performed in 3-mL Teflon-capped glass vials.

Molecular mechanics calculations were performed using the SYBYL software package (version 5.32, Tripos Associates, Inc. a subsidiary of Evans & Sutherland) operating on a Digital Equipment Corp. (DEC) microVAX workstation and an Evans & Sutherland PS-330 graphics terminal.

Synthesis of Standards. Ecgonine-2-d_1 methyl ester (**5d**) was prepared as previously described.[22] The 2-deuterioecgonine methyl ester (**5d**) was isolated following the procedure of Casale[11] to give 24.5 mg of the crystalline hydrochloride salt (41% yield). The 2-deuterio analog of cocaine (**1d**) was synthesized from 2-deuterioecgonine methyl ester (**5d**) following the benzoylation procedure of Sinnema.[5]

The 2-deuterio analogs of pseudoecgonine methyl ester (**7d**) and pseudococaine (**2d**) were synthesized following the procedures of Carroll[6] and Sinnema,[5] respectively. Unlabeled ecgonine methyl ester (**5**), pseudoecgonine methyl ester (**7**), cocaine (**1**), and pseudococaine (**2**) were obtained from this laboratory and were part of an authenticated reference collection of the S.B.I. Drug Laboratory.

Deuterium Incorporation and Epimerization. Into three separate 3-mL vials was placed 25 mg of unlabeled ecgonine methyl ester (**5**) (0.126 umol), 1.00 mL of MeOD (40.2 mmol), and 3.0 mg of NaOMe (0.0555 mmol), and the vials were sealed under nitrogen with septa caps. One vial was kept at 7 °C (vial A), one at 25 °C (vial B), and one at 65 °C (vial C). Into the fourth and fifth vials were placed 25 mg of pseudoecgonine methyl ester (**7**) (0.126 mmol), 1.00 mL of MeOD (40.2 mmol), and 3.0 mg of NaOMe (0.0555 mmol), and the vials were sealed under N_2 and kept at 25 °C (vial D) and 65 °C (vial E). Aliquots of 50 μL were removed from vials A–E in intervals as outlined in Tables I–IV. Each aliquot was quenched with 10 μL of D_2O (500 μmol) and extracted once with $CHCl_3$ (1 mL); the extracts were washed with 5% $NaHCO_3$ (0.5 mL), dried over Na_2SO_4, filtered, and subjected to both GC and GC/MS analysis. Reactions involving the methyl 3β-phenyltropane-2-carboxylates were performed in an identical manner at 65 °C (Tables V and VI).

Molecular Modeling. Ecgonine methyl ester (**5anti**) with the *N*-methyl group anti to the three-carbon bridge (i.e., equatorial to the piperidine ring) was constructed using the TRIPOS fragment library. The structure was subjected to MAXIMIN2 followed by MNDO with full geometry optimization. The resulting geometry was used as the starting point for constructing ecgonine methyl ester (**5**) with the *N*-methyl group syn to the three-carbon bridge, as well as anti and syn pseudoecgonine methyl ester. Each structure was then optimized using MNDO, AM1, and MAXIMIN2. The MNDO-optimized structures and the AM1-optimized structures were each optimized using MM2. The MNDO-optimized structures were subjected to conformational search (defining as rotatable the bonds RB1, from C-2 to the carbomethoxy group; RB2, from the carbonyl to the methoxy group; and RB3, from C-3 to the hydroxy group) within a 1-kcal window. Each of the resulting conformers was then subjected to MAXIMIN2, MNDO, and MM2. The rotatable bonds RB1, RB2, and RB3 were not optimized in these calculations. The energies obtained were used in a program called BOLTS, developed in our laboratories (J.P.B.), which allows the analysis of conformational populations based on energy differences according to the Boltzman equation (Table IX). The MNDO-optimized structures were also used to obtain the corresponding C-2 anions; each of these was optimized by MNDO as well. *anti*-Ecgonine methyl ester (**5anti**) was also constructed using the X-ray coordinates for cocaine (**1**), removing the benzoyl group and adding the hydrogen atoms; the MNDO-optimized form of this structure was then modified to *syn*-ecgonine methyl ester (**5syn**), *anti*-pseudoecgonine methyl ester (**7anti**), and *syn*-pseudoecgonine methyl ester (**7syn**). Each of these structures was also optimized using MNDO. The heats of formation (or the energies, in the case of MAXIMIN2) are shown in Table VII. The equilibrium concentrations of ecgonine methyl ester (**5**) and pseudoecgonine methyl ester (**7**) at 65 °C, predicted by the energies obtained from the optimizations, were calcualted using BOLTS and are shown in Table VIII.

(22) Casale, J. F.; Lewin, A. H.; Raney, H. T.; Cooper, D. A. *J. Label. Cmpds Radiopharm.* **1991**, *19*, 327–335.

Acknowledgment. We wish to thank H. T. Raney of the S.B.I. Drug Laboratory for recording the mass spectra presented in this paper and John Gorst (U.G.A.) for his thoughtful discussion. This work was supported in part by Grant 170-188-E6-D009 from the U.S. Department of Justice to J.F.C. and by Grant DA05477 from the National Institute on Drug Abuse to F.I.C.

Inter- and Intramolecular [4 + 2] Cycloadditions of Nitroalkenes with Olefins. 2-Nitrostyrenes

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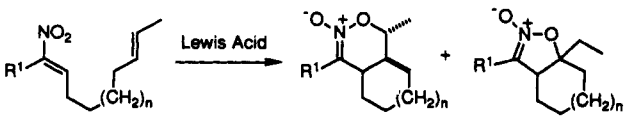
Aromatic nitroalkenes **9–12** underwent Lewis acid catalyzed cycloadditions with various cyclic alkenes to afford high yields of nitronates **25–30** with exclusive anti selectivity. Hammett studies helped to further delineate the role of the Lewis acid. Reaction of nitroalkenes **8** and **10** with various cyclic dienes in the presence of a Lewis acid demonstrated the ability of nitroalkenes to behave as dienes in cycloadditions. The major products were the syn diastereomers which arise from an endo-folded transition structure. Finally, intramolecular cycloaddition of **36–39** allowed a correlation between the stereochemical course of the reaction and positions of sp^2 centers in the tether to be addressed.

Introduction

Within the realm of ring-forming reactions, cycloadditions have secured an immutable and well-deserved stature in the minds and hands of chemists. The introduction of heterodienes[1] has extended the synthetic versatility of cycloaddition reactions by allowing rapid access to various heterocycles. Within these laboratories, we have extensively examined the use of nitroalkenes as dienes in [4 + 2] cycloadditions.

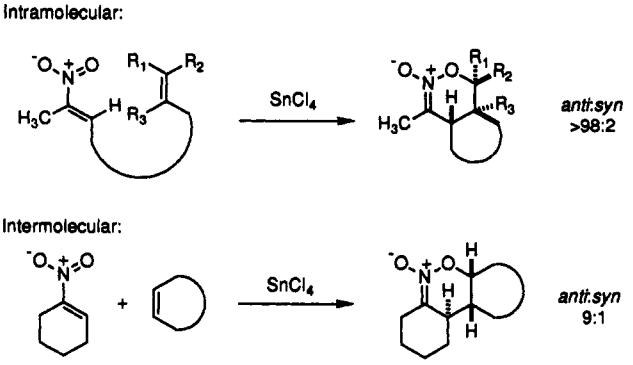
Scheme I



(1) Weinreb, S. M.; Boger, D. B. *Hetero Diels–Alder Methodology in Organic Synthesis*; Academic Press: Orlando, 1987.

0022-3263/92/1957-4912$03.00/0

Scheme II



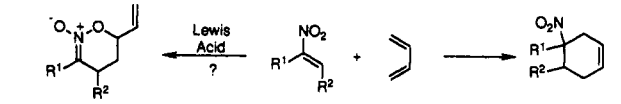
Nitroalkenes have been used as Michael acceptors with a wide range of nucleophiles including enamines,[2] silyl enol ethers,[3] and silyl ketene acetals,[4] as well as 2π components in [2 + 2] cycloadditions.[5] Seebach has shown that enamines react with nitroalkenes to afford cyclobutanes, the product of a formal [2 + 2] cycloaddition. The fact that both *E* and *Z* enamines afford the same product suggests both the intermediacy of a common zwitterionic species and the reversibility of the initial C–C bond-forming event.

In contrast, work in our laboratories has established that the Lewis acid catalyzed cyclization of nitroalkenes with dienophiles in a [4 + 2] fashion occurs with *preservation* of dienophile geometry (Scheme I).[6] Isolation of a five-membered ring nitronate indicates that, although not synchronous, the reaction must maintain a high degree of pericyclic character in order to preserve dienophile geometry.

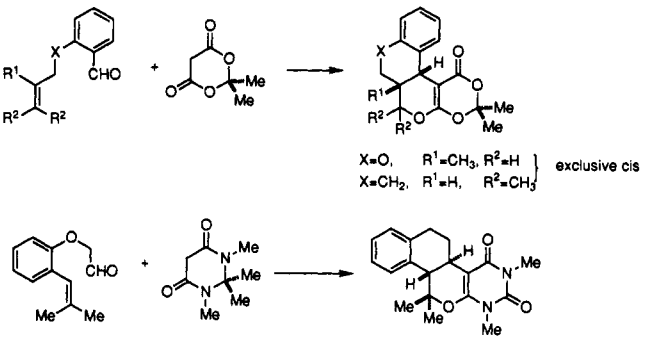
Previous work in these laboratories has shown the utility of the intramolecular [4 + 2] cycloaddition with regard to stereoselectivity, stereospecificity, and substitution pattern.[7] The major nitronate product formed in these cycloadditions predictably possesses anti ring fusions that arise via an exo-folding of the side chain in the transition structure in which nonbonded interactions are minimized (Scheme II). This reaction was further extended to the intermolecular variant using aliphatic nitroalkenes and cyclic dienophiles.[8] Consistent with the above case, the major product was always the anti-fused nitronate; however, the magnitude of the anti–syn selectivity was lower for the intermolecular variant (90:10) as opposed to the intramolecular case (>98:2).

A substitution pattern not yet examined, and one which would allow further exploration of the many facets of this reaction, would be nitrostyrenes. On the basis of frontier molecular orbital arguments, the exo vs endo selectivity of the intermolecular [4 + 2] cycloaddition should be increased by replacing an aliphatic substituent on the nitroalkene with an aromatic one. Another reaction parameter that warranted investigation concerned the influence of the Lewis acid on the reaction rate. The use of para-substituted nitrostyrenes in a Hammett study would allow

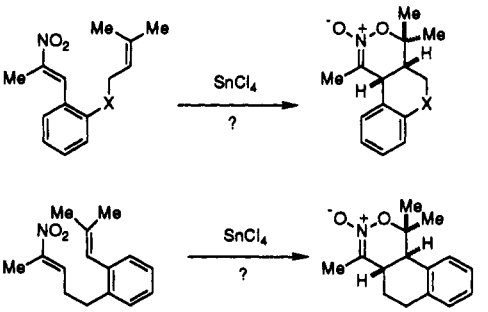
Scheme III



Scheme IV



Scheme V



investigation of electronic effects in these Lewis acid catalyzed cycloadditions.

An additional influence the role of the Lewis acid plays in this cycloaddition involves the periselectivity with dienes. Nitroalkenes are known to react thermally with dienes to afford the [4 + 2] cycloadduct in which the nitroalkene behaves as the dienophile.[9] Periselectivity has never been examined with a diene in the presence of a Lewis acid (Scheme III).

Finally, the effect of sp^2 centers in the connecting tether on the stereochemical course of the intramolecular [4 + 2] cycloaddition was planned. Tietze[10] has shown that the intramolecular cycloaddition of benzylidenepyrazolones proceeds with syn-selectivity when the diene is conjugated with the double bond in the connecting tether (in this case, from a benzene ring). Anti selectivity is observed if the double bond is in a nonconjugated position (Scheme IV). We were intrigued as to whether our systems would behave analogously given the previously noted propensity for formation of anti cycloadducts (Scheme V).

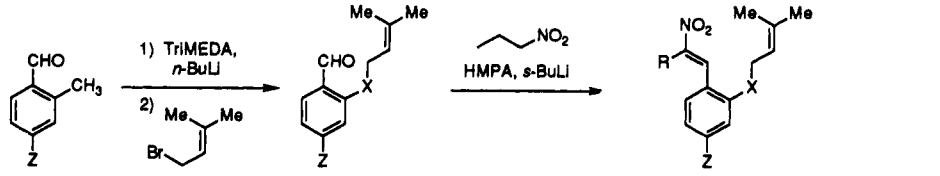
Results

A. Preparation of Nitroalkenes. Nitroalkenes can be readily prepared by a modified Henry reaction[11] between the appropriate aldehyde and nitroalkane. The resulting nitro alcohols can be acetylated and dehydroacetylated in a one- or two-pot procedure to give nitroalkenes.

1. Synthesis of Nitroalkenes for Intermolecular Reactions. Nitroalkenes 7–12 were prepared by con-

(2) Seebach, D.; Beck, A. K.; Golifiski, J.; Hay, J. N.; Laube, T. *Helv. Chim. Acta* **1985**, *68*, 162.
(3) (a) Miyashita, M.; Yanami, T.; Kumazawa, T.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1984**, *106*, 2149. (b) Seebach, D.; Brook, M. A. *Helv. Chim. Acta* **1985**, *68*, 319.
(4) Miyashita, M.; Kumazawa, T.; Yoshikoshi, A. *Chem. Lett.* **1980**, 1043.
(5) Corey, E. J.; Estreicher, H. *Tetrahedron Lett.* **1981**, 603.
(6) (a) Dappen, M. S., Ph.D. Thesis, University of Illinois, Urbana, 1985. (b) Denmark, S. E.; Dappen, M. S.; Cramer, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 1306.
(7) Denmark, S. E.; Moon, Y.-C.; Cramer, C. J.; Dappen, M. S.; Senanayake, C. B. W. *Tetrahedron* **1990**, *46*, 7373.
(8) Denmark, S. E.; Cramer, C. J.; Sternberg, J. A. *Helv. Chim. Acta* **1986**, *69*, 1971.
(9) (a) Parham, W. E.; Hunter, W. T.; Hanson, R. *J. Am. Chem. Soc.* **1951**, *73*, 5068. (b) Weinstock, J.; Schwartz, N.; Kormendy, M. F. *J. Org. Chem.* **1961**, *26*, 5247.
(10) Tietze, L. F.; Brumby, T.; Pretor, M.; Remberg, G. *J. Org. Chem.* **1988**, *53*, 810.
(11) Wollenberg, R. H.; Miller, S. J. *Tetrahedron Lett.* **1978**, 3219.

Scheme VI

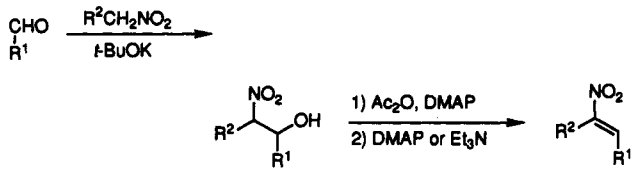


13, Z=H
16, Z=OCH_3

14, 74% (X=CH_2, Z=H)
17, 54% (X=CH_2, Z=OCH_3)
19, X=O, Z=H

15, 34% (R=Et, X=CH_2, Z=H)
18, 20% (23% 17) (R=Et, X=CH_2, Z=OCH_3)
20, X=O 84% (R=Me, X=O, Z=H)

Table I. Preparation of Nitroalkenes



R^1	R^2	nitro alcohol	yield, %	nitro-alkene	yield, %
cyclohexyl	CH_3	1	94	7	84
C_6H_5	H	2	89	8	84
C_6H_5	CH_3	3	89	9	88
4-$CH_3OC_6H_4$	CH_3	4	82	10	88
4-$CF_3C_6H_4$	CH_3	5	95	11	82
4-$NO_2C_6H_4$	CH_3	6	78	12	77

densing the appropriate aldehydes and either nitromethane or nitroethane with a catalytic amount of potassium *tert*-butoxide. As expected, an electron-withdrawing group in the para position facilitated nitro alcohol formation (room temperature, 1 h), whereas a donating group retarded it (incomplete after 2 days). The nitro alcohols could then be dehydrated by acetylation with acetic anhydride/4-(dimethylamino)pyridine (DMAP) followed by elimination with either triethylamine or DMAP.

