Supporting information

Chlorination of conjugated nitroalkenes with PhICl$_2$ and SO$_2$Cl$_2$
for the synthesis of α-chloronitroalkenes

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List of starting nitroalkenes 1:

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Nitroalkenes 1a, 1l, 1q, 1s were prepared by literature procedures.

**General procedure 1 for the synthesis of starting nitroalkenes 1b-i,k,m-p,t,u.**

Nitroalkenes 1b-i,k,m-p,t,u were prepared similar to literature procedure$^4$ as follows:

Solution of aldehyde (1 equiv.), nitromethane (3 equiv.) and ethylenediammonium bistrifluoroacetate (0.05 equiv.) in DMSO (0.25 mL / 1 mmol of aldehyde) were maintained at 110 °C (oil bath) for 7-22 hours. Reaction mixture was poured into water (ca. 10 mL / 1 mmol of starting aldehyde). Formed precipitate (unless otherwise mentioned) was filtered and recrystallized from EtOH to give target nitroalkenes 1.
General procedure 2 for the synthesis of starting nitroalkenes 1j,r.

Nitroalkenes 1j,r were prepared similar to literature procedure2 as follows:

Solution of aldehyde (1 equiv.), nitromethane (2.75 equiv.) and ammonium acetate (2.2 equiv.) in AcOH (2.8 mL / 1 mmol of aldehyde) were refluxed for 8-21 hours. After cooling to r.t., the resultant mixture was diluted with H2O, and extracted with EtOAc. The combined organic layers were washed with NaHCO3, brine, dried over Na2SO4 and concentrated in vacuo. The residue was recrystallized from EtOH to give target nitroalkenes 1.

**(E)-1-(Benzyloxy)-4-(2-nitrovinyl)benzene (1b)**

![Structure](image)

Obtained from p-benzyloxybenzaldehyde5 (1.06 g, 5 mmol) according to general procedure 1. Reaction time – 22 h. Recrystallization afforded 0.96 g (76%) of target nitroalkene as brownish powder.

1H NMR (300 MHz, CDCl3): δ = 8.00 (d, J = 13.5 Hz, 1H, =CH–C Ar), 7.34-7.64 (m, 8H, CH Ph, CHAr and =CH–NO2), 7.05 (d, J = 8.4 Hz, 2H, CHAr), 5.16 (s, 2H, CH2–Ph).

NMR matches previously reported data.s6

**(E)-1,2-Dimethoxy-4-(2-nitrovinyl)benzene (1c)**

![Structure](image)

Obtained from 3,4-dimethoxybenzaldehyde (1.66 g, 10 mmol) according to general procedure 1. Reaction time – 18 h. Recrystallization afforded 1.45 g (76%) of target nitroalkene as yellow crystals.

1H NMR (300 MHz, CDCl3): δ = 7.98 (d, J = 13.5 Hz, 1H, =CH–C Ar), 7.54 (d, J = 13.6 Hz, 1H, =CH–NO2), 7.19 (dd, J = 8.3, 2.0 Hz, 1H, CHAr), 7.02 (d, J = 2.0 Hz, 1H, CHAr), 6.93 (d, J = 8.3 Hz, 1H, CHAr), 3.96 (s, 3H, Me), 3.94 (s, 3H, Me).

NMR matches previously reported data.s7

**(E)-2-(Cyclopentyloxy)-1-methoxy-4-(2-nitrovinyl)benzene (1d)**

![Structure](image)

Obtained from 3-cyclopentyloxy-4-methoxybenzaldehyde7 (2.2 g, 10 mmol) according to general procedure 1. Reaction time – 8 h. Recrystallization afforded 1.66 g (63%) of target nitroalkene as yellow crystals.

1H NMR (300 MHz, CDCl3): δ = 7.97 (d, J = 13.6 Hz, 1H, =CH–C Ar), 7.52 (d, J = 13.6 Hz, 1H, =CH–NO2), 7.16 (dd, J = 8.4, 2.1 Hz, 1H, CHAr), 7.03 (d, J = 2.1 Hz, 1H, CHAr), 6.91 (d, J = 8.4 Hz, 1H, CHAr), 4.78-4.84 (m, 1H, CH–O), 3.92 (s, 3H, Me), 1.79-2.07 (m, 6H, CH2), 1.59-1.74 (m, 2H, CH2).

