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Au(I)-Catalyzed Cyclization of Enynes Bearing an Olefinic Cycle

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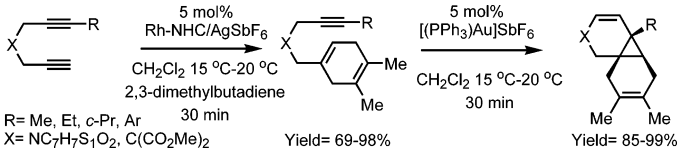

Gold(I)-catalyzed cyclization of enynes containing an olefinic cycle has been studied. The introduction of an olefinic ring instead of a terminal alkene in enynes dramatically increased the yield of the reaction. Enynes having an olefinic cycle were prepared by a rhodium-catalyzed intermolecular [4 + 2] cycloaddition of diynes with butadiene. Consecutive rhodium-catalyzed Diels−Alder/gold(I)-catalyzed cycloisomerization reactions were integrated in a one-pot reaction.

Introduction

Transition-metal-catalyzed cycloisomerizations of enynes provide rapid and efficient access to a variety of cyclic structural motifs with a broad range of synthetically useful applications.[1] Among them, the latest advances in gold(I)[2] catalysis are particularly noteworthy. For this reason, gold complexes have recently emerged as valuable catalysts in the conversion of various types of enynes into a range of useful structural motifs.[3] Under these circumstances, while we were pursuing the improvement of the gold(I)-catalyzed enyne cycloisomerization yields, we found that the introduction of an olefinic cycle instead of a terminal alkene dramatically improved the yield of the reaction. Herein, we report our results on the gold(I)-catalyzed cycloisomerization of enynes having an olefinic cycle and integration of the generation and cycloisomerization of enynes bearing an olefinic cycle into a "one-pot" transformation.

Results and Discussion

For reference purposes, the yields from the cycloisomerization of enynes obtained in our laboratory are summarized in Scheme 1. Interestingly, when the reaction time was lengthened, a reductive dimerization occurred. The reductive dimerized product (**2a′**) was confirmed by an X-ray study (Figure 1). We surmised that the extra hydrogens found in **2a′** was derived from adventitious water under our reaction conditions. When an enyne (**3e**) bearing a cyclic olefin at the terminal olefin and an internal alkyne was used, the yield of the reaction was dramatically improved to 98% within 30 min. Moreover, no dimerization was observed. This dramatic increase in the yield was presumably in part due to the conformational restriction of the carbon−carbon double bond in the cyclic olefin compared to that of the C═C bond in the terminal olefin.

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(3) (a) Gagosz, F. *Org. Lett.* **2005**, *7*, 4129−4132. (b) Mezailles, N.; Ricard, L.; Gagosz, F. *Org. Lett.* **2005**, *7*, 4133−4136. (c) Muñoz, M.; Adrio, J.; Carretero, J. C.; Echavarren, A. M. *Organometallics* **2005**, *24*, 1293−1300. (d) Zhang, L.; Kozmin, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 6962−6963. (e) Luzung, M. R.; Markham, J. P.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 10858−10859. (f) Zhang, L.; Kozmin, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 11806−11807. (g) Mamane, V.; Gress, T.; Krause, H.; Fürstner, A. *J. Am. Chem. Soc.* **2004**, *126*, 8654−8655.

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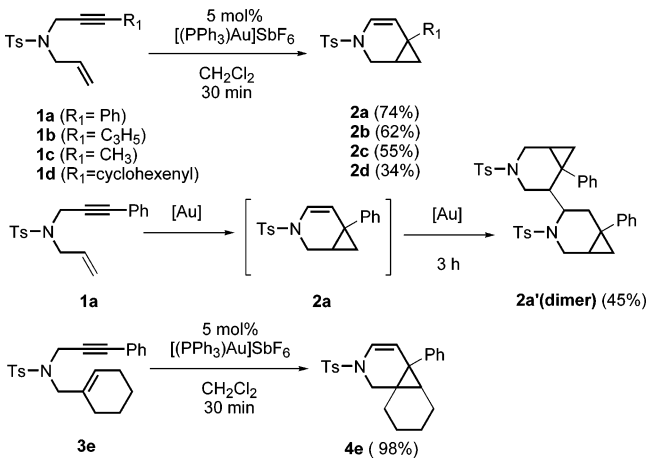
SCHEME 1

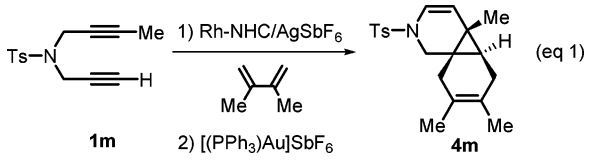


The steric hindrance might enable the C=C bond to participate easily in the cycloisomerization. Similar tricyclic compounds bearing a cyclopropane had been reported by Trost's, Fürstner's, and Echavarren's groups.[2a,c,4] They studied a platinum- and gold-catalyzed cycloisomerization of enynes containing a heteroatom in the tether and a cyclic olefin. Thus, we decided to study the gold(I)-catalyzed cycloisomerization of enynes bearing a cyclic olefin in detail.

Enynes (**3**) bearing a cyclic olefin used in this study were easily synthesized by a Diels−Alder reaction of suitable diynes (**1**) with 2,3-dimethylbutadiene in the presence of [Rh(NHC)-(cod)Cl]/$AgSbF_6$ (NHC=*N*,*N*′-bis(2,6-diisopropropyl)imidazole-2-yilidene) (Table 1).[5] Most of the Diels−Alder reactions studied went to completion within 30 min in high yields. The reaction time and yield were dependent upon the substituent on the alkyne unit. Compared to those of alkyl substituents, relatively high yields were obtained for aryl substitutents. The rhodium does not catalyze the second cycloisomerization under the reaction conditions.

Next, we screened the gold-catalyzed cycloisomerization of various enynes (**3**) (Table 2). As shown in Table 2, the enynes studied produced quite good results. Formation of the cyclopropanated compounds (**4**) was confirmed by an X-ray study of **4i** (Figure 2). However, when R_1 was a cyclopropyl (entry 10), the expected product (**4o**) was obtained in 46% yield with the concomitant formation of an isomerized 5,4,6-tricyclic diene compound (**5**) in 48% yield. Similar gold- and platinum-catalyzed [2 + 2] cycloaddition reactions of enynes were reported by Echavarren's and Füstner's groups.[6] Moreover, when R_1 was a cyclohexenyl, a 6,5,6,6-tetracyclic triene compound (**6**) was obtained in 85% yield. The structures of **5** and **6** were confirmed by ^1H and ^{13}C NMR studies, including HMBC and HMQC.

Next we investigated the possibility of integrating the Diels−Alder reaction and the cycloisomerization into a "one-pot" transformation (eq 1).



In a tandem reaction, each catalyst must be compatible with the substrates, intermediates, and other catalysts and must also exhibit reaction sequence selectivity.[7] Thus, when the tandem reaction was initiated, both catalysts, Rh and Au, coexisted with the substrates. Diyne **1m** (0.162 g, 0.62 mmol) and 2,3-dimethylbutadiene (0.11 mL, 0.93 mmol) were reacted in the presence of [Rh(NHC)(cod)Cl] (20 mg, 5 mol %), $Au(PPh_3)Cl$ (15 mg, 5 mol %), and $AgSbF_6$ (30 mg, 15 mol %) in dichloromethane at room temperature. After the reaction, **4m** was obtained in a 50% yield. The overall yield was low compared to those of the two separate reactions combined (69% and 99%, respectively), presumably due to the decomposition of diynes in the presence of $Au(PPh_3)Cl/AgSbF_6$. Thus, to improve the yield of the reaction, a one-pot tandem reaction via a sequential addition of rhodium(I) and gold(I) catalysts was tried. After completion of the Diels−Alder reaction of **1m** (0.162 mg, 0.62 mmol) in the presence of [Rh(NHC)(cod)Cl] (20 mg, 5 mol %)/$AgSbF_6$ (15 mg, 7 mol %), $Au(PPh_3)Cl$ (15 mg, 7 mol %) and $AgSbF_6$ (13 mg, 7 mol %) were added, and the whole mixture was stirred at the same temperature for 1 h. Chromatography on a silica gel column eluting with hexane/ethyl acetate (v/v, 3:1) gave **4m** in a 66% yield. Thus, a two-step, one-pot reaction was realized in dichloromethane in a reasonable period of time.

