Electrochemical Nitration with Nitrite

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Electrochemical Nitration with Nitrite

Stephan P. Blum[a], Christean Nickel[a], Lukas Schäffer[a], Tarik Karakaya[a], Siegfried R. Waldvogel[a]∗

Abstract: Aromatic nitration has tremendous importance in organic chemistry as nitroaromatic compounds serve as versatile building blocks. We present the electrochemical aromatic nitration with NBu₄NO₂, which serves a dual role as supporting electrolyte and safe, readily available as well as easy to handle nitro source. Stoichiometric amounts of 1,1,1-3,3,3-hexafluoropropan-2-ol (HFIP) in MeCN significantly increased the yield by solvent control. In this protocol, the reaction mechanism is based on electrochemical oxidation of nitrite to NO₂⁻, which initiates the nitration reaction in a divided electrolysis cell with inexpensive graphite electrodes. Overall, the reaction has been demonstrated for 20 examples with yields up to 88%. Scalability has been proven by a 13-fold scale-up.

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1. **General Information**

All reagents and solvents used were obtained as analytical grade from commercial suppliers or purified with standard methods.\(^1\) Electrochemical reactions were carried out at graphite (C\(_{gr}\)) electrodes. Isostatic graphite Sigrafine® electrodes V2100 were obtained from SGL Carbon (Bonn-Bad Godesberg, Germany). BDD electrodes (DIACHEM®, 15 μm boron-doped diamond layer on 3 mm silicon support/wafer) were purchased from CONDIAS GmbH, Itzhoe, Germany. The glass frits were purchased from ROBU® Glasfilter-Geräte GmbH (VitraPOR filter-disc; centred; porosity: P4; diameter: 10 mm; thickness standard: approx. 2.8 mm). Glassy carbon electrodes were obtained from SIGRADUR® G, HTW, Thierhaupten, Germany.

**Column chromatography** was performed on silica gel 60 m (0.040–0.063 mm, Macherey-Nagel GmbH & Co, Düren, Germany). Therefore, a preparative chromatography system (Büchi, Flawil, Switzerland) was used with a Büchi Control Unit C-620, an UV detector Büchi UV photometer C-635, a Büchi fraction collector C-660 and two Pump Modules C-605 for adjusting the solvent mixtures. As eluent, mixtures of cyclohexane and ethyl acetate were employed. Silica gel 60 sheets on aluminium (F254, Merck KGaA, Darmstadt, Germany) were employed for thin layer chromatography.

**Gas chromatography** was performed on a Shimadzu GC-2025 (Shimadzu, Japan) using a HP-5 column (Agilent Technologies, Santa Clara, California; length: 30 m, inner diameter: 0.25 mm, film: 0.25 μm, carrier gas: hydrogen). GC-MS measurements were carried out on a Shimadzu GC-2010 (Shimadzu, Japan) using a HP-1 column (Agilent Technologies, Santa Clara, California; length: 30 m, inner diameter: 0.25 mm, film: 0.25 μm, carrier gas: helium). The chromatograph was coupled to a mass spectrometer Shimadzu GC-MS-QP2010.

**Melting points** were determined with a Melting Point Apparatus B-565 (Büchi, Flawil, Switzerland) and are uncorrected. Heating rate: 1 °C/min.

**NMR spectra** of \(^1\)H (400 MHz), \(^{13}\)C\({}^\text{\text{1}}\)H (101 MHz), and \(^{19}\)F (376 MHz) were recorded at 23 °C by Bruker Avance II 400 (400 MHz, 5 mm BBFO-SmartProbe with z gradient and ATM, SampleXPress 60 sample changer, Analytische Messtechnik, Karlsruhe, Germany). Chemical
shifts (δ) are reported in parts per million (ppm) relative to traces of CHCl₃ (7.26 ppm in ¹H, 77.16 ppm in ¹³C{¹H}). For ¹⁹F spectra CFCl₃ serves as reference compound.²

**NMR spectra** of ¹H (300.13 MHz), ¹⁹F (282.38 MHz) and ¹³C{¹H} (75.48 MHz) were recorded at 23 °C by Bruker Avance III HD spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of CHCl₃ (7.26 ppm in ¹H, 77.16 ppm in ¹³C{¹H}). For ¹⁹F spectra CFCl₃ serves as reference compound.²

**High-resolution mass spectra** were obtained with QT of Ultima 3 (Waters, Milford, Massachusetts) using electrospray ionization (ESI) and atmospheric-pressure chemical ionization (APCI) mode.

