Completing the Redox-Series of Silicon Trisdioxolene: ortho-Quinone and Lewis Superacid Make a Powerful Redox Catalyst

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1. Experimental Procedures

1.1. General Information

The chemicals used for this work were purchased from commercial suppliers. Prior to use, the solid chemicals were dried overnight under reduced pressure and the liquids were degassed by an Ar flow and stored over activated molecular sieve (3 Å or 4 Å) in the glovebox. All solvents were rigorously dried by applying standard procedures, freshly degassed by three freeze-pump-thaw cycles and stored over molecular sieve (3 Å or 4 Å) prior to use. Unless otherwise stated, all reactions were either performed in flame-dried standard laboratory glassware under Ar atmosphere using standard Schlenk techniques or in a glovebox (Mbraun LABmaster dp, MB-20G or SylaTech Y05G) under N₂ atmosphere. All glassware, syringes, magnetic stirring bars and needles were thoroughly dried. o-Tetrachlorocatechol (H₂Cat) and 1 were prepared according to literature.[1] The silicon tris(perchloro)catecholate dianions [1][M]₂ were synthesized analogous to the procedure of RAO et al., as specified in the following section. The substrates for the oxidative lactonization studies were generated according to JACOBSEN et al.[3] 3,3',4,4'-Tetramethoxy-o-terphenyl, which was synthesized following literature procedures,[4] was provided by Ute Wild from the working group HIMMEL (Heidelberg). All air sensitive compounds were handled and stored in a glovebox under N₂ atmosphere. Purity and identity of the compounds were confirmed by NMR spectroscopy, EPR spectroscopy, mass spectrometry, elemental analysis and X-ray diffraction analysis, if possible. 

¹H, ¹¹B, ¹³C, ¹⁹F and ²⁹Si INVGATE NMR spectra were recorded at 298 K with a Bruker (DPX) 200, Bruker Avance II 400 or Bruker 2 Avance III 600 NMR spectrometer and referenced to the respective solvent in use.[5] Chemical shifts δ are reported in parts per million (ppm) and coupling constants J are given in Hertz (Hz). EPR measurements were performed at the magenettech MiniScope MS400 spectrometer at room temperature in the X-band frequency range (9.30-9.55 GHz) with a modulation frequency of 100 kHz. IR spectra were measured in the glovebox SylaTech Y05G on an Agilent Cary 630 spectrometer equipped with a diamond ATR unit. HRMS (ESI) measurements were performed in dichloromethane with a Bruker micrOTOF II: ESI Mass Spectrometer. Elemental analysis for the determination of the CHN content were carried out by the microanalysis laboratory of the Institute of Organic Chemistry (Heidelberg) on a vario MICRO cube from Elementar Analysensysteme GmbH.
1.2. Synthesis

\[ [\text{Si(diox}^\text{Cl})_3][\text{H}_2\text{N}(n-\text{Pr}_2)_2] - [1][\text{H}_2\text{N}(n-\text{Pr}_2)_2] \]

Di-n-propylamine (109 mg, 148 µL, 1.08 mmol, 2 eq.) was slowly dropped to a solution of o-tetrachlorocatechol (402 mg, 1.62 mmol, 3 eq.) in acetonitrile (6.0 mL). The reaction mixture turned red brown. Tetraethyl orthosilicate (113 mg, 121 µL, 541 µmol, 1 eq.) was slowly added. The reaction was stirred for 1 h at r.t. and heated to 90 °C for 2 h. After cooling to r.t., a colorless solid precipitated. Cooling to −20 °C for 1 h promoted further precipitation. The solids were filtered off, washed several times with diethyl ether and dried under reduced pressure to give the product \([1][\text{H}_2\text{N}(n-\text{Pr}_2)_2]\) as colorless crystalline solids (268 mg, 276 µmol, 51 %).

\[ ^1H \text{NMR (600 MHz, CD}_2\text{Cl}_2): \delta = 7.43 (s, 4H), 3.23 (t, } J = 7.4 \text{ Hz, } 8H), 1.71 \text{ (sex, } J = 7.5 \text{ Hz, } 4H), 0.96 \text{ (t, } J = 7.4 \text{ Hz, } 6H). \]

\[ ^{13}C \text{ NMR (151 MHz, CD}_2\text{Cl}_2): \delta = 146.7, 120.3, 114.2, 49.2, 19.7, 10.9. \]

\[ ^{29}\text{Si INVGATE NMR (119 MHz, CD}_3\text{CN): } \delta = -143.7. \]

\[ \text{IR (ATR): } 3230 \text{ (br), } 2970 \text{ (br), } 2806 \text{ (br), } 1568, 1456, 1387, 1305, 1244, 1237, 1001, 984, 806, 754. \]

\[ \text{Anal.: Calcd. for } \text{C}_{30}\text{H}_{32}\text{Cl}_{12}\text{N}_{2}O_{6}\text{Si: C 37.14, H 3.33, N 2.89, found: C 37.69, H 3.49, N 3.01.} \]

\[ ^{1H} \text{NMR (200 MHz, CD}_2\text{Cl}_2): \delta = 7.37 \text{ (s, } 2H), 3.48 \text{ (t, } J = 5.6 \text{ Hz, } 12H), 1.26 \text{ (t, } J = 7.2 \text{ Hz, } 18H). \]

\[ ^{13}C \text{ NMR (151 MHz, CD}_2\text{Cl}_2): \delta = 147.6, 119.9, 113.8, 48.2, 9.0. \]

\[ ^{29}\text{Si INVGATE NMR (119 MHz, CD}_2\text{CN): } \delta = -138.3. \]

\[ \text{IR (ATR): } 3118 \text{ (br), } 2982, 2946, 1571, 1552, 1453, 1396, 1382, 1304, 1245, 1231, 1032, 983, 805. \]

\[ \text{Anal.: Calcd. for } \text{C}_{30}\text{H}_{32}\text{Cl}_{12}\text{N}_{2}\text{O}_{6}\text{Si: C 37.14, H 3.33, N 2.89, found: C 37.48, H 3.49, N 3.15.} \]

\[ [\text{Si(diox}^\text{Cl})_3][\text{HNEt}_3] - [1][\text{HNEt}_3] \]