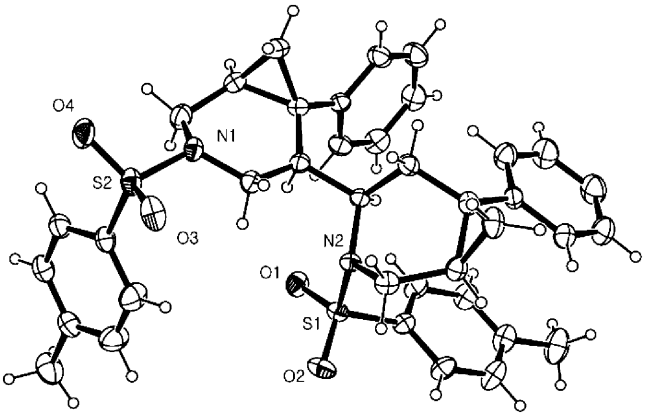


FIGURE 1. X-ray structure of **2a′** (30% thermal ellipsoid).

Scheme 2 shows that the product distributions depended on the structure of the substrates. When an enyne (**1r**) with a terminal alkyne was subjected to the reaction conditions, polymerized compounds were obtained before a gold-catalyzed reaction occurred. Reaction of diphenyl-substituted diyne (**1s**) with the rhodium catalyst yielded an enyne (**3s**) in 78% yield. However, treatment of **1s** with the gold catalyst produced an intramolecular [3 + 2] cycloadduct, **7**, in 85% yield.[8a] Diynes (**1t** and **1u**) having tethers lengthened by one carbon were also studied. Diels−Alder reaction products (**3t** and **3u**) were obtained in 98% and 85% yields, respectively. However, they

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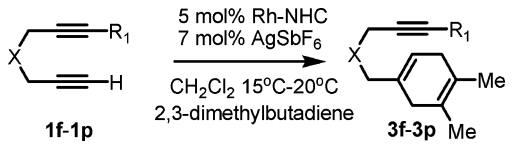
(6) (a) Nieto-Oberhuber, C.; López, S.; Muñoz, M. P.; Cárdenas, D. J.; Buñuel, E.; Nevado, C.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 6146−6148. (b) Fürstner, A.; Davies, P. W.; Gress, T. *J. Am. Chem. Soc.* **2005**, *127*, 8244−8245. (c) Trost, B. M.; Chang, V. K. *Synthesis* **1993**, *8*, 824−832.

(7) For recent reviews, see: (a) Wasilke, J.-C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001−1020. (b) Fogg, D. E.; dos Santos, E. N. *Coord. Chem. Rev.* **2004**, *248*, 2365−2379. (c) Lee, J. M.; Na, Y.; Han, H.; Chang, S. *Chem. Soc. Rev.* **2004**, *33*, 302−312. (d) Ajamian, A.; Gleason, J. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 3754−3760.

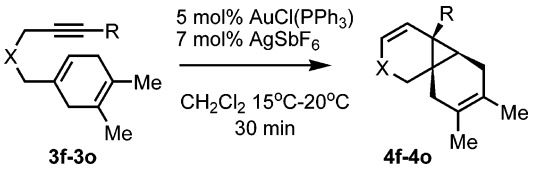
TABLE 1. Rh(I)-Catalyzed Intermolecular [4 + 2] Cycloaddition of Diynes[a]



entry		X	R_1	time	yield (%)[b]
1	**1f**	NTs	Ph	30 min	98 (**3f**)
2	**1g**	$C(CO_2Me)_2$	Ph	30 min	85 (**3g**)
3	**1h**	NTs	*p*-iolyl	30 min	89 (**3h**)
4	**1i**	NTs	4-methoxyphenyl	30 min	82 (**3i**)
5	**1j**	NTs	2-bromophenyl	30 min	84 (**3j**)
6	**1k**	NTs	3,5-dimethylphenyl	30 min	86 (**3k**)
7	**1i**	NTs	naphthalene	30 min	97 (**3l**)
8	**1m**	NTs	Me	30 mn	69 (**3m**)
9	**1n**	NTs	Et	30 min	81 (**3n**)
10	**1o**	NTs	*c*-Pr(C_3H_5)	3 h	68 (**3o**)
11	**1p**	NTs	cyclohexynyl	1 h	58 (**3p**)

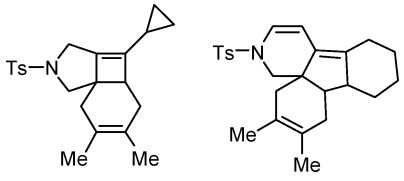
[a] 0.52 mmol of substrate (0.1 M), 5 mol % of Rh−NHC, and 7 mol % of $AgSbF_6$ were used. [b] Isolated yield.

TABLE 2. Au(I)-Catalyzed Cycloisomerization of Enynes[a]



entry		X	R_1	time (min)	yield (%)[b]
1	**3f**	NTs	Ph	30	99 (**4f**)
2	**3g**	$C(CO_2Me)_2$	Ph	30	N/A[c]
3	**3h**	NTs	*p*-tolyl	30	91 (**4h**)
4	**31**	NTs	4-methoxyphenyl	30	85 (**4i**)
5	**3j**	NTs	2-bromophenyl	30	93 (**4j**)
6	**3k**	NTs	3,5-dimethylphenyl	30	85 (**4k**)
7	**3l**	NTs	naphthalene	30	85 (**4l**)
8	**3m**	NTs	Me	30	99 (**4m**)
9	**3n**	NTs	Et	30	98 (**4n**)
10	**3o**	NTs	*c*-Pr(C_3H_5)	30	46 (**4o**)

[a] 0.52 mmol of substrate (0.1 M), 5 mol % of $(PPh_3)AuCl$, and 7 mol % of $AgSbF_6$ were used. [b] Isolated yield. [c] Polymerized products were obtained.



were completely inert to the cycloisomerization. Thus, the chain length between a C−C triple bond and a C−C double bond seems to be quite important for a successful reaction.

The above studies dealt only with an intermolecular Diels−Alder reaction product. As an extension of the above study, we devised an intramolecular Diels−Alder reaction to generate an enyne with a cyclic olefin (Scheme 3). Thus, the synthesized diendiyne **1v** was first treated with $[Rh(NHC)(cod)Cl]/AgSbF_6$. After reaction, the expected enyne **2v** having a cyclic olefin was isolated in 98% yield. The structure of **2v** was confirmed by an X-ray diffraction study (see the Supporting Information). Treatment of **2v** with $[(PPh_3)Au]Cl$ and $AgSbF_6$ afforded the expected tetracyclic diene compound **4v** in 93% yield.

