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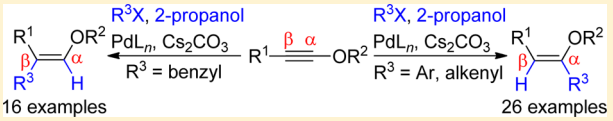
Palladium-Catalyzed Hydroarylation, Hydroalkenylation, and Hydrobenzylation of Ynol Ethers with Organohalides: A Regio- and Stereoselective Entry to α,β- and β,β-Disubstituted Alkenyl Ethers

Weijian Cui, Jing Yin, Renwei Zheng, Cungui Cheng, Yihui Bai, and Gangguo Zhu*

Department of Chemistry, Zhejiang Normal University, 688 Yingbin Road, Jinhua 321004, China

Supporting Information

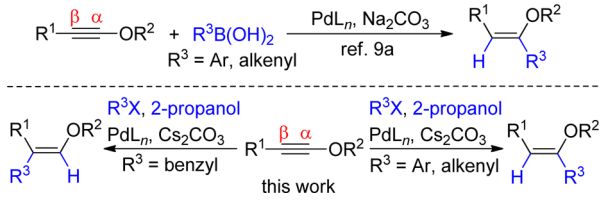
ABSTRACT: A Pd-catalyzed reductive addition of organohalides, including aryl, alkenyl, and benzyl halides, to ynol ethers has been realized in the presence of 2-propanol, giving α,β- and β,β-disubstituted olefinic ethers in satisfactory yields with excellent regio- and stereoselectivity. It represents the first highly regio- and stereoselective hydroarylation, hydroalkenylation, and hydrobenzylation of ynol ethers.



INTRODUCTION

The development of operationally simple and general methods for the preparation of alkenyl ethers is of importance in organic chemistry, and consequently, a variety of protocols have been described.[1] However, there is still an urgent need for the discovery of regio- and stereoselective approaches to this framework, especially the catalytic versions. Recently, the functionalization of ynol ethers has emerged as a straightforward and effective protocol for constructing stereodefined vinylic ethers, including the hydrohalogenation,[2] hydroboration,[3] chloroallylation,[4] reduction,[5] carbometalation,[6] cycloaddition,[7] and radical reactions.[8] In a previous work, we reported a highly regio- and stereoselective approach to α,β-disubstituted enol ethers featuring the Pd-catalyzed addition of boronic acids to ynol ethers (Scheme 1).[9a] Compared with the

Scheme 1. Summary of Our Efforts to Access Alkenyl Ethers



prevalence of alkyne hydroarylation using boronic acids,[10] surprisingly, transition-metal-catalyzed hydroarylation of alkynes with organohalides[11] has received much less attention, despite that the latter ones are more accessible. Recently, alcohols stand out as a convenient reductant[12] for the capture of carbopalladation intermediates. Thus, we envisioned that carbopalladation of ynol ethers, followed by reduction with 2-propanol as the hydride source,[12] would provide an expeditious alternative to multisubstituted enol ethers. Herein, we wish to demonstrate a highly regio- and stereoselective synthesis of α,β- or β,β-disubstituted alkenyl ethers via the reductive addition of organohalides to ynol ethers[13] in the presence of 2-propanol, in which the regioselectivity is found to be determined by the choice of organic halides. Indeed, it represents the first regio- and stereoselective hydroarylation, hydroalkenylation, and hydrobenzylation of ynol ethers.

RESULTS AND DISCCUSION

Initially, we examined the hydroarylation reaction of ynol ether **1a** with iodobenzene (**2a**) by employing isopropanol as the hydride source in THF (Table 1). Screening of the base revealed that Cs_2CO_3 was more effective than K_2CO_3, $NaHCO_3$, and other bases (Table 1, entries 1−5). Gratifyingly, a better yield was obtained by utilizing PCy_3 instead of PPh_3 as the ligand, giving α,β-disubstituted alkenyl ether **3aa**[9a] in 72% yield, and no other regio- and stereoisomers were detected by NMR and GC−MS analysis (Table 1, entry 14). We then decided to evaluate the solvent with PCy_3 acting as the ligand, and finally, the optimum reaction conditions were determined as: ynol ether (0.5 mmol), organohalides (0.75 mmol), $Pd(OAc)_2$ (5 mol %), $PCy_3{\cdot}HBF_4$ (10 mol %), Cs_2CO_3 (1.0 mmol), 2-propanol (0.75 mmol), and dioxane (2 mL) at 50 °C for 10 h, which produced 94% of **3aa** upon isolation (Table 1, entry 16). In contrast, the reaction of PhBr only provided **3aa** in 68% yield under the reaction conditions.[14]

The synthetic merit of this protocol was demonstrated by varying the substrates, and the results are included in Table 2. A wide range of organic halides were found to be compatible with this transformation. In particular, 4-, 3-, and 2-iodotoluenes (**2b**−**2d**) smoothly coupled with **1a** to deliver enol ethers **3ab**−**3ad** in comparable yields (92, 91, and 91%), indicating that the steric effects of organohalides have little influence on the yield (Table 2, **3ab**−**3ad**). Various substituents, including electron-donating groups, such as methyl (**2b**−**2d**) and methoxy (**2i** and **2j**), and electron-withdrawing groups, such as trifluoromethyl (**2f**), chloride (**2g**), acetyl (**2k**), and ester (**2n**), were tolerated

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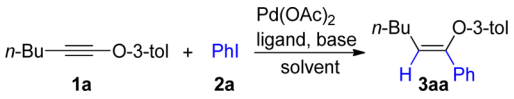
Table 1. Optimization of the Reaction Parameters[a]

