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Asymmetric Au-catalyzed domino cyclization/nucleophile addition reactions of enynes in the presence of water, methanol and electron-rich aromatic derivatives

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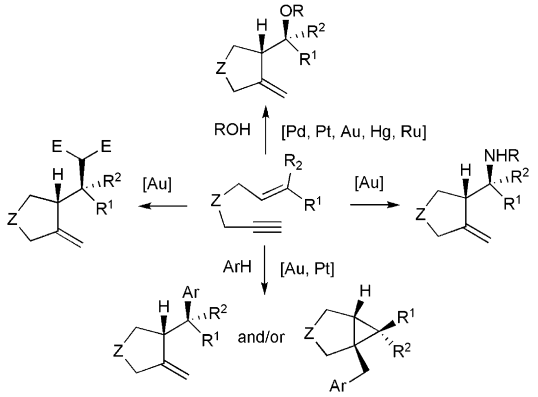
ABSTRACT

An efficient Au(I) catalytic system is described for the asymmetric domino cyclization/functionalization reactions of functionalized 1,6-enynes in the presence of an external nucleophile. The use of (*R*)-4-MeO-3,5-(*t*-Bu)$_2$-MeOBIHEP ligand associated with gold led to clean rearrangements implying the formal addition of an oxygen or carbon nucleophile to an alkene followed by a cyclization process. The enantiomeric excesses were highly dependant on the substrate/nucleophile combination. Very good enantiomeric excesses up to 98% were obtained in the case of substrates bearing larger groups (hindered diesters and disulfones) and in the case of hindered carbon nucleophiles.

1. Introduction

Metal-catalyzed cycloisomerization reactions of 1,*n*-enynes have appeared as conceptually and chemically highly attractive processes as they contribute to the concept of atom economy and offer the opportunity to develop new reactions.[1] The recent emergence of interest associated with the studies involving carbophilic Lewis acids, such as gold or platinum opened the way to the development of families of highly active and selective catalysts presenting a unique reactivity.[2,3] A wide variety of carbo- and heterocycles presenting a high degree of structural complexity can be formed using those new catalytic systems. The development of enantioselective variants of these transformations are still rare,[4] probably because of a highly substrate-dependency encountered with these systems. Among the numerous 1,*n*-enynes cycloisomerization transformations, we[5] and others[6] have been interested in domino processes implying an external nucleophile (oxygen, amino or aromatic derivative) and leading to functionalized cyclic cyclopentenes (Scheme 1). The first enantioselective versions have been described, respectively, in the presence of platinum and gold for the alkoxycyclization reactions in 2004[7] and 2005.[8] We expanded these methodologies for the hydroarylation/cyclization domino process and obtained high enantiomeric excesses in the presence of two systems: one based on Pt(II) catalyst associated with a monophosphane (Ph–Binepine ligand)[9] and one based on a dinuclear gold complex associated with the atropisomeric 4-MeO-3,5-(*t*-Bu)$_2$-MeOBIPHEP ligand.[10] Other groups have recently described chiral gold-based systems for domino processes, such as phenoxycyclization, intramolecular hydroarylation/cyclization reactions or 1,3-dipolar cycloaddition, for example.[11] In this paper, we wish to disclose a comprehensive study on gold-catalyzed enantioselective domino nucleophile addition/cyclization reactions putting the stress on the scope and limitations of such systems.



Scheme 1. Domino cyclization/functionalization reactions implying oxygen, amino and carbon nucleophiles.

2. Results and discussion

In order to find the optimized catalytic system, enyne **1a** as the substrate and *N*-methylindole as the nucleophile were reacted in the presence of various cationic bimetallic gold complexes formed from L*(AuCl)$_2$ and 2 equiv of halide scavenging agents (Table 1).

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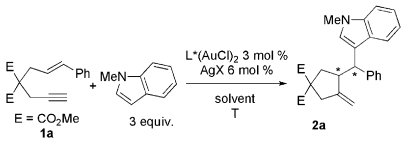
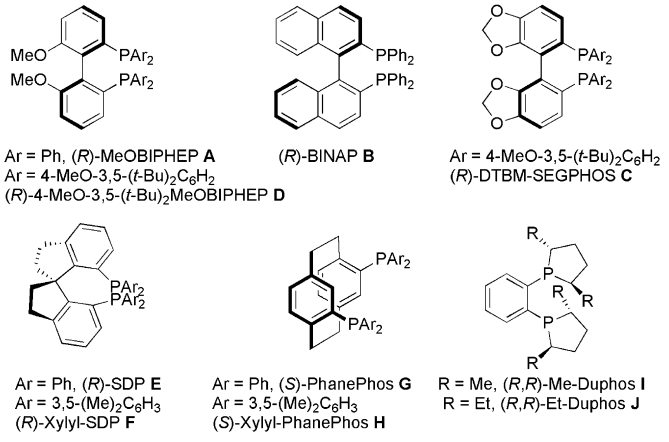
We selected various ligands L* including atropisomeric ligands, such as MeOBIPHEP (**A**, **D**), BINAP (**B**) and SEGPHOS (**C**) ligands and other chiral ones presenting different chirality properties, such as chiral spiro ligands SDP (**E**, **F**), PhanePhos (**G**, **H**) and DuPhos (**I**, **J**) ligands (Scheme 2). We prepared the bimetallic gold complexes starting from (tht)AuCl according to reported procedures.[8,12]

