Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 101

www.rsc.org/obc

PAPER

A combined mechanistic and computational study of the gold(I)-catalyzed formation of substituted indenes†

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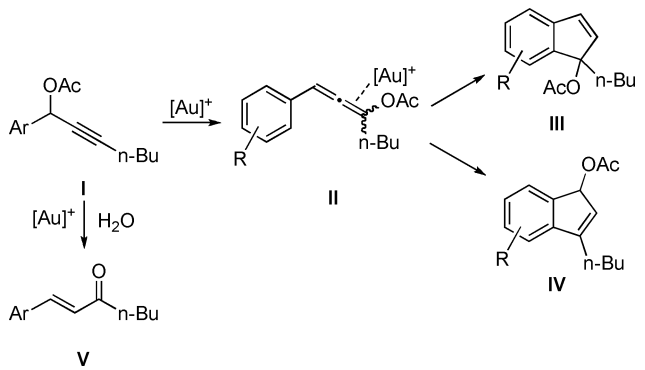
Received 21st September 2010, Accepted 28th September 2010
DOI: 10.1039/c0ob00758g

Substituted indenes can be prepared after a sequence [1,3] O-acyl shift-hydroarylation-[1,3] O-acyl shift. Each step is catalyzed by a cationic NHC-Gold(I) species generated *in situ* after reaction between [(IPr)AuOH] and $HBF_4{\cdot}OEt_2$. This interesting silver-free way is fully supported by a computational study justifying the formation of each intermediate.

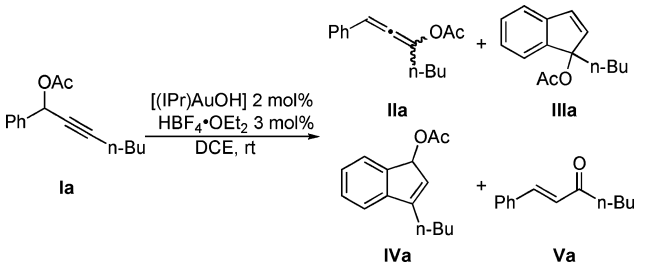
Introduction

The use of gold as a molecular assembly strategy is growing rapidly in interest as attested by the expanding related literature.[1] Among the most prevalent transformations examined, those involving alkynes,[2] with specific examples making use of propargylic esters, are most common.[3]

Propargylic acetates **I** have already been shown to react in the presence of $[(IPr)AuCl]/AgBF_4$ (IPr = 1,3-bis(diisopropyl)-phenylimidazol-2-ylidene) through a tandem [3,3] rearrangement-intramolecular hydroarylation to give either indenes **III** or **IV**.[4] The same reaction in presence of water leads to enone **V** (Scheme 1).[5] We recently described the synthesis and characterization of a NHC-gold(I) hydroxide complex.[6] This compound displays a strong Brønsted basic character and can react with acids to generate a cationic gold(I) species.[7] This catalytic system is user-friendly and circumvents the need of silver salts in association with gold to generate the putative $[NHC–Au]^+$ species. In the present study, this simple activation protocol ($[(IPr)AuOH] + HBF_4{\cdot}OEt_2$) was examined in a skeleton rearrangement reaction involving propargylic acetates. (Scheme 2).[8]



Scheme 1 Transformations of propargylic acetates.



Scheme 2 Formation of allene **IIa**, enone **IIIa**, and indenes **IVa** and **Va** from propargylic acetate **Ia**.

Results and discussion

Propargylic acetate **Ia** was fully converted after 5 min at RT in the presence of $[(IPr)Au]^+$ formed *in situ* using the acid activation method described above.

