DOI: 10.1002/hlca.202000198

FULL PAPER

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Mono-Gold(I)-Catalyzed Enantioselective Intermolecular Reaction of Ynones with Styrenes: Tandem *Diels–Alder* and Ene Sequence

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Dedicated to Professor *Antonio Togni*

Gold-catalyzed intermolecular reaction leading to dihydronaphthalene derivatives in one pot from two equivalents of ynones with respect to styrene is uncovered. The [4 + 2] *Diels–Alder* cycloaddition of ynones and styrenes is catalyzed by a mono-gold(I) complex and the conjugated acid to provide an unstable 3,8a-dihydronaphthalene to subsequently undergo an intermolecular ene-type reaction with the π-activated ynone to afford multi-component coupling dihydronaphthalene products. Linear relationships between chiral ligand-gold complexes and chiral dihydronaphthalene products proves mono-gold catalysis that triggers an asymmetric tandem *Diels–Alder* and ene reaction sequence.

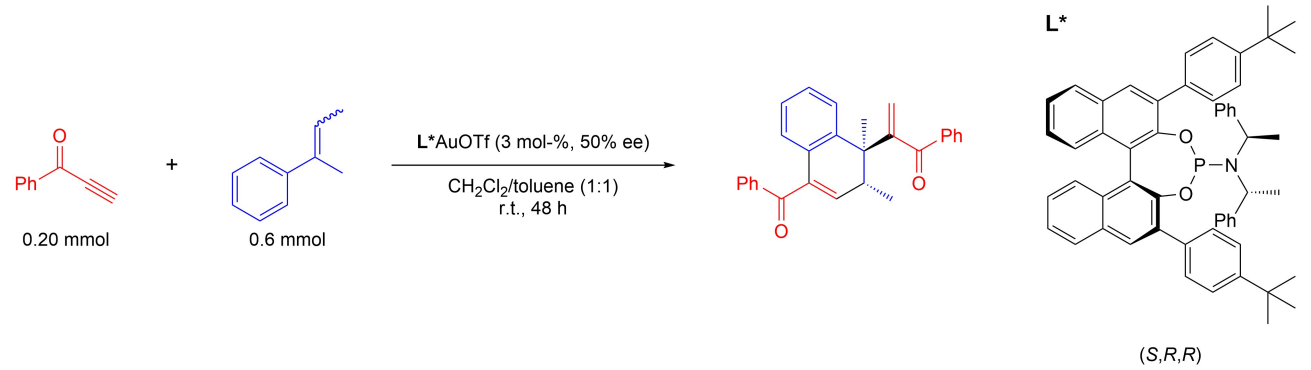
Keywords: asymmetric gold catalysis, intermolecular reaction, ene reaction, multicomponent reaction, *Diels–Alder* reaction.

Introduction

Metal-catalyzed intermolecular cyclization reactions are the most powerful tools for the efficient construction of complicated cyclic frameworks in short synthetic operation.[1,2] These processes have obvious advantages that greatly improve synthetic step efficiency[3,4] and atom economy[5,6] to waste much less chemicals. Gold provides a promising complex for the construction of carbo- and hetero-cyclic compounds with high step and atom economies under mild reaction conditions. The development of gold(I)-catalyzed reactions relied especially on intramolecular reactions of 1,*n*-enynes and their allene analogues.[7–14] In contrast, much less attention is paid for the corresponding intermolecular versions.[15] In the last few years, several intermolecular reactions with significant synthetic potential have been reported.[16–18] However, the chiral gold-catalyzed intermolecular reaction is still challenging due to its so far low reactivity and enantioselectivity.[19]

We have reported a highly enantioselective [4 + 2] *Diels–Alder* (D–A) cycloaddition reaction of ynones with less sterically demanding cyclic dienes catalyzed by chiral cationic phosphoramidite-di-gold complexes.[20] We anticipated that the enantioselective D–A cycloaddition could be extended to styrenes with the same di-gold catalysts and ynones. To our surprise, ynones reacted with α-methylstyrene in particular to form dihydronaphthalenes of synthetic importance[21] (*Scheme 1*). Herein, we report our discovery of mono-gold-catalyzed intermolecular tandem D–A and ene reaction sequence[22–26] of ynones and styrenes, and mechanistic proof thereof. Linear relationships[27–33] between chiral ligand-gold complexes and chiral dihydronaphthalene products clarifies mono-gold catalysis that triggers an asymmetric tandem D–A[34–37] and ene[38–42] reaction sequence of styrenes with two equivalents of ynones.

Supporting information for this article is available on the WWW under https://doi.org/10.1002/hlca.202000198

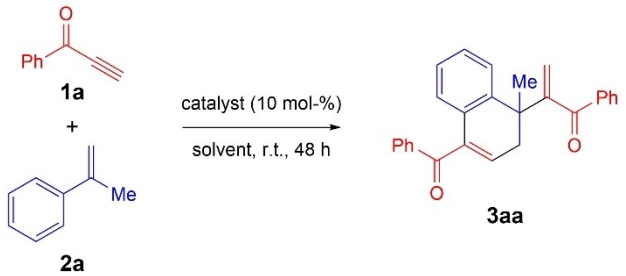


Scheme 1. Intermolecular three components coupling reaction of styrene with two equivalents of ynones.

Results and Discussion

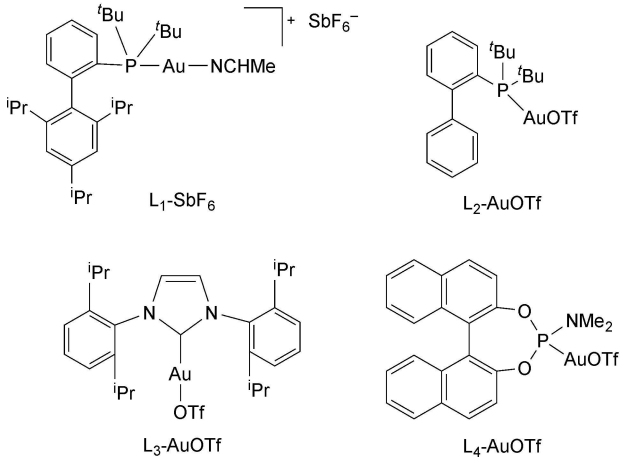
The initial assays were carried out with ynone **1a** and styrene **2a** in CH_2Cl_2 with various gold(I) catalysts (*Table 1*). No reaction was observed with commercially available cationic gold(I) salts such as bulky L_1-$AuSbF_6$ (*entry 1*). In contrast, dihydronaphthalene **3aa** was obtained as a single regioisomer with L_2-AuOTf bearing bulky dialkylbiarylphosphine ligand, L_2 (*entry 2*). NHC-gold(I) complex L_3-AuOTf was also effective to give dihydronaphthalene **3aa** (*entry 3*). The best result was obtained using phosphoramidite-gold(I) complex, L_4-AuOTf (*entry 4*).

Table 1. Gold(I)-catalyzed reaction of **1a** with **2a**.[a]



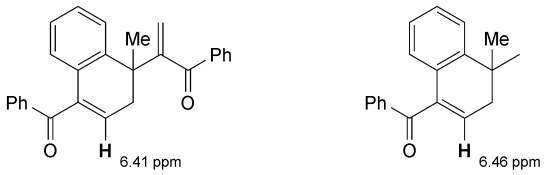
Entry	Catalyst	Solvent	**1a**:**2a**	Yield[b] [%]
1	L_1-$AuSbF_6$	CH_2Cl_2	1:1	0
2	L_2-AuOTf	CH_2Cl_2	1:1	16
3	L_3-AuOTf	CH_2Cl_2	1:1	13
4	L_4-AuOTf	CH_2Cl_2	1:1	22
5	L_4-$AuBF_4$	CH_2Cl_2	1:1	12
6	L_4-AuOPNB	CH_2Cl_2	1:1	0
7	L_4-AuOTs	CH_2Cl_2	1:1	0
8	TfOH	CH_2Cl_2	1:1	0
9[c]	L_4-AuOTf	CH_2Cl_2/ toluene (1:1)	1:3	38
10	L_4-$AuNTf_2$	CH_2Cl_2	1:1	0

[a] Ynone **1a** (0.2 mmol), styrene **2a** (0.2 mmol.) and catalyst (10 mol-%) were used in 1 mL of solvent at r.t. for 48 h.[b] Yields were determined by ^{1}H-NMR analysis using tetrachloroethane as an internal standard.[c] Ynone **1a** (0.2 mmol), styrene **2a** (0.6 mmol.) and catalyst (3 mol-%) were used in 1 mL of solvent at r.t. for 48 h.



