Electronic Supplementary Material (ESI) for Green Chemistry.

Improving process efficiency of Gold-Catalyzed Hydration of Alkynes: Merging Catalysis with Membrane Separation.

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[c]

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General information

The solvents used in this study were methanol, 1,4-dioxane (dioxane), tetrahydrofuran (THF) and 2-methyltetrahydrofuran (Me-THF), all of technical grade purchased from VWR (Belgium) and used without prior purification. Water was reverse osmosis purified water. Commercially available membranes selected for this study were Inopor ceramic membranes from Inopor (Veilsdorf, Germany). The C_8 modified ceramic membranes were Inopor membranes modified in house to have n-alkyl chains on the membranes top layer. The membranes used in this work were asymmetric tubular TiO_2 membranes; length 120 mm or 250 mm outer diameter 10 mm, inner diameter 7 mm and top layer thickness of about 50 nm. All membrane experiments were performed in a cross-flow filtration unit made in-house, pressurized with nitrogen gas. Filtration experiments were performed with crossflow velocity of 2 m/s for ceramic membranes and 0.3 m/s for polymeric membranes and unless otherwise stated a transmembrane pressure of 20 bar for polymeric membranes and 10 bar for ceramic membranes.. Prior to use Starmem membranes require preconditioning. To this end the a volume of solvent equivalent to 50L/m^2 of membrane surface was permeated through the membrane, this removes preservatives from the membrane pores. Though ceramic and the Borsig membranes do not require preconditioning sole of the solvent used in the membrane filtration was permeated through the membrane prior to use to simply ensure they were free of any residue remaining from the membrane preparation. All experiments containing reagents of air and moisture-sensitive materials were performed in the glovebox and using a flamed dry Schlenk glassware on a Schlenk line, connected to vaccum pump. ^{1}H, and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a bruker-500 and 400 MHz spectrometer at ambient temperature in CD_2Cl_2 and $CDCl_3$. Chemical shifts expressed in parts per million and they are referenced to residual solvent peaks ($CDCl_3$: δ_H= 7.26 ppm, δ_C= 77.16 ppm; CD_2Cl_2: δ_H= 5.32 ppm, δ_C= 53.84 ppm). Coupling constants, J, are given in hertz. Elemental analysis was performed at London Metropolitan University 166- 220 Holloway Road, London, N7 8DB. High resolution mass spectra (HRMS) were recorded in QTOF with an Agilent 6220A under electron spray ionization (ESI).

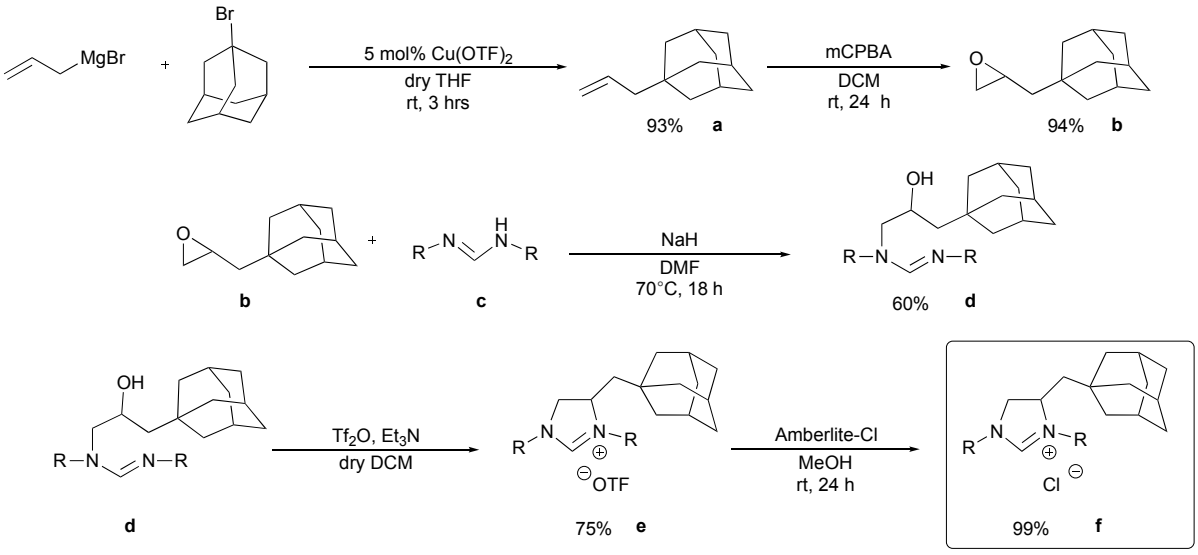
Alkyne hydration reactions were analyzed on a waters UPLC with a UV/Vis PDA detector. A Waters Acquity BEH C18 column with dimensions of 2.1 x 50 mm, 1.7µm and a gradient of water, acetonitrile buffered with 4mM ammonium acetate. The column temperature was 40°C and the detector was used at a wavelengths of 280 and 243 nm.

Analysis of Au species was carried out using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). After evaporation of the solvent from the sample the residue was digested using *aqua regia* and diluted with deionized water to the required concentration range. The samples were then analysed for metal content.

Thin layer chromatography (TLC) was carried out on silica-gel plates (Merck F254). Spots were detected with UV light and revealed with $KMnO_4$ or ninhydrin solutions.

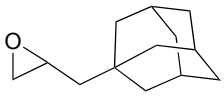
Gold complexes [Au(OTf)(IPr)] **3**, [Au(OH)(IPr)] **4**, [(Au(CH_2COCH_3)(IPr)] **5**, [{Au(IPr)}$_2$(µ-OH)][BF_4] **6**, were prepared according to literature.[1]

Steps for the synthesis of ligand f



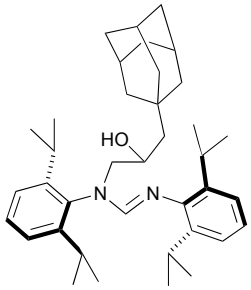
a and **c** were prepared according to literature.[2]

Preparation of epoxide b



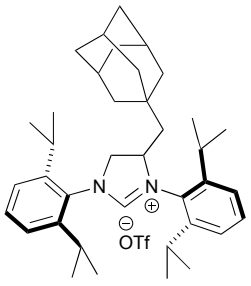
Allyladamantyl (1 g, 5.67 mmol, 1 eq.) is dissolved in DCM (28 mL, 0.2 M). *m*CPBA (3.79 g, 11.34 mmol, 2 eq.) is added and the reaction is allowed to stir at room temperature for 24 h. The reaction is quenched with 40 mL of a saturated $NaHSO_3$ solution; the organics are separated and are further washed with saturated $NaHCO_3$ (2 x 40 mL), 50 mL of brine and dried with anhydrous $MgSO_4$. The solvent was removed under vacuum to afford the formation of a yellow oil (1 g, 94%).) **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 3.02-2.97 (m, 1H, OCH), 2.74 (dd, $J_{H\text{-}H}$ = 5.1, 2.8 Hz, 1H, OCH_2), 2.39 (dd, $J_{H\text{-}H}$ = 5.1, 2.8 Hz, 1H OCH_2), 1.97 (s, 3H, $CH_{Adamantyl}$), 1.76-1.60 (m, 12H, $CH_{2\ Adamantyl}$), 1.34-1.22 (m, 2H, CH_2). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 48.8 (OCH), 47.4 (OCH_2), 47.0 (CH_2), 42.9 ($CH_{2\ Admantyl}$), 37.15 ($CH_{2\ Adamantyl}$), 32.84 ($C_{Adamantyl}$), 28.74 ($CH_{Adamantyl}$).[3]