As previously observed,[4,9] products **IIa** and **IIIa** were formed along with trace amounts (<5%) of enone **Va**.[5] The reaction mixture was analyzed after 5 h and surprisingly another compound identified as indene **IVa** appeared in a **IIIa**/**IVa** ratio 87 : 13. After 24 h this ratio evolved to 70 : 30 (**IIIa**/**IVa**). These results led us to reconsider the previously proposed mechanism for this transformation. Indeed, indene **IVa** appears to be a rearranged product of **IIIa** and not a product obtained directly from allene **IIa**. The influence of temperature on conversion of **Ia** into **IVa** was next investigated. Complete conversion at 25 °C, 35 °C and 45 °C was reached after 30 h, 14 h and 4 h, respectively. Monitoring the progress of the reaction by ^1H NMR spectroscopy clearly illustrates the progress of the transformation (Fig. 1).

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† Electronic supplementary information (ESI) available: Computational data and NMR spectra. See DOI: 10.1039/c0ob00758g

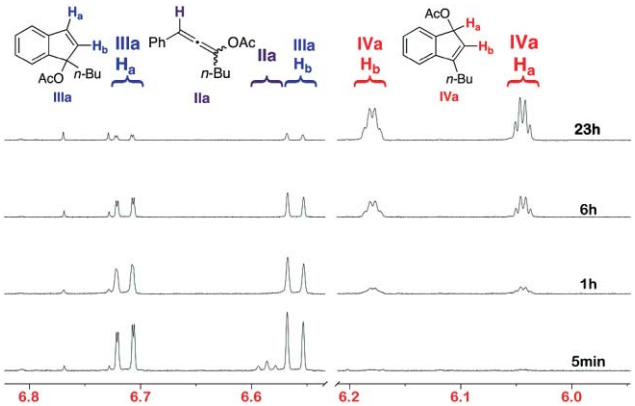


Fig. 1 ^{1}H NMR of the reaction mixture at room temperature.

After 5 min., complete conversion of **Ia** into the allene **IIa** (triplet at 6.58 ppm), indene **IIIa** (doublets at 6.70 and 6.56 ppm) and enone **Va** (doublet at 6.75 ppm) was observed. After 1 h, allene **IIa** was totally converted into indene **IIIa**. After 6 h and 23 h, a constant increase of the proportion of **IVa** linked to a decrease of **IIIa** was noticed. No intermediate between these two compounds was observed, suggesting that a direct [1,3]-shift of the acetate group is involved in the transformation.

To further support the proposed mechanism, a computational analysis was performed.[10] Fig. 2 illustrates all the intermediates found for the **Ia** → **IIa** → **IIIa** → **IVa** isomerization.

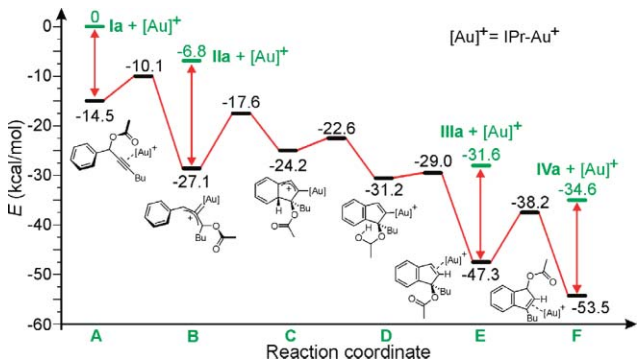


Fig. 2 Energy profile for the **Ia** → **IIa** → **IIIa** → **IVa** conversion.

