hydroxy deriv), 123834-66-2; **29**, 123834-86-6; **30**, 123834-87-7; **31**, 30315-04-9; **32**, 123834-88-8; **33**, 123834-89-9; **34**, 123834-90-2; **35**, 123834-91-3; **36**, 123834-92-4; **37**, 123834-93-5; **38**, 123834-89-9; **39**, 123834-94-6; **40**, 123834-88-8; **41**, 123834-95-7; **41** (20-alcohol), 111324-69-7; **42**, 123835-02-9; **43**, 123834-96-8; **44**, 123857-41-0; **45**, 123834-97-9; (*E*)-CH_2=C(OTMS)C(CH_3)=$CHOCH_3$, 54125-02-9; (±)-$BrCH_2CH(OMe)Br$, 66556-47-6; 20-(benzoyloxy)-1β-*tert*-butyldimethylsilyloxy-18-ethoxy-18-nor-9β-picrasan-12-one, 123929-84-0; 20-(benzoyloxy)-16-ethoxy-1β-hydroxy-18-nor-9β-picrasan-12-one, 123834-71-9.

Supplementary Material Available: Experimental details for the preparation of compounds **7**, **8**, **32–41**, and **43** (9 pages). Ordering information is given on any current masthead page.

Synthesis and Application of Tertiary Allylic Nitro Compounds

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A new procedure was developed for the synthesis of tertiary allylic nitro compounds. Secondary nitroalkanes (comprising nitrocyclohexane, 2-nitroheptane, 4-nitro-1-pentene, and 2-nitropropane) were treated with 1.5 equiv of electron-deficient acetylenes (including methyl propiolate, dimethyl acetylenedicarboxylate, and 3-butyn-2-one) to give the corresponding tertiary allylic nitro adducts in 62–90% yields. These reactions required 5.0 equiv of potassium fluoride as the base, 1.0 equiv of tetra-*n*-butylammonium chloride as the phase-transfer catalyst, and dimethyl sulfoxide as the solvent. Tertiary allylic nitro compounds were also synthesized by the double Michael addition of 1 equiv of primary nitroalkanes to 2 equiv of electron-deficient acetylenes in the presence of potassium fluoride, tetra-*n*-butylammonium chloride, and dimethyl sulfoxide. Thus, nitroethane and methyl 4-nitrobutyrate (**5**) individually reacted with 3.0–3.5 equiv of methyl propiolate to give dimethyl 3-methyl-3-nitro-1,4-pentadiene-1,5-dicarboxylate (**6**) in 75% yield and dimethyl 3-[2-(methoxycarbonyl)ethyl]-3-nitro-1,4-pentadiene-1,5-dicarboxylate (**7**) in 53% yield, respectively. Furthermore, the double Michael addition proceeded well when two different Michael acceptors were added sequentially: acetylenes followed by electron-deficient alkenes. Reaction of nitroethane with 1.0 equiv of methyl propiolate or 3-butyn-2-one and then with 2.0 equiv of methyl vinyl ketone afforded (*E*)-methyl 4-methyl-4-nitro-7-oxo-2-octenoate (**8**) in 60% yield and (*E*)-5-methyl-5-nitro-3-nonene-2,8-dione (**9**) in 52% yield, respectively. Alkenes containing an electron-withdrawing substituent and an alkyl group at the α- or the β-position were also employed in the double Michael addition; however, they must be used as the first Michael acceptor. Thus, nitroethane reacted with 1.0 equiv of ethyl methacrylate and then with 1.5 equiv of methyl propiolate to give (*E*)-methyl 6-(ethoxycarbonyl)-4-methyl-4-nitro-2-heptenoate (**10**) in 41% yield. In a similar reaction involving 2-cyclohexen-1-one, instead of ethyl methacrylate, a mixture of (*E*)- and (*Z*)-methyl 4-nitro-4-(3-oxocyclohexyl)-2-pentenoate (**11**) was obtained in 50% yield. The newly developed double Michael addition was used as the key step in a total synthesis of (±)-norsolanadione, a biologically active terpenoid.

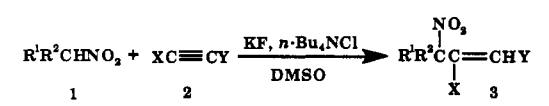
Introduction

The nitro group in organic compounds plays an important role in carbon–carbon bond formation and functionality transformation.[1,2] In the latter category, tertiary allylic nitro compounds are versatile synthetic intermediates because they can be easily transformed to different classes of organic materials. The tertiary allylic nitro group can be readily replaced by nucleophiles, such as amines,[3] enolates,[3-5] lithium dialkylcuprates,[6] sulfinates,[7] and thiolates.[7] Also, the nitro group can be reduced to an amine[2] or be replaced by a hydride.[8] The applicability of tertiary allylic nitro compounds in synthesis is nevertheless limited because only a few *general* methods exist for their preparation. We therefore sought a new, efficient method for the synthesis of tertiary allylic nitro compounds.

Tanikaga et al. reported a procedure for the preparation of tertiary allylic nitro compounds from nitroalkanes and phenyl vinyl sulfoxide.[9] This procedure requires two steps and high reaction temperature (180 °C). Ono, Tamura, and co-workers developed another method, in which nitroalkenes react with aldehydes or electron-deficient olefins.[10,11] Preparation of the starting material nitroalkanes usually requires two steps or more.[12]

We report herein that the Michael addition of secondary nitroalkanes to electron-deficient acetylenes gave good to excellent yields of tertiary allylic nitro compounds. This class of compounds also can be obtained by an unprecedented double Michael addition of primary nitroalkanes

Scheme I



† Research fellow of the Alfred P. Sloan Foundation (1986–1990).

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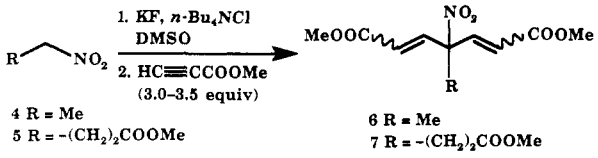
Table I. Synthesis of Tertiary Allylic Nitro Compounds 3 by the Michael Addition of Secondary Nitroalkanes 1 to Acetylenes 2[a]

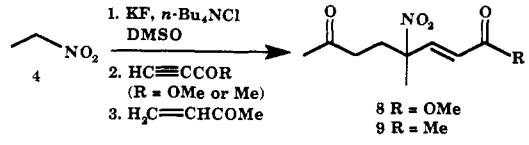
R^1	R^2	X	Y	adduct	% yield[b]
Me	Me	H	COOMe	**3a**	90
	$-(CH_2)_5-$	H	COOMe	**3b**	89
Me	n-C_5H_{11}	H	COOMe	**3c**	86
Me	CH_2=$CHCH_2$	H	COOMe	**3d**	82
Me	Me	COOMe	COOMe	**3e**	62
	$-(CH_2)_5-$	COOMe	COOMe	**3f**	75
Me	Me	H	COMe	**3g**	80
	$-(CH_2)_5-$	H	COMe	**3h**	80

[a] Reaction conditions: KF, n-Bu_4NCl, and $R^1R^2HNO_2$ (molar ratio = 5:1:1) were stirred in DMSO (1.0 M) for 0.5 h; the acetylene (XC≡CY, 1.5 equiv) was then added, and stirring was continued for an additional hour. [b] Yields refer to pure, isolated products.

