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Synthesis of 2-Naphthols via Carbonylative Stille Coupling Reaction of 2-Bromobenzyl Bromides with Tributylallylstannane Followed by the Heck Reaction

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Supporting Information

ABSTRACT: A method for the synthesis of 2-naphthols **4** is described. The carbonylative Stille coupling reactions of 2-bromobenzyl bromides with tributylallylstannane to produce 2-bromobenzyl β,γ-unsaturated ketones **2** in satisfactory to excellent yields has been achieved. The isomerization of 2-bromobenzyl β,γ-unsaturated ketones **2** can readily occur under basic conditions to generate 2-bromobenzyl α,β-unsaturated ketones **3**. The 2-bromobenzyl α,β-unsaturated ketones **3** can be transformed into 2-naphthols **4** via intramolecular Heck reaction in satisfactory to good yields.

INTRODUCTION

The development of convenient and efficient methods for the synthesis of 2-naphthols has attracted considerable attention. 2-Naphthols can be utilized as versatile and key synthetic intermediates for the preparation of several natural products, bioactive compounds, and chiral ligands.[1] Over the past three decades, two main methods have been developed for the preparation of 2-naphthols. One method involves intramolecular cyclization reactions, such as electrophilic cyclization,[2] cyclodehydration,[3] oxidative cyclization,[4] rhodium(II)-catalyzed cycloisomerization,[5] photo- or thermal-promoted cyclization,[6] and intramolecular Aldol condensation[7] and Dieckmann condensation.[8] The other method involves intermolecular cyclization reactions such as palladium(II)-catalyzed annulation reactions.[9] Although mono- and polysubstituted-2-naphthols can be obtained using these methods, the synthesis frequently suffers from drawbacks such as multistep reactions, harsh reaction conditions, and special starting materials.

In the course of our continuous research on the η^3-benzylpalladium chemistry,[10] we found that benzyl α,β-unsaturated ketones **3**[11] can be readily obtained from the isomerization reaction of benzyl β,γ-unsaturated ketones **2**[12] under basic conditions. The ketones **2** are generated from the carbonylative Stille coupling reaction of 2-bromobenzyl bromides **1** with tributylallylstannane. The ketones **3** can be transformed into 2-naphthols **4** via an intramolecular Heck reaction (Scheme 1). In the present paper, we report a method of preparing 2-naphthols using simple and readily available starting materials, such as 2-bromobenzyl bromides, tributylallylstannane, and carbon monoxide (CO).

RESULTS AND DISCUSSION

Synthesis of Benzyl β,γ-Unsaturated Ketones 2. In our initial studies, the reaction of 2-bromobenzyl bromide (**1a**), tributylallylstannane, and CO was chosen as a model to optimize the reaction conditions. The optimization included selecting the most suitable palladium catalysts and solvents at 80 °C (Table 1). Several palladium catalysts were tested in acetonitrile (MeCN) under 0.3 MPa CO pressure. These catalysts include Pd(II) chloride ($PdCl_2$)/PPh_3, Pd(II) acetate [$Pd(OAc)_2$]/PPh_3, Pd(II) acetylacetonate [$Pd(acac)_2$]/PPh_3, tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$]/PPh_3, and tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] (entries 1−5). $Pd(PPh_3)_4$ exhibited higher catalytic activity than the others and gave the desired benzyl β,γ-unsaturated ketone, 1-(2-bromophenyl)pent-4-en-2-one (**2a**), in 87% ^{1}H NMR yield (entry 5). The solvents were then screened using $Pd(PPh_3)_4$ as the catalyst (entries 5−9). Both polar [MeCN, 1-methyl-2-pyrrolidinone (NMP), dioxane, and tetrahydrofuran (THF)] and nonpolar (toluene) solvents were examined, and MeCN proved to be the best solvent (entry 5). The yield of **2a** decreased with decreased $Pd(PPh_3)_4$ loading (entry 10), lowered reaction temperature (entry 11), and decreased CO pressure (entry 12).

Scheme 1. Synthesis of 2-Naphthols 4 Using 2-Bromobenzyl Bromides, Tributylallylstannane, and CO as Starting Materials

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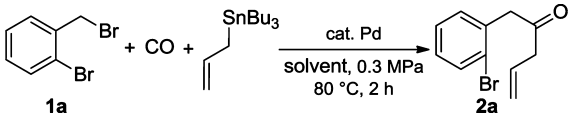
Table 1. Optimization of Reaction Conditions for the Carbonylative Stille Coupling Reaction of 2-Halogenbenzyl Halides 1 with Tributylallylstannane[a]



entry	catalyst	solvent	yield[b] (%)
1	$PdCl_2/PPh_3$	MeCN	85
2	$Pd(OAc)_2/PPh_3$	MeCN	80
3	$Pd(acac)_2/PPh_3$	MeCN	81
4	$Pd_2(dba)_3/PPh_3$	MeCN	84
5	$Pd(PPh_3)_4$	MeCN	87
6	$Pd(PPh_3)_4$	NMP	15
7	$Pd(PPh_3)_4$	dioxane	81
8	$Pd(PPh_3)_4$	THF	83
9	$Pd(PPh_3)_4$	toluene	60
10[c]	$Pd(PPh_3)_4$	MeCN	79
11[d]	$Pd(PPh_3)_4$	MeCN	80
12[e]	$Pd(PPh_3)_4$	MeCN	81

[a]Reaction conditions: 3 mmol each of **1a** and tributylallylstannane, 2 mol % of Pd, and 8 mol % of PPh_3 in 12 mL of solvent under 0.3 MPa CO pressure at 80 °C for 2 h; all reactions were performed in a 75 mL autoclave. [b]^{1}H NMR yield, mesitylene was used as an internal standard. [c]1 mol % of $Pd(PPh_3)_4$ was used. [d]The reaction was performed at 70 °C. [e]The reaction was performed under 0.2 MPa CO pressure.

Therefore, the subsequent reactions of the 2-halogenbenzyl halides **1** with tributylallylstannane were performed in MeCN at 80 °C under 0.3 MPa CO pressure in the presence of $Pd(PPh_3)_4$ as the catalyst.

The carbonylative Stille coupling reactions of 2-halogenbenzyl halides **1a**−**i** with tributylallylstannane were performed under the optimized conditions, and the results are summarized in Table 2. The reactions of 2-bromobenzyl bromide (**1a**) and 1-bromo-2-(bromomethyl)naphthalene (**1b**), a polycyclic analogue of **1a**, with tributylallylstannane and CO smoothly proceeded to furnish the corresponding β,γ-unsaturated ketones, **2a** and **2b** in good yields (86% and 77%, respectively; entries 1 and 2). Substrates **1c**−**e**, which bear the electron-donating groups methyl and methoxyl on the benzene ring, exhibited almost the same reactivities as those of substrates **1a** and **1b** to give β,γ-unsaturated ketones **2c**−**e** in satisfactory yields (90%, 73%, and 68%, respectively; entries 3−5). Substrates **1f**−**h**, bearing halogen atoms F, Cl, and Br on the benzene ring, also smoothly underwent the desired reactions to give products **2f**−**h** in good yields (84%, 76%, and 84%, respectively, entries 6−8). These results indicate that the reaction yield was not affected by the electronic property of the substituent linked to the benzene ring of the substrate. As expected, the reaction of 2-chlorobenzyl chloride (**1i**) gave β,γ-unsaturated ketone **2i** in good yield (82%, entry 9). Notably, the Cl and Br atoms linked to the aromatic ring were maintained in the structures of the products **2** under the carbonylative Stille coupling reaction conditions.[13] Although the formation of α,β-unsaturated ketones **3** in all cases was detected via ^{1}H NMR analysis of the product mixture, **3** were not isolated because the amount formed was considered too small.

