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Functionalized Allyl Aryl Ethers Synthesis from Benzoic Acids Using Dearomatization and Decarboxylative Allylation Approach

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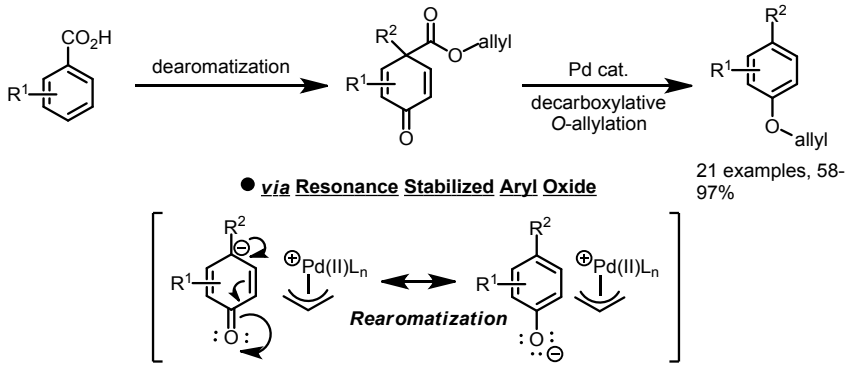
Supporting Information Placeholder



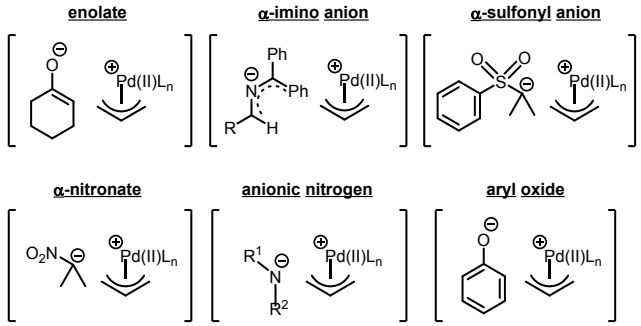
ABSTRACT: A strategy towards the preparation of substituted allyl aryl ethers from benzoic acids via a dearomatization and decarboxylative allylation (DcA) reaction is presented. The benzoic acids undergo a dearomatization to give alkylated 2,5-cyclohexadienyl ketoesters which are subjected to a palladium-catalyzed DcA reaction providing a variety of functionalized allyl aryl ethers. In addition, the combination of resonance stabilized DcA reaction with a Claisen rearrangement for the synthesis of multi-substituted phenols and applying to dihydroplicatin B derivative synthesis is also presented.

INTRODUCTION

Functionalized arenes are important scaffolds for the preparation of natural products, pharmaceuticals, and functional materials. Among all of the functionalized arenes, allyl aryl ethers particularly draw our attention because they are key precursors used in natural product synthesis.[1] For instance, allyl aryl ethers can undergo aryl-Claisen [3,3]-sigmatropic rearrangements[2] providing *ortho*-allyl phenols followed by cyclization to give dihydrobenzofurans,[3] which are important backbones in many biologically active molecules.[4] Moreover, isochroman and dioxabicyclooctane scaffolds can be prepared through Friedel-Crafts type cyclizations of allyl aryl ethers.[5]

Generally, the Williamson ether synthesis is a classical method for the preparation of allyl aryl ethers.[6] This protocol involves the S_N2 attack of a phenoxide with allyl halides or tosylates. However, a stoichiometric amount of a base and an unhindered alkylating reagent are often required under these reaction conditions. Recently, the transition metal-catalyzed decarboxylative allylation (DcA) of allyl aryl carbonates or vinyl cyclic carbonates have been used to prepare allyl aryl ethers with advantages over the Williamson ether synthesis. These catalytic process are conducted under neutral conditions with broad substrate scope of allyl moieties in a regioselective and/or enantioselective manner.[7] Typically, allyl aryl carbonates are prepared by reaction of phenols with allyl chloroformates under basic conditions.[7f] Nevertheless, some phenolic substrates bearing multi-substituents are not readily available. Hence, extending the substrate scope of highly substituted allyl aryl ethers to improve the synthetic potentials in bioactive molecules synthesis is of particular interests.

Scheme 1. Various Intermediates in DcA Reactions

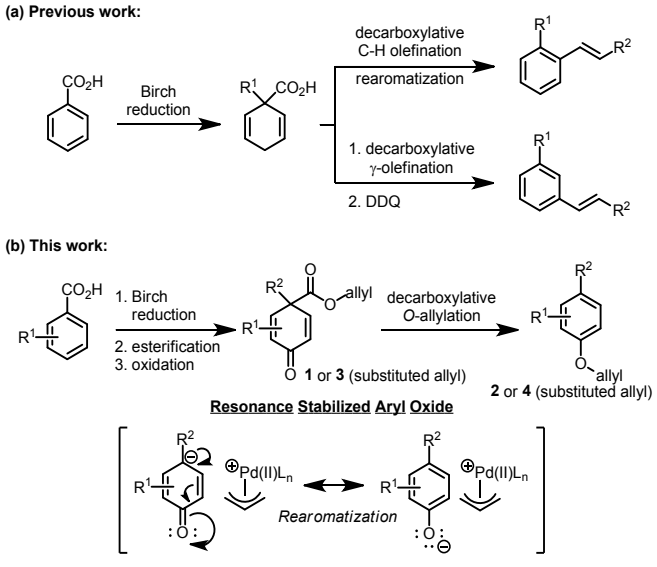


Earlier studies have shown that DcA reactions can be carried out using a wide range of starting materials. During the DcA process, it is thought that the reactants can form a stable carbon or heteroatom nucleophiles *via* decarboxylation.[8] For example, enolates,[9] α-imino anions,[10] α-sulfonyl anions,[11] α-nitronates,[12] anionic nitrogens,[13] and aryl oxides[7] can act as good

nucleophiles toward Pd-π-allyl-complexes in DcA reactions to furnish carbon-carbon or carbon-heteroatom bond formations (Scheme 1). We recently developed two protocols for the preparation of *ortho*-alkylated vinylarenes or *meta*-alkylated vinylarenes through the dearomatization of benzoic acids affording alkylated 2,5-cyclohexadiene-1-carboxylic acids followed by decarboxylative C-H olefination[14] and decarboxylative γ−olefination/rearomatization,[15] respectively (Scheme 2a).

In light of the above, we investigated ways in which to expand the reaction repertoire of alkylated 2,5-cyclohexadiene-1-carboxylic acids.[14-16] We envisioned that the cross-conjugated ketoesters **1** or **3** derived from alkylated 2,5-cyclohexadiene-1-carboxylic acids by sequential Birch reduction, esterification and oxidation, (see Supporting Information (SI) for details), can be utilized in Pd-catalyzed decarboxylative allylic etherification reactions. During the DcA reaction, the aromaticity of the products can be regained due to the formation of a resonance stabilized aryl oxide intermediate (Scheme 2b). This reaction will be referred to as the resonance stabilized DcA (RSDcA) reaction. Upon reaction of an aryl oxide with a Pd-π-allyl complex, highly substituted allyl aryl ethers **2** or **4** were formed in high yield (58-97%) with good regioselectivity (Table 2 and 3). Herein, we reported a Pd-catalyzed decarboxylative allylic etherification of cross-conjugated ketoesters via a resonance stabilized intermediate for preparation of functionalized allyl aryl ethers, and its potential application to dihydroplicatin B synthesis.

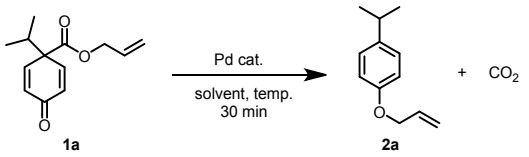
Scheme 2. Regioselective Functionalization of Arenes via Decarboxylative Couplings Approach



RESULTS AND DISCUSSION

We began our investigation of the RSDcA reaction using starting material **1a** in various solvents at elevated or room temperature. By using 5 mol % of $Pd(PPh_3)_4$ in toluene at 110 °C for 1 h, the decarboxylative *O*-allylation product **2a** was obtained and isolated in 8% yield (Table 1, entry 1). We also isolated 2-allyl-4-isopropylphenol (48%) and 4-isopropylphenol (44%) as byproducts, produced from a Claisen rearrangement of compound **2a**. Next, we replaced the $Pd(PPh_3)_4$ with $Pd(dba)_2$. However, the yield dropped dramatically and compound **1a** was recovered, regardless of which of the three solvents (toluene, tetrahydrofuran, acetonitrile) that were used (entries 2-4). Pleasingly, we obtained up to 95% yield by simply lowering the reaction temperature to room temperature in the presence of $Pd(PPh_3)_4$ (entry 5). The effect of various solvents at room temperature was also studied and the resulting product yields were nearly the same. To study the effect of catalyst loading, 1 mol % of $Pd(PPh_3)_4$ was tested, but resulted in poorer yield (entry 8). Therefore, we used 5 mol % of $Pd(PPh_3)_4$ in acetonitrile at rt as the standard conditions in the following experiments.

Table 1. Optimization of the Pd-Catalyzed RSDcA Reaction[a]



entry	Pd (mol %)	solvent	T (°C)	yield (%)[b]
1	$Pd(PPh_3)_4$ (5)	toluene	110	8[c]
2	$Pd(dba)_2$ (5)	toluene	r.t.	<5[d]
3	$Pd(dba)_2$ (5)	THF	r.t.	<5[d]
4	$Pd(dba)_2$ (5)	acetonitrile	r.t.	<5[d]
5	$Pd(PPh_3)_4$ (5)	toluene	r.t.	95
6	$Pd(PPh_3)_4$ (5)	THF	r.t.	95
7	$Pd(PPh_3)_4$ (5)	acetonitrile	r.t.	95
8	$Pd(PPh_3)_4$ (1)	acetonitrile	r.t.	<1[d]

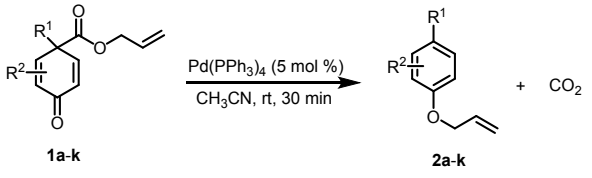
[a]Reaction conditions: **1a**, 0.1 mmol in 1.0 mL solvent under argon atmosphere. [b]Isolated yield. [c]2-Allyl-4-isopropylphenol and 4-isopropylphenol were isolated as byproducts. [d]Recovering of **1a**.

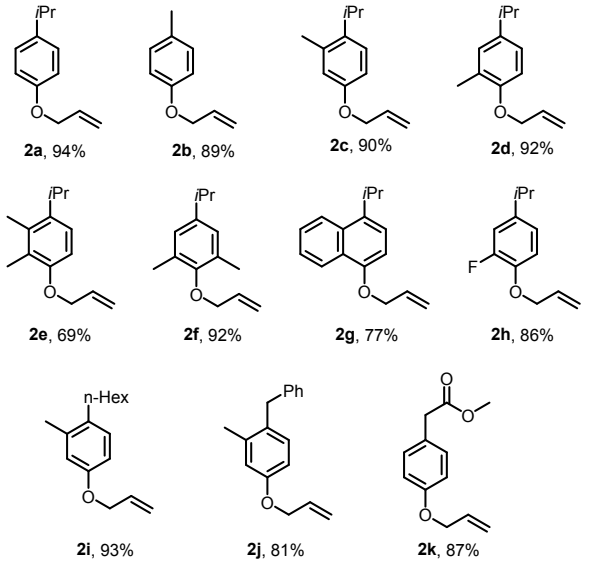
With the optimized reaction conditions in hand, the substrate scope of the RSDcA reaction shown in Scheme 2B was investigated. As is shown in Table 2, a series of cross-conjugated ketoesters **1** were prepared and applied under the optimized conditions to give substituted allyl aryl ethers **2a**−**2k** in good to excellent yields. The reaction tolerates a wide range of substituents at the 1-position of compound **1** including, methyl, isopropyl, *n*-hexyl, benzyl, and methylene methyl ester groups (**2a**, **2b**, **2i**, **2j**, and **2k**). An additional methyl or fluoro substituent at the 2- or 3-position of the cross-conjugated ketoester was well tolerated and the reaction furnished tri-substituted aryl allyl ethers (**2c**, **2d**, **2h**, **2i**, and **2j**) in 70-90% isolated yields. In addition, highly substituted substrates, **1e** and **1g**, were compatible with this procedure, providing corresponding compounds **2e** and **2g** in good yield. Notably, the sterically hindered substrate **1f**, afforded the corresponding 2,4,6-substituted aryl allyl ether **2f** in 92% yield under our RSDcA reaction conditions.

