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Recyclable heterogeneous gold(I)-catalyzed oxidative ring expansion of alkynyl quinols: a practical access to tropone and its analogues†

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The heterogeneous gold(I)-catalyzed oxidative ring expansion of alkynyl quinols has been achieved by using a benzyldiphenylphosphine-modified MCM-41-immobilized gold(I) complex [MCM-41–$BnPh_2P$–$AuNTf_2$] as the catalyst and 8-methylquinoline *N*-oxide as the oxidant under mild reaction conditions, yielding a variety of functionalized tropone derivatives in good to excellent yields. Extension of this methodology allows for facile construction of other seven- or six-membered ring systems including dibenzotropones, dibenzooxepines, phenanthrenes, and quinolin-2(1*H*)-ones. This new heterogeneous gold(I) complex can be readily recovered through a simple filtration process and recycled at least eight times without any apparent decrease in catalytic efficiency.

Introduction

Tropones and tropolones as nonbenzenoid aromatic seven-membered rings are pharmaceutically important structural motifs, and these compounds have attracted considerable interest owing to their structural diversity and their existence in a variety of natural products with a broad spectrum of biological activities.[1] For instance, colchicine containing a tropolone nucleus is used clinically for the treatment of gout and familial Mediterranean fever.[2] The cage-like diterpenoid natural product harringtonolide bearing a tropone nucleus was found to be antineoplastically and antivirally active and to have potent cytotoxic activities.[3] Theaflavic acid from black tea was shown to exhibit significant anti-inflammatory and cytotoxic activities.[4] In addition, tropones are also a class of highly valuable building blocks for the higher order cycloaddition reactions[5] and work as four-, six-, or eight-member synthons to afford [4 + 2],[6] [6 + 3],[7] [6 + 4],[8] [8 + 2],[9] or [8 + 3][10] fused ring products that are very useful in the construction of bioactive compounds and natural products. As a result, many methods have been developed for the construction of tropone and its derivatives,[1e,11] and among those, various cycloaddition reactions such as [3 + 2],[3c] [4 + 2],[12] [4 + 3],[13] and [5 + 2][14] cyclizations are already well represented. Recently, Salacz *et al.* described a rhodium-catalyzed [2 + 2 + 2 + 1] carbonylative cycloaddition of triynes for the synthesis of polyheterocyclic tropones.[15] However, these cycloaddition strategies require multistep synthesis for either the substrates or the desired tropone rings. In addition, ring expansion reactions of six-membered ring compounds through cyclopropanation/ring-expansion sequence also proved to be the most often utilized approach,[1e,16] and have been successfully employed to synthesize tropones and natural products bearing tropolone nucleus.[11f,g] But, these ring-expansion reactions also suffer from multistep synthesis for either the cyclopropanation precursors or the target products, moderate yields, and in some cases, the use of unstable reagents such as diazo-compounds or dihalocarbenes for efficient cyclopropanation. Therefore, the development of more efficient methods for the construction of tropone and its derivatives is highly desirable.

Over the past two decades, organic reactions catalyzed by homogeneous gold complexes have drawn much attention and have been widely applied to the synthesis of a wide range of complex molecules owing to their high efficiencies and relatively milder reaction conditions.[17] Gold carbenes formed through inter- or intramolecular oxygen transfer are usually involved as the key intermediates in many transformations, which often display unique reactivity and selectivity in comparison with that of other transition metals such as Rh, Pd, and Cu.[18] Recently, Liu and coworkers have developed a gold(I)-catalyzed highly regioselective oxidative ring expansion of 2-alkynyl-1,2-dihydro-pyridines and alkynyl quinols towards azepine and tropone derivatives, respectively in high yields by using pyridine or 8-methylquinoline *N*-oxides as oxidants.[19] However, homogeneous gold catalysis suffers from some serious drawbacks such as the high cost, difficulty with separ-

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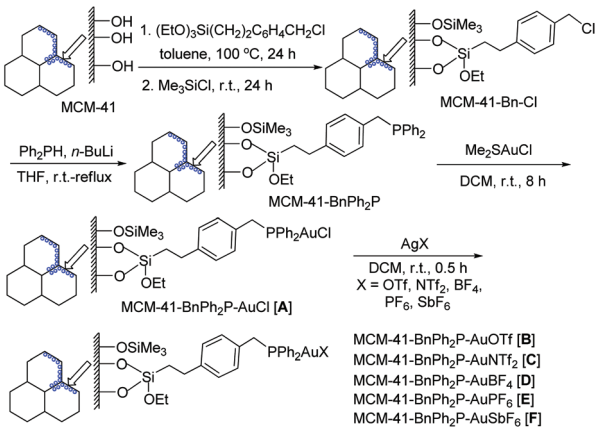
ation, and non-recyclability of gold catalysts as well as the decay of cationic gold, which largely restrict their practical applications in large-scale synthesis or in industry. Anchoring homogeneous gold catalysts through covalent bond formation onto a solid support is one of the possible ways to solve these problems, employment of the supported catalysts in organic reactions could lead to convenient separation, recovery, and recycle of the gold catalysts, thereby preventing contamination of the desired product from gold and minimizing waste derived from reaction workup.[20] The use of nano-sized mesoporous materials with high surface areas as the supports is particularly attractive in this regard.

Mesoporous silica MCM-41 materials have proven to be ideal and powerful supports for anchoring homogeneous catalysts because of their unique properties including high surface areas, high thermal stability, big pore volumes, and homogeneity of the pores compared to other solid supports.[21] Recently, various functionalized MCM-41-anchored gold(I) or gold(III) catalysts have been applied successfully to the construction of carbon–carbon and carbon-heteroatom bonds.[22] In continuation of our efforts to develop highly efficient and recyclable catalytic systems for homogeneous gold-catalyzed organic transformations,[22d–g] herein we report the synthesis of a benzyldiphenylphosphine-modified MCM-41-immobilized gold(I) complex [MCM-41–$BnPh_2P$–$AuNTf_2$] and its catalytic behaviour in highly regio-selective oxidative ring expansion reaction of alkynyl quinols towards functionalized tropone derivatives (Scheme 1). This new heterogeneous gold(I) catalyst exhibits high catalytic activity under mild conditions and can be readily separated from the desired product and recovered through a simple filtration process and recycled at least eight times without any apparent loss of catalytic efficiency.

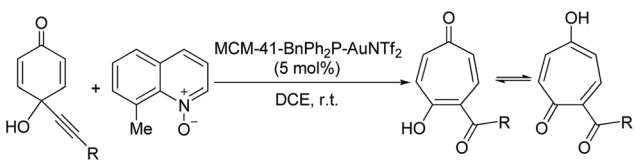
Results and discussion

Several benzyldiphenylphosphine-modified MCM-41-immobilized gold(I) complexes [MCM-41–$BnPh_2P$–AuX, X = Cl, OTf, NTf_2, BF_4, PF_6, and SbF_6] were readily synthesized according to the route depicted in Scheme 2. First, the condensation of mesoporous MCM-41 with commercially available 2-(4-chloromethylphenyl)ethyltriethoxysilane in dry toluene at reflux for 24 h, followed by treating with Me_3SiCl in dry toluene at room temperature provided a 4-chloromethylphenyl-functionalized mesoporous MCM-41 (MCM-41–Bn–Cl). Subsequent reaction of MCM-41–Bn–Cl with Ph_2PLi generated *in situ* from Ph_2PH and *n*-BuLi in THF delivered the benzyldiphenylphosphine-modified MCM-41 (MCM-41–$BnPh_2P$). The latter underwent the coordination reaction with Me_2SAuCl in dichloromethane (DCM) at room temperature to afford MCM-41–$BnPh_2P$–AuCl [**A**]. Finally, MCM-41–$BnPh_2P$–AuCl [**A**] was reacted with different silver salts (AgX = AgOTf, $AgNTf_2$, $AgBF_4$, $AgPF_6$, and $AgSbF_6$) in DCM to give several benzyldiphenylphosphine-modified MCM-41-immobilized gold(I) complexes (MCM-41–$BnPh_2P$–AuX, X = OTf [**B**], NTf_2 [**C**], BF_4 [**D**], PF_6 [**E**], and SbF_6 [**F**]) as gray powders.



