Electrochemical Dearomatizing Spirolactonization and Spiroetherification of Free Arenols

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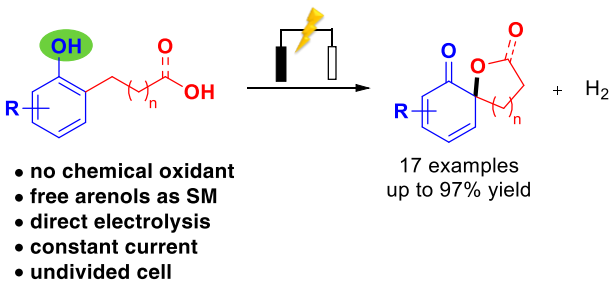
Abstract

An electrochemical oxidative *ortho*-dearomatization of naphthols and phenols with an intramolecular C–O bond formation has been developed. A careful optimization of the reaction parameters allowed for the application of free arenols as the starting materials, in contrast to the existing alternative procedures necessitating aryl methyl ethers substrates. The reaction delivers an array of spirolactones and spiroethers in yields up to 97%, under simple experimental conditions: in a constant current mode, using an undivided cell, and without an inert atmosphere. The method avoids using catalysts or stoichiometric oxidants (e.g., hypervalent iodine reagents), generating hydrogen as the sole side-product.



Introduction

Spiro-oxacyclic moieties are prevalent in numerous natural products and compounds of biological and medicinal relevance, including alkaloids and antibiotics (Figure 1A).[1] A very powerful synthetic strategy that is routinely employed to construct spiro-oxacyclic compounds relies on the oxidative dearomatization of arenols that proceeds through the intramolecular addition of a tethered oxygen nucleophile (Figure 1B).[2] Hypervalent iodine reagents have been most commonly used to promote such dearomatization reactions,[3] but other oxidants have been employed for that purpose as well.[4] In particular, over the last decade, a significant progress has been made in the area of enantioselective intramolecular spirolactonization and spiroetherification of arenols using the catalysis with chiral iodoarenes.[5]

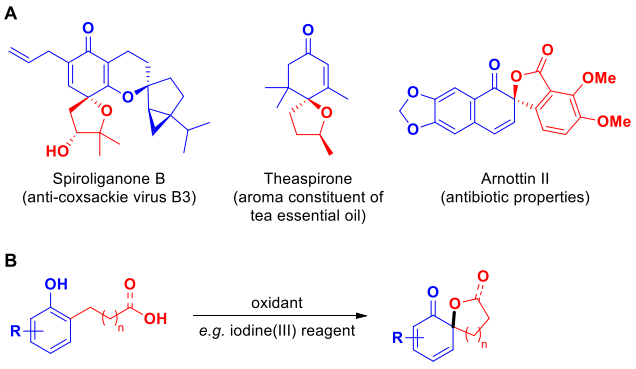
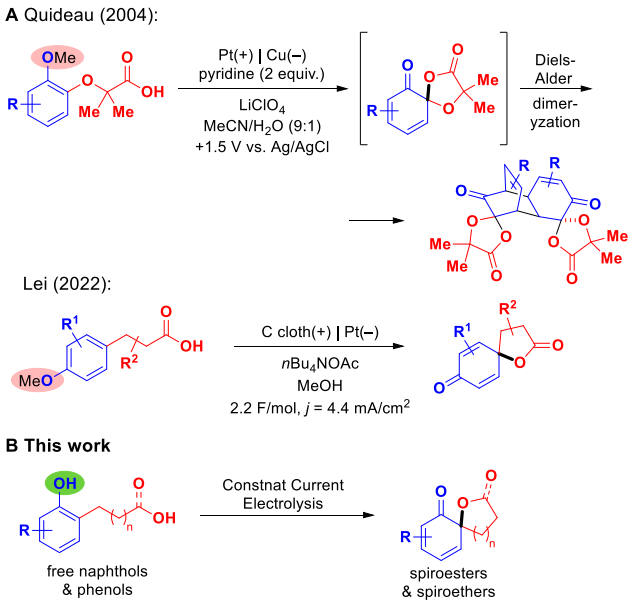


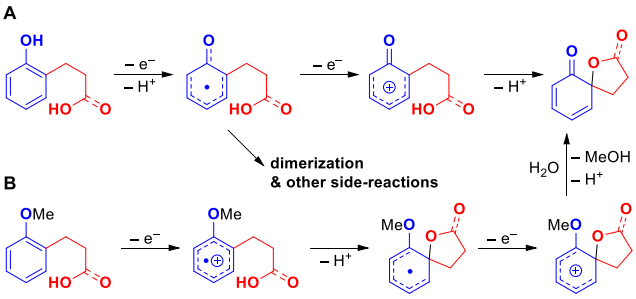
Figure 1. (A) Examples of bioactive natural products containing a spirolactone or spiroether moiety and (B) the oxidative dearomatization of arenols with the intramolecular addition of tethered oxygen nucleophiles.

Due to the emergence of easily accessible standardized instrumentation, electrochemistry has in recent years become a handy and valuable synthetic tool for conducting organic redox transformations.[6] One of its major advantages is the sustainability that stems from the exchange of stoichiometric amounts of often toxic, expensive, and high energy redox

reagents, additionally accompanied by likewise problematic waste streams, with electrical stimuli that both moves the electrons and provides the driving force for the reaction. However, despite phenols being common substrates in electrochemical transformations,[7] the anodic oxidative dearomatization of arenols leading to spiro-oxacyclic compounds has not been systematically investigated. Reports of isolated examples of such a process are scarce and are exclusively confined to *para*-dearomatizations.[8,9] Instead, an analogous approach employing aryl methyl ethers rather than arenols has been pursued by Quideau and, more recently, by Lei (Scheme 1A).[9g,10] This is due to the fact that upon the initial single-electron oxidation, phenols are converted into phenoxyl radicals, which are prone to dimerization and other side-processes (Scheme 2A).[7a,7c-e] These undesired pathways mitigate the efficiency of the spiro-oxacyclization by competing with the second oxidation step that is required to generate a phenoxenium ion, priming the ring for the addition of the oxygen nucleophile. Conversely, the SET oxidation of aryl methyl ethers affords the corresponding radical cations (Scheme 2B), which are readily quenched by the nucleophile, preventing the formation of side-products.



Scheme 1. Existing procedures for the synthesis of spirolactones via electrochemical oxidative dearomatizations of aryl methyl ethers (A) and the developed direct electrochemical dearomatizing oxidation of free arenols leading to spirolactones and spiroethers (B).



Scheme 2. Comparison of mechanistic pathways for the anodic oxidation of (A) free arenols and (B) aryl methyl ethers with a tethered oxygen nucleophile. The two protons and two electrons removed in each of the pathways are combined at the cathode to generate H_2.