Triethylamine (136 mg, 188 µL, 1.35 mmol, 2 eq.) was slowly dropped to a solution of o-tetrachlorocatechol (500 mg, 2.02 mmol, 3 eq.) in acetonitrile (40 mL). The reaction mixture turned reddish. Then tetraethyl orthosilicate (140 mg, 149 µL, 672 µmol, 1 eq.) was slowly added. The reaction was stirred for 2 h at r.t. and heated to 88 °C for 18 h. After cooling to r.t., colorless solids precipitated. Cooling to −20 °C for 1–2 h promoted further precipitation. The solids were filtered off, washed with diethyl ether and pentane, and dried under reduced pressure to give the product \([1][\text{HNEt}_3]\) as colorless powder (400 mg, 412 µmol, 61 %).

\[ ^{1H} \text{NMR (200 MHz, CD}_2\text{Cl}_2): \delta = 7.37 \text{ (s, } 2H), 3.48 \text{ (t, } J = 5.6 \text{ Hz, } 12H), 1.26 \text{ (t, } J = 7.2 \text{ Hz, } 18H). \]

\[ ^{13}C \text{ NMR (151 MHz, CD}_2\text{Cl}_2): \delta = 147.6, 119.9, 113.8, 48.2, 9.0. \]

\[ ^{29}\text{Si INVGATE NMR (119 MHz, CD}_2\text{CN): } \delta = -138.3. \]

\[ \text{IR (ATR): } 3118 \text{ (br), } 2982, 2946, 1571, 1552, 1453, 1396, 1382, 1304, 1245, 1231, 1032, 983, 805. \]

\[ \text{Anal.: Calcd. for } \text{C}_{30}\text{H}_{32}\text{Cl}_{12}\text{N}_{2}\text{O}_{6}\text{Si: C 37.14, H 3.33, N 2.89, found: C 37.48, H 3.49, N 3.15.} \]

\[ \text{HRMS (ESI neg.): [Si(diox}^\text{Cl})_3+H]}^{-}, \text{ m/z} \text{ calcd. 766.5722, found 766.5751.} \]
[Si(dioxC\textsubscript{3})\textsubscript{3}[NBu\textsubscript{4}]\textsubscript{2} = [1][NBu\textsubscript{4}]\textsubscript{2}

To a suspension of [1][HNEt\textsubscript{3}]\textsubscript{2} (388 mg, 400 µmol, 1 eq.) in dichloromethane (50 mL), tetrabutylammonium chloride (222 mg, 800 µmol, 2 eq.) was added. The clear and colorless solution was stirred vigorously for 2 h and cooled down to −20 °C overnight to precipitate the side product triethylammonium chloride. Colorless crystals were obtained and removed. The filtrate was washed with distilled water (3x50 mL). The organic phase was then dried over anhydrous MgSO\textsubscript{4} and the solvent removed under reduced pressure. The resulting solids were dried in vacuo to give the product [1][NBu\textsubscript{4}]\textsubscript{2} as colorless powder (370 mg, 296 µmol, 74 %).

\textsuperscript{1}H NMR (600 MHz, CD\textsubscript{2}Cl\textsubscript{2}): δ = 3.22 (t, J = 8.5 Hz, 16H), 1.69-1.63 (m, 16H), 1.25 (sext, J = 7.2 Hz, 24H), 0.85 (t, J = 7.4 Hz, 16H).

\textsuperscript{13}C NMR (151 MHz, CD\textsubscript{2}Cl\textsubscript{2}): δ = 149.2, 117.9, 112.6, 59.6, 24.4, 20.2, 13.7.

\textsuperscript{29}Si INVGATE NMR (119 MHz, CD\textsubscript{3}CN): δ = −138.2.

IR (ATR): 2961, 2932, 2875, 1568, 1549, 1462, 1379, 1304, 1240, 985, 879, 808, 738.

Anal.: Calcd. for C\textsubscript{50}H\textsubscript{72}Cl\textsubscript{12}N\textsubscript{2}O\textsubscript{6}Si: C 48.02, H 5.80, N 2.24. Found: C 48.24, H 5.91, N 2.18.

HRMS (ESI neg.): [Si(dioxC\textsubscript{3})\textsubscript{3}+H]\textsuperscript{-}, m/z calcd. 382.7824, found 382.7813; [Si(dioxC\textsubscript{3})\textsubscript{3}+NBu\textsubscript{4}]\textsuperscript{-}, m/z calcd. 1007.8491, found 1007.8511.

[Si(dioxC\textsubscript{3})\textsubscript{3}[NBu\textsubscript{4}] = [1][NBu\textsubscript{4}]

[1][NBu\textsubscript{4}]\textsubscript{2} (54.0 mg, 43.2 µmol, 1 eq.) was dissolved in dichloromethane (2.0 mL) and cooled down to −40 °C. To the colorless solution, silicon trisperchloro(dioxolene) \textsuperscript{1} (33.1 mg, 43.2 µmol, 1 eq.) was added. Immediately, an intense black-green colored reaction mixture was observed. The reaction was maintained at −40 °C without stirring. After 24 h black-green crystals were obtained. The supernatant solution was removed. The crystalline solids were dried under reduced pressure to finally yield the product [1][NBu\textsubscript{4}]\textsubscript{2} as intense green powder (55.4 mg, 55.0 µmol, 64 %). SCXRD analysis and elemental analysis revealed one equivalent of dichloromethane per structural unit of [1][NBu\textsubscript{4}].