Scheme 2 Synthesis of MCM-41–$BnPh_2P$–AuX.

The MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] complex was then fully characterized by using different physico-chemical techniques. Fig. 1 shows low angle X-ray diffraction (XRD) patterns of MCM-41 and MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**]. The XRD pattern of MCM-41 exhibits a strong diffraction peak (100) at 2θ = 2.19 and two additional high order weak diffraction peaks (110 and 200) at 2θ = 3.79 and 4.37, respectively.[21a] The XRD pattern of MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] was similar to that of MCM-41, which indicating that MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] also contains the hexagonally-ordered mesoporous structures.



Scheme 1 Heterogeneous gold(I)-catalyzed oxidative ring expansion reaction of alkynyl quinols.

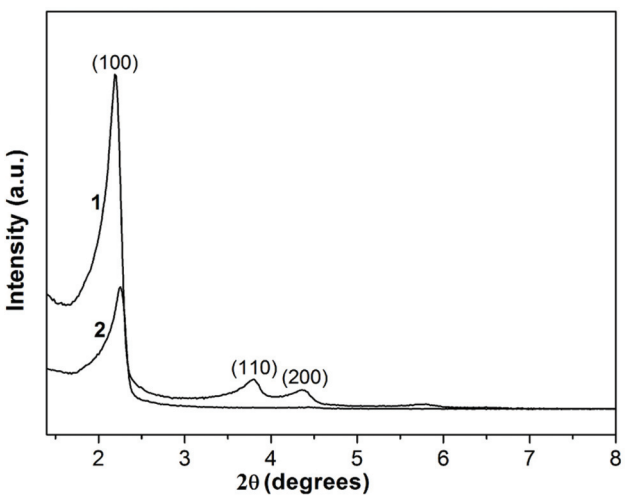


Fig. 1 XRD patterns of MCM-41 (**1**) and MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] (**2**).

However, after anchoring the benzyldiphenylphosphine gold(I) complexes, the (100) diffraction peak intensity of MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] decreased significantly, and the two high order (110) and (200) diffraction peaks disappeared, which showed that the benzyldiphenylphosphine gold(I) complexes were mainly anchored onto the inner walls of mesopore channels. These results indicated that the textural characteristics of MCM-41 were preserved during the supported gold(I) catalyst preparation and the mesopore channels remained accessible.

N_2 adsorption/desorption isotherms are usually used to provide information about the pore structures of mesoporous materials. Fig. 2 presents the N_2 isotherms of MCM-41 and MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] recorded at 77 K. MCM-41 showed a type IV isotherm[21a] (definition by IUPAC), which is a typical character of mesoporous materials with pore diameters between 2 and 50 nm. A rapid increase in the adsorption volume of N_2 between the relative pressures of 0.25 and 0.35 should be attributed to capillary condensation. Compared to the parent MCM-41, MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] exhibits a decreased N_2 uptake due to the incorporation of the benzyldiphenylphosphine gold(I) complexes into the inner channels and the silylation of the modified material with Me_3SiCl.

The BJH pore size distributions of MCM-41 and MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] are shown in Fig. 3. Both pore volume and size of MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] reduced obviously in comparison with the parent MCM-41, also verifying that the organic moieties (benzyldiphenylphosphine gold(I) complexes and Me_3Si groups) were introduced into the inner channels, but a narrow pore size distribution could still be observed for MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**]. After anchoring the benzyldiphenylphosphine gold(I) complexes, the surface area and average pore diameter of MCM-41 decreased from 887 $m^2\ g^{-1}$ and 2.4 nm to 561 $m^2\ g^{-1}$ and 2.0 nm, respectively, further indicating that the hexagonally-ordered mesoporous structures of the parent MCM-41 were preserved during the preparation of MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**].

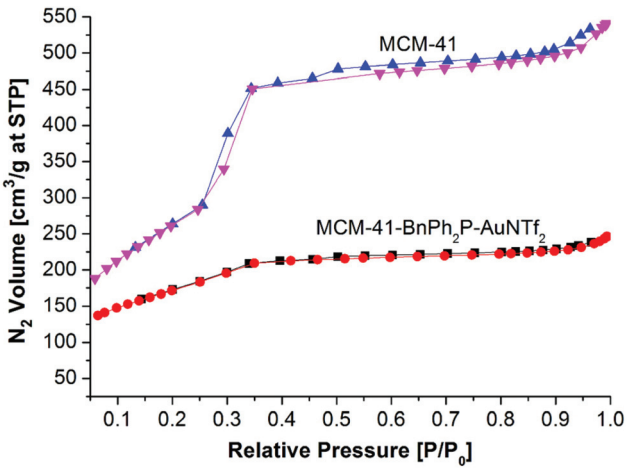


Fig. 2 N_2 adsorption/desorption isotherms of MCM-41 and MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**].

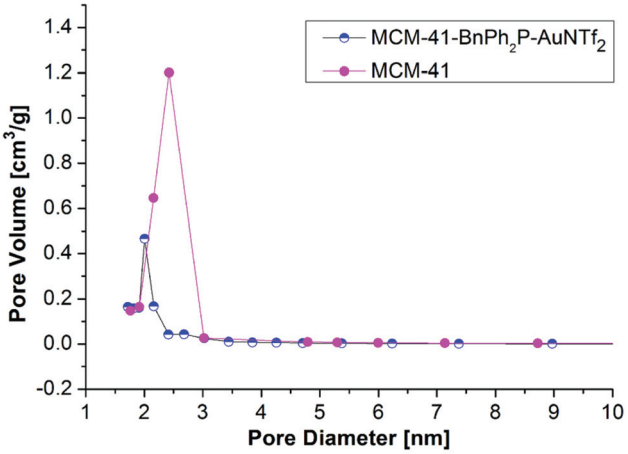


Fig. 3 Pore size distributions of MCM-41 and MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**].

The energy dispersive X-ray spectroscopy (EDS) is usually used to analyze the elemental components of the material. EDS spectrum of MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] indicates the existence of C, N, O, F, Si, P, S and Au elements (Fig. 4). The structure of MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] was further identified by X-ray photoelectron spectroscopy (XPS). The XPS spectrum of MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] (Fig. 5) displays the spin orbit pair at 85.3 eV (Au $4f^{7/2}$) and 89.0 eV (Au $4f^{5/2}$), which revealing that the oxidation state of gold in MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] was Au(I).

The MCM-41–$BnPh_2P$–AuX complexes were then utilized as catalysts for oxidative ring expansion of alkynyl quinols. Initial experiments with 4-hydroxy-4-(phenylethynyl)cyclohexa-2,5-dienone (**1a**) as the substrate were conducted to optimize the reaction conditions including catalysts, *N*-oxides, and solvents. The results are listed in Table 1. First, the effect of several heterogeneous gold(I) catalysts on the model reaction was examined in DCE as solvent with 8-methylquinoline *N*-oxide (**2a**) as the oxidant at room temperature (entries 1–6). As expected, the use of MCM-41–$BnPh_2P$–AuCl [**A**] as catalyst did not give the ring-expanded 4-benzoyl-5-hydroxycyclohepta-2,4,6-trien-1-one (**3a**) and the substrate **1a** was recovered in

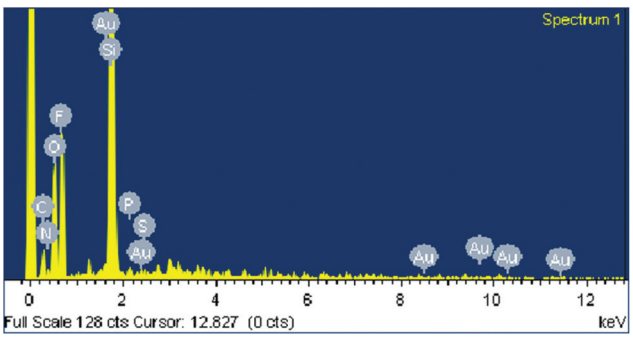


Fig. 4 Energy dispersive spectrum (EDS) of MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**].

