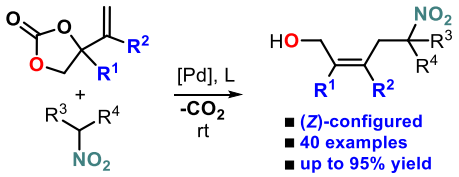
Palladium-Catalyzed (*Z*)-Selective Allylation of Nitroalkanes: Access to Highly Functionalized Homoallylic Scaffolds

Àlex Cristòfol,[†,‡] Eduardo C. Escudero-Adán[†] and Arjan W. Kleij*[,†,§]

[†]Institute of Chemical Research of Catalonia (ICIQ), the Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 – Tarragona, Spain, and [‡]Universitat Rovira i Virgili, Departament de Química Analítica i Química Orgànica, c/Marcel·lí Domingo, 1, 43007 Tarragona, Spain

[§]Catalan Institute of Research and Advanced Studies (ICREA), Pg. Lluís Companys 23, 08010 – Barcelona, Spain



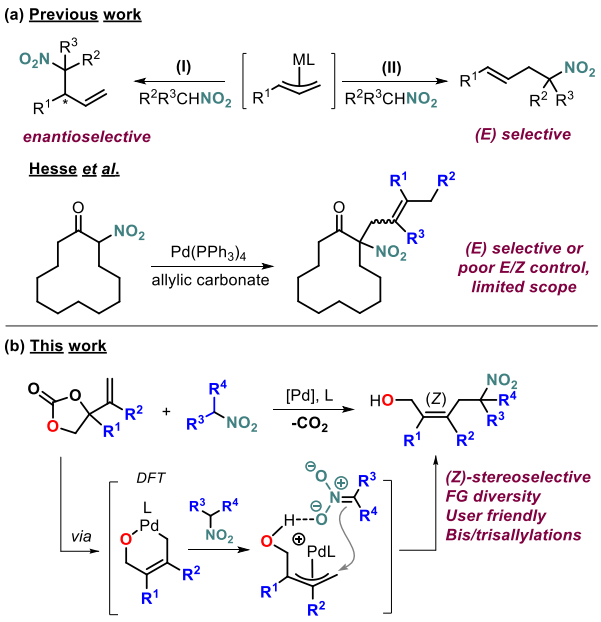
ABSTRACT: Nitroalkanes undergo decarboxylative allylation in the presence of vinyl-substituted cyclic carbonates providing a wide variety of functionalized homoallylated compounds with exquisite stereocontrol. This Pd-mediated procedure features operational simplicity, versatile substrate combinations and also allows for the sequential introduction of different allyl groups in the nitroalkane scaffolds with high levels of stereocontrol through the intermediacy of a (*Z*)-configured palladacyclic intermediate. As far as we know, the developed protocol is the first general Pd-mediated methodology towards (*Z*)-configured homoallylic nitroalkanes with attractive functional group diversity.

■ INTRODUCTION

Stereoselective synthesis of highly functionalized tri- and tetrasubstituted olefin scaffolds still remains a highly challenging and attractive objective.[1] Homoallylic nitroalkanes, an important subclass of alkenes, are versatile building blocks in organic synthesis and provide precursors to amines relevant to biologically active N-containing compounds.[2] Metal-catalyzed allylic alkylation reactions have become popular towards the preparation of functionalized olefins under mild reaction conditions.[3] In this respect, Tsuji-Trost type allylation of nitroalkanes has received much attention since the resultant homoallylic products are precursors to their homoallylic amine congeners.[4]

While enantioselective allylations of nitroalkanes have been frequently investigated (Scheme 1a, route **I**),[5] stereoselective allylations have been less studied (Scheme 1a, route **II**).[6] In most reported cases, the resulting olefin unit in the homoallylic nitroalkane product is mostly disubstituted while having an (*E*) configuration. In 1985, Hesse and coworker reported the allylation of 2-nitrocycloalkanones using substituted allylic carbonates affording rare examples of trisubstituted derivatives (Scheme 1a, lower part).[7] However, either a stereoisomeric mixture or formation of expected stereochemistry (*E*) was noted for the targeted products. Thus, despite notable progress the stereoselective construction of tri- and tetrasubstituted (*Z*)-configured homoallylic nitroalkanes using metal-catalyzed allylic substitution reactions remains undeveloped. An approach that successfully addresses these issues would expand on the variety of available homoallylic scaffolds that cannot be easily accessed through other known methodologies.[1,8] Owing to the versatility of the nitro group, it can be anticipated that their use would be further amplified in synthetic chemistry.

Scheme 1. Previous Metal-Catalyzed Allylation of Nitroalkanes and Current Approach towards Tri- and Tetrasubstituted Homoallylic Nitroalkanes

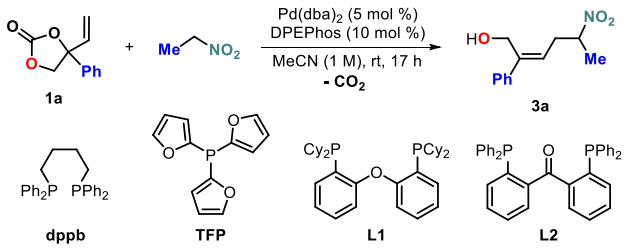


We recently reported that regio- and enantioselective Pd-catalyzed allylic substitutions of vinyl-substituted cyclic carbonates (VCCs)[9] in the presence of N-,[10] O-[11] and S-derived nucleophiles[12] are ligand-controlled transformations providing either linear or branched allylic compounds under high stereocontrol. Computational analysis afforded useful mechanistic insight into the origin of the stereocontrol, and moreover illustrated that a (*Z*)-palladacyclic intermediate (which was supported

by DFT analysis)[10a] acts a key species incorporating a basic function (*cf*., Scheme 1b) for the activation of pronucleophiles.

With this design element in mind, we envisioned that nitronate species should be easily formed from nitroalkanes in the presence of this formal Pd(allyl) intermediate without the requirement of a basic additive. Suitable ligands should be able to bias the double bond configuration in the allylated nitroalkanes towards the desired stereoisomer.[13] Importantly, the targeted (*Z*)-configured homoallylic compounds would incorporate additional functionality providing interesting product diversification potential from a wide array of homoallylic structures that are not easily accessible via other preparative routes.

Table 1. Optimized Reaction Conditions towards the Stereoselective Formation of Homoallylic Product 3a[a]



entry	deviation[b]	yield of **3a** (%)[c]	Z:E[d]
1	none	85 (50)[e]	>99:1
2	$Pd(PPh_3)_4$/THF	41	93:7
3	White catalyst/THF	18	87:13
4	Toluene as solvent	59	93:7
5	DMF as solvent	76	98:2
6	dppb as ligand	74	>99:1
7	TFP as ligand	69	68:32
8	**L1** as ligand	53	>99:1
9	**L2** as ligand	56	87:13

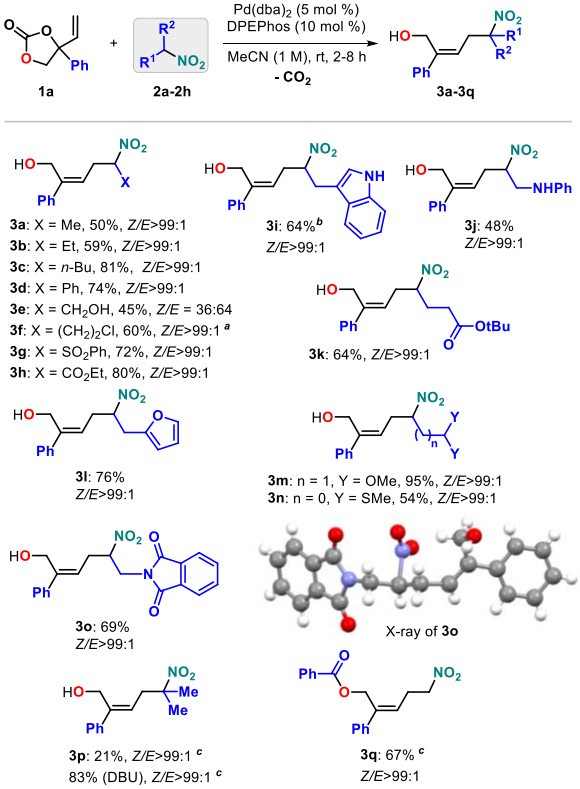
[a]Reaction conditions: 0.20 mmol of cyclic carbonate **1a**, 0.30 mmol of nitroethane, 200 μL of solvent, rt, open to air; the White catalyst is a bis-sulfoxide ligated $Pd(OAc)_2$. [b]Deviation from standard conditions. [c]NMR yield using mesitylene as an internal standard. [d]Determined by ^{1}H NMR. [e]Yield of isolated product.

■ RESULTS AND DISCUSSION

Screening Studies. Various conditions were screened towards the formation of the targeted (*Z*)-product **3a** taking vinyl cyclic carbonate **1a** and nitroethane as benchmark substrates. The nature of the Pd precursor, ligand, solvent, relative amount of nitroethane and catalyst loading were optimized (see Table 1 and Tables S1–S5, see the Supporting Information: SI). The optimized conditions reported in Table 1 gave the best NMR yield (Table 1, entry 1; 85%, isolated 50%)[14] and stereoselectivity (*Z*/*E*>99:1) of homoallylic nitroalkane product **3a**. The presence of other Pd-precursors, solvents or ligands (Table 1, entries 2–9) gave inferior results in terms of yield and/or stereocontrol, and are not discussed in detail here.

Scope in Nitroalkane Reagent. With these optimized conditions in hand, the scope of reaction partners was then examined, and first the nitroalkane reagent (*cf*., **2a–2h**, see SI for details on the preparation of the non-commercial examples) was varied (Scheme 2; note that isolated yields are reported) providing access to functional homoallylic nitroalkanes **3a–3q** in excellent (except for 3e)[15] stereoselectivity. Apart from simple alkyl or aryl groups (R^1 and R^2) in the nitroalkane reagent (*cf*., synthesis of **3a–d**), also synthetically more attractive functionalities could be readily introduced into the allylated targets including alcohol (**3e**), alkyl chloride (**3f**), aryl sulfone (**3g**), ester (**3h**, **3k**), indole (**3i**), aromatic amine (**3j**), furan (**3l**), (dithio)acetal (**3m-n**) and imide (**3o**) groups. Most of these products were isolated in moderate to high yields, and apart from the desired compound typically bisallylated nitroalkanes[16] and minor amounts (<5%) of a vinyl carbonate cross-coupled derivative[17] were noted. The presence of a free alcohol unit in the nitroalkane reagent leading to product **3e** (*Z*/*E* = 36:64) is not well-tolerated as illustrated by a significant lower stereoselectivity. This may be ascribed to undesired interaction of the alcohol with the intermediate (allyl)Pd species, and adversely influencing the stereochemical course of the allylation process.

Scheme 2. Variation of Nitroalkane Reagent to afford Homoallylic Compounds 3a-3q

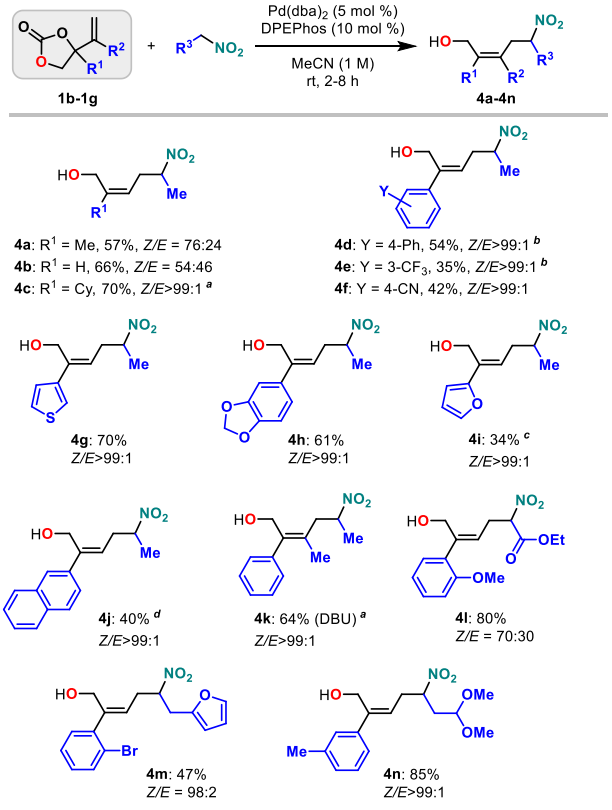


Conditions: cyclic carbonate (1.0 mmol), nitroalkane (1.5 equiv.), rt, 2-8 h, open to air. [a] 0.23 mmol scale. [b] 0.58 mmol scale. [c] 0.20 mmol scale.

Apart from various primary nitroalkanes, also a more challenging secondary derivative could be allylated though with much lower efficiency (**3p**; 21 % yield). To improve the formation of **3p**, the use of a base (DBU; 1,8-diazabicyclo[5.4.0]undec-7-ene) markedly improved the yield to 83%, showing that the reactivity of the nitronate anion may be influenced by the counter cation.[18]

Finally, when benzoyl nitromethane was employed, we observed a post-synthetic shift of the phenyl ketone group to the alcohol unit resulting in the formation of the phenyl ester based allylated nitroalkane **3q** isolated in 67% yield.[19] The assigned stereochemistry of all products was fully consistent with their 2D NMR data (see ^{1}H-^{1}H NOESY NMR for **3d**; SI), and in the case of **3o**, it was further confirmed by X-ray diffraction (see inset in Scheme 2 and SI).

Scheme 3. Variation of the VCC Reagent to afford Homoallylic Compounds 4a-4n

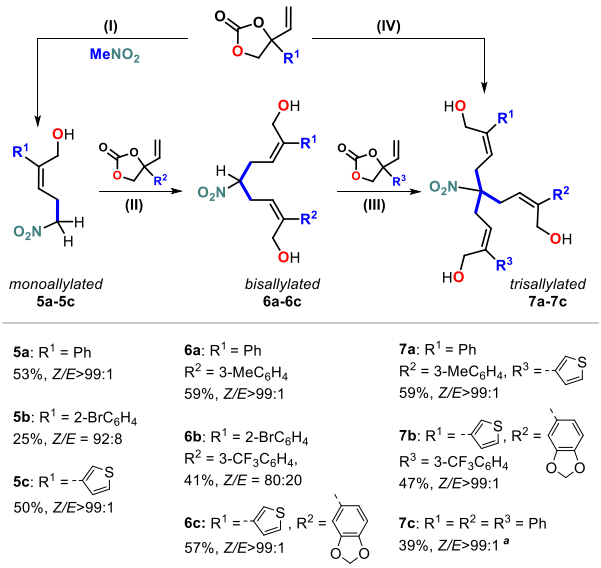


Conditions: cyclic carbonate (1.0 mmol), nitroalkane (1.5 equiv.), rt, 2-8 h, open to air. Note that formally product **4i** has an (*E*)-configuration, but has the same spatial orientation around the olefin unit as the other products. [a] 0.20 mmol scale. [b] The reaction in the presence of DBU (10 mol %) showed no improvement (32% isolated, *Z*/*E*>99:1). [c] 0.46 mmol scale. [d] 0.22 mmol scale.

Scope in VCC Reagent. Next, the VCC was varied using a selection of nitroalkanes as coupling partners and this afforded the homoallylated derivatives **4a–4n** (Scheme 3). Apart from those cases where the VCC reagent was minimally substituted or having *ortho*-substituents in the aryl groups (*cf*., the synthesis of **4a–b**, **4l** with **4m** being an exception), exclusive formation of the (*Z*) isomer was noted. Alkyl-substituted VCCs show an apparent size-influence on the stereoselectivity of the reaction with the presence of larger groups such as cyclohexyl (*cf*., synthesis of **4c**) providing much higher *Z*/*E* control. We previously reported the formal hydration of similar (allyl)Pd intermediates obtained after decarboxylation of VCCs[11a] giving rise to (*Z*)-butene-1,4-diol formation. This latter work showed that hyper conjugation between the VCC aryl substituent and the Pd(allyl) fragment is crucial towards the overall reactivity and (*Z*) stereobias. Interestingly, the hydration of alkyl-based Me- and cyclohexyl-substituted VCCs proved to be unproductive substrates in this hydration process, whereas in the present work the use of nitroalkanes as pronucleophiles was feasible towards product formation. Thus, both electronic as well as steric effects are operative in these kind of allylic transformations, and the type of nucleophile also plays an important role.

