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RESEARCH FRONT

Aust. J. Chem. **2019**, *72*, 881–889
https://doi.org/10.1071/CH19330

Full Paper

Gold-Catalysed Oxidative Cycloisomerisation of 1,6-Diyne Acetates to 1-Naphthyl Ketones

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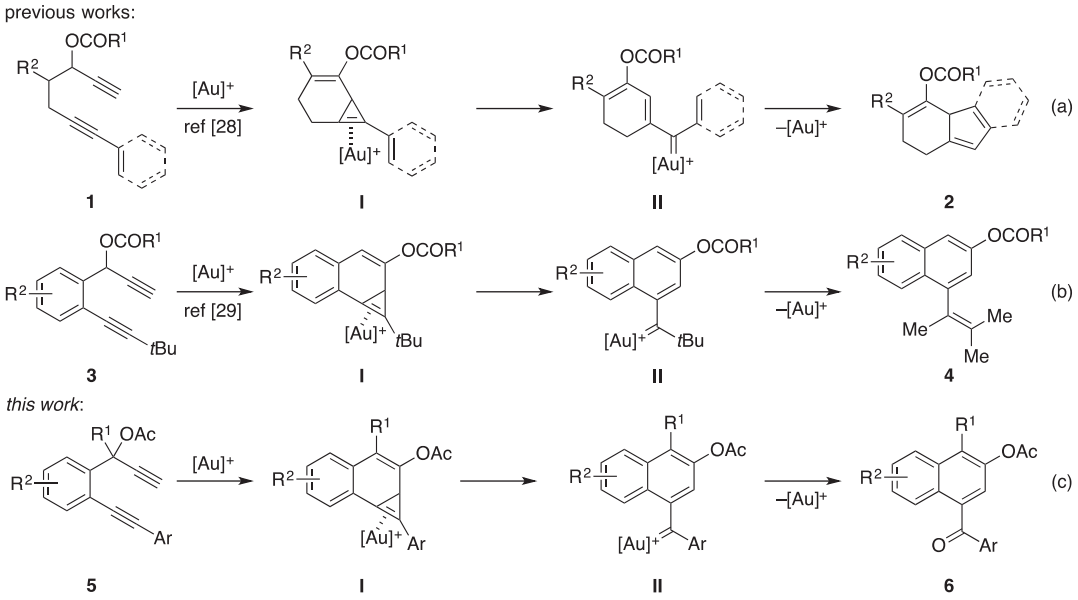
A synthetic method to prepare 1-naphthyl ketones from gold(I)-catalysed oxidative cycloisomerisation of 1,6-diyne acetates is described. The proposed mechanism involves cyclopropenation–cycloreversion of the 1,6-diyne motif initiated by a 1,2-acyloxy migration. This is followed by nucleophilic attack of the ensuing gold carbenoid species by a molecule of water and autoxidation to give the aromatic product.

Manuscript received: 16 July 2019.
Manuscript accepted: 27 August 2019.
Published online: 14 October 2019.

Introduction

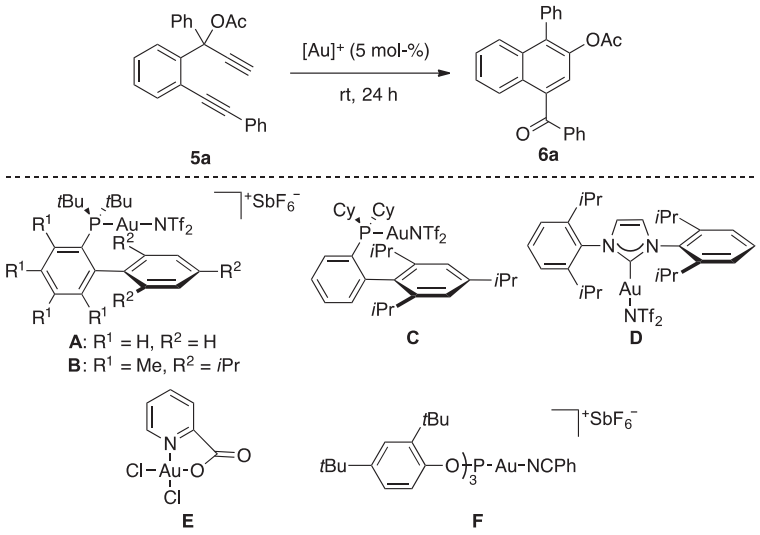
An emerging synthetic tool in organic synthesis to rapidly achieve molecular complexity and diversity is homogeneous gold catalysis.[1–54] In recent years, the field has witnessed a myriad of elegant methods to assemble an array of compounds of potential synthetic value, such as carbocycles and heterocycles, from readily accessible propargyl substrates in a single step.[18,30] An example of this is the gold(I)-catalysed preparation of 2,4a-dihydro-1*H*-fluorenes from 1,6-diyne esters in which computational studies revealed the likely involvement of the cyclopropene adduct **I** and gold carbenoid species **II** (Scheme 1a).[28] Closely following this work, the participation of these type of intermediates was proposed in the cycloisomerisation of 1,6-diyne esters to vinyl-substituted β-napthols (Scheme 1b).[29] Building on these initial studies, we were drawn to the potential reactivity of aryl-substituted 1,6-diyne esters containing a benzene tether (Scheme 1c). We anticipated that such substrates would form the corresponding cyclopropene intermediate **I** in the presence of a gold(I) complex.[47] Cycloreversion might then give the gold carbenoid species **II**. In the absence of a pronucleophilic motif or external reagent, this newly formed organogold species might then be susceptible to hydrolysis and autoxidation to give the 1-naphthyl ketone derivative **6**. Herein, we describe the details of this chemistry,



Scheme 1. Gold(I)-catalysed reactivities of 1,6-diyne esters.

Table 1. Optimisation of the reaction conditions

All reactions were performed at 0.05-mmol scale with catalyst : **5a** ratio = 1 : 20 in given solvent at room temperature (rt) for 24 h



Entry	Catalyst	Solvent	Yield [%][A]
1	**A**	CH_2Cl_2	62[B]
2	**B**	CH_2Cl_2	37
3	**C**	CH_2Cl_2	45
4	$(Ph_3P)AuNTf_2$	CH_2Cl_2	7
5	**D**	CH_2Cl_2	23 (48)[C]
6	**E**	CH_2Cl_2	37 (45)[C]
7	**F**	CH_2Cl_2	(99)[C]
8	AuCl	CH_2Cl_2	90
9	**A**	$(CH_2Cl)_2$	43
10	**A**	Chloroform	25
11	**A**	1,3-Dioxane	33
12	**A**	Acetonitrile	42
13	**A**	H_2O	31[D]
14	**A**	CH_2Cl_2	58[E]
15	**A**	CH_2Cl_2	32[F]
16	**A**	CH_2Cl_2	(99)[C,G]
17	**A**	CH_2Cl_2	40[F,H]
18	**A**	CH_2Cl_2	37[H]

[A]Yield determined by ^{1}H NMR measurements with 1,2-dibromomethane as the internal standard.
[B]Isolated yield.
[C]Values in parentheses denote the yield of recovered starting material.
[D]Reaction carried out at 80°C.
[E]Reaction was carried out in the presence of 3 equiv. of H_2O.
[F]Reaction was carried out in the presence of 10 equiv. of H_2O.
[G]Reaction conducted in the presence of 4-Å MS.
[H]Reaction carried out at reflux temperature.

which provides an expedient route to the aromatic carbonyl compound under reaction conditions that did not require an external oxidant.