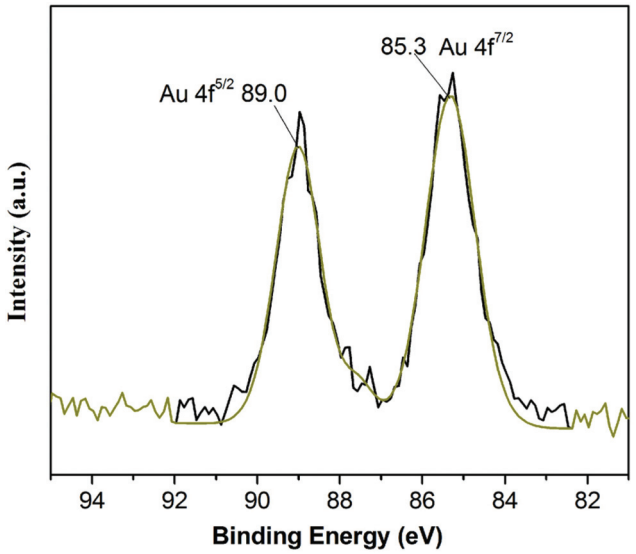
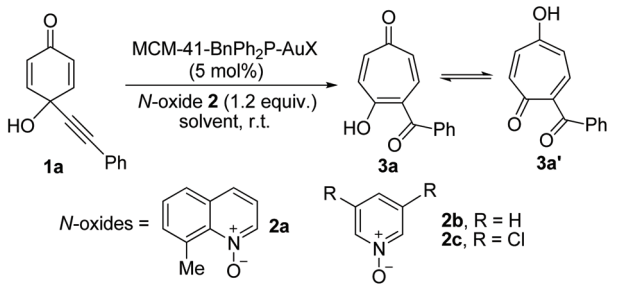


Fig. 5 XPS spectrum of MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**].

Table 1 Optimization of the reaction conditions[a]



Entry	X	*N*-Oxide	Solvent	Time (h)	Yield[b] (%)
1	Cl	**2a**	DCE	24	0
2	OTf	**2a**	DCE	4	82
3	NTf_2	**2a**	DCE	4	91
4	BF_4	**2a**	DCE	4	83
5	PF_6	**2a**	DCE	4	84
6	SbF_6	**2a**	DCE	4	89
7[c]	—	**2a**	DCE	24	0
8	NTf_2	**2b**	DCE	24	69
9	NTf_2	**2c**	DCE	12	43
10	NTf_2	**2a**	Toluene	4	87
11	NTf_2	**2a**	THF	4	79
12	NTf_2	**2a**	DCM	4	84
13[d]	NTf_2	**2a**	DCE	12	65
14[e]	NTf_2	**2a**	DCE	2	92
15[f]	—	**2a**	DCE	4	91
16[g]	—	**2a**	DCE	4	78
17[h]	—	**2a**	DCE	4	86

[a] Reaction conditions: **1a** (0.3 mmol), *N*-oxide (0.36 mmol), solvent (3.0 mL) at room temperature under Ar. [b] Isolated yield. [c] 5 mol% $AgNTf_2$ alone was used as the catalyst. [d] 2 mol% **C** was used. [e] 10 mol% **C** was used. [f] 5 mol% $Ph_3PAuNTf_2$ was used as the catalyst. [g] 5 mol% MCM-41–$EtPh_2P$–$AuNTf_2$ was used as the catalyst. [h] 5 mol% MCM-41–Ph_3P–$AuNTf_2$ was used as the catalyst.

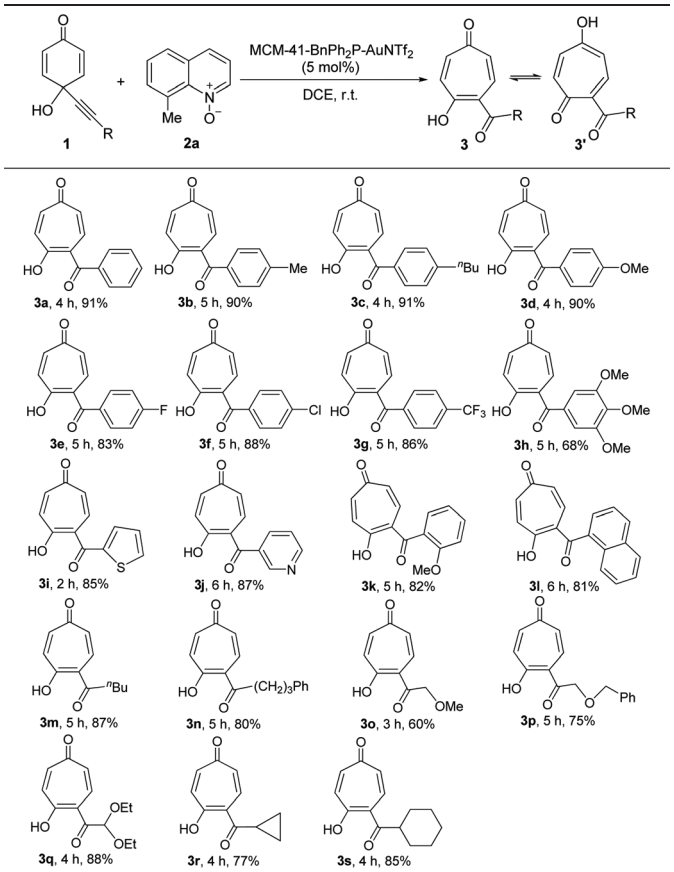
95% yield (entry 1). To our delight, changing the counterion (Cl^-) of the MCM-41–$BnPh_2P$–AuCl [**A**] catalyst to OTf^-, NTf_2^-, BF_4^-, PF_6^-, or SbF_6^- have a very important influence on the reaction.[23] When MCM-41–$BnPh_2P$–AuOTf [**B**], MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**], MCM-41–$BnPh_2P$–$AuBF_4$ [**D**], MCM-41–$BnPh_2P$–$AuPF_6$ [**E**], or MCM-41–$BnPh_2P$–$AuSbF_6$ [**F**] was used as the catalyst, the reaction afforded the desired product **3a** in 82–91% yields and MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] gave the best result (entries 2–6). Control experiment with $AgNTf_2$ alone did not produce the desired product (entry 7), revealing the special catalytic role of gold(I) catalysts in this reaction. Replacement of **2a** with pyridine *N*-oxide (**2b**) or 3,5-dichloropyridine *N*-oxide (**2c**) as the oxidant resulted in a decreased yield of **3a** and a long reaction time was needed (entries 8 and 9). The use of toluene, THF, or DCM as the solvent also produced the desired **3a** in good yields of 79–87% (entries 10–12), but DCE was the best choice (entry 3). Further screening of the catalyst quantities revealed that the use of 5 mol% MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] was the optimal choice. Reducing the amount of the catalyst [**C**] to 2 mol% led to a remarkable decrease in the yield of **3a** and required a long reaction time (entry 13), whilst increasing the amount of the catalyst [**C**] to 10 mol% could enhance the reaction rate significantly, but did not increase the yield of **3a** obviously (entry 14). The use of $Ph_3PAuNTf_2$ (5 mol%) as the catalyst also delivered the desired **3a** in 91% yield (entry 15), which indicating that MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] exhibits a similar catalytic efficiency as homogeneous $Ph_3PAuNTf_2$. Next, we also examined the catalytic behaviour of the other heterogeneous gold catalysts reported previously by us in this transformation. Replacement of MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] with an MCM-41–silyl-bridged ethylPh_2P–$AuNTf_2$ [MCM-41–$EtPh_2P$–$AuNTf_2$][22f,g] resulted in a decreased yield of **3a**, probably due to poorer swelling capacity of the catalytic center in DCE caused by a short carbon linker (entry 16). When an MCM-41–silyl-bridged 4-(3-propylureido) phenylPh_2P–$AuNTf_2$ [MCM-41–Ph_3P–$AuNTf_2$][22d] was used as the catalyst, the desired **3a** was also obtained in a slightly lower yield of 86% (entry 17), but the catalyst preparation required the use of commercially unavailable 4-aminophenyldiphenylphosphine as the starting material. By contrast, MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] exhibited higher catalytic activity than MCM-41–$EtPh_2P$–$AuNTf_2$ or MCM-41–Ph_3P–$AuNTf_2$ in the reaction. Thus, the optimal reaction conditions for this oxidative ring expansion reaction were the use of 5 mol% MCM-41–$BnPh_2P$–$AuNTf_2$ in DCE with 1.2 equiv. of 8-methylquinoline *N*-oxide as oxidant at room temperature under Ar for 4 h (entry 3). As demonstrated in Liu's work,[19b] tropone **3a** in $CDCl_3$ is confirmed to be the dominant formation by HMBC experiments, possibly due to the intramolecular H-bonding. On the other hand, the X-ray crystallographic analysis of **3a** displayed a structure of 2-benzoyl-5-hydroxyltropone (**3a′**), which showed that **3a′** predominates in its solid form, probably due to the intermolecular H-bonding for a better crystal stacking.