EPR (\nu\textsuperscript{X} = 9.449144 GHz, CH\textsubscript{2}Cl\textsubscript{2}): g = 2.0046. IR (ATR): 2961, 2932, 2960, 1528, 1448, 1385, 1300, 1240, 985, 879, 808, 733, 690, 669. Anal.: Calcd. for C\textsubscript{34}H\textsubscript{36}Cl\textsubscript{12}NO\textsubscript{6}Si x CH\textsubscript{2}Cl\textsubscript{2}: C 38.46, H 3.50, N 1.28. Found: C 38.49, H 3.53, N 1.28.

HRMS (ESI neg.): [Si(dioxC\textsubscript{3})\textsubscript{3}+H]\textsuperscript{-}, m/z calcd. 766.5722, found 766.5645.
1 (14.2 mg, 18.6 µmol, 1 eq.) and [1][H₂N(n-Pr₂)]₂ (18.0 mg, 18.6 µmol, 1 eq.) were mixed in dichloromethane-d₂. A green solution was obtained at first and then turned orange, indicating liberation of QCl. The product [3][H₂N(n-Pr₂)]₂ was crystallized with pentane by gas diffusion, giving light brownish crystals (21.1 mg, 14.2 µmol, 76%).

**1H NMR** (400 MHz, CD₂Cl₂): δ = 7.02 (s, 4H), 3.34 (s, 8H), 1.87-1.81 (m, 8H), 1.03 (t, J = 7.3 Hz, 6H).  
**13C NMR** (151 MHz, CD₂Cl₂): δ = 145.1, 126.5, 124.0, 49.0, 19.5, 11.0.  
**29Si-INVGate NMR** (119 MHz, CD₂Cl₂): δ = −109.6.  
**IR (ATR):** 3190 (br), 3096 (br), 2972 (br), 2937, 2881, 1584 (br), 1449, 1387, 1300, 1232, 986, 849, 836, 814, 751, 737, 710, 665.  
**Anal.:** Calcd. for C₄₂H₃₂Cl₂N₂O₁₀Si₂: C 33.6, H 2.16, N 1.88, found: C 33.93, H 2.37, N 2.04.  
**HRMS (ESI neg.)** was attempted but only fragments could be detected: [Si(diox³)₃+H⁺], m/z calc. 766.5722, found 766.5747.
2. NMR Spectra

Figure S1. $^1$H NMR spectrum ($^*CD_2Cl_2$) of [1][H$_2$N(n-Pr)$_2$].

Figure S2. $^{13}$C NMR spectrum ($^*CD_2Cl_2$) of [1][H$_2$N(n-Pr)$_2$].
Figure S3. $^{29}$Si INVGATE NMR spectrum (CD$_2$Cl$_2$) of [1][H$_2$N(n-Pr)$_2$].
Figure S4. $^1$H NMR spectrum ($^*\text{CD}_2\text{Cl}_2$) of [1][HNEt$_3$]. Contains residual $^*$water and $^*$silicone grease.

Figure S5. $^{13}$C NMR spectrum ($^*\text{CD}_2\text{Cl}_2$) of [1][HNEt$_3$]. Contains residual $^*$silicon grease.
Figure S6. $^{29}$Si INVGATE NMR spectrum (CD$_3$CN) of [1][HNEt$_3$]$_2$. 
Figure S7. $^1$H NMR spectrum ($^*$CD$_2$Cl$_2$) of [1][NBu$_4$].

Figure S8. $^{13}$C NMR spectrum ($^*$CD$_2$Cl$_2$) of [1][NBu$_4$].
Figure S9. $^{29}$Si INVGATE NMR spectrum (CD$_3$CN) of [1][NBu$_4$].
Figure S10. $^1$H NMR spectrum ($^*$CD$_2$Cl$_2$) of [3][H$_2$N(n-Pro)]$^+$. 

Figure S11. $^{13}$C NMR spectrum ($^*$CD$_2$Cl$_2$) of [3][H$_2$N(n-Pro)]$^+$. 

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Figure S12. $^{29}$Si INVGATE NMR spectrum (CD$_2$Cl$_2$) of [3]H$_2$N(r-Pr)$_2$].
3. Electrochemical Investigations

Potentiodynamic electrochemical measurements were investigated with the EmStat3+ Blue from PalmSens Compact Electrochemical Interfaces. The program PSTrace 5.7 was used to record all measurements. The experiments were conducted in the glovebox SylaTech Y05G under N₂ atmosphere in a glass cell using a three-electrode configuration. A glassy carbon electrode, with a working area of 0.07 cm², was used as working electrode, a platinic wire as counter electrode; and a silver wire served as quasi reference electrode. As internal standard ferrocene was measured at the very end of each measurement. The spectra were plotted with OriginPro 2019 (9.6.0).

The CV spectra were collected at room temperature at a scan rate of 100 mV/s in dichloromethane, unless otherwise stated. The electrolytes of choice were NBu₄BARF₂₀ or NBu₄PF₆. Prior to use, NBu₄BARF₂₀ was recrystallized from dichloromethane/hexane. The electrolytes were dried overnight under reduced pressure and stored in the glovebox. The concentration of the electrolyte solutions was 0.1 M in a total electrolyte volume of 5 mL. The solutions were stirred between each CV measurement and kept under N₂ atmosphere throughout the measurements.

3.1. Stability Test of 1 with Electrolyte NBu₄BARF₂₀

The reaction conditions for the stability test of 1 in the presence of the electrolyte NBu₄BARF₂₀ were chosen similar to the ones during a CV measurement. 1 (0.4 mg, 0.54 µmol, 0.01 eq.) was added to a solution of NBu₄BARF₂₀ (50.0 mg, 54.3 µmol, 1 eq.) in dichloromethane-d₂ (0.5 mL). After 18 h, the integrity of 1 was verified by the absence of diamagnetic reaction products (QCl or H₂CatCl) via NMR spectroscopy.