Preparation of alcohol d



To a cooled solution at 0°C of **c** (1 g, 2.74 mmol, 1.2 eq.) in dry DMF (17 mL) NaH (82.27 mg, 3.42 mmol, 1.5 eq.) was added, the mixture was warmed to room temperature and stirred for 45 mins. After that, the reaction mixture was cooled to 0 °C and epoxide **b** (439 mg, 2.28 mmol, 1eq.) was added and the reaction is allowed to stir 70 °C for overnight. After that 50 mL of H_2O was added and the mixture was extracted 3 times with 35 mL ethylacetate, the combined organic face was washed with 100 mL of brine and dried with anhydrous $MgSO_4$. After evaporating the solvent, the crude was purified by column chromatography on silica gel using 1:9 ethylacetate/hexane to afford **c** as an off-white solid (762 mg, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.32 (t, J_{H-H}=7.7 Hz, 1H, CH_{Ar}), 7.25 (s, 1H, NCHN), 7.22-7.14 (m, 2H, CH_{Ar}, overlapping peaks), 7.10-7.07 (m, 2H, CH_{Ar}), 7.04-7.00 (m, 1H, C_{Ar}), 6.48 (s,1H,O*H*), 4.31-4.21 (m, 2H, NCH_2), 3.57-3.49 (m, 1H, C*H*$(CH_3)_2$), 3.27-3.05 (m, 4H, overlapping peaks 3H, C*H*$(CH_3)_2$, and 1H, C*H*OH), 1.92 (s, 3H, $CH_{Adamantyl}$), 1.70-1.45 (m, 13H, $CH_{Adamantyl}$), 1.33-1.26 (m, 6H, CH(C*H*$_3)_2$), 1.22-1.17 (m, 14 H, overlapping peaks 12H, CH(C*H*$_3)_2$, and 2H, C*H*$_2$), 1.13 (d, J_{H-H}=6.9 Hz, 3H, CH(C*H*$_3)_2$) . **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 154.7 (NCN), 147.8 (C_{Ar}), 147.4 (C_{Ar}), 145.6 (C_{Ar}), 140.6 (C_{Ar}), 140.2 (C_{Ar}), 129.0 (CH_{Ar}), 124.7 (CH_{Ar}), 124.5 (CH_{Ar}), 123.6 (CH_{Ar}), 122.9 (CH_{Ar}), 68.0 (*C*HOH), 62.9 (NCH_2), 50.8 ($C_{Adamentyl}$), 43.1 ($CH_{2\ Adamantyl}$), 37.2 ($CH_{2\ Adamantyl}$), 32.5 (CH_2), 28.9 ($CH_{Adamantyl}$), 28.6 (*C*H$(CH_3)_2$), 28.3 (*C*H$(CH_3)_2$), 28.1 (*C*H$(CH_3)_2$), 25.1 (CH(*C*H$_3)_2$), 25.1 (CH(*C*H$_3)_2$), 25.0 CH(*C*H$_3)_2$), 24.7 CH(*C*H$_3)_2$), 24.6 CH(*C*H$_3)_2$), 23.9 CH(*C*H$_3)_2$), 23.7 CH(*C*H$_3)_2$).
HRMS (ESI) Calculated for $C_{38}H_{57}N_2O^+$ (M^++ H^+) 557.4465; Found 557.4475.

Preparation of imidazolinlium trifluoromethanesulfonate e

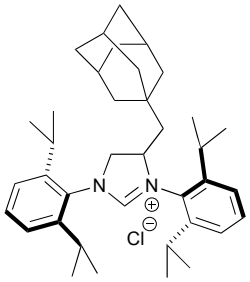


d (1g, 1.79 mmol, 1 eq.) was dissolved in 15 mL of dry dichloromethane, the mixture was cooled to 0°C and Et_3N (0.27 mL, 1.97 mmol, 1.1 eq) was added dropwise. After that the reaction mixture was cooled to 0 °C and Tf_2O (554 mg, 1.97 mmol, 1.1 eq) was added. The reaction is allowed to stir at room temperature for overnight. After evaporating the solvent, the crude was purified by column chromatography on silica gel (dichloromethane/ethanol = 10:0.5) to afford **e** as off-white solid (925 mg, 75%) **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.52 (s, 1H, NC*H*N), 7.50-7.45 (m, 2H, CH_{Ar}, overlapping peaks), 7.32-7.26 (m, 4H, CH_{Ar}, overlapping peaks), 4.97-4.86 (m, 2H, CH_{2imid}), 3.93 (t, J_{H-H}=9.3 Hz, 1H, $CH_{2\ imid}$), 3.18-2.85 (m, 4H, C*H*$(CH_3)_2$), 1.94 (s, 3H, $CH_{Adamantyl}$), 1.69-1.24 (m, 38H, overlapping peaks 24H, CH(C*H*$_3)_2$, 2H, C*H*$_2$, and 14H, $CH_{Adamantyl}$). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 159.1 (NCN), 147.2 (C_{Ar}), 147.1 (C_{Ar}), 146.8 (C_{Ar}), 145.7 (C_{Ar}), 131.7 (CH_{Ar}), 131.6 (CH_{Ar}), 129.4 (C_{Ar}), 127.1 (C_{Ar}), 125.7 (CH_{Ar}), 125.3 (CH_{Ar}), 125.0 (CH_{Ar}), 124.9 (CH_{Ar}), 62.8 (CH_{imid}), 61.2 ($CH_{2\ imid}$), 48.3

(CH_2), 42.4 ($CH_{2\ Adamantyl}$), 36.5 ($CH_{2\ Adamantyl}$), 32.1 ($C_{Adamantyl}$), 29.5 ($CH(CH_3)_2$), 29.4 ($CH(CH_3)_2$), 29.3 ($CH(CH_3)_2$), 29.3 ($CH(CH_3)_2$), 28.3 ($CH_{Adamantyl}$), 25.7 ($CH(CH_3)_2$), 25.4 $CH(CH_3)_2$), 25.0 $CH(CH_3)_2$), 24.9 $CH(CH_3)_2$), 24.4 $CH(CH_3)_2$), 24.2 $CH(CH_3)_2$), 23.6 $CH(CH_3)_2$), 23.5 $CH(CH_3)_2$). **^{19}F NMR** ($CDCl_3$, 500 MHz): δ (ppm) = -78.5.

HRMS (ESI) Calculated for $C_{38}H_{55}N_2^+$ (M^+-OTf^-) 539.4359; Found 539.4369.

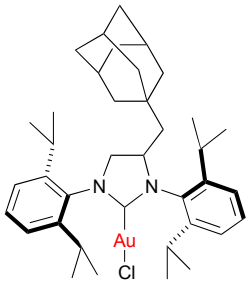
Preparation of imidazolinlium chloride f



