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General information

All reagents were used in analytical grades and were obtained from commercial sources. Solvents were purified by standard methods.\(^1\) For electrochemical reactions, different electrode materials were used: isostatic graphite electrodes were obtained from SGL carbon, Bonn, Germany.

**Column chromatography** was performed on silica gel 60 M (0.040-0.063 mm, Macherey-Nagel GmbH & Co, Düren, Germany) with a maximum pressure of 2.0 bar. Either a glass column or a preparative chromatography system (Büchi-Labortechnik GmbH, Essen, Germany) were used with a Büchi Control Unit C-620, an UV detector Büchi UV photometer C-635, Büchi fraction collector C-660 and two Pump Modules C-605 for adjusting the solvent mixtures. Mixtures of hexane and ethyl acetate (7:1) or cyclohexane and ethyl acetate (10:1) were used as eluents. Silica gel 60 sheets on aluminium (F254, Merck, Darmstadt, Germany) were employed for thin layer chromatography.

**Gas chromatography** was performed on a Shimadzu GC-2025 (Shimadzu, Japan) using a Zebron ZB-5MSi column (Phenomenex, USA; length: 30 m, inner diameter: 0.25 mm, film: 0.25 µm, pre-column: 5 m, carrier gas: hydrogen). GC-MS measurements were carried out on a Shimadzu GC-2010 (Shimadzu, Japan) using a Zebron ZB-5MSi column (Phenomenex, USA; length: 30 m, inner diameter: 0.25 mm, film: 0.25 µm, pre-column: 5 m, carrier gas: helium) combined with a GCMS-QP2010.

**Microanalysis** was performed by a VarioMICRO cube (Elementar Analysesysteme, Hanau, Germany).

**Melting points** were determined by a Melting Point Apparatus SMP3 (Stuart Scientific, Staffordshire, U.K.) and are uncorrected.

**Spectroscopy and Spectrometry:** \(^1\)H NMR, \(^{13}\)C NMR and \(^{19}\)F spectra were recorded at 25 °C by using a Bruker Avance II 400 or a Bruker Avance III HD 400 (Analytische Messtechnik, Karlsruhe, Germany). Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS as internal standard or traces of CHCl₃ or DMSO in the corresponding deuterated solvent. For the \(^{19}\)F spectra, α-trifluorotoluene served as external standard (δ = −63.9 ppm).\(^2\) Mass spectra and high resolution mass spectra were obtained by using a QTof Ultima 3 (Waters, Milford, Massachusetts) apparatus employing ESI+.

**X-ray analysis:** All data were collected on a STOE IPDS2T diffractometer (Oxford Cryostream 700er series, Oxford Cryosystems) using graphite monochromated Mo K\(_\alpha\) radiation (λ = 0.71073 Å). Intensities were measured using fine-slicing \(\omega\) and \(\varphi\)-scans and corrected for background, polarization and Lorentz effects. The structures were solved by direct methods and refined anisotropically by the least-squares procedure implemented in the SHELX program system.\(^3\)

The supplementary crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Deposition numbers and further details are given with the individual characterization data.

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Electrolysis protocols

General electrolysis protocol A in 25 mL three-necked flasks

A solution of 0.4 mmol anilide derivative and 38 mg tetrabutylammonium hexafluorophosphate (0.01 M) in 10 mL hexafluoroisopropanol (HFIP) is placed in a 25 mL three-necked round-bottom flask. A reticulated vitreous carbon (100 PPI) anode and a platinum wire cathode is placed in the solution and sonicated for 30 s. The solution is electrolyzed with a constant current of 8.4 mA until 2 F are applied. Full conversion is checked by TLC. After electrolysis, the solvent is removed via distillation and product is isolated via column chromatography with mixtures of hexanes and ethyl acetate.