Scheme II



Scheme III



to electron-deficient acetylenes and alkenes. We applied the double Michael addition to a total synthesis of (±)-norsolanadione, a biologically active terpenoid.

Results

We reacted secondary nitroalkanes **1** and 1.5 equiv of activated acetylenes **2** in the presence of 5.0 equiv of potassium fluoride (KF) and 1.0 equiv of tetra-n-butylammonium chloride (n-Bu_4NCl) in dimethyl sulfoxide (DMSO) at room temperature (Scheme I). Tertiary allylic nitro compounds **3** were obtained in good to excellent yields (62–90%, Table I). When 3-butyn-2-one and dimethyl acetylenedicarboxylate were used as Michael acceptors, much heat was generated. Therefore, it was necessary to add these acetylenes to the nitroalkanes slowly.

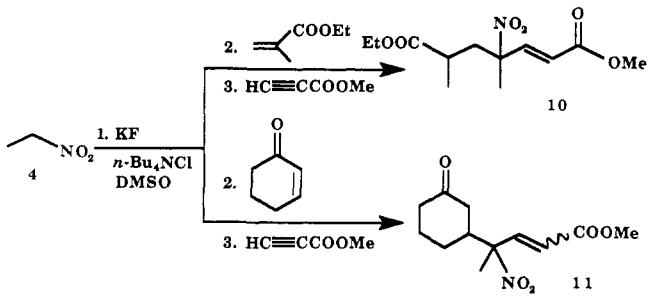
When 2-nitropropane, nitrocyclohexane, 2-nitroheptane, and 4-nitro-1-pentene individually reacted with methyl propiolate, the E/Z ratios of adducts **3a–d** were approximately 4:1. The ratios did not change with reaction time. Compared with the Z isomers, the E isomers had longer retention time of GC, smaller R_f values for TLC, and larger coupling constants for the olefinic protons ($J \approx 16.0$ Hz for the E isomers and 12.6 Hz for the Z isomers). We were able to separate the E and the Z isomers of **3d** by radial thin-layer chromatography.

The Michael addition of nitroethane and nitrocyclohexane to 3-butyn-2-one gave adducts **3g** and **3h**, respectively, as a mixture of E and Z isomers. The E/Z ratio was dependent upon the reaction time. For **3g**, the E/Z ratio was 62:38 after 1 h; an 80% yield of the E isomer was isolated as the only adduct after 72 h. For **3h**, mainly the Z isomer was obtained within 3 h; the E/Z ratio changed to 86:14 after 72 h. Furthermore, reaction of 2-nitropropane and nitrocyclohexane with dimethyl acetylenedicarboxylate produced **3e** and **3f**, respectively, as single isomers. Their stereoconfigurations were not identified.

We found that primary nitroalkanes **4** and **5** individually reacted with excess methyl propiolate, in the presence of KF and n-Bu_4NCl, to give double Michael adducts **6** (75%) and **7** (53%, Scheme II). Both **6** and **7** were obtained as a mixture of stereoisomers.

Next we explored the feasibility of the double Michael addition of a primary nitro compound with an acetylene and then with a second Michael acceptor in situ (Scheme III). To a stirred solution of 1.0 equiv of nitroethane, 5.0 equiv of KF, and 1.0 equiv of n-Bu_4NCl in DMSO were added 1.0 equiv of methyl propiolate and then 2.0 equiv of methyl vinyl ketone. The double Michael adduct **8** was obtained as the only enedione in 60% yield. Based on the coupling constant ($J \approx 16.1$ Hz) of the olefinic protons, we identified **8** as the E isomer. By adding 1.0 equiv of 3-butyn-2-one and 2.0 equiv of methyl vinyl ketone in sequence to 1.0 equiv of nitroethane, we obtained allylic nitro compound **9** exclusively in the E form in 52% yield.

Scheme IV



We found that electron-deficient alkenes with an alkyl substituent at either the α- or the β-position were also suitable Michael acceptors (Scheme IV). Thus, 1.0 equiv of nitroethane reacted sequentially with 1.0 equiv of ethyl methacrylate and 1.0 equiv of methyl propiolate in the presence of 5.0 equiv of KF, 1.0 equiv of n-Bu_4NCl, and DMSO to afford a 41% yield of adduct **10**, which was a 2:3 mixture of diastereomers. The ^1H NMR spectrum of **10** indicated that only the E isomer was obtained ($J_{CH=CH}$ = 16.0 Hz). Compound **10** was unstable to GC conditions. Furthermore, use of 1.0 equiv of 2-cyclohexen-1-one and 1.0 equiv of methyl propiolate as Michael acceptors gave adduct **11** in 50% yield (Scheme IV).

We used the new procedure of the double Michael addition as the key step in a total synthesis of (±)-norsolanadione (**14**). (−)-Norsolanadione was isolated from aged Burley,[13,14] Turkish,[15] and Greek[16] tobacco leaves. The yield (<0.02%) is generally low.[15] Norsolanadione is an attractant for *tabakoshibanmushi*, a pest insect that infests stored foods and tobacco.[17] In additon, norsolanadione is a flavorant and flavor enhancer for tobacco.[18]

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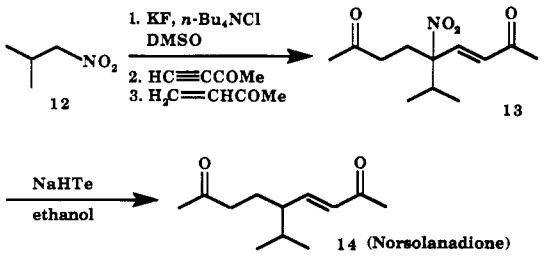
Scheme V



Racemic norsolanadione was first synthesized in 1965 by Johnson et al.[19] An improved synthesis[20] and a patented method[21] were published later.

We treated 1.0 equiv of 2-methyl-1-nitropropane (**12**)[22] with 1.0 equiv of 3-butyn-2-one and then with 2.0 equiv of methyl vinyl ketone in the presence of 5.0 equiv of KF, 1.0 equiv of n-Bu_4NCl, and DMSO (Scheme V). The double Michael adduct **13** was obtained in 51% yield. By using the procedure developed by Suzuki et al.,[23] we reduced allylic nitro compound **13** with sodium hydrogen telluride (NaHTe)[24] to give (±)-norsolanadione (**14**) in 64% yield. Although NaHTe can reduce α,β-unsaturated ketones to the corresponding saturated carbonyl compounds,[25] the nitro group was apparently more reactive in our case.

Discussion

Battersby et al.[26] found that secondary nitro compound 2-nitro-1,3-diphenylpropane adds to methyl propiolate in the presence of $KF{\cdot}2H_2O$, n-Bu_4NCl, and dimethylformamide. However, this procedure cannot be generalized for the preparation of various tertiary allylic nitro compounds.[26] In order to solve this problem, we used KF as the base, n-Bu_4NCl as the phase-transfer catalyst, and DMSO as the solvent for the reaction of nitroalkanes with electron-deficient acetylenes. Consequently, tertiary allylic nitro compounds were obtained in good to excellent yields.