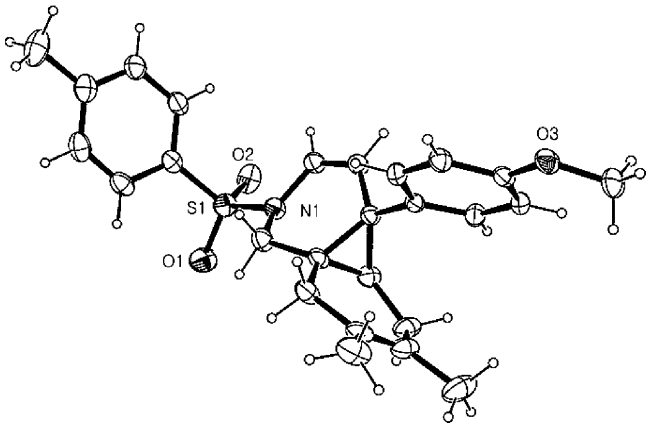
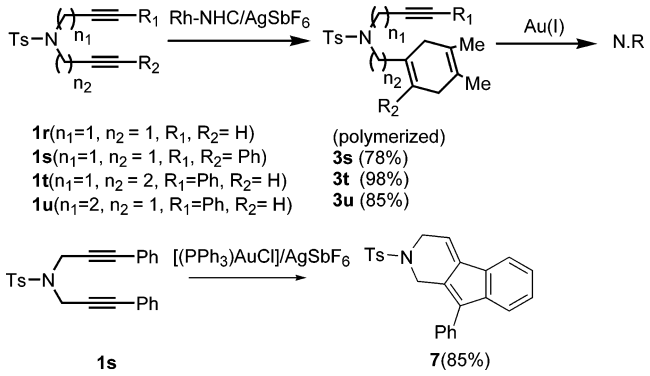
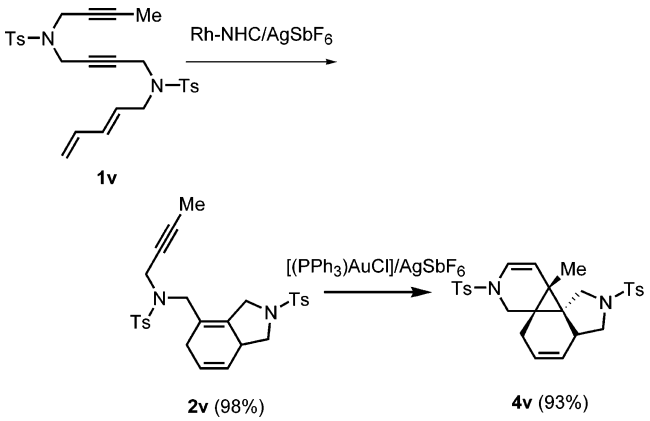


FIGURE 2. X-ray structure of **4i** (30% thermal ellipsoid).

SCHEME 2



SCHEME 3



Conclusion

We have developed a highly efficient gold-catalyzed cycloisomerization of enynes bearing a cyclic olefin. The reaction proceed at room temperature, in contrast with that found in reactions catalyzed by Pt(II), which require heating at 80 °C. This catalytic process provides rapid access to highly fused polycyclic diene compounds.

(8) Recently, the formation of **7** was reported. (a) Lian, J.-J.; Chen, P.-C. Ting, H.-P. Liu, R.-S. *J. Am. Chem. Soc.* **2006**, *128*, 11372−11373. Similar reactions were reported by Echavarren's, Gagosz's, and Shibata's groups. See ref 3b. (b) Nieto-Oberhuber, C.; López, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178−6179. (c) Shibata, T.; Fujiwara, R.; Takano, D. *Synlett* **2005**, 2062−2066.

Experimental Section

General Procedure for Rh−NHC-Catalyzed Intermolecular [4 + 2] Cycloaddition. To a flame-dried 15 mL Schlenk flask capped with a rubber septum was injected 5 mL of dichloromethane via syringe under N_2 flow. Rh−NHC (13 mg, 5 mol %) and $AgSbF_6$ (16 mg, 7 mol %) were added sequentially. The Rh−NHC solution was stirred for 10 min. A diene (1.5 equiv, 1 mmol) was injected in the flask by 1 mL syringe. A diyne (0.52 mmol) was put into the flask under N_2 flow. The reaction was monitored by thin-layer chromatography. After the reactant disappeared, solvent was removed under reduced pressure. Flash chromatography on a silica gel eluting with hexane and ethyl acetate (v/v, 10:1) gave the product.

General Procedure for Au(I)-Catalyzed Cycloisomerization of Enyne. To a flame-dried 15 mL Schlenk flask capped with a rubber septum was injected 5 mL of dichloromethane via syringe under N_2 flow. $(PPh_3)AuCl$ (13 mg, 5 mol %) and $AgSbF_6$ (16 mg, 7 mol %) were added sequentially. The Au solution was stirred for 10 min. A enyne (0.52 mmol) was put into the flask under N_2 flow. The reaction was monitored by thin-layer chromatography. After the reactant disappeared, solvent was removed under reduced pressure. Flash chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 10:1) gave the product.

2a′: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.60 (t, J = 5.0 Hz, 1 H), 0.70 (m, 1 H), 0.90−1.10 (m, 3 H), 1.46 (m, 1 H), 1.66 (dd, J = 4.8 Hz, 8.9 Hz, 1 H), 2.13 (s, 3 H), 2.43 (s, 3 H), 2.72 (m, 2 H), 3.09 (dd, J = 3.2 Hz, 11.2 Hz, 1 H), 3.93 (m, 2 H), 4.39 (dd, J = 7.4 Hz, 16.0 Hz, 1 H), 5.83 (m, 2 H), 6.68 (m, 2 H), 6.80 (m, 2 H), 6.90 (m, 2 H), 7.28 (m, 2 H), 7.36 (m, 7 H), 7.80 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.6, 20.0, 21.6, 21.8, 23.2, 23.5, 25.6, 26.6, 36.9, 41.1, 46.0, 53.7, 118.8, 124.3, 124.9, 126.5, 127.0, 127.3, 127.7, 127.9, 128.7, 129.3, 130.1, 134.1, 135.8, 141.5, 142.8, 142.9, 144.1; exact mass for $C_{38}H_{40}N_2S_2O_4$ (EI) calcd 652.2429, found 652.2424; CCDC no. 603263; IR (cm^{-1}) 2956 (w), 2863 (w), 2121 (w), 1965 (w), 1915 (w), 1737 (br), 1658 (s), 1597 (s).

***N*-Allyl-*N*-(3-cyclopropylprop-2-ynyl)-4-methylbenzenesulfonamide (1b):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.28 (m, 1 H), 0.59 (m, 1 H), 0.91 (m, 1 H), 2.41 (s, 3 H), 3.77 (d, J = 6.3 Hz, 1 H), 4.00 (d, J = 1.7 Hz, 1 H), 5.22 (m, 2 H), 5.70 (m, 1 H), 7.28 (d, J = 8.1 Hz, 2 H), 7.69 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −0.9, 7.9, 21.6, 36.4, 49.0, 67.6, 89.4, 119.7, 127.8, 129.4, 132.2, 136.2, 143.4; exact mass for $C_{16}H_{19}N_1S_1O_2$ (EI) calcd 289.1137, found 289.1139; IR (cm^{-1}) 2944 (w), 2848 (w), 2224 (m), 1721 (s), 1635 (s), 1590 (w).

