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Lewis Acid Mediated Domino Intramolecular Cyclization: Synthesis of Dihydrobenzo[*a*]fluorenes

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ABSTRACT: An efficient and facile method for the regioselective synthesis of novel dihydrobenzo[*a*]fluorenes from readily accessible alkynols is presented. The current strategy triggers the formation of a dual C−C bond intramolecularly via Lewis acid catalysis under mild reaction conditions. Notably, secondary as well as tertiary alcohols bearing an alkyne moiety have been smoothly transformed into the corresponding products. As a result, novel tetracyclic dihydrobenzo[*a*]fluorenes have been accomplished using this approach.

INTRODUCTION

Benzo[*a*]fluorenes are nonalternant polycyclic aromatic hydrocarbons (PAH) with potential applications in material science. In addition, these structural motifs can serve as ligands in the fields of organometallics and coordination chemistry.[1] Although the synthesis of benzo[*a*]fluorenes has been greatly explored, the accomplishment of saturated analogues of benzo[*a*]fluorenes (i.e., dihydrobenzo[*a*]fluorenes and tetrahydrobenzo[*a*]fluorenes) has not. In addition, the saturated benzo[*a*]fluorene skeletal core constitutes various carbocyclic natural products.[2] This tetracyclic core skeleton has gained much attention owing to its interesting biological and pharmacological activities, namely in isoprekinamycin,[3] veratramine,[4] pelorol,[5] and dasyscyphin B.[6] In addition, the synthetic tetracyclic core of the THBF analogue having a piperidinyl-ethoxypheny side chain (Figure 1) is known to show interesting properties, for instance, as estrogen receptor or bone loss inhibitors.[7]

Cascade or tandem reactions are highly efficient chemical processes wherein several reactions sequentially take place in the same pot and, as a result, bring in sufficient molecular complexity instantly.[8] In recent years, electrophilic cascade reactions have gained more attention in the domain of synthetic organic chemistry.[9] However, the literature precedence disclosing the synthesis of fused tetracyclic dihydrobenzo[*a*]fluorene derivatives is very limited. To the best of our knowledge, until now, only a very few reports are known in the literature for the synthesis of dihydrobenzo[*a*]-fluorenes.

Among them, an efficient gold-catalyzed intramolecular [3 + 3] cycloaddition of *o*-alkynylstyrene was demonstrated for the synthesis of dihydrobenzo[*a*]fluororenes by Sanz et al.[10] In yet another report, the research group of Anand established the synthesis of dihydrobenzo[*a*]fluorenes starting from alkynated *p*-quinonemethides and styrenes.[11] Although these previous reports were found to be effective but suffer from some limitations like being utilized a precious catalysts, with limited substrate scope and longer reaction times. Thus, there is always enough space for establishing new and efficient strategies utilizing mild conditions. As part of our ongoing interest centered on transition-metal catalysis and acid-mediated domino electrophilic cyclizations,[12] herein we disclose an

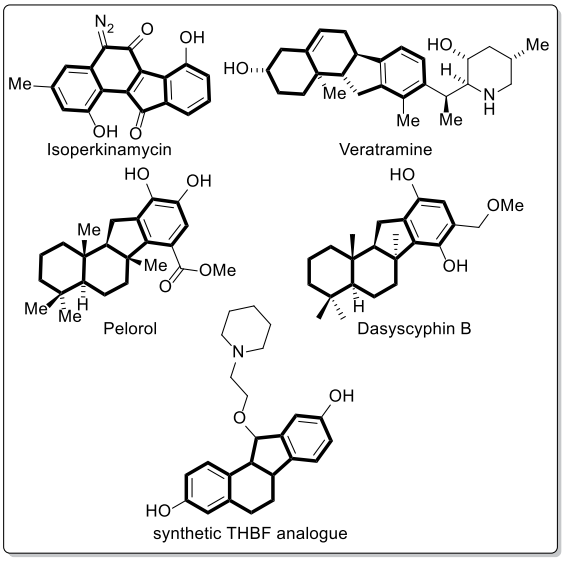

Figure 1. Representative natural/unnatural products bearing benzo-[*a*]fluorene skeleton.

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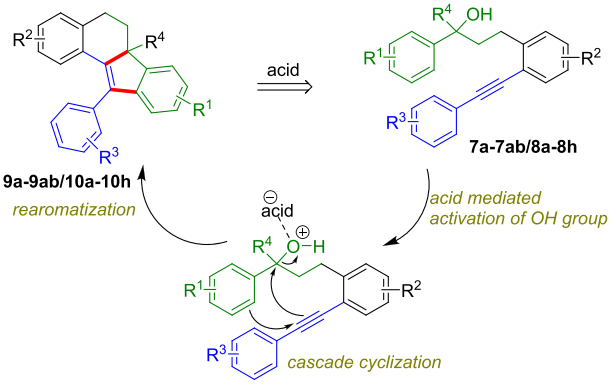
intramolecular electrophilic cascade cyclization reaction of alkynol promoted by simple Lewis acid $BF_3{\cdot}OEt_2$, which affords the novel 11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluorene derivatives under mild conditions.

RESULT AND DISCUSSION

It was intended that in the presence of an appropriate acid catalyst the synthetic precursor with suitably positioned hydroxyl and alkyne functional groups (alkynols) would undergo the activation of the hydroxyl group, which in turn initiate the tandem intramolecular cyclization to furnish dihydrobenzo[*a*]fluorenes. Thus, the novel tetracyclic products **9a−9ab/10a−10h** could be accomplished from alkynols **7a−7ab/8a−8h** in the presence of an acid, as outlined in Scheme 1.

Scheme 1. Anticipated Mode of Tandem Cyclization Path to Yield Tetracyclic Products 9a−9ab/10a−10h



The required starting material secondary alkynols **7a−7ac** have been readily achieved by adopting a two-pot synthesis, as depicted in Scheme 2. Thus, the secondary alcohols **4a−4m** were prepared using a sequential one-pot process *via* one-pot Heck coupling between allylic alcohols **1a−1j** and iodoarenes **2a−2c** and reduction sequence.[12f] Subsequently, an intermolecular Sonogashira coupling between secondary alcohols **4a−4m** and terminal aromatic acetylenes **6a−6i** afforded the required synthetic precursors alkynols **7a−7ac** (Scheme 2). On the other hand, the tertiary alkynol precursors **8a−8h** were synthesized by treating the simple Heck products (ketones **3a**, **3g**, and **3h**) with Grignard reagents (to give tertiary alcohols **5a−5f**) and then by intermolecular Sonogashira coupling of tertiary alcohols **5a−5f** with terminal acetylenes **6a**, **6d**, and **6f** (Scheme 2).

At the outset, we began our optimization studies with simple 1-phenyl-3-(2-(phenylethynyl)phenyl)propan-1-ol **7a** (62.4 mg, 0.2 mmol) for its conversion into the desired tetracyclic product **9a**. This, based on our previous experience with acid catalysis, led us to choose 1,2-DCE as solvents. Thus, initially, alkynol **7a** was treated with *p*-toluenesulfonic acid with varying quantities (50 mol % and 1 equiv) at 0 °C to room temperature. However, the product was formed in moderate and fair yields, respectively (Table 1, entries 1 and 2), while the starting material was decomposed with *p*-TSA at a temperature of 80 °C (Table 1, entry 3). Thus, switching to the Lewis acid ZnI_2 at ambient temperature furnished the desired tetracyclic product **9a**, but in very poor yield (Table 1, entry 4). A slightly elevated temperature of 50 °C gave a moderate yield of 34% of **9a** (Table 1, entry 5). The presence of Lewis acids $ZnCl_2/ZnBr_2$ at ambient temperature and 50 °C showed little improvement (Table 1, entries 6−9). Notably, the Lewis acid $FeCl_3$ at room temperature drove the reaction to give **9a** in 50% yield (Table 1, entry 10). Further improvement was noted with the same $FeCl_3$ catalyst at a slightly elevated temperature of 50 °C (Table 1, entry 11). In contrast, the hydrated $FeCl_3$ Lewis acid was found to be much inferior when compared with the anhydrous one (Table 1, entry 12). To our delight, when 50 mol % of $BF_3{\cdot}OEt_2$ (Table 1, entry 13) was used as the Lewis acid at 50 °C, the tetracyclic product **9a** was acquired in 65% yield. The reaction with a decreased loading of catalyst $BF_3{\cdot}OEt_2$ to 30 mol % and decreased temperature to 0 °C, gratifyingly, increased the yield of **9a** to 79% (Table 1, entry 14). However, the reaction became sluggish upon further decreasing the amount of the catalyst $BF_3{\cdot}OEt_2$ at room temperature (Table 1, entry 15). In contrast, the attempt with $AlCl_3$ was found to be inferior (Table 1, entries 16). Also, when the reaction was conducted with 20 and 40 mol % of $BF_3{\cdot}OEt_2$ under similar conditions of entry 14 at 0 °C to rt for 1 h, the product **9a** was observed in 52% and 60% yields, respectively (Table 1, entries 17 and 18), while a moderate yield of the product **9a** was observed when TfOH was used as the Bronsted acid at low temperature (Table 1, entry 19). The attempts to increase the yield were successful when $AgSbF_6$ was used as an additive under the standard conditions (entry 14) and obtained 81% **9a** (Table 1, entry 20).

Scheme 2. Synthesis of Alkynols 7a−7ac/8a−8h Starting from Allylic Alcohols 1a−1j and 1-Bromo-2-iodoarenes 2a−2c

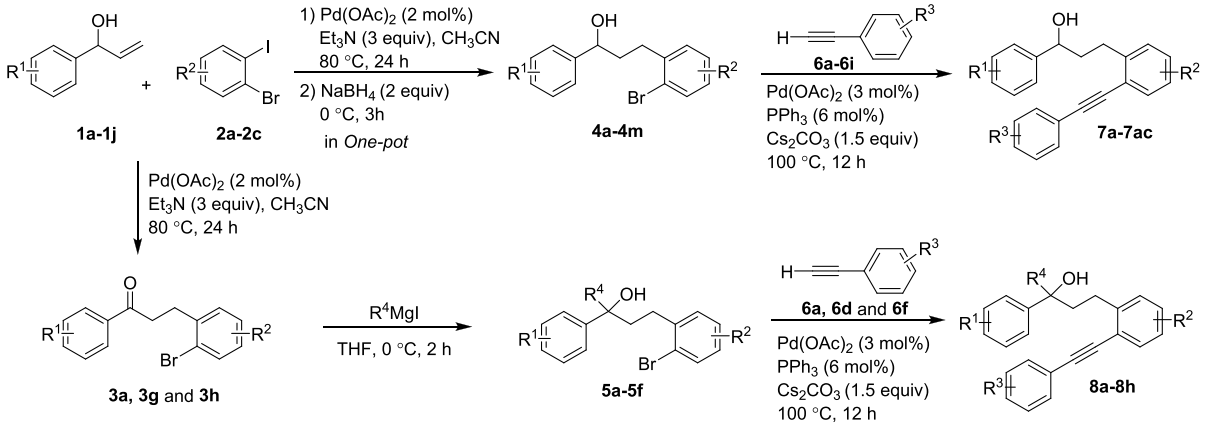


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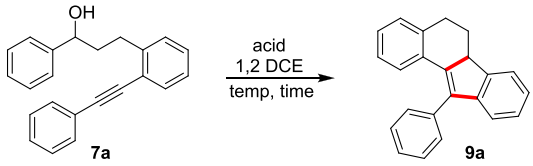
Table 1. Screening Conditions for the Formation of Tetracyclic Product 9a[a−c]



entry	acid catalyst	temp (°C)	time	yield **9a** (%)
1	*p*-TsOH (50 mol %)	0 to rt	12 h	42
2	*p*-TsOH (1 equiv)	rt	12 h	65
3	*p*-TsOH (1 equiv)	80	2 h	
4	ZnI_2 (50 mol %)	rt	6 h	18
5	ZnI_2 (50 mol %)	50	3 h	34
6	$ZnCl_2$ (50 mol %)	rt	6 h	38
7	$ZnCl_2$ (50 mol %)	50	3 h	48
8	$ZnBr_2$ (50 mol %)	rt	6 h	32
9	$ZnBr_2$ (50 mol %)	50	3 h	41
10	$FeCl_3$ (50 mol %)	rt	3 h	50
11	$FeCl_3$ (50 mol %)	50	3 h	61
12	$FeCl_3{\cdot}6H_2O$ (50 mol %)	rt	6 h	36
13	$BF_3{\cdot}OEt_2$ (50 mol %)	50	30 min	65
14	$BF_3{\cdot}OEt_2$ (30 mol %)	0 to rt	1 h	79
15	$BF_3{\cdot}OEt_2$ (10 mol %)	rt	3 h	62
16	$AlCl_3$ (50 mol %)	rt	10 min	
17	$BF_3{\cdot}OEt_2$ (20 mol %)	0 to rt	1 h	52
18	$BF_3{\cdot}OEt_2$ (40 mol %)	0 to rt	1 h	60
19	TfOH (30 mol %)	−10	50 min	62
20[c]	$BF_3{\cdot}OEt_2$ (30 mol %)	0 to rt	1 h	81

[a]Conditions to synthesize dihydrobenzo[*a*]fluorene: Reactions were conducted at ambient temperatures and 50 °C using 62.4 mg (0.20 mmol) of 1-phenyl-3-(2-(phenylethynyl)phenyl)propan-1-ol, in solvent 1,2 DCE (1 mL). [b]Yields in parentheses are isolated yields of the tetracyclic product **9a**. [c]$AgSbF_6$ (20 mol %) is used as additive.

