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Oxidant-Dependent Chemoselectivity in the Gold-Catalyzed Oxidative Cyclizations of 3,4,6,6-Tetrasubstituted 3,5-Dien-1-ynes

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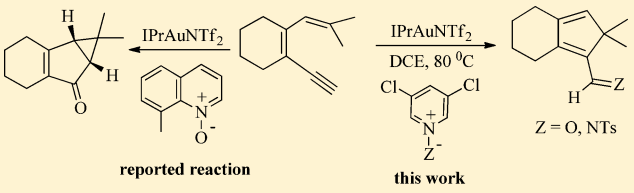
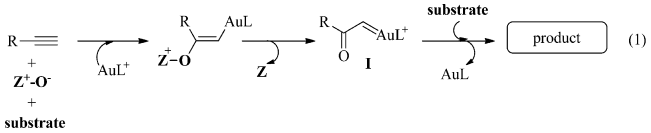
Supporting Information

ABSTRACT: A distinct chemoselectivity in the gold-catalyzed oxidative cyclization of 3,5-dien-1-ynes was observed when 3,5-dichloropyridine *N*-oxide replaced 8-methylquinoline *N*-oxide as the oxidant; the resulting cyclopentadienyl aldehydes were obtained in good yields. The altered chemoselectivity is attributed to a prior enyne cyclization in the presence of 3,5-dichloropyridine *N*-oxides. The use of *N*-iminopyridium ylide enables a similar iminocyclization reaction to give cyclopentadienyl imines efficiently. Our experimental data support a prior gold-catalyzed cyclization of 3,5-dien-1-ynes to form gold carbene, followed by the oxidation with *N*-oxide.



INTRODUCTION

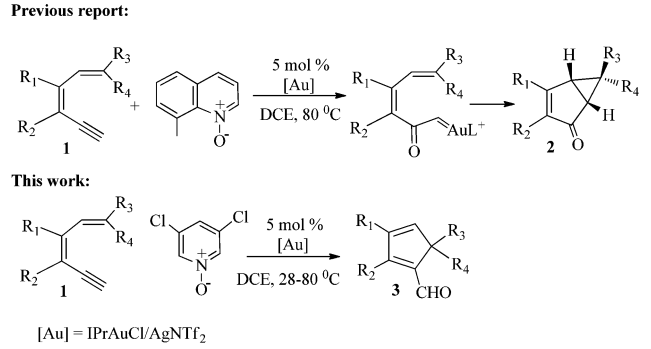
Gold-catalyzed intermolecular oxidation of terminal alkynes with pyridine-based oxides is a powerful tool to access α-functionalized carbonyl compounds (eq 1).[1−3] This oxidation



involves an initial attack of *N*-oxides at the alkynyl C(2)-carbon to generate α-oxo gold carbenes **I** that are trapped *in situ* with a suitable substrate (**S**).[1,2] The chemoselectivity in this alkyne oxidation is generally invariant with diverse derivatives of pyridine-based oxides. We are aware of no report in which the reaction chemoselectivity varied with a change of *N*-oxide. In this work, we report a distinct chemoselectivity in the oxidative cyclization of 3,5-dien-1-ynes with alterable pyridine-based *N*-oxides.

Shown in Scheme 1 is the oxidant-dependent chemoselectivity. We reported that gold-catalyzed reactions between 3,5-dien-1-ynes and 8-methylquinoline *N*-oxide (8-MQO) resulted in an oxidative cyclopropanation with high stereospecificity;[2b] this process involves α-oxo gold carbenes as intermediates.[1,2] Herein, we report the use of 3,5-dichloropyridine *N*-oxide in the reactions to give cyclopentadienyl aldehydes **3** instead and present experimental results to clarify the reaction mechanisms.

Scheme 1. Two Distinct Oxidative Cyclizations



RESULTS AND DISCUSSION

Table 1 (entry 1) shows our previously reported reaction between dienyne **1a**, IPrAuCl/$AgNTf_2$ (5 mol %, IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene), and 8-methylquinoline *N*-oxide (8-MQO, 1.2 equiv) in hot DCE (80 °C, 0.33 h), resulting in an oxidative cyclopropanation product **2a** in 60% yield.[2b] The yield was increased to 78% using the same *N*-oxidant in a large proportion (3 equiv). We tested the reactions with alterable pyridine-based *N*-oxides; Brønsted acids were excluded here to avoid the polymerization of starting **1a**. With pyridine *N*-oxide and its 2-ethyl derivative (1.2 equiv) in hot DCE (80 °C, 24−48 h), we obtained a new compound, cyclopentadienyl aldehyde **3a**, in low yield (<35%) together with indanone **2a** and unreacted **1a** in a substantial proportions (>18%, entries 2 and 3). The yields of aldehyde **3a** were enhanced to 56−60% yields with electron-deficient pyridine *N*-oxides bearing a chloro or bromo substituent at the C(2)- or C(3)-carbons (entries 4−6). To our pleasure, the use of 3,5-dichloropyridine *N*-oxide in hot DCE (80 °C, 0.33 h) effected a complete suppression of cyclopropyl indanone **2a** to deliver compound **3a** with 83% yield (entry 7). IPrAuCl/$AgSbF_6$ also maintained a high efficiency to give aldehyde **3a** in 76% yield (entry 9). P(*t*-Bu)$_2$(*o*-biphenyl)AuCl/$AgNTf_2$ and PPh_3AuCl/$AgNTf_2$ were less chemoselective in giving compound **3a** in less yield together with undesired **2a** in 16−22% yields (entries 10

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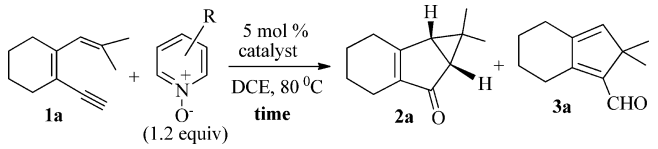
Table 1. Reactions with Various *N*-Oxides and Gold Catalysts



