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Au-Catalyzed Tandem Cyclization/[1,2]-Alkyl Migration Reaction of Epoxy Alkynes: Synthesis of Spiropyranones

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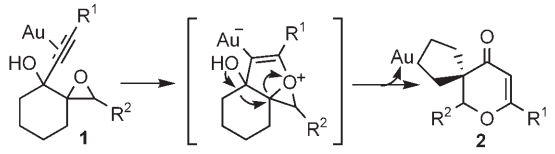
Abstract: A novel gold-catalyzed tandem cyclization/[1,2]-alkyl migration process of epoxy alkynes to spiropyranones has been discovered. From this process, the construction of adjacent multiple stereocenters with a new quaternary carbon atom is achieved. The gold-catalyzed domino process is stereospecific with respect to the migrating carbon atom. A type of unusual C–C bond cleavage of epoxide systems has also been discovered, which can lead to the formation of two *Z* alkenes and a carbonyl functional group in one step with excellent stereoselectivity. Furthermore, this efficient domino process could be achieved in the presence of the simplest and least expensive gold catalyst $[NaAuCl_4]\cdot 2H_2O$ with a low catalyst loading.

Keywords: epoxy alkynes · gold · migration · rearrangement · spiropyrane

Introduction

In the field of organic synthesis, it is very desirable to facilitate two- or multistep bond formations in one pot with a single catalyst to achieve economically useful transformations.[1] One of the most effective ways of achieving this synthetic efficiency is to implement tandem reactions.[2] Recently, Au catalysis[3] has elicited new excitement in this active research area, and a number of consecutive C–X (X = heteroatom) and C–C bond-forming processes have been effective.[4] In this context, tandem cyclization/migration reactions would present a valuable opportunity.[5] Although, much attention has been paid to ether[5a,c] and carbonyl groups,[6] other functional groups, such as aziridines and epoxides, which are among the most versatile intermediates in organic synthesis,[7] have not been explored until now.

In the context of our ongoing efforts to develop tandem reactions,[8] we found that oxonium ions formed from alkynes and epoxides might be perfect intermediates in a domino process.[9] We hypothesize that gold-activated epoxy alkynes may undergo an *anti-endo-dig* cyclization to afford the intermediate oxonium ions, which might induce the migration of neighboring groups when assisted with the hydroxy group (Scheme 1). Herein, we report a novel gold-catalyzed tandem cyclization/[1,2]-alky migration process to spiropyranones. In this reaction, the [1,2]-migration of the alkyl groups was a key step and the construction of adjacent multiple stereocenters with a new quaternary carbon atom was also achieved.



Scheme 1. The hypothesized activation of epoxy alkynes with gold.

Results and Discussion

Optimization studies of this transformation began with epoxy alkyne **1a** (Table 1), which was readily prepared from the corresponding enone in two steps.[10] The cyclization of **1a** proceeded effectively with $[NaAuCl_4]\cdot 2H_2O$ (5 mol%) in toluene at 80 °C and gave the expected 4(2*H*)-pyranone **2a**

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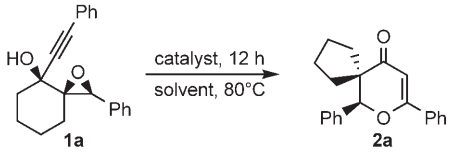
Table 1. Optimization of the reaction conditions for the cyclization of **1a**.[a]



Entry	Catalyst	Catalyst loading [mol%]	Solvent	Yield [%][b]
1	$[NaAuCl_4]\cdot 2H_2O$	5	toluene	80
2	$[HAuCl_4]\cdot 4H_2O$	5	toluene	52
3	$AuCl_3$	5	toluene	71
4	AuCl	5	toluene	67
5	$AuCl_3$, $AgSbF_6$	5, 15	toluene	trace
6	AuCl, $AgSbF_6$	5, 5	toluene	trace
7	$PtCl_2$	5	toluene	56
8	$[Pd(tfa)_2]$	5	toluene	48
9	$[NaAuCl_4]\cdot 2H_2O$	5	xylene	72
10	$[NaAuCl_4]\cdot 2H_2O$	5	*n*-hexane	46
11	$[NaAuCl_4]\cdot 2H_2O$	5	benzene	93
12	$[NaAuCl_4]\cdot 2H_2O$	2	benzene	92
13	$[NaAuCl_4]\cdot 2H_2O$	1	benzene	83

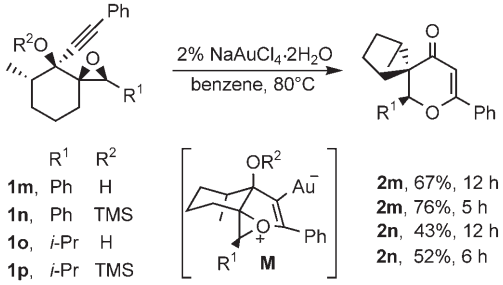
[a] Reactions conditions: **1a** (0.3 mmol), solvent (2 mL), 80 °C, 12 h. [b] Yield of isolated product.

in 80% yield after 12 h (Table 1, entry 1). With other gold catalysts, such as $[HAuCl_4]\cdot 4H_2O$, $AuCl_3$, and AuCl, no superior results were obtained (Table 1, entries 2–4). The addition of a silver salt led to a dramatic decomposition of the starting material (Table 1, entries 5 and 6). $PtCl_2$ and $[Pd(tfa)_2]$ (tfa = trifluoroacetate) also showed considerable catalytic activity, whereas moderate yields were obtained (Table 1, entries 7 and 8). On the other hand, an excellent yield of **2a** was obtained by switching the solvent to benzene (Table 1, entry 11).[11] A similar result was also achieved when 2 mol% of $[NaAuCl_4]\cdot 2H_2O$ was used (Table 1, entry 12).

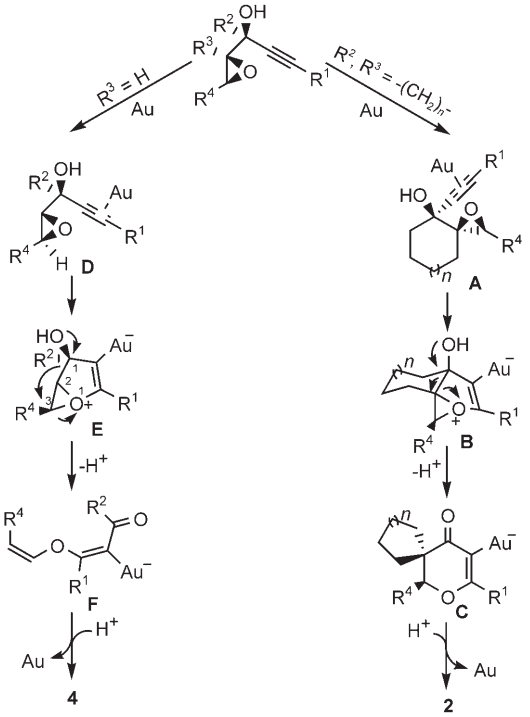
With these optimal conditions in hand, we examined the scope of this reaction (Table 2). Various aryl groups and alkyl substituent on the oxirane ring were tolerated (Table 2, entries 1–4 and 11). An electron-withdrawing aryl group gave a better result relative to electron-rich groups (Table 2, entries 2 versus 3 and 4), which might be ascribed to the intermediate oxonium ions (Scheme 1). After being stabilized effectively, the ability of oxonium ions to induce the migration of an adjacent group will be decreased. Alkynes with different aryl groups were compatible with this reaction (Table 2, entries 5 and 6). If aliphatic and heteroaromatic alkynes were used, the reaction proceeds much faster to afford higher yields of the desired products (Table 2, entries 7 and 8). On the other hand, the reaction efficiency was consistent with the ring strain. Larger-membered ring systems gave higher yields of corresponding products in a shorter time (Table 2, entries 9–11). If the hydroxy group was protected with trimethylsilylether, then the reaction proceeded efficiently in the presence of three equivalents of H_2O and gave a superior result to tertiary alcohol **1a** (Table 2, entry 12 versus 1).

