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$GaCl_3$-Catalyzed Allenyne Cycloisomerizations to Allenenes

Sang Ick Lee, So Hee Sim, Soo Min Kim, Kwang Kim, and Young Keun Chung*

Intelligent Textile System Research Center and Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-747, Korea

ykchung@snu.ac.kr

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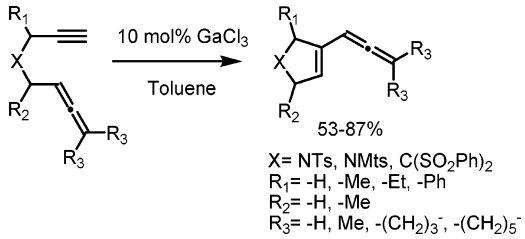

Cycloisomerizations of allenynes to allenenes have been studied in the presence of catalytic amounts of $[Au(PPh_3)]SbF_6$ in dichloromethane or $GaCl_3$ in toluene. Both catalytic systems are quite effective for terminal 1,6-allenynes. However, they showed different reactivities toward allenynes with di-substituents at the allenic terminal carbon. For the $GaCl_3$-catalyzed reactions, allenenes were obtained in reasonable to high yields. However, for a Au(I)-catalyzed reaction, a triene was obtained in a poor yield. Thus, $GaCl_3$ serves as an effective catalyst for the cycloisomerization of allenynes bearing a terminal alkyne to give cyclic allenenes in reasonable to high yields.

The transition-metal-catalyzed cyclization of enyne systems has recently experienced tremendous developments.[1] Allenynes are quite attractive substrates due to their use in diverse synthetic applications as well as in new reactions of unsaturated systems.[2] Recently, they have been widely used in intramolecular Pauson−Khand reactions.[3] However, allenynes still have been much less involved in the transition-metal-catalyzed (or -mediated) cyclizations than their enyne analogues. Particularly, transition-metal-catalyzed intramolecular cycloisomerizations of enynes have recently been widely studied.[4] However, the use of allenynes in the metal-catalyzed cycloisomerization is quite rare. Recently, $PtCl_2$-catalyzed cycloisomerizations of allenynes were reported by Murakami's and Malacria's groups.[5] We initially studied the use of gold-catalyzed cycloisomerization of allenynes. However, the expected reaction did not proceed in many cases. This limitation prompted us to investigate an alternative, more reactive catalytic system. Herein, we describe a cycloisomerization of allenynes upon treatment with a catalytic amount of $GaCl_3$. Recently, the Chatani group reported[6] that $GaCl_3$ is a highly active catalyst for the skeletal rearrangement of 1,6-enynes and 1,7-enynes.

We initially screened various metal catalysts such as the Grubbs catalyst,[7] Au(L)Cl/AgX,[4] $FeCl_3$,[8] $PtCl_2$,[5] $InCl_3$,[9] $GaCl_3$,[6] and $[Mn(CO)_5]BF_4$[10] for the cycloisomerization of allenynes (Table 1).

Unfortunately, when $PtCl_2$, $[Mn(CO)_5]BF_4$, or $FeCl_3$ was used as a catalyst, the reactant was recovered. The use of Grubbs catalyst led to polymerization of the reactant. When $InCl_3$ was used as a catalyst, 45% of the cycloisomerized product was isolated with a recovery of 40% of the reactant. However, when $[Au(PPh_3)]SbF_6$ and $GaCl_3$ were used as a catalyst, the metath-

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(10) Recently, we found that $[Mn(CO)_5]BF_4$ was active in the cycloisomerization of some enyne substrates. Lee, S. I.; Baek, J. Y.; Chung, Y. K. Manuscript in preparation.

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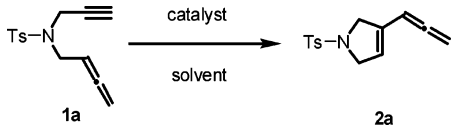
TABLE 1. Allenyne Metathesis by Various Catalysts[a]



entry	catalyst	solvent	*T* (°C)	*t* (h)	yield (%)[b]
1	5 mol % $RuCl_2(PCy_3)_2$-(benzylidene)	CH_2Cl_2	15−20	6	N/A
2	5 mol % $[Mn(CO)_5]BF_4$	DCE	60	24	NR
3	5 mol % $FeCl_3$	toluene	80	24	NR
4	5 mol % $PtCl_2$	toluene	80	24	NR
5	10 mol % $InCl_3$	toluene	80	24	45(40)
6	5 mol % [Au(PPh3)]SbF_6	CH_2Cl_2	15-20	0.5	75
7	10 mol % $GaCl_3$	toluene	15−20	2	81

[a] 0.2 g (0.691 mmol) of **1a** in 5 mL of solvent was used. [b] Isolated yield. [c] DCE = 1,2-dichloroethane. [d] Yield in parentheses is reactant recovered.

