A General Method for the Preparation of 2,2-Disubstituted 1-Nitroalkenes

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A general and expeditious route for the preparation of functionalized 2,2-disubstituted 1-nitroalkenes has been developed. Conjugate 1,4-addition of complex zinc cuprates (RCu(CN)ZnI) to easily obtained (*E*)-1-nitroalkenes, followed by trapping with phenylselenenyl bromide and subsequent oxidative elimination, afforded the corresponding 2,2-disubstituted 1-nitroalkenes in good yields. 2-Alkyl-2-aryl- and 2,2-dialkyl nitroalkenes **4b–g** were prepared in 76–88% yield and obtained as *E*/*Z* isomeric mixtures, slightly favoring the *Z* isomer (~1.0:1.5, *E*/*Z*).

Introduction and Background

Conjugated nitroalkenes are useful and versatile intermediates in organic synthesis.[1] Due to the powerful electron withdrawing properties of the nitro group, they have found widespread application as Michael acceptors for the addition of stabilized carbon nucleophiles, such as enamines,[2] lithium enolates,[3] silyl enol ethers, and silyl ketene acetals.[4] In recent years, significant advances have been reported on the addition of nonstabilized organometallics derived from lithium,[5] magnesium,[6] zinc,[7] aluminum,[8] and copper.[9] In addition, nitroalkenes have found notable utility as electron-deficient dienophiles in Diels–Alder reactions.[10] Regardless of the application, the versatility of the chemistry of the nitro group stems from the ability to transform nitro-containing compounds into a variety of functionalized products such as, aldehydes, ketones, oximes, nitrones, hydroxylamines, and amines.[11]

For several years, we have developed the use of conjugated nitroalkenes as electron-deficient heterodienes in Lewis acid-promoted [4 + 2] cycloaddition reactions.[12] Most of these studies have involved 2-substituted nitroalkenes, as well as 1,2-disubstituted 1-nitroalkenes. In connection with planned total syntheses of alkaloid natural products,[13] we became interested in exploring [4 + 2] cycloadditions of 2,2-disubstituted 1-nitroalkenes.[14] Therefore, we required a general route for the preparation of various 2,2-disubstituted 1-nitroalkenes. However, it became evident that a general and practical route for the preparation of this class of compounds was lacking.[1a,9d–f,15]

Classically, nitroalkenes are prepared by a Henry reaction of a nitroalkane with a carbonyl compound,[11] followed by dehydration of the resultant 2-nitro alcohol,[16]

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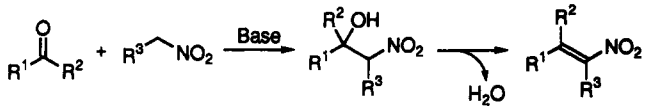
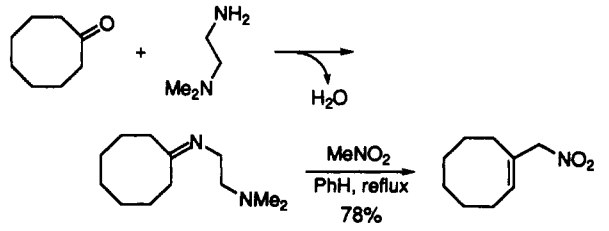
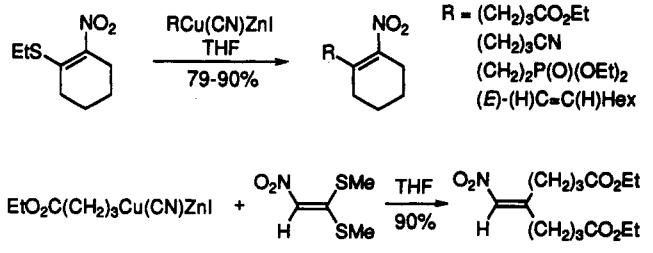
Scheme I



Scheme II



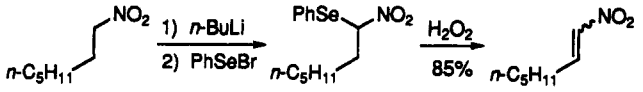
Scheme III



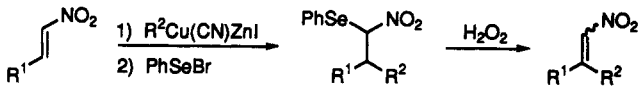
Scheme I. Unfortunately, the nitro-aldol approach is impractical for the synthesis of 2,2-disubstituted 1-nitroalkenes due to the reversibility of the reaction when ketones are employed as substrates.[17] In fact, Tamura and co-workers have utilized *N,N*-dimethylethylenediamine to drive the condensation of ketones with nitroalkanes, but the β,γ-unsaturated tautomers are the major products, Scheme II.[17c]

Very recently, Knochel and co-workers described the preparation of 2,2-disubstituted 1-nitroalkenes from the addition/elimination of copper–zinc organometallic reagents to nitroalkenes substituted with leaving groups at the β-position, Scheme III.[9d-f,18] This procedure allows for high-yield preparation of functionalized nitroalkenes, but is dependent upon the availability or ease of preparation of the starting nitro olefins. Also, when the starting nitro olefin contains two leaving groups, as with 2,2-bis(methylthio)-1-nitroethylene, only 2,2-disubstituted 1-nitroalkenes with identical 2-substituents can be prepared. Because we desired acyclic 2,2-disubstituted 1-nitroalkenes with different 2-substituents, this route was unsuitable for our needs.

Scheme IV



Scheme V



In 1981, Sakakibara et al. reported the preparation of 1-nitroalkenes from nitroalkanes utilizing selenium chemistry.[19] It was found that nitronates, generated in situ from treatment of nitroalkanes with *n*-butyllithium, were trapped upon quenching with phenylselenenyl bromide to afford the corresponding nitro selenides, Scheme IV. The selenides were oxidized with hydrogen peroxide to the selenoxides which spontaneously underwent elimination at room temperature to afford α,β-unsaturated 1-nitroalkenes in good yield.

We have developed a synthesis of 2,2-disubstituted 1-nitroalkenes, which is an amalgamation of Knochel's and Sakakibara's work, involving the conjugate addition of copper–zinc organometallics to 1-nitro olefins, followed by phenylselenation and oxidative elimination, Scheme V.[20]

Results

Initial studies were conducted with (*E*)-2-nitrostyrene[21] (**1a**) and (*E*)-1-(3,4-dimethoxyphenyl)-2-nitroethene[22] (**1b**), Table I. Utilizing a procedure developed by Knochel,[9c] organometallic reagents of the type, $R^2Cu(CN)ZnI$ (from the corresponding alkyl iodide),[23] added in a Michael-type reaction to the nitroalkenes **1** to afford, after acidic workup, the nitroalkanes **2** in 75–95% yield. The purified nitroalkanes were treated with *n*-butyllithium and the resulting lithium nitronates were quenched by the addition of phenylselenenyl bromide. The resulting selenides **3** were obtained in moderate yield (59–71%) after purification. Finally, hydrogen peroxide oxidation of the nitro selenides, at room temperature, afforded the bright yellow nitroalkenes **4** in good yield (77-93%). The nitroalkenes were obtained as *E*/*Z* isomeric mixtures, slightly enriched in the *Z* isomer (~1.0:1.5 (*E*/*Z*)). Multigram portions of the isomeric mixtures were separated by silica gel column chromatography.

The olefin geometry in **4a–d** was assigned by the ^1H NMR chemical shifts of the allylic methylene protons. For example, when the allylic methylene protons in **4b** are cis to the nitro group (*E* isomer), they are deshielded by a through-space interaction with the electron-poor nitro functionality and appear further downfield (δ = 3.06 ppm), with respect to the corresponding allylic methylene protons in the *Z* isomer (δ = 2.50 ppm), Figure 1.

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(20) Vicarious nucleophilic substitution has been employed for the preparation of 2,2-disubstituted nitroalkenes from 1-nitroalkenes using phenyl chloromethyl sulfone. Makosza, M.; Kwast, A. *Tetrahedron* **1991**, *47*, 5001–5018.

