CSIRO PUBLISHING

RESEARCH FRONT

Aust. J. Chem. **2014**, *67*, 481–499
http://dx.doi.org/10.1071/CH13552

Full Paper

Gold Catalysis: Biarylphosphine Ligands as Key for the Synthesis of Dihydroisocoumarins

A. Stephen K. Hashmi,[A,B,D] *Benjamin Bechem,*[A] *Annette Loos,*[A] *Melissa Hamzic,*[A] *Frank Rominger,*[A] *and Hassan Rabaa*[C]

[A]Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany.
[B]Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia.
[C]Université Ibn Tofail, LCTA, Département de Chimie, PO Box 133, Kénitra 14000, Morocco.
[D]Corresponding author. Email: hashmi@hashmi.de

A gold-catalyzed phenol synthesis was successfully used in the synthesis of dihydroisocoumarins for the first time. A large number of gold(I) complexes were prepared and tested; only complexes based on the biarylphosphine motif were successful.

Manuscript received: 11 October 2013.
Manuscript accepted: 29 January 2014.
Published online: 27 February 2014.

Introduction

The gold-catalyzed synthesis of phenols[1–24] (Scheme 1) has proved to be an excellent tool for the synthesis of benzoanellated carbo- and heterocycles **2** from easily available substrates **1** and is probably one of the most reliable gold-catalyzed organic reactions with a broad scope.[25–36] The positioning of the hydroxyl group *ortho* to the anellation point is difficult to achieve by classical anellation strategies, which usually direct an intramolecular electrophile to the *para* and not to the *ortho* position of the phenolic hydroxyl group. Depending on the length of the tether, both benzo-anellated five- and six-membered rings can be prepared.

Dihydroisocoumarin natural products are interesting targets; along with examples like mellein,[37] phyllodulcin,[37] hydrangenol,[37] ochratoxin B,[38]] amicoumacin C,[39] gamahorin,[40] in the last decade ajudazol A has been a prominent target. Ajudazol A is an antimicrobial compound from myxobacteria *Chondromyces crocatus* that inhibits mitochondrial electron transport. It was first isolated by Höfele et al.[41] The eastern part of the molecule has already been synthesized by Taylor et al. (C12–C28)[42] and Rizzacasa et al. (C9–C29)[43] (Fig. 1); biosynthesis has been investigated by Müller et al.[44]

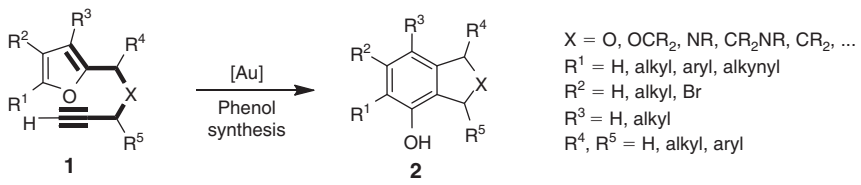
The western part looks like an ideal target for gold-catalyzed phenol synthesis, but all initial efforts to form the dihydroisocoumarin skeleton with the gold catalysts usually used in phenol synthesis failed.[45]

Recently, a synthesis of the core of the western part of Ajudazol A was published by Marquez et al.[46a] and the total synthesis was reported by Menche.[46b] This has prompted us to disclose our efforts in the development of a methodology for the part of the natural product that is of general interest for that type of building block. We report here that only gold(I) phosphine complexes with a biaryl substituent on phosphorus efficiently catalyze phenol synthesis to the dihydroisocoumarin skeleton, one more potential application of gold catalysis in total synthesis.[47]

Results and Discussion

The synthesis of the 1,7-enyne substructure of the substrates for gold catalysis begins with the regioselective ring-opening of the epoxides **4** with lithiated 2-methylfuran **3**. This delivers the furylethanols **5** (Table 1).

The next step was the synthesis of the propiolic acid esters. The alcohols **5** were coupled with propiolic acid using di(cyclohexyl)



Scheme 1. The gold-catalysed phenol synthesis; the enyne substructure is shown in bold.

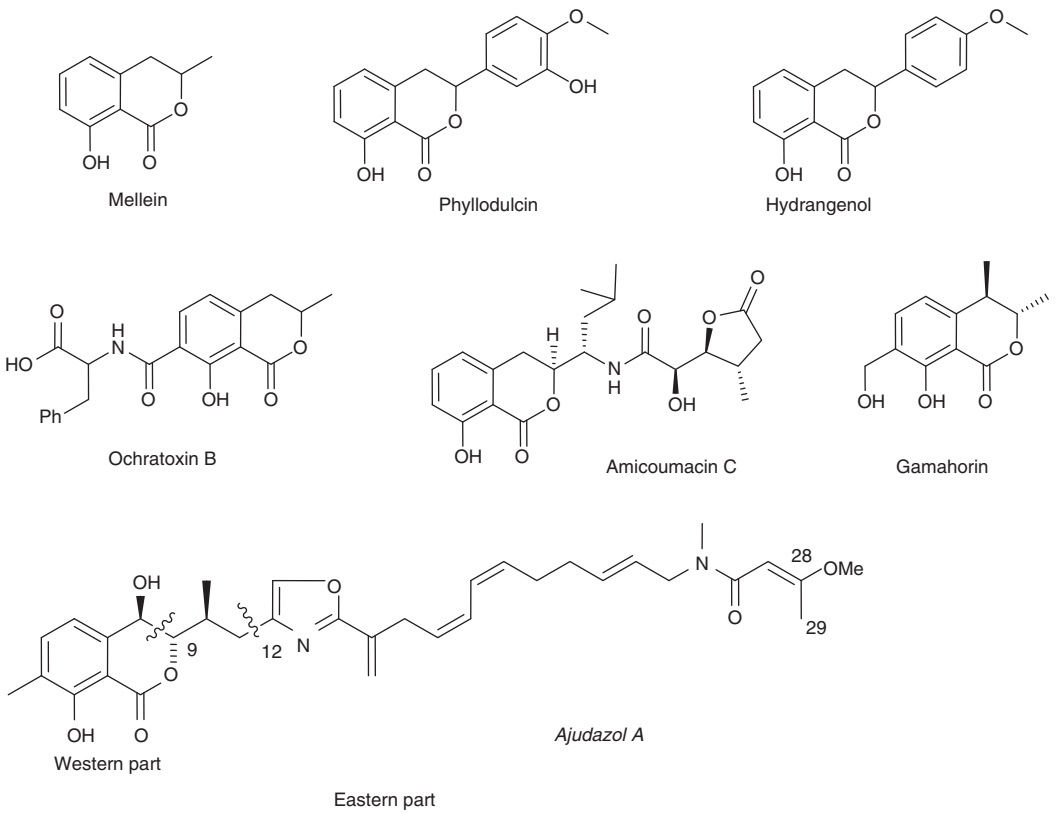
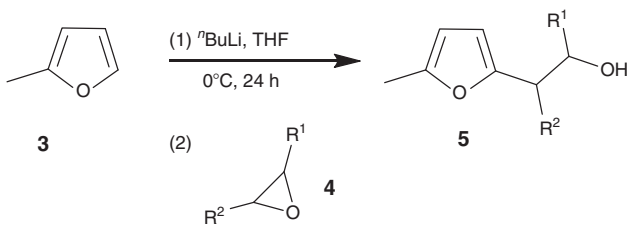


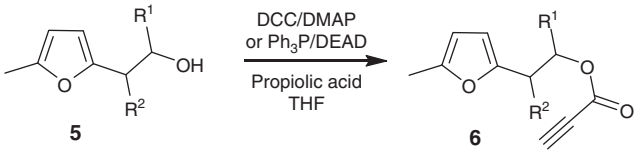
Fig. 1. Dihydroisocoumarine-substructures in natural products.

Table 1. Epoxide opening with lithiated 2-methylfuran



Entry	R^1 in **4**	R^2 in **4**	Product (yield)
1	Me	H	**5a** (67 %)
2	Pr	H	**5b** (34 %)
3	Bu	H	**5c** (45 %)
4	Ph	H	**5d** (42 %)
5	CH_2-OPh	H	**5e** (42 %)
6	CH_2-(2-methylfuryl)	H	**5f** (43 %)
7	Ph	CH_2OH	**5g** (9 %)
8	4-$NO_2C_6H_4$	H	–

Table 2. Esterification of alcohols 5 with propiolic acid

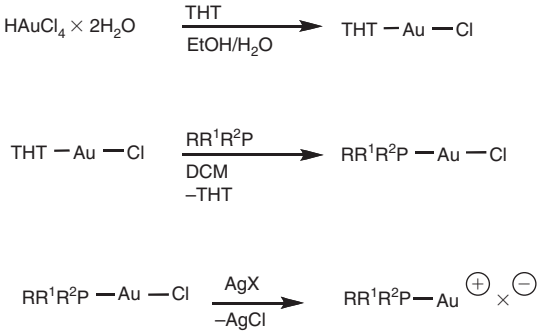


Entry	R^1 in **5**	R^2 in **5**	Product (yield)
1	Me	H	**6a** (16 %)
2	Pr	H	**6b** (25 or 58 %[A])
3	Bu	H	**6c** (30 %)
4	Bu	H	**6c** (86 %)[A]
5	Ph	H	**6d** (29 %)
6	CH_2-OPh	H	**6e** (25 %)
7	CH_2-(2-methylfuryl)	H	**6f** (17 or 39 %[A])
8	Ph	CH_2OH	**6g** (57 %)

[A]Obtained by Mitsunobu coupling.

carbodiimide (DCC)/4-*N*,*N*-dimethylaminopyridine (DMAP) (Table 2). The alternative Mitsunobu coupling turned out to be more efficient.

For this investigation, a series of different gold(I) complexes was prepared by the normal route for the synthesis of these compounds: formation of tetrahydrothiophengold(I) chloride from tetraauric acid and subsequent ligand exchange with phosphine ligands (Scheme 2). For the catalysis reactions, these complexes were converted into the catalytically active cationic form by the addition of the corresponding silver salt (Scheme 2).



Scheme 2. General synthesis of gold phosphine complexes (THT, tetrahydrothiophen) and activation of gold phosphine complexes by silver salts.

The six different complexes prepared initially are shown in Table 3; four of these could be characterized by X-ray structure analyses.[48] Au-PhosphineB with the butyl cataCXium ligand in the crystal shows a disordering of the butyl side chain and close contact of gold and nitrogen. Au-PhosphineC during the crystallization process delivers Au-PhosphineC_2 with two phosphine ligands on gold; the chloride is not coordinated to the gold centre. The benzyl cataCXium ligand in Au-PhosphineD does not show disorder similar to Au-PhosphineB, the benzyl group occupying a defined position in the crystals. Au-BiarylA like Au-PhosphineB also shows a gold–nitrogen contact and the distal aryl group of the biaryl unit is close to the gold centre.

Having the substrates **6** and the catalysts Au-PhosphineA–Au-PhosphineD, Au-BiarylA and Au-BiarylB at hand, we now could finally investigate the essential point, the cycloisomerization of **6** to dihydroisocoumarins. For the initial catalyst screening, we used substrate **6c**. As observed previously,[45] the formation of dihydroisocoumarins is a challenge in the field of gold-catalyzed phenol synthesis. Simple gold complexes like $AuCl_3$ and AuCl (Table 4, entries 1–4), which usually show at least some activity, were completely inactive even at temperatures up to 70°C; the starting material was recovered. The same was true for most of the gold(I) phosphine complexes; this applied for both the preformed catalysts with the bis(trifluoromethylsulfonyl)imide (NTf_2^-) counter ion and for in situ activated gold(I) complexes, in both dichloromethane and acetonitrile (entries 5–13). With the biaryl ligand in a complex with the weakly coordinating NTf_2^- counter ion (Au-Biaryl A), we observed traces of the product (entry 15), but only in dichloromethane and not in acetonitrile (entry 14). We were delighted to see that Au-BiarylB in situ after activation with the non-coordinating BF_4^- counter ion, when going from room temperature to 70°C, delivered a 50 % yield of the desired product (entry 17). Again, in acetonitrile the same system showed no conversion (entry 16). This could even be slightly improved to 57 % when the reaction was done at 25°C, where it was slower (entry 20). Again, in acetonitrile the same system showed no conversion (entry 16). THF also inhibited the reaction and starting at 70°C immediately led to decomposition of the catalyst (entry 18). Buchwald-type biaryl ligands have received increasing interest in gold-catalyzed reactions. The number of publications where Au-biaryl complexes play a substantial role in either reactivity or selectivity is continually growing.[49]

Based on the success of the biarylphosphine ligands, 16 different complexes containing the biaryl motif were prepared by the methods mentioned above. These are shown in Table 5; 12 of these complexes could even be characterized by X-ray structure analysis.[48]

These Buchwald-type biaryl ligands were tested in the reaction of **6c**. The results obtained with the biaryl-biscyclohexyl phosphines are shown in Table 6. The unsubstituted Au-BiarylD gave a decent yield of **7c**, at both 50°C and at room temperature (entries 1 and 2). With the methyl-substituted Au-BiarylE, a slightly better yield of **7c** was obtained (entry 3). With stronger donors in the same position of the biaryl unit, like the dimethylamino group in Au-BiarylF (entry 4), the dimethoxy derivative Au-BiarylG (entry 5), the di(isopropoxy) derivative Au-BiarylH (entry 6) or the tri(isopropyl) derivative Au-BiarylI (entry 7), no improvement was achieved. However, acceptors on the biaryl unit, as in Au-BiarylJ (entry 8) and Au-BiarylK (entry 9), led to a complete failure to catalyze this reaction. The highly substituted Au-BiarylC (entry 10) gave the best results.

Turning to the biaryl-bis-*tert*-butyl phosphines in Table 7, we used the same substrate to allow comparison. With the *tert*-butyl substitutent on the phosphine, the difference between the unsubstituted biaryl system in Au-BiarylB (entry 1) and the methyl-substituted biaryl system in Au-BiarylL (entries 2 and 3) is less significant than with the cyclohexyl substituent on the phosphine. The other donor substitutents are also not as beneficial as those shown in Table 6; the dimethylamino group in Au-BiarylM (entry 4) and the isopropyl groups in Au-BiarylN (entry 5) show reduced yields only. The binaphthyl group in Au-BiarylO (entries 6 and 7), however, gives yields similar to entries 1–3.

Now it was also interesting to compare the phosphines with available identical biaryl units that had different substituents on phosphorous, which was the case for the dimethylamino group. In Table 8, these are compared: it is obvious that the dicyclohexyl derivative is most active (entry 1), the di-*tert*-butyl derivative significantly less active (entry 2), and the phenyl group is inactive (entry 3).

Next we explored the influence of a pyrrole subunit in the biaryl moiety. Table 9 shows two such catalysts. These show some activity and completely converted the substrate **6c**, but the in situ ^{1}H NMR spectra showed mainly polymerization; only low yields were obtained with both pyrrole-based catalysts. This once more underlines the difficulties that can be observed with this class of substrates and the unique advantages of catalysts like Au-BiarylC, which efficiently convert **6c** into the dihydroisocoumarin **7c**.

As Au-BiarylC was the best catalyst, we used this complex for the conversion of the other substrates. Table 10 shows the results obtained with the substrates **6a**–**6g**. Whereas the alkyl-substituted **6a**–**6c** gave quite comparable yields of **7a**–**7c** (entries 1–3), with **6d**–**6f**, only reduced amounts of **7d**–**7f** (entries 4–6) were formed. The disubstituted **6g** with a free hydroxy group failed to be converted.

The structures of the synthetic intermediate **5e**, the substrate **6e**, and the product **7e** were unambiguously proved by crystal structure analyses (Fig. 2).[48] In the solid-state structure of **7e**, a hydrogen bond between the phenolic hydroxy group and the ester carbonyl group is visible, probably a typical feature of the whole family of these products.

From efforts to prepare the cationic variant of the Au-BiarylF catalyst by addition of silver tetrafluoroborate, we isolated some material that separated by spontaneous crystallization. Crystal structure analysis showed that both dimethylamino groups are protonated and that this dinuclear complex, Au-BiarylS, connects two gold(I) centres by a chloro bridge (Fig. 3).[48] The charge is compensated for by BF_4^- units in the crystal lattice. Typical bond lengths and bond angles are shown in Table 11. The coordination geometry at both gold centres is almost linear; the two gold centres are quite close, the Au–Cl–Au angle being only 86°. The other values are normal; only the short contact distance between the plane of the distal ring of the biaryl unit and the gold centre is remarkable.

In explaining the unusual reactivity of the Au-Biaryl catalysts, this short gold–arene contact may be the key. In addition to related work of Gray,[50,51] we started a theoretical investigation of the geometries and the resulting reactivity effects of these complexes.[52] Initial calculations nicely confirm the structural features of Au-BiarylF (see Supplementary Material), but significantly more work is necessary to understand the quite short arene–gold contact and its impact on catalyst activity.

