Alkynyliodonium Salts in Organic Synthesis. Preparation of Annelated Dihydropyrroles by Cascade Addition/Bicyclization of Dienyltosylamide Anions with Phenyl(propynyl)iodonium Triflate

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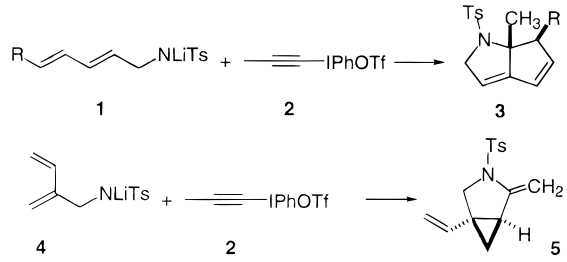
The addition of simple pentadienyltosylamide derivatives to the two-carbon electrophile phenyl(propynyl)iodonium triflate initiates a sequence of transformations that furnishes complex, highly functionalized cyclopentenannelated dihydropyrrole products in moderate yields with complete stereoselection. This sequence demonstrates that diyls resulting from homolytic scission of alkylidene carbene−alkene adducts can be readily accessed under mild experimental conditions and that, in the presence of appropriate pendant functionality, these diyls can productively cyclize. The isomeric isoprene-derived tosylamides follow an abbreviated reaction course and deliver azabicyclo[3.1.0]-hexanes via an isomerization that competes with diyl formation.

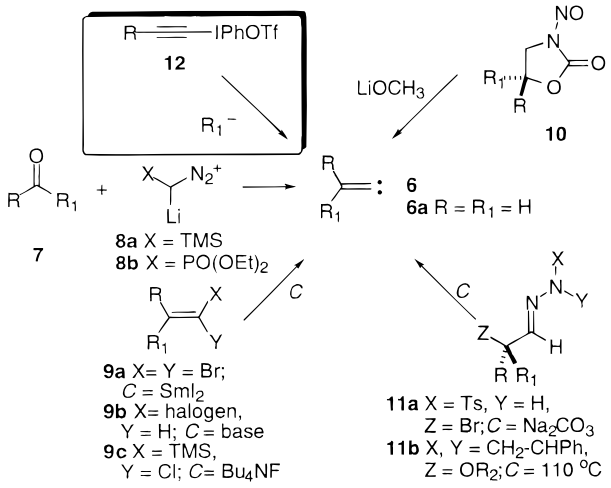
Serial cyclization of polyolefinic substrates via propagating reactive intermediates remains among the most efficient of the canonical strategies for converting simple acyclic precursors into polycyclic products. Whereas the bulk of the efforts in this area have utilized either anionic, cationic, or radical intermediates, one recent unconventional example of this process was proposed to proceed in succession through an alkylidene carbene and then a trimethylenemethane diyl en route to the cyclopentannelated pyrroles **3** from the pentadienyl substrates **1** and the alkynyliodonium salt **2**.[1] Intramolecular capture of these reactive species limits both regiochemical and stereochemical options, and consequently these transformations proceed with high levels of selectivity for the products **3** and **5** (Scheme 1). A detailed account of this work is presented, including descriptions of substrate synthesis, presentation of addition/cyclization results, and analysis of mechanistic/selectivity issues.

The ready accessibility and high reactivity of alkylidene carbenes has encouraged their use in several C−C bond forming processes.[2] Estimates of the ΔH_f of the parent species, vinylidene $H_2C{=}C{:}$ **6a**, converge on a value (101 ± 6 kcal/mol) even greater than one of the most reactive organic intermediates known, singlet methylene.[3] High level computational analysis of **6a** describes a geometry (C=C = 1.33 Å, C−H = 1.09 Å) not remarkably different than ethylene.[4] Electronic structure calculations support assignment of a singlet ground state separated by a 48 kcal/mol barrier from the nearly inaccessible triplet isomer.[3b] The dominant reactivity profile exhibited by a free alkylidene carbene **6** is mild electrophilicity, as indicated by a $\rho = -0.64$ for cycloaddition with substituted styrenes (compare $\rho^+ = -0.62$ for $Cl_2C{:}$ addition to styrenes).[5]

Scheme 1



Scheme 2



Low-temperature methods for the preparation of these transient intermediates utilize a wide variety of unrelated precursors, Scheme 2. Ketonic **7** or alkenic **9** precursors have documented utility in delivering a range of substituted alkylidene carbenes under mild conditions, whereas the more exotic *N*-nitrosooxazolindones **10** or hydrazone derivatives **11** have seen less service in this regard.[2a] A more recent entry point into alkylidene carbene chemistry, the alkynyliodonium salts **12**,[7] have

(1) (a) Feldman, K. S.; Mareska, D. A.; *J. Am. Chem. Soc.* **1998**, *120*, 4027. (b) Feldman, K. S.; Mareska, D. A. *Tetrahedron Lett.* **1998**, *39*, 4781.

(2) Kirmse, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1164. (b) Stang, P. J. *Chem. Rev.* **1978**, *78*, 333.

(3) (a) Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Phys. Chem.* **1989**, *91*, 5974. (b) Bodor, N.; Dewar, M. J. S.; Wasson, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9095.

(4) Gallo, M. M.; Hamilton, J. P.; Schaeffer, H. F. III *J. Am. Chem. Soc.* **1990**, *112*, 8714.

(5) Gilbert, J. C.; Giamalva, D. H. *J. Org. Chem.* **1992**, *57*, 4185.

(6) Seyferth, D.; Mui, J. Y. P.; Damrauer, R. *J. Am. Chem. Soc.* **1968**, *90*, 6182.

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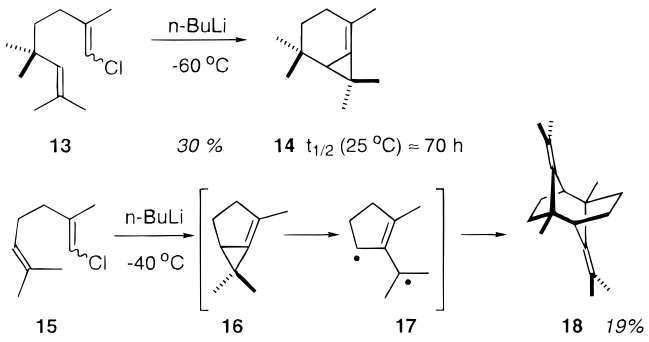
Scheme 3

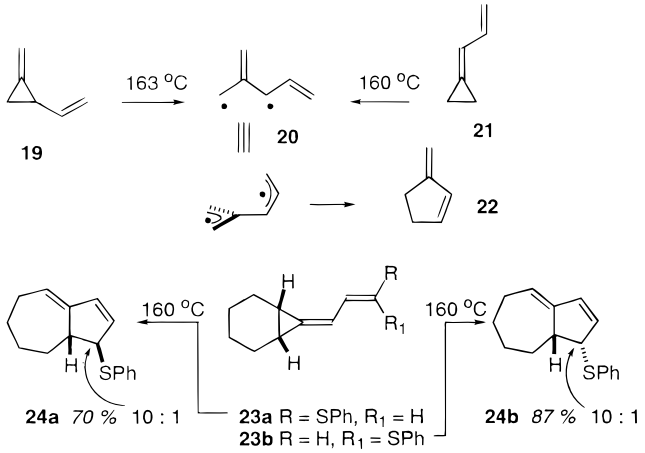


received increasing attention plausibly due to their versatility. Unique among the alkylidene carbene precursors, these salts offer the opportunity to bring together two distinct R- and R_1-containing components during preparation of the free carbene. This advantage becomes particularly significant when alkylidene carbenes bearing heteroatoms (R_1 = N, O, S species) are required.

These monosubstituted carbon species participate in the types of reactions usually reserved for highly reactive and electrophilic disubstituted carbenes, including formal dimerization, intermolecular X−H, or intramolecular 1,5 C−H insertion, 1,2 substituent shift, and alkene cycloaddition.[2b] When either R or R_1 (cf. **6**) is H, Ar, or SiR'_3, the 1,2 substituent shift precedes all other options and an alkyne product is formed.[2b,7] Alkyl or heteroatom substituents on an alkylidene carbene raise the barrier for this shift and permit the slower X−H or C−H insertions to prevail. The selectivity among C−H bonds (tertiary > secondary > primary)[8] is in accord with the expectations of reaction through an electron deficient transition state.[5] Only when both 1,2 shift and 1,5 C−H insertion have been suppressed can alkene cycloaddition emerge as the major reaction pathway. Numerous studies have shown that alkene geometry is faithfully translated into product stereochemistry as befitting a concerted cycloaddition between two singlet species.[2b,5]

An intramolecular variant of the alkylidene carbene/alkene cycloaddition was explored by Köbrich et al. (Scheme 3), who discovered that this high energy intermediate was capable of delivering materially strained alkenes **14** and **16**.[9] Whereas the bicyclo[4.1.0]heptene species **14** was isolable, the existence of the lower homologue **16** could only be inferred from formation of the dimerization product **18**. Later studies by Berson and Salinero provided unequivocal evidence for the intermediacy of a trimethylenemethane diyl **17**.[10] This transformation, while of little preparative value, did reveal that (1) intramolecular cycloaddition of an alkylidene carbene with a pendant alkene is capable of generating highly strained bicycloalkene products, and (2) the imbedded methylenecyclopropane constructs so formed are prone to facile homolytic C−C bond scission to furnish

Scheme 4



trimethylenemethane-type diyls. This latter point is not without merit, as the cleavage temperature of **16** is strikingly lower than that for the comparable bond rupture in an unstrained methylenecyclopropane system (≥200 °C).[11]

This situation might be improved, however, by presenting the intermediate diyl with a suitable internal trap. Much effort has been directed toward developing tethered alkene/trimethylenemethane diyl cycloadditions as an effective polyquinane synthesis strategy by Little and co-workers.[12] A trap in the form of an adjacent alkene offers a more direct pathway for conversion of a reactive diyl intermediate into an stable product. This chemistry has been explored in seminal thermolysis studies on both vinylmethylenecyclopropane isomers **19** and **21**, Scheme 4.[13] Much mechanistic inquiry ultimately provided a coherent picture of these thermolyses that featured a common intermediate, the orthogonal vinyltrimethylenemethane species **20**,[14] as the precursor to methylenecyclopentene product formation. Recently, Cohen et al. have developed this rearrangement into a useful and stereoselective cyclopentene annelation sequence, **23a**/**b** → **24a**/**b**.[15] The relatively high temperatures required for reorganization in these comparatively unstrained systems are in sharp contrast to the Köbrich work where the vinylmethylenecyclopropane cleaves at < −40 °C.

Thus, the basic stratagem underlying the synthesis of dihydropyrroles **3** involves choosing the appropriate unsaturated substrate **1** that will deliver, upon combination with **2**, an alkylidene carbene whose primary reactivity option is limited to internal alkene addition. Once this addition occurs, the strained bicyclo[3.1.0]hexene product can cleave to furnish a reactive trimethylenemethane diyl through chemistry analogous to the Köbrich/Berson work (e.g., **16** → **17**). However, unlike the

(7) (a) Stang, P. J.; Zhdankin, V. V. *Tetrahedron* **1998**, *54*, 10927. (b) Stang, P. J. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; Wiley-VCH: Weinheim, Germany, 1995.