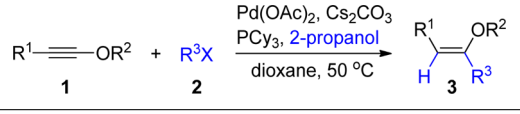


1a 2a 3aa

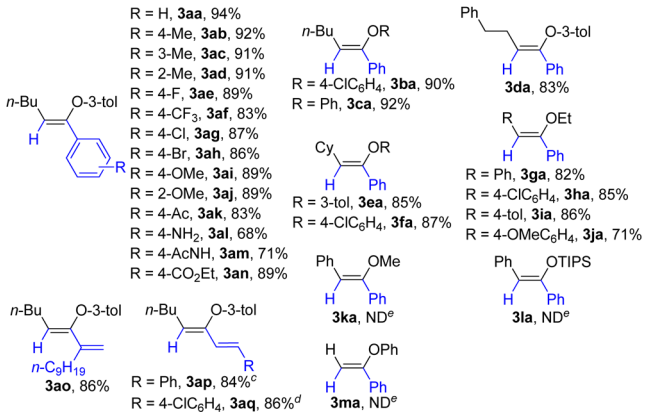
entry	ligand	base	solvent	yield (%)[b]
1	PPh_3	K_3PO_4	THF	15
2	PPh_3	*t*-BuOK	THF	<10
3	PPh_3	$NaHCO_3$	THF	<10
4	PPh_3	K_2CO_3	THF	31
5	PPh_3	Cs_2CO_3	THF	40
6	P(4-OMe-C_6H_4)$_3$	Cs_2CO_3	THF	36
7	P(2-furyl)$_3$	Cs_2CO_3	THF	15
8	P(C_6F_5)$_3$	Cs_2CO_3	THF	trace
9	dppp	Cs_2CO_3	THF	<10
10	P(4-tol)$_3$	Cs_2CO_3	THF	33
11	P(3-tol)$_3$	Cs_2CO_3	THF	16
12	P(2-tol)$_3$	Cs_2CO_3	THF	67
13	Xphos	Cs_2CO_3	THF	43
14	PCy_3[c]	Cs_2CO_3	THF	72
15	PCy_3[c]	Cs_2CO_3	toluene	55
16	PCy_3[c]	Cs_2CO_3	dioxane	94 (68)[d]
17	PCy_3[c]	Cs_2CO_3	DMF	38

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.5 mmol), **2a** (0.75 mmol), $Pd(OAc)_2$ (5 mol %), ligand (10 mol %), base (1.0 mmol), 2-propanol (0.75 mmol), solvent (2 mL), 50 °C, 10 h. [b]Isolated yield. [c]Generated in situ from PCy_3·HBF_4. [d]PhBr was used instead of PhI.

Table 2. Synthesis of α,β-Disubstituted Alkenyl Ethers via the Hydroarylation or Hydroalkenylation of Ynol Ethers[a,b,c,d,e]



1 2 3

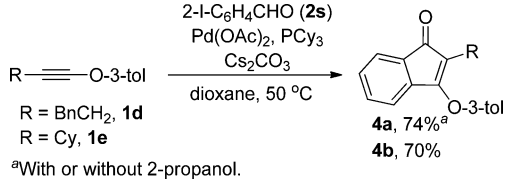


[a]Unless otherwise noted, all reactions were carried out with **1** (0.5 mmol), **2** (0.75 mmol), $Pd(OAc)_2$ (5 mol %), PCy_3·HBF_4 (10 mol %), 2-propanol (0.75 mmol), Cs_2CO_3 (1.0 mmol), dioxane, 50 °C, 10 h. [b]Isolated yield. [c]rr = 91:9. [d]rr = 95:5. [e]A complex mixture of products was formed. ND = not detected. TIPS = Si(*i*-Pr)$_3$. **2** = PhI (**2a**), 4-MeC_6H_4I (**2b**), 3-MeC_6H_4I (**2c**), 2-MeC_6H_4I (**2d**), 4-FC_6H_4I (**2e**), 4-$CF_3C_6H_4I$ (**2f**), 4-ClC_6H_4I (**2g**), 4-BrC_6H_4I (**2h**), 4-$OMeC_6H_4I$ (**2i**), 2-$OMeC_6H_4I$ (**2j**), 4-$CH_3COC_6H_4I$ (**2k**), 4-$NH_2C_6H_4I$ (**2l**), 4-$AcNHC_6H_4I$ (**2m**), 4-$CO_2EtC_6H_4Br$ (**2n**), CH_2=CI-*n*-C_9H_{19} (**2o**), (*E*)-styryl bromide (**2p**), or (*E*)-4−Cl-C_6H_4CH=CHBr (**2q**).

under the reaction conditions. Furthermore, the free NH_2 group proved to be tolerated, giving rise to **3al** in good yield (Table 2, **3al**). Notably, the hydroalkenylation of ynol ethers could also be achieved by using olefinic halides as the coupling partners. For example, 2-iodoundec-1-ene (**2o**) was converted into dienyl ether **3ao** in quite high yield (Table 2, **3ao**). In addition to alkenyl iodides, alkenyl bromides, such as (*E*)-styryl bromide (**2p**) and (*E*)-*p*-chloro-*β*-bromostyrene (**2q**), also furnished the corresponding products in high yields, albeit with slightly reduced regioselectivity (Table 2, **3ap** and **3aq**).

Interestingly, when 2-iodobenzaldehyde (**2s**) was subjected to the standard conditions, the cyclic products **4**, instead of the desired vinylic ethers **3**, were obtained. As an example, the reaction of **1d** afforded 1*H*-inden-1-ones **4a** in 74% yield, in the presence or absence of 2-propanol, thus providing an efficient and convenient access to 1*H*-inden-1-one derivatives (Scheme 2).[15] Likewise, **4b** was synthesized from **1e** in a good yield.

Scheme 2. Synthesis of 1*H*-Inden-1-one Derivatives



[a]With or without 2-propanol.

These results indicated that the intramolecular insertion of the C−Pd bond of intermediate **B** (see the proposed mechanism) into the carbonyl group should be predominant over the intermolecular reduction with isopropanol.

Then, we briefly investigated the scope of this reaction with regard to ynol ethers by using **2a** as the substrate. Alkyl alkynyl ethers, including the steric demanding **1e** and **1f**, turned out to be effective substrates for this hydrophenylation reaction (Table 2, **3ba**−**3fa**). The reaction was also applicable to ether ynol ethers, as demonstrated by the reaction of **1g**−**1j** (Table 2, **3ga**−**3ja**). In contrast, methyl ynol ether (**1k**), silyl ynol ether (**1l**), and ethynyl phenyl ether (**1m**) all failed to provide the desired products under the standard reaction conditions (Table 2, **3ka**−**3ma**).

On the other hand, subjection of BnBr (**5a**)[16] to the reductive addition process led to 89% yield of *β*,*β*-disubstituted alkenyl ether **6aa** as a single isomer, as evidenced by NMR and NOE experiments (see the Supporting Information) (Table 3, **6aa**). Notably, it represents a rare example of catalytic hydrobenzylation of alkynes.[17] As such, we further examined the scope and limitations of this hydrobenzylation reaction. Pleasingly, various benzyl bromides bearing F, Cl, OMe, alkyl, and aryl groups were amenable to this reaction (Table 3, **6ab**−**6ah**). On the contrary, 4-nitrobenzyl bromide (**5i**) did not yield the desired product under the reaction conditions (Table 3, **6ai**). Reductive addition of benzyl chloride (**5k**) to **1a** proceeded as well, albeit in a prolonged reaction time (18 h) and relatively decreased yield (Table 3, **6aa**). Additionally, the scope of this hydrobenzylation reaction with respect to ynol ethers was investigated. For instance, the steric hindered alkynyl ethers **1e** and **1f** delivered *β*,*β*-disubstituted vinylic ethers **6ea** and **6fa** in high yields (Table 3, **6ea** and **6fa**). Moreover, the transformation of ethyl ynol ether **1g** with **5a** provided 60% yield of **6ga** (Table 3, **6ga**). Unfortunately, the reaction of methyl ynol ether (**1k**), silyl ynol ether (**1l**), and ethynyl phenyl ether (**1m**) all led to unsatisfactory results (Table 3, **6ka**−**6ma**).

