Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2012, **10**, 1686

www.rsc.org/obc

PAPER

Palladium-catalyzed cross-coupling reactions of organogold(I) phosphanes with allylic electrophiles†‡

Miguel Peña-López, Miguel Ayán-Varela, Luis A. Sarandeses* and José Pérez Sestelo*

Received 24th October 2011, Accepted 6th December 2011
DOI: 10.1039/c2ob06788a

Aryl and alkenylgold(I) phosphanes react regioselectively with allylic electrophiles such as cinnamyl and geranyl halides (bromide, chloride and acetates) under palladium catalysis in THF at 80 °C to afford the α-substitution product with moderate to high yields. When the reaction is performed with a chiral enantiopure secondary acetate, the α-substituted cross-coupling product is obtained with complete inversion of the stereochemistry.

Introduction

During recent years the use of gold reagents in organic synthesis has increased exponentially following the discovery that cationic complexes can catalyze the nucleophilic addition to unsaturated C–C bonds.[1] In this reaction gold(I) organometallics are synthetic intermediates that usually suffer protodeauration to regenerate the gold(I) catalyst, but in some cases can be isolated[2] and even used in further organic transformations.[3] Although the properties and reaction patterns of gold compounds have been studied throughout the last few decades,[4] their utility in organic synthesis is very limited probably due to their cost and low nucleophilicity.[5] Nowadays, transition metal-catalyzed reactions offer a new opportunity for discovering novel synthetic transformations using gold reagents in stoichiometric or catalytic amounts.[6] Recently, important contributions from different groups have demonstrated that gold organometallics are useful reagents in metal-catalyzed cross-coupling reactions.[7] In our group, we reported that organogold(I) phosphanes ($RAuPPh_3$, R = alkyl, alkynyl, alkenyl and aryl) react efficiently with aryl halides (iodides, bromides and triflates), β-bromostyrene, benzyl bromide and benzoyl chloride under palladium catalysis.[8] The main features of gold organometallics in this reaction are the stability in air atmosphere, reactivity at room temperature, and high chemoselectivity. These findings confirm organogold(I) compounds as useful reagents for transmetalating organic groups to palladium, and the possibility to develop gold-palladium catalyzed processes. As part of a project aimed at studying the utility of gold organometallics in metal-catalyzed reactions, we herein report the reactivity of gold(I) organometallics with allylic electrophiles under palladium catalysis.

The allylic substitution reaction is a key transformation in organic synthesis due to the high reactivity and bidentate electrophilicity of allylic substrates.[9] The control of the regio- and stereoselectivity are fundamental aspects that can be modulated by selecting the reaction partners (nucleophile, catalyst or allylic electrophile). Transition metal-catalyzed cross-coupling reactions of allylic substrates involving the oxidative addition, transmetalation and reductive elimination sequence have been performed using several organometallics and provide a synthetically useful methodology.[10] However, the reactivity of gold organometallics with allylic electrophiles is limited to some isolated examples. First, Blum reported a palladium-catalyzed cross-coupling of an alkenylgold(I) phosphane, obtained by alkyne carboauration, with allyl bromide.[6c] More recently, Hashmi reported that alkenylgold(I) phosphane, prepared by gold-catalyzed cyclization of an allenoate, react with allyl iodide under palladium catalysis, but other allylic electrophiles such as allyl bromide or cinnamyl bromide and acetate failed.[7b] In a different approach, Blum has also reported a dual-catalytic (Au–Pd) cross-coupling reaction where an alkenyl gold phosphane, intermediate in a gold-catalyzed cyclization, reacts with an allyl palladium complex.[6d]

Results and discussion

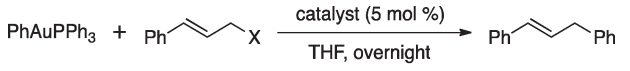
Guided by our experience in allylic cross-coupling reactions,[11] we decided to study the reactivity of organogold(I) phosphanes ($RAuPPh_3$) with allylic electrophiles. Gold(I) organometallics (RAuL) are air stable compounds that can be prepared from organolithium, Grignard reagents, or boronic acids.[12] In our first reaction, we observed that phenyl(triphenylphosphine)gold ($PhAuPPh_3$, **1a**, 110 mol %) reacts slowly with (*E*)-cinnamyl bromide (**2a**) at room temperature affording, after 24 h, the S_N2 product **3a** in 15% yield (Table 1, entry 1). However, longer reaction times (up to 48h) or higher temperatures did not

Departamento de Química Fundamental, Universidade da Coruña, E-15071 A Coruña, Spain. E-mail: sestelo@udc.es, qfsarand@udc.es; Fax: +34 981 167 065

† This paper is dedicated to the memory of Prof. Rafael Suau

‡ Electronic supplementary information (ESI) available. See DOI: 10.1039/c2ob06788a

Table 1 Reaction of phenyl(triphenylphosphine)gold with (*E*)-cinnamyl halides[a]

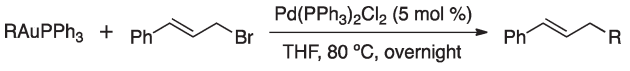


1a **2a–c** **3a**

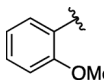
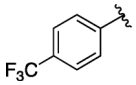
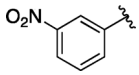
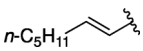
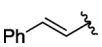
Entry	X	Catalyst	*T*/°C	Yield (%)[b]
1	Br (**2a**)	No cat.	25	15
2	Br (**2a**)	No cat.	80	15
3	Br (**2a**)	$Pd(PPh_3)_2Cl_2$	25	20
4	Br (**2a**)	$Pd_2(dba)_3$	25	18
5	Br (**2a**)	$Pd(PPh_3)_2Cl_2$	80	75
6	Br (**2a**)	$Pd_2(dba)_3$	80	80
7	Br (**2a**)	$Pd(PPh_3)_4$	80	78
8	Cl (**2b**)	No cat.	80	—
9	Cl (**2b**)	$Pd(PPh_3)_2Cl_2$	80	84
10	Cl (**2b**)	$Pd_2(dba)_3$	80	77
11	OAc (**2c**)	$Pd(PPh_3)_2Cl_2$	80	83
12	OAc (**2c**)	No cat.	80	—
13	OAc (**2c**)	$Pd_2(dba)_3$	80	84
14	OAc (**2c**)	$Pd(PPh_3)_2Cl_2$	80	85[c]

[a] All the reactions were conducted using 110 mol % of $PhAuPPh_3$. [b] Isolated yield. [c] Reaction performed in THF/H_2O (1 : 1).

Table 2 Reaction of organogold(I) phosphanes with (*E*)-cinnamyl bromide



1b–h **2a** **3b–h**

Entry	R		Product	Yield (%)[a]
1		(**1b**)	**3b**	93
2		(**1c**)	**3c**	76
3		(**1d**)	**3d**	83
4		(**1e**)	**3e**	56
5		(**1f**)	**3f**	75
6		(**1g**)[b]	**3g**[c]	87
7		(**1h**)[d]	**3h**[e]	90

[a] Isolated yield. [b] As a *E*/*Z* (82 : 18) mixture by ^1H NMR. [c] As a 4*E*/4*Z* (82 : 18) mixture by ^1H NMR. [d] As a *E*/*Z* (92 : 8) mixture by ^1H NMR. [e] As a 4*E*/4*Z* (91 : 9) mixture by ^1H NMR.

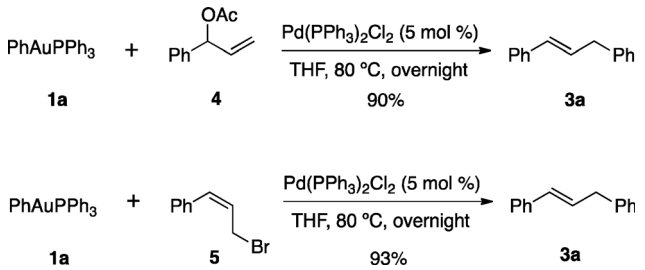
improve the transformation, producing significant amounts of the biphenyl from oxidative dimerization of the organogold reagent (Table 1, entry 2). When the coupling reaction was tried under palladium catalysis at room temperature using 5 mol % of $Pd(PPh_3)_2Cl_2$ or $Pd_2(dba)_3$ complexes the yield remained unaltered, but at 80 °C the α-substitution product **3a** was obtained in high yields (75–80%, Table 1, entries 5–7). The ^1H NMR of the reaction crude showed that the reaction proceeds with high regioselectivity (the γ-substitution product was undetectable) and without isomerization of the double bond. When the reaction conditions were extended to other cinnamyl derivatives such as chloride (**2b**) and acetate (**2c**) the α-coupling product **3a** was obtained as a single product with high yields (77–84%) using several Pd(0) or Pd(II) complexes (Table 1, entries 8–13).[13] Besides the high efficiency and regioselectivity observed, it is interesting to note that $PhAuPPh_3$ is a stable reagent at air atmosphere and the reaction with cinnamyl acetate (**2c**) can be performed in aqueous media (1 : 1, THF/H_2O) with similar yield (85%, Table 1, entry 14).

