JOC The Journal of Organic Chemistry

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Gold(I)-Catalyzed Ring-Expanding Spiroannulation of Cyclopropenones with Enynes

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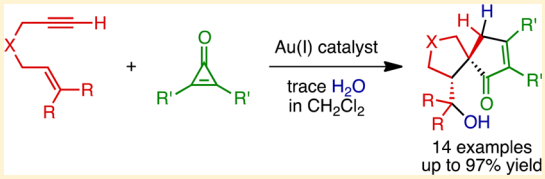
Supporting Information

ABSTRACT: The gold(I)-catalyzed ring-expanding spiroannulation of cyclopropenones with enynes is reported here. A molecule of water is incorporated into the products during the spiroannulation to afford spirocyclic cyclopentenones containing an alcohol functionality.



The transition-metal-catalyzed cyclization of enynes represents fertile ground for the discovery of new reactions and the preparation of diverse cyclic molecules.[1] In particular, the gold- and platinum-catalyzed cyclizations of enynes have been extensively studied in the past decade to expand the synthetic repertoire.

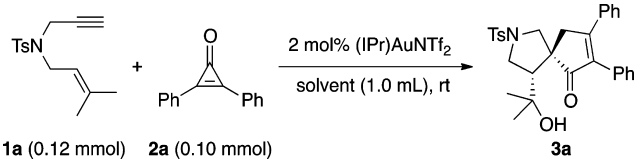
The transition-metal-catalyzed reactions of small-ring compounds involving the cleavage of a strained C−C bond have also been an active research area,[2] and diverse ring-opening/expanding reactions have been developed. However, the transition-metal-catalyzed reactions of cyclopropenones remain relatively unexplored.[3] Recently, we reported the palladium-catalyzed ring-opening alkynylation of cyclopropenones with terminal alkynes and the application of this reaction to the [3 + 2] annulation giving cyclopentenones.[4] Herein, we report the successful utilization of cyclopropenones in the gold(I)-catalyzed ring expansion, which is accompanied by the spiroannulation with enynes affording spiro[4.4]octane skeletons.

N-Prenyl-*N*-propargyltosylamide (**1a**) and diphenylcyclopropenone (**2a**) were selected as the substrates for our studies. The reaction of **1a** with **2a** (**1a**:**2a** = 1:1) in DCE (1,2-dichloroethane) in the presence of 2 mol % (SPhos)$AuNTf_2$[5] at room temperature for 12 h afforded **3a** (Scheme 1). However, the structure of **3a** could not be determined from its NMR spectrum. The crystals suitable for the X-ray diffraction analysis were obtained by the crystallization of mesylamide counterpart **3b** (*vide infra*). The product was identified as a spirocyclic ketone containing an alcohol functionality; the yield of **3a** was 53%. The three-membered ring of **2a** expanded to form the cyclopentenone ring of the spirocyclic skeleton. A hydroxy group was introduced to **3a** by the incorporation of a water molecule to the product. The traces of water present in the solvent used were probably responsible for this incorporation of water. ^{1}H NMR spectral analysis showed the formation of only one diastereomer of the product in this reaction.

Scheme 1. Gold(I)-Catalyzed Reaction of 1,6-Enyne 1a and Cyclopropenone 2a

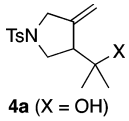
Next, the reaction conditions were optimized for the gold(I)-catalyzed ring-expanding spiroannulation using **1a** and **2a** (Table 1). The use of (IPr)$AuNTf_2$[5] as the catalyst significantly

Table 1. Optimization of Reaction Conditions for Gold(I)-Catalyzed Ring-Expanding Spiroannulation



entry	1a:2a	solvent	time	yield of 3a[a]
1	1:1	DCE	12	77%
2	1:1	DCM	12	85%
3	1:1	toluene	24	64%[b]
4	1:1	$MeNO_2$	24	40%[c]
5	1.2:1	DCM	12	92%
6	1.2:1	MeOH	12	–[d]
7[e]	1.2:1	DCM	12	48%[f]
8[g]	1.2:1	DCM	12	–[h]

[a]Isolated yield. [b]**3a**:**4a** = 69:31. [c]**3a**:**4a** = 48:52. [d]**4b** was isolated in 65% yield. [e]The reaction was performed in the presence of 5 equiv of H_2O. [f]**3a**:**4a** = 56:44. [g]The reaction was performed in the presence of 5 equiv of MeOH. [h]**4b** was isolated in 64% yield.



4a (X = OH)
4b (X = OMe)

Received: January 9, 2014
Published: February 26, 2014

dx.doi.org/10.1021/jo500045n | J. Org. Chem. 2014, 79, 2739−2745

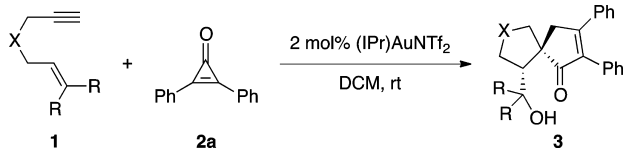
improved the yield of **3a** to 77% yield (entry 1).[6] When the solvent was replaced with DCM (dichloromethane), the yield of **3a** further increased to 85% (entry 2).[7] The reactions performed in other solvents such as toluene and nitromethane formed byproduct **4a**, resulting from the hydroxycyclization of enyne **1a** in the presence of the gold(I) catalyst (entries 3 and 4).[8] Finally, a slight excess (1.2 equiv) of **1a** was found to be the optimal quantity, resulting in a 92% yield of **3a** (entry 5). When the reaction was examined in MeOH as the solvent, in an attempt to incorporate MeOH instead of water to the product, enyne **1a** afforded alkoxycyclization product **4b** (65% yield) without any detectable amount of the expected corresponding spiro compound (entry 6). The reaction of **1a** with **2a** was also conducted in the presence of added water or MeOH. The addition of 5 equiv of water reduced the yield of spiro product **3a** (48%) due to the competing hydroxycyclization of **1a** affording **4a** (37%) (entry 7). On the other hand, exclusive alkoxycyclization occurred when 5 equiv of MeOH were added to the reaction mixture (entry 8).