Next, the regioselectivity of the RSDcA reaction was investigated by varying the allyl substituents of compounds **3**, and the resulting decarboxylative *O*-allylation products of **4** are shown in Table 3. The non-fluorinated or fluorinated cross-

conjugated ketone esters with prenyl substituent provided the branched allylation products exclusively in good yields (entries 1 and 2). The 1-methylallyl substrate gave branched allylation products with moderate regioselectivies and yields (entries 3 and 4). 3-alkyl-substituted allyl substrate was also compatible with this procedure and resulted in 92% yield but with nearly no regioselectivity (entry 5). The RSDcA reaction of 2-methylallyl derivatives proceeded smoothly and provided products in good yields (entries 6 and 7). Notably, cinnamyl substrate **3h** and 1-phenylallyl substrate **3j** both gave linear allylation product **4h** exclusively in good yields. However, the reaction of fluorinated cinnamyl substrate **3i** showed poor regioselectivity and resulted in linear product to branched product in 1/0.57 ratio. These results suggest that the regioselectivity of the RSDcA reaction is highly dependent on the structures of the starting materials, strongly suggesting that product formation is under kinetic control. This conclusion is consistent with the iron-catalyzed decarboxylative etherification of carbonates reported by Tunge's group in 2009.[7d]

Table 2. Substrate Scope for the RSDcA Reaction[a,b]

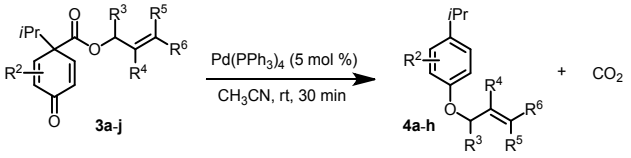


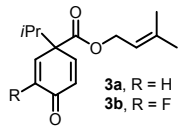
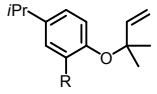
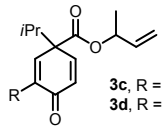
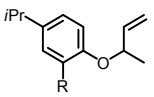
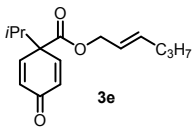
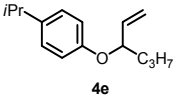
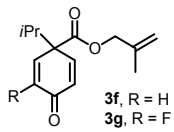
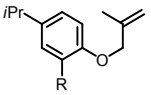
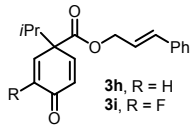
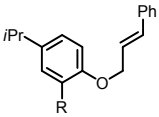
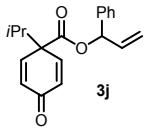
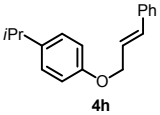


[a]Reaction was performed with **1** (0.2-0.5 mmol), and 5 mol % of $Pd(PPh_3)_4$ in 1 mL of acetonitrile. [b]Isolated yields.

Based on our experiment results, we propose a plausible mechanism for the RSDcA (Scheme 3). The reaction substrate **3** is first ionized by the Pd(0) catalyst to afford a Pd–π–allyl species and carboxylate ion pair **A**. Next, the decarboxylation of carboxylate occurs to give the cyclohexadienone anion and Pd–π–allyl species ion pair **B**. The cyclohexadienone anion then rearomatizatizes generating a stable aryloxide intermediate **C**. Finally, the *O*-allylation of aryloxide occurs with Pd–π–allyl species to afford a branched or linear allyl aryl ether **4** as a kinetic product, regenerating the Pd(0) catalyst completing the catalytic cycle.

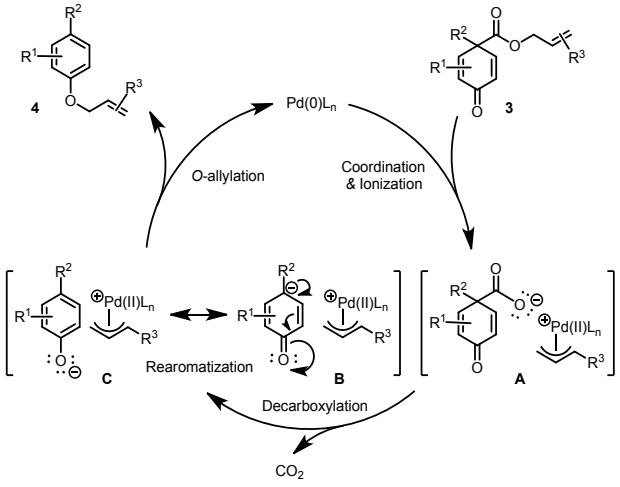
Table 3. Substrate Scope of Allyl Electrophiles[a]



Entry	Substrate	Product	Yield (%)[b]
1, 2	 **3a**, R = H **3b**, R = F		**4a**, R = H, 70%[c] **4b**, R = F, 80%[c]
3, 4	 **3c**, R = H **3d**, R = F		**4c**, R = H, 78%[c] (l:b = 0.31:1)[d] **4d**, R = F, 73%[c] (l:b = 0.23:1)[d]
5	 **3e**	 **4e**	92% (l:b = 0.95:1)[d]
6, 7	 **3f**, R = H **3g**, R = F		**4f**, R = H, 91% **4g**, R = F, 92%
8, 9	 **3h**, R = H **3i**, R = F		**4h**, R = H, 97% **4i**, R = F, 95% (l:b = 1:0.57)[d]
10	 **3j**	 **4h**	90%

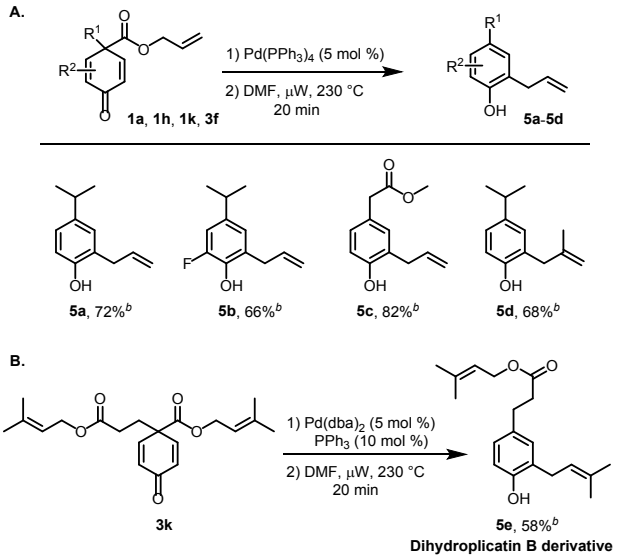
[a]Reaction was performed with **3** (0.1-0.2 mmol), and 5 mol % of $Pd(PPh_3)_4$ in 1 mL of acetonitrile. [b]Isolated yields. [c]5 mol % of $Pd(dba)_2$ and 10 mol % of PPh_3 was used. [d]Ratio was determined by ^1H NMR, l: linear, b: branched.

Scheme 3. Proposed Mechanism for the RSDcA Reaction



The Claisen rearrangement of allyl aryl ethers is a useful method in natural product synthesis.[2] Hence, we investigate the *O*-allylation products of **1a**, **1h**, **1k**, and **3f** under microwave assisted Claisen rearrangement (Scheme 4A). The product yields of this reaction towards highly substituted phenols are considerably high (**5a**−**d**, 66-82%). Furthermore, we utilized this protocol for the synthesis of dihydroplicatin B derivative (Scheme 4B, **5e**), whereas its methyl ester analogues have antimutagenic activity.[17] Satisfyingly, this synthetic strategy achieved dihydroplicatin B derivative in about 30% overall yield in five steps starting from commercially available benzoic acid (see details in the SI).

Scheme 4. (A) RSDcA and Microwave Assistance Claisen Rearrangement. (B) Approach to Dihydroplicatin B Derivative (5e)[a]



[a]Step 2 were performed on 0.23-0.63 mmol reaction scale in 1 mL of DMF. [b]Combined yields of two steps.

CONCLUSIONS

In conclusion, we have developed a protocol for the synthesis of versatile allyl aryl ethers from readily available benzoic acids. This reaction protocol consists of a dearomatization of benzoic acids by Birch reductive alkylation, and rearomatization of the alkylated 2,5-cyclohexadienyl ketoesters by a Pd-catalyzed decarboxylative allylic etherification. The yields of the RSDcA reaction are generally high and provided diverse allyl aryl ethers with good regioselectivity. Moreover, we utilized the RSDcA reaction with a Claisen rearrangement for the synthesis of dihydroplicatin B derivative. We anticipate the concept of RSDcA reaction can be further applied on carbon−carbon or other carbon−heteroaton bond forming reactions. Indeed, the study of these aforementioned reactions is currently being investigated in our laboratory.

EXPERIMENTAL SECTION

General information. All solvents and reagents were purified according to standard procedures or were used as received from Aldrich, Fluka, Acros, or Lancaster. ^{1}H NMR (300 MHz) spectrum, ^{13}C{^{1}H} NMR (75 MHz) spectrum, and ^{19}F NMR (282 MHz) spectrum were obtained on a Varian-Mercury-300 spectrometer. Chemical shifts for ^{1}H NMR spectrum are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) and are referenced to residual protium in the NMR solvent ($CDCl_3$, δ 7.26). Chemical shifts for ^{13}C NMR spectrum are reported in ppm downfield from TMS and were referenced to the carbon resonances of the solvent ($CDCl_3$, δ 77.0 ppm). Data are represented as follows: chemical shift, multiplicity (s= singlet, d= doublet, t= triplet, q= quartet, p= pentet, m = multiplet), coupling constants in Hertz (Hz), integration. Spectrum were calibrated related to the solvent residual proton and carbon, chemical shift: $CDCl_3$ (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Thin-layer chromatography (TLC) was performed using Merck silica gel 60 F-254 plates, the detection of compounds was performed using ultra violet (UV) light or immerse in a solution of potassium permanganate (1.5 g of $KMnO_4$, 5 g $NaHCO_3$, and 400 mL H_2O) followed by heating the TLC plates. Flash column chromatography was performed using Merck silica gel 60 (40-63 μm) with an applied pressure of 0.5 bar. High Resolution Mass (**HRMS**) Spectra were obtained on a Finnigan/Thermo Quest MAT 95XL (EI), Thermo Scientific TSQ Quantum Triple Quadrupole (ESI and APCI), JEOL JMS-700 (FAB). Melting points were obtained using a Fargo MP-2D capillary melting point apparatus. The microwave assisted reactions were performed using a CEM discover SP microwave synthesis system with a sealed reaction vessels, the reaction temperature was monitored through external surface sensor.

General procedure of Birch reductive alkylation. To a 250 mL round bottle benzoic acid/benzoic acid derivatives (1 equiv.) was added. The bottle was vacuumed and filled with Argon (Ar) gas. Then started to condense liquid ammonia at -78 °C. Lithium metal (Li) (2.5 equiv.) was added in to the solution, the color of solution became dark blue after the addition of lithium was finished. After 1 hour, the alkyl halide (3 equiv.) was added in to the solution and reaction for 1 hour. The liquid ammonia was evaporated overnight, and the residue was dissolved in 200 mL of water. Concentrated hydrochloric acid (HCl) was added until pH 1-2. After the addition of HCl, solution was extracted with diethyl ether. The organic phase was washed with 10% $NaHCO_{3(aq)}$ and saturated $NaCl_{(aq)}$. The organic phase was dried over $MgSO_4$ and concentrated by rotary evaporator. Compound **1aa-1ka**,[14] or **3ka** were purified by recrystallization or column chromatography (see chemical structures in the SI).