![Figure S13](image_url) ¹H NMR spectrum (CD₂Cl₂) of NBu₄BARF₂₀ with 1. Signals for H₂CatCl or other side products were not observed.
Figure S14. $^{13}$C NMR spectrum ($^1$CD$_2$Cl$_2$) of NBu$_4$BArF$_{20}$ with 1. Signals indicating the liberation of Q$^+$ were not observed.

Figure S15. $^{11}$B NMR spectrum (CD$_2$Cl$_2$) of NBu$_4$BArF$_{20}$ with 1.
3.2. Cyclic Voltammetry Experiments

3.2.1. [1][NBu₄]₂

Figure S16. ¹⁹F NMR spectrum (CD₂Cl₂) of NBu₄BArF₂₀ with 1.

Figure S17. Left: CV measurement of the first quasi reversible redox wave of [1][NBu₄]₂ at 500 mV/s (red trace), measuring up to the second redox event leads to two separated non-reversible redox waves (black trace). Right: CV measurement of the first quasi reversible redox wave of [1][NBu₄]₂ at different scan rates (50 mV/s – 500 mV/s).
3.2.2. [1][NBu₄]

Figure S18. Left: CV measurement of the two separated quasi reversible redox waves of [1][NBu₄] at different scan rates (100 mV/s – 700 mV/s). Right: CV measurement of the second quasi reversible redox wave of [1][NBu₄] at different scan rates (50 mV/s – 700 mV/s).

3.2.3. α-Perchloroquinone (QCl)

Figure S19. CV measurement of QCl in dichloromethane with NBu₄BArF20 at 100 mV/s.
3.2.4. Comparing [1][NBu₄] with Q⁺

![Graph comparing redox waves of Q⁺ and [1][NBu₄]]

Figure S20. Comparison of the (quasi) reversible redox waves of Q⁺ (100 mV/s) and of [1][NBu₄] (500 mV/s).

3.2.5. Thianthrene

![Graph showing CV measurement of thianthrene in dichloromethane with NBu₄PF₆ at 100 mV/s.]

Figure S21. CV measurement of thianthrene in dichloromethane with NBu₄PF₆ at 100 mV/s.
3.2.6. Tris(4-bromophenyl)amine (amine-Br)

![Graph showing CV measurement of amine-Br.](image)

*Figure S22. CV measurement of amine-Br in dichloromethane with NBu₄PF₆ at 100 mV/s.*

3.2.7. Tris(2,4-dibromophenyl)amine (amine-Br₂)

![Graph showing CV measurement of amine-Br₂.](image)

*Figure S23. CV measurement of amine-Br₂ in dichloromethane with NBu₄PF₆ at 100 mV/s.*
3.2.8. Hexamethylbenzene (HMB)

Figure S24. CV measurement of HMB in dichloromethane with NBu₄PF₆ at 100 mV/s.

3.2.9. Pentamethylbenzene (PMB)

Figure S25. CV measurement of PMB in dichloromethane with NBu₄PF₆ at 100 mV/s.
3.2.10. 1,2,3,4-Tetramethylbenzene (prehnitene)

![Graph showing CV measurement of prehnitene in dichloromethane with NBu$_4$PF$_6$ at 100 mV/s.]

Figure S26. CV measurement of prehnitene in dichloromethane with NBu$_4$PF$_6$ at 100 mV/s.

### 3.3. Redox Potential Values

**Table S1.** Redox potential values from CV experiments of following compounds using the respective electrolyte (0.1 M) in dichloromethane vs. Fc/Fc$^+$ (internal reference).

| Compound     | $E_{1/2}$ / V | Compound     | $E_{ox}$ / V |
|--------------|---------------|--------------|--------------|
| 1            | 0.43$^a$/ 0.88$^a$ | HMB          | 1.14$^a$     |
| Q$^{a}$      | $-1.19^b$ / $-0.33^b$ | PMB          | 1.27$^b$     |
| thianthrene  | 0.84$^b$      | prehnitene   | 1.65$^b$     |
| amine-Br     | 0.72$^b$      |              |              |
| amine-Br$_2$ | 1.12$^b$      |              |              |

*NBu$^+_4$BArF$_2$, NBu$_4$PF$_6$.\(^{a,b}\)
4. Oxidation Reactions

General Procedure:
1 (10.0 mg, 13.1 µmol, 1 eq.) and a substrate (13.1 µmol, 1 eq.) were mixed and the respective solvent (0.5 mL) was added. After stirring for some minutes, a change of color in the reaction mixture was observed. The reaction course was then monitored by $^1$H and $^{13}$C NMR or EPR spectroscopy. The conversions were confirmed by the disappearance of the respective signals in the $^1$H NMR spectrum and by the resulting EPR spectrum with the specific hyperfine coupling.

Table S2. Oxidation reactions of 1 with the following substrates.

| Entry | Substrate | Solvent    | Reaction Colour |
|-------|-----------|------------|-----------------|
| 1     | thianthrene | CD$_2$Cl$_2$ | dark purple    |
| 2     | amine-Br   | CD$_2$Cl$_2$ | dark blue      |
| 3     | HMB        | o-DCB      | dark brown     |
| 4     | PMB        | CD$_2$Cl$_2$ | red violet     |
| 5     | prehnitene | CD$_2$Cl$_2$ | magenta       |

4.1. Reaction of 1 with Tris(2,4-dibromophenyl)amine

1 (10.0 mg, 13.1 µmol, 1 eq.) and tris(2,4-dibromophenyl)amine (9.39 mg, 13.1 µmol, 1 eq.) were mixed and dichloromethane-d$_2$ (0.5 mL) was added to give a green suspension. Broad signals were observed in the $^1$H NMR spectrum indicating a possible equilibrated electron transfer between the starting materials.