6-Cyclopropyl-3-tosyl-3-azabicyclo[4.1.0]hept-4-ene (2b): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.02 (m, 2 H), 0.31 (m, 2 H), 0.40 (m, 1 H), 0.54 (m, 1 H), 1.00 (m, 1 H), 2.44 (s, 3 H), 2.99 (dd, J = 2.5 Hz, 11.5 Hz, 1 H), 3.87 (d, J = 11.4 Hz, 1 H), 5.37 (d, J = 8.1 Hz, 1 H), 6.35 (d, J = 8.1 Hz, 1 H), 7.33 (d, J = 8.4 Hz, 1 H), 7.67 (d, J = 8.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 2.1, 2.2, 15.1, 17.1, 18.0, 21.6, 23.4, 40.9, 116.0, 120.4, 127.0, 129.7, 134.9, 143.7; exact mass for $C_{16}H_{19}N_1S_1O_2$ (EI) calcd 289.1137, found 289.1137; IR (cm^{-1}) 2960 (w), 2912 (w), 2840 (m), 2288 (w), 1615 (s), 1580 (w).

***N*-Allyl-*N*-(3-cyclohexenylprop-2-ynyl)-4-methylbenzenesulfonamide (1d):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.53 (m, 4 H), 1.80 (m, 2 H), 2.02 (m, 2 H), 2.41 (s, 3 H), 3.81 (d, J = 6.4 Hz, 2 H), 4.18 (s, 2 H), 5.26 (m, 2 H), 5.75 (m, 2 H), 7.29 (d, J = 8.1 Hz, 2 H), 7.73 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 21.6, 22.3, 29.0, 36.8, 49.1, 78.8, 87.7, 119.86, 119.9, 127.9, 129.6, 132.2, 135.2, 136.2, 143.4; exact mass for $C_{19}H_{23}N_1S_1O_2$ (EI) calcd 329.1450, found 329.1449; IR (cm^{-1}) 2912 (w), 2864 (w), 2208 (m), 1638 (w), 1587 (w).

6-Cyclohexenyl-3-tosyl-3-azabicyclo[4.1.0]hept-4-ene (2d): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.53 (m, 1 H), 0.98 (m, 1 H), 1.55 (m, 5 H), 1.87 (m, 2 H), 1.97 (m, 2 H), 2.44 (s, 3 H), 3.05 (dd, J = 2.7 Hz, 11.6 Hz, 1 H), 3.92 (d, J = 11.4 Hz, 1 H), 5.31 (d, J = 8.3 Hz, 1 H), 5.46 (m, 1 H), 6.37 (d, J = 8.2 Hz, 1 H), 7.32 (d, J = 8.1 Hz, 2 H), 7.67 (d, J = 8.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.3, 21.7, 22.5, 23.0, 23.4, 25.2, 25.3, 26.7, 41.1, 114.8, 120.9, 122.3, 127.2, 129.9, 135.1, 138.6, 143.8; exact mass for $C_{19}H_{23}N_1S_1O_2$ (EI) calcd 329.1450, found 329.1451; IR (cm^{-1}) 2912 (w), 2864 (w), 1620 (s), 1530 (s).

***N*-(Cyclohexenylmethyl)-4-methyl-*N*-(3-phenylprop-2-ynyl)-benzenesulfonamide (3e):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.64 (m, 4 H), 2.05 (m, 4 H), 2.33 (s, 3 H), 3.75 (s, 2 H), 4.24 (s, 2 H), 5.74 (s, 1 H), 7.05 (d, J = 6.6 Hz, 2 H), 7.26 (m, 5 H), 7.78 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 22.4, 22.7, 25.4, 26.1, 36.3, 53.2, 82.0, 85.7, 122.4, 127.8, 127.9, 128.2, 128.4, 129.6, 131.6, 131.9, 136.2, 143.4; exact mass for $C_{23}H_{25}N_1S_1O_2$ (EI) calcd 379.1606, found 379.1601; IR (cm^{-1}) 2930 (w), 2832 (w), 2210 (m), 2128 (w), 1638 (w), 1587 (w).

4e: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.65 (m, 2 H), 1.02 (m, 2 H), 1.24 (m, 1 H), 1.66 (m, 4 H), 2.45 (s, 3 H), 2.90 (d, J = 11.6 Hz, 1 H), 3.91 (d, J = 11.6 Hz, 1 H), 5.19 (d, J = 8.0 Hz, 1 H), 6.24 (d, J = 8.0 Hz, 1 H), 7.13 (d, J = 6.8 Hz, 1 H), 7.20 (t, J = 7.0 Hz, 2 H), 7.27 (d, J = 7.8 Hz, 2 H), 7.34 (d, J = 8.2 Hz, 2 H), 7.69 (d, J = 8.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.6, 20.9, 21.2, 21.6, 25.1, 28.6, 29.2, 32.7, 47.0, 118.7, 120.5, 126.4, 127.1, 128.6, 129.9, 130.6, 134.9, 140.4, 143.7; exact mass for $C_{23}H_{25}N_1S_1O_2$ (EI) calcd 379.1606, found 379.1601; IR (cm^{-1}) 2948 (w), 2822 (w), 1620 (s), 1515 (s).

4f: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.03 (s, 3 H), 1.08 (s, 3 H), 1.33 (d, J = 4.7 Hz, 1 H), 2.16 (m, 4 H), 2.45 (s, 3 H), 2.94 (d, J = 11.5 Hz, 1 H), 3.93 (d, J = 11.5 Hz, 1 H), 5.16 (d, J = 7.9 Hz, 1 H), 6.28 (d, J = 7.9 Hz, 1 H), 7.00 (d, J = 7.8 Hz, 2 H), 7.15 (m, 2 H), 7.35 (m, 3 H), 7.69 (d, J = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.4, 21.6, 27.6, 29.5, 29.8, 32.7, 34.0, 46.0, 119.0, 119.2, 122.2, 123.5, 126.1, 127.1, 127.5, 127.8, 129.9, 134.9, 140.5, 143.7; exact mass for $C_{25}H_{27}S_1O_2N_1$ (EI) calcd 393.1762, obsd 393.1764; IR (cm^{-1}) 3080 (w), 3057 (w), 3022 (w), 2997 (w), 2908 (m), 2862 (m), 1948 (w), 1925 (w), 1899 (w), 1813 (w), 1699 (w), 1628 (s), 1595 (s).

3g: IR (cm^{-1}) 1754; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.60 (s, 3 H), 1.61 (s, 3 H), 2.40 (m, 2 H), 2.62 (m, 2 H), 2.87 (m, 2 H), 3.04 (s, 2 H), 3.76 (s, 6 H), 5.61 (s, 1 H), 7.28 (m, 3 H), 7.38 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.3, 18.6, 34.1, 36.9, 39.4, 52.9, 57.0, 84.0, 85.0, 122.8, 122.9, 123.4, 125.2, 128.1, 128.4, 129.8, 131.8, 171.1; exact mass for $C_{23}H_{26}O_4$ (EI) calcd 366.1831, found 366.4501.

4-Methyl-*N*-(prop-2-ynyl)-*N*-(3-*p*-tolylprop-2-ynyl)benzenesulfonamide (1h): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.20 (s, 1 H), 2.33 (s, 3 H), 2.37 (s, 3 H), 4.20 (s, 2 H), 4.40 (s, 2 H), 7.06 (m, 4 H), 7.27 (d, J = 7.1 Hz, 2 H), 7.75 (d, J = 8.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.43, 21.46, 36.5, 37.2, 73.9, 80.6, 86.0, 100.0, 119.1, 127.9, 128.9, 129.6, 131.5, 135.4, 138.7, 143.8; exact mass for $C_{20}H_{19}N_1S_1O_2$ (EI) calcd 337.1136, found 337.1139; IR (cm^{-1}) 2966 (w), 2914 (w), 2239 (m), 2123 (w), 1655 (w), 1595 (s).

