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Michael monoadditions of nitromethane or nitroethane with electrophilic *gem*-disubstituted alkenes over alumina under microwave irradiation

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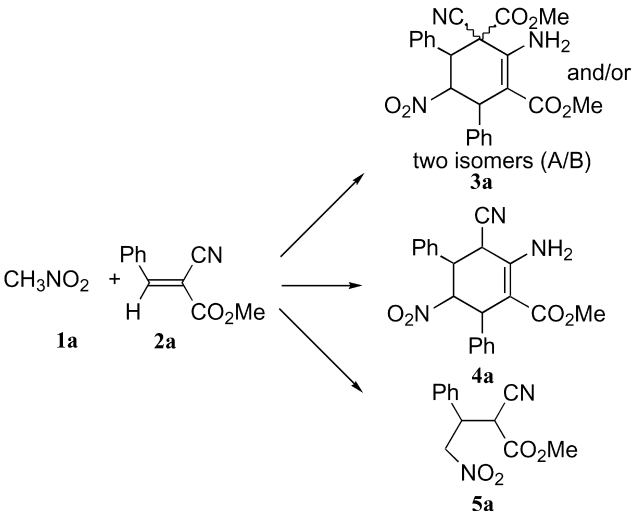
Abstract—Nitromethane **1a** or nitroethane **1b** react with electrophilic alkenes **2a–i** RCH=C(CN)(Y) with Y=CO_2R', CN, $CONH_2$ adsorbed on alumina to give selectively at room temperature or under focused microwave irradiation new Michael monoadducts **5** (two diastereoisomers) or **6** (four diastereoisomers) after a few minutes. It is possible to obtain only two diastereoisomers of **6** by reaction of the corresponding nitroalkene and methylcyanoacetate in the presence of catalytic amounts of piperidine. Mechanisms are proposed. Some examples of addition of nitroalkanes with electron-deficient alkynes in dry media coupled with microwave irradiation conditions are also described.

1. Introduction

Michael addition of nitroalkanes with electron-deficient alkenes has been extensively used in organic synthesis and largely reviewed.[1–3] A wide variety of catalysts[4–8] has been used in various experimental conditions. However, the reactions of nitromethane or nitroethane are not very clean and lead to many side-products owing to polymerization after long heating time under classical conditions (oil-bath).

We reported recently the reactions Michael Michael Induced Ring Closure (MIMIRC) of nitromethane **1a** with electrophilic alkenes **2a–i** in solvent-free reaction under microwave irradiation.[9,10] The course of the reaction was strongly depending on the experimental conditions. We showed that it was possible to isolate the acyclic intermediate **5a** when nitromethane **1a** in excess (3 equiv.) or in stoichiometric amount in a polar solvent as acetonitrile and methyl benzylidene cyanoacetate **2a** were mixed in the presence of piperidine (3% towards the alkene) (Scheme 1). However, the presence of some amount of cyclohexene **3a** (10%) made the purification of the product **5a** tedious. The preliminary results related to the Michael monoaddition of nitromethane **1a** or nitroethane **1b** in reaction with electrophilic alkenes **2a–i** RCH=C(CN)(Y) by simple adsorption over alumina being already published,[11] we now report the full paper dealing with the synthesis of these new



Scheme 1. Ref. 9.

Michael adducts in dry media under microwave irradiation;[12] the optimization of the addition, a proposition of mechanism, a discussion of the diastereoselectivity and the extension of the reactions are described.

2. Results and discussion

The model reaction of nitromethane **1a** with methyl benzylidene cyanoacetate **2a** was carried out with various catalysts in order to study the factors which govern the ratio of the final products **5a** and **3a**: nature and mass of the

Keywords: microwave heating; Michael additions; nitrocompounds; electrophilic alkenes; solvent-free reactions; green chemistry.

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Table 1. Reaction of nitromethane with alkene **2a** and various catalysts under microwave irradiation

Entry	Catalyst	Mass (g)	Percent completion[a] (%)	**3a** (%)	**5a** (%)
1	K10[b]	1.5	0	0	0
2	*i*-Pr_2NEt	0.026	73	51	22
3	NEt_3	0.02	5	0	5
4	*t*BuOK	0.02	55	10	44
5	Al_2O_3	1	66	~0	66

[a] Calculated with respect to nitromethane.
[b] Montmorillonite (clay).

and the reaction time: at 120°C with 0.5 g of alumina, the percent completion is 70% but, at 90°C, the percent completion is 79% (and is stable for a longer time 76% after 16 min). The reaction, at room temperature, is nearly quantitative (95% completion) but the percentage of cyclohexene **3a** is significant (15%). After examination of these various experimental conditions, we decided to run the reaction with 0.5 g of alumina during 11 min at 90°C reached after 3 min (Fig. 1) with an excess of nitromethane[9] (3 equiv. with respect to methyl benzylidene cyanoacetate **2a**) which favoured the formation of **5a**. Pure monoadduct **5a** (two diastereoisomers A and B: 50/50) was isolated in 70% yield after slow crystallization from ether/pentane

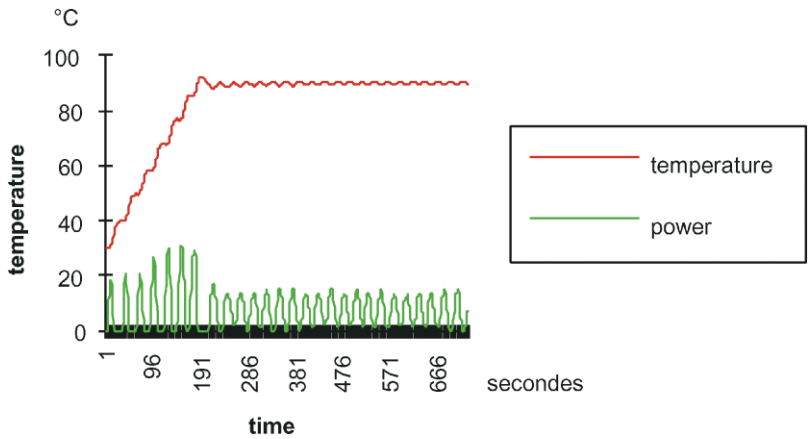


Figure 1. Temperature profile under microwave irradiation.

catalyst, temperature (final temperature assigned by computer of the PROLABO Synthewave 402®),[13,14] irradiation time.

First, we have studied the nature of the catalyst (Table 1). The alkene **2a** (5 mmol) and nitromethane **1a** (2.5 mmol) were mixed, the catalyst added and the mixture irradiated at a power of 150 W with a temperature of 90°C (temperature previously used and optimized for the cyclohexene synthesis) reached after 3 min and maintained for 11 min.

The experimental results show that solid alumina is an efficient and selective catalyst: no cyclohexene **3a** was detected (<5%). We can also note that *i*-Pr_2NEt, an homogeneous base, acts as piperidine[9] which favoured **3a** but is less efficient (73% completion).

So, we studied the influence of the mass of alumina. The reaction was realized at 120°C (in order to try to eliminate completely the cyclohexene formation which is disfavoured when temperature is increased) with an equimolar mixture of 2.5 mmol of nitromethane **1a** and methylbenzylidene cyanoacetate **2a**. The reaction proceeds during 11 min and final temperature was reached after 3 min. The mass of alumina in the range of 0.5 g (2 equiv.), 1 g (4 equiv.) and 1.5 g (6 equiv.) gave respectively, 70, 58 and 49% of the adduct **5a** at 120°C. An excess of alumina (2 equiv.) is necessary but a large one (6 equiv.) made the reaction slower by dilution of reactants.

Then, we were interested in the influence of the temperature (95/5), the crude yield estimated by ^1H NMR being 95%. The spectroscopic data for **5a** were reported in Ref. 10.

