Advanced Synthesis & Catalysis

Very Important Publication

DOI: 10.1002/adsc.201400849

Gold-Catalyzed Carbenoid Transfer Reactions of Diynes – Pinacol Rearrangement *versus* Retro-Buchner Reaction

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Received: August 27, 2014; Revised: November 19, 2014; Published online: ■■ ■■, 0000

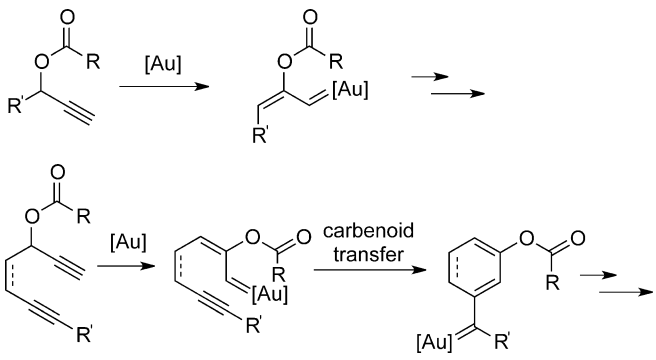
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201400849.

Abstract: Aromatic diyne systems bearing one terminal propargylic acetate moiety and one tertiary propargylic alcohol subunit were converted in the presence of a gold catalyst. After an initial 1,2-migration of the acetoxy group at the *terminal* alkyne, a gold carbenoid is formed which is then transferred onto the *internal* alkyne of the propargylic alcohol. This combination enables the use of propargylic acetates as precursors for a gold-catalyzed pinacol-type rearrangement. In the final pinacol-like step the shift of an alkyl or aryl moiety onto an electrophilic gold carbenoid/cation terminates the reaction and 1-naphthyl ketones are obtained as products. If electron-rich aromatic backbones are used, a mechanistically interesting alternative pathway including a retro-Buchner reaction is opened.

Keywords: carbenoid transfer; gold carbenoids; naphthalenes; pinacol rearrangement; retro-Buchner reaction

Introduction

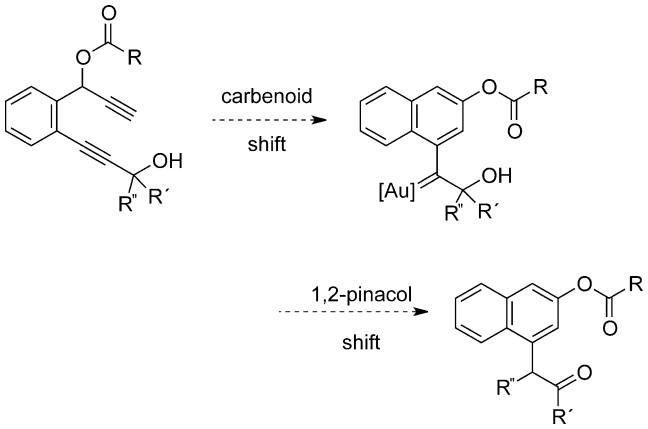
Among the key fundamental reactions in the field of gold catalysis, the generation of gold carbenoids *via* a 1,2-acyl migration of propargylic acetates plays an important role (Scheme 1, *upper part*). Due to the easy access to the starting materials combined with the diverse reactivity of the carbenoid centre, many useful organic transformations following this reactivity principle have been developed.[1]



Scheme 1. *Upper part:* generation of gold carbenoids *via* 1,2-acyl migration. *Lower part:* subsequent carbenoid transfer *via* a pendant alkyne.

A valuable expansion of this methodology was discovered only recently by the groups of Hirao/Chan, Oh and ourselves. If a second alkyne is offered in an appropriate distance, a transfer of the carbenoid is possible and further transformations with the newly generated vinyl gold carbenoids are possible (Scheme 1, *lower part*).[2] Carbenoid transfer reactions to an adjacent alkyne were also reported for gold carbenoids derived either from diazo compounds[3] or from *N*-oxides *via* intermolecular oxygen transfer.[4]

As a part of our studies concerning naphthyl gold carbenoids generated *via* carbenoid transfer reactions, we considered the possibility of a pinacol-type rearrangement as terminating step of the reaction cascade (Scheme 2). Pinacol-like reactions are known in the field of gold chemistry. So far the carbenoid intermediates were generated by oxygen transfer from *N*-oxides,[5] by an initial enyne cyclization,[6] or by the generation of allyl cations from allylic alcohol derivatives.[7] So far, no approaches using 1,2-acyl migrations have been reported, which is most probably based on the fact that internal alkynes, which would serve as



