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Synthesis and Characterization of Multiple Functionalized Cyclohexanone Using Diels–Alder Reaction of α-Nitrocinnamate

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Abstract: A systematic study of the Diels–Alder reaction of α-nitrocinnamate was performed. The reaction of *p*-substituted α-nitrocinnamate with 2,3-dimethyl-1,3-butadienes smoothly proceeded regardless of the *p*-substituent, which was either an electron-donating or -withdrawing group. A control reaction revealed that α-nitrocinnamate isomerized during the reaction. Danishefsly's diene (1-methoxy-3-trimethylsiloxy-1,3-butadiene) facilitated cycloaddition under mild conditions to afford a cycloadduct without the alternation of the diastereomeric ratio. Moreover, the desilylation of the cycloadduct furnished multiple functionalized cyclohexanones.

Keywords: α-nitrocinnamate; Diels–Alder reaction; multiple functionalized cyclohexanones

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1. Introduction

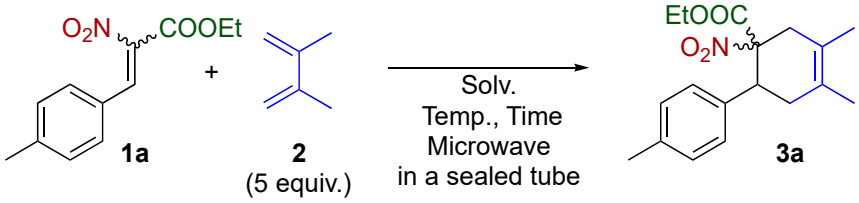
Nitroalkenes are one of the important building blocks for multiple functionalized compounds. The electron-withdrawing effect of the nitro group enhances the electron acceptability of the alkene moiety, which facilitates conjugate addition [1,2], the Diels–Alder reaction [1,3,4] and 1,3-dipolar cycloaddition [5]. Further chemical conversions of the conjugate adducts and cycloadducts can furnish amines [6], alkenes [1,7], and carbonyl compounds (Nef reaction) [8] via reduction, denitration, and hydrolysis, respectively. The introduction of an electron-withdrawing group such as a carbonyl functionality at the α position of nitroalkenes enhances electron acceptability [9]. For instance, α-nitrocinnamate **1** facilitates conjugate addition by hetero-aromatic compounds, which are less nucleophilic species [10,11]. α-carbonylated nitroalkenes should also be suitable for the Diels–Alder reaction as dienophiles because the carbonyl group decreases the LUMO level of the nitroalkenes. However, there have been few examples of the Diels–Alder reaction using α-carbonylated nitroalkenes [12–19] despite abundant studies on that using α-unsubstituted nitroalkenes [1,3,4]. However, related studies of heterocyclic compounds such as coumarin [20,21], quinolone [22–24], pyridone [24] and pyridazine [25] possessing an α-carbonylated nitroalkene moiety as a partial structure have been reported. Accordingly, systematic studies using α-carbonylated nitroalkene can help expand the synthetic utility of the Diels–Alder reaction. In the present work, a series of α-nitrocinnamates **1** were reacted with dienes, and their reactivity and regioselectivity were investigated.

2. Results and Discussion

When a toluene solution of ethyl α-nitrocinnamate **1a** was heated with 1,3-butadiene **2** at 150 °C under microwave irradiation, product **3a** was isolated in a 13% yield (Table 1, Entry 1). In the ^{1}H NMR of **3a**, two singlet signals were inequivalently observed at around 1.7 ppm, indicating that symmetrical butadiene was converted into an unsymmetrical structure. Other spectral data also supported the idea that difunctionalized cyclohexene **3a** was successfully obtained. To increase the yield of **3a**, several solvents were tested,

and acetonitrile was found to be the most suitable (Entries 1–4). Though six hours were necessary to consume **1a** at 150 °C (Entry 5), the reaction was completed within two hours when the reaction temperature was elevated to 180 °C (Entry 6).

Table 1. Optimal conditions of the Diels–Alder reaction with ethyl α-nitrocinnamate **1a** and 2,3-dimethyl-1,3-butadiene (**2**).