To briefly examine the proposed proto-demetalation step to set the gold catalyst free, under the standard conditions ether **1l** was subjected to an excess of D_2O as an additive, and the desired incorporation of the deuterium atom into 4-(2*H*)-pyranone **2l** at C5 was observed. This result is consistent with our proposed mechanism (Scheme 3), in which proto-demetalation at C5 is believed to be the final step.

Additionally, the gold-catalyzed domino process is stereospecific with respect to the migrating carbon atom (Scheme 2). The methyl-substituted compounds **1m**,[12] and **1n**–**1p** reacted smoothly to afford the only isomer of spiropyranones **2m**[13] and **2n** in moderate yields. Better results were obtained when the alcohols were protected with trimethylsilylether. We think the rearrangement proceeded via the oxonium ion as the intermediate **M**, although no direct experimental proof exists.

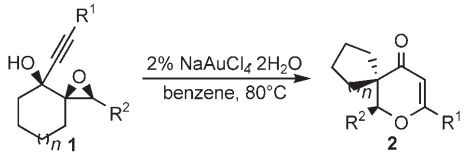


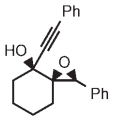
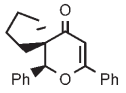
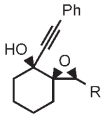
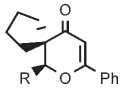
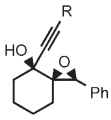
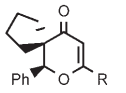
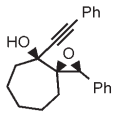
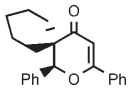
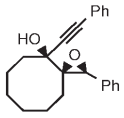
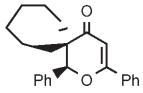
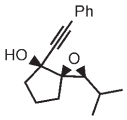
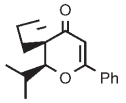
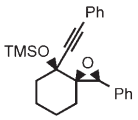
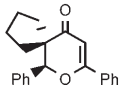
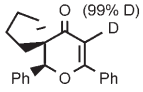
Scheme 2. Stereospecific study of the gold-catalyzed domino process.



Scheme 3. Proposed mechanism for the gold-catalyzed reactions to form **2** and **4**.

Table 2. Gold-catalyzed tandem reactions of various epoxy alkynes.[a]



Entry	Substrate	R	t [h]	Product	Yield[b] [%]
1		**1a**	12	 **2a**	92
2		**1b** p-ClC_6H_4	12	 **2b**	84
3		**1c** p-$CH_3C_6H_4$	12	**2c**	75
4		**1d** m-$CH_3C_6H_4$	36	**2d**	63
5		**1e** p-ClC_6H_4	7	 **2e**	75
6		**1f** p-$CH_3C_6H_4$	10	**2f**	85
7		**1g** n-C_5H_{11}	4	**2g**	97
8		**1h** 2-thienyl	6	**2h**	95
9		**1i**	2	 **2i**	75
10		**1j**	20 min	 **2j**	85
11[c]		**1k**	12	 **2k**	44
12[d]		**1l**	3	 **2a**	90
13[e]			6	 **2l**	73

[a] Unless noted, all the reactions were carried out using **1** (0.3 mmol) with $[NaAuCl_4]\cdot 2H_2O$ (2 mol%) in benzene (2.0 mL) at 80°C. [b] Yield of the isolated product. [c] Reaction run with $AuCl_3$ (2 mol%). [d] Addition of H_2O (3 equiv). [e] Reaction was carried out in benzene/D_2O (10:1).

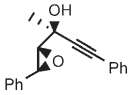
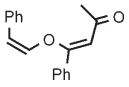
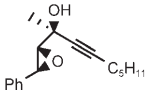
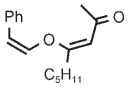
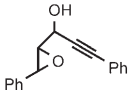
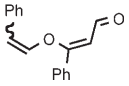
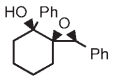
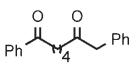
Interestingly, a type of novel C–C bond cleavage of epoxides was discovered when acyclic systems were introduced under standard conditions (Table 3).[14] Two *Z* alkenes and a carbonyl functional group were formed in one step with excellent stereoselectivity from this process. For example, compounds **3a** and **3b** underwent the domino process to give the corresponding products efficiently (Table 3, entries 1 and 2). And the *syn*/*anti* mixtures of **3c** led to the products **4c** in a 3:1 ratio (Table 3, entry 3). [15] Moreover, no desired product was observed when substrate **3d** was employed to study the semipinacol rearrangement[16] under the optimal conditions, whereas the same C–C bond cleavage was observed (Table 3, entry 4).[17]

On the basis of the above results, a plausible mechanism for this transformation is proposed in Scheme 3.[18] The coordination of the gold center to epoxy alkynes afforded complexes **A** and **D**. The subsequent nucleophilic attack of the epoxide on the alkynyl moiety leads to the formation of intermediates **B** and **E**. The oxonium ion[19] **B** might trigger the [1,2]-migration of an adjacent group, when assisted by the hydroxy group, to give **C** which underwent protonation to regenerate the gold catalyst and produce 4(2*H*)-pyranone **2**. However, with more difficult migration systems, such as acyclic compounds, the oxonium ion **E** induced the cleavage of the C^1–C^2 and C^3–O^1 bonds instead of the migration process, which leads to the formation of alkenyl ethers **4**.

Conclusion

We have developed an efficient approach to spiropyranones by utilizing a gold-catalyzed tandem cyclization/[1,2]-alkyl migration reaction of epoxy alkynes, which were readily prepared from the corresponding enones in two steps. In this reaction, the construction of adjacent multiple stereocenters with a new quaternary carbon atom was achieved. Furthermore, the gold-catalyzed domino process is stereospecific with respect to the migrating carbon atom. On the other hand, the stable, simplest, and least expensive gold catalyst $[NaAuCl_4]\cdot 2H_2O$ shows excellent catalytic activity in the reaction with low catalyst loading. When acyclic epoxide systems were introduced under the standard conditions, a type of unusual C–C bond cleavage of epoxy alkynes were also discovered. In this process, two *Z* alkenes and a carbonyl functional group were obtained in one step with excellent stereoselectivity. The same C–C bond cleavage was also observed when an α-hydroxy epoxide was used under the optimum conditions.

