
volume = '60 mL'
rinsing_solvent = 'Toluene'
rinsing_volume = '5 mL'
rinsing_repeats = '2'

/\Stir
vessel = 'NaFlask'
time = '20 h'
stir_speed = '400'

/\!-- Step 3: Setup Rig for Day 2 -->
/\!-- IsolationFlask (see SI) -->
/\Confirm
msg = 'Connected IsolationFlask?'

/\SchlenkFlaskTapOpen
pneumatic_controller = 'Line'
position = 'top'

/\CConnect
from_vessel = 'IsolationFlask'
to_vessel = 'Pump2'

/\SchlenkLineTapOpenVacuum
pneumatic_controller = 'Line'
port = '1'

/\Confirm
msg = 'Connected Precipitation Flask?'

/\SchlenkLineTapOpenVacuum
pneumatic_controller = 'Line'
port = '3'

/\CConnect
from_vessel = 'PrecipitationFlask'
to_vessel = 'Pump1'

/\Wait
time = '2 mins'

/\Async
/\EvacuateAndRefill
vessel = 'IsolationFlask'
after_vacuum_wait_time = '3 minutes'
repeats = '3'
gas = 'high'

/\</Async
/\Async
/\EvacuateAndRefill
vessel = 'PrecipitationFlask'
after_vacuum_wait_time = '5 minutes'
repeats = '3'
gas = 'high'

/\</Async
/\Async
/\EvacuateAndRefill
vessel='PneumaticSplitter'
after_vacuum_wait_time='3 minutes'
repeats='3'
gas='high'
</Async>
<Wait
time = '13 mins'
/>
<StartPurge
vessel = 'NaFlask'
/>
<Confirm
msg = 'Is toluene connected to the liquid handling backbone?'
/>
<ResetHandling
solvent='Toluene'
repeats='3'
volume='5mL'
/>
<!-- Step 3: Isolate reduced species -->
<StopStir
vessel = 'NaFlask'
/>
<StartStir
vessel = 'PrecipitationFlask'
stir_speed = '220'
/>
<Transfer
from_vessel='NaFlask'
from_port = '0'
to_vessel='PrecipitationFlask'
to_port = '1'
volume = '120 mL'
aspiration_speed = '5'
/>
<Add
vessel = 'NaFlask'
reagent = 'Toluene'
volume = '30 mL'
stir = 'true'
stir_speed='250'
port='1'
/>
<StartStir
vessel = 'PrecipitationFlask'
stir_speed = '400'
/>
<SchlenkLineTapOpenVacuum
pneumatic_controller = 'Line'
port = '3'
/>
<Wait
time = '90 mins'
/>
<SchlenkLineTapOpenArgon
pneumatic_controller = 'Line'
port = '3'
/>
<ResetHandling
solvent='Hexane'
repeats='3'
volume='5mL'
/>
<Add
vessel = 'PrecipitationFlask'
port = '1'
reagent = 'Hexane'
volume = '15 mL'
stir = 'true'
stir_speed = '180'
/>
vessel='PrecipitationFlask'
time = '10 mins'
stir_speed = '250'

<Transfer
    from_vessel = 'PrecipitationFlask'
    from_port = '1'
    to_vessel = 'IsolationFlask'
    to_port = '0'
    volume = '30 mL'
    aspiration_speed = '5'
/>

<Wait
time = '2 mins'
/>

<SchlenkLineTapOpenVacuum
    pneumatic_controller = 'Line'
    port = '1'
/>

<Wait
time = '60 mins'
/>

<SchlenkFlaskTapClose
    pneumatic_controller = 'Line'
    position = 'top'
/>

<-- Quench Na(0) with 15% iPrOH in Toluene -->

<Confirm
    msg = 'Product dry and Killing solution connected?'
/>

<SchlenkLineTapOpenArgon
    pneumatic_controller = 'Line'
    port = '1'
/>

<AddDynamic
    vessel = 'NaFlask'
    reagent = 'Killing Solution'
    volume = '25 mL'
    sensor = "rtd"
    max_temp = "50"
    wait_after_reading = "1"
    safety_margin = "10"
    aliquot_volume = "0.25 mL"
    stir = 'true'
    stir_speed = '90'
/>

<Stir
    vessel = 'NaFlask'
    time = '1h'
    stir_speed = '200'
/>

</Procedure>
</Synthesis>
1.5.2 NMR Data for [(DippNacNac)Mg]$_2$ (4)

Figure S30: $^1$H NMR of crude [(DippNacNac)Mg]$_2$ (4) in C$_6$D$_6$ isolated from automated synthesis corresponding to literature values for the same compound. Sample prepared in nitrogen filled glovebox.