The optimized reaction conditions were used to investigate the substrate scope of the gold(I)-catalyzed spiroannulation of diverse enynes **1** with **2a**. The reaction of enyne **1a**-*d* with a deuterium atom at the alkyne terminus provided single diastereomer **3a**-*d* in 87% yield (Table 2, entry 1).[9] Similar to *N*-tosyl enyne **1a**, nitrogen-tethered 1,6-enynes **1b–d** with different *N*-sulfonyl protecting groups smoothly afforded the corresponding spiro products **3b–d** in excellent yields (entries 2–4), whereas the reaction of *N*-phenyl derivative **1e** resulted in a low yield (entry 5). Oxygen- and carbon-tethered enynes **1f** and **1g** also reacted with **2a** to give **3f** and **3g** in 68% and 41% yields, respectively (entries 6 and 7). The reaction of enyne **1h** bearing a cyclohexylidene moiety with **2a** gave **3h** in 77% yield (entry 8), and 3,3-diphenylallyl derivative **1i** also participated in the reaction (entry 9). The reaction was only found to be applicable to the enynes bearing a prenyl-type group; the attempted reactions of the *N*-allyl, *N*-cyclohex-2-en-1-yl, *N*-cinnamyl, and *N*-methallyl derivatives with **2a** failed under the reaction conditions.[10] In addition, no reaction was observed for the enynes with an internal alkyne moiety.

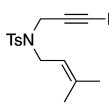
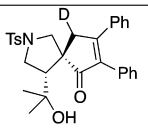
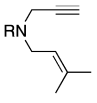
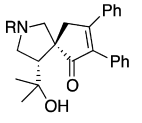
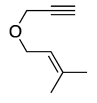
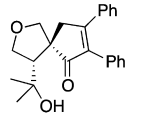
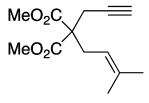
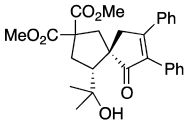
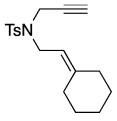
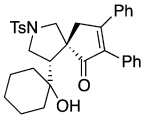
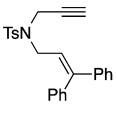
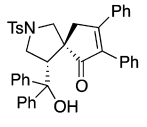
The reaction of other cyclopropenones **2b–e** was also examined using **1a** as the coupling partner (Table 3). The ring-expanding spiroannulation of enyne **1a** with diarylcyclopropenones **2b** and **2c** afforded the corresponding spirocyclic ketones **3j** and **3k**, respectively, in high yields (entries 1 and 2). Dipropylcyclopropenone **2d** also underwent the spiroannulation with **1a** to afford **3l** in 85% yield (entry 3). Single regioisomer **3m** was obtained in an excellent yield by the reaction of unsymmetrically substituted cyclopropenone **2e** with **1a** (entry 4).[11] In this case, clean conversion was achieved by performing the reaction at 0 °C. However, an attempted reaction using monosubstituted phenylcyclopropenone gave only a complex mixture of products.

The gold(I)-catalyzed reactions of enynes with carbonyl compounds have been reported.[12] Echavarren et al. reported the gold(I)-catalyzed reaction of 1,6-enynes with aldehydes[12f] and found that the reaction proceeded via the formation of (cyclopropylcarbene)gold(I) species, affording an oxocarbenium ion by the ring opening of the cyclopropane ring with an aldehyde. Based on their proposed mechanism, the following catalytic cycle may have operated in our spiroannulation reaction (Scheme 2).[13] Similar to the case for the reaction with aldehydes, (cyclopropylcarbene)gold(I) species **A** is produced by the reaction of enyne **1** with the Au(I) catalyst; then the carbonyl group of cyclopropenone **2** opens the cyclopropane ring of **A** to generate oxocarbenium ion intermediate **B**. The resulting alkenylgold(I) moiety of **B** attacks the carbonyl sp^2 carbon with the β-carbon to form carbenegold(I) **C** with a 3-oxabicyclo[3.3.0]octane system with a spirocyclic cyclopropene moiety.[14] Then, the cyclopropene sp^2 carbon migrates onto the carbon α to the Au(I), resulting in the ring expansion to generate tricyclic oxocarbenium ion **D**. The cyclopentene

Table 2. Substrate Scope of Enynes 1[a]



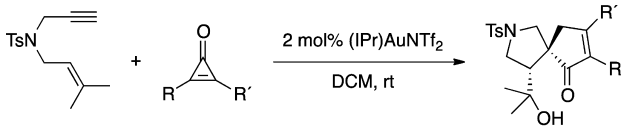
1 **2a** **3**

entry	enyne **1**	product **3**	yield[b]
1	 **1a**-*d*	 **3a**-*d*[c]	87%
2	 **1b** (R = Ms)	 **3b**	91%
3	**1c** (R = Ns[d])	**3c**	79%
4	**1d** (R = $BnSO_2$)	**3d**	86%
5	**1e** (R = Ph)	**3e**	11%
6	 **1f**	 **3f**	68%
7[e]	 **1g**	 **3g**	41%
8	 **1h**	 **3h**	77%
9	 **1i**	 **3i**	53%

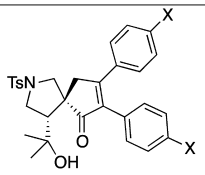
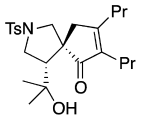
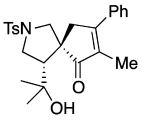
[a]Enyne **1** and cyclopropenone **2a** (**1**:**2a** = 1.2:1) were reacted in DCM at room temperature in the presence of (IPr)$AuNTf_2$ (2 mol %). [b]Isolated yield. [c]Obtained as a single diastereomer. [d]Ns = (2-nitrophenyl)sulfonyl. [e]The reaction was performed at 0 °C.

dx.doi.org/10.1021/jo500045n | J. Org. Chem. 2014, 79, 2739–2745

Table 3. Substrate Scope of Cyclopropenones 2[a]

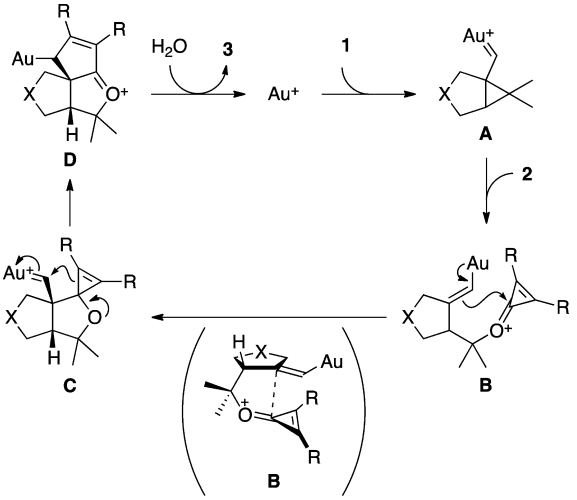


1a 2 3

entry	cyclopropenone **2** (R, R′)	product **3**	yield[b]
			
1	**2b** (4-MeC$_6$H$_4$, 4-MeC$_6$H$_4$)	**3j** (X = Me)	95%
2	**2c** (4-MeOC$_6$H$_4$, 4-MeOC$_6$H$_4$)	**3k** (X = OMe)	97%
3	**2d** (Pr, Pr)	 **3l**	85%
4[c]	**2e** (Me, Ph)	 **3m**	85%

[a]Enyne **1** and cyclopropenone **2a** (**1**:**2a** = 1.2:1) were reacted in DCM at room temperature in the presence of (IPr)AuNTf$_2$ (2 mol %). [b]Isolated yield. [c]The reaction was performed at 0 °C.