Figure S27. $^1$H NMR ($^1$CD$_2$Cl$_2$) of tris(2,4-dibromophenyl)amine with 1. Contains residual *pentane.
5. EPR Spectroscopy

5.1. [1][NBu₄]

![EPR spectrum of [1][NBu₄] in dichloromethane. EPR parameters: B₀ = 3368 G, sweep = 25 G, sweep time = 30 s, modulation = 2000 mG, microwave power = 10 mW, gain = 3.]

**Figure S28.** EPR spectrum of [1][NBu₄] in dichloromethane. EPR parameters: $B_0 = 3368$ G, sweep = 25 G, sweep time = 30 s, modulation = 2000 mG, microwave power = 10 mW, gain = 3.

5.2. Oxidation Reactions

![EPR spectrum of the reaction of 1 and thianthrene at r.t. in dichloromethane. The observed EPR spectrum from the reaction of thianthrene with 1 is in agreement with previous studies of the thianthrene radical cation. EPR parameters: $B_0 = 3364$ G, sweep = 100 G, sweep time = 20 s, modulation = 2000 mG, microwave power = 10 mW, gain = 7.]

**Figure S29.** EPR spectrum of the reaction of 1 and thianthrene at r.t. in dichloromethane. The observed EPR spectrum from the reaction of thianthrene with 1 is in agreement with previous studies of the thianthrene radical cation. EPR parameters: $B_0 = 3364$ G, sweep = 100 G, sweep time = 20 s, modulation = 2000 mG, microwave power = 10 mW, gain = 7.
Figure S30. EPR spectrum of the reaction of 1 and tris(4-bromophenyl)amine at r.t. in dichloromethane. The observed EPR spectrum shows a broad triplet signal indicating a radical localized at the nitrogen. EPR parameters: $B_0 = 33.70$ G, sweep = 200 G, sweep time = 20 s, modulation = 2000 mG, microwave power = 10 mW, gain = 9.

Figure S31. EPR spectrum of the reaction of 1 and HMB at r.t. in dichloromethane. The observed EPR spectrum is in agreement with previous studies of the hexamethylbenzene radical cation. The asymmetry in the signal can be explained by the presence of the underlying radical anion of 1. EPR parameters: $B_0 = 33.77$ G, sweep = 100 G, sweep time = 40 s, modulation = 2000 mG, microwave power = 1 mW, gain = 9$ \times 10^2$. 
Figure S32. EPR spectra of the reaction of 1 and PMB (left) and of 1 and prehnitene (right) at r.t. in dichloromethane. The observed EPR spectra show the formation of radicals with hyperfine coupling, thus validating the successful oxidation reactions of the alkylated aromatics. The asymmetry in the signal can be explained by the presence of the underlying radical anion of 1. Due to the short-lived nature and light-sensitivity of the primary oxidation products, no further characterization was attempted. EPR parameters for the reaction of 1 with PMB: $B_0 = 3370$ G, sweep = 100 G, sweep time = 20 s, modulation = 2000 mG, microwave power = 10 mW, gain = $4 \cdot 10^2$. EPR parameters for the reaction of 1 with prehnitene: $B_0 = 3370$ G, sweep = 100 G, sweep time = 30 s, modulation = 2000 mG, microwave power = 10 mW, gain = $2 \cdot 10^2$. 

[Diagram of EPR spectra with labels and parameters]
6. IR Spectroscopy

Figure S33. IR (ATR) spectrum of [1][H$_2$N(n-Pr)$_2$]$_2$.

Figure S34. IR (ATR) spectrum of [1][HNEt]$_2$. 
Figure S35. IR (ATR) spectrum of [1][NBu4].

Figure S36. IR (ATR) spectrum of [1][NBu].
Figure S37. IR (ATR) spectrum of $[3][\text{H}_2\text{N}(\text{n-Pr})_2]_2$. 

$[3][\text{H}_2\text{N}(\text{n-Pr})_2]_2$
7. UV-Vis-NIR Spectroscopy

UV-Vis-NIR spectra were recorded at room temperature with the Agilent Varian Cary 5000 UV-Vis-NIR spectrophotometer. The solutions were prepared in a Schlenk quartz cuvette (10.00 x 10.00 mm) in a glovebox in dichloromethane. Before each measurement, a background spectrum of the solvent was recorded and a baseline correction was conducted. The spectra were plotted and evaluated with OriginPro 2019 (9.6.0).

![UV-Vis spectrum](image1.png)

Figure S38. UV-Vis spectrum of [1][NBu₄] in dichloromethane in various concentrations.

![Near-IR spectrum](image2.png)

Figure S39. Near-IR spectrum of [1][NBu₄] (10⁻³ M) in dichloromethane. The sharp irregularities in the baseline from 1600 nm to 2800 nm arise due to the subtraction of the strong near-IR absorptions of the solvent. Several broad bands at 2400 nm, 2800 nm and 2950 nm were assigned to intervalence charge transfer bands.
Figure S40. Extinction coefficient $\varepsilon_{456\text{nm}} = 1320.4 \pm 77.7 \, \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ of [1][NBu$_4$] in dichloromethane.
8. Oxidative Lactonization Studies

8.1. Substrate Synthesis

2-(4-Methoxybenzoyl)benzoic acid

\[
\text{MeO} \quad \text{MgBr} + \text{O} \quad \text{O} \quad \text{THF} \quad 0 \^\circ\text{C to r.t.} \quad \text{MeO} \quad \text{CO}_2\text{H}
\]