f was prepared by resin anionic exchange. A solution of the trifluoromethanesulfonate **e** (500 mg, 0.72 mmol) with 5g of Amberlite® IRA402 chloride form in 50 mL of MeOH were stirred for overnight at room temperature. The resin was filtered and washed with 25 mL of MeOH. The filtrate were evaporated, and the product was dried under vacuum to afford an off-white solid. (410 mg, 99%) **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 10.77 (s, 1H, NC*H*N), 7.48-7.42 (m, 2H, CH_{Ar}, overlapping peaks), 7.28-7.23 (m, 4H, CH_{Ar}, overlapping peaks), 4.87-4.75 (m, 2H, CH_{2imid}), 3.86 (t, J_{H-H} = 10.3 Hz, 1H, $CH_{2\ imid}$), 3.19-2.84 (m, 4H, $CH(CH_3)_2$), 1.93 (s, 3H, $CH_{Adamantyl}$), 1.66-1.24 (m, 38H, overlapping peaks 24H, $CH(CH_3)_2$, 2H, CH_2, and 14H, $CH_{Adamantyl}$). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 161.2 (NCN), 147.4 (C_{Ar}), 146.7 (C_{Ar}), 146.6 (C_{Ar}), 145.8 (C_{Ar}), 131.5 (CH_{Ar}), 131.4 (CH_{Ar}), 129.8 (C_{Ar}), 127.5 (C_{Ar}), 125.4 (CH_{Ar}), 125.1 (CH_{Ar}), 124.8 (CH_{Ar}), 62.4 (CH_{imid}), 61.4 ($CH_{2\ imid}$), 48.1 (CH_2), 42.5 ($CH_{2\ Adamantyl}$), 36.5 ($CH_{2\ Adamantyl}$), 32.0 ($C_{Adamantyl}$), 29.6 ($CH(CH_3)_2$), 29.6 ($CH(CH_3)_2$), 29.5 ($CH(CH_3)_2$), 28.3 ($CH_{Adamantyl}$), 26.1 ($CH(CH_3)_2$), 25.7 $CH(CH_3)_2$), 25.5 $CH(CH_3)_2$), 25.4 $CH(CH_3)_2$), 24.2 $CH(CH_3)_2$), 24.1 $CH(CH_3)_2$), 23.5 $CH(CH_3)_2$), 23.3 $CH(CH_3)_2$).

HRMS (ESI) Calculated for $C_{38}H_{55}N_2^+$ (M^+-Cl^-) 539.4359; Found 539.4366.

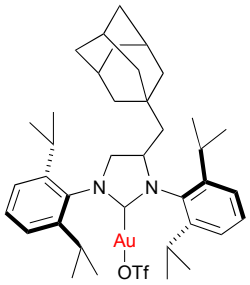
Synthesis of [Au(Cl)(SIPr$^{Me\text{-}Ad}$)]



A vial was charged, under air, with the imidazolium chloride **f** (500 mg, 0.87 mmol, eq.), [Au(DMS)Cl] (255 mg, 0.87 mmol, 1 eq.), and acetone (4 mL, 0.2 M) the vial was closed in a needle-pierced cap, the mixture was stirred initially at 30 °C for 10 minutes. Afterwards, K_2CO_3 (360 mg, 2.6 mmol, 3 eq.) was added to the reaction mixture and the vial was sealed and stirred for 2 hours at 60 °C. After this time, the mixture was filtered through a pad of silica and the silica was washed with dichloromethane. The solvent was then concentrated and pentane was added to precipitate the complex, the obtained solid was washed with further portions of pentane and dried under vacuum to afford the formation of an off-white solid (604 mg, 90%.). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.44-7.38 (m, 2H, CH_{Ar}, overlapping peaks), 7.26-7.18 (m, 4H, CH_{Ar}, overlapping peaks), 4.31 (q, J_{H-}

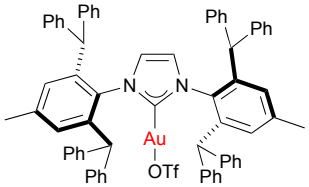
$_H$=10.9 Hz, 1H, CH_{imid}), 4.17 (t, J_{H-H}=10.9 Hz, 1H, $CH_{2\ imid}$), 3.56 (t, J_{H-H}=10.8 Hz, 1H, $CH_{2\ imid}$), 3.18-3.10 (m, 2H, C*H*$(CH_3)_2$), 3.00-2.89 (m, 2H, C*H*$(CH_3)_2$), 1.91 (s, 3H, $CH_{Adamantyl}$), 1.69-1.66 (m, 3H, $CH_{Adamantyl}$),1.57-1.53 (m, 3H, $CH_{Adamantyl}$), 1.46-1.26 (m, 32H, overlapping peaks 24H, CH(C*H*$_3)_2$, 2H, C*H*$_2$, and 6H, $CH_{Adamantyl}$). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 195.5 (C-Au), 148.3 (C_{Ar}), 146.8 (C_{Ar}), 146.7 (C_{Ar}), 146.5 (C_{Ar}), 134.4 (C_{Ar}), 132.4 (C_{Ar}), 130.1 (CH_{Ar}), 130.0 (CH_{Ar}), 124.93 (CH_{Ar}), 124.89 (CH_{Ar}), 124.7 (CH_{Ar}), 124.5(CH_{Ar}), 61.7 (CH_{imid}), 61.3 ($CH_{2\ imid}$), 48.9 (CH_2), 42.7($CH_{2\ Adamantyl}$), 36.7 ($CH_{2\ Adamantyl}$), 31.9 ($C_{Adamantyl}$), 29.2 ($CH_{Adamantyl}$), 29.0 ($CH_{Adamantyl}$), 28.9 ($CH_{Adamantyl}$), 28.4 ($CH_{Adamantyl}$), 26.1 (*C*H$(CH_3)_2$), 25.5 ($CH_{Adamantyl}$), 25.2 (*C*H$(CH_3)_2$), 24.6 CH(*C*H$_3)_2$), 24.3 CH(*C*H$_3)_2$), 23.9 CH(*C*H$_3)_2$), 23.6 CH(*C*H$_3)_2$).
Anal. Calcd. for $C_{38}H_{54}AuClN_2$: C 59.18; N 3.63; H 7.06. Found: C 58.86; N 3.53; H 7.17.

Synthesis of [Au(OTf)(SIPr$^{Me\text{-}Ad}$)] 7



In a glovebox, a vial equipped with a stir bar was charged with [Au(Cl)(SIPr$^{Me\text{-}Ad}$)] (100 mg, 0.130 mmol, 1eq.) and silver(I) trifluoromethanesulfonate (33.3 mg, 0.130 mmol, 1 eq.) in anhydrous dichloromethane (6 mL). The resulting white suspension was stirred in the dark for 20 min. then filtered through Celite. The solvent was then evaporated affording **7** as a white solid (104 mg, 90%). **^{1}H NMR** (CD_2Cl_2, 400 MHz): δ (ppm) = 7.51-7.46 (m, 2H, CH_{Ar}, overlapping peaks), 7.32-7.28 (m, 4H, CH_{Ar}, overlapping peaks), 4.49-4.40 (m, 1H, CH_{imid}), 4.30 (t, J_{H-H}=11.1 Hz, 1H, $CH_{2\ imid}$), 3.68 (t, J_{H-H}=11.1 Hz, 1H, $CH_{2\ imid}$), 3.17-3.05 (m, 2H, C*H*$(CH_3)_2$), 2.96-2.85 (m, 2H, C*H*$(CH_3)_2$), 1.91 (s, 3H, $CH_{Adamantyl}$), 1.70-1.67 (m, 4H, $CH_{Adamantyl}$),1.59-1.53 (m, 4H, $CH_{Adamantyl}$), 1.50-1.27 (m, 30H, overlapping peaks 24H, CH(C*H*$_3)_2$, 2H, C*H*$_2$, and 4H, $CH_{Adamantyl}$). **^{13}C NMR** (101 MHz, CD_2Cl_2): δ (ppm) = 184.1 (C-Au), 148.7 (C_{Ar}), 147.4 (C_{Ar}), 147.3(C_{Ar}), 147.1 (C_{Ar}), 134.4 (C_{Ar}), 132.3 (C_{Ar}), 130.8 (CH_{Ar}), 130.78 (CH_{Ar}), 125.5 (CH_{Ar}), 125.4 (CH_{Ar}), 125.2 (CH_{Ar}), 124.5 (CH_{Ar}), 125.1 (CH_{Ar}), 62.7 (CH_{imid}), 61.7 ($CH_{2\ imid}$), 49.2 (CH_2), 43.0 ($CH_{2\ Adamantyl}$), 37.1 ($CH_{2\ Adamantyl}$), 32.3 ($C_{Adamantyl}$), 29.6 ($CH_{\ Adamantyl}$), 29.4 ($CH_{Adamantyl}$), 29.0 ($CH_{Adamantyl}$), 26.1 ($C_{Adamantyl}$), 25.4 (*C*H$(CH_3)_2$), 25.3 (*C*H$(CH_3)_2$), 25.1 ($CH_{\ Adamantyl}$), 24.9 CH(*C*H$_3)_2$), 24.6 CH(*C*H$_3)_2$), 24.1 CH(*C*H$_3)_2$), 23.7 CH(*C*H$_3)_2$). **^{19}F NMR** (CD_2Cl_2, 500 MHz): δ (ppm) = -77.9.
Anal. Calcd. for $C_{39}H_{54}AuF_3N_2O_3S$: C 52.94; N 3.17; H 6.15. Found: C 52.81; N 3.08; H 6.19.

