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# Metal-Free Oxidative C−C Bond Functionalization of Methylenecyclopropanes with Ethers Leading to 2-Substituted 3,4-Dihydronaphthalenes

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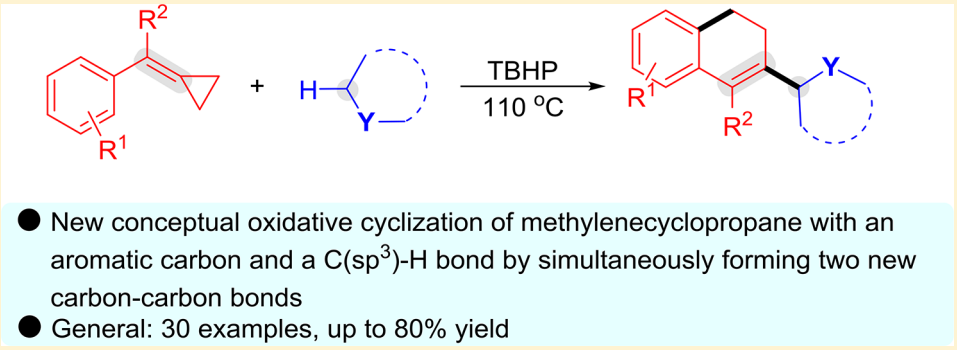
Supporting Information




**ABSTRACT:** A novel metal-free oxidative ring-opening/cyclization of methylenecyclopropanes with ethers was established for the synthesis of diverse 2-substituted 3,4-dihydronaphthalenes with high selectivity and efficiency. This oxidative cyclization is achieved by C($sp^3$)-H functionalization, ring-opening, and cyclization, and this method represents a new example of methylenecyclopropane oxidative cyclization with an aromatic carbon and a C($sp^3$)-H bond by simultaneously forming two new carbon−carbon bonds.

## INTRODUCTION

Carbon−carbon $\sigma$-bond activation and functionalization possess great potential for the synthesis of complex biological and natural product scaffolds.[1,2] A number of synthetically useful methods featuring C−C bond cleavage and subsequent formation of one or more new C−C bonds have been recently developed and applied to a wide variety of substrates.[3] In particular, three- and four-membered carbocycles[4] are perfect substrates for synthesizing fused carbocycles, key motifs in various biologically important natural products.

Methylenecyclopropanes (MCPs) are highly strained three-membered carbocycles but readily accessible molecules and have been used very frequently as important building blocks in organic synthesis.[5] Herein, we report a new C−C bond cleavage strategy for selective synthesis of 2-substituted 3,4-dihydronaphthalene architectures by metal-free oxidative C−C bond functionalization of methylenecyclopropane oxidative cyclization with an aromatic carbon and a C($sp^3$)-H bond of ether; this tandem reaction is triggered by the TBHP and involves the use of MCPs as radical acceptors to trap the ether radicals (Scheme 1c).

Simple ethers, as very important basic chemical buildings, are widely used solvents in organic synthesis and industry because of their chemical inertness under many conditions. However, use of transition-metal catalysts or oxidants affords the opportunity to use them as reactive reagents. As ethers, particularly cyclic ethers, frequently exist within the framework of many biologically active molecules,[6] many transition-metal-catalyzed methods employing simple ethers to construct higher-functionalized ethers through a C−C bond forming process have been investigated.[7−10] In this field, the reactions proceed via single electron transfer (SET) strategy and mainly focus on the reactions of the C($sp^3$)-H bonds adjacent to an oxygen atom (ethers) with C(sp)-H bonds (alkynes),[7] C($sp^2$)-H bonds,[8] and C($sp^3$)-H bonds.[9] Reactions of ethers with alkynes[7a] (Scheme 1a) and alkenes[8e] (Scheme 1b) have also been developed by Li's group. However, methods for the oxidative ring-opening/cyclization of methylenecyclopropane with an aromatic carbon and a C($sp^3$)-H bonds adjacent to an oxygen atom (ethers) are lacking.

## RESULTS AND DISCUSSION

We began our investigation by examining the reaction between 1-(benzyloxy)-2-(cyclopropylidene-methyl)benzene (**1a**) and tetrahydrofuran (THF, **2a**) (Table 1). Initially, treatment of substrate **1a** with THF **2a** and TBHP (*tert*-butyl hydroperoxide, 5.0 M in decane) (2.0 equiv) afforded the desired product **3aa**

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**Scheme 1. Reactions of C($sp^3$)-H Bonds Adjacent to an Oxygen Atom (Ethers)**

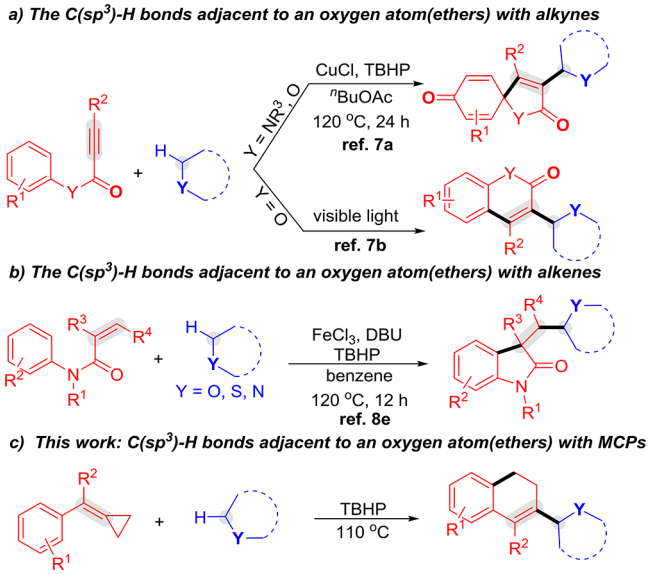
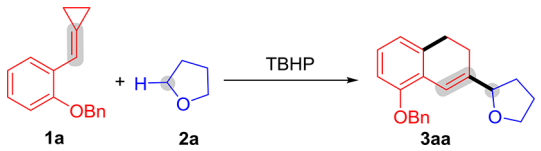



**Table 1. Screening Optimal Conditions**[a]




| entry | variation from the standard conditions | yield (%) |
|---|---|---|
| 1 | none | 75 |
| 2 | without TBHP | 0 |
| 3 | TBHP (1.5 equiv) | 67 |
| 4 | TBHP (2.5 equiv) | 73 |
| 5 | DCP instead of TBHP | 0 |
| 6 | DTBP instead of TBHP | 0 |
| 7 | BPO instead of TBHP | 0 |
| 8 | CHP instead of TBHP | 18 |
| 9 | TAHP instead of TBHP | 51 |
| 10 | TBHP (70% in water) instead of TBHP | 36 |
| 11 | BuOAc (1.5 mL) was added | 41 |
| 12 | benzene (1.5 mL) was added | 50 |
| 13 | air instead of Ar | 64 |
| 14 | 100 °C | 72 |
| 15 | 120 °C | 68 |
| 16 | 36 h | 74 |
| 17[b] | none | 67 |

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (15 mmol), TBHP (2.0 equiv), 110 °C, under argon, 24 h. [b]**1a** (10 mmol, 2.36 g).

in 75% yield under 110 °C (entry 1). A screening of the TBHP effect revealed that the absence of TBHP resulted in no detectable product **3aa** (entry 2), and the amount of TBHP affected the reaction. The results suggested that the reaction at 2.0 equiv TBHP was revealed as the most effective loading (entries 1, 3, and 4). Subsequently, a series of other oxidants such as DCP (dicumyl peroxide), DTBP (di-*tert*-butyl peroxide), BPO (benzoyl peroxide), CHP (cumene hydroperoxide), TAHP (*tert*-amyl hydroperoxide), and TBHP (70% in water) were subsequently examined (entries 5−10). We were surprised to find that only hydroperoxides (CHP, TAHP, and aqueous TBHP) afforded the target products **3aa** (entries 8−10). Gratifyingly, the product **3aa** was obtained in a slightly diminishing yield when adding 1.5 mL BuOAc or benzene to the reaction system (entries 11 and 12). It is noteworthy that a good yield is still achieved in air atmosphere (entry 13). Unfortunately, a lower temperature (100 °C) or a higher temperature (120 °C) could not promote the reaction (entries 1, 14, and 15), and extending the time also could not improve the yield (entry 16). Notably, 10 mmol of substrate **1a** was successfully converted in good yield (entry 17).