General procedure of the allylation of cyclohexadiene carboxylic acids. Allyl bromide (1.5 equiv.) was added into a solution contain K_2CO_3 (1.2 equiv.) and compounds **1aa-1ka** in dry dimethylformamide (DMF) under Ar gas at room temperature. The solution was then heated up to 75 °C for 30 minutes. After 30 minutes, the reaction mixture was cool to room temperature by ice-water bath. Water was added into the reaction solution, then extracted with diethyl ether. Organic phase was washed with 10% $NaHCO_{3(aq)}$, saturated $NaCl_{(aq)}$, and dried over $MgSO_4$. Concentrated by rotary evaporator to give compounds **1ab-1kb** without further purification. Compounds **1ab-1kb** were synthesized from a modified literature procedure.[18]

General procedure of the allylation of cyclohexadiene carboxylic acids to give substituted allyl esters. Oxalyl chloride (2 equiv.) was added to a solution of compound **1aa** or **1ha** (1 equiv.) in dry DCM under Ar gas. The solution was put into ice-water bath, then added few drops of DMF. The reaction mixture then started to bubble. After 1 hour, the solvent was removed under vacuum. Yellow-white solid was obtained. Dry DCM was added into the reaction container under Ar gas. A solution contained substituted allyl alcohol (1.1 equiv.), pyridine (1.2 equiv.), DMAP (catalytic amount) in DCM was added and the reaction was carried out overnight under Ar gas. 10% HCl was added to the reaction mixture and extracted with diethyl ether. The organic phase was washed by 10% $NaHCO_{3(aq)}$, saturated $NaCl_{(aq)}$, and dried over $MgSO_4$. Concentrated by rotary evaporator to give compounds

3ab-3jb with further purification by column chromatography. Compounds **3ab-3jb** were synthesized from a modified literature procedure.[19]

General procedure of the allylic oxidation of cyclohexadiene esters. Method A, cooper iodide (0.03 equiv.) was added into the solution contain compound **1ab-1kb** or **3ab-3gb** or **3kb** (1 equiv.) in acetonitrile. *tert*-Butyl hydroperoxide (TBHP) (7 equiv.) was added into the solution. The reaction mixture was reflux overnight. 10% of $Na_2S_2O_3$ was added to the solution after cooling down to room temperature. The solution was extracted with diethyl ether. Organic phase was washed by 10% $NaHCO_{3(aq)}$ and saturated $NaCl_{(aq)}$, then dried over $MgSO_4$. The solvent was removed by rotary evaporator to give compounds **1a-1k** or **3a-3g** or **3k** with further purification by column chromatography. Compounds **1a-1k** or **3a-3g** or **3k** were synthesized from a modified literature procedure.[20]

General procedure of the allylic oxidation of cyclohexadiene esters. Method B, 3,5-dimethylpyrazole (3,5-DMP) (1 equiv.) and chromium trioxide (CrO_3) (1 equiv.) was added into dry DCM at −20 °C and stirred at −20 °C for 10 minutes. Compound **3eb** or **3hb-3jb** was added into the solution and stir overnight at room temperature. The solution was cooled to 0 °C and $NaOH_{(aq)}$ (5 M) was added. The solution was extracted with diethyl ether. Organic phase was washed by 10% $NaHCO_{3(aq)}$ and saturated $NaCl_{(aq)}$, then dried over $MgSO_4$. The solvent was removed by rotary evaporator to give compounds **3e** or **3h-3j** with further purification by column chromatography. Compounds **3e** or **3h-3j** were synthesized from a modified literature procedure.[21]

General procedure of the Pd-catalyzed RSDcA reaction for allyl aryl ethers synthesis. Compounds **1a-1k** or **3a-3k** and $Pd(PPh_3)_4$ (5 mol%) or $Pd(dba)_2$ (5 mol%) were added into the reaction container. Acetonitrile was added into the container under Ar gas. The reaction was traced by TLC, after 1 hour at room temperature showed full conversion of the reactant. The mixture was filtered with celite to give the crude reaction mixture, then purified by silicagel column chromatography to afford the allyl aryl ether products**2a-2k** or **4a-4j**.

General procedure of the microwave-assisted Claisen rearrangement for allyl aryl ethers. Compound **2a**, **2h**, **2k**, **4f**, or **4k** was added to reaction vessel contain DMF and magnetic stirring bar. Followed by microwave-assisted Claisen rearrangement in a sealed reaction vessel, the solution undergoes microwave irradiation at 230 °C for 20 minutes. Saturated $NaHCO_{3(aq)}$ was added to the reaction mixture, then extracted with diethyl ether. The combined organic phase was washed by saturated $NaCl_{(aq)}$ and dried over $MgSO_4$. The solvent was removed through rotary evaporator to give compounds **5a-5e** with further purification by column chromatography. Compounds **5a-5e** were synthesized from a modified literature procedure.[22]

*Allyl 1-isopropylcyclohexa-2,5-dienecarboxylate **(1ab)***. According to general procedure, compound **1aa** (670 mg, 4 mmol), allyl bromide (0.52 mL, 6.0 mmol), and K_2CO_3 (663 mg, 4.8 mmol) in dry DMF (10 mL). Compound **1ab** was achieved as colorless liquid without further purification (817 mg, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.11-5.87 (m, 3H), 5.85-5.66 (m, 2H), 5.41-5.14 (m, 2H), 4.60 (d, *J*= 5.6 Hz, 2H), 2.62 (s, 2H), 2.12 (m, 1H), 0.83 (d, *J*= 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.5, 132.2, 126.4, 125.7, 118.0, 65.1, 52.0, 35.8, 26.5, 17.3. HRMS (EI) calculated for $C_{13}H_{18}O_2$ ([M]$^+$): 206.1307. Found: 206.1305.

*Allyl 1-methylcyclohexa-2,5-dienecarboxylate **(1bb)***. According to general procedure, compound **1ba** (600 mg, 4.3 mmol), allyl bromide (0.56 mL, 6.5 mmol), and K_2CO_3 (709 mg, 5.2 mmol) in dry DMF (10 mL). Compound **1bb** was achieved as colorless liquid without further purification (750 mg, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.97-5.76 (m, 5H), 5.30 (m, 1H), 5.23-5.19 (m, 1H), 4.59-4.57 (m, 2H) , 2.67-2.64 (m, 2H), 1.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.8, 132.1, 128.5, 124.5, 117.7, 65.2, 43.8, 27.3, 25.8. HRMS (ESI) calculated for $C_{11}H_{14}NaO_2$ ([M+Na]$^+$): 201.0891. Found: 201.0886.

*Allyl 1-isopropyl-2-methylcyclohexa-2,5-dienecarboxylate **(1cb)***. According to general procedure, compound **1ca** (500 mg, 2.8 mmol), allyl bromide (0.36 mL, 4.2 mmol), and K_2CO_3 (459 mg, 3.3 mmol) in dry DMF (10 mL). Compound **1cb** was achieved as colorless liquid without further purification (591 mg, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.01-5.84 (m, 2H), 5.66-5.63 (m, 2H), 5.33-5.26 (m, 1H), 5.22-5.18 (m, 1H) , 4.61-4.58 (m, 2H), 2.68-2.64 (m, 2H), 2.60-2.46 (m, 1H), 1.70 (s, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.72 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 132.3, 131.5, 126.3, 124.0, 123.4, 117.7, 65.1, 55.4, 31.4, 26.9, 19.5, 17.8, 17.1. HRMS (EI) calculated for $C_{14}H_{20}O_2$ ([M]$^+$): 220.1463. Found: 220.1461.

*Allyl 1-isopropyl-3-methylcyclohexa-2,5-dienecarboxylate **(1db)***. According to general procedure, compound **1da** (500 mg, 2.8 mmol), allyl bromide (0.36 mL, 4.2 mmol), and K_2CO_3 (459 mg, 3.3 mmol) in dry DMF (10 mL). Compound **1db** was achieved as colorless liquid with further purification by flash column chromatography (EA/Hexane) (397 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.99-5.86 (m, 2H), 5.78-5.73 (m, 1H), 5.46-5.45(m, 1H), 5.35-5.28 (m, 1H), 5.24-5.19 (m, 1H), 4.57-4.60 (m, 2H), 2.52 (s, 2H), 2.16-2.07 (m, 1H), 1.7 (s, 3H), 0.82 (d, *J* = 3.7 Hz, 3H), 0.79 (d, *J* = 3.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.8, 133.7, 132.3, 126.3, 125.2, 120.5, 117.8, 65.1, 53.2, 36.0, 31.3, 23.2, 17.3. HRMS (EI) calculated for $C_{14}H_{20}O_2$ ([M]$^+$): 220.1463. Found: 220.1470.

*Allyl 1-isopropyl-2,3-dimethylcyclohexa-2,5-dienecarboxylate **(1eb)***. According to general procedure, compound **1ea** (500 mg, 2.6 mmol), allyl bromide (0.33 mL, 3.9 mmol), and K_2CO_3 (426 mg, 3.1 mmol) in dry DMF (10 mL). Compound **1eb** was achieved as colorless liquid with further purification by flash column chromatography (EA/Hexane) (429 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.02-5.80 (m, 2H), 5.66-5.55 (m, 1H), 5.32-5.13 (m, 2H), 4.58 (d, *J* = 5.5 Hz, 2H), 2.67-2.43 (m, 3H), 1.68 (s, 3H), 1.62 (s, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.66 (d, *J* = 6.9 Hz,3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.9, 132.4, 128.1, 126.3, 124.1, 123.8, 117.6, 65.0, 56.4, 33.1, 31.9, 19.4, 18.1, 17.3, 13.5. HRMS (EI) calculated for $C_{15}H_{22}O_2$ ([M]$^+$): 234.1620. Found: 234.1623.

*Allyl 1-isopropyl-3,5-dimethylcyclohexa-2,5-dienecarboxylate **(1fb)***. According to general procedure, compound **1fa** (500.0 mg, 2.6 mmol), allyl bromide (0.33 mL, 3.9 mmol), and K_2CO_3 (426 mg, 3.1 mmol) in dry DMF (10 mL). Compound **1fb** was achieved as colorless liquid without further purification (596 mg, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.99-5.86 (m, 1H), 5.45 (s, 2H), 5.34-5.19 (m, 2H), 4.58 (d, *J* = 5.5 Hz, 2H), 2.43 (s, 2H), 2.17-2.03 (m, 1H), 1.76 (s, 6H), 0.78 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.2, 133.6, 132.4, 120.0, 117.7, 65.0, 54.4, 36.2, 23.0, 17.4. HRMS (EI) calculated for $C_{15}H_{22}O_2$ ([M]$^+$): 234.1620. Found: 234.1627.

*Allyl 1-isopropyl-1,4-dihydronaphthalene-1-carboxylate **(1gb)***. According to general procedure, compound **1ga** (500 mg, 2.3 mmol), allyl bromide (0.30 mL, 3.5 mmol), and K_2CO_3 (382 mg, 2.8 mmol) in dry DMF (10 mL). Compound **1gb** was achieved as colorless liquid without further purification (565 mg, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54-7.51 (m, 1H), 7.21-7.11 (m, 3H), 6.23-6.17 (m, 1H), 5.91-5.78 (m, 2H), 5.23-5.12 (m, 2H), 4.65-4.50 (m, 2H), 3.42-3.39 (m, 2H), 2.79-2.66 (m, 1H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.54 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.0, 135.2, 134.3, 132.0, 128.3, 126.5, 126.4, 126.3, 123.7, 117.7, 65.4, 54.8, 37.6, 29.7, 18.5, 17.0. HRMS (EI) calculated for $C_{17}H_{20}O_2$ ([M]$^+$): 256.1463. Found: 256.1465.

*Allyl 3-fluoro-1-isopropylcyclohexa-2,5-dienecarboxylate **(1hb)***. According to general procedure, compound **1ha** (600 mg, 3.3 mmol), allyl bromide (0.42 mL, 4.9 mmol), and K_2CO_3 (540 mg, 3.9 mmol) in dry DMF (10 mL). Compound **1hb** was achieved as colorless liquid without further purification (738 mg, 99%). ^{1}H

NMR (300 MHz, $CDCl_3$): δ 5.98-5.71 (m, 3H), 5.38-5.34 (m, 1H), 5.32-5.28 (m, 1H), 5.21-5.26 (m, 1H), 4.61-4.58 (m, 2H), 2.82-2.80 (m, 2H), 2.19-2.10 (m, 1H), 0.83 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.8, 158.6 (d, *J* = 255.2 Hz), 131.9, 126.6 (d, *J* = 2.8 Hz), 123.7 (d, *J* = 10.5 Hz), 118.3, 101.6 (d, *J* = 17.6 Hz), 65.4, 55.0 (d, *J* = 7.6 Hz),, 35.8, 27.1 (d, *J* = 26.6 Hz), 17.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ −102.7 (ddd, *J* = 17.9, 7.6, 2.8 Hz). HRMS (EI) calculated for $C_{13}H_{17}FO_2$ ($[M]^+$): 224.1213. Found: 224.1217.

*Allyl 1-hexyl-2-methylcyclohexa-2,5-dienecarboxylate (**1ib**)*. According to general procedure, compound **1ia** (500 mg, 2.3 mmol), allyl bromide (0.30 mL, 3.4 mmol), and K_2CO_3 (373 mg, 2.7 mmol) in dry DMF (10 mL). Compound **1ib** was achieved as colorless liquid with further purification by flash column chromatography (EA/ Hexane) (354 mg, 60%). ^1H NMR (300 MHz, $CDCl_3$) δ 6.05-5.76 (m, 2H), 5.72-5.58 (m, 1H), 5.45 (d, J= 9.9 Hz, 1H), 5.35-5.13 (m, 2H), 4.67-4.47 (m, 2H), 2.80-2.55 (m, 2H), 1.98-1.80 (m, 1H), 1.56-1.75 (m, 4H), 1.36-1.20 (m, 6H), 1.18-0.93 (m, 2H), 0.92-0.76 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2, 132.2, 131.1, 127.7, 126.0, 123.1, 117.6, 65.2, 51.7, 34.5, 31.7, 29.5, 26.9, 23.8, 22.6, 19.7, 14.0. HRMS (EI) calculated for $C_{17}H_{26}O_2$ ($[M]^+$): 262.1933. Found: 262.1923.