NMR matches previously reported data.s8
(E)-1-Bromo-4,5-dimethoxy-2-(2-nitrovinyl)benzene (1e)

\[ \text{MeO} \quad \text{Br} \quad \text{MeO} \quad \text{NO}_2 \]

Obtained from 2-bromo-4,5-dimethoxybenzaldehyde\(^{9}\) (1.2 g, 5 mmol) according to general procedure 1. Reaction time – 9 h. Recrystallization afforded 1.01 g (70%) of target nitroalkene as yellow crystals.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 8.36 \text{ (d, } J = 13.5 \text{ Hz, } 1\text{H, } =\text{CH–C}_\text{Ar}) \), 7.53 (d, \(J = 13.5 \text{ Hz, } 1\text{H, } =\text{CH–NO}_2\) ), 7.12 (s, 1H, CH\(_\text{Ar}\) ), 7.01 (s, 1H, CH\(_\text{Ar}\) ), 3.95 (s, 3H, Me ), 3.93 (s, 3H, Me).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 152.9 \text{ (C) } \), 148.9 (C ), 137.7 (C ), 136.9 (C ), 122.0 (C ), 119.3 (C ), 116.1 (CH), 109.6 (CH), 56.4 (OMe), 56.2 (OMe).

NMR matches previously reported data.\(^{10}\)

(E)-2-Bromo-5-(2-nitrovinyl)thiophene (1f)

\[ \text{Br} \quad \text{S} \quad =\text{NO}_2 \]

Obtained from 5-bromothiophencarbaldehyde\(^{11}\) (1.91 g, 10 mmol) according to general procedure 1. Reaction time – 11 h. Recrystallization afforded 1.44 g (62%) of target nitroalkene as brownish powder.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 8.04 \text{ (d, } J = 13.4 \text{ Hz, } 1\text{H, } =\text{CH–C}_\text{Ar}) \), 7.40 (d, \(J = 13.4 \text{ Hz, } 1\text{H, } =\text{CH–NO}_2\) ), 7.3 (d, \(J = 3.9 \text{ Hz, } 1\text{H, CH}_\text{Ar}\) ), 7.14 (d, \(J = 3.9 \text{ Hz, } 1\text{H, CH}_\text{Ar}\) ).

NMR matches previously reported data.\(^{12}\)

(E)-5-(2-Nitrovinyl)benzo[d][1,3]dioxole (1g)

\[ \text{O} \quad \text{O} \quad \text{NO}_2 \]

Obtained from corresponding benzaldehyde (1.5 g, 10 mmol) according to general procedure 1. Reaction time – 22 h. Recrystallization afforded 1.35 g (70%) of target nitroalkene as yellow powder.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.95 \text{ (d, } J = 13.6 \text{ Hz, } 1\text{H, } =\text{CH–C}_\text{Ar}) \), 7.49 (d, \(J = 13.6 \text{ Hz, } 1\text{H, } =\text{CH–NO}_2\) ), 7.10 (dd, \(J = 8.0, 1.7 \text{ Hz, } 1\text{H, CH}_\text{Ar}\) ), 7.02 (d, \(J = 1.7 \text{ Hz, } 1\text{H, CH}_\text{Ar}\) ), 6.90 (d, \(J = 8.0 \text{ Hz, } 1\text{H, CH}_\text{Ar}\) ), 6.08 (s, 2H, CH\(_2\) ).

NMR matches previously reported data.\(^{7}\)

Methyl (E)-4-(4-(2-nitrovinyl)phenoxy)butanoate (1h)

\[ \text{MeO} \quad \text{O} \quad \text{NO}_2 \]

Obtained from corresponding benzaldehyde (1.11 g, 5 mmol) according to general procedure 1. Reaction time – 19 h. Recrystallization afforded 0.80 g (61%) of target nitroalkene as yellow powder. mp = 112-115 °C (EtOH).

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.99 \text{ (d, } J = 13.6 \text{ Hz, } 1\text{H, } =\text{CH–C}_\text{Ar}) \), 7.54 (d, \(J = 13.6 \text{ Hz, } 1\text{H, } =\text{CH–NO}_2\) ), 7.51 (d, \(J = 8.6 \text{ Hz, } 2\text{H, CH}_\text{Ar}\) ), 6.96 (d, \(J = 8.5 \text{ Hz, } 2\text{H, CH}_\text{Ar}\) ), 4.10 (t, \(J = 6.0 \text{ Hz, } 2\text{H, CH}_2–\text{O}\) ), 3.72 (s, 3H, Me), 2.56 (t, \(J = 7.2 \text{ Hz, } 2\text{H, CH}_2–\text{CO}_2\text{Me}\) ), 2.12-2.21 (m, 2H, CH\(_2–\text{C}_2–\text{CH}_2\) )

\(^{13}\)C NMR (75 MHz, CDCl\(_3\), DEPT): \(\delta = 173.5 \text{ (C=O) } \), 162.2 (C\(_\text{Ar}–\text{O}\) ), 139.0 (=CH), 135.1 (CH–NO\(_2\) ), 131.2 (CH\(_\text{Ar}\) ), 122.6 (C\(_\text{Ar}\) ), 115.4 (C\(_\text{Ar}\) ), 67.0 (CH\(_2–\text{O}\) ), 51.7 (OMe), 30.3 (CH\(_2–\text{CO}_2\text{Me}\) ), 24.4 (CH\(_2–\text{C}_2–\text{CH}_2\) ).