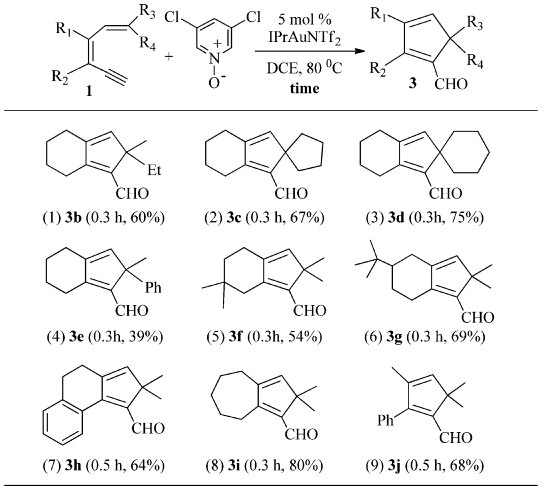
entry	catalyst[a] (mol %)	*N*-oxide[b]	°C/h	compounds (yields)[c] 1a	2a	3a
1	$IPrAuCl/AgNTf_2$	8-MQO	80/0.3		60 (78)[d]	
2	$IPrAuCl/AgNTf_2$	R = H	80/48	59	24	6
3	$IPrAuC1/AgNTf_2$	R = 2-Et	80/24	25	35	18
4	$IPrAuCl/AgNTf_2$	R = 2-Br	80/0.7		24	60
5	$IPrAuCVAgNTf_2$	R = 3-Br	80/0.2		26	57
6	$IPrAuCyAgNTf_2$	R = 2-C1	80/0.3		30	56
7	$IPrAuCl/AgNTf_2$	R = 3,5-Cl_2	80/0.3			83
8	$IPrAuCVAgNTf_2$	R = 3,5-Cl_2	25/0.6			81
9	$IPrAuCl/AgSbF_6$	R = 3,5-Cl_2	25/0.8			76
10	$LAuCl/AgNTf_2$	R = 3,5-Cl_2	25/1.0		22	57
11	$PPh_3AuCl/AgNTf_2$	R = 3,5-Cl_2	25/1.2		16	56
12	Ph_2SO	Ph_2SO	25/0.5			*e*

[a]8-MQO = 8-methylquinoline *N*-oxide, IPr = l,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, L = P(*t*-Bu)$_2$(*o*-biphenyl), [**la**] = 0.05 M. [b]*N*-Oxide (1.2 equiv). [c]Product yields are reported after separation on a silica column. [d]This value corresponds to 8-MQO with 3.0 equiv. [e]Polymerization of starting **la** was observed.

and 11). We tested the reaction with Ph_2SO (1.2 equiv),[4] which led to a polymerization of starting **1a** (entry 12); the same polymerization was observed in the absence of oxides, reflecting the sensitivity of starting **1a** toward an acidic gold catalyst. Only basic *N*-oxides can reduce the acidity of $IPrAuNTf_2$ to secure the stability of starting **1a.**

Table 2 shows the gold-catalyzed reactions between various 3,5-dien-ynes **1b**−**1j** with 3,5-dichloropyridine *N*-oxide, giving only cyclopentadienyl aldehydes **3b**−**3j**, whereas competitive cyclopropyl indanones **2** were completely suppressed. In entries 1 and 4, starting **1b** was prepared as a mixture of *E*/*Z* isomers (*E*/*Z* = 1.4), whereas species **1e** was prepared as the *E*-isomer. Entries 1−4 show the applicability of this new oxidative

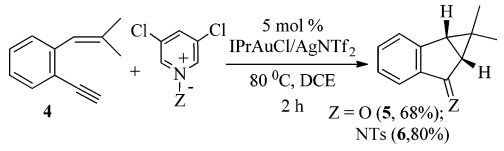
Table 2. Oxidative Cyclization with Various 3,5-Dien-1-ynes[a]



[a]IPr = l,3-bis(2,6-dii8opropylphenyl)imidazol-2-ylidene, L = P(*t*-Bu)$_2$(*o*-biphenyl), [**la**] = 0.05 M, *N*-oxide (1.2 equiv). Product yields are reported after separation on a silica column. **1b**, *E*/*Z* = 1.4. **1e** is *E*-isomer.

cyclization to 3,5-dien-1-ynes **1b**−**1e** bearing various substituted alkenes; the resulting aldehydes **3b**−**3d** were obtained in satisfactory yields (60−75%) with the exception of compound **3e** that was obtained in a low yield (39%). We tested the reactions on 3,5-dien-1-ynes **1f**−**1h** bearing a substituted cyclohexenyl bridge; the corresponding products **3f**−**3h** were produced with 54−69% yields. This reaction was applicable also to substrate **1i** bearing a cycloheptenyl bridge, giving desired product **3i** in 80% yield. For an acyclic 3,5-dien-1-yne **1j**, its gold-catalyzed reaction delivered cyclopentadienyl aldehyde **3j** in 68% yield. Our attempted reaction on 3,5-dien-1-yne bearing a single phenyl substituent in the 6-position, unlike compound **1e**, gave a complicated mixture of products.[5]

We examined the reaction of a benzenoid substrate **4** with 3,5-dichloropyridine *N*-oxide, which delivered cyclopropyl indanone **5** instead (eq 1). The same reaction pattern was observed using *N*-iminopyridium ylide[6,7] to afford cyclopropyl indanimine **6** in 80% yield (eq 2), whereas for non-benzenoid



(2)

3,5-dien-1-yne **1a**, a different chemoselectivity occurred to give cyclopentadienyl imine **7a** in 84% yield (eq 3). $NaBH_3CN$-reduction of imine species **7a** provided primary imine **8a** in 67% yield, which was characterized by X-ray diffraction (eq 3).[8]

Table 3 shows the gold-catalyzed synthesis of cyclopentadienyl imines from the same 3,5-dien-1-ynes **1b**−**1j** as in Table 2. The reaction proceeded with high chemoselectivity to afford cyclopentadienyl imines **7b**−**7j** exclusively. For 3,5-dien-1-ynes **1b**−**1e** bearing various trisubstituted alkenes, their resulting cyclopentadienyl imines **7b**−**7e** were produced in 57−76% yields (entries 1−4). This iminocyclization was operable with additional 3,5-dien-1-ynes **1f**−**1h** bearing a varied cyclohexenyl bridge, giving desired imines **7f**−**7h** with 66−

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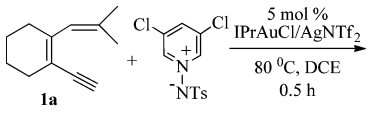
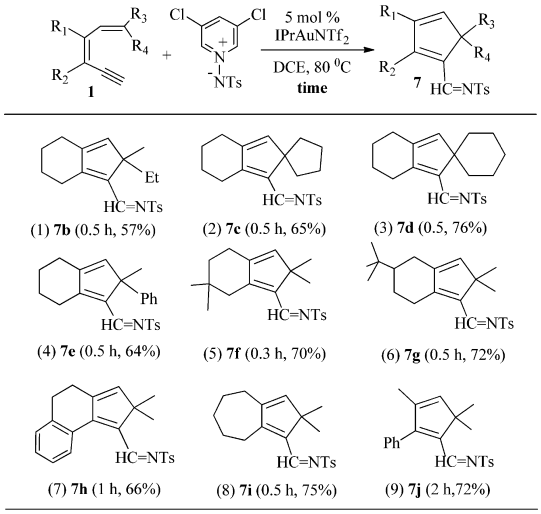


Table 3. Scope for Gold-Catalyzed Iminocyclizations[a]

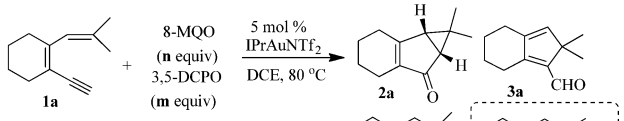


[a]IPr = l,3-bis(2,6-diisopropylphenyl)imidazol-2-ylideiie, L = P(*t*-Bu)$_2$(*o*-biphenyl), [**la**] = 0.05 M. *N*-oxide (1.2 equiv). Product yields are reported after separation on a silica column. **1b**, *E*/*Z* = 1.4. **1e**, *E*/*Z* = 1.0.