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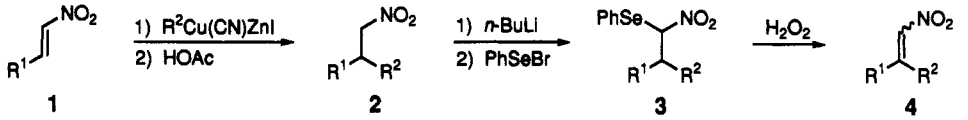
Table I. Preparation of 2,2-Disubstituted 1-Nitroalkenes



1 2 3 4

entry	R^1	R^2	nitroalkane 2 (%)	nitroselenide 3 (%)	nitroalkene 4 (%)	E/Z ratio[a]
a	phenyl	ethyl	92	59	77	1.0:2.8
b	3,4-dimethoxyphenyl	ethyl	84	68	90	1.0:1.6
c	3,4-dimethoxyphenyl	*n*-butyl	95	60	93	1.0:1.7
d	3,4-dimethoxyphenyl	*i*-butyl	75	71	80	1.0:1.4

[a] Values represent isolated ratios.

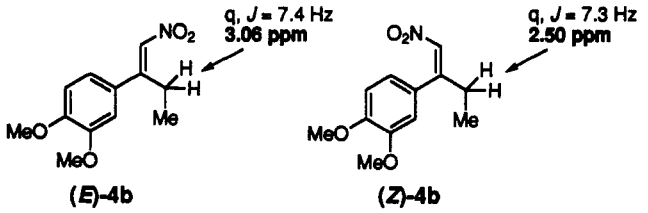
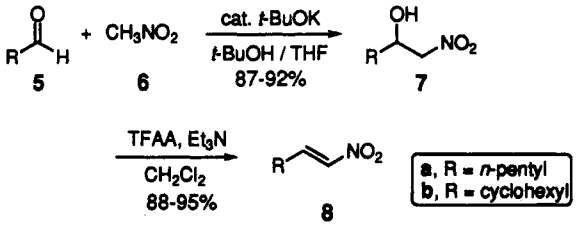


Figure 1. Characteristic ^1H NMR data.

Scheme VI

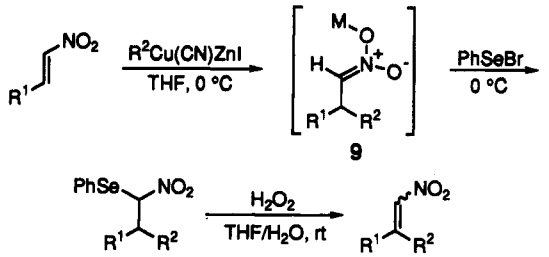


5 6 7 8

To further explore the general utility of this procedure, we sought to prepare 2,2-dialkyl-1-nitroalkenes. This synthesis required the conjugate addition of zinc–copper organometallic reagents to 2-alkyl-substituted 1-nitroalkenes. Substrates **8a** and **8b** with *n*-pentyl and cyclohexyl substituents, respectively, were prepared in high yields utilizing standard procedures, Scheme VI. A potassium *tert*-butoxide-catalyzed nitro-aldol condensation between nitromethane (**6**) and the corresponding aldehyde **5** afforded the nitro alcohols **7** in good yield (87–92%). Dehydration of the alcohols was effected upon treatment with trifluoroacetic anhydride[24] and triethylamine to afford the slightly yellow nitroalkenes **8a** and **8b**, exclusively as the trans isomers, in high yield (88–95%). The conversion of **8a** and **8b** to 2,2-dialkyl-1-nitroalkenes was accomplished by use of a streamlined "one-pot" procedure described below.

The synthesis of all 2,2-disubstituted 1-nitroalkenes (2-aryl and 2-alkyl) could be optimized by streamlining the process into a three-step, "one-pot" procedure, Table II. The improved procedure involved the direct trapping of the Michael addition products, metallonitronates **9**, with 1.5 equiv of phenylselenenyl bromide. The crude selenides **3** were isolated after aqueous workup and passage of the organic concentrate through a pad of silica gel, for removal of residual metal species. Hydrogen peroxide oxidation of the unpurified selenides in aqueous THF, at room temperature, proceeded smoothly with spontaneous selenoxide elimination to afford the desired nitroalkenes in good yield (76–83% over three steps). A comparison to

Table II. "One-Pot" Procedure for the Synthesis of 2,2-Disubstituted 1-Nitroalkenes



9 3 4

entry	R^1	R^2	nitroalkene 4 (%)	E/Z ratio[a]
b	3,4-dimethoxyphenyl	ethyl	78	1.0:1.3
c	3,4-dimethoxyphenyl	*n*-butyl	88	1.0:1.6
d	3,4-dimethoxyphenyl	*i*-butyl	83	1.0:1.5
e	phenyl	$(CH_2)_4CO_2Et$	85	1.0:1.8
f	*n*-pentyl	ethyl	76	*b*
g	cyclohexyl	ethyl	77	1.0:1.2

[a] Determined by ^1H NMR integration. [b] Unable to determine by ^1H NMR.

the previously utilized sequence reveals an increase in yield of purified nitroalkenes on the order of 27–43% for compounds **4b–d**.

Discussion

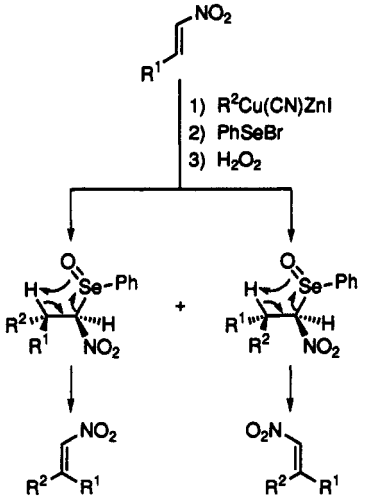
The described synthesis of 2,2-disubstituted 1-nitroalkenes is mainly a fusion of Knochel's and Sakakibara's methods and employs easily obtained starting materials and allows for the synthesis of 1-nitroalkenes with different 2-substituents. Furthermore, this route allows for the synthesis of highly functionalized 1-nitroalkenes, such as the ester-containing nitroalkene **4e**, as well as others not explicitly prepared.[10] One drawback to the procedure is that the nitroalkenes are obtained unselectively as *E*/*Z* isomeric mixtures. The isomeric mixtures of nitroalkenes were suitable for our subsequent purposes,[13] however, the isomers are usually separable by silica gel column chromatography is so desired.

In all the examples studied, the *E*/*Z* ratio of isomers was found to slightly favor the *Z* isomer. Since, selenoxide elimination is believed to be a syn-concerted process,[25] the ratio must reflect the diasteroselectivity of the initial Michael addition and selenide trapping. The two resulting nitro selenoxide diastereomers would afford the corresponding *E*- or *Z*-trisubstituted nitroalkenes as depicted in Scheme VII.

(24) The TFAA/Et_3N dehydration procedure was developed in these laboratories: Moon, Y.-C. Ph.D. Thesis, Univ. of Illinois, Urbana, IL, 1991.

(25) Sharpless, K. B.; Young, M. W.; Lauer, R. F. *Tetrahedron Lett.* 1973, *14*, 1979–1982.

Scheme VII



Conclusion

In summary, we have developed a general and high-yield route for the synthesis of functionalized 2,2-disubstituted 1-nitroalkenes. We have demonstrated the utility of this method by the synthesis of 2-aryl, 2-alkyl and α-branched 2-alkyl 2,2-disubstituted nitroalkenes **4a–g**. The nitroalkenes were obtained as E/Z isomeric mixtures, slightly favoring the Z isomer ($\sim$1.0:1.5, E/Z). The use of these nitroalkenes as substrates for [4 + 2] cycloaddition and subsequent manipulations is the subject of the following article in this issue.