4-Methoxyphenylmagnesium bromide (9.46 mL, 0.50 M in THF, 4.73 mmol, 1.00 eq) was added dropwise to a solution of phthalic anhydride (701 mg, 4.73 mmol, 1.00 eq) in THF (10 mL) at 0 °C. The light-yellow reaction was warmed to room temperature after 1 h, and stirred for 24 h. The blurry and colourless reaction mixture was quenched with 1M HCl (aq) and extracted with diethyl ether. The combined organic phases were extracted twice with 1 M NaOH (aq) and the resulting aqueous phases were acidified with concentrated HCl. The mixture was then extracted with diethyl ether, washed with brine solution and dried over MgSO\(_4\). The solvent was removed under reduced pressure to obtain the crude product (857 mg, 3.34 mmol, 71 %). Recrystallisation in diethyl ether yielded the product as colourless crystals (464 mg, 1.81 mmol, 38 % yield). The spectral data matched with previously reported ones.\(^9\)

Figure S41. \(^1\)H and \(^{13}\)C NMR spectrum (\(^*\)CD\(_2\)Cl\(_2\)) of 2-(4-methoxybenzoyl)benzoic acid. Contains residual \(^*\)silicon grease.
Trifluoroacetic acid (3.00 mL) was added dropwise to a solution of 2-(4-methoxybenzyl)benzoic acid (460 mg, 1.80 mmol, 1.00 eq) and triethylsilane (860 µL, 5.39 mmol, 3.00 eq) in chloroform (3.00 mL) at 0 ºC. Then the solution was warmed up to r.t. and heated at reflux for 19 h. After the reaction was cooled down to room temperature, it was diluted with diethyl ether and washed twice with 1M HCl (aq). The combined organic phases were extracted twice with 1 M NaOH (aq) and the resulting aqueous phases were acidified with concentrated HCl. The mixture was then extracted with diethyl ether, washed with brine solution and dried over MgSO₄. The solvent was removed under reduced pressure to yield the product 4 as colorless solids (380 mg, 1.57 mmol, 87% yield). The spectral data of 4 matched with previously reported ones.\[9a\]
8.2. Catalysis

![Chemical structure](image)

1 (2.50 mg, 3.27 µmol, 5 mol%) and QCl (20.9 mg, 84.9 µmol, 1.3 eq.) were mixed and cooled down to −40 °C. Cold dichloromethane-d₂ (0.5 mL) was slowly added. The reaction mixture was maintained for 5 min at 4 °C and then stirred at r.t. Over time the reaction turned from intense dark red to yellow. Within less than 95 min the reaction was completed. Product conversions were determined by ¹H NMR analysis of the crude reaction. 5 is a known compound and the spectral data matched with previously reported ones.[10]

![NMR spectra](image)

Figure S43. ¹H NMR spectra (CD₂Cl₂) of the reaction course of the lactonization of 4 to 5 with 5 mol% of 1. Contains o-tetrachlorocatechol (respective signal lies beneath the product signal).
8.3. *in situ* Catalysis

Silicon tetraiodide (1.70 mg, 3.10 µmol, 5 mol%) and QCl (19.8 mg, 80.5 µmol, 1.3 eq.) were mixed and dichloromethane-d2 (0.25 mL) was added. A bright red solution was obtained. After 30 min, a solution of 4 (15.0 mg, 61.9 µmol, 1.0 eq) in dichloromethane-d2 (0.25 mL) was added to the reaction. Within less than 80 min the reaction was completed. Product conversions were determined by ¹H NMR analysis of the crude reaction. 5 is a known compound and the spectral data matched with previously reported ones.[10]

**Figure S44.** ¹H NMR spectra (*CD2Cl2*) of the reaction course of the lactonization of 4 to 5 by *in situ* synthesis of 1 with 5 mol% of SiI₄. Contains *o*-tetrachlorocatechol (respective signal lies beneath the product signal).
9. Dehydrogenative Coupling of 3,3′′',4,4′′-Tetramethoxy-o-terphenyl 7

9.1. Catalysis

1 (2.00 mg, 2.61 µmol, 10 mol%), QCl (8.35 mg, 34.0 µmol, 1.3 eq.) and 3,3′′,4,4′′-tetramethoxy-o-terphenyl 7 (9.15 mg, 26.1 µmol, 1 eq.) were mixed and cooled down to −40 °C. Cold dichloromethane-d2 (0.5 mL) was added and a black green solution was obtained. It was maintained for 5 min at −40 °C, then it was slowly warmed up to r.t. The reaction was stirred for 24 h, then colorless crystals precipitated. The supernatant solution was removed. The crystals were dried under reduced pressure to give the product 2,3,10,11-tetramethoxytriphenyle 8 co-crystallized with H2CatCl as light brown powder in quantitative yields. 8 is a known compound and the spectral data matched with previously reported ones.[11] Product identity was also confirmed by SCXRD analysis (Figure S46).

Figure S45. 1H NMR spectra (CD2Cl2) of the reaction course of the oxidative coupling of 7 to 8 with 10 mol% of 1. Contains "o-tetrachlorocatechol and residual "water after reaction quenching.
Figure S46. Molecular structure of 8 as ORTEP plot with one o-tetrachlorocatechol per structural unit.
10. Oxidation of 9,10-Dihydroanthracene 9

1 (2.00 mg, 2.61 µmol, 5 mol%), QCl (16.1 mg, 65.3 µmol, 2.5 eq.) and 9,10-dihydroanthracene 9 (4.70 mg, 26.1 µmol, 1 eq.) were mixed and dichloromethane-d$_2$ (0.5 mL) was added. A dark red solution was obtained, which decolored within few minutes to a colorless to light yellow suspension. It was stirred at r.t. After 65 h the reaction was completed. Product conversions were determined by $^1$H NMR analysis of the crude reaction. Anthracene 10 is a known compound and the spectral data matched with previously reported ones.\[12\]

Figure S47. $^1$H NMR spectra of the reaction course of the oxidation of 9 to 10 with 10 mol% of 1. Contains $^*$-tetrachlorocatechol and residual $^*$pentane. Secondary oxidation products are framed in the blue box.
11. Computational Details: Transition State for Catecholate Shuffling.