(8) Gilbert, J. C.; Giamalva, D. H.; Weerasooriya, U. *J. Org. Chem.* **1983**, *48*, 5251.

(9) (a) Köbrich, G.; Heinemann, H. *J. Chem. Soc., Chem. Commun.* **1969**, 493. (b) Köbrich, G.; Baumann, M. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 52.

(10) (a) Salinero, R. F.; Berson, J. A. *Tetrahedron Lett.* **1982**, *23*, 1447. (b) Salinero, R. F.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7094.

(11) Chesick, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 220.

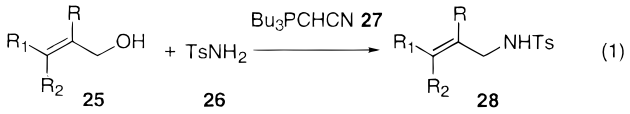
(12) (a) Little, R. D. *Chem. Rev.* **1996**, *96*, 93. (b) Little, R. D. *Chem. Rev.* **1986**, *86*, 875.

(13) (a) Billups, W. E.; Leavell, K. H.; Lewis, E. S.; Vanderpool, S. *J. Am. Chem. Soc.* **1973**, *95*, 8096. (b) Kende, A. S.; Riecki, E. E. *J. Am. Chem. Soc.* **1972**, *94*, 1397. (c) Roth, W. R.; Schmidt, T. *Tetrahedron Lett.* **1971**, 3639. (d) Pikulin, S.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 8274. (e) Shields, T. C.; Billups, W. E.; Lepley, A. R. *J. Am. Chem. Soc.* **1968**, *90*, 4749. (f) Gilbert, J. C.; Higley, D. P. *Tetrahedron Lett.* **1973**, 2075.

(14) Direct (IR) detection of triplet-4-methylene-2-pentene-1,5-diyl: Maier, G.; Senger, S. *J. Am. Chem. Soc.* **1997**, *119*, 5852.

(15) (a) Davidson, E. R.; Gajewski, J. J.; Shook, C. A.; Cohen, T. *J. Am. Chem. Soc.* **1995**, *33*, 8495. (b) Shook, C. A.; Romberger, M. L.; Jung, S.-H.; Xiao, M.; Sherbine, J. P.; Zhang, B.; Lin, F.-T.; Cohen, T. *J. Am. Chem. Soc.* **1993**, *115*, 10754.

Table 1. Synthesis of the Dienyltosylamides 28 from the Corresponding Alcohols 25



entry	dienol	R	R_1	R_2	tosylamide	yield (%)
a	**25a**	H	(*E*)-$H_3CCH{=}CH$	H	**28a**	59
b	**25b**	H	$(H_3C)_2C{=}CH$	H	**28b**	17
c	**25c**	H	(*E*)-TMSCH=CH	H	**28c**	46
d	**25d**	H	(*E*)-PhCH=CH	H	**28d**	26
e	**25e**	H	(*E*)-*p*-$(O_2N)C_6H_4$ CH=CH	H	**28e**	37
f	**25f**	H	(*Z*)-PhCH=CH-	H	**28f**	42
g	**25g**	H	H	(*E*)-PhCH=CH	**28g**	26
h	**25h**	$CH{=}CH_2$	H	H	**28h**	53

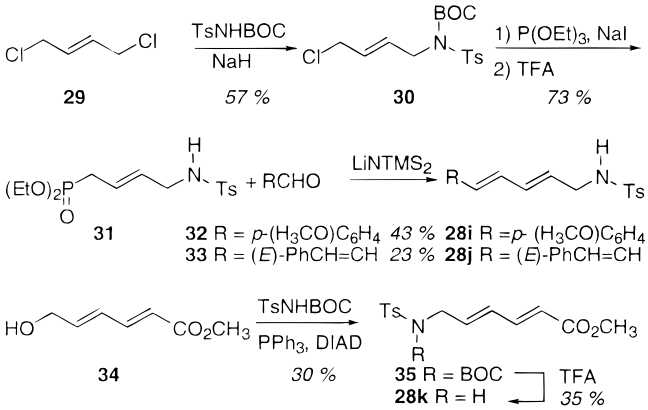
earlier studies, incorporation of the second (adjacent) alkene into the substrate provides a low-energy pathway for intramolecular quenching of the diyl that leads to methylenecyclopentene formation. The reduction of this hypothesis to practice is described below.

Results and Discussion

The lack of relevant precedents for all of the projected reaction steps after alkylidene carbene generation from dienyltosylamide **1** and alkynyliodonium salt **2** suggested that a thorough examination of both substrate substituents and reaction parameters would be necessary to develop fully the desired bicyclization sequence. The earlier work of Köbrich and Berson demonstrated that cyclopropyl substituents profoundly influenced the facility of C−C bond scission within an annelated methylenecyclopropane substructure.[9,10] Thus, the electronic properties of the distal substituent R in **1** may play a decisive role in the completion of the planned reaction cascade. Similarly, the connectivity pattern in isomer **4** may introduce different reaction options to a putative bicyclo[3.1.0]hexene intermediate, as will become apparent as the cyclization studies unfold. Finally, the level of stereochemical control inherent in this transform will be probed with alkene isomers of the prototype (*E*,*E*)-diene. A comparison between the diastereoselectivity observed upon formation of **3** from these isomeric substrates and the related Cohen work will illuminate some of the subtle control elements that contribute to stereoselectivity upon cyclization of an orthogonal bis allylic radical related to **20**. For simplicity of analysis, the readily available and stable alkynyliodonium salt **2** will be used in all cases.

Functional group incompatibilities that emerged for certain substituents R during substrate synthesis necessitated the development of two distinct approaches to the panel of desired tosylamides. The majority of the desired dienyltosylamides, **28a**−**h**, were prepared from the readily available alcohol precursors **25**, eq 1 in Table 1. Initial efforts at direct displacement of the alcohol-derived tosylates or mesylates with the anion of toluenesulfonamide were uniformly disappointing. Classical Mitsunobu approaches likewise were frustrated by low yields and the predominance of S_N2'-like products. Eventual recourse to the highly activated Mitsunobu reagent cyanomethylenetributylphosphorane (CMBP, **27**) developed by Tsunoda[16] provided the dienyltosylamide derivatives in an acceptable compromise between yield and ease of

Scheme 5



product isolation, Table 1. Diallylation of tosylamide **26** was occasionally a problem, and the transformation failed entirely for substrates **25** with R_1 = *p*-$(H_3CO)C_6H_4CH{=}$CH and $PhHC{=}CH{-}CH{=}CH$ (R = R_2 = H). In the former case, S_N2'-type products predominantly were formed.

The two substrates **28i** and **28j** were prepared by phosphonate-mediated olefination of the requisite aldehydes **32** and **33**, respectively, using the allylic phosphonate reagent **31**, Scheme 5. The N-BOC analogue of tosylamide **31** has been reported to condense smoothly with aldehyde **32**.[17] In both cases examined, the desired polyalkenylated product was formed with complete (*E*) selectivity, albeit in modest yields. The methyl sorbate derivative **28k** was prepared via the Mitsunobu-generated N-BOC intermediate **35** in overall modest yield.

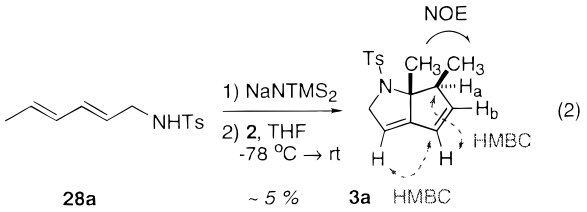
The initial attempts at addition/bicyclization utilized the sorbyltosylamide **28a** and iodonium salt **2** under conditions previously identified as conducive to alkylidene carbene generation.[18] A complex product mixture ensued, from which a single bicyclic material was isolated, eq 2. Subsequent careful examination of the crude reaction mixture (^{1}H NMR, extensive chromatography) did not provide any evidence for alternative cyclization products such as the putative methylenecyclopropane intermediate **43** (R = CH_3, R_1 = H) or the regioisomeric diyl closure product **47** (R, R_1 = CH_3, H) (cf. Scheme 7, vide infra). The overall framework connectivity, as well as the stereochemical details, was deduced from application of HMQC, HMBC, and DNOE NMR techniques, cf.

(16) Tsunoda, T.; Yamamoto, H.; Goda, K.; Ito, S. *Tetrahedron Lett.* **1996**, *37*, 2457.

(17) Connell, R. D.; Helquist, P.; Akermark, B. *J. Org. Chem.* **1989**, *54*, 3359.

(18) Feldman, K. S.; Bruendl, M. M.; Schildknegt, K.; Bohnstedt, A. C. *J. Org. Chem.* **1996**, *61*, 5440.

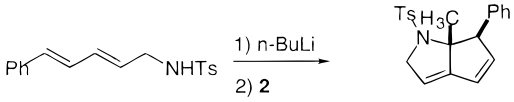
3a. The cis stereochemical assignment implied by the DNOE results was corroborated by the near zero coupling observed between H_a and H_b. The formation of this bicyclic product was consistent with the gross expectations outlined earlier, although both stereochemical and regiochemical control elements remain unidentified at this juncture.



(2)

The inherent low yield and difficulty in chromatographic isolation of the bicyclic product **3a** hindered optimization studies with **28a**. Subsequent cyclization experiments with the phenyl analogue **28d** revealed that not only were the preliminary yields of bicyclic product better, but the chromatography was cleaner as well. Thus, this substrate was chosen for extensive yield optimization studies, eq 3. Variables examined in these experiments included concentration, reagent ratio (**28d**:**2**), rate and order of addition, base, solvent, temperature, and time. The results of these trials indicated that the yield of bicycle **3d** did not vary significantly as concentration (0.01 to 0.1 M), addition rate (0.3 to 4 h), or base ($LiNTMS_2$, $KNTMS_2$, $NaNTMS_2$, or n-BuLi) were changed. However, the order of addition did matter, and the yield of **3d** was highest when a solution of **2** was added to **28d**/base and not the reverse. Three experimental parameters did modestly influence product yield: reagent ratio, solvent, and temperature. A survey of these variables, all examined at 0.01−0.05 M concentration with n-BuLi as base and an addition time of 4−5 h, is presented in Table 2. The upshot of these yield optimization studies with the phenyl-bearing substrate **28d** follows: 1.5 equiv of phenyl(propynyl)iodonium triflate (**2**) in THF added to the preformed tosylamide anion (1 equiv of n-BuLi) in refluxing THF (total concentration = 0.05 M) over 4−5 h maximizes the yield of the annelated dihydropyrrole product **3d**.