Experimental Section

General. For general methods see supplementary material or ref 12h.

Materials. Solvents for extraction and chromatography were technical grade and distilled from the indicated drying agents; hexane, dichloroethane ($CaCl_2$), *tert*-butyl methyl ether (TBDME, $FeSO_4$), ethyl acetate (K_2CO_3). Tetrahydrofuran (THF) used in anhydrous reactions was distilled from sodium and benzophenone. Ethyl iodide, 1-iodobutane, 1-iodo-2-methylpropane, 1,2-dibromoethane, and ethyl 5-bromovalerate were obtained from commercial sources and distilled from CaH_2 prior to use. Hexanal, pentanal, *tert*-butanol, and chlorotrimethylsilane were obtained from commercial sources and fractionally distilled prior to use. Nitromethane was distilled from $CaCl_2$. Copper(I) cyanide (Baker) was washed with boiling H_2O, followed by EtOH, and then dried under high vacuum. Zn metal dust (Mallinckrodt, 97.1% purity), lithium chloride (Fisher), and H_2O_2 (Fisher, 30% aqueous) were used as obtained. *n*-Butyllithium (Aldrich, 2 M/hexane) was titrated prior to use. Brine refers to a saturated aqueous solution of NaCl.

Ethyl 5-iodovalerate,[26] (*E*)-2-nitrostyrene[21] (**1a**) and (*E*)-1-(3′,4′-dimethoxyphenyl)-2-nitroethane[22] (**1b**) were prepared by literature methods.

^{1}H and ^{13}C NMR chemical shifts are reported as δ values and IR absorption frequencies in cm^{-1}.

General Procedure for the Preparation of 2,2-Disubstituted 1-Nitroalkanes (2a–d) (General Procedure I). The preparation of 2-(3′,4′-dimethoxyphenyl)-1-nitrobutane (**2b**) from (*E*)-1-(3′,4′-dimethoxyphenyl)-2-nitroethene (**1b**) will serve to illustrate the general procedure utilized.

2-(3′,4′-Dimethoxyphenyl)-1-nitrobutane (2b). A suspension of zinc dust (1.70 g, 26.0 mmol, 1.45 equiv) in THF (2.0 mL) containing 1,2-dibromoethane (86.0 μL, 1.0 mmol, 0.06 equiv) was heated to 65 °C for 1 min and allowed to cool to room temperature, and chlorotrimethylsilane (102 μL, 0.80 mmol, 0.04 equiv) was added. After 15 min at room temperature, a solution of ethyl iodide (2.0 mL, 25.0 mmol, 1.4 equiv) in THF (10 mL) was slowly added. After complete addition, the reaction mixture was stirred for 12 h at 35–40 °C (some unreacted zinc remained). The resulting cloudy, gray solution was cooled to −10 °C, and a solution of copper(I) cyanide (1.97 g, 22.0 mmol, 1.23 equiv) and lithium chloride (1.87 g, 44.0 mmol, 2.46 equiv) in THF (22 mL) was rapidly added. The resulting brown mixture was stirred at 0 °C for 10 min, cooled to −78 °C, and then ready for use. A solution of **1b** (3.76 g, 17.9 mmol) in THF (65 mL) was rapidly added to the prepared organometallic reagent at −78 °C and the mixture immediately warmed to 0 °C. After stirring 4 h at 0 °C, the reaction was cooled to −78 °C, quenched by the addition of an acetic acid solution (2 mL HOAc/5 mL of THF), warmed up to 0 °C, and poured into water (100 mL). The resulting solution was extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered through a pad of Celite, and concentrated. The resulting yellow oil was purified by silica gel column chromatography (hexane/EtOAc, (3/1)) and bulb-to-bulb distillation to afford 3.59 g (84%) of analytically pure **2b** as a clear, colorless oil, which solidified after standing several hours at room temperature: bp 200 °C (0.1 Torr); mp 49–50.5 °C; ^{1}H NMR (300 MHz) 6.83 (d, J = 8.3, 1 H, HC(5′)), 6.37 (dd, J = 1.5, J = 8.3, 1 H, HC(6′)), 6.67 (d, J = 1.5, 1 H, HC(2′)), 4.53 (m, 2 H, H_2C(1)), 3.88 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 3.30 (m, 1 H, HC(2)), 1.70 (m, 2 H, H_2C(3)), 0.85 (t, J = 7.3, 3 H, H_3C(4)); ^{13}C NMR (75.5 MHz) 148.99 (C(3′)), 148.18 (C(4′)), 131.56 (C(1′)), 119.44 (C(6′)), 111.24 (C(5′)), 110.53 (C(2′)), 80.85 (C(1)), 55.77 (OCH_3), 55.70 (OCH_3), 45.60 (C(2)), 26.05 (C(3)), 11.47 (C(4)); IR (CCl_4) 2965 (s), 1554 (s), 1377 (s); MS (70 eV) 239 (M^+, 31); TLC R_f 0.40 (hexane/EtOAc, (2/1)). Anal. Calcd for $C_{12}H_{17}NO_4$ (239.27): C, 60.24; H, 7.16; N, 5.85. Found: C, 60.26; H, 7.14; N, 5.85.

2-Phenyl-1-nitrobutane (2a). General Procedure I. A solution of **1a** (2.34 g, 15.7 mmol) was allowed to react with EtCu(CN)ZnI (22.0 mmol, 1.4 equiv) to afford, after acidic workup, a yellow oil. The oil was purified by silica gel column chromatography (hexane/EtOAc, (6/1)) and bulb-to-bulb distillation to afford 2.58 g (92%) of **2a** as a clear, colorless oil: bp 125 °C (0.2 Torr); ^{1}H NMR (300 MHz) 7.36–7.17 (m, 5 H, Ph), 4.56 (m, 2 H, H_2C(1)), 3.36 (m, 1 H, HC(2)), 1.68 (m, 2 H, H_2C(3)), 0.84 (t, J = 7.4, 3 H, H_3C(4)); IR (neat) 2968(s), 1547 (s), 1380 (s); MS (10 eV) 179 (M^+, 4), 133 (11), 132 (100), 117 (5), 91 (15); TLC R_f 0.43 (hexane/EtOAc, (4/1)). The spectral data matches that reported in the literature.[27]

2-(3′,4′-Dimethoxyphenyl)-1-nitrohexane (2c). General Procedure I. A solution of **1b** (3.29 g, 15.7 mmol) was allowed to react with *n*-BuCu(CN)ZnI (22.0 mmol, 1.4 equiv) to afford, after acidic workup, a yellow oil. The oil was purified by silica gel column chromatography (hexane/EtOAc, (5/1)) and bulb-to-bulb distillation to afford 4.00 g (95%) of **2c** as a clear, colorless oil, which solidified after standing several hours at room temperature: bp 200 °C (0.2 Torr); mp 64.5–65.5 °C; ^{1}H NMR (300 MHz) 6.82 (d, J = 8.2, 1 H, HC(5′)), 6.73 (dd, J = 1.8, J = 8.2, 1 H, HC(6′)), 6.67 (d, J = 1.8, 1 H, HC(2′)), 4.52 (m, 2 H, H_2C(1)), 3.88 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 3.37 (m, 1 H, HC(2)), 1.65 (m, 2 H, H_2C(3)), 1.29–1.13 (m, 4 H, H_2C(4), H_2C(5)), 0.84 (t, J = 7.2, 3 H, H_3C(6)); ^{13}C NMR (75.5 MHz) 148.97 (C(3′)), 148.13 (C(4′)), 131.82 (C(1′)), 119.38 (C(6′)), 111.22 (C(5′)), 110.45 (C(2′)), 81.09 (C(1)), 55.76 (OCH_3), 55.68 (OCH_3), 43.94 (C(2)), 33.56 (C(3)), 28.94 (C(4)), 22.72 (C(5)), 13.73 (C(6)); IR (CCl_4) 2934 (s), 1555 (m), 1377 (m); MS (70 eV) 267 (M^+, 23); TLC R_f 0.48 (hexane/EtOAc, (2/1)). Anal. Calcd for $C_{14}H_{21}NO_4$ (267.32): C, 62.90; H, 7.92; N, 5.24. Found: C, 63.04; H, 8.04; N, 5.25.