Looking for a possible specific microwave effect, we realized the reaction in an oil-bath at 90°C with a temperature profile close to the one observed under microwaves (Fig. 2). The crude yield estimated by ^1H NMR being 93%, no specific effect was detected. However, the use of microwave heating is easier, cleaner, instantaneous, with a great reproductibility and precision in the assigned temperature.

The second part of our discussion is focused on the mechanism of the formation of **5a** by adsorption on alumina and the diastereoselectivity of the formation of the isomers A and B. The reaction takes place at the solid–liquid interface: the reactive species interact with the acidic and

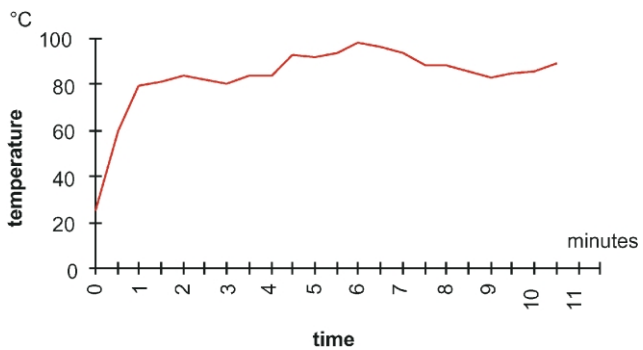
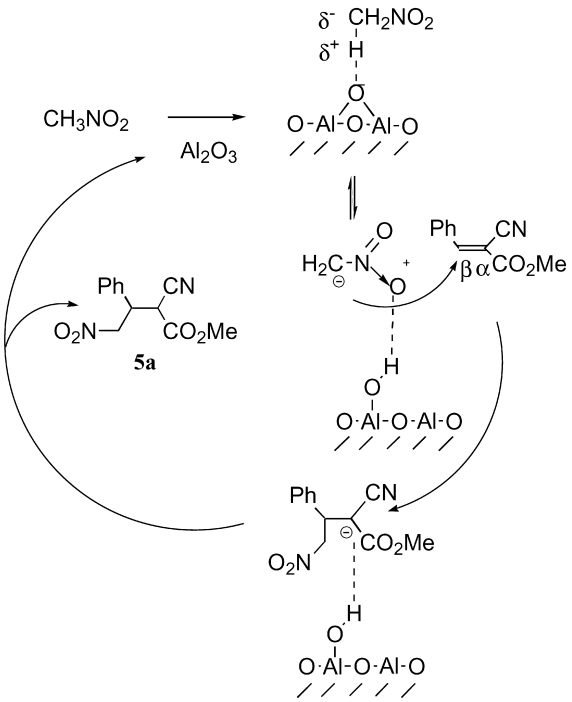


Figure 2. Temperature profile under classical heating.

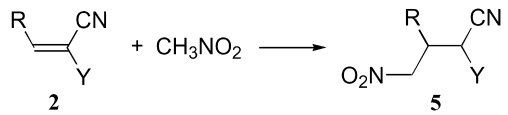


Scheme 2.

basic sites of the catalyst. Acidic nitromethane is deprotonated to form the corresponding planar anion stabilized by resonance. This anion attacks the β-carbon of the nitrile group of the alkene **2a** in the perpendicular plane with the same probability. Nucleophilic addition occurs upon the surface of alumina where **2a** and the nitroanion were adsorbed before the protonation of the latter (Scheme 2).

The ^{1}H NMR analysis of the final crude reaction mixture showed the presence of two diastereoisomers A and B (55/45) of **5a**: R–CH^2(CH_2NO_2)–CH^1(CN)(CO_2Me) evaluated by the integration of the methyl ester group (3.67 ppm for A and 3.75 ppm for B) and proton H^1 (δH^1=4.15 ppm, $^3J_{HH}$=5.8 Hz for A and δH^1=3.96 ppm, $^3J_{HH}$=5.4 Hz for B). A and B were formed after the non-stereoselective protonation of the stabilized planar carbanionic intermediates I and II (Scheme 3).

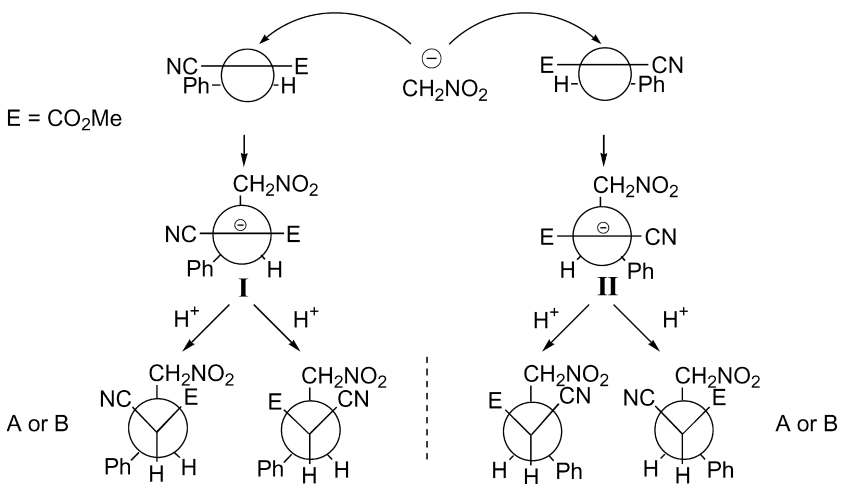
Table 2. Preparation of monoadducts **5a–i** on alumina under microwave irradiation



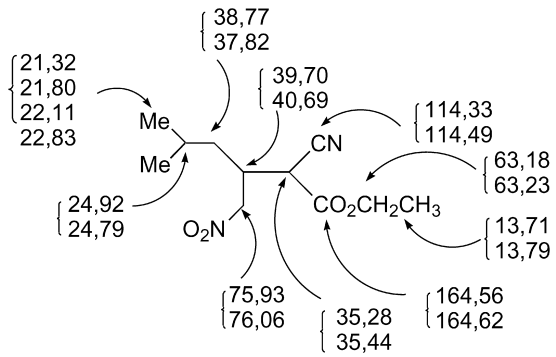
Y	R	Compounds	Molecular formula	**5a–i**[a] Yield (%)
CO_2Me	C_6H_5	**5a**	$C_{12}H_{12}N_2O_4$	70
CO_2Me	*p*-Cl C_6H_4	**5b**	$C_{12}H_{11}N_2O_4Cl$	72
CO_2Me	*o*-Br C_6H_4	**5c**	$C_{12}H_{11}N_2O_4Br$	83
CO_2Me	*o*-F C_6H_4	**5d**	$C_{12}H_{11}N_2O_4F$	70
CO_2Me	*m*-F C_6H_4	**5e**	$C_{12}H_{11}N_2O_4F$	72
CO_2Et	*iso*-Bu	**5f**	$C_{11}H_{18}N_2O_4$	70
CO_2Me	2-Cl-5-NO_2 C_6H_3	**5g**	$C_{12}H_{10}N_3O_6Cl$	70
CN	C_6H_5	**5h**	$C_{11}H_9N_3O_2$	63[b]
$CONH_2$	C_6H_5	**5i**	$C_{11}H_{11}N_3O_3$	68

[a] Two diastereoisomers A and B are present (50/50).
[b] 15 equiv. of nitromethane are used (3 equiv. otherwise); presence of the corresponding cyclohexene (20%).