Transformation of β,γ-Unsaturated Ketones 2 into α,β-Unsaturated Ketones 3. The β,γ-unsaturated ketones **2** obtained from the synthesis via carbonylative Stille coupling reactions of benzyl halides with tributylallylstannane were very stable under thermal and acidic conditions but can be easily transformed into α,β-unsaturated ketones **3** under basic conditions. The carbonylative Stille coupling reactions of **1a**−**i** with tributylallylstannane were again performed to obtain **3** for the synthesis of the 2-naphthols **4**. The results are shown in Table 3. After the reactions were completed, mixtures of the β,γ-unsaturated ketones **2** and a small amount of **3** were obtained via silica gel column chromatography. The isomerization of the **2** easily occurred when the resulting mixtures were passed through a short basic alumina column to give **3**. The *cis*- and *trans*-isomers of **3** were then separated via silica gel column chromatography using the appropriate eluents.

Synthesis of 2-Naphthols 4. In our initial studies, we have chosen the reaction of a *trans*-isomer **3aE** of the α,β-unsaturated ketone **3a** as a model to screen the reaction conditions. The results are shown in Table 4. When the intramolecular Heck reaction of **3aE** was performed in NMP at 120 °C for 3 h using various Pd sources and $NaHCO_3$ as a base, $Pd(PPh_3)_4$ was found to be the optimal catalyst (entries 1−5). The desired 2-naphthol, 4-methylnaphthalen-2-ol (**4a**), was obtained in 87% GC yield (entry 5). Evaluation of the bases and solvents (entries 5−13) reveal $NaHCO_3$ and NMP to be the optimal. The use of the tertiary amines NEt_3 and N^nBu_3 as bases resulted in a reductive Heck reaction product **5**, a byproduct, in the same (or almost the same) yield as that of **4a** (40% GC yield, entries 8 and 9).[14] The yield of **4a** decreased with decreased $Pd(PPh_3)_4$ loading (5 mol %, entry 14) and lowered reaction temperature (110 °C, entry 15).

The intramolecular Heck reactions of the α,β-unsaturated ketones **3** were performed under the optimized conditions, and the results are summarized in Table 5. The reaction of **3aE** was completed within 3 h to afford the desired product **4a** in 86% yield (entry 1). The reactions of α,β-unsaturated ketones **3bE**, **3cE**, **3dE**, and **3eE** also proceeded smoothly to furnish the corresponding 2-naphthols **4b**−**e** in moderate to good yields (63%−89%, entries 2−5). Low yields were observed from the reactions of α,β-unsaturated ketones **3fE** and **3gE**, which bear a F and Cl atom on the benzene ring, respectively (entries 6 and 7). The 2-naphthols **4f** and **4g** were obtained in 35% and 21% yields, respectively. Decomposition or no reaction was observed when the starting materials **3hE** and **3iE** were treated under the same conditions (entries 8 and 9). The 2-naphthol **4a** was also obtained in good yield when the *cis*- isomer **3aZ** of **3a** was used (82%, entry 10).

The direct use of the β,γ-unsaturated ketone **2a** and one-pot reactions of **1a**, tributylallylstannane, and CO were attempted for preparation of the 2-naphthol **4a**. The results are shown in Scheme 2. As expected, the β,γ-unsaturated ketone **2a** underwent the desired reaction smoothly to provide the 2-naphthol **4a** in 85% yield (eq 1). The three successive one-pot reactions (carbonylative Stille coupling, isomerization, and Heck reaction) of **1a**, tributylallylstannane, and CO led to the formation of a mixture of **4a** and (*E*)-3-(prop-1-en-1-yl)-1*H*-isochromen-1-one (**6**), an isocoumarin derivative.[15] Products **4a** and **6** were isolated in 29% and 18% yields, respectively (eq 2).

Finally, tributylvinylstannane was employed instead of tributylallylstannane as a starting material for the three-component coupling reaction. The results are shown in Scheme 3. As expected, the carbonylative Stille coupling product **7** was obtained in moderate yield (69%) under the same reaction conditions. The yield of **7** was improved to 75% when the catalyst loading was increased to 4 mol %. The desired product 2-naphthol **8** was finally obtained in moderate yield (59%) under the modified reaction conditions.

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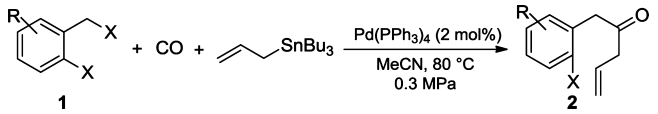
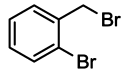
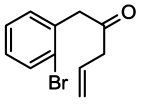
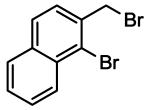
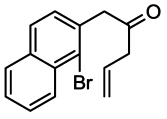
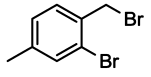
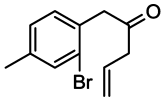
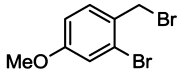
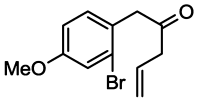
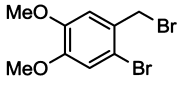
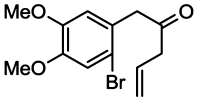
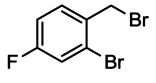
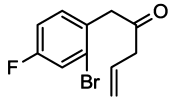
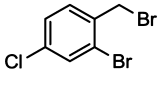
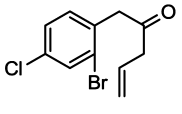
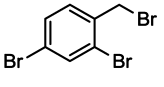
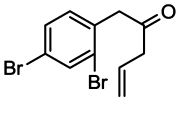
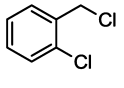
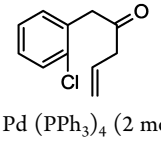
Table 2. Carbonylative Stille Coupling Reactions of 2-Halogenbenzyl Halides 1 with Tributylallylstannane[a]



Entry	Substrate 1		Time (h)	Product 2		Yield (%)[b]
1		**1a**	2		**2a**	86
2		**1b**	2		**2b**	77
3		**1c**	3		**2c**	90
4		**1d**	3		**2d**	73
5		**1e**	4		**2e**	68
6		**1f**	2		**2f**	84
7		**1g**	2		**2g**	76
8		**1h**	2		**2h**	84
9		**1i**	4		**2i**	82

[a]A mixture of 2-halogenbenzyl halide **1a**–**i** (3 mmol), tributylallylstannane (3 mmol), and Pd $(PPh_3)_4$ (2 mol %) in MeCN (12 mL) was stirred at 80 °C under 0.3 MPa CO pressure for the period indicated in the table; all reactions were performed in a 75 mL autoclave. [b]Crude products were purified via silica gel column chromatography.

CONCLUSION

In conclusion, we have developed a new, highly efficient protocol to synthesize 2-naphthols under very mild reaction conditions. The present methodology utilizes simple and readily available starting materials, namely, 2-bromobenzyl bromides, tributylallylstannane, and CO, and generally affords products in good yields. We have also developed a convenient and efficient method for the preparation of the benzyl β,γ-unsaturated ketone and benzyl α,β-unsaturated ketone intermediates.

EXPERIMENTAL SECTION

General Methods. All solvents were dried according to standard literature procedures. All reagents were purchased from commercial sources and used without further purification. 1-Bromo-2-(bromomethyl)-benzene (**1a**) and 1-chloro-2-(chloromethyl) benzene (**1i**) are commercially available. 1-Bromo-2-(bromomethyl)naphthalene (**1b**),[16] 1-bromo-2-(bromomethyl)-4,5-dimethoxybenzene (**1e**),[17] 2-bromo-1-(bromomethyl)-4-fluorobenzene (**1f**),[18] 2-bromo-1-(bromomethyl)-4-chlorobenzene (**1g**),[19] and 2,4-dibromo-1-(bromomethyl)benzene (**1h**)[20] were prepared following literature procedures. ^1H and ^{13}C NMR

