Supporting Information

for

Synthesis, characterization and initial evaluation of 5-nitro-1-(trifluoromethyl)-3H-1\(^\lambda^3\),2-benziodaoxol-3-one

Nico Santschi, Roman C. Sarott, Elisabeth Otth, Reinhard Kissner and Antonio Togni*  
Address: Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology (ETH Zürich), Wolfgang-Pauli-Str. 10, CH-8093 Zürich, Switzerland  
Email: Antonio Togni* - atogni@ethz.ch  
* Corresponding author  

Experimental details, crystallographic data (selected intermolecular bond lengths) as well as a description of the \(^{19}\)F NMR monitoring experiments and data analysis

Table of Contents  
Experimental details........................................................................................................................................S2  
Crystallographic details .................................................................................................................................S3  
\(^{19}\)F NMR monitoring setup ..........................................................................................................................S7  
Cyclic voltammetry spectrum of 3......................................................................................................................S8  
References.......................................................................................................................................................S9
Experimental details

NMR spectra were recorded on Bruker Avance III HD Nanobay-300 and Avance III HD Nanobay-400 spectrometers. $^1$H and $^{13}$C chemical shifts are referenced to residual solvent signals. $^{19}$F chemical shifts are referenced to external CFCl$_3$. Mass spectra (EI) were measured by the MS-service of the Laboratory of Organic Chemistry (ETH Zurich). Elemental analyses were carried out by the Laboratory of Micro elemental Analysis (ETH Zurich). Melting points were determined on a Büchi Melting Point B-540 apparatus and are uncorrected. UV–vis spectra were obtained with an Analytik Jena Specord 200 spectrometer. DSC traces were recorded on a NETZSCH DSC 404 apparatus. CV was performed on a Metrohm Autolab PGSTAT128N with a Pt 100 μm BAS working electrode and a Ag/Ag$^+$ (0.1 M AgBF$_4$ in MeCN) reference electrode. X-ray intensity data of single crystals glued to a glass capillary were collected at the given temperature (usually 100 K) on a Bruker SMART APEX platform with CCD detector and graphite monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). The program SMART served for data collection; integration was performed with the software SAINT (SAINT+, Software for CCD Diffractometers, v. 6.01; Bruker AXS, Inc., Madison, WI, 2001 and SAINT, v. 6.02). The structures were solved by direct methods or Patterson methods, respectively, using the program SHELXS-97 [1]. The refinement and all further calculations were carried out using SHELXL-97 [2]. All non-hydrogen atoms were refined anisotropically using weighted full-matrix least-squares on $F^2$. The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. In the end absorption correction was applied (SADABS) [3] and weights were optimized in the final refinement cycles. The standard uncertainties (s.u.) are rounded according to the “Notes for Authors” of Acta Crystallographica [4].
Crystallographic details

The crystal structures of 6 and 3 have been deposited at the Cambridge Crystallographic Data Center as CCDC 958118 and CCDC 958117, respectively.

Crystallographic data for compound 6

CCDC 958118
Empirical formula C7H3ClINO4
Formula Weight 327.45
Temperature 100(2) K
Wavelength 0.71073 Å
Crystal system, space group Orthorhombic, Pnma
Unit cell dimensions a = 9.8332(10) Å  α = 90°
b = 6.3159(6) Å  β = 90°
c = 14.5737(14) Å  γ = 90°
Volume 905.11(15) Å³
Z, Calculated density 4, 2.403 Mg/m³
Absorption coefficient 3.818 mm⁻¹
F(000) 616
Crystal size 0.17 x 0.14 x 0.08 mm
Data collection Siemens SMART PLATFORM with CCD Detector
Graphite monochromator
Detector distance 50 mm
Method; exposure time/frame omega-scans; t = 10 sec
Solution by direct methods
Refinement method full matrix least-squares on F², SHELXTL
Theta range for data collection 2.50 to 29.13°
Limiting indices -13<=h<=13, -8<=k<=8, -19<=l<=19
Reflections collected / unique 12511 / 1323 [R(int) = 0.0312]
Completeness to θ = 29.13 100.0%
Absorption correction Empirical
Max. and min. transmission 0.7601 and 0.5681
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 1323 / 0 / 85
Goodness-of-fit on F² 0.748
Final R indices [I>2σ(I)] R₁ = 0.0213, wR₂ = 0.0793
R indices (all data) R₁ = 0.0247, wR₂ = 0.0855
Largest diff. peak and hole 1.822 and -1.574 e.Å⁻³
Crystallographic data for compound 3

CCDC 958117
Empirical formula C₈H₃F₃INO₄
Formula Weight 361.01
Temperature 100(2) K
Wavelength 0.71073 Å
Crystal system, space group Orthorhombic, \( Pbca \)
Unit cell dimensions \( a = 11.0917(5) \) Å \( \alpha = 90^\circ \)
\( b = 7.2595(4) \) Å \( \beta = 90^\circ \)
\( c = 24.7955(12) \) Å \( \gamma = 90^\circ \)
Volume 1996.54(17) Å³
Z, Calculated density 8, 2.402 Mg/m³
Absorption coefficient 3.257 mm⁻¹
F(000) 1360
Crystal size 0.18 x 0.09 x 0.06 mm
Data collection Siemens SMART PLATFORM with CCD Detector
Graphite monochromator
Detector distance 50 mm
Method; exposure time/frame omega-scans; t = 10 sec
Solution by direct methods
Refinement method full matrix least-squares on \( F^2 \), SHELXTL
Theta range for data collection 2.46 to 30.05°
Limiting indices \(-15 \leq h \leq 13, -10 \leq k \leq 7, -32 \leq l \leq 34\)
Reflections collected / unique 14217 / 2928 [R(int) = 0.0671]
Completeness to \( \theta = 29.13^\circ \) 99.9%
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.8412 and 0.5917
Refinement method Full-matrix least-squares on \( F^2 \)
Data / restraints / parameters 2928 / 0 / 154
Goodness-of-fit on \( F^2 \) 1.016
Final R indices [I>2\sigma(I)] \( R_1 = 0.0483, wR_2 = 0.0804 \)
R indices (all data) \( R_1 = 0.0958, wR_2 = 0.0925 \)
Largest diff. peak and hole 1.823 and -1.078 e.Å⁻³
Selected intermolecular short contacts for 6