Overall, out of all the reaction conditions screened, the conditions of entry 14 from Table 1 were good pertaining to the yield of dihydrobenzo[*a*]fluorene **9a**, where the Lewis acid $BF_3{\cdot}OEt_2$ was used as the sole acid catalyst. Thus, we set out to explore the scope and limitations of the present strategy on different precursors, in particular, with regard to various functional groups that are flanked all three aryl rings. First, we scrutinized the substrate scope concerning the arene ring derived from allylic alcohol (i.e., with R^1 functional moieties). As anticipated, the reaction is quite compatible with simple activating alkyl groups (Me, Et, and ^{i}Pr) placed at the *para*-position to the aromatic ring and gave the products **9b**, **9c**, and **9d** in 70%, 65%, and 68% yields, respectively (Table 2). In addition, the residence of strong electron-donating groups like dimethoxy and methylenedioxy functional groups facilitated the formation of the corresponding tetracyclic products **9e**−**9g** in fair to good yields (Table 2). Notably, the reaction was also amenable with electron-deactivating Cl and F substituents but witnessed a slight decrease in yields (**9h** and **9i**, Table 2). This is probably due to the electron-deactivating nature of Cl and F groups, which would impede the activation of the hydroxyl group that is in conjugation to that aromatic ring (i.e., as R^1). It is worth mentioning that the reaction with naphthalene as the R^1 substituent did not give the desired product; instead, it gave the isomerized product **9j′**. Overall, different R^1 substituents with electron-deactivating, simple electron-donating, and strong electron-donating properties enabled the formation of desired products smoothly. Encouraged by these results, we next turned our attention to checking the substrate scope on the alkyne-bearing ring (i.e., an aromatic ring with R^3 substituents). Consequently, simple functional groups such as Me- and Et-containing alkynyl arene ring synthetic precursors were amenable and afforded the products in fair to very good yields ranging from 64 to 80% (**9l**, **9o**, **9p**, **9t**, **9w**, and **9y**). On the other hand, alkynols possessing electron-donating alkoxy substituents on the arene ring originating from the terminal alkyne were also well-tolerated and gave the final products **9k**, **9m**, **9n**, **9q**, **9r**, **9u**, and **9x** as anticipated. The structure of **9m** was unambiguously confirmed by X-ray crystallography. However, in the case of *o*-anisyl alkyne, the product **9v** seemed to accompany its stereoisomer, which may be attributed to atropisomerism. In addition, the reaction is quite successful with electron-withdrawing fluoro (R^3) groups containing an arene alkyne and afforded the corresponding product **9s** in 68% of yield. It is worth mentioning that the reactions were unsuccessful with aliphatic alkyne and *p*-amino alkynes **9ac**. Furthermore, focus on the substituents of the arene ring originated from 1-bromo-2-iodoarene (i.e., R^2 group-containing aromatic ring). Notably, electron-donating OMe, as well as fluoro moieties holding precursors, were smoothly transformed into the corresponding tetracyclic products **9z**, **9aa**, and **9ab** in 79%, 68%, and 79% yields, respectively (Table 2).

Furthermore, it was speculated that the reaction would successful if alkyl or aryl groups are introduced as R^4 in the form of their tertiary alcohols or not. If the reaction becomes successful, dihydrobenzo[*a*]fluorenes will be obtained with a quaternary center. As shown above, the ketones **3a**, **3g**, and **3h** have been smoothly transformed into the tertiary alkynols **8a**−**8h** via the corresponding tertiary alcohols **5a**−**5f** by Grignard addition and Sonogashira couplings. Gratifyingly, the reaction of methyl and ethyl tertiary alcohols **8a**, **8b**, **8c**, **8e**, **8f**, **8g**, and **8h** was quite successful and delivered dihydrobenzo[*a*]-fluorenes with different R^1 and R^3 substituents (**10a**, **10b**, **10c**, **10e**, **10f**, **10g**, and **10h**) in yields ranging from 78 to 82% in 30 min as shown in Table 3. It is also worth mentioning that the reaction was amenable with aryl tertiary alcohol **8d** and furnished the product dihydrobenzo[*a*]fluorene **10d** in 79% yield (Table 3).

Further, to check the synthetic utility of the current method, the reaction was also conducted on a molar scale (1.35 mmol of **7a**) experiment for the synthesis of **9a**. As expected, **9a** was isolated in 63% yield as outlined in Scheme 3.

In conclusion, we have demonstrated a concise and efficient method for the synthesis of novel dihydrobenzo[*a*]fluorene via an intramolecular cascade cyclization. It was illustrated that mild Lewis acid $BF_3{\cdot}OEt_2$ was able to trigger the dual cyclization process and constructed two C−C bonds effectively. The strategy showed a broad substrate scope and quite successful in delivering a variety of dihydrobenzo[*a*]-fluorenes.

EXPERIMENTAL SECTION

General Methods. IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (hertz) are reported in standard fashion concerning either internal standard tetramethylsilane (TMS) (δ_H = 0.00 ppm) or $CDCl_3$ (δ_H = 7.25 ppm). $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer at rt in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CDCl_3$ [δ_C = 77.00 ppm (central line of the triplet)]. In the

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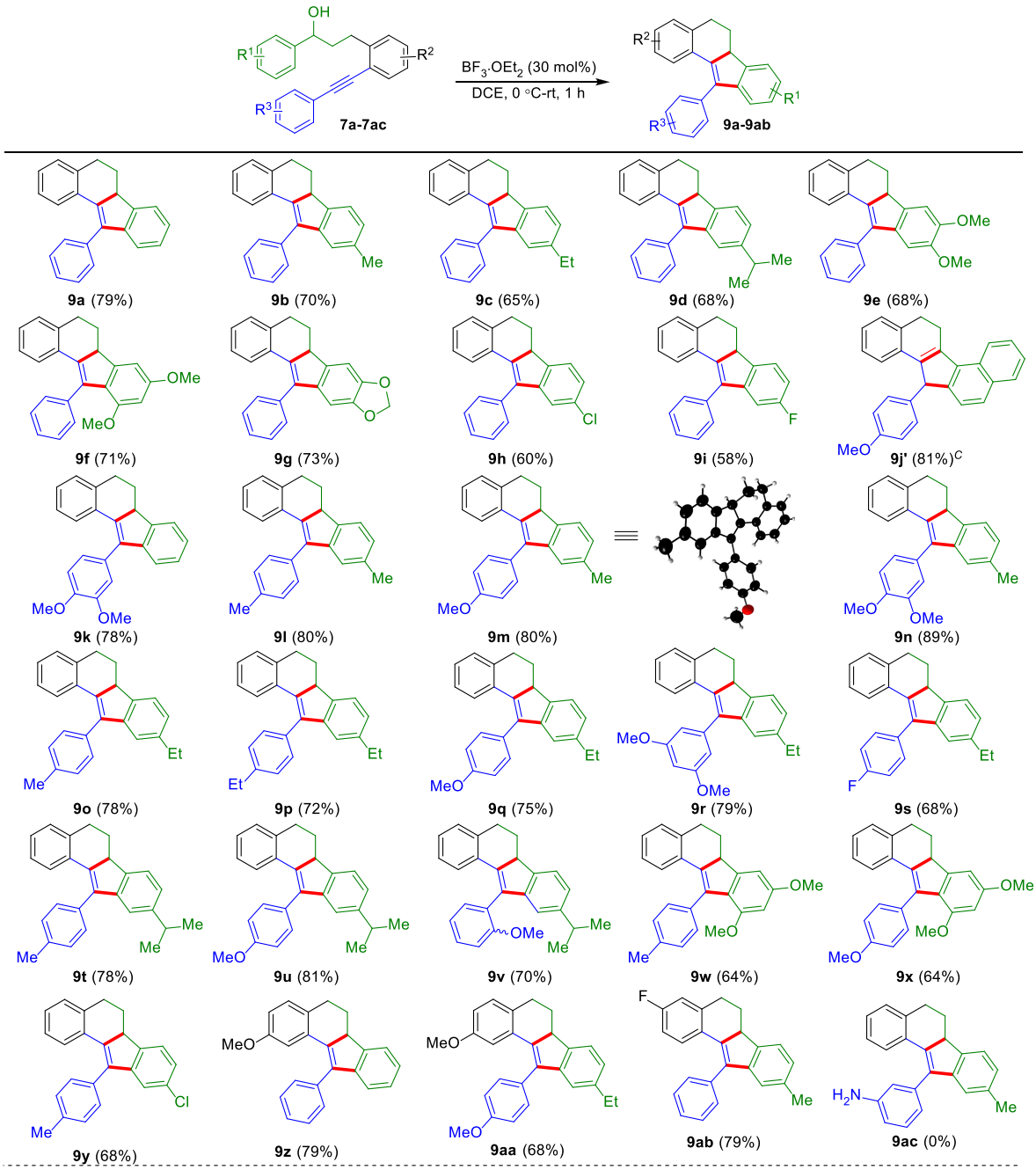
Table 2. Substrate Scope of Dihydrobenzo[*a*]fluorenes 9a–9ab[a,b]



[a]Reaction conditions: compound **7a–7ac** (0.2 mmol), $BF_3{\cdot}OEt_2$ (30 mol %), DCE (1 mL), 0 °C to rt, 1 h. [b]Isolated yields of the products **9a–9ab**. [c]Double bond is isomerized product **9j′** was obtained.

$^{13}C\{^1H\}$ NMR, the nature of carbons (C, CH, CH_2, and CH_3) was determined by recording the DEPT-135 spectra and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2), and q = quartet (for CH_3). In the ^1H NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sept = septet, dd = doublet of doublet, m = multiplet, and br s = broad singlet. The assignment of signals was confirmed by ^1H, $^{13}C\{^1H\}$ CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. All small-scale reactions were carried out using a Schlenk tube. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Solvents were distilled before use; petroleum ether with a boiling range of 60–80 °C was used. $Pd(OAc)_2$, cesium carbonate, triphenylphosphine (TPP), sodium borohydride, and $BF_3{\cdot}OEt_2$ (48–50% essay) were purchased from Sigma-Aldrich and used as received. Substituted benzaldehydes, vinyl magnesium bromide in THF, 1-alkynes, and triethylamine were purchased from Sigma/TCI/local. Solvent THF was dried over sodium metal, whereas DMF was dried over calcium hydride. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per 1 g of crude material).

General Procedure 1 (GP-1): Preparation of 3-(2-Bromophenyl)-1-phenylpropan-1-ols) 4a–4m. To an oven-dried Schlenk tube under nitrogen atmosphere were added allylic alcohol **1a–1j** (134–194 mg, 1 mmol), 1-iodo-2-bromoarene **2a–2c** (346–382 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), and triethylamine

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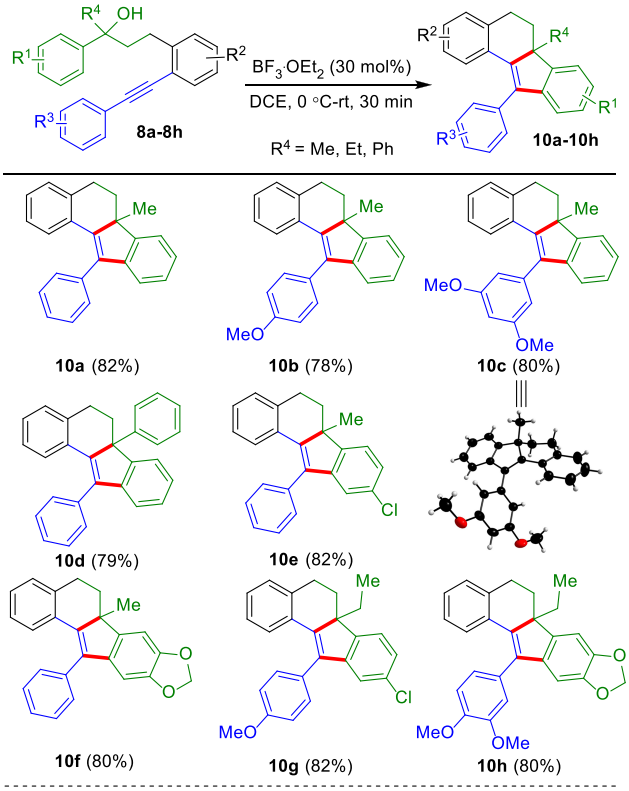
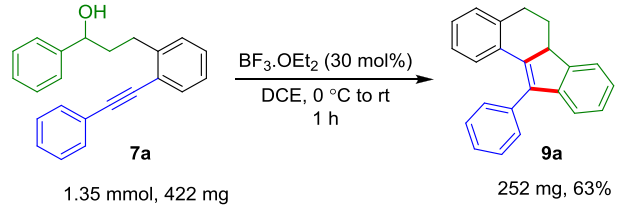
Table 3. Synthesis of Dihydrobenzo[*a*]fluorenes with a Quaternary Center[a,b]



[a]Reaction conditions: compound **8a−8h** (0.2 mmol), $BF_3{\cdot}OEt_2$ (30 mol %), DCE (1 mL), room temperature, 30 min. [b]Isolated yields of tetracyclic products **10a−10h**.

Scheme 3. Scale-up Experiment on 9a



(303 mg, 3 equiv) followed by dry acetonitrile (2 mL). The resulting reaction mixture was stirred at 80 °C for 24 h. The progress of the reaction was monitored by TLC until the reaction was completed. To the cooled reaction mixture at 0 °C was added $NaBH_4$ (2.0 mmol), and the reaction mixture was stirred at room temperature for 3 h, with completion of the reduction monitored by TLC. Then the mixture was quenched by the addition of an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the alcohols **4a−4m** (65−84%) as a viscous liquid.

