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Regioselective and Stereoselective Entry to β,β-Disubstituted Vinyl Ethers via the Sequential Hydroboration/Suzuki−Miyaura Coupling of Ynol Ethers

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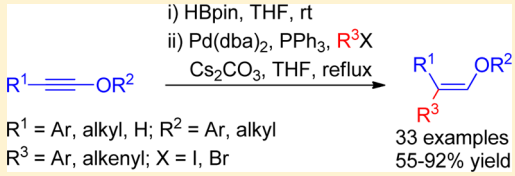
Supporting Information

ABSTRACT: A highly regio- and stereoselective synthesis of stereodefined β,β-disubstituted alkenyl ethers featuring the sequential hydroboration/Suzuki−Miyaura coupling of ynol ethers has been described. A number of functional groups, including OMe, Ac, CO_2Et, CN, halides, and alkyl, (hetero)aryl, and alkenyl groups, are well-tolerated under the reaction conditions. Furthermore, it allows a facile entry to the labile diarylacetaldehydes by TFA-mediated hydrolysis of β,β-disubstituted vinyl ethers.



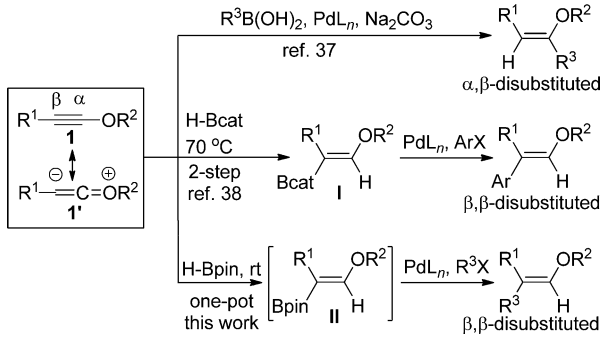
INTRODUCTION

Alkenyl ethers possess versatile reactivity in organic chemistry,[1] and there are a diverse array of methods that exist for the assembly of these motifs, such as the olefination of carbonyl compounds, elimination reaction, hydroalkoxylation of acetylenes, C−O bond formation, and other transformations.[2−10] In particular, the C−O bond coupling strategy[2−6] provides a highly regio- and stereoselective approach to prepare vinyl ethers; however, the construction of stereodefined alkenyl coupling precursors, especially the thermodynamically unfavorable *Z*-isomers, is difficult to achieve in many cases. Hence, the development of a simple and general method for the access of stereodefined multisubstituted vinyl ethers is still highly desirable.

On the other hand, the functionalization of ynol ethers[11−19] has attracted considerable attention over the past decades and provides a straightforward and effective alternative to access alkenyl ethers.[20−28] As an example, Greene and co-workers[20] reported that (*Z*)- or (*E*)-vinyl ethers could be synthesized via the reduction of ynol ethers by Lindlar catalyst or $LiAlH_4$, respectively. Marek[21] described an effective regiodivergent synthesis of vinyl ethers featuring the carbocupration of ynol ethers, in which the regioselectivity was determined by the nature of heteroatom substituents. Remarkably, a range of densely substituted vinyl ethers were found to be assembled by the Al-catalyzed,[22] Au-catalyzed,[23] Ni-catalyzed,[24] or Rh-catalyzed[25,26] cycloaddition of ynol ethers, respectively reported by Ready,[22] Hashimi,[23] Saito,[24] and Tanaka.[25,26] In addition, Daoust et al.[27,28] demonstrated that either intermolecular or intramolecular radical addition to ynol ethers proceeded regioselectively, providing α-iodovinyl ethers in good yields.

As part of our ongoing interest in the functionalization of heteroatom-substituted alkynes,[29−35] we have reported a regio- and stereoselective protocol for the preparation of (1*E*)-α-chloroenol ethers via Pd-catalyzed chloroallyaltion of aromatic alkynyl ethers.[36] Quite recently, we implemented a facile and concise synthesis of α,β-disubstituted vinyl ethers by the Pd-catalyzed stereospecific addition of boronic acids to ynol ethers.[37] Despite the significant success in assembling α,β-disubstituted vinyl ethers, the regio- and stereoselective synthesis of β,β-disubstituted vinyl ethers constitutes a formidable challenge. Indeed, in 1987, a seminal work done by Suzuki and co-workers[38] disclosed a two-step procedure for the synthesis of β,β-disubstituted vinyl ethers involving a regioselective hydroboration of ynol ethers using catecholborane (HBcat) followed by a Pd-catalyzed Suzuki−Miyaura coupling[39,40] with aryl halides (Scheme 1). However, it was

Scheme 1. Complementary Approaches to Vinyl Ethers



reported that alkenylboronates **I** obtained by the hydroboration of ynol ethers with HBcat were air-sensitive,[41] therefore significantly limiting the synthetic utility of this protocol. Meanwhile, since the report by Knochel,[42] pinacolborane (HBpin) has been widely employed in acetylenic hydroboration reaction[43−54] due to the improved reactivity and stability. For example, the regioselective hydroboration of ynol ethers with HBpin was realized by Hoffman,[48] including the catalytic

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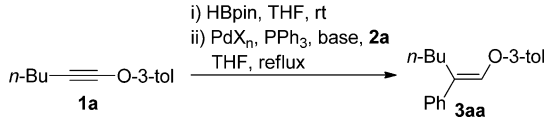
reaction using Cp_2ZrHCl as the catalyst and the noncatalytic version, although only one example was reported in the latter case. In light of these advances, we envisioned that the regioselective hydroboration of ynol ethers with HBpin[48] followed by a subsequent Suzuki–Miyaura coupling reaction[39,40] would provide an operationally simple, highly efficient, and one-pot method for the synthesis of β,β-disubstituted vinyl ethers (Scheme 1). Clearly, compared with our previous report,[37] it may provide a complementary method to assemble polysubstituted vinyl ethers.