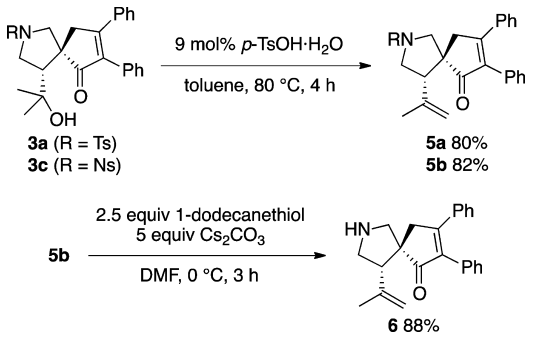
Scheme 2. Proposed Mechanism for the Gold(I)-Catalyzed Spiroannulation



structure of **D** is formed by the stepwise intramolecular [3 + 2] annulation of the vinylgold with the cyclopropene moieties of **B** via **C**. Finally, **D** is hydrolyzed with water present in the solvent to furnish product **3**,[15] and the Au(I) catalyst is regenerated. The results of the deuterium-labeling experiment indicate that both the ring expansion and protodeauration steps proceeded in diastereoselective manners.

The spirocyclic products were derivatized (Scheme 3). The 2-hydroxypropan-2-yl groups of **3a** and **3c** were dehydrated

Scheme 3. Derivatization of Spiroannulation Products 3



with 9 mol % *p*-toluenesulfonic acid in toluene at 80 °C to produce the corresponding alkenes **5a** and **5b**, respectively, in good yields. The (2-nitrophenyl)sulfonyl group of **5b** was removed by reacting with 1-dodecanethiol and Cs_2CO_3 in DMF to furnish **6** in 88% yield.[16]

In summary, we have developed a gold(I)-catalyzed spiroannulation reaction of enynes with cyclopropenones involving ring expansion of the cyclopropenone ring. The reaction proceeds with the incorporation of a water molecule to afford [4.4]-spirocyclic cyclopentenones containing an alcohol functionality, in excellent yields and with high diastereoselectivity.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out with standard Schlenk techniques under an argon atmosphere. Proton chemical shifts were referenced to a residual $CHCl_3$ signal at 7.26 ppm. Carbon chemical shifts were referenced to $CDCl_3$ at 77.0 ppm. Gold complexes,[17] enynes (**1a**,[18] **1e**,[19] **1f**,[20] and **1g**[21]), and cyclopropenones (**2b**,[22] **2c**,[23] **2d**,[24] and **2e**[3c]) were prepared according to the literature methods.

4-Methyl-*N*-(3-methylbut-2-en-1-yl)-*N*-[(3-^{2}H)prop-2-yn-1-yl]benzenesulfonamide (1a-*d*). The deuteration of **1a** was performed according to the reported procedure.[25] White solid, mp 60–61 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.67 (s, 3H), 1.72 (s, 3H), 1.98 (t, J = 2.6 Hz, 90% D), 2.42 (s, 3H), 3.81 (d, J = 12.5 Hz, 2H), 4.06 (s, 2H), 5.06–5.14 (m, 1H), 7.29 (d, J = 7.8 Hz, 2H), 7.70–7.76 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 17.8, 21.5, 25.8, 35.3, 43.8, 73.1 (t, J = 38.4 Hz), 76.5 (t, J = 7.2 Hz), 117.8, 127.7, 129.3, 136.0, 139.0, 143.3; HRMS (ESI) calcd for $C_{15}H_{18}DNNaO_2S$ $[M + Na]^+$ 301.1091, found 301.1087.

***N*-(3-Methylbut-2-en-1-yl)-*N*-(prop-2-yn-1-yl)methanesulfonamide (1b).** Step 1: Prenyl chloride (523 mg, 5.00 mmol) was added to a suspension of methanesulfonamide (713 mg, 7.50 mmol) and K_2CO_3 (691 mg, 5.00 mmol) in acetone (10 mL), and the resulting mixture was heated at 60 °C for 12 h. The reaction mixture was filtered, and the filtrate was concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 5:1) to afford *N*-prenylmethanesulfonamide (498 mg, 3.05 mmol, 61%).

Step 2: Propargyl bromide (535 mg, 4.50 mmol) was added to a mixture of *N*-prenylmethanesulfonamide (489 mg, 3.00 mmol) and K_2CO_3 (622 mg, 4.50 mmol) in acetonitrile (10 mL), and the resulting mixture was heated at 80 °C for 12 h. The reaction mixture was filtered, and the filtrate was concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 10:1) to afford **1b** (531 mg, 2.64 mmol, 88%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.75 (s, 3H), 1.77 (s, 3H), 2.35 (t, J = 2.5 Hz, 1H), 2.95 (s, 3H), 3.88 (d, J = 7.5 Hz, 2H), 4.04 (d, J = 2.0 Hz, 2H), 5.19 (t, J = 7.2 Hz, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 17.8, 25.9, 35.3, 38.0, 43.9,

dx.doi.org/10.1021/jo500045n | J. Org. Chem. 2014, 79, 2739–2745

74.0, 77.6, 117.7, 139.5; HRMS (ESI) calcd for $C_9H_{15}NNaO_2S$ $[M + Na]^+$ 224.0716, found 224.0718.

***N*-(3-Methylbut-2-en-1-yl)-2-nitro-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1c).** The title compound was prepared according to the procedure described for **1b**, starting with 2-nitrobenzenesulfonamide (Step 1: 432 mg, 32%; Step 2: 308 mg, 62%). White solid, mp 49−51 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.69 (s, 3H), 1.72 (s, 3H), 2.14 (t, J = 2.4 Hz, 1H), 4.00 (d, J = 7.5 Hz, 2H), 4.12 (d, J = 2.4 Hz, 2H), 5.03−5.11 (m, 1H), 7.60−7.74 (m, 3H), 8.02−8.08 (m, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 17.8, 25.8, 35.6, 44.4, 73.3, 77.3, 117.5, 124.1, 130.9, 131.6, 133.0, 133.6, 139.7, 148.2; HRMS (ESI) calcd for $C_{14}H_{16}N_2NaO_4S$ $[M + Na]^+$ 331.0723, found 331.0722.