The structural feature of dihydronaphthalene core of **3aa** was confirmed by the separate synthesis of a similar dihydronaphthalene **4** (*Figure 1*) from 4-methyl-1-tetralone; olefinic proton at 6.45 ppm in dihydronaphthalene **3aa** is in good agreement with that of **4** at 6.4 ppm.

The cyclization of ynone and styrene leading to dihydronaphthalene core can be rationalized by the D–A reaction involving the styrene as a diene component. However, a gold/conjugated acid complex[43,44] is responsible for an anomalous regioselectivity in the gold-catalyzed D–A reaction. Generally, a nucleophile adds to highly substituted carbon of terminal alkynes activated by gold complexes. This reversal is supported by the fact that H^+ (the conjugated acid) is essential for the progress of the D–A reaction. The presence of tertiary amine totally



3aa 4

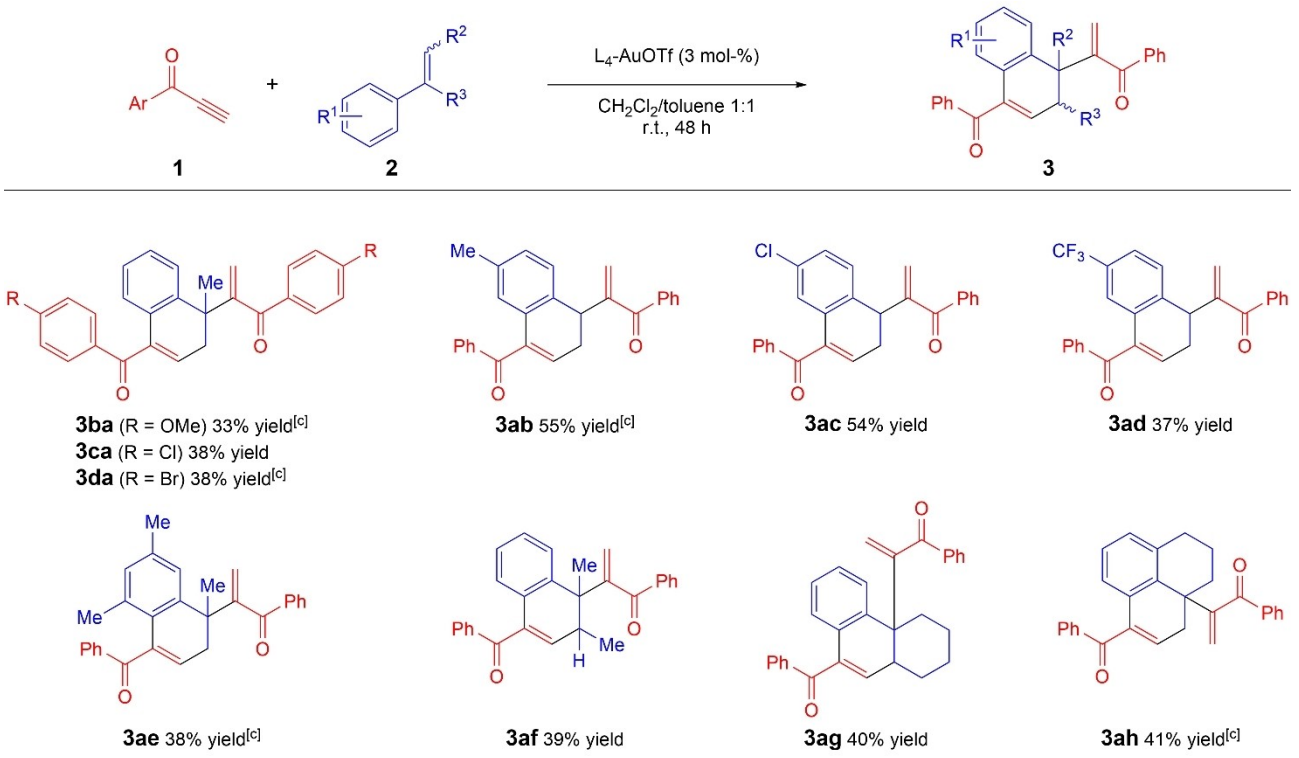
Figure 1. Dihydronaphthalenes **3aa** and **4**.

inhibits the progress of the reaction by trapping H^+ of the conjugated acid (*vide infra*).[20]

The effect of counter anion was further investigated. L_4–$AuBF_4$ promoted the reaction but in lower yield than L_4–AuOTf (*entry 5*). When the reaction was performed with L_4–Au–OPNB and –OTs, the product was not obtained (*entries 6* and *7*). However, the conjugated acid, TfOH itself did not catalyze the present reaction (*entry 8*). It was uncovered that the mixed solvent of CH_2Cl_2 and toluene was the best to give the highest yield of the desired product **3aa**. To improve the reactivity, the reaction conditions were further improved to increase the concentration of styrene and to use 3 mol-% of L_4–AuOTf for the best yield (*entry 9*). In this case, however, further elevating amounts of the catalyst led to lower yields due to dimerization of **2a**.

Under the optimized reaction conditions (*Table 1*, *entry 9*), a variety of ynones and styrenes were examined (*Table 2*). Reaction of electron donating groups and halides on the aryl ynones, such as 4–OMe (**1b**), 4–Cl (**1c**), 4–Br (**1d**), with α-methylstyrene **2a** led to the corresponding dihydronaphthalenes **3ba**–**3da** in moderate yields. A variety of substituted **2** with electron donating and halogen groups, such as 4–Me (**2b**) and 4–Cl (**2c**) gave the corresponding dihydronaphthalenes **3ab** and **3ac** in 55 and 54% yield, respectively. When aryl substituent in **2** was replaced with electron withdrawing groups such as 4–CF_3 (**2d**) and more bulky 3,5-dimethyl (**2e**), yields were lowered (**3ad**: 37% and **3ae**: 38%, resp.). The alkyl substituents were further varied with α,β-dimethylstyrene **2f** ((*E*/*Z*) mixture) to give the desired dihydronaphthalene **3af** in 39% yield. Even cyclic styrene derivatives such as 1-phenylcyclohexene **2g** and 1-methylene-1,2,3,4-tetra-

Table 2. Gold(I)-catalyzed reaction of **1** with **2**.[a,b]



[a] Ynone **1** (0.2 mmol), styrene **2** (0.6 mmol) and catalyst (3 mol-%) were used in 1 mL of solvent at r.t. for 48 h.[b] Yield of isolated product.[c] L_4-$AuBF_4$ was used as catalyst.

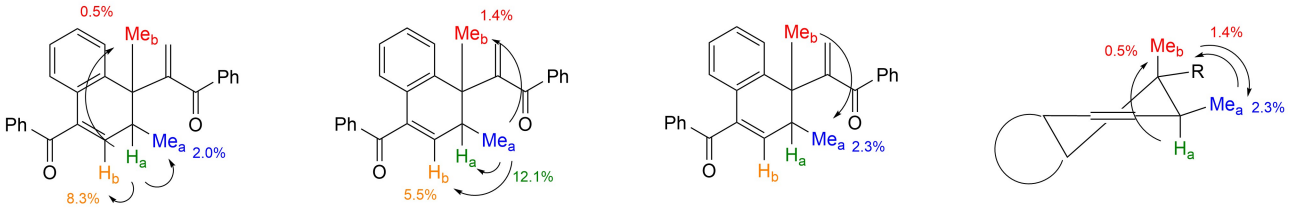


Figure 2. NOE analysis and proposed conformation of **3af**.

hydronaphthalene **2h** afforded the corresponding tetrahydrophenanthrene **3ag** and dihydro-1*H*-phenalene **3ah** in 40 and 41 % yields, respectively.