After coordination of **Ia** to the Au center, the proposed [1,3] shift of the acetyl group requires to overcome of a barrier of only 4.4 kcal mol^{-1}, evolving the system into intermediate **B**. Intermediate **B** has a strong Au-carbenoid character, as indicated by the strongly bent allene moiety (the C–C–C allene angle in **B** is 127.8°). Dissociation of **IIa** from **B** requires 20.3 kcal mol^{-1}. The hydroarylation **B–C** step is endothermic by 9.5 kcal mol^{-1}, and leads to intermediate **C**, which proceeds with a low barrier to intermediate **D**, recovering the aromaticity of the arene ring of the substrate. The hydrogen of the hydroxyl group of **D** then migrates to the C atom σ-bonded to the metal in **D**. The **D–E** step is nearly thermoneutral, and **E** is the first intermediate that is remarkably more stable than **B**. Dissociation of **IIIa** from **E** costs 15.7 kcal mol^{-1}. Finally, a second [1,3] shift migration of the acetyl group of **E** occurs into the final position in **F** with a barrier of 9.1 kcal mol^{-1} only. Dissociation of the most stable product **IVa** from **F** is endothermic by 18.9 kcal mol^{-1}. In short, the proposed reaction pathway is fully supported by the theoretical analysis. All barriers connecting **Ia** to **IVa** are lower than 10 kcal mol^{-1}, and product **IVa** is the most stable product. Further, the mechanistic sequence **Ia** → **IIa** → **IIIa** → **IVa** is in agreement with the NMR analysis of Fig. 1. On the other hand, direct hydroarylation from **A**, *i.e.* without the initial [1,3] shift of the acetyl group, has the high barrier of 17.8 kcal mol^{-1}. Similarly, the direct H transfer from **B**, *i.e.* before the hydroarylation, has a barrier of 44.0 kcal mol^{-1}. This indicates that the sequence of steps illustrated in Fig. 2 is the only viable one. Finally, the barrier of 32.4 kcal mol^{-1} for the **IIIa** → **IVa** isomerization in the absence of the Au-catalyst, excludes the possibility of this transformation proceeding in the absence of gold.

This reaction was extended to other propargylic acetates leading to a variety of indenes (Fig. 3).[11] Various substitutions, electron withdrawing or donating, on the aromatic ring as well as the effect of a more hindered O-Acyl group (**IVh**) instead of the acetate were studied.

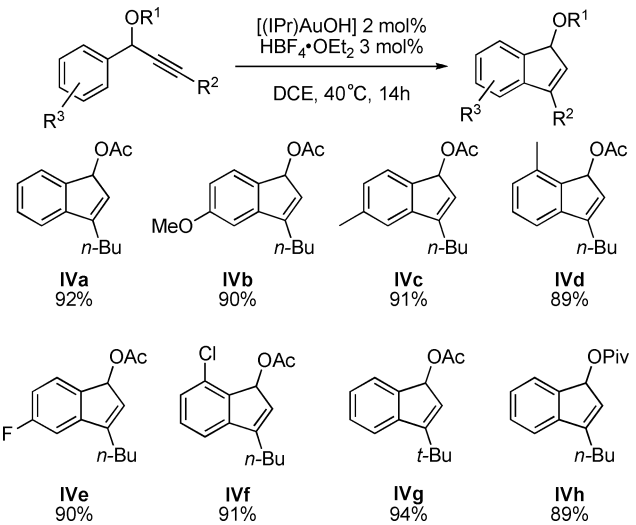
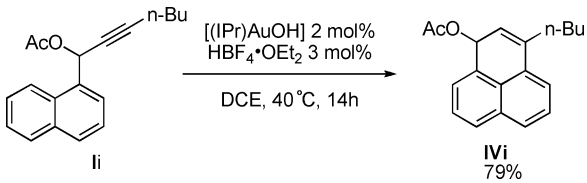


Fig. 3 Gold-catalyzed synthesis of indenes.

In all cases, the sequential formation of allene **II**, kinetic indene **III** and then thermodynamic indene **IV** was observed by ^{1}H NMR spectroscopy. The presence of electron donating (**IVa–d**) as well as halogenes (**IVe–f**) on the aromatic ring in *ortho* and in *para* positions showed no effect on the hydroarylation step leading to the corresponding indenes in high yields (>89%). The reaction is also quite efficient if the n-butyl chain is replaced by a more sterically demanding t-butyl (**IVg**). We also investigated the reactivity of a pivaloyl substituent as a migrating group, with no notable effect of the more hindered substitution (**IVh**).