Table 1
Optimization of the catalytic system for the hydroarylation/cyclization reaction



Entry	L*[a]	AgX	Solvent	T [°C]	t [h]	Yield [%]	ee [%][b]
1	**A**	$AgSbF_6$	Ether	rt	0.3	96	26 (+)
2	**A**	AgOBz	Ether	rt	240	0	/
3	**A**	AgOTf	Ether	rt	20	96	46 (+)
4	**A**	$AgNTf_2$	Ether	rt	0.3	91	45 (+)
5	**A**	AgOTf	CH_2Cl_2	rt	48	91	48 (+)
6	**A**	$AgNTf_2$	CH_2Cl_2	rt	0.2	89	43 (+)
7	**A**	AgOTf	Ether	0	24	71	54 (+)
8	**A**	$AgNTf_2$	Ether	0	21	84	58 (+)
9	**A**	$AgNTf_2$	Ether	−10	15	76	56 (+)
10	**A**	$AgNTf_2$	Ether	−20	15	39	55 (+)
11	**B**	AgOTf	Ether	0	36	46	12 (+)
12	**B**	$AgNTf_2$	Ether	0	24	99	20 (+)
13	**C**	AgOTf	Ether	rt	20	58	47 (+)
14	**D**	AgOTf	Ether	0	2	91	80 (+)
15	**D**	$AgNTf_2$	Ether	0	24	90	71 (+)
16	**D**	AgOTf	Ether	rt	48	99	83 (+)
17	**D**	AgOTf	CH_2Cl_2	rt	48	96	63 (+)
18	**E**	AgOTf	Ether	rt	48	65	20 (+)
19	**F**	AgOTf	Ether	rt	48	61	18 (−)
20	**G**	AgOTf	Ether	rt	48	43	7 (−)
21	**H**	AgOTf	Ether	rt	48	41	20 (+)
22	**I**	AgOTf	Ether	rt	48	43	7 (/)
23	**J**	AgOTf	Ether	rt	48	64	2 (/)

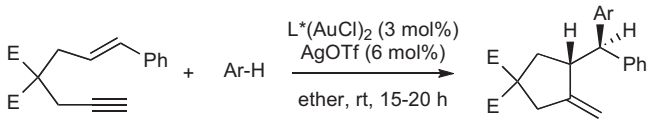
[a] A=(*R*)-MeOBIPHEP, B=(*R*)-BINAP, C=(*R*)-DTBM-SEGPHOS, D=(*R*)-4-MeO-3,5-(*t*-Bu)$_2$-MeOBIPHEP, E=(*R*)-SDP, F=(*R*)-Xylyl-SDP, G=(*S*)-PhanePhos, H=(*S*)-Xylyl-PhanePhos, I=(*R*,*R*)-Me-DuPhos, J=(*R*,*R*)-EtDuPhos.
[b] Determined by HPLC analysis OD-H, hexane/*i*-PrOH 98/2, 1 mL/min.



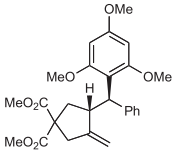
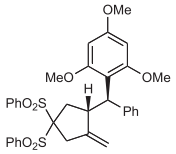
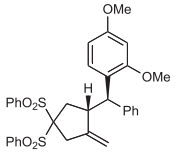
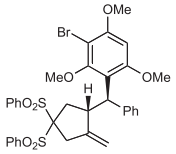
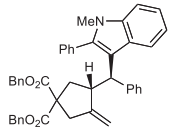
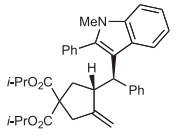
Scheme 2. Chiral ligands.

The use of (*R*)-MeOBIPHEP-$(AuCl)_2$[12] associated with silver salt $AgSbF_6$ in ether has allowed the formation of the desired product **2a** in excellent yield and 26% ee (Table 1, entry 1). The influence of silver salts was investigated (Table 1, entries 2–4), silver triflate and silver bis(trifluoromethanesulfonyl)imidate giving the best results.

Table 2
Asymmetric hydroarylation/cyclization in the presence of electron-rich aromatic rings



L* = (*R*)-4-MeO-3,5-(*t*-Bu)$_2$MeOBIPHEP
1a E = CO_2Me; **1b** E = CO_2*i*-Pr; **1c** E = CO_2Bn
2 E = SO_2Ph

Entry	Product		Yield[a] [%]	ee [b] [%]
1		**3a**	92	72 (−)
2		**4**	85	94 (−)
3		**5**	86	98 (−)
4		**6**	85	94 (−)
5		**7**	99	82 (−)
6		**8**	99	95 (−)

[a] Isolated yield.
[b] Determined by HPLC analysis.