Having established the optimal reaction conditions, we next evaluated the substrate scope of this oxidative ring expan-

sion reaction catalyzed by heterogeneous gold(I) catalyst under the reaction conditions shown in Table 1, entry 3 and the results are given in Table 2. As seen from Table 2, this oxidative ring expansion reaction was found to be quite general for a wide variety of diversely substituted aromatic alkynes and aliphatic alkynes, and the desired tropone derivatives **3a–3s** were obtained in mostly good to excellent yields. In the case of aromatic alkynes, various functional groups such as methyl, butyl, methoxy, fluoro, chloro, and trifluoromethyl on the benzene ring were well tolerated during the reaction. For example, both electron-rich (*p*-Me, *p*-Bu, *p*-MeO, 3,4,5-tri (MeO)) and electron-deficient (*p*-F, *p*-Cl, *p*-CF_3) aromatic alkynes underwent oxidative ring-expansion reaction smoothly under mild conditions to afford the desired tropone derivatives **3b–3h** in 68–91% yields, which indicating that the electronic nature of the aryl substituents on the alkyne terminus had limited influence on the ring expansion reaction of alkynyl quinols catalyzed by heterogeneous gold(I). Heteroaryl-substituted alkynes such as thienyl- or pyridinyl-substituted ones were suitable for this reaction, furnishing the expected products **3i–3j** in high yields of 85–87%. Notably, sterically hindered 2-methoxyphenyl and bulky 1-naphthyl groups were also compatible with the optimized conditions and the corresponding products **3k** and **3l** were obtained in good yields. The ring expansion reaction also proceeded effectively with aliphatic alkynes. For instance, alkynyl quinols **1m** and **1n** bearing a linear alkyl group such as butyl or phenylpropyl on the alkyne terminus gave the target products **3m** and **3n** in 87 and 80% yields, respectively. In addition, aliphatic alkynes with a methyl- or benzyl-protected alcohol moiety **1o** and **1p** could be transformed into the corresponding products **3o** and **3p** in 60–75% yields. Interestingly, an alkyne bearing an acetal group also reacted well in this transformation, giving the expected **3q** in 88% yield. A cycloalkyl group such as cyclopropyl- or cyclohexyl-substituted alkynes were also compatible in this ring expansion reaction, affording the desired **3r** and **3s** in 77 and 85% yields, respectively.

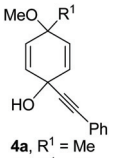
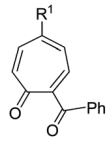
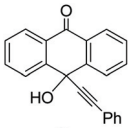
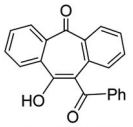
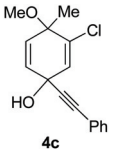
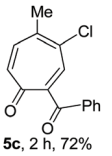
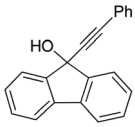
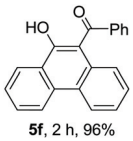
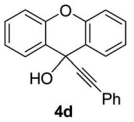
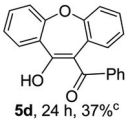
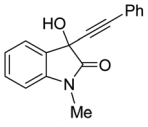
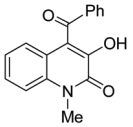
Encouraged by the above results, we next extended the scope of this ring expansion reaction to various appropriate cyclic compounds having a propargyl alcohol moiety for the synthesis of novel carbo- or heterocycles with one-carbon ring expansion. The representative results are summarized in Table 3. We were pleased to observe that the ring expansion reaction of alkynyl quinol derivatives **4a** and **4b** bearing a methoxy group at the C-4 position proceeded effectively under the optimized conditions to furnish the desired tropones **5a** and **5b** in 85 and 88% yields, respectively. Both alkyl and aryl groups as R^1 substituents were compatible in this reaction. The results also showed that the reaction involved a gold-assisted elimination of methoxy group during the ring expansion process. In the case of alkynyl quinol derivative **4c** having a chlorine substituent, 2-benzoyl-4-chloro-5-methylcyclohepta-

Table 2 Heterogeneous gold(I)-catalyzed ring expansion of alkynyl quinols toward tropone derivatives[a,b]



[a] Reaction conditions: **1** (0.3 mmol), **2a** (0.36 mmol), MCM-41–$BnPh_2P$–$AuNTf_2$ (5 mol%), DCE (3 mL) at room temperature under Ar. [b] Isolated yield.

Table 3 Heterogeneous gold(I)-catalyzed ring expansion of various carbo- or heterocycles[a,b]

Substrate	Product	Substrate	Product
 **4a**, R^1 = Me **4b**, R^1 = Ph	 **5a**, 1 h, 85% **5b**, 2 h, 88%	 **4e**	 **5e**, 5 h, 94%[c]
 **4c**	 **5c**, 2 h, 72%	 **4f**	 **5f**, 2 h, 96%
 **4d**	 **5d**, 24 h, 37%[c]	 **4g**	 **5g**, 2 h, 81%

[a] Reaction conditions: **4** (0.3 mmol), **2a** (0.36 mmol), MCM-41–$BnPh_2P$–$AuNTf_2$ (5 mol%), DCE (3 mL) at room temperature under Ar. [b] Isolated yield. [c] Pyridine *N*-oxide (0.36 mmol) was used.