**Cyclic voltammetry** was performed in a 10 mL snap-cap vial equipped with an Autolab PGSTAT101 potentiostat (Metrohm AG, Herisau, Switzerland). **WE:** glassy carbon electrode tip, 2 mm diameter; **CE:** glassy carbon rod; **RE:** Ag/AgCl in saturated LiCl/EtOH. Solvent: MeCN (5 mL), ν = 100 mV/s, room temperature, c = 0.01 M, supporting electrolyte: NBu₄BF₄, c (NBu₄BF₄) = 0.1 M (165 mg, 0.50 mmol). Ferrocene/ferrocenium (FcH/FcH⁺) was used as internal reference (half-wave potential 0.58 V versus Ag/AgCl).
2. Experimental Procedures

Experimental setup (screening cells):
The electrochemical conversion was conducted in divided cells made of Teflon™ according to Figure 1.[3] A porous glass frit (porosity: P4) was used as separator, sealed by an EPDM ring. As cathode and anode material, graphite electrodes (Cgr) were utilized, which can be fixed by Teflon™ screws. One round-shaped stirring bar is placed in each compartment of the cell. In total, six divided cells can be placed in a screening block, which can be located on a magnetic stirrer. This reaction set-up can be commercially obtained as IKA® screening system package (6 cells) from IKA®-Werke GmbH & Co. KG, Staufen, Germany.

![Diagram of screening system with 6 divided electrolysis cells fitting on a common magnetic stirrer; electrode gap: 2 cm; active surface of each planar electrode: 3.2 cm².](image)

**Figure 1.** Screening system with 6 divided electrolysis cells fitting on a common magnetic stirrer; electrode gap: 2 cm; active surface of each planar electrode: 3.2 cm².

**Scale-up Electrolysis:**
The scale-up reaction was performed in an H-type glass cell, which is divided by a glass frit (P4) and can be seen in Figure 2. Total volume was 160 mL (80 mL in each compartment). A star-shaped stirring bar was used on each side for efficient mixing. Graphite electrodes (dimensions: (6 x 2 x 0.3) cm) were employed. Dimensions of the H-type divided glass cell: (16 x 5 x 14) cm. The electrode gap is 11.5 cm.
Preparation of NBu₄NO₂:
A flask was charged with (NBu₄)₂SO₄ (50 mL (equals 25 g), 43.3 mmol, 1.00 eq., 50 wt-% solution). NaNO₂ (8.91 g, 129.1 mmol, 3.00 eq.) was added and the reaction mixture was stirred at 10 °C until full dissolution of NaNO₂. The precipitation of excess Na₂SO₄ can be observed during this process. The mixture was filtered to remove the precipitated Na₂SO₄. To the crude reaction mixture was added distilled water (50 mL). NBu₄NO₂ was extracted in CH₂Cl₂ (2x 60 mL). The aqueous phase was back-washed with CH₂Cl₂ (2x 25 mL). The combined organic phases were dried over Na₂SO₄ and filtered. The solvent was removed under reduced pressure. The desired salt (Figure 3) was afforded as a pale-yellow salt (23.23 g, 80.5 mmol, 93%).

Please consider: Occasionally, the formation of low amounts of nitrous gases was observed during removal of the organic solvent at reduced pressure. Therefore, the use of rotary evaporation in a fume hood is highly recommended. Additionally, it also has to be considered that NBu₄NO₂ is hygroscopic. Therefore, storage in well-sealed container is recommended.
Figure 3. NBu4NO2 obtained from salt metathesis.

General procedure for optimization reactions (GP1):
The anodic compartment of a divided PTFE screening cell was charged with 1,4-dimethoxybenzene (83 mg, 0.60 mmol, 1.00 eq.) and NBu4NO2 (519 mg, 1.8 mmol, 3.00 eq.). The cathodic compartment was charged with NBu4BF4 (395 mg, 1.2 mmol, 2.00 eq.), MeCN (5.5 mL), and HFIP (0.5 mL). Into the anodic compartment were added MeCN (5.5 mL) and HFIP (94 μL, 0.90 mmol, 1.50 eq.). The graphite electrodes were connected to a galvanostat and the electrolysis was carried out under constant stirring (300 rpm). After termination of the electrolysis (108 min for j = 7 mA/cm², 2.5 F), the reaction mixture was further stirred for 30 min. 1,3,5-Trimethoxybenzene (101 mg, 0.60 mmol, 1.00 eq.) was added as internal NMR standard. An aliquot (1–2 mL) of the crude reaction mixture was taken and the solvents were removed under reduced pressure. The NMR yield of the product (4) was determined by integral ratio to the internal standard (1,3,5-trimethoxybenzene).

General procedure for the electrochemical synthesis of nitroaromatic compounds (GP2):
The anodic compartment of a divided PTFE screening cell was charged with the aromatic compound (0.60 mmol, 1.00 eq.) and NBu4NO2 (519 mg, 1.8 mmol, 3.00 eq.). The cathodic compartment was charged with NBu4BF4 (395 mg, 1.2 mmol, 2.00 eq.), MeCN (5.5 mL), and HFIP (0.5 mL). Into the anodic compartment were added MeCN (5.5 mL) and HFIP (94 μL, 0.90 mmol, 1.50 eq.). The graphite electrodes were connected to a galvanostat and the electrolysis (j = 15 mA/cm², Q = 2.5 F) was carried out under stirring (300 rpm) at room temperature. During this process, the terminal voltage was ~13.5 V. After termination of the electrolysis (50 min), the reaction mixture was further stirred for 30 min. Ethyl acetate (30 mL) was added to the reaction
mixture. The organic layer was washed with distilled water (3x 25 mL). The aqueous phases were back-washed with ethyl acetate (2x 25 mL). The combined organic fractions were dried over Na₂SO₄ and filtered. The organic solvent was removed under reduced pressure. The crude product was separated via column chromatography by using an ethyl acetate/cyclohexane solvent gradient (mostly 2:98 to 1:1).

