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Ligand-Effect in Gold(I)-Catalyzed Rautenstrauch Rearrangement: Regio- and Stereoselective Synthesis of Bicyclo[3.2.1]octa-3,6-dienes through Cyclodimerization of 1-Ethynyl-2-propenyl Esters

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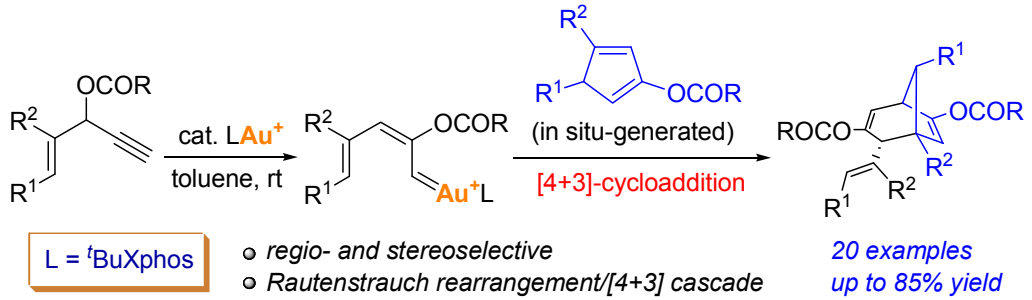


Abstract: Gold(I) complexes bearing sterically demanding phosphine ligands such as ^{t}BuXphos catalyze the cascade Rantenstrauch rearrangement/[4+3] cycloaddition of 1-ethynyl-2-propenyl esters. The reaction provides an efficient and straightforward route to bicyclo[3.2.1]octa-3,6-dienes with high regio- and stereoselectivity. The formation of the [4+3] cycloadducts likely proceeds through the cycloaddition of a gold(I)

carbenoid/gold-stabilized allyl cation intermediate with cyclopentadiene arised from Rantenstrauch rearrangement.

INTRODUCTION

The bridged bicyclo[3.2.1]octanes represent a ubiquitous structural motif existed in many families of biologically active natural compounds[1] such as Enaimeone A, Clavubicyclone, and Ialibinone A. For example, Clavubicyclone showed a moderate growth inhibition activity toward tumor cells.[1b] Ialibinone A exhibited an antioxidant activity in polymorphonuclear cells.[1c] In addition, bicyclo[3.2.1]octa-3,6-dien-2-yl anion or cation have also attracted much attention because they have often been used for the study of the bishomoaromaticity or bishomoantiaromaticity due to their unique structures (Figure 1).[2] Although various methods have been developed to construct these carbon bridged seven-membered rings,[3] most of them require multistep synthesis or their synthetic methods are restricted to to specific substrates. Therefore, the straightforward access to bicyclo[3.2.1]octane cores from readily available building blocks under mild reaction conditions is highly desired.

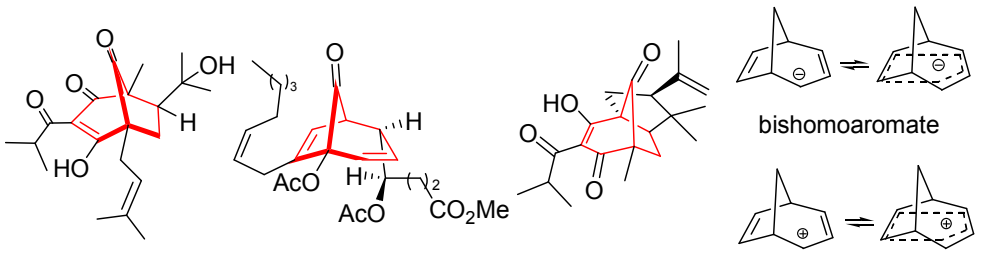
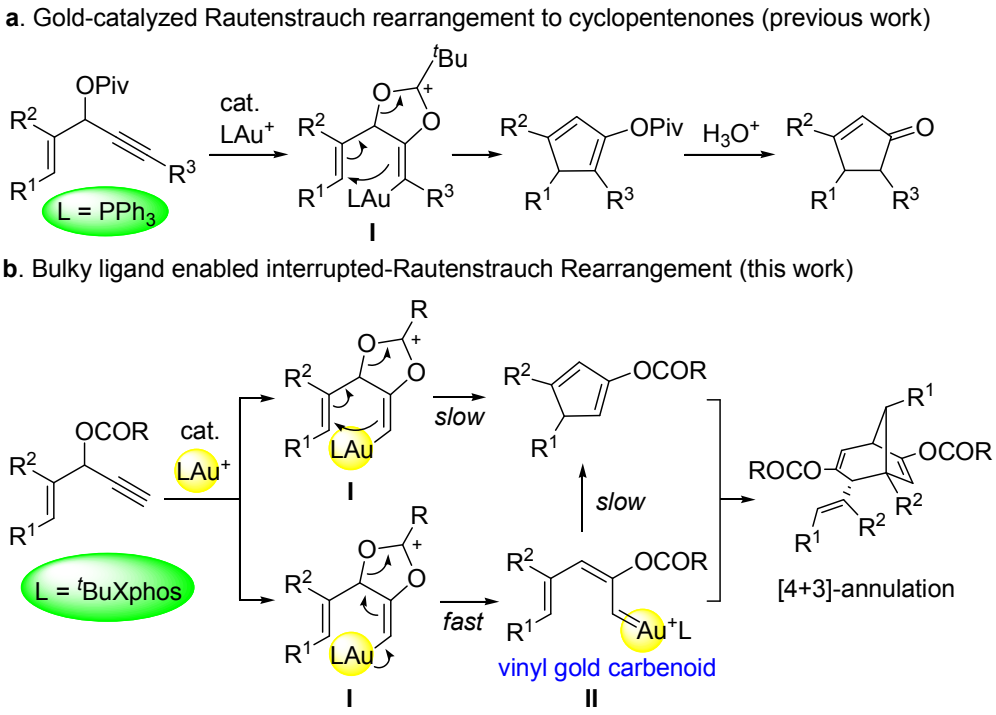


Figure 1. Representative Compounds Containing Bicyclo[3.2.1]octane Core

Homogeneous gold catalysis has emerged as one of the most powerful tools for the rapid and efficient construction of highly functionalized and architecturally complex molecules from simple starting materials.[4] A particularly attractive strategy is based on the gold-catalyzed 1,2-acyloxy migration of propargyl esters.[5] For example, in 2005, Toste[6a] and Gagosz[6b] reported that PPh_3-ligated gold(I) complex could catalyze Rautenstrauch rearrangement[7] of 1-ethynyl-2-propenyl pivaloates to cyclopentenones[8] (Scheme 1**a**). Recently, Hashmi and Lautens expanded the scope of this reaction by addition of a proton source into the reaction mixture to facilitate the hydrolysis of the enol ester intermediate.[9] Generally, these reactions are initiated through the activation of the propargyl moiety by gold catalyst to trigger an efficient generation of a vinyl gold species **I**. Subsequent Nazarov-like cyclization/1,2-acyloxy migration and hydrolysis furnish the desired cyclopentenones.[9,10] An excellent chirality transfer found in these reactions indicated that a gold carbenoid species might not be involved.[6a] Later in 2015, the Toste group has also disclosed a gold-catalyzed highly enantioselective dearomative Rautenstrauch rearrangement of the indole-derived propargyl acetals,[11] in which a vinyl gold carbenoid or its resonance structure was proposed as a reaction intermediate. During our studies on gold-catalyzed cyclization of functionalized alkynes, we found that the steric and electronic properties of ancillary ligands on gold catalyst could have a significant impact on the reaction course such as tuning

the reactivity of gold catalysts, stabilizing the active gold-containing intermediates or improving the reaction selectivity.[12] Ligand effects have also been found in many excellent reports described by other groups.[13] We found here that when sterically demanding ligands such as ^{t}BuXphos were employed instead of PPh_3 in the gold-catalyzed Rautenstrauch rearrangement, an unexpected product of bicyclo[3.2.1]octa-3,6-diene was formed with high regio- and stereoselectivity (Scheme 1**b**). We rationalized that an increase of the steric interaction between the vinyl moiety and gold in intermediate **I** caused by the bulky ligand on the gold metal could slow down the Nazarov cyclization process. This may result in a facile formation of a vinyl gold(I) carbenoid **II**. The ligand should have played a crucial role in the stability of gold(I) carbenoid **II**. The [4+3] cycloaddition of cycopentadiene intermediate with **II** thus affords the cyclodimerized product.[14] Herein, we disclose the details of this reaction.

Scheme 1. Gold-catalyzed Rautenstrauch Rearrangement

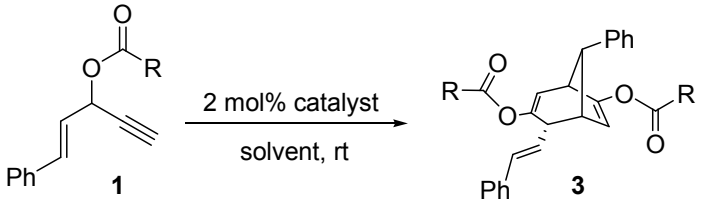


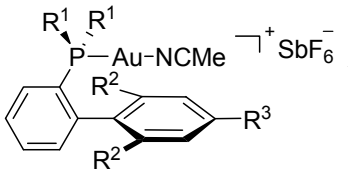
RESULTS AND DISCUSSION

We initially investigated gold-catalyzed Rautenstrauch rearrangement of phenyl-substituted 1-ethynyl-2-propenyl benzoate **1a** in the presence of various gold catalysts. Treatment of **1a** with 2 mol% PPh_3AuNTf_2 in toluene resulted in a non-clean reaction mixture, among which, only 11% NMR yield of the double bond isomerized cyclopentenone **2a** was formed, which could not be separated from other byproducts through column chromatography (Table 1, entry 1). Gratifyingly, the cyclization using [LAu(MeCN)]SbF_6 bearing a Buchwald ligand in toluene afforded a cyclodimerized product **3a** containing a bicyclo[3.2.1]octa-3,6-diene skeleton in satisfactory yields. For example, the gold catalyst with a Johnphos, Sphos or ^{t}BuXphos as the ligand provided **3a** in 62%, 55% and 70% yields, respectively

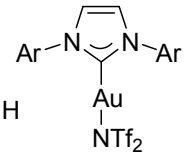
(entries 2-4). **3a** was isolated as a single diastereomer in which the bridging atom is oriented *trans* with respect to the styryl group, and the phenyl group on the bridgehead is *cis* with right side ring. The use of a *N*-heterocyclic carbene-gold(I) complex IPrAuNTf$_2$ as the catalyst afforded a complex reaction mixture, and **3a** was observed in 22% NMR yield (entry 5). We next examined the effect of the protecting groups on this reaction. Propargyl benzoates bearing an electron-donating group (*p*-MeO) or electron-withdrawing group (*p*-CF_3) on the aryl ring provided the corresponding **3b** and **3c** in similar yields (60-69%, entries 6-7), indicating that the electronic nature on the aryl ring have a little influence on the reaction process. Interestingly, the replacement of a phenyl substituent on the protecting group by a thienyl ring resulted in a higher yield of **3e** (81%, entry 9). Propargyl acetate (**1f**) and pivaloate (**1g**) were also transformed into the desired cyclodimerized products **3f** and **3g** smoothly in 63-71% yields (entries 10-11). Changing the counterions of the gold catalysts from SbF_6^- to OTf^-, BF_4^- afforded **3e** in 44% and 72% yields, respectively (entries 12-13). The use of DCE or THF as the solvent led to the diminished yields of **3e** (17-53%, entries 14-15). It was noted that in most cases of the above reactions, small amounts of inseparable isomers or byproducts were also observed.[15] Control experiments run with ^{t}BuXphosAuCl or $AgSbF_6$ alone did not give the desired products (entries 16-17).