HRMS (ESI): \(m/z\) calcd for C\(_{13}\)H\(_{16}\)NO\(_5\) [M + H\(^+\)]: 266.1023; found: 266.1030.
Ethyl (E)-2-methyl-2-(4-(2-nitrovinyl)phenoxy)propanoate (1i)

\[ \text{EtO}_2\text{C} \begin{array}{c} \text{NO}_2 \\ \end{array} \]

Obtained from corresponding substituted benzaldehyde\(^{13}\) (1.18 g, 5 mmol) according to general procedure 1. Reaction time – 20 h. Recrystallization afforded 0.54 g (40%) of target nitroalkene as yellow powder.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.97 \text{ (d, } J = 13.7 \text{ Hz, 1H, } =\text{CH–C}_{\text{Ar}}), 7.53 \text{ (d, } J = 13.7 \text{ Hz, 1H, } =\text{CH–NO}_2), 7.47 \text{ (d, } J = 8.7 \text{ Hz, 2H, } \text{CH}_2\), 6.87 (d, \(J = 8.7 \text{ Hz, 2H, CH}_{\text{Ar}}\), 4.25 (q, \(J = 7.1 \text{ Hz, 2H, } \text{CH}_2\)), 1.67 (s, 6H, Me), 1.25 (t, \(J = 7.1 \text{ Hz, 3H, CH}_3\)).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\), DEPT, HSQC, HMBC): \(\delta = 173.5 \text{ (C=O), 159.2 (C}_{\text{Ar–O}}, 138.7 (=\text{C–C}_{\text{Ar}}), 135.4 (=\text{C–NO}_2), 130.7 \text{ (CH}_{\text{Ar}}, 123.2 \text{ (C}_{\text{Ar–C–C}}, 118.6 \text{ (CH}_{\text{Ar}}, 79.5 \text{ (CMe}_2), 61.7 \text{ (CH}_2), 25.4 \text{ (CMe}_2), 14.0 \text{ (CH}_2\text{Me).}

NMR matches previously reported data.\(^{14}\)

(E)-2-Bromo-1-methoxy-4-(2-nitrovinyl)benzene (1j)

\[ \text{Br} \begin{array}{c} \text{MeO} \end{array} \]

Obtained from 3-bromo-4-methoxybenzaldehyde\(^{15}\) (1.94 g, 9 mmol) according to general procedure 2. Reaction time – 18 h. Recrystallization afforded 1.01 g (44%) of brownish powder.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.92 \text{ (d, } J = 13.6 \text{ Hz, 1H, } =\text{CH–C}_{\text{Ar}}), 7.78 \text{ (d, } J = 2.3 \text{ Hz, 1H, CH}_{\text{Ar}}, 7.43-7.57 \text{ (m, 2H, CH}_{\text{Ar}} \text{ and } =\text{CH–NO}_2), 6.97 \text{ (d, } J = 8.6 \text{ Hz, 1H, CH}_{\text{Ar}}, 3.98 \text{ (s, 3H, OMe).}

NMR matches previously reported data.\(^{16}\)

4-(4-Chlorophenoxy)benzaldehyde

To a solution of 4-fluorobenzaldehyde (1.24 g, 10 mmol) and 4-chlorophenol (1.41 g, 11 mmol) in DMF (12 mL) was added powdered K\(_2\)CO\(_3\) (2.76 g, 20 mmol), and the mixture was stirred at 120°C for 21 h. After cooling to r.t., the resulting mixture was extracted with EtOAc/H\(_2\)O. The aqueous layer was washed with EtOAc. Combined organic layers were washed with aqueous NaOH solution (3M), saturated NaCl solution, dried with anhydrous Na\(_2\)SO\(_4\) and concentrated in vacuo to give 2.04 g (88%) of target 4-(4-chlorophenoxy)benzaldehyde that was further used without additional purification.