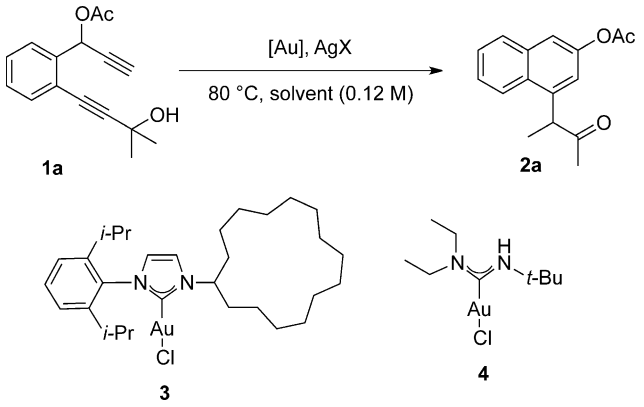
Scheme 2. Desired carbenoid shift/carbenoid transfer/pinacol rearrangement cascade.

precursors, are known to favour a competing allene formation *via* 1,3-acyl migration instead of the formation of a gold carbenoid.[8] We envisioned that diynes as starting materials would be ideal to circumvent this intrinsic problem. By employing this strategy, one could generate a gold carbenoid by a 1,2-acyl migration at one terminal alkyne, which can then be transferred by a carbenoid transfer onto a second internal alkyne that bears a propargylic subunit which eventually is able to undergo a pinacol-like rearrangement (Scheme 2).

Results and Discussion

For a screening of the reaction conditions we applied diyne **1a** which was available in three steps from 2-bromobenzaldehyde *via* a Sonogashira coupling, an addition of ethynylmagnesium bromide and an acylation. A first series of experiments with PPh_3AuNTf_2 in different solvents delivered only poor results (Table 1, entries 1–5), no matter whether preactivated or *in situ* generated catalysts were applied. A variation of the counterion at the gold catalyst gave a first improvement, but yields of about 15% with hexafluoroantimonate (entry 7) and with tetrafluoroborate (entry 8) were still unsatisfactory. Triflate gave only traces of product (entry 9). Simple gold chloride (entry 10) and complexes bearing Buchwald-type ligands (entries 11 and 12) showed only a minor improvement with yields up to 24%. The same was the case with the frequently used IPr ligand (entry 13). Slightly better results were obtained with unsaturated NHC complex **3** (entry 14).[9] By far the best results were obtained by the use of nitrogen acyclic carbene (NAC) **4** (entry 15).[10] Attempts to further improve the yield by changing the concentration (entries 16–18) failed. Finally, we tested the reaction with only a non-activated catalyst or with only the silver salt,

Table 1. Screening of the reaction conditions.



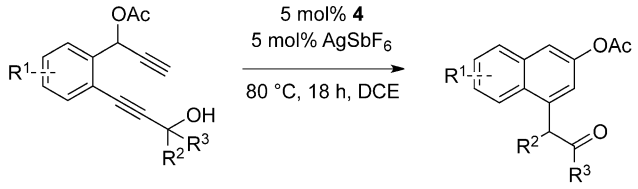
Entry	[Au] [5 mol%]	AgX [5 mol%]	Solvent	Yield[a]
1	PPh_3AuNTf_2	–	DCE	4%
2	PPh_3AuNTf_2	–	benzene	2%
3	PPh_3AuNTf_2	–	toluene	traces
4	PPh_3AuNTf_2	–	MeCN	traces
5	PPh_3AuCl	$AgNTf_2$	DCE	traces
6	PPh_3AuCl	$AgPF_6$	DCE	traces
7	PPh_3AuCl	$AgSbF_6$	DCE	18%
8	PPh_3AuCl	$AgBF_4$	DCE	15%
9	PPh_3AuCl	AgOTf	DCE	traces
10	AuCl	–	DCE	15%
11	XPhosAuCl	$AgSbF_6$	DCE	15%
12	SPhosAuCl	$AgSbF_6$	DCE	24%
13	IPrAuCl	$AgSbF_6$	DCE	23%
14	**3**	$AgSbF_6$	DCE	35%
15	**4**	**$AgSbF_6$**	**DCE**	**60%**
16[b]	**4**	$AgSbF_6$	DCE	41%
17[c]	**4**	$AgSbF_6$	DCE	40%
18[d]	**4**	$AgSbF_6$	DCE	traces
19	**4**	–	DCE	–
20	–	$AgSbF_6$	DCE	–