***N*-(3-Methylbut-2-en-1-yl)-1-phenyl-*N*-(prop-2-yn-1-yl)methanesulfonamide (1d).** The title compound was prepared according to the procedure described for **1b**, starting with phenylmethanesulfonamide (Step 1: 526 mg, 44%; Step 2: 494 mg, 89%). White solid, mp 49−50 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.68 (s, 3H), 1.73 (s, 3H), 2.38 (t, J = 2.5 Hz, 1H), 3.72 (d, J = 7.0 Hz, 2H), 3.98 (d, J = 2.5 Hz, 2H), 4.30 (s, 2H), 5.08 (t, J = 7.7 Hz, 1H), 7.35−7.40 (m, 3H), 7.44−7.49 (m, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 17.7, 25.8, 35.4, 44.6, 58.4, 73.5, 78.5, 118.4, 128.57, 128.59, 128.7, 130.9, 138.8; HRMS (ESI) calcd for $C_{15}H_{19}N_2NaO_2S$ $[M + Na]^+$ 300.1029, found 300.1032.

***N*-(3-Methylbut-2-en-1-yl)-*N*-(prop-2-yn-1-yl)aniline (1e).** Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.76 (s, 6H), 2.17 (t, J = 2.2 Hz, 1H), 3.93 (d, J = 6.5 Hz, 2H), 4.01 (d, J = 2.5 Hz, 2H), 5.24−5.30 (m, 1H), 6.80 (t, J = 7.2 Hz, 1H), 6.89 (d, J = 8.0 Hz, 2H), 7.27 (t, J = 7.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 18.0, 25.8, 39.4, 48.7, 71.6, 80.1, 114.6, 118.2, 120.8, 129.1, 135.7, 148.6; HRMS (ESI) calcd for $C_{14}H_{18}N$ $[M + H]^+$ 200.1434, found 200.1434.

3-Methyl-1-(prop-2-yn-1-yloxy)but-2-ene (1f). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70 (s, 3H), 1.75 (s, 3H), 2.41 (t, J = 2.2 Hz, 1H), 4.05 (d, J = 7.2 Hz, 2H), 4.12 (d, J = 2.4 Hz, 2H), 5.28−5.37 (m, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 18.0, 25.8, 56.7, 65.9, 74.1, 80.0, 120.1, 138.4; HRMS (ESI) calcd for $C_8H_{12}NaO$ $[M + Na]^+$ 147.0780, found 147.0782.

***N*-(2-Cyclohexylideneethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1h).** A solution of diisopropyl azodicarboxylate (1.0 M toluene solution, 1.1 mL, 1.1 mmol) was added dropwise to a mixture of 2-cyclohexylideneethan-1-ol[26] (139 mg, 1.10 mmol), 4-methyl-*N*-propargylbenzenesulfonamide (209 mg, 1.00 mmol), and PPh_3 (288 mg, 1.10 mmol) in THF (11 mL) at 0 °C, and then the resulting mixture was warmed to room temperature and further stirred for 12 h. The reaction mixture was concentrated in vacuo, and the residue was purified by column chromatography on silica gel (hexane/AcOEt = 15:1) to afford **1h** (222 mg, 0.699 mmol, 70%) as a white solid. Mp 71−72 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41−1.59 (m, 6H), 1.96 (t, J = 2.4 Hz, 1H), 2.01−2.20 (m, 4H), 2.42 (s, 3H), 3.81 (d, J = 7.5 Hz, 2H), 4.07 (d, J = 2.1 Hz, 2H), 5.04 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 21.5, 26.6, 27.9, 28.5, 28.7, 35.2, 37.2, 43.0, 73.3, 76.9, 114.4, 127.8, 129.4, 136.1, 143.3, 147.2; HRMS (ESI) calcd for $C_{18}H_{23}NNaO_2S$ $[M + Na]^+$ 340.1342, found 340.1346.

***N*-(3,3-Diphenylallyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1i).** The title compound was prepared according to the procedure described for **1h**, starting with 3,3-diphenylprop-2-en-1-ol[27] (313 mg, 78%). Pale yellow solid, mp 88−90 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.89 (t, J = 2.5 Hz, 1H), 2.40 (s, 3H), 3.95 (d, J = 7.0 Hz, 2H), 4.11 (d, J = 7.2 Hz, 2H), 6.02 (t, J = 7.0 Hz, 1H), 7.12−7.38 (m, 12H), 7.69 (d, J = 8.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4, 36.4, 45.7, 73.5, 76.7, 122.7, 127.3, 127.5, 127.7, 128.1, 128.17, 128.20, 128.9, 129.4, 129.7, 136.1, 138.3, 143.4, 146.0; HRMS (ESI) calcd for $C_{25}H_{23}NNaO_2S$ $[M + Na]^+$ 424.1342, found 424.1342.

General Procedure for Gold-Catalyzed Reaction of Enynes 1 and Cyclopropenones 2. A Schlenk tube was charged with (IPr)AuNTf$_2$ (2.0 μmol), enyne **1** (0.12 mmol), and cyclopropenone **2** (0.10 mmol), and the tube was evacuated and backfilled with argon. DCM (1.0 mL) was added via a syringe through the septum, and the mixture was stirred at 25 °C for 12 h. Then, the reaction mixture was concentrated under reduced pressure, and the residue was purified by preparative TLC on silica gel to afford spirocyclic cyclopentenones **3**.

(4*R,5*S**)-4-(2-Hydroxypropan-2-yl)-7,8-diphenyl-2-tosyl-2-azaspiro[4.4]non-7-en-6-one (3a).** The general procedure was followed using **1a** (33.2 mg, 0.120 mmol) and **2a** (20.6 mg, 0.100 mmol). The purification by preparative TLC on silica gel (hexane/AcOEt = 2:1) afforded **3a** (46.0 mg, 0.092 mmol, 92%) as a white solid. Mp 122−124 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (s, 3H), 1.17 (s, 3H), 2.44 (s, 3H), 2.61 (dd, J = 9.0, 8.0 Hz, 1H), 3.11 (d, J = 10.0 Hz, 1H), 3.18 (d, J = 18.0 Hz, 1H), 3.27 (t, J = 9.5 Hz, 1H), 3.38 (d, J = 18.5 Hz, 1H), 3.51 (d, J = 9.0 Hz, 1H), 3.77−3.84 (m, 2H), 7.14−7.19 (m, 2H), 7.26−7.40 (m, 10H), 7.72 (d, J = 8.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.6, 29.3, 29.4, 48.7, 50.2, 56.1, 59.6, 61.2, 70.6, 128.0, 128.4, 128.6, 128.7, 129.3, 129.9, 130.9, 131.5, 131.8, 134.1, 139.0, 144.0, 166.6, 210.2; HRMS (ESI) calcd for $C_{30}H_{31}NNaO_4S$ $[M + Na]^+$ 524.1866, found 524.1868; IR (ν/cm^{-1}): 3448, 1689, 1350, 1157.