*Allyl 1-benzyl-2-methylcyclohexa-2,5-dienecarboxylate (**1jb**)*. According to general procedure, compound **1ja** (500 mg, 2.2 mmol), allyl bromide (0.27 mL, 3.3 mmol), and K_2CO_3 (364 mg, 2.64 mmol) in dry DMF (10 mL). Compound **1jb** was achieved without further purification (550 mg, 93%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.33-7.02 (m, 5H), 6.02-5.85 (m, 1H), 5.84-5.71 (m, 1H), 5.68-5.47 (m, 2H), 5.39-5.15 (m, 2H), 4.77-4.55 (m, 2H), 3.28-3.02 (m, 2H), 2.57-2.37 (m, 1H), 2.13-1.93 (m, 1H), 1.92-1.72 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8, 137.2, 132.1, 130.5, 130.3, 127.3, 126.9, 126.3, 126.0, 124.2, 118.1, 77.4, 77.0, 76.5, 65.5, 53.0, 40.5, 26.5, 20.0. HRMS (EI) calculated for $C_{18}H_{20}O_2$ ($[M]^+$): 268.1463. Found: 268.1469.

*Allyl 1-(2-methoxy-2-oxoethyl)cyclohexa-2,5-dienecarboxylate (**1kb**)*. According to general procedure, compound **1ka** (500 mg, 2.6 mmol), allyl bromide (0.33 mL, 3.8 mmol), and K_2CO_3 (422 mg, 3.1 mmol) in dry DMF (10 mL). Compound **1kb** was achieved as colorless liquid without further purification (524 mg, 87%). ^1H NMR (300 MHz, $CDCl_3$): δ 5.97- 5.80 (m, 5H), 5.35-5.28 (m, 1H), 5.24-5.19 (m, 1H), 4.63-4.61 (m, 2H), 3.65 (s, 3H), 2.76 (s, 2H), 2.70-2.66 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.1, 170.8, 132.0, 126.4, 126.2, 117.8, 65.7, 51.6, 51.6, 45.7, 44.2, 26.0. HRMS (EI) calculated for $C_{13}H_{16}O_4$ ($[M]^+$): 236.1044. Found: 236.1052.

*Allyl 1-isopropyl-4-oxocyclohexa-2,5-dienecarboxylate (**1a**)*. According to general procedure, compound **1ab** (2.1 g, 10.2 mmol), CuI (59 mg, 0.31 mmol), and TBHP (9.87 mL, 71.7 mmol) in CH_3CN (35 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **1a** as colorless liquid (1.3 g, 56%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.07-7.04 (d, 2H), 6.43-6.39 (d, 2H), 5.97-5.84 (m, 1H), 5.36-5.26 (m, 2H), 4.66-4.63 (m, 2H), 2.53-2.44 (m, 1H), 0.93 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.2, 170.0, 147.0, 130.9, 119.3, 109.9, 66.4, 56.5, 36.6, 17.6. HRMS (EI) calculated for $C_{13}H_{16}O_3$ ($[M]^+$): 220.1099. Found: 220.1097.

*Allyl 1-methyl-4-oxocyclohexa-2,5-dienecarboxylate (**1b**)*. According to general procedure, compound **1bb** (831 mg, 4.7 mmol), CuI (27 mg, 0.14 mmol), and TBHP (3.30 mL, 32.6 mmol) in CH_3CN (23.3 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **1b** as colorless liquid (480 mg, 54%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.06 (d, *J* = 10.2 Hz, 2H), 6.31 (d, *J* = 10.4 Hz, 2H), 5.95-5.82 (m, 1H), 5.33-5.24 (m, 2H), 4.64-4.61 (m, 2H), 1.57 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.9, 170.3, 148.8, 131.1, 129.0, 119.0, 66.5, 48.2, 24.8. HRMS (EI) calculated for $C_{11}H_{12}O_3$ ($[M]^+$): 192.0786. Found: 192.0784.

*Allyl 1-isopropyl-2-methyl-4-oxocyclohexa-2,5-dienecarboxylate (**1c**)*. According to general procedure, compound **1cb** (500 mg, 2.3 mmol), CuI (14 mg, 0.07 mmol), and TBHP (1.99 mL, 15.9 mmol) in CH_3CN (11.35 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **1c** as colorless liquid (268 mg, 50%). ^1H NMR (300 MHz, $CDCl_3$): δ 6.97 (d, *J* = 10.3 Hz, 1H), 6.46 (d, *J* = 10.3, 1H), 6.28-6.25 (m, 1H), 5.91-5.78 (m, 1H), 5.31-5.21 (m, 2H), 4.61-4.58 (m, 2H), 2.78-2.69 (m, 1H), 2.01 (s, 3H), 1.12 (d, *J* = 6.7 Hz, 3H), 0.68 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.6, 169.5, 156.3, 145.4, 131.1, 130.7, 130.5, 118.9, 66.3, 59.6, 33.7, 19.9, 18.9, 16.4. HRMS (EI) calculated for $C_{14}H_{18}O_3$ ($[M]^+$): 234.1256. Found: 234.1253.

*Allyl 1-isopropyl-3-methyl-4-oxocyclohexa-2,5-dienecarboxylate (**1d**)*. According to general procedure, compound **1db** (364 mg, 1.8 mmol), CuI (10 mg, 0.05 mmol), and TBHP (1.58 mL, 12.6 mmol) in CH_3CN (9.00 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **1d** as colorless liquid (219 mg, 52%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.04-6.98 (m, 1H), 6.82-6.79 (m, 1H), 6.41-6.36 (m, 1H), 5.97-5.82 (m, 1H), 5.36-5.23 (m, 2H), 4.65-4.61 (m, 2H), 2.50-2.39 (m, 1H), 1.95-1.93 (m, 3H), 0.93-0.87 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.9, 170.5, 146.5, 142.3, 137.4, 131.3, 130.6, 119.0, 66.2, 56.4, 36.6, 17.7, 17.6, 16.1. HRMS (EI) calculated for $C_{14}H_{18}O_3$ ($[M]^+$): 234.1256. Found: 234.1263.

*Allyl 1-isopropyl-2,3-dimethyl-4-oxocyclohexa-2,5-dienecarboxylate (**1e**)*. According to general procedure, compound **1eb** (388 mg, 1.7 mmol), CuI (10 mg, 0.05 mmol), and TBHP (1.49 mL, 11.9 mmol) in CH_3CN (9.00 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **1e** as colorless liquid (236 mg, 56%). ^1H NMR (300 MHz, $CDCl_3$): δ 6.90 (d, *J* = 10.2 Hz, 1H), 6.49 (d, *J* = 10.2 Hz, 1H), 5.91-5.76 (m, 1H), 5.27-5.19 (m, 2H), 4.6-4.54 (m, 2H), 2.81-2.67 (m, 1H), 1.93 (d, *J* = 9.3, 6H), 1.11 (d, *J* = 6.8 Hz, 3H), 0.60 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.0, 170.0, 149.7, 144.3, 135.0, 131.3, 130.4, 118.6, 66.0, 59.5, 33.4, 19.1, 16.6, 15.9, 11.2. HRMS (EI) calculated for $C_{15}H_{20}O_3$ ($[M]^+$): 248.1412. Found: 248.1417.

*Allyl 1-isopropyl-3,5-dimethyl-4-oxocyclohexa-2,5-dienecarboxylate (**1f**)*. According to general procedure, compound **1fb** (596 mg, 2.5 mmol), CuI (15 mg, 0.076 mmol), and TBHP (2.23 mL, 17.8 mmol) in CH_3CN (10.00 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **1f** as colorless liquid (334 mg, 53%). ^1H NMR (300 MHz, $CDCl_3$): δ 6.79 (s, 2H), 5.98-5.85 (m, 1H), 5.35-5.25 (m, 2H), 4.64-4.62 (m, 2H), 2.47-2.38 (m, 1H), 1.95 (s, 6H), 0.88 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.5, 171.1, 141.9, 137.0, 131.5, 118.9, 66.1, 55.8, 36.6, 29.6, 17.7, 16.3. HRMS (EI) calculated for $C_{15}H_{20}O_3$ ($[M]^+$): 248.1412. Found: 248.1408.

*Allyl 1-isopropyl-4-oxo-1,4-dihydronaphthalene-1-carboxylate (**1g**)*. According to general procedure, compound **1gb** (566 mg, 2.2 mmol), CuI (13 mg, 0.066 mmol), and TBHP (1.93 mL, 15.4 mmol) in CH_3CN (10.00 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **1g** as colorless liquid (439 mg, 74%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.19 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.62-7.56 (m, 1H), 7.49-7.41 (m, 1H), 7.14 (d, *J* = 10.5 Hz, 1H), 6.68 (d, *J* = 10.5 Hz, 1H), 5.87-5.74 (m, 1H), 5.22-5.14 (m, 2H), 4.67-4.50 (m, 2H), 2.98-2.86 (m, 1H), 1.16 (d, *J* = 6.8 Hz, 3H), 0.46 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.2, 171.4, 145.0, 141.5, 132.9, 132.0, 131.2, 130.5, 127.8, 126.6, 126.4, 118.6, 66.2, 56.3, 38.3, 19.3, 16.5. HRMS (EI) calculated for $C_{17}H_{18}O_3$ ($[M]^+$): 270.1256. Found: 270.1257.

*Allyl 3-fluoro-1-isopropyl-4-oxocyclohexa-2,5-dienecarboxylate (**1h**)*. According to general procedure, compound **1hb** (738 mg, 3.3 mmol), CuI (19 mg, 0.099 mmol), and TBHP (2.88 mL, 23.0 mmol) in CH_3CN (15.00 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **1h** as

colorless liquid (433 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.07 (d, *J* = 10.1, 1H), 6.61 (d, *J* = 13.3, 1H), 6.48-6.40 (m, 1H), 5.96-5.84 (m, 1H), 5.37-5.28 (m, 2H), 4.68-4.63 (m, 2H), 2.59-2.47 (m, 1H), 0.95 (d, *J* = 13.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ177.9 (d, *J* = 21.7 Hz), 169.4, 154.8 (d, *J* = 264.5 Hz), 148.1 (d, *J* = 2.3 Hz), 130.7 (d, *J*= 44.25 Hz), 122.5 (d, *J* = 15.4 Hz), 119.6, 66.8, 57.9 (d, *J* = 5.5 Hz), 36.9, 17.7 (d, *J* = 25.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −126.90 (dt, *J* = 13.4, 7.8 Hz). HRMS (FAB) calculated for $C_{13}H_{15}FO_3$ ([M]$^+$): 238.1005. Found: 238.1003.

*Allyl 1-hexyl-2-methyl-4-oxocyclohexa-2,5-dienecarboxylate **(1i)***. According to general procedure, compound **1ib** (300 mg, 1.1 mmol), CuI (7 mg, 0.034 mmol), and TBHP (1.00 mL, 8.0 mmol) in CH_3CN (5.0 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **1i** as colorless liquid (194 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.74 (d, *J* = 10.0 Hz, 1H), 6.38 (d, *J* = 10.0, 1H), 6.29-6.25 (m, 1H), 5.90-5.77 (m, 1H), 5.30-5.21 (m, 2H), 4.60-4.56 (m, 2H), 2.17-1.93 (m, 5H), 1.31-1.16 (m, 8H), 0.87-0.83 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.1, 169.9, 156.4, 148.0, 131.1, 130.4, 130.1, 119.0, 66.4, 56.0, 34.4, 31.4, 29.1, 23.1, 22.5, 20.2, 13.9. HRMS (EI) calculated for $C_{17}H_{24}O_3$ ([M]$^+$): 276.1725. Found: 276.1730.

*Allyl 1-benzyl-2-methyl-4-oxocyclohexa-2,5-dienecarboxylate **(1j)***. According to general procedure, compound **1jb** (400 mg, 1.5 mmol), CuI (9 mg, 0.045 mmol), and TBHP (1.31 mL, 10.5 mmol) in CH_3CN (5.0 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **1j** as colorless liquid (259 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20-7.16 (m, 3H), 7.04-7.01 (m, 2H), 6.82 (d, *J* = 10.0 Hz, 1H), 6.25 (d, *J* = 10.0 Hz, 1H), 6.20-6.10 (m, 1H), 5.92-5.79 (m, 1H), 5.32-5.22 (m, 2H), 4.69-4.56 (m, 2H), 3.50 (d, *J* = 13.9 Hz, 1H), 3.28 (d, *J* = 13.9 Hz, 1H), 2.13 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.5, 169.6, 155.2, 147.4, 134.4, 130.9, 130.4, 130.0, 129.7, 128.0, 127.2, 119.2, 66.6, 56.8, 41.1, 20.6. HRMS (EI) calculated for $C_{18}H_{18}O_3$ ([M]$^+$): 282.1256. Found: 282.1252.

*Allyl 1-(2-methoxy-2-oxoethyl)-4-oxocyclohexa-2,5-dienecarboxylate **(1k)***. According to general procedure, compound **1kb** (523 mg, 2.2 mmol), CuI (13 mg, 0.066 mmol), and TBHP (1.94 mL, 15.5 mmol) in CH_3CN (10.0 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **1k** as colorless liquid (360 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11-7.05 (m, 2H), 6.41-6.36 (m, 2H), 5.94-5.81 (m, 1H), 5.34-5.23 (m, 2H), 4.65-4.63 (m, 2H), 3.70 (s, 3H), 2.89 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.6, 169.7, 169.1, 146.1, 131.0, 130.5, 119.0, 52.2, 49.5, 41.3. HRMS (EI) calculated for $C_{13}H_{14}O_5$ ([M]$^+$): 250.0841. Found: 250.0848.