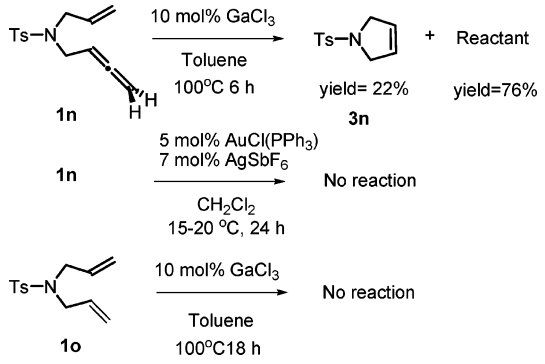
esis product was isolated in 75% and 81% yield, respectively. The obtained cycloisomerized product (**1A**) was the same type as those obtained by the molybdenum alkylidene complex-catalyzed ring-closing metathesis (RCM) of allenynes[11] but quite different from those obtained by $PtCl_2$-catalyzed cycloisomerization of allenynes.[5] Encouraged by this result, several allenynes were examined for $GaCl_3$- and Au(I)-catalyzed metathesis reactions (Table 2).

Terminal allenynes **1a**−**1c** having sulfonamide or sulfone in a tether were found to serve as good substrates for both $GaCl_3$- and Au(I)-catalyzed reactions (entries 1−5). This is in sharp contrast to previously reported results on the Mo-catalyzed RCM of allenynes,[11] where no reaction occurred with allenynes bearing the allenic terminus unsubstituted. Allenynes **1d**−**1g** having a substituent on the 3 position (entries 6−10) or having a substituent on the 5 position (entries 11 and 12) were also good substrates. However, allenynes with di-substituents at the allenic terminal carbon showed a different behavior depending upon the catalyst used. When $GaCl_3$ was used as catalyst, an allenyne (**1h**) (entry 13) afforded the product **2h** in 60% yield and allenynes **1i** and **1j** bearing a cyclic group on the allenic terminal carbon (entries 14 and 15) were also good substrates and led to the isolation of the products **2i** and **2j** in 53% and 83% yields, respectively. Thus, substantial structural variations can be accommodated. Interestingly, when **1j** was reacted with [Au(PPh_3)]SbF_6, a cycloisomerized product (**3j**) was isolated in low yield (38%). This transformation is similar to the $PtCl_2$-catalyzed cycloisomerization of allenynes reported by Murakami's group.[5a] Thus, $GaCl_3$ is a better catalyst for the cycloisomerization of allenynes with di-substituents at the allenic terminal carbon. Unfortunately, no reaction was observed for allenynes having a substituent (**1k** and **1l**) on the alkyne terminal position (entries 17−19) and a 1,7-allenyne (**1m**) (entries 20 and 21) under the conditions described here.

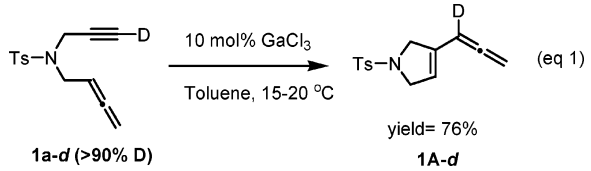
When allenene (**1n**) was reacted in the presence of $GaCl_3$ catalyst (Scheme 1), an RCM product (**3n**) was obtained in 22% yield with recovery of reactant in 76% yield. However, no reaction was observed in the presence of Au(I) catalyst. Treatment of 1,6-diene (**1o**) under the same reaction conditions gave no reaction product. Thus, the $GaCl_3$- and Au(I)-catalyzed cycloisomerization were unique to allenyne substrates.

