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Supporting Information for

Allenylidene Au(I) Catalyst Derived From Triazole Unit & Its Initial Application

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1. General Condition

All reactions were run under an inert atmosphere (Ar) with flame-dried glassware using standard techniques for manipulating air-sensitive compounds. All solvents were dried and purified before use by standard procedures. Commercial reagents were used as supplied or purified by standard techniques where necessary. Column chromatography was performed using 200-300 mesh silica with the proper solvent system according to TLC analysis and UV light to visualize the reaction components. Unless otherwise noted, nuclear magnetic resonance spectra were recorded on 400 MHz spectrometer. NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet- doublet, t = triplet, m = multiplet and bs = broad singlet), coupling constant in Hz and integration. Chemical shifts of ¹H NMR spectra were recorded in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.26 ppm). Chemical shifts for ¹³C NMR spectra were recorded in parts per million from tetramethylsilane using the central peak of CDCl₃ (77.16 ppm) as the internal standard. HR-MS data were obtained using ESI ionization with 100,000 (FWHM) maximum resolution. M.p. data were measured with micro melting point apparatus.

X-ray Crystallographic Studies: Data collections for them were performed on a Bruker APEX-II CCD' diffractometer, using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Using Olex21, the structures were solved with the ShelXT2 structure solution program using Intrinsic Phasing and refined with the ShelXL3 refinement package using Least Squares minimization. Refinement was performed on F2 anisotropically for all the non-hydrogen atoms by the full-matrix least squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for compounds were summarized. Accession Codes CCDC (1) 1903172 (2a), (2) 1903174 (3a), (3) 1903173 (3d) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Alkynyl triazole salt $1g^{[1]}$, Substrate dienone $4^{[2]}$, Arylenone $6a-f^{[3]}$ and $8^{[4]}$ were prepared according to the published methods.

2 X-ray chromatograph for complexes 2a, 3a, 3d and complex S1

I. 2a's crystal were obtained by slow diffusion of ether into a dilute dichloromethane solution of 2a.



SFigure 1. ORTEP picture of compound 2a with the displacement ellipsoid drawn at 50% probability. {CCDC: 1903172}

STable 1. Selected Bond Lengths for 2a			
Atom	Atom	Length/Å	
C1	C4	1.3683(17)	
C1	C2	1.4194(18)	
N1	N2	1.3220(14)	
C2	C3	1.1800(2)	
N1	C4	1.3491(15)	
N3	N2	1.3127(15)	
N3	C1	1.3604(16)	

II. 3a's crystal was obtained by slow diffusion of ether into a dilute dichloromethane solution of 3a.



SFigure 2. ORTEP picture of compound 3a with the displacement ellipsoid drawn at 50% probability. {CCDC: 1903174}

 STable 2. Selected Bond Lengths for 3a

 Atom
 Atom

Aul	Cl1	2.2844(13)
Au1	C3	1.944(6)
N1	N2	1.316(6)
N1	C4	1.356(6)
N2	N3	1.317(6)
N3	C1	1.367(7)
C2	C3	1.221(8)
C1	C2	1.403(8)
C4	C1	1.371(8)

III. 3d's crystal was obtained by slow diffusion of ether into a dilute dichloromethane solution of 3d.



SFigure 3. ORTEP picture of compound 3d with the displacement ellipsoid drawn at 50% probability. {CCDC: 1903173}

		0	
Atom	Atom	Length/Å	
Cl1	Au1	2.280(3)	
N3	N2	1.334(14)	
N3	C4	1.333(13)	
C1	N1	1.352(14)	
N2	N1	1.327(10)	
C3	C2	1.204(13)	
C3	Au1	1.954(8)	
C4	C1	1.368(17)	
C1	C2	1.408(15)	

STable 3. Selected Bond Lengths for 3d

IV. Complex **S1**'s crystal was obtained by slow diffusion of ether into a dilute dichloromethane solution of **S1**.



SFigure 4. ORTEP picture of complex S1 with the displacement ellipsoid drawn at 50% probability. {CCDC: 1906049}

Atom	Atom	Length/Å
Aul	P1	2.2781(9)
Aul	C3	2.003(4)
N1	C4	1.345(4)
N1	N2	1.352(4)
C3	C2	1.198(5)
C2	C1	1.427(4)
N3	C1	1.369(4)
N3	N2	1.309(4)
<u>C4</u>	C1	1.372(4)

STable 4. Selected Bond Lengths for S1

3. DFT calculation results for ligand A's σ -donating orbital (HOMO) and π -accepting orbital (LUMO+1)

Description : Result description DFT calculations were carried out with the Gaussian 16 package^[9]. In order to reduce the computational cost, the phenyl groups were replaced by methyl groups. Geometry optimizations were performed with the density functional theory (DFT)/ (BP86). The TZVP basis set was used for all the atoms. Frequency calculations at the same level of theory were performed. The positive frequencies obtained for all the vibrational modes of the systems considered ensure the minima on the potential energy surface.