Our choice of KF is based on previous findings[27,28] that fluoride ions can catalyze the Michael addition of nitroalkanes to electron-deficient alkenes. We used DMSO as the solvent because KF would be an effective base in polar, aprotic media.[29] However, the phase-transfer catalyst n-Bu_4NCl is needed to bring the fluoride anions into the organic solvent.[29]

Battersby et al. attempted to obtain tertiary allylic nitro compounds by reacting nitroalkanes with dimethyl acetylenedicarboxylate, but was not successful.[26] Nevertheless, we were able to obtain **3e** and **3f** in 62% and 75% yields, respectively. Belyaev et al. prepared **3h** from sodium cyclohexylnitronate and methyl 2-chlorovinyl ketone in 61% yield.[30] Our method led to **3h** in a better yield (80%).

The double Michael addition occurs between primary nitroalkanes and 2 equiv of electron-deficient olefins.[31] Primary nitroalkanes can also react sequentially with two different C–C double bonds in the same molecule.[32-34] However, to the best of our knowledge, the double Michael addition is unprecedented between primary nitroalkanes and acetylenes.[35] Our results demonstrate the feasibility of the double Michael addition of nitroalkanes to two electron-deficient acetylenes or to one electron-deficient acetylene and one alkene (Schemes II and III).

We found that electron-deficient alkenes with an alkyl substituent at either the α- or the β-position were also suitable Michael acceptors (Scheme IV). It is difficult to add secondary nitronates to alkenes that contain an electron-withdrawing group and an alkyl group at either the α- or the β-position.[27,36] Thus, such alkenes must be used as the first Michael acceptor in the newly developed double addition procedure.

Conclusion

Michael additions of secondary nitroalkanes to electron-deficient acetylenes in the presence of KF, n-Bu_4NCl, and DMSO gave tertiary allylic nitro compounds in good to excellent yields. Nitro compounds in this family were also generated from primary nitroalkanes and electron-deficient acetylenes and alkenes by a double Michael addition. This unprecedented double Michael addition was applied as the key step in a total synthesis of terpeniod (±)-norsolanadione.

Experimental Section

Infrared (IR) spectra were measured on a Perkin-Elmer 599B, 710B, or a Fourier-Transform 1600 spectrophotometer. The wavenumbers reported are referenced to the polystyrene 1601-cm^{-1} absorption. Infrared absorption intensities are designated by use of the following abbreviations: s, strong; m, medium; w, weak. Proton NMR spectra were obtained on a Varian CFT-20 (80 MHz) spectrometer by use of chloroform-d as solvent and Me_4Si as internal standard. Multiplicities are recorded by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; J, coupling constant (hertz). High-resolution mass spectra were obtained with a VG Analytical 70-S mass spectrometer. Ethyl acetate and hexanes from Tilley Chemical Co. were dried and distilled over CaH_2. Ethanol (anhydrous, 200 proof) was purchased from the Warner-Graham Co. and used directly. 2-Methyl-1-nitropropane,[22] 4-nitro-1-pentane,[37] and 2-nitroheptane[38] were prepared by following the published procedures. All other nitro compounds, all acetylenes, all alkenes, potassium fluoride, sodium borohydride, tetra-n-butylammonium chloride, and tri-n-butyltin hydride were purchased from Aldrich Chemical Co. and were used directly without purification. Tellurium (−30 mesh) was purchased from Alfa Products and was used directly without purification. Dimethyl sulfoxide was purchased from J. T. Baker Chemical Co. and dried over 4A molecular sieves. Melting points were obtained with a Büchi 510 melting point apparatus and are uncorrected. Analytical thin-layer chromatography (TLC) was performed on precoated plates (silica gel GHLF), purchased from Analtech Inc. Visualization of spots

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on TLC plates was done by use of UV light and/or 2.5% phosphomolybdic acid in ethanol with heating. Mixtures of ethyl acetate and hexanes were used as eluants. Gas chromatography analyses were performed on a Hewlett-Packard 5794 instrument equipped with a 12.5-m cross-linked methyl silicone gum capillary column (0.2-mm i.d.). Purification by gravity column chromatography was carried out by use of EM Reagents silica gel 60 (particle size 0.063–0.200 mm, 70–230 mesh ASTM). Separations by radial thin-layer chromatography were performed on a Model 7924T Chromatotron from Harrison Research. The plates (1- or 2-mm thickness) were coated with EM Reagents silica gel 60 PF_{254} containing gypsum.

General Procedure for the Preparation of Allylic Nitro Compounds. To a 10-mL pear-shaped flask were added tetra-*n*-butylammonium chloride (1.0 equiv), potassium fluoride (5.0 equiv), DMSO (1.0 M), and the nitro compound (1.0 equiv). After the solution was stirred for 30 min at room temperature, the acetylene was added, and stirring was continued for an additional hour. The reaction was quenched with water, and the solution was extracted two times with diethyl ether. The combined organic layers were washed with 10% aqueous HCl and brine, dried over $MgSO_4$, filtered, and concentrated to give an oil. The oil was chromatographed to afford the desired allylic nitro compound.

(*E*)- and (*Z*)-Methyl 4-Methyl-4-nitro-2-pentenoate (3a). The general procedure was followed. Reagents added into the reaction flask were tetra-*n*-butylammonium chloride (145 mg, 0.523 mmol, 1.0 equiv), potassium fluoride (152 mg, 2.62 mmol, 1.0 equiv), DMSO (0.52 mL), 2-nitropropane (46.6 mg, 0.523 mmol, 1.0 equiv), and methyl propiolate (66.2 mg, 0.785 mmol, 1.5 equiv). After workup and purification by gravity column chromatography (20% EtOAc in hexanes as eluant), the isomeric allylic nitro compounds **3a** were obtained as a yellow oil in 90% yield (81.7 mg, 0.472 mmol, *E* isomer:*Z* isomer = 73:26): TLC R_f 0.47 (*Z* isomer) and 0.41 (*E* isomer) (20% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 100 °C) t_R 3.13 min (*Z* isomer) and 4.26 min (*E* isomer); ^1H NMR ($CDCl_3$) δ 1.76 (s, 6 H, $(CH_3)_2CNO_2$, *E* isomer), 1.86 (s, 6 H, $(CH_3)_2CNO_2$, *Z* isomer), 3.70 (s, 3 H, CO_2CH_3, *Z* isomer), 3.78 (s, 3 H, CO_2CH_3, *E* isomer), 5.95 (d, J = 12.6 Hz, 1 H, C=$CHCO_2$, *Z* isomer), 6.00 (d, J = 16.0 Hz, 1 H, C=$CHCO_2$, *E* isomer), 6.38 (d, J = 12.6 Hz, 1 H, CH=C, *Z* isomer), 7.19 (d, J = 16.0 Hz, 1 H, CH=C, *E* isomer); IR (neat) 2975 (m), 2925 (m), 2850 (w), 1710 (s, C=O), 1650 (w), 1530 (s, NO_2), 1450 (m), 1420 (m), 1380 (m), 1360 (s, NO_2), 1330 (m), 1300 (s), 1280 (m), 1190 (s), 1160 (m), 1120 (m), 1020 (w), 990 (w), 960 (w), 820 (w), 800 (w) cm^{-1}; exact mass calcd for $C_6H_8NO_3$ ($M^{\bullet+}$ – $^{\bullet}OMe$) 142.0504, found 142.0509.