2-(3′,4′-Dimethoxyphenyl)-4-methyl-1-nitropentane (2d). General Procedure I. A solution of **1b** (0.395 g, 1.89 mmol) was allowed to react with *i*-BuCu(CN)ZnI (2.64 mmol, 1.4 equiv) to afford, after acidic workup, a yellow oil. The oil was purified by silica gel column chromatography (hexane/EtOAc, (4/1)) and bulb-to-bulb distillation to afford 0.380 g (75%) of analytically pure **2d** as a clear, colorless oil: bp 160 °C (0.1 Torr); ^{1}H NMR (400 MHz) 6.81 (d, J = 8.2, 1 H, HC(5′)), 6.75 (dd, J = 2.0, J = 8.2, 1 H, HC(6′)), 6.67 (d, J = 2.0, 1 H, HC(2′)), 4.48 (m, 2 H,

(26) House, H. O., Babad, H. *J. Org. Chem.* **1963**, *28*, 90–92.

(27) Ohta, H.; Kobayashi, N.; Ozaki, K. *J. Org. Chem.* **1989**, *54*, 1802–1804.

$H_2C(1)$), 3.87 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 3.47 (m, 1 H, HC(4)), 1.39 (m, 2 H, $H_2C(3)$), 0.87 (m, 6 H, $H_3C(5)$, $H_3C(6)$); ^{13}C NMR (75.5 MHz) 149.07 (C(3')), 148.25 (C(4''), 131.74 (C(1')), 119.54 (C(6')), 111.31 (C(5'), 110.51 (C(2')), 81.49 (C(1)), 55.87 (OCH_3), 55.76 (OCH_3), 41.97 (C(2)), 41.82 (C(3)), 25.01 (C(4)), 23.32 (C(5) or C(6)), 21.31 (C(6) or C(5)); IR (neat) 2957 (s), 1551 (s), 1379 (s); MS (70 eV) 267 (M^+, 22); TLC R_f 0.25 (hexane/EtOAc, (4/1)). Anal. Calcd for $C_{14}H_{21}NO_4$ (267.32): C, 62.90; H, 7.92; N, 5.24. Found: C, 62.99; H, 7.95; N, 5.27.

General Procedure for the Preparation of 2,2-Disubstituted 1-Nitroalkenes (4a–d) from the Corresponding 2,2-Disubstituted 1-Nitroalkanes (2a–d) (General Procedure II). The preparation of 1-nitro-2-(3',4'-dimethoxyphenyl)-1-butene (**4b**) from nitroalkane **2b** will serve to illustrate the general procedure utilized.

(*E*)-1-Nitro-2-(3',4'-dimethoxyphenyl)-1-butene ((*E*)-4b) and (*Z*)-1-Nitro-2-(3',4'-dimethoxyphenyl)-1-butene ((*Z*)-4b). A solution of *n*-butyllithium (1.4 M in hexane, 5.0 mL, 6.90 mmol, 1.1 equiv) was slowly added over 5 min to a solution of **2b** (1.5 g, 6.27 mmol, 1.0 equiv) in THF (13 mL) at 0 °C. After stirring 15 min at 0 °C, a solution of PhSeBr (2.96 g, 12.5 mmol, 2.0 equiv) in THF (7 mL) was quickly added, and the resulting brown reaction mixture was left to stir 40 min at 0 °C. The reaction was quenched by the addition of water (5 mL) at 0 °C, poured into water (100 mL), and extracted with EtOAc (3 × 150 mL). The combined organic layers were dried (Na_2SO_4), filtered through a pad of Celite, and concentrated. The resulting brown oil was purified by silica gel column chromatography (hexane/EtOAc, (5/1)) to afford 1.67 g (68%) of selenide **3b** as a heavy yellow oil. The selenide was not characterized, but directly subjected to oxidation conditions. A 30% aqueous solution of hydrogen peroxide (3.8 mL) was added to a solution of **3b** (1.67 g, 4.24 mmol) in THF (20 mL) at room temperature. After stirring 3 h at room temperature, the reaction mixture was poured into water (150 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with water and brine (1 × 30 mL, 1 × 30 mL), dried ($MgSO_4$), filtered through a pad of Celite, and concentrated. The resulting yellow oil was purified by silica gel column chromatography (hexane/EtOAc, (3/1)) to afford 0.912 g (90%) of a mixture of (*E*)- and (*Z*)-nitroalkenes **4b** as a heavy bright yellow oil. The isomers were separated by MPLC (15% acetone/hexane) to give 0.308 g of (*E*)-**4b** as a yellow liquid and 0.483 g of (*Z*)-**4b** as a yellow solid, plus 0.040 g of combined isomers (1:1.6, *E*/*Z* isolated ratio). An analytical sample of (*E*)-**4b** was obtained after diffusion pump (1×10^{-4} Torr) bulb-to-bulb distillation. Recrystallization of (*Z*)-**4b** (hexane/EtOAc) afforded yellow prisms: (*E*)-**4b**: bp 100 °C (1×10^{-4} Torr); ^1H NMR (300 MHz) 7.22 (s, 1 H, HC(1)), 7.06 (dd, J = 2.1, J = 8.5, 1 H, HC(6')), 6.90 (m, 2 H, HC(2'), HC(5')), 3.92 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 3.06 (q, J = 7.4, 2 H, $H_2C(3)$), 1.16 (t, J = 7.4, 3 H, $H_3C(4)$); ^{13}C NMR (75.5 MHz) 153.73 (C(2)), 151.03 (C(3')), 149.13 (C(4')), 134.62 (C(1')), 129.13 (C(1)), 120.40 (C(6')), 111.13 (C(5')), 109.77 (C(2')), 55.95 (OCH_3), 55.93 (OCH_3), 24.46 (C(3)), 13.00 (C(4)); IR (neat) 1514 (s), 1333 (s); MS (70 eV) 237 (M^+, 100); TLC R_f 0.29 (15% acetone/hexane). Anal. Calcd for $C_{12}H_{15}NO_4$ (237.25): C, 60.75; H, 6.37; N, 5.90. Found: C, 60.62; H, 6.39; N, 5.86. (*Z*)-**4b**: mp 81–82 °C (hexane/EtOAc); ^1H NMR (300 MHz) 7.00 (s, 1 H, HC(1)), 6.88 (d, J = 8.2, 1 H, HC(5')), 6.76 (dd, J = 1.8, J = 8.2, 1 H, HC(6')), 6.68 (d, J = 1.8, 1 H, HC(2')), 3.90 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 2.50 (q, J = 7.3, 2 H, $H_2C(3)$), 1.08 (t, J = 7.3, 3 H, $H_3C(4)$); ^{13}C NMR (75.5 MHz) 153.24 (C(2)), 149.30 (C(3')), 148.67 (C(4')), 133.67 (C(1')), 128.29 (C(1)), 119.26 (C(6')), 110.82 (C(5')), 109.98 (C(2')), 55.81 (OCH_3), 55.63 (OCH_3), 30.73 (C(3)), 11.84 (C(4)); IR (CCl_4) 1526 (s), 1340 (m); MS (70 eV) 238 (M^+, 14); TLC R_f 0.23 (15% acetone/hexane). Anal. Calcd for $C_{12}H_{15}NO_4$ (237.25): C, 60.75; H, 6.37; N, 5.90. Found: C, 60.76; H, 6.40; N, 5.92.