[a] Yield was determined by GCMS using hexamethylbenzene as internal standard.
[b] 0.06 M solution.
[c] 0.24 M solution.
[d] 0.48 M solution.

both of these control experiments showed no conversion (entries 19 and 20). A competing oligomerization/polymerization[11] is observed in all entries, accounting for the reduced yields. The reason for the superiority of the carbene complexes **3** and **4** is unknown.[12]

With the optimized conditions we evaluated the substrate scope. The results are summarized in Table 2. With test substrate **1a** a yield of 54% of the desired pinacol rearrangement product **2a** could be obtained (entry 1). A different picture was observed with aromatic backbones containing electron-rich oxygen donors as substituents. With substrates **1b–1d** (entries 2–4) mixtures of two different compounds were obtained. Unfortunately, the yields were unsatisfactory for these substrates. Besides the expected pi-

Table 2. Scope of the reaction.



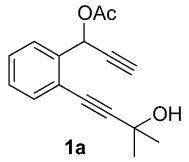
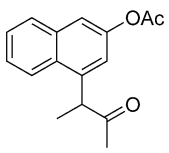
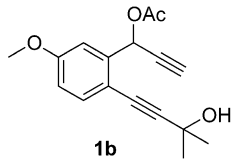
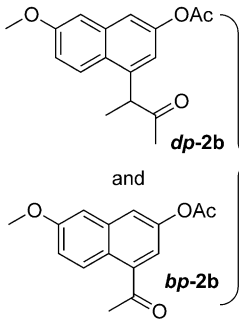
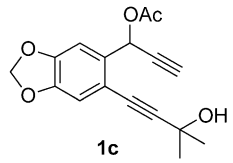
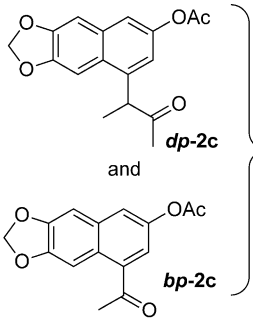
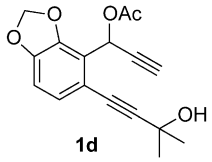
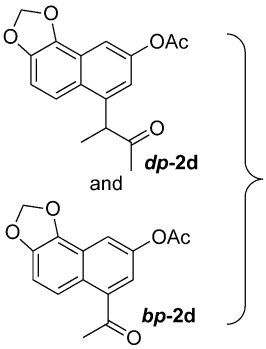
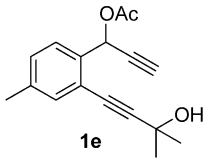
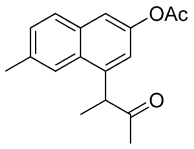
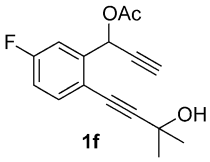
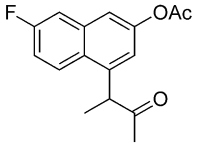
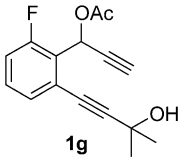
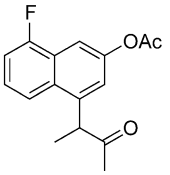
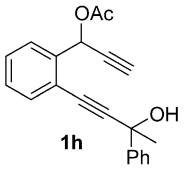
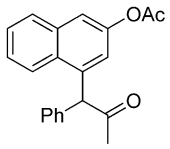
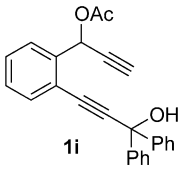
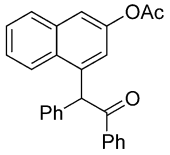
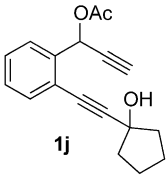
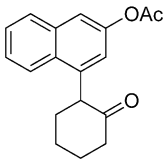
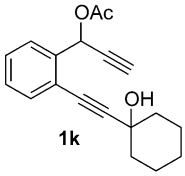
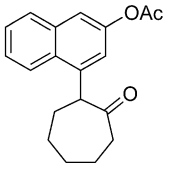
Entry	Substrate	Product (Yield)
1		 **2a** (54%)
2		 ***dp*-2b** and ***bp*-2b** (11%)[a]
3		 ***dp*-2c** and ***bp*-2c** (16%)[a]
4		 ***dp*-2d** and ***bp*-2d** (27%)[a]