2. Synthesis of Nitroalkenes for Intramolecular Reactions. Initial attempts to prepare 14 and 17 focused on alkylation of the oxazoline derived from benzaldehyde with prenyl bromide according to the method of Meyers.[12] This route was largely unsuccessful; however, after lengthy experimentation, compounds 13 and 16 were successfully alkylated following the method of Commins.[13] This method has the advantage that the aldehyde can remain as such during the reaction, eliminating subsequent manipulations of the oxazolines. Thus, alkylation of *o*-tolualdehyde with the allylic bromide afforded 14 in 74% yield. Similarly, reaction of 16 produced 54% of aldehyde 17.

For aldehydes 14 and 17, condensation with nitroethane was only marginally successful. The Henry reaction is known to give variable results, in part due to its ease of reversibility. A solution to this problem is to "trap" the nitro alcohol such that the retrograde process is not a viable option. Toward this end, Seebach has reported two methods.[14] The first involves the use of silyl nitronates and a catalytic amount of fluoride. The product is trapped as the siloxy nitroalkane. The preparation of the reagent was straightforward as reported by Seebach, but reaction with 14 led to only a low recovery of starting material. The second method involves the use of a dianion "trap". The immediate product of alkylation still possesses anionic character on the α-carbon and is therefore less prone to reversion. In fact, treatment of 1-nitropropane in THF/HMPA (5:1) at −90 °C with 2 equiv of *s*-BuLi resulted in a lemon-yellow solution that, when treated with 14 and quenched with acetic anhydride, afforded 34% of nitroalkene 15 directly. Aldehyde 17 was not as amenable to these conditions, providing nitroalkene 18 in only 20% yield. The final conjugated substrate 20 was prepared from the known aldehyde[10] by the standard Henry reaction, followed by acetylation and elimination to afford nitroalkene 20 in 84% overall yield.

Scheme VII

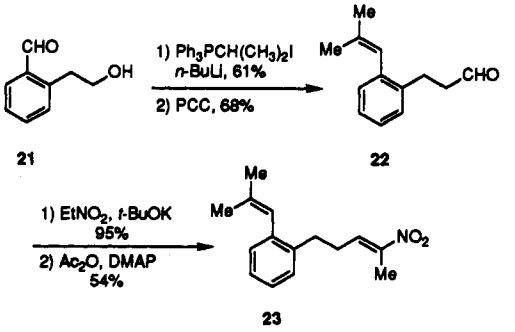
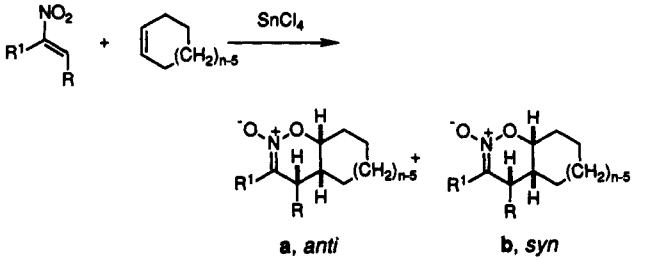


Table II. Reaction of Nitroalkenes with Cycloalkenes



R	nitro-alkene	n	nitronate	time, h	anti:syn	yield, %
cyclohexyl	7	5	24		90:10	92
C_6H_5	9	5	25	0.8	100:0	93
4-$CH_3OC_6H_4$	10	5	26	0.5	100:0	96
4-$CF_3C_6H_4$	11	5	27		100:0	85[a]
4-$NO_2C_6H_4$	12	5	28	7	100:0	38[b]
4-$CH_3OC_6H_4$	10	6	29	3	100:0	87
4-$CH_3OC_6H_4$	10	7	30	0.5	100:0	99

[a] Required warming to −30 °C for complete reaction. [b] Recovered 38% of 12.

The synthesis of nonconjugated substrate 23 began with hydroxy aldehyde 21 (Scheme VII). Treatment with the anion of isopropyltriphenylphosphonium iodide afforded hydroxy alkene 21a (61%), which was subsequently oxidized with prydinium chlorochromate to afford aldehyde 22 in 68% yield. Standard protocol for conversion to nitroalkene 23 proceeded in 51% overall yield.

B. Intermolecular Cycloadditions. 1. Cyclic Dienophiles. For comparison to the aromatic variants, aliphatic nitroalkene 7 was allowed to react with cyclopentene in the presence of $SnCl_4$ to afford a 9:1 mixture of nitronates 24a and b, arising from exo and endo ap-

(12) Meyers, A. I.; Knaus, G.; Kamata, K. *J. Am. Chem. Soc.* **1974**, *95*, 268.
(13) Comins, D. L.; Brown, J. D. *J. Org. Chem.* **1984**, *49*, 1078.
(14) (a) Colvin, E. W.; Beck, A. K.; Seebach, D. *Helv. Chim. Acta* **1981**, *64*, 2264. (b) Seebach, D.; Lehr, F. *Helv. Chim. Acta* **1979**, *62*, 2239.

proach, respectively (Table II). Gratifyingly, *aromatic nitroalkene 9 reacted with cyclopentene in 30 min to afford exclusively nitronate 25 in excellent yield.* In fact, nitroalkenes **10–12** all behaved similarly to afford only anti cycloadducts. These results will be discussed later. There are, however, several points that deserve further comment. Nitroalkene **10** displayed an interesting color change during the course of the reaction which made this substrate particularly convenient to utilize in subsequent reactions. The pale yellow solution of nitroalkene consistently turned red upon addition of 1 drop of $SnCl_4$, becoming almost colorless again after ~5 s. This phenomenon was observed until 0.5–0.7 equiv of $SnCl_4$ had been added, at which time the solution remained a white emulsion.

As mentioned previously, a para electron-withdrawing group facilitates nitro alcohol formation. However, in the cycloaddition, a marked decelerating effect is observed for such substituents. For example, the reaction of **12** was allowed to warm to room temperature for 7 h and still 38% of the starting material was recovered. The implications of this will be discussed later.

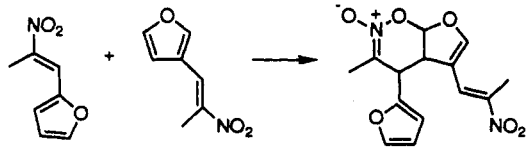
We have previously[8] noted that the aliphatic intermolecular cycloadditions of nitroalkenes with cycloalkenes exhibited the poorest selectivity (1:1) with cycloheptene. Surprisingly, reaction of aromatic nitroalkene **10** was completely selective for the anti nitronate with both cycloheptene and cyclohexene, albeit the rate of the reaction was slower in the latter case. The relative reaction rates of the three cycloalkenes (5, 7 > 6) correlate both with ring-strain energies and carbocation stabilities as discussed earlier.[8] Interestingly, the nitroalkene derived from furfural did cyclize with cyclopentene to produce 34% of nitronate product; however, the major product observed arose from intermolecular reaction between nitroalkenes.[15]

2. Competition Studies. Nitroalkenes **9–12** were initially chosen for the competition experiments. However, it was evident upon their initial cyclization with cyclopentene that nitroalkene **12** was too sluggish to be included. Thus, remaining substrates **10** and **11** were individually compared to parent nitroalkene **9**.

Equimolar amounts of the two nitroalkenes to be compared were combined in five separate flasks and cooled to −78 °C. An excess (110 equiv) of cyclopentene was added to ensure pseudo-first-order kinetics. A solution of $SnCl_4$ was freshly prepared immediately before use with CH_2Cl_2 that had been passed through a plug of basic alumina. Two equivalents of the $SnCl_4$ solution was added to each flask, and the reactions were quenched after 1, 2, 10, 30, and 80 min, respectively, with saturated aqueous $NaHCO_3$ solution. The reaction progress was monitored by HPLC analysis of the mixtures after workup. A plot of log (100 − % conversion) versus time showed that nitroalkene **10** reacts 6 times faster than **9**, which in turn reacts 77 times faster than **11**.

3. Cyclic Dienes as Dienophiles. The enhanced reactivity and selectivity of aromatic nitroalkenes with olefins stimulated investigation of their reactivity with dienes.

(15) This is not suprising since we have utilized vinyl ethers as dienophiles; see: (a) Denmark, S. E.; Senenayake, C. B. W.; Ho, G.-D. *Tetrahedron* **1990**, *46*, 4857. (b) Denmark, S. E.; Moon, Y.-C.; Senanayake, C. B. W. *J. Am. Chem. Soc.* **1990**, *112*, 311. (c) Denmark, S. E.; Schnute, M. E. *J. Org. Chem.* **1991**, *56*, 6738.



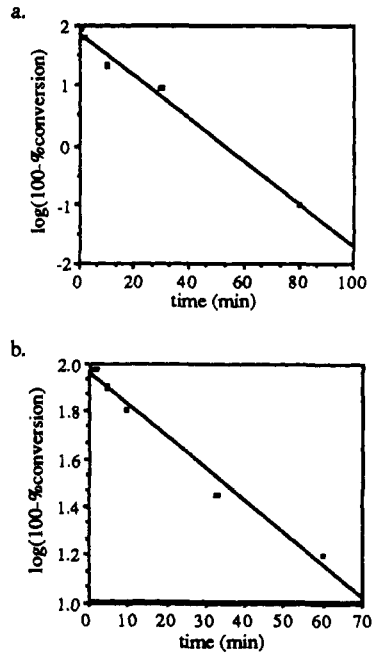
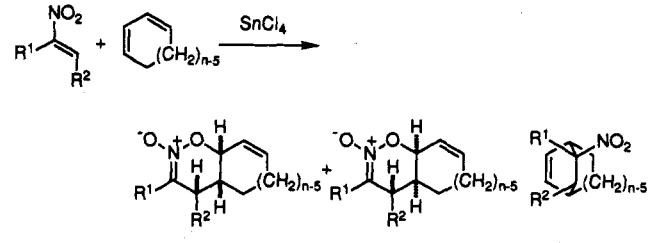


Figure 1. Graphs of (a) nitroalkene **10** versus **9** and (b) nitroalkene **9** versus **11**.

Table III. Reactions of Nitroalkenes with Dienes



syn-**31-34** *anti*-**31-34** **35**

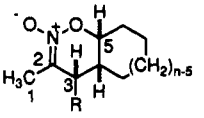
R^1	R^2	nitroalkene	n	nitronate	syn:anti	yield, %
CH_3	4-$CH_3OC_6H_4$	**10**	6	**31**	80:20	53
CH_3	4-$CH_3OC_6H_4$	**10**	5	**32**	80:20	22
H	C_6H_5	**8**	6	**33**	66:33	83
H	C_6H_5	**8**	5	**34**	75:25	66

Dienes are known[16] to engage in thermal cycloadditions as 4π-components with a nitrostyrene dienophile. In striking contrast, the Lewis acid catalyzed cycloaddition of nitroalkene **10** with cyclohexadiene afforded two isomeric nitronates, *syn*-**31** and *anti*-**31**, in a 80:20 ratio, the major isomer arising from an endo transition state (Table III). Likewise, cycloaddition of nitroalkene **8** with either cyclopentadiene or cyclohexadiene affords a predominance of nitronate *syn*-**33** and *syn*-**34**. In no instance was cycloadduct **35**, the product in which the nitroalkene participates as the dienophile, observed.

C. Structural Analysis. The structural assignment of nitronates **25–30** was based on spectroscopic methods and by analogy to previous results in these laboratories. Representative structural data are collected in Table IV. The chemical shifts in both the ^1H and ^{13}C NMR spectra are indicative of the type of ring system, e.g., 6/5, 6/6, or 6/7. The protons HC(1) are consistently between 1.85 and

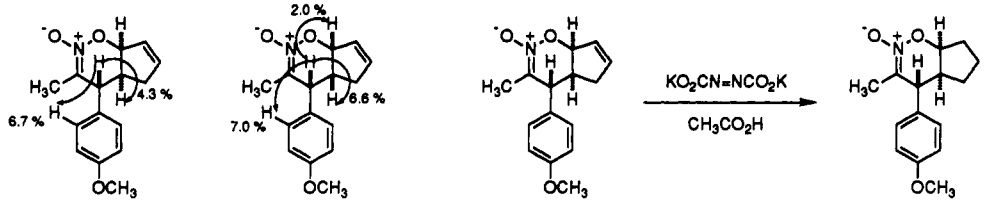
(16) (a) Bendetti, F.; Pitacco, G.; Valentin, E. *Tetrahedron* **1979**, *35*, 2293. (b) Allen, C. F. H.; Bell, A. *J. Am. Chem. Soc.* **1939**, *61*, 521. (c) Parham, W. E.; Hunter, W. T.; Hanson, R. *J. Am. Chem. Soc.* **1951**, *73*, 5068. (d) Wildman, W. C.; Wildman, R. B. *J. Org. Chem.* **1952**, *17*, 581. (e) Allen, C. F. H.; Bell, A.; Gates, J. W., Jr. *J. Org. Chem.* **1943**, *8*, 373. (f) Wildman, W. C.; Hemminger, C. H. *J. Org. Chem.* **1952**, *17*, 1641.

Table IV. Structural Data for Cycloadducts from Cyclic Alkenes



compd	R	n	IR (cm^{-1}) C=N	δ ^{1}H NMR (ppm), J (Hz) H$_3$C(1)	HC(3)	HC(5)	$J_{3,4}$	δ ^{13}C NMR (ppm)
25	C_6H_5	5	1601	1.86	3.55	4.90	5.0	83.99
26	4-$CH_3OC_6H_4$	5	1599	1.85	3.49	4.89	5.6	84.39
27	4-$CF_3C_6H_4$	5	1603	1.89	3.66	4.92	4.5	84.70
28	4-$NO_2C_6H_4$	5	1592	1.89	3.71	4.92	4.8	84.73
29	4-$CH_3OC_6H_4$	6		1.95	3.33	4.58	0	74.85
30	4-$CH_3OC_6H_4$	7	1608	1.91	3.80	4.59	0	79.40

Scheme VIII



anti-32 *syn*-32 *anti*-32 26

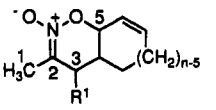
1.89 ppm in the 6/5 systems, moving downfield as the ring size increases (1.91–1.95 ppm). Particularly sensitive to ring size are HC(3) and HC(5). In the former, the 6/5 system resonates between 3.49 and 3.71 ppm, moving upfield in the 6/6 (3.33 ppm) and downfield (3.80 ppm) in the 6/7 system. Most dramatic is the effect on HC(5) which typically falls between 4.89 and 4.92 for 6/5 systems and moves noticeably upfield (4.58–4.59) in both 6/6 and 6/7 systems. Unfortunately, the coupling constants (0–4.8 Hz) did not allow unambiguous assignment of the ring fusion as anti or syn. Inspection of Dreiding models reveals both a syn and anti cycloadduct conformation that could afford couplings within this range. We prefer that, by analogy with the aliphatic systems, the observance of a single stereoisomer must arise from a similar exo transition structure rather than a complete change in mechanism. The extreme selectivity in these cycloadditions precluded comparisons to other isomers. In the ^{13}C NMR spectra, C(5) is again the most diagnostic resonance, typically falling between 83.99 and 84.73 ppm for 6/5 ring fused nitronates, with a noticeable upfield shift for the 6/6 and 6/7 systems (74.85, 79.40 ppm).

In the cycloadditions with dienes, the major stereoisomer was tentatively assigned as the syn adduct! This was most conclusive in the comparison of *syn*-31 and *anti*-31 as the diagnostic couplings of 2.7 and 9.0 Hz are so different. In addition, NOE studies (shown for the benzylic methine) supported these assignments. To unambiguously confirm these results, the olefin in nitronate *syn*-32 and *anti*-32 was reduced using diimide prepared in situ from potassium azodicarboxylate and acetic acid.[17] Indeed, minor nitronate *anti*-32 was identical to independently prepared 26 (Scheme VIII).

