32. 2′-Nitro-2′-propen-1′-yl 2,2-Dimethylpropanoate (NPP), A Multiple Coupling Reagent

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Dedicated to Dr. *Arnold Brossi* on the occasion of his 60th birthday

(24.X.83)

Summary

The title compound **1** (NPP) is prepared from formaldehyde, nitromethane, and pivaloyl chloride. It is shown to be a versatile nitroallylating reagent combining with nucleophiles as different as anilines, indoles, enolates, and organolithium compounds. This is documented by *ca.* 40 examples (**2–30**). The mechanism of the reaction is discussed. Some examples of addition of two different nucleophiles to the C_3-moiety of NPP are described (**35–46**). This demonstrates the usefulness of NPP as a multiple coupling reagent for convergent syntheses, also of products not containing nitro groups *(Scheme 4)*.

A. Introduction. – In a convergent synthesis, (*a*) in *Scheme 1*, two components A and B are synthesized in a number of steps, *n* and *m*, respectively, and combined in a key-step to form the target skeleton. Normally, a specific activation is necessary to achieve the crucial step of combination. Instead of activating A_n and/or B_m, the synthesis can also be planned so that a highly reactive coupling reagent is used to join non-activated A_n- and B_m-moieties, (*b*) in *Scheme 1*. Since such reagents may be constructed to join two or more components, we call them *multiple coupling reagents* (MCR)[2]).

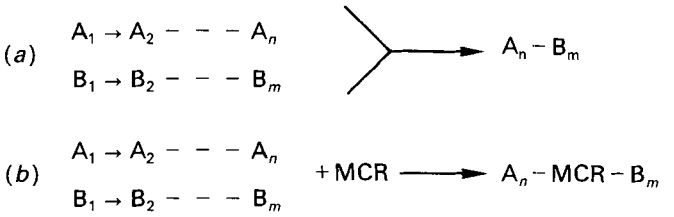
There are only few ideal MCR's, because high reactivity is normally associated with low selectivity. The major requiremets for MCR's are the following (see *Scheme 2*): *i*) It must furnish a C-skeleton and a functionality pattern which are part of many target molecules. *ii*) It must allow for selective, sequential intermolecular formation of two or more new bonds to take place, (*a*). *iii*) If it contains constitutionally heterotopic sites, these must be well-differentiated, (*b*). *iv*) No mixtures of diastereomers should be

[1]) Part of the Ph. D. Thesis of *P. K.*, ETH Diss. No. 7170 (1982). Present address of Dr. *P. K.*: Laboratoire de Chimie des Organoéléments, Université Pierre et Marie Curie, Tour 44–45 – 4, Place Jussieu, F–76230 Paris Cédex 05.

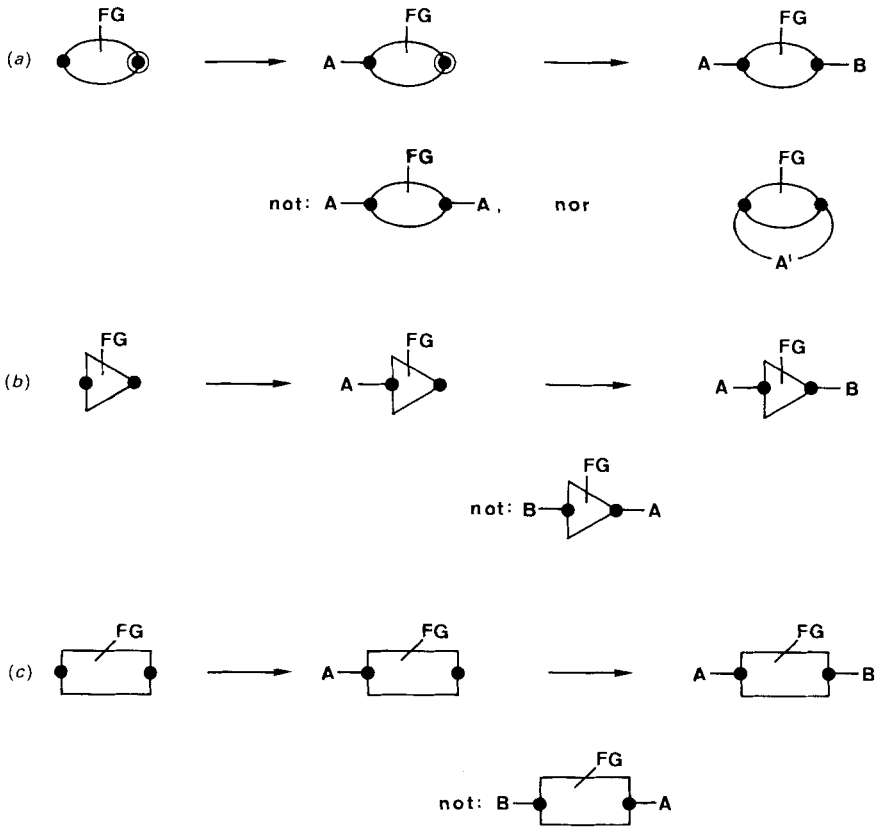
[2]) The term *conjunctive reagent* was used in a recent paper [13c]. In German we use the word *Verknüpfungsreagenz* (VR).

formed, if the reactive sites are diastereotopic, (*c*). Some more or less deliberately chosen examples[3]) of MCRs are given in *Table 1*.

Scheme 1



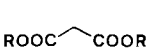
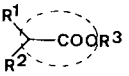
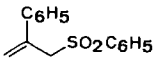
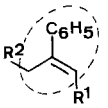
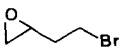
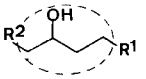
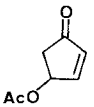
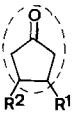
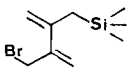
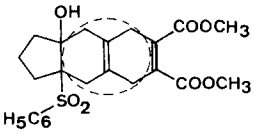
Scheme 2[a])



[a]) FG = functional group, which must not be the same in the MCR and in the final product.

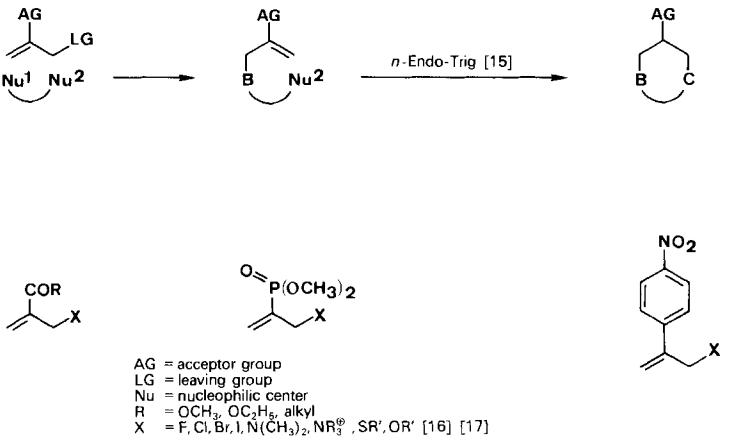
[3]) Epichlorohydrine is used extensively as MCR, mainly for heteroatomic nucleophiles, *cf.* the syntheses of β-blockers in textbooks of pharmaceutical and medicinal chemistry.

Table 1. *Examples of Multiple Coupling Reagents (MCR) with One to Six C-Atoms*

MCR				
Number of C-atoms	Reagent	Reactivity	Product	Ref.
1		d^1, d^1		[1–4]
1		a^1, d^1		[5]
2		d^2, d^2		
2		a^1, d^2		[6]
3		d^1, a^3		[7]
4		a^3, $a^{2'}$		[8]
5		a^3, $a^{3'}$		[9]
6		a^1, d^4, *Diels-Alder*		[10]

Bifunctional reagents which are used for *cyclizations* must have different properties; they are meant to combine with bifunctional substrates, with an intermolecular coupling being followed by an intramolecular step. For examples see the recently developed a^1,d^n-reagents with n = 2, 3, 4, providing two, three, and four C-atoms for five- and six-ring annulations [11–14], and last entry of *Table 1*. Also, the C_3-reagents with a *Michael*-acceptor and an electrophilic alkylating center in 1,3-positions (a^1, a^3) have mostly been employed for cyclizations, see *Scheme 3*. This principle was first realized by *Nelson & Lawton* [16a], and culminated in the use of 2-(*p*-nitrophenyl)-3-hetero-substituted 1-propenes for the cross-linking of proteins by *Mitra & Lawton* [16c].

Scheme 3



In the course of our work with nitroolefins [18], it occured to us[1])[4]) that a multiple coupling reagent with two acceptor centers in 1,3-position could be developed: normally, a nitroalkene double bond is a more reactive electrophile than a typical S_N^2-type alkylating reagent. Also, the stability of a nitronate is large enough, so that it tolerates β-leaving groups such as $OSiR_3$ at low enough temperatures [20]. We therefore hoped to find a nitropropene **A** *(Scheme 4)* to which nucleophiles would add to form a nitronate **B**, stable under the reaction conditions. This intermediate **B** would have to lose the $X^{\ominus}$-group to give the nitroolefin **C** in a separate step, and thus allow the subsequent selective addition of a second, different nucleophile (**C**→**D**→**F** in *Scheme 4*). Also, it was conceivable, that the X-group in **A** might activate the nitroolefin sufficiently to make it more reactive than a 'normal' terminal nitroolefin such as **C**. This would also provide for a selective 'mono-addition' **A**→**C**, and open the possibility of adding two different nucleophiles to give **F**. The well-known conversions of nitroalkanes to amines, ketones, alcohols, and olefins (see a recent review [18]), as well as the facile *Diels-Alder* reactions of nitroolefins (→**E**) would thus make the reagent **A** correspond to the synthons shown inside the box of *Scheme 4*.

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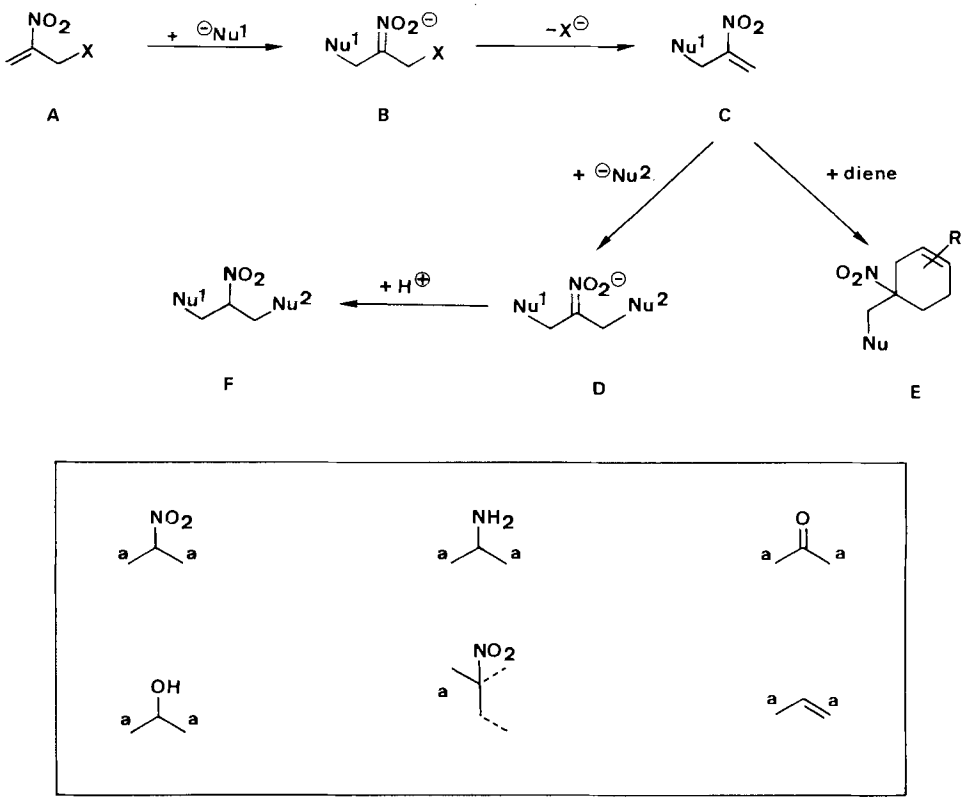
[4]) A first, preliminary communication [19] was submitted in October 1980.

Scheme 4



We describe here the preparation and reactions of a parent nitropropene derivative of type **A**[5]), while analogues with larger C-skeletons[6]) will be covered in a separate paper [24].

B. Preparation of 2′-Nitro-2′-propen-1′-yl 2,2-Dimethyl-propionate (NPP). – Among the nitropropenyl derivatives **A** in *Scheme 4* which we prepared, the chloride and bromide (**A**, X = Cl, Br) were so reactive that they could not be handled. The acetate (**A**, X = $OCOCH_3$), which had been described before [25] [26], and for which an improved procedure was elaborated[1]), turned out to be attacked at the carbonyl C-atom rather than at the nitroolefin group by the more reactive nucleophiles. This limitation was avoided[7]) by using the pivalate **1** (NPP). Its preparation is outlined in

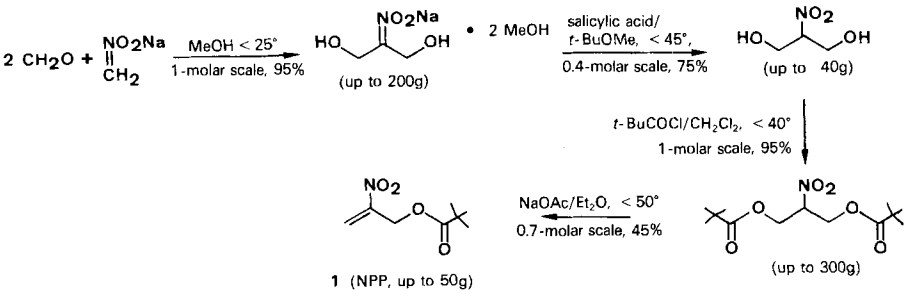
[5]) For preliminary communications on 2′-nitro-2′-propen-1′-yl 2,2-dimethylpropionate (NPP), see [19] [21].

[6]) For a communication about a phenyl-substituted nitropropene derivative and about analogous nitrocyclohexene derivatives, see [22] [23].

[7]) For discussions of optimizations of leaving groups in other, related cases, see [9] [13b].

Scheme 5. The scales at which the single steps were carried out by us, are also given, documenting that NPP is available on a 50-gram scale[8]). We have stored the colorless, distilled material (m.p. 18°) in a refrigerator (+5°) or in a freezer (−20°) for many months.

Scheme 5[8])



C. Nitroallylations with NPP (1). – The pivaloyloxy-nitropropene **1** proved to be a nitroallylating reagent (*cf.* **A**→**C** in *Scheme 4*) with a great variety of nucleophiles. The products **2–30** of nitroallylation were isolated after purification by flash chromatography [27] in good to excellent yields, generally ranging around and above 70%. These yields were realized by adding NPP to solutions of the less reactive nucleophiles (→**2–16**) or by inverse addition of the more reactive nucleophiles such as aryl-, vinyl-, and alkyllithium derivatives at temperatures[9]) between −110° and +20°. The nucleophiles were used as commercially available or were generated by standard methods[10]) which are indicated in the *Exper. Part.* All products were identified by NMR, IR, and mass spectra, and most also by elemental analyses. In the product *formulae*, the newly formed C-heteroatom (**2–4**) or C-C bonds (**5–30**) are indicated by a heavy line.