General Procedure 2 (GP-2): Preparation of Tertiary Alcohols 5a−5f. To the ketone **3a**, **3g**, and **3h** (224−249 mg, 0.75 mmol) in a round-bottomed flask in dry diethyl ether or dry THF (10 mL) at 0 °C was added freshly prepared alkyl magnesium iodide or arylmagnesium bromide (2.25 mmol) [alkyl/arylmagnesium halide (bromide or iodide) was prepared from magnesium (45 mg, 1.8 mmol), alkyl halide (142−158 mg, 1.8 mmol), and a catalytic amount of iodine in 8 mL of dry ether]. The reaction mixture was stirred at 0 °C for 4 h. Progress of the reaction was monitored by TLC. It was then quenched with saturated aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 30 mL). The organic layers were washed with saturated NaCl solution, dried over Na_2SO_4, and filtered. Evaporation of the solvent and purification of the residue over a silica gel column using petroleum ether/ethyl acetate as eluent furnished the tertiary alcohols **5a−5f** (85−93%).

General Procedure 3 (GP-3): Preparation of Alkynols (7a−7ac). The appropriate arylacetylene **6a−6i** (1.5 equiv) was added to a solution of bromo-secondary/bromo-tertiary alcohol **4a−4m** (0.3 mmol), Cs_2CO_3 (1.5 equiv), $Pd(OAc)_2$ (0.03 mmol, 3 mol %), and triphenylphosphine (0.06 mmol, 6 mol %) in DMF (2 mL). The resulting mixture was heated in a 100 °C oil bath with rapid stirring until bromo-secondary alcohol was consumed as determined by TLC. The crude mixture was partitioned between water and ethyl acetate (3 × 30 mL). The organic layers were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered, and the solvents were removed under reduced pressure. Purification of the residue over silica gel column using petroleum ether/ethyl acetate as eluent furnished the corresponding alkynols **7a−7ac**/**8a−8h** (68−89%).

General Procedure 4 (GP-4): Synthesis of Dihydrobenzo-[*a*]fluorenes (9a−9ab/10a−10h). To a cold solution (0 °C) of secondary/tertiary alkynols **7a−7ab**/**8a−8h** (62.4 mg to 88.8 mg, 0.2 mmol) in a Schlenk tube in dry DCE (2 mL) was added $BF_3{\cdot}OEt_2$ (30 mol %) and the reaction mixture stirred at 0 °C to room temperature. Completion of the reaction was monitored by TLC (2:98 ethyl acetate and hexane) for 1−3 h. The reaction mixture was quenched with aqueous ammonium chloride and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with brine, dried over (Na_2SO_4), and evaporated under reduced pressure. Purification of the crude residue by column chromatography on silica gel (100−200 mesh) by using a hexane/ethyl acetate solvent system as eluent afforded the cyclized product **9a−9ab**/**10a−10h** (58−82%).

3-(2-Bromophenyl)-1-(4-chlorophenyl)propan-1-one (3h). GP-1 (GP-1 was carried out until ketone stage without further performing the reduction sequence) was carried out with allylic alcohol **1h** (168 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv), and dry acetonitrile (2 mL) at 80 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 98:1 to 99:2) furnished the ketone **3h** (245.5 mg, 76%) as a viscous liquid. TLC (petroleum ether/ethyl acetate 98:2, R_f(**1h**) = 0.2, R_f(**3h**) = 0.75, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3092, 3020, 2842, 1680, 1063, 951, 881, 567 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.75−7.72 (m, 2H, ArH), 7.37 (m, 1H, ArH), 7.26−7.24 (m, 2H, ArH), 7.13 (dd, J = 7.6 and 1.7 Hz, 1H, ArH), 7.07 (ddd, J = 8.8, 6.3, and 2.5 Hz, 1H, ArH), 6.93−6.89 (m, 1H, Ar-H), 3.12−3.09 (m, 2H, CH_2), 3.02−2.99 (m, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 197.6, 140.3, 137.3, 139.5, 134.9, 132.8, 130.7, 129.5 (2 × CH), 128.9 (2 × CH), 128.0, 126.6, 124.3, 38.5, 30.6 ppm.

3-(2-Bromophenyl)-1-(*p*-tolyl)propan-1-ol (4b). GP-1 was carried out with allylic alcohol **1b** (148 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv), and dry acetonitrile (2 mL) at 80 °C for 24 h and subsequently with $NaBH_4$ (75.6 mg, 2.0 mmol) at room temperature for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished the alcohol **4b** (231.5 mg, 76%) as a viscous liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**1b**) = 0.45, R_f(**4b**) = 0.35, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3334, 3064, 2968, 1642, 1463, 1371, 1268, 1085, 938, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.53 (d, J = 7.9 Hz, 1H, ArH), 7.30−7.24 (m, 2H, ArH), 7.23 (d, J = 4.2 Hz, 2H, ArH), 7.17 (d, J = 7.9 Hz, 2H, ArH), 7.10−7.02 (m, 1H, ArH), 4.69 (dd, J = 7.6 and 5.5 Hz, 1H, ArC*H*(OH)), 2.89 (ddd, J = 13.9, 10.1, and 5.6 Hz, 1H, CH), 2.76 (ddd, J = 13.7, 9.9, and 6.5 Hz, 1H, CH), 2.36 (s, 3H, ArCH_3), 2.19−1.94 (m, 3H, CH_2 and OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 141.3, 141.1, 137.3, 132.8, 130.4, 129.1 (2 × CH), 127.5, 127.4, 125.9 (2 × CH), 124.4, 73.7, 38.7, 32.6, 21.1 ppm. HRMS (ESI) m/z:

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J. Org. Chem. 2021, 86, 8706−8725

$[M + K]^+$ calcd for $C_{16}H_{17}Br^{79}KO$ 343.0094; Found 343.0092; $[M + K]^+$ calcd for $C_{16}H_{17}Br^{81}KO$ 345.0074; Found 345.0075.

3-(2-Bromophenyl)-1-(4-ethylphenyl)propan-1-ol (4c). GP-1 was carried out with allylic alcohol **1c** (162 mg, 1.0 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv), and dry acetonitrile (2 mL) at 80 °C for 24 h and subsequently with $NaBH_4$ (75.6 mg, 2.0 mmol) at room temperature for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished the alcohol **4c** (257.6 mg, 81%) as a viscous liquid. TLC control (petroleum ether/ethyl acetate 90:10), R_f(**1c**) = 0.45, R_f(**4c**) = 0.35, UV detection. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3382, 2930, 2963, 1455, 1471, 1046, 1022, 832 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.52 (d, J = 7.7 Hz, 1H, ArH), 7.31−7.29 (m, 2H, ArH), 7.24−7.16 (m, 4H, ArH), 7.07−7.03 (m, 1H, ArH), 4.70 (t, J = 5.5 Hz, 1H, ArC*H*(OH)), 2.94−2.87 (m, 1H, CH), 2.81−2.74 (m, 1H, CH), 2.65 (q, J = 7.6 Hz, 2H, CH_2CH_3), 2.13−2.01 (m, 2H, CH_2), 1.89 (s, 1H, OH), 1.24 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 143.8, 141.6, 141.2, 132.8, 130.4, 128.0 (2 × CH), 127.6, 127.4, 125.9 (2 × CH), 124.4, 73.8, 38.7, 32.6, 28.5, 15.6 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ calcd for $C_{17}H_{18}Br^{79}$ 301.0586; Found 301.0576; $[(M + H) + (-H_2O)]^+$ calcd for $C_{17}H_{18}Br^{81}$ 303.0566; Found 303.0557.

3-(2-Bromophenyl)-1-(4-isopropylphenyl)propan-1-ol (4d). GP-1 was carried out with allylic alcohol **1d** (176 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (212.1 mg, 3 equiv), and dry acetonitrile (2 mL) at 80 °C for 24 h and subsequently with $NaBH_4$ (75.6 mg, 2.0 mmol) at room temperature for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished the alcohol **4d** (270.5 mg, 78%) as a viscous liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**1d**) = 0.45, R_f(**4d**) = 0.35, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3385, 3017, 2957, 2874, 1636, 1511, 1454, 1030, 921, 833, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.49 (d, J = 8.0 Hz, 1H, ArH), 7.31−7.24 (m, 2H, ArH), 7.24−7.15 (m, 4H, ArH), 7.05−6.99 (m, 1H, ArH), 4.67−4.64 (m, 1H, ArC*H*(OH)), 2.96−2.83 (m, 2H, CH_2), 2.75 (ddd, J = 13.7, 9.7, and 6.6 Hz, 1H, Ar*CH*$(CH_3)_2$), 2.12−1.95 (m, 3H, CH_2 and OH), 1.24 (d, J = 5.8 Hz, 6H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 148.3, 141.8, 141.2, 132.7, 130.3, 127.5, 127.3, 126.5 (2 × CH), 125.9 (2 × CH), 124.4, 73.7, 38.7, 33.8, 32.7, 24.0 (2 × CH_3) ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ calcd for $C_{18}H_{20}Br^{79}$ 315.0743; Found 315.0745; $[(M + H) + (-H_2O)]^+$ calcd for $C_{18}H_{20}Br^{81}$ 317.0743; Found 317.0726.

3-(2-Bromophenyl)-1-(3,5-dimethoxyphenyl)propan-1-ol (4f). GP-1 was carried out with allylic alcohol **1f** (194.1 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv), and dry acetonitrile (2 mL) at 80 °C for 24 h and subsequently with $NaBH_4$ (75.6 mg, 2.0 mmol) at room temperature for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 85:15 to 80:20) furnished the alcohol **4f** (280.3 mg, 80%) as a viscous liquid. TLC (petroleum ether/ethyl acetate 80:20, R_f(**1f**) = 0.50, R_f(**4f**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3421, 3000, 2935, 2837, 1595, 1469, 1428, 1203, 1152, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.52 (d, J = 7.7 Hz, 1H, ArH), 7.25−7.18 (m, 2H, ArH), 7.05 (ddd, J = 8.0 Hz, 5.7 and 3.4 Hz, 1H, ArH), 6.54 (d, J = 2.2 Hz, 2H, ArH), 6.37 (t, J = 7.3 Hz, 1H, ArH), 4.67 (dd, J = 7.4 and 5.6 Hz, 1H, ArC*H*(OH)), 3.80 (s, 6H, 2 × $ArOCH_3$), 2.93−2.86 (m, 1H, CH), 2.82−2.75 (m, 1H, CH), 2.08−2.01 (m, 3H, CH_2 and OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 160.8 (2 × C), 146.9, 141.1, 132.8, 130.4, 127.6, 127.4, 124.3, 103.7 (2 × CH), 99.6, 73.9, 55.4 (2 × OCH_3), 38.7, 32.5 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ calcd for $C_{17}H_{18}Br^{79}O_2$ 333.0484; Found 333.0485; $[(M + H) + (-H_2O)]^+$ calcd for $C_{17}H_{18}Br^{81}O_2$ 335.0464; Found 335.0468.

3-(2-Bromophenyl)-1-(4-chlorophenyl)propan-1-ol (4h). GP-1 was carried out with allylic alcohol **1h** (168.0 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303.0 mg, 3 equiv), and dry acetonitrile (2 mL) at 80 °C for 24 h and subsequently with $NaBH_4$ (75.6 mg, 2.0 mmol) at room temperature for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished the alcohol **4h** (220.2 mg, 68%) as a viscous liquid. TLC control (petroleum ether/ethyl acetate 90:10), R_f(**1h**) = 0.45, R_f(**4h**) = 0.35, UV detection. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3382, 3010, 2963, 1606, 1471, 1046, 1022, 832, 750 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.56−7.49 (m, 1H, ArH), 7.34−7.24 (m, 4H, ArH), 7.24−7.18 (m, 2H, ArH), 7.06 (ddd, J = 8.0 Hz, 6.3 and 2.8 Hz, 1H, ArH), 4.70 (dd, J = 7.5 and 5.5 Hz, 1H, ArC*H*(OH)), 2.96−2.79 (m, 1H, CH), 2.79−2.63 (m, 1H, CH), 2.16 (s, 1H, OH), 2.07−1.91 (m, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 142.7, 140.8, 133.2, 132.8, 130.3, 128.6 (2 × CH), 127.7, 127.5, 127.2 (2 × CH), 124.3, 73.1, 38.8, 32.4 ppm. HRMS (ESI) m/z: $[(M + NH_4) + (-H_2O)]^+$ calcd for $C_{15}H_{16}Br^{79}ClN$ 324.0149; Found 324.0139; $[(M+NH_4)+ (-H_2O)]^+$ calcd for $C_{15}H_{16}Br^{81}ClN$ 326.0128; Found 326.0117.