RESULTS AND DISCUSSION

At the outset, the ynol ether **1a**, which was easily prepared by Evano's method,[55] was chosen for examining the reaction. By treating a solution of **1a** in THF with 1.1 equiv of neat HBpin at room temperature for 1 h, 5 mol % $Pd(PPh_3)_2Cl_2$, 2.0 equiv of Cs_2CO_3, and 1.2 equiv of PhI (**2a**) were added. To our delight, the β,β-disubstituted vinyl ether **3aa** was obtained in 45% yield (Table 1, entry 1), and no other regio- and stereoisomers were observed by NMR and GC–MS analysis. Encouraged by this result, we further investigated other conditions for this sequential reaction.

Table 1. Screening of the Reaction Conditions[a]



entry	PdX_n	base	solvent	yield[b] (%)
1	$Pd(PPh_3)_2Cl_2$	Cs_2CO_3	THF	45
2	$Pd(OAc)_2$	Cs_2CO_3	THF	78
3	$Pd(dba)_2$	Cs_2CO_3	THF	92
4	$Pd(PPh_3)_4$	Cs_2CO_3	THF	86
5	$Pd_2(dba)_3$	Cs_2CO_3	THF	85
6	$Pd(dba)_2$	Cs_2CO_3	THF	89 (92:8)[c,d]
7	$Pd(dba)_2$	Cs_2CO_3	THF	84[e]
8	$Pd(dba)_2$	Cs_2CO_3	THF	5[f]
9	$Pd(dba)_2$	K_2CO_3	THF	84
10	$Pd(dba)_2$	K_3PO_4	THF	76
11	$Pd(dba)_2$	*t*-BuOK	THF	74
12	$Pd(dba)_2$	Na_2CO_3	THF	67
13	$Pd(dba)_2$	KF	THF	76
14	$Pd(dba)_2$	CsF	THF	69
15	$Pd(dba)_2$	Cs_2CO_3	dioxane	55
16	$Pd(dba)_2$	Cs_2CO_3	toluene	67

[a]Reaction conditions: (i) **1a** (0.5 mmol), HBPin (0.55 mmol), rt, 1–2 h; (ii) **2a** (0.6 mmol), PdX_n (5 mol %), PPh_3 (10 mol %), base (1.0 mmol), reflux, 4 h. [b]Isolated yield. [c]PdL_n was added in step i. [d]The regioisomeric ratio (rr = 92:8) was determined by GC. [e]A 1 equiv portion of Cs_2CO_3 was used. [f]Without PPh_3.

Pleasingly, the combination of 5 mol % $Pd(dba)_2$ and 10 mol % PPh_3 worked better and resulted in **3aa** in 92% yield, while the omission of PPh_3 ligand furnished only a very low (5%) yield (Table 1, entries 3 and 8). Other palladium catalysts, including $Pd(PPh_3)_4$ and $Pd_2(dba)_3$, led to **3aa** in slightly reduced yields (Table 1, entries 4 and 5). Noteworthy, it was reported by Miyaura and Suzuki[40] that palladium complexes could catalyze the hydroboration of alkynes. As such, we tried the reaction utilizing $Pd(dba)_2$ and PPh_3 as the catalyst for both the hydroboration and coupling reaction; however, the hydroboration/coupling sequence produced 89% **3aa** with a lower regioselectivity (92:8) (Table 1, entry 6), indicating that an uncatalyzed hydroboration[56] followed a subsequent Suzuki–Miyaura coupling appeared to be the most suitable procedure. Next we employed $Pd(dba)_2$ together with PPh_3 to perform further optimization. Of the bases we examined, Cs_2CO_3 seemed to be the most effective, although other bases such as K_2CO_3, K_3PO_4, and *t*-BuOK also produced **3aa** in good yields (Table 1, entries 3 and 9–14). Additionally, the reaction performed in other solvents, including dioxane and toluene, just led to decreased yields (Table 1, entries 15 and 16). Therefore, further substrate screening was carried out using 5 mol % $Pd(dba)_2$, 10 mol % PPh_3, and 2 equiv of Cs_2CO_3 in THF at reflux for 4 h.

As shown in Table 2, the scope of this reaction with respect to halide electrophiles (R^3X) was found to be quite satisfactory. Both electron-rich and electron-poor organic halides proved to be effective coupling partners, giving desired β,β-disubstituted vinyl ethers in good yields (Table 2). In particular, the reaction of 4-MeC_6H_4I (**2b**), 3-MeC_6H_4I (**2c**), and 2-MeC_6H_4I (**2d**) afforded the desired products **3ab–ad** in 84%, 82%, and 78% yield, respectively, indicating that the steric effect had little influence on this sequential reaction (Table 2, entries 2–4). A number of functional groups, including Me, OMe, Ac, CO_2Et, CN, halides, and heteroaryl and alkenyl groups, were found to be very compatible under the reaction conditions. It should be noted that, as for 4-BrC_6H_4I (**2g**), the competitive coupling of the C–Br bond was also observed (<20%), thereby leading to a slight decrease of the yield of **3ag** (Table 2, entry 7).

Besides that of iodobenzenes, the reaction of bromobenzenes and bromoalkenes proceeded smoothly as well and generated β,β-disubstituted vinyl ethers in excellent regioselectivity. In particular, the reaction of 3-thienyl bromide (**2p**) led to **3ap** in reasonable yield (Table 2, entry 16). Notably, the coupling of **1a** with vinyl bromides **2q–s** furnished the stereodefined dienyl ethers **3aq–as** in good yields (Table 2, entries 17–19). On the other hand, the ynol ether component was varied, and as a result, ynol ether (**1d**) coupled successfully with **2a** to form **3da** in an excellent yield (Table 2, entry 22). In contrast, ynol ethers **1e** and **1f**, bearing a terminal alkene functionality, gave the corresponding vinyl ethers **3ea** and **3fa** in respective yields of 65% and 64%, together with formation of some (<15%) byproducts resulting from the competitive alkenyl hydroboration followed by the Suzuki–Miyaura coupling reaction (Table 2, entries 23 and 24). Interestingly, the sequential reaction of sterically demanding substrate **1g** with **2a** produced 86% **3ga** as a mixture of two regioisomers at a ratio of 5:1. This implied that the sterically demanding Cy group might disfavor the β-phenylation of ynol ethers, therefore resulting in decreased regioselectivity (Table 2, entry 25).