72% yields (entries 5−7). The reaction worked also with substrate **1i** bearing a cycloheptenyl bridge, giving the corresponding product **7i** in 75% yield (entry 8). Acyclic 3,5-dien-1-yne **1j** was also suitable for this iminocyclization, giving desired **7j** in 72% yield (entry 9).

As shown in Scheme 2, we performed a reaction with 8-methylquinoline *N*-oxide and 3,5-dichloropyridine *N*-oxide in

Scheme 2. Oxidation Properties of *N*-Oxides

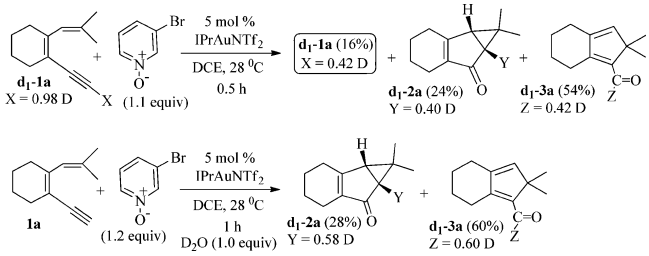


entry	n	m	yields (%) 2a	3a	9
1	1.5	3.0	33	trace	39
2	1.1	3.0	34	15	29

equal proportions ((3,5-DCPO, 1.5 equiv, Scheme 2) and obtained desired cyclopropyl indanone **2a** together with a new product **9** in 33% and 39% yields respectively; cyclopentadienyl aldehyde **3a** was obtained in a negligible proportion. Pyranyl aldehyde **9** was generated with 6-π electrocyclization of α-carbonyl aldehyde **9′** that resulted from a second oxidation of gold carbenes **C** (*vide ante*, Scheme 4).[9] Compound **3a** were generated in 15% yield with a decreasing loading of 8-methylquinoline *N*-oxide (1.1 equiv, entry 2). These data provide insight into the effects of two *N*-oxides, namely, that 8-methylquinoline *N*-oxide is more active than 3,5-dichloropyridine *N*-oxide for the alkyne oxidation and is inactive toward the carbene oxidation.

Scheme 3 shows the deuterium labeling experiments. The treatment of deuterated d_1-**1a** with 3-bromopyridine *N*-oxide

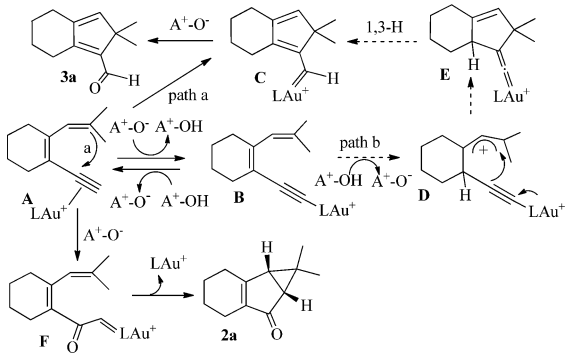
Scheme 3. Deuterium Labeling Experiments



(1.1 equiv) in DCE at 28 °C (0.5 h) led to a 80% conversion, giving unreacted d_1-**1a** and cyclopropyl indanone d_1-**2a** and cyclopentadienyl aldehyde d_1-**3a** in 16%, 24%, and 54% recovery or yields, respectively. Notably, the deuterium contents X, Y, and Z are nearly the same (40−42%). Alternatively, the use of undeuterated **1a** and D_2O (1.0 equiv) in this reaction also provided deuterated d_1-**2a** and d_1-**3a** with the same level of deuterium contents (58−60%). These results indicates that the loss of deuterium content of d_1-**2a** and d_1-**3a** is attributed to a quick equilibrium between π-alkyne **A** and alkynyl gold **B** (Scheme 4). This **A**/**B** equilibrium allows a quick change between d_1-**1a** and water before the production of d_1-**2a** and d_1-**3a.**

Scheme 4 depicts possible mechanisms to rationalize the formation of cyclopropyl indanone **2a** and cyclopentadienyl

Scheme 4. Possible Reaction Mechanisms



aldehyde **3a**; the latter was produced with less nucleophlic *N*-oxides that attack π-alkyne **A** inefficiently. The deuterium labeling experiments in Scheme 3 indicate that an equilibrium[10,11] between π-alkyne **A** and alkynylgold species **B** is rapidly attained before products **2a** and **3a** are formed. *N*-Oxides are reported to catalyze this **A**/**B** equibrium.[10]

Besides a prior cyclization route (path **a**) involving the transformation π-alkyne **A** → gold carbene **C**, a small portion of species **B** might undergo protonation at the dienyl C(3)-carbon to give an allylic cation **D** (path **b**), which induces a cyclization to generate gold allenylidene **E**, ultimately giving gold carbene **C**. We sought suitable experiments to probe the feasibility of the two paths (**a** and **b**).

We assessed the role of alkynylgold intermediate **B** to participate the alkyne oxidation, as depicted in path **b**. As depicted in Table 4, we prepared alkynylgold species **10**[12] and

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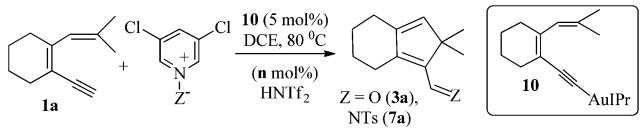
Table 4. Alkynylgold Species as the Catalysts[a]

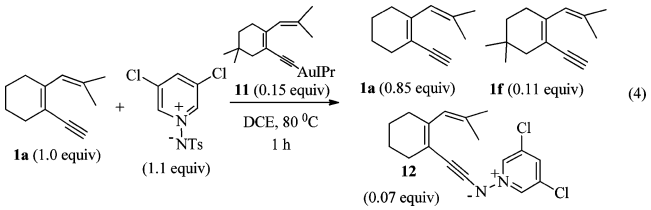


entry	oxidant	mol % $HNTf_2$	min	yield[b]
1	Z = NTs	1.0	20	**7a** (86%)
2	Z = NTs	0	600	**7a** (56%)
3	Z = O	1.0	120	**3a** (75%)
4	Z = O	0	600	**1a** (55%)

[a][**1a**] = 0.05 M. *N*-oxide (1.2 equiv). [b]Product yields are reported after separation on a silica column.