According to these results, we have applied the methodology to the alkenes RCH=C(CN)Y **2a–i** with various substituents on the aromatic ring and electron-withdrawing groups Y and easily prepared the monoadducts **5a–i** (Table 2). The assignment of the ^{13}C NMR signals of **5f** was achieved by selective irradiation: the chemical shifts are reported in Scheme 4. In the same way, we prepared the new monoadducts **6** (for example, **6b**,**e** and **6f**) by using nitroethane and an alkene **2b**,**e** and **2f** (Table 3). The reaction times are longer in comparison with nitromethane (40 min). In this case, four diastereoisomers are present: the percentage of A, B, C, D was estimated by the ^{1}H NMR of proton H^1. The reversibility of the monoaddition was shown experimentally by irradiation of a mixture of monoadduct **6e** (5 mmol), alumina (0.1 g) and nitroethane (2 equiv.) during 12 min at 90°C reached after 3 min: the initial alkene **2e** is formed (30%). The reaction under these conditions is thermodynamically controlled. Indeed, a longer time (55 min) does not affect the final yield and the stereoselectivity. It is interesting to note that 2-nitropropane is unreactive under these conditions.

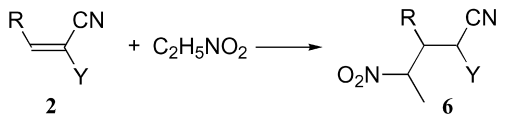


Scheme 3.



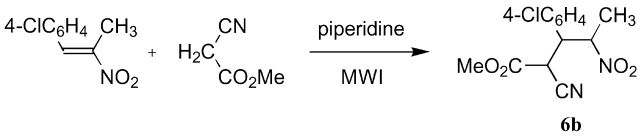
Scheme 4.

Table 3. Preparation of monoadducts **6b**,**e** and **6f** on alumina under microwave irradiation



Compounds	Yield (%)	A (%)[a]	B (%)[a]	C (%)[a]	D (%)[a]
6b	100[a,b]	43.5	28	17.5	11
6e	72[c]	40	29	19	12
6f	70[c]	36	23	21	20

[a] Estimated by ^{1}H NMR (±5%).
[b] Oily mixture.
[c] Pure product.



Scheme 5.

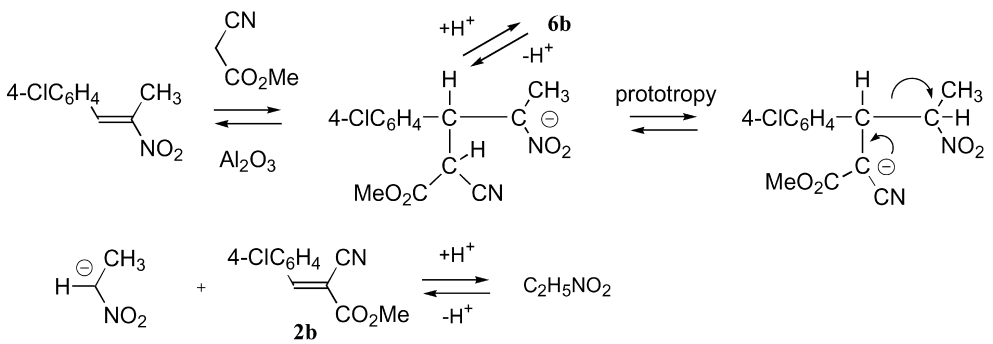
It was possible to prepare only two among the four diastereoisomers:[18] for instance **6b** (A/D: 75/25) are formed by reaction of the corresponding nitroalkene (15 mmol) and methylcyanoacetate (20 mmol) without solvent at room temperature in presence of piperidine (10%). **6b** is isolated in 85% yield after 4 h (65% under microwaves after 2 min at 90°C): the isomer A (mp: 156°C) is crystallized in ether (Scheme 5). The planar conjugated carbanion of methyl-cyanoacetate attacks the nitroalkene in a direction parallel to the plane of the molecules and the regioselectivity should be favoured by the interaction between the phenyl and the ester groups.

In this case, alumina was useless (0% of **6b**): the alkene **2b** was recovered after Michael retro-addition which took place on alumina (Scheme 6). Prototropy is possible owing to the close values of pK_a of the nitroalkyl and the cyanoacetate anion. Indeed, under microwaves at 90°C (30 W), a partial degradation of the adduct **6b** obtained with piperidine is observed: after 2 min, the yield of **6b** is 65% and decreased to 53% after 7 min.

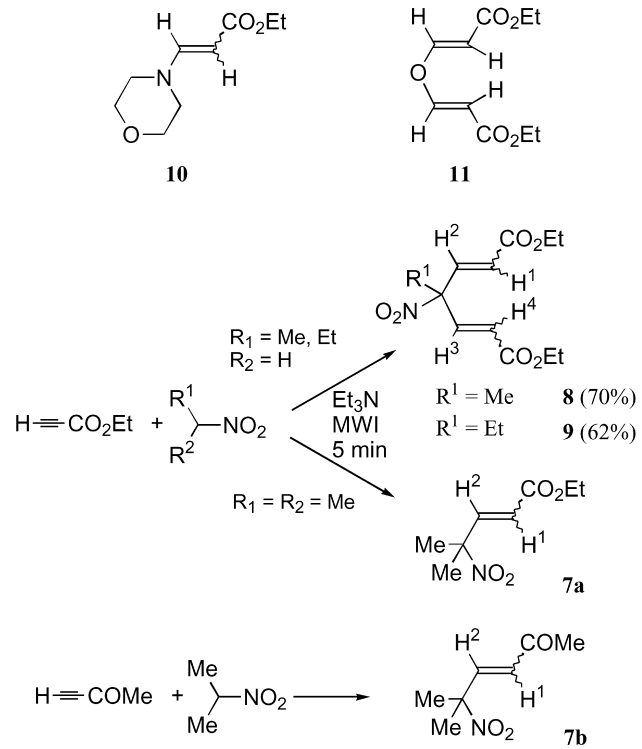
With the aim to widen the scope of the Michael addition of nitroalkanes to electron-withdrawing substituted alkynes, we have realized the reaction of nitromethane, nitroethane and 2-nitropropane with ethyl propiolate or 3-butyn-2-one (Scheme 7). It is necessary to realize the addition under dry inert atmosphere to avoid the formation of divinylether **11** after the hydrolysis of the starting ethyl propiolate.[19–22] Otherwise, the experimental conditions should be strictly controlled because of the polymerisations. A non-nucleophilic amine as NEt_3 must be used to avoid the formation of enamine **10**[23](for example, with morpholine). The reaction mixture must be cooled during the addition of NEt_3 and irradiated for 5 min at a monitored temperature of 60 or 70°C.

The two *E* and *Z* isomers of the monoadducts **7a**,**b** from 2-nitropropane are formed in similar ratio (60/40). Nitroethane and 1-nitropropane lead to the bis-adducts **8** and **9**[25] as three isomers A (*E*,*E*), B (*Z*,*E*) and C (*Z*,*Z*) formed in small amount (11%) because of steric hindrance. The assignments of ^{1}H NMR signals were based upon the comparison of coupling constants ($^3J_{trans}$~16 Hz, $^3J_{cis}$~12 Hz). Nitromethane gives non-identified side-products. The selective preparation of monoadducts from primary nitroalkanes was not observed in our experimental conditions.