Encouraged by these results, we explored the versatility of the reaction using substituted arylgold reagents. In this case we found that the reaction of *o*-methoxyphenyl (**1b**), *p*-trifluoromethylphenyl (**1c**) and *m*-nitrophenyl (**1d**) gold phosphanes with (*E*)-cinnamyl bromide gave regioselectively the *trans* α-substituted products **3b–d** in high yields (76–93%, Table 2, entries 1–3). Analogously, the reaction using the heteroarylgold(I) reagent **1e**, furnished with the furyl group, afforded the coupling product **3e** in 56% yield (Table 2, entry 4). In this way we demonstrate that the allylic cross-coupling can be efficiently performed with *ortho*-, *meta*- and *para*-substituted arylgold reagents furnished with electron donating or withdrawing groups.

Our next step was to study the reactivity of alkenylgold(I) organometallics. Under the previously developed conditions, the reaction of vinylgold(I) phosphane **1f** with cinnamyl bromide gave the 1,4-diene **3f** in 75% yield as a single reaction product without isomerization by ^1H NMR (Table 2, entry 5). Likewise, the cross-coupling reaction using the stereodefined (*E*/*Z* = 82 : 18) 1-heptenylgold phosphane **1g**, proceeded efficiently to give the (1*E*,4*E*)-diene **3g** in 87% as major stereoisomer with retention of the configuration (4*E*/4*Z* = 82 : 18, Table 2, entry 6). When the reaction was performed using the styrylgold reagent **1h** (*E*/*Z* = 92 : 8), the coupling product **3h** (4*E*/4*Z* = 91 : 9) was also obtained stereospecifically in 90% yield (Table 2, entry 7). These results are particularly interesting since several alkenylgold species have been isolated as intermediates in different gold-catalyzed reactions, and the development of metal-catalyzed tandem reactions using one or two metals is an attractive goal in organic synthesis.[6]

In the course of our research we also tested the ability of organogold reagents for transferring alkynyl and alkyl groups to allylic electrophiles under palladium catalysis. However, the reaction of phenylethynyl(triphenylphosphine)gold (**1i**) with cinnamyl bromide at 80 °C using 5 mol % of $Pd(PPh_3)_2Cl_2$, only led to the diyne resulting from dimerization of the organogold reagent. The same result was reproduced using $Pd_2(dba)_3$ as catalyst and when cinnamyl chloride or acetate were used as electrophiles. This reactivity contrasts with the high efficiency exhibited by **1i** in the palladium-catalyzed cross-coupling reaction with aryl, benzyl and benzoyl electrophiles.[8] On the other hand, we studied the reactivity of alkylgold reagents using n-butyl(triphenylphosphine)gold (**1j**). In this case, the reaction of **1j** with cinnamyl bromide provided the reductive homocoupling of the starting bromide in 76% yield.[14] A result related with the reductive dimerization observed in the palladium-catalyzed cross-coupling of **1j** with 4-iodotoluene.[8]

To study the regio- and stereoselectivity of the allylic substitution reaction using organogold(I) reagents, 1-phenylallyl



Scheme 1 Reaction of phenyl(triphenylphosphine)gold with 1-phenylallyl acetate (**4**) and (*Z*)-cinnamyl bromide (**5**).

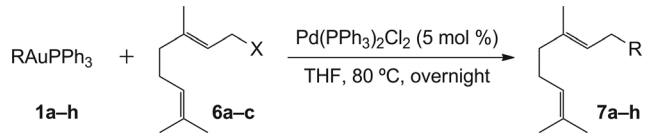
acetate (**4**) and (*Z*)-cinnamyl bromide (**5**)[15] were chosen as allylic electrophiles. Interestingly, the palladium-catalyzed reaction of **1a** with **4** afforded the S_N2' type product (**3a**) in 90% yield as the only regioisomer (Scheme 1). Moreover, the reaction of **1a** with **5** provided the α-coupling product (S_N2) in high yield (93%), but with complete isomerization of the double bond to the most stable *trans* isomer. These results support the formation of a π-allylpalladium intermediate during the cross-coupling reaction.

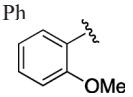
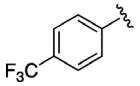
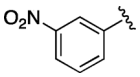
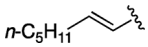
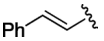
To expand the scope of the methodology, we tested the reactivity of aliphatic allylic electrophiles such as geranyl bromide (**6a**), a substrate previously explored in metal-catalyzed cross-coupling reactions of organometallic reagents with allylic eletrophiles.[11] Under the previously developed conditions, the reaction of $PhAuPPh_3$ with **6a** in the presence of $Pd(PPh_3)_2Cl_2$ (5 mol%) as catalyst afforded the α-coupling product **7a** in 60% yield as major regioisomer with only traces (less than 2% by ^1H NMR) of the γ-coupling product (Table 3, entry 1). Analogously, the reaction using geranyl chloride or acetate as electrophiles provided similar yields and other reaction conditions varying the catalyst [$Pd(PPh_3)_2Cl_2$ or $Pd_2(dba)_3$], or the temperature did not improve the efficiency of the tranformation (50% and 52%, Table 3, entries 2 and 3, respectively). The reaction of the arylgold reagents **1b–e** with geranyl bromide provided the α-cross-coupling products in moderate yields (40–51%, Table 3, entries 4–7). However, the reaction using the heptenylgold reagent **1g** afforded the (*E*,*E*)-1,4-diene (*E*/*Z* = 84 : 16) coupling product stereoselectively in 89% yield, and using the (*E*)-styrylgold phosphane **1h** the coupling product **7h** (*E*/*Z* = 92 : 8) was isolated in 54% yield (Table 3, entries 8 and 9).

In an effort to determine if the additional olefin present in the geranyl derivatives was responsible for the lower isolated yields, we also tested the reactivity of allylic bromide derived from phytol.[16] However, the reaction of $PhAuPPh_3$ provided the S_N2 product in a similar yield (61%), what seems to indicate that the lower yields obtained with geranyl derivatives can also be attributed to the structure of the allylic moiety.

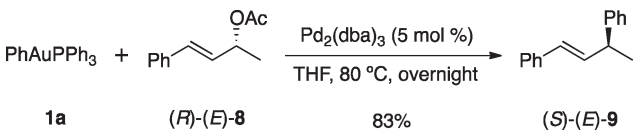
To gain insight into the reaction mechanism of this palladium-catalyzed allylic substitution, we tested the reactivity of the organogold reagents with the enantiomerically pure (>99% ee) secondary acetate (*R*)-(*E*)-**8**.[17] In this case, the reaction of $PhAuPPh_3$ with (*R*)-(*E*)-**8**, using Pd_2dba_3 (5 mol %) at 80 °C proceeded efficiently to afford the α-coupling product (*S*)-(*E*)-**9** (>99% ee) in 83% yield with complete inversion of the configuration (Scheme 2).[13,18] This stereochemical result is coherent with the general mechanism proposed for palladium-catalyzed allylic substitution using organometallic reagents,[19] and can be explained through a nucleophilic addition of the Pd(0) catalyst with inversion, followed by a transmetallation and reductive elimination with retention of configuration. In addition, these results demonstrate the efficiency of the palladium-catalyzed cross-coupling of organogold reagents with secondary allylic acetates.

Table 3 Reaction of organogold(I) phosphanes with geranyl derivatives



Entry	X	R		Product	Yield (%)[a]
1	Br (**6a**)	Ph	(**1a**)	**7a**	60
2	Cl (**6b**)	Ph	(**1a**)	**7a**	50
3	OAc (**6c**)	Ph	(**1a**)	**7a**	52
4	Br (**6a**)		(**1b**)	**7b**	51
5	Br (**6a**)		(**1c**)	**7c**	45
6	Br (**6a**)		(**1d**)	**7d**	40
7	Br (**6a**)		(**1e**)	**7e**	40
8	Br (**6a**)		(**1g**)[b]	**7g**[c]	89
9	Br (**6a**)		(**1h**)[d]	**7h**[e]	54

[a] Isolated yield. [b] As a *E*/*Z* (82 : 18) mixture by ^1H NMR. [c] As a *E*/*Z* (84 : 16) mixture by ^1H NMR. [d] As a *E*/*Z* (92 : 8) mixture by ^1H NMR. [e] As a *E*/*Z* (92 : 8) mixture by ^1H NMR.



Scheme 2 Reaction of phenyl(triphenylphosphine)gold with secondary acetate (*R*)-(*E*)-**8**.