Although considerably more challenging, the preparation of spiro-oxacycles under the electrochemical conditions directly from free arenols would benefit from much greater

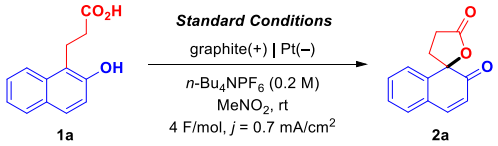
availability of the starting materials and shorter, thus more economical and greener, synthetic sequence. For instance, introducing a methyl group onto an arenol to merely facilitate the electrochemical dearomatization constitutes an additional synthetic step, utilizing extra reagents and resources necessary for carrying out the reaction as well as the isolation and purification of the methyl ether intermediate. Therefore, we set out to develop the direct electrochemical oxidative dearomatization of free arenols toward the formation of spirolactones and spiroethers (Scheme 1B). Given the existence of scarce precedents,[8] we assumed that since electrochemistry offers many possibilities to control the course of the reaction and its outcome by the choice of the respective electrolytic parameters, we would be able to find conditions, under which the SET oxidation of the phenolxyl radical prevails over the alternative undesired side-processes. Specifically, we focused on the *ortho*-dearomatizations, which have never been realized before via the electrochemically-promoted oxidation of free arenols.

Result and discussion

We began with our investigations by optimizing the reaction conditions for the electrochemical spirolactonization of a model 2-naphthol-derived carboxylic acid **1a**. Indeed, for this generic substrate, we were able to identify a set of parameters that secures a nearly quantitative formation of the desired product **2a** (Table 2, entry 1). This consists of a constant current electrolysis (CCE) of the solution of the substrate in nitromethane in an undivided cell, using a graphite anode and a platinum cathode at a current density of 0.7 mA/cm^2, with 4 F/mol of total charge passed. *n*-Bu_4NPF_6 is employed as a supporting electrolyte and the electrolysis is carried out at room temperature under air. The impact of different parameters

on the efficacy of the electrochemical spirolactonization of **2a** is shown in Table 1. To this end, replacing $MeNO_2$ with MeCN as the reaction solvent results in the yield of spirolactone **2a** being reduced to 78% (entry 2). The application of other solvents, such as 1,1,1,3,3,3-hexafloroisopropanol (HFIP), 2,2,2-trifluoroethanol (TFE), and dichloromethane was found to be detrimental for the reaction (entries 3-5). When the electrolysis was carried out using $LiClO_4$, instead of *n*-Bu_4NPF_6, as the supporting electrolyte, the yield was decreased to 75% (entry 6). Lowering the concentration of *n*-Bu_4NPF_6 from 0.2 M (5 equiv. relative to the substrate) to 0.12 M (3 equiv.) leads to a diminished efficiency of the spirolactonization (entry 7), and only a trace amount of **2a** is obtained in the absence of the supporting electrolyte (entry 8). Regarding the materials of the electrodes, utilizing glassy carbon in place of graphite as the anode results in a very low yield of the product, while replacing the platinum cathode with a graphite one decreases the yield to 71% (entries 9 and 10, respectively). To effect a quantitative spirolactonization, as much as 4 F/mol of charge need to be passed through the electrodes, while lowering this value to 3 F/mol already affects the yield considerably (entry 11). The reaction affords the product in an unchanged yield under an inert atmosphere (entry 12), demonstrating that oxygen is not involved in the reaction. Finally, no product was observed in the absence of the electric stimuli (entry 13).

Table 1. Effect of reaction parameters on the electrochemical spirolactonization of 2-naphthol-derived carboxylic acid **1a**.

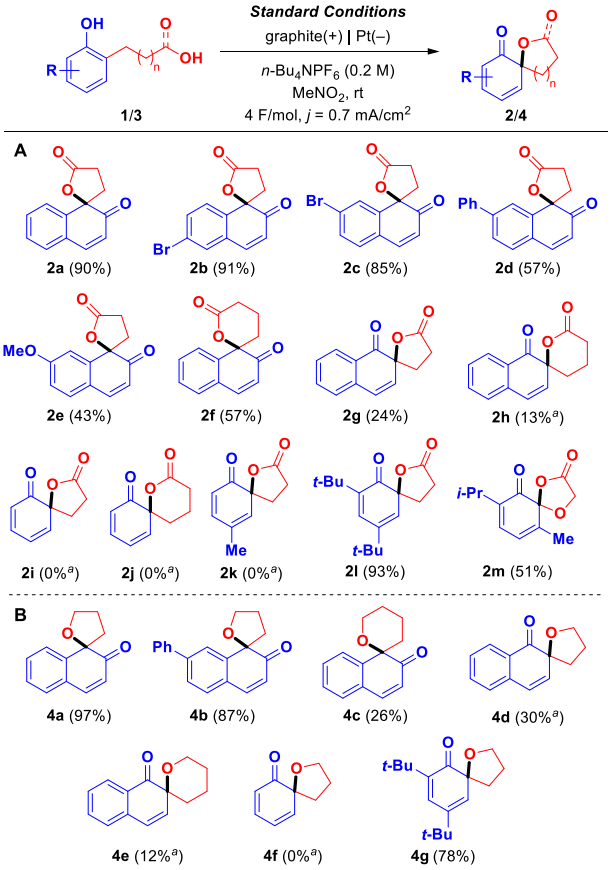


Entry	Variation from the Standard Conditions	Yield (%)[a]
1	none	96
2	CH_3CN, instead of $MeNO_2$	78
3	HFIP, instead of $MeNO_2$	30
4	TFE, instead of $MeNO_2$	9
5	CH_2Cl_2, instead of $MeNO_2$	3
6	$LiClO_4$, instead of *n*-Bu_4NPF_6	75
7	0.12 M *n*-Bu_4NPF_6, instead of 0.2 M	85
8	no *n*-Bu_4NPF_6	trace
9	glassy carbon as anode, instead of graphite	10
10	graphite as cathode, instead of Pt	71
11	3 F/mol charge passed, instead of 4 F/mol	58
12	under N_2 atmosphere	94
13	no electric current	no reaction

[a] Determined by ^1H NMR spectroscopy.