Both substituted aryl- and alkyl-substituted VCCs (R^1 and R^2; **4a–4f**) could be used, though the presence of electron-poor aryl groups lowered the yields of the homoallylic targets (**4e–4f**). Various heterocyclic groups (**4g–4i**) were also readily incorporated, though the isolated yield of **4i** was low (34%) due to the instability of the carbonate reagent. Other combinations of substituted VCCs and nitroalkanes were also probed furnishing the allylated nitroalkanes **4j–4n** in up to 85% yield. Notably, product **4k** (64%, using DBU as additive) comprises a tetrasubstituted double bond, and stereoselective formation of such compounds with four different substituents is generally difficult.[1]

Scheme 4. Stereoselective Synthesis of Mono-, Bis- and Trisallylated Compounds.

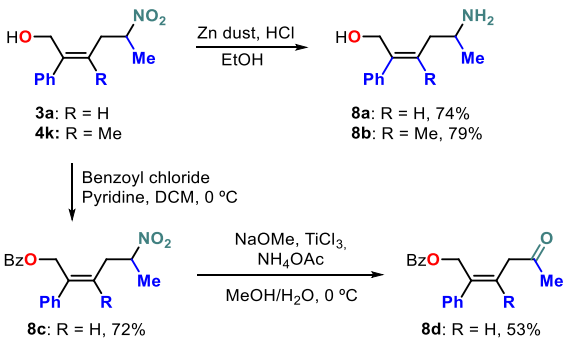


Conditions: (I) cyclic carbonate (1.0 mmol), $[Pd(allyl)Cl]_2$ (2.5 mol %), DPEPhos (10 mol %), CH_3NO_2 (1.0 mL), rt, open to air; (II) cyclic carbonate (1.0 equiv.), nitroalkane (1.5 equiv.), $Pd(dba)_2$ (5.0 mol %), DPEPhos (10 mol %), MeCN (1 M), rt, open to air; (III) cyclic carbonate (1.0 equiv.), nitroalkane (1.5 equiv.), $Pd(dba)_2$ (5.0 mol %), DPEPhos (10 mol %), DBU (10 mol %), MeCN (1 M), rt, open to air; (IV) cyclic carbonate (3.1 equiv.), nitromethane (1.0 equiv.), $Pd(dba)_2$ (5.0 mol %), DPEPhos (10 mol %), DBU (10 mol %), MeCN (1 M), rt, open to air. [a] The reaction was repeated with DBU (30 mol %) without improvement of the yield (40 %, *Z*/*E*>99:1).

Synthesis of Multi-Allylated Nitroalkanes. Multiple allylation was then also investigated to see whether the stereoselectivity could be retained upon introduction of different allyl groups (Scheme 4). It was necessary to devise new reaction conditions for the synthesis of mono-allylated products **5a–c**, as bisallylation was more competitive compared to the use of other primary nitroalkanes (see Tables S6–S8, SI). After finding suitable reaction conditions, nitroalkanes **5a–5c** were prepared under excellent stereocontrol (Scheme 4, Route I). Subsequent allylation using standard conditions gave hetero-bisallylated nitroalkanes **6a** and **6c** with high *Z/E* ratios while for **6b** a lower degree of stereocontrol was noted (Scheme 4, Route II).

Hetero-trisallylation also proved be feasible (*cf*., **7a** and **7b**) and despite the higher steric demand of the intermediate carbon nucleophile (Scheme 4, Route III), excellent levels of stereocontrol were observed. Moreover, homo-trisallylated product **7c** could be directly prepared in one-step from nitromethane with exquisite stereoselectivity (Scheme 4, Route IV). These results underpin the robust nature of these stereocontrolled conversions towards more elaborate functional scaffolds.

Scheme 5. Synthesis of highly Substituted Homoallylic Amines 8a and 8b.



The allylation process could be easily scaled up (6 mmol of VCC used, 1.14 g) using the same experimental procedure thus allowing to obtain larger amounts of homoallylic nitroalkane **3a** without affecting the efficiency of the process (62% yield, *Z/E* >99:1). The conversion of homoallylic nitroalkanes **3a** and **4k** into their homoallylic amines **8a** and **8b** (Scheme 5) was straightforward and these compounds were isolated in good yields. As far as we know, the synthesis of **8b** represents the first example of a (*Z*) configured homoallylic amine incorporating a tetrasubstituted double bond. Further to this, a combined protection/Nef reaction sequence (see the Experimental Section for details) leading to ketone **8d** illustrates that elusive β,γ-unsaturated (*Z*)-configured ketones can be easily accessed without any observed double bond isomerization.

■ CONCLUSION

In summary, a general (*Z*)-stereoselective methodology for highly substituted homoallylic nitroalkanes is reported that features attractive functional group diversity and operational simplicity. These (*Z*)-homoallylic compounds can be prepared from readily accessible starting materials, which were also shown to offer entries towards bis- and trisallylated functional homoallylic scaffolds while maintaining excellent stereocontrol.

■ EXPERIMENTAL SECTION

General methods. Air and water-sensitive reactions were carried out in flame-dried glassware under an argon atmosphere using standard Schlenk manifold techniques. Reactions were monitored by TLC or ^{1}H NMR. TLC was carried out on 0.25 mm Merck aluminum backed sheets coated with 60 F254 silica gel. Visualization of the silica plates was achieved using a UV lamp (λ = 254 nm) and/or by heating plates that were dipped in a $KMnO_4$ or ceric ammonium molybdate stains. Flash chromatography was carried out on Sigma-Aldrich silica gel 60 (70-230 mesh) using the indicated eluent system. In the screening phase, the internal standard was added after the reaction. Hereafter, an aliquot of the resulting mixture was taken and the yield was determined by means of ^{1}H NMR spectroscopy using $CDCl_3$ as the solvent.

Commercially available reagents and solvents were purchased from Sigma-Aldrich, TCI, Strem Chemicals, Abcr GmbH, Acros Organics or Alfa Aesar, and were used without further purification. Zinc dust was activated using a previously reported procedure.[20]

Solvents were dried using an Innovative Technology PURE SOLV solvent purification system. ^{1}H NMR, ^{13}C NMR, DEPT-90, DEPT-135, and related 2D NMR (gCOSY90, gHMQC, gHMBC and gNOESY) spectra were recorded at room temperature on a Bruker AV-300, AV-400 or AV-500 spectrometer and referenced to their residual deuterated solvent signals. ^{19}F NMR spectra were recorded on a Bruker AV-400. Coupling constants (*J*) are reported in Hertz with the following splitting abbreviations: s = singlet, d = doublet, t = triplet, q = quadruplet, quint = quintet, sextet = sext, br = broad and app = apparent. All reported NMR values are given in parts per million (ppm). FT-IR measurements were carried out on a Bruker Optics FTIR Alpha spectrometer. Mass spectrometric and X-ray analyses were performed by the Research Support Group at ICIQ.

Vinyl cyclic carbonate synthesis. The following cyclic carbonates were prepared according to a previously reported literature:[10a] 4-methyl-4-vinyl-1,3-dioxolan-2-one, 4-cyclohexyl-4-vinyl-1,3-dioxolan-2-one, 4-(naphthalen-2-yl)-4-vinyl-1,3-dioxolan-2-one, 4-([1,1'-biphenyl]-4-yl)-4-vinyl-1,3-dioxolan-2-one, 4-(furan-2-yl)-4-vinyl-1,3-dioxolan-2-one, 4-(thiophen-3-yl)-4-vinyl-1,3-dioxolan-2-one and 4-(benzo[d][1,3]dioxol-5-yl)-4-vinyl-1,3-dioxolan-2-one. Otherwise, the cyclic carbonates were prepared following a previously reported literature procedure with minor modifications.[21]

Step 1: In a flame-dried round-bottomed flask, organocatalyst **A** (10 mol %) and paraformaldehyde (3.0 equiv.) were suspended in dry THF (0.25 M) under Ar. Then, the aldehyde (1.0 equiv.) and DIPEA (20 mol %) were added, respectively. The mixture was stirred at 60°C (oil bath) for 24 h. Hereafter, the mixture was concentrated in *vacuo* and the residue was purified by flash chromatography on silica gel to afford the corresponding hydroxymethyl ketone.

Step 2: In a flame-dried Schlenk flask, the corresponding hydroxymethyl ketone (1.0 equiv.) was dissolved in dry THF (0.4 M) under Ar. The solution was cooled to 0°C (ice-water bath) and vinyl magnesium bromide (2.5 equiv., 1.0 M in THF) was added dropwise over 20 minutes. After the addition, the

mixture was allowed to warm to room temperature and was stirred for 2.5-5 h. The reaction was quenched at 0°C (ice-water bath) with NH_4Cl (aq, sat) and the phases were separated. The aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated in *vacuo*. The crude product was used in the next step without further purification.

Step 3: In a flame-dried Schlenk flask, the crude product from step 2 was dissolved in dry CH_2Cl_2 (0.33 M) under Ar. Then, anhydrous pyridine (6.0 equiv.) was added, and the mixture was cooled to -72 °C (dry ice-ethanol bath). Then, a solution of triphosgene (0.5 equiv.) in dry CH_2Cl_2 (0.5 M) was cannulated to the mixture dropwise over 20-30 minutes. After that, the mixture was stirred for 30 min, and the reaction was monitored by TLC. If the reaction had not gone to completion, it was allowed to warm to room temperature and was stirred for further 30 min - 2 h. The reaction was quenched at 0°C (ice-water bath) with NH_4Cl (aq, sat) and the phases were separated. The aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with 1 M HCl, $NaHCO_3$ (aq, sat), brine, and were dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by flash chromatography on silica gel to afford the corresponding cyclic carbonate. Note: the reported yields of the cyclic carbonates are always referred to combined steps 2 and 3.

4-Methyl-4-vinyl-1,3-dioxolan-2-one and cyclic carbonate **1a** were prepared from their commercially available hydroxymethyl ketones. Cyclic carbonate **1g** was prepared using isopropenyl magnesium bromide. The organocatalyst (**A**: perchlorate salt of 3-mesityl-4,5,6,7-tetrahydrobenzo[d]thiazol-3-ium) used in the first step was prepared according to a slightly modified literature procedure,[22] the only change being that the products was purified by trituration using hot *i*-PrOH (70 °C), instead of recrystallization from a mixture of $MeOH/CH_2Cl_2/Et_2O$.

*4-Phenyl-4-vinyl-1,3-dioxolan-2-one (**1a**)*. Compound **1a** was prepared following the general procedure from 2-hydroxyacetophenone (2.72 g, 20.0 mmol). The product was purified by flash chromatography on silica gel using EtOAc/cyclohexane (1:9) to afford the title compound (2.63 g, 69 % yield) as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δH 7.46-7.34 (m, 5H), 6.16 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.43 (d, *J* = 10.7 Hz, 1H), 5.42 (d, *J* = 17.2 Hz, 1H), 4.66 (d, *J* = 8.4 Hz, 1H), 4.58 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.2, 138.5, 136.6, 129.1, 129.0, 125.0, 117.6, 85.6, 74.6. Spectroscopic data are in agreement with published data.[9c]

*4-(m-Tolyl)-4-vinyl-1,3-dioxolan-2-one (**1b**)*. Compound **1b** was prepared following general procedure from *m*-tolualdehyde (1.82 mL, 15.0 mmol). The product was purified by flash chromatography on silica gel using 5 % EtOAc/cyclohexane to afford the title compound (1.86 g, 75 % yield) as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ7.31-7.27 (m, 1H), 7.19-7.16 (m, 2H), 7.13-7.10 (m, 1H), 6.15 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.42 (d, *J* = 17.2 Hz, 1H), 5.41 (d, *J* = 10.8 Hz, 1H), 4.64 (d, *J* = 8.4 Hz, 1H), 4.56 (d, *J* = 8.4 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ154.2, 139.0, 138.5, 136.7, 129.7, 129.0, 125.5, 122.0, 117.5, 85.6, 74.7, 21.6. Spectroscopic data are in agreement with published data.[11a]

*4-(3-(Trifluoromethyl)phenyl)-4-vinyl-1,3-dioxolan-2-one (**1c**)*. Compound **1c** was prepared following the general procedure from 3-(trifluoromethyl)benzaldehyde (2.0 mL, 15.0 mmol). The product was purified by flash chromatography on silica gel using 20 % EtOAc/cyclohexane to afford the title compound (1.28 g, 51 % yield) as a light orange oil. R_f 0.25 (EtOAc/cyclohexane 2:8). IR (neat): 2924, 1801, 1481, 1446, 1414, 1378, 1332, 1251, 1167, 1122, 1055, 986, 940, 902, 805, 768, 701, 654 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.70-7.64 (m, 1H), 7.63-7.60 (m, 1H), 7.60-7.55 (m, 2H), 6.16 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.49 (d, *J* = 10.8 Hz, 1H), 5.44 (d, *J* = 17.2 Hz, 1H), 4.71 (d, *J* = 8.6 Hz, 1H), 4.56 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ153.7, 139.8, 136.0, 131.7 (q, *J* = 32.7 Hz), 129.9, 128.4, 126.0 (q, *J* = 3.8 Hz), 122.0 (q, *J* = 3.8 Hz), 118.6, 85.1, 74.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ-62.9. HRMS (ESI+/TOF) Calcd for $C_{12}H_9F_3O_3Na^+$ [M + Na]$^+$: 281.0396. Found: 281.0400.

*4-(2-Methoxyphenyl)-4-vinyl-1,3-dioxolan-2-one (**1d**)*. Compound **1d** was prepared following the general procedure from *o*-anisaldehyde (1.81 mL, 15.0 mmol). The product was purified by flash chromatography on silica gel using 20 % EtOAc/cyclohexane to afford the title compound (1.66 g, 89 % yield) as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.35 (ddd, *J* = 8.2, 7.5, 1.7 Hz, 1H), 7.02 (td, *J* = 7.6, 1.1 Hz, 1H), 6.94 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.23 (dd, *J* = 17.1, 10.7 Hz, 1H), 5.40 (d, *J* = 17.1 Hz, 1H), 5.25 (d, *J* =10.7 Hz, 1H), 4.74 (d, *J* = 8.8 Hz, 1H), 4.54 (d, *J* = 8.8 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.9, 154.3, 136.4, 130.1, 127.6, 125.7, 121.4, 115.6, 111.2, 84.8, 75.2, 55.6. Spectroscopic data are in agreement with published data.[9c]

*4-(2-Bromophenyl)-4-vinyl-1,3-dioxolan-2-one (**1e**)*. Compound **1e** was prepared following the general procedure from 2-bromobenzaldehyde (1.80 mL, 15.0 mmol). The product was purified by flash chromatography on silica gel using 15-20 % EtOAc/cyclohexane to afford the title compound (1.92 g, 57 % yield) as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.41 (td, *J* = 7.8, 1.2 Hz, 1H), 7.25 (td, *J* = 7.8, 1.9 Hz, 1H), 6.36 (dd, *J* = 17.0, 10.6 Hz, 1H), 5.40 (d, *J* = 10.6 Hz, 1H), 5.40 (d, *J* = 17.0 Hz, 1H), 4.97 (d, *J* = 9.0 Hz, 1H), 4.73 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.5, 138.8, 135.1, 134.4, 130.5, 128.2, 127.5, 119.1, 118.6, 85.6, 74.6. Spectroscopic data are in agreement with published data.[9c]

*4-(2-Oxo-4-vinyl-1,3-dioxolan-4-yl)benzonitrile (**1f**)*. Compound **1f** was prepared following the general procedure from 4-cyanobenzaldehyde (1.97 g, 15.0 mmol), except that dry THF was used as solvent instead of CH_2Cl_2 in step 3 because of solubility problems. The product was purified by flash chromatography on silica gel using 20-30 % EtOAc/cyclohexane to afford the title compound (277.9 mg, 24 % yield) as a light orange solid. R_f 0.13 (EtOAc/cyclohexane 2:8). IR (neat): 3103, 3055, 2985, 2923, 2231, 1794, 1610, 1507, 1473, 1418, 1389, 1320, 1213, 1117, 1063, 985, 949, 841, 760, 740 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.77–7.68 (m, 2H), 7.53–7.43 (m, 2H), 6.12 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.46 (d, *J* = 10.8 Hz, 1H), 5.41 (d, *J* = 17.2 Hz, 1H), 4.70 (d, *J* = 8.7 Hz, 1H), 4.53 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ153.4, 143.5, 135.6, 132.9, 125.8, 118.7, 118.0, 113.1, 84.9, 74.2. HRMS (ESI+/TOF) Calcd for $C_{12}H_9NO_3Na^+$ [M + Na]$^+$: 238.0475. Found: 238.0483.