In Fig. 4, the molecular structures obtained from the X-ray crystal structure analysis of Au-BiarylC, D, E, F, G, H, I, M, N, O, Q, and R are superimposed. The structural characteristics match the analogous complexes described in the literature.[50,51,53]

Table 3. Gold(I) phosphine complexes used in this investigation

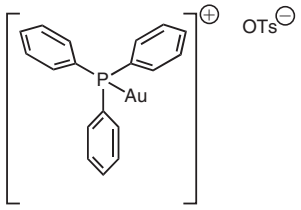
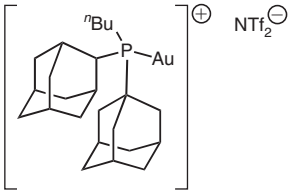
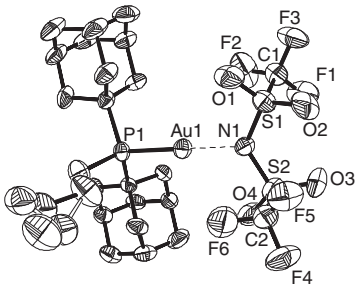
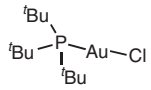
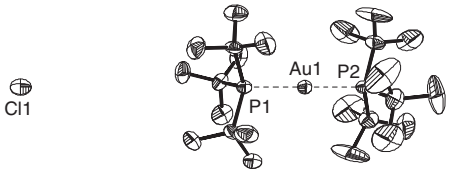
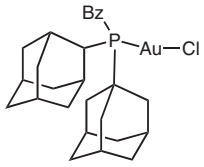
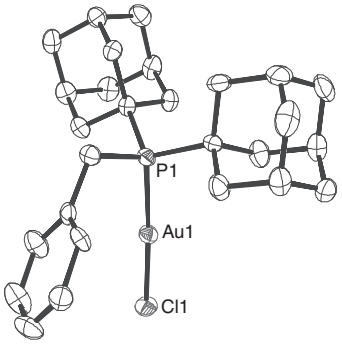
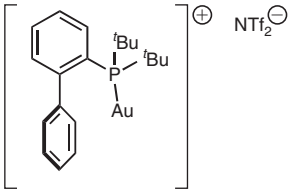
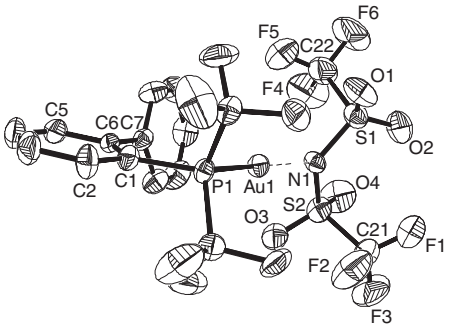
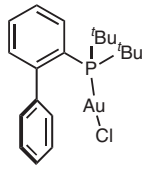
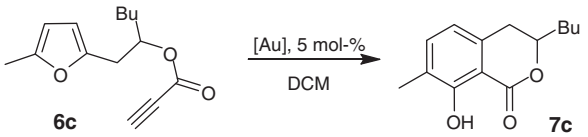
Entry	Structure	X-ray structure analysis
1	 Au-PhosphineA	
2	 Au-PhosphineB	
3	 Au-PhosphineC	 Au-PhosphineC$_2$
4	 Au-PhosphineD	
5	 Au-BiarylA	
6	 Au-BiarylB	–

Table 4. Catalyst development stage 1 – general catalyst screening
CD_3CN, acetonitrile-D_3; CD_2Cl_2, dichloromethane-D_2; $AgNTf_2$, silver(I) bis(trifluormethansulfon)imide



Entry	Catalyst	Additive	Solvent	Temperature [°C][A]	Yield of **7c**[B]
1	5 mol-% $AuCl_3$	–	CDCN	25–70	–
2	10 mol-% $AuCl_3$	–	CDCN	25–70	–
3	10 mol %$AuCl_3$	10 mol-% BF_3OEt_2	CDCN	25–70	–
4	5 mol-% AuCl	5 mol-% $AgBF_4$	CDCl	25–70	–
5	5 mol-% Au-PhosphineA	5 mol-% $AgNTf_2$	CDCl	25–70	–
6	5 mol-% Au-PhosphineB	–	CDCl	25–70	–
7	5 mol-% Au-PhosphineB	–	CDCl	25	–
8	5 mol-% Au-PhosphineB	–	CDCl	70	–
9	5 mol-% Au-PhosphineB	–	CDCN	25–70	–
10	5 mol-% Au-PhosphineC	$AgBF_4$	CDCl	25–70	–
11	5 mol-% Au-PhosphineC	$AgBF_4$	CDCN	25–70	–
12	5 mol-% Au-PhosphineD	$AgBF_4$	CDCl	25–70	–
13	5 mol-% Au-PhosphineD	$AgBF_4$	CDCN	25–70	–
14	5 mol-% Au-BiarylA	–	CDCN	25–70	–
15	5 mol-% Au-BiarylA	–	CDCl	25–70	traces
16	5 mol-% Au-BiarylB	$AgBF_4$	CDCN	25–70	–
17	5 mol-% Au-BiarylB	$AgBF_4$	CDCl	25–70	50 %
18	5 mol-% Au-BiarylB	$AgBF_4$	CDCl	70	–
19	5 mol-% Au-BiarylB	$AgBF_4$	d^8-THF	70	–
20	5 mol-% Au-BiarylB	$AgBF_4$	CDCl	25	57 %

[A]25–70°C: the temperature was increased stepwise, first to 30°C and then in steps of 10°C.
[B]Yield by ^{1}H NMR integration.

In the plot, the second aryl group of the Buchwald ligand is fixed for superimposition of the structures and the variety of flexible side arms with the P–Au–Cl unit is demonstrated. The general motif comprises the almost-linear coordination of the Au^I atom to the chloride and the phosphorus atom of the ligand. The second feature consists of the Au^I–π arene interaction with the coordinating aryl moiety of the Buchwald ligand. Aurophilic interactions are not present owing to the fact that the Au–Au distance for any complex is larger than the corresponding bond length of ~3 Å.[54]

The most important data for the Au-Biaryl complexes are summarized in Table 12. For further clarity and understanding, the haptacity of the Au centre was calculated using the method developed by Kochi and coworkers.[55] The measured Au–P bond length of all complexes varies from 2.22 to 2.25 Å, the Au–Cl bond length from 2.28 to 2.30 Å.

The existence of an Au–C interaction to the flanking biaryl moieties is validated by the measured distance in the solid state and is therefore is therefore shorter than the sum of the Van der Waals radii (3.36 Å).[56]

In most cases, Au–C_{ipso} is shorter than the Au–C_{ortho} distance and ranges from 2.96 Å for Au-BiarylC to 3.26 Å for Au-BiarylR (Table 12: entries 1 and 12). For the ligands containing an amino group in the *ortho* position of the coordinating second aryl group, the Au^I atom is directed to the C_{ortho} position. The Au–C_{ortho} distances are 3.17 and 3.12 Å, and the Au–N distances are 3.58 and 3.30 Å for Au-BiarylF and Au-BiarylM respectively (Table 12: entries 4 and 8).

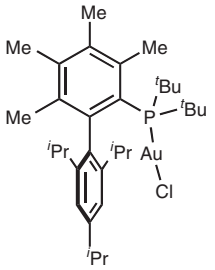
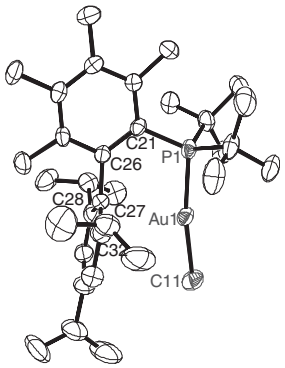
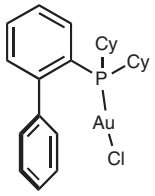
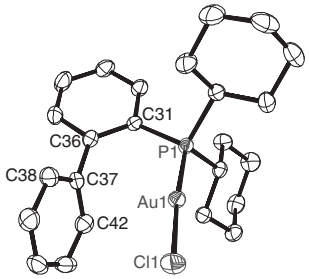
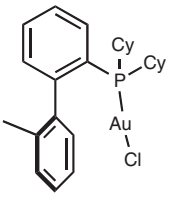
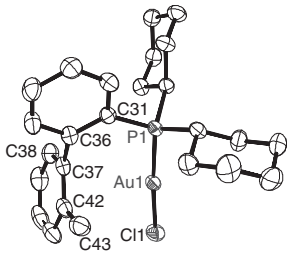
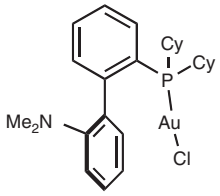
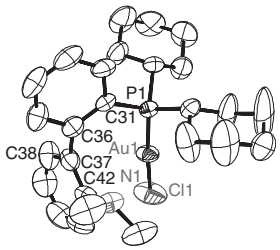
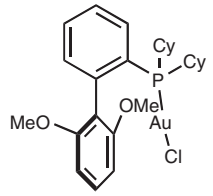
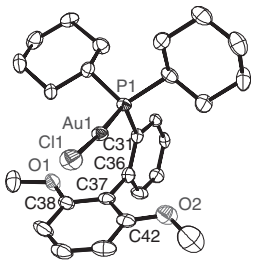
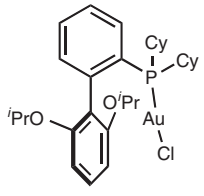
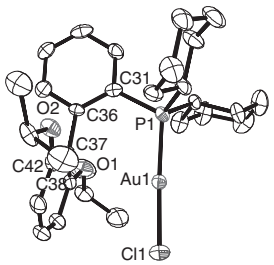
If the second phenyl ring of the Buchwald ligand has just one *ortho*-substituted position, the Au^I centre of Au-BiarylE, F, and M is interacting with the more highly substituted π-bond (Table 12: entries 3,4, and 8). This is totally different in the Beller-type ligand[57]] system Au-BiarylR where the Au^I centre is interacting with the non-substituted π-bond of the biphenyl (Table 12: entry 12). The distance between gold and the phenyl plane of the biaryl is 3.10 Å on average (Au–biaryl plane: 2.955–3.220 Å).

The linear geometry of P–Au–Cl in every complex is slightly distorted, which is seen in the average angle of P–Au–Cl = 175.0° (P–Au–Cl: 169.5° (Au-BiarylC) to 176.6° (Au-BiarylO)). Au-BiarylC has with 169.5° the highest deviation from the expected 180° for a linear-coordinated Au^I complex (Table 12: entry 1). This is a result of steric hindrance between the substituents of the phosphorus atom of the ligand. The tetramethyl-substituted phenyl ring in BiarylC on one side repulses the di-*tert*-butyl moieties on the other side. Therefore the gold centre is pushed towards the mean plane of the second phenyl ring and further distorted from the ideal linear geometry.

Another outcome of this effect is the low value for hapticity η in Au-BiarylC with $\eta_{calc} = 1.13$. The average hapticity of the other mentioned Au-Biaryl complexes is $\eta_{calc/average} = 1.70$, which clearly demonstrates the favoured haptacity of η^2-Au^I complexes. Au-BiarylF with $\eta_{calc} = 1.91$ has the highest calculated hapticity.

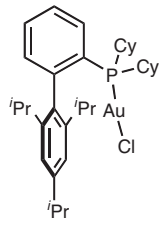
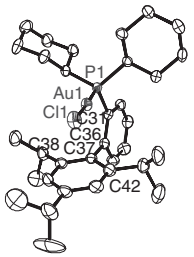
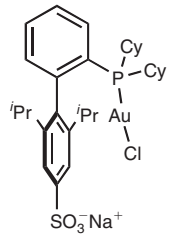
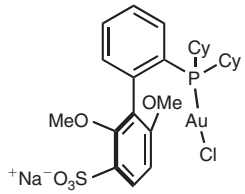
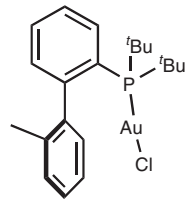
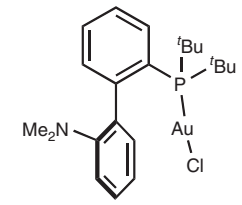
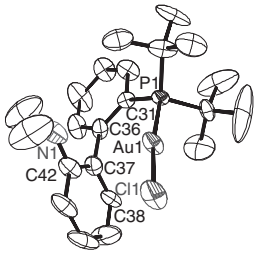
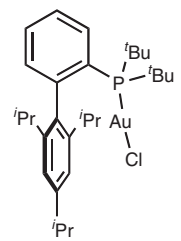
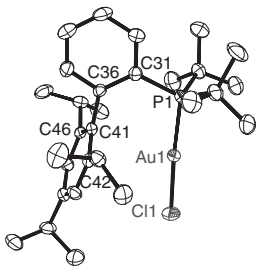
Interestingly, the Au-BiarylC complex is the most effective in our studies in the phenol synthesis of dihydroisocoumarins (Table 12). We think that the high effectiveness is a result of the stabilization of Au^I in the transition state by the side-on interaction with the mean plane with the flanking phenyl ring of the ligand. The fact that different kinds of catalytic systems either lead to decomposition of the substrate or do not react at all must be a reliable indicator for reactivity and selectivity.

Table 5. More gold(I) biarylphosphine complexes used in this investigation
Cy, cyclohexyl

Entry	Structure	X-ray structure analysis
1	 Au-BiarylC	
2	 Au-BiarylD	
3	 Au-BiarylE	
4	 Au-BiarylF	
5	 Au-BiarylG	
6	 Au-BiarylH	

(*Continued*)

Table 5. (Continued)

Entry	Structure	X-ray structure analysis
7	 Au-BiarylI	
8	 Au-BiarylJ	–
9	 Au-BiarylK	–
10	 Au-BiarylL	–
11	 Au-BiarylM	
12	 Au-BiarylN	

(*Continued*)

Table 5. (Continued)

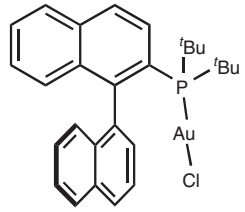
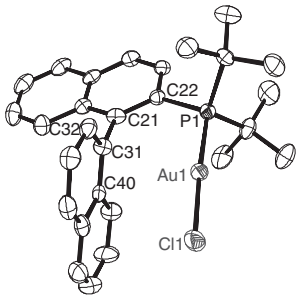
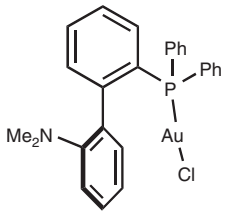
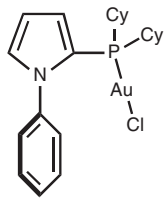
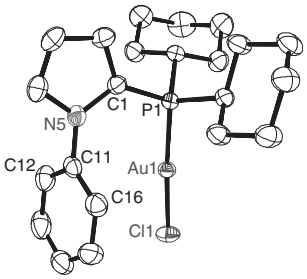
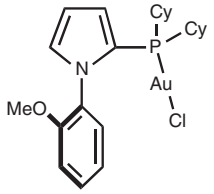
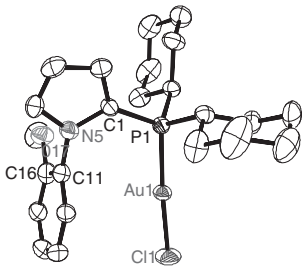
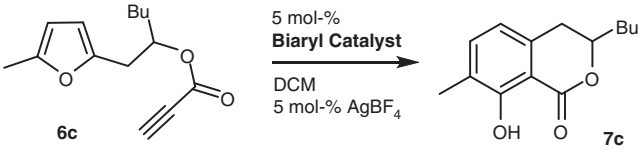
Entry	Structure	X-ray structure analysis
13	 Au-BiarylO	
14	 Au-BiarylP	–
15	 Au-BiarylQ	
16	 Au-BiarylR	

Table 6. Catalyst development stage 2 – screening of biaryl phosphine ligands with two cyclohexyl groups on phosphorus

Entry	Ligand	Temperature [°C]	Time [days]	Yield of **7c**[A]
1	Au-BiarylD	25–50	4	71 %
2	Au-BiarylD	25	5	67 %
3	Au-BiarylE	25–50	3	72 %
4	Au-BiarylF	25	6	64 %
5	Au-BiarylG	25–70	4	58 %
6	Au-BiarylH	25–70	6	50 %
7	Au-BiarylI	25–70	14	65 %
8	Au-BiarylJ	25–70	5	–
9	Au-BiarylK	25–70	7	–
10	Au-BiarylC	25	3	75 %

[A]Yield determined by ^{1}H NMR integration.

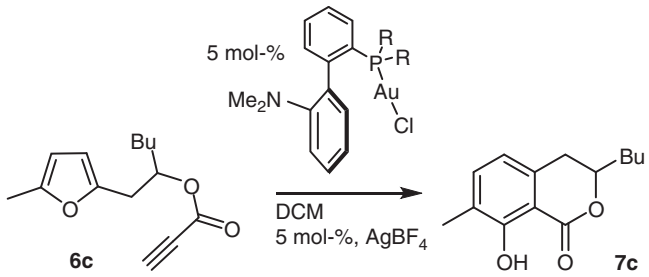
Table 7. Catalyst development stage 3 – screening of biaryl phosphine ligands with two *tert*-butyl groups on phosphorus



Entry	Ligand	Temperature [°C]	Time	Yield of **7c**[A]
1	Au-BiarylB	25–50	5 days	64 %
2	Au-BiarylL	25	5 days	64 %
3	Au-BiarylL	25–50	4 days	63 %
4	Au-BiarylM	25	30 h[B]	43 %
5	Au-BiarylN	25–70	10 days	44 %
6	Au-BiarylO	25–50	4 days	66 %
7	Au-BiarylO	25	5 days	68 %

[A]Yield by ^{1}H NMR integration.
[B] decomposition of the substrate after 30 h.