Results and Discussion

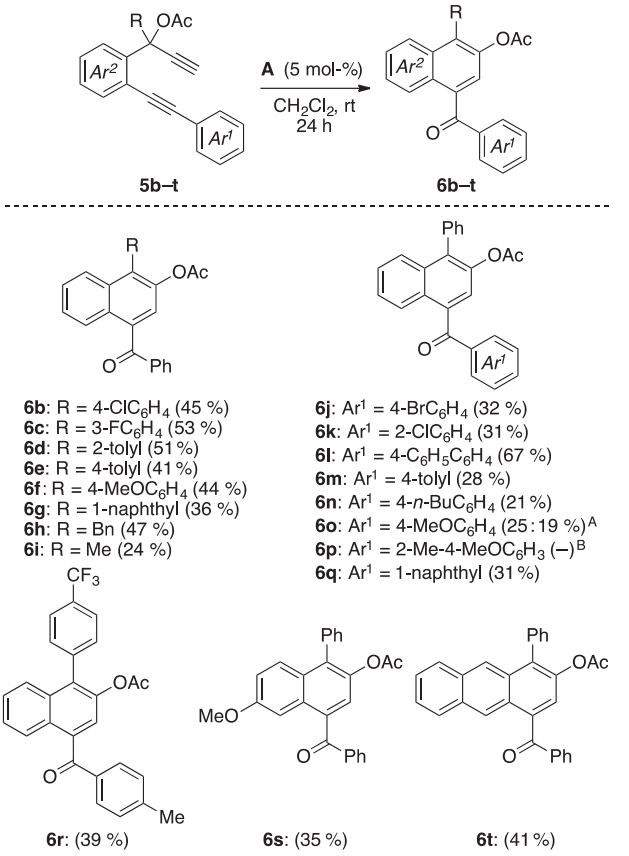
We began our investigations by examining the gold-catalysed cycloisomerisations of 1,6-diyne ester **5a** to establish the optimum reaction conditions (Table 1). This initially revealed subjecting the substrate to 5 mol-% of gold(I) phosphine complex **A** in dichloromethane at room temperature for 24 h gave the best result (entry 1). Under these conditions, the desired 1-naphthyl ketone **6a** was afforded in 62 % yield. Lower product yields of 7–45 % were obtained on repeating the reaction with the gold(I) phosphine complexes **B**, **C**, and $PPh_3PAuNTf_2$ (Tf = triflate) in place of **A** as the catalyst (entries 2–4). Control experiments with the NHC-Au^{I} (NHC = *N*-heterocyclic carbene) complex **D** or gold(III) complex **E** were found to result in incomplete consumption of the starting material, which was obtained along with **6a** in respective yields of 48 and 23 %, and 45 and 37 % (entries 5 and 6). In contrast, the use of the gold(I) phosphite complex **F** as the catalyst was found to lead to no reaction and the near-quantitative recovery of the substrate (entry 7). Although the analogous reaction mediated by AuCl was initially found to give a product yield of 90 %, unfortunately

this could not be consistently replicated (entry 8). A survey of other solvents such as 1,2-dichloroethane, chloroform, 1,3-dioxane or acetonitrile in place of dichloromethane was shown to give product yields of 25–43 % (entry 9–12). Likewise, comparable product yields of 31–58 % were afforded in control reactions in dichloromethane with 3 or 10 equiv. of water or only the latter as the solvent (entries 13–15). In a final set of control experiments, the introduction of 4-Å molecular sieves (MS) was observed to result in no reaction and near-quantitative recovery of the substrate (entry 16). On the other hand, conducting the reaction at reflux temperature in dichloromethane or the chlorinated solvent containing 10 equiv. of H_2O was found to provide product yields of 40 and 37 %, respectively (entries 17 and 18).

The generality of the transformation was next investigated with a variety of 1,6-diyne esters (Table 2). With gold(I) phosphine complex **A** as the catalyst, the reaction conditions were found to be broad, and a range of 1-naphthyl ketones with a variety of substitution patterns were furnished in 21–67 % yield from the corresponding substrates **5b**–**t**. Reactions of substrates where the ester carbon centre contained a phenyl motif with an electron-withdrawing (**5b** and **5c**) or donating (**5d**–**f**) group at either the *o*-, *m*- or *p*-position of the ring were shown to be well tolerated and gave **6b**–**f** in 41–53 % yield. Likewise, 1,6-diyne acetates with a 1-naphthyl (**5g**), methyl (**5h**) or benzyl (**5i**) substituent at the R position were found to proceed well and give **6g**–**i** in 24–47 % yield. Reactions with the introduction of other phenyl-substituted motifs (**5j**–**n**) or a 1-naphthyl group (**5q**) at the Ar^1 position of the starting acetate were also found to proceed well, affording the corresponding products **6j**–**n** and **6q** in 21–67 % yield. The reactions of substrates containing a *p*-anisyl (**5o**) or 2-Me-4-MeO-substituted phenyl (**5p**) group at the Ar^1 position were observed to be the only exceptions. In the case of the former, an inseparable mixture of **6o** and the starting material in a ratio of 4 : 3 and 44 % overall yield was observed. For the latter, no reaction was found and the starting material was recovered in near-quantitative yield. In contrast, reaction of a substrate containing both a *p*-CF_3 and *p*-Me substituent on the phenyl rings at the respective R and Ar^1 positions (**5r**) was found to give corresponding ketone **6r** in 39 % yield. Similarly, reactions of substrates in which the Ar^2 of the substrate is a *p*-anisyl (**5s**) or 2-naphthyl (**5t**) moiety were found to proceed well. Under the gold(I)-catalysed standard reaction conditions, these experiments gave the anticipated aryl ketone adducts **6s** and **6t** in respective yields of 35 and 41 %.

A tentative mechanism for the present gold(I)-catalysed 1-naphthyl ketone forming reaction is outlined in Scheme 2. With **5a** as a representative example, this may initially involve activation of the propargyl moiety of the substrate by the Au^I catalyst to give the gold(I)-coordinated complex **IIIa**. This results in the [2,3]-sigmatropic rearrangement of the acetyl functional group to produce the gold carbenoid species **Va** via the 1,3-dioxin-1-ium intermediate **IVa**. Trapping of this newly formed organogold species by the remaining alkyne motif may then provide the putative cyclopropene adduct **VIa**.[47,55] Further coordination of the Group 11 metal complex to the C=C bond of the tricyclic intermediate may next provide the gold(I)-activated species **Ia**. Ensuing electrophilic ring-opening of the gold(I)-activated three-membered ring in **Ia** would deliver the dibenzyl-stabilised gold carbenoid species **IIa** and its gold-stabilised allylic carbocation isomer **IIa′**. This is the active species that is prone to intermolecular nucleophilic attack by a molecule of water to form the hydrated organogold intermediate **VIIa**.[59] A sequential deprotonation and protodeauration process

Table 2. Cycloisomerisation of 1,6-diyne esters 5b–t catalysed by A
All reactions were performed at the 0.018–0.23-mmol scale with **A** : **5** = 1 : 20 in CH_2Cl_2 at room temperature (rt) for 24 h. Values in parentheses denote isolated yields

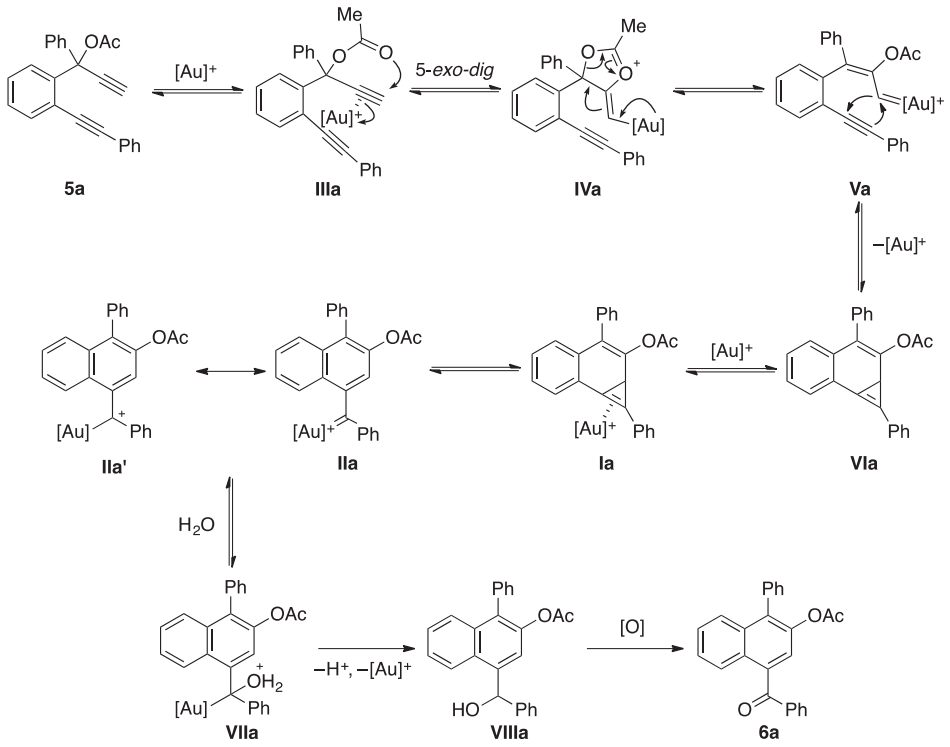


[A]Isolated as an inseparable mixture of product and starting material in a ratio of 4 : 3.
[B]No reaction detected by TLC analysis and ^1H NMR measurements with starting material recovered in near-quantitative yield.