SFigure 5. Energy (eV) of ligand A's σ -donating orbital (HOMO), LUMO orbital and π -accepting orbital (LUMO+1) at the BP86/ TZVP level.

4. Stable 5. Aryl enone 6a's Nazarov reaction by using complexes 3a-f and Au(III) complex.^{a, b}



entry	Condition	Temp	time	yield
1	$3a/AgSbF_{6}(1/2)$	35	12h	85%
2	$3b/AgSbF_{6}(1/2)$	35	12h	96%
3	$3c/AgSbF_{6}(1/2)$	35	12h	40%
4	$3d/AgSbF_{6}(1/2)$	35	12h	91%
5	$3e/AgSbF_{6}(1/2)$	35	12h	81%
6	$3f/AgSbF_{6}(1/2)$	35	12h	80%
7	$AuCl_3/AgSbF_6$ (1/2)	35	12h	97%

^a Unless noted, all reactions were carried out on a 0.1 mmol scale in 2 mL of solvent at 35°C with the addition of 2 mol% of Au(I)/silver salt catalyst. ^b The reaction yields were determined by ${}^{1}H$ NMR method.

Description: Less reactive aryl enone **8a**'s Nazarov reaction was investigated to evaluate complexes **3a-f**'s catalytic activity variation. As compared with the phenyl group and *p*-chlorophenyl group substituted triazolylidene vinylidene Au(I) complexes **3a** (Stable 8, entry 1) and **3c** (Stable 8, entry 3), the relatively electron-rich *p*-methyl phenyl group and benzyl group substituted analogues **3b** (Stable 8, entry 2) and **3d** (Stable 8, entry 4) seemed to have much higher catalytic activity. Furthermore, a site preference could be observed from **3b** and **3e**'s catalytic performance. It was found that the allenylidene moiety, locating in the different position of the triazole ring, would lead to an obvious different inducing activity (Stable 8, entry 2 and 5). Among all these complexes tested, complex **3b** provide a highest reaction yield.

5. General procedure for complex 3b mediated arylenone's Nazarov reaction:



To a suspension of 2 mol% of $3b/AgSbF_6(1/2)$ in CH_2Cl_2 (2 mL) at 35 °C, was added aryl enone **6a** (29.6mg, 0.1 mmol). The reaction was then kept at 35 °C with TLC monitoring until complete consumption of the starting material. Concentration of the reaction mixture, followed by purification product through flash chromatography (petroleum/EtOAc = 10/1 to 5/1 as the eluent) afforded **7a** as a white solid (28 mg, 96% yield).

6. Complexes 3a-f's preparation

6.1 1,4-disubstitued 1,2,3-triazole 1a-c, 1,5-disubstitued 1,2,3-triazole 1d-e and 1,4,5-trisubstituted 1,2,3-triazole 1f's preparation

7.1a General synthetic route for preparation of 1-alkynyl triazole derivatives 1a-c and 1f:



I General procedure for preparation of 1-phenyl-4-hydoxymethyl-1H-1,2,3-triazole S5a:

To a solution of phenylazide **S4a** (595 mg, 5 mmol) in DMF/MeOH=9/1 (5 mL), was added 2propyn-1-ol (840 mg, 3 mmoL) and CuI (57 mg, 0.3 mmol). Stirring at rt with TLC monitoring until complete consumption of the starting material **S1a**, the reaction mixture was then poured into cold ice water (20 ml) and extracted with ethyl acetate (3×10 ml). The combined organic layers were washed with distilled water (2×10 ml), brine (10 ml) and dried over anhydrous sodium sulphate. After filtration and concentration under reduced pressure, the crude product was purified by column chromatography (SiO₂; eluent: ethyl acetate/hexane = 1/1) to give product **S2a** as a white solid (778 mg, 89% yield)



(1-phenyl-1H-1,2,3-triazol-4-yl)methanol S2a: ¹H NMR (600 MHz, CD₃CN) δ 8.21 (s, 1H), 7.82 – 7.77 (m, 2H), 7.58 – 7.54 (m, 3H), 7.50 – 7.44 (m, 1H), 4.72 (s, 2H), 3.39 (s, 1H). ¹³C NMR (151 MHz, CD₃CN) δ 149.60, 137.91, 130.45, 129.31, 121.40, 121.13, 118.00, 56.22. HR-MS (ESI) calcd for [C₉H₉N₃O], [M+Na]⁺: m/z= 198.0638; Found: 198.0639.

S5b, **S5c**, **S5f** were prepared according to the published methods.^[6]



II General procedure for preparation of alkynyl triazole 1a-c and 1f:

To a solution of (1-phenyl-1H-1,2,3-triazol-4-yl)methanol S5a (875mg, 5 mmol) in DCM, was

added MnO_2 (4.3g, 50 mmol). The mixture was stirred at 35°C with TLC monitoring until complete consumption of **S2a**. Afterwards, the solution was filtered, and concentrated *in vacuo* to give a triazolyl aldehyde product,^[7] which was directly utilized in the next step without further purification.