Table 1. Optimization of Reaction Conditions





A, R^1 = ^{t}Bu, R^2 = R^3 = H
B, R^1 = Cy, R^2 = MeO, R^3 = H
C, R^1 = ^{t}Bu, R^2 = R^3 = ^{i}Pr

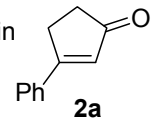


Ar = 2,6-(^{i}Pr)$_2$C$_6$H$_3$

D

entry	R	catalyst	solvent	time (h)	product	yield (%)[a]
1	Ph (**1a**)	PPh_3AuNTf_2	toluene	24	-[b]	-[b]
2	Ph (**1a**)	**A**	toluene	1	**3a**	62
3	Ph (**1a**)	**B**	toluene	1	**3a**	55
4	Ph (**1a**)	**C**	toluene	1	**3a**	70
5	Ph (**1a**)	**D**	toluene	24	**3a**	22[c]
6	*p*-$OMeC_6H_4$ (**1b**)	**C**	toluene	2	**3b**	60
7	*p*-$CF_3C_6H_4$ (**1c**)	**C**	toluene	2	**3c**	69
8	2-furanyl (**1d**)	**C**	toluene	3	**3d**	47
9	2-thienyl (**1e**)	**C**	toluene	2	**3e**	81
10	Me (**1f**)	**C**	toluene	2	**3f**	63
11	^{t}Bu (**1g**)	**C**	toluene	1	**3g**	71
12	2-thienyl (**1e**)	^{t}BuXphosAuCl/AgOTf	toluene	5	**3e**	44
13	2-thienyl (**1e**)	^{t}BuXphosAuCl/$AgBF_4$	toluene	3	**3e**	72
14	2-thienyl (**1e**)	**C**	DCE	6	**3e**	53
15	2-thienyl (**1e**)	**C**	THF	5	**3e**	17
16	2-thienyl (**1e**)	^{t}BuXphosAuCl	toluene	12	**3e**	0 (62)[d]
17	2-thienyl (**1e**)	$AgSbF_6$	toluene	12	**3e**	0 (85[e])[d]

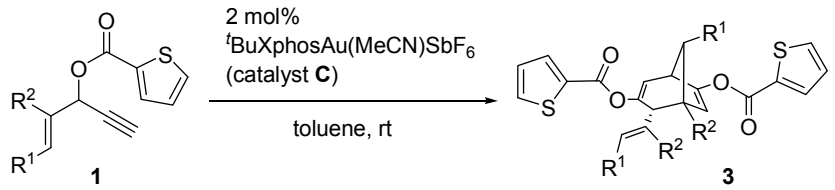
[a]Isolated yields. [b]Complicated reaction mixture. **2a** was observed in 11% NMR yield. [c]NMR yield. [d]The yields of the recovered **1e** are shown in parentheses. [e]Containing small amounts of impurity.

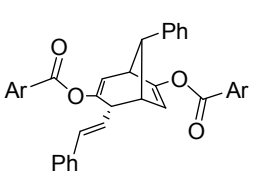


2a

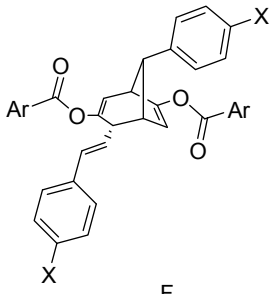
Having established the effective catalytic system, we proceeded to explore the substrate scope of this novel cascade reaction. As shown in Scheme 2, a wide range of 1-ethynyl-2-propenyl esters containing an aryl substituent at the alkene terminus were suitable for this reaction, and the desired bicyclo[3.2.1]octa-3,6-dienes **3h-r** and **3t** were obtained in moderate to good yields within short reaction times at room temperature. The process is also highly stereoselective, as *trans* products were obtained as the major isomers. Both electron-deficient (*p*-Br, *p*-F, *p*-CF_3) and electron-rich substituents (*p*-Me, 3,4,5-$(MeO)_3$) on the aryl rings tolerated well during the reaction, leading to **3h-3l** in 56-72% yields. Substrates bearing an *ortho* substituent (*o*-F) or meta-substituent (*m*-Cl) on the aryl rings were also compatible, leading to **3m** and **3n** in 55% and 77% yields, respectively. Interestingly, the substrate tethered with an alkynyl functional group could be efficiently converted to the desired product **3o** in moderate yield (55%), and the alkynyl group remained intact. A sterically demanding 2-naphthyl group as R^1 was well accommodated to give the product **3p** in 71% yield. Cyclization of the substrates bearing an alkyl group as R^2 such as methyl or n-hexyl group occurred smoothly to give the corresponding **3q** and **3r** in 85% and 74% yields, respectively. However, when a substrate bearing an alkyl group such as a methyl group on the alkene terminus was employed, only low yield (28%) of the desired product **3s** was obtained, possibly due to the lower stability of the gold-carbenoid/gold-stabilized allyl cation intermediate. The structure of the

Scheme 2. Scope of Gold-catalyzed Rautenstrauch Rearrangement/[4+3] Cascade[a]





3e, 2 h, 81%

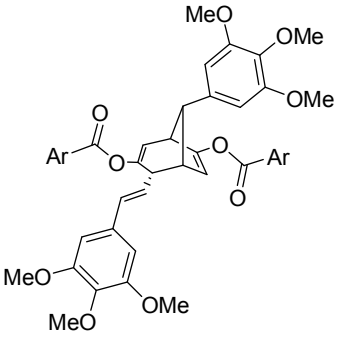


3h, X = Br, 2 h, 72%

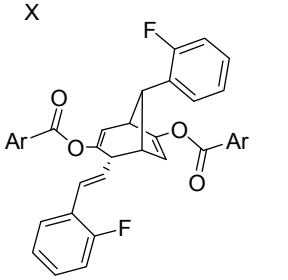
3i, X = F, 2 h, 71%

3j, X = CF_3, 2 h, 65%

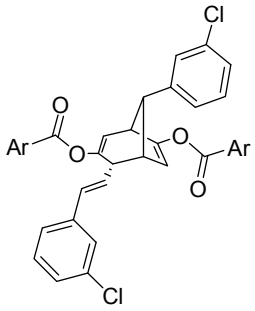
3k, X = Me, 1 h, 56%



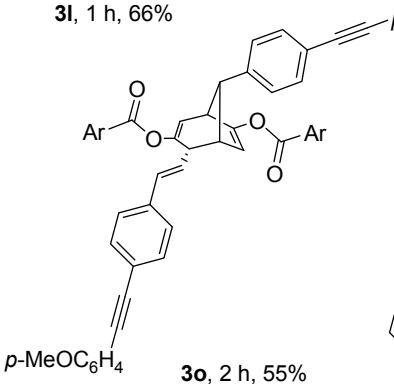
3l, 1 h, 66%



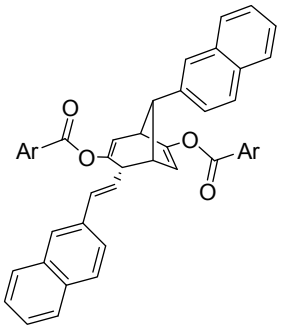
3m, 1 h, 55%



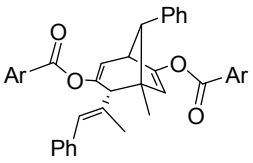
3n, 2 h, 77%



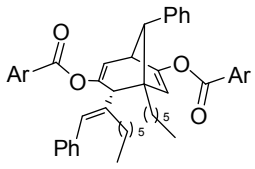
3o, 2 h, 55%



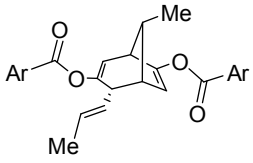
3p, 2 h, 71%



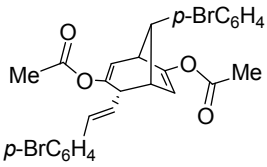
3q, 4 h, 85%



3r, 6 h 74%



3s, 1 h, 28%



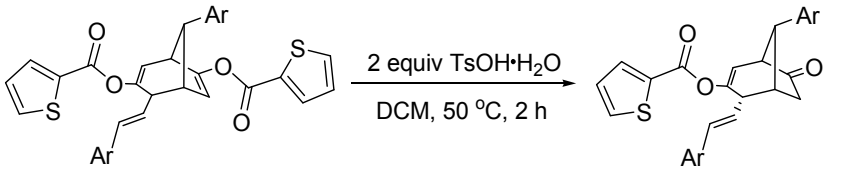
3t[b], 1 h, 67%

[a]Isolated yields. Ar = 2-thienyl. [b]Propargyl acetate was used as the substrate.

dimerized products was unambiguously confirmed by the X-ray crystallographic analyses of **3a**, **3q** and **3t**.[16]

The utility of the bicyclo[3.2.1]octa-3,6-dienes **3** was demonstrated by the deprotection reactions of **3e** and **3l** (Scheme 3). Treatment of **3e** with 2.0 equiv *p*-toluenesulfonic acid monohydrate in DCM resulted in the formation of ketone **4e** in 66% yield. The results indicated that only the protecting group at the same side with the Ar group was removed selectively. The chemoselectivity of this reaction is possibly influenced by the steric effect. Similarly, **4l** was obtained in moderate yield, and its structure was determined by X-ray crystallography.[16] This process may enlarge the utility in subsequent modification and transformations. However, deprotection attempts of the remaining acyl group by various methods failed.

Scheme 3. Removal of the Protecting Group



3e or **3l**

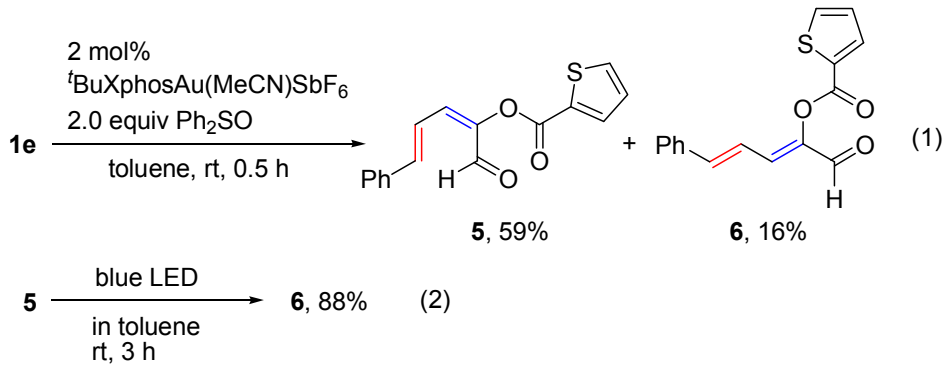
4e, Ar = Ph, 66%

4l, Ar = 3,4,5-$(OMe)_3C_6H_2$, 60%

In order to validate the proposed gold(I)-carbenoid intermediate, the gold-catalyzed oxidative rearrangement reaction of ester **1e** was performed. As we expected, aldehyde **5** was formed in 59% yield as a (*E*,*E*)-isomer (determined by 2D NOESY NMR spectroscopy), together with 16% of (*E*,*Z*)-isomer **6** in the presence

of diphenylsulfoxide as the oxidant (Scheme 4, eq 1).[17] We noted that **5** could undergo a double-bond isomerization slowly when standing a solution of **5** in organic solvents. Interestingly, **5** could be readily isomerized to **6** within 3 h under the irradiation of the blue light, indicating that the process was caused by the photo-induced isomerization (Scheme 4, eq 2)[18,19] The structure of **6** was confirmed by the X-ray crystallographic analysis of its imine derivative (compound **7**).[16]