Inspection of the *formulae* **2–30** reveals the following remarkable facets of the nitroallylation reaction.

i) It occurs with nucleophiles derived from acids of pK_A-values ranging from below 4 to above 40. Arylamines (→**2, 3**), lithium thiophenolate (→**4**), indoles (→**5**), lithium enolates of ketones (→**6–12**) and esters (→**13–15**), lithiodithiane (→**16**), aryl- (→**17–22**), as well as alkynyl- (→**23**), vinyl- (→**24–26**) and primary (→**27**), secondary (→**28, 29**), and tertiary (→**30**) alkyllithium derivatives are all converted to nitroolefins with substitution of the pivaloyloxy group of NPP.

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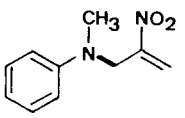
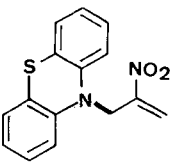
[8]) Calorimetric measurements of the stabilities of all intermediates indicate, that the conditions given here should be carefully obeyed, especially in large-scale preparations. We thank Dr. *E. Galantay* of the *Sandoz AG*, Basel, for the safety tests.

[9]) For a review with detailed descriptions of techniques for carrying out preparative reactions at temperatures below −80°, see [28].

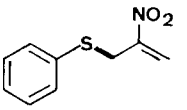
[10]) Enolates were generated with lithium diisopropylamide (LDA; review, see *e.g.* [29]), lithiodithianes with BuLi (reviews [3]), vinyl- and aryllithium compounds by H/Li-([30], for the preparation of **17**) or preferably by Br/Li or I/Li-exchange [31–33], alkyllithium derivatives from the corresponding chloroalkanes and lithium *p,p'*-di(*tert*-butyl)biphenylide [34].



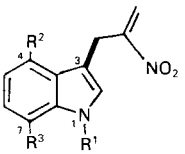
2 (86%)



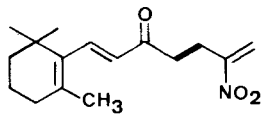
3 (95%)



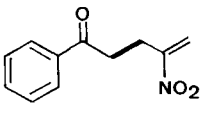
4 (62%)



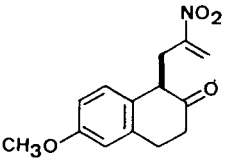
5a $R^1 = R^2 = R^3 = H$ (69%)
5b $R^1 = CH_3$, $R^2 = R^3 = H$ (92%)
5c $R^1 = H$, $R^2 = CHO$, $R^3 = H$ (30%)
5d $R^1 = H$, $R^2 = OCH_2C_6H_5$, $R^3 = (CH_2)_2OH$ (66%)
5e $R^1 = Me$, $R^2 = OCH_2C_6H_5$, $R^3 = (CH_2)_2OCH_3$ (80%)



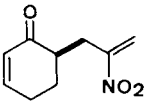
6 (77%)



7 (81%)



8 (44%)



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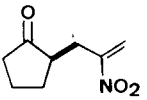
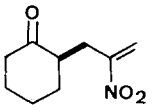
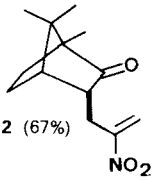


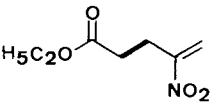
10 (90%)



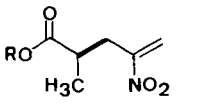
11 (87%)



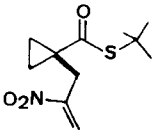
12 (67%)



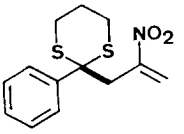
13 (87%)



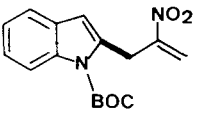
14a $R = C_2H_5$ (68%)
14b $R = t\text{-}C_4H_9$ (83%)



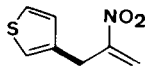
15 (82%)



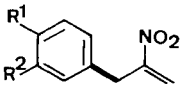
16 (85%)



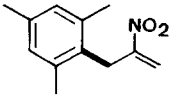
17 (73%)



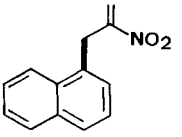
18 (69%)



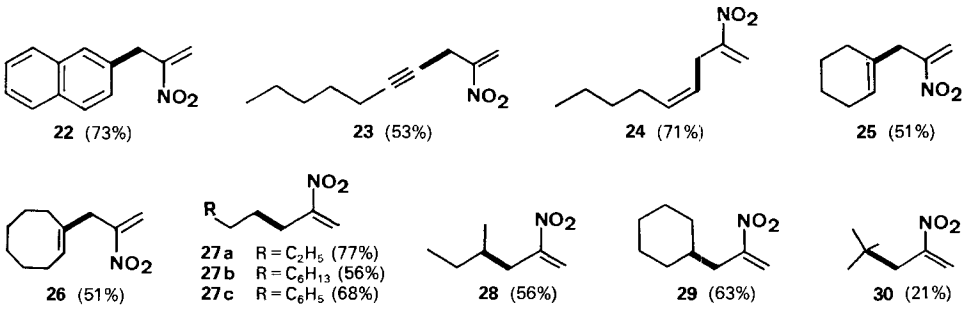
19a $R^1 = R^2 = H$ (77%)
19b $R^1 = OCH_3$, $R^2 = H$ (71%)
19c $R^1 = F$, $R^2 = H$ (74%)
19d $R^1 = H$, $R^2 = CF_3$ (78%)



20 (78%)



21 (88%)



ii) The yields of nitroallylation by NPP with the most reactive nucleophiles such as aromatic and aliphatic lithium compounds (→**17–30**) are higher than those of addition of the same nucleophiles to simple 2-nitro-1-alkenes [18]. Thus, the rule emerges that with the multiple coupling reagent **1** the more reactive organometallic substrate is added first, followed by less reactive substrates such as enolates (see *Section D*).

iii) As can be seen from the yields of addition of the camphor enolate (→**12**) and of mesityllithium (→**20**), the reaction is not hampered by bulky nucleophiles.

iv) With alkynyl-, alkenyl- and aryl-nucleophiles we did not observe any products with conjugated π-systems arising from double bond shifts (see **5** and **17–26**). The result of the reaction is a clean nitroallylation.

v) Finally, the (*Z*)-configuration of the product **24** formed from NPP and (*Z*)-1-lithio-1-hexene suggests that the reaction does not involve free radicals [35].

D. Mechanism(s) of the Nitroallylation with NPP. – A discussion of possible mechanisms of the nitroallylation of nucleophiles by NPP must take into account that *both*, the highly reactive alkyllithium compounds and the slowly-reacting indoles can be employed. Thus, no diadducts were discovered in the addition of cyclohexyllithium to NPP with a reaction time of 20 minutes at −90° (→63% of **29**). The most obvious interpretation of this result is that the primary adduct of type **32** does not eliminate lithium pivalate (→**31**) until all RLi has been consumed, a 'stop-and-go' mechanism, see *Scheme 6* und compare with *Scheme 4*. When, on the other hand, reaction mixtures of NPP with organolithium compounds were quenched by addition of acid after short reaction times at low temperatures, no adduct pivalates of type **33** were isolated. Instead, only NPP and product **31** could be detected. This result is compatible[11]) with a fast elimination (**32**→**31**) or with a direct S_N2'-substitution[12]) of lithium pivalate to give the product **31**, which does not compete with NPP for unreacted RLi.

Reaction times of several hours at room temperature are required for the 1:1 nitroallylation of indoles with NPP (→**5**); again no double addition was detected. This is also *not* in agreement with a 'stop-and-go' mechanism, *Scheme 7*, because the primary adduct such as **34** ist not expected to survive in the apolar reaction medium until all NPP has been consumed. Rather, the nitroallylation product **5b**, be it formed by direct

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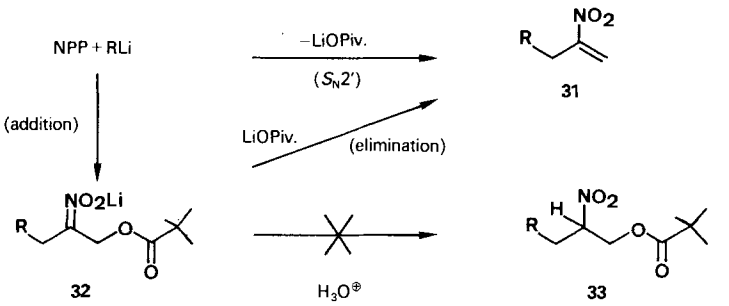
[11]) Spontaneous elimination (**33**→**31**) under the quenching and workup conditions is unlikely.

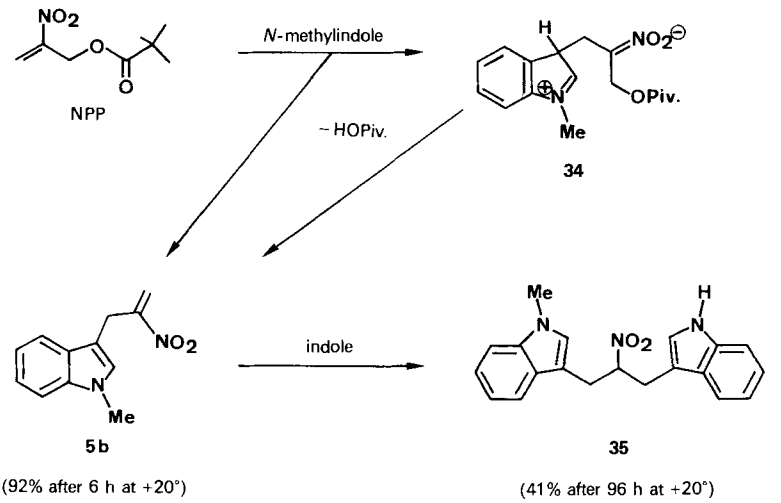
[12]) From the results of reactions of substituted nitroallylating reagents [22] [24], we can exclude the possibility of a direct S_N2-substitution of lithium pivalate without double-bond shift.

Scheme 6



substitution or through the zwitterion **34**, must be less reactive than NPP itself, and does not successfully compete for unreacted indole. The increased reactivity of NPP as compared to indolyl-nitropropene **5b** was exploited in the preparation of the diindolyl-nitropropane **35**, see the drastically different reaction times of the two sequential steps (NPP→**5b** and **5b**→**35** in *Scheme 7*).

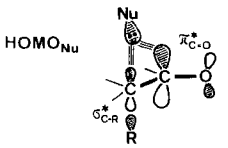
Scheme 7



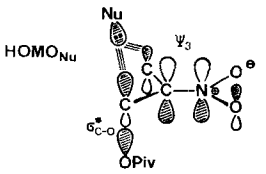
From the results of these – admittedly few – mechanistic tests, we presently favour the view that NPP is a selective nitroallylating reagent in all cases, because it is more reactive than its nitroolefinic products[13]). By which effect does the pivaloyloxy group activate the nitroolefin? There is certainly an inductive effect on the σ-skeleton by the electronegative RCOO-group. In addition, a stereoelectronic effect might be operative, analogous to that proposed to explain *Cram*'s rule [36], see **G**. In this simple-minded

[13]) We would not be surprised if different mechanisms would eventually be found for the reactions of NPP with different types of such nucleophiles.

analysis it is assumed that the nucleophile interacts simultaneously with the LUMO of the nitroolefin (ψ_3) *and* with the σ^*-orbital of the C-OPiv bond, see **H**. This requires that the C-OPiv bond is located in a plane which is approximately perpendicular to the plane of the atoms of the conjugated system $C{=}C{-}NO_2$. Further experiments with substituted NPP-derivatives are necessary to test this hypothesis.

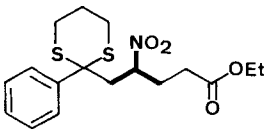


G

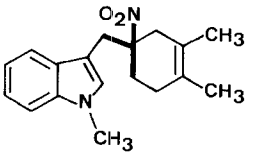


H

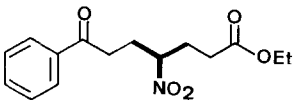
E. Products of Coupling of NPP with Two Different Substrates. – To demonstrate that NPP is a powerful multiple coupling reagent, we have prepared a number of products arising from its combination with two different substrates[14]). Although not in high yields, *in situ* reactions with two nucleophiles are possible: sequential one-pot addition of 2-lithio-2-phenyl-1,3-dithiane and of the lithium enolate of ethyl acetate to



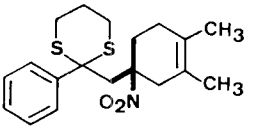
36 (66%)



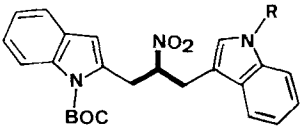
37 (71% from **5b**)



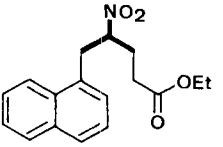
38 (70% from **13**)



39 (85% from **16**)

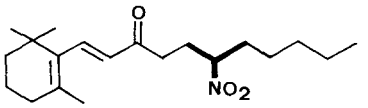


40a R = H (65% from **17**)
40b R = CH_3 (60% from **17**)

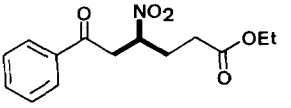


41 (66% from **21**)

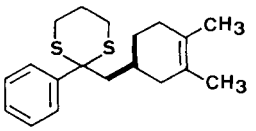
[14]) The addition of a dienophile or of a second nucleophile to the products **2–30**, which are more or less simple 2-nitro-l-alkenes, is well-precedented in the literature. Examples from our own work are described in references [14] [18] [37–42].



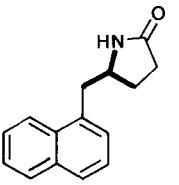
42 (75% from **27a**)



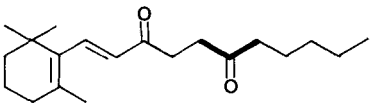
43 (54% from **36** with $HgO/BF_3 \cdot Et_2O$, THF/H_2O [43a] 69% with excess MeI [43b])



44 (95% from **39** with Bu_3SnH in C_6H_6 [44])



45 (82% from **41** and *Raney*-Ni/H_2)



46 (78% from **42** with NaOMe/MeOH, then H_2SO_4/OH, −35° [45])

NPP furnishes the keto-nitro-ester derivative **36** (66%). The products **37–42** were prepared from isolated and purified precursors which are indicated underneath the *formulae*. Finally, four products (**43–46**) of further conversions are given. In the *formulae* of the compounds **36–46**, the moiety stemming from NPP is marked by heavy lines. The variety of C-skeletons and of functional group patterns proves the usefulness of NPP as a multiple coupling reagent.

Experimental Part

General. For techniques and instruments used see our recent full papers [12] [14] [20] [42].