To our surprise, the dihydronaphthalene **3af** was found to be diastereopure even starting from the (*E*/*Z*) mixture of α,β-dimethylstyrene **2f**. We performed several NOE studies on the dihydronaphthalene product **3af** at the methine proton and methyl groups of the dihydronaphthalene ring. The orientation of two methyl groups was thus determined to be *cis* by NOE correlation with H_a. As shown in *Figure 2*, the irradiation of Me_a, represented by arrow, gave 1.4 % NOE to Me_b. On the other hand, the irradiation of Me_b gave 2.3 % NOE to Me_a. The NOE correlation between Me_a and Me_b showed that two methyl groups likely possess *cis*-orientation.

In order to gain insight into reaction mechanism, deuterium experiments were exerted. First, the position of two terminal vinyl hydrogen atoms of **3ac** was determined by NOE analysis. As shown in *Figure 3*, the irradiation of Me, represented by arrow, gave 3.5 % NOE to the *syn* vinyl hydrogen atom of which the ^{1}H-NMR signal appeared at 5.41 ppm.

The use of aromatic deuterated α-methylstyrene ((D$_5$)-**2a**) under the optimal reaction conditions led to (D$_5$)-**3ca** in 39 % yield with 98 % deuterium at *syn* vinyl hydrogen and no deuterium was found at vinyl proton of dihydronaphthalene and *anti* vinyl hydrogen (*Scheme 2*, *eqn. 1*). Surprisingly, the exposure of terminal deuterated ynone (D$_1$)-**1c** to the optimal reaction conditions led to (D$_2$)-**3ca** with a 90 % deuterium at *anti* vinyl hydrogen (*Scheme 2*, *eqn. 2*).

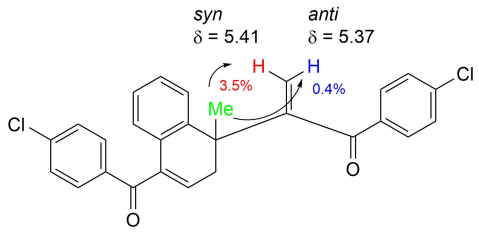
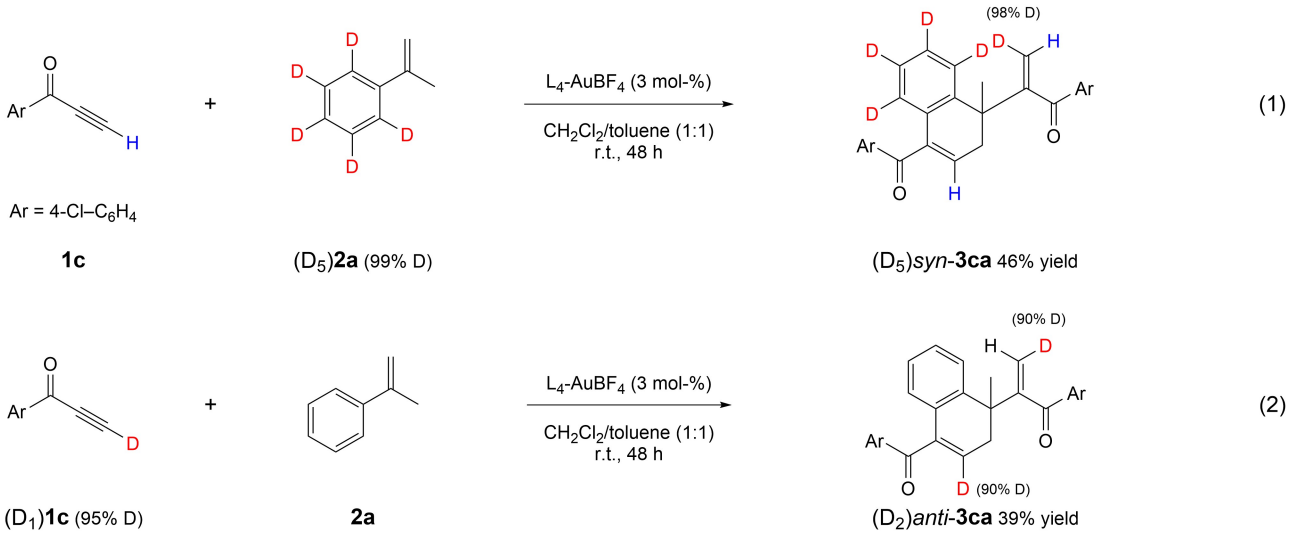


Figure 3. NOE analysis of dihydronaphthalene compound **3ac**.

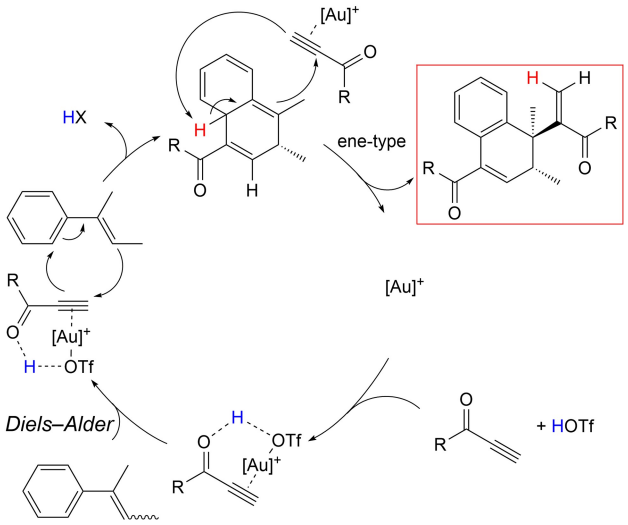


Scheme 2. Deuterium labelling experiments.

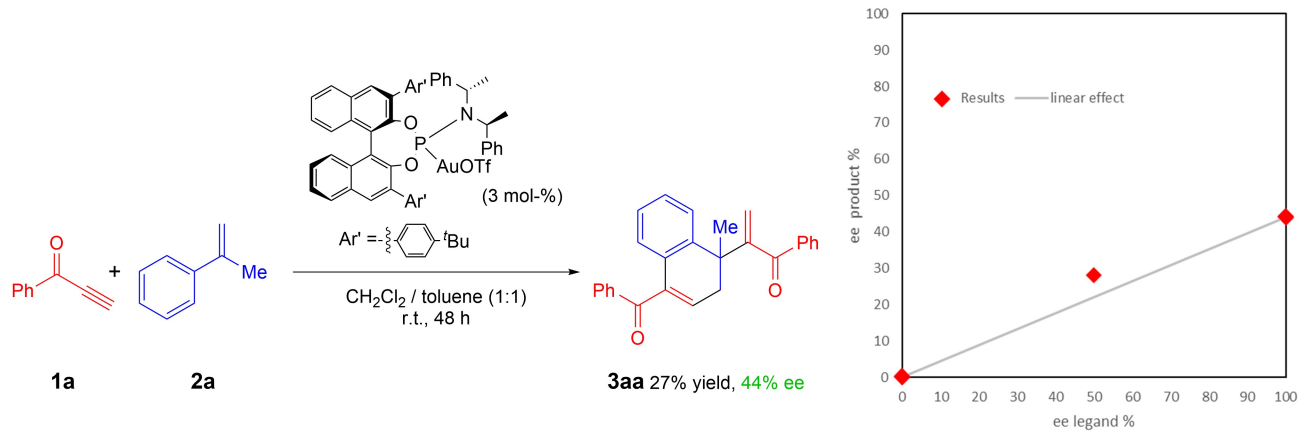
These facts clearly demonstrated that this reaction was regioselectively promoted with π-activated gold(I) complex and hence that this reaction did not proceed with di-gold acetylide complex.[20] Furthermore, the reaction took place with additional catalytic amount of the conjugated acid. Both gold(I) catalysts and conjugated acids complexed therewith were required for the present three components coupling reaction (*vide supra*). The regioselectivity of the dihydronaphthalene can then be controlled by the presence of the conjugated acid that coordinated with the gold catalyst to acidify thereof for triggering the D–A reaction. Hence, 3,8a-dihydronaphthalene intermediate would form with or without involvement of benzylic positive charge through activation of carbonyl functionality of ynones.