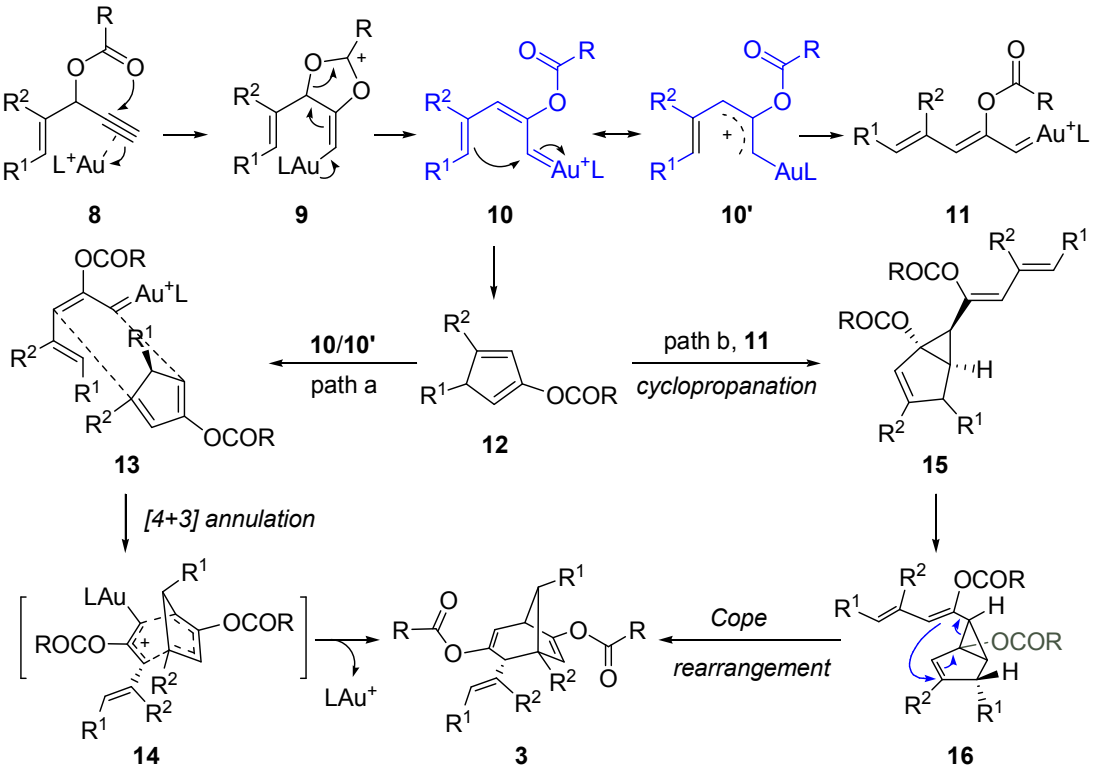
Scheme 4. Formation of Enals



Although the full mechanistic details of the current cyclization reactions remain to be elucidated, a plausible mechanism for the formation of bicyclo[3.2.1]octa-3,6-dienes is proposed based on the above results and the literature reports (Scheme 5). Initially, nucleophilic attack of the carbonyl of the ester group to the gold-coordinated alkyne leads to the formation of vinyl gold species **9**. Although the Toste's work supported a concerted process from **9** to cyclopentadiene **12**, our study prefers that vinyl gold-carbenoid **10** or its resonance structure gold-stabilized allyl cation **10'** is formed due to the stabilizing effect of the

bulky ligand. **10** might isomerize to (*E*,*Z*)-isomer **11** according to the experiment shown in Scheme 4, eq 1. Cyclization of **9** or **10**/**10'** followed by elimination of the gold catalyst gives cyclopentadiene **12**. The subsequent [4+3] cycloaddition between cyclopentadiene **12** and **10**/**10'**[20] from another substrate occurs followed by deauration to deliver the product **3** (path a). The stereoselectivity observed in **3** can be understood through a transition state (**13**/**14**). In this process, cyclopentadiene **12** is considered to react with the (*E*,*E*)-isomer **10** selectively since that **10** is formed as the major isomer. In **13**, R^1 group on the bridgehead oriented *trans* with the diene moiety to avoid the steric hindrance. Furthermore, a secondary orbital interaction between the alkene moiety and cyclopentadiene might be involved, making the *endo*-product **3** to be the major isomer. In addition, the electron rich vinyl ester moiety may prefer to attack the gold carbenoid, thus affording the cycloadduct with high regioselectivity. We also can not exclude the pathway through a cyclopropanation/Cope rearrangement cascade[5c] as indicated in path b. In this reaction pathway, cyclopentadiene **12** may react with the thermodynamically more stable (*E*,*Z*)-isomer **11** preferencially[5d] due to the less steric hindrance of gold-carbenoid moiety to give the *cis*-cyclopropane intermediate **15**[21], which undergoes Cope rearrangement[22] to deliver the product **3**. It is reported that the Cope rearrangement of divinylcyclopropanes proceeds through a boat transition state.[5c,23] Thus a boatlike transition state **16** is proposed to account for the observed stereoselectivity.

Scheme 5. Possible Reaction Mechanism



CONCLUSION

In summary, we have developed a gold(I)-catalyzed regio- and stereoselective synthesis of bicyclo[3.2.1]octa-3,6-dienes through the cyclodimerization of 1-ethynyl-2-propenyl esters by modulating the steric and electronic properties of the ligands on the gold(I) catalyst. This reaction provides a new strategy for the construction of complex molecules from simple building blocks. The formation of the [4+3] cycloadducts likely arises from the cycloaddition of a gold(I) carbenoid/gold-stabilized allyl cation with cyclopentadiene intermediate.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out using standard Schlenk technique under argon unless noted. DCM and DCE were distilled from CaH_2. Toluene was distilled from sodium and benzophenone. THF was distilled from sodium and benzophenone or purified using Innovative Technology Solvent Purifier (for the synthesis of substrates). MeCN was purified using Innovative Technology Solvent Purifier. Unless noted, all commercial reagents were used without further purification. (Acetonitrile)[(2-biphenyl)di-*tert*-butylphosphine]gold(I)hexafluoroantimonate (catalyst **A**) was purchased from Chemical Company. Gold complex **B-C** were prepared by stirring the [Au(L)Cl] complex with $AgSbF_6$ in MeCN at room temperature.[24] PPh_3AuNTf_2[25] and $IPrAuNTf_2$[26] were prepared according to the published methods. ^1H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ (containing 0.03% TMS), Acetonitrile-d_3 (containing 0.03% TMS), or Toluene-d_8 on Varian XL-400 MHz spectrometer or Agilent 400 MHz NMR spectrometer. ^1H NMR spectra were recorded at 400 MHz, ^{13}C NMR spectra were recorded at 100 MHz. ^1H NMR spectra were recorded with tetramethylsilane (δ = 0.00 ppm) or solvent residual peak ($CDCl_3$: 7.26 ppm) as internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. High-resolution mass spectra was performed on a mass spectrometer with a TOF or FT analyzer. Melting points were uncorrected. Single crystal X-ray diffraction data were collected at 296(2) K for **3a**, 293(2) K for **3q**, 296(2) K for **3t**, 273(2) for **4l** and 293(2) K for **7**. Photochemical reactions were carried with 15 W blue LED (456 nm peak wavelength, 23.8 nm spectral half-wave width, composed of 30 LED units.

Method A: Synthesis of 1-ethynyl-2-propenyl esters 1a-1i, 1q, 1o, 1s and 1t.

Typical procedure for the synthesis of (*E*)-1-phenylpent-1-en-4-yn-3-yl benzoate (1a).

To a solution of cinnamaldehyde (660.8 mg, 5.0 mmol) in THF (10 mL) was added ethynylmagnesium bromide (0.5 M in THF, 12.0 mL, 6.0 mmol) at 0 ^{o}C, and the resulting solution was stirred at room temperature for 1 h. After the starting material was consumed, the mixture was quenched with water, extracted with ethyl acetate, washed with brine solution and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford the desired propargyl alcohol, which was used directly for the next step.

Under air, to a mixture of above propargyl alcohol, DCM (20 mL), Et_3N (1.52g, 15.0 mmol), DMAP (61.1 mg, 0.5 mmol) was added benzoyl chloride (1.41 g, 10 mmol) at 0 ^{o}C. The resulting solution was warmed up to room temperature and stirred for 6 h. After the starting material was consumed, the mixture was quenched with saturated NH_4Cl solution, extracted with dichloromethane, washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) to afford **1a** (1.03 g, 79% yield) as a yellow oil.

Method B: Synthesis of 1-ethynyl-2-propenyl esters 1j-1k, 1m-1n, 1p and 1r.

Typical procedure for the synthesis of (*E*)-1-(*p*-tolyl)pent-1-en-4-yn-3-yl thiophene-2-carboxylate (1k).

To a solution of (*E*)-3-(*p*-tolyl)acrylaldehyde (438.6 mg, 3.0 mmol) in THF (10 mL) was added ethynylmagnesium bromide (0.5 M in THF, 7.2 mL, 3.6 mmol) at 0 ^{o}C, and the resulting solution was stirred at room temperature for 1 h. After the starting material was consumed, the mixture was quenched with water, extracted with ethyl acetate, washed with brine solution and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) to afford the desired propargyl alcohol, which was used directly for the next step.

Under air, to a mixture of above propargyl alcohol, DCM (10 mL), pyridine (1.19 g, 15.0 mmol) was added thiophene-2-carbonyl chloride (879.5 mg, 6 mmol) at 0 ^{o}C. The resulting solution was warmed up to room temperature and stirred for 4 h. After the starting material was consumed, the mixture was quenched with saturated NH_4Cl solution, extracted with dichloromethane, washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) to afford **1k** (762.2 mg, 90% yield) as a white amorphous solid.

(*E*)-1-Phenylpent-1-en-4-yn-3-yl benzoate (1a). Method A was used. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45-7.42 (m, 4H), 7.34-7.22 (m, 3H), 6.97 (d, *J* = 14.8 Hz, 1H), 6.38-6.30 (m, 2H), 2.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 135.5, 134.9, 133.3, 129.8, 129.5, 128.6, 128.5, 128.4, 126.9, 123.3, 79.3, 75.6, 64.5. The spectroscopic data is in agreement with that previously reported.[27]

(*E*)-1-Phenylpent-1-en-4-yn-3-yl 4-methoxybenzoate (1b). Method A was used. 3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) afforded the title product in 82% yield (720.5 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.35-7.24 (m, 3H), 6.96 (d, J = 15.6 Hz, 1H), 6.91 (d, J = 8.4 Hz, 2H), 6.36 (dd, J = 15.6 Hz, 6.4 Hz, 1H), 6.29 (dd, J = 6.4 Hz, 0.8 Hz, 1H), 3.83 (s, 3H), 2.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 163.6, 135.5, 134.6, 131.9, 128.6, 128.4, 126.9, 123.5, 121.8, 113.6, 79.5, 75.4, 64.1, 55.3. IR (neat): 3291, 3026, 2837, 2121, 1712, 1604, 1249, 1090, 768 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{19}H_{16}O_3$ 292.1099; Found 292.1102.

(*E*)-1-Phenylpent-1-en-4-yn-3-yl 4-(trifluoromethyl)benzoate (1c). Method A was used. 3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) afforded the title product in 75% yield (741.8 mg) as a light yellow amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 7.6 Hz, 2H), 7.36-7.27 (m, 3H), 6.99 (d, J = 15.2 Hz, 1H), 6.39-6.31 (m, 2H), 2.73 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 135.5, 135.3, 134.7 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 132.8, 130.2, 128.7, 127.0, 125.4 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 123.5 (q, $^1J_{C\text{-}F}$ = 271.8 Hz), 122.8, 78.9, 76.0, 65.2. IR (neat): 3294, 3056, 2923, 2126, 1721, 1246, 1094, 773 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{19}H_{13}O_2F_3$ 330.0868; Found 330.0873.