2'-Nitro-2'-propen-1'-yl 2,2-dimethylpropanoate (*NPP*) (**1**). *a) Sodium Salt of* 2-aci-*Nitro-1,3-propandiol.* Na (26 g, 1.13 mol) was slowly added with stirring to 200 ml of MeOH at 5°. When the H_2-evolution slowed down the mixture was warmed for 3 h at 40° (30 ml of MeOH were added after 1.5 h at 40°). The solution was cooled and added slowly to a stirred mixture of 60 g (2 mol) of paraformaldehyde and 61 g (1 mol) of nitromethane in 370 ml of MeOH at 0°. The temperature never exceeded 6° during the addition. After 12 h between 0–6°, the Na-salt was filtered, washed with MeOH and dried at 25–30°/10 Torr for 4 h to yield 197 g (95%) of the Na-salt of 2-*aci*-nitro-1,3-propandiol containing 2 molecules of MeOH.

b) 2-Nitro-1,3-propandiol. A solution of 55.2 g (0.4 mol) of salicylic acid in 400 ml of *tert*-butyl methyl ether was quickly added to a vigorously stirred mixture of 82.8 g (0.4 mol) of the Na-salt of 2-*aci*-nitro-1,3-propandiol in 600 ml of *tert*-butyl methyl ether at 25°. After 0.5 h, the mixture was heated at 40–45° for 0.75 h, then cooled, and the sodium salicylate filtered. The solution was concentrated to 60 ml by evaporation, cooled for 12 h at 0° and the colourless crystals of 2-nitro-1,3-propandiol (34–38 g; 70–80%) were filtered, m.p. 53–55°. ^{1}H-NMR (CD_3COCD_3): 4.00 (*m*, 4H, 2 OH, H–C(1), H–C(3)); 4.33 (*t*, J = 5, 2H, H–C(1), H–C(3)); 4.8 (*m*, 1H, H–C(2)).

c) 2'-Nitrotrimethylene Bis(2,2-dimethylpropanoate). A suspension of 129.7 g (1.07 mol) of 2-nitro-1,3-propandiol in 430 ml of CH_2Cl_2 was refluxed, and 400 g (3.32 mol) of pivaloyl chloride were slowly added with vigorous stirring. The HCl-evolution was monitored by a bubbler. After 3 h at 40°, no more HCl was formed

and the homogeneous mixture was cooled and allowed to stand for 12 h at 25°. The solvent was evaporated first on a rotatory evaporator, then with a pump (0.1 Torr) to remove the excess of pivaloyl chloride. The yellow-brown residue was dissolved in 700 ml of CH_2Cl_2 and washed with 0.2M NaOH (3 × 100 ml) and H_2O until the aq. layer was neutral. The crude product (308.9 g, 95%) was isolated as a yellow oil after drying ($MgSO_4$) and evaporating the solvent. ^{1}H-NMR (CCl_4): 1.20 (*s*, 18H, $2(CH_3)_3C$); 4.47 (*m*, 4H, 2H–C(1'), 2H–C(3')); 4.88 (*m*, 1H, H–C(2')).

d) 2'-Nitro-2'-propen-1'-yl 2,2-Dimethylpropanoate (NPP) (**1**). A mixture of 187 g (0.646 mol) of crude 2'-nitrotrimethylene bis(2,2-dimethylpropanoate) and 80 g (0.97 mol) of AcONa in 1700 ml Et_2O were *vigorously* stirred at 25° until the conversion reached 55% (usually 5–9 h). After 3 h stirring, aliquots of the mixture were removed, quenched by addition to CH_2Cl_2, washed with aq. $NaHCO_3$, H_2O, dried ($MgSO_4$), and analyzed by ^{1}H-NMR. Longer stirring lowered the yield and led to the polymerization of **1**. The solvent was evaporated to 300 ml and the resulting yellow mixture was washed with aq. $NaHCO_3$ until all the pivalic acid was removed (checked by ^{1}H-NMR). The Et_2O-solution was washed with H_2O, dried ($MgSO_4$), evaporated and the residue was distilled at 40–45°/0.01 Torr to give 52 g (43%) of **1** as a yellow liquid which crystallized in the refrigerator (m.p. 18°). The use of *tert*-butyl methyl ether instead of Et_2O allowed a better control of the reaction (less polymerization, better yield). NPP can be stored at −10° for more than 6 months without any decomposition. IR (CCl_4): 2970, 2950, 2900, 2865, 1740, 1530, 1480, 1450, 1398, 1361, 1348, 1279, 1249, 1138, 1035, 988, 942, 861, 692. ^{1}H-NMR (CCl_4): 1.22 (*s*, 9H, $(CH_3)_3C$); 5.03 (*s*, 2H, 2H–C(1')); 5.93 (br. *s*, 1H, olef. H *trans* to NO_2); 6.70 (*m*, 1H, olef. H *cis* to NO_2). Anal. calc. for $C_8H_{13}NO_4$ (187.20): C 51.33, H 7.00, N 7.48; found: C 51.47, H 7.19, N 7.45.

General Procedure for the Addition of a Nucleophile with NPP (**1**). – *a) Method A: Direct Addition (Addition of NPP-Solution to the Nucleophile).* A dry one-necked flask with a side arm (rubber septum, a pressure-equilizing dropping funnel, a magnetic stirrer and a three-way stopcock) was flushed with dry Ar. Diisopropylamine (10.5 mmol) and 30 ml of dry THF were added through the rubber septum using syringe-techniques. The stirred mixture was cooled to −78° (acetone/dry ice) and 10.3 mmol of BuLi (1.6M in hexane) was added dropwise with a syringe. After 0.5 h at −78°, a solution of a ketone or ester (10.2 mmol) in 4 ml of THF was slowly added to the stirred LDA solution. The *lithium enolate* was formed after 1–1.5 h stirring at −78°. Then, a solution of **1** (10 mmol) in 50 ml of THF was added within 20 min through a pressure-equalizing dropping funnel. After 1–3 h at −78°, the mixture was warmed up to −30° within 10 min, poured into 125 ml of 2% AcOH and extracted with CH_2Cl_2 (4 × 100 ml). The org. layer was washed successively with aq. $NaHCO_3$ (3 × 100 ml), with H_2O (2 × 100 ml), and NaCl-solution, dried ($MgSO_4$) and filtered. The solvent was evaporated and the residue was rapidly purified by flash chromatography [27] (20 × 8-cm column eluted mostly with CH_2Cl_2/hexane mixtures).

b) Method B: Inverse Addition (Addition of the Nucleophile to a NPP-Solution). Following the previously described technique [12b] [28] a flask A with the *lithium* or *magnesium* reagent was cooled to between −50° and −80°. A second flask B contained a stirred solution of **1** (8 mmol) in THF (50 ml) at −100° (acetone/Et_2O/N_2) and to this the contents of flask A were transferred through *Teflon* tubing (diameter 1 mm) within 20 min by Ar overpressure. The rate of addition could be controlled by a balloon attached on the three-way stopcock of flask B. After stirring for 15–60 min (depending on the nucleophile) at −78°, the mixture was warmed to −30° within 10 min and worked up as above.

N-*Methyl*-N-*(2'-nitro-2'-propenyl)aniline* (**2**). A solution of 1 g (5.34 mmol) of **1** in 5 ml of THF was added to a stirred solution of 0.572 g (5.34 mmol) of *N*-methylaniline in 15 ml of THF at −78° and stirring was continued for 2 h. Usual workup and flash chromatography yielded 0.884 g (86%) of pure **2**. IR (CCl_4): 3080, 3060, 3020, 2940, 2890, 2842, 2817, 1595, 1572, 1520, 1500, 1440, 1420, 1365, 1336, 1246, 1209, 1190, 1158, 1119, 1030, 1000, 984, 948, 901, 860, 690, 670, 630. ^{1}H-NMR (CCl_4): 2.99 (*s*, 3H, CH_3N); 4.4 (*m*, 2H, 2H–C(1')); 5.51 (br. *s*, 1H, olef. H *trans* to NO_2); 6.46 (*m*, 1H, olef. H *cis* to NO_2); 6.68 (*m*, 3H, 3 arom. H); 7.13 (*m*, 2H, 2 arom. H). MS (72 eV): 192 (40), 149 (7), 146 (20), 145 (20), 144 (100), 131 (8), 120 (25), 107 (7), 106 (20), 105 (17), 104 (15), 79 (5), 78 (5), 77 (35), 51 (7), 39 (3).

N-*(2'-Nitro-2'-propenyl)phenothiazine* (**3**). A solution of 1.4 g (7.48 mmol) of **1** in 5 ml of THF was added to a stirred solution of 1.491 g (7.48 mmol) of phenothiazine in 30 ml of THF at −78°. The mixture was warmed up to 25° and stirring was continued for 12 d. Usual workup and flash chromatography (CH_2Cl_2/hexane 1:4) of the dark red liquid yielded 1.97 g (99%) of **3**, m.p. 54–55°. IR (CCl_4): 3060, 2958, 1590, 1570, 1522, 1462, 1440, 1360, 1340, 1280, 1255, 1245, 1218, 1160, 1140, 1130, 1110, 1050, 950, 900, 860, 692, 660, 600. ^{1}H-NMR (CCl_4): 4.92 (*m*, 2H, 2H–C(1')); 5.70 (*m*, 1H, olefin. H *trans* to NO_2); 6.69 (*m*, 3H, olef. H *cis* to NO_2, 2 arom. H); 6.96 (*m*, 6H, 6 arom. H). MS (72 eV): 284 (20), 199 (45), 198 (100), 167 (15), 154 (5), 149 (5), 121 (25), 119 (60), 117 (60), 84 (6), 82 (10), 47 (5), 43 (7).

2-Nitro-3-phenylthio-1-propene (**4**). A solution of (7.48 mmol) of BuLi in hexane (1.6M) was added to a stirred solution of 0.824 g (7.48 mmol) of thiophenol in 23 ml of THF at −78° and the stirring was continued for 10 min. Then, a solution of 1.4 g (7.48 mmol) of **1** in 30 ml THF was added dropwise at −78°. The yellow mixture was stirred for 0.5 h at −78° and then warmed up to −30° within 10 min. After the usual workup and flash chromatography (CH_2Cl_2/hexane 1:1) yielded 0.900 g (61.5%) of **4**. IR (CCl_4): 3058, 2945, 1522, 1477, 1435, 1408, 1340, 1243, 1220, 1021, 938, 860, 690. ^{1}H-NMR (CCl_4): 3.95 (*s*, 2H, 2H−C(3)); 5.5 (*s*, 1H, olef. H *trans* to NO_2); 6.40 (*m*, 1H, olef. H *cis* to NO_2); 7.32 (*m*, 5H, 5 arom. H).

3-(2'-Nitro-2'-propenyl)indole (**5a**). A solution of 1.4 g (7.48 mmol) of **1** in 5 ml of benzene was added to a solution of 875 mg (7.48 mmol) of indole in 15 ml of benzene and stirring of the brown mixture continued for 6 h at 25°. The solution was left overnight at −35°. Usual workup and flash chromatography (CH_2Cl_2) of the dark brown liquid yielded 1.04 g (69%) of **5a**. IR ($CHCl_3$): 3470, 1610, 1518, 1450, 1412, 1340, 1090, 1003, 942, 861. ^{1}H-NMR (CCl_4 + $CHCl_3$): 4.01 (*s*, 2H, 2H−C(1')); 5.44 (*s*, 1H, olef. H *trans* to NO_2); 6.45 (*s*, 1H, olef. H *cis* to NO_2); 7.0–7.55 (*m*, 5H, 5 arom. H); 8.00 (br. *s*, 1H, H−N(1)).

N-*Methyl-3-(2'-nitro-2'-propenyl)indole* (**5b**). A solution of 1.4 g (7.48 mmol) of **1** in 5 ml of benzene was added to a solution of 0.97 g (7.47 mmol) of *N*-methylindole in 15 ml of benzene and stirring of the brown-yellow mixture continued for 3.5 h at 25°. Usual workup and flash chromatography (CH_2Cl_2/pentane 4:1) of the brown liquid yielded 1.478 g (91.5%) of **5b**, m.p. 63° (yellow crystals). IR ($CDCl_3$): 3045, 2930, 2910, 2890, 1610, 1520, 1465, 1421, 1370, 1340, 1250, 1155, 1130, 1088, 1058, 1010, 880, 640. ^{1}H-NMR ($CDCl_3$): 3.70 (*s*, 3H, CH_3N); 4.02 (*s*, 2H, 2H−C(1')); 5.45 (*m*, 1H, olef. H *trans* to NO_2); 6.43 (*m*, 1H, olef. H *cis* to NO_2); 6.95 (H−C(2)); 7.25 (*m*, 4H, 4 arom. H). MS (72 eV): 216 (41), 204 (3), 185 (5), 170 (22), 169 (100), 168 (46), 158 (25), 156 (25), 144 (35), 130 (15), 129 (15), 128 (15), 115 (10), 102 (9), 89 (3), 77 (15), 63 (7), 51 (5), 44 (15), 30 (55). Anal. calc. for $C_{12}H_{12}N_2O_2$ (216.24): C 66.65, H 5.59, N 12.96; found: C 66.64, H 5.58, N 12.97.

3-(2'-Nitro-2'-propenyl)indole-4-carbaldehyde (**5c**). A solution of 1.4 g (7.48 mmol) of **1** in 5 ml of THF was added to a stirred solution of 1.08 g (7.47 mmol) of indole-4-carbaldehyde in 15 ml of THF and stirring continued for 2 weeks at 25°. Usual workup and flash chromatography (AcOEt/CH_2Cl_2 5:95) yielded 0.52 g (30%) of **5c**, m.p. 147°. IR (KBr): 3240, 3130, 3110, 3060, 3040, 2860, 2760, 1675, 1560, 1515, 1498, 1450, 1420, 1410, 1360, 1340, 1338, 1290, 1258, 1218, 1161, 1142, 1128, 1069, 1034, 948, 940, 928, 870, 842, 795, 770, 740, 698, 660, 594, 575, 565. ^{1}H-NMR ($CDCl_3$ + 5% CD_3COCD_3): 2.35 (*s*, 1H, NH); 4.50 (*s*, 2H, 2H−C(1')); 5.28 (*m*, 1H, olef. H *trans* to NO_2); 6.40 (*s*, 1H, olef. H *cis* to NO_2); 7.30 (*m*, 2H, 2 arom. H); 7.7 (*m*, 1H, 1 arom. H); 10.1 (*s*, 1H, CHO)). MS (72 eV): 230 (45), 184 (21), 183 (65), 182 (7), 174 (10), 156 (15), 155 (45), 154 (100), 130 (10), 129 (28), 128 (28), 127 (40), 117 (10), 77 (25), 51 (7), 39 (3). Anal. calc. for $C_{12}H_{10}N_2O_3$ (230.22): C 62.61, H 4.38, N 12.17; found: C 62.63, H 4.39, N 12.16.

4-Benzyloxy-3-(2'-nitro-2'-propenyl)indole-7-ethanol (**5d**). A solution of 198 mg (1.06 mmol) of **1** in 1.5 ml of benzene was added to a solution of 284.7 mg (1.06 mmol) of 4-(benzyloxy)indole-7-ethanol in 2 ml of benzene and stirring continued for 3 h at 25°. Usual workup and flash chromatography (CH_2Cl_2/AcOEt 1:4) yielded 373.5 mg (66%) of **5d**, m.p. 124–126°. IR ($CDCl_3$): 3580, 3480, 3340, 2920, 2870, 1603, 1595, 1510, 1450, 1415, 1340, 1259, 1170, 1065, 940, 690. ^{1}H-NMR ($CDCl_3$): 1.8 (br. *s*, 1H, OH); 3.00 (*t*, J = 6, 2H, CH_2CH_2OH); 3.96 (*t*, J = 6, 2H, CH_2CH_2OH); 4.18 (*s*, 2H, 2H−C(1')); 5.11 (*s*, 2H, $PhCH_2$); 5.22 (*s*, 1H, olef. H *trans* to NO_2); 6.30 (*s*, 1H, olef. H *cis* to NO_2); 6.5 (*d*, part of an *AB*-system, J = 8, 1H, 1H−C(5)); 6.90 (*d*, J = 8, part of an *AB*-system, 1H, 1H−C(6)); 7.00 (*m*, 1H, H−C(2)); 7.4 (*s*, 5H, 5 arom. H). MS (72 eV): 352 (75), 305 (7), 261 (98), 231 (36), 215 (68), 196 (8), 184 (100), 156 (7), 154 (7), 129 (8), 128 (8), 115 (3), 91 (72), 77 (3), 65 (7), 30 (3).