When allenyne **1a**-*d* with the alkyne terminus deuterated was used, the deuterium was labeled at the 1-position of the produced

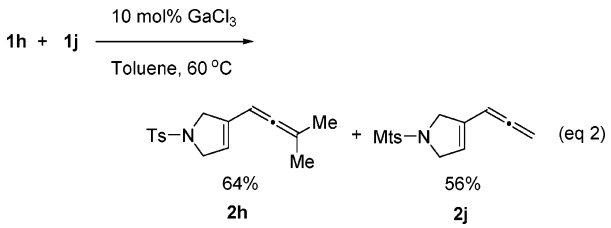
SCHEME 1



allene (eq 1). Murakami et al.[11] also observed the formation of the same deuterated reaction product.



Next, when a crossover reaction using a mixture of **1h** and **1j** was carried out in the presence of $GaCl_3$, no crossover products were obtained (eq 2). This observation was quite different from the results observed in the molybdenum-catalyzed reaction, where the crossover products were isolated.[6]



A general mechanistic view has so far remained elusive. However, our experimental observations suggest that the mechanism will be different from that proposed by Murakami[11] but will follow the general process depicted by Chatani[6] (Scheme 2).[12]

In conclusion, we have shown that the unprecedented $GaCl_3$- and Au(I)-catalyzed cycloisomerization of allenyne systems is a highly versatile tool for obtaining products that cannot be easily attained with other metals. Both catalytic systems are quite effective for terminal 1,6-allenynes. However, they showed different reactivities toward allenynes with di-substituents at the allenic terminal carbon.

Experimental Section

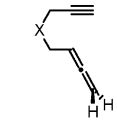
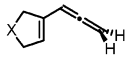
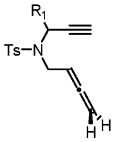
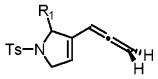
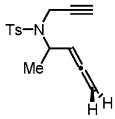
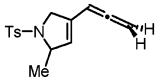
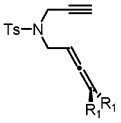
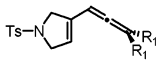
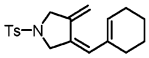
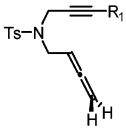
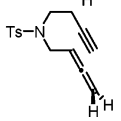
General Procedure for $GaCl_3$-Catalyzed Metathesis of Allenyne. To a flame-dried 10 mL Schlenk containing 5 mL of toluene were added $GaCl_3$ (10 mol %, 14 mg) and allenyne (0.7 mmol) sequentially. After the reactant disappeared, 1 mL of diisopropylamine was added. After the reaction mixture was quenched, the solvent was removed under reduced pressure. Flash column chromatography gave the product.

General Procedure for AuCl(PPh_3)/$AgSbF_6$-Catalyzed Metathesis of Allenyne. To a flame-dried 10 mL Schlenk containing

(11) Murakami, M.; Kadowaki, S.; Matsuda, T. *Org. Lett*. **2005**, *7*, 3953.

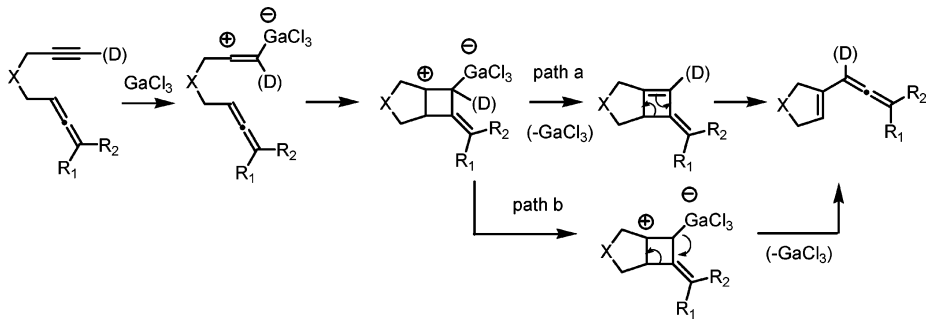
(12) One of the referees suggested an alternative, path "b", as a possible reaction path.