(*E*)- and (*Z*)-Methyl 3-(1-Nitrocyclohexyl)-2-propenoate (3b). The general procedure was followed. Reagents added into the reaction flask were tetra-*n*-butylammonium chloride (443 mg, 1.59 mmol, 1.0 equiv), potassium fluoride (463 mg, 7.97 mmol, 5.0 equiv), DMSO (1.60 mL), nitrocyclohexane (206 mg, 1.59 mmol, 1.0 equiv), and methyl propiolate (201 mg, 2.39 mmol, 1.5 equiv). After workup and purification by gravity column chromatography (20% EtOAc in hexanes as eluant), the isomeric allylic nitro compounds **3b** were obtained as a yellow oil in 89% yield (303 mg, 1.42 mmol, *E* isomer:*Z* isomer = 78:22): TLC R_f 0.48 (*Z* isomer) and 0.41 (*E* isomer) (20% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 150 °C) t_R 3.68 min (*Z* isomer) and 4.39 min (*E* isomer); ^1H NMR ($CDCl_3$) δ 1.05–2.50 (m, 10 H, $(CH_2)_5$), 3.69 (s, 3 H, CO_2CH_3, *Z* isomer), 3.76 (s, 3 H, CO_2CH_3, *E* isomer), 6.01 (d, J = 12.6 Hz, 1 H, C=$CHCO_2$, *Z* isomer), 6.01 (d, J = 16.0 Hz, C=$CHCO_2$, *E* isomer), 6.27 (d, J = 12.6 Hz, 1 H, CH=C, *Z* isomer), 6.93 (d, J = 16.0 Hz, 1 H, CH=C, *E* isomer); IR (neat) 2940 (s), 2860 (m), 1720 (s, C=O), 1650 (w), 1540 (s, NO_2), 1440 (m), 1430 (m), 1380 (w), 1340 (m, NO_2), 1310 (m), 1270 (m), 1190 (m), 1170 (m), 1030 (w), 1000 (w), 970 (w), 900 (w), 830 (w), 810 (w), 720 (w) cm^{-1}; exact mass calcd for $C_9H_{12}NO_3$ ($M^{\bullet+}$ – $^{\bullet}OMe$) 182.0817, found 182.0822.

(*E*)- and (*Z*)-Methyl 4-Methyl-4-nitro-2-nonenoate (3c). The general procedure was followed. Reagents added into the reaction flask were tetra-*n*-butylammonium chloride (334 mg, 1.20 mmol, 1.0 equiv), potassium fluoride (349 mg, 6.00 mmol, 5.0 equiv), DMSO (1.20 mL), 2-nitroheptane[38] (175 mg, 1.20 mmol, 1.0 equiv), and methyl propiolate (152 mg, 1.80 mmol, 1.5 equiv). After workup and purification by gravity column chromatography (10% EtOAc in hexanes as eluant), the isomeric allylic nitro compounds **3c** were obtained as a yellow oil in 86% yield (237 mg, 1.03 mmol, *E* isomer:*Z* isomer = 76:24): TLC R_f 0.41 (*Z* isomer) and 0.34 (*E* isomer) (10% EtOAc in hexanes); ^1H NMR ($CDCl_3$) δ 0.60–0.95 (m, 3 H, CH_3), 1.00–1.40 (m, 6 H, $(CH_2)_3$), 1.71 (s, 3 H, CH_3CNO_2, *E* isomer), 1.84 (s, 3 H, CH_3CNO_2, *Z* isomer), 1.90–2.25 (m, 2 H, CH_2CNO_2), 3.70 (s, 3 H, CO_2CH_3, *Z* isomer), 3.78 (s, 3 H, CO_2CH_3, *E* isomer), 5.95 (d, J = 16.0 Hz, 1 H, C=$CHCO_2$, *E* isomer), 5.96 (d, J = 12.8 Hz, 1 H, C=$CHCO_2$, *Z* isomer), 6.45 (d, J = 12.8 Hz, 1 H, CH=C, *Z* isomer), 7.24 (d, J = 16.0 Hz, 1 H, CH=C, *E* isomer); IR (neat) 2950 (m), 2860 (w), 1725 (s, C=O), 1650 (w), 1540 (s, NO_2), 1460 (w), 1435 (m), 1385 (w), 1345 (m, NO_2), 1325 (m), 1280 (m), 1200 (m), 1180 (m), 1020 (w), 980 (w), 845 (w), 820 (w) cm^{-1}; exact mass calcd for $C_{10}H_{16}NO_3$ ($M^{\bullet+}$ – $^{\bullet}OMe$) 198.1130, found 198.1133.

(*E*)- and (*Z*)-Methyl 4-Methyl-4-nitro-2,6-heptadienoate (3d). The general procedure was followed. Reagents added into the reaction flask were tetra-*n*-butylammonium chloride (135 mg, 0.484 mmol, 1.0 equiv), potassium fluoride (141 mg, 2.42 mmol, 5.0 equiv), DMSO (0.48 mL), 4-nitro-1-pentene[37] (55.7 mg, 0.484 mmol, 1.0 equiv), and methyl propiolate (61.0 mg, 0.726 mmol, 1.5 equiv). After workup and purification by gravity column chromatography (20% EtOAc in hexanes as eluant), the isomeric allyic nitro compounds **3d** were obtained as a colorless oil in 82% yield (79.1 mg, 0.397 mmol, *E* isomer:*Z* isomer = 78:22). The isomers were separated by Chromatotron (1-mm plate; 20% EtOAc in hexanes as eluant).

For (*E*)-**3d**: 64% yield (61.7 mg, 0.310 mmol); TLC R_f 0.48 (20% EtOAc, in hexanes); ^1H NMR ($CDCl_3$) δ 1.72 (s, 3 H, CH_3CNO_2), 2.79 (d, J = 6.6 Hz, 2 H, CH_2), 3.78 (s, 3 H, CO_2CH_3), 5.00–5.75 (m, 3 H, CH_2=CH), 5.98 (d, J = 16.0 Hz, 1 H, C=$CHCO_2$), 7.21 (d, J = 16.0 Hz, 1 H, CH=C); IR (neat) 3000 (w), 2960 (w), 1730 (s, C=O), 1660 (w), 1550 (s, NO_2), 1440 (m), 1390 (m), 1350 (m, NO_2), 1320 (s), 1280 (m), 1205 (m), 1180 (m), 1110 (w), 980 (w), 945 (w), 910 (w), 840 (w) cm^{-1}; exact mass calcd for $C_8H_{10}NO_3$ ($M^{\bullet+}$ – $^{\bullet}OMe$) 168.0661, found 168.0662.

For (*Z*)-**3d**: 18% yield (17.4 mg, 0.0873 mmol); TLC R_f 0.55 (20% EtOAc in hexanes); ^1H NMR ($CDCl_3$) δ 1.85 (s, 3 H, CH_3CNO_2), 2.94 (d, J = 6.6 Hz, 2 H, CH_2), 3.71 (s, 3 H, CO_2CH_3), 5.00–5.90 (m, 3 H, CH_2=CH), 5.99 (d, J = 12.6 Hz, 1 H, C=$CHCO_2$), 6.41 (d, J = 12.6 Hz, 1 H, CH=C); IR (neat) 2995 (w), 2950 (w), 1725 (s, C=O), 1640 (w), 1550 (s, NO_2), 1440 (m), 1410 (m), 1380 (m), 1350 (m, NO_2), 1210 (s), 1180 (s), 1000 (m), 930 (m), 860 (w), 825 (m) cm^{-1}; exact mass calcd for $C_8H_{10}NO_3$ ($M^{\bullet+}$ – $^{\bullet}OMe$) 168.0661, found 168.0660.