Having established the standard reaction conditions, we explored the scope of oxidative cyclization with respect to methylenecyclopropanes **1** (Table 2). Substrates **1** with a variety of substituents at the aromatic rings were successfully converted into the desired products in the yields ranging from 49 to 77%. In general, the impact of substituents at the *para*-position on the aromatic ring was investigated (products **3ba**−**ia**). Methylenecyclopropanes with an electron-donating group (OBn, OBu, OMe, Ph, or $^t$Bu) or an electron-withdrawing group (Cl or $CF_3$) at the *para*-position on the aromatic ring of MCPs were all well-tolerated (products **3ba**−**ha**), but a *p*-$NO_2$ resulted in no reaction (product **3ia**), presumably due to its instability in the presence of large amount of oxidant. Interestingly, the reaction of substrates with substituents at other positions on the aromatic ring (*o*-OMe or *m*-OMe) proceeded smoothly to afford the corresponding products in moderate yields (products **3ja** and **3ka**). To our surprise, only product **3ka** was obtained when the substrate **1k** reacted with THF **2a**. Subsequently, MCPs with two methoxy on the aromatic rings (2,4-dimethoxy, 3,4-dimethoxy, or 2,5-dimethoxy) were consistent with the optimal conditions, giving the desired products **3la**, **3ma**, and **3na** in good yields. It should be also noted the cases of **1m**, two cyclization regioisomers were formed at the same time.

Gratifyingly, a series of 2-bromo-substitution substrates were investigated and revealed as suitable substrates (**3oa**−**sa**). For example, the substrates **1o**−**q**, in which the aromatic ring had two halogen substituents, and the corresponding products **3oa**-**qa** were formed in 51−75% yields. The trisubstituted substrate **1r** produced the corresponding product **3ra** in 68% yield, and a 2-bromo-substitution substrate **1s** also showed the same activity (product **3sa**). A substrate containing only a phenyl has been also utilized for this reaction. However, we found that no desired product was formed under the standard conditions. As for the substrate **1t**, it was unstable because it could easily decompose even at low temperature under an argon atmosphere. As for four-menbered carbocyclic substrate (methylenecyclobutane **1u**), the reaction did not take place under the standard conditions.

To our delight, in the case of diphenylmethylenecyclopropanes **1v**−**z**, in which $R^2$ = H was replaced by phenyl groups, the reactions carried out under the optimal conditions to give the desired products **3va**−**za** in good yields. The diphenylmethylenecyclopropanes with a series of substituents on the two aromatic rings (methyl, methoxy, fluoro, and chloro) were compatible in this transformation.

We next set out to examine the possibility of generating 2-substituted 3,4-dihydronaphthalenes by the oxidative cyclization reaction of various ethers **2** in the presence of (cyclopropylidenemethylene)dibenzene **1v** and TBHP (Table 3). Common simple ethers such as tetrahydrofuran (**2a**), 1,2-dimethoxyethane (**2b**), 1,3-dioxolane (**2c**), and diethyl ether (**2d**) all reacted smoothly with **1v** to generate the corresponding substituted 3,4-dihydronaphthalenes (**3va**−**vd**)


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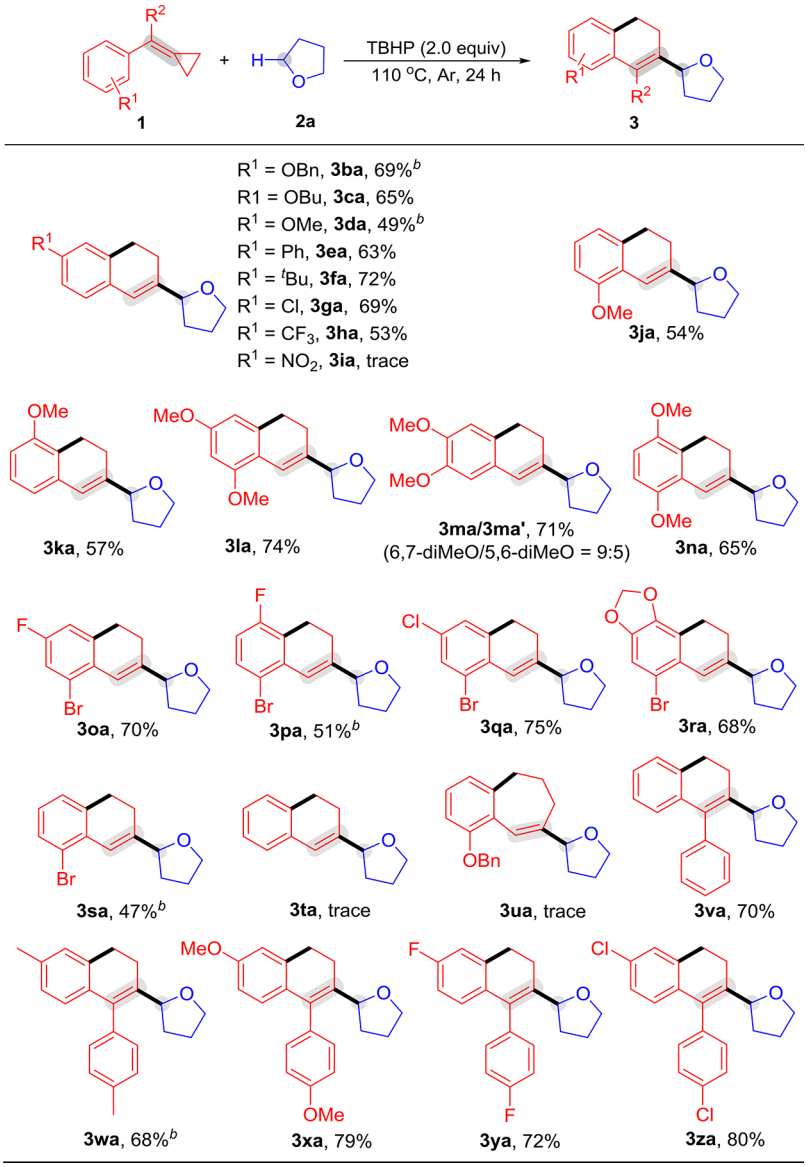
**Table 2. Screening Scope of MCPs (1)**[a]




[a]Reaction conditions: **1** (0.3 mmol), **2a** (15 mmol), TBHP (2.0 equiv), 110 °C, under argon, 24 h. [b]The byproduct was cyclization of MCPs, detected by GC−MS.

in moderate to good yields (36−71%); the reactions of 1,2-dimethoxyethane (**2b**) and diethyl ether (**2d**) proceeded regioselectively at the $CH_2$ position (products **3vb** and **3vd**). However, when tetrahydropynan and tetrahydrothiopyran were used to test this transformation, no target products were obtained, and the substrate **1v** mainly decomposed into benzophenone. Additionally, the cyclopentane, cyclohexane, anisole, and *N*-methylmorpholine were tested under the standard reaction conditions instead of ether. However, none of them gave the desired substituted 3,4-dihydronaphthalene products, and most of the raw starting materials were recovered.