To a solution of the triazolyl aldehyde (obtained in the previous step) in MeOH (20 mL) at 0 °C, was added dimethyl acetyldiazomethylphosphonate (960 mg, 5 mmol) and K_2CO_3 (1.38 g, 10mmol). The reaction mixture was stirred at 0 °C for 1 hour and then at rt for 12 hours. After removal of the solvent, the crude product was purified by column chromatography over SiO₂ (Hex/EtOAc=5/1) to give 4-ethynyl-1-phenyl-1H-1,2,3-triazole **1a** as a white solid (786 mg, 93% yield for two steps).^[8]



4-ethynyl-1-phenyl-1H-1,2,3-triazole 1a: ¹H NMR (600 MHz, CDCl₃) δ 8.05 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 15.7 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.55 (d, J = 15.6 Hz, 1H), 7.44 – 7.37 (m, 3H), 6.99 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H).¹³C NMR (151 MHz, CDCl₃) δ 136.44, 130.74, 129.89, 129.22, 124.74, 120.63, 81.78, 77.26, 77.05, 76.84, 72.75. HR-MS (ESI) calcd for [C₁₀H₇N₃], [M+H]⁺: m/z= 170.0713; Found: 170.0709.



4-ethynyl-1-(p-tolyl)-1H-1,2,3-triazole 1b: Obtained as a white solid in 87% yield by using the same preparation method of **1a**. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (s, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 3.30 (s, 1H), 2.39 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 139.28, 134.00, 130.42, 130.23, 124.69, 120.34, 81.58, 72.78, 20.98. HR-MS (ESI) calcd for [C₁₁H₉N₃], [M+H]⁺: m/z= 184.0869; Found: 184.0866



1-(4-chlorophenyl)-4-ethynyl-1H-1,2,3-triazole 1c: Obtained as a white solid in 85% yield by using the same preparation method of **1a.** ¹H NMR (600 MHz, CDCl₃) δ 8.08 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 3.32 (s, 1H).¹³C NMR (151 MHz, CDCl₃) δ 135.17, 135.02, 131.10, 130.16, 124.57, 121.87, 82.02, 72.57. HR-MS (ESI) calcd for [C₁₀H₆N₃Cl], [M+H]⁺: m/z= 204.0323; Found: 204.0325.



5-ethynyl-4-phenyl-1-(p-tolyl)-1H-1,2,3-triazole 1f: Obtained as a white solid in 75% yield by using the same preparation method of **1a.** ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 3.80 (s, 1H), 2.46 (s, 3H).¹³C NMR (101 MHz, CDCl₃) δ 149.57, 139.88, 133.90, 129.90, 128.96, 128.74, 126.56, 123.90, 90.75, 21.32. HR-MS (ESI) calcd for [C₁₇H₁₃N₃], [M+H]⁺: m/z= 260.1182; Found: 260.1181

6.1b General synthetic route for preparation of 1-alkynyl triazole derivatives 1d and 1e:



To a solution of Cp*RuCl(PPh₃)₂ (79 mg, 0.05 mmol) dissolved in 5 mL of dioxane, was added a solution of buta-1,3-diyn-1-yltrimethylsilane (134 mg, 1.1 mmol) and benzyl azide **S4d** (133mg, 1 mmol) in 6 mL of dioxane. The vial was purged with Argon, sealed and heated in an oil bath at 75 °C for 12h, until complete consumption of the azide starting materials with TLC monitoring. Removal of the solvent under reduced pressure followed by purification through column chromatography over SiO₂ (eluted by Hex/EtOAc=5/1) afforded 1-benzyl-5-((trimethylsilyl) ethynyl)-H-1,2,3- triazole **S5d** as a white solid (142 mg, 56% yield). ^[5]

To a solution of 1-benzyl-5-((trimethylsilyl)ethynyl)-1H-1,2,3-triazole **S5d** (142mg, 0.56 mmol) in anhydrous MeOH (3 mL), was added anhydrous potassium carbonate (77 mg, 0.56 mmol) under argon protection. After stirring at 25 °C for 3 h, the solvent was evaporated under reduced pressure. The residue was mixed with 2 mL of aqueous sodium bicarbonate and extracted with DCM (3×10 mL). The combined organic fractions were dried over MgSO₄, and concentrated. The residue was purified by flash chromatography on silica gel (eluted by n-Hexane/EtOAc=5/1) to give alkynyl triazole **1d** as a white solid (91 mg, 89% yield).



1-benzyl-5-((trimethylsilyl)ethynyl)-1H-1,2,3-triazole S5d: ¹H NMR (600 MHz, CDCl₃) δ 7.76 (s, 1H), 7.38 – 7.27 (m, 5H), 5.57 (s, 2H), 0.25 (s, 9H) ¹³C NMR (151 MHz, CDCl₃) δ 137.02, 134.63, 128.90, 128.81, 128.53, 128.25, 128.05, 108.05, 89.23, 88.90, 52.77, -0.51. HR-MS (ESI) calcd for [C₁₄H₁₇N₃Si], [M+H]⁺: m/z= 256.1265; Found: 256.1265.