The use of dichloromethane instead of ether did not improve the enantioselectivity (Table 1, entries 5 and 6). As the reaction time was generally short, we decided to compare the efficiency of the domino process at lower temperature. Indeed the reactivity was still observed at 0 °C, −10 °C and even −20 °C, unfortunately the influence on the ee was moderate (Table 1, entries 7–10). The use of BINAP (**B**)[13] induced a marked decrease of the observed ee (Table 1, entries 11–12). The outcome of the reaction was positively influenced by hindered MeOBIPHEP or SEGPHOS analogous ligands (**D**, **C**), which previously showed very interesting activities in gold-catalyzed asymmetric reactions.[4,12,14] The analogue of SEGPHOS ligand **C** did not lead to better results compared to MeOBIPHEP ligand **A** (Table 1, entry 13 compared to 3). The use of 4-MeO-3,5-(*t*-Bu)$_2$-MeOBIPHEP ligand **D** afforded a consistent gap of the ee as the desired arylated product **2a** was isolated in 80% ee (Table 1, entry 14). We tried to optimize the conditions by changing the temperature, the silver salts or the solvent. The best result was obtained in

the presence of 3 mol % of (*R*)-**D**$(AuCl)_2$, 6 mol % of AgOTf in ether at room temperature (Table 1, entry 16). We therefore tested the efficiency of other chiral skeletons under the optimized conditions. The SDP ligands **E**, **F** and PhanePhos ligands **G**, **H** did not induce good levels of enantioselectivities (Table 1, entries 18 and 19, respectively, 20 and 21). One may notice the influence of the substitution of the aryl groups on the phosphine in both cases as the sense of enantioselectivity is reversed for ligands bearing xylyl groups (**F** and **H**, respectively) The bis gold complex derived from (*R*,*R*)-Me-Duphos ligand **I**, which was recently evaluated in the hydrogenation of C=O and C=N bonds,[15] was engaged in the domino process, but disappointing results were obtained either with Me- or Et-substituted ligand (Table 1, entries 22 and 23). The best catalytic system was therefore found to be (*R*)-4-MeO-3,5-(*t*-Bu)$_2$-MeOBIPHEP$(AuCl)_2$ (ligand **D**). It's also noteworthy that encouraging results were also obtained in the presence of the parent complex (*R*)-MeOBIPHEP-$(AuCl)_2$ (ligand **A**).

We also screened carbon nucleophiles and treated them with various 1,6-enynes in the presence of the optimized system (Table 2). A good reactivity was observed in all cases as the isolated yields were between 85% and 99%. The enantioselectivities were more dependent on the substrates. For the addition of 1,3,5-trimethoxybenzene (Table 2, entries 1 and 2), the best result was obtained for the disulfone tethered substrate as 94% ee was reached compared to 72% for enyne **1a**. The excellent enantioselectivity in the case of substrate **2** (E=SO_2Ph) was confirmed by engaging 1,3-dimethoxybenzene and 4-bromo-1,3,5-trimethoxybenzene (Table 2, entries 3, 4). The arylated derivatives **5** and **6** were obtained in 98% and 94% ee, respectively.

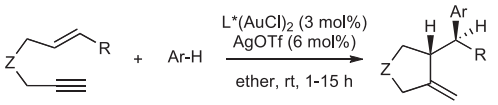
A similar trend was observed when treating hindered diesters, such as benzyl **1b** or *iso*-propyl **1c** substituted diesters with hindered 1-methyl-2-phenylindole as nucleophile (Table 2, entries 5 and 6). The corresponding arylated cyclized adducts **7** and **8** were obtained in good to excellent enantiomeric excesses, 82% and 95%, respectively. For selected substrates we compared the activity of catalysts derived from MeOBIPHEP ligands **A** and **D** (Table 3).

Through the examples depicted in Table 3, we highlighted the strong dependence of the chiral ligands. When replacing MeOBIPHEP ligand **A** by 4-MeO-3,5-(*t*-Bu)$_2$-MeOBIPHEP **D**, the enantiomeric excesses increased, the gap being always over 30 units for ee. In the case of enynes **1a**, **1b** and **1c**, good activities were observed for both chiral catalytic systems (Table 3, entries 1–3). The best ee was observed in the case of the *iso*-propyl-substituted diester **1b** with 1-methylindole, compound **11** being obtained in 94% yield and 95% ee (Table 3, entry 2). The challenging case of oxygen-tethered 1,6-enyne was then evaluated. The additions of 1-methylindole, 1-methyl-2-phenylindole or free indole led to the formation of the desired products **13**–**16** in low enantiomeric excesses in the presence of (*R*)-**A**$(AuCl)_2$ catalyst (Table 3, entries 4–7). Encouraging results were obtained in the presence of (*R*)-**D**$(AuCl)_2$ chiral catalysts, especially for 1-methyl-2-phenylindole and 1,3,5-trimethoxybenzene as nucleophiles. Functionalized heterocycles **14** and **16** were isolated in good yields and enantiomeric excesses around 60% (Table 3, entries 5 and 7). These results may be explained by the conjunction of the use of a hindered chiral ligand (**D**) and a hindered nucleophile, as the substrate offers a poor intrinsic steric congestion.