*3-Methylbut-2-en-1-yl 1-isopropylcyclohexa-2,5-diene-1-carboxylate **(3ab)***. According to general procedure, compound **1aa** (500 mg, 3.0 mmol), oxalyl chloride (0.6 mL, 6.0 mmol), DMF (catalytic amount), 3-Methyl-2-buten-1-ol (0.33 mL, 3.3 mmol), pyridine (0.29 mL, 3.6 mmol), and DMAP (catalytic amount) in dry DCM (20 mL). Purification by flash column chromatography (DCM/ Hexane) to give compound **3ab** as colorless liquid (429 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.94-5.88 (m, 2H), 5.77-5.73 (m, 2H), 5.35-5.31 (m, 1H), 4.58 (d, *J* = 7.1 Hz, 2H), 2.64-2.59 (m, 2H), 2.16-2.03 (m, 1H), 1.72 (d, *J* = 14.0 Hz, 6H), 0.82 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.9, 169.8, 138.7, 126.2, 125.9, 118.7, 61.6, 51.9, 35.8, 26.5, 25.7, 18.0, 17.3. HRMS (APCI) calculated for $C_{15}H_{23}O_2$ ([M]$^+$): 235.1693. Found: 235.1698.

*3-Methylbut-2-en-1-yl 3-fluoro-1-isopropylcyclohexa-2,5-diene-1-carboxylate **(3bb)***. According to general procedure, compound **1ha** (500 mg, 2.7 mmol), oxalyl chloride (0.47 mL, 5.4 mmol), DMF (catalytic amount), 3-Methyl-2-buten-1-ol (0.27 mL, 2.7 mmol), pyridine (0.24 mL, 3.0 mmol), and DMAP (catalytic amount) in dry DCM (20 mL). Purification by flash column chromatography (DCM/ Hexane) to give compound **3bb** as colorless liquid (362 mg, 53%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.85-5.70 (m, 1H), 5.36-5.30 (m, 2H), 4.58 (d, *J* = 7.0 Hz, 2H), 2.80 (s, 2H), 2.17-2.07 (m, 1H), 1.72 (d, *J* = 14.5 Hz, 6H), 0.81 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.2, 158.4 (d, *J* = 255.0 Hz), 139.1, 126.7 (d, *J* = 2.7 Hz), 123.5 (d, *J* = 10.8 Hz), 118.4, 101.8 (d, *J* = 17.4 Hz), 61.8, 54.9 (d, *J* = 7.5 Hz), 35.8, 29.6, 27.1 (d, *J* = 26.6 Hz), 26.9, 25.7, 18.0, 17.3 (d, *J* = 5.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −102.92 (ddd, *J* = 17.7, 7.7, 3.1 Hz). HRMS (EI) calculated for $C_{15}H_{21}FO_2$ ([M]$^+$): 252.1526. Found: 252.1530.

*But-3-en-2-yl 1-isopropylcyclohexa-2,5-diene-1-carboxylate **(3cb)***. According to general procedure, compound **1aa** (500 mg, 3.0 mmol), oxalyl chloride (0.6 mL, 6.0 mmol), DMF (catalytic amount), 3-Buten-2-ol (0.28 mL, 3.3 mmol), pyridine (0.29 mL, 3.6 mmol), and DMAP (catalytic amount) in dry DCM (20 mL). Purification by flash column chromatography (DCM/ Hexane) to give compound **3cb** as colorless liquid (271 mg, 41%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.94-5.73 (m, 5H), 5.40-5.32 (m, 1H), 5.28-5.21 (m, 1H), 5.14-5.10 (m, 1H), 2.64-2.59 (m, 2H), 2.17-2.07 (m, 1H), 1.31 (d, *J* = 6.5 Hz, 3H), 0.83 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.0, 137.6, 126.3, 125.8, 115.6, 70.9, 51.9, 35.7, 26.5, 19.8, 17.3. HRMS (EI) calculated for $C_{14}H_{20}O_2$ ([M]$^+$): 220.1463. Found: 220.1466.

*But-3-en-2-yl 3-fluoro-1-isopropylcyclohexa-2,5-diene-1-carboxylate **(3db)***. According to general procedure, compound **1ha** (500 mg, 2.7 mmol), oxalyl chloride (0.47 mL, 5.4 mmol), DMF (catalytic amount), 3-Buten-2-ol (0.26 mL, 3.0 mmol), pyridine (0.26 mL, 3.3 mmol), and DMAP (catalytic amount) in dry DCM (20 mL). Purification by flash column chromatography (DCM/Hexane) to give compound **3db** as colorless liquid (336 mg, 52%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.89-5.70 (m, 3H), 5.37-5.11 (m, 4H) 2.80 (s, 2H) 2.19-2.09 (m, 1H), 1.31 (d, *J* = 6.5 Hz, 3H), 0.83 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.3, 158.5 (d, *J* = 254.9 Hz), 137.4, 126.6, 123.6 (d, *J* = 10.6 Hz), 115.9, 101.7 (d, *J* = 18.0 Hz), 71.4, 55.1, 35.7, 27.1 (d, *J* = 26.6 Hz), 19.8, 17.3 (d, *J* = 6.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −102.86 (dd, *J* = 17.9, 7.5 Hz). HRMS (EI) calculated for $C_{14}H_{19}FO_2$ ([M]$^+$): 238.1369. Found: 238.1362.

*(E)-Hex-2-en-1-yl 1-isopropylcyclohexa-2,5-dienecarboxylate **(3eb)***. According to general procedure, compound **1aa** (1.00 g, 6.0 mmol), oxalyl chloride (0.75 mL, 9.0 mmol), DMF (catalytic amount), (*E*)-hex-2-en-1-ol (0.79 mL, 6.6 mmol), pyridine (0.58 mL, 7.2 mmol), and DMAP (catalytic amount) in dry DCM (20 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **3eb** as colorless liquid (1.17 g, 79%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.94-5.89 (m, 2H), 5.78-5.71 (m, 2H), 5.60-5.51 (m, 1H), 4.54 (d, *J* = 6.3 Hz, 2H), 2.64-2.60 (m, 2H), 2.17-1.98 (m, 3H), 1.46-1.34 (m, 2H), 0.91-0.86 (m, 4H), 0.82 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.7, 136.2, 126.3, 125.9, 123.9, 65.4, 51.9, 35.8, 34.3, 26.5, 22.0, 17.3, 13.6. HRMS (ESI) calculated for $C_{16}H_{24}NaO_2$ ([M+Na]$^+$): 271.1669. Found: 271.1669.

*2-Methylallyl 1-isopropylcyclohexa-2,5-diene-1-carboxylate **(3fb)***. According to general procedure, compound **1aa** (1.0 g, 6.0 mmol), oxalyl chloride (0.60 mL, 9.0 mmol), DMF (catalytic amount), 2-Methyl-2-propen-1-ol (0.56 mL, 6.6 mmol), pyridine (0.58 mL, 7.2 mmol), and DMAP (catalytic amount) in dry DCM (20 mL). Purification by flash column chromatography (DCM/ Hexane) to give compound **3fb** as colorless liquid (755 mg, 57%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.96-5.79 (m, 2H), 5.79-5.74 (m, 2H), 4.99-4.91 (m, 2H), 4.51 (s, 2H), 2.65-2.61 (m, 2H), 2.18-2.09 (m, 1H), 1.76-1.75 (m, 3H), 0.84 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.4, 139.9, 126.4, 125.7, 112.7, 67.7, 52.1, 35.7, 26.5, 19.5, 17.3. HRMS (EI) calculated for $C_{14}H_{20}O_2$ ([M]$^+$): 220.1463. Found: 220.1467.

*2-Methylallyl 3-fluoro-1-isopropylcyclohexa-2,5-diene-1-carboxylate **(3gb)***. According to general procedure, compound **1ha** (1.0 g, 5.4 mmol), oxalyl chloride (0.93 mL, 10.9 mmol), DMF

(catalytic amount), 2-Methyl-2-propen-1-ol (0.51 mL, 6.0 mmol), pyridine (0.52 mL, 6.5 mmol), and DMAP (catalytic amount) in dry DCM (20 mL). Purification by flash column chromatography (DCM/ Hexane) to give compound **3gb** as colorless liquid (740 mg, 57%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.87-5.71 (m, 2H), 5.34 (d, *J* = 18.1 Hz, 1H), 4.95 (d, *J* = 15.9 Hz, 2H), 4.51 (s, 2H), 2.81 (s, 2H), 2.23-2.09 (m, 1H), 1.75 (s, 3H), 0.84 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.8, 158.6 (d, *J* = 255.3 Hz), 139.7, 126.6, 123.7 (d, *J* = 10.6 Hz), 113.0, 101.6 (d, *J* = 19.6 Hz), 68.0, 55.1 (d, *J* = 7.5 Hz), 35.7, 27.1 (d, *J* = 26.7 Hz), 19.5, 17.4 (d, *J* = 3.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −102.70 (ddd, *J* = 17.9, 7.6, 2.7 Hz). HRMS (EI) calculated for $C_{14}H_{19}FO_2$ ([M]$^+$): 238.1369. Found: 238.1364.

*Cinnamyl 1-isopropylcyclohexa-2,5-dienecarboxylate (**3hb**)*. According to general procedure, compound **1aa** (0.97 g, 5.8 mmol), oxalyl chloride (0.75 mL, 8.7 mmol), DMF (catalytic amount), (*E*)-3-phenylprop-2-en-1-ol (0.82 mL, 6.4 mmol), pyridine (0.56 mL, 7.0 mmol), and DMAP (catalytic amount) in dry DCM (20 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **3hb** as colorless liquid (1.3 g, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.27 (m, 5H), 6.65 (d, *J* = 15.9 Hz, 1H), 6.34-6.24 (m, 1H), 5.97-5.91 (m, 2H), 5.81-5.76 (m, 2H), 4.76 (d, *J* = 6.3 Hz, 2H), 2.66-2.10 (m, 1H), 0.85 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.7, 136.3, 133.9, 128.6, 128.0, 126.6, 126.5, 125.8, 123.3, 65.2, 52.0, 35.9, 26.5, 17.4. HRMS (EI) calculated for $C_{19}H_{22}O_2$ ([M]$^+$): 282.1620. Found: 282.1628.

*Cinnamyl 3-fluoro-1-isopropylcyclohexa-2,5-dienecarboxylate (**3ib**)*. According to general procedure, compound **1ha** (500 mg, 2.7 mmol), oxalyl chloride (0.47 mL, 5.4 mmol), DMF (catalytic amount), (*E*)-3-phenylprop-2-en-1-ol (0.4 mL, 3.0 mmol), pyridine (0.26 mL, 3.25 mmol), and DMAP (catalytic amount) in dry DCM (20 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **3ib** as colorless liquid (214 mg, 26%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.29 (m, 5H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.34-6.22 (m, 1H), 5.87-5.73 (m, 2H), 5.37 (d, *J* = 18.0 Hz, 1H), 4.76 (d, *J* = 6.4 Hz, 2H), 2.82 (s, 2H), 2.21-2.12 (m, 1H), 0.84 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.9, 158.6 (d, *J* = 255.3 Hz), 136.2, 134.3, 128.6, 128.1, 126.6, 123.7 (d, *J* = 10.7 Hz), 122.9, 101.7 (d, *J* = 16.9 Hz), 65.5, 55.1 (d, *J* = 7.4 Hz), 35.9, 27.1 (d, *J* = 26.6 Hz), 17.4 (d, *J* = 3.3 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −102.63 (ddd, *J* = 17.2, 7.3, 2.4 Hz). HRMS (EI) calculated for $C_{19}H_{21}FO_2$ ([M]$^+$): 300.1526. Found: 300.1520.

*1-Phenylallyl 1-isopropylcyclohexa-2,5-dienecarboxylate (**3jb**)*. According to general procedure, compound **1aa** (1g, 6.0 mmol), oxalyl chloride (0.77 mL, 9.0 mmol), DMF (catalytic amount), 1-phenylprop-2-en-1-ol (085 mL, 6.6 mmol), pyridine (0.58 mL, 7.2 mmol), and DMAP (catalytic amount) in dry DCM (20 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **3jb** as colorless liquid (440 mg, 26%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.26 (m, 5H), 6.28 (d, *J*= 5.9, 1H), 6.09-5.87 (m, 3H), 5.86-5.69 (m, 2H), 5.39-5.18 (m, 2H), 2.76-2.52 (m, 2H), 2.15 (hept, *J*= 7.0, 1H), 0.79 (d, *J*= 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 138.9, 136.2, 128.4, 127.9, 127.0, 126.4, 125.5, 116.9, 76.0, 52.0, 35.7, 26.5, 17.2. HRMS (EI) calculated for $C_{19}H_{22}O_2$ ([M]$^+$): 282.1620. Found: 282.1614.

