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Medium-Sized Heterocycle Synthesis by the Use of Synergistic Effects of Ni-NHC and γ-Coordination in Cycloisomerization

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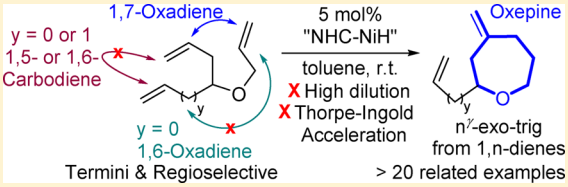
Supporting Information

ABSTRACT: This paper describes a new approach in transition-metal-catalyzed unsymmetric cycloisomerization for medium-sized heterocycles. The steric and electronic effects of an NHC−NiH catalyst and γ-heteroatom chelation were used together as a basis for 1,*n*-diene termini differentiation and for n^{γ}-*exo-trig* (head-to-tail) product selectivity. Heterocycles bearing an exocyclic methylene such as oxepines, thiepines, siloxepines, and oxocanes were synthesized from the corresponding 1,*n*-dienes by a fine-tuning of the NHC properties. The implication of the underlying hypothesis was further demonstrated in a competition experiment in which strained oxepines were formed preferentially over other competing oxa-/carbocycles. Under more forcing physical conditions and the use of a suitable NHC ligand, the exocyclic methylene products were isomerized further into endocyclic olefin products regioselectively in one pot.



INTRODUCTION

Catalytic cycloisomerization is important in organic chemistry as an expedient way of constructing relevant frameworks for further applications. A commonly used C−C forming approach involves the use of 1,*n*-dienes as cycloisomerization substrates.[1] The products obtained through these methods may complement ring-closing metathesis, which also uses 1,*n*-dienes as substrates for chemical library synthesis and for efficient structure−activity relationship (SAR) studies (Figure 1).[2] However, the full potential of this complementarity has yet to be realized.

Current cycloisomerization technology is effective for only a subset of the possible range of 1,*n*-dienes. Oligomerization or isomerization often complicates the reaction, and rings with lower strains are the preferred outcomes. As such, the most efficient cases are those either with a 1,6-relationship, with templates for conformational freedom reduction or with Thorpe−Ingold acceleration.[3] Few protocols for medium-sized rings (1,*n* > 6 dienes) with a freely rotating linear tether have been discovered.[4] Other than in cases governed by ring closure constraints (e.g., *n* = 5), systems giving *n*- over (*n* − 1)-*exo-trig* cycloisomerization products from 1,*n*-dienes, which require a head-to-tail over typical tail-to-tail cycloisomerization, are rare (Figure 1, eqs 1 and 2).[5,6] This is because, in an approach based on oxidative cyclometalation in early transition metals, n-*exo-trig* product formation often first requires a geometrically relatively more constrained diene−M coordination. In contrast, in cases based on olefin insertion to M−H, such formation generally faces strong hydrometalation regioselective competition and also a catalyst deactivation pathway related to γ-heteroatom chelation, which significantly hampers the synthesis of heterocycles (Figure 1, eq 3).[5c] Another persistent challenge in the M−H approach is tether differentiation. Unlike approaches that employ two tethers with differences in their degree of unsaturation,[7,8] the progress for an effective differentiation of structurally and electronically similar termini in 1,*n*-dienes is mostly limited to (*n* − 1)-*exo-trig* cases on a steric basis.[9,10]

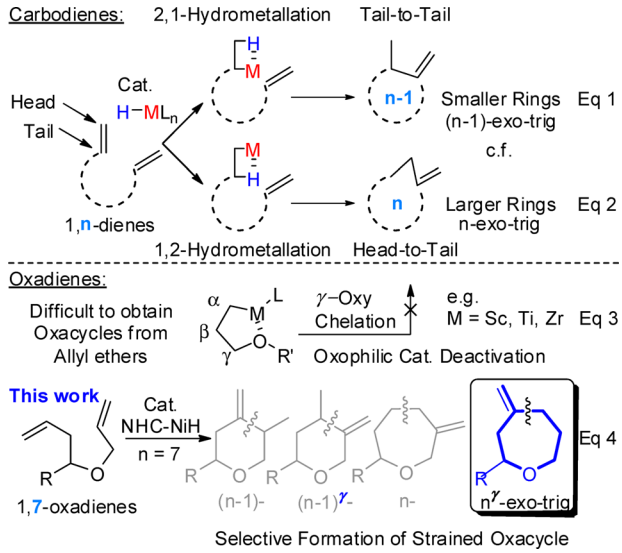


Figure 1. New approach for 1,7-oxadienes selective cycloisomerization.

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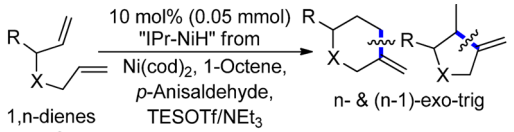
In this context and as part of our continuing programs that aim to discover new applications for N-heterocyclic carbene (NHC) in transition-metal catalysis, we became interested in the potential of NHC−Ni interactions with heteroatoms for selective C−C forming reactions. In this paper, we are interested in expanding the scope of current cycloisomerization, particularly in the synthesis of medium-sized heterocycles (Figure 1, eq 4). We surmise that γ-heteroatom chelation could be used as a strong directing effect for C−C forming activity if we could mitigate its strength to an optimal level by using a strongly electron-donating NHC ligand. Accordingly, we believe that the formation of *n*-/(*n* − 1)-*exo-trig* types of products would be less favorable than products formed via a n^{γ}-/$(n-1)^{\gamma}$-*exo-trig* (γ denoted as the cases with the help of γ-heteroatom chelation). Furthermore, by using the strong steric effect of NHC substituents as an ancillary factor to favor a 1,2-hydrometalation and to disfavor a secondary carbocenter on Ni for tether insertion, this approach should as a whole be able to provide n^{γ}- over a $(n-1)^{\gamma}$-*exo-trig* product highly selectively.[11]

RESULTS AND DISCUSSION

First, we studied the basic activities of NHC−NiH in cycloisomerization by subjecting several 1,6-dienes to an in situ generated [IPr-NiH(OTf)] used for cross-hydroalkenylation at rt in toluene.[12,13] This showed that, in relation to simple 1,6-dienes without an allyl heteroatom, the sterically demanding catalyst generally favored *n*- over (*n* − 1)-*exo-trig* but that this ratio was only moderate unless a Thorpe-Ingold effect was in force (Table 1, entries 1−4). This finding suggests that the use of steric interaction between an open-chained substrate and NHC substituents to favor a high ratio may not be generally applicable. In relation to diallylamines, the ratio observed was found to be tunable according to the electron-donating ability of the N-substituents (entries 5 and 6). This plausibly supported the possibility of a positive role for a γ-heteroatom chelation with Ni−NHC at this stage. There are several protocols for termini-selective (*n* − 1)-*exo-trig* cycloisomerization.[5,6,9,10] Unusually, our system enabled a termini-selective *n*-*exo-trig* cycloisomerization and favored a less sterically demanding tether insertion (entry 7). We suggest that this selectivity was due either to the creation by IPr of large steric differences in *n*-*exo-trig* ring-closure barriers between the two 1,2-hydrometalated species or the relatively faster isomerization on the less sterically demanding tether. In relation to diallyl ethers, the most commonly observed activities reported in previous attempts were (1) the deactivation of highly oxophilic catalysts, (2) the decomposition of substrates by the use of NHC−Pd(allyl) catalysts,[14] or (3) the successful cycloisomerization at a high (*n* − 1)-:*n*-*exo-trig* selectivity by the use of P−NiH.[5c] In this experiment, we were pleased to find that our system not only allowed C−C formation in the absence of nucleophilic or Lewis acidic additives but also changed its preference in terms of selectivity to favor a high *n*-:(*n* − 1)-*exo-trig* selectivity (entries 8 and 9). Nevertheless, the pyran synthesis efficiency was low due to nonselective iso-/oligomerization competition, and we cannot conclude at this stage whether the consistent termini-selectivity noted in entries 7−9 was related to the heteroatoms or was entirely based on steric reason (see below).

Table 1. IPr-NiH Effect on 1,6-Diene Cycloisomerization[a]



Entry[a]			Product	Conver.%	Yield	n-:(n-1)-exo-trig
	R = H	X =				
1		$C(COOEt)_2$	**6a**	73	73	4.2:1
2[b,c]		$C(CH_2OBn)_2$	**6b**	89	89	7.9:1
3[d]		2,2-(α-tetralone)	**6c**	100	95	19.0:1[e]
4		CH(OBn)	**6d**	82	81	0.5:1
5		N-Ts	**6e**	70	57	3.1:1[f]
6[b]		N-(Mesityl)	**6f**	88	86	16.2:1
	R =	X =				
7[b]	Pentyl	N-(2,6-Xylene)	**6g**	58	50	19.0:1[h]
8[g]	Ph	O	**6h**	38	32	19.0:1[h]
9[g]	Pentyl	O	**6i**	100	60	19.0:1[h]

[a]See the Experimental Section for details of the procedure for cycloisomerization. The yields of the desired products from *n*-*exo-trig* were determined by ^{1}H NMR and isolation. Unless otherwise indicated, no other cyclic products (<5%) were detected by ^{1}H NMR and isolation. Other conversions of 1,*n*-dienes were found due to nonselective isomerization and oligomerization. [b]35 °C. [c]36 h. [d]5 mol % of catalyst. [e]dr of (*n* − 1)-*exo-trig* products, syn/anti = 2.1. [f]NMR yield. [g]20 mol % of catalyst. [h]The alternative *n*- or (*n* − 1)-*exo-trig* isomers via a 1,2- or 2,1-hydrometalation at a terminus without an α-branch R was not detected by ^{1}H NMR.

To study the effect of tether length and to obtain much less readily accessible but strained medium-sized oxacycle targets with an exocyclic *gem*-olefin by an n^{γ}-*exo-trig* selective cycloisomerization, several 1,7-oxadienes (i.e., 1,7-dienes with a simple allyl ether terminus) were then tested (Table 2, entries 1−12). In the absence of conformational constraints, such as Thorpe−Ingold acceleration and high-dilution conditions (run at 0.5 M, cf. a general 0.1−6 × 10^{-3} M required in 1,*n* < 7 dienes cycloisomerization) to combat a relatively higher entropy stress, the same NHC catalyst as above can provide n^{γ}-*exo-trig*-type cycloisomerization products effectively. This concurrently achieved prominent chemoselectivity (cycloisomerization vs homohydroalkenylation), regioselectivity (1,2- vs 2,1-hydrometalation), and termini selectivity (allyl vs homoallyl ether) to give a single oxepine with an isolated yield of 84−89% (R = nonyl, Bn, ^{i}Bu, ^{c}Hex) from a vast number of other competitive outcomes. In addition, this reaction can be achieved in a shorter reaction time (14−18 h) at 5 mol % catalyst loading. Other than 5−10% nonselective starting material isomerization and <5% product isomerization, no other cyclic products that could be formed via such a pathway were detected by ^{1}H NMR from the crude mixture (~19:1), except in entries 6 and 7. Even the purification of the isomeric mixture is difficult in some 1,*n*-diene cycloisomerization systems, the high selectivity of our system and the higher polarity of the n^{γ}-*exo-trig* product compared with the other types of products made purification easy. Strategically, the exocyclic methylene products obtained here offers an easy channel to access related structures and complements the endocyclic olefin products obtained from 1,7-oxadiene RCM. For instance, a 4-oxepanone was obtained by ozonolysis at a 78% yield from **7a**.