Table 3. Gold-catalyzed novel C–C bond cleavage of the epoxy alkynes.[a]

Entry	Substrate[b]		t [h]	Product		Yield[c] [%]
1		**3a**	3		**4a**	86
2		**3b**	3		**4b**	96
3		**3c**[d]	3		**4c**[e]	75
4		**3d**	8		**4d**	62

[a] All reactions were carried out using **3** (0.3 mmol) with $NaAuCl_4 \cdot 2H_2O$ (2 mol%) in benzene (2.0 mL) at 80°C. [b] Ref. [15]. [c] Yield of the isolated product. [d] *Syn*/*anti* mixtures (2:1) of the substrates were used and the ratio was determined by ^1H NMR spectroscopic analysis. [e] *Z*/*E* mixtures (3:1) of the products were obtained.

Experimental Section

General: Column chromatography was carried out on silica gel. Unless noted, the ^1H NMR spectra were recorded at 300 or 400 MHz in $CDCl_3$ and the ^{13}C NMR spectra were recorded at 75 or 100 MHz in $CDCl_3$ with trimethylsilane (TMS) as an internal standard. IR spectra were recorded on a FT-IR spectrometer, and only the major peaks are reported (in cm^{-1}). Melting points were determined on a microscopic apparatus and are uncorrected. All new compounds were further characterized by element analysis; copies of their ^1H and ^{13}C NMR spectra are provided. Detailed data of the ^1H NMR NOE interaction experiments of **2m** and X-ray crystallographic studies of **1m** are also provided. Commercially available reagents and solvents were used without further purification. THF was distilled immediately before use from Na/benzophenone.

Materials: The known *E* enones, as substrates **1a**–**1i**,[20] **1l**–**1p**,[20] **3d**,[20] **1j**,[21] and **1k**[22] were prepared according to previous methods. Epoxy alkynes **1a**–**1k**, **1m**, **1o**, and **3a**–**3c** and epoxide **3d** were prepared according to previous methods.[8d]

2-Phenyl-4-(2-phenylethynyl)-1-oxaspiro[2.5]oct-4-ol (1a): Solid; m.p. 90–92°C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.48$–7.46 (m, 2H), 7.37–7.25 (m, 8H), 4.59 (s, 1H), 2.57 (s, 1H), 2.25–2.21 (m, 1H), 1.91–1.69 (m, 4H), 1.57–1.46 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 135.2$, 131.8, 128.6, 128.3, 128.1, 127.5, 126.3, 122.4, 88.7, 86.3, 69.6, 68.1, 60.3, 39.9, 25.4, 23.1, 23.0 ppm; IR (KBr): $\tilde{\nu} = 3435$, 2948, 1666, 1621, 1449, 993, 756 cm^{-1}; elemental analysis (%) calcd for $C_{21}H_{20}O_2$: C 82.86, H 6.62; found: C 82.89, H 6.54.

2-(4-Chlorophenyl)-4-(2-phenylethynyl)-1-oxaspiro[2.5]oct-4-ol (1b): Solid; m.p. 122–124°C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.47$–7.45 (m, 2H), 7.33–7.31 (m, 5H), 7.26–7.24 (m, 2H), 4.56 (s, 1H), 2.64 (s, 1H), 2.22–2.19 (m, 1H), 1.90–1.67 (m, 4H), 1.55–1.43 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 133.8$, 133.3, 131.7, 128.6, 128.3, 127.7, 122.3, 88.5, 86.4, 69.6, 68.2, 59.7, 39.8, 25.3, 23.1, 22.9 ppm; IR (KBr): $\tilde{\nu} = 3453$, 2938, 2859, 1492, 1443, 1088, 757 cm^{-1}; elemental analysis (%) calcd for $C_{21}H_{19}ClO_2$: C 74.44, H 5.65; found: C 74.52, H 5.48.

2-(4-Methylphenyl)-4-(2-phenylethynyl)-1-oxaspiro[2.5]oct-4-ol (1c): Solid; m.p. 76–77°C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.48$–7.44 (m, 2H), 7.31–7.29 (m, 3H), 7.23–7.20 (d, $J = 7.5$ Hz, 2H), 7.16–7.13 (d, $J = 7.5$ Hz, 2H), 4.58 (s, 1H), 2.77 (s, 1H), 2.33 (s, 3H), 2.26–2.18 (m, 1H), 1.93–1.67 (m, 4H), 1.55–1.48 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 137.0$, 132.1, 131.7, 128.7, 128.4, 128.2, 126.2, 122.4, 88.8, 86.2, 69.6, 68.0, 60.2, 39.8, 25.3, 23.1, 22.9, 21.1 ppm; IR (KBr): $\tilde{\nu} = 3455$, 2938, 2860, 2247, 1828, 1443, 1086, 758 cm^{-1}; elemental analysis (%) calcd for $C_{22}H_{22}O_2$: C 82.99, H 6.96; found: C 82.86, H 6.92.

2-(3-Methylphenyl)-4-(2-phenylethynyl)-1-oxaspiro[2.5]oct-4-ol (1d): Oil; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.48$–7.46 (m, 2H), 7.31–7.29 (m, 3H), 7.25–7.21 (m, 1H), 7.13–7.08 (m, 3H), 4.57 (s, 1H), 2.71 (s, 1H), 2.35 (s, 3H), 2.25–2.18 (m, 1H), 1.91–1.70 (m, 4H), 1.57–1.49 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 137.7$, 135.1, 131.7, 128.5, 128.2, 127.9, 126.9, 123.3, 122.4, 109.7, 88.8, 86.2, 69.6, 68.0, 60.3, 39.8, 25.3, 23.1, 23.0, 21.4 ppm; IR (neat): $\tilde{\nu} = 3452$, 2937, 2860, 1606, 1489, 1443, 1085, 757 cm^{-1}; elemental analysis (%) calcd for $C_{22}H_{22}O_2$: C 82.99, H 6.96; found: C 83.09, H 6.87.

4-[2-(4-Chlorophenyl)ethynyl]-2-phenyl-1-oxaspiro[2.5]oct-4-ol (1e): Solid; m.p. 105–107°C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.40$–7.25 (m, 9H), 4.58 (s, 1H), 2.74 (s, 1H), 2.22–2.17 (m, 1H), 1.93–1.63 (m, 4H), 1.56–1.48 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 135.0$, 134.6, 133.0, 128.6, 128.1, 127.5, 126.2, 120.8, 89.7, 85.1, 69.6, 68.0, 60.3, 39.8, 25.3, 23.1, 22.9 ppm; IR (KBr): $\tilde{\nu} = 3448$, 2939, 1490, 1448, 1088, 829, 755 cm^{-1}; elemental analysis (%) calcd for $C_{21}H_{19}ClO_2$: C 74.44, H 5.65; found: C 74.52, H 5.69.