Table 2. (Continued)

Entry	Substrate	Product (Yield)
5		 **2e** (54%)
6		 **2f** (22%)
7		 **2g** (37%)
8		 **2h** (33%)
9		 **1i** (54%)
10		 **2j** (41%)
11		 **2k** (62%)

[a] A mixture of the desired product (*dp*) and inseparable by-product (*bp*) was obtained

nacol-type product, a second product was obtained in significant amounts. Mass spectrometry revealed that a formal ethene elimination leads to this by-product. NMR analysis of the compounds together with the results of a X-ray crystal structure analysis allowed a safe structural assignment (Figure 1).[13] For all of the by-products two carbon atoms are missing and the acyl group is directly attached to the naphthalene system. A methyl substitution at the aromatic backbone selectively delivered the pinacol product in moderate yields (entry 5). Electron-deficient fluorine substituents were also tolerated, but yields were sig-

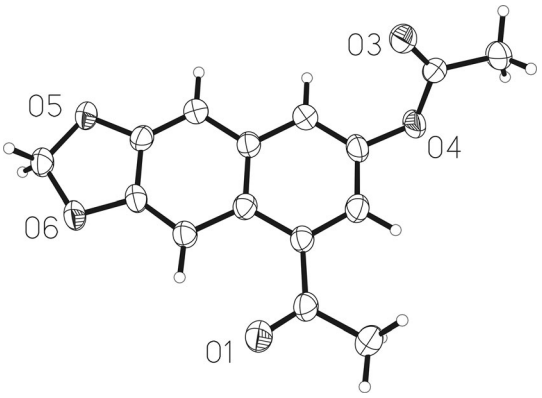


Figure 1. Solid state molecular structure of the by-product ***bp*-2c**.

nificantly lower (entries 6 and 7). Next we investigated different substitution patterns at the propargylic position. With mixed aromatic/aliphatic tertiary alcohol **1h** as the starting material, a selective migration of the phenyl group took place delivering product **2h** in moderate yield. Two phenyl groups in propargylic positions were also tolerated and product **2i** was obtained in comparable yield (54%) to the corresponding methyl-substituted substrate **2a**. Finally, we investigated the possibility of a ring expansion reaction. Fortunately both five- and six-membered ring systems could be converted leading to the corresponding six- and seven-membered products in yields of 41% (**2j**) and 62% (**2k**). The solid state molecular structure of **2k**, obtained by another X-ray crystal structure analysis, nicely confirms the constitution of the ring expansion product obtained (Figure 2).[13]

A plausible mechanistic picture[14] for the formation of the two products is depicted in Scheme 3. The reaction cascade is initiated *via* the known 1,2-acyl migration that delivers carbenoid **III** as intermediate. A subsequent cyclopropenation delivers key intermediate **IV**.[15] The ring opening of the so formed cyclopropene then determines the product selectivity. Path A describes the formation of the desired pinacol rearrangement product. Coordination of the cationic gold catalyst to the cyclopropene double bond delivers stabilized benzylic cation **V**, which under aromatization delivers naphthyl carbenoid **VI**. Finally, the reaction is terminated by an alkyl migration onto the electrophilic carbenoid carbon which delivers the desired products ***dp*-2**. Pathways B and C provide possible explanations for the formation of by-product ***bp*-2**. In the case of path B the gold catalyst adds to the opposite end of the cyclopropene double bond and the homoallyl cation **VII** is formed. Ring opening of the cyclopropyl unit then delivers gold carbenoid **IXa/b** which can also be regarded as a gold-stabilized tropylium cation. Pathway C would also lead to the same intermediate **IXa/b**, but breaking of the aromatic system under formation of bent allene **VIII** and subsequent addition to the cationic gold complex should be less favoured. The final sequence of both pathways B and C is initiated *via* an alkyl migration[16] onto the carbenoid carbon atom followed by a retro-Buchner reaction[17] from norcaradiene **XI** that is in equilibrium with cycloheptatriene **X**. Finally, by-product ***bp*-2** is formed under release of ethene and the gold catalyst.

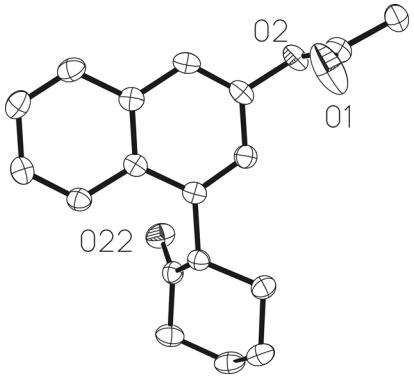


Figure 2. Solid state molecular structure of **2j**.

