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Regioselectivity Switch: Gold(I)-Catalyzed Oxidative Rearrangement of Propargyl Alcohols to 1,3-Diketones

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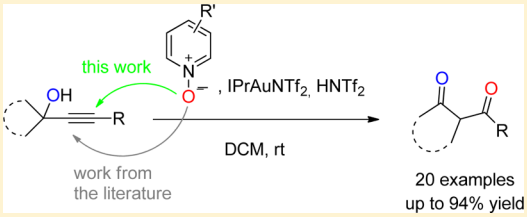
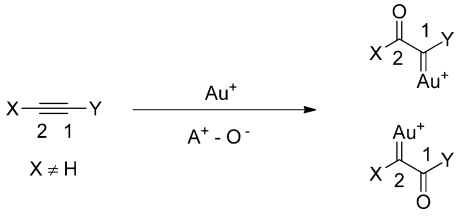
Supporting Information

ABSTRACT: The gold(I)-catalyzed oxidative rearrangement of propargyl alcohols provides an efficient and selective route to 1,3-diketones under mild conditions. Pyridine-*N*-oxides were used as external oxidants with, different from related substrates, no alkylidenecycloalkanones or oxetan-3-ones formed as side-products.



In the recent past, gold-catalyzed oxidative rearrangements have significantly enriched the arsenal of gold-catalyzed methodology for organic synthesis.[1] Diphenylsulfoxide, pyridine-*N*-oxides and nitrones are often used as *O*-donors in the oxidative rearrangements of alkyne-containing substrates, such as 1,6-enynes,[2] 1,5-enynes,[3] propargyl esters,[2a] alkynylcyclopropanes,[4] homopropargylic alcohols[5] and propargyl alcohols.[6] α-Carbonyl carbenoids are proposed as common key intermediates in these reactions (Scheme 1) undergoing an

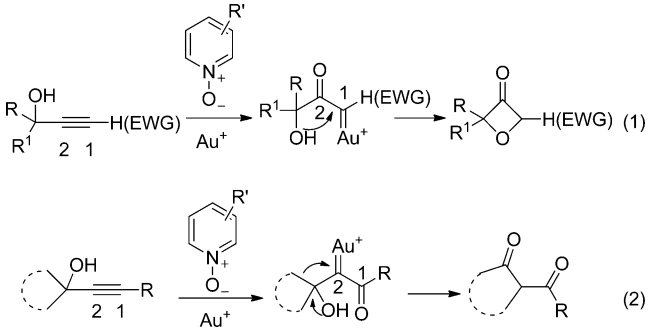
Scheme 1. Generation of α-Carbonyl Carbenoids



array of versatile transformations. In this process, terminal alkynes (Y = H) favor the oxidation at the C2 alkynyl carbon atom but internal alkynes (Y ≠ H) show little selectivity.[7]

In 2010, Liming Zhang et al. reported the gold-catalyzed synthesis of oxetan-3-ones from propargyl alcohols and pyridine-*N*-oxides via the C2 carbonylated α-carbonyl carbenoids (Scheme 2, eq 1).[6c] In their work, terminal alkynes showed high selectivity in the transformation of secondary propargyl alcohols and a primary alcohol, but for the transformation of tertiary alcohols, electron withdrawing groups were required at the alkyne terminus. We envisioned that by changing the groups at the alkyne terminus, 1,3-diketones should be obtained via the C1 carbonylated α-carbonyl carbenoids (Scheme 2, eq 2). As part of our efforts to develop gold-catalyzed reactions and mechanistic aspects,[8] we herein report a different regio-selectivity for the gold(I)-catalyzed oxidative rearrangement of propargyl alcohols to 1,3-diketones, by using pyridine-*N*-oxides as external oxidants. 1,3-Diketones

Scheme 2. Known Reactivity Pattern (eq 1) and Initial Hypothesis for a Switch in Chemoselectivity by Introducing the R Group (eq 2)



are important intermediates for various heterocyclic compounds[9] and key structural units in many chelating ligands for lanthanide and transition metals.[10]

We began our study by examining 1-(phenylethynyl)-cyclobutanol (**1a**) and 3,5-dichloropyridine-1-oxide (**2a**) in presence of various gold(I) catalysts (Table 1, entries 1−5). To our delight, the desired product 2-benzoylcyclopentanone (**3a**) was obtained in moderate yields, and no formation of oxetan-3-one was observed. Among the gold catalysts, $IPrAuNTf_2$ gave the best result (entry 3, 65%) and was chosen for the screening of a series of different pyridine-*N*-oxides. But no improvement of the yield was possible (entries 6−8). When relatively electron-rich pyridine *N*-oxides were added, the consumption of the starting material was incomplete. It was assumed that the basic pyridine derivative formed during the reaction was inhibiting the gold catalyst;[5] thus, acid was added to retain the catalytic activity. Indeed, the reaction proceeded well when triflimide ($HNTf_2$) was added as additive in combination with 4-picoline-*N*-oxide (**2b**), 2-benzoylcyclopentanone (**3a**) was

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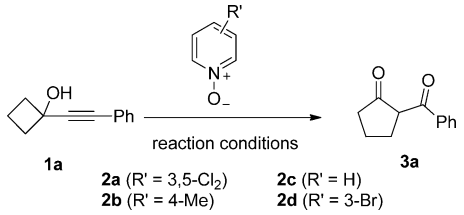
Table 1. Optimization of the Reaction Conditions[a]



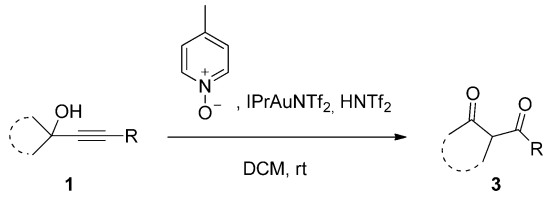
entry	catalyst	*N*-oxide	acid	solvent/time (h)	yield (%)[b]
1	$Ph_3PAuCl/AgNTf_2$	**2a**		DCM/19	40 (45)
2	$Ph_3PAuCl/AgSbF_6$	**2a**		DCM/10	60
3	$IPrAuCl/AgNTf_2$	**2a**		DCM/19	65
4	$IPrAuCl/AgSbF_6$	**2a**		DCM/5	56
5	IPrAuCl/AgOTf	**2a**		DCM/19	35 (51)
6	$IPrAuCl/AgNTf_2$	**2b**		DCM/19	46 (50)
7	$IPrAuCl/AgNTf_2$	**2c**		DCM/19	43 (50)
8	$IPrAuCl/AgNTf_2$	**2d**		DCM/19	38 (48)
9	$Ph_3PAuCl/AgSbF_6$	2b	$HNTf_2$	DCM/16	83
10	**$IPrAuCl/AgNTf_2$**	**2b**	**$HNTf_2$**	**DCM/16**	**85**
11	$IPrAuCl/AgNTf_2$	**2a**	$HNTf_2$	DCM/16	69
12	$IPrAuCl/AgNTf_2$	**2b**	$HNTf_2$	DCE/16	80
13	$IPrAuCl/AgNTf_2$	**2b**	$HNTf_2$	CH_3CN/16	51 (40)
14	$IPrAuCl/AgNTf_2$	**2b**	$HNTf_2$	THF/16	61 (32)
15	$IPrAuCl/AgNTf_2$	**2b**	$HNTf_2$	Toluene/16	49
16	$IPrAuCl/AgNTf_2$	**2b**	PTSA	DCM/26	76
17	$IPrAuCl/AgNTf_2$	**2b**	MsOH	**DCM/20**	80
18	$IPrAuCl/AgNTf_2$	**2b**	TFA	**DCM/24**	77