A plausible reaction mechanism to rationalize the termination of dihydronaphthalene formation is depicted in *Scheme 3*. The coordination of the triple bond to gold(I) complexes and conjugated acids could effectively enhance the electrophilicity of ynones. Subsequently, nucleophilic attack of the olefin portion of less sterically demanding (*E*)-α,β-dimethylstyrene to the electron-deficient ynones in either stepwise or [4 + 2] concerted ways would form 3,8a-dihydronaphthalene. The *cis*-ene addition[38–40] of the unstable 3,8a-dihydronaphthalene to the π-activated ynone, as shown with arrows, should afford the dihydronaphthalene products and recycle the Au catalyst. Due to the instability of 3,8a-dihydronaphthalene, the 3,8a-dihydronaphthalene should be trapped by the second π-activated ynones on generation.

As a proof of the *mono*-gold catalysis, linear relationships between chiral ligand-gold complexes and chiral dihydronaphthalene products was clarified rather than non-linear relationships (*Scheme 4*). The linear relationship was indeed validated between *ee*'s of chiral BINOL-derived phosphoramidite ligands, (*R,S,S*)-**L*** with bulky chiral (*S,S*)-bis(1-phenylethyl) amine and cycloadducts **3af** through a range of *ee* values ((*R,S,S*)-**L***-Au: 0, 50, and 100% *ee*; **3af**: 0, 28 (27%), and 44% *ee* (28%), resp.). The linear relationships clearly prove the intervention of the *mono*-gold-activated alkyne as a triggering species. A chiral and large amine moiety in the ligand played a positive role on the enantioselectivity of the reaction. Although the enantiomeric excess was moderate, the result showed



Scheme 3. Plausible tandem *Diels–Alder* and ene reaction mechanism.



Scheme 4. Asymmetric three components reaction.

that mono-gold chiral catalyst was concerned with a catalytic cycle.

Conclusions

In summary, this work shows that the mono-gold(I)-catalyzed reaction of two alkynes with respect to one molecule of styrenes leads to dihydronaphthalenes of synthetic importance. Key for the success in this tandem reaction is the selective *cis*-ene addition of the unstable intermolecular D–A intermediates to π-activated ynones by gold(I) complexes. The present tandem D–A and ene reaction sequence opens new opportunities for the invention of related intermolecular chiral gold(I)-catalyzed (tandem) processes.

Experimental Section

General Information

^{1}H-, ^{13}C-, and ^{19}F-NMR spectra were measured on *Bruker AV300 M* (300 MHz) spectrometers. Chemical shifts of ^{1}H-NMR were expressed in parts per million relative to the *singlet* ($\delta = 7.26$) for $CDCl_3$. Chemical shifts of ^{13}C-NMR were expressed in parts per million relative to the central line of the *triplet* ($\delta = 77.0$) for $CDCl_3$. Chemical shifts of ^{31}P-NMR were expressed in parts per million downfield from 85% H_3PO_4 as an external standard ($\delta = 0.00$) in $CDCl_3$. Chemical shifts of ^{19}F-NMR were expressed in parts per million downfield from BTF as an external standard ($\delta = -63.24$) in $CDCl_3$. Analytical thin layer chromatography (TLC) was performed on glass plates pre-coated with silica-gel (*Merck Kieselgel 60 F_{254}*, layer thickness 0.25 mm). Visualization was accomplished by UV light (254 nm), anisaldehyde, $KMnO_4$, phosphomolybdic acid. Column chromatography was performed on *KANTO Silica Gel 60 N* (spherical, neutral). IR Spectra were measured on a *JASCO FT/IR-4200* spectrometer. High performance liquid chromatography (HPLC) was conducted on *JASCO PU-980*, *LG-980-02*, *DG-980-50*, *MD-2010*, and *CO-966* instrument equipped with model *UV-975* spectrometers as an ultraviolet light. Peak areas were calculated by JASCO chrom NAV (Windows 7) as an automatic integrator. *DAICEL CHIRALPAK AD-3*, *DAICEL CHIRALPAK AD-H*, *DAICEL CHIRALPAK AS-H*, *DAICEL CHIRALCEL OD-3*, and *DAICEL CHIRALCEL OJ-3* were used as chiral columns. Mass spectra were measured on a *JEOL JMS-T100CS* (Accu-TOF) spectrometer. Optical rotations were measured on a *JASCO P-1020*. X-Ray crystal analyses were measured on *Bruker APEX CCD* area detector (MoKα radiation, graphite monochromator, $\lambda = 0.71073$ Å; *Bruker AXS K.K.*). All experiments were carried out under argon atmosphere unless otherwise noted.

Typical Synthetic Procedure for α-Alkylstyrene

Styrenes **2a** and **2g** were purchased from *Aldrich*. Other styrenes were prepared according to the literature.

To a solution of triphenylphosphonium bromide (2.1 g, 6 mmol, 1.2 equiv.) in dry Et_2O (30 mL) under Ar atmosphere was added 2.6 M of BuLi in hexane (2.3 mL, 6 mmol, 1.2 equiv.) at room temperature and the mixture was stirred for 1 h. A solution of corresponding ketone (5 mmol, 1.0 equiv.) in Et_2O (5 mL) was added dropwise and the resulting mixture was stirred at room temperature for 24 h. The mixture was poured into aq. NH_4Cl (50 mL) and the organic layer was extracted by dichloromethane (40 mL ×2). The combined organic phase was washed with brine (20 mL×1), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica-gel (hexane only), affording the corresponding α-methylstyrene product.

4,α-Dimethylstyrene (= **1-Methyl-4-(prop-1-en-2-yl)benzene**; **2b**).[45] Colorless liquid (39% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): 2.40 (*s*, 3 H, Me); 2.59 (*s*, 3 H, Me); 5.30 (*s*, 1 H, vinyl); 5.62 (*s*, 1 H, vinyl); 7.37 (*d*, J= 7.9, 2 H, arom.); 7.62 (*d*, J=8.0, 2 H, arom.). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): 21.3; 22.1; 111.8; 125.7; 129.2; 137.3; 138.6; 143.3.

4-Chloro-α-methylstyrene (= **1-Chloro-4-(prop-1-en-2-yl)benzene**; **2c**).[45] Yellow liquid (32% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): 2.21 (*s*, 3 H, Me); 5.19 (*s*, 1 H, vinyl); 5.45 (*s*, 1 H, vinyl); 7.08 (*d*, J=8.8, 2 H, arom.); 7.65 (*d*, J=8.8, 2 H, arom.). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): 22.0; 55.1; 110.7; 113.8; 126.8; 133.8; 142.7; 159.4.

4-Trifluoromethyl-α-methylstyrene (= **1-(Prop-1-en-2-yl)-4-(trifluoromethyl)benzene**; **2d**).[46] Colorless solid (75% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): 2.22 (*s*, 3 H, Me); 5.26 (*s*, 1 H, vinyl); 5.51 (*s*, 1 H, vinyl); 7.62 (*dd*, J=8.8, 13.8, 4 H, arom.). ^{19}F{^{1}H}-NMR (282 MHz, $CDCl_3$): −62.6 (*s*). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): 21.5; 114.5; 122.6; 125.2 (*q*, J_{CF}=3.8); 125.8; 126.2; 129.4 (*q*, J_{CF}= 32.3); 142.2; 144.8.

3,5-Dimethyl-α-methylstyrene (= **1,3-Dimethyl-5-(prop-1-en-2-yl)benzene**; **2e**).[47] Colorless liquid (70% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): 2.54 (*s*, 3 H, Me); 2.71 (*s*, 6 H, Me); 5.46 (*s*, 1 H, vinyl); 5.76 (*s*, 1 H, vinyl); 7.29 (*s*, 1 H, arom.); 7.50 (*s*, 1 H, arom.). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): 21.6; 22.2; 112.3; 123.8; 129.3; 137.8; 141.6; 143.8.