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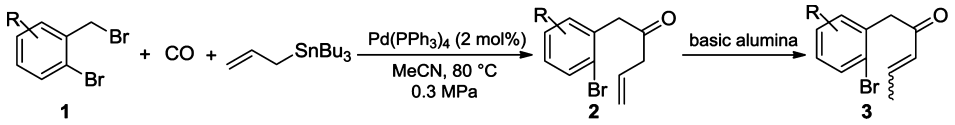
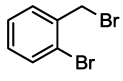
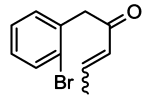
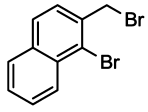
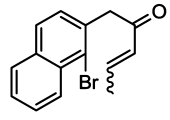
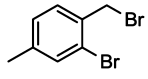
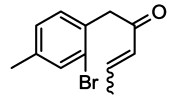
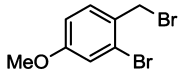
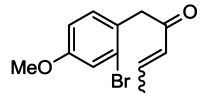
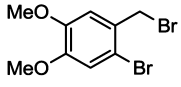
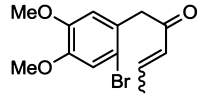
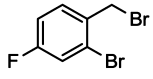
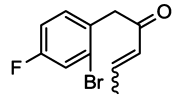
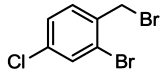
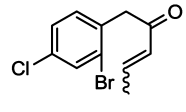
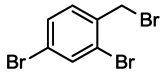
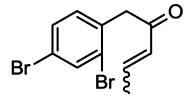
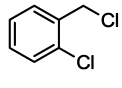
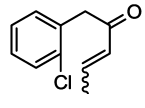
Table 3. Preparation of Benzyl α,β-Unsaturated Ketones 3[a]



1 2 3

Entry	Substrate 1		Time (h)	Product 3		Yield (%)[b]	Z/E[c]
1		**1a**	2		**3a**	95	12/88
2		**1b**	2		**3b**	87	10/90
3		**1c**	3		**3c**	99	8/92
4		**1d**	3		**3d**	85	9/91
5		**1e**	4		**3e**	78	13/87
6		**1f**	2		**3f**	94	11/89
7		**1g**	2		**3g**	83	10/90
8		**1h**	2		**3h**	91	8/92
9		**1i**	4		**3i**	95	11/89

[a]A mixture of 2-halogenbenzyl halide **1a–i** (3 mmol), tributylallylstannane (3 mmol), and Pd $(PPh_3)_4$ (2 mol %) in MeCN (12 mL) was stirred at 80 °C under 0.3 MPa CO pressure for the period indicated in the table; all reactions were performed in a 75 mL autoclave. [b]Crude products were purified via silica gel column chromatography and a short basic alumina column. [c]The ratio of the *cis*- to *trans*-isomers was determined via ^{1}H NMR analysis.

(proton decoupled) spectra were recorded in $CDCl_3$ solvent on a 400 MHz NMR spectrometer. Chemical shifts (δ) were reported in parts per million (ppm) with respect to TMS as an internal standard. Coupling constants (J) are quoted in hertz (Hz). IR spectra were recorded on FT-IR spectrometer. The high-resolution mass spectra were recorded on a mass spectrometer equipped with a Z-spray ionization source. Thin-layer chromatography (TLC) was performed on SiO_2 (silica gel 60 F_{254}), and the spots were detected with UV light

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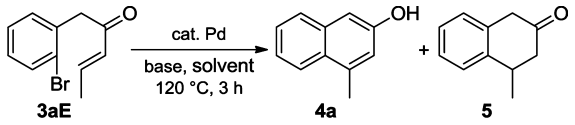
Table 4. Optimization of Reaction Conditions for the Intramolecular Heck Reaction of 2-Bromobenzyl α,β-Unsaturated Ketones 3[a]



3aE 4a 5

				yield[b] (%)	
entry	Pd source	base	solvent	4a	5
1	$PdCl_2$	$NaHCO_3$	NMP	81	ND[c]
2	$Pd(OAc)_2$	$NaHCO_3$	NMP	81	ND[c]
3	$Pd(acac)_2$	$NaHCO_3$	NMP	55	ND[c]
4	$Pd_2(dba)_3$	$NaHCO_3$	NMP	78	ND[c]
5	$Pd(PPh_3)_4$	$NaHCO_3$	NMP	87	ND[c]
6	$Pd(PPh_3)_4$	NaOAc	NMP	67	4
7	$Pd(PPh_3)_4$	K_3PO_4	NMP	3	ND[c]
8	$Pd(PPh_3)_4$	NEt_3	NMP	45	40
9	$Pd(PPh_3)_4$	N^nBu_3	NMP	40	40
10	$Pd(PPh_3)_4$	$NaHCO_3$	MeCN	40	trace
11	$Pd(PPh_3)_4$	$NaHCO_3$	dioxane	12	ND[c]
12	$Pd(PPh_3)_4$	$NaHCO_3$	DMF	79	ND[c]
13	$Pd(PPh_3)_4$	$NaHCO_3$	toluene	trace	ND[c]
14[d]	$Pd(PPh_3)_4$	$NaHCO_3$	NMP	50	ND[c]
15[e]	$Pd(PPh_3)_4$	$NaHCO_3$	NMP	61	ND[c]

[a]Reaction conditions: 0.5 mmol of **3aE**, 1.0 mmol of base, 10 mol % of Pd, and 40 mol % of PPh_3 [combined with $PdCl_2$, $Pd(OAc)_2$, $Pd(acac)_2$, or $Pd_2(dba)_3$] in 5 mL of solvent at 120 °C for 3 h; all reactions were performed in a 25 mL Schlenk reactor. [b]GC yield; 1-naphthol was used as an internal standard. [c]Not determined. [d]5 mol % of $Pd(PPh_3)_4$ was used. [e]The reaction was performed at 110 °C.

or 1% aqueous $KMnO_4$. Flash chromatography was also performed on either SiO_2 (silica gel 60, 200−300 mesh) or basic alumina (Al_2O_3 90, 100−200 mesh). Melting points were determined using a micro-melting point apparatus and are uncorrected.

Preparation of 2-Bromo-1-(bromomethyl)-4-methylbenzene (1c). To a solution of 2-bromo-4-methylbenzaldehyde[21] (12.2 g, 61 mmol) in 200 mL of MeOH at 0 °C was added $NaBH_4$ (2.7 g, 72 mmol) portionwise within 10 min. After the mixture was stirred for 10 min, an aqueous HCl (1 M) was added to quench the reaction and neutralize the resulting solution. The solvents were removed under vacuum, and the residue obtained was then extracted with dichloromethane (50 mL × 3). The combined organic layers were dried over Na_2SO_4, and the solvent was removed under reduced pressure to give a crude product, (2-bromo-4-methylphenyl)methanol, as an oil . This oil was used without further purification in the next step. To a solution of (2-bromo-4-methylphenyl)methanol in anhydrous Et_2O (200 mL) at 0 °C was added PBr_3 (6.7 g, 22 mmol) dropwise, and the resulting solution was stirred at room temperature for 3 h. The resultant mixture was neutralized with an aqueous $NaHCO_3$, and the product was extracted with Et_2O (100 mL × 2). The organic layers were dried over Na_2SO_4, and the solvent was removed under vacuum. The crude product was recrystallized from petroleum ether to give **1c** (14.7 g, 91%) as a colorless solid: mp 58−60 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.09 (d, J = 7.8 Hz, 1H), 4.59 (s, 2H), 2.32 (s, 3H).[22]

Preparation of 2-Bromo-1-(bromomethyl)-4-methoxybenzene (1d). To a solution of 2-bromo-4-methoxy-1-methylbenzene[23] (9.2 g, 46 mmol) in 150 mL of CCl_4 were added *N*-bromosuccinimide (NBS, 8.2 g, 46 mmol) and azobisisobutyronitrile (AIBN, 755 mg, 4.6 mmol). The reaction mixture was stirred under reflux for 12 h. After being cooled to room temperature, the mixture was washed with an aqueous sodium thiosulfate (NaS_2O_3, 5 wt %). The organic layer was dried over Na_2SO_4, and the solvent was removed under vacuum. The crude product was recrystallized from petroleum ether to give **1d** (7.9 g, 62%) as a white solid: mp 54−56 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.5 Hz, 1H), 7.12 (d, J = 2.6 Hz, 1H), 6.84 (dd, J = 8.5, 2.6 Hz, 1H), 4.60 (s, 2H), 3.80 (s, 3H).[24]

Representative Procedure for the Preparation of Benzyl β,γ-Unsaturated Ketones 2. $Pd(PPh_3)_4$ (69 mg, 0.06 mmol, 2 mol %), **1a** (750 mg, 3 mmol), tributylallylstannane (993 mg, 3 mmol), and MeCN (12 mL) were placed in a 75 mL autoclave with a magnetic stir bar under a N_2 atmosphere. The autoclave was purged with CO three times, filled with CO to 0.3 MPa pressure, and heated to 80 °C for 2 h. The autoclave was allowed to cool to room temperature and the remaining CO was vented. The resultant mixture was evaporated in vacuo to give the crude product, which was then purified via silica gel chromatography (eluent: ethyl acetate/petroleum ether = 1:20) to afford **2a** as a light yellow oil.