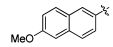
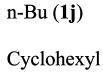
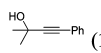
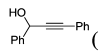
[a]Reaction conditions: **1a** (400 μmol), **2** (800 μmol), [Au/Ag] (5.0 mol %), acid (480 μmol, if added in the reaction), solvent (4 mL), room temperature. [b]Percentage of **1a** recovered after column is in parentheses.

obtained in 85% yield after 16 h (entry 10), and the same reaction with the PPh_3 ligand on gold gave a slightly lower yield (entry 9). The yield was slightly improved when triflimide was added with 3,5-dichloropyridine-1-oxide (**2a**) (entry 11). Different solvents were examined but failed to improve the reaction (entries 12−15). A comparative study with PTSA (entry 16), MsOH (entry 17) and TFA (entry 18) gave no superior results. Thus, 5 mol % of $IPrAuNTf_2$, 2 equivalents of 4-picoline-*N*-oxide (**2b**) and 1.2 equivalents of triflimide in dichloromethane at room temperature were chosen as the optimal conditions for the transformation of propargyl alcohols to 1,3-diketones. The role of the acid might simply be to protonate the pryidine that is set free in the course of the reaction—it is only important that the acid forms a weakly coordinating conjugated base in order to avoid deactivation of the catalyst. With less than 1 equivalent of acid, no efficient conversion is observed.

Under these optimized reaction conditions, a wide variety of propargyl alcohols **1** were examined and the results are summarized in Table 2. First, cyclobutanols bearing various ethynyl groups were examined (entries 1−11). The reaction of this type of substrate proceeded smoothly to deliver the oxidation/ring-expansion products in moderate to excellent yields, no matter if the substituents at the acetylenic terminus were aromatic groups (entries 1−8) or alkyl groups (entries 9−11). To expand the substrate scope, different cycloalkanols were then tested (entries 12−16). Cyclopropanol derivative (**1m**) gave the expected product 2-benzoylcyclobutanone (**3m**)

Table 2. Scope of the Reaction of Propargyl Alcohols[a]



Entry	**1**	Time (h)	**3**	Yield (%)
1	R=4-MeC_6H_4 (**1b**)	25	**3b**	83
2	4-$OMeC_6H_4$ (**1c**)	19	**3c**	79
3	4-FC_6H_4 (**1d**)	21	**3d**	80
4	3-ClC_6H_4 (**1e**)	24	**3e**	84
5	3,5-$(OMe)_2C_6H_3$ (**1f**)	25	**3f**	81
6	3,5-$(CF_3)_2C_6H_3$ (**1g**)	75	**3g**	59
7	2,4,5-$(CH_3)_3C_6H_4$ (**1h**)	68	**3h**	70
8	 (**1i**)	22	**3i**	94
9	n-Bu (**1j**)	25	**3j**	71
10	Cyclohexyl (**1k**)	20	**3k**	66
11	 (**1l**)	30	**3l**	61
12[b]	n = 0 (**1m**)	19	**3m**	35(82)[c]
13	n = 2 (**1n**)	24		NR[d]
14	n = 3 (**1o**)	24		NR[d]
15	n = 9 (**1p**)	24	**3p**	65
16	n = 12 (**1q**)	24	**3q**	70
17	 (**1r**)	20	 **3r**	78
18	 (**1s**)	24	 **3s**	50
			 **3s'**	26
19	 (**1t**)	24	 **3t**	80%
			 **3t'**	(**3t**+**3t'**)[e]
20	 (**1u**)	28	 **3u**	57
			 **3u'**	16

[a]Reaction conditions: **1** (400 μmol), **2b** (800 μmol), $IPrAuNTf_2$ (5.0 mol %), $HNTf_2$ (480 μmol), DCM (4 mL). [b]**2d** was used as oxidant and no $HNTf_2$ was added. [c]NMR yield, CH_2Br_2 was added as an internal standard, and the product is not stable upon column chromatography.[12] [d]No reaction. [e]**3t**/**3t'** = 10:1.

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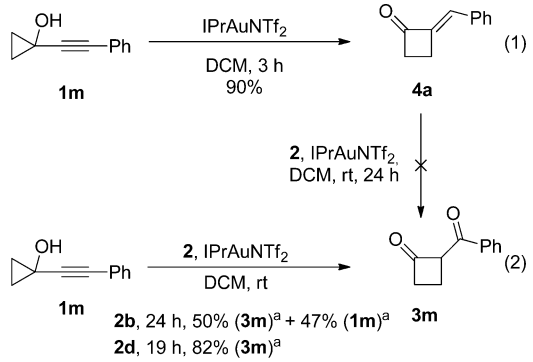
in 82% NMR yield. Unfortunately, cyclopentanol (**1n**) and cyclohexanol derivative (**1o**) could not undergo the reaction under the reaction conditions. The ring strain of cyclobutanol and cyclopropanol, which usually is the driving force for the ring expansion of these small ring compounds, might explain these results. The larger steric hindrance of cyclopentanol and cyclohexanol if compared to cyclobutanol and cyclopropanol might play a role, too.[11] To further investigate the reaction, more flexible cycloalcohol substrates were examined under the same reaction conditions. To our delight, they were converted with good yields to the corresponding diketone products (entries 15 and 16). This indicates that, in addition to angular strain, steric hindrance of the substrates is also a crucial factor in the reaction. Noncyclic alcohols were examined last. 2-Methyl-4-phenylbut-3-yn-2-ol (**1r**) gave the 1,2-methyl shift product (**3r**) in 78% yield (entry 17). Hydride migration was favored in the reaction of 4-phenylbut-3-yn-2-ol (**1s**) (entry 18) but was less favored in 1,3-diphenylprop-2-yn-1-ol (**1t**) (entry 19). The phenyl group showed stronger migration ability than the methyl group in 2,4-diphenylbut-3-yn-2-ol (**1u**) (entry 20) as well. The migration ability inferred from the results of entries 18 and 19 (Ph > H > CH_3) was not corroborated by the results of entries 19 and 20, where methyl migration is slightly favored over hydride.