(*E*)-1-Nitro-2-phenyl-1-butene ((*E*)-4a) and (*Z*)-1-Nitro-2-phenyl-1-butene ((*Z*)-4a). General Procedure II. A solution of **2a** (2.45 g, 13.7 mmol) was treated with *n*-butyllithium (1.3 M, 11.6 mL, 15.0 mmol, 1.1 equiv) followed by a solution of PhSeBr (6.47 g, 27.4 mmol, 2.0 equiv) in THF (10 mL). The resulting oil was purified by silica gel column chromatography (hexane/EtOAc, (20/1)) to afford 2.72 g (59%) of **3a** as a slightly yellow, heavy oil. After treatment with H_2O_2 (30% aqueous, 8.1 mL) and workup, the crude organic concentrate was purified by silica gel column chromatography (hexane/EtOAc, (50/1)) to give 0.260 g of (*E*)-**4a** as a yellow oil, and 0.726 g of (*Z*)-**4a** as a yellow oil, plus 0.126 g of mixed isomers (1:2.8, *E*/*Z* isolated ratio) for an overall combined yield of 1.11g (77%). An analytical sample of (*Z*)-**4a** was obtained after bulb-to-bulb distillation. (*Z*)-**4a**: bp 100 °C (0.2 Torr); ^1H NMR (400 MHz) 7.43–7.38 (m, 3 H, Ph), 7.19–7.16 (m, 2 H, Ph), 7.04 (t, J = 1.3, 1 H, HC(1)), 2.50 (dq, J_d = 1.3, J_q = 7.3, 2 H, $H_2C(3)$), 1.08 (t, J = 7.3, 3 H, $H_3C((4))$; ^{13}C NMR (100.6 MHz) 153.78 (C(2)), 136.38 (C(1')), 134.02 (C(1)), 128.38 (C(3')), 128.31 (C(4')), 126.31 (C(2')), 30.84 (C(3)), 11.58 (C(4)); IR (neat) 2975 (m), 1520 (s), 1345 (s); MS (10 eV) 177 (M^+, 43); TLC R_f 0.18 (hexane/EtOAc, (20/1)). Anal. Calcd for $C_{10}H_{11}NO_2$ (177.20): C, 67.78; H, 6.26; H, 6.26; N, 7.90. Found: C, 67.77; H, 6.26; N, 7.90. (*E*)-**4a**: ^1H NMR (300 MHz) 7.46–7.19 (m, 6 H, HC(1), Ph), 3.09 (q, J = 7.5, 2 H, $H_2C(3)$), 1.16 (t, J = 7.5, 3 H, $H_3C(4)$; IR (neat) 1514 (s), 1337 (s); MS (10 eV) 177 (M^+, 55); TLC R_f 0.29 (hexane/EtOAc, (20/1)). The spectral data for (*E*)-**4a** matches that reported in the literature.[27]

(*E*)-1-Nitro-2-(3',4'-dimethoxyphenyl)-1-hexene ((*E*)-4c) and (*Z*)-1-Nitro-2-(3',4'-dimethoxyphenyl)-1-hexene ((*Z*)-4c). General Procedure II. A solution of **2c** (3.40 g, 12.7 mmol) was treated with *n*-butyllithium (1.3 M, 10.8 mL, 14.0 mmol, 1.1 equiv) followed by a solution of PhSeBr (6.00 g, 27.4 mmol, 2.0 equiv) in THF (10 mL). The resulting oil was purified by silica gel column chromatography (hexane/EtOAc, (6/1)) to afford 3.21 g (60%) of selenide **3c** as a heavy yellow oil. After treatment with H_2O_2 (30% aqueous, 7.5 mL) and workup, the crude concentrate was purified by silica gel column chromatography (hexane/EtOAc, (4/1)) to afford 1.86 g (93%) of a mixture of (*E*)- and (*Z*)-nitroalkenes **4c** as a thin yellow oil. The isomers of a 0.912-g of **4c** were separated by MPLC (10% acetone/hexane) to give 0.263 g of (*E*)-**4c** as a yellow oil and 0.434 g of (*Z*)-**4c** as a yellow oil, plus 0.195 g of combined isomers (1:1.7, *E*/*Z* isolated ratio). A second MPLC (10% acetone/hexane) purification of (*E*)-**4c** provided an analytically pure sample. An analytical sample of (*Z*)-**4c** was obtained after bulb-to-bulb distillation. (*E*)-**4c**: ^1H NMR (300 MHz) 7.24 (s, 1 H, HC(1)), 7.06 (dd, J = 2.2, J = 8.4, 1 H, HC(6')), 6.92–6.89 (m, 2 H, HC(3'), HC(5')), 3.92 (s, 6 H, OCH_3, OCH_3), 3.03 (t, J = 7.6, 2 H, $H_2C(3)$), 1.53–1.37 (m, 4 H, $H_2C(4)$, $H_2C(5)$), 0.91 (t, J = 7.1, 3 H, $H_3C(6)$); ^{13}C NMR (75.5 MHz) 154.71 (C(2)), 151.02 (C(3')), 149.16 (C(4')), 134.92 (C(1')), 129.57 (C(1)), 120.35 (C(6')), 111.17 (C(5')), 109.81 (C(2')), 55.99 (OCH_3), 55.95 (OCH_3), 30.76, 30.74, 22.84 (C(5)), 13.70 (C(6)); IR (neat) 2958 (s), 1516 (s), 1334 (s); (MS 70 eV) 265 (M^+, 85); TLC R_f 0.18 (10% acetone/hexane). Anal. Calcd for $C_{14}H_{19}NO_4$ (265.31): C, 63.38; H, 7.22; N, 5.28. Found: C, 63.56; H, 7.27; N, 5.29. (*Z*)-**4c**: bp 175 °C (0.1 Torr); ^1H NMR (300 MHz) 7.00 (s, 1 H, HC(1)), 6.88 (d, J = 8.3, 1 H, HC(5')), 6.75 (dd, J = 2.0, J = 8.3, 1 H, HC(6')), 6.67 (d, J = 2.0, 1 H, HC(2')), 3.90 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 2.45 (t, J = 6.7, 2 H, $H_2C(3)$), 1.42–1.25 (m, 4 H, $H_2C(4)$, $H_2C(5)$), 0.88 (t, J = 7.1, 3 H, $H_3C(6)$); ^{13}C NMR (75.5 MHz) 152.05 (C(2)), 149.39 (C(3')), 148.70 (C(4')), 133.99 (C(1')), 128.19 (C(1)), 119.41 (C(6')), 110.85 (C(5')), 110.12 (C(2')), 55.87 (OCH_3), 55.72 (OCH_3), 37.12 (C(3)), 29.02 (C(4)), 22.00 (C(5)), 13.60 (C(6)); IR (neat) 2957 (s), 1520 (s), 1340 (s); MS (70 eV) 265 (M^+, 100); TLC R_f 0.14 (10% acetone/hexane). Anal. Calcd for $C_{14}H_{19}NO_4$ (265.31): C, 63.38; H, 7.22; N, 5.28. Found: C, 63.61; H, 7.28; N, 5.34.