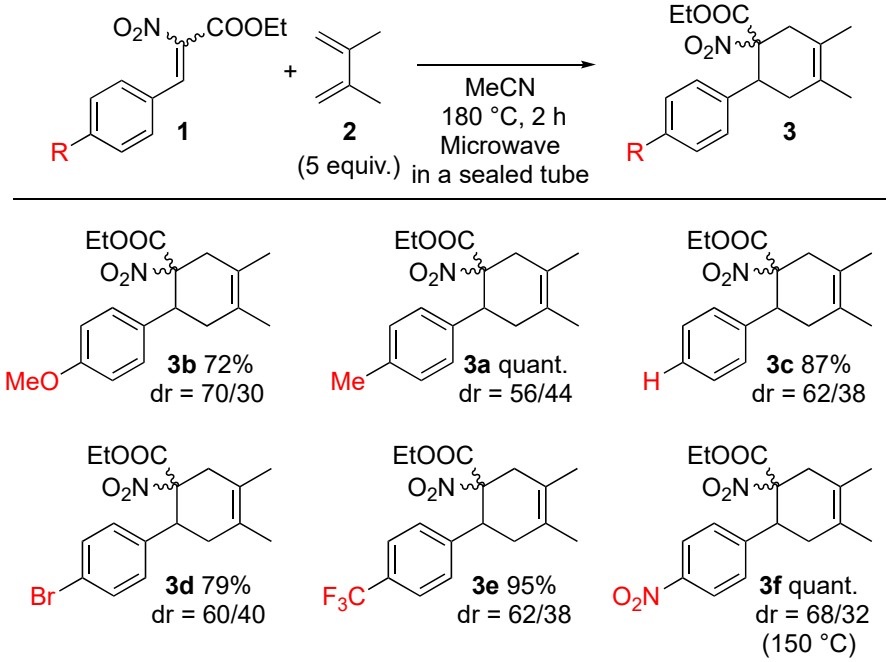


Entry	Solv.	Temp. (°C)	Time (h)	Yield of 3a (%) [1,2]	Recovery of 1a (%) [1]
1	toluene	150	1.5	13(13) [3]	86
2	THF	150	1.5	29	61
3	$CHCl_3$	150	1.5	57	40
4	MeCN	150	1.5	67	32
5	MeCN	150	6.0	96	0
6	MeCN	180	2.0	quant.	0

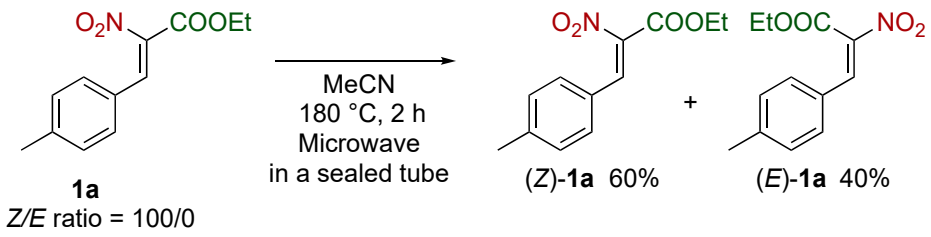
[1] Determined by ^{1}H NMR using internal standard (1,1,2,2-tetrachloroethane); [2] total yield of diastereoisomers; [3] isolated yield.

The optimal conditions were applied to several ethyl α-nitrocinnamates **1b–f** possessing different substituent at the *para* position (Scheme 1). Each reaction used two diastereomeric products with different positions of the nitro and ethoxycarbonyl groups at the 3 position. Reactions efficiently proceeded, with substrates substituting either the electron-donating or -withdrawing group to afford the corresponding products **3b–e**; however, the reaction of nitro-substituted substrate **1f** was complicated due to overreactions such as the elimination of a nitrous acid and subsequent oxidation. This disadvantage was overcome by reducing the reaction temperature to 150 °C, and cycloadduct **3f** was quantitatively obtained. Among substrates **1a–f**, methoxy- and bromo-substituted cinnamates **1b** and **1d** were the least reactive, which was presumably due to the electron-donating resonance effect that increased the single bond character of the double-bond moiety. Systematic studies showed that the diastereomeric ratio of products **3a–f** was about 60/40 even when only a Z isomer was used as a starting material, which means that isomerization occurred during the reaction. To reveal this phenomenon, only the Z isomer of **1a** was heated at 180 °C, which afforded a *Z*/*E* mixture of **1a** with a 60/40 ratio (Scheme 2). This result indicated that the isomerization of **1** occurred under reaction conditions and not during the Diels–Alder reaction.

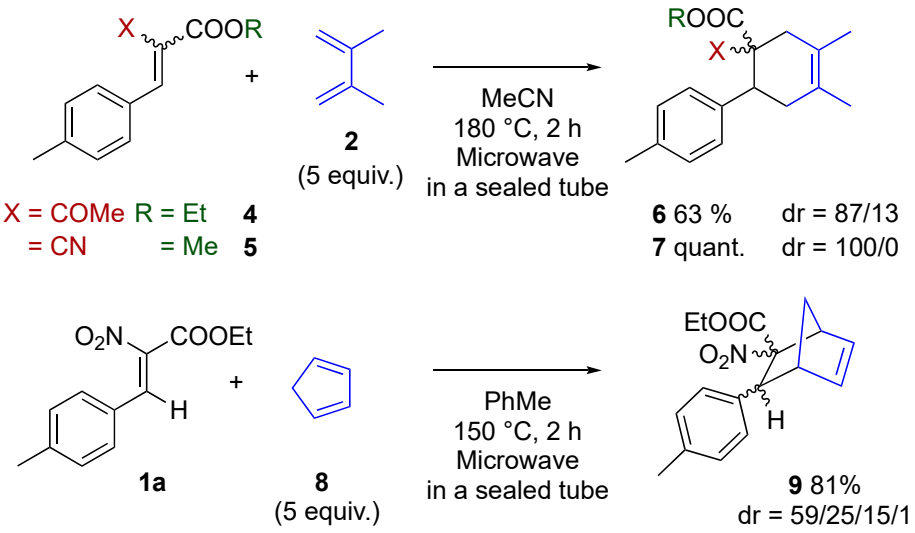
Next, α-cyano and α-acetylcinnamates **4** and **5** were employed as dienophiles instead of α-nitro derivative **1** (Scheme 3). Even when the nitro group was replaced with less electron-withdrawing acetyl groups, the cycloaddition proceeded to furnish the corresponding cycloadduct **6** with a 87/13 diastereomeric ratio. In the case of substrate **5** with a less hindered cyano group, cycloadduct **7** was quantitatively produced as a single isomer because the *E* isomer was not converted into an unstable *Z* isomer, even under conditions of progressive isomerization. When cyclopenta-1,3-diene **8** was subjected to the reaction with **1a**, cycloadduct **9** was obtained in a 81% yield as a mixture of four diastereomers.