In 2005, Toste et al. reported a gold(I)-catalyzed ring expansion of cyclopropanols and cyclobutanols to alkylidenecycloalkanones,[13] but such products were not observed in the oxidative rearrangement process described here. It is noteworthy that some of the substrates are prone to undergo ring expansion in the absence of the oxidant to give alkylidenecycloalkanones. For example 1-(phenylethynyl)cyclopropanol (**1m**) was rapidly converted to (**4a**) in presence of $IPrAuNTf_2$ (Scheme 3, eq 1), while in the presence of the oxidant **2** the

Scheme 3. Product 4a from the Gold-catalyzed Rearrangement of 1m Does Not Provide 3m with the Gold Catalyst and 2

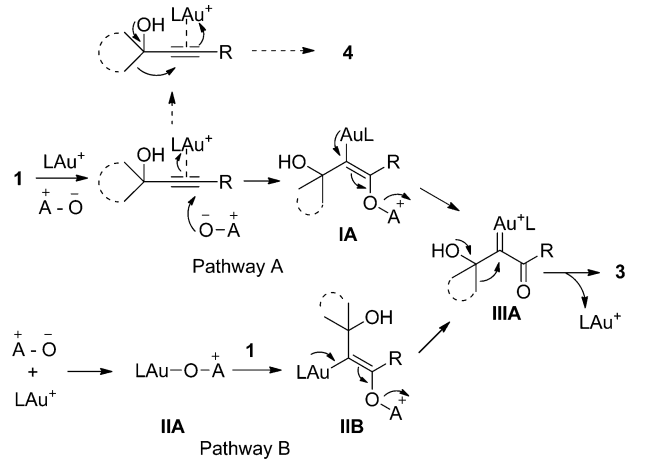


[a]NMR yield, CH_2Br_2 was added as an internal standard.

dicarbonyl compound **3m** is formed (Scheme 3, eq 2). The conversion of **4a** to **3m** under these oxidative conditions (**2**, $IPrAuNTf_2$) is not possible.

Two plausible pathways that account for the oxidative rearrangement of propargyl alcohols are depicted in Scheme 4. In pathway A, coordination of the cationic gold(I) to the alkyne moiety induces the nucleophilic attack of pyridine-*N*-oxide on the triple bond to give vinyl-gold intermediate **IA**, which undergoes fragmentation to gold carbenoid **IIIA**. Rearrangement of gold carbenoid **IIIA** finally affords the 1,3-diketone (**3**).

Scheme 4. Plausible Mechanisms for the Conversion of 1 to 3



In pathway B, pyridine-*N*-oxide coordinates to cationic gold(I) to form gold complex **IIA**. Syn addition of this moiety to the alkyne gives vinyl-gold intermediate **IIB**, which undergoes fragmentation to gold carbenoid **IIIA** and, finally, to 1,3-diketone (**3**).

Generally in this type of gold-catalyzed alkyne oxidation, an α-carbonyl carbenoid is proposed to be generated from nucleophilic attack of *N*-oxide on alkyne which is activated by cationic gold catalyst (pathway A). However, coordination of the gold complex to the alkyne moiety is liable to undergo intramolecular reaction leading to alkylidenecycloalkanone (**4**), which was not observed in the reaction. Calculations predicted that coordination of gold to the *N*-oxide was favored over coordination to the alkyne in an intramolecular oxidative rearrangement of acetylenic amine *N*-oxide.[14] Thus, pathway B is considered as a reasonable mechanism for this reaction. Efforts to grow single crystals of *N*-oxide complex of gold failed; but the coordination of *N*-oxide to the gold complex was indeed revealed by a series of NMR experiments[15] (Supporting Information).

CONCLUSION

We have developed an efficient gold(I)-catalyzed oxidative rearrangement of propargyl alcohols to 1,3-diketones under mild conditions. Pyridine-*N*-oxides were used as external oxidants. The reaction shows high selectivity to 1,3-diketones and no alkylidenecycloalkanones[13] or oxetan-3-ones[6c] were observed. NMR experiments indicated a coordination of the gold catalyst to pyridine-*N*-oxide.

EXPERIMENTAL SECTION

Propargyl Alcohols Were Prepared According to Literature Procedures.[16] To a solution of terminal alkyne (6 mmol) in tetrahydrofuran (30 mL), *n*-butyllithium (2.5 M in hexane, 2.4 mL, 6 mmol) was added dropwise by syringe at −78 °C. After stirring for 30 min, a solution of ketone (5 mmol) in THF (5 mL) was added dropwise and the mixture stirred at the same temperature for 1 h. The solution was allowed to warm to room temperature and was quenched with saturated aqueous NH_4Cl and was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over magnesium sulfate and concentrated under vaccuo. The crude residue was purified by flash chromatography on silica gel (petrol ether/EtOAc) to give the expected propargyl alcohol.

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*1-(Phenylethynyl)cyclobutanol (**1a**).* Yield: 732 mg, 85%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46−7.42 (m, 2 H); 7.33−7.28 (m, 3 H); 2.58−2.30 (m, 5 H); 1.93−1.82 (m, 2 H). **1a** is known.[17]

*1-(p-Tolylethynyl)cyclobutanol (**1b**).* Yield: 810 mg, 87%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (d, 2 H, J = 8.1 Hz); 7.10 (d, 2 H, J = 7.9 Hz); 2.57−2.48 (m, 3 H), 2.40−2.29 (m, 5 H), 1.92−1.81 (m, 2 H). **1b** is known.[16]

*1-((4-Methoxyphenyl)ethynyl)cyclobutanol (**1c**).* Yield: 800 mg, colorless oil, 79%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39−7.34 (m, 2 H); 6.85−6.80 (m, 2 H); 3.80 (s, 3 H), 2.56−2.46 (m, 2 H); 2.42 (br, 1 H), 2.38−2.28 (m, 2 H); 1.91−1.80 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.6, 133.1, 114.8, 113.9, 91.1, 83.3, 68.4, 55.2, 38.7, 12.9 ppm, IR (film): $\tilde{\nu}$ = 3373, 2992, 2941, 2838, 2228, 1607, 1572, 1510, 1462, 1442, 1419, 1286, 1249, 1175, 1155, 1107, 1031, 961, 914, 833, 807, 596, 542, 470 cm^{-1}; HRMS (EI+): $C_{13}H_{14}O_2$ calcd 202.0994; found 202.0998.