Synthesis of [Au(OTf)(IPr*)] 4



In a glovebox, a vial equipped with a stir bar was charged with [Au(Cl)(IPr*)] (200 mg, 0.174 mmol, 1eq.) and silver(I) trifluoromethanesulfonate (44.8 mg, 0.174 mmol, 1 eq.) in anhydrous dichloromethane (9 mL). The resulting white suspension was stirred in the dark for 20 min. then filtered through Celite. The solvent was then concentrated and pentane was added to precipitate the complex, affording **7** as a white solid (209 mg, 95%). **^{1}H NMR** (CD_2Cl_2, 400 MHz): δ (ppm) = 7.21-

7.18 (m, 24H, CH_{Ar}), 7.03-7.0 (m, 8H,CH_{Ar}), 6.93 (s, 4H, CH_{Ar}), 6.91-6.89 (m, 8H, C_{Ar})), 5.96 (s, 2H, CH_{imid}), 5.15 (s, 4H, $CHPh_2$), 2.25 (s, 6H, CH_3). **^{13}C NMR** (101 MHz, CD_2Cl_2): δ (ppm) = 162.0 (C-Au), 143.3 (C_{Ar}), 142.7 (C_{Ar}), 141.4 (C_{Ar}), 133.74 (C_{Ar}), 130.9 (C_{Ar}), 130.1 (CH_{Ar}), 129.9 (CH_{Ar}), 129.1 (CH_{Ar}), 129.0 (CH_{Ar}), 127.4 (CH_{Ar}), 127.3 (CH_{Ar}), 124.6 (CH_{imid}), 51.9 ($CHPh_2$), 22.1 (CH_3). **^{19}F NMR** ($CDCl_3$, 500 MHz): δ (ppm) = -76.9.
Anal. Calcd. for $C_{70}H_{56}AuF_3N_2O_3S$: C 66.77; N 2.22; H 4.48. Found: C 66.82; N 2.26; H 4.31.

General procedure for rejection profiling in Dioxane/H_2O and MeOH/H_2O using [Au(OH)(IPr)]

To a solution of gold catalyst (2 mol %, 50 mg, 0.083 mmol) in a mixture Dioxane/H_2O (2:1) (12 mL) was added a tetrafluoroboric acid solution in water(48 % wt in H_2O) (2 mol %, 0.083 mmol, 30 mg). The reaction mixture was stirred at rt for 5 min and diphenylacetylene (4.15 mmol, 740 mg, 1 eq) was added. The reaction mixture was stirred at 65 °C for 2 h, TLC showed complete conversion.
The reaction mixture was then dissolved in 750 mL of a mixture Dioxane/H_2O (2:1) and the resulting solution was added to the filtration unit fitted with the required membrane and ready for use. The circulation pump was switch on, and the mixture circulated at a nitrogen pressure of 0.5 bar until the internal temperature was 25 °C. The pressure was increased to 10 bar for ceramics and 20 bar for polymeric membranes. Once a stable flux had been reached a further 50 to 100 mL of solvent was allowed to permeate. Sample were taken from the retentate and permeate for analysis.

To a solution of gold catalyst (2 mol %, 50 mg, 0.083 mmol) in a mixture methanol/H_2O (2:1) (12 mL) was added a tetrafluoroboric acid solution in water(48 % wt in H_2O) (2 mol %, 0.083 mmol, 30 mg). The reaction mixture was stirred at rt for 5 min and Diphenylacetylene (4.15 mmol, 740 mg, 1 eq) was added. The reaction mixture was stirred at 65 °C for 2 h, TLC showed complete conversion.
The reaction mixture was then dissolved in 750 mL of a mixture methanol/H_2O (2:1) and the resulting solution was added to the filtration unit fitted with the required membrane and ready for use. The circulation pump was switch on, and the mixture circulated at a nitrogen pressure of 0.5 bar until the internal temperature was 25 °C. The pressure was increased to 10 bar for ceramics and 20 bar for polymeric membranes. Once a stable flux had been reached a further 50 to 100 mL of solvent was allowed to permeate. Sample were taken from the retentate and permeate for both ICP and UPLC analysis.

General procedure for rejection profiling in Dioxane/H_2O and MeOH/H_2O using [{Au(IPr)}$_2$(μ-OH)][BF_4]

To a solution of gold catalyst (2 mol %, 50 mg, 0.083 mmol) in a mixture Dioxane/H_2O (2:1) (12 mL)) diphenylacetylene (4.15 mmol, 740 mg, 1 eq) was added. The reaction mixture was stirred at 65 °C for 2 h, TLC showed complete conversion. Then the filtration was done in the same manner as the one explained for [Au(OH)(IPr)] in Dioxane/H_2O.
To a solution of gold catalyst (2 mol %, 50 mg, 0.083 mmol) in a mixture methanol/H_2O (2:1) (12 mL) diphenylacetylene (4.15 mmol, 740 mg, 1 eq) was added. The reaction mixture was stirred at 65 °C for 2 h, TLC showed complete conversion. Then the filtration was done in the same way as the one explained for [Au(OH)(IPr)] in MeOH/H_2O.

General procedure for rejection profiling in THF/H_2O using [Au(OTf)(IPr)], [Au(OTf)(IPr*)], [Au(OTf)($SIPr^{Me-Ad}$)]

To a solution of diphenylacetylene (5.2 mmol) in THF/H_2O (10:1) (0.25M) 1 mol% of the catalyst was added to the reaction mixture, the reaction mixture was heated to 60 °C. The reaction was sampled regularly and analyze by UPLC.

The reaction mixture was then dissolved in 500 mL in THF and the resulting solution was added to the filtration unit fitted with the required membrane and ready for use. The circulation pump was switch on, and the mixture circulated at a nitrogen pressure of 0.5 bar until the internal temperature was 25 °C. The pressure was increased to 20 bar for the polymeric membranes used. Once a stable flux had been reached a further around 150 to 200 mL of solvent was allowed to permeate. Sample were taken from the retentate and permeate for both ICP and UPLC analysis.

General procedure for rejection profiling in THF/H_2O using [Au(OH)(IPr)] and [Au (CH_2COCH_3)(IPr)]

To a solution of diphenylacetylene (5.2 mmol) in THF/H_2O (10:1) (0.25M) 1 mol% of the catalyst was added to the reaction mixture followed by the addition of 1 mol% of tetrafluoroboric acid solution in water (48 % wt in H_2O), the reaction mixture was heated to 60 °C. The reaction was sampled regularly and analyze by UPLC.

The reaction mixture was then dissolved in 500 mL in THF and the resulting solution was added to the filtration unit fitted with the required membrane and ready for use. The circulation pump was switch on, and the mixture circulated at a nitrogen pressure of 0.5 bar until the internal temperature was 25°C. The pressure was increased to 20 bar for the polymeric membranes used. Once a stable flux had been reached a further around 150 to 200 mL of solvent was allowed to permeate. Sample were taken from the retentate and permeate for both ICP and UPLC analysis.