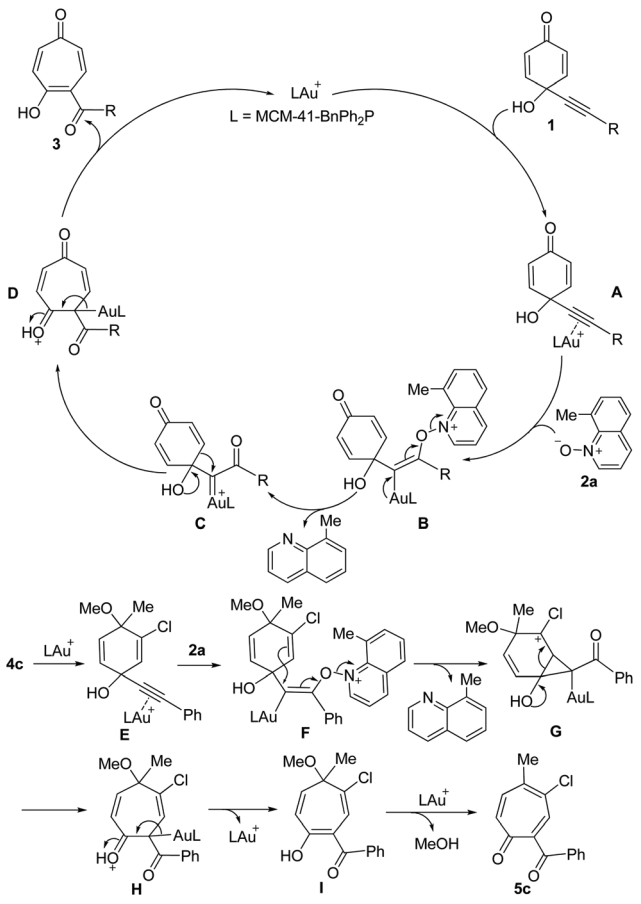
2,4,6-trienone (**5c**) was obtained exclusively in 72% yield, which reveals that the attack of the double bond bearing a chlorine substituent on the vinylgold moiety in intermediate **F** occurred preferentially since chlorine can stabilize the cation intermediate **G** better (Scheme 3). Ring expansion of substrate **4d** derived from 9*H*-xanthen-9-one with pyridine *N*-oxide as the oxidant was also observed, but the desired benzooxepine **5d** was obtained in a low yield of 37%. Substrate **4e** derived from anthracene-9,10-dione underwent the ring expansion reaction smoothly in the presence of pyridine *N*-oxide as the oxidant to afford dibenzotropone **5e** in 94% yield. Ring expansion reaction of substrate **4f** derived from 9-fluorenone proceeded quite effectively to give 9-hydroxyphenanthrene **5f** in excellent yield of 96%. Notably, substrate **4g** derived from isatin proved to be also suitable for this transformation and could undergo a highly selective 1,2-phenyl migration to yield exclusively 3-hydroxyquinolin-2(1*H*)-one derivative **5g** in 81% yield. 3-Hydroxyquinolinone and its derivatives are important structural units presented in many natural products and a wide variety of bioactive molecules.[24] They are usually prepared *via* aldol-type condensation of ethyl diazoacetate with isatin and subsequent Lewis acid-mediated ring expansion.[25] The present method offers potential advantages such as the elimination of the hazardous diazo compounds, mild conditions and good yields. As seen from Table 3, the developed methodology can provide a novel, general, efficient and practical route for the construction of various types of carbo- or heterocycles, particularly for medium-sized ring systems that are difficult to obtain.

To verify whether the observed reaction resulted from the supported gold catalyst MCM-41–$BnPh_2P$–$AuNTf_2$ or a gold species leached from the catalyst in solution, we performed the ring expansion reaction of 4-hydroxy-4-(phenylethynyl) cyclohexa-2,5-dienone (**1a**), and the gold catalyst was then filtered off from the reaction mixture at about 50% conversion of **1a**. The catalyst-free filtrate was again stirred at room temperature under argon for 4 h. In this case, further increase in conversion of **1a** was not observed, which revealing that leached gold species from the MCM-41–$BnPh_2P$–$AuNTf_2$ catalyst (if any) should not be responsible for the observed catalysis. It was also identified based on ICP-AES analysis that the filtrate did not contain any gold species (below the detection limit). The above results demonstrated that the real catalytic species should be MCM-41–$BnPh_2P$–$AuNTf_2$ and not the leached gold species in the solution, thereby supporting the heterogeneous nature of the reaction.

A possible mechanism[19b,26] for this oxidative ring expansion reaction of alkynyl quinols under the heterogeneous gold (I) catalysis is illustrated in Scheme 3. First, coordination of the MCM-41–$BnPh_2P$–$AuNTf_2$ complex to the alkyne moiety in alkynyl quinol **1** occurs to provide an MCM-41-bound $BnPh_2P$–Au alkyne complex **A**. The latter reacts with 8-methylquinoline *N*-oxide (**2a**) to form an MCM-41-bound vinylgold intermediate **B**, which undergoes an elimination reaction to generate an MCM-41-bound α-carbonyl gold carbenoid intermediate **C**. Subsequently, intermediate **C** undergoes 1,2-migration of the alkenyl moiety (pinacol type) to produce intermediate **D**. Finally, the deauration of intermediate **D** affords the tropone derivative **3** and regenerates the MCM-41–$BnPh_2P$–$AuNTf_2$ complex to complete the catalytic cycle.

However, in the case of the reactants lacking a carbonyl group such as **4a–d**, **4f** and **4g**, the reaction may proceed through an alternative pathway, which involving the formation of a cyclopropylcarbinyl cation intermediate. For example, coordination of MCM-41–$BnPh_2P$–$AuNTf_2$ to the alkyne moiety in **4c** provides an MCM-41-bound $BnPh_2P$–Au alkyne complex **E**, which reacts with **2a** to give intermediate **F**. Then a cyclopropylcarbinyl cation intermediate **G** might be generated through attack of the double bond bearing a chlorine substituent on the vinylgold moiety in intermediate **F**. Intermediate **G** undergoes the ring-opening reaction and subsequent deauration to give intermediate **I**. Finally, a gold-assisted elimination of methoxy group in intermediate **I** occurs to afford the desired **5c**.[19b]

As gold catalysts are quite expensive, from the viewpoints of both economy and environment, the recovery and reusability of supported gold catalysts are significant factors that need to be examined for their practical applications. The MCM-41–$BnPh_2P$–$AuNTf_2$ catalyst can be readily separated from the product and recovered through a simple filtration process. We next evaluated the recycle efficiency of the MCM-41–$BnPh_2P$–



Scheme 3 Proposed catalytic cycle.

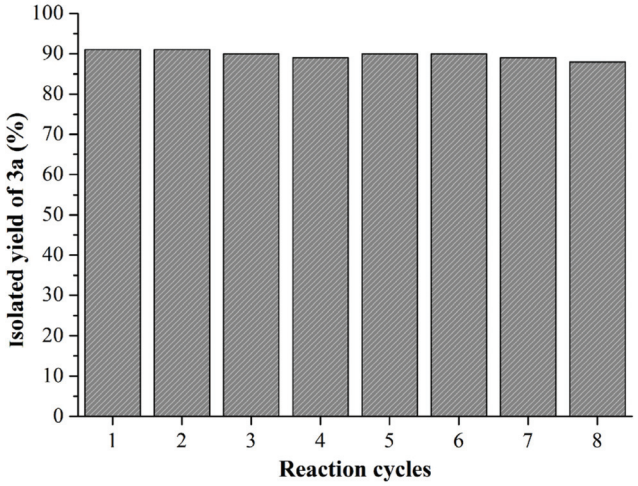


Fig. 6 Recycle of MCM-41–$BnPh_2P$–$AuNTf_2$.

$AuNTf_2$ catalyst in the ring expansion reaction of 4-hydroxy-4-(phenylethynyl)cyclohexa-2,5-dienone (**1a**) under the standard conditions and the results are presented in Fig. 6. After the first reaction cycle was completed, the gold catalyst was recovered by simple filtration of the reaction mixture, followed by washing with DCE and acetone, and dried at 70 °C *in vacuo* for 2 h. In the recycling experiments, the recovered gold catalyst was recharged with fresh substrate **1a** for the next reaction cycle under the identical conditions. It was found that the supported gold(I) catalyst still remained highly active even after being recycled eight times and the yield of the desired **3a** was over 88% in eight consecutive cycles. Besides, the gold content of the MCM-41–$BnPh_2P$–$AuNTf_2$ catalyst after recycling eight times was measured to be 0.32 mmol g^{-1} based on ICP-AES analysis, thus, the gold leaching appeared to be negligible compared with the fresh catalyst with gold content of 0.33 mmol g^{-1}.