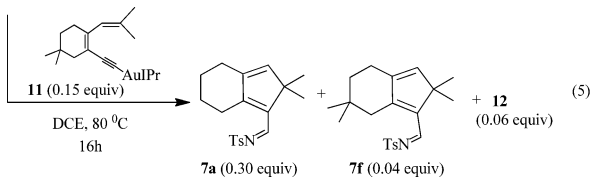
used it as a catalyst (5 mol %) in both oxidation and nitrene reactions. In the nitrene reaction, we obtained excellent yields (86%) for desired product **7a** with $HNTf_2$ (1 mol %). To our surprise, the catalytic reaction still proceeded in the absence of $HNTf_2$ to give compound **7a** in 56% yield over a protracted period (10 h, entry 2). In contrast, $HNTf_2$ was required for the oxidation reactions using alkynylgold **10** catalyst (entries 3 and 4).

To understand the role of alkynylgold species **B** in path **b**, we performed a control experiment in eq 4, involving **1a** (1 equiv),



(4)

N-iminopyridium ylide (1 equiv) and alkynylgold species **11** (0.15 equiv). Heating this mixture in hot DCE for a brief period (1 h) gave no desired iminocyclization products **7a** and **7f**, but we obtained a mixture of 3,5-dien-1-ynes **1a** and **1f** with a **1a**/**1f** ratio of 7.7/1. Accordingly, alkynylgold species **B** preferably underwent protonation to produce gold-π-alkyne species **A**, rather than giving gold-vinylidene **E**, thus excluding the route **b** in Scheme 4. Herein, *N*-iminopyridium ylide serves as a proton shuttle with dien-1-yne **1a** as the proton source. At a protracted period (16 h), the same reaction gave desired iminocylization products **7a** and **7f**, albeit in low yields (30−35%); in this case, alkynylamide **12** was obtained in minor proportion (eq 5). This



(5)

result reveals that alkynylgold species **11** was a poor catalyst for this iminocyclization; the corresponding mechanism might be different. The isolation of alkynylamide **12** allows us to understand the reaction mechanism in eq 4.[13]

CONCLUSIONS

A distinct chemoselectivity in the gold-catalyzed oxidative cyclization of 3,5-dien-1-ynes occurred when 8-methylquinoline *N*-oxide was replaced with 3,5-dichloropyridine *N*-oxide; the resulting cyclopentadienyl aldehydes were obtained in satisfactory yields. The change of chemoselectivity is attributed to the weak nucleophilicity of 3,5-dichloropyridine *N*-oxide such that a prior cyclization of 3,5-dien-1-ynes occurs preferably. The reactions were extensible to their iminocyclizations when the same 3,5-dien-1-ynes were treated with *N*-iminopyridium ylide. Our experimental results support a prior gold-catalyzed cyclization of 3,5-dien-1-ynes to form gold carbene **C**, followed by the oxidation with *N*-oxide.[14] In a case involving alkynylgold as the catalyst, a prior protonation of alkynylgold to give π-alkyne occurred preferably.

EXPERIMENTAL SECTION

General Comments. Unless otherwise noted, all reactions to prepare the substrates were performed in oven-dried glassware under a nitrogen atmosphere with freshly distilled solvents. The catalytic reactions were performed under a nitrogen atmosphere. Toluene, DCE, and methanol were distilled from CaH_2 under nitrogen. Methanol and triethylamine (Et_3N) were stored over molecular sieves (4 Å) before use. All other commercial reagents were used without further purification, unless otherwise indicated. ^1H NMR and ^{13}C NMR spectra were recorded on 400 and 600 MHz spectrometers using chloroform-d_1 ($CDCl_3$), CD_2Cl_2, or DMSO-d_6 as the internal standard. EI/MS-MS, ESI/FTMS, and ESI/orbitrap mass spectrometry were used for the HRMS measurements. All 1,5-enynes (**1a**−**1i**) were prepared from the reported procedure in the literature.[15]

General Procedure for Gold-Catalyzed Oxidative Cyclization between 1,5-Enyne (1a) and 3,5-Dichloropyridine *N*-Oxide. A 1,2-dichloroethane solution (4.2 mL) of compound **1a** (50 mg, 0.31 mmol) and 3,5-dichloropyridine *N*-oxide (60.7 mg, 0.37 mmol) was added to a 1,2-dichloroethane solution (2.0 mL) of $IPrAuNTf_2$ (13.9 mg, 0.016 mmol). The mixture was heated to 80 °C for 0.5 h before it was filtered over a short silica bed. The solvent was evaporated under reduced pressure; the crude product was eluted through a silica gel column to afford **3a** as a yellow oil (45.4 mg, 0.26 mmol, 83%).

General Procedure for Gold-Catalyzed Oxidative Cyclization between 1,5-Enyne (1a) and (3,5-Dichloro-pyridinium-1-yl)-tosylamide. To a 1,2-dichloroethane solution (4.2 mL) of compound **1a** (50 mg, 0.31 mmol) and (3,5-dichloro-pyridinium-1-yl)tosylamide (117.4 mg, 0.37 mmol) was added a 1,2- dichloroethane solution (2.0 mL) of $IPrAuNTf_2$ (13.9 mg, 0.016 mmol); the mixture was heated to 80 °C for 0.5 h before it was filtered over a short silica bed. The solvent was evaporated under reduced pressure; the crude product was eluted through a silica column to afford **7a** as an orange red oil (85.8 mg, 0.26 mmol, 84%).

Procedure for Gold-Catalyzed Oxidative Cyclization between Deuterated 1-Ethynyl-2-(2-methylprop-1-en-1-yl)-cyclohex-1-ene (d_1-1a) and 3-Bromo Pyridine *N*-Oxide. A 1,2-dichloroethane solution (3.7 mL) of compound d_1-**1a** (50 mg, 0.31 mmol) and 3-bromopyridine *N*-oxide (64.4 mg, 0.37 mmol) was added to a 1,2-dichloroethane solution (2.5 mL) of $IPrAuNTf_2$ (13.8 mg, 0.016 mmol). The mixture was heated to 80 °C for 0.5 h before it was filtered over a short silica bed. The solvent was evaporated under reduced pressure; the crude product was eluted through a silica gel column to afford compound d_1-**1a** as a pale yellow oil (8.0 mg, 0.05 mol, 16%), compound d_1-**2a** as a colorless oil (13.2 mg, 0.07 mmol, 24%), and compound d_1-**3a** as a yellow oil (29.7 mg, 0.17 mmol, 54%).

Synthesis of *N*-((2,2-Dimethyl-4,5,6,7-tetrahydro-2*H*-inden-1-yl)methyl)-4-methylbenzenesulfonamide (8a). To a THF solution (5.2 mL) of compound **7a** (86 mg, 0.26 mmol) was added $NaBH_3CN$ (18 mg, 0.26 mmol), and the mixture was stirrred for 4 h at room temperature, quenched with water, and extracted with ethyl acetate (20 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated on an evaporator. The residue was eluted through a short pad of silica column to afford compound **8a** as pale yellow solid (58 mg, 0.17 mmol, 67%).