*4-Phenyl-4-(prop-1-en-2-yl)-1,3-dioxolan-2-one (**1g**)*. Compound **1g** was prepared following the general procedure from 2-hydroxyacetophenone (1.36 g, 10.0 mmol). The product was purified by flash chromatography on silica gel using 10 % EtOAc/cyclohexane to afford the title compound (1.31 g, 64 %

yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.33 (m, 5H), 5.19 (s, 1H), 5.16 (s, 1H), 4.79 (d, J = 8.5 Hz, 1H), 4.63 (d, J = 8.5 Hz, 1H), 1.73 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 154.1, 143.0, 138.5, 129.0, 125.1, 114.1, 88.1, 73.2, 18.6. Spectroscopic data are in agreement with published data.[11a]

Nitroalkane synthesis. 3-(2-Nitroethyl)-1*H*-indole (**2a**),[23] *tert*-butyl 4-nitrobutanoate (**2b**)[24], 2-(2-nitroethyl)furan (**2c**),[25] *N*-(2-nitroethyl)aniline (**2d**),[25] 1,1-dimethoxy-3-nitropropane (**2e**)[26] and 1-chloro-3-nitropropane (**2h**)[27] were prepared following previously reported protocols. Nitroalkanes **2f** and **2g** were prepared as indicated below.

*N-(2-Nitroethyl)phthalimide (**2f**)*. The following procedure was adapted from a previously reported procedure.[24b] In an oven-dried 100 mL round-bottomed flask, PPh_3 (4.72 g, 18.0 mmol) and imidazole (1.38 g, 19.5 mmol) were dissolved in dry CH_2Cl_2 under Ar. The mixture was cooled to 0 °C (ice-water bath), and I_2 was added. After stirring the mixture for 15 minutes, *N*-(2-hydroxyethyl)phthalimide (2.87 g, 15.0 mmol) was added. The mixture was stirred at 0 °C for 30 minutes and then at room temperature for 4 h. After that, the reaction was diluted with H_2O and the layers were separated. The aqueous phase was extracted with CH_2Cl_2, and the combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel using 10 % EtOAc/hexane to afford *N*-(2-iodoethyl)phthalimide as a white solid (4.19 g, 93 % yield).

In a 100 mL round-bottomed flask, *N*-(2-iodoethyl)phthalimide (3.77 g, 12.51 mmol) was suspended in H_2O (25 mL) and then, $AgNO_2$ (7.70 g, 50.04 mmol) was added. The flask was wrapped with aluminum foil and the mixture was heated at 60 °C (oil-bath) for 6 h. After that, the mixture was filtered through a pad of Celite, and the filtrate was extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel using 20-30 % EtOAc/cyclohexane to afford the title compound as a white solid (645 mg, 23 % yield). R_f 0.35 (EtOAc/cyclohexane 3:7). IR (neat): 3463, 3096, 3066, 3031, 3004, 2965, 2927, 1771, 1701, 1608, 1549, 1418, 1394, 1343, 1302, 1229, 1186, 1143, 1087, 1043, 1018, 961, 877, 806, 717 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91–7.84 (m, 2H), 7.79 – 7.72 (m, 2H), 4.72 (app t, J = 6.1 Hz, 2H), 4.32 (app t, J = 6.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.6, 134.6, 131.8, 123.9, 72.3, 35.3. HRMS (ESI+/TOF) Calcd for $C_{10}H_8N_2O_4Na^+$ [M + Na]$^+$: 243.0376. Found: 243.0374.

*(2-Nitroethane-1,1-diyl)bis(methylsulfane) (**2g**)*. The following procedure was adapted from a previously reported procedure.[27] In a flame-dried 100 mL round-bottomed flask, $NaBH_4$ (454 mg, 12.0 mmol) was dissolved in dry THF (11 mL) and dry MeOH (3.8 mL) under Ar. The solution was cooled to 0 °C (ice-water bath) and a solution of 1,1-bis(methylthio)-2-nitroethylene (1.65 g, 10.0 mmol) in dry THF (15 mL) was added. The mixture was warmed to room temperature and was stirred for 24 h. The reaction was quenched with NH_4Cl (aq, sat), was diluted with H_2O and was extracted with EtOAc. The organic phase was washed with H_2O and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel using 3 % EtOAc/cyclohexane to afford the title compound as a colorless oil (768.5 mg, 46 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.61 (d, J = 7.7 Hz, 2H), 4.36 (t, J = 7.7 Hz, 1H), 2.19 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 77.9, 50.2, 13.2. Spectroscopic data are in agreement with published data.[28]

General allylation procedure. In a 5 mL vial, cyclic carbonate (1.0 equiv.), $Pd(dba)_2$ (5.0 mol %), DPEPhos (10 mol %) and nitroalkane (1.5 equiv.) were dissolved in MeCN (1.0 M). The vial was sealed with a septum and a needle was placed through the septum to release gaseous CO_2. The mixture was stirred for 2–8 h at rt open to air. After that, the solvent was evaporated with a stream of N_2 and the residue was purified by flash chromatography on silica gel to afford the corresponding homoallylic nitroalkane. All homoallylic nitroalkanes apart from products **3p**, **4k**, **5a-5c** and **7a-7c** were prepared using this protocol.

*(Z)-5-Nitro-2-phenylhex-2-en-1-ol (**3a**)*. Compound **3a** was prepared following the general procedure from cyclic carbonate **1a** (190.2 mg, 1.0 mmol) and nitroethane. The product was purified by flash chromatography on silica gel using 20-30 % EtOAc/cyclohexane to afford the title compound (110.0 mg, 50 % yield) as a yellowish oil. R_f 0.31 (EtOAc/cyclohexane 3:7). IR (neat): 3573, 3387, 3058, 2938, 1543, 1493, 1446, 1388, 1359, 1312, 999, 767, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.26 (m, 5H), 5.74 (dd, J = 8.2, 7.2 Hz, 1H), 4.71 (dqd, J = 8.2, 6.7, 5.4 Hz, 1H), 4.61–4.50 (m, 2H), 3.02 (dt, J = 15.0, 8.2 Hz, 1H), 2.74 (ddd, J = 15.0, 7.2, 5.4 Hz, 1H), 1.62 (d, J = 6.7 Hz, 3H), 1.52–1.46 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.6, 140.3, 128.7, 128.0, 126.7, 124.3, 83.3, 59.9, 34.0, 19.1. HRMS (ESI+/TOF) Calcd for $C_{12}H_{15}NO_3Na^+$ [M + Na]$^+$: 244.0950. Found: 244.0944.

*(Z)-5-Nitro-2-phenylhept-2-en-1-ol (**3b**)*. Compound **3b** was prepared following the general procedure from cyclic carbonate **1a** (190.2 mg, 1.0 mmol) and 1-nitropropane. The product was purified by flash chromatography on silica gel using 20 % EtOAc/cyclohexane to afford the title compound (138.2 mg, 59 % yield) as a yellowish oil. R_f 0.39 (EtOAc/cyclohexane 3:7). IR (neat): 3574, 3403, 3057, 2973, 2937, 1543, 1493, 1460, 1443, 1373, 1326, 1011, 909, 766, 731, 697 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.37 (m, 2H), 7.36–7.32 (m, 2H), 7.31–7.26 (m, 1H), 5.73 (dd, J = 8.8, 6.9 Hz, 1H), 4.59–4.49 (m, 3H), 3.01 (dt, J = 15.0, 8.8 Hz, 1H), 2.72 (ddd, J = 15.0, 6.9, 4.8 Hz, 1H), 2.07 (ddq, J = 14.6, 9.2, 7.4 Hz, 1H), 1.89 (dqd, J = 14.6, 7.4, 4.7 Hz, 1H), 1.52 (br t, J = 5.8 Hz, 1H), 1.01 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δC 143.5, 140.4, 128.7, 127.9, 126.7, 124.5, 90.2, 59.9, 32.6, 27.1, 10.4; HRMS (ESI+/TOF) Calcd for $C_{13}H_{17}NO_3Na^+$ [M + Na]$^+$: 258.1101. Found: 258.1106.

*(Z)-5-Nitro-2-phenylnon-2-en-1-ol (**3c**)*. Compound **3c** was prepared following the general procedure from cyclic carbonate **1a** (190.2 mg, 1.0 mmol) and 1-nitropentane. The product was purified by flash chromatography on silica gel using 10-20 % EtOAc/cyclohexane to afford the title compound (212.2 mg, 81 % yield) as a dark red oil. R_f 0.31 (EtOAc/cyclohexane 2:8). IR (neat): 3577, 3400, 3057, 2958, 2930, 2872, 1545, 1493, 1465, 1436, 1366, 1266, 1016, 764, 736, 697 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.37 (m, 2H), 7.36–7.31 (m, 2H), 7.31–7.26 (m, 1H), 5.73 (dd, J = 8.5, 6.9 Hz, 1H), 4.64–4.49 (m, 3H), 3.01 (ddd, J = 15.0, 9.2, 8.5 Hz, 1H), 2.71 (ddd, J = 15.0, 6.9, 4.7 Hz, 1H), 2.11–2.01 (m, 1H), 1.85–1.77 (m, 1H), 1.49 (app dd, J = 6.5, 5.2 Hz, 1H), 1.41–1.30 (m, 4H), 0.95–0.89 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δC 143.5, 140.4, 128.7, 127.9, 126.7, 124.5, 88.8, 59.9, 33.5, 32.9, 28.0, 22.2, 13.9. HRMS (ESI+/TOF) Calcd for $C_{15}H_{21}NO_3Na^+$ [M + Na]$^+$: 286.1414. Found: 286.1416.

*(Z)-5-Nitro-2,5-diphenylpent-2-en-1-ol (**3d**)*. Compound **3d** was prepared following the general procedure from cyclic carbonate **1a** (190.2 mg, 1.0 mmol) and (nitromethyl)benzene. The product was purified by flash chromatography on silica gel using 10-20 % EtOAc/cyclohexane to afford the title compound (209.4 mg, 74 % yield) as a yellowish oil. R_f 0.26 (EtOAc/cyclohexane 2:8). IR (neat): 3574, 3402, 3061, 3032, 2899, 1546, 1494, 1455, 1364, 1010, 909, 765, 717, 694 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54–7.49 (m, 2H), 7.46–7.41 (m, 3H), 7.38–7.26 (m, 5H), 5.72 (dd, J = 8.2, 6.9 Hz, 1H), 5.60 (dd, J = 9.1, 6.0 Hz, 1H), 4.57 (d, J = 12.5 Hz, 1H), 4.53 (d, J = 12.5 Hz, 1H), 3.53 (ddd, J = 15.0, 9.1, 8.2 Hz, 1H), 3.03 (ddd, J = 15.0, 6.9, 6.0 Hz, 1H), 1.60 (br s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.6, 140.3, 134.1, 130.2, 129.3, 128.7, 127.9, 127.7, 126.6, 124.2, 91.1, 60.0, 33.3. HRMS (ESI+/TOF) Calcd for $C_{17}H_{17}NO_3Na^+$ [M + Na]$^+$: 306.1101. Found: 306.1110.

*5-Nitro-2-phenylhex-2-ene-1,6-diol (**3e**)*. Compound **3e** was prepared following the general procedure from cyclic carbonate **1a** (190.2 mg, 1.0 mmol) and 2-nitroethanol. The product was purified by flash chromatography on silica gel using 30-35 % EtOAc/cyclohexane to afford the title compound (106.5 mg, 45 % yield) as a yellowish oil. R_f 0.16 (EtOAc/cyclohexane 4:6). IR (neat): 3338, 3082, 3056, 3027, 2928, 2893, 2477, 2071, 1542, 1493, 1445, 1362, 1012, 972, 853, 766, 697 cm^{-1}. ^{1}H NMR (500 MHz, CD_3OD): δ 7.47–7.37 (m, 2H), 7.31 (ddt, J = 8.1, 6.3, 1.5 Hz, 2H), 7.27–7.21 (m, 1H), 5.76 (t, J = 7.7 Hz, 1H), 4.76 (tdd, J = 8.1, 5.9, 3.7 Hz, 1H), 4.49–4.42 (m, 2H), 4.00 (dd, J = 12.2, 7.8 Hz, 1H), 3.93 (dd, J = 12.2, 3.7 Hz, 1H), 2.94 (dt, J = 15.0, 8.1 Hz, 1H), 2.82 (ddd, J = 15.0, 7.6, 5.9 Hz, 1H). ^{13}C NMR (126 MHz, CD_3OD): δ 144.5, 142.5, 129.3, 128.3, 127.5, 125.6, 95.8, 64.5, 59.8, 29.7. Note: NMR resonances reported correspond to the (*Z*) isomer. HRMS (ESI+/TOF) Calcd for $C_{12}H_{15}NO_4Na^+$ [M + Na]$^+$: 260.0893. Found: 260.0896.

*(Z)-7-Chloro-5-nitro-2-phenylhept-2-en-1-ol (**3f**)*. Compound **3f** was prepared following the general procedure from cyclic carbonate **1a** (44.5 mg, 0.23 mmol) and nitroalkane **2h**. The product was purified by flash chromatography on silica gel using 10-20 % EtOAc/cyclohexane to afford the title compound (38.0 mg, 60 % yield) as a yellowish oil. R_f 0.15 (EtOAc/cyclohexane 2:8). IR (neat): 3575, 3383, 3082, 3057, 3028, 2924, 2853, 1545, 1493, 1445, 1375, 1331, 1293, 1010, 971, 910, 767, 735, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.27 (m, 5H), 5.73 (dd, J = 8.2, 7.1 Hz, 1H), 4.91 (tdd, J = 9.1, 5.2, 4.0 Hz, 1H), 4.55 (d, J = 12.7 Hz, 1H), 4.50 (d, J = 12.7 Hz, 1H), 3.65 (dt, J = 11.3, 5.5 Hz, 1H), 3.52 (ddd, J = 11.6, 9.1, 4.9 Hz, 1H), 3.02 (dt, J = 15.0, 8.4 Hz, 1H), 2.81 (ddd, J = 15.0, 7.1, 5.2 Hz, 1H), 2.58 (ddt, J = 14.8, 9.9, 5.1 Hz, 1H), 2.22 (dddd, J = 15.0, 9.4, 5.7, 4.0 Hz, 1H), 1.67 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.0, 140.2, 128.7, 128.0, 126.6, 123.6, 85.2, 59.9, 40.4, 35.7, 32.6. HRMS (ESI+/TOF) Calcd for $C_{13}H_{16}ClNO_3Na^+$ [M + Na]$^+$: 292.0711. Found: 292.0713.

*(Z)-5-Nitro-2-phenyl-5-(phenylsulfonyl)pent-2-en-1-ol (**3g**)*. Compound **3g** was prepared following the general procedure from cyclic carbonate **1a** (190.2 mg, 1.0 mmol) and nitromethyl phenyl sulfone. The product was purified by flash chromatography on silica gel using 20 % EtOAc/cyclohexane to afford the title compound (249.2 mg, 72 % yield) as a yellowish oil. R_f 0.22 (EtOAc/cyclohexane 3:7). IR (neat): 3563, 3064, 2963, 1558, 1493, 1448, 1334, 1221, 1154, 1082, 999, 908, 757, 724, 684, 600, 574, 530 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ H 7.96–7.89 (m, 2H), 7.81–7.74 (m, 1H), 7.67–7.59 (m, 2H), 7.36–7.26 (m, 5H), 5.71 (dd, J = 9.2, 5.3 Hz, 1H), 5.65 (t, J = 7.7 Hz, 1H), 4.55 (d, J = 12.7 Hz, 1H), 4.51 (d, J = 12.7 Hz, 1H), 3.38–3.24 (m, 2H), 1.88 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.6, 139.9, 135.8, 134.1, 130.0, 129.8, 128.7, 128.2, 126.6, 120.8, 101.6, 60.2, 27.3. HRMS (ESI+/TOF) Calcd for $C_{17}H_{17}NO_5SNa^+$ [M + Na]$^+$: 370.0720. Found: 370.0729.