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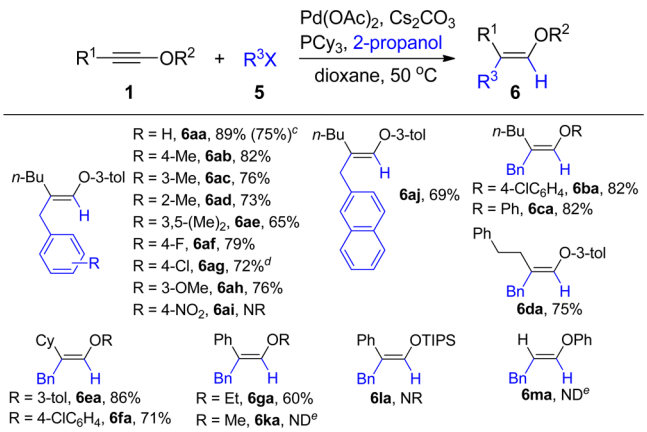
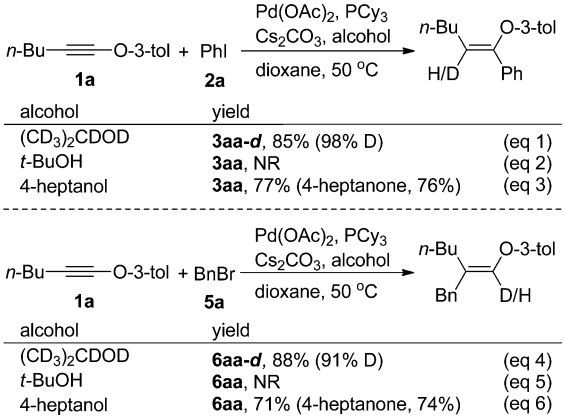
Table 3. Synthesis of *β,β*-Disubstituted Enol Ethers via the Hydrobenzylation of Ynol Ethers[a,b,c,d,e]



[a]Unless otherwise noted, all reactions were carried out with **1** (0.5 mmol), **5** (1.1 mmol), $Pd(OAc)_2$ (5 mol %), $PCy_3{\cdot}HBF_4$ (10 mol %), 2-propanol (0.75 mmol), Cs_2CO_3 (1.0 mmol), dioxane, 50 °C, 10 h. [b]Isolated yield. [c]BnCl (**5k**) was used instead of BnBr (**5a**). [d]rr = 94:6. [e]A complex mixture of products was formed. NR = no reaction. **5** = BnBr (**5a**), 4-$MeC_6H_4CH_2Br$ (**5b**), 3-$MeC_6H_4CH_2Br$ (**5c**), 2-$MeC_6H_4CH_2Br$ (**5d**), 3,5-$(Me)_2C_6H_3CH_2Br$ (**5e**), 4-$FC_6H_4CH_2Br$ (**5f**), 4-$ClC_6H_4CH_2Br$ (**5g**), 3-$OMeC_6H_4CH_2Br$ (**5h**), 4-$NO_2C_6H_4$-CH_2Br (**5i**), or 2-(bromomethyl)naphthalene (**5j**).

To gain some insight into the mechanism of this reductive addition reaction, ynol ether **1a** was treated with 1.5 equiv of $(CD_3)_2CDOD$, 5 mol % of $Pd(OAc)_2$, 10 mol % of $PCy_3{\cdot}HBF_4$, 2.0 equiv of Cs_2CO_3, and 1.5 equiv of **2a** in 2 mL of dioxane at 50 °C for 10 h, providing **3aa-*d*** in 85% yield with 98% deuterium incorporation (Scheme 3, eq 1). In contrast, no

Scheme 3. The Deuteration and Related Experiments



reaction occurred when $(CD_3)_2CDOD$ was replaced by *t*-BuOH (Scheme 3, eq 2), indicating that the protonolysis mechanism might be less likely in this reaction. Furthermore, when 4-heptanol was employed instead of 2-propanol as the hydride source, the desired product **3aa** was obtained in 77% yield, together with the formation of a good yield of 4-heptanone (Scheme 3, eq 3). Likewise, **6aa-*d*** was isolated in excellent yield with 91% deuterium incorporation by treating **1a** with $(CD_3)_2CDOD$ under the hydrobenzylation conditions, whereas the reaction did not proceed in the presence of *t*-BuOH (Scheme 3, eqs 4 and 5). These results indicated that 2-propanol might act as the hydride donor via the *β*-H elimination reaction.

As such, a possible mechanism is proposed in Scheme 4 for this regiocontrolled reductive addition of organohalides to ynol ethers. First, the oxidative addition of Pd(0) with aryl or alkenyl halides affords a species **A**, which is regio- and stereoselectively converted into the intermediate **B** by *cis*-carbopalladation of ynol ethers. The highly polarized C−C triple bonds of **1**, stemmed from the formation of a ketene-like mesomer **1′**,[7c] may account for the regioselective *α*-arylation or *α*-alkenylation. Then, in the presence of Cs_2CO_3, the reaction of 2-propanol with **B** gives the intermediate **C**, followed by a *β*-H elimination/reductive elimination sequence to produce *α,β*-disubstituted vinylic ethers **3** with concurrent formation of the Pd(0) catalyst (Scheme 4, path a).

On the other hand, the benzylpalladium intermediate **E**, generated by the oxidative addition of Pd(0) with benzyl halides, may undergo the *cis*-carbopalladation with **1** to form an alkenylpalladium intermediate **F**. The reversed regioselectivity at this carbopalladation step is still unclear at the current stage. A possible reason may be attributed to the unique properties of benzylpalladium complexes, which usually act as electrophiles rather than nucleophiles.[18] As such, the external nucleophilic attack of the *β*-carbon of ynol ethers leads to the regioselective *β*-benzylation. Subsequently, reduction of the C−Pd bond of **F** furnishes the *β,β*-disubstituted alkenyl ethers **6** with the regeneration of Pd(0) species (Scheme 4, path b).