Conclusion

In summary, we have successfully developed a novel, convenient and practical route for the construction of functionalized tropone derivatives through a heterogeneous gold(I)-catalyzed oxidative ring expansion of alkynyl quinols by using a benzyldiphenylphosphine-modified MCM-41-immobilized gold(I) complex [MCM-41–$BnPh_2P$–$AuNTf_2$] as the catalyst and 8-methylquinoline *N*-oxide as the oxidant. The reaction proceeds smoothly *via* a heterogeneous gold(I)-catalyzed regioselective oxidation of alkynes, followed by the 1,2-migration of an alkenyl moiety under mild conditions, generating a variety of tropone derivatives in mostly good to excellent yields. Extension of this methodology allows for facile construction of other seven- or six-membered ring compounds such as dibenzotropones, dibenzooxepines, phenanthrenes, and quinolin-2(1*H*)-ones. Furthermore, this new supported gold(I) catalyst can be readily prepared from commercially easily available materials, and reused at least seven times without any apparent decrease in catalytic efficiency. Therefore, the current method provides a general, efficient and practical procedure for the synthesis of functionalized tropone derivatives and various types of seven- or six-membered carbo- or heterocycles.

Experimental

General comments

All starting matrials and mesoporous MCM-41 were purchased from different commercial suppliers and used without further purification prior to use. Alkynyl quinols **1a–1s** and substrates **4a–4g** were prepared according to a literature procedure.[19b] Dichloroethane (DCE) and dichloromethane (DCM) were dried over P_2O_5 and distilled before use. Toluene and THF were dried over sodium and distilled. All reactions were performed under an atmosphere of argon in oven-dried glassware. The products were purified by column chromatography on silica gel. Mixture of petroleum ether, EtOAc and DCM was generally used as eluent. All products were characterized by comparison of their spectra and physical data with authentic samples. ^1H and ^{13}C NMR spectra were recorded at 400 or 100 MHz with $CDCl_3$ or C_6D_6 as the solvent and TMS as an internal standard. Chemical shifts are given as δ values relative to TMS. HRMS spectra were recorded on a Q-T of spectrometer with micromass MS software using electrospray ionization (ESI). Melting points are uncorrected. Gold contents of the catalysts were measured by ICP-AES analysis.

Preparation of MCM-41–$BnPh_2P$–$AuNTf_2$ [C]

A mixture of 2-(4-chloromethylphenyl)ethyltriethoxysilane (0.476 g, 1.5 mmol) and mesoporous MCM-41 (2.0 g) in dry toluene (120 mL) was stirred at reflux for 24 h under an atmosphere of argon. The resulting product was filtered, washed with toluene (30 mL), and dried at 140 °C *in vacuo* for 4 h. The powdery solid obtained was then stirred with a solution of Me_3SiCl (3.5 g) in dry toluene (100 mL) at room temperature for 24 h. The powdery solid was filtered, washed with toluene (30 mL), acetone (2 × 30 mL), and dried at 110 °C *in vacuo* for 2 h to furnish 2.312 g of the 4-chloromethylphenyl-functionalized mesoporous MCM-41 (MCM-41–Bn–Cl) with chlorine content of 0.43 mmol g^{-1} based on elemental analysis.

To a solution of diphenylphosphine (0.224 g, 1.2 mmol) in dry THF (50 mL) was added *n*-BuLi (2.5 M in hexane, 0.48 mL, 1.2 mmol) at room temperature under argon. After stirring for 1 h at the same temperature, MCM-41–Bn–Cl (2.0 g) was added and the resulting mixture was stirred at reflux for 24 h. The product was filtered, washed by THF (20 mL), distilled water (2 × 20 mL), and acetone (2 × 20 mL), and dried under vacuum at 80 °C for 5 h to give 2.123 g of the benzyldiphenylphosphine-modified MCM-41 (MCM-41–$BnPh_2P$) with phosphorus content of 0.38 mmol g^{-1} based on elemental analysis.

A mixture of MCM-41–$BnPh_2P$ (1.10 g) and Me_2SAuCl (112 mg, 0.38 mmol) in dry CH_2Cl_2 (35 mL) was stirred under argon at room temperature for 8 h to generate MCM-41–

$BnPh_2P$–AuCl [**A**]. Then MCM-41–$BnPh_2P$–AuCl [**A**] was stirred with $AgNTf_2$ (153 mg, 0.39 mmol) at room temperature for 0.5 h. The resulting product was filtered, followed by washing with 25 wt% $NH_3{\cdot}H_2O$ (2 × 20 mL), deionized water (20 mL), and acetone (2 × 20 mL) and dried at 70 °C *in vacuo* to afford 1.137 g of MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] as the gray powdery solid with gold content of 0.33 mmol g^{-1} based on ICP-AES analysis.

Similarly, MCM-41–$BnPh_2P$–AuOTf [**B**], MCM-41–$BnPh_2P$–$AuBF_4$ [**D**], MCM-41–$BnPh_2P$–$AuPF_6$ [**E**] and MCM-41–$BnPh_2P$–$AuSbF_6$ [**F**] were also prepared by using MCM-41–$BnPh_2P$ (1.10 g), Me_2SAuCl (0.38 mmol), and various silver salts (0.39 mmol) as the starting materials. The gold contents were measured to be 0.35 mmol g^{-1}, 0.32 mmol g^{-1}, 0.31 mmol g^{-1}, and 0.34 mmol g^{-1} based on ICP-AES analysis, respectively.

General procedure for the heterogeneous gold(I)-catalyzed oxidative ring expansion reaction of alkynyl quinols and various carbo- or heterocycles

To a solution of substrate **1** or **4** (0.3 mmol) and 8-methylquinoline *N*-oxide **2a** (57 mg, 0.36 mmol) in DCE (3 mL) was added MCM-41–$BnPh_2P$–$AuNTf_2$ [**C**] (45 mg, 0.015 mmol) under an atmosphere of argon. After stirring at room temperature for 1–24 h (monitored by TLC), the reaction mixture was diluted with DCE (3 mL) and filtered. The gold(I) catalyst was washed with DCE (2 × 3 mL), acetone (2 × 3 mL) and dried at 70 °C *in vacuo* for 2 h, and reused in the next cycle. In the case of substrates **1a–1s** and **4g**, the filtrate was then quenched with 0.5 M NaOH solution (5 mL) and the water phase was washed with dichloromethane. Then 1.0 M HCl solution (5 mL) was added to the water phase to produce a large amount of yellow solid. Then dichloromethane was added to dissolve the precipitate, and the resulting mixture was extracted with dichloromethane, washed with water until the pH = 7, and dried over anhydrous $MgSO_4$. After evaporating the solvent under the reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether : ethyl acetate : dichloromethane = 10 : 1 : 1 to 2 : 1 : 1) to afford the desired products **3a–3s** or **5g**. In the case of substrates **4a–4f**, the filtrate was directly concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1 to 5 : 1) to afford the desired products **5a–5f**.

4-Benzoyl-5-hydroxycyclohepta-2,4,6-trien-1-one 3a. Yellow solid, m.p. 174–176 °C (ref. 19*b* m.p. 175–177 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 15.85 (s, 1H), 7.64–7.58 (m, 3H), 7.53 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 12.8 Hz, 1H), 7.22–7.13 (m, 2H), 6.50 (dd, J = 12.8, 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.6, 186.0, 174.9, 145.8, 137.5, 137.2, 135.3, 132.5, 129.0, 128.9, 128.8, 115.8.