It is believed that the reaction proceeded via a radical-type pathway on the basis of previously reported literature.[11] Then, the control experiments with radical inhibitors BHT and TEMPO were performed, as shown in Scheme 2. The results show that the formation of the corresponding etherified product was significantly suppressed (eqs 1 and 2). A stoichiometric amount of TEMPO resulted in no conversion of substrate **1a**; moreover, THF **2a** was converted into 2,2,6,6-tetramethyl-1-(tetrahydrofuran-2-yloxy)piperidine **4** (eq 2). These results imply that the tandem reaction includes a radical process.

Consequently, we proposed a working mechanism as outlined in Scheme 3 on the basis of the present results and literature.[5b,7−9,11] Initially, alkyl radical **B** is formed from THF **2a** by a SET from TBHP under the condition of heating. Then, alkylation of carbon−carbon double bond of MCPs **1a** with alkyl radical **B** affords the more stable benzyl radical intermediate **C**, which undergoes a ring-opening process to give the alkyl radical intermediate **D**. The key intermediate **D** undergoes direct radical cyclization with an aromatic ring to afford intermediate **E**. Finally, hydrogen abstraction of radical intermediate **E** by radicals **A** offers 2-substituted 3,4-dihydronaphthalene **3aa**.



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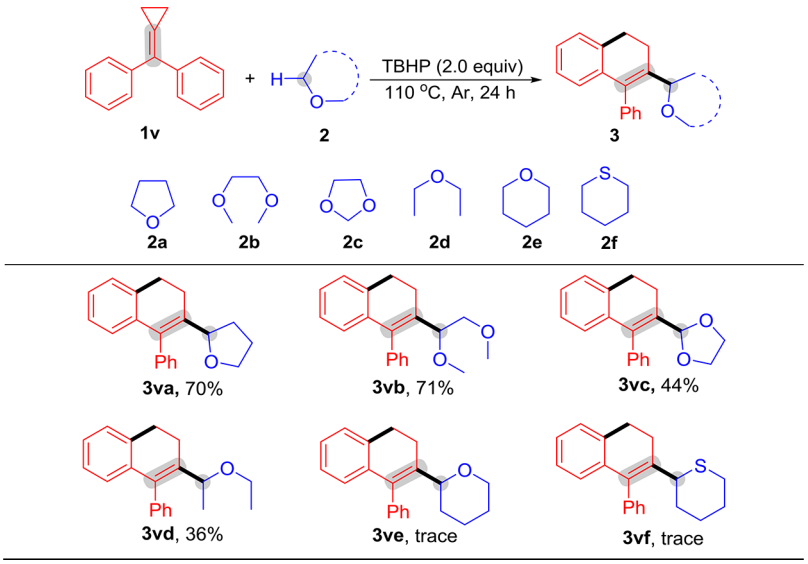
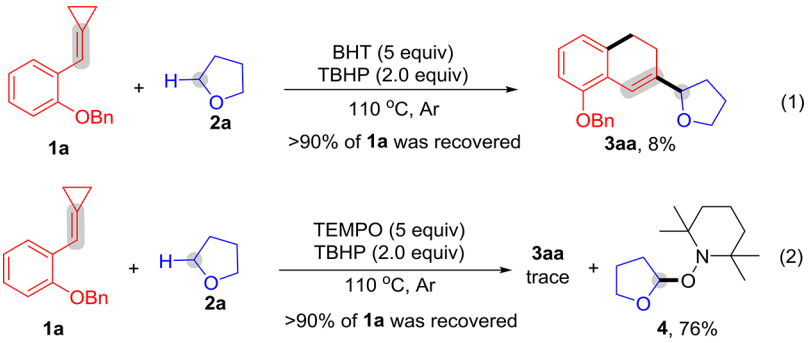
**Table 3. Screening Scope of Ethers (2)**[a]

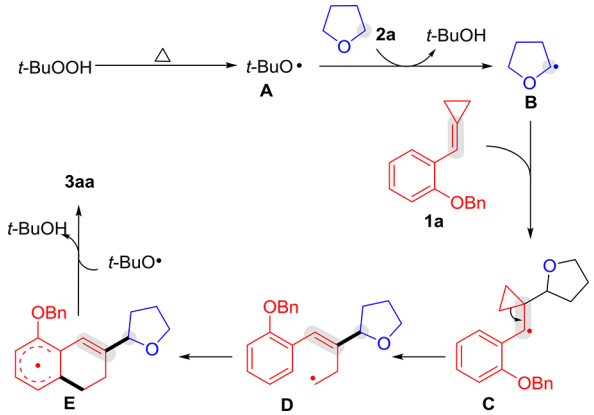



[a]Reaction conditions: **1v** (0.3 mmol), **2** (15 mmol), TBHP (2.0 equiv), 110 °C, under argon, 24 h.

**Scheme 2. Control Experiments**




**Scheme 3. Possible Mechanisms**




## CONCLUSIONS

In summary, we disclosed a novel synthetic protocol for the construction of 2-substituted 3,4-dihydronaphthalenes through an efficient metal-free oxidative ring-opening/cyclization of methylenecyclopropanes with ethers. Mechanistic studies suggested that a radical process is involved, and the reaction proceeded through an ether radical addition to the C−C double bond of MCP, followed by sequential ring opening and oxidative cyclization to afford the desired product. Importantly, this tandem method makes the construction of higher-functionalized ethers from simple ethers easy by a C($sp^3$)-H oxidative functionalization strategy and represents the first example of methylenecyclopropane oxidative cyclization with an aromatic carbon and a C($sp^3$)-H bond by simultaneously forming two new carbon−carbon bonds. Studies on the application of this new methodology to synthesize interesting biologically active compounds are currently underway in our laboratory.

## EXPERIMENTAL SECTION

**General Considerations.** $^1$H and $^{13}$C NMR spectra were recorded in $CDCl_3$ solvent on a NMR spectrometer using TMS as internal standard. LRMS was performed on a GC−MS instrument, and HRMS was measured on an ESI apparatus using TOF mass spectrometry. Melting points are uncorrected.

*Preparation of Methylenecyclopropanes (1).* All methylenecyclopropanes (**1**) were synthesized according to the known methods.[12]

*1-Butoxy-4-(cyclopropylidenemethyl)benzene (**1c**).* Colorless oil; NMR data and spectra of **1c** are not provided as the product was a mixture (contained **1c** and $PPh_3$) which was very difficult to separate. LRMS (EI, 70 eV): *m*/*z* (%) 203 ($M^+$ + 1, 4), 202 ($M^+$, 28), 145 (100), 131 (52); HRMS (ESI-TOF): *m*/*z* $C_{14}H_{19}O$ $(M + H)^+$ calcd for 203.1430, found 203.1437.

*1-(Cyclopropylidenemethyl)-4-methoxybenzene (**1k**).* Colorless oil; NMR data and spectra of **1k** are not provided as the product



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was a mixture (contained **1k** and $PPh_3$) which was very difficult to separate. LRMS (EI, 70 eV): *m/z* (%) 161 ($M^+$ + 1, 12), 160 ($M^+$, 100), 145 (66), 128 (30), 115 (88); HRMS (ESI-TOF): *m/z* $C_{11}H_{13}O$ $(M + H)^+$ calcd for 161.0961, found 161.0970.