With the optimized conditions established, we proceeded to investigate the substrate scope of the electrochemical spiro-oxacylization of arenols (Scheme 3A). First, we explored the spirolactonization of 2-naphthol derivatives with a propionic acid moiety tethered at position 1, affording the corresponding five-membered oxacyclic esters. Thus, the preparative electrolysis of the model substrate **1a** provides spirolactone **2a** in 90% isolated yield. The synthesis of analogous dearomatized spirolactones with a bromine substituent at either position 6 or 7 of the naphthalene ring also proceeds uneventfully, affording the respective products **2b** and **2c** in excellent yields (91% and 85%, respectively). A slightly reduced

reaction efficiency was observed for the 2-naphthol substrates containing a phenyl and a methoxy substituent at position 7 (**2d** and **2e**). Interestingly, we were also able to successfully obtain a dearomatized product **2f** possessing a six-membered lactone ring in a moderate yield of 57% under the electrochemical conditions. Next, we tested substrates derived from 1-naphthol, which, unfortunately, were found to undergo the reaction with a considerably lower efficiency. Namely, products **2g** and **2h** containing a five- and six-membered lactone rings are generated in only 24% and 13%, respectively. Finally, we evaluated the developed procedure for the *ortho*-spirolactonization of phenol derivatives. Thus, phenols furnishing easily dimerizing radicals do not provide the corresponding lactones at all (**2i-k**). Conversely, the desired spiro-oxacyclic product is afforded in an excellent 93% yield from the phenol with alkyl substituents in positions 4 and 6 (**2l**), and in 51% yield for the phenol containing a 3,6-substitution pattern (**2m**).

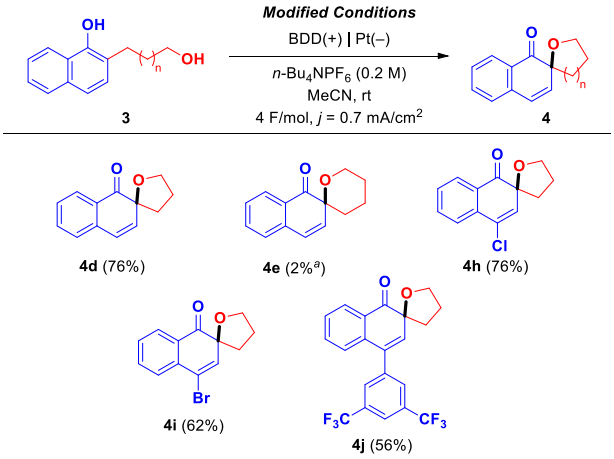


Scheme 3. Scope of the electrochemical oxidative spirolactonization and spiroetherification of arenols under the Standard Conditions (isolated yields).

[a] NMR yield.

Next, we moved to examine the anodic *ortho*-dearomatization of arenols with tethered alcohols, leading to spiroethers (Scheme 3B). In this regard, both unsubstituted and 7-phenyl-substituted 2-naphthol-derived alcohols undergo a facile electrochemical dearomatization, providing the corresponding five-membered cyclic ethers in high yields (**4a** and **4b**, respectively). On the other hand, the six-membered tetrahydropyran counterpart is not generated efficiently (**4c**). Similarly to the case of the spirolactonization described above, also the alcohol derivatives of 1-napthol were found to not be suitable substrates for the reaction under the developed conditions (**4d-e**). Finally, the electrochemical spiroetherification involving an alcohol moiety tethered to the unsubstituted phenol does not lead to the desired

products (**4f**), whereas upon the introduction of large alkyl substituents, hindering the dimerization of the radical intermediate, the corresponding product is generated in a good yield (**4g**).



Scheme 4. Scope of the electrochemical oxidative spiroetherification of substrates derived from 1-naphthol under the Modified Conditions (isolated yields).

[a] NMR yield.

The somewhat disappointing results obtained for the 1-napthol derivatives prompted us to attempt to reoptimize the reaction conditions specifically for this class of substrates. Thus, we established that a slight modification of the electrochemical parameters can indeed considerably improve the efficacy of the spiroetherification of 1-naphthol-derived compounds (the efforts to enhance the corresponding spirolactonization were not successful). In particular, the material of the anode was changed to boron-doped diamond (BDD) and nitromethane was replaced by acetonitrile as the solvent (Scheme 4). Under these conditions, the dearomative spiroetherification of 1-naphthol-derived alcohols proceeds much better, providing the desired products in good yields (**4d**, **4h-j**), with the exception of the 6-membered spiroether **4e**.

Conclusions

In conclusion, we developed an electrochemical oxidative *ortho*-spirolactonization and *ortho*-spiroetherification of free arenols. The method constitutes a chemical oxidant-free entry to important molecular scaffolds, generating hydrogen as the sole side-product. The reaction displays a broad scope, encompassing both naphthol and phenol derivatives, with the exception of ones furnishing easily dimerizing radicals. It provides moderate to high yields and proceeds under simple constant current conditions in an undivided cell.

Experimental section

General Information. Unless stated otherwise, all materials were purchased from commercial suppliers and used without purification. Anhydrous DME, MeCN, and $MeNO_2$ were purchased in septa-sealed bottles and were stored under nitrogen. Anhydrous CH_2Cl_2 and THF were purified prior to use by passage through a column of neutral alumina under nitrogen. Et_3N was rendered anhydrous by storing over molecular sieves 4 Å. The electrochemical experiments were carried with IKA Electrasyn 2.0, using standard vials and rectangular cuboid electrodes purchased from IKA. NMR spectroscopic data was collected on Varian 400 MHz and Bruker 500 MHz spectrometers at ambient temperature. The chemical shifts are reported in ppm (referenced to solvent peaks). Mass spectra were recorded on Thermo QExactive mass spectrometer in ESI ionization mode with TOF mass analyzer. IR spectra were recorded on Shimadzu FT-IR spectrometer equipped with an ATR unit.

Preparation of Starting Materials. Compounds **1i** and **3f** are commercially available. Compounds **1a-b**,[5k] **1c**,[11] **1e**,[5k] **1g**,[5b] **1k**,[12] **1l**,[5f] **1m**,[5g] **3a**,[4c] **3d**,[5j] **3g**,[13] and **3h-j**[5j] were prepared according to published procedures. The preparation of compounds **1d**, **1f**, **1h**, **1j**, **3b-c**, and **3e** is described in the Supporting Information.

Electrochemical Spirolactonization and Spiroetherification of Arenols; General Procedure A (Standard Conditions). A 10-mL glass vial was charged with substrate (0.30 mmol) and *n*-Bu_4NPF_6 (1.50 mmol, 5 equiv.). Anhydrous $MeNO_2$ (7.5 mL) was added and the vial was closed with a cap fitted with a graphite anode and a platinum (coated on copper) cathode. The electrolysis was carried out at a constant current of 3.7 mA, with stirring at room temperature, until 4.0 F/mol was passed. The solvent was removed under reduced pressure and the product was purified by column chromatography.

Electrochemical Spiroetherification of 1-Napthol Derivatives; General Procedure B (Modified Conditions). A 10-mL glass vial was charged with substrate (0.30 mmoland *n*-Bu_4NPF_6 (1.50 mmol, 5 equiv.). Anhydrous MeCN (7.5 mL) was added and the vial was closed with a cap fitted with a BDD anode and a platinum (coated on copper) cathode. The electrolysis was carried out at a constant current of 3.7 mA, with stirring at room temperature, until 4.0 F/mol was passed. The solvent was removed under reduced pressure and the product was purified by column chromatography.