TABLE 2. $GaCl_3$- and $[Au(PPh_3)]SbF_6$-Catalyzed Metathesis of Allenyne[a]

Entry	Reactant	Product	Catalyst	T(°C)	t	Yield(%)[b]
1	 X= NTs (**1a**)	 X= NTs (**2a**)	$GaCl_3$	20	2 h	81
2	(**1a**)	(**2a**)	$[Au(PPh_3)]SbF_6$	20	30 min	75
3	X= NMts[c] (**1b**)	X= NMts (**2b**)	$GaCl_3$	60	30 min	73
4	X=$C(SO_2Ph)_2$ (**1c**)	X=$C(SO_2Ph)_2$ (**2c**)	$GaCl_3$	20	2 h	73
5	(**1c**)	(**2c**)	$[Au(PPh_3)]SbF_6$	20	30 min	56
6	 R_1=Me (**1d**)	 R_1=Me (**2d**)	$GaCl_3$	60	1 h	87
7	(**1d**)	(**2d**)	$[Au(PPh_3)]SbF_6$	20	30 min	78
8	R_1=Et (**1e**)	R_1=Et (**2e**)	$GaCl_3$	60	1 h	65
9	R_1=Ph (**1f**)	R_1=Ph (**2f**)	$GaCl_3$	60	1 h	58
10	(**1f**)	(**2f**)	$[Au(PPh_3)]SbF_6$	20	30 min	62
11	 (**1g**)	 (**2g**)	$GaCl_3$	20	2 h	77
12	(**1g**)	(**2g**)	$[Au(PPh_3)]SbF_6$	20	30 min	75
13[c]	 R_1=Me (**1h**)	 R_1=Me (**2h**)	$GaCl_3$	20	1.5 h	60
14	R_1=-$(CH_2)_3$- (**1i**)	R_1=-$(CH_2)_3$- (**2i**)	$GaCl_3$	20	1.5 h	53
15	R_1=-$(CH_2)_5$- (**1j**)	R_1=-$(CH_2)_5$- (**2j**)	$GaCl_3$	20	1.5 h	83
16	(**1j**)	 (**3j**)	$[Au(PPh_3)]SbF_6$	20	1 h	38
17	 R_1=Me (**1k**)	N/A	$GaCl_3$	60	24 h	N.R[d]
18	(**1k**)	N/A	$[Au(PPh_3)]SbF_6$	20	24 h	N.R
19	R_1=Ph (**1l**)	N/A	$GaCl_3$	60	24 h	N.R
20	 (**1m**)	N/A	$GaCl_3$	60	24 h	N.R
21	(**1m**)	N/A	$[Au(PPh_3)]SbF_6$	20	24 h	N.R

[a] Condition A: 0.2 g (0.691 mmol) of allenyne and 10 mol % $GaCl_3$ in 5 mL of toluene were used. Condition B: 0.2 g (0.691 mmol) of allenyne, 5 mol % $AuCl(PPh_3)$, and 7 mol % $AgSbF_6$ in 5 mL of CH_2Cl_2 were used. [b] Isolated yield. [c] 20 mol % $GaCl_3$ was used. [d] No reaction.

SCHEME 2



5 mL of CH_2Cl_2 were added $AuCl(PPh_3)$ (5 mol %, 9 mg), $AgSbF_6$ (7 mol %, 10 mg), and allenyne (0.7 mmol) sequentially. After the reactant disappeared, the solvent was removed under reduced pressure. A flash column chromatography gave the product.

3-(Propa-1,2-dienyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2a). ^1H NMR ($CDCl_3$, 300 MHz) δ 2.35 (s, 3 H), 4.02 (m, 2 H), 4.09 (m, 2 H), 4.93 (m, 2 H), 5.42 (s, 1 H), 5.80 (t, J = 6.6 Hz, 1 H), 7.25 (d, J = 8.0 Hz, 2 H), 7.65 (d, J = 8.2 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.7, 54.8, 55.7, 78.5, 87.8, 120.7, 127.6, 130.0, 133.0, 134.2, 143.7, 211.0 ppm. Exact mass for ($C_{14}H_{15}N_1S_1O_2$, EI): (calcd) 261.0823, (found) 261.0825.

***N*-(Buta-2,3-dienyl)-2,4,6-trimethyl-*N*-(prop-2-ynyl)benzenesulfonamide (1b).** ^1H NMR ($CDCl_3$, 300 MHz) δ 2.19 (t, J = 2.2 Hz, 1 H), 2.29 (s, 3 H), 2.57 (s, 6 H), 3.85 (m, 2 H), 4.01(d, J = 2.2 Hz, 2 H), 4.77 (m, 2 H), 5.02 (m, 1 H), 6.92 (s, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.0, 22.8, 34.6, 44.7, 73.0, 76.3, 85.3, 132.0, 132.3, 140.5, 142.8, 209.9 ppm. Exact mass for ($C_{16}H_{19}N_1S_1O_2$, EI): (calcd) 289.1137, (found) 289.1133.