Table 2. Optimization of 3d Formation from 28d and 2

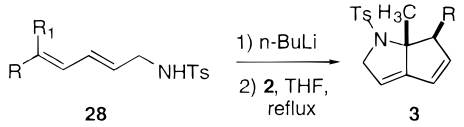


(3)

entry	solvent	equiv **2**	temp (°C)	yield **3d** (%)	recovered **28d** (%)
a	DME	1.0	85	36	34
b	PhH	1.0	80	41	15
c	$PhCH_3$	1.0	110	38	26
d	THF	1.0	65	52	14
e	**THF**	**1.5**	**65**	**58**	**14**
f	THF	2.0	65	49	17
g	THF	1.0	−78 → 25	27	20
h	THF	1.0	25	24	7

Finally, nucleophilic additives designed to temper the reactivity of the putative intermediate alkylidene carbene were included in a few scouting experiments. The presence of either 1 equiv of Ph_3P or Ph_2S in the reaction of **28d** with **2**, however, did not lead to any meaningful difference in the yield of **3d** (or amount of recovered diene) compared to the unperturbed reaction.

Table 3. Addition/Bicyclization of Dienyltosylamides 28 with Phenylpropynyliodonium Triflate (2) To Furnish Annelated Dihydropyrrole Products 3



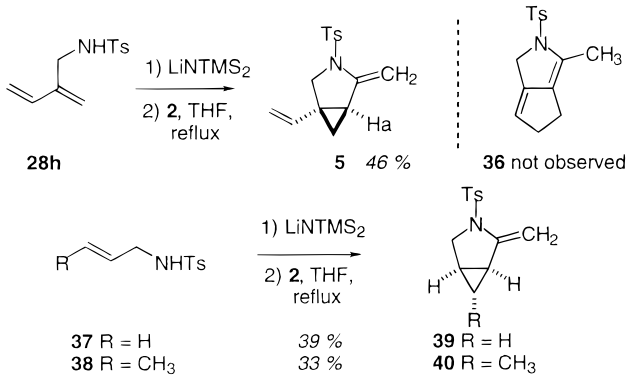
(4)

entry	diethyl-tosyl-amide	R	R_1	bicyclic product **3**	yield (%)	recovered **28** (%)
a	**28a**	CH_3	H	**3a**	24	17
b	**28b**	CH_3	CH	−	−	16
c	**28c**	TMS	H	**3c**	27	20
d	**28d**	Ph	H	**3d**	58	14
e	**28e**	*p*-$(O_2N)C_6H_4$	H	**3e**	12	29
f	**28f**	*p*-$(H_3CO)C_6H_4$	H	**3i**	51	10
g	**28g**	(*E*)-PhCH=CH	H	**3j**	35	21
h	**28h**	CO_2CH_3	H	−	−	50

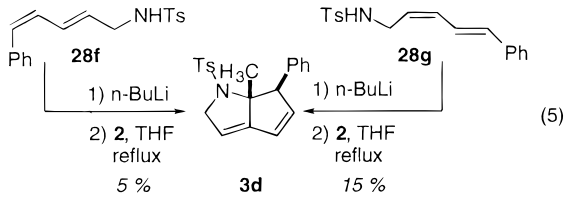
The optimized conditions described in Table 2, entry e, were exported to addition/bicyclization reactions for the remainder of the dienyltosylamide substrates **28a**−**c**,**e**,**i**−**k**, eq 4 and Table 3. While it is difficult to draw sweeping generalizations from this limited data set, it does appear that those dienyltosylamide substrates (**28a** and **28c**) whose substituent R cannot engage in conjugative radical stabilization (Table 3, entry a, R = CH_3, and entry c, R = TMS) did not perform as well as the R = aryl or R = vinyl analogues. For example, the *p*-methoxyphenyl-substituted dienyltosylamide **28i** and iodonium salt **2** combined with nearly equal efficiency as did the carefully optimized phenyl case **28d**. Dienyltosylamide substrates bearing electron-withdrawing functionality (Table 3, entry e, R = *p*-nitrophenyl, and entry h, = CO_2CH_3) participated poorly, if at all, in this transformation. It is possible that either intramolecular or intermolecular competitive conjugate addition reactions between the tosylamide anion and the Michael acceptor portion of these species diverted substrate from the desired reaction channel. The terminally disubstituted dienyltosylamide **28b** failed to provide characterizable product(s) upon combination with **2**, an observation that draws attention to the role of steric hindrance at a site of eventual bond formation (vide infra). The vinylogue of **28d**, trienyltosylamide **28j**, was only moderately successful in delivering the desired bicyclic product **3j**, a result that may in part reflect the sensitive nature of the triene unit. An overall requirement for radical-stabilizing groups that are at the same time immune to nucleophilic addition seems to characterize the higher yielding examples of this addition/bicyclization cascade.

The isomeric (*E*, *Z*)- and (*Z*, *E*)-dienyltosylamide substrates **28f** and **28g**, respectively, were designed to probe the relationship between starting alkene geometry and product stereochemistry. Extrapolation from the Cohen work (Scheme 4) would lead to the expectation that at least **28f** might afford a bicyclic product featuring a trans disposition between CH_3 and Ph. From this perspective, it was surprising to discover that both diene geometrical isomers furnished the same cis-substituted bicyclic product **3d** already in hand from the (*E*,*E*) isomer **28d**. No evidence for alternative products was forthcoming upon careful examination of the crude reaction mixture, although the conspicuously low yields still leave open the possibility that minor isomers escaped detection. Appar-

Scheme 6

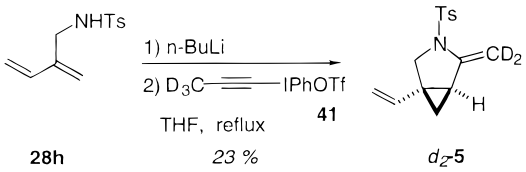


ently, there must be some mechanistic divergence between the Cohen examples and the reactions described in eq 5.



A very different type of product was observed upon use of a 2-substituted dienyltosylamide substrate in place of the 1-substituted analogues. The isoprenyltosylamide substrate **28h** was allowed to react with iodonium salt **2** under the optimized conditions with the anticipation that an annelated dihydropyrrole product **36** would emerge following sequential passage through an alkylidene carbene, a strained azabicyclo[3.1.0]hexene, and an orthogonal bis allylic radical, Scheme 6. However, the reality was very different. A single bicyclic product, the azabicyclo[3.1.0]hex*ane* species **5**, was isolated in moderate yield. This unexpected reaction course was not anomalous, as formation of the similar products **39** and **40** from the simple allylic tosylamides **37** and **38**, respectively, was observed as well. Evidently, the lack of a vinyl substituent at the alkene terminus of the allylic tosylamide is sufficient to divert this complex cascade down an alternative pathway when compared to the 1-dienyl-containing substrates.

An attempt to determine the origin of the unexpected ring juncture hydrogen H_a in **5** was pursued with the trideuterated version of **2**, the iodonium salt **41**, eq 6. Combining **28h** with **41** under standard conditions afforded only the *di*deuterioazabicyclo[3.1.0]hexane product d_2-**5**, eq 6. This result disqualifies the methyl group of **2** as the source of H_a. A few subsequent experiments extended the search for the origin of H_a. Combination of **28h** with **2** in d_8-THF did not afford any deuterated **5**, while treatment of **5** with $LiNTMS_2$ and then D_2O returned only unchanged **5**. Use of n-BuLi instead of $LiNTMS_2$ as base led to identical results, suggesting that the presence of *H*-$NTMS_2$ in the reaction medium was not crucial for the deprotonation/reprotonation sequence. Finally, reaction of the *phenyl*sulfonyl analogue of **28h** with **2** delivered the $PhSO_2$ analogue of **5** in 31% yield. Since this product is formed in the absence of the tolyl's methyl group, this latter experiment rules out $H_3C-PhSO_2N$ as the H_a donor in the **28h**/**2** reaction. It is conceivable that either the arylsulfonyl *ortho* protons or the CH_2 unit of **28h** might serve as the source of this hydrogen, but no labeling studies to test these hypotheses were conducted.

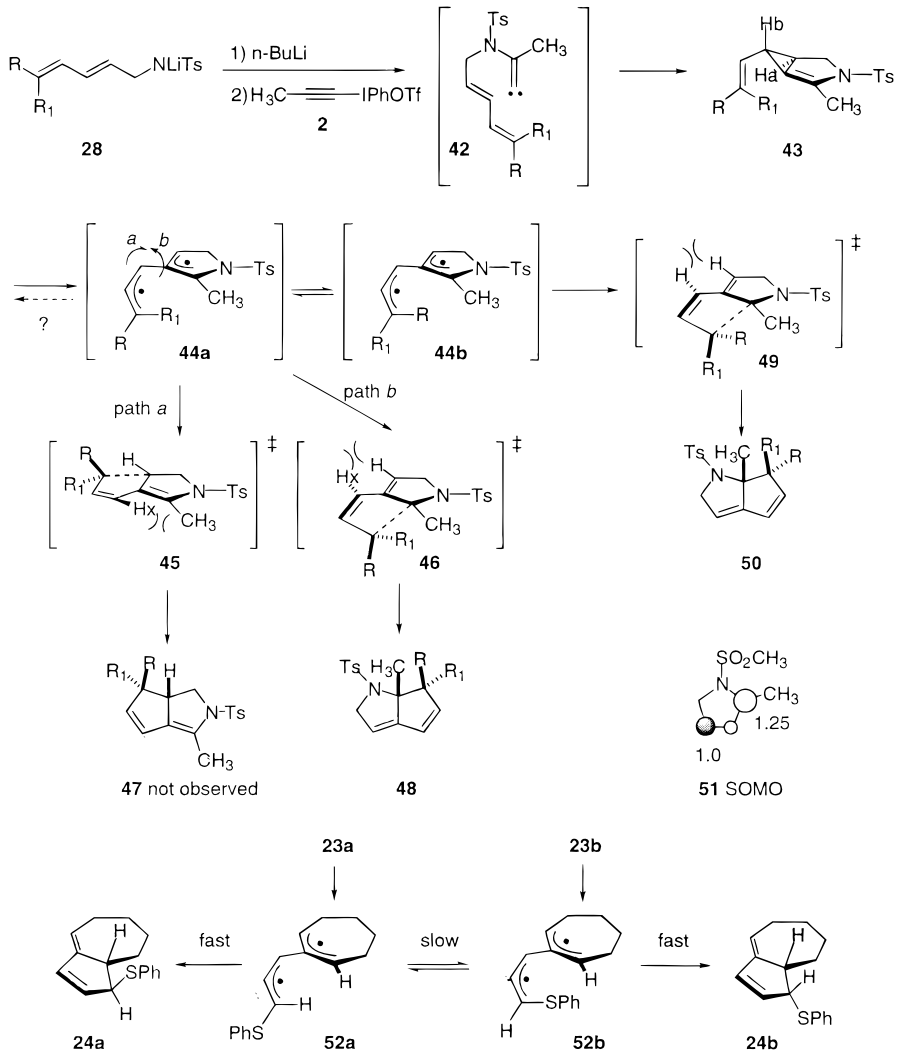


The accumulated experimental evidence from the studies described herein and from prior work in bis allylic radical chemistry[13,15] permit formulation of an inclusive mechanistic picture that rationalizes both the regiochemistry and the stereochemistry of cyclopentenannelated dihydropyrrole synthesis from the penta-2,4-dienyltosylamide derivative **28**, Scheme 7. Initial conjugate addition of the amide anion derived from **28** to the iodonium salt **2** proceeds through the putative alkylidene carbene **42** to furnish the highly strained azabicyclo[3.1.0]hexene derivative **43**, which formally contains a trans alkene in a six-membered ring. Note that the trans arrangement of H_a and H_b on the cyclopropyl core precludes direct [3,3] sigmatropic reorganization leading to **48**. Scission of the labile cyclopropane C−C bond in **43** then affords an intermediate orthogonal bis allylic radical **44a**. This pivotal species can continue down one of two competing pathways: (1) diyl cyclization, along either rotational direction a or b to furnish the cyclopentene products **47** or **48**, respectively, or (2) allyl radical bond rotation to access the isomeric diradical **44b**. Diradical **44b** could then proceed along similar channels to provide the stereoisomeric product **50** (or its regioisomer similar to **47**, not pictured).