2'H,3H-Spiro[furan-2,1'-naphthalene]-2',5(4H)-dione (2a). Prepared from 3-(2-hydroxynaphthalen-1-yl)propanoic acid (**1a**)[5k] according to General Procedure A. After purification by column chromatography (silica; hexane-EtOAc = 1:2), the product was obtained as a white solid (57 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 10.0 Hz, 1H), 7.48 − 7.45 (m, 2H), 7.39 (t, *J* = 5.0 Hz, 1H), 7.35 (d, *J* = 10.0 Hz, 1H), 6.17 (d, *J* = 10.0 Hz, 1H), 2.86 − 2.82 (m, 1H), 2.68 − 2.61 (m, 2H), 2.18 − 2.11 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 197.5, 176.4, 146, 140.6, 131.0, 129.7, 129.2, 129.1, 125.7, 122.5, 85.8, 35.8, 26.6. The characterization data is consistent with that reported previously.[5k]

6'-Bromo-2'H,3H-spiro[furan-2,1'-naphthalene]-2',5(4H)- dione (2b). Prepared from 3-(6-bromo-2-hydroxynaphthalen-1-yl)propanoic acid (**1b**)[5k] according to General Procedure A. After purification by column chromatography (silica; hexane-EtOAc = 1:2), the product was

obtained as a white solid (80 mg, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 10.0, 1.5 Hz, 1H), 7.51 (s, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.40 (d, *J* = 10.0 Hz, 1H), 6.22 (d, *J* = 10.0 Hz, 1H), 2.87 − 2.80 (m, 1H), 2.67 − 2.62 (m, 2H), 2.15 − 2.08 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 197.7, 176.0, 144.3, 139.3, 133.7, 132.3, 131.0, 127.5, 123.8, 123.2, 85.4, 35.6, 26.5. The characterization data is consistent with that reported previously.[5k]

7'-Bromo-2'H,3H-spiro[furan-2,1'-naphthalene]-2',5(4H)-dione (2c). Prepared from 3-(7-bromo-2-hydroxynaphthalen-1-yl)propanoic acid (**1c**)[11] according to General Procedure A. After purification by column chromatography (silica; hexane-EtOAc = 1:2), the product was obtained as a white solid (74 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 1.9 Hz, 1H), 7.54 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.43 (d, *J* = 10.0 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 1H), 6.19 (d, *J* = 10.0 Hz, 1H), 2.87 − 2.79 (m, 1H), 2.68 − 2.63 (m, 2H), 2.18 − 2.11 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 196.5, 175.9, 144.8, 142.3, 132.4, 130.9, 129.1, 128.0, 125.8, 122.8, 85.1, 35.7, 26.4. The characterization data is consistent with that reported previously.[11]

7'-Phenyl -2'H,3H-spiro[furan-2,1'-naphthalene]-2',5(4H)-dione (2d). Prepared from 3-(7-phenyl-2-hydroxynaphthalen-1-yl)propanoic acid (**1d**)[14] according to General Procedure A. After purification by column chromatography (silica; hexane-EtOAc = 1:2), the product was obtained as a white solid (49 mg, 57%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 1.6 Hz, 1H), 7.63 − 7.61 (m, 3H), 7.52 (d, *J* = 10.0 Hz, 1H), 7.49 − 7.46 (m, 2H), 7.44 − 7.41 (m, 2H), 6.19 (d, *J* = 10.0 Hz, 1H), 2.91 − 2.83 (m, 1H), 2.73 − 2.64 (m, 2H), 2.24 − 2.17 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 197.4, 176.4, 145.6, 144.0, 141.2, 139.3, 130.2, 129.0, 128.4, 128.0, 127.6, 127.1, 124.5, 122.3, 85.9, 36.0, 26.6. FT-IR (ATR): 1780, 1772, 1677, 1675, 1606, 1222, 1167, 1062, 846, 755 cm^{-1}. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{15}O_3$ 291.1017; Found 291.1015.

7'-Methoxy-2'H,3H-spiro[furan-2,1'-naphthalene]-2',5(4H)-dione (2e). Prepared from 3-(2-hydroxy-7-methoxynaphthalen-1-yl)propanoic acid (**1e**)[5k] according to General Procedure

A. After purification by column chromatography (silica; hexane-EtOAc = 1:2), the product was obtained as a white solid (31 mg, 43%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, *J* = 10.0 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.78 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.04 (d, *J* = 10.0 Hz, 1H), 3.87 (s, 3H), 2.88 − 2.80 (m, 1H), 2.68 − 2.60 (m, 2H), 2.16 − 2.09 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 197.6, 176.6, 182.3, 146.1, 143.2, 131.7, 122.3, 120.0, 114.6, 111.7, 86.1, 55.9, 36.3, 26.7. The characterization data is consistent with that reported previously.[5k]

4',5'-dihydro-2H-spiro[naphthalene-1,2'-pyran]-2,6'(3'H)-dione (2f). Prepared from 4-(2-hydroxynaphthalen-1-yl)-butyric acid (**1f**)[14] according to General Procedure A. After purification by column chromatography (silica; hexane-EtOAc = 1:0→3:2), the product was obtained as a viscous colorless oil (39 mg, 57%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.8, 1.2 Hz, 1H), 7.47 – 7.31 (m, 4H), 6.12 (d, *J* = 9.9 Hz, 1H), 2.82 – 2.77 (m, 1H), 2.58 – 2.51 (m, 1H), 2.17 – 2.13 (m, 1H), 1.93 – 1.75 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 198.8, 170.8, 145.7, 142.0, 131.1, 129.9, 129.0, 128.8, 126.4, 122.7, 87.5, 34.6, 28.9, 16.5. FT-IR (ATR): 1735, 1669, 1221, 1211, 1192, 1055, 818, 758 cm^{-1}. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{13}O_3$ 229.0859; Found 229.0857.