Additionally, the reaction of aryl ynol ethers occurred uneventfully and generated the desired products in good yields. For instance, 1-ethoxy-2-phenylacetylene (**1h**) coupled with **2a**, **2b**, and **2f** smoothly to provide the corresponding β,β-disubstituted vinyl ethers in good yields and perfect regioselectivity (Table 2, entries 26–28). Notably, the reaction of **1j** afforded **3ja** in 78% yield with a slightly decreased regioselectivity (rr = 9:1), whereas **1k** furnished an 88% yield of **3ka** in a single β-regioisomer (Table 2, entries 30 and 31), indicating that the utilization of sterically hindered R^2 group could increase the regioselectivity of β-substitution of ynol ethers, probably owing to the steric interaction in the hydroboration step. Furthermore, we were pleased to find that the hydroxy group was well tolerated, although only a

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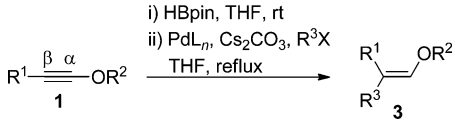
Table 2. Scope and Limitations[a]



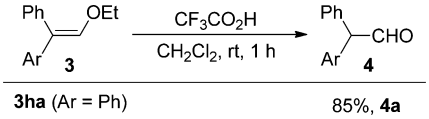
entry	R^1/R^2 (1)	R^3X (2)	yield[b] (%)
1	*n*-Bu/3-tol (**1a**)	PhI (**2a**)	92 (**3aa**)
2	**1a**	4-MeC_6H_4I (**2b**)	84 (**3ab**)
3	**1a**	3-MeC_6H_4I (**2c**)	82 (**3ac**)
4	**1a**	2-MeC_6H_4I (**2d**)	78 (**3ad**)
5	**1a**	4-FC_6H_4I (**2e**)	90 (**3ae**)
6	**1a**	4-ClC_6H_4I (**2f**)	85 (**3af**)
7	**1a**	4-BrC_6H_4I (**2g**)	55 (**3ag**)
8	**1a**	4-OMeC_6H_4I (**2h**)	75 (**3ah**)
9	**1a**	4-$CH_3COC_6H_4$I (**2i**)	70 (**3ai**)
10	**1a**	PhBr (**2j**)	86 (**3aa**)
11	**1a**	4-MeC_6H_4Br (**2k**)	80 (**3ab**)
12	**1a**	4-FC_6H_4Br (**2l**)	88 (**3ae**)
13	**1a**	4-OMeC_6H_4Br (**2m**)	67 (**3ah**)
14	**1a**	4-CO_2EtC_6H_4Br (**2n**)	73 (**3an**)
15	**1a**	3-CNC_6H_4Br (**2o**)	81 (**3ao**)
16	**1a**	3-thienyl bromide (**2p**)	60 (**3ap**)
17	**1a**	(*E*)-styryl bromide (**2q**)	71 (**3aq**)
18	**1a**	(*E*)-4-ClC_6H_4CH=CHBr (**2r**)	70 (**3ar**)
19	**1a**	(*E*)-4-OMeC_6H_4CH=CHBr (**2s**)	62 (**3as**)
20	*n*-Bu/Ph (**1b**)	**2a**	86 (**3ba**)
21	*n*-Bu/4-ClC_6H_4 (**1c**)	**2a**	88 (**3ca**)
22	PhCH_2CH_2/3-tol (**1d**)	**2a**	92 (**3da**)
23	CH_2=$CHCH_2$/Ph (**1e**)	**2a**	65 (**3ea**)
24	CH_2=$CHCH_2$/3-tol (**1f**)	**2a**	64 (**3fa**)
25	Cy/3-tol (**1g**)	**2a**	86[c] (**3ga**)
26	Ph/Et (**1h**)	**2a**	81 (**3ha**)
27	Ph/Et (**1h**)	**2b**	80 (**3hb**)
28	Ph/Et (**1h**)	**2f**	84 (**3hf**)
29	4-OMeC_6H_4/Et (**1i**)	**2a**	87 (**3ia**)
30	4-ClC_6H_4/Et (**1j**)	**2a**	78[d] (**3ja**)
31	4-ClC_6H_4/*t*-Bu (**1k**)	**2a**	88 (**3ka**)
32	CH_2OH/*t*-Bu (**1l**)	**2a**	55 (**3la**)
33	H/Ph (**1m**)	**2a**	62 (**3ma**)

[a]Reaction conditions: see Table 1. [b]Isolated yield. [c]Combined yield of two regioisomers at a ratio of 5:1. [d]Combined yield of two regioisomers at a ratio of 9:1.

moderate yield was observed (Table 2, entry 32). Finally, the terminal alkynyl ether **1m** also underwent the sequential hydroboration/Suzuki–Miyaura coupling reaction smoothly and gave **3ma** in a reasonable yield (Table 2, entry 33). The regio- and stereochemistry of *β*,*β*-disubstituted vinyl ethers **3** was determined by NOE measurements.[57] Therefore, we have realized an operationally simple and effective protocol for the elaboration of stereodefined *β*,*β*-disubstituted vinyl ethers from the readily available ynol ethers,[20,55,58] which is highlighted by the broad substrate scope, mild reaction conditions, and excellent regio- and stereocontrol.

Next the synthetic utility of this method was explored by treating vinyl ether **3ha** with 5 equiv of CF_3CO_2H (TFA) in CH_2Cl_2 at room temperature. After being stirred for 1 h, the reaction mixture was quenched with saturated $NaHCO_3$ solution, followed by extraction and concentration to give 2,2-diphenylacetaldehyde (**4a**)[59] in 85% yield (note that **4a** will decompose in the presence of silica gel) (Scheme 2). Furthermore, the reaction worked well for other *β*,*β*-disubstituted vinyl ethers, including **3hb** and **3hf**, producing

Scheme 2. Preparation of Diarylacetaldehydes from 3



3ha (Ar = Ph) 85%, **4a**
3hb (Ar = 4-Me-C_6H_4) 89%, **4b**
3hf (Ar = 4-Cl-C_6H_4) 97%, **4c**

α-branched aldehydes **4b**[60] and **4c** in excellent yields. It is worth mentioning that diarylacetaldehydes are usually a class of air- and light-sensitive compounds in organic chemistry.[61] As such, the method developed here provides an effective and mild protocol for the synthesis of diarylacetaldehydes in excellent yields with satisfactory purity.