(E)-1-Chloro-4-(4-(2-nitrovinyl)phenoxy)benzene (1k)

\[ \text{Cl} \begin{array}{c} \text{NO}_2 \end{array} \]

Obtained from 4-(p-chlorophenoxy)-benzaldehyde (1162 mg, 5 mmol) according to general procedure 1. Reaction time – 22 h. Recrystallization afforded 916 mg (67%) of orange powder. mp = 80-82 °C.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 8.00 \text{ (d, } J = 13.7 \text{ Hz, 1H, } =\text{CH–C}_{\text{Ar}}), 7.50-7.61 \text{ (m, 3H, CH}_{\text{Ar}} \text{ and } =\text{CH–NO}_2), 7.39 \text{ (d, } J = 8.9 \text{ Hz, 2H, CH}_{\text{Ar}}, 7.02-7.05 \text{ (m, 4H, CH}_{\text{Ar}}).}

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 160.9 \text{ (C}_{\text{Ar–O}}, 154.0 \text{ (C}_{\text{Ar–O}}, 138.3 (=\text{C–CH}_{\text{Ar}}), 136.1 (=\text{C–NO}_2), 131.2 \text{ (CH}_{\text{Ar}}, 130.2 \text{ (CH}_{\text{Ar}}, 129.9 \text{ (CH}_{\text{Ar}}, 124.8 \text{ (C}_{\text{Ar}}, 121.4 \text{ (CH}_{\text{Ar}}, 118.4 \text{ (CH}_{\text{Ar}}.}

HRMS (ESI): \(m/z\) calcd for C\(_{14}\)H\(_{10}\)ClNO\(_3\)Na \([\text{M + H}^+\]): 298.0241; found: 298.0232.
(E)-1-Fluoro-4-(2-nitrovinyl)benzene (1m)

Obtained from p-fluorobenzaldehyde (620 mg, 5 mmol) according to general procedure 1. Reaction time – 17 h. Recrystallization afforded 455 mg (54%) of target nitroalkene as pale yellow crystals.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 8.00$ (d, $J = 13.7$ Hz, 1H, =CH–CAr), 7.65 – 7.49 (m, 3H, CHAr and =CH–NO$_2$), 7.18 (t, $J = 8.6$ Hz, 2H, CHAr).

NMR matches previously reported data.$^{s7}$

(E)-1-Chloro-4-(2-nitrovinyl)benzene (1n)

Obtained from p-chlorobenzaldehyde (2.1 g, 15 mmol) according to general procedure 1. Reaction time – 13 h. Recrystallization afforded 1.7 g (63%) of target nitroalkene as brownish powder.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.98$ (d, $J = 13.7$ Hz, 1H, =CH–CAr), 7.58 (d, $J = 13.7$ Hz, 1H, =CH–NO$_2$), 7.52 (d, $J = 8.6$ Hz, 2H, CHAr), 7.45 (d, $J = 8.6$ Hz, 2H, CHAr).

NMR matches previously reported data.$^{s17}$

(E)-1-Bromo-4-(2-nitrovinyl)benzene (1o)

Obtained from p-bromobenzaldehyde (2.77 g, 15 mmol) according to general procedure 1. Reaction time – 10 h. Recrystallization afforded 2.31 g (67%) of target nitroalkene as brownish crystals.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.97$ (d, $J = 13.7$ Hz, 1H, =CH–CAr), 7.65 – 7.53 (m, 3H, CHAr and =CH–NO$_2$), 7.44 (d, $J = 8.5$ Hz, 2H, CHAr).

NMR matches previously reported data.$^{s7}$

(E)-1-Methyl-4-(2-nitrovinyl)benzene (1p)

Obtained from p-methylbenzaldehyde (1.2 g, 10 mmol) according to general procedure 1. Reaction time – 8 h. Recrystallization afforded 0.96 g (59%) of target nitroalkene as pale yellow crystals.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 8.01$ (d, $J = 13.6$ Hz, 1H, =CH–CAr), 7.59 (d, $J = 13.6$ Hz, 1H, =CH–NO$_2$), 7.47 (d, $J = 8.0$ Hz, 2H, CHAr), 7.28 (d, $J = 8.0$ Hz, 2H, CHAr), 2.43 (s, 3H, Me).