D. Intramolecular Cycloadditions. 1. Lewis Acid Catalyzed vs Thermal Conditions. Nitroalkenes 15 and 18 were both subjected to intramolecular cycloaddition using $SnCl_4$ (2 equiv) in toluene at −78 °C. The reactions were quenched with 0.5 N NaOH in MeOH after 1 h when judged complete by TLC analysis. Purification by column chromatography afforded a single isomer in both cases in

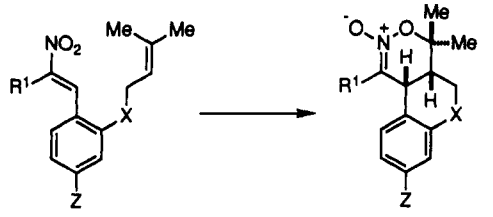
(17) Tamelen, E. E. van; Dewey, R. S.; Timmons, R. J. *J. Am. Chem. Soc.* **1961**, *83*, 3725.

Table V. Structural Data for Cycloadducts of Cyclic Dienes



nitronate	R^1	n	δ ^{1}H NMR (ppm) H$_3$C(1)	HC(3)	HC(5)	$J_{3,4}$
syn-32	4-$CH_3OC_6H_4$	5	1.93	4.03	5.51	6.9
anti-32	4-$CH_3OC_6H_4$	5	1.87	3.52	5.56	8.2
syn-31	4-$CH_3OC_6H_4$	6	1.84	3.31	4.82	2.7
anti-31	4-$CH_3OC_6H_4$	6	1.89	4.12	4.83	9.0

Table VI. Results from Intramolecular Cycloadditions

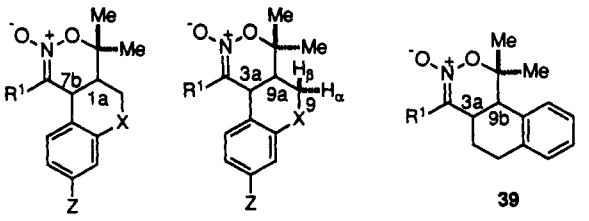


nitroalkene	R^1	Z	X	condns	product	yield, %
15	CH_3CH_2–	H	CH_2	$SnCl_4$	36	68
18	CH_3CH_2–	CH_3O–	CH_2	$SnCl_4$	37	46
20	CH_3	H	O	mesitylene, heat	38	35

68 and 46% yield, respectively. Examination of the coupling constant between HC(4a) and HC(1a) led to the conclusion that the ring fusion was syn. To ascertain any influence of the Lewis acid on the product stereochemistry, nitroalkene 20 was cyclized thermally at 210 °C in mesitylene for 30 min with $CaCO_3$ added as an acid scavenger. Purification by column chromatography afforded 35% of only a single compound, again assigned as syn on the basis of a small coupling constant.

Contrariwise, cyclization of nitroalkene 23 with 2 equiv of $SnCl_4$ in CH_2Cl_2 at −78 °C afforded a 57% yield of nitronate 39 after chromatography. Inspection of the ^{1}H NMR spectrum revealed a 79:21 mixture of anti- and

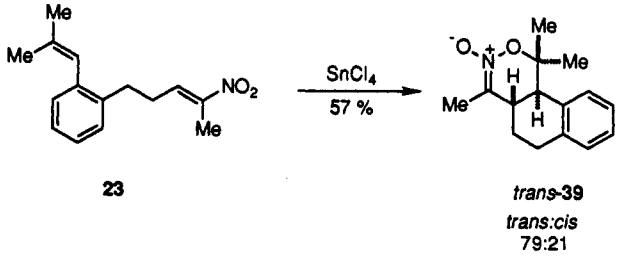
Table VII. Structural Data for Intramolecular Cycloadducts



36, 37 38 39

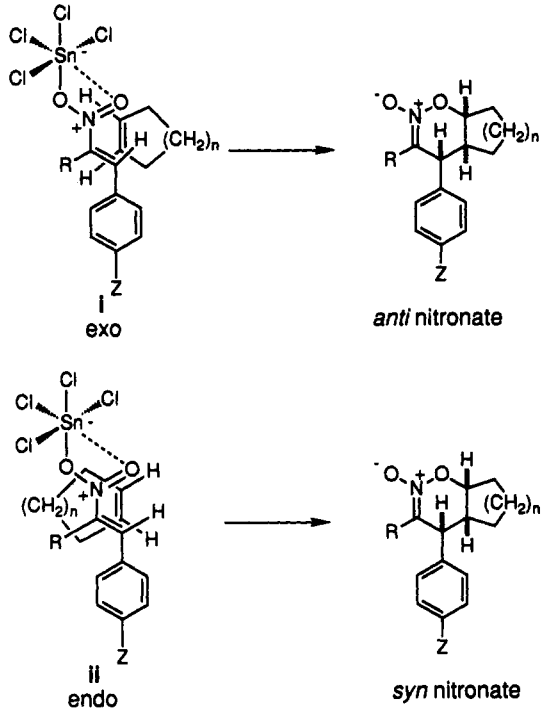
				δ ^{1}H NMR (ppm), J (Hz)			
compd	R^1	X	Z	HC(7b or 3a)	$J_{7b,1a}$	H(9b)	$J_{9b,3a}$
36	CH_3CH_2–	CH_2	H	3.91	5.8		
37	CH_3CH_2–	CH_2	CH_3O	3.85	5.8		
38	CH_3	O	H	3.85	5.3		
anti-**39**						2.99	11.6
syn-**39**						3.28	6.2

Scheme IX



23 *trans*-**39** *trans:cis* 79:21

Scheme X



syn-fused nitronates (Scheme IX). Interestingly, no products of 1,2-hydrogen migration to form 5-membered nitronates were observed. Such a rearrangement would have proceeded through the intermediacy of a tertiary benzylic carbonium ion.

2. Structure Assignment. Nitronates **36**, **37**, and **38** all afforded syn ring fusion adducts as judged by the $^3J_{7b,1a}$ coupling of 5.3–5.8 Hz. Tietze reports a similar range for his substrates (5–6 Hz). In the case of nitronate **38**, the $J_{3a,9a}$ coupling was obtained by irradiation of $H_bC(9)$ which was W-coupled to HC(3a).

Nitronate **39** was isolated as an inseparable mixture of trans and cis ring fused isomers (79:21). The coupling constants of 11.6 and 6.2 are consistent with the trans- and cis-fused structures, respectively (Tietze reports trans couplings of 10.5–11.2 Hz).[1d]

Discussion

A. Mechanism. The discussion of mechanism must begin with the role of the Lewis acid and its probable location in the transition structure. Cramer[18] first investigated this question using variable-temperature NMR. He found the complexation of $SnCl_4$ with 1-nitrocyclohexene is 1:1, but that this complex is still dynamic even at −120 °C. Seebach and Dunitz[19] studied silyl esters of nitronic acids and concluded by VT-NMR that the silicon moves rapidly between the two oxygen atoms. An X-ray analysis also showed that the silicon was within van der Waals radius with the oxygen to which it was not attached. X-ray studies of nitromethane and $TiCl_4$ show formation of 1:1 adducts with only one oxygen atom of the nitro group bound to titanium.[20] Finally, a recent report by Strauss[21] provides the first crystallographic evidence that nitrobenzene can act as both a mono- and bidentate ligand with Zn(II). Although a definitive answer regarding Lewis acid complexation with nitro compounds is still to be firmly established, we prefer to picture the $SnCl_4$ at least loosely associated with the second oxygen in an unsymmetrical fashion (Scheme X).

The very high exo selectivity of these reactions must arise from the ability of the nitroalkene–tin complex to discriminate between the two possible approaches of the dienophile shown in Scheme X. Two nonbonded interactions exist in **ii** that are not present in **i**, namely, (1) R with the dienophile and (2) $SnCl_4$ with the dienophile.

B. Kinetics. This reaction can be characterized as an inverse electron demand cycloaddition, thus focusing attention on the LUMO of the diene and the HOMO of the dienophile. As such, there should be a pronounced acceleration of rate, as in the inverse electron demand Diels–Alder reaction, with the use of Lewis acids.[22] This

(18) Cramer, C. J., Ph.D. Thesis, University of Illinois, Urbana, 1988.
(19) Colvin, E. W.; Beck, A. K.; Bastani, B.; Seebach, D.; Kai, Y.; Dunitz, J. D. *Helv. Chim. Acta* **1980**, *63*, 697.
(20) Boyer, M.; Jeannin, Y.; Rocchiccioli-Deltcheff, C.; Thouvenot, R. *J. Coord. Chem.* **1978**, *7*, 219.
(21) Hurlburt, P. K.; Kellett, P. J.; Anderson, O. P.; Strauss, S. H. *J. Chem. Soc., Chem. Commun.* **1990**, 576.

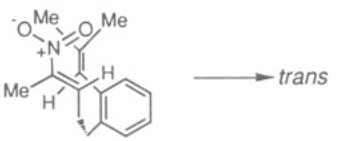
effect arises from the lowering of the LUMO which occurs upon complexation of the nitroalkene with the Lewis acid, thereby decreasing the HOMO–LUMO energy gap.

In planning the Hammett study, we recognized that electron-donating substituents should facilitate Lewis acid complexation but retard the actual cycloaddition event. In fact, we found that *p*-methoxy-substituted nitroalkene **10** reacted *six times faster* than parent nitroalkene **9** which in turn reacted *77 times faster* than *p*-trifluoromethyl derivative **11**. The 4-nitrophenyl nitroalkene was so slow as to be eliminated from the competition experiments.

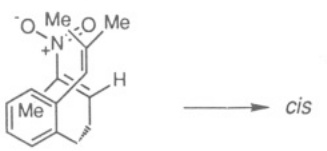
The orbital coefficients for the complex with tin tetrachloride will be different depending upon the nature of the 4-substituent. Examination of the complexes themselves might lead one to predict that an electron-withdrawing group should react faster based on frontier molecular orbital theory. However, the results imply that even though complexation occurs to differing extents depending upon the 4-substituent, the overall lowering of the LUMO that does occur upon complexations outweighs the electronic deceleration of a 4-methoxy group in the cycloaddition event. Analogous results have been obtained by Desmoni[22] and co-workers in the Diels–Alder reaction using electron-deficient dienes.

C. Stereochemistry. The exclusive formation of anti cycloadducts with nitrostyrenes and cycloalkenes can be adequately explained by transition structures **i** and **ii** in Scheme X. An increase in the severity of nonbonded interactions with aromatic nitroalkenes derives in part from the fewer degrees of freedom present in the nitroalkene as compared to the completely aliphatic version. Moreover, the cycloadditions with the aromatic substrates could be conducted at lower temperatures, thus accentuating differences in $\Delta\Delta G^{\ddagger}$.

Similar arguments hold for the intramolecular cyclization of nitroalkene **23**. Again, possible exo- and endo-folding transition states **iii** and **iv** clearly show a bad interaction between the phenyl group and the methyl of the nitroalkene in **iv**.

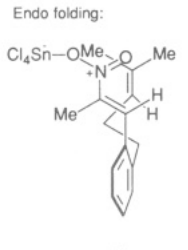


iii

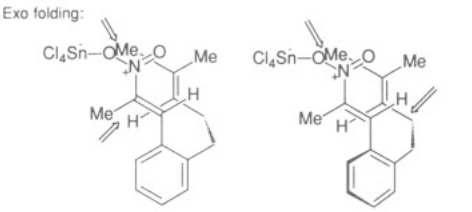


iv

The factors effecting exo and endo selectivity in the transition structures for **15**, **18**, and **20** clearly must be stronger as only one isomer, that arising from endo folding, is produced. The exact position of an sp^2 carbon in the connecting tether is crucial in determining the stereochemical outcome of the cycloaddition. If the sp^2 carbon is not conjugated with the heterodiene, as in **23**, the normal product of exo folding in the transition state is observed. However, movement of that sp^2 carbon into conjugation with the heterodiene conformationally immobilizes the system enough that the exo-folded structures **vi** and **vii** experience nonbonded interactions and torsional strain, such that reaction via **v** now becomes the lower energy pathway. An endo-folded structure that maintains conjugation of the phenyl ring with the nitroolefin is geometrically impossible.

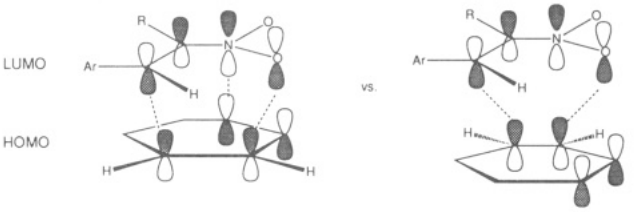


v



vi vii

The preference for syn-fused cycloadducts when nitrostyrenes react with cyclic dienes can be understood by considering secondary orbital interactions. A representation of the frontier molecular orbital diagram shows a possible secondary orbital overlap in endo-positioned structure **viii**, not available in structure **ix**. The added energy stabilization this overlap provides in the transition structure allows a switch in the syn–anti selectivity to manifest itself.



endo viii exo ix

D. Periselectivity. Nitrostyrene is known to react thermally with cyclohexadiene,[16b] cyclopentadiene,[16c,d] butadiene,[16e] and 2,3-dimethylbutadiene,[9b,16f] to afford adducts where the nitrostyrene participates as the dienophile. Our observations show that nitrostyrenes can react with the opposite periselectivity. In the thermal cycloadditions, the $HOMO_{(diene)}$–$LUMO_{(nitroalkene)}$ is the smallest energy gap to be considered. Consideration of the frontier orbital diagram shows that complexation of the nitroalkene by a Lewis acid serves only to enhance this overlap, leading to the same product, and thus cannot adequately explain the opposite periselectivity observed. The generally good yields obtained with cyclic dienes, and more importantly, the failure to observe any of **35**, must be a direct consequence of the Lewis acid employed.

In an uncomplexed nitroalkene, the charge on oxygen is evenly dispersed within the O–N–O bonding array.[23] As a result, the nitroalkene cannot electronically participate as a diene in the cycloaddition event. However, the situation changes upon the addition of a Lewis acid. Coor-

(22) Desimoni, G.; Gamba, A.; Monticelli, M.; Nicola, M.; Tacconi, G. *J. Am. Chem. Soc.* **1976**, *98*, 2947.

(23) For example, the two N–O bond lengths in *p*-nitrophenol are 2.232 and 1.236 Å; see: Sorriso, S. Structural Chemistry. In *The Chemistry of Functional Groups, Supplement F: The Chemistry of Amino, Nitroso and Nitro Compounds and their Derivatives*; Patai, S., Ed.; Wiley: New York, 1982; Part 1, pp 32–40.

dination of the Lewis acid with *one* of the oxygen atoms of the nitro group, as evidenced in the $RNO_2 \cdot TiCl_4$ crystal structure,[20] serves to localize double-bond character. While we are uncertain about the ground-state structure of the $SnCl_4$ complexes involved herein (see Discussion above) we suggest that the reactive form more resembles monodentate coordination. This species is best described as an *N*-alkoxylvinylnitrosonium cation and can now function as a heterodiene.[24]

Conclusions

The cycloaddition of nitroalkenes with dienophiles generally proceeds with a high degree of diastereoselectivity and always preserves dienophile geometry. Intermolecular cyclizations of nitrostyrenes afford exclusively anti-fused cycloadducts with alkenes. A reversal of selectivity occurs with dienes, due to secondary orbital interactions, to provide syn-fused cycloadducts. Noteworthy is the effect that a Lewis acid has on the periselectivity of the reaction with dienes.

Intramolecular cycloadditions are noticeably influenced by the hybridization of the atoms in the connecting tether. An sp^2 carbon that is not conjugated with the heterodiene allows the reaction to proceed through the anti manifold, whereas a conjugated sp^2 carbon can exert enough steric and torsional leverage in the transition state to reverse the selectivity.