Ligand screening indicated that the efficient oxepine formation was not simply a direct result of optimal tether length and γ-oxy chelation with Ni. This finding was supported by a control that used a P−NiH equivalent generated from PPh_3/$[(allyl)NiCl]_2$/AgOTf, in which a 78% **7a** precursor was isomerized to a mixture of noncyclic products. In addition, the

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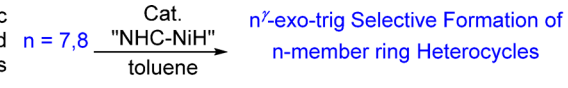
Table 2. Termini and Regioselective Heterosubstituted 1,7- and 1,8-Diene Cycloisomerization[a]



Entry	NHC	Hours	°C	Cat mol%	Substrates	Products		Conversion %	n^{γ}-exo-trig Yield %	(n-1)-exo-trig Yield %
1	IPr	14	r.t.	5			**7a** R = Nonyl	100	85	
	IMes	14	r.t.	5				90	25	
	SIPr	14	r.t.	5				100	75 (20)[b]	
2	IPr	18	r.t.	5			**7b** R = Bn	100	89	
3	IPr	18	r.t.	5			**7c** R = Cy	100	87	
4	IPr	14	r.t.	5			**7d** R = *iso*-Bu	100	84	
5	IPr	14	r.t.	5			**7e** R = CH_2OPh	100	78	
6	IPr	14	r.t.	5			**7f** R= Ph	100	60	20[c]
7	IPr	14	r.t.	5			**7g** R = *p*-Anisyl	100	55	10[c]
8	IPr	20	r.t.	10			**7h**	55	46	
	IPr	20	35	10				100	68	
9	IPr	14	r.t.	5			**7i** R = H	100	92	
10	IPr	20	50	20			**7j** R = Me	62	54	
11	IPr	20	r.t.	10			**7k**	70	66	
12	SIPr	24	r.t.	10			**7l**	100	55	8[c]
13	SIPr	18	r.t.	5			**7m** R = H	95	60[d]	
	SIPr	24	r.t.	20			**7n** R = n-Pentyl	72	60[d]	
14	SIPr	24	35	20			**7o** R = OBn	86	84	
	IPr	24	35	20				44	42	
	SIPr	24	35	20			**7p** R = Octyl	80	70 (9)[b]	
15	IPr	24	r.t.	10			**8a**	75	32	
16	SIPr	40	35	20			**8b**	78	71	

[a]See the Experimental Section for the detailed cycloisomerization procedure. All of the 1,*n*-dienes are in racemic form, and the products shown are in relative configurations. The yields of the desired products from n^{γ}-*exo-trig* were determined by ^{1}H NMR and isolation. Other than 5−10% nonselective 1,7-oxadiene isomerization and <5% product isomerization, no other cyclic products that could be formed from these substrates were detected by ^{1}H NMR and isolation unless otherwise indicated. [b]Yield of endocyclic 4-oxepine **7a′** and **7p′**, respectively (see later section). [c]Mixture of $(n-1)$-*exo-trig* products. [d]By NMR, the product was not stable on the column. Attempts to recover the decomposed products failed.

reactivity was found to be sensitive to both the NHC electronic properties and to its substituents, where using IMes resulted in mainly nonselective isomerization and oligomerization (entry 1, footnote b). Moreover, screening a 1,7-diene with the Thorpe−Ingold effect but without γ-oxy chelation, diethyl (homoallyl)-allylmalonate, did not form n-*exo-trig* product under our experimental conditions and provided only nonselective oligomerization. This indicated that the oxepine formation was not merely the direct result of optimal tether length and NHC steric effect directed 1,2-hydrometalation, but that the γ-oxy chelation was assumed to have a substantial role. Together with the high n^{γ}-:$(n-1)^{\gamma}$-*exo-trig* selectivity observed, we believe that the tether length, γ-oxy chelation, and NHC steric effects were intercorrelated factors that are important to the success described above.

We then directed our efforts to delineating the generality and scope of this approach with respect to the ***steric effect*** next to the olefin, such as the incorporation of α-substituents or a cyclic template (entries 8−12). We found that our approach was remarkably powerful in its effects on an n^{γ}-*exo-trig* cycloisomerization. Our system did not follow the predictions entirely based on conventional steric rationales or the relative olefin isomerization rate (vs the trend observed in Table 1, entries 7−9). Although the tethers involved were sterically more challenging than the former and the desired n^{γ}-*exo-trig* selectivity may be affected according to the relative fused ring

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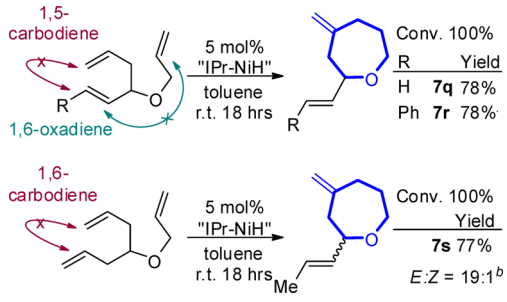
strains (entries 10−12),[4,11] the system consistently gave n^{γ}-*exo-trig* product as the dominant mode and allowed the diastereoselective formation of oxepine. In other words, an increase in steric effect around the olefin substituents as shown cannot supersede the selectivity on γ-oxy chelation and an NHC steric basis and cannot reprioritize the preference for favoring *n-exo-trig* or $(n-1)^{\gamma}$-*exo-trig*. To a limited extent, this finding also suggests that the high *n*-:$(n-1)$-*exo-trig* cycloisomerization observed in Table 1, entries 7−9, may be strongly related to the γ-heteroatom chelation rather than to the effect of R alone. As such, the R may be the key factor to differentiate the two competing n^{γ}-*exo-trig* pathways on steric and rate of isomerization basis, since both of which have a primary (1°) carbocenter on Ni.

Having studied the system with respect to ***allyl heteroatoms*** below, we found that the strength of the heteroatom−Ni chelation was tunable through the use of the electronic properties of NHC. The use of a more electron-rich NHC ligand SIPr led to a significant improvement in reactivity and functional group compatibility and solved issues related to catalyst deactivation by a stronger γ-heteroatom chelation or simply by σ-coordination. This expanded the scope of our findings to other heterocycles such as siloxepine and thiephine,[15] further highlighting the potential of this approach (entries 13 and 14). However, using commercially available ligands at this stage, the cycloisomerization system only resulted in limited success when using 1,8-oxadiene substrates without a cyclic backbone (entries 15 vs 16). Nevertheless, the selective oxocane over oxepine formation showed again that the success was related to γ-oxy chelation and the NHC effect and was not a direct result of relative ring strain or tether length.

In Scheme 1, by subjecting precursors with an extra terminus for competition, the results further showed that our approach

Scheme 1. Competitive Oxa- and Carbocycles Synthesis[a]



[a]See the Experimental Section for the detailed cycloisomerization procedure. The yields of the desired products from 7^{γ}-*exo-trig* were determined by ^{1}H NMR and isolation. No other oxacycle regioisomers and carbocycles (<5%) were detected by ^{1}H NMR and isolation. [b]The exocyclic homoallyl ether terminus was isomerized to give allyl ether (*E*:*Z* = 19:1 by ^{1}H NMR).

was exceptionally suited to directing a n^{γ}-*exo-trig* compared with other cycloisomerization modes.

The formation of strained oxepines was preferable to all of the other possible oxacycles (e.g., pyrans), and also outperformed all of the other highly competitive, less strained, smaller ordinary carbocycle formation pathways (e.g., cyclopentanes/hexanes). As such, a *high oxa- to carbocycle ratio was achieved*. This set of observations is notable given that both 1,5- and 1,6-carbodienes are often regarded as more efficient substrates than their heterosubstituted counterparts in traditional Lewis acidic cationic catalyst systems[1,5a] and the fact that our system also catalyzes the carbodiene cycloisomerization as shown in Table 1.

Although a precise cycloisomerization mechanism awaits further study, we believe that our initial proposal was reasonable in that the optimal γ-heteroatom chelation with Ni−NHC has a fundamental role in accounting for the observations. The use of an electron-rich NHC ligand may result in a weaker σ-heteroatom−Ni chelation than a P ligand, and a syn 1,2-hydrometalation on an allyl ether terminus could be favored (Figure 2). The hydrometalated species is then

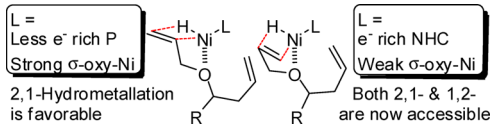


Figure 2. Effect of ligand and σ-oxy-Ni chelation on regioselective hydrometalation of allyl ether.

stabilized by a γ-heteroatom−Ni chelation in the form of heteronickelacyclopentane.[16,17] Next, this stabilized intermediate allows ring closure in an n^{γ}-*exo-trig* manner. The rest of the mechanism is expected to resemble that described in a typical P−NiH-catalyzed 1,*n*-diene case, in which the Ni−H is regenerated after a typical syn β-H elimination. The n^{γ}- over $(n-1)^{\gamma}$-*exo-trig* selectivity observed could be a result of a more difficult 2,1-hydrometalation on an homoallylether terminus or the higher ring closure barriers in a secondary (2°) over a 1° carbocenter on Ni−NHC.[18] Overall, the cycloisomerization selectivity could be a balance between the challenges of hydrometalation under the σ-heteroatom−Ni chelation effect, the stability of the resulted heteronickelacycles (Figure 3), and the NHC steric effect on ring closure.

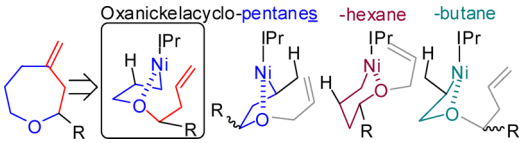


Figure 3. n^{γ}-*Exo-trig* directed by NHC steric effect and γ-oxy stabilization.

It should be noted that, in the presence of a σ-heteroatom−Ni chelation, the allyl ether terminus could be quite difficult to adopt a desired conformation for a *syn* 1,2-hydrometalation under mild conditions. Indeed, the crystallographic data of several bulky P-ligated oxanickelacyclopentanes reported in the literature also suggested this conjecture.[16a,b] This inspired us to hypothesize an alternative mechanism that involves a contrasting progression. Unlike many chelation-controlled reactions sequences, we hypothesize that the reaction may first undergo a NHC steric effect directed 1,2-hydrometalation followed by γ-heteroatom *stabilization*. The reversible nature of hydrometalation (Scheme 2) and the NHC steric effect may allow the system to sort out the optimal stabilization and tether for the desired ring closure selectivity. As such, eventually, a stabilized oxa-/thio-/siloxanickelacyclopentane intermediate (Figure 3) as described in the above reaction mechanism can be obtained on the allyl ether terminus *after* a 1,2-hydrometalation favored by the NHC steric effect. However, we do not have direct evidence for this new reaction sequence.

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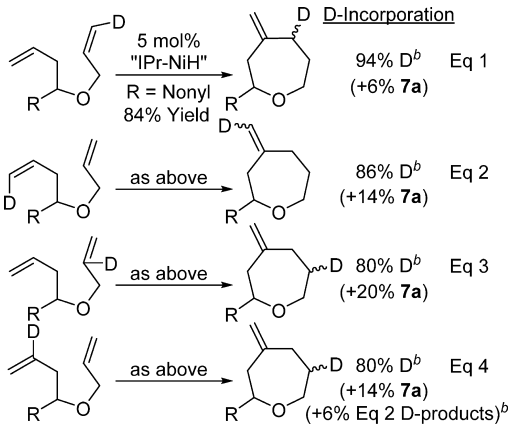
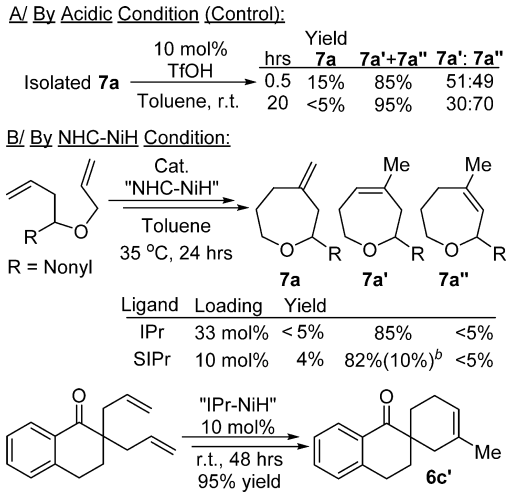
Scheme 2. Labeling Experiments[a]



[a]The cycloisomerization procedure employed was the same as the 7a preparation in Table 2. Products ratios were determined by NMR [b]A mixture of D-labeled isomers was obtained in ca. 1:1.