***N*-((4,5-Dimethylcyclohexa-1,4-dienyl)methyl)-4-methyl-*N*-(3-*p*-tolylprop-2-ynyl)benzenesulfonamide (3h):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.63 (s, 3 H), 1.65 (s, 3 H), 2.32 (s, 6 H), 2.63 (s, 4 H), 3.78 (s, 2 H), 4.22 (s, 2 H), 5.71 (s, 1 H), 6.94 (d, J = 7.5 Hz, 2 H), 7.03 (d, J = 7.5 Hz, 1 H), 7.23 (d, J = 7.9 Hz, 2 H), 7.77 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.1, 18.4, 21.4, 33.7, 33.8, 36.3, 52.3, 81.1, 85.7, 119.3, 122.4, 123.2, 125.1, 127.8, 128.8, 129.4, 129.5, 131.4, 136.2, 138.4, 143.3; exact mass for $C_{26}H_{29}N_1S_1O_2$ (EI) calcd 419.1919, found 419.1924; IR (cm^{-1}) 2970 (w), 2918 (w), 2046 (m), 1606 (s), 1508 (s).

4h: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.05 (s, 3 H), 1.10 (s, 3 H), 1.29 (d, J = 4.6 Hz, 1 H), 2.17 (m, 4 H), 2.25 (s, 3 H), 2.45 (s, 3 H), 2.93 (d, J = 11.5 Hz, 1 H), 3.91 (d, J = 11.5 Hz, 1 H), 5.12 (t, J = 10.5 Hz, 1 H), 6.26 (d, J = 7.9 Hz, 1 H), 6.88 (d, J = 8.0 Hz, 2 H), 6.96 (d, J = 7.8 Hz, 2 H), 7.34 (d, J = 8.0 Hz, 1 H),

7.69 (d, J = 8.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.4, 21.0, 21.6, 27.3, 29.5, 29.8, 32.7, 33.9, 46.1, 118.9, 119.6, 122.1, 123.3, 127.1, 127.4, 128.5, 129.8, 135.1, 135.4, 137.4, 143.6; exact mass for $C_{26}H_{29}N_1S_1O_2$ (EI) calcd 419.1919, found 419.1920; IR (cm^{-1}) 3080 (w), 3057 (w), 3022 (w), 2997 (w), 2908 (m), 2862 (m), 1948 (w), 1925 (w), 1899 (w), 1813 (w), 1699 (w), 1628 (s), 1595 (s).

***N*-(3-(4-Methoxyphenyl)prop-2-ynyl)-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (1i):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.20 (t, J = 2.2 Hz, 1 H), 2.36 (s, 3 H), 3.79 (s, 3 H), 4.19 (d, J = 2.2 Hz, 1 H), 4.38 (s, 2 H), 6.77 (d, J = 8.7 Hz, 2 H), 7.11 (d, J = 8.7 Hz, 2 H), 7.27 (d, J = 8.0 Hz, 2 H), 7.74 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 36.5, 37.3, 55.3, 74.0, 76.6, 79.8, 85.8, 113.8, 114.2, 127.9, 129.6, 133.1, 135.2, 143.9, 159.8; exact mass for $C_{20}H_{19}N_1S_1O_3$ (EI) calcd 353.1086, found 353.1083; IR (cm^{-1}) 2970 (w), 2931 (w), 2241 (m), 2121 (m), 1606 (s).

3i: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.63 (s, 3 H), 1.65 (s, 3 H), 2.31 (s, 3 H), 2.32 (s, 3 H), 2.63 (s, 4 H), 3.78 (s, 2 H), 4.22 (s, 2 H), 5.71 (s, 1 H), 6.92 (d, J = 7.9 Hz, 2 H), 7.03 (d, J = 7.8 Hz, 2 H), 7.23 (d, J = 8.0 Hz, 2 H), 7.77 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.2, 18.4, 21.4, 33.7, 33.8, 36.3, 52.3, 81.1, 85.8, 119.3, 122.4, 123.2, 125.1, 127.8, 128.8, 129.4, 129.5, 131.4, 138.4, 143.3; exact mass for $C_{26}H_{29}N_1S_1O_3$ (EI) calc 435.1868, found 435.1873; IR (cm^{-1}) 2962 (w), 2924 (w), 2241 (m), 1605 (m), 1592 (s).

4i: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.07 (s, 3 H), 1.12 (s, 3 H), 1.28 (m, 1 H) 2.15 (m, 4 H), 2.45 (s, 3 H), 2.93 (d, J = 11.6 Hz, 1 H), 3.74 (s, 3 H), 3.91 (d, J = 11.6 Hz, 1 H), 5.14 (d, J = 7.9 Hz, 1 H), 6.25 (d, J = 7.9 Hz, 1 H), 6.71 (d, J = 8.7 Hz, 2 H), 6.93 (d, J = 8.7 Hz, 1 H), 7.34 (d, J = 8.0 Hz, 1 H), 7.69 (d, J = 8.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.39, 18.43, 21.6, 26.9, 29.5, 29.8, 32.7, 34.0, 46.1, 55.2, 113.3, 118.9, 119.6, 122.1, 123.3, 127.1, 128.5, 129.8, 132.9, 135.0, 143.7, 157.9; exact mass for $C_{26}H_{29}N_1S_1O_3$ (EI) calcd 435.1868, found 435.1873; CCDC no. 603264; IR (cm^{-1}) 2992 (w), 2908 (w), 1607 (m), 1513 (s).

3j: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.63 (s, 3 H), 1.66 (s, 3 H), 2.22 (s, 3 H), 2.63 (m, 4 H), 3.84 (s, 2 H), 4.28 (s, 2 H), 5.78 (s, 1 H), 7.14 (m, 5 H), 7.50 (d, J = 7.7 Hz, 1 H), 7.76 (d, J = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.1, 18.4, 21.3, 33.7, 33.8, 36.2, 52.3, 84.1, 86.7, 122.4, 123.2, 124.0, 125.1, 125.5, 126.7, 127.8, 129.3, 129.4, 132.2, 133.4, 136.0, 143.4; exact mass for $C_{25}H_{26}N_1S_1O_2Br_1$ (EI) calcd 483.0868, found 483.0864; IR (cm^{-1}) 2910 (w), 2868 (w), 2843 (w), 2812 (w), 1969 (w), 1927 (m), 1664 (m), 1628 (m), 1597 (s).

4j: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.87 (m, 1 H), 1.06 (s, 3 H), 1.20 (s, 3 H), 2.32 (m, 4 H), 2.45 (s, 3 H), 3.29 (d, J = 11.7 Hz, 1 H), 3.90 (d, J = 11.7 Hz, 1 H), 5.08 (d, J = 7.9 Hz, 1 H), 6.39 (d, J = 7.9 Hz, 1 H), 7.00 (m, 2 H), 7.12 (m, 2 H), 7.34 (m, 1 H), 7.41 (d, J = 7.9 Hz, 1 H), 7.70 (d, J = 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.4, 18.43, 21.6, 29.9, 30.1, 32.7, 35.0, 44.8, 117.5, 117.6, 120.1, 122.2, 124.2, 124.5, 126.6, 127.1, 127.14, 127.9, 129.8, 129.82, 133.0, 133.2, 135.2, 140.8, 143.6; exact mass for $C_{25}H_{26}N_1S_1O_2Br_1$ (EI) calc 483.0868, found 483.0864; IR (cm^{-1}) 2989 (w), 2912 (w), 1637 (s), 1599 (s).

1k: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.20 (t, J = 2.5 Hz, 1 H), 2.24 (s, 6 H), 2.36 (s, 3 H), 4.18 (d, J = 2.4 Hz, 1 H), 4.39 (s, 2 H), 6.79 (s, 2 H), 6.91 (s, 1 H), 7.27 (d, J = 7.8 Hz, 2 H), 7.75 (d, J = 8.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.1, 21.6, 36.6, 37.3, 74.1, 76.7, 80.6, 86.4, 121.9, 128.1, 129.4, 129.7, 130.5, 135.5, 137.8, 143.9; exact mass for $C_{21}H_{21}N_1S_1O_2$ (EI) calcd 351.1293, found 351.1295; IR (cm^{-1}) 3033 (w), 2218 (m), 2133 (m), 1927 (m).