4-[2-(4-Methylphenyl)ethynyl]-2-phenyl-1-oxaspiro[2.5]oct-4-ol (1f): solid; m.p. 116–118°C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.37$–7.25 (m, 7H), 7.13–7.11 (m, 2H), 4.59 (s, 1H), 2.56 (s, 1H), 2.35 (s, 3H), 2.24–2.19 (m, 1H), 1.89–1.69 (m, 4H), 1.56–1.45 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.7$, 135.3, 131.7, 129.0, 128.0, 127.4, 126.3, 119.3, 87.9, 86.5, 69.6, 68.1, 60.3, 39.9, 25.4, 23.1, 23.0, 21.4 ppm; IR (KBr): $\tilde{\nu} = 3430$, 2948, 1505, 1447, 1387, 990, 816 cm^{-1}; elemental analysis (%) calcd for $C_{22}H_{22}O_2$: C 82.99, H 6.96; found: C 82.85, H 7.02.

4-(Hept-1-ynyl)-2-phenyl-1-oxaspiro[2.5]oct-4-ol (1g): Oil; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.37$–7.21 (m, 5H), 4.51 (s, 1H), 2.53 (s, 1H), 2.28–2.23 (m, 2H), 2.10–2.05 (m, 1H), 1.80–1.29 (m, 13H), 0.91–0.87 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 135.4$, 127.9, 127.3, 126.2, 87.0, 79.8, 69.0, 68.2, 60.1, 40.0, 30.9, 28.2, 25.3, 23.1, 23.0, 22.1, 18.6, 13.9 ppm; IR (neat): $\tilde{\nu} = 3463$, 2934, 2862, 1449, 1084, 701 cm^{-1}; elemental analysis (%) calcd for $C_{20}H_{26}O_2$: C 80.50, H 8.78; found: C 80.66, H 8.67.

2-Phenyl-4-[2-(thienyl)ethynyl]-1-oxaspiro[2.5]oct-4-ol (1h): Oil; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.40$–7.23 (m, 7H), 6.99–6.96 (m, 1H), 4.57 (s, 1H), 2.59 (s, 1H), 2.23–2.17 (m, 1H), 1.91–1.63 (m, 4H), 1.59–1.46 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 135.1$, 132.5, 128.1, 127.5, 127.4, 126.9, 126.3, 122.2, 92.5, 79.6, 69.8, 67.9, 60.3, 39.7, 25.3, 23.1, 22.9 ppm; IR (neat): $\tilde{\nu} = 3449$, 2938, 2860, 1773, 1447, 1193, 1084, 702 cm^{-1}; elemental analysis (%) calcd for $C_{19}H_{18}O_2S$: C 73.52, H 5.84; found: C 73.64, H 5.89.

2-Phenyl-4-(2-phenylethynyl)-1-oxaspiro[2.6]non-4-ol (1i): Solid; m.p. 41–43°C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.49$–7.44 (m, 2H), 7.39–7.24 (m, 8H), 4.49 (s, 1H), 3.33 (s, 1H), 2.34–2.26 (m, 1H), 2.18–2.10 (m, 1H), 1.78–1.58 (m, 6H), 1.52–1.42 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 135.2$, 131.7, 128.4, 128.2, 128.2, 127.6, 126.4, 122.5, 90.7, 84.4, 71.2, 69.9, 62.3, 42.2, 29.7, 24.4, 23.7, 22.2 ppm; IR (KBr): $\tilde{\nu} = 3456$, 2940, 2361, 1447, 1150, 754 cm^{-1}; elemental analysis (%) calcd for $C_{22}H_{22}O_2$: C 82.99, H 6.96; found: C 83.06, H 6.88.

2-Phenyl-4-(2-phenylethynyl)-1-oxaspiro[2.7]dec-4-ol (1j): Solid; m.p. 83–85°C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.46$–7.43 (m, 2H), 7.41–7.24 (m, 8H), 4.60 (s, 1H), 2.98 (s, 1H), 2.25–2.16 (m, 2H), 1.82–1.61 (m, 7H), 1.42–1.39 (m, 2H), 1.29–1.26 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 135.6$, 131.8, 128.4, 128.2, 128.2, 127.6, 126.3, 122.5, 90.3, 84.5, 71.7, 68.5, 63.9, 35.0, 25.6, 24.4, 24.0, 24.0, 22.1 ppm; IR (KBr): $\tilde{\nu} = 3474$, 2918, 2865, 1491, 1446, 1117, 764, 696 cm^{-1}; elemental analysis (%) calcd for $C_{23}H_{24}O_2$: C 83.10, H 7.28; found: C 83.24; 7.22.

2-Isopropyl-4-(2-phenylethynyl)-1-oxaspiro[2.4]hept-4-ol (1k): Solid; m.p. 71–73 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.39 (m, 2H), 7.31–7.26 (m, 3H), 3.03–2.99 (m, 1H), 2.81 (s, 1H), 2.26–1.95 (m, 4H), 1.86–1.78 (m, 2H), 1.50–1.42 (m, 1H,) 1.14–1.10 (m, 3H), 1.04–1.00 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.6, 128.3, 128.2, 122.6, 89.6, 85.0, 72.8, 67.5, 41.0, 29.1, 26.6, 20.2, 19.8, 18.3 ppm; IR (KBr): $\tilde{\nu}$ = 3490, 2963, 1485, 1061, 760 cm^{-1}; elemental analysis (%) calcd for $C_{17}H_{20}O_2$: C 79.65, H 7.86; found: C 79.73, H 7.72.

2-Phenyl-4-(2-phenylethynyl)-4-trimethylsiloxy-1-oxaspiro[2.5]octane (1l): Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.45 (m, 2H), 7.36–7.26 (m, 8H), 4.49 (s, 1H), 2.12–2.08 (m, 1H), 2.04–1.96 (m, 1H), 1.78–1.65 (m, 3H), 1.61–1.48 (m, 2H), 1.36–1.31 (m, 1H), 0.32–0.30 ppm (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.0, 131.5, 128.5, 128.4, 127.9, 127.2, 126.3, 122.6, 90.1, 87.0, 72.1, 68.0, 60.3, 40.8, 25.0, 23.5, 21.8, 1.88 ppm; IR (neat): $\tilde{\nu}$ = 2944, 2860, 1447, 1252, 1110, 1033, 910, 843, 755, 696 cm^{-1}; elemental analysis (%) calcd for $C_{24}H_{28}O_2Si$: C 76.55, H 7.49; found: C 76.62, H 7.53.

5-Methyl-2-phenyl-4-(2-phenylethynyl)-1-oxaspiro[2.5]oct-4-ol (1m): Solid; m.p. 90–92 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.44 (m, 2H), 7.38–7.23 (m, 8H), 4.59 (s, 1H), 2.39 (s, 1H), 1.91–1.80 (m, 2H), 1.75–1.72 (m, 1H), 1.65–1.47 (m, 3H), 1.36–1.21 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.4, 131.8, 128.5, 128.2, 128.0, 127.4, 126.2, 122.5, 87.4, 86.6, 73.0, 68.4, 59.5, 42.8, 31.8, 25.8, 22.5, 16.1 ppm; IR (KBr): $\tilde{\nu}$ = 3428, 2931, 2863, 1450, 1078, 750 cm^{-1}; elemental analysis (%) calcd for $C_{22}H_{22}O_2$: C 82.99, H 6.96; found: C 82.86, H 6.88.