4-Benzyloxy-7-(2-methoxyethyl)-N-*methyl-3-(2'-nitro-2'-propenyl)indole* (**5e**). A solution of 174 mg (0.93 mmol) of **1** in 1 ml of THF was added to a solution of 275 mg (0.93 mmol) of 4-benzyloxy-7-(2-methoxyethyl)-*N*-methylindole in 1 ml of THF and stirring continued for 1.5 h at 25°. Usual workup and flash chromatography (CH_2Cl_2/pentane 4:1) yielded 281.8 mg (80%) of **5e**. IR ($CDCl_3$): 3020, 2920, 2860, 2820, 1585, 1518, 1505, 1441, 1413, 1395, 1375, 1340, 1260, 1205, 1198, 1145, 1102, 1070, 1050, 1020, 787. ^{1}H-NMR ($CDCl_3$): 3.31 (*m*, 2H, $CH_2CH_2OCH_3$); 3.40 (*s*, 3H, CH_3N); 3.67 (*m*, 2H, $CH_2CH_2OCH_3$); 3.95 (*s*, 3H, CH_3O); 4.10 (*s*, 2H, 2H−C(1')); 5.08 (*s*, 2H, $PhCH_2$); 5.21 (*m*, 1H, olef. H *trans* to NO_2); 6.30 (*s*, 1H, olef. H *cis* to NO_2); 6.5 (*d*, part of an *AB*-system, J = 8, 1H, H−C(6)); 6.75 (*s*, 1H, H−C(2)); 6.90 (*d*, part of an *AB*-system, J = 8, 1H, 1H−C(5)); 7.4 (*s*, 5H, 5 arom. H).

(E)-6-Nitro-1-(2',6',6'-trimethyl-1'-cyclohexenyl)-1,6-heptadien-3-one (**6**; *Method A*). A solution of 1.438 g (7.48 mmol) of β-ionone (purity by GC: 95%) in 2 ml of THF was added within 10 min to 7.48 mmol of LDA in 20 ml of THF at −78°. Stirring was continued for 1.5 h at −78°. A solution of 1.4 g (7.48 mmol) of **1** in 35 ml

of THF was added within 15 min to the stirred lithium enolate solution at −78° and after 4 h at −78° the mixture was warmed to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2/pentane 7:3) yielded 1.520 g (77%) of **6**. IR (CCl_4): 2959, 2927, 2860, 1690, 1670, 1602, 1590, 1525, 1460, 1430, 1360, 1340, 1250, 1190, 1140, 1090, 1020, 980, 945, 860, 690. ^{1}H-NMR (CCl_4): 1.05 (*s*, 6H, 2CH$_3$−C(6′)); 1.52 (*m*, 4H, 2H−C(5′), 2H−C(4′)); 1.78 (*s*, 3H, CH$_3$−C(2′)); 2.10 (*m*, 2H, 2H−C(3′)); 2.86 (4-line system, 4H, 2H−C(4), 2H−C(5)); 5.65 (*s*, 1H, olef. H *trans* to NO_2); 6.03 (*d*, part of an *AB*-system, J = 16.5, 1H, H−C(1)); 6.4 (*m*, 1H, olef. H *cis* to NO_2); 7.22 (*d*, part of an *AB*-system, J = 16.5, 1H, 1H−C(2)). MS (72 eV): 277 (5), 263 (17), 262 (100), 231 (3), 220 (3), 215 (2), 177 (4), 176 (3), 161 (3), 149 (5), 133 (7), 128 (4), 121 (5), 119 (5), 107 (5), 105 (5), 95 (5), 93 (5), 91 (7), 79 (7), 77 (5), 69 (5), 55 (7), 53 (6), 41 (10). Anal. calc. for $C_{16}H_{23}NO_3$ (277.36): C 69.29, H 8.36, N 5.05; found: C 68.92, H 8.67, N 5.13.

4-Nitro-1-phenyl-4-penten-1-one (**7**; *Method A*). A solution of 0.87 g (7.24 mmol) of acetophenone in 2 ml of THF was added within 10 min to 7.4 mmol of LDA in 25 ml of THF at −78° and stirring continued for 1.5 h at −78°. A solution of 1.40 g (7.48 mmol) of **1** in 30 ml of THF was added within 15 min to the stirred lithium enolate solution at −78° and after 2.75 h at −78° the mixture was warmed to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2) yielded 1.20 g (80.5%) of **6**, m.p. 108°. IR ($CHCl_3$): 3060, 3030, 3010, 2910, 2858, 1685, 1598, 1580, 1522, 1450, 1431, 1390, 1345, 1320, 1300, 1180, 1001, 980, 950, 890, 870, 831, 690. ^{1}H-NMR ($CDCl_3$): 3.15 (*m*, 4H, 2H−C(2), 2H−C(3)); 5.72 (*s*, 1H, olef. H *trans* to NO_2); 6.54 (*m*, 1H, olef. H *cis* to NO_2); 7.54 (*m*, 3H, 3 arom. H); 7.99 (*m*, 2H, 2 arom. H). MS (72 eV): 205 (1), 159 (65), 106 (6), 105 (100), 77 (55), 51 (15). Anal. calc. for $C_{11}H_{11}NO_3$ (205.21): C 64.38, H 5.40, N 6.83; found: C 64.43, H 5.40, N 6.78.

6-Methoxy-1-(2′-nitro-2′-propenyl)-3,4-dihydro-2(1H)-naphthalenone (**8**; *Method A*). A solution of 1.313 g (7.45 mmol) of 6-methoxy-3,4-dihydro-2(1*H*)-naphthalenone in 2 ml of THF was added within 10 min to 7.5 mmol of LDA in 25 ml of THF at −78°. Stirring was continued for 15 min at −78°. A solution of 1.4 g (7.48 mmol) of **1** in 30 ml THF was added over 15 min to the stirred lithium enolate solution at −78° and after 2.5 h at −78° the mixture was warmed to −30° in 10 min. Usual workup and flash chromatography (AcOEt/CH_2Cl_2 1:9) yielded 846 mg (44%) of **8**. IR ($CDCl_3$): 2930, 2900, 2830, 1710, 1607, 1565, 1520, 1495, 1460, 1435, 1340, 1260, 1150, 1118, 1030, 945, 905, 850. ^{1}H-NMR ($CDCl_3$): 2.55 (*m*, 2H, 2H−C(4)); 3.10 (*m*, 4H, 2H−C(3), 2H−C(1′)); 3.70 (*m*, 1H, H−C(1)); 3.79 (*s*, 3H, CH$_3$O); 5.55 (*m*, 1H, olef. H *trans* to NO_2); 6.43 (*m*, 1H, olef. H *cis* to NO_2), 6.80 (*m*, 2H, H−C(7), H−C(8)); 7.02 (*m*, 1H, H−C(5)).

6-(2′-Nitro-2′-propenyl)-2-cyclohexen-1-one (**9**; *Method A*). A solution of 719 mg (7.48 mmol) of cyclohexenone in 2 ml of THF was added within 10 min to 7.48 mmol of LDA in 20 ml of THF. Stirring was continued for 1.5 h at −78°. A solution of 1.4 g (7.48 mmol) of **1** in 35 ml of THF was added over 20 min to the stirred lithium enolate solution at −78° and after 4 h at −78° the mixture was warmed to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2) yielded 868 mg (64%) of **6**, m.p. 32°. IR (CCl_4): 3130, 3040, 2940, 2860, 2830, 1682, 1524, 1452, 1430, 1388, 1343, 1282, 1250, 1230, 1218, 1210, 1140, 1130, 1090, 1003, 946, 920, 910, 898, 867, 698, 660, 632. ^{1}H-NMR (CCl_4): 1.5–2.2 (*m*, 2H, 2H−C(5)); 2.5 (*m*, 4H, 2H−C(4), 2H−C(1′)); 3.2 (*m*, 1H, H−C(6)); 5.71 (*s*, 1H, olef. H *trans* to NO_2); 5.99 (*dt*, ^3J = 10, ^4J = 1, 1H, H−C(2)); 6.45 (*s*, 1H, olef. H *cis* to NO_2); 6.9 (*m*, 1H, H−C(3)). Anal. calc. for $C_9H_{11}NO_3$ (181.19): C 59.65, H 6.12, N 7.73; found: C 59.52, H 6.24, N 7.71.

2-(2′-Nitro-2′-propenyl)-1-cyclopentanone (**10**; *Method A*). A solution of 614 mg (7.3 mmol) of cyclopentanone in 2 ml of THF was added within 10 min to 7.4 mmol of LDA in 25 ml THF at −40°, stirring was continued for 15 min. The mixture was then warmed to 25° and stirred for 1 h at this temperature. A solution of 1.4 g (7.48 mmol) of **1** in 30 ml THF was added within 20 min to the stirred lithium enolate solution at −78°. After 2.5 h at −78°, the mixture was warmed to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2) yielded 1.11 g (89.7%) of **10**, b.p. 78°/0.003 Torr. IR (CCl_4): 2950, 2875, 1740, 1520, 1448, 1425, 1401, 1387, 1340, 1270, 1244, 1150, 1105, 1000, 940, 860, 692. ^{1}H-NMR (CCl_4): 1.3–2.7 (*m*, 8H, 2H−C(3), 2H−C(4), 2H−C(5), 2H−C(1′)); 3.05 (*m*, 1H, H−C(2)); 5.63 (*s*, 1H, olef. H *trans* to NO_2); 6.43 (*s*, 1H, olef. H *cis* to NO_2). MS (72 eV): 168 (3), 166 (3), 164 (3), 123 (100), 95 (30), 81 (10), 79 (35), 77 (25), 71 (20), 67 (35), 66 (30), 55 (60), 43 (30), 41 (60). Anal. calc. for $C_8H_{11}NO_3$ (169.18): C 56.80, H 6.55, N 8.28; found: C 56.39, H 6.68, N 8.17.

2-(2′-Nitro-2′-propenyl)-1-cyclohexanone (**11**; *Method A*). A solution of 0.716 g (7.3 mmol) of cyclohexanone in 2 ml of THF was added within 10 min to 7.4 mmol of LDA in 25 ml of THF at −40° and stirring continued for 15 min. The mixture was then warmed to 25° and stirred for 1 h at this temperature. A solution of 1.4 g (7.48 mmol) of **1** in 30 ml THF was added within 15 min to the stirred lithium enolate solution at −78°. After 2.5 h at −78°, the mixture was warmed to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2) yielded 1.16 g (86.7%) of **11**, b.p. 80°/0.001 Torr. IR (CCl_4): 2935, 2858, 1710, 1520, 1442, 1421, 1340,

1125, 945, 859. ^{1}H-NMR (CCl_4): 1.2–2.8 (*m*, 10H, $4CH_2$, 2H–C(1')); 3.18 (*m*, 4-line system, 1H, H–C(2)); 5.70 (*s*, 1H, olef. H *trans* to NO_2); 6.47 (*s*, 1H, olef. H *cis* to NO_2). MS (72 eV): 178, 137 (100), 95 (13), 93 (15), 91 (12), 79 (20), 77 (10), 67 (35), 55 (32), 41 (30), 30 (10), 27 (12). Anal. calc. for $C_9H_{13}NO_3$ (183.21): C 59.00, H 7.15, N 7.65; found: C 58.97, H 7.15, N 7.52.

endo-*3-(2'-Nitro-2'-propenyl)-2-bornanone* (**12**; *Method A*). A solution of 1.11 g (7.3 mmol) of camphor in 2 ml of THF was added within 10 min to 7.4 mmol of LDA in 25 ml of THF at −40° and stirring continued for 15 min. The mixture was then warmed to 25° and stirred for 1 h at this temperature. A solution of 1.4 g (7.48 mmol) of **1** in 30 ml of THF was added to the stirred lithium enolate solution over 15 min at −78°. After 3 h at −78°, the mixture was warmed to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2/hexane) yielded 1.16 g (67%) of **12**, m.p. 51°. IR (CCl_4): 2950, 2890, 2870, 1740, 1524, 1430, 1390, 1370, 1340, 1320, 1280, 1246, 1015, 939, 908, 860, 691. ^{1}H-NMR (CCl_4): 0.98 (*m*, 9H, $3CH_3$); 1.2–3.0 (*m*, 8H, H–C(3), H–C(4), 2H–C(5), 2H–C(6), 2H–C(1')); 5.62 (br. *s*, 1H, olef. H *trans* to NO_2); 6.45 (*m*, 1H, olef. H *cis* to NO_2). MS (72 eV): 237 (5), 220 (4), 209 (3), 194 (2), 192 (10), 191 (70), 175 (1), 166 (1), 161 (1), 151 (6), 147 (8), 139 (7), 133 (6), 123 (10), 121 (15), 119 (10), 110 (10), 109 (25), 108 (30), 105 (10), 95 (80), 93 (15), 91 (25), 83 (100), 79 (25), 77 (25), 69 (50), 55 (55), 41 (60). Anal. calc. for $C_{13}H_{19}NO_3$ (237.30): C 65.80, H 8.07, N 5.90; found: C 65.64, H 7.98, N 5.80.

Ethyl 4-Nitro-4-pentenoate (**13**; *Method A*). A solution of 660 mg (7.51 mmol) of AcOEt in 2 ml of THF was added within 10 min to 7.51 mmol of LDA in 20 ml of THF at −78°. Stirring was continued for 1 h at −78°. A solution of 1.4 g (7.48 mmol) of **1** in 30 ml of THF was added over 20 min to the stirred lithium enolate solution at −78°, and after 40 min at −78° the mixture was warmed to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2) yielded 1.15 g (87%) of **13**, b.p. 60°/0.01 Torr. IR (CCl_4): 2980, 2950, 1736, 1546, 1529, 1430, 1372, 1342, 1249, 1188, 698. ^{1}H-NMR (CCl_4): 1.22 (*t*, J = 6, 3H, CH_3CH_2O); 2.52 (*t*, J = 7, 2H, 2H–C(3)); 2.90 (*t*, J = 7, 2H, 2H–C(2)); 4.10 (*q*, J = 6, 2H, CH_3CH_2O); 5.62 (*s*, 1H, olef. H *trans* to NO_2); 6.5 (*s*, 1H, olef. H *cis* to NO_2). MS (72 eV): 174 (1), 173 (1), 156 (1), 149 (5), 128 (90), 100 (35), 99 (100), 84 (5), 81 (7), 71 (25), 60 (20), 53 (45), 43 (80), 29 (60). Anal. calc. for $C_7H_{11}NO_4$ (173.17): C 48.55, H 6.40, N 8.09; found: C 48.65, H 6.54, N 8.25.