Interestingly, product **IVi** can also be prepared from propargylic acetate **Ii** through the same sequence after formation of a 6-membered ring preceding the [1,3] O-acyl shift but without any indene formation (eqn (1)).



(1)

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To support our mechanistic hypothesis, isolated allene **IIa** and indene **IIIa** were reacted under catalytic conditions. As expected, in the presence of our catalytic system, **IIa** or **IIIa** led quantitatively to indene **IVa**. Simple heating of these substrates with or without $HBF_4{\cdot}OEt_2$ (3 mol%) did not yield **IVa**, excluding the simple thermal or acid-catalyzed rearrangement reaction pathway.

Conclusion

In conclusion, the pre-catalyst [(IPr)AuOH] is shown to be useful in the preparation of substituted indenes in an entirely silver-free manner *via* activation with $HBF_4{\cdot}OEt_2$ as a Brønsted acid to generate the active species *in situ*. The use of this new catalytic system permitted the examination of individual steps involved in the transformation and to correct the previously proposed mechanism. The proposed steps are fully supported by a computational study. The transformation involves firstly a [1,3] O-acyl shift to form an allene, then hydroarylation to produce a kinetically favored indene and finally another [1,3] O-acyl shift generates a more stable substituted indene.

Experimental section

All reagents and solvents were used as purchased. NMR spectra were recorded on a 400 MHz Varian Gemini spectrometer. High Resolution Mass Spectrometry analyses were performed by St Andrews analytical services.

Complex [(IPr)AuOH][6] and propargylic acetates[4,5,12] were prepared according to literature procedures. For computational data see supporting information.†

Computational details

All the DFT static calculations were performed at the GGA level with the Gaussian03 set of programs,[13] using the BP86 functional of Becke and Perdew.[14] The electronic configuration of the molecular systems was described with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers for H, C, N, and O (SVP keyword in gaussian).[15] For Au we used the small-core, quasi-relativistic Stuttgart/Dresden effective core potential, with an associated valence basis set contracted (standard SDD keywords in gaussian03).[16] The geometry optimizations were performed without symmetry constraints, and the characterization of the located stationary points was performed by analytical frequency calculations. The energies discussed throughout the text contain zero point energy (ZPE) corrections. Solvent effects including contributions of non electrostatic terms have been estimated in single point calculations on the gas phase optimized structures, based on the polarizable continuous solvation model PCM using dichloroethane as solvent.[17]

General procedure for the synthesis of indenes

In a flame-dried Schlenk, 2.4 mg of IPrAuOH (6.10^{-3} mmol, 2 mol%) is diluted in 8 ml of 1,2-dichloroethane, then 84 µl of a 1% solution of $HBF_4{\cdot}OEt_2$ in dichloroethane (9.10^{-3} mmol, 3 mol%) is added. Mixture is stirred at room temperature for 5 min, then a solution of propargylic acetate (0.3 mmol, 1 eq) in 2 ml of dichloroethane is added. Reaction is heated overnight at 40 °C. The solvent is evaporated and the crude product diluted in pentane and filtered over a plug of silica to remove catalyst or purified on column chromatography if needed.

3-Butyl-1*H*-inden-1-yl acetate[3] (IVa). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.3 Hz, 1H), 7.35–7.30 (m, 1H), 7.25 (d, J = 7.2 Hz, 1H), 7.21 (dt, J = 7.3 Hz, J = 0.9 Hz, H^{Ar}), 6.19 (m, 1H), 6.05 (m, 1H), 2.51–2.45 (m, 2H), 2.15 (s, 3H), 1.70–1.62 (m, 2H), 1.49–1.39 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 148.5, 144.2, 142.8, 128.8, 126.7, 126.3, 124.2, 119.6, 76.8, 29.6, 27.3, 22.8, 21.3, 14.1. HRMS calcd for $C_{15}H_{18}O_2Na$: 253.1204. Found: 253.1201.