Dimethyl 2-(1-Nitro-1-methylethyl)-2-butenedioate (3e). The general procedure was followed except dimethyl acetylenedicarboxylate was added over a 30-min period. Reagents added into the reaction flask were tetra-*n*-butylammonium chloride (291 mg, 1.05 mmol, 1.0 equiv), potassium fluoride (304 mg, 5.23 mmol, 5.0 equiv), DMSO (1.00 mL), 2-nitropropane (93.2 mg, 1.05 mmol, 1.0 equiv), and dimethyl acetylenedicarboxylate (297 mg, 2.09 mmol, 2.0 equiv). After workup and purification by Chromatotron (2-mm plate; 20% EtOAc in hexanes as eluant), allylic nitro compound **3e** was obtained as a yellow oil in 62% yield (151 mg, 0.653 mmol): TLC R_f 0.26 (20% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 70 °C, duration 2.00 min; increment rate 10 °C/min; final temperature 250 °C) t_R 9.82 min; ^1H NMR ($CDCl_3$) δ 1.83 (s, 6 H, $(CH_3)_2CNO_2$), 3.77 (s, 3 H, CO_2CH_3), 3.82 (s, 3 H, CO_2CH_3), 6.19 (s, 1 H, C=$CHCO_2$); IR (neat) 3000 (w), 2980 (w), 2920 (w), 1730 (s, C=O), 1645 (w), 1550 (s, NO_2), 1460 (m), 1440 (m), 1400 (w), 1380 (m), 1350 (m, NO_2), 1275 (m), 1205 (m), 1180 (m), 1065 (w), 1020 (w), 970 (w), 890 (w), 855 (w) cm^{-1}; exact mass calcd for $C_8H_{10}NO_5$ ($M^{\bullet+}$ – $^{\bullet}OMe$) 200.0559, found 200.0567.

Dimethyl 2-(1-Nitrocyclohexyl)-2-butenedioate (3f). The general procedure was followed except dimethyl acetylenedicarboxylate was added over a 30-min period. Reagents added into the reaction flask were tetra-*n*-butylammonium chloride (221 mg, 0.797 mmol, 1.0 equiv), potassium fluoride (232 mg, 3.98 mmol, 5.0 equiv), DMSO (0.80 mL), nitrocyclohexane (103 mg, 0.797 mmol, 1.0 equiv), and dimethyl acetylenedicarboxylate (227 mg, 1.59 mmol, 2.0 equiv). After workup and purification by Chromatotron (2-mm plate; 20% EtOAc in hexanes as eluant), allylic nitro compound **3f** was obtained as a colorless oil in 75% yield (161 mg, 0.594 mmol): TLC R_f 0.32 (20% EtOAc in hexanes); GC (injector temperture 260 °C; column temperature program:

initial temperature 70 °C, duration 2.00 min; increment rate 10 °C/min; final temperature 250 °C) t_R 13.85 min; ^{1}H NMR ($CDCl_3$) δ 1.15–2.80 (m, 10 H, $(CH_2)_5$), 3.74 (s, 3 H, CO_2CH_3), 3.83 (s, 3 H, CO_2CH_3), 6.11 (s, 1 H, C=$CHCO_2$); IR (neat) 2950 (m), 2870 (w), 1735, (s, C=O), 1640 (w), 1550 (s, NO_2), 1440 (m), 1360 (m, NO_2), 1265 (m), 1205 (m), 1180 (m), 1010 (w), 880 (w), 850 (w) cm^{-1}; exact mass calcd for $C_{11}H_{14}NO_5$ ($M^{\bullet+}$ – $^{\bullet}$OMe) 240.0872, found 240.0874.

(*E*)-5-Methyl-5-nitro-3-hexen-2-one (3g). The general procedure was followed except 3-butyn-2-one was added over a 30-min period, and the reaction was then stirred for 72 h. Reagents added into the reaction flask were tetra-*n*-butylammonium chloride (72.8 mg, 0.262 mmol, 1.0 equiv), potassium fluoride (76.1 mg, 1.31 mmol, 5.0 equiv), DMSO (0.20 mL), 2-nitropropane (23.3 mg, 0.262 mmol, 1.0 equiv), and 3-butyn-2-one (26.8 mg, 0.393 mmol, 1.5 equiv). After workup and purification by Chromatotron (1-mm plate; 20% EtOAc in hexanes as eluant), allyic nitro compound **3g** was obtained as a colorless oil in 80% yield (33.1 mg, 0.211 mmol): TLC R_f 0.22 (20% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 100 °C) t_R 2.92 min; ^{1}H NMR ($CDCl_3$) δ 1.77 (s, 6 H, $(CH_3)_2CNO_2$), 2.32 (s, 3 H, CH_3C=O), 6.20 (d, J = 16.3 Hz, C=CHC=O), 7.02 (d, J = 16.3 Hz, CH=C); IR (neat) 2996 (w), 2942 (w), 2878 (w), 1705 (m), 1684 (s, C=O), 1636 (m), 1544 (s, NO_2), 1466 (w), 1396 (m), 1370 (m), 1346 (s, NO_2), 1254 (m), 1181 (m), 1136 (m), 978 (w), 856 (w), 846 (w) cm^{-1}; exact mass calcd from $C_7H_{11}O$ ($M^{\bullet+}$ – $^{\bullet}NO_2$) 111.0810, found 111.0812.

(*E*)- and (*Z*)-4-(1-Nitrocyclohexyl)-3-buten-2-one (3h).[30] The general procedure was followed except 3-butyn-2-one was added over a 30-min period, and the reaction was then stirred for 72 h. Reagents added into the reaction flask were tetra-*n*-butylammonium chloride (55.3 mg, 0.199 mmol, 1.0 equiv), potassium fluoride (57.8 mg, 0.995 mmol, 5.0 equiv), DMSO (0.20 mL), nitrocyclohexane (25.7 mg, 0.199 mmol, 1.0 equiv), and 3-butyn-2-one (20.3 mg, 0.299 mmol, 1.5 equiv). After workup and purification by Chromatotron (1-mm plate; 20% EtOAc in hexanes as eluant), isomeric allylic nitro compounds **3h** were obtained as an oil in 80% yield (31.4 mg, 0.159 mmol, *E* isomer:*Z* isomer = 86:14): TLC R_f 0.39 (20% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 150 °C) t_R 2.76 min (*Z* isomer) and 3.26 min (*E* isomer); ^{1}H NMR ($CDCl_3$) δ 1.25–1.80 (m, 10 H, $(CH_2)_5$), 2.22 (s, 3 H, CH_3C=O, *Z* isomer), 2.28 (s, 3 H, CH_3C=O, *E* isomer), 5.97 (d, J = 12.6 Hz, 1 H, C=CHC=O, *Z* isomer), 6.18 (d, J = 12.6 Hz, 1 H, CH=C, *Z* isomer), 6.21 (d, J = 16.2 Hz, 1 H, CHC=O, *E* isomer), 6.75 (d, J = 16.2 Hz, 1 H, CH=C, *E* isomer); IR (neat) 2941 (s), 2865 (m), 1701 (s, C=O), 1683 (s), 1629 (m), 1542 (s, NO_2), 1450 (m), 1427 (m), 1362 (m, NO_2), 1300 (w), 1253 (w), 1181 (s), 1148 (w), 980 (w), 912 (w), 844 (w) cm^{-1}; exact mass calcd for $C_{10}H_{15}O$ ($M^{\bullet+}$ – $^{\bullet}NO_2$) 151.1123, found 151.1126.