3-(2-Bromophenyl)-1-(4-fluorophenyl)propan-1-ol (4i). GP-1 was carried out with allylic alcohol **1i** (152.1 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv), and dry acetonitrile (2 mL) at 80 °C for 24 h and subsequently with $NaBH_4$ (75.6 mg, 2.0 mmol) at room temperature for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished the alcohol **4i** (200.2 mg, 65%) as yellow viscous liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**1i**) = 0.45, R_f(**4i**) = 0.40, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3351, 3061, 2932, 2869, 1653, 1604, 1508, 1223, 1020, 834, 750, 703 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.55−7.50 (m, 1H, ArH), 7.37−7.31 (m, 2H, ArH), 7.24−7.20 (m, 2H, ArH), 7.11−6.96 (m, 3H, ArH), 4.81−4.60 (m, 1H, ArC*H*(OH)), 2.88 (ddd, J = 13.7, 10.1, and 5.6 Hz, 1H, CH), 2.75 (ddd, J = 13.7, 9.8, and 6.5 Hz, 1H, CH), 2.15−1.93 (m, 3H, CH_2 and O*H*) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.3 (J_{C-F} = 244 Hz), 141.9, 140.1 (J_{C-F} = 3 Hz), 132.9, 130.4, 127.5, 127.6, 127.5 (J_{C-F} = 2 Hz, 2 × CH), 124.4, 115.3 (J_{C-F} = 21 Hz, 2 × CH), 73.3, 39.0, 32.5 ppm. HRMS (ESI) m/z: $[(M+NH_4)+ (-H_2O)]^+$ calcd for $C_{15}H_{16}Br^{79}NF$ 308.0444; Found 308.0449; $[(M + NH_4) + (-H_2O)]^+$ calcd for $C_{15}H_{16}Br^{81}NF$ 310.0424; Found 310.0406.

3-(2-Bromophenyl)-1-(naphthalen-1-yl) propan-1-ol (4j). GP-1 was carried out with allylic alcohol **1j** (184.1 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv), and dry acetonitrile (2 mL) at 80 °C for 24 h and subsequently with $NaBH_4$ (75.6 mg, 2.0 mmol) at room temperature for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 88:12) furnished the alcohol **4j** (248.2 mg, 73%) as a yellow viscous liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**1j**) = 0.55, R_f(**4j**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3386, 3056, 2928, 2862, 1597, 1510, 1456, 1385, 1025, 778 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.97 (dt, J = 6.8 and 3.4 Hz, 1H, ArH), 7.91−7.84 (m, 1H, ArH), 7.78 (d, J = 8.2 Hz, 1H, ArH), 7.70 (d, J = 7.1 Hz, 1H, ArH), 7.55 (dd, J = 8.0 and 1.1 Hz, 1H, ArH), 7.50−7.45 (dt, J = 7.1 and 2.8 Hz, 3H, ArH), 7.26−7.23 (m, 2H, ArH), 7.07 (ddd, J = 7.9, 7.2, and 2.1 Hz, 1H, ArH), 5.51 (dd, J = 8.6 and 3.8 Hz, 1H, ArC*H*(OH)), 3.11−2.91 (m, 2H, CH_2), 2.37−2.23 (m, 1H, CH), 2.23−2.11 (m, 1H, CH), 2.04 (d, J = 6.1 Hz, 1H, ArCH(O*H*)) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 141.1, 140.1, 133.8, 132.8, 130.5, 130.3, 128.9, 128.0, 127.7, 127.4, 126.0, 125.5, 125.4, 124.5, 123.0, 122.7, 70.5, 38.2, 33.0 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ calcd for $C_{19}H_{16}Br^{79}$ 323.0430; Found 323.0430; $[(M + H) + (-H_2O)]^+$ calcd for $C_{19}H_{16}Br^{81}$ 325.0430; Found 325.0411.

3-(2-Bromo-4-methoxyphenyl)-1-phenylpropan-1-ol (4k). GP-1 was carried out with allylic alcohol **1k** (134.1 mg, 1 mmol), 2-bromo-1-iodo-4-methoxybenzene **2b** (382.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv), and dry acetonitrile (2 mL) at 80 °C for 24 h and subsequently with $NaBH_4$ (75.6 mg, 2.0 mmol) at room temperature for 3 h. Purification

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J. Org. Chem. 2021, 86, 8706−8725

of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 85:15) furnished the alcohol **4k** (249.6 mg, 78%) as a viscous liquid. TLC control (petroleum ether/ethyl acetate 85:15), R_f(**1k**) = 0.55, R_f(**4k**) = 0.45, UV detection. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3374, 2922, 1604, 1578, 1469, 1234, 1028, 816 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.40−7.32 (m, 4H, ArH), 7.29−7.27 (m, 1H, ArH), 7.13 (d, J = 8.5 Hz, 1H, ArH), 7.09 (d, J = 2.6 Hz, 1H, ArH), 6.79 (dd, J = 8.5 and 2.6 Hz, 1H, ArH), 4.71 (t, J = 6.4 Hz, 1H, ArC*H*(OH)), 3.77 (s, 3H, $ArOCH_3$), 2.85−2.79 (m, 1H, CH), 2.77−2.65 (m, 1H, CH), 2.12−1.94 (m, 3H, CH_2 and OH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 158.3, 144.4, 133.0, 130.6, 128.5 (2 × CH), 127.6, 125.9 (2 × CH), 124.5, 117.9, 113.6, 73.9, 55.5, 39.1, 31.6 ppm. HRMS (ESI) m/z: $[(M+NH_4)+(-H_2O)]^+$ calcd for $C_{16}H_{19}Br^{79}NO$ 320.0644; Found 320.0637; $[(M + NH_4) + (-H_2O)]^+$ calcd for $C_{16}H_{19}Br^{81}NO$ 322.0624; Found 322.0617.

3-(2-Bromo-4-methoxyphenyl)-1-(4-ethylphenyl)propan-1-ol (4l). GP-1 was carried out with allylic alcohol **1c** (162.2 mg, 1 mmol), 2-bromo-1-iodo-4-methoxybenzene **2b** (382.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv), and dry acetonitrile (2 mL) at 80 °C for 24 h and subsequently with $NaBH_4$ (75.6 mg, 2.0 mmol) at room temperature for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 85:15) furnished the alcohol **4l** (281.9 mg, 81%) as a viscous liquid. TLC (petroleum ether/ethyl acetate 85:15, R_f(**1c**) = 0.50, R_f(**4l**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3382, 2906, 2809, 1581, 1446, 1456, 1415, 1187, 1138 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.32−7.26 (dd, J = 8.6 and 6.9 Hz, 2H, ArH), 7.19 (d, J = 8.1 Hz, 2H, ArH), 7.13 (d, J = 8.5 Hz, 1H, ArH), 7.08 (d, J = 2.6 Hz, 1H, ArH), 6.78 (dd, J = 8.5 and 2.6 Hz, 1H, ArH), 4.68 (dd, J = 7.8 and 5.4 Hz, 1H, ArC*H*(OH)), 3.77 (s, 3H, $ArOCH_3$), 2.83 (ddd, J = 14.0, 9.9, and 5.6 Hz, 1H, CH), 2.75−2.62 (m, 3H, CH, $ArCH_2CH_3$), 2.14−2.00 (m, 2H, CH_2), 1.95 (br.s, 1H, O*H*), 1.30 (t, J = 7.6 Hz, 3H, $ArCH_2CH_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 158.3, 143.7, 141.7, 133.1, 130.7, 128.0 (2 × CH), 126.0 (2 × CH), 124.5, 117.9, 113.6, 73.7, 55.5, 39.0, 31.7, 28.6, 15.6 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ calcd for $C_{18}H_{20}Br^{79}O$ 331.0692; Found 331.0679; $[(M + H) + (-H_2O)]^+$ calcd for $C_{18}H_{20}Br^{81}O$ 333.0671; Found 333.0662.

3-(2-Bromo-5-fluorophenyl)-1-(*p*-tolyl)propan-1-ol (4m). GP-1 was carried out with allylic alcohol **1b** (150 mg, 1 mmol), 1-bromo-4-fluoro-2-iodobenzene **2c** (382.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv), and dry acetonitrile (2 mL) at 80 °C for 24 h and subsequently with $NaBH_4$ (75.6 mg, 2.0 mmol) at room temperature for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished the alcohol **4m** (257.6 mg, 80%) as a viscous liquid. TLC control (petroleum ether/ethyl acetate 90:10), R_f(**1b**) = 0.45, R_f(**4m**) = 0.35, UV detection. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3430, 2924, 1607, 1597, 1457, 1470, 1155, 1061, 751 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.32 (m, 1H, ArH), 7.11 (d, J = 8.1 Hz, 2H, ArH), 7.03 (d, J = 8.0 Hz, 2H, ArH), 6.81 (dd, J = 9.4 and 3.0 Hz, 1H, ArH), 6.65 (td, J = 8.5 and 3.0 Hz, 1H, ArH), 4.52 (dd, J = 7.6 and 5.5 Hz, 1H, ArC*H*(OH)), 2.78−2.66 (m, 1H, CH), 2.61−2.54 (m, 1H, CH), 2.22−2.10 (m, 4H, $ArCH_3$, OH), 1.97−1.83 (m, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 162.0 (J_{C-F} = 245 Hz), 143.4 (J_{C-F} = 7 Hz), 141.3, 137.5, 133.8 (J = 9 Hz), 129.3 (2 × CH), 125.9 (2 × CH), 118.5 (J = 3 Hz), 117.2 (J = 23 Hz), 114.7 (J = 22 Hz), 73.7, 38.4, 32.7, 21.2 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ calcd for $C_{16}H_{15}Br^{79}F$ 305.0335; Found 305.0324; $[(M + H) + (-H_2O)]^+$ calcd for $C_{16}H_{15}Br^{81}F$ 307.0315; Found 307.0305.

4-(2-Bromophenyl)-2-phenylbutan-2-ol (5a). GP-2 was carried out with ketone **3a** (288.1 mg, 1 mmol), MeMgI [prepared from Mg (48, 2.0 mmol), MeI (300 mg, 2.0 mmol), and dry diethyl ether (10 mL)] in diethyl ether (2 mL) at 0 °C for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished the alcohol **5a** (270.6 mg, 89%) as a viscous liquid. TLC control (petroleum ether/ethyl acetate 93:07), R_f(**3a**) = 0.85, R_f(**5a**) = 0.55, UV detection. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3529, 3026, 2939, 2898, 1429, 1358, 1330, 1251, 1115, 928, 879 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.54−7.46 (m, 3H, ArH), 7.40−7.33 (m, 2H, ArH), 7.29−7.23 (m, 1H, ArH), 7.20−7.15 (m, 1H, ArH), 7.13 (dd, J = 7.6 Hz, 1.9 Hz, 1H, CH), 7.05−6.97 (m, 1H, ArH), 2.80−2.72 (m, 1H, CH), 2.60−2.52 (m, 1H, CH), 2.17−2.06 (m, 2H, CH_2), 1.85 (s, 1H, OH), 1.63 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 147.3, 141.6, 132.7, 130.3, 128.2 (2 × CH), 127.5, 127.5, 126.7, 124.8 (2 × CH), 124.3, 74.6, 44.3, 31.1, 30.3 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ calcd for $C_{16}H_{16}Br^{79}$ 287.0430; Found 287.0431; $[(M + H) + (-H_2O)]^+$ calcd for $C_{16}H_{16}Br^{81}$ 289.0409; Found 289.0411.

3-(2-Bromophenyl)-1,1-diphenylpropan-1-ol (5b). GP-2 was carried out with ketone **3a** (288.1 mg, 1 mmol) and PhMgBr [prepared from Mg (48, 2.0 mmol), PhBr (312 mg, 2.0 mmol), and dry diethyl ether (10 mL)] in diethyl ether (2 mL) at 0 °C for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished the alcohol **5b** (311.1 mg, 85%) as a viscous liquid. TLC control (petroleum ether/ethyl acetate 95:05), R_f(**3a**) = 0.8, R_f(**5b**) = 0.45, UV detection. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3385, 2921, 1596, 1580, 1497, 1273, 1227, 1067, 959, 818, 755 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.53−7.46 (m, 5H, ArH), 7.36−7.30 (m, 4H, ArH), 7.27−7.20 (m, 3H, ArH), 7.19−7.14 (m, 1H, ArH), 7.07−7.00 (m, 1H, CH), 2.78−2.68 (m, 2H, CH_2), 2.62−2.53 (m, 2H, CH_2), 2.23 (s, 1H, OH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 146.6 (2 × C), 141.7, 132.8, 130.5, 128.2 (4 × CH), 127.6, 127.5, 127.0 (2 × CH), 126.9, 126.0 (3 × CH), 124.3, 78.0, 42.3, 30.9 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ calcd for $C_{21}H_{18}Br^{79}$ 349.0586; Found 349.0575; $[(M + H) + (-H_2O)]^+$ calcd for $C_{21}H_{18}Br^{81}$ 351.0566; Found 351.0556.

4-(2-Bromophenyl)-2-(4-chlorophenyl)butan-2-ol (5c). GP-2 was carried out with ketone **3h** (321 mg, 1 mmol) and MeMgI [prepared from Mg (48, 2.0 mmol), MeI (312 mg, 2.0 mmol), and dry diethyl ether (10 mL)] in diethyl ether (2 mL) at 0 °C for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished the alcohol **5c** (304.2 mg, 90%) as a viscous liquid. TLC control (petroleum ether/ethyl acetate 95:05), R_f(**3h**) = 0.80, R_f(**5c**) = 0.45, UV detection. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3434, 2972, 1595, 1566, 1488, 1470, 1170, 1093, 930, 888, 832 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.49 (dd, J = 8.0 and 1.2 Hz, 1H, ArH), 7.46−7.42 (m, 2H, ArH), 7.36−7.31 (m, 2H, ArH), 7.19 (td, J = 7.4 and 1.2 Hz, 1H, ArH), 7.13 (dd, J = 7.6 and 1.8 Hz, 1H, ArH), 7.07−6.98 (m, 1H, ArH), 2.78−2.66 (m, 1H, CH), 2.61−2.54 (m, 1H, CH), 2.12−2.04 (m, 2H, CH_2), 1.82 (s, 1H, OH), 1.62 (s, 3H, $ArCH_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 145.9, 141.3, 132.8, 132.5, 130.3, 128.3 (2 × CH), 127.6, 127.5, 126.4 (2 × CH), 124.3, 74.3, 44.2, 31.0, 30.5 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ calcd for $C_{16}H_{15}Br^{79}Cl$ 321.0040; Found 321.0025; $[(M + H) + (-H_2O)]^+$ calcd for $C_{16}H_{15}Br^{81}Cl$ 323.0019; Found 323.0004.