Synthesis of 3,3-Dimethyl-5,6,7,8-tetrahydro-3*H*-isochromene-1-carbaldehyde (9). A 1,2-dichloroethane solution (3.7 mL) of compound **1a** (50 mg, 0.31 mmol), 8-methylquinoline *N*-oxide (74.8 mg, 0.47 mmol), and 3,5-dichloropyridine *N*-oxide (152.5

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mg, 0.93 mmol) was added to a 1,2-dichloroethane solution (2.5 mL) of $IPrAuNTf_2$ (13.8 mg, 0.016 mmol). The mixture was heated to 80 °C for 0.5 h before it was filtered over a short silica bed. The solvent was evaporated under reduced pressure; the crude product was eluted through a silica gel column to afford compound **2a** as a pale yellow oil (18 mg, 0.10 mol, 33%), compound **9** as a yellow oil (23.0 mg, 0.12 mmol, 39%), and a trace amount of compound **3a** with yellow oil.

Synthesis of 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene((2-(2-methylprop-1-en-1-yl)cyclohex-1-en-1-yl)-ethynyl)gold (10). A round-bottom flask (10 mL) was charged with 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene gold chloride (76.7 mg, 0.12 mmol) and NaOH (9.6 mg, 0.24 mmol). After the flask was evacuated and refilled with nitrogen, methanol (3.0 mL) was added by syringe, and the reaction mixture was stirred for 20 min. Dichloromethane (1.5 mL) was added until a homogeneous solution was obtained. Compound **1a** (20.0 mg, 0.12 mmol) was added directly to this solution. The reaction was covered in foil and stirred for 36 h followed by removal of the volatiles under vacuum and extraction of the residue with benzene (10 mL × 3). After filtration to remove insoluble salts and purification by recrystallization (benzene and pentane), the desired compound **10** was obtained as white solid (61.0 mg, 0.082 mmol, 68%).

Synthesis of 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene((5,5-dimethyl-2-(2-methylprop-en-1-yl)cyclohex-1-en-1-yl)ethynyl)gold (11). A MeOH solution (4.2 mL) of NaO^tBu (15.4 mg, 0.16 mmol) and compound **1f** (30.0 mg, 0.16 mmol) was stirred for 10 min before addition of a MeOH solution (2.0 mL) of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene gold chloride (49.7 mg, 0.08 mmol). The reaction was covered in foil and stirred for 48 h followed by removal of the volatiles under vacuum and extraction of the residue with dichloromethane (10 mL × 3). After filtration to remove insoluble salts and purification by recrystallization (benzene and pentane), the desired compound **11** was obtained as a pale yellow solid (84.0 mg, 0.11 mmol, 68%).

Synthesis of (3,5-Dichloropyridin-1-ium-1-yl)((2-(2-methylprop-1-en-1-yl)cyclohex-1-en-1-yl)ethynyl)amide (12). To a 1,2-dichloroethane solution (4.2 mL) of compound **1a** (50 mg, 0.31 mmol) and (3,5-dichloro-pyridinium-1-yl)tosylamide (104.7 mg, 0.33 mmol) was added a 1,2-dichloroethane solution (2.0 mL) of compound **11** (36.0 mg, 0.047 mmol); the mixture was heated to 80 °C for 1 h before it was filtered over a short silica bed. The solvent was evaporated under reduced pressure; the crude product was eluted through a silica column to afford compound **1a** as a yellow oil (42 mg, 0.26 mmol, 85%), compound **1f** as a yellow oil (6.5 mg, 0.034 mmol, 0.11 equiv), and compound **12** as a yellow oil (7.0 mg, 0.022 mmol, 0.07 equiv).

Deuterated 1,1-Dimethyl-1,2,3,4,5,6a-hexahydrocyclopropa[*a*]inden-6(1a*H*)-one (d_1-2a). Pale yellow oil; (13 mg, 24%); ^1H NMR (400 MHz, $CDCl_3$) δ 2.40−2.34 (m, 1 H), 2.17−2.11 (m, 2 H), 2.10−2.03 (m, 2 H), 1.92 (d, J = 4.4 Hz, 0.6 H), 1.70−1.61 (m, 3 H), 1.52−1.48 (m, 1 H), 1.17 (s, 3 H), 1.04 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.3, 168.8, 137.3, 48.3, 48.2, 38.1, 37.9 (t, J = 26 Hz), 37.3, 37.2, 28.7, 27.2, 27.1, 22.2, 21.7, 19.5, 14.3; HRMS calcd for $C_{12}H_{16}O$ 176.1201, found 176.1197, 177.1262.

2,2-Dimethyl-4,5,6,7-tetrahydro-2*H*-indene-1-carbaldehyde (3a). Yellow oil; (45 mg, 83%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1 H), 6.28 (s, 1 H), 2.86 (t, J = 6.4 Hz, 2 H), 2.47 (td, J = 6.4, 2.0 Hz, 2 H), 1.72−1.59 (m, 4 H), 1.21 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8, 160.6, 151.1, 145.5, 139.3, 51.1, 24.8, 24.0, 22.8, 22.4, 21.8; HRMS calcd for $C_{12}H_{16}O$ 176.1201, found 176.1195.

Deuterated 2,2-Dimethyl-4,5,6,7-tetrahydro-2*H*-indene-1-carbaldehyde (d_1-3a). Pale yellow oil; (30 mg, 54%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 0.58 H), 6.29 (s, 1 H), 2.87 (t, J = 6.0 Hz, 2 H), 2.47 (t, J = 5.6 Hz, 2 H), 1.72−1.63 (m, 4 H), 1.22 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.8, 183.5 (t, J = 102 Hz), 160.6, 151.1, 145.4, 139.3, 51.1, 24.7, 24.0, 22.8, 22.4, 21.8; HRMS calcd for $C_{12}H_{16}O$ 176.1201, found 176.1206, 177.1268.

2-Ethyl-2-methyl-4,5,6,7-tetrahydro-2*H*-indene-1-carbaldehyde (3b). Yellow oil; (36 mg, 60%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1 H), 6.27 (s, 1 H), 2.88 (t, J = 5.6 Hz, 2 H), 2.48 (t, J = 5.2 Hz, 2 H), 1.78 (q, J = 7.2 Hz, 2 H), 1.71−1.64 (m, 4 H), 1.21 (s, 3 H), 0.57 (td, J = 7.2 Hz, 0.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.7, 161.8, 149.2, 144.4, 140.6, 55.5, 28.8, 24.7, 24.0, 22.9, 22.5, 20.6, 9.4; HRMS calcd for $C_{13}H_{18}O$ 190.1358, found 190.1364.

4′,5′,6′,7′-Tetrahydrospiro[cyclopentane-1,2′-indene]-1′-carbaldehyde (3c). Yellow oil; (36 mg, 67%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1 H), 6.50 (s, 1 H), 2.87 (t, J = 6.0 Hz, 2 H), 2.46 (t, J = 6.0 Hz, 2 H), 2.20−2.13 (m, 2 H), 1.98−1.93 (m, 2 H), 1.80−1.62 (m, 6 H), 1.45−1.41 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.7, 161.6, 148.4, 142.7, 139.0, 61.7, 32.4, 26.2, 24.8, 24.1, 22.9, 22.4; HRMS calcd for $C_{14}H_{18}O$ 202.1358, found 202.1350.