(*E*)-1-Phenylpent-1-en-4-yn-3-yl furan-2-carboxylate (1d). Method A was used. 3 mmol

scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) afforded the title product in 75% yield (568.4 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.35-7.25 (m, 4H), 6.96 (d, *J* = 15.2 Hz, 1H), 6.51 (dd, *J* = 1.8 Hz , 1.2 Hz, 1H), 6.36-6.28 (m, 2H), 2.72 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 146.7, 143.8, 135.3, 135.3, 128.5, 128.5, 126.9, 122.8, 118.8, 111.9, 78.9, 76.0, 64.4. IR (neat): 3280, 3128, 2940, 2118, 1715, 1579, 1165, 754 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{16}H_{12}O_3$ 252.0786; Found 252.0781.

(*E*)-1-Phenylpent-1-en-4-yn-3-yl thiophene-2-carboxylate (1e). Method A was used. 10 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 86% yield (2.31 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 3.6 Hz, 1H), 7.57 (d, *J* = 4.8 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.35-7.23 (m, 3H), 7.09 (t, *J* = 4.4 Hz, 1H), 6.95 (d, *J* = 15.6 Hz, 1H), 6.33 (dd, *J* = 15.6 Hz, 6.4 Hz, 1H), 6.27-6.25 (m, 1H), 2.70 (d, *J* = 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 135.4, 135.0, 134.1, 133.1, 132.9, 128.6, 128.5, 127.8, 126.9, 123.1, 79.1, 75.8, 64.7. IR (neat): 3290, 3087, 3023, 2124, 1706, 1250, 1069, 745 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{16}H_{12}O_2S$ 268.0558; Found 268.0560.

(*E*)-1-Phenylpent-1-en-4-yn-3-yl acetate (1f). Method A was used. 3 mmol scale, acetic anhydride (2 equiv) was used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 91% yield (545.9 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.35-7.25 (m, 3H), 6.89 (d, *J* =

15.6 Hz, 1H), 6.24 (dd, *J* = 16.0 Hz, 6.4 Hz, 1H), 6.05 (d, *J* = 6.4 Hz, 1H), 2.65 (d, *J* = 2.0 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 135.3, 134.6, 128.4, 128.3, 126.7, 123.1, 79.2, 75.3, 63.7, 20.8. The spectroscopic data is in agreement with that previously reported.[28]

(*E*)-1-Phenylpent-1-en-4-yn-3-yl pivalate (1g). Method A was used. 2 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 86% yield (416.5 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.34-7.25 (m, 3H), 6.87 (d, *J* = 15.6 Hz, 1H), 6.22 (dd, *J* = 15.8 Hz, 6.4 Hz, 1H), 6.03 (d, *J* = 6.4 Hz, 1H), 2.61 (d, *J* = 1.2 Hz, 1H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 135.6, 134.3, 128.6, 128.4, 126.9, 123.5, 79.5, 75.0, 63.7, 38.7, 27.0. IR (neat): 3292, 3029, 2972, 2871, 2122, 1729, 1272, 1136, 747 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{16}H_{18}O_2$ 242.1307; Found 242.1311.

(*E*)-1-(4-Bromophenyl)pent-1-en-4-yn-3-yl thiophene-2-carboxylate (1h). Method A was used. 3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 77% yield (802.6 mg) as a yellow amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.87 (m, 1H), 7.60 (d, *J* = 5.2 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.12 (t, *J* = 4.0 Hz, 1H), 6.90 (d, *J* = 15.6 Hz, 1H), 6.33 (dd, *J* = 15.6 Hz, 6.4 Hz, 1H), 6.25 (d, *J* = 6.4 Hz, 1H), 2.71 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 134.4, 134.2, 133.8, 133.2, 132.8, 131.8, 128.5, 127.9, 123.9, 122.5, 78.8, 76.0, 64.5. IR (neat): 3258, 3042, 2121, 1719, 1246, 1067,

745 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{16}H_{11}O_2SBr$ 345.9663; Found 345.9673.

(*E*)-1-(4-Fluorophenyl)pent-1-en-4-yn-3-yl thiophene-2-carboxylate (1i). Method A was used. 3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 69% yield (591.3 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 3.6 Hz, 0.8 Hz, 1H), 7.60-7.59 (m, 1H), 7.43-7.38 (m, 2H), 7.12-7.10 (m, 1H), 7.06-7.00 (m, 2H), 6.95-6.89 (m, 1H), 6.29-6.23 (m, 2H), 2.70 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, $^1J_{C\text{-}F}$ = 246.8 Hz), 160.9, 134.1, 133.8, 133.1, 132.8, 131.6 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 128.6 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 127.8, 122.9 (d, $^5J_{C\text{-}F}$ = 2.3 Hz), 115.6 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 79.0, 75.9, 64.6. IR (neat): 3295, 3106, 3045, 2124, 1706, 1601, 1222, 1069, 747 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{16}H_{11}O_2SF$ 286.0464; Found 286.0470.

(*E*)-1-(4-(Trifluoromethyl)phenyl)pent-1-en-4-yn-3-yl thiophene-2-carboxylate (1j). Method B was used. 2 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded **1j** in 73% yield (491.8 mg) as a light yellow amorphous solid. M.p. 73-75 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.87 (m, 1H), 7.60-7.57 (m, 3H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.11 (dd, *J* = 4.4 Hz, 4.0 Hz, 1H), 6.99 (d, *J* = 16.0 Hz, 1H), 6.43 (dd, *J* = 15.8 Hz, 6.4 Hz, 1H), 6.29 (d, *J* = 6.0 Hz, 1H), 2.74 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 138.9, 134.2, 133.3, 133.2, 132.7, 130.1 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 127.9, 127.1, 125.8, 125.5 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.0 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 78.6, 76.2, 64.2. IR (neat): 3287, 3098, 2920, 2124, 1708, 1610, 1156, 1071, 757 cm^{-1}.

HRMS (EI-TOF) m/z: M^+ calcd for $C_{17}H_{11}O_2F_3S$ 336.0432; Found 336.0431.

(*E*)-1-(*p*-Tolyl)pent-1-en-4-yn-3-yl thiophene-2-carboxylate (1k). Method B was used. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 3.8 Hz, 1.2 Hz, 1H), 7.57 (dd, *J* = 5.0 Hz, 0.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.09 (dd, *J* = 4.8 Hz, 4.0 Hz, 1H), 6.92 (d, *J* = 14.8 Hz, 1H), 6.31-6.24 (m, 2H), 2.69 (d, *J* = 1.6 Hz, 1H), 2.33 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 138.5, 135.0, 134.0, 133.0, 132.6, 129.3, 127.8, 126.9, 122.0, 79.2, 75.7, 64.8, 21.2. IR(neat): 3266, 3112, 2920, 2118, 1710, 1244, 1066, 748 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{17}H_{14}O_2S$ 282.0715; Found 282.0718.

(*E*)-1-(3,4,5-Trimethoxyphenyl)pent-1-en-4-yn-3-yl thiophene-2-carboxylate (1l). Method B was used. 2 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded **1l** in 62% yield (446.1 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 3.6 Hz, 1H), 7.60 (d, *J* = 5.2 Hz, 1H), 7.11 (t, *J* = 4.4 Hz, 1H), 6.91-6.86 (m, 1H), 6.67 (s, 2H), 6.29-6.23 (m, 2H), 3.88 (s, 6H), 3.85 (s, 3H), 2.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 153.2, 138.5, 135.1, 134.0, 133.0, 132.9, 131.1, 127.8, 122.5, 104.0, 79.0, 75.8, 64.6, 60.8, 56.0. IR (neat): 3287, 3095, 2838, 2118, 1707, 1582, 1246, 1069, 747 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{19}H_{18}O_5S$ 358.0875; Found 358.0869.

(*E*)-1-(2-Fluorophenyl)pent-1-en-4-yn-3-yl thiophene-2-carboxylate (1m). Method B was used. 3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether:

ethyl acetate = 20:1) afforded the title product in 82% yield (701.3 mg) as a white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 3.8 Hz, 1.2 Hz, 1H), 7.59 (dd, *J* = 5.2 Hz, 1.2 Hz, 1H), 7.49-7.45 (m, 1H), 7.28-7.22 (m, 1H), 7.13-7.07 (m, 3H), 7.05-7.02 (m, 1H), 6.44 (dd, *J* = 16.0 Hz, 6.4 Hz, 1H), 6.28-6.26 (m, 1H), 2.72 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 160.5 (d, $^{1}J_{C\text{-}F}$ = 249.7 Hz), 134.1, 133.1, 132.8, 129.9 (d, $^{3}J_{C\text{-}F}$ = 9.1 Hz), 128.0 (d, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 127.8, 127.5 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 125.6 (d, $^{3}J_{C\text{-}F}$ = 5.3 Hz), 124.1 (d, $^{4}J_{C\text{-}F}$ = 3.8 Hz), 123.3 (d, $^{2}J_{C\text{-}F}$ = 12.1 Hz), 115.8 (d, $^{2}J_{C\text{-}F}$ = 21.2 Hz), 78.8, 76.0, 64.7. IR (neat): 3260, 3095, 2920, 2121, 1716, 1219, 1066, 745 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{16}H_{11}O_2FS$ 286.0464; Found 286.0467.

(*E*)-1-(3-Chlorophenyl)pent-1-en-4-yn-3-yl thiophene-2-carboxylate (1n). Method B was used. 3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 52% yield (468.5 mg) as a white solid. M.p. 64-65 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 3.8 Hz, 1.2 Hz, 1H), 7.57 (dd, *J* = 5.0 Hz, 1.2 Hz, 1H), 7.39 (s, 1H), 7.28-7.22 (m, 3H), 7.09 (dd, *J* = 4.8 Hz, 4.0 Hz, 1H), 6.88 (d, *J* = 15.6 Hz, 1H), 6.33 (dd, *J* = 15.6 Hz, 6.4 Hz, 1H), 6.27-6.25 (m, 1H), 2.73 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 137.2, 134.4, 134.1, 133.4, 133.1, 132.6, 129.8, 128.3, 127.8, 126.7, 125.1, 124.5, 78.7, 76.1, 64.3. IR (neat): 3291, 3109, 2909, 2121, 1707, 1247, 1066, 746 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{16}H_{11}O_2SCl$ 302.0168; Found 302.0164.

(*E*)-1-(4-((4-Methoxyphenyl)ethynyl)phenyl)pent-1-en-4-yn-3-yl-thiophene-2-carboxyl

ate (1o). Method A was used. 1 mmol scale, 1.5 equiv thiophene-2-carbonyl chloride, 2.0 equiv Et_3N and 10 mol% DMAP were used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 68% yield (271.7 mg) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.86 (m, 1H), 7.58 (d, *J* = 4.8 Hz, 1H), 7.47 (t, *J* = 5.6 Hz, 4H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.11-7.09 (m, 1H), 6.94 (d, *J* = 15.6 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.35 (dd, *J* = 15.6 Hz, 6.4 Hz, 1H), 6.27 (d, *J* = 6.4 Hz, 1H), 3.81 (s, 3H), 2.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 159.6, 135.0, 134.4, 134.1, 133.1, 133.0, 132.9, 131.6, 127.8, 126.9, 123.8, 123.7, 115.1, 114.0, 90.6, 88.0, 79.0, 75.9, 64.6, 55.2. IR (neat): 3276, 3004, 2915, 2840, 2212, 1711, 1606, 1265, 1066, 756 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{25}H_{19}O_3S$ 399.1049; Found 399.1048.