(1-Methylpropen-1-yl)benzene (**2f**).[48] (1-Methylpropen-1-yl)benzene was prepared from acetophenone and ethyltriphenylphosphonium bromide in a similar manner to 4-methoxy-α-methylstyrene as colorless liquid ((*E/Z*) mixture, 64% yield).

1-Methylidene-1,2,3,4-tetrahydronaphthalene (**2h**).[49] Colorless liquid (76% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): 2.17–2.25 (*m*, 2 H, CH_2); 2.87–2.91 (*m*, 2 H, CH_2); 3.14–3.18 (*m*, 2 H, CH_2); 5.31 (*d*, J = 1.3, 1 H, vinyl); 5.85 (*d*, J = 0.8, 1 H, vinyl); 7.40–7.53 (*m*, 3 H, arom.); 7.99-8.02 (*m*, 1 H, arom.). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): 24.1; 30.7; 33.5; 108.0; 124.4; 126.1; 127.8; 129.4; 134.9; 137.4; 143.6.

(D_5)-α-Methylstyrene (= **1-(Prop-1-en-2-yl)($^2H_5$) benzene**; (D_5)**2a**).[50] Colorless liquid (86% yield, 99% D). ^{1}H-NMR (300 MHz, $CDCl_3$): 2.36 (*s*, 3 H, Me); 5.28 (*s*, 1 H, vinyl); 5.58 (*s*, 1 H, vinyl); 7.44 (*s*, 0.01 H, arom.); 7.50 (*s*, 0.02 H, arom.); 7.66 (*s*, 0.02 H, arom.). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): 21.8; 112.3; 125.2 (*t*, J = 23.6); 126.9 (*t*, J = 24.0); 127.8 (*t*, J = 24.0); 141.3; 143.4.

Typical Synthetic Procedure for Ynones: **1-(4-Chlorophenyl)(^{2}H)prop-2-yn-1-one** ((D_1)**1c**).[20] To a solution of trimethylsilylacetylene (1.6 mL, 11 mmol) in dry THF (20 mL) under Ar atmosphere was added butyllithium (4.2 mL, 11 mmol, 2.6 M solution in hexane, 1 M = 1 mol dm^{-3}) at −78 °C and the mixture was stirred for 15 min. 4-Chlorobenzaldehyde (703 mg, 5 mmol) in THF (5 mL) was added to the solution, and the mixture was warmed up to room temperature. After stirring at that temperature (monitored by TLC), the reaction was quenched with saturated aq. NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with Et_2O three times. The combined organic layers were washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure.

After concentration, the crude mixture was dissolved by MeOH (30 mL) under air at room temperature. Then, potassium carbonate (8.3 g, 60 mmol) was added, and the reaction mixture was stirred for 1 h at that temperature (monitored by TLC). Then, the mixture was filtrated over *Celite*. The residue was washed with diethyl ether (10 mL). The collected filtrate was concentrated in vacuo and the residue purified by column chromatography over silica-gel (hexane/AcOEt 10:1–3:1), affording the corresponding ynol product.

To the solution of crude alcohol in dry THF (20 mL) under Ar atmosphere was added butyllithium (4.2 mL, 11 mmol, 2.6 M solution in hexane, 1 M = 1 mol dm^{-3}) at −78 °C, and the mixture was stirred for 15 min. After this time, the reaction was quenched by D_2O (1 mL) and warmed up to room temperature. The organic layer was separated, and the aqueous layer was extracted with Et_2O three times. The combined organic layers were washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure.

To the solution of crude alcohol in acetone at 0 °C, *Jones'* reagent (10.8 mL, 0.54 M solution in water, 1 M = 1 mol dm^{-3}) was added slowly, and the mixture was stirred at that temperature (monitored by TLC). The mixture was warmed to room temperature and quenched with ^{i}PrOH (10 mL). The mixture was diluted with $CHCl_3$ (20 mL) and water (20 mL). The organic phase was separated, and the aqueous layer was extracted with $CHCl_3$ (20 mL × 2). The combined organic layers were washed with brine (20 mL × 1), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica-gel (hexane/AcOEt 30:1) to yield the corresponding compounds. Ynones **1a**–**1d** were similarly synthesized[51].

Yellow solid (477 mg, 57% yield, 95% D). ^{1}H-NMR (300 MHz, $CDCl_3$): 3.52 (*s*, 0.05H, CH); 7.44 (*d*, J = 7.2, 2 arom.); 8.06 (*d*, J = 7.2, 2 arom.). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): 79.7 (*t*, J = 7.1); 81.4 (*t*, J = 39.0); 129.3; 131.2; 134.7; 141.4; 176.3. HR-APCI-TOF-MS: 166.0175 ($C_9H_5DNaClO^+$, $[M+H]^+$; calc. 166.0167. FT-IR (KBr pellets): 1575, 1725, 2875, 2932, 2966.

Typical Procedure for Three Component Coupling

A solution of alkyne (0.2 mmol) in CH_2Cl_2/toluene (1:1, 0.2 mL) and styrene (0.6 mmol) was added to a solution of gold(I) catalyst (3 mol-%) in CH_2Cl_2/toluene (1:1, 0.8 mL). The mixture was stirred at room temperature for 48 h. The mixture was directly loaded onto a silica-gel short column (hexane/AcOEt 3:1) to remove the catalyst, and then the solution was concentrated

under reduced pressure. The residue was purified by silica-gel chromatography (hexane/AcOEt 10:1).

2-(4-Benzoyl-1-methyl-1,2-dihydronaphthalen-1-yl)-1-phenylprop-2-en-1-one (**3aa**). Yellow liquid (17.2 mg, 43% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.80 (*s*, 3 H, Me); 2.48 (*dd*, *J* = 3.3, 17.3, 1 H, CH_2); 3.20 (*dd*, *J* = 6.2, 17.3, 1 H, CH_2); 5.40 (*s*, 2 H, vinyl); 6.41 (*dd*, *J* = 3.3, 6.9, 1 H, vinyl); 7.22–7.54 (*m*, 10 H, arom.); 7.56–7.79 (*m*, 2 H, arom.); 7.86–7.89 (*m*, 2 H, arom.). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): 26.6; 35.4; 42.7; 124.4; 126.0; 126.9; 127.3; 128.4; 128.6; 130.1; 130.2; 132.1; 133.0; 133.1; 136.1; 138.0; 138.2; 139.4; 141.3; 152.8; 196.9; 199.1. HR-ESI-TOF-MS: 401.1518 ($C_{27}H_{22}NaO_2^+$, $[M+Na]^+$; calc. 401.1518). FT-IR (neat): 1266, 1454, 1600, 1668, 1717, 2928, 2954, 3025, 3067. HPLC analysis (column, *CHIRALPAK AD-3*, hexane/2-propanol 99:1, flow rate 1.0 mL/min, 20 °C, detection UV 220 nm light); t_R of major-isomer 10.5 min, t_R of minor-isomer 11.9 min.

2-[4-(4-Methoxybenzoyl)-1-methyl-1,2-dihydronaphthalen-1-yl]-1-(4-methoxyphenyl)prop-2-en-1-one (**3ba**). Yellow liquid (15.3 mg, 35% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): 3.43 (*s*, 3 H); 2.47 (*d*, *J* = 17.3, 1 H); 3.12 (*dd*, *J* = 17.0, 5.6, 1 H); 3.85 (*s*, 3 H); 3.88 (*s*, 3 H); 5.31 (*d*, *J* = 6.4, 2 H); 6.32 (*s*, 1 H); 6.86 (*d*, *J* = 8.2, 2 H); 6.93 (*d*, *J* = 8.3, 2 H); 7.23–7.32 (*m*, 3 H); 7.47 (*d*, *J* = 7.2, 1 H); 7.82 (*d*, *J* = 8.2, 2 H); 7.92 (*d*, *J* = 8.2, 2 H). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): 26.5; 35.1; 42.5; 55.5 ;113.4; 113.6; 122.0; 125.9; 126.5; 127.0; 128.2; 130.4; 130.6; 132.3; 132.4; 133.7; 139.3; 140.9; 152.9; 163.5; 163.6; 195.6; 197.8. HR-ESI-TOF-MS: 461.1735 ($C_{29}H_{26}NaO_4^+$, $[M+Na]^+$; calc. 461.1723). FT-IR (neat): 1303, 1461, 1593, 1650, 1732, 1755, 2861, 2936.