Experimental Section

General. Melting points (mp) were determined on a capillary melting point apparatus and are corrected. Boiling points (bp) for bulb to bulb distillations refer to air-bath temperatures and are uncorrected. Analytical TLC was performed on silica gel plates with QF-254 indicator. Visualization was accomplished with UV light, *p*-anisaldehyde/sulfuric acid, iodine, phosphomolybdic acid, $KMnO_4$, and/or vanillin. Solvents for extraction and chromatography were technical grade and distilled from the indicated drying agents: hexane, pentane, dichloromethane ($CaCl_2$); ether ($CaSO_4/FeSO_4$); ethyl acetate (K_2CO_3). Solvents for recrystallization were spectral grade. Column (flash) chromatography was performed using 32–63-μm Woelm silica gel. Analytical gas chromatography was performed using the following columns: (A) 3% Silicone OV-17 on 60–80 Chromosorb Q (6 ft by $^1/_8$ in.), (B) 5% OV-17 capillary (50 m), (C) 5% Carbowax 20M on 60–80 Chromosorb G (6 ft by $^1/_8$ in.). Analytical high-pressure liquid chromatography (HPLC) was performed using a Supelco LC-Si 5m column; the detector wavelength = 254 nm, the flow rate = 1 mL/min unless otherwise indicated, and the solvent systems were as denoted. Solvent system 1 was a gradient solvent system reported as (time, flow rate (mL/min), % EtOAc/hexane): (0, 0.8, 10/90), (9, 0.8, 11/89), (11, 1.0, 30/70), (15, 1.5, 60/40). Solvent system 2 was a gradient solvent system reported as (time, flow rate, % *tert*-butyl methyl ether/EtOAc/hexane): (0, 0.5, 0.5/0/99.5), (11, 0.6, 0/1/99), (13, 1.0, 0/10/90), (15, 1.5, 0/50/50), (17, 1.5, 0/70/30). *sec*-, and n-Butyllithium were titrated according to the method of Gilman.[25] All reactions were performed in oven (140 °C) and/or flame-dried glassware under an inert atmosphere of dry N_2, except those which contained water, which were performed in air. Infrared spectra (IR) were obtained in carbon tetrachloride solution. Peaks are reported in cm^{-1} with the following relative intensities: s (strong, 67–100%), m (medium, 34–66%), w (weak, 0–33%). ^1H NMR and ^{13}C NMR spectra were recorded in deuterochloroform with chloroform as an internal standard (d = 7.26 for ^1H) unless otherwise stated. Chemical shifts are given in ppm (d); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broadened), and exch (D_2O exchangeable). Coupling constants, *J*, are reported in Hz. Mass spectra were obtained with ionization voltages of 70 or 10 eV. Data are reported in the form *m/z* (intensity relative to base = 100). Elemental combustion analyses were performed by the University of Illinois Microanalytical Service Laboratory.

General Procedure for the Synthesis of Nitro Alcohols. An oven-dried, round-bottomed flask was charged with the aldehyde, nitroalkane, *t*-BuOH, and THF. After the mixture was cooled to 0 °C, the *t*-BuOK was added and the mixture stirred for the indicated time. The mixture was then diluted with Et_2O and water. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine. The aqueous layers were back-extracted with Et_2O, dried with $MgSO_4$, filtered, and concentrated in vacuo to afford oils.

1-Cyclohexyl-2-nitro-1-propanol (1). Cyclohexanecarboxaldehyde (0.46 g, 0.50 mL, 4.1 mmol), nitroethane (0.78 g, 0.75 mL, 7.4 mmol, 1.8 equiv), *t*-BuOH/THF (3.0 mL each), and *t*-BuOK (42 mg, 0.23 mmol, 0.060 equiv) were stirred for 4 h to afford 724.5 mg (94%) of 1 as a 55:45 mixture of isomers after purification by column chromatography (silica gel; hexane, 200 mL; hexane/EtOAc (10:1), 150 mL; hexane/EtOAc (5:1), 150 mL; hexane/EtOAc (10:3), 150 mL): ^1H NMR (300 MHz) major isomer 4.64 (qd, *J* = 6.7, 3.1, 1 H, HC(2)), 3.94 (dd, *J* = 8.3, 3.1, 1 H, HC(1)), 2.16 (br s, 1 H, HC(1)), 1.76–1.65 (m, 4 H, $H_{eq}C(5)$, $H_{eq}C(6)$, $H_{eq}C(8)$, $H_{eq}C(9)$), 1.53 (d, *J* = 6.7, 3 H, $H_3C(3)$), 1.48–0.94 (m, 7 H, HO, $H_{ax}C(5)$, $H_{ax}C(6)$, $H_2C(7)$, $H_{ax}C(8)$, $H_{ax}C(9)$); minor isomer 4.71 (quintet, *J* = 6.8, 1 H, HC(2)), 3.64 (dd, *J* = 7.0, 4.7, 1 H, HC(1)), 2.07 (br s, 1 H, HC(1)), 1.76–1.65 (m, 4 H, $H_{eq}C(5)$, $H_{eq}C(6)$, $H_{eq}C(8)$, $H_{eq}C(9)$), 1.53 (d, *J* = 6.7, 3 H, $H_3C(3)$), 1.48–0.94 (m, 7 H, HO, $H_{ax}C(5)$, $H_{ax}C(6)$, $H_2C(7)$, $H_{ax}C(8)$, $H_{ax}C(9)$); ^{13}C NMR (75.5 MHz) major isomer 85.6 (C(2)), 76.7 (C(1)), 39.4 (C(4)), 28.7 (C(5), C(9)), 25.6 (C(6), C(8)), 25.4 (C(7)), 16.1 (C(3)); minor isomer 84.1 (C(2)), 76.3 (C(1)), 40.1 (C(4)), 29.7 (C(5), C(9)), 26.0 (C(6), C(8)), 25.9 (C(7)), 11.4 (C(3)); IR (CCl_4) 3619 (free OH) m, 3551 (br, OH) m, 1555 (NO_2) s, 1360 (NO_2) s; TLC R_f 0.34 (hexane/EtOAc (10:3)).

2-Nitro-1-phenyl-1-propanol (3). Benzaldehyde (2.09 g, 2.00 mL, 19.7 mmol), nitroethane (2.96 g, 2.83 mL, 39.4 mmol, 2.00 equiv), *t*-BuOH/THF (5 mL each), and *t*-BuOK·*t*-BuOH (1:1 complex, 184 mg, 0.990 mmol, 0.05 equiv) were stirred for 16 h to afford 3.57 g (100%) of a colorless oil. Purification by flash column chromatography (silica gel; hexane, 200 mL; hexane/EtOAc (10:1) 200 mL; hexane/EtOAc (5:1), 200 mL; hexane/EtOAc (10:3), 100 mL; hexane/EtOAc (5:2), 100 mL) afforded 3.18 g (89%) of 3: ^1H NMR (300 MHz) 7.38 (m, 5 H, HC(5), HC(6), HC(7), HC(8), HC(9)), 5.02 (dd, *J* = 9.0, 3.9, 1 H, HC(1)), 4.77 (dt, *J* = 9.0, 6.9, 1 H, HC(2)), 2.63 (d, *J* = 3.9, 1 H, HC(1)), 1.31 (d, *J* = 6.9, 3 H, $H_3C(3)$); ^{13}C NMR (75.5 MHz) major isomer 138.3 (C(4)), 128.8 (C(6), C(8)), 128.6 (C(5), C(9)), 125.9 (C(7)), 88.3 (C(2)), 76.1 (C(1)), 16.3 (C(3)); minor isomer 138.5 (C(4)), 129.0 (C(6), C(8)), 128.3 (C(5), C(9)), 126.9 (C(7)), 87.3 (C(2)), 73.9 (C(1)), 12.0 (C(3)); IR (CCl_4) 3619 (free OH) m, 3551 (OH) m, 1555 (NO_2) s, 1360 (NO_2) s; TLC R_f 0.23 (hexane/EtOAc (10:3)).

2-Nitro-1-(4-methoxyphenyl)-1-propanol (4). A mixture of *p*-methoxybenzaldehyde (2.72 g, 2.43 mL, 20.0 mmol), nitroethane (3.00 g, 2.87 mL, 40.0 mmol, 2.00 equiv), *t*-BuOK (catalytic amount), and *t*-BuOH/THF (2 mL each) was allowed to warm to room temperature, which afforded 3.48 g (82%) of 4 as a mixture of diastereomers: ^1H NMR (200 MHz) 7.28 (d, *J* = 8.6, 2 H, HC(5), HC(9)), 6.92 (m, 2 H, HC(6), HC(8)), 5.29 (m, 0.5 H, HC(2)), 4.91 (m, 0.5 H, HC(2)), 4.74 (m, 1 H, HC(3)), 3.88 (s, 3 H, HC(10)), 3.04 (s, 1 H, OH), 1.48 (d, 1.5 H, HC(1)), 1.26 (d, *J* = 3.4, 1.5 H, HC(1)); IR (CCl_4) 3450 (OH) w, 2840 (OCH_3) m, 1555 (NO_2) s, 1360 (NO_2) m; TLC R_f 0.23 (hexane/EtOAc (4:1)).

2-Nitro-1-[4-(trifluoromethyl)phenyl]-1-propanol (5). A mixture of α,α,α-trifluoro-*p*-tolualdehyde (1.75 g, 1.37 mL, 10.0 mmol), nitroethane (1.50 g, 1.44 mL, 20.0 mmol, 2.00 equiv), *t*-BuOK (catalytic amount), and *t*-BuOH/THF (2 mL each) was allowed to warm to room temperature to afford 5 (2.37 g, 95%) as a mixture of diastereomers: ^1H NMR (200 MHz) 7.67 (d, 2 H, HC(6), HC(8)), 7.53 (d, 2 H, HC(5), HC(9)), 5.49 (s, 0.5 H, HC(2)), 5.12 (m, 0.5 H, HC(2)), 4.70 (m, 1 H, HC(3)), 2.85 (d, 0.5 H, OH), 2.73 (d, 0.5 H, OH), 1.46 (d, *J* = 7.0, 1.5 H, HC(1)), 1.31 (d, *J* = 6.7, 1.5 H, HC(1)); IR (CCl_4) 3619 (OH) m, 1555 (NO_2) s, 1362 (NO_2) m; TLC R_f 0.33 (hexane/EtOAc (4:1)).

2-Nitro-1-(4-nitrophenyl)-1-propanol (6). A mixture of *p*-nitrobenzaldehyde (2.27 g, 15.0 mmol), nitroethane (2.25 g, 2.15 mL, 30.0 mmol, 2.00 equiv), *t*-BuOK (catalytic amount), and

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t-BuOH/THF (4 mL each) was allowed to warm to room temperature to afford 2.65 g (78%) of **6** as a mixture of diastereomers: ^{1}H NMR (200 MHz) 8.29 (d, J = 2.3, 2 H, HC(6), HC(8)), 8.24 (d, J = 2.3, 2 H, HC(5), HC(9)), 5.57 (t, J = 3.5, 0.7 H, HC(2)), 5.20 (m, 0.3 H, HC(2)), 4.74 (m, 1 H, HC(3)), 3.06 (d, J = 4.4, 0.7 H, OH), 3.00 (d, J = 4.3, 0.3 H, OH), 1.50 (d, J = 6.5, 2.2 H, HC(1)), 1.39 (d, J = 7.1, 0.8 H, HC(1)); IR (CCl_4) 3604 (OH) m, 1609 (NO_2) s, 1393 (NO_2) s.

General Procedure for the Preparation of Nitroalkenes. The crude nitro alcohols were taken up in Et_2O and treated with acetic anhydride and DMAP (catalytic). After being stirred for the specified time, the mixture was concentrated and the crude nitroacetates were taken up in CH_2Cl_2 and treated with stoichiometric amounts of DMAP. The mixture was diluted with CH_2Cl_2 and washed with water, 0.1 N HCl, and brine. The aqueous layers were back-extracted with CH_2Cl_2 (2x), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated in vacuo. Liquid nitroalkenes were purified by distillation, and solids were recrystallized from the solvents indicated.

1-Cyclohexyl-2-nitropropene (7). A mixture of nitro alcohol **1** (598 mg, 3.19 mmol), DMAP (5.00 mg, 0.05 equiv), Et_2O (4 mL), and acetic anhydride (0.370 g, 340 μL, 3.60 mmol, 1.13 equiv) was stirred for 3 h and then concentrated. The crude nitro acetate (715 mg, 3.11 mmol), CH_2Cl_2 (4 mL), and DMAP (520 mg, 4.26 mmol, 1.37 equiv) were stirred for 3 h to afford a yellow oil. Purification by column chromatography (silica gel; hexane, 200 mL; hexane/EtOAc (20:1), 200 mL) gave 441 mg (84%) of **7** as a pale yellow oil. An analytical sample was obtained by bulb to bulb distillation: bp 45 °C (0.03 Torr); ^{1}H NMR (300 MHz) 6.95 (d, J = 10.3, 1 H, HC(1)), 2.28–2.20 (m, 1 H, HC(4)), 2.16 (s, 3 H, H_3C(3)), 1.80–1.66 (m, 5 H, H_{eq}C(5), H_{eq}C(6), H_{eq}C(7), H_{eq}C(8), H_{eq}C(9)), 1.34–1.15 (m, 5 H, H_{ax}C(5), H_{ax}C(6), H_{ax}C(7), H_{ax}C(8), H_{ax}C(9)); ^{13}C NMR (75.5 MHz) 146.1 (C(2)), 140.6 (C(1)), 37.4 (C(4)), 31.6 (C(5), C(9)), 25.4 (C(7)), 25.1 (C(6), C(8)), 12.4 (C(3)); IR (CCl_4) 1674 (C=C) w, 1524 (NO_2) s, 1330 (NO_2) s; TLC R_f 0.65 (hexane/EtOAc (10:3)). Anal. Calcd for $C_9H_{15}NO_2$ (169.23): C, 63.88; H, 8.94; N, 8.28. Found: C, 63.72; H, 8.86; N, 8.40.

(*E*)-1-Nitro-2-phenylethene (8). A mixture of benzaldehyde (2.09 g, 2.00 mL, 19.7 mmol), nitromethane (3.60 g, 3.20 mL, 59.0 mmol, 3.00 equiv), *t*-BuOH/THF (10 mL each), and *t*-BuOK (111 mg, 0.990 mmol, 0.05 equiv) was stirred for 16 h at 10 °C to afford a colorless oil. Purification by column chromatography (silica gel; hexane, 200 mL; hexane/EtOAc (10:1), 200 mL; hexane/EtOAc (5:1), 200 mL; hexane/EtOAc (10:3) 100 mL; hexane/EtOAc (5:2), 100 mL) afforded 2.82 g (89%) of nitro alcohol **2**. A mixture of crude nitro alcohol **2** (2.82 g, 16.9 mmol), DMAP (16.9 mg, 0.130 mmol, 0.01 equiv), acetic anhydride (1.89 g, 1.75 mL, 18.6 mmol, 1.10 equiv), and Et_2O (17 mL) was stirred for 4 h and then concentrated. The crude nitro acetate (16.9 mmol) in CH_2Cl_2 (33 mL, 0.5 M) was treated with triethylamine (1.72 g, 2.40 mL, 17.0 mmol) in CH_2Cl_2 (5 mL). After 6 h the mixture was diluted with CH_2Cl_2 (40 mL) and washed with water (30 mL), saturated aqueous $NaHCO_3$ (30 mL), and brine (30 mL). The aqueous layers were back-extracted with CH_2Cl_2 (2×). The combined organic layers were dried and concentrated to afford a yellow oil. Purification by column chromatography (silica gel; hexane, 200 mL; hexane/EtOAc (20:1), 200 mL; hexane/EtOAc (20:1), 200 mL) gave 2.12 mg (84%) of **8** as pale-yellow crystals: mp 62.5–63.5 °C (hexane); ^{1}H NMR (300 MHz) 8.01 (d, J = 13.6, 1 H, HC(1)), 7.59 (d, J = 13.9, 1 H, HC(1)), 7.55 (d, J = 8.7, 2 H, HC(4), HC(8)), 7.48 (dd, J = 8.7, 8.2, 2 H, HC(5), HC(7)), 7.43 (t, J = 8.2, 1 H, HC(6)); ^{13}C NMR (75.5 MHz) 138.5 (C(2)), 136.5 (C(1)), 131.7 (C(6)), 129.6 (C(3)), 128.84 (C(5), C(7)), 128.77 (C(4), C(8)); TLC R_f 0.67 (hexane/EtOAc (10:3)).