General electrolysis protocol B in 25 mL glass cells

Undivided 25 mL glass electrolysis cells were used (Figure 1). A solution of 1.0 mmol anilide derivative and 97 mg tetrabutylammonium hexafluorophosphate is electrolyzed with a current density of 2.5 mA/cm² using an isostatic graphite anode and a platinum cathode, until 2 F are applied. Full conversion is checked via TLC. For optimization studies, different currents were applied. The electrode area in solution is 8.0 cm² After electrolysis, the solvent is recovered by distillation and the product is isolated via column chromatography with mixtures of cyclohexane and ethyl acetate.

Tested solvents and non-convertible anilides

Table 1: Tested solvents and their applicability for the conversion.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFIP</td>
<td>✓</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>product traces</td>
</tr>
<tr>
<td>methanol</td>
<td>no product formation</td>
</tr>
</tbody>
</table>
Scheme 1: Non-convertible anilides.
Synthesis of starting materials

Substituted Benzanilides and pivalanilides were prepared from acid chlorides and corresponding anilines according to the literature.\(^4\)

**N-(4-Trifluoromethansulfonylphenyl)benzamide**

![Chemical structure of N-(4-Trifluoromethansulfonylphenyl)benzamide](image)

To a solution of 426 mg N-(4-hydroxyphenyl)benzamide (2 mmol) in 10 mL pyridine was added 404 μL trifluoromethansulfonic anhydride (2.4 mmol) dropwise at 0 °C. The mixture was allowed to stir at 0 °C for 10 minutes and 12 h at room temperature. 20 mL ethyl acetate was added and the organic layer was washed with aqueous 1 M CuSO\(_4\) solution (3 x 20 mL) and water (1 x 40 mL). The organic layer was dried with MgSO\(_4\) and the solvent was removed under reduced pressure the yield 654 mg of the pure triflate as orange solid (yield: 95%, 1.89 mmol)

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta = 10.53\) (s, 1H), 7.99 – 7.92 (m, 4H), 7.64 – 7.59 (m, 1H), 7.58 – 7.52 (m, 2H), 7.52 – 7.48 (m, 2H).

\(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta = 165.84, 144.50, 139.58, 134.51, 131.85, 128.45, 127.73, 121.78, 121.75, 118.26\) (q, \(J = 321.1\) Hz).

\(^{19}\)F NMR (377 MHz, DMSO-\(d_6\)) \(\delta = -73.90\).

HRMS for C\(_{14}\)H\(_{10}\)F\(_3\)NO\(_4\)S (ESI\(^+\)) [M+Na\(^+\)]: calc.: 368.0180, found: 368.0172.

Synthesis of benzoxazoles (2a-i)

Some benzoxazoles were prepared according to electrolysis protocol A and electrolysis protocol B. For these compounds, only one protocol is named.

**6-Chloro-2-phenyl-1,3-benzoxazole (2a)**

![Chemical structure of 6-Chloro-2-phenyl-1,3-benzoxazole](image)

According to electrolysis protocol B, 232 mg N-(4-chlorophenyl)benzamide (1.0 mmol) are electrolyzed until 2 F are applied. Column chromatography yielded 152 mg product as colorless solid (yield: 66%, 0.66 mmol).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.23 – 8.20\) (m, 2H), 7.66 (d, \(J = 8.5\) Hz, 1H), 7.58 (d, \(J = 2.0\) Hz, 1H), 7.54 – 7.50f (m, 3H), 7.32 (dd, \(J = 8.5, 2.0\) Hz, 1H).

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$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 163.64, 150.86, 140.84, 131.76, 130.62, 128.93, 127.61, 126.65, 125.24, 120.42, 111.20.

HRMS for C$_{13}$H$_8$ClNO (ESI$^+$) [M+H$^+$]: calc.: 230.0373, found: 230.0373.