Figure S31: $^1$H NMR of recrystallised [(DippNacNac)Mg]$_2$ (4) measured in $d_8$-THF. Sample prepared in nitrogen filled glovebox.
2 Hardware

2.1 AutoSchlenk Line

Table S1: Bill of Materials for AutoSchlenk Line build

<table>
<thead>
<tr>
<th>CHEMPU PART NO.</th>
<th>PART DESCRIPTION</th>
<th>SUPPLIER</th>
<th>ORDER CODE</th>
<th>QUANTITY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vacutap 1-way bore 9mm, side arm standard / automated</td>
<td>Louwers Hanique</td>
<td>LH1040550 0</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>DURAN® Threaded Sockets, reinforced, NS 19/26</td>
<td>DWK Life Sciences / VWR</td>
<td>286581909</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>DURAN® Threaded Sockets, reinforced, NS 34/35</td>
<td>DWK Life Sciences / VWR</td>
<td>286583404</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Smiths Medical™ Portex™ Yellow PVC Tubing 6.4 mm 800/021/300/706</td>
<td>VWR / Smiths Medical</td>
<td>13120873</td>
<td>1 x 30 m</td>
</tr>
<tr>
<td></td>
<td>Edwards Rotary Vane Pump</td>
<td>Edwards</td>
<td>A65301903</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>ADC Active Digital Controller</td>
<td>Edwards</td>
<td>D39590000</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>3M Cable Assembly</td>
<td>Edwards</td>
<td>D40001030</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>APG100-XLC Active linear Pirani vacuum gauge</td>
<td>Edwards</td>
<td>D02604000</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2m Line cord with UK plug for Microstar Compact Water Vapor Pump</td>
<td>Edwards</td>
<td>D40013025</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>NW25 Nozzle Aluminium</td>
<td>Edwards</td>
<td>C10514645</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>NW25 Centring Ring</td>
<td>Edwards</td>
<td>C10514395</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>NW25 Clamping Ring Stainless Steel</td>
<td>Edwards</td>
<td>C1051440</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Adapter Flange KFGroundCone Stainless Steel, DN 25 KF NS 19/26 joint.</td>
<td>Fisher</td>
<td>10550453</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Idex Quick Connect Adapter UPP678</td>
<td>Fisher</td>
<td>05700367</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Masterflex Fitting, PVDF, Straight, Female Luer to Hose Barb Adapter, 3/32”; 25/P</td>
<td>Cole Palmer</td>
<td>UY-45512-02</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Idex XP-315 Flangeless Fitting, Standard Knurl, Natural ETFE, 1/8&quot; OD Tubing, 1/4-28 Flat-Bottom</td>
<td>Cole Palmer</td>
<td>UY-02020-94</td>
<td>10</td>
</tr>
</tbody>
</table>
Manifold consists of two glass lines each appended with 5 Louwers Hanique Taps through a glass connection providing a hose barb from which to attached Portex tubing to a Schlenk flask. Each line is terminated with a female 19/26 Rodavis joint. The vacuum line (front) is thus connected to a straight J-Youngs tapped joint which allows connection to the Edwards RV5 vacuum pump through a cryogenic trap consisting of a 34/35 Rodavis connection. The gas line is appended on both ends with a straight HP Rotaflo keyed 3mm joint. Finally the RHS terminus of the line is connected to an Edwards Pirani Vacuum Gauge through a Leybold Adapter Flange.

Figure S32: AutoSchlenk glass manifold with 5 ports on each line of vacuum (front) and inert gas (back).