2-(Benzo[*d*][1,3]dioxol-5-yl)-4-(2-bromophenyl)butan-2-ol (5d). GP-2 was carried out with ketone **3g** (332.2 mg, 1 mmol) and MeMgI [prepared from Mg (48, 2.0 mmol), MeI (312 mg, 2.0 mmol), and dry diethyl ether (10 mL)] in diethyl ether (2 mL) at 0 °C for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished the alcohol **5g** (306.2 mg, 88%) as a viscous liquid. TLC control (petroleum ether/ethyl acetate 90:10), R_f(**3g**) = 0.80, R_f(**5g**) = 0.65, UV detection. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3386, 2905, 1585, 1551, 1480, 1436, 1305, 1264, 1176, 847, 812 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.49 (dd, J = 8.0 and 1.2 Hz, 1H, ArH), 7.26−7.14 (m, 2H, ArH), 7.06−7.03 (m, 2H, ArH), 6.97 (d, J = 8.1 and 1.9 Hz, 1H, ArH), 6.80 (d, J = 8.1 Hz, 1H, ArH), 6.00−5.91(m, 2H, $-OCH_2O-$), 2.78−2.68 (m, 1H, CH), 2.62−2.54 (m, 1H, CH), 2.11−1.98 (m, 2H, CH_2), 1.87 (s, 1H, OH), 1.61 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 147.5, 146.2, 141.6, 141.5, 132.7, 130.3, 127.5 (2 × CH), 124.3, 117.9, 107.8, 105.9, 100.9, 74.5, 44.3, 31.1, 30.4 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ calcd for $C_{17}H_{16}Br^{79}O_2$ 331.0328; Found 331.0276; [(M

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J. Org. Chem. 2021, 86, 8706−8725

+ H) + (−H_2O)]$^+$ calcd for $C_{17}H_{16}Br^{81}O_2$ 333.0307; Found 333.0255.

1-(2-Bromophenyl)-3-(4-chlorophenyl)pentan-3-ol (5e). GP-2 was carried out with ketone **3h** (321 mg, 1 mmol) and EtMgI [prepared from Mg (48, 2.0 mmol), CH_2CH_3I (312 mg, 2.0 mmol), and dry diethyl ether (10 mL)] in diethyl ether (2 mL) at 0 °C for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished the alcohol **5e** (327.4 mg, 93%) as a viscous liquid. TLC control (petroleum ether/ethyl acetate 95:05), R_f(**3h**) = 0.80, R_f(**5e**) = 0.55, UV detection. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3468, 3056, 2878, 1566, 1470, 1093, 1012, 1024, 1094, 827, 753 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.49 (dd, J = 8.0 and 1.2 Hz, 1H, ArH), 7.43−7.38 (m, 2H, ArH), 7.37−7.31 (m, 2H, ArH), 7.21−7.16 (m, 1H, ArH), 7.12 (dd, J = 7.6 and 1.8 Hz, 1H, ArH), 7.07−6.98 (m, 1H, ArH), 2.80−2.73 (m, 1H, CH), 2.47−2.40 (m, 1H, CH), 2.12−2.01 (m, 2H, CH_2), 1.92−1.82 (m, 2H, CH_2) 1.76 (s, 1H, OH), 0.78 (s, 3H, CH_2CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 143.8, 141.5, 132.8, 132.3, 130.3, 128.2 (2 × CH), 127.6, 127.5, 126.9 (2 × CH), 124.3, 76.9, 42.9, 35.7, 31.0, 7.6 ppm. HRMS (ESI) m/z: [(M + H) + (−H_2O)]$^+$ calcd for $C_{17}H_{17}Br^{79}Cl$ 335.0196; Found 335.0181; [(M + H) + (−H_2O)]$^+$ calcd for $C_{17}H_{17}Br^{81}Cl$ 337.0176; Found 337.0161.

3-(Benzo[*d*][1,3]dioxol-5-yl)-1-(2-(phenylethynyl)phenyl)-pentan-3-ol (5f). GP-2 was carried out with ketone **3g** (332.2 mg, 1 mmol), EtMgI [prepared from Mg (48, 2.0 mmol), and CH_2CH_3I (312 mg, 2.0 mmol) and dry diethyl ether (10 mL)] in diethyl ether (2 mL) at 0 °C for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished the alcohol **5f** (333.1 mg, 92%) as a viscous liquid. TLC control (petroleum ether/ethyl acetate 90:10), R_f(**3g**) = 0.60, R_f(**5f**) = 0.45, UV detection. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3559, 2878, 1503, 1487, 1238, 1040, 1025, 752, 731 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (dd, J = 8.0 and 1.2 Hz, 1H, ArH), 7.19 (td, J = 7.5 and 1.2 Hz, 1H, ArH), 7.14 (dd, J = 7.6 and 1.9 Hz, 1H, ArH), 7.06−7.00 (m, 1H, ArH), 6.97 (d, J = 1.8 Hz, 1H, ArH), 6.92 (dd, J = 8.1 and 1.8 Hz, 1H, ArH), 6.81 (d, J = 8.1 Hz, 1H, ArH), 5.97 (s, 2H, ArOCH_2O), 2.80−2.72 (m, 1H, CH), 2.52−2.47 (m, 1H, CH), 2.10−2.01 (m, 2H, CH_2), 1.94−1.78 (m, 2H, CH_2), 1.75 (s, 1H, ArC(O*H*)), 0.80 (t, J = 7.4 Hz, 3H, CH_2CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 147.6, 146.0, 141.7, 139.4, 132.7, 130.4, 127.5, 127.4, 124.3, 118.5, 107.7, 106.3, 100.9, 77.0, 43.0, 35.7, 30.7, 7.7 ppm. HRMS (ESI) m/z: [(M + H) + (−H_2O)]$^+$ calcd for $C_{18}H_{18}Br^{79}O_2$ 345.0484; Found 345.0475; [(M + H) + (−H_2O)]$^+$ calcd for $C_{18}H_{18}Br^{81}O_2$ 347.0464; Found 347.0456.

1-Phenyl-3-(2-(phenylethynyl)phenyl)propan-1-ol (7a). GP-3 was carried out with 3-(2-bromophenyl)-1-phenylpropan-1-ol **4a** (87.0 mg, 0.3 mmol), ethynylbenzene **6a** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 93:07 to 90:10) furnished the product **7a** (73.9 mg, 79%) as a brown liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**4a**) = 0.50, R_f(**6a**) = 0.95, R_f(**7a**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3387, 3064, 2922, 1599, 1492, 1452, 1057, 755, 700 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51−7.45 (m, 3H, Ar-H), 7.38−7.32 (m, 5H, Ar-H), 7.29−7.27 (m, 2H, Ar-H), 7.26−7.22 (m, 3H, Ar−H), 7.18 (ddd, J = 7.5, 6.2, and 2.6 Hz, 1H, Ar-H), 4.73 (t, J = 5.2 Hz, 1H, ArC*H*(OH)), 3.06−2.87 (m, 2H, CH_2), 2.27−2.04 (m, 2H, CH_2), 1.99 (d, J = 2.9 Hz, 1H, OH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ = 144.5, 143.9, 132.3, 131.5 (2 × CH), 128.9, 128.5, 128.4 (2 × CH), 128.3 (2 × CH), 128.2, 127.5, 126.0, 125.9 (2× CH), 123.3, 122.6, 93.0, 88.1, 74.0, 39.8, 31.0 ppm. HRMS (ESI) m/z: [(M + H) + (−H_2O)]$^+$ Calcd for $C_{23}H_{19}$ 295.1481; Found 295.1487.

3-(2-(Phenylethynyl)phenyl)-1-(*p*-tolyl)propan-1-ol (7b). GP-3 was carried out with 3-(2-bromophenyl)-1-(*p*-tolyl)propan-1-ol **4b** (91.2 mg, 0.3 mmol), ethynylbenzene **6a** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 93:07 to 90:10) furnished the product **7b** (80.2 mg, 80%) as a brown oil. TLC (petroleum ether/ethyl acetate 90:10, R_f(**4b**) = 0.50, R_f(**6a**) = 0.95, R_f(**7b**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3753, 3414, 3053, 2925, 1683, 1603, 1449, 1267, 814, 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52−7.47 (m, 3H, Ar-H), 7.36−7.32 (m, 3H, Ar-H), 7.26−7.23 (m, 3H, Ar-H), 7.23−7.17 (m, 2H, Ar-H), 7.11 (d, J = 7.9 Hz, 2H, Ar-H), 4.71−4.66 (m, 1H, ArC*H*(OH)), 3.01−2.87 (m, 2H, CH_2), 2.32 (s, 3H, Ar-CH_3), 2.20−2.09 (m, 2H, CH_2), 2.01 (d, J = 2.9 Hz, 1H, OH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ = 143.9, 141.4, 137.1, 132.2, 131.5 (2 × CH), 129.1 (2 × CH), 128.7, 128.4, 128.3 (2 × CH), 128.2, 125.9, 125.8 (2 × CH), 123.3, 122.5, 93.0, 88.1, 73.8, 39.6, 31.0, 21.1 ppm. HRMS (ESI) m/z: [(M + H) + (−H_2O)]$^+$ Calcd for $C_{24}H_{21}$ 309.1637; Found 309.1637.

1-(4-Ethylphenyl)-3-(2-(phenylethynyl)phenyl)propan-1-ol (7c). GP-3 was carried out with 3-(2-bromophenyl)-1-(4-ethylphenyl)propan-1-ol **4c** (95.4 mg, 0.3 mmol), ethynylbenzene **6a** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 93:07 to 90:10) furnished the product **7c** (84.6 mg, 83%) as a brown liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**4c**) = 0.50, R_f(**6a**) = 0.95, R_f(**7c**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3366, 3021, 2960, 2926, 2209, 1496, 1447, 1057, 832, 754 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51−7.46 (m, 3H, Ar-H), 7.36−7.31 (m, 3H, Ar-H), 7.24−7.22 (m, 4H, Ar-H), 7.20−7.15 (m, 1H, Ar-H), 7.14−7.12 (m, 2H, Ar-H), 4.69 (t, 1H, J = 6.3 Hz, ArC*H*(OH)), 3.03−2.90 (m, 2H, CH_2), 2.61 (q, J = 7.6 Hz, 2H, CH_2CH_3), 2.24−2.21 (m, 2H, CH_2), 1.96 (s, 1H, OH), 1.20 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ = 144.0, 143.5, 141.7, 132.2, 131.5 (2 × CH), 128.9, 128.5, 128.3 (2 × CH), 128.2, 127.9 (2 × CH), 125.9 (2 × CH), 125.9, 123.4, 122.6, 93.2, 88.1, 73.9, 39.6, 31.0, 28.5, 15.5 ppm. HRMS (ESI) m/z: [(M + H) + (−H_2O)]$^+$ Calcd for $C_{25}H_{23}$ 323.1794; Found 323.1797.

1-(4-Isopropylphenyl)-3-(2-(phenylethynyl)phenyl)propan-1-ol (7d). GP-3 was carried out with 3-(2-bromophenyl)-1-(4-isopropylphenyl)propan-1-ol **4d** (99.6 mg, 0.3 mmol), ethynylbenzene **6a** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 93:07 to 90:10) furnished the product **7d** (73.3 mg, 69%) as a brown liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**4d**) = 0.50, R_f(**6a**) = 0.95, R_f(**7d**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3350, 2894, 2827, 1476, 1251, 1078, 820, 743 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51−7.48 (m, 3H, Ar-H), 7.37−7.32 (m, 3H, Ar-H), 7.28−7.23 (m, 4H, Ar-H), 7.20−7.15 (m, 3H, Ar-H), 4.71−4.68 (m, 1H, ArC*H*(OH)), 3.03−2.83 (m, 3H, CH_2 and C*H*$(CH_3)_2$), 2.24−2.12 (m, 2H, CH_2), 1.96 (s, 1H, OH), 1.22 (d, J = 6.9 Hz, 6H, CH$(CH_3)_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 148.2, 143.9, 141.8, 132.2, 131.5 (2× CH), 128.9, 128.5, 128.3 (2 × CH), 128.2, 126.5 (2 × CH), 125.9 (2 × CH), 125.8, 123.4, 122.6, 93.0, 88.1, 73.9, 39.6, 33.8, 31.1, 23.9 (2 × CH_3) ppm. HRMS (ESI) m/z: [(M + H) + (−H_2O)]$^+$ Calcd for $C_{26}H_{25}$ 337.1950; Found 337.1937.