The regiochemical outcome of this diyl cyclization is determined by the direction of rotation (*a* or *b*) taken by **44a** (or **44b**, if applicable). Two independent types of steric interactions that can impact on the direction of rotation chosen can be identified. Rotation along pathway a introduces a burgeoning H_x/H_3C $A^{1,3}$ steric interaction as the forming bond closes (cf. **45**). In contrast, rotation in the alternate b direction engenders only a presumably less penalizing H_x/H $A^{1,3}$ steric interaction upon diradical closure. The second identifiable type of steric interaction stems from incipient crowding along the forming bonds in both **45** and **46**. These interactions plausibly favor cyclization at the secondary site in **45** over closure at a tertiary carbon in **46**. It would seem that these two distinct types of steric interactions are in opposition, but which effect dominates? The exclusive formation of **48** (path b) supports a hypothesis that identifies the $A^{1,3}$ steric elements as major determinants of product regiochemistry while at the same time relegating the steric interactions at the site of bond formation itself to only a minor role. An electronic component to this regiochemical preference for **48** over **47** may arise as well. 6-31G*//6-31G**MP2-level calculations on the simple allylic radical model system **51** revealed that the tertiary carbon bears higher electron density in the SOMO than does the secondary carbon. This observation is consistent with a model for diyl collapse in which reaction at the tertiary radical site is intrinsically favored.

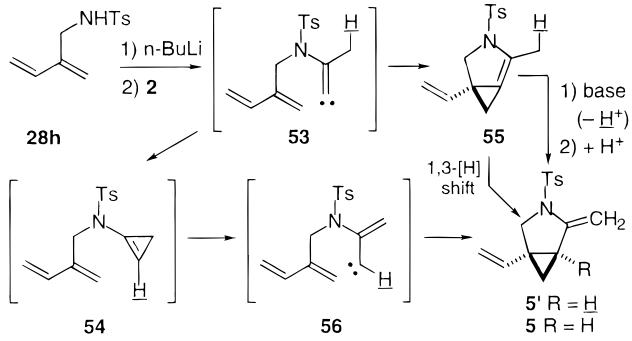
The stereochemical outcome of diyl cyclization depends on the relative rates of allylic radical isomerization (**44a** → **44b**) and cyclization (**44a** → **48**). Retention of stereo-

Scheme 7



chemical information when the strained vinylmethylenecyclopropane **43** is converted to bicyclic product **48** requires that the cyclization rate exceeds the isomerization rate. Since preservation of starting alkene geometry upon addition/bicyclization was *not* observed (cf. **28d** and **28f** → **3d**), it is apparent that equilibration of the allylic radicals **44a** and **44b** must be faster than closure. Thus, the curious case of **28f** cyclization to give the cis stereochemical arrangement of CH_3 and Ph in product **3d** can be rationalized. In this instance, the first-formed diyl **44a** (R = H, R_1 = Ph) places a bulky phenyl substituent directly under the five-membered ring. As the radical termini approach each other, the growing repulsive interactions between R_1 = Ph and the ring in **46** must retard the rate of bond formation. The alternative isomerization pathway to **44b** is evidently favored, and this diyl (R_1 = Ph, R = H), which positions only a hydrogen under the five-membered ring, then rapidly closes to furnish the "wrong" stereoisomer **50** (R_1 = Ph, R = H). The Cohen chemistry provides an interesting counterpoint to this behavior. In that series, stereochemical integrity is largely maintained upon diyl formation and cyclization, indicating that closure of either of the bis allylic radicals **52a** or **52b** is faster than equilibration. Apparently, placing a SPh substituent under the cycloheptenyl ring in **52b** is not as energetically penalizing as forcing a phenyl ring under the cyclopentenyl ring of **44a** (R_1 = Ph).

Scheme 8



Two mechanistic hypotheses can be offered to explain the formation of the azabicyclo[3.1.0]hexane **5** from isoprenyltosylamide **28h** and iodonium salt **2**, Scheme 8. The point of departure from the pentadienyltosylamide chemistry might come as early as the alkylidene carbene stage, wherein sluggish addition of the carbene in **53** to the adjacent 1,1-disubstituted alkene may permit emergence of a normally slower 1,3-[H] shift (**53** → **56**, via **54**).[19] Ring opening of the derived cyclopropene in **54** provides access to vinylcarbene **56**,[20] which can cyclize by intramolecular cyclopropanation to generate **5**. Alter-

natively, the carbene **53** may, in fact, follow the expected course and generate the strained azabicyclo[3.1.0]hexene **55**. Carbon−carbon bond homolysis may be energetically prohibitive in this case since the cyclopropyl methylene carbon entirely lacks a radical-stabilizing group (compare to **43**, which has a vinyl appendage at this position). In this scenario, an alternative pathway for strain relief involving a formal 1,3-[H] shift becomes manifest. This 1,3-[H] shift could, in principle, occur through either an intramolecular pathway (**55** → **5′**) or through a stepwise intermolecular proton-transfer sequence (**55** → **5**). In support of this latter proposition, many instances of base-mediated isomerization of methylenecyclopropanes into vinylcyclopropanes have been recorded.[21] The complete absence of deuterium incorporation at the ring juncture position R in **5** upon combination of **28h** and **41** (Scheme 6) permits exclusion of both the vinylcarbene pathway and the intramolecular 1,3-[H] shift. By default, the bimolecular proton transfer sequence, presumably mediated by the anion derived from **28h**, appears to be the most likely route by which **5** is formed.

Experimental Section

Moisture and oxygen sensitive reactions were carried out in flame-dried glassware under an argon atmosphere. Tetrahydrofuran (THF), dimethoxyethane (DME), and dioxane were distilled from sodium benzophenone ketyl under an argon atmosphere immediately before use. Toluene, benzene (C_6H_6), and dichloromethane (CH_2Cl_2) were distilled from calcium hydride (CaH_2) under an argon atmosphere immediately before use. *n*-Butyllithium (2.5 M hexanes), lithium hexamethylsilylamide (1.0 M THF), sodium hexamethylsilylamide (1.0 M THF), potassium hexamethylsilylamide (0.5 M toluene), sodium hydride (NaH, 60% in oil), and methyllithium (1.6 M Et_2O) were used as purchased. Purification of products via flash chromatography[22] was performed with 32−63 mm silica gel and the solvent systems indicated. Hexane and diethyl ether (Et_2O) used in flash chromatography were distilled from CaH_2 prior to use, whereas ethyl acetate (EtOAc) was used as purchased. Melting points are uncorrected. Chemical impact mass spectra (CIMS) were obtained with isobutane as the reagent gas. Copies of ^1H and ^{13}C NMR spectra are provided in the Supporting Information to establish purity for those compounds that were not subjected to combustion analyses.

General Procedure A: Synthesis of Derivatives of Penta-2,4-dienyltoluenesulfonamides 28a−h via Mitsunobu Reactions. *p*-Toluenesulfonamide (1.0 equiv) was added to a solution of dienol (1.0 equiv) in C_6H_6 or CH_2Cl_2, and the mixture was purged with inert gas. CMBP (1.5 equiv) dissolved in like solvent was added over several minutes via syringe, and the resulting solution was stirred overnight at room temperature. Concentration of the crude reaction mixture in vacuo followed by purification via flash chromatography on silica gel with the indicated solvent system and recrystallization yielded the desired penta-2,4-dienyltoluenesulfonamides.

General Procedure B for Synthesis of Derivatives of Penta-2,4-dienyltoluenesulfonamides via Horner−Emmons Wittig Reactions. Sodium hexamethylsilylamide (2.0 equiv) was added via syringe over 5 min to [4-(toluenesulfonamide)-(2*E*)-butenyl)]phosphonic acid diethyl ester **31** (1.0 equiv) in THF at −78 °C, and the solution was stirred for 15 min. The appropriate aldehyde (0.90 equiv) was added over 15 min, and the reaction solution was warmed to room temperature over 2 h and then stirred for an additional 1 h. After dilution with EtOAc, the organic layer was poured into an ice-cold mixture of 1:1 saturated $NaHCO_3$ solution and brine. The aqueous phase was extracted twice with EtOAc, and the combined organic phases were dried with $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude product via flash chromatography with the indicated solvent system followed by recrystallization from the mobile phase yielded the desired penta-2,4-dienyltoluenesulfonamides.

***N*-(2*E*,4*E*)-Hexa-2,4-dienyltoluenesulfonamide (28a).** Following general procedure A, sorbyl alcohol (**25a**) (1.17 g, 11.9 mmol) was dissolved in 50 mL of C_6H_6 followed by the addition of *p*-toluenesulfonamide (2.74 g, 16.0 mmol) and CMBP (3.87 g, 16.0 mmol). The crude product was chromatographed with 3:7 Et_2O/hexane followed by recrystallization from the mobile phase to yield 1.80 g of pure **28a** (59%) as a white solid. mp 88−89 °C; IR ($CDCl_3$) 3383, 1662, 1332, 1169 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 2 H), 7.29 (d, J = 8.1 Hz, 2 H), 5.97 (m, 2 H), 5.62 (m, 1 H), 5.35 (dt, J = 6.5, 14.8 Hz, 1 H), 4.59 (t, J = 5.9 Hz, 1 H), 3.57 (t, J = 6.3 Hz, 2 H), 2.42 (s, 3 H), 1.71 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.4, 137.0, 133.6, 130.6, 130.2, 129.7, 127.1, 124.4, 45.2, 21.5, 18.0; CIMS *m*/*z* (relative intensity) 252 (MH^+, 44), 184 (95), 81 (100). Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57; S, 12.76; found: C, 62.30; H, 6.80; N, 5.66; S, 12.76.