(*E*)-1-Nitro-2-(3',4'-dimethoxyphenyl)-4-methyl-1-pentene ((*E*)-4d) and (*Z*)-1-Nitro-2-(3',4'-dimethoxyphenyl)-4-methyl-1-pentene ((*Z*)-4d). General Procedure II. A solution of **2d** (2.36 g, 8.83 mmol) was treated with *n*-butyllithium (1.3 M, 7.5 mL, 9.71 mmol, 1.1 equiv) followed by a solution of PhSeBr (4.17 g, 17.7 mmol, 2.0 equiv) in THF (5 mL). The resulting oil was purified by silica gel column chromatography (hexane/EtOAc, (8/1)) to afford 2.65 g (71%) of selenide **3d** as a heavy yellow oil. After treatment with H_2O_2 (30% aqueous, 6.3 mL) and workup, the crude concentrate was purified by silica gel column chromatography (hexane/EtOAc, (8/1)) to afford 1.33 g (80%) of a mixture of (*E*)- and (*Z*)-nitroalkenes **4d** as a thin, yellow oil. The isomers, of a 0.680-g sample of **4d**, were separated by MPLC (10% acetone/hexane) to give 0.223 g of (*E*)-**4d** as a yellow solid and 0.307 g of (*Z*)-**4d** as a yellow oil (1.0:1.4, *E*:*Z* isolated ratio). Recrystallization (hexane) of (*E*)-**4d** afforded analytically pure bright yellow prisms. An analytical sample of (*Z*)-**4d** was obtained after bulb-to-bulb distillation. (*E*)-**4d**: mp 79–80 °C; ^1H NMR

(300 MHz) 7.28 (s, 1 H, HC(1)), 7.04 (dd, J = 2.0, J = 8.3, 1 H, HC(6')), 6.90 (m, 2 H, HC(2'), HC(5')), 3.93 (m, 6 H, OCH_3, OCH_3), 3.05 (d, J = 7.2, 2 H, $H_2C(3)$), 1.69 (m, 1 H, HC(4)), 0.91 (d, J = 6.7, 6 H, $H_3C(5)$, $H_3C(6)$); ^{13}C NMR (75.5 MHz) 153.73 (C(2)), 150.86 (C(3')), 149.14 (C(4')), 135.78 (C(1')), 129.86 (C(2)), 120.31 (C(6')), 111.13 (C(5')), 109.84 (C(2')), 56.00 (OCH_3), 55.91 (OCH_3), 38.54 (C(4)), 28.39 (C(3)), 22.38 (C(5), C(6)); IR (neat) 2960 (s), 1518 (s), 1338 (s); MS (70 eV) 265 (M^+, 100); TLC R_f 0.18 (10% acetone/hexane). Anal. Calcd for $C_{14}H_{19}NO_4$ (265.31): C, 63.38; H, 7.22; N, 5.28. Found: C, 63.40; H, 7.32; N, 5.20. (*Z*)-**4d**: bp 175 °C (0.1 Torr); ^1H NMR (300 MHz) 6.99 (s, 1 H, HC(1)), 6.88 (d, J = 8.3, 1 H, HC(5')), 6.77 (dd, J = 1.8, J = 8.3, 1 H, HC(6')), 6.68 (d, J = 1.8, 1 H, HC(2')), 3.90 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 2.31 (d, J = 7.3, 2 H, $H_2C(3)$), 1.59 (m, 1 H, HC(4)), 0.91 (d, J = 6.6, 6 H, $H_3C(5)$, $H_3C(6)$); ^{13}C NMR (75.5 MHz) 150.85 (C(2)), 149.52 (C(3')), 148.74 (C(4')), 134.50 (C(1')), 127.94 (C(1)), 119.64 (C(6')), 110.87 (C(5')), 110.29 (C(2')), 55.93 (OCH_3), 55.74 (OCH_3), 46.41 (C(4)), 26.00 (C(3)), 22.09 (C(5), C(6)); IR (neat) 2957 (s), 1518 (s), 1338 (s); MS (70 eV) 265 (M^+, 100); TLC R_f 0.15 (10% acetone/hexane). Anal. Calcd for $C_{14}H_{19}NO_4$ (265.31): C, 63.38; H, 7.22; N, 5.28. Found: C, 63.38; H, 7.24; N, 5.27.

1-Nitroheptan-2-ol (7a). Potassium *tert*-butoxide (0.168 g, 3.0 mmol, 0.1 equiv) was added to a stirred solution of hexanal (**5a**) (3.00 g, 30 mmol), nitromethane (**6**) (2.44 mL, 45 mmol, 1.5 equiv), THF (7.5 mL), and *tert*-butanol (7.5 mL) at 0 °C. The stirred mixture was allowed to warm to room temperature over 2 h and stirred an additional 8 h. The mixture was poured into water (100 mL) and extracted with TBDME (3 × 100 mL). The combined organic layers were washed with water and brine (1 × 100 mL, 1 × 75 mL), dried ($MgSO_4$), filtered through pad of Celite, and concentrated. The resulting slightly yellow oil was purified by bulb-to-bulb distillation to afford 4.21 g (87%) **7a** as a clear viscous oil: bp 115 °C (0.4 Torr); ^1H NMR (400 MHz) 4.45–4.29 (m, 3 H, $H_2C(1)$, HC(2)), 2.65 (br, 1 H, OH), 1.56–1.26 (m, 8 H, $H_2C(3)$, $H_2C(4)$, $H_2C(5)$, $H_2C(6)$), 0.89 (t, J = 7.0, 3 H, $H_3C(7)$); ^{13}C NMR (100.6 MHz) 80.63 (C(1)), 68.66 (C(2)), 33.63 (C(3)), 31.41 (C(4)), 24.79 (C(5)), 22.41 (C(6)), 13.89 (C(7)); IR (neat) 3418 (br, s), 2932 (s), 1553 (s), 1381 (s); MS (CI) 162 (M^+ + 1, 49); TLC R_f 0.39 (hexane/EtOAc, (4/1)). Anal. Calcd for $C_7H_{15}NO_3$ (161.20): C, 52.16; H, 9.38; N, 8.69. Found: C, 52.14; H, 9.46; N, 8.70.

1-Cyclohexyl-2-nitroethanol (7b). Potassium *tert*-butoxide (0.150 g, 2.7 mmol, 0.1 equiv) was added to a stirred solution of cyclohexanecarboxaldehyde (**5b**) (3.00 g, 26.7 mmol), nitromethane (**6**) (2.20 mL, 40.1 mmol, 1.5 equiv), THF (7.0 mL), and *tert*-butanol (7.0 mL) at 0 °C. The stirred mixture was allowed to warm to room temperature over 2 h and stirred an additional 10 h. The mixture was poured into water (100 mL) and extracted with TBDME (3 × 100 mL). The combined organic layers were washed with brine (1 × 50 mL), dried ($MgSO_4$), filtered through a pad of Celite, and concentrated. The resulting oil was purified by bulb-to-bulb distillation to afford 4.23 g (92%) of **7b** as a clear viscous oil: bp 100 °C (0.4 Torr); ^1H NMR (400 MHz) 4.44 (m, 2 H, $H_2C(2)$), 4.05 (m, 1 H, HC(1)), 2.81 (br, 1 H, OH), 1.81–1.61 (m, 5 H), 1.42 (m, 1 H), 1.27–0.99 (m, 5 H); ^{13}C NMR (100.6 MHz) 79.26 (C(2)), 72.78 (C(1)), 41.30 (C(1')), 28.63 (C(2') or C(6')), 27.82 (C(6') or C(2')), 25.95 (C(4')), 25.74 (C(3') or C(5')), 25.61 (C(5') or C(3')); IR (neat) 3426 (br, s), 2928 (s), 1553 (s), 1385 (m); MS (CI) 174 (M^+ + 1, 6); TLC R_f 0.50 (hexane/EtOAc, (4/1)). Anal. Calcd for $C_8H_{15}NO_3$ (173.21): C, 55.47; H, 8.73; N, 8.09. Found: C, 55.55; H, 8.84; N, 8.15.