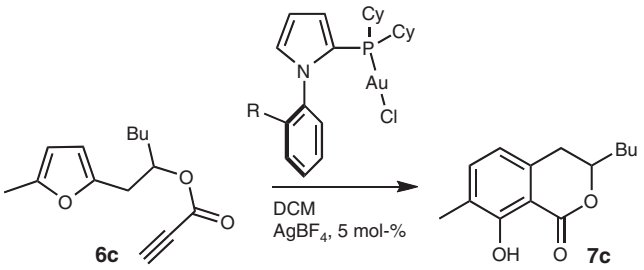
Table 8. Catalyst development stage 4 – comparison of different groups on phosphorus for a specific biaryl unit



Entry	Ligand	R	T [°C]	Time	Yield of **7c**[A]
1	Au-BiarylF	Cy	25	6 days	64 %
2	Au-BiarylM	*tert*-Butyl	25	30 h[B]	43 %
3	Au-BiarylP	Phenyl	25–70	5 days	–

[A]Yield by ^{1}H NMR integration.
[B]Decomposition of the substrate after 30 h.

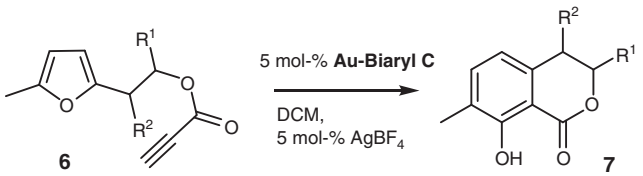
Table 9. Catalyst development stage 5 – properties of pyrrole-based biaryl units



Entry	Ligand	R	Temperature [°C]	Time [h]	Yield of **7c**[A]
1	Au-BiarylQ	H	25	10	14 %
2	Au-BiarylR	OMe	25	27	15 %

[A]Yield by ^{1}H NMR integration.

Table 10. Gold-catalyzed synthesis of dihydroisocoumarins 7



Entry	Substrate	R^1	R^2	Product (yield)[A]
1	**6a**	Methyl	H	**7a** (48 %)
2	**6b**	Propyl	H	**7b** (51 %)
3	**6c**	Butyl	H	**7c** (57 %)
4	**6d**	Phenyl	H	**7d** (40 %)
5	**6e**	CH_2-OPh	H	**7e** (28 %)
6	**6f**	CH_2-(2-Methylfuryl)	H	**7f** (35 %)
7	**6g**	Phenyl	CH_2OH	–

[A]Yield after workup.

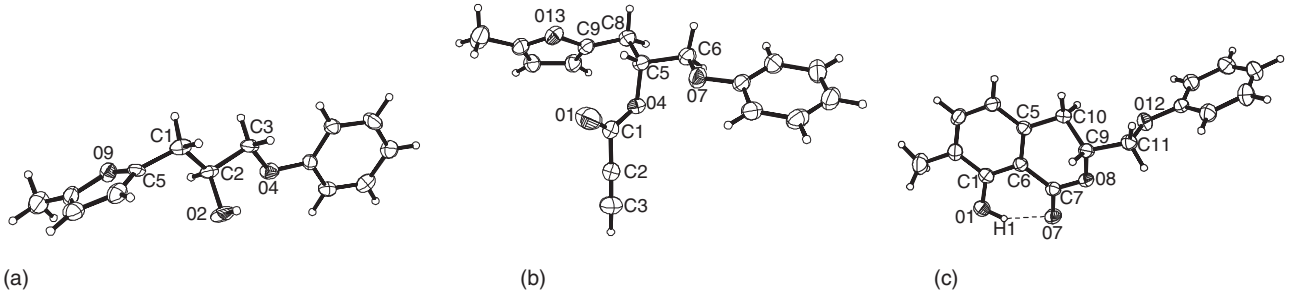


Fig. 2. Molecular structure of (a) **5e**; (b) **6e**; and (c) **7e** in the solid state.

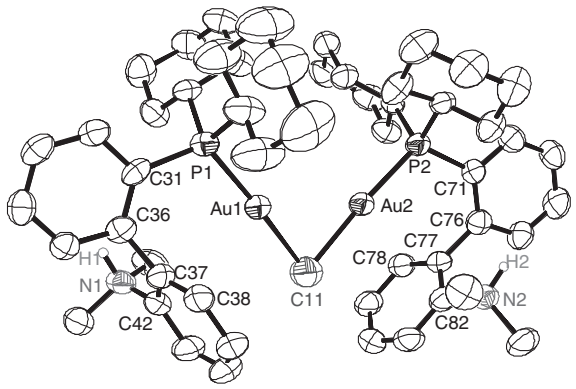


Fig. 3. Structure of Au-BiarylS in the solid state.

Table 11. Selected structural data for Au-BiarylS

Au1–P1	2.234(2) Å
Au1–Cl1	2.324(3) Å
Au1–Au2	3.1616(5) Å
Au2–P2	2.227(2) Å
Au2–Cl1	2.333(3) Å
Au1–C37	3.070 Å
Au2–C77	3.060 Å
Au1–plane1 of the distal ring of the biaryl unit	3.058 Å
Au1–plane2 of the distal ring of the biaryl unit	3.052 Å
P1–Au1–Cl1	177.14(9)°
P1–Au1–Au2	135.36(6)°
Cl1–Au1–Au2	47.37(7)°
P2–Au2–Cl1	175.56(10)°
P2–Au2–Au1	135.10(6)°
Cl1–Au2–Au1	47.13(7)°
Au1–Cl1–Au2	85.49(10)°

Conclusion

We identified a class of biarylphosphinegold(I) complexes that for the first time allows the cycloisomerization of notoriously difficult substrates for dihydroisocoumarins. This might be useful for total synthesis, the western part of ajudazol being just one potential target.

Experimental

General Procedures

General Procedure A: Synthesis of Hydroxyfurans

In a dry Schlenk flask under an inert gas atmosphere, a solution of 2-methylfuran in dry THF was prepared. The solution was cooled to 0°C. Then nBuLi was added dropwise, and the solution turned slightly yellow. The solution was allowed to stir for 2 h at room temperature (RT) before the oxirane derivative was added dropwise at 0°C. Then the mixture was allowed to warm slowly to RT and stirred for 14 h; the solution turned orange-reddish. Subsequently, the solution was hydrolyzed with 20 mL of water. The aqueous phase was extracted thrice with dichloromethane (DCM) before the combined organic phases were dried over Na_2SO_4, filtered and

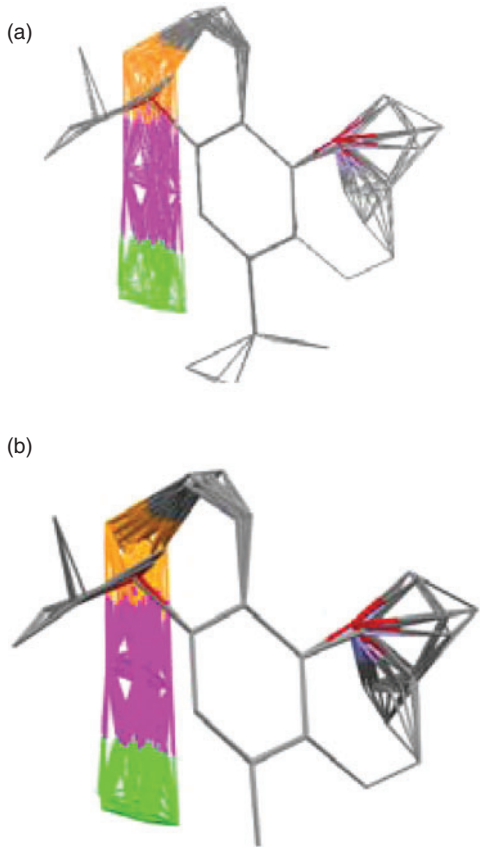


Fig. 4. Fit of superimposed Au-biaryl complexes analysed by X-ray crystal structure determination. Linear subunit: top = phosphorous; middle = gold; bottom = chlorine.

concentrated under vacuum. The residue was purified by flash column chromatography on silica gel.

General Procedure B: Synthesis of Alkynylesters with 1,7-Enyne Substructure

DCC coupling. In a dry Schlenk flask under an inert gas atmosphere, a solution of hydroxyfuran (from General Procedure A) and propiolic acid in dry DCM was prepared. The solution was cooled to 0°C. A second solution of DCC and DMAP in DCM was added within 1 h at 0°C. The resulting mixture was stirred for 5 h at RT. A precipitate formed, which was filtered off and washed with diethyl ether. The resulting filtrate was washed with brine and the combined organic layers were dried over Mg_2SO_4. The solid was removed by filtration and the solution was concentrated under vacuum. The residue was purified by flash column chromatography on silica gel.

Mitsunobu Reaction. The alcohol was dissolved in THF and the solution was cooled to −10°C. The solution was treated with PPh_3 and propiolic acid at that temperature. The resulting solution was stirred for 10 min at which point diethylazodicarboxylatge (DEAD) was added slowly. The mixture was allowed to slowly warm to room temperature. The conversion was monitored by TLC and after total consumption of the starting material, the solvent was removed under vacuum. The crude product was directly purified by column chromatography.

General Procedure C: Gold-catalyzed Cycloisomerization of 1,7-Enynes

The enyne derivative was dissolved in [D2]DCM and an NMR spectrum was taken as a reference. Then 5 mol-% of the catalyst and 5 mol-% of silver salt were added. The reaction progress was monitored by 1H NMR spectroscopy. Then the

Table 12. Selected crystallographic data and haptacity from Kochi et al.[55]

Entry	Au–P [Å]	Au–Cl [Å]	Angle P–Au–Cl [°]	Au–C_{ortho} [Å]	Au–C_{ipso} [Å]	Au–plane [Å]	Hapticity η_{calc}
1 Au-BiarylC	2.241	2.291	169.48	3.171 3.354	2.956	2.955	1.13
2 Au-BiarylD	2.228	2.283	175.45	3.317 3.538	3.160	3.140	1.50[C]
3 Au-BiarylE	2.233	2.288	175.49	3.266[A] 3.699	3.194	3.132	1.81[C]
4 Au-BiarylF	2.231	2.286	175.38	3.167[A] 3.641	3.193	3.104	1.91
5 Au-BiarylG	2.235	2.297	173.42	3.253 3.605	3.193	3.145	1.81
6 Au-BiarylH	2.224	2.281	176.33	3.195 3.583	3.113	3.060	1.77
7 Au-BiarylI	2.228	2.283	176.36	3.206 3.474	3.121	3.076	1.74[C]
8 Au-BiarylM	2.238	2.294	172.94	3.116[A] 3.546	3.266	3.091	1.54
9 Au-BiarylN	2.239	2.285	176.19	3.229 3.732	3.135	3.046	1.82
10 Au-BiarylO	2.246	2.289	176.64	3.227 3.358	3.052	3.037	1.43
11 Au-BiarylQ	2.233	2.289	176.37	3.345 3.544	3.215	3.188	1.58
12 Au- BiarylR	2.232	2.287	175.38	3.674 3.333[B]	3.259	3.220	1.74

[A]Distance to the ortho-substituted biphenyl.
[B]Distance to the unsubstituted ortho position of the biphenyl.
[C]In good agreement with the experimental data described in the literature.[50,58]

solvent was evaporated and the resulting residue was purified by flash column chromatography on silica gel.

General Procedure D: Preparation of Au^{I} Complexes with Phosphine Ligands

Tetrahydrothiophengold(I) chloride (1 equiv.) was dissolved in dichloromethane and the phosphine ligand (1 equiv.) was slowly added (~45 min) to this solution with stirring. After 60 min, the solid was filtered off, washed with dichloromethane and dried under vacuum.

Single Crystals for X-Ray Crystal Structure Analyses

All single crystals were grown by slow evaporation of the solvent.

Syntheses

1-(5-Methylfuran-2-yl)propan-2-ol (**5a**)

According to General Procedure A, 2-methylfuran (4.51 mL, 50.0 mmol) was treated with ^{n}BuLi in hexanes (20.0 mL, 2.5 M, 50.0 mmol) and 1,2-epoxypropane (2.13 mL, 50.0 mmol) in 20 mL THF. The crude product was purified by silica gel flash chromatography (hexane/methyltertbutylehter (MTBE) 5 : 1) to give **5a** (4.70 g, 33.5 mmol, 67 %) as a colourless oil. R_f (hexanes/MTBE, 5 : 1) 0.14. δ_H (CDCl, 300 MHz) 1.20 (d, *J* 6.2, 3H), 1.92 (s, 1H), 2.23 (s, 3H), 2.67 (dq, *J* 7.6, 4.5, 2H), 3.97–4.05 (m, 1H), 5.84 (d, *J* 2.9, 1H), 5.94 (d, *J* 3.0, 1H). δ_C (CDCl, 75 MHz) 13.5 (s), 22.6 (s), 37.9 (d), 66.7 (t), 106.0 (t), 107.7 (t), 150.9 (q), 151.1 (q).

1-(5-Methylfuran-2-yl)pentan-2-ol (**5b**)

According to General Procedure A, 2-methylfuran (4.51 mL, 50.0 mmol) was treated with ^{n}BuLi in hexanes (20.0 mL, 2.5 M, 50.0 mmol) and 1,2-epoxypentane (5.19 mL, 50.0 mmol) in 20 mL THF. The crude product was purified by silica gel flash chromatography (hexane/MTBE 5 : 1) to give **5b** (2.86 g, 17.0 mmol, 34 %) as a slightly yellow oil. *R* (hexanes/ MTBE 5 : 1) 0.19. ν_{max} (film)/cm^{-1} 3384, 2959, 2927, 2873, 1570, 1454, 1219, 1123, 1021, 782. δ_H ($CDCl_3$, 300 MHz) 0.91 (t, $^3J_{H,H}$ 7.0, 3H), 1.44 (m, 4H), 1.98 (s, 1H), 2.22 (s, 3H), 2.68 (qd, $^3J_{H,H}$ 8.0 and $^2J_{H,H}$ 4.1, 2H), 3.83 (m, 1H), 5.83 (d, $^3J_{H,H}$ 2.9, 1H), 5.94 (d, $^3J_{H,H}$ 3.0, 1H). δ_C ($CDCl_3$, 75 MHz) 13.4 (q), 14.0 (q), 18.8 (t), 36.2 (t), 38.8 (t), 70.1 (d), 106.0 (d), 107.6 (d), 151.0 (s), 151.0 (s). *m*/*z* (electrospray ionization (EI)) 168 (24 %) [M$^+$], 151 (11), 96 (100), 95 (69), 81 (17); *m*/*z* (high-resolution (HR)-MS, 70eV) 168.1166; calc. for $C_{10}H_{16}O_2$: 168.1150.

1-(5-Methylfuran-2-yl)hexan-2-ol (**5c**)

According to General Procedure A, 2-methylfuran (3.97 mL, 44.0 mmol) was treated with ^{n}Buli in hexanes (17.6 mL, 2.5 M, 44.0 mmol) and 1,2-epoxyhexane (5.30 mL, 44.0 mmol) in 20 mL THF. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate/DCM 20 : 1 : 2) to give **5c** (3.61 g, 19.8 mmol, 45 %) as a slightly yellow oil. *R* (light petroleum/ethyl acetate/DCM, 20 : 1 : 2) 0.20. ν_{max} (film)/cm^{-1} 3484, 2965, 2932, 2872, 1759, 1706, 1431, 1381, 1242, 1169, 1096 cm. δ_H ($CDCl_3$, 500 MHz) 0.88 (t, $^3J_{H,H}$ 7.1, 3H), 1.31–1.49 (m, 6H), 1.86 (s, 1H), 2.23 (s, 3H), 2.69 (dq, $^3J_{H,H}$ 8.0, 4.1, 2H), 3.82 (m, 1H), 5.85 (s, 1H), 5.95 (d, $^3J_{H,H}$ 3.0, 1H). δ_C ($CDCl_3$, 125 MHz) 13.5 (q), 14.0 (q), 22.7 (t), 27.8 (t), 36.3 (t), 70.4 (d), 106.0 (d), 107.7 (d), 151.0 (s), 151.1 (s). *m*/*z* (EI) 182 (23 %) [M$^+$], 151 (12), 113 (9), 96 (100), 95 (58), 81 (14); *m*/*z* (HR-MS, 70eV) 182.1334; calc. for $C_{11}H_{18}O_2$: 182.1307.