General procedure for rejection profiling in THF/H_2O using [{Au(IPr)}$_2$(μ-OH)][BF_4]

To a solution of diphenylacetylene (5.2 mmol) in THF/H_2O (10:1) (0.25M) 0.5 mol% of the catalyst was added to the reaction mixture, the reaction mixture was heated to 60 °C. The reaction was sampled regularly and analyze by UPLC .

The reaction mixture was then dissolved in 500 mL in THF and the resulting solution was added to the filtration unit fitted with the required membrane and ready for use. The circulation pump was switch on, and the mixture circulated at a nitrogen pressure of 0.5 bar until the internal temperature was 25 °C. The pressure was increased to 20 bar for the polymeric membranes used. Once a stable flux had been reached a further around 150 to 200 mL of solvent was allowed to permeate. Sample were taken from the retentate and permeate for both ICP and UPLC analysis.

Rejection profiling in Me-THF/H_2O using [Au(IPr)(OTf)]

To a solution of diphenylacetylene (5.2 mmol) in THF/H_2O (10:1) (0.25M) 1 mol% of [Au(IPr)(OTf)] **3** was added to the reaction mixture, the reaction mixture was heated to 60 °C. The reaction was sampled regularly and analyze by UPLC.

The reaction mixture was then dissolved in 500 mL in Me-THF and the resulting solution was added to the filtration unit fitted with the required membrane and ready for use. The circulation pump was switch on, and the mixture circulated at a nitrogen pressure of 0.5 bar until the internal temperature

was 25 °C. The pressure was increased to 20 bar for the polymeric membranes used. Once a stable flux had been reached a further around 200 mL of solvent was allowed to permeate. Sample were taken from the retentate and permeate for both ICP and UPLC analysis. The kinetic profile of the reaction done in THF *vs* the one done in Me-THF is shown in Figure S1.

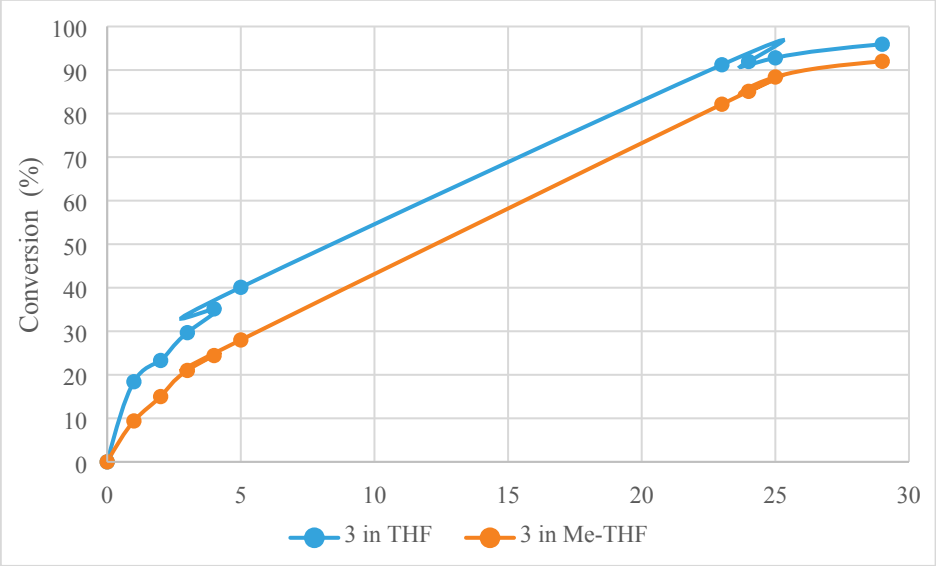


Figure S1. Kinetic profile of the hydration reaction of **1** with catalyst **3** in THF and Me-THF.

Reusability test

The reaction was performed inside the membrane unit in which diphenylacetylene (109.9 mmol) and the catalyst (1.099 mmol) in 10:1 THF/H_2O (0.25M) mixture were inserted inside the tank and circulated through the system at a flow of 294-300 Kg/h (~2m/s). The reaction mixture was then heated to 60 °C and allowed to circulate inside the process setup for 24 hrs **(1st cycle)**. The reaction mixture was then diverted over the Borsig *oNF-1* membrane and subjected to diafiltration at a flow of 45-52 Kg/h (0.3 m/s) in which 7 diafiltration volumes were washed over the membrane.

To the solution left in the retained phase diphenyacetylene (109.9 mmol) in THF/H_2O was added inside the tank and circulate through the system at a flow of 294-300 Kg/h (~2m/s) The reaction mixture was then heated to 60 °C and allowed to circulate inside the process setup for 24 hrs **(2nd cycle)**. The reaction mixture was then diverted over the Borsig *oNF-1* membrane and subjected to diafiltration at a flow of 45-52 Kg/h (0.3 m/s) in which 7 diafiltration volumes were washed over the membrane.

In the same manner the 3rd and the 4th cycle were done.

In all the cycles and the filtrations regular sampling were taken for both UPLC and ICP analysis.

Catalyst recovery treatment

After the last diafiltration, the solvent in the retained phase was concentrated and pentane was added to precipitate a brown solid compound. ^{1}H NMR of the compound shows the presence of the decomposition product [Au(IPr)$_2$]OTf, however the other peaks were difficult to identify. Treating the solid with HCl (2M HCl in diethyl ether) led to convert the unidentified peaks into [Au(IPr)(Cl)] and [Au(IPr)$_2$]OTf was not affected by the acid addition. Filtration over silica gel gave the pure [Au(IPr)(Cl)] in 44% yield.