Louwers Hanique taps are connected to the programmable solenoid manifold (see below) with 1/8" PTFE tubing via a Flangeless fitting connected through an Idex Quick connect fitting to a MasterFlex Luer to hose barb connector which allowed connection to the supplier Louwers Hanique tubing.

Figure S33: Assembled AutoSchlenk Line with Liquid N₂ Trap and attached Vacuum pressure gauge.
**Figure S1:** Additional Photos of manifold build and setting within ChemPU frame.

Waste bottle is connected to the output (RHS) of the gas line, to the ChemPU valve waste output (daisy chained) and subsequently to the bubbler. A long coil of tubing is used between the bubbler and waste bottle to prevent oil suckback.
2.2 Solenoid manifold Build

For build details see the Supplementary Materials associated with Cronin et al., Nat. Chem., 2021 with key differences in the build of this manifold detailed below.\textsuperscript{10}

2.2.1 Programmable solenoid manifold

Table S2: Bill of Materials for the programmable solenoid manifold.

<table>
<thead>
<tr>
<th>PART NO.</th>
<th>PART DESCRIPTION</th>
<th>SUPPLIER</th>
<th>ORDER CODE</th>
<th>QUANTITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHEMP0280</td>
<td>Series V100, S41 Type 6-position Manifold</td>
<td>SMC</td>
<td>VV100-S41-06-M5</td>
<td>1</td>
</tr>
<tr>
<td>CHEMP0281</td>
<td>3 Port Direct Operated Solenoid Valve - Large flow</td>
<td>SMC</td>
<td>V114A-6LOU</td>
<td>6</td>
</tr>
<tr>
<td>CHEMP0282</td>
<td>One-touch Fitting Nickel Plated - 4 mm Hexagon socket head male connector</td>
<td>SMC</td>
<td>KQ2S04-M5N</td>
<td>12</td>
</tr>
<tr>
<td>CHEMP0284</td>
<td>One-touch Fitting White Color - 6 mm Male Elbow</td>
<td>SMC</td>
<td>KQ2L06-M5N</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>One-touch Fitting White Color - 6 mm Male Straight</td>
<td>SMC</td>
<td>KQ2H06-M5A</td>
<td>1</td>
</tr>
<tr>
<td>CHEMP0283</td>
<td>One-touch Fitting White Color - 4 mm Male Elbow</td>
<td>SMC</td>
<td>KQ2L04-M5N</td>
<td>7</td>
</tr>
<tr>
<td>CHEMP0285</td>
<td>3 Port Direct Operated Solenoid Valve - Large flow - with backplate</td>
<td>SMC</td>
<td>V114A-6LOU-M5</td>
<td>6</td>
</tr>
<tr>
<td>CHEMP0286</td>
<td>One-touch Fitting White Color - 6mm-6mm- M5 Male Branch Tee</td>
<td>SMC</td>
<td>KQ2T06-M5A</td>
<td>4</td>
</tr>
<tr>
<td>CHEMP0287</td>
<td>One-touch Fitting White Color - 6-6-8 Different Diameter Tee</td>
<td>SMC</td>
<td>KQ2T06-08A</td>
<td>1</td>
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<tr>
<td>CHEMP0338</td>
<td>FEP Fluoropolymer tubing 6mm</td>
<td>RS Components</td>
<td>2550255657</td>
<td>Varies</td>
</tr>
<tr>
<td>CHEMP0291</td>
<td>One-touch Fittings Manifold Series - Port A One-touch Fitting, Port B One-touch Fitting</td>
<td>SMC</td>
<td>KM11-04-08-10</td>
<td>1</td>
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<tr>
<td>CHEMP0339</td>
<td>Pneumatic Straight Tube-to-Tube Adapter, Plug In 6 mm</td>
<td>RS Components</td>
<td>771-5612</td>
<td>2</td>
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<tr>
<td>CHEMP0331</td>
<td>M2.5 x 12mm Hex Socket Cap Screw Black, Self-Colour Steel</td>
<td>RS Components</td>
<td>281-653</td>
<td>12</td>
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<tr>
<td>CHEMP0110</td>
<td>M4 x 30mm Cap Head Screws (DIN 912) - A4 Stainless Steel</td>
<td>Accu</td>
<td>SSC-M4-30-A4</td>
<td>4</td>
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<tr>
<td>CHEMP0128</td>
<td>M4 x 10mm Low Head Cap Screws (DIN 7984) - A4 Stainless Steel</td>
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<td>186-636</td>
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<tr>
<td>CHEMP0289</td>
<td>Finger Valve 6-6</td>
<td>SMC</td>
<td>VHK3-06F-06F</td>