Figure S1: ORTEP representation with thermal ellipsoids set to 50% probability. Selected bond lengths (Å): C\textsuperscript{2}–O\textsuperscript{4} 2.46, C\textsuperscript{3}–O\textsuperscript{3} 2.56, I\textsuperscript{1}–O\textsuperscript{2} 2.84.
Selected intermolecular short contacts for 3

Figure S2: ORTEP representation with thermal ellipsoids set to 50% probability. Selected bond lengths (Å): C²–O¹ 2.41, C³–O³ 2.92, ¹¹–O² 2.76.
**19F NMR monitoring setup**

All reactions were monitored by 19F NMR spectroscopy using TopSpin on a Bruker Avance III HD Nanobay-400 spectrometer operating at 376 MHz. The experimental temperature was set to 298 K and maintained by a Bruker BCU II -80/60 temperature control unit. Initially, the temperature was equilibrated with a standard sample containing the appropriate reagent (2, 3) and α,α,α-trifluorotoluene as internal standard. The shim was optimized using “topshim”. The actual samples were prepared by mixing a reagent stock solution (3, 250 μL, 10.8 mM in MeCN-d3 containing ~41 mM α,α,α-trifluorotoluene or 2, 250 μL, 11.4 mM in MeCN-d3 containing ~41 mM α,α,α-trifluorotoluene) and a stock solution of p-toluenesulfonic acid monohydrate (250 μL, 11.8 mM in MeCN) in a 0.5 mm NMR tube. The sample was then inserted into the magnet and the acquisition was started. Sequential 19F NMR spectra measured every 60 s (“multi_zgvd” command, ds = 0, ns = 8) were used to monitor the reaction. Thus, a data point was obtained every 75 s along the reaction coordinate. The data obtained were processed (ef, phc0, phc1, pk, abs) using the batch processing command “multicmd” with phasing parameters determined for the last spectrum measured. Then, for every measuring point the integral for the signals of reagent and internal standard (α,α,α-trifluorotoluene) were determined and exported (“multi_integ3”). The exported data were then imported into R 2.14.0, a time scale was generated by multiplying the data row number by 75 s. In addition, for both reagents a blank spectrum only containing reagent and standard was measured (Iblank,2 and Iblank,3) in order to normalize the data. Intensity data were converted to concentrations according to $c(A) = \frac{0.0055 M \times (I(A)/I(S)) \times I_{\text{blank}}}{I_{\text{blank}}}$, where $c(A)$ refers to the concentration values of 2 or 3, I(A) are the intensity values of 2 or 3 and I(S) the intensity values of the internal standard. $I_{\text{blank}}$ refers to either $I_{\text{blank,2}}$ or $I_{\text{blank,3}}$. Every experiment was carried out at least 6 times to ensure reproducibility and allow for error estimation. As reagent 3 decayed exponentially, the rate constant $k_3$ was obtained by considering $\ln([3]) = -k_3 \times t + \ln([3]_0)$. For reagent 2, the approach of initial rates was applied and $v_0$ transformed to $k_2$ under the assumption of an exponential decay ($k_2 = v_0/[2]_0$). A summary of the data obtained is given in Table S1. Sample decays of 2 and 3 are depicted in Figure 3.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>$k_1$ [s$^{-1}$]</th>
<th>$k_2$ [s$^{-1}$]</th>
<th>$k_3$ [s$^{-1}$]</th>
<th>$k_4$ [s$^{-1}$]</th>
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<td>6.120 x 10$^{-4}$</td>
<td>8.981 x 10$^{-4}$</td>
<td>3.931 x 10$^{-4}$</td>
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<tr>
<td></td>
<td>$k_5$ [s$^{-1}$]</td>
<td>$k_6$ [s$^{-1}$]</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>5.919 x 10$^{-4}$</td>
<td>2.389 x 10$^{-4}$</td>
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<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Reagent</th>
<th>$k_1$ [s$^{-1}$]</th>
<th>$k_2$ [s$^{-1}$]</th>
<th>$k_3$ [s$^{-1}$]</th>
<th>$k_4$ [s$^{-1}$]</th>
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<td>3</td>
<td>2.256 x 10$^{-3}$</td>
<td>4.427 x 10$^{-3}$</td>
<td>6.280 x 10$^{-3}$</td>
<td>5.984 x 10$^{-3}$</td>
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<tr>
<td></td>
<td>$k_5$ [s$^{-1}$]</td>
<td>$k_6$ [s$^{-1}$]</td>
<td>$k_7$ [s$^{-1}$]</td>
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<tr>
<td></td>
<td>7.487 x 10$^{-3}$</td>
<td>2.191 x 10$^{-3}$</td>
<td>2.772 x 10$^{-3}$</td>
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</tbody>
</table>
Figure S3: Sample decays of 2 (left) and 3 (right) and resulting fits (dashed lines).

Cyclic voltammetry spectrum of 3

Figure S4: Unprocessed CV spectrum of reagent 3 (1 mM) in anhydrous MeCN + 0.1 M Bu₄NBF₄, platinum electrode, Ag/Ag⁺ reference electrode, scan rate = 0.1 V/s.
References