1-(3,4-Dimethoxyphenyl)-3-(2-(phenylethynyl)phenyl)-propan-1-ol (7e). GP-3 was carried out with 3-(2-bromophenyl)-1-(3,4-dimethoxyphenyl)propan-1-ol **4e** (105.0 mg, 0.3 mmol), ethynylbenzene **6a** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 85:15 to 80:20) furnished the product **7e** (90.3 mg, 81%) as a brown liquid. TLC (petroleum ether/ethyl acetate 75:25, R_f(**4e**) = 0.50, R_f(**6a**) = 0.95, R_f(**7e**) = 0.42, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3466, 2933, 1594, 1516, 1462, 1263, 1234, 1027, 757, 691 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (d, J = 7.5 Hz, 1H, Ar-H), 7.48−7.46 (m, 2H, Ar-H), 7.36−7.34 (m, 3H, Ar-H), 7.29−7.23 (m, 2H, Ar-H), 7.20−7.16 (m, 1H, Ar-H), 6.89−6.85

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(m, 2H, Ar-H), 6.77 (d, J = 8.1 Hz, 1H, Ar-H), 4.68 (dd, J = 7.5 and 5.6 Hz, 1H, ArC*H*(OH)), 3.84 (s, 3H, $ArOCH_3$), 3.81 (s, 3H, $ArOCH_3$), 3.06−2.88 (m, 2H, CH_2), 2.27−2.04 (m, 3H, CH_2 and OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 149.0, 148.4, 143.9, 137.1, 132.3, 131.5 (2 × CH), 128.9, 128.6, 128.4 (2 × CH), 128.3, 125.9, 123.3, 122.6, 118.2, 110.9, 109.1, 93.0, 88.1, 73.9, 55.8, 55.7, 39.6, 31.1 ppm. HRMS (ESI) m/z: $[M+NH_4]^+$ Calcd for $C_{25}H_{28}NO_3$ 390.2064; Found 390.2049.

1-(3,5-Dimethoxyphenyl)-3-(2-(phenylethynyl)phenyl)-propan-1-ol (7f). GP-3 was carried out with 3-(2-bromophenyl)-1-(3,5-dimethoxyphenyl)propan-1-ol **4f** (105 mg, 0.3 mmol), ethynylbenzene **6a** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 85:15 to 80:20) furnished the product **7f** (92.6 mg, 83%) as a brown liquid. TLC (petroleum ether/ethyl acetate 75:25, R_f(**4f**) = 0.50, R_f(**6a**) = 0.95, R_f(**7f**) = 0.42 UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3022, 1582, 1439, 1250, 1040, 723, 659 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.53−7.49 (m, 3H, Ar-H), 7.37−7.33 (m, 3H, Ar-H), 7.28−7.26 (m, 2H, Ar-H), 7.22−7.17 (m, 1H, Ar-H), 6.52 (d, J = 2.3 Hz, 2H, Ar-H), 6.35 (t, J = 2.3 Hz, 1H, Ar-H), 4.69 (dd, J = 7.4 and 5.5 Hz, 1H, ArC*H*(OH)), 3.73 (s, 6H, 2 × $ArOCH_3$), 3.04−2.93 (m, 2H, CH_2), 2.19−2.05 (m, 3H, CH_2 and OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 160.8 (2× C), 147.1, 143.8, 132.2, 131.5 (2 × CH), 128.9, 128.5, 128.3 (2 × CH), 128.2, 125.9, 123.3, 122.6, 103.6 (2 × CH), 99.5, 93.1, 88.1, 74.1, 55.2 (2 × OCH_3), 39.6, 31.1 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{25}O_3$ 373.1798; Found 373.1776.

1-(Benzo[*d*][1,3]dioxol-5-yl)-3-(2-(phenylethynyl)phenyl)-propan-1-ol (7g). GP-3 was carried out with 1-(benzo[*d*][1,3]-dioxol-5-yl)-3-(2-bromophenyl)propan-1-ol **4g** (100.2 mg, 0.3 mmol), ethynylbenzene **6a** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 85:15) furnished the product **7g** (75.7 mg, 71%) as a brown liquid. TLC (petroleum ether/ethyl acetate 85:15, R_f(**4g**) = 0.50, R_f(**6a**) = 0.95, R_f(**7g**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3567, 3056, 2969, 1598, 1487, 1434, 1373, 1039, 916 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.50−7.44 (m, 3H, Ar-H), 7.35−7.30 (m, 3H, Ar-H), 7.26−7.21 (m, 2H, Ar-H), 7.18−7.13 (m, 1H, Ar-H), 6.84 (d, J = 1.6 Hz, 1H, Ar-H), 6.79−6.72 (m, 1H, Ar-H), 6.69 (d, J = 7.9 Hz, 1H, Ar-H), 5.85 (d, J = 1.5 Hz, 1H, $-OCH_aCH_bO-$), 5.84 (d, J = 1.5 Hz, 1H, $-OCH_aCH_bO-$), 4.60 (dd, J = 7.4 and 5.7 Hz, 1H, ArC*H*(OH)), 3.00−2.80 (m, 2H, CH_2), 2.22−1.98 (m, 3H, CH_2 and OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.7, 146.8, 143.8, 138.5, 132.2, 131.4 (2 × CH), 128.8, 128.4, 128.3 (2 × CH), 128.2, 125.9, 123.3, 122.5, 119.3, 108.0, 106.4, 100.9, 93.0, 88.0, 73.8, 39.7, 30.9 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{24}H_{19}O_2$ 339.1379; Found 339.1372.

1-(4-Chlorophenyl)-3-(2-(phenylethynyl)phenyl)propan-1-ol (7h). GP-3 was carried out with 3-(2-bromophenyl)-1-(4-chlorophenyl)propan-1-ol **4h** (97.2 mg, 0.3 mmol), ethynylbenzene **6a** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 93:07 to 90:10) furnished the product **7h** (78.1 mg, 75%) as a brown liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**4h**) = 0.50, R_f(**6a**) = 0.95, R_f(**7h**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3566, 3368, 2924, 2318, 1596, 1491, 1445, 1082, 1013, 755 cm^{-1}. ^1H NMR ($CDCl_3$ 400 MHz) δ = 7.50 (d, 1H, J = 7.5 and 0.9 Hz, Ar-H), 7.46−7.43 (m, 2H, Ar-H), 7.38−7.33 (m, 3H, Ar-H), 7.28−7.21 (m, 6H, Ar-H), 7.19−7.14 (m, 1H, Ar-H), 4.69 (t, 1H, J = 5.9 Hz, ArC*H*(OH)), 2.95−2.87 (m, 2H, CH_2), 2.19−2.03 (m, 3H, CH_2 and OH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ = 143.6, 142.9, 133.1, 132.3, 131.4 (2 × CH), 128.9, 128.6, 128.6 (2 × CH), 128.4 (2 × CH), 128.3, 127.3 (2 × CH), 126.0, 123.2, 122.6, 93.1, 88.0, 73.2, 39.8, 30.7 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{23}H_{18}Cl$ 329.1091; Found 329.1084.

1-(4-Fluorophenyl)-3-(2-(phenylethynyl)phenyl)propan-1-ol (7i). GP-3 was carried out with 3-(2-bromophenyl)-1-(4-fluorophenyl)propan-1-ol **4i** (92.4 mg, 0.3 mmol), ethynylbenzene **6a** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 93:07 to 90:10) furnished the product **7i** (71.3 mg, 72%) as a brown liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**4i**) = 0.50, R_f(**6a**) = 0.95, R_f(**7i**) = 0.42, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3387, 3058, 2927, 1678, 1601, 1468, 1267, 1139, 748 cm^{-1}. ^1H NMR ($CDCl_3$ 400 MHz) δ = 7.51−7.49 (d, 1H, J = 7.5 and 0.9 Hz, Ar-H), 7.48−7.43 (m, 2H, Ar-H), 7.37−7.33 (m, 3H, Ar-H), 7.33−7.28 (m, 2H, Ar-H), 7.27−7.22 (m, 2H, Ar-H), 7.21−7.15 (m, 1H, Ar-H), 6.99−6.94 (m, 2H, Ar-H), 4.72 (t, 1H, J = 6.4 Hz, ArC*H*(OH)), 2.96−2.89 (m, 2H, CH_2), 2.25−2.00 (m, 3H, CH_2 and OH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ = 162.1 (J_{C-F} = 244 Hz), 143.7, 140.1, 132.3, 131.5 (2 × CH), 128.9, 128.6, 128.4 (2× CH), 128.3, 126.6 (J_{C-F} = 8.0 Hz, 2 × Ar-CH), 126.0, 123.2, 122.6, 115.3 (J_{C-F} = 21.2 Hz, 2 × Ar-CH), 93.0, 87.9, 73.2, 39.9, 30.9 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{23}H_{18}F$ 313.1387; Found 313.1393.

3-(2-((4-Methoxyphenyl)ethynyl)phenyl)-1-(naphthalen-1-yl)propan-1-ol (7j). GP-3 was carried out with 3-(2-bromophenyl)-1-(naphthalen-1-yl)propan-1-ol **4j** (102 mg, 0.3 mmol), 1-ethynyl-4-methoxybenzene **6d** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 88:12 to 85:15) furnished the product **7j** (90.2 mg, 83%) as a brown liquid. TLC (petroleum ether/ethyl acetate 88:12, R_f(**4j**) = 0.50, R_f(**6d**) = 0.90, R_f(**7j**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3431, 2930, 2368, 1605, 1509, 1248, 1030, 801 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.89 (d, J = 8.5 Hz, 1H, Ar-H), 7.84 (d, J = 8.1 Hz, 1H, Ar-H), 7.75 (d, J = 8.2 Hz, 1H, Ar-H), 7.70 (d, J = 7.1 Hz, 1H, Ar-H), 7.54−7.50 (d, J = 7.2 Hz, 1H, Ar-H), 7.46 (d, J = 7.2 Hz, 1H, Ar-H), 7.44−7.37 (m, 3H, Ar-H), 7.34−7.23 (m, 3H, Ar-H), 7.23−7.17 (m, 1H, Ar-H), 6.91−6.83 (m, 2H, Ar-H), 5.53 (d, J = 8.3 Hz, 1H, ArC*H*(OH)), 3.84 (s, 3H, $ArOCH_3$), 3.26−3.05 (m, 2H, CH_2), 2.41−2.22 (m, 2H, CH_2), 2.17 (s, 1H, OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.6 (s, Ar-C), 143.6 (s, Ar-C), 140.2 (s, Ar-C), 133.7 (s, Ar-C), 132.9 (d, 2 × Ar-CH), 132.1 (d, Ar-CH), 130.2 (s, Ar-C), 129.0 (d, Ar-CH), 128.8 (d, Ar-CH), 128.2 (d, Ar-CH), 127.8 (d, Ar-CH), 126.0 (d, Ar-CH), 125.9 (d, Ar-CH), 125.4 (d, 2 × Ar-CH), 123.0 (d, Ar-CH), 123.0 (s, Ar-C), 122.6 (d, Ar-CH), 115.4 (s, Ar-C), 114.0 (d, 2 × Ar-CH), 93.0 (s, C≡C), 86.8 (s, C≡C), 70.4 (d, ArCH(OH)), 55.3 (s, $ArOCH_3$), 39.3 (t, CH_2), 31.4 (t, CH_2) ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{28}H_{23}O$ 375.1743; Found 375.1730.

3-(2-((3,4-Dimethoxyphenyl)ethynyl)phenyl)-1-phenylpropan-1-ol (7k). GP-3 was carried out with 3-(2-bromophenyl)-1-phenylpropan-1-ol **4a** (87.2 mg, 0.3 mmol), 4-ethynyl-1,2-dimethoxybenzene **6e** (72.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 85:15 to 80:20) furnished the product **7k** (88.1 mg, 79%) as a brown liquid. TLC (petroleum ether/ethyl acetate 75:25, R_f(**4a**) = 0.50, R_f(**6e**) = 0.9, R_f(**7k**) = 0.48, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3516, 2934, 1597, 1513, 1453, 1249, 1132, 1024, 759 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.48 (d, J = 7.3 Hz, 1H, Ar-H), 7.36−7.32 (m, 2H, Ar-H), 7.28 (ddd, J = 5.9, 2.4, and 0.6 Hz, 2H, Ar-H), 7.26−7.20 (m, 3H, Ar-H), 7.16 (ddd, J = 7.6, 5.7, and 3.1 Hz, 1H, Ar-H), 7.08 (dd, J = 8.3 and 1.9 Hz, 1H, Ar-H), 7.02 (d, J = 1.9 Hz, 1H, Ar-H), 6.83 (d, J = 8.3 Hz, 1H, Ar-H), 4.71 (dd, J = 8.0 and 5.0 Hz, 1H, ArCH(OH)), 3.88 (s, 3H, $ArOCH_3$), 3.87 (s, 3H, $ArOCH_3$), 2.97 (dddd, J = 16.1, 13.4, 9.5, and 6.2 Hz, 2H, CH_2), 2.25−2.09 (m, 2H, CH_2), 2.08 (s, 1H, OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz,

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J. Org. Chem. 2021, 86, 8706−8725

$CDCl_3$) δ 149.5, 148.6, 144.5, 143.7, 132.1, 128.9, 128.4 (2 × CH), 128.3, 127.4, 125.9, 125.8 (2 × CH), 124.8, 122.8, 115.5, 114.1, 111.0, 93.1, 86.6, 73.9, 55.9, 55.8, 39.8, 31.1 ppm. HRMS (ESI) *m/z*: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{25}H_{23}O_2$ 355.1692; Found 355.1675.