Scheme 1. Diels–Alder reactions of ethyl α-nitrocinnamates possessing a *para*-substituent.



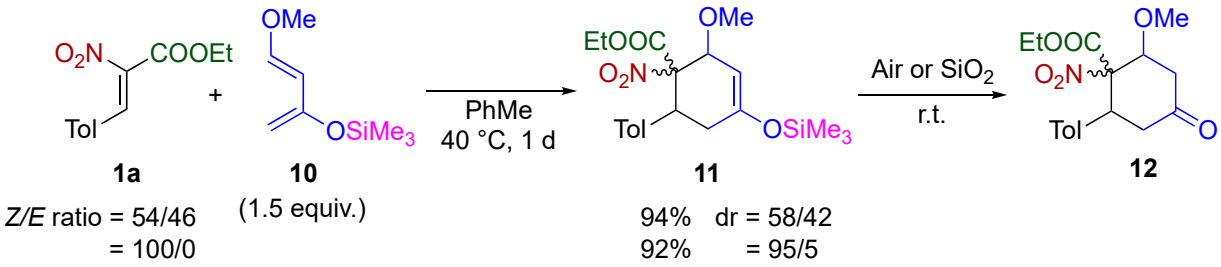
Scheme 2. Isomerization of **1a** at 180 °C.



Scheme 3. Diels–Alder reactions using other dienophiles and diene.

So far, nitrocinnamate **1** was found to serve as an excellent dienophile that could efficiently undergo the Diels–Alder reaction, which led to multiple substituted cyclohexene **3** products. Our next challenge was focused on the synthesis of more densely functionalized cyclohexenes. For this purpose, 1-methoxy-3-trimethylsiloxy-1,3-butadiene (Danishefsky's diene, CAS No. 54125-02-9) **10** was employed because its silyl enol ether moiety can be

converted into a carbonyl group upon desilylation and two electron-donating groups can improve its reactivity. The Diels–Alder reaction of **1a** with diene **10** efficiently proceeded without heating to yield cycloadduct **11** regardless of the *Z*/*E* ratio of **1a** (Scheme 4). The diastereomeric ratio of **11** was consistent with the *Z*/*E* ratio of **1a**, and close to a single isomer (95/5) was obtained when only the *Z* form of **1a** was used. Cycloadduct **11** easily underwent desilylation to afford cyclohexanone **12** in air or during treatment with chromatography on silica gel. The formation of **12** was confirmed by NMR and IR measurements. In the ^{1}H NMR spectra, a doublet at 5.2 ppm assigned to an alkenyl proton of **11** disappeared, and the absorption of a carbonyl group newly appeared in the IR spectrum.



Scheme 4. Diels–Alder reaction of ethyl α-nitrocinnamate **1a** with Danishefsky's diene **10**.

Since cyclohexanone **12** is an oil, it was converted into solid hydrazone **13** to determine its stereochemistry with single X-ray crystallography. A single diastereomer of cyclohexanone **12** obtained from the *Z* isomer of **1a** was reacted with 2,4-dinitrophylhydrazine in ethanol in the presence of hydrochloric acid, which afforded hydrazone **13** without any stereochemical isomerization. During the reaction, methanol was eliminated. The recrystallization of **13** from toluene–hexane successfully yielded orange needles as a single crystal, and X-ray crystallography revealed that the nitro group and 4-methylphenyl group were substituted in the *cis* form, which was the same relationship as the Z form in **1a** (Figure 1, Supplementary Materials). These results confirmed that the Diels–Alder reaction concertedly proceeded.

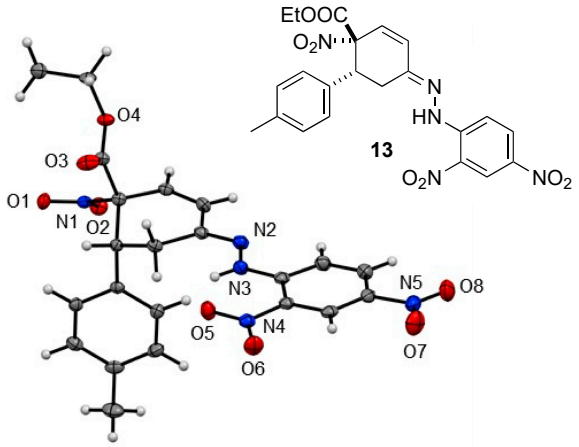


Figure 1. The crystal structure of **13** with ORTEP drawing (50% probability). Atoms are colored as follows: carbon, gray; nitrogen, blue; oxygen, red. Triclinic, *P*-1, *Z* = 2, GOF = 1.062, $R_1[I > 2\sigma(I)] = 0.0369$, wR_2 (all data) = 0.1055.

3. Conclusions

A systematic study of the Diels–Alder reactions of α-nitrocinnamate **1** was performed. Cinnamate **1** efficiently reacted with 2,3-dimethyl-1,3-butadiene **2** to afford cyclohexene **3** in high yields. This reaction was not influenced by the *p*-substituent of the phenyl group. Cycloadduct **3** was obtained as a mixture of stereoisomers, which was found to be due to *E*/*Z* isomerization at high temperatures. In the case of the more electron-rich Danishefsly's

diene **10**, cycloaddition efficiently proceeded under mild conditions, which furnished highly functionalized cyclohexene **11**. Multiple functionalized cyclohexanones **12** were obtained via the subsequent desilylation of **11**. The insights obtained in this study are surely valuable in the field of organic synthesis.