3-Butyl-5-methoxy-1*H*-inden-1-yl acetate[4] (IVb). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 8.1 Hz, 1H), 6.80 (d, J = 2.3 Hz, 1H), 6.70 (dd, J = 2.3 Hz, J = 8.1 Hz), 6.12 (m, 1H), 6.06 (m, 1H), 3.83 (s, 3H), 2.47–2.43 (m, 2H), 2.13 (s, 3H), 1.69–1.61 (m, 2H), 1.48–1.39 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 160.8, 148.1, 146.0, 134.8, 128.1, 125.0, 110.4, 106.7, 76.4, 55.6, 29.6, 27.3, 22.7, 21.3, 14.1. HRMS calcd for $C_{16}H_{20}O_3Na$: 283.1310. Found: 283.1310.

3-Butyl-7-methyl-1*H*-inden-1-yl acetate[4] (IVc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 7.6 Hz, 1H), 7.06–7.04 (m, 1H), 7.01 (d, J = 7.5 Hz), 6.15–6.13 (m, 1H), 6.03–6.01 (m, 1H), 2.49–2.43 (m, 2H), 2.38 (s, 3H), 2.13 (s, 3H), 1.69–1.60 (m, 2H), 1.48–1.38 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 148.4, 144.4, 139.9, 138.7, 127.0, 126.8, 124.0, 120.5, 76.6, 29.6, 27.3, 22.8, 21.7, 21.3, 14.1. HRMS calcd for $C_{16}H_{20}O_2Na$: 267.1361. Found: 267.1359.

3-Butyl-7-methyl-1*H*-inden-1-yl acetate[4] (IVd). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (t, J = 7.5 Hz, 1H), 7.11 (d, J = 7.2 Hz, 1H), 7.01 (d, J = 7.6 Hz), 6.25 (m, 1H), 6.08 (m, 1H), 2.47 (dd, J = 7.2 Hz, J = 7.9 Hz, 2H), 2.33 (s, 3H), 2.15 (s, 3H), 1.69–1.61 (m, 2H), 1.49–1.39 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 148.4, 144.3, 140.1, 134.3, 129.1, 128.1, 126.5, 117.3, 76.4, 29.6, 27.4, 22.7, 21.1, 18.0, 14.1. HRMS calcd for $C_{16}H_{20}O_2Na$: 267.1361. Found: 267.1357.

3-Butyl-5-fluoro-1*H*-inden-1-yl acetate (IVe). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (dd, J = 8.0 Hz, J = 5.0 Hz, 1H), 6.92 (dd, J = 8.8 Hz, J = 2.3 Hz, 1H), 6.90–6.84 (m, 1H), 6.12 (m, 2H), 2.46–2.41 (m, 2H), 2.14 (s, 3H), 1.68–1.60 (m, 2H), 1.48–1.38 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 162.4 (d, J = 245.0 Hz), 147.6 (d, J = 2.7 Hz), 146.7 (d, J = 8.7 Hz), 138.2 (d, J = 2.7 Hz), 128.9, 125.3 (d, J = 9.2 Hz), 112.5 (d, J = 23.0 Hz), 107.4 (d, J = 23.7 Hz), 76.1, 29.5, 27.3, 22.7, 21.3, 14.1. HRMS calcd for $C_{15}H_{17}FO_2Na$: 271.1110. Found: 271.1115.

3-Butyl-7-chloro-1*H*-inden-1-yl acetate (IVf). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.24 (m, 1H), 7.16 (dd, J = 0.9 Hz, J = 8.1 Hz, 1H), 7.14 (dd, J = 0.9 Hz, J = 7.2 Hz, 1H), 6.37–6.33 (m, 1H), 6.09–6.06 (m, 1H), 2.48–2.41 (m, 2H), 2.15 (s, 3H), 1.69–1.57 (m, 2H), 1.49–1.35 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 147.8, 146.5, 139.4, 130.7, 130.6, 127.7, 127.0, 118.1, 75.6, 29.6, 27.4, 22.7, 21.0, 14.1. HRMS calcd for $C_{15}H_{17}ClO_2Na$: 287.0815. Found: 287.0815.