NMR matches previously reported data.$^{s7}$

(E)-2-Chloro-1-methoxy-4-(2-nitrovinyl)benzene (1r)

Obtained from 3-chloro-4-methoxybenzaldehyde$^{s18}$ (853 mg, 5 mmol) according to general procedure 2. Reaction time – 21 h. Recrystallization afforded 734 mg (69%) of brownish crystals.
$^1$H NMR (300 MHz, CDCl$_3$): 7.94 (d, $J = 13.6$ Hz, 1H, =CH–C$_{Ar}$), 7.61 (d, $J = 2.2$ Hz, 1H, C$_{Ar}$), 7.53 (d, $J = 13.7$ Hz, 1H, =CH–NO$_2$), 7.47 (dd, $J = 8.6$, 2.2 Hz, 1H, C$_{Ar}$), 7.01 (d, $J = 8.6$ Hz, 1H, C$_{Ar}$), 3.98 (s, 3H, OMe).

NMR matches previously reported data.$^{s19}$

**(E)-1-(2-Nitrovinyl)-4-phenoxybenzene (1t)**

Obtained from corresponding benzaldehyde$^{s20}$ (990 mg, 5 mmol) according to general procedure 1. Reaction time – 9 h. Recrystallization afforded 811 mg (67%) of target nitroalkene as brownish crystals. mp = 89-95 °C (EtOH) (Lit.$^{s21}$ 102 °C (EtOH)).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 8.01$ (d, $J = 13.6$ Hz, 1H, =CH–C$_{Ar}$), 7.52-7.58 (m, 3H, C$_{Ar}$ and =CH–NO$_2$), 7.43 (t, $J = 7.6$ Hz, 2H, C$_{Ar}$), 7.24 (app t, $J = 7.3$ Hz, 1H, C$_{Ar}$), 7.10 (d, $J = 7.9$ Hz, 2H, C$_{Ar}$), 7.04 (d, $J = 8.4$ Hz, 2H, C$_{Ar}$).

$^{13}$C NMR (75 MHz, CDCl$_3$, HSQC): $\delta = 161.4$ (C$_{Ar}$–O), 155.3 (C$_{Ar}$–O), 138.5 (=CH–C$_{Ar}$), 135.9 (=CH–NO$_2$), 131.1 (C$_{Ar}$), 130.1 (C$_{Ar}$), 124.8 (C$_{Ar}$), 124.4 (C$_{Ar}$–C=C), 120.2 (CH$_{Ar}$), 118.4 (CH$_{Ar}$).

NMR matches previously reported data.$^{s22}$

**(E)-1,2,3-trimethoxy-5-(2-nitrovinyl)benzene (1u)**

Obtained from 3,4,5-trimethoxybenzaldehyde (2.94 g, 15 mmol) according to general procedure 1. Reaction time – 7 h. Recrystallization afforded 2.39 g (67%) of target nitroalkene as yellow crystals.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.95$ (d, $J = 13.5$ Hz, 1H, =CH–C$_{Ar}$), 7.55 (d, $J = 13.5$ Hz, 1H, =CH–NO$_2$), 6.78 (s, 2H, C$_{Ar}$), 3.93 (s, 3H, Me), 3.92 (s, 6H, Me).

NMR matches previously reported data.$^{s7}$
Data for Figure 1:
For the reaction without HCl:
Nitroalkene 1a (179 mg, 1 mmol) and methyl 3,5-dinitrobenzoate (75 mg, 0.33 mmol, as internal standard) were dissolved in CH₂Cl₂ (2 mL), the solution was cooled to 0 °C (ice-water bath) under argon atmosphere, and then SO₂Cl₂ (90 µL, 1.1 equiv.) was added. The mixture was stirred at the same temperature. Aliquots were taken at the specified time and worked up (extracted with EtOAc/H₂O, washed with saturated NaCl, dried with anhydrous Na₂SO₄). After concentration in vacuo reaction mixture was analyzed by ¹H NMR.

For the HCl-promoted reaction:
Procedure the same as above, albeit HCl (25 µL of 4M sol in 1,4-dioxane, 0.1 mmol, 0.1 equiv.) was added before addition of SO₂Cl₂.

Reaction without addition of HCl:

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Reaction with addition of HCl (0.1 equiv.):

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References:

(E)-1-(Benzyloxy)-4-(2-nitrovinyl)benzene (1b)

\[ ^1H \text{NMR} \]
(E)-1,2-Dimethoxy-4-(2-nitrovinyl)benzene (1c)

$^1H$ NMR

![Chemical structure of (E)-1,2-Dimethoxy-4-(2-nitrovinyl)benzene (1c)](attachment:image)

- $8.00, 7.95$ (apparent as a single peak)
- $7.56, 7.52, 7.20, 7.18, 7.03, 6.94, 6.92$ (apparent as a multiplet)
- $3.94, 3.96$ (apparent as a doublet)

Peaks at $7.03, 7.18, 7.20, 7.52, 7.56, 7.56, 7.95, 8.00$ correspond to protons from aromatic rings and vinyl group.