1-benzyl-5-ethynyl-1H-1,2,3-triazole 1d: ¹H NMR (400 MHz, CDCl3) δ 7.82 (s, 1H), 7.35 (m, 5H), 5.58 (s, 2H), 3.72 (s, 1H).13C NMR (101 MHz, CDCl3) δ 137.33, 134.33, 128.73, 128.41, 127.88, 120.15, 89.35, 68.65, 52.46. HR-MS (ESI) calcd for [C11H9N3] , [M+H]+: m/z= 184.0869; Found: 184.0870.



1-(p-tolyl)-5-((trimethylsilyl)ethynyl)-1H-1,2,3-triazole S5e: Obtained as a white solid in 77% yield by using the same preparation method of **S5d**. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 2.44 (s, 3H), 0.22 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 139.44, 137.75, 134.01, 129.63, 123.20, 120.58, 107.72, 89.64, 21.22, -0.65. HR-MS (ESI) calcd for [C₁₄H₁₇N₃Si], [M+H]⁺: m/z= 256.1265; Found: 256.1265.



5-ethynyl-1-(p-tolyl)-1H-1,2,3-triazole 1e: Obtained as a white solid in 81% yield by using the same preparation method of **1d**. ¹H NMR (600 MHz, CDCl₃) δ 7.95 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 3.60 (s, 1H), 2.44 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 139.82, 138.40, 133.80, 129.90, 123.56, 119.93, 88.78, 69.45, 21.25. HR-MS (ESI) calcd for [C₁₁H₉N₃], [M+H]⁺: m/z= 184.0869; Found: 184.0870.

6.2 General procedure for preparation of alkynyl triazole salts 2a-f:

To a solution of **1a** (169 mg, 1 mmol) in a mixture of dry DCM/MeCN (10 mL, 1/1), was added Me_3OBF_4 (444 mg, 3 mmol) under Ar protection. The solution was stirred at 65 °C for 16 h. After the completion by TLC monitoring, the reaction was quenched by the addition of MeOH (3 mL) at 0°C. Removal of the solvent in vacuo followed by purification through flash chromatography over silica gel column using DCM/MeOH (100/1) as the eluent afforded alkynyl triazole salt **2a** as a white solid (211 mg, 78% yield).



4-ethynyl-3-methyl-1-phenyl-1H-1,2,3-triazol-3-ium 2a: M.p. 183-186 °C. ¹H NMR (400 MHz, CD₃CN) δ 8.97 (s, 1H), 7.72 (d, J = 8.6 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 4.58 (s, 1H), 4.35 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 135.41, 133.05, 131.61, 131.26, 127.53, 122.60, 118.00, 95.35, 64.51, 39.79. HR-MS (ESI) calcd for[C₁₁H₁₀N₃BF₄], [[M-BF₄]⁺: m/z= 184.0869; Found: 184.0863.



4-ethynyl-3-methyl-1-(p-tolyl)-1H-1,2,3-triazol-3-ium 2b: Obtained as a white solid in 67% yield by using the same preparation method of **2a**. M.p. 169-171 °C. ¹H NMR (400 MHz, CD₃CN) δ 8.97 (s, 1H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 4.58 (s, 1H), 4.35 (s, 3H) , 2.46 (s, 3H). ¹³C NMR (101 MHz, CD₃CN) δ 143.90, 132.98, 131.51, 131.41, 127.28, 122.14, 95.15, 64.48, 39.58, 20.92. HR-MS (ESI) calcd for [C₁₂H₁₂N₃BF₄], [[M-BF₄]⁺: m/z= 198.1026; Found: 198.1017.



1-(4-chlorophenyl)-4-ethynyl-3-methyl-1H-1,2,3-triazol-3-ium 2c: Obtained as a white solid in 77% yield by using the same preparation method of **2a**. M.p. 168-170 °C. ¹H NMR (400 MHz, CD₃CN) δ 9.00 (s, 1H), 7.86 – 7.82 (m, 2H), 7.73 – 7.68 (m, 2H), 4.58 (s, 1H), 4.37 (s, 3H). ¹³C NMR (101 MHz, CD₃CN) δ 138.34, 133.95, 131.74, 131.17, 127.49, 124.15, 95.35, 64.37, 39.72 HR-MS (ESI) calcd for[C₁₁H₉N₃ClBF₄], [[M-BF₄]⁺: m/z= 218.0480; Found: 218.0475.



1-benzyl-5-ethynyl-3-methyl-1H-1,2,3-triazol-3-ium 2d: Obtained as a white solid in 67% yield by using the same preparation method of **2a**. M.p. 162-165 °C. ¹H NMR (400 MHz, CD₃CN) δ 8.57 (s, 1H), 7.48 (s, 5H), 5.81 (s, 2H), 4.55 (s, 1H), 4.28 (s, 3H). ¹³C NMR (101 MHz, CD₃CN) δ 134.63, 132.09, 130.21, 129.73, 125.79, 95.44, 64.67, 56.45, 41.16. HR-MS (ESI) calcd for[C₁₂H₁₂N₃BF₄], [M-BF₄]⁺: m/z= 198.1026; Found: 198.1027.