3a-*d*. The general procedure was followed using **1a**-*d* (32.8 mg, 0.118 mmol) and **2a** (20.6 mg, 0.100 mmol). The purification by preparative TLC on silica gel (hexane/AcOEt = 2:1) afforded **3a**-*d* (43.9 mg, 0.087 mmol, 87%) as a white solid. Mp 117−119 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (s, 3H), 1.17 (s, 3H), 2.44 (s, 3H), 2.61 (dd, J = 9.8, 7.8 Hz, 1H), 3.11 (d, J = 9.5 Hz, 1H), 3.16 (s, 1H), 3.27 (t, J = 9.5 Hz, 1H), 3.51 (d, J = 9.5 Hz, 1H), 3.78−3.83 (m, 2H), 7.14−7.18 (m, 2H), 7.24−7.40 (m, 10H), 7.70−7.73 (m, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 21.6, 29.3, 29.4, 48.2 (t), 50.2, 56.0, 59.5, 61.1, 70.5, 127.9, 128.0, 128.4, 128.59, 128.65, 129.3, 129.9, 130.9, 131.5, 131.8, 134.1, 139.0, 144.0, 166.5, 210.2; HRMS (ESI) calcd for $C_{30}H_{30}DNNaO_4S$ $[M + Na]^+$ 525.1929, found 525.1928; IR (ν/cm^{-1}): 3502, 3433, 1689, 1342, 1157.

(4*R,5*S**)-4-(2-Hydroxypropan-2-yl)-2-(methylsulfonyl)-7,8-diphenyl-2-azaspiro[4.4]non-7-en-6-one (3b).** The general procedure was followed using **1b** (23.9 mg, 0.119 mmol) and **2a** (20.6 mg, 0.100 mmol). The purification by preparative TLC on silica gel (hexane/AcOEt = 2:1) afforded **3b** (38.8 mg, 0.091 mmol, 91%) as pale yellow crystals. Mp 176−178 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18 (s, 3H), 1.22 (s, 3H), 2.46 (br s, 1H), 2.67 (dd, J = 10.3, 7.8 Hz, 1H), 2.94 (s, 3H), 3.17 (d, J = 18.0 Hz, 1H), 3.30 (d, J = 18.5 Hz, 1H), 3.54 (d, J = 9.5 Hz, 1H), 3.58 (d, J = 11.0 Hz, 1H), 3.64−3.69 (m, 1H), 3.72−3.76 (m, 1H), 7.15−7.34 (m, 10H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 29.7, 30.0, 35.0, 43.7, 49.1, 54.5, 58.3, 58.4, 71.1, 128.2, 128.3, 128.6, 128.7, 129.3, 130.5, 131.8, 134.5, 139.0, 165.3, 209.8; HRMS (ESI) calcd for $C_{24}H_{27}NNaO_4S$ $[M + Na]^+$ 448.1553, found 448.1554; IR (ν/cm^{-1}): 3487, 1689, 1327, 1149.

(4*R,5*S**)-4-(2-Hydroxypropan-2-yl)-2-[(2-nitrophenyl)-sulfonyl]-7,8-diphenyl-2-azaspiro[4.4]non-7-en-6-one (3c).** The general procedure was followed using **1c** (36.7 mg, 0.119 mmol) and **2a** (20.6 mg, 0.100 mmol). The purification by preparative TLC on silica gel (hexane/AcOEt = 1:1) afforded **3c** (42.0 mg, 0.079 mmol, 79%) as a white solid. Mp 155−156 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (s, 3H), 1.24 (s, 3H), 2.68 (dd, J = 10.5, 8.0 Hz, 1H), 3.22 (br s, 1H), 3.30 (s, 2H), 3.71 (s, 2H), 3.78 (t, J = 10.0 Hz, 1H), 3.94 (dd, J = 9.5, 8.0 Hz, 1H), 7.16−7.20 (m, 2H), 7.27−7.40 (m, 8H), 7.63−7.67 (m, 1H), 7.69−7.74 (m, 2H), 8.10−8.13 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 29.56, 29.63, 46.1, 49.8, 55.6, 59.0, 59.7, 70.9, 124.2, 128.3, 128.6, 128.7, 129.3, 130.68, 130.74, 131.4, 131.6, 131.9, 133.7, 134.3, 139.0, 148.5, 165.9, 209.5; HRMS (ESI) calcd for $C_{29}H_{28}N_2NaO_6S$ $[M + Na]^+$ 555.1560, found 555.1558; IR (ν/cm^{-1}): 3548, 3525, 1689, 1543, 1365, 1165.

(4*R,5*S**)-2-(Benzylsulfonyl)-4-(2-hydroxypropan-2-yl)-7,8-diphenyl-2-azaspiro[4.4]non-7-en-6-one (3d).** The general procedure was followed using **1d** (33.4 mg, 0.120 mmol) and **2a** (20.6 mg, 0.100 mmol). The purification by preparative TLC on silica gel (hexane/AcOEt = 2:1) afforded **3d** (43.1 mg, 0.086 mmol, 86%) as a white solid. Mp 148−150 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16 (s, 3H), 1.20 (s, 3H), 2.59 (dd, J = 10.3, 7.8 Hz, 1H), 3.17 (d, J = 18.0 Hz, 1H), 3.23 (d, J = 18.5 Hz, 1H), 3.47 (d, J = 11.0 Hz, 1H), 3.52 (d, J = 10.0 Hz, 1H), 3.67−3.72 (m, 1H), 3.73−3.78 (m, 1H), 4.29 (d, J = 15.0 Hz, 1H), 4.36 (d, J = 13.5 Hz, 1H), 7.14−7.19 (m, 2H), 7.21−7.36 (m, 11H), 7.39−7.43 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ

dx.doi.org/10.1021/jo500045n | J. Org. Chem. 2014, 79, 2739−2745

29.7, 29.8, 45.0, 49.5, 55.4, 56.3, 58.9, 59.2, 71.0, 128.28, 128.31, 128.5, 128.6, 128.68, 128.72, 128.8, 129.3, 130.6, 130.9, 131.7, 134.4, 139.0, 165.7, 209.9; HRMS (ESI) calcd for $C_{30}H_{31}NNaO_4S$ $[M + Na]^+$ 524.1866, found 524.1863; IR (ν/cm^{-1}): 3502, 1682, 1342, 1149, 694.