Peaks at $3.94, 3.96$ correspond to methoxy groups.

Peaks at $7.03, 7.18, 7.20, 7.52, 7.56, 7.56, 7.95, 8.00$ are typical for aromatic protons.

Peaks at $3.94, 3.96$ are typical for methoxy protons.
(E)-2-(Cyclopentyloxy)-1-methoxy-4-(2-nitrovinyl)benzene (1d)

$^1$H NMR
(E)-1-Bromo-4,5-dimethoxy-2-(2-nitrovinyl)benzene (1e)

$^1$H NMR

$8.38 \rightarrow 8.34 \rightarrow 7.55 \rightarrow 7.12 \rightarrow 7.01 \rightarrow 3.95 \rightarrow 3.93$
$^{13}$C NMR

MeO$_2$C\(\text{Br}\)NO$_2$
(E)-2-Bromo-5-(2-nitrovinyl)thiophene (1f)

$^1$H NMR

![NMR Spectrogram](image-url)
(E)-5-(2-Nitovinyl)benzo[d][1,3]dioxole (1g)

$^1$H NMR

![NMR Spectrogram](image-url)
Methyl (E)-4-(2-nitrovinyl)phenoxybutanoate (1h)

$^1$H NMR

\[
\text{MeO}_2C-\text{CH(OH)}-\text{C}(\equiv\text{C})-\text{NO}_2
\]
$^{13}$C NMR

MeO$_2$C

\[ \text{CH}_2\text{CH}_2\text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{NO}_2 \]

\[ \text{H}_2\text{C} = \]

\[ \text{H}_2\text{C} = \]

\[ \text{H}_2\text{C} = \]

\[ \text{H}_2\text{C} = \]

\[ \text{H}_2\text{C} = \]
13C NMR DEPT

MeO$_2$C - O

- 138.99
- 135.06
- 131.17
- 115.37
- 67.03
- 66.88
- 51.72
- 30.34
- 24.40
Ethyl (E)-2-methyl-2-(4-(2-nitrovinyl)phenoxy)propanoate (1i)

$^1$H NMR
$^{13}$C NMR

EtO₂C

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]
$^{13}$C NMR DEPT

EtO$_2$C

$\text{O}$

$\text{NO}_2$

The diagram shows a $^{13}$C NMR DEPT spectrum for a compound with the structural formula shown. The spectrum displays peaks at various chemical shifts indicated by the labels 138.75, 135.44, 130.72, 118.61, -61.72, -25.38, and -14.04.
$^{1}H-^{13}C$ HMBC
(E)-2-Bromo-1-methoxy-4-(2-nitrovinyl)benzene (1j)

$^1$H NMR
(E)-1-Chloro-4-(4-(2-nitrovinyl)phenoxy)benzene (1k)

$^1$H NMR
$^{13}$C NMR

![Chemical structure and NMR spectrum](image-url)
(E)-1-Fluoro-4-(2-nitrovinyl)benzene (1m)

$^1$H NMR

![NMR Spectrogram](image)
(E)-1-Chloro-4-(2-nitrovinyl)benzene (1n)

$^1$H NMR
(E)-1-Bromo-4-(2-nitrovinyl)benzene (1o)

$^1$H NMR

\[
\begin{align*}
\text{Br} & \quad \text{NO}_2 \\
\end{align*}
\]
(E)-1-Methyl-4-(2-nitrovinyl)benzene (1p)

$^1$H NMR
(E)-2-Chloro-1-methoxy-4-(2-nitrovinyl)benzene (1r)

1H NMR
(E)-1-(2-Nitrovinyl)-4-phenoxybenzene (1t)

$^1$H NMR

![NMR Spectrum](image)
$^{13}$C NMR

\[
\text{NO}_2
\]

- 161.39
- 155.34
- 138.54
- 135.85
- 131.12
- 130.12
- 124.78
- 124.36
- 120.17
- 118.39
$^1\text{H}-^{13}\text{C}$ HSQC
(E)-1,2,3-trimethoxy-5-(2-nitrovinyl)benzene (1u)

$^1$H NMR

$\begin{align*}
7.97, 7.93, 7.53, 6.78, 3.92, 3.93
\end{align*}$

\[ \text{MeO} \quad \text{NO}_2 \]

\[ \text{MeO} \quad \text{OMe} \]
(Z)-1-(2-Chloro-2-nitrovinyl)-4-methoxybenzene (2a)