As noted in Table 2 entry 1, there is a regioselective formation of a minor endocyclic methylene product 7a′ when SIPr is used; we therefore studied the system further hoping to understand and to develop a more efficient one-pot process after optimization (Scheme 3).[19] First, we confirmed the

Scheme 3. One-Pot Selective Cycloisomerization to Endocyclic Products[a]



[a]See the Experimental Section for the detailed procedures. The yields of the products were determined by ^{1}H NMR and isolation. No other cycloisomerization products and other olefin regioisomers (<5%) were detected by ^{1}H NMR and isolation. [b]Yield of less hindered 7a′ isomer, assigned by comparison with related literatures.[20]

observation is not a direct result of an acid-catalyzed isomerization. By subjecting an isolated oxepine **7a** to a TfOH-catalyzed olefin isomerization condition, we found that a new trisubstituted olefin **7a″** was formed as a major product rather than a highly selective formation of **7a′** observed (Scheme 3, A). Second, we found that the isomerization efficiency was related to the NHC electronic properties, in which the use of sterically similar but more electron rich NHC ligand SIPr was significantly more efficient than IPr in the isomerization of exo- to endocyclic olefin product (Table 2, entry 1). Third, we found that the reaction was also sensitive to the steric effect around the exocyclic methylene. A greater steric hindrance closed to exocyclic methylene of the oxepine resulted a more difficult exo- to endo-isomerization of the olefin (Table 2, **7h,j,m−n**). Finally, it should be noted that the isomerization was sensitive toward the electronic property of the product substituents. It was more difficult in cases having better electron-donating heteroatoms for σ-coordination (Table 2, **7o−p**), but it was easier in the isomerization of oxepines and carbocycle such as **6c** to **6c′**. Overall, the above experiments and analysis suggested that the selective formation of **7a′** was a result of a NHC−NiH catalyzed isomerization of **7a**, where the isomerization efficiency and regioselectivity were related to both the electronic and the steric properties of the catalyst and the heterocycle. Since the 2,1-hydrometalation step required for the isomerization is expected to be difficult with a bulky NHC ligated NiH, the optimized catalytic one-pot synthesis of the endocyclic product required an elevated temperature or in a longer period of reaction time than the normal cycloisomerization procedure (Scheme 3, B).

CONCLUSION

In summary, the γ-oxy deactivation[5a] was transformed into a valuable asset for a highly site- and regioselective C−C forming reaction by using NHC as an optimal ligand to balance the high oxophilicity of hydrometalation catalyst. The new reactivity profile realized from this pairing provides not only the first 1,7-heterodiene unsymmetric n^{γ}-*exo-trig* cycloisomerization but also a novel means of circumventing the typical 1,*n*-diene cycloisomerization preferences that normally favor a lower ring strain product. With this method, larger heterocycles with a higher strain can be formed *preferentially* over the ordinary less strained hetero-/carbocycles observed in conventional systems. This new approach and its implications will encourage subsequent optimization and allow the paradigm to achieve its full potential. The n^{γ}-*exo-trig* cycloisomerization outcomes offered in this work should complement the products obtained from $(n-1)$-*exo-trig* cycloisomerization and olefin RCM, and this may further facilitate SAR study in drug synthesis.

EXPERIMENTAL SECTION

General Methods. Unless otherwise indicated, all reactions were performed under a nitrogen atmosphere from which oxygen and moisture were rigidly excluded from the reagents and glassware. IPr [1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene], $Ni(cod)_2$ [bis-(cyclooctadienyl)nickel(0)], IMes [1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene], and SIPr [1,3-bis(2,6-diisopropylphenyl)-imidazolidin-2-ylidene] were used as received from commercial sources and stored in a glovebox. Triethylsilyl trifluoromethanesulfonate (TESOTf), *p*-anisaldehyde, and triethylamine (NEt_3) were distilled before use. Toluene was distilled over sodium before use. 1,*n*-Dienes were dried with CaH_2 or $CaCl_2$ before use. Unless otherwise indicated, they were synthesized according to the procedures in the literature. Analytical thin-layer chromatography (TLC) was performed with the use of silica gel 60 F254 plates. The developed chromatogram was analyzed by UV lamp (254 nm), ethanolic phosphomolybdic acid (PMA), or potassium permanganate ($KMnO_4$). Flash liquid chromatography was performed on a coarse fritted glass column packed with silica gel (230−400 mesh, 0.040−0.063 mm). The cycloisomerization products were found to be unstable to acidic aqueous conditions.[21] We therefore did not use HCl-washed sand to pack the silica gel column, and we recommend the use of fritted glass column. The cycloisomerization products, except those with α-branch to the exocyclic olefin, were found to be unstable upon storage in general and will decompose or isomerize upon heating. The preferred water bath temperature for rotavap is

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below 40 °C. NMR spectra were recorded with a 400 NMR spectrometer for ^{1}H NMR and 100 MHz for ^{13}C NMR. Chemical shifts in ^{1}H NMR spectra are reported in ppm on the δ scale from an internal standard of residual chloroform (7.27 ppm). Chemical shifts of ^{13}C NMR spectra are reported in ppm from the central peak of $CDCl_3$ (77.16 ppm) on the δ scale. Cycloisomerization precursors conversion and products ratio was determined by integration of areas of selected peaks in crude ^{1}H NMR with relaxation time d_1 = 10 s and nitromethane as standard. High-resolution mass spectra (HRMS) data were obtained by electron-impact (EI) ionization or electrospray ionization (ESI) with the mass analyzer of magnetic sector used.

NHC−NiH Catalyst Generation. In a glovebox, Ni(cod)$_2$ and IPr or SIPr or IMes (0.05 mmol, 5 mol % each) were added to an oven-dried test tube equipped with a stir bar. After being sealed with a septum and brought out of the glovebox, the tube was connected to a N_2 line. The mixture was dissolved in 2 mL of dried degassed toluene and stirred at rt for 1 h. 1-Octene (25 mol %), NEt_3 (0.3 mmol), *p*-anisaldehyde (5 mol %), and TESOTf (10 mol %) were then added sequentially and stirred for 45 min at rt.[12] The catalyst can be generated by using conventional methods analogous to the P systems carefully.[9b,13a] However, technically we strongly recommend the above procedure for high consistency. The presence of small amounts of catalytically active impurities, such as other NiH or its equivalent, may consume the cycloisomerization precursors more readily than our desired pathway with the NHC catalyst.

General Cycloisomerization Procedure in Tables 1 and 2 and Schemes 1 and 2. The 1,*n*-diene (1.0 mmol or indicated amount) was added to the above catalyst at rt. After the mixture was stirred at the temperature and time indicated, a spatula of Na_2CO_3(s) was added, and the mixture was diluted with 4 mL of hexane and stirred in open air for 30 min. The mixture was then filtered through a short plug of silica gel and rinsed with 75 mL of 80% ether/hexane. The solvent was removed under a vacuum. Purification via silica gel column chromatography (hexane/DCM 5:1, 4:1, 3:1, 2:1, 1:1) yielded the cycloisomerization product as a colorless oil, and the 7$^{\gamma}$-*exo-trig* cycloisomerization products were found to be *more polar* than the 1,7-oxadienes and the isomerization product mixtures on TLC by using DCM/Hex as eluent in silica gel in general. In cases where there were minor 6-*exo-trig* cycloisomerization products observed, e.g., in Table 2, R = aryl, they were found to be less polar than the starting material, and thus, the purification is not difficult. For reactions carried out at a higher temperature, we preheated the oil bath to the required temperature before immersing the reaction tube.

Table 1, **6a**,**d**,**e**, are literature compounds, and they were obtained in 59% (70.8 mg), 27% (27.3 mg), and 43% (54.2 mg) yield, respectively.[22]

*Table 1, Entry 2, **6b***. 132 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34−7.24 (m, 10H), 4.66 (s, 1H), 4.59 (s, 1H), 4.49 (s, 4H), 3.41−3.33 (m, 4H), 2.12−2.09 (m, 4H), 1.58−1.53 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.7, 139.2, 139.0, 128.4, 128.1, 127.5, 127.4, 124.8, 109.2, 73.6, 73.3, 41.0, 39.8, 35.0, 29.5, 22.7. HRMS−ESI (*m*/*z*): [M + Na]$^+$ calcd for $C_{23}H_{28}O_2$ 359.1982, found 359.1980.

*Table 1, Entry 3, **6c***. 204 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04−8.02 (m, 1H), 7.46−7.42 (m, 1H), 7.31−7.29 (m, 1H), 7.27−7.20 (m, 1H), 4.79 (s, 1H), 4.67 (s, 1H), 2.98−2.87 (m, 2H), 2.55−2.51 (m, 1H), 2.31−2.28 (m, 1H), 2.18−2.15 (m, 1H), 2.10−1.96 (m, 2H), 1.87−1.74 (m, 2H), 1.70−1.04 (m, 1H), 1.62−1.51 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.1, 145.9, 143.3, 133.2, 131.9, 128.8, 128.2, 126.7, 109.9, 46.5, 40.7, 34.6, 30.8, 29.6, 24.9, 22.8. HRMS−EI (*m*/*z*): [M]$^+$ calcd for $C_{16}H_{18}O$ 226.1358, found 226.1356.

*Table 1, Entry 6, **6f***. 81% NMR yield, 50 mg, 47% isolated yield, it was found to be unstable on column. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.81 (s, 2H), 4.69 (s, 1H), 4.67 (s, 1H), 3.51 (s, 2H), 3.09 (t, 2H, *J* = 5.2 Hz), 2.28−2.25 (m, 2H), 2.26 (s, 6H), 2.23 (s, 3H), 1.75−1.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.4, 146.0, 137.1, 134.5, 129.6, 107.0, 57.4, 50.8, 33.3, 28.5, 20.8, 19.6. HRMS−ESI (*m*/*z*): [M + H]$^+$ calcd for $C_{15}H_{22}N$ 216.1747, found 216.1752.

*Table 1, Entry 7, **6g***. 64 mg, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.04−6.89 (m, 3H), 4.68 (s, 1H), 4.66 (s, 1H), 3.69 (d, 1H, *J* = 12.4 Hz), 3.27 (d, 1H, *J* = 12.4 Hz), 3.23−3.19 (m, 1H), 2.49−2.45 (m, 1H), 2.29 (s, 3H), 2.26 (s, 3H), 1.97−1.94 (m, 1H), 1.35−1.11 (8H), 0.80 (t, 3H, *J* = 6.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.2, 137.9, 129.0, 128.3, 125.2, 106.5, 58.1, 57.5, 33.5, 33.4, 33.1, 32.1, 25.7, 22.7, 20.0, 19.8, 19.6, 14.0. HRMS−ESI (*m*/*z*): [M + H]$^+$ calcd for $C_{19}H_{30}N$ 272.2373, found 272.2378.

*Table 1, Entry 8, **6h***. 14 mg, 30% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38−7.32 (m, 4H), 7.29−7.25 (m, 1H), 4.88 (d, 1H, *J* = 1.5 Hz), 4.84 (s, 1H), 4.48 (dd, 1H, *J* = 11.2, 2.1 Hz), 4.36 (dd, 1H, *J* = 12.4, 1.5 Hz), 4.17 (d, 1H, *J* = 12.4 Hz), 2.56−2.42 (m, 2H), 2.18−1.97 (m, 1H), 1.81−1.71 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.5, 142.5, 128.5, 127.6, 126.1, 109.7, 79.8, 73.0, 35.6, 32.2. HRMS−EI (*m*/*z*): [M]$^+$ calcd for $C_{12}H_{14}O$ 174.1045, found 174.1055.