*1-((4-Fluorophenyl)ethynyl)cyclobutanol (**1d**).* Yield: 856 mg, colorless oil, 90%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45−7.38 (m, 2 H); 7.04−6.96 (m, 2 H); 2.57−2.47 (m, 2 H); 2.39−2.28 (m, 3 H); 1.92−1.81 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.5 (d, J_{FC} = 247.5 Hz), 133.6 (d, J_{FC} = 8.3 Hz), 118.8 (d, J_{FC} = 3.8 Hz), 115.5 (d, J_{FC} = 21.8 Hz), 92.2 (d, J_{FC} = 1.5 Hz), 82.4, 68.3, 38.6, 12.9 ppm, IR (film): $\tilde{\nu}$ = 3344, 2992, 2944, 2875, 2366, 1893, 1601, 1507, 1422, 1294, 1231, 1155, 1109, 1013, 962, 915, 836, 817, 591, 538, 453 cm^{-1}; HRMS (EI+): $C_{12}H_{11}FO$ calcd 190.0794; found 190.0755.

*1-((3-Chlorophenyl)ethynyl)cyclobutanol (**1e**).* Yield: 753 mg, colorless oil, 75%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49−7.48 (m, 1 H); 7.34−7.28 (m, 3 H); 2.63−2.52 (m, 3 H); 2.46−2.35 (m, 2 H); 1.99−1.93 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.1, 131.5, 129.7, 129.5, 128.5, 124.4, 93.7, 82.1 68.2, 38.5, 12.9 ppm, IR (film): $\tilde{\nu}$ = 3322, 3068, 2993, 2944, 2873, 2849, 1593, 1562, 1475, 1207, 1302, 1288, 1245, 1213, 1158, 1112, 1091, 1079, 998, 963, 929, 881, 808, 784, 708, 682, 477 cm^{-1}; HRMS (EI+): $C_{12}H_{11}ClO$ calcd 206.0498; found 206.0520.

*1-((3,5-Dimethoxyphenyl)ethynyl)cyclobutanol (**1f**).* Yield: 894 mg, colorless oil, 77%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.58 (d, 2 H, J = 2.4 Hz); 6.42 (t, 1 H, J = 2.4 Hz); 3.76 (s, 6 H), 2.76 (br, 1 H), 2.56−2.46 (m, 2 H); 2.39−2.28 (m, 2 H); 1.91−1.80 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.4 124.0, 109.4, 101.7, 92.1, 83.3, 68.2, 55.3, 38.5, 12.9 ppm, IR (film): $\tilde{\nu}$ = 3386, 2994, 2940, 2839, 1597, 1457, 1421, 1352, 1301, 1261, 1206, 1178, 1157, 1107, 1065, 992, 954, 928, 895, 834, 703, 682, 654, 540 cm^{-1}; HRMS (EI+): $C_{14}H_{16}O_3$ calcd 232.1099; found 232.1078.

*1-((3,5-Bis(trifluoromethyl)phenyl)ethynyl)cyclobutanol (**1g**).* Yield: 1.16 g, white crystalline solid, 75%; mp 36−37 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (s, 2 H); 7.80 (s, 1 H); 2.60−2.50 (m, 2 H); 2.42−2.31 (m, 3 H); 1.96−1.85 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.9 (q, J_{FC} = 33.5 Hz), 131.6 (d, J_{FC} = 3.0 Hz), 125.1, 122.9 (q, J_{FC} = 271.0 Hz), 121.8−121.6 (m, 1 C), 96.1, 80.7, 68.2, 38.4, 13.0 ppm, IR (KBr): $\tilde{\nu}$ = 3556, 3399, 2999, 2947, 1616, 1464, 1384, 1281, 1247, 1176, 1135, 1107, 969, 898, 848, 700, 684, 424 cm^{-1}; HRMS (EI+): $C_{14}H_{10}F_6O$ calcd 308.0636; found 308.0630.

*1-((2,4,5-Trimethylphenyl)ethynyl)cyclobutanol (**1h**).* Yield: 868 mg, colorless oil, 81%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19 (s, 1 H); 6.97 (s, 1 H); 2.57−2.49 (m, 2 H); 2.42−2.31 (m, 6 H); 2.23 (s, 3 H); 2.19 (s, 3 H); 1.93−1.82 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.4, 137.1, 133.6, 132.8, 130.8, 119.6, 95.5, 82.5, 68.5, 38.9, 19.9, 19.6, 19.0, 12.9 ppm, IR (film): $\tilde{\nu}$ = 3326, 2989, 2941, 2869, 2222, 1617, 1504, 1455, 1422, 1381, 1297, 1246, 1161, 1116, 1070, 1000, 960, 910, 877, 795, 710, 528, 503, 457 cm^{-1}; HRMS (EI+): $C_{15}H_{18}O$ calcd 214.1358; found 214.1345.

*1-((6-Methoxynaphthalen-2-yl)ethynyl)cyclobutanol (**1i**).* Yield: 883 mg, white crystalline solid, 70%; mp 103−104 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (s, 1 H); 7.69−7.64 (m, 2 H); 7.45 (dd, 1 H, J = 1.8 Hz, 8.5 Hz); 7.17−7.09 (m, 2 H); 3.92 (s, 3 H); 2.62−2.53 (m, 2 H); 2.43−2.32 (m, 3 H); 1.96−1.85 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.3, 134.1, 131.4, 129.3, 129.0, 128.4, 126.7, 119.4, 117.6, 105.8, 92.1, 83.9, 68.4, 55.3, 38.7, 13.0 ppm, IR (KBr): $\tilde{\nu}$ = 3368, 2993, 2942, 2846, 1628, 1601, 1499, 1483, 1464, 1410, 1387, 1370, 1330, 1292, 1259, 1227, 1197, 1184, 1164, 1151, 1122, 1112, 1025, 971, 961, 942, 889, 859, 813, 755, 702, 666, 539, 476, 424 cm^{-1}; HRMS (EI+): $C_{17}H_{16}O_2$ calcd 252.1150; found 252.1156.

*1-(Hex-1-yn-1-yl)cyclobutanol (**1i**).* Yield: 518 mg, colorless oil, 68%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41−2.31 (m, 2 H); 2.27−2.17 (m, 5 H); 1.82−1.71 (m, 2 H), 1.54−1.34 (m, 4 H), 0.91 (t, 3 H, J = 7.1 Hz). **1j** is known.[18]

*1-(Cyclohexylethynyl)cyclobutanol (**1k**).* Yield: 606 mg, colorless oil, 68%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.44−2.31 (m, 3 H); 2.28−2.17 (m, 3 H); 1.82−1.64 (m, 6 H); 1.55−1.22 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 88.1, 83.8, 68.1, 38.9, 32.7, 29.0, 25.9, 24.8, 12.8 ppm, IR (film): $\tilde{\nu}$ = 3323, 2989, 2932, 2854, 2664, 2232, 1448, 1422, 1363, 1318, 1299, 1246, 1175, 1125, 1065, 1012, 979, 955, 933, 891, 850, 823, 778, 738, 641, 515, 480, 422 cm^{-1}; HRMS (EI+): $C_{12}H_{18}O$ calcd 178.1358; found 178.1359.