(1*E*,4*E*)-, (1*E*,4*Z*)-, and (1*Z*,4*Z*)-Dimethyl 3-Methyl-3-nitro-1,4-pentadiene-1,5-dicarboxylate (6). The general procedure was followed except methyl propiolate was added over a 30-min period. Reagents added into the reaction flask were tetra-*n*-butylammonium chloride (371 mg, 1.34 mmol, 1.0 equiv), potassium fluoride (388 mg, 6.68 mmol, 5.0 equiv), DMSO (1.40 mL), nitroethane (100.3 mg, 1.34 mmol, 1.0 equiv), and methyl propiolate (337 mg, 4.01 mmol, 3.0 equiv). After workup and purification by Chromatotron (2-mm plate; 40% EtOAc in hexanes as eluant), the mixture of stereoisomeric allylic nitro compounds **6** was obtained as an oil in 75% yield (244 mg, 1.00 mmol, 60% *E,E* isomer, 40% *E,Z* and *Z,Z* isomers): TLC R_f 0.52 (40% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$) δ 1.91 (s, 3 H, CH_3CNO_2, *E,E* isomer), 1.99 (s, 3 H, CH_3CNO_2, *E,Z* isomer), 2.03 (s, 3 H, CH_3CNO_2, *Z,Z* isomer), 3.69 (s, 3 H, CO_2CH_3), 3.77 (s, 3 H, CO_2CH_3), 3.79 (s, 3 H, CO_2CH_3, *E,E* isomer), 5.88–6.46 (m, 2 H, C=$CHCO_2$, *E,Z* and *Z,Z* isomers), 6.03 (d, J = 16.0 Hz, 1 H, C=$CHCO_2$, *E,E* isomer), 7.09–7.55 (m, 2 H, CH=C, *E,Z* and *Z,Z* isomers), 7.19 (d, J = 16.0 Hz, 1 H, CH=C, *E,E* isomer); IR (neat) 3000 (w), 2960 (w), 1720 (s, C=O), 1655 (m), 1550 (s, NO_2), 1440 (s), 1385 (m, NO_2), 1345 (m), 1320 (s), 1280 (s), 1205 (s), 1180 (s), 1080 (w), 1030 (w), 1010 (m), 980 (m), 920 (w), 850 (w), 830 (w), 770 (w), 715 (w) cm^{-1}; exact mass calcd for $C_{10}H_{13}O_4$ ($M^{\bullet+}$ – $^{\bullet}NO_2$) 197.0814, found 197.0817.

The pure *E,Z* isomer was crystallized from ether/hexanes as white crystals: mp 85–86 °C; TLC R_f 0.50 (40% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$) δ 1.99 (s, 3 H, CH_3CNO_2), 3.69 (s, 3 H, CO_2CH_3), 3.77 (s, 3 H, CO_2CH_3), 5.98 (d, J = 16.0 Hz, 1 H, C=$CHCO_2$ in *E* form), 6.10 (d, J = 12.2 Hz, 1 H, C=$CHCO_2$ in *Z* form), 6.39 (d, J = 12.2 Hz, 1 H, CH=C in *Z* form), 7.45 (d, J = 16.0 Hz, 1 H, CH=C in *E* form); IR ($CHCl_3$) 3002 (w), 2956 (w), 2840 (w), 1723 (s, C=O), 1708 (s), 1656 (w), 1557 (s, NO_2), 1464 (m), 1443 (m), 1434 (m), 1387 (m, NO_2), 1320 (s), 1284 (m), 1211 (s), 1181 (m), 1085 (w), 1004 (m), 994 (m), 917 (w), 823 (m), 770 (w) cm^{-1}.

(1*E*,4*E*)-, (1*E*,4*Z*)-, and (1*Z*,4*Z*)-Dimethyl 3-[2-(Methoxycarbonyl)ethyl]-3-nitro-1,4-pentadiene-1,5-dicarboxylate (7). The general procedure was followed except methyl propiolate was added over a 30-min period. Reagents added into the reaction flask were tetra-*n*-butylammonium chloride (174 mg, 0.625 mmol, 1.0 equiv), potassium fluoride (182 mg, 3.13 mmol, 5.0 equiv), DMSO (0.60 mL), methyl 4-nitrobutyrate (80%, 115 mg, 0.625 mmol, 1.0 equiv), and methyl propiolate (184 mg, 2.19 mmol, 3.5 equiv). After workup and purification by Chromatotron (2-mm plate; 40% EtOAc in hexanes as eluant), the mixture of stereoisomeric allylic nitro compounds **7** was obtained as a yellow oil in 53% yield (105 mg, 0.333 mmol): TLC R_f 0.48, 0.43, 0.38 (40% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$) δ 2.10–2.75 (m, 4 H, $(CH_2)_2$), 3.69 (s, 3 H, CO_2CH_3), 3.77 (s, 3 H, CO_2CH_3), 3.79 (s, 3 H, CO_2CH_3, *E,E* isomer), 5.82–6.50 (m, 2 H, C=$CHCO_2$, *E,Z* and *Z,Z* isomers), 6.03 (d, J = 16.1 Hz, 1 H, C=$CHCO_2$, *E,E* isomer), 7.08–7.66 (m, 2 H, CH=C, *E,Z* and *Z,Z* isomers), 7.18 (d, J = 16.1 Hz, 1 H, CH=C, *E,E* isomer); IR (neat) 3003 (w), 2956 (w), 1732 (s, C=O), 1658 (w), 1555 (s, NO_2), 1438 (m), 1380 (m, NO_2), 1322 (s), 1283 (s), 1203 (s), 1180 (s), 982 (m), 918 (w), 844 (w), 806 (w), 732 (w) cm^{-1}; exact mass calcd for $C_{13}H_{17}O_6$ ($M^{\bullet+}$ – $^{\bullet}NO_2$) 269.1025, found 269.1022.

(*E*)-Methyl 4-Methyl-4-nitro-7-oxo-2-octenoate (8). To a 10-mL pear-shaped flask were added tetra-*n*-butylammonium chloride (371 mg, 1.34 mmol, 1.0 equiv), potassium fluoride (388 mg, 6.68 mmol, 5.0 equiv), DMSO (1.40 mL), and nitroethane (100.3 mg, 1.34 mmol, 1.0 equiv). After the solution was stirred for 30 min at room temperature, methyl propiolate (112 mg, 1.34 mmol, 1.0 equiv) was added over a 2-h period, and stirring was continued for 1 more hour. Methyl vinyl ketone (187 mg, 2.67 mmol, 2.0 equiv) was added, and stirring was continued for an additional 2 h. The reaction was quenched with water (5 mL), and the solution was extracted with diethyl ether (2 × 15 mL). The combined organic layers were washed with 10% aqueous HCl (10 mL) and brine (10 mL), dried over $MgSO_4$, filtered, and concentrated to give an oil. The oil was purified by Chromatotron (2-mm plate; 40% EtOAc in hexanes as eluant) to give pure allylic nitro compound **8** as a colorless oil in 60% yield (183 mg, 0.798 mmol): TLC R_f 0.37 (40% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 70 °C, duration 2.00 min; increment rate 10 °C/min; final temperature 250 °C) t_R 11.61 min; ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 3 H, CH_3CNO_2), 2.15 (s, 3 H, CH_3CO), 2.37–2.45 (m, 4 H, $(CH_2)_2$), 3.78 (s, 3 H, CO_2CH_3), 5.98 (d, J = 16.1 Hz, 1 H, C=$CHCO_2$), 7.21 (d, J = 16.1 Hz, 1 H, CH=C); IR (neat) 3000 (w), 2975 (w), 2950 (w), 1720 (s, C=O), 1660 (w), 1545 (s, NO_2), 1440 (m), 1390 (w), 1350 (m, NO_2), 1320 (m), 1285 (m), 1205 (m), 1175 (m), 1040 (w), 1015 (w), 985 (w), 920 (w), 810 (w) cm^{-1}; exact mass calcd for $C_9H_{12}NO_4$ ($M^{\bullet+}$ – $^{\bullet}$OMe) 198.0766, found 198.0768.