4′,5′,6′,7′-Tetrahydrospiro[cyclohexane-1,2′-indene]-1′-carbaldehyde (3d). Pale yellow solid; (40 mg, 75%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1 H), 6.92 (s, 1 H), 2.84 (t, J = 6.0 Hz, 2 H), 2.47 (t, J = 5.6 Hz, 2 H), 2.15 (td, J = 12.8, 3.2 Hz, 2 H), 1.76−1.61 (m, 6 H), 1.48−1.33 (m, 4 H), 1.05−1.02 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.0, 160.7, 146.8, 145.6, 140.8, 56.1, 31.4, 25.6, 25.0, 24.9, 24.1, 22.8, 22.4; HRMS calcd for $C_{15}H_{20}O$ 216.1514, found 216.1512.

2-Methyl-2-phenyl-4,5,6,7-tetrahydro-2*H*-indene-1-carbaldehyde (3e). Yellow oil; (29 mg, 39%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1 H), 7.23−7.12 (m, 5 H), 6.44 (s, 1 H), 3.03−2.88 (m, 2 H), 2.54−2.52 (m, 2 H), 1.78−1.68 (m, 4 H), 1.65 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.6, 161.6, 150.2, 146.0, 140.2, 139.9, 128.2, 126.3, 125.9, 57.6, 24.7, 24.3, 22.8, 22.4, 20.1; HRMS calcd for $C_{17}H_{18}O$ 238.1358, found 238.1355.

2,2,6,6-Tetramethyl-4,5,6,7-tetrahydro-2*H*-indene-1-carbaldehyde (3f). Yellow oil; (29 mg, 54%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1 H), 6.31 (s, 1 H), 2.60 (s, 2 H), 2.50 (td, J = 6.8, 1.2 Hz, 2 H), 1.49 (t, J = 6.8 Hz, 2 H), 1.21 (s, 6 H), 0.96 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8, 160.9, 151.3, 146.1, 138.0, 51.7, 37.7, 35.4, 29.8, 28.0, 21.9, 20.8; HRMS calcd for $C_{14}H_{20}O$ 204.1514, found 204.1507.

5-(*tert*-Butyl)-2,2-dimethyl-4,5,6,7-tetrahydro-2*H*-indene-1-carbaldehyde (3g). Yellow oil; (37 mg, 69%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1 H), 6.28 (s, 1 H), 3.21 (ddd, J = 18.4, 4.4, 2.4 Hz, 1 H), 2.68−2.62 (m, 1 H), 2.53 (ddd, J = 18.4, 12.4, 5.2 Hz, 1 H), 2.07 (ddd, J = 16.4, 12.4, 2.4 Hz, 1 H), 1.98−1.92 (m, 1 H), 1.28 (ddd, J = 12.4, 4.4, 1.6 Hz, 1 H), 1.31 (s, 3 H), 1.20−1.16 (m, 4 H), 0.89 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8, 160.7, 151.3, 145.0, 140.5, 51.5, 45.1, 32.4, 27.2, 26.2, 24.5, 24.1, 21.8 (2 × CH_3); HRMS calcd for $C_{16}H_{24}O$ 232.1827, found 232.1815.

2,2-Dimethyl-4,5-dihydro-2*H*-cyclopenta[*a*]naphthalene-1-carbaldehyde (3h). Yellow oil; (35 mg, 64%); ^1H NMR (400 MHz, $CDCl_3$) δ 10.20 (s,1 H), 7.69 (dd, J = 6.0, 2.0 Hz, 1 H), 7.37−7.33 (m, 1 H), 7.31−7.28 (m, 2 H), 6.38 (s, 1 H), 2.84 (t, J = 6.0 Hz, 2 H), 2.59−2.55 (m, 2 H), 1.35 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 153.0, 148.2, 144.9, 140.8, 140.2, 130.2, 130.0 (2 × CH), 128.9, 126.9, 52.8, 30.6, 23.8, 22.4; HRMS calcd for $C_{16}H_{16}O$ 224.1201, found 224.1198.

2,2-Dimethyl-2,4,5,6,7,8-hexahydroazulene-1-carbaldehyde (3i). Yellow oil; (44 mg, 80%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1 H), 6.24 (s, 1 H), 2.77 (br, 2 H), 2.41−2.39 (m, 2 H), 1.72−1.70 (m, 2 H), 1.65−1.62 (m, 2 H), 1.57−1.54 (m, 2 H), 1.20 (s 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.0, 165.5, 151.2, 146.0, 145.4, 50.8, 32.2, 30.1, 29.4, 28.7, 27.0, 21.8; HRMS calcd for $C_{13}H_{18}O$ 190.1358, found 190.1361.

3,5,5-Trimethyl-2-phenylcyclopenta-1,3-dienecarbaldehyde (3j). Yellow oil; (37 mg, 68%); ^1H NMR (400 MHz, $CDCl_3$) δ9.49 (s, 1 H), 7.42−7.39 (m, 3 H), 7.30−7.28 (m, 2 H), 6.43 (s, 1 H), 1.85 (s, 3 H), 1.32 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ187.0, 162.4, 152.6, 148.6, 138.0, 133.0, 129.3, 128.6, 128.2, 51.0, 21.7, 13.8; HRMS calcd for $C_{15}H_{16}O$ 212.1201, found 212.1205.

***N*-((2,2-Dimethyl-4,5,6,7-tetrahydro-2*H*-inden-1-yl)-methylene)-4-methylbenzenesulfonamide (7a).** Orange red oil; (86 mg, 84%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1 H), 7.81 (d, J = 8.4 Hz, 2 H), 7.27 (d, J = 8.4 Hz, 2 H), 6.45 (s, 1 H), 2.79 (t, J = 6.0 Hz, 2 H), 2.46 (t, J = 5.6 Hz, 2 H), 2.39 (s, 3 H), 1.73−1.63 (m, 4 H), 1.19 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 158.8, 154.4, 143.3, 142.1, 140.2, 137.2, 129.4, 127.2, 51.6, 24.8, 24.5, 22.7, 22.2, 21.9, 21.5; HRMS calcd for $C_{19}H_{23}NO_2S$ 329.1449, found 329.1447.