2-Phenyl-4-(2-phenylethynyl)-5-methyl-4-trimethylsiloxy-1-oxaspiro-[2.5]octane (1n): Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.44 (m, 2H), 7.40–7.26 (m, 8H), 4.45 (s, 1H), 2.15–2.09 (m, 1H), 1.81–1.70 (m, 2H), 1.61–1.54 (m, 3H), 1.49–1.39 (m, 1H), 1.19–1.17 (d, J = 6.6 Hz, 3H), 0.34 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.2, 131.4, 128.6, 128.4, 128.0, 127.3, 126.2, 122.5, 89.2, 88.5, 75.5, 68.1, 60.0, 42.2, 30.6, 25.6, 21.8, 16.4, 2.19 ppm; IR (neat): $\tilde{\nu}$ = 3405, 2936, 1449, 1252, 1108, 843, 753 cm^{-1}; elemental analysis (%) calcd for $C_{25}H_{30}O_2Si$: C 76.88, H 7.74; found: C 76.95, H 7.79.

2-Isopropyl-5-methyl-4-(2-phenylethynyl)-1-oxaspiro[2.5]oct-4-ol (1o): Solid; m.p. 93–95 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.42 (m, 2H), 7.32–7.26 (m, 3H), 3.14–3.11 (d, J = 9.3 Hz, 1H), 2.22–2.16 (m, 2H), 1.73–1.46 (m, 7H), 1.20–1.18 (d, J = 6.6 Hz, 3H), 1.13–1.10 (d, J = 6.3 Hz, 3H), 1.00–0.97 ppm (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.8, 128.4, 128.2, 122.6, 87.1, 86.9, 72.6, 66.4, 65.0, 42.4, 31.7, 27.0, 26.3, 22.5, 20.2, 18.5, 16.2 ppm; IR (KBr): $\tilde{\nu}$ = 3447, 2962, 2928, 2865, 1455, 1074, 755 cm^{-1}; elemental analysis (%) calcd for $C_{19}H_{24}O_2$: C 80.24, H 8.51; found: C 80.32, H 8.45.

2-Isopropyl-4-(2-phenylethynyl)-5-methyl-4-trimethylsiloxy-1-oxaspiro-[2.5]octane (1p): Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.42 (m, 2H), 7.35–7.33 (m, 3H), 3.00–2.97 (m, 1H), 2.18–2.12 (m, 1H), 2.00–1.94 (m, 1H), 1.76–1.50 (m, 6H), 1.13–1.07 (m, 6H), 1.00–0.98 (m, 3H), 0.29–0.22 ppm (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.4, 128.5, 128.4, 122.6, 89.2, 88.8, 75.2, 66.5, 65.5, 41.5, 31.2, 27.1, 26.7, 22.3, 20.3, 18.8, 16.6, 2.23 ppm; IR (neat): $\tilde{\nu}$ = 3399, 2961, 1453, 1251, 1116, 842, 756 cm^{-1}; elemental analysis (%) calcd for $C_{22}H_{32}O_2Si$: C 74.10, H 9.05; found: C 74.23, H 9.11.

(*S*)-4-Phenyl-2-[(2*R*,3*S*)-3-phenyloxiran-2-yl]but-3-yn-2-ol (3a): Solid; m.p. 74–76 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.42 (m, 2H), 7.35–7.24 (m, 8H), 4.17 (m, 1H), 3.30–3.29 (m, 1H), 2.68 (s, 1H), 1.72 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.3, 131.8, 128.6, 128.5, 128.4, 128.2, 125.9, 122.0, 88.3, 85.2, 67.1, 67.1, 56.7, 27.4 ppm; IR (KBr): $\tilde{\nu}$ = 3425, 2986, 1600, 1492, 1365, 1132, 1068, 899, 755, 695 cm^{-1}; elemental analysis (%) calcd for $C_{18}H_{16}O_2$: C 81.79, H 6.10; found: C 81.72, H 6.19.

(*S*)-2-[(2*R*,3*S*)-3-Phenyloxiran-2-yl]non-3-yn-2-ol (3b): Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.28 (m, 5H), 4.08–4.07 (d, J = 1.8 Hz, 1H), 3.18–3.17 (d, J = 2.4 Hz, 1H), 2.44 (s, 1H), 2.22–1.18 (m, 2H), 1.59 (s, 3H), 1.53–1.46 (m, 2H), 1.37–1.26 (m, 4H), 0.90–0.85 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.5, 128.5, 128.3, 125.8, 86.2, 79.5, 67.3, 66.6, 56.6, 31.0, 28.1, 27.6, 22.1, 18.6, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 3444, 2929, 2862, 1719, 1459, 1369, 898, 699 cm^{-1}; elemental analysis (%) calcd for $C_{17}H_{22}O_2$: C 79.03, H 8.58; found: C 79.15, H 8.51.

3-Phenyl-1-(3-phenyloxiran-2-yl)prop-2-yn-1-ol (3c) (2:1 mixture of *syn*/*anti* diastereoisomers): Oil; ^{1}H NMR (300 MHz, $CDCl_3$, 2:1 mixture of diastereoisomers): δ = 7.46–7.43 (m, 2H), 7.37–7.23 (m, 8H), [4.96–4.94 (m), 4.77–4.73 (m), 1 H], [4.14–4.13 (d, J = 2.4 Hz), 4.04–4.03 (d, J = 2.4 Hz), 1 H], 3.43–3.40 (m, 1H), 2.88–2.86 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 2:1 mixture of diastereoisomers) δ = 136.1, 135.9, 131.8, 128.7, 128.5, 128.4, 128.2, 125.9, 121.9, 86.7, 85.9, 85.1, 64.0, 63.3, 62.1, 61.5, 56.2, 55.9 ppm; IR (neat): $\tilde{\nu}$ = 3430, 3060, 2923, 2230, 1638, 1491, 1265, 1032 cm^{-1}; elemental analysis (%) calcd for $C_{17}H_{14}O_2$: C 81.58, H 5.64; found: C 81.43, H 5.77.

2,4-Diphenyl-1-oxaspiro[2.5]oct-4-ol (3d): Solid; m.p. 119–120 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.58 (m, 2H), 7.44–7.29 (m, 8H), 4.56 (s, 1H), 2.68–2.61 (m, 1H), 2.50 (s, 1H), 1.93–1.84 (m, 1H), 1.80–1.74 (m, 1H), 1.65–1.32 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.7, 135.4, 128.6, 128.2, 128.0, 127.6, 127.3, 126.3, 74.1, 68.5, 61.0, 38.4, 25.7, 23.6, 23.1 ppm; IR (KBr): $\tilde{\nu}$ = 3467, 2938, 2862, 1495, 1449, 1077, 755, 699 cm^{-1}; elemental analysis (%) calcd for $C_{19}H_{20}O_2$: C 81.40, H 7.19; found: C 81.27, H 7.36.