**Important Considerations**

The anodic compartment of the divided PTFE cells was sealed with Parafilm™ as shown in Figure 4. The graphite electrodes were occasionally grinded with sand paper and washed with DMSO.

![Figure 4](image.png)

**Figure 4.** Compartments were sealed with Parafilm™. The cathodic compartment was not fully sealed due to H₂ gas evolution.
3. **Mechanistic Proposal**

Cyclic voltammetry experiments (Graph 1) were conducted to support the suggested reaction mechanism. Firstly, it is noticeable that the oxidation potential of nitrite (ranging from 0.13 V–0.40 V) increases upon addition of HFIP, which can be explained by hydrogen bonding effects. Secondly, the CV data suggests the initial oxidation of the nitrite prior to the arene, as 1,4-dimethoxybenzene is oxidized at 0.94 V. As expected, the oxidation potential of 4 is significantly higher compared to 1,4-dimethoxybenzene due to the electron-withdrawing effect of the nitro group.

**Graph 1.** Cyclic Voltammetry measurements of N Bu NO 2 with different HFIP concentrations (no HFIP, 0.01 M, 0.1 M), 1,4-dimethoxybenzene, and nitroarene 4 (ν = 100 mV/s).
As outlined in the manuscript, NO could be recycled with atmospheric oxygen to NO$_2$.
Alternatively, the recycling of NO to NO$_2$/N$_2$O$_4$ could also proceed as shown in scheme 1, which was postulated by Wartel and co-workers in 1987.$^{[4]}$
Protons are considered to induce the ionic dissociation of N$_2$O$_4$ to [NO$^+$][NO$_3^-$]. After formation of the [arene–NO$^+$] complex, subsequent oxidation to the arene radical cation, and final reaction to the nitroarene with NO$_2$/N$_2$O$_4$ (and H$^+$ abstraction), the in-situ generated NO and NO$_2$/N$_2$O$_4$ form N$_2$O$_3$. The conversion of the latter with HNO$_3$ gives N$_2$O$_4$ and nitrous acid (HNO$_2$). (In their work, the nitration of naphthalene has been accomplished by anodic oxidation of NO$_2$/N$_2$O$_4$ to NO$_2^+$ inducing an initial nitration reaction with H$^+$ generation to induce the catalytic cycle as shown in Scheme 1.)$^{[4]}$
Finally, we conducted several control experiments with the chemical oxidant NOBF$_4$ to further investigate the reaction mechanism.

Scheme 2. Experiments conducted with NOBF$_4$ as chemical oxidant.

Table 1. Variations from the conditions shown in Scheme 2.

| Entry | NOBF$_4$ | NBu$_4$NO$_2$ | Ar atmosphere | SM$[^a]$ | NMR yield$[^a]$ |
|-------|---------|--------------|---------------|---------|-----------------|
| 1     | –       | –            | –             | 100%    | –               |
| 2     | –       | ✓            | –             | 100%    | –               |
| 3     | ✓       | –            | –             | 20%     | 29%             |
| 4     | ✓       | ✓            | –             | 60%     | 31%             |
| 5     | ✓       | ✓            | ✓             | 64%     | 31%             |
| 6     | ✓       | –            | ✓             | 23%     | 19%             |

[a]: Yield determined by internal NMR standard (1,3,5-trimethoxybenzene); SM = starting material.

As expected, no reaction occurred in the reactions of entry 1 and 2 (Table 1) due to the missing chemical oxidant NO$^+$ (also so Figure 5, A and B). In entry 3, the nitrite salt was omitted, which resulted in 29% NMR yield due to the addition of NOBF$_4$. However, starting material degradation (brown/dark reaction mixture, Figure 5, C) occurred as only 20% of 1,4-dimethoxybenzene was detected in the crude NMR results. Interestingly, in the reaction of entry 4, less starting material degradation occurred due to the presence of the nitrite salt. Furthermore, the NO gas evolution was clearly recognizable (Figure 5, D), which turned brown (NO$_2$) upon contact with atmospheric oxygen. The reaction in Ar atmosphere (entry 5) showed almost the same results compared to entry 4, indicating that nitrite could be also eligible as nucleophile for the reaction to nitroarenes as depicted in the manuscript. Significantly less NMR yield and starting material were detected in Ar atmosphere and when nitrite was omitted (entry 6) possibly due to missing/less atmospheric oxygen for the formation of NO$_2$ from NO.
Figure 5. A corresponds to the reaction mixture of entry 1 in Table 1; B corresponds to entry 2; C corresponds to entry 3; D corresponds to entry 4.
4. Further Optimization Reactions

Scheme 3. Test reaction (equals to Scheme 3 in the manuscript).