(*E*)-1-(Naphthalen-2-yl)pent-1-en-4-yn-3-yl thiophene-2-carboxylate (1p). Method B was used. 1 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded **1p** in 94% yield (298.2 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 4.0 Hz, 1.2 Hz, 1H), 7.79-7.75 (m, 4H), 7.59-7.57 (m, 1H), 7.55-7.53 (m, 1H), 7.47-7.41 (m, 2H), 7.11-7.05 (m, 2H), 6.44 (dd, *J* = 15.4 Hz, 6.0 Hz, 1H), 6.32-6.30 (m, 1H), 2.72 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 135.1, 134.1, 133.3, 133.1, 132.9, 132.8, 128.3, 128.1, 127.8, 127.6, 127.5, 126.3, 126.3, 123.4, 123.3, 79.1, 75.9, 64.7. IR (neat): 3279, 3109, 2948, 2121, 1682, 1269, 1091, 745 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{20}H_{14}O_2S$ 318.0715; Found 318.0718.

(*E*)-2-Methyl-1-phenylpent-1-en-4-yn-3-yl thiophene-2-carboxylate (1q). Method A

was used. 3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 79% yield (667 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 3.6 Hz, 1H), 7.56 (d, *J* = 5.2 Hz, 1H), 7.36-7.30 (m, 4H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.09 (dd, *J* = 4.4 Hz, 4.2 Hz, 1H), 6.84 (s, 1H), 6.16 (d, *J* = 0.8 Hz, 1H), 2.65 (d, *J* = 2.0 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 136.3, 134.0, 133.0, 132.4, 130.1, 129.0, 128.1, 127.8, 127.1, 79.3, 75.4, 69.6, 14.2. IR (neat): 3290, 3020, 2915, 2124, 1708, 1249, 1070, 745 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{17}H_{14}O_2S$ 282.0715; Found 282.0728.

(*E*)-4-Benzylidenedec-1-yn-3-yl thiophene-2-carboxylate (1r). Method B was used. 3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 69% yield (725.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 3.6 Hz, 1.2 Hz, 1H), 7.52-7.51 (m, 1H), 7.34-7.24 (m, 4H), 7.22-7.21 (m, 1H), 7.06-7.04 (m, 1H), 6.92 (s, 1H), 6.27-6.26 (m, 1H), 2.68 (d, *J* = 2.4 Hz, 1H), 2.52-2.37 (m, 2H), 1.70-1.52 (m, 2H), 1.34-1.19 (m, 6H), 0.84 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 136.8, 136.4, 133.8, 132.9, 130.4, 128.5, 128.1, 127.7, 127.0, 79.4, 75.7, 68.1, 31.2, 29.2, 28.3, 28.3, 22.3, 13.9. IR (neat): 3292, 3020, 2954, 2927, 2124, 1712, 1249, 1085, 746 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{22}H_{24}O_2S$ 352.1497; Found 352.1501.

(*E*)-Hex-4-en-1-yn-3-yl thiophene-2-carboxylate (1s). Method A was used. 10 mmol scale, 1.5 equiv thiophene-2-carbonyl chloride, 2.0 equiv Et_3N and 10 mol% DMAP were

used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 15:1) afforded the title product in 67% yield (1.39 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.833-7.826 (m, 1H), 7.57 (d, *J* = 4.8 Hz, 1H), 7.10-7.08 (m, 1H), 6.14-6.06 (m, 1H), 6.03 (d, *J* = 6.4 Hz, 1H), 5.67 (dd, *J* = 15.2 Hz, 6.4 Hz, 1H), 2.63 (s, 1H), 1.77 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 133.8, 133.1, 132.8, 132.1, 127.7, 125.5, 79.5, 75.1, 64.6, 17.5. IR (neat): 3292, 3103, 2918, 2124, 1706, 1250, 1070, 747 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{11}H_{10}O_2S$ 206.0402; Found 206.0401.

(*E*)-1-(4-Bromophenyl)pent-1-en-4-yn-3-yl acetate (1t). Method A was used. 2 mmol scale, 2.0 equiv acetic anhydride, 3.0 equiv Et_3N and 10 mol% DMAP were used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) afforded the title product in 67% yield (371.8 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 16.0 Hz, 1H), 6.22 (dd, *J* = 15.6 Hz, 6.4 Hz, 1H), 6.03 (d, *J* = 6.4 Hz, 1H), 2.68 (d, *J* = 2.0 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169. 4, 134.3, 133.4, 131.6, 128.3, 123.9, 122.3, 79.0, 75.5, 63.6, 20.9. IR (neat): 3293, 3034, 2931, 2125, 1736, 1219, 1008, 801 cm^{-1}. HRMS (EI-TOF) m/z: M^+ calcd for $C_{13}H_{11}O_2Br$ 277.9942; Found 277.9948.

Synthesis of Bicyclo[3.2.1]octa-3,6-dienes 3.

Typical procedure for the synthesis of (1*R,2*S**,5*R**,8*R**)-8-phenyl-2-((*E*)-styryl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl dibenzoate 3a.**

To a solution of (*E*)-1-phenylpent-1-en-4-yn-3-yl benzoate **1a** (78.7 mg, 0.3 mmol) in toluene (3 mL) was added ^{t}BuXphosAu(MeCN)SbF$_6$ (5.4 mg, 0.006 mmol). The resulting solution was stirred at room temperature for 1 h. Then the mixture was filtered through a pad of silica gel. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 100:1 to 20:1) to afford the product **3a** in 70% yield (54.9 mg) as a white solid.

(1*R,2*S**,5*R**,8*R**)-8-Phenyl-2-((*E*)-styryl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl dibenzoate (3a).** M.p. 122-124 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.6 Hz, 2H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.51-7.44 (m, 3H), 7.37-7.16 (m, 12H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.48 (d, *J* = 6.4 Hz, 1H), 6.20 (dd, *J* = 15.8 Hz, 9.6 Hz, 1H), 5.67 (d, *J* = 2.8 Hz, 1H), 3.99 (dd, *J* = 9.2 Hz, 4.0 Hz, 1H), 3.70 (s, 1H), 3.35-3.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 163.6, 159.7, 148.8, 141.8, 137.0, 133.5, 133.3, 133.2, 130.0, 129.8, 129.6, 129.3, 128.5, 128.40, 128.36, 128.1, 127.6, 127.3, 126.6, 126.30, 126.25, 121.7, 107.3, 56.3, 49.1, 47.1, 44.5. IR (neat): 3056, 3023, 2942, 1740, 1717, 1175, 1056, 743 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{36}H_{32}NO_4$ 542.2326; Found 542.2324.

(1*R,2*S**,5*R**,8*R**)-8-Phenyl-2-((*E*)-styryl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl bis(4-methoxybenzoate) (3b).** 0.3 mmol scale, **1b** (87.7 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF$_6$ (5.4 mg, 0.006 mmol) were used. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: DCM = 1:1) afforded

the title product in 60% yield (52.3 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.38-7.18 (m, 10H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.44 (d, *J* = 6.8 Hz, 1H), 6.20 (dd, *J* = 15.6 Hz, 9.6 Hz, 1H), 5.62 (d, *J* = 2.4 Hz, 1H), 3.97 (dd, *J* = 9.2 Hz, 5.2 Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.69 (s, 1H), 3.33-3.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 163.8, 163.5, 163.4, 159.8, 148.7, 142.0, 137. 1, 133.1, 132.2, 131.9, 128.4, 128.1, 127.7, 127.2, 126.8, 126.3, 121.9, 121.6, 121.6, 113.7, 113.6, 106.8, 56.2, 55.5, 55.4, 49.1, 47.2, 44.6. IR (neat): 3059, 3023, 2937, 2843, 1728, 1603, 1252, 1045, 763 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{38}H_{36}NO_6$ 602.2537; Found 602.2534.

(1*R,2*S**,5*R**,8*R**)-8-Phenyl-2-((*E*)-styryl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl bis(4-(trifluoromethyl)benzoate) (3c).** 0.3 mmol scale, **1c** (99.1 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF_6 (5.4 mg, 0.006 mmol) were used. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: DCM = 5:1) afforded the title product in 69% yield (68.7 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.37-7.18 (m, 10H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.52 (d, *J* = 6.8 Hz, 1H), 6.19 (dd, *J* = 15.8 Hz, 9.2 Hz, 1H), 5.72 (d, *J* = 2.0 Hz, 1H), 4.00 (dd, *J* = 9.2 Hz, 4.8 Hz, 1H), 3.71 (s, 1H), 3.38-3.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 162.4, 159.4, 148.7, 141.5, 136.8, 134.9 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 134.7 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 133.6, 132.8, 132.5, 130.4, 130.2, 128.5, 128.2, 127.59, 127.55, 126.47, 126.2, 126.1, 125.5 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.4 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 123.5 (q, $^1J_{C\text{-}F}$ = 270.9 Hz), 121.9, 108.1, 56.3, 48.8,

47.1, 44.6. IR (neat): 3067, 3026, 2945, 1737, 1264, 1067, 732 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{38}H_{30}F_6NO_4$ 678.2074; Found 678.2067.

(1*R,2*S**,5*R**,8*R**)-8-phenyl-2-((*E*)-styryl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl bis(furan-2-carboxylate) (3d).** 0.3 mmol scale, **1d** (75.7 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF_6 (5.4 mg, 0.006 mmol) were used. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: DCM = 1:2) afforded the title product in 47% yield (35.6 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.54 (s, 1H), 7.35-7.20 (m, 11H), 7.13 (d, *J* = 2.8 Hz, 1H), 6.57 (d, *J* = 15.6 Hz, 2H), 6.45 (d, *J* = 7.2 Hz, 2H), 6.16 (dd, *J* = 15.6 Hz, 9.6 Hz, 1H), 5.63 (s, 1H), 3.98 (dd, *J* = 8.2 Hz, 4.4 Hz, 1H), 3.65 (s, 1H), 3.32-3.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 156.8, 155.4, 148.3, 147.1, 146.8, 143.8, 143.6, 141.6, 137.0, 133.4, 128.4, 128.1, 127.6, 127.4, 126.33, 126.28, 126.22, 121.8, 119.4, 118.9, 112.2, 112.0, 107.6, 56.0, 49.1, 47.1, 44.4. IR (neat): 3140, 3026, 2931, 1732, 1575, 1288, 1068, 750 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{32}H_{28}NO_6$ 522.1911; Found 522.1907.

(1*R,2*S**,5*R**,8*R**)-8-Phenyl-2-((*E*)-styryl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl bis(thiophene-2-carboxylate) (3e).** 0.3 mmol scale, **1e** (80.5 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF_6 (5.4 mg, 0.006 mmol) were used. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: DCM = 1:1) afforded the title product in 81% yield (65.3 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 3.6 Hz, 1H), 7.77 (d, *J* = 3.6 Hz, 1H), 7.61 (d, *J* = 4.8 Hz, 1H), 7.49 (d, *J* = 4.8

Hz, 1H), 7.35-7.17 (m, 10H), 7.12 (t, *J* = 4.4 Hz, 1H), 7.02 (t, *J* = 4.0 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.47 (d, *J* = 6.8 Hz, 1H), 6.17 (dd, *J* = 16.0 Hz, 9.2 Hz, 1H), 5.62 (d, *J* = 2.0 Hz, 1H), 3.95 (dd, *J* = 8.8 Hz, 4.8 Hz, 1H), 3.65 (s, 1H), 3.33-3.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 159.3, 159.1, 148.4, 141.7, 137.0, 134.5, 134.2, 133.6, 133.4, 133.1, 132.8, 132.6, 128.4, 128.1, 128.0, 127.8, 127.6, 127.3, 126.3, 126.31, 126.26, 121.8, 107.3, 56.1, 48.9, 47.1, 44.4. IR (neat): 3106, 3023, 2934, 1719, 1246, 1053, 736 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{32}H_{28}NO_4S_2$ 554.1454; Found 554.1453.