*1-(2-Bromophenyl)pent-4-en-2-one (**2a**):* 617 mg, 86% yield, light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.0 Hz, 1H), 7.33−7.10 (m, 3H), 5.95 (ddt, J = 17.2, 10.2, 7.0 Hz, 1H), 5.20 (d, J = 9.5 Hz, 1H), 5.16 (dd, J = 17.1, 1.2 Hz, 1H), 3.89 (s, 2H), 3.27 (d, J = 7.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.7, 134.6, 132.9, 131.8, 130.3, 128.9, 127.7, 125.0, 119.2, 49.5, 47.4; IR (neat) 3073, 3017, 2958, 2922, 1720, 1470, 1440, 1331, 1054, 1026, 920, 750 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{11}BrO$ 237.9993 $[M]^+$, found 238.0004.

*1-(1-Bromonaphthalen-2-yl)pent-4-en-2-one (**2b**):* 668 mg, 77% yield, light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.4 Hz, 1H), 7.81 (dd, J = 15.7, 8.2 Hz, 2H), 7.60 (t, J = 7.7 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 5.97 (dt, J = 17.1, 6.7 Hz, 1H), 5.21 (d, J = 10.2 Hz, 1H), 5.16 (d, J = 17.2 Hz, 1H), 4.14 (s, 2H), 3.30 (d, J = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, CD_3Cl) δ 204.3, 133.3, 132.6, 132.1, 130.2, 128.4, 127.9, 127.6, 127.3, 127.0, 126.2, 124.7, 118.8, 50.5, 47.1; IR (neat) 3053, 2908, 1718, 1501, 1410, 1329, 1055, 981, 921, 811, 755 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{13}ONaBr$ 311.0047 $[M + Na]^+$, found 311.0050.

*1-(2-Bromo-4-methylphenyl)pent-4-en-2-one (**2c**):* 683 mg, 90% yield, light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.09 (s, 2H), 5.95 (ddt, J = 17.1, 10.3, 7.0 Hz, 1H), 5.21−5.13 (m, 2H), 3.85 (s, 2H), 3.25 (d, J = 6.9 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3, 138.6, 132.9, 131.2, 130.2, 128.2, 124.4, 118.6, 48.8, 46.9, 20.4; IR (neat) 3078, 3004, 2979, 2919, 1720, 1683, 1636, 1598, 1392, 1038, 966, 923, 811, 705 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{13}ONaBr$ 275.0047 $[M + Na]^+$, found 275.0050.

*1-(2-Bromo-4-methoxyphenyl)pent-4-en-2-one (**2d**):* 589 mg, 73% yield, light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (dd, J = 7.5, 5.6 Hz, 2H), 6.84 (dd, J = 8.5, 2.6 Hz, 1H), 5.94 (ddt, J = 17.2, 10.2, 7.0 Hz, 1H), 5.20 (dd, J = 10.2, 1.3 Hz, 1H), 5.15 (dd, J = 17.1, 1.5 Hz, 1H), 3.82 (s, 2H), 3.79 (s, 3H), 3.25 (d, J = 7.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.8, 159.0, 131. 9, 130.3, 126.3, 124.9, 118.7, 117.8, 113.4, 55.3, 48.3, 46.9; IR (neat) 3079, 3006, 2942, 2905, 1716, 1605, 1440, 1245, 1029, 921, 863, 676 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{13}O_2NaBr$ 290.9997 $[M + Na]^+$, found 291.0001.

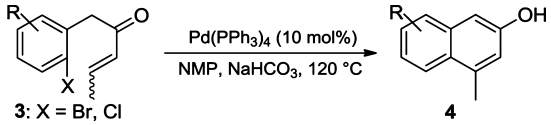
*1-(2-Bromo-4,5-dimethoxyphenyl)pent-4-en-2-one (**2e**):* 610 mg, 68% yield, white solid; mp 65−66 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 1H), 6.70 (s, 1H), 5.95 (ddt, J = 17.2, 10.2, 7.0 Hz, 1H), 5.20 (dd, J = 10.2, 1.3 Hz, 1H), 5.16 (dd, J = 17.1, 1.5 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.82 (s, 2H), 3.26 (d, J = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.8, 148.6, 148.3, 130.2, 126.1, 118.8, 115.3, 114.7, 113.9, 56.0, 55.9, 48.9, 46.9; IR (KBr) 3078, 3002, 2935, 2840, 1719, 1603, 1508, 1382, 1259, 1217, 1032, 921 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{15}O_3NaBr$ 321.0102 $[M + Na]^+$, found 321.0094.

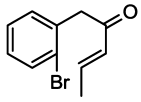
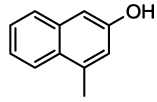
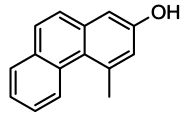
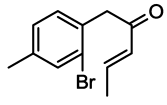
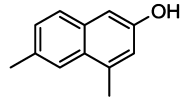
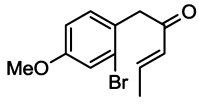
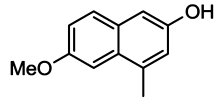
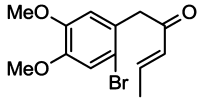
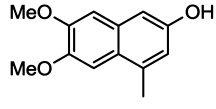
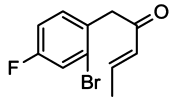
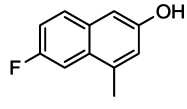
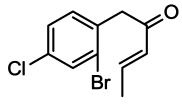
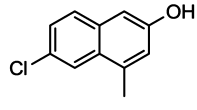
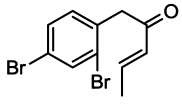
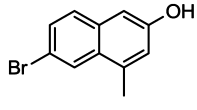
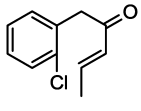
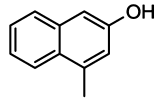
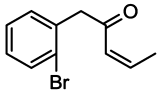
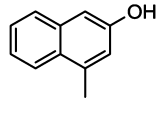
*1-(2-Bromo-4-fluorophenyl)pent-4-en-2-one (**2f**):* 648 mg, 84% yield, light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 8.2, 2.4 Hz, 1H), 7.18 (dd, J = 8.3, 6.1 Hz, 1H), 7.01 (td, J = 8.3, 2.4 Hz, 1H), 5.95 (ddt, J = 17.2, 10.2, 7.0 Hz, 1H), 5.28−5.11 (m, 2H), 3.87 (s, 2H), 3.27 (d, J = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2, 161.4 (d, J_{CF} = 250.2 Hz), 132.5 (d, J_{CF} = 8.3 Hz), 130.5 (d, J_{CF} = 3.2 Hz), 130.2, 124.8 (d, J_{CF} = 9.5 Hz), 119.9 (d, J_{CF} = 24.5 Hz), 119.1, 114.7 (d, J_{CF} = 21.0 Hz), 48.4, 47.3; IR (neat) 3084, 2919, 2840, 1719, 1600, 1488, 1231, 1055, 1032, 921 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{10}OFNaBr$ 278.9797 $[M + Na]^+$, found 278.9800.