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***N*-((2-Ethyl-2-methyl-4,5,6,7-tetrahydro-2*H*-inden-1-yl)-methylene)-4-methylbenzenesulfonamide (7b).** Orange red oil; (61 mg, 57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.80 (d, J = 8.4 Hz, 2 H), 7.26 (d, J = 8.4 Hz, 2 H), 6.43 (s, 1 H), 2.80 (t, J = 6.4 Hz, 2 H), 2.47 (t, J = 6.4 Hz, 2 H), 2.39 (s, 3 H), 1.78 (q, J = 7.2 Hz, 2 H), 1.71−1.65 (m, 4 H), 1.17 (s, 3 H), 0.46 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 158.9, 152.7, 143.3, 141.6, 140.9, 137.2, 129.4, 127.1, 56.1, 28.9, 24.8, 24.5, 22.7, 22.2, 21.5, 20.8, 9.2; HRMS calcd for $C_{20}H_{25}NO_2S$ 343.1606, found 343.1608.

4-Methyl-*N*-((4′,5′,6′,7′-tetrahydrospiro[cyclopentane-1,2′-inden]-1′-yl)methylene)benzenesulfonamide (7c). Orange red oil; (72 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1 H), 7.80 (d, J = 8.4 Hz, 2 H), 7.26 (d, J = 8.4 Hz, 2 H), 6.67 (s, 1 H), 2.81 (t, J = 6.0 Hz, 2 H), 2.46 (t, J = 5.6 Hz, 2 H), 2.39 (s, 3 H), 2.19−2.12 (m, 2 H), 1.98−1.90 (m, 2 H), 1.75−1.65 (m, 6 H), 1.42−1.37 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 158.7, 152.1, 143.3, 140.0, 139.5, 137.3, 129.4, 127.2, 62.1, 32.8, 26.2, 24.9, 24.6, 22.8, 22.2, 21.5; HRMS calcd for $C_{21}H_{25}NO_2S$ 355.1606, found 355.1607.

4-Methyl-*N*-((4′,5′,6′,7′-tetrahydrospiro[cyclohexane-1,2′-inden]-1′-yl)methylene)benzenesulfonamide (7d). Orange red oil; (88 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1 H), 7.81 (d, J = 7.6 Hz, 2 H), 7.28 (d, J = 7.6 Hz, 2 H), 7.09 (s, 1 H), 2.78 (t, J = 6.0 Hz, 2 H), 2.48 (t, J = 6.0 Hz, 2 H), 2.40 (s, 3 H), 2.20 (td, J = 13.2 Hz, 3.2 Hz, 2 H), 1.76−1.65 (m, 6 H), 1.48−1.30 (m, 4 H), 0.98 (d, J = 13.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ165.1, 159.1, 150.6, 143.3, 142.3, 141.7, 137.1, 129.4, 127.2, 56.7, 31.5, 25.5, 24.9, 24.8, 24.7, 22.7, 22.2, 21.5; HRMS calcd for $C_{22}H_{27}NO_2S$ 369.1762, found 369.1770.

4-Methyl-*N*-((2-methyl-2-phenyl-4,5,6,7-tetrahydro-2*H*-inden-1-yl)methylene)benzenesulfonamide (7e). Orange red oil; (78 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1 H), 7.43 (d, J = 8.4 Hz, 2 H), 7.11 (d, J = 8.4 Hz, 2 H), 7.08−7.07 (m, 3 H), 7.03−7.01 (m, 2 H), 6.58 (s, 1 H), 2.95−2.80 (m, 2 H), 2.54−2.52 (m, 2 H), 2.35 (s, 3 H), 1.75−1.69 (m, 4 H), 1.67 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 159.0, 153.2, 143.2, 142.9, 141.1, 139.3, 137.2, 129.1, 128.0, 126.7, 126.2, 126.1, 58.1, 25.1, 24.6, 22.7, 22.2, 21.4, 20.0; HRMS (ESI (+)) $C_{24}H_{25}NO_2S$, calcd 391.1606 [M], found 391.1606.

4-Methyl-*N*-((2,2,6,6-tetramethyl-4,5,6,7-tetrahydro-2*H*-inden-1-yl)methylene)benzenesulfonamide (7f). Orange red oil; (78 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1 H), 7.83 (d, J = 8.0 Hz, 2 H), 7.27 (d, J = 8.0 Hz, 2 H), 6.48 (s, 1 H), 2.54 (s, 2 H), 2.51 (t, J = 6.8 Hz, 2 H), 2.40 (s, 3 H), 1.50 (t, J = 6.8 Hz, 2 H), 1.19 (s, 6 H), 0.96 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 158.8, 154.7, 143.3, 142.7, 138.9, 137.4, 129.4, 127.2, 52.2, 38.4, 35.3, 29.9, 27.9, 22.0, 21.5, 20.7; HRMS calcd for $C_{21}H_{27}NO_2S$ 357.1762, found 357.1761.

***N*-((5-(*tert*-Butyl)-2,2-dimethyl-4,5,6,7-tetrahydro-2*H*-inden-1-yl)methylene)-4-methylbenzenesulfonamide (7g).** Orange red oil; (87 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1 H), 7.82 (d, J = 8.0 Hz, 2 H), 7.27 (d, J = 8.0 Hz, 2 H), 6.46 (s, 1 H), 3.14−3.09 (m, 1 H), 2.67−2.63 (m, 1 H), 2.54−2.45 (m, 1 H), 2.40 (s, 3 H), 2.12−2.05 (m, 1 H), 2.01−1.97 (m, 1 H), 1.36−1.27 (m, 2 H), 1.20 (s, 3 H), 1.18 (s, 3 H), 0.90 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 158.8, 154.6, 143.3, 141.7, 141.4, 137.2, 129.4, 127.2, 52.0, 45.0, 32.4, 27.2, 26.0, 25.3, 23.8, 22.0, 21.9, 21.5; HRMS calcd for $C_{23}H_{31}NO_2S$ 385.2075, found 385.2070.

***N*-((2,2-Dimethyl-4,5-dihydro-2*H*-cyclopenta[*a*]naphthalene-1-yl)methylene)-4-methylbenzenesulfonamide (7h).** Orange red oil; (78 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1 H), 7.84 (d, J = 8.4 Hz, 2 H), 7.56 (d, J = 7.2 Hz, 1 H), 7.38−7.33 (m, 2 H), 7.31−7.28 (m,3 H), 6.50 (s, 1 H), 2.82 (t, J = 6.0 Hz, 2 H), 2.59−2.55 (m, 2 H), 2.41 (s, 3 H), 1.31 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 157.0, 151.0, 143.5, 141.0, 140.8 (2 × C), 136.8, 130.5, 130.1, 129.5, 129.4, 129.0, 127.4 (2 × CH), 53.2, 30.4, 23.7, 22.5, 21.5; HRMS calcd for $C_{23}H_{23}NO_2S$ 377.1449, found 377.1447.

***N*-((2,2-Dimethyl-2,4,5,6,7,8-hexahydroazulen-1-yl)methylene)-4-methylbenzenesulfonamide (7i).** Orange red oil; (80 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1 H), 7.82 (d, J = 8.4 Hz, 2 H), 7.27 (d, J = 8.4 Hz, 2 H), 6.41 (s, 1 H), 2.73−2.71 (m, 2 H), 2.44−2.41 (m, 2 H), 2.40 (s, 3 H), 1.75−1.72 (m, 2 H), 1.64−1.63 (m,2 H), 1.57−1.55 (m,2 H), 1.19 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 159.3, 154.3, 146.0, 143.3, 142.3, 137.2, 129.4, 127.2, 51.2, 32.1, 30.0, 29.2, 28.5, 28.1, 21.9, 21.5; HRMS calcd for $C_{20}H_{25}NO_2S$ 343.1606, found 343.1609.