*2-Bromo-1-(cyclopropylidenemethyl)-4-fluorobenzene (**1o**).* Yield: 1152.6 mg, 51%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.77 (t, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.07 (s, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 1.40 (t, *J* = 8.0 Hz, 2H), 1.22 (t, *J* = 8.0 Hz, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 161.1 (d, *J* = 248.7 Hz, 1C), 133.7, 133.6, 128.2, 128.1, 127.1, 122.9, 122.8, 119.9, 119.6, 115.9, 114.5, 3.8, 0.9; $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −114.0 (s, 1F); LRMS (EI, 70 eV): *m/z* (%) 228 (2), 227 ($M^+$ + 1, 1), 226 ($M^+$, 2), 147 (100), 127 (25); HRMS (ESI-TOF): *m/z* $C_{10}H_9{}^{19}F^{79}Br$ $(M + Na)^+$ calcd for 248.9686, found 248.9692.

*Bromo-2-(cyclopropylidenemethyl)-5-fluorobenzene (**1p**).* Yield: 971 mg, 43%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.51−7.47 (m, 2H), 7.09 (s, 1H), 6.82−6.77 (m, 1H), 1.44 (t, *J* = 8.0 Hz, 2H), 1.23 (t, *J* = 8.0 Hz, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 162.0 (d, *J* = 243.9 Hz, 1C), 139.1 (2C), 134.0, 133.9, 129.1, 117.3, 117.2, 116.5, 116.4, 115.3, 115.1, 113.9, 113.7, 3.9, 0.9; $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −115.2 (s, 1F); LRMS (EI, 70 eV): *m/z* (%) 228 (2), 227 ($M^+$ + 1, 1), 226 ($M^+$, 2), 147 (100), 127 (25); HRMS (ESI-TOF): *m/z* $C_{10}H_9{}^{19}F^{79}Br$ $(M + Na)^+$ calcd for 248.9686, found 248.9692.

*2-Bromo-4-chloro-1-(cyclopropylidenemethyl)benzene (**1q**).* Yield: 1587.6 mg, 63%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.72 (t, *J* = 8.4 Hz, 1H), 7.56 (s, 1H), 7.23 (t, *J* = 8.4 Hz, 1H), 7.07 (s, 1H), 1.40 (t, *J* = 8.0 Hz, 2H), 1.22 (t, *J* = 8.0 Hz, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 135.9, 132.7, 132.4, 128.2, 127.9, 127.5, 123.2, 116.1, 3.9, 0.9; LRMS (EI, 70 eV): *m/z* (%) 244 (2), 243 ($M^+$ + 1, 1), 242 ($M^+$, 1), 207 (41), 163 (25), 128 (100); HRMS (ESI-TOF): *m/z* $C_{10}H_9{}^{79}Br^{35}Cl$ $(M + H)^+$ calcd for 242.9571, found 242.9574.

*5-Bromo-6-(cyclopropylidenemethyl)benzo[d][1,3]dioxole (**1r**).* Yield: 1436.4 mg, 57%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.32 (s, 1H), 7.05 (s, 1H), 7.00 (s, 1H), 5.95 (s, 2H) 1.38 (t, *J* = 7.6 Hz, 2H), 1.18 (t, *J* = 8.0 Hz, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 147.5, 147.1, 133.8, 133.6, 128.4, 116.8, 112.5, 106.6, 101.6, 3.9, 0.7; LRMS (EI, 70 eV): *m/z* (%) 253 ($M^+$ + 1, 2), 252 ($M^+$, 7), 224 (15), 173 (79), 143 (41), 115 (100); HRMS (ESI-TOF): *m/z* $C_{11}H_{10}{}^{79}BrO_2$ $(M + H)^+$ calcd for 252.9859, found 252.9866.

**Typical Experimental Procedure for the TBHP-Mediated Synthesis of 2-Substituted 3,4-Dihydronaphthalenes from Methylenecyclopropanes with Ethers.** To a Schlenk tube were added **1** (0.3 mmol), **2** (15 mmol), and TBHP (*tert*-butyl hydroperoxide, 5.0 M in decane) (0.12 mL, 2.0 equiv). Then, the mixture was stirred at 110 °C (oil bath temperature) under nitrogen atmosphere (1 atm) for 24 h until complete consumption of starting material, as monitored by TLC and GC−MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over $Na_2SO_4$ and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 30/1) to afford the desired products **3**.

*2-(8-(Benzyloxy)-3,4-dihydronaphthalen-2-yl)tetrahydrofuran (**3aa**).* Yield: 68.9 mg, 75%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.44−7.37 (m, 2H), 7.35−7.32 (m, 2H), 7.31−7.24 (m, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.91 (s, 1H), 6.80−6.70 (m, 2H), 5.08 (s, 2H), 4.82 (t, *J* = 7.2 Hz, 1H), 4.00−3.95 (m, 1H), 3.88−3.83 (m, 1H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.35−2.19 (m, 2H), 2.09−2.01 (m, 1H), 1.96−1.91 (m, 2H), 1.79−1.72 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 153.9, 140.6, 137.5, 136.9, 128.5, 127.7, 127.2, 127.1, 123.5, 120.2, 116.7, 110.4, 82.2, 70.2, 68.6, 30.6, 28.4, 26.1, 22.6; LRMS (EI, 70 eV): *m/z* (%) 307 ($M^+$ + 1, 7), 306 ($M^+$, 34), 215 (36), 91 (100); HRMS (ESI-TOF): *m/z* $C_{21}H_{22}NaO_2$ $(M + Na)^+$ calcd for 329.1512, found 329.1534.

*2-(6-(Benzyloxy)-3,4-dihydronaphthalen-2-yl)tetrahydrofuran (**3ba**).* Yield: 63.6 mg, 69%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.43−7.35 (m, 4H), 7.33−7.29 (m, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.76−6.73 (m, 2H), 6.40 (s, 1H), 5.03 (s, 2H), 4.42 (t, *J* = 7.2 Hz, 1H), 4.00−3.95 (m, 1H), 3.88−3.84 (m, 1H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.27−2.20 (m, 2H), 2.06−2.03 (m, 1H), 1.97−1.92 (m, 2H), 1.75−1.72 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 157.7, 139.0, 137.1, 136.8, 128.5, 127.8, 127.6, 127.4, 126.9, 121.5, 114.4, 112.0, 81.7, 69.9, 68.5, 30.6, 28.5, 26.0, 23.0; LRMS (EI, 70 eV): *m/z* (%)307 ($M^+$ + 1, 7), 306 ($M^+$, 34), 215 (36), 91 (100); HRMS (ESI-TOF): *m/z* $C_{21}H_{22}NaO_2$ $(M + Na)^+$ calcd for 329.1512, found 329.1534.

*2-(6-Butoxy-3,4-dihydronaphthalen-2-yl)tetrahydrofuran (**3ca**).* Yield: 53.0 mg, 65%; colorless oil; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 6.95 (d, *J* = 7.5 Hz, 1H), 6.68−6.66 (m, 2H), 6.40 (s, 1H), 4.43 (t, *J* = 7.0 Hz, 1H), 3.99−3.88 (m, 3H), 3.86 (t, *J* = 7.0 Hz, 1H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.28−2.21 (m, 2H), 2.07−2.04 (m, 1H), 1.97−1.93 (m, 2H), 1.78−1.71 (m, 3H), 1.51−1.47 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$): $\delta$ 158.0, 138.6, 136.7, 127.2, 126.9, 114.1, 111.7, 81.7, 68.4, 67.6, 31.1, 30.6, 28.6, 26.0, 23.1, 19.2, 13.8; LRMS (EI, 70 eV): *m/z* (%) 272 ($M^+$, 41), 199 (100), 128 (32); HRMS (ESI-TOF): *m/z* $C_{18}H_{25}O_2$ $(M + H)^+$ calcd for 273.1849, found 273.1855.