2-(5-Methylfuran-2-yl)-1-phenylethanol (**5d**)

According to General Procedure A, 2-methylfuran (3.97 mL, 44.0 mmol) was treated with ^{n}Buli in hexanes (17.6 mL, 2.5 M, 44.0 mmol) and 1,2-epoxystyrene (5.02 mL, 44.0 mmol) in 25 mL THF. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate/DCM 15 : 1 : 2) to give **5d** (3.73 g, 18.5 mmol, 42 %) as a slightly yellow oil. *R* (light petroleum/ethyl acetate/DCM, 15 : 1 : 2) 0.10. ν_{max} (film)/cm^{-1} 3418, 3066, 3033, 2920, 1709, 1609, 1568, 1494, 1452, 1218, 1051, 1024, 784 cm. δ_H ($CDCl_3$, 500 MHz) 2.27 (s, 4H), 2.97 (m, 2H), 4.95 (dd, *J* 8.5 and 3.9, 1H), 5.88 (d, *J* 2.8, 1H), 5.96 (d, *J* 2.9, 1H), 7.28 (t, $^3J_{H,H}$ 6.8, 1H), 7.36 (m, 4H). δ_C ($CDCl_3$, 125 MHz) 13.5 (q), 38.5 (t), 72.8 (d), 106.1 (d), 108.1 (d), 125.7 (d), 127.6 (d), 128.3 (d), 143.4 (s), 150.4 (s), 151.2 (s). *m*/*z* (EI) 202 (5 %) [M$^+$], 107 (24), 96 (100), 95 (55), 79 (20), 77 (12); *m*/*z* (HR-MS, 70eV) 202.0994; calc. for $C_{13}H_{14}O_2$: 202.0975. Anal. calc. for $C_{13}H_{14}O_2$ (202.1): C 77.20, H 6.98. Found: C 77.14, H 6.85 %.

1-(5-Methylfuran-2-yl)-3-phenoxypropan-2-ol (**5e**)

According to General Procedure A, 2-methylfuran (3.97 mL, 44.0 mmol) was treated with ^{n}Buli in hexanes (17.6 mL, 2.5 M, 44.0 mmol) and 1,2-epoxy-3-phenoxypropane (8.94 mL, 66.0 mmol) in 35 mL THF. The crude product was purified by recrystallization in hexane to give **5e** (4.31 g, 18.5 mmol, 42 %) as a white solid. Mp 70–71°C. ν_{max} (KBr)/cm^{-1} 3449, 3066, 2832, 1602, 1499, 1252, 1043. δ_H ($CDCl_3$, 300 MHz) 2.24 (s, 3H), 2.39 (d, $^3J_{H,H}$ 4.3, 1H), 2.91 (d,$^3J_{H,H}$ 6.5, 2H), 3.91 (dd, *J* 9.4, *J* 6.5, 1H), 3.99 (dd, *J* 9.4, 4.0, 1H), 4.27 (m, *J* 4.1, 2.4, 1H), 5.86 (d, *J* 2.9, 1H), 6.00 (d, *J* 3.0, 1H), 6.89 (m, 1H), 6.91 (m, 1H), 6.95 (tt, *J* 7.3, 1.0, 1H), 7.26 (d, *J* 7.5, 1H), 7.28 (d, *J* 7.5, 1H). δ_C (CDCl, 75 MHz) 13.6 (q), 32.5 (t), 69.1 (t), 71.1 (d), 106.2 (d), 108.1 (d), 114.6 (d), 121.2 (d), 129.5 (d), 149.8 (s), 151.3 (s), 158.6 (s). *m*/*z* (EI) 232 (58 %) [M$^+$], 162 (5), 160 (7), 121 (42), 119 (8), 113 (6), 96 (38), 95 (100), 94 (6), 91 (5); *m*/*z* (HR-MS, 70eV) 232.1082; calc. for $C_{14}H_{16}O_3$: 232.1099. Anal. calc. for $C_{14}H_{16}O_3$ (232.1): C 72.39, H 6.94. Found: C 72.16, H 6.93 %.

1,3-Bis(5-methylfuran-2-yl)propan-2-ol (**5f**)

(a) 2-Methyl-5-(oxiran-2-ylmethyl)furan. According to General Procedure A, 2-methylfuran (3.08 mL, 37.5 mmol) was treated with ^{n}BuLi in hexanes (15.0 mL, 2.5 M, 37.5 mmol) and 2-(chloromethyl)oxirane (4.40 mL, 56.3 mmol) in 30 mL THF. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate/DCM 15 : 1 : 2) to give 2-methyl-5-(oxiran-2-ylmethyl)furan **5f** (2.68 g, 19.4 mmol, 41 %) as a colourless oil. *R* (light petroleum/ethyl acetate (EE)/DCM 15 : 1 : 2) 0.13. ν_{max} (KBr)/cm^{-1} 3418, 2954, 2923, 1757, 1715, 1569, 1430, 1216. δ_H ($CDCl_3$, 300 MHz) 5.97 (d, *J* 3.0, 1H), 5.84 (m, 1H), 3.13 (m, 1H), 2.89 (dd, *J* 15.5, 5.5, 1H), 2.72 (m, 2H), 2.52 (dd, *J* 5.0, 2.6, 2H), 2.23 (s, 3H). δ_C (CDCl, 75 MHz) 151.0 (q), 149.2 (q), 107.2 (t), 106.0 (t), 50.46 (t), 46.7 (d), 31.5 (d), 13.4 (s). *m*/*z* (EI) 138 (40 %) [M$^+$], 95 (100), 43 (14); *m*/*z* (HR-MS, 70eV) 138.0680; calc. for $C_8H_{10}O_2$: 138.0681.

(b) ***5f***. According to General Procedure A, 2-methylfuran (164 mg, 2.00 mmol) was treated with ^{n}BuLi in hexanes (800 µL, 2.5 M, 2.00 mmol) and 2-methyl-5-(oxiran-2-ylmethyl)furan

(276 mg, 2.00 mmol) in 10 mL THF. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate/DCM 20 : 1 : 2) to give **5f** (189 mg, 0.86 mmol, 43 %). *R* (light petroleum/ethyl acetate/DCM, 20 : 1 : 2) 0.13. ν_{max} (film)/cm^{-1} 3418, 2922, 1710, 1570, 1431, 1384, 1218, 1177, 1046, 1023, 996, 962, 935, 784. δ_H ($CDCl_3$, 300 MHz) 2.21 (bs, 1H), 2.24 (s, 6H), 2.76 (m, 4H), 4.12 (m, 1H), 5.86 (dd, *J* 2.9, 1.0, 2H), 5.98 (d, *J* 2.9, 2H). δ_C ($CDCl_3$, 75 MHz) 13.5 (q, 2C), 35.4 (t, 2C), 69.3 (d, 2C), 106.1 (d, 2C), 107.9 (d, 2C), 150.5 (s, 2C), 151.1 (s, 2C). *m/z* (EI) 220 (89 %) [M$^+$], 202 (7), 161 (9), 151 (9), 125 (19), 124 (33), 97 (16), 96 (76), 95 (100), 83 (20), 81 (14); *m/z* (HR-MS, 70eV) 220.1068; calc. for $C_{13}H_{16}O_3$: 220.1099. Anal. calc. for $C_{13}H_{16}O_3$ (220.3): C 70.89, H 7.32. Found: C 70.22, H 7.36 %.

*(2S,3S)-3-(5-Methylfuran-2-yl)-3-phenylpropane-1,2-diol (**5g**)*

In an oven-dried Schlenk flask under an inert gas atmosphere, a solution of 2-methylfuran (3.97 mL, 44.0 mmol) in dry THF (30.0 mL) was prepared. The solution was cooled to 0°C. Then ^{n}BuLi in hexanes (2.5 M, 17.6 mL, 44.0 mmol) was added dropwise and the solution turned slightly yellow. Afterwards the solution was stirred for 2 h at RT before ((2*R*,3*R*)-3-phenyloxiran-2-yl)methanol (7.56 mL, 33.0 mmol) was added dropwise at 0°C. Then the mixture was allowed to warm slowly to RT and stirred for 14 h and the solution turned orange-reddish. Subsequently the solution was hydrolyzed with water (20 mL). The aqueous phase was extracted with DCM (15 mL) before the combined organic phases were dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification of the product by column chromatography (SiO_2, light petroleum/ethyl acetate/DCM 3 : 1 : 2) provided **5 g** (700 mg, 3.01 mmol) as a slightly yellow oil in 9 % yield (only one diastereoisomer observed). R_f (light petroleum/EE/DCM 3 : 1 : 2) 0.08. ν_{max} (film)/cm^{-1} 3420, 2949, 2910, 1616, 1566, 1496, 1453, 1220, 1025, 779, 747, 708, 615. δ_H ($CDCl_3$, 300 MHz) 2.23 (s, 3H), 2.80 (s, 2H), 3.42 (dd, *J* 11.5, 6.7, 1H), 3.59 (dd, *J* 11.5, 2.9, 1H), 3.97 (d, *J* 8.8, 1H), 4.23 (m, 1H), 5.84 (d, *J* 2.9, 1H), 5.97 (d, *J* 3.0, 1H), 7.28 (m, 5H). δ_C ($CDCl_3$, 75 MHz) 13.5 (q), 48.5 (d), 64.7 (t), 73.6 (d), 106.0 (d), 107.5 (d), 127.0 (d, 2C), 128.5 (d, 2C), 128.8 (d), 139.1 (d), 151.1 (s), 152.3 (s). *m/z* (EI) 232 (5 %) [M$^+$], 201 (4), 173 (4), 172 (38), 171 (100), 163 (5), 162 (7), 151 (9), 128 (6), 113 (6), 107 (6), 105 (5), 91 (7), 77 (4); *m/z* (HR-MS, 70eV) 232.1114; calc. for $C_{14}H_{16}O_3$: 232.1099.

*1-Methyl-2-(5-methylfuran-2-yl)ethylprop-2-ynoate (**6a**)*

According to General Procedure B, **5a** (2.00 g, 14.0 mmol) was treated with propiolic acid (879 µL, 14.0 mmol), DCC (2.94 g, 14.0 mmol), and DMAP (18 mg, 140 µmol) in 50 mL DCM. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate/DCM 10 : 1 : 2) to give **6a** (1.05 g, 5.46 mmol, 39 %) as a colourless oil. *R* (light petroleum/ethyl acetate/DCM, 10 : 1 : 2) 0.47. ν_{max} (film)/cm^{-1} 3276, 2925, 2118, 1799, 1570, 1452, 1384, 1235, 1190, 1134, 1049, 1021, 786, 757. δ_H ($CDCl_3$, 300 MHz) 1.26 (d, $^3J_{H,H}$ 6.3, 3H), 2.19 (s, 3H), 2.84 (dq, *J* 6.5, 2H), 2.86 (s, 1H), 5.18 (sext, $^3J_{H,H}$ 6.4, 1H), 5.80 (dd, *J* 2.9, 1.0, 1H), 5.92 (d, *J* 3.0, 1H). δ_C (CDCl, 75 MHz) 13.3 (q), 19.2 (q), 34.2 (t), 71.9 (d), 74.4 (d), 74.8 (s), 106.0 (d), 107.9 (d), 148.8 (s), 151.0 (s), 151.9 (s). *m/z* (EI) 192 (6 %) [M$^+$], 163 (6), 162 (8), 151 (10), 123 (14), 122 (95), 121 (6), 107 (8), 96 (7), 95 (100), 91 (5); *m/z* (HR-MS, 70eV) 192.0795; calc. for $C_{11}H_{12}O_3$: 192.0786.

*1-(5-Methylfuran-2-yl)pentan-2-yl Propiolate (**6b**)*

According to General Procedure B, **5b** (1.68 g, 10.0 mmol) was treated with propiolic acid (616 µL, 10.0 mmol), DCC (2.06 g, 10.0 mmol), and DMAP (31.0 mg, 250 µmol) in 15 mL DCM. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate 20 : 1) to give **6b** (550 mg, 2.50 mmol, 25 %) as a colourless oil. *R* (light petroleum/ethyl acetate, 20 : 1) 0.27. ν_{max} (film)/cm^{-1} 3267, 2962, 2936, 2876, 2118, 1713, 1383, 1361, 1233, 1022, 786, 756. δ_H ($CDCl_3$, 300 MHz) 0.89 (t, $^3J_{H,H}$ 7.3, 3H), 1.37 (m, 2H), 1.58 (m, 2H), 2.22 (s, 3H), 2.84 (d, *J* 6.2, 2H), 2.84 (s, 1H), 5.17 (m, 1H), 5.82 (d, $^3J_{H,H}$ 2.8, 1H), 5.92 (d, *J* 2.9, 1H). δ_C ($CDCl_3$, 75 MHz) 13.6 (q), 13.9 (q), 18.6 (t), 32.9 (t), 35.7 (t), 74.6 (d), 75.3 (d), 75.5 (s), 106.2 (d), 108.1 (d), 149.2 (s), 151.3 (s), 152.4 (s). *m/z* (EI) 220 (5 %) [M$^+$], 150 (68), 121 (72), 95 (100); *m/z* (HR-MS, 70eV) 220.1089; calc. for $C_{13}H_{16}O_3$: 220.1099.

*1-(5-Methylfuran-2-yl)hexan-2-yl Propiolate (**6c**)*

According to General Procedure B, **5c** (729 g, 4.0 mmol) was treated with propiolic acid (246 µL, 4.00 mmol), DCC (825 mg, 4.00 mmol), and DMAP (12.0 mg, 100 µmol) in 15 mL DCM. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate 30 : 1) to give **6c** (281 mg, 1.20 mmol, 30 %) as a yellow oil. *R* (light petroleum/ethyl acetate, 30 : 1) 0.14. ν_{max} (film)/cm^{-1} 3281, 2959, 2933, 2863, 2117, 1714, 1570, 1235, 1022, 785, 735. δ_H ($CDCl_3$, 500 MHz) 0.87 (t, $^3J_{H,H}$ 7.0, 3H), 1.29 (m, 4H), 1.60 (m, 2H), 2.22 (s, 3H), 2.84 (m, 3H), 5.16 (quin, $^3J_{H,H}$ 6.3, 1H), 5.83 (d, $^3J_{H,H}$ 2.7, 1H), 5.93 (d, *J* 2.9, 1H). δ_C ($CDCl_3$, 75 MHz) 13.5 (q), 14.0 (q), 22.7 (t), 33.0 (t), 33.4 (t), 74.6 (d), 75.1 (s), 75.7 (d),106.3 (d), 108.2 (d), 147.6 (s), 149.6 (s), 152.5 (s). *m/z* (EI) 234 (7 %) [M$^+$], 216 (5), 213 (8), 212 (5), 201 (9), 165 (14), 164 (96), 161 (13), 151 (20), 121 (75), 113 (13), 108 (11), 96 (9), 95 (100), 92 (18), 91 (25); *m/z* (HR-MS, 70eV) 234.1290; calc. for $C_{14}H_{18}O_3$: 234.1256.

*2-(5-Methylfuran-2-yl)-1-phenylethyl propiolate (**6d**)*

According to General Procedure B, **5d** (809 mg, 4.00 mmol) was treated with propiolic acid (246 µL, 4.00 mmol), DCC (825 mg, 4.00 mmol), and DMAP (12 mg, 100 µmol) in 15 mL DCM. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate 10 : 1) to give **6d** (295 mg, 1.16 mmol, 29 %) as a colourless oil. *R* (light petroleum/ethyl acetate, 10 : 1) 0.35. ν_{max} (film)/cm^{-1} 3278, 2920, 2119, 1721, 1230, 1026, 754, 701. δ_H (CD_2Cl_2, 300 MHz) 2.23 (s, 3H), 2.97 (s, 1H), 3.09 (dd, *J* 5.8, 1H), 3.24 (dd, *J* 8.1, 1H), 5.85 (m, 1H), 5.89 (d, *J* 7, 1H), 6.06 (m, 1H), 7.35 (m, 5H). δ_C (CD_2Cl_2, 75 MHz) 13.5 (q), 35.3 (t), 74.8 (s), 75.1 (d), 76.9 (d), 106.4 (d), 108.5 (d), 126.9 (d), 128.8 (d), 128.8 (s), 139.1 (d), 148.9 (s), 151.7 (s), ester carbon not detected. *m/z* (EI) 254 (3 %) [M$^+$], 185 (11), 184 (45), 159 (40), 96 (7), 95 (100); *m/z* (HR-MS, 70eV) 254.0970; calc. for $C_{16}H_{14}O_3$: 254.0943.

*2-(5-Methylfuran-2-yl)-1-(phenoxymethyl)ethyl Prop-2-ynoate (**6e**)*

According to General Procedure B, **5e** (1.64 g, 7.00 mmol) was treated with propiolic acid (430 µL, 7.00 mmol), DCC (1.45 g, 7.00 mmol), and DMAP (9.0 mg, 70 µmol) in 48 mL DCM. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate 25 : 1) to give **6e** (497 mg, 1.75 mmol, 25 %) as a colourless oil. *R* (light petroleum/ethyl acetate, 25 : 1) 0.13. ν_{max} (film)/cm^{-1} 3272,

2924, 2119, 1717, 1548, 1496, 1228, 1044, 754, 692. δ_H ($CDCl_3$, 300 MHz) 2.28 (s, 3H), 2.97 (s, 1H), 3.12 (m, *J* 15.2, 6.5, 2H), 4.12 (m, *J* 10.5, 3.5, 2H), 5.56 (m, 1H), 5.91 (d, *J* 3.0, 1H), 6.05 (d, *J* 3.0, 1H), 6.93 (d, *J* 8.8, 2H), 7.01 (t, *J* 7.4, 1H), 7.32 (m, *J* 8.7, 2H). δ_C ($CDCl_3$, 75 MHz) 13.2 (q), 29.2 (t), 67.4 (t), 72.7 (d), 74.3 (s), 75.5 (d), 106.1 (d), 108.3 (d), 114.4 (d, 2C), 121.1 (d), 129.3 (d, 2C), 147.8 (s), 151.2 (s), 151.7 (s), 158.1 (s). *m/z* (EI) 284 (4 %) [M^+], 151 (4), 122 (9), 121 (100), 95 (33), 77 (7); *m/z* (HR-MS, 70eV) 284.1041; calc. for $C_{17}H_{16}O_4$: 284.1049. Anal. calc. for $C_{17}H_{16}O_4$ (284.3): C 71.82, H 5.67. Found: C 71.71, H 5.74 %.