1'H,3H-Spiro[furan-2,2'-naphthalene]-1',5(4H)-dione (2g). Prepared from 3-(1-hydroxynaphthalen-2-yl)propanoic acid (**1g**)[5b] according to General Procedure A. After purification by column chromatography (silica; hexane-EtOAc = 3:1), the product was obtained as a white solid (15 mg, 24%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01(d, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 10.0 Hz, 1H), 6.20 (d, *J* = 10.0 Hz, 1H), 2.95 − 2.87 (m, 1H), 2.62 − 2.56 (m, 1H), 2.45 − 2.40 (m, 1H), 2.22 − 2.15 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 196.7, 176.7, 137.0, 135.9, 132.5, 129.2, 128.1, 128.0, 127.7, 127.6, 83.6, 31.5, 26.7. The characterization data is consistent with that reported previously.[5b]

7,9-Di-tert-butyl-1-oxaspiro[4.5]deca-7,9-diene-2,6-dione (2l). Prepared from 3-(3,5-di-*tert*-butyl-2-hydroxyphenyl)propanoic acid (**1l**)[5f] according to General Procedure A. After purification by column chromatography (silica; hexane-EtOAc = 3:1), the product was obtained as a yellow solid (81 mg, 98%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.89 (d, *J* = 2.4 Hz, 1H), 5.98 (d, *J* = 2.4 Hz, 1H), 2.80 − 2.72 (m, 1H), 2.53 − 2.47 (m, 1H), 2.35 − 2.30 (m, 1H), 2.05 − 1.98 (m, 1 H), 1.23 (s, 9H), 1.14 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 199.0, 176.6, 143.8, 142.8, 135.8, 128.2, 84.5, 34.5, 34.5, 30.2, 29.0 (3C), 28.4 (3C), 26.1. The characterization data is consistent with that reported previously.[5f]

7-Isopropyl-10-methyl-1,4-dioxaspiro[4.5]deca-7,9-diene-2,6-dione (2m). Prepared from 2-(2-hydroxy-3-isopropyl-6-methylphenoxy)acetic acid (**1m**)[5g] according to General Procedure A. After purification by column chromatography (silica; hexane-EtOAc = 1:0→4:1), the product was obtained as a yellow oil (34 mg, 51%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.65 (d, *J* = 6.5 Hz, 1H), 6.17 (dd, *J* = 6.5, 1.8 Hz, 1H), 4.50 (q, *J* = 14.3 Hz, 2H), 2.83 (hept, *J* = 6.9 Hz, 1H), 1.93 (d, *J* = 1.7 Hz, 3H), 1.07 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 194.7, 171.5, 140.6, 140.2, 134.9, 125.7, 98.1, 63.0, 26.3, 21.6, 21.6, 16.2. The characterization data is consistent with that reported previously.[5g]

4,5-Dihydro-2'H,3H-spiro[furan-2,1'-naphthalen]-2'-one (4a). Prepared from 1-(3-hydroxypropyl)naphthalen-2-ol (**3a**)[4c] according to General Procedure A. After purification by column chromatography (silica; hexane-EtOAc = 4:1), the product was obtained as a yellow oil (58 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8 Hz, 1H), 7.39 − 7.34 (m, 2H), 7.30 − 7.25 (m, 2H), 6.09 (d, *J* = 10 Hz, 1H), 4.44 − 4.35 (m, 2H), 2.46 − 2.41 (m, 1H), 2.20-2.03 (m, 2H), 1.90 − 1.84 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 209.9, 145.6, 144.7, 130.3, 129.8, 129.2, 127.9, 125.6, 124.2, 88.0, 72.1, 40.8, 24.7. The characterization data is consistent with that reported previously.[4c]

7'-Phenyl -4,5-Dihydro-2'H,3H-spiro[furan-2,1'-naphthalen]-2'-one (4b). Prepared from 7-phenyl-2-(3-hydroxypropyl)naphthalene-1-ol (**3b**)[14] according to General Procedure A. After purification by column chromatography (silica; hexane-EtOAc = 4:1), the product was obtained as a yellow oil (72 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 1.8 Hz, 1H), 7.63 − 7.61 (m, 2H), 7.51 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.40 − 7.36 (m, 2H), 7.34 (d, *J* = 7.8 Hz, 1H), 6.11 (d, *J* = 9.8 Hz, 1H), 4.47 − 4.39 (m, 2H), 2.50 − 2.45 (m, 1H), 2.22 − 2.13 (m, 1H), 2.12 − 2.05 (m, 1H), 1.95 − 1.89 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 203.6, 146.0, 144.1, 143.0, 140.2, 129.6, 128.9, 128.7, 127.9, 127.1, 126.4, 124.2, 123.8, 88.0, 71.9, 40.7, 24.5. FT-IR (ATR): 2899, 1674, 1669, 1604, 1390, 1063, 1037, 965, 848, 764 cm^{-1}. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{17}O_2$ 277.1220; Found 277.1224.

3',4',5',6'-tetrahydro-2H-spiro[naphthalene-1,2'-pyran]-2-one (4c). Prepared from 1-(3-hydroxypropyl)naphthalen-2-ol (**3c**)[14] according to General Procedure A. After purification by column chromatography (silica; hexane-EtOAc = 1:0→6:1), the product was obtained as a viscous yellow oil (17 mg, 26%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.73 (d, *J* = 7.8 Hz, 1H), 7.40 (td, *J* = 7.6, 1.5 Hz, 1H), 7.28 – 7.21 (m, 3H), 5.97 (d, *J* = 9.9 Hz, 1H), 4.95 – 4.89 (m, 1H), 4.09 – 4.05 (m, 1H), 2.15 – 2.12 (m, 1H), 1.73 – 1.57 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 206.3, 146.4, 143.4, 130.6, 129.4, 129.0, 127.8, 126.1, 124.8, 80.0, 56.8, 37.2, 25.7, 18.3. FT-IR (ATR): 2954, 1675, 1614, 1467, 1287, 1229, 1176, 1082, 908, 825, 752 cm^{-1}. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{15}O_2$ 215.1067; Found 215.1065.

4,5-Dihydro-1'H,3H-spiro[furan-2,2'-naphthalen]-1'-one (4d). Prepared from 2-(3-hydroxypropyl)naphthalen-1-ol (**3d**)[5j] according to General Procedure B. After purification by column chromatography (silica; hexane-EtOAc = 1:1), the product was obtained as a colorless oil (45 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 6.51 (d, *J* = 10.0 Hz, 1H), 6.17 (d, *J* = 10.0 Hz, 1H), 4.34 − 4.30 (m, 1H), 4.18 − 4.13 (m, 1H), 2.27 − 2.17 (m, 2H),

2.07 − 2.02 (m, 1H), 1.93 − 1.89 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 202.0, 137.6, 136.7, 134.8, 129.1, 128.2, 127.4, 127.3, 125.8, 84.3, 70.8, 36.7, 25.4. The characterization data is consistent with that reported previously.[5j]

7,9-Di-tert-butyl-1-oxaspiro[4.5]deca-7,9-diene-6-one (4g). Prepared from 2,4-di-*tert*-butyl-6-(3-hydroxypropyl)phenol (**3g**)[13] according to General Procedure A. After purification by column chromatography (silica; hexane-EtOAc = 4:1), the product was obtained as a yellow oil (61 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.78 (d, *J* = 2.4 Hz, 1H), 5.95 (d, *J* = 2.4 Hz, 1H), 4.25 − 2.21 (m, 1H), 4.12 − 4.07 (m, 1H), 2.16 − 2.06 (m, 2H), 1.97 − 1.92 (m, 1 H), 1.76 − 1.71 (m, 1H), 1.21 (s, 9H), 1.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 204.8, 143.3, 141.4, 134.7, 132.0, 86.7, 70.5, 35.7, 34.2, 34.1, 29.2, 28.6, 24.7. The characterization data is consistent with that reported previously.[15]