*Table 1, Entry 9, **6i***. 24 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.78 (s, 1H), 4.76 (s, 1H), 4.18 (d, 1H, *J* = 12.3 Hz), 3.96 (d, 1H, *J* = 12.3 Hz), 3.38−3.35 (m, 1H), 2.42−2.39 (m, 1H), 2.29−2.23 (m, 1H), 1.78−1.73 (m, 1H), 1.51−1.48 (m, 8H), 0.89 (t, 3H, *J* = 6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.3, 109.1, 77.6, 72.6, 36.2, 33.5, 32.1, 31.8, 25.5, 22.8, 14.2. HRMS−EI (*m*/*z*): [M + H]$^+$ calcd for $C_{11}H_{21}O$ 169.1587, found 169.1589.

*Table 2, Entry 1, **7a***. 202 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.78 (s, 1H), 4.71 (s, 1H), 4.05−3.95 (m, 1H), 3.50−3.40 (m, 1H), 3.40−3.33 (m, 1H), 2.49−2.41 (m, 1H), 2.41−2.35 (m, 1H), 2.35−2.28 (m, 1H), 2.28−2.21 (m, 1H), 1.85−1.73 (m, 1H), 1.73−1.69 (m, 1H), 1.46−1.38 (m, 2H), 1.35−1.20 (m, 14H), 0.87 (t, 3H, *J* = 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.6, 112.1, 80.3, 70.6, 44.8, 36.9, 34.8, 32.1, 30.6, 29.8, 29.8, 29.7, 29.4, 26.2, 22.8, 14.3. HRMS−EI (*m*/*z*): [M]$^+$ calcd for $C_{16}H_{30}O$ 238.2297, found 238.2296.

*Table 2, Entry 2, **7b***. 180 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31−7.19 (m, 5H), 4.79 (s, 1H), 4.70 (s, 1H), 3.97 (dt, 1H, *J* = 12.4, 4.6 Hz), 3.70−3.63 (m, 1H), 3.44−3.37 (m, 1H), 2.87 (dd, 1H, *J* = 13.8, 7.4 Hz), 2.69 (dd, 1H, 13.8, 5.7 Hz), 2.50−2.45 (m, 1H), 2.42−2.26 (m, 3H), 1.91−1.73 (m, 1H), 1.71−1.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.0, 147.3, 129.6, 121.0, 114.8, 113.1, 78.0, 71.0, 70.8, 40.8, 35.0, 30.5. HRMS−ESI (*m*/*z*): [M + H]$^+$ calcd for $C_{14}H_{19}O$ 203.1430, found 203.1430.

*Table 2, Entry 3, **7c***. 169 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.78 (s, 1H), 4.72 (s, 1H), 4.00 (dt, 1H, *J* = 12.2, 4.7 Hz), 3.45−3.39 (m, 1H), 3.15−3.10 (m, 1H), 2.47−2.26 (m, 4H), 1.91 (d, 1H, *J* = 12.2 Hz), 1.82−1.64 (m, 6H), 1.39−0.93 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.2, 112.1, 84.6, 71.2, 43.8, 41.8, 34.7, 30.9, 29.5, 28.9, 26.7, 26.5, 26.4. HRMS−ESI (*m*/*z*): [M + H]$^+$ calcd for $C_{13}H_{23}O$ 195.1743, found 195.1746.

*Table 2, Entry 4, **7d***. 141 mg, 84% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.78 (s, 1H), 4.72 (s, 1H), 3.99 (dt, 1H, *J* = 12.3, 4.6 Hz), 3.50−3.40 (m, 2H), 2.44−2.18 (m, 4H), 1.84−1.70 (m, 3H), 1.52−1.44 (m, 1H), 1.20−1.13 (m, 1H), 0.91 (d, 3H, *J* = 3.2 Hz), 0.89 (d, 3H, *J* = 3.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.7, 112.2, 78.3, 70.6, 46.0, 45.2, 34.8, 30.6, 24.8, 23.5, 22.4. HRMS−ESI (*m*/*z*): [M + H]$^+$ calcd for $C_{11}H_{21}O$: 169.1587, found 169.1588.

*Table 2, Entry 5, **7e***. 170 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30−7.27 (m, 2H), 6.96−6.91 (m, 3H), 4.86 (s, 1H), 4.79 (s, 1H), 4.09 (dt, 1H, *J* = 12.3, 4.5 Hz), 4.04−3.92 (m, 1H), 3.90−3.84 (m, 2H), 3.62−3.54 (m, 1H), 2.62 (dd, 1H, *J* = 14.4, 2.4 Hz), 2.53−2.41 (m, 2H), 2.37−2.31 (m 1H), 1.87−1.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.0, 147.3, 129.6, 121.0, 114.8, 113.1, 78.0, 71.0, 70.8, 40.8, 35.0, 30.5. HRMS−ESI (*m*/*z*): [M + Na]$^+$ calcd for $C_{14}H_{18}O_2Na$ 241.1199, found 241.1200.

*Table 2, Entry 6, **7f***. 113 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35−7.23 (m, 5H), 4.87 (s, 1H), 4.78 (s, 1H), 4.49 (dd, 1H, *J* = 10.28 Hz, 3.08 Hz), 4.16−4.10 (m, 1H), 3.68−3.62 (m, 1H), 2.73−2.69 (m, 1H), 2.64−2.57 (m, 1H), 2.49−2.44 (m, 2H), 1.95−1.79 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.0, 143.8, 128.5, 127.3, 125.8, 113.0, 82.5, 70.9, 46.9, 34.8, 30.3. HRMS−EI (*m*/*z*): [M + Na]$^+$ calcd for $C_{13}H_{16}NaO$ 211.1093, found 211.1095

*Table 2, Entry 7, **7g***. 120 mg, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (d, 2H, *J* = 8.5 Hz), 6.87 (d, 2H, *J* = 8.5 Hz), 4.86 (s, 1H), 4.78 (s, 1H), 4.44 (dd, 1H, *J* = 9.8, 2.8 Hz), 4.11 (dt, 1H, *J* = 12.4, 4.4 Hz), 3.80 (s, 3H), 3.66−3.60 (m, 1H), 2.82−2.57 (m, 2H), 2.52−2.36 (m, 2H), 2.08−1.87 (m, 1H), 1.82−1.69 (m, 1H). ^{13}C

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NMR (100 MHz, $CDCl_3$) δ: 158.9, 148.1, 136.1, 127.1, 113.8, 113.0, 82.1, 70.7, 55.4, 46.8, 34.7, 30.2. HRMS−ESI (m/z): $[M + H]^+$ calcd for $C_{14}H_{19}O_2$ 219.1380, found 219.1382.

*Table 2, Entry 8, **7h***. Rac-, relative configuration only, 85 mg, 68% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 4.77 (s, 1H), 4.73 (s, 1H), 4.12 (d, 1H, J = 11.8 Hz), 3.37−3.30 (m, 1H), 2.97 (t, 1H, J = 9.1 Hz), 2.44−2.15 (m, 3H), 1.73−1.66 (m, 2H), 1.54−1.50 (m, 2H), 1.40−1.22 (m, 14H), 1.00 (d, 3H, J = 6.9 Hz), 0.88 (t, 3H, J = 5.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.9, 111.6, 87.0, 73.7, 48.2, 34.9, 33.7, 32.2, 32.1, 29.9, 29.8, 29.8, 29.5, 26.3, 22.8, 19.6, 14.3. HRMS−ESI (m/z): $[M + H]^+$ calcd for $C_{17}H_{33}O$ 253.2526, found 253.2525.

*Table 2, Entry 9, **7i***. Rac-, relative configuration only, 153 mg, 92% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 4.86 (s, 1H), 4.76 (s, 1H), 4.06−4.01 (m, 1H), 3.50−3.43 (m, 1H), 3.04−2.98 (m, 1H), 2.39−2.26 (m, 2H), 2.12−2.07 (m, 1H), 1.97−1.95 (m, 1H), 1.80−1.69 (m, 5H), 1.43−1.18 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.0 111.2 84.7 71.3 52.3 34.3 34.2 32.9 31.8 26.0 25.5. HRMS−ESI (m/z): $[M + H]^+$ calcd for $C_{11}H_{19}O$ 167.1430, found 167.1432.

*Table 2, Entry 10, **7j***. Rac-, relative configuration determined by NOESY, 24 mg, 54% yield. Major diastereomer. ^1H NMR (400 MHz, $CDCl_3$) δ: 4.85 (s, 1H), 4.78 (s, 1H), 3.94 (dd, 1H, J = 12.2, 5.1 Hz), 3.08−3.00 (m, 2H), 2.29 (dd, 1H, J = 12.9, 4.0 Hz), 2.16−2.10 (m, 2H), 1.96−1.90 (m, 2H), 1.78−1.67 (m, 3H), 1.33−1.22 (m, 4H), 0.83 (d, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.5, 112.2, 85.2, 78.4, 52.8, 42.3, 37.0, 34.1, 33.3, 26.0, 25.5, 17.5. HRMS−ESI (m/z): $[M + H]^+$ calcd for $C_{12}H_{21}O$ 181.1587, found 181.1589. Minor diastereomer, ∼3% yield as determined by NMR. Isolation was not successful, and the following data was deduced from a product mixture roughly purified on a short plug of silica gel. ^1H NMR (400 MHz, $CDCl_3$) δ: 4.82 (s, 1H), 4.78 (s, 1H), 3.72 (dd, 1H, J = 12.1, 2.4 Hz), 3.58 (dd, 1H, J = 12.2, 4.2 Hz), 3.46 (d, 1H, J = 11.0 Hz), 3.19 (d, 1H, J = 11.0 Hz), 2.94 (dd, 1H, J = 12.8, 9.1 Hz), 2.52 (dd, 1H, J = 12.8, 5.0 Hz), 1.96−1.67 (m, 5H), 1.33−1.22 (m, 4H), 0.97 (d, 3H, J = 7.0 Hz). ^{135}DEPT NMR (100 MHz, $CDCl_3$) δ: 111.0, 85.8, 76.5, 52.1, 42.5, 37.0, 32.1, 31.9, 29.9, 28.5, 14.3.

*Table 2, Entry 11, **7k***. Rac-, relative configuration only, 50 mg, 66% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 4.80 (s, 1H), 4.67 (s, 1H), 4.01 (ddd, 1H, J = 12.0, 5.1, 3.3 Hz), 3.63 (dd, 1H, J = 14.9, 8.5 Hz), 3.53−3.47 (m, 1H), 2.60−2.48 (m, 3H), 2.10−2.01 (m, 1H), 1.98−1.91 (m, 1H), 1.90−1.80 (m, 1H), 1.77−1.72 (m, 2H), 1.68−1.50 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.1, 108.6, 85.1, 71.6, 52.6, 36.4, 32.5, 29.6, 29.2, 21.6. HRMS−ESI (m/z): $[M + H]^+$ calcd for $C_{10}H_{17}O$ 153.1274, found 153.1273.

*Table 2, Entry 12, **7l***. Rac-, relative configuration only, 55 mg, 55% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.21−7.19 (m, 4H), 4.99 (s, 1H), 4.98 (s, 1H), 4.09 (dd, 1H, J = 11.7, 5.5 Hz), 3.95 (dd, 1H, J = 17.7, 8.5 Hz), 3.83 (d, 1H, J = 8.5 Hz), 3.56 (m, 1H), 3.20 (dd, 1H, J = 15.0, 7.5 Hz), 2.89 (dd, 1H, J = 15.0, 9.8 Hz), 2.73−2.69 (m, 1H), 2.61−2.53 (m, 1H), 2.09−1.98 (m, 1H), 1.96−1.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.6, 141.2, 141.0, 127.0, 126.6, 125.8, 124.8, 110.5, 90.4, 70.4, 56.2, 38.1, 35.5, 28.3. HRMS−EI (m/z): [M]+ calcd for $C_{14}H_{16}O$ 200.1196, found 200.1195.