Ethyl 2-Methyl-4-nitro-4-pentenoate (**14a**; *Method A*). A solution of 746 mg (7.3 mmol) of ethyl propionate in 2 ml of THF was added within 10 min to 7.4 mmol of LDA in 25 ml of THF at −78° and stirring continued for 1 h at −78°. A solution of 1.4 g (7.48 mmol) of **1** in 30 ml THF was added over 20 min to the stirred lithium enolate solution at −78°, and after 50 min at −78° the mixture was warmed to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2) yielded 930 mg (68%) of **14a**, b.p. 60°/0.01 Torr. IR (CCl_4): 2980, 2950, 2880, 1730, 1528, 1460, 1422, 1341, 1283, 1248, 1185, 1160, 1110, 1050, 1005, 945, 912, 695. ^{1}H-NMR (CCl_4): 1.21 (*m*, 6H, $2CH_3$); 2.76 (*m*, 3H, 1H–C(2), 2H–C(3)); 4.07 (*q*, J = 6, 2H, CH_3CH_2O); 5.61 (*s*, 1H, olef. H *trans* to NO_2); 6.44 (*m*, 1H, olef. H *cis* to NO_2). MS (72 eV): 188 (1), 170 (1), 156 (1), 142 (45), 141 (25), 125 (2), 114 (30), 113 (85), 97 (8), 95 (13), 85 (8), 74 (6), 67 (100), 57 (20), 43 (40), 41 (40), 29 (50). Anal. calc. for $C_8H_{13}NO_4$ (187.20): C 51.83, H 7.00, N 7.48; found: C 51.23, H 6.99, N 7.44.

tert-*Butyl 2-Methyl-4-nitro-4-pentenoate* (**14b**; *Method A*). A solution of 950 mg (7.30 mmol) of *tert*-butyl propionate in 2 ml of THF was added within 10 min to 7.4 mmol of LDA in 25 ml of THF at −78° and stirring continued for 1 h at −78°. A solution of 1.4 g (7.48 mmol) of **1** in 35 ml of THF was added over 15 min to the stirred lithium enolate solution at −78°, and after 1 h at −78° the mixture was warmed to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2) yielded 1.304 g (83%) of **14b**, b.p. 60°/0.01 Torr. IR (CCl_4): 2970, 2950, 1722, 1524, 1450, 1420, 1390, 1375, 1362, 1340, 1245, 1150, 940, 910, 860, 842, 692. ^{1}H-NMR (CCl_4): 1.20 (*d*, J = 7, 3H, CH_3–C(2)); 1.44 (*s*, 9H, $(CH_3)_3C$); 2.78 (*m*, 3H, H–C(2), 2H–C(3)); 5.62 (br. *s*, 1H, olef. H *trans* to NO_2); 6.45 (*s*, 1H, olef. H *cis* to NO_2). MS (72 eV): 215 (1), 160 (1), 142 (50), 135 (1), 125 (3), 114 (8), 113 (5), 98 (1), 95 (1), 67 (37), 57 (100), 41 (38), 29 (20). Anal. calc. for $C_{10}H_{17}NO_4$ (215.249): C 55.80, H 7.96, N 6.51; found: C 55.74, H 7.83, N 6.37.

S-tert-*Butyl 1-(2'-nitro-2'-propenyl)cyclopropane-1-carbothioate* (**15**; *Method A*). A solution of 1.15 g (7.26 mmol) of *S-tert*-butyl cyclopropanecarbothioate in 2 ml of THF was added within 10 min to 7.48 mmol of LDA in 25 ml of THF at −78°. Stirring was continued for 1 h at −78°. A solution of 1.4 g (7.48 mmol) of **1** in 30 ml of THF was added to the stirred lithium enthiolate solution at −78° 15 min, and after 1.5 h at −78° the mixture was warmed to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2) yielded 1.45 g (82%) of **15**, b.p. 120°/0.02 Torr. IR (CCl_4): 2960, 2920, 2860, 1660, 1525, 1450, 1413, 1360, 1340, 1156, 1038, 1008, 951, 900, 851. ^{1}H-NMR (CCl_4): 0.87 (4-line system, 4H, 2H–C(2), 2H–C(3)); 1.43 (*s*, 9H, $(CH_3)_3C$); 2.98 (*s*, 2H, 2H–C(1')); 5.72 (*m*, 1H, olef. H *trans* to NO_2); 6.52 (*m*, 1H, olef. H *cis* to NO_2). MS (72 eV): 187 (10), 181 (1), 169 (2), 157 (7), 154 (100), 141 (30), 131 (15), 119 (2), 95 (7), 85 (3), 79 (10), 77 (12), 69 (30), 57 (75), 41

(20). Anal. calc. for $C_{11}H_{17}NO_3S$ (243.33): C 54.30, H 7.04, N 5.76, S 13.18; found: C 54.16, H 6.95, N 5.69, S 13.08.

2-(2'-Nitro-2'-propenyl)-2-phenyl-1,3-dithiane (**16**). *a) Direct Addition (Method A).* A solution of 4.58 ml (7.32 mmol) of BuLi in hexane (*ca.* 1.6M) was added slowly to a solution of 890 mg (7.32 mmol) of 2-phenyl-1,3-dithiane in 15 ml of THF at −78°. Stirring was continued for 2 h at −78°. A solution of 1.4 g (7.48 mmol) of **1** in 30 ml of THF was added to the stirred lithium dithianide solution at −78° within 15 min, and after 3 h at −78° the mixture was warmed to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2) yielded 1.18 g (78%, purity by GC 90%) of **16**.

b) Inverse Addition (Method B). A solution of 7.4 mmol of 2-lithio-2-phenyl-1,3-dithiane (prepared as above) was cooled to −78° and transferred within 20 min into a flask containing a stirred solution of 1.4 g (7.48 mmol) of **1** at −100°. After stirring for 2 h at −78°, the mixture was allowed to warm to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2) yielded 1.77 g (85%) of pure **16**. IR (CCl_4): 3050, 2940, 2920, 2900, 1525, 1440, 1420, 1338, 1273, 1031, 945, 700. ^{1}H-NMR ($CDCl_3$): 1.91 (*m*, 2H, 2H–C(5)); 2.71 (3-line system, 4H, 2H–C(4), 2H–C(6)); 3.43 (*s*, 2H, 2H–C(1')); 5.33 (*m*, 1H, olef. H *trans* to NO_2); 6.42 (*s*, 1H, olef. H *cis* to NO_2); 7.32 (*m*, 3H, 3 arom. H); 7.85 (*m*, 2H, 2 arom. H).

N-(tert-Butoxycarbonyl)-2-(2'-nitro-2'-propenyl)indole (**17**; *Method B*). A solution of 1.61 g (7.40 mmol) of *N-(tert*-butoxycarbonyl)indole in 2 ml of THF was added dropwise to 7.77 mmol of *t*-BuLi in 20 ml of THF and *ca.* 5 ml of hexane at −78° [30]. Stirring was continued for 0.75 h at −78°. This mixture was then transferred, within 20 min, into a flask containing a stirred solution of 1.4 g (7.48 mmol) of **1** in 50 ml of THF at −100°. After stirring for 1 h at −78°, the mixture was allowed to warm to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2/pentane 1:1) yielded 2.237 g (72.6%) of **17**, m.p. 59°. IR (CCl_4): 3058, 2990, 2938, 1738, 1529, 1451, 1380, 1370, 1341, 1331, 1250, 1220, 1160, 1120, 1090, 968, 942, 865, 848. ^{1}H-NMR (CCl_4): 1.62 (*s*, 9H, $(CH_3)_3C$); 4.28 (*s*, 2H, 2H–C(1')); 5.32 (*m*, 1H, olef. H *trans* to NO_2); 6.42 (*s*, 2H, olef. H *cis* to NO_2, H–C(3)); 7.19 (*m*, 2H, 2 arom. H); 7.40 (*m*, 1H, 1 arom. H); 8.04 (*m*, 1H, 1 arom. H). MS (72 eV): 302 (15), 246 (30), 202 (20), 199 (25), 185 (10), 155 (100), 154 (25), 149 (20), 130 (5), 127 (5), 77 (5), 57 (60), 41 (40). Anal. calc. for $C_{16}H_{18}N_2O_4$ (302.33): C 63.56, H 6.00, N 9.27; found: C 63.57, H 6.17, N 9.17.

3-(2'-Nitro-2'-propenyl)thiophene (**18**; *Method B*). A solution of 1.232 g (7.55 mmol) of 3-bromothiophene in 2 ml of THF was added dropwise to 7.6 mmol of BuLi in 5 ml of hexane THF 1:9 at −100° [32]. Stirring was continued for 0.25 h at −100°. The solution was then warmed to −78° and stirred at this temp. for 0.25 h. This mixture was transferred within 15 min into a flask containing a stirred solution of 1.4 g (7.48 mmol) of **1** in 50 ml of THF at −100°. After stirring for 1 h at −80°, the mixture was allowed to warm to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2/pentane 1:3) yielded 0.87 g (69%) of **18**, b.p. 80°/0.15 Torr. IR (CCl_4): 3120, 3095, 2942, 2842, 1521, 1420, 1338, 1241, 1145, 1075, 940, 860, 830, 718, 690, 682. ^{1}H-NMR (CCl_4): 3.88 (*s*, 2H, 2H–C(1')); 5.41 (*s*, 1H, olef, H *trans* to NO_2); 6.43 (*s*, 1H, olef. H *cis* to NO_2); 6.9 (*m*, 1H, 1 arom. H); 7.09 (*m*, 1H, 1 arom. H); 7.30 (*m*, 1H, 1 arom. H). MS (72 eV): 169 (27), 123 (18), 122 (100), 97 (10), 79 (15), 78 (10), 77 (15), 45 (21). Anal. calc. for $C_7H_7NO_2S$ (169.202): C 49.69, H 4.17, N 8.28, S 18.95; found: C 49.62, H 4.26, N 8.05, S 18.78.

(2'-Nitro-2'-propenyl)benzene (**19a**; *Method B*). A solution of 4.94 ml (7.6 mmol) of BuLi in hexane (1.54M) was added dropwise to 1.185 g (7.55 mmol) of bromobenzene in 50 ml of THF at −90° [32]. Stirring was continued for 1 h at −90°. This mixture was then transferred within 20 min into a flask containing a stirred solution of 1.4 g (7.48 mmol) of **1** in 50 ml of THF at −100°. After stirring for 0.5 h at −90°, the mixture was allowed to warm to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2/pentane 3:7) yielded 936 mg (76.7%) of **19a**, b.p. 80°/0.2 Torr. IR (CCl_4): 3060, 3020, 2940, 2845, 1521, 1490, 1448, 1421, 1340, 1241, 1149, 940, 860, 698. ^{1}H-NMR (CCl_4): 3.85 (*s*, 2H, 2H–C(1')); 5.33 (*s*, 1H, olef. H *trans* to NO_2); 6.42 (*s*, 1H, olef. H *cis* to NO_2); 7.4 (*m*, 5H, 5 arom. H). MS (72 eV): 163 (11), 116 (100), 115 (53), 91 (20), 77 (1), 65 (6), 57,5 (6), 51 (6), 39 (6). Anal. calc. for $C_9H_9NO_2$ (163.18): C 66.25, H 5.56, N 8.58; found: C 66.24, H 5.63, N 8.52.

1-Methoxy-4-(2'-nitro-2'-propenyl)benzene (**19b**; *Method B*). A solution of 4.88 ml (7.5 mmol) of BuLi in hexane (1.54M) was added dropwise to 1.384 g (7.4 mmol) of 1-bromo-4-methoxybenzene in 50 ml of THF at −100° [32]. Stirring was continued for 1 h at −90°. A white precipitate was formed that redissolved on rapid warming to −40°. This mixture was cooled to −80° and then transferred within 10 min into a flask containing a stirred solution of 1.4 g (7.48 mmol) of **1** in 50 ml of THF at −100°. After stirring for 0.5 h at −90°, the mixture was allowed to warm to −40° in 10 min. Usual workup and flash chromatography (CH_2Cl_2/pentane 7:3) yielded 1.011 g (70.7%) of **19b**, b.p. 130°/0.02 Torr. IR (CCl_4): 3000, 2940, 2920, 2900, 2820, 1608, 1580, 1521, 1508, 1458, 1421, 1340, 1298, 1241, 1171, 1142, 1101, 1035, 940, 860, 690. ^{1}H-NMR (CCl_4): 3.75 (*s*, 3H, CH_3O); 3.82

(*s*, 2H, 2H–C(1')); 5.35 (*s*, 1H, olef. H *trans* to NO_2); 6.42 (*s*, 1H, olef. H *cis* to NO_2); 6.98 (*m*, 4H, 4 arom. H). MS (72 eV): 193 (18), 167 (1), 146 (100), 137 (1), 131 (30), 121 (6), 115 (18), 103 (30), 91 (7), 78 (10), 77 (15), 65 (5), 63 (7), 51 (8), 39 (3). Anal. calc. for $C_{10}H_{11}NO_3$ (193.20): C 62.17, H 5.74, N 7.25; found: C 62.00, H 5.86, N 7.11.

1-Fluoro-4-(2'-nitro-2'-propenyl)benzene (**19c**). A solution of 4.94 ml (7.6 mmol) of BuLi in hexane (1.54M) was added dropwise to 1.321 g (7.4 mmol) of 1-bromo-4-fluorobenzene in 50 ml of THF at −90°. Stirring was continued for 0.75 h at −90°. This mixture was then transferred within 20 min into a flask containing a stirred solution of 1.4 g (7.48 mmol) of **1** in 50 ml of THF at −100°. After stirring for 1 h at −100°, the mixture was allowed to warm to −30° in 10 min. Usual workup and flask chromatography (CH_2Cl_2/hexane 3:7) yielded 0.994 g (74%) of **19c**, b.p. 100°/0.2 Torr. IR (CCl_4): 3035, 2945, 2880, 1600, 1595, 1524, 1505, 1421, 1340, 1242, 1230, 1221, 1151, 1090, 1010, 940, 860, 690. ^{1}H-NMR (CCl_4): 3.90 (*s*, 2H, 2H–C(1')); 5.40 (*s*, 1H, olef. H *trans* to NO_2); 6.48 (*s*, 1H, olef. H *cis* to NO_2); 7.12 (*m*, 4H, 4 arom. H). MS (72 eV): 181 (7), 135 (20), 134 (100), 133 (80), 123 (5), 115 (19), 109 (36), 107 (7), 89 (1), 83 (11), 75 (4), 66,5 (5), 57 (6), 39 (7). Anal. calc. for $C_9H_8NO_2F$ (181.17): C 59.67, H 4.45, N 7.73; found: C 59.77, H 4.58, N 7.60.

1-(2'-Nitro-2'-propenyl)-3-(trifluoromethyl)benzene (**19d**). A solution of 4.94 ml (7.6 mmol) of BuLi in hexane (1.54M) was added dropwise to 1.699 g (7.55 mmol) of 1-bromo-3-(trifluoromethyl)benzene in 50 ml of THF at −90°. Stirring was continued for 0.75 h at −90°. This yellow mixture was then transferred within 20 min into a flask containing a stirred solution of 1.4 g (7.48 mmol) of **1** in 50 ml of THF at −100°. After stirring for 1 h at −90°, the mixture was allowed to warm to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2/hexane 4:1) yielded 1.345 g (77.8%) of **19d**, b.p. 80°/0.15 Torr. IR (CCl_4): 3120, 3050, 2945, 2850, 1524, 1443, 1421, 1340, 1330, 1242, 1195, 1188, 1175, 1165, 1130, 1090, 1071, 940, 910, 860, 700, 652. ^{1}H-NMR (CCl_4): 3.98 (*s*, 2H, 2H–C(1')); 5.46 (*s*, 1H, olef. H *trans* to NO_2); 6.55 (*s*, 1H, olef. H *cis* to NO_2); 7.50 (*m*, 4H, 4 arom. H). MS (72 eV): 213 (26), 196 (4), 166 (35), 165 (100), 152 (16), 141 (4), 139 (5), 128 (4), 115 (8), 82.5 (6). Anal. calc. for $C_{10}H_8NO_2F_3$ (231.17): C 51.96, H 3.49, N 6.06; found: C 52.03, H 3.54, N 6.01.

