JOC The Journal of Organic Chemistry

Article

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Understanding the Reactivity of Enol Ether Radical Cations: Investigation of Anodic Four-Membered Carbon Ring Formation

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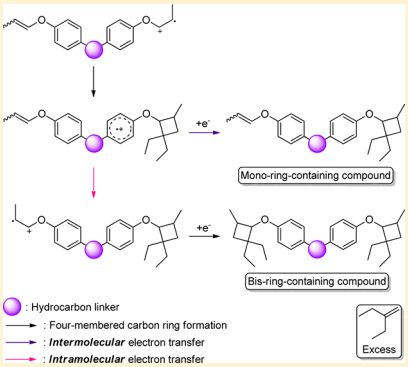
Supporting Information

ABSTRACT: The reactivity of enol ether radical cations was investigated in anodic four-membered carbon ring formations, advancing the mechanistic understanding of these reactions. The mono-ring-containing aromatic cations were reduced through inter- or intramolecular electron transfer to give mono- or bis-ring-containing compounds, respectively. Small structural changes in the hydrocarbon linkers tethering two aromatic rings exerted a powerful effect on the efficiency of such electron transfer events.



INTRODUCTION

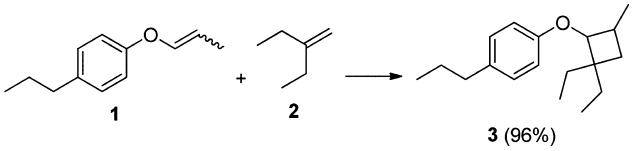
In the field of organic chemistry, a remarkable array of powerful reactions and transformations has been added to the growing toolbox. The modern synthetic landscape has been dominated largely by the use of conventional intermediates, including carbanions, carbocations, radicals, and carbenes, and the chemoselectivity of such reactive species is well established. Electron-transfer-induced reactions that involve transient radical ions, typically generated using photochemical approaches, one-electron-redox reagents, and electrochemical processes, are also potential candidates for the design of sophisticated new synthetic sequences based on the distinctive reactivity unique to them.[1] A mechanistic understanding of the behavior of such radical ions would be a great aid for their installation into the framework of existing organic synthesis.

Enol ether radical cations can be produced readily via either oxidative or nonoxidative reactions and constitute one of the simplest members of the radical cation family. The nonoxidative generation of enol ether radical cations involves heterolytic fragmentation of an α-alkoxy radical containing a β-leaving group, and such an entry to enol ether radical cations has been introduced creatively into ribose scaffolds, affording studies of electron transfer in DNA that are implicated in its degradation.[2] In addition, the nonoxidative access to enol ether radical cations has been well-combined with radical clock methods, leading to an accurate kinetic understanding.[3]

On the other hand, the oxidative generation of enol ether radical cations is an umpolung process in which the polarity of nucleophilic enol ethers is reversed such that they function as electrophilic radical cations.[4] In particular, the chemoselectivity of electrochemically generated enol ether radical cations has been investigated directly on the basis of competition study methods using alcohols and sulfonamides as trapping groups, which has provided clear-cut mechanistic insights.[5]

In this context, we have been developing four-membered carbon ring formation reactions initiated via the anodic umpolung process of enol ethers, which generate radical cations that are then trapped by several unactivated olefin nucleophiles.[6] For example, the anodic oxidation of 1-(prop-1-en-1-yloxy)-4-propylbenzene (**1**) in the presence of 3-methylenepentane (**2**) gave the four-membered carbon ring containing compound **3** (Scheme 1).[7] Our previous studies

Scheme 1. Anodic Four-Membered Carbon Ring Formation[a]

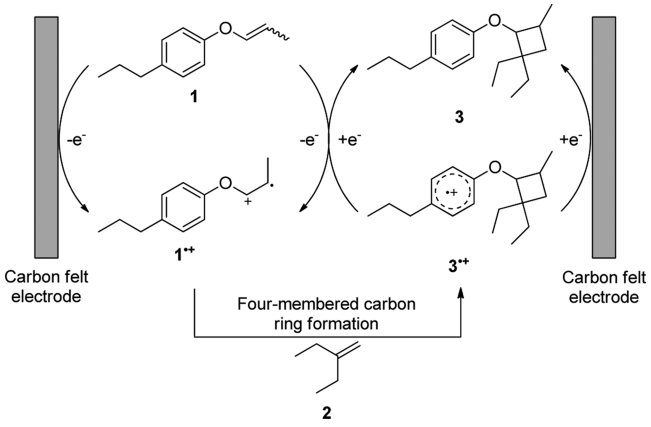


[a]Reagents and conditions: (a) $LiClO_4$, $MeNO_2$, carbon felt electrodes 1.2 V vs Ag/AgCl, room temperature.

have indicated that the aromatic radical cation ($\mathbf{3}^{\bullet+}$) constructed through intermolecular carbon−carbon bond formation between the enol ether radical cation ($\mathbf{1}^{\bullet+}$) and 3-methylenepentane (**2**) was reduced to give the ring-containing compound **3** (Scheme 2). For the aromatic radical cation ($\mathbf{3}^{\bullet+}$) to be reduced, there are two possible pathways, including the oxidation of 1-(prop-1-en-1-yloxy)-4-propylbenzene (**1**) and

Received: December 30, 2012
Published: February 26, 2013

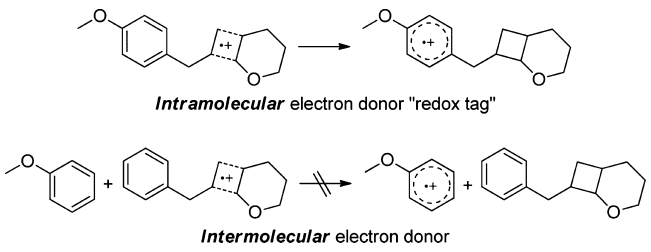
Scheme 2. Proposed Reaction Mechanism for Anodic Four-Membered Carbon Ring Formation



the electrode process. While the oxidation of 1-(prop-1-en-1-yloxy)-4-propylbenzene (**1**) can lead to the generation of the further enol ether radical cation $\mathbf{1}^{\bullet+}$ in order to drive the overall reaction cycle with a catalytic amount of electricity, the electrode process was not effective unless an anodic backward discharge took place. Because both of these reductions are intermolecular electron transfer events, a higher concentration of 1-(prop-1-en-1-yloxy)-4-propylbenzene (**1**) is effective for preferentially driving the electrocatalytic route over the electrode process; however, undesired dimerization also competes under such reaction conditions.[8]

With respect to kinetic aspects, intramolecular electron transfer generally has an advantage over intermolecular variants. Indeed, our previous studies clearly demonstrated that intramolecular electron donors completed the formation of four-membered carbon rings, while intermolecular variants did not (Scheme 3).[9] On the basis of these observations, we

Scheme 3. Comparison of the Reactivity of Intra- and Intermolecular Electron Donors for Anodic Four-Membered Carbon Ring Formation



envisioned that an intramolecular, tethered enol ether should be an efficient electron donor that could lead to the regeneration of an enol ether radical cation, affording bis four-membered carbon ring containing compounds using a catalytic amount of electricity (Scheme 4). Described herein is the further investigation of the reactivity of enol ether radical cations toward anodic four-membered carbon ring formation.

RESULTS AND DISCUSSION

The present study began with the synthesis of 1,3-bis(4-(prop-1-en-1-yloxy)phenyl)propane (**4**) as a model bis-enol ether, which was prepared via the simple addition of a second enol ether moiety at the end of the propyl group of 1-(prop-1-en-1-yloxy)-4-propylbenzene (**1**) (Scheme 5). A Grignard reaction between (4-methoxyphenyl)magnesium bromide and 1,3-dibromopropane followed by deprotection of the phenolic methyl ethers provided the corresponding bis-phenol precursor **5**, which was then allylated. Isomerization of the allyl groups gave 1,3-bis(4-(prop-1-en-1-yloxy)phenyl)propane (**4**).

The anodic oxidation of 1,3-bis(4-(prop-1-en-1-yloxy)-phenyl)propane (**4**) in the presence of 3-methylenepentane (**2**) as an unactivated olefinic nucleophile was expected to provide the mono-ring-containing compound **6** or the bis-ring-containing compound **7** (Scheme 6). In particular, the formation of the bis-ring-containing compound (**7**) should involve the transformation from the aromatic radical cation ($\mathbf{6}_a^{\bullet+}$) to the enol ether radical cation ($\mathbf{6}_e^{\bullet+}$) via intramolecular electron transfer, such that the reaction would be completed with a catalytic amount of electricity. When the reaction at 0.5 F (i.e., 0.5 F for every one enol ether) was monitored using GC-MS, however, 28% of 1,3-bis(4-(prop-1-en-1-yloxy)-phenyl)propane (**4**) was recovered, and the peak associated with the mono-ring-containing compound **6** was predominant, with only a small peak associated with the bis-ring-containing compound **7** observed (Figure S1, Supporting Information). Intramolecular four-membered carbon ring formation via the trapping of the enol ether radical cation by the additional enol ether group in the molecule was not observed, apparently because of the conformational restriction. At 1.0 F, the 1,3-bis(4-(prop-1-en-1-yloxy)phenyl)propane (**4**) was almost completely consumed, and the peak associated with the mono-ring-containing compound **6** remained the major product (Figure S1, Supporting Information). At 2.0 F, however, both 1,3-bis(4-(prop-1-en-1-yloxy)phenyl)propane (**4**) and the peak associated with the mono-ring-containing compound **6** finally disappeared, and that associated with the bis-ring-containing compound **7** was observed as the predominant product (Figure S1, Supporting Information). These results suggested that the transformation from the aromatic radical cation $\mathbf{6}_a^{\bullet+}$ to the enol ether radical cation $\mathbf{6}_e^{\bullet+}$ via intramolecular electron transfer barely took place and that the aromatic radical cation $\mathbf{6}_a^{\bullet+}$ was reduced once via intermolecular electron transfer to give the mono-ring-containing compound **6**, which then underwent further anodic oxidation, leading to construction of the bis-ring-containing compound **7**.