General procedure for the preparation of spiropyranones 2a–2n, ethers 4a–4c, and ketone 4d: $[NaAuCl_4]\cdot 2H_2O$ (2.37 mg, 2 mol%) was added to a stirred solution of epoxide (0.30 mmol) in benzene (2.0 mL) under air at 80 °C. When the reaction was considered to be complete, as determined by TLC analysis, the reaction mixture was diluted with ethyl acetate (10 mL) and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford the corresponding products.

6,8-Diphenyl-7-oxaspiro[4.5]dec-8-en-10-one (2a): Prepared by using the above method in 92% yield as a solid. M.p. 122–124 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76–7.73 (m, 2H), 7.50–7.25 (m, 8H), 6.06 (s, 1H), 5.42 (s, 1H), 2.30–2.19 (m, 1H), 1.98–1.88 (m, 1H), 1.81–1.48 (m, 4H), 1.32–1.22 (m, 1H), 1.17–1.06 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.7, 168.3, 136.0, 132.6, 131.4, 128.5, 128.5, 128.3, 128.1, 126.4, 100.4, 87.0, 54.9, 31.4, 30.1, 26.0, 25.9 ppm; IR (KBr): $\tilde{\nu}$ = 3434, 2943, 2862, 1660, 1607, 1362, 1040, 696 cm^{-1}; elemental analysis (%) calcd for $C_{21}H_{20}O_2$: C 82.86, H 6.62; found: C 82.98, H 6.54.

6-(4-Chlorophenyl)-8-phenyl-7-oxaspiro[4.5]dec-8-en-10-one (2b): Prepared by using the above method in 84% yield as a solid. M.p. 122–124 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.70 (m, 2H), 7.47–7.37 (m, 7H), 6.05–6.03 (m, 1H), 5.40–5.38 (m, 1H), 2.26–2.20 (m, 1H), 1.85–1.55 (m, 5H), 1.33–1.14 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.3, 168.1, 134.6, 134.5, 132.5, 131.5, 129.7, 128.6, 128.4, 126.4, 100.5, 86.4, 54.9, 31.6, 30.2, 26.0 ppm; IR (KBr): $\tilde{\nu}$ = 2950, 2864, 1657, 1603, 1360, 828, 689 cm^{-1}; elemental analysis (%) calcd for $C_{21}H_{19}ClO_2$: C 74.44, H 5.65; found: C 74.62, H 5.69.

6-(4-Methylphenyl)-8-phenyl-7-oxaspiro[4.5]dec-8-en-10-one (2c): Prepared by using the above method in 75% yield as a solid. M.p. 113–114 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75–7.72 (m, 2H), 7.47–7.35 (m, 5H), 7.20–7.18 (m, 2H), 6.04 (s, 1H), 5.39 (s, 1H), 2.37 (s, 3H), 2.24–2.19 (m, 1H), 1.92–1.51 (m, 5H), 1.35–1.29 (m, 1H), 1.22–1.11 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.8, 168.3, 138.3, 133.1, 132.8, 131.3, 128.8, 128.5, 128.3, 126.4, 100.4, 87.1, 55.0, 31.8, 30.2, 26.0, 21.1 ppm; IR (KBr): $\tilde{\nu}$ = 3406, 2949, 2863, 1658, 1607, 1367, 1043, 692 cm^{-1}; elemental analysis (%) calcd for $C_{22}H_{22}O_2$: C 82.99, H 6.96; found: C 82.87, H 7.02.

6-(3-Methylphenyl)-8-phenyl-7-oxaspiro[4.5]dec-8-en-10-one (2d): Prepared by using the above method in 63% yield as a solid. M.p. 71–72 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75–7.73 (d, J = 6.9 Hz, 2H), 7.47–7.36 (m, 3H), 7.28–7.27 (m, 3H), 7.19–7.18 (m, 1H), 6.04 (s, 1H), 5.38 (s, 1H), 2.38–2.36 (m, 3H), 2.24–2.20 (m, 1H), 1.95–1.88 (m, 1H), 1.81–1.51 (m, 4H), 1.34–1.28 (m, 1H), 1.18–1.12 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.7, 168.3, 137.7, 136.0, 132.7, 131.3, 129.2, 129.1, 128.5, 128.0, 126.4, 125.5, 100.4, 87.2, 55.0, 31.5, 30.2, 25.9, 25.9, 21.5 ppm; IR (KBr): $\tilde{\nu}$ = 3432, 2952, 2868, 1659, 1606, 1373, 1050, 693 cm^{-1}; elemental analysis (%) calcd for $C_{22}H_{22}O_2$: C 82.99, H 6.96; found: C 83.13, H 6.82.

8-(4-Chlorophenyl)-6-phenyl-7-oxaspiro[4.5]dec-8-en-10-one (2e): Prepared by using the above method in 75% yield as a solid. M.p. 168–169 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69–7.65 (m, 2H), 7.48–7.35 (m, 7H), 6.01 (s, 1H), 5.41 (s, 1H), 2.25–2.21 (m, 1H), 1.94–1.51 (m, 5H), 1.33–1.29 (m, 1H), 1.15–1.10 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$):

δ = 198.5, 167.1, 137.5, 135.9, 131.1, 128.8, 128.6, 128.4, 128.2, 127.7, 100.6, 87.2, 55.0, 31.5, 30.2, 26.0 ppm; IR (KBr): $\tilde{\nu}$ = 3405, 2929, 2860, 1656, 1605, 1088, 825 cm^{-1}; elemental analysis (%) calcd for $C_{21}H_{19}ClO_2$: C 74.44, H 5.65; found: C 74.61, H 5.52.

8-(4-Methylphenyl)-6-phenyl-7-oxaspiro[4.5]dec-8-en-10-one (2f): Prepared by using the above method in 85% yield as a solid. M.p. 141–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65–7.62 (m, 2H), 7.48–7.46 (m, 2H), 7.41–7.36 (m, 3H), 7.21–7.18 (m, 2H), 6.02–6.01 (m, 1H), 5.40–5.39 (m, 1H), 2.37–2.36 (m, 3H), 2.26–2.21 (m, 1H), 1.94–1.50 (m, 5H), 1.26 (m, 1H), 1.12–1.08 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.7, 168.5, 142.0, 136.2, 129.8, 129.3, 128.5, 128.4, 128.1, 126.4, 99.8, 87.0, 55.0, 31.5, 30.2, 26.0, 21.4 ppm; IR (KBr): $\tilde{\nu}$ = 2953, 2861, 1656, 1606, 1360, 1046, 821, 706 cm^{-1}; elemental analysis (%) calcd for $C_{22}H_{22}O_2$: C 82.99, H 6.96; found: C 83.06, H 6.88.