*1-(3-Phenoxyprop-1-yn-1-yl)cyclobutanol (**1l**).* Yield: 708 mg, colorless oil, 70%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34−7.26 (m, 2 H); 7.02−6.97 (m, 3 H); 4.74 (s, 2 H), 2.45−2.19 (m, 5 H); 1.88−1.75 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.7, 129.4, 121.4, 115.0, 90.8, 78.4, 67.8, 56.2, 38.2, 12.8 ppm, IR (film): $\tilde{\nu}$ = 3346, 3064, 2992, 2945, 2871, 2243, 1937, 1598, 1495, 1456, 1422, 1375, 1337, 1304, 1265, 1216, 1175, 1125, 1080, 1046, 1008, 990, 957, 886, 811, 778, 754, 691, 645, 507 cm^{-1}; HRMS (EI+): $C_{13}H_{14}O_2$ calcd 202.0994; found 202.1016.

*1-(Phenylethynyl)cyclopropanol (**1m**).* Yield: 475 mg, colorless oil, 60%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44−7.38 (m, 2 H); 7.33−7.27 (m, 3 H); 2.61 (br, 1 H), 1.21−1.07 (m, 4 H). **1m** is known.[19]

*1-(Phenylethynyl)cyclopentanol (**1n**).* Yield: 829 mg, colorless oil, 89%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54−7.39 (m, 2 H); 7.32−7.27 (m, 3 H); 2.11−1.98 (m, 5 H); 1.94−1.72 (m, 4 H). **1n** is known.[20]

*1-(Phenylethynyl)cyclohexanol (**1o**).* Yield: 851 mg, colorless oil, 85%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45−7.40 (m, 2 H); 7.32−7.27 (m, 3 H); 2.17 (br, 1 H), 2.04−1.95 (m, 2 H); 1.77−1.56 (m, 7 H); 1.32−1.26 (m, 2 H). **1o** is known.[17]

*1-(Phenylethynyl)cyclododecanol (**1p**).* Yield: 1.04 g, 73%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45−7.38 (m, 2 H); 7.32- 7.27 (m, 3 H); 1.99−1.89 (m, 2 H); 1.83−1.72 (m, 3 H); 1.61−1.56 (m, 2 H), 1.38 (s, 16 H). **1p** is known.[20]

*1-(Phenylethynyl)cyclopentadecanol (**1q**).* Yield: 1.14 g, white crystalline solid, 70%; mp 52−53 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45−7.39 (m, 2 H); 7.32−7.27 (m, 3 H); 1.94 (s, 1 H), 1.88−1.79 (m, 4 H); 1.46−1.35 (m, 24 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.7, 128.2, 128.1, 122.9, 93.5, 83.5, 71.3, 39.7, 27.4, 26.9, 26.7, 26.7, 26.4, 22.2 ppm, IR (film): $\tilde{\nu}$ = 3382, 3057, 2930, 2856, 1741, 1599, 1573, 1490, 1459, 1445, 1373, 1351, 1253, 1154, 1070, 1045, 1001, 940, 914, 756, 691, 591, 525 cm^{-1}; HRMS (EI+): $C_{23}H_{34}O$ calcd 326.2610; found 326.2602.

*2-Methyl-4-phenylbut-3-yn-2-ol (**1r**).* Yield: 609 mg, 76%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43−7.39 (m, 2 H); 7.32−7.27 (m, 3 H); 2.03 (s, 1 H), 1.62 (s, 6 H). **1r** is known.[17]

*4-Phenylbut-3-yn-2-ol (**1s**).* Yield: 446 mg, 61%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45−7.41 (m, 2 H); 7.33−7.28 (m, 3 H); 4.76 (q, 1 H, J = 6.6 Hz), 2.01 (br, 1 H); 1.55 (d, 3 H, J = 6.6 Hz). **1s** is known.[21]

*1,3-Diphenylprop-2-yn-1-ol (**1t**).* Yield: 833 mg, 80%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65−7.61 (m, 2 H); 7.51−7.30 (m, 8 H); 5.70 (d, 1 H, J = 6.3 Hz), 2.36 (d, 1 H, J = 6.3 Hz). **1t** is known.[17]

*2,4-Diphenylbut-3-yn-2-ol (**1u**).* Yield: 834 mg, 75%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77−7.73 (m, 2 H); 7.53−7.46 (m, 2 H); 7.43−7.29 (m, 6 H); 2.55 (s, 1 H); 1.89 (s, 3 H). **1u** is known.[22]

Typical Procedure for Gold(I)-Catalyzed Oxidative Rearrangement of Propargyl Alcohols. 4-Picoline-*N*-oxide (0.8 mmol) was added to a stirring suspension of IPrAuCl (0.02 mmol) and $AgNTf_2$ (0.02 mmol) in dichloromethane (4 mL) and stirred for 5 min at room temperature. After that, $HNTf_2$ (0.48 mmol) was added and the mixture was allowed to stir for additional 5 min. To the resulting solution propargyl alcohol (0.4 mmol) was added and the combined solution was then stirred at rt until the reaction was completed (monitored by TLC). After evaporation, the residue was purified by

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column chromatography on silica gel (petrol ether/EtOAc = 10:1) afforded the desired product.