Herein, we present further optimization reactions (Table 1) for the test substrates (Scheme 3), which are not presented in the manuscript. The reaction procedure has been executed according to GP1.

Table 1. Further optimization reactions for the electrochemical nitration. Standard conditions are displayed in Scheme 3. Composition of the catholyte: NBu$_4$BF$_4$ (2.0 eq.), HFIP (0.5 mL), MeCN (5.5 mL).

| Entry | Deviations from the standard conditions | NMR yield$^{[a]}$ |
|-------|----------------------------------------|------------------|
| 1     | 7 mA/cm$^2$, no HFIP in anolyte, 0.5 mL AcOH in catholyte (instead of HFIP) | 29%              |
| 2     | O$_2$ atmosphere, 2 F                   | 86%              |
| 3     | O$_2$ atmosphere                        | 76%              |
| 4     | 3.0 F (instead of 2.5 F)                | 52%              |
| 5     | 4.0 F (instead of 2.5 F)               | traces           |
| 6     | 5 mA/cm$^2$ (instead of 15 mA/cm$^2$)   | 82%              |
| 7     | 10 mA/cm$^2$ (instead of 15 mA/cm$^2$)  | 86%              |
| 8     | 12 mA/cm$^2$ (instead of 15 mA/cm$^2$)  | 91%              |
| 9     | anodic compartment not sealed with Parafilm™ | 65%              |

[a] Yield was determined by internal NMR standard (1,3,5-trimethoxybenzene).

Omitting of HFIP in the anolyte and simultaneous substitution of HFIP by AcOH in the catholyte significantly reduced the NMR yield to 29% (Table 1, entry 1). Oxygen atmosphere in the anolyte and the application of 2 F (entry 2) interestingly gave higher yields compared to 2.5 F in entry 3 possibly due to excess formation of NO$_2$ in the latter. Higher amounts of charge ($Q$) significantly reduced the yield (entry 4 and 5). It is noteworthy that double nitration of 4 was not observed. Modulation of the current density ($j$) resulted in comparable yields, whereas higher current densities seemed to be slightly superior. Finally, when the anodic compartment was not sealed with Parafilm™ as shown in Figure 4, the yield drastically reduced to 65% (entry 9). A possible explanation for this could be the leakage of the in-situ formed NO gas in unsealed cells, which is supposed to be (partially) recycled to the system (in form of NO$_2$).
5. Product Characterization

5.1 1,4-Dimethoxy-2-nitrobenzene (4)

According to GP2, 1,4-dimethoxybenzene (83 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 → 50:50), 4 (97 mg, 0.53 mmol, 88%) was isolated as yellow crystalline solid.

Scale-up of the electrolysis:
The anode compartment of a divided H-type glass cell was charged with 1,4-dimethoxybenzene (1.11 g, 8.0 mmol, 1.00 eq.) and NBu₄NO₂ (6.92 g, 24.0 mmol, 3.00 eq.). Into the cathode compartment was added NBu₄BF₄ (5.3 mg, 16 mmol, 2.00 eq.). Subsequently, MeCN (73.5 mL) and HFIP (6.5 mL) were transferred into the cathode compartment. The anode compartment was filled with MeCN (71.5 mL) and HFIP (1.26 mL, 12 mmol, 1.50 eq.). The graphite electrodes were connected to a galvanostat. The electrolysis (15 mA/cm², 2.5 F) was started and the reaction mixture was stirred (300 rpm) at room temperature. During the electrolysis the terminal voltage was 34 V. After 268 min, the electrolysis was completed and the reaction was further stirred overnight (in total: 14 h). The reaction solutions of both compartments were transferred into a separating funnel and rinsed with 250 mL ethyl acetate and distilled water (250 mL) was added. The organic layer was washed with distilled water (2x 150 mL). The aqueous fractions were combined and back-washed with ethyl acetate (2x 100 mL). The organic fractions were combined, dried over Na₂SO₄ and filtered. The organic solvent was removed under reduced pressure. The crude product was separated via column chromatography using an Ethyl acetate/cyclohexane solvent gradient (2:98 to 1:1). The title compound (1.25 mg, 6.81 mmol, 85%) was obtained as a yellow crystalline solid.

4:

^1^H NMR (300 MHz, CDCl₃) δ [ppm] = 7.35 (d, J = 3.1 Hz, 1H), 7.09 (dd, J = 9.2, 3.1 Hz, 1H), 7.01 (d, J = 9.2 Hz, 1H), 3.89 (s, 3H), 3.79 (s, 3H); ^13^C NMR (75 MHz, CDCl₃) δ [ppm] = 152.9, 147.4, 139.5, 120.9, 115.2, 110.15, 57.1, 56.1; m.R: 70–71 ºC; HRMS for C₈H₉NO₄ (APCI+) [M⁺]: calc.: 183.0527, found: 183.0534.
Analytical data of 4 correspond to those reported in the literature.\textsuperscript{[5]}

5.2 1-Bromo-2,5-dimethoxy-4-nitrobenzene (5)

![Chemical structure of 5]

According to GP2, 1-bromo-2,5-dimethoxybenzene (157 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 $\rightarrow$ 50:50). The title compound (95 mg, 0.36 mmol, 60\%) was obtained as yellow solid.