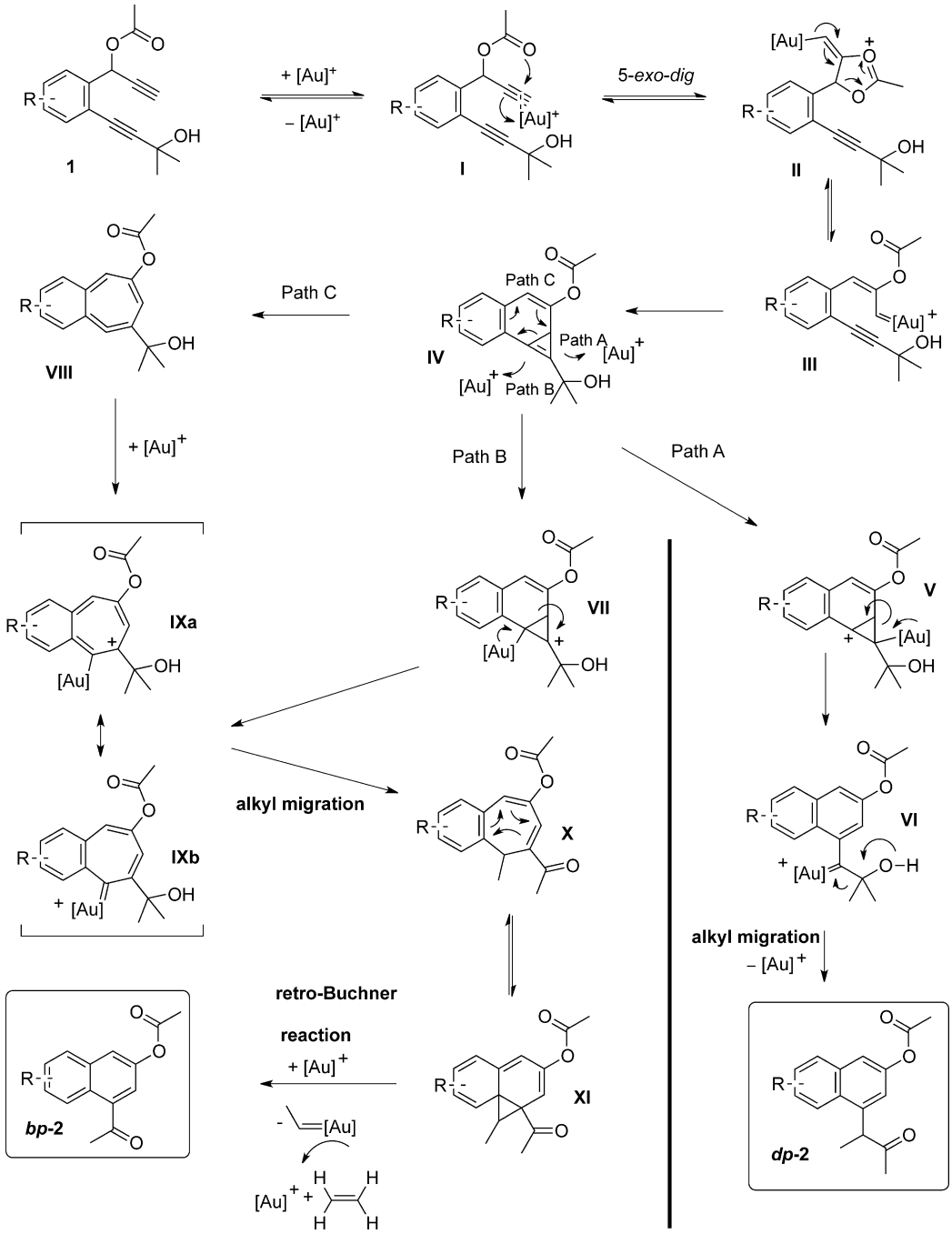
Conclusions

In conclusion, we have presented the first example of a gold-catalyzed pinacol-type reaction that is based on a 1,2-acetoxy migration as initiating step. By the use of diyne systems the gold carbenoid can be generated at one *terminal* alkyne (which is crucial for the formation of a gold carbenoid) and can then be transferred onto a second *internal* alkyne. This pendant tertiary propargyl alcohol subunit enables the pinacol rearrangement. In dependency of the substitution pattern of the aromatic backbone an alternative retro-Buchner reaction can take place under elimination of ethene.