References

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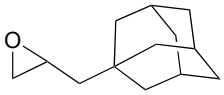
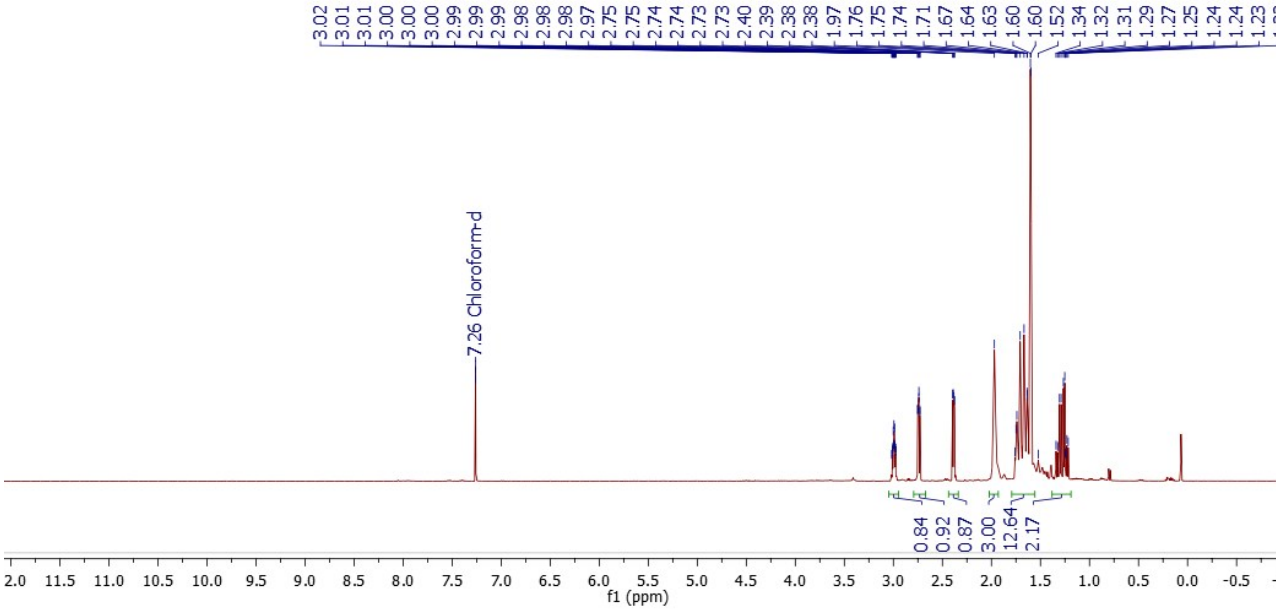
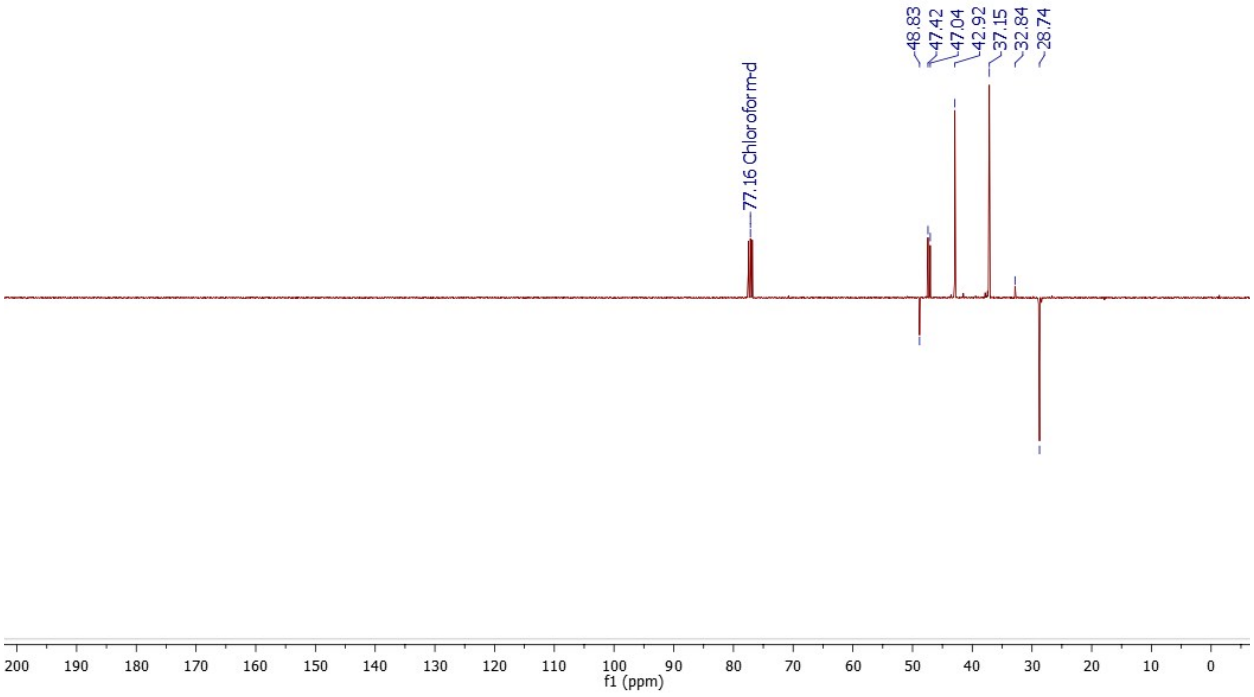
2. a) M. Sai, H. Yorimitsu and K. Oshima, *Bull. Chem. Soc. Jpn.*, 2009, **82**, 1194-1196; b) K. Hirano, S. Urban, C. Wang and F. Glorius, *Org. Lett.*, 2009, **11**, 1019-1022.
3. Product is commercially available, for more details and COA download : see https://www.enaminestore.com/catalog (Catalog ID = EN300-1841300).

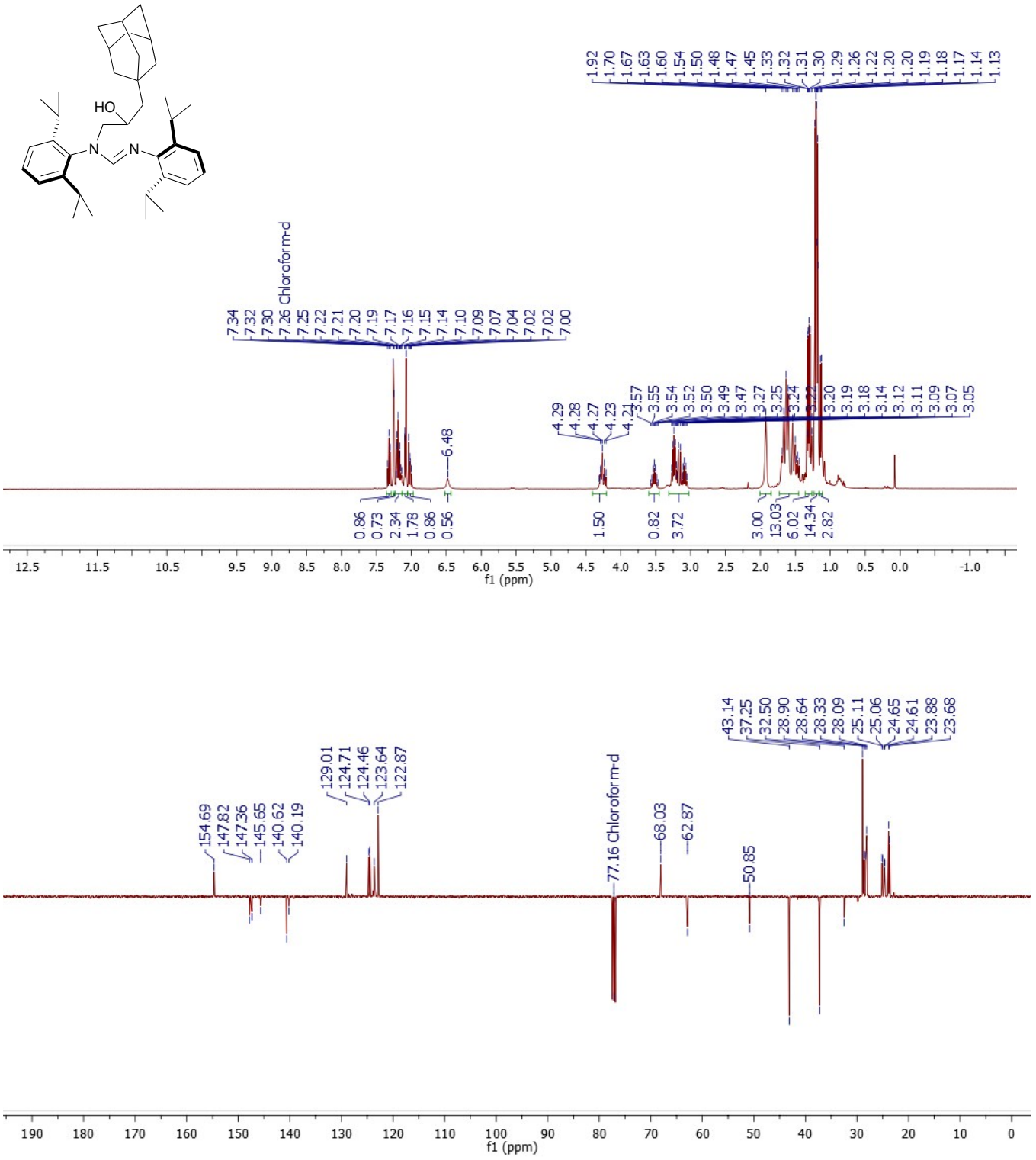
^{1}H and ^{13}C APT {^{1}H} NMR of epoxide d: ($CDCl_3$)