2-[4-(4-Chlorobenzoyl)-1-methyl-1,2-dihydronaphthalen-1-yl]-1-(4-chlorophenyl)prop-2-en-1-one (**3ca**). Yellow liquid (16.9 mg, 38% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.80 (*s*, 3 H, Me); 2.48 (*dd*, *J* = 3.1, 17.4, 1 H, CH_2); 3.17 (*dd*, *J* = 6.3, 17.4, 1 H, CH_2); 5.39 (*d*, *J* = 11.8, 2 H, vinyl); 6.39 (*dd*, *J* = 3.2, 6.2, 1 H, vinyl); 7.25–7.47 (*m*, 7 H, arom.), 7.71 (*d*, *J* = 8.5, 2 H, arom.); 7.84 (*d*, *J* = 8.5, 2 H, arom.). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): 26.7; 35.4; 42.7; 124.1; 126.1; 127.0; 127.5; 128.9; 128.9; 129.1; 131.6; 131.6; 132.0; 136.0; 136.3; 136.5; 139.3; 139.7; 139.8; 141.1; 152.6; 195.7; 197.8. HR-ESI-TOF-MS: 469.0739 ($C_{27}H_{20}Cl_2NaO_2^+$, $[M+Na]^+$; calc. 469.0738). FT-IR (neat): 1389, 1582, 1654, 2861, 2927, 2965, 3066.

2-[4-(4-Bromobenzoyl)-1-methyl-1,2-dihydronaphthalen-1-yl]-1-(4-bromophenyl)prop-2-en-1-one (**3da**). Yellow solid (20.4 mg, 38% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.79 (*s*, 3 H, Me); 2.48 (*dd*, *J* = 3.2, 17.4, 1 H, CH_2); 3.17 (*dd*, *J* = 6.3, 17.4, 1 H, CH_2); 5.39 (*d*, *J* = 12.0, 2 H, vinyl); 6.38 (*dd*, *J* = 3.3, 6.3, 1 H, vinyl); 7.23–7.37 (*m*, 3 H, arom.); 7.45 (*d*, *J* = 7.3, 1 H, arom.); 7.52 (*d*, *J* = 7.7, 2 H, arom.); 7.56–7.64 (*m*, 4 H, arom.); 7.78 (*d*, *J* = 8.5, 2 H, arom.). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): 26.4; 35.1; 42.4; 123.9; 125.8; 126.7; 127.2; 128.2; 128.6; 131.3; 131.4; 131.6; 131.7; 131.8; 135.8; 136.3; 136.6; 139.0; 140.8; 152.2; 195.6; 197.7. HR-ESI-TOF-MS: 556.9749 ($C_{27}H_{20}Br_2NaO_2^+$, $[M+Na]^+$; calc. 556.9728). FT-IR (KBr): 1575, 1650, 1728, 2853, 2889, 2920, 2974.

2-(4-Benzoyl-1,6-dimethyl-1,2-dihydronaphthalen-1-yl)-1-phenylprop-2-en-1-one (**3ab**). Yellow liquid (22.9 mg, 55% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.77 (*s*, 3 H, Me); 2.29 (*s*, 3 H, Me); 2.44 (*dd*, *J* = 3.3, 17.3, 1 H, CH_2); 3.17 (*dd*, *J* = 6.3, 17.3, 1 H, CH_2); 5.38 (*d*, *J* = 7.7, 2 H, vinyl); 6.36 (*dd*, *J* = 3.3, 6.3, 1 H, vinyl); 7.13–7.19 (*m*, 2 H, arom.); 7.33–7.58 (*m*, 7 H, arom.); 7.74–7.77 (*m*, 2 H, arom.); 7.86–7.89 (*m*, 2 H, arom.). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): 21.4; 26.8; 35.6; 42.5; 124.5; 126.0; 127.7; 128.5; 128.7; 129.4; 130.2; 130.3; 132.2; 133.1; 133.2; 136.1; 137.0; 138.2; 138.4; 138.6; 139.6; 153.1; 197.2; 199.3. HR-ESI-TOF-MS: 415.1680 ($C_{28}H_{24}NaO_2^+$, $[M+Na]^+$; calc. 415.1674). FT-IR (neat): 1450, 1589, 1652, 1732, 2871, 2917, 2962, 3026, 3060.

2-(4-Benzoyl-6-chloro-1-methyl-1,2-dihydronaphthalen-1-yl)-1-phenylprop-2-en-1-one (**3ac**). Yellow liquid (21.5 mg, 54% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.78 (*s*, 3 H, Me); 2.47 (*dd*, *J* = 3.3, 17.4, 1 H, CH_2); 3.24 (*dd*, *J* = 6.1, 17.5, 1 H, CH_2); 5.36 (*d*, *J* = 1.1, 2 H, vinyl); 6.48 (*dd*, *J* = 3.5, 6.0, 1 H, vinyl); 7.28–7.32 (*m*, 1 H, arom.); 7.37–7.62 (*m*, 8 H, arom.); 7.76–7.78 (*m*, 2 H, arom.); 7.86–7.89 (*m*, 2 H, arom.). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): 26.8; 35.6; 42.5; 124.9; 127.0; 127.5; 128.5; 128.6; 128.8; 130.2; 130.3; 133.3; 133.3; 133.4; 133.6; 137.8; 138.0; 138.1; 138.3; 139.9; 152.4; 196.4; 198.9. HR-ESI-TOF-MS: 435.1137 ($C_{27}H_{21}ClNaO_2^+$, $[M+Na]^+$; calc. 435.1128). FT-IR (neat): 1452, 1586, 1661, 1712, 2857, 2920, 2969, 3066.

2-[4-Benzoyl-1-methyl-6-(trifluoromethyl)-1,2-dihydronaphthalen-1-yl]-1-phenylprop-2-en-1-one (**3ad**). Yellow liquid (16.4 mg, 37% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.78 (*s*, 3 H, Me); 2.47 (*dd*, *J* = 3.2, 17.6, 1 H, CH_2); 3.28 (*dd*, *J* = 5.8, 17.6, 1 H, CH_2); 5.50 (*d*, *J* = 4.8, 2 H, vinyl); 6.52 (*t*, *J* = 4.3, 1 H, vinyl); 7.37–7.60

(*m*, 8 H, arom.); 7.74–7.77 (*m*, 3 H, arom.); 7.86 (*d*, *J*= 7.5, 2 H, arom.). $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): 26.4; 35.2; 42.5; 123.6 (*q*, J_{CF} = 3.8); 125.0 (*q*, J_{CF} = 3.8); 125.1; 125.8; 126.2; 128.3; 128.5; 129.1; 129.5; 129.8; 129.9; 132.2; 133.0; 133.1; 137.6; 137.7; 138.0; 145.1; 151.7; 195.9; 198.4. HR-ESI-TOF-MS: 469.1380 ($C_{28}H_{21}NaF_3O_2^+$, $[M+Na]^+$; calc. 469.1391). FT-IR (neat): 1416, 1577, 1660, 1717, 2863, 2921, 2954, 3060.