(4*R,5*S**)-4-(2-Hydroxypropan-2-yl)-2,7,8-triphenyl-2-azaspiro[4.4]non-7-en-6-one (3e).** The general procedure was followed using **1e** (24.1 mg, 0.121 mmol) and **2a** (20.6 mg, 0.100 mmol). The purification by preparative TLC on silica gel (hexane/AcOEt = 5:1) afforded **3e** (4.6 mg, 0.011 mmol, 11%) as a yellow solid. Mp 138−139 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (s, 3H), 1.32 (s, 3H), 2.69 (t, J = 8.0 Hz, 1H), 3.22 (br s, 1H), 3.24 (d, J = 18.0 Hz, 1H), 3.36 (d, J = 7.2 Hz, 1H), 3.51 (d, J = 9.0 Hz, 1H), 3.70−3.74 (m, 3H), 6.64 (dd, J = 8.5, 1.0 Hz, 2H), 6.73 (t, J = 7.5 Hz, 1H), 7.22−7.38 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 28.9, 29.9, 47.0, 50.3, 55.9, 58.6, 60.1, 71.7, 112.4, 116.7, 128.2, 128.3, 128.5, 128.6, 129.1, 129.4, 130.4, 131.9, 134.8, 139.1, 147.6, 165.0, 210.5; HRMS (ESI) calcd for $C_{29}H_{30}NO_2$ $[M + H]^+$ 424.2271, found 424.2272; IR (ν/cm^{-1}): 3502, 1689, 1597, 1504, 1365, 748, 694.

(4*R,5*S**)-4-(2-Hydroxypropan-2-yl)-7,8-diphenyl-2-oxaspiro[4.4]non-7-en-6-one (3f).** The general procedure was followed using **1f** (15.2 mg, 0.122 mmol) and **2a** (20.6 mg, 0.100 mmol). The purification by preparative TLC on silica gel (hexane/AcOEt = 10:1) afforded **3f** (23.8 mg, 0.068 mmol, 68%) as a yellow solid. Mp 111−112 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14 (s, 3H), 1.22 (s, 3H), 2.55 (t, J = 8.5 Hz, 1H), 3.16 (d, J = 18.0 Hz, 1H), 3.30 (d, J = 18.5 Hz, 1H), 3.85 (d, J = 8.5 Hz, 1H), 3.94 (d, J = 8.5 Hz, 1H), 4.19−4.27 (m, 2H), 4.48 (br s, 1H), 7.13−7.36 (m, 10H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 29.9, 48.9, 58.5, 61.7, 70.3, 71.1, 81.7, 128.3, 128.6, 128.7, 129.4, 130.6, 131.8, 134.5, 139.6, 166.6, 211.1; HRMS (ESI) calcd for $C_{23}H_{24}NaO_3$ $[M + Na]^+$ 371.1618, found 371.1619; IR (ν/cm^{-1}): 3433, 1674, 1350, 694.

Dimethyl (4*R,5*S**)-4-(2-hydroxypropan-2-yl)-6-oxo-7,8-diphenylspiro[4.4]non-7-ene-2,2-dicarboxylate (3g).** The general procedure was followed using **1g** (28.3 mg, 0.119 mmol) and **2a** (20.6 mg, 0.100 mmol). The purification by preparative TLC on silica gel (hexane/AcOEt = 3:1) afforded **3g** (18.9 mg, 0.041 mmol, 41%) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19 (s, 3H), 1.21 (s, 3H), 2.44−2.51 (m, 2H), 2.60 (ddd, J = 13.1, 6.6, 1.4 Hz, 1H), 2.76 (d, J = 14.0 Hz, 1H), 2.81 (t, J = 12.8 Hz, 1H), 3.18 (d, J = 18.5 Hz, 1H), 3.25 (d, J = 18.0 Hz, 1H), 3.75 (s, 3H), 3.80 (s, 3H + 1H), 7.20 (dd, J = 7.5, 1.5 Hz, 2H), 7.26−7.38 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 29.0, 30.5, 36.4, 48.5, 48.8, 52.9, 53.0, 55.8, 58.8, 58.9, 71.0, 128.2, 128.2, 128.5, 128.6, 129.3, 130.4, 131.9, 134.7, 138.8, 166.1, 171.2, 172.8, 213.5; HRMS (ESI) calcd for $C_{28}H_{30}NaO_6$ $[M + Na]^+$ 485.1935, found 485.1935; IR (ν/cm^{-1}): 3448, 2962, 1736, 1682, 1442, 1265, 756, 694.

(4*R,5*S**)-4-(1-Hydroxycyclohexyl)-7,8-diphenyl-2-tosyl-2-azaspiro[4.4]non-7-en-6-one (3h).** The general procedure was followed using **1h** (38.2 mg, 0.120 mmol) and **2a** (20.6 mg, 0.100 mmol). The purification by preparative TLC on silica gel (hexane/AcOEt = 2:1) afforded **3h** (41.8 mg, 0.077 mmol, 77%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.08−1.65 (m, 10H), 2.44 (s, 3H), 2.63 (dd, J = 10.3, 7.8 Hz, 1H), 3.03 (d, J = 9.5 Hz, 1H), 3.19 (d, J = 18.5 Hz, 1H), 3.22 (t, J = 9.8 Hz, 1H), 3.39 (d, J = 18.5 Hz, 1H), 3.50 (d, J = 10.0 Hz, 1H), 3.72−3.82 (m, 2H), 7.14−7.19 (m, 2H), 7.27−7.40 (m, 10H), 7.70 (d, J = 8.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.51, 21.54, 21.6, 25.5, 36.7, 37.0, 48.9, 49.7, 56.0, 59.2, 61.6, 71.4, 128.0, 128.3, 128.56, 128.63, 129.3, 129.9, 130.8, 131.5, 134.1, 138.9, 144.0, 166.4, 210.5; HRMS (ESI) calcd for $C_{33}H_{35}NNaO_4S$ $[M + Na]^+$ 564.2179, found 564.2182; IR (ν/cm^{-1}): 3425, 2931, 1689, 1350, 1165, 756.