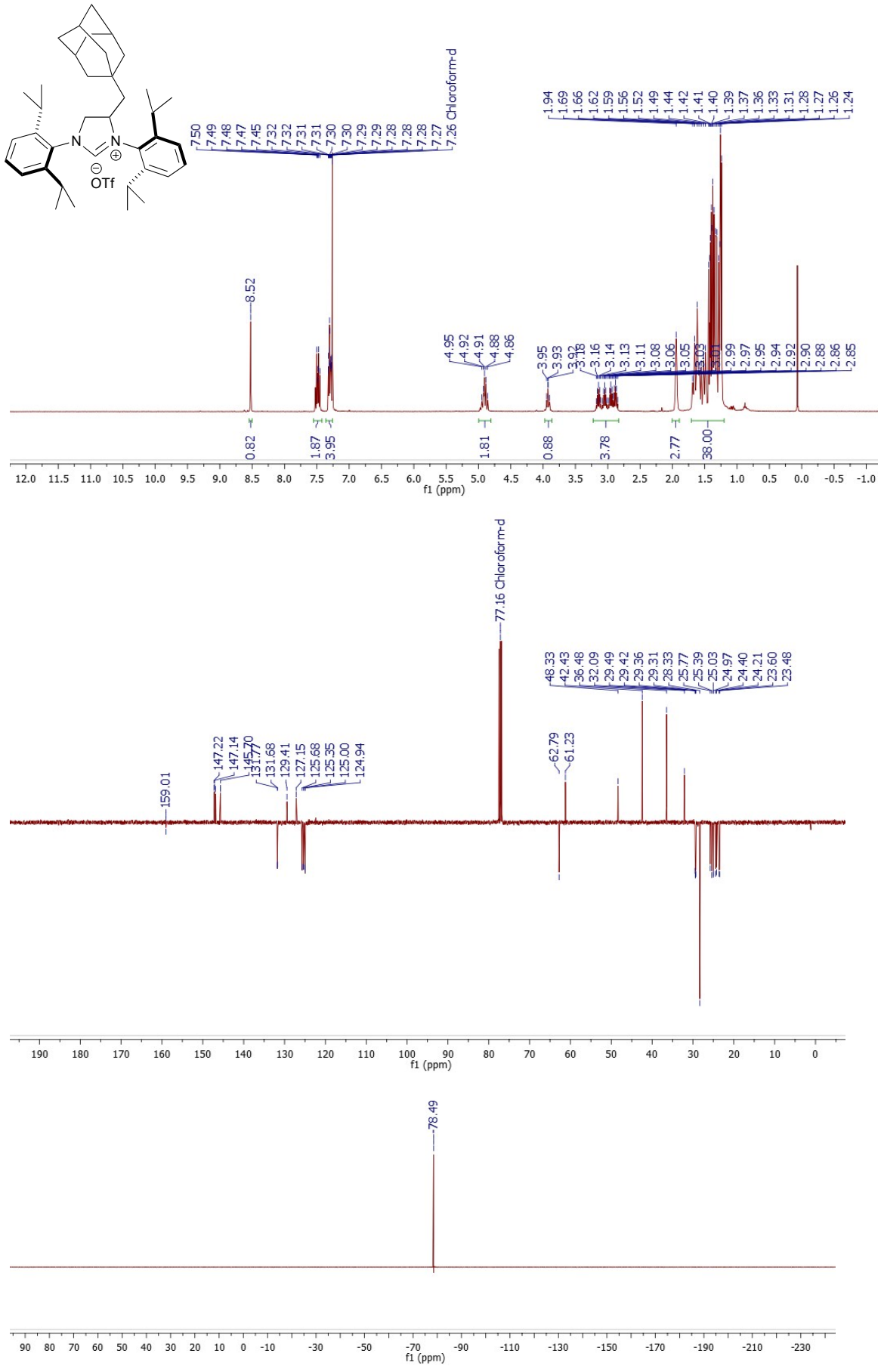




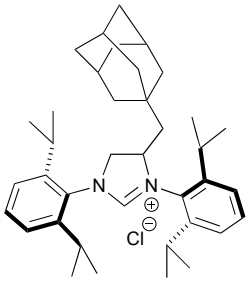
^{1}H and ^{13}C APT {^{1}H} NMR of alcohol d: ($CDCl_3$)

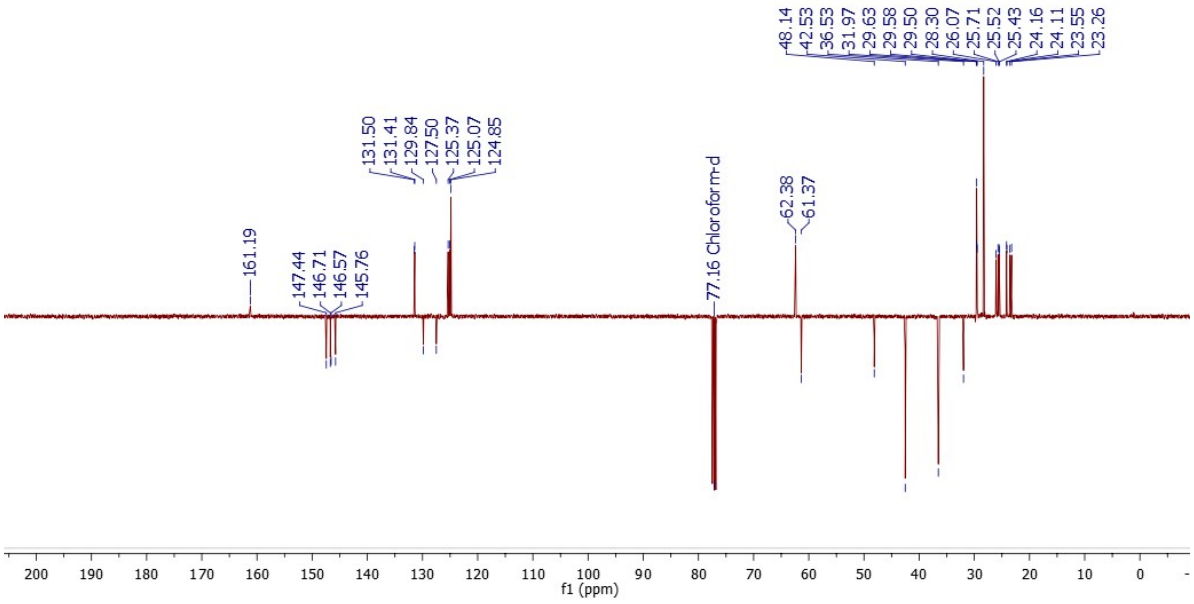


^{1}H, ^{13}C APT {^{1}H} and ^{19}F {^{1}H} NMR of imidazolinlium trifluoromethanesulfonate e: ($CDCl_3$)

