JOC*Article*

Rhodium *N*-Heterocyclic Carbene-Catalyzed [4 + 2] and [5 + 2] Cycloaddition Reactions

Sang Ick Lee, Se Yeoun Park, Ji Hoon Park, Il Gu Jung, Soo Young Choi, and Young Keun Chung*

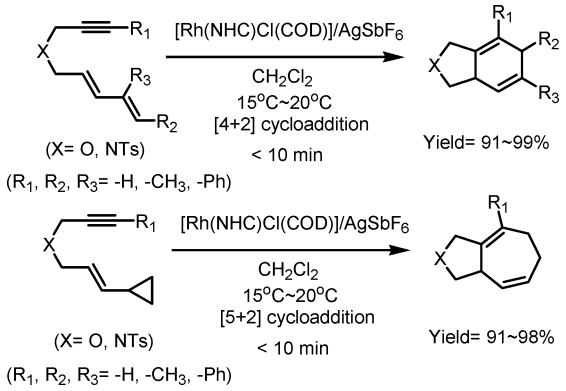
Intelligent Textile System Research Center, Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-747, Korea

Bun Yeoul Lee

Department of Molecular Science and Technology, Ajou University, Suwon 442-749, Korea

ykchung@plaza.snu.ac.kr

Received August 10, 2005



A rhodium complex of *N*-heterocyclic carbene (NHC) has been developed for intra- and intermolecular [4 + 2] and intramolecular [5 + 2] cycloaddition reactions. This is the first use of a transition-metal NHC complex in a Diels−Alder-type reaction. For the intramolecular [4 + 2] cycloaddition reactions, all the dienynes studied were converted to their corresponding cycloadducts in 91−99% yields within 10 min. Moreover, up to 1900 turnovers have been obtained for the intramolecular [4 + 2] cycloaddition at 15− 20 °C. For the intermolecular [4 + 2] cycloadditions, high yields (71−99%) of the corresponding cycloaddition products were obtained. The reaction time and yield were highly dependent upon the diene and the dienophile. For the intramolecular [5 + 2] cycloaddition reactions, all the alkyne vinylcyclopropanes studied were converted to their corresponding cycloadducts in 91−98% yields within 10 min. However, the catalytic system was not effective for an intermolecular [5 + 2] cycloaddition reaction.

Introduction

Development of effective cyclization reactions for the synthesis of carbocycles and heterocycles has been the subject of extensive study because of their relevance to medicines and other functional materials.[1] Among the numerous methods available, the transition-metal-promoted cyclization reaction has attracted a lot of attention and has become one of the most popular.[2] However, considerable effort is still being devoted to the development of more efficient and practical methods of

(1) (a) Langer, P.; Freiberg, W. *Chem. Rev.* **2004**, *104*, 4125−4150. (b) Deiters, A.; Martin, S. F. *Chem. Rev.* **2004**, *104*, 2199−2238. (c) Rassu, G.; Auzzas, L.; Battistini, L.; Casiraghi, G. *Mini-Rev. Org. Chem.* **2004**, *1*, 343−357. (d) Maryanoff, B. E.; Zhang, H.-C.; Cohen, J. H.; Turchi, I. J.; Maryanoff, C. A. *Chem. Rev.* **2004**, *104*, 1431−1628.

(2) (a) Evans, P. A. *Rhodium-Catalyzed Organic Reactions*; Wiley-VCH: Weinheim, 2005. (b) Nakamura, I.; Yamamoto, Y. *Chem. Rev.* **2004**, *104*, 2127−2198. (c) Montgomery, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 3891−3908. (d) Fairlamb, I. J. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1048−1052. (e) Gabriele, B.; Salermo, G.; Costa, M. *Synlett.* **2004**, 2468−2483. (f) Schmidt, B. *Angew. Chem., Int. Ed.* **2003**, *42*, 4996−4999. (g) Murakami, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 718−720. (h) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813−834. (i) Negeshi, E.-I.; Copéret, C.; Ma, S.; Liou, S.-Y.; Liu, F. *Chem. Rev.* **1996**, *96*, 365−394. (j) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635−662. (k) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49−92.

10.1021/jo051685u CCC: $33.50
Published on Web 11/19/2005

synthesizing polycyclic organic compounds from readily available starting materials.

Recently, *N*-heterocyclic carbenes (NHCs) have emerged as a group of promising materials for the design of new homogeneous catalysts.[3] The promise of being able to predetermine the structure and chemical properties of a metal complex has been the main driving force in the design of new ligand systems. Moreover, the donor power of NHC ligands is considered to be even greater than that of phosphines, prompting a range of investigations seeking to exploit their properties in homogeneous catalysis. Carbene ligand precursors are easy to prepare, and their chemical and topological versatility allows the preparation of a wide variety of complexes whose chemical properties can be easily modulated. Despite the intense interest in the catalytic properties of NHC complexes,[4] reports of the use of transition metal NHC complexes in cyclization, other than in metathesis,[5] are still rare.[6] Until now, the Rh NHC complex (Rh-NHC) catalyzed cycloaddition reactions such as Diels−Alder-type reactions have not been reported. Very recently, Evans reported[7] a diastereoselective Rh-NHC-catalyzed [4 + 2 + 2] carbocyclization. Some years ago, in situ generated Ni(II)-NHC had been used as a catalyst in the reaction of 1,3-dienes and aldehydes.[8] As a further step in our program toward the development of cycloaddition reactions catalyzed by transition-metal complexes,[9] we initiated a study on the use of transition-metal NHC complexes in cyclization. Here, we report on Rh-NHC-catalyzed intra- and intermolecular [4 + 2] and intramolecular [5 + 2] cycloaddition reactions. This catalytic system has several advantages, such as mild reaction conditions, high yields, and high TON.

Results and Discussion

Complex **1**, RhCl(IPMes)(COD) (IPMes= *N*,*N*′-bis(2,6-diisopropyl)imidazole-2-yilidene), showed a high catalytic activity in hydrosilylation[10] and was used as a precatalyst for our reactions. The catalyst [Rh(IPMes)(COD)(solvent)]$^+$ was generated in situ by the reaction of **1** with $AgSbF_6$ at 15−20 °C for 5 min. Without a silver salt, the reaction did not proceed. Using **2a** as a dienyne model compound, we studied an intramolecular [4 + 2] cycloaddition reaction (Scheme 1).