3k: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.63 (s, 3 H), 1.66 (s, 3 H), 2.25 (s, 6 H), 2.35 (s, 3 H), 2.64 (m, 4 H), 3.77 (s, 2 H), 4.22 (s, 2 H), 5.70 (s, 1 H), 6.64 (s, 2 H), 6.91 (s, 1 H), 7.27 (d, J = 8.0 Hz, 1 H), 7.78 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.4, 18.6, 21.3, 21.7, 33.8, 33.9, 36.4, 52.4, 81.0, 86.1, 122.1, 122.6, 123.4, 125.4, 128.0, 129.3, 129.5, 129.6, 130.4, 136.2, 137.8, 143.4; exact mass for $C_{27}H_{31}N_1S_1O_2$ (EI) calcd 433.2075, found 433.2076; IR (cm^{-1}) 3039 (w), 2968 (w), 2908 (m), 2858 (m), 2851 (m), 2218 (w), 1597 (s).

4k: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.02 (s, 3 H), 1.07 (s, 3 H), 1.27 (m, 1 H), 2.14 (m, 4 H), 2.21 (s, 6 H), 2.45 (s, 3 H), 2.92 (d, J = 11.5 Hz, 1 H), 3.92 (d, J = 11.6 Hz, 1 H), 5.16 (d, J = 7.9 Hz, 1 H), 6.26 (d, J = 7.2 Hz, 1 H), 6.61 (s, 2 H), 6.75 (s, 1 H), 7.34 (d, J = 7.9 Hz, 2 H), 7.69 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.5, 18.54, 21.4, 21.8, 27.5, 30.0, 32.9, 34.2, 46.2, 119.1, 119.5, 122.3, 123.6, 125.3, 127.2, 127.9, 130.0, 135.0, 137.3, 140.5, 143.8; exact mass for $C_{27}H_{31}N_1S_1O_2$ (EI) calcd 433.2075, found 433.2074; IR (cm^{-1}) 3026 (w), 2997 (w), 2966 (w), 1639 (s), 1599 (s).

3l: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.63 (s, 3 H), 1.67 (s, 3 H), 2.11 (s, 3 H), 2.66 (m, 4 H), 3.88 (s, 2 H), 4.41 (s, 2 H), 5.77 (s, 1 H), 7.12 (d, J = 8.0 Hz, 2 H), 7.27 (d, J = 7.9 Hz, 1 H), 7.34 (t, J = 7.6 Hz, 1 H), 7.47 (m, 2 H), 7.80 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.2, 18.5, 21.2, 33.8, 33.9, 36.5, 52.5, 83.9, 86.8, 120.1, 122.5, 123.2, 125.0, 125.4, 125.9, 126.4, 126.7, 127.7, 128.3, 128.8, 129.5, 130.6, 133.0, 133.1, 136.1, 143.5; exact mass for $C_{29}H_{29}N_1S_1O_2$ (EI) calcd 455.1919, found 455.1915; IR (cm^{-1}) 2979 (m), 2910 (m), 2860 (m), 2816 (m), 1728 (s), 1655 (w), 1597 (s).

***N*-(But-2-ynyl)-*N*-((4,5-dimethylcyclohexa-1,4-dienyl)methyl)-4-methylbenzenesulfonamide (3l):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.49 (t, J = 2.1 Hz, 3 H), 1.61 (s, 3 H), 1.63 (s, 3 H), 2.41 (s, 3 H), 2.58 (m, 4 H), 3.67 (s, 2 H), 3.94 (d, J = 2.1 Hz, 2 H), 5.64 (s, 1 H), 7.28 (d, J = 8.1 Hz, 2 H), 7.73 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 3.4, 18.3, 18.6, 21.7, 33.8, 33.9, 36.0, 52.2, 71.8, 81.6, 122.5, 123.3, 125.0, 128.1, 129.3, 129.7, 136.4, 143.3; exact mass for $C_{20}H_{25}N_1S_1O_2$ (EI) calcd 343.1606, found 343.1610; IR (cm^{-1}) 3053 (w), 3026 (w), 2979 (m), 2918 (s), 2858 (s), 2817 (s), 2299 (m), 2252 (m), 1628 (s), 1597 (s).

4l: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.81 (s, 3 H), 0.89 (d, J = 7.2 Hz, 1 H), 1.54 (s, 3 H), 1.55 (s, 3 H), 1.88 (m, 1 H), 1.96 (m, 2 H), 2.12 (m, 1 H), 2.42 (s, 3 H), 2.76 (d, J = 11.3 Hz, 1 H), 3.80 (d, J = 11.3 Hz, 1 H), 5.17 (d, J = 7.9 Hz, 1 H), 6.22 (d, J = 7.9 Hz, 1 H), 7.31 (d, J = 7.9 Hz, 2 H), 7.64 (d, J = 7.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.1, 18.7, 18.9, 19.3, 21.7, 25.4, 27.8, 29.7, 31.1, 46.1, 119.3, 120.0, 122.6, 124.2, 127.2, 129.9, 135.1, 143.7; exact mass for $C_{20}H_{25}N_1S_1O_2$ (EI) calcd 343.1606, found 343.1610; IR (cm^{-1}) 2991 (w), 2958 (w), 2920 (w), 2858 (w), 1651 (s), 1595 (s), 1493 (s).

3n: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.87 (t, J = 7.5 Hz, 3 H), 1.63 (s, 3 H), 1.65 (s, 3 H), 1.87 (tq, J = 2.2 Hz, 7.4 Hz 1 H,), 2.42 (s, 3 H), 2.58 (m, 4 H), 3.70 (s, 2 H), 3.98 (d, J = 2.2 Hz, 2 H), 5.66 (s, 1 H), 7.29 (d, J = 8.2 Hz, 2 H), 7.74 (d, J = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.3, 13.7, 18.3, 18.6, 21.7, 33.8, 33.9, 36.0, 52.1, 71.8, 87.6, 122.5, 123.3, 125.0, 128.0, 129.4, 129.7, 136.5, 143.3; exact mass for $C_{21}H_{27}N_1S_1O_2$ (EI) calcd 357.1763, found 357.1756; IR (cm^{-1}) 2987 (w), 2914 (w), 2289 (s), 2227 (s), 1932 (s), 1816 (s), 1741 (s), 1702 (s), 1664 (s).

4n: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.91 (t, J = 7.5 Hz, 3 H), 1.16 (m, 1 H), 1.55 (s, 3 H), 1.57 (s, 3 H), 2.00 (q, J = 7.4 Hz, 2 H), 2.43 (s, 3 H), 2.82 (d, J = 11.4 Hz, 1 H), 3.80 (d, J = 11.4 Hz, 1 H), 5.30 (d, J = 8.1 Hz, 1 H), 6.32 (d, J = 8.0 Hz, 1 H), 7.32 (d, J = 8.1 Hz, 2 H), 7.66 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.6, 18.5, 18.7, 19.4, 21.5, 24.3, 25.9, 27.8, 30.1, 31.1, 46.4, 117.3, 120.0, 122.7, 124.2, 127.0, 129.7, 135.2, 143.5; exact mass for $C_{21}H_{27}N_1S_1O_2$ (EI) calcd 357.1763, found 357.1756; IR (cm^{-1}) 2970 (w), 2920 (w), 1928 (w), 1816 (w), 1647 (s), 1598 (s).