*2-(5-Methylfuran-2-yl)-1-[(5-methylfuran-2-yl)methyl] ethyl Prop-2-ynoate (**6f**)*

According to General Procedure B, **5f** (1.00 g, 4.54 mmol) was treated with propiolic acid (280 µL, 4.54 mmol), DCC (938 g, 4.54 mmol), and DMAP (6 mg, 45 µmol) in 25 mL DCM. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate/DCM 15 : 1 : 1) to give **6f** (210 mg, 772 µmol, 17 %) as a colourless oil. *R* (light petroleum/ethyl acetate/DCM, 15 : 1 : 1) 0.67. ν_{max} (film)/cm^{-1} 3271, 2923, 2118, 1716, 1616, 1569, 1234, 1190, 1023, 995, 786, 751. δ_H ($CDCl_3$, 300 MHz) 2.23 (s, 6H), 2.83 (s, 1H), 2.85–2.96 (m, 4H), 5.36 (q, *J* 6.3, 1H), 5.83 (m, 2H), 5.97 (d, *J* 3.0, 2H). δ_C ($CDCl_3$, 75 MHz) 13.5 (q), 32.1 (t), 70.9 (s), 73.5 (d), 74.6 (d), 106.1 (d), 108.3 (d), 148.6 (s), 151.3 (s), 151.9 (s). *m/z* (EI) 272 (17 %) [M^+], 218 (8), 203 (11), 202 (76), 187 (7), 162 (7), 160 (10), 159 (57), 151 (8), 145 (6), 121 (30), 113 (6), 96 (7), 95 (100), 91 (6); *m/z* (HR-MS, 70eV) 272.1049; calc. for $C_{16}H_{16}O_4$: 272.1049. Anal. calc. for $C_{16}H_{16}O_4$ (272.3): C 70.57, H 5.92. Found: C 70.77, H 5.98 %.

*(2S,3S)-3-(5-Methylfuran-2-yl)-3-phenylpropane-1,2-diyl Dipropiolate (**6g**)*

In an oven-dried Schlenk flask under an inert gas atmosphere, a solution of **5g** (480 mg, 2.07 mmol) and propiolic acid (250 µL, 4.11 mmol) in dry DCM (15 mL) was prepared. The solution was cooled to 0°C. A solution of DCC (500 mg, 2.43 mmol) and DMAP (5.0 mg, 41 µmol) in DCM (5 mL) was added within 1 h at 0°C. The resulting mixture was stirred for 5 h at RT. Then the obtained precipitate was filtered off and washed with diethyl ether. The resulting filtrate was washed with brine and the combined organic layers dried over Mg_2SO_4. The solid was removed by filtration and the solution was concentrated under vacuum. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate/DCM 15 : 1 : 2) to provide **6g** (100 mg, 0.30 mmol, 15 %) as a colourless oil. R_f (light petroleum/EE/DCM 15 : 1 : 2) 0.11. ν_{max} (film)/cm^{-1} 3536, 3484, 3429, 3410, 3284, 3266, 2123, 1719, 1243, 1207, 1166, 1060, 755, 744, 701. δ_H ($CDCl_3$, 300 MHz) 2.24 (s, 3H), 2.81 (s, 1H), 2.91 (s, 1H), 4.19 (dd, *J* 12.2, 6.3, 1H), 4.29 (d, *J* 9.2, 1H), 4.38 (dd, *J* 12.2, 2.9, 1H), 5.85 (m, *J* 3.0, 2H), 6.03 (d, *J* 3.1, 1H), 7.30 (m, 5H). δ_C ($CDCl_3$, 75 MHz) 13.5 (q), 46.2 (d), 65.2 (t), 73.7 (s), 73.9 (s), 74.1 (s), 75.7 (d, 2C), 106. 3 (d), 108.7 (d), 127.5 (d), 128.5 (d, 2C), 128.6 (d, 2C), 137.2 (s), 149.9 (s), 151.5 (s), 152.1 (s), 152.1 (s). *m/z* (EI) 336 (3 %) [M^+], 266 (26), 237 (8), 221 (7), 208 (9), 179 (11), 172 (45), 171 (100), 161 (7), 151 (9), 141 (612), 128 (15), 125 (15), 115 (11), 91 (9); *m/z* (HR-MS, 70eV) 336.1010; calc. for $C_{20}H_{16}O_5$: 336.0998.

*8-Hydroxy-3,7-dimethylisochroman-1-one (**7a**)*

According to General Procedure C, **6g** (82.0 mg, 427 µmol) was treated with di-*tert*-butyl-(2′,4′,6′-triisopropyl-3,4,5,6-tetramethylbiphenyl-2-yl)phospinegold(I) chloride (15 mg, 21 µmol) and silver tetrafluoroborate (4.0 mg, 21 µmol) in 1 mL [D2]DCM. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate/DCM 15 : 1 : 1) to give **7g** (39.0 mg, 205 µmol, 48 %) as a white solid. Mp 75–76°C. *R* (light petroleum/ethyl acetate/DCM, 15 : 1 : 1) 0.45. δ_H ($CDCl_3$, 300 MHz) 1.50 (d, $^3J_{H,H}$ 6.3, 3H), 2.22 (s, 3H), 2.87 (d, $^3J_{H,H}$ 7.2, 2H), 4.69 (sext, $^3J_{H,H}$ 6.4 and 7.2, 1H), 6.57 (d, $^3J_{H,H}$ 7.5, 1H), 7.25 (d, $^3J_{H,H}$ 7.4, 1H), 11.24 (s, 1H). δ_C ($CDCl_3$, 75 MHz) 15.4 (q), 20.7 (q), 34.5 (t), 76.3 (d), 107.5 (s), 117.1 (d), 125.3 (s), 136.5 (s), 136.8 (d), 160.5 (s), 170.4 (s). *m/z* (EI) 192 (100 %) [M^+], 174 (35), 173 (7), 163 (18), 162 (8), 159 (21), 151 (12), 149 (8), 148 (33), 146 (9), 145 (7), 131 (9), 120 (11), 119 (5), 113 (8), 92 (12), 91 (27), 77 (6); *m/z* (HR-MS, 70eV) 192.0788; calc. for $C_{11}H_{12}O_3$: 192.0786.

*8-Hydroxy-7-methyl-3-propylisochroman-1-one (**7b**)*

According to General Procedure C, **6b** (35.0 mg, 159 µmol) was treated with di-*tert*-butyl-(2′,4′,6′-triisopropyl-3,4,5,6-tetramethylbiphenyl-2-yl)phospinegold(I) chloride (6 mg, 8 µmol) and silver tetrafluoroborate (2 mg, 8 µmol) in 1 mL [D2]DCM. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate 15 : 1) to give **7b** (18 mg, 37 µmol, 53 %) as a white solid. Mp 76°C. *R* (light petroleum/ethyl acetate, 15 : 1) 0.33. ν_{max} (film)/cm^{-1} 3438, 3059, 2946, 2929, 1664, 1623, 1463, 1429, 1377, 1253, 1175, 1150, 1131, 807, 763. δ_H ($CDCl_3$, 500 MHz) 0.96 (t, $^3J_{H,H}$ 7.3, 3H), 1.44–1.61 (m, 3H), 1.85 (m, 1H), 2.22 (s, 3H), 2.87 (m, 2H), 4.54 (m, 1H), 6.57 (d, $^3J_{H,H}$ 7.4, 1H), 7.24 (d, $^3J_{H,H}$ 7.4, 1H), 11.24 (s, 1H). δ_C ($CDCl_3$, 125 MHz) 13.8 (q), 15.4 (q), 18.1 (t), 32.8 (t), 36.8 (t), 79.7 (d), 107.7 (s), 117.1 (d), 125.2 (s), 136.7 (s), 136.7 (d), 160.5 (s), 170.4 (s). *m/z* (EI) 221 (14 %) [(M + H)$^+$], 220 (100) [M^+], 202 (35), 187 (10), 184 (15), 177 (9), 173 (22), 165 (9), 164 (7), 163 (8), 161 (23), 160 (11), 149 (19), 148 (27), 120 (7), 91 (13); *m/z* (HR-MS, 70eV) 220.1082; calc. for $C_{13}H_{16}O_3$: 220.1099. Anal. calc. for $C_{13}H_{16}O_3$ (220.3): C 70.89, H 7.32. Found: C 70.20, H 7.22 %.

*3-Butyl-8-hydroxy-7-methyl-isochroman-1-one (**7c**)*

According to General Procedure C, **6c** (35 mg, 149 µmol) was treated with di-*tert*-butyl-(2′,4′,6′-triisopropyl-3,4,5,6-tetramethylbiphenyl-2-yl)phospinegold(I) chloride (5 mg, 7 µmol) and silver tetrafluoroborate (1 mg, 7 µmol) in 1 mL [D2]DCM. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate 10 : 1) to give **7c** (20 mg, 85 µmol, 57 %) as a white solid. Mp 52°C. *R* (light petroleum/DCM, 10 : 1) 0.23. ν_{max} (film)/cm^{-1} 3450, 2953, 2934, 2859, 1665, 1457, 1438, 1255, 1174, 1147, 1127, 806, 729. δ_H ($CDCl_3$, 500 MHz) 0.91 (t, $^3J_{H,H}$ 7.2, 3H), 1.32–1.47 (m, 3H), 1.47–1.52 (m, 1H), 1.65–1.74 (m, 1H), 1.81–1.91 (m, 1H), 2.22 (s, 3H), 2.87 (m, 2H), 4.52 (m, 1H), 6.57 (d, $^3J_{H,H}$ 7.4, 1H), 7.24 (d, $^3J_{H,H}$ 7.4, 1H), 11.24 (s, 1H). δ_C ($CDCl_3$, 125 MHz) 13.9 (q), 15.4 (q), 22.4 (t), 27.0 (t), 32.8 (t), 34.5 (t), 80.0 (d), 107.7 (s), 117.1 (d), 125.2 (s), 136.7 (q), 136.7 (d), 160.5 (q), 170.4 (q). *m/z* (EI) 234 (100 %) [M^+], 216 (22), 201 (9), 177 (10), 174 (13), 173 (11), 165 (9), 164 (7), 163 (6), 162 (14), 161 (30), 160 (8), 149 (17), 148 (25), 120 (6), 119 (5), 91 (11); *m/z* (HR-MS, 70eV) 234.1250; calc. for $C_{14}H_{18}O_3$: 234.1256. Found: C 71.77, H 7.74. Found: C 71.23, H 7.54 %.

*8-Hydroxy-7-methyl-3-phenylisochroman-1-one (**7d**)*

According to General Procedure C, **6d** (35 mg, 140 µmol) was treated with di-*tert*-butyl-(2′,4′,6′-triisopropyl-3,4,5,

6-tetramethylbiphenyl-2-yl)phospinegold(I) chloride (5 mg, 7 µmol) and silver tetrafluoroborate (1 mg, 7 µmol) in 1 mL [D2]DCM. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate/DCM 25 : 1 : 4) to give **7d** (14 mg, 56 µmol, 40 %) as a white solid. *R* (light petroleum/ethyl acetate/DCM, 25 : 1 : 4) 0.38. ν_{max} (film)/cm^{-1} 3443, 2940, 1676, 1616, 1458, 1420, 1226, 1128, 802, 777, 705. δ_H ($CDCl_3$, 500 MHz) 2.25 (s, 3H), 3.08 (dd, *J* 16.4 and *J* 3.2, 1H), 3.27 (dd, *J* 16.3, 4.1, 1H), 5.56 (dd, *J* 12.2, 3.2, 1H), 6.63 (d, $^3J_{H,H}$ 7.4, 1H), 7.29 (d, $^3J_{H,H}$ 7.4, 1H), 7.34–7.46 (m, 5H), 11.21 (s, 1H). δ_C ($CDCl_3$, 125 MHz) 15.5 (q), 35.1 (t), 81.0 (d), 117.1 (d), 125.5 (s), 126.1 (d, 2C), 128.7 (d, 2C), 128.8 (d, 2C), 136.4 (s), 137.0 (d), 138.1 (s), 160.6 (s), 170.2 (s). *m/z* (EI) 254 (79 %) [M$^+$], 237 (17), 236 (100), 235 (13), 208 (28), 207 (9), 180 (5), 179 (13), 178 (10), 165 (17), 163 (7), 162 (8), 151 (13), 148 (9), 113 (9), 91 (7); *m/z* (HR-MS, 70eV) 254.0922; calc. for $C_{16}H_{14}O_3$: 254.0922.

*8-Hydroxy-7-methyl-3-(phenoxymethyl)isochroman-1-one (**7e**)*

According to General Procedure C, **6e** (225 mg, 791 µmol) was treated with di-*tert*-butyl-(2′,4′,6′-triisopropyl-3,4,5,6-tetramethylbiphenyl-2-yl)phospinegold(I) chloride (28 mg, 40 µmol) and silver tetrafluoroborate (8 mg, 40 µmol) in 10 mL DCM. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate/DCM 10 : 1 : 2) to give **7e** (63 mg, 221 µmol, 28 %) as a white solid. Mp 95°C. *R* (light petroleum/ethyl acetate/DCM, 10 : 1 : 2) 0.43. ν_{max} (film)/cm^{-1} 3170, 2924, 1673, 1619, 1498, 1455, 1426, 1385, 1362, 1290, 1254, 1223, 1170, 1141, 1121, 1090, 801, 752, 732, 691. δ_H ($CDCl_3$, 300 MHz) 2.24 (s, 3H), 3.05 (dd, *J* 16.3, 3.7, 1H), 3.21 (dd, *J* 11.3, 5.1, 1H), 4.23 (dq, *J* 10.1, 5.4, 1H), 4.90 (m, 1H), 6.64 (d, $^3J_{H,H}$ 7.4, 1H), 6.90 (m, 1H), 6.92 (m, 1H), 6.97 (tt, *J* 7.4, 1.0, 1H), 7.24–7.32 (m, 4H), 11.13 (s, 1H). δ_C ($CDCl_3$, 75 MHz) 15.5 (q), 29.7 (t), 68.5 (t), 77.2 (d), 107.5 (s), 114.6 (d, 2C), 117.4 (d), 121.5 (d), 125.5 (s), 129.6 (d, 2C), 135.8 (s), 137.1 (d), 158.1 (s), 160.6 (s), 169.5 (s). *m/z* (EI) 284 (100 %) [M$^+$], 266 (6), 200 (6), 191 (13), 190 (19), 177 (20), 174 (9), 173 (74), 163 (10), 162 (10), 161 (23), 151 (13), 149 (74), 148 (8), 121 (9), 113 (11), 91 (17); *m/z* (HR-MS, 70eV) 284.1047; calc. for $C_{17}H_{16}O_4$: 284.1049. Anal. calc. for $C_{17}H_{16}O_4$ (284.3): C 71.82, H 5.67. Found: C 71.69, H 5.87 %.

*8-Hydroxy-7-methyl-3-[(5-methylfuran-2-yl)methyl]-3,4-dihydro-1*H*-isochromen-1-one (**7f**)*

According to General Procedure C, **6f** (20 mg, 73 µmol) was treated with di-*tert*-butyl-(2′,4′,6′-triisopropyl-3,4,5,6-tetramethylbiphenyl-2-yl)phospinegold(I) chloride (3 mg, 4 µmol) and silver tetrafluoroborate (1 mg, 4 µmol) in 5 mL DCM. The crude product was purified by silica gel flash chromatography (light petroleum/ethyl acetate/DCM 15 : 1 : 1) to give **7f** (7 mg, 26 µmol, 35 %) as a white solid. *R* (light petroleum/ethyl acetate/DCM, 15 : 1 : 1) 0.49. ν_{max} (film)/cm^{-1} 3438, 2948, 2924, 1671, 1621, 1426, 1253, 1173, 1138. δ_H (CD_2Cl_2, 300 MHz) 2.21 (s, 3H), 2.24 (s, 3H), 2.93 (d, $^3J_{H,H}$ 7.5, 2H), 3.01 (dd, *J* 15.1, 6.8, 1H), 3.15 (dd, *J* 15.1, 6.1, 1H), 4.80 (quin, $^3J_{H,H}$ 6.8, 1H) 5.91 (d, $^3J_{H,H}$ 2.7, 1H), 6.06 (d, $^3J_{H,H}$ 3.0, 1H), 6.61 (d, $^3J_{H,H}$ 7.5, 1H), 7.28 (d, $^3J_{H,H}$ 7.5, 1H), 11.17 (s, 1H). δ_C (CD_2Cl_2, 75 MHz) 12.8 (q), 14.7 (q), 31.7 (t), 33.1 (t), 77.7 (d), 105.8 (d), 107.2 (s), 108.2 (d), 116.9 (d), 124.6 (s), 136.1 (s), 136.4 (d), 147.7 (s), 151.2 (s), 159.9 (s), 169.6 (s). *m/z* (EI) 272 (55 %) [M$^+$], 178 (6), 177 (48), 150 (10), 149 (100), 135 (7), 96 (10), 95 (26), 91 (10); *m/z* (HR-MS, 70eV) 272.1055; calc. for $C_{16}H_{16}O_4$: 272.1049.