SCHEME 1

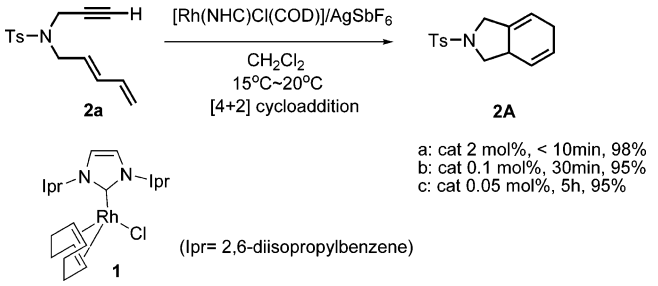


TABLE 1. Rh(NHC)-Catalyzed Intramolecular [4 + 2] Cycloaddition[a]

entry	reactant	product	time	yield(%)[b]
1	**3a**	**3A**	<10min	91
			5h	90[c]
2	**4a**	**4A**	<10min	98
3	**5a**	**5A**	<10min	91
4	**6a**	**6A**	<10min	99
5	**7a**	**7A**	<10min	99
6	**8a**	**8A**	<10min	97

[a] 0.52 mmol of substrate, 2 mol % of catalyst, and 3 mol % of $AgSbF_6$ were used. [b] Isolated yield. [c] 2.5 mol % of [Rh(dppb)(solvent)]$^+$ was used; see ref 11.

When 2 mol % of **1**/$AgSbF_6$ was used at 15−20 °C, the reaction went to completion within several minutes, although the exact reaction time was not determined. The yield was up to 95∼98%. Thus, we cut down the amount of catalyst to 0.1 mol %. In this case, the reaction went to completion within 30 min and the yield was 95%. When the catalyst was cut down to 0.05 mol %, the reaction went to completion within 5 h and the yield was 95%. Thus, the maximum TON should be higher than 1900. For practical purposes, when 1.0 g of the substrate (**2a**) was reacted under the same reaction conditions, a 91% yield of the corresponding product was obtained within 45 min. Several years ago, Zhang et al.[11] reported on rhodium diphos-

(3) (a) Wang, A. E.; Xie, H. H.; Wang, L. X.; Zhou, Q. L. *Tetrahedron* **2005**, *61*, 259−266. (b) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247−2273. (c) Cesar, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Chem.* Soc. Rev. **2004**, *33*, 619−636. (d) Cavell, K. J.; McGuinness, D. S. *Coord. Chem. Rev.* **2004**, *248*, 671−681. (e) Lebel, H.; Janes, M. K.; Charette, A. B.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5046−5047. (f) Herrmann, W. A.; Kocher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2163. (g) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−92. (h) Crabtree, R. H. *Pure Appl. Chem.* **2003**, *75*, 435. (i) Arduengo, A. J. *Acc. Chem. Res.* **1999**, *32*, 913−921.

(4) (a) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239−2246. (b) Herrmann, W. A.; Ofele, K.; von Preysing, D.; Schneider, S. K. *J. Organomet. Chem.* **2003**, *687*, 229−248. (c) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951−961. (d) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309.

(5) (a) Despagnet-Ayoub, E.; Grubbs, R. H. *Organometallics* **2005**, *24*, 338−340. (b) Yang, L.; Mayr, M.; Wurst, K.; Buchmeiser, M. R. *Chem. Eur. J.* **2004**, *10*, 5761−5770. (c) Choi, T.-L.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 1743−1746. (d) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546−2558. (e) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29. (f) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2490−2493.

(6) (a) Louie, J.; Gibby, J. E.; Farnworth, M. V.; Tekavec, T. N. *J. Am. Chem. Soc.* **2002**, *124*, 15188−15189. (b) Tekavec, T. N.; Arif, A. M.; Louie, J. *Tetrahedron* **2004**, *60*, 7431−7437.

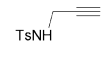
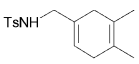
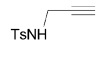
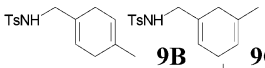
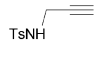
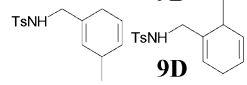
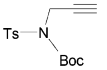
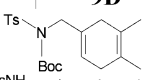
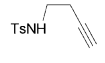
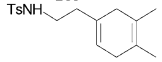
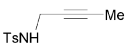
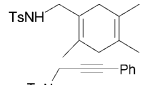
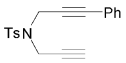
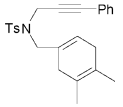
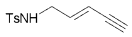
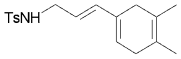
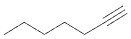
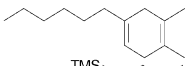
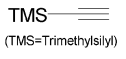
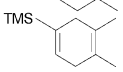
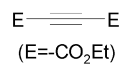
(7) Evans, P. A.; Baum, E. W.; Fazal, A. N.; Pink, M. *Chem. Commun.* **2005**, 63−65.

(8) Sato, Y.; Sawaki, R.; Mori, M. *Organometallics* **2001**, *20*, 5510−5512.

(9) (a) Lee, S. I.; Park, J. H.; Chung, Y. K.; Lee, S.-G. *J. Am. Chem. Soc.* **2004**, *126*, 10190. (b) Park, K. H.; Jung, I. G.; Kim, S. Y.; Chung, Y. K. *Org. Lett.* **2003**, *5*, 4967−4970. (c) Son, S. U.; Park, K, H.; Lee, S. J.; Kim, B. M.; Chung, Y. K. *Synlett* **2003**, 1101−1104. (d) Lee, S. I.; Son, S. U.; Choi, M. R.; Chung, Y. K. *Tetrahedron Lett.* **2003**, *44*, 4705−4709.

(10) Park, K. H.; Kim, S. Y.; Son, S. U.; Chung, Y. K. *Eur. J. Org. Chem.* **2003**, 4341−4345.