(1*R,2*S**,5*R**,8*R**)-8-Phenyl-2-((*E*)-styryl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl diacetate (3f).** 0.3 mmol scale, **1f** (60.1 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF_6 (5.4 mg, 0.006 mmol) were used. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product in 63% yield (37.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.32-7.19 (m, 8H), 6.53 (d, *J* = 15.6 Hz, 1H), 6.22 (dd, *J* = 7.0 Hz, 2.0 Hz, 1H), 6.07 (dd, *J* = 15.8 Hz, 9.6 Hz, 1H), 5.44 (d, *J* = 2.8 Hz, 1H), 3.83 (dd, *J* = 9.0 Hz, 3.6 Hz, 1H), 3.52 (s, 1H), 3.22-3.21 (m, 1H), 3.10 (d, *J* = 6.8 Hz, 1H), 2.15 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.50, 167.73, 159.45, 148.54, 141.78, 136.95, 133.05, 128.52, 128.06, 127.55, 127.46, 126.64, 126.27, 126.25, 121.19, 106.66, 55.92, 48.89, 46.99, 44.29, 21.23, 20.81. IR (neat): 3059, 3023, 2937, 1756, 1192, 1006, 733 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{26}H_{28}NO_4$ 418.2013; Found 418.2008.

(1*R,2*S**,5*R**,8*R**)-8-Phenyl-2-((*E*)-styryl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl bis(2,2-dimethylpropanoate) (3g).** 0.3 mmol scale, **1g** (72.7 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF_6 (5.4 mg, 0.006 mmol) were used. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: DCM = 2:1) afforded the title product in 71% yield (51.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.21 (m, 10H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.19 (d, *J* = 6.4 Hz, 1H), 6.07 (dd, *J* = 16.0 Hz, 10.0 Hz, 1H), 5.37 (s, 1H), 3.86 (dd, *J* = 9.4 Hz, 4.4 Hz, 1H), 3.54 (s, 1H), 3.18 (s, 1H), 3.11 (d, *J* = 6.8 Hz, 1H), 1.27 (s, 9H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 175.5, 160.3, 148.6, 142.0, 137.0, 133.3, 128.5, 128.1, 127.5, 127.4, 126.8, 126.3, 126.2, 121.0, 106.2, 56.4, 49.2, 47.2, 43.9, 39.2, 38.8, 27.2, 27.0. IR (neat): 3059, 3026, 2971, 2933, 1743, 1644, 1123, 1096, 750 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{32}H_{40}NO_4$ 502.2952; Found 502.2944.

In this case, a clean byproduct, possibly, the isomer of **3g**, was also isolated in 13% yield (9.8 mg). The structure of this product was not defined yet. The characterization data of this byproduct: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.34-7.24 (m, 8H), 7.23-7.18 (m, 2H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.17 (dd, *J* = 6.8 Hz, 2.0 Hz, 1H), 6.08 (d, *J* = 3.2 Hz, 1H), 6.01 (dd, *J* = 15.8 Hz, 9.6 Hz, 1H), 3.91-3.87 (m, 1H), 3.58 (s, 1H), 3.31-3.30 (m, 1H), 3.08 (dd, *J* = 6.4 Hz, 2.8 Hz, 1H), 1.12 (s, 9H), 1.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 175.7, 148.5, 147.8, 141.9, 136.8, 132.9, 128.4, 128.1, 127.6, 127.6, 127.4, 126.23, 126.20, 122.2, 119.7, 56.1, 51.3, 46.9, 41.8, 39.0, 38.8, 27.10, 26.8. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{32}H_{40}NO_4$ 502.2952; Found 502.2942.

(1*R,2*S**,5*R**,8*R**)-8-(4-Bromophenyl)-2-((*E*)-4-bromostyryl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl bis(thiophene-2-carboxylate) (3h).** 0.3 mmol scale, **1h** (104.2 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF_6 (5.4 mg, 0.006 mmol) were used. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: DCM = 1:1) afforded the title product in 72% yield (75.3 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 3.6 Hz, 1H), 7.77 (d, *J* = 3.2 Hz, 1H), 7.63 (d, *J* = 5.2 Hz, 1H), 7.51 (d, *J* = 4.8 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.16-7.12 (m, 3H), 7.03 (dd, *J* = 4.4 Hz, 4.4 Hz, 1H), 6.49 (d, *J* = 15.6 Hz, 1H), 6.45 (d, *J* = 7.2 Hz, 1H), 6.14 (dd, *J* = 15.8 Hz, 9.2 Hz, 1H), 5.59 (d, *J* = 2.8 Hz, 1H), 3.92 (dd, *J* = 9.0 Hz, 5.2 Hz, 1H), 3.58 (s, 1H), 3.29-3.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 159.3, 159.1, 148.2, 140.6, 135.8, 134.7, 134.3, 133.7, 133.3, 132.6, 132.39, 132.36, 131.5, 131.2, 129.4, 128.0, 127.9, 127.8, 126.9, 121.7, 121.1, 120.3, 107.2, 55.6, 48.6, 46.9, 44.3. IR (neat): 3099, 3021, 2951, 2926, 1713, 1246, 1055, 738 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{32}H_{26}Br_2NO_4S_2$ 709.9665; Found 709.9656.

(1*R,2*S**,5*R**,8*R**)-8-(4-Fluorophenyl)-2-((*E*)-4-fluorostyryl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl bis(thiophene-2-carboxylate) (3i).** 0.3 mmol scale, **1i** (85.9 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF_6 (5.4 mg, 0.006 mmol) were used. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: DCM = 1:1) afforded the title product in 71% yield (60.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 3.6 Hz, 1H), 7.78 (d, *J* = 3.6 Hz, 1H), 7.63 (d, *J* = 5.2 Hz, 1H), 7.51 (d, *J* = 4.8 Hz, 1H), 7.32-7.24 (m, 4H), 7.13 (dd, *J* = 4.4 Hz, 4.2 Hz, 1H), 7.05-6,92 (m,

5H), 6.52 (d, J = 16.0 Hz, 1H), 6.45 (d, J = 6.8 Hz, 1H), 6.06 (dd, J = 15.6 Hz, 9.2 Hz, 1H), 5.61 (d, J = 2.0 Hz, 1H), 3.92 (dd, J = 8.8 Hz, 4.4 Hz, 1H), 3.62 (s, 1H), 3.29-3.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, $^1J_{C\text{-}F}$ = 245.2 Hz), 161.5 (d, $^1J_{C\text{-}F}$ = 243.7 Hz), 160.5, 159.4, 159.1, 148.4, 137.4 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 134.6, 134.2, 133.7, 133.2, 133.1 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 132.7, 132.5, 132.3, 129.1 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 128.0, 127.8, 127.8 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 125.9 (d, $^5J_{C\text{-}F}$ = 2.3 Hz), 121.7, 115.3 (d, $^2J_{C\text{-}F}$ = 22.1 Hz), 114.9 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 107.3, 55.5, 48.9, 47.0, 44.6. IR (neat): 3098, 2920, 1708, 1614, 1250, 1094, 754 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{32}H_{23}O_4F_2S_2$ 573.1000; Found 573.0999.

(1*R,2*S**,5*R**,8*R**)-8-(4-(Trifluoromethyl)phenyl)-2-((*E*)-4-(trifluoromethyl)styryl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl bis(thiophene-2-carboxylate) (3j).** 0.3 mmol scale, **1j** (100.9 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF_6 (5.4 mg, 0.006 mmol) were used. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: DCM = 1:1) afforded the title product in 65% yield (65.5 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.89 (m, 1H), 7.79-7.78 (m, 1H), 7.65-7.63 (m, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.53-7.46 (m, 5H), 7.39 (d, J = 8.0 Hz, 2H), 7.14 (dd, J = 4.8 Hz, 4.4 Hz, 1H), 7.05 (dd, J = 4.8 Hz, 4.2 Hz, 1H), 6.62 (d, J = 16.0 Hz, 1H), 6.50-6.49 (m, 1H), 6.27 (dd, J = 15.8 Hz, 9.6 Hz, 1H), 5.61 (d, J = 2.8 Hz, 1H), 4.01 (dd, J = 8.6 Hz, 4.8 Hz, 1H), 3.70 (s, 1H), 3.37-3.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 159.3, 159.1, 148.1, 145.56 (q, $^4J_{C\text{-}F}$ = 1.5 Hz), 140.3 (q, $^4J_{C\text{-}F}$ = 1.5 Hz), 134.8, 134.4, 133.9, 133.4, 132.5, 132.4, 132.3, 129.2 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 128.5 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 128.8, 128.1, 128.0, 127.9, 126.4, 125.4 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.1 (q, $^3J_{C\text{-}F}$ = 3.8 Hz),

124.2 (q, $^{1}J_{C\text{-}F}$ = 271.0 Hz), 124.1 (q, $^{1}J_{C\text{-}F}$ = 270.3 Hz), 121.8, 107.0, 55.9, 48.6, 46.9, 44.2. IR (neat): 3106, 2959, 2918, 2848, 1720, 1616, 1248, 1066, 736 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{34}H_{26}F_6NO_4S_2$ 690.1202; Found 690.1201.

(1*R,2*S**,5*R**,8*R**)-2-((*E*)-4-Methylstyryl)-8-(*p*-tolyl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl bis(thiophene-2-carboxylate) (3k).** 0.3 mmol scale, **1k** (84.7 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF_6 (5.4 mg, 0.006 mmol) were used. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: DCM = 1:1) afforded the title product in 56% yield (47.6 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 3.8 Hz, 0.8 Hz, 1H), 7.76 (dd, *J* = 3.8 Hz, 0.8 Hz, 1H), 7.60 (dd, *J* = 4.8 Hz, 1.2 Hz, 1H), 7.48 (dd, *J* = 5.2 Hz, 1.2 Hz, 1H), 7.24-7.19 (m, 4H), 7.13-7.10 (m, 3H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.01 (dd, *J* = 4.8 Hz, 4.0 Hz, 1H), 6.53 (d, *J* = 15.6 Hz, 1H), 6.46-6.44 (m, 1H), 6.11 (dd, *J* = 15.6 Hz, 9.6 Hz, 1H), 5.61 (d, *J* = 2.8 Hz, 1H), 3.92 (dd, *J* = 9.2 Hz, 4.4 Hz, 1H), 3.62 (s, 1H), 3.30-3.28 (m, 2H), 2.31 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 159.4, 159.1, 148.5, 138.7, 137.1, 135.8, 134.5, 134.3, 134.2, 133.5, 133.1, 133.1, 132.9, 132.7, 129.1, 128.8, 128.0, 127.8, 127.5, 126.2, 125.3, 121.8, 107.4, 55.8, 49.0, 47.1, 44.5, 21.1, 21.0. IR (neat): 3095, 3020, 2919, 1720, 1248, 1054, 736 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{34}H_{32}NO_4S_2$ 582.1767; Found 582.1765.

