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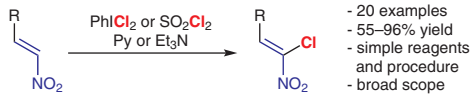
Chlorination of Conjugated Nitroalkenes with $PhICl_2$ and SO_2Cl_2 for the Synthesis of α-Chloronitroalkenes

Anastasia A. Fadeeva[a,b]
Sema L. Ioffe[a]
Andrey A. Tabolin*[a]

[a] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prosp. 47, Moscow 119991, Russian Federation
atabolin@ioc.ac.ru
tabolin87@mail.ru
[b] Higher Chemical College, D. Mendeleev University of Chemical Technology of Russia, Miusskaya sq. 9, Moscow 125047, Russian Federation



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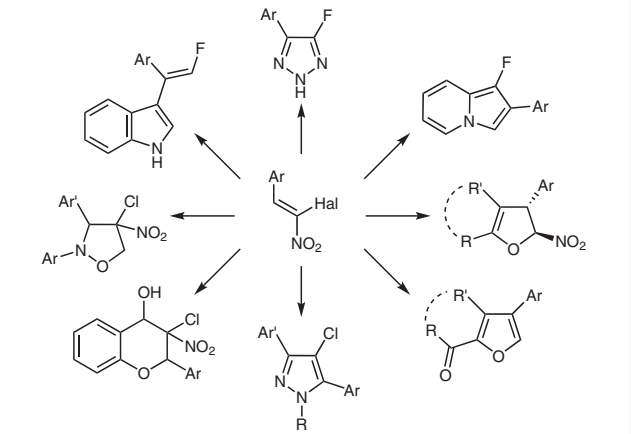
Abstract Chlorination of conjugated nitroalkenes with iodobenzene dichloride or sulfuryl chloride to give target α-chloronitroalkenes in good yields is described. Details of the procedure depend on the donating ability of the nitroalkene substituents. The activity of the described chlorinating agents increases in order '$PhICl_2$/Py' < 'SO_2Cl_2' < 'SO_2Cl_2/HCl' with the former producing the best yields for highly donating substrates and the latter for non-activated groups. An autocatalytic role of hydrogen chloride and the chemoselectivity of chlorination were also demonstrated.

Key words nitroalkenes, halogenation, chlorination, nitro compounds, chemoselectivity

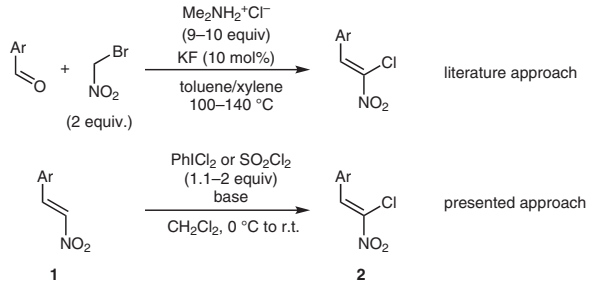
Conjugated nitroalkenes serve as versatile intermediates for organic synthesis. The high electrophilicity of these substrates gives rise to diverse chemical transformations such as Michael addition, Diels–Alder cycloaddition, (3+2)-cycloaddition and other ring-forming reactions, including their asymmetric variants.[1] Importantly, the high activating ability of the nitro group allows for installation of the prerequisite functionality into the target molecule using appropriately functionalized substrates. Thus, α-halonitroalkenes are used in the synthesis of halonitroalkyl-substituted products and (after elimination of HHal and/or HNO_2) halovinyl-substituted products and aromatics (Scheme 1).[2] In such a manner, fluorinated 1,2,3-triazoles,[3] fluorinated indolizines and their derivatives,[4] various fluorovinyl derivatives,[5] chlorinated flavone derivatives,[6] chloropyrazoles,[7] chloroisoxazolidines,[8] furane derivatives[9] and many other compounds were prepared.[10] However, α-halonitroalkenes are not always readily available substrates. Indeed, electrophilic substitution in the respective non-halogenated substrates **1** could be considered as the most straightforward pathway toward halonitroalkenes **2**. Nevertheless, this procedure is widely used only for bromination;[11] the synthesis of other α-halonitroalkenes often requires indirect routes.[12] For instance, chlorination of nitroalkenes is poorly described in the literature, presumably because of the dangerous nature of gaseous chlorine.[13–15] Particularly, Zhao et al. reported a few examples of the formation of chloronitroalkenes during attempted chloroformyloxylation of alkenes using the $PhICl_2$/DMF/H_2O system.[15] Therefore, the most popular procedure for the preparation of chloronitroalkenes is the Dauzonne method, starting from aromatic aldehydes and bromonitromethane (Scheme 2).[16] Despite a broad substrate scope, it has drawbacks such as the use of large amounts of reagents (e.g., 10-fold excess of $Me_2NH_2^+Cl^-$) and formation of variable amounts of the corresponding bromo-derivatives as side-products.[9a] Thus, considering the importance of organochlorine compounds,[17] development of new methods for the synthesis of α-chloronitroalkenes is desirable. We envisioned that



Scheme 1 Application of α-halogenated nitroalkenes in organic synthesis

Georg Thieme Verlag KG, Rüdigerstraße 14, 70469 Stuttgart, Germany

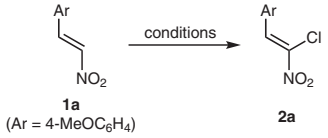
employment of a suitable, readily available equivalent of Cl_2 would allow direct chlorination of conjugated nitroalkenes. Here, we describe our results on the use of $PhICl_2$ and SO_2Cl_2 for the preparation of α-chloronitroalkenes.



Scheme 2 Approaches toward α-chloronitroalkenes

We started our study with the model reaction of nitroalkene **1a**. Various commercial or readily available chlorinating agents were tested under different conditions (Table 1). *A priori* electron-withdrawing nitro group should drastically deactivate a C=C double bond toward electrophilic substitution. Indeed, for cases of N-chlorosuccinimide and 1,3-dichloro-5,5-dimethylhydantoin (entries 1–3), incomplete consumption of starting material was observed, indicating insufficient activity of the chlorinating agent. *tert*-Butyl hypochlorite and trichloroisocyanuric acid gave higher conversion, albeit with moderate yields (entries 4–6). Much better results were obtained using iodobenzene dichloride, which provided good yields of target product **2a**. Further variations showed little dependence on the solvent (entries 7–9) and pyridine was an appropriate base (entries 7 and 11). Apart from $PhICl_2$, another positive result was obtained with commercially available reagent, sulfuryl chloride, which also provided the target chlorinated alkene **2a** in >90% yield (entry 16). Here, higher yield was obtained with triethylamine as base and separation of chlorination and elimination steps (see Scheme 4 below for further details). Notably, for both $PhICl_2$ and SO_2Cl_2, immediate addition of Et_3N and chlorinating reagent to alkene **1** gave inferior results (entries 11 and 13) due to higher sensitivity of the amine toward oxidation compared to substrate **1a**. In turn, the ability of Et_3N to quench SO_2Cl_2 was useful to prevent side reactions. For instance, quenching with pyridine resulted in lower yield, which we ascribed to chlorination of the C=C bond in the target conjugated nitroalkene **2a** (entry

Table 1 Screening of the Reaction Conditions for the Synthesis of Nitroalkene **2a**