Conclusions

In summary, we have shown that aryl- and alkenylgold(I) phosphanes react regio- and stereoselectively with allylic electrophiles such as cinnamyl halides and acetates and geranyl bromide, under palladium catalysis at 80 °C, to afford the α-substituted cross-coupling product, in moderate to good yields. When the reaction is performed with an enantiomerically pure secondary acetate, the α-substituted product is obtained with inversion of configuration. These results support the use of the aryl and alkenylgold intermediates of gold-catalyzed reactions in allylic palladium-catalyzed cross-coupling reactions. The main features of this methodology relay in the air stability of the

organogold reagents what opens the posibility to perform cross-coupling reaction in water and in the presence of wide number of functional groups. Further developments of this methodology are currently underway in our laboratories.

Experimental

General methods

Unless otherwise is stated, all reactions were conducted in flame-dried glassware under a positive pressure of argon. Reaction temperatures refer to external bath temperatures. Anhydrous THF was obtained by distillation from the sodium/benzophenone. All other commercially available reagents were used as received. Organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated by using a rotary evaporator at aspirator pressure (20–30 mmHg). TLC was effected on silica gel 60 F_{254} (layer thickness 0.2 mm) and components were located by observation under UV light and/or by treating the plates with a phosphomolybdic acid, or *p*-anisaldehyde reagent followed by heating. Column chromatography was performed on silica gel (230–400 mesh).[20] NMR spectra were performed in a Bruker Avance 300 spectrometer using the residual solvent signal as internal standard. DEPT was used to assign carbon types. The low resolution electron-impact mass spectra were measured on a Thermo Finnigan Trace MS spectrometer at 70 eV. The high resolution mass spectra were measured on a Thermo Finnigan MAT 95XP spectrometer. Infrared spectra were taken with a Bruker Vector 22 and with ATR ("attenuated total reflectance"). Optical rotation values were determined at room temperature in a JASCO DIP-1000 Digital polarimeter. HPLC analyses were performed on an Agilent 1200 Series system by using a Daicel CHIRALCEL OD-H column (0.46 cm Ø × 25 cm).

General procedure for the preparation of organogold compounds

To a cooled solution of Ph_3PAuCl (75 mg, 0.152 mmol) in dry THF (3 mL) at −20 °C, a solution of RLi or RMgBr (0.182 mmol, 1.0–2.0 M) in THF was added dropwise. The mixture was stirred 20 min, the cooling bath was removed, and the reaction mixture stirred for 1 h at room temperature. The solvent was evaporated under reduced pressure and benzene (5 mL) was added. The mixture was filtered through Celite, concentrated at reduced pressure to dryness, washed with pentane and dried. The solid was re-extracted with a minimum of benzene, filtered, washed with pentane and dried under high-vacuum.

Phenyl(triphenylphosphine)gold (1a)[21]

Following the general procedure, **1a** was isolated as a white powder (74.8 mg, 0.139 mmol, 92%). M.p. 160–161 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 6.88–6.97 (m, 9H), 7.26 (t, J = 7.4 Hz, 1H), 7.37–7.44 (m, 6H), 7.52 (t, J = 7.5 Hz, 2H), 8.11 (d, J = 7.0 Hz, 2H) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ 125.9 (s, 2 × CH), 127.5 (s, 3 × C), 127.7 (s, C), 127.7 (br s, 2 × CH), 128.7 (d, J (C,P) = 10.5 Hz, 6 × CH), 130.6 (br s, CH), 134.2 (d, J (C, P) = 13.9 Hz, 6 × CH), 140.0 (s, 3 × CH) ppm; ^{31}P NMR (121.5 MHz, C_6D_6) δ 43.99 (s) ppm; IR (ATR) 3051, 3006, 2922, 2851, 1571, 1478, 1434 cm^{-1}; MS (EI) m/z (%): 536 (M^+, 71), 459 (M^+ − C_6H_5, 100); HRMS (EI) m/z: calcd for $C_{24}H_{20}PAu$ (M^+) 536.0963, found 536.0944.

2-Methoxyphenyl(triphenylphosphine)gold (1b)

Following the general procedure, **1b** was isolated as a white powder (69.3 mg, 0.122 mmol, 81%). M.p. 140–142 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 3.65 (s, 3H), 6.89–7.00 (m, 10H), 7.22–7.33 (m, 2H), 7.44–7.51 (m, 6H), 8.09 (dt, J (C,P) = 1.9, 6.5 Hz, 1H) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ 55.0 (s, CH_3), 110.0 (d, J (C,P) = 4.3 Hz, CH), 120.9 (d, J (C,P) = 6.0 Hz, CH), 126.6 (s, CH), 128.7 (d, J (C,P) = 10.6 Hz, 6 × CH), 130.5 (d, J (C,P) = 2.1 Hz, 3 × CH), 131.6 (d, J (C,P) = 48.8 Hz, 3 × C), 134.3 (d, J (C,P) = 13.8 Hz, 6 × CH), 140.2 (s, CH), 160.5 (d, J (C,P) = 112.8 Hz, C), 166.1 (d, J (C,P) = 0.9 Hz, C) ppm; ^{31}P NMR (121.5 MHz, C_6D_6) δ 44.25 (s) ppm; IR (ATR) 3054, 2944, 2828, 1566, 1479 cm^{-1}; MS (EI) m/z (%): 566 (M^+, 1), 459 (M^+ − C_7H_7O, 2), 262 (M^+ − C_7H_7OAu, 100); HRMS (EI) m/z: calcd for $C_{25}H_{22}OPAu$ (M^+) 566.1068, found 566.1063.

4-Trifluoromethylphenyl(triphenylphosphine)gold (1c)[6c]

Following the general procedure, **1c** was isolated as a brown powder (72.6 mg, 0.120 mmol, 79%). M.p. 155–157 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 6.91–6.99 (m, 9H), 7.33–7.41 (m, 6H), 7.66 (d, J = 7.7 Hz, 2H), 7.95 (t, J = 6.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ 123.6 (m, 2 × CH), 127.6 (s, 3 × C), 128.9 (d, J (C,P) = 10.9 Hz, 6 × CH), 130.5 (s, C), 130.8 (d, J (C,P) = 2.1 Hz, 2 × CH), 131.2 (s, C), 134.2 (d, J (C,P) = 13.7 Hz, 6 × CH), 139.9 (s, 3 × CH), 178.3 (d, J (C,P) = 116.8 Hz, C) ppm; ^{31}P NMR (121.5 MHz, C_6D_6) δ 43.62 (s) ppm; IR (ATR) 3057, 1591, 1556, 1479, 1322 cm^{-1}; MS (EI) m/z (%): 604 (M^+, 1), 459 (M^+ − $C_7H_4F_3$, 3), 262 (M^+ − $C_7H_4F_3Au$, 100); HRMS (EI) m/z: calcd for $C_{25}H_{19}F_3PAu$ (M^+) 604.0837, found 604.0808.

3-Nitrophenyl(triphenylphosphine)gold (1d)[21]

Cs_2CO_3 (236.9 mg, 0.727 mmol) and Ph_3PAuCl (180 mg, 0.363 mmol) were added successively to a solution of 3-nitrophenylboronic acid (121.4 mg, 0.727 mmol) in dry isopropyl alcohol (5 mL). The resultant white suspension was stirred at 50 °C for 24 h and taken to dryness *via* rotary evaporation. The solid was extracted with benzene, filtered through Celite, concentrated *in vacuo* to dryness, washed with pentane and dried. The solid was re-extracted with a minimum of benzene, filtered, washed with pentane and dried under high-vacuum, to give the organogold phosphane **1d** as a white powder (192.5 mg, 0.331 mmol, 91%). M.p. 170–171 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (dd, J = 7.3, 8.1 Hz, 1H), 7.46–7.64 (m, 15H), 7.87–7.94 (m, 2H), 8.45 (br s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 120.5 (s, CH), 127.5 (s, CH), 129.2 (d, J (C,P) = 10.8 Hz, 6 × CH), 130.2 (s, C), 130.9 (s, C), 131.3 (d, J (C,P) = 2.2 Hz, CH), 133.5 (s, CH), 134.3 (d, J (C,P) = 13.8 Hz, 6 × CH), 146.0 (s, 3 × CH), 147.5 (s, 3 × C) ppm; ^{31}P NMR (121.5 MHz,

$CDCl_3$) δ 43.36 (s) ppm; IR (ATR) 3052, 2923, 2852, 1509, 1479, 1435 cm^{-1}; MS (EI) *m/z* (%): 581 (M^+, 3), 459 ($M^+ - C_6H_4NO_2$, 12), 262 ($M^+ - C_7H_4F_3Au$, 100); HRMS (EI) *m/z*: calcd for $C_{24}H_{19}NO_2PAu$ (M^+) 581.0813, found 581.0823.