*3-Methylbut-2-en-1-yl 1-isopropyl-4-oxocyclohexa-2,5-diene-1-carboxylate (**3a**)*. According to general procedure, compound **3ab** (234 mg, 1.0 mmol), CuI (6 mg, 0.003 mmol), and TBHP (0.88 mL, 7.0 mmol) in CH_3CN (5.00 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **3a** as colorless liquid (139 mg, 56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.07-7.02 (m, 2H), 6.41-6.36 (m, 2H), 5.35-5.30 (m, 1H), 4.63 (d, *J* = 7.3 Hz, 2H), 2.53-2.39 (m, 1H), 1.73 (d, *J* = 15.2 Hz, 6H), 0.92 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.3, 170.3, 147.3, 140.2, 130.8, 117.7, 62.8, 56.5, 36.6, 25.7, 18.0, 17.6. HRMS (EI) calculated for $C_{15}H_{20}O_3$ ([M]$^+$): 248.1412. Found: 248.1408.

*3-Methylbut-2-en-1-yl 3-fluoro-1-isopropyl-4-oxocyclohexa-2,5-diene-1-carboxylate (**3b**)*. According to general procedure, compound **3bb** (300 mg, 1.2 mmol), CuI (7 mg, 0.036 mmol), and TBHP (1.01 mL, 8.4 mmol) in CH_3CN (5.00 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **3b** as colorless liquid (166 mg, 52%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.06 (d, *J* = 10.2 Hz, 1H), 6.62-6.57 (d, *J* = 13.4 Hz, 1H), 6.42 (d, *J* = 10.1 Hz, 1H), 5.35-5.29 (m, 1H), 4.65 (d, *J* = 7.2 Hz, 2H), 2.56-2.42 (m, 1H), 1.74 (d, *J* = 15.4 Hz, 6H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.9 (d, *J* = 21.8 Hz), 169.7, 154.7 (d, *J* = 264.0 Hz), 148.4, 140.6, 130.2, 122.8 (d, *J* = 15.4 Hz), 117.4, 63.1, 57.9 (d, *J* = 5.3 Hz), 25.7, 18.0, 17.6 (d, *J* = 23.7 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): −127.18 (dd, *J*= 14.0, 7.0 Hz). HRMS (EI) calculated for $C_{15}H_{19}FO_3$ ([M]$^+$): 266.1318. Found: 266.1320.

*But-3-en-2-yl 1-isopropyl-4-oxocyclohexa-2,5-diene-1-carboxylate (**3c**)*. According to general procedure, compound **3cb** (225 mg, 1.0 mmol), CuI (6 mg, 0.031 mmol), and TBHP (0.88 mL, 7.1 mmol) in CH_3CN (10.00 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **3c** as colorless liquid (160 mg, 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.07- 7.01 (m, 2H), 6.42-6.36 (m, 2H), 5.81 (d, *J* = 17.2 Hz, 1H), 5.39 (p, *J* = 6.5 Hz, 1H), 5.30-5.15 (m, 2H), 2.54-2.40 (m, 1H), 1.34 (d, *J* = 6.5 Hz, 3H), 0.93 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.2, 169.4, 147.2, 136.6, 130.8, 116.8, 72.8, 56.5, 36.5, 19.7, 17.6. HRMS (EI) calculated for $C_{14}H_{18}O_3$ ([M]$^+$): 234.1256. Found: 234.1252.

*But-3-en-2-yl 3-fluoro-1-isopropyl-4-oxocyclohexa-2,5-diene-1-carboxylate (**3d**)*. According to general procedure, compound **3db** (324 mg, 1.4 mmol), CuI (8 mg, 0.0041 mmol), and TBHP (1.1 mL, 8.5 mmol) in CH_3CN (5.00 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **3d** as colorless liquid (158 mg, 46%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08-7.04 (m, 1H), 6.63-6.57 (m, 1H), 6.46-6.40 (m, 1H), 5.88-5.76 (m, 1H), 5.44-5.17 (m, 3H), 2.55-2.47 (m, 1H), 1.35 (d, *J* = 6.5 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.9 (d, *J* = 21.7 Hz), 168.9, 154.7 (d, *J* = 264.5 Hz), 148.2, 136.4, 130.3 (d, *J* = 4.3 Hz), 122.7 (d, *J* = 16.0 Hz), 117.1, 73.4, 36.9, 19.8, 17.7, 17.4. ^{19}F NMR (282 MHz, $CDCl_3$): −127.05 (m). HRMS (EI) calculated for $C_{14}H_{17}FO_3$ ([M]$^+$): 252.1162. Found: 252.1169.

*(E)-Hex-2-en-1-yl 1-isopropyl-4-oxocyclohexa-2,5-dienecarboxylate (**3e**)*. According to general procedure, compound **3eb** (80 mg, 0.3 mmol), CrO_3 (32 mg, 0.3 mmol), and 3,5-DMP (31 mg, 0.3 mmol) in dry DCM (1.60 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **3e** as colorless liquid (28 mg, 33%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (d, *J* = 10.4 Hz, 2H), 6.39 (d, *J* = 10.3 Hz, 2H), 5.84-5.74 (m, 1H), 5.59-5.50 (m, 1H), 4.59 (d, *J* = 6.6 Hz, 2H), 2.47 (p, *J* = 6.9 Hz, 1H), 2.03 (q, *J* = 7.1 Hz, 2H), 1.40 (h, *J* = 7.4 Hz, 2H), 0.93-0.89 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.4, 170.2, 147.3, 137.7, 130.8, 123.0, 66.7, 56.6, 36.6, 34.2, 21.9, 17.6, 13.6. HRMS (EI) calculated for $C_{16}H_{22}O_3$ ([M]$^+$): 262.1569. Found: 262.1564.

*2-Methylallyl 1-isopropyl-4-oxocyclohexa-2,5-diene-1-carboxylate (**3f**)*. According to general procedure, compound **3fb** (620 mg, 2.8 mmol), CuI (16 mg, 0.084 mmol), and TBHP (2.36 mL, 19.7 mmol) in CH_3CN (10.00 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **3b** as colorless liquid (348 mg, 53%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08-7.02 (m, 2H), 6.43-6.38 (m, 2H), 4.97 (s, 2H), 4.56 (s, 2H), 2.54-2.42 (m, 1H), 1.74 (s, 3H), 0.94 (d, *J* = 7.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.2, 170.0, 147.0, 138.9, 130.9, 113.9, 69.0, 56.6, 36.5, 19.4, 17.6. HRMS (EI) calculated for $C_{14}H_{18}O_3$ ([M]$^+$): 234.1256. Found: 234.1252.

*2-Methylallyl 3-fluoro-1-isopropyl-4-oxocyclohexa-2,5-diene-1-carboxylate (**3g**)*. According to general procedure, compound **3gb** (710 mg, 3.0 mmol), CuI (17 mg, 0.089 mmol), and TBHP

(2.51 mL, 20.9 mmol) in CH_3CN (15.00 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **3g** as colorless liquid (428 mg, 57%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.07 (dd, *J* = 10.2, 2.7 Hz, 1H), 6.61 (dd, *J* = 13.3, 2.7 Hz, 1H), 6.44 (dd, *J* = 10.1, 6.9 Hz, 1H), 4.98 (s, 2H), 4.58 (s, 2H), 2.58-2.48 (m, 1H), 1.75 (s, 3H), 0.98 (d, *J* = 6.9 Hz, 3H) , 0.93 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ177.9 (d, *J* = 21.9 Hz), 169.4, 154.8 (d, *J* = 264.6 Hz), 148.0, 138.7, 130.4, 122.5 (d, *J* = 15.3 Hz), 114.2, 69.4, 58.0 (d, *J* = 5.4 Hz), 36.9, 19.4, 17.7 (d, *J* = 25.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −126.89 (dd, *J* = 13.3, 6.9 Hz). HRMS (EI) calculated for $C_{14}H_{17}FO_3$ ([M]$^+$): 252.1162. Found: 252.1156.

*Cinnamyl 1-isopropyl-4-oxocyclohexa-2,5-dienecarboxylate **(3h)***. According to general procedure, compound **3hb** (911 mg, 3.2 mmol), CrO_3 (384 mg, 3.84 mmol), and 3,5-DMP (338 mg, 3.52 mmol) in dry DCM (20 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **3h** as colorless liquid (304 mg, 32%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.23 (m, 5H), 7.07 (d, *J* = 10.4 Hz, 2H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.41 (d, *J* = 10.4 Hz, 2H), 6.26 (dt, *J* = 15.8, 6.6 Hz, 1H), 4.80 (d, *J* = 6.6 Hz, 2H), 2.50 (hept, *J* = 6.9 Hz, 1H), 0.94 (d, J = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.2, 170.1, 147.0, 135.7, 135.3, 130.9, 128.6, 128.3, 126.6, 121.9, 66.5, 56.5, 36.6, 17.6. HRMS (EI) calculated for $C_{19}H_{20}O_3$ ([M]$^+$): 296.1412. Found: 296.1416.

*Cinnamyl 3-fluoro-1-isopropyl-4-oxocyclohexa-2,5-dienecarboxylate **(3i)***. According to general procedure, compound **3ib** (100 mg, 0.3 mmol), CrO_3 (7 mg, 0.3 mmol), and 3,5-DMP (32 mg, 0.3 mmol) in dry DCM (1.65 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **3i** as colorless liquid (16 mg, 15%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41-7.29 (m, 5H), 7.09 (dd, *J* = 10.2, 2.7 Hz, 1H), 6.71-6.60 (m, 2H), 6.45 (dd, *J* = 9.9, 6.6 Hz, 1H), 6.26 (dt, *J* = 15.8, 7.0 Hz, 1H), 4.82 (d, *J* = 6.7 Hz, 2H), 2.54 (dt, *J* = 13.8, 6.9 Hz, 1H), 0.95 (dd, *J* = 14.6, 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.9 (d, *J* = 21.8 Hz), 169.6, 154.7 (d, *J* = 264.5 Hz), 148.1, 147.1, 135.8, 130.42, 128.7, 128.4, 126.7, 122.5 (d, *J* = 15.4 Hz), 121.6, 66.9, 57.9 (d, *J* = 5.4 Hz), 37.0, 17.7 (d, *J* = 26.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −126.83 (dd, *J* = 13.0, 6.5 Hz). HRMS (EI) calculated for $C_{19}H_{19}FO_3$ ([M]$^+$): 314.1318. Found: 314.1315.

*1-Phenylallyl 1-isopropyl-4-oxocyclohexa-2,5-dienecarboxylate **(3j)***. According to general procedure, compound **3jb** (280 mg, 1 mmol), CrO_3 (120 mg, 1.2 mmol), and 3,5-DMP (105 mg, 1.1 mmol) in dry DCM (20 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **3j** as colorless liquid (70 mg, 15%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49-7.24 (m, 5H), 7.06 (d, *J* = 10.5 Hz, 2H), 6.41 (d, *J* = 10.2 Hz, 2H), 6.29 (d, *J* = 6.0 Hz, 1H), 6.10 – 5.89 (m, 1H), 5.39-5.20 (m, 2H), 2.48 (hept, *J* = 6.9 Hz, 1H), 0.87 (dd, J = 6.9, 3.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.2, 169.2, 146.9, 137.9, 135.3, 130.9, 128.6, 128.5, 127.0, 117.8, 77.8, 56.6, 36.5, 17.5. HRMS (EI) calculated for $C_{19}H_{20}O_3$ ([M]$^+$): 296.1412. Found: 296.1418.

*1-(Allyloxy)-4-isopropylbenzene **(2a)***.[23] According to the general procedure, compound **1a** (50 mg, 0.2 mmol), and $Pd(PPh_3)_4$ (14 mg, 0.012 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound 2a as colorless liquid (38 mg, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16-7.11 (m, 2H), 6.88-6.83 (m, 2H), 6.13-6.00 (m, 1H), 5.45-5.37 (m, 1H), 5.30-5.25 (m, 1H), 4.53-4.50 (m, 2H), 2.90-2.81 (m, 1H), 1.22 (d, *J* = 7.0 Hz, 6H).

*1-(Allyloxy)-4-methylbenzene **(2b)***.[24] According to the general procedure, compound **1b** (100 mg, 0.5 mmol), and $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound 2b as colorless liquid (68.4 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10-7.07 (m, 2H), 6.85-6.80 (m, 2H), 6.13-6.00 (m, 1H), 5.45-5.37 (m, 1H), 5.30-5.25 (m, 1H), 4.53-4.50 (m, 2H), 2.29 (s, 3H).

*4-(Allyloxy)-1-isopropyl-2-methylbenzene **(2c)***. According to the general procedure, compound **1c** (100 mg, 0.4 mmol), and $Pd(PPh_3)_4$ (25 mg, 0.021 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound **2c** as colorless liquid (73 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.15 (d, *J* = 8.2 Hz, 1H), 6.77-6.72 (m, 2H), 6.13-6.01 (m, 1H), 5.41 (d, *J* = 17.2, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 4.53-4.50 (m, 2H), 3.15-3.01 (m, 1H), 2.32 (s, 3H), 1.21 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.2, 139.2, 136.2, 133.6, 133.6, 125.5, 117.3, 116.5, 111.9, 68.7, 28.6, 23.4, 19.4. HRMS (EI) calculated for $C_{13}H_{18}O$ ([M]$^+$): 190.1358. Found: 190.1358.