TABLE 2. Rh(NHC)-Catalyzed Intermolecular [4 + 2] Cycloaddition[a]

entry	dienophile	diene[b]	product	time	yield(%)[c]
1	 **9a**		 **9A**	15min	98
2	 **9a**		 **9B** **9C**	15min	99(3.2:1)[d]
3	 **9a**		 **9D** **9E**	45min	76(5.7:1)[e]
4	 **10a**		 **10A**	15min	99
5	 **11a**		 **11A**	45min	71
6	 **12a**		 **12A**	2h	80
7[f]	 **13a**		 **13A**	1h	97
8	 **14a**		 **14A**	1h	72
9	 **15a**		 **15A**	2hr	50(25)[g]
10	 **16a**		 **16A**	2hr	61(17)[h]
11	 **17a**		 **17A**	30min	99

[a] 0.52 mmol of dienophile, 3 mol % of catalyst, and 4 mol % of $AgSbF_6$ were used. [b] 2 equiv of diene was used. [c] Isolated yield. [d,e]Ratio was determined by ^1H NMR. [f] 1 equiv of diene was used. [g,h] Yields for dehydrated products are shown in parentheses.

phine cationic complex-catalyzed intramolecular [4 + 2] cycloaddition. Among them, they obtained the best results when they used $[Rh(dppb)(solvent)]^+$ (dppb= 1,4-bis(diphenylphosphino)butane) as a catalyst. Using $[Rh(dppb)(solvent)]^+$ (generated in situ by the reaction of $[Rh(dppb)Cl]_2$ and $AgSbF_6$) as a catalyst at room temperature for 4 h, up to 1000 turnovers were observed. They did not obtain the maximum turnovers under the optimized reaction conditions. Thus, it was not simple to compare directly our turnovers with theirs.

As shown in Table 1, all the dienynes studied were converted to their corresponding cycloadducts in 91−99% yields within 10 min. Our results show that the catalytic system can tolerate the oxygen and nitrogen tether in the substrate. Any change of terminal substituents in the alkyne (entries 5 and 6) and in the diene (entries 1−4) has little effect on the efficiency of the cycloaddition reaction. When the reaction of 1-prop-2-ynyloxyhexa-2,4-diene (entry 3) in Table 1 was carried out using 2.5 mol % of $[Rh(dppb)(solvent)]^+$ as a catalyst at room temperature, the time taken to reach 90% completion of the reaction was ca. 5 h.[11]

We also investigated an intermolecular [4 + 2] cycloaddition reaction (Table 2). In general, high yields of the corresponding cycloaddition products were obtained. Interestingly, the reaction time and yield were highly dependent upon the diene and the dienophile. When the reaction between 2,3-dimethyl-1,3-butadiene and **9a** (a reaction time of 15 min and a yield of 98%) was studied as a model reaction, the use of a terminal alkene (entry 2) had no effect on either the reaction time or the yield (15 min and 99%). Due to the unsymmetric nature of a diene, an isomeric mixture was obtained in the ratio of 3.2:1.[12] However, the use of an internal alkene (entry 3) resulted in an isomeric mixture (5.7:1) with a diminished yield of 76% and a lengthening of the reaction time to 45 min.[13] Substitution of a hydrogen on the nitrogen with a Boc group (entry 4) had no effect on the reaction time and yield (15 min and 99%). Interestingly, the increase of the chain length between an alkyne and a nitrogen atom of an amine (entry 5) led to a decrease of the yield (71%) and an increase of the reaction time (45 min). When an internal alkyne (entry 6) was used as a dienophile, the yield decreased to 80% and the reaction time increased to 2 h.

When enynes were reacted with dienes in the presence of Rh-NHC, it was known that [4 + 2 + 2] cycloaddition reactions proceeded.[7] Similarly, we first expected [4 + 2 + 2] cycloadditon between diyne and diene. However, we could get the [4 + 2] cycloaddition reaction product only (entry 7). These results agreed with entries 1 and 6. The structure of **13A** was confirmed by X-ray structure.[14] When an enyne with a terminal alkyne (entry 8) was used as a dienophile the terminal alkyne reacted

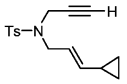
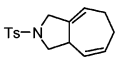
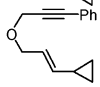
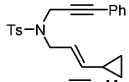
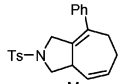
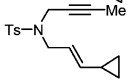
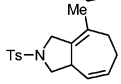
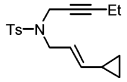
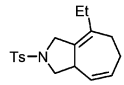
(11) Wang, B.; Cao, P.; Zhang, X. *Tetrahedron Lett.* **2000**, *41*, 8041−8044.

(12) Paik, S.-J.; Son, S. U.; Chung, Y. K. *Org. Lett.* **1999**, *1*, 2045−2047.

(13) $[(\eta^6\text{-}C_{10}H_8)Rh(COD)]BF_4$ showed similar selectivities for the intermolecular [4 + 2] cycloaddition. See ref 11.

(14) Crystal system, triclinic, *P*1, unit cell dimensions, $a = 9.42870(40)$ Å, $b = 11.28010(40)$ Å, $c = 11.75760(50)$ Å, $\alpha = 93.0232(21)°$, $\beta = 111.2617(20)°$, $\gamma = 98.4089(23)°$. Final *R* indices [$I > 2\sigma(I)$], $R_1 = 0.0223$, $wR_2 = 0.0320$. CCDC reference no.: 271994.

TABLE 3. Rh(NHC)-Catalyzed Intermolecular [5 + 2] Cycloaddition[a]

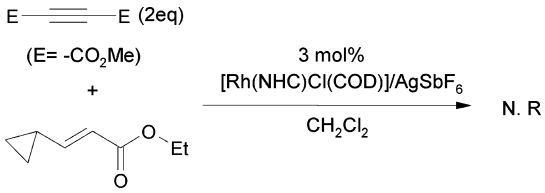
entry	reactant	product	time	yield(%)[b]
1	 **18a**	 **18A**	< 10min	98
2	 **19a**	 **19A**	< 10min	91
3	 **20a**	 **20A**	< 10min	96
4	 **21a**	 **21A**	< 10min	95
5	 **22a**	 **22A**	< 10min	93
6	 **23a**	 **23A**	< 10min	94

[a] 0.52 mmol of substrate, 2 mol % of catalyst, and 3 mol % of $AgSbF_6$ were used. [b] Isolated yield.

with a diene to give a cyclohexadiene bearing a side chain with a double bond in 72% yield within 1 h. Interestingly, when a terminal alkyne having a linear alkyl chain or a TMS group (entry 9 and 10) was used as a dienophile, the reaction time increased to 2 h and the reaction product was obtained as a mixture of a cycloadduct and an arene, a dehydrogenated cycloadduct, in a ratio of 2:1−3.6:1. The generation of aromatic compounds via oxidation of the Diels−Alder reaction product is not unusual.[15] When the reaction of entry 10 in Table 2 was carried out in the presence of 1 mol % of [(η^6-$C_{10}H_8$)Rh(COD)]-BF_4 at 15−20 °C for 15 min, the corresponding cycloaddition product was obtained in 94% yield without any dehydrogenated compounds.[12] When a diester-substituted alkyne (entry 11) was used as a dienophile, the reaction time increased to 30 min with a quantitative yield. However, all of the reactions went to completion within 2 h.