■ CONCLUSION

In summary, we have realized a novel method for the highly regio- and stereoselective synthesis of *β*,*β*-disubstituted vinyl ethers from the readily accessible ynol ethers via a hydro-

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boration/Suzuki−Miyaura coupling sequence. The notable features of this reaction include the readily available catalytic system, broad substrate scope, high efficiency, and excellent regio- and stereoselectivity. Moreover, it offers a very effective access to the labile diarylacetaldehydes via the hydrolysis of β,β-disubstituted vinyl ethers promoted by TFA. As such, we believe that it will contribute to the progress of synthetic chemistry.

EXPERIMENTAL SECTION

General Procedures. Toluene, THF, and dioxane were distilled from sodium prior to use. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Commercial available neat pinacolborane (HBpin) was employed as the hydroborating reagent. $^{13}C\{^1H\}$ NMR spectra were measured on a 400 or 600 MHz NMR spectrometer using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard. Chemical shifts are given in δ relative to TMS, and the coupling constants are given in hertz. Column chromatography was performed using silica gel (300−400 mesh). High-resolution mass spectral (HRMS) analyses were carried out using a TOF MS instrument with an EI or ESI source.

General Procedure for the Sequential Hydroboration/Suzuki−Miyaura Coupling of Ynol Ethers. To a solution of **1a** (94 mg, 0.5 mmol) in 1 mL of THF was added neat HBpin (71 mg, 0.55 mmol) under a nitrogen atmosphere. After the resulting mixture was stirred at rt for around 1.5 h (determined by GC), $Pd(dba)_2$ (14 mg, 0.025 mmol), PPh_3 (13 mg, 0.05 mmol), Cs_2CO_3 (326 mg, 1.0 mmol), and PhI (123 mg, 0.6 mmol) were added. After being stirred at reflux for 4 h, the reaction mixture was concentrated and purified by column chromatography on silica gel (petroleum ethers:EtOAc = 50:1) to give 122 mg (92% yield) of **3aa** as a colorless oil. Compound **3aa** was also prepared from **2j** in 86% yield (114 mg): ^1H NMR (400 MHz, $CDCl_3$) δ 7.45−7.34 (m, 4 H), 7.33−7.21 (m, 2 H), 6.94−6.87 (m, 3 H), 6.76 (s, 1 H), 2.70 (t, J = 7.4 Hz, 2 H), 2.39 (s, 3 H), 1.52−1.34 (m, 4 H), 0.94 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 139.8, 139.1, 139.0, 129.3, 128.4, 126.6, 126.3, 125.7, 123.4, 117.0, 113.3, 30.3, 26.8, 22.5, 21.4, 13.9; MS (EI, m/z) 266 (M^+, 53), 223 (23), 195 (88), 180 (54), 117 (100); HRMS (EI, m/z) calcd for $C_{19}H_{22}O$ (M^+) 266.1671, found 266.1673.

Data for compound ***3ab****:* 117 mg, 84% yield from **2b**, colorless oil; it was also prepared from **2k** in 80% yield (112 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.28 (m, 2 H), 7.28−7.17 (m, 3 H), 6.95−6.85 (m, 3 H), 6.73 (s, 1 H), 2.68 (t, J = 6.4 Hz, 2 H), 2.40 (s, 3 H), 2.39 (s, 3 H), 1.53−1.34 (m, 4 H), 0.94 (t, J = 6.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 139.7, 138.4, 136.3, 136.1, 129.3, 129.1, 126.2, 125.7, 123.3, 117.0, 113.2, 30.3, 26.8, 22.5, 21.4, 21.1, 13.9; MS (EI, m/z) 280 (M^+, 100), 237 (23), 223 (22), 209 (68), 179 (48); HRMS (EI, m/z) calcd for $C_{20}H_{24}O$ (M^+) 280.1827, found 280.1826.

Data for compound ***3ac****:* 115 mg, 82% yield, colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33−7.21 (m, 4 H), 7.18−7.10 (m, 1 H), 6.96−6.89 (m, 3 H), 6.77 (s, 1 H), 2.71 (t, J = 7.4 Hz, 2 H), 2.43 (s, 3 H), 2.41 (s, 3 H), 1.54−1.37 (m, 4 H), 0.96 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 139.7, 139.1, 138.9, 137.9, 129.3, 128.3, 127.4, 127.0, 125.8, 123.4, 123.3, 117.0, 113.3, 30.3, 26.9, 22.5, 21.5, 21.4, 13.9; MS (EI, m/z) 280 (M^+, 100), 237 (20), 209 (51), 194 (20), 179 (27); HRMS (EI, m/z) calcd for $C_{20}H_{24}O$ (M^+) 280.1827, found 280.1832.

Data for compound ***3ad****:* 109 mg, 78% yield, colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.19 (m, 5 H), 6.95−6.85 (m, 3 H), 6.41 (s, 1 H), 2.58 (t, J = 6.6 Hz, 2 H), 2.44 (s, 3 H), 2.41 (s, 3 H), 1.44−1.36 (m, 4 H), 0.97−0.90 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 139.7, 139.1, 139.0, 136.6, 130.1, 130.1, 129.3, 127.0, 126.1, 125.4, 123.1, 116.8, 113.0, 29.8, 28.9, 22.7, 21.4, 20.2, 13.9; MS (EI, m/z) 280 (M^+, 100), 237 (29), 209 (48), 194 (17), 179 (38); HRMS (EI, m/z) calcd for $C_{20}H_{24}O$ (M^+) 280.1827, found 280.1830.