Geometry optimizations and single point energy calculations have been performed with ORCA 4.2. The structures of all involved compounds were optimized with the PBEh-3c/def2-mSVP as implemented in ORCA, using grid5 settings, and confirmed as energetic minima on the potential energy surface by analytical calculation of harmonic frequencies, revealing only positive Hessian eigenvalues, or one negative in case of the transition state. Enthalpies at 298.15 K have been calculated at the same level of theory by using the rigid-rotor harmonic oscillator (RRHO) approximation as implemented in ORCA. The gas phase single point computations were calculated with the hybrid meta exchange-correlation functional PW6B95-D3(BJ), in combination with the very large def2-QZVPP basis set. SCF settings were tightSCF and integration was performed at a very fine grid. The RIJCOSX Fock-matrix formation algorithm was used as implemented in Orca along with the respective automatically generated auxiliary basis sets (AutoAux). Enthalpies at 298.15 K were calculated with the total thermal and zero-point energy correction from the PBEh-3c calculation combined with the electronic single point energies obtained on the PW6B95-D3(BJ)/def2-QZVPP level of theory.

Table S3. Computational details on the energies of $3^2$ and the transition state (TS).

|                  | Thermal + ZPE correction from PBEh-3c [kJ mol$^{-1}$] | Entropy$^\text{298K}$ from PBEh-3c [kJ mol$^{-1}$] | $E$ (Hartree) PW6B95-D3(BJ)/def2-QZVPP | $E$ [kJ mol$^{-1}$] | $H$ [kJ mol$^{-1}$] | $G$ [kJ mol$^{-1}$] |
|------------------|------------------------------------------------------|-----------------------------------------------|----------------------------------------|---------------------|-------------------|-------------------|
| $3^2$            | 848.8                                                | 379.9                                         | -11690.5                                | -30693465.2         | -30692616.4       | -30692996.2       |
| TS               | 845.6                                                | 369.4                                         | -11690.5                                | -30693423.0         | -30692577.4       | -30692946.7       |

|                  | $\Delta E$ | $\Delta H$ | $\Delta G$ |
|------------------|------------|------------|------------|
| Exchange         | 42.3       | 39.1       | 49.5       |

$3^2$ global min.
rel. $G = 0$ kJ mol$^{-1}$

$3^2$ transition state for interchange of bridging (B) with external catecholate (A)
rel. $G = 49.5$ kJ mol$^{-1}$
12. Computation of MOS

The MOS was calculated by means of the Excel sheet provided in the supporting information of: S. N. Brown, Inorg. Chem. 2012, 51, 1251-1260.

Table S4. Calculated Metrical Oxidation State (MOS) for the following compounds.

| Compound | Dioxolene | C-O average | C1-C2 | C2-C3 avg | C3-C4 avg | C4-C5 | Calc. MOS |
|----------|-----------|-------------|-------|-----------|-----------|-------|-----------|
| [1][NBu₄] | Ring 1    | 1.2805      | 1.447 | 1.4135    | 1.376     | 1.437 | -1.05     |
|          | Ring 2    | 1.3435      | 1.409 | 1.3765    | 1.403     | 1.386 | -1.97     |
|          | Ring 3    | 1.346       | 1.397 | 1.381     | 1.4025    | 1.391 | -1.99     |
|          | sum       |             |       |           |           |       | -5.01     |
| [1][H₂N(n-Pr)₂] | Ring 1 | 1.343 | 1.409 | 1.3775 | 1.4025 | 1.389 | -1.95 |
|          | Ring 2    | 1.34      | 1.399 | 1.391    | 1.403     | 1.388 | -1.93     |
|          | Ring 3    | 1.343     | 1.409 | 1.3775   | 1.4025    | 1.389 | -1.95     |
|          | sum       |             |       |           |           |       | -5.82     |
| [3][H₂N(n-Pr)₂] | Ring 1 | 1.362 | 1.382 | 1.379    | 1.3965    | 1.397 | -2.11     |
|          | Ring 2    | 1.3565    | 1.387 | 1.378    | 1.393     | 1.397 | -2.06     |
|          | Ring 3 (linker) | 1.3685 | 1.394 | 1.388    | 1.3835    | 1.386 | -2.11     |
|          | Ring 4    | 1.363     | 1.391 | 1.3785   | 1.395     | 1.39  | -2.12     |
|          | Ring 5    | 1.3575    | 1.395 | 1.3685   | 1.3985    | 1.4   | -2.07     |
|          | sum       |             |       |           |           |       | -10.48    |
13. X-ray Crystal Structure Determination

Suitable crystals for single-crystal structure determination were taken directly from the mother liquor, taken up in perfluorinated polyether oil and fixed on a cryo loop. Full shells of intensity data were collected at low temperature with a Bruker D8 Venture diffractometer, dual-source (Mo- or Cu-Kα radiation, microfocus X-ray tube, Photon III detector). Data were processed with the standard Bruker (SAINT, APEX3) software package. Multiscan absorption correction was applied using the SADABS program. The structures were solved by intrinsic phasing and refined using the SHELXTL software package (Version 2014/6 and 2018/3). Graphical handling of the structural data during solution and refinement was performed with OLEX2. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms bound to carbon were input at calculated positions and refined with a riding model. CCDC 2035360-2035362 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre's and FIZ Karlsruhe's joint Access Service via https://www.ccdc.cam.ac.uk/structures/.