MP: 102.0–103.0 °C (CH$_2$Cl$_2$)

6-Methoxy-2-phenyl-1,3-benzoxazole (2b)

According to electrolysis protocol A, 227 mg N-(4-chlorophenyl)benzamide (0.4 mmol) are electrolyzed until 2 F are applied. Column chromatography yielded 77 mg product as colorless solid (yield: 86%, 0.34 mmol).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.27 – 8.11 (m, 2H), 7.62 (d, $J$ = 8.8 Hz, 1H), 7.55 – 7.38 (m, 3H), 7.05 (d, $J$ = 2.4 Hz, 1H), 6.92 (dd, $J$ = 8.8, 2.4 Hz, 1H), 3.81 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 162.01, 158.11, 151.46, 135.71, 130.88, 128.69, 127.01, 119.80, 112.64, 95.24, 55.72.

HRMS for C$_{14}$H$_{11}$NO$_2$ (ESI$^+$) [M+H$^+$]: calc.: 226.0868, found: 226.0867.

MP: 66.0–67.0 °C (CH$_2$Cl$_2$)

6-Trifluormethansulfonat-2-phenyl-1,3-benzoxazole (2c)

According to electrolysis protocol B, 138 mg N-(4-trifluormethansulfonylphenyl)benzamide (0.4 mmol) are electrolyzed until 2 F are applied. Column chromatography yielded 82 mg product as colorless solid (yield: 60%, 0.24 mmol).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.37 – 8.17 (m, 2H), 7.81 (d, $J$ = 8.7 Hz, 1H), 7.65 – 7.47 (m, 4H), 7.30 (dd, $J$ = 8.7, 2.4 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 165.22, 150.33, 146.31, 141.98, 132.24, 129.08, 127.82, 126.31, 120.65, 118.76 (q, $J$ = 321.0 Hz), 118.23, 105.06.

$^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ = -73.67.

HRMS for C$_{14}$H$_8$F$_3$NO$_3$S (ESI$^+$) [M+H$^+$]: calc.: 344.0204, found: 344.0207.

MP: 92.0–93.0 °C (EtOH)

Anal. Calcd for C$_{14}$H$_8$F$_3$NO$_3$S: C, 48.99; H, 2.35; N, 4.08; S, 9.34. Found: C, 49.03; H, 2.30; N, 4.10; S, 9.80
Crystal structure determination of 2c (CCDC 1530094): C_{14}H_{8}F_{3}NO_{4}S, \( M_r = 343.2 \) g/mol, colorless block (0.09 x 0.33 x 0.42 mm\(^3\)), P 2\( \overline{1} \)/c (monoklin), \( a = 16.5356 \) Å, \( b = 7.3275 \) Å, \( c = 11.8114 \) Å, \( V = 1364.76 \) Å\(^3\), \( Z = 4 \), \( F(000) = 696 \), \( \rho = 1.669 \) g/cm\(^3\), \( \mu = 0.290 \) mm\(^{-1}\), Mo-K\( \alpha \) graphite monochromator (0.71073 Å), 120 K, 107.5 °, 7371 reflections, 3288 independent reflections, \( wR_2 = 0.0843 \), \( R_1 = 0.0338 \), 0.37 e/Å\(^3\), –0.33 e/Å\(^3\), GoF = 1.021

![Molecular structure of derivative 2c by X-ray analysis](image1)

**Figure 2:** Molecular structure of derivative 2c by X-ray analysis (up: top view; down: side view).

![Packing of 2c in the solid state](image2)

**Figure 3** Packing of 2c in the solid state.

Single crystals for structure determination were obtained by recrystallization from ethanol at room temperature. In the packing, a significant \( \pi - \pi \) interaction between the benzoxazole and phenyl moieties is present.
**6-Fluoro-2-phenyl-1,3-benzoxazole (2d)**