Data for compound ***3ae****:* 128 mg, 90% yield from **2e**, colorless oil; it was also prepared from **2l** in 88% yield (125 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.40 (dd, J = 8.2, 5.6 Hz, 2 H), 7.28 (t, J = 7.9 Hz, 1 H), 7.10 (t, J = 8.6 Hz, 2 H), 7.00−6.90 (m, 3 H), 6.74 (s, 1 H), 2.72 (t, J = 7.3 Hz, 2 H), 2.43 (s, 3 H), 1.53−1.38 (m, 4 H), 0.98 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.9 (d, J = 245.4 Hz), 157.6, 139.8, 138.8, 135.1, 129.3, 127.8 (d, J = 7.7 Hz), 124.8, 123.6, 117.0, 115.3 (d, J = 21.3 Hz), 113.3, 30.2, 27.0, 22.4, 21.4, 13.9; ^{19}F NMR (565 MHz, $CDCl_3$) δ −116.18; MS (EI, m/z) 284 (M^+, 100), 265 (69), 293 (47), 207 (37); HRMS (EI, m/z) calcd for $C_{19}H_{21}FO$ (M^+) 284.1576, found 284.1570.

Data for compound ***3af****:* 128 mg, 85% yield, colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.31 (m, 4 H), 7.30−7.22 (m, 1 H), 6.97−6.87 (m, 3 H), 6.76 (s, 1 H), 2.68 (t, J = 7.2 Hz, 2 H), 2.40 (s, 3 H), 1.52−1.35 (m, 4 H), 0.95 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 139.8, 139.4, 137.6, 132.3, 129.4, 128.6, 127.5, 124.5, 123.6, 117.1, 113.4, 30.2, 26.7, 22.4, 21.4, 13.9; MS (EI, m/z) 302 (15), 300 (M^+, 48), 194 (59), 151 (49), 125 (100); HRMS (EI, m/z) calcd for $C_{19}H_{21}ClO$ (M^+) 300.1281, found 300.1278.

Data for compound ***3ag****:* 95 mg, 55% yield, colorless oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.50−7.44 (m, 2 H), 7.29−7.20 (m, 3 H), 6.93−6.85 (m, 3 H), 6.73 (s, 1 H), 2.64 (t, J = 7.2 Hz, 2 H), 2.37 (s, 3 H), 1.46−1.31 (m, 4 H), 0.91 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.5, 139.8, 139.4, 138.1, 131.5, 129.4, 127.8, 124.5, 123.6, 120.3, 117.1, 113.4, 30.2, 26.7, 22.4, 21.4, 13.9; MS (EI, m/z) 346 (4), 344 (M^+, 4), 221 (5), 194 (100), 179 (61); HRMS (EI, m/z) calcd for $C_{19}H_{21}BrO$ (M^+) 344.0776, found 344.0778.

Data for compound ***3ah****:* 111 mg, 75% yield from **2h**, colorless oil; it was prepared from **2m** in 67% yield (99 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39−7.31 (m, 2 H), 7.28−7.20 (m, 1 H), 6.98−6.86 (m, 5 H), 6.69 (s, 1 H), 3.86 (s, 3 H), 2.67 (t, J = 7.2 Hz, 2 H), 2.39 (s, 3 H), 1.51−1.34 (m, 4 H), 0.94 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 157.7, 139.7, 137.9, 131.5, 129.3, 127.3, 125.5, 123.2, 116.9, 113.9, 113.2, 55.2, 30.3, 27.0, 22.5, 21.4, 13.9; MS (EI, m/z) 296 (M^+, 100), 253 (8), 239 (13), 145 (37), 121 (72); HRMS (EI, m/z) calcd for $C_{20}H_{24}O_2$ (M^+) 296.1776, found 296.1780.

Data for compound ***3ai****:* 108 mg, 70% yield, colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 2 H), 7.53 (d, J = 8.4 Hz, 2 H), 7.26−7.20 (m, 1 H), 6.94−6.83 (m, 4 H), 2.70 (t, J = 7.4 Hz, 2 H), 2.62 (s, 3 H), 2.37 (s, 3 H), 1.50−1.32 (m, 4 H), 0.91 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 157.4, 144.2, 140.9, 139.9, 135.2, 129.4, 128.7, 125.9, 124.2, 123.9, 117.3, 113.5, 30.3, 26.5, 26.4, 22.4, 21.4, 13.9; MS (EI, m/z) 308 (M^+, 10), 265 (87), 250 (13), 175 (43), 117 (100); HRMS (EI, m/z) calcd for $C_{21}H_{24}O_2$ (M^+) 308.1776, found 308.1777.

Data for compound ***3an****:* 123 mg, 73% yield, colorless oil; ^1H NMR (600 MHz, $CDCl_3$) δ 8.08−8.04 (m, 2 H), 7.48 (d, J = 8.3 Hz, 2 H), 7.26 (t, J = 7.8 Hz, 1 H), 6.98−6.86 (m, 4 H), 4.43 (q, J = 7.1 Hz, 2 H), 2.73 (t, J = 7.5 Hz, 2 H), 2.40 (s, 3 H), 1.51−1.37 (m, 7 H), 0.95 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 157.4, 143.9, 140.6, 139.8, 129.7, 129.4, 128.5, 125.7, 124.4, 123.8, 117.2, 113.5, 60.8, 30.3, 26.4, 22.4, 21.4, 14.3, 13.8; MS (EI, m/z) 338 (M^+, 27), 221 (21), 195 (39), 178 (50), 163 (100); HRMS (EI, m/z) calcd for $C_{22}H_{26}O_3$ (M^+) 338.1882, found 338.1886.