Synthesis of (tetrahydrothiophene)AuCl

$HAuCl_4 \cdot 2H_2O$ (1.13 g, 3 mmol) was dissolved in H_2O/EtOH (15 mL, 4 : 1) and tetrahydrothiophene (tht) (790 mg, 9 mmol) was added dropwise. The yellow solution became colourless and (tht)AuCl precipitated. It was filtered and dried under high vacuum. (tht)AuCl (780 mg, 2.43 mmol, 81 %) was obtained as a white powder. δ_H (250 MHz, $CDCl_3$) 2.16–2.27 (m, 4H), 3.39–3.49 (m, 4H)

Triphenylphosphinegold(I) p*-Tolylsulfonate (Au-PhosphineA)*

A mixture of (triphenylphosphine)gold(I) chloride (40 mg, 0.15 mmol) and silver(I) tosylate (AgOTs) (43 mg, 0.15 mmol) was suspended in DCM. The reaction mixture was stirred at room temperature for 1 h, the solvent was evaporated, and the crude product was dissolved in DCM. The mixture was then filtered through a pad of Celite, and the solvent evaporated under reduced pressure to give Au-PhosphineA as a white solid. Yield 98 %. δ_H ($CDCl_3$, 500 MHz) 2.34 (s, 3H), 7.11–7.82 (m, 19H). δ_P ($CDCl_3$, 202 MHz) 30.34.

Data agree with literature.[59]

Di(1-adamantyl)butylphosphinegold(I) Bis(trifluoromethanesulfonyl)imidate (Au-PhosphineB)

A mixture of di(1-adamantyl)butylphosphinegold(I) chloride (1.40 g, 2.38 mmol) and $AgNTf_2$ (1.20, 2.38 mmol) was suspended in DCM. The reaction mixture was stirred at room temperature for 1 h, the solvent was evaporated, and the crude product was dissolved in DCM. The mixture was then filtered through a pad of Celite and the solvent was evaporated under reduced pressure to give Au-PhosphineB as a white solid. Yield 99 %. Mp 150–170°C. ν_{max} (film)/cm^{-1} 2909, 2853, 1449, 1397, 1377, 1346, 1216, 1187, 1133, 1054, 965, 895, 823, 789, 709. δ_H ($CDCl_3$, 500 MHz) 0.94 (t, *J* 7.2, 3H), 1.57 (m, 2H), 1.76–1.79 (m, 16 H), 2.09–2.10 (m, 18H). δ_C ($CDCl_3$, 125 MHz) 13.7 (q), 24.48 (t), 28.63–28.75 (d, adamantyl), 33.60 (s, adamantyl), 33.62 (t), 34.38 (t), 36.38 (t, adamantyl), 40.01 (d), 40.22 (d), 41.15 (t, adamantyl). δ_P (202 MHz, $CDCl_3$) 69.18. *m/z* (HR-MS electrospray ionisation (ESI)) 555.2449 [M$^+$]; calc. for $C_{24}H_{39}AuP$: 555.2455; *m/z* (HR-MS ESI) 279.9167, calc. for $C_2F_6N_1O_4S_2$: 279.91. Anal. calc. for $C_{26}H_{39}AuF_6NO_4PS_2$ (835.65): C 37.37, H 4.70, N 1.68. Found C 37.46, H 4.78, N 1.70 %.

*Tris(*tert*-butyl)phosphinegold(I) Complex (Au-PhosphineC)*

(Chloro(tetrahydrothiophen)gold(I)) (500 mg, 1.56 mmol) was dissolved in DCM and the phosphane ligand (333 mg, 1.56 mmol) was slowly added (~45 min) to this solution with stirring. After 60 min, the solid was filtered off, washed with DCM and dried under vacuum. Yield 99 %. Mp 260°C. ν_{max} (film)/cm^{-1} 2992, 2944, 2869, 1473, 1395, 1367, 1172, 1027, 931, 809, 747. δ_H ($CDCl_3$, 500 MHz) 1.61 (s, 27H), δ_C ($CDCl_3$, 125 MHz) 32.73 (q, 9C), 54.83, 54.05, 54.27 (s, 3C). δ_P ($CDCl_3$, 202 MHz) 96.51. *m/z* (HR-MS ESI) 457.1097 [M + Na]$^+$, calc. for $C_{12}H_{27}AuPClNa$: 457.1102.

Di(1-adamantyl)benzylphosphinegold(I) Chloride (Au-PhosphineD)

Tht-gold(I) chloride (408 mg, 1.27 mmol) was dissolved in DCM and the phosphane ligand (500 mg, 1.27 mmol) was slowly added (~45 min) to this solution with stirring. After 60 min, the solid was filtered off, washed with DCM and dried

under vacuum. Yield 99 %. Mp 268–270°C. ν_{max} (film)/cm^{-1} 2898, 2847, 1599, 1494, 1449, 1342, 1302, 1256, 1103, 1070, 1049, 971, 882, 834. δ_H ($CDCl_3$, 500 MHz) 1.68–2.16 (m, 30H, adamantyl), 3.26 (d, 2H, *J* 11.12), 7.23–7.29 (m, 1H), 7.31–7.32 (t, *J* 7.7, 2H), 7.57–7.59 (d, 2H, *J* 7.8). δ_C ($CDCl_3$, 125 MHz) 24.3 (d), 28.27 (s), 28.34 (d), 31.83 (s, adamantyl), 36.20 (t, adamantyl), 40.81 (t, adamantyl), 127.03 (d), 128.87 (s), 130.63 (d, 2C, aromatic), 130.67 (d, 2C, aromatic). δ_P ($CDCl_3$, 202 MHz) 67.74. *m/z* (HR-MS ESI) 647.1879 $[M + Na]^+$; calc. for $C_{27}H_{37}AuClNaP$: 647.1914.

Biphenyl-2-yl-di-tert-*butylphosphinegold(I) NTf_2 Salt (Au-BiarylA)*

A mixture of biphenyl-2-yldi-*tert*-butylphosphinegold(I) chloride (970 mg, 1.83 mmol) and $AgNTf_2$ (922 mg,1.83 mmol) was suspended in DCM. The reaction mixture was stirred at RT for 1 h, the solvent was evaporated, and the crude product was dissolved in DCM. The mixture was then filtered through a pad of Celite, and the solvent was evaporated under reduced pressure to give Au-BiarylA as a white solid. Yield 98 %. ν_{max} (film)/cm^{-1} 3423, 2955, 2187, 1470, 1442, 1393, 1373, 1184, 1125, 1059, 997, 956, 884, 826, 807, 774, 751, 697. δ_H ($CDCl_3$, 500 MHz) 1.44 (d, *J* 15.5, 18H), 7.19 (dd, *J* 7.57 and 2.22, 2H), 7.31–7.34 (m, 1H), 7.53–7.66 (m, 5H), 7.91 (t, *J* 7.31Hz, 1H). δ_C ($CDCl_3$, 125 MHz) 30.70 (q, 6C), 38.25 (s), 38.46 (s), 126.86 (d, 2C), 127.90 (d, 3C), 129.06 (d, 2C), 129.45 (d, 2C), 131.13 (s, 2C), 180.52 (s). δ_P ($CDCl_3$, 202 MHz) 57.75. *m/z* (HR-MS ESI) 495.1510 $[M^+]$; calc. for $C_{20}H_{27}AuP$: 495.1516.

2-(Di-tert-*butylphosphino)-1,1′-biphenylgold(I) Chloride (Au-BiarylB)*

According to General Procedure D, (tht)AuCl (64 mg, 200 µmol) was treated with 2-(di-*tert*-butylphosphino)-1,1′-biphenyl (60 mg, 200 µmol) in 1 mL DCM. Au-BiphenylB (105 mg, 198 µmol, 99 %) was obtained as a white solid. ν_{max} (film)/cm^{-1} 3443, 3423, 2928, 2852, 1627, 1447, 748. δ_H ($CDCl_3$, 300 MHz) 1.40 (d, *J* 15.6, 18H), 7.14 (d, $^3J_{H,H}$ 7.3, 2H), 7.28 (m, 1H), 7.38 (t, $^3J_{H,H}$ 7.5, 2H), 7.50 (m, 3H), 7.89 (t, $^3J_{H,H}$ 7.2, 1H). δ_C (CD_2Cl_2, 75 MHz) 30.1 (q, 3C), 30.2 (q, 3C), 37.0 (s), 37.4 (s), 126.2 (d), 127.4 (d), 128.0 (2C), 128.8 (d), 130.0 (d), 132.6 (s), 132.7 (d), 133.3 (d), 142.0 (s), 149.6 (s). δ_P (CD_2Cl_2, 122 MHz) 60.0.

Di-tert-*butyl-(2′,4′,6′-triisopropyl-3,4,5,6-tetramethylbiphenyl-2-yl)phospinegold(I) Chloride (Au-BiarylC)*

Tht-gold(I) chloride (100 mg, 0.31 mmol) was dissolved in DCM and the phosphane ligand (150 mg, 0.31 mmol) was slowly added (~45 min) to this solution with stirring. After 60 min, the solid was filtered off, washed with DCM and dried under vacuum. Yield 99 %. ν_{max} (film)/cm^{-1} 3436, 2960, 2925, 2867, 1754, 1608, 1460, 1392, 1383, 1362, 1313, 1250, 1164, 1067, 1023, 875, 770, 608, 536, 510. δ_H ($CDCl_3$, 500 MHz) 0.79 (d, *J* 6.5, 6H), 1.22 (d, *J* 6.8, 6H), 1.31 (d, *J* 6.9, 6H), 1.44 (s, 9H), 1.47 (s, 9H), 2.17 (s, 6H), 2.24 (s, 3H), 2.28–2.34 (sept, *J* 6.9, 6.8, 2H), 2.54 (s, 3H), 2.89–2.95 (sept, *J* 6.5, 1H), 6.97 (s, 2H). δ_C ($CDCl_3$, 125 MHz) 17.30 (q), 17.77 (q, 2C), 22.25 (q), 24.65 (q, 2C), 25.07 (q, 2C), 25.19 (q, 2C), 28.02 (d), 30.02 (s, 2C), 30.67 (d), 33.42 (s, 6C), 34.23 (d), 122. 53 (d, 2C), 128.00 (s), 140.22 (s), 145.74 (s, 2C), 150.24 (s). δ_P ($CDCl_3$, 202 MHz) 77.00. *m/z* (HR-MS ESI) 735.3131 $[M+Na]^+$; calc. for $C_{33}H_{53}AuClNaP$: 735.3137.

Biphenyl-2-yl(dicyclohexyl)phosphinegold(I) Chloride (Au-BiarylD)

According to General Procedure D, (tht)AuCl (64.1 mg, 0.2 mmol) and phosphine (70.1 mg, 0.2 mmol) were stirred in DCM. Au-BiarylD (119 mg, 203 µmol, quant.) was obtained as a white powder. δ_H ($CDCl_3$, 250 MHz,) 1.01–2.02 (m, 22 H), 7.14–7.20 (m, 2 H), 7.27–7.34 (m, 1 H), 7.40–7.59 (m, 5 H), 7.67–7.77 (m, 1 H). δ_P ($CDCl_3$, 101 MHz) 45.14.

Dicyclohexyl(2′-methylbiphenyl-2-yl)phosphinegold(I) Chloride (Au-BiarylE)

According to General Procedure D, (tht)AuCl (64.13 mg, 0.2 mmol) and phosphine (72.90 mg, 0.2 mmol) were stirred in DCM. Au-BiarylE (123.86 mg, 0.2 mmol, quant.) was obtained as a white powder. Mp 260–263°C. ν_{max} (KBr)/cm^{-1} 3056, 2928, 2851, 1628, 1467, 1448, 1004, 853, 755, 723, 669, 542. δ_H ($CDCl_3$, 500 MHz,) 1.04–1.40 (m, 10 H), 1.50–1.89 (m, 10 H), 1.90–1.99 (m, 2 H), 1.96 (s, 3 H), 7.00 (dd, *J* 7.5, *J* 1.1, 1 H), 7.22–7.26 (m, 2 H), 7.32 (d, 7.7, 1 H), 7.44–7.55 (m, 3 H), 7.60 (td, *J* 8.7, *J* 1.4, 1 H). δ_C ($CDCl_3$,125 MHz) 20.97 (q), 25,74 (t), 25.83 (t), 26.42 (t), 26.60 (t), 26.84 (t), 26.91 (t), 28.93 (t), 29.58 (t), 30.87 (t), 30.96 (t), 35.38 (d), 37.49 (d), 125.12 (s, $^1J_{C,P}$ 51.7), 125.57 (d), 127.47 (d, $^3J_{C,P}$ 7.7), 128.77 (d), 129.94 (d), 131.08 (d, $^4J_{C,P}$ 1.9), 131.38 (d), 132.58 (d, $^3J_{C,P}$ 7.9), 132.84 (d, $^4J_{C,P}$ 4.3), 135.64 (s), 140.87 (s, $^3J_{C,P}$ 6.2),149.16 (s, $^2J_{C,P}$ 12.8). δ_P ($CDCl_3$, 202 MHz) 38.2. *m/z* (fast atom bombardment (FAB)$^+$) 619.2 $[M + Na]^+$, 596.2 $[M^+]$, 561.2 $[M^+ - Cl]$. Anal. calc. for $C_{25}H_{33}AuClP$ (596.92): C 50.30, H 5.57, Cl 5.94, P 5.19. Found: C 50.22, H 5.67, Cl 5.73, P 5.03 %.

2-(Dicyclohexylphosphino)-2′-(N,N-dimethylamino)-1,1′-biphenylgold Chloride (Au-BiarylF)

According to General Procedure D, (tht)AuCl (160 mg, 500 µmol) was treated with 2-(dicyclohexylphosphino)-2′-(*N,N*-dimethylamino)-1,1′-biphenyl (197 mg, 500 µmol) in 10 mL DCM. Au-BiarylF (309 mg, 495 µmol, 99 %) was obtained as a white solid. Mp 190–193°C (decomp.). ν_{max} (KBr)/cm^{-1} 3434, 2961, 1629, 1471, 1174, 755. δ_H (CD_2Cl_2, 500 MHz) 7.59 (d, $^3J_{H,H}$ 7.8, 1H), 7.54 (t, $^3J_{H,H}$ 7.4, 1H), 7.46 (t, $^3J_{H,H}$ 7.5, 1H), 7.42 (t, $^3J_{H,H}$ 7.5, 1H), 7.35 (d, $^3J_{H,H}$ 7.6, 1H), 7.07 (d, $^3J_{H,H}$ 8.2, 1H), 7.04 (t, $^3J_{H,H}$ 7.4, 1H), 6.99 (d, $^3J_{H,H}$ 7.2, 1H), 2.79 (m, 1H), 2.47 (s, 6H), 2.34 (tt, *J* 12.0, 3.0, 1H), 1.99–2.10 (m, 3H), 1.86–1.92 (m, 1H), 1.66–1.81 (m, 5H), 1.59 (dq, *J* 12.4, 3.3, 2H), 1.06–1.43 (m, 9H). δ_C (CD_2Cl_2, 125 MHz) 25.3 (t), 25.4 (t), 26.2 (t, 2C), 26.3 (t), 26.4 (t), 28.6 (t), 29.7 (t), 30.1 (t), 30.6 (t), 35.3 (d), 37.5 (d), 43.1 (q, 2C), 119.3 (d), 121.2 (d), 125.2 (s), 126.5 (d), 128.7 (d), 130.4 (d), 131.1 (d), 132.1 (d), 133.1 (d), 134.6 (s), 148.1 (s), 151.0 (s). δ_P (CD_2Cl_2, 202 MHz) 39.5. *m/z* (FAB$^+$) 627 (20 %) $[M^+, {}^{37}Cl]$, 626 (21), 625 (49) $[M^+, {}^{35}Cl]$), 624 (12), 591 (29), 590 (100) $[(M - Cl)^+]$, 589 (17), 588 (21), 574 (12), 506 (6) *m/z* (HR-MS, 70eV) 625.1939; calc. for $C_{26}H_{36}^{35}ClNPAu$: 625.1921; *m/z* 590.2238; calc. for $C_{26}H_{36}NPAu$: 590.2251. Anal. calc. for $C_{26}H_{36}ClNPAu$ (625.96): C 49.89, H 5.80, N 2.24. Found: C 50.29, H 6.03, N 2.18 %.

Dicyclohexyl(2′,6′-dimethoxybiphenyl-2-yl) phosphinegold Chloride (Au-BiarylG)

According to General Procedure D, (tht)AuCl (64.13 mg, 0.2 mmol) and phosphine (82.11 mg, 0.2 mmol) were stirred in DCM. Au-BiarylG (134 mg, 0.21 mmol, quant.) was obtained as a white powder. δ_H ($CDCl_3$, 250 MHz,) 1.16–1.46 (m, 7 H), 1.60–1.87 (m, 8 H), 1.90–2.23 (m, 7 H), 3.70 (s, 6 H), 6.66

(d, *J* 8.4, 2 H), 7.16–7.25 (m, 1 H), 7.45–7.60 (m, 4 H). δ_P ($CDCl_3$, 101 MHz) 39.83.