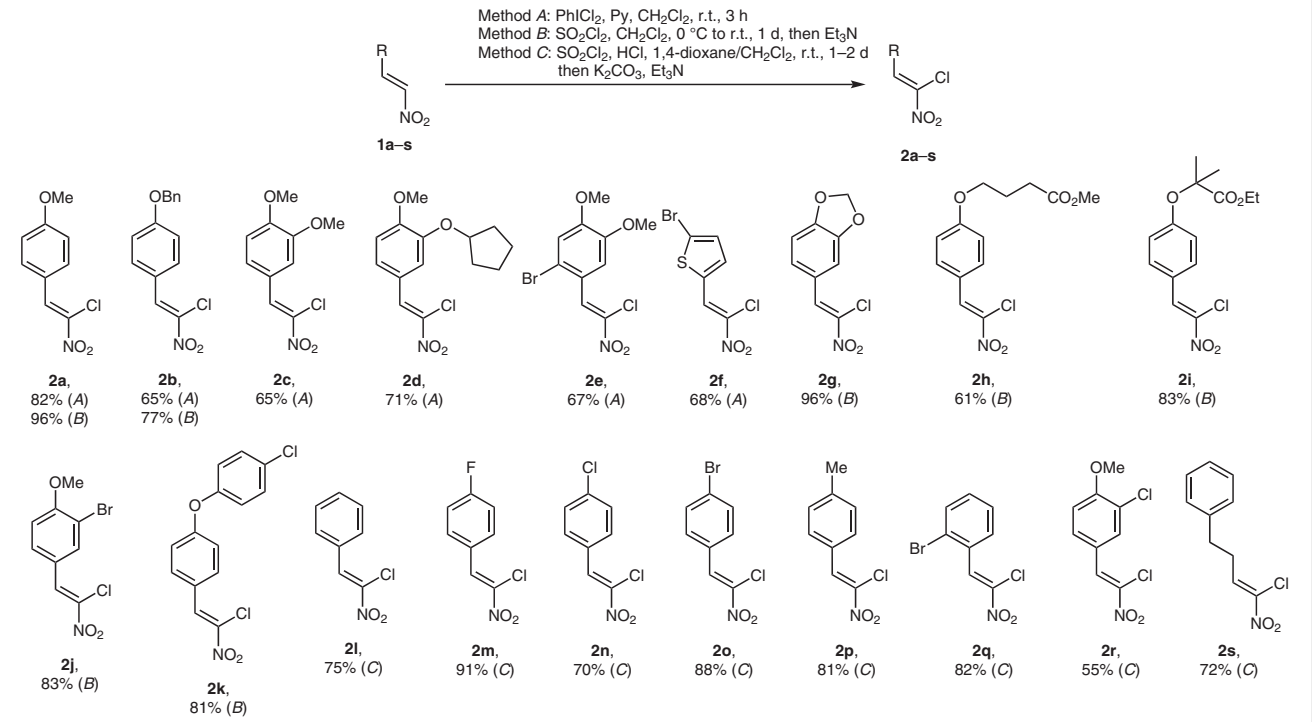
Entry	Reagents (equivalents)	Solvent, temperature, time	Recovery of **1a** (%)[a]	Yield **2a** (%)[a]
1	NCS (1.2), Py (2)	CH_2Cl_2, r.t., 3 h	71	14
2	NCS (1.2), Py (2)	$ClCH_2CH_2Cl$, 70 °C, 15 h	34	58
3	1,3-dichloro-5,5-dimethylhydantoin (1.2), Py (2)	CH_2Cl_2, r.t., 3 h	65	11
4	$(CONCl)_3$ (0.4), Py (2)	CH_2Cl_2, r.t., 4 h	51	34
5	$(CONCl)_3$ (1.2), Py (2)	CH_2Cl_2, r.t., 3 h	0	31
6	*t*-BuOCl (2), Py (2)	CH_2Cl_2, r.t., 2 d	5	66
7	**$PhICl_2$ (1.2), Py (2)**	**CH_2Cl_2, r.t., 3 h**	**0**	**87**
8	$PhICl_2$ (1.2), Py (2)	THF, r.t., 3 h	0	85
9	$PhICl_2$ (1.2), Py (2)	MeCN, r.t., 3 h	0	82
10	$PhICl_2$ (1.2), Py (2)	CH_2Cl_2, 0 °C, 3 h	17	69
11	$PhICl_2$ (1.2), Et_3N (2)	CH_2Cl_2, r.t., 4 d	82	2
12	SO_2Cl_2 (1.1), Py (2)	CH_2Cl_2, r.t., 3 d	15	82
13	SO_2Cl_2 (1.1), Et_3N (2)	CH_2Cl_2, r.t., 3 h	63	33
14	SO_2Cl_2 (1.1), then Py (2)	CH_2Cl_2, r.t., 3 h, then 1.5 h	0	52
15	SO_2Cl_2 (1.1), then Et_3N (1.7)	CH_2Cl_2, r.t., 3 h, then 1 h	0	96
16	**SO_2Cl_2 (1.1), then Et_3N (1.7)**	**CH_2Cl_2, 0 °C, 1 d, then 1 h**	0	**96**

[a] Based on ^1H NMR spectroscopic analysis with internal standard (methyl 3,5-dinitrobenzoate).

14). Overall, two procedures (entries 7 and 16) were chosen for further investigation.

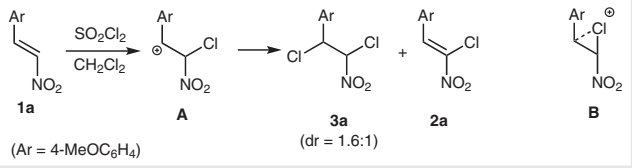
For the determination of substrate scope, a wide variety of nitroalkenes **1** was selected (Scheme 3). The $PhICl_2$-based procedure (method A) was found to give good yields of target products **2** for rather electron-rich substrates, e.g., those possessing *p*-methoxy-substituent. In such a way, nitroalkenes **2a–f** were obtained. However, the sensitivity of the reaction to the electronic demand of the aromatic ring was rather high; for example, attempted syntheses of products **2g** and **2j** resulted in incomplete consumption of starting material. In the absence of donating substituent, such as in the case of *p*-halogen-nitrostyrenes **1m–o**, the chlorination with $PhICl_2$ failed; this is consistent with Zhao's results, wherein incomplete consumption of starting materials was also reported in such cases.[15] The SO_2Cl_2-based procedure (method B) was found to be complementary to the $PhICl_2$-based approach. Thus, by using SO_2Cl_2 as a chlorinating agent, products **2a**, **2b**, and **2g–k** were successfully prepared. In contrast to method A, the use of method B for excessively electron-rich substrates (e.g., **1c** and **1d**) resulted in mixtures of products, presumably because of chlorination of the aromatic ring. Scalability of the process was demonstrated with the preparation of gram quantities of product **2a**. Overall, chlorination with methods A and B gave products **2a–k**, including those with a thiophene ring and pharmaceutically relevant catechol substituents.[18] An additional advantage of the SO_2Cl_2-procedure is the rather easy purification of target compounds **2** since ionic (e.g., triethylammonium salts) and volatile (e.g., SO_2) by-products are removed via extractive work-up and evaporation. The structures of target nitroalkenes **2** were supported by ^1H and ^{13}C NMR spectroscopic analysis as well as by HRMS or elemental analysis data. In all cases, a single isomer at the C=C double bond was observed, the *Z*-configuration of which was assigned by comparison with reported data.[16a]