*2-(6-Methoxy-3,4-dihydronaphthalen-2-yl)tetrahydrofuran (**3da**).* Yield: 33.7 mg, 49%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.11 (t, *J* = 7.6 Hz, 1H), 6.75−6.71 (m, 2H), 6.42 (s, 1H), 4.45 (t, *J* = 7.2 Hz, 1H), 4.02−3.97 (m, 1H), 3.88−3.83 (m, 1H), 3.81 (s, 3H), 2.89−2.78 (m, 2H), 2.30−2.16 (m, 2H), 2.09−2.01 (m, 1H), 1.99−1.89 (m, 2H), 1.79−1.70 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 156.0, 141.8, 135.3, 126.7, 122.7, 121.7, 119.1, 109.3, 81.6, 68.6, 55.5, 30.7, 26.0, 22.8, 20.2; LRMS (EI, 70 eV): *m/z* (%) 230 ($M^+$, 97), 229 (38), 199 (100); HRMS (ESI-TOF): *m/z* $C_{15}H_{18}NaO_2$ $(M + Na)^+$ calcd for 253.1199, found 253.1210.

*2-(6-Phenyl-3,4-dihydronaphthalen-2-yl)tetrahydrofuran (**3ea**).* Yield: 52.2 mg, 63%; colorless oil; $^1H$ NMR (500 MHz, $CDCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.60 (d, *J* = 7.5 Hz, 2H), 7.45−7.31 (m, 5H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.52 (s, 1H), 4.49 (t, *J* = 7.5 Hz, 1H), 4.04−4.00 (m, 1H), 3.92−3.88 (m, 1H), 2.91 (t, *J* = 8.0 Hz, 2H), 2.38−2.27 (m, 2H), 2.13−2.07 (m, 1H), 2.01−1.96 (m, 2H), 1.80−1.75 (m, 1H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$): $\delta$ 141.9, 141.1, 139.4, 135.5, 133.5, 128.7, 127.0, 126.9, 126.3, 126.0, 125.2, 121.5, 81.6, 68.6, 30.8, 28.2, 26.0, 23.4; LRMS (EI, 70 eV): *m/z* (%) 277 ($M^+$ + 1, 17), 276 ($M^+$, 86), 233 (26), 217 (29), 199 (100); HRMS (ESI-TOF): *m/z* $C_{20}H_{21}O$ $(M + H)^+$ calcd for 277.1578, found 277.1586.

*2-(6-(tert-Butyl)-3,4-dihydronaphthalen-2-yl)tetrahydrofuran (**3fa**).* Yield: 55.3 mg, 72%; colorless oil; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.18−7.14 (m, 2H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.44 (s, 1H), 4.45 (t, *J* = 7.5 Hz, 1H), 4.02−3.97 (m, 1H), 3.90−3.85 (m, 1H), 2.83 (t, *J* = 8.0 Hz, 2H), 2.33−2.22 (m, 2H), 2.09−2.04 (m, 1H), 1.98−1.93 (m, 2H), 1.77−1.71 (m, 1H), 1.31 (s, 9H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$): $\delta$ 149.6, 140.8, 134.7, 131.7, 125.6, 124.4, 123.2, 121.7, 81.7, 68.5, 34.5, 31.3, 30.7, 28.5, 25.9, 23.4; LRMS (EI, 70 eV): *m/z* (%) 256 ($M^+$, 49), 199(97), 128 (100); HRMS (ESI-TOF): *m/z* $C_{18}H_{25}O$ $(M + H)^+$ calcd for 257.1900, found 257.1907.

*2-(6-Chloro-3,4-dihydronaphthalen-2-yl)tetrahydrofuran (**3ga**).* Yield: 47.8 mg, 69%; colorless oil; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.10−7.08 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.42 (s, 1H), 4.43 (t, *J* = 7.5 Hz, 1H), 4.01−3.96 (m, 1H), 3.89−3.85 (m, 1H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.30−2.19 (m, 2H), 2.11−2.05 (m, 1H), 1.98−1.93 (m, 2H), 1.74−1.68 (m, 1H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$): $\delta$ 142.2, 136.8, 132.7, 131.7, 127.3, 127.0, 126.4, 120.9, 81.4, 68.6, 30.8, 27.9, 25.9, 23.1; LRMS (EI, 70 eV): *m/z* (%) 235 ($M^+$ + 1, 7), 234 ($M^+$, 22), 199 (56), 128 (100); HRMS (ESI-TOF): *m/z* $C_{14}H_{16}{}^{35}ClO$ $(M + H)^+$ calcd for 235.0884, found 235.0891.

*2-(6-(Trifluoromethyl)-3,4-dihydronaphthalen-2-yl)-tetrahydrofuran (**3ha**).* Yield: 42.6 mg, 53%; colorless oil, $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.38 (d, *J* = 8.0 Hz, 1H), 7.33(s, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.50 (s, 1H), 4.46 (t, *J* = 7.2 Hz, 1H), 4.03−4.00 (m, 1H), 3.92−3.86 (m, 1H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.37−2.23 (m, 2H), 2.17−2.06 (m, 1H), 2.00−1.93 (m, 2H), 1.77−1.69 (m, 1H); $^{13}C-\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 144.8, 137.6, 135.5, 128.4, 128.0, 125.9, 125.4, 123.9 (2C), 123.5, 123.4, 123.0, 120.7, 81.2, 68.7, 30.9, 27.8, 25.9, 23.3; $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −62.3 (s, 3F); LRMS (EI, 70 eV): *m/z* (%) 268 ($M^+$, 100), 267 (31), 177 (52); HRMS



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(ESI-TOF): $m/z$ $C_{15}H_{16}{}^{19}F_3O$ $(M + H)^+$ calcd for 269.1148, found 269.1155.

*2-(8-Methoxy-3,4-dihydronaphthalen-2-yl)tetrahydrofuran (**3ja**).* Yield: 37.3 mg, 54%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.07 (d, $J$ = 7.6 Hz, 1H), 6.83 (s, 1H), 6.73 (t, $J$ = 8.0 Hz, 2H), 4.48 (t, $J$ = 7.2 Hz, 1H), 4.02−3.97 (m, 1H), 3.94−3.82 (m, 1H), 3.81 (s, 3H), 2.80 (t, $J$ = 8.0 Hz, 2H), 2.33−2.18 (m, 2H), 2.10−2.03 (m, 1H), 1.97−1.91 (m, 2H), 1.80−17.1 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 154.7, 140.6, 136.7, 127.1, 122.9, 119.9, 116.2, 108.7, 82.1, 68.6, 55.5, 30.7, 28.4, 26.1, 22.7; LRMS (EI, 70 eV): $m/z$ (%) 230 ($M^+$, 97), 229 (38), 199 (100); HRMS (ESI-TOF): $m/z$ $C_{15}H_{18}NaO_2$ $(M + Na)^+$ calcd for 253.1199, found 253.1210.

*2-(5-Methoxy-3,4-dihydronaphthalen-2-yl)tetrahydrofuran (**3ka**).* Yield: 39.3 mg, 57%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.96 (d, $J$ = 8.8 Hz, 1H), 6.68−6.67 (m, 2H), 6.40 (m, 1H), 4.43 (t, $J$ = 7.2 Hz, 1H), 4.01−3.96 (m, 1H), 3.89−3.84 (m, 1H), 3.79 (s, 3H), 2.81 (t, $J$ = 8.0 Hz, 2H), 2.32−2.16 (m, 2H), 2.10−2.02 (m, 1H), 1.98−1.93 (m, 2H), 1.78−1.71 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 158.4, 138.8, 136.8, 127.4, 126.9, 121.6, 113.5, 111.1, 81.7, 68.5, 55.2, 30.6, 28.6, 26.0, 23.1; LRMS (EI, 70 eV): $m/z$ (%) 230 ($M^+$, 97), 229 (38), 199 (100); HRMS (ESI-TOF): $m/z$ $C_{15}H_{18}NaO_2$ $(M + Na)^+$ calcd for 253.1199, found 253.1210.

