Supporting Information:

Single-Electron-Transfer Oxidation of Trifluoroborates and Silicates with Organic Reagents: A Comparative Study

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I. General informations

Unless otherwise noted, reactions were carried out under an argon atmosphere in oven-dried glassware. Methanol was distilled over CaH$_2$, THF and diethyl ether were distilled over sodium/benzophenone, triethylamine over potassium hydroxide. Catechol was purchased from commercial source and purified by crystallization from toluene followed by sublimation. Reagents and chemicals were purchased from commercial sources and used as received. Infrared (IR) spectra were recorded on a Bruker Tensor 27 (ATR diamond) spectrophotometer. Melting points were determined on a melting point apparatus SMP3 (Stuart scientific) and are uncorrected. $^1$H, $^{19}$F, $^{13}$C NMR spectra were recorded at room temperature at 400, 377 and 100 MHz respectively, on a Bruker AVANCE 400 spectrometer. $^{29}$Si NMR spectra were recorded at 119 MHz on a Bruker AVANCE III 600 spectrometer. Chemical shifts (δ) are reported in ppm and coupling constants (J) are given in Hertz (Hz). Abbreviations used for peak multiplicity are: s (singlet); bs (broad singlet); d (doublet); t (triplet); q (quartet); quint (quintet); sept (septet); m (multiplet). Thin layer chromatographies (TLC) were performed on Merck silica gel 60 F 254 and revealed with a UV lamp (λ = 254 nm) and KMnO$_4$ staining. Flash Column Chromatographies were conducted on silica Geduran® Si 60 Å (40 – 63 µm). High resolution mass spectrometries were performed on a microTOF (ESI).
II. General procedures

1. **Synthesis of organotrifluoroborate salt (1):**

   All organotrifluoroborate salts were prepared following previously reported procedures.\[^{1,2}\]

2. **General procedure for bis(catecholato)-silicate synthesis (4):**

   All organobis(catecholato)silicate salts were prepared following previously reported procedures.\[^{3}\]

3. **General oxidation procedures for TEMPO adducts formation (5):**

   **General procedure for stoechiometric oxidation of organotrifluoroborate and organobis(catecholato)silicate (GPA)**

   To a schlenk flask was added the appropriate trifluoroborate salt or silicate salt (0.3 mmol), the oxidizing agent (0.3 mmol) and TEMPO (0.9 mmol, 141 mg). The schlenk flask was sealed with a rubber septum, and evacuated / purged with vacuum / argon three times. Degassed DMF or diethyl ether (3 mL) was introduced followed by two freeze-pump-thaw cycles. The reaction mixture was stirred at room temperature for 24h under an argon atmosphere. The reaction mixture was diluted with diethyl ether (50 mL), washed with water (2 times), brine (2 times), dried over MgSO\(_4\) and evaporated under reduced pressure. The reaction residue was purified by flash column chromatography on silica gel.

   For compound 6, the same experimental procedure was applied but methyl vinyl ketone (5 equiv) was used instead of TEMPO.
General procedure for photooxidation of organotrifluoroborate or organobis(catecholato)silicate (GPB)

![Chemical structure](image)

To a schlenk flask was added the appropriate trifluoroborate salt or silicate salt (0.3 mmol), the organophotocatalyst (0.03 mmol) and TEMPO (0.66 mmol, 103 mg). The schlenk flask was sealed with a rubber septum, and evacuated / purged with vacuum / argon three times. Degassed DMF (3 mL) was introduced followed by two freeze-pump-thaw cycles. The reaction mixture was stirred at room temperature under blue LEDs irradiation for 24h under an argon atmosphere. The reaction mixture was diluted with diethyl ether (50 mL), washed with saturated NaHCO₃ (2 times), brine (2 times), dried over MgSO₄ and evaporated under reduced pressure. The reaction residue was purified by flash column chromatography on silica gel.
III. Compound characterizations

Potassium benzyltrifluoroborate (1a)

\[
\begin{array}{c}
\text{BF}_3\text{K} \\
\text{phenyl}
\end{array}
\]