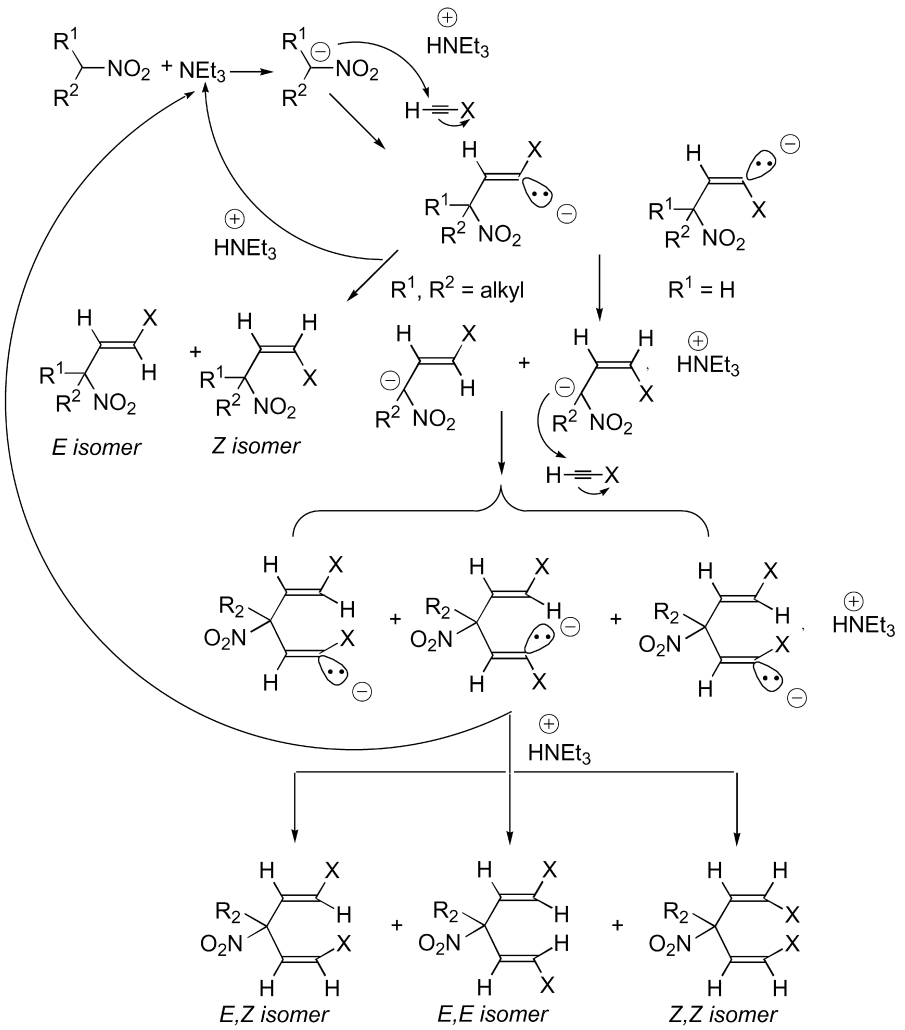
The general mechanism is proposed in Scheme 8: triethylamine promotes a regiospecific nucleophilic addition-Michael type-of nitroalkane with the alkyne to give a vinylic intermediate which leads to the monoadduct (*E* and *Z*) after protonation. In the presence of two acidic hydrogens, a second addition occurs spontaneously to generate the bis-adduct (*EZ*,*EE*,*ZZ*-minor-). No cyclization was observed.



Scheme 6.



Scheme 7.



Scheme 8.

3. Conclusion

We have reported in this paper the selective, new and efficient Michael monoaddition of nitromethane or nitroethane upon electrophilic alkenes RCH=C(CN)(Y) with (Y=CO_2R', CN, $CONH_2$) by simple adsorption on chromatographic alumina, without solvent under microwave irradiation within a few minutes to obtain these, up to now, unknown monoadducts.

We have also proposed a useful alternative for the preparation of some allylic nitrocompounds by microwave heating during 5 min, under dry nitrogen atmosphere and triethylamine in catalytic amount. This work is another example of organic synthesis in the area of Green Chemistry which offers clean, economical and ecofriendly processes.

4. Experimental

4.1. General methods

Melting points were determined on a Kofler melting point apparatus and are uncorrected. IR spectra were taken with a PERKIN–ELMER 1420 spectrometer. ^{1}H NMR spectra were recorded on BRUKER ARX 200 (200 MHz),

BRUKER AC 300 P (300 MHz) spectrometers and ^{13}C NMR spectra on BRUKER AC 300 P (75 MHz) spectrometer. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. The mass spectra (MS) were taken on a VARIAN MAT 311 at an ionizing potential of 70 eV in the Centre de Mesures Physiques de l'Ouest (CRMPO, Rennes). Elemental analysis were performed at the Laboratoire Central de Microanalyses-CNRS (Lyon). For preparative column chromatography, silica gel 60 Merck (230–240 Mesh ASTM) or alumina 90 Merck was used. Reactions under microwave irradiation were performed in a PROLABO Synthewave 402® (2.45 GHz) microwave reactor with a single focused system.[13,14] All solvents and reagents were purchased from Acros Organics and Aldrich Chimie and used without further purification unless otherwise stated.

Electrophilic alkenes **2a–i** were readily prepared by literature methods.[15,16]

4.2. General procedure for the preparation of Michael adducts 5: R–CH²(CH₂NO₂)–CH¹(CN) Y and 6: R–CH²(CH(CH₃)NO₂)–CH¹(CN) Y

The nitroalkane (nitromethane **1a** or nitroethane **1b**) and the alkene **2a–i** (5 mmol) previously adsorbed on alumina (1 g) were placed in a quartz tube (diameter: 26 mm), with a refluxing condenser, introduced into the Synthewave 402® reactor fitted with rotational system, adjustable power within the range 20–300 W and a wave guide (monomode T_{01}). The temperature consign is programmed with the computer of the oven. (Maximum temperature=90°C reached after 3 min and maintained 9 min for nitromethane; maximum temperature=80°C reached after 3 min and maintained 37 min for nitroethane **1b** for the method A.) After cooling to room temperature, the crude product is extracted with CH_2Cl_2, alumina is removed by filtration, and the solvent evaporated under vacuum. The product is analyzed by ^1H NMR. Two diastereoisomers A and B were isolated after crystallization from cold diethyl ether, chromatography on silica gel (eluent CH_2Cl_2) or purification in a Kugelrohr apparatus.

4.2.1. 2-Cyano-4-nitro-3-phenyl-methylbutanoate (5a). Mp=64°C; A/B=50/50. Yield=70%; ^1H and ^{13}C NMR, HRMS data are reported in Ref. 11. IR (nujol): 1740, 2240 cm^{-1}. Anal. calcd for $C_{12}H_{12}N_2O_4$: C, 58.06; H, 4.87; N, 11.28. Found C, 58.08; H, 4.87; N, 11.30.

4.2.2. 2-Cyano-4-nitro-3-(4-chlorophenyl)-methylbutanoate (5b). Mp=73°C; A/B=45/55. Yield=72%; ^1H NMR ($CDCl_3$, 300 MHz) δ: 3.70 (A) and 3.77 (B) (s, 3H, OCH_3); 3.95 (B) and 4.15 (A) (d, 1H, H^1, ^3J=5.4, 5.6 Hz); 4.18–4.27 (m, 1H, H^2); 4.77–5.04 (m, 2H, CH_2NO_2); 7.24–7.38 (m, 4H arom.). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 41.29 (A) and 41.33 (B) (dm, CH^1, ^1J=136.8, 136.8 Hz); 41.99 (A) and 42.35 (B) (dm, CH^2); 53.96 (A) and 54.14 (B) (q, O–CH_3, ^1J=149.1 Hz); 75.67 (B) and 76.02 (A) (tm, CH_2NO_2); 114.12 (A) and 114.25 (B) (m, CN); 129.03–135.46 (m, =CH arom.); 164.16 (B) and 164.32 (A) (m, CO). IR (nujol): 1530, 1745, 2250 cm^{-1}. HRMS calcd for $C_{12}H_{10}NO_2Cl$: $M^+\cdot-HNO_2$: 282.041, found 282.039. Anal. calcd for $C_{12}H_{11}N_2O_4Cl$: C, 50.98; H, 3.92; N, 9.91. Found C, 51.07; H, 3.94; N, 9.83.