5: 
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ [ppm] = 7.44 (s, 1H), 7.31 (s, 1H), 3.92 (s, 3H), 3.90 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ [ppm] = 149.6, 147.6, 138.1, 119.3, 118.6, 108.7, 57.4, 57.1; mR: 150–152 °C; HRMS for C$_8$H$_8$BrNO$_4$ (APCI+) [M+H]$^+$: calc.: 260.9637, found: 260.9625.

Analytical data of 5 correspond to those reported in the literature.\textsuperscript{[6]}

5.3 1-Chloro-2,5-dimethoxy-4-nitrobenzene (6)

![Chemical structure of 6]

According to GP2, 1-chloro-2,5-dimethoxybenzene (104 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 $\rightarrow$ 50:50), 6 (76 mg, 0.35 mmol, 58\%) was obtained as yellow solid.

6:
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ [ppm] = 7.49 (s, 1H), 7.14 (s, 1H), 3.92 (s, 3H), 3.90 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 148.6, 147.7, 137.4, 129.3, 116.2, 109.2, 57.4, 57.0; $\text{mp}$: 136–138 °C; HRMS for C$_8$H$_8$FNO$_4$ (APCI+) [M$^+$]: calc.: 217.0137, found: 217.0131. Reported melting range: 147–148 °C. $^1$H NMR, $^{13}$C NMR and HRMS data correspond to those reported in the literature.[7]

5.4 1-Fluoro-2,5-dimethoxy-4-nitrobenzene (7)

According to GP2, 2-fluoro-1,4-dimethoxybenzene (94 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 → 50:50), 7 (86 mg, 0.43 mmol, 71%) was obtained as yellow solid.

7: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ [ppm] = 7.61 (d, $J$ = 8.7 Hz, 1H), 6.88 (d, $J$ = 12.2 Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 155.8 (d, $J$ = 258.0 Hz), 149.0 (d, $J$ = 9.3 Hz), 141.1 (d, $J$ = 12.1 Hz), 134.5, 111.5 (d, $J$ = 4.5 Hz), 103.0 (d, $J$ = 23.5 Hz), 57.3, 57.1; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ [ppm] = −121.94 (dd, $J$ = 12.1, 8.7 Hz); $\text{mp}$: 113–115 °C; HRMS for C$_8$H$_9$FNO$_4$+ (APCI+) [M+H$^+$]: calc.: 202.0510, found: 202.0495. Analytical data correspond to those reported in the literature.[8]

5.5 1,2,4-Trimethoxy-5-nitrobenzene (8)
According to GP2, 1,2,4-trimethoxybenzene (101 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 → 50:50), 8 (97 mg, 0.45 mmol, 76%) was obtained as yellow solid.

8:
\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta [ppm] = 7.52 (s, 1H), 6.53 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.85 (s, 3H); ^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta [ppm] = 154.9, 150.5, 142.3, 130.8, 108.9, 97.5, 57.2, 56.5, 56.5; 121–123 °C; HRMS for C\(_9\)H\(_{12}\)NO\(_5\)\(^{+}\) (ESI\(^{+}\)) [M+H]\(^{+}\): calc.: 214.0710, found: 214.0715.

Analytical data correspond to those reported in the literature.\(^9\)

5.6 1,2-Dimethoxy-4-nitrobenzene (9)

According to GP2, veratrole (83 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 → 50:50), 9 (86 mg, 0.47 mmol, 78%) was obtained as yellow solid.

9:
\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta [ppm] = 7.92 (dd, J = 8.9, 2.6 Hz, 1H), 7.75 (d, J = 2.6 Hz, 1H), 6.91 (d, J = 8.9 Hz, 1H), 3.98 (s, 3H), 3.97 (s, 3H); ^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 154.6, 149.0, 141.6, 118.0, 110.0, 106.6, 56.6, 56.5; mR: 95–96 °C; HRMS for C\(_8\)H\(_{10}\)NO\(_4\)\(^{+}\) (APCI\(^{+}\)) [M+H]\(^{+}\): calc.: 184.0605, found: 184.0603.

Analytical data correspond to those reported in the literature.\(^10\)
5.7 1-Fluoro-4,5-dimethoxy-2-nitrobenzene (10)

According to GP2, 4-fluoroveratrole (94 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 → 50:50), 10 (65 mg, 0.32 mmol, 54%) was obtained as yellow solid.

10:
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ [ppm] = 7.58 (d, $J = 7.1$ Hz, 1H), 6.73 (d, $J = 12.3$ Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 155.2 (d, $J = 9.3$ Hz), 153.9, 150.4, 145.1, 107.4 (d, $J = 2.0$ Hz), 101.0 (d, $J = 26.7$ Hz), 57.0, 56.8; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ [ppm] = −121.90 (dd, $J = 12.3$, 7.1 Hz); mR: 142–144 °C; HRMS for C$_8$H$_8$FNO$_4$ (APCI+) [M$^+$]: calc.: 201.0432, found: 201.0423.