*Table 2, Entry 13, **7m***. Low boiling, purified in DCM/pentane. 60% NMR yield, 54 mg, 35% isolated yield, it was found not stable on column. ^1H NMR (400 MHz, $CDCl_3$) δ: 4.67−4.66 (m, 1H), 4.57−4.56 (m, 1H), 3.85−3.83 (m, 2H), 2.26−2.23 (m, 2H), 1.79−1.74 (m, 2H), 1.72 (s, 2H), 0.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.0, 109.0, 64.7, 38.7, 32.8, 28.9, −1.3. HRMS−ESI (m/z): $[2M + Na]^+$ calcd for $C_{16}H_{32}NaO_2Si_2$ 335.1833, found 335.1835.

*Table 2, Entry 13, **7n***. 60% NMR yield, 17 mg, 30% isolated yield, it was found not stable on column. ^1H NMR (400 MHz, $CDCl_3$) δ: 4.63 (s, 1H), 4.56 (s, 1H), 3.73−3.69 (m, 1H), 2.42−2.36 (m, 1H), 2.11−2.01 (m, 1H), 1.76−1.66 (m, 3H), 1.58−1.18 (m, 11H), 0.88 (t, 3H, J = 6.6 Hz), 0.14 (s, 3H), 0.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.3, 108.6, 74.1, 38.8, 37.9, 37.7, 31.9, 29.4, 25.8, 22.8, 14.2, −1.0, −1.2. HRMS−EI (m/z): $[M]^+$ calcd for $C_{13}H_{26}OSi$ 226.1747, found 226.1745.

*Table 2, Entry 14, **7o***. 52 mg, 84% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.36−7.28 (m, 5H), 4.88 (s, 1H), 4.84 (s, 1H), 4.60−4.53 (m, 2H), 3.59−3.48 (m, 2H), 3.08−3.01 (m, 1H), 2.84−2.78 (m, 2H), 2.63−2.56 (m, 1H), 2.43−2.32 (m, 2H), 2.21−2.15 (m, 1H), 2.09−1.97 (m, 1H), 1.87−1.75 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.8, 138.3, 128.5, 127.8, 127.8, 114.4, 73.4, 73.3, 46.2, 42.6, 35.2, 32.6, 32.0. HRMS−ESI (m/z): $[M + Na]^+$ calcd for $C_{15}H_{20}OSNa$ 271.1127, found 271.1126.

*Table 2, Entry 14, **7p***. 44 mg, 70% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 4.85 (s, 1H), 4.81 (s, 1H), 2.79 (dt, 1H, J = 14.6, 4.3 Hz), 2.75−2.67 (m, 2H), 2.60−2.52 (m, 1H), 2.45−2.39 (m, 1H), 2.26−2.13 (m, 2H), 2.05−1.99 (m, 1H), 1.82−1.71 (m, 1H), 1.53−1.48 (m, 2H), 1.48−1.40 (m, 1H), 1.30−1.26 (m, 12H), 0.88 (t, 3H, J = 6.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.8, 113.9, 47.6, 47.0, 36.3, 34.8, 32.5, 32.3, 32.0, 29.7, 29.5, 27.7, 22.8, 14.3. HRMS−EI (m/z): [M]+ calcd for $C_{16}H_{30}S$ 254.2063, found 254.2063.

*Table 2, Entry 15, **8a***. (31 mg, 32% yield) ^1H NMR (400 MHz, $CDCl_3$) δ: 4.78 (s, 1H), 4.74 (s, 1H), 3.83−3.77 (m, 1H), 3.57−3.51 (m, 1H), 3.40−3.35 (m, 1H), 2.41−2.31 (m, 1H), 2.30−2.26 (m, 2H), 2.11−2.04 (m, 1H), 1.98−1.91 (m, 1H), 1.82−1.75 (m, 1H), 1.66−1.62 (m, 1H), 1.61−1.51 (m, 1H), 1.47−1.38 (m, 2H), 1.36−1.24 (m, 6H), 0.88 (t, 3H, J = 6.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.0, 109.9, 78.9, 69.5, 36.6, 36.0, 34.3, 32.4, 32.1, 29.4, 25.9, 22.8, 14.2. HRMS−EI (m/z): $[M + H]^+$ calcd for $C_{13}H_{25}O$: 197.1905, found 197.1904.

*Table 2, Entry 16, **8b***. 61 mg, 70% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.21−7.14 (m, 2H), 7.07−7.01 (m, 2H), 4.82 (s, 1H), 4.68 (s, 1H), 4.15−4.12 (m, 2H), 3.50−3.41 (m, 2H), 2.32- 2.30 (m, 2H), 1.62−1.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.6, 150.6, 135.8, 130.2, 128.5, 125.1, 122.4, 111.9, 77.8, 39.7, 36.1, 28.7. HRMS−ESI (m/z): $[M + H]^+$ calcd for $C_{12}H_{15}O$ 175.1117, found 175.1113.

*Scheme 1, **7q***. 107 mg, 78% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 5.97−5.87 (m, 1H), 5.29−5.14 (m, 2H), 4.88 (m, 2H), 4.00−3.96 (m, 3H), 2.55−2.35 (m, 3H), 2.28−2.17 (m, 1H), 1.88−1.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.9, 135.4, 116.7, 106.6, 80.0, 70.0, 39.6, 32.2, 30.2. HRMS−ESI (m/z): $[M + H]^+$ calcd for $C_9H_{15}O$ 139.1123, found 139.1120.

*Scheme 1, **7r***. 167 mg, 78% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.42−7.20 (m, 5H), 6.59 (d, 1H, J = 16.0 Hz), 6.27−6.22 (m, 1H), 4.86 (s, 1H), 4.80 (s, 1H), 4.17−4.10 (m, 1H), 4.09−4.05 (m, 1H), 3.64−3.58 (m, 1H), 2.61 (dd, 1H, J = 14.7, 2.9 Hz), 2.48−2.34 (m, 3H), 1.89−1.81 (m, 1H), 1.80−1.70 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6, 137.1, 130.9, 129.6, 128.6, 127.6, 126.6, 113.0, 80.3, 70.1, 44.7, 34.9, 30.3. HRMS−EI (m/z): $[M]^+$ calcd for $C_{15}H_{18}O$ 214.1358, found 214.1346.

*Scheme 1, **7s***. *E* configuration, 111 mg, 73% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 5.70−5.50 (m, 2H), 4.81 (s, 1H), 4.76 (s, 1H), 4.03−3.98 (m, 1H), 3.92−3.86 (m, 1H), 3.56−3.50 (m, 1H), 2.51−2.47 (m, 1H), 2.42−2.30 (m, 3H), 1.84−1.76 (m, 1H), 1.74−1.69 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.9, 132.6, 126.3, 112.7, 80.6, 70.0, 44.8, 34.9, 30.3, 17.9. HRMS−EI (m/z): $[M + H]^+$ calcd for $C_{10}H_{17}O$ 153.1279, found 153.1275.

In Scheme 2, each of those D-labeled oxepines is not separable by column and were isolated with the **7a** obtained together. The peaks corresponding only to **7a** were identified and indicated in parentheses as shown below.

*Scheme 2, D-Labeled **7a** in eq 1*. Mixed with **7a**, 200 mg, 84% yield. ^1H NMR (700 MHz, $CDCl_3$) δ: 4.78 (s, 1H), 4.71 (s, 1H), 4.03−3.97 (m, 1H), 3.50−3.43 (m, 1H), 3.43−3.35 (m, 1H), 2.46−2.42 (m, 1H), 2.38−2.35 (m, 0.5H) [**7a**: 2.41−2.35 (m, 1H)], 2.31−2.27 (m, 0.5H) [**7a**: 2.34−2.27 (m, 1H)], 2.27−2.22 (m, 1H), 1.81−1.73 (m, 1H), 1.72−1.67 (m, 1H), 1.52−1.47 (m, 1H), 1.42−1.38 (m, 1H), 1.35−1.20 (m, 14H), 0.88 (t, 3H, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.6, 112.1, 80.3, 70.7, 70.6, 44.8, 36.9, 34.5 (t, J = 19.3 Hz), 34.4 (t, J = 19.3 Hz) [**7a**: 34.8], 32.1, 30.5, 30.5 [**7a**: 30.6], 29.8, 29.8, 29.7, 29.4, 26.2, 22.8, 14.3. HRMS−EI (m/z): $[M]^+$ calcd for $C_{16}H_{29}DO$ 239.2354, found 239.2352.

*Scheme 2, D-Labeled **7a** in eq 2*. Mixed with **7a**, 199 mg, 84% yield. ^1H NMR (700 MHz, $CDCl_3$) δ: 4.77 (s, 0.43H) [**7a**: 4.78 (s, 0.14H)], 4.70 (s, 0.43H) [**7a**: 4.71 (s, 0.14H)], 3.50−3.43 (m, 1H), 3.43−3.35 (m, 1H), 2.46−2.42 (m, 1H), 2.41−2.35 (m, 1H), 2.34−2.27 (m, 1H), 2.27−2.22 (m, 1H), 1.81−1.73 (m, 1H), 1.72−1.67 (m, 1H), 1.52−1.47 (m, 1H), 1.42−1.38 (m, 1H), 1.35−1.20 (m, 14H),

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0.88 (t, 3H, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.6, 111.9 (t, J = 23.7 Hz) [**7a**: 112.1], 80.3, 70.6, 44.7, 36.9, 34.8, 32.1, 30.6, 29.8, 29.8, 29.7, 29.5, 26.2, 22.8, 14.3. HRMS−ESI (m/z): $[M + H]^+$ calcd for $C_{16}H_{30}DO$ 240.2432, found 240.2430.

*Scheme 2, D-Labeled **7a** in eqs 3 and 4.* Mixed with **7a**, 199 mg, 84% yield. ^{1}H NMR (700 MHz, $CDCl_3$) δ: 4.78 (s, 1H), 4.71 (s, 1H), 3.50−3.43 (m, 1H), 3.43−3.35 (m, 1H), 2.46−2.42 (m, 1H), 2.41−2.35 (m, 1H), 2.34−2.27 (m, 1H), 2.27−2.22 (m, 1H), 1.81−1.73 (m, 0.4H) [**7a**: 1.81−1.73 (m, 0.2H)], 1.72−1.67 (m, 0.4H) [**7a**: 1.72−1.67 (m, 0.2H)], 1.52−1.47 (m, 1H), 1.42−1.38 (m, 1H), 1.35−1.20 (m, 14H), 0.88 (t, 3H, J = 7.0 Hz. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.7 [**7a**: 148.6], 112.1, 112.1, 80.3, 80.3, 70.6, 70.6 [**7a**: 70.6], 44.7, 36.9, 34.7 [**7a**: 34.8], 32.1, 30.2 (t, J = 19.6 Hz) [**7a**: 30.6], 29.8, 29.8, 29.7, 29.5, 26.2, 22.8, 14.3. HRMS−ESI (m/z): $[M + H]^+$ calcd for $C_{16}H_{30}DO$ 240.2432, found 240.2429.

Triflic Acid Catalyzed Isomerization of 7a to Endocyclic Olefins 7a′ and 7a″ in Scheme 3, Part A. Triflic acid (10 mol %) was added to a toluene solution of isolated **7a** and stirred at rt for the indicated reaction time. The mixture was then added a spatula of Na_2CO_3(s). After the solution was filtered through a short plug of silica gel and rinsed with 75 mL of 80% ether/hexane, the solvent was removed under vacuum. Purification via silica gel column chromatography (hexane/DCM, 3:1, 2:1, 1:1) yielded the endocyclic olefin products. The products obtained from the NHC catalyst and from the acid catalyzed isomerization are respectively less polar and more polar than the original exocyclic methylene, i.e., typical polarity trend: **7a″** > **7a** > **7a′**.