Data for compound ***3ao****:* 118 mg, 81% yield, colorless oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.67 (t, J = 1.5 Hz, 1 H), 7.63−7.60 (m, 1 H), 7.57−7.54 (m, 1 H), 7.46 (t, J = 7.8 Hz, 1 H), 7.25 (t, J = 7.8 Hz, 1 H), 6.95 (d, J = 7.5 Hz, 1 H), 6.91−6.86 (m, 2 H), 6.80 (s, 1 H), 2.78 (t, J = 7.2 Hz, 2 H), 2.39 (s, 3 H), 1.47−1.34 (m, 4 H), 0.93 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.3, 140.7, 140.6, 139.9, 130.4, 129.9, 129.6, 129.4, 129.3, 124.0, 123.3, 119.0, 117.2, 113.5, 112.6, 30.1, 26.5, 22.4, 21.4, 13.8; MS (EI, m/z) 291 (M^+, 24), 270 (10), 195 (56), 180 (45), 174 (100); HRMS (EI, m/z) calcd for $C_{20}H_{21}NO$ (M^+) 291.1623, found 291.1615.

Data for compound ***3ap****:* 82 mg, 60% yield, colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23−7.16 (m, 1 H), 7.11−7.06 (m, 1 H), 6.99−6.95 (m, 2 H), 6.91 (s, 1 H), 6.90−6.82 (m, 3 H), 2.61 (t, J = 7.6 Hz, 2 H), 2.34 (s, 3 H), 1.59−1.49 (m, 2 H), 1.45−1.33 (m, 2 H), 0.92 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 142.8, 139.8, 138.4, 129.4, 127.2, 123.6, 122.4, 122.3, 120.1, 117.2, 113.4, 30.6, 27.9, 22.5, 21.4, 13.9; MS (EI, m/z) 273 (17), 272 (M^+, 100), 243 (12), 215 (50), 167 (71); HRMS (EI, m/z) calcd for $C_{17}H_{20}OS$ (M^+) 272.1235, found 272.1232.

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Data for compound ***3aq:*** 104 mg, 71% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.6 Hz, 2 H), 7.34 (t, J = 7.6 Hz, 2 H), 7.28−7.18 (m, 2 H), 6.96−6.85 (m, 3 H), 6.79−6.71 (m, 2 H), 6.56 (d, J = 16.1 Hz, 1 H), 2.53 (t, J = 7.5 Hz, 2 H), 2.39 (s, 3 H), 1.61−1.40 (m, 4 H), 1.02−0.94 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 143.4, 139.8, 138.0, 129.4, 128.6, 127.4, 126.7, 125.9, 125.2, 124.2, 123.7, 117.2, 113.5, 30.6, 23.9, 22.7, 21.4, 14.0; MS (EI, m/z) 292 (M^+, 71), 235 (6), 184 (42), 141 (93), 129 (100); HRMS (EI, m/z) calcd for $C_{21}H_{24}O$ (M^+) 292.1827, found 292.1828.

Data for compound ***3ar:*** 114 mg, 70% yield, white solid, mp 77−79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.17 (m, 5 H), 6.92−6.80 (m, 3 H), 6.74−6.63 (m, 2 H), 6.45 (d, J = 16.0 Hz, 1 H), 2.48 (t, J = 7.5 Hz, 2 H), 2.35 (s, 3 H), 1.58−1.35 (m, 4 H), 0.94 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 143.8, 139.8, 136.5, 132.0, 129.4, 128.7, 128.1, 127.0, 123.9, 123.8, 123.7, 117.2, 113.5, 30.5, 23.9, 22.7, 21.4, 14.0; MS (EI, m/z) 328 (17), 326 (M^+, 56), 283 (100), 235 (34), 172 (17); HRMS (EI, m/z) calcd for $C_{21}H_{23}ClO$ (M^+) 326.1437, found 326.1435.

Data for compound ***3as:*** 100 mg, 62% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.7 Hz, 2 H), 7.25 (t, J = 7.9 Hz, 1 H), 7.00−6.80 (m, 5 H), 6.72 (s, 1 H), 6.64 (d, J = 16.1 Hz, 1 H), 6.52 (d, J = 16.1 Hz, 1 H), 3.84 (s, 3 H), 2.52 (t, J = 7.5 Hz, 2 H), 2.39 (s, 3 H), 1.62−1.40 (m, 4 H), 0.98 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 157.4, 142.5, 139.8, 130.8, 129.3, 126.9, 125.3, 124.7, 124.4, 123.5, 117.1, 114.0, 113.4, 55.2, 30.6, 23.9, 22.7, 21.4, 14.0; MS (EI, m/z) 322 (M^+, 12), 307 (80), 234 (45), 214 (100), 198 (87); HRMS (EI, m/z) calcd for $C_{22}H_{26}O_2$ (M^+) 322.1933, found 322.1923.

Data for compound ***3ba:*** 108 mg, 86% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, J = 7.8 Hz, 2 H), 7.42−7.37 (m, 4 H), 7.35−7.31 (m, 1 H), 7.15−7.10 (m, 3 H), 6.79 (s, 1 H), 2.73 (t, J = 7.5 Hz, 2 H), 1.54−1.39 (m, 4 H), 0.96 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7, 139.1, 138.9, 129.6, 128.4, 126.7, 126.3, 126.0, 122.6, 116.3, 30.3, 26.9, 22.5, 13.9; MS (EI, m/z) 252 (M^+, 100), 209 (19), 181 (63), 166 (27), 131 (12); HRMS (EI, m/z) calcd for $C_{18}H_{20}O$ (M^+) 252.1514, found 252.1512.

Data for compound ***3ca:*** 125 mg, 88% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45−7.38 (m, 4 H), 7.34−7.32 (m, 3 H), 7.07−7.02 (m, 2 H), 6.70 (s, 1 H), 2.71 (t, J = 7.6 Hz, 2 H), 1.50−1.37 (m, 4 H), 0.94 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.2, 138.4, 129.5, 129.4, 128.5, 126.9, 126.3, 125.1, 117.5, 116.7, 30.2, 26.9, 22.5, 13.9; MS (EI, m/z) 288 (31), 286 (M^+, 100), 215 (30), 179 (42), 165 (17); HRMS (EI, m/z) calcd for $C_{18}H_{19}ClO$ (M^+) 286.1124, found 286.1125.