According to electrolysis protocol B, 215 mg N-(4-fluorophenyl)benzamide (1.0 mmol) are electrolyzed until 2 F are applied. Column chromatography yielded 125 mg product as colorless solid (yield: 59%, 0.59 mmol).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.25 - 8.19\) (m, 2H), 7.70 (dd, \(J = 8.7, 4.9\) Hz, 1H), 7.58 – 7.49 (m, 3H), 7.31 (dd, \(J = 7.9, 2.4\) Hz, 1H), 7.11 (ddd, \(J = 9.6, 8.7, 2.4\) Hz, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 163.69\) (d, \(J = 3.4\) Hz), 160.65 (d, \(J = 244.1\) Hz), 150.69 (d, \(J = 14.7\) Hz), 138.40 (d, \(J = 1.9\) Hz), 131.59, 128.94, 127.46, 126.87, 120.23 (d, \(J = 10.2\) Hz), 112.53 (d, \(J = 24.7\) Hz), 98.67 (d, \(J = 28.3\) Hz).

\(^{19}\)F NMR (377 MHz, CDCl\(_3\)) \(\delta = -116.22\).

HRMS for C\(_{13}\)H\(_8\)FNO (ESI\(^+\)) [M+H\(^+\)]: calc.: 214.0668, found: 214.0660.

MP: 105.0–106.0 °C (CH\(_2\)Cl\(_2\))

**6-Methoxy-2-(4-methylphenyl)-1,3-benzoxazole (2e)**

According to electrolysis protocol B, 241 mg 4-Methyl-N-(4-methoxyphenyl)benzamide (1.0 mmol) are electrolyzed until 2 F are applied. Column chromatography yielded 134 mg product as colorless solid (yield: 56%, 0.56 mmol).

\(^1\)H NMR (400 MHz, DMSO) \(\delta = 8.12 - 8.06\) (m, 2H), 7.62 (d, \(J = 8.7\) Hz, 1H), 7.33 – 7.28 (m, 2H), 7.10 (d, \(J = 2.3\) Hz, 1H), 6.94 (dd, \(J = 8.7, 2.4\) Hz, 1H), 3.87 (s, 3H), 2.43 (s, 4H).

\(^{13}\)C NMR (101 MHz, DMSO) \(\delta = 162.47, 158.07, 151.51, 141.50, 135.90, 129.57, 127.12, 124.56, 119.76, 112.58, 95.41, 55.91, 21.58\).

HRMS for C\(_{15}\)H\(_{13}\)NO\(_2\) (ESI\(^+\)) [M+H\(^+\)]: calc.: 240.1025, found: 240.1025.

MP: 90.0–91.0 °C (CH\(_2\)Cl\(_2\))

**2-(4-Fluorophenyl)-6-methoxy-1,3-benzoxazole (2f)**

According to electrolysis protocol B, 245 mg 4-Fluoro-N-(4-methoxyphenyl)benzamide (1.0 mmol) are electrolyzed until 2 F are applied. Column chromatography yielded 160 mg product as colorless solid (yield: 66%, 0.66 mmol).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.22 - 8.15\) (m, 2H), 7.62 (d, \(J = 8.7\) Hz, 1H), 7.23 – 7.14 (m, 2H), 7.10 (d, \(J = 2.3\) Hz, 1H), 6.96 (dd, \(J = 8.7, 2.4\) Hz, 1H), 3.88 (s, 3H).
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 165.75, 162.29 (d, $J = 191.3$ Hz), 158.27, 151.63, 135.79, 129.32 (d, $J = 8.8$ Hz), 123.68 (d, $J = 3.4$ Hz), 119.93, 116.10 (d, $J = 22.2$ Hz), 112.82, 95.43, 55.94.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = –109.38.

HRMS for C$_{14}$H$_{10}$FNO$_2$ (ESI$^+$) [M+H$^+$]: calc.: 244.0774, found: 244.0776.