4-Hydroxy-5-(4-methylbenzoyl)cyclohepta-2,4,6-trien-1-one 3b. Yellow solid, m.p. 176–178 °C (ref. 19*b* m.p. 175–177 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 15.83 (brs, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 12.8 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.22–7.13 (m, 2H), 6.51 (dd, J = 12.8, 2.4 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.2, 185.9, 174.8, 145.5, 143.6, 137.8, 135.5, 134.3, 129.4, 129.2, 128.6, 116.1, 21.7.

4-(4-Butylbenzoyl)-5-hydroxycyclohepta-2,4,6-trien-1-one 3c. Yellow solid, m.p. 153–155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 15.80 (brs, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 12.8 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.20–7.11 (m, 2H), 6.51 (dd, J = 12.8, 2.0 Hz, 1H), 2.71 (t, J = 7.8 Hz, 2H), 1.68–1.62 (m, 2H), 1.43–1.35 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.3, 185.9, 174.7, 148.6, 145.6, 137.7, 135.4, 134.5, 129.3, 128.8, 128.5, 116.1, 35.7, 33.2, 22.4, 13.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O_3$, 283.1334; found, 283.1336.

4-Hydroxy-5-(4-methoxybenzoyl)cyclohepta-2,4,6-trien-1-one 3d. Yellow solid, m.p. 186–188 °C (ref. 19*b* m.p. 185–187 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 15.73 (brs, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 12.8 Hz, 1H), 7.21–7.14 (m, 2H), 7.01 (d, J = 8.4 Hz, 2H), 6.53 (dd, J = 13.0, 2.2 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.9, 186.1, 174.3, 163.5, 145.5, 137.7, 135.4, 131.8, 129.4, 128.8, 115.8, 114.1, 55.6.

4-(4-Fluorobenzoyl)-5-hydroxycyclohepta-2,4,6-trien-1-one 3e. Yellow solid, m.p. 195–197 °C (ref. 19*b* m.p. 196–198 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 15.68 (s, 1H), 7.65 (dd, J = 8.0, 5.6 Hz, 2H), 7.32 (d, J = 13.2 Hz, 1H), 7.26–7.16 (m, 4H), 6.52 (d, J = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.0, 185.9, 174.8, 165.3 (d, J = 253.9 Hz), 145.9, 137.1, 135.2, 133.3 (d, J = 3.2 Hz), 131.7 (d, J = 9.0 Hz), 129.1, 116.1 (d, J = 21.9 Hz), 115.6.

4-(4-Chlorobenzoyl)-5-hydroxycyclohepta-2,4,6-trien-1-one 3f. Yellow solid, m.p. 216–218 °C (ref. 19*b* m.p. 215–217 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 15.70 (brs, 1H), 7.56 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 12.8 Hz, 1H), 7.22–7.13 (m, 2H), 6.51 (d, J = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.2, 185.8, 175.0, 145.9, 139.1, 137.0, 135.4, 135.3, 130.4, 129.2, 129.0, 116.2.

4-Hydroxy-5-(4-(trifluoromethyl)benzoyl)cyclohepta-2,4,6-trien-1-one 3g. Yellow solid, m.p. 212–214 °C (ref. 19*b* m.p. 213–215 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 15.73 (s, 1H), 7.81 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.24–7.14 (m, 3H), 6.50 (dd, J = 13.0, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.4, 185.8, 175.4, 146.3, 140.4, 136.5, 135.0, 133.9 (q, J = 32.9 Hz), 129.4, 129.0, 125.9 (q, J = 3.7 Hz), 123.4 (q, J = 271.2 Hz), 115.4.

4-Hydroxy-5-(3,4,5-trimethoxybenzoyl)cyclohepta-2,4,6-trien-1-one (3h). Yellow solid, m.p. 224–226 °C (ref. 19*b* m.p. 223–225 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 15.63 (brs, 1H), 7.44 (d, J = 12.8 Hz, 1H), 7.20–7.13 (m, 2H), 6.84 (s, 2H), 6.54 (dd, J = 13.0, 2.2 Hz, 1H), 3.95 (s, 3H), 3.90 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.5, 186.1, 174.5, 153.2, 145.7, 142.0, 137.6, 135.3, 131.9, 128.8, 115.8, 106.7, 61.1, 56.4.

4-Hydroxy-5-(thiophene-2-carbonyl)cyclohepta-2,4,6-trien-1-one 3i. Yellow solid, m.p. 157–159 °C (ref. 19*b* m.p. 158–160 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 15.25 (brs, 1H), 7.81 (dd, J = 4.8, 0.8 Hz, 1H), 7.73 (d, J = 12.8 Hz, 1H), 7.66 (dd, J = 3.6, 0.8 Hz, 1H), 7.24–7.20 (m, 1H), 7.18–7.13 (m, 2H), 6.63 (dd, J = 13.2, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.9, 186.0, 173.6, 145.4, 141.3, 136.5, 135.2, 134.9, 129.4, 128.3, 115.6.

4-Hydroxy-5-nicotinoylcyclohepta-2,4,6-trien-1-one 3j. Yellow solid, m.p. 236–238 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 15.79 (brs, 1H), 8.87–8.83 (m, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.50 (dd, J = 7.6, 4.8 Hz, 1H), 7.27 (d, J = 12.8 Hz, 1H), 7.21–7.16 (m, 2H), 6.53 (dd, J = 12.8, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.2, 186.1, 175.5, 152.9, 149.4, 146.2, 136.4, 135.1, 133.2, 129.3, 123.5, 115.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{10}NO_3$, 228.0661; found, 228.0664.

4-Hydroxy-5-(2-methoxybenzoyl)cyclohepta-2,4,6-trien-1-one 3k. Yellow solid, m.p. 129–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 15.95 (s, 1H), 7.48–7.42 (m, 1H), 7.25 (dd, J = 7.4, 1.4 Hz, 1H), 7.09–6.99 (m, 4H), 6.93 (d, J = 8.4 Hz, 1H), 6.37 (dd, J = 12.8, 2.4 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.1, 186.0, 174.2, 156.1, 145.7, 138.2, 135.4, 132.9, 129.0, 128.9, 126.9, 121.2, 117.3, 111.4, 55.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{13}O_4$, 257.0814; found, 257.0819.

4-(1-Naphthoyl)-5-hydroxycyclohepta-2,4,6-trien-1-one 3l. Yellow solid, m.p. 228–229 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 16.37 (s, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.97–7.94 (m, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.62–7.48 (m, 4H), 7.24 (d, J = 13.2 Hz, 1H), 7.16 (dd, J = 13.2, 2.4 Hz, 1H), 7.07 (d, J = 12.8 Hz, 1H), 6.32 (dd, J = 13.0, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.8, 186.0, 175.5, 146.2, 137.5, 135.4, 134.9, 133.5, 131.5, 129.7, 129.2, 128.8, 127.8, 127.0, 126.1, 124.7, 117.2, 116.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}O_3$, 277.0865; found, 277.0867.

4-Hydroxy-5-pentanoylcyclohepta-2,4,6-trien-1-one 3m. Yellow oil.[19b] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 16.23 (s, 1H), 7.41 (d, J = 12.8 Hz, 1H), 6.98–6.91 (m, 2H), 6.48 (dd, J = 13.0, 2.2 Hz, 1H), 2.86 (t, J = 7.4 Hz, 2H), 1.65–1.57 (m, 2H), 1.36–1.28 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.9, 185.8, 174.0, 145.0, 135.6, 134.6, 129.5, 115.8, 39.1, 26.5, 22.2, 13.7.