5.8 1-Bromo-4,5-dimethoxy-2-nitrobenzene (11)

According to GP2, 4-bromoveratrole (130 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 → 50:50), 11 (44 mg, 0.17 mmol, 28%) was obtained as yellow solid.

11:
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ [ppm] = 7.57 (s, 1H), 7.11 (s, 1H), 3.96 (s, 3H), 3.94 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ [ppm] = 153.0, 148.4, 141.9, 116.7, 109.2, 107.7, 56.9, 56.6; mR: 151–153 °C; HRMS for C$_8$H$_8$BrNO$_4$ (APCI+) [M$^+$]: calc.: 260.9632, found: 260.9625.

Analytical data correspond to those reported in the literature.$^{[11]}$
5.9  2,3-Dihydro-6-Nitrobenzo[1,4]dioxine (12)

According to GP2, benzo-1,4-dioxane (82 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 → 50:50), 12 (63 mg, 0.35 mmol, 58%) was obtained as beige solid.

12:  
$^1$H NMR (300 MHz, CDCl$_3$) δ [ppm] = 7.80–7.74 (m, 2H), 6.98–6.89 (m, 1H), 4.38–4.28 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ [ppm] = 149.5, 143.3, 141.9, 117.8, 117.4, 113.6, 64.8, 64.2; mR: 118–120 °C; HRMS for C$_8$H$_8$NO$_4^+$ (ESI+) [M+H]: calc.: 182.0448, found: 182.0438.

Analytical data correspond to those reported in the literature.$^{[10b,12]}$

5.10  5-Nitrobenzo[1,3]dioxole (13)

According to GP2, 1,3-benzodioxole (73 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 → 50:50), 13 (28 mg, 0.17 mmol, 28%) was obtained as beige solid.

13:  
$^1$H NMR (300 MHz, CDCl$_3$) δ [ppm] = 7.89 (dd, $J = 8.6$, 2.3 Hz, 1H), 7.66 (d, $J = 2.3$ Hz, 1H), 6.86 (d, $J = 8.6$ Hz, 1H), 6.14 (s, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ [ppm] = 153.3, 148.3, 143.0, 120.0, 107.7, 104.6, 103.2; mR: 144–146 °C; HRMS for C$_7$H$_6$NO$_4^+$ (APCI+) [M+H]: calc.: 268.0292, found: 268.0286.

Analytical data correspond to those reported in the literature.$^{[13]}$
5.11 2-Methoxy-4-methyl-6-nitrophenol (14)

According to GP2, 2-methoxy-4-methylphenol (83 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 → 50:50), 14 (39 mg, 0.21 mmol, 35%) was obtained as yellow solid.

14:

1H NMR (400 MHz, CDCl₃) δ [ppm] = 10.62 (s, 1H), 7.47–7.48 (m, 1H), 6.94 (d, J = 1.6 Hz, 1H), 3.92 (s, 3H), 2.33 (s, 3H); 13C NMR (101 MHz, CDCl₃) δ [ppm] = 149.6, 144.4, 133.5, 129.0, 119.2, 115.3, 56.7, 21.0; mR: 77–78 °C; HRMS for C₈H₉NO₄ (APCI+) [M⁺]: calc.: 183.0527, found: 183.0523.

Analytical data correspond to those reported in the literature.[14]

5.12 2,4-Di-tert-butyl-6-nitrophenol (15)

According to GP2, 2,4-di-tert-butylphenol (124 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 0:100 → 50:50), 15 (34 mg, 0.14 mmol, 23%) was obtained as highly viscous yellow oil.

15:

1H NMR (400 MHz, CDCl₃) δ [ppm] = 11.45 (s, 1H), 7.96 (d, J = 2.5 Hz, 1H), 7.65 (d, J = 2.5 Hz, 1H), 1.45 (s, 9H), 1.32 (s, 9H); 13C NMR (101 MHz, CDCl₃) δ [ppm] = 153.2, 142.1, 140.0, 133.8, 132.7, 119.0, 35.9, 34.7, 31.2, 29.5; HRMS for C₁₄H₂₆NO₃⁻ (ESI⁻) [M–H]⁻: calc.: 250.1448, found: 250.1465.
5.13 4-Bromo-2-methyl-6-nitrophenol (16)

According to GP2, 4-bromo-2-methylphenol (112 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 → 50:50), 16 (20 mg, 0.09 mmol, 14%) was obtained as yellow solid.

16:
$^1$H NMR (400 MHz, CDCl$_3$) δ [ppm] = 10.82 (s, 1H), 8.10 (d, $J = 2.5$ Hz, 1H), 7.55 (m, 1H), 2.33 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ [ppm] = 153.0, 140.8, 133.9, 131.9, 124.9, 111.1, 15.9; m${}_R$: 87–88 °C; HRMS for C$_7$H$_6^{79}$BrNO$_3^-$ (ESI−) [M−H]$^-$: calc.: 229.9458, found: 229.9456.