(1*R,2*S**,5*R**,8*R**)-8-(3,4,5-Trimethoxyphenyl)-2-((*E*)-3,4,5-trimethoxystyryl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl bis(thiophene-2-carboxylate) (3l).** 0.5 mmol scale, **1l**

(179.2 mg, 0.5 mmol), toluene (5 mL), ^{t}BuXphosAu(MeCN)SbF$_6$ (9.0 mg, 0.01 mmol) were used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 3:1) afforded the title product in 66% yield (117.9 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 1.2 Hz, 1H), 7.80 (d, *J* = 1.2 Hz, 1H), 7.64 (d, *J* = 4.4 Hz, 1H), 7.54 (d, *J* = 4.4 Hz, 1H), 7.138-7.131 (m, 1H), 7.06 (s, 1H), 6.64 (s, 2H), 6.53 (s, 2H), 6.50-6.47 (m, 2H), 6.07 (dd, *J* = 15.6 Hz, 9.2 Hz, 1H), 5.61 (s, 1H), 4.00-3.98 (m, 1H), 3.87 (s, 6H), 3.85 (s, 9H), 3.82 (s, 3H), 3.63 (s, 1H), 3.36 (d, *J* = 7.2 Hz, 1H), 3.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 159.8, 159.0, 153.1, 152.8, 148.4, 137.5, 137.4, 136.4, 134.6, 134.2, 133.6, 133.4, 133. 1, 132.7, 132.6, 132.3, 128.0, 127.8, 125.5, 121.9, 107.5, 104.7, 103.2, 60.7, 60.7, 56.7, 56.0, 55.9, 49.3, 47.0, 44.3. IR (neat): 3099, 2995, 2937, 2833, 1722, 1247, 1122, 740 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{38}H_{40}NO_{10}S_2$ 734.2088; Found 734.2083.

(1*R,2*S**,5*R**,8*R**)-8-(2-Fluorophenyl)-2-((*E*)-2-fluorostyryl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl bis(thiophene-2-carboxylate) (3m).** 0.3 mmol scale, **1m** (85.9 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF$_6$ (5.4 mg, 0.006 mmol) were used. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: DCM = 1:1) afforded the title product in 55% yield (47.5 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 4.0 Hz, 1.2 Hz, 1H), 7.79 (dd, *J* = 3.8 Hz, 1.2 Hz, 1H), 7.63 (dd, *J* = 5.2 Hz, 1.2 Hz, 1H), 7.51 (dd, *J* = 5.2 Hz, 1.2 Hz, 1H), 7.41-7.37 (m, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.25-7.12 (m, 3H), 7.10-7.02 (m, 4H), 6.99-6.94 (m, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.50-6.48 (m, 1H), 6.24 (dd, *J* = 16.0 Hz, 9.6 Hz, 1H), 5.62 (d, *J* = 2.8 Hz, 1H), 3.99

(dd, J = 9.2 Hz, 4.4 Hz, 1H), 3.85 (s, 1H), 3.34-3.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6 (d, $^{1}J_{C\text{-}F}$ = 244.4 Hz), 160.4, 159.9 (d, $^{1}J_{C\text{-}F}$ = 247.5Hz), 159.6, 159.1, 148.2, 134.6, 134.2, 133.7, 133.12, 132.8, 132.5, 128.9 (d, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 128.8 (d, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 128.6 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 128.5 (d, $^{2}J_{C\text{-}F}$ = 12.9 Hz), 128.1, 128.0, 127.8, 127.4 (d, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 125.9 (d, $^{3}J_{C\text{-}F}$ = 3.1 Hz), 125.0 (d, $^{2}J_{C\text{-}F}$ = 12.1 Hz), 124.0 (d, $^{4}J_{C\text{-}F}$ = 3.1 Hz), 123.7 (d, $^{4}J_{C\text{-}F}$ = 3.1 Hz), 121.7, 115.5 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 115.1 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 107.3, 50.2 (d, $^{3}J_{C\text{-}F}$ = 3.1 Hz), 47.8, 47.2, 43.2. IR (neat): 3103, 3042, 2931, 1775, 1717, 1248, 1008, 754 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{32}H_{26}F_2NO_4S_2$ 590.1266; Found 590.1264.

(1*R,2*S**,5*R**,8*R**)-8-(3-Chlorophenyl)-2-((*E*)-3-chlorostyryl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl bis(thiophene-2-carboxylate) (3n).** 0.3 mmol scale, **1n** (90.8 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF_6 (5.4 mg, 0.006 mmol) were used. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: DCM = 1:1) afforded the title product in 77% yield (69.9 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 3.6 Hz, 0.8 Hz, 1H), 7.78 (dd, J = 3.8 Hz, 1.2 Hz, 1H), 7.63 (dd, J = 5.0 Hz, 1.2 Hz, 1H), 7.53 (dd, J = 5.0 Hz, 1.2 Hz, 1H), 7.33 (s, 1H), 7.27-7.12 (m, 8H), 7.05 (dd, J = 4.8 Hz, 4.0 Hz, 1H), 6.51 (d, J = 15.6 Hz, 1H), 6.46 (dd, J = 7.0 Hz, 2.0 Hz, 1H), 6.16 (dd, J = 15.6 Hz, 9.2 Hz, 1H), 5.60 (d, J = 2.4 Hz, 1H), 3.94 (dd, J = 8.2 Hz, 4.8 Hz, 1H), 3.61 (s, 1H), 3.32-3.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 159.4, 159.1, 148.2, 143.7, 138.8, 134.7, 134.4, 134.3, 134.0, 133.7, 133.3, 132.6, 132.4, 132.3, 129.7, 129.4, 128.0, 127.89, 127.87, 127.7, 127.4, 126.6, 126.2, 125.8, 124.5, 121.8, 107.1,

55.8, 48.5, 46.9, 44.4. IR (neat): 3101, 3026, 2931, 1720, 1246, 1053, 720 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{32}H_{26}Cl_2NO_4S_2$ 622.0675; Found 622.0670.

(1*R,2*S**,5*R**,8*R**)-8-(4-((4-Methoxyphenyl)ethynyl)phenyl)-2-((*E*)-4-((4-methoxyphenyl)ethynyl)styryl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl bis(thiophene-2-carboxylate) (3o).** 0.3 mmol scale, **1o** (119.5 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF_6 (5.4 mg, 0.006 mmol) were used. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: DCM = 1:1) afforded the title product in 55% yield (65.6 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 3.2 Hz, 1H), 7.77 (d, *J* = 2.8 Hz, 1H), 7.61 (d, *J* = 4.8 Hz, 1H), 7.51-7.39 (m, 9H), 7.31-7.25 (m, 4H), 7.12 (dd, *J* = 3.6 Hz, 3.6 Hz, 1H), 7.02 (dd, *J* = 3.8 Hz, 3.6 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 4H), 6.55 (d, *J* = 15.6 Hz, 1H), 6.47 (d, *J* = 6.8 Hz, 1H), 6.18 (dd, *J* = 15.6 Hz, 9.6 Hz, 1H), 5.62 (s, 1H), 3.96-3.94 (m, 1H), 3.80 (s, 6H), 3.63 (s, 1H), 3.32-3.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 159.54, 159.47, 159.4, 159.1, 148.3, 141.6, 136.6, 134.6, 134.2, 133.6, 133.2, 133.0, 132.7, 132.5, 131.5, 131.2, 128.0, 127.8, 127.6, 127.0, 126.2, 122.4, 121.7, 121.6, 115.4, 115.3, 114.0, 113.9, 107.3, 90.0, 89.2, 88.2, 88.0, 56.1, 55.2, 48.7, 47.1, 44.4. IR (neat): 3034, 3001, 2931, 2834, 2212, 1712, 1602, 1245, 1027, 738 cm^{-1}. HRMS (MALDI/DHB-Stiral) m/z: $[M+Na]^+$ calcd for $C_{50}H_{36}O_6NaS_2$ 819.1846; Found 819.1837.

(1*R,2*S**,5*R**,8*R**)-8-(Naphthalen-2-yl)-2-((*E*)-2-(naphthalen-2-yl)vinyl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl bis(thiophene-2-carboxylate) (3p).** 0.3 mmol scale, **1p** (95.5 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF_6 (5.4 mg, 0.006 mmol) were used.

Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: ethyl acetate = 6:1) afforded the title product in 71% yield (68.2 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 2.8 Hz, 1H), 7.83-7.72 (m, 8H), 7.64 (s, 1H), 7.61 (d, *J* = 4.4 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.51-7.38 (m, 6H), 7.12 (t, *J* = 4.4 Hz, 1H), 7.00 (t, *J* = 4.4 Hz, 1H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.53 (d, *J* = 7.2 Hz, 1H), 6.33 (dd, *J* = 15.6 Hz, 9.6 Hz, 1H), 5.70 (s, 1H), 4.06 (dd, *J* = 8.8 Hz, 4.8 Hz, 1H), 3.84 (s, 1H), 3.48 – 3.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 159.5, 159.1, 148.5, 139.0, 134.6, 134.5, 134.2, 133.6, 133.5, 133.2, 133.1, 132.8, 132.8, 132.6, 132.1, 128.0, 128.0, 127.9, 127.9, 127.7, 127.6, 127.4, 126.7, 126.5, 126.1, 126.0, 125.9, 125.7, 125.5, 123.6, 121.9, 107.4, 56.4, 48.7, 47.3, 44.6. IR (neat): 3095, 3056, 2931, 1713, 1598, 1247, 1053, 738 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{40}H_{32}NO_4S_2$ 654.1767; Found 654.1762.

(1*S,2*S**,5*R**,8*R**)-1-Methyl-8-phenyl-2-((*E*)-1-phenylprop-1-en-2-yl)bicyclo[3.2.1]oct a-3,6-diene-3,6-diyl bis(thiophene-2-carboxylate) (3q).** 0.3 mmol scale, **1q** (84.7 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF_6 (5.4 mg, 0.006 mmol) were used. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: DCM = 1:1) afforded the title product in 85% yield (72.2 mg) as a white solid. M.p. 164-166 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 3.6 Hz, 1H), 7.79 (d, *J* = 3.6 Hz, 1H), 7.64 (d, *J* = 4.8 Hz, 1H), 7.51 (d, *J* = 4.8 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 3H), 7.16-7.10 (m, 4H), 7.05 (dd, *J* = 4.2 Hz, 3.6 Hz, 1H), 6.50 (d, *J* = 6.8 Hz, 1H), 6.38 (s, 1H), 5.33 (s, 1H), 3.67 (s, 1H), 3.39 (s, 1H), 3.28 (d,

J = 6.8 Hz, 1H), 1.87 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 159.2, 155.8, 149.3, 140.6, 137.8, 134.6, 134.2, 134.1, 133.6, 133.0, 132.9, 132.6, 131.8, 128.8, 128.0, 127.92, 127.87, 127.8, 126.7, 126.1, 121.6, 112.6, 62.8, 60.8, 52.5, 45.1, 21.1, 17.2. IR (neat): 3059, 3026, 2962, 2918, 1720, 1248, 1049, 737 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{34}H_{32}NO_4S_2$ 582.1767; Found 582.1764.

(1*S,2*S**,5*R**,8*R**)-1-Hexyl-8-phenyl-2-((*E*)-1-phenyloct-1-en-2-yl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl bis(thiophene-2-carboxylate) (3r).** 0.3 mmol scale, **1r** (105.7 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF_6 (5.4 mg, 0.006 mmol) were used. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: DCM = 2:1) afforded the title product in 74% yield (77.8 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 3.8 Hz, 1.2 Hz, 1H), 7.82 (dd, *J* = 3.6 Hz, 0.8 Hz, 1H), 7.61 (dd, *J* = 4.8 Hz, 1.2 Hz, 1H), 7.55 (dd, *J* = 4.8 Hz, 0.8 Hz, 1H), 7.51 (d, *J* = 6.8 Hz, 2H), 7.28-7.07 (m, 10H), 6.45-6.43 (m, 2H), 5.54 (s, 1H), 3.79 (s, 1H), 3.46 (s, 1H), 3.15 (d, *J* = 7.2 Hz, 1H), 1.63-1.60 (m, 2H), 1.51-1.45 (m, 2H), 1.26-0.88 (m, 16H), 0.78-0.74 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 159.1, 155.5, 150.5, 140.9, 138.4, 134.5, 134.1, 133.4, 133.3, 133.0, 132.8, 128.9, 128.5, 128.0, 128.0, 127.8, 126.9, 126.0, 121.9, 113.7, 62.0, 56.6, 49.3, 46.7, 32.4, 31.4, 31.3, 29.5, 29.3, 28.7, 22.8, 22.4, 22.3, 14.0, 13.9. IR (neat): 3059, 3023, 2927, 2856, 1724, 1244, 1049, 738 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{44}H_{52}NO_4S_2$ 722.3332; Found 722.3329.