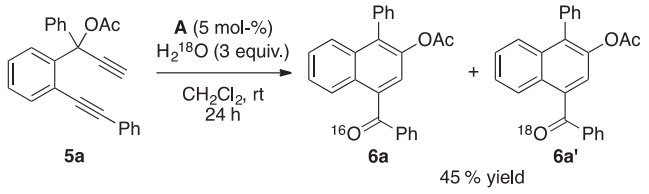
may then be anticipated to give the benzylic alcohol species **VIIIa**, which undergoes autoxidation to yield the 1-naphthyl ketone **6a**. The proposed role of water in providing the oxygen source for the carbonyl functional group formation through addition to the gold carbenoid species **IIa** would be in good agreement with our earlier findings described in Table 1, entry 16 showing no reaction when 4-Å MS were added to the reaction conditions. It is also supported by the following control experiment (Scheme 3). Treatment of **5a** with 3 equiv. of $H_2{}^{18}O$ in distilled dichloromethane predried using 4-Å MS yielded the desired 1-naphthyl ketones **6a** and **6a′** as an inseparable mixture of isotopic isomers in an overall yield of 45 %. The incorporation of ^{18}O-content in **6a′** was detected by mass spectrometric measurements.

Conclusion

In summary, we have demonstrated that propargyl esters containing a benzene-tethered alkyne undergo a 1,2-acyloxy migration–cyclopropenation–ring-opening sequence to access a dibenzyl-stabilised gold-carbenoid intermediate. In the absence of a pronucleophilic group or external reagent, addition of a molecule of water is followed by a deprotonation–protodeauration–autoxidation cascade to give access to a range of 1-naphthyl ketones.



Scheme 2. Proposed mechanism for Au^{I}-catalysed cycloisomerisation of 1,6-diyne esters represented by **1a**.



Scheme 3. Control experiment conducted with **5a** and $H_2{}^{18}O$.

This successful utilisation of stabilised gold-carbenoid intermediates of this type should potentially lead to further useful transformations to compounds of synthetic value.

Experimental

General Considerations

Unless specified, all reagents, solvents, and starting materials were purchased from commercial sources and used as received. The propargyl alcohol precursor to substrate **5** was prepared following literature procedures.[28] Analytical thin-layer chromatography (TLC) was performed using precoated silica gel plates and visualisation was achieved with UV light (254 nm). Flash chromatography was performed using silica gel and a gradient solvent system (toluene or EtOAc/*n*-hexane as eluent). ^{1}H and ^{13}C spectra were measured on 400 and 600 MHz spectrometers. Chemical shifts (ppm) were recorded with respect to TMS in CD_2Cl_2 and $CDCl_3$. Multiplicities are given as: s (singlet), brs (broad singlet), d (doublet), dd (doublet of doublets), ddd (doublet of doublets of doublets), t (triplet), dt (doublet of triplets), q (quartet) or m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H. Coupling constants are reported as a *J* value in hertz. Infrared spectra were recorded on an IR spectrometer. Low- and high-resolution mass spectra (electrospray ionisation, ESI) were obtained using a liquid chromatography/high resolution mass spectrometry-time-of-flight (LC/HRMS TOF) spectrometer fitted with an analytical electrospray source using NaI for accurate mass calibration. Mass spectral data are reported in units of mass to charge ratio (*m*/*z*).

General Experimental Procedure for the Preparation of 1,6-Diyne Acetate Substrate 5[28]

To a solution of the propargyl alcohol (1equiv.) and 4-dimethylaminopyridine (DMAP, 0.6 equiv.) in distilled CH_2Cl_2 (1 mL per 0.1 mmol) were sequentially added *N*,*N*-diisopropylethylamine (DIPEA, 4 equiv.) and acetic anhydride (3 equiv.). The reaction mixture was stirred at room temperature for 18 h. On completion, the reaction mixture was quenched by adding saturated aqueous NH_4Cl (10 mL) and extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were washed with saturated aqueous NH_4Cl (2 × 20 mL), H_2O (15 mL), and brine (15 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude mixture by flash column chromatography on silica gel (eluent: *n*-hexanes/EtOAc, gradient 14 : 1 to 9 : 1) gave the 1,6-diyne acetate substrate.

1-Phenyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl Acetate (5a)

Orange solid (438 mg, 98 % yield); mp 155.5–156.3°C. δ_H (600 MHz, CD_2Cl_2) 7.99 (s, 1H), 7.56–7.51 (m, 3H), 7.42 (td, *J* 7.7, 1.5, 1H), 7.39–7.25 (m, 9H), 3.05 (s, 1H), 2.12 (s, 3H). δ_C (151 MHz, CD_2Cl_2) 168.44, 142.49, 142.48, 141.67, 141.66, 134.94, 134.93, 131.48, 131.46, 128.80, 128.78, 128.77, 128.55, 128.41, 128.30, 128.29, 127.08, 123.67, 121.12, 95.78, 88.46, 82.32, 79.14, 78.59, 21.65. ν_{max} (NaCl, neat)/cm^{-1} 3252, 2113, 1745, 1491, 1442, 1364, 1226. *m*/*z* (HRMS ESI) 351.1277 $[M + H]^+$; calc. for $C_{25}H_{18}O_2$: 351.1385.

*1-(4-Chlorophenyl)-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl Acetate (**5b**)*

Yellow solid (386 mg, 96 % yield); mp 114.0–116.0°C. δ_H (600 MHz, CD_2Cl_2) 7.99 (dd, *J* 8.0, 0.9, 1H), 7.53 (dd, *J* 7.6, 1.5, 1H), 7.50–7.47 (m, 2H), 7.43 (td, *J* 7.7, 1.5, 1H), 7.38–7.34 (m, 6H), 7.30–7.26 (m, 2H), 3.06 (s, 1H), 2.12 (s, 3H). δ_C (151 MHz, $CDCl_3$) 168.26, 141.66, 139.87, 134.86, 134.02, 131.20, 128.54, 128.53, 128.45, 128.42, 128.24, 127.88, 123.41, 120.94, 95.85, 88.21, 81.62, 78.71, 78.52, 21.63. ν_{max} (NaCl, neat)/cm^{-1} 3267, 2221, 2113, 1740, 1490, 1442, 1228. *m/z* (HRMS ESI) 385.0963 $[M + H]^+$; calc. for $C_{25}H_{17}ClO_2$: 385.0995.

*1-(3-Fluorophenyl)-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl Acetate (**5c**)*

Beige solid (275 mg, 81 % yield); mp 146.7–148.2°C. δ_H (600 MHz, CD_2Cl_2) 8.03–8.00 (m, 1H), 7.54 (dd, *J* 7.6, 1.1, 1H), 7.45 (td, *J* 7.7, 1.5, 1H), 7.41–7.33 (m, 7H), 7.31–7.27 (m, 2H), 7.03–6.96 (m, 1H), 3.08 (s, 1H), 2.14 (s, 3H). δ_C (151 MHz, $CDCl_3$) 168.30, 163.59, 161.97, 144.32, 141.88, 135.01, 131.46, 129.91, 128.84, 128.77, 128.50, 128.34, 123.54, 122.94, 121.12, 115.25, 115.10, 114.52, 114.36, 95.96, 88.25, 81.79, 78.95, 78.53, 21.60. ν_{max} (NaCl, neat)/cm^{-1} 3250, 1742, 1592, 1491, 1441, 1368, 1223. *m/z* (HRMS ESI) 369.1285 $[M + H]^+$ calc. for $C_{25}H_{17}FO_2$: 369.1291.

*1-(2-(Phenylethynyl)phenyl)-1-(o-tolyl)prop-2-yn-1-yl Acetate (**5d**)*

Yellow oil (85 mg, 84 % yield). δ_H (600 MHz, CD_2Cl_2) 7.90–7.86 (m, 1H), 7.71 (dd, *J* 8.0, 1.4, 1H), 7.60–7.54 (m, 1H), 7.41–7.35 (m, 2H), 7.22 (td, *J* 7.4, 1.3, 1H), 7.19–7.15 (m, 1H), 7.15–7.10 (m, 1H), 3.09 (s, 1H), 2.23 (s, 3H), 2.09 (s, 3H). δ_C (151 MHz, CD_2Cl_2) 168.22, 141.75, 138.45, 136.55, 134.99, 132.73, 131.51, 129.52, 129.22, 128.71, 128.66, 128.59, 128.05, 125.47, 123.75, 121.76, 96.01, 88.61, 81.39, 79.77, 78.94, 21.66, 21.60. ν_{max} (NaCl, neat)/cm^{-1} 3284, 2931, 2114, 1750, 1598, 1570, 1492, 1442, 1365, 1223. *m/z* (HRMS ESI) 365.1520 $[M + H]^+$; calc. for $C_{26}H_{20}O_2$: 365.1542.