$^1$H NMR
(Z)-1-(Benzyloxy)-4-(2-chloro-2-nitrovinyl)benzene (2b)

$^1$H NMR
$^{13}$C NMR

![Chemical Structure](image-url)

Labels:
- BnO
- Cl
- NO$_2$
$^1\text{H}^1\text{C} \text{ HSQC}$
$^{1}H-^{13}C$ HMBC
MS spectra (EI)

![MS Spectra Graph]

Chemical structure:

BnO

\begin{align*}
\text{Cl} & \rightarrow \\
\text{NO}_2 & \rightarrow \\
\end{align*}
(Z)-4-(2-Chloro-2-nitrovinyl)-1,2-dimethoxybenzene (2c)

$^1$H NMR

[Chemical structure image]
$^{13}$C NMR

![NMR Spectrum](image)

- 152.55
- 149.16
- 131.89
- 126.83
- 122.31
- 113.04
- 111.19
- 56.10
- 56.01
$\text{H-}^{13}\text{C HMBC}$
(Z)-4-(2-Chloro-2-nitrovinyl)-2-(cyclopentyloxy)-1-methoxybenzene (2d)

$^1$H NMR
$^{13}$C NMR

![Chemical Structure Image]
$^{1}H^{13}C$ HSQC
$^1$H-$^{13}$C HMBC
MS spectra (EI)
(Z)-1-Bromo-2-(2-chloro-2-nitrovinyl)-4,5-dimethoxybenzene (2e)

$^1$H NMR
$^{13}$C NMR
$^{1}H^{13}C$ HSQC

![Chemical structure diagram](attachment:image.png)

- MeO
- NO$_2$
- Br
- Cl
MS spectra (EI)

[Image of a molecular structure]

[Graph showing a mass spectrum with peaks at various m/z values]
(Z)-2-Bromo-5-(2-chloro-2-nitrovinyl)thiophene (2f)

$^1$H NMR
$^{13}$C NMR
MS spectra (EI)
(Z)-5-(2-Chloro-2-nitrovinyl)benzo[d][1,3]dioxole (2g)

$^1$H NMR

![NMR spectrum](image)
$^{13}$C NMR

![Chemical Structure Image]
$^{13}$C NMR DEPT

![Chemical Structure](image)

- 131.67
- 128.97
- 109.55
- 108.96
- 102.15
MS spectra (EI)

![Chemical structure]

- M+ = 227
- M+ - Cl = 180
- M+ - NO2 = 146
- M+ - C6H5 = 123
- M+ - C6H4NO = 73
- M+ - C6H4Cl = 62

Peak intensities at 62, 73, 87, 123, 146, 180, and 227.
Methyl (Z)-4-(4-(2-chloro-2-nitrovinyl)phenoxy)butanoate (2h)

$^1$H NMR

MeO$_2$C

Cl

NO$_2$
$^{13}$C NMR

MeO$_2$C\(-\)CH$_2$O\(-\)Cl, $\text{NO}_2$

Peak Values: 173.40, 161.91, 150.62, 122.14, 115.12, 67.04, 51.71, 30.33, 24.40
MS spectra (EI)

![MS spectrum diagram](image)

Chemical structure: MeO₂C - O - C₆H₄ - Cl - C₆H₄ - NO₂
Ethyl (Z)-2-(4-(2-chloro-2-nitrovinyl)phenoxy)-2-methylpropanoate (2i)

$^1$H NMR
$^{13}$C NMR

EtO$_2$C

\[ \text{Cl} \]

\[ \text{NO}_2 \]
$^{13}$C NMR DEPT

EtO$_2$C

O

Cl

NO$_2$
MS spectra (EI)

![Chemical Structure](image)

**Peak Intensities:**
- 59
- 87
- 101
- 118
- 125
- 141
- 152
- 199
- 240
- 313

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

$^1$H NMR

![NMR spectrum of (Z)-2-Bromo-4-(2-chloro-2-nitrovinyl)-1-methoxybenzene (2j)](image-url)
$^{13}$C NMR
$^{13}$C NMR DEPT

![Chemical Structure](image)
MS spectra (EI)
(Z)-1-Chloro-4-(4-(2-chloro-2-nitrovinyl)phenoxy)benzene (2k)

$^1$H NMR
$^{13}$C NMR

Cl-\(\text{O}\)-\(\text{NO}_2\)-\(\text{Cl}\)
$^{13}$C NMR DEPT

[Chemical Structure Image]
$^1$H-$^{13}$C HMBC
(Z)-(2-Chloro-2-nitrovinyl)benzene (2l)