4. Experimental Section

All reagents were purchased from commercial sources and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded with Bruker DPX-400 and JEOL JMN-ECZ400S spectrometers (400 MHz and 100 MHz, respectively) using TMS as an internal standard. The assignments of the ^{13}C NMR spectra were performed with DEPT experiments. IR spectra were recorded with a JASCO FT/IR-4200 spectrometer equipped with an ATM detector. High-resolution mass spectra were obtained with an AB SCEIX Triplet TOF 4600 mass spectrometer. Microwave heating was performed with an Anton Paar Microwave 300 (850 W, 2455 MHz) and an Anton Paar Microwave 400 (850 W, 2450 MHz) using a 10 mL glass vessel. Diffraction data were collected at 93 K under a cold N_2 gas stream with a Rigaku XtaLAB Synergy-S/Mo system (λ = 0.71073 Å (Mo-Kα)). The integrated data were analyzed by using a Yadokari-XG software package. The structures were solved with the ShelXT structure solution program using intrinsic phasing and refined with the ShelXL refinement package using least-squares minimization. Anisotropic refinement was performed for all non-hydrogen atoms, and all the hydrogen atoms were put in calculated positions.

Synthesis of α-nitrocinnamate 1a. α-Nitrocinnamate **1** was synthesized using a somewhat modified method previously described in the literature. Aniline (0.91 mL, 10.0 mmol) and magnesium sulfate (400 mg) were added to a solution of 4-methylbenzaldehyde (10.0 mmol) in THF (5 mL), and the mixture was stirred at room temperature for 5 h. After filtrations of magnesium sulfate, the filtrate was concentrated under reduced pressure to afford imine (2.0 g, 9.7 mmol, 97%) as a brown solid, which was used for the next step without further purification. A solution of imine (2.0 g, 9.7 mmol) and nitroacetate (1.08 mL, 9.7 mmol, CAS No. 626-35-7) in acetic anhydride (5 mL) was heated at 60 °C for 18 h. The reaction mixture was poured into water (100 mL) and extracted with dichloromethane (50 mL × 3). Organic layers were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was treated with flash column chromatography on silica gel (hexane/ethyl acetate = 9/1) to afford α-nitrocinnamate **1a** (1520 mg, 6.5 mmol, 65%) as a yellow oil. When the aldehyde could not be completely separated, distillation was performed to remove it. The recrystallization of the product using hexane/chloroform afforded (*Z*) isomer. Other cinnamates **1b–f**, **4**, and **5** were synthesized in the same way.

Ethyl 3-(4-methylphenyl)-2-nitropropenoate (1a) [26]. Yellow plates. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 4.37 (q, *J* = 7.3 Hz, 2H), 2.39 (s, 3H) 1.36 (t, *J* = 7.3 Hz, 3H).

Ethyl 3-(4-methylphenyl)-2-nitropropenoate (1b) [27]. Brown plates. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.39 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 4.36 (q, *J* = 7.3 Hz, 2H), 3.85 (s, 3H), 1.36 (t, *J* = 7.3 Hz, 3H).

Ethyl 2-nitro-3-phenylpropenoate (1c) [26]. Yellow plates. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.40–7.51 (m, 5H), 4.39 (q, *J* = 6.9 Hz, 2H), 1.37 (t, *J* = 6.9 Hz, 3H).

Ethyl 3-(4-bromophenyl)-2-nitropropenoate (1d) [26]. Yellow plates. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.47 (s, 1H), 7.28 (d, *J* = 8.5 Hz, 2H), 4.29 (q, *J* = 7.3 Hz, 2H), 1.37 (t, *J* = 7.3 Hz, 3H).

Ethyl 3-[(4-trifluoromethyl)phenyl]-2-nitropropenoate (1e) [26]. Yellow plates. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.50 (s, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 4.05 (q, *J* = 7.0 Hz, 2H), 1.38 (t, *J* = 7.0 Hz, 3H).

Ethyl 2-nitro-3-(4-nitrophenyl)propenoate (1f) [27]. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.7 Hz, 2H), 7.60 (s, 1H), 7.59 (d, *J* = 8.7 Hz, 2H), 4.42 (q, *J* = 6.9 Hz, 2H), 1.39 (t, *J* = 6.9 Hz, 3H).

Ethyl 2-ethanoyl-3-(4-methylphenyl)propenoate (4) [28]. Colorless plates. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 4.29 (q, *J* = 7.0 Hz, 2H), 2.36 (s, 3H), 2.35 (s, 3H), 1.32 (t, *J* = 7.0 Hz, 3H).

Ethyl 2-cyano-3-(4-methylphenyl)propenoate (5) [29]. Colorless needles. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 3H), 2.44 (s, 3H).

Diels–Alder reaction of α-nitrocinnamate. 2,3-dimethyl-1,3-butadiene **2** (0.28 mL, 2.5 mmol) was added to a solution of α-nitrocinnamate **1a** (117 mg, 0.5 mmol) in MeCN (1 mL), and the resultant solution was heated at 180 °C for 2 h under microwave irradiation. After the removal of the solvent under reduced pressure, the residue was subjected to flash column chromatography on silica gel (hexane/ethyl acetate = 95/5) to afford cycloadduct **3a** (151 mg, 0.475 mmol, 95%) as a pale-yellow oil. When other substrates were used or conditions were changed, the reaction was conducted in the same way.