1-(*p*-Tolyl)-3-(2-(*p*-tolylethynyl)phenyl)propan-1-ol (7l). GP-3 was carried out with 3-(2-bromophenyl)-1-(*p*-tolyl)propan-1-ol **4b** (91.2 mg, 0.3 mmol), 1-ethynyl-4-methylbenzene **6b** (52.2 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 93:07 to 90:10) furnished the product **7l** (76.5 mg, 75%) as a brown liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**4b**) = 0.50, R_f(**6b**) = 0.95, R_f(**7l**) = 0.30, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3391, 3055, 2919, 2213, 1605, 1509, 1058, 816, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.4 Hz, 1H, Ar-H), 7.39 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.30−7.25 (m, 4H, Ar-H), 7.22−7.10 (m, 5H, Ar-H), 4.72−4.69 (m, 1H, ArC*H*(OH)), 3.09−2.82 (m, 2H, CH_2), 2.39 (s, 3H, $ArCH_3$), 2.34 (s, 3H, $ArCH_3$), 2.28−2.07 (m, 2H, CH_2), 2.00 (s, 1H, OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.8, 141.5, 138.3, 137.1, 132.1, 131.4 (2 × CH), 129.1 (2 × CH), 129.0 (2 × CH), 128.8, 128.3, 125.8 (3 × CH), 122.7, 120.2, 93.2, 87.4, 73.8, 39.7, 31.1, 21.6, 21.2 ppm. HRMS (ESI) *m/z*: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{25}H_{23}$ 323.1794; Found 323.1775.

3-(2-((4-Methoxyphenyl)ethynyl)phenyl)-1-(*p*-tolyl)propan-1-ol (7m). GP-3 was carried out with 3-(2-bromophenyl)-1-(*p*-tolyl)propan-1-ol **4b** (91.2 mg, 0.3 mmol), 1-ethynyl-4-methoxybenzene **6d** (59.4 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 85:15) furnished the product **7m** (87.6 mg, 82%) as a brown liquid. TLC (petroleum ether/ethyl acetate 85:15, R_f(**4b**) = 0.60, R_f(**6d**) = 0.90, R_f(**7m**) = 0.55, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3384, 2915, 2825, 2150, 2061, 1361, 1238, 1172, 946, 888 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, *J* = 7.4 Hz, 1H, Ar-H), 7.42−7.38 (m, 2H, Ar-H), 7.24−7.20 (m, 4H, Ar-H), 7.16 (ddd, *J* = 7.6, 5.2, and 3.7 Hz, 1H, Ar-H), 7.11 (d, *J* = 7.8 Hz, 2H, Ar-H), 6.90−6.84 (m, 2H, Ar-H), 4.69 (dd, *J* = 7.5 and 5.5 Hz, 1H, ArC*H*(OH)), 3.82 (s, 3H, $ArOCH_3$), 3.06−2.81 (m, 2H, CH_2), 2.31 (s, 3H, $ArCH_3$), 2.27−2.05 (m, 2H, CH_2), 2.02 (s, 1H, OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 159.6, 143.7, 141.5, 137.1, 132.9 (2 × CH), 132.0, 129.1 (2 × CH), 128.8, 128.1, 125.9 (3 × CH), 122.9, 115.5, 113.9 (2 × CH), 93.1, 86.8, 73.8, 55.3, 39.7, 31.0, 21.1 ppm. HRMS (ESI) *m/z*: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{25}H_{23}O$ 339.1743; Found 339.1732.

3-(2-((3,4-Dimethoxyphenyl)ethynyl)phenyl)-1-(*p*-tolyl)propan-1-ol (7n). GP-3 was carried out with 3-(2-bromophenyl)-1-(*p*-tolyl)propan-1-ol **4b** (91.2 mg, 0.3 mmol), 4-ethynyl-1,2-dimethoxybenzene **6e** (72.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 85:15 to 80:20) furnished the product **7n** (90.3 mg, 78%) as a brown liquid. TLC (petroleum ether/ethyl acetate 75:25, R_f(**4b**) = 0.50, R_f(**6e**) = 0.90, R_f(**7n**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3389, 2927, 1584, 1449, 1484, 1251, 1227, 1041, 822 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51−7.49 (m, 1H, Ar-H), 7.25−7.21 (m, 4H, Ar-H), 7.18 (ddd, *J* = 7.6, 5.7, and 3.2 Hz, 1H, Ar-H), 7.13−7.07 (m, 3H, Ar-H), 7.05 (d, *J* = 1.8 Hz, 1H, Ar-H), 6.84 (d, *J* = 8.3 Hz, 1H, Ar-H), 4.70 (dd, *J* = 8.0 and 5.0 Hz, 1H, ArC*H*(OH)), 3.91 (s, 3H, $ArOCH_3$), 3.90 (s, 3H, $ArOCH_3$), 2.97 (dddd, *J* = 16.1, 13.4, 9.6, and 6.1 Hz, 2H, CH_2), 2.32 (s, 3H, $ArCH_3$), 2.16 (ddddd, *J* = 13.7, 11.8, 9.8, 7.4, and 5.3 Hz, 2H, CH_2), 1.97 (s, 1H, OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 149.4, 148.7, 143.8, 141.5, 137.1, 132.1, 129.1 (2 × CH), 128.9, 128.3, 125.9, 125.8 (2 × CH), 124.8, 122.8, 115.6, 114.2, 111.1, 93.1, 86.7, 73.8, 55.9, 55.9, 39.7, 31.1, 21.1 ppm. HRMS (ESI) *m/z*: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{26}H_{25}O_2$ 369.1849; Found 369.1837.

1-(4-Ethylphenyl)-3-(2-(*p*-tolylethynyl)phenyl)propan-1-ol (7o). GP-3 was carried out with 3-(2-bromophenyl)-1-(4-ethylphenyl)propan-1-ol **4c** (95.4 mg, 0.3 mmol), 1-ethynyl-4-methylbenzene **6b** (52.6 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 93:07 to 90:10) furnished the product **7o** (83.9 mg, 79%) as a brown liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**4c**) = 0.50, R_f(**6b**) = 0.95, R_f(**7o**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3409, 2964, 2928, 2313, 1509, 1451, 1045, 816, 706 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.49 (d, *J* = 7.4 Hz, 1H, Ar-H), 7.39 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.28 (s, 1H, Ar-H), 7.27−7.22 (m, 3H, Ar-H), 7.20−7.17 (m, 1H, Ar-H), 7.15 (dd, *J* = 7.8, 5.8 Hz, 4H, Ar-H), 4.70 (dd, *J* = 7.6 and 5.5 Hz, 1H, ArC*H*(OH)), 3.05−2.88 (m, 2H, CH_2), 2.61 (q, *J* = 7.6 Hz, 2H, CH_2CH_3), 2.38 (s, 3H, $ArCH_3$), 2.28−2.10 (m, 2H, CH_2), 1.96 (s, 1H, OH), 1.22 (t, *J* = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 143.9, 143.5, 141.7, 138.3, 132.2, 131.4 (2 × CH), 129.1 (2 × CH), 128.8, 128.3, 127.9 (2 × CH), 125.9 (2 × CH), 125.8, 122.8, 120.3, 93.2, 87.5, 73.9, 39.7, 31.1, 28.5, 21.5, 15.5 ppm. HRMS (ESI) *m/z*: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{26}H_{25}$ 337.1950; Found 337.1940.

1-(4-Ethylphenyl)-3-(2-((4-ethylphenyl)ethynyl)phenyl)-propan-1-ol (7p). GP-3 was carried out with 3-(2-bromophenyl)-1-(4-ethylphenyl)propan-1-ol **4c** (95.4 mg, 0.3 mmol), 1-ethyl-4-ethynylbenzene **6c** (58.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 88:12) furnished the product **7p** (79.5 mg, 72%) as a brown liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**4c**) = 0.50, R_f(**6c**) = 0.95 R_f(**7p**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3736, 2964, 1590, 1456, 1205, 1156, 1064, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50−7.48 (m, 1H, Ar-H), 7.42−7.39 (m, 2H, Ar-H), 7.27 (s, 1H, Ar-H), 7.26−7.22 (m, 3H, Ar-H), 7.20−7.15 (m, 3H, Ar-H), 7.15−7.13 (m, 2H, Ar-H), 4.69 (m, 1H, ArC*H*(OH)), 3.00−2.88 (m, 2H, CH_2), 2.66 (q, *J* = 7.6 Hz, 2H, CH_2CH_3), 2.61 (q, *J* = 7.7 Hz, 2H, CH_2CH_3), 2.20−2.10 (m, 2H, CH_2), 1.97 (d, *J* = 3.2 Hz, 1H, OH), 1.24 (t, *J* = 7.6 Hz, 3H, CH_2CH_3), 1.20 (t, *J* = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 144.6, 143.9, 143.5, 141.8, 132.2, 131.5 (2 × CH), 128.9, 128.3, 127.9 (2 × CH), 127.9 (2 × CH), 125.9 (2 × CH), 125.8, 122.8, 120.5, 93.2, 87.4, 73.8, 39.6, 31.0, 28.8, 28.5, 15.5, 15.5 ppm. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{27}H_{28}ONa$ 391.2032; Found 391.2030.

1-(4-Ethylphenyl)-3-(2-((4-methoxyphenyl)ethynyl)phenyl)-propan-1-ol (7q). GP-3 was carried out with 3-(2-bromophenyl)-1-(4-ethylphenyl)propan-1-ol **4c** (95.4 mg, 0.3 mmol), 1-ethynyl-4-methoxybenzene **6d** (59.4 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 88:12) furnished the product **7q** (83.2 mg, 75%) as a brown liquid. TLC (petroleum ether/ethyl acetate 85:15, R_f(**4c**) = 0.50, R_f(**6d**) = 0.9, R_f(**7q**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3374, 2923, 2859, 2323, 1492, 1446, 1051, 753, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.48−7.46 (m, 1H, Ar-H), 7.45−7.40 (m, 2H, Ar-H), 7.27−7.26 (m, 2H, Ar-H), 7.23 (dd, *J* = 4.9 and 1.1 Hz, 2H, Ar-H), 7.17−7.14 (m, 1H, Ar-H), 7.12 (t, *J* = 8.1 Hz, 2H, Ar-H), 6.91−6.84 (m, 2H, Ar-H), 4.68 (dd, *J* = 7.7 and 5.4 Hz, 1H, ArC*H*(OH)), 3.81 (s, 3H, $ArOCH_3$), 2.97−2.88 (m, 2H, CH_2), 2.61 (q, *J* = 7.6 Hz, 2H, CH_2CH_3), 2.27−2.05 (m, 2H, CH_2), 2.02 (s, 1H, OH), 1.22 (t, *J* = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 159.6, 143.7, 143.5, 141.7, 132.9 (2 × CH), 132.0, 128.8, 128.1, 127.9 (2 × CH), 125.9 (2 × CH), 125.8, 122.9, 115.5, 114.0 (2 × CH), 93.0, 86.8, 73.8, 55.3, 39.6, 31.0, 28.5, 15.5 ppm. HRMS (ESI) *m/z*: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{26}H_{25}O$ 353.1900; Found 353.1903.

3-(2-((3,5-Dimethoxyphenyl)ethynyl)phenyl)-1-(4-ethylphenyl)propan-1-ol (7r). GP-3 was carried out with 3-(2-

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J. Org. Chem. 2021, 86, 8706−8725

bromophenyl)-1-(4-ethylphenyl)propan-1-ol **4c** (95.4 mg, 0.3 mmol), 1-ethynyl-3,5-dimethoxybenzene **6f** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 85:15 to 80:20) furnished the product **7r** (94.8 mg, 79%) as a brown liquid. TLC (petroleum ether/ethyl acetate 75:25, R_f(**4c**) = 0.50, R_f(**6f**) = 0.90, R_f(**7r**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3338, 2895, 2836, 1496, 1250, 1016, 801, 729 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 7.2 and 0.8 Hz, 1H, Ar-H), 7.21−7.13 (m, 4H, Ar-H), 7.12−7.08 (m, 1H, Ar-H), 7.05 (t, J = 6.7 Hz, 2H, Ar-H), 6.61 (d, J = 2.3 Hz, 2H, Ar-H), 6.38 (t, J = 2.3 Hz, 1H, Ar-H), 4.62 (dd, J = 8.0 and 5.1 Hz, 1H, ArC*H*(OH)), 3.72 (s, 6H, 2 × $ArOCH_3$), 2.93−2.82 (m, 2H, CH_2), 2.52 (q, J = 7.6 Hz, 3H, CH_2CH_3 and OH), 2.19−1.99 (m, 2H, CH_2), 1.12 (t, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.5 (2 × C), 144.1, 143.6, 141.7, 132.3, 128.9, 128.5, 127.9 (2 × CH), 125.9 (3 × CH), 124.7, 122.4, 109.4 (2 × CH), 101.6, 93.0, 87.7, 73.9, 55.4 (2 × OCH_3), 39.6, 31.2, 28.5, 15.5 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{27}H_{27}O_2$ 383.2005; Found 383.2007.