4.2.3. 2-Cyano-4-nitro-3-(2-bromophenyl)-methylbutanoate (5c). Mp=111°C; A/B=50/50. Yield=83%; ^1H NMR (CD_3CN, 200 MHz) δ: 3.76 (B) and 3.81 (A) (s, 3H, OCH_3); 4.07 (A) and 4.32 (B) (d, 1H, H^1, ^3J=4.7, 6.6 Hz); 4.75–5.12 (m, 3H, CH^2 and CH_2NO_2); 7.21–7.68 (m, 4H arom.). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 41.45 (A) and 41.74 (B) (dm, CH^1, ^1J=100.6, 115.5 Hz); 42.04 (A) and 42.12 (B) (dm, CH^2, ^1J=119.5 Hz); 54.68 (A) and 54.84 (B) (q, O–CH_3, ^1J=149 Hz); 75.94 (B) and 77.20 (A) (tm, CH_2NO_2, ^1J=149.5 Hz); 115.35 (A) and 115.70 (B) (m, CN); 125.75–135.58 (m, 6C arom.); 165.68 (B) and 165.83 (A) (m, C=O). IR (nujol): 1540, 1730, 2240 cm^{-1}. HRMS calcd for $C_{12}H_{11}N_2O_4Br$: 325.990, found M+·325.991. Anal. calcd for $C_{12}H_{11}N_2O_4Br$: C, 44.06; H, 3.39; N, 8.56. Found C, 44.19; H, 3.51; N, 8.30.

4.2.4. 2-Cyano-4-nitro-3-(2-fluorophenyl) methylbutanoate (5d). Mp=109°C; A/B=50/50. Yield=70%; ^1H NMR ($CDCl_3$, 300 MHz) δ: 3.71 (A) and 3.72 (B) (s, 3H, OCH_3); 4.05 (B) and 4.2 (A) (d, 1H, CH^1,^3J=6.6, 7.3 Hz); 4.47–4.55 (m, 1H, CH^2); 4.76–5.03 (m, 2H, CH_2NO_2); 7.07–7.19 (m, 2H arom.); 7.30–7.39 (m, 2H arom.).^{13}C NMR ($CDCl_3$, 75 MHz) δ: 37.27 (A) (dm, CH^2, ^1J=137.1 Hz; $^3J_{CF}$=1.7 Hz); 37.48 (B) (dm, CH^2, ^1J=137.8 Hz; $^3J_{CF}$=1.9 Hz); 40.20 (A) and 40.23 (B) (dm, CH^1, ^1J=137.3, 137 Hz); 53.97 (A) and 54.03 (B) (q, O–CH_3, ^1J=149 Hz); 74.87 and 75.55 (A and/or B) (tm, CH_2NO_2, $^4J_{CF}$=2.1, 2.3 Hz); 114.27 (s, CN); 116.18–131.29 (m, 5C arom.); 160.50 (B) and 160.59 (A) (dm, =C–F, $^1J_{CF}$=247.5 Hz); 164.33 (B) and 164.50 (A) (m, CO). IR (nujol): 1540, 1730, 2240 cm^{-1}. HRMS calcd for $C_{12}H_{11}N_2O_4F$: 266.072, found $M^+\cdot$266.069. Anal. calcd for $C_{12}H_{11}N_2O_4F$: C, 54.14; H, 4.16; N, 10.52. Found C, 54.12; H, 4.24; N, 10.62.

4.2.5. 2-Cyano-4-nitro-3-(3-fluorophenyl) methylbutanoate (5e). Mp=74°C; A/B=45/55. Yield=72%; ^1H NMR ($CDCl_3$, 300 MHz) δ: 3.74 (A) and 3.81 (B) (s, 3H, OCH_3); 3.94 (B) and 4.14 (A) (d, 1H, CH^1, ^3J=5.4, 5.7 Hz); 4.20–4.28 (m, 1H, CH^2); 4.79–5.05 (m, 2H, CH_2NO_2); 7.02–7.42 (m, 4H arom.). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 41.27 (A) and 41.33 (B) (dm, CH^1, ^1J=137.2 Hz); 42.26 (A) and 42.53 (B) (dm, CH^2, $^4J_{CF}$=1.7 Hz); 53.98 (A) and 54.17 (B) (q, O–CH_3, ^1J=149 Hz); 75.62 (B) and 75.99 (A) (tm, CH_2NO_2); 114.09–136.98 (m, CN and 5C arom.); 161.23 (A) and 161.34 (B) (dm, =C–F, $^1J_{CF}$=248 Hz); 164.18 (A) and 164.34 (B) (m, CO). IR (nujol): 1725, 2240 cm^{-1}. HRMS calcd for $C_{12}H_{10}NO_2F$: $M^+\cdot-HNO_2$: 219.069, found 219.070. Anal. calcd for $C_{12}H_{11}N_2O_4F$: C, 54.14; H, 4.16; N, 10.52. Found C, 53.85; H, 4.15; N, 10.57.

4.2.6. 2-Cyano-5-methyl-3-nitromethyl-ethylhexanoate (5f). Bp 0.05 Torr=120°C; A/B=50/50. Yield=70%; ^1H NMR ($CDCl_3$, 300 MHz) δ: 0.93–1.00 (m, 6H, $(CH_3)_2C$); 1.35 (t, 3H, CH_3CH_2O, ^3J=7.1 Hz); 1.30–1.46 (m, 2H, $CHCH_2$); 1.65–1.70 (m, 1H, $(CH_3)_2CH$); 3.00–3.10 (m, 1H, CH^2); 3.82 and 3.95 (d, 1H, CH^1, ^3J=4.1, 4.0 Hz); 4.29 and 4.31 (q, 2H, O–CH_2, ^3J=7.1 Hz); 4.42–4.63 (m, 2H, CH_2NO_2). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.71 and 13.79 (qm, OCH_2CH_3, ^1J=127.5 Hz); 21.32, 21.80, 22.11 and 22.83 (qm, CH_3CH, ^1J=136.5 Hz); 24.79 and 24.92 (dm, CH, ^1J=124 Hz); 35.28 and 35.44 (dm, CH^1, ^1J=136 Hz); 37.82 and 38.78 (tm, CH_2, ^1J=145 Hz); 39.70 and 39.74 (dm, CH^2, ^1J=136.5 Hz); 40.64 and 40.69 (dm, CH^2,

^1J=136.5 Hz); 63.18 and 63.23 (tm, OCH_2, ^1J=149 Hz); 75.93 and 76.07 (tm, CH_2NO_2, ^1J=147 Hz); 114.33 and 114.49 (m, CN); 164.56 and 164.62 (m, C=O). IR (nujol): 1540, 1730, 2250 cm^{-1}. HRMS calcd for $C_9H_{13}N_2O_3$: $M^{+\cdot}-C_2H_5O$: 197.O95, found 197.093. Anal. calcd for $C_{11}H_{18}N_2O_4$: C, 54.53 H, 7.49; N, 11.56. Found C, 54.36; H, 7.49; N, 11.56.

This compound was analyzed by F.A.B mode:[17] $(C_{11}H_{19}N_2O_4)^+$: (M^+; +H) calcd: 243.135, found 243.135.