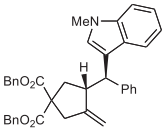
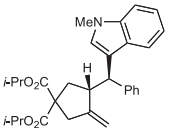
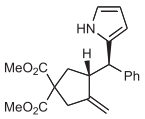
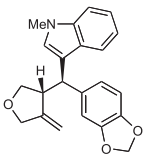
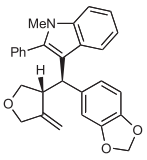
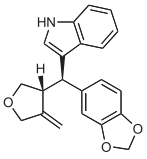
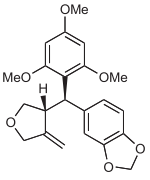
The intramolecular version of the asymmetric hydroarylation/cyclization reaction afforded high enantiomeric excesses in the case of a prenyl side chain (substrates **17a**,**b**, Scheme 3). The tricyclic adducts **18a** and **18b** were, respectively, isolated in excellent yields and in ee>90%. A disappointing result was obtained for cinnamyl substituted 1,6-enyne **1a**, despite the fact the desired adduct **20** was prepared in 86% yield.

We then turned our attention towards the addition of oxygen nucleophiles. We selected carbon tethered enynes **1a**, **1b** and **1d** bearing increasing hindered ester groups (CO_2Me, CO_2*i*-Pr and CO_2*t*-Bu) and studied the influence of both chiral complexes derived from MeOBIPHEP **A** and 4-MeO-3,5-(*t*-Bu)$_2$-MeOBIPHEP **D** ligands (Scheme 4). As anticipated, the same trend as previously observed in the case of electron-rich aromatic rings nucleophiles was demonstrated. Quite surprisingly, the addition of water to enyne **1a** led to the formation of the alcohol **21a** in 54% and 58% enantiomeric excesses with the MeOBIPHEP **A** and **D** derived catalytic systems. Lower enantiomeric excesses were observed when 1,6-enynes **1b** (R=*i*-Bu) and **1d** (R=*t*-Bu) were engaged in the

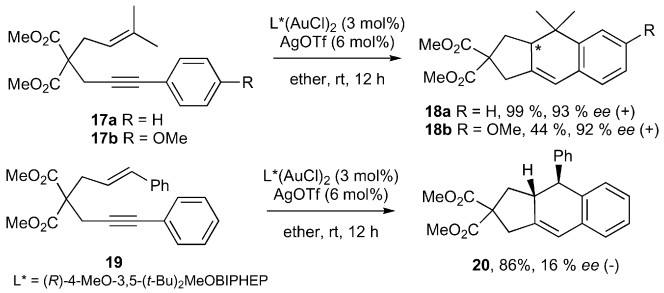
Table 3
Comparison of the enantioselectivity for the hydroarylation/cyclization in the presence of (*R*)-**A**$(AuCl)_2$ and (*R*)-**D**$(AuCl)_2$ complexes



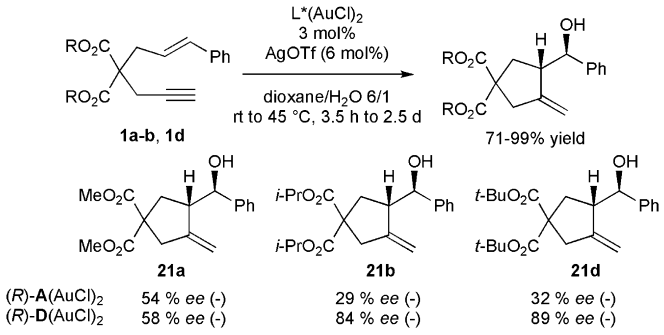
L* = (*R*)-4-MeO-3,5-(*t*-Bu)$_2$MeOBIPHEP
1a Z = $C(CO_2Me)_2$, R = Ph; **1b** Z = $C(CO_2i\text{-}Pr)_2$, R = Ph; **1c** Z = $C(CO_2Bn)_2$, R = Ph
9 Z = O, R = 3,4-$(OCH_2O)C_6H_3$

Entry	Product		Complex (*R*)-**A**$(AuCl)_2$ Yield,[a] ee[b] [%]	Complex (*R*)-**D**$(AuCl)_2$ Yield,[a] ee[b] [%]
1		**10**	65, 51 (+)	99, 81 (+)
2		**11**	79, 40 (+)	94, 95 (+)
3[c]		**12**	68, 29 (−)	84, 80 (−)
4		**13**	89, 13 (−)	99, 53 (−)
5		**14**	29, 14 (−)	88, 61 (−)
6		**15**	98, 5 (−)	97, 36 (−)
7		**16**	96, 6 (−)	96, 59 (−)

[a] Isolated yield.
[b] Determined by HPLC analysis.
[c] C2 isomer isolated from C2/C3 mixture (86/14).



Scheme 3. Intramolecular hydroarylation/cyclization in the presence of (*R*)-**D**$(AuCl)_2$ catalyst.



Scheme 4.

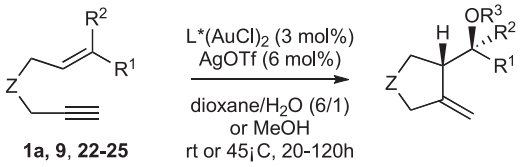
presence of (*R*)-**A**$(AuCl)_2$ catalyst (ee around 30%). Gratifyingly a good substrate/catalyst matching operates when performing the reaction in the presence of (*R*)-**D**$(AuCl)_2$ catalyst. The alcohols **21b** and **21d** were isolated in, respectively, 84% and 89% ee.