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<tr>
<td>CHEMP0293</td>
<td>In-line Air Filter with One-touch Fitting</td>
<td>SMC</td>
<td>ZFC54-B</td>
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<td>M4 x 10mm Low Head Cap Screws (DIN 7984) - A4 Stainless Steel</td>
<td>Accu</td>
<td>SSC-M4-10-A4</td>
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<tr>
<td>CHEMP0174</td>
<td>D-Link DPE-301GS PoE Splitter</td>
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<td>PCB hex spacer 20 mm</td>
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<td>Rotameter, 0.04-0.5 LPM air, with valve</td>
<td>Omega</td>
<td>FL-2011</td>
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<tr>
<td>-----------</td>
<td>----------------------------------------</td>
<td>-------</td>
<td>---------</td>
<td>---</td>
</tr>
<tr>
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<td>Threaded-to-Tube Elbow Connector Uni 1/8 to Push In 6 mm</td>
<td>RS Components</td>
<td>771-5386</td>
<td>4</td>
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<td>In-house - laser cut</td>
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<tr>
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<td>M4 x 20mm Penny Washers - A2 Stainless Steel</td>
<td>Accu</td>
<td>HYW-M4-20-A2</td>
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<td>CHEMP0290</td>
<td>Regulator Single Unit Type</td>
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<td>One-touch Fitting White Color - Different diameter union &quot;Y&quot; 8-6-6</td>
<td>SMC</td>
<td>KQ2U06-08A</td>
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<td>CHEMP0302</td>
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<td>In-house - laser cut</td>
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<td>M3 x 16mm Full Thread Cap Head Screws (DIN 912) - A2 Stainless Steel</td>
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<td>SSCF-M3-16-A2</td>
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<td>RS Components</td>
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<tr>
<td>CHEMP0088</td>
<td>Polymer Blanking Plug</td>
<td>RS Components</td>
<td>722-047</td>
<td>Varies</td>
</tr>
<tr>
<td>CHEMP0308</td>
<td>SMC Cable, Plug, 600mm</td>
<td>RS Components</td>
<td>701-3019</td>
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<tr>
<td>CHEMP0035</td>
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<td>RS Components</td>
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<td>Accu</td>
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<td>RS Components</td>
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<tr>
<td>CHEMP0344</td>
<td>M4 x 8mm Vented Socket Cup Point Set / Grub Screws (DIN 916) - Black A2 Stainless Steel</td>
<td>Accu</td>
<td>SSUV-M4-8-A2-BL</td>
<td>4</td>
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<tr>
<td>CHEMP0300</td>
<td>Thumb screw</td>
<td>Accu</td>
<td>SKT-M4-12-A1</td>
<td>4</td>
</tr>
</tbody>
</table>
2.2.2 Build differences from published design

1. Only one Rotameter with flow valve (CHEMP0309) required which is placed on the RHS position of the backplate (Figure S35).

Figure S35: Solenoid manifold Build without tubing showing an upper and lower line of solenoid valves.

Figure S36: Solenoid manifold with Flask Operating Solenoids highlighted (red). The other 10 solenoids control the AutoSchlenk line with the top set controlling the gas line and the bottom set controlling the vacuum line.
2. Tubing connects directly from left hand regulator (CHEMP0290) to port 3 on manifold (CHEMP0280) via adaptor (CHEMP0284) (Yellow, Figure S37). The right hand regulator (CHEMP0290) is connected to the gas distribution manifold (CHEMP0291) via adaptor (CHEMP0339).