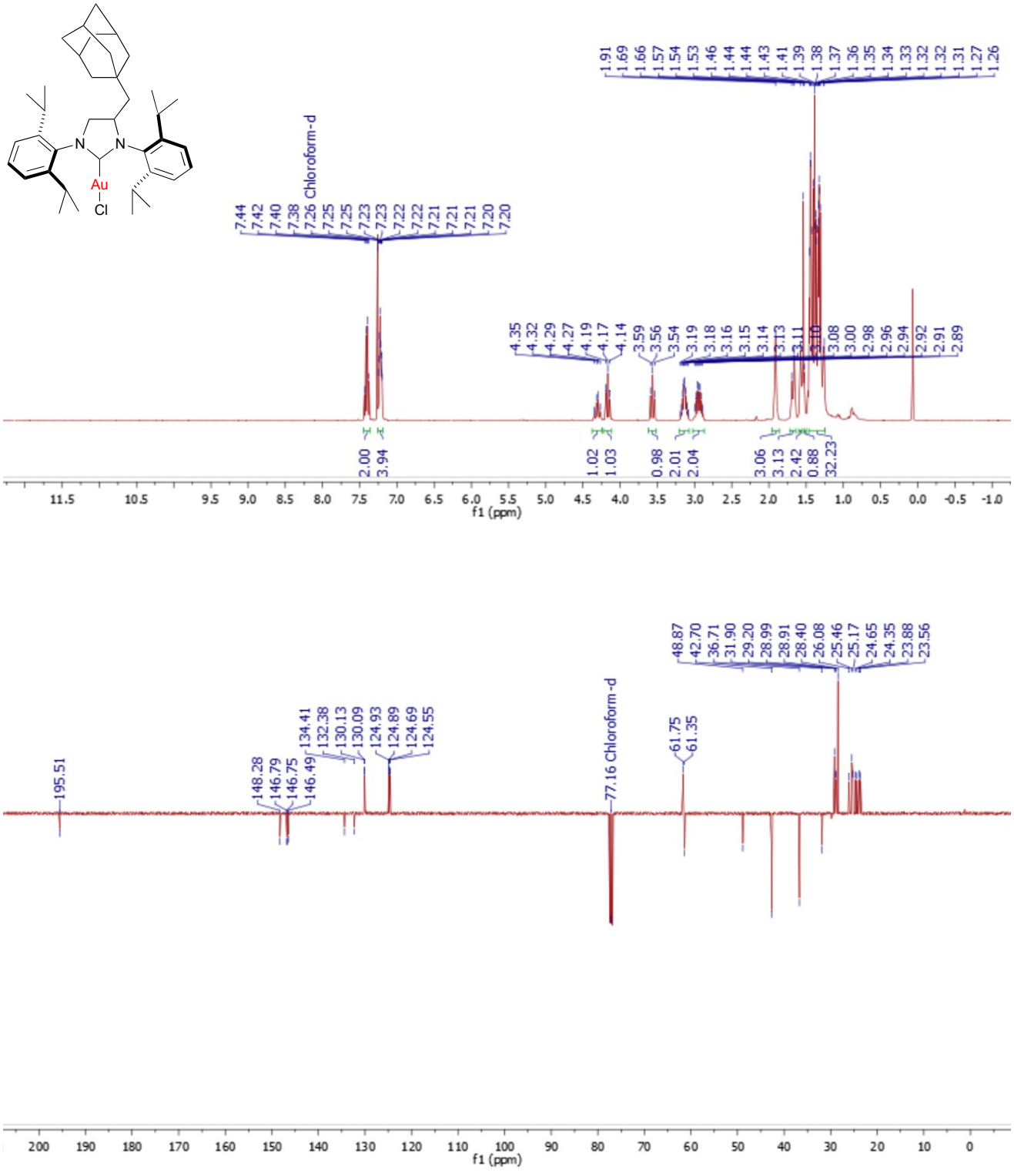


^{1}H and ^{13}C APT {^{1}H} NMR of imidazolinlium chloride f: ($CDCl_3$)

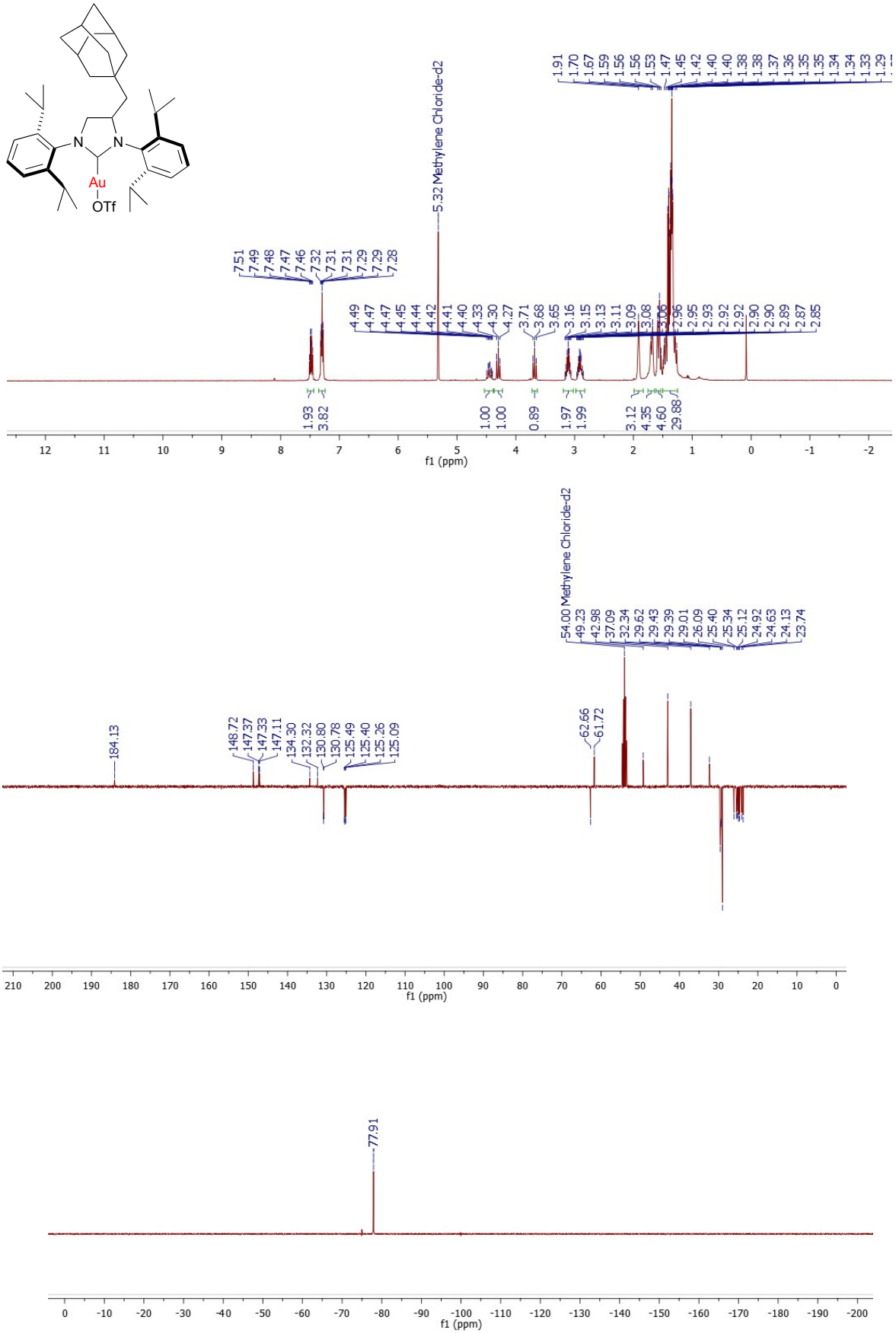




^{1}H and ^{13}C APT {^{1}H} NMR of [Au(Cl)(SIPr$^{Me\text{-}Ad}$)]: ($CDCl_3$)



^{1}H, ^{13}C APT {^{1}H} and ^{19}F {^{1}H} NMR of [Au(OTf)(SIPr$^{Me\text{-}Ad}$)] 7: (CD_2Cl_2)



^{1}H, ^{13}C APT {^{1}H} in (CD_2Cl_2) and ^{19}F {^{1}H} in $CDCl_3$ NMR of [Au(OTf)(IPr*)] 4