4.2.7. 2-Cyano-4-nitro-3-(2-chloro-5-nitrophenyl)-methylbutanoate (5g). Mp=166°C; A/B=50/50. Yield=70%; ^{1}H NMR (DMSO *d*-6, 300 MHz) δ: 3.74 (B) and 3.78 (A) (s, 3H, OCH_3); 4.79–4.96 (m, 2H, CH^1 and CH^2, ^3J=5.8, 7.3 Hz); 5.28–5.52 (m, 2H, CH_2NO_2); 7.87–8.71 (m, 3H arom.). ^{13}C NMR (DMSO-*d*6, 75 MHz) δ: 35.85 and 35.99 (dm, CH^1 and CH^2 not discerned because masked by DMSO); 53.74 (q, O–CH_3, ^1J=149 Hz); 75.07 and 75.62 (tm, CH_2NO_2, ^1J=152.5, 148 Hz); 114.69 and 114.77 (B) (m, CN); 123.25–131.28 (m, 3C arom.); 140.80–146.87 (m, 3C quat. arom.); 164.33 and 164.56 (m, C=O). IR (nujol): 1530, 1730, 2220 cm^{-1}. HRMS calcd for $C_{12}H_{10}N_3O_6$: $M^{+\cdot}-Cl$ 292.057, found 292.057. Anal. calcd for $C_{12}H_{10}N_3O_6Cl$: C, 43.98; H, 3.07; N, 12.82. Found C, 43.82; H, 3.28; N, 12.55.

4.2.8. 3-Nitro-2-phenylpropane dicarbonitrile (5h). Mp=58°C; A/B=50/50. Yield=63%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.08 (dd, 1H, CH^2, ^3J=13.9, 6 Hz); 4.44 (d, 1H, CH^1, ^3J=6 Hz); 4.82–4.98 (m, 2H, CH_2NO_2); 7.24–7.45 (m, 5H arom.).^{13}C NMR (CD_3CN, 75 MHz) δ: 27.66 (ddt, CH^1, ^1J=143.5 Hz, ^2J=4.4 Hz); 43.36 (dmt, CH^2, ^1J=139 Hz); 75.19 (tdd, CH_2NO_2, ^1J=148.5 Hz); 110.83 and 111.43 (m, CN); 127.87–132.16 (m, 6C arom.). IR (nujol): 1665, 2225, 3170–3430 cm^{-1}. HRMS calcd for $C_{11}H_9N_3O_2$: 215.069, found $M^{+\cdot}$215.069. Anal. calcd for $C_{11}H_9N_3O_2$: C, 61.39; H, 4.19; N, 19.53. Found C, 61.25; H, 4.21; N, 19.69.

4.2.9. 2-Cyano-4-nitro-3-phenyl butanamide (5i). Mp=125°C; A/B=50/50. Yield=68%; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 3.88 (A) and 3.99 (B) (d, 1H, CH^1, ^3J=4.7, 5.8 Hz); 4.22–4.32 (m, 1H, CH^2); 4.76–5.10 (m, 2H, CH_2NO_2); 5.90–6.19 (m, 2H, $CONH_2$); 7.26–7.45 (m, 5H, arom.). ^{13}C NMR (CD_3CN, 50 MHz) δ: 41.01 and 41.32 (dm, CH^2, ^1J=138 Hz); 42.87 and 42.90 (dm, CH^1, ^1J=138 Hz); 76.50 and 76.62 (tm, CH_2NO_2, ^1J=148.5 Hz); 115.79 and 115.83 (m, CN); 127.53–135.11 (m, 6C arom.). IR (nujol): 1665, 2225, 3170–3430 cm^{-1}. HRMS calcd for $C_{11}H_{10}N_2O_2$: $M^{+\cdot}-HNO_2$ 186.079, found 186.079. Anal. calcd for $C_{11}H_{11}N_3O_3$: C, 56.65; H, 4.75; N, 18.01. Found C, 56.46; H, 4.83; N, 18.24.

4.2.10. 2-Cyano-4-methyl-4-nitro-3-(4-chlorophenyl)-methylbutanoate (6b). *Method A*. Four diastereoisomers A (43.5%), B (28%), C (17.5%) and D (11%) were obtained.

Yield=100% (estimated by ^{1}H NMR, the final product being an oil). A (mp=156°C) is obtained after slow crystallization in a mixture of cold ether and pentane (95/5).

Method B.[18] Two diastereoisomers A (75%) and D (25%) were obtained after the mixture of 1-(4-chlorophenyl)-2-nitroprop-1-ene (15 mmol)[15] and methylcyanoacetate (20 mmol) in presence of piperidine (10%) was allowed to stand at room temperature during 4 h (85% yield) or irradiated 2 min at 90°C under P_{max}=30 W (65% yield).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.41 (A), 1.42 (D), 1.60 (C) and 1.71 (B) (d, 3H, CH_3CH, ^1J=6.65, 6.75, 6.65, 6.65 Hz); 3.61 (A), 3.65 (B), 3.69 (C) and 3.77 (D) (s, 3H, O–CH_3); 3.83–3.96 (A and D) (m, 2H, CH^1 and CH^2); 3.83–3.96 (C and B) (m, 1H, CH^2); 4.15 (D) and 4.16 (C) (d, 1H, CH^1, ^3J=5.8, 7 Hz), 5.17 (A and B), 5.31 (C) and 5.37 (D) (m, $CHNO_2$), 7.19–7.42 (m, 4H arom.). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 17.44 (C), 17.90 (B),18.23 (D) and 18.44 (A) (qm, CH_3CH, ^1J=130.6, 131, 131, 131.5 Hz); 39.97 (B) (ddd, CH^1, ^1J=136.5 Hz, ^2J=3.3 Hz); 40.73 (C) (ddd, CH^1, ^1J=136 Hz, ^2J=3.3 Hz); 41.17 (A and D) (ddd, CH^1, ^1J=135.5 Hz, ^2J=3.3 Hz); 47.89 (B), 48.00 (A), 48.42 (D) and 48.61 (C) (dm, CH^2, ^1J=135 Hz); 53.50 (A), 53.76 (D), 53.92 (B) and 53.97 (C) (q, O–CH_3, ^1J=149 Hz); 83.04 (D), 83.62 (C), 84.17 (A) and 84.47 (B) (dm, $CHNO_2$, ^1J=150 Hz); 114.14 (B), 114.21 (A), 114.78 (C) and 115.32 (D) (m, CN); 128.81–139.60 (m, 6C arom.); 164.00 (D), 164.10 (A), 164.27 (B) and 164.68 (m, C=O). IR (nujol): 1540; 1730; 2250 cm^{-1}. HRMS calcd for $C_{13}H_{13}N_2O_4Cl$: 296.056, found $M^{+\cdot}$296.056. Anal. calcd for $C_{13}H_{13}N_2O_4Cl$: C, 52.62; H, 4.41, N, 9.44. Found C, 52.36; H, 4.45; N, 9.35.

4.2.11. 2-Cyano-4-methyl-4-nitro-3-(3-fluorophenyl)-methylbutanoate (6e). Four diastereoisomers A (40%), B (29%), C (19%) and D (12%) were obtained as a solid (Mp=108°C) after crystallization in a mixture ether/pentane (95/5) in 72% yield.