3. On the right hand side of the front end manifold the elbow joint (CHEM0284) is replaced with a 3 way joint (CHEMP0286, Figure S37, Red Circle). At the same time the RHS Port 1 on the part CHEMP0280 is replaced with a straight fitting (KQ2H06-M5A). This allows connection of the vacuum line (Blue, Figure S37) between the two manifolds.

![Figure S37: Solenoid manifold with inlet tubing for gas (yellow) and vacuum (blue).](image-url)

4. Outlet tubing from rotameter connects to gas line on AutoSchlenk manifold via a non-return valve (CHEMP0083) (Figure S38).
Figure S38: Solenoid manifold with outlet tubing to flasks (red), AutoSchlenk gas line taps (pale yellow/cream), AutoSchlenk Vacuum Line Taps (Pale Blue).

Figure S39: Photograph of the solenoid manifold without outlet tubing as built.
2.3 Glassware Build

2.3.1 Isolation Flask

250 mL RBF appended with a Louwers Hanique Tap. The side arm is also appended with a screw thread joint for a GL14 adaptor and as such can either be connected to Portex tubing (as shown) or directly to liquid handling (see below) depending on the use. The terminal O-ring on the tap was replaced with an FFKM80 O-ring (Barnwell Services, MBMS0085 4.76 mm ID, 1.78 mm thick) to avoid swelling upon solvent exposure.

2.3.2 Schlenk (Filter) Flask

A medium porosity filter flask is appended with two Louwers Hanique taps on either end. In turn the side arms are appended with GL14 threaded joints for connection to liquid handling system (as shown) or alternately, Portex tubing (see above). The terminal O-rings on both taps are replaced with FFKM80 O-rings (Barnwell Services, MBMS0085 4.76 mm ID, 1.78 mm thick) to avoid swelling upon solvent exposure.
2.4 Other Hardware

2.4.1 Pneumatic Splitter

Table S3: Bill of Materials

<table>
<thead>
<tr>
<th>PART DESCRIPTION</th>
<th>SUPPLIER</th>
<th>ORDER CODE</th>
<th>QUANTITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless Steel Pipe Fitting, Cross, 3/8 in. Female NPT</td>
<td>Swagelock</td>
<td>SS-6-CS</td>
<td>1</td>
</tr>
<tr>
<td>RS PRO Straight Brass Hose Connector, 3/8 in G Male</td>
<td>RS Components</td>
<td>506-7250</td>
<td>4</td>
</tr>
</tbody>
</table>

In order to connect all solvent bottles to the AutoSchlenk system at once the gas/vacuum line was split using a Swagelock 4-way fitting appended with four hose connectors sealed with PTFE tape.

2.4.2 Tube-in-Tube Splitter

Table S4: Bill of Materials

<table>
<thead>
<tr>
<th>PART NO.</th>
<th>PART DESCRIPTION</th>
<th>SUPPLIER</th>
<th>ORDER CODE</th>
<th>QUANTITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS PRO Manifold, G 1/4 Female to G 1/4 Female</td>
<td>RS Components</td>
<td>176-1098</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>RS PRO Straight Brass Hose Connector, 1/4 in G Male</td>
<td>RS Components</td>
<td>506-7200</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>RS PRO Thermocouple Compression Fitting for use with Thermocouple With 3.175mm Probe Diameter, 1/4 BSP</td>
<td>RS Components</td>
<td>178-0962</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>RS PRO NBR G 1/4 Male Blanking Plug</td>
<td>RS Components</td>
<td>176-1049</td>
<td>1</td>
<td></td>
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</tbody>
</table>

A 4-way manifold was appended with two brass hose connectors, a blocking plug and a thermocouple compression fitting. The hose connectors were appended with Portex tubing. 1/8” PTFE tubing was threaded through the thermocouple compression fitting and through the Portex tubing until it was slightly longer than the outer tubing and the compression fitting was tightened.

Figure S43: Tube in Tube solvent/gas handling
2.4.3 Inline Filters for liquid handling system

Where applicable the use of these is indicated in the .json file for each reaction and is associated with a specific port on a flask meaning the tubing in this port was appended with a filter as shown.