(*E*)-5-Methyl-5-nitro-3-nonene-2,8-dione (9). To a 5-mL pear-shaped flask were added tetra-*n*-butylammonium chloride (92.8 mg, 0.334 mmol, 1.0 equiv), potassium fluoride (97.0 mg, 1.67 mmol, 5.0 equiv), DMSO (0.33 mL), and nitroethane (25.1 mg, 0.334 mmol, 1.0 equiv). After the solution was stirred for 30 min at room temperature, 3-butyn-2-one (22.7 mg, 0.334 mmol, 1.0 equiv) was added over a 2-h period and stirring was continued for an additional hour. Methyl vinyl ketone (46.8 mg, 0.668 mmol, 2.0 equiv) was then added, and stirring was continued for an additional 3 h. The reaction was quenched with water (5 mL), and the solution was extracted with diethyl ether (2 × 10 mL). The combined organic layers were washed with 10% aqueous HCl (5 mL) and brine (5 mL), dried over $MgSO_4$, filtered, and concentrated to give an oil. The oil was purified by Chromatotron (1-mm plate; 40% EtOAc in hexanes as eluant) to yield pure allylic nitro compound **9** as a yellow oil in 52% yield (37.2 mg, 0.174 mmol): TLC R_f 0.28 (40% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial tem-

perature 70 °C, duration 2.00 min; increment rate 10 °C/min; final temperature 250 °C) t_R 11.24 min; ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 3 H, CH_3CNO_2), 1.95–2.55 (m, 2 H, CH_2CNO_2), 2.15 (s, 3 H, CH_3COCH_2), 2.32 (s, 3 H, CH_3COCH=C), 2.38–2.49 (m, 2 H, CH_2CO), 6.18 (d, J = 16.4 Hz, 1 H, C=$CHCO_2$), 7.03 (d, J = 16.4 Hz, 1 H, CH=C); IR (neat) 3001 (w), 2942 (w), 1716 (s, C=O), 1683 (s), 1633 (m), 1542 (s, NO_2), 1422 (m), 1390 (m), 1357 (s, NO_2), 1256 (m), 1169 (m), 1096 (w), 982 (s), 846 (w) cm^{-1}; exact mass calcd for $C_{10}H_{15}O_2$ ($M^{\bullet+}$ – $^{\bullet}NO_2$) 167.1072, found 167.1069.

(*E*)-Methyl 6-(Ethoxycarbonyl)-4-methyl-4-nitro-2-heptenoate (10). To a 10-mL pear-shaped flask were added tetra-*n*-butylammonium chloride (371 mg, 1.34 mmol, 1.0 equiv), potassium fluoride (388 mg, 6.68 mmol, 5.0 equiv), DMSO (1.4 mL), and nitroethane (100.3 mg, 1.34 mmol, 1.0 equiv). After the solution was stirred for 30 min at room temperature, ethyl methacrylate (153 mg, 1.34 mmol, 1.0 equiv) was added over a 2-h period, and stirring was continued for an additional 24 h. Methyl propiolate (112 mg, 1.34 mmol, 1.0 equiv) was then added, and stirring was continued for 1 more hour. The reaction was quenched with water (10 mL), and the solution was extracted with diethyl ether (2 × 15 mL). The combined organic layers were washed wth 10% aqueous HCl (10 mL) and brine (10 mL), dried over $MgSO_4$, filtered, and concentrated to give an oil. The oil was purified by Chromatotron (2-mm plate; 20% EtOAc in hexanes as eluant) to yield pure allylic nitro compound **10** as a yellow oil in 41% yield (150 mg, 0.549 mmol): TLC R_f 0.34 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$) δ 1.24 (t, J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.70 (s, 3 H, CH_3CNO_2), 1.73 (s, 3 H, CH_3CNO_2), 2.01–2.98 (m, 3 H, CH_2CH), 3.77 (s, 3 H, CO_2CH_3), 4.11 (q, J = 7.2 Hz, 2 H, CO_2CH_2), 5.96 (d, J = 16.0 Hz, 1 H, C=$CHCO_2$), 7.18 (d, J = 16.0 Hz, 1 H, CH=C); IR (neat) 2960 (w), 1725 (s, C=O), 1545 (s, NO_2), 1460 (w), 1440 (w), 1390 (w), 1340 (m, NO_2), 1310 (m), 1280 (m), 1200 (m), 1180 (m), 1050 (w), 1020 (w), 980 (w), 850 (w) cm^{-1}; exact mass calcd for $C_{11}H_{16}NO_5$ ($M^{\bullet+}$ – $^{\bullet}OMe$) 242.1028, found 242.1030.

(*E*)- and (*Z*)-Methyl 4-Nitro-4-(3-oxocyclohexyl)-2-pentenoate (11). To a 5-mL pear-shaped flask were added tetra-*n*-butylammonium chloride (186 mg, 0.668 mmol, 1.0 equiv), potassium fluoride (194 mg, 3.34 mmol, 5.0 equiv), DMSO (0.67 mL), and nitroethane (50.2 mg, 0.668 mmol, 1.0 equiv). After the solution was stirred for 30 min at room temperature, 2-cyclohexen-1-one (64.2 mg, 0.668 mmol, 1.0 equiv) was added, and stirring was continued for an additional 24 h. Methyl propiolate (56.2 mg, 0.668 mmol, 1.0 equiv) was then added, and stirring was continued for 3 more hours. The reaction was quenched with water (5 mL), and the solution was extracted with diethyl ether (2 × 10 mL). The combined organic layers were washed with 10% aqueous HCl (5 mL) and brine (10 mL), dried over $MgSO_4$, filtered, and concentrated to give an oil. The oil was purified by Chromatotron (1-mm plate; 40% EtOAc in hexanes as eluant) to yield a mixture of isomeric allylic nitro compounds **11** as a yellow oil in 50% yield (85.7 mg, 0.336 mmol): TLC R_f 0.35 (40% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$) δ 1.40–2.75 (m, 9 H, CH + 4 CH_2), 1.71 (s, 3 H, CH_3CNO_2, *E* isomer), 3.71 (s, 3 H, CO_2CH_3, *Z* isomer), 3.79 (s, 3 H, CO_2CH_3, *E* isomer), 5.80–6.40 (m, 1 H, C=$CHCO_2$), 7.05–7.35 (m, 1 H, CH=C); IR (neat) 2953 (m), 2871 (w), 1718 (s, C=O), 1545 (s, NO_2), 1437 (m), 1391 (m), 1346 (m, NO_2), 1316 (m), 1284 (m), 1203 (m), 1107 (w), 985 (w), 852 (w); exact mass calcd for $C_{11}H_{14}NO_4$ ($M^{\bullet+}$ – $^{\bullet}OMe$) 224.0923, found 224.0926.