4-Ethoxycarbonyl-1,2-dimethyl-5-(4-methylphenyl)-4-nitrocyclohexene (3a). Pale-yellow oil (*dr* = 56/44). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.9–7.9 (m, 4H), 4.07 (q, *J* = 7.2 Hz, 2H), 4.05 (d, *J* = 8.0 Hz, 1H), 2.7–3.0 (m, 3H), 2.30 (s, 3H), 2.28 (br d, *J* = 18.8 Hz, 1H), 1.72 (s, 3H), 1.68 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (C), 137.6 (C), 137.1 (C), 129.5 (CH), 128.4 (CH), 125.7 (C), 121.2 (C), 95.7 (C), 62.7 (CH_2), 42.8 (CH), 36.2 (CH_2), 34.0 (CH_2), 21.2 (CH_3), 19.2 (CH_3), 18.6 (CH_3), 13.8 (CH_3). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.9–7.9 (m, 4H), 4.24 (dq, *J* = 7.2, 14.4 Hz, 1H), 4.21 (dq, *J* = 7.2, 14.4 Hz, 1H), 3.95 (d, *J* = 7.6 Hz, 1H), 2.7–3.0 (m, 3H), 2.39 (br d, *J* = 17.2 Hz, 1H), 2.30 (s, 3H), 1.74 (s, 3H), 1.69 (s, 3H), 1.22 (dd, *J* = 7.2, 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 (C), 137.6 (C), 136.5 (C), 129.4 (CH), 128.4 (CH), 126.4 (C), 121.2 (C), 95.3 (C), 62.8 (CH_2), 43.8 (CH), 37.7 (CH_2), 33.9 (CH_2), 21.2 (CH_3), 19.4 (CH_3), 18.4 (CH_3), 13.8 (CH_3). IR (KBr/cm^{-1}) 1753, 1553; HRMS (ESI/TOF) calculated for (M + H^+) $C_{18}H_{24}NO_4$: 318.1700, found: 318.1696.

4-Ethoxycarbonyl-5-(4-methoxyphenyl)-1,2-dimethyl-4-nitrocyclohexene (3b). Pale-yellow oil (*dr* = 70/30). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 4.05 (d, *J* = 7.6 Hz, 1H), 3.77 (s, 3H), 2.7–3.1 (m, 3H), 2.27 (br d, *J* = 18.4 Hz, 1H), 1.72 (s, 3H), 1.67 (s, 3H), 1.56 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (C), 159.2 (C), 132.1 (C), 129.6 (CH), 125.7 (C), 121.2 (C), 114.2 (CH), 95.6 (C), 62.7 (CH_2), 55.3 (CH_3), 42.4 (CH), 36.3 (CH_2), 34.0 (CH_2), 19.2 (CH_3), 18.6 (CH_3), 13.9 (CH_3). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 4.23 (dq, *J* = 7.2, 14.4 Hz, 1H),4.22 (dq, *J* = 7.2, 14.4 Hz, 1H), 3.93 (d, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 2.7–3.1 (m, 3H), 2.27 (br d, *J* = 17.2 Hz, 1H), 1.72 (s, 3H), 1.67 (s, 3H), 1.22 (dd, *J* = 7.2, 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 (C), 159.2 (C), 131.5 (C), 129.6 (CH), 125.7 (C), 121.2 (C), 114.0 (CH), 95.3 (C), 62.7 (CH_2), 55.3 (CH_3), 43.5 (CH), 37.8 (CH_2), 34.0 (CH_2), 19.4 (CH_3), 18.4 (CH_3), 13.9 (CH_3); HRMS (ESI/TOF) calculated for (M + H^+) $C_{18}H_{24}NO_5$: 334.1649, found: 334.1648.

4-Ethoxycarbonyl-1,2-dimethyl-4-nitro-5-phenylcyclohexene (3c). Pale-yellow oil (*dr* = 62/38). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.10 (m, 5H), 4.08 (br d, *J* = 7.3 Hz, 1H), 4.05 (q, *J* = 7.3 Hz, 2H), 2.72–3.00 (m, 3H), 2.30 (br d, *J* = 18.3 Hz, 1H), 1.68 (s, 3H), 1.72 (s, 3H), 1.12 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (C), 140.2 (C), 128.8 (CH), 128.5 (CH), 127.9 (CH), 125.7 (C), 121.3 (C), 95.6 (C), 62.7 (CH_2), 43.1 (CH), 36.1 (CH_2), 33.9 (CH_2), 19.3 (CH_3), 18.6 (CH_3), 13.8 (CH_3). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.10 (m, 5H), 4.22 (dq, J = 7.3, 10.6 Hz, 1H), 4.21 (dq, *J* = 7.3, 10.6 Hz, 1H), 3.97 (br dd, *J* = 7.8, 2.3 Hz, 1H), 2.72–3.00 (m, 3H), 2.41 (br d, *J* = 17.4 Hz, 1H), 1.73 (s, 3H), 1.69 (s, 3H), 1.12 (dd, *J* = 7.3, 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 (C), 139.5 (C), 128.7 (CH), 128.5 (CH), 127.9 (CH), 126.4 (C), 121.2 (C), 95.2 (C), 62.9 (CH_2), 44.2 (CH), 37.6 (CH_2), 34.0 (CH_2), 19.5 (CH_3), 18.4 (CH_3), 13.8 (CH_3); HRMS (ESI/TOF) calculated for (M + H^+) $C_{17}H_{22}NO_4$: 304.1543, found: 304.1540.