5-ethynyl-3-methyl-1-(p-tolyl)-1H-1,2,3-triazol-3-ium 2e: Obtained as a white solid in 73% yield by using the same preparation method of **2a**. M.p. 162-165 °C. ¹H NMR (600 MHz, CD₃CN) δ 8.67 (s, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 4.35 (s, 3H), 4.34 (s, 1H), 2.48 (s, 3H). ¹³C NMR (151 MHz, CD₃CN) δ 144.40, 135.08, 131.99, 131.30, 126.14, 125.16, 118.00, 94.57, 65.30, 41.43, 21.12. HR-MS (ESI) calcd for[C₁₂H₁₂N₃BF₄], [M-BF₄]⁺: m/z= 198.1026; Found: 198.1027.



5-ethynyl-3-methyl-4-phenyl-1-(p-tolyl)-1H-1,2,3-triazol-3-ium 2f: Obtained as a white solid in 57% yield by using the same preparation method of **2a**. M.p. 162-164 °C. ¹H NMR (400 MHz, CD₃CN) δ 7.82 – 7.69 (m, 7H), 7.55 (d, *J* = 8.2 Hz, 2H), 4.27 (s, 3H), 4.26 (s, 1H), 2.50 (s, 3H). ¹³C NMR (101 MHz, CD₃CN) δ 146.28, 144.40, 133.19, 132.22, 131.38, 130.61, 130.42, 130.31, 129.69, 129.57, 126.82, 125.14, 124.82, 124.53, 122.01, 94.79, 66.11, 39.82, 21.16. HR-MS (ESI) calcd for[C₁₈H₁₆N₃BF₄], [M-BF₄]⁺: m/z= 198.1026; Found: 198.1027.

6.3 General procedure for preparation of (allenylidene)(carbene) Au(I) complexes 3a-f:

To a solution of alynyl triazole salt **2a** (13.5 mg, 0.05 mmol) in a mixture of dry DCM/MeCN (2 mL, 1/1), was added Ag₂O (11.5 mg, 0.05 mmol) at rt under Ar protection. After stirred at rt in the dark overnight, Au(SMe₂)Cl (14.7 mg, 0.05 mmol) was added. 2h later, the solution was filtered through celite and concentrated in vacuo. The mixture was purified by flash chromatography over Al₂O₃ column using DCM/MeOH (100/1) as the eluent afforded the allenylidene Au(I) complex **3a** as a white solid (10 mg, 49% yield).



((3-methyl-1-phenyl-2,3-dihydro-1H-1,2,3-triazol-4-yl)ethynyl)gold(I) chloride 3a: M.p. 206-208 °C. ¹H NMR (600 MHz, DMSO) δ 9.52 (s, 1H), 7.95 (d, J = 6.9 Hz, 2H), 7.77 – 7.68 (m, 3H), 4.28 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 174.03, 36.48, 135.35, 132.13, 130.84, 129.51, 128.79, 121.87, 78.24, 38.49. (N-CH₃). HR-MS (ESI) calcd for [C₁₁H₉N₃AuCl], [M+Na]⁺: m/z= 438.0043; Found: 438.0045. Anal. Calcd for C₁₁H₉N₃AuCl+0.5(MeOH): C, 32.00; H, 2.57; N, 9.73; Found: C, 32.54; H, 2.86; N, 9.73



((3-methyl-1-(p-tolyl)-1H-1,2,3-triazol-4-yl)ethynyl)gold(I) chloride 3b: Obtained as a white solid in 79% yield by using the same preparation method of 3a. M.p. 256-257 °C. ¹H NMR (600 MHz, DMSO) δ 9.47 (s, 1H), 7.83 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 4.26 (s, 3H), 2.43 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 174.76(C-Au), 142.31, 136.39, 133.07, 131.14, 130.14, 129.45, 128.52, 121.60, 78.25, 38.41(N-CH₃), 21.23. HR-MS (ESI) calcd for [C₁₂H₁₁N₃AuCl], [M+Na]⁺: m/z= 452.0199; Found: 452.0188.Anal. Calcd for C₁₂H₁₁N₃AuCl +1(H₂O): C, 32.20; H, 2.93; N, 9.39; Found: C, 32.43; H, 3.08; N, 9.38



mono(((1-(4-chlorophenyl)-3-methyl-2,3-dihydro-1H-1,2,3-triazol-4-yl)ethynyl)gold(I))mono--chloride 3c: Obtained as a white solid in 43% yield by using the same preparation method of 3a. M.p. 282-283 °C. ¹H NMR (600 MHz, DMSO) δ 9.51 (s, 1H), 7.98 (d, J = 8.9 Hz, 2H), 7.83 (d, J = 8.9 Hz, 2H), 4.28 (s, 2H). ¹³C NMR (126 MHz, DMSO) δ 174.78(C-Au), 136.69, 134.15, 130.85, 129.53, 128.99, 126.76, 123.77, 78.16, 38.54. (N-CH3). HR-MS (ESI) calcd for [C₁₁H₈N₃AuCl₂], [M+Na]+: m/z= 471.9653; Found: 471.9663.Anal. Calcd for C₁₁H₈N₃AuCl₂ + 0.3(CH₂Cl₂): C, 28.48; H, 1.83; N, 8.78; Found: C, 28.72; H, 1.79; N, 8.22