2-Furyl(triphenylphosphine)gold (1e)[22]

Following the general procedure, **1e** was isolated as a white powder (74.2 mg, 0.141 mmol, 93%). M.p. 157–159 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 6.68 (dd, J = 1.6, 3.0 Hz, 1H), 6.83–7.00 (m, 10H), 7.25–7.33 (m, 6H), 7.90 (d, J = 1.5 Hz, 1H) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ 108.4 (s, CH), 118.9 (br s, CH), 127.6 (s, 3 × C), 128.8 (d, J (C,P) = 10.8 Hz, 6 × CH), 130.6 (d, J (C,P) = 2.3 Hz, 51.5 Hz, C), 130.8 (d, J (C,P) = 2.3 Hz, CH), 134.2 (d, J (C,P) = 13.8 Hz, 6 × CH), 144.2 (s, 3 × CH) ppm; ^{31}P NMR (121.5 MHz, C_6D_6) δ 43.90 (s) ppm; IR (ATR) 3062, 1478, 1433, 1350 cm^{-1}; MS (EI) *m/z* (%): 526 (M^+, 1), 459 ($M^+ - C_4H_3O$, 2), 262 ($M^+ - C_4H_3OAu$, 100); HRMS (EI) *m/z*: calcd for $C_{22}H_{18}OPAu$ (M^+) 526.0755, found 526.0740.

Ethenyl(triphenylphosphine)gold (1f)[6c]

Following the general procedure, **1f** was isolated as a white powder (66.5 mg, 0.137 mmol, 90%). M.p. 124–125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.49–5.57 (dd, J = 4.9, 20.7 Hz, 1H), 6.00–6.07 (dd, J = 4.9, 14.0 Hz, 1H), 7.15–7.26 (dd, J = 14.0, 20.7 Hz, 1H), 7.41–7.59 (m, 15H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.0 (d, J (C,P) = 10.9 Hz, 6 × CH), 130.7 (d, J (C,P) = 51.2 Hz, 3 × C), 131.2 (d, J (C,P) = 2.1 Hz, 3 × CH), 131.4 (s, CH_2), 134.3 (d, J (C,P) = 13.7 Hz, 6 × CH), 168.0 (m, CH) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 45.09 (s) ppm; IR (ATR) 3638, 3055, 2955, 1480, 1434 cm^{-1}; MS (EI) *m/z* (%): 486 (M^+, 5), 459 ($M^+ - C_2H_3$, 17), 262 ($M^+ - C_2H_3Au$, 100); HRMS (EI) *m/z*: calcd for $C_{20}H_{18}PAu$ (M^+) 486.0806, found 486.0804.

(*E*)-1-Hepten-1-yl(triphenylphosphine)gold (1g)

Following the general procedure, a solution of (*E*)-1-heptenyllithium, prepared from (*E*)-1-iodo-1-heptene (40.8 mg, 0.182 mmol, *E*/*Z* 82 : 18) and *t*BuLi (0.215 mL, 1.7 M in pentane, 0.364 mmol), was added to a solution of Ph_3PAuCl (90 mg, 0.182 mmol) in THF (3 mL) and the resulting organogold phosphane **1g** was used directly in the palladium-catalyzed cross-coupling reaction. Alternatively, **1g** can be prepared from (*E*)-1-heptenylboronic acid: Cs_2CO_3 (105.4 mg, 0.323 mmol) and Ph_3PAuCl (80 mg, 0.161 mmol) were added successively to a solution of (*E*)-1-heptenylboronic acid (45.9 mg, 0.323 mmol) in dry isopropyl alcohol (5 mL). The resultant white suspension was stirred at 50 °C for 24 h and taken to dryness *via* rotary evaporation. The solid was extracted with benzene, filtered through Celite, concentrated *in vacuo* to dryness, washed with pentane and dried. The solid was re-extracted with a minimum of benzene, filtered, washed with pentane and dried under high-vacuum, to give the organogold phosphane **1g** as a pale brown solid (80.7 mg, 0.145 mmol, 90%). M.p. 91–93 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 0.87 (t, J = 7.2 Hz, 3H), 1.26–1.49 (m, 4H), 1.61–1.71 (m, 2H), 2.56 (q, J = 6.9 Hz, 2H), 6.43–6.56 (m, 1H), 6.85–6.97 (m, 9H), 7.35–7.43 (m, 6H), 7.53 (dd, J = 18.4, 5.1 Hz, 1H) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ 14.0 (s, CH_3), 22.8 (s, 2 × CH_2), 30.2 (s, CH_2), 31.7 (s, CH_2), 128.7 (d, J (C,P) = 10.5 Hz, 6 × CH), 130.5 (s, CH), 131.7 (d, J (C,P) = 47.2 Hz, 3 × C), 134.2 (d, J (C,P) = 13.8 Hz, 6 × CH), 144.4 (s, CH), 146.4 (s, 3 × CH) ppm; ^{31}P NMR (121.5 MHz, C_6D_6) δ 45.41 (s) ppm; IR (ATR) 3053, 2952, 2916, 2849, 1583, 1479 cm^{-1}; MS (EI) *m/z* (%): 556 (M^+, 1), 459 ($M^+ - C_7H_{13}$, 2), 262 ($M^+ - C_7H_{13}Au$, 100).

(*E*)-2-Phenylethenyl(triphenylphosphine)gold (1h)[21]

Following the general procedure, **1h** was isolated as a brown powder (81.2 mg, 0.144 mmol, 95%, *E*/*Z* 92 : 8). M.p. 144–146 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 6.88–6.97 (m, 9H), 7.04 (t, J = 7.3 Hz, 1H), 7.21 (t, J = 7.6 Hz, 2H), 7.31–7.45 (m, 6H), 7.51 (d, J = 19.2 Hz, 1H), 7.66 (d, J = 7.3 Hz, 2H), 8.49 (d, J = 19.2 Hz, 1H) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ 125.8 (s, 2 × CH), 126.0 (s, CH), 128.0 (s, 3 × C), 128.4 (s, 2 × CH), 128.8 (d, J (C,P) = 10.6 Hz, 6 × CH), 130.7 (d, J (C,P) = 1.8 Hz, 2 × CH), 134.2 (d, J (C,P) = 13.8 Hz, 6 × CH), 141.4 (s, C), 144.4 (s, 3 × CH) ppm; ^{31}P NMR (121.5 MHz, C_6D_6) δ 45.21 (s) ppm; IR (ATR) 3052, 2010, 1593, 1551, 1478 cm^{-1}; MS (EI) *m/z* (%): 562 (M^+, 1), 459 ($M^+ - C_8H_7$, 4), 262 ($M^+ - C_8H_7Au$, 100); HRMS (EI) *m/z*: calcd for $C_{26}H_{22}PAu$ (M^+) 562.1125, found 562.1121.

2-Phenylethynyl(triphenylphosphine)gold (1i)[23]

Following the general procedure, **1i** was isolated as a white powder (84.3 mg, 0.150 mmol, 99%). M.p. 161–162 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 6.84–6.98 (m, 9H), 7.02–7.08 (m, 3H), 7.19–7.26 (m, 6H), 7.84 (d, J = 7.9 Hz, 2H) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ 126.1 (s, CH), 127.5 (s, C), 127.8 (s, C), 128.1 (d, J (C,P) = 12.2 Hz, CH), 128.8 (d, J (C,P) = 11.2 Hz, CH), 129.9 (s, C), 130.6 (s, C), 130.8 (d, J (C,P) = 2.2 Hz, CH), 132.4 (s, CH), 134.1 (d, J (C,P) = 13.9 Hz, CH) ppm; ^{31}P NMR (121.5 MHz, C_6D_6) δ 41.98 (s) ppm; IR (ATR) 3053, 2923, 2357, 1595, 1483, 1435, 1331 cm^{-1}; MS (EI) *m/z* (%): 560 (M^+, 18), 459 ($M^+ - C_8H_5$, 1), 404 (100); HRMS (EI) *m/z*: calcd for $C_{26}H_{20}PAu$ (M^+) 560.0963, found 560.0985.

Butyl(triphenylphosphine)gold (1j)[24]

Following the general procedure, **1j** was isolated as a colorless oil (64.7 mg, 0.125 mmol, 83%).^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, J = 7.3 Hz, 3H), 1.43–1.55 (m, 4H), 1.82–1.96 (m, 4H), 7.42–7.59 (m, 15H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3 (s, CH_3), 29.5 (d, J (C,P) = 5.3 Hz, CH_2), 30.8 (d, J (C,P) = 94.9 Hz, CH_2), 34.1 (d, J (C,P) = 3.8 Hz, CH_2), 128.9 (d, J (C,P) = 10.3 Hz, CH), 130.7 (d, J (C,P) = 2.1 Hz, CH), 131.8 (d, J (C,P) = 45.1 Hz, C), 134.3 (d, J (C,P) = 13.7 Hz, CH) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 46.37 (s) ppm; IR (ATR) 3640, 2952, 2914, 2867, 1479, 1434, 1381 cm^{-1}; MS (EI) *m/z* (%): 516 (M^+, 7), 487 ($M^+ - C_2H_5$, 15), 459 ($M^+ - C_4H_9$, 100); HRMS (EI) *m/z*: calcd for $C_{22}H_{24}PAu$ (M^+) 516.1276, found 516.1251.