*2-Benzoylcyclopentanone (**3a**).* Yield: 64 mg as a mixture of a keto and an enol forms (keto/enol = 22:78 by ^{1}H NMR), 85%; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 22:78) δ = 14.49 (s, 1 H, enol), 8.02−7.41 (m, 5 H, keto and enol), 4.27 (t, 1 H, J = 7.8 Hz, keto), 2.90−1.94 (m, 6 H, keto and enol). **3a** is known.[23]

*2-(4-Methylbenzoyl)cyclopentanone (**3b**).* Yield: 67 mg as a mixture of a keto and an enol forms (keto/enol = 38:62 by ^{1}H NMR), red solid, 83%; mp 37−38 °C; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 38:62) δ = 14.60 (s, 1 H, enol), 7.94−7.26 (m, 4 H, keto and enol), 4.26 (t, 1 H, J = 7.8 Hz, keto), 2.92−1.93 (m, 9 H, keto and enol). ^{13}C NMR (75 MHz, $CDCl_3$, keto and enol): δ = 213.5 (keto), 210.0 (enol), 195.1 (keto), 169.0 (enol), 144.3, 141.5, 134.0, 131.7, 129.5, 129.2, 129.0, 128.1, 108.7, 57.0, 38.9, 37.5, 28.4, 27.2, 21.6, 21.5, 21.2, 21.1 ppm. IR (film): $\tilde{\nu}$ = 3462, 2961, 1741, 1670, 1611, 1565, 1508, 1449, 1409, 1379, 1310, 1279, 1253, 1184, 1151, 1117, 1068, 900, 827, 785, 730, 680, 632, 600, 556, 501, 469 cm^{-1}; HRMS (EI+): $C_{13}H_{14}O_2$ calcd 202.0994; found 202.0973. **3b** is known but not fully characterized.[24]

*2-(4-Methoxybenzoyl)cyclopentanone (**3c**).* Yield: 69 mg as a mixture of a keto and an enol forms (keto/enol = 53:47 by ^{1}H NMR), 79%; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 53:47) δ = 14.74 (s, 1 H, enol), 7.98 (d, 1 H, J = 8.7 Hz, keto and enol), 7.77 (d, 1 H, J = 8.7 Hz, keto and enol), 6.95 (d, 2 H, J = 8.7 Hz, keto and enol),4.20 (t, 1 H, J = 7.8 Hz, keto), 3.87 (s, 3 H, keto), 3.86 (s, 3 H, enol), 2.90−1.88 (m, 6 H, keto and enol). **3c** is known.[25]

*2-(4-Fluorobenzoyl)cyclopentanone (**3d**).* Yield: 66 mg as a mixture of a keto and an enol forms (keto/enol = 20:80 by ^{1}H NMR), 80%; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 20:80) δ = 14.54 (s, 1 H, enol), 8.06−8.01 (m, 1 H, keto), 7.81−7.75 (m, 1 H, enol), 7.19−7.08 (m, 2 H, keto and enol), 4.21 (t, 1 H, J = 7.8 Hz, keto), 2.88−1.92 (m, 6 H, keto and enol). **3d** is known.[26]

*2-(3-Chlorobenzoyl)cyclopentanone (**3e**).* Yield: 75 mg as a mixture of a keto and an enol forms (keto/enol = 5:95 by ^{1}H NMR), white solid, 84%; mp 54−56 °C; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 5:95) δ = 14.37 (s, 1 H, enol), 7.98−7.35 (m, 5 H, keto and enol), 4.21 (t, 1 H, J = 7.8 Hz, keto), 2.86 (t, 2 H, J = 7.1 Hz, enol), 2.50 (t, 2 H, J = 7.8 Hz, enol), 2.04−1.93 (m, 2 H, enol). ^{13}C NMR (75 MHz, $CDCl_3$, enol): δ = 210.8, 166.6, 136.3, 134.5, 130.9, 129.6, 128.1, 126.1, 109.7, 37.6, 28.2, 21.2 ppm, IR (film): $\tilde{\nu}$ = 3425, 3064, 2974, 2904, 2855, 1741, 1638, 1606, 1562, 1480, 1468, 1449, 1413, 1365, 1315, 1282, 1269, 1240, 1223, 1184, 1154, 1130, 1098, 1071, 1024, 916, 895, 876, 831, 795, 741, 715, 686, 675, 514 cm^{-1}; HRMS (EI+): $C_{12}H_{11}ClO_2$ calcd 222.0448; found 222.0452.

*2-(3,5-Dimethoxybenzoyl)cyclopentanone (**3f**).* Yield: 81 mg as a mixture of a keto and an enol forms (keto/enol = 35:65 by ^{1}H NMR), white solid, 81%; mp 75−77 °C; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 35:65) δ = 14.50 (s, 1 H, enol), 7.13−6.55 (m, 3 H, keto and enol), 4.18 (t, 1 H, J = 8.1 Hz, keto), 3.83 (s, 6 H, keto), 3.82 (s, 6 H, enol), 2.89−1.91 (m, 6 H, keto and enol). ^{13}C NMR (75 MHz, $CDCl_3$, keto and enol): δ = 213.2 (keto), 210.3 (enol), 195.5 (keto), 168.5 (enol), 160.8, 160.6, 138.5, 136.4, 109.3, 107.1, 106.1, 105.8, 103.2, 57.3, 55.5, 55.4, 38.9, 37.5, 28.4, 27.5, 21.2, 21.0 ppm, IR (film): $\tilde{\nu}$ = 3422, 3101, 3007, 2965, 2941, 2842, 1741, 1626, 1567, 1471, 1450, 1431, 1410, 1361, 1319, 1283, 1217, 1203, 1186, 1165, 1082, 1062, 1051, 945, 929, 919, 892, 875, 847, 838, 731, 677, 511 cm^{-1}; HRMS (EI+): $C_{14}H_{16}O_4$ calcd 248.1049; found 248.1042. **3f** is known but not fully characterized.[27]

*2-(3,5-Bis(trifluoromethyl)benzoyl)cyclopentanone (**3g**).* Yield: 77 mg as a mixture of a keto and an enol forms (keto/enol = 20:80 by ^{1}H NMR), red oil, 59%; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 20:80) δ = 14.29 (br, 1 H, enol), 8.52−7.96 (m, 3 H, keto and enol), 4.28 (t, 1 H, J = 8.1 Hz, keto), 2.93−1.99 (m, 6 H, keto and enol). ^{13}C NMR (75 MHz, $CDCl_3$, keto and enol): δ = 211.8 (keto), 211.4 (enol), 192.5 (keto), 164.0 (enol), 137.9, 136.7, 132.7, 132.2, 131.8, 129.6, 128.0, 128.0, 124.8, 124.1, 124.1, 121.2, 110.6, 57.7, 39.0, 37.6, 28.0, 26.4, 21.2, 20.9 ppm, IR (film): $\tilde{\nu}$ = 3474, 3099, 2970, 2361, 1745, 1690, 1653, 1626, 1601, 1453, 1385, 1340, 1280, 1240, 1179, 1136, 1080, 1024, 904, 846, 766, 742, 700, 682, 637, 515, 447 cm^{-1}; HRMS (EI+): $C_{14}H_{10}F_6O_2$ calcd 324.0585; found 324.0586.