((1-benzyl-3-methyl-1H-1,2,3-triazol-5-yl)ethynyl)gold(I) chloride 3d: Obtained as a white solid in 80% yield by using the same preparation method of 3a. M.p. 229-230°C. ¹H NMR (600 MHz, DMSO) δ 8.81 (s, 1H), 7.47 – 7.39 (m, 5H), 5.75 (s, 2H), 4.21 (s, 3H). ¹³C NMR (151 MHz, DMSO) δ 174.35(C-Au), 136.07, 133.06, 131.33, 129.72, 129.09, 129.03, 128.82, 127.62, 77.84, 53.76, 40.27. HR-MS (ESI) calcd for [C₁₂H₁₁N₃AuCl], [M+Na]⁺: m/z= 452.0199; Found: 452.0195.Anal. Calcd for C₁₂H₁₁N₃AuCl + 0.3(CH₃OH): C,33.64; H, 2.82; N, 9.54; Found: C, 33.55; H, 2.58; N, 9.78



((3-methyl-1-(p-tolyl)-1H-1,2,3-triazol-5-yl)ethynyl)gold(I)chloride 3e: Obtained as a white solid in 75% yield by using the same preparation method of 3a. M.p.218-223 °C.¹H NMR (600 MHz, DMSO) δ 8.96 (s, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H), 4.31 (s, 3H), 2.44 (s, 3H). ¹³C NMR (151 MHz, DMSO) δ 174.61(C-Au), 142.19, 136.18, 132.40, 132.06, 130.52, 130.00, 127.77, 124.73, 78.60, 40.59(N-CH₃), 21.21. HR-MS (ESI) calcd for[C₁₂H₁₁N₃AuCl], [M+Na]⁺: m/z= 452.0199; Found: 452.0202.Anal. Calcd for C₁₂H₁₁N₃AuCl + 0.3(CH₂Cl₂): C, 31.80; H, 2.56; N, 8.90; Found: C, 31.56; H, 2.58; N, 8.78.



((1-methyl-3,5-diphenyl-2,3-dihydro-1H-1,2,3-triazol-4-yl)ethynyl)gold(I) chloride 3f: Obtained as a white solid in 58% yield by using the same preparation method of 3a. M.p. 292-293 °C.¹H NMR (600 MHz, DMSO) δ 7.85 – 7.80 (m, 4H), 7.74 – 7.68 (m, 3H), 7.57 (d, J = 8.2 Hz, 2H), 4.28 (s, 3H), 2.47 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 174.78(C-Au), 142.45, 142.19, 139.69, 136.99, 132.41, 131.97, 130.77, 130.15, 130.11, 129.78, 126.06, 125.41, 124.89, 123.22, 79.30, 40.61(N-CH₃), 21.39. HR-MS (ESI) calcd for[C₁₈H₁₅N₃AuCl], [M+Na]⁺: m/z= 528.0512; Found: 528.0525. Anal. Calcd for C₁₈H₁₅N₃AuCl + 0.5(CH₂Cl₂)+0.5(MeOH): C, 41.46; H, 3.15; N, 7.71; Found: C, 41.97; H, 3.55; N, 7.80.

6.4 procedure for the synthesis of ((1-phenyl-1H-1,2,3-triazol-4-yl)ethynyl)gold(I) triphenylphosphane S1:^[10]



To a mixture solution of Au(PPh₃)Cl (25mg 0.05mol) and 4-ethynyl-1-phenyl-1H-1,2,3triazole **1a** (8.5 mg, 0.05mmol) in MeOH (10 mL), was added 2 mL of NaOH solution (0.4 mmol, prepared by dissolving 0.10 g NaOH in 12.5 mL dry MeOH) dropwisely. The reaction mixture was stirred for 4 hours at rt. The solution was filtered through celite and concentrated in vacuo. The mixture was purified by silica gel with petroleum/ethyl acetate as the eluent afforded complex **S1** as a white solid (28 mg, 89% yield).

$$\overset{\mathsf{Ph}}{\underset{N=N}{\overset{\mathsf{h}}{\longrightarrow}}} \mathsf{Au-\mathsf{PPh}}_3$$