Experimental Section

4-(2-Oxo-1,2-diphenylethyl)naphthalen-2-yl Acetate (2i)

120 mg (315 μmol) of **1i** were dissolved in 2.6 mL of DCE. 6.13 mg (15.8 μmol) of NACAuCl (**4**) and 5.42 mg (15.8 μmol) of $AgSbF_6$ were added and the mixture was stirred at 80 °C for 18 h. After this time the solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2, PE:EA, 10:1) to afford **2i** as a brown solid; yield: 65.0 mg (171 μmol, 54%). R_f (PE:EA = 5:1) = 0.08; ^{1}H NMR (500 MHz, C_6D_6): δ = 1.59 (s, 3H), 6.72 (s, 1H), 6.89 (t, J = 7.5 Hz, 2H), 6.95–7.00 (m, 2H), 7.05 (t, J = 7.6 Hz, 2H), 7.12–7.14 (m, 1H), 7.17–7.18 (m, 1H), 7.25 (d, J = 7.5 Hz, 2H), 7.37 (d, J = 2.3 Hz, 1H),



Scheme 3. Mechanistic proposal for the formation of the ethene elimination products.

7.50–7.52 (m, 2H), 7.98–8.01 (m, 3H); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 20.5$ (q), 56.3 (q), 60.1 (d), 119.0 (d), 123.3 (d), 126.5 (d), 126.7 (d), 127.6 (d), 128.9 (d, 2C), 129.1 (d, 2C), 129.1 (d, 2C), 129.3 (d), 130.1 (d, 2C), 133.1 (d), 133.1 (d), 135.2 (s), 137.1 (s), 138.2 (s), 138.2 (s), 148.7 (s), 168.4 (s), 197.4 (s); IR (film): $\nu = 3062$, 2933, 1759, 1682, 1625, 1598, 1581, 1512, 1495, 1448, 1431, 1394, 1367, 1294, 1271, 1200, 1131, 1078, 1032, 1013, 912, 887, 845, 800, 774, 745, 726, 696, 657, 626 cm^{-1}; HR -MS [DART (+)]: $m/z = 398.1770$, calcd. for $[C_{26}H_{24}O_3N]^+$, $[M+NH_4]^+$: 398.1756.

4-(2-Oxocycloheptyl)naphthalen-2-yl Acetate (2k)

120 mg (405 μmol) of **1k** were dissolved in 3.40 mL of DCE. 7.87 mg (20.3 μmol) of NACAuCl and 6.96 mg (20.3 μmol) of $AgSbF_6$ were added and the mixture was stirred at 80 °C for 16 h. After this time the solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2, PE:EA, 10:1) to afford **2k** as an orange oil; yield: 74.0 mg (250 μmol, 62%). R_f (PE:EA = 5:1) = 0.09; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.46$–1.65 (m, 3H), 1.76–1.86 (m, 1H), 2.02- 2.14 (m, 3H), 2.24–2.31 (m, 1H), 2.35 (s, 3H), 2.66–2.73 (m, 1H), 2.76–2.83 (m, 1H),

4.58 (dd, $J=11.1$ Hz, $J=3.5$ Hz, 1H),7.18 (d, $J=2.3$ Hz, 1H), 7.47–7.51 (m, 3H), 7.79–7.81 (m, 1H), 7.97–7.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=21.4$ (q), 25.2 (t), 29.4 (t), 29.9 (t), 32.1 (t), 43.3 (t), 53.7 (d), 118.0 (d), 120.5 (d), 123.6 (d), 126.1 (d), 126.5 (d), 128.9 (d), 129.9 (s), 134.5 (s), 139.4 (s), 148.0 (s), 169.9 (s), 213.0 (s); IR (film): $\nu=3503$, 3066, 2391, 2856, 1768, 1705, 1625, 1602, 1582, 1512, 1454, 1432, 1392, 1369, 1344, 1315, 1218, 1169, 1150, 1131, 1014, 983, 934, 915, 889, 843, 799, 773, 745 cm^{-1}; HR-MS [DART (+)]: $m/z=314.1759$, calcd. for $[C_{18}H_{22}O_3N]^+$, $[M+NH_4^+]$: 314.1756.

Acknowledgements

H.T. is grateful for support by the "Engineering Science Student Dispatch Program" of the Graduate School of Engineering Science, Osaka University. Gold salts were generously donated by Umicore AG & Co. KG.

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