8-Pentyl-6-phenyl-7-oxaspiro[4.5]dec-8-en-10-one (2g): Prepared by using the above method in 97% yield as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.33 (m, 5H), 5.35 (s, 1H), 5.20 (s, 1H), 2.26–2.12 (m, 3H), 1.87–1.45 (m, 8H), 1.20–1.08 (m, 2H), 0.94–0.83 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.2, 175.5, 136.2, 128.4, 128.4, 128.0, 102.6, 86.9, 54.4, 34.4, 31.9, 31.0, 30.2, 26.0, 25.9, 22.2, 13.8 ppm; IR (neat): $\tilde{\nu}$ = 3400, 2927, 2860, 1667, 1616, 1457, 1388, 1005, 704 cm^{-1}; elemental analysis (%) calcd for $C_{20}H_{26}O_2$: C 80.50, H 8.78; found: C 80.57, H 8.73.

6-Phenyl-8-(2-thienyl)-7-oxaspiro[4.5]dec-8-en-10-one (2h): Prepared by using the above method in 95% yield as a solid. M.p. 129–130 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.36 (m, 7H), 7.08–7.05 (m, 1H), 5.93 (s, 1H), 5.41 (s, 1H), 2.24–2.16 (m, 1H), 1.91–1.51 (m, 5H), 1.31–1.26 (m, 1H), 1.17–1.11 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.1, 163.4, 136.6, 135.9, 130.0, 128.6, 128.4, 128.2, 128.1, 99.4, 87.3, 55.2, 31.9, 30.3, 26.0 ppm; IR (KBr): $\tilde{\nu}$ = 3399, 2948, 2864, 1655, 1594, 1384, 1317, 707 cm^{-1}; elemental analysis (%) calcd for $C_{19}H_{18}O_2S$: C 73.52, H 5.84; found: C 73.63, H 5.79.

1,3-Diphenyl-2-oxaspiro[5.5]undec-3-en-5-one (2i): Prepared by using the above method in 75% yield as a solid. M.p. 150–151 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.71 (m, 2H), 7.48–7.33 (m, 8H), 5.97 (s, 1H), 5.39 (s, 1H), 2.08–2.01 (m, 1H), 1.95–1.91 (m, 1H), 1.82–1.78 (m, 1H), 1.57–1.51 (m, 2H), 1.43–1.22 (m, 4H), 1.07 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.0, 167.3, 135.6, 132.5, 131.3, 128.7, 128.6, 128.5, 128.1, 126.4, 100.6, 88.5, 46.2, 30.6, 26.7, 25.6, 22.3, 21.3 ppm; IR (KBr): $\tilde{\nu}$ = 2924, 2852, 2349, 1661, 1611, 1366, 776, 705 cm^{-1}; elemental analysis (%) calcd for $C_{22}H_{22}O_2$: C 82.99, H 6.96; found: C 82.87, H 7.06.

1,3-Diphenyl-2-oxaspiro[5.6]dodec-3-en-5-one (2j): Prepared by using the above method in 85% yield as a solid. M.p. 147–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.74 (m, 2H), 7.53–7.26 (m, 8H), 6.03 (m, 1H), 5.27 (s, 1H), 2.37–2.31 (m, 1H), 1.96–1.91 (m, 1H), 1.72–1.60 (m, 4H), 1.49–1.28 (m, 4H), 1.02–0.96 (m, 1H), 0.49–0.44 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.3, 168.2, 135.9, 132.5, 131.4, 128.6, 128.4, 128.1, 126.4, 100.2, 89.3, 50.6, 31.3, 31.0, 30.5, 28.5, 23.5, 22.4 ppm; IR (KBr): $\tilde{\nu}$ = 2924, 2856, 1661, 1609, 1350, 776, 705 cm^{-1}; elemental analysis (%) calcd for $C_{23}H_{24}O_2$: C 83.10, H 7.28; found: C 83.19, H 7.26.

5-Isopropyl-7-phenyl-6-oxaspiro[3.5]non-7-en-9-one (2k): Prepared by using the above method, but with $AuCl_3$ as the catalyst, in 44% yield as an oil. ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 7.61–7.57 (m, 2H), 7.39–7.31 (m, 3H), 5.49 (s, 1H), 4.13–4.09 (d, J = 9.6 Hz, 1H), 2.45–2.30 (m, 3H), 2.15–1.98 (m, 4H), 1.12–1.09 (m, 3H), 0.88–0.83 ppm (m, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3): δ = 217.3, 157.0, 131.4, 129.2, 128.9, 125.7, 101.4, 94.6, 62.6, 39.0, 38.8, 20.2, 20.1, 19.4 ppm; IR (neat): $\tilde{\nu}$ = 3452, 2962, 2871, 1735, 1641, 1450, 1045, 733 cm^{-1}; elemental analysis (%) calcd for $C_{17}H_{20}O_2$: C 79.65, H 7.86; found: C 79.59, H 7.88.

[9D]6,8-Diphenyl-7-oxaspiro[4.5]dec-8-en-10-one (2l): Prepared by using the above method, but using benzene/H_2O (10:1 v/v) as the solvent, in 73% yield as a solid. M.p. 122–124 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76–7.73 (m, 2H), 7.50–7.25 (m, 8H), 6.06 (s, 0.01H), 5.43 (s, 1H), 2.29–2.22 (m, 1H), 2.19–1.89 (m, 1H), 1.82–1.50 (m, 4H), 1.32–1.26 (m, 1H), 1.17–1.06 ppm (m, 1H); IR (KBr): $\tilde{\nu}$ = 2948, 2866, 1657, 1598, 1566, 1353, 1292, 697 cm^{-1}.

1-Methyl-6,8-diphenyl-7-oxaspiro[4.5]dec-8-en-10-one (2m): Prepared by using the above method in 67% yield from **1m**. When substrate **1n** was used, H_2O (3 equiv) was added to afford **2m** in 76% yield as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67–7.64 (m, 2H), 7.42–7.25 (m, 8H), 6.05 (s, 1H), 5.60 (s, 1H), 2.40–2.34 (m, 1H), 2.22–2.13 (m, 1H), 1.90–1.72 (m, 2H), 1.67–1.60 (m, 1H), 1.47–1.24 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.0, 167.0, 137.4, 133.1, 131.3, 128.9, 128.7, 128.5, 128.4, 126.5, 101.2, 84.7, 56.7, 43.7, 33.1, 30.4, 23.2, 16.1 ppm; IR (neat): $\tilde{\nu}$ = 2955, 2874, 1656, 1606, 1377, 1031, 695 cm^{-1}; elemental analysis (%) calcd for $C_{22}H_{22}O_2$: C 82.99, H 6.96; found: C 82.83, H 7.08.

6-Isopropyl-1-methyl-8-phenyl-7-oxaspiro[4.5]dec-8-en-10-one (2n): Prepared by using the above method in 43% yield from **1o**. When substrate **1p** was used, H_2O (3 equiv) was added to afford **2n** in 52% yield as a solid. M.p. 68–70 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78–7.75 (m, 2H), 7.48–7.27 (m, 3H), 5.89 (s, 1H), 4.51–4.49 (d, J = 4.2 Hz, 1H), 2.27–2.10 (m, 3H), 1.89–1.68 (m, 3H), 1.57–1.48 (m, 1H), 1.35–1.30 (m, 1H), 1.17–1.15 (d, J = 6.9 Hz, 3H), 1.10–1.08 (d, J = 7.5 Hz, 3H), 0.95–0.93 ppm (d, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.4, 167.8, 133.1, 131.2, 128.6, 126.3, 100.2, 86.8, 57.1, 43.7, 32.4, 30.9, 28.2, 23.0, 21.6, 18.5, 16.5 ppm; IR (KBr): $\tilde{\nu}$ = 3301, 2961, 2875, 1658, 1608, 1456, 1385, 1341, 1043, 692 cm^{-1}; elemental analysis (%) calcd for $C_{19}H_{24}O_2$: C 80.24, H 8.51; found: C 80.31, H 8.44.