General procedure for the allylic palladium-catalyzed cross-coupling reaction

To a mixture of the allylic substrate (1.0 equiv) and palladium catalyst (5 mol %) in dry THF (4 mL), a THF solution of freshly prepared $RAuPPh_3$ (1.1 equiv) was added. The resulting mixture was stirred at 80 °C under argon overnight until the starting material was consumed (TLC). The reaction mixture was concentrated under reduced pressure and Et_2O (20 mL) was added. The ethereal phase was washed with brine (10 mL), dried with $MgSO_4$, filtered, and concentrated to a reduced volume at reduced pressure. The residue was purified by flash chromatography to afford, after concentration and high-vacuum drying, the corresponding allylic substitution product in the reported yield.

(*E*)-1,3-Diphenylpropene (3a)[11b]

Following the general procedure, **3a** was obtained as a colorless oil (20.0 mg, 0.103 mmol, 75% from cinnamyl bromide; 22.4 mg, 0.115 mmol, 84% from cinnamyl chloride; 22.2 mg, 0.114 mmol, 83% from cinnamyl acetate).^{1}H NMR (300 MHz, $CDCl_3$) δ 3.58 (d, J = 6.3 Hz, 2H), 6.39 (dt, J = 6.3, 15.7 Hz, 1H), 6.49 (d, J = 15.8 Hz, 1H), 7.20–7.41 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.4 (CH_2), 126.1 (2 × CH), 126.2 (CH), 127.1 (CH), 128.5 (4 × CH), 128.7 (2 × CH), 129.2 (CH), 131.1 (CH), 137.5 (C), 140.2 (C) ppm; IR (ATR) 3059, 3025, 2897, 1600, 1494, 1451 cm^{-1}; MS (EI) m/z (%): 194 (M^+, 64), 117 ($M^+ - C_6H_5$, 50); HRMS (EI) m/z: calcd for $C_{15}H_{14}$ (M^+) 194.1090, found 194.1092.

(*E*)-1-Phenyl-3-(2-methoxyphenyl)propene (3b)[25]

Following the general procedure, **3b** was obtained as a colorless oil (28.7 mg, 0.128 mmol, 93%).^{1}H NMR (300 MHz, $CDCl_3$) δ 3.57 (d, J = 5.3 Hz, 2H), 3.87 (s, 3H), 6.36–6.50 (m, 2H), 6.89–6.96 (m, 2H), 7.18–7.40 (m, 7H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.4 (CH_2), 55.4 (CH_3), 110.4 (CH), 120.6 (CH), 126.1 (2 × CH), 126.9 (CH), 127.4 (CH), 128.4 (2 × CH), 128.9 (CH), 129.9 (CH), 130.7 (CH), 137.8 (C), 157.3 (C) ppm; IR (ATR) 3025, 2923, 2852, 1599, 1492, 1463, 1437 cm^{-1}; MS (EI) m/z (%): 224 (M^+, 100), 193 ($M^+ - CH_3O$, 37); HRMS (EI) m/z: calcd for $C_{16}H_{16}O$ (M^+) 224.1196, found 224.1194.

(*E*)-1-Phenyl-3-(4-trifluoromethylphenyl)propene (3c)[26]

Following the general procedure, **3c** was obtained as a colorless oil (25.9 mg, 0.099 mmol, 76%).^{1}H NMR (300 MHz, $CDCl_3$) δ 3.62 (d, J = 6.7 Hz, 2H), 6.34 (dt, J = 6.7, 15.8 Hz, 1H), 6.50 (d, J = 15.8 Hz, 1H), 7.21–7.40 (m, 7H), 7.59 (d, J = 8.0 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.1 (CH_2), 125.4 (q, J = 3.8 Hz, CF_3), 125.4 (C), 126.2 (4 × CH), 127.4 (CH), 127.9 (CH), 128.6 (2 × CH), 128.9 (2 × CH), 131.9 (CH), 137.1 (C), 144.3 (d, J = 1.3 Hz, C) ppm; IR (ATR) 3029, 1620, 1601, 1497, 1323 cm^{-1}; MS (EI) m/z (%): 262 (M^+, 100), 193 ($M^+ - CF_3$, 25); HRMS (EI) m/z: calcd for $C_{16}H_{13}F_3$ (M^+) 262.0964, found 262.0957.

(*E*)-1-Phenyl-3-(3-nitrophenyl)propene (3d)[27]

Following the general procedure, **3d** was obtained as a white powder (32.0 mg, 0.134 mmol, 83%). M.p. 53–54 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (d, J = 6.9 Hz, 2H), 6.33 (dt, J = 6.9, 15.8 Hz, 1H), 6.52 (d, J = 15.8 Hz, 1H), 7.21–7.39 (m, 5H), 7.49 (t, J = 7.8 Hz, 1H), 7.59 (d, J = 7.7 Hz, 1H), 8.02–8.14 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.9 (CH_2), 121.4 (CH), 123.5 (CH), 126.2 (2 × CH), 127.2 (CH), 127.5 (CH), 128.6 (2 × CH), 129.3 (CH), 132.5 (CH), 134.9 (CH), 136.9 (C), 142.2 (C), 148.5 (C) ppm; IR (ATR) 3026, 2923, 2853, 1525, 1349 cm^{-1}; MS (EI) m/z (%): 239 (M^+, 100), 193 ($M^+ - NO_2$, 21); HRMS (EI) m/z: calcd for $C_{15}H_{13}NO_2$ (M^+) 239.0941, found 239.0942.

(*E*)-1-Phenyl-3-(furan-2-yl)propene (3e)[28]

Following the general procedure, **3e** was obtained as a colorless oil (11.6 mg, 0.063 mmol, 56%).^{1}H NMR (300 MHz, $CDCl_3$) δ 3.57 (d, J = 6.7 Hz, 2H), 6.09 (dd, J = 0.8, 3.2 Hz, 1H), 6.27–6.38 (m, 2H), 6.51 (d, J = 15.8 Hz, 1H), 7.20–7.40 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.8 (CH_2), 105.6 (CH), 110.3 (CH), 125.6 (CH), 126.2 (2 × CH), 127.3 (CH), 128.5 (2 × CH), 132.0 (CH), 137.2 (C), 141.4 (CH), 153.9 (C) ppm; IR (ATR) 3082, 3059, 3027, 1596, 1504, 1448 cm^{-1}; MS (EI) m/z (%): 184 (M^+, 100), 155 ($M^+ - CHO$, 31); HRMS (EI) m/z: calcd for $C_{13}H_{12}O$ (M^+) 184.0883, found 184.0874.

(*E*)-1-Phenyl-1,4-pentadiene (3f)[11b]

Following the general procedure, **3f** was obtained as a colorless oil (13.3 mg, 0.092 mmol, 75%).^{1}H NMR (300 MHz, $CDCl_3$) δ 2.98 (tc, J = 1.4, 6.5 Hz, 2H), 5.05–5.17 (m, 2H), 5.86–5.99 (m, 1H), 6.24 (dt, J = 6.5, 15.8 Hz, 1H), 6.43 (d, J = 15.8 Hz, 1H), 7.18–7.39 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.0 (CH_2), 115.7 (CH_2), 126.0 (2 × CH), 127.0 (CH), 128.2 (CH), 128.5 (2 × CH), 130.8 (CH), 136.5 (CH), 137.6 (C) ppm; IR (ATR) 3080, 3061, 3026, 2924, 2853, 1736 cm^{-1}; MS (EI) m/z (%): 144 (M^+, 53), 129 ($M^+ - CH_3$, 100); HRMS (EI) m/z: calcd for $C_{11}H_{12}$ (M^+) 144.0934, found 144.0927.

(1*E*,4*E*)-1-Phenyl-1,4-decadiene (3g)

Following the general procedure, **3g** was obtained as a colorless oil (23.6 mg, 0.110 mmol, 87%, 4*E*/4*Z* 82 : 18).^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J = 6.8 Hz, 3H), 1.25–1.44 (m, 6H), 2.00–2.07 (m, 2H), 2.90–2.94 (m, 2H), 5.44–5.59 (m, 2H), 6.24 (dt, J = 6.5, 15.8 Hz, 1H), 6.41 (d, J = 15.8 Hz, 1H), 7.18–7.39 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.6 (CH_2), 29.2 (CH_2), 31.4 (CH_2), 32.6 (CH_2), 35.9 (CH_2), 126.0 (2 × CH), 126.9 (CH), 127.5 (CH), 128.5 (2 × CH), 129.4 (CH), 130.2 (CH), 132.1 (CH), 137.8 (C) ppm; IR (ATR) 3025, 2955, 2923, 2871, 2854, 1494, 1448 cm^{-1}; MS (EI) m/z (%): 214 (M^+, 47), 143 ($M^+ - C_5H_{11}$, 100), 130 ($M^+ - C_6H_{12}$, 43); HRMS (EI) m/z: calcd for $C_{16}H_{22}$ (M^+) 214.1716, found 214.1711.