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.43 (A), 1.44 (D), 1.64 (C) and 1.75 (B) (d, 3H, CH_3CH, ^1J=6.7 Hz); 3.64 (A), 3.68 (B), 3.73 (C) and 3.76 (D) (s, 3H, O–CH_3); 3.87–3.98 (A and D) (m, 2H, CH^1 and CH^2); 3.87–3.98 (C and B) (m, 1H, CH^2), 4.16 (C) and 4.17 (B) (d, 1H, CH^1, ^3J=5.8, 7 Hz), 5.15–5.23 (m, $CHNO_2$), 7.03–7.37 (m, 4H arom.). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 17.53 (C), 17.93 (D), 18.31 (B) and 18.48 (A) (qm, CH_3CH, ^1J=131 Hz); 39.97 (D) (dm, CH^1, ^1J=135.5 Hz); 40.79 (C) (dm, CH^1, ^1J=139.5 Hz); 41.14 (A and B) (dm, CH^1, ^1J=136 Hz); 48.15 (D), 48.24 (A), 48.27 (B) and 48.73 (C) (dm, CH^2, ^1J=137.5 Hz); 53.59 (A), 53.79 (B), 53.95 (D) and 54.04 (C) (q, O–CH_3, ^1J=149 Hz); 83.02 (B), 83.67 (C), 84.15 (A) and 84.40 (D) (dm, $CHNO_2$, ^1J=150.5 Hz); 114.08 (D), 114.13 (A), 114.69 (C) and 115.46 (B) (m, CN); 115.80–135.35 (m, 5C arom.); 162.70–163.00 (A), 164.08 (D) and 164.41 (m, C=O). IR (nujol): 1530, 1730, 2225 cm^{-1}. HRMS calcd for $C_{13}H_{13}N_2O_4F$: 280.086, found $M^{+\cdot}$280.087. Anal. calcd for $C_{13}H_{13}N_2O_4F$: C, 55.71; H, 4.67, N, 9.99. Found C, 55.86; H, 4.79; N, 10.03.

4.2.12. 2-Cyano-5-methyl-3-(1-methyl-nitromethyl)-ethylhexanoate (6k). Four diastereoisomers A (36%), B (23%), C (21%) and D (20%) were obtained as an oil (Bp 0.03 Torr=150°C) after short-path purification with Kugelrohr apparatus in 70% yield without possibility of assignment.

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 0.92–1.00 (A, B, C and D)

(m, 6H, $(CH_3)_2C$); 1.30–1.67 (A, B, C and D) (t, 9H, $(CH_3CH,CH_3CH_2O$, $CHCH_2$ and CH_3CNO_2); 2.83–3.03 (A, B, C and D) (m, 1H, CH^2); 3.68 (A) 3.76 (B), 3.77 (C) and 3.85 (D) (d, 1H, CH^1, ^1J=2.7, 4.7, 4.2, 2.8 Hz); 4.25–4.35 (A, B, C and D) (m, 2H, $O-CH_2$); 4.64–4.75 (m, 1H, $CHNO_2$). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 13.78 and 13.80 (A, B, C and D) (qt, OCH_2CH_3, ^1J=128 Hz; ^2J=2.4 Hz); 14.69, 15.82, 16.32 and 16.84 (A, B, C and D) (qm, CH_3CHNO_2, ^1J=126.5 Hz); 20.95, 20.98, 21.97, 22.03, 22.35, 22.47, 22.99 and 23.19 (A, B, C and D) (qm, CH_3CH, ^1J=125.5 Hz); 25.04, 25.17, 25.21 and 25.55 (A, B, C and D) (dm, CH, ^1J=126 Hz); 36.16, 37.42, 38.31, 38.43, 38.64, 38.76, 39.38, 39.73, 39.85, 40.04 and 40.07 (A, B, C and D) (dm, tm and dm, CH^1, CH_2 and CH^2); 63.32 and 63.37 (A, B, C and D) (tq, OCH_2, ^1J=149 Hz, ^2J=4.4 Hz); 83.39 (D), 84.08 (A), 84.76 (B) and 85.36 (C) (tm, CH_2NO_2); 114.16 (B), 114.32 (D), 114.63 (C) and 114.92 (A) (m, CN); 164.69 (D) and 164.95 (A),165.06 (B) and 165.13 (C) (m, C=O). IR (nujol): 1540; 1730; 2250 cm^{-1}. HRMS calcd for $C_{12}H_{20}NO_2$: $M^{+\cdot}-NO_2$ 210.149, found 210.149. Anal. calcd for $C_{12}H_{20}N_2O_4$: C, 56.23; H, 7.86, N, 10.93. Found C, 55.84; H, 7.72; N, 10.85.

4.3. General procedure for the preparation of Michael adducts 7–9

The alkyne (2 mmol) and nitroalkane (1.33 equiv. unless otherwise stated) are successively introduced in the cylindrical quartz reactor under nitrogen. Triethylamine (5 μL) is then added to the previously ice cooled medium. After warming back to room temperature, the reaction mixture is irradiated during 5 min in the microwave oven S402® (final temperature: 60°C unless otherwise stated). Crude product is extracted with dichloromethane which is removed under vacuum and analyzed by ^1H NMR (200 MHz, $CDCl_3$). The compounds are purified by filtration on Florisil or chromatography on alumina 90 or silica gel.

4.3.1. 4-Methyl-4-nitro-hex-2-ene-ethylcarboxylate (7a). Two diastereoisomers A (*E*: 60%) and B (*Z*: 40%) were obtained as an oil (Bp 0.028 Torr=110°C) after filtration on Florisil and short-path purification with Kugelrohr apparatus in 70% yield.

^1H NMR ($CDCl_3$, 200 MHz) δ: 1.27 (B) and 1.31 (A) (t, 3H, CH_3CH_2, ^3J=7.1 Hz); 1.77 (A) and 1.85 (B) (s, 6H, $C-(CH_3)_2$); 4.15–4.23 (m, 2H, CH_3CH_2, ^3J=7.1 Hz); 5.96 (B) and 6.01 (A) (d, 2H, CH^1, $^3J_{cis}$=12.6 Hz, $^3J_{trans}$=16 Hz); 6.34 (B) and 7.17 (A) (d, 2H, CH^2, $^3J_{cis}$=12.6 Hz, $^3J_{trans}$=16 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 14.04 (B) and 14.18 (A) (qt, CH_3CH_2, ^1J=127.5, 127 Hz, ^2J=2.70, 2.50 Hz); 25.62 (B) and 27.28 (A) (qdd, $(CH_3)_2$, ^1J=130.60, 130.50 Hz, ^3J=7.60, 6.75 Hz, ^4J=2.85, 2.70 Hz); 60.84 and 61.06 (B and A) (tq, $O-CH_2$, ^1J=143.5, 148 Hz, ^2J=4.5 Hz); 87.05 (B) and 87.09 (A) (m, $C-NO_2$); 122.63 (A) and 122.67 (B) (d, $=CH^1$, ^1J=164, 163.5 Hz); 144.70 (A) (dhept, $=CH^2$, ^1J=158.2 Hz, ^3J=4 Hz); 145.23 (B) (dhept, $=CH^2$, ^1J=162.4 Hz, ^3J=1.8 Hz); 164.66 (B) and 165.36 (A) (m, C=O). IR (nujol): 1520, 1610, 1710, 2980 cm^{-1}. HRMS calcd for $C_8H_{13}O_2$: M^+; $-NO_2$: 141.089, found 141.091. Anal. calcd for $C_8H_{13}NO_4$: C, 51.83; H, 7.13, N, 7.38. Found C, 51.33; H, 7.00; N, 7.48.