Although the bis-ring-containing compound **7** was selectively obtained with an excess amount of electricity, enabling the confirmation of the structural identity, the mono-ring-containing compound **6** was not readily separable. Therefore, the mono-ring-containing compound **6** was synthesized alternatively to confirm the structural identity of the compound produced in the reaction (Scheme 7). The monoallylation of bis-phenol precursor **5** followed by isomerization of the allyl group provided a monoenol ether, which was then further allylated. Subsequent anodic oxidation constructed a mono-ring-containing intermediate bearing an allyl group, which was then isomerized to give the mono-ring-containing compound **6**. The synthesized compound **6** was then coinjected with the reaction mixture obtained from the anodic oxidation of 1,3-bis(4-(prop-1-en-1-yloxy)phenyl)propane (**4**) in the presence of 3-methylenepentane (**2**), confirming the postulated structure (Figure S2, Supporting Information).

With the fully characterized four-membered carbon ring containing compounds **6** and **7** in hand, the anodic oxidation of 1,3-bis(4-(prop-1-en-1-yloxy)phenyl)propane (**4**) in the presence of 3-methylenepentane (**2**) was carefully remonitored using GC-MS (Figure 1). These results clearly illustrated that

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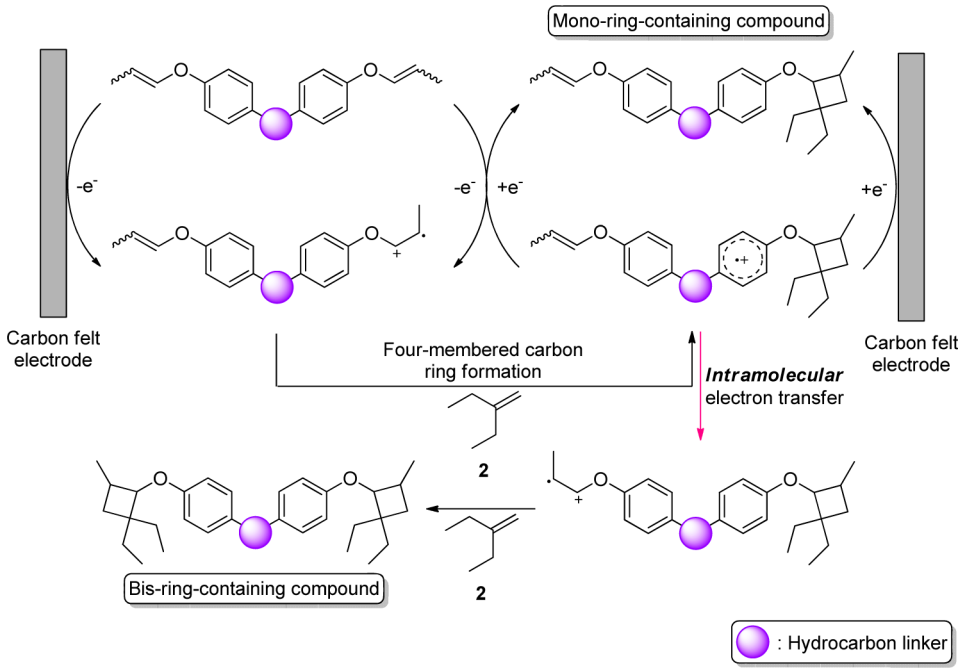
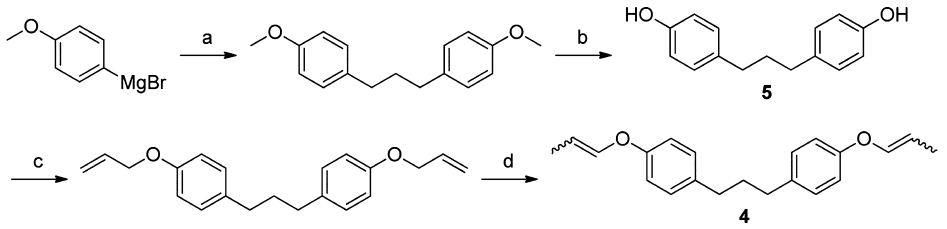
Scheme 4. General Strategy of This Study



Scheme 5. Synthesis of 1,3-Bis(4-(prop-1-en-1-yloxy)phenyl)propane (4)[a]



[a]Reagents and conditions: (a) 1,3-Dibromopropane, Li_2CuCl_4, THF, 0 °C to room temperature, 99%; (b) BBr_3, CH_2Cl_2, 0 °C to room temperature, 90%; (c) allyl bromide, K_2CO_3, DMF, 60 °C; (d) ^{t}BuOK, DMSO, room temperature.

the formation of the four-membered carbon rings took place in a stepwise manner. Thus, the mono-ring-containing compound **6** was initially accumulated in the early stages of the reaction and was then reoxidized at the anode to complete the formation of the bis-ring-containing compound **7**. Moreover, cyclic voltammograms of 1,3-bis(4-(prop-1-en-1-yloxy)phenyl)-propane (**4**) and the mono-ring-containing compound **6** were recorded, and the peak oxidation potentials were determined to be 1.22 and 1.14 V vs Ag/AgCl, respectively, clearly indicating that the reactivities toward anodic oxidation of the enol ether moieties in both 1,3-bis(4-(prop-1-en-1-yloxy)phenyl)propane (**4**) and the mono-ring-containing compound **6** were similar (Figure S3, Supporting Information). This similarity ruled out the possibility that the mono-ring-containing compound **6** was accumulated because of its low reactivity. Indeed, the anodic oxidation of the mono-ring-containing compound **6** in the presence of 3-methylenepentane (**2**) at 1.0 F also gave the bis-ring-containing compound **7** in 72% yield, and no mono-ring-containing compound **6** was recovered. Therefore, in this case, intermolecular electron transfer has some advantage over the intramolecular variant for the reduction of the aromatic radical cation $\mathbf{6}_a^{\bullet+}$.

In general, the efficiency of electron transfer events depends to a large extent on the orientation of the electron donor and the electron acceptor. Although the conformation of the aromatic radical cation ($\mathbf{6}_a^{\bullet+}$) was unclear in the reaction mixture, the contraction of the propylene linker that tethered the two aromatic rings would affect the intramolecular electron transfer significantly. For this reason, additional bis-enol ethers (**8** and **9**) were designed and synthesized from the corresponding bis-phenol precursors (Schemes 8 and 9).

The anodic oxidation of 1,2-bis(4-(prop-1-en-1-yloxy)-phenyl)ethane (**8**) in the presence of 3-methylenepentane (**2**) was then monitored using GC-MS. Although the yields of the mono- and bis-ring-containing compounds **12** and **13**, respectively, were both moderately decreased in comparison to those obtained from 1,3-bis(4-(prop-1-en-1-yloxy)phenyl)-propane (**4**), their ratios changed significantly (Figure 2). The bis-/mono-ring-containing compound values were 0.09 at 0.5 F and 0.24 at 1.0 F, respectively, when 1,3-bis(4-(prop-1-en-1-yloxy)phenyl)propane (**4**) was used and increased to 0.15 and 0.63, respectively, in the case of 1,2-bis(4-(prop-1-en-1-yloxy)phenyl)ethane (**8**). (The structural identity of the mono-ring-containing compound **12** was confirmed through its alternative synthesis (Scheme 10)). Notably, the anodic oxidation of mono-ring-containing compound **12** in the presence of 3-methylenepentane (**2**) at 1.0 F gave the bis-ring-containing compound **13** in only 4% yield, and 64% of the mono-ring-containing compound **12** was recovered (Scheme 11). Apparently, the bis-ring-containing compound **13** was

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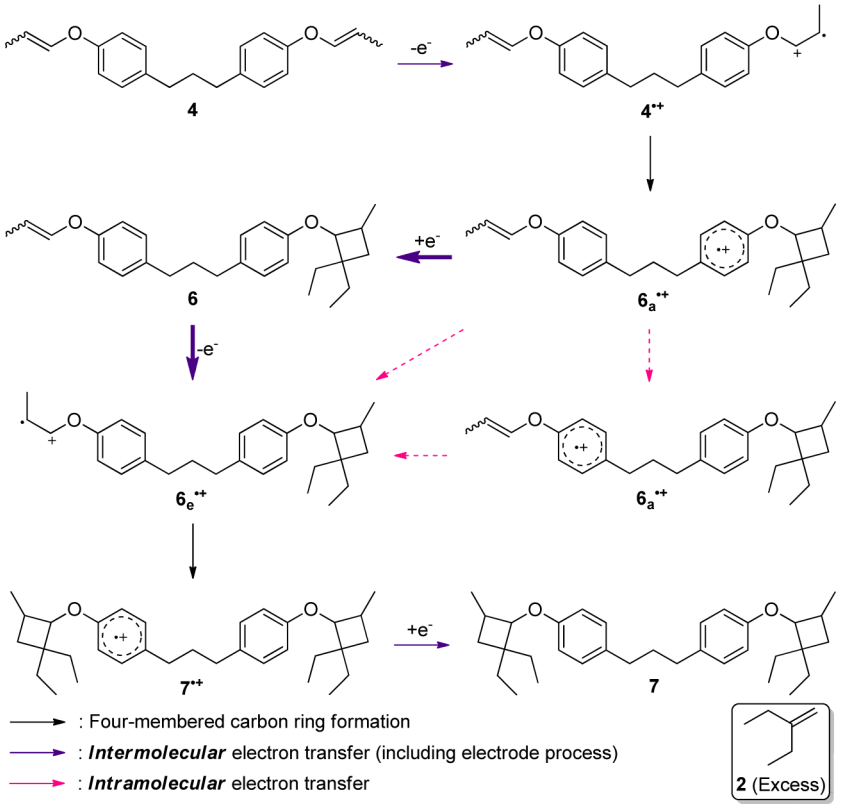
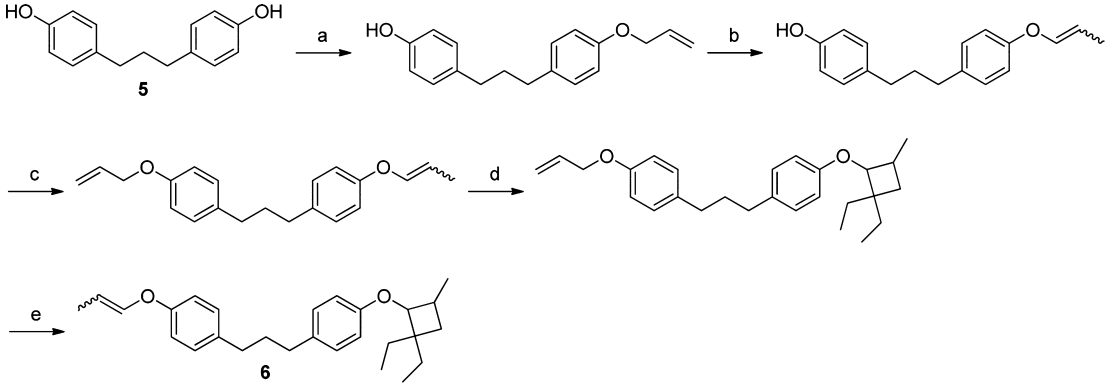
Scheme 6. Proposed Reaction Mechanism for the Anodic Four-Membered Carbon Ring Formation Starting from 1,3-Bis(4-(prop-1-en-1-yloxy)phenyl)propane (4)