***N*-(2*E*,4*E*)-5-Methylhexa-2,4-dienyltoluenesulfonamide (28b).** Following general procedure A, (*E*)-5-methylhexa-2,4-dienol (**25b**)[23] (0.54 g, 4.8 mmol) was dissolved in 24 mL of C_6H_6 followed by the addition of *p*-toluenesulfonamide (0.82 g, 4.8 mmol) and CMBP (1.74 g, 7.2 mmol). The crude product was purified on silica gel with 3:7 Et_2O/hexane followed by recrystallization from the mobile phase to yield 0.21 g of pure **28b** (17%) as a white solid. mp 92−94 °C; IR ($CDCl_3$) 3378, 1331, 1161 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H), 6.28 (dd, J = 10.9, 15.0 Hz, 1 H), 5.71 (d, J = 11.0, 1 H), 5.37 (dt, J = 6.5, 15.0 Hz, 1 H), 4.27 (t, J = 5.8 Hz, 1H), 3.62 (t, J = 6.3 Hz, 2 H), 2.43 (s, 3 H), 1.75 (s, 3 H), 1.69 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.4, 137.0, 136.9, 130.1, 129.7, 127.2, 124.1, 123.7, 45.5, 25.9, 21.5, 18.3; CIMS *m*/*z* (relative intensity) 266 (MH^+, 7), 184 (98), 95 (100). Anal. Calcd for $C_{14}H_{19}NO_2S$: C, 63.37; H, 7.22; N, 5.28; S, 12.08. Found: C, 63.31; H, 7.20; N, 5.34; S, 12.18.

***N*-(2*E*,4*E*)-(5-Trimethylsilyl)-penta-2,4-dienyltoluenesulfonamide (28c).** Following general procedure A, dienol **25c**[24] (0.24 g, 1.56 mmol) was dissolved in 8 mL of C_6H_6 followed by the addition of *p*-toluenesulfonamide (0.27 g, 1.6 mmol) and CMBP (0.56 g, 2.3 mmol). The crude product was chromatographed with 3:7 Et_2O/hexane and recrystallized from the mobile phase to yield 0.22 g of pure **28c** (46%) as a white solid. mp 74−75 °C; IR ($CDCl_3$) 3389, 1331, 1155 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J = 8.3 Hz, 2 H), 7.31 (d, J = 8.4 Hz, 2 H), 6.38 (dd, J = 10.0, 18.3 Hz, 1 H), 6.08 (dd, J = 10.0, 15.2 Hz, 1 H), 5.80 (d, J = 18.3 Hz, 1 H), 5.53 (dt, J = 6.3, 15.2 Hz, 1 H), 4.55 (t, J = 6.1 Hz, 1 H), 3.61 (t, J = 6.2 Hz, 2 H), 2.43 (s, 3 H), 0.05 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.5, 142.5, 137.0, 136.0, 135.7, 129.7, 127.8, 127.2, 45.0, 21.5, −1.4; CIMS *m*/*z* (relative intensity) 310 (MH^+, 23), 172 (100). Anal. Calcd for $C_{15}H_{23}NO_2SSi$: C, 58.21; H, 7.49; N, 4.53; S, 10.36; found: C, 58.09; H, 7.52; N, 4.61; S, 10.31.

***N*-(2*E*,4*E*)-5-Phenylpenta-2,4-dienyltoluenesulfonamide (28d).** Following general procedure A, (2*E*,4*E*)-5-phenylpenta-2,4-dienol (**25d**)[25] (0.59 g, 3.7 mmol) was dissolved in 18 mL of C_6H_6 followed by the addition of *p*-toluenesulfona-

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mide (0.63 g, 3.7 mmol) and CMBP (1.35 g, 5.6 mmol). The crude product was chromatographed with 1:1 Et_2O/hexane followed by recrystallization from the mobile phase to yield 0.31 g of pure **28d** (26%) as a white solid. mp 124−126 °C; IR ($CDCl_3$) 3386, 1335, 1161 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.76 (d, J = 8.3 Hz, 2 H), 7.39−7.22 (m, 7 H), 6.66 (dd, J = 10.0, 15.6 Hz, 1 H), 6.47 (d, J = 15.6 Hz, 1 H), 6.26 (dd, J = 10.0, 15.1 Hz, 1 H), 5.63 (dt, J = 6.4, 15.1 Hz, 1 H), 4.44 (bs, 1 H), 3.69 (t, J = 6.3 Hz, 2 H), 2.43 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.5, 137.0, 136.8, 133.4, 133.2, 129.7, 128.6, 127.8, 127.7, 127.5, 127.1, 126.4, 45.1, 21.5; CIMS *m/z* (relative intensity) 314 (MH^+, 13), 184 (100). Anal. Calcd for $C_{18}H_{19}NO_2S$: C, 68.98; H, 6.11; N, 4.47; S, 10.23; found: C, 68.71; H, 6.01; N, 4.53; S, 10.38.

***N*-(2*E*,4*E*)-5-(4-Nitrophenyl)penta-2,4-dienyltoluenesulfonamide (28e).** DIBAL in toluene (24.5 mL of a 1 M solution, 24.5 mmol) was added to a solution of ethyl (2*E*,4*E*)-5-(4-nitrophenyl)penta-2,4-dienoate[26] (3.0 g, 12.1 mmol) in 30 mL of benzene at room temperature. After 18 h at room temperature, the solution was cooled to 0 °C and excess DIBAL was quenched with CH_3OH. This solution was poured into 10% aqueous HCl, and the mixture was extracted three times with EtOAc. The combined organic phases were washed with brine, dried with $MgSO_4$, filtered, and concentrated in vacuo. Chromatography of the residue on silica gel with 1:1 EtOAc/hexane as eluent furnished 1.62 g of the dienol **25e** (65%). IR ($CDCl_3$) 3695, 3613, 1513, 1378 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, J = 8.9 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 6.92 (dd, J = 15.6, 11 Hz, 1H), 6.56 (d, J = 15.7 Hz, 1H), 6.45 (dd, J = 15.2, 10.4 Hz, 1H), 6.09 (dt, J = 15.3, 5.5 Hz, 1H), 4.29 (d, J = 5.5 Hz, 2H), 1.73 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.7, 143.7, 136.0, 132.7, 130.2, 130.0, 126.7, 124.0, 63.0.

Following general procedure A, (2*E*,4*E*)-5-(4-nitrophenyl)-penta-2,4-dienol (**25e**) (1.33 g, 6.5 mmol) was dissolved in 32 mL of CH_2Cl_2 followed by the addition of *p*-toluenesulfonamide (1.11 g, 6.5 mmol) and CMBP (2.36 g, 9.8 mmol). The crude product was chromatographed with 1:1 EtOAc/hexane followed by recrystallization from the mobile phase to yield 0.71 g of pure **28e** (30%) as a yellow microcrystalline solid. mp 174−179 °C; IR ($CDCl_3$) 3389, 1519, 1343, 1161 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.16 (d, J = 8.9 Hz, 2 H), 7.77 (d, J = 8.3 Hz, 2 H), 7.47 (d, J = 8.8 Hz, 2 H), 7.33 (d, J = 8.0 Hz, 2 H), 6.81 (dd, J = 10.3, 15.6 Hz, 1 H), 6.52 (d, J = 15.7 Hz, 1 H), 6.32 (dd, J = 10.4, 15.2 Hz, 1 H), 5.81 (dt, J = 6.2, 15.2 Hz, 1 H), 4.46 (t, J = 5.8 Hz, 1 H), 3.72 (t, J = 6.1 Hz, 2 H), 2.44 (s, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 146.9, 143.7, 143.3, 137.0, 132.4, 131.9, 131.4, 130.8, 129.8, 127.2, 126.8, 124.1, 45.0, 21.5; CIMS *m/z* (relative intensity) 359 (MH^+, 26), 184 (87) 172 (100). Anal. Calcd for $C_{18}H_{18}N_2O_4S$: C, 60.32; H, 5.06; N, 7.82; S, 8.94; found: C, 60.25; H, 5.01; N, 7.70; S, 8.67.

***N*-(2*E*,4*Z*)-5-Phenylpenta-2,4-dienyltoluenesulfonamide (28f).** DIBAL in toluene (7.0 mL of a 1 M solution, 7.0 mmol) was added to a solution of methyl (2*E*,4*Z*)-5-phenylpenta-2,4-dienoate[27] (0.64 g, 3.4 mmol) in 17 mL of benzene at room temperature. After 2 h at room temperature, the solution was cooled to 0 °C and excess DIBAL was quenched with CH_3OH. This solution was poured into 10% aqueous HCl, and the mixture was extracted twice with EtOAc. The combined organic phases were washed with brine, dried with $MgSO_4$, filtered, and concentrated in vacuo. Chromatography of the residue on silica gel with 1:1 EtOAc/hexane as eluent furnished 378 mg of the dienol **25f** (69%). ^1H NMR (200 MHz, $CDCl_3$) δ 7.3 (m, 5 H), 6.82 (ddd, J = 16, 12, 1 Hz, 1 H), 6.49 (d, J = 12 Hz, 1 H), 6.37 (t, J = 12 Hz, 1 H), 6.01 (dt, J = 15, 5 Hz, 1 H), 4.22 (dd, J = 6, 1 Hz, 2 H), 1.48 (bs, 1 H).

Following general procedure A, dienol **25f** (0.27 g, 1.7 mmol) was dissolved in 8 mL of C_6H_6 followed by the addition of *p*-toluenesulfonamide (0.29 g, 1.7 mmol) and CMBP (0.60 g, 2.5 mmol). The crude product was chromatographed with 2:3 Et_2O/hexane to yield 0.22 g of pure **28f** (42%) as a thick oil. IR ($CDCl_3$) 3378, 1332, 1162 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 2 H), 7.35−7.20 (m, 7 H), 6.58 (dd, J = 11.2, 15.1 Hz, 1 H), 6.40 (d, J = 11.5 Hz, 1 H), 6.10 (dd, J = 11.4 Hz, 1 H), 5.66 (dt, J = 6.5, 15.1 Hz, 1 H), 4.90 (t, J = 6.2 Hz, 1 H), 3.63 (t, J = 6.3 Hz, 2 H), 2.38 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 137.0, 136.8, 130.7, 130.1, 129.6, 129.1, 128.8, 128.7, 128.2, 127.1 (2 C), 45.1, 21.4; EIMS *m/z* (relative intensity) 313 (M^+, 3); HRMS calcd for $C_{18}H_{19}NO_2S$ 313.1034, found 313.0980.

***N*-(2*Z*,4*E*)-5-Phenylpenta-2,4-dienyltoluenesulfonamide (28 g).** DIBAL in toluene (10.9 mL of a 1 M solution, 10.9 mmol) was added to a solution of methyl (2*Z*,4*E*)-5-phenylpenta-2,4-dienoate[28] (1.0 g, 5.3 mmol) in 18 mL of benzene at room temperature. After 10 h at room temperature, the solution was cooled to 0 °C and excess DIBAL was quenched with CH_3OH. This solution was poured into 10% aqueous HCl, and the mixture was extracted twice with EtOAc. The combined organic phases were washed with brine, dried with $MgSO_4$, filtered, and concentrated in vacuo. Chromatography of the residue on silica gel with 1:1 Et_2O/hexane as eluent afforded 747 mg of the dienol **25g** (88%). ^1H NMR (200 MHz, $CDCl_3$) δ 7.3 (m, 5 H), 7.11 (dd, J = 15, 10 Hz, 1 H), 6.73 (d, J = 15 Hz, 1 H), 6.31 (t, J = 10 Hz, 1 H), 5.73 (dt, J = 10, 5 Hz, 1 H), 4.45 (d, J = 5 Hz, 2 H), 1.77 (bs, 1 H).