To take a deeper look at the chlorination of nitroalkenes with sulfuryl chloride, we analyzed the content of the reaction mixture (**1a**+SO_2Cl_2) prior to the addition of triethylamine. Interestingly, it consisted of two diastereomers of dichloride **3a** (dr = 1.6:1, total yield 75% according to ^1H NMR analysis) and chloronitroalkene **2a** (21% yield according to ^1H NMR analysis) (see Scheme 4). The low diastereoselectivity of **3a** provided evidence for the intermediacy of benzylic cation **A**, rather than chloronium structure **B**, stabilized by a *p*-methoxy substituent.[19] During the course of the reaction, **A** can add a chloride anion from either side of the plane of the molecule. Moreover, prolonged exposure of the reaction mixture did not change the **2a**/**3a** ratio. This also accounted for the formation of cation **A**, which can suffer elimination of a proton, leading to **2a**. In turn, formation of **2a** meant the accumulation of hydrogen chloride in the reaction mixture. Therefore, we performed qualitative experiments to check whether HCl could influence the chlorination process (Scheme 4, Figure 1). Indeed, addition of 0.1 equivalent of HCl (as 4 M soln in 1,4-dioxane) resulted in



Scheme 3 Synthesis of α-chloronitroalkenes **2** via chlorination of nitroalkenes **1**

significant acceleration of the reaction. At 0 °C (ice-water bath) nearly full consumption of staring nitroalkene was achieved within ca. 6 h, whereas in the absence of HCl the reaction proceeded longer.[20] Thus, it can be concluded that chlorination of **1a** is autocatalytic since HCl is released during the process. We suppose that HCl may form a hydrogen bond with an oxygen atom of SO_2Cl_2, producing a more electrophilic chlorinating species.[21]



Scheme 4 Chlorination of nitroalkene **1a** with SO_2Cl_2 without Et_3N

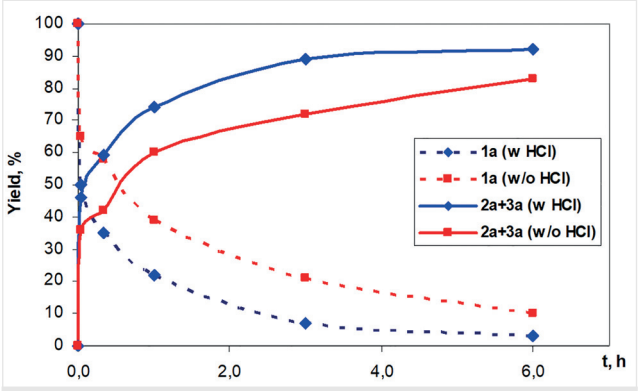
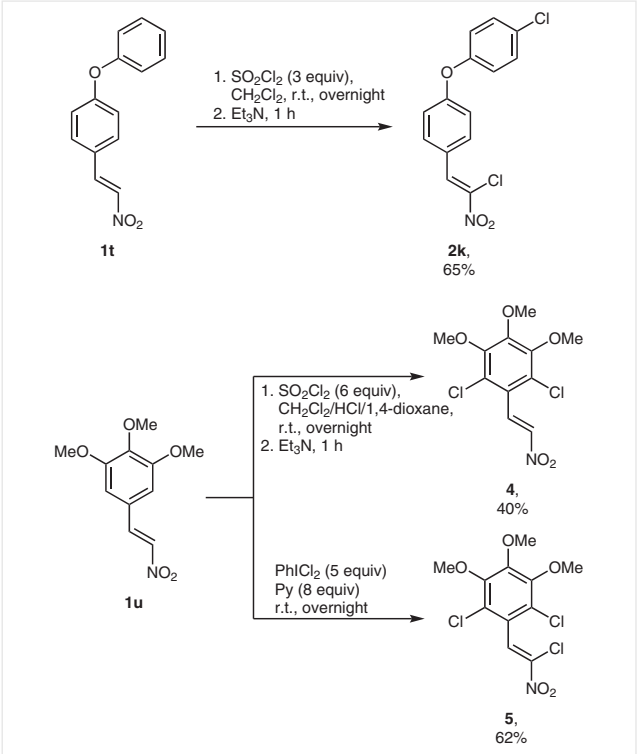


Figure 1 Time dependences of yields of reaction components for chlorination of **1a** (1 mmol in 2 mL of CH_2Cl_2) by SO_2Cl_2 (1.1 mmol) at 0 °C with and without 0.1 equiv of HCl (Scheme 4, see the Supporting Information for full data).

The revelation of the critical importance of hydrogen chloride allowed the chlorination of a wider scope of nitroalkenes **1** to be achieved. As was noted above, SO_2Cl_2 itself (method B) successfully chlorinated only electron-rich substrates. Increase of the acidity of the medium and performing the reaction in the presence of 4 equivalents of HCl (Scheme 3, Method C) resulted in good yields of chloronitroalkenes **2l–r**, possessing, for example, *p*-chloro-, *p*-bromo-, or *o*-bromo-phenyl substituents. Moreover, aliphatic nitroalkene **2s** was also prepared in reasonable yield. We also noted that formation of cations of type **A** is suppressed in these cases; no nitroalkenes **2** was observed before treatment with Et_3N and the diastereoselectivity of the formation of dichloride **3n** (based on ^1H NMR spectroscopic analysis, dr = 9:1) was high (see the experimental part). These conditions could account for increased participation of chloronium cation of type **B** in the reaction.

Finally, we should note the selectivity of the proposed method for the chlorination. As was already mentioned, for aromatic nitroalkenes, electrophilic aromatic substitution could compete with the target addition to the side-chain double bond. For the cases presented in Scheme 3 we observed selective introduction of one chlorine atom to form the C(Cl)–NO_2 moiety. In contrast, this was not the case for substrates where the activating substituent on the benzene ring is weaker (or not) conjugated with the C=C–NO_2 moiety, but also significantly activate the benzene ring. Thus, *o*- and *m*-methoxy substituted nitroalkenes **1** (Ar = 3-$MeOC_6H_4$, 2-$MeOC_6H_4$) failed to selectively give target nitroalkenes **2** due to concomitant chlorination of the aromatic ring. However, in some cases, we achieved the selective formation of polychlorinated products in reasonable yields. Thus, *p*-phenoxy-substituted substrate **1t** gave rise to chlorination of both C=C–NO_2 and the *p*-position of the benzene ring, ultimately leading to product **2k** (Scheme 5). Highly electron-donating 3,4,5-trimethoxyphenyl substituent also resulted in aromatic chlorination: for SO_2Cl_2, product **4** was isolated, whereas for $PhICl_2$ exhaustive chlorination was observed with the incorporation of three chlorine atoms in product **5**.[22]



Scheme 5 Chlorination of nitroalkenes **1t** and **1u**

In conclusion, we have demonstrated that conjugated nitroalkenes are chlorinated by either iodobenzene dichloride or sulfuryl chloride, leading to the corresponding α-chloronitroalkenes in high yields. Appropriate reaction conditions depend on the electronic demands of the substrate. The most electron-rich substrates required the $PhICl_2$/pyridine system, less electron-rich substrates used the SO_2Cl_2

system, and electron neutral substrates required the SO_2Cl_2/HCl system. The role of hydrogen chloride in promoting the reaction with SO_2Cl_2 was determined.