CONCLUSION

In summary, we have developed a highly effective Pd-catalyzed reductive addition of organohalides, including aryl, alkenyl, and benzyl halides, to ynol ethers for the first time. It proceeds under mild reaction conditions with the use of readily available 2-propanol as the hydride source, giving *α,β*- and *β,β*-disubstituted alkenyl ethers in satisfactory yields with excellent regio- and stereoselectivity. The regioselectivity of this reaction is found to be determined by the organic halides employed. It constitutes a significant advance in the exploration of regiocontrolled hydroarylation, hydroalkenylation, and hydrobenzylation of internal alkynes using the readily accessible organohalides as coupling partners, and we believe that it will be of value for organic synthesis.

EXPERIMENTAL SECTION

General. THF, dioxane, and toluene were distilled from sodium prior to use. Unless otherwise noted, commercially available materials and reagents were used directly without further purification. ^1H and ^{13}C NMR spectra were measured on 400 or 600 MHz NMR spectrometers utilizing $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were given in *δ* relative to TMS, while the coupling constants were given in Hz. High-resolution mass spectra (HRMS) analyses were performed employing a TOF MS instrument with an EI or ESI source. Column chromatography was carried out using silica gel (300−400 mesh).

General Procedure for the Pd-Catalyzed Reductive Addition of Organohalides to Ynol Ethers. To a mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), $PCy_3{\cdot}HBF_4$ (18.4 mg, 0.05 mmol), and Cs_2CO_3 (326 mg, 1.0 mmol) was added a solution of **1a** (94 mg, 0.5 mmol), PhI (153 mg, 0.75 mmol), and 2-propanol (45 mg, 0.75 mmol) in 2 mL of dioxane under a nitrogen atmosphere. After stirring for 10 h at 50 °C, the reaction mixture was concentrated and purified by column chromatography on silica (petroleum ether) to give 125 mg (94% yield) of **3aa**[9a] as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$) *δ* 7.50 (d, *J* = 7.8 Hz, 2H), 7.32−7.15 (m, 3H), 7.09 (t, *J* = 7.9 Hz, 1H),

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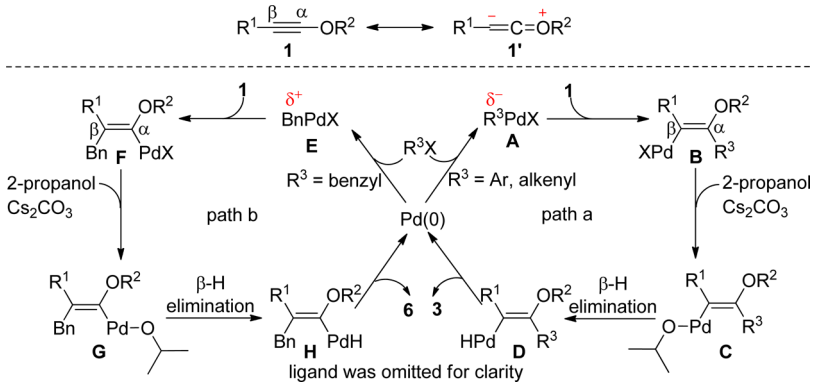
Scheme 4. Proposed Mechanism



6.79−6.73 (m, 3H), 5.87 (t, *J* = 7.4 Hz, 1H), 2.31 (s, 3H), 2.22 (q, *J* = 7.3 Hz, 2H), 1.46−1.30 (m, 4H), 0.89 (t, *J* = 7.3 Hz, 3H).

Compound ***3aa-d:***[9a] The title compound was obtained by replacing 2-propanol with $(CD_3)_2CDOD$ under the standard conditions, 113 mg, 85% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.9 Hz, 1H), 6.79 (s, 1H), 6.73 (m, 2H), 2.27 (s, 3H), 2.20 (q, *J* = 7.3 Hz, 2H), 1.44−1.30 (m, 4H), 0.87 (t, *J* = 7.3 Hz, 3H).

Compound ***3ab:***[9a] 129 mg, 92% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.10−7.03 (m, 3H), 6.79 (s, 1H), 6.72 (d, *J* = 7.9 Hz, 2H), 5.79 (t, *J* = 7.4 Hz, 1H), 2.29 (s, 3H), 2.27 (s, 3H), 2.18 (q, *J* = 7.3 Hz, 2H), 1.43−1.25 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H).

Compound ***3ac:***[9a] 127 mg, 91% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.24 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.79 (s, 1H), 6.73 (d, *J* = 8.0 Hz, 2H), 5.84 (t, *J* = 7.4 Hz, 1H), 2.30 (s, 3H), 2.28 (s, 3H), 2.18 (q, *J* = 7.3 Hz, 2H), 1.44−1.28 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H).

Compound ***3ad:***[9a] 127 mg, 91% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.32 (m, 1H), 7.15−7.00 (m, 4H), 6.74 (s, 1H), 6.72−6.65 (m, 2H), 5.33 (t, *J* = 7.4 Hz, 1H), 2.42 (s, 3H), 2.30−2.19 (m, 5H), 1.49−1.33 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H).

Compound ***3ae:***[9a] 126 mg, 89% yield, yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47−7.42 (m, 2H), 7.10 (t, *J* = 7.7 Hz, 1H), 6.97−6.92 (m, 2H), 6.78−6.70 (m, 3H), 5.76 (t, *J* = 7.4 Hz, 1H), 2.29 (s, 3H), 2.18 (q, *J* = 7.4 Hz, 2H), 1.43−1.28 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 3H).

Compound ***3af:***[9a] 138 mg, 83% yield, yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 1H), 6.79−6.74 (m, 2H), 6.75 (d, *J* = 7.0 Hz, 1H), 6.00 (t, *J* = 7.4 Hz, 1H), 2.32 (s, 3H), 2.27 (q, *J* = 7.4 Hz, 2H), 1.49−1.39 (m, 2H), 1.38−1.31 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).

Compound ***3ag:***[9a] 130 mg, 87% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.26−7.17 (m, 2H), 7.09 (t, *J* = 7.9 Hz, 1H), 6.76−6.65 (m, 3H), 5.83 (t, *J* = 7.4 Hz, 1H), 2.28 (s, 3H), 2.19 (q, *J* = 7.3 Hz, 2H), 1.45−1.27 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H).