Data for compound ***3da:*** 144 mg, 92% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39−7.32 (m, 4 H), 7.28−7.22 (m, 3 H), 7.21−7.13 (m, 4 H), 6.86 (d, J = 7.5 Hz, 1 H), 6.80−6.76 (m, 2 H), 6.71 (s, 1 H), 2.96 (dd, J = 9.4, 6.8 Hz, 2 H), 2.76 (dd, J = 9.4, 6.8 Hz, 2 H), 2.32 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.5, 142.0, 139.7, 139.6, 138.7, 129.3, 128.5, 128.5, 128.2, 126.8, 126.2, 125.7, 124.5, 123.5, 117.1, 113.4, 34.4, 29.2, 21.4; MS (EI, m/z) 314 (M^+, 63), 223 (69), 195 (100), 180 (30), 165 (44); HRMS (EI, m/z) calcd for $C_{23}H_{22}O$ (M^+) 314.1671, found 314.1662.

Data for compound ***3ea:*** 77 mg, 65% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.0 Hz, 2 H), 7.43−7.35 (m, 4 H), 7.34−7.30 (m, 1 H), 7.17−7.10 (m, 3 H), 6.92 (s, 1 H), 6.04−5.90 (m, 1 H), 5.21 (dd, J = 17.1, 1.5 Hz, 1 H), 5.08 (dd, J = 10.1, 1.3 Hz, 1 H), 3.49 (d, J = 6.0 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.5, 139.7, 138.7, 135.8, 129.6, 128.4, 126.8, 126.0, 122.8, 122.7, 116.5, 115.5, 31.9; MS (EI, m/z) 236 (M^+, 13), 212 (43), 159 (100), 142 (32); HRMS (EI, m/z) calcd for $C_{17}H_{16}O$ (M^+) 236.1201, found 236.1201.

Data for compound ***3fa:*** 80 mg, 64% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.41 (m, 2 H), 7.39−7.33 (m, 2 H), 7.31−7.22 (m, 2 H), 6.96−6.86 (m, 4 H), 5.99−5.87 (m, 1 H), 5.17 (dd, J = 17.1, 1.7 Hz, 1 H), 5.04 (dd, J = 10.1, 1.6 Hz, 1 H), 3.44 (d, J = 6.1 Hz, 2 H), 2.38 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.5, 139.8, 138.8, 135.9, 129.4, 128.4, 126.7, 126.0, 125.4, 123.6, 122.5, 117.2, 115.4, 113.4, 31.9, 21.4; MS (EI, m/z) 250 (M^+, 32), 226 (64), 172 (100), 156 (25); HRMS (EI, m/z) calcd for $C_{18}H_{18}O$ (M^+) 250.1358, found 250.1356.

Data for compound ***3ga:*** 126 mg, 86% yield, colorless oil, rr = 5:1; ^{1}H NMR (600 MHz, $CDCl_3$) (β-regioisomer) δ 7.44−7.34 (m, 5 H), 7.33−7.27 (m, 1 H), 7.00−6.95 (m, 3 H), 6.49 (s, 1 H), 2.92 (ddt, J = 15.3, 12.3, 3.1 Hz, 1 H), 2.44 (s, 3 H), 1.94−1.61 (m, 6 H), 1.49−1.19 (m, 4 H); ^{13}C NMR (150 MHz, $CDCl_3$) (β-regioisomer) δ 157.6, 139.7, 139.6, 138.8, 131.4, 129.3, 128.7, 127.9, 126.6, 123.3, 117.0, 113.2, 39.7, 31.4, 26.9, 26.1, 21.4; MS (EI, m/z) 291 (M^+, 100), 249 (2), 185 (28), 155 (11), 141 (47); HRMS (EI, m/z) calcd for $C_{21}H_{24}O$ (M^+) 292.1827, found 292.1826.

Data for compound ***3ha:*** 91 mg, 81% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.47 (m, 2 H), 7.42−7.26 (m, 8 H), 6.57 (s, 1 H), 4.05 (q, J = 7.1 Hz, 2 H), 1.41 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 140.7, 137.8, 129.8, 128.3, 128.2, 127.8, 126.3, 126.3, 120.2, 68.9, 15.4; MS (EI, m/z) 225 (14), 224 (M^+, 87), 196 (42), 195 (25), 167 (100); HRMS (EI, m/z) calcd for $C_{16}H_{16}O$ (M^+) 224.1201, found 224.1203.

Data for compound ***3hb:*** 95 mg, 80% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.38 (m, 2 H), 7.34−7.27 (m, 2 H), 7.26−7.21 (m, 1 H), 7.20−7.02 (m, 4 H), 6.47 (s, 1 H), 3.97 (q, J = 7.1 Hz, 2 H), 2.34 (s, 3 H), 1.33 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 137.9, 137.8, 136.0, 129.8, 128.9, 128.3, 127.8, 126.3, 120.0, 68.8, 21.1, 15.4; MS (EI, m/z) 238 (M^+, 74), 209 (29), 181 (93), 165 (100); HRMS (EI, m/z) calcd for $C_{17}H_{18}O$ (M^+) 238.1358, found 238.1356.

Data for compound ***3hf:*** 108 mg, 84% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.28 (m, 4 H), 7.27−7.19 (m, 3 H), 7.17−7.12 (m, 2 H), 6.48 (s, 1 H), 3.99 (q, J = 7.1 Hz, 2 H), 1.34 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 139.2, 137.3, 132.0, 129.7, 129.5, 128.3, 128.0, 126.6, 119.2, 69.1, 15.4; MS (EI, m/z) 260 (18), 258 (M^+, 57), 230 (25), 203 (16), 165 (100); HRMS (EI, m/z) calcd for $C_{16}H_{15}ClO$ (M^+) 258.0811, found 258.0814.

Data for compound ***3ia:*** 110 mg, 87% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37−7.32 (m, 2 H), 7.28−7.24 (m, 2 H), 7.23−7.19 (m, 3 H), 6.87−6.83 (m, 2 H), 6.43 (s, 1 H), 3.95 (q, J = 7.1 Hz, 2 H), 3.78 (s, 3 H), 1.32 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0, 144.3, 140.9, 130.9, 130.2, 128.3, 128.1, 126.2, 119.8, 113.3, 68.7, 55.1, 15.4; MS (EI, m/z) 254 (M^+, 21), 239 (12), 210 (15), 194 (100), 178 (41); HRMS (EI, m/z) calcd for $C_{17}H_{18}O_2$ (M^+) 254.1307, found 254.1306.