Scheme 7. Synthesis of the Mono-Ring-Containing Compound 6[a]



[a]Reagents and conditions: (a) allyl bromide, K_2CO_3, DMF, 60 °C; (b) ^{t}BuOK, DMSO, room temperature; (c) allyl bromide, K_2CO_3, DMF, 60 °C; (d) 3-methylenepentane, $LiClO_4$, $MeNO_2$, carbon felt electrodes, 1.2 V vs Ag/AgCl, room temperature; (e) ^{t}BuOK, DMSO, room temperature.

formed mainly from 1,2-bis(4-(prop-1-en-1-yloxy)phenyl)-ethane (**8**) in a direct manner, not via formation of the mono-ring-containing compound **12**, which would involve transformation from the aromatic radical cation $\mathbf{12}_a^{\bullet+}$ to the enol ether radical cation $\mathbf{12}_e^{\bullet+}$ via intramolecular electron transfer (Scheme 12).

The synthesis of enol ether bis(4-(prop-1-en-1-yloxy)-phenyl)methane (**9**) was not as straightforward as that of **4** and **8**. The standard synthetic scheme for the enol ethers, including allylation and basic isomerization, had to be modified. Because of the relatively high acidity of the benzylic protons of bis(4-(allyloxy)phenyl)methane (**11**), its treatment with base resulted in a messy mixture. To address this issue, a ruthenium catalyst was used to isomerize the allyl groups of bis(4-(allyloxy)phenyl)methane (**11**). This method has proven to be a highly versatile and successful approach for obtaining bis(4-(prop-1-en-1-yloxy)phenyl)methane (**9**). Reaction monitoring of the anodic oxidation of bis(4-(prop-1-en-1-yloxy)phenyl)-methane (**9**) in the presence of 3-methylenepentane (**2**) using GC-MS was disappointing, because the mono-ring-containing compound **14** was the predominant product, even at 2 F, with only a small amount of the bis-ring-containing compound **15** observed (Figure 3). (The mono-ring-containing compound **14** was also synthesized alternatively to confirm its structural identity; see Scheme 13.). These results were presumably due to the stability of the corresponding diarylcarbenium ion, which can be generated and accumulated by the low-temperature anodic oxidation of diarylmethanes.[10] There was the possibility

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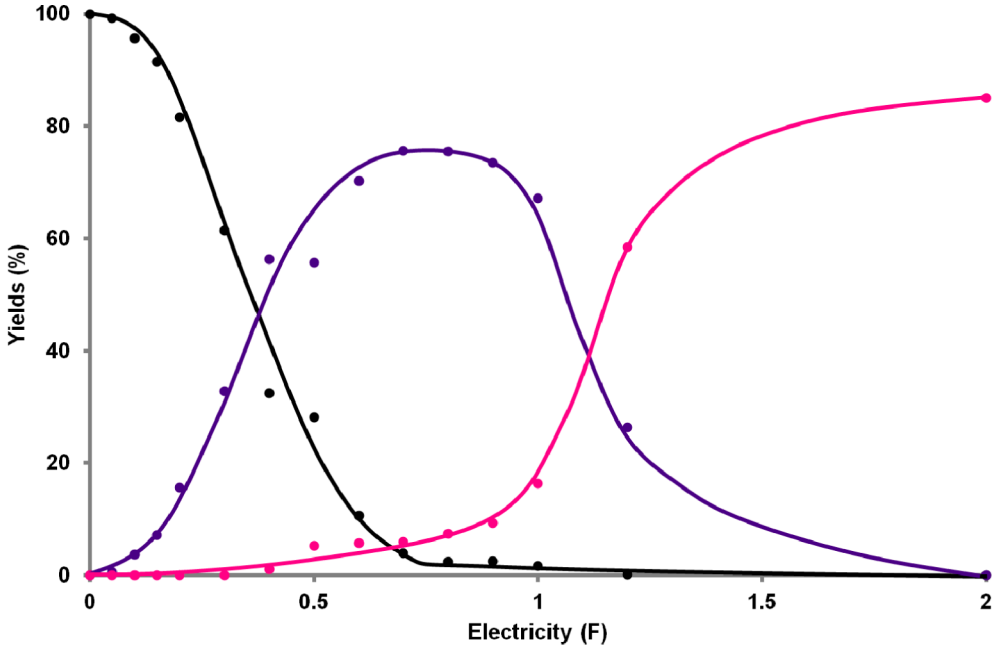
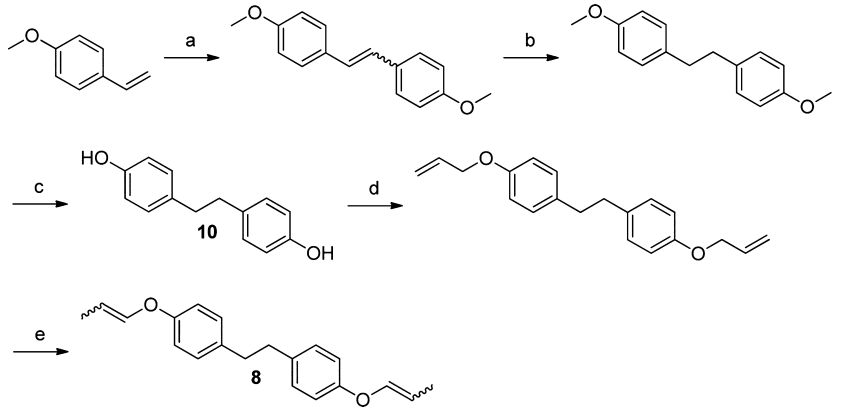


	electricity (F)														
	0	0.05	0.1	0.15	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2	2.0
4	100	99	96	92	82	61	33	28	11	4	3	2	2	<1	0
6	0	<1	4	7	16	33	56	56	70	76	76	74	67	26	0
7	0	0	0	0	0	0	1	5 (0.09)	6	6	7	9	16 (0.24)	58	85

Yields determined by GC-MS (%). **7/6** values are described in parenthesis.

Figure 1. Monitoring of the reaction of **4** via GC-MS: (black line) 1,3-bis(4-(prop-1-en-1-yloxy)phenyl)propane (**4**); (purple line) mono-ring-containing compound **6**; (pink line) bis-ring-containing compound **7**.

Scheme 8. Synthesis of 1,2-Bis(4-(prop-1-en-1-yloxy)phenyl)ethane (8)[a]



[a]Reagents and conditions: (a) Grubbs second-generation catalyst, CH_2Cl_2, 40 °C, 93%; (b) H_2, Pd/C, THF, room temperature, 84%; (c) BF_3SMe_2, CH_2Cl_2, room temperature, 96%; (d) allyl bromide, K_2CO_3, DMF, 60 °C; (e) ^{t}BuOK, DMSO, room temperature.

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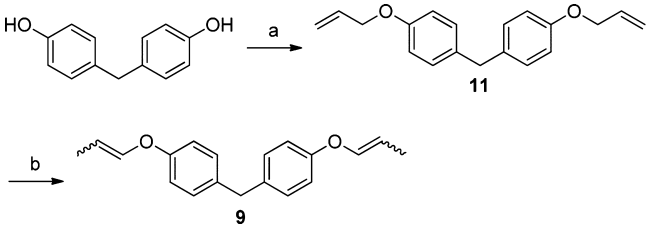
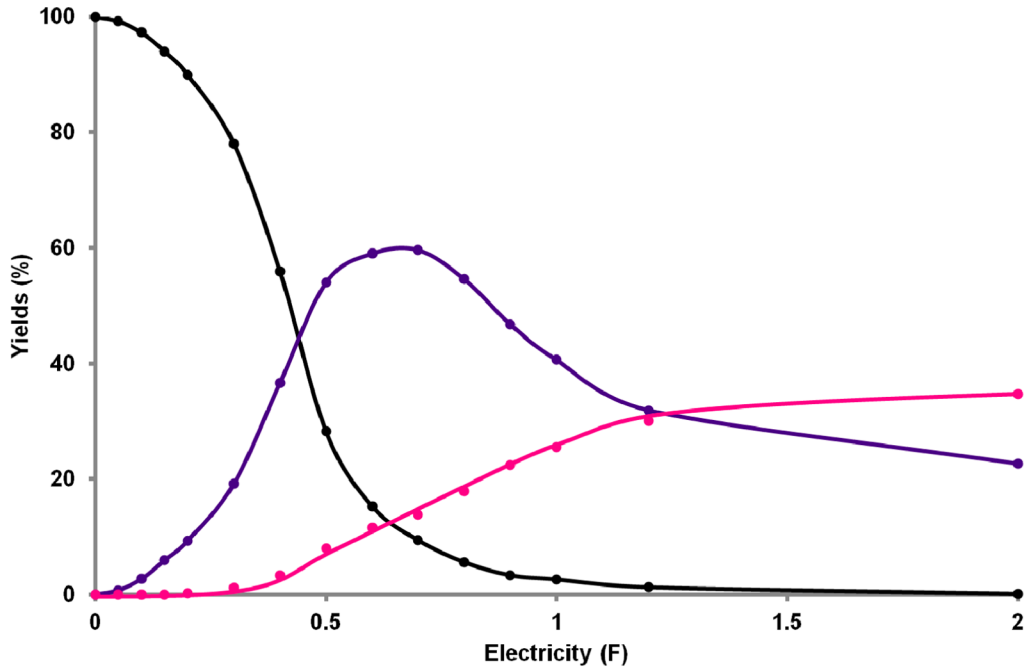
Scheme 9. Synthesis of Bis(4-(prop-1-en-1-yloxy)phenyl)methane (9)[a]

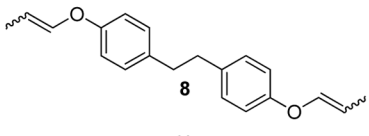
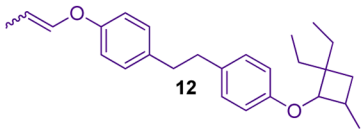
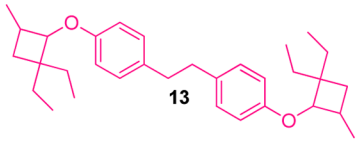


[a]Reagents and conditions: (a) allyl bromide, K_2CO_3, DMF, 60 °C; (b) $(Ph_3P)_3RuCl_2$, toluene, reflux, 90%.

that both the aromatic radical cation $14_a^{\bullet+}$ and the mono-ring-containing compound **14** could undergo transformation to the diarylcarbenium ion 14^+ via anodic oxidation accompanied by deprotonation, which seemed not to afford the bis-ring-containing compound **15** even on reaction with 3-methylenepentane (**2**) (Scheme 14). Therefore, 4,4′-(propane-2,2-diyl)bis((prop-1-en-1-yloxy)benzene) (**16**), in which the acidic benzylic protons were preliminarily abstracted, was finally designed and synthesized (Scheme 15).