1-(Mesitylsulfonyl)-3-(propa-1,2-dienyl)-2,5-dihydro-1*H*-pyrrole (2b). ^1H NMR ($CDCl_3$, 300 MHz) δ 2.29 (s, 3 H), 2.63 (s, 6 H), 4.09 (m, 2 H), 4.13 (m, 2 H), 4.98 (m, 1 H), 5.59 (s, 1 H), 5.94 (m, 1 H), 6.96 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.0,

22.9, 53.3, 54.3, 78.3, 87.8, 120.6, 131.9, 132.6, 132.7, 140.2, 142.5, 210.8. Exact mass for ($C_{16}H_{19}N_1S_1O_2$, EI): (calcd) 289.1137, (found) 289.1140.

1c. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.94 (t, J = 2.1 Hz, 1 H), 2.93 (m, 2 H), 3.03 (d, J = 2.1 Hz, 2 H), 4.63 (m, 2 H), 5.26 (m, 1 H), 7.40 (m, 4 H), 7.53 (d, J = 7.4 Hz, 2 H), 7.95 (d, J = 8.0 Hz, 4 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.9, 29.2, 74.5, 75.7, 76.0, 83.0, 88.4, 128.7, 131.5, 135.0, 136.4, 210.5 ppm. Exact mass for ($C_{20}H_{18}N_1S_1O_2$, EI): (calcd) 386.0647, (found) 386.0651.

2c. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.36−3.37 (m, 4 H), 4.97 (m, 2 H), 5.11 (s, 1 H), 5.66 (m, 1 H), 7.54 (m, 4 H), 7.67 (m, 2 H), 7.97 (m, 4 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 39.1, 39.5, 78.4, 89.3, 91.3, 122.8,129.0, 131.0, 134.9, 135.1, 137.0, 211.3 ppm. Exact mass for ($C_{20}H_{18}N_1S_1O_2$, EI): (calcd) 386.0647, (found) 386.0651.

***N*-(But-3-yn-2-yl)-*N*-(buta-2,3-dienyl)-4-methylbenzenesulfonamide (1d).** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.49 (d, J = 7.1 Hz, 3 H), 2.15 (d, J = 2.2 Hz, 1 H), 2.43 (s, 3 H), 3.78 (m, 1 H), 3.97 (m, 1 H), 4.78 (m, 2 H), 4.90 (dd, J = 7.1, 2.2 Hz, 1 H), 5.23 (m, 1 H), 7.30 (d, J = 8.0 Hz, 2 H), 7.74 (d, J = 7.9 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.8, 22.8, 44.0, 46.0, 73.4, 76.6, 81.5, 89.3, 127.7, 129.7, 136.6, 143.6, 208.9 ppm. Exact mass for ($C_{15}H_{16}N_1S_1O_2$, EI): (calcd) 275.0980, (found) 275.0982.

2-Methyl-3-(propa-1,2-dienyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2d). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.49 (d, J = 6.6 Hz, 3 H), 2.43 (s, 3 H), 4.07−4.24 (m, 2 H), 4.54 (m, 1 H), 5.01 (m, 2 H), 5.45 (s, 1 H), 5.82 (t, J = 6.6 Hz, 1 H), 7.31 (d, J = 8.0 Hz, 2 H), 7.72 (d, J = 7.9 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 22.3, 54.5, 63.0, 78.5, 87.4, 120.3, 127.3, 129.8, 135.1, 143.5, 210.7 ppm. Exact mass for ($C_{15}H_{16}N_1S_1O_2$, EI): (calcd) 275.0980, (found) 275.0982.

***N*-(Buta-2,3-dienyl)-4-methyl-*N*-(pent-1-yn-3-yl)benzenesulfonamide (1e).** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.02 (t, J = 7.7 Hz, 3 H), 1.77 (qd, J = 7.7, 3.3 Hz, 2 H), 2.13 (d, J = 2.2 Hz, 1 H), 2.41 (s, 3 H), 3.72 (m, 1 H), 3.91 (m, 1 H), 4.60 (td, J = 7.6, 2.1 Hz, 1 H), 4.75 (m, 2 H), 5.26 (m, 1 H), 7.28 (d, J = 7.9 Hz, 2 H), 7.73 (d, J = 7.9 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.7, 21.5, 29.0, 44.0, 52.2, 73.8, 76.2, 80.5, 88.9, 127.6, 129.4, 136.5, 143.4, 208.6 ppm. Exact mass for ($C_{16}H_{19}N_1S_1O_2$, EI): (calcd) 289.1137 (found) 289.1135.