Following general procedure A, dienol **25g** (0.75 g, 4.7 mmol) was dissolved in 24 mL of C_6H_6 followed by the addition of *p*-toluenesulfonamide (0.80 g, 4.7 mmol) and CMBP (1.71 g, 7.1 mmol). The crude product was chromatographed with 1:1 Et_2O/hexane followed by recrystallization from the mobile phase to yield 0.39 g of pure **28g** (26%) as a white solid. mp 88−90 °C; IR ($CDCl_3$) 3378, 1336, 1161 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.78 (d, J = 8.2 Hz, 2 H), 7.35−7.22 (m, 7 H), 6.79 (dd, J = 11.2, 15.4 Hz, 1 H), 6.53 (d, J = 15.4 Hz, 1 H), 6.19 (dd, J = 11.0 Hz, 1 H), 5.35 (dt, J = 3.3, 10.6 Hz, 1 H), 4.69 (t, 1 H), 3.82 (t, J = 7.1 Hz, 2 H), 2.41 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 136.8, 136.7, 135.1, 132.4, 129.7, 128.6, 128.0, 127.2, 126.6, 125.0, 122.5, 40.4, 21.5; CIMS *m/z* (relative intensity) 314 (MH^+, 9), 184 (74), 67 (100). Anal. Calcd for $C_{18}H_{19}NO_2S$: C, 68.98; H, 6.11; N, 4.47; S, 10.23; found: C, 69.33; H, 6.29; N, 4.48; S, 10.22.

***N*-2-Methylenebut-3-enyltoluenesulfonamide (28h).** Following general procedure A, 2-methylene-3-butenol[29] (0.34 g, 4.0 mmol) was dissolved in 50 mL of C_6H_6 followed by the addition of *p*-toluenesulfonamide (0.94 g, 5.5 mmol) and CMBP (1.33 g, 5.5 mmol). The crude product was chromatographed with 3:7 Et_2O/hexane to yield 0.50 g of pure **28h** (53%) as a white solid. mp 45−47 °C; IR ($CDCl_3$) 3365, 1337 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (dd, J = 1.8, 6.5 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H), 6.29 (dd, J = 11.0, 17.7 Hz, 1 H), 5.13 (m, 4 H), 3.73 (d, J = 6.2 Hz, 2 H), 2.43 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 140.7, 136.7, 136.0, 129.7, 127.1, 118.1, 114.8, 44.1, 21.5; CIMS *m/z* (relative intensity) 238 (MH^+, 100); HRMS calcd for $C_{12}H_{15}NO_2S$ 237.0823, found 237.0816.

***N*-(2*E*,4*E*)-5-(4-Methoxyphenyl)penta-2,4-dienyltoluenesulfonamide (28i).** Following general procedure B, sodium hexamethylsilylamide (1.3 mL, 1.3 mmol) was added to phosphonate sulfonamide **31** (0.23 g, 0.64 mmol) followed by *p*-methoxybenzaldehyde (**32**) (0.078 g, 0.58 mmol). The crude product was chromatographed with 1:1 Et_2O/hexane and recrystallized from the mobile phase to yield 0.096 g of pure **28i** (43%) as a white solid. mp 137−140 °C; IR ($CDCl_3$) 3389, 1333, 1169 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 2 H), 7.32−7.26 (m, 4 H), 6.84 (d, J = 8.6 Hz, 2 H), 6.52 (dd, J = 9.9, 15.6 Hz, 1 H), 6.42 (d, J = 15.6 Hz, 1 H), 6.22 (dd, J = 9.9, 15.1 Hz, 1 H), 5.57 (dt, J = 6.6, 15.0 Hz, 1 H), 4.43 (t, J = 6.0 Hz, 1 H), 3.69 (t, J = 6.3 Hz, 2 H), 3.81 (s, 3 H), 2.43 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 143.5, 137.0, 133.9, 133.0, 129.7, 129.6, 127.7, 127.2, 126.4, 125.4, 114.1, 55.3, 45.3, 21.5; CIMS *m/z* (relative intensity) 344 (MH^+, 68), 172 (100). Anal. Calcd for $C_{19}H_{21}NO_3S$: C, 66.45; H, 6.16; N, 4.08; S, 9.33; found: C, 66.16; H, 6.32; N, 4.05; S, 9.27.

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***N*-(2*E*,4*E*,6*E*)-7-Phenylhepta-2,4,6-trienyltoluenesulfonamide (28j).** Following general procedure B, sodium hexamethylsilylamide (1.4 mL, 1.4 mmol) was added to the phosphonate sulfonamide (0.25 g, 0.7 mmol) followed by cinnamaldehyde (0.085 g, 0.64 mmol). The crude product was chromatographed with 1:1 Et_2O/hexane and recrystallized from the mobile phase to yield 0.051 g of pure **28i** (23%) as light yellow flakes. mp 138−143 °C; IR ($CDCl_3$) 3378, 1335, 1162 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.76 (d, J = 8.3 Hz, 2 H), 7.39−7.20 (m, 7 H), 6.77 (dd, J = 10.0, 15.5 Hz, 1 H,), 6.55 (d, J = 15.6 Hz, 1 H), 6.35−6.14 (m, J = 10.0, 15.1 Hz, 1 H), 5.56 (dt, J = 6.5, 14.3 Hz, 1 H), 4.46 (t, J = 5.9 Hz, 1 H), 3.66 (t, J = 6.3 Hz, 2 H), 2.43 (s, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 143.5, 137.1, 137.0, 134.0, 133.4, 133.4, 131.5, 129.7, 128.6, 128.5, 127.7, 127.5, 127.2, 126.4, 45.3, 21.5; CIMS *m*/*z* (relative intensity) 340 (MH^+, 44), 169 (100); HRMS calcd for $C_{20}H_{21}NO_2S$ 339.1293, found 339.1282.

Methyl (*E*,*E*)-6-Toluenesulfonylaminohexa-2,4-dienoate (28k). Triphenylphosphine (5.42 g, 20.7 mmol), *N*-*tert*-butoxycarbonyl-*p*-toluenesulfonamide (2.51 g, 9.3 mmol), and ester alcohol **34**[30] (1.47 g, 10.3 mmol) were dissolved in 60 mL of THF at room temperature. Diisopropyl azodicarboxylate (5.1 mL, 25.7 mmol) was added dropwise, and the reaction solution was stirred overnight. After concentration in vacuo, the crude product was purified via flash chromatography with 1:4 EtOAc/hexane to yield pure **35** (30%) as a white solid. mp 99−101 °C; IR ($CDCl_3$) 1720, 1372, 1154 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H), 7.27 (m, 1 H), 6.37 (dd, J = 11.1, 15.2 Hz, 1 H), 6.14 (dt, J = 6.1, 15.3 Hz, 1 H), 5.90 (d, J = 15.4 Hz, 1 H), 4.53 (d, J = 6.0 Hz, 2 H), 3.76 (s, 3 H), 2.43 (s, 3 H), 1.35 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 150.6, 144.4, 143.5, 137.0, 136.7, 130.9, 129.3, 128.1, 121.8, 84.7, 51.6, 47.8, 27.9, 21.6; CIMS *m*/*z* (relative intensity) 339 (MH^+, − *t*-Bu). Anal. Calcd For $C_{19}H_{25}NO_6S$: C, 57.71; H, 6.37; N, 3.54; S, 8.11. Found: C, 57.67; H, 6.38; N, 3.52; S, 8.07.

The BOC-sulfonamide **35** (1.21 g, 3.1 mmol) was dissolved in CH_2Cl_2 and purged with Ar. Trifluoroacetic acid (1.74 g, 15.3 mmol) was added, and the reaction solution was stirred at room temperature for 21 h. The crude product was diluted with EtOAc and poured into ice cold saturated aqueous sodium bicarbonate. The aqueous phase was extracted twice with EtOAc, and the combined organic phases were washed with saturated sodium chloride, dried with anhydrous Na_2SO_4, filtered, and concentrated. The crude product was then purified via flash chromatography with 2:3 EtOAc/hexane to yield pure **28k** as a white solid (35%). mp 132−135 °C; IR ($CDCl_3$) 3392, 1332, 1162 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H), 7.14 (dd, J = 11.0. 18.6 Hz, 1 H), 6.24 (dd, J = 11.0, 15.1 Hz, 1 H), 5.90 (dt, J = 5.9, 15.3 Hz, 1 H), 5.81 (d, J = 15.4 Hz, 1 H), 3.74 (s, 3 H), 3.71 (t, J = 5.9 Hz, 2 H), 2.43 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 143.8, 143.1, 136.9, 136.4, 130.1, 129.8, 127.1, 121.8, 51.6, 44.7, 21.5; CIMS *m*/*z* (relative intensity) 296 (MH^+, 100). Anal. Calcd for $C_{14}H_{17}NO_4S$: C, 56.97; H, 5.80; N, 4.74; S, 10.85. Found: C, 56.81; H, 5.96; N, 4.81; S, 10.91.

***N*,*N*-(*tert*-Butoxycarbonyl)-(4-chloro-(*E*)-2-butenyl)-toluenesulfonamide (30).** *N*,*N*-Dimethylformamide (DMF, 9 mL) was added at 0 °C to NaH (0.19 g, 4.8 mmol) and *tert*-butoxycarbonyl-*p*-toluenesulfonamide (1.09 g, 4.0 mmol), and the solution was stirred for 15 min. (*E*)-1,4-Dichloro-2-butene (1.5 g, 12.0 mmol) in 3 mL of DMF was added via syringe all at once. The orange solution was stirred for 10 min and then heated at 65 °C for 3 h. After cooling the reaction solution to room temperature, 5 mL of H_2O was added to quench any remaining NaH. Ethyl acetate was used to partition the phases, and the organic layers were washed sequentially with saturated solutions of sodium thiosulfite and 1:1 $NaHCO_3$/brine. All aqueous layers were extracted twice with EtOAc, and the combined organic phases were dried with Na_2SO_4, filtered, and concentrated. The crude product was purified via flash chromatography with 3:7 Et_2O/hexane and recrystallized from the mobile phase to yield 0.82 g of pure **30** (57%) as a white solid. mp 82−83 °C; IR ($CDCl_3$) 1727, 1367, 1155 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, J = 8.4 Hz, 2 H), 7.30 (d, J = 8.2 Hz, 2 H), 5.91 (m, 2 H), 4.45 (d, J = 4.4 Hz, 2 H), 4.08 (d, J = 4.3 Hz, 2 H), 2.44 (s, 3 H), 1.36 (s, 9 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 150.6, 144.3, 137.0, 129.7, 129.2 (2 C), 128.2, 84.5, 47.3, 44.1, 27.9, 21.6; CIMS *m*/*z* (relative intensity) 303 (MH^+ − t-Bu, 100), 268 (MH^+ − t-Bu and Cl, 63). Anal. Calcd for $C_{16}H_{22}NO_4SCl$: C, 53.40; H, 6.16; Cl, 9.85; N, 3.89; S, 8.91; found: C, 53.02; H, 6.16; Cl, 9.72; N, 3.87; S, 9.22.