All reactions were performed in oven-dried (150 °C) glassware. Most of the chemicals were acquired from commercial sources and used as received. Petroleum ether (PE) and EtOAc for column chromatography were distilled. CH_2Cl_2 was distilled from CaH_2 prior to use. Brine refers to saturated aqueous solution of NaCl. Starting nitroalkenes **1** were obtained from the corresponding aldehydes and nitromethane using reported procedures (see the Supporting Information for details). $PhICl_2$ was prepared upon treatment of PhI in concd aq HCl with NaClO solution.[23] TLC were performed on silica coated on aluminum with UV254 indicator. Visualization was accomplished with UV light. Column chromatography was performed on silica (0.04–0.063 mm, 60 Å). NMR spectra were recorded at 300 K with Bruker AM300 and Fourier 300HD spectrometers at the spectrometer frequencies of 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR). Multiplicities are assigned as s (singlet), d (doublet), t (triplet), q (quadruplet), quint (quintet), m (multiplet), app (apparent). Assignment of $=CHC_{Ar}$ and $=CHNO_2$ for starting nitroalkenes **1** was made on the basis of 2D NMR analysis for **1i**. Assignment of *Z*-configuration of chloronitroalkenes **2** and **5** was made on the basis of the chemical shifts for $=CHC_{Ar}$ and comparison to reported data.[16a] Note: For chloronitroalkenes **2** the signal of $=C(Cl)NO_2$ is not always clearly visible in regular ^{13}C NMR spectra due to quadrupole broadening/low intensity, although it can be assigned on the basis of ^{1}H-^{13}C HMBC. High-resolution mass spectra were acquired with a Bruker micrOTOF spectrometer using electrospray ionization (ESI). Elemental analyses were performed in the Analytical laboratory of N. D. Zelinsky Institute. Low-resolution mass spectra were acquired at Chromatec-Crystal instrument using electron impact (EI) ionization (200 °C, ionization energy – 70 eV). Intensities relative to the most intensive peak are reported in parentheses. Melting points were determined with a Kofler melting point apparatus and are uncorrected.

Chloronitroalkenes 2a–g (Scheme 3, Method A); General Procedure

Nitroalkene **1a–g** (1 equiv) and pyridine (2 equiv) were dissolved in CH_2Cl_2 (2 mL/1 mmol of nitroalkene), and then $PhICl_2$ (1.2 equiv) was added. The mixture was stirred at r.t. for 3 h (unless otherwise stated) and extracted with EtOAc/H_2O. The aqueous layer was washed with EtOAc. Combined organic layers were washed with saturated NaCl solution, dried with anhydrous Na_2SO_4 and concentrated in vacuo to give the crude chloronitroalkene **2**.

Chloronitroalkenes 2a, 2b, 2h–k (Scheme 3, Method B); General Procedure

Nitroalkene **1a**, **1b**, **1h–k** (1 equiv) was dissolved in CH_2Cl_2 (2 mL/1 mmol of nitroalkene), the solution was cooled in an ice bath under argon atmosphere, and then SO_2Cl_2 (1.1 equiv) was added. The mixture was stirred at 0 °C for 1 d (unless otherwise stated). After completion of the reaction, Et_3N (1.7 equiv) was added and the mixture was stirred at r.t. for 1 h, and then extracted with EtOAc/H_2O. The aqueous layer was washed with EtOAc. Combined organic layers were washed with saturated NaCl solution, dried with anhydrous Na_2SO_4 and concentrated in vacuo to give the crude chloronitroalkene **2**.

Chloronitroalkenes 2l–s (Scheme 3, Method C); General Procedure

Nitroalkene **1l–s** (1 equiv) was dissolved in CH_2Cl_2 (2 mL/1 mmol of nitroalkene), and then SO_2Cl_2 (2 equiv) and HCl/dioxane (4 M, 4 equiv) were added under argon atmosphere. The mixture was stirred at r.t. for 1–2 d. After completion of the reaction, K_2CO_3 (4 equiv) was added and the mixture was stirred at r.t. for 1 h, then cooled in an ice bath, and Et_3N (3 equiv) was added. After stirring at r.t. for 1 h, the reaction mixture was extracted with EtOAc/H_2O. The aqueous layer was washed with EtOAc. Combined organic layers were washed with saturated NaCl solution, dried with anhydrous Na_2SO_4 and concentrated in vacuo to give the crude chloronitroalkene **2**.

(*Z*)-1-(2-Chloro-2-nitrovinyl)-4-methoxybenzene (2a)

Obtained from nitroalkene **1a** (358 mg, 2 mmol) according to Method A. Reaction time: 3 h. The crude product was subjected to column chromatography (eluent: 10:1, PE/EtOAc) to give the target nitroalkene **2a** (348 mg, 82%) as yellow crystals.

Obtained from nitroalkene **1a** (895 mg, 5 mmol) according to Method B. Reaction time: 1 d. The crude product was crystallized from EtOH to give target nitroalkene **2a** (1021 mg, 96%) as yellow crystals.

R_f = 0.38 (9:1, PE/EtOAc) (UV); mp 78–81 °C (Lit.[16a] 74–75 °C (hexane)).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.38 (s, 1 H, =CH), 7.89 (d, *J* = 8.9 Hz, 2 H, CH_{Ar}), 7.03 (d, *J* = 8.9 Hz, 2 H, CH_{Ar}), 3.91 (s, 3 H, OMe).

NMR matches previously reported data.[16a]

(*Z*)-1-(Benzyloxy)-4-(2-chloro-2-nitrovinyl)benzene (2b)

Obtained from nitroalkene **1b** (255 mg, 1 mmol) according to Method A with $PhICl_2$ (2 equiv). Reaction time: 3 h. The crude product was crystallized from EtOAc to give the target nitroalkene **2b** (188 mg, 65%) as yellow crystals.

Obtained from nitroalkene **1b** (255 mg, 1 mmol) according to Method B. Reaction time: 1 d. The crude product was crystallized from EtOH to give the target nitroalkene **2b** (221 mg, 77%) as yellow crystals.

R_f = 0.43 (9:1, PE/EtOAc) (UV); mp 160–161 °C (EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ = 8.38 (s, 1 H, =CH), 7.89 (d, *J* = 8.6 Hz, 2 H, CH_{Ar}), 7.51–7.33 (m, 5 H, CH_{Ph}), 7.10 (d, *J* = 8.8 Hz, 2 H, CH_{Ar}), 5.18 (s, 2 H, CH_2Ph).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HMBC, HSQC): δ = 161.8 ($C_{Ar}O$), 136.0 (C_{Ph}), 135.4 (CNO_2), 133.6 (CH_{Ar}), 131.6 (=CH), 128.8 (CH_{Ph}), 128.4 (CH_{Ph}), 127.5 (CH_{Ph}), 122.3 (C_{Ar}), 115.5 (CH_{Ar}), 70.3 (CH_2Ph).

MS (EI, 70 eV): *m*/*z* (%) = 291 (1) $[M + 2]^+$, 289 (3) $[M]^+$, 91 (100) $[C_7H_7]^+$.

Anal. Calcd. for $C_{15}H_{12}ClNO_3$: C, 62.19; H, 4.18; N, 4.83. Found: C, 62.18; H, 4.05; N, 4.81.

(*Z*)-4-(2-Chloro-2-nitrovinyl)-1,2-dimethoxybenzene (2c)

Obtained from nitroalkene **1c** (209 mg, 2 mmol) according to Method A. Reaction time: 3 h. The crude product was subjected to column chromatography (eluent: 10:1, PE/EtOAc) to give the target nitroalkene **2c** (314 mg, 65%) as orange crystals.

R_f = 0.22 (9:1, PE/EtOAc) (UV); mp 108–110 °C (EtOH) (Lit.[24] 113–114 °C (heptane)).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.37 (s, 1 H, =CH), 7.48–7.51 (m, 2 H, CH_{Ar}(3 and 5)), 6.99 (d, *J* = 9.1 Hz, 1 H, CH_{Ar}(6)), 3.98 (s, 3 H, OMe), 3.96 (s, 3 H, OMe).

^{13}C NMR (75 MHz, $CDCl_3$, HSQC, HMBC): δ = 152.6 (C_{Ar}(1)O), 149.2 (C_{Ar}(2)O), 135.3 (CNO_2), 131.9 (=CH), 126.8 (CH_{Ar}(3 or 5)), 122.3 (C_{Ar}(4)), 113.0 (CH_{Ar}(3 or 5)), 111.2 (CH_{Ar}(6)), 56.1 (OMe), 56.0 (OMe).