***N*-(3-Cyclopropylprop-2-ynyl)-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (1o):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.37 (m, 2 H), 0.61 (m, 2 H), 1.02 (m, 1 H), 2.12 (t, J = 2.1 Hz, 1 H), 2.38 (s, 3 H), 4.02 (m, 4 H), 7.27 (d, J = 7.9 Hz, 2 H), 7.63 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −0.7, 8.0, 21.6, 36.2, 36.8, 67.2, 73.8, 76.6, 89.7, 127.9, 129.5, 135.3, 143.9; exact mass for $C_{16}H_{17}N_1S_1O_2$ (EI) calcd 287.0980, found 287.0985; IR (cm^{-1}) 3010 (w), 2970 (w), 2921 (w), 2848 (w), 2368 (m), 2247 (m), 1635 (s), 1590 (w).

3o: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.28 (m, 2 H), 0.57 (m, 2 H), 1.64 (s, 3 H), 1.66 (s, 3 H), 2.43 (s, 3 H), 2.55−2.60 (m, 4 H), 3.68 (s, 2 H), 3.95 (s, 2 H), 5.64 (s, 1 H), 7.27 (d, J = 7.9 Hz, 2 H), 7.63 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −0.7, 8.0, 18.4, 18.6, 21.7, 33.8, 36.0, 52.1, 67.8, 89.4, 122.5, 123.4, 125.0, 128.0, 129.5, 129.7, 136.5, 143.3; exact mass for $C_{22}H_{27}N_1S_1O_2$ (EI) calcd 369.1763, found 369.1760; IR (cm^{-1}) 2995 (w), 2916 (w), 2852 (w), 2809 (w), 2310 (w), 2251 (w), 1932 (w), 1836 (w), 1670 (s), 1597 (s).

4o: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.33 (m, 4 H), 0.94 (m, 1 H), 0.97(d, J = 5.5 Hz, 1 H), 1.55 (s, 3 H), 1.58 (s, 3 H), 2.00 (m, 4 H), 2.42 (s, 3 H), 2.97 (d, J = 11.4 Hz, 1 H), 3.81 (d, J = 11.4 Hz, 1 H), 4.79 (d, J = 8.3 Hz, 1 H), 6.11 (d, J = 8.3 Hz, 1 H), 7.30 (d, J = 8.0 Hz, 2 H), 7.64 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −0.1, 1.3, 6.1, 19.0, 21.8, 23.4, 26.7, 27.9, 30.8, 31.3, 46.1, 112.5, 120.4, 122.9, 124.5, 127.2, 129.9, 135.1, 143.7; exact mass for $C_{22}H_{27}N_1S_1O_2$ (EI) calcd 369.1763, found 369.1761; IR (cm^{-1}) 2991 (w), 2958 (w), 2920 (w), 2858 (w), 1651 (s), 1595 (s), 1493 (s).

5: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.34 (m, 2 H), 0.64 (m, 2 H), 0.88 (m, 1 H), 1.18 (m, 1 H), 1.51 (s, 3 H), 1.62 (s 3 H), 1.84 (m, 2 H), 2.04 (m, 1 H), 2.31 (m, 1 H), 2.44 (s, 3 H), 2.85 (d, J = 9.8 Hz, 1 H), 3.35 (d, J = 9.8 Hz, 1 H), 3.71 (m, 2 H), 7.33 (d, J = 8.0 Hz, 2 H), 7.72 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −0.1, 1.3, 6.1, 19.0, 21.8, 23.4, 26.7, 27.9, 30.8, 31.3, 46.1, 112.5, 120.4, 122.9, 124.5, 127.2, 129.9, 135.1, 143.7; exact mass for $C_{22}H_{27}N_1S_1O_2$ (EI) calcd 369.1763, found 369.1765; IR (cm^{-1}) 2993 (w), 2960 (w), 2920 (w), 2858 (w), 1639 (s), 1584 (s), 1467 (s).

***N*-(3-Cyclohexenylprop-2-ynyl)-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (1p):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.54 (m, 4 H), 1.88 (m, 2 H), 2.00 (m, 2 H), 2.15 (t, J = 2.1 Hz, 1 H), 2.42 (s, 3 H), 4.31 (d, J = 2.1 Hz, 2 H), 4.28 (s, 2 H), 5.88 (s, 1 H), 7.29 (d, J = 7.9 Hz, 2 H), 7.72 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 21.6, 22.1, 25.5, 28.9, 36.2, 37.1, 73.8, 76.5, 78.3, 87.7, 119.8, 127.9, 129.5, 135.3, 135.6, 143.8; exact mass for $C_{21}H_{23}N_1S_1O_2$ (EI) calcd 327.1293, found 327.1293; IR (cm^{-1}) 2928 (w), 2880 (w), 2352 (m), 2176 (m), 1590 (w), 1484 (w).

3p: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.53 (m, 4 H), 1.63 (s, 3 H), 1.64 (s, 3 H), 1.76 (m, 2 H), 1.98 (m, 2 H), 2.43 (s, 3 H), 2.60 (m, 4 H), 3.71 (s, 2 H), 4.20 (s, 2 H), 5.66 (s, 1 H), 5.73 (m, 1 H), 7.30 (d, J = 7.9 Hz, 2 H), 7.74 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 3.4, 18.3, 18.6, 21.7, 33.8, 33.9, 36.0, 52.2, 71.8, 81.6, 122.5, 123.3, 125.0, 128.1, 129.3, 129.7, 136.4, 143.3; exact mass for $C_{25}H_{31}N_1S_1O_2$ (EI) calcd 409.2076, found 409.2073; IR (cm^{-1}) 2976 (w), 2920 (w), 2852 (w), 2817 (w), 2372 (w), 2345 (w), 2302 (w), 2221 (w), 1637 (m), 1598 (m).

6: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89 (m, 1 H), 1.20 (m, 3 H), 1.40 (m, 1 H), 1.50 (s, 3 H), 1.63 (s, 3 H), 1.76 (m, 3 H), 1.82 (m, 2 H), 1.99 (m, 2 H), 2.22 (m, 2 H), 2.41 (s, 3 H), 2.43 (m, 1 H), 2.51 (m, 1 H), 3.81 (d, J = 10.7 Hz, 1 H), 5.57 (d, J = 8.1 Hz, 1 H), 6.69(d, J = 8.1 Hz, 1 H), 7.29 (d, J = 7.9 Hz, 2 H), 7.67 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.4, 19.6, 21.7, 25.5, 25.7, 25.9, 31.0, 33.0, 36.6, 44.4, 49.7, 53.6, 102.3, 123.0, 124.2, 124.4, 127.1, 130.0, 132.3, 135.1, 135.7, 143.8; exact mass for $C_{25}H_{31}N_1S_1O_2$ (EI) calcd 409.2076, found 409.2075; IR (cm^{-1}) 2991 (w), 2940 (w), 2920 (w), 2858 (w), 1655 (s), 1590 (s), 1458 (s).

3s: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.63 (s, 3 H), 1.72 (s, 3 H), 2.19 (s, 3 H), 2.87 (m, 4 H), 3.84 (s, 2 H), 4.14 (s, 2 H), 6.72 (m, 2 H), 7.02−7.22 (m, 10 H), 7.64 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0, 18.3, 21.5, 34.9, 35.6, 41.4, 48.1, 82.0, 85.4, 122.4, 122.6, 123.7, 124.8, 126.8, 127.8, 127.9, 128.2, 128.4, 129.5, 131.6, 136.3, 137.3, 141.3, 143.4; exact mass for $C_{31}H_{21}N_1S_1O_2$ (EI) calcd 481.2075, found 481.2074; IR (cm^{-1}) 3080 (w), 3057 (w), 3022 (w), 2997 (w), 2908 (m), 2862 (m), 1948 (w), 1925 (w), 1899 (w), 1813 (w), 1699 (w), 1628 (s), 1595 (s).