4.3.2. 5-Methyl-5-nitro-hex-3-ene-2-one (7b).[24] Two diastereoisomers B (*Z*: 55%) and A (*E*: 45%) were obtained as an oil (Bp 0.028 Torr=90°C) after filtration on Alumina 90 and short-path purification with Kugelrohr apparatus in 56% yield (1.77 equiv. of 3-butyn-2-one). ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.78 (A) and 1.81 (B) (s, 6H, $(CH_3)_2-$); 2.24 (B) and 2.34 (A) (s, 3H, $COCH_3$); 6.12 and 6.23 (B and A) (d, 1H, $=CH^1$, $^3J_{trans}$=16.2 Hz, $^3J_{cis}$=12.4 Hz); 6.31 and 7.03 (Band A) (d, 1H, $=CH^2$, $^3J_{cis}$=12.4 Hz, $^3J_{trans}$=16.2 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 25.55 and 27.01 (B and A) (qm, $(CH_3)_2-$, ^1J=130.8 Hz); 27.57 (B) (qd, $COCH_3$, ^1J=127.5 Hz, ^4J=1.6 Hz); 31.18 (A) (q, $COCH_3$, ^1J=127.5 Hz); 87.16 and 87.27 (B and A) (m, $C-NO_2$); 128.67 (B) (dm, $=C^1-H$, ^1J=159.5 Hz, ^2J=3.7 Hz); 130.30 (A) (dm, $=C^1-H$, ^1J=158.5 Hz); 142.04 (B) (dm, $=C^2-H$, ^1J=162.5 Hz, ^2J=3.2 Hz); 143.78 (A) (dm, $=C^2-H$, ^1J=161 Hz); 197.55 (A) (m, C=O, ^2J=6.9 Hz); 198.30 (B) (m, C=O, ^2J=11.3 Hz, ^3J=4.6 Hz). IR (nujol): 1520, 1620, 1680, 2980 cm^{-1}. HRMS calcd for $C_7H_{11}O$: $M^{+\cdot}-NO_2$: 111.081, found 111.081.

4.3.3. 4-Methyl-4-nitro-hept-2,5-diene-1,7-diethyldicarboxylate (8).[25] Three diastereoisomers A (2*E*,5*E*: 48%), B (2*Z*,5*E*: 41%) and C (2*Z*,5*Z*: 11%) were obtained in 70% yield at a final temperature of 70°C with 1 equiv. of nitroethane (0.15 g) and purification by chromatography on silica gel (eluent: CH_2Cl_2, R_f=0.6). The NMR data of the too minor isomer C could not be determined accurately. ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.12–1.38 (A and B) (m, 3H, CH_2CH_3); 1.93 (B) (s, 3H, CH_3-CNO_2); 1.99 (A) (s, 3H, CH_3-CNO_2); 4.11–4.30 (A and B) (m, 4H, OCH_2); 5.99 (A) (d, 1H, CH^4, $^3J_{trans}$=16 Hz); 6.04 (A) (d, 1H, CH^5, $^3J_{trans}$=16 Hz); 6.12 (B) (d, 1H, CH^1, $^3J_{cis}$=12.2 Hz); 6.35 (B) (d, 1H, CH^2, $^3J_{cis}$=12.2 Hz); 7.19 (A) (d, 1H, CH^6, $^3J_{trans}$=16 Hz); 7.47 (B) (d, 1H, CH^3, $^3J_{trans}$=16 Hz).^{13}C NMR ($CDCl_3$, 50 MHz) δ: 13.96 (B) and 14.16 (A) (qm, CH_3CH_2O, ^1J=127 Hz); 22.82 (B) and 26.62 (A) (qm, CH_3-CNO_2, ^1J=132 Hz); 61.05, (B), 61.17 (A) and 61.32 (B) (tm, OCH_2, ^1J=148 Hz); 88.91 and 89.61 (A and B) (m, CNO_2); 123.37 and 125.02 (B and A) (d, C^1, C^4, ^1J=161.5, 166 Hz); 140.91, 141.89 and 143.47 (A and B) (d, C^2, C^3, ^1J=164.71, 169.6, 171.5 Hz); 164.21, 164.82 and 165.29 (A and B) (m, C=O). IR (nujol): 1530, 1640, 1710, 2980 cm^{-1}. HRMS calcd for $C_{12}H_{17}O_4$: $M^{+\cdot}-NO_2$: 225.112, found 225.112. Anal. calcd for $C_{12}H_{17}NO_6$: C, 53.13; H, 6.31; N, 5.16. Found C, 53.19; H, 6.52; N, 5.08.

4.3.4. 4-Ethyl-4-nitro-hept-2,5-diene-1,7-diethyldicarboxylate (9).[25] Three diastereoisomers A (2*E*,5*E*: 46%), B (2*Z*,5*E*: 43%) and C (2*Z*,5*Z*: 11%) were obtained in 62% yield at a final temperature of 70°C with 1.125 equiv. of 1-nitropropane (0.20 g) and purification by chromatography on silica gel (eluent: CH_2Cl_2, R_f=0.6). The NMR data of the minor isomer C could not be determined. ^1H NMR ($CDCl_3$, 200 MHz) δ: 0.96 and 0.98 (A, B and C) (t, 3H, $CH_3CH_2-CNO_2$, ^3J=7.30 Hz); 1.20–1.38 (A, B and C) (m, 6H, OCH_2CH_3); 2.31 (A, B and C) (q, 2H, CH_2-CNO_2, ^3J=7.3 Hz); 4.07–4.49 (A, B and C) (m, 4H, OCH_2CH_3); 5.85 (B) (d, 1H, CH^4, $^3J_{trans}$=16.2 Hz); 5.98 (A) (d, 1H, CH^6, $^3J_{trans}$=16.1 Hz); 6.17 (B) (d, 1H, CH^1, $^3J_{cis}$=12.1 Hz); 6.35 (B) (d, 1H, CH^2, $^3J_{cis}$=12.1 Hz); 7.20 (A) (d, 1H, CH^2, $^3J_{trans}$=16.1 Hz); 7.63 (B) (d, 1H, CH^3, $^3J_{trans}$=16.2 Hz).^{13}C NMR ($CDCl_3$, 50 MHz) δ: 8.46 (A and B) (q,

CH_3CH_2O, ^1J=127.5 Hz); 13.93 (A) and 14.17 (B) (q, CH_3-CH_2, ^1J=127.5 Hz); 60.97, 61.14 and 61.30 (A and B) (t, OCH_2CH_3, ^1J=145.5 Hz); 92.46 and 93.82 (A and B) (m, CNO_2); 122.67 and 125.37 and 125.81 (A and B) (d, C^1, C^4, ^1J=157.5, 162, 158.5 Hz); 139.93, 140.99 and 143.42 (A and B) (d, C^2, C^3, ^1J=167 Hz); 164.17, 164.88 and 165.35 (A and B) (m, C=O). IR (nujol): 1530, 1600, 1720, 3000 cm^{-1}. HRMS calcd for $C_{13}H_{19}O_4$: $M^{+}\cdot-NO_2$: 239.128, found 239.128. Anal. calcd for $C_{13}H_{19}NO_6$: C, 54.73; H, 6.71; N, 4.91. Found C, 55.00; H, 6.80; N, 4.90.

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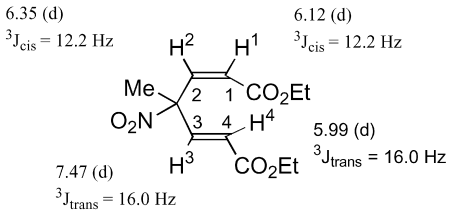
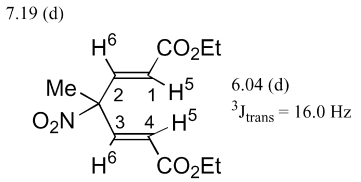
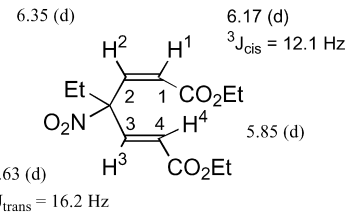


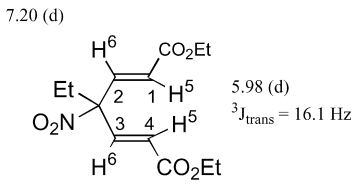
8B (Z, E)
41%



8A (E, E)
48%



9B (Z, E)
43%



9A (E, E)
46%