General Cycloisomerization Procedure for the One-pot Preparation of the Endocyclic Olefin Product in Scheme 3, Part B. The NHC−NiH-catalyzed reactions were performed by following the general cycloisomerization procedure except with the use of the indicated ligands, time, temperature, and catalyst loading. Product structures were assigned by NMR and by comparison with literature[20]

*Scheme 3, Part A, 3-Endocyclic Methylene Product **7a″**.* 79 mg, 67% yield. Obtained by acid-catalyzed isomerization, it is more polar than the below 4-endocyclic methylene product **7a′**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.57 (dt, 1H, J = 15.5, 7.0 Hz), 5.45 (d, 1H, J = 15.5 Hz), 3.90−3.86 (m, 2H), 2.03−1.81 (m, 5H), 1.70−1.63 (m, 1H), 1.35−1.26 (m, 17H), 0.88 (t, 3H, J = 6.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.4, 128.1, 82.2, 67.4, 37.7, 32.4, 32.1, 29.7, 29.6, 29.5, 29.5, 29.3, 26.7, 25.9, 22.8, 14.3. HRMS−ESI (m/z): $[M + Na]^+$ calcd for $C_{16}H_{30}ONa$ 261.2189, found 261.2189.

We found that the cycloisomerization cascade could provide two column separable 4-endocyclic methylene product **7a′** isomers by using SIPr.

*Scheme 3, Part B, **7a′**.* Major isomer, less polar, 98 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.56 (s, 1H), 4.0−3.95 (m, 1H), 3.47−3.37 (m, 2H), 2.44−2.34 (m, 2H), 2.12−2.05 (m, 1H), 1.98 (d, 1H, J = 16.1 Hz), 1.74 (s, 3H), 1.53−1.26 (m, 16H), 0.88 (t, 3H, J = 6.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.4, 124.7, 78.9, 70.0, 42.9, 37.2, 32.1, 31.4, 29.8, 29.8, 29.7, 29.5, 26.8, 26.2, 22.8, 14.3. HRMS m/z): $[M + H]^+$ calcd for $C_{16}H_{31}O$ 239.2369, found 239.2363. Minor isomer, more polar, 12 mg, 10% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.33 (s, 1H), 4.09−4.03 (m, 1H), 3.95−3.90 (m, 1H), 3.74−3.68 (m, 1H), 2.26−2.24 (m, 2H), 1.81−1.70 (m, 2H), 1.75 (s, 3H), 1.49−1.11 (m, 16H), 0.88 (t, 3H, J = 6.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.4, 129.4, 77.0, 72.3, 36.8, 32.7, 32.1, 29.8, 29.8, 29.7, 29.5, 28.2, 26.3, 25.8, 22.8, 14.3. HRMS−ESI (m/z): $[M + H]^+$ calcd for $C_{16}H_{31}O$ 239.2369, found 239.2371.

*Scheme 3, Part B, **6c′**.* 107 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05−8.03 (m, 1H), 7.47−7.43 (m, 1H), 7.32−7.28 (m, 1H), 7.26−7.21 (m, 1H), 5.41−5.39 (m, 1H), 3.08−3.00 (m, 1H), 2.93−2.86 (m, 1H), 2.64−2.60 (m, 1H), 2.10−1.93 (m, 4H), 1.77−1.71(m, 2H), 1.70 (s, 3H), 1.69−1.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.7, 143.3, 133.1, 132.1, 131.9, 128.8, 128.2, 126.7, 119.2, 44.0, 36.6, 30.7, 27.3, 25.4, 24.0, 22.6. HRMS−EI (m/z): $[M]^+$ calcd for $C_{16}H_{18}O$ 226.1358, found 226.1356.

Synthesis of 4-Oxepanone.[23] The ozonolysis followed a typical procedure. A solution of **7a** (36 mg, 0.15 mmol) in CH_2Cl_2 (6 mL) at −78 °C was sparged with ozone (O_3) until a blue color was obtained (∼20 min). After being stirred for 1 h at −78 °C, it was sparged with nitrogen until no trace of blue color remained (about 5 min). Triphenylphosphine (0.75 mmol) was then added, and the reaction was allowed to reach rt gradually by stirring overnight. Removal of solvent in vacuum followed by flash chromatography on silica gel (10% EtOAc/hexanes) afforded the desired product as colorless oil (78% yield, 28 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.21−4.16 (m, 1H), 3.66−3.61 (m, 1H), 3.59−3.52 (m, 1H), 2.73−2.55 (m, 4H), 1.95−1.80 (m, 2H), 1.57−1.27 (m, 16H), 0.88 (t, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 211.8, 76.9, 72.5, 52.2, 43.0, 36.8, 32.0, 29.7, 29.6, 29.4, 27.0, 25.8, 22.8, 14.3. HRMS−ESI (m/z): $[M + Na]^+$ calcd for $C_{15}H_{28}O_2Na$ 263.1982, found 263.1981.

General Procedure for the 1,*n*-Diene (P) Syntheses. Allylation was the last step in most of the 1,n-dienes syntheses. All the carbodienes were prepared according to the literature procedures. Most of the other 1,*n*-dienes (**P**), including **P6(a−i)** in Table 1 and **P7(a−s)**, **P8(a,b)** in Table 2 and Schemes 1−3 were prepared according to the literature procedures or in analogy except the following:[24,25]

Allylation General Procedure. The 1,*n*-dienes (**P**) were synthesized by adding NaH (1.5 equiv., 60% in mineral oil) to a solution of corresponding allylic/homoallylic alcohol, thiol, or amine (10 mmol) in DMF (20 mL) at 0 °C and stirred for 5 min. Two equivalents of allyl bromide (or the corresponding halides, e.g., 3-chloro-2-methyl-1-propene, 5-bromo-1-pentene, or the corresponding 2-D-labeled allyl bromide) was then added to the above mixture. After being stirred overnight at rt, the reaction mixture was quenched with 30 mL of ice−water, extracted with diethyl ether (3 × 50 mL), washed with brine, dried over Na_2SO_4, filtered, and concentrated. Purification via silica gel column chromatography (hexane/DCM 5:1, 3:1, 2:1) afforded the corresponding 1,*n*-oxadiene as a colorless oil for cycloisomerization.

*Table 2, Entry 1, **P7a**.* Allylation of the 1- tridecen-4-ol with allyl bromide by following the allylation general procedure gave **P7a** (2.1 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.97−5.78 (m, 2H), 5.29−5.03 (m, 4H), 4.03 (dd, 1H, J = 12.4, 5.6 Hz), 3.97 (dd, 1H, J = 12.6, 5.7 Hz), 3.36−3.33 (m, 1H), 2.26 (m, 2H), 1.47−1.26 (m, 16H), 0.88 (t, 3H, J = 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.62, 135.29, 116.86, 116.62, 78.73, 70,13, 38.51, 33.97, 32.05, 29.90, 29.77, 29.73, 29.47, 25.51, 22.83, 14.27. HRMS−ESI (m/z): $[M + Na]^+$ calcd for $C_{16}H_{30}ONa$ 261.2189, found 261.2184.

*Table 2, Entry 2, **P7b**.* Allylation of the 5-phenylpent-1-en-4-ol with allyl bromide by following the allylation general procedure gave **P7b** (1.8 g, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29−7.17 (m, 5H), 5.92−5.76 (m, 2H), 5.22−5.06 (m, 4H), 3.99−3.88 (m, 2H), 3.58 (m, 1H), 2.80 (dd, 1H, J = 30.6, 13.7 Hz), 2.78 (dd, 1H, J = 29.9, 13.7 Hz), 2.27−2.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.1, 135.2, 134.9, 129.6, 128.3, 126.2, 117.3, 116.7, 79.9, 70.5, 40.5, 38.3. HRMS−ESI (m/z): $[M + H]^+$ calcd for $C_{14}H_{19}O$ 203.1430, found 203.1430.

*Table 2, Entry 4, **P7d**.* Allylation of the 6-methyl-1-hepten-4-ol with allyl bromide by following the allylation general procedure gave **P7d** (1.5 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.07−5.70 (m, 2H), 5.29−5.03 (m, 4H), 4.07 (dd, 1H, J = 12.6, 5.8 Hz), 3.94 (dd, 1H, J = 5.8, 12.6 Hz), 3.46−3.40 (m, 1H), 2.28−2.25 (m, 2H), 1.82−1.72 (m, 1H), 1.50−1.43 (m, 1H), 1.26−1.20 (m, 1H), 0.90 (d, 3H, J = 4.6 Hz), 0.89 (d, 3H, J = 4.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.5, 135.1, 117.0, 116.6, 76.8, 70.0, 43.6, 38.8, 24.6, 23.4, 22.5. HRMS−ESI (m/z): $[M + Na]^+$ calcd for $C_{11}H_{20}ONa$ 191.1406, found 191.1403.

*Table 2, Entry 5, **P7e**.* Allylation of the 1-phenoxypent-4-en-2-ol with allyl bromide by following the allylation general procedure gave **P7e** (1.9 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35−7.31 (m, 2H), 7.02−6.96 (m, 3H), 6.18−5.84 (m, 2H), 5.55−5.02 (m, 4H), 4.44−4.32 (m, 2H), 4.26−4.11 (m, 2H), 4.07−3.80 (m, 1H), 2.55−2.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.9, 135.2, 134.3, 129.5, 120.9, 117.7, 117.1, 114.7, 76.9, 71.2, 69.7, 36.4. HRMS−ESI (m/z): $[M + Na]^+$ calcd for $C_{14}H_{18}O_2Na$ 241.1199, found 241.1199.

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*Table 2, Entry 8, **P7h**.* Allylation of the alcohol (1.1 g, 5 mmol) with allyl bromide by following the allylation general procedure gave **P7h** (1.1 g, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.01−5.73 (m, 2H), 5.28−4.99 (m, 4H), 4.04−3.96 (m, 2H), 3.19−3.13 (m, 1H), 2.44−2.38 (m, 1H), 1.43−1.35 (m, 2H), 1.34−1.16 (m, 14H), 1.02−0.99 (m, 3H), 0.88 (t, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.2, 135.7, 116.5, 114.5, 83.1, 71.2, 40.7, 32.1, 31.0, 30.0, 29.8, 29.8, 29.5, 26.1, 22.8, 15.1, 14.3. HRMS−ESI (m/z): $[M + Na]^+$ calcd for $C_{17}H_{32}ONa$ 275.2345, found 275.2345.

*Table 2, Entry 10, **P7j**.* Allylation of the *trans*-2-vinylcyclohexanol with 3-chloro-2-methyl-1-propene by following the allylation general procedure gave **P7j** (1.5 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.94−5.85 (m, 1H), 5.08−4.99 (m, 2H), 4.96 (s, 1H), 4.84 (s, 1H), 3.97 (d, 1H, J = 12.3 Hz), 3.82 (d, 1H, J = 12.3 Hz), 3.01−2.97 (m, 1H), 2.09−2.08 (m, 2H), 1.73 (s, 3H), 1.73−1.68 (m, 3H), 1.22−1.17 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.1, 141.9, 114.1, 112.0, 81.2, 72.9, 47.9, 31.3, 31.2, 25.2, 24.7, 19.8. HRMS−ESI (m/z): $[M + Na]^+$ calcd for $C_{12}H_{20}ONa$: 203.1406, found 203.1405.