*(Z)-Ethyl-6-hydroxy-2-nitro-5-phenylhex-4-enoate (**3h**)*. Compound **3h** was prepared following the general procedure from cyclic carbonate **1a** (190.2 mg, 1.0 mmol) and ethyl nitroacetate. The product was purified by flash chromatography on silica gel using 20 % EtOAc/cyclohexane to afford the title compound (223.0 mg, 80 % yield) as a yellowish oil. R_f 0.30 (EtOAc/cyclohexane 3:7). IR (neat): 3576, 2984, 1745, 1557, 1493, 1445, 1371, 1260, 1209, 1013, 857, 766, 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 5H), 5.73 (app t, J = 7.7 Hz, 1H), 5.26 (dd, J = 8.6, 6.0 Hz, 1H), 4.60 (d, J = 12.6 Hz, 1H), 4.56 (d, J = 12.6 Hz, 1H), 4.31 (qd, J = 7.2, 1.8 Hz, 2H), 3.29 (dt, J = 15.1, 8.3 Hz, 1H), 3.17 (ddd, J = 15.1, 7.4, 6.0 Hz, 1H), 1.81 (br s, 1H), 1.31 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.2, 144.5, 140.2, 128.7, 128.1, 126.6, 122.7, 87.6, 63.5, 60.0, 29.7, 14.0. HRMS (ESI+/TOF) Calcd for $C_{14}H_{17}NO_5Na$ [M + Na]$^+$: 302.0999. Found: 302.0996.

*(Z)-6-(1H-Indol-3-yl)-5-nitro-2-phenylhex-2-en-1-ol (**3i**)*. Compound **3i** was prepared following the general procedure from cyclic carbonate **1a** (111.1 mg, 0.58 mmol) and nitroalkane **2a**. The product was purified by flash chromatography on silica gel using 20-30 % EtOAc/cyclohexane to afford the title compound (126.7 mg, 64 % yield) as a yellowish oil. R_f 0.08 (EtOAc/cyclohexane 2:8). IR (neat): 3556, 3415, 3056, 2924, 1747, 1543, 1492, 1457, 1370, 1339, 1279, 1230, 1097, 1010, 743, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (br s, 1H), 7.59 (dt, J = 7.9, 1.0 Hz, 1H), 7.41–7.27 (m, 6H), 7.23 (ddd, J = 8.1, 7.0, 1.2 Hz, 1H), 7.17 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 7.04 (d, J = 2.5 Hz, 1H), 5.75 (dd, J = 8.6, 6.7 Hz, 1H), 4.96 (dddd, J = 9.2, 7.7, 6.5, 4.5 Hz, 1H), 4.53 (d, J = 12.5 Hz, 1H), 4.48 (d, J = 12.5 Hz, 1H), 3.54 (ddd, J = 14.8, 7.7, 0.8 Hz, 1H), 3.32 (ddd, J = 14.8, 6.5, 0.7 Hz, 1H), 3.08 (dt, J = 15.2, 8.9 Hz, 1H), 2.80 (ddd, J = 15.2, 6.8, 4.5 Hz, 1H), 1.51 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.5, 140.3, 136.3, 128.7, 127.9, 126.9, 126.6, 124.5, 123.2, 122.7, 120.1, 118.3, 111.6, 109.6, 88.8, 59.9, 32.5, 30.0. HRMS (ESI+/TOF) Calcd for $C_{20}H_{20}N_2O_3Na^+$ [M + Na]$^+$: 359.1366. Found: 359.1367.

*(Z)-5-Nitro-2-phenyl-6-(phenylamino)hex-2-en-1-ol (**3j**)*. Compound **3j** was prepared following the general procedure from cyclic carbonate **1a** (190.2 mg, 1.0 mmol) and nitroalkane **2d**. The product was purified by flash chromatography on silica gel using 10-20 % EtOAc/cyclohexane to afford the title compound (150.6 mg, 48 % yield) as a yellowish oil. R_f 0.18 (EtOAc/cyclohexane 2:8). IR (neat): 3567, 3408, 3055, 3026, 2922, 1602, 1544, 1497, 1444, 1381, 1355, 1314, 1256, 1182, 992, 908, 750, 692 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.27 (m, 6H), 7.24 – 7.17 (m, 2H), 6.78 (tt, J = 7.4, 1.1 Hz, 1H), 6.66–6.59 (m, 2H), 5.77 (dd, J = 8.2, 7.4 Hz, 1H), 4.88 (tdd, J = 8.0, 5.6, 4.5 Hz, 1H), 4.56 (s, 2H), 4.13 (br s, 1H), 3.81 (dd, J = 14.7, 7.9 Hz, 1H), 3.65 (dd, J = 14.8, 4.5 Hz, 1H), 3.06 (dt, J = 15.0, 8.1 Hz, 1H), 2.90 (ddd, J = 15.0, 7.4, 5.6 Hz, 1H), 1.66 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.4, 143.9, 140.3, 129.7, 128.8, 128.0, 126.6, 123.8, 118.9, 113.2, 86.5, 60.0, 46.4, 30.4. HRMS (ESI+/TOF) Calcd for $C_{18}H_{21}N_2O_3$ [M + H]$^+$: 313.1547. Found: 313.1545.

*(Z)-tert-Butyl-8-hydroxy-4-nitro-7-phenyloct-6-enoate (**3k**)*. Compound **3k** was prepared following the general procedure from cyclic carbonate **1a** (190.2 mg, 1.0 mmol) and nitroalkane **2b**. The product was purified by flash chromatography on silica gel using 10-20 % EtOAc/cyclohexane to afford the title compound (215.7 mg, 64 % yield) as a yellowish oil. R_f 0.17 (EtOAc/cyclohexane 2:8). IR (neat): 3566, 3434, 3083, 3059, 2979, 2933, 1724, 1547, 1493, 1445, 1367, 1320, 1251, 1150, 1009, 911, 844, 766, 732, 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.25 (m, 5H), 5.72 (dd, J = 8.3, 7.1 Hz, 1H), 4.74–4.64 (m, 1H), 4.57–4.46 (m, 2H), 2.99 (dt, J =15.0, 8.6 Hz, 1H), 2.74 (ddd, J = 15.0, 7.1, 5.0 Hz, 1H), 2.40–2.08 (m, 4H), 1.88 (br t, J = 5.1 Hz, 1H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.3, 143.7, 140.4, 128.6, 127.8, 126.6, 124.0, 87.6, 81.4, 59.8, 32.8, 31.4, 28.6, 28.1. HRMS (ESI+/TOF) Calcd for $C_{18}H_{25}NO_5Na^+$ [M + Na]$^+$: 358.1625. Found: 358.1633.

*(Z)-6-(Furan-2-yl)-5-nitro-2-phenylhex-2-en-1-ol (**3l**)*. Compound **3l** was prepared following the general procedure from cyclic carbonate **1a** (190.2 mg, 1.0 mmol) and nitroalkane **2c**. The product was purified by flash chromatography on silica gel using 10-20 % EtOAc/cyclohexane to afford the title compound (218.3 mg, 76 % yield) as a yellowish oil. R_f 0.22 (EtOAc/cyclohexane 2:8). IR (neat): 3574, 3398, 3027, 2920, 1599, 1547, 1506, 1493, 1429, 1371, 1325, 1208, 1145, 1077, 1010, 911, 732, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.26 (m, 6H), 6.31 (dd, J = 3.2, 1.9 Hz, 1H), 6.19–6.13 (m, 1H), 5.73 (dd, J = 8.4, 7.0 Hz, 1H), 4.91 (dddd, J = 8.8, 7.9, 6.0, 4.9 Hz, 1H), 4.54–4.45 (m, 2H), 3.40 (dd, J = 15.4, 7.9 Hz, 1H), 3.20 (dd, J = 15.4, 6.0 Hz, 1H), 3.01 (dt, J = 15.2, 8.6 Hz, 1H), 2.79 (ddd, J = 15.2, 7.1, 4.9 Hz, 1H), 1.80 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.1, 143.7, 142.5, 140.3, 128.6, 127.9, 126.6, 123.8, 110.7, 108.3, 86.6, 59.7, 32.1, 31.9. HRMS (ESI+/TOF) Calcd for $C_{16}H_{17}NO_4Na^+$ [M + Na]$^+$: 310.1050. Found: 310.1046.

*(Z)-7,7-Dimethoxy-5-nitro-2-phenylhept-2-en-1-ol (**3m**)*. Compound **3m** was prepared following the general procedure from cyclic carbonate **1a** (190.2 mg, 1.0 mmol) and nitroalkane **2e**. The product was purified by flash chromatography on silica gel using 20-30 % EtOAc/cyclohexane to afford the title compound (281.0 mg, 95 % yield) as a yellowish oil. R_f 0.08 (EtOAc/cyclohexane 2:8). IR (neat): 3568, 3422, 3081, 3058, 3029, 2992, 2937, 2911, 2836, 2251, 1548, 1493, 1445, 1370, 1325, 1267, 1194, 1127, 1065, 1023, 949, 909, 768, 730, 698 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.37 (m, 2H), 7.37–7.32 (m, 2H), 7.31–7.27 (m, 1H), 5.73 (dd, J = 8.3, 7.1 Hz, 1H), 4.77 (tdd, J = 9.1, 5.1, 4.2 Hz, 1H), 4.58–4.47 (m, 2H), 4.41 (dd, J = 6.3, 4.5 Hz, 1H), 3.37 (s, 3H), 3.35 (s, 3H), 2.99 (dt, J = 14.9, 8.5 Hz, 1H), 2.79 (ddd, J = 15.0, 7.1, 5.1 Hz, 1H), 2.45 (ddd, J = 14.7, 9.2, 4.5 Hz, 1H), 2.05 (ddd, J = 14.7, 6.3, 4.2 Hz, 1H), 1.53 (br t, J = 4.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.8, 140.3, 128.7, 128.0, 126.7, 124.0, 102.1, 84.5, 59.9, 54.5, 54.1, 36.4, 33.1. HRMS (ESI+/TOF) Calcd for $C_{15}H_{21}NO_5Na$ [M + Na]$^+$: 318.1312. Found: 318.1321.

*(Z)-6,6-Bis(methylthio)-5-nitro-2-phenylhex-2-en-1-ol (**3n**)*. Compound **3n** was prepared following the general procedure from cyclic carbonate **1a** (190.2 mg, 1.0 mmol) and nitroalkane **2g**. The product was purified by flash chromatography on silica gel using 10 % EtOAc/cyclohexane to afford the title compound (170.3 mg, 54 % yield) as a yellowish oil. R_f 0.22 (EtOAc/cyclohexane 2:8). IR (neat): 3565, 3396, 3081, 3055, 3026, 2919, 2854, 1550, 1493, 1423, 1365, 1308, 1011, 975, 957, 766, 698 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.37 (m, 2H), 7.37–7.31 (m, 2H), 7.31–7.27 (m, 1H), 5.76 (dd, J = 8.7, 6.7 Hz, 1H), 4.70 (td, J = 9.7, 3.7 Hz, 1H), 4.57 (dd, J = 12.7, 3.4 Hz, 1H), 4.53 (dd, J = 12.7, 5.2 Hz, 1H), 4.13 (d, J = 9.6 Hz, 1H), 3.19 (ddd, J = 15.3, 6.7, 3.7 Hz, 1H), 3.09 (app dt, J = 15.3, 9.3 Hz, 1H), 2.21 (s, 3H), 2.19 (s, 3H), 1.57 (overlapped, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.1, 140.3, 128.7, 128.0, 126.7, 123.8, 90.7, 60.0, 55.7, 31.5, 13.7, 13.5; HRMS (ESI+/TOF) Calcd for $C_{14}H_{19}NO_3S_2Na^+$ [M + Na]$^+$: 336.0699. Found: 336.0700.

*(Z)-2-(6-Hydroxy-2-nitro-5-phenylhex-4-en-1-yl)isoindoline-1,3-dione (**3o**)*. Compound **3o** was prepared following the general procedure from cyclic carbonate **1a** (190.2 mg, 1.0 mmol) and nitroalkane **2f**. The product was purified by flash chromatography on silica gel using 20-30 % EtOAc/cyclohexane to afford the title compound (251.1 mg, 69 % yield) as a pale yellow solid. R_f 0.11 (EtOAc/cyclohexane 3:7). IR (neat): 3455, 3090, 3060, 3029, 2954, 2897, 1774, 1702, 1611, 1552, 1473, 1423, 1396, 1339, 1296, 1256, 1192, 1088, 1017, 992, 969, 931, 904, 881, 851, 771, 715, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.81 (m, 2H), 7.79–7.71 (m, 2H), 7.40–7.27 (m, 5H), 5.75 (t, J = 7.6 Hz, 1H), 5.06 (tt, J = 8.4, 5.1 Hz, 1H), 4.57 (d, J = 4.8 Hz, 2H), 4.42 (dd, J = 14.5, 8.3 Hz, 1H), 4.06 (dd, J = 14.5, 4.8 Hz, 1H), 3.11 (dt, J = 15.2, 8.3 Hz, 1H), 2.90 (ddd, J = 15.2, 7.2, 5.3 Hz, 1H), 1.66 (br t, J = 5.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.7, 144.3, 140.1, 134.7, 131.7, 128.7, 128.0, 126.6, 123.9, 122.9, 84.9, 60.0, 40.0, 30.6. HRMS (ESI+/TOF) Calcd for $C_{20}H_{18}N_2O_5Na^+$ [M + Na]$^+$: 389.1108. Found: 389.1111.

*(Z)-5-Nitro-2-phenylpent-2-en-1-yl benzoate (**3q**)*. Compound **3q** was prepared following the general procedure from cyclic carbonate **1a** (38.0 mg, 0.20 mmol) and benzoyl nitromethane. The product was purified by flash chromatography on silica gel using 5 % EtOAc/cyclohexane to afford the title compound (41.9 mg, 67 % yield) as a brownish oil. R_f 0.26 (EtOAc/cyclohexane 1:9). IR (neat): 3061, 3031, 2962, 2918, 1807, 1713, 1600, 1548, 1493, 1450, 1377, 1315, 1265, 1176, 1106, 1069, 1025, 954, 763, 710 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98–7.91 (m, 2H), 7.54 (app dt, J = 8.8, 1.4 Hz, 1H), 7.45–7.27 (m, 7H), 5.96 (t, J = 7.6 Hz, 1H), 5.28 (s, 2H), 4.55 (t, J = 6.8 Hz, 2H), 3.12 (q, J = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.5, 140.0, 138.9, 133.3, 130.0, 129.8, 128.7, 128.6, 128.0, 127.3, 126.5, 74.9, 61.6, 26.8. HRMS (ESI+/TOF) Calcd for $C_{18}H_{17}NO_4Na^+$ [M + Na]$^+$: 334.1050. Found: 334.1054.

*2-Methyl-5-nitrohex-2-en-1-ol (**4a**)*. Compound **4a** was prepared following the general procedure from 4-methyl-4-vinyl-1,3-dioxolan-2-one (128.1 mg, 1.0 mmol) and nitroethane. The product was purified by flash chromatography on silica gel using 20-30 % EtOAc/cyclohexane to afford the title compound (90.0 mg, 57 % yield) as a yellowish oil. R_f 0.31 (EtOAc/cyclohexane 3:7). IR (neat): 3377, 2976, 2941, 1542, 1451, 1388, 1361, 1008 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.25–5.17 (m, 1H), 4.62–4.51 (m, 1H), 4.13 (app d, J = 12.3 Hz, 1H), 4.06 (dd, J = 12.6, 3.4 Hz, 1H), 2.85–2.70 (m, 1H), 2.55–2.42 (m, 1H), 1.80 (q, J = 1.2 Hz, 3H), 1.53 (d, J = 6.7 Hz, 3H), 1.51 (overlapped, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.9, 120.6, 83.6, 61.4, 33.4, 21.6, 18.9. Note: the NMR resonances reported correspond to the (*Z*) isomer. HRMS (ESI+/TOF) Calcd for $C_7H_{13}NO_3Na^+$ [M + Na]$^+$: 182.0788. Found: 182.0787.

*5-Nitrohex-2-en-1-ol (**4b**)*. Compound **4b** was prepared following the general procedure from 4-vinyl-1,3-dioxolan-2-one

(114.1 mg, 1.0 mmol) and nitroethane. The product was purified by flash chromatography on silica gel using 20-30 % EtOAc/cyclohexane to afford the title compound (96.1 mg, 66 % yield) as a yellowish oil. R_f 0.16 (EtOAc/cyclohexane 3:7). IR (neat): 3570, 3353, 2940, 1543, 1451, 1389, 1361, 1314, 1004, 973, 857 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) : δ 5.78 (overlapped, 1H), 5.46 (dddt, J = 11.1, 8.5, 7.2, 1.5 Hz, 1H), 4.63–4.55 (m, 1H), 4.25–4.14 (m, 2H), 2.86–2.77 (m, 1H), 2.52 (overlapped, 1H), 1.56 (dd, J = 12.1, 6.7 Hz, 3H), 1.45 (br s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 133.4, 125.1, 83.0, 58.4, 33.1, 18.9. Note: NMR resonances reported correspond to the (*Z*) isomer. HRMS (ESI+/TOF) Calcd for $C_6H_{11}NO_3Na^+$ [M + Na]$^+$: 168.0631. Found: 168.0632.