NMR matches previously reported data.[24]

(*Z*)-4-(2-Chloro-2-nitrovinyl)-2-(cyclopentyloxy)-1-methoxybenzene (2d)

Obtained from nitroalkene **2d** (132 mg, 0.5 mmol) according to Method A. Reaction time: 3 h. The crude product was subjected to column chromatography (eluent: 15:1, PE/EtOAc) to give the target nitroalkene **2d** (106 mg, 71%) as yellow crystals.

R_f = 0.28 (9:1, PE/EtOAc) (UV); mp 85–87 °C (EtOH).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.35 (s, 1 H, =CH), 7.52 (d, *J* = 2.1 Hz, 1 H, CH_{Ar}(3)), 7.44 (dd, *J* = 8.5, 2.1 Hz, 1 H, CH_{Ar}(5)), 6.96 (d, *J* = 8.5 Hz, 1 H, CH_{Ar}(6)), 4.78–4.85 (m, 1 H, CHO), 3.93 (s, 3 H, OMe), 2.10–1.77 (m, 6 H, 3 × CH_2), 1.75–1.56 (m, 2 H, CH_2).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC, HMBC): δ = 153.6 (C_{Ar}(1)O), 147.8 (C_{Ar}(2)O), 135.1 (CNO_2), 132.1 (=CH), 126.7 (CH_{Ar}(5)), 122.1 (C_{Ar}(4)), 116.2 (CH_{Ar}(3)), 111.6 (CH_{Ar}(6)), 80.8 (CHO), 56.1 (Me), 32.8 (CH_2), 24.2 (CH_2).

MS (EI, 70 eV): *m*/*z* (%) = 299 (7) $[M + 2]^+$, 297 (31) $[M]^+$, 231 (36) $[M + 2 - C_5H_{10}]^+$, 229 (100) $[M - C_5H_{10}]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{17}ClNO_4$: 298.0841; found: 298.0848.

(*Z*)-1-Bromo-2-(2-chloro-2-nitrovinyl)-4,5-dimethoxybenzene (2e)

Obtained from nitroalkene **1e** (288 mg, 1 mmol) according to Method A with $PhICl_2$ (2 equiv). Reaction time: 3 h. The crude product was subjected to column chromatography (eluent: 5:1, PE/EtOAc) to give the target nitroalkene **2e** (216 mg, 67%) as orange crystals.

R_f = 0.48 (3:1, PE/EtOAc) (UV); mp 142–144 °C (EtOH).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (s, 1 H, =CH), 7.28 (s, 1 H, CH_{Ar}), 7.18 (s, 1 H, CH_{Ar}), 3.96 (s, 3 H, Me), 3.94 (s, 3 H, Me).

^{13}C NMR (75 MHz, $CDCl_3$, HSQC): δ = 152.3 (C_{Ar}O), 148.3 (C_{Ar}O), 137.5 (CNO_2), 130.7 (=CH), 121.8 (C_{Ar}), 119.6 (C_{Ar}), 115.9 (CH_{Ar}), 112.3 (CH_{Ar}), 56.4 (OMe), 56.2 (OMe).

MS (EI, 70 eV): *m*/*z* (%) = 325 (10) $[M + 4]^+$, 323 (44) $[M + 2]^+$, 321 (28) $[M]^+$, 276 (15) $[M + 2 - HNO_2]^+$, 274 (11) $[M - HNO_2]^+$, 242 (85) [M^+ – Br or $M^+ + 2 - NO_2Cl$], 240 (16) $[M - NO_2Cl]^+$, 212 (100), 197 (70), 196 (34).

Anal. Calcd for $C_{10}H_9BrClNO_4$: C, 37.24; H, 2.81; N, 4.34. Found: C, 37.15; H, 2.90; N, 4.19.

(*Z*)-2-Bromo-5-(2-chloro-2-nitrovinyl)thiophene (2f)

Obtained from nitroalkene **1f** (117 mg, 0.5 mmol) according to Method A. Reaction time: 1 d. The crude product was subjected to column chromatography (eluent: 4:1, PE/toluene) to give the target nitroalkene **2f** (91 mg, 68%) as yellow crystals.

R_f = 0.47 (1:1, PE/toluene) (UV); mp 140–143 °C (EtOH).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.51 (s, 1 H, =CH), 7.41 (d, *J* = 4.0 Hz, 1 H, CH(4)), 7.23 (d, *J* = 4.1 Hz, 1 H, CH(3)).

^{13}C NMR (75 MHz, $CDCl_3$, HMBC): δ = 137.2 (CH(4)), 135.0 and 134.9 (C(5) and CNO_2), 131.2 (CH(3)), 125.6 (=CH), 123.3 (C(2)Br).

MS (EI, 70 eV): *m*/*z* (%) = 271 (9) $[M + 4]^+$, 269 (30) $[M + 2]^+$, 267 (22) $[M]^+$, 222 (19) $[M + 2 - HNO_2]^+$, 220 (12) $[M - HNO_2]^+$, 188 (29) $[M + 2 - NO_2Cl]^+$, 186 (17) $[M - NO_2Cl]^+$, 142 (100).

Anal. Calcd for $C_6H_3BrClNO_2S$: C, 26.84; H, 1.13; N, 5.22. Found: C, 26.69; H, 1.09; N, 5.09.

(*Z*)-5-(2-Chloro-2-nitrovinyl)benzo[*d*][1,3]dioxole (2g)

Obtained from nitroalkene **1g** (386 mg, 2 mmol) according to Method B. Reaction time: 3 d. The crude product was crystallized from EtOH to give the target nitroalkene **2g** (436 mg, 96%) as a yellow powder.

R_f = 0.48 (5:1, PE/EtOAc) (UV); mp 98–100 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.32 (s, 1 H, =CH), 7.54 (d, *J* = 1.8 Hz, 1 H, CH_{Ar}), 7.33 (dd, *J* = 8.2, 1.8 Hz, 1 H, CH_{Ar}), 6.93 (d, *J* = 8.2 Hz, 1 H, CH_{Ar}), 6.10 (s, 2 H, CH_2).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HMBC): δ = 151.1 (C_{Ar}O), 148.5 (C_{Ar}O), 135.5 (CNO_2), 131.7 (=CH), 128.9 (CH_{Ar}), 123.6 (C_{Ar}), 109.5 (CH_{Ar}), 108.9 (CH_{Ar}), 102.2 (CH_2).

MS (EI, 70 eV): *m*/*z* (%) = 229 (27) $[M + 2]^+$, 227 (95) $[M]^+$, 182 (15) $[M + 2 - HNO_2]^+$, 181 (20) $[M - NO_2]^+$, 180 (43) $[M - HNO_2]^+$, 146 (100) $[M - NO_2Cl]^+$.

Anal. Calcd for $C_9H_6ClNO_4$: C, 47.50; H, 2.66; N, 6.15. Found: C, 47.43; H, 2.77; N, 6.24.

Methyl (*Z*)-4-(4-(2-Chloro-2-nitrovinyl)phenoxy)butanoate (2h)

Obtained from nitroalkene **1h** (133 mg, 0.5 mmol) according to Method B. Reaction time: 3 h. The crude product was subjected to column chromatography (eluent: 8:1, PE/EtOAc) to give the target nitroalkene **2h** (91 mg, 61%) as yellow crystals.