*1-(Allyloxy)-4-isopropyl-2-methylbenzene **(2d)***. According to the general procedure, compound **1d** (100 mg, 0.4 mmol), and $Pd(PPh_3)_4$ (25 mg, 0.021 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound **2d** as colorless liquid (75 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.01-6.97 (m, 1H), 6.77-6.74 (m, 1H), 6.14-6.02 (m, 1H), 5.43 (d, *J* = 17.3 Hz, 1H), 5.27 (d, *J* = 10.5 Hz, 1H), 4.53 (d, *J* = 5.0 Hz, 2H), 2.88-2.79 (m, 1H), 2.25 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.8, 140.8, 133.8, 128.8, 126.6, 124.1, 116.7, 111.2, 68.8, 33.2, 29.6, 24.2, 16.3. HRMS (EI) calculated for $C_{13}H_{18}O$ ([M]$^+$): 190.1358. Found: 190.1361.

*1-(Allyloxy)-4-isopropyl-2,3-dimethylbenzene **(2e)***. According to the general procedure, compound **1e** (50 mg, 0.2 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound **2e** as colorless liquid (28 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.05 (d, *J* = 8.6 Hz, 1H), 6.72 (d, *J* = 8.6 Hz, 1H), 6.15-6.02 (m, 1H), 5.43 (d, *J* = 17.3 Hz, 1H), 5.26 (d, *J* = 10.5Hz, 1H), 4.51 (d, *J* = 5.1 Hz, 2H), 3.20-3.11 (m, 1H), 2.24 (d, *J* = 9.1 Hz, 6H), 1.21 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.3, 139.0, 135.1, 134.0, 125.4, 122.2, 116.6, 109.3, 69.1, 29.6, 29.1, 23.5, 15.0, 12.3. HRMS (EI) calculated for $C_{14}H_{20}O$ ([M]$^+$): 204.1514. Found: 204.1512.

*2-(Allyloxy)-5-isopropyl-1,3-dimethylbenzene **(2f)***. According to the general procedure, compound **1f** (50 mg, 0.2 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound **2f** as colorless liquid (38 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.86 (s, 2H), 6.18-6.05 (m, 1H), 5.43 (d, *J* = 17.2 Hz, 1H), 5.25 (d, *J* = 10.4 Hz, 1H), 4.29 (d, *J* = 5.5 Hz, 2H), 2.84- 2.75 (m, 1H), 2.27 (s, 6H), 1.22 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.8, 144.1, 134.3, 130.5, 126.6, 116.9, 73.0, 33.4, 29.6, 24.1, 16.4. HRMS (EI) calculated for $C_{14}H_{20}O$ ([M]$^+$): 204.1514. Found: 204.1508.

*1-(Allyloxy)-4-isopropylnaphthalene **(2g)***. According to the general procedure, compound **1g** (100 mg, 0.4 mmol), and $Pd(PPh_3)_4$ (21 mg, 0.019 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound **2g** as colorless liquid (65 mg, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.1 Hz, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.57-7.45 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.25-6.12 (m, 1H), 5.53 (d, *J* = 17.3 Hz, 1H), 5.33 (d, *J* = 10.4 Hz, 1H), 4.71 (d, *J* = 5.1 Hz, 2H), 3.73-3.60 (m, 1H), 1.38 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.5, 136.6, 133.5, 132.2, 126.1, 124.5, 123.0, 122.7, 121.3, 117.2, 104.7, 68.9, 28.0, 23.6. HRMS (EI) calculated for $C_{16}H_{18}O$ ([M]$^+$): 226.1358. Found: 226.1356.

*1-(Allyloxy)-2-fluoro-4-isopropylbenzene **(2h)***. According to the general procedure, compound **1h** (100 mg, 0.4 mmol), and $Pd(PPh_3)_4$ (24 mg, 0.021 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound **2h** as colorless liquid (70 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.02-6.80 (m, 3H), 6.13-6.07 (m, 1H), 5.42 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.29 (d, *J* = 10.5 Hz, 1H), 4.58 (d, *J* = 5.4 Hz, 2H), 2.84 (hept, *J* = 6.8 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.7 (d, *J* = 245.0 Hz), 144.3 (d, *J* = 10.8 Hz), 142.6 (d, *J* = 5.6 Hz), 133.1, 121.6, 117.9, 115.4, 114.2 (d, *J* = 18.4 Hz), 70.4, 33.2,

23.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ −134.42 (m). HRMS (EI) calculated for $C_{12}H_{15}FO$ ($[M]^+$): 194.1107. Found: 194.1099.

*4-(Allyloxy)-1-hexyl-2-methylbenzene (**2i**)*. According to the general procedure, compound **1i** (100 mg, 0.4 mmol), and $Pd(PPh_3)_4$ (21 mg, 0.018 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound **2i** as colorless liquid (78 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.02 (d, *J* = 8.2 Hz, 1H), 6.73-6.67 (m, 2H), 6.12-6.01 (m, 1H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.27 (d, *J* = 10.5 Hz, 1H), 4.50 (d, *J* = 5.3 Hz, 2H), 2.54-2.49 (m, 2H), 2.27 (s, 3H), 1.53-1.48 (m, 1H), 1.38-1.26 (m, 7H), 0.91-0.87 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.5, 137.0, 133.6, 133.5, 129.5, 117.3, 116.5, 111.7, 68.7, 32.5, 31.7, 30.5, 29.3, 22.6, 19.5, 14.1. HRMS (EI) calculated for $C_{16}H_{24}O$ ($[M]^+$): 232.1827. Found: 232.1828.

*4-(Allyloxy)-1-benzyl-2-methylbenzene (**2j**)*. According to the general procedure, compound **1j** (55 mg, 0.20 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound **2j** as colorless liquid (40 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.10 (m, 5H), 7.00 (d, *J* = 8.3 Hz, 1Hz), 6.76 (d, *J* = 2.6 Hz, 1H), 6.70 (d, *J* = 8.3 Hz, 1H), 6.12-6.01 (m, 1H), 5.41 (d, *J* = 17.3 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 4.51 (d, *J* = 5.3 Hz, 2H), 3.92 (s, 2H), 2.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.0, 140.7, 137.9, 133.4, 131.3, 130.7, 128.5, 128.3, 125.8, 117.5, 116.7, 111.6, 68.7, 38.6, 29.6, 19.9. HRMS (EI) calculated for $C_{17}H_{18}O$ ($[M]^+$): 238.1358. Found: 238.1363.

*Methyl 2-(4-(allyloxy)phenyl)acetate (**2k**)*. According to the general procedure, compound **1k** (50 mg, 0.2 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound **2k** as colorless liquid (36 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21-7.16 (m, 2H), 6.90-6.85 (m, 2H), 6.12-5.99 (m, 1H), 5.41 (d, *J* = 17.3 Hz, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 4.52 (d, *J* = 5.3 Hz, 2H), 3.69 (s, 3H), 3.57 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 157.7, 133.2, 130.2, 126.1, 117.6, 114.8, 68.8, 52.0, 40.2, 40.2. HRMS (EI) calculated for $C_{12}H_{14}O_3$ ($[M]^+$): 206.0943. Found: 206.0953.

*1-Isopropyl-4-((2-methylbut-3-en-2-yl)oxy)benzene (**4a**)*. According to the general procedure, compound **3a** (20 mg, 0.1 mmol), $Pd(dba)_2$ (4 mg, 0.004 mmol), and PPh_3 (2 mg, 0.008 mmol) in CH_3CN (0.3 mL). Purification by flash column chromatography (Hexane) to give compound **4a** as colorless liquid (12 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09-7.04 (m, 2H), 6.92-6.87 (m, 2H), 6.19-6.09 (m, 1H), 5.19-5.10 (m, 2H), 2.89-2.80 (m, 1H), 1.43 (s, 6H), 1.22 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.7, 144.6, 142.5, 126.5, 121.6, 113.1, 79.1, 33.3, 26.9, 24.1. HRMS (EI) calculated for $C_{14}H_{20}O$ ($[M]^+$): 204.1514. Found: 204.1512.

*2-Fluoro-4-isopropyl-1-((2-methylbut-3-en-2-yl)oxy)benzene (**4b**)*. According to the general procedure, compound **3b** (22 mg, 0.05 mmol), $Pd(dba)_2$ (3 mg, 0.0038 mmol), and PPh_3 (2 mg, 0.0075 mmol) in CH_3CN (0.3 mL). Purification by flash column chromatography (Hexane) to give compound **4b** as colorless liquid (13 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.99-6.80 (m, 3H), 6.18-6.08 (m, 1H), 5.18-5.09 (m, 2H), 2.91-2.77 (m, 1H), 1.44 (s, 6H), 1.21 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ177.9 (d, *J* = 21.7 Hz), 169.7, 154.6 (d, *J* = 264.1 Hz), 148.4 (d, *J* = 2.1 Hz), 140.6, 130.2 (d, *J* = 4.4 Hz), 122.8 (d, *J* = 15.3 Hz), 117.5, 63.1, 57.9 (d, *J* = 5.2 Hz), 36.9, 25.7, 18.0, 17.6 (d, *J* = 23.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −127.20 (dd, *J* = 13.4, 6.9 Hz). HRMS (EI) calculated for $C_{14}H_{19}FO$ ($[M]^+$): 222.1420. Found: 222.1425.

*1-(But-3-en-2-yloxy)-4-isopropylbenzene (**4c**), (E)-1-(but-2-en-1-yloxy)-4-isopropylbenzene (**4c'**) (**4c**:**4c'** = 1:0.31)*. According to the general procedure, compound **3c** (50 mg, 0.2 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound **4c** and **4c'** (mixture) as colorless liquid (31 mg, 78%, **4c**:**4c'** = 1:0.31). ^{1}H NMR (300 MHz, $CDCl_3$): 7.13-7.08 (m, 2H), 6.87-6.81 (m, 2H), 5.99-5.85 (m, 1H), 5.34-5.12 (m, 2H), 4.82-4.71 (m, 1H), 2.92-2.78 (m, 1H), 1.42 (d, *J* = 6.4 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 6H). HRMS (EI) calculated for $C_{13}H_{18}O$ ($[M]^+$): 190.1358. Found: 190.1362.

*1-(But-3-en-2-yloxy)-2-fluoro-4-isopropylbenzene (**4d**), (E)-1-(but-2-en-1-yloxy)-2-fluoro-4-isopropylbenzene (**4d'**) (**4d**:**4d'** = 1:0.23)*. According to the general procedure, compound **3d** (50 mg, 0.2 mmol), and $Pd(PPh_3)_4$ (11 mg, 0.0099 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound **4d** and **4d'** (mixture) as colorless liquid (30 mg, 73%, **4d**:**4d'** = 1:0.23). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.01-6.81 (m, 3H), 5.93 (m, 1H), 5.21 (m, 2H), 4.78-4.67 (m, 1H), 2.83 (hept, *J* = 6.9 Hz, 1H), 1.46 (d, *J* = 6.4 Hz, 3H), 1.21 (d, *J* = 6.9 Hz, 6H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −133.27 (dd, *J*= 13.9, 7.89 Hz) (4d), −134.46 (m) (4d'). HRMS (EI) calculated for $C_{13}H_{17}FO$ ($[M]^+$): 208.1263. Found: 208.1270.

*1-(Hex-1-en-3-yloxy)-4-isopropylbenzene (**4e**), (E)-1-(hex-2-en-1-yloxy)-4-isopropylbenzene (**4e**:**4e'** = 1:0.95)*. According to the general procedure, compound **4e** (28 mg, 0.1 mmol), and $Pd(PPh_3)_4$ (6 mg, 0.005 mmol) in CH_3CN (0.5 mL). Purification by flash column chromatography (Hexane) to give compound **4e** and **4e'** (mixture) as colorless liquid (21 mg, 92%, **4e**:**4e'** = 1:0.95). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19-7.08 (m, 2H), 6.75-6.91 (m, 2H), 6.00-5.80 (m, 1H), 5.31-5.15 (m, 1H), 4.60-4.52 (m, 4e, 1H), 4.45 (d, *J*= 6 Hz, 4e', 2H), 2.90-2.76 (m, 1H), 1.48-1.29 (m, 3H), 1.20-1.48 (m, 6H), 0.98-0.88 (m, 4H). HRMS (EI) calculated for $C_{15}H_{22}O$ ($[M]^+$): 218.1671. Found: 218.1676.