(Z)-2-Cyclohexyl-5-nitrohex-2-en-1-ol ***(4c)***. Compound **4c** was prepared following the general procedure from 4-cyclohexyl-4-vinyl-1,3-dioxolan-2-one (39.3 mg, 0.20 mmol) and nitroethane. The product was purified by flash chromatography on silica gel using 20 % EtOAc/cyclohexane to afford the title compound (32.0 mg, 70 % yield) as a brownish oil. R_f 0.42 (EtOAc/cyclohexane 3:7). IR (neat): 3287, 3221, 2923, 2851, 1545, 1448, 1387, 1360, 998 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.23 (ddd, J = 8.1, 6.9, 1.0 Hz, 1H), 4.60 (dqd, J = 8.3, 6.7, 5.4 Hz, 1H), 4.14 (dd, J = 11.9, 4.6 Hz, 1H), 4.09 (dd, J = 11.9, 5.7 Hz, 1H), 2.83 (dt, J = 14.7, 8.3 Hz, 1H), 2.55 (dt, J = 14.7, 6.7, 5.7 Hz, 1H), 2.09–1.98 (m, 1H), 1.83–1.63 (m, 6H), 1.55 (d, J = 6.7 Hz, 3H), 1.35–1.05 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.2, 119.8, 83.8, 59.7, 43.6, 33.5, 32.7, 32.6, 26.82, 26.79, 26.3, 19.0. HRMS (ESI+/TOF) Calcd for $C_{12}H_{21}NO_3Na^+$ [M + Na]$^+$: 250.1414. Found: 250.1412.

(Z)-2-([1,1'-Biphenyl]-4-yl)-5-nitrohex-2-en-1-ol ***(4d)***. Compound **4d** was prepared following the general procedure from 4-([1,1'-biphenyl]-4-yl)-4-vinyl-1,3-dioxolan-2-one (57.6 mg, 0.22 mmol) and nitroethane. The product was purified by flash chromatography on silica gel using 20-30 % EtOAc/cyclohexane to afford the title compound (34.6 mg, 54 % yield) as a yellowish oil. R_f 0.30 (EtOAc/cyclohexane 3:7). IR (neat): 3428, 3029, 2924, 1538, 1486, 1448, 1388, 1357, 1000, 837, 763, 730, 692 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.62–7.56 (m, 4H), 7.51–7.47 (m, 2H), 7.47– .42 (m, 2H), 7.38–7.33 (m, 1H), 5.81 (dd, J = 8.3, 7.2 Hz, 1H), 4.73 (dqd, J = 8.1, 6.6, 5.3 Hz, 1H), 4.62 (d, J = 12.5 Hz, 1H), 4.58 (d, J = 12.5 Hz, 1H), 3.05 (dt, J = 14.9, 8.3 Hz, 1H), 2.77 (ddd, J = 14.9, 7.2, 5.4 Hz, 1H), 1.64 (d, J = 6.7 Hz, 3H), 1.56 (br s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.1, 140.8, 140.7, 139.2, 128.9, 127.5, 127.4, 127.1, 127.0, 124.3, 83.3, 59.8, 34.1, 19.1. HRMS (ESI+/TOF) Calcd for $C_{18}H_{19}NO_3Na^+$ [M + Na]$^+$: 320.1257. Found: 320.1271.

(Z)-5-Nitro-2-(3-(trifluoromethyl)phenyl)hex-2-en-1-ol ***(4e)***. Compound **4e** was prepared following the general procedure from cyclic carbonate **1c** (258.2 mg, 1.0 mmol) and nitroethane. The product was purified by flash chromatography on silica gel using 20-30 % EtOAc/cyclohexane to afford the title compound (100.0 mg, 35 % yield) as a yellowish oil. R_f 0.19 (EtOAc/cyclohexane 3:7). IR (neat): 3578, 3371, 3077, 2992, 2924, 2899, 2854, 1806, 1547, 1489, 1436, 1390, 1331, 1262, 1164, 1118, 1075, 1066, 907, 800, 733, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 1.8 Hz, 1H), 7.62–7.52 (m, 2H), 7.45 (d, J = 7.7 Hz, 1H), 5.80 (dd, J = 8.4, 7.0 Hz, 1H), 4.73 (dqd, J = 8.5, 6.6, 5.1 Hz, 1H), 4.59 (dd, J = 12.6, 4.3 Hz, 1H), 4.53 (dd, J = 12.5, 5.5 Hz, 1H), 3.05 (dt, J = 15.0, 8.5 Hz, 1H), 2.75 (ddd, J = 15.0, 7.0, 5.2 Hz, 1H), 1.64 (d, J = 6.7 Hz, 3H), 1.56 (br t, J = 5.6 Hz, 1H). 13C NMR (101 MHz, $CDCl_3$): δ 142.5, 141.4, 131.0 (q, J = 32.4 Hz), 130.1, 129.1, 126.0, 125.5, 124.6 (q, J = 3.8 Hz), 123.4 (q, J = 4.0 Hz), 122.8, 83.2, 59.8, 34.0, 19.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.7. HRMS (ESI+/TOF) Calcd for $C_{13}H_{14}F_3NO_3Na^+$ [M + Na]$^+$: 312.0818. Found: 312.0819.

(Z)-4-(1-Hydroxy-5-nitrohex-2-en-2-yl)benzonitrile ***(4f)***. Compound **4f** was prepared following the general procedure from cyclic carbonate **1f** (215.2 mg, 1.0 mmol) and nitroethane. The product was purified by flash chromatography on silica gel using 30-40 % EtOAc/cyclohexane to afford the title compound (104.0 mg, 42 % yield) as a yellowish oil. R_f 0.08 (EtOAc/cyclohexane 3:7). IR (neat): 3494, 2989, 2939, 2898, 2227, 1605, 1544, 1504, 1449, 1389, 1360, 1312, 1008, 910, 830, 729 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63–7.58 (m, 2H), 7.54–7.48 (m, 2H), 5.85 (dd, J = 8.5, 7.0 Hz, 1H), 4.73 (dqd, J = 8.5, 6.7, 5.0 Hz, 1H), 4.56 (d, J = 12.6 Hz, 1H), 4.51 (d, J = 12.6 Hz, 1H), 3.04 (dt, J = 15.1, 8.5 Hz, 1H), 2.75 (ddd, J = 15.1, 7.0, 5.0 Hz, 1H), 1.73 (br s, 1H), 1.63 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.2, 142.2, 132.4, 127.3, 127.2, 118.9, 111.3, 83.1, 59.4, 34.0, 19.2. HRMS (ESI+/TOF) Calcd for $C_{13}H_{14}N_2O_3Na^+$ [M + Na]$^+$: 269.0897. Found: 269.0907.

(Z)-5-Nitro-2-(thiophen-3-yl)hex-2-en-1-ol ***(4g)***. Compound **4g** was prepared following the general procedure from 4-(thiophen-3-yl)-4-vinyl-1,3-dioxolan-2-one (196.2 mg, 1.0 mmol) and nitroethane. The product was purified by flash chromatography on silica gel using 20-25 % EtOAc/cyclohexane to afford the title compound (159.3 mg, 70 % yield) as a yellowish oil. Rf 0.09 (EtOAc/cyclohexane 2:8). IR (neat): 3567, 3381, 3108, 2988, 2938, 2897, 2248, 1678, 1544, 1449, 1388, 1360, 1312, 1004, 908, 861, 781, 728 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.33 (dd, J = 3.0, 1.4 Hz, 1H), 7.28 (dd, J = 5.1, 2.9 Hz, 1H), 7.19 (dd, J = 5.1, 1.4 Hz, 1H), 5.85 (dd, J = 8.3, 7.3 Hz, 1H), 4.68 (dqd, J = 8.1, 6.7, 5.3 Hz, 1H), 4.51 (d, J = 12.2 Hz, 1H), 4.46 (d, J = 12.2 Hz, 1H), 2.99 (dt, J = 15.0, 8.3 Hz, 1H), 2.71 (ddd, J = 15.0, 7.2, 5.4 Hz, 1H), 1.73 (br s, 1H), 1.60 (d, J = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 141.2, 138.0, 126.1, 125.7, 122.8, 121.4, 83.3, 59.8, 33.7, 19.1. HRMS (ESI+/TOF) Calcd for $C_{10}H_{13}NO_3SNa^+$ [M + Na]$^+$: 250.0508. Found: 250.0506.

(Z)-2-(Benzo[d][1,3]dioxol-5-yl)-5-nitrohex-2-en-1-ol ***(4h)***. Compound **4h** was prepared following the general procedure from 4-(benzo[d][1,3]dioxol-5-yl)-4-vinyl-1,3-dioxolan-2-one (234.2 mg, 1.0 mmol) and nitroethane. The product was purified by flash chromatography on silica gel using 20-30 % EtOAc/cyclohexane to afford the title compound (162.4 mg, 61 % yield) as a yellowish oil. R_f 0.09 (EtOAc/cyclohexane 2:8). IR (neat): 3567, 3401, 3068, 2989, 2897, 2779, 1720, 1606, 1545, 1503, 1486, 1436, 1388, 1360, 1326, 1232, 1110, 1036, 932, 891, 862, 808, 732 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.91–6.84 (m, 2H), 6.77 (dd, J = 7.8, 0.6 Hz, 1H), 5.95 (s, 2H), 5.64 (dd, J = 8.3, 7.2 Hz, 1H), 4.68 (dqd, J = 8.3, 6.7, 5.4 Hz, 1H), 4.50 (d, J = 12.4 Hz, 1H), 4.46 (d, J = 12.4 Hz, 1H), 2.97 (dt, J = 15.0, 8.2 Hz, 1H), 2.70 (ddd, J = 15.0, 7.2, 5.4 Hz, 1H), 1.60 (d, J = 6.7 Hz, 3H), 1.58 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.0, 147.4, 143.1, 134.5, 123.3, 120.2, 108.4, 107.2, 101.3, 83.3, 59.9, 34.0, 19.0. HRMS (ESI+/TOF) Calcd for $C_{13}H_{15}NO_5Na^+$ [M + Na]$^+$: 288.0842. Found: 288.0840.

(E)-2-(Furan-2-yl)-5-nitrohex-2-en-1-ol ***(4i)***. Compound **4i** was prepared following the general procedure from 4-(furan-2-yl)-4-vinyl-1,3-dioxolan-2-one (83.4 mg, 0.46 mmol) and nitroethane. The product was purified by flash chromatography on silica gel using 20-25 % EtOAc/cyclohexane to afford the

title compound (33.3 mg, 34 % yield) as a yellowish oil. R_f 0.11 (EtOAc/cyclohexane 2:8). IR (neat): 3577, 3390, 3152, 3138, 3119, 2987, 2938, 2900, 1544, 1459, 1388, 1360, 1313, 1320, 1159, 1013, 905, 884, 805, 731 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, J = 1.8 Hz, 1H), 6.42 (app d, J = 3.4 Hz, 1H), 6.40 (dd, J = 3.4, 1.8 Hz, 1H), 6.07 (t, J = 8.0 Hz, 1H), 4.69 (dqd, J = 8.0, 6.7, 5.5 Hz, 1H), 4.47 (d, J = 12.3 Hz, 1H), 4.42 (d, J = 12.3 Hz, 1H), 3.03 (dt, J = 15.0, 8.2 Hz, 1H), 2.74 (ddd, J = 15.0, 7.5, 5.6 Hz, 1H), 1.61 (overlapped, 1H), 1.61 (d, J = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.3, 142.4, 132.9, 120.9, 111.6, 106.9, 83.2, 58.2, 33.4, 19.1. HRMS (ESI+/TOF) Calcd for $C_{10}H_{13}NO_4Na^+$ [M + Na]$^+$: 234.0737. Found: 234.0730.

(Z)-2-(Naphthalen-2-yl)-5-nitrohex-2-en-1-ol ***(4j)***. Compound **4j** was prepared following the general procedure from 4-(naphthalen-2-yl)-4-vinyl-1,3-dioxolan-2-one (240.3 mg, 1.0 mmol) and nitroethane. The product was purified by flash chromatography on silica gel using 20 % EtOAc/cyclohexane to afford the title compound (108.3 mg, 40 % yield) as a yellowish oil. R_f 0.29 (EtOAc/cyclohexane 3:7). IR (neat): 3574, 3390, 3057, 2939, 1543, 1448, 1388, 1360, 1013, 909, 802, 778, 730 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89–7.82 (m, 2H), 7.80 (app d, J = 8.3 Hz, 1H), 7.53–7.46 (m, 2H), 7.43 (dd, J = 8.3, 7.0 Hz, 1H), 7.28 (dd, J = 7.0, 1.2 Hz, 1H), 5.60 (dd, J = 8.3, 7.1 Hz, 1H), 4.79–4.69 (m, 1H), 4.58–4.48 (m, 2H), 3.12 (dt, J = 14.7, 8.3 Hz, 1H), 2.83 (ddd, J = 14.8, 7.0, 5.4 Hz, 1H), 1.66 (d, J = 6.7 Hz, 3H), 1.53 (br s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.6, 139.1, 133.8, 131.6, 128.5, 128.1, 126.7, 126.42, 126.40, 126.1, 125.43, 125.40, 83.3, 61.8, 33.9, 19.1. HRMS (ESI+/TOF) Calcd for $C_{16}H_{17}NO_3Na^+$ [M + Na]$^+$: 294.1101. Found: 294.1101.

Ethyl 6-hydroxy-5-(2-methoxyphenyl)-2-nitrohex-4-enoate ***(4l)***. Compound **4l** was prepared following the general procedure B from cyclic carbonate **1d** (220.2 mg, 1.0 mmol) and ethyl nitroacetate. The product was purified by flash chromatography on silica gel using 20 % EtOAc/cyclohexane to afford the title compound (247.2 mg, 80 % yield) as a yellowish oil. R_f 0.11 (EtOAc/cyclohexane 2:8). IR (neat): 3570, 2982, 2963, 2940, 2838, 1747, 1598, 1558, 1489, 1464, 1435, 1373, 1240, 1119, 1050, 1021, 910, 858, 755, 730 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30–7.25 (m, 1H), 7.08 (dd, J = 7.5, 1.8 Hz, 1H), 6.96–6.91 (m, 1H), 6.89 (d, J = 8.2 Hz, 1H), 5.58 (t, J = 7.5 Hz, 1H), 5.32 (dd, J = 9.2, 5.7 Hz, 1H), 4.39 (dd, J = 12.5, 7.1 Hz, 1H), 4.33 (overlapped, 1H), 4.29 (qd, J = 7.2, 1.2 Hz, 2H), 3.85 (s, 3H), 3.28 (ddd, J = 15.1, 9.2, 7.8 Hz, 1H), 3.16 (ddd, J = 15.3, 7.4, 5.7 Hz, 1H), 2.47 (t, J = 6.5 Hz, 1H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 164.2, 156.3, 144.7, 131.1, 130.3, 129.2, 125.4, 121.3, 110.7, 87.8, 63.2, 61.0, 55.7, 29.2, 14.0. Note: the NMR resonances reported correspond to the (*Z*) isomer. HRMS (ESI+/TOF) Calcd for $C_{15}H_{19}NO_6Na^+$ [M + Na]$^+$: 332.1105. Found: 332.1106.