*2-(6,8-Dimethoxy-3,4-dihydronaphthalen-2-yl)tetrahydrofuran (**3la**).* Yield: 47.7 mg, 74%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.72 (s, 1H), 6.30 (s, 2H), 4.45 (t, $J$ = 7.2 Hz, 1H), 3.98−3.96 (m, 1H), 3.90−3.83 (m, 1H), 3.79 (s, 6H), 2.76 (t, $J$ = 8.0 Hz, 2H), 2.31−2.14 (m, 2H), 2.08−2.00 (m, 1H), 1.96−1.91 (m, 2H), 1.79−1.70 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 159.3, 155.9, 137.8, 137.6, 116.3, 116.2, 104.5, 96.3, 82.2, 68.5, 55.5, 55.3, 30.6, 29.1, 26.1, 22.7; LRMS (EI, 70 eV): $m/z$ (%) 260 ($M^+$, 24), 229 (71), 198 (100); HRMS (ESI-TOF): $m/z$ $C_{16}H_{20}NaO_3$ $(M + Na)^+$ calcd for 283.1305, found 283.1287.

*2-(6,7-Dimethoxy-3,4-dihydronaphthalen-2-yl)tetrahydrofuran (**3ma**).* Yield: 29.7 mg, 46%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.67 (s, 1H), 6.61 (s, 1H), 6.37 (s, 1H), 4.44 (t, $J$ = 7.2 Hz, 1H), 4.01−3.89 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.76 (t, $J$ = 8.0 Hz, 2H), 2.30−2.16 (m, 2H), 2.11−2.03 (m, 1H), 1.99−1.94 (m, 2H), 1.78−1.69 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 147.5, 147.3, 139.5, 127.5, 127.0, 121.6, 111.2, 109.9, 81.7, 68.5, 56.0 (2C), 30.7, 27.8, 26.0, 23.4; LRMS (EI, 70 eV): $m/z$ (%) 260 ($M^+$, 24), 229 (71), 198 (100); HRMS (ESI-TOF): $m/z$ $C_{16}H_{20}NaO_3$ $(M + Na)^+$ calcd for 283.1305, found 283.1287.

*2-(5,6-Dimethoxy-3,4-dihydronaphthalen-2-yl)tetrahydrofuran (**3ma′**).* Yield: 19.5 mg, 25%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.77 (d, $J$ = 8.0 Hz, 1H), 6.69 (d, $J$ = 8.0 Hz, 1H), 6.39 (s, 1H), 4.01−3.96 (m, 2H), 3.89−3.85 (m, 4H), 3.79 (s, 3H), 2.94−2.83 (m, 2H), 2.30−2.11 (m, 2H), 2.10−2.03 (m, 1H), 1.99−1.93 (m, 2H), 1.78−1.69 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 151.9, 145.8, 139.3, 128.8, 128.3, 121.8, 121.5, 109.5, 81.7, 68.5, 60.4, 55.7, 30.7, 26.0, 22.6, 21.2; LRMS (EI, 70 eV): $m/z$ (%) 260 ($M^+$, 24), 229 (71), 198 (100); HRMS (ESI-TOF): $m/z$ $C_{16}H_{20}NaO_3$ $(M + Na)^+$ calcd for 283.1305, found 283.1287.

*2-(5,8-Dimethoxy-3,4-dihydronaphthalen-2-yl)tetrahydrofuran (**3na**).* Yield: 41.9 mg, 65%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.80 (s, 1H), 6.69−6.64 (m, 2H), 4.80 (t, $J$ = 7.2 Hz, 1H), 4.01−3.95 (m, 1H), 3.90−3.86 (m, 1H), 3.78 (s, 6H), 2.88−2.82 (m, 1H), 2.77−2.73 (m, 1H), 2.31−2.11 (m, 2H), 2.10−2.04 (m, 1H), 1.97−1.90 (m, 2H), 1.80−1.73(m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 150.4, 149.5, 141.0, 124.5, 124.2, 116.1, 109.6, 108.6, 82.0, 68.6, 56.0 (2C), 30.7, 26.0, 22.1, 20.8; LRMS (EI, 70 eV): $m/z$ (%) 260 ($M^+$, 24), 229 (71), 198 (100); HRMS (ESI-TOF): $m/z$ $C_{16}H_{20}NaO_3$ $(M + Na)^+$ calcd for 283.1305, found 283.1287.

*2-(8-Bromo-6-fluoro-3,4-dihydronaphthalen-2-yl)-tetrahydrofuran (**3oa**).* Yield: 62.2 mg, 70%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.11 (d, $J$ = 8.0 Hz, 1H), 6.79 (d, $J$ = 8.4 Hz, 1H), 6.75 (s, 1H), 4.48 (t, $J$ = 7.2 Hz, 1H), 4.03−3.97 (m, 1H), 3.91−3.86 (m, 1H), 2.80 (t, $J$ = 8.0 Hz, 2H), 2.30−2.16 (m, 2H), 2.13−2.07 (m, 1H), 2.00−1.92 (m, 2H), 1.78−1.71 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 160.6 (d, $J$ = 248 Hz, 1C), 143.4, 143.3, 139.3, 139.2, 129.6 (2C), 121.5, 121.4, 120.0, 117.6, 117.4, 114.0, 113.8, 81.5, 68.7, 30.8, 29.2, 26.0, 22.5; $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −114.3 (s, 1F); LRMS (EI, 70 eV): $m/z$ (%) 298 ($M^+$ + 2, 58), 297 ($M^+$ + 1, 26), 296 ($M^+$, 57), 217 (45), 146 (100); HRMS (ESI-TOF): $m/z$ $C_{14}H_{14}{}^{79}Br^{19}FNaO$ $(M + Na)^+$ calcd for 319.0104, found 319.0110.

*2-(8-Bromo-5-fluoro-3,4-dihydronaphthalen-2-yl)-tetrahydrofuran (**3pa**).* Yield: 45.4 mg, 51%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.33−7.29 (m, 1H), 6.78−6.73 (m, 2H), 4.97 (t, $J$ = 7.2 Hz, 1H), 4.02−3.99 (m, 1H), 3.92−3.89 (m, 1H), 2.88−2.78 (m, 2H), 2.31−2.17 (m, 2H), 2.15−2.09 (m, 1H), 1.99−1.96 (m, 2H), 1.78−1.72 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 158.7 (d, $J$ = 242 Hz, 1C), 145.3, 135.0, 131.0, 130.9, 123.8, 123.6, 120.4, 120.3, 116.0, 115.0, 114.8, 81.4, 68.7, 30.8, 25.9, 22.0, 20.4; $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −121.3 (s, 1F), −123.1 (s, 1F); LRMS (EI, 70 eV): $m/z$ (%)298 ($M^+$ + 2, 58), 297 ($M^+$ + 1, 26), 296 ($M^+$, 57), 217 (45), 146 (100); HRMS (ESI-TOF): $m/z$ $C_{14}H_{14}{}^{79}Br^{19}FNaO$ $(M + Na)^+$ calcd for 319.0104, found 319.0110.