1,3,5-Trimethyl-2-(2'-nitro-2'-propenyl)benzene (**20**). A solution of 4.94 ml (7.6 mmol) of BuLi in hexane (1.54M) was added dropwise to 1.503 g (7.55 mmol) of 2-bromo-1,3,5-trimethylbenzene in 50 ml of THF at −90° [32]. Stirring was continued for 1.5 h at −78°. This mixture was then transferred within 15 min into a flask containing a stirred solution of 1.4 g (7.48 mmol) of **1** in 50 ml of THF at −100°. After stirring for 1 h at −78°, the mixture was allowed to warm to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2/pentane 1:4) yielded 1.190 g (77.5%) of **20**, m.p. 42–43°. IR (CCl_4): 3000, 2945, 2920, 2850, 1655, 1610, 1520, 1480, 1440, 1420, 1340, 1242, 1150, 1028, 940, 912, 860, 850, 690, 650. ^{1}H-NMR (CCl_4): 2.18 (*s*, 6H, CH_3–C(1), CH_3–C(3)); 2.28 (*s*, CH_3–C(5)); 3.85 (*m*, 2H, 2H–C(1)); 4.9 (*m*, 1H, olef. H *trans* to NO_2); 6.35 (*m*, 1H, olef. H *cis* to NO_2); 6.8 (*s*, 2H, 2 arom. H). MS (72 eV): 205 (30), 190 (5), 188 (4), 158 (32), 144 (25), 143 (100), 129 (25), 128 (25), 115 (14), 105 (6), 91 (12), 77 (7), 65 (5). Anal. calc. for $C_{12}H_{15}NO_2$ (205.26): C 70.22, H 7.37, N 6.82; found: C 70.07, H 7.48, N 6.83.

1-(2'-Nitro-2'-propenyl)naphthalene (**21**; *Method B*). A solution of 4.94 ml (7.6 mmol) of BuLi in hexane (1.54M) was added dropwise to 1.563 g (7.55 mmol) of 1-bromonaphthalene in 60 ml of THF at −90° [32]. Stirring was continued for 1 h at −60°. This mixture was then transferred within 15 min into a flask containing a stirred solution of 1.4 g (7.48 mmol) of **1** in 50 ml of THF at −100°. After stirring for 0.5 h at −90°, the mixture was allowed to warm to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2/pentane 3:7) yielded 1.403 g (88%) of **21**, m.p. 63°. IR (CCl_4): 3120, 3060, 3040, 3000, 2942, 2840, 1591, 1520, 1435, 1425, 1392, 1375, 1338, 1242, 1160, 1145, 1010, 960, 900, 860, 690, 670. ^{1}H-NMR (CCl_4): 4.3 (*s*, 2H, 2H–C(1')); 5.02 (*s*, 1H, olef. H *trans* to NO_2); 6.45 (*s*, 1H, olef. H *cis* to NO_2); 7.5 (*m*, 4 arom. H); 7.82 (*m*, 3H, 3 arom. H). MS (72 eV): 213 (26), 196 (4), 166 (35), 165 (100), 152 (16), 141 (4), 139 (5), 128 (4), 115 (8), 82.5 (6). Anal. calc. for $C_{13}H_{11}NO_2$ (213.24): C 73.23, H 5.20, N 6.57; found: C 73.23, H 5.23, N 6.53.

2-(2'-Nitro-2'-propenyl)naphthalene (**22**; *Method B*). A solution of 4.87 ml (7.5 mmol) of BuLi in hexane (1.54M) was added dropwise to 1.543 g (7.45 mmol) of 2-bromonaphthalene in 70 ml of THF at −90° [32]. Stirring was continued for 0.5 h at −70°. This mixture was then transferred within 15 min into a flask containing a stirred solution of 1.4 g (7.48 mmol) of **1** in 50 ml of THF at −100°. After stirring for 1.5 h at −70°, the mixture was allowed to warm to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2/pentane 1:4) yielded 1.257 g (73%) of **22**, m.p. 35°. IR (CCl_4): 3120, 3042, 3005, 2940, 2840, 1595, 1520, 1502, 1420, 1371, 1337, 1262, 1240, 1145, 1120, 1010, 940, 930, 860, 845. ^{1}H-NMR (CCl_4): 3.95 (*s*, 2H, 2H–C(1')); 5.32 (*s*, 1H, olef. H *trans* to NO_2); 6.40 (*s*, 1H, olef. H *cis* to NO_2); 7.15–7.85 (*m*, 7H, 7 arom. H). MS (72 eV): 199 (1), 182 (7), 151 (7), 128 (6), 109 (35), 95 (85), 89 (28), 83 (27), 81 (65), 69 (20), 67 (55), 57 (40), 55 (90), 43 (80), 41 (100), 39 (22), 29 (35). Anal. calc. for $C_{13}H_{11}NO_2$ (213.24): C 73.23, H 5.20, N 6.57; found: C 73.14, H 5.24, N 6.57.

2-Nitro-1-decen-4-yne (**23**; *Method B*). A solution of 4.81 ml (7.4 mmol) of BuLi in hexane (1.54M) was added dropwise to 721 mg (7.5 mmol) of 1-heptyne in 40 ml of THF at −50°. Stirring was continued for 1.5 h at −20°. This mixture was then transferred within 5 min into a flask containing a stirred solution of 1.4 g (7.48 mmol) of **1** in 50 ml of THF at −100°. After stirring for 1 h at −90°, the mixture was allowed to warm to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2/pentane 3:1) yielded 0.702 g (52.3%) of **23**, b.p. 78°/0.07 Torr. IR (CCl_4): 3130, 2960, 2925, 2860, 2235, 1660, 1525, 1462, 1455, 1430, 1413, 1371, 1342, 1247, 1155, 1140, 948, 930, 914, 861, 691, 660. ^{1}H-NMR (CCl_4): 0.93 (*m*, 3H, 3H−C(10)); 1.45 (*m*, 6H, 2H−C(9), 2H−C(8), 2H−C(7)); 2.23 (*m*, 2H, 2H−C(6)); 3.52 (*m*, 2H, 2H−C(3)); 6.01 (*m*, 1H, olef. H *trans* to NO_2); 6.6 (*m*, 1H, olef, H *cis* to NO_2). MS (72 eV): 134 (3), 119 (7), 111 (20), 105 (22), 95 (7), 91 (38), 83 (35), 79 (35), 67 (25), 65 (20), 63 (12), 55 (100), 54 (10), 53 (20), 52 (20), 51 (30), 49 (10), 41 (65), 39 (45), 29 (30). Anal. calc. for $C_{10}H_{15}NO_2$ (181.24): C 66.27, H 8.34, N 7.73; found: C 66.14, H 8.21, N 7.67.

(Z)-*2-Nitro-1,4-nonadiene* (**24**; *Method B*). A solution of 4.94 ml (7.6 mmol) of BuLi in hexane (1.54M) was added dropwise to 1.586 g (7.55 mmol) of *(Z)*-1-iodo-1-hexene [33] in 50 ml of Et_2O at −78° [31]. Stirring was continued for 0.5 h at −60°. This mixture was then transferred within 15 min into a flask containing a stirred solution of 1.4 g (7.48 mmol) of **1** in 50 ml of Et_2O at −100°. After stirring for 1.5 h at −80°, the mixture was allowed to warm to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2/pentane 4:1) yielded 893 mg (70.6%) of **24**, b.p. 50°/0.06 Torr. IR (CCl_4): 3010, 2960, 2955, 2922, 1522, 1460, 1420, 1375, 1340, 1245, 1150, 938, 860, 691. ^{1}H-NMR (CCl_4): 0.95 (*m*, 3H, 3H−C(9)); 1.35 (*m*, 4H, 2H−C(7), 2H−C(8)); 2.10 (*m*, 2H, 2H−C(6)); 3.31 (*d*, J = 8, 2H, 2H−C(3)); 5.5 (*m*, 3H, olef. H *trans* to NO_2, H−C(4), H−C(5)); 6.4 (*s*, 1H, olef. H *cis* to NO_2. MS (72 eV): 169 (1), 148 (1), 138 (1), 122 (20), 107 (7), 99 (21), 93 (30), 91 (25), 83 (8), 81 (37), 80 (37), 79 (100), 77 (70), 71 (15), 69 (30), 67 (40), 66 (30), 55 (75), 51 (11), 43 (41), 41 (95), 39 (55), 29 (30), 27 (42). Anal. calc. for $C_9H_{15}NO_2$ (169.22): C 53.88, H 8.93, N 8.28; found: C 63.90, H 9.16, N 8.38.

1-(2'-Nitro-2'-propenyl)cyclohexene (**25**). A solution of 4.94 ml (7.6 mmol) of BuLi in hexane (1.54M) was added dropwise to a stirred solution of 1.57 g (7.55 mmol) of 1-iodocyclohexane in 50 ml of Et_2O at −70° [33]. Stirring was continued for 1 h at −60°. This mixture was then transferred within 15 min into a flask containing a stirred solution of 1.4 g (7.48 mmol) of **1** in 50 ml of Et_2O at −100°. After stirring for 1.25 h at −90°, the mixture was allowed to warm to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2/pentane 3:7) yielded 622 mg (50.4%) of **25**, b.p. 50°/0.01 Torr. IR (CCl_4): 2915, 2859, 2839, 1526, 1448, 1438, 1421, 1341, 1248, 1150, 938, 920, 861, 692. ^{1}H-NMR (CCl_4): 1.60 (*m*, 4H, 2H−C(4), 2H−C(5)); 1.99 (*m*, 4H, 2H−C(3), 2H−C(6)); 3.21 (*s*, 2H, 2H−C(1')); 5.46 (*s*, 1H, olef. H *trans* to NO_2); 5.52 (*s*, 1H, H−C(2)); 6.38 (*s*, 1H, olef. H *cis* to NO_2). MS (72 eV): 167 (3), 151 (4), 150 (4), 137 (30), 120 (50), 119 (18), 117 (7), 105 (33), 97 (24), 95 (20), 93 (35), 92 (50), 91 (100), 81 (65), 80 (77), 77 (52), 69 (25), 67 (63), 55 (40), 53 (30), 41 (75), 39 (35). Anal. calc. for $C_9H_{13}NO_2$ (167.21): C 64.35, H 7.84, N 8.38; found: C 64.38, H 7.89, N 8.31.

1-(2'-Nitro-2'-propenyl)cyclooctene (**26**). A solution of 9.64 ml (14.94 mmol) of *t*-BuLi in hexane (1.55M) was added dropwise to a stirred solution of 1.4 g (6.47 mmol) of 1-bromocyclooctene (purity by GC: 85%) in 40 ml of THF at −80° [31]. Stirring was continued for 1.25 h at −78°. This mixture was then transferred within 15 min into a flask containing a stirred solution of 1.40 g (7.48 mmol) of **1** in 50 ml of THF at −100°. After stirring for 0.5 h at −90° the mixture was allowed to warm to −35° in 10 min. Usual workup and flash chromatography (CH_2Cl_2/pentane 3:7) yielded 637 mg (50.4%) of **26**, b.p. 90°/0.08 Torr. IR (CCl_4): 2960, 2925, 2850, 1655, 1522, 1468, 1450, 1422, 1340, 1248, 1150, 939, 861, 691. ^{1}H-NMR (CCl_4): 1.5 (br. *s*, 8H, 2H−C(7), 2H−C(5), 2H−C(6), 2H−C(4)); 2.15 (*m*, 4H, 2H−C(3), 2H−C(8)); 3.25 (*s*, 2H, 2H−C(1')); 5.50 (*m*, 2H, H−C(2), olef. H *trans* to NO_2); 6.4 (*s*, 1H, olef. H *cis* to NO_2). MS (72 eV): 195 (1), 178 (1), 165 (30), 148 (7), 133 (15), 125 (12), 120 (22), 107 (30), 105 (35), 97 (15), 95 (25), 93 (25), 91 (59), 83 (20), 81 (55), 79 (72), 77 (33), 69 (20), 67 (70), 55 (100), 41 (75), 29 (15), Anal. calc. for $C_{11}H_{17}NO_2$ (195.26): C 67.66, H 8.78, N 7.17; found: C 67.39, H 8.90, N 7.07.

2-Nitro-1-heptene (**27a**). A solution of 4.86 ml (7.48 mmol) of BuLi in hexane (1.54M) was added to 40 ml of THF at −80°. This mixture was then transferred within 15 min into a flask containing a stirred solution of 1.4 g (7.48 mmol) of **1** in 45 ml of THF at −100°. After stirring for 30 min at −80°, the mixture was allowed to warm to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2/hexane) yielded 820 mg (76.6%) of **27a**. Under the same conditions but using BuMgBr in THF (prepared from BuBr and Mg in THF) instead of BuLi 580 mg (54%) of **27a** were obtained IR (CCl_4): 2950, 2921, 2858, 1520, 1455, 1428, 1375, 1340, 1242, 932, 860, 690. ^{1}H-NMR (CCl_4): 0.92 (*t*, J = 5, 3H, 3H−C(7)); 1.40 (*m*, 6H, 2H−C(4), 2H−C(5), 2H−C(6)); 2.58 (*t*, J = 6, 2H, 2H−C(3)); 5.42 (*s*, 1H, olef. H *trans* to NO_2); 6.33 (*s*, 1H, olef. H *cis* to NO_2).

2-Nitro-1-undecene (**27b**). At 0°, 110.7 mg (15.95 mmol) of freshly cut Li were added to 4.512 g (16.94 mmol) of 4,4'-di(*tert*-butyl)biphenyl in 100 ml of THF and stirring was continued at 0° until most of the Li was

dissolved (17 h) [34]. The blue solution was then cooled to −78°, and 1.182 g (7.97 mmol) of 1-chlorooctane in 2 ml of THF were added dropwise with stirring. After stirring for 15 min at −78°, the deep red mixture was transferred over 35 min into a stirred solution of 1.356 g (7.245 mmol) of **1** in 50 ml of THF at −100°. After stirring for 2 h at −80°, the mixture was allowed to warm to −30° in 10 min. Usual workup and flash chromatography (pentane (separation of 4,4'-di(*tert*-butyl)biphenyl), then CH_2Cl_2/pentane 3:7) yielded 805 mg (56%) of **27b**, b.p. 80°/0.1 Torr.

Using octylmagnesium chloride in THF instead of octyllithium yielded 464 mg (32.3%) of **27b**. IR (CCl_4): 2950, 2920, 2855, 1525, 1460, 1439, 1340, 1245, 935, 860, 690. ^{1}H-NMR (CCl_4): 0.94 (*m*, 3H−C(11)); 1.40 (*m*, 14H, 2H−C(4), 2H−C(5), 2H−C(6), 2H−C(7), 2H−C(8), 2H−C(9), 2H−C(10)); 2.67 (3-line system, 2H, 2H−C(3)); 5.49 (*s*, 1H, olef. H *trans* to NO_2); 6.39 (*s*, 1H, olef. H *cis* to NO_2). MS (72 eV): 200 (1), 182 (7), 151 (7), 128 (5), 109 (34), 95 (84), 89 (26), 83 (25), 81 (60), 71 (20), 69 (75), 67 (55), 57 (40), 55 (90), 43 (75), 41 (100), 39 (21), 29 (33). Anal. calc. for $C_{11}H_{21}NO_2$ (199.29): C 66.29, H 10.62, N 7.03; found: C 66.30, H 10.74, N 7.04.