*1-(2-Bromo-4-chlorophenyl)pent-4-en-2-one (**2g**):* 624 mg, 76% yield, light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H),

dx.doi.org/10.1021/jo201907t | J. Org. Chem. 2011, 76, 10068−10077

Table 5. Preparation of 2-Naphthols 4 via Intramolecular Heck Reaction of α,β-Unsaturated Ketones 3[a]



Entry	Substrate 3		Time (h)	Product 4		Yield (%)[b]
1		**3aE**	3		**4a**	86
2		**3bE**	3		**4b**	63
3		**3cE**	3		**4c**	86
4		**3dE**	3		**4d**	89
5		**3eE**	3		**4e**	81
6		**3fE**	12		**4f**	35
7		**3gE**	7		**4g**	21
8		**3hE**	8		**4h**	DC[c]
9		**3iE**	3		**4a**	NR[d]
10		**3aZ**	3		**4a**	82

[a]A mixture of α,β-unsaturated ketone **3** (0.5 mmol), $NaHCO_3$ (1.0 mmol), and $Pd(PPh_3)_4$ (10 mol %) in NMP (5 mL) was stirred at 120 °C under a N_2 atmosphere for the period indicated in the table. [b]Crude products were purified via silica gel column chromatography. [c]The starting material **3hE** was decomposed. [d]No reaction; the starting material **3iE** was recovered.

7.27 (d, J = 7.4 Hz, 1H), 7.13 (d, J = 8.2 Hz, 1H), 5.95 (ddt, J = 17.2, 10.0, 7.0 Hz, 1H), 5.22 (d, J = 10.3 Hz, 1H), 5.18 (d, J = 17.2 Hz, 1H), 3.87 (s, 2H), 3.27 (d, J = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 133.5, 133.1, 132.4, 132.2, 130.0, 127.7, 125.1, 119.1, 48.5, 47.3; IR (neat) 3081, 2908, 2840, 1720, 1586, 1471, 1411, 1101, 1054, 1039, 921, 747 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{10}OClNaBr$ 294.9500 $[M + Na]^+$, found 294.9504.

*1-(2,4-Dibromophenyl)pent-4-en-2-one (**2h**):* 801 mg, 84% yield, light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 1.7 Hz, 1H), 7.41 (dd, J = 8.2, 1.7 Hz, 1H), 7.08 (d, J = 8.2 Hz, 1H), 5.95 (ddt,

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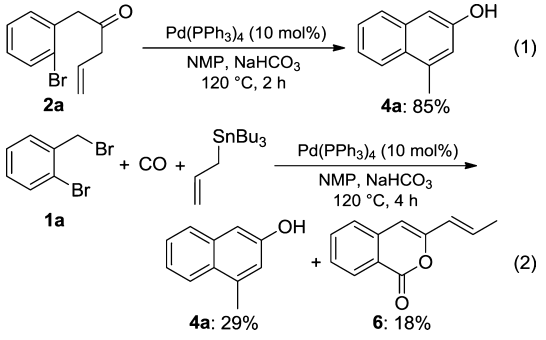
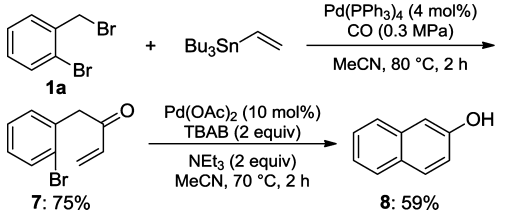
Scheme 2. Direct Use of the β,γ-Unsaturated Ketone 2a and One-Pot Reactions for Preparation of the 2-Naphthol 4a



Scheme 3. Synthesis of 2-Naphthol 8 Using 2-Bromobenzyl Bromide 1a, Tributylvinylstannane, and CO as Starting Materials



J = 17.1, 10.2, 7.0 Hz, 1H), 5.22 (d, J = 10.2 Hz, 1H), 5.18 (d, J = 17.2 Hz, 1H), 3.85 (s, 2H), 3.27 (d, J = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.7, 134.9, 133.6, 132.8, 130.6, 130.0, 125.5, 121.3, 119.2, 48.6, 47.3; IR (neat) 3080, 2907, 1719, 1580, 1467, 1053, 1036, 920, 731 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{10}ONaBr_2$ 338.8996 [M + Na]$^+$, found 338.8994.

*1-(2-Chlorophenyl)pent-4-en-2-one (**2i**):* 479 mg, 82% yield, light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.37 (m, 1H), 7.25−7.19 (m, 3H), 5.95 (ddt, J = 17.2, 10.2, 7.0 Hz, 1H), 5.20 (ddd, J = 10.3, 2.6, 1.2 Hz, 1H), 5.15 (ddd, J = 17.1, 2.9, 1.4 Hz, 1H), 3.87 (s, 2H), 3.26 (d, J = 7.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.7, 134.4, 132.7, 131.8, 130.3, 129.6, 128.7, 127.0, 119.1, 47.3, 47.1; IR (neat) 3076, 3020, 2981, 2909, 1720, 1638, 1474, 1444, 1330, 1053, 921, 752 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{11}OCl$ 194.0498 [M]$^+$, found 194.0498.

Representative Procedure for the Preparation of Benzyl α,β-Unsaturated Ketones 3. The carbonylative Stille coupling reaction of **1a** with tributylallylstannane [$Pd(PPh_3)_4$: 69 mg, 0.06 mmol, 2 mol %; **1a**: 750 mg, 3 mmol; tributylallylstannane: 993 mg, 3 mmol; CO: 0.3 MPa; MeCN: 12 mL] was performed according to the procedure described in the above section. When the reaction was completed, a 689 mg (96% yield) mixture of benzyl β,γ-unsaturated ketone **2a** and a small amount of benzyl α,β-unsaturated ketone **3a** were obtained via silica gel column chromatography (eluent: ethyl acetate/petroleum ether =1:20). The resultant mixture in ethyl acetate (20 mL) was passed through a short basic alumina column to give **3a** in 95% yield (681 mg) with a 12:88 Z/E ratio. The *cis*- and *trans*-isomers of **3a** were then separated via silica gel column chromatography using ethyl acetate/petroleum ether (1:20) as an eluent.

*(Z)-1-(2-Bromophenyl)pent-3-en-2-one (**3aZ**):* 82 mg, 11% yield, light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, J = 8.0, 0.8 Hz, 1H), 7.32−7.25 (m, 1H), 7.23 (dd, J = 7.6, 1.8 Hz, 1H), 7.13 (td, J = 7.8, 1.9 Hz, 1H), 6.31−6.19 (m, 2H), 3.91 (s, 2H), 2.13 (d, J = 5.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 144.6, 135.0, 132.8, 131.7, 128.7, 127.6, 126.9, 125.1, 51.1, 16.1; IR (neat) 3058, 3025, 2910, 1696, 1618, 1470, 1439, 1074, 1026, 919, 742 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{11}ONaBr$ 260.9891 [M + Na]$^+$, found 260.9891.

*(E)-1-(2-Bromophenyl)pent-3-en-2-one (**3aE**):* 599 mg, 84% yield, light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, J = 8.0, 1.0 Hz, 1H), 7.28 (dt, J = 7.3, 1.3 Hz, 1H), 7.22 (dd, J = 7.6, 1.8 Hz, 1H), 7.13 (td, J = 7.8, 1.8 Hz, 1H), 6.99 (dq, J = 15.6, 6.9 Hz, 1H), 6.21 (dq, J = 15.6, 1.5 Hz, 1H), 3.99 (s, 2H), 1.91 (dd, J = 6.9, 1.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 143.7, 134.9, 132.8, 131.7, 131.0, 128.7, 127.6, 125.1, 47.5, 18.4; IR (neat) 3055, 2912, 1682, 1629, 1471, 1439, 1336, 1187, 1026, 968, 749 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{11}BrO$ 237.9993 [M]$^+$, found 237.9985.

*(Z)-1-(1-Bromonaphthalen-2-yl)pent-3-en-2-one (**3bZ**):* 75 mg, 9% yield, light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.61−7.49 (m, 2H), 7.33 (d, J = 8.4 Hz, 1H), 6.29−6.19 (m, 2H), 4.16 (s, 2H), 2.13 (d, J = 5.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 144.8, 133.8, 133.3, 132.7, 128.7, 128.24, 127.9, 127.7, 127.6, 127.0, 126.5, 125.2, 52.1, 16.2; IR (neat) 3053, 2922, 1716, 1692, 1619, 1501, 1433, 1074, 812, 759 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{13}BrO$ 288.0150 [M]$^+$, found 288.0151.