Trifluoroborate 1a was synthesized as described. The spectroscopic data are in agreement with those reported in the literature. \[1\]

Potassium benzyltrifluoroborate (1b)

\[
\begin{array}{c}
\text{BF}_3\text{K} \\
\text{allyl}
\end{array}
\]

Trifluoroborate 1b was synthesized as described. The spectroscopic data are in agreement with those reported in the literature. \[1\]

Potassium 5-hexenyl-1-trifluoroborate (1d)

\[
\begin{array}{c}
\text{BF}_3\text{K} \\
\text{alkyl}
\end{array}
\]

Trifluoroborate 1d was synthesized as described. The spectroscopic data are in agreement with those reported in the literature. \[1\]

Potassium ((1R,2S,3R,5R)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)trifluoroborate (1e)

\[
\begin{array}{c}
\text{BF}_3\text{K} \\
\text{cycloheptane}
\end{array}
\]

Trifluoroborate 1e was synthesized as described. The spectroscopic data are in agreement with those reported in the literature. \[1\]

Potassium tert-butyltrifluoroborate (1f)

\[
\begin{array}{c}
\text{BF}_3\text{K} \\
\text{tert-butyl}
\end{array}
\]

Trifluoroborate 1f was synthesized as described. The spectroscopic data are in agreement with those reported in the literature. \[1\]
Potassium (1S,2R,3S,6R)-3,7,7-trimethylbicyclo[4.1.0]heptan-2-trifluoroborate (1g)

Trifluoroborate 1g was synthesized as described. The spectroscopic data are in agreement with those reported in the literature. [1]

Potassium indanyl-2-trifluoroborate (1i)

Trifluoroborate 1i was synthesized as described. The spectroscopic data are in agreement with those reported in the literature. [2]

Potassium [18-Crown-6] bis(catecholato)-benzylsilicate (3a)

Silicate 4a was synthesized as described. The spectroscopic data are in agreement with those reported in the literature. [3]

Potassium [18-Crown-6] bis(catecholato)-allylsilicate (3b)

Silicate 4b was synthesized as described. The spectroscopic data are in agreement with those reported in the literature. [3]
Potassium [18-Crown-6] bis(catecholato)-hexenylsilicate (3d)

![Potassium [18-Crown-6] bis(catecholato)-hexenylsilicate (3d)](image)

Silicate 4d was synthesized as described. The spectroscopic data are in agreement with those reported in the literature. \[^3\]

Potassium [18-Crown-6] bis(catecholato)-cyclohexylsilicate (3h)

![Potassium [18-Crown-6] bis(catecholato)-cyclohexylsilicate (3h)](image)

Silicate 4j was synthesized as described. The spectroscopic data are in agreement with those reported in the literature. \[^3\]

1-(benzyloxy)-2,2,6,6-tetramethylpiperidine (4a)

![1-(benzyloxy)-2,2,6,6-tetramethylpiperidine (4a)](image)

Following general procedure A with potassium benzyl trifluoroborate 1a (0.3 mmol, 59 mg) and triphenylcarbenium tetrafluoroborate (0.3 mmol, 99 mg) in diethyl ether. The crude product was purified by flash column chromatography (pentane/diethyl ether, 99/1) to afford 4a as a colorless oil (48 mg, 65%). The spectroscopic data are in agreement with those reported in the literature. \[^1\]

\[^1\]H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 1.04 (s, 6H), 1.14 (s, 6H), 1.21-1.50 (m, 6H), 4.71 (s, 2H), 7.11-7.26 (m, 5H). \[^13\]C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 17.1, 20.3(2 C), 33.1(2 C), 39.7(2 C), 60.0(2 C), 78.7, 127.3, 127.4(2 C), 128.2(2 C), 138.3.
1-(allyloxy)-2,2,6,6-tetramethylpiperidine (4b)

Following general procedure B with potassium allyl trifluoroborate 1b (0.3 mmol, 44 mg) and 9-mesityl-10-methylacridinium perchlorate (0.03 mmol, 12.4 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 98/2) to afford 4b as a colorless oil (19 mg, 32%). Following the same procedure with potassium [18-Crown-6] bis(catecholato)-allylsilicate 3b (0.3 mmol, 177 mg) gave 4b (18 mg, 31%). The spectroscopic data are in agreement with those reported in the literature. [1]