(*E*)-5-Isopropyl-5-nitro-3-nonene-2,8-dione (13). To a 5-mL pear-shaped flask were added tetra-*n*-butylammonium chloride (228 mg, 0.821 mmol, 1.0 equiv), potassium fluoride (239 mg, 4.11 mmol, 5.0 equiv), DMSO (0.82 mL), and 2-methyl-1-nitropropane[22] (84.6 mg, 0.821 mmol, 1.0 equiv). After the solution was stirred for 30 min at room temperature, 3-butyn-2-one (55.9 mg, 0.821 mmol, 1.0 equiv) was added over a 2-h period, and stirring was continued for an additional hour. Methyl vinyl ketone (115 mg, 1.64 mmol, 2.0 equiv) was then added, and stirring was continued for an additonal 3 h. The reaction was quenched with water (5 mL), and the solution was extracted with diethyl ether (2 × 10 mL). The combined organic layers were washed with 10% aqueous HCl (5 mL) and brine (5 mL), dried over $MgSO_4$, filtered, and concentrated to give an oil. The oil was purified by Chromatotron (1-mm plate; 40% EtOAc in hexanes as eluant) to yield pure allylic nitro compound **13** as a yellow oil in 51% yield (101 mg, 0.419 mmol): TLC R_f 0.40 (40% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 70 °C, duration 2.00 min; increment rate 10 °C/min; final temperature 250 °C) t_R 12.20 min; ^{1}H NMR ($CDCl_3$) δ 0.93 (d, J = 6.8 Hz, 6 H, $(CH_3)_2CH$), 1.95–2.55 (m, 2 H, CH_2CNO_2), 2.12 (s, 3 H, CH_3COCH_2), 2.35 (s, 3 H, CH_3COCH=C), 2.33–2.45 (m, 2 H, CH_2CO), 6.05 (d, J = 16.8 Hz, 1 H, C=$CHCO_2$), 7.17 (d, J = 16.8 Hz, 1 H, CH=C); IR (neat) 2975 (m), 2942 (w), 2882 (w), 1716 (s, C=O), 1683 (s), 1631 (m), 1543 (s, NO_2), 1468 (m), 1424 (m), 1395 (m), 1360 (s), NO_2), 1255 (m), 1173 (m), 1125 (w), 1099 (w), 985 (m), 846 (w) cm^{-1}; exact mass calcd for $C_{12}H_{19}O_2$ ($M^{\bullet+}$ – $^{\bullet}NO_2$) 195.1385, found 195.1391.

Norsolanadione (14, (*E*)-5-Isopropyl-3-nonene-2,8-dione). The conditions used were a modification of Suzuki's.[23] A solution of tertiary nitro compound **13** (47.6 mg, 0.197 mmol, 1.0 equiv) in ethanol (2.0 mL) was added at room temperature under nitrogen atmosphere to a solution of NaHTe,[24] prepared in situ by reacting tellurium powder (62.8 mg, 0.493 mmol, 2.5 equiv) and sodium borohydride (44.8 mg, 1.18 mmol, 6.0 equiv) for 1 h in refluxing ethanol (2.0 mL). After 5 h, water (3.0 mL) was added, and the resulting mixture was stirred under air for 1 h. It was then filtered through Celite, and the filtrate was extracted with dichloromethane (3 × 5 mL). The combined organic layers were washed with water (5 mL) and brine (5 mL), dried over $MgSO_4$, filtered, and concentrated to give a yellow oil. The oil was purified by Chromatotron (1-mm plate; 40% EtOAc in hexanes as eluant) to yield pure **14** as an oil in 64% yield (24.9 mg, 0.126 mmol): TLC R_f 0.37 (40% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 130 °C) t_R 3.64 min; ^{1}H NMR ($CDCl_3$) δ 0.87 (d, J = 6.4 Hz, 3 H, CH_3CH), 0.92 (d, J = 6.4 Hz, 3 H, CH_3CH), 1.45–2.05 (m, 3 H, CH_2CH), 2.10 (s, 3 H, CH_3COCH_2), 2.24 (s, 3 H, CH_3COCH=C), 2.35 (t, J = 6.9 Hz, 2 H, CH_2CO), 6.00 (d, J = 16.0 Hz, 1 H, C=$CHCO_2$), 6.56 (dd, J = 8.7 and 16.0 Hz, 1 H, CH=C); IR (neat) 2960 (s), 2874 (w), 1716 (s, C=O), 1675 (s, C=O), 1624 (w), 1419 (w), 1362 (s), 1255 (s), 1164 (m), 989 (m) cm^{-1}; MS *m/e* (relative intensity) 196 ($M^{\bullet+}$, 0.2), 135 (7), 126 (11), 123 (7), 121 (5), 120 (8), 111 (8), 97 (31), 95 (16), 93 (9), 55 (5), 43 (100), 41 (16). The spectroscopic data of this compound were consistent with those reported in the literature.[39]

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Registry No. (*E*)-**3a**, 123239-98-5; (*Z*)-**3a**, 123239-99-6; (*E*)-**3b**, 123240-00-6; (*Z*)-**3b**, 123240-01-7; (*E*)-**3c**, 123240-02-8; (*Z*)-**3c**, 123240-03-9; (*E*)-**3d**, 123240-04-0; (*Z*)-**3d**, 123240-05-1; **3e**, 123240-06-2; **3f**, 123240-07-3; (*E*)-**3g**, 123240-08-4; (*E*)-**3h**, 123240-09-5; (*Z*)-**3h**, 123240-10-8; **4**, 79-24-3; **5**, 13013-02-0; (*E,E*)-**6**, 123240-11-9; (*E,Z*)-**6**, 123240-12-0; (*Z,Z*)-**6**, 123240-13-1; (*E,E*)-**7**, 123240-14-2; (*E,Z*)-**7**, 123240-15-3; (*Z,Z*)-**7**, 123240-16-4; (*E*)-**8**, 123263-94-5; (*E*)-**9**, 123240-17-5; (*E*)-**10**, 123263-95-6; (*E*)-**11**, 123240-18-6; (*Z*)-**11**, 123240-19-7; (*E*)-**13**, 123240-20-0; (±)-(*E*)-**14**, 58001-08-4; $CH_3CH(NO_2)CH_3$, 79-46-9; $CH_3CH(NO_2)(CH_2)_4CH_3$, 617-72-1; CH_2=$CHCH_2CH(NO_2)CH_3$, 86246-21-1; CH≡CCO_2Me, 922-67-8; MeO_2CC≡CCO_2Me, 762-42-5; CH≡$CCOCH_3$, 1423-60-5; CH_3COCH=CH_2, 78-94-4; CH_2=$C(CH_3)CO_2Et$, 97-63-2; $CH_3CH(CH_3)CH_2NO_2$, 625-74-1; nitrocyclohexane, 1122-60-7; 2-cyclohexen-1-one, 930-68-7.

Supplementary Material Available: Elemental analysis data (C, H, N) for **3a–h**, **6–11**, and **13** (1 page). Ordering information is given on any current masthead page.

(39) Aasen, A. J.; Enzell, C. R. *Acta Chem. Scand. B* **1975**, *29*, 528.