(4'-Nitro-4'-pentenyl)benzene (**27c**). At 0°, 93.4 mg (13.47 mmol) of freshly cut Li were added to 5.128 g (19.25 mmol) of 4,4'-di(*tert*-butyl)biphenyl in 100 ml of THF at 0° until most of the Li was dissolved (17 h) [34]. The blue solution was cooled to −78°, and a solution of 947 mg (6.73 mmol) of 2-chloroethylbenzene in 2 ml was added dropwise with stirring. After 15 min stirring at −78° the deep red mixture was transferred within 25 min into a stirred solution of 1.15 g (6.12 mmol) of **1** in 50 ml of THF at −100°. After stirring for 30 min at −90°, the mixture was allowed to warm to −40° in 10 min. Usual workup and flash chromatography (pentane (separation of 4,4'-di(*tert*-butyl)biphenyl), then CH_2Cl_2/pentane 1:4) yielded 790 mg (67.5%) of **27c**, b.p. 80°/0.02 Torr. IR (CCl_4): 3010, 2940, 2860, 1600, 1524, 1491, 1450, 1430, 1382, 1341, 1248, 1078, 1030, 940, 860, 700. ^{1}H-NMR (CCl_4): 1.90 (*m*, 2H, 2H−C(2')); 2.6 (4-line system, 4H, 2H−C(1'), 2H−C(3')); 5.40 (*s*, 1H, olef. H *trans* to NO_2); 6.35 (*s*, 1H, olef. H *cis* to NO_2); 7.13 (*m*, 5H, 5 arom. H). MS (72 eV): 191, 174 (15), 162 (13), 143 (25), 128 (57), 117 (17), 115 (15), 105 (25), 91 (100), 79 (16), 77 (16), 65 (19). Anal. calc. for $C_{11}H_{13}NO_2$ (191.23): C 69.09, H 6.85, N 7.32; found: C 69.15, H 6.98, N 7.23.

4-Methyl-2-Nitro-1-hexene (**28**). A solution of 7.06 ml (7.48 mmol) of *sec*-BuLi in hexane (1.06M) was added to 40 ml of THF at −80°. This mixture was transferred within 20 min into a flask containing a stirred solution of 1.40 g (7.48 mmol) of **1** in 50 ml THF at −100°. After stirring for 0.5 h at −90°, the mixture was allowed to warm to −30° in 10 min. Usual workup and flash chromatography (CH_2Cl_2/pentane 1:4) yielded 598 mg (55.8%) of **28**, b.p. 80°/13 Torr. IR (CCl_4): 2960, 2920, 2878, 2850, 1522, 1460, 1430, 1380, 1342, 1248, 1090, 939, 860. ^{1}H-NMR (CCl_4): 0.95 (*m*, 6H, $2CH_3$); 1.10–1.90 (*m*, 3H, 2H−C(5), H−C(4)); 2.5 (*AB*-part of an *ABX*-system, $J_{AB} = 14.5$, $J_{AX} = J_{BX} = 6$, 2H, 2H−C(3)); 5.45 (br. *s*, 1H, olef. H *trans* to NO_2); 6.35 (*s*, 1H, olef. H *cis* to NO_2). MS (72 eV): 143 (1), 95 (3), 91 (3), 87 (26), 67 (12), 57 (100), 55 (29), 43 (19), 41 (52), 39 (15), 29 (40).

(2'-Nitro-2'-propenyl)cyclohexane (**29**). At 0°, 93.5 mg (15.41 mmol) of freshly cut Li were added to 4.31 g (16.94 mmol) of 4,4'-di(*tert*-butyl)biphenyl in 100 ml of THF until most of the Li was dissolved (17–50 h) [34]. The blue solution was cooled to −78°, and a solution of 730 mg (7.70 mmol) of chlorocyclohexane in 2 ml of THF was added dropwise with stirring. After 15 min stirring at −78° the deep red mixture was transferred within 20 min into a stirred solution of 1.037 g (5.54 mmol) of **1** in 50 ml of THF at −100°. After stirring for 20 min at −100°, the mixture was allowed to warm to −40° within 10 min. Usual workup and flash chromatography (pentane (separation of 4,4'-di(*tert*-butyl)biphenyl), then CH_2Cl_2/pentane 3:7) yielded 590 mg (63%) of **29**, b.p. 40°/0.03 Torr. IR (CCl_4): 2960, 2943, 1525, 1450, 1429, 1341, 1390, 940, 860, 695, 600. ^{1}H-NMR (CCl_4): 1.16–1.72 (*m*, 11H, H-(6-membered ring); 2.47 (*d*, $J = 6$, 2H, 2H−C(1')); 5.38 (*s*, 1H, olef. H *trans* to NO_2); 6.32 (*s*, 1H, olef. H *cis* to NO_2). MS (72 eV): 169 (1), 149 (3), 121 (2), 99 (7), 84 (8), 83 (100), 81 (15), 79 (6), 67 (6), 55 (55), 41 (20), 39 (7), 29 (4). Anal. calc. for $C_9H_{15}NO_2$ (169.22): C 63.88, H 8.93, N 8.28; found: C 63.76, H 9.04, N 8.22.

4,4-Dimethyl-2-nitro-1-pentene (**30**). A solution of 4.84 ml (7.5 mmol) of *t*-BuLi in hexane (1.55M) was added to 50 ml of THF at −100°. The mixture was transferred within 20 min into a flask containing a stirred solution of 1.4 g (7.48 mmol) of **1** in 50 ml of THF at −100°. After stirring for 0.5 h at −90°, the mixture was allowed to warm to −30° within 10 min. Usual workup and flash chromatography (CH_2Cl_2/hexane 1:4) yielded 221 mg (20.6%) of **30**. IR (CCl_4): 2955, 2860, 1650, 1520, 1470, 1462, 1428, 1385, 1362, 1340, 1260, 1242, 1231, 1198, 1121, 935, 890, 860, 691. ^{1}H-NMR (CCl_4): 1.00 (*s*, 9H, $(CH_3)_3C$); 2.6 (*s*, 2H, 2H−C(3)); 5.46 (br. *s*, 1H, olef. H *trans* to NO_2); 6.43 (*s*, 1H, olef. H *cis* to NO_2). MS (72 eV): 143, 106 (2), 105 (2), 91 (9), 81 (21), 71 (7), 57 (100), 56 (7), 55 (6), 43 (8), 41 (28), 39 (10), 29 (15).

1-Methyl-3,3'-(2-nitrotrimethylene)diindole (**35**). A solution of 2.376 g (10.9 mmol) of **5b** and 1.276 g (10.9 mmol) of indole was stirred for 90 h at −25° in the dark and under Ar. Purification by flash chromatography

(Et_2O/hexane 1:1) yielded 1.48 g (40.7%) of **35**, m.p. 129–130°. IR ($CHCl_3$): 3480, 3060, 3010, 2923, 1620, 1550, 1478, 1460, 1440, 1422, 1378, 1360, 1332, 1160, 1138, 1128, 1100, 1075, 1045, 1017, 911, 860, 652, 620. ^{1}H-NMR ($CDCl_3$): 3.31 (9-line system, 4H, $CH_2CH(NO_2)CH_2$); 3.61 (*s*, 3H, $CH_3N(1)$); 5.14 (*m*, 1H, $CH_2CH(NO_2)CH_2$); 6.8 (*s*, 1H, H–C(2')); 6.86 (*d*, *J* = 3, 1H, H–C(2')); 7.0–7.3 (*m*, 6H, 6 arom. H); 7.3–7.55 (*m*, 2H, 2 arom. H); 7.88 (br. *s*, 1H, H–N(1')). MS (72 eV): 334 (10), 333 (52), 287 (5), 286 (19), 285 (10), 259 (5), 187 (3), 170 (31), 157 (12), 156 (74), 145 (15), 144 (100), 143 (15), 131 (10), 130 (67), 129 (5), 128 (5), 115 (5), 103 (5), 102 (2), 89 (1), 77 (10), 42 (1). Anal. calc. for $C_{20}H_{19}N_3O_2$ (333.39): C 72.05, H 5.74, N 12.60; found: C 72.00, H 5.80, N 12.59.

One-Pot Synthesis of Ethyl 4-Nitro-6-phenyl-6,6-(trimethylenedithio)hexanoate (**36**) *from Ethyl Acetate, 2-Phenyl-1,3-dithiane and* **1**. A solution of 4.72 ml (7.4 mmol) of BuLi in hexane (1.57M) was added slowly to a stirred solution of 1.45 g (7.4 mmol) of 2-phenyl-1,3-dithiane in 23 ml of THF under Ar at −78°. Stirring was continued for 1.5 h at −78°. A solution of **1** (1.4 g, 7.48 mmol) in 25 ml of THF was added to the stirred lithium dithiane solution within 20 min at −78°. After 2 h at −78°, the mixture was warmed to −30° in 10 min and stirring was continued for 15 min at −35°. The solution was then cooled at −78° and transferred within 20 min into a flask containing 7.4 mmol of the lithium enolate of AcOEt (prepared from 0.76 g (7.5 mmol) of diisopropylamine, 7.4 mmol of BuLi in hexane and 650 mg (7.4 mmol) of AcOEt in 20 ml of THF; see synthesis of **13**). Stirring was continued for 1.25 h at −78°. A solution of 2 ml of AcOH in 3 ml of THF was added and the mixture was allowed to warm to −40° in 20 min. The solution was poured into 100 ml of H_2O, extracted with CH_2Cl_2 (4 × 100 ml). The org. layer was washed with aq. $NaHCO_3$ (2 × 100 ml), H_2O (2 × 100 ml), brine (100 ml), dried ($MgSO_4$) and evaporated. Flash chromatography (CH_2Cl_2/pentane 1:1) yielded 1.816 g (66.4%) of **36**. IR (CCl_4): 3050, 2950, 2910, 2860, 2820, 1733, 1540, 1475, 1440, 1420, 1365, 1275, 1245, 1180, 1065, 1025, 905, 860, 700. ^{1}H-NMR (CCl_4): 1.2 (*t*, *J* = 6, 3H, CH_3CH_2O); 1.80–3.20 (*m*, 12H); 4.60 (*m*, 1H, H–C(4)); 4.10 (*q*, *J* = 6, CH_3CH_2O); 7.35 (*m*, 3H, 3 arom. H); 7.80 (*m*, 2H, 2 arom. H). MS (72 eV): 369 (98), 339 (10), 323 (55), 277 (55), 249 (25), 233 (15), 203 (40), 195 (75), 187 (20), 173 (35), 160 (75), 141 (20), 121 (42), 106 (60), 105 (100), 99 (21), 91 (15), 77 (30), 73 (20), 57 (50), 35 (40), 29 (32).

*3-(3',4'-Dimethyl-1'-nitro-3'-cyclohexenyl)methyl-*N*-methylindole* (**37**). A solution of 1.081 g (5 mmol) of **5b** and 10 mg of hydroquinone in 10 ml of 2,3-dimethylbutadiene was heated at −70° for 21 h. After evaporation, flash chromatography (CH_2Cl_2) yielded 1.059 g (71%) of **37**, m.p. 95°. IR ($CDCl_3$): 3020, 2980, 2930, 1600, 1540, 1470, 1445, 1380, 1370, 1335, 1050, 880. ^{1}H-NMR ($CDCl_3$): 1.60 (*s*, 6H, CH_3–C(3'), CH_3–C(4')); 1.95–2.9 (*m*, 6H, 2H–C(2'), 2H–C(5'), 2H–C(6')); 3.34 (*d*, *J* = 1, 2H, CH_2–C(3)); 3.70 (*s*, 3H, CH_3–N(1)); 6.82 (*s*, 1H, H–C(2)); 7.0–7.4 (*m*, 3H, 3 arom. H); 7.5 (*m*, 1H, H–C(7)). MS (72 eV): 299.5 (1.5), 298 (6.8), 251 (5), 145 (13), 144 (100), 132 (7.6), 131 (8.3), 121 (24.2), 105 (6.7), 103 (5), 91 (6), 77 (8.9), 57 (6.3), 41 (10), 28 (13.9), 18 (6.4). Anal. calc. for $C_{18}H_{22}N_2O_2$ (298.39): C 72.46, H 7.43, N 9.39; found: C 72.43, H 7.59, N 9.56.

Ethyl 4-Nitro-7-oxo-7-phenylheptanoate (**38**). A solution of 1.00 g (5.86 mmol) of **13** in 30 ml of THF was added within 20 min under Ar to a solution of 5.86 mmol of lithium enolate of acetophenone at −78° (prepared from 704 mg (5.86 mmol) of acetophenone, 20 ml of THF, 0.6 g (5.9 mmol) of diisopropylamine and 5.87 mmol of BuLi in hexane (1.54M); see synthesis of **7**). After stirring for 3 h at −78°, 2 ml of AcOH in 3 ml of THF was added and the mixture was allowed to warm to −40° within 20 min. Usual workup and flash chromatography yielded 1.187 g (70.1%) of **38**, m.p. 25°. IR (CCl_4): 2950, 2890, 1732, 1686, 1540, 1441, 1415, 1370, 1350, 1320, 1245, 1205, 1178, 1021, 999, 961, 860, 691, 687. ^{1}H-NMR (CCl_4): 1.23 (*t*, *J* = 7, 3H, CH_3CH_2O); 2.35 (*m*, 6H, 2H–C(2), 2H–C(3), 2H–C(5)); 3.00 (*t*, *J* = 6, 2H, 2H–C(6)); 4.10 (*q*, *J* = 7, 2H, CH_3CH_2); 4.61 (*m*, 1H, H–C(4)); 7.5 (*m*, 3H, 3 arom. H); 7.91 (*m*, 2H, 2 arom. H). MS (72 eV): 248 (5), 247 (10), 246 (20), 218 (4), 217 (4), 201 (5), 173 (3), 159 (5), 155 (3), 106 (18), 105 (100), 91 (3), 81 (3), 77 (50), 51 (7). Anal. calc. for $C_{15}H_{19}NO_5$ (293.32): C 61.42, H 6.53, N 4.78; found: C 61.34, H 6.50, N 4.69.

2-(3',4'-Dimethyl-1'-nitro-3'-cyclohexenyl)methyl-2-phenyl-1,3-dithiane (**39**). A solution of 1.2 g (4.7 mmol) of **16** and 30 mg of hydroquinone in 5 ml of 2,3-dimethylbutadiene was heated at 80° for 28 h. After evaporation flash chromatography (CH_2Cl_2) yielded 1.452 g (85%) of **39**, m.p. 131°. IR ($CDCl_3$): 2970, 2900, 2850, 1590, 1535, 1485, 1440, 1410, 1365, 1345, 1275, 1195, 910, 705, 695, 660. ^{1}H-NMR ($CDCl_3$): 1.48 (*s*, 6H, CH_3–C(3'), CH_3–C(4')); 1.7–2.8 (*m*, 12H); 2.9 (*dd*, AB-system, *J* = 15, 2H, CH_2–C(2)); 7.25–7.5 (*m*, 3H, 3 arom. H); 7.8–8.0 (*m*, 2H, 2 arom. H). MS (72 eV): 363 (3), 317 (4), 241 (5), 225 (5), 211 (18), 209 (19), 197 (6), 196 (8), 195 (58), 122 (5), 121 (53), 117 (7), 115 (5), 108 (11), 107 (100), 106 (29), 105 (74), 104 (6), 103 (47), 93 (9), 91 (25), 79 (7), 77 (24), 73 (5). Anal. calc. for $C_{19}H_{25}NO_2S_2$ (363.54): C 62.77, H 6.93, N 3.85, S 17.64; found: C 62.66, H 6.95, N 3.94, S 17.84.