(1*E*,4*E*)-1,5-Diphenyl-1,4-pentadiene (3h)[29]

Following the general procedure, **3h** was obtained as a colorless oil (29.7 mg, 0.135 mmol, 90%, 4*E*/4*Z* 91 : 9).^{1}H NMR (300 MHz, $CDCl_3$) δ 3.14 (t, J = 6.5 Hz, 2H), 6.31 (dt, J = 6.5, 15.8 Hz, 2H), 6.49 (d, J = 15.8 Hz, 2H), 7.20–7.41 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.2 (CH_2), 126.1 (4 × CH), 127.1 (2 × CH), 128.2 (2 × CH), 128.5 (4 × CH), 131.0 (2 × CH), 137.6 (2 × C) ppm; IR (ATR) 3080, 3058, 3024, 1648, 1597, 1494, 1446 cm^{-1}; MS (EI) *m*/*z* (%): 220 (M^+, 100), 129 ($M^+ - C_7H_7$, 43); HRMS (EI) *m*/*z*: calcd for $C_{17}H_{16}$ (M^+) 220.1247, found 220.1245.

(*E*)-1,4-Diphenyl-1,5-hexadiene (3j)[14a]

Following the general procedure, **3j** was obtained as a colorless oil (14.2 mg, 0.061 mmol, 76%).^{1}H NMR (300 MHz, $CDCl_3$) δ 2.66 (br t, J = 7.2 Hz, 2H), 3.45 (q, J = 7.4 Hz, 1H), 5.02–5.12 (m, 2H), 5.99–6.19 (m, 2H), 6.40 (br d, J = 15.8 Hz, 1H), 7.17–7.36 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.0 (CH_2), 50.0 (CH), 114.7 (CH_2), 126.0 (2 × CH), 126.3 (CH), 126.9 (CH), 127.7 (2 × CH), 128.4 (2 × CH), 128.5 (2 × CH), 131.4 (2 × CH), 137.6 (C), 141.5 (CH), 143.7 (C) ppm; IR (ATR) 3059, 2975, 2360, 2340, 1636, 1493 cm^{-1}; MS (EI) *m*/*z* (%): 234 (M^+, 15), 117 ($M^+ - C_9H_9$, 97), 115 (100); HRMS (EI) *m*/*z*: calcd for $C_{18}H_{18}$ (M^+) 234.1403, found 234.1395.

(*E*)-3,7-Dimethyl-1-phenyl-2,6-octadiene (7a)[11b]

Following the general procedure, **7a** was obtained as colorless oil (19.0 mg, 0.089 mmol, 60% from geranyl bromide; 15.8 mg, 0.074 mmol, 50% from geranyl chloride; 16.4 mg, 0.077 mmol, 52% from geranyl acetate).^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63 (s, 3H), 1.71 (s, 3H), 1.74 (s, 3H), 2.06–2.18 (m, 4H), 3.39 (d, J = 7.3 Hz, 2H), 5.11–5.18 (m, 1H), 5.34–5.40 (m, 1H), 7.17–7.22 (m, 3H), 7.27–7.33 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.1 (CH_3), 17.7 (CH_3), 25.7 (CH_3), 26.6 (CH_2), 34.2 (CH_2), 39.7 (CH_2), 123.0 (CH), 124.3 (CH), 125.7 (CH), 128.3 (2 × CH), 128.3 (2 × CH), 131.5 (C), 136.2 (C), 141.8 (C) ppm; IR (ATR) 3029, 2968, 2916, 2856, 1495, 1453 cm^{-1}; MS (EI) *m*/*z* (%): 214 (M^+, 76), 145 ($M^+ - C_5H_9$, 100), 91 ($M^+ - C_9H_{15}$, 25); HRMS (EI) *m*/*z*: calcd for $C_{16}H_{22}$ (M^+) 214.1716, found 214.1710.

(*E*)-1-(3,7-Dimethylocta-2,6-dienyl)-2-methoxybenzene (7b)[30]

Following the general procedure, **7b** was obtained as colouless oil (13.7 mg, 0.056 mmol, 51%).^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61 (s, 3H), 1.69 (s, 3H), 1.71 (s, 3H), 2.01–2.19 (m, 4H), 3.34 (d, J = 7.3 Hz, 2H), 3.84 (s, 3H), 5.08–5.18 (m, 1H), 5.33 (t, J = 7.3 Hz, 1H), 6.84–6.92 (m, 2H), 7.13–7.24 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.0 (CH_3), 17.7 (CH_3), 25.7 (CH_3), 26.7 (CH_2), 28.1 (CH_2), 39.8 (CH_2), 55.3 (CH_3), 110.1 (CH), 120.4 (CH), 122.4 (CH), 124.4 (CH), 126.8 (CH), 129.2 (CH), 130.1 (C), 131.3 (C), 136.1 (C), 157.3 (C) ppm; IR (ATR) 2963, 2914, 1600, 1587, 1491, 1462, 1239 cm^{-1}; MS (EI) *m*/*z* (%): 244 (M^+, 34), 175 ($M^+ - C_5H_9$, 100); HRMS (EI) *m*/*z*: calcd for $C_{17}H_{24}O$ (M^+) 244.1822, found 244.1830.

(*E*)-1-(3,7-Dimethylocta-2,6-dienyl)-4-(trifluoromethyl)benzene (7c)

Following the general procedure, **7c** was obtained as colorless oil (17.0 mg, 0.060 mmol, 45%).^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61 (s, 3H), 1.69 (s, 3H), 1.71 (s, 3H), 2.06–2.18 (m, 4H), 3.42 (d, J = 7.4 Hz, 2H), 5.07–5.14 (m, 1H), 5.29–5.35 (m, 1H), 7.29 (d, J = 7.9 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.1 (CH_3), 17.7 (CH_3), 25.7 (CH_3), 26.5 (CH_2), 34.0 (CH_2), 39.6 (CH_2), 121.9 (CH), 122.6 (C), 124.1 (CH), 125.2 (CH), 127.6 (CH), 128.6 (2 × CH), 131.6 (C), 137.3 (C), 145.9 (C) ppm; IR (ATR) 2967, 2918, 2856, 1618, 1321 cm^{-1}; MS (EI) *m*/*z* (%): 282 (M^+, 27), 213 ($M^+ - CF_3$, 28), 123 ($M^+ - C_8H_6F_3$, 100); HRMS (EI) *m*/*z*: calcd for $C_{17}H_{21}F_3$ (M^+) 282.1590, found 282.1587.

(*E*)-1-(3,7-dimethylocta-2,6-dien-1-yl)-3-nitrobenzene (7d)

Following the general procedure, **7d** was obtained as a yellow oil (29.0 mg, 0.112 mmol, 40%).^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61 (s, 3H), 1.69 (s, 3H), 1.73 (s, 3H), 2.05–2.19 (m, 4H), 3.47 (d, J = 7.3 Hz, 2H), 5.07–5.14 (m, 1H), 5.30–5.37 (m, 1H), 7.41–7.54 (m, 2H), 8.03–8.07 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.2 (CH_3), 17.7 (CH_3), 25.7 (CH_3), 26.5 (CH_2), 33.8 (CH_2), 39.6 (CH_2), 120.9 (CH), 121.3 (CH), 123.2 (CH), 123.9 (CH), 129.1 (CH), 132.0 (C), 134.6 (CH), 138.0 (C), 143.8 (C), 148.4 (C) ppm; IR (ATR) 2961, 2923, 2854, 1728, 1528 cm^{-1}; MS (EI) *m*/*z* (%): 259 (M^+, 9), 149 ($M^+ - C_6H_4NO_2$, 45), 69 (100); HRMS (EI) *m*/*z*: calcd for $C_{16}H_{21}NO_2$ (M^+) 259.1567, found 259.1569.

(*E*)-2-(3,7-Dimethylocta-2,6-dienyl)furan (7e)[31]

Following the general procedure, **7e** was obtained as a colorless oil (11.8 mg, 0.058 mmol, 40%).^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62 (s, 3H), 1.70 (s, 6H), 2.03–2.16 (m, 4H), 3.36 (d, J = 7.1 Hz, 2H), 5.09–5.14 (m, 1H), 5.32–5.37 (m, 1H), 5.96–5.98 (m, 1H), 6.28–6.30 (dd, J = 1.8, 3.1 Hz, 1H), 7.30–7.32 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.1 (CH_3), 17.7 (CH_3), 25.7 (CH_3), 26.6 (CH_2), 27.0 (CH_2), 39.6 (CH_2), 104.6 (CH), 110.1 (CH), 119.2 (CH), 124.1 (CH), 131.5 (C), 137.6 (C), 140.9 (CH), 155.3 (C) ppm; IR (ATR) 2966, 2920, 2855, 1594, 1505 cm^{-1}; MS (EI) *m*/*z* (%): 204 (M^+, 13), 162 ($M^+ - C_3H_6$, 2), 69 (100); HRMS (EI) *m*/*z*: calcd for $C_{14}H_{20}O$ (M^+) 204.1509, found 204.1508.