We evaluated the activity of (*R*)-**D**$(AuCl)_2$ chiral catalyst towards other 1,6-enynes in both hydroxy- and methoxycyclization reactions (Table 4). Moderate enantiomeric excesses were obtained in the case of enynes **22** and **23** (Table 4, entries 1 and 2). Once again a higher ee was observed in the case of the hindered disulfone substrate **23**.

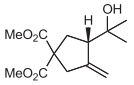
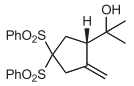
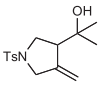
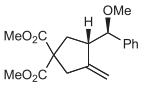
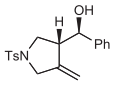
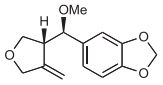
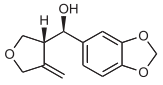
The nitrogen- and oxygen-tethered 1,6-enynes were reacted in the presence of water or methanol as nucleophiles, but either racemic derivatives or low enantiomeric excesses were obtained (Table 4, entries 3, 5–7). The influence of the nucleophilic partner in the domino process was further demonstrated by conducting the methoxycyclization of enyne **1a** (Table 4, entry 4). Whereas the indole-substituted adduct **2a** was obtained in 83% ee (Table 1), the methoxycyclization reaction afforded the desired ether **29** in 11% ee.

Finally, a comparison was performed in the case of already studied enynes **22** and **33** (Scheme 5). The results proved that higher enantioselectivity may be obtained in the presence of 4-MeO-3,5-(*t*-Bu)$_2$-MeOBIPHEP ligand compared to Tol-BINAP ligand, but this observation was limited to the dimethylmalonate substrate **22**. The ether **34** was isolated in 44% ee compared to 2% in the presence of Tol-BINAP$(AuCl)_2$ catalyst. Unexpectively, a lower ee was obtained for the methoxycyclization of phenyl-substituted enyne **33**.

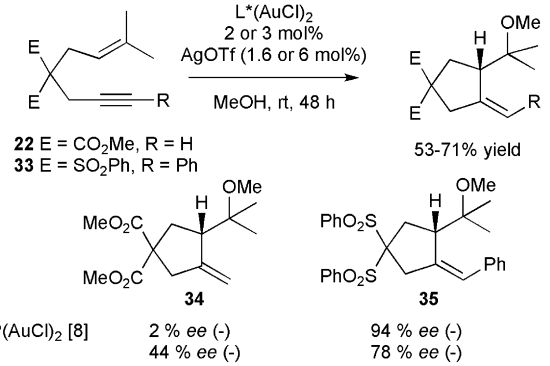
Table 4
Asymmetric hydroxy- and methoxycyclization reactions of 1,6-enynes



L* = (*R*)-4-MeO-3,5-(*t*-Bu)$_2$MeOBIPHEP
R^1 = R^2 = Me: **22** Z = $C(CO_2Me)_2$, **23** Z = $C(SO_2Ph)_2$, **24** Z = NTs
R^1 = Ph, R^2 = H: **25** Z = NTs

Entry	Product		Solvent	Yield[a] [%]	ee [b] [%]
1		**26**	Dioxane/H_2O	99	46 (−)
2		**27**	Dioxane/H_2O	99	68 (−)
3[c]		**28**	Dioxane/H_2O	64	0 (/)
4		**29**	MeOH	99	11 (−)
5[c]		**30**	Dioxane/H_2O	46	23 (−)
6		**31**	MeOH	84	0 (/)
7		**32**	Dioxane/H_2O	54	38 (−)

[a] Isolated yield.
[b] Determined by HPLC analysis.
[c] 45 °C.



Scheme 5. Comparison of Au catalysts in the methoxycyclization reaction.

3. Conclusion

We have therefore shown that the asymmetric gold-catalyzed domino cyclization/functionalization reactions of 1,6-enynes in the presence of an external nucleophile ring leads to carbo- and heterocycles in good to excellent yields and enantiomeric excesses when electron-rich aromatic rings are engaged. A comparison of the activity of two MeOBIPHEP-derived catalysts for various enyne/nucleophile combinations highlighted the general higher efficiency of the 4-MeO-3,5-(*t*-Bu)$_2$-MeOBIPHEP ligand, but also a strong dependency of both the intrinsic hindrance generated by the enyne and the nucleophile. The addition of oxygen nucleophiles, such as water and methanol could be challenged, the best enantiomeric excesses being obtained for the hydroxycyclization reaction of a di-*tert*-butyl-ester-tethered enyne. All the collected results therefore tend to show that increasing the steric hindrance of both the phosphane-metal fragment and the enyne substrate favourably influences the chiral recognition. The use of various nucleophilic

partners (excess of aromatic rings or polar alcohols as solvents or co-solvents) has also an influence on the enantioselectivity that cannot be rigorously quantified. Such mechanistic issues would need to be challenged by theoretical studies involving solvent effects. Further studies will be dedicated to the still challenging enantioselective construction of heterocyclic units from oxygen- or nitrogen-tethered enynes, whose skeleton could be integrated in pharmaceutically active compounds.