2-Ethyl-3-(propa-1,2-dienyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2e). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.82 (t, J = 7.3 Hz, 3 H), 1.78 (m, 1 H), 1.98 (m, 1 H), 2.40 (s, 3 H), 4.11 (m, 2 H), 4.62 (m, 1 H), 4.99 (m, 1 H), 5.48 (m, 1 H), 5.78 (m, 1 H), 7.27 (d, J = 7.8 Hz, 2 H), 7.69 (d, J = 7.8 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.1, 21.5, 26.4, 55.4, 67.5, 78.2, 82.2, 121.5, 127.2, 129.6, 135.1, 135.2, 143.3, 210.4 ppm. Exact mass for ($C_{16}H_{19}N_1S_1O_2$, HRFAB): (calcd) 290.1215, (found) 290.1213.

***N*-(Buta-2,3-dienyl)-4-methyl-*N*-(1-phenylprop-2-ynyl)benzenesulfonamide (1f).** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.40 (d, J = 2.2 Hz, 1 H), 2.44 (s, 3 H), 3.71−3.77 (m, 2 H), 4.42 (m, 1 H), 4.51 (m, 1 H), 4.77 (m, 1 H), 6.11 (d, J = 2.2 Hz, 1 H), 7.33 (m, 5 H), 7.60 (d, J = 6.9 Hz, 2 H), 7.79 (d, J = 8.0 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.8, 44.6, 53.3, 76.0, 78.4, 87.9, 128.0, 128.3, 128.6, 128.63, 128.7, 129.7, 136.0, 136.6, 143.8 ppm. Exact mass for ($C_{20}H_{19}N_1S_1O_2$, EI): (calcd) 337.1137, (found) 337.1137.

2-Phenyl-3-(propa-1,2-dienyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2f). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.42 (s, 3 H), 4.34 (m, 1 H), 4.45 (m, 1 H), 4.61 (m, 1 H), 4.91 (m, 1 H), 5.59 (m, 1 H), 5.76 (m, 1 H), 5.81 (m, 1 H), 7.17 (d, J = 8.0 Hz, 2 H), 7.27 (m, 5 H), 7.43 (d, J = 8.0 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ ?21.6, 54.9, 55.0, 70.3, 78.7, 87.2, 121.2, 127.2, 127.9, 128.2, 128.5, 129.5, 136.2, 136.5, 140.0, 143.0, 211.4 ppm. Exact mass for ($C_{20}H_{19}N_1S_1O_2$, EI): (calcd) 337.1137, (found) 337.1137.

4-Methyl-*N*-(penta-3,4-dien-2-yl)-*N*-(prop-2-ynyl)benzenesulfonamide (1g). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.26 (d, J = 6.2 Hz, 3 H), 2.17 (t, J = 2.2 Hz, 1 H), 2.43 (s, 3 H), 3.96 (dd, J = 18.5, 2.2 Hz, 1 H), 4.15 (dd, J = 18.5, 2.2 Hz, 1 H), 4.60 (m, 1 H), 4.82 (m, 2 H), 5.07 (q, J = 6.2 Hz, 1 H), 7.29 (d, J = 8.0 Hz, 2 H), 7.80 (d, J = 8.0 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.1, 21.7, 32.2, 52.0, 72.4, 78.1, 80.4, 91.8, 127.7, 129.7, 137.8, 143.6, 208.9 ppm. Exact mass for ($C_{15}H_{17}N_1S_1O_2$, EI): (calcd) 275.0980, (found) 275.0982.

2-Methyl-4-(propa-1,2-dienyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2g). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.41 (d, J = 6.2 Hz, 3 H), 2.42 (s, 3 H), 4.04 (m, 1 H), 4.16 (m, 1 H), 4.51 (m, 1 H), 4.99 (m, 2 H), 5.40 (m, 1 H), 5.88 (m, 1 H), 7.31 (d, J = 8.0 Hz, 2 H), 7.72 (d, J = 8.0 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.7, 23.0, 55.3, 64.0, 78.5, 87.7, 127.1, 127.6, 129.9, 131.4, 135.0, 143.6, 211.1 ppm. Exact mass for ($C_{15}H_{17}N_1S_1O_2$, EI): (calcd) 275.0980, (found) 275.0982.