4'-Chloro-4,5-dihydro-1'H,3H-spiro[furan-2,2'-naphthalen]-1'-one (4h). Prepared from 4-chloro-2-(3-hydroxypropyl)-naphthalen-1-ol (**3h**)[5j] according to General Procedure B. After purification by column chromatography (silica; hexane-EtOAc = 4:1), the product was obtained as a colorless oil (53 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.71 − 7.64 (m, 2H), 7.44 (td, *J* = 7.5, 1.4 Hz, 1H), 6.35 (s, 1H), 4.29 − 4.25 (m, 1H), 4.16 − 4.12 (m, 1H), 2.28 − 2.20 (m, 2H), 2.08 − 2.04 (m, 1H), 1.99 − 1.95 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 199.5, 134.9, 134.8, 133.2, 129.2, 129.1, 128.8, 127.4, 125.2, 84.5, 70.6, 36.5, 25.3. The characterization data is consistent with that reported previously.[5j]

4'-Bromo-4,5-dihydro-1'H,3H-spiro[furan-2,2'-naphthalen]-1'-one (4i). Prepared from 4-bromo-2-(3-hydroxypropyl)naphthalene-1-ol (**3i**)[5j] according to General Procedure B. After purification by column chromatography (silica; hexane-EtOAc = 4:1), the product was obtained as a colorless oil (52 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.8 Hz, 1H), 7.69 − 7.64 (m, 2H), 7.44 − 7.41 (m, 1H), 6.62 (s, 1H), 4.30 − 4.26 (m, 1H), 4.17 − 4.13 (m, 1H), 2.29 − 2.17 (m, 2H), 2.11 − 1.94 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 199.8,

137.9, 135.8, 135.1, 129.5, 129.1, 128.3, 127.5, 119.9, 85.7, 70.8, 36.6, 25.5. The characterization data is consistent with that reported previously.[5j]

4'-(3,5-Bis(trifluoromethyl)phenyl)-4,5-dihydro-1'H,3H-spiro[furan-2,2'-naphthalen]-1'-one (4j). Prepared from 4-(3,5-bis(trifluoromethyl)phenyl)-2-(3-hydroxypropyl)naphthalen-1-ol (**3j**)[5j] according to General Procedure B. After purification by column chromatography (silica; hexane-EtOAc = 4:1), the product was obtained as a colorless oil (69 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.8 Hz, 1H), 7.93 (s, 1H), 7.82 (s, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.19 (s, 1H), 4.36 − 4.32 (m, 1H), 4.20 − 4.16 (m, 1H), 2.38 − 2.24 (m, 2H), 2.13 − 2.01 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 200.6, 140.7, 137.3, 136.3, 135.3, 134.7, 132.2 (q, *J* = 34 Hz), 129.1 (br), 128.9, 128.1, 125.8, 123.2 (q, *J* = 274 Hz), 122.1, 122.0 − 121.9 (m), 84.2, 70.7, 36.6, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.8. The characterization data is consistent with that reported previously.[5j]

Supporting Information

The Supporting Information file contains: preparation of starting materials and NMR spectra of products.

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Notes

The authors declare no competing financial interest.

Acknowledgements

We acknowledge financial support from the National Science Centre, Poland (grant no. 2020/37/B/ST4/01162). Generous access to an NMR spectrometer was granted by the Faculty of Physics of the University of Warsaw.

References

1. (a) Wipf, P.; Kim, Y.; Fritch, P. C. Total Synthesis and Structure Assignment of the Antitumor Antibiotic Aranorosin. *J. Org. Chem.* **1993**, *58*, 7195-7203. (b) Voss, F.; Schunk, S.; Steinhagen, H. In *Privileged Scaffolds in Medicinal Chemistry: Design, Synthesis, Evaluation*, 1st ed.; Bräse, S., Ed. The Royal Society of Chemistry: Cambridge, UK, 2016; pp 450-453. (c) Quintavalla, A. Spirolactones: Recent Advances in Natural Products, Bioactive Compounds and Synthetic Strategies. *Curr. Med. Chem.* **2018**, *25*, 917-962. (d) Thorat, S. S.; Kontham, R. Recent Advances in the Synthesis of Oxaspirolactones and Their Application in the Total Synthesis of Related Natural Products. *Org. Biomol. Chem.* **2019**, *17*, 7270-7292.
2. (a) Quideau, S.; Pouységu, L.; Deffieux, D. Oxidative Dearomatization of Phenols: Why, How and What For? *Synlett* **2008**, 467-495. (b) Roche, S. P.; Porco, J. A. Dearomatization Strategies in the Synthesis of Complex Natural Products. *Angew. Chem. Int. Ed.* **2011**, *50*, 4068-4093. (c) Bartoli, A.; Rodier, F.; Commeiras, L.; Parrain,

J.-L.; Chouraqui, G. Construction of Spirolactones with Concomitant Formation of the Fused Quaternary Centre – Application to the Synthesis of Natural Products. *Nat. Prod. Rep.* **2011**, *28*, 763-782. (d) Zhuo, C.-X.; Zhang, W.; You, S.-L. Catalytic Asymmetric Dearomatization Reactions. *Angew. Chem. Int. Ed.* **2012**, *51*, 12662-12686. (e) Ding, Q.; Ye, Y.; Fan, R. Recent Advances in Phenol Dearomatization and Its Application in Complex Syntheses. *Synthesis* **2013**, *45*, 1-16. (f) Sun, W.; Li, G.; Hong, L.; Wang, R. Asymmetric Dearomatization of Phenols. *Org. Biomol. Chem.* **2016**, *14*, 2164-2176. (g) Wu, W.-T.; Zhang, L.; You, S.-L. Catalytic Asymmetric Dearomatization (CADA) Reactions of Phenol and Aniline Derivatives. *Chem. Soc. Rev.* **2016**, *45*, 1570-1580. (h) Pantaine, L.; Moreau, X.; Coeffard, V.; Greck, C. The Impact of Asymmetric Organocatalysis in Dearomatization and Aromatization of Carbocycles: Increasing Molecular Complexity and Diversity. *Tetrahedron Lett.* **2016**, *57*, 2567-2574.