1-Methyl-1-nitro-2-phenylethene (9). A mixture of nitro alcohol **3** (1.06 g, 10.0 mmol), Et_2O (2 mL), acetic anhydride (1.12 g, 1.04 mL, 11.0 mmol, 1.10 equiv), and DMAP (10 mg) was stirred for 1 h at which time another 10 mg of DMAP was added. After 30 min, workup afforded a mixture of diastereomers as a blue-green oil (1.30 g, 58%). Data: ^{1}H NMR (300 MHz) 7.38 (s, 5 H, aromatic H), 6.34 (d, J = 3.0, 0.43 H, HC(3)), 6.05 (d, J = 9.0, 0.57 H, HC(3)), 4.93 (m, 0.57 H, HC(2)), 4.81 (m, 0.43 H, HC(2)), 2.22 (s, 1.2 H, HC(12)), 2.02 (s, 1.8 H, HC(12)), 1.56 (d, J = 6.0, 1.26 H, HC(1)), 1.34 (d, J = 6.0, 1.74 H, HC(1)).

The crude nitro acetates (1.0 g, 4.5 mmol), DMAP (0.66 g, 5.4 mmol, 1.2 equiv), and CH_2Cl_2 were stirred for 3 h to afford green-yellow crystals (0.69 g, 93%). Purification by column chromatography afforded 0.65 g (88%) of **9**[26a–d] as yellow crystals which were recrystallized: mp 60–62 °C (hexane/EtOAc); ^{1}H NMR (300 MHz) 8.10 (s, 1 H, HC(3)), 7.44 (s, 5 H, aromatic H), 2.46 (s, 3 H, H_3C(1)); IR (CCl_4) 1665 (C=C) m, 1526 (NO_2) s, 1325 (NO_2) s; UV λ_{max} = 230 nm (14 359.8) in CH_2Cl_2; HPLC t_R = 5.31 min (solvent system 1), 9.28 (solvent system 2); TLC R_f 0.41 (hexane/EtOAC (4:1)). Anal. Calcd for $C_9H_9NO_2$ (163.17): C, 66.25; H, 5.56; N, 8.58. Found: C, 66.38; H, 5.43; N, 8.49.

1-Methyl-1-nitro-(4-methoxyphenyl)ethene (10). A mixture of nitro alcohol **4** (0.54 g, 2.5 mmol), Et_2O (2 mL), acetic anhydride (0.29 g, 0.26 mL, 2.8 mmol, 1.1 equiv), and DMAP (10 mg) was stirred for 5 h to afford a blue-green oil (0.47 g, 73%) containing both nitro acetate and nitroalkene. Purification on a chromatotron plate afforded 0.22 g (34%) of diastereomer 1 and 0.10 g (16%) of diastereomer 2: ^{1}H NMR (200 MHz) diastereomer 1 7.30 (d, 2 H, HC(5), HC(9)), 6.92 (d, 2 H, HC(6), HC(8)), 6.01 (d, 1 H, HC(3)), 4.92 (m, 1 H, HC(2)), 3.81 (s, 3 H, H_3C(12)), 2.00 (s, 3 H, H_3C(10)), 1.34 (d, 3 H, H_3C(1)); diastereomer 2 7.23 (d, 2 H, HC(5), HC(9)), 6.87 (d, 2 H, HC(6), HC(8)), 6.22 (d, 1 H, HC(3)), 4.80 (m, 1 H, HC(2)), 3.78 (s, 3 H, H_3C(12)), 2.11 (s, 3 H, H_3C(10)), 1.56 (d, 3 H, H_3C(1)).

A mixture of the crude nitro acetates (0.37 g, 1.5 mmol), DMAP (0.21 g, 1.7 mmol, 1.2 equiv), and CH_2Cl_2 (2 mL) was stirred for 30 min to afford 0.25 g (88%) of **10** as yellow crystals: mp 43–45 °C (hexane/EtOAc); ^{1}H NMR (300 MHz) 8.08 (s, 1 H, HC(3)), 7.43 (d, J = 8.8, 2 H, HC(6), HC(8)), 6.98 (d, J = 8.7, 2 H, HC(5), HC(9)), 3.87 (s, 3 H, H_3C(10)), 2.48 (s, 3 H, H_3C(1)); ^{13}C NMR (75.5 MHz) 161.07 (C(7)), 145.63 (C(2)), 133.62 (C(3)), 132.09 (C(6 and 8)), 124.66 (C(4)), 114.44 (C(5 and 9)), 55.41 (C(10)), 14.11 (C(1)); UV λ_{max} = 346 nm (3728.3) in CH_2Cl_2; HPLC t_R = 7.36 min (solvent system 1); TLC R_f 0.33 (hexane/EtOAc (4:1)). Anal. Calcd for $C_{10}H_{11}NO_3$ (193.20): C, 62.17; H, 5.74; N, 7.25. Found: C, 62.24; H, 5.77; N, 7.19.

1-Methyl-1-nitro-2-[4-(trifluoromethyl)phenyl]ethene (11). A mixture of nitro alcohol **5** (0.45 g, 1.8 mmol), Et_2O (2 mL), acetic anhydride (0.20 g, 0.19 mL, 2.0 mmol, 1.1 equiv), and DMAP (10 mg) was stirred for 2 h to afford a mixture of diastereomers (0.50 g, 95%): ^{1}H NMR (200 MHz) 7.67 (m, 2 H, HC(6), HC(8)), 7.49 (m, 2 H, HC(5), HC(9)), 6.36 (d, J = 5.5, 0.4 H, HC(3)), 6.09 (d, J = 9.9, 0.6 H, HC(3)), 4.92 (m, 1 H, HC(2)), 2.17 (s, 1.2 H, HC(12)), 2.05 (s, 1.8 H, HC(12)), 1.58 (d, J = 6.5, 1.2 H, HC(1)), 2.74 (d, J = 7.0, 1.8 H, HC(1)); IR (CCl_4) 1763 (C=O) s, 1561 (NO_2) s, 1325 (NO_2) s, 1219 (COC stretch) s.

A mixture of the crude nitro acetates (0.50 g, 1.7 mmol), DMAP (0.25 g, 2.1 mmol, 1.2 equiv), and CH_2Cl_2 (2.5 mL) was stirred for 2.5 h to afford greenish crystals (0.34 g, 86%). Purification on the chromatotron afforded **11** as yellow crystals (0.33 g, 82%) which were recrystallized: mp 36–38.5 °C (hexane/EtOAc); ^{1}H NMR (200 MHz) 8.08 (s, 1 H, HC(3)), 7.72 (d, J = 8.3, 2 H, HC(6), HC(8)), 7.53 (d, J = 7.9, 2 H, HC(5), HC(9)), 2.44 (s, 3 H, H_3C(1)); ^{13}C NMR (75.5 MHz) 149.40 (C(2)), 136.04 (C(3)), 131.74 (aromatics), 131.29, 130.02, 125.88 (aromatics), 123.70 (C(10), J = 272.4 Hz), 13.99 (C(1)); HPLC t_R = 10.3 (solvent system 2); TLC R_f 0.32 (hexane/EtOAc (4:1)). Anal. Calcd for $C_{10}H_8F_3NO_2$ (231.18): C, 51.96; H, 3.49; F, 24.65; N, 6.06. Found: C, 51.90; H, 3.42; F, 24.74; N, 6.07.

1-Methyl-1-nitro-2-(4-nitrophenyl)ethene (12). A mixture of nitro alcohol **6** (2.62 g, 11.6 mmol), Et_2O (8 mL), acetic anhydride (1.30 g, 1.20 mL, 12.8 mmol, 1.1 equiv), and DMAP (20 mg) was stirred for 3 h to afford light-blue crystals (88%) as a mixture of diastereomers after purification by column chromatography. Data: ^{1}H NMR (200 MHz) 8.27 (m, 2 H, HC(6), HC(8)), 7.55 (m, 2 H, HC(5), HC(9)), 6.36 (d, J = 5.5, 0.5 H, HC(3)), 6.13 (d, J = 9.5, 0.5 H, HC(3)), 4.93 (m, 1 H, HC(2)), 2.18 (s, 1.5 H, HC(12)), 2.06 (s, 1.5 H, HC(12)), 1.59 (d, J = 6.6, 1.5 H, HC(1)), 1.38 (d, J = 7.1, 1.5 H, HC(1)); IR (CCl_4) 1765 (C=O) m, 1561 (aliphatic NO_2) s, 1456 (aromatic NO_2) w.

DMAP (0.24 g, 2.0 mmol, 1.2 equiv) was added to the crude nitro acetate (0.44 g, 1.6 mmol) in CH_2Cl_2 (2 mL) and allowed

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to stir for 45 min to afford 0.27 g (77%) of 12[26c,d] as yellow-brown crystals: mp 103.5–105 °C (hexane/EtOAc); ^{1}H NMR (200 MHz) 8.33 (m, 1 H, HC(6), HC(8)), 8.10 (s, 1 H, HC(3)), 7.59 (d, 2 H, HC(5), HC(9)), 2.46 (s, 3 H, H_3C(1)); IR (CCl_4) 1532 (NO_2) s; TLC R_f 0.31 (hexane/EtOAc (4:1)).

General Procedure for the Trimethylethylenediamine (TriMEDA)-Assisted Alkylation. A three-necked flask was fitted with an addition funnel and flame-dried. Tetrahydrofuran and TriMEDA were added to the flask and chilled to −20 °C, at which time *n*-BuLi was added dropwise. After 15 min, the aldehyde was added, followed 15 min later by 3 equiv of *n*-BuLi. The reaction mixture turned dark orange and was allowed to stir at −20 °C for 1.5 h. The mixture was chilled to −65 °C followed by dropwise addition of the alkyl halide. The solution turned colorless upon being warmed slowly to room temperature. The reaction was quenched by pouring it into cold, stirred 1 N HCl and extraction with Et_2O. The combined organic layers were washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo to afford oils.

2-(4-Methyl-3-pentenyl)benzaldehyde (14). To a solution of THF (32 mL) and TriMEDA (1.31 g, 1.64 mL, 12.8 mmol, 1.1 equiv) was added *n*-BuLi (1.59 M, 7.60 mL, 12.0 mmol) followed by 2-methylbenzaldehyde (1.44 g, 1.39 mL, 12.0 mmol). Three equiv of *n*-BuLi were added followed by the alkyl halide (10.7 g, 72.0 mmol, 6.00 equiv). The resulting oil was purified by MPLC (hexane/EtOAc (100:1)) to afford 1.67 g (74%) of **14** as a colorless oil: bp 125 °C (0.3 Torr); ^{1}H NMR (300 MHz) 10.25 (s, 1 H, HC(1)), 7.82 (dd, J = 6.5, 0.9, 1 H, HC(3)), 7.49 (ddd, J = 6.3, 1.1, 1 H, HC(5)), 7.34 (t, J = 7.4, 1 H, HC(4)), 7.26 (d, J = 7.6, 1 H, HC(6)), 5.17 (t, J = 7.3, 1 H, HC(10)), 3.04 (t, J = 7.7, 2 H, H_2C(8)), 2.29 (q, J = 7.5, 2 H, H_2C(9)), 1.66 (s, 3 H, H_3C(13)), 1.44 (s, 3 H, H_3C(12)); ^{13}C NMR (75.5 MHz) 191.8 (C(1)), 144.9 (C(7)), 133.7 (C(5)), 133.6 (C(2)), 131.0 (C(3) or C(6)), 130.9 (C(3) or C(6)), 126.4 (C(4)), 122.7 (C(10)), 32.3 (CH_2), 30.5 (CH_2), 25.6 (C(13)), 17.4 (C(12)); TLC R_f 0.62 (hexane/EtOAc (4:1)).

4-Methoxy-2-(4-methyl-3-pentenyl)benzaldehyde (17). To a solution of THF (3.5 mL) and TriMEDA (0.19 mL, 1.5 mmol, 1.1 equiv) was added *s*-BuLi (1.1 mL, 1.3 M, 1.5 mmol, 1.1 equiv) followed by 4-methoxy-2-methylbenzaldehyde (0.20 g, 1.3 mmol). Three equiv of *s*-BuLi was added followed by the bromide (1.2 g, 8.0 mmol, 6.0 equiv). The resulting yellow oil was purified by flash column chromatography (50 cm; hexane/EtOAc (10:1), hexane/EtOAc (4:1)) followed by distillation to afford 0.16 g (54%) of **17** as a yellow oil: bp 140 °C (0.3 Torr); ^{1}H NMR (300 MHz) 10.10 (s, 1 H, HC(1)), 7.78 (d, J = 8.5, 1 H, HC(3)), 6.84 (dd, J = 8.6, 2.5, 1 H, HC(4)), 6.74 (d, J = 2.4, 1 H, HC(6)), 5.18 (t, 1 H, HC(10)), 3.85 (s, 3 H, H_3C(14)), 3.02 (t, J = 7.7, 2 H, H_2C(8)), 2.29 (q, J = 7.5, 2 H, H_2C(9)), 1.67 (s, 3 H, H_3C(12)), 1.49 (s, 3 H, H_3C(13)); ^{13}C NMR (75.5 MHz) 190.30 (C(1)), 163.57 (C(5)), 147.50 (C(7)), 133.93 (C(3)), 132.79 (C(11)), 127.32 (C(2)), 122.86 (C(10)), 116.01 (C(6)), 111.54 (C(4)), 55.25 (C(14)), 32.58 (CH_2), 30.17 (CH_2), 25.53 (C(13)), 17.42 (C(12)); IR (CCl_4) 1694 (CHO) s, 1601 s; TLC R_f 0.47 (hexane/EtOAc (4:1)). Anal. Calcd for $C_{14}H_{18}O_2$ (218.30): C, 77.03; H, 8.31. Found: C, 77.06; H, 8.22.

General Procedure for the Preparation of 15 and 18. A three-necked flask with addition funnel was flame-dried and charged with THF/HMPA (5:1) and nitropropane and cooled to −90 °C. The *s*-BuLi was added dropwise and stirred for 15 min while the temperature was maintained between −90 and −80 °C. The aldehyde was added to the yellow solution and allowed to warm slowly to −60 °C. The reaction was quenched with acetic anhydride (3 equiv) after 30 min, extracted with pentane, and washed with water, and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated in vacuo to afford yellow oils.

(*E*)-2-(4-Methyl-3-pentenyl)-1-(2-nitro-1-butenyl)benzene (15). Nitropropane (1.06 g, 1.06 mL, 11.9 mmol) in THF/HMPA (70 mL) was treated with *s*-BuLi (18.7 mL, 1.27 M, 23.7 mmol, 2 equiv) and aldehyde **14** (2.23 g, 11.9 mmol) to afford 3.65 g of a yellow oil. Purification by MPLC (hexane/EtOAc (100:1)) gave 1.03 g (34%) of **15** as a bright yellow oil: bp 160 °C (0.35 Torr); ^{1}H NMR (300 MHz) 8.16 (s, 1 H, HC(4)), 7.27 (m, 4 H, H_2C(6), H_2C(9)), 5.13 (m, 1 H, HC(13)), 2.72 (q, J = 7.4, 2 H, H_2C(2)), 2.64 (t, J = 7.8, 2 H, H_2C(11)), 2.21 (q, J = 7.6, 2 H, H_2C(12)), 1.66 (s, 3 H, H_3C(15)), 1.51 (s, 3 H, H_3C(16)), 1.20 (t, J = 7.4, 3 H, H_3C(1)); ^{13}C NMR (75.5 MHz) 153.82 (C(3)), 141.88 (C(10)), 132.87 (C(5)), 132.40 (C(4)), 131.34 (C(14)), 129.70 (C(6) or C(9)), 129.59 (C(6) or C(9)), 128.33 (C(13)), 126.16 (C(8)), 122.81 (C(7)), 33.89 (CH_2), 29.39 (CH_2), 25.60 (C(16)), 20.50 (CH_2), 17.42 (C(15)), 12.58 (C(1)); IR (CCl_4) 1653 (C=C) m, 1524 (NO_2 asym) s, 1377 (NO_2 sym) s, 1335 (NO_2 sym) s; TLC R_f 0.41 (hexane/EtOAc (4:1)). Anal. Calcd for $C_{16}H_{21}NO_2$ (259.35): C, 74.10; H, 8.16; N, 5.40. Found: C, 74.14; H, 8.15; N, 5.37.