This structural change had the desired effect on the synthetic outcome and confirmed our suspicions about the previous failed synthetic effort with bis(4-(prop-1-en-1-yloxy)phenyl)-methane (**9**). Reaction monitoring of the anodic oxidation of 4,4′-(propane-2,2-diyl)bis((prop-1-en-1-yloxy)benzene) (**16**) in the presence of 3-methylenepentane (**2**) using GC-MS



	electricity (F)														
	0	0.05	0.1	0.15	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2	2.0
 8	100	99	97	94	90	78	56	28	15	9	6	3	3	1	<1
 12	0	<1	3	6	9	19	37	54	59	60	55	47	41	32	23
 13	0	0	0	0	<1	1	3	8 (0.15)	12	14	18	22	26 (0.63)	30	35

Yields determined by GC-MS (%). **13**/**12** values are described in parenthesis.

Figure 2. Monitoring of the reaction of **8** via GC-MS: (black line) 1,2-bis(4-(prop-1-en-1-yloxy)phenyl)ethane (**8**); (purple line) mono-ring-containing compound **12**; (pink line) bis-ring-containing compound **13**.

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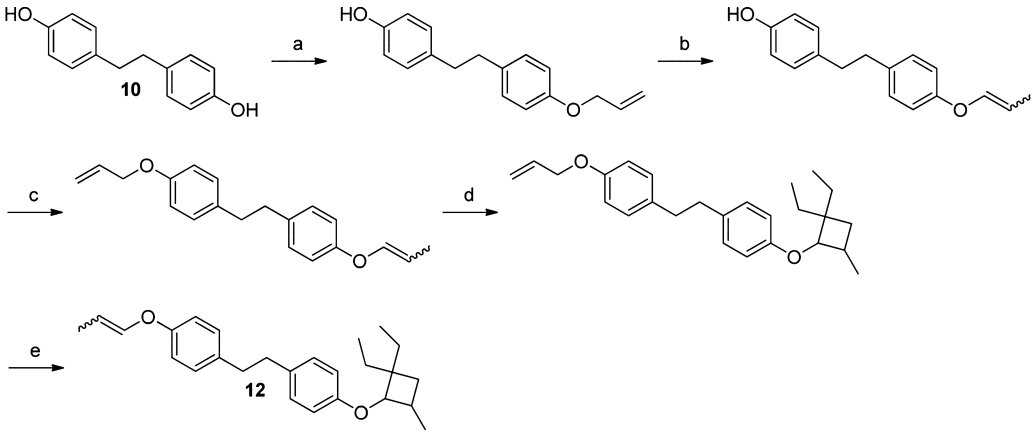
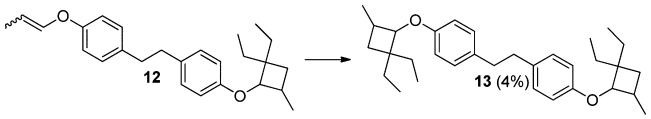
Scheme 10. Synthesis of the Mono-Ring-Containing Compound 12[a]



[a]Reagents and conditions: (a) allyl bromide, K_2CO_3, DMF, 60 °C; (b) ^{t}BuOK, DMSO, room temperature; (c) allyl bromide, K_2CO_3, DMF, 60 °C; (d) 3-methylenepentane, $LiClO_4$, $MeNO_2$, carbon felt electrodes, 1.2 V vs Ag/AgCl, room temperature; (e) ^{t}BuOK, DMSO, room temperature.

Scheme 11. Anodic Four-Membered Carbon Ring Formation of the Mono-Ring-Containing Compound 12[a]



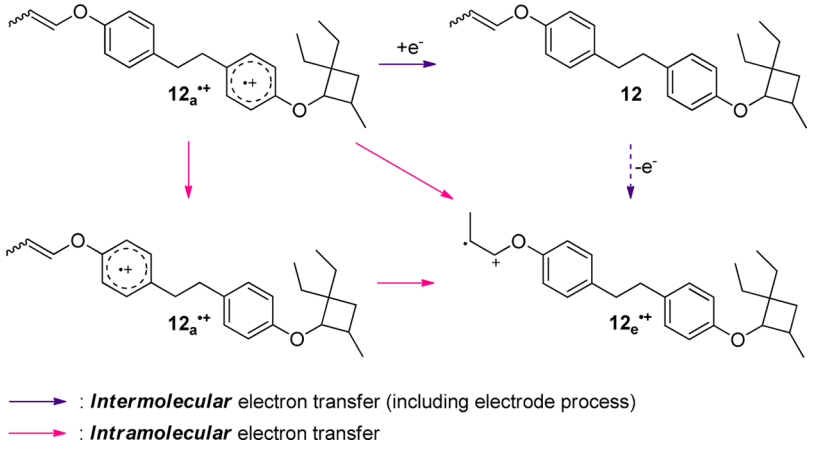
[a]Reagents and conditions: 3-methylenepentane, $LiClO_4$, $MeNO_2$, carbon felt electrodes, 1.2 V vs Ag/AgCl, 1.0 F/mol, room temperature.

showed that the bis-ring-containing compound **18** was predominantly observed, even at 0.5 F, with generation of only a minor amount of the mono-ring-containing compound **17**. At 1.0 F, the ratio of the bis- and mono-ring-containing compounds **18** and **17**, respectively, was 8.4, and almost no mono-ring-containing compound **17** was detected (Figure 4). The structural identity of the mono-ring-containing compound **17** was confirmed through its alternative synthesis (Scheme 16). On the basis of these observations, it can be rationalized that transformation from the aromatic radical cation $\mathbf{17}_a^{\bullet+}$ to the enol ether radical cation $\mathbf{17}_e^{\bullet+}$ occurred rapidly via intramolecular electron transfer, and the resulting enol ether radical cation $\mathbf{17}_e^{\bullet+}$ was then trapped by 3-methylenepentane (**2**) to construct the bis-ring-containing compound **18** in a direct manner (Scheme 17). In this case, a hopping mechanism using a second aromatic ring as relay station was also possible for the intramolecular electron transfer.[11] The peak oxidation potentials of 4,4′-(propane-2,2-diyl)bis((prop-1-en-1-yloxy)-benzene) (**16**) and the mono-ring-containing compound **17** are 1.25 and 1.27 V vs Ag/AgCl, respectively, clearly indicating that the selective anodic oxidation of the mono-ring-containing compound **17** in the presence of 4,4′-(propane-2,2-diyl)bis-((prop-1-en-1-yloxy)benzene) (**16**) was barely achieved (Figure S4, Supporting Information). In this case, intramolecular electron transfer was strongly preferred over the intermolecular variant for reduction of the aromatic radical cation $\mathbf{17}_a^{\bullet+}$.

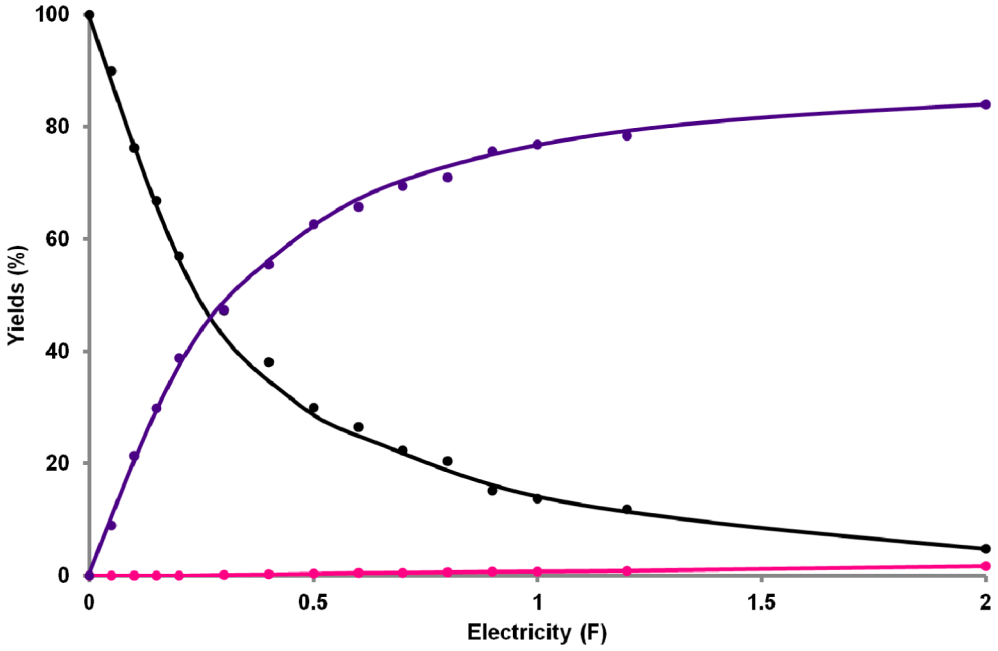
CONCLUSION

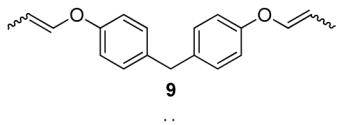
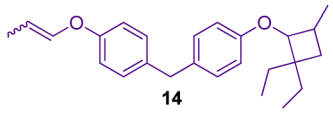
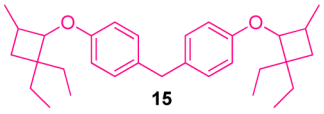
The experimental results presented herein successfully advanced the mechanistic understanding of the reactivity of enol ether radical cations for anodic four-membered carbon ring formation (Scheme 18). The anodically generated enol ether radical cations were trapped by olefinic nucleophiles in order to afford the corresponding mono-ring-containing aromatic radical cations. There are two possible pathways for such aromatic radical cations to be reduced, inter- and intramolecular electron transfers, and both were directly investigated through the synthetic outcomes. The intermolec-