*2-(8-Bromo-6-chloro-3,4-dihydronaphthalen-2-yl)-tetrahydrofuran (**3qa**).* Yield: 70.0 mg, 75%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.38 (s, 1H), 7.03 (s, 1H), 6.76 (s, 1H), 4.48 (t, $J$ = 7.2 Hz, 1H), 4.03−3.97 (m, 1H), 3.91−3.86 (m, 1H), 2.78 (t, $J$ = 8.0 Hz, 2H), 2.30−2.16 (m, 2H), 2.14−2.07 (m, 1H), 2.00−1.89 (m, 2H), 1.77−1.70 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 144.7, 138.7, 131.9, 130.1, 126.6, 126.4, 121.8, 120.0, 81.4, 68.7, 30.8, 28.8, 26.0, 22.7; LRMS (EI, 70 eV): $m/z$ (%)312 ($M^+$, 86), 311 (25), 310 (60), 271 (100); HRMS (ESI-TOF): $m/z$ $C_{14}H_{15}{}^{79}Br^{35}ClO$ $(M + H)^+$ calcd for 312.9989, found 312.9995.

*5-Bromo-7-(tetrahydrofuran-2-yl)-8,9-dihydronaphtho[1,2-d]-[1,3]dioxole (**3ra**).* Yield: 65.7 mg, 68%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.84 (s, 1H), 6.72 (s, 1H), 5.94 (s, 2H), 4.46 (t, $J$ = 7.2 Hz, 1H), 4.02−3.96 (m, 1H), 3.90−3.84 (m, 1H), 2.77−2.71 (m, 2H), 2.28−2.16 (m, 2H), 2.12−2.05 (m, 1H), 1.99−1.94 (m, 2H), 1.76−1.70 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 146.6, 143.9, 141.4, 127.3, 120.9, 117.8, 112.7, 110.2, 101.4, 81.8, 68.6, 30.7, 26.0, 21.8, 21.6; LRMS (EI, 70 eV): $m/z$ (%) 324 ($M^+$ + 2, 64), 322 ($M^+$, 73), 243 (100); HRMS (ESI-TOF): $m/z$ $C_{15}H_{16}{}^{79}BrO_3$ $(M + H)^+$ calcd for 323.0277, found 323.0285.

*2-(8-Bromo-3,4-dihydronaphthalen-2-yl)tetrahydrofuran (**3sa**).* Yield: 42 mg, 47%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.36 (d, $J$ = 8.0 Hz, 1H), 7.03 (d, $J$ = 7.2 Hz, 1H), 6.94 (t, $J$ = 8.0 Hz, 1H), 6.82 (s, 1H), 4.50 (t, $J$ = 7.2 Hz, 1H), 4.04−3.89 (m, 1H), 3.92−3.87 (m, 1H), 2.81 (t, $J$ = 8.0 Hz, 2H), 2.29−2.18 (m, 2H), 2.13−2.07 (m, 1H), 2.00−1.95 (m, 2H), 1.79−1.70 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 144.3, 137.7, 133.2, 130.7, 127.5, 126.3, 121.9, 120.8, 81.6, 68.7, 30.8, 28.9, 26.0, 22.9; LRMS (EI, 70 eV): $m/z$ (%) 279 ($M^+$ + 1, 19), 278 ($M^+$, 45), 199 (70), 128 (100); HRMS (ESI-TOF): $m/z$ $C_{14}H_{15}{}^{79}BrNaO$ $(M + Na)^+$ calcd for 301.0198, found 301.0221.

*2-(1-Phenyl-3,4-dihydronaphthalen-2-yl)tetrahydrofuran (**3va**).* Yield: 58.0 mg, 70%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.42−7.33 (m, 3H), 7.23−7.07 (m, 4H), 7.01 (t, $J$ = 7.2 Hz, 1H), 6.57 (d, $J$ = 7.6 Hz, 1H), 4.34 (t, $J$ = 8.0 Hz, 1H), 3.94−3.89 (m, 1H), 3.75−3.70 (m, 1H), 2.99−2.81 (m, 2H), 2.61−2.54 (m, 1H), 2.37−2.29 (m, 1H), 1.94−1.64 (m, 4H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 138.8, 137.5, 136.5, 135.9, 135.4, 129.9, 128.0, 127.0, 126.8, 126.6, 126.1, (2C), 78.7, 68.8, 30.8, 28.5, 26.7, 21.5; LRMS (EI, 70 eV): $m/z$ (%) 277 ($M^+$ + 1, 17), 276 ($M^+$, 86), 233 (26), 217 (29), 199 (100); HRMS (ESI-TOF): $m/z$ $C_{20}H_{21}O$ $(M + H)^+$ calcd for 277.1578, found 277.1586.

*2-(6-Methyl-1-(p-tolyl)-3,4-dihydronaphthalen-2-yl)-tetrahydrofuran (**3wa**).* Yield: 62.4 mg, 68%; colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.27−7.25(m, 1H), 7.23−7.17 (m, 2H), 7.11−7.09 (m, 1H), 6.98 (br, 1H), 6.82 (d, $J$ = 7.6 Hz, 1H), 6.49 (d, $J$ = 8.0 Hz, 1H), 4.36 (t, $J$ = 7.2 Hz, 1H), 3.91−3.88 (m, 1H), 3.74−3.71 (m, 1H), 2.94−2.86 (m, 1H), 2.81−2.78 (m, 1H), 2.56−2.52 (m, 1H), 2.39 (s, 3H), 2.33−2.28 (m, 4H), 1.93−1.81 (m, 3H), 1.80−1.68 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 136.3, 136.2, 135.9, 135.2, 134.0, 130.1, 129.3, 128.9, 127.9, 126.6, 126.2, 126.1, 78.7, 68.7, 30.7, 28.6, 26.7, 21.6, 21.2, 21.0; LRMS (EI, 70 eV): $m/z$ (%) 305 ($M^+$ + 1, 22), 304 ($M^+$, 100), 289 (25), 261 (61), 213 (84); HRMS (ESI-TOF): $m/z$ $C_{22}H_{25}O$ $(M + H)^+$ calcd for 305.1900, found 305.1911.



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*2-(6-Methoxy-1-(4-methoxyphenyl)-3,4-dihydronaphthalen-2-yl)tetrahydrofuran (**3xa**).* Yield: 79.6 mg, 79%; colorless oil; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.15−6.98 (m, 2H), 6.91 (d, $J$ = 8.5 Hz, 2H), 6.73 (s, 1H), 6.56−6.53 (m, 2H), 4.38−4.35 (m, 1H), 2.92−3.89 (m, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 3.74−3.70 (m, 1H), 2.94−2.88 (m, 1H), 2.83−2.73 (m, 1H), 2.56−2.50 (m, 1H), 2.33−2.26 (m, 1H), 1.95−1.88 (m, 1H), 1.87−1.79 (m, 2H), 1.75−1.69 (m, 1H); $^{13}$C{$^1$H}NMR (125 MHz, $CDCl_3$): $\delta$ 158.4, 158.3, 137.8, 134.8, 134.7, 131.2, 130.0, 127.5, 127.3, 114.0, 113.2, 110.7, 78.8, 68.7, 55.2 (2C), 30.7, 29.0, 26.7, 21.6; LRMS (EI, 70 eV): $m/z$ (%) 337 ($M^+$ + 1, 15), 335 ($M^+$, 43), 305 (25), 274 (100); HRMS (ESI-TOF): $m/z$ $C_{22}H_{25}O_3$ $(M + H)^+$ calcd for 337.1798, found 337.1794.