(*E*)-2-(4-Methyl-3-pentenyl)-1-(2-nitro-1-butenyl)-4-methoxybenzene (18). Nitropropane (0.49 g, 0.49 mL, 5.5 mmol) in THF/HMPA (30 mL) was treated with *t*-BuLi (7.0 mL, 1.7 M, 12 mmol, 2.2 equiv) and aldehyde **17** (1.2 g, 11 mmol, 2.0 equiv) to afford 7 g of a yellow oil. Purification by flash column chromatography (hexane/EtOAc (10:1)) afforded 0.31 g (20%) of **18** as a yellow oil (23% of starting material was recovered). Data for **18**: bp 190 °C (1.2 Torr); ^{1}H NMR (300 MHz) 8.17 (s, 1 H, HC(4)), 7.21 (m, 1 H, HC(6)), 6.81 (m, 2 H, HC(7), HC(9)), 5.13 (dt, J = 1.2, 6.1, 1 H, HC(13)), 3.84 (s, 3 H, H_3C(17)), 2.77 (q, J = 7.4, 2 H, H_2C(2)), 2.65 (t, J = 7.8, 2 H, H_2C(11)), 2.22 (q, J = 7.6, 2 H, H_2C(12)), 1.68 (s, 3 H, H_3C(16)), 1.52 (s, 3 H, H_3C(15)), 1.21 (t, J = 7.1, 3 H, HC(1)); ^{13}C NMR (75.5 MHz) 160.71 (C(3)), 152.39 (C(8)), 144.37 (C(10)), 132.05 (C(4)), 129.94 (C(6)), 123.46 (C(5)), 122.65 (C(13)), 115.32 (C(9)), 111.45 (C(7)), 55.13 (C(17)), 34.11 (C(11)), 29.37 (C(12)), 20.53 (C(2)), 15.14 (C(15), C(16)), 12.50 (C(1)); IR (CCl_4) 1604 (C=C) s, 1570 (NO_2 asym) m, 1522 (NO_2 asym) s, 1381 (NO_2 sym) s, 1331 (NO_2 sym) s; TLC R_f 0.51 (hexane/EtOAc (4:1)). Anal. Calcd for $C_{17}H_{23}NO_3$ (289.38): C, 70.56; H, 8.01; N, 4.84. Found: C, 70.53; H, 7.98; N, 4.77.

(*E*)-1-[2′-[(3″-Methyl-2″-butenyl)oxy]phenyl]-2-nitropropene (20). According to the general procedure for the preparation of nitro alcohols, a mixture of aldehyde **19** (0.27 g, 1.4 mmol), nitroethane (0.53 g, 0.51 mL, 7.1 mmol, 5.0 equiv), *t*-BuOH/THF (5 mL each), and *t*-BuOK (catalytic amount) was stirred for 1 h to afford 0.36 g (95%) of a yellow oil: ^{1}H NMR (300 MHz) 7.31 (m, 2 H, HC(5), HC(7)), 6.94 (m, 2 H, HC(6), HC(8)), 5.47 (m, 1 H, HC(11)), 4.99 (m, 1 H, HC(2)), 4.60 (m, 2 H, H_2C(10)), 3.41 (d, J = 6.0, 1 H, HC(3), 1 diastereomer), 3.16 (d, J = 5.7, 1 H, HC(3), 1 diastereomer), 1.81 (d, J = 6.0, 3 H, H_3C(13)), 1.76 (d, J = 4.9, 3 H, H_3C(12)), 1.51 (d, J = 6.9, 3 H, H_3C(1), 1 diastereomer), 1.33 (d, J = 6.6, 3 H, H_3C(1), 1 diastereomer); TLC R_f 0.30 (hexane/EtOAc (10:1)).

According to the general procedure for the preparation of nitroalkenes, a mixture of the crude nitro alcohol (0.35 g, 1.3 mmol), Et_2O (11 mL), acetic anhydride (0.15 g, 0.14 mL, 1.5 mmol, 1.1 equiv), and DMAP (30 mg) was stirred for 2 h and concentrated. The crude nitroacetate in CH_2Cl_2 (5.7 mL) at 0 °C was treated with triethylamine (0.13 g, 0.19 mL, 1.3 mmol, 1 equiv based on theoretical yield) and stirred for 2 h to afford 0.37 g of yellow crystals. Purification by flash column chromatography (silica gel; hexane/EtOAc (4:1)) afforded 0.29 g (88%) of **20** as viscous yellow oil: ^{1}H MMR (300 MHz) 8.28 (s, 1 H, HC(1)), 7.37 (m, 1 H, HC(6′)), 7.28 (t, J = 6.0, 1 H, HC(4′)), 6.97 (m, 2 H, HC(5′), HC(3′)), 5.47 (dd, J = 6.0, 9.0, 1 H, HC(2″)), 4.58 (d, J = 6.0, 2 H, H_2C(1″)), 2.38 (s, 3 H, H_3C(3)), 1.79 (s, 3 H, H_3C(5″)), 1.74 (s, 3 H, H_3C(4″)); ^{13}C NMR (75.5 MHz) 157.51 (C(2)), 147.44 (C(2′)), 138.20 (C(1′)), 131.37 (C(4′, 6′, or 1)), 130.16 (C(4′, 6′, or 1)), 130.10 (C(4′, 6′, or 1)), 121.87 (C(3″)), 120.34 (C(2″ or 5′)), 119.28 (C(2″ or 5′)), 112.17 (C(3′)), 65.47 (C(1″)), 25.78 (C(3)), 18.29 (C(4″ or 5″)), 14.24 (C(4″ or 5″)); IR (CCl_4) 1653 (C=C) w, 1599 (C=CN) m, 1522 (NO_2) s, 1325 (NO_2) s. Anal. Calcd for $C_{14}H_{17}NO_3$ (247.30): C, 68.00; H, 6.93; N, 5.66. Found: C, 67.98; H, 6.89; N, 5.64.

3-[2′-(2-Methyl-1-propenyl)phenyl]propanal (22). A 250-mL, three-necked flask was charged with the phosphonium iodide (15.1 g, 34.9 mmol, 2.50 equiv) and THF (114 mL) and cooled to 0 °C. Then *n*-BuLi (20.9 mL, 33.5 mmol, 2.40 equiv, 1.6 M) was added dropwise and stirring continued for 30 min. Aldehyde **21** (2.29 g, 14.0 mmol) in 28 mL of THF was added dropwise via an addition funnel to the blood-red solution. After 4 h the mixture was extracted with *tert*-butyl methyl ether (3 × 250 mL) and washed with water (100 mL) and brine (100 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by column chromatography (silica gel; hexane/EtOAc (4:1); hexane/EtOAc (2:1)) afforded 1.62 g of **21a** (61%) as a colorless oil: bp 150 °C (2 Torr); ^{1}H NMR (300 MHz) 7.14 (m, 4 H, HC(5–8)), 6.29 (s, 1 H, HC(10)), 3.61 (t, J = 6.4, 2 H, H_2C(1)), 2.65 (t, J = 7.7, 2 H, H_2C(3)), 1.90 (s, 3 H, H_3C(12)), 1.80 (m, 2 H, H_2C(2)), 1.69 (s, 3 H, H_3C(13)); ^{13}C NMR (75.5 MHz)

139.97 (C(4)), 137.48 (C(11)), 135.52 (C(9)), 129.95, 128.74, 126.44, 125.50, 123.74 (C(7)), 62.25 (C(1)), 33.31 (C(2)), 29.43 (C(3)), 26.01 (C(13)), 19.20 (C(12)); TLC R_f 0.27 (hexane/EtOAc (2:1)). Anal. Calcd for $C_{13}H_{18}O$ (190.29): C, 82.06; H, 9.53. Found: C, 81.85; H, 9.49.

A dry 250-mL, three-necked flask was charged with pyridinium chlorochromate (3.53 g, 16.4 mmol, 2 equiv) and evacuated for 15 min. Molecular sieves (9.30 g) and CH_2Cl_2 (82 mL) were added followed by the above alcohol (1.56 g, 8.20 mmol) in 32 mL of CH_2Cl_2. After 4 h, the reaction was filtered through Fluorosil and washed with 300 mL of CH_2Cl_2 and the filtrate concentrated in vacuo to afford a dark brown liquid. Purification by column chromatography (silica gel; hexane/EtOAc (4:1)) afforded 1.05 g (68%) of **22** as a colorless oil: ^{1}H NMR (300 MHz) 9.78 (t, J = 1.2, 1 H, HC(1)), 7.14 (m, 4 H, HC(5–8)), 6.24 (s, 1 H, HC(10)), 2.91 (t, J = 7.6, 2 H, $H_2C(2)$), 2.67 (m, 2 H, $H_2C(3)$), 1.90 (s, 3 H, $H_3C(12)$), 1.68 (s, 3 H, $H_3C(13)$); ^{13}C NMR (75.5 MHz) 201.97 (C(1)), 138.51 (C(4)), 137.58 (C(11)), 136.13 (C(9)), 130.18, 128.64, 126.66, 126.03, 123.30, 44.47 (C(2)), 26.03 (C(13)), 25.96 (C(3)), 19.25 (C(12)); TLC R_f 0.53 (hexane/EtOAc (4:1)). Anal. Calcd for $C_{13}H_{16}O$ (188.27): C, 82.94; H, 8.57. Found: C, 82.85; H, 8.63.

(*E*)-5-[2′-(2″-Methyl-1″-propenyl)phenyl]-2-nitropent-2-ene (23). Aldehyde **22** (1.05 g, 5.58 mmol), nitroethane (2.09 g, 2.00 mL, 27.9 mmol, 5.00 equiv), *t*-BuOH/THF (20 mL each), and *t*-BuOK (63.0 mg, 0.600 mmol, 0.1 equiv) were stirred for 3 h to afford 1.40 g (95%) of a colorless oil: ^{1}H NMR (300 MHz) 7.14 (m, 4 H, HC(7-10)), 6.28 (s, 1 H, HC(12)), 4.47 (m, 1 H, HC(2)), 4.12 (m, 1 H, 1 diastereomer, HC(3)), 3.84 (m, 1 H, 1 diastereomer, HC(3)), 2.75 (m, 4 H, $H_2C(4)$, $H_2C(5)$), 1.91 (s, 3 H, $H_3C(14)$), 1.68 (s, 3 H, $H_3C(15)$), 1.52 (d, J = 6.8, 3 H, 1 diastereomer, $H_3C(1)$), 1.49 (d, J = 6.9, 3 H, 1 diastereomer, $H_3C(1)$); IR (CCl_4) 3569 m, 2932 m, 1551 s, 1450 w, 1393 w, 1358 w, 1254 w, 1003.

A mixture of the crude nitro alcohol (400 mg, 1.52 mmol), acetic anhydride (0.190 g, 0.170 mL, 1.82 mmol, 1.20 equiv), and DMAP (0.450 g, 3.65 mmol. 2.40 equiv) in CH_2Cl_2 (8 mL) was stirred for 2 h to afford an orange oil. Purification by flash column chromatography (silica gel; hexane/EtOAc (20:1)) afforded 200 mg (54%) of **23** as a yellow liquid: ^{1}H NMR (300 MHz) 7.15 (m, 5 H, HC(7-10), HC(3)), 6.26 (bs, 1 H, HC(12)), 2.76 (t, J = 7.6, 2 H, $H_2C(5)$), 2.45 (m, 2 H, $H_2C(4)$), 2.02 (d, J = 0.6, 3 H, $H_3C(1)$), 1.92 (d, J = 0.6, 3 H, $H_3C(14)$), 1.69 (d, J = 0.9, 3 H, $H_3C(15)$); ^{13}C NMR (75.5 MHz) 147.86 (C(2)), 138.31 (C(6)), 137.50 (C(13)), 136.20 (C(3)), 135.26 (C(11)), 130.23, 128.84, 126.66, 126.19, 123.28 (C(9)), 31.97, 29.16 (C(5)), 26.05 (C(15)), 19.20 (C(14)), 12.22; IR (CCl_4) 1526 (NO_2, asym) s, 1335 (NO_2, sym) s; TLC R_f 0.48 (hexane/EtOAc (4:1); 2×). Anal. Calcd for $C_{15}H_{19}NO_2$ (245.32): C, 73.44; H, 7.81; N, 5.71. Found: C, 73.45; H, 7.81; N, 5.71.

General Procedure for the Preparation of 25–28. To a cold (−78 °C) solution of nitroalkene and cylcopentene in CH_2Cl_2 was added $SnCl_4$ (0.320 g, 0.144 mL, 1.23 mmol, 2 equiv), and the solution was stirred for the indicated time. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$ and diluted with EtOAc. After being warmed to room temperature with vigorous stirring, the mixture was filtered through a medium porous glass filter. The white viscous material was washed with EtOAc (2 × 20 mL), and the combined heterogeneous solution was washed with saturated aqueous $NaHCO_3$, 0.1 N NaOH, and brine. The aqueous layers were back-extracted with EtOAc, and the combined organic layers were dried (Na_2SO_4), filtered, and concentrated.

[*R*,*S*]-(3a*l*,7*l*,7a*l*)-1,2,3,3a,7,7a-Hexahydro-6-methyl-7-phenylcyclopent[*e*][1,2]oxazine *N*-Oxide (25). A mixture of nitroalkene **9** (100 mg, 0.613 mmol), cyclopentene (83.8 mg, 0.110 mL, 1.23 mmol, 2.00 equiv), CH_2Cl_2 (2 mL), and $SnCl_4$ (0.320 g, 0.144 mL, 1.23 mmol, 2.00 equiv) was stirred for 45 min to afford an oil that was purified by flash column chromatography to afford 120 mg (85%) of **25** as white crystals: mp 102–103.5 °C (hexane/EtOAc); ^{1}H NMR (300 MHz) 7.31–7.41 (m, 3 H, HC(10), HC(10′), HC(11)), 7.20 (d, J = 6.8, 2 H, HC(9), HC(9′)), 4.91 (m, 1 H, HC(3a)), 3.57 (d, J = 4.6, 1 H, HC(7)), 2.38–2.43 (m, 1 H, HC(7a)), 1.84–2.03 (m, 4 H, $H_2C(1)$, $H_2C(3)$), 1.87 (s, 3 H, $H_3C(13)$), 1.58–1.66 (m, 2 H, $H_2C(2)$); ^{13}C NMR (75.5 MHz) 140.09 (C(6)), 129.11 (C(10), C(10′)), 128.20 (C(9), C(9′)), 127.62 (C(7a)), 124.31 (C(11)), 84.66 (C(3a)), 48.01, 46.80, 31.90, 30.41, 22.37 (C(2)), 17.11 (C(13)); IR (CCl_4) 1601 (C=N) s; UV l_{max} = 236 nm (2051.4) in CH_2Cl_2; HPLC t_R = 20.4 min (solvent system 1 and 2); TLC R_f 0.17 (hexane/EtOAc (1:1)). Anal. Calcd for $C_{14}H_{17}NO_2$ (231.29): C, 72.70; H, 7.41; N, 6.06. Found: C, 72.66; H, 7.42; N, 6.12.