![Figure S5: Filter Tip for tubing.](image)

2.5 Benchtop NMR

**Spinsolve 43 Carbon from Magritek**

- Frequency: 43 MHz Proton
- Resolution: 50% linewidth < 0.5 Hz
- Linewidth: 0.55% linewidth < 20 Hz
- $^1$H Sensitivity: >120:1 for 1% ethyl benzene
- Dimensions: 58 x 43 x 40 cm
- Weight: 60 kg
- Magnet: Permanent and cryogen free
- Stray field: < 2 G all around system

![Figure S45: Spinsolve 43 Carbon benchtop NMR unit with an NMR tube connected to the Schlenkputer liquid handling backbone via PTFE tubing.](image)

The instrument is equipped with a flow-cell (Spinsolve SPSFC) to allow online analysis. The cell is fed through the instrument and its location places the NMR tube at the centre of the magnets. Both inlet (bottom) and outlet (top) are connected to 1/8” PTFE tubing with IDEX screw fittings (Figure S45) which is also connected to one of the ChemPU valves. The flow cell allows automatic reaction monitoring in real time by pumping 9 ml of solution from the reaction mixture. In order to inertize the tubing clean, dry solvent (10 mL) is pumped in and out of the flow cell in triplicate before analysis is conducted.
2.6 Temperature Sensor Setup

Table S5: Bill of Materials

<table>
<thead>
<tr>
<th>PART NO.</th>
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<th>SUPPLIER</th>
<th>ORDER CODE</th>
<th>QUANTITY</th>
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<tr>
<td>CHEMP0035</td>
<td>Arduino Duo with headers</td>
<td>RS Components</td>
<td>769-7412</td>
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</tr>
<tr>
<td>CHEMP0174</td>
<td>D-Link DPE-301GS PoE Splitter</td>
<td>Insight</td>
<td>6338009</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Adafruit PT100 RTD Temperature Sensor Amplifier with MAX31865</td>
<td>Adafruit</td>
<td>3328</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Bola Temperature Probe Lemo (PT100)</td>
<td>VWR</td>
<td>P1760-15</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Custom Made MOSFET shield</td>
<td>Cronin Group</td>
<td>NA</td>
<td>1</td>
</tr>
</tbody>
</table>

2.6.1 SensorHub

As with the solenoid manifold above our SensorHub system allows communication with the temperature sensors over ethernet. SensorHub consists of an Arduino fitted with a custom-design MOSFET shield (Figure S46) with built-in Ethernet module for control over an IP network (full details on the Arduino firmware, the design of the MOSFET shield and detailed assembly instructions are available on request). Overall, it allows installation of up to 8 analog sensors, 8 sensors with I²C communication (achieved using an I²C multiplexer, thus allowing installation of devices with same addresses), several sensors with SPI communication (achieved via “software SPI” Arduino feature) and up to 12 PWM devices.

Figure S46: SensorHub board used to power & control temperature sensor.
2.6.2 Reaction temperature sensor (RTD)

The MAX31865 RTD-to-Digital Converter was selected to simplify the interfacing the SensorHub with resistance temperature detector (RTD, or temperature probe). The unit has a built-in 15-bit ADC, input protection, a digital controller, and an SPI-compatible interface. We have selected Adafruit PT100 RTD Temperature Sensor Amplifier as an evaluation board for the MAX31865 converter (Figure S47b) and 4-wire PTFE-encapsulated PT100 temperature probe (Figure S47a, BOLA, part No. P1750-15) installed via screw fitting (BOLA, part No. D629-54 for GL18 glass thread) on the round bottom flask. An installation example is shown below (Figure S48).

![Figure S47: a - PT100 temperature probe connected to b – RTD-to-Digital converter.](image)

![Figure S48: Example setup of 3-necked RBF with temperature probe.](image)
2.7 Ultra Low Temperature Chiller Setup

Temperature control in the synthesis platform was achieved using a Huber TC 100EF immersion cooling chiller incorporated using an RS232 to USB adaptor. The chiller can achieve temperatures as low as -100°C through automated control. Full details of the code used to control the system can be found at https://github.com/croningp.