5-(4-Bromophenyl)-4-ethoxycarbonyl-1,2-dimethyl-4-nitrocyclohexene (3d). Pale-yellow solid (*dr* = 52/48). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 4.23 (dq, *J* = 7.2, 10.8 Hz, 1H), 4.20 (dq, *J* = 7.2, 10.8 Hz, 1H),

3.94 (d, *J* = 7.2 Hz,1H), 2.7–3.1 (m, 3H), 2.36 (br d, *J* = 18.0 Hz, 1H), 1.72 (s, 3H), 1.68 (s, 3H), 1.21 (dd, *J* = 7.2, 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (C), 138.5 (C), 131.8 (CH), 130.3 (CH), 126.1 (C), 122.0 (C), 121.4 (C), 94.9 (C), 63.0 (CH_2), 43.6 (CH), 37.3 (CH_2), 34.1 (CH_2), 19.4 (CH_3), 18.4 (CH_3), 13.8 (CH_3). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 4.08 (q, *J* = 7.2 Hz, 2H), 4.03 (br d, *J* = 7.6 Hz, 1H), 2.7–3.1 (m, 3H), 2.26 (br d, *J* = 19.2 Hz, 1H), 1.72 (s, 3H), 1.67 (s, 3H), 1.56 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6 (C) 139.1 (C), 131.9 (CH), 130.3 (CH), 125.5 (C), 122.0 (C), 121.4 (C), 95.2 (C), 62.8 (CH_2), 42.8 (CH), 35.9 (CH_2), 34.1 (CH_2), 19.2 (CH_3), 18.5 (CH_3), 13.8 (CH_3). IR (KBr/cm^{-1}) 1752, 1554; HRMS (ESI/TOF) calculated for (M + H$^+$) $C_{17}H_{20}BrNO_4$: 382.0649, found: 382.0644.

4-Ethoxycarbonyl-5-[4-(trifluoromethyl)phenyl]-1,2-dimethyl-4-nitrocyclohexene (3e). Pale-yellow oil (*dr* = 62/38). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 4.15 (d, *J* = 7.2 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 2.6–3.1 (m, 3H), 2.31 (d, *J* = 18.4 Hz, 1H), 1.74 (s, 3H), 1.69 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6 (C), 144.2 (C), 130.2 (C, q, *J* = 33 Hz), 129.1 (CH), 125.7 (CH, q, *J* = 4 Hz), 125.5 (C), 124.1 (C, q, *J* = 270 Hz), 121.6 (C), 95.1 (C), 62.9 (CH_2), 43.2 (CH), 35.9 (CH_2), 34.1 (CH_2), 19.2 (CH_3), 18.5 (CH_3), 13.7 (CH_3). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 4.25 (dq, *J* = 7.2, 10.8 Hz, 1H), 4.21 (dq, *J* = 7.2, 10.8 Hz, 1H), 4.04 (dd, *J* = 2.8, 7.2 Hz, 1H), 2.6–3.1 (m, 3H), 2.41 (d, *J* = 18.8 Hz, 1H), 1.74 (s, 3H), 1.69 (s, 3H), 1.21 (dd, *J* = 7.2, 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (C), 144.2 (C), 130.2 (C, q, *J* = 32 Hz), 129.1 (CH), 126.1 (C), 125.6 (CH, q, *J* = 4 Hz), 124.1 (C, q, *J* = 271 Hz), 121.5 (C), 94.8 (C), 63.1 (CH_2), 44.0 (CH), 37.2 (CH_2), 33.9 (CH_2), 19.4 (CH_3), 18.4 (CH_3), 13.8 (CH_3); IR (KBr/cm^{-1}) 1753, 1556, 1167, 1326; HRMS (ESI/TOF) calculated for (M + Na$^+$) $C_{18}H_{19}NO_4F_3Na$: 394.1237, found: 339.1237.

4-Ethoxycarbonyl-1,2-dimethyl-4-nitro-5-[4-nitrophenyl]cyclohexene (3f). Pale-yellow oil (*dr* = 65/35). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 4.18 (d, *J* = 7.3 Hz, 1H), 4.10 (q, *J* = 7.3 Hz, 2H), 2.80–3.09 (m, 3H), 2.33 (d, *J* = 17.8 Hz, 1H), 1.75 (s, 3H), 1.70 (s, 3H), 1.22 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3 (C), 147.6 (C), 147.4 (C), 129.7 (CH), 125.4 (C), 124.0 (CH), 121.7 (C), 94.8 (C), 63.1 (CH_2), 43.3 (CH), 35.8 (CH_2), 34.3 (CH_2), 19.2 (CH_3), 18.6 (CH_3), 13.9 (CH_3). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 4.25 (dq, *J* = 7.3, 10.5 Hz, 1H), 4.22 (dq, *J* = 7.3, 10.5 Hz, 1H), 2.80–3.09 (m, 3H), 2.40 (d, *J* = 18.3 Hz, 1H), 1.76 (s, 3H), 1.71 (s, 3H), 1.22 (dd, *J* = 7.3, 7.3 Hz, 3H), One signal could not be observed presumably due to overlapping; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6 (C), 147.6 (C), 146.8 (C), 129.7 (CH), 125.9 (C), 123.8 (CH), 121.6 (C), 94.6 (C), 63.3 (CH_2), 43.9 (CH), 37.0 (CH_2), 34.2 (CH_2), 19.4 (CH_3), 18.4 (CH_3), 13.9 (CH_3); HRMS (ESI/TOF) calculated for (M + Na$^+$) $C_{17}H_{20}N_2O_6Na$: 371.1214, found: 371.1210.