[*R*,*S*]-(3a*l*,7*l*,7a*l*)-1,2,3,3a,7,7a-Hexahydro-6-methyl-7-(4-methoxyphenyl)cyclopent[*e*][1,2]oxazine *N*-Oxide (26). A mixture of nitroalkene **10** (0.10 g, 0.52 mmol), cyclopentene (71 mg, 92 μL, 1.0 mmol, 2.0 equiv), CH_2Cl_2 (2 mL), and $SnCl_4$ (0.27 g, 0.12 mL, 1.0 mmol, 2.0 equiv) was stirred for 20 min to afford an oil that was purified by flash column chromatography to afford 0.11 g (79%) of **26** as white crystals: mp 122–124 °C (hexane/EtOAc); ^{1}H NMR (300 MHz) 7.12 (d, J = 8.6, 2 H, HC(9), HC(9′)), 6.90 (d, J = 8.6, 2 H, HC(10), HC(10′)), 4.89–4.92 (m, 1 H, HC(3a)), 3.82 (s, 3 H, $H_3C(12)$), 3.51 (d, J = 4.8, 1 H, HC(7)), 2.39 (m, 1 H, HC(7a)), 1.81–2.00 (m, 4 H, $H_2C(1)$, $H_2C(3)$), 1.86 (s, 3 H, $H_3C(13)$), 1.58–1.67 (m, 2 H, $H_2C(2)$); ^{13}C NMR (75.5 MHz) 158.97 (C(11)), 131.94 (C(6)), 129.32 (C(9), C(9′)), 124.96 (C(7)), 114.43 (C(10), C(10′)), 84.83 (C(3a)), 55.31 (C(12)), 47.32, 47.08, 32.04, 30.47, 22.48 (C(2)), 16.97 (C(13)); IR (CCl_4) 1599 (C=N) s; UV l_{max} = 234 nm (2320.5) in CH_2Cl_2; HPLC t_R = 22.2 (solvent system 1); TLC R_f 0.13 (hexane/EtOAc (1:1)). Anal. Calcd for $C_{15}H_{19}NO_3$ (261.32): C, 68.94; H, 7.33; N, 5.36. Found: C, 68.76; H, 7.41; N, 5.17.

[*R*,*S*]-(3a*l*,7*l*,7a*l*)-1,2,3,3a,7,7a-Hexahydro-6-methyl-7-[4-(trifluoromethyl)phenyl]cyclopent[*e*][1,2]oxazine *N*-Oxide (27). Nitroalkene **11** (0.10 g, 0.43 mmol), cyclopentene (59 mg, 0.080 mL, 0.87 mmol, 2.0 equiv), CH_2Cl_2 (2 mL), and $SnCl_4$ (0.23 g, 0.10 mL, 0.87 mmol, 2.0 equiv) were combined at −78 °C. It was necessary to warm the flasks to −30 °C to achieve complete reaction. The resulting oil was purified by flash column chromatography to afford 0.11 g (85%) of **27** as white crystals: mp 91.5–93 °C (hexane/EtOAc); ^{1}H NMR (300 MHz) 7.66 (d, J = 8.1, 2 H, HC(10), HC(10′)), 7.35 (d, J = 8.1, 2 H, HC(9), HC(9′)), 4.92 (m, 1 H, HC(3a)), 3.66 (d, J = 4.5, 1 H, HC(7)), 2.40 (m, 1 H, HC(7a)), 1.91–2.03 (m, 4 H, $H_2C(1)$, $H_2C(3)$), 1.89 (s, 3 H, $H_3C(13)$), 1.60–1.66 (m, 2 H, $H_2C(2)$); ^{13}C NMR (75.5 MHz) 144.15, 128.68 (aromatics), 126.21, 126.16, 126.12, 123.25, 84.70 (C(3a)), 47.93, 46.80, 31.90, 30.50, 22.43 (C(2)), 17.18 (C(13)); IR (CCl_4) 1603 (C=N) s; UV l_{max} = 236 nm (4057.92) in CH_2Cl_2; HPLC t_R = 20.0 (solvent system 2); TLC R_f 0.04 (hexane/EtOAc (4:1)). Anal. Calcd for $C_{15}H_{16}F_3NO_2$ (299.30): C, 60.20; H, 5.39; F, 19.04, N, 4.68. Found: C, 60.10; H, 5.36; F, 18.94; N, 4.62.

[*R*,*S*]-(3a*l*,7*l*,7a*l*)-1,2,3,3a,7,7a-Hexahydro-6-methyl-7-(4-nitrophenyl)cyclopent[*e*][1,2]oxazine *N*-Oxide (28). Nitroalkene **12** (0.52 g, 2.5 mmol), cyclopentene (0.34 g, 0.44 mL, 5.0 mmol, 2.0 equiv), CH_2Cl_2 (3 mL), and $SnCl_4$ (1.3 g, 0.59 mL, 5.0 mmol, 2.0 equiv) were combined at −78 °C. Warming the reaction slowly to room temperature and continued stirring for 7 h was necessary for complete reaction. The resulting oil was purified by flash column chromatography to afford 0.26 g (38%) of **28** as shiny pale yellow crystals along with 38% of recovered starting material: mp 161–164 °C (hexane/EtOAc); ^{1}H NMR (300 MHz) 8.26 (d, J = 8.6, 2 H, HC(10), HC(10′)), 7.41 (d, J = 8.6, 2 H, HC(9), HC(9′)), 4.92 (m, 1 H, HC(3a)), 3.71 (d, J = 4.8, 1 H, HC(7)), 2.41 (m, 1 H, HC(7a)), 1.86–2.04 (m, 4 H, $H_2C(1)$, $H_2C(3)$), 1.89 (s, 3 H, $H_3C(11)$), 1.56–1.69 (m, 2 H, $H_2C(2)$); ^{13}C NMR (75.5 MHz) 147.39 (C(12)), 129.22 (C(7a)), 124.44 (C(7)), 123.00 (C(6)), 106.04, 84.73 (C(3a)), 47.99, 46.78, 31.92, 30.61, 22.49 (C(2)), 17.21 (C(13)); IR (KBr) 1592 (C=N) s; TLC R_f 0.15 (hexane/EtOAc (4:1)). Anal. Calcd for $C_{14}H_{16}N_2O_4$ (276.30): C, 60.86; H, 5.84; N, 10.14. Found: C, 60.95; H, 5.94; N, 9.99.

General Procedure for Preparation of 29, 30, 31, 33. To a solution of the nitroalkene and cycloalkadiene in CH_2Cl_2 was added $SnCl_4$ (2.0 equiv) at −78 °C. When one drop of $SnCl_4$ added, the solution turned red and very slowly lightened to pink. The reaction was stirred for the indicated time and then quenched with saturated aqueous $NaHCO_3$ and diluted with EtOAc. The heterogeneous mixture obtained from filtration was washed with 0.1 N NaOH (30 mL), saturated aqueous $NaHCO_3$ (30 mL), and brine (30 mL). The aqueous layers were back-extracted with EtOAc (2 × 40 mL) and the combined organic layers dried, concentrated, and filtered. Purification of the oil by column chromatography (silica gel; hexane/EtOAc (5:1), 100 mL; hexane/EtOAc (10:3), 300 mL; hexane/EtOAc (2:1), 200 mL) afforded crystalline products.

Cycloaddition of Nitroalkene 10 with Cyclohexene 29. From nitroalkene **10** (148 mg, 0.776 mmol), cyclohexene (0.140 g, 155 μL, 1.53 mmol, 2.00 equiv), and $SnCl_4$ (0.400 g, 180 μL, 1.53

mmol, 2.00 equiv) in CH_2Cl_2 (1.53 mL) for 3 h was obtained 184 mg (87%) of **29** after flash column chromatography: ^1H NMR (300 MHz) 7.05 (d, J = 8.6, 2 H, HC(11), HC(13)), 6.87 (d, J = 8.6, 2 H, HC(10), HC(14)), 4.58 (s, 1 H, HC(8a)), 3.78 (s, 3 H, H_3C(15)), 3.33 (s, 1 H, HC(4)), 2.06–2.01 (m, 1 H, HC(4a)), 1.95 (s, 3 H, H_3C(14)), 1.79–1.46 (m, 5 H), 1.42–1.30 (m, 4 H); ^{13}C NMR (75.5 MHz) 158.4 (C(11)), 132.9 (C(9)), 128.3 (C(10), C(14)), 119.6 (C(3)), 113.9 (C(11), C(13)), 74.9 (C(8a)), 54.8 (C(15)), 48.8 (C(4)), 39.5 (C(4a)), 28.2 (C(8)), 26.9 (C(5)), 24.1 (C(6)), 19.4 (C(7)), 18.3 (C(14)).

Cycloaddition of Nitroalkene 10 with Cycloheptene 30. From nitroalkene **10** (127 mg, 0.660 mmol), cycloheptene (0.130 g, 154 μL, 1.32 mmol, 2.00 equiv), and $SnCl_4$ (0.340 g, 154 μL, 1.32 mmol, 2.00 equiv) in CH_2Cl_2 for 30 min was obtained 192 mg (100%) of **30** after flash column chromatography: ^1H NMR (300 MHz) 7.07 (d, J = 8.6, 2 H, HC(12), HC(14)), 6.88 (d, J = 8.6, 2 H, HC(11), HC(15)), 4.59 (m, 1 H, HC(9a)), 3.80 (s, 3 H, H_3C-(16)), 3.39 (1 H, HC(4a)), 1.91 (s, 3 H, H_3C(17)), 2.00–1.34 (m, 11 H); ^{13}C NMR (75.5 MHz) 158.5 (C(13)), 132.4 (C(10)), 128.8 (C(11), C(15)), 121.5 (C(3)), 113.9 (C(12), C(14)), 79.4 (C(9a)), 54.8 (C(16)), 50.4 (C(4)), 43.8 (C(4a)), 30.9 (C(9)), 28.5 (C(5)), 27.8 (C(7)), 26.0 (C(8)), 21.3 (C(6)), 17.7 (C(17)); TLC R_f 0.16 (hexane/EtOAc (5:3)).

Cycloaddition of Nitroalkene 10 with Cyclohexadiene 31. From nitroalkene **10** (132 mg, 0.680 mmol), 1,3-cyclohexadiene (0.110 g, 130 μL, 1.37 mmol, 2.00 equiv), and $SnCl_4$ (0.110 g, 50.0 μL, 0.430 mmol, 0.630 equiv) in CH_2Cl_2 (4.0 mL) for 15 min was obtained 79.3 mg (43%) of nitronate *syn*-**31** and 18.1 mg (10%) of nitronate *anti*-**31**. Data for *syn*-**31**: ^1H NMR (300 MHz) 6.97 (d, J = 8.6, 2 H, HC(10), HC(14)), 6.86 (d, J = 8.6, 2 H, HC(11), HC(13)), 6.10 (m, 1 H, HC(7)), 5.81 (m, 1 H, HC(8)), 4.83 (d, J = 6.0, 1 H, HC(8a)), 4.12 (d, J = 9.0, 1 H, HC(4)), 3.80 (s, 3 H, H_3C(15)), 2.21–2.08 (m, 2 H, HC(4a), HC(6)), 1.94–1.82 (m, 1 H, HC(6)), 1.89 (s, 3 H, H_3C(16)), 1.50 (m, 1 H, HC(5)), 0.90 (m, 1 H, HC(5)). Data for *anti*-**31**: ^1H NMR (300 MHz) 7.06 (d, J = 8.6, 2 H, HC(10), HC(14)), 6.84 (d, J = 8.6, 2 H, HC(11), HC(13)), 6.01 (dt, J = 9.6, 3.4, 1 H, HC(7)), 5.77 (dd, J = 9.6, 1.8, 1 H, HC(8)), 4.82 (br s, 1 H, HC(8a)), 3.75 (s, 3 H, H_3C(15)), 3.33 (d, J = 2.7, 1 H, HC(4)), 2.25–1.63 (m, 5 H), 1.84 (s, 3 H, H_3C(16)).

Cycloaddition of Nitroalkene 8 with Cyclohexadiene 33. From nitroalkene **8** (306 mg, 2.05 mmol), 1,3-cyclohexadiene (0.330 g, 390 μL, 4.10 mmol, 2.00 equiv), and $SnCl_4$ (1.07 g, 480 μL, 4.10 mmol, 2.00 equiv) in toluene (13 mL) for 20 min was obtained 267 mg (57%) of nitronate *syn*-**33** and 122 mg (26%) of nitronate *anti*-**33**. Data for *syn*-**33**: ^1H NMR (300 MHz) 7.41–7.21 (m, 5 H, aromatics), 6.42 (d, J = 3.8, 1 H, HC(3)), 6.11 (m, 1 H, HC(7)), 5.85 (m, 1 H, HC(8)), 4.83 (br s, 1 H, HC(8a)), 3.49 (t, J = 3.8, 1 H, HC(4)), 2.33–2.24 (m, 1 H), 2.17–2.04 (m, 2 H), 1.92–1.75 (m, 2 H); ^{13}C NMR (75.5 MHz) 141.1 (C(9)), 135.7 (C(3)), 129.2 (C(11), C(13)), 127.7 (C(12)), 127.6 (C(10), C(14)), 122.0 (C(8)), 114.1 (C(7)), 75.9 (C(8a)), 45.1 (C(4)), 38.9 (C(4a)), 24.5 (C(5)), 23.4 (C(6)); TLC R_f 0.38 (hexane/EtOAc (1:1)). Data for *anti*-**33**: ^1H NMR (300 MHz) 7.40–7.16 (m, 5 H, aromatics), 6.45 (d, J = 3.3, 1 H, HC(3)), 6.14 (ddd, J = 9.5, 4.8, 2.0, 1 H, HC(7)), 5.84 (m, 1 H, HC(8)), 4.98 (d, J = 5.4, 1 H, HC(8a)), 4.29 (dd, J = 7.5, 3.3, 1 H, HC(4)), 1.95, 1.55 (qd, J = 13.1, 5.7, 1 H, H_aC(5)), 0.98 (1 H, H_bC(5)); ^{13}C NMR (75.5 MHz) 136.8 (C(3)), 136.7 (C(9)), 128.5 (C(11), C(13)), 128.0 (C(10), C(14)), 127.3 (C(12)), 120.8 (C(8)), 113.1 (C(7)), 76.6 (C(8a)), 43.8 (C(4)), 33.6 (C(4a)), 25.4 (C(6)), 18.3 (C(5)); TLC R_f 0.26 (hexane/EtOAc (5:3)).

Cycloaddition of Nitroalkene 8 with Cyclopentadiene 34. To nitroalkene **8** (324 mg, 2.17 mmol) and 1,3-cyclopentadiene (freshly distilled, 0.240 g, 300 μL, 3.64 mmol, 1.70 equiv) at −78 °C was added $SnCl_4$ (1.13 g, 507 μL, 4.33 mmol, 2.00 equiv). The mixture became pale pink then yellow then orange. After 10 min an additional 300 μL of cyclopentadiene was added, at which time a yellow color persisted. After 30 min the mixture was quenched with saturated aqueous $NaHCO_3$ (30 mL) and diluted with EtOAc (50 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 50 mL) and brine (50 mL). The aqueous layers were back-extracted with EtOAc (2 × 50 mL), dried (Na_2SO_4), filtered, and concentrated. Purification by flash column chromatography (silica gel; CH_2Cl_2, 50 mL; hexane/EtOAc (5:3), 600 mL) afforded 73.3 mg (15.7%) of nitronate *anti*-**34** and 235 mg (50.2%) of nitronate *syn*-**34**. Data for *syn*-**34**: ^1H NMR (300 MHz) 7.42–7.31 (m, 3 H, HC(10), HC(11), HC(12)), 7.30–7.24 (m, 2 H, HC(9), HC(13)), 6.56 (d, J = 4.0, 1 H, HC(3)), 6.20–6.17 (m, 1 H, HC(6)), 5.85–5.80 (m, 1 H, HC(7)), 5.60 (d, J = 7.8, 1 H, HC(7a)), 3.41 (dd, J = 9.7, 4.0, 1 H, HC(4)), 2.91 (tdd, J = 9.4, 8.1, 3.9, 1 H, HC(4a)), 2.53 (ddt, J = 17.9, 8.4, 3.9, 1 H, HC(5)), 2.39 (dq, J = 17.9, 2.7, 1 H, HC(5)); TLC R_f 0.36 (hexane/EtOAc (1:1)). Data for *anti*-**34**: ^1H NMR (300 MHz) 7.40 (dd, J = 7.5, 6.9, 2 H, HC(10), HC(12)), 7.31 (t, J = 6.9, 1 H, HC(11)), 7.23 (d, J = 7.5, 2 H, HC(9), HC(13)), 6.74 (d, J = 4.4, 1 H, HC(3)), 6.16 (d, J = 6.3, 1 H, HC(6)), 5.92–5.90 (m, 1 H, HC(7)), 5.68 (d, J = 8.6, 1 H, HC(7a)), 4.06 (dd, J = 5.5, 4.4, 1 H, HC(4)), 3.42 (m, 1 H, HC(4a)), 2.33 (d, J = 18.3, 1 H, HC(5)), 2.18 (dd, J = 18.3, 8.3, 1 H, HC(5)); ^{13}C NMR (75.5 MHz) 139.74 (C(3)), 136.47 (C(8)), 128.96 (C(10), C(12)), 127.52 (C(9), C(13)), 127.33 (C(11)), 127.23 C(7)), 117.71 (C(6)), 91.75 (C(7a)), 43.06 (C(4)), 41.81 (C(4a)), 34.61 (C(5)); TLC R_f 0.24 (hexane/EtOAc (1:1)).