Next we examined an intramolecular [5 + 2] cycloaddition reaction (Table 3). We used Wender's alkyne vinylcyclopropanes as substrates.[16] Heteroatom (O and NTs) tethers are good substrates. The presence of a substitutent on the alkyne did no harm to either the yield or the reaction time. The Rh-NHC catalytic system displayed a greatly enhanced cycloaddition activity compared to other rhodium catalytic systems[11,17] in the cycloaddition reaction of the substrate. For example, in the cycloaddition of the substrate (entry 3), the time taken to reach complete conversion to a bicyclic diene was less than 10 min in the presence of Rh-NHC. However, no other rhodium catalytic systems went to completion within 10 min under our reaction conditions. Thus, our catalytic system seems to be quite effective for the intramolecular [5 + 2] cycloaddition reaction.

SCHEME 2



We attempted to develop an intermolecular version of the [5 + 2] cycloaddition reaction (Scheme 2). However, after workup, the reactant was recovered. Unfortunately, the catalytic system has not proved to be effective for an intermolecular reaction. Further study will hopefully disclose a catalytic system that is effective for an intermolecular reaction.

Conclusion

We have found a useful catalytic system that is especially active for the intra- and intermolecular [4 + 2] and intramolecular [5 + 2] cycloaddition reactions. Up to 1900 turnovers have been obtained for the intramolecular [4 + 2] cycloaddition at 15 °C∼ 20 °C. Compared to other rhodium catalytic systems, the Rh-NHC system is a preferred catalyst for the intramolecular [5 + 2] cycloaddition of tethered alkyne vinylcyclopropanes. We are currently investigating asymmetric catalysts based on NHC ligands and tandem [4 + 2]/[5 + 2] cyclization using Rh-NHC.

Experimental Section

A Typical Procedure for the Synthesis of Rh-NHC Complex (1). 1,3-Bis(2,6-diisopropylphenyl)-1*H*-imidazole chloride (0.72 g, 0.41 mmol) and Ag_2O (0.1 g, 0.4 mmol) were dissolved in a flame-dried 100 mL of Schlenk flask, covered with aluminum foil, containing anhydrous dichloromethane (20 mL) at room temperature (rt). After the solution was stirred for 4 h, the solution was filtered through the vacuum-dried Celite. The filtrate was evaporated under reduced pressure. The obtained crude Ag-carbene salt and [RhCl-(cod)]$_2$ (cod = 1,5-cyclooctadiene) (0.2 g, 0.4 mmol) were added to a flask containing 30 mL of dichloromethane. The resulting solution was stirred at room temperature for 4 h. Removal of the solvent followed by chromatography on a silica gel eluting with hexane and diethyl ether (v/v, 10:1) gave yellow solid **1** (0.216 g, 0.34 mmol) in 85% yield: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.11 (d, J = 6.8 Hz, 6H, CH_3), 1.24−1.54 (br, 6H, CH_3), 1.40−1.60 (m, 2H, CH_2), 1.66−1.78 (m, 1H, COD), 1.78−1.92 (m, 1H, COD), 2.40−2.70 (br, 1 H, CH), 3.26 (s, 1H, COD), 3.46−3.76 (br, 1 H, CH), 4.38 (s, 1H, COD), 7.03 (s, 1H, ═CH), 7.20−7.50 (br, 2H, *m*-iPr_2C_6), 7.51 (t, J = 7.6 Hz, 1H, *p*-iPr_2C_6); ^{13}C{1H} NMR (C_6D_6): δ 22.68 (br, CH), 24.02 (br, CH), 26.97 (br, CH_3), 28.85 (COD), 29.35 (CH_3), 33.36 (COD), 67.55 (d, $^2J_{CRh}$ = 14 Hz, COD), 96.44 (d, $^2J_{CRh}$ = 7.6 Hz, COD), 122.92 (br, *m*-iPr_2C_6), 124.69 (═CH), 125.22 (br, *m*-iPr_2C_6), 130.15 (*p*-iPr_2C_6), 136.85 (*ipso*-iPr_2C_6), 145.56 (br, *o*-iPr_2C_6), 148.44 (br, *o*-iPr_2C_6), 187.51 (d, $^2J_{CRh}$ = 52 Hz, C═Rh). Anal. found (calcd for $C_{37}H_{48}N_2Rh_1Cl_1$): C, 66.41 (66.22); H, 7.59 (7.63); N, 4.37 (4.42).

General Procedure for Rh-NHC-Catalyzed Intramolecular [4 + 2] and [5 + 2] Cycloaddition. To a flame-dried 15 mL Schlenk flask capped with a rubber septum was added 5 mL of dichloromethane via syringe under N_2 flow. Then, Rh-NHC (8 mg, 2 mol %) and $AgSbF_6$ (7 mg, 3 mol %) were added sequentially. After the solution was stirred for 10 min, a substrate (0.52 mmol) was added to the solution under N_2 flow. The reaction was

(15) (a) Hilt, G.; du Mesnil, F.-X. *Tetrahedron Lett.* **2000**, *41*, 6757−6761. (b) Levy, L. A. *J. Org. Chem.* **1978**, *43*, 3068−3069.

(16) (a) Wender, P. A.; Takahashi, H.; Witulski, B. *J. Am. Chem. Soc.* **1995**, *117*, 4720−4721. (b) Wender, P. A.; Husfeld, C. O.; Langkopf, E.; Love, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 1940−1941. (c) Wender, P. A.; Glorius, F.; Husfeld, C. O.; Langkopf, E.; Love, J. A. *J. Am. Chem. Soc.* **1999**, *121*, 5348−5349. (d) Wender, P. A.; Dyckman, A. J.; Husfeld, C. O.; Kadereit, D.; Love, J. A. *J. Am. Chem. Soc.* **1999**, *121*, 10442−10443. (e) Wender, P A.; Dyckman, A J. *Org. Lett.* **1999**, *1*, 2089−2092. (f) Wender, P A.; Zhang, L. *Org. Lett.* **2000**, *2*, 2323−2326. (g) Wender, P A.; Barzilay, C M.; Dyckman, A J. *J. Am. Chem. Soc.* **2001**, *123*, 179−180. (h) Wender, P A.; Pedersen, T M.; Scanio, M J. C. *J. Am. Chem. Soc.* **2002**, *124*, 15154−15155.