MP: 105.0–106.0 °C (CH$_2$Cl$_2$)

**2-(4-Chlorophenyl)-6-methoxy-1,3-benzoxazole (2g)**

According to electrolysis protocol A, 105 mg 4-Chloro-N-(4-methoxyphenyl)benzamide (0.4 mmol) are electrolyzed until 2 F are applied. Column chromatography yielded 83 mg product as colorless solid (yield: 80%, 0.32 mmol).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.09 – 8.03 (m, 2H), 7.59 (d, $J = 8.7$ Hz, 1H), 7.45 – 7.40 (m, 2H), 7.04 (d, $J = 2.4$ Hz, 1H), 6.93 (dd, $J = 8.7$, 2.4 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 161.07, 158.33, 151.52, 137.08, 135.65, 129.07, 128.26, 125.72, 119.95, 112.90, 95.28, 55.82.

HRMS for C$_{14}$H$_{10}$ClNO$_2$ (ESI$^+$) [M+H$^+$]: calc.: 260.0478, found: 260.0475.

MP: 134.0–135.0 °C (CH$_2$Cl$_2$)

**6-Methoxy-2-(4-methoxyphenyl)-1,3-benzoxazole (2h)**

According to electrolysis protocol A, 103 mg 4-Methoxy-N-(4-methoxyphenyl)benzamide (0.4 mmol) are electrolyzed until 2 F are applied. Column chromatography yielded 80 mg product as colorless solid (yield: 78%, 0.31 mmol).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.15 – 8.06 (m, 2H), 7.58 (d, $J = 8.7$ Hz, 1H), 7.05 (d, $J = 2.4$ Hz, 1H), 7.01 – 6.94 (m, 2H), 6.91 (dd, $J = 8.7$, 2.4 Hz, 1H), 3.84 (s, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 162.27, 161.86, 157.81, 151.40, 135.93, 128.80, 119.82, 119.44, 114.19, 112.31, 95.36, 55.82, 55.30.

HRMS for C$_{15}$H$_{13}$NO$_3$ (ESI$^+$) [M+Na$^+$]: calc.: 278.0793, found: 278.0797.

MP: 108.5–109.5 °C (CH$_2$Cl$_2$)
**2-(2,2-Dimethylethyl)-6-methoxy-1,3-benzoxazole (2i)**

According to electrolysis protocol A, 85 mg N-(4-chlorophenyl)pivalamide (0.4 mmol) are electrolyzed until 2 F are applied. Column chromatography yielded 51 mg product as colorless liquid (yield: 61%, 0.24 mmol).

$^1$H NMR (400 MHz, DMSO) δ = 7.59 (dd, $J = 8.4$, 0.5 Hz, 1H), 7.50 (dd, $J = 2.0$, 0.5 Hz, 1H), 7.27 (dd, $J = 8.4$, 1.9 Hz, 1H), 1.48 (s, 9H)

$^{13}$C NMR (75 MHz, DMSO) δ = 174.23, 151.00, 139.99, 130.01, 124.61, 120.15, 111.02, 34.24, 28.38.

HRMS for C$_{11}$H$_{12}$ClN$_1$O (ESI+) [M+H$^+$]: calc.: 210.0686, found: 210.0696.
NMR spectra

N-(4-Trifluoromethansulfonylphenyl)benzamide
6-Chloro-2-phenyl-1,3-benzoxazole (2a)

$^1$H NMR (CDCl$_3$):

$^{13}$C NMR (CDCl$_3$):
6-Methoxy-2-phenyl-1,3-benzoxazole (2b)

$^1$H NMR (CDCl$_3$):

$^{13}$C NMR (CDCl$_3$):
6-Trifluormethansulfonat-2-phenyl-1,3-benzoxazole (2c)
6-Fluoro-2-phenyl-1,3-benzoxazole (2d)
6-Methoxy-2-(4-methylphenyl)-1,3-benzoxazole (2e)
2-(4-Fluorophenyl)-6-methoxy-1,3-benzoxazole (2f)
2-(4-Chlorophenyl)-6-methoxy-1,3-benzoxazole (2g)
6-Methoxy-2-(4-methoxyphenyl)-1,3-benzoxazole (2h)
2-(2,2-Dimethyllethyl)-6-methoxy-1,3-benoxazole (2i)