(6*E*,9*E*)-2,6-Dimethylpentadeca-2,6,9-triene (7g)

Following the general procedure, **7g** was obtained as colorless oil (26.5 mg, 0.113 mmol, 89%, 9*E*/9*Z* 84 : 16).^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 6.8 Hz, 3H), 1.25–1.40 (m, 6H), 1.61 (s, 6H), 1.69 (s, 3H), 1.95–2.13 (m, 6H), 2.70 (t, J = 5.8 Hz, 2H), 5.09–5.18 (m, 2H), 5.32–5.48 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0 (CH_3), 15.9 (CH_2), 17.7 (CH_3), 22.6 (CH_2), 25.7 (CH_3), 26.7 (CH_2), 29.3 (CH_2), 31.1 (CH_2), 31.4 (CH_2), 32.6 (CH_2), 39.7 (CH_2), 122.5 (CH), 124.3 (CH), 128.6 (CH), 130.4 (CH), 131.3 (C), 135.6 (C) ppm; IR (ATR) 2959, 2923, 2872, 2855, 1450, 1377 cm^{-1}; MS (EI) *m*/*z* (%):

234 (M^+, 68), 219 ($M^+ - CH_3$, 34), 191 ($M^+ - C_3H_7$, 87); HRMS (EI) *m/z*: calcd for $C_{17}H_{30}$ (M^+), 234.2342, found 234.2339.

(1*E*,4*E*)-(5,9-Dimethyldeca-1,4,8-trienyl)benzene (7h)[32]

Following the general procedure, **7h** was obtained as colorless oil (15.4 mg, 0.064 mmol, 54%, 1*E*/1*Z* 92 : 8).^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63 (s, 3H), 1.68 (s, 3H), 1.71 (s, 3H), 2.02–2.14 (m, 4H), 2.93 (t, J = 6.8 Hz, 2H), 5.11–5.17 (m, 1H), 5.22–5.28 (m, 1H), 6.17–6.26 (dt, J = 6.3, 15.8 Hz, 1H), 6.40 (d, J = 15.8 Hz, 1H), 7.17–7.38 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.1 (CH_3), 17,7 (CH_3), 25.7 (CH_3), 26.7 (CH_2), 31.5 (CH_2), 39.7 (CH_2), 121.4 (CH), 124.3 (CH), 125.9 (2 × CH), 126.8 (CH), 128.4 (2 × CH), 129.5 (2 × CH), 131.5 (C), 136.7 (C), 137.9 (C) ppm; IR (ATR) 2962, 2922, 2853, 1493, 1446, 1376 cm^{-1}; MS (EI) *m/z* (%): 240 (M^+, 10), 171 ($M^+ - C_5H_9$, 14), 91 (100); HRMS (EI) *m/z*: calcd for $C_{18}H_{24}$ (M^+) 240.1873, found 240.1875.

(*R*)-(*E*)-4-Phenyl-3-buten-2-ol[17]

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (d, J = 6.4 Hz, 3H), 4.51 (quint, J = 6.3 Hz, 1H), 6.28 (dd, J = 6.1, 15.9 Hz, 1H), 6.58 (d, J = 16.0 Hz, 1H), 7.22–7.41 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.4 (CH_3), 68.9 (CH), 126.4 (2 × CH), 127.6 (CH), 128.6 (2 × CH), 129.4 (CH), 133.5 (CH), 136.7 (C) ppm; IR (ATR) 3356, 3026, 2972, 2925, 1403, 1448 cm^{-1}; MS (EI) *m/z* (%): 148 (M^+, 85), 133 ($M^+ - CH_3$, 34), 105 (100); HRMS (EI) *m/z*: calcd for $C_{10}H_{12}O$ (M^+) 148.0883, found 148.0878; $[\alpha]_D^{20}$ = +33.2 (c 0.55, $CHCl_3$), lit. $[\alpha]_D^{20}$ = +31.4 (c 1.38, $CHCl_3$).

(*R*)-(*E*)-4-Phenyl-3-buten-2-yl acetate ((*R*)-(*E*)-8)[33]

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.42 (d, J = 6.5 Hz, 3H), 2.09 (s, 3H), 5.49–5.59 (m, 1H), 6.20 (dd, J = 6.7, 16.0 Hz, 1H), 6.61 (d, J = 16.0 Hz, 1H), 7.22–7.41 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.4 (CH_3), 21.4 (CH_3), 71.0 (CH), 126.5 (2 × CH), 127.9 (CH), 128.6 (2 × CH), 128.8 (CH), 131.5 (CH), 136.3 (C), 170.3 (C) ppm; IR (ATR) 3027, 2980, 2931, 1731 cm^{-1}; MS (EI) *m/z* (%): 190 (M^+, 13), 148 (100), 147 ($M^+ - C_2H_3O$, 68); HRMS (EI) *m/z*: calcd for $C_{12}H_{14}O_2$ (M^+) 190.0988, found 190.0993; $[\alpha]_D^{20}$ = +148.7 (c 0.64, $CHCl_3$), lit. $[\alpha]_D^{20}$ = +142.2 (c 1.0, $CHCl_3$); HPLC (Chiralcel OD-H, hexanes, 1.0 mL min^{-1}): $t_r(R)$ = 35.4 min, $t_r(S)$ = 50.4 min.

(*S*)-(*E*)-1,3-Diphenyl-1-butene ((*S*)-(*E*)-9)[34]

Following the general procedure, **(*S*)-(*E*)-9** was obtained as colorless oil (29.0 mg, 0.139 mmol, 83%, >99% ee).^{1}H NMR (300 MHz, $CDCl_3$) δ 1.50 (d, J = 6.9 Hz, 3H), 3.63–3.72 (m, 1H), 6.42–6.44 (m, 2H), 7.19–7.40 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2 (CH_3), 42.6 (CH), 126.1 (2 × CH), 126.2 (CH), 127.0 (CH), 127.3 (2 × CH), 128.5 (4 × CH), 128.6 (CH), 135.3 (CH), 137.6 (C), 145.6 (C) ppm; IR (ATR) 3027, 2961, 2924, 2853, 1602, 1494 cm^{-1}; MS (EI) *m/z* (%): 208 (M^+, 100), 193 ($M^+ - CH_3$, 89); HRMS (EI) *m/z*: calcd for $C_{16}H_{16}$ (M^+) 208.1247, found 208.1246; $[\alpha]_D^{20}$ −31.4 (*c* 2.50, $CHCl_3$), lit. $[\alpha]_D^{20}$ −39.3 (*c* 2.51, $CHCl_3$); HPLC (Chiralcel OD-H, hexanes, 0.5 mL min^{-1}): $t_r(R)$ = 24.5 min, $t_r(S)$ = 25.4 min.

Acknowledgements

We are grateful to the Xunta de Galicia (INCITE08P-XIB103167PR) and Ministerio de Ciencia e Innovación (CTQ2009-07180) for financial support. M.P.L. thanks Ministerio de Ciencia e Innovación for an FPU predoctoral fellowship.

Notes and references

1 For recent reviews about gold-catalyzed reactions, see: (*a*) A. Corma, A. Leyva-Pérez and M. J. Sabater, *Chem. Rev.*, 2011, **111**, 1657; (*b*) A. S. K. Hashmi and M. Bührle, *Aldrichimica Acta*, 2010, **43**, 27; (*c*) A. Fürstner, *Chem. Soc. Rev.*, 2009, **38**, 3208; (*d*) Z. Li, C. Brouwer and C. He, *Chem. Rev.*, 2008, **108**, 3239; (*e*) A. Arcadi, *Chem. Rev.*, 2008, **108**, 3266; (*f*) E. Jiménez-Núñez and A. M. Echavarren, *Chem. Rev.*, 2008, **108**, 3326; (*g*) A. S. K. Hashmi and M. Rudolph, *Chem. Soc. Rev.*, 2008, **37**, 1766.

2 (*a*) L.-P. Liu, B. Xu, M. S. Mashuta and G. B. Hammond, *J. Am. Chem. Soc.*, 2008, **130**, 17642; (*b*) D. Weber, M. A. Tarselli and M. R. Gagné, *Angew. Chem. Int. Ed.*, 2009, **48**, 5733; (*c*) A. S. K. Hashmi, A. M. Schuster and F. Rominger, *Angew. Chem. Int. Ed.*, 2009, **48**, 8247; (*d*) R. L. LaLonde, W. E. Brenzovich, Jr., D. Benitez, E. Tkatchouk, K. Kelley, W. A. Goddard III and F. D. Toste, *Chem. Sci.*, 2010, **1**, 226; (*e*) A. S. K. Hashmi, *Angew. Chem. Int. Ed.*, 2010, **49**, 5232; (*f*) W. E. Brenzovich, Jr., D. Benitez, A. D. Lackner, H. P. Shunatona, E. Tkatchouk, W. A. Goddard III and F. D. Toste, *Angew. Chem. Int. Ed.*, 2010, **49**, 5519; (*g*) N. P. Mankad and F. D. Toste, *J. Am. Chem. Soc.*, 2010, **132**, 12859; (*h*) D. Weber and M. R. Gagné, *Chem. Commun.*, 2011, 5172.