*Table 2, Entry 11, **P7k**.* Allylation of the *trans*-2-vinylcyclopentanol with allyl bromide by following the allylation general procedure gave **P7k** (1.3 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.04−5.74 (m, 2H), 5.29−4.96 (m, 4H), 3.99 (d, 2H, J = 5.5 Hz), 3.66 (dd, 1H, J = 11.1, 5.5 Hz), 2.57−2.49 (m, 1H), 1.94−1.83 (m, 2H), 1.78−1.60 (m, 3H), 1.45−1.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.4, 135.5, 116.7, 114.1, 85.6, 70.5, 50.1, 31.7, 30.4, 22.5. HRMS−ESI (m/z): $[M + H]^+$ calcd for $C_{10}H_{17}O$ 153.1274, found 153.1273.

*Table 2, Entry 12, **P7l**.* Allylation of the *trans*-1-vinyl-2,3-dihydro-1*H*-inden-2-ol with allyl bromide by following the allylation general procedure gave **P7l** (1.7 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18−7.09 (m, 4H), 5.99−5.83 (m, 2H), 5.33−5.17 (m, 4H), 4.17−4.11 (m, 3H), 3.81−3.77 (m, 1H), 3.23 (dd, 1H, J = 15.6, 7.0 Hz), 2.91 (dd, 1H, J = 15.6, 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.8, 140.1, 139.0, 135.1, 127.3, 126.9, 124.8, 124.7, 117.2, 117.1, 85.8, 70.9, 56.0, 38.1. HRMS−EI (m/z): [M]+ calcd for C $_{14}H_{16}O$ 200.1196, found 200.1199.

*Table 2, Entry 15, **P8a**.* Alkylation of 1-octen-3-ol with 5-bromo-1-pentene by following the allylation general procedure gave **P8a** (1.5 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.87−5.62 (m, 2H), 5.17−5.10 (m, 2H), 5.04−4.94 (m, 2H), 3.60−3.47 (m, 2H), 3.29−3.23 (m, 1H), 2.15−2.09 (m, 2H), 1.69−1.62 (m, 2H), 1.59−1.56 (m, 1H), 1.47−1.37 (m, 2H), 1.35−1.28 (m, 5H), 0.88 (t, 3H, J = 6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.8, 138.6, 116.3, 114.7, 81.5, 67.9, 35.6, 31.9, 30.6, 29.3, 25.2, 22.8, 14.2. HRMS−EI (m/z): $[M + H]^+$ calcd for $C_{13}H_{25}O$ 197.1905, found 197.1898.

*Scheme 1, **P7s**.* Allylation of 1,6-heptadien-4-ol with allyl bromide by following the allylation general procedure gave **P7s** (1.3 g, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.96−5.78 (m, 3H), 5.30−5.25 (m, 1H), 5.16−5.05 (m, 5H), 4.02 (d, 2H, J = 5.6 Hz), 3.43 (quin, 1H, J = 5.9 Hz), 2.30−2.27 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.4, 134.9, 117.1, 116.7, 78.1, 70.2, 38.2. HRMS−EI (m/z): $[M + H]^+$ calcd for $C_{10}H_{17}O$ 153.1279, found 153.1275.

Procedure for the Preparation of 1,7-Siloxadiene.[26] *Table 2, Entry 13, **P7n**.* Allylchlorodimethylsilane (10.5 mmol) was added to a solution of 1-octen-3-ol (10 mmol), triethylamine (12 mmol), and 4-(dimethylamino)pyridine (0.6 mmol) in 50 mL of dry CH_2Cl_2 at rt. The reaction was stirred overnight and then quenched with 50 mL of water, the organic layer was removed, and the aqueous layer was extracted with ether (3 × 50 mL). The organic layers were combined, washed with brine, dried over Na_2SO_4, and concentrated. Purification via a NEt_3 buffered silica gel column chromatography (10% Et_2O/*n*-pentane) afforded the title 1,7-siloxadiene **P7n** (1.8 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.85−5.74 (m, 2H), 5.16−4.84 (m, 4H), 4.07 (dd, 1H, J = 12.5, 6.1 Hz), 1.63 (d, 2H, J = 18.1 Hz), 1.48−1.40 (m, 2H), 1.38−1.27 (m, 6H), 0.88 (t, 3H, J = 6.5 Hz), 0.12 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.7, 134.4, 113.9, 113.7, 74.3, 38.0, 31.9, 25.2, 25.2, 22.8, 14.2, −1.7, −1.8. HRMS−EI (m/z): $[M]^+$ calcd for $C_{13}H_{26}OSi$ 226.1747, found 226.1743.

Procedure for the Preparation of 1,7-Thiodienes.[27] *Table 2, Entry 14, **P7o**.* The allylation was performed by adding NaH (2.4 equiv) followed by allyl bromide (2.5 equiv) to a solution of ethyl thioglycolate (20 mmol) in THF (60 mL) at 0 °C, and the reaction was then stirred at rt overnight. After being quenched with water, the mixture was extracted with diethyl ether. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure and then purified over silica gel column chromatography with 10% EtOAc/*n*-hexane as the eluent. After a typical ester reduction with $LiAlH_4$ (1.2 equiv) in THF (50 mL) at 0 °C and stirring at rt for 5 h, the purified alcohol was protected with benzyl bromide (1.5 equiv) and NaH (2 equiv) in THF (50 mL) at 0 °C and stirred at rt for overnight. After a normal aqueous workup, the mixture was purified over silica gel column chromatography by using 10% EtOAc/*n*-hexane as the eluent and afforded the title 1,7-thiodiene **P7o** (2.6 g, 53% isolated yield over three steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37−7.25 (m, 5H), 5.88−5.75 (m, 2H), 5.11−5.05 (m, 4H), 4.53 (s, 2H), 3.60−3.57 (m, 1H), 3.52−3.48 (m, 1H), 3.24−3.14 (m, 2H), 2.91−2.85 (m, 1H), 2.55−2.48 (m, 1H), 2.36−2.29 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.2, 135.2, 134.7, 128.4, 127.6, 117.2, 117.0, 73.0, 72.7, 43.3, 36.2, 34.4. HRMS−ESI (m/z): $[M + Na]^+$ calcd for $C_{15}H_{20}OSNa$ 271.1127, found 271.1127.

*Table 2, Entry 14, **P7p**.* Diisopropyl azodicarboxylate (20 mmol, 2 equiv) was added to a solution of triphenylphosphine (20 mmol, 2 equiv) in THF (50 mL) at 0 °C. After 0.5 h, a solution of 1-tridecen-4-ol (10 mmol, 1 equiv) and thioacetic acid (20 mmol, 2 equiv) in THF (10 mL) was added, and the reaction mixture was stirred at rt overnight. After the volatiles were removed under vacuum, trituration of the residue in hexane, filtration, concentration of the filtrate, and chromatography of the residue afforded the thioester (6 mmol, 60% isolated yield) by using DCM/*n*-hexane (1:2) as the eluent. After a typical ester reduction with $LiAlH_4$ (12 mmol, 2 equiv) in THF (30 mL) from 0 °C to rt, the roughly purified 1-tridecen-4-thiol was treated with allyl bromide (9 mmol, 1.5 equiv) and NaH (12 mmol, 2 equiv) in DMF (15 mL) from 0 °C to rt for overnight. After aqueous workup as described in Allylation General Procedure, the mixture was purified over silica gel column chromatography with DCM/*n*-hexane (1:4) as the eluent and afforded the title 1,7-thiodiene **P7p** (0.9 g, 35% yield over three steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.89−5.76 (m, 2H), 5.12−5.05 (m, 4H), 3.15 (dd, 2H, J = 7.1, 0.9 Hz), 2.68−2.62 (m, 1H), 2.38−2.30 (m, 2H), 1.61−1.26 (m, 16H), 0.88 (t, 3H, J = 6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.9, 135.1, 116.8, 116.7, 43.9, 39.1, 34.1, 33.9, 32.0, 29.7, 29.7, 29.4, 26.7, 22.8, 14.2. HRMS−EI (m/z): [M]+ calcd for $C_{16}H_{30}S$: 254.2063, found 254.2062.

Procedure for the Preparation of 1,*n*-Azadienes.[28] *Table 1, Entry 7, **P6g**.* By following the standard Buchwald amination procedure, 3-aminooct-1-ene (5 mmol, 1 equiv), 2,6-dimethylbromobenzene (5 mmol, 1 equiv), (±)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (0.25 mmol, 0.05 equiv), and sodium *tert*-butoxide (15 mmol, 3 equiv) were mixed in a sealed tube with 10 mL of toluene, and the mixture was stirred at 90 °C for 24 h. The crude reaction mixture was filtered through Celite, washed with CH_2Cl_2, concentrated, and purified by column chromatography (30% DCM/*n*-hexane) the product obtained was then followed by typical allylation conditions as described in the Allylation General Procedure and afforded the branched 1,6-azadiene **P6g** (0.9 g, 70% isolated yield over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.99−6.92 (m, 3H), 5.80−5.70 (m, 1H), 5.68−5.59 (m, 1H), 5.09−5.04 (m, 2H), 4.94−4.81 (m, 2H), 3.71 (dd, 1H, J = 14.3, 6.1 Hz), 3.59 (dd, 1H, J = 14.3, 7.4 Hz), 3.55−3.50 (m, 1H), 2.28 (s, 3H), 2.26 (s, 3H), 1.39−1.11 (m, 8H), 0.82 (t, 3H, J = 6.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.1, 141.6, 139.7, 139.0, 137.7, 128.7, 128.3, 125.5, 115.9, 115.1, 66.5, 55.0, 33.1, 32.0, 26.2, 22.8, 20.1, 14.2. HRMS−ESI (m/z): $[M + H]^+$ calcd for $C_{19}H_{30}N$: 272.2373, found 272.2378.

Scheme 2, Procedures for the Preparation of D-Labeled 1,7-Oxadiene. *1,7-Oxadienes Labeled with a D at the Alkene Terminal Position in eqs 1 and 2 (Scheme 2).* were prepared from the corresponding enynes (4-(prop-2-yn − 1-yloxy)tridec-1-ene for eq 1, Scheme 2, 4-(allyloxy)tridec-1-yne for eq 2, Scheme 2) by a typical deprotonation with *n*-BuLi, followed by quenching with D_2O, and finally a partial hydrogenation (Lindlar catalyst).[29] *n*-BuLi (1.6 M in hexane, 1.2 equiv) was added dropwise to a solution of the corresponding 1,7-oxaenyne (6 mmol) in dry THF (30 mL) at −78

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°C. The reaction mixture was allowed to warm slowly and to reach 0 °C, followed by D_2O quenching (1 mL). After being stirred overnight at rt, the reaction mixture was diluted with 20 mL of Et_2O, dried over Na_2SO_4, filtered through a short pad of silica gel, and washed thoroughly with Et_2O. The filtrate was concentrated under reduced pressure to afford the corresponding deuterated 1,7-oxaenyne and used directly in the next step without further purification. The deuterated 1,7-oxaenyne above was treated with quinoline (6 mmol) and Lindlar catalyst (palladium 5 wt % on calcium carbonate poisoned with lead, 2 mol % Pd, 255 mg) in 30 mL of ethyl acetate. The reaction flask was then degassed and backfilled with H_2. A H_2 balloon was then attached, and the reaction mixture was allowed to stirred at rt for 15 min. The reaction progress was closely monitored by NMR to avoid over-reduction. The reaction was stopped by remove the H_2 balloon and vacuum for 5 min. The reaction mixture was filtered through a short pad of silica gel, washed with Et_2O, and the filtrate was concentrated under reduced pressure. Purification via silica gel column chromatography (20% DCM/hexane) afforded the corresponding deuterated 1,7-oxadiene in 58% (0.83 g) and 50% (0.72 g) isolated yield over two steps in eqs 1 and 2 (Scheme 2), respectively.