*2-(6-Fluoro-1-(4-fluorophenyl)-3,4-dihydronaphthalen-2-yl)-tetrahydrofuran (**3ya**).* Yield: 67.4 mg, 72%; colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.14−6.98 (m, 4H), 6.87 (d, $J$ = 8.8 Hz, 1H), 6.70 (t, $J$ = 8.4 Hz, 1H), 6.50 (t, $J$ = 7.2 Hz, 1H), 4.30 (t, $J$ = 8.0 Hz, 1H), 3.95−3.89 (m, 1H), 3.76−3.71 (m, 1H), 2.90−2.82 (m, 2H), 2.59−2.52 (m, 1H), 2.35−2.27 (m, 1H), 1.98−1.90 (m, 1H), 1.88−1.80 (m, 2H), 1.79−1.70 (m, 1H); $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$): $\delta$ 163.2, 162.8, 160.7, 160.3, 138.4 (2C), 137.2, 134.4 (2C), 133.7, 132.6, 131.5, 128.0, 127.5, 127.4, 115.7, 115.5, 114.3, 114.1, 112.6, 112.4, 106.6, 78.5, 68.8, 30.8, 28.6, 26.7, 21.3; LRMS (EI, 70 eV): $m/z$ (%) 314 ($M^+$ + 2, 100), 312 ($M^+$, 81), 268 (54), 162 (92); HRMS (ESI-TOF): $m/z$ $C_{20}H_{19}{}^{19}F_2O$ $(M + H)^+$ calcd for 313.1398, found 313.1396.

*2-(6-Chloro-1-(4-chlorophenyl)-3,4-dihydronaphthalen-2-yl)-tetrahydrofuran (**3za**).* Yield: 82.6 mg, 80%; colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.37 (d, $J$ = 8.4 Hz, 2H), 7.14−7.04 (m, 3H), 6.97 (d, $J$ = 8.0 Hz, 1H), 6.46 (d, $J$ = 8.0 Hz, 1H), 4.29 (t, $J$ = 7.2 Hz, 1H), 3.92−3.88 (m, 1H), 3.76−3.73 (m, 1H), 2.90−2.78−6.95 (m, 2H), 2.58−2.53 (m, 1H), 2.35−2.31 (m, 1H), 1.96−1.82(m, 3H), 1.72−1.69 (m, 1H); $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$): $\delta$ 138.5, 137.7, 136.8, 134.6, 133.5, 133.1, 132.2, 131.5, 128.8, 127.2, 127.1, 126.1, 78.4, 68.9, 30.8, 28.2, 26.7, 21.4; LRMS (EI, 70 eV): $m/z$ (%) 346 ($M^+$ + 2, 46), 344 ($M^+$, 69), 301 (33), 233 (100); HRMS (ESI-TOF): $m/z$ $C_{20}H_{19}{}^{35}Cl_2O$ $(M + H)^+$ calcd for 345.0807, found 345.0815.

*3-(1,2-Dimethoxyethyl)-4-phenyl-1,2-dihydronaphthalene (**3vb**).* Yield: 62.6 mg, 71%; colorless oil; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.43−7.40 (m, 2H), 7.36−7.33 (m, 1H), 7.17−7.11 (m, 4H), 7.05−7.02 (m, 1H), 6.59 (d, $J$ = 4.0 Hz, 1H), 4.09−4.06 (m, 1H), 3.54−3.52 (m, 1H), 3.39−3.38 (m, 1H), 3.29 (s, 3H), 3.23 (s, 3H), 2.89−2.85 (m, 2H), 2.55−2.50 (m, 1H), 2.34−2.27 (m, 1H); $^{13}$C{$^1$H}NMR (125 MHz, $CDCl_3$): $\delta$ 138.7, 138.4, 136.3, 136.0, 133.9, 130.5, 129.3, 128.5, 127.1, 127.0, 126.3 (2C), 79.2, 74.1, 59.1, 56.3, 28.3, 21.8; LRMS (EI, 70 eV): $m/z$ (%) 295 ($M^+$ + 1, 12), 294 ($M^+$, 42), 205 (88), 128 (100); HRMS (ESI-TOF): $m/z$ $C_{20}H_{23}O_2$ $(M + H)^+$ calcd for 295.1693, found 295.1699.

*2-(1-Phenyl-3,4-dihydronaphthalen-2-yl)-1,3-dioxolane (**3vc**).* Yield: 36.7 mg, 44%; colorless oil; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.41−7.34 (m, 3H), 7.26−7.22 (m, 2H), 7.19−7.13 (m, 2H), 7.03 (t, $J$ = 7.5 Hz, 1H), 6.64 (d, $J$ = 7.5 Hz, 1H), 5.21 (s, 1H), 4.06−3.99 (m, 2H), 3.85−3.79 (m, 2H), 2.91 (t, $J$ = 8.0 Hz, 2H), 2.48 (t, $J$ = 8.0 Hz, 2H); $^{13}$C{$^1$H}NMR (125 MHz, $CDCl_3$): $\delta$ 140.1, 137.5, 136.6, 135.9, 132.4, 130.2, 128.2, 127.5, 127.2 (2C), 126.6, 126.1, 102.3, 65.5, 28.2, 20.6; LRMS (EI, 70 eV): $m/z$ (%)279 ($M^+$ + 1, 26), 278 ($M^+$, 55), 205 (100), 128 (49); HRMS (ESI-TOF): $m/z$ $C_{19}H_{19}O_2$ $(M + H)^+$ calcd for 279.1380, found 279.1385.

*3-(1-Ethoxyethyl)-4-phenyl-1,2-dihydronaphthalene (**3vd**).* Yield: 30.0 mg, 36%; colorless oil; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.40−7.37 (m, 2H), 7.34−7.31 (m, 1H), 7.23−7.08 (m, 4H), 7.01 (t, $J$ = 9.5 Hz, 1H), 6.57 (d, $J$ = 9.5 Hz, 1H), 4.06−4.02 (m, 1H), 3.49−3.44 (m, 1H), 3.15−3.11 (m, 3H), 2.81 (t, $J$ = 9.0 Hz, 2H), 1.12 (d, $J$ = 8.0 Hz, 3H), 1.10 (t, $J$ = 7.0 Hz, 3H); $^{13}$C{$^1$H}NMR (125 MHz, $CDCl_3$): $\delta$ 142.0, 138.8, 138.4, 136.4, 135.8, 132.3, 130.0, 128.6, 128.2, 126.8, 126.3, 126.0, 73.9, 63.2, 28.3, 25.5, 19.8, 15.4; LRMS (EI, 70 eV): $m/z$ (%) 279 ($M^+$ + 1, 26), 278 ($M^+$, 55), 205 (100), 128 (49); HRMS (ESI-TOF): $m/z$ $C_{20}H_{23}O$ $(M + H)^+$ calcd for 279.1743, found 279.1748.

*2,2,6,6-Tetramethyl-1-((tetrahydrofuran-2-yl)oxy)piperidine (**4**).* Yield: 258 mg, 76%; colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.35−5.33 (m, 1H), 3.88−3.77 (m, 2H), 1.99−1.86 (m, 3H), 1.79−1.72 (m, 1H), 1.48−1.41 (m, 6H), 1.34−1.20 (m, 3H), 1.12−1.02 (m, 9H); $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$): $\delta$ 109.5, 66.6, 40.1, 39.6, 33.8, 33.3, 31.2, 23.9, 20.4, 20.0, 17.2; LRMS (EI, 70 eV): $m/z$ (%) 227 ($M^+$, 2), 142 (100), 71 (54); HRMS (ESI-TOF): $m/z$ $C_{13}H_{26}NO_2$ $(M + H)^+$ calcd for 228.1958, found 228.1964.

## ■ ASSOCIATED CONTENT

### Supporting Information

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Copies of spectra (PDF)

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### Notes

The authors declare no competing financial interest.

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