3. Pouységu, L.; Deffieux, D.; Quideau, S. Hypervalent Iodine-Mediated Phenol Dearomatization in Natural Product Synthesis. *Tetrahedron* **2010**, *66*, 2235-2261.
4. (a) Kotoku, N.; Tsujita, H.; Hiramatsu, A.; Mori, C.; Koizumi, N.; Kobayashi, M. Efficient Total Synthesis of Bastadin 6, an Anti-Angiogenic Brominated Tyrosine-Derived Metabolite from Marine Sponge. *Tetrahedron* **2005**, *61*, 7211-7218. (b) Oguma, T.; Katsuki, T. Iron-Catalysed Asymmetric Tandem Spiro-Cyclization Using Dioxygen in Air as the Hydrogen Acceptor. *Chem. Commun.* **2014**, *50*, 5053-5056. (c) Sarkar, D.; Ghosh, M. K.; Rout, N. Phenyl Trimethyl Ammonium Tribromide Mediated Robust One-Pot Synthesis of Spiro-oxacycles – An Economic Route – Stereoselective Synthesis of Oxaspirohexacyclodieneones. *Org. Biomol. Chem.* **2016**, *14*, 7883-7898. (d) Sarkar, D.; Rout, N. Ruthenium(VIII)-Catalyzed *ipso*-Dearomative Spiro-Etherification and Spiro-Amidation of Phenols. *Org. Lett.* **2019**, *21*, 4132-4136. (e) Sarkar, D.; Kuila, P.; Sood, D. Controlling Stereoselectivity in Tribromide Mediated

Oxidative Dearomatisations – Synthesis of Selective Spirofurano-naphthalones. *Eur. J. Org. Chem.* **2019**, *2019*, 5894-5904. (f) Sahoo, S. R.; Sarkar, D. Stereoselective Synthesis of *para*-Quinone Monoketals through Tri-bromide (TBr) Mediated Oxidative Dearomatization of Phenols. *Tetrahedron Lett.* **2020**, *61*, 151646.

5. (a) Dohi, T.; Maruyama, A.; Takenaga, N.; Senami, K.; Minamitsuji, Y.; Fujioka, H.; Caemmerer, S. B.; Kita, Y. A Chiral Hypervalent Iodine(III) Reagent for Enantioselective Dearomatization of Phenols. *Angew. Chem. Int. Ed.* **2008**, *47*, 3787-3790. (b) Uyanik, M.; Yasui, T.; Ishihara, K. Enantioselective Kita Oxidative Spirolactonization Catalyzed by In Situ Generated Chiral Hypervalent Iodine(III) Species. *Angew. Chem. Int. Ed.* **2010**, *49*, 2175-2177. (c) Uyanik, M.; Yasui, T.; Ishihara, K. Chiral Hypervalent Iodine-Catalyzed Enantioselective Oxidative Kita Spirolactonization of 1-Naphthol Derivatives and One-Pot Diastereoselective Oxidation to Epoxyspirolactones. *Tetrahedron* **2010**, *66*, 5841-5851. (d) Dohi, T.; Takenaga, N.; Nakae, T.; Toyoda, Y.; Yamasaki, M.; Shiro, M.; Fujioka, H.; Maruyama, A.; Kita, Y. Asymmetric Dearomatizing Spirolactonization of Naphthols Catalyzed by Spirobiindane-Based Chiral Hypervalent Iodine Species. *J. Am. Chem. Soc.* **2013**, *135*, 4558-4566. (e) Volp, K. A.; Harned, A. M. Chiral Aryl Iodide Catalysts for the Enantioselective Synthesis of *para*-Quinols. *Chem. Commun.* **2013**, *49*, 3001-3003. (f) Uyanik, M.; Yasui, T.; Ishihara, K. Hydrogen Bonding and Alcohol Effects in Asymmetric Hypervalent Iodine Catalysis: Enantioselective Oxidative Dearomatization of Phenols. *Angew. Chem. Int. Ed.* **2013**, *52*, 9215-9218. (g) Uyanik, M.; Sasakura, N.; Mizuno, M.; Ishihara, K. Enantioselective Synthesis of Masked Benzoquinones Using Designer Chiral Hypervalent Organoiodine(III) Catalysis. *ACS Catal.* **2017**, *7*, 872-876. (h) Dohi, T.; Sasa, H.; Miyazaki, K.; Fujitake, M.; Takenaga, N.; Kita, Y. Chiral Atropisomeric 8,8′-Diiodobinaphthalene for Asymmetric Dearomatizing

Spirolactonizations in Hypervalent Iodine Oxidations. *J. Org. Chem.* **2017**, *82*, 11954-11960. (i) Ogasawara, M.; Sasa, H.; Hu, H.; Amano, Y.; Nakajima, H.; Takenaga, N.; Nakajima, K.; Kita, Y.; Takahashi, T.; Dohi, T. Atropisomeric Chiral Diiododienes *(Z,Z)*-2,3-Di(1-iodoalkylidene)tetralins: Synthesis, Enantiomeric Resolution, and Application in Asymmetric Catalysis. *Org. Lett.* **2017**, *19*, 4102-4105. (j) Jain, N.; Xu, S.; Ciufolini, M. A. Asymmetric Oxidative Cycloetherification of Naphtholic Alcohols. *Chem. Eur. J.* **2017**, *23*, 4542-4546. (k) Uyanik, M.; Yasui, T.; Ishihara, K. Chiral Hypervalent Organoiodine-Catalyzed Enantioselective Oxidative Spirolactonization of Naphthol Derivatives. *J. Org. Chem.* **2017**, *82*, 11946-11953.

6. (a) Horn, E. J.; Rosen, B. R.; Baran, P. S. Synthetic Organic Electrochemistry: An Enabling and Innately Sustainable Method. *ACS Cent. Sci.* **2016**, *2*, 302-308. (b) Yan, M.; Kawamata, Y.; Baran, P. S. Synthetic Organic Electrochemical Methods Since 2000: On the Verge of a Renaissance. *Chem. Rev.* **2017**, *117*, 13230-13319. (c) Yoshida, J.-i.; Shimizu, A.; Hayashi, R. Electrogenerated Cationic Reactive Intermediates: The Pool Method and Further Advances. *Chem. Rev.* **2018**, *118*, 4702-4730. (d) Jiang, Y.; Xu, K.; Zeng, C. Use of Electrochemistry in the Synthesis of Heterocyclic Structures. *Chem. Rev.* **2018**, *118*, 4485-4540. (e) Shatskiy, A.; Lundberg, H.; Kärkäs, M. D. Organic Electrosynthesis: Applications in Complex Molecule Synthesis. *ChemElectroChem* **2019**, *6*, 4067-4092. (f) Meyer, T. H.; Choi, I.; Tian, C.; Ackermann, L. Powering the Future: How Can Electrochemistry Make a Difference in Organic Synthesis? *Chem* **2020**, *6*, 2484-2496. (g) Pollok, D.; Waldvogel, S. R. Electro-organic Synthesis – A 21st Century Technique. *Chem. Sci.* **2020**, *11*, 12386-12400. (h) Zhu, C.; Ang, N. W. J.; Meyer, T. H.; Qiu, Y.; Ackermann, L. Organic Electrochemistry: Molecular Syntheses with Potential. *ACS Cent. Sci.* **2021**, *7*, 415-431.