(4*R,5*S**)-4-(Hydroxydiphenylmethyl)-7,8-diphenyl-2-tosyl-2-azaspiro[4.4]non-7-en-6-one (3i).** The general procedure was followed using **1i** (47.3 mg, 0.118 mmol) and **2a** (20.6 mg, 0.100 mmol). The purification by preparative TLC on silica gel (hexane/AcOEt = 2:1) afforded **3i** (33.2 mg, 0.053 mmol, 53%) as a white solid. Mp 126−127 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.50 (s, 3H), 3.11 (d, J = 9.5 Hz, 1H), 3.17 (dd, J = 9.8, 8.2 Hz, 1H), 3.34 (d, J = 19.5 Hz, 1H), 3.42 (t, J = 9.3 Hz, 1H), 3.53 (d, J = 9.0 Hz, 1H), 3.71 (d, J = 19.5 Hz, 1H), 3.93 (t, J = 8.5 Hz, 1H), 6.41−6.44 (m, 2H), 7.12−7.42 (m, 20H), 7.65 (d, J = 8.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.7, 49.9, 51.4, 56.4, 58.0, 61.8, 78.2, 124.9, 125.3, 126.5, 127.0, 128.0, 128.06, 128.14, 128.2, 128.3, 128.6, 128.7, 129.2, 129.8, 130.8, 130.9, 131.3, 134.3, 139.6, 144.1, 145.3, 147.0, 166.9, 209.1; HRMS (ESI) calcd for $C_{40}H_{35}NNaO_4S$ $[M + Na]^+$ 648.2179, found 648.2179; IR (ν/cm^{-1}): 3363, 1674, 1350, 1165, 748, 702, 663.

(4*R,5*S**)-4-(2-Hydroxypropan-2-yl)-7,8-bis(4-methylphenyl)-2-tosyl-2-azaspiro[4.4]non-7-en-6-one (3j).** The general procedure was followed using **1a** (33.2 mg, 0.120 mmol) and **2b** (22.4 mg, 0.096 mmol). The purification by preparative TLC on silica gel (hexane/AcOEt = 2:1) afforded **3j** (48.0 mg, 0.091 mmol, 95%) as a pale yellow solid. Mp 141−143 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12 (s, 3H), 1.15 (s, 3H), 2.35 (s, 3H), 2.36 (s, 3H), 2.44 (s, 3H), 2.60 (dd, J = 9.5, 8.0 Hz, 1H), 3.06 (d, J = 9.5 Hz, 1H), 3.14 (d, J = 18.5 Hz, 1H), 3.24 (t, J = 9.7 Hz, 1H), 3.36 (d, J = 18.0 Hz, 1H), 3.48 (d, J = 10.0 Hz, 1H), 3.80 (t, J = 8.5 Hz, 1H), 7.06 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 9.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4, 21.5, 21.6, 29.2, 29.5, 48.8, 50.3, 56.1, 59.6, 61.5, 70.4, 128.0, 128.4, 128.7, 129.1, 129.3, 129.4, 129.9, 131.3, 131.6, 138.2, 138.3, 141.6, 144.0, 166.3, 210.5; HRMS (ESI) calcd for $C_{32}H_{35}NNaO_4S$ $[M + Na]^+$ 552.2179, found 552.2182; IR (ν/cm^{-1}): 3471, 1689, 1350, 1165, 818, 663.

(4*R,5*S**)-4-(2-Hydroxypropan-2-yl)-7,8-bis(4-methoxyphenyl)-2-tosyl-2-azaspiro[4.4]non-7-en-6-one (3k).** The general procedure was followed using **1a** (33.2 mg, 0.120 mmol) and **2c** (25.5 mg, 0.096 mmol). The purification by preparative TLC on silica gel (hexane/AcOEt = 2:1) afforded **3k** (52.2 mg, 0.093 mmol, 97%) as a pale yellow solid. Mp 149−152 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 (s, 3H), 1.15 (s, 3H), 2.44 (s, 3H), 2.59 (dd, J = 9.5, 8.0 Hz, 1H), 3.03 (d, J = 10.0 Hz, 1H), 3.12 (d, J = 18.5 Hz, 1H), 3.22 (t, J = 9.8 Hz, 1H), 3.37 (d, J = 18.5 Hz, 1H), 3.46 (d, J = 10.0 Hz, 1H), 3.77−3.82 (m, 1H), 3.82 (s, 3H + 3H), 4.11 (br s, 1H), 6.78−6.82 (m, 2H), 6.88−6.91 (m, 2H), 7.10−7.13 (m, 2H), 7.33−7.36 (m, 4H), 7.69−7.71 (m, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 21.6, 29.2, 29.5, 48.8, 50.3, 55.2, 55.4, 56.0, 59.7, 61.6, 70.4, 114.0, 114.3, 124.2, 126.6, 128.0, 129.9, 130.3, 130.6, 131.5, 136.9, 144.0, 159.5, 161.7, 165.5, 210.4; HRMS (ESI) calcd for $C_{32}H_{35}NNaO_6S$ $[M + Na]^+$ 584.2077, found 584.2079; IR (ν/cm^{-1}): 3448, 1597, 1512, 1350, 1257, 1165.

(4*R,5*S**)-4-(2-Hydroxypropan-2-yl)-7,8-dipropyl-2-tosyl-2-azaspiro[4.4]non-7-en-6-one (3l).** The general procedure was followed using **1a** (33.2 mg, 0.120 mmol) and **2d** (13.8 mg, 0.100 mmol). The purification by preparative TLC on silica gel (hexane/AcOEt = 2:1) afforded **3l** (36.8 mg, 0.085 mmol, 85%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, J = 7.3 Hz, 3H), 0.95 (t, J = 7.3 Hz, 3H), 1.01 (s, 3H), 1.05 (s, 3H), 1.20−1.61 (m, 4H), 2.12 (t, J = 7.6 Hz, 2H), 2.32−2.50 (m, 6H), 2.60 (d, J = 18.9 Hz, 1H), 2.79−2.87 (m, 2H), 3.11−3.22 (m, 2H), 3.71 (t, J = 8.5 Hz, 1H), 4.17 (s, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.97, 14.03, 20.6, 21.49, 21.51, 25.11, 28.8, 29.4, 32.8, 49.3, 50.3, 55.7, 59.0, 61.6, 70.3, 127.9, 129.8, 131.7, 140.3, 143.9, 174.2, 212.4; HRMS (ESI) calcd for $C_{24}H_{35}NNaO_4S$ $[M + Na]^+$ 456.2179, found 456.2179; IR (ν/cm^{-1}): 3410, 2962, 1682, 1628, 1342, 1165, 756, 663.