Scheme 12. Proposed Electron Transfer in the Mono-Ring-Containing Compound 12



dx.doi.org/10.1021/jo3028246 | J. Org. Chem. 2013, 78, 2626−2638

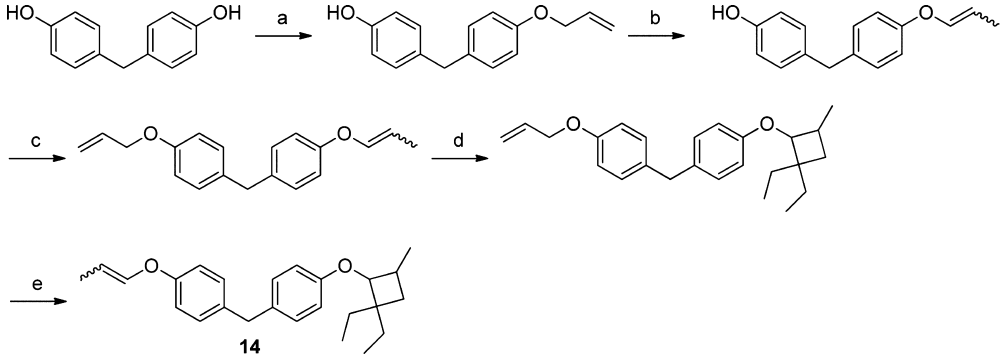


	electricity (F)														
	0	0.05	0.1	0.15	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2	2.0
 9	100	90	76	67	57	47	38	30	26	22	20	15	14	12	5
 14	0	9	21	30	39	47	55	63	66	69	71	76	77	78	84
 15	0	0	0	0	0	<1	<1	<1	<1	<1	<1	<1	<1	<1	2

Yields determined by GC-MS (%).

Figure 3. Monitoring of the reaction of **9** via GC-MS: (black line) bis(4-(prop-1-en-1-yloxy)phenyl)methane (**9**); (purple line) mono-ring-containing compound **14**; (pink line) bis-ring-containing compound **15**.

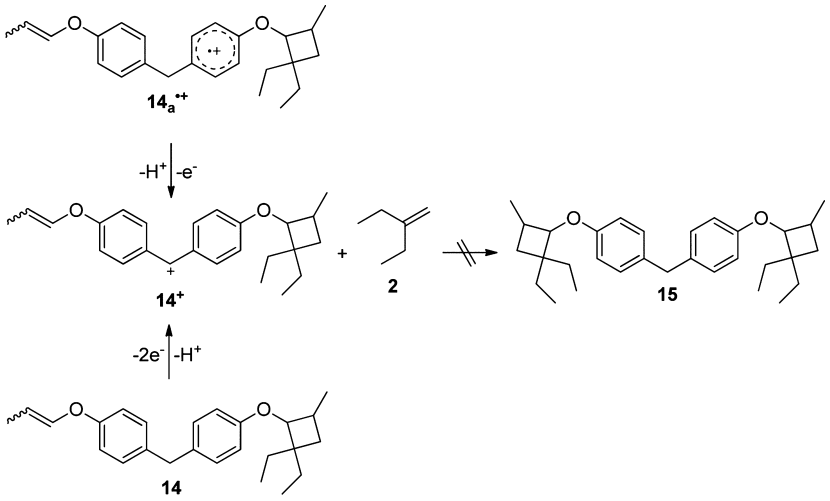
Scheme 13. Synthesis of the Mono-Ring-Containing Compound 14[a]



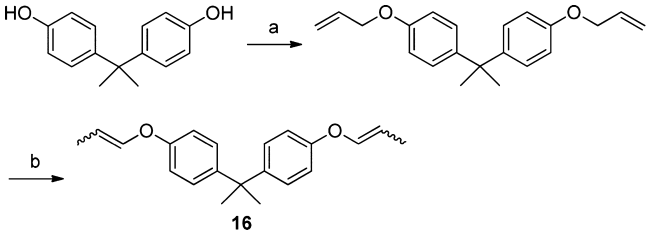
[a]Reagents and conditions: (a) allyl bromide, K_2CO_3, DMF, 60 °C; (b) $(Ph_3P)_3RuCl_2$, toluene, reflux; (c) allyl bromide, K_2CO_3, DMF, 60 °C,; (d) 3-methylenepentane, $LiClO_4$, $MeNO_2$, carbon felt electrodes, 1.2 V vs Ag/AgCl, room temperature; (e) $(Ph_3P)_3RuCl_2$, toluene, reflux.

dx.doi.org/10.1021/jo3028246 | J. Org. Chem. 2013, 78, 2626−2638

Scheme 14. Possible Formation of the Diarylcarbenium Ion 14^+



Scheme 15. Synthesis of 4,4′-(Propane-2,2-diyl)bis((prop-1-en-1-yloxy)benzene) (16)[a]



[a]Reagents and conditions: (a) allyl bromide, K_2CO_3, DMF, 60 °C; (b) ^{t}BuOK, DMSO, room temperature.

ular reduction simply gave the mono-ring-containing compound that could be further oxidized. The intramolecular reduction triggered the regeneration of the enol ether radical cations, affording the bis-ring-containing compounds. The information gained about the tether between the aromatic rings influencing the relative rates of inter- and intramolecular electron transfer will be critical for the design of new synthetic sequences that aim to capitalize on the distinctive reactivity unique to enol ether radical cations in combination with the use of more conventional reactive intermediates.

EXPERIMENTAL SECTION

All solvents and reagents were from commercial source and were used without further purification. ^{1}H NMR spectra were collected on a 600 MHz NMR spectrometer using the deuterated solvent as an internal deuterium reference. Chemical shift data are given in δ units calibrated with residual protic solvent. The multiplicity of a signal is indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. ^{13}C NMR spectra were collected on a 150 MHz spectrometer with proton decoupling using the deuterated solvent as an internal carbon reference. Chemical shift data are given in δ units calibrated with residual solvent. Only selected absorbances are reported in the IR spectra. HRMS analysis was performed in DARTTOF mode.[12] The reaction yields were determined by NMR or GC-MS.

General Procedure for the Preparation of Bis Enol Ethers. Unless otherwise stated, all enol ether substrates were prepared from the corresponding bis-phenol precursors through a previously described procedure in the literature.[13] To a solution of the bis-phenol precursor in DMF, allyl bromide (3.0 equiv for every one phenol) and K_2CO_3 (4.5 equiv for every one phenol) were added. The resulting reaction mixture was stirred at 60 °C until completion of the reaction (determined by TLC), followed by dilution with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification by silica gel column chromatography (EtOAc/hexanes) gave the desired bis-allylated compounds. To a solution of the resulting bis-allylated compound in DMSO, ^{t}BuOK (8.0 equiv for every one phenol) was added. The resulting reaction mixture was stirred at room temperature for 6 h, followed by dilution with hexane. The layers were separated, the DMSO layer was extracted several times with hexane, and the combined hexane phases were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification by silica gel column chromatography (EtOAc/hexanes) gave the desired bis-enol ethers.

General Procedure for the Anodic Four-Membered Carbon Ring Formations. To a solution of lithium perchlorate (1.0 M) in $MeNO_2$, the enol ether substrate (0.10 mmol) and 3-methylenepentane (**2**; 0.50 M) were added. Carbon felt electrodes (20 mm × 20 mm) were inserted into the solution, and electrolysis was performed using an undivided cell with stirring at a constant potential of 1.2 V vs Ag/AgCl under room-temperature conditions. The reaction progress was monitored by TLC and GC-MS. If it was desired to obtain the bis-ring-containing compounds selectively, an excess amount of electric charge (5−10 F) was passed through the solution to consume the mono-ring-containing compounds, followed by dilution with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification by silica gel column chromatography (EtOAc/hexanes) gave the desired bis-ring-containing compounds.

General Procedure for the Preparation of the Mono-Ring-Containing Compounds. All mono-ring-containing compounds were synthesized from the corresponding bis-phenol precursors through the combined procedures described above. To a solution of the bis-phenol precursor in DMF were added allyl bromide (1.1 equiv) and K_2CO_3 (4.5 equiv). The resulting reaction mixture was stirred at 60 °C until completion of the reaction (determined by TLC), followed by dilution with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification by silica gel column chromatography (EtOAc/hexanes) gave the desired mono-allylated compounds. To a solution of the resulting monoallylated compound in DMSO was added ^{t}BuOK (8.0 equiv). The resulting reaction mixture was stirred at room temperature for 6 h, followed by dilution with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification by silica gel column chromatography (EtOAc/hexanes) gave the desired mono enol ethers. The remaining phenol was similarly allylated, followed by the anodic four-membered carbon ring formation, and the remaining allyl group was isomerized. Purification by silica gel column chromatography (EtOAc/hexanes) gave the desired mono-ring-containing compounds.