After cooling the most efficient reheating method for reactor flasks was found to involve simple siphoning off of the cooling bath solvent, since this most closely mirrors the manual action of removing an RBF from a cooling bath, warming to room temp in ca 90-120 mins. This was achieved using a partitioned pump/valve setup as shown for Pump3/Valve4 in Fig.s S19 & S29.

Figure S6: Huber TC100E immersion cooling chiller.

Figure S50: Setup for replacement of acetone cooling bath.
3 Software

3.1 XDL General
All Code associated with this platform and paper, including XDL files as executed, can be found at https://github.com/croningp/Inertputer and is based upon the language outlined in Cronin et al.\textsuperscript{11}

3.2 XDL Steps Description

Table S1. $\chi$DL synthesis steps implemented in the platform.

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>Add</td>
<td>Adds given volume of given reagent/solvent to given vessel</td>
</tr>
<tr>
<td>AddSolid</td>
<td>Stops run to allow solid to be added manually with user confirmation</td>
</tr>
<tr>
<td>Transfer</td>
<td>Transfers solution from one flask to another</td>
</tr>
<tr>
<td>StartPurge</td>
<td>Opens Schlenk Line Tap to place flask under a blanket of N$_2$</td>
</tr>
<tr>
<td>EvacuateAndRefil</td>
<td>Sequentially opens and closes vacuum and gas line taps on</td>
</tr>
<tr>
<td></td>
<td>AutoSchlenk line to cycle and inertise a flask/line</td>
</tr>
<tr>
<td>StartStir</td>
<td>Sets stir rate and begins stirring through hotplate</td>
</tr>
<tr>
<td>HeatChill</td>
<td>Heat/Chill given cartridge to given temperature for given time</td>
</tr>
<tr>
<td>WashSolid</td>
<td>Washes solid in given cartridge by adding solvent and filtering $n$ times</td>
</tr>
<tr>
<td>CConnect</td>
<td>Turns the valve so that a specific flask has a direct pathway between</td>
</tr>
<tr>
<td></td>
<td>the flask and pump. Used to evacuate liquid handling system.</td>
</tr>
<tr>
<td>ResetHandling</td>
<td>Washes the liquid handling backbone with solvent. Also helps to purge air</td>
</tr>
<tr>
<td></td>
<td>from valve connections.</td>
</tr>
<tr>
<td>Confirm</td>
<td>Takes no action until the user confirms</td>
</tr>
<tr>
<td>PrimePumpforAdd</td>
<td>Aspirates 3 mL (default) of reagent into lines to ensure accurate</td>
</tr>
<tr>
<td></td>
<td>dispensing during add steps.</td>
</tr>
<tr>
<td>SchlenkLineTapOpenVacuum</td>
<td>Opens the Louwers Hanique tap on the Vacuum line of the AutoSchlenk line at the defined position.</td>
</tr>
<tr>
<td>SchlenkLineTapOpenArgon</td>
<td>Opens the Louwers Hanique tap on the Inert Gas line of the</td>
</tr>
<tr>
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<td>AutoSchlenk line at the defined position.</td>
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<tr>
<td>SchlenkLineTapClose</td>
<td>Closes both Louwers Hanique taps on the AutoSchlenk line at the defined</td>
</tr>
<tr>
<td></td>
<td>position.</td>
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<tr>
<td>SchlenkFlaskTapOpen</td>
<td>Opens the Louwers Hanique tap on the Inertputer Flask at the defined</td>
</tr>
<tr>
<td></td>
<td>position.</td>
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<tr>
<td>SchlenkFlaskTapClose</td>
<td>Closes the Louwers Hanique tap on the Inertputer Flask at the defined</td>
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<tr>
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<td>position.</td>
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<tr>
<td>Async</td>
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3.3 New/Custom Graph Nodes

3.3.1 NMR Machine

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            "id": "name",
            "units": "",
            "type": "str"
        }
    },
    "name": "nmr",
    "class": "ChemputerNMR"
}
```
3.3.2 Pneumatic Splitter
4 References