2-(4-Benzoyl-1,5,7-trimethyl-1,2-dihydronaphthalen-1-yl)-1-phenylprop-2-en-1-one (**3ae**). Yellow liquid (15.2 mg, 38% yield). ^1H-NMR (300 MHz, $CDCl_3$): 1.79 (*s*, 3 H, Me); 2.11 (*s*, 3 H, Me); 2.30–2.37 (*m*, 1 H, CH_2); 2.39 (*s*, 3 H, Me); 3.07 (*dd*, *J*= 7.1, 16.3, 1 H, CH); 5.34 (*s*, 1 H, vinyl); 5.49 (*s*, 1 H, vinyl); 6.98 (*s*, 1 H, arom.); 7.18 (*s*, 1 H, arom.); 7.30–7.35 (*m*, 2 H, arom.); 7.40–7.47 (*m*, 3 H, arom.); 7.52–7.57 (*m*, 1 H, arom.); 7.72 (*d*, *J*= 7.2, 2 H, arom.); 7.92 (*d*, *J*= 7.2, 2 H, arom.). $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): 21.9; 22.9; 34.8; 44.2; 124.5; 125.9; 128.5; 128.7; 129.9; 130.3; 130.5; 131.0; 133.0; 133.1; 135.3; 137.4; 137.9; 138.1; 138.3; 141.6; 143.9; 152.7; 196.4; 199.2. HR-ESI-TOF-MS: 429.1843 ($C_{29}H_{26}NaO_2^+$, $[M+Na]^+$; calc. 429.1831). FT-IR (neat): 1589, 1653, 1721, 2875, 2921, 2970, 3056.

2-(4-Benzoyl-1,2-dimethyl-1,2-dihydronaphthalen-1-yl)-1-phenylprop-2-en-1-one (**3af**). Yellow liquid (15.5 mg, 39% yield). ^1H-NMR (300 MHz, $CDCl_3$): 1.03 (*d*, *J*= 7.1, 3 H, Me); 1.74 (*s*, 3 H, Me); 3.34 (*dt*, *J*= 1.2, 14.1, 1 H, CH); 5.51 (*d*, *J*= 11.0, 2 H, vinyl); 7.22–7.60 (*m*, 12 H, arom.); 7.80 (*d*, *J*= 8.5, 2 H, arom.); 7.89 (*d*, *J*= 8.5, 2 H, arom.). $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): 13.4; 22.6; 35.9; 47.0; 125.4; 126.9; 127.0; 127.3; 128.5; 128.7; 128.8; 130.2; 130.4; 130.6; 133.1; 133.2; 137.7; 138.2; 138.4; 140.7; 142.3; 154.2; 197.2; 199.2. HR-ESI-TOF-MS: 415.1694 ($C_{28}H_{24}NaO_2^+$, $[M+Na]^+$; calc. 415.1674). FT-IR (neat): 1454, 1601, 1656, 1728, 2913, 2973, 3030, 3060.

2-(9-Benzoyl-1,3,4,10a-tetrahydrophenanthren-4a(2*H*)-yl)-1-phenylprop-2-en-1-one (**3ag**). Yellow liquid (17.1 mg, 40% yield). ^1H-NMR (300 MHz, $CDCl_3$): 1.16–1.78 (*m*, 6 H, alkyl); 2.26–2.33 (*m*, 1 H, alkyl); 2.60 (*d*, *J*= 14.1, 1 H, alkyl); 3.08 (*dd*, *J*= 4.6, 8.8, 1 H, CH); 5.24 (*s*, 2 H, CH_2); 6.38 (*d*, *J*= 6.38, 1 H, CH); 7.26–7.59 (*m*, 10 H, arom.); 7.62 (*d*, *J*= 7.6, 2 H, arom.); 7.87 (*d*, *J*= 7.6, 2 H, arom.). $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): 22.4; 25.5; 33.4; 38.9; 47.8; 123.1; 127.2; 127.4; 128.0; 128.5; 128.6; 128.7; 130.2; 130.6; 132.6; 133.2; 133.2; 137.4; 137.7; 137.8; 138.4; 141.1; 154.3; 197.3; 199.7. HR-ESI-TOF-MS: 441.1850 ($C_{29}H_{26}NaO_2^+$, $[M+Na]^+$; calc. 441.1831). FT-IR (neat): 1450, 1601, 1660, 1721, 2857, 2936, 3033, 3063.

2-(6-Benzoyl-2,3-dihydro-1*H*-phenalen-3a(4*H*)-yl)-1-phenylprop-2-en-1-one (**3ah**). Yellow liquid (17.2 mg, 41% yield). ^1H-NMR (300 MHz, $CDCl_3$): 1.68–1.80 (*m*, 1 H, alkyl); 1.84–1.89 (*m*, 2 H, alkyl); 2.37 (*dd*, *J*= 2.7, 17.1, 1 H, CH_2); 2.74–2.78 (*m*, 1 H, alkyl); 2.87–2.93 (*m*, 2 H, alkyl); 3.11 (*dd*, *J*= 7.2, 17.3, 1 H, CH_2); 5.19 (*s*, 1 H, vinyl); 5.54 (*s*, 1 H, vinyl); 7.12–7.22 (*m*, 3 H, arom.); 7.29–7.35 (*m*, 2 H, arom.); 7.39–7.57 (*m*, 4 H, arom.); 7.76–7.79 (*m*, 2 H, arom.); 7.85–7.87 (*m*, 2 H, arom.). $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): 18.6; 29.4; 33.8. 34.9; 43.0; 124.9; 127.2; 128.5; 128.7; 128.9; 129.6; 130.1; 130.4; 132.6; 133.1; 133.2; 136.2; 136.4; 137.0; 138.2; 138.3; 140.6; 151.6; 197.3; 198.4. HR-ESI-TOF-MS: 441.1850 ($C_{29}H_{24}NaO_2^+$, $[M+Na]^+$; calc. 441.1831). FT-IR (neat): 1450, 1601, 1660, 1721, 2875, 2939, 3026, 3063.

(2*E*)-2-[4-(4-Chlorobenzoyl)-1-methyl-(5,6,7,8-$^2H_4$)-1,2-dihydronaphthalen-1-yl]-1-(4-chlorophenyl)(3-$^2H_1$)prop-2-en-1-one ((D_5)**3ac**). Yellow liquid (20.7 mg, 46% yield). ^1H-NMR (300 MHz, $CDCl_3$): 1.80 (*s*, 3 H, Me); 2.48 (*dd*, 1 H, *J*= 17.5, 2.9, alkyl); 3.18 (*dd*, 1 H, *J*= 17.4, 6.1, alkyl); 5.35 (*s*, 1 H, vinyl); 5.40 (*s*, 0.06 H, vinyl); 6.39 (*q*, 1 H, *J*= 3.0, vinyl); 7.36 (*d*, *J*= 8.3, 2 H, arom.); 7.44 (*d*, *J*= 8.3, 2 H, arom.); 7.71 (*d*, *J*= 8.3, 2 H, arom.); 7.84 (*d*, 2 H, *J*= 8.3, arom.). $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): 26.7; 35.5; 42.7; 123.8 (t; J_{CD} = 22.1); 128.9; 129.1; 131.6; 131.7; 131.9; 136.1; 136.3; 136.5; 139.3; 139.75; 139.8; 141.0; 152.5; 195.7; 197.9 (J_{CD} vinyl coupling pattern was not assigned). HR-ESI-TOF-MS: 474.1035 ($C_{27}H_{15}D_5Cl_2NaO_2^+$, $[M+Na]^+$; calc. 474.1052). FT-IR (neat): 1427, 1577, 1668, 1732, 2883, 2924, 2966, 3075.