Compound ***3ah:*** 148 mg, 86% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.35 (m, 4H), 7.16−7.10 (m, 1H), 6.83−6.71 (m, 3H), 5.88 (t, *J* = 7.4 Hz, 1H), 2.32 (s, 3H), 2.23 (td, *J* = 7.3, 7.3 Hz, 2H), 1.49−1.34 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 147.8, 139.7, 134.6, 131.5, 129.2, 126.8, 122.4, 121.6, 118.9, 116.1, 112.2, 31.3, 25.6, 22.4, 21.5, 13.9; MS (EI, *m*/*z*) 346 (14), 344 (M^+, 17), 303 (10), 301 (10), 238 (21); HRMS (EI) calcd for $C_{19}H_{21}BrO$ (M^+) 344.0776, found 344.0773.

Compound ***3ai:***[9a] 132 mg, 89% yield, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.7 Hz, 2H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.84−6.76 (m, 3H), 6.75−6.70 (m, 2H), 5.75 (t, *J* = 7.4 Hz, 1H), 3.80 (s, 3H), 2.28 (s, 3H), 2.17 (q, *J* = 7.1 Hz, 2H), 1.44−1.28 (m, 4H), 0.87 (t, *J* = 7.3 Hz, 3H).

Compound ***3aj:*** 132 mg, 89% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.7 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.95−6.91 (m, 2H), 6.87 (s, 1H), 6.83−6.76 (m, 2H), 6.05 (t, *J* = 7.3 Hz, 1H), 3.93 (s, 3H), 2.34−2.29 (m, 5H), 1.53−1.41 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.4, 157.1, 145.1, 139.2, 128.9, 128.9, 128.6, 124.5, 122.4, 122.0, 120.4, 116.5, 112.6, 111.1, 55.4, 31.6, 25.7, 22.4, 21.4, 13.9; MS (EI, *m*/*z*) 296 (M^+, 43), 189 (95), 147 (68), 135 (64); HRMS (EI) calcd for $C_{20}H_{24}O_2$ (M^+) 296.1776, found 296.1784.

Compound ***3ak:***[9a] 128 mg, 83% yield, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.12 (t, *J* = 7.9 Hz, 1H), 6.81−6.69 (m, 3H), 6.04 (t, *J* = 7.4 Hz, 1H), 2.58 (s, 3H), 2.31 (s, 3H), 2.26 (dd, *J* = 14.7, 7.4 Hz, 2H), 1.41 (m, 1.49−1.34, 4H), 0.91 (t, *J* = 7.2 Hz, 3H).

Compound ***3al:*** 96 mg, 68% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33−7.29 (m, 2H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.81 (s, 1H), 6.76 (dd, *J* = 7.9, 1.8 Hz, 2H), 6.63−6.58 (m, 2H), 5.67 (t, *J* = 7.3 Hz, 1H), 3.70 (br, 2H), 2.31 (s, 3H), 2.21−2.16 (m, 2H), 1.44−1.34 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.6, 148.7, 146.0, 139.4, 129.1, 126.4, 126.1, 121.9, 116.2, 114.9, 114.8, 112.4, 31.6, 25.4, 22.4, 21.5, 13.9; MS (EI, *m*/*z*) 281 (M^+, 43), 238 (18), 207 (10), 195 (2), 174 (100); HRMS (EI) calcd for $C_{19}H_{23}NO$ (M^+) 281.1780, found 281.1778.

Compound ***3am:*** 115 mg, 71% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48−7.42 (m, 3H), 7.35−7.30 (m, 1H), 7.13−7.09 (m, 1H), 6.81−6.73 (m, 3H), 5.81 (t, *J* = 7.4 Hz, 1H), 2.30 (s, 3H), 2.23−2.19 (m, 2H), 2.15 (d, *J* = 7.0 Hz, 3H), 1.46−1.41 (m, 2H), 1.39−1.33 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 157.4, 148.1, 139.5, 131.6, 129.1, 128.9, 125.8, 122.2, 119.7, 117.5, 116.1, 112.3, 31.4, 25.5, 24.5, 22.4, 21.4, 13.9; MS (EI, *m*/*z*) 323 (M^+, 32), 280 (18), 216 (100), 207 (8); HRMS (EI) calcd for $C_{21}H_{25}NO_2$ (M^+) 323.1885, found 323.1884.

Compound ***3an:*** 150 mg, 89% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.14−7.10 (m, 1H), 6.81−6.72 (m, 3H), 6.02 (t, *J* = 7.4 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 2.28−2.24 (m, 2H), 1.50−1.36 (m, 7H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.2, 157.2, 148.0, 139.9, 139.6, 129.7, 129.5, 129.2, 125.0, 122.4, 120.7, 116.1, 112.2, 60.8, 31.2, 25.7, 22.4, 21.4, 14.3, 13.8; MS (EI, *m*/*z*) 338 (M^+, 17), 295 (19), 230 (38), 215 (13), 177 (47); HRMS (EI) calcd for $C_{22}H_{26}O_3$ (M^+) 338.1882, found 338.1882.

Compound ***3ao:*** 147 mg, 86% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.8 Hz, 1H), 6.82−6.72 (m, 3H), 5.53 (t, *J* = 7.3 Hz, 1H), 5.19 (s, 1H), 4.92 (s, 1H), 2.35 (s, 3H), 2.30−2.26 (m, 2H), 2.15−2.09 (m, 2H), 1.59 (t, *J* = 7.1 Hz, 2H), 1.41−1.31 (m, 16H), 0.94 (t, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.9, 149.2, 141.7, 139.4, 129.1, 121.8, 118.8, 115.6, 112.4, 111.7, 32.9, 31.9, 31.3, 29.6, 29.5, 29.5, 29.3, 28.5, 25.5, 22.7, 22.4, 21.5, 14.1, 13.9; MS (EI, *m*/*z*) 342 (M^+, 21), 229 (16), 215 (13), 187 (14), 173 (19); HRMS (EI) calcd for $C_{24}H_{38}O$ (M^+) 342.2923, found 342.2925.

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Compound ***3ap:*** 123 mg, 84% yield, colorless oil; rr = 91:9; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, J = 7.4 Hz, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.26−7.17 (m, 2H), 6.88−6.81 (m, 3H), 6.72 (d, J = 15.9 Hz, 1H), 6.59 (d, J = 15.9 Hz, 1H), 5.51 (t, J = 7.5 Hz, 1H), 2.36 (s, 3H), 2.14 (td, J = 7.3, 7.3 Hz, 2H), 1.43−1.31 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7, 148.9, 139.6, 136.8, 129.2, 128.5, 128.2, 127.5, 126.5, 123.9, 123.5, 122.1, 115.6, 111.9, 31.2, 25.7, 22.3, 21.5, 13.8; MS (EI, m/z) 292 (M^+, 23), 263 (7), 249 (100), 221 (76); HRMS (EI) calcd for $C_{21}H_{24}O$ (M^+) 292.1827, found 292.1824.