Diethyl [4-(Toluenesulfonamide)-(*E*)-2-butenyl)]phosphonate (31). Chlorosulfonamide **30** (1.47 g, 4.1 mmol), sodium iodide (0.12 g, 0.82 mmol), and triethyl phosphite (1.5 g, 9.0 mmol) were added to a thick-walled Schlenk tube equipped with a Teflon stopcock. This mixture was sealed under vacuum and heated to 110 °C for 22 h, at which time it was cooled to room temperature and diluted with EtOAc. This solution was washed three times with a saturated solution of sodium thiosulfite and once with brine. All aqueous phases were extracted twice with EtOAc, and the combined organic layers were dried with Na_2SO_4, filtered, and concentrated. The crude product was purified via flash chromatography with EtOAc to yield two products: 1.24 g of pure N−Boc derivative of **31** (66%) and 0.24 g of **31** (16%), both as colorless oils.

Trifluoroacetic acid (0.67 g, 5.9 mmol) was added to a solution of the BOC-protected derivative of **31** (0.54 g, 1.2 mmol) in 5 mL of CH_2Cl_2. After being refluxed for 20 h, the solution was diluted with EtOAc and poured into an ice cold saturated solution of $NaHCO_3$. The aqueous layer was extracted twice with EtOAc, and the combined organic phases were dried with Na_2SO_4, filtered, and concentrated. The crude product was purified via flash chromatography to yield 0.37 g of pure **31** (86%) as a colorless oil. IR ($CDCl_3$) 1708, 1166 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.74 (d, J = 8.3 Hz, 2 H), 7.30 (d, J = 8.8 Hz, 2 H), 5.57 (m, 2 H), 5.04 (t, J = 6.1 Hz, 1 H), 4.04 (m, 4 H), 3.54 (m, 2 H), 2.51 (dd, J = 5.6, 21.8, 2 H), 2.43 (s, 3 H), 1.30 (t, J = 7.0 Hz, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.3, 137.0, 130.2 (d, J = 14.5 Hz), 129.6, 127.1, 122.9 (d, J = 10.9 Hz); 61.9 (d, J = 6.6 Hz), 44.9 (d, J = 2.1 Hz), 30.0 (d, J = 139.5 Hz), 21.5, 16.4 (d, J = 5.9 Hz); CIMS *m*/*z* (relative intensity) 362 (MH^+, 100); HRMS calcd for $C_{15}H_{24}NO_5PS$ 362.1191, found 362.1190.

General Procedure C for the Addition/Cyclization of Dienyltosylamides 28 with Phenyl(propynyl)iodonium Triflate (2). *n*-BuLi (1 equiv, 2.5 M in hexane) was added over several minutes to a deoxygenated, stirring solution of the appropriate sulfonamide in the indicated solvent (∼0.01 M) at −78 °C. The reaction was warmed to 0 °C for 0.5 h and then heated to reflux and held there. Phenyl(propynyl)-iodonium triflate **2**[31] (indicated equiv) was added dropwise via syringe over 4 h as a ∼0.4 M solution in the indicated solvent. Stirring was maintained for an additional 1 h, at which time the solution was cooled to room temperature, diluted with Et_2O, and washed with brine. The aqueous layer was extracted twice with Et_2O, and the combined organic phases were dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The resulting residue was purified via flash chromatography with the indicated solvent system.

***N*-(Toluenesulfonamide)-6,6a-dimethyl-1,2,6,6a-tetrahydrocyclopenta[*b*]pyrrole (3a).** Following general procedure C, *n*-BuLi (0.20 mmol) was added to sulfonamide **28a** (50 mg, 0.20 mmol) in 20 mL of THF. Phenyl(propynyl)iodonium triflate (**2**) (120 mg, 0.30 mmol) was dissolved in ∼0.5 mL of THF and added via syringe over 4 h. The crude mixture was chromatographed with 2:23 Et_2O/hexane and 3:7 Et_2O/hexane to yield 14 mg of pure **3a** (24%) as a foam and recovered **28a** (8.5 mg, 17%). IR ($CDCl_3$) 3045, 1599, 1335, 1159 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.3 Hz, 2 H), 7.28 (d, J = 8.4 Hz, 2 H), 6.05 (dd, J = 2.7, 5.9 Hz, 1 H), 5.92 (d, J = 6.0 Hz, 1 H), 5.25 (bs, 1 H), 4.32 (dd, J = 13.9, 1.0 Hz, 1 H), 4.27

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(ddd, J = 13.9, 3.3, 1.1 Hz, 1 H), 3.02 (bq, J = 7.3 Hz, 1 H), 2.42 (s, 3 H), 1.29 (d, J = 7.3 Hz, 3 H), 1.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1, 147.1, 143.0, 138.0, 129.5, 127.4, 123.2, 107.9, 80.2, 58.7, 46.9, 21.5, 18.3, 13.2; CIMS m/z (relative intensity) 291 (MH^+, 100); HRMS calcd for $C_{16}H_{19}NO_2$: 290.1215, found 290.1210.

***N*-(Toluenesulfonamide)-6a-methyl-6-(trimethylsilyl)-1,2,6,6a-tetrahydrocyclopenta[*b*]pyrrole (3c).** Following general procedure C, *n*-BuLi (0.16 mmol) was added to sulfonamide **28c** (50 mg, 0.16 mmol) in 16 mL of THF. Phenyl(propynyl)iodonium triflate (**2**) (95 mg, 0.24 mmol) was dissolved in ~0.5 mL of THF and added via syringe over 4 h. The crude mixture was chromatographed with 2:23 Et_2O/hexane and 3:7 Et_2O/hexane to yield 15 mg of pure **3c** (27%) as an oil and recovered **28c** (10.0 mg, 20%). IR ($CDCl_3$) 1336, 1157 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 7.83 (d, J = 8.3 Hz, 2 H), 6.78 (d, J = 8.4 Hz, 2 H), 5.88 (m, 1 H), 5.80 (dd, J = 2.9, 5.4 Hz, 1 H), 4.88 (bs, 1 H), 4.17 (m, 2 H), 2.76 (bs, 1 H), 1.89 (s, 3 H), 1.31 (s, 3 H), 0.26 (s, 9 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 159.8, 144.2, 142.9, 138.1, 129.4, 127.3, 121.8, 108.2, 79.9, 51.8, 44.4, 22.4, 21.5, 0.1; EIMS m/z (relative intensity) 347 (MH^+, 5), 73 (100); HRMS calcd for $C_{18}H_{25}NO_2SSi$ 347.1375, found 347.1369.

***N*-(Toluenesulfonamide)-6a-methyl-6-phenyl-1,2,6,6a-tetrahydrocyclopenta[*b*]pyrrole (3d).** Following general procedure C, *n*-BuLi (0.16 mmol) was added to sulfonamide **28d** (50 mg, 0.16 mmol) in 16 mL of THF. Phenyl(propynyl)-iodonium triflate (**2**) (94 mg, 0.24 mmol) was dissolved in ~0.5 mL of THF and added via syringe over 4 h. The crude mixture was chromatographed with 2:23 Et_2O/hexane and 3:7 Et_2O/hexane to yield 33 mg of pure **3d** (58%) as a colorless foam and recovered **28d** (7 mg, 14%). IR ($CDCl_3$) 3032, 1599, 1337, 1158 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz, 2 H), 7.43 (m, 2 H), 7.31 (m, 3 H), 7.19 (d, J = 8.4 Hz, 2 H), 6.29 (dd, J = 5.9, 2.7 Hz, 1 H), 6.11 (dd, J = 5.6, 1.8 Hz, 1 H), 5.38 (t, J = 1.3, 0.9 Hz, 1 H), 4.32 (m, 3 H), 2.37 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 156.4, 145.6, 143.1, 138.6, 137.3, 131.0, 129.3, 127.7, 127.4, 126.9, 124.6, 108.7, 81.5, 59.0, 58.8, 21.4, 19.6; CIMS m/z (relative intensity) 353 (MH^+, 100); HRMS calcd for $C_{21}H_{21}NO_2S$ 352.1371, found 352.1370.

***N*-(Toluenesulfonamide)-6-(4-nitrophenyl)-6a-methyl-1,2,6,6a-tetrahydrocyclopenta[*b*]pyrrole (3e).** Following general procedure C, *n*-BuLi (0.14 mmol) was added to sulfonamide **28e** (50 mg, 0.14 mmol) in 14 mL of THF. Phenyl(propynyl)iodonium triflate (**2**) (82 mg, 0.21 mmol) was dissolved in ~0.5 mL of THF and added via syringe over 4 h. The crude mixture was chromatographed with 2:23 EtOAc/hexane and 3:7 EtOAc/hexane to yield 7 mg of pure **3e** (12%) as an oil and recovered **28e** (29%). IR ($CDCl_3$) 3049, 1599, 1348, 1159 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.19 (d, J = 8.8 Hz, 2 H), 7.60 (d, J = 8.9 Hz, 2 H), 7.59 (d, J = 8.3 Hz, 2 H), 7.23 (d, J = 8.4 Hz, 2 H), 6.37 (dd, J = 6.0, 2.8 Hz, 1 H), 6.07 (d, J = 6.0 Hz, 1 H), 5.44 (s, 1 H), 4.47 (s, 1 H), 4.35 (dd, J = 14.5, 2.9 Hz, 1 H), 4.28 (d, J = 13.4 Hz, 1 H), 2.39 (s, 3 H), 0.97 (s, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 155.3, 147.1, 146.5, 143.6, 143.5, 136.9, 131.9, 129.5, 127.7, 125.8, 122.6, 109.9, 81.5, 58.9 (2C), 21.5, 19.6; CIMS m/z (relative intensity) 397 (MH^+, 100); HRMS calcd for $C_{21}H_{20}N_2O_4S$ 396.1148, found 396.1144.

***N*-(Toluenesulfonamide)-6-(4-methoxyphenyl)-6a-methyl-1,2,6,6a-tetrahydrocyclopenta[*b*]pyrrole (3i).** Following general procedure C, *n*-BuLi (0.12 mmol) was added to sulfonamide **28i** (41 mg, 0.12 mmol) in 12 mL of THF. Phenyl(propynyl)iodonium triflate (**2**) (70 mg, 0.18 mmol) was dissolved in ~0.5 mL of THF and added via syringe over 4 h. The crude mixture was chromatographed with 1:10 Et_2O/hexane and 1:1 Et_2O/hexane to yield 23 mg of pure **3i** (51%) as a foam and recovered **28i** (10 mg, 25%). IR ($CDCl_3$) 3049, 1602, 1337, 1249, 1155 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 7.67 (d, J = 8.3 Hz, 2 H), 7.49 (d, J = 8.8 Hz, 2 H), 6.88 (d, J = 8.8 Hz, 2 H), 6.65 (d, J = 8.4 Hz, 2 H), 5.87 (dd, J = 5.9, 2.7 Hz, 1 H), 5.80 (d, J = 5.9 Hz, 1 H), 4.89 (d, J = 2.3 Hz, 1 H), 4.51 (s, 1 H), 4.33 (dd, J = 14.0, 3.5 Hz, 1 H), 4.11 (d, J = 14.0 Hz, 1 H), 3.35 (s, 3 H), 1.82 (s, 3 H), 0.97 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 159.3, 156.8, 146.2, 142.5, 138.6, 132.5, 130.9, 129.4, 128.1, 124.5, 113.3, 109.0, 81.4, 59.2, 58.4, 54.7, 21.0, 19.8; CIMS m/z (relative intensity) 382 (MH^+, 100); HRMS calcd for $C_{22}H_{23}NO_3S$ 381.1399, found 381.1388.