(*E*)-1-Nitro-1-heptene (8a). Trifluoroacetic anhydride (2.19 mL, 15.5 mmol, 1 equiv) was added to a solution of β-nitro alcohol **7a** (2.50 g, 15.5 mmol) in dichloromethane (18 mL) at −10 °C. The resulting solution was allowed to stir 2 min, and then triethylamine (4.32 mL, 31.0 mmol, 2 equiv) was slowly added dropwise over 15 min and the reaction mixture stirred for an additional 30 min at −10 °C. The resulting mixture was poured into dichloromethane (125 mL) and washed with saturated aqueous NH_4Cl solution (2 × 50 mL). The aqueous layers were back-extracted with dichloromethane (2 × 30 mL) and the combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), filtered through a pad of Celite, and concentrated. The resulting yellow oil was passed through a pad of silica gel (hexanes/EtOAc, (20/1)) and purified by bulb-to-bulb distillation to afford 2.12 g (95%) of (*E*)-**8a** as a thin yellow oil: bp 80 °C (0.5 Torr); ^1H NMR (400 MHz) 7.22 (dt, J_d = 7.5, J_t = 13.4, 1 H, HC(2)), 6.93 (d, J = 13.4, 1 H, HC(1)), 2.21 (m, 2 H, $H_2C(3)$), 1.45 (m, 2 H, $H_2C(4)$), 1.26 (m, 4 H, $H_2C(5)$, $H_2C(6)$), 0.84 (t, J = 7.1, 3 H, $H_3C(7)$); ^{13}C NMR (100.6 MHz) 142.71 (C(2)), 139.33 (C(1)), 31.02 (C(3)), 28.17 (C(4)), 27.18 (C(5)), 22.10 (C(6)), 13.63 (C(7)); IR (neat) 2957 (s), 1649 (m), 1524 (s), 1352 (s); MS (CI) 144 (M^+ + 1, 100); TLC R_f 0.30 (hexane/EtOAc, (20/1)). Anal. Calcd for $C_7H_{13}NO_2$ (MW 143.19): C, 58.72; H, 9.15; N, 9.78. Found: C, 58.46; H, 9.08; N, 9.70.

(*E*)-1-Nitro-1-cyclohexylethene (8b). Trifluoroacetic anhydride (5.13 mL, 36.3 mmol, 1.05 equiv) was added to a solution of the β-nitro alcohol **7b** (6.00g g, 34.6 mmol) in dichloromethane (43 mL) at −10 °C. The resulting solution was allowed to stir 2 min, and then triethylamine (10.1 mL, 72.7 mmol, 2.1 equiv) was slowly added dropwise over 15 min and the reaction mixture was stirred for an additional 30 min at −10 °C. The resulting mixture was poured into dichloromethane (250 mL) and washed with saturated aqueous NH_4Cl solution (2 × 100 mL). The aqueous layers were back-extracted with dichloromethane (2 × 50 mL) and the combined organic layers were washed with brine (75 mL), dried ($MgSO_4$), filtered through a pad of Celite, and concentrated. The resulting yellow oil was passed through a pad of silica gel (hexanes/EtOAc, (20/1)) and purified by bulb-to-bulb distillation to afford 4.73 g (88%) of (*E*)-**8b** as a thin yellow oil: bp 100 °C (0.4 Torr); ^1H NMR (400 MHz) 7.16 (dd, J = 7.3, J = 13.4, 1 H, HC(2)), 6.89 (d, J = 13.4, 1 H HC(1)), 2.21 (m, 1 H, HC(1')), 1.77–1.63 (m, 5 H), 1.33–1.09 (m, 5 H); ^{13}C NMR (100.6 MHz) 147.12 (C(2)), 138.04 (C(1)), 37.33 (C(1')), 31.19 (C(2')), 25.41 (C(4')), 25.24 (C(3')); IR (neat) 2928 (s), 1645 (s), 1520 (s), 1350 (s); MS (CI) 156 (M^+ + 1, 100); TLC R_f 0.28 (hexane/EtOAc, (20/1)). Anal. Calcd for $C_8H_{13}NO_2$ (155.20): C, 61.91; H, 8.44; N, 9.03. Found: C, 61.85; H, 8.46; N, 8.95.

"One Pot" Procedure for the Preparation of 2,2-Disubstituted 1-Nitroalkenes (General Procedure III). The preparation of 1-nitro-2-(3',4'-dimethoxyphenyl)-1-butene (**4a**) from (*E*)-1-(3',4'-dimethoxyphenyl)-2-nitroethene (**1b**) will serve to illustrate the general procedure utilized.

1-Nitro-2-(3',4'-dimethoxyphenyl)-1-butene (28a). A suspension of zinc dust (2.71 g, 41.4 mmol, 1.66 equiv) in THF (3 mL) was sonicated for 30 min at room temperature in an ultrasonic cleaning bath. The ultrasonic bath was removed and replaced with a magnetic stirring apparatus. Dibromoethane (0.137 mL, 1.60 mmol, 0.06 equiv) was added and the stirred suspension heated at 65 °C for 2 min. After cooling to room temperature, chlorotrimethylsilane (0.161 mL, 1.30 mmol, 0.05 equiv) was added and the mixture stirred for 15 min, before the addition of a solution of ethyl iodide (3.18 mL, 39.8 mmol, 1.60 equiv) in THF (16 mL). The resulting suspension was stirred for 12 h at 38 °C (some unreacted zinc remained). The resulting cloudy gray solution was cooled to −10 °C, and a solution of copper(I) cyanide (3.13 g, 35.0 mmol, 1.4 equiv) and lithium chloride (2.97 g, 70.0 mmol, 2.8 equiv) in THF (35 mL) was rapidly added. The brown mixture was stirred for 10 min at 0 °C, cooled to −30 °C, and then ready for use. A solution of **1b** (5.22 g, 25.0 mmol) in THF (90 mL) was added to the prepared organometallic reagent at −30 °C. The mixture was allowed to warm to 0 °C and stirred for 2 h and then quenched with a solution of PhSeBr (8.25 g, 35.0 mmol, 1.40 equiv) in THF (16 mL). After one additional hour, the reaction mixture was poured into water (150 mL) and extracted with TBDME (3 × 100 mL). The combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), concentrated, and passed through a pad of silica gel (hexanes/EtOAc, (4/1)) to afford the crude selenide **3b** as a brown oil. Crude **3b** was dissolved in THF (100 mL) and treated with a 30% aqueous solution of H_2O_2 (25 mL) at room temperature. The stirred solution warmed internally as the brown color dissipated to a bright yellow. After 2 h, the reaction mixture was poured into water (100 mL) and extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed with water and brine (1 × 50 mL, 1 × 50 mL), dried ($MgSO_4$), filtered through a pad of Celite, and concentrated. The crude concentrate was purifed by silica gel column chromatography (hexanes/EtOAc, (3/1)) to afford 4.62 g (78%) of **4b** as a bright yellow oil. The product was determined to be a 1.0:1.3 (*E*/*Z*) mixture of isomers

by ^{1}H NMR integration. The spectral data was in agreement with that previously reported for compounds (*E*)-**4a** and (*Z*)-**4a**.

1-Nitro-2-(3′,4′-dimethoxyphenyl)-1-hexene (4c). General Procedure III. A solution of **1b** (1.58 g, 7.54 mmol) in THF (27 mL) was allowed to react with *n*-BuC(CN)ZnI (10.6 mmol, 1.4 equiv) and quenched with a solution of PhSeBr (2.49 g, 10.56 mmol, 1.4 equiv) in THF (6 mL). After workup, the crude selenide **3c** was passed through a silica gel plug (hexane/EtOAc (4/1)) and concentrated and treated with H_2O_2 (30% aqueous 7.5 mL). After aqueous workup, the crude organic concentrate was purified by silica gel column chromatography (hexanes/EtOAc, (4/1)) to afford 1.75 g (88%) of **4c** as a bright yellow oil. The product was determined to be a 1.0:1.6 (*E*/*Z*) mixture of isomers by ^{1}H NMR integration. The spectral data was in agreement with that previously reported for compounds (*E*)-**4c** and (*Z*)-**4c**.

1-Nitro-2-(3′,4′-dimethoxyphenyl)-4-methyl-1-pentene (4d). General Procedure III. A solution of **1b** (1.58 g, 7.54 mmol) in THF (27 mL) was allowed to react with *n*-BuCu(CN)ZnI (10.6 mmol, 1.4 equiv) and quenched with a solution of PhSeBr (2.49 g, 10.56 mmol, 1.4 equiv) in THF (6 mL). After workup, the crude selenide **3d** was passed through a silica gel plug (hexane/EtOAc (4/1)), concentrated, and treated with H_2O_2 (30% aqueous, 7.5 mL). After aqueous workup, the crude organic concentrate was purified by silica gel column chromatography (hexanes/EtOAc, (4/1)) to afford 1.66 g (83%) of **4d** as a bright yellow oil. The product was determined to be a 1.0:1.5 (*E*/*Z*) mixture of isomers by ^{1}H NMR integration. The spectral data was in agreement with that previously reported for compounds (*E*)-**4d** and (*Z*)-**4d**.