**Figure S49.** Molecular structure of [1][NBu4] as ORTEP plot, protons omitted.

| Property                  | Value                        |
|---------------------------|------------------------------|
| **Empirical formula**     | C_{35}H_{38}Cl_{14}NO_{6}Si  |
| **Formula weight**        | 1093.05                      |
| **Temperature/K**         | 101.0                        |
| **Crystal system**        | triclinic                    |
| **Space group**           | P-1                          |
| **Cell parameters**       |                              |
| a/Å                       | 10.9650(8)                   |
| b/Å                       | 12.4668(9)                   |
| c/Å                       | 17.8053(13)                  |
| α/°                       | 101.534(3)                   |
| β/°                       | 100.805(3)                   |
| γ/°                       | 102.979(3)                   |
| **Volume/Å³**             | 2254.0(3)                    |
| **Z**                     | 2                            |
| **ρ_cal(g/cm³)**          | 1.611                        |
| **μ/mm²**                 | 0.927                        |
| **F(000)**                | 1110.0                       |
| **Crystal size/mm³**      | 0.181 × 0.089 × 0.062        |
| **Radiation**             | MoKα (λ = 0.71073)           |
| **2θ range for data collection** | 3.686 to 54.326 |
| **Index ranges**          | -14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -22 ≤ l ≤ 22 |
| **Reflections collected** | 71748                        |
| **Independent reflections** | 9956 [R_{int} = 0.0599, R_{exp} = 0.0332] |
| **Data/restraints/parameters** | 9956/0/518                   |
| **Goodness-of-fit on F²** | 1.049                        |
| **Final R indexes [I>2σ (I)]** | R₁ = 0.0398, wR₂ = 0.0910 |
| **Final R indexes [all data]** | R₁ = 0.0513, wR₂ = 0.0979 |
| **Largest diff. peak/hole/e Å³** | 0.69/-0.61                  |
Figure S50. Molecular structure of \([\text{1}]\text{H}_2\text{N(n-Pr)}_2\) as ORTEP plot.

| Property                | Value                     |
|-------------------------|---------------------------|
| Empirical formula       | \(\text{C}_{30}\text{H}_{32}\text{Cl}_{12}\text{N}_{2}\text{O}_{6}\text{Si}\) |
| Formula weight          | 970.06                    |
| Temperature/K           | 120                       |
| Crystal system          | monoclinic                |
| Space group             | \(\text{C2/c}\)            |
| \(a/\text{Å}\)          | 20.646(4)                 |
| \(b/\text{Å}\)          | 12.467(3)                 |
| \(c/\text{Å}\)          | 16.175(3)                 |
| \(\alpha/\degree\)      | 90                        |
| \(\beta/\degree\)       | 108.56(3)                 |
| \(\gamma/\degree\)      | 90                        |
| Volume/\(\text{Å}^3\)   | 3946.8(15)                |
| \(Z\)                   | 4                         |
| \(\rho_{\text{calc}}/\text{g/cm}^3\) | 1.633                     |
| \(\mu/\text{mm}^{-1}\)  | 0.917                     |
| \(F(000)\)              | 1968.0                    |
| Crystal size/mm\(^2\)   | 0.13 \times 0.12 \times 0.11 |
| Radiation               | \(\text{MoK\(\alpha\)} (\lambda = 0.71073)\) |
| 2\(\theta\) range for data collection\(^n\) | 3.874 to 60.09 |
| Index ranges            | -29 \(\leq h \leq 29\), -17 \(\leq k \leq 17\), -22 \(\leq l \leq 22\) |
| Reflections collected   | 10939                     |
| Independent reflections | 5772 [R\(_{\text{int}}\) = 0.0376, R\(_{\text{exp}}\) = 0.0528] |
| Data/restraints/parameters | 5772/0/244               |
| Goodness-of-fit on \(F^2\) | 1.034                     |
| Final R indexes [\(l \geq 2\sigma (l)\)] | \(R_1 = 0.0415\), \(wR_2 = 0.0920\) |
| Final R indexes [all data] | \(R_1 = 0.0699\), \(wR_2 = 0.1021\) |
| Largest diff. peak/hole \(e \text{ Å}^3\) | 0.69\/-0.59 |
Figure S51. Molecular structure of $[\text{H}_2\text{N}(\sigma\text{-Pr})]_2$ as ORTEP plot (A: without cations. B: with cations).

Empirical formula: $\text{C}_{42}\text{H}_{32}\text{N}_2\text{O}_{10}\text{Si}_2\text{Cl}_{20}$

Formula weight: 1489.87

Temperature/K: 293(2)

Crystal system: triclinic

Space group: $P\overline{1}$

$a$/Å: 11.029(2)

$b$/Å: 15.799(3)

$c$/Å: 17.369(4)

$\alpha$/°: 87.78(3)

$\beta$/°: 74.42(3)

$\gamma$/°: 85.75(3)

Volume/Å³: 2906.8(11)

$Z$: 2

$\rho_{calc}$/g/cm³: 1.702

$\mu$/mm⁻¹: 1.035

$F(000)$: 1492.0

Crystal size/mm: $0.105 \times 0.09 \times 0.085$

Radiation: MoKα ($\lambda = 0.71073$)

2θ range for data collection/°: 2.586 to 55

Index ranges: $-14 \leq h \leq 14$, $-20 \leq k \leq 20$, $-22 \leq l \leq 22$

Reflections collected: 24720

Independent reflections: 13332 [$R_{int} = 0.0797, R_{restr} = 0.1439$]

Data/restraints/parameters: 13332/0/689

Goodness-of-fit on $F^2$: 0.923

Final R indexes [I>$2\sigma$(I)]: $R_I = 0.0523$, $wR_I = 0.0913$

Final R indexes [all data]: $R_I = 0.1631$, $wR_I = 0.1195$

Largest diff. peak/hole / e Å⁻³: 0.44/-0.34
Figure S52. Molecular structure of [1][NBu₄] as ORTEP plot, connectivity shown only, protons omitted.
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