*1-Isopropyl-4-((2-methylallyl)oxy)benzene (**4f**)*. According to the general procedure, compound **3f** (50 mg, 0.2 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound **4f** as colorless liquid (37 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16-7.11 (m, 2H), 6.88-6.83 (m, 2H), 5.09 (s, 1H), 4.98 (s, 1H), 4.41 (s, 2H), 2.91-2.79 (m, 1H), 1.83 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.8, 141.1, 127.1, 114.5, 112.5, 71.8, 33.2, 24.1, 19.4. HRMS (EI) calculated for $C_{13}H_{18}O$ ($[M]^+$): 190.1358. Found: 190.1367.

*2-Fluoro-4-isopropyl-1-((2-methylallyl)oxy)benzene (**4g**)*. According to the general procedure, compound **3g** (50 mg, 0.2 mmol), and $Pd(PPh_3)_4$ (11 mg, 0.0099 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound **4g** as colorless liquid (38 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.97-6.93 (m, 1H), 6.89-6.87 (m, 2H), 5.10 (s, 1H), 4.99 (s, 1H), 4.48 (s, 2H), 2.91-2.77 (m, 1H), 1.84 (s, 3H), 1.21 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ152.7 (d, *J* = 245.0 Hz), 144.5 (d, *J* = 10.8 Hz), 142.6 (d, *J* = 5.6 Hz), 140.7, 121.7 (d, *J* = 3.3 Hz), 115.4 (d, *J* = 2.1 Hz), 114.2 (d, *J* = 18.1 Hz), 112.9, 73.3, 33.2, 29.6, 23.9, 19.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ −134.37 (m). HRMS (EI) calculated for $C_{13}H_{17}FO$ ($[M]^+$): 208.1263. Found: 208.1270.

*1-(Cinnamyloxy)-4-isopropylbenzene (**4h**)*. According to the general procedure, compound **3h** (50 mg, 0.2 mmol), and $Pd(PPh_3)_4$ (9.7 mg, 0.0084 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound **4h** as white solid (41 mg, 97%). Compound **3j** (40 mg, 0.13 mmol), and $Pd(PPh_3)_4$ (7.5 mg, 0.0065 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound **4h** as white solid (29 mg, 90%). mp = 66-68 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64-7.25 (m, 5H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 16.0 Hz, 2H), 6.79 (d, *J* = 16.0 Hz, 1H), 6.48 (dt, *J* = 16.0, 5.8 Hz, 1H), 4.74 (d, *J* = 7.1 Hz, 2H), 2.94 (hept, *J* = 6.8 Hz, 1H), 1.31 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.6, 141.2, 136.4, 132.7, 128.5, 127.7, 127.2, 126.5, 124.6, 114.5, 68.6, 33.2, 24.1. HRMS (EI) calculated for $C_{18}H_{20}O$ ($[M]^+$): 252.1514. Found: 252.1506.

*1-(Cinnamyloxy)-2-fluoro-4-isopropylbenzene (**4i**), 2-fluoro-4-isopropyl-1-((1-phenylallyl)oxy)benzene (**4i'**) (**4i**:**4i'** = 1:0.57)*. According to the general procedure, compound **3i** (50 mg, 0.16 mmol), and $Pd(PPh_3)_4$ (9.2 mg, 0.008 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (Hexane) to give compound **4i** and **4i'** (mixture) as colorless liquid (41 mg, 95%, **4i**:**4i'** = 1:0.57). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48-7.24 (m, 5H), 7.05-6.83 (m, 3H), 6.51-6.36 (m, 1H), 4.80-4.72 (m, 2H), 2.96-2.75 (m, 1H), 1.24-1.18 (m, 6H). ^{19}F NMR (282 MHz, $CDCl_3$): −134.16 (m). HRMS (EI) calculated for $C_{18}H_{19}FO$ ($[M]^+$): 270.1420. Found: 270.1424.

*1-(2-Carboxyethyl)cyclohexa-2,5-dienecarboxylic acid (**3ka**)*. According to the general procedure, benzoic acid (5 g, 41 mmol), 3-Bromopropionic acid (18.8 g, 123 mmol), and Li (0.71g, 102.3 mmol). Compound **3ka** was achieved after recrystallization as white solid (7.8 g, 98%). mp = 162-164 °C. ^{1}H NMR (300 MHz, DMSO-d6): δ 12.46-12.16 (broad, 2H), 5.86 (d, *J* = 10.5 Hz, 2H), 5.61 (d, *J* = 10.5 Hz, 2H), 2.58 (s, 2H), 2.12-2.00 (m, 2H), 1.88-1.78 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d6) δ 175.8, 174.8, 127.4, 126.4, 47.1, 34.1, 29.7, 26.2. HRMS (ESI) calculated for $C_{10}H_{11}O_4$ ($[M-H]^-$): 195.0652. Found: 195.0649.

*3-Methylbut-2-en-1-yl 1-(3-((3-methylbut-2-en-1-yl)oxy)-3-oxopropyl)cyclohexa-2,5-dienecarboxylate (**3kb**)*. According to the general procedure, compound **3ka** (2 g, 10.2 mmol), oxalyl chloride (2.62 mL, 0.6 mmol, 3 equiv.), DMF (catalytic amount), 3-Methyl-2-buten-1-ol (2.56 mL, 25.5 mmol, 2.5 equiv.), pyridine (1.97 mL, 24.5 mmol, 2.4 equiv.), and DMAP (catalytic amount) in dry DCM (40 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **3kb** as yellow liquid (3.2 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.90 (d, *J* = 10.5 Hz, 2H), 5.68 (d, *J* = 10.5 Hz, 2H), 5.36-5.25 (m, 2H), 4.62-4.48 (m, 4H), 2.67-2.58 (m, 2H), 2.27-2.17 (m, 2H), 2.06-1.96 (m, 2H), 1.72 (d, *J* = 16.9 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.3, 173.5, 139.1, 138.9, 127.2, 126.6, 126.3, 125.7, 118.5, 118.4, 62.0, 61.3, 47.3, 33.7, 29.6, 26.1, 25.8, 18.1, 17.9. HRMS (ESI) calculated for $C_{20}H_{28}NaO_4$ ($[M+Na]^+$): 355.1880. Found: 355.1884.

*3-Methylbut-2-en-1-yl 1-(3-((3-methylbut-2-en-1-yl)oxy)-3-oxopropyl)-4-oxocyclohexa-2,5-dienecarboxylate (**3k**)*. According to general procedure, compound **3kb** (320 mg, 0.96 mmol), CuI (5.5 mg, 0.029 mmol), and TBHP (0.92 mL, 6.72 mmol) in CH_3CN (3.00 mL). Purification by flash column chromatography (EA/ Hexane) to give compound **3k** as colorless liquid (183 mg, 55%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 6.99 (d, *J* = 10.3 Hz, 2H), 6.36 (d, *J* = 10.3 Hz, 2H), 5.34-5.22 (m, 2H), 4.62 (d, *J* = 7.3 Hz, 2H), 4.53 (d, *J* = 7.3 Hz, 2H), 2.41-2.28 (m, 2H), 2.23-2.12 (m, 2H), 1.71 (d, *J* = 19.1 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.9, 172.1, 169.8, 147.2, 140.4, 139.6, 130.8, 118.1, 117.5, 63.2, 61.7, 51.7, 32.4, 28.9, 25.8, 18.1, 17.9. HRMS (ESI) calculated for $C_{20}H_{26}NaO_5$ ($[M+Na]^+$): 369.1672. Found: 369.1682.

*3-Methylbut-2-en-1-yl 3-(4-((2-methylbut-3-en-2-yl)oxy)phenyl)propanoate **(4j)***. According to the general procedure, compound **3k** (80 mg, 0.23 mmol), $Pd(dba)_2$ (11 mg, 0.012 mmol), and PPh_3 (6.3 mg, 0.024 mmol) in CH_3CN (1 mL). Purification by flash column chromatography (EA/Hexane) to give compound **4j** as colorless liquid (40 mg, 58%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.03 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.12 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.38-5.26 (m, 1H), 5.2-5.07 (m, 2H), 4.56 (d, *J* = 7.2 Hz, 2H), 2.95-2.80 (m, 2H), 2.67-2.51 (m, 2H), 1.73 (d, *J* = 18.4 Hz, 6H), 1.42 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.1, 154.2, 144.4, 139.1, 134.3, 128.5, 121.8, 118.5, 113.3, 79.3, 61.4, 36.1, 30.2, 29.7, 26.9, 25.8, 18.0. HRMS (EI) calculated for $C_{19}H_{26}O_3$ ($[M]^+$): 302.1882. Found: 302.1880.

*2-Allyl-4-isopropylphenol (**5a**)*. According to the general procedure, compound **2a** (50 mg, 0.28 mmol), DMF (1 mL). Purification by flash column chromatography (EA/Hexane) to give compound **5a** (36 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03-6.91 (m, 2H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.11-5.94 (m, 1H), 5.23-5.10 (m, 2H), 3.40 (d, *J* = 6.3 Hz, 2H), 2.83 (sept, *J* = 6 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.1, 141.4, 136.6, 128.4, 125.5, 124.8, 116.4, 115.6, 35.4, 33.3, 24.2. HRMS (EI) calculated for $C_{12}H_{16}O$ ($[M]^+$): 176.1201. Found: 176.1200.

*2-Allyl-6-fluoro-4-isopropylphenol (**5b**)*. According to the general procedure, compound **2h** (100 mg, 0.51 mmol), DMF (1 mL). Compound **5b** (98 mg, 98%) was achieved without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.9-6.7 (m, 2H), 6.09-5.91 (m, 1H), 5.18-5.03 (m, 2H), 3.41 (d, *J* = 6.5 Hz, 2H), 2.87-2.72 (m, 1H), 1.20 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ150.9 (d, *J* = 235.9 Hz), 141.2 (d, *J* = 5.7 Hz), 139.2 (d, *J* = 14.3 Hz), 136.2, 127.9, 123.2 (d, *J* = 2.5 Hz), 115.9, 110.9 (d, *J* = 18.2 Hz), 34.1, 33.4, 24.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ −141.30 (d, *J* = 11.5 Hz). HRMS (EI) calculated for $C_{12}H_{15}FO$ ($[M]^+$): 194.1107. Found: 194.1101.

*Methyl 2-(3-allyl-4-hydroxyphenyl)acetate (**5c**)*. According to the general procedure, compound **2k** (60 mg, 0.3 mmol), DMF (1 mL). Compound **5c** (59 mg, 98%) was achieved without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17-6.92 (m, 2H), 6.72 (d, *J* = 8.8 Hz, 1H), 6.11-5.89 (m, 1H), 5.23-5.07 (m, 2H), 3.69 (s, 3H), 3.54 (s, 2H), 3.38 (d, *J* = 6.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.7, 153.3, 136.2, 131.2, 128.5, 126.0, 125.6, 116.5, 115.9, 52.1, 40.3, 34.9. HRMS (EI) calculated for $C_{12}H_{14}O_3$ ($[M]^+$): 206.0943. Found: 206.0946.

*4-Isopropyl-2-(2-methylallyl)phenol (**5d**)*. According to the general procedure, compound **4f** (120 mg, 0.63 mmol), DMF (1 mL). Purification by flash column chromatography (EA/Hexane) to give compound **5d** (81.6 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11-6.87 (m, 2H), 6.77 (d, *J* = 8.2 Hz, 1H), 4.93 (s, 1H), 4.86 (s, 1H), 3.37 (s, 2H), 2.84 (hept, *J* = 7.2 Hz, 1H), 1.76 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 144.8, 141.2, 128.9, 125.6, 124.4, 115.8, 112.2, 40.1, 33.2, 24.2, 22.1. HRMS (EI) calculated for $C_{13}H_{18}O$ ($[M]^+$): 190.1358. Found: 190.1360.

*3-Methylbut-2-en-1-yl 3-(4-hydroxy-3-(3-methylbut-2-en-1-yl)phenyl)propanoate (**5e**)*. According to general procedure, compound **4j** (40 mg, 0.13 mmol), DMF (1 mL). Compound **5e** (40 mg, 99%) was achieved without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99-6.85 (m, 2H) 6.71 (d, *J* = 8.7 Hz,1H), 5.40-5.21 (m, 2H), 4.57 (d, *J* = 7.2 Hz, 2H), 3.31 (d, *J* = 7.2 Hz, 2H), 2.85(t, *J* = 7.9 Hz, 2H), 2.58 (t, *J* = 7.9 Hz, 2H), 1.96-1.58 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2, 152.7, 139.1, 134.6, 132.6, 129.8, 127.1, 126.8, 121.8, 118.5, 115.6, 61.4, 36.3, 30.2, 29.8, 25.8, 17.9, 17.8. HRMS (EI) calculated for $C_{19}H_{26}O_3$ ($[M]^+$): 302.1882. Found: 302.1888.

1 mmol scale test for RSDcA reaction. According to general procedure, compound **3f** (234 mg, 1 mmol), and $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol) in CH_3CN (3 mL). Purification by flash column chromatography (Hexane) to give compound **4f** as colorless liquid (167 mg, 88%).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Scheme of synthetic methods, ^{1}H, ^{13}C, and ^{19}F NMR spectra for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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