*1-(2-(Phenylethynyl)phenyl)-1-(p-tolyl)prop-2-yn-1-yl Acetate (**5e**)*

White oil (132 mg, 97 % yield). δ_H (400 MHz, $CDCl_3$) 7.94 (dd, *J* 7.9, 1.3, 1H), 7.52 (dt, *J* 7.6, 1.0, 1H), 7.47–7.42 (m, 2H), 7.41–7.28 (m, 7H), 7.14–7.09 (m, 2H), 2.99 (d, *J* 0.9, 1H), 2.32 (s, 3H), 2.13 (d, *J* 0.8, 3H). δ_C (101 MHz, $CDCl_3$) 168.44, 142.35, 138.36, 137.83, 134.77, 131.27, 128.81, 128.44, 128.33, 128.13, 128.11, 127.96, 126.81, 123.71, 120.99, 95.55, 88.56, 82.24, 79.08, 78.22, 77.48, 77.36, 77.16, 76.84, 21.67, 21.25, 1.17. ν_{max} (NaCl, neat)/cm^{-1} 3283, 2923, 2113, 1751, 1492, 1365, 1224. *m/z* (HRMS ESI) 365.1532 $[M + H]^+$; calc. for $C_{26}H_{20}O_2$: 365.1542.

*1-(4-Methoxyphenyl)-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl Acetate (**5f**)*

Yellow oil (70.5 mg, 97 % yield). δ_H (600 MHz, $CDCl_3$) 7.93 (d, *J* 8.0, 1H), 7.53 (dd, *J* 7.6, 1.1, 1H), 7.49–7.46 (m, 2H), 7.40–7.35 (m, 3H), 7.34–7.29 (m, 4H), 6.85–6.81 (m, 2H), 3.76 (s, 3H), 3.00 (s, 1H), 2.13 (s, 3H). δ_C (151 MHz, $CDCl_3$) 168.41, 159.26, 142.38, 134.71, 133.39, 131.23, 128.41, 128.32, 128.27, 128.10, 128.07, 127.76, 123.61, 120.96, 113.37, 95.60, 88.47, 82.16, 78.87, 78.12, 77.38, 77.17, 76.96, 55.31, 55.27, 29.81, 21.66. ν_{max} (NaCl, neat)/cm^{-1} 3286, 2927, 1752, 1608, 1510, 1494, 1443, 1368, 1229, 1176. *m/z* (HRMS ESI) 381.1481 $[M + H]^+$; calc. for $C_{26}H_{20}O_3$: 381.1491.

*1-(Naphthalen-2-yl)-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl Acetate (**5g**)*

Yellow oil (87 mg, 87 % yield). δ_H (400 MHz, $CDCl_3$) 8.11 (s, 1H), 8.01 (dt, *J* 8.0, 1.6, 1H), 7.80–7.68 (m, 3H), 7.57 (dt, *J* 8.7, 2.0, 1H), 7.50 (dt, *J* 7.6, 1.6, 1H), 7.46–7.36 (m, 3H), 7.33–7.18 (m, 7H), 3.04 (d, *J* 1.6, 1H), 2.17 (d, *J* 1.2, 3H). δ_C (101 MHz, $CDCl_3$) 168.32, 141.95, 138.12, 134.72, 132.89, 132.72, 131.18, 128.53, 128.32, 128.27, 128.23, 128.11, 127.97, 127.89, 127.58, 126.42, 126.21, 126.03, 124.51, 123.41, 120.96, 95.67, 88.34, 81.92, 79.11, 78.62, 77.42, 77.10, 76.78, 21.60, 21.11, 14.26, 1.10. ν_{max} (NaCl, neat)/cm^{-1} 3286, 2169, 1751, 1600, 1494, 1226. *m/z* (HRMS ESI) 401.1523 $[M + H]^+$; calc. for $C_{29}H_{20}O_2$: 401.1542.

*1-Phenyl-2-(2-(phenylethynyl)phenyl)but-3-yn-2-yl Acetate (**5h**)*

Yellow oil (211 mg, 86 % yield). δ_H (600 MHz, $CDCl_3$) 7.64–7.58 (m, 3H), 7.43–7.36 (m, 3H), 7.28 (dd, *J* 7.5, 1.4, 1H), 7.24–7.22 (m, 1H), 7.21–7.15 (m, 4H), 7.11–7.07 (m, 2H), 3.79 (d, *J* 13.2, 1H), 3.67 (d, *J* 13.3, 1H), 2.85 (s, 1H), 2.08 (s, 3H). δ_C (101 MHz, $CDCl_3$) 168.57, 140.70, 134.83, 134.55, 131.26, 131.15, 128.58, 128.53, 128.50, 128.12, 127.82, 127.55, 126.91, 123.49, 119.01, 95.13, 88.54, 81.39, 79.43, 77.93, 77.34, 77.03, 76.71, 46.61, 21.27. ν_{max} (NaCl, neat)/cm^{-1} 2184, 2162, 2140, 1750, 1559, 1540, 1522, 1507, 1496, 1457, 1437, 1419, 1225. *m/z* (HRMS ESI) 365.1532 $[M + H]^+$; calc. for $C_{26}H_{20}O_2$: 365.1541.

*2-(2-(Phenylethynyl)phenyl)but-3-yn-2-yl Acetate (**5i**)*

Yellow oil (121 mg, 71 % yield). δ_H (600 MHz, CD_2Cl_2) 7.90 (dd, *J* 7.9, 0.9, 1H), 7.58–7.53 (m, 3H), 7.42–7.35 (m, 4H), 7.31 (td, *J* 7.5, 1.2, 1H), 2.89 (s, 1H), 2.10 (s, 3H), 2.02 (s, 3H). δ_C (151 MHz, CD_2Cl_2) 168.95, 142.97, 134.74, 131.58, 128.92, 128.87, 128.66, 128.12, 127.44, 123.81, 119.45, 95.36, 88.52, 83.45, 76.14, 75.82, 29.93, 21.37. ν_{max} (NaCl, neat)/cm^{-1} 3283, 2933, 2116, 1744, 1598, 1570, 1493, 1441, 1224. *m/z* (HRMS ESI) 289.1211 $[M + H]^+$; calc. for $C_{20}H_{16}O_2$: 289.1229.

*1-(2-((4-Bromophenyl)ethynyl)phenyl)-1-phenylprop-2-yn-1-yl Acetate (**5j**)*

Yellow solid (480 mg, 78 % yield); mp 133.2–135.2°C. δ_H (600 MHz, CD_2Cl_2) 7.98 (dd, *J* 9.2, 0.4, 1H), 7.53–7.49 (m, 3H), 7.49–7.47 (m, 2H), 7.44 (td, *J* 7.7, 1.5, 1H), 7.35 (td, *J* 7.5, 1.3, 1H), 7.33–7.26 (m, 3H), 7.24–7.20 (m, 2H), 3.05 (s, 1H), 2.11 (s, 3H). δ_C (151 MHz, CD_2Cl_2) 168.40, 142.58, 141.63, 134.88, 132.93, 132.04, 128.64, 128.59, 128.38, 128.32, 127.08, 122.87, 122.70, 120.84, 94.67, 89.62, 82.21, 79.08, 78.69, 21.66. ν_{max} (NaCl, neat)/cm^{-1} 3269, 211, 1742, 1491, 1441, 1235, 1192. *m/z* (HRMS ESI) 429.0479 $[M + H]^+$; calc. for $C_{25}H_{17}BrO_2$: 429.0490.

*1-(2-((2-Chlorophenyl)ethynyl)phenyl)-1-phenylprop-2-yn-1-yl Acetate (**5k**)*

Yellow oil (87 mg, 86 % yield). δ_H (400 MHz, $CDCl_3$) 7.94 (ddd, *J* 8.0, 1.3, 0.5, 1H), 7.59 (ddd, *J* 7.5, 1.5, 0.5, 1H), 7.56–7.52 (m, 2H), 7.44–7.34 (m, 3H), 7.33–7.27 (m, 4H), 7.25–7.17 (m, 2H), 3.01 (s, 1H), 2.14 (s, 3H). δ_C (101 MHz, CD_2Cl_2) 168.55, 142.50, 141.58, 135.74, 135.34, 133.34, 129.84, 129.67, 128.80, 128.56, 128.41, 128.37, 128.34, 127.10, 126.96, 123.51, 120.74, 93.43, 92.48, 82.30, 79.11, 78.75, 21.67. ν_{max} (NaCl, neat)/cm^{-1} 3288, 2921, 1752, 1487, 1227. *m/z* (HRMS ESI) 325.0767 $[M - OAc]^-$; calc. for $C_{25}H_{17}ClO_2$: 325.0784.

*1-(2-([1,1′-Biphenyl]-4-ylethynyl)phenyl)-1-phenylprop-2-yn-1-yl Acetate (**5l**)*

White oil (98 mg, 87 % yield). δ_H (600 MHz, CD_2Cl_2) 7.99 (d, *J* 8.0, 1H), 7.65–7.58 (m, 4H), 7.58–7.52 (m, 3H), 7.49–7.41 (m, 5H), 7.40–7.26 (m, 5H), 3.07 (s, 1H), 2.14 (s, 3H). δ_C (151 MHz, CD_2Cl_2) 168.47, 142.49, 141.68, 141.39, 140.56, 134.93, 131.92, 129.29, 128.56, 128.42, 128.36, 128.32, 128.12, 127.40, 127.31, 127.11, 122.60, 121.16, 95.73, 89.21, 82.34, 79.16, 78.61, 21.70. ν_{max} (NaCl, neat)/cm^{-1} 3284, 2925, 1725, 1599, 1489, 1448, 1226. *m/z* (HRMS ESI) 367.1471 $[M - OAc]^-$; calc. for $C_{31}H_{22}O_2$: 367.1487.