Compound ***3aq:*** 140 mg, 86% yield, colorless oil; rr = 95:5; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31−7.25 (m, 4H), 7.18 (t, J = 7.8 Hz, 1H), 6.87−6.80 (m, 3H), 6.67 (d, J = 15.9 Hz, 1H), 6.52 (d, J = 15.9 Hz, 1H), 5.52 (t, J = 7.5 Hz, 1H), 2.36 (s, 3H), 2.13 (td, J = 7.4 Hz, J = 7.4 Hz, 2H), 1.42−1.30 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.6, 148.7, 139.6, 133.0, 129.2, 128.7, 127.6, 127.5, 126.8, 124.6, 124.2, 122.2, 115.5, 111.8, 31.1, 25.7, 22.3, 21.5, 13.8; MS (EI, m/z) 328 (11), 326 (M^+, 36), 283 (39), 271 (26), 239 (25); HRMS (EI) calcd for $C_{21}H_{23}ClO$ (M^+) 326.1437, found 326.1435.

Compound ***3ba:***[9a] 128 mg, 90% yield, yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48−7.40 (m, 2H), 7.31−7.23 (m, 3H), 7.20−7.15 (m, 2H), 6.95−6.82 (m, 2H), 5.87 (t, J = 7.4 Hz, 1H), 2.19 (q, J = 7.4 Hz, 2H), 1.47−1.31 (m, 4H), 0.90 (t, J = 7.3 Hz, 3H).

Compound ***3ca:***[9a] 116 mg, 92% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56−7.52 (m, 2H), 7.36−7.24 (m, 5H), 7.05−6.93 (m, 3H), 5.92 (t, J = 7.4 Hz, 1H), 2.27 (q, J = 7.4 Hz, 2H), 1.51−1.37 (m, 4H), 0.94 (t, J = 7.3 Hz, 3H).

Compound ***3da:***[9a] 130 mg, 83% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.0 Hz, 2H), 7.27−7.14 (m, 8H), 7.05 (t, J = 7.8 Hz, 1H), 6.76−6.64 (m, 3H), 5.85 (t, J = 7.3 Hz, 1H), 2.73 (t, J = 7.7 Hz, 2H), 2.52 (q, J = 7.6 Hz, 2H), 2.25 (s, 3H).

Compound ***3ea:***[9a] 124 mg, 85% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, J = 7.4 Hz, 2H), 7.26−7.14 (m, 3H), 7.10−7.04 (m, 1H), 6.80 (s, 1H), 6.73−6.71 (m, 2H), 5.67 (d, J = 9.4 Hz, 1H), 2.56−2.48 (m, 1H), 2.26 (s, 3H), 1.74−1.65 (m, 4H), 1.29−1.12 (m, 6H).

Compound ***3fa:***[9a] 136 mg, 87% yield, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.41 (m, 2H), 7.27−7.13 (m, 5H), 6.89−6.85 (m, 2H), 5.69 (d, J = 9.4 Hz, 1H), 2.51−2.43 (m, 1H), 1.70−1.67 (m, 4H), 1.26−1.11 (m, 6H).

Compound ***3ga:***[9a] 92 mg, 82% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, J = 7.4 Hz, 2H), 7.58 (d, J = 7.4 Hz, 2H), 7.45−7.29 (m, 5H), 7.23 (t, J = 7.4 Hz, 1H), 6.18 (s, 1H), 3.90 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.0 Hz, 3H).

Compound ***3ha:***[9a] 110 mg, 85% yield, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.6 Hz, 2H), 7.55 (m, J = 8.4 Hz, 2H), 7.43−7.35 (m, 3H), 7.29 (d, J = 8.6 Hz, 2H), 6.01 (s, 1H), 3.86 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H).

Compound ***3ia:***[9a] 102 mg, 86% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.1 Hz, 2H), 7.63−7.58 (m, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.37 (d, J = 7.2 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 6.15 (s, 1H), 3.87 (q, J = 7.0 Hz, 2H), 2.40 (s, 3H), 1.39 (t, J = 7.0 Hz, 3H).

Compound ***3ja:***[9a] 90 mg, 71% yield, yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 7.5 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.28 (t, J = 7.3 Hz, 1H), 6.87 (d, J = 8.8 Hz, 2H), 6.06 (s, 1H), 3.82−3.77 (m, 5H), 1.33 (t, J = 7.0 Hz, 3H).

Compound ***4a:*** The title compound was obtained by replacing PhI with *o*-iodobenzaldehyde under the standard conditions with or without 2-propanol, 125 mg, 74% yield, yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48−7.44 (m, 1H), 7.29−7.22 (m, 5H), 7.18 (d, J = 7.4 Hz, 1H), 7.08 (d, J = 7.3 Hz, 3H), 6.88 (d, J = 6.3 Hz, 2H), 6.74−6.70 (m, 1H), 2.74−2.68 (m, 2H), 2.40−2.36 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.5, 169.6, 154.8, 141.5, 140.0, 139.6, 132.4, 132.1, 129.4, 129.0, 128.4, 128.2, 125.9, 125.8, 121.2, 119.8, 119.5, 116.2, 34.6, 23.6, 21.3; MS (EI, m/z) 340 (M^+, 2), 250 (16), 249 (100), 221 (38), 193 (7); HRMS (EI) calcd for $C_{24}H_{20}O_2$ (M^+) 340.1463, found 340.1464.

Compound ***4b:*** 111 mg, 70% yield, yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, J = 7.0 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H), 7.14 (t, J = 7.3 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 7.6 Hz, 1H), 6.95 (s, 1H), 6.92−6.89 (m, 1H), 6.38 (d, J = 7.2 Hz, 1H), 2.47−2.41 (m, 1H), 2.36 (s, 3H), 1.72−1.63 (m, 6H), 1.24 (d, J = 14.2 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.3, 168.1, 155.2, 140.1, 139.1, 132.2, 129.5, 128.6, 125.6, 125.1, 121.2, 120.0, 118.7, 115.0, 33.2, 30.7, 26.6, 25.8, 21.4; MS (EI, m/z) 318 (M^+, 100), 275 (26), 262 (15), 249 (37), 181 (46); HRMS (EI) calcd for $C_{22}H_{22}O_2$ (M^+) 318.1620, found 318.1624.