*(E)-1-(1-Bromonaphthalen-2-yl)pent-3-en-2-one (**3bE**):* 679 mg, 78% yield, white solid; mp 76−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.02 (dq, J = 13.9, 6.8 Hz, 1H), 6.24 (dd, J = 15.4, 1.4 Hz, 1H), 4.24 (s, 2H), 1.90 (d, J = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 144.0, 133.8, 133.2, 132.7, 131.1, 128.7, 128.3, 127.9, 127.7, 127.6, 126.5, 125.1, 49.1, 18.5; IR (KBr) 3052, 2911, 1676, 1630, 1501, 1438, 1325, 1189, 968, 808, 761 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{13}BrO$ 288.0150 [M]$^+$, found 288.0149.

*(Z)-1-(2-Bromo-4-methylphenyl)pent-3-en-2-one (**3cZ**):* 60 mg, 8% yield, light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.12−7.07 (m, 2H), 6.28−6.19 (m, 2H), 3.86 (s, 2H), 2.32 (s, 3H), 2.12 (d, J = 5.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 144.4, 138.8, 133.3, 131.8, 131.4, 128.5, 126.8, 124.8, 50.7, 20.7, 16.0; IR (neat) 3025, 2920, 1693, 1620, 1492, 1435, 1317, 1074, 1040, 920, 870, 819, 743, 702 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{13}ONaBr$ 275.0047 [M + Na]$^+$, found 275.0045.

*(E)-1-(2-Bromo-4-methylphenyl)pent-3-en-2-one (**3cE**):* 692 mg, 91% yield, light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.11−6.93 (m, 3H), 6.20 (dd, J = 15.7, 1.6 Hz, 1H), 3.94 (s, 2H), 2.31 (s, 3H), 1.91 (dd, J = 6.9, 1.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 143.6, 138.8, 133.2, 131.7, 131.3, 131.0, 128.4, 124.8, 47.1, 20.7, 18.4; IR (neat) 3034, 2969, 2914, 2868, 1681, 1632, 1492, 1441, 1332, 1187, 1073, 1041, 968, 867, 798, 674 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{13}ONaBr$ 275.0047 [M + Na]$^+$, found 275.0042.

*(Z)-1-(2-Bromo-4-methoxyphenyl)pent-3-en-2-one (**3dZ**):* 62 mg, 8% yield, white solid; mp 30−31 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14−7.10 (m, 2H), 6.84 (dd, J = 8.5, 2.6 Hz, 1H), 6.28−6.19 (m, 2H), 3.83 (s, 2H), 3.79 (s, 3H), 2.12 (d, J = 5.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 159.2, 144.3, 132.0, 126.9, 126.8, 125.2, 118.1, 113.8, 55.5, 50.2, 16.0; IR (KBr) 3069, 3005, 2940, 2912, 2836, 1639, 1605, 1494, 1439, 1282, 1243, 1074, 1029, 920, 862, 840 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{13}O_2Br$ 268.0099 [M]$^+$, found 268.0105.

*(E)-1-(2-Bromo-4-methoxyphenyl)pent-3-en-2-one (**3dE**):* 625 mg, 77%, white solid; mp 58−60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13−7.10 (m, 2H), 6.97 (dq, J = 13.7, 6.9 Hz, 1H), 6.83 (dd, J = 8.5, 2.5 Hz, 1H), 6.20 (dd, J = 15.7, 1.5 Hz, 1H), 3.91 (s, 2H), 3.79 (s, 3H), 1.90 (dd, J = 6.8, 1.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 159.2, 143.5, 131.9, 130.9, 126.8, 125.2, 118.1, 113.7, 55.5, 46.6, 18.3; IR (KBr) 3006, 2941, 2910, 2836, 1686, 1631, 1605, 1495, 1440, 1243, 1185, 1028, 969, 864 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{13}O_2Br$ 268.0099 [M]$^+$, found 268.0096.

*(Z)-1-(2-Bromo-4,5-dimethoxyphenyl)pent-3-en-2-one (**3eZ**):* 91 mg, 10% yield, white solid; mp 64−66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 1H), 6.72 (s, 1H), 6.30−6.21 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 3.83 (s, 2H), 2.13 (d, J = 5.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 148.6, 148. 5, 144.6, 126.8, 126.7, 115.5, 115.0, 113.9, 56.2, 56.0, 50.7, 16.0; IR (KBr) 3077, 3002, 2935, 2909, 2839, 1692, 1619, 1508, 1464, 1439, 1381, 1259, 1219, 1165, 1075, 1032, 967, 924, 852, 801 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{15}O_3Br$ 298.0205 [M]$^+$, found 298.0211.

*(E)-1-(2-Bromo-4,5-dimethoxyphenyl)pent-3-en-2-one (**3eE**):* 609 mg, 68% yield, white solid; mp 62−64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04−6.95 (m, 2H), 6.71 (s, 1H), 6.21 (dq, J = 15.6, 1.5 Hz, 1H), 3.91

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(s, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 1.91 (dd, J = 6.9, 1.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 148.6, 148.4, 143.7, 130.8, 126.6, 115.4, 114.9, 113.9, 56.1, 56.0, 47.0, 18.3; IR (KBr) 2935, 2840, 1685, 1630, 1507, 1439, 1382, 1259, 1218, 1165, 1031, 969, 807 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{15}O_3Br$ 298.0205 $[M]^+$, found 298.0207.

(Z)-1-(2-Bromo-4-fluorophenyl)pent-3-en-2-one (**3fZ**): 80 mg, 10% yield, white solid; mp 58−60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 8.2, 2.6 Hz, 1H), 7.19 (dd, J = 8.5, 6.0 Hz, 1H), 7.01 (td, J = 8.3, 2.6 Hz, 1H), 6.32−6.18 (m, 2H), 3.88 (s, 2H), 2.15−2.11 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.97, 161.4 (d, J_{CF} = 250.0 Hz), 144.7, 132.4 (d, J_{CF} = 8.4 Hz), 131.0 (d, J_{CF} = 3.6 Hz), 126.7, 125.0 (d, J_{CF} = 9.5 Hz), 120.0 (d, J_{CF} = 24.4 Hz), 114.7 (d, J_{CF} = 21.0 Hz), 50.1, 16.0; IR (KBr) 3069, 3027, 2956, 2923, 2871, 1696, 1621, 1600, 1488, 1299, 1074, 921, 884, 858 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{10}BrFO$ 255.9899 $[M]^+$, found 255.9907.

(E)-1-(2-Bromo-4-fluorophenyl)pent-3-en-2-one (**3fE**): 645 mg, 84%, light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, J = 8.2, 2.6 Hz, 1H), 7.18 (dd, J = 8.5, 6.0 Hz, 1H), 7.03−6.94 (m, 2H), 6.21 (dd, J = 15.7, 1.6 Hz, 1H), 3.95 (s, 2H), 1.92 (dd, J = 6.9, 1.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 161.4 (d, J_{CF} = 249.9 Hz), 143.8, 132.4 (d, J_{CF} = 8.4 Hz), 130.94, 130.89 (d, J_{CF} = 3.7 Hz), 124.9 (d, J_{CF} = 9.5 Hz), 119.9 (d, J_{CF} = 24.4 Hz), 114.7 (d, J_{CF} = 21.0 Hz), 46.5, 18.3; IR (neat) 3067, 3038, 2971, 2913, 2852, 1684, 1633, 1600, 1488, 1231, 969, 881, 859 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{10}BrFO$ 255.9899 $[M]^+$, found 255.9906.