(Z)-2-(2-Bromophenyl)-6-(furan-2-yl)-5-nitrohex-2-en-1-ol ***(4m)***. Compound **4m** was prepared following the general procedure from cyclic carbonate **1e** (269.1 mg, 1.0 mmol) and nitroalkane **2c**. The product was purified by flash chromatography on silica gel using 10-20 % EtOAc/cyclohexane to afford the title compound (173.0 mg, 47 % yield) as a yellowish oil. R_f 0.32 (EtOAc/cyclohexane 2:8). IR (neat): 3581, 3407, 3119, 3055, 2919, 1548, 1506, 1468, 1431, 1370, 1145, 1010, 908, 728 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59–7.53 (m, 1H), 7.35 (d, J = 2.0 Hz, 1H), 7.31–7.24 (m, 1H), 7.18–7.13 (m, 2H), 6.31 (dd, J = 3.2, 2.0 Hz, 1H), 6.17 (d, J = 3.3 Hz, 1H), 5.49 (t, J = 7.7 Hz, 1H), 4.91 (tt, J = 8.2, 5.5 Hz, 1H), 4.42 (d, J = 6.1 Hz, 2H), 3.42 (dd, J = 15.4, 8.0 Hz, 1H), 3.24 (dd, J = 15.5, 6.0 Hz, 1H), 3.04 (dt, J = 15.1, 8.5 Hz, 1H), 2.82 (ddd, J = 15.1, 7.1, 5.0 Hz, 1H), 1.72 (t, J = 6.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.1, 144.9, 142.5, 142.1, 132.7, 131.2, 129.2, 127.5, 126.7, 122.4, 110.7, 108.3, 86.4, 60.8, 31.9, 31.8. HRMS (ESI+/TOF) Calcd for $C_{16}H_{16}BrNO_4Na^+$ [M + Na]$^+$: 388.0155. Found: 388.0149.

(Z)-7,7-Dimethoxy-5-nitro-2-(m-tolyl)hept-2-en-1-ol ***(4n)***. Compound **4n** was prepared following the general procedure from cyclic carbonate **1b** (204.2 mg, 1.0 mmol) and nitroalkane **2e**. The product was purified by flash chromatography on silica gel using 20-30 % EtOAc/cyclohexane to afford the title compound (263.1 mg, 85 % yield) as a yellowish oil. R_f 0.12 (EtOAc/cyclohexane 3:7). IR (neat): 3576, 3441, 2937, 2835, 2250, 1603, 1548, 1446, 1370, 1192, 1127, 1066, 1010, 909, 786, 729, 702 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.16 (m, 3H), 7.13–7.08 (m, 1H), 5.70 (dd, J = 8.3, 7.1 Hz, 1H), 4.76 (tdd, J = 9.1, 5.2, 4.1 Hz, 1H), 4.52 (dd, J = 14.5, 12.6 Hz, 1H), 4.48 (d, J = 12.6 Hz, 1H), 4.40 (dd, J = 6.3, 4.5 Hz, 1H), 3.36 (s, 3H), 3.34 (s, 3H), 2.97 (dt, J = 14.9, 8.4 Hz, 1H), 2.77 (ddd, J = 15.0, 7.1, 5.2 Hz, 1H), 2.44 (ddd, J = 14.7, 9.2, 4.5 Hz, 1H), 2.35 (s, 3H), 2.04 (ddd, J = 14.8, 6.3, 4.1 Hz, 1H), 1.72 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.9, 140.3, 138.3, 128.6, 128.5, 127.4, 123.73, 123.71, 102.1, 84.5, 59.8, 54.4, 54.0, 36.3, 33.1, 21.6. HRMS (ESI+/TOF) Calcd for $C_{16}H_{23}NO_5Na^+$ [M + Na]$^+$: 332.1468. Found: 332.1466.

(2Z,7Z)-5-Nitro-2-phenyl-8-(m-tolyl)nona-2,7-diene-1,9-diol ***(6a)***. Compound **6a** was prepared following the general procedure from cyclic carbonate **1b** (72.3 mg, 0.35 mmol) and mono-allylated nitroalkane **5a**. The product was purified by flash chromatography on silica gel using 30-50 % EtOAc/cyclohexane to afford the title compound (73.3 mg, 59 % yield) as a yellowish foam. R_f 0.09 (EtOAc/cyclohexane 4:6). IR (neat): 3575, 3376, 3080, 3056, 3028, 2920, 2249, 1602, 1546, 1491, 1436, 1371, 1323, 1220, 1008, 907, 786, 727, 697, 648 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.37 (m, 2H), 7.36–7.31 (m, 2H), 7.31–7.27 (m, 1H), 7.23 (t, J = 7.5 Hz, 1H), 7.21–7.16 (m, 2H), 7.11 (d, J = 7.3 Hz, 1H), 5.75 (t, J = 7.9 Hz, 1H), 5.72 (t, J = 7.9 Hz, 1H), 4.75 (tt, J = 8.2, 5.4 Hz, 1H), 4.54 (s, 2H), 4.53 (s, 2H), 3.06 (dtd, J = 15.0, 8.1, 3.4 Hz, 2H), 2.87 (dddd, J = 15.1, 7.6, 5.4, 2.4 Hz, 2H), 2.35 (s, 3H), 1.84 (br s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.9, 143.8, 140.33, 140.27, 138.4, 128.8, 128.7, 128.6, 128.0, 127.4, 126.7, 124.0, 123.7, 87.9, 59.94, 59.91, 32.3, 21.6. HRMS (ESI+/TOF) Calcd for $C_{22}H_{25}NO_4Na^+$ [M + Na]$^+$: 390.1676. Found: 390.1681.

(7Z)-2-(2-Bromophenyl)-5-nitro-8-(3-(trifluoromethyl)phenyl)nona-2,7-diene-1,9-diol ***(6b)***. Compound **6b** was prepared following the general procedure from cyclic carbonate **1c** (43.9 mg, 0.17 mmol) and mono-allylated nitroalkane **5b**. The product was purified by flash chromatography on silica gel using 30-40 % EtOAc/cyclohexane to afford the title compound (35.0 mg, 41 % yield) as a yellowish foam. R_f 0.07 (EtOAc/cyclohexane 4:6). IR (neat): 3574, 3364, 3056, 2924, 1546, 1468, 1433, 1372, 1332, 1265, 1164, 1119, 1074, 1021, 800, 754, 700, 657 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (app s, 1H), 7.63–7.50 (m, 3H), 7.46 (t, J = 7.6 Hz, 1H), 7.30–7.25 (m, 1H), 7.19–7.12 (m, 2H), 5.83 (dd, J = 8.4, 7.0 Hz, 1H), 5.51 (t, J = 7.7 Hz, 1H), 4.78 (tt, J = 8.3, 5.3 Hz, 1H), 4.60 (d, J = 12.5 Hz, 1H), 4.56 (d, J = 12.5 Hz, 1H), 4.48 (d, J = 13.3 Hz, 1H), 4.44 (d, J = 13.3 Hz, 1H), 3.19–3.04 (m, 2H), 2.97–2.86 (m, 2H), 1.75 (br s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.0, 142.8, 142.0,

141.4, 132.8, 131.2, 131.1 (q, J = 32.5 Hz), 130.1, 129.3, 129.2, 127.6, 126.9, 125.7, 124.6 (q, J = 3.9 Hz), 123.4 (q, J = 3.5 Hz), 122.5, 87.6, 61.0, 59.8, 32.3, 32.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.7. HRMS (ESI+/TOF) Calcd for $C_{22}H_{21}BrF_3NO_4Na^+$ $[M + Na]^+$: 522.0498. Found: 522.0521.

*(2Z,7Z)-2-(Benzo[d][1,3]dioxol-5-yl)-5-nitro-8-(thiophen-3-yl)nona-2,7-diene-1,9-diol (**6c**)*. Compound **6c** was prepared following the general procedure from 4-(benzo[d][1,3]dioxol-5-yl)-4-vinyl-1,3-dioxolan-2-one (77.8 mg, 0.33 mmol) and mono-allylated nitroalkane **5c**. The product was purified by flash chromatography on silica gel using 30-50 % EtOAc/cyclohexane to afford the title compound (76.4 mg, 57 % yield) as a yellowish foam. R_f 0.10 (EtOAc/cyclohexane 1:1). IR (neat): 3561, 3353, 3107, 2894, 1606, 1544, 1502, 1486, 1434, 1370, 1325, 1233, 1102, 1035, 932, 892, 862, 810, 781, 729 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, J = 2.9, 1.4 Hz, 1H), 7.29 (dd, J = 5.1, 3.0 Hz, 1H), 7.19 (dd, J = 5.0, 1.4 Hz, 1H), 6.88 (t, J = 1.7 Hz, 1H), 6.85 (overlapped, 1H), 6.77 (d, J = 7.9 Hz, 1H), 5.95 (s, 2H), 5.87 (t, J = 7.7 Hz, 1H), 5.65 (t, J = 7.7 Hz, 1H), 4.72 (tt, J = 8.2, 5.5 Hz, 1H), 4.50 (d, J = 12.4 Hz, 1H), 4.47 (d, J = 12.4 Hz, 1H), 4.46 (s, 2H), 3.10–2.95 (m, 2H), 2.89–2.76 (m, 2H), 1.88 (br s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.0, 147.5, 143.2, 141.2, 138.3, 134.5, 126.1, 125.7, 123.0, 122.4, 121.5, 120.2, 108.4, 107.2, 101.3, 87.9, 59.9, 59.8, 32.2, 32.0. HRMS (ESI+/TOF) Calcd for $C_{20}H_{21}NO_6SNa^+$ $[M + Na]^+$: 426.0982. Found: 426.0982.

Synthesis of mono-allylated nitroalkanes. In a 5 mL vial, the respective cyclic carbonate (1.0 equiv.), $[Pd(allyl)Cl]_2$ (2.5 mol %) and DPEPhos (10 mol %) were dissolved in CH_3NO_2 (1.0 M). The vial was sealed with a septum and a needle was placed through the septum to release gaseous CO_2. The mixture was stirred for 2–8 h at rt open to air. After that, the solvent was evaporated with a stream of N_2 and the residue was purified by flash chromatography on silica gel to afford the corresponding mono-allylated nitroalkane. Compounds **5a–5c** were prepared using this approach.

*(Z)-5-Nitro-2-phenylpent-2-en-1-ol (**5a**)*. Compound **5a** was prepared following the general procedure from cyclic carbonate **1a** (190.2 mg, 1.0 mmol). The product was purified by flash chromatography on silica gel using 20-30 % EtOAc/cyclohexane to afford the title compound (110.1 mg, 53 % yield) as a yellowish oil. R_f 0.16 (EtOAc/cyclohexane 3:7). IR (neat): 3563, 3376, 3082, 3056, 3028, 2924, 2852, 1545, 1492, 1430, 1376, 1190, 999, 955, 766, 697 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43–7.39 (m, 2H), 7.37–7.33 (m, 2H), 7.32–7.27 (m, 1H), 5.77 (t, J = 7.6 Hz, 1H), 4.59 (s, 2H), 4.53 (t, J = 6.9 Hz, 2H), 3.02 (q, J = 7.0 Hz, 2H), 1.54 (br s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.5, 140.3, 128.8, 128.0, 126.6, 124.6, 75.2, 60.1, 26.6. HRMS (ESI+/TOF) Calcd for $C_{11}H_{13}NO_3Na^+$ $[M + Na]^+$: 230.0788. Found: 230.0790.

*2-(2-Bromophenyl)-5-nitropent-2-en-1-ol (**5b**)*. Compound **5b** was prepared following the general procedure from cyclic carbonate **1e** (269.1 mg, 1.0 mmol). The product was purified by flash chromatography on silica gel using 20-30 % EtOAc/cyclohexane to afford the title compound (73.0 mg, 25 % yield) as an orange oil. R_f 0.14 (EtOAc/cyclohexane 3:7). IR (neat): 3570, 3384, 3055, 2919, 1546, 1467, 1428, 1376, 1264, 1192, 1118, 1023, 752 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.54 (m, 1H), 7.31–7.26 (m, 1H), 7.20–7.13 (m, 2H), 5.52 (t, J = 7.6 Hz, 1H), 4.54 (t, J = 6.8 Hz, 2H), 4.49 (d, J = 6.3 Hz, 2H), 3.03 (q, J = 7.0 Hz, 2H), 1.65 (t, J = 6.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.5, 142.1, 132.8, 131.2, 129.3, 127.7, 127.6, 122.5, 74.9, 61.0, 26.3. Note: the NMR resonances reported correspond to the (*Z*) isomer. HRMS (ESI+/TOF) Calcd for $C_{11}H_{12}BrNO_3Na^+$ $[M + Na]^+$: 307.9893. Found: 307.9891.

*(Z)-5-Nitro-2-(thiophen-3-yl)pent-2-en-1-ol (**5c**)*. Compound **5c** was prepared following the general procedure from 4-(thiophen-3-yl)-4-vinyl-1,3-dioxolan-2-one (196.2 mg, 1.0 mmol). The product was purified by flash chromatography on silica gel using 20-30 % EtOAc/cyclohexane to afford the title compound (106.3 mg, 50 % yield) as a yellowish oil. R_f 0.11 (EtOAc/cyclohexane 3:7). IR (neat): 3565, 3376, 3106, 2916, 1544, 1428, 1376, 1336, 1267, 1178, 1001, 957, 861, 779, 734 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (dd, J = 3.0, 1.4 Hz, 1H), 7.30 (dd, J = 5.1, 2.9 Hz, 1H), 7.20 (dd, J = 5.2, 1.4 Hz, 1H), 5.89 (t, J = 7.7 Hz, 1H), 4.54 (s, 2H), 4.51 (t, J = 6.8 Hz, 2H), 2.99 (q, J = 7.0 Hz, 2H), 1.64 (br s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 141.2, 138.0, 126.2, 125.7, 123.1, 121.4, 75.1, 59.9, 26.3. HRMS (ESI+/TOF) Calcd for $C_9H_{11}NO_3SNa^+$ $[M + Na]^+$: 236.0352. Found: 236.0356.

Synthesis of 3p, 4k and tris-allylated nitroalkanes 7a-c. In a 5 mL vial, cyclic carbonate (1.0 equiv.), $Pd(dba)_2$ (5 mol %), DPEPhos (10 mol %) and nitroalkane (1.5 equiv.) were dissolved in MeCN (1.0 M). Then, DBU (10 mol %) was added. The vial was sealed with a septum and a needle was placed through the septum to release gaseous CO_2. The mixture was stirred for 2–8 h at rt open to air. After that, the solvent was evaporated with a stream of N_2 and the residue was purified by flash chromatography on silica gel to afford the corresponding nitroalkane.

*(Z)-5-Methyl-5-nitro-2-phenylhex-2-en-1-ol (**3p**)*. Compound **3p** was prepared following the general procedure from cyclic carbonate **1a** (38.0 mg, 0.20 mmol) and 2-nitropropane. The product was purified by flash chromatography on silica gel using 20-30 % EtOAc/cyclohexane to afford the title compound (39.0 mg, 83 % yield) as a yellowish oil. R_f 0.08 (EtOAc/cyclohexane 2:8). IR (neat): 3575, 3405, 3057, 2987, 2930, 1533, 1493, 1468, 1445, 1396, 1372, 1347, 1261, 1137, 1019, 855, 766, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.27 (m, 5H), 5.72 (t, J = 7.9 Hz, 1H), 4.55 (s, 2H), 2.91 (d, J = 7.9 Hz, 2H), 1.67 (s, 6H), 1.49 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.8, 140.5, 128.7, 127.9, 126.7, 123.9, 88.3, 59.9, 39.5, 26.0. HRMS (ESI+/TOF) Calcd for $C_{13}H_{17}NO_3Na^+$ $[M + Na]^+$: 258.1101. Found: 258.1106.

*(Z)-3-Methyl-5-nitro-2-phenylhex-2-en-1-ol (**4k**)*. Compound **4k** was prepared following the general procedure from cyclic carbonate **1g** (40.8 mg, 0.20 mmol) and nitroethane. The product was purified by flash chromatography on silica gel using 10-20 % EtOAc/cyclohexane to afford the title compound (30.1 mg, 64 % yield) as a yellowish oil. R_f 0.15 (EtOAc/cyclohexane 2:8). IR (neat): 3568, 3396, 3080, 3057, 3021, 2989, 2937, 2921, 2861, 1599, 1546, 1492, 1442, 1388, 1361, 1314, 1218, 1118, 1051, 995, 910, 854, 768, 731, 701 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.32 (m, 2H), 7.29–7.25 (m, 1H), 7.15–7.10 (m, 2H), 4.86 (dquint, J = 9.0, 6.5 Hz, 1H), 4.34 (d, J = 5.0 Hz, 2H), 3.13 (dd, J = 14.1, 9.0 Hz, 1H), 2.56 (dd, J = 14.1, 5.7 Hz, 1H), 1.64 (d, J = 6.6 Hz, 3H), 1.61 (s, 3H), 1.36 (br t, J = 6.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 140.8, 140.3, 129.8, 128.9, 128.6, 127.2, 82.4, 62.9, 39.7, 20.2, 19.3. HRMS (ESI+/TOF) Calcd for $C_{13}H_{17}NO_3Na^+$ $[M + Na]^+$: 258.1101. Found: 258.1108.