3 (*a*) G. Zhang, Y. Peng, L. Cui and L. Zhang, *Angew. Chem. Int. Ed.*, 2009, **48**, 3112; (*b*) P. Garcia, M. Malacria, C. Aubert, V. Gandon and L. Fensterbank, *ChemCatChem.*, 2010, **2**, 493; (*c*) G. Siedel, C. W. Lehmann and A. Fürstner, *Angew. Chem., Int. Ed.*, 2010, **49**, 8466; (*d*) G. Zhang, L. Cui, Y. Wang and L. Zhang, *J. Am. Chem. Soc.*, 2010, **132**, 1474; (*e*) C. de Haro and C. Nevado, *Angew. Chem., Int. Ed.*, 2011, **50**, 906.

4 H. Schmidbaur and A. Schier, in *Comprehensive Organometallic Chemistry III*, eds. D. M. P. Mingos and R. H. Crabtree, Elsevier, Oxford, UK, 2007, Vol. 2, Chapter 2.05, p. 251.

5 M. Murakami, M. Inouye, M. Suginome and Y. Ito, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 3649.

6 (*a*) S. Porcel, V. López-Carrillo, C. García-Yebra and A. M. Echavarren, *Angew. Chem. Int. Ed.*, 2008, **47**, 1883; (*b*) Y. Shi, S. M. Peterson, W. W. Haberaecker III and S. A. Blum, *J. Am. Chem. Soc.*, 2008, **130**, 2168; (*c*) Y. Shi, S. D. Ramgren and S. A. Blum, *Organometallics*, 2009, **28**, 1275; (*d*) Y. Shi, K. E. Roth, S. D. Ramgren and S. A. Blum, *J. Am. Chem. Soc.*, 2009, **131**, 18022.

7 (*a*) A. S. K. Hashmi, C. Lothschütz, R. Döpp, M. Rudolph, T. D. Ramamurthi and F. Rominger, *Angew. Chem., Int. Ed.*, 2009, **48**, 8243; (*b*) A. S. K. Hashmi, R. Döpp, C. Lothschütz, M. Rudolph, D. Riedel and F. Rominger, *Adv. Synth. Catal.*, 2010, **352**, 1307; (*c*) J. J. Hirner and S. A. Blum, *Organometallics*, 2011, **30**, 1299; (*d*) Y. Shi and S. A. Blum, *Organometallics*, 2011, **30**, 1776; (*e*) J. J. Hirner, Y. Shi and S. A. Blum, *Acc. Chem. Res.*, 2011, **44**, 603; (*f*) A. S. K. Hashmi and L. Molinari, *Organometallics*, 2011, **30**, 3457; (*g*) H. A. Wegner and M. Auzias, *Angew. Chem. Int. Ed.*, 2011, **50**, 8236.

8 M. Peña-López, M. Ayán-Varela, L. A. Sarandeses and J. Pérez Sestelo, *Chem.—Eur. J.*, 2010, **16**, 9905.

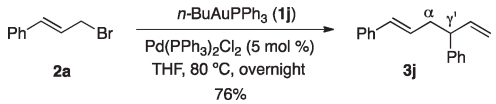
9 For a general overview, see: T. Tsuji, *Transition Metal Reagents and Catalysts*, Wiley, New York, 2000, Chapter 4, p. 109.

10 E. Negishi and F. Liu, in *Handbook of Organopalladium Chemistry for Organic Chemistry*, ed. E. Negishi, Wiley, New York, 2002, vol 1, Part III, chapter 2.9, p. 551.

11 (*a*) D. Rodríguez, J. Pérez Sestelo and L. A. Sarandeses, *J. Org. Chem.*, 2003, **68**, 2518; (*b*) D. Rodríguez, J. Pérez Sestelo and L. A. Sarandeses, *J. Org. Chem.*, 2004, **69**, 8136.

12 (*a*) C. Croix, A. Balland-Longeau, H. Allouchi, M. Giorgi, A. Duchêne and J. Thibonnet, *J. Organomet. Chem.*, 2005, **690**, 4835;

(*b*) D. V. Partyka, M. Zeller, A. D. Hunter and T. G. Gray, *Angew. Chem. Int. Ed.*, 2006, **45**, 8188; (*c*) D. V. Partyka, J. B. Updegraff, M. Zeller, A. D. Hunter and T. G. Gray, *Organometallics*, 2009, **28**, 1666.
13 No reaction was observed in the absence of a palladium catalyst.
14 The homocoupling product (**3j**) corresponds to α-γ′ dimerization. For examples of reductive homocoupling of allylic halides, see: (*a*) A. F. Barrero, M. M. Herrador, J. F. Quílez del Moral, P. Arteaga, J. F. Arteaga, H. R. Diéguez and E. M. Sánchez, *J. Org. Chem.*, 2007, **72**, 2988; (*b*) S. Mukhopadhyay, G. Rothenberg, D. Gitis and Y. Sasson, *J. Org. Chem.*, 2000, **65**, 3107



.

15 S. G. Jarboe and P. Beak, *Org. Lett.*, 2000, **2**, 357.
16 (*a*) A. Vik, E. Hedner, C. Charnock, L. W. Tangen, Ø. Samuelsen, R. Larsson, L. Bohlin and L-L. Gundersen, *Bioorg. Med. Chem.*, 2007, **15**, 4016; (*b*) J. Esnault, J-M. Mallet, Y. Zhang, P. Sinay, T. Le Bouar, F. Pincet and E. Perez, *Eur. J. Org. Chem.*, 2001, 253.
17 The (2*R*,3*E*)-4-phenyl-3-buten-2-ol precursor of (*R*)-(*E*)-**6** was prepared by a Sharpless kinetic resolution: (*a*) Y. Gao, R. M. Hanson, J. M. Klunder, S. Y. Ko, H. Masamune and K. B. Sharpless, *J. Am. Chem. Soc.*, 1987, **109**, 5765; (*b*) P. R. Carlier, W. S. Mungall, G. Schröder and K.B. Sharpless, *J. Am. Chem. Soc.*, 1988, **110**, 2978.
18 The ee was measured by HPLC, for further experimental details see the ESI.
19 Y. Nishibayashi and S. Uemura, in *Comprehensive Organometallic Chemistry III*, eds. D. M. P. Mingos and R. H. Crabtree, Elsevier, Oxford, UK, 2007; Vol. 11, Chapter 11.02, p. 75.
20 W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923.
21 A. S. K. Hashmi, T. D. Ramamurthi and F. Rominger, *J. Organomet. Chem.*, 2009, **694**, 592.
22 H. A. Porter, A. Schier and H. Schmidbaur, *Organometallics*, 2003, **22**, 4922.
23 R. J. Cross and M. F. Davidson, *J. Chem. Soc., Dalton Trans.*, 1986, 411.
24 H. G. Raubenheimer, M. W. Esterhuysen, G. Frenking, A. Y. Timoshkin, C. Esterhuysen and U. E. I. Horvath, *Dalton Trans.*, 2006, 4580.
25 Y. Yamamoto and K. Itonaga, *Chem.—Eur. J.*, 2008, **14**, 10705.
26 H. Tsukamoto, M. Sato and Y. Kondo, *Chem. Commun.*, 2004, 1200.
27 D. Bouyssi, V. Gerusz and G. Balme, *Eur. J. Org. Chem.*, 2002, 2445.
28 Z. Yang, P. Tang, J. F. Gauuan and B. F. Molino, *J. Org. Chem.*, 2009, **74**, 9546.
29 E. Alacid and C. Nájera, *J. Org. Chem.*, 2009, **74**, 2321.
30 S. Araki, S. Manabe and Y. Butsugan, *Chem. Lett.*, 1982, 797.
31 A. Takeda, K. Shinhama and S. Tsuboi, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1903.
32 B. Moreau, J. Y. Wu and T. Ritter, *Org. Lett.*, 2009, **11**, 337.
33 (*a*) U. Kazmaier and F. L. Zumpe, *Eur. J. Org. Chem.*, 2001, 4067; (*b*) S. Akai, R. Hanada, N. Fujiwara, Y. Kita and M. Egi, *Org. Lett.*, 2010, **12**, 4900.
34 (*a*) L. Schwink and P. Knochel, *Chem.—Eur. J.*, 1998, **4**, 950; (*b*) J. Norinder, K. Bogár, L. Kanupp and J.-E. Bäckvall, *Org. Lett.*, 2007, **9**, 5095.