1,7-Oxadienes Labeled with a D at the Alkene Terminal Position in eq 1 (Scheme 2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.95−5.78 (m, 2H), 5.14−5.03 (m, 3H), 4.06−3.94 (m, 2H), 3.38−3.32 (m, 1H), 2.32−2.21 (m, 2H), 1.49−1.46 (m, 2H), 1.43−1.26 (m, 14H), 0.88 (t, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.4, 135.0, 116.6, 115.8 (t, J = 23.8 Hz), 78.5, 69.9, 38.4, 33.9, 32.0, 29.8, 29.7, 29.6, 29.4, 25.4, 22.8, 14.1. HRMS−ESI (m/z): [M + Na]$^+$ calcd for $C_{16}H_{29}DONa$ 262.2252, found 262.2256.

1,7-Oxadienes Labeled with a D at the Alkene Terminal Position in eq 2 (Scheme 2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.97−5.81 (m, 2H), 5.29−5.01 (m, 3H), 4.05−3.94 (m, 2H), 3.38−3.32 (m, 1H), 2.30−2.23 (m, 2H), 1.49−1.26 (m, 16H), 0.88 (t, 3H, J = 6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.5, 134.9, 116.3 (t, J = 23.5 Hz), 116.1, 78.6, 70.0, 38.4, 33.9, 32.0, 29.8, 29.7, 29.6, 29.4, 25.4, 22.7, 14.1. HRMS−ESI (m/z): [M + Na]$^+$ calcd for $C_{16}H_{29}DONa$ 262.2252, found 262.2254.

Procedure for the Enyne 4-(Prop-2-yn − 1-yloxy)tridec-1-ene. NaH (1.5 equiv, 60% in mineral oil) was added to a solution of 1-tridecen-4-ol (15 mmol) in DMF (30 mL) at 0 °C and stirred for 15 min. Propargyl chloride (2 equiv) was then added to the above mixture. After being stirred overnight at rt, the mixture was quenched with 30 mL of ice−water, extracted with diethyl ether (3 × 50 mL), washed with brine, dried over Na_2SO_4, filtered, and concentrated. Purification via silica gel column chromatography (20% DCM/Hexane) afforded the 1,7-oxaenyne (1.8 g, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.89−5.78 (m, 1H), 5.11−5.05 (m, 2H), 4.22 (s, 2H), 3.56−3.51 (m, 1H), 2.39 (t, 1H, J = 2.3 Hz), 2.29 (t, 2H, J = 6.3 Hz), 1.50−1.46 (m, 2H), 1.44−1.26 (m, 14H), 0.88 (t, 3H, J = 6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.9, 117.2, 80.6, 78.4, 73.8, 56.3, 38.1, 33.7, 32.1, 29.9, 29.7, 29.7, 29.5, 25.3, 22.8, 14.3. HRMS−ESI (m/z): [M + Na]$^+$ calcd for $C_{16}H_{28}ONa$ 259.2032, found 259.2035.

Procedure for the Enyne 4-(Allyloxy)tridec-1-yne. Allylation of 1-tridecyn-4-ol (9 mmol) with allyl bromide by following the Allylation General Procedure afforded the title 1,7-oxaenyne (1.7 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.97−5.87 (m, 1H), 5.31−5.15 (m, 2H), 4.13−4.08 (m, 1H), 4.02−3.96 (m, 1H), 3.45−3.43 (m, 1H), 2.46−2.33 (m, 2H), 1.99 (t, 1H, J = 2.7 Hz), 1.63−1.59 (m, 2H), 1.42−1.27 (m, 14H), 0.88 (t, 3H, J = 6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.3, 117.0, 81.5, 77.3, 70.6, 69.9, 34.1, 32.0, 29.8, 29.7, 29.7, 29.5, 25.4, 24.0, 22.8, 14.3. HRMS−ESI (m/z): [M + Na]$^+$ calcd for $C_{16}H_{28}ONa$ 259.2032, found 259.2037.

1,7-Oxadienes Labeled with a D at the Alkene Internal Position in eq 3 (Scheme 2). was prepared by allylation of 1-tridecen-4-ol with 2-D-labeled allyl bromide[30] following the Allylation General Procedure (0.8 g, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.89−5.77 (m, 1H), 5.25−5.02 (m, 4H), 4.04−3.94 (m, 2H), 3.37−3.32 (m, 1H), 2.32−2.21 (m, 2H), 1.49−1.39 (m, 2H), 1.39−1.23 (m, 14H), 0.88 (t, 3H, J = 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.3 (t, J = 23.6 Hz), 135.2, 116.8, 116.4, 78.7, 70.0, 38.5, 34.0, 32.0, 29.9, 29.8, 29.7, 29.5, 25.5, 22.8, 14.2. HRMS−ESI (m/z): [M + Na]$^+$ calcd for $C_{16}H_{29}DONa$ 262.2252, found 262.2254.

1,7-Oxadienes Labeled with a D at the Alkene Internal Position in eq 4 (Scheme 2). was prepared by allylation of 1-tridecen-2-deuterio-4-ol (3.2 mmol) with allyl bromide following the Allylation General Procedure (0.65 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.97−5.87 (m, 1H), 5.28−5.04 (m, 4H), 4.05−3.94 (m, 2H), 3.38−3.32 (m, 1H), 2.31−2.22 (m, 2H), 1.49−1.39 (m, 2H), 1.39−1.26 (m, 14 H), 0.88 (t, 3H, J = 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.6, 134.8 (t, J = 23.3 Hz), 116.6, 116.1, 78.6, 70.0, 38.4, 33.9, 32.0, 29.8, 29.7, 29.6, 29.4, 25.4, 22.7, 14.1. HRMS−ESI (m/z): [M + Na]$^+$ calcd for $C_{16}H_{29}DONa$ 262.2252, found 262.2256.

Procedure for the D-Labeled Alcohol, 1-Tridecen-2-deuterio-4-ol.[25c] Decyl aldehyde (8 mmol), the 2-D-labeled allyl bromide above (~0.3 M in Et_2O, 35 mL), tin powder (10 mmol) in HCl (60 mL, 0.6 mol L^{-1}), and 15 mL of THF were stirred at 35 °C for overnight and then extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Purification via silica gel column chromatography (10% EA/Hexane) afforded the 2-D-labeled 1-tridecen-4-ol (0.64 g, 40% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.12 (s, 2H), 3.61−3.69 (m, 1H), 2.32−2.28 (m, 1H), 2.16−2.11 (m, 1H), 1.49−1.45 (m, 2H), 1.43−1.26 (m, 14H), 0.88 (t, 3H, J = 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.7 (t, J = 23.2 Hz), 117.7, 70.8, 41.9, 36.9, 32.0, 29.8, 29.7, 29.7, 29.4, 25.8, 22.7, 14.2. HRMS−ESI (m/z): [M + Na]$^+$ calcd for $C_{13}H_{25}DONa$ 222.1939, found 222.1943.

Additional Experiments with 1,*n*-Azadienes (Employed in ref 15). Most of the cycloisomerization products and precursors are literature compounds except the following:[31,32]

6-*Exo*-*Trig* Product from *N*,*N*-Diallyl-2,6-diisopropylaniline. 131 mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18−7.14 (m, 1H), 7.10−7.08 (m, 2H), 4.70 (s, 1H), 4.66 (s, 1H), 3.54 (s, 2H), 3.43 (hept, 2H, J = 6.9 Hz), 3.14 (t, 2H, J = 5.2 Hz), 2.29 (t, 2H, J = 6.2 Hz), 1,77−1.71 (m, 2H), 1.19 (d, 6H, J = 6.9 Hz), 1.19 (d, 6H, J = 6.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4, 146.5, 145.7, 126.5, 124.0, 107.0, 58.6, 51.8, 33.2, 28.4, 28.2, 24.5, 24.4. HRMS−ESI (m/z): [M + H]$^+$ calcd for $C_{18}H_{28}N$ 258.2216, found 258.2212.

6-*Exo*-*Trig* Product from *N*-Allyl-*N*-homoallyltosylamine. 42 mg, 16% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, 2H, J = 8.0 Hz), 7.31 (d, 2H, J = 7.8 Hz), 4.71 (s, 1H), 4.67 (s, 1H), 3.51−3.49 (m, 2H), 2.60−2.53 (m, 1H), 2.45−2.40 (m, 1H), 2.42 (s, 3H), 2.39−2.31 (m, 2H), 2.24−2.18 (m, 1H), 1.06 (d, 3H, J = 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.1, 143.6, 133.4, 129.7, 127.7, 107.9, 53.8, 48.0, 36.4, 34.0, 21.6, 15.6. HRMS−ESI (m/z): [M + Na]$^+$ calcd for $C_{14}H_{19}NO_2SNa$ 288.1029, found 288.1025.

7$^\gamma$-*Exo*-*Trig* and 6$^\gamma$-*Exo*-*Trig* Products from *N*-Allyl-*N*-homoallyltosylamine. Inseparable mixture, yield was determined by NMR ratio. **6$^\gamma$-*exo*-*trig*** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, 2H, J = 8.2 Hz), 7.33 (d, 2H, J = 7.6 Hz), 4.96 (s, 1H), 4.81 (s, 1H), 4.07 (d, 1H, J = 12.1 Hz), 3.70−3.67 (m, 1H), 2.96 (d, 1H, J = 12.1 Hz), 2.56−2.49 (m, 1H), 2.44 (s, 3H), 1.99−1.97 (m, 1H), 1.84−1.73 (m, 1H), 1.43−1.30 (m, 1H), 1.04 (d, 3H, J = 6.6 Hz). **7$^\gamma$-*exo*-*trig*** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, 2H, J = 8.2 Hz), 7.33 (d, 2H, J = 7.7 Hz), 4.78 (s, 1H), 4.73 (s, 1H), 3.28−3.24 (m, 4H), 2.44−2.40 (m, 2H), 2.42 (s, 3H), 2.30−2.27 (m, 2H), 1.82−1.74 (m, 2H). HRMS−ESI (m/z): [M + Na]$^+$ calcd for $C_{14}H_{19}NO_2SNa$ 288.1029, found 288.1024.

***N*,*N*-Diallyl-2,6-diisopropylaniline.** The compound was prepared in one step from 2,6-diisopropylaniline (NH_2-DIPP, 10 mmol), NaH (23 mmol, 2.3 equiv), and allyl bromide (23 mmol, 2.3 equiv) by following the Allylation General Procedure (0.8 g, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17−7.14 (m, 1H), 7.08−7.06 (m, 2H), 5.92−5.82 (m, 2H), 5.09−5.00 (m, 4H), 3.64 (d, 4H, J = 6.4 Hz), 3.44 (sept, 2H, J = 6.9 Hz), 1.19 (d, 12H, J = 6.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.2, 145.7, 137.3, 126.6, 124.1, 116.2, 58.1, 28.2, 24.6. HRMS−ESI (m/z): [M + H]$^+$ calcd for $C_{18}H_{28}N$ 258.2216, found 258.2218.

***N*-Allyl-*N*-homoallyl-2,4,6-trimethylaniline.** The compound was prepared in two steps by allylation of 2,4,6-trimethylaniline (10

mmol) with allyl bromide (12 mmol) following the Allylation General Procedure and followed by homoallylation of the obtained *N*-allyl-2,4,6-trimethylaniline with 4-bromopentene (15 mmol) refluxing in MeCN in the presence of K_2CO_3 (20 mmol) in 50% yield over two steps (1.1 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.80 (s, 2H), 5.92−5.82 (m, 1H), 5.79−5.68 (m, 1H), 5.15−5.10 (m, 1H), 5.02−4.92 (m, 3H), 3.60 (d, 2H, J = 6.5 Hz), 3.06 (t, 2H, J = 7.7 Hz), 2.25 (s, 6H), 2.22 (s, 3H), 2.17−2.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.6, 137.6, 137.5, 137.1, 134.5, 129.6, 115.8, 115.6, 57.7, 52.7, 34.2, 20.9, 19.7. HRMS−ESI (m/z): $[M + H]^+$ calcd for $C_{16}H_{24}N$ 230.1903, found 230.1908.

■ ASSOCIATED CONTENT

Supporting Information

Additional experiments as described in ref 15 and NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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