***N*-(3-Cyclobutylideneallyl)-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (1i).** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.93 (m, 2 H), 2.01 (t, J = 2.2 Hz, 1 H), 2.42 (s, 3 H), 2.81−2.87 (m, 4 H), 3.81 (s, 1 H), 3.83 (s, 1 H), 4.13 (d, J = 2.2 Hz, 2 H), 4.98 (m, 1 H), 7.28 (d, J = 8.0 Hz, 2 H), 7.73 (d, J = 8.0 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.5, 21.6, 29.6, 35.6, 46.6, 73.4, 77.2, 87.8, 103.0, 127.7, 129.5, 136.1, 143.5, 197.5 ppm. Exact mass for ($C_{17}H_{19}N_1S_1O_2$, EI): (calcd) 301.1137, (found) 301.1134.

3-(2-Cyclobutylidenevinyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2i). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.91 (m, 2 H), 2.33 (s, 3 H), 2.80 (m, 4 H), 4.03 (m, 2 H), 4.06 (m, 2 H), 5.38 (s, 1 H), 5.73 (m, 1 H), 7.23 (d, J = 8.0 Hz, 2 H), 7.64 (d, J = 8.0 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.4, 21.5, 29.9, 54.8, 55.5, 89.8, 103.9, 120.1, 127.2, 129.7, 134.3, 135.2, 143.4, 197.4 ppm. Exact mass for ($C_{17}H_{19}N_1S_1O_2$, EI): (calcd) 301.1137, (found) 301.1136.

(*E*)-3-(Cyclohexenylmethylene)-4-methylene-1-tosylpyrrolidine (3j). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.61 (m, 4 H), 1.93 (m, 2 H), 2.06 (m, 2 H), 2.45 (s, 3 H), 3.81 (m, 2 H), 3.85 (m, 2 H), 5.01 (s, 1 H), 5.02 (s, 1 H), 5.41−5.46 (m, 2 H), 7.30 (d, J = 8.0 Hz, 2 H), 7.67 (d, J = 8.0 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.7, 22.3, 23.1, 25.4, 28.9, 45.8, 49.8, 113.3, 120.7, 126.6, 128.1, 129.7, 133.9, 136.3, 136.5, 141.4, 143.7 ppm. Exact mass for ($C_{19}H_{23}N_1S_1O_2$, EI): (calcd) 329.1449, (found) 329.1448.

***N*-(But-2-ynyl)-*N*-(buta-2,3-dienyl)-4-methylbenzenesulfonamide (1k).** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.49 (t, J = 2.6 Hz, 3 H), 2.35 (s, 3 H), 3.77 (m, 2 H), 4.00 (q, J = 2.6 Hz, 2 H), 4.69 (m, 2 H), 4.97 (m, 1 H), 7.21 (d, J = 8.0 Hz, 2 H), 7.65 (d, J = 8.0 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ ?3.4, 21.7, 36.6, 45.7, 71.8, 81.7, 85.8, 128.0, 129.5, 136.4, 143.5, 209.9 ppm. Exact mass for ($C_{15}H_{17}N_1S_1O_2$, EI): (calcd) 275.0980, (found) 275.0981.

***N*-(But-3-ynyl)-*N*-(buta-2,3-dienyl)-4-methylbenzenesulfonamide (1m).** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.87 (t, J = 2.3 Hz, 1 H), 2.29 (s, 3 H), 2.36 (td, J = 7.6 Hz, 2.3 Hz, 2 H), 3.22 (t, J = 7.6 Hz, 2 H), 3.77 (m, 2 H), 4.60 (m, 2 H), 4.83 (m, 1 H), 7.17 (d, J = 8.0 Hz, 2 H), 7.57 (d, J = 8.0 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ ?19.4, 21.7, 46.0, 47.5, 70.3, 76.7, 81.2, 86.1, 128.5, 129.9, 137.2, 143.6, 209.7 ppm. Exact mass for ($C_{15}H_{17}N_1S_1O_2$, EI): (calcd) 275.0980, (found) 275.0977.

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Supporting Information Available: Characterization of new compounds and ^{1}H and ^{13}C NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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