(17) Wender, P. A.; Williams, T. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 4550−4552.

monitored by thin-layer chromatography (TLC). After the reactant completely disappeared, the solvent was removed under reduced pressure. Flash chromatography on silica gel eluting with hexane and ethyl acetate (or diethyl ether) gave a product.

General Procedure for Rh-NHC-Catalyzed Intermolecular [4 + 2] Cycloaddition. To a flame-dried 15 mL Schlenk flask capped with a rubber septum was added 5 mL of dichloromethane via syringe under N_2 flow. Rh-NHC (10 mg, 3 mol %) and $AgSbF_6$ (9 mg, 4 mol %) were added sequentially to the above solution. After the resulting solution was stirred for 10 min, diene (1 mmol, 2 equiv) was added by syringe (1 mL). The color of solution turned to orange. Dienophile (0.52 mmol) was added to the above solution under N_2 flow. The reaction was monitored by TLC. After the reactant was completely disappeared, the solvent was removed under reduced pressure. Flash chromatography on a silica gel column eluting with hexane and ethyl acetate (or diethyl ether) gave a product.

4-Methyl-*N*-penta-2,4-dienyl-*N*-prop-2-ynylbenzenesulfonamide (2a). To a solution of anhydrous DMF (30 mL) were added NaH (0.2 g, 5.0 mmol, 60 wt % stabilized mineral oil) and 4-methyl-*N*-penta-2, 4-dienyl-benzenesulfonamide (1.0 g, 4.2 mmol) at 0 °C. After the solution was stirred for 1 h, 1.3 equiv of propargyl bromide (0.58 mL, 5.4 mmol, 80 wt % in toluene) was added at 0 °C. After the resulting solution was stirred at room temperature for 6 h, the reaction mixture was extracted with saturated NaCl aqueous solution and diethyl ether. Flash column chromatography gave **2a** (6.35 g, 2.3 mmol) in 55% yield as a white solid (TLC R_f = 0.8, hexane/ethyl acetate = 3:1): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.42 (s, 3 H), 3.85 (d, 6.9 Hz, 2 H), 4.08 (d, 2.0 Hz, 2 H), 5.12 (d, 9.8 Hz, 1 H), 5.22 (d, 16.7 Hz, 1 H), 5.57 (m, 1 H), 6.28 (m, 2 H), 7.29 (d, 7.9 Hz, 2 H), 7.73 (d, 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.8, 36.0, 48.2, 74.0, 76.3, 118.7, 127.0, 128.0, 129.7, 135.8, 135.9, 136.1, 143.8; IR (in $CHCl_3$) 3296 (w), 3152 (w), 2968 (w), 2256 (s), 1795 (w), 1595 (br); HRMS (EI) calcd for ($C_{15}H_{17}S_1O_2N_1$) 275.0980, found 275. 0981.

2-(Toluene-4-sulfonyl)-2,3,3a,6-tetrahydro-1*H*-isoindole (2A): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.10 (m, 3 H), 2.42 (s, 3 H), 2.44 (m, 1 H), 2.90 (t, 10.6 Hz, 1 H), 3.20 (m, 1 H), 3.88 (t, 9.96 Hz, 1 H), 5.42 (d, 9.96 Hz, 1 H), 5.60 (m, 1 H), 6.10 (s, 1 H), 7.28 (d, 7.9 Hz, 2 H), 7.66 (d, 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6, 26.9, 51.0, 53.1, 117.3, 123.5, 126.9, 127.7, 129.9, 135.2, 143.6; IR (in $CHCl_3$) 3296 (w), 3152 (w), 2968 (w), 2256 (s), 1795 (w), 1595 (br); HRMS (EI) calcd for ($C_{15}H_{17}S_1O_2N_1$) 275.0980, found 275. 0982

(5-Prop-2-ynyloxypenta-1,3-dienyl)benzene (5a). To a solution of anhydrous THF (30 mL) were added 1.1 equiv (1.16 mL, 6.31 mmol) of HMPT (hexamethylphosphorus triamide), 1.2 equiv of NaH (0.30 g, 7.49 mmol, 60 wt % stabilized mineral oil), and 5-phenylpenta-2, 4-dien-1-ol (1.0 g, 6.2 mmol) at 0 °C. After the solution was stirred for 1 h, 1.3 equiv of propargyl bromide (0.88 mL, 8.11 mmol, 80 wt % in toluene) was added at 0 °C. After the resulting solution was stirred at room temperature for 6 h, the reaction mixture was extracted with aqueous NH_4Cl solution and Et_2O. Flash column chromatography gave colorless oil **5a** (1.0 g, 5.3 mmol) in 85% yield (TLC R_f = 0.75, hexane/Et_2O = 2:1): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.48 (m, 1 H), 4.19 (d, 1.0 Hz, 2 H), 4.21 (d, 2.4 Hz, 2 H), 5.90 (dt, 15.2 Hz, 6.3 Hz, 1 H), 6.48 (dd, 15.2 Hz, 10.4 Hz, 1 H), 6.60 (d, 15.6 Hz, 1 H), 6.82 (dd, 15.6 Hz, 10.4 Hz, 1 H), 7.27 (m, 1 H), 7.35 (m, 1 H), 7.42 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 57.2, 70.1, 74.7, 79.9, 126.6, 127.9, 128.3, 128.8, 129.2, 133.3, 134.0, 137.3; IR (cm^{-1}, in $CHCl_3$) 3313 (s), 3040, 2864, 2256 (s), 1642 (w), 1446 (m), 1382 (m); HRMS (EI) calcd for ($C_{14}H_{14}O_1$) 198.1045, found 198.1044.