Ethyl 7-Nitro-6-phenyl-1-heptenoate (4e). General Procedure III. A solution of **1a** (0.93 g, 6.23 mmol) in THF (5 mL) was allowed to react with $EtO_2C(CH_2)_4Cu(CN)ZnI$ (8.72 mmol, 1.4 equiv) and quenched with a solution of PhSeBr (2.06 g, 8.72 mmol, 1.5 equiv) in THF (4 mL). After workup, the crude selenide **3e** was passed through a silica gel plug (hexane/EtOAc (4/1)), concentrated, and treated with H_2O_2 (30% aqueous, 6.2 mL). After aqueous workup, the crude organic concentrate was purified by silica gel column chromatography (hexanes/EtOAc, (7/1)) to afford 1.47 g (85%) of analytically pure **4e** as yellow oil. The product was determined to be a 1.0:1.8 (*E*/*Z*) mixture of isomers by ^{1}H NMR integration: ^{1}H NMR (400 MHz) 7.44–7.04 (m, 6 H, Ph, HC(7)), 4.09 (m, 2 H, OCH_2CH_3), 3.08 (t, J = 7.8, 0.72 H, $H_2C_E(5)$), 2.48 (t, J = 7.5, 1.28 H, $H_2C_Z(5)$), 2.27 (m, 2 H, $H_2C(2)$), 1.73–1.40 (m, 4 H, $H_2C(3)$, $H_2C(4)$), 1.22 (m, 3 H, OCH_2CH_3); ^{13}C NMR (100.6 MHz) (*Z*)-**4e**: 173.08 (C(1)), 151.87 (C(6)), 136.12 (Ph), 134.56 (C(7)), 129.04 (Ph), 128.48 (Ph), 126.43 (Ph), 60.35 (OCH_2CH_3), 37.23 (C(5)), 33.72 (C(2)), 26.30, 24.17. (*E*)-**4e**: 173.25 (C(1)), 154.03 (C(6), 137.00 (Ph), 135.97 (C(7)), 130.28 (Ph), 128.65 (Ph), 127.02 (Ph), 60.26 (OCH_2CH_3), 33.78 (C(5)), 30.83 (C(2)), 27.68, 24.80. (*Z*)-**4e**, (*E*)-**4e**: 14.16 (OCH_2CH_3); IR (neat) 2942 (m), 1730 (s), 1520 (s), 1341 (s); MS (CI) 278 (M^+ + 1, 46); TLC R_f 0.27 and 0.18 (hexane/EtOAc, (7/1)). Anal. Calcd for $C_{15}H_{19}NO_4$ (277.32): C, 64.97; H, 6.91; N, 5.05. Found: C, 64.95; H, 6.96; N, 5.04.

1-Nitro-2-ethyl-1-heptene (4f). General Procedure III. A solution of **8a** (2.00 g, 14.0 mmol) in THF (8 mL) was allowed to react with EtCu(CN)ZnI (21.0 mmol, 1.5 equiv) and quenched with a solution of PhSeBr (4.96 g, 21.0 mmol, 1.5 equiv) in THF (10 mL). After workup, the crude selenide **3f** was passed through a silica gel plug (hexane/EtOAc (50/1)), concentrated, and treated with H_2O_2 (30% aqueous, 14 mL). After aqueous workup, the crude organic concentrate was purified by silica gel column chromatography (hexanes/EtOAc, 50/1) to afford, after bulb-to-bulb distillation, 1.83 g (76%) of analytically pure **4f** as slightly yellow oil. The *Z*/*E* ratio could not be unambiguously determined by ^{1}H NMR. (*E*/*Z*)-**4f**: bp 80 °C (0.4 Torr); ^{1}H NMR (400 MHz) 7.26 (s, 1 H, HC(1)), 2.61 (m, 2 H, $H_2C(3)$, $H_2C(1')$), 2.21 (m, 2 H, $H_2C(3)$, $H_2C(8)$), 1.49 (m, 2 H, $H_2C(4)$), 1.32 (M, 4 H, $H_2C(5)$, $H_2C(6)$), 1.12 (m, 3 H, $H_3C(7)$). 0.89 (m, 3 H, $H_3C(2')$); ^{13}C NMR (100.6 MHz) (**a**) 159.00 (C(2)), 134.34 (C(1)), 35.52 (C(3)), 31.33 (C(1′)), 27.65 (C(4)), 26.90 (C(5)), 22.31 (C(6)), 13.87 (C(7)), 12.21 (C(2′)); (**b**) 158.94 (C(2)), 134.55 (C(1)), 31.98 (C(3)), 31.66 (C(1′)), 29.18 (C(4)), 24.84 (C(5)), 22.34 (C(6)), 13.98 (C(7)), 11.75 (C(2′)); IR (neat) 2959 (s), 1634 (m), 1518 (s), 1343 (s); MS (CI) 172 (M^+ + 1, 100); TLC R_f 0.24 (hexane/EtOAc, (50/1)). Anal. Calcd for $C_8H_{17}NO_2$ (171.24): C, 63.13; H, 10.01; N, 8.21. Found: C, 63.05; H, 10.01; N, 8.19.

1-Nitro-2-cyclohexyl-1-butene (4g). General Procedure III. A solution of **8b** (2.17 g, 14.0 mmol) in THF (8 mL) was allowed to react with EtCu(CN)ZnI (21.0 mmol, 1.5 equiv) and quenched with a solution of PhSeBr (4.96 g, 21.0 mmol, 1.5 equiv) in THF (10 mL). After workup, the crude selenide **3f** was passed through a silica gel plug (hexane/EtOAc (50/1)), concentrated, and treated with H_2O_2 (30% aqueous, 14 mL). After aqueous workup, the crude organic concentrate was purified by silica gel column chromatography (hexanes/EtOAc, 50/1) to afford, after bulb-to-bulb distillation, 1.99 g (77%) of analytically pure **4g** as a slightly yellow oil. The product was determined to be a 1.0:1.2 (*E*/*Z*) mixture of isomers by ^{1}H NMR integration: (*E*/*Z*)-**4g**: bp 73–75 °C (0.1 Torr); ^{1}H NMR (400 MHz) 6.85 (s, 0.57 H, $HC_Z(1)$), 6.76 (s, 0.43 H, $HC_E(1)$), 3.44 (m, 0.57 H, $HC_Z(1')$), 2.58 (q, J = 7.6, 1.14 H, $H_2C_E(3)$), 2.24 (dq, J_d = 1.5, J_q = 7.3, 0.86 H, $H_2C_Z(3)$), 2.05 (m, 0.43 H, $HC_E(1')$), 1.83–1.64 (m, 5 H), 1.40–1.05 (m, 8 H); ^{13}C NMR (100.6 MHz) (*E*)-**4g**: 163.32 (C(2)), 134.56 (C(1)), 45.00 (C(1′)), 31.53 (C(2′)), 26.19 (C(3′)), 25.73, 23.94, 12.61 (C(4)). (*Z*)-**4g**: 161.79 (C(2)), 133.74 (C(1)), 38.86 (C(1′)), 30.39 (C(2′)), 26.02 (C(3′)), 25.80, 24.30, 11.88 (C(4)); IR (neat) 2930 (s), 1628 (m), 1516 (s), 1341 (s); MS (CI) 184 (M^+ + 1, 100); TLC R_f 0.23 (hexane/EtOAc, (50/1)). Anal. Calcd for $C_{10}H_{17}NO_2$ (183.25): C, 65.54; H, 9.35; N, 7.64. Found: C, 65.66; H, 9.50; N, 7.42.

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Supplementary Material Available: A description of general experimental methods along with complete listings of infrared absorbances and mass spectral fragments for all compounds described are provided (4 pages). This material is contained in 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.