Compound ***6aa:*** The title compound was prepared from **1a** and **5a** according to the general procedure except that 2.2 equiv of **5a** was used, 124 mg, 89% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, J = 7.5 Hz, 2H), 7.26−7.16 (m, 4H), 6.83 (d, J = 7.5 Hz, 1H), 6.81−6.77 (m, 2H), 6.28 (s, 1H), 3.32 (s, 2H), 2.34 (s, 3H), 2.12−2.08 (m, 2H), 1.40−1.35 (m, 2H), 1.34−1.28 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8, 139.8, 139.6, 137.4, 129.2, 128.9, 128.3, 126.1, 124.6, 122.9, 116.8, 112.9, 37.9, 29.7, 26.5, 22.5, 21.4, 13.9; MS (EI, m/z) 280 (M^+, 31), 223 (7), 181 (10), 159 (8), 129 (100); HRMS (EI) calcd for $C_{20}H_{24}O$ (M^+) 280.1827, found 280.1825.

Compound ***6aa-d:*** 123 mg, 88% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, J = 7.5 Hz, 2H), 7.27−7.16 (m, 4H), 6.86−6.76 (m, 3H), 6.28 (s, 0.09H), 3.32 (s, 2H), 2.34 (s, 3H), 2.10 (t, J = 7.6 Hz, 2H), 1.42−1.35 (m, 2H), 1.33−1.25 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H); MS (EI, m/z) 282 (11), 281 (M^+, 59), 224 (11), 190 (3), 130 (100).

Compound ***6ab:*** 121 mg, 82% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19−7.17 (m, 1H), 7.16−7.12 (m, 4H), 6.80 (d, J = 7.5 Hz, 1H), 6.74 (s, 1H), 6.70 (dd, J = 8.1, 2.2 Hz, 1H), 6.00 (s, 1H), 3.32 (s, 2H), 2.34 (s, 3H), 2.31 (s, 3H), 2.18−2.14 (m, 2H), 1.46−1.42 (m, 2H), 1.34−1.30 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8, 139.6, 137.6, 136.6, 130.2, 129.7, 129.2, 126.3, 125.9, 122.8, 116.7, 112.7, 35.4, 29.9, 27.3, 22.5, 21.4, 19.4, 14.0; MS (EI, m/z) 294 (M^+, 20), 237 (4), 207 (6), 195 (8), 143 (100); HRMS (EI) calcd for $C_{21}H_{26}O$ (M^+) 294.1984, found 294.1985.

Compound ***6ac:*** 112 mg, 76% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24−7.20 (m, 2H), 7.11−7.04 (m, 3H), 6.89−6.80 (m, 3H), 6.31 (s, 1H), 3.32 (s, 2H), 2.38 (m, 6H), 2.16−2.11 (m, 2H), 1.32−1.42 (m, 4H), 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8, 139.7, 139.6, 137.9, 137.3, 129.6, 129.2, 128.2, 126.9, 125.9, 124.7, 122.8, 116.7, 112.9, 37.8, 29.7, 26.5, 22.5, 21.5, 21.4, 13.9; MS (EI, m/z) 294 (M^+, 12), 237 (32), 207 (7), 195 (12), 143 (100); HRMS (EI) calcd for $C_{21}H_{26}O$ (M^+) 294.1984, found 294.1986.

Compound ***6ad:*** 107 mg, 73% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (t, J = 7.8 Hz, 1H), 7.19−7.14 (m, 4H), 6.83 (d, J = 7.5 Hz, 1H), 6.80 (s, 1H), 6.78 (d, J = 8.1 Hz, 1H), 6.26 (s, 1H), 3.28 (s, 2H), 2.33 (s, 3H), 2.32 (s, 3H), 2.11−2.06 (m, 2H), 1.40−1.34 (m, 2H), 1.32−1.24 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8, 139.6, 137.2, 136.6, 135.6, 129.2, 129.0, 128.7, 128.3, 124.8, 122.8, 116.8, 112.9, 37.4, 29.7, 26.4, 22.5, 21.4, 21.0, 13.9; MS (EI, m/z) 294 (M^+, 8), 237 (23), 207 (8), 195 (10), 143 (100); HRMS (EI) calcd for $C_{21}H_{26}O$ (M^+) 294.1984, found 294.1983.

Compound ***6ae:*** 100 mg, 65% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (t, J = 7.8 Hz, 1H), 6.91−6.83 (m, 6H), 6.31 (s, 1H), 3.29 (s, 2H), 2.38 (s, 3H), 2.34 (s, 6H), 2.17−2.12 (m, 2H), 1.46−1.40 (m, 2H), 1.36−1.30 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8, 139.6, 137.7, 137.3, 129.2, 127.8, 126.7, 126.2, 124.8, 122.8, 116.7, 112.9, 37.7, 29.7, 26.5, 22.4, 21.4, 21.3, 13.9; MS (EI, m/z) 308 (M^+, 12), 251 (32), 221 (24), 207 (45), 143 (100); HRMS (EI) calcd for $C_{22}H_{28}O$ (M^+) 308.2140, found 308.2135.

Compound ***6af:*** 118 mg, 79% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26−7.20 (m, 3H), 7.07−7.01 (m, 2H), 6.89 (d, J = 7.5 Hz, 1H), 6.83−6.81 (m, 2H), 6.31 (s, 1H), 3.33 (s, 2H), 2.39 (s, 3H), 2.18−2.10 (m, 2H), 1.47−1.28 (m, 4H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.5 (d, J = 242.3 Hz), 157.7, 139.7, 137.5, 135.3 (d, J = 3.1 Hz), 130.2 (d, J = 7.8 Hz), 129.3, 124.3, 123.0, 116.8, 115.1 (d, J = 21.0 Hz), 112.9, 37.1, 29.6, 26.4, 22.4, 21.4, 13.9;

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MS (EI, *m*/*z*) 298 (M^+, 42), 255 (8), 241 (11), 199 (13), 147 (60); HRMS (EI) calcd for $C_{20}H_{23}FO$ (M^+) 298.1733, found 298.1731.

Compound ***6ag:*** 113 mg, 72% yield, colorless oil; rr = 94:6; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, J = 7.7 Hz, 2H), 7.24−7.19 (m, 3H), 6.90−6.80 (m, 3H), 6.31 (s, 1H), 3.32 (s, 2H), 2.38 (s, 3H), 2.14−2.09 (m, 2H), 1.43−1.29 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.6, 139.7, 138.3, 137.7, 131.9, 130.2, 129.3, 128.4, 123.9, 123.0, 116.8, 112.9, 37.3, 29.6, 26.4, 22.4, 21.5, 13.9; MS (EI, *m*/*z*) 316 (14), 314 (M^+, 42), 271 (9), 257 (12), 214 (14); HRMS (EI) calcd for $C_{20}H_{23}ClO$ (M^+) 314.1437, found 314.1431.