4-Ethanoyl-4-ethoxycarbonyl-5-(4-methylphenyl)-1,2-dimethylcyclohexene (6). Pale-yellow oil (*dr* = 58/42). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04–6.99 (m, 4H), 4.01 (dq, *J* = 7.3, 10.6 Hz, 1H), 4.06 (dq, *J* = 7.3, 10.6 Hz, 1H), 3.77 (br d, *J* = 7.3 Hz, 1H), 2.87–2.43 (m, 3H), 2.29 (s, 3H), 2.17–2.10 (m, 1H), 2.08 (s, 3H), 1.74 (s, 3H), 1.64 (s, 3H), 1.18 (dd, 7.3, 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0 (C), 170.5 (C), 140.0 (C), 136.4 (C), 129.0 (CH), 128.5 (CH), 126.7 (C), 122.5 (C), 64.1 (C), 61.3 (CH_2), 41.7 (CH), 36.4 (CH_2), 32.4 (CH_2), 26.5 (CH_3), 21.1 (CH_3), 19.6 (CH_3), 18.7 (CH_3), 14.1 (CH_3). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04–6.99 (m, 4H), 4.18 (dq, *J* = 7.3, 10.6 Hz, 1H), 4.14 (dq, *J* = 7.3, 10.6 Hz, 1H), 3.77 (br d, *J* = 7.3 Hz, 1H), 2.87–2.43 (m, 3H), 2.28 (s, 3H), 2.17–2.10 (m, 1H), 1.95 (s, 3H), 1.74 (s, 3H), 1.65 (s, 3H), 1.19 (dd, 7.3, 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.4 (C), 171.7 (C), 139.3 (C), 136.5 (C), 129.1 (CH), 128.4 (CH), 125.6 (C), 123.3 (C), 64.2 (C), 61.4 (CH_2), 42.7 (CH), 37.0 (CH_2), 32.4 (CH_2), 27.4 (CH_3), 21.1 (CH_3), 19.5 (CH_3), 18.7 (CH_3), 14.1 (CH_3); HRMS (ESI/TOF) calculated for (M + Na$^+$) $C_{20}H_{26}O_3Na$: 337.1774, found: 337.1774.

4-Cyano-4-methoxycarbonyl-1,2-dimethyl-5-(4-methylphenyl)cyclohexene (7). Pale-yellow oil (*dr* = 100/0). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 3.49 (s, 3H), 3.22 (dd, *J* = 7.2, 12.0 Hz, 1H), 2.92 (br d, *J* = 16.8 Hz, 1H), 2.73 (br dd, *J* = 17.6, 12.0 Hz, 1H), 2.46 (d, *J* = 16.8 Hz, 1H), 2.32 (s, 3H), 2.23 (dd,

J = 7.2, 17.6 Hz, 1H), 1.71 (br s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4 (C), 137.7 (C), 136.1 (C), 129.4 (CH), 127.9 (CH), 126.5 (C), 121.0 (C), 118.7 (C), 53.2 (CH_3), 50.6 (C), 45.9 (CH), 41.0 (CH_2), 36.3 (CH_2), 21.2 (CH_3), 18.9 (CH_3), 18.6 (CH_3); IR (KBr/cm^{-1}) 1740; HRMS (ESI/TOF) calculated for (M + H$^+$) $C_{18}H_{22}NO_2$: 284.1645, found: 284.1645.

5-Ethoxycarbonyl-6-(4-methylphenyl)-5-nitrobicyclo [2.2.1]hept-2-ene (9). Yellow oil (*dr* = 59/25/15/1). ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 7.20 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.66 (dd, *J* = 3.2, 5.5 Hz, 1H), 6.07 (dd, *J* = 2.7, 5.5 Hz, 1H), 4.04 (d, *J* = 2.7 Hz, 1H), 3.76 (d, *J* = 2.7 Hz, 1H), 3.73 (dq, *J* = 7.3, 10.5 Hz, 1H), 3.61 (dq, *J* = 7.3, 10.5 Hz, 1H), 3.16 (br s, 1H), 2.72 (d, *J* = 9.6 Hz, 1H), 2.30 (s, 3H), 1.95 (d, *J* = 9.6 Hz, 1H), 0.82 (dd, *J* = 7.3, 7.3 Hz, 3H); Minor isomer 1: δ 7.02 (d, *J* = 8.2 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.66–6.69 (m, 1H), 6.49 (dd, *J* = 3.2, 5.5 Hz, 1H), 4.58 (d, *J* = 3.2 Hz, 1H), 4.30 (q, *J* = 6.9 Hz, 2H), 3.62–3.64 (m, 1H), 3.10–3.15 (m, 1H), 2.27 (s, 3H), 1.62–1.70 (m, 2H), 1.28 (t, *J* = 6.9 Hz, 3H); Minor isomer 2: δ 7.02–7.07 (m, 4H), 6.62–6.65 (m, 1H), 6.47 (dd, *J* = 2.7, 5.5 Hz, 1H), 4.74 (d, *J* = 3.2 Hz, 1H), 3.80–3.83 (m, 1H), 3.58–3.79 (m, 2H), 3.11–3.14 (m, 1H), 2.28 (s, 3H), 1.62–1.70 (m, 2H), 0.69 (t, *J* = 7.3 Hz, 3H); HRMS (ESI/TOF) calculated for (M + H$^+$) $C_{17}H_{19}NO_4$: 324.1206, found: 324.1196.