2-(Dicyclohexylphosphino)-2′,6′-(diisopropoxy)-1,1′-biphenylgold(I) Chloride (Au-BiarylH)

According to General Procedure D, (tht)AuCl (160 mg, 500 µmol) was treated with 2-(dicyclohexylphosphino)-2′,6′-diisopropyl-1,1′-biphenyl (233 mg, 500 µmol) in 10 mL DCM. Au-BiarylH (346 mg, 495 µmol, 99 %) was obtained as a white solid. Mp 180–183°C (decomp.). ν_{max} (KBr)/cm^{-1} 3431, 2974, 2928, 2852, 1626, 1594, 1459, 1383, 1248, 1116, 1064, 772, 727. δ_H (CD_2Cl_2, 500 MHz) 1.01 (d, $^3J_{H,H}$ 6.0, 6H), 1.18 (d, $^3J_{H,H}$ 6.0, 6H), 1.20–1.37 (m, 8H), 1.44 (dq, *J* 12.4, 3.4, 2H), 1.63–1.76 (m, 6H), 1.80 (m, 2H), 2.01 (m, 2H), 2.18 (tt, *J* 12.0, 3.0, 2H), 4.48 (sept, $^3J_{H,H}$ 6.0, 2H), 6.58 (d, $^3J_{H,H}$ 8.4, 2H), 7.08 (d, $^3J_{H,H}$ 7.6, 1H), 7.35 (t, $^3J_{H,H}$ 8.4, 1H), 7.42 (t, $^3J_{H,H}$ 7.6, 1H), 7.48 (t, $^3J_{H,H}$ 7.4, 1H), 7.53 (d, $^3J_{H,H}$ 7.7, 1H). δ_C (CD_2Cl_2, 125 MHz) 21.3 (q, 2C), 21.9 (q, 2C), 25.4 (t, 2C), 26.1 (t, 2C), 29.4 (t, 2C), 30.4 (t, 2C), 36.1 (d, 4C), 69.7 (d, 2C), 105.9 (d, 2C), 121.0 (s), 126.1 (d), 127.0 (s), 128.9 (d), 129.9 (d), 131.2 (d), 132.8 (d), 143.4 (s), 155.9 (s, 2C). δ_P (CD_2Cl_2, 202 MHz) 39.1. *m/z* (FAB^+) 700 (9 %) [M^+, ^{37}Cl], 699 (8), 698 (23) [M^+, ^{35}Cl]), 665 (6), 664 (33), 663 (100) [$(M - Cl)^+$], 662 (15), 661 (6), 659 (7), 621 (6), 620 (6), 619 (12), 579 (8). *m/z* (HR-MS, 70eV) 698.2330; calc. for $C_{30}H_{43}^{35}ClO_2PAu$: 698.2355; *m/z* 663.2658; calc. for $C_{30}H_{43}O_2PAu$: 663.2666. Anal. calc. for $C_{30}H_{43}O_2ClPAu$ (699.05): C 51.54, H 6.20, Cl 5.07, P 4.43. Found: C 51.50, H 6.28, Cl 4.95, P 4.44 %.

2-Cyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenylgold(I) Chloride (Au-BiarylI)

According to General Procedure D, (tht)AuCl (96 mg, 300 µmol) was treated with 2-cyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl (143 mg, 300 µmol) in 5 mL DCM. Au-BiarylI (211 mg, 297 µmol, 99 %) was obtained as a white solid. Mp 207–208°C. ν_{max} (KBr)/cm^{-1} 3440, 2957, 2929, 2854, 1629, 1609, 1463, 1448, 1382, 1361, 770. δ_H (CD_2Cl_2, 500 MHz) 0.92 (d, $^3J_{H,H}$ 6.7, 6H), 1.19–1.25 (m, 5H), 1.28 (d, $^3J_{H,H}$ 6.9, 6H), 1.34 (d, $^3J_{H,H}$ 6.9, 7H), 1.47 (dq, *J* 12.3, 3.4, 2H), 1.66 (m, 2H), 1.75–1.84 (m, 6H), 1.91 (m, 1H), 2.06–2.14 (m, 4H), 2.25 (sept, $^3J_{H,H}$ 6.8, 2H), 2.79 (m, 1H), 2.94 (sept, $^3J_{H,H}$ 6.9, 1H), 7.06 (s, 2H), 7.22 (m, 1H), 7.50 (m, 2H), 7.63 (m, 1H). δ_C (CD_2Cl_2, 125 MHz) 22.4, 23.7, 25.0, 25.3 (t), 26.2 (t), 26.5 (t), 29.8 (t), 30.4, 34.0, 36.8, 121.1 (d), 126.7 (d), 130.0 (d), 131.9 (d), 133.3 (d), 145.3 (s), 146.9 (s), 149.5 (s). δ_P (CD_2Cl_2, 202 MHz) 35.8. *m/z* (FAB^+) 710 (1 %) [M^+, ^{37}Cl], 708 (1), [M^+, ^{35}Cl]), 673 (100) [$(M - Cl)^+$], 657 (9), 655 (6). *m/z* (HR-MS, 70eV) 708.2919; calc. for $C_{33}H_{49}^{35}ClPAu$: 708.2926.

Sodium 2-Cyclohexylphosphino-2′,6′-diisopropyl-4′-sulfonato-1,1′-biphenylgold(I) Chloride (Au-BiarylJ)

According to General Procedure D, (tht)AuCl (64.1 mg, 0.20 mmol) and phosphine (107 mg, 0.20 mmol) were stirred in DCM. Au-BiarylJ (159 mg, 0.2 mmol, quant.) was obtained as a yellowish oil. ν_{max} (KBr)/cm^{-1} 3400, 2929, 2853, 1635, 1464, 1197, 1042, 772, 646. *m/z* (HR FAB^+) 769.1892 $[M + H]^+$; calc. for $C_{30}H_{43}AuClO_3SPNa$: 769.1922.

Sodium 2-Cyclohexylphosphino-2′,6′-dimethoxy-3′-sulfonato-1,1′-biphenylgold(I) Chloride (Au-BiarylK)

According to General Procedure D, (tht)AuCl (96.0 mg, 0.30 mmol) and phosphine (154 mg, 0.30 mmol) were stirred in DCM. Au-BiarylK (224 mg, 0.3 mmol, quant.) was obtained as a colourless oil. ν_{max} (KBr)/cm^{-1} 3423, 2930, 2851, 1631, 1451, 1399, 1228, 1100, 1020, 595. *m/z* (HR-MS ESI) 721.1224 $[M - Na]^-$; calc. for $C_{26}H_{34}AuClO_5SP$: 721.1219.

Di-tert-butyl(2′-methylbiphenyl-2-yl)phosphinegold(I) Chloride (Au-BiarylL)

According to General Procedure D, (tht)AuCl (64.1 mg, 0.2 mmol) and phosphine (62.5 mg, 0.2 mmol) were stirred in DCM. Au-BiarylL (108 mg, 199 µmol, 99 %) was obtained as a white powder. Mp 273–275°C. ν_{max} (KBr)/cm^{-1} 3060, 2998, 2970, 2864, 1635, 1472, 1464, 1427, 1390, 1367, 1174, 810, 774, 754, 739, 723. δ_H ($CDCl_3$, 300 MHz,) 1.41 (d, $J_{H,P}$ 15.5, 9H), 1.43 (d, $J_{H,P}$ 15.5, 9H), 2.02 (s, 3 H), 6.98 (dd, *J* 7.6, 1.1, 1H), 7.17–7.28 (m, 2H), 7.32 (d, *J* 7.7, 1H), 7.44–7.57 (m, 3H), 7.87 (dt, *J* 7.6, 1.5, 1H). δ_C ($CDCl_3$,75 MHz) 20.80 (s), 30.78 (q, $^2J_{C,P}$ 6.4, 3 C), 31.59 (q, $^2J_{C,P}$ 6.8, 3 C), 37.98 (s, $^1J_{C,P}$ 26.0), 38.07 (s, $^1J_{C,P}$ 25.9), 125.46 (d), 126.73 (d, $^3J_{C,P}$ 6.9), 126.90 (s, $^1J_{C,P}$ 45.0), 128.73 (d), 130.25 (d), 131.00 (d, $^4J_{C,P}$ 2.3), 131.33 (d), 133.43 (d, $^3J_{C,P}$ 7.7), 133.96 (d, $^4J_{C,P}$ 2.9), 135.52 (s), 141.28 (s, $^3J_{C,P}$ 6.4),149.71 (s, $^2J_{C,P}$ 13.9). δ_P (121 MHz, $CDCl_3$) 59.79. *m/z* (FAB^+) 567.2 $[M + Na]^+$, 544.2 $[M^+]$, 509.3 $[M^+ - Cl]$. Anal. calc. for $C_{21}H_{29}AuClP$ (544.85): C 46.29, H 5.36, Cl 6.51, P 5.68. Found C 46.18, H 5.31, Cl 6.71, P 5.68 %.

2-(Di-tert-butylphosphino)-2′-(N,N-dimethylamino)-1,1′-biphenylgold(I) Chloride (Au-BiarylM)

According to General Procedure D, (tht)AuCl (96 mg, 300 µmol) was treated with 2-(di-*tert*-butylphosphino)-2′-(*N,N*-dimethylamino)-1,1′-biphenyl (102 mg, 300 µmol) in 5 mL DCM. Au-BiarylM (170 mg, 297 µmol, 99 %) was obtained as a white solid. Mp 250–252°C. ν_{max} (KBr)/cm^{-1} 3442, 2996, 2773, 1628, 1494, 1472, 1172, 1053, 946, 761, 749. δ_H (CD_2Cl_2, 500 MHz) 1.23 (s, 9H), 1.52 (s, 9H), 2.45 (s, 6H), 6.97 (d, $^3J_{H,H}$ 7.5, 1H), 7.04 (t, $^3J_{H,H}$ 7.4, 1H), 7.08 (d, $^3J_{H,H}$ 8.2, 1H), 7.31 (d, $^3J_{H,H}$ 7.7, 1H), 7.45 (m, 2H), 7.55 (t, $^3J_{H,H}$ 7.5, 1H), 7.86 (d, $^3J_{H,H}$ 8.0, 1H). δ_C (CD_2Cl_2, 125 MHz) 29.5 (q), 30.9 (q), 37.0 (s), 37.5 (s), 43.2 (q), 120.5 (d), 121.5 (d), 126.4 (s), 128.6 (d), 130.4 (d), 130.9 (s), 133.6 (d), 134.0 (d), 136.1 (s), 148.5 (s), 150.9 (s). δ_P (CD_2Cl_2, 202 MHz) 62.0. *m/z* (FAB^+) 575 (24 %) [M^+, ^{37}Cl], 573 (63), [M^+, ^{35}Cl]), 572 (9), 539 (24), 538 (100), 537 (11). *m/z* (HR-MS, 70eV) 573.1616; calc. for $C_{22}H_{32}N^{35}ClPAu$: 573.1626.

2-(Di-tert-butylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenylgold(I) Chloride (Au-BiarylN)

According to General Procedure D, (tht)AuCl (76 mg, 240 µmol) was treated with di-*tert*-butyl-phosphino-2′,4′,6′-triisopropylbiphenyl (100 mg, 240 µmol) in 7 mL DCM. Au-BiarylN (158 mg, 238 µmol, 99 %) was obtained as a white solid. ν_{max} (KBr)/cm^{-1} 3054, 2958, 2865, 1609, 1458, 1425, 1383, 1360, 1169, 1098, 1023, 770. δ_H (CD_2Cl_2, 300 MHz) 0.90 (d, $^3J_{H,H}$ 6.64, 6H), 1.27 (d, $^3J_{H,H}$ 6.8, 6H), 1.34 (d, $^3J_{H,H}$ 6.9, 6H), 1.38 (s, 9H), 1.43 (s, 9H), 2.35 (sept, $^3J_{H,H}$ 6.7, 2H), 2.94 (sept, $^3J_{H,H}$ 6.9, 1H), 7.05 (s, 2H), 7.28 (m, 1H), 7.50 (m, 2H), 7.89 (m, 1H). δ_C (CD_2Cl_2, 75 MHz) 23.1 (q), 24.5 (q), 26.2 (q), 31.2 (d), 31.4 (q), 31.5 (q), 34.7 (d), 38.4 (s) 38.8 (s), 122.1 (d), 126.8 (d, *J* 6.9), 128.3 (d), 128.9 (d), 130.6 (d, *J* 2.4), 135.0 (d, *J* 3.1), 135.3 (d, *J* 8.1), 146.3 (s, *J* 1.4), 148.6 (s), 150.4 (s). δ_P (CD_2Cl_2, 122 MHz) 58.76. *m/z* (EI) 658 (2) [M^+], 656 (4 %) [M^+], 621 (53), 620 (100), 521 (6), 423 (9), 382 (12), 381(29), 269 (7), 267 (11), 201 (5). *m/z* (HR-MS, 70eV) 656.2607; calc.

for $C_{29}H_{45}PAu^{35}Cl$: 656.2613. *m/z* (HR-MS, 70eV) 658.2569; calc. for $C_{29}H_{45}PAu^{37}Cl$: 658.2597.

1,1′-Binaphthalen-2-yl(di-tert-butyl)phosphinegold(I) Chloride (Au-BiarylO)

According to General Procedure D, (tht)AuCl (80.0 mg, 0.2 mmol) and phosphine (64.1 mg, 0.2 mmol) were stirred in DCM. Au-BiarylO (127 mg, 0.2 mmol, quant.) was obtained as a white powder. Mp 282–285°C (decomp.) ν_{max} (KBr)/cm^{-1} 3060, 2556, 2898, 1473, 1367, 1170, 823, 802, 780, 772, 749. δ_H ($CDCl_3$, 300 MHz) 1.42 (d, $J_{H,P}$ 15.6, 9 H), 1.45 (d, $J_{H,P}$ 15.4, 9 H), 6.96 (t, *J* 9.7, 2 H), 7.19–7.25 (m, 2 H), 7.32 (dd, *J* 7.1, *J* 1.0, 1 H), 7.43–7.62 (m, 3 H), 7.89–8.05 (m, 4 H), 8.23 (d, *J* 8.3, 1 H). δ_C ($CDCl_3$,75 MHz) 30.92 (q, $^2J_{C,P}$ 6.5, 3 C), 31.82 (q, $^2J_{C,P}$ 7.0, 3 C), 38.03 (s, $^1J_{C,P}$ 25.3), 38.25 (s, $^1J_{C,P}$ 25.6), 124.97 (d), 125.47 (s, $^1J_{C,P}$ 45.9), 126.12 (d), 126.18 (d), 126.26 (d), 127.16 (d, $^4J_{C,P}$ 1.1), 127.43 (d, $^3J_{C,P}$ 7.1), 127.69 (d), 128.29 (d), 128.64 (d, $^4J_{C,P}$ 1.5), 128.85 (d, $^4J_{C,P}$ 3.5) 129.36 (d), 129.49 (d), 129.72 (d), 133.53 (s), 134.10 (d, $^4J_{C,P}$ 1.9), 134.37 (s), 134.67 (s, $^3J_{C,P}$ 8.9), 136.24 (s, $^3J_{C,P}$ 7.9),147.87 (s, $^2J_{C,P}$ 13.1). δ_P (121 MHz, $CDCl_3$) 62.05. *m/z* (FAB$^+$) 653.2 [M + Na]$^+$, 630.2 [M$^+$], 595.2 [M$^+$ – Cl]. Anal. calc. for $C_{28}H_{31}AuClP$ (630.94): C 53.30, H 4.95, Cl 5.62, P 4.91. Found C 53.17, H 4.87, Cl 5.90, P 4.83 %.

2′-(Diphenylphosphinyl)-N,N-dimethylbiphenyl-2-aminegold(I) Chloride (Au-BiarylP)

According to General Procedure D, (tht)AuCl (64.13 mg, 0.2 mmol) and phosphine (76.29 mg, 0.2 mmol) were stirred in DCM. Au-BiarylP (124.45 mg, 0.2 mmol, quant.) was obtained as a white powder. Mp 218–220°C. ν_{max} (KBr)/cm^{-1} 3054, 2940, 2828, 1594, 1494, 1436, 1315, 1100, 945, 747, 722, 707, 696. δ_H ($CDCl_3$, 500 MHz) 2.05 (s, 6 H), 6.98–7.02 (m, 2H), 7.06 (td, *J* 7.4, *J* 0.9, 1H), 7.20 (ddd, *J* 11.0, *J* 7.9, *J* 1.0, 1 H), 7.25–7.31 (m, 2H), 7.32–7.38 (m, 3H), 7.39–7.44 (m, 1H), 7.45–7.65 (m, 8H). δ_C ($CDCl_3$,125 MHz) 40.83 (d, 2 C), 118.79 (d), 122.54 (d), 126.64 (s, $^1J_{C,P}$ 63.6), 127.07 (d, $^3J_{C,P}$ 8.6), 128.96 (d, $^3J_{C,P}$ 11.7, 3 C), 130.02 (s, $^1J_{C,P}$ 64.4), 130.21 (d), 131.07 (d), 131.17 (d), 131.72 (d), 131.89 (d, $^4J_{C,P}$ 1.8), 132.99 (d), 132.99 (s, $^1J_{C,P}$ 60.3), 133.47 (s, $^3J_{C,P}$ 5.8), 133.64 (d, $^2J_{C,P}$ 13.3, 2 C), 133.74 (d, $^2J_{C,P}$ 12.8, 2 C), 135.79 (d, $^3J_{C,P}$ 5.6), 147.98 (s, $^2J_{C,P}$ 16.1), 152.07 (s). δ_P (202 MHz, $CDCl_3$) 24.95. *m/z* (FAB$^+$) 639.2 [M + Na]$^+$, 613.2 [M$^+$], 578.2 [M$^+$ – Cl]. Anal. calc. for $C_{26}H_{24}AuClNP$ (613.87): C 50.87, H 3.94, N 2.28, Cl 5.78, P 5.05. Found C 50.64, H 3.99, N 2.17, Cl 5.84, P 4.99 %.