$^1$H NMR

![NMR Spectrum](image-url)
(Z)-1-(2-Chloro-2-nitrovinyl)-4-fluorobenzene (2m)

$^1$H NMR
$^{13}$C NMR

![Chemical Structure](image)

- 166.21
- 162.83
- 133.56
- 130.44
- 125.85
- 116.64
- 116.35
$^1$H-$^{13}$C HMBC
(Z)-1-Chloro-4-(2-chloro-2-nitrovinyl)benzene (2n)

$^{1}H$ NMR
$^{13}$C NMR
(Z)-1-Bromo-4-(2-chloro-2-nitrovinyl)benzene (2o)

$^1$H NMR

\[
\begin{align*}
\text{Br} & \quad & \text{Cl} \\
& \quad & \quad \text{NO}_2
\end{align*}
\]
(Z)-1-(2-Chloro-2-nitrovinyl)-4-methylbenzene (2p)

$^1$H NMR
$^{13}$C NMR
$^{1}H^{13}C$ HMBC
(Z)-1-Bromo-2-(2-chloro-2-nitrovinyl)benzene (2q)

$^1$H NMR
$\text{Br}$

$\text{NO}_2$

$\text{Cl}$

$\text{C NMR}$

$\text{13C NMR}$
$^{1}H-^{13}C$ HSQC
$^{1}H^{13}C$ HMBC
(Z)-2-Chloro-4-(2-chloro-2-nitrovinyl)-1-methoxybenzene (2r)

^{1}H NMR
$^{13}$C NMR

![Chemical structure diagram]
$^1$H-$^1$C HSQC
MS spectra (EI)
(Z)-(4-Chloro-4-nitrobut-3-enyl)benzene (2s)

$^1$H NMR
$^{13}$C NMR

![Chemical Structure](image)

- 140.39 ppm
- 139.48 ppm
- 134.93 ppm
- 128.77 ppm
- 128.27 ppm
- 126.72 ppm
- 33.44 ppm
- 30.72 ppm
$^{13}$C NMR DEPT

\[ \text{Structure:} \]

\[ \text{Chemical Shifts:} \]

- 134.93 ppm
- 128.77 ppm
- 128.27 ppm
- 126.72 ppm
- 33.44 ppm
- 30.72 ppm
$^1$H-$^3$H COSY
$^1$H-$^{13}$C HMBC
MS spectra (EI)

\[\text{NO}_2\]

\[\text{Cl}\]

![MS spectrum graph](image_url)
Crude reaction mixture for 1a+SO₂Cl₂ without quenching with NEt₃. Major component: 1-(1,2-Dichloro-2-nitroethyl)-4-methoxybenzene (3a) (2 diastereomers)

¹H NMR
$^{13}$C NMR

![Chemical Structure](image)

- Peak at 122.11 ppm
- Peak at 133.57 ppm
- Peak at 131.68 ppm
- Peak at 129.66 ppm
- Peak at 129.27 ppm
- Peak at 125.55 ppm
- Peak at 125.24 ppm

Peaks labeled 2a, 3a, 3a', and 3a''
$^{\text{1H-13C}}$ HSQC
$^{1}H-^{13}C$ HMBC

![Chemical Structure](Image)

...
Crude reaction mixture for 1n+SO$_2$Cl$_2$ without quenching with NEt$_3$. Major component: 1-Chloro-4-(1,2-dichloro-2-nitroethyl)benzene (3n)
$^{13}$C NMR

![Chemical structure diagram with NMR spectrum]
$^{13}$C NMR DEPT

![Chemical structure diagram]
(E)-1,3-Dichloro-4,5,6-trimethoxy-2-(2-nitrovinyl)benzene (4)

$^1$H NMR
$^{13}$C NMR

![Chemical structure image]

Spectroscopic data:
- $61.28$
- $61.50$
- $122$
- $149.68$
- $142.41$
- $132.33$
- $125.57$
- $123.01$

Chemical shifts and peak assignments for the compound.
MS spectra (EI)

Chemical structure:

- MeO
- OMe
- NO2
- OMe
- Cl
- Cl
- Cl

Mass values:
- 59
- 97
- 131
- 186
- 217
- 245
- 260
- 307
(Z)-1,3-Dichloro-2-(2-chloro-2-nitrovinyl)-4,5,6-trimethoxybenzene (5)

$^1$H NMR

![NMR spectrum diagram]
$^{13}$C NMR

![Chemical Structure](image)

Frequency: 149.64, 149.01, 127.98, 124.36, 123.00, 61.46, 61.36
\(^1\text{H-\(^{13}\text{C}\)}\) HMBC