$^1$H NMR (400MHz, CDCl$_3$): δ 1.16 (s, 6H), 1.33 (s, 6H), 1.30-1.58 (m, 6H), 4.28 (dt, $J = 5.5$, 1.5 Hz, 2H), 5.09-5.30 (m, 1H), 5.26 (dq, $J = 17.3$, 3.6 Hz, 1H), 5.84-5.94 (m, 1H). $^{13}$C NMR (100MHz, CDCl$_3$): δ 17.2, 20.1 (2 C), 32.9 (2 C), 39.7 (2 C), 59.7 (2 C), 78.3, 115.9, 134.2.

2,2,6,6-Tetramethyl-N-(O-5-hexenyl)-piperidine (4d) and 2,2,6,6-Tetramethyl-N-(O-cyclomethylpentyl)-piperidine (4d’)

Following general procedure B with potassium 5-hexenyl-1-trifluoroborate 1d (0.3 mmol, 57 mg) and 9-mesityl-10-methylacridinium perchlorate (0.03 mmol, 12.4 mg). The crude product was purified by flash column chromatography (pentane) to afford a mixture of 4d and 4d’ as a colorless oil (10 mg, 14%) with the ratio 4d/4d’: 20/1.

Following general procedure A with potassium 5-hexenyl-1-trifluoroborate 1d (0.3 mmol, 57 mg) and triphenylcarbenium tetrafluoroborate (0.3 mmol, 99 mg) in diethyl ether. The crude product was purified by flash column chromatography (pentane) to afford a mixture of 4d and 4d’ as a colorless oil (41 mg, 57%) with a ratio 4d/4d’: 89/11.

Following the same procedure with potassium [18-Crown-6] bis(catecholato)- 5-hexenyl-1-silicate 3d (0.3 mmol, 189 mg) in DMF gave 4d and 4d’ as a colorless oil (37%*) with the ratio 4d/4d’: 10/1. Replacing the oxidizing agent by tris(4-bromophenyl)ammoniumyl hexachloroantimonate (0.3 mmol, 245 mg), the products were obtained (61%*) with the same ratio.

S8
*Yield determined by NMR with butadiene sulfone as internal standard.
The spectroscopic data are in agreement with those reported in the literature.[1]

$^1$H NMR for 5d (400MHz, CDCl$_3$): $\delta$ 1.09 (s, 6H), 1.14 (s, 6H), 1.20-1.55 (m, 10H), 2.07 (q, $J = 7.2$ Hz, 2H), 3.73 (t, $J = 6.1$ Hz, 2H), 4.94 (m, 1H), 5.01 (m, 1H), 5.82 (m, 1H). Characteristic signal for 5d’: 3.64 (d, $J = 6.8$ Hz, 2H).

$^{13}$C NMR for 5d (100MHz, CDCl$_3$): $\delta$ 17.3, 20.3 (2 C), 25.9, 28.4, 33.2 (2 C), 34.0, 39.7 (2 C), 59.8, 59.9, 80.8, 114.5, 139.1. Characteristic signal for 5d’: 76.7.

2,2,6,6-Tetramethyl-1-((1R,2R,3R,5S)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yloxy)piperidine (4e)

Following general procedure B with potassium ((1R,2S,3R,5R)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)trifluoroborate 1e (0.3 mmol, 74 mg) and 9-mesityl-10-methylacridinium perchlorate (0.03 mmol, 12.4 mg). The crude product was purified by flash column chromatography (pentane) to afford 4e as a colorless oil (61 mg, 69%).

Following general procedure A with potassium ((1R,2S,3R,5R)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)trifluoroborate 1e (0.3 mmol, 74 mg) and triphenylcarbenium tetrafluoroborate (0.3 mmol, 99 mg) in diethyl ether. The crude product was purified by flash column chromatography (pentane) to afford 4e as a colorless oil (57 mg, 64%). Replacing the oxidizing agent by tris(4-bromophenyl)ammoniumyl hexachloroantimonate (0.3 mmol, 245 mg) in DMF, 4e was obtained with 27%* yield.