4. Experimental

4.1. General

(tht)AuCl was prepared from $HAuCl_4$ according to known procedure[16] and was used for the synthesis of bimetallic catalysts. All manipulations were carried out under argon. ^1H NMR, ^{13}C NMR and ^{31}P NMR were recorded on a Bruker AV 300 instrument. All signals were expressed as parts per miilion (δ) and internally referenced to residual protio solvent signals. Coupling constants (J) are reported in hertz and refer to apparent peak multiplicities. Mass spectrometry analyses (direct introduction by chemical ionization with ammoniac or electrospray) were performed at the Ecole Nationale Supérieure de Chimie de Paris, Chimie ParisTech. High resolution mass spectra were performed at the University Pierre et Marie Curie in Paris. Enynes **1a**–**d**, **2**, **9**, **17a**,**b**, **19** and **22**–**25** were prepared according to published procedures.[5f–h,6f–h,8] ^1H, ^{13}C NMR and mass spectroscopy data for compounds **2a**–**3a**,[5f,10a] **4**–**8**,[5f,10a] **10**–**16**,[5f,10a] **18a**,**b**,[10a] **20**,[6h] **21a**,[6h] **26**–**32**[5g,h,6c,d] and **34**, **35**[8] were described elsewhere.

Gold complexes derived from (*R*)-SDP **E** and (*R*)-Xylyl-SDP **F** ligands. (*R*)-**E**$(AuCl)_2$: ^1H NMR (300 MHz, $CDCl_3$) δ 7.54–7.49 (m, 4H), 7.42–7.29 (m, 12H), 7.10–6.99 (m, 8H), 7.91–7.86 (m, 2H), 3.19–3.13 (m, 2H), 2.95–2.90 (m, 2H), 2.48–2.41 (m, 2H), 2.16–2.08 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 153.0, 147.3, 147.2, 136.0, 135.3, 135.1, 133.3, 133.1, 132.3, 131.7, 131.4, 131.2, 129.2, 129.0, 128.9, 128.7, 128.5, 128.3, 127.9, 123.0, 122.3, 64.7, 39.7, 30.6. ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.1. (*R*)-**F**$(AuCl)_2$: ^1H NMR (300 MHz, $CDCl_3$) δ 7.53–7.50 (m, 2H), 7.43 (t, J=7.5 Hz, 2H), 7.08 (s, 2H), 6.99 (s, 2H), 6.84 (d, J=13.5 Hz, 4H), 6.62 (d, J=13.2 Hz, 4H), 3.18–3.07 (m, 2H), 2.99–2.82 (m, 2H), 2.56–2.40 (m, 2H), 2.25 (s, 12H), 2.19 (s, 2H), 2.07–1.97 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.1, 147.0, 138.5, 138.3, 138.2, 138.0, 135.7, 133.8, 133.1, 132.9, 132.4, 131.0, 130.9, 130.6, 128.5, 128.1, 127.7, 123.5, 64.7, 39.8, 39.5, 30.6, 21.4, 21.3. ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.8.

Gold complexes derived from (*S*)-PhanePhos **G** and (*S*)-Xylyl-PhanePhos **H** ligands. (*S*)-**G**$(AuCl)_2$: ^1H NMR (300 MHz, $CDCl_3$) δ 7.69–7.62 (m, 10H), 7.49–7.18 (m, 12H), 6.80–6.68 (m, 4H), 3.80 (s, 2H), 3.40 (t, J=12.2 Hz, 2H), 3.09 (t, J=11.6 Hz, 2H), 2.83–2.73 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.5, 144.3, 140.4, 137.2, 135.9, 135.7, 134.8, 133.6, 133.4, 131.5, 129.9, 129.7, 128.9, 128.8, 34.6, 34.1. ^{31}P NMR (121 MHz, $CDCl_3$) δ 31.2. (*S*)-**H**$(AuCl)_2$: ^1H NMR (300 MHz, $CDCl_3$) δ 7.28–7.18 (m, 6H), 7.09–7.00 (m, 6H),6.80–6.67 (m, 4H), 3.88–3.78 (m, 2H), 3.35 (t, J=12 Hz, 2H), 3.07 (t, J=12 Hz, 2H), 3.82–3.70 (m, 2H), 2.45 (s, 6H), 2.20 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 143.4, 139.3, 139.1, 138.4, 138.2, 137.4, 137.3, 135.9, 134.7, 134.1, 134.0, 133.7, 133.6, 132.3, 132.1, 131.9, 131.4, 130.5, 130.3, 130.1, 126.6, 126.5, 125.8, 125.7, 33.6, 33.0, 20.8, 20.3. ^{31}P NMR (121 MHz, $CDCl_3$) δ 31.5.

Gold complex derived from (*R*,*R*)-EtDuPhos **J**: (*R*,*R*)-**J**$(AuCl)_2$. ^1H NMR (300 MHz, $CDCl_3$) δ 7.78–7.70 (m, 2H), 7.66–7.61 (m, 2H), 3.37 (q, J=1.3 Hz, 2H), 2.80–2.74 (m, 2H), 2.61–2.42 (m, 2H), 2.39–2.11 (m, 2H), 1.86–1.75 (m, 8H), 0.96–0.88 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.9, 134.8, 132.5, 132.2, 131.2, 44.9, 44.7, 44.5, 42.8, 42.6, 42.3, 33.0, 31.7, 31.6, 28.7, 28.3, 14.1, 12.7, 12.6. ^{31}P NMR (121 MHz, $CDCl_3$) δ 39.9.