Data for compound ***3ja:*** 101 mg, 78% yield, colorless oil, rr = 9:1; ^{1}H NMR (400 MHz, $CDCl_3$) (β-regioisomer) δ 7.42−7.36 (m, 2 H), 7.36−7.27 (m, 5 H), 7.26−7.20 (m, 2 H), 6.53 (s, 1 H), 4.03 (q, J = 7.1 Hz, 2 H), 1.38 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) (β-regioisomer) δ 145.5, 140.2, 136.2, 131.9, 131.1, 128.4, 128.3, 128.0, 126.5, 119.1, 69.1, 15.4; MS (EI, m/z) 260 (19), 258 (M^+, 56), 230 (34), 203 (32), 165 (100); HRMS (EI, m/z) calcd for $C_{16}H_{15}ClO$ (M^+) 258.0811, found 258.0814.

Data for compound ***3ka:*** 126 mg, 88% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42−7.22 (m, 9 H), 6.73 (s, 1 H), 1.41 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.0, 140.2, 136.6, 133.8, 133.7, 131.1, 128.6, 128.3, 127.9, 126.4, 77.7, 28.2; MS (EI, m/z) 288 (4), 286 (M^+, 13), 229 (100), 195 (20), 165 (69); HRMS (EI, m/z) calcd for $C_{18}H_{19}ClO$ (M^+) 286.1124, found 286.1131.

Data for compound ***3la:*** 57 mg, 55% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.31 (m, 5 H), 6.74 (s, 1 H), 4.64 (d, J = 6.1 Hz, 2 H), 2.04 (t, J = 6.2 Hz, 1 H), 1.39 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 138.6, 128.5, 126.2, 125.7, 119.9, 77.6, 59.3, 28.1; MS (EI, m/z) 206 (M^+, 9), 182 (20), 150 (31), 132 (100), 119 (58); HRMS (EI, m/z) calcd for $C_{13}H_{18}O_2$ (M^+) 206.1307, found 206.1308.

Data for compound ***3ma:*** 61 mg, 62% yield, colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44−7.34 (m, 6 H), 7.29−7.22 (m, 2 H), 7.19−7.11 (m, 3 H), 6.42 (d, J = 12.4 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.1, 143.4, 135.1, 129.7, 128.7, 126.6, 125.6, 123.2, 116.9, 113.6; MS (EI, m/z) 196 (M^+, 100), 119 (87), 103 (36), 101 (31); HRMS (EI, m/z) calcd for $C_{14}H_{12}O$ (M^+) 196.0888, found 196.0888.

General Procedure for the Synthesis of Diarylacetaldehydes via TFA-Promoted Hydrolysis of β,β-Disubstituted Vinyl

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Ethers. To a solution of **3ha** (112 mg, 0.5 mmol) in 2 mL of CH_2Cl_2 was added CF_3CO_2H (285 mg, 2.5 mmol). After being stirred at room temperature for 1 h, the reaction mixture was quenched with saturated $NaHCO_3$ solution, extracted with CH_2Cl_2, washed with brine, and dried. Concentration gave 83 mg (85% yield) of compound **4a**[59] as a pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (d, J = 2.4 Hz, 1 H), 7.41 (t, J = 7.4 Hz, 4 H), 7.35 (d, J = 7.2 Hz, 2 H), 7.26 (d, J = 7.2 Hz, 4 H), 4.93 (d, J = 2.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 136.3, 129.1, 129.0, 127.6, 64.1; MS (EI, m/z) 196 (M^+, 11), 167 (100), 152 (63), 139 (12), 115 (13).

Data for compound ***4b***:[60] 94 mg, 89% yield, pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (d, J = 2.5 Hz, 1 H), 7.42−7.36 (m, 2 H), 7.35−7.32 (m, 1 H), 7.27−7.19 (m, 4 H), 7.13 (d, J = 8.1 Hz, 2 H), 4.88 (d, J = 2.2 Hz, 1 H), 2.37 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 137.4, 136.5, 133.2, 129.7, 129.1, 129.0, 128.9, 127.5, 63.7, 21.1; MS (EI, m/z) 210 (M^+, 3), 181 (100), 165 (43), 152 (6).

Data for compound ***4c***: 112 mg, 97% yield, pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (d, J = 2.2 Hz, 1 H), 7.46−7.33 (m, 5 H), 7.26−7.21 (m, 2 H), 7.21−7.15 (d, J = 8.4 Hz, 2 H), 4.91 (d, J = 1.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 135.7, 134.8, 133.6, 130.4, 129.2, 129.1, 129.0, 127.8, 63.3; MS (EI, m/z) 232 (2), 230 (M^+, 6), 201 (100), 165 (78), 139 (10); HRMS (EI, m/z) calcd for $C_{14}H_{11}ClO$ (M^+) 230.0498, found 230.0493.

■ ASSOCIATED CONTENT

Supporting Information

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

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Notes

The authors declare no competing financial interest.

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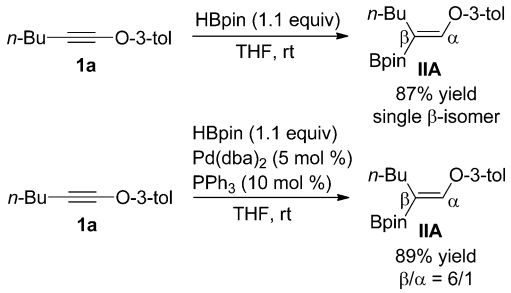
(56) The following control experiments indicated that the hydroboration of ynol ethers in this paper should be an uncatalyzed reaction. For details on the hydroboration product **IIA**, see the Supporting Information.



(57) Selected NOE data are provided in the Supporting Information. Although we cannot obtain all NOE data of the products due to the peak overlap in the NMR spectra in some cases, the stereochemistry of other products should be reasonably deduced.

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