*Yield determined by NMR with butadiene sulfone as internal standard.
The spectroscopic data are in agreement with those reported in the literature.[1]

$^1$H NMR (400MHz, CDCl$_3$): $\delta$ 0.88 (s, 3H), 1.02 (d, $J = 9.3$ Hz, 1H), 1.06-1.25 (m, 18H), 1.40-1.45 (m, 6H), 1.73 (td, $J = 5.9$, 2.4 Hz), 1.85-1.91 (m, 1H), 2.05-2.14 (m, 1H), 2.20-2.37 (m, 3H), 4.21 (dt, $J = 9.4$, 4.5 Hz, 1H). $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ 17.5, 20.5 (2 C), 22.0, 23.9, 27.6, 33.1, 34.7 (3 C), 38.5, 40.6, 40.8, 41.6, 44.5, 48.0, 59.9 (2 C), 82.4.
1-tert-Butoxy-2,2,6,6-tetramethylpiperidine (4f)

Following general procedure A with potassium tert-butyltrifluoroborate 1f (0.3 mmol, 49 mg) and triphenylcarbenium tetrafluoroborate (0.3 mmol, 99 mg) in diethyl ether. The crude product was purified by flash column chromatography (pentane/diethyl ether : 99/1) to afford 4f as a colorless oil (16 mg, 25%). The spectroscopic data are in agreement with those reported in the literature.\[1\]

$^1$H NMR (400MHz, CDCl$_3$): $\delta$ 1.07 (s, 6H), 1.12 (s, 6H), 1.18 (s, 9H), 1.44-1.48 (m, 6H).

$^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ 17.5, 20.7 (2 C), 29.7 (3 C), 35.1 (2 C), 41.1 (2 C), 59.4 (2 C), 77.3.

2,2,6,6-Tetramethyl-1-((1R,4S)-4-methylcyclohex-2-enyl)propan-2-yloxy)piperidine (4g)

Following general procedure A with potassium (1S,2R,3S,6R)-3,7,7-trimethylbicyclo[4.1.0]heptan-2-trifluoroborate 1g (0.3 mmol, 65 mg) and triphenylcarbenium tetrafluoroborate (0.3 mmol, 99 mg) in diethyl ether. The crude product was purified by flash column chromatography (pentane/diethyl ether : 99/1) to afford 4f as a colorless oil (48 mg, 67%).

Following general procedure B with potassium (1S,2R,3S,6R)-3,7,7-trimethylbicyclo[4.1.0]heptan-2-trifluoroborate 1g (0.3 mmol, 65 mg) and 9-mesityl-10-methylacridinium perchlorate (0.03 mmol, 12.4 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether : 99/1) to afford 4f as a colorless oil (16 mg, 18%). The spectroscopic data are in agreement with those reported in the literature.\[1\]

$^1$H NMR (400MHz, CDCl$_3$): $\delta$ 0.98 (d, $J = 7.2$ Hz, 3H), 1.09 (s, 3H), 1.10 (s, 3H), 1.12 (s, 6H), 1.20 (s, 3H), 1.21 (s, 3H), 1.24-1.30 (m, 2H), 1.40-1.57 (m, 6H), 1.65-1.74 (m, 2H), 2.18 (m, 1H), 2.53 (m, 1H), 5.67 (m, 1H), 5.76 (m, 1H). $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ 17.3, 20.7, 21.0 (2 C), 21.2, 23.8, 24.0, 29.0, 29.3, 35.1, 35.3, 41.2 (2 C), 47.2, 59.5 (2 C), 81.1, 128.8, 133.9.
1-Cyclohexyloxy-2,2,6,6-tetramethylpiperidine (4h)

Following general procedure A with potassium [18-Crown-6] bis(catecholato)-cyclohexylsilicate 3h (0.3 mmol, 189 mg) and triphenylcarbenium tetrafluoroborate (0.3 mmol, 99 mg) in DMF. The crude product was purified by flash column chromatography (pentane/diethyl ether, 98/2) to afford 4h (53%). Replacing the oxidizing agent by tris(4-bromophenyl)ammoniumyl hexachloroantimonate (0.3 mmol, 245 mg) in DMF, 4h was obtained with 44% yield.