Cycloaddition of Nitroalkene 10 with Cyclopentadiene 32. A dry, 50-mL, two-necked flask was charged with nitroalkene **10** (0.50 g, 2.6 mmol) and 26 mL of toluene and cooled to −78 °C. Cyclopentadiene (freshly distilled into a −78 °C collecting flask, 5.2 mmol, 2.0 equiv) was added followed by $SnCl_4$ (0.45 g, 0.20 mL, 1.7 mmol, 0.67 equiv). Another 2 equiv of cyclopentadiene was added, followed by the remaining $SnCl_4$ (0.90 g, 0.41 mL, 3.5 mmol, 1.3 equiv). After 20 min, a final 2 equiv of cyclopentadiene was added. After 4 h, the reaction was quenched with 4 mL of saturated aqueous $NaHCO_3$ and was allowed to warm to room temperature. The mixture was extracted with CH_2Cl_2 (3 × 150 mL) and washed with 0.1 N NaOH (100 mL), saturated aqueous $NaHCO_3$ (100 mL), and brine (100 mL). The combined organic layers were dried (Na_2SO_4/$MgSO_4$), filtered, and concentrated in vacuo to afford a yellow-orange liquid. Purification by flash column chromatography (silica gel; hexane/EtOAc, then EtOAc) afforded 33 mg (5%) of *anti*-**32** as pale yellow crystals which were recrystallized from *tert*-butyl methyl ether/hexane and 118 mg of *syn*-**32** (18%) as white crystals which were similarly recrystallized. Data for *anti*-**32**: ^1H NMR (500 MHz) 7.15 (d, J = 8.6, 2 H, HC(10), HC(10′)), 6.90 (d, J = 8.6, 2 H, HC(11), HC(11′)), 6.14 (m, 1 H, HC(6)), 5.82 (m, 1 H, HC(7)), 5.56 (d, J = 8.0, 1 H, HC(5)), 3.81 (s, 3 H, H_3C(13)), 3.52 (d, J = 8.2, 1 H, HC(3)), 3.09 (m, 1 H, HC(4)), 2.58 (dddd, J = 17.8, 8.6, 2.0, 2.0, 1 H, H_AC(8)), 2.24 (dddd, J = 18.0, 2.8, 1 H, H_BC(8)), 1.87 (d, J = 1.1, 3 H, H_3C(1)); ^{13}C NMR (125 MHz) 159.06 (C(12)), 138.49 (C(6)), 129.72 (C(10)), 129.42 (C(2)), 129.11 (C(9)), 126.72 (C(7)), 114.36 (C(11)), 90.69 (C(5)), 55.30 (C(13)), 49.37 (C(3)), 44.42 (C(4)), 38.62 (C(8)), 16.30 (C(1)); IR ($CDCl_3$) 1597 (C=O) s, 1514 (C=N) s; TLC R_f 0.43 (EtOAc). Anal. Calcd for $C_{15}H_{17}NO_3$ (259.31): C, 69.48; H, 6.61; N, 5.40. Found: C, 69.62; H, 6.68; N, 5.30. Data for *syn*-**32**; mp 142–143 °C (hexane/*tert*-butyl methyl ether); ^1H NMR (500 MHz) 7.14 (d, J = 8.6, 2 H, HC(10), HC(10′)), 6.86 (d, J = 8.7, 2 H, HC(11), HC(11′)), 6.15 (m, 1 H, HC(6)), 5.88 (m, 1 H, HC(7)), 5.51 (dt, J = 7.6, 2.3, 1 H, HC(5)), 4.03 (d, J = 6.9, 1 H, HC(3)), 3.79 (s, 3 H, H_3C(13)), 3.23 (dddd, J = 7.2, 7.1, 7.1, 7.1, 1 H, HC(4)), 2.44 (dddd, J = 17.6, 8.7, 2.3, 2.3, 1 H, H_AC(8)), 2.24 (dddd, J = 17.6, 2.6, 2.5, 1 H, H_BC(8)), 1.93 (d, J = 0.9, 3 H, H_3C(1)); ^{13}C NMR (125 MHz) 158.88 (C(12)), 140.30 (C(6)), 129.95 (C(10)), 128.97 (C(2)), 128.01 (C(9)), 127.03 (C(7)), 114.15 (C(11)), 91.14 (C(5)), 55.24 (C(13)), 45.84 (C(3)), 41.09 (C(4)), 35.67 (C(8)), 17.04 (C(1)); IR ($CDCl_3$) 1512 (C=N) s; TLC R_f 0.33 (EtOAc). Anal. Calcd for $C_{15}H_{17}NO_3$ (259.31): C, 69.48; H, 6.61; N, 5.40. Found: C, 69.68; H, 6.68; N, 5.47.

General Procedure for the Preparation of 36, 37, and 39. A solution of the nitroolefin in toluene was chilled to −75 °C, and tin tetrachloride was added dropwise. After the indicated time, the mixture was quenched with 0.5 N NaOH in MeOH. The white mixture was poured into saturated aqueous $NaHCO_3$, extracted with EtOAc, and washed with saturated aqueous $NaHCO_3$. The combined organic layers were dried ($MgSO_4$), filtered, and concentrated in vacuo to afford crude oils.

[*R*,*S*]-(4a*l*,1a*u*)-1,1-Dimethyl-4-ethyl-5a,8a-phenyl-1a,4a,5a,8a,9,10-hexahydro-1*H*-benz[*d*][1,2]oxazine *N*-Oxide (36). From nitroolefin **15** (0.10 g, 0.39 mmol) and tin tetrachloride (0.09 mL, 0.77 mmol, 2.0 equiv) in toluene (3 mL) for 40 min was obtained a pale yellow oil (0.15 g). Flash column chromatography (20 cm; hexane/EtOAc (10:1), 100 mL; EtOAc) afforded 68 mg (68%) of **36** as white crystals: mp 94–96 °C; ^1H NMR (500 MHz) 7.22 (m, 4 H, aromatics), 3.91 (d, J = 5.8, 1 H, HC(4a)), 2.87 (dt, J = 5.5, 1 H, HC(9)), 2.76 (ddd, 1 H, HC(9)), 2.34 (m, 2 H,

$H_2C(13)$), 2.11 (m, 1 H, HC(10)), 1.96 (m, 1 H, HC(10)), 1.76 (m, 1 H, HC(1a)), 1.49 (s, 3 H, $H_3C(11)$ or C(12)), 1.41 (s, 3 H, $H_3C(11)$ or $H_3C(12)$), 0.84 (t, J = 7.4, 3 H, $H_3C(14)$); ^{13}C NMR (125 MHz) 133.01, 130.27, 128.54, 127.74, 126.04, 83.83 (C(1)), 76.60 (C(1a) or C(4a)), 76.55 (C(1a) or C(4a)), 40.15, 39.92, 28.30, 25.92, 23.85, 23.32, 22.18, 8.56 (C(14)), carbon 4 not found; IR (CCl_4) 1592 (C=N) s; TLC R_f 0.39 (EtOAc). Anal. Calcd for $C_{16}H_{21}NO_2$ (259.35): C, 74.10; H, 8.16; N, 5.40. Found: C, 74.09; H, 8.20; N, 5.34.

[*R*,*S*]-(4a*l*,1a*u*)-1,1-Dimethyl-4-ethyl-5a,8a-(4-methoxyphenyl)-1,4a,5a,8a,9,10-hexahydro-1*H*-benz[*d*][1,2]oxazine *N*-Oxide (37). From nitroalkene **18** (0.14 g, 0.47 mmol) and tin tetrachloride (0.25 g, 0.11 mL, 0.95 mmol, 2.0 equiv) in toluene (4 mL) for 1 h was obtained a yellow oil. Purification by flash column chromatography (10 cm; hexane/EtOAc (10:1); EtOAc) afforded 63 mg (46%) of **37** as a pale yellow oil. Data for **37**: ^1H NMR (300 MHz) 7.08 (d, J = 8.4, 1 H, HC(5)), 6.74 (m, 2 H, HC(6), HC(8)), 3.85 (d, J = 5.8, 1 H, HC(4a)), 3.79 (s, 3 H, $H_3C(15)$), 2.49–2.86 (m, 3 H, $H_3C(11)$ or $H_3C(12)$), 1.40 (s, 3 H, $H_3C(11$ or $12)$), 0.83 (t, J = 7.4, 3 H, $H_3C(14)$); TLC R_f 0.37 (EtOAc).

3a*H*,9*H*,9a*H*-Trihydro-3,10,10-trimethyl[3]benzopyrano-[3,2-*d*]-1,2-oxazine *N*-Oxide (38). Nitroalkene **20** (68 mg) was taken up in mesitylene (3.5 mL) and heated for 15 min in a preheated 210 °C oil bath in a sealed vial (20 mg of $CaCO_3$ was added as an acid scavenger). The solution turned orange-brown, and TLC analysis indicated the formation of product. The vial was heated for an additional 15 min, and the contents were concentrated. Purification by column chromatography (silica gel; hexane/EtOAc (2:1), EtOAc) afforded 35% of only one possible diastereomer: ^1H NMR (300 MHz) 7.20 (m, 2 H, HC(4), HC(6)), 6.92 (m, 2 H, HC(5), HC(7)), 4.42 (ddd, J = 1.7, 3.8, 11.4, 1 H, $HC(9_A)$), 3.90 (dd, J = 11.3, 1 H, $HC(9_B)$), 3.85 (m, 1 H, HC(3a)), 2.33 (m, 1 H, HC(9a)), 2.12 (s, 3 H, $H_3C(13)$), 1.54 (s, 3 H, $H_3C(11$ or $12)$), 1.46 (s, 3 H, $H_3C(11$ or $12)$); ^{13}C NMR (75.5 MHz) 154.20 (C(7a)), 131.74 (C(3)), 129.45, 122.37, 120.56, 117.43, 117.22, 82.09 (C(10)), 63.90 (C(9)), 38.05, 37.96, 36.63, 25.88, 23.53, 16.63; HRMS calcd for 247.120700, found 247.120844; TLC R_f 0.31 (EtOAc).

6*H*-3,10,10-Trimethylnaphth[10,1,9b,3a,4,5-*d*]oxazine *N*-Oxide (39). From nitroalkene **23** (242 mg, 0.990 mmol) and $SnCl_4$ (0.510 g, 0.230 mL, 1.97 mmol, 2.00 equiv) in CH_2Cl_2 (12 mL) for 3 h was obtained a very viscous yellow oil. Purification by flash column chromatography (silica gel; EtOAc) afforded 138 mg (57%) of a viscous oil. Crystallization was induced by suspending this oil in hexane and cooling in liquid nitrogen: mp 95–98 °C (hexane); ^1H NMR (300 MHz) trans adduct 7.18 (m, 4 H, HC(6–9)), 2.99 (d, J = 11.6, 1 H, HC(9b)), 2.92 (m, 2 H, $H_2C(5)$), 2.47 (m, 1 H, HC(3a)), 2.27 (m, 1 H, HC(4)), 2.11 (d, J = 1.5, 3 H, $H_3C(13)$), 1.83 (s, 3 H, $H_3C(11$ or $12)$), 1.72 (m, 1 H, HC(4)), 1.34 (s, 3 H, $H_3C(11$ or $12)$); cis adduct 7.18 (m, 4 H, HC(6-9)), 3.28 (d, J = 6.2, 1 H, HC(9b)), 2.92 (m, 2 H, $H_2C(5)$), 2.79 (m, 1 H, HC(3a)), 2.27 (m, 1 H, HC(4)), 2.20 (s, 3 H, $H_3C(13)$), 1.88 (m, 1 H, HC(4)), 1.65 (s, 3 H, $H_3C(11$ or $12)$), 1.04 (s, 3 H, $H_3C(11$ or $12)$); ^{13}C NMR (75.5 MHz) trans adduct 137.35 (C(9a)), 135.27 (C(5a)), 129.32 (C(7)), 126.73 (C(3)), 125.93, 125.68, 86.10 (C(10)), 49.76 (C(3a)), 38.49 (C(4)), 29.43 (C(5)), 28.88, 24.44, 20.54 (C(13)), 13.85 (C(11), C(12)); TLC R_f 0.22 (EtOAc). Anal. Calcd for $C_{15}H_{19}NO_2$ (245.32): C, 73.44; H, 7.81; N, 5.71. Found: C, 73.56; H, 7.89; N, 5.90.

Competition Experiments with 1-Methyl-1-nitro-2-phenylethene and 1-Methyl-1-nitro-(4-methoxyphenyl)-ethene (9 and 10). Five 25-mL, two-necked, round-bottomed flasks with stir bars were oven-dried and cooled under vacuum. Solutions of each nitroalkene in CH_2Cl_2 were freshly prepared to contain 1 mg/mL. Each of the nitroalkenes (5.0 mL **9**, 5.9 mL **10**, 0.03 mmol) was added and chilled to −78 °C followed by addition of cyclopentene (0.65 mg, 0.50 mL, 9.5 mmol, 243 equiv). The $SnCl_4$ (1.0 mL) was diluted to 10 mL with CH_2Cl_2 which was previously passed through a pipet filled with alumina under N_2. The $SnCl_4$ needed for *all five* reactions was drawn up into the syringe at once and dispensed quickly to each reaction vessel (16 mg, 72 μL, 0.61 mmol, 2.0 equiv). Indication that reactions had occurred was noted by the dark orange color that appeared on the addition of the $SnCl_4$ (M_F = 0.005). The reactions were then quenched after 1, 2, 10, 30, and 80 min, respectively, with saturated aqueous $NaHCO_3$ and allowed to warm with stirring. The reaction mixtures were diluted with EtOAc and then washed with saturated aqueous $NaHCO_3$, 0.1 M NaOH, and brine. The combined aqueous layers were extracted once with EtOAc. The combined organic extracts were dried ($MgSO_4$), filtered, concentrated in vacuo and put through a pipet of silica gel before being injected onto the HPLC. Solvent system 1 was used.

Competition Experiment with 1-Methyl-1-nitro-2-phenylethene and 1-Methyl-1-nitro-[4-(trifluoromethyl)-phenyl]ethene (9 and 11). Five 10-mL, two-necked, round-bottomed flasks with stir bars were oven-dried and then cooled under vacuum. Solutions of each nitroalkene in CH_2Cl_2 were freshly prepared to contain 1.0 mg/mL. Each of the nitroalkenes (1.0 mL **9**, 1.3 mL **11**, 0.043 mmol) was added and chilled to −78 °C followed by addition of cyclopentene (0.32 mg, 0.25 mL, 4.8 mmol, 110 equiv). The $SnCl_4$ (1.0 mL) was diluted to 10 mL with CH_2Cl_2 which had been previously passed through a pipet filled with alumina under N_2. The $SnCl_4$ needed for *all five* reactions was drawn up into the syringe at once and dispensed quickly to each reaction vessel (100 μL, 22.5 mg, 0.09 mmol, 2 quiv). Indication that reactions had occurred was noted by a yellow color that appeared on addition of the $SnCl_4$ (M_F = 0.033). The reactions were quenched after 2, 5, 10, 33, and 60 min, respectively, with saturated aqueous $NaHCO_3$ and allowed to warm with stirring. The reaction mixtures were diluted with EtOAc and then washed with saturated aqueous $NaHCO_3$, 0.1 M NaOH, and brine. The combined aqueous layers were extracted once with EtOAc. The combined organic extracts were dried ($MgSO_4$), filtered, concentrated in vacuo and put through a pipet of silica gel before being injected onto the HPLC. Solvent system 2 was used.

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Supplementary Material Available: Complete listings of infrared absorbances and mass spectral fragments for all compounds described are provided (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.