(Z)-1-(2-Bromo-4-chlorophenyl)pent-3-en-2-one (**3gZ**): 68 mg, 8% yield, light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 2.1 Hz, 1H), 7.27 (dd, J = 8.4, 1.9 Hz, 1H), 7.16 (d, J = 8.2 Hz, 1H), 6.32−6.20 (m, 2H), 3.88 (s, 2H), 2.13 (dd, J = 6.9, 1.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 145.1, 133.6, 132.4, 132.4, 127.8, 126.7, 125.4, 50.37, 16.11; IR (neat) 3026, 2912, 2852, 1694, 1621, 1471, 1435, 1314, 1074, 1038, 921, 866, 837, 817 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{10}BrClNaO$ 294.9501 $[M + Na]^+$, found 294.9502.

(E)-1-(2-Bromo-4-chlorophenyl)pent-3-en-2-one (**3gE**): 613 mg, 75% yield, white solid; mp 32−34 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 2.1 Hz, 1H), 7.28−7.25 (m, 1H), 7.15 (d, J = 8.2 Hz, 1H), 6.99 (dq, J = 15.6, 6.9 Hz, 1H), 6.21 (dq, J = 15.7, 1.6 Hz, 1H), 3.96 (s, 2H), 1.93 (dd, J = 6.9, 1.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 144.1, 133.6, 133.5, 132.4, 130.93, 127.8, 125.3, 46.7, 18.4; IR (KBr) 3036, 2912, 2852, 1691, 1674, 1632, 1588, 1471, 1440, 1378, 1327, 1187, 1039, 968, 864 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{10}BrClNaO$ 294.9501 $[M + Na]^+$, found 294.9499.

(Z)-1-(2,4-Dibromophenyl)pent-3-en-2-one (**3hZ**): 69 mg, 7% yield, light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 1.8 Hz, 1H), 7.41 (dd, J = 8.1, 1.8 Hz, 1H), 7.10 (d, J = 8.2 Hz, 1H), 6.30−6.20 (m, 2H), 3.87 (s, 2H), 2.13 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 145.0, 135.1 134.1, 132.8, 130.7, 126.7, 125.7, 121.3, 50.4, 16.1; IR (neat) 3077, 3025, 2909, 1694, 1620, 1580, 1467, 1072, 1036, 921, 867, 832, 813 704 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{10}OBr_2$ 315.9098 $[M]^+$, found 315.9093.

(E)-1-(2,4-Dibromophenyl)pent-3-en-2-one (**3hE**): 799 mg, 84% yield, white solid; mp 42−44 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 1.8 Hz, 1H), 7.42−7.39 m, 1H), 7.09 (d, J = 8.2 Hz, 1H), 6.99 (dq, J = 13.7, 6.8 Hz, 1H), 6.20 (dd, J = 15.7, 1.4 Hz, 1H), 3.94 (s, 2H), 1.93 (dd, J = 6.9, 1.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 144.0, 135.1, 134.0, 132.8, 130.9, 130.7, 125.6, 121.3, 46.8, 18.4; IR (KBr) 3036, 2969, 2911, 1688, 1672, 1631, 1579, 1468, 1326, 1187, 1036, 968, 812 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{10}OBr_2$ 315.9098 $[M]^+$, found 315.9091.

(Z)-1-(2-Chlorophenyl)pent-3-en-2-one (**3iZ**): 61 mg, 10% yield, light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 6.6, 2.7 Hz, 1H), 7.23−7.20 (m, 3H), 6.29−6.20 (m, 2H), 3.89 (s, 2H), 2.12 (d, J = 5.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 144.5, 134.5, 133.1, 131.7, 129.5, 128.5, 127.0, 126.8, 48.7 16.0; IR (neat) 3061, 3025, 2955, 2923, 2870, 1697, 1619, 1474, 1443, 1075, 1053, 920, 745 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{11}OCl$ 194.0498 $[M]^+$, found 194.0510.

(E)-1-(2-Chlorophenyl)pent-3-en-2-one (**3iE**): 494 mg, 85% yield, light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.37 (m, 1H), 7.23−7.21 (m, 3H), 6.98 (dq, J = 15.7, 6.9 Hz, 1H), 6.21 (dd, J = 15.7, 1.6 Hz, 1H), 3.97 (s, 2H), 1.91 (dd, J = 6.9, 1.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 143.9, 134.6, 133.2, 131.8, 131.1, 129.7, 128.7, 127.1, 45.1, 18.5; IR (neat) 3060, 2969, 2912, 1683, 1630, 1474, 1443, 1333, 1187, 1053, 968, 751 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{11}OCl$ 194.0498 $[M]^+$, found 194.0508.

Representative Procedure for the Preparation of 2-Naphthols 4. A mixture of $Pd(PPh_3)_4$ (58 mg, 0.05 mmol, 10 mol %), $NaHCO_3$ (84 mg, 1.0 mmol, 2.0 equiv), **3aE** (120 mg, 0.5 mmol), and NMP (5 mL) was stirred at 120 °C under a N_2 atmosphere. The reaction progress was monitored via TLC. TLC analysis indicated that the reaction was complete after the mixture was stirred for 3 h. The mixture was then allowed to cool to room temperature. Water (20 mL) was added to the resultant mixture, and the product was extracted with ethyl acetate (10 mL × 3). The combined extracts were washed with brine (10 mL × 2), dried over Na_2SO_4, and evaporated in vacuo. The residue obtained was purified via silica gel chromatography (eluent: ethyl acetate/petroleum ether = 1:10) to give **3a** as a red solid.

4-Methylnaphthalen-2-ol (**4a**):.[25] 68 mg, 86% yield, red solid; mp 72−74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.3 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 6.98−6.95 (m, 2H), 5.24 (s, 1H), 2.63 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 136.9, 134.9, 128.3, 127.1, 126.3, 124.1, 123.5, 118.6, 107.8, 19.3; IR (KBr) 3369, 3066, 2920, 2859, 1622, 1602, 1512, 1462, 1349, 1282, 1233, 1172, 1133, 1000, 857, 769, 745 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{10}O$ 158.0732 $[M]^+$, found 158.0737.

4-Methylphenanthren-2-ol (**4b**): 66 mg, 63% yield, red solid; mp 126−128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, J = 8.5 Hz, 1H), 7.88−7.85 (m, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.62−7.48 (m, 3H), 7.08 (dd, J = 28.3, 2.6 Hz, 2H), 3.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 138.0, 135.5, 132.5, 131.8, 128.8, 127.9, 127.3, 126.7, 125.8, 125.0, 124.6, 120.8, 110.9, 27.4; IR (KBr) 3318, 3050, 2962, 2874, 1613, 1602, 1467, 1453, 1265, 1173, 993, 866, 856, 806, 744, 707 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{12}O$ 208.0888 $[M]^+$, found 208.0878.

4-Methylphenanthren-2-ol (**4c**): 74 mg, 86% yield, red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.57 (d, J = 8.3 Hz, 1H), 7.29−7.25 (m, 1H), 6.97−6.93 (m, 2H), 4.99 (s, 1H), 2.63 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 136.0, 133.1, 132.8, 128.5, 128.4, 127.0, 123.3, 118.8, 107.8, 21.9, 19.4; IR (neat) 3373, 3048, 2920, 2858, 1634, 1612, 1512, 1440, 1395, 1287, 1139, 970, 854, 732 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{12}O$ 172.0888 $[M]^+$, found 172.0881.

6-Methoxy-4-methylnaphthalen-2-ol (**4d**): 84 mg, 89% yield, red solid; mp 108−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.9 Hz, 1H), 7.17−7.11 (m, 2H), 6.96 (d, J = 6.3 Hz, 2H), 4.95 (s, 1H), 3.92 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 151.5, 135.2, 130.1, 128.9, 128.6, 119.1, 118.4, 108.0, 103.3, 55.4, 19.5; IR (KBr) 3404, 2933, 2833, 1608, 1514, 1444, 1397, 1249, 1160, 1036, 851 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{12}O_2$ 188.0837 $[M]^+$, found 188.0835.