*Yield determined by NMR with butadiene sulfone as internal standard.

The spectroscopic data are in agreement with those reported in the literature.\(^{[4]}\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 3.61-3.55 (m, 1 H), 2.07-2.02 (m, 2 H), 1.77-1.75 (m, 2 H), 1.70-1.20 (m, 12 H), 1.12 (s, 12 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 81.5, 59.3, 40.1, 34.3, 32.6, 25.7, 24.8, 19.9, 17.1.

1-(indan-2-yloxy)-2,2,6,6-tetramethylpiperidine (4i)

Following general procedure B with potassium indanyl-2-trifluoroborate 1i (0.3 mmol, 67 mg) and 9-mesityl-10-methylacridinium perchlorate (0.03 mmol, 12.4 mg). The crude product was purified by flash column chromatography (pentane) to afford 4e as a colorless oil (27 mg, 33%).

The spectroscopic data are in agreement with those reported in the literature.\(^{[2]}\)

\(^1\)H NMR (300MHz, CDCl\(_3\)): \(\delta\) 1.11 (s, 6H), 1.21 (s, 6H), 1.30-1.54 (m, 6H), 3.04 (dd, \(J = 7.7, 15.8\) Hz, 2H), 3.28 (dd, \(J = 7.7, 15.8\) Hz, 2H), 4.77 (p, \(J = 7.7\) Hz, 2H), 7.14 (m, 4H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 17.3, 20.3(2 C), 34.1(2 C), 39.6(2 C), 40.2, 59.5(2 C), 87.4, 124.4(2 C), 126.3(2 C), 141.11(2 C). HRMS (m/z): [C\(_{18}\)H\(_{28}\)NO\(^+\)], calc. 274.2165, found 274.2166.
4-isopinocamphenyl-2-butanone (5)

Potassium \(((1R,2S,3R,5R)-2,6,6-\text{trimethylbicyclo}[3.1.1]\text{heptan-3-yl})\text{trifluoroborate} \) 1e (1 mmol, 244 mg), methyl vinyl ketone (0.4 mL, 5 mmol), and triphenylcarbenium tetrafluoroborate (1 mmol, 330 mg) were added to a schlenk flask. The schlenk flask was sealed with a rubber septum, and evacuated / purged with vacuum / argon three times. Degassed diethyl ether (10 mL) was introduced followed by two freeze-pump-thaw cycles. The reaction mixture was stirred at room temperature for 24h under an argon atmosphere. The reaction was diluted with diethyl ether (50 mL), washed with water (2 times) and brine (2 times). The organic layer was dried over MgSO\(_4\) and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford 5 as a colorless oil (131 mg, 63%). The spectroscopic data are in agreement with those reported in the literature.\(^{[1]}\)

\(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta\) 0.70 (d, \(J = 9.7\) Hz, 1H), 0.96 (s, 3H), 0.99 (d, \(J = 7.0\) Hz, 3H), 1.16 (s, 3H), 1.34-1.45 (m, 2H), 1.50-1.68 (m, 2H), 1.70-1.85 (m, 2H), 1.85-1.91 (m, 1H), 2.06-2.15 (m, 1H), 2.13 (s, 3H), 2.22-2.30 (m, 1H), 2.34 (ddd, \(J = 16.5, 10.4, 5.1\) Hz, 1H), 2.46 (ddd, \(J = 16.5, 10.1, 5.9\) Hz, 1H). \(^{13}\)C NMR (100MHz, CDCl\(_3\)): \(\delta\) 21.7, 23.0, 28.1, 30.0, 34.1, 34.5, 34.8, 36.1, 38.8, 42.0, 42.3, 43.7, 48.2, 209.5.
IV. References