((1-phenyl-1H-1,2,3-triazol-4-yl)ethynyl)gold(I) triphenylphosphane S1: M.p. 259-261 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.99 – 7.94 (m, 2H), 7.84 (s, 1H), 7.56 – 7.43 (m, 18H).. ¹³C NMR (151 MHz, CDCl₃) δ 137.89, 137.03, 134.31, 134.22, 131.77, 129.55, 129.31, 129.24, 129.17, 129.10, 128.66, 123.49, 122.01, 87.45. ³¹P NMR (243 MHz, CDCl₃) δ 41.45. HR-MS (ESI) calcd for[C₂₈H₂₁N₃AuP], [M+Na]⁺: m/z= 650.1031.Found 650.1039.Anal. Calcd for C₂₈H₂₁N₃AuP + 0.5(C₄H₈O₂: C, 53.71; H, 4.09; N, 5.87. Found: C, 53.97; H, 3.95; N, 5.80

7. Characterization Data for all new compounds obtained from Nazarov reaction,



Methyl (18,2R)-5-methoxy-3-oxo-1-phenyl-2,3-dihydro-1H-indene-2-carboxylate 9a: obtained as a colorless oil in 96% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.31 (m, 3H), 7.24 (s, m,2H), 7.20 – 7.13 (m, 3H), 4.93 (d, J = 4.4 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.70 (d, J = 4.4 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 198.45, 168.90, 160.15, 149.23, 142.06, 136.32, 129.06, 127.83, 127.52, 127.49, 125.31, 105.21, 77.26, 77.05, 76.84, 64.12, 55.74, 52.81, 48.05. HR-MS (ESI) calcd. for [C₁₈H₁₆O₆], [M+H]⁺: m/z = 297.1121; Found: 297.1116.



Ethyl (1S,2R)-5-methoxy-3-oxo-1-phenyl-2,3-dihydro-1H-indene-2-carboxylate 9b: obtained as a colorless oil in 89% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.28 (m, 3H), 7.23-7.15 (m, 1H), 7.16-7.12 (m, 4H), 4.90 (d, *J* = 4.5 Hz, 1H), 4.31-4.21 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 3.60 (d, *J* = 4.5 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 198.62, 168.44, 160.05, 149.23, 142.09, 136.33, 129.01, 127.82, 127.49, 127.42, 125.23, 105.09, 64.25, 61.80, 55.69, 48.02, 14.22. HR-MS (ESI) calcd for [C₁₉H₁₈O₄], [M+H]⁺: m/z = 310.1278; Found: 310.1274.



Ethyl (18,2R)-5-methoxy-3-oxo-1-(p-tolyl)-2,3-dihydro-1H-indene-2-carboxylate 9c: obtained as a colorless oil in 90% yield; ¹H NMR (600 MHz, CDCl₃) δ 7.23-7.11 (m, 5H), 7.03 (d, J = 7.9 Hz, 2H), 4.88 (d, J = 4.4 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 3.65 (d, J = 4.4 Hz, 1H), 2.33 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 198.74, 168.54, 160.07, 149.48, 139.14, 137.14, 136.38, 129.70, 127.72, 127.49, 125.19, 105.14, 64.40, 61.76, 55.73, 47.77, 21.06, 14.25. HR-MS (ESI) calcd for [C₂₀H₂₀O₄], [M+H]⁺: m/z = 325.1434; Found: 325.1430.



Ethyl(18,2R)-5-methoxy-1-(4-methoxyphenyl)-3-oxo-2,3-dihydro-1H-indene-2- carboxylate 9d: obtained as a colorless oil in 92% yield. ¹H NMR (600 MHz, CDCl₃) δ 7.23-7.14 (m, 3H), 7.06 (d, J = 8.3 Hz, 2H), 6.85 (d, J = 8.3 Hz, 2H), 4.87 (d, J = 4.3 Hz, 1H), 4.31- 4.21 (q, J = 7.2 Hz, 2H), 3.86 (s, 3H), 3.79 (s, 3H), 3.63 (d, J = 4.4 Hz, 1H), 1.31 (t, J = 7.2 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 198.72, 168.56, 160.08, 158.97, 149.53, 136.36, 134.18, 128.87, 127.47, 125.19, 114.43, 105.12, 64.51, 61.75, 55.73, 55.33, 47.42, 14.26. HR-MS (ESI) calcd for [C₂₀H₂₀O₅], [M+H]⁺: m/z= 341.1385; Found: 341.1378.



Ethyl(1S,2R)-1-(4-chlorophenyl)-5-methoxy-3-oxo-2,3-dihydro-1H-indene-2

carboxylate 9e: obtained as a colorless oil in 89% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.28 (m, 2H), 7.23-7.15 (m, 2H), 7.16-7.12 (m, 1H), 7.10-7.07 (m, 2H), 4.90 (d, J = 4.5 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 3.60 (d, J = 4.5 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 198.10, 168.22, 160.23, 148.51, 140.62, 133.34, 130.75, 129.22, 128.42, 127.36, 125.32, 105.28, 64.18, 61.93, 55.75, 47.36, 14.24. HR-MS (ESI) calcd for [C₁₉H₁₇ClO₄], [M+H]⁺: m/z = 345.0888; Found: 345.0883.