(1*R,2*S**,5*R**,8*R**)-8-Methyl-2-((*E*)-prop-1-en-1-yl)bicyclo[3.2.1]octa-3,6-diene-3,6-di**

yl bis(thiophene-2-carboxylate) (3s). 0.3 mmol scale, **1s** (61.9 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF_6 (5.4 mg, 0.006 mmol) were used. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether: DCM = 1:1) afforded the title product in 28% yield (17.3 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.8 Hz, 1H), 7.79-7.78 (m, 1H), 7.62 (d, *J* = 5.2 Hz, 1H), 7.56 (d, *J* = 4.8 Hz, 1H), 7.14 (dd, *J* = 4.8 Hz, 4.2 Hz, 1H), 7.09 (dd, *J* = 4.4 Hz, 4.2 Hz, 1H), 6.21 (d, *J* = 6.8 Hz, 1H), 5.59-5.50 (m, 1H), 5.45 (s, 1H), 5.33 (dd, *J* = 14.6 Hz, 9.2 Hz, 1H), 3.52 (dd, *J* = 9.0 Hz, 4.8 Hz, 1H), 2.71-2.67 (m, 2H), 2.45 (q, *J* = 6.4 Hz, 1H), 1.57 (d, *J* = 6.4 Hz, 3H), 1.17 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 160.5, 159.6, 148.6, 134.4, 133.9, 133.4, 133.3, 132.9, 132.8, 128.7, 128.0, 127.7, 127.4, 121.6, 108.1, 49.6, 47.5, 46.6, 44.9, 17.8, 17.4. IR (neat): 3106, 2957, 2917, 2851, 1716, 1653, 1268, 1049, 735 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{22}H_{24}NO_4S_2$ 430.1141; Found 430.1134.

(1*R,2*S**,5*R**,8*R**)-8-(4-Bromophenyl)-2-((*E*)-4-bromostyryl)bicyclo[3.2.1]octa-3,6-diene-3,6-diyl diacetate (3t).** 0.3 mmol scale, **1t** (83.7 mg, 0.3 mmol), toluene (3 mL), ^{t}BuXphosAu(MeCN)SbF_6 (5.4 mg, 0.006 mmol) were used. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 67% yield (56.0 mg) as a white solid. M.p. 142-144 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 8.0 Hz, 4H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.20 (dd, *J* = 7.0 Hz, 2.0 Hz, 1H), 6.04 (dd, *J* = 15.6 Hz, 9.6 Hz, 1H), 5.40 (d, *J* = 2.8 Hz, 1H), 3.80 (dd, *J* = 9.0 Hz, 4.4 Hz, 1H), 3.45 (s, 1H), 3.16-3.15 (m, 1H), 3.06 (d, *J* = 6.8 Hz, 1H), 2.15 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 167.7, 159.4, 148.3,

140.7, 135.8, 132.0, 131.6, 131.2, 129.3, 127.8, 127.2, 121.3, 121.1, 120.2, 106.5, 55.4, 48.6, 46.9, 44.2, 21.2, 20.8. IR (neat): 3050, 3021, 2959, 2931, 1758, 1644, 1194, 1009, 827 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{26}H_{26}Br_2NO_4$ 574.0223; Found 574.0220.

Removal of the protecting group: synthesis of 4e and 4l.

Typical procedure for the synthesis of (1*R,4*S**,5*S**,8*R**)-7-oxo-8-phenyl-4-((*E*)-styryl)bicyclo[3.2.1]oct-2-en-3-yl thiophene-2-carboxylate (4e).**

To a sealable tube were added **3e** (107.3 mg, 0.2 mmol), DCM (2 mL) and *p*-toluenesulfonic acid monohydrate (76.1 mg, 0.4 mmol). The tube was sealed and immersed into an oil bath preheated at 50 ^oC. After stirring for 2 h, the mixture was cooled down to room temperature, then filtered through a pad of silica gel. The solvent was evaporated under the reduced pressure and the residue was purified by preparative TLC on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) to afford the title product **4e** in 66% yield (56.6 mg) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 3.8 Hz, 1.2 Hz, 1H), 7.54 (dd, *J* = 5.0 Hz, 0.8 Hz, 1H), 7.36-7.19 (m, 10H), 7.06 (t, *J* = 4.0 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.15 (dd, *J* = 16.0 Hz, 8.4 Hz, 1H), 5.90 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 4.26 (bs, 1H), 3.66 (s, 1H), 3.36 (d, *J* = 8.0 Hz, 1H), 2.88 (t, *J* = 5.2 Hz, 1H), 2.63 (dd, *J* = 19.2 Hz, 1.6 Hz, 1H), 2.20 (dd, *J* = 19.2 Hz, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.4, 159.8, 150.5, 140.6, 136.7, 134.5, 134.4, 133.5, 132.2, 128.8, 128.5, 127.9, 127.6, 126.9, 126.6, 126.2, 125.0, 114.7, 49.4, 49.4, 47.9, 44.0, 35.0. IR (neat): 3088, 3060, 3024,

2975, 1740, 1720, 1247, 1047, 737 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{27}H_{26}NO_3S$ 444.1628; Found 444.1623.

(1*R,4*S**,5*S**,8*R**)-7-Oxo-8-(3,4,5-trimethoxyphenyl)-4-((*E*)-3,4,5-trimethoxystyryl)bicyclo[3.2.1]oct-2-en-3-yl thiophene-2-carboxylate (4l).** 0.2 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 2:1) afforded the title product **4l** in 60% yield as a light yellow solid. M.p. 150-152 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.82-7.81 (m, 1H), 7.58 (d, *J* = 4.8 Hz, 1H), 7.09 (t, *J* = 4.0 Hz, 1H), 6.56-6.50 (m, 3H), 6.41 (s, 2H), 6.06 (dd, *J* = 15.8 Hz, 8.4 Hz, 1H), 5.89 (d, *J* = 8.0 Hz, 1H), 4.26 (t, *J* = 4 Hz, 1H), 3.86 (s, 6H), 3.83 (s, 9H), 3.82 (s, 3H), 3.61 (s, 1H), 3.34 (d, *J* = 8.0 Hz, 1H), 2.86 (s, 1H), 2.66 (d, *J* = 19.2 Hz, 1H), 2.26 (dd, *J* = 19.2 Hz, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.5, 159.8, 153.4, 153.2, 150.5, 137.9, 136.9, 136.3, 134.6, 134.5, 133.6, 132.4, 132.2, 128.0, 124.4, 114.6, 103.7, 103.3, 60.9, 60.8, 56.1, 56.0, 49.61, 49.57, 47.8, 44.2, 35.1. IR (neat): 3096, 2993, 2936, 2838, 1740, 1714, 1254, 1002, 730 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ calcd for $C_{33}H_{38}NO_9S$ 624.2262; Found 624.2258.

Synthesis of 5 and 6.

To a solution of **1e** (53.7 mg, 0.2 mmol) in toluene (2 mL) were added phenyl sulfoxide (80.9 mg, 0.4 mmol) and ^{t}BuXphosAu(MeCN)SbF_6 (3.6 mg, 0.004 mmol). The resulting solution was stirred at room temperature for 0.5 h. Then the mixture was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford **5** in

59% yield (33.5 mg) as a light yellow amorphous solid and **6** in 16% yield (8.9 mg) as a light yellow oil.

When the reaction was carried out in the absence of light by wrapping the tube with aluminum paper, the products **5** and **6** were formed in 64% and 11% NMR yields.

(2*E*,4*E*)-1-Oxo-5-phenylpenta-2,4-dien-2-yl thiophene-2-carboxylate (5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.95 (d, J = 2.4 Hz, 1H), 7.71-7.64 (m, 2H), 7.52 (d, J = 6.8 Hz, 2H), 7.43-7.37 (m, 3H), 7.16 (bs, 1H), 6.98, (d, J = 13.6 Hz, 1H), 6.94 (d, J = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.3, 160.1, 143.3, 142.7, 136.0, 135.5, 135.1, 133.9, 131.5, 129.6, 128.8, 128.0, 127.4, 119.0. IR (neat): 3096, 3060, 3021, 2864, 1726, 1674, 1248, 1056, 739 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{13}O_3S$ 285.0580; Found 285.0580.

(2*Z*,4*E*)-1-Oxo-5-phenylpenta-2,4-dien-2-yl thiophene-2-carboxylate (6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.01-8.00 (m, 1H), 7.69 (d, J = 4.8 Hz, 1H), 7.50-7.48 (m, 2H), 7.37-7.33 (m, 3H), 7.19 (dd, J = 4.4 Hz, 4.4 Hz, 1H), 7.15-7.05 (m, 2H), 7.01 (dd, J = 8.8 Hz, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.4, 159.0, 145.1, 143.1, 137.5, 135.4, 135.3, 134.1, 131.3, 129.9, 128.8, 128.1, 127.7, 119.8. IR (neat): 3099, 3039, 2923, 2848, 1727, 1679, 1623, 1242, 1056, 743 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{13}O_3S$ 285.0580; Found 285.0579.

Isomerization of 5 to 6 by blue light.

A 8 mL vial equipped with a magneticstir bar were charged with **5** (56.9 mg, 0.2 mmol) and toluene (2 mL). The vial was placed at a distance of 5 cm from the blue LEDs. The mixture was stirred and irradiated by blue LEDs for 3 h. After the reaction was complete, the solvent was evaporated under the reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford **6** in 88% yield (50 mg) as a colorless oil.

Synthesis of (2*Z*,4*E*)-1-((4-bromophenyl)imino)-5-phenylpenta-2,4-dien-2-yl thiophene-2-carboxylate 7.

Under air, to a solution of **6** (56.9 mg, 0.2 mmol) in DCM (5 mL) were added *p*-$BrC_6H_4NH_2$ (34.4 mg, 0.2 mmol) and $MgSO_4$ (7.2 mg, 0.06 mmol). The resulting solution was stirred at room temperature for 18 h. Then the mixture was filtered through a pad of celite. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel which was treated with petroleum ether: Et_3N = 4:1 and then petroleum ether before loading the sample (eluent: petroleum ether: ethyl acetate = 10:1) to afford the title product **7** in 62% yield (54.7 mg) as a yellow solid. M.p. 156-158 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 3.8 Hz, 0.8 Hz, 1H), 8.01 (s, 1H), 7.69 (dd, *J* = 5.0 Hz, 1.6 Hz, 1H), 7.45-7.40 (m, 4H), 7.34-7.25 (m, 3H), 7.20 (dd, *J* = 4.8 Hz, 4.0 Hz, 1H), 7.10 (dd, *J* = 15.6 Hz, 11.2 Hz, 1H), 7.01-6.97 (m, 2H), 6.90 (d, *J* = 15.6 Hz, 1H), 6.74 (d, *J* = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 153.5, 149.9, 145.1, 139.2, 136.1, 135.0, 133.7, 132.2, 132.0, 131.2, 129.1, 128.7, 128.1, 127.3, 122.8, 120.8, 119.7. IR (neat): 2957, 2923, 2851, 1719, 1611, 1244, 1059, 752 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{17}BrNO_2S$ 438.0158; Found 438.0155.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallography of compounds **3a**, **3q**, **3t**, **4l** and **7**, and NMR spectra of all new compounds are given in the Supporting Information. 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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(18) When the reaction shown in eq 1 was carried out in the absence of light, **5** and **6** were obtained in 64% and 11% NMR yields, respectively. The results indicated that **6** was formed under gold catalysis in this reaction.

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