N-Phenyl-2-(dicyclohexylphosphino)pyrrolegold(I) Chloride (Au-BiarylQ)

According to General Procedure D, (tht)AuCl (98 mg, 290 µmol) was treated with *N*-phenyl-2-(dicyclohexylphosphino)pyrrole (100 mg, 290 µmol) in 5 mL DCM. Concentration by evaporation in vacuum yielded a white powder. Crystals were obtained by slow evaporation of DCM at RT. Mp 201–203°C. ν_{max} (KBr)/cm^{-1} 3452, 2928, 2851, 1636, 1511, 1448, 760. δ_H (CD_2Cl_2, 500 MHz) 1.18 (m, 2H), 1.29 (m, 8H), 1.69 (m, 4H), 1.80 (m, 4H), 1.94 (m, 2H), 2.05 (m, 2H), 6.42 (m, 1H), 6.71 (m, 1H), 7.05 (m, 1H), 7.26 (d, *J* 8.0, 2H), 7.48 (m, 2H), 7.56 (m, 1H). δ_C (CD_2Cl_2, 125 MHz) 26.20, 26.77, 26.78, 26.88, 29.13, 30.76, 30.79 (t, 10C), 36.62 (d, *J* 38.5, 2C), 109.81 (d, 1C), 118.02 (s, *J* 70.3, 1C), 121.13 (d, 1C), 128.78 (d, 2C), 129.68 (d, 1C), 129.87 (d, 2C), 130.99 (d, 1C), 140.28 (s, 1C). δ_P (CD_2Cl_2, 121 MHz) 24.09. *m/z* (HR-MS ESI+) 1107.3243; calc. for $C_{44}H_{60}Au_2Cl_1N_2P_2$: 1107.3251.

1-(2-Methoxyphenyl)-2-(dicyclohexylphosphino) pyrrolegold(I) Chloride (Au-BiarylR)

According to General Procedure D, (tht)AuCl (87 mg, 270 µmol) was treated with 1-(2-methoxyphenyl)-2-(dicyclohexylphosphino)pyrrole (100 mg, 270 µmol) in 10 mL DCM. Concentration yielded a white powder. Crystals were obtained by slow evaporation of DCM at RT. Mp 206–207°C (decomp.). ν_{max} (KBr)/cm^{-1} 3449, 2927, 2850, 1599, 1513, 1448, 749, 727. δ_H (CD_2Cl_2, 300 MHz) 1.25 (m, 10H), 1.80 (m, 11H), 2.14 (m, 1H), 3.77 (s, 3H), 6.43 (m, 1H), 6.66 (m, 1H), 6.92 (m, 1H), 7.05 (m, 1H), 7.18 (dd, *J* 7.9 and 1.8, 1H), 7.55 (dt, *J* 8.3 and 1.8, 1H). δ_C (CD_2Cl_2, 75 MHz) 26.25, 26.78, 26.87, 26.95, 27.02, 28.42, 29.81, 30.24, 30.73 (t, 10C), 36.25 (d, *J* 58.0, 1C), 36.77 (d, *J* 56.3, 1C), 55.74 (q, 1C), 109.85 (d, 1C), 113,06 (d, 1C), 119.91 (d, 1C), 120.87 (d, 1C), 130.16 (d, 1C), 130.67 (d, 1C), 156.10 (s, 1C). δ_P (CD_2Cl_2, 121 MHz) 23.56. *m/z* (HR-MS ESI+) 935.4106; calc. for $C_{46}H_{64}Au_1N_2O_2P_2$: 935.4109; *m/z* 1167.3243; calc. for $C_{46}H_{64}Au_2Cl_1N_2O_2P_2$: 1167.3463.

Supplementary Material

Computational results on Au-BiarylF are available on the Journal's website.

References

[1] A. S. K. Hashmi, T. M. Frost, J. W. Bats, *J. Am. Chem. Soc.* **2000**, *122*, 11553. doi:10.1021/JA005570D

[2] B. Martín-Matute, C. D. J. Cárdenas, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2001**, *40*, 4754. doi:10.1002/1521-3773(20011217)40:24<4754::AID-ANIE4754>3.0.CO;2-9

[3] A. S. K. Hashmi, T. M. Frost, J. W. Bats, *Org. Lett.* **2001**, *3*, 3769. doi:10.1021/OL016734D

[4] M. Méndez, M. P. Munoz, C. Nevade, D. J. Cárdenas, A. M. Echavarren, *J. Am. Chem. Soc.* **2001**, *123*, 10511. doi:10.1021/JA0112184

[5] A. S. K. Hashmi, T. M. Frost, J. W. Bats, *Catal. Today* **2002**, *72*, 19. doi:10.1016/S0920-5861(01)00474-6

[6] B. Martín-Matute, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *J. Am. Chem. Soc.* **2003**, *125*, 5757. doi:10.1021/JA029125P

[7] A. S. K. Hashmi, L. Ding, J. W. Bats, P. Fischer, W. Frey, *Chem. Eur. J.* **2003**, *9*, 4339. doi:10.1002/CHEM.200305092

[8] A. S. K. Hashmi, J. P. Weyrauch, M. Rudolph, E. Kurpejovic, *Angew. Chem.* **2004**, *116*, 6707. doi:10.1002/ANGE.200460232

[9] A. S. K. Hashmi, L. Grundl, *Tetrahedron* **2005**, *61*, 6231. doi:10.1016/J.TET.2005.03.103

[10] A. S. K. Hashmi, M. Rudolph, J. P. Weyrauch, M. Wölfle, W. Frey, J. W. Bats, *Angew. Chem. Int. Ed.* **2005**, *44*, 2798. doi:10.1002/ANIE.200462672

[11] A. S. K. Hashmi, M. C. Blanco, E. Kurpejovic, W. Frey, J. W. Bats, *Adv. Synth. Catal.* **2006**, *348*, 709. doi:10.1002/ADSC.200606012

[12] A. S. K. Hashmi, P. Haufe, C. Schmid, A. Rivas Nass, W. Frey, *Chem. Eur. J.* **2006**, *12*, 5376. doi:10.1002/CHEM.200600192

[13] A. S. K. Hashmi, J. P. Weyrauch, E. Kurpejovic, T. M. Frost, B. Miehlich, W. Frey, J. W. Bats, *Chem. Eur. J.* **2006**, *12*, 5806. doi:10.1002/CHEM.200501268

[14] A. S. K. Hashmi, M. Wölfle, F. Ata, M. Hamzic, R. Salathé, W. Frey, *Adv. Synth. Catal.* **2006**, *348*, 2501. doi:10.1002/ADSC.200600367

[15] S. Carrettin, M. C. Blanco, A. Corma, A. S. K. Hashmi, *Adv. Synth. Catal.* **2006**, *348*, 1283. doi:10.1002/ADSC.200606099

[16] A. S. K. Hashmi, R. Salathé, W. Frey, *Chem. Eur. J.* **2006**, *12*, 6991. doi:10.1002/CHEM.200600533

[17] A. S. K. Hashmi, E. Kurpejovic, W. Frey, J. W. Bats, *Tetrahedron* **2007**, *63*, 5879. doi:10.1016/J.TET.2007.02.108

[18] A. S. K. Hashmi, M. Wölfle, J. H. Teles, W. Frey, *Synlett* **2007**, 1747. doi:10.1055/S-2007-982569

[19] A. S. K. Hashmi, F. Ata, E. Kurpejovic, J. Huck, M. Rudolph, *Top. Catal.* **2007**, *44*, 245. doi:10.1007/S11244-007-0297-5

[20] A. S. K. Hashmi, E. Kurpejovic, M. Wölfle, W. Frey, J. W. Bats, *Adv. Synth. Catal.* **2007**, *349*, 1743. doi:10.1002/ADSC.200600653

[21] A. S. K. Hashmi, M. Rudolph, H.-U. Siehl, M. Tanaka, J. W. Bats, W. Frey, *Chem. Eur. J.* **2008**, *14*, 3703. doi:10.1002/CHEM.200701795

[22] A. S. K. Hashmi, M. Rudolph, J. W. Bats, W. Frey, F. Rominger, T. Oeser, *Chem. Eur. J.* **2008**, *14*, 6672. doi:10.1002/CHEM.200800210

[23] A. S. K. Hashmi, E. Enns, T. M. Frost, S. Schäfer, A. Schuster, W. Frey, F. Rominger, *Synthesis* **2008**, 2707. doi:10.1055/S-2008-1067227

[24] A. S. K. Hashmi, S. Schäfer, J. W. Bats, W. Frey, F. Rominger, *Eur. J. Org. Chem.* **2008**, 4891.

[25] A. S. K. Hashmi, *Gold Bull.* **2003**, *36*, 3. doi:10.1007/BF03214859

[26] A. S. K. Hashmi, *Gold Bull.* **2004**, *37*, 51. doi:10.1007/BF03215517

[27] A. Hoffmann-Röder, N. Krause, *Org. Biomol. Chem.* **2005**, *3*, 387. doi:10.1039/B416516K

[28] A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2005**, *44*, 6990. doi:10.1002/ANIE.200502735

[29] L. Zhang, J. Sun, S. Kozmin, *Adv. Synth. Catal.* **2006**, *348*, 2271. doi:10.1002/ADSC.200600368

[30] A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem. Int. Ed.* **2006**, *45*, 7896. doi:10.1002/ANIE.200602454

[31] A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180. doi:10.1021/CR000436X

[32] A. Fürstner, P. W. Davies, *Angew. Chem. Int. Ed.* **2007**, *46*, 3410. doi:10.1002/ANIE.200604335

[33] D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395. doi:10.1038/NATURE05592

[34] E. Jiménez-Núñez, A. M. Echavarren, *Chem. Commun.* **2007**, 333. doi:10.1039/B612008C

[35] V. Michelet, P. Y. Toullec, J.-P. Genêt, *Angew. Chem. Int. Ed.* **2008**, *47*, 4268. doi:10.1002/ANIE.200701589

[36] (a) H. C. Shen, *Tetrahedron* **2008**, *64*, 3885. doi:10.1016/J.TET.2008.01.081
(b) H. C. Shen, *Tetrahedron* **2008**, *64*, 7847. doi:10.1016/J.TET.2008.05.082

[37] R. S. Mali, P. G. Jagtap, S. R. Patil, P. N. Pawar, *J. Chem. Soc. Chem. Commun.* **1992**, 883. doi:10.1039/C39920000883

[38] K. J. van der Merwe, P. S. Steyn, L. Fourie, *J. Chem. Soc.* **1965**, 7083. doi:10.1039/JR9650007083

[39] Y. Shimojima, H. Hayashi, T. Ooka, M. Shibukawa, Y. Iitaka, *Tetrahedron* **1984**, *40*, 2519. doi:10.1016/S0040-4020(01)83504-3

[40] H. Koshino, T. Yoshihara, M. Okuno, S. Sakamura, A. Tajimi, T. Shimanuki, *Biosci. Biotechnol. Biochem.* **1992**, *56*, 1096. doi:10.1271/BBB.56.1096

[41] R. Jansen, B. Kunze, H. Reichenbach, G. Höfle, *Eur. J. Org. Chem.* **2002**, 917. doi:10.1002/1099-0690(200203)2002:5<917::AID-EJOC917>3.0.CO;2-Z

[42] O. Krebs, R. J. K. Taylor, *Org. Lett.* **2005**, *7*, 1063. doi:10.1021/OL047313+

[43] D. Ganame, T. Quach, C. Poole, M. A. Rizzacasa, *Tetrahedron Lett.* **2007**, *48*, 5841. doi:10.1016/J.TETLET.2007.06.072

[44] K. Buntin, S. Rachid, M. Scharfe, H. Blöcker, K. J. Weissman, R. Müller, *Angew. Chem. Int. Ed.* **2008**, *47*, 4595. doi:10.1002/ANIE.200705569

[45] R. Salathé, Synthesepotential und Grenzen in der Goldkatalyse, PhD thesis, Universität Stuttgart, **2007**.

[46] (a) S. J. Hobson, A. Parkin, R. Marquez, *Org. Lett.* **2008**, *10*, 2813. doi:10.1021/OL8009336
(b) S. Essig, S. Bretzke, R. Müller, D. Menche, *J. Am. Chem. Soc.* **2012**, *134*, 19362. doi:10.1021/JA309685N

[47] A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2008**, *37*, 1766. doi:10.1039/B615629K

[48] CCDC 746941 (**5e**), 746942 (Au-PhosphineB), 746943 (Au-PhosphineC_2), 746944 (Au-PhosphineD), 746945 (Au-BiarylA), 746946 (Au-BiarylC), 746947 (Au-BiarylD), 746948 (Au-BiarylE), 746949 (Au-BiarylF), 746950 (Au-BiarylG), 746951 (Au-BiarylH), 746952 (Au-BiarylI), 746953 (Au-BiarylM), 746954 (Au-BiarylN), 746955 (Au-BiarylO), 746956 (Au-BiarylQ), 746957 (Au-BiarylR), 746958 (**6e**), 746959 (**7e**), and 746960 (Au-BiarylS) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif [accessed 13 February 2014].

[49] (a) C. Nieto-Oberhuber, S. Lopez, M. P. Munoz, E. Jimenez-Nunez, I. Bunuel, D. J. Cardenas, A. M. Echavarren, *Chem. Eur. J.* **2006**, *12*, 1694. doi:10.1002/CHEM.200501089
(b) C. Nieto-Oberhuber, M. P. Munoz, S. Lopez, E. Jimenez-Nunez, C. Nevado, E. Herrero-Gomez, M. Raducan, A. M. Echavarren, *Chem. Eur. J.* **2006**, *12*, 1677. doi:10.1002/CHEM.200501088
(c) C. Ferrer, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2006**, *45*, 1105. doi:10.1002/ANIE.200503484
(d) C. Nieto-Oberhuber, S. Lopez, M. P. Munoz, D. J. Cardenas, E. Bunuel, C. Nevado, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2005**, *44*, 6146. doi:10.1002/ANIE.200501937
(e) C. Nieto-Oberhuber, S. Lopez, A. M. Echevarren, *J. Am. Chem. Soc.* **2005**, *127*, 6178. doi:10.1021/JA042257T
(f) Z. Zhang, C. Liu, R. I. Kinder, X. Han, H. Qian, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2006**, *128*, 9066. doi:10.1021/JA062045R
(g) X. Han, R. A. Widenhoefer, *Angew. Chem. Int. Ed.* **2006**, *45*, 1747. doi:10.1002/ANIE.200600052

[50] D. V. Partyka, T. J. Robilotto, M. Zeller, A. D. Hunter, T. G. Gray, *Organometallics* **2008**, *27*, 28. doi:10.1021/OM700517Q

[51] D. V. Partyka, J. B. Updegraff III, M. Zeller, A. D. Hunter, T. G. Gray, *Organometallics* **2009**, *28*, 1666. doi:10.1021/OM800746U

[52] E. Herrero-Gómez, C. Nieto-Oberhuber, S. Lopez, J. Benet-Buchholz, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2006**, *45*, 5455. doi:10.1002/ANIE.200601688

[53] M. Touil, B. Bechem, A. S. K. Hashmi, B. Engels, M. A. Omary, H. Rabaâ, *Theochem* **2010**, *957*, 21. doi:10.1016/J.THEOCHEM.2010.06.030

[54] H. Schmidbaur, *Gold Bull.* **2000**, *33*, 3. doi:10.1007/BF03215477

[55] A. V. Vasilyev, S. V. Lindeman, J. K. Kochi, *Chem. Commun.* **2001**, 909. doi:10.1039/B102148F

[56] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441. doi:10.1021/J100785A001

[57] A. Zapf, R. Jackstell, F. Rataboul, T. Riermeier, A. Monsees, C. Fuhrmann, N. Shaikh, U. Dingerdissen, M. Beller, *Chem. Commun.* **2004**, 38. doi:10.1039/B311268N

[58] E. Herrero-Gómez, C. Nieto-Oberhuber, S. Lopez, J. Benet-Buchholz, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2006**, *45*, 5455. doi:10.1002/ANIE.200601688

[59] P. Römbke, A. Schier, H. Schmidbaur, *J. Chem. Soc., Dalton Trans.* **2001**, 2482. doi:10.1039/B104001B