R_f = 0.30 (3:1, PE/EtOAc) (UV); mp 81–84 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.37 (s, 1 H, =CH), 7.87 (d, *J* = 8.8 Hz, 2 H, CH_{Ar}), 7.01 (d, *J* = 8.8 Hz, 2 H, CH_{Ar}), 4.12 (t, *J* = 6.1 Hz, 2 H, CH_2O), 3.72 (s, 3 H, OMe), 2.57 (t, *J* = 7.2 Hz, 2 H, CH_2CO_2Me), 2.17 (app quint, *J* = 6.6 Hz, 2 H, $CH_2\underline{CH_2}CH_2$).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HMBC): δ = 173.4 (C=O), 161.9 (C_{Ar}O), 135.3 (CNO_2), 133.5 (CH_{Ar}), 131.6 (=CH), 122.1 (C_{Ar}), 115.1 (CH_{Ar}), 67.0 (CH_2O), 51.7 (OMe), 30.3 ($\underline{CH_2}CO_2Me$), 24.4 ($CH_2\underline{CH_2}CH_2$).

MS (EI, 70 eV): *m*/*z* (%) = 301 (1) $[M + 2]^+$, 299 (2) $[M]^+$, 101 (100).

Anal. Calcd for $C_{13}H_{14}ClNO_5$: C, 52.10; H, 4.71; N, 4.67. Found: C, 52.27; H, 4.57; N, 4.72.

Ethyl (*Z*)-2-(4-(2-Chloro-2-nitrovinyl)phenoxy)-2-methylpropanoate (2i)

Obtained from nitroalkene **1i** (452 mg, 1.62 mmol) according to Method B. Reaction time: 1 d. The crude product was subjected to column chromatography (eluent: 30:1, PE/EtOAc) to give the target nitroalkene **2i** (420 mg, 83%) as a yellow oil.

R_f = 0.33 (9:1, PE/EtOAc) (UV).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.35 (s, 1 H, =CH), 7.82 (d, *J* = 8.9 Hz, 2 H, CH_{Ar}), 6.91 (d, *J* = 8.8 Hz, 2 H, CH_{Ar}), 4.26 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.69 (s, 6 H, Me), 1.25 (t, *J* = 7.1 Hz, 3 H, $C\underline{H_3}CH_2$).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ = 173.5 (C=O), 159.0 (C_{Ar}O), 135.7 (CNO_2), 133.1 (CH_{Ar}), 131.4 (=CH), 122.7 (C_{Ar}), 118.2 (CH_{Ar}), 79.6 (CO), 61.7 (CH_2), 25.4 (Me), 14.0 ($\underline{CH_3}CH_2$).

MS (EI, 70 eV): *m*/*z* (%) = 315 (14) $[M + 2]^+$, 313 (36) $[M]^+$, 242 (16) $[M + 2 - CO_2Et]^+$, 240 (41) $[M - CO_2Et]^+$, 201 (39) $[M + 2 - CH_3C(=CH_2)CO_2Et]^+$, 199 (100) $[M - CH_3C(=CH_2)CO_2Et]^+$, 152 (100).

Anal. Calcd for $C_{14}H_{16}ClNO_5$: C, 53.60; H, 5.14; N, 4.46. Found: C, 53.68; H, 5.31; N, 4.45.

(*Z*)-2-Bromo-4-(2-chloro-2-nitrovinyl)-1-methoxybenzene (2j)

Obtained from nitroalkene **1j** (453 mg, 1.76 mmol) according to Method B. Reaction was performed at r.t. Reaction time: 1 d. The crude product was crystallized from EtOH to give the target nitroalkene **2j** (428 mg, 83%) as a yellow powder.

R_f = 0.42 (5:1, PE/EtOAc) (UV); mp 102–103 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.30 (s, 1 H, =CH), 8.14 (d, *J* = 2.3 Hz, 1 H, CH_{Ar}), 7.84 (dd, *J* = 8.6, 2.3 Hz, 1 H, CH_{Ar}), 7.02 (d, *J* = 8.6 Hz, 1 H, CH_{Ar}), 4.00 (s, 3 H, OMe).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ = 158.7 ($C_{Ar}O$), 136.3 (CNO_2), 135.9 (CH_{Ar}), 132.6 (CH_{Ar}), 130.1 (=CH), 123.3 (C_{Ar}), 112.6 ($C_{Ar}Br$), 111.9 (CH_{Ar}), 56.6 (OMe).

MS (EI, 70 eV): *m*/*z* (%) = 295 (21) $[M + 4]^+$, 293 (74) $[M + 2]^+$, 291 (62) $[M]^+$, 248 (26), 247 (31), 246 (100), 245 (25) and 244 (71) [(M^+ + 4 or M^++2 or M^+) – (HNO_2 or NO_2)], 212 (61) $[M + 2 – NO_2Cl]^+$, 210 (59) $[M + 2 – NO_2Cl]^+$.

Anal. Calcd for $C_9H_7BrClNO_3$: C, 36.96; H, 2.41; N, 4.79. Found: C, 36.98; H, 2.39; N, 4.80.

(*Z*)-1-Chloro-4-(4-(2-chloro-2-nitrovinyl)phenoxy)benzene (2k)

Obtained from nitroalkene **1k** (551 mg, 2 mmol) according to Method B. Reaction was performed at r.t. Reaction time: 1 d. The crude product was crystallized from EtOH to give the target nitroalkene **2k** (500 mg, 81%) as a yellow powder.

Obtained from nitroalkene **1t** (120 mg, 0.5 mmol) according to Method B with SO_2Cl_2 (3 equiv) and then Et_3N (5 equiv). Reaction was performed at r.t. Reaction time: 1 d. The crude product was subjected to column chromatography (eluent: 25:1, PE/EtOAc) to give the target nitroalkene **2k** (100 mg, 65%) as a yellow powder.

R_f = 0.51 (9:1, PE/EtOAc) (UV); mp 88–90 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.37 (s, 1 H, =CH), 7.88 (d, *J* = 8.5 Hz, 2 H, CH_{Ar}), 7.39 (d, *J* = 8.3 Hz, 2 H, CH_{Ar}), 7.04–7.09 (m, 4 H, CH_{Ar}).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HMBC): δ = 160.6 ($C_{Ar}O$), 153.9 ($C_{Ar}O$), 136.4 (CNO_2), 133.4 (CH_{Ar}), 131.0 (=CH), 130.2 (CH_{Ar}), 130.0 (C_{Ar}), 124.3 (C_{Ar}), 121.5 (CH_{Ar}), 118.0 (CH_{Ar}).

MS (EI, 70 eV): *m*/*z* (%) = 311 (68) $[M + 2]^+$, 309 (100) $[M]^+$, 265 (27) $[M + 2 – NO_2]^+$, 264 (53) $[M^+ + 2 – HNO_2]$, 263 (33) $[M – NO_2]^+$, 262 (66) $[M – HNO_2]^+$, 230 (34) $[M + 2 – NO_2Cl]^+$, 228 (87) $[M – NO_2Cl]^+$, 165 (66).

Anal. Calcd for $C_{14}H_9Cl_2NO_3$: C, 54.22; H, 2.93; N, 4.52. Found: C, 54.13; H, 2.80; N, 4.37.

(*Z*)-(2-Chloro-2-nitrovinyl)benzene (2l)

Obtained from nitroalkene **1l** (149 mg, 1 mmol) according to Method C. Reaction time: 1 d. The crude product was subjected to column chromatography (eluent: 15:1, PE/EtOAc) to give the target nitroalkene **2l** (138 mg, 75%) as yellow crystals.

R_f = 0.49 (9:1, PE/EtOAc) (UV); mp 35–37 °C (EtOH) (Lit.[15] 43–45 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.40 (s, 1 H, =CH), 7.86–7.90 (m, 2 H, CH_{Ar}), 7.46–7.57 (m, 3 H, CH_{Ar}).