4-Methyl-*N*-((3,5,5-trimethyl-2-phenylcyclopenta-1,3-dien-1-yl)methylene)benzenesulfonamide (7j). Orange red solid; (82 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1 H), 7.77 (d, J = 8.4 Hz, 2 H), 7.43−7.42 (m, 3 H), 7.26 (d, J = 8.4 Hz, 2 H), 7.20−7.18 (m, 2 H), 6.56 (s, 1 H), 2.39 (s, 3 H), 1.87 (s, 3 H), 1.29 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 162.0, 155.6, 145.0, 143.5, 138.7, 136.6, 132.7, 129.4, 129.0 (2 × CH), 128.5, 127.4, 51.5, 21.9, 21.5, 13.9; HRMS calcd for $C_{22}H_{23}NO_2S$ 365.1449, found 365.1444.

***N*-((2,2-Dimethyl-4,5,6,7-tetrahydro-2*H*-inden-1-yl)methyl)-4-methylbenzenesulfonamide (8a).** Pale yellow solid; (58 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2 H), 7.31 (d, J = 8.4 Hz, 2 H), 5.73 (s, 1 H), 3.97 (br, 1 H), 3.65 (d, J = 5.2 Hz, 2 H), 2.43 (s, 3 H), 2.35−2.34 (m, 2 H), 2.18 (br, 2 H), 1.53−1.51 (m, 4 H), 0.98 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 140.2, 139.5, 138.4, 136.5, 129.6 (2 × CH), 127.2, 51.5, 37.8, 25.3, 23.5, 23.4, 23.2, 22.2, 21.5; HRMS calcd for $C_{19}H_{25}NO_2S$ 331.1606, found 331.1602.

3,3-Dimethyl-5,6,7,8-tetrahydro-3*H*-isochromene-1-carbaldehyde (9). Yellow oil; (23 mg, 39%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1 H), 5.35 (s, 1 H), 2.74 (t, J = 6.0 Hz, 2 H), 2.28 (t, J = 6.0 Hz, 2 H), 1.67−1.56 (m, 4 H), 1.31 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.4, 149.2, 142.9, 131.1, 129.4, 75.2, 29.1, 26.7, 23.3, 23.0, 22.8; HRMS calcd for $C_{12}H_{16}O_2$: 192.1150, found 192.1147.

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene((2-(2-methylprop-1-en-1-yl) cyclohex-1-en-1-yl)ethynyl)gold (10). White solid; (61 mg, 68%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (t, J = 7.8 Hz, 2 H), 7.24 (d, J = 7.8 Hz, 4 H), 7.08 (s, 2 H), 5.96 (s, 1 H), 2.59−2.55 (m, 4 H), 2.10−2.08 (m, 4 H), 1.62 (s, 3 H), 1.58 (s, 3 H), 1.45−1.44 (m, 4 H), 1.33 (d, J = 7.2 Hz, 12 H), 1.18 (d, J = 7.2 Hz, 12 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.7, 145.7, 138.9, 134.4, 132.7, 131.6, 130.4, 127.1, 124.1, 123.0, 118.8, 105.6, 31.5, 30.0, 28.8, 27.0, 24.5, 24.0, 22.9, 22.7, 20.7; HRMS calcd for $C_{39}H_{51}AuN_2$: 744.3718, found 744.3712.

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene((5,5-dimethyl-2-(2-methylprop-1-en-1-yl)cyclohex-1-en-1-yl)-ethynyl)gold (11). Pale yellow solid; (84 mg, 68%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (t, J = 7.8 Hz, 2 H), 7.24 (d, J = 7.8 Hz, 4 H), 7.08 (s, 2 H), 5.95 (s, 1 H), 2.59−2.55 (m, 4 H), 2.10 (t, J = 6.6 Hz, 2 H), 1.90 (s, 2 H), 1.63 (s, 3 H), 1.59 (s, 3 H), 1.33 (d, J = 7.2 Hz, 12 H), 1.21 (t, J = 6.6 Hz, 2 H), 1.18 (d, J = 7.2 Hz, 12 H), 0.78 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.7, 145.6, 137.2, 134.4, 132.9, 131.1, 130.3, 126.6, 124.1, 123.0, 118.0, 105.8, 45.1, 35.6, 28.8, 28.7, 28.0, 27.5, 27.0, 24.5, 24.0, 20.7; HRMS (ESI (+)) $C_{41}H_{56}AuN_2^+$, calcd 773.4104 [M + H]$^+$, found 773.4128.

(3,5-Dichloropyridin-1-ium-1-yl)((2-(2-methylprop-1-en-1-yl)cyclohex-1-en-1-yl)ethynyl)amide (12). Yellow oil; (7 mg, 7%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (s, 1 H), 7.05 (d, J = 1.2 Hz, 1 H), 6.64 (d, J = 0.6 Hz, 1 H), 5.80 (s, 1 H), 2.59−2.56 (m, 2 H), 2.19−2.18 (m, 2 H), 1.77−1.67 (m, 7 H), 1.43 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.5, 137.9, 137.3, 133.6, 126.7, 125.6, 125.1, 123.5, 123.2, 117.6, 97.7, 31.5, 28.7, 25.6, 22.9, 22.7, 19.3; HRMS calcd for $C_{17}H_{18}Cl_2N_2$ 320.0847, found 320.0854.

■ ASSOCIATED CONTENT

Supporting Information

HRMS ^{1}H and ^{13}C NMR spectra of compounds d_1-**2a**, **3a**−**3j**, d_1-**3a**, **7a**−**7j**, **8a**, **9**, **10**, **11**, and **12**, and crystallographic data for compound **8a**. 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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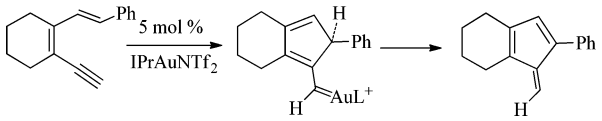

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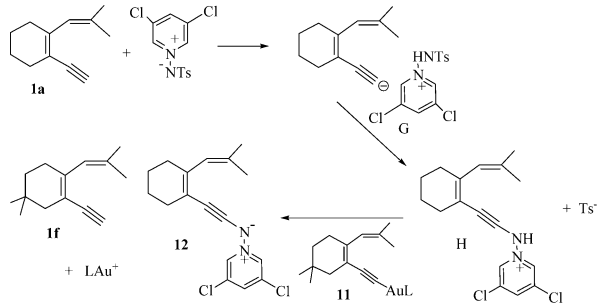

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