Compound ***6ah:*** 118 mg, 76% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (t, J = 7.9 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 6.90−6.87 (m, 2H), 6.85−6.79 (m, 4H), 6.33 (s, 1H), 3.85 (s, 3H), 3.34 (s, 2H), 2.38 (s, 3H), 2.16−2.12 (m, 2H), 1.44−1.32 (m, 4H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 157.7, 141.5, 139.6, 137.4, 129.3, 129.2, 124.3, 122.9, 121.3, 116.7, 114.6, 112.9, 111.4, 55.1, 37.9, 29.7, 26.4, 22.5, 21.4, 13.9; MS (EI, *m*/*z*) 310 (M^+, 17), 203 (7), 173 (16), 159 (100), 147 (21); HRMS (EI) calcd for $C_{21}H_{26}O_2$ (M^+) 310.1933, found 310.1935.

Compound ***6aj:*** 114 mg, 69% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87−7.83 (m, 3H), 7.73 (s, 1H), 7.52−7.44 (m, 3H), 7.24 (t, J = 7.8 Hz, 1H), 6.92−6.84 (m, 3H), 6.40 (s, 1H), 3.54 (s, 2H), 2.40 (s, 3H), 2.22−2.17 (m, 2H), 1.50−1.44 (m, 2H), 1.38−1.32 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8, 139.6, 137.7, 137.3, 133.6, 132.2, 129.2, 127.9, 127.6, 127.5, 127.4, 127.1, 125.9, 125.3, 124.4, 122.9, 116.8, 112.9, 38.1, 29.7, 26.6, 22.5, 21.4, 13.9; MS (EI, *m*/*z*) 330 (M^+, 25), 193 (11), 179 (100), 167 (52); HRMS (EI) calcd for $C_{24}H_{26}O$ (M^+) 330.1984, found 330.1987.

Compound ***6ba:*** 123 mg, 82% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36−7.24 (m, 7H), 6.95 (d, J = 8.8 Hz, 2H), 6.26 (s, 1H), 3.37 (s, 2H), 2.15 (t, J = 7.6 Hz, 2H), 1.46−1.38 (m, 2H), 1.36−1.30 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.3, 139.4, 137.0, 129.4, 128.8, 128.5, 128.4, 128.3, 126.2, 117.1, 37.8, 29.6, 26.5, 22.4, 13.9; MS (EI, *m*/*z*) 302 (5), 300 (M^+, 16), 243 (2), 179 (3), 129 (100); HRMS (EI) calcd for $C_{19}H_{21}ClO$ (M^+) 300.1281, found 300.1284.

Compound ***6ca:*** 109 mg, 82% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.26 (m, 7H), 7.09−7.00 (m, 3H), 6.33 (s, 1H), 3.38 (s, 2H), 2.20−2.12 (m, 2H), 1.46−1.31 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 139.7, 137.3, 129.5, 128.9, 128.3, 126.2, 124.9, 122.0, 116.0, 37.9, 29.7, 26.5, 22.4, 13.9; MS (EI, *m*/*z*) 266 (M^+, 26), 244 (11), 207 (7), 185 (14), 129 (100); HRMS (EI) calcd for $C_{19}H_{22}O$ (M^+) 266.1671, found 266.1669.

Compound ***6da:*** 123 mg, 75% yield, colorless oil; H NMR (400 MHz, $CDCl_3$) δ 7.39−7.33 (m, 2H), 7.32−7.18 (m, 9H), 6.91−6.78 (m, 3H), 6.35 (s, 1H), 3.35 (s, 2H), 2.79−2.71 (m, 2H), 2.51−2.44 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 142.1, 139.6, 139.5, 138.0, 129.2, 128.9, 128.4, 128.4, 128.2, 126.2, 125.7, 123.5, 123.0, 116.9, 113.0, 38.2, 34.0, 28.9, 21.4; MS (EI, *m*/*z*) 328 (M^+, 3), 237 (8), 207 (4), 159 (4), 129 (100); HRMS (EI) calcd for $C_{24}H_{24}O$ (M^+) 328.1827, found 328.1823.

Compound ***6ea:*** 132 mg, 86% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37−7.30 (m, 4H), 7.26−7.20 (m, 2H), 6.88 (d, J = 7.5 Hz, 1H), 6.84 (s, 1H), 6.82−6.79 (m, 1H), 6.05 (s, 1H), 3.36 (s, 2H), 2.62 (tt, J = 12.1, 3.3 Hz, 1H), 2.38 (s, 3H), 1.75−1.70 (m, 2H), 1.68−1.64 (m, 1H), 1.63−1.59 (m, 2H), 1.41 (qd, J = 12.6, 3.1 Hz, 2H), 1.32−1.25 (m, 2H), 1.15 (tt, J = 12.9, 3.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8, 140.3, 139.6, 137.7, 129.2, 129.2, 129.0, 128.2, 126.0, 122.8, 116.8, 112.9, 38.2, 36.2, 31.1, 26.7, 26.2, 21.4; MS (EI, *m*/*z*) 306 (M^+, 100), 223 (26), 155 (65), 129 (64); HRMS (EI) calcd for $C_{22}H_{26}O$ (M^+) 306.1984, found 306.1982.

Compound ***6fa:*** 138 mg, 71% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36−7.21 (m, 7H), 6.92−6.88 (m, 2H), 5.94 (s, 1H), 3.34 (s, 2H), 2.60−2.56 (m, 1H), 1.75−1.68 (m, 3H), 1.62−1.53 (m, 2H), 1.41−1.34 (m, 2H), 1.30−1.24 (m, 2H), 1.15−1.10 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.4, 139.9, 137.3, 130.5, 129.4, 129.0, 128.3, 126.9, 126.1, 117.2, 38.2, 36.1, 31.0, 26.7, 26.1; MS (EI, *m*/*z*) 328 (16), 326 (M^+, 51), 235 (54), 207 (14), 147 (32); HRMS (EI) calcd for $C_{21}H_{23}ClO$ (M^+) 326.1437, found 326.1436.

Compound ***6ga:*** 71 mg, 60% yield, yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54−7.32 (m, 2H), 7.30−7.20 (m, 8H), 6.22 (s, 1H), 3.92 (q, J = 7.1 Hz, 2H), 3.65 (s, 2H), 1.32 (t, J = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.5, 141.8, 140.7, 129.7, 128.4, 128.4, 128.3, 128.0, 127.8, 125.5, 68.6, 38.6, 15.4; MS (EI, *m*/*z*) 238 (M^+, 100), 209 (15), 193 (12), 181 (30), 131 (20); HRMS (EI) calcd for $C_{17}H_{18}O$ (M^+) 238.1358, found 238.1361.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectroscopic data of compounds **3**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: gangguo@zjnu.cn.

Notes

The authors declare no competing financial interest.

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