3-*tert*-Butyl-1*H*-inden-1-yl acetate (IVg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 7.3 Hz, 1H), 7.30 (dt, J = 7.6 Hz, J = 1.2 Hz, 1H), 7.19 (dt, J = 7.4 Hz, J = 1.0 Hz), 6.14 (d, J = 2.1 Hz, 1H), 6.03 (d, J = 2.1 Hz,

1H), 2.15 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 156.8, 144.0, 142.6, 128.5, 125.8, 125.4, 124.4, 122.8, 76.2, 33.3, 29.1, 21.3. HRMS calcd for $C_{15}H_{18}O_2Na$: 253.1204. Found: 253.1199.

3-Butyl-1*H*-inden-1-yl pivalate[3a] (IVh). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.35 (m, 1H), 7.31 (dd, J = 1.1 Hz, J = 7.4 Hz, 1H), 7.24 (d, J = 7.2 Hz, 1H), 7.19 (dt, J = 7.3 Hz, J = 1.2 Hz, 1H), 6.17 (dd, J = 1.8 Hz J = 3.7 Hz, 1H), 6.03 (dd, J = 1.7 Hz, J = 3.5 Hz, 1H), 2.51–2.45 (m, 2H), 1.70–1.60 (m, 2H), 1.47–1.38 (m, 2H), 1.23 (s, 9H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.1, 147.9, 144.1, 143.2, 128., 127.0, 126.1, 123.8, 119.4, 76.6, 43.5, 39.0, 29.5, 27.2, 22.7, 14.0. HRMS calcd for $C_{18}H_{24}O_2Na$: 295.1674. Found: 295.1681.

3-Butyl-1*H*-phenalen-1-yl acetate (IVi). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.3 Hz, 2H), 7.81 (d, J = 9.1 Hz, 1H), 7.52–7.38 (m, 3H), 6.55–6.53 (m, 1H), 6.19 (dd, J = 1.7 Hz, J = 3.5 Hz, 1H), 2.61–2.53 (m, 2H), 2.20 (s, 3H), 1.76–1.65 (m, 2H), 1.51–1.40 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 148.4, 142.3, 137.7, 132.7, 129.9, 129.5, 129.0, 127.0, 126.7, 125.2, 123.5, 118.6, 76.4, 29.7, 27.6, 22.7, 21.4, 14.0. HRMS calcd for $C_{19}H_{20}O_2Na$: 303.1361. Found: 303.1360.

Acknowledgements

The ERC (Advanced Investigator Award to SPN) and the EPSRC are gratefully acknowledged for support of this work. Umicore AG are thanked for their generous gifts of materials. LC thanks the HPC team of Enea (www.enea.it) for using the ENEA-GRID and the HPC facilities CRESCO (www.cresco.enea.it) in Portici, Italy. AP thanks the Spanish MICINN for a Ramón y Cajal contract. SPN is a Royal Society-Wolfson Research Merit Award holder.

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8 The amount of acid used (3 mol%) was selected for ease of manipulation. Background reactions conducted with acid only did not lead to product formation and permitted recovery of starting material.

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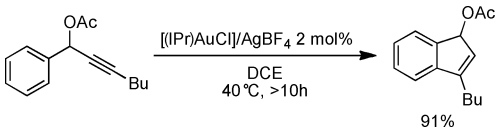
10 The BP86 DFT calculations were performed with the Gaussian03 package using a SVP basis set on main group atoms, and the SDD-ECP basis set on Ru. Solvent effects, dichloroethane, were included with the PCM approach. Further details in the Supporting Information.

11 The reaction below conducted under identical catalytic conditions but with the use of a Au–Cl precursor activated by a silver salt yields comparable results (thermodynamic indene) but with apparent slower kinetics as under optimised conditions this transformation mediated by [(IPr)AuOH] and acid reaches completion after 4 h.



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