*1-Phenyl-1-(2-(p-tolylethynyl)phenyl)prop-2-yn-1-yl Acetate (**5m**)*

Yellow solid (211 mg, 83 % yield); mp 142.0–143.2°C. δ_H (600 MHz, CD_2Cl_2) 7.97 (dd, *J* 8.0, 1.3, 1H), 7.55–7.52 (m, 2H), 7.50 (dd, *J* 7.6, 1.5, 1H), 7.41 (td, *J* 7.7, 1.5, 1H), 7.35–7.24 (m, 6H), 7.18–7.14 (m, 2H), 3.05 (s, 1H), 2.36 (s, 3H), 2.12 (s, 3H). δ_C (151 MHz, CD_2Cl_2) 168.46, 142.35, 141.68, 139.16, 134.84, 131.34, 129.54, 128.50, 128.29, 128.27, 128.24, 128.20, 127.08, 121.32, 120.59, 96.04, 87.84, 82.37, 79.15, 78.51, 21.66, 21.62. ν_{max} (NaCl, neat)/cm^{-1} 3269, 2920, 2855, 2213, 2116, 1743, 1509, 1440, 1363, 1238. *m/z* (HRMS ESI) 365.1519 $[M + H]^+$; calc. For $C_{26}H_{20}O_2$: 365.1542.

*1-(2-((4-Butylphenyl)ethynyl)phenyl)-1-phenylprop-2-yn-1-yl Acetate (**5n**)*

Yellow oil (498 mg, 73 % yield). δ_H (600 MHz, CD_2Cl_2) 7.99 (d, *J* 8.0, 1H), 7.59–7.55 (m, 2H), 7.55–7.51 (m, 1H), 7.42 (td, *J* 7.8, 1.5, 1H), 7.37–7.27 (m, 6H), 7.18 (d, *J* 8.2, 2H), 3.06 (s, 1H), 2.67–2.61 (m, 2H), 2.14 (s, 3H), 1.65–1.58 (m, 2H), 1.38 (h, *J* 7.4, 2H), 0.96 (t, *J* 7.4, 3H). δ_C (151 MHz, CD_2Cl_2) 168.46, 144.16, 142.35, 141.69, 134.88, 131.37, 128.92, 128.72, 128.51, 128.30, 128.29, 128.25, 128.20, 127.10, 126.29, 121.36, 120.80, 96.12, 87.87, 82.39, 79.18, 78.54, 35.95, 33.85, 22.77, 21.68, 14.12. ν_{max} (NaCl, neat)/cm^{-1} 3283, 2955, 2927, 2215, 2117, 1725, 1509 1449, 1225. *m/z* (HRMS ESI) 407.1992 $[M + H]^+$; calc. for $C_{29}H_{26}O_2$: 407.2011.

*1-(2-((4-Methoxyphenyl)ethynyl)phenyl)-1-phenylprop-2-yn-1-yl Acetate (**5o**)*

Yellow solid (134 mg, 98 % yield); mp 121.0–122.0°C. δ_H (600 MHz, CD_2Cl_2) 7.96 (dd, *J* 8.0, 0.9, 1H), 7.55–7.52 (m, 2H), 7.49 (dd, *J* 7.6, 1.1, 1H), 7.39 (td, *J* 7.7, 1.5, 1H), 7.35–7.25 (m, 6H), 6.90–6.84 (m, 2H), 3.82 (s, 3H), 3.04 (s, 1H), 2.12 (s, 3H). δ_C (151 MHz, CD_2Cl_2) 168.18, 159.95, 141.91, 141.43, 134.42, 132.65, 128.22, 128.02, 127.99, 127.95, 127.74, 126.81, 121.21, 115.46, 114.15, 95.68, 86.94, 82.11, 78.90, 78.21, 55.44, 21.39. ν_{max} (NaCl, neat)/cm^{-1} 3271, 2935, 2842, 2218, 2113, 1741, 1508, 1442, 1363, 1247, 1224, 1181. *m/z* (HRMS ESI) 380.1441 $[M]^+$; calc. for $C_{26}H_{20}O_3$: 380.1413.

*1-(2-((4-Methoxy-2-methylphenyl)ethynyl)phenyl)-1-phenylprop-2-yn-1-yl Acetate (**5p**)*

Yellow solid (155 mg, 81 % yield); mp 131.7–132.7°C. δ_H (600 MHz, CD_2Cl_2) 7.96 (dd, *J* 7.9, 1.0, 1H), 7.54–7.50 (m, 3H), 7.40 (td, *J* 7.7, 1.5, 1H), 7.35 (dd, *J* 7.5, 1.4, 1H), 7.33–7.26 (m, 3H), 7.25 (d, *J* 8.4, 1H), 6.74 (d, *J* 2.6, 1H), 6.71 (dd, *J* 8.4, 2.6, 1H), 3.79 (s, 3H), 3.05 (s, 1H), 2.29 (s, 3H), 2.11 (s, 3H). δ_C (151 MHz, CD_2Cl_2) 168.54, 160.14, 142.28, 141.72, 141.64, 134.93, 133.19, 128.48, 128.34, 128.30, 127.93, 127.17, 121.82, 115.66, 115.37, 111.67, 95.04, 90.89, 82.55, 79.32, 78.59, 55.62, 21.65, 20.97. ν_{max} (NaCl, neat)/cm^{-1} 3283, 2936, 2837, 2207, 1751, 1604, 1501, 1449, 1237. *m/z* (HRMS ESI) 395.1660 $[M + H]^+$; calc. for $C_{27}H_{22}O_3$: 395.1647.

*1-(2-(Naphthalen-1-ylethynyl)phenyl)-1-phenylprop-2-yn-1-yl Acetate (**5q**)*

White oil (40.2 mg, 77 % yield). δ_H (600 MHz, $CDCl_3$) 8.14–8.10 (m, 1H), 8.02 (ddd, *J* 7.9, 1.3, 0.5, 1H), 7.83 (ddt, *J* 12.4, 8.6, 0.9, 2H), 7.70 (ddd, *J* 7.6, 1.5, 0.5, 1H), 7.61–7.56 (m, 3H), 7.53–7.47 (m, 2H), 7.47–7.42 (m, 2H), 7.39 (td, *J* 7.5, 1.3, 1H), 7.36–7.28 (m, 3H), 3.05 (s, 1H), 2.10 (s, 3H). δ_C (151 MHz, $CDCl_3$) 168.65, 141.62, 141.57, 141.30, 135.10, 133.27, 130.13, 128.82, 128.60, 128.38, 128.27, 128.23, 128.20, 128.18, 127.78, 127.67, 127.03, 126.71, 126.60, 126.55, 125.37, 29.86. ν_{max} (NaCl, neat)/cm^{-1} 3234, 2918, 1749, 1558, 1506, 1228. *m/z* (HRMS ESI) 341.1316 $[M - OAc]^-$; calc. for $C_{29}H_{20}O_2$: 341.13303.

*1-(2-(p-Tolylethynyl)phenyl)-1-(4-(trifluoromethyl)phenyl)-prop-2-yn-1-yl Acetate (**5r**)*

Orange oil (43 mg, 39 % yield). δ_H (600 MHz, $CDCl_3$) 7.99 (dd, *J* 8.0, 1.0, 1H), 7.63 (d, *J* 8.2, 2H), 7.51 (d, *J* 8.3, 2H), 7.47 (ddd, *J* 7.6, 1.5, 0.5, 1H), 7.38 (td, *J* 7.7, 1.5, 1H), 7.30 (td, *J* 7.5, 1.3, 1H), 7.16–7.13 (m, 2H), 7.10 (d, *J* 7.9, 2H), 3.00 (s, 1H), 2.34 (s, 3H), 2.13 (s, 3H). δ_C (151 MHz, $CDCl_3$) 168.20, 145.12, 141.18, 138.82, 134.83, 131.06, 129.32, 128.61, 128.14, 128.03, 127.34, 125.08, 125.06, 121.13, 120.20, 96.21, 87.42, 81.42, 79.05, 29.86, 22.34, 21.67, 21.60. ν_{max} (NaCl, neat)/cm^{-1} 3297, 2921, 2210, 2182, 1755, 1326, 1226. *m/z* (HRMS ESI) 373.1187 $[M - OAc]^-$; calc. for $C_{27}H_{19}F_3O_2$: 373.1204.