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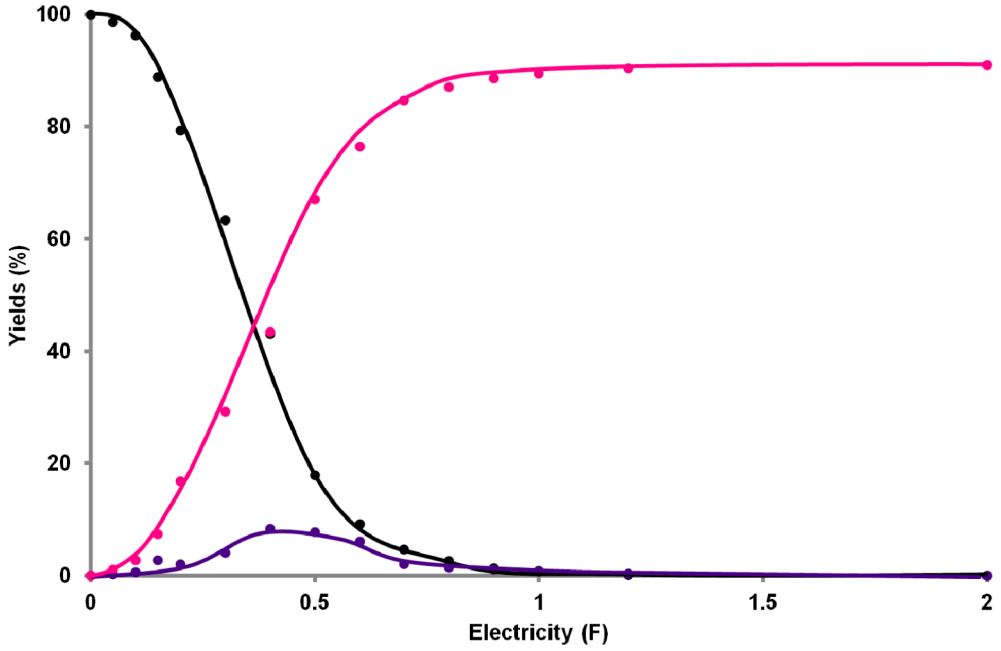

	electricity (F)														
	0	0.05	0.1	0.15	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2	2.0
16	100	99	96	89	79	63	43	18	9	5	3	1	<1	<1	0
17	0	<1	<1	3	3	4	8	8	6	2	2	1	<1	<1	0
18	0	1	3	7	17	29	43	67 (8.4)	76	85	87	89	89 (-)	90	91

Yields determined by GC-MS (%). **18**/**17** values are described in parenthesis.

Figure 4. Monitoring of the reaction of **16** via GC-MS: (black line) 4,4′-(propane-2,2-diyl)bis((prop-1-en-1-yloxy)benzene) (**16**); (purple line) mono-ring-containing compound **17**; (pink line) bis-ring-containing compound **18**.

Preparation of 4,4′-(Propane-1,3-diyl)diphenol (5). To a solution of 1,3-dibromopropane (2.04 mL, 20.0 mmol) in THF (20 mL) was added lithium tetrachlorocuprate(II) (0.10 M in THF, 1.20 mL, 0.120 mmol), and the mixture was cooled with an ice bath. (4-Methoxyphenyl)magnesium bromide (1.0 M in THF, 70.0 mL, 70.0 mmol) was added dropwise, and the resulting reaction mixture was stirred at room temperature for 16 h, followed by dilution with cold water and Et_2O. The layers were separated, the aqueous layer was extracted several times with Et_2O, and the combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated in vacuo to give 5.08 g of 1,3-bis(4-methoxyphenyl)propane (99% yield). This compound was finally purified by recrystallization from EtOH. 1,3-Bis(4-methoxyphenyl)propane was then dissolved in CH_2Cl_2 (100 mL) and cooled with an ice bath. BBr_3 (1.0 M in CH_2Cl_2, 3.0 equiv.) was added dropwise, and the resulting reaction mixture was stirred at room temperature for 16 h. The reaction mixture was poured into water, and the layers were separated. The aqueous layer was extracted several times with CH_2Cl_2, and the combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated in vacuo to give 4.07 g of 4,4′-(propane-1,3-diyl)diphenol (**5**) (90% yield). This compound was finally purified by silica gel column chromatography (EtOAc/hexanes).

Preparation of 4,4′-(Ethane-1,2-diyl)diphenol (10). 1,2-Bis(4-methoxyphenyl)ethane was prepared from 1-methoxy-4-vinylbenzene through a procedure previously described in the literature.[14] To a solution of 1-methoxy-4-vinylbenzene (2.68 mL, 20 mmol) in CH_2Cl_2 (40 mL) was added Grubbs' second-generation catalyst (5 mol %). The resulting reaction mixture was stirred at 40 °C for 2 h and concentrated in vacuo to give 2.23 g of 1,2-bis(4-methoxyphenyl)-ethane (93% yield). This compound was finally purified by silica gel column chromatography (EtOAc/hexanes). 1,2-Bis(4-methoxyphenyl)ethane was then dissolved in THF (40 mL). 5% Pd/C (112 mg) was added and the mixture purged with hydrogen gas. The resulting reaction mixture was vigorously stirred under a hydrogen atmosphere for 6 h at room temperature. The reaction mixture was then filtered and concentrated in vacuo to give 1.89 g of 1,2-bis(4-

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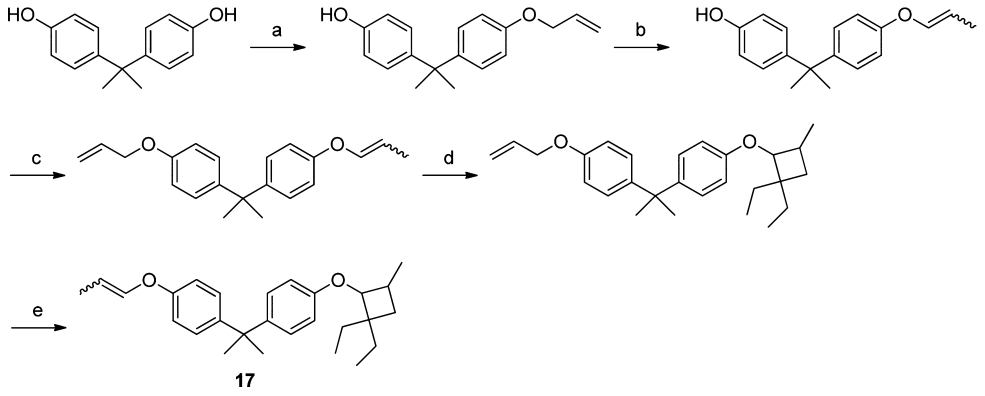
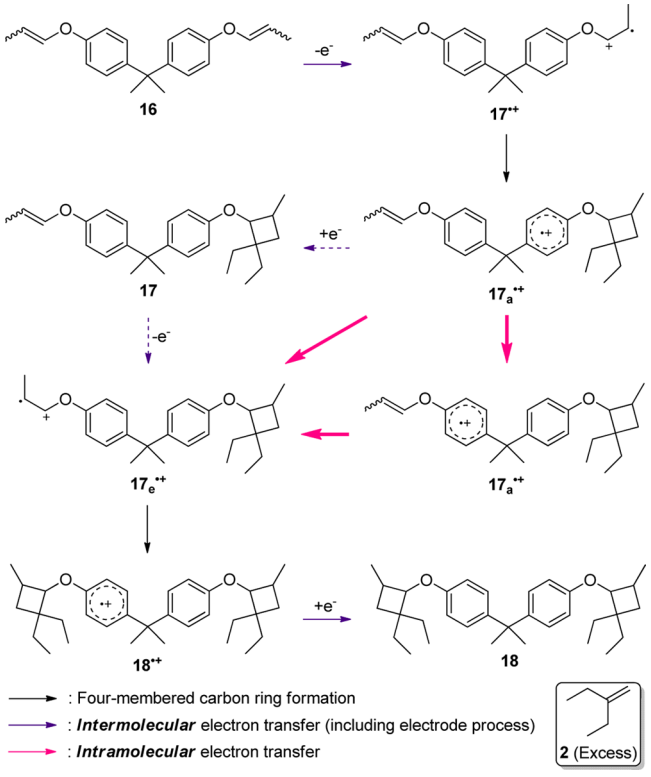
Scheme 16. Synthesis of the Mono-Ring-Containing Compound 16[a]

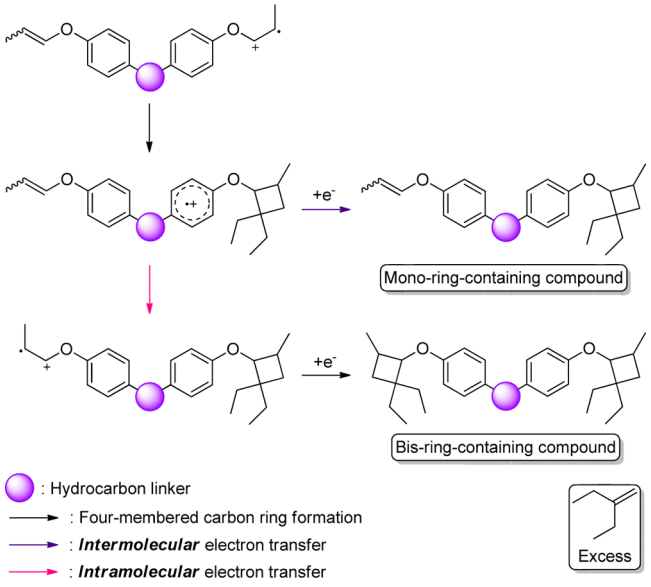


[a]Reagents and condition: (a) Allylbromide, K_2CO_3, DMF, 60 °C. (b) ^{t}BuOK, DMSO, room temperature. (c) Allylbromide, K_2CO_3, DMF, 60 °C, (d) 3-Methylenepentane, $LiClO_4$, $MeNO_2$, carbon felt electrodes, 1.2 V vs Ag/AgCl, room temperature. (e) ^{t}BuOK, DMSO, room temperature.

Scheme 17. Proposed Reaction Mechanism for Anodic Four-Membered Carbon Ring Formation Starting from 4,4′-(Propane-2,2-diyl)bis((prop-1-en-1-yloxy)benzene) (16)



Scheme 18. Mechanistic Understanding of the Behavior of Enol Ether Radical Cations during Anodic Four-Membered Carbon Ring Formation



methoxyphenyl)ethane (84% yield). This compound was finally purified by silica gel column chromatography (EtOAc/hexanes). 4,4′-(Ethane-1,2-diyl)diphenol (**10**) was prepared from 1,2-bis(4-methoxyphenyl)ethane through a procedure previously described in the literature.[15] To a solution of 1,2-bis(4-methoxyphenyl)ethane in CH_2Cl_2 (40 mL) was added boron trifluoride–dimethyl sulfide complex (5.0 equiv for every one methoxy group) dropwise, and the resulting reaction mixture was stirred at room temperature for 12 h, followed by dilution with CH_2Cl_2 and 2.0 M HCl. The layers were separated, the aqueous layer was extracted several times with CH_2Cl_2, and the combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated in vacuo to give 1.61 g of 4,4′-(ethane-1,2-diyl)diphenol (**10**) (96% yield). This compound was finally purified by silica gel column chromatography (EtOAc/hexanes).