*(2Z,7Z)-5-((Z)-4-Hydroxy-3-(m-tolyl)but-2-en-1-yl)-5-nitro-2-phenyl-8-(thiophen-3-yl)nona-2,7-diene-1,9-diol (**7a**)*.

Compound **7a** was prepared following the general procedure from 4-(thiophen-3-yl)-4-vinyl-1,3-dioxolan-2-one (26.1 mg, 0.13 mmol) and bis-allylated nitroalkane **6a**. The product was purified by flash chromatography on silica gel using 90-100 % Et_2O/cyclohexane to afford the title compound (40.9 mg, 59 % yield) as a yellowish foam. R_f 0.13 (Et_2O). IR (neat): 3559, 3336, 3106, 3028, 2921, 1719, 1601, 1535, 1486, 1433, 1357, 1286, 1230, 1122, 1076, 1010, 847, 780, 697 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.40–7.24 (m, 7H), 7.24–7.14 (m, 4H), 7.10 (d, J = 7.4 Hz, 1H), 5.83 (t, J = 7.4 Hz, 1H), 5.72–5.64 (m, 2H), 4.48 (d, J = 3.3 Hz, 4H), 4.43 (s, 2H), 3.07 (d, J = 7.4 Hz, 6H), 2.47 (s, 3H), 2.43 (br s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.0, 141.3, 140.4, 140.3, 138.6, 138.5, 131.1, 129.0, 128.9, 128.8, 128.7, 128.0, 127.4, 126.7, 126.1, 125.8, 125.7, 123.8, 123.0, 122.7, 121.6, 121.4, 94.4, 59.93, 59.90, 59.85, 34.8, 34.6, 30.5, 21.7. HRMS (ESI+/TOF) Calcd for $C_{30}H_{33}NO_5SNa^+$ $[M + Na]^+$: 542.1972. Found: 542.1982.

(2*Z*,7*Z*)-2-(Benzo[d][1,3]dioxol-5-yl)-5-((*Z*)-4-hydroxy-3-(3-(trifluoromethyl)phenyl)but-2-en-1-yl)-5-nitro-8-(thiophen-3-yl)nona-2,7-diene-1,9-diol (**7b**). Compound **7b** was prepared following the general procedure from cyclic carbonate **1c** (32.6 mg, 0.13 mmol) and bis-allylated nitroalkane **6c**. The product was purified by flash chromatography on silica gel using Et_2O to afford the title compound (36.3 mg, 47 % yield) as a yellowish foam. R_f 0.06 (Et_2O). IR (neat): 3642, 3559, 3350, 2954, 2922, 1722, 1607, 1536, 1503, 1487, 1433, 1334, 1233, 1163, 1119, 1075, 1036, 933, 893, 860, 780, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.54 (app t, J = 8.8 Hz, 2H), 7.42 (t, J = 7.8 Hz, 1H), 7.30 (dd, J = 2.9, 1.4 Hz, 1H), 7.28–7.24 (m, 1H), 7.18 (dd, J = 5.1, 1.4 Hz, 1H), 6.89–6.81 (m, 2H), 6.80–6.71 (m, 1H), 5.93 (s, 2H), 5.82 (t, J = 7.5 Hz, 1H), 5.75 (t, J = 7.3 Hz, 1H), 5.60 (t, J = 7.4 Hz, 1H), 4.48 (s, 2H), 4.45 (s, 2H), 4.43 (s, 2H), 3.12–3.01 (m, 6H), 2.55 (br s, 3H). 13C NMR (126 MHz, $CDCl_3$): δ 148.0, 147.5, 143.3, 142.6, 141.5, 141.3, 138.3, 135.9, 134.6, 130.9 (q, J = 32.2 Hz), 130.1, 129.1, 126.1, 125.8, 125.6, 124.8, 124.5 (q, J = 3.7 Hz), 123.3 (q, J = 3.8 Hz), 122.1, 121.5, 120.2, 108.5, 107.2, 101.3, 94.2, 59.8, 59.7, 59.6, 34.9, 34.8, 34.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.7. HRMS (ESI+/TOF) Calcd for $C_{31}H_{30}F_3NO_7SNa^+$ $[M + Na]^+$: 640.1587. Found: 640.1582.

*(2Z,7Z)-5-((Z)-4-Hydroxy-3-phenylbut-2-en-1-yl)-5-nitro-2,8-diphenylnona-2,7-diene-1,9-diol (**7c**).* Compound **7c** was prepared following the general procedure from nitromethane (10.8 μL, 0.20 mmol) and cyclic carbonate **1a** (117.9 mg, 0.62 mmol). The product was purified by flash chromatography on silica gel using 30-70 % EtOAc/cyclohexane to afford the title compound (38.8 mg, 39 % yield) as a yellowish foam. R_f 0.05 (EtOAc/cyclohexane 1:1). IR (neat): 3568, 3326, 3055, 3024, 2953, 2922, 2851, 1598, 1534, 1492, 1443, 1353, 1013, 948, 847, 765, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41–7.28 (m, 15H), 5.70 (t, J = 7.4 Hz, 3H), 4.54 (s, 6H), 3.12 (d, J = 7.4 Hz, 6H), 1.78 (br s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.1, 140.4, 128.8, 128.0, 126.7, 123.0, 94.4, 59.9, 34.8. HRMS (ESI+/TOF) Calcd for $C_{31}H_{33}NO_5Na^+$ $[M + Na]^+$: 522.2251. Found: 522.2254.

Synthesis of homoallylic amines 8a and 8b. In a 25 mL round-bottomed flask, the homoallylic nitroalkane substrate (1.0 equiv.) was dissolved in EtOH (0.15 M) under Ar. Then, 1 M HCl (0.1 M) was added dropwise, followed by the addition of activated zinc dust (30 equiv.). The mixture was stirred at rt for 8 h. The mixture was basified with $NaHCO_3$ (aq, sat) and the solids were removed by filtration. The aqueous phase was extracted three times with EtOAc (20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel to afford the corresponding homoallylic amine. See the SI for full analysis of these two compounds.

*(Z)-5-amino-2-phenylhex-2-en-1-ol (**8a**).* Compound **8a** was prepared following the general procedure from homoallylic nitroalkane **3a** (66.4 mg, 0.30 mmol). The product was purified by flash chromatography on silica gel using 10-20 % MeOH/CH_2Cl_2 to afford the title compound (42.5 mg, 74 % yield) as a yellowish oil. R_f 0.03 (MeOH/CH_2Cl_2 1:9). IR (neat): 3344, 3283, 3080, 3055, 3025, 2959, 2925, 2871, 1727, 1597, 1493, 1445, 1374, 1343, 1009, 940, 765, 696 cm^{-1}. ^1H NMR (500 MHz, CD_3OD): δ 7.50–7.43 (m, 2H), 7.34–7.27 (m, 2H), 7.26–7.19 (m, 1H), 5.90 (t, J = 7.7 Hz, 1H), 4.53 (d, J = 12.1 Hz, 1H), 4.50 (d, J = 12.1 Hz, 1H), 3.11 (sext, J = 6.5 Hz, 1H), 2.51–2.35 (m, 2H), 1.20 (d, J = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, CD_3OD): δ 143.0, 129.2, 129.1, 128.0, 127.5, 127.4, 59.7, 48.3, 38.2, 22.2. HRMS (ESI+/TOF) Calcd for $C_{12}H_{18}NO^+$ $[M + H]^+$: 192.1383. Found: 192.1390.

*(Z)-5-amino-3-methyl-2-phenylhex-2-en-1-ol (**8b**).* Compound **8b** was prepared following the general procedure from homoallylic nitroalkane **4k** (32.6 mg, 0.13 mmol). The product was purified by flash chromatography on silica gel using 10-20 % MeOH/CH_2Cl_2 to afford the title compound (48.7 mg, 79 % yield) as a yellowish oil. R_f 0.06 (MeOH/CH_2Cl_2 1:9). IR (neat): 3375, 3051, 3019, 2974, 2931, 2506, 2188, 1600, 1492, 1441, 1386, 1202, 1156, 1109, 1058, 993, 768, 720, 701 cm^{-1}. ^1H NMR (500 MHz, CD_3OD): δ 7.37–7.31 (m, 2H), 7.28–7.23 (m, 1H), 7.23–7.19 (m, 2H), 4.45 (d, J = 12.0 Hz, 1H), 4.25 (d, J = 12.0 Hz, 1H), 3.53 (sext, J = 6.9 Hz, 1H), 2.69 (dd, J = 13.6, 7.3 Hz, 1H), 2.54 (dd, J = 13.6, 7.4 Hz, 1H), 1.64 (s, 3H), 1.38 (d, J = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, CD_3OD): δ 143.3, 140.9, 132.3, 129.8, 129.2, 127.7, 63.2, 47.3, 40.3, 20.4, 19.3. HRMS (ESI+/TOF) Calcd for $C_{13}H_{19}NONa^+$ $[M + Na]^+$: 228.1359. Found: 228.1364.

Synthesis of derivatives 8c and 8d.

*(Z)-5-nitro-2-phenylhex-2-en-1-yl benzoate (**8c**).* In a flame-dried 25 mL round-bottomed flask, compound **3a** (170.0 mg, 0.77 mmol) was dissolved in dry CH_2Cl_2 (2.3 mL) under Ar. Then, pyridine (249 μL, 3.07 mmol) was added dropwise and the mixture was cooled to 0 ºC. Thereafter, benzoyl chloride (107 μL, 0.92 mmol) was added dropwise, and the mixture was allowed to warm to rt and was stirred for 14 h. The reaction was quenched with 1M HCl and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with $NaHCO_3$ (aq, sat) and brine (1 × 15 mL), and were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel using 5% Et_2O/hexane to afford compound **8c** (178.9 mg, 72% yield) as a colorless oil. R_f 0.26 (Et_2O/hexane 1:9). IR (neat): 3061, 3032, 2990, 2938, 2899, 1714, 1601, 1546, 1492, 1449, 1389, 1359, 1313, 1264, 1214, 1176, 1107, 1098, 1070, 1024, 958, 762, 738, 710, 697 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.97–7.92 (m, 2H), 7.56–7.51 (m, 1H), 7.44–7.38 (m, 4H), 7.37–7.32 (m, 2H), 7.32–7.27 (m, 1H), 5.92 (t, J = 7.6 Hz, 1H), 5.30 (app d, J = 12.5 Hz, 1H), 5.19 (app d, J = 12.5 Hz, 1H), 4.71 (dqd, J = 8.1, 6.7, 5.5 Hz, 1H), 3.10 (dt, J = 15.2, 7.9 Hz, 1H), 2.88 (ddd, J = 15.2, 7.5, 5.5 Hz, 1H), 1.63 (d, J = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.5, 140.1, 139.0, 133.2, 130.0, 129.8, 128.6, 128.5, 128.0, 127.1,

126.5, 83.0, 61.5, 34.1, 19.1. HRMS (ESI+/TOF) Calcd for $C_{19}H_{19}NNaO_4$ $[M + Na]^+$: 348.1206. Found: 348.1215.

(Z)-5-oxo-2-phenylhex-2-en-1-yl benzoate ***(8d)***.[29] In an argon-flushed 25 mL round-bottomed flask, compound **8c** (65.1 mg, 0.20 mmol) was dissolved in MeOH (3.0 mL) under Ar. The solution was cooled to 0 ºC and NaOMe (137 μL, 0.60 mmol, 25% in MeOH) was added. In a separate flask, NH_4OAc (531.9 mg, 6.90 mmol) was dissolved in H_2O (1.2 mL) and $TiCl_3$ (1.1 mL, 1.10 mmol, 12% in HCl) was added dropwise. After that, the mixture of $TiCl_3$ was transferred with a cannula to the other reaction flask in 5 minutes. The mixture was stirred at 0 ºC for 3 h. Hereafter, the product was extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with $NaHCO_3$ (2 × 10 mL) and brine (1 × 10 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel using 5-15% EtOAc/Hexane to afford compound **8d** (31.1 mg, 53 % yield) as a colorless oil. R_f 0.30 (EtOAc/Hexane 2:8). IR (neat): 3060, 3032, 2960, 2924, 2854, 1713, 1601, 1493, 1451, 1356, 1315, 1264, 1175, 1159, 1107, 1098, 1070, 1024, 952, 759, 710, 697 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.99–7.91 (m, 2H), 7.56–7.51 (m, 1H), 7.51–7.48 (m, 2H), 7.42–7.38 (m, 2H), 7.37–7.32 (m, 2H), 7.31–7.26 (m, 1H), 6.30 (t, J = 7.2 Hz, 1H), 5.24 (s, 2H), 3.59 (d, J = 7.2 Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 205.5, 166.6, 140.2, 137.4, 133.2, 130.1, 129.8, 128.6, 128.5, 127.8, 126.4, 125.9, 62.0, 43.3, 30.1. HRMS (ESI+/TOF) Calcd for $C_{19}H_{18}NaO_3$ $[M + Na]^+$: 317.1148. Found: 317.1149.

Crystallographic Studies. The measured crystal of **3o** was stable under atmospheric conditions; nevertheless, it was treated under inert conditions immersed in perfluoro-polyether as protecting oil for manipulation. Data Collection: measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX II 4K CCD area detector, a FR591 rotating anode with MoKα radiation, Montel mirrors and a Kryoflex low temperature device (T = −173 °C). Full-sphere data collection was used with ω and φ scans. Programs used: Data collection Apex2 V2011.3 (Bruker-Nonius 2008), data reduction Saint+Version 7.60A (Bruker AXS 2008) and absorption correction SADABS V. 2008−1 (2008). Structure Solution: SHELXTL Version 6.10 (Sheldrick, 2000) was used.[30] Structure Refinement: SHELXTL-97-UNIX VERSION.

Crystal data for homoallylic nitroalkane 3o. $C_{21.5}H_{21}N_2O_{5.5}$, M_r = 395.40, monoclinic, $P2(1)/n$, a = 13.6502(8) Å, b = 5.5638(3) Å, c = 25.477(2) Å, α = 90º, β = 93.556(6)º, γ = 90º, V = 1931.2(2) $Å^3$, Z = 4, ρ = 1.360 mg·M^{-3}, μ = 0.099 mm^{-1}, λ = 0.71073 Å, T = 100(2) K, F(000) = 832, crystal size = 0.20 × 0.10 × 0.05 mm, θ(min) = 1.74°, θ(max) = 27.80°, 5097 reflections collected, 5097 reflections unique, GoF = 0.932, R_1 = 0.0418 and wR_2 = 0.0854 [$I > 2\sigma(I)$], R_1 = 0.0761 and wR_2 = 0.0970 (all indices), min/max residual density = −0.202/0.245 [e·$Å^{-3}$]. Completeness to θ(27.80°) = 88.6%. CCDC number 1837204.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsjoc.###

Catalysis screening data, NMR spectra for all known and new products (PDF), X-ray data for compound **3o** (CIF).

■ AUTHOR INFORMATION

Corresponding Author

* E-mail: akleij@iciq.es

ORCID

Àlex Cristòfol: 0000-0001-6931-6423

Arjan W. Kleij: 0000-0002-7402-4764

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENT

We thank the Cerca program/Generalitat de Catalunya, ICREA, MINECO (CTQ2017-88920-P) and AGAUR (2017-SGR-232) for support.

■ REFERENCES

(1) (a) Itami, K.; Yoshida, J. Platform Synthesis: A Useful Strategy for Rapid and Systematic Generation of Molecular Diversity. *Chem. Eur. J.* **2006**, *12* (15), 3966-3974. (b) Flynn, A. B.; Ogilvie, W. W. Stereocontrolled Synthesis of Tetrasubstituted Olefins. *Chem. Rev.* **2007**, *107* (11), 4698-4745. (c) Negishi, E.; Huang, Z.; Wang, G.; Mohan, S.; Wang, C.; Hattori, H. Recent Advances in Efficient and Selective Synthesis of Di-, Tri-, and Tetrasubstituted Alkenes via Pd-Catalyzed Alkenylation-Carbonyl Olefination Synergy. *Acc. Chem. Res.* **2008**, *41* (11), 1474-1485. (d) Shindo, M.; Mori, S. Torquoselective Olefination of Carbonyl Compounds with Ynolates: Highly Efficient Stereoselective Synthesis of Tetrasubstituted Alkenes. *Synlett*, **2008**, (15), 2231-2243.