(3*Z*)-4-Phenyl-4-(styryloxy)but-3-en-2-one (4a): Prepared by using the above method in 86% yield as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91–7.88 (m, 2H), 7.59–7.25 (m, 8H), 6.56–6.54 (d, J = 6.3 Hz, 1H), 6.48 (s, 1H), 5.83–5.81 (d, J = 6.9 Hz, 1H), 2.57 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.2, 170.8, 139.7, 137.9, 133.7, 132.2, 129.0, 128.5, 127.8, 127.5, 114.4, 101.2, 19.2 ppm; IR (neat): $\tilde{\nu}$ = 3399, 3059, 1658, 1594, 1392, 1175, 1062, 697 cm^{-1}; elemental analysis (%) calcd for $C_{18}H_{16}O_2$: C 81.79, H 6.10; found: C 81.91, H 6.02.

(3*Z*)-4-(Styryloxy)non-3-en-2-one (4b): Prepared by using the above method in 96% yield as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.24 (m, 5H), 6.95–6.92 (d, J = 9.0 Hz, 1H), 6.39–6.36 (d, J = 9.3 Hz, 1H), 5.62 (s, 1H), 2.81–2.77 (m, 2H), 2.16 (s, 3H), 1.64–1.56 (m, 2H), 1.38–1.34 (m, 4H), 0.94–0.84 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.4, 173.6, 139.8, 134.0, 128.7, 127.5, 126.1, 117.4, 103.4, 32.0, 31.5, 31.4, 26.8, 22.4, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 3454, 3058, 2930, 2862, 1684, 1588, 1380, 1152, 947 cm^{-1}; elemental analysis (%) calcd for $C_{17}H_{22}O_2$: C 79.03, H 8.58; found: C 78.92, H 8.66.

(2*Z*)-3-Phenyl-3-(styryloxy)acrylaldehyde (4c): Compound **4c** (3:1 of *Z*/*E* mixtures) was prepared by using the above method in 75% yield as an oil, but *syn*/*anti* mixtures (2:1) of the substrates were used: ^{1}H NMR (3:1 of *Z*/*E* mixtures, 300 MHz, $CDCl_3$): δ = [10.20–10.17 (m), 9.55–9.52 (m), 1 H], 7.62–7.37 (m, 5H), 7.35–7.17 (m, 5H), [7.15–7.11 (m), 7.07–7.02 (d, J = 13.5 Hz), 1 H], [6.53–6.49 (d, J = 12.3 Hz), 6.33–6.29 (d, J = 12.3 Hz), 1 H], [6.02–5.99 (m), 5.88–5.85 (m), 1 H] ppm; ^{13}C NMR (3:1 of *Z*/*E* mixtures, 75 MHz, $CDCl_3$): δ = 191.8, 189.9, 174.2, 168.2, 144.6, 139.9, 133.9, 133.3, 132.5, 131.8, 131.6, 131.4, 129.9, 128.9, 128.7, 128.6, 128.4, 127.7, 127.5, 127.0, 126.1, 125.6, 118.4, 113.9, 113.2, 109.1 ppm; IR (neat): $\tilde{\nu}$ = 3452, 3059, 2848, 1960, 1658, 1607, 1347, 1212, 1127, 752 cm^{-1}; elemental analysis (%) calcd for $C_{17}H_{14}O_2$: C 81.58, H 5.64; found: C 81.71, H 5.57.

1,7-Diphenylheptane-1,6-dione (4d): Prepared by using the above method in 62% yield as a solid. M.p. 56–57 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93–7.91 (m, 2H), 7.55–7.52 (m, 1H), 7.47–7.42 (m, 2H), 7.35–7.19 (m, 5H), 3.69 (s, 2H), 2.95–2.91 (t, J = 7.2 Hz, 2H), 2.53–2.49 (t, J = 6.9 Hz, 2H), 1.69–1.62 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.1, 199.9, 136.8, 134.2, 132.9, 129.3, 128.7, 128.5, 127.9, 127.0, 50.1, 41.7, 38.2, 23.5, 23.2 ppm; IR (KBr): $\tilde{\nu}$ = 3397, 2940, 1704, 1675, 1450, 1402, 1256, 696 cm^{-1}; elemental analysis (%) calcd for $C_{19}H_{20}O_2$: C 81.40, H 7.19; found: C 81.49, H 7.13.

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[10] See the Supporting Information for details.

[11] The result was improved efficiently by switching the solvent to benzene; however, the toxicity of the benzene should be noted.

[12] The molecular structure of the corresponding product **1m** was determined by means of X-ray crystallographic studies; for details, see the Supporting Information; CCDC 668682 (**1m**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] The structure of **2m** was determined by means of an NOE interaction study; see the Supporting Information for detailed data of the ^{1}H NMR NOE interaction studies.

[14] Marson and co-workers reported that acyclic epoxy alkynes could undergo a 1,2-hydride shift to afford 2,3-dihydro-4*H*-pyran-4-ones in the presence of Hg^{II}; see: ref. [9b].

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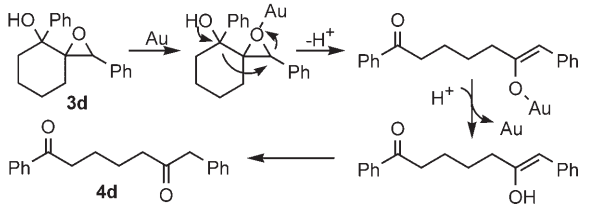
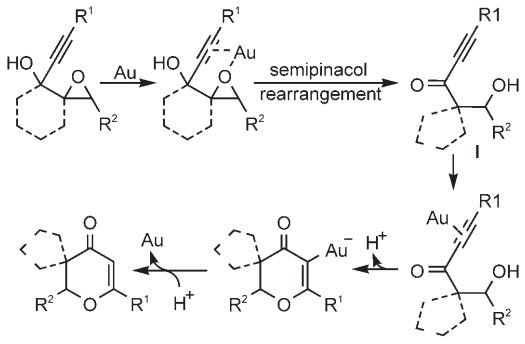


[18] Although we could not exclude the semipinacol rearrangement from the mechanism, we still insist that the oxonium ion is an the intermediate in the process. The results of acyclic systems are most consistent with our hypothesis (Table 3, entries 1–3), and the high stereoselectivity of the transformation is also consistent with this hypothesis; furthermore, we studied the semipinacol rearrangement of **3d** and no semipinacol rearrangement product was detected (Table 3, entry 4). We also did not observe any semipinacol rearrangement product **I**, which might have been detected in the reaction. For an alternate mechanism by semipinacol rearrangement, see:



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