(2*E*)-2-[4-(4-Chlorobenzoyl)-1-methyl(3-^2H)-1,2-dihydronaphthalen-1-yl]-1-(4-chlorophenyl)(3-$^2H_1$)-prop-2-en-1-one ((D_2)**3ac**). Yellow liquid (17.4 mg, 39% yield). ^1H-NMR (300 MHz, $CDCl_3$): 1.80 (*s*, 3 H, Me); 2.48 (*d*, 1 H, *J*= 17.2, alkyl); 3.18 (*d*, 1 H, *J*= 17.5, alkyl); 5.37 (*s*, 1 H, vinyl); 5.39 (*s*, 1 H, vinyl); 6.39 (*s*, 1 H, vinyl); 7.23–7.28 (*m*, 1 H, arom.); 7.35 (*t*, *J*= 8.6, 4 H, arom.); 7.42-7.45 (*m*, 3 H, arom.); 7.71 (*d*, *J*= 8.2, 2 H, arom.); 7.84 (*d*, *J*= 8.1, 2 H, arom.). $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): 26.7; 35.3; 42.7; 124.1 (*t*, J_{CD} = 18.7, vinyl); 126.1; 127.0; 127.5; 128.9; 129.1; 131.6; 131.7; 132.0; 136.3; 136.5; 139.2; 139.75; 139.8; 141.1; 152.5; 195.7; 197.8 (J_{CD} aromatic coupling patterns were not assigned.). HR-ESI-TOF-MS: 471.0873 ($C_{27}H_{15}D_5\ Cl_2NaO_2^+$, $[M+$

Na]$^+$; calc. 471.0864). FT-IR (neat): 1469, 1608, 1656, 1717, 2871, 2917, 2966, 3063.

Synthesis of **4-Bromo-1-methyl-1,2-dihydronaphthalene**

4-Bromo-1-methyl-1,2-dihydronaphthalene was synthesized employing the procedure reported.[51] Yellow liquid (51% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.45 (*d*, *J* = 7.5, 3 H, Me); 2.27–2.37 (*m*, 1 H, alkyl); 2.63–2.72 (*m*, 1 H, alkyl); 3.07–3.19 (*m*, 1 H, alkyl); 6.55 (*t*, *J* = 4.8, 1 H, vinyl); 7.30–7.33 (*m*, 1 H, arom.); 7.40–7.45 (*m*, 2 H, arom.); 7.81–7.84 (*m*, 1 H, arom.). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): 20.3; 32.1; 33.5; 121.1; 126.1; 126.8; 127.0; 128.8; 129.5; 132.3; 141.3.

Synthesis of **(4-Methyl-3,4-dihydronaphthalen-1-yl)(phenyl)methanone** (**4**). To a solution of 4-bromo-1-methyl-1,2-dihydronaphthalene (222 mg, 1 mmol) in dry THF (10 mL) under Ar atmosphere was added butyllithium (0.42 mL, 1.1 mmol, 2.6 M solution in hexane, 1 M = 1 mol dm^{-3}) at −78 °C and the mixture was stirred for 15 min. *N*,*N*-Dimethylbenzamide (194 mg, 1.3 mmol) in THF (5 mL) was added to the solution, and the mixture was warmed up to room temperature. After stirring at that temperature for 1 h, the reaction was quenched with saturated aq. NH_4Cl. The organic layer was separated, and the aqueous layer was extracted Et_2O three times. The combined organic layers were washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography over silica-gel (hexane/AcOEt 10:1) to yield the corresponding compounds. Yellow liquid (109.0 mg, 44% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.36 (*d*, *J* = 6.9, 3 H, Me); 2.30–2.39 (*m*, 1 H, alkyl); 2.64–2.73 (*m*, 1 H, alkyl); 3.03–3.10 (*m*, 1 H, alkyl); 6.46 (*t*, *J* = 4.4, 1 H, vinyl); 7.18–7.32 (*m*, 2 H, arom.); 7.46 (*t*, *J* = 7.3, 2 H, arom.), 7.58 (*t*, *J* = 7.1, 1 H, arom.); 7.91 (*d*, *J* = 7.5, 2 H, arom.). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): 20.5; 31.5; 32.1; 126.3; 126.7; 126.8; 128.5; 130.2; 131.4; 133.1; 135.4; 138.3; 138.7; 140.9. HR-ESI-TOF-MS: 271.1092 ($C_{18}H_{16}NaO^+$, $[M+Na]^+$; calc. 271.1099). FT-IR (neat): 1465, 1660, 1721, 2871, 2927, 2958, 3026, 3063.

Preparation of Chiral Au(I) Complex[20]

To a mixture of (Me_2S)AuCl (28.0 mg, 0.095 mmol) and chiral phosphoramidite (*S*,*R*,*R*)-**L$_7$**[20] (0.10 mmol) was added CH_2Cl_2 (1 mL) under Ar atmosphere at room temperature, and the mixture was stirred for 1 h at that temperature. After evaporation under reduced pressure, the resultant residue was washed with hexane (1 mL) three times and dried *in vacuo*. The residue was purified by silica-gel column chromatography (hexane/AcOEt 100:0 – hexane/AcOEt 5:1) to give the corresponding chiral phosphoramidite-Au(I) complex as colorless solid (99% yield).

(*R*,*R*,*R*)-**L$_7$-AuCl**.[20] Pale yellow solid (99% yield). ^{1}H-NMR (300 MHz, CDCl3): 1.09–1.14 (*s*, 36 H, alkyl); 1.40–1.49 (*m*, 6 H, CH); 2.08 (*s*, 3 H, Me); 2.12 (*s*, 3 H, Me); 7.34–7.46 (*m*, 2 H, arom.); 7.53–7.57 (*m*, 4 H, arom.); 7.60–7.71 (*m*, 8 H, arom.); 8.00–8.04 (*m*, 2 H, arom.); 8.15 (*d*, *J* = 4.2, 2 H, arom.). ^{31}P{^{1}H}-NMR (121 MHz, $CDCl_3$): 125.3 (*s*). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): 19.3; 29.9; 31.65; 31.72; 34.9; 35.0; 55.1; 55.3; 122.78; 122.82; 124.58; 124.64; 125.6; 126.0; 126.2; 126.4; 126.8; 126.9; 127.1; 127.6; 127.7; 128.1; 128.4; 128.5; 129.0; 130.4; 130.7; 131.1; 131.2; 131.8; 132.2; 132.3; 132.38; 132.40; 132.56; 132.58; 133.3; 133.87; 133.90; 134.3; 134.65; 134.70; 140.75; 140.81; 144.9; 145.0; 146.8; 147.0; 151.0; 151.7 (As the coupling patterns could not be determined, all peaks were shown.). HR-ESI-TOF-MS: 1058.3128 ($C_{56}H_{54}AuClNNaO_2P^+$, $[M+Na]^+$; calc. 1058.3144). FT-IR (KBr): 1201, 1393, 1725, 1803, 2868, 2904, 2962, 3030; Anal. calc. for $C_{56}H_{54}AuClNO_2P$: C 64.91, H 5.22, N 1.35; found C 63.99, H 5.32, N 1.29. Optical Rotation: $[\alpha]^{D26} = -250.8$ ($c = 0.33$, $CHCl_3$).

(*S*,*R*,*R*)-**L$_7$-AuCl**. ^{31}P{^{1}H}-NMR (121 MHz, $CDCl_3$): 127.7 (*s*).

Observation of Linear Relationships

A solution of 1-phenylprop-2-yn-1-one (**1a**; 0.1 mmol) in CH_2Cl_2 (0.5 mL) and (but-2-en-2-yl)benzene (**2f**; 0.6 mmol) was added to a solution of (*S*,*R*,*R*)-**L$_7$-AuPF$_6$** (5 mol-%) in CH_2Cl_2 (0.5 mL) at 0 °C. The mixture was stirred at the same temperature for 32 h. The mixture was directly loaded onto a silica-gel short column (hexane/AcOEt 3:1) to remove the catalyst, and then the solution was concentrated under reduced pressure. Purification by silica-gel chromatography (hexane/AcOEt 10:1) gave 2-(4-benzoyl-1,2-dimethyl-1,2-dihydronaphthalen-1-yl)-1-phenylprop-2-en-1-one (**3af**) (28% yield, 44% ee).

Acknowledgements

This work was financially supported by a grant program 'Advanced Catalytic Transformation program for Carbon utilization (ACT–C)' from the Japan Science

and Technology Agency (JST). We thank Profs. *Shigekazu Ito* and *Kohsuke Aikawa* of Tokyo Institute of Technology for valuable discussions.

Author Contribution Statement

M. Nanko, *Y. Inaba*, *K. Sekine*, and *K. Mikami* performed the experiments, analyzed the data and wrote the paper.

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Received October 15, 2020
Accepted December 21, 2020