*1-(4-Methoxy-2-(phenylethynyl)phenyl)-1-phenylprop-2-yn-1-yl Acetate (**5s**)*

Brown solid (83 mg, 74 % yield); mp 116.6–117.1°C. δ_H (600 MHz, $CDCl_3$) 7.79 (dd, *J* 8.8, 1.4, 1H), 7.49 (dt, *J* 8.2, 1.6, 2H), 7.30–7.24 (m, 7H), 7.23–7.19 (m, 1H), 7.00 (dd, *J* 2.6, 1.1, 1H), 6.86 (dd, *J* 8.8, 2.7, 1H), 3.76 (s, 3H), 2.95 (s, 1H), 2.07 (s, 3H). δ_C (151 MHz, $CDCl_3$) 168.47, 159.05, 141.65, 134.51, 131.23, 129.76, 128.39, 128.04, 127.95, 126.71, 123.40, 122.11, 119.31, 114.01, 95.22, 88.23, 82.29, 78.81, 78.37, 55.49, 29.80, 21.65. ν_{max} (NaCl, neat)/cm^{-1} 3283, 2925, 1752, 1601, 1569, 1225. *m/z* (HRMS ESI) 381.1448 $[M + H]^+$; calc. for $C_{26}H_{20}O_3$: 381.1491.

*1-Phenyl-1-(3-(phenylethynyl)naphthalen-2-yl)prop-2-yn-1-yl Acetate (**5t**)*

White oil (10 mg, 42 % yield). δ_H (600 MHz, $CDCl_3$) 8.40 (s, 1H), 8.06 (s, 1H), 7.90 (dd, *J* 6.3, 2.9, 1H), 7.78 (dd, *J* 6.3, 2.7, 1H), 7.60–7.56 (m, 2H), 7.56–7.50 (m, 2H), 7.39–7.27 (m, 8H), 3.08 (d, *J* 0.7, 1H), 2.17 (d, *J* 0.8, 3H). δ_C (151 MHz, $CDCl_3$) 168.55, 141.15, 138.12, 135.16, 132.66, 132.17, 131.29, 128.72, 128.46, 128.32, 128.17, 128.13, 127.87, 127.38, 127.36, 127.28, 127.03, 123.68, 118.55, 94.58, 88.84, 82.18, 79.24, 78.84, 77.37, 77.16, 76.95, 21.82. ν_{max} (NaCl, neat)/cm^{-1} 3286, 2225, 1752, 1598, 1495, 1449, 1226. *m/z* (HRMS ESI) 401.1528 $[M + H]^+$; calc. for $C_{29}H_{20}O_2$: 401.1542.

*General Experimental Procedure for the Gold(I)-Catalysed Oxidative Cycloisomerisation of **5***

To a reaction vessel containing the 1,6-diyne acetate substrate **5** (0.1 mmol) and gold(I) phosphine complex **A** (5 mol-%) under

atmospheric conditions was added CH_2Cl_2 (2 mL) and the resulting reaction mixture was stirred for 24 h. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc 14 : 1) to give the 1-naphthyl ketone product **6**.

*4-Benzoyl-1-phenylnaphthalen-2-yl Acetate (**6a**)*

Yellow solid (33 mg, 62 % yield); mp 126.1–127.8°C. δ_H (400 MHz, $CDCl_3$) 8.19–8.13 (m, 1H), 8.00–7.95 (m, 2H), 7.70–7.60 (m, 2H), 7.55–7.42 (m, 8H), 7.41–7.35 (m, 3H), 1.97 (s, 3H). δ_C (151 MHz, CD_2Cl_2) 196.83, 169.86, 144.57, 138.33, 137.51, 135.01, 134.46, 134.28, 133.88, 130.75, 130.48, 129.80, 128.97, 128.72, 128.42, 127.42, 127.06, 126.14, 123.88, 20.69. ν_{max} (NaCl, neat)/cm^{-1} 2923, 1761, 1494, 1197, 1176. *m/z* (HRMS ESI) 367.1333 $[M + H]^+$; calc. for $C_{25}H_{18}O_3$: 367.1334.

*4-Benzoyl-1-(4-chlorophenyl)naphthalen-2-yl Acetate (**6b**)*

Yellow oil (24 mg, 45 % yield). δ_H (600 MHz, CD_2Cl_2) 8.13–8.09 (m, 1H), 7.95–7.90 (m, 2H), 7.67–7.62 (m, 2H), 7.54–7.47 (m, 6H), 7.38 (s, 1H), 7.35–7.32 (m, 2H), 2.00 (s, 3H). δ_C (151 MHz, CD_2Cl_2) 196.74, 169.75, 144.62, 138.22, 137.92, 134.44, 134.08, 133.95, 133.58, 133.10, 132.02, 130.74, 129.76, 129.01, 127.63, 127.17, 126.73, 126.23, 123.69, 20.74. ν_{max} (NaCl, neat)/cm^{-1} 2924, 1763, 1661, 1491, 1197, 1176. *m/z* (HRMS ESI) 401.0930 $[M + H]^+$; calc. for $C_{25}H_{17}ClO_3$: 401.0945.

*4-Benzoyl-1-(3-fluorophenyl)naphthalen-2-yl Acetate (**6c**)*

White oil (28.5 mg, 53 % yield). δ_H (400 MHz, CD_2Cl_2) 8.12–8.06 (m, 1H), 7.95–7.89 (m, 2H), 7.68–7.60 (m, 2H), 7.55–7.44 (m, 5H), 7.38 (s, 1H), 7.25–7.08 (m, 4H), 1.99 (s, 3H). δ_C (101 MHz, CD_2Cl_2) 196.73, 169.73, 164.30, 161.85, 144.58, 138.22, 138.02, 137.29, 137.21, 133.99, 133.97, 132.96, 132.94, 130.75, 130.49, 130.41, 129.74, 129.01, 127.66, 127.19, 126.74, 126.49, 126.46, 126.22, 123.69, 117.66, 117.44, 115.47, 115.26, 54.24, 20.70. ν_{max} (NaCl, neat)/cm^{-1} 1764, 1582, 1489, 1449, 1437, 1369, 1338, 1269, 1242, 1201, 1172, 1123, 1020. *m/z* (HRMS ESI) 385.1233 $[M + H]^+$; calc. for $C_{25}H_{17}FO_3$: 385.1240.

*4-Benzoyl-1-(o-tolyl)naphthalen-2-yl Acetate (**6d**)*

White oil (17 mg, 51 % yield). δ_H (400 MHz, $CDCl_3$) 8.18 (dt, *J* 8.4, 1.1, 1H), 8.00–7.95 (m, 2H), 7.63 (ddt, *J* 7.9, 6.9, 1.3, 1H), 7.54–7.36 (m, 8H), 7.34–7.28 (m, 1H), 7.20 (dd, *J* 7.2, 1.2, 1H), 2.02 (s, 3H), 1.92 (s, 3H). δ_C (151 MHz, $CDCl_3$) 196.87, 169.58, 144.74, 138.37, 137.70, 137.37, 134.48, 134.10, 134.04, 133.85, 130.78, 130.44, 129.71, 128.96, 128.68, 127.54, 127.09, 126.78, 126.26, 126.03, 124.06, 30.09, 20.61, 19.86. ν_{max} (NaCl, neat)/cm^{-1} 2920, 2851, 1765, 1663, 1449, 1201. *m/z* (HRMS ESI) 381.1467 $[M + H]^+$; calc. for $C_{26}H_{20}O_3$: 381.1491.

*4-Benzoyl-1-(p-tolyl)naphthalen-2-yl Acetate (**6e**)*

Yellow oil (18 mg, 41 % yield). δ_H (400 MHz, $CDCl_3$) 8.15 (dd, *J* 8.3, 1.6, 1H), 7.96 (dt, *J* 7.1, 1.4, 2H), 7.72–7.58 (m, 2H), 7.53–7.40 (m, 4H), 7.37 (s, 1H), 7.32 (d, *J* 7.8, 2H), 7.28–7.22 (m, 2H), 2.46 (s, 3H), 1.99 (s, 3H). δ_C (101 MHz, $CDCl_3$) 196.63, 169.55, 144.09, 137.95, 137.70, 136.86, 134.23, 134.10, 133.42, 131.56, 130.53, 129.96, 129.57, 129.02, 128.57, 126.92, 126.79, 126.71, 125.81, 123.58, 77.33, 77.01, 76.69, 21.36, 20.57, 1.02. ν_{max} (NaCl, neat)/cm^{-1} 2957, 2923, 1763, 1661, 1595, 1579, 1508, 1449, 1231, 1200. *m/z* (HRMS ESI) 381.1487 $[M + H]^+$; calc. for $C_{26}H_{20}O_3$: 381.1491.