NMR matches previously reported data.[15]

(*Z*)-1-(2-Chloro-2-nitrovinyl)-4-fluorobenzene (2m)

Obtained from nitroalkene **1m** (167 mg, 1 mmol) according to Method C. Reaction time: 2 d. The crude product was subjected to column chromatography (eluent: 15:1, PE/EtOAc) to give the target nitroalkene **2m** (183 mg (91%) as pale-yellow crystals.

R_f = 0.44 (9:1, PE/EtOAc) (UV); mp 66–68 °C (EtOH) (Lit.[24] 76–77 °C (hexane)).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.38 (s, 1 H, =CH), 7.91 (dd, *J* = 8.7, 5.3 Hz, 2 H, CH_{Ar}), 7.22 (t, *J* = 8.7 Hz, 2 H, CH_{Ar}).

^{13}C NMR (75 MHz, $CDCl_3$, HMBC): δ = 164.5 (d, $^1J_{CF}$ = 255.6 Hz, CF), 137.3 (CNO_2), 133.5 (d, $^3J_{CF}$ = 8.9 Hz, CH_{Ar}), 130.4 (=CH), 125.9 (d, $^4J_{CF}$ = 3.5 Hz, C_{Ar}), 116.5 (d, $^2J_{CF}$ = 22.0 Hz, CH_{Ar}).

NMR matches previously reported data.[24]

(*Z*)-1-Chloro-4-(2-chloro-2-nitrovinyl)benzene (2n)

Obtained from nitroalkene **1n** (184 mg, 1 mmol) according to Method C. Reaction time: 1 d. The crude product was crystallized from EtOH to give the target nitroalkene **2n** (152 mg, 70%) as pale-yellow crystals.

R_f = 0.49 (9:1, PE/EtOAc) (UV); mp 98–100 °C (Lit.[16a] 107–108 °C (heptane)).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.35 (s, 1 H, =CH), 7.82 (d, *J* = 8.4 Hz, 2 H, CH_{Ar}), 7.50 (d, *J* = 8.4 Hz, 2 H, CH_{Ar}).

^{13}C NMR (75 MHz, $CDCl_3$, HMBC): δ = 138.2 ($C_{Ar}Cl$), 137.9 (CNO_2), 132.3 (CH_{Ar}), 130.3 (=CH), 129.5 (CH_{Ar}), 128.1 (C_{Ar}).

NMR matches previously reported data.[16a]

(*Z*)-1-Bromo-4-(2-chloro-2-nitrovinyl)benzene (2o)

Obtained from nitroalkene **1o** (228 mg, 1 mmol) according to Method C. Reaction time: 2 d. The crude product was crystallized from EtOH to give the target nitroalkene **2o** (232 mg, 88%) as pale-yellow crystals.

R_f = 0.58 (9:1, PE/EtOAc) (UV); mp 116–119 °C (Lit.[15] 58–60 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (s, 1 H, =CH), 7.74 (d, *J* = 8.3 Hz, 2 H, CH_{Ar}), 7.66 (d, *J* = 8.3 Hz, 2 H, CH_{Ar}).

Anal. Calcd for $C_8H_5BrClNO_2$: C, 36.61; H, 1.92; N, 5.34. Found: C, 36.67; H, 1.80; N, 5.24.

NMR matches previously reported data.[15]

(*Z*)-1-(2-Chloro-2-nitrovinyl)-4-methylbenzene (2p)

Obtained from nitroalkene **1p** (163 mg, 1 mmol) according to Method C. Reaction time: 1 d. The crude product was subjected to column chromatography (eluent: 15:1, PE/EtOAc) to give the target nitroalkene **2p** (160 mg, 81%) as pale-yellow crystals.

R_f = 0.48 (9:1, PE/EtOAc) (UV); mp 68–70 °C (EtOH) (Lit.[14] 82–83 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.38 (s, 1 H, =CH), 7.79 (d, *J* = 8.1 Hz, 2 H, CH_{Ar}), 7.33 (d, *J* = 8.1 Hz, 2 H, CH_{Ar}), 2.45 (s, 3 H, Me).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HMBC): δ = 143.0 (CMe), 136.7 (CNO_2), 131.8 (=CH), 131.4 (CH_{Ar}), 129.9 (CH_{Ar}), 126.9 (C_{Ar}), 21.7 (Me).

NMR matches previously reported data.[14]

(*Z*)-1-Bromo-2-(2-chloro-2-nitrovinyl)benzene (2q)

Obtained from nitroalkene **1q** (228 mg, 1 mmol) according to Method C. Reaction time: 1 d. The crude product was subjected to column chromatography (eluent: 15:1, PE/EtOAc) to give the target nitroalkene **2q** (215 mg, 82%) as pale-yellow crystals.

R_f = 0.50 (9:1, PE/EtOAc) (UV); mp 38–40 °C (EtOH) (Lit.[9a] 50–51 °C).

^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ = 8.64 (s, 1 H, =CH), 7.93 (dd, *J* = 7.8, 1.4 Hz, 1 H, CH_{Ar}), 7.73 (dd, *J* = 8.0, 1.0 Hz, 1 H, CH_{Ar}), 7.46 (dt, *J* = 7.8, 3.9 Hz, 1 H, CH_{Ar}), 7.37 (dt, *J* = 7.7, 1.6 Hz, 1 H, CH_{Ar}).

^{13}C NMR (75 MHz, $CDCl_3$, HSQC, HMBC): δ = 139.6 (CNO_2), 133.4 (CH_{Ar}), 132.3 (CH_{Ar}), 130.7 (=CH), 130.5 (CH_{Ar}), 130.4 (C_{Ar}), 127.6 (CH_{Ar}), 126.1 ($C_{Ar}Br$).

Anal. Calcd for $C_8H_5BrClNO_2$: C, 36.61; H, 1.92; N, 5.34. Found: C, 36.82; H, 1.68; N, 5.15.

NMR matches previously reported data.[9a]

(*Z*)-2-Chloro-4-(2-chloro-2-nitrovinyl)-1-methoxybenzene (2r)

Obtained from nitroalkene **1r** (87 mg, 0.4 mmol) according to Method C. Reaction time: 1 d. The crude product was crystallized from EtOH to give the target nitroalkene **2r** (54 mg, 55%) as brownish crystals.

R_f = 0.33 (9:1, PE/EtOAc) (UV); mp 89–91 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31 (s, 1 H, =CH), 7.99 (d, *J* = 2.2 Hz, 1 H, CH_{Ar}), 7.78 (dd, *J* = 8.7, 2.3 Hz, 1 H, CH_{Ar}), 7.05 (d, *J* = 8.7 Hz, 1 H, CH_{Ar}), 4.01 (s, 3 H, OMe).

^{13}C NMR (75 MHz, $CDCl_3$, HSQC, HMBC): δ = 157.8 ($C_{Ar}O$), 136.4 (CNO_2), 132.7 (CH_{Ar}), 132.0 (CH_{Ar}), 130.2 (=CH), 123.5 and 122.8 ($C_{Ar}Cl$ and C_{Ar}), 112.1 (CH_{Ar}), 56.4 (OMe).

MS (EI, 70 eV): *m*/*z* (%) = 249 (42) $[M + 2]^+$, 247 (77) $[M]^+$, 202 (36) $[M + 2 – HNO_2]^+$, 200 (56) $[M–HNO_2]^+$, 168 (30) $[M + 2 – NO_2Cl]^+$, 166 (100) $[M – NO_2Cl]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_9H_7Cl_2NO_3Na$: 269.9695; found: 269.9696.