4.2. General procedure for the hydroarylation/cyclization, hydroxy- and methoxycyclization reactions

A mixture of (*R*)-4-MeO-3,5-(*t*-Bu)$_2$-MeOBIPHEP$(AuCl)_2$ (3 mol %) and AgOTf (6 mol %) in distilled diethyl ether (10^{-2} M) was stirred under argon atmosphere at room temperature for 30 min. The aromatic nucleophile (3 equiv) was then added and the mixture was stirred for 5 min. Enyne (1 equiv) was finally added and the mixture was stirred until completion of the reaction. The mixture was then filtered through a short pad of silica to eliminate the catalyst (EtOAc) and the solvents were evaporated under reduced pressure. The crude product was purified by silica gel flash chromatography (petroleum ether/ethyl acetate, 90/10 to 70/30 v/v) if necessary.

A mixture of (*R*)-4-MeO-3,5-(*t*-Bu)$_2$-MeOBIPHEP$(AuCl)_2$ (3 mol %) and AgOTf (6 mol %) in degassed aqueous dioxane (14% v/v water) (10^{-2} M) or degassed methanol (10^{-2} M) was stirred under argon atmosphere at room temperature for 30 min. Enyne (1 equiv) was added and the mixture was stirred until completion of the reaction. The mixture was then filtered through a short pad of silica to eliminate the catalyst (EtOAc) and the solvents were evaporated under reduced pressure. The crude product was purified by silica gel flash chromatography (petroleum ether/ethyl acetate, 90/10 to 70/30 v/v) if necessary.

4.2.1. Di(tert-butyl) 2-(3-phenylprop-2-enyl)-2-(prop-2-ynyl) malonate ***1d***. ^1H NMR ($CDCl_3$, 300 MHz; δ ppm): 1.46 (s, 18H), 2.04 (t, J=2.7 Hz, 1H), 2.74 (d, J=2.7 Hz, 2H), 2.87 (dd, J=7.6, 1.2 Hz, 2H), 6.04 (dt, J=15.7, 7.6 Hz, 1H), 6.51 (d, J=15.7 Hz, 1H), 7.20–7.35 (m, 5H). ^{13}C ($CDCl_3$, 75 MHz; δ ppm): 22.8, 27.9 (6C), 35.6, 57.6, 71.2, 79.3, 81.7 (2C), 123.8, 126.2 (2C), 127.3, 128.5 (2C), 134.1, 137.2, 168.9 (2C). MS-CI (NH_3): m/z 393.4 $[M+Na]^+$, 371.3 $[M+H]^+$. ESI-HRMS calculated for $C_{23}H_{31}O_4$: 371.2222. Observed: 371.2221.

4.2.2. 3-((R)-Benzo[d][1,3]dioxol-5-yl((R)-4-methylenetetrahy-drofuran-3-yl)methyl)-1H-indole ***15***. $[\alpha]_{D^{23}}$ −17.3 (*c* 0.72, $CHCl_3$) for ee=36%. HPLC (Chiralcel OD-H, hexane/propan-2-ol (90/10), 1.0 mL/min, λ=215 nm): t_R 36.0 and 48.0 min, ee 36%.

4.2.3. Dimethyl 4-phenyl-3a,4-dihydro-1H-cyclopenta[b]na-phthalene-2,2(3H)-dicarboxylate ***20***. $[\alpha]_{D^{23}}$ +34.2 (*c* 1.12, $CHCl_3$) for ee=16%. HPLC (Chiralcel OD-H, hexane/propan-2-ol (99/1), 1.0 mL/min, λ=215 nm): t_R 15.1 and 22.0 min, ee 16%.

4.2.4. Dimethyl4-(1-hydroxyphenylmethyl)-3-methylenecyclo pentane-1,1-dicarboxylate ***21a***. $[\alpha]_{D^{22}}$ −44 (*c* 1.14, $CHCl_3$) for 58% ee. HPLC Chiralcel OD-H (*n*-hexane/2-propanol: 90/10, 1.0 mL/min, λ=215 nm): t_R 18.8 and 25.2 min, ee 58%.

4.2.5. Di-iso-propyl4-(1-hydroxyphenylmethyl)-3-methylene cyclopentane-1,1-dicarboxylate ***21b***. ^1H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, J=6.0 Hz, 6H), 1.21 (dd, J=6.3, 2.7 Hz, 6H), 2.16–2.29 (m, 3H), 2.94 (d, J=1.5 Hz, 2H), 3.05 (sl, 1H), 4.88 (q, J=2.4 Hz, 1H), 4.96–5.07 (m, 3H), 5.11 (q, J=2.4 Hz, 1H), 7.22–7.38 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4 (2C), 21.5 (2C), 33.4, 41.9, 49.7, 58.3, 68.7, 68.9, 73.9, 108.0, 125.8 (2C), 127.2, 128.2 (2C), 142.5, 149.2, 171.1, 171.3. CI-MS (NH_3) (m/z): 378 $[M+NH_4]^+$, 361 $[M+H]^+$, 343 $[M+H-H_2O]^+$. $[\alpha]_{D^{22}}$ −52.7 (*c* 0.99, $CHCl_3$) for 84% ee. HPLC Chiralcel OD-H (*n*-hexane/2-propanol: 90/10, 1.0 mL/min, λ=215 nm): t_R 16.8 and 20.5 min, ee 84%.