*2-(2,4,5-Trimethylbenzoyl)cyclopentanone (**3h**).* Yield: 65 mg as a mixture of a keto and an enol forms (keto/enol = 20:80 by ^{1}H NMR), red solid, 70%; mp 77−79 °C; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 20:80) δ = 13.86 (br, 1 H, enol), 7.52 (s, 1 H, keto), 7.06 (s, 1 H, enol), 7.02 (s, 1 H, keto and enol), 4.17 (t, 1 H, J = 8.1 Hz, keto), 2.52−1.85 (m, 15 H, keto and enol). ^{13}C NMR (75 MHz, $CDCl_3$, keto and enol): δ = 214. Two (keto), 209.5 (enol), 199.3 (keto), 171.9 (enol), 141.0, 138.5, 136.6, 134.8, 133.7, 133.6, 133.5, 133.4, 132.1, 131.5, 131.5, 129.0, 110.6, 59.3, 38.9, 37.9, 27.8, 27.1, 21.1, 21.0, 21.0, 19.7, 19.5, 19.3, 19.2, 19.1 ppm, IR (film): $\tilde{\nu}$ = 3451, 2948, 2920, 2862, 2361, 1634, 1498, 1448, 1399, 1370, 1312, 1295, 1270, 1225, 1184, 1163, 1024, 912, 886, 871, 819, 781, 675, 634, 611, 527, 506, 444 cm^{-1}; HRMS (EI+): $C_{15}H_{18}O_2$ calcd 230.1307; found 230.1316.

*2-(6-Methoxy-2-naphthoyl)cyclopentanone (**3i**).* Yield: 101 mg as a mixture of a keto and an enol forms (keto/enol = 38:62 by ^{1}H NMR), yellow solid, 94%; 122−124 °C; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 38:62) δ = 14.72 (s, 1 H, enol), 8.45−7.15 (m, 6 H, keto and enol), 4.39 (t, 1 H, J = 8.0 Hz, keto), 3.94 (s, 3 H, keto and enol), 3.00−1.95 (m, 6 H, keto and enol). ^{13}C NMR (75 MHz, $CDCl_3$, keto and enol): δ = 213.7 (keto), 209.9 (enol), 195.2 (keto), 169.2 (enol), 159.9, 159.2, 137.5, 135.9, 132.0, 131.7, 131.4, 130.6, 129.7, 128.9, 128.0, 127.8, 127.0, 126.8, 125.2, 125.0, 119.7, 119.6, 109.0, 105.7, 105.6, 57.0, 55.4, 55.4, 39.0, 37.5, 28.6, 27.3, 21.3, 21.1 ppm, IR (film): $\tilde{\nu}$ = 3428, 2966, 2863, 1813, 1741, 1625, 1590, 1481, 1457, 1440, 1411, 1362, 1326, 1308, 1272, 1248, 1210, 1167, 1136, 1069, 1026, 961, 941, 908, 855, 847, 817, 779, 764, 717, 639, 511, 476, 462 cm^{-1}; HRMS (EI+): $C_{17}H_{16}O_3$ calcd 268.1099; found 268.1098.

*2-Pentanoylcyclopentanone (**3j**).* Yield: 48 mg as a mixture of a keto and an enol forms (keto/enol = 41:59 by ^{1}H NMR), red oil, 71%; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 41:59) δ = 13.63 (s, 1 H, enol), 3.37 (t, 1 H, J = 7.8 Hz, keto), 2.83−0.87 (m, 15 H, keto and enol). ^{13}C NMR (75 MHz, $CDCl_3$, keto and enol): δ = 213.2 (keto), 205.0 (keto), 204.8 (enol), 179.4 (enol), 109.4 (enol), 61.8, 42.8, 38.8, 36.9, 34.2, 27.6, 25.7, 25.4, 25.3, 22.4, 22.2, 20.8, 20.3, 13.8, 13.8 ppm, IR (film): $\tilde{\nu}$ = 2960, 2934, 2873, 1743, 1710, 1656, 1612, 1465, 1408, 1378, 1282, 1234, 1201, 1122, 1029, 1003, 909, 883, 829, 757, 478 cm^{-1}; HRMS (EI+): $C_{10}H_{16}O_2$ calcd 168.1150; found 168.1152. **3j** is known but not fully characterized.[28]

*2-(Cyclohexanecarbonyl)cyclopentanone (**3k**).* Yield: 51 mg as a mixture of a keto and an enol forms (keto/enol = 33:67 by ^{1}H NMR), red oil, 66%; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 33:67) δ = 13.84 (s, 1 H, enol), 3.55 (t, 1 H, J = 7.8 Hz, keto), 2.79 - 1.15 (m, 17 H, keto and enol). ^{13}C NMR (75 MHz, $CDCl_3$, keto and enol): δ = 213.6 (keto), 208.3 (keto), 205.2 (enol), 183.0 (enol), 108.1 (enol), 59.8, 50.4, 43.2, 38.8, 36.8, 30.9, 28.9, 28.5, 27.2, 26.0, 25.9, 25.8, 25.8, 25.7, 25.5, 25.1, 20.9, 20.4 ppm, IR (film): $\tilde{\nu}$ = 3458, 2933, 2855, 1810, 1744, 1704, 1647, 1613, 1450, 1378, 1351, 1310, 1269, 1236, 1140, 1084, 1026, 1001, 945, 910, 893, 849, 831, 760, 668, 630, 556, 520, 477 cm^{-1}; HRMS (EI+): $C_{12}H_{18}O_2$ calcd 194.1307; found 194.1298. **3k** is known but not fully characterized.[29]

*2-(2-Phenoxyacetyl)cyclopentanone (**3l**).* Yield: 53 mg as a mixture of a keto and an enol forms (keto/enol = 35:65 by ^{1}H NMR), red oil, 61%; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 35:65) δ = 13.40 (br, 1H, enol), 7.25−6.80 (m, 5 H, keto and enol), 4.91−4.57 (m, 2 H, keto and enol), 3.55 (t, 1 H, J = 8.6 Hz, keto), 2.60−1.73 (m, 6 H, keto and enol). ^{13}C NMR (75 MHz, $CDCl_3$, keto and enol): δ = 212.5 (keto), 205.1 (enol), 200.8 (keto), 173.7 (enol), 158.0, 157.6, 129.6, 121.7, 121.5, 114.6, 114.4, 109.8, 72.6, 67.4, 58.8, 38.6, 36.3, 25.3, 25.0, 20.9, 20.5 ppm, IR (film): $\tilde{\nu}$ = 3448, 3063, 2969, 2916, 1746, 1721, 1667, 1599, 1495, 1455, 1430, 1404, 1365, 1328, 1292, 1268, 1223, 1173, 1132, 1083, 1012, 909, 886, 822, 786, 755, 692, 613, 569, 508 cm^{-1}; HRMS (EI+): $C_{13}H_{14}O_3$ calcd 218.0943; found 218.0937. **3l** is known.[30]