7: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.28 (s, 3 H), 4.15 (d, J = 4.1 Hz, 2 H), 4.44 (s, 2 H), 6.58 (t, J = 4.1 Hz, 1 H), 7.14−7.60 (m, 13 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 44.1, 45.4, 119.9, 120.1, 122.0, 125.4, 127.5, 127.8, 128.2, 128.2, 128.5, 129.0, 129.7, 133.8, 133.9, 134.4, 137.5, 139.0, 142.1, 143.8; exact mass for $C_{25}H_{21}N_1S_1O_2$ (EI) calcd 399.1293, found 399.1297

1t: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.03 (t, J = 2.7 Hz, 1 H), 2.35 (s, 3 H), 2.58 (dt, J = 2.7 Hz, 7.3 Hz, 2 H), 3.44 (t, J = 7.3 Hz, 2 H), 4.42 (s, 2 H), 7.08 (m, 2 H), 7.27 (m, 5 H), 7.76 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.3, 21.6, 38.4, 45.7, 70.6, 81.0, 82.0, 85.9, 122.2, 127.9, 128.4, 128.8, 131.7, 136.0, 143.7; exact mass for $C_{20}H_{19}N_1S_1O_2$ (EI) calcd 337.1136, found 337.1141; IR (cm^{-1}) 2976 (w), 3269 (w), 2991 (w), 2947 (w), 2237 (w), 1967 (m), 1924 (w), 1660 (m), 1595 (s).

3t: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.61 (s, 6 H), 2.30 (m, 5 H), 2.56 (m, 4 H), 3.36 (m, 2 H), 4.36 (s, 2 H), 5.49 (s, 1 H), 7.02 (m, 2 H), 7.21 (m, 5 H), 7.76 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.4, 18.7, 21.6, 34.0, 35.4, 35.8, 37.2, 44.9, 81.9, 85.9, 121.6, 122.3, 123.0, 123.1, 127.9, 128.3, 128.6, 129.7, 131.7, 132.0, 135.9, 143.6; exact mass for $C_{26}H_{29}N_1S_1O_2$ (EI) calcd 419.1919, found 419.1927; IR (cm^{-1}) 2922 (w), 2857 (w), 2807 (w), 1920 (w), 1735 (w), 1598 (m).

4-Methyl-*N*-(4-phenylbut-3-ynyl)-*N*-(prop-2-ynyl)benzenesulfonamide (1u): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.02 (t, J = 2.2 Hz, 1 H), 2.41 (s, 3 H), 2.75 (t, J = 7.2 Hz, 2 H), 3.46 (t, J = 7.2 Hz, 2 H), 4.25 (d, J = 2.2 Hz, 2 H), 7.27 (m, 5 H), 7.37 (m, 2 H), 7.76 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.0, 21.6, 37.4, 45.6, 74.0, 76.6, 82.4, 86.3, 123.2, 127.7, 128.0, 129.6, 131.6, 135.9, 143.7; exact mass for $C_{20}H_{19}N_1S_1O_2$ (EI) calcd 337.1136, found 337.1143; IR (cm^{-1}) 2976 (w), 3269 (w), 2991 (w), 2947 (w), 2237 (w), 1967 (m), 1924 (w), 1660 (m), 1595 (s).

***N*-((4,5-Dimethylcyclohexa-1,4-dienyl)methyl)-4-methyl-*N*-(4-phenylbut-3-ynyl)benzenesulfonamide (3u):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.58 (s, 3 H), 1.60 (s, 3 H), 2.41 (s, 3 H), 2.46 (m, 2 H), 2.62 (m, 4 H), 3.33 (m, 2 H), 3.76 (s, 2 H), 5.62 (s, 2 H), 7.27 (m, 5 H), 7.34 (m, 2 H), 7.72 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.3, 18.5, 20.1, 21.6, 33.9, 46.6, 54.9, 82.3, 86.9, 122.6, 123.0, 123.6, 124.6, 127.3, 128.0, 128.4, 129.8, 130.8, 131.7, 143.4; exact mass for $C_{26}H_{29}N_1S_1O_2$ (EI) calcd 419.1919, found 419.1927; IR (cm^{-1}) 2983 (w), 2947 (w), 2237 (w), 1967 (m), 1924 (w), 1660 (m), 1595 (s).

1v: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.53 (s, 3 H), 2.32 (s, 3 H), 2.36 (s, 3 H), 3.36 (s, 2 H), 3.76−3.83 (m, 4 H), 3.87 (s, 2 H), 5.10 (m, 2 H), 5.45 (m, 1 H), 6.10 (m, 2 H), 7.22 (m, 4 H), 7.62 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 3.5, 21.64, 21.68, 22.1, 36.1, 36.3, 36.7, 48.3, 71.3, 78.3, 78.6, 82.1, 118.7, 126.9, 127.8, 127.9, 129.5, 129.7, 134.6, 135.4, 136.7, 135.8, 135.9, 143.9; exact mass for $C_{27}H_{30}N_2S_2O_4$ (EI) calcd 510.1647, found 510.1648; IR (cm^{-1}) 2976 (w), 2912 (w), 2304 (s), 1910 (br), 1795 (w), 1686 (m).

2v: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.56 (s, 3H), 2.41 (s, 3H), 2.45 (s, 3H), 2.58 (m, 2H), 2.75 (m, 1H), 3.02 (m, 1H), 3.55−4.02 (m, 7 H), 5.60 (m, 1 H), 5.80 (m, 1 H), 7.27 (m, 4 H), 7.67 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 3.44, 21.71, 28.13, 36.26, 39.57, 47.65, 48.85, 52.40, 71.62, 82.46, 122.69, 122.93, 127.07, 127.65, 128.03, 129.50, 129.89, 133.63, 134.70, 135.79, 143.70, 143.84; exact mass for $C_{27}H_{30}N_2S_2O_4$ (EI) calcd 510.1647, found 510.1648; CCDC no. 603266; IR (cm^{-1}) 2912 (s), 1910 (w), 1790 (w), 1596 (s), 1488 (m).

4v: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.87 (s, 3 H), 1.84 (m, 1 H), 1.97 (m, 1 H), 2.42 (m, 3 H), 2.43 (s, 3 H), 2.45 (s, 3 H), 2.98 (d, J = 11.5 Hz, 1 H), 3.37 (d, J = 11.5 Hz, 1 H), 3.38 (d, J = 11.5 Hz, 1 H), 3.94 (m, 1 H), 4.95 (d, J = 8.1 Hz, 1 H), 5.50 (m, 1 H), 5.57 (m, 1 H), 6.50 (d, J = 8.1 Hz, 1 H), 7.35 (m, 4 H), 7.64 (d, J = 8.0 Hz, 2 H), 7.71 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.2. 21.86, 21.89, 22.1, 25.0, 27.6, 35.5, 36.7, 44.3, 49.5, 54.8, 112.2, 121.5, 124.8, 125.8, 127.4, 128.5, 129.9, 130.0, 130.1, 130.2, 132.2, 134.4, 143.8, 144.4; exact mass for $C_{27}H_{30}N_2S_2O_4$

(EI) calcd 510.1647, found 510.1649; IR (cm^{-1}) 2912 (s), 1638 (m), 1590 (s), 1542 (w), 1488 (m).

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Supporting Information Available: Detailed experimental procedures, new characterization data, ^{1}H and ^{13}C NMR spectra of all compounds, and crystallographic data (CIF) of **2a′**, **2v**, and **4i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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