5.14 5-Iodo-4-methoxy-2-nitrophenol (17)

According to GP2, 3-iodo-4-methoxyphenol (150 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 0:100 → 50:50), 17 (24 mg, 0.08 mmol, 14%) was obtained as yellow solid.

17:
$^1$H NMR (400 MHz, CDCl$_3$) δ [ppm] = 10.24 (s, 1H), 7.71 (s, 1H), 7.39 (s, 1H), 3.90 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ [ppm] = 151.9, 149.5, 133.2, 130.9, 130.6, 100.2, 57.3; m${}_R$: 116–118 °C, HRMS for C$_7$H$_5$INO$_4^-$ (APCI−) [M−H]$^-$: calc.: 293.9269, found: 293.9262.
5.15  \( N-(4,5\text{-Dimethoxy-2-nitrophenyl})\text{acetamide (18)} \)

According to GP2, \( N-(3,4\text{-dimethoxyphenyl})\text{acetamide (117 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 → 50:50), 18 (96 mg, 0.40 mmol, 67\%) was obtained as yellow solid. \)

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18:
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) [ppm] = 10.75 (s, 1H), 8.50 (s, 1H), 7.68 (s, 1H), 4.00 (s, 3H), 3.92 (s, 3H), 2.29 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) [ppm] = 169.5, 156.0, 144.5, 132.3, 128.5, 107.2, 103.2, 56.8, 56.4, 26.0; mR: 192–194 °C; HRMS for C\(_{10}\)H\(_{13}\)N\(_2\)O\(_5\) (ESI\(^+\)) [M+H]\(^+\) : calc.: 241.0819, found: 241.0820.

5.16  \( N-(4,5\text{-Dimethoxy-2-nitrophenyl})\text{benzamide (19)} \)

According to GP2, \( N-(3,4\text{-dimethoxyphenyl})\text{benzamide (154 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 → 50:50), 19 (89 mg, 0.29 mmol, 49\%) was obtained as yellow solid. \)

\[
19:
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\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) [ppm] = 11.79 (s, 1H), 8.75 (s, 1H), 8.03–7.96 (m, 2H), 7.74 (s, 1H), 7.64–7.58 (m, 1H), 7.58–7.50 (m, 2H), 4.06 (s, 3H), 3.94 (s, 3H); \(^{13}\)C NMR (101 MHz,
5.17 tert-Butyl (4,5-dimethoxy-2-nitrophenyl)carbamate (20)

According to GP2, tert-butyl (3,4-dimethoxyphenyl)carbamate (152 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 → 50:50), 20 (139 mg, 0.47 mmol, 78%) was obtained as yellow solid.

20:

$^1$H NMR (400 MHz, CDCl$_3$) δ [ppm] = 10.07 (s, 1H), 8.22 (s, 1H), 7.66 (s, 1H), 4.00 (s, 3H), 3.90 (s, 3H), 1.54 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ [ppm] = 156.0, 152.6, 143.7, 133.5, 128.0, 107.2, 101.7, 81.9, 56.7, 56.4, 28.4; m.p.: 168–170 °C; HRMS for C$_{13}$H$_{18}$N$_2$O$_6$ (ESI$^+$) [M+H]$^+$: calc.: 321.1057, found: 321.1065.

5.18 2,2,2-Trifluoro-$N$-(5-methoxy-4-methyl-2-nitrophenyl)acetamide (21)

According to GP2, 2,2,2-trifluoro-$N$-(3-methoxy-4-methylphenyl)acetamide (140 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl
acetate:cyclohexane = 2:98 → 50:50), 21 (35 mg, 0.13 mmol, 21%) was obtained as yellow solid.

21:
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ [ppm] = 11.82 (s, 1H), 8.27 (s, 1H), 8.11 (d, $J$ = 1.0 Hz, 1H), 3.98 (s, 3H), 2.24 (s, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ [ppm] = 164.2, 155.7 (q, $J$ = 38 Hz), 133.2, 129.5, 128.0, 125.1, 115.5 (q, $J$ = 289 Hz), 102.3, 56.6, 15.9; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ [ppm] = −77.44; m$_R$: 121–122 °C; HRMS for C$_{10}$H$_8$F$_3$N$_2$O$_4^−$ (ESI−) [M−H]$^−$: calc.: 277.0441, found: 277.0449.

5.19 $N$-(4-Methoxy-2-nitrophenyl)acetamide (22)

According to GP2, $N$-(4-methoxy-2-nitrophenyl)acetamide (99 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 → 50:50), 22 (8 mg, 0.04 mmol, 6%) was obtained as orange solid.

22:
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ [ppm] = 10.04 (s, 1H), 8.61 (d, $J$ = 9.3 Hz, 1H), 7.64 (d, $J$ = 3.1 Hz, 1H), 7.22 (dd, $J$ = 9.3, 3.1 Hz, 1H), 3.84 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ [ppm] = 168.9, 155.0, 137.1, 128.6, 124.0, 123.5, 108.6, 56.0, 25.5; m$_R$: 110–112 °C; HRMS for C$_9$H$_{10}$N$_2$O$_4$ (APCI+) [M$^+$]: calc.: 210.0636, found: 210.0641.