*2-Benzoylcyclobutanone (**3m**).* Yield: 25 mg, 35%; ^{1}H NMR (300 MHz, CD_2Cl_2, keto/enol >99:1) δ = 8.06−8.02 (m, 2 H), 7.64−7.58 (m, 1 H), 7.55−7.48 (m, 2 H), 5.25−5.19 (m, 1 H), 3.22−3.14 (m, 2 H), 2.84−2.76 (m, 1 H), 2.26−2.16 (m, 1 H). **3m** is known.[12,31]

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*2-Benzoylcyclotridecanone (**3p**).* Yield: 78 mg, white solid, 65%; mp 102−103 °C; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol > 99:1) δ = 7.97−7.93 (m, 2H), 7.60−7.54 (m, 1 H), 7.49−7.44 (m, 2 H), 4.46 (dd, 1 H, J = 3.0 Hz, 10.2 Hz), 2.70−2.60 (m, 1 H), 2.37−2.27 (m, 1 H), 2.19−2.15 (m, 1 H), 1.86−1.24 (m, 19 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 207.1, 196.3, 136.3, 133.5, 128.8, 128.5, 63.0, 39.7, 27.9, 26.9, 26.2, 26.1, 25.5, 25.1, 24.9, 24.9, 24.3, 22.4 ppm, IR (film): $\tilde{\nu}$ = 3422, 2923, 2862, 1708, 1679, 1596, 1580, 1461, 1448, 1410, 1363, 1327, 1294, 1280, 1264, 1250, 1206, 1175, 1104, 1066, 1021, 1003, 980, 965, 936, 795, 764, 739, 706, 694, 660, 603, 567, 494 cm^{-1}; HRMS (EI+): $C_{20}H_{28}O_2$ calcd 300.2089; found 300.2081.

*2-Benzoylcyclohexadecanone (**3q**).* Yield: 96 mg, white solid, 70%; mp 71−73 °C; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol > 99:1) δ = 7.97−7.94 (m, 2 H), 7.59−7.53 (m, 1 H), 7.48−7.42 (m, 2 H), 4.45 (q, 1 H, J = 4.8 Hz), 2.67−2.56 (m, 1 H), 2.32−2.09 (m, 2 H), 1.89−1.79 (m, 1 H), 1.64−1.53 (m, 2 H), 1.30 (s, 22 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.9, 196.1, 136.3, 133.5, 128.8, 128.6, 63.2, 39.6, 28.8, 27.5, 27.4, 27.1, 27.0, 26.7, 26.5, 26.5, 26.4, 26.4, 26.2, 26.1, 22.4 ppm, IR (film): $\tilde{\nu}$ = 3439, 2929, 2856, 1713, 1679, 1596, 1581, 1449, 1400, 1351, 1234, 1114, 1078, 1048, 1001, 953, 765, 699, 690, 598 cm^{-1}; HRMS (EI+): $C_{23}H_{34}O_2$ calcd 342.2559; found 342.2536.

*2-Methyl-1-phenylbutane-1,3-dione (**3r**).* Yield: 55 mg as a mixture of a keto and an enol forms (keto/enol = 87:13 by ^{1}H NMR), 78%; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 87:13) δ = 16.60 (s, 1 H, enol), 7.98−7.36 (m, 5 H, keto and enol), 4.48 (q, 1 H, J = 7.2 Hz, keto), 2.25 (s, 3 H, enol), 2.14 (s, 3 H, keto), 1.92 (s, 3 H, enol), 1.44 (d, 3 H, J = 7.2 Hz, keto). **3r** is known.[32]

*1-Phenylbutane-1,3-dione (**3s**).* Yield: 33 mg as a mixture of a keto and an enol forms (keto/enol = 8:92 by ^{1}H NMR), 50%; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 8:92) δ = 16.16 (s, 1 H, enol), 7.95−7.41 (m, 5 H, keto and enol), 6.18 (s, 1 H, enol), 4.10 (s, 2 H, keto), 2.30 (s, 3 H, keto), 2.20 (s, 3 H, enol). **3s** is known.[33]

*2-Methyl-3-oxo-3-phenylpropanal (**3s′**).* Yield: 26 mg as a mixture of a keto and an enol forms (keto/enol = 30:70 by ^{1}H NMR), 26%; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 30:70) δ = 15.39 (d, 1 H, enol), 9.76 (d, 1 H, J = 2.3 Hz, keto), 8.60 (d, 1 H, J = 4.8 Hz, enol), 7.99−7.41 (m, 5 H, keto and enol), 4.40 (qd, 1 H, J = 2.3 Hz, 6.9 Hz, keto), 1.99 (s, 3 H, enol), 1.48 (d, 3 H, J = 6.9 Hz, keto). **3s′** is known.[34]

*3-Oxo-2,3-diphenylpropanal (**3t**).* Yield: 65 mg as a mixture of a keto and an enol forms (keto/enol = 3:97 by ^{1}H NMR), 73%; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 3:97) δ = 15.91 (d, 1 H, J = 5.4 Hz, enol), 9.98 (d, 1 H, J = 3.6 Hz, keto), 8.63 (d, 1 H, J = 5.4 Hz, enol), 8.01−7.07 (m, 10 H, keto and enol), 5.39 (d, 1 H, J = 3.6 Hz, keto). **3t** is known.[35]

*1,2-Diphenylbutane-1,3-dione (**3u**).* Yield: 54 mg as a mixture of a keto and an enol forms (keto/enol = 27:73 by ^{1}H NMR), 57%; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 27:73) δ = 17.48 (s, 1 H, enol), 8.09−7.19 (m, 10 H, keto and enol), 5.78 (s, 1 H, keto), 2.36 (s, 3 H, keto), 2.15 (s, 3 H, enol). **3u** is known.[36]

*2-Methyl-1,3-diphenylpropane-1,3-dione (**3u′**).* Yield: 15 mg, 16%; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol > 99:1) δ = 7.97−7.94 (m, 4 H), 7.60−7.54 (m, 2 H), 7.48−7.42 (m, 4 H), 5.26 (q, 1 H, J = 6.9 Hz), 1.61 (d, 3 H, J = 6.9 Hz). **3u′** is known.[33]

*(E)-2-Benzylidenecyclobutanone (**4a**).* Yield: 60 mg, 95%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.54−7.49 (m, 2 H), 7.44−7.37 (m, 3 H), 7.05−7.02 (m, 1 H), 3.18−3.09 (m, 2 H), 3.04−2.96 (m, 2 H). **4a** is known.[13]

■ ASSOCIATED CONTENT

Supporting Information

Spectra for compounds **1a−u**, **3a−u**, **3u′**, **4a** as well as ^{1}H and ^{31}P NMR spectra of $Ph_3PAuNTf_2$ and different ratios of pyridine-*N*-oxide and $Ph_3PAuNTf_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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