(2) (a) Ono, N. *The Nitro Group in Organic Synthesis*; John Wiley & Sons: New York, 2001. (b) Ballini, R.; Bosica, G.; Fiorini, D.; Palmieri, A.; Petrini, M. Conjugate Additions of Nitroalkanes to Electron-Poor Alkenes: Recent Results. *Chem. Rev.* **2005**, *105* (3), 933-972. (c) Ballini, R.; Petrini, M.; Rosini, G. Nitroalkanes as Central Reagents in the Synthesis of Spiroketals. *Molecules* **2008**, *13* (2), 319-330.

(3) For selected reviews see: (a) Trost, B. M. Metal Catalyzed Allylic Alkylation: Its Development in the Trost Laboratories. *Tetrahedron* **2015**, *71* (35), 5708-5733. (b) Butt, N. A.; Zhang, W. Transition Metal-Catalyzed Allylic Substitution Reactions with Unactivated Allylic Substrates. *Chem. Soc. Rev.* **2015**, *44* (22), 7929-7967. (c) Qu, J.; Helmchen, G. Applications of Iridium-Catalyzed Asymmetric Allylic Substitution Reactions in Target-Oriented Synthesis. *Acc. Chem. Res.* **2017**, *50* (10), 2539-2555. (d) Bayeh, L.; Tambar, U. K. Catalytic Asymmetric Intermolecular Allylic Functionalization of Unactivated Internal Alkenes. *ACS Catal.* **2017**, *7* (12), 8533-8543.

(4) For the synthetic importance and utility of homoallylic amines see: (a) Ochoa Puentes, C.; Kouznetsov, V. Recent Advancements in the Homoallylamine Chemistry. *J. Heterocyclic Chem.* **2002**, *39* (4), 595-614. (b) Ding, H.; Friestad, G. K. Asymmetric Addition of Allylic Nucleophiles to Imino Compounds. *Synthesis* **2005**, (17), 2815-2829. (c) Shibasaki, M.; Kanai, M. Asymmetric Synthesis of Tertiary Alcohols and α-Tertiary Amines via Cu-Catalyzed C−C Bond Formation to Ketones and Ketimines. *Chem. Rev.* **2008**, *108* (8), 2853-2873. (d) Batey, R.; Ramadhar, T. Allylation of Imines and Their Derivatives with Organoboron Reagents: Stereocontrolled Synthesis of Homoallylic Amines. *Synthesis* **2011**, (9), 1321-1346. (e) Gandhi, S.; List, B. Catalytic Asymmetric Three-Component Synthesis of Homoallylic Amines. *Angew. Chem. Int. Ed.* **2013**, *52* (9), 2573-2576. (f) Niu, D.; Wan, L.; Tian, L.; Liu, J. Iridium-Catalyzed Asymmetric Umpolung Allylation of N-Fluorenyl Imines to Prepare 1,4-Disubstituted Homoallylic Amines. *Synlett* **2017**, *28* (16), 2051-2056.

(5) (a) Rieck, H.; Helmchen, G. Palladium Complex Catalyzed Asymmetric Allylic Substitutions with Nitromethane: Enantioselectivities Exceeding 99.9% ee. *Angew. Chem. Int. Ed. Engl.* **1996**, *34* (23-

24), 2687-2698. (b) Trost, B. M.; Surivet, J.-P. Diastereo- and Enantioselective Allylation of Substituted Nitroalkanes. *J. Am. Chem. Soc.* **2000**, *122* (26), 6291-6292. (c) Trost, B. M.; Jiang, C. Atom Economic Asymmetric Creation of Quaternary Carbon: Regio- and Enantioselective Reactions of a Vinylepoxide with a Carbon Nucleophile. *J. Am. Chem. Soc.* **2001**, *123* (51), 12907-12908. (d) Uozumi, Y.; Suzuka, T. π-Allylic C1-Substitution in Water with Nitromethane Using Amphiphilic Resin-Supported Palladium Complexes. *J. Org. Chem.* **2006**, *71* (22), 8644-8646. (e) Ohmatsu, K.; Ito, M.; Kunieda, T.; Ooi, T. Ion-Paired Chiral Ligands for Asymmetric Palladium Catalysis. *Nat. Chem.* **2012**, *4*, 473-477. (f) Yang, X.-F.; Yu, W.-H.; Ding, C.-H.; Ding, Q.-P.; Wan, S.-L.; Hou, X.-L.; Dai, L.-X.; Wang, P.-J. Palladium-Catalyzed Regio-, Diastereo-, and Enantioselective Allylation of Nitroalkanes with Monosubstituted Allylic Substrates. *J. Org. Chem.* **2013**, *78* (13), 6503-6509. (g) Chaudhuri, S.; Bhunia, S.; Roy, A.; Das, M. K.; Bisai, A. Biomimetic Total Syntheses of Clavine Alkaloids. *Org. Lett.* **2018**, *20* (1), 288-291.

(6) (a) Aleksandrowicz, P.; Piotrowska, H.; Sas, W. Palladium catalyzed C-allylation of nitroalkanes. *Tetrahedron Lett.* **1982**, *38* (9), 1321-1327. (b) Maki, K.; Kanai, M.; Shibasaki, M. Pd-Catalyzed Allylic Alkylation of Secondary Nitroalkanes. *Tetrahedron Lett.* **2007**, *63* (20), 4250-4257. (c) Grenning, A. J.; Tunge, J. A. Rapid Decarboxylative Allylation of Nitroalkanes. *Org. Lett.* **2010**, *12* (4), 740-742. (d) Grenning, A. J.; Tunge, J. A. Deacylative Allylation of Nitroalkanes: Unsymmetric Bisallylation by a Three-Component Coupling. *Angew. Chem. Int. Ed.* **2011**, *50* (7), 1688-1691. (e) Lang, S. B.; Locascio, T. M.; Tunge, J. A. Activation of Alcohols with Carbon Dioxide: Intermolecular Allylation of Weakly Acidic Pronucleophiles. *Org. Lett.* **2014**, *16* (16), 4308-4311. (f) Chang, C.-Y.; Wu, Y.-K. Palladium-Catalyzed α-Allylation of Secondary Nitroalkanes with Allylic Alcohols and Strategic Exploitation of Seebach's Reagent for the Total Synthesis of (±)-Adalinine. *J. Org. Chem*. **2018**, *83* (11), 6217-6224. For an intramolecular example see: (g) Genet, J. P.; Grisoni, S. Ergoline Precursors 2. An Efficient Synthesis of c Ring by Palladium (0) Catalyzed Reactions. *Tetrahedron Lett.* **1986**, *27* (35), 4165-4168.

(7) Ognyanov, V.; Hesse, M. Palladium-Catalyzed Synthesis of 2-Allyl-2-nitrocycloalkanones. *Synthesis* **1985**, (6-7), 645-647.

(8) Chen, M. Z.; McLaughlin, M.; Takahashi, M.; Tarselli, M. A.; Yang, D.; Umemura, S.; Micalizio, G. C. Preparation of Stereodefined Homoallylic Amines from the Reductive Cross-Coupling of Allylic Alcohols with Imines. *J. Org. Chem*. **2010**, *75* (23), 8048-8059.

(9) For selected seminal contributions: (a) Bando, T.; Harayama, H.; Fukazawa, Y.; Shiro, M.; Fugami, K.; Tanaka, S.; Tamaru, Y. Regio- and Stereoselective Synthesis of 1,3-Hydroxyl Amines via Palladium-Catalyzed Carbonate-Carbamate Transformation with Unique Stereoselectivity: Synthesis of 3-Amino-4-penten-1-ols. *J. Org. Chem.* **1994**, *59* (6), 1465-1474. (b) Ohmatsu, K.; Imagawa, N.; Ooi, T. Ligand-Enabled Multiple Absolute Stereocontrol in Metal-Catalysed Cycloaddition for Construction of Contiguous All-Carbon Quaternary Stereocentres. *Nat. Chem*. **2014**, *6*, 47-51. (c) Khan, A.; Zheng, R.; Kan, Y.; Ye, J.; Xing, J.; Zhang, Y. J. Palladium-Catalyzed Decarboxylative Cycloaddition of Vinylethylene Carbonates with Formaldehyde: Enantioselective Construction of Tertiary Vinylglycols. *Angew. Chem. Int. Ed*. **2014**, *53* (25), 6439-6442. (d) Zhang, Y. J.; Yang, J. H.; Kim, S. H.; Krische, M. J. *anti*-Diastereo- and Enantioselective Carbonyl (Hydroxymethyl)allylation from the Alcohol or Aldehyde Oxidation Level: Allyl Carbonates as Allylmetal Surrogates. *J. Am. Chem. Soc*. **2010**, *132* (13), 4562-4563.

(10) (a) Guo, W.; Martínez-Rodríguez, L.; Kuniyil, R.; Martin, E.; Escudero-Adán, E. C.; Maseras, F.; Kleij, A. W. Stereoselective and Versatile Preparation of Tri- and Tetra-Substituted Allylic Amine Scaffolds under Mild Conditions. *J. Am. Chem. Soc.* **2016**, *138* (36), 11970-11978. (b) Cai, A.; Guo, W.; Martínez-Rodríguez, L.; Kleij, A. W. Palladium-Catalyzed Regio- and Enantio-Selective Synthesis of Allylic Amines Featuring Tetrasubstituted Tertiary Carbons. *J. Am. Chem. Soc*. **2016**, *138* (43), 14194-14197. (c) Guo, W.; Cai, A.; Xie, J.; Kleij, A. W. Asymmetric Synthesis of α,α-Disubstituted Allylic Amines through Palladium-Catalyzed Allylic Substitution. *Angew. Chem. Int. Ed*. **2017**, *56* (39), 11797-11801.

(11) (a) Guo, W.; Martínez-Rodríguez, L.; Martín, E.; Escudero-Adán, E. C.; Kleij, A. W. Highly Efficient Catalytic Formation of (Z)-1,4-But-2-ene Diols using Water as a Nucleophile. *Angew. Chem. Int. Ed*. **2016**, *55* (37), 11037-11040. (b) Xie, J.; Guo, W.; Cai, A.; Escudero-Adán, E. C.; Kleij, A. W. Pd-Catalyzed Enantio- and Regioselective Formation of Allylic Aryl Ethers. *Org. Lett*. **2017**, *19* (23), 6388-6391.

(12) Gómez, J. E.; Guo, W.; Kleij, A. W. Palladium-Catalyzed Stereoselective Formation of Substituted Allylic Thioethers and Sulfones. *Org. Lett*. **2016**, *18* (23), 6042-6045.

(13) The preparation of (*Z*)-configured products from the allylation of nitroalkanes is not well-developed, see ref. 7.

(14) The isolated yield of **3a** through column purification could not be improved despite several attempts.

(15) The low stereoselectivity towards **3e** is ascribed to possible interference of the alcohol group of the nitroalkane with the catalytic species formed after decarboxylation of the VCC, see Scheme 1.

(16) Since a number of the resultant monoallylated nitroalkanes still incorporate an α-acidic hydrogen, the products are susceptible towards double allylation. Such "over-allylation" has been observed by other authors, see for instance ref. 5a. Interestingly, Tunge and coworkers also reported a selective and sequential approach towards unsymmetrical bis-allylated nitroalkanes, see ref. 6c.

(17) We recently reported the cross-coupling of VCCs, see: W. Guo, W.; Kuniyil, R.; Gómez, J. E.; Maseras, F.; Kleij, A. W. A Domino Process towards Functionally Dense Quaternary Carbons through Pd-Catalyzed Decarboxylative Csp3-Csp3 Bond Formation. *J. Am. Chem. Soc*. **2018**, *140* (11), 3981-3987.

(18) The group of Shibasaki reported that a basic additive is needed to boost the reactivity of the nitronate anion when secondary nitroalkanes are used, see ref. 6b.

(19) Benzoyl nitromethane is regarded as a synthetic equivalent to nitromethane. Intramolecular acyl transfer has been postulated as an operating mechanism, see: (a) Gao, Y.; Ren, Q.; Siau, W.-Y.; Wang, J. Asymmetric Organocatalytic Cascade Michael/Hemiketalization/Retro-Henry reaction of β,γ-Unsaturated Ketoesters with α-Nitroketones. *Chem. Commun*. **2011**, *47* (20) 5819-5821. (b) Lu, R.-J.; Yan, Y.-Y.; Wang, J.-J.; Du, Q.-S.; Nie, S.-Z.; Yan, M. Organocatalytic Asymmetric Conjugate Addition and Cascade Acyl Transfer Reaction of α-Nitroketones. *J. Org. Chem*. **2011**, *76* (15), 6230-6239. (c) Giorgi, G.; López-Alvarado, P.; Miranda, S.; Rodriguez, J.; Menéndez, J. C. Michael Additions in Aqueous Media: "On-Water" and "In-Water" Processes from α-Nitro Ketones and Their Anions. *Eur. J. Org. Chem*. **2013**, (7), 1327-1336.

(20) Yamamura, S.; Toda, M.; Hirata, Y. Modified Clemmensen Reduction: Cholestane. *Org. Synth*. **1973**, *53*, 86.

(21) Burk, R. M.; Roof, M. B. A Safe and Efficient Method for Conversion of 1,2- and 1,3-Diols to Cyclic Carbonates Utilizing Triphosgene. *Tetrahedron Lett*. **1993**, *34* (3), 395-398.

(22) Piel, I.; Pawelczyk, M. D.; Hirano, K.; Fröhlich, R.; Glorius, F. A Family of Thiazolium Salt Derived N-Heterocyclic Carbenes (NHCs) for Organocatalysis: Synthesis, Investigation and Application in Cross-Benzoin Condensation. *Eur. J. Org. Chem*. **2011**, (28), 5475-5484.

(23) Cai, S.; Zhao, X.; Wang, X.; Liu, Q.; Li, Z.; Wang, D. Z. Visible-light-promoted C-C bond cleavage: photocatalytic generation of iminium ions and amino radicals. *Angew. Chem. Int. Ed*. **2012**, *51* (32), 8050-8053.

(24) (a) Newkome, G. R.; Kim, H. J.; Moorefield, C. N.; Maddi, H.; Yoo, K.-S. Syntheses of New 1 → (2 + 1) C-Branched Monomers for the Construction of Multifunctional Dendrimers. *Macromolecules* **2003**, *36* (12), 4345-4354. (b) Rezazadeh, S.; Devannah, V.; Watson, D. A. Nickel-Catalyzed C-Alkylation of Nitroalkanes with Unactivated Alkyl Iodides. *J. Am. Chem. Soc*. **2017**, *139* (24), 8110-8113.

(25) Manna, M. S.; Mukherjee, S. Organocatalytic Enantioselective Formal C(sp2)–H Alkylation. *J. Am. Chem. Soc*. **2015**, *137* (1), 130-133.

(26) Griesser, H.; Öhrlein, R.; Schwab, W.; Ehrler, R.; Jäger, V. 3-Nitropropanal, 3-Nitropropanol, And 3-Nitropropanal Dimethyl Acetal. *Org. Synth*. **2000**, *77*, 236.

(27) Hamberger, H.; Stütz, P.; Schulz, G. Polare Äthylene II die Synthese von Nitro- und Amino-Acetaldehyddithioacetalen. *Tetrahedron Lett*. **1977**, *18* (41), 3623-3624.

(28) (a) Kai, Y.; Knochel, P.; Kwiatkowski, S.; Dunitz, J. D.; Oth, J. F. M.; Seebach, D.; Kalinowski, H.-O. Structure, Synthesis, and Properties of Some Persubstituted 1,2-Dinitroethanes. In Quest of Nitrocyclopropyl-Anion Derivatives. *Helv. Chim. Acta* **1982**, *65* (1), 137-161. (b) Zhao, M.; Lu, W. Visible Light-Induced Oxidative Chlorination of Alkyl sp3 C-H Bonds with NaCl/Oxone at Room Temperature. *Org. Lett.* **2017**, *19* (17), 4560-4563.

(29) Ballini, R.; Petrini, M. The Nitro to Carbonyl Conversion (Nef Reaction): New Perspectives for a Classical Transformation. *Adv. Synth. Catal.* **2015**, *357* (11), 2371-2402.

(30) G. M. Sheldrick, SHELXTL Crystallographic System, version 6.10; Bruker AXS, Inc.: Madison, WI, **2000**.