(*Z*)-(4-Chloro-4-nitrobut-3-enyl)benzene (2s)

Obtained from nitroalkene **1s** (177 mg, 1 mmol) according to Method C. Reaction time: 1 d. The crude product was subjected to column chromatography (eluent: 15:1, PE/EtOAc) to give the target nitroalkene **2s** (153 mg, 72%) as a yellow oil.

R_f = 0.44 (9:1, PE/EtOAc) (UV).

^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ = 7.49 (t, *J* = 7.5 Hz, 1 H, =CH), 7.21–7.38 (m, 5 H, Ph), 2.90 (t, *J* = 7.5 Hz, 2 H, CH_2Ph), 2.75 (q, *J* = 7.5 Hz, 2 H, CH_2CH=).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HMBC): δ = 140.4 (CNO_2), 139.5 (C_{Ph}), 134.9 (=CH), 128.8 (CH_{Ph}), 128.3 (CH_{Ph}), 126.7 (CH_{Ph}), 33.4 (CH_2Ph), 30.7 (CH_2CH=).

MS (EI, 70 eV): *m*/*z* (%) = 196 (8) $[M + 2 – OH]^+$, 194 (24) $[M – OH]^+$, 129 (19), 91 (100) $[C_7H_7]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{10}H_{10}ClNO_2$: 234.0292; found: 234.0281.

1-(1,2-Dichloro-2-nitroethyl)-4-methoxybenzene (3a)

Nitroalkene **1a** was subjected to Method B, but the reaction was worked up without quenching with Et_3N.

Dichloride (**3a**) was characterized as a crude reaction mixture. Ratio **3a**/**2a** = 3.6:1. dr (**3a**) = 1.6:1. Configuration of diastereomers was not determined. Attempts to purify **3a** by column chromatography led to partial elimination of HCl, resulting in chloronitroalkene **2a**. ESI-HRMS also detected only **2a**.

Major Diastereomer

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 8.7 Hz, 1 H, CH_{Ar}), 6.96 (d, *J* = 8.7 Hz, 1 H, CH_{Ar}), 6.07 (d, *J* = 9.6 Hz, 1 H, $CHClNO_2$), 5.37 (d, *J* = 9.6 Hz, 1 H, CHClAr), 3.86 (s, 3 H, OMe).

^{13}C NMR (75 MHz, $CDCl_3$, HSQC, HMBC): δ = 160.9 ($C_{Ar}O$), 129.7 (CH_{Ar}), 125.2 (C_{Ar}), 114.6 (CH_{Ar}), 92.2 ($CHClNO_2$), 60.9 (CHClAr), 55.4 (OMe).

Minor Diastereomer

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.7 Hz, 1 H, CH_{Ar}), 6.93 (d, *J* = 8.7 Hz, 1 H, CH_{Ar}), 6.09 (d, *J* = 6.7 Hz, 1 H, $CHClNO_2$), 5.54 (d, *J* = 6.7 Hz, 1 H, CHClAr), 3.84 (s, 3 H, OMe).

^{13}C NMR (75 MHz, $CDCl_3$, HSQC, HMBC): δ = 160.9 ($C_{Ar}O$), 129.3 (CH_{Ar}), 125.6 (C_{Ar}), 114.5 (CH_{Ar}), 94.7 ($CHClNO_2$), 62.5 (CHClAr), 55.4 (OMe).

1-Chloro-4-(1,2-dichloro-2-nitroethyl)benzene (3n)

Nitroalkene **1n** was subjected to method C, but the reaction was worked up without quenching with K_2CO_3 and Et_3N.

Dichloride (**3n**) was characterized as the crude reaction mixture. dr = 9:1. Configuration of diastereomers was not determined. Attempts to purify **3n** by column chromatography led to partial elimination of HCl, resulting in chloronitroalkene **2n**.

Major Diastereomer

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.46 (m, 4 H, CH_{Ar}), 6.05 (d, *J* = 9.5 Hz, 1 H, $CHClNO_2$), 5.39 (d, *J* = 9.6 Hz, 1 H, CHClAr).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HMBC): δ = 136.4 (C_{Ar}), 131.9 (C_{Ar}), 129.7 (CH_{Ar}), 129.5 (CH_{Ar}), 91.9 ($CHClNO_2$), 60.2 (CHClAr).

Minor Diastereomer

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.46 (m, 4 H, CH_{Ar}), 6.08 (d, *J* = 6.2 Hz, 1 H, $CHClNO_2$), 5.60 (d, *J* = 6.2 Hz, 1 H, CHClAr).

(*E*)-1,3-Dichloro-4,5,6-trimethoxy-2-(2-nitrovinyl)benzene (4)

Obtained from nitroalkene **1u** (120 mg, 0.5 mmol) according to Method C with SO_2Cl_2 (6 equiv) and HCl/dioxane (4 equiv). Reaction time: 1 d. The crude product was subjected to column chromatography (eluent: 15:1, PE/EtOAc) to give the target nitroalkene **4** (61 mg, 40%) as yellow crystals.

R_f = 0.34 (5:1, PE/EtOAc) (UV); mp 78–83 °C (EtOH).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 13.9 Hz, 1 H, $=CHC_{Ar}$), 7.86 (d, *J* = 13.9 Hz, 1 H, $=CHNO_2$), 4.03 (s, 3 H, Me), 3.93 (s, 6 H, Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.9 ($C_{Ar}O$), 149.7 ($C_{Ar}O$), 142.4 ($=CHC_{Ar}$), 132.3 ($=CHNO_2$), 125.6 (C_{Ar}), 123.0 (C_{Ar}), 61.5 (OMe), 61.3 (OMe).

MS (EI, 70 eV): *m*/*z* (%) = 309 (65) $[M + 2]^+$, 307 (100) $[M]^+$, 274 (32) $[M + 2 – Cl]^+$, 272 (82) $[M – Cl]^+$, 262 (26) $[M + 2 – HNO_2]^+$, 260 (36) $[M – HNO_2]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{11}H_{12}Cl_2NO_5$: 308.0087; found: 308.0080.

(*Z*)-1,3-Dichloro-2-(2-chloro-2-nitrovinyl)-4,5,6-trimethoxybenzene (5)

Obtained from nitroalkene **1u** (120 mg, 0.5 mmol) according to Method A with Py (8 equiv) and $PhICl_2$ (5 equiv). Reaction time: 1 d. The crude product was subjected to column chromatography (eluent: 20:1, PE/EtOAc) to give the target nitroalkene **5** (105 mg, 62%) as pale-yellow crystals.

R_f = 0.50 (5:1, PE/EtOAc) (UV); mp 69–70 °C (PE).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16 (s, 1 H, =CH), 4.01 (s, 3 H, Me), 3.94 (s, 6 H, Me).

^{13}C NMR (75 MHz, $CDCl_3$, HMBC): δ = 149.6 ($C_{Ar}O$), 149.0 ($C_{Ar}O$), 143.2 (CNO_2), 128.0 (=CH), 124.4 (C_{Ar}), 123.0 (C_{Ar}), 61.5 (OMe), 61.4 (OMe).

MS (EI, 70 eV): *m*/*z* (%) = 345 (26) $[M + 4]^+$, 343 (84) $[M + 2]^+$, 341 (89) $[M]^+$, 308 (70) $[M + 2 – Cl]^+$, 306 (100) $[M – Cl]^+$, 278 (52), 261 (58), 245 (76), 228 (63).

Anal. Calcd for $C_{11}H_{10}Cl_3NO_5$: C, 38.57; H, 2.94; N, 4.09. Found: C, 38.63; H, 2.88; N, 4.06.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1707396.

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