4.2.6. Di-tert-butyl-(1-hydroxyphenylmethyl)-3-methylene cyclopentane-1,1-dicarboxylate ***21d***. ^1H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 9H), 1.43 (s, 9H), 2.04–2.23 (m, 3H), 2.87 (d, J=1.5 Hz, 2H), 3.00–3.08 (sl, 1H), 4.86 (q, J=2.1 Hz, 1H), 4.96 (d, J=4.2 Hz, 1H), 5.09 (q, J=2.1 Hz, 1H), 7.21–7.38 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.7

(3C), 27.8 (3C), 33.2, 41.9, 49.7, 59.4, 73.8, 81.1, 81.4, 107.7, 125.8 (2C), 127.1, 128.2 (2C), 142.7, 149.4, 170.8, 171.1. CI-MS (NH_3) (*m*/*z*): 389 $[M+H]^+$, 371 $[M+H-H_2O]^+$, 350 $[M+NH_4-C_4H_8]^+$. $[\alpha]_{D^{22}}$ −61.9 (*c* 1, $CHCl_3$) for 89% ee. HPLC Chiralcel OD-H (*n*-hexane/2-propanol: 90/10, 1.0 mL/min, λ=215 nm): t_R 21.5 and 26.6 min, ee 89%.

4.2.7. Dimethyl 4-(1-hydroxymethylethyl)-3-methylenecyclo pentane-1,1-dicarboxylate ***26***. $[\alpha]_{D^{22}}$ −38.0 (*c* 0.16, $CHCl_3$) for 46% ee. HPLC Chiralcel OD-H (*n*-hexane/2-propanol: 98/2, 1.0 mL/min, λ=215 nm): t_R 18.0 and 19.9 min, ee 46%.

4.2.8. 1,1-Bis(phenylsulfonyl)-4-(1-hydroxymethylethyl)-3-methylenecyclopentane ***27***. $[\alpha]_{D^{22}}$ −30.8 (*c* 0.81, $CHCl_3$) for 68% ee. HPLC Chiralpak AS-H (*n*-hexane/2-propanol: 90/10, 1.0 mL/min, λ=215 nm): t_R 61.9 and 71.2 min, ee 68%.

4.2.9. 3-[1-Hydroxymethylethyl]-4-methylene-N-tosylpyrrolidine ***28***. HPLC Chiralcel OD-H (*n*-hexane/2-propanol: 95/5, 1.0 mL/min, λ=215 nm): t_R 21.4 and 25.6 min, ee 0%.

4.2.10. Dimethyl 4-(1-methoxyphenylmethyl)-3-methylenecyclo pentane-1,1-dicarboxylate ***29***. $[\alpha]_{D^{22}}$ −17.2 (*c* 0.78, $CHCl_3$) for 11% ee. HPLC Chiralcel OD (*n*-hexane/2-propanol: 99/1, 1.0 mL/min, λ=215 nm): t_R 16.5 and 17.8 min, ee 11%.

4.2.11. 3-[1-Hydroxyphenylmethyl]-4-methylene-N-tosylpyrrolidine ***30***. $[\alpha]_{D^{22}}$ −23.3 (*c* 0.67, $CHCl_3$) for 23% ee. HPLC Chiralpak AS-H (*n*-hexane/2-propanol: 90/10, 1.0 mL/min, λ=215 nm): t_R 42.7 and 48.3 min, ee 23%.

4.2.12. 4-[1-Methoxy-(3,4-methylenedioxy)phenylmethyl]-3-methylenetetrahydrofurane ***31***. HPLC Chiralpak AS-H (*n*-hexane/2-propanol: 95/5, 1.0 mL/min, λ=215 nm): t_R 9.2 and 9.9 min, ee 0%.

4.2.13. 4-[1-Hydroxy-(3,4-methylenedioxy)phenylmethyl]-3-methylenetetrahydrofurane ***32***. $[\alpha]_{D^{22}}$ −13.6 (*c* 0.66, $CHCl_3$) for 38% ee. HPLC Chiralpak AS-H (*n*-hexane/2-propanol: 98/2, 1.0 mL/min, λ=215 nm): t_R 49.8 and 63.4 min, ee 38%.

4.2.14. Dimethyl 4-(1-methoxymethylethyl)-3-methylenecyclo pentane-1,1-dicarboxylate ***34***. $[\alpha]_{D^{22}}$ −2.0 (*c* 0.65, $CHCl_3$) for 44% ee. HPLC Chiralcel OJ (*n*-hexane/2-propanol: 99/1, 1.0 mL/min, λ=215 nm): t_R 16.5 and 18.4 min, ee 44%.

4.2.15. (Z)-(3-Benzylidene-4-(2-methoxypropan-2-yl)cyclopen tanedisulfonyl)dibenzene ***35***. $[\alpha]_{D^{22}}$ −218.1 (*c* 1.05, $CHCl_3$) for 78% ee. HPLC Chiralpak AS-H (*n*-hexane/2-propanol: 90/10, 1.0 mL/min, λ=215 nm): t_R 22.9 and 29.9 min, ee 78%.

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