In the literature, the melting point is reported to be 118 °C.$^{[15]}$
According to GP3, 4-methoxy-\(N,N\)-dimethylaniline (91 mg, 0.60 mmol, 1.00 eq.) was used as substrate. After product purification via column chromatography (ethyl acetate:cyclohexane = 2:98 → 50:50), 23 (86 mg, 0.36 mmol, 59\%) was obtained as orange solid.

23:

\(^1\text{H NMR}\) (300 MHz, CDCl\(_3\)) \(\delta\) [ppm] = 7.33 (s, 2H), 3.86 (s, 3H), 2.75 (s, 6H); \(^{13}\text{C NMR}\) (75 MHz, CDCl\(_3\)) \(\delta\) [ppm] = 154.8, 149.2, 133.2, 113.9, 56.6, 42.9; \(\text{mR}: 88–89 \, ^\circ\text{C}\); HRMS for \(\text{C}_9\text{H}_{12}\text{N}_3\text{O}_5^+\) (ESI+) [M+H]^+: calc.: 242.0772, found: 242.0778.
6. NMR Spectra of all Isolated Compounds

$^1$H NMR (300 MHz, CDCl$_3$/298 K): 4

$^{13}$C NMR (75 MHz, CDCl$_3$/298 K): 4
$^1$H NMR (300 MHz, CDCl$_3$/298 K): 5

$^{13}$C NMR (75 MHz, CDCl$_3$/298 K): 5
**SUPPORTING INFORMATION**

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

\[^1H\text{ NMR (300 MHz, CDCl}_3/298 \text{ K): 6}\]

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

\[^{13}\text{C NMR (75 MHz, CDCl}_3/298 \text{ K): 6}\]
$^1$H NMR (300 MHz, CDCl$_3$/298 K): 7

$^{13}$C NMR (75 MHz, CDCl$_3$/298 K): 7
$^1$H NMR (300 MHz, CDCl$_3$/298 K): 8

$^{19}$F NMR (282 MHz, CDCl$_3$/298 K): 7
$^{13}$C NMR (75 MHz, CDCl$_3$/298 K): 8

$^1$H NMR (300 MHz, CDCl$_3$/298 K): 9
$^{13}$C NMR (75 MHz, CDCl$_3$/298 K): 9

$^1$H NMR (300 MHz, CDCl$_3$/298 K): 10
$^{13}$C NMR (75 MHz, CDCl$_3$/298 K): 10

$^{19}$F NMR (282 MHz, CDCl$_3$/298 K): 10
\[ \text{Supporting Information} \]

1H NMR (400 MHz, CDCl\textsubscript{3}/298 K): 11

\[ \text{13C NMR (101 MHz, CDCl}\textsubscript{3}/298 K): 11 \]
$^{1}H$ NMR (300 MHz, CDCl$_3$/298 K): 12

$^{13}C$ NMR (75 MHz, CDCl$_3$/298 K): 12
$^{1}H$ NMR (300 MHz, CDCl$_3$/298 K): 13

$^{13}C$ NMR (75 MHz, CDCl$_3$/298 K): 13


$\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3/298 \text{ K): 14}$

$\text{\textsuperscript{13}C NMR (101 MHz, CDCl}_3/298 \text{ K): 14}$
$^1$H NMR (400 MHz, CDCl$_3$/298 K): 15

$^{13}$C NMR (101 MHz, CDCl$_3$/298 K): 15
$^1$H NMR (400 MHz, CDCl$_3$/298 K): 16

$^{13}$C NMR (101 MHz, CDCl$_3$/298 K): 16
$^1$H NMR (400 MHz, CDCl$_3$/298 K): 17

$^{13}$C NMR (101 MHz, CDCl$_3$/298 K): 17
$^1$H NMR (400 MHz, CDCl$_3$/298 K): 18

$^{13}$C NMR (101 MHz, CDCl$_3$/298 K): 18
**Supporting Information**

**1H NMR (400 MHz, CDCl₃/298 K):** 19

![1H NMR spectrum](image)

**13C NMR (101 MHz, CDCl₃/298 K):** 19

![13C NMR spectrum](image)
$^1$H NMR (400 MHz, CDCl$_3$/298 K): 20

$^{13}$C NMR (101 MHz, CDCl$_3$/298 K): 20
$^1$H NMR (400 MHz, CDCl$_3$/298 K): 21

$^{13}$C NMR (101 MHz, CDCl$_3$/298 K): 21
$^{19}$F NMR (376 MHz, CDCl$_3$/298 K): 21

$^1$H NMR (400 MHz, CDCl$_3$/298 K): 22
SUPPORTING INFORMATION

\[\text{13C NMR (101 MHz, CDCy/298 K): 22}\]

\[\text{1H NMR (300 MHz, CDCy/298 K): 23}\]
$^{13}$C NMR (75 MHz, CDCl$_3$/298 K): 23
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