6-Phenyl-1,3,3a,6-tetrahydroisobenzofuran (5A): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.21 (m, 1 H), 3.38 (dd, 11.1 Hz, 7.3 Hz, 1 H), 4.05 (m, 1 H), 4.31 (m, 2 H), 4.49 (m, 1 H), 5.57 (m, 1 H), 5.88 (m, 2 H), 7.22 (m, 2 H), 7.29 (m, 1 H), 7.36 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 39.4, 43.5, 69.5, 72.4, 119.5, 122.4, 126.7, 128.2, 128.8, 131.9, 138.9, 145.2; IR (cm^{-1}, in $CHCl_3$) 3360 (br), 2884, 2056 (s), 1792 (w), 1635 (w), 1462 (m), 1382 (m); HRMS (EI) calcd for ($C_{14}H_{14}O_1$) 198.1045, found 198.1044.

(2-Methyl-5-prop-2-ynyloxypenta-1,3-dienyl)benzene (6a). To a solution of anhydrous THF (30 mL) were added 1.1 equiv of HMPT (1.16 mL, 6.31 mmol), 1.2 equiv of NaH (0.28 g, 6.9 mmol, 60 wt % stabilized mineral oil), and 4-methyl-5-phenylpenta-2, 4-dien-1-ol (1.0 g, 5.7 mmol) at 0 °C. After the solution was stirred for 1 h, 1.3 equiv of propargyl bromide (0.80 mL, 7.5 mmol, 80 wt % in toluene) was added at 0 °C. After the resulting solution was stirred at room temperature for 6 h, the reaction mixture was extracted with aqueous NH_4Cl solution and Et_2O. Flash column chromatography gave colorless oil **6a** (1.0 g, 4.9 mmol) in 85% yield (TLC: R_f = 0.75, hexane/Et_2O = 2:1): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.02 (s, 3 H), 2.47 (s, 1 H), 4.19 (m, 4 H), 5.89 (m, 1 H), 6.46 (s, 1 H), 6.53 (d, 10.3 Hz, 1 H), 7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.0, 57.1, 70.5, 74.6, 79.9, 124.3, 126.8, 128.3, 129.3, 132.2, 135.0, 137.7, 139.0; IR (cm^{-1}, in $CHCl_3$): 3313 (s), 3040, 2864, 2256 (s), 1642 (w), 1446 (m), 1382 (m); HRMS (EI) calcd for ($C_{15}H_{16}O_1$) 212.1201, found 212.1200.

5-Methyl-6-phenyl-1,3,3a,6-tetrahydroisobenzofuran (6A): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.48 (s, 3 H), 3.25 (m, 1 H), 3.38 (dd, 11 Hz, 7 Hz, 1 H), 3.88 (d, 9.7 Hz, 1 H), 4.30 (dd, 14 Hz, 6.8 Hz, 2 H), 4.46 (ddt, 11.8 Hz, 3.3 Hz, 1.7 Hz, 1 H), 5.49 (s, 1 H), 5.64 (s, 1 H), 7.26 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.3, 40.7, 62.3, 73.5, 118.3, 120.0, 126.6, 128.3, 128.6, 128.7, 137.0, 144.5; IR (cm^{-1}, in $CHCl_3$) 3056 (s), 2976 (s), 2303 (m), 1600 (w), 1424 (s), 1260 (s); HRMS (EI) calcd for ($C_{15}H_{16}O_1$) 212.1201, found 212.1201.

***N*-(4,5-Dimethylcyclohexa-1,4-dienylmethyl)-4-methylbenzenesulfonamide (9A):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.58 (s, 6 H), 2.42 (s, 3 H), 2.43 (m, 2 H), 2.53 (m, 2 H), 3.47 (m, 2 H), 4.33 (m, 1 H), 5.53 (m, 1 H), 7.28 (d, 7.9 Hz, 2 H), 7.74 (d, 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.3, 18.5, 21.6, 33.8, 34.1, 49.1, 122.8, 123.1, 127.4, 129.8, 131.0, 137.7, 143.4; IR (cm^{-1}, in $CHCl_3$) 3376 (w), 3152 (w), 2978 (w), 2256 (s), 1808 (w), 1795 (w), 1635 (w), 1465 (m), 1382 (m), 1324 (br), 1155 (s), 1091 (s); HRMS (EI) calcd for ($C_{16}H_{21}S_1O_2N_1$) 290.1294, found 290.1293.

4-Methyl-*N*-(4-methylcyclohexa-1,4-dienylmethyl)benzenesulfonamide (9B): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.62 (s, 3 H), 2.38 (s, 3 H), 2.4 (m, 4 H), 3.48 (m, 2 H), 4.5 (m, 1 H), 5.34 (m, 1 H), 5.55 (m, 1 H), 7.28 (m, 2 H), 7.73 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.9, 21.9, 31.4, 31.6, 48.2, 117.2, 118.1, 125.7, 129.6, 135.7, 136.8, 141.2; HRMS (EI) calcd for ($C_{15}H_{19}S_1O_2N_1$) 277.1136, found 277.1136.

4-Methyl-*N*-(5-methylcyclohexa-1,4-dienylmethyl)benzenesulfonamide (9C): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.62 (s, 3 H), 2.38 (s, 3 H), 2.4 (m, 4 H), 3.48 (m, 2 H), 4.5 (m, 1 H), 5.34 (m, 1 H), 5.55 (m, 1 H), 7.28 (d, 7.9 Hz, 2 H), 7.73 (d, 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.9, 23.2, 29.2, 38.9, 48.5, 116.9, 117.9, 125.4, 129.5, 134.7, 136.3, 140.9; HRMS (EI) calcd for ($C_{15}H_{19}S_1O_2N_1$) 277.1136, found 277.1138.

4-Methyl-*N*-(3-methylcyclohexa-1,4-dienylmethyl)benzenesulfonamide (9D): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.61 (s, 3 H), 2.45 (s, 3 H), 2.50 (m, 4 H), 3.45 (m, 2 H), 4.90 (m, 1 H), 5.35 (m, 1 H), 5.54 (s, 1 H), 7.27 (d, 7.9 Hz, 2 H), 7.74 (d, 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.8, 21.2, 31.4, 31.7, 48.5, 121.9, 124.8, 125.7, 129.9, 135.9, 137.3, 141.00; HRMS (EI) calcd for ($C_{15}H_{19}S_1O_2N_1$) 277.1136, found 277.1138.