Ethyl(1R,2R)-5-methoxy-1-(1-methyl-1H-indol-3-yl)-3-oxo-2,3-dihydro-1H-indene-2-carboxylate 9f: obtained as a yellow oil in 75% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 2.3 Hz, 1H), 7.25-7.16 (m, 3H), 7.05-6.98 (m, 1H), 6.87 (s, 1H), 5.20 (d, J = 4.4 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 3.83 (d, J = 4.4 Hz, 1H), 3.75 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 198.99, 169.05, 160.01, 149.35, 137.53, 136.17, 127.45, 126.94, 125.07, 122.06, 119.29, 119.11, 115.02, 109.55, 105.14, 63.45, 61.72, 55.73, 39.99, 32.76, 14.27. HR-MS (ESI) calcd for [C₂₂H₂₁NO₄], [M+H]⁺: m/z = 364.1543; Found: 364.1535.



Ethyl(1R,2R)-1-(furan-2-yl)-5-methoxy-3-oxo-2,3-dihydro-1H-indene-2-carboxylate 9g: obtained as a colorless oil in 93% yield; ¹H NMR (600 MHz, CDCl₃) δ 7.28 (d, *J* = 8.0 Hz, 1H), 7.21-7.16 (m, 1H), 7.15-7.13 (m, 2H), 6.24 (dd, *J* = 2.9, 1.9 Hz, 1H), 6.10 (d, *J* = 3.1 Hz, 1H), 4.94 (d, *J* = 4.4 Hz, 1H), 4.19(q, *J* = 7.1 Hz, 2H), 3.79 (d, *J* = 4.4 Hz, 1H), 3.76 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 197.66, 168.20, 160.39, 153.71, 146.21, 142.55, 135.99, 127.13, 125.07, 110.35, 106.75, 105.57, 61.97, 60.46, 55.75, 41.41, 14.23. HR-MS (ESI) calcd for [C₁₇H₁₆O₅], [M+H]⁺: m/z = 301.1070; Found: 301.1065.



Compound 9h, 9i have been reported in the previous research.^[6b]

Ethyl (2R,3S)-5,6-dimethoxy-1-oxo-3-phenyl-2,3-dihydro-1H-indene-2-carboxylate 9j: obtained as a colorless oil in 95% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.27 (m, 3H), 7.22 (s, 1H), 7.17-7.12 (m, 2H), 6.64 (s, 1H), 4.89 (d, *J* = 4.0 Hz, 1H), 4.26 (q, *J* = 7.1, 2H), 3.93 (s, 3H), 3.85 (s, 3H), 3.61 (d, *J* = 4.1 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.11, 168.74, 156.37, 151.83, 150.20, 142.10, 129.08, 127.87, 127.46, 107.32, 104.32, 77.37, 77.05, 76.73, 63.85, 61.78, 56.40, 56.23, 48.42, 14.25. HR-MS (ESI) calcd. for [C₂₀H₂₀O₅], [M+H]⁺: m/z = 341.1384; Found: 341.1379.



Ethyl(2R,3S)-1-oxo-3-phenyl-2,3-dihydro-1H-cyclopenta[b]naphthalene-2-carboxylate 9k: obtained as a white solid in 91% yield. M.p. 59-61 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.85 (dd, J = 14.3, 8.3 Hz, 2H), 7.75 (d, J = 8.5 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.19 (m, 3H), 7.04 (d, J = 7.2 Hz, 2H), 5.35 (t, J = 3.1 Hz, 1H), 4.24 – 4.17 (q, J = 7.1 Hz, 2H), 3.65 (d, J = 3.1 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 198.44, 168.38, 156.29, 142.72, 137.68, 133.85, 130.15, 129.95, 129.34, 129.25, 129.07, 127.54, 127.41, 127.33, 127.18, 126.15, 119.55, 77.26, 77.05, 76.84, 64.43, 61.97, 48.23, 14.27. HR-MS (ESI) calcd. For [C₁₈H₁₆O₆], [M+H]⁺: m/z = 297.1121; Found: 297.1116.

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9. ¹H NMR and C¹³ NMR spectra



















































10. Detailed results for DFT calculation

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1.09784512	-0.44444307	0.00021013
-1.09808804	- 0.44396250	-0.00012588
-2.47444723	0.03800427	0.00006213
-2.43429744	1.13544136	-0.00270988
-3.00190820	-0.31362786	-0.89785394
-3.00019220	-0.30884286	0.90090219
2.47442412	0.03689224	-0.00006388
3.00002523	-0.31045669	-0.90075694
2.43477791	1.13434831	0.00254013
3.00170123	-0.31473069	0.89800019
	0.00006388 -0.68283575 0.68201235 -1.38680064 1.38562656 0.00037761 0.00086636 1.09784512 -1.09808804 -2.47444723 -2.43429744 -3.00190820 -3.00019220 2.47442412 3.00002523 2.43477791 3.00170123	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$

%chk=E:\5\mi1.chk # opt freq bp86 tzvp Title Card Required

01			
С	-0.68194135	1.22171885	-0.00001152
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Ν	-1.06616175	-0.11936090	-0.00003377