*1-(*tert*-Butoxycarbonyl)-2,3'-(2-nitrotrimethylene)diindole* (**40a**). A solution of 199 mg (0.66 mmol) of **17** and 77.1 mg (0.658 mmol) of indole in 1 ml of benzene was stirred for 4 days at +25° under Ar and in the dark.

Flash chromatography (CH_2Cl_2/pentane 1:1) of this solution yielded 179.1 mg (65%) of **40a**, m.p. 157°. IR ($CHCl_3$): 3480, 3000, 2980, 2935, 1725, 1550, 1472, 1452, 1431, 1420, 1372, 1330, 1307, 1255, 1160, 1120, 1090, 1010, 860, 840, 810. ^{1}H-NMR ($CDCl_3$): 1.72 (*s*, 9H, $(CH_3)_3C$); 3.45 (*m*, 2H, $CH_2CH(NO_2)CH_2C(3')$); 3.70 (*m*, 2H, $CH_2CH(NO_2)CH_2C(3')$); 5.32 (9-line system, 1H, $CH_2CH(NO_2)CH_2C(3')$); 6.4 (*s*, 1H, H–C(3)); 6.95 (*m*, 1H, H–C(2')); 7.03–7.70 (*m*, 7H, 7 arom. H); 7.99 (*m*, 2H, 1 arom. H, H–N(1')). MS (72 eV): 419 (1), 363 (1), 319 (50), 273 (35), 272 (30), 271 (20), 257, 245, 156 (95), 149 (15), 143 (20), 131 (30), 130 (100), 115 (10), 103 (15), 77 (20), 56 (60), 44 (80). Anal. calc. for $C_{24}H_{25}N_3O_4$ (419.48): C 68.72, H 6.01, N 10.02; found: C 68.57, H 5.96, N 9.89.

*1-(*tert*-Butoxycarbonyl)-1'-methyl-2,3'-(2-nitrotrimethylene)diindole* (**40b**). A solution of 536 mg (1.773 mmol) of **17** and 232.5 mg (1.773 mmol) of 1-methylindole in 5 ml of benzene was stirred for 30 days at 25° under Ar and in the dark. Flash chromatography (CH_2Cl_2/pentane 3:7) of this solution yielded 461 mg (60%) of **40b**, m.p. 136°. IR (CCl_4): 3055, 2960, 1728, 1549, 1462, 1451, 1422, 1389, 1370, 1330, 1250, 1218, 1160, 1120, 1089, 910, 861, 698. ^{1}H-NMR (CCl_4): 1.66 (*s*, 9H, $(CH_3)_3C$); 3.23–3.7 (*m*, 4H, $CH_2CH(NO_2)CH_2$); 3.6 (*s*, 3H, CH_3–N(1')); 5.1 (*m*, 1H, $CH_2CH(NO_2)CH_2$); 6.32 (*s*, 1H, H–C(3)); 6.65 (*s*, 1H, H–C(2)); 7.03 (*m*, 5H, 5 arom. H); 7.35 (*m*, 2H, 2 arom. H); 7.82 (*m*, 1H, 1 arom. H). MS (72 eV): 434 (7.9), 433 (27.4), 377 (12.5), 334 (7.0), 333 (29.8), 330 (6.0), 288 (7.4), 287 (34.6), 286 (29.5), 285 (12.3), 271 (5.1), 259 (5.5), 200 (25.4), 171 (8.5), 170 (59.2), 1687 (6.8), 157 (24.2), 156 (73.7), 155 (6.4), 154 (7.6), 145 (13.5), 144 (100), 143 (17.9), 131 (18.5), 130 (63.8), 129 (8.5), 128 (8.2), 115 (10.7), 103 (8.8), 77 (10.9), 57 (50.2), 56 (48.6), 44 (20.8), 41 (33), 29 (8). Anal. calc. for $C_{25}H_{27}N_3O_4$ (433.51): C 69.27, H 6.28, N 9.69; found: C 69.33, H 6.20, N 9.64.

Ethyl 5-(α-Naphtyl)-4-nitrovalerate (**41**). A solution of 1.173 g (5.5 mmol) of **21** in 35 ml of THF was added within 20 min to 5.7 mmol of the lithium enolate of AcOEt at −78° (prepared from 502 mg (5.7 mmol) of AcOEt, 0.59 g (5.8 mmol) of diisopropylamine, and 5.75 mmol of BuLi in hexane (1.54M); see synthesis of **13**). After stirring for 0.75 h at −78°, 1.5 ml of AcOH in 3 ml of THF were added and the mixture was allowed to warm to −40° within 20 min. Usual workup and flash chromatography (CH_2Cl_2/pentane 4:1) yielded 1.095 g (66.1%) of **41**, b.p. 230°/1.5×10^{-4} Torr. IR (CCl_4): 3060, 2990, 2940, 1738, 1550, 1375, 1182, 1020, 863. ^{1}H-NMR (CCl_4): 1.12 (*t*, J = 7, 3H, CH_3CH_2O); 2.22 (*m*, 4H, 2H–C(2), 2H–C(3)); 3.57 (8-line system, *AB*-part of *ABX*-system, $J_{AX} = J_{BX} = 8$, $J_{AB} = 15$, 2H, 2H–C(5)); 4.00 (*q*, J = 7, 2H, CH_3CH_2O); 4.87 (*m*, 1H, H–C(4)); 7.18–8.00 (*m*, 7H, 7 arom. H). MS (72 eV): 301 (15), 254 (60), 226 (20), 209 (15), 181 (15), 180 (25), 167 (100), 166 (80), 165 (30), 153 (20), 149 (30), 141 (70), 115 (20), 85 (10), 77 (5), 57 (5), 29 (20). Anal. calc. for $C_{17}H_{19}NO_4$ (301.34): C 67.76, H 6.36, N 4.65; found: C 67.94, H 6.50, N 4.67.

6-Nitro-1-(2',6',6'-trimethyl-1-cyclohexenyl)-1-undecen-3-one (**42**). A solution of 859 mg (6 mmol) of **27a** in 35 ml of THF was added within 20 min to a solution of 6 mmol of lithium enolate of β-ionone, at −78° (prepared from 1.15 g (6 mmol) of β-ionone, 607 mg (6 mmol) of diisopropylamine, 20 ml of THF, and 6 mmol of BuLi in hexane (1.54M); see synthesis of **6**). After stirring for 1.5 h at −78°, 2 ml of AcOH in 3 ml of THF were added, and the mixture was allowed to warm to −40° within 20 min. Usual workup and flash chromatography (CH_2Cl_2/pentane 1:1) gave 1.50 g (75%) of **42**, b.p. 230°/0.02 Torr. IR (CCl_4): 2960, 2935, 2862, 1690, 1670, 1605, 1587, 1546, 1455, 1440, 1375, 1360, 1258, 1248, 1201, 1170, 978, 862. ^{1}H-NMR (CCl_4): 0.90 (*m*, 3H, 3H–C(11)); 1.08 (*s*, 6H, $2CH_3$–C(6')); 1.2–1.7 (*m*, 10H, 2H–C(8), 2H–C(9), 2H–C(10), 2H–C(4'), 2H–C(5')); 1.78 (*s*, 3H, CH_3–C(2')); 2.10 (*m*, 6H, 2H–C(5), 2H–C(7), 2H–C(3')); 4.45 (7-line system, 1H, H–C(6)); 6.04 (*d*, part of an *AB*-system, J = 16.5, 1H, H–C(1)); 7.24 (br. *d*, part of an *AB*-system, J = 16.5, 1H, H–C(2)). MS (72 eV): 335 (5), 321 (21), 320 (100), 289 (7), 278 (3), 273 (7), 189 (5), 190 (5), 177 (10), 176 (10), 161 (4), 149 (7), 133 (6), 121 (7), 107 (5), 105 (5), 93 (5), 81 (4), 77 (4), 69 (10), 55 (13), 43 (7), 41 (10). Anal. calc. for $C_{20}H_{33}NO_3$ (335.49): C 71.60, H 9.92, N 4.18; found: C 71.72, H 9.75, N 4.16.

Ethyl 4-Nitro-6-oxo-6-phenylhexanoate (**43**). *a) Method A.* A solution of 685 mg (1.85 mmol) of **36** in 1 ml of THF was added dropwise under Ar to 0.87 g (4 mmol) of yellow HgO and 568 mg (4 mmol) of $BF_3 \cdot Et_2O$ in 5 ml of THF (containing 15% of H_2O) at 0° [**43b**]. After 0.75 h at 0°, the mixture was pourred into 100 ml of Et_2O, filtered and washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography (CH_2Cl_2) yielded 280 mg (54%) of **43**.

b) Method B. A solution of 1.174 g (3.17 mmol) of **36** and 4 ml of MeI in 20 ml of EtOH (containing 4% of H_2O) was refluxed under Ar for 22 h [**43b**]. The solvents were evaporated, and the residue was treated with 3 ml of H_2O and extracted with Et_2O. The org. layer was washed with aq. NaOH (0.1N), water, brine, dried ($MgSO_4$), and evaporated. Flash chromatography as above, yielded 611 mg (69%) of **43**. IR (CCl_4): 2980, 2930, 1732, 1690, 1595, 1545, 1446, 1418, 1368, 1260, 1210, 1180, 1095, 1020, 1000, 982, 858, 689. ^{1}H-NMR (CCl_4): 1.20 (*t*, J = 7, 3H, CH_3CH_2O); 2.30 (*m*, 4H, 2H–C(2), 2H–C(3)); 3.5 (8-line system, 2H, 2H–C(5)); 4.05 (*q*, J = 6, 2H, CH_3CH_2O); 5.06 (*m*, 1H, H–C(4)); 7.45 (*m*, 2H, 2 arom. H); 7.91 (*m*, 3H, 3 arom. H).

2-(3',4'-Dimethyl-3'-cyclohexenyl)methyl-2-phenyl-1,3-dithiane (**44**). A solution of 294 mg (0.808 mmol) of **39**, 22 mg of azodiisobutyronitrile and 282 mg (0.97 mmol) of Bu_3SnH in benzene was refluxed for 1 h [44]. Evaporation and flash chromatography yielded 245 mg (95%) of **44**, m.p. 83–84°. IR ($CHCl_3$): 2970, 2900, 2850, 2820, 1595, 1480, 1440, 1430, 1420, 1410, 1375, 1275, 1175, 1030, 905, 860, 695, 655. ^{1}H-NMR (CCl_4): 1.5 (br. *s*, 6H, CH_3–C(3'), CH_3–C(4')); 1.4–1.8 (*m*, 7H); 2.0 (*m*, 4H, 2H–C(2'), 2H–C(5')); 2.7 (*m*, 4H, 2H–C(4), 2H–C(6)); 7.35 (*m*, 3H, 3 arom. H); 7.98 (2-line system, 2H, 2 arom. H). MS (72 eV): 318 (6), 243 (20), 212 (6), 211 (13), 195 (17), 161 (17), 121 (7), 109 (11), 108 (100), 107 (13), 106 (6), 103 (9), 93 (20), 91 (8), 77 (6), 67 (5), 41 (6), 18 (6). Anal.calc. for $C_{19}H_{26}S_2$ (318.55): C 71.64, H 8.23; found: C 71.14, H 8.00.

5-(α-Naphthyl)methyl-2-pyrrolidone (**45**). A suspension of 0.7 g of *Raney* Ni, 352.8 mg (1.17 mmol) of **41** in 10 ml of Et_2O/EtOH 1:1 was shaken at 50° (for 15 h) under 25 atm. of H_2. The mixture was filtered and evaporated. The residue was dissolved in 25 ml of toluene and refluxed for 10 h. The solution was evaporated and the residue purified by flash chromatography (CH_2Cl_2/methanol 95:5): Yield of **45**: 217.5 mg (82.5%). IR ($CDCl_3$): 3660, 3435, 3210, 3070, 2940, 2890, 1690, 1595, 1510, 1455, 1417, 1398, 1378, 1303, 1262, 1200, 1080, 790. ^{1}H-NMR ($CDCl_3$): 1.80 (br. *m*, 2H, 2H–C(4)); 2.30 (br. *m*, 2H, 2H–C(3)); 2.70 (*m*, 2H, CH_2–C(5)); 4.00 (*m*, 1H, H–C(5)); 6.7 (br. *m*, 1H, H–N(1)); 6.8–8.1 (*m*, 7H, 7 arom. H). MS (72 eV): 225 (7), 205 (1), 153 (2), 146 (9), 142 (49), 128 (5), 115 (16), 105 (2), 98 (1), 91 (3), 84 (100), 77 (3), 63 (3), 56 (11), 51 (3), 41 (24). Anal. calc. for $C_{15}H_{15}NO$ (225.29): C 79.97, H 6.71, N 6.22; found: C 79.47, H 7.07, N 6.20.

1-(2',6',6'-Trimethyl-1'-cyclohexenyl)-1-undecene-3,6-dione (**46**). A solution of 0.732 g (2.27 mmol) of **42** in 2 ml of MeOH was added to 5.40 ml (2.69 mmol) of MeONa in MeOH (0.5M). This mixture was then added with a syringe to a stirred solution of 5.31 ml (96 mmol) of H_2SO_4 (18M) in 20 ml of MeOH at −40° and under Ar. After 1 min, the mixture was poured into 120 ml of CH_2Cl_2 and washed successively with a mixture of H_2O, ice and brine (50 ml), aq. Na_2CO_3-solution (2 × 50 ml), and brine (2 × 50 ml). The org. layer was dried ($MgSO_4$) and the solvent was removed on a rotatory evaporator. Flash chromatography (CH_2Cl_2) yielded 542.6 mg (78.4%) of **46**, b.p. 135°/5 × 10^{-5} Torr. IR (CCl_4): 2960, 2930, 2865, 1718, 1690, 1669, 1605, 1585, 1455, 1410, 1360, 1247, 1190, 1060, 978, 860. ^{1}H-NMR (CCl_4): 0.90 (*t*, *J* = 5, 3H, 3H–C(11)); 1.06 (*s*, 6H, $2CH_3$–C(6')); 1.15–1.7 (*m*, 10H, 2H–C(8), 2H–C(9), 2H–C(10), 2H–C(4'), 2H–C(5')); 1.77 (*s*, 3H, CH_3–C(2')); 2.01 (*m*, 2H, 2H–C(3')); 2.40 (3-line system, 2H, 2H–C(4)); 2.69 (6-line system, 4H, 2H–C(5), 2H–C(7)); 6.02 (*d*, part of an *AB*-system, *J* = 16.5, 1 H, H–C(1)); 7.20 (br. *d*, part of an *AB*-system, *J* = 16.5, 1H, H–C(2)). MS (72 eV): 304 (5), 289 (100), 271 (5), 247 (4), 233 (3), 200 (10), 190 (7), 177 (9), 175 (8), 172 (9), 155 (10), 149 (10), 121 (10), 119 (10), 107 (10), 99 (7), 95 (8), 91 (15), 81 (10), 77 (10), 69 (11), 55 (15), 43 (25). Anal. calc. for $C_{20}H_{32}O_2$ (304.47): C 78.90, H 10.59; found: C 79.26, H 10.66.

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