*4-Benzoyl-1-(4-methoxyphenyl)naphthalen-2-yl Acetate (**6f**)*

White oil (32.3 mg, 44 % yield). δ_H (600 MHz, $CDCl_3$) 8.16 (d, *J* 8.4, 1H), 7.96 (d, *J* 8.2, 2H), 7.71 (d, *J* 8.4, 1H), 7.64–7.60 (m, 1H), 7.53–7.42 (m, 4H), 7.37 (s, 1H), 7.32–7.28 (m, 2H), 7.08–7.03 (m, 2H), 3.91 (s, 3H), 2.01 (s, 3H). δ_C (151 MHz, $CDCl_3$) 196.78, 169.71, 159.47, 144.37, 138.07, 136.95, 134.38, 134.11, 133.58, 131.44, 130.67, 129.73, 128.72, 127.09, 126.89, 126.87, 126.78, 125.97, 123.71, 55.46, 20.74. ν_{max} (NaCl, neat)/cm^{-1} 2927, 1759, 1578, 1507, 1448, 1366, 1244, 1196, 1172. *m/z* (HRMS ESI) 397.1412 $[M + H]^+$; calc. for $C_{26}H_{20}O_4$: 397.1440.

*4-Benzoyl-(1,1′-binaphthalen)-2-yl Acetate (**6g**)*

White oil (20 mg, 36 % yield). δ_H (600 MHz, CD_2Cl_2) 8.14 (d, *J* 8.1, 1H), 8.02 (d, *J* 8.4, 1H), 7.99–7.91 (m, 4H), 7.87 (s, 1H), 7.71–7.68 (m, 1H), 7.66 (tt, *J* 7.8, 1.3, 1H), 7.61–7.56 (m, 2H), 7.55–7.48 (m, 4H), 7.47–7.42 (m, 2H), 1.91 (s, 3H). δ_C (151 MHz, CD_2Cl_2) 196.84, 169.87, 144.78, 138.34, 137.62, 134.39, 134.30, 133.90, 133.60, 133.32, 132.55, 130.77, 129.83, 129.67, 128.99, 128.49, 128.36, 128.31, 128.16, 127.49, 127.13, 127.11, 126.89, 126.82, 126.19, 123.93, 54.02, 20.72. ν_{max} (NaCl, neat)/cm^{-1} 2925, 1763, 1662, 1200, 1175. *m/z* (HRMS ESI) 417.1451 $[M + H]^+$; calc. for $C_{29}H_{20}O_3$: 417.1491.

*4-Benzoyl-1-benzylnaphthalen-2-yl Acetate (**6h**)*

Yellow oil (5.8 mg, 47 % yield). δ_H (600 MHz, $CDCl_3$) 8.17–8.12 (m, 1H), 8.06–8.02 (m, 1H), 7.96–7.91 (m, 2H), 7.62 (ddt, *J* 7.7, 7.1, 1.3, 1H), 7.52–7.44 (m, 4H), 7.38 (s, 1H), 7.28–7.23 (m, 2H), 7.21–7.16 (m, 3H), 4.45 (s, 2H), 2.27 (s, 3H). δ_C (125 MHz, $CDCl_3$) 194.83, 170.61, 142.99, 139.17, 136.56, 133.85, 132.69, 130.42, 129.99, 128.51, 126.78, 126.37, 125.43, 33.51, 20.02. ν_{max} (NaCl, neat)/cm^{-1} 3062, 3028, 2922, 2853, 2360, 2341, 2250, 1761, 1659, 1594, 1515, 1495, 1449, 1368, 1339, 1281, 1255, 1199, 1176, 1082, 1011, 907. *m/z* (HRMS ESI) 381.1483 $[M + H]^+$; calc. for $C_{26}H_{20}O_3$: 380.1412.

*4-Benzoyl-1-methylnaphthalen-2-yl Acetate (**6i**)*

White oil (15 mg, 24 % yield). δ_H (400 MHz, $CDCl_3$) 8.16 (ddd, *J* 8.5, 1.4, 0.7, 1H), 8.09 (ddd, *J* 8.6, 1.3, 0.7, 1H), 7.91–7.87 (m, 2H), 7.63–7.57 (m, 2H), 7.53–7.44 (m, 3H), 7.30 (s, 1H), 2.58 (s, 3H), 2.37 (s, 3H). δ_C (151 MHz, CD_2Cl_2) 169.68, 145.17, 143.66, 138.55, 135.72, 134.22, 133.67, 130.68, 129.57, 128.97, 128.87, 127.33, 126.88, 126.61, 124.94, 124.03, 100.40, 30.09, 21.04, 12.27. ν_{max} (NaCl, neat)/cm^{-1} 2922, 2853, 1759, 1594, 1199. *m/z* (HRMS ESI) 305.1170 $[M + H]^+$; calc. for $C_{20}H_{16}O_3$: 305.1178.

*4-(4-Bromobenzoyl)-1-phenylnaphthalen-2-yl Acetate (**6j**)*

Yellow oil (20 mg, 32 % yield). δ_H (400 MHz, $CDCl_3$) 8.14 (ddd, *J* 8.4, 1.5, 0.7, 1H), 7.86–7.79 (m, 2H), 7.69–7.63 (m, 3H), 7.55–7.42 (m, 6H), 7.39–7.34 (m, 3H), 1.98 (s, 3H). δ_C (151 MHz, CD_2Cl_2) 195.78, 169.86, 144.53, 137.19, 136.81, 134.90, 134.80, 134.31, 132.30, 132.26, 130.44, 129.69, 129.01, 128.74, 128.47, 127.51, 127.21, 127.11, 126.02, 124.08, 70.87, 20.68. ν_{max} (NaCl, neat)/cm^{-1} 2865, 1763, 1583, 1201. *m/z* (HRMS ESI) 445.0431 $[M + H]^+$; calc. for $C_{25}H_{17}BrO_3$: 445.0440.

*4-(2-Chlorobenzoyl)-1-phenylnaphthalen-2-yl Acetate (**6k**)*

Brown solid (24 mg, 31 % yield); mp 137.0–138.0°C. δ_H (400 MHz, $CDCl_3$) 8.87 (d, *J* 8.6, 1H), 7.70–7.61 (m, 2H), 7.58

(d, *J* 7.2, 1H), 7.55–7.44 (m, 6H), 7.43–7.32 (m, 4H), 1.93 (s, 3H). δ_C (151 MHz, CD_2Cl_2) 196.09, 169.70, 144.59, 139.65, 136.89, 135.76, 134.83, 134.54, 132.45, 132.40, 130.84, 130.34, 129.78, 128.69, 128.53, 128.07, 127.59, 127.33, 127.18, 127.15, 126.33, 20.63. ν_{max} (NaCl, neat)/cm^{-1} 2926, 1751, 1674, 1582, 1197. *m*/*z* (HRMS ESI) 401.0938 $[M+H]^+$; calc. for $C_{25}H_{17}ClO_3$: 401.0945.

*4-([1,1′-Biphenyl]-4-carbonyl)-1-phenylnaphthalen-2-yl Acetate (**6l**)*

Yellow solid (20 mg, 67 % yield); mp 126.4–127.2°C. δ_H (600 MHz, $CDCl_3$) 8.18 (d, *J* 8.4, 1H), 8.08–8.03 (m, 2H), 7.73 (d, *J* 8.2, 2H), 7.69–7.64 (m, 3H), 7.54–7.37 (m, 11H), 1.99 (s, 3H). δ_C (151 MHz, $CDCl_3$) 196.34, 169.72, 146.37, 144.22, 139.96, 137.32, 136.67, 134.80, 134.23, 134.10, 131.30, 130.24, 129.67, 129.14, 128.48, 128.15, 127.48, 127.40, 127.20, 126.94, 126.86, 126.00, 123.56, 20.67. ν_{max} (NaCl, neat)/cm^{-1} 2923, 1761, 1655, 1600, 1260, 1198, 1176. *m*/*z* (HRMS ESI) 443.1641 $[M+H]^+$; calc. for $C_{31}H_{22}O_3$: 443.1647.

*4-(4-Methylbenzoyl)-1-phenylnaphthalen-2-yl Acetate (**6m**)*

Yellow oil (14.9 mg, 28 % yield). δ_H (400 MHz, $CDCl_3$) 8.16–8.10 (m, 1H), 7.92–7.85 (m, 2H), 7.68–7.63 (m, 1H), 7.54–7.41 (m, 5H), 7.39–7.35 (m, 3H), 7.32–7.28 (m, 2H), 2.45 (s, 3H), 1.98 (s, 3H). δ_C (101 MHz, $CDCl_3$) 196.42, 169.64, 144.63, 144.19, 137.56, 135.43, 134.81, 134.01, 133.94, 130.82, 130.22, 129.62, 129.42, 128.42, 128.08, 127.08, 126.77, 125.97, 123.28, 77.45, 77.33, 77.13, 76.81, 21.88, 20.62, 1.14. ν_{max} (NaCl, neat)/cm^{-1} 2926, 1763, 1604, 1495, 1201. *m*/*z* (HRMS ESI) 381.1461 $[M+H]^+$; calc. for $C_{26}H_{20}O_3$: 381.1491.