(4*R,5*S**)-4-(2-Hydroxypropan-2-yl)-8-methyl-7-phenyl-2-tosyl-2-azaspiro[4.4]non-7-en-6-one (3m).** The general procedure was followed using **1a** (33.2 mg, 0.120 mmol) and **2e** (14.6 mg, 0.101 mmol) at 0 °C. The purification by preparative TLC on silica gel (hexane/AcOEt = 2:1) afforded **3m** (38.0 mg, 0.086 mmol, 85%) as a pale yellow solid. Mp 89−91 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.09 (s, 3H), 1.12 (s, 3H), 2.19 (s, 3H), 2.43 (s, 3H), 2.52 (dd, J = 10.5, 8.0 Hz, 1H), 2.81 (d, J = 19.0 Hz, 1H), 2.98 (d, J = 10.0 Hz, 1H), 3.01 (d, J = 20.5 Hz, 1H), 3.20 (t, J = 9.8 Hz, 1H), 3.39 (d, J = 10.0 Hz, 1H), 3.74−3.78 (m, 1H), 3.92 (br s, 1H), 7.20−7.24 (m, 2H), 7.31−7.36 (m, 3H), 7.37−7.42 (m, 2H), 7.68 (d, J = 8.5 Hz, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 18.2, 21.5, 29.1, 29.4, 50.2, 51.4, 56.1, 59.2, 61.3, 70.4, 127.9, 128.1, 128.4, 128.9, 129.8, 130.6, 131.6, 139.9, 144.0, 171.6, 210.2; HRMS (ESI) calcd for $C_{25}H_{29}NNaO_4S$ $[M + Na]^+$ 462.1710, found 462.1709; IR (ν/cm^{-1}): 3896, 3417, 2978, 1689, 1342, 1157, 756, 663.

dx.doi.org/10.1021/jo500045n | J. Org. Chem. 2014, 79, 2739−2745

(4*R,5*S**)-7,8-Diphenyl-4-(prop-1-en-2-yl)-2-tosyl-2-azaspiro[4.4]non-7-en-6-one (5a).** Toluene (0.6 mL) was added to a Schlenk tube containing *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H_2O, 1.0 mg, 5.3 μmol) and **3a** (30.1 mg, 0.060 mmol) via a syringe through the septum, and the mixture was heated at 80 °C for 4 h. The reaction mixture was passed through a plug of Florisil and eluted with hexane−AcOEt (1:1). The eluate was concentrated under reduced pressure, and the residue was purified by preparative TLC on silica gel (hexane/AcOEt = 3:1) to afford **5a** (23.2 mg, 0.048 mmol, 80%) as a white solid. Mp 156−158 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.61 (s, 3H), 2.44 (s, 3H), 2.93 (dd, J = 9.5, 7.0 Hz, 1H), 3.01−3.11 (m, 2H), 3.58−3.73 (m, 4H), 4.72 (s, 1H), 4.85 (t, J = 1.5 Hz, 1H), 7.04−7.09 (m, 2H), 7.22−7.37 (m, 10H), 7.78−7.82 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.6, 22.3, 43.0, 50.6, 55.1, 55.5, 114.7, 127.6, 128.0, 128.45, 128.51, 129.3, 129.7, 130.2, 131.7, 134.2, 134.7, 138.4, 140.0, 143.5, 164.1, 206.1; HRMS (ESI) calcd for $C_{30}H_{29}NNaO_3S$ $[M + Na]^+$ 506.1760, found 506.1762; IR (ν/cm^{-1}): 1697, 1342, 1157.

(4*R,5*S**)-2-[(2-Nitrophenyl)sulfonyl]-7,8-diphenyl-4-(prop-1-en-2-yl)-2-azaspiro[4.4]non-7-en-6-one (5b).** The title compound was prepared in a similar manner as described for **5a**, using **3c** (31.9 mg, 0.060 mmol) to afford **5b** (25.3 mg, 0.049 mmol, 82%) as a white solid. Mp 172−175 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.67 (s, 3H), 3.09 (dd, J = 10.7, 6.7 Hz, 1H), 3.13−3.22 (m, 2H), 3.74 (d, J = 10.0 Hz, 1H), 3.83 (dd, J = 9.0, 7.0 Hz, 1H), 3.95 (d, J = 10.0 Hz, 1H), 3.95 (dd, J = 10.8, 9.2 Hz, 1H), 4.85 (s, 1H), 4.91 (t, J = 1.5 Hz, 1H), 7.09−7.13 (m, 2H), 7.27−7.37 (m, 8H), 7.64−7.75 (m, 3H), 8.20 (dd, J = 7.7, 1.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.2, 41.2, 50.3, 54.6, 54.9, 55.3, 115.3, 124.2, 128.1, 128.50, 128.55, 129.3, 130.31, 130.35, 131.7, 131.9, 132.3, 133.3, 134.6, 138.4, 139.1, 148.3, 164.7, 206.8; HRMS (ESI) calcd for $C_{29}H_{26}N_2NaO_5S$ $[M + Na]^+$ 537.1455, found 537.1456; IR (ν/cm^{-1}): 1704, 1350, 1165.

(4*R,5*S**)-7,8-Diphenyl-4-(prop-1-en-2-yl)-2-azaspiro[4.4]non-7-en-6-one (6).** A solution of 1-dodecanethiol (19.4 mg, 0.096 mmol) and **5b** (20.6 mg, 0.040 mmol) in DMF (0.40 mL) was added to a Schlenk tube containing Cs_2CO_3 (65.2 mg, 0.200 mmol) via a syringe through the septum, and the mixture was stirred at 0 °C for 3 h. Then, the reaction mixture was concentrated under reduced pressure, and the residue was purified by preparative TLC on silica gel ($CHCl_3$/MeOH/28% NH_3 solution = 45:3:1) to afford **6** (11.6 mg, 0.035 mmol, 88%) as a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70 (s, 3H), 2.62 (br s, 1H), 3.02−3.08 (m, 1H), 3.11 (d, J = 18.5 Hz, 1H), 3.16 (d, J = 11.0 Hz, 1H), 3.18 (d, J = 17.5 Hz, 1H), 3.25−3.31 (m, 1H), 3.43 (d, J = 11.5 Hz, 1H), 3.51 (t, J = 10.5 Hz, 1H), 4.82 (s, 1H), 4.86 (s, 1H), 7.14−7.19 (m, 2H), 7.26−7.36 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.2, 41.2, 49.8, 56.9, 57.0, 57.1, 113.9, 127.9, 128.1, 128.5, 129.3, 130.0, 132.1, 135.1, 138.6, 141.2, 165.2, 209.0; HRMS (ESI) calcd for $C_{23}H_{24}NO$ $[M + H]^+$ 330.1852, found 330.1853; IR (ν/cm^{-1}): 2924, 1689, 1350, 694.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of new compounds and X-ray crystallographic data for **3b** (ORTEP drawing and CIF). 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.

■ ACKNOWLEDGMENTS

This work was supported in part by a Grant-in-Aid for Scientific Research (C) (25410054) from MEXT, Japan.

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(5) Abbreviations: SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene

(6) Product **3a** was obtained in 29% yield using $PtCl_2$ (10 mol%), and 1,2,6,7-tetraphenyl-4-oxaspiro[2.4]hepta-1,6-dien-5-one was obtained in 66% yield by the dimerization of **2a** (ref 3e) when a mixture of **1a** and **2a** was treated with $AgNTf_2$ (10 mol%).

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(9) The stereochemical configuration has not been assigned.

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