Preparation of Bis(4-(prop-1-en-1-yloxy)phenyl)methane (9). To a solution of bis(4-(allyloxy)phenyl)methane (**11**; 2.80 g, 10.0 mmol) in toluene (10 mL) was added tris(triphenylphosphine)-ruthenium(II) dichloride (10 mol %). The resulting reaction mixture was stirred under reflux conditions for 12 h. The reaction mixture was concentrated in vacuo to give 2.52 g of bis(4-(prop-1-en-1-yloxy)-phenyl)methane (**9**) (90% yield). This compound was finally purified by silica gel column chromatography (EtOAc/hexanes).

*1,3-Bis(4-(prop-1-en-1-yloxy)phenyl)propane (**4**), mixture of diastereomers (oil):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.11–7.08 (4H, m), 6.92–6.86 (4H, m), 6.41–6.36 (0.2H, m) 6.36–6.33 (1.8H, m), 5.30 (0.2H, dq, J = 12.4, 6.9 Hz), 4.83 (1.8H, dq, J = 6.9, 6.5 Hz), 2.58 (4H, t, J = 7.6 Hz), 1.92–1.86 (2H, m), 1.70 (5.4H, dd, J = 6.9, 2.1 Hz), 1.65 (0.6H, dd, J = 6.8, 1.7 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 155.8, 141.3, 136.3, 129.5, 128.0, 116.3, 116.2, 107.8, 107.0, 34.6, 33.4, 12.3, 9.4; IR (NaCl, cm^{-1}) 3036, 2921, 2857, 1668, 1607, 1509, 1234, 1021; HRMS $[M + H]^+$ calcd for $C_{21}H_{25}O_2$ 309.1855, found 309.1854.

*1-(2,2-Diethyl-4-methylcyclobutoxy)-4-(3-(4-(prop-1-en-1-yloxy)-phenyl)propyl)benzene (**6**), mixture of diastereomers (oil):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.12–6.99 (4H, m), 6.94–6.86 (2H, m), 6.81–6.77 (1H, m), 6.75–6.71 (1H, m), 6.43–6.28 (1H, m), 5.36–5.28 (0.2H, m), 4.87–4.79 (0.8H, m), 4.31 (0.6H, d, J = 6.9 Hz), 3.96 (0.4H, d, J = 6.9 Hz), 2.71–2.64 (0.6H, m), 2.60–2.51 (4H, m), 2.43–

dx.doi.org/10.1021/jo3028246 | J. Org. Chem. 2013, 78, 2626–2638

2.32 (0.4H, m), 1.91−1.83 (2H, m), 1.81−1.72 (2H, m), 1.70 (2.6H, dd, J = 6.9, 2.1 Hz), 1.65 (0.4H, dd, J = 6.9, 1.4 Hz), 1.64−1.54 (1H, m), 1.52−1.43 (2H, m), 1.39 (0.6H, dd, J = 11.7, 6.2 Hz), 1.15 (1.2H, d, J = 6.2 Hz), 1.01 (1.8H, d, J = 7.6 Hz), 0.99−0.90 (0.4H, m), 0.84−0.76 (6H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.5, 157.2, 155.7, 141.3, 136.5, 134.3, 133.8, 129.5, 129.2, 129.1, 116.3, 116.1, 115.8, 114.5, 107.0, 85.2, 79.6, 45.4, 45.2, 41.0, 35.5, 34.6, 33.7, 33.4, 31.8, 31.0, 30.1, 30.0, 24.8, 24.0, 20.0, 19.9, 15.8, 13.9, 12.3, 9.4, 8.5, 8.4, 8.3, 7.8; IR (NaCl, cm^{-1}) 3029, 2960, 2929, 2858, 1672, 1607, 1509, 1238, 1021; HRMS $[M + H]^+$ calcd for $C_{27}H_{37}O_2$ 393.2794, found 393.2793.

*1,3-Bis(4-(2,2-diethyl-4-methylcyclobutoxy)phenyl)propane (**7**), mixture of diastereomers (oil):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.08−7.01 (4H, m), 6.86−6.77 (2H, m), 6.76−6.72 (2H, m), 4.32 (1.6H, d, J = 7.3 Hz), 3.96 (0.4H, d, J = 7.3 Hz), 2.74−2.62 (1.6H, m), 2.55 (4H, t, J = 7.3 Hz), 2.42−2.32 (0.4H, m), 1.91−1.83 (2H, m), 1.80−1.68 (4H,m), 1.65−1.55 (2H, m), 1.50−1.44 (4H, m), 1.40 (1.6H, dd, J = 11.5, 6.0 Hz), 1.15 (1.2H, d, J = 6.9 Hz), 1.01 (4.8H, m), 0.99−0.90 (0.4H, m), 0.85−0.76 (12H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.5, 157.1, 134.5, 134.0, 129.3, 129.2, 129.1, 115.9, 114.8, 85.2, 79.8, 45.4, 45.2, 35.5, 34.6, 33.8, 33.5, 31.8, 31.0, 30.6, 30.1, 24.8, 24.0, 20.0, 15.8, 8.5, 8.4, 8.3, 7.8; IR (NaCl, cm^{-1}) 2964, 2929, 2873, 1607, 1509, 1458, 1241, 826; HRMS $[M + H]^+$ calcd for $C_{33}H_{49}O_2$ 477.3733, found 477.3731.

*1,2-Bis(4-(prop-1-en-1-yloxy)phenyl)ethane (**8**), mixture of diastereomers (amorphous solid):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.09−7.05 (4H, m), 6.91−6.80 (4H, m), 6.40−6.37 (0.2H, m) 6.35−6.33 (1.8H, m), 5.33 (0.2H, dq, J = 12.4, 6.9 Hz), 4.84 (1.8H, dq, J = 6.9, 6.5 Hz), 2.84 (4H, s), 1.71 (5.4H, dd, J = 6.9, 2.1 Hz), 1.65 (0.6H, dd, J = 6.8, 1.7 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 155.9, 142.4, 141.3, 135.7, 129.6, 116.3, 116.1, 107.9, 107.1, 37.3, 12.3, 9.4; IR (NaCl, cm^{-1}) 3044, 2929, 2849, 1671, 1607, 1509, 1234, 1024; HRMS $[M + H]^+$ calcd for $C_{20}H_{23}O_2$ 295.1698, found 295,1695; mp 71−76 °C.

*1-(2,2-Diethyl-4-methylcyclobutoxy)-4-(4-(prop-1-en-1-yloxy)-phenethyl)benzene (**12**), mixture of diastereomers (oil):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.12−7.06 (2H, m), 7.02 (2H, d, J = 8.7 Hz), 6.92−6.86 (2H, m), 6.82−6.76 (1H, m), 6.74 (1H, d, J = 8.7 Hz), 6.43−6.31 (1H, m), 5.38−5.28 (0.1H, m), 4.88−4.78 (0.9H, m), 4.32 (0.6H, d, J = 6.9 Hz), 3.96 (0.4H, d, J = 6.9 Hz), 2.81 (4H, m), 2.74−2.62 (0.6H, m), 2.43−2.30 (0.4H, m), 1.83 −1.73 (2H, m), 1.70 (2.7H, dd, J = 6.9, 2.1 Hz), 1.67−1.57 (1.3H, m), 1.52−1.43 (2H, m), 1.40 (0.6H, dd, J = 11.7, 6.2 Hz), 1.15 (1.2H, d, J = 6.2 Hz), 1.01 (1.8H, d, J = 7.6 Hz), 0.99−0.90 (0.4H, m), 0.85−0.75 (6H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.6, 157.3, 155.9, 155.7, 141.3, 136.0, 135.9, 133.8, 133.3, 129.5, 129.3, 129.2, 116.1, 115.9, 114.9, 107.0, 85.2, 79.6, 45.4, 45.2, 37.5, 37.4, 37.3, 35.5, 33.7, 31.8, 31.0, 30.1, 29.9, 24.8, 24.0, 19.9, 15.8, 12.3, 9.5, 8.5, 8.4, 8.3, 7.8; IR (NaCl, cm^{-1}) 3030, 2954, 2929, 2863, 1672, 1608, 1509, 1234, 1021; HRMS $[M + H]^+$ calcd for $C_{26}H_{35}O_2$ 379.2637, found 379.2637.

*1,2-Bis(4-(2,2-diethyl-4-methylcyclobutoxy)phenyl)ethane (**13**), one diastereomer (oil):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.03 (4H, dd, J = 8.3, 2.1 Hz), 6.73 (4H, d, J = 7.6 Hz), 4.31 (2H, d, J = 7.6 Hz), 2.79 (4H, s), 2.72−2.63 (2H, m), 1.79−1.72 (4H, m), 1.65−1.57 (2H,m), 1.52−1.46 (4H, m), 1.39 (2H, dd, J = 11.7, 5.6 Hz), 1.01 (6H, d, J = 6.9 Hz), 0.79 (12H, dt, J = 11.0, 7.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.6, 133.6, 129.2, 114.9, 79.6, 45.2, 37.4, 35.5, 30.0, 29.9, 24.8, 15.8, 8.2, 7.7; IR (NaCl, cm^{-1}) 2961, 2931, 2870, 1607, 1516, 1448, 1241, 825; HRMS $[M + H]^+$ calcd for $C_{32}H_{47}O_2$ 463.3576, found 463.3575.

*1,2-Bis(4-(2,2-diethyl-4-methylcyclobutoxy)phenyl)ethane (**13**), mixture of other diastereomers (oil):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.09−6.99 (4H, m), 6.85−6.69 (4H, m), 4.31 (1H, d, J = 7.6 Hz), 3.96 (1H, d, J = 7.6 Hz), 2.79 (4H, s), 2.71−2.64 (1H, m), 2.39−2.29 (1H, m), 1.82−1.68 (4H, m), 1.65−1.56 (2H, m), 1.52−1.44 (4H, m), 1.40 (1H, dd, J = 11.7, 6.2 Hz), 1.14 (3H, d, J = 6.2 Hz), 1.01 (3H, d, J = 6.9 Hz), 0.99−0.95 (1H, m), 0.83−0.76 (12H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.6, 157.2, 134.1, 133.6, 129.4, 129.2, 115.8, 114.9, 85.2, 79.6, 45.4, 45.1, 37.5, 37.4, 35.5, 33.7, 31.8, 30.9, 30.0, 29.9, 24.8, 24.0, 19.9, 15.8, 8.5, 8.4, 8.3, 7.7; IR (NaCl, cm^{-1}) 2964, 2930, 2872, 1607, 1509, 1457, 1241, 826; HRMS $[M + H]^+$ calcd for $C_{32}H_{47}O_2$ 463.3576, found 463.3575.