***N*-(Toluenesulfonamide)-6a-methyl-6-styryl-1,2,6,6a-tetrahydrocyclopenta[*b*]pyrrole (3j).** Following general procedure C, *n*-BuLi (0.15 mmol) was added to sulfonamide **28j** (50 mg, 0.15 mmol) in 15 mL of THF. Phenyl(propynyl)-iodonium triflate (**2**) (86 mg, 0.22 mmol) was dissolved in ~0.5 mL of THF and added via syringe over 4 h. The crude mixture was chromatographed with 2:23 Et_2O/hexane and 3:7 Et_2O/hexane to yield 20 mg of pure **5d** (35%) as a colorless foam and recovered **1d** (11 mg, 21%). IR ($CDCl_3$) 3025, 1599, 1338, 1157 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 7.80 (d, J = 8.3 Hz, 2 H), 7.47 (d, J = 7.2 Hz, 2 H), 7.20−7.04 (m, 4 H), 6.71 (d, J = 8.5 Hz, 2 H), 6.53 (d, J = 16.3 Hz, 1 H), 5.91 (d, J = 6.0 Hz, 1 H), 5.83 (dd, J = 6.0, 2.6 Hz, 1 H), 4.82 (s, 1 H), 4.22 (ddd, J = 14.0, 3.3, 1.2 Hz, 1 H), 4.13 (dd, J = 14.0, 0.9 Hz, 1 H), 4.00 (m, 1 H), 1.85 (s, 3 H), 1.17 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 143.2, 143.1, 137.7, 137.6, 131.5, 129.5, 128.5, 127.9, 127.6, 127.2, 126.3, 124.8, 108.8, 80.3, 58.6, 54.8, 21.4, 19.8; CIMS m/z (relative intensity) 378 (MH^+, 6), 91 (100); HRMS calcd for $C_{23}H_{23}NO_2S$ 377.1449, found 377.1443.

3-Toluenesulfonyl-4-methylene-1-vinyl-3-azabicyclo-[3.1.0]hexane (5). Dienyltosylamide **28h** (50 mg, 0.21 mmol) was dissolved in 4.5 mL of THF and cooled to 0 °C. Lithium hexamethylsilylamide (0.21 mL of a 1 M solution in THF, 0.21 mmol) was added slowly, and the reaction solution was stirred for 30 min at 0 °C before being brought to reflux. Phenyl-(propynyl)iodonium triflate (**2**) (82 mg, 0.21 mmol) was dissolved in THF to a total volume of 0.5 mL and added via syringe over ~15 min. After refluxing an additional 30 min, the mixture was diluted with Et_2O and washed with brine. The organic phases were dried with $MgSO_4$, filtered, concentrated, and chromatographed with 2:25 Et_2O/hexane to yield 27 mg of pure **5** (46%) as a colorless oil. IR ($CDCl_3$) 3090, 1643, 1349, 1167 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 7.71 (d, J = 8.4 Hz, 2 H), 6.70 (d, J = 8.0 Hz, 2 H), 5.47 (s, 1 H), 5.12 (dd, J = 10.7, 17.3 Hz, 1 H), 4.73 (dd, J = 0.9, 10.7 Hz, 1 H), 4.64 (dd, J = 0.9, 17.3 Hz, 1 H), 4.44 (s, 2 H), 3.76 (s, 1 H), 1.82 (s, 3 H), 1.43 (dd, J = 4.0, 8.2 Hz, 1 H), 0.46 (m, 1 H), −0.49 (m, 1 H); ^{13}C NMR (75 MHz, C_6D_6) δ 145.4, 143.5, 136.8, 136.4, 129.5, 127.5, 113.5, 90.8, 54.8, 31.8, 27.4, 21.1, 17.5; EIMS m/z (relative intensity) 275 (M^+, 6), 120 (62), 91 (100); HRMS calcd for $C_{15}H_{17}NO_2S$ 275.0980, found 275.0979.

3-Toluenesulfonyl-2-methylene-3-azabicyclo[3.1.0]-hexane (39). Tosylamide **37**[32] (100 mg, 0.47 mmol) was dissolved in 10 mL of THF and cooled to 0 °C. Lithium hexamethylsilylamide (0.50 mL of a 1 M solution in THF, 0.50 mmol) was added slowly and the reaction stirred 30 min at 0 °C before being brought to reflux. Phenyl(propynyl)iodonium triflate (**2**) (196 mg, 0.50 mmol) was dissolved in THF to a total volume of 0.5 mL and added via syringe over ~15 min. After refluxing an additional 30 min, the mixture was diluted with Et_2O and washed with brine. The organic phases were dried with $MgSO_4$, filtered, concentrated, and chromatographed with 2:25 Et_2O/hexane to yield 47 mg of pure **39** (39%) as a colorless oil. IR ($CDCl_3$) 3048, 1637, 1343, 1161 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2 H), 7.29 (d, J = 8.0 Hz, 2 H), 5.02 (s, 1 H), 4.44 (s, 1 H), 3.81 (dd, J = 4.6, 10.3 Hz, 1 H), 3.76 (d, J = 10.3 Hz, 1 H), 2.42 (s, 3 H), 1.90 (m, 1 H), 1.57 (m, 1 H), 0.69 (m, 1 H), −0.25 (m, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 145.4, 143.9, 135.2, 129.5, 127.1, 90.2, 53.2, 22.7, 21.5, 13.2, 11.0; EIMS m/z (relative intensity) 249 (M^+, 6), 184 (100); HRMS calcd for $C_{13}H_{15}NO_2S$ 249.0823, found 249.0830.

3-Toluenesulfonyl-6-methyl-2-methylene-3-azabicyclo-[3.1.0]hexane (40). Tosylamide **38**[16] (100 mg, 0.44 mmol) was dissolved in 9 mL of THF and cooled to 0 °C. Lithium hexamethylsilylamide (0.47 mL of a 1 M solution in THF, 0.47 mmol) was added slowly, and the reaction solution was stirred for 30 min at 0 °C before being brought to reflux. Phenyl-(propynyl)iodonium triflate (**2**) (184 mg, 0.47 mmol) was dissolved in THF to a total volume of 0.5 mL and added via

(32) Sanghavi, N. M.; Parab, V. L.; Patravale, B. S. Patel, M. N. *Synth. Commun.* **1989**, *19*, 1499.

syringe over ~15 min. After refluxing an additional 30 min, the mixture was diluted with Et_2O and washed with brine. The organic layers were dried with $MgSO_4$, filtered, concentrated, and chromatographed with 2:25 Et_2O/hexane to yield 47 mg of pure **40** (33%) as a colorless oil. IR ($CDCl_3$) 3049, 1643, 1349, 1167 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 7.74 (d, J = 8.3 Hz, 2 H), 6.71 (d, J = 8.0 Hz, 2 H), 5.46 (s, 1 H), 4.44 (s, 1 H), 3.65 (d, J = 10.3 Hz, 1 H), 3.51 (dd, J = 5.0, 10.3 Hz, 1 H), 1.81 (s, 3 H), 1.22 (m, 1 H), 0.59 (m, 1 H), 0.46 (d, J = 6.1 Hz, 3 H), 0.02 (m, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 145.4, 143.8, 135.3, 129.5, 127.2, 89.2, 76.3, 53.4, 31.0, 21.1, 19.1, 15.9; EIMS m/z (relative intensity) 263 (M^+, 6), 198 (100); HRMS calcd for $C_{14}H_{17}NO_2S$ 263.0980, found 263.0984.

***d*$_3$-Propynyl(phenyl)iodonium Triflate (41).** n-BuLi (2.8 mL of a 2.5 M solution in hexane, 6.9 mmol) was added to a stirring solution of (trimethylsilyl)acetylene (0.68 g, 6.9 mmol) in 7 mL of THF and 7 mL of DMPU at 0 °C. D_3CI (1.07 g, 7.4 mmol) was added slowly (exothermic), and the reaction solution was stirred at 0 °C for 14 h. The mixture was poured into ice-cold H_2O and extracted twice with pentane. The organic layers were dried over $MgSO_4$, filtered, and the pentane/THF was removed by short-path distillation at 1 atm. The residue (~0.45 g, ~3.9 mmol) of crude (trimethylsilyl)propyne-d_3 was used directly in the next step.

This crude sample of (trimethylsilyl)propyne-d_3 and bis tributyltin oxide (0.94 g, 1.57 mmol) in 10 mL of THF was treated with n-Bu_4NF (0.079 mL of a 1 M solution in THF, 0.079 mmol), and the reaction solution was brought to reflux. After 2.5 h at reflux, the mixture was cooled to room temperature and concentrated in vacuo. Purification of the residue by chromatography on SiO_2 with 1:19 Et_2O/hexane furnished 690 mg of (tributylstannyl)propyne-d_3 (66%) as a colorless oil. The material was used immediately in the next step.

A 50 mL Schlenk flask was charged with cyano(phenyl)-iodonium triflate (0.72 g, 1.9 mmol) and dichloromethane. The mixture was purged with Ar and cooled to −45 °C. (Tributylstannyl)propyne-d_3 (0.69 g, 2.1 mmol) was dissolved in 3 mL of CH_2Cl_2 and added over 15 min to the cold reaction mixture. The reaction solution was then stirred for 1.25 h at −45 °C → −25 °C, after which time 50 mL of freshly distilled hexane was added via cannula, which caused the iodonium salt to precipitate. The microcrystalline solid was collected without exposure to air, rinsed with hexane, and then recrystallized with the precipitation method mentioned above (CH_2Cl_2/hexane) to yield 0.48 g of **41** (58%) as a white solid. mp = 112 °C; IR ($CDCl_3$) 2179 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (m, 2 H), 7.65 (m, 1 H), 7.54 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.0, 132.5, 132.3, 121.9, 116.1, 106.8, 20.8; LR MALDI m/z (cation) 245.9811; HRMS calcd for $C_{10}H_5D_3I$ 245.9859, found 245.9871.

Supporting Information Available: Copies of ^1H and ^{13}C NMR spectra for compounds **3a**,**c**−**e**,**i**−**j**, **5**, **28f**,**h**,**j**, **31**, **39**, and **40**. This material is available free of charge via the Internet at http://pubs.acs.org.

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