4-Hydroxy-5-(4-phenylbutanoyl)cyclohepta-2,4,6-trien-1-one 3n. Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 16.29 (s, 1H), 7.38–7.31 (m, 3H), 7.26–7.21 (m, 3H), 7.10 (s, 2H), 6.57 (d, J = 13.2 Hz, 1H), 2.94 (t, J = 7.4 Hz, 2H), 2.76 (t, J = 7.4 Hz, 2H), 2.15–2.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.5, 186.0, 174.1, 145.2, 140.9, 135.7, 134.5, 129.6, 128.6, 128.5, 126.3, 115.9, 38.5, 34.9, 25.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}O_3$, 269.1178; found, 269.1177.

4-Hydroxy-5-(2-methoxyacetyl)cyclohepta-2,4,6-trien-1-one 3o. Yellow oil.[19b] ^{1}H NMR (400 MHz, C_6D_6): δ = 15.93 (s, 1H), 6.68 (d, J = 13.2 Hz, 1H), 6.45–6.37 (m, 3H), 3.71 (s, 2H), 3.01 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6): δ = 202.9, 185.0, 173.8, 145.3, 134.0, 132.0, 129.8, 114.1, 74.3, 58.6.

4-(2-(Benzyloxy)acetyl)-5-hydroxycyclohepta-2,4,6-trien-1-one 3p. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 15.70 (brs, 1H), 7.38–7.31 (m, 5H), 7.29 (d, J = 13.2 Hz, 1H), 7.09 (s, 2H), 6.56 (d, J = 12.8 Hz, 1H), 4.67 (s, 2H), 4.63 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.9, 186.1, 174.3, 145.6, 136.5, 135.5, 133.7, 130.0, 128.7, 128.4, 128.2, 116.2, 73.8, 72.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{15}O_4$, 271.0970; found, 271.0967.

4-(2,2-Diethoxyacetyl)-5-hydroxycyclohepta-2,4,6-trien-1-one 3q. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 15.49 (s, 1H), 8.01 (d, J = 13.2 Hz, 1H), 7.13–7.06 (m, 2H), 6.60 (dd, J = 13.0, 1.0 Hz, 1H), 5.10 (s, 1H), 3.87–3.78 (m, 2H), 3.69–3.60 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.5, 186.4, 175.6, 145.8, 135.6, 135.1, 129.5, 114.2, 104.7, 64.7, 15.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{17}O_5$, 253.1076; found, 253.1072.

4-(Cyclopropanecarbonyl)-5-hydroxycyclohepta-2,4,6-trien-1-one 3r. Yellow oil.[19b] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 16.30 (s, 1H), 7.78 (d, J = 12.8 Hz, 1H), 7.12–7.06 (m, 2H), 6.64 (d, J = 12.8 Hz, 1H), 2.58–2.51 (m, 1H), 1.39–1.33 (m, 2H), 1.24–1.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.6, 186.0, 173.5, 145.0, 135.8, 135.0, 129.6, 116.7, 17.8, 13.3.

4-(Cyclohexanecarbonyl)-5-hydroxycyclohepta-2,4,6-trien-1-one 3s. Yellow solid, m.p. 89–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 16.55 (s, 1H), 7.45 (d, J = 12.8 Hz, 1H), 7.07–6.99 (m, 2H), 6.56 (dd, J = 12.8, 2.0 Hz, 1H), 3.15–3.09 (m, 1H), 1.86–1.71 (m, 5H), 1.53–1.28 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.9, 186.1, 175.1, 145.1, 136.0, 134.4, 129.5, 114.9, 45.9, 29.5, 25.7, 25.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{17}O_3$, 233.1178; found, 233.1179.

2-Benzoyl-5-methylcyclohepta-2,4,6-trienone 5a. Yellow solid, m.p. 74–75 °C (ref. 19*b* m.p. 75–76 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, J = 7.6 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.18 (d, J = 8.8 Hz, 1H), 7.12 (dd, J = 12.4, 1.6 Hz, 1H), 7.04 (d, J = 12.4 Hz, 1H), 6.93 (d, J = 9.2 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.4, 185.4, 148.9, 148.1, 142.1, 140.0, 135.9, 135.7, 133.4, 132.0, 129.3, 128.6, 26.5.

2-Benzoyl-5-phenylcyclohepta-2,4,6-trien-1-one 5b. Yellow solid, m.p. 131–132 °C (ref. 19*b* m.p. 130–132 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.87 (m, 2H), 7.58–7.40 (m, 10H), 7.27–7.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.2, 185.2, 149.9, 149.6, 142.9, 141.4, 138.2, 135.9, 135.6, 133.6, 131.9, 129.4, 129.3, 129.2, 128.7, 127.5.

2-Benzoyl-4-chloro-5-methylcyclohepta-2,4,6-trienone 5c. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.82 (m, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.47–7.41 (m, 3H), 7.20 (d, J = 12.8 Hz, 1H), 6.99 (d, J = 12.8 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.9, 183.9, 147.3, 143.6, 139.8, 139.5, 138.6, 138.3, 135.4, 133.8, 129.4, 128.7, 26.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{12}ClO_2$, 259.0526; found, 259.0525.

(11-Hydroxydibenzo[*b*,*f*]oxepin-10-yl)(phenyl)methanone 5d. Yellow solid, m.p. 169–171 °C (ref. 19*b* m.p. 170–172 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (dd, J = 8.0, 1.6 Hz, 1H), 7.54–7.45 (m, 3H), 7.37 (t, J = 7.4 Hz, 1H), 7.31–7.22 (m, 5H), 7.14–7.09 (m, 1H), 6.77–6.73 (m, 1H), 6.65 (dd, J = 7.8, 1.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 178.8, 161.2, 158.2, 137.4, 134.2, 132.9, 131.4, 130.4, 129.8, 128.8, 128.2, 128.1, 127.9, 125.3, 124.6, 120.9, 120.8, 111.4.

10-Benzoyl-11-hydroxy-10,11-dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-one 5e. Yellow solid, m.p. 125–127 °C (ref. 19*b* m.p. 126–128 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 16.75 (s, 1H), 8.26–8.23 (m, 1H), 7.79–7.76 (m, 1H), 7.70–7.62 (m, 3H), 7.34–7.28 (m, 3H), 7.26–7.18 (m, 3H), 7.01 (t, J = 7.0 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 197.1, 174.9, 142.4, 141.5, 138.1, 132.7, 132.5, 132.2, 131.9, 131.7, 131.5, 129.7, 129.6, 129.5, 128.0, 127.3, 127.1, 126.7, 112.3.

(10-Hydroxyphenanthren-9-yl)(phenyl)methanone 5f. Yellow oil.[19b] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.74 (s, 1H), 8.55 (t, J = 8.4 Hz, 2H), 8.46 (d, J = 8.0 Hz, 1H), 7.82–7.77 (m, 1H), 7.69–7.64 (m, 1H), 7.63–7.59 (m, 2H), 7.54–7.49 (m, 1H), 7.40–7.32 (m, 4H), 7.18–7.12 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.2, 160.7, 140.4, 134.0, 132.5, 130.6, 130.3, 129.5, 128.5, 127.7, 127.1, 126.2, 125.9, 125.2, 125.1, 124.4, 122.9, 122.6, 111.0.

4-Benzoyl-3-hydroxy-1-methylquinolin-2(1*H*)-one 5g. Yellow solid, m.p. 206–207 °C (ref. 19*b* m.p. 206–207 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.52–7.40 (m, 5H), 7.34 (d, J = 8.0 Hz, 1H), 7.20 (t, J = 7.0 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 158.8, 140.8, 136.4, 134.5, 134.4, 129.8, 128.9, 127.9, 125.4, 123.8, 121.0, 119.4, 114.6, 30.7.

Author contributions

M. Cai designed the project. Y. Du, B. Huang, and J. Zeng carried out the experiments together. B. Huang performed the structure characterization of the heterogeneous gold complex. M. Cai and Y. Du analyzed the data and wrote the paper. All authors discussed the results and made comments and edits to the manuscript.

Conflicts of interest

There are no conflicts to declare.

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