*Bis(4-(prop-1-en-1-yloxy)phenyl)methane (**9**), mixture of diastereomers (oil):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.11 (4H, d, J = 8.4 Hz), 6.95−6.89 (4H, m), 6.43−6.39 (1.7H, m) 6.38−6.34 (0.3H, m), 5.36 (1.7H, dq, J = 12.4, 6.9 Hz), 4.89 (0.3H, dq, J = 6.9, 6.5 Hz), 3.90 (2H, s), 1.73 (0.9H, dd, J = 6.9, 2.1 Hz), 1.67 (5.1H, dd, J = 6.8, 1.7 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 155.9, 142.3, 141.2, 135.4, 130.0, 116.5, 116.3, 108.0, 107.3, 40.4, 12.4, 9.5; IR (NaCl, cm^{-1}) 3036, 2918, 2857, 1672, 1607, 1509, 1234, 1173; HRMS $[M + H]^+$ calcd for $C_{19}H_{21}O_2$ 281.1542, found 281.1540.

*1-(2,2-Diethyl-4-methylcyclobutoxy)-4-(4-(prop-1-en-1-yloxy)-benzyl)benzene (**14**), mixture of diastereomers (oil):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.14−6.99 (4H, m), 6.92−6.70 (4H, m), 6.39−6.36 (0.8H, m), 6.35−6.31 (0.2H, m), 5.36−5.29 (0.8H, m), 4.86−4.80 (0.2H, m), 4.30 (0.7H, d, J = 6.9 Hz), 3.95 (0.3H, d, J = 6.9 Hz), 3.85 (2H, m), 2.71−2.62 (0.7H, m), 2.39−2.32 (0.3H, m), 1.82 −1.71 (2H, m), 1.70 (0.6H, dd, J = 6.9, 2.1 Hz), 1.64 (2.4H, m), 1.62−1.55 (1H, m), 1.52−1.44 (2H, m), 1.39 (0.7H, dd, J = 11.7, 6.2 Hz), 1.14 (0.9H, d, J = 6.2 Hz), 1.01 (2.1H, d, J = 7.6 Hz), 0.99−0.94 (0.3H, m), 0.83−0.76 (6H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.6, 157.4, 155.9, 155.8, 142.5, 141.2, 135.8, 133.4, 132.9, 129.9, 129.7, 129.6, 116.4, 116.3, 116.2, 115.9, 115.0, 107.9, 107.1, 85.1, 79.6, 45.4, 45.1, 40.3, 35.5, 33.7, 31.7, 31.0, 30.0, 29.9, 24.8, 24.0, 20.0, 15.8, 12.3, 9.4, 8.5, 8.4, 8.3, 7.7; IR (NaCl, cm^{-1}) 3029, 2955, 2929, 2863, 1672, 1608, 1504, 1229, 1021; HRMS $[M + H]^+$ calcd for $C_{25}H_{33}O_2$ 365.2481, found 365.2483.

*Bis(4-(2,2-diethyl-4-methylcyclobutoxy)phenyl)methane (**15**), mixture of diastereomers (oil):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.07−6.99 (4H, m), 6.81−6.70 (4H, m), 4.30 (1.5H, d, J = 7.6 Hz), 3.94 (0.5H, d, J = 7.6 Hz), 3.82 (2H, s), 2.71−2.62 (1.5H, m), 2.38−2.31 (0.5H, m), 1.80−1.69 (4H, m), 1.64−1.57 (2H, m), 1.52−1.41 (4H, m), 1.39 (1.5H, dd, J = 11.7, 6.2 Hz), 1.13 (1.5H, d, J = 6.2 Hz), 1.03−0.93 (5H, m), 0.83−0.75 (12H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.7, 157.3, 133.7, 133.3, 129.7, 129.6, 115.8, 115.0, 85.1, 79.6, 45.3, 45.1, 40.2, 35.5, 33.7, 31.7, 31.0, 30.0, 29.9, 24.8, 24.0, 19.9, 15.8, 8.5, 8.4, 8.2, 7.7; IR (NaCl, cm^{-1}) 2964, 2929, 2872, 1610, 1510, 1452, 1241, 824; HRMS $[M + H]^+$ calcd for $C_{31}H_{45}O_2$ 449.3420, found 449.3423.

*4,4′-(Propane-2,2-diyl)bis((prop-1-en-1-yloxy)benzene) (**16**), mixture of diastereomers (oil):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.16 (4H, m), 6.90−6.83 (4H, m), 6.40−6.37 (0.2H, m) 6.36−6.31 (1.8H, m), 5.33 (0.2H, dq, J = 12.4, 6.9 Hz), 4.84 (1.8H, dq, J = 6.9, 6.5 Hz), 1.69 (5.4H, dd, J = 6.9, 2.1 Hz), 1.67 −1.59 (6.6H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 155.5, 144.8, 142.2, 141.1 127.9, 115.8, 115.6, 108.0, 107.2, 42.0, 31.3, 12.4, 9.5; IR (NaCl, cm^{-1}) 3043, 2970, 2863, 1672, 1607, 1505, 1253, 1231; HRMS $[M + H]^+$ calcd for $C_{21}H_{25}O_2$ 309.1855, found 309.1856.

*1-(2,2-Diethyl-4-methylcyclobutoxy)-4-(2-(4-(prop-1-en-1-yloxy)-phenyl)propan-2-yl)benzene (**17**), mixture of diastereomers (oil):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.19−7.05 (4H, m), 6.91−6.84 (2H, m), 6.801−6.75 (1H, m), 6.72 (1H, d, J = 8.9 Hz), 6.42−6.38 (0.2H, m),6.37−6.34 (0.8H, m) 5.37−5.28 (0.2H, m), 4.84 (0.8H, dq, J = 6.9, 6.5 Hz), 4.31 (0.6H, d, J = 6.9 Hz), 3.97 (0.4H, d, J = 7.6 Hz), 2.72−2.62 (0.6H, m), 2.41−2.32 (0.4H, m), 1.81−1.72 (2H, m), 1.70 (2.4H, dd, J = 6.9, 2.1 Hz), 1.65−1.60 (6.6H, m), 1.61−1.45(3H, m), 1.40 (0.6H, dd, J = 11.7, 6.2 Hz), 1.16 (1.2H, d, J = 6.2 Hz), 1.02 (1.8H, d, J = 7.6 Hz), 0.99−0.90 (0.4H, m), 0.85−0.76 (6H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.2, 156.9, 155.4, 145.2, 145.1, 142.8, 142.4, 142.3, 141.4, 127.9, 127.7, 127.6, 127.5, 115.7, 115.6, 115.2, 114.5, 114.0, 107.9, 107.1, 85.0, 79.6, 45.3, 45.2, 41.9, 41.8, 41.0, 35.5, 33.7, 31.7, 31.5, 31.1, 31.0, 30.1, 30.0, 24.8, 24.1, 20.0, 15.9, 13.1, 12.9, 12.4, 9.4, 8.5, 8.4, 8.3, 7.8; IR (NaCl, cm^{-1}) 3036, 2964, 2929, 2872, 1668, 1607, 1509, 1254, 1179; HRMS $[M + H]^+$ calcd for $C_{27}H_{37}O_2$ 393.2794, found 393.2791.

*4,4′-(Propane-2,2-diyl)bis((2,2-diethyl-4-methylcyclobutoxy)-benzene) (**18**), one diastereomer (oil):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.10−7.03 (4H, m), 6.72−6.65 (4H, m), 4.30 (2H, d, J = 7.6 Hz), 2.70−2.65 (2H, m), 1.79−1.70 (4H, m), 1.65−1.56 (8H, m), 1.48 (4H, q, J = 7.6 Hz), 1.38 (2H, dd, J = 11.7, 5.6 Hz), 1.01 6H, d, J = 6.9 Hz), 0.79 (12H, dt, J = 11.0, 7.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.1, 142.7, 127.6, 114.4, 79.6, 45.2, 41.7, 35.4, 31.2, 30.1, 30.0, 24.9,

dx.doi.org/10.1021/jo3028246 | J. Org. Chem. 2013, 78, 2626−2638

15.9, 8.3, 7.8; IR (NaCl, cm^{-1}) 2958, 2932, 2870, 1609, 1512, 1448, 1240, 826; HRMS $[M + H]^+$ calcd for $C_{33}H_{49}O_2$ 477.3733, found 477.3731.

*4,4′-(Propane-2,2-diyl)bis((2,2-diethyl-4-methylcyclobutoxy)-benzene) (**18**), mixture of other diastereomers (oil):* ^1H NMR ($CDCl_3$, 600 MHz) δ 7.13−7.05 (4H, m), 6.79−6.67 (4H, m), 4.30 (1.2H, d, J = 7.6 Hz), 3.95 (0.8H, d, J = 7.6 Hz), 2.70−2.61 (1.2H, m), 2.40−2.29 (0.8H, m), 1.79−1.70 (4H, m), 1.65−1.56 (8H, m), 1.51−1.46 (4H, m), 1.38 (1.2H, dd, J = 11.7, 5.6 Hz), 1.14 (2.4H, d, J = 6.2 Hz), 1.01 (3.6H, d, J = 6.9 Hz), 0.99−0.95 (0.8H, m), 0.79 (12H, dt, J = 11.0, 7.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.6, 156.8, 143.1, 142.6, 127.7, 127.6, 115.1, 114.4, 84.9, 79.6, 45.3, 45.1, 41.7, 35.5, 33.7, 31.7, 31.2, 30.9, 30.1, 30.0, 24.8, 24.1, 20.0, 15.9, 8.5, 8.4, 8.3, 7.8; IR (NaCl, cm^{-1}) 2961, 2931, 2870, 1607, 1516, 1448, 1241, 825; HRMS $[M + H]^+$ calcd for $C_{33}H_{49}O_2$ 477.3733, found 477.3731.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving additional data and ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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