4-Methyl-*N*-(6-methylcyclohexa-1,4-dienylmethyl)benzenesulfonamide (9E): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.61 (s, 3 H), 2.45 (s, 3 H), 2.50 (m, 4 H), 3.45(m, 2H), 4.90 (m, 1 H), 5.35 (m, 1 H), 5.54 (s, 1 H), 7.27 (d, 7.9 Hz, 2 H), 7.74 (d, 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.3, 20.8, 30.1, 32.3, 45.8, 116.7, 124.8, 125.7, 129.9, 136.6, 140.2, 140.9, 141.2; HRMS (EI) calcd for ($C_{15}H_{19}S_1O_2N_1$) calcd 277.1136, found 277.1138.

***N*-Boc-*N*-(4,5-dimethylcyclohexa-1,4-dienylmethyl)-4-methyl-*N*-(3-phenylprop-2-ynyl)benzenesulfonamide (10A):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.32 (s, 9 H), 1.58 (s, 3 H), 1.61 (s, 3 H), 2.39 (s, 3 H), 2.45 (t, 7.5 Hz, 2 H), 2.62 (s, 2 H), 4.36 (s, 2 H),

5.62 (s, 1 H), 7.23 (d, 8 Hz, 2 H), 7.76(d, 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.3, 18.6, 21.7, 28.0, 33.7, 33.9, 51.6, 81.2, 122.1, 122.5, 122.8, 128.3, 129.7, 130.9, 137.2, 144.2, 151.2; IR (cm^{-1}, NaCl) 2312 (s), 1723 (s), 1548 (w), 1419 (br); HRMS (EI) calcd for ($C_{21}H_{29}S_1O_4N_1$) 391.1817, obsd 391.1818.

***N*-[2-(4,5-Dimethylcyclohexa-1,4-dienyl)ethyl]-4-methylbenzenesulfonamide (11A):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.56 (s, 3 H), 1.60 (s, 3 H), 2.10 (t, 6.5 Hz, 2 H), 2.20 (m, 2 H), 2.42 (s, 3 H), 2.56 (m, 2 H), 3.03 (dd, 12 Hz, 6 Hz, 2 H), 4.50 (t, 5.5 Hz, 1 H), 5.38 (s, 1 H), 7.28 (d, 8 Hz, 2 H), 7.72(d, 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.3, 18.5, 21.7, 33.9, 35.4, 36.5, 40.6, 122.5, 122.7, 123.1, 127.3, 129.8, 131.2, 137.1, 143.5; HRMS (EI) calcd for ($C_{17}H_{23}S_1O_2N_1$) 305.1449, obsd 305.1448.

4-Methyl-*N*-(2,4,5-trimethylcyclohexa-1,4-dienylmethyl)benzenesulfonamide (12A): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.53 (s, 3 H), 1.54 (s, 3 H), 1.56 (s, 3 H), 2.42 (s, 3 H), 2.44 (s, 4 H), 3.54 (d, 5.8 Hz, 2 H), 4.49 (t, 5.8 Hz, 1 H), 7.30 (d, 8 Hz, 2 H), 7.75 (d, 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.9, 18.0, 18.1, 21.7, 36.1, 40.2, 44.3, 122.7, 122.9, 123.2, 127.3, 129.7, 130.3, 137.1, 143.5; HRMS (EI) calcd for ($C_{17}H_{23}S_1O_2N_1$) (EI, *m*/*z*) 305.1449, obsd 305.1448.

***N*-(4,5-Dimethylcyclohexa-1,4-dienylmethyl)-4-methyl-*N*-(3-phenylprop-2-ynyl)benzenesulfonamide (13A):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.63 (s, 3 H), 1.65 (s, 3 H), 2.31 (s, 3 H), 2.63 (s, 4 H), 3.78 (s, 2 H), 4.23 (s, 2 H), 5.70 (s, 1 H), 7.03 (d, 8.0 Hz, 2 H), 7.22 (m, 5 H), 7.77 (d, 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.3, 18.6, 34.0, 34.1, 52.6, 82.2, 85.8, 122.6, 123.4, 128.0, 128.2, 128.7, 129.6, 131.7, 136.6, 143.5; HRMS (EI) calcd for ($C_{25}H_{27}S_1O_2N_1$) 405.1762, obsd 405.1764.

4-Methyl-*N*-pent-2-en-4-ynylbenzenesulfonamide (14a). To a flame-dried 50 mL Schlenk flask capped with a rubber septum were added *N*-Boc-4-methyl-*N*-pent-2-en-4-ynylbenzenesulfonamide (1.0 g, 3.0 mmol) and 5 equiv of TFA (1.11 mL, 14.9 mmol) sequentially. After the solution was stirred for 3 h at room temperature, the solution was evaporated under reduced pressure. Flash chromatography on a silica gel column eluting with hexane and ethyl acetate (v/v, 10:1) gave brown solid **14a** (0.35 g, 1.5 mmol) in 50% yield (TLC R_f = 0.55, hexane/ethyl acetate = 3:1): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.35 (s, 3 H), 2.98 (s, 1 H), 3.83 (m, 2 H), 4.32 (m, 1 H), 5.62 (s, 1 H), 6.12 (m, 1 H), 7.34 (d, 8.0 Hz, 2 H), 7.81 (d, 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.9, 42.5, 80.0, 82.8, 113.9, 125.4, 129.5, 136.3, 140.2, 140.9; IR (cm^{-1}, in $CHCl_3$) 3408 (br), 3296 (s), 3168 (w), 3008 (w), 2240 (s), 1916 (w), 1792 (w), 1593 (m), 1465 (br), 1408 (br), 1328 (s), 1158 (s), 1092 (s); HRMS (EI) calcd for ($C_{12}H_{13}S_1O_2N_1$) 235.0667, obsd 235.0667.

***N*-[3-(4,5-Dimethylcyclohexa-1,4-dienyl)allyl]-4-methylbenzenesulfonamide (14A):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.71 (s, 6 H), 2.35 (m, 4 H), 2.63 (s, 3 H), 5.29 (m, 1 H), 5.74 (m, 1 H), 6.15 (m, 1 H), 7.24 (m, 2 H), 7.81 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.4, 16.8, 20.9, 36.5, 41.3, 44.1, 118.3, 125.4, 127.3, 129.5, 128.5, 136.3, 140.9; IR (cm^{-1}, in $CHCl_3$) 3360 (br), 2256 (m), 1808 (w), 1459 (m), 1155 (s), 1094 (s); HRMS (EI) calcd for ($C_{18}H_{23}S_1O_2N_1$) 317.1449, obsd 317.1450.