4-Ethoxycarbonyl-3-methoxy-5-(4-methylphenyl)-1-(trimethylsiloxy)-4-nitrocyclohexene (11). Pale-yellow oil (*dr* = 86/14). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.17 (d, *J* = 4.0 Hz, 1H), 4.54 (d, *J* = 4.0 Hz, 1H), 4.24 (dq, *J* = 7.2, 10.8 Hz, 1H), 4.16 (dq, *J* = 7.2, 10.8 Hz, 1H), 3.94 (dd, *J* = 6.4, 8.0 Hz, 1H), 3.41 (s, 3H), 2.38 (dd, *J* = 6.4, 18.0 Hz, 1H), 2.39 (dd, *J* = 8.0, 18.0 Hz, 1H), 2.32 (s, 3H), 1.23 (dd, *J* = 7.2, 7.2 Hz, 3H), 0.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5 (C), 153.5 (C), 137.7 (C), 135.3 (C), 129.4 (CH), 128.9 (CH), 100.3 (CH), 96.2 (C), 76.4 (CH), 62.3 (CH_2), 57.4 (CH_3), 42.7 (CH), 35.3 (CH_2), 21.2 (CH_3), 14.0 (CH_3), 0.4 (CH_3); IR (KBr/cm^{-1}) 1766, 1733, 1549, 1244, 1220, 1084, 849; HRMS (ESI/TOF) calculated for (M + Na$^+$) $C_{20}H_{29}NO_6SiNa$: 430.1656, found: 430.1651.

4-Ethoxycarbonyl-3-methoxy-5-(4-methylphenyl)-4-nitrocyclohexanone (12). Pale-yellow oil (*dr* = 95/5). ^{1}H NMR (400 MHz, CD_3Cl) δ 7.06 (s, 4H), 4.49 (dd, *J* = 4.1, 4.1 Hz, 1H), 4.27 (dq, *J* = 7.3, 11.0 Hz, 1H), 4.21 (dd, *J* = 5.5, 11.4 Hz, 1H), 4.20 (dq, *J* = 7.3, 11.0 Hz, 1H), 3.39 (dd, *J* = 4.1, 15.6 Hz, 1H), 3.35 (3H, s), 2.90 (dd, *J* = 11.4, 15.6 Hz, 1H), 2.81 (ddd, *J* = 1.8, 4.1, 15.6 Hz, 1H), 2.72 (ddd, *J* = 1.8, 5.5, 15.6 Hz, 1H), 2.28 (s, 3H), 1.23 (dd, *J* = 7.3, 7.3 Hz, 3H); ^{13}C NMR (101 MHz) δ 205.5 (C), 163.9 (C), 137.9 (C), 134.0 (C), 128.9 (CH), 128.6 (CH), 95.5 (C), 79.4 (CH), 62.6 (CH_2), 57.6 (CH), 43.9 (CH_3), 43.5 (CH_2), 41.1 (CH_2), 20.9 (CH_3), 13.7 (CH_3); IR (KBr/cm^{-1}) 1766, 1729, 1548, 1243, 1083; HRMS (ESI/TOF) calculated for (M + H$^+$) $C_{17}H_{22}NO_6$: 336.1442, found: 336.1443.

3-Ethoxycarbonyl-4-(4-methylphenyl)-3-nitro-6-[(2,4dinitrophenyl)hydrazino)]cyclohexene (13). Orange needles, m.p. 110–111 °C. ^{1}H NMR (400 MHz, CD_3Cl) δ 11.24 (br s, 1H), 9.11 (d, *J* = 2.4 Hz, 1H), 8.37 (dd, *J* = 2.4, 9.6 Hz, 1H), 8.06 (d, *J* = 9.6 Hz, 1H), 7.05 (s, 4H), 6.83 (d, *J* = 9.2 Hz, 1H), 6.65 (dd, *J* = 0.9, 9.2 Hz, 1H), 4.42 (dq, *J* = 7.3, 10.1 Hz, 1H), 4.42 (ddd, *J* = 0.9, 2.7, 6.9 Hz, 1H), 4.30 (dq, *J* = 7.3, 10.1 Hz, 1H), 3.42 (dd, *J* = 6.9, 17.4 Hz, 1H), 3.04 (dd, *J* = 2.7, 17.4 Hz, 1H), 2.27 (s, 3H), 1.29 (dd, *J* = 7.3, 7.3 Hz, 3H); ^{13}C NMR (101 MHz, CD_3Cl) δ 164.8 (C), 148.1 (C), 144.4 (C), 139.2(C), 138.7 (C), 134.4 (C), 132.1 (CH), 130.5 (C), 130.3 (CH), 129.8 (CH), 128.3 (CH), 127.1 (CH), 123.4 (CH), 116.8 (CH), 93.8 (C), 63.9 (CH_2), 43.3 (CH), 28.9 (CH_2), 21.2 (CH_3), 13.9 (CH_3); IR (KBr/cm^{-1}) 1750, 1616, 1337, 771; HRMS (ESI/TOF) calculated for (M + H$^+$) $C_{22}H_{22}NO_2$: 484.1463, found: 484.1453.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/reactions3040041/s1. Copies of the NMR and HRMS spectra of compounds **1**, **3**, **6**, **7**, **9**, and **11**–**13**, as well as the crystallographic data of **13**.

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