*4-(4-Butylbenzoyl)-1-phenylnaphthalen-2-yl Acetate (**6n**)*

Orange oil (12.7 mg, 21 % yield). δ_H (400 MHz, $CDCl_3$) 8.05 (d, *J* 8.1, 1H), 7.82 (d, *J* 8.3, 2H), 7.61–7.54 (m, 1H), 7.46–7.34 (m, 5H), 7.32–7.28 (m, 3H), 7.26–7.20 (m, 2H), 2.66–2.59 (m, 2H), 1.90 (s, 3H), 1.63–1.53 (m, 2H), 1.31 (dq, *J* 14.7, 7.3, 3H), 0.87 (t, *J* 7.3, 3H). δ_C (151 MHz, CD_2Cl_2) 168.47, 145.15, 144.45, 144.15, 142.33, 141.67, 134.88, 134.47, 131.46, 131.35, 128.92, 128.86, 128.72, 128.51, 128.49, 128.39, 128.32, 128.28, 128.18, 127.08, 126.91, 126.27, 35.93, 33.81, 22.75, 21.67, 14.09. ν_{max} (NaCl, neat)/cm^{-1} 2925, 2859, 1765, 1605, 1456, 1201. *m*/*z* (HRMS ESI) 423.1929 $[M+H]^+$; calc. for $C_{29}H_{26}O_3$: 423.19604.

*4-(4-Methoxybenzoyl)-1-phenylnaphthalen-2-yl Acetate (**6o**)*

Orange oil (42 mg, 25 % yield, obtained as inseparable mixture of **5o** and **6o** in a ratio 4 : 1). δ_H (400 MHz, CD_2Cl_2) 8.07–8.02 (m, 1H), 7.95–7.91 (m, 2H), 7.73–7.65 (m, 2H), 7.57–7.27 (m, 7H), 7.02–6.97 (m, 2H), 3.89 (s, 3H), 1.98 (s, 3H). δ_C (101 MHz, CD_2Cl_2) 169.89, 164.50, 156.57, 144.62, 142.18, 134.69, 133.12, 132.92, 131.29, 131.04, 130.51, 128.26, 128.22, 128.01, 126.98, 126.84, 126.17, 123.00, 87.21, 82.38, 79.16, 78.50, 56.01, 55.69, 21.67. ν_{max} (NaCl, neat)/cm^{-1} 3282, 2959, 2934, 2214, 2114, 1751, 1511, 1247, 1226. *m*/*z* (HRMS ESI) 397.1417 $[M+H]^+$; calc. for $C_{26}H_{20}O_4$: 397.1440.

*4-(1-Naphthoyl)-1-phenylnaphthalen-2-yl Acetate (**6q**)*

Yellow oil (12.9 mg, 31 % yield). δ_H (600 MHz, $CDCl_3$) 8.69 (d, *J* 8.4, 1H), 8.54 (d, *J* 8.5, 1H), 8.06 (d, *J* 8.2, 1H), 7.96 (d, *J* 7.6, 1H), 7.74 (dd, *J* 7.1, 1.1, 1H), 7.68 (d, *J* 8.5, 2H), 7.60 (ddd, *J* 8.1, 6.8, 1.3, 1H), 7.55 (ddd, *J* 8.4, 6.8, 1.4, 1H), 7.53–7.45 (m, 5H), 7.40 (s, 1H), 7.38–7.33 (m, 2H), 1.91 (s, 3H). δ_C (151 MHz, $CDCl_3$) 198.48, 169.59, 144.25, 138.36, 136.49, 135.37, 134.76, 134.19, 134.08, 133.14, 131.38, 130.18, 130.00, 128.66, 128.46, 128.29, 128.19, 127.39, 127.25, 126.90, 126.84, 126.17, 126.04, 125.74, 124.57, 14.27. ν_{max} (NaCl, neat)/cm^{-1} 2920, 1745, 1653, 1578, 1173. *m*/*z* (HRMS ESI) 417.1489 $[M+H]^+$; calc. for $C_{29}H_{20}O_3$: 417.1491.

*4-(4-Methylbenzoyl)-1-(4-(trifluoromethyl)phenyl)-naphthalen-2-yl Acetate (**6r**)*

Orange solid (20 mg, 35 % yield); mp 75.0–76.0°C. δ_H (600 MHz, $CDCl_3$) 8.12 (d, *J* 8.6, 1H), 7.87 (d, *J* 8.2, 2H), 7.79 (d, *J* 8.0, 2H), 7.56–7.44 (m, 6H), 7.37 (s, 1H), 7.32–7.29 (m, 2H), 2.45 (s, 3H), 2.00 (s, 3H). δ_C (151 MHz, $CDCl_3$) 196.25, 169.50, 144.88, 144.22, 138.85, 138.41, 135.26, 133.57, 132.25, 130.84, 130.82, 129.59, 129.52, 127.53, 127.03, 126.27, 126.20, 125.51, 125.48, 125.45, 125.43, 123.38, 123.02, 21.94, 20.67. ν_{max} (NaCl, neat)/cm^{-1} 2918, 1766, 1574, 1323, 1176. *m*/*z* (HRMS ESI) 365.1159 $[M+H]^+$; calc. for $C_{23}H_{15}F_3O$: 365.1153.

*4-Benzoyl-6-methoxy-1-phenylnaphthalen-2-yl Acetate (**6s**)*

Orange oil (30 mg, 35 % yield). δ_H (600 MHz, $CDCl_3$) 7.96 (d, *J* 7.2, 2H), 7.67 (d, *J* 2.5, 1H), 7.65–7.61 (m, 1H), 7.57–7.44 (m, 7H), 7.39 (s, 1H), 7.37–7.33 (m, 2H), 7.11 (dd, *J* 9.3, 2.6, 1H), 3.83 (s, 3H), 1.96 (s, 3H). δ_C (151 MHz, $CDCl_3$) 197.08, 169.83, 158.65, 142.43, 138.43, 134.93, 134.91, 134.89, 133.39, 131.28, 130.65, 130.15, 129.44, 128.70, 128.43, 128.31, 128.13, 125.15, 120.03, 104.28, 55.46, 20.63. ν_{max} (NaCl, neat)/cm^{-1} 2931, 1765, 1513, 1471, 1203. *m*/*z* (HRMS ESI) 397.1418 $[M+H]^+$; calc. for $C_{26}H_{20}O_4$: 397.1440.

*4-Benzoyl-1-phenylanthracen-2-yl Acetate (**6t**)*

White oil (3 mg, 41 % yield). δ_H (600 MHz, $CDCl_3$) 8.84 (s, 1H), 8.19 (s, 1H), 8.04 (s, 2H), 7.96–7.92 (m, 1H), 7.84–7.80 (m, 1H), 7.67–7.62 (m, 1H), 7.60–7.56 (m, 2H), 7.55–7.51 (m, 3H), 7.48–7.42 (m, 4H), 7.40 (s, 1H), 2.00 (s, 3H). δ_C (151 MHz, $CDCl_3$) 196.81, 169.77, 143.27, 138.21, 137.08, 134.95, 133.80, 133.64, 132.13, 132.04, 131.93, 130.75, 130.31, 128.78, 128.71, 128.61, 128.28, 127.56, 126.52, 126.31, 125.95, 125.48, 124.85, 29.90, 20.70, 14.28. ν_{max} (NaCl, neat)/cm^{-1} 1758, 1655, 1459, 1258. *m*/*z* (HRMS ESI) 417.1468 $[M+H]^+$; calc. for $C_{29}H_{20}O_3$: 417.1491.

*General Experimental Procedure for the Gold(I)-Catalysed Oxidative Cycloisomerisation of **5a***

To a reaction vessel containing the 1,6-diyne acetate substrate **5a** (41.2 mg, 0.1 mmol), $H_2{}^{18}O$ (6.4 μL, 0.3 mmol), and gold(I) phosphine complex **A** (4.5 mg, 5 mol-%) under atmospheric conditions was added CH_2Cl_2 (2 mL) and the resulting reaction mixture was stirred for 24 h. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc 14 : 1) to give an inseparable mixture of the 1-naphthyl ketone products **6a** and **6a′** (19.6 mg, 45 % yield).

Supplementary Material

^1H and ^{13}C NMR spectra for all starting materials and products are available on the Journal's website.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgements

This work was supported by a Discovery Project Grant (DP160101682) from the Australian Research Council.

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