***N*-(3-Cyclopropylallyl)-4-methyl-*N*-(3-phenylprop-2-ynyl)benzenesulfonamide (21a).** To a flame-dried 100 mL Schlenk flask containing 3-cyclopropylprop-2-en-1-ol (1.0 g, 10 mmol) and THF (30 mL) at −78 °C was added 1.2 equiv of *n*-BuLi (4.8 mL, 2.5 M in hexane). After the solution was stirred for 10 min, 1.2 equiv of methanesulfonyl chloride (0.95 mL, 12 mmol) and 1.3 equiv of lithium bromide (1.11 g, 13 mmol) were added in one portion. After the solution was stirred for 30 min, it was transferred via cannula to the DMF solution containing 4-methyl-*N*-(3-phenyl-prop-2-ynyl)-benzenesulfonamide (2.85 g, 10 mmol) and NaH (12 mmol, 0.48 g, 60 wt % in mineral oil). To a second flame-dried 100 mL Schlenk flask charged with 4-methyl-*N*-(3-phenylprop-2-ynyl)benzenesulfonamide (2.85 g, 10 mmol) was added NaH (12 mmol, 0.48 g, 60 wt % in mineral oil) slowly at 0 °C. After the solution was stirred for 30 min at room temperature, the solution was cooled to −78 °C. The bromide solution prepared above was transferred via cannula into the second flask. The resulting solution was stirred at −78 °C for 2 h and at room temperature for 4 h. Quenching with NaCl solution, extraction with diethyl ether, drying over $MgSO_4$, and evaporation gave a crude product. Flash chromatography on a silica gel eluting with hexane and ethyl acetate (v/v, 10:1) gave white solid **21a** (TLC: R_f = 0.7, hexane/ethyl acetate = 2:1): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.36 (m, 2 H), 0.72 (m, 2 H), 1.44 (m, 1 H), 2.32 (s, 3 H), 3.80 (d, 6.7 Hz, 2 H), 4.29 (s, 2 H), 5.21 (m, 1 H), 5.46 (m, 1 H), 7.02 (d, 7.9 Hz, 2 H), 7.24 (m, 5 H), 7.74 (d, 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.1, 13.7, 21.6, 36.6, 46.7, 82.0, 85.7, 120.8, 122.5, 128.0, 128.3, 128.5, 129.7, 131.6, 136.1, 140.9, 143.6; IR (cm^{-1}, in $CHCl_3$) 3064 (s), 2304 (m), 1419 (s), 1344 (w), 1264 (s), 1161 (m); HRMS (EI) calcd for ($C_{22}H_{23}S_1O_2N_1$) 365.1449, obsd 365.1450.

8-Phenyl-2-(toluene-4-sulfonyl)-1,2,3,3a,6,7-hexahydrocyclohepta[*c*]pyrrole (21A): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.25 (m, 3 H), 2.45s, 3 H), 2.78 (dd, 9 Hz, 9 Hz, 1 H), 2.87 (m, 1 H), 3.60 (d, 14 Hz, 1 H), 3.73 (dd, 9 Hz, 9 Hz, 1 H), 3.85 (d, 14 Hz, 1 H), 3.93 (m. 1 H), 5.64 (m, 1 H), 6.65(m, 1 H), 7.08 (d, 8.0 Hz, 2 H), 7.30 (m, 5 H), 7.65 (d, 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.8, 26.7, 32.8, 40.6, 52.4, 55.0, 127.1, 127.2, 128.2, 128.3, 128.6, 129.8, 131.0, 131.9, 135.6, 136.9, 142.6, 144.0; IR (cm^{-1}, in $CHCl_3$) 3056 (s), 2970 (s), 2304 (m), 1420 (s), 1264 (s), 1158 (m); HRMS (EI) calcd for ($C_{22}H_{23}S_1O_2N_1$) 365.1449, obsd 365.1448.

***N*-(3-Cyclopropyl-allyl)-4-methyl-*N*-pent-2-ynylbenzenesulfonamide (23a):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.34 (m, 2 H), 0.70 (m, 2 H), 0.88 (t, 7.4 Hz, 3 H), 1.40 (m, 1 H), 1.90 (m, 2 H), 2.40 (s, 3 H), 3.72 (d, 6.7 Hz, 2 H), 4.30 (t, 2.2 Hz, 2 H), 5.21 (m, 1 H), 5.38 (m.1 H), 7.27 (d. 7.9 Hz, 2 H), 7.72 (d, 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 6.9, 12.2, 13.4, 13.6, 21.6, 36.1, 48.3, 72.1, 87.4, 117.2, 121.0, 127.9, 129.3, 136.6, 140.3, 143.2; IR (cm^{-1}, in $CHCl_3$) 3408 (br), 3168 (m), 2960 (s), 1795 (w), 1596 (m), 1459 (s), 1340 (s); HRMS (EI) calcd for ($C_{18}H_{23}S_1O_2N_1$) 317.1449, obsd 317.1449.

8-Ethyl-2-(toluene-4-sulfonyl)-1,2,3,3a,6,7-hexahydrocyclohepta-[*c*]pyrrole (23A): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.95 (t, 7.5 Hz, 3 H), 1.93 (m, 3 H), 1.97 (m, 1 H), 2.21 (m, 1 H), 2.44 (s, 3 H), 2.49 (m, 1 H), 2.63 (m, 1 H), 3.53 (d, 13.1 Hz, 1 H), 3.69 (m, 2 H), 3.98 (d, 13.1 Hz, 1 H), 5.30 (m, 1 H), 5.61 (m, 1 H), 7.34 (d, 7.9 Hz, 2 H), 7.70 (d, 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.0, 21.6, 26.5, 28.5, 29.5, 40.2, 51.1, 54.8, 128.1, 129.7, 130.9, 131.6, 132.1, 135.8, 143.8; HRMS (EI) calcd for ($C_{18}H_{23}S_1O_2N_1$) (EI, *m*/*z*) 317.1449, found 317.1448.

Acknowledgment. This work was supported by the Korean Research Foundation Grant funded by the Korean Government (MOEHRD) (R02-2004-000-10005-0). S.I.L, S.Y.P., and J.H.P. acknowledge BK21 fellowships. J.H.P. acknowledges a GSI-1 fellowship.

Supporting Information Available: Procedures, spectral data for new compounds, and details for the crystal structures of **1**, **5A**, and **13A**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO051685U