6,7-Dimethoxy-4-methylnaphthalen-2-ol (**4e**):.[26] 88 mg, 81% yield, light red solid; mp 164−166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 1H), 6.98 (s, 1H), 6.92 (d, J = 2.3 Hz, 1H), 6.83 (d, J = 1.6 Hz, 1H), 4.80 (s, 1H), 3.99 (s, 3H), 3.98 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 149.8, 147.5, 135.0, 130.6, 123.18, 116.5, 107.1, 105.9, 103.3, 55.82, 55.79, 19.6; IR (KBr) 3452, 3002, 2956, 2829, 1633, 1510, 1399, 1272, 1250, 1162, 1063, 862, 771 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{14}O_3$ 218.0943 $[M]^+$, found 218.0934.

6-Fluoro-4-methylnaphthalen-2-ol (**4f**): 31 mg, 35% yield, light yellow solid; mp 86−88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 9.0, 5.8 Hz, 1H), 7.51 (d, J = 10.9 Hz, 1H), 7.22 (t, J = 8.7 Hz, 1H), 7.00 (d, J = 4.5 Hz, 2H), 4.93 (s, 1H), 2.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5 (d, J_{CF} = 242.4 Hz), 152.4, 136.3 (d, J_{CF} = 5.4 Hz), 131.8, 129.2 (d, J_{CF} = 8.6 Hz), 128.9 (d, J_{CF} = 8.1 Hz), 119.6, 116.5 (d, J_{CF} = 25.1 Hz), 107.96 (d, J_{CF} = 21.0 Hz), 107.95, 19.4; IR (KBr) 3287, 2924, 2862, 1613, 1519, 1450, 1278, 1242, 1156, 852 cm^{-1}; HRMS (EI) calcd for $C_{11}H_9FO$ 176.0637 $[M]^+$, found 176.0638.

6-Chloro-4-methylnaphthalen-2-ol (**4g**): 20 mg, 21% yield, yellow solid; mp 90−92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 1.6 Hz, 1H), 7.60 (d, J = 8.7 Hz, 1H), 7.36 (dd, J = 8.7, 2.0 Hz, 1H), 6.98 (s, 2H), 5.15 (s, 1H), 2.62 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

153.3, 136.2, 133.3, 129.2, 129.0, 128.6, 127.2, 123.4, 119.7, 107.8, 19.4; IR (KBr) 3373, 2923, 2852, 1624, 1598, 1502, 1470, 1134, 1089, 889 cm^{-1}; HRMS (EI) calcd for $C_{11}H_9ClO$ 192.0342 $[M]^+$, found 192.0339.

*4-Methyl-3,4-dihydronaphthalen-2(1H)-one (**5**):*.[27] 32 mg, 40% yield, light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30−7.21 (m, 3H), 7.13 (d, J = 7.2 Hz, 1H), 3.68−3.56 (m, 2H), 3.32−3.24 (m, 1H), 2.71 (dd, J = 16.6, 5.2 Hz, 1H), 2.34 (dd, J = 16.6, 7.5 Hz, 1H), 1.34 (d, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.4, 141.2, 132.8, 128.4, 127.0, 126.8, 126.0, 46.3, 44.6, 33.5, 20.1; IR (neat) 3023, 2961, 2874, 1718, 1489, 1458, 1236, 1107, 756 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{12}O$ 160.0888 $[M]^+$, found 160.0883.

One-Pot Reactions of 1a, Tributylallylstannane, and CO. Pd$(PPh_3)_4$ (347 mg, 0.30 mmol, 10 mol %), **1a** (750 mg, 3 mmol), tributylallylstannane (993 mg, 3 mmol), $NaHCO_3$ (504 mg, 6 mmol), and NMP (30 mL) were placed in a 75 mL autoclave with a magnetic stir bar under a N_2 atmosphere. The autoclave was purged with CO three times and then filled with CO to 0.3 MPa pressure. The autoclave was heated to 120 °C for 4 h. It was allowed to cool to room temperature, and the remaining CO was vented. Water (20 mL) was added to the resultant mixture, and the products were extracted with ethyl acetate (10 mL × 3). The combined extracts were washed with brine (20 mL × 2) and dried over Na_2SO_4. The solvent was removed in vacuo. The residue obtained was purified via silica gel chromatography (eluent: ethyl acetate/petroleum ether = 1:20) to give **4a** (140 mg) and **6** (100 mg) in 29% and 18% yields, respectively.

*(E)-3-(Prop-1-en-1-yl)-1H-isochromen-1-one (**6**):* 100 mg, 18% yield, white solid; mp 89−90 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.0 Hz, 1H), 7.65 (td, J = 7.9, 1.3 Hz, 1H), 7.42 (td, J = 8.0, 1.1 Hz, 1H), 7.36 (d, J = 7.9 Hz, 1H), 6.63 (dq, J = 13.8, 6.9 Hz, 1H), 6.24 (s, 1H), 6.05 (dd, J = 15.4, 1.7 Hz, 1H), 1.91 (dd, J = 6.9, 1.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 152.7, 137.9, 134.8, 131.8, 129.8, 127.8, 125.7, 123.4, 120.8, 103.5, 18.5; IR (KBr) 3439, 3061, 2967, 2939, 2910, 1723, 1311, 1164, 1058, 959, 763 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{10}O_2$ 186.0681 $[M]^+$, found 186.0675.

Synthesis of 2-Naphthol 8 Using 2-Bromobenzyl Bromide 1a, Tributylvinylstannane, and CO as Starting Materials. Pd$(PPh_3)_4$ (139 mg, 0.12 mmol, 4 mol %), **1a** (750 mg, 3 mmol), tributylvinylstannane (951 mg, 3 mmol), and MeCN (12 mL) were placed in a 75 mL autoclave with a magnetic stir bar under a N_2 atmosphere. The autoclave was purged with CO three times, filled with CO to 0.3 MPa pressure, and heated to 80 °C for 2 h. The autoclave was allowed to cool to room temperature and the remaining CO was vented. The resultant mixture was evaporated in vacuo to give the crude product, which was then purified via silica gel chromatography (eluent: ethyl acetate/petroleum ether = 1:20) to afford **7** as a light yellow oil.

A mixture of $Pd(OAc)_2$ (11 mg, 0.05 mmol, 10 mol %), TBAB [tetra-*n*-butylammonium bromide, 322 mg, 0.1 mmol, 2 equiv], Et_3N (101 mg, 1.0 mmol, 2 equiv), **7** (113 mg, 0.5 mmol), and MeCN (10 mL) was stirred at 70 °C under a N_2 atmosphere. The reaction progress was monitored via TLC. TLC analysis indicated that the reaction was complete after the mixture was stirred for 2 h. The mixture was then allowed to cool to room temperature. Water (20 mL) was added to the resultant mixture, and the product was extracted with ethyl acetate (10 mL × 3). The combined extracts were washed with brine (10 mL × 2), dried over Na_2SO_4, and evaporated in vacuo. The residue obtained was purified via silica gel chromatography (eluent: ethyl acetate/petroleum ether = 1:10) to give **8** as a light yellow solid.

*1-(2-Bromophenyl)but-3-en-2-one (**7**):* 506 mg, 75% yield, light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.0 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.22 (dd, J = 7.5, 1.5 Hz, 1H), 7.15 (td, J = 7.8, 1.7 Hz, 1H), 6.45 (dd, J = 17.6, 10.1 Hz, 1H), 6.36 (dd, J = 17.5, 1.3 Hz, 1H), 5.88 (dd, J = 10.1, 1.4 Hz, 1H), 4.06 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 135.6, 134.5, 132.8, 131.8, 129.1, 128.8, 127.6, 125.0, 47.1; IR (neat) 3057, 3019, 2910, 1692, 1471, 1440, 1397, 1334, 1078, 1026, 986, 749 cm^{-1}; HRMS (EI) calcd for $C_{10}H_9BrO$ 223.9837 $[M]^+$, found 223.9826.

*Naphthalen-2-ol (**8**):*.[28] 43 mg, 59% yield, light yellow solid; mp 100−102 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (t, J = 7.6 Hz, 2H), 7.68 (d, J = 8.2 Hz, 1H), 7.45−7.40 (m, 1H), 7.35−7.30 (m, 1H), 7.15 (d, J = 2.3 Hz, 1H), 7.10 (dd, J = 8.8, 2.5 Hz, 1H), 5.06 (s, 1H).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General information and copies of spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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