7. (a) Yamamura, S.; Nishiyama, S. Anodic Oxidation of Phenols Towards the Synthesis of Bioactive Natural Products. *Synlett* **2002**, 533-543. (b) Quideau, S.; Pouysegu, L.; Deffieux, D. Chemical and Electrochemical Oxidative Activation of Arenol Derivatives for Carbon-Carbon Bond Formation. *Curr. Org. Chem.* **2004**, *8*, 113-148. (c) Yamamura, S., Oxidation of Phenols. In *PATAI'S Chemistry of Functional Groups*, Rappoport, Z., Ed. John Wiley & Sons, Ltd.: 2009; pp 1-40. (d) Waldvogel, S. R.; Lips, S.; Selt, M.; Riehl, B.; Kampf, C. J. Electrochemical Arylation Reaction. *Chem. Rev.* **2018**, *118*, 6706-6765. (e) Röckl, J. L.; Pollok, D.; Franke, R.; Waldvogel, S. R. A Decade of Electrochemical Dehydrogenative C,C-Coupling of Aryls. *Acc. Chem. Res.* **2020**, *53*, 45-61. (f) Medici, F.; Resta, S.; Puglisi, A.; Rossi, S.; Raimondi, L.; Benaglia, M. Electrochemical Organic Synthesis of Electron-Rich Biaryl Scaffolds: An Update. *Molecules* **2021**, *26*. (g) Fatykhov, R.; Khalymbadzha, I.; Chupakhin, O. Cross-Dehydrogenative Coupling Reactions between Phenols and Hetarenes: Modern Trends in Cross-Coupling Chemistry of Phenols. *Adv. Synth. Catal.* **2022**, *364*, 1052-1068.

8. (a) Noda, H.; Niwa, M.; Yamamura, S. Biomimetic Oxidation of Methyl 3,5-Dibromo-4-Hydroxyphenylpyruvate Oxime and Related Phenols. *Tetrahedron Lett.* **1981**, *22*, 3247-3248. (b) Hutinec, A.; Ziogas, A.; El-Mobayed, M.; Rieker, A. Spirolactones of Tyrosine: Synthesis and Reaction with Nucleophiles. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2201-2208. (c) Mori, K.; Takahashi, M.; Yamamura, S.; Nishiyama, S. Anodic Oxidation of Monohalogenated Phenols. *Tetrahedron* **2001**, *57*, 5527-5532.

9. For examples of few existing related electrochemical oxidative dearomatizations of phenols with an intermolecular addition of nucleophiles, see: (a) Nilsson, A.; Ronlán, A.; Parker, V. D. A Novel Synthesis of 4-Chloro-4-methylcyclohexa-2,5-dienone and 4,4-Dimethoxycyclohexa-2,5-dienone. *Tetrahedron Lett.* **1975**, *16*, 1107-1110. (b)

Nilsson, A.; Palmquist, U.; Pettersson, T.; Ronlán, A. Anodic Oxidation of Phenolic Compounds. Part 5. Anodic Methoxylation of Phenols. A Simple Synthesis of Quinones, Quinone Acetals, and 4-Methyl-α-methoxycyclohexa-2,5-dienones. *J. Chem. Soc., Perkin Trans. 1* **1978**, 696-707. (c) Shizuri, Y.; Nakamura, K.; Yamamura, S.; Ohba, S.; Yamashita, H.; Saito, Y. Total Syntheses of Isodihydrofutoquinol A, Futoquinol, and Isofutoquinol A and B. *Tetrahedron Lett.* **1986**, *27*, 727-730. (d) Yamamura, S.; Shizuri, Y.; Shigemori, H.; Okuno, Y.; Ohkubo, M. Natural Products Syntheses Using Anodic Oxidation of Phenols as a Key Step. *Tetrahedron* **1991**, *47*, 635-644. (e) Rieker, A.; Beisswenger, R.; Regier, K. Syntheses via Anodically Produced Phenoxenium Ions. Applications in the Field of Peptides and Carbohydrates. *Tetrahedron* **1991**, *47*, 645-654. (f) Quideau, S.; Pouysegu, L.; Deffieux, D.; Ozanne, A.; Gagnepain, J.; Fabre, I.; Oxoby, M. Iodane-Mediated and Electrochemical Oxidative Transformations of 2-Methoxy- and 2-Methylphenols. *ARKIVOC* **2003**, *vi*, 106-119. (g) Deffieux, D.; Fabre, I.; Titz, A.; Léger, J.-M.; Quideau, S. Electrochemical Synthesis of Dimerizing and Nondimerizing Orthoquinone Monoketals. *J. Org. Chem.* **2004**, *69*, 8731-8738.

10. (a) Deffieux, D.; Fabre, I.; Courseille, C.; Quideau, S. Electrochemically-Induced Spirolactonization of α-(Methoxyphenoxy)alkanoic Acids into Quinone Ketals. *J. Org. Chem.* **2002**, *67*, 4458-4465. (b) Zhang, C.; Bu, F.; Zeng, C.; Wang, D.; Lu, L.; Zhang, H.; Lei, A. Electrochemical Oxidation Dearomatization of Anisol Derivatives toward Spiropyrrolidines and Spirolactones. *CCS Chem.* **2022**, *4*, 1199-1207.
11. Ishihara, K.; Uyanik, M.; Takeshi, Y. Iodoarene Derivative, Method for Producing Optically Active Spirolactone Compound Using Same, and Method for Producing Optically Active Cyclization Adduct. EP 2684863 A1, 2014.

12. Drutu, I.; Njardarson, J. T.; Wood, J. L. Reactive Dienes: Intramolecular Aromatic Oxidation of 3-(2-Hydroxyphenyl)-propionic Acids. *Org. Lett.* **2002**, *4*, 493-496.

13. Oleynik, A. S.; Kuprina, T. S.; Pevneva, N. Y.; Markov, A. F.; Kandalintseva, N. V.; Prosenko, A. E.; Grigor'ev, I. A. Synthesis and Antioxidant Properties of Sodium *S*-[3-(Hydroxyaryl)propyl] Thiosulfates and [3-(Hydroxyaryl)propane]-1-sulfonates. *Russ. Chem. Bull.* **2007**, *56*, 1135-1143.

14. See the Supporting Information for details.

15. Uyanik, M.; Sahara, N.; Katade, O.; Ishihara, K. Chemoselective Oxidative Spiroetherification and Spiroamination of Arenols Using I^+/Oxone Catalysis. *Org. Lett.* **2020**, *22*, 560-564.