1-(4-Ethylphenyl)-3-(2-((4-fluorophenyl)ethynyl)phenyl)-propan-1-ol (7s). GP-3 was carried out with 3-(2-bromophenyl)-1-(4-ethylphenyl)propan-1-ol **4c** (95.4 mg, 0.3 mmol), 1-ethynyl-4-fluorobenzene **6g** (54.2 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 93:07 to 90:10) furnished the product **7s** (73.0 mg, 68%) as a brown liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**4c**) = 0.50, R_f(**6g**) = 0.95, R_f(**7s**) = 0.46, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3352, 2988, 2930, 1582, 1492, 1277, 1215, 825, 749 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.53−7.47 (m, 3H, Ar-H), 7.31−7.28 (m, 4H, Ar-H), 7.23−7.18 (m, 1H, Ar-H), 7.17 (d, J = 4.9 and 1.1 Hz, 2H, Ar-H), 7.10−7.05 (m, 2H, Ar-H), 4.73 (dd, J = 7.7 and 5.4 Hz, 1H, ArC*H*(OH)), 3.04−2.92 (m, 2H, CH_2), 2.66 (q, J = 7.6 Hz, 2H, CH_2CH_3), 2.24−2.14 (m, 2H, CH_2), 2.02 (s, 1H, OH), 1.25 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.4 (J_{C-F} = 248 Hz), 143.9, 143.6, 141.7, 133.3 (J_{C-F} = 8.0 Hz, 2 × CH), 132.6, 128.9, 128.5, 127.9 (2 × CH), 125.9 (2 × CH), 125.9, 122.4, 119.4 (J_{C-F} = 4.0 Hz), 115.5 (J_{C-F} = 22 Hz, 2 × CH), 91.9, 87.8, 73.9, 39.6, 31.1, 28.5, 15.5 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{25}H_{22}F$ 341.1700; Found 341.1689.

1-(4-Isopropylphenyl)-3-(2-(*p*-tolylethynyl)phenyl)propan-1-ol (7t). GP-3 was carried out with 3-(2-bromophenyl)-1-(4-isopropylphenyl)propan-1-ol **4d** (99.6 mg, 0.3 mmol), 1-ethynyl-4-methylbenzene **6b** (52.6 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 93:07 to 90:10) furnished the product **7t** (86.2 mg, 78%) as a brown liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**4d**) = 0.50, R_f(**6b**) = 0.95, R_f(**7t**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3390, 2939, 2898, 1451, 1429, 1251, 1057, 741, 693 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.4 Hz, 1H, Ar-H), 7.51−7.44 (m, 2H, Ar-H), 7.34 (d, J = 8.1 Hz, 2H, Ar-H), 7.32−7.29 (m, 2H, Ar-H), 7.28−7.23 (m, 5H, Ar-H), 4.76 (dd, J = 7.3 and 5.7 Hz, 1H, ArC*H*(OH)), 3.09−2.87 (m, 3H, CH_2 and CH), 2.44 (s, 3H, $ArCH_3$), 2.32−2.12 (m, 2H, CH_2), 2.05 (s, 1H, OH), 1.29 (d, 6H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 148.2, 143.8, 141.8, 138.3, 132.2, 131.4 (2 × CH), 129.1 (2 × CH), 128.8, 128.3, 126.5 (2 × CH), 125.9 (2 × CH), 125.8, 122.8, 120.3, 93.2, 87.4, 73.8, 39.6, 33.8, 31.1, 23.9 (2 × CH_3), 21.6 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{27}H_{27}$ 351.2107; Found 351.2086.

1-(4-Isopropylphenyl)-3-(2-((4-methoxyphenyl)ethynyl)-phenyl)propan-1-ol (7u). GP-3 was carried out with 3-(2-bromophenyl)-1-(4-isopropylphenyl)propan-1-ol **4d** (99.6 mg, 0.3 mmol), 1-ethynyl-4-methoxybenzene **6d** (59.4 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 85:15) furnished the product **7u** (93.3 mg, 81%) as a brown liquid. TLC (petroleum ether/ethyl acetate 85:15, R_f(**4d**) = 0.50, R_f(**6d**) = 0.90, R_f(**7u**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3410, 2958, 2372, 1606, 1509, 1287, 1248, 831, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.4 Hz, 1H, Ar-H), 7.47−7.43 (m, 2H, Ar-H), 7.30−7.28 (m, 2H, Ar-H), 7.27−7.23 (m, 2H, Ar-H), 7.21−7.16 (m, 3H, Ar-H), 6.91−6.87 (m, 2H, Ar-H), 4.71 (dd, J = 6.2 Hz, 1H, ArC*H*(OH)), 3.84 (s, 3H, $ArOCH_3$), 3.09−2.82 (m, 3H, CH_2 and $CH(CH_3)_2$), 2.26−2.07 (m, 2H, CH_2), 1.99 (s, 1H, OH), 1.24 (d, J = 6.9 Hz, 6H, $CH(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.6, 148.2, 143.7, 141.9, 132.9 (2 × CH), 132.0, 128.8, 128.2, 126.5 (2 × CH), 125.9 (2 × CH), 125.9, 122.9, 115.5, 113.9 (2 × CH), 93.0, 86.8, 73.8, 55.3, 39.6, 33.8, 31.1, 23.9, 23.8 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{27}H_{27}O$ 367.2056; Found 367.2036.

1-(4-Isopropylphenyl)-3-(2-((2-methoxyphenyl)ethynyl)-phenyl)propan-1-ol (7v). GP-3 was carried out with 3-(2-bromophenyl)-1-(4-isopropylphenyl)propan-1-ol **4d** (99.6 mg, 0.3 mmol), 1-ethynyl-2-methoxybenzene **6h** (59.4 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 85:15) furnished the product **7v** (91.0 mg, 79%) as a brown liquid. TLC (petroleum ether/ethyl acetate 85:15, R_f(**4d**) = 0.50, R_f(**6h**) = 0.90, R_f(**7v**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3441, 2933, 1596, 1493, 1455, 1204, 1154, 1060, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.4 Hz, 1H, Ar-H), 7.52 (dd, J = 7.6, 1.7 Hz, 1H, Ar-H), 7.40−7.15 (m, 8H, Ar-H), 6.98 (td, J = 7.5, 0.9 Hz, 1H, Ar-H), 6.94 (d, J = 8.3 Hz, 1H, Ar-H), 4.73 (s, 1H, ArC*H*(OH)), 3.92 (s, 3H, $ArOCH_3$), 3.07 (t, J = 7.7 Hz, 2H, CH_2), 2.90 (dt, J = 13.8, 6.9 Hz, 1H, ArC*H*$(CH_3)_2$), 2.40 (br. s, 1H, OH), 2.34−2.08 (m, 2H, CH_2), 1.25 (d, J = 6.9 Hz, 6H, $ArCH(CH_3)_2$) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 159.7, 148.0, 144.0, 142.0, 133.4, 132.3, 129.7, 129.0, 128.4, 126.4 (2 × CH), 125.8 (2 × CH), 125.8, 123.0, 120.6, 112.7, 110.8, 92.4, 89.4, 73.3, 55.9, 40.1, 33.8, 31.0, 24.0 (2× CH_3) ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{27}H_{29}O_2$ 385.2162, Found 385.2184.

1-(3,5-Dimethoxyphenyl)-3-(2-(*p*-tolylethynyl)phenyl)-propan-1-ol (7w). GP-3 was carried out with 3-(2-bromophenyl)-1-(3,5-dimethoxyphenyl)propan-1-ol **4f** (105.0 mg, 0.3 mmol), 1-ethynyl-4-methylbenzene **6b** (52.5 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 85:15 to 80:20) furnished the product **7w** (96.1 mg, 83%) as a brown liquid. TLC (petroleum ether/ethyl acetate 75:25, R_f(**4f**) = 0.50, R_f(**6b**) = 0.98, R_f(**7w**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3399, 2966, 2901, 1583, 1445, 1250, 1141, 1047, 724 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.4 Hz, 1H, Ar-H), 7.41 (d, J = 8.1 Hz, 2H, Ar-H), 7.31−7.24 (m, 2H, Ar-H), 7.22−7.12 (m, 3H, Ar-H), 6.53 (d, 2H, Ar-H), 6.37 (t, J = 2.3 Hz, 1H, Ar-H), 4.73−4.63 (m, 1H, ArC*H*(OH)), 3.75 (s, 6H, 2 × $ArOCH_3$), 3.07−2.95 (m, 2H, CH_2), 2.39 (s, 3H, Ar-CH_3), 2.15 (ddt, J = 9.7 Hz, 7.2 and 5.4 Hz, 3H, CH_2 and OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.9 (2 × C), 147.2, 143.8, 138.4, 132.2, 131.4 (2 × CH), 129.2 (2 × CH), 128.9, 128.4, 125.4, 122.9, 120.3, 103.8 (2 × CH), 99.5, 93.3, 87.5, 74.1, 55.3 (2 × OCH_3), 39.7, 31.1, 21.5 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{26}H_{25}O_2$ 369.1849; Found 369.1829.

1-(3,5-Dimethoxyphenyl)-3-(2-((4-methoxyphenyl)ethynyl)-phenyl)propan-1-ol (7x). GP-3 was carried out with 3-(2-bromophenyl)-1-(3,5-dimethoxyphenyl)propan-1-ol **4f** (105 mg, 0.3 mmol), 1-ethynyl-4-methoxybenzene **6d** (59.4 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatog-

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raphy (petroleum ether/ethyl acetate 85:15 to 80:20) furnished the product **7x** (92.9 mg, 77%) as a brown liquid. TLC (petroleum ether/ethyl acetate 75:25, R_f(**4f**) = 0.50, R_f(**6d**) = 0.98, R_f(**7x**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3452, 2936, 2367, 1596, 1606, 1456, 1248, 1155, 832, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.4 Hz, 1H, Ar-H), 7.45−7.40 (m, 2H, Ar-H), 7.24 (dd, J = 4.2 and 3.4 Hz, 2H, Ar-H), 7.21−7.15 (m, 1H, Ar-H), 6.90−6.85 (m, 2H, Ar-H), 6.51 (d, J = 2.2 Hz, 2H, Ar-H), 6.35 (t, J = 2.3 Hz, 1H, Ar-H), 4.68 (t, J = 5.3 Hz, 1H, ArC*H*(OH)), 3.83 (s, 3H, $ArOCH_3$), 3.74 (s, 6H, 2 × $ArOCH_3$), 3.04−2.89 (m, 2H, CH_2), 2.21−2.08 (m, 2H, CH_2), 2.03 (s, 1H, OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.8 (2 × C), 159.6, 147.2, 143.6, 132.9 (2 × CH), 132.0, 128.8, 128.2, 125.9, 122.9, 115.4, 114.0 (2 × CH), 103.7 (2 × CH), 99.4, 93.1, 86.8, 74.1, 55.3, 55.3 (2 × OCH_3), 39.7, 31.0 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{27}O_4$ 403.1904; Found 403.1882.

1-(4-Chlorophenyl)-3-(2-(*p*-tolylethynyl)phenyl)propan-1-ol (7y). GP-3 was carried out with 3-(2-bromophenyl)-1-(4-chlorophenyl)propan-1-ol **4h** (97.2 mg, 0.3 mmol), 1-ethynyl-4-methylbenzene **6b** (53.1 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 93:07 to 90:10) furnished the product **7y** (91.8 mg, 85%) as a brown liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**4h**) = 0.50, R_f(**6b**) = 0.95, R_f(**7y**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3410, 3340, 3029, 2927, 1598, 1456, 1257, 813 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.5 Hz, 1H, Ar-H), 7.37 (d, J = 8.1 Hz, 2H, Ar-H), 7.30−7.24 (m, 5H, Ar-H), 7.24−7.21 (m, 1H, Ar-H), 7.21−7.16 (m, 3H, Ar-H), 4.71 (dd, J = 7.5 and 5.4 Hz, 1H, ArC*H*(OH)), 2.94 (dd, J = 9.1 and 6.8 Hz, 2H, CH_2), 2.38 (s, 3H, Ar-C*H*$_3$), 2.21−2.04 (m, 3H, CH_2 and OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 143.5, 142.9, 138.4, 133.0, 132.2, 131.3 (2 × CH), 129.2 (2 × CH), 128.8, 128.5 (2 × CH), 128.3, 127.3 (2 × CH), 126.0, 122.7, 120.1, 93.3, 87.3, 73.2, 39.8, 30.7, 21.5 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{24}H_{20}Cl$ 343.1248; Found 343.1252.

3-(4-Methoxy-2-(phenylethynyl)phenyl)-1-phenylpropan-1-ol (7z). GP-3 was carried out with 3-(2-bromo-4-methoxyphenyl)-1-phenylpropan-1-ol **4k** (96.0 mg, 0.3 mmol), ethynylbenzene **6a** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 85:15) furnished the product **7z** (81.1 mg, 79%) as a brown liquid. TLC (petroleum ether/ethyl acetate 85:15, R_f(**4k**) = 0.50, R_f(**6a**) = 0.95, R_f(**7z**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3338, 2895, 2836, 1496, 1250, 1016, 861, 725 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, J = 6.6 and 3.1 Hz, 2H, Ar-H), 7.34−7.27 (m, 6H, Ar-H), 7.25−7.19 (m, 2H, Ar-H), 7.13−7.06 (m, 1H, Ar-H), 7.01 (d, J = 2.7 Hz, 1H, Ar-H), 6.80 (dd, J = 8.5 and 2.8 Hz, 1H, Ar-H), 4.67 (dd, J = 7.6 and 5.4 Hz, 1H, ArC*H*(OH)), 3.75 (s, 3H, $ArOCH_3$), 2.86 (td, J = 9.0 and 6.4 Hz, 2H, CH_2), 2.22−1.91 (m, 3H, CH_2 and OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.4, 144.5, 136.2, 131.5 (2 × CH), 129.9, 128.4 (2 × CH), 128.3 (2 × CH), 128.2, 127.4, 125.9 (2 × CH), 123.2, 123.1, 116.5, 115.3, 92.7, 88.1, 73.9, 55.3, 39.9, 30.0 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{24}H_{21}O$ 325.1587; Found 325.1578.

1-(4-Ethylphenyl)-3-(4-methoxy-2-((4-methoxyphenyl)-ethynyl)phenyl)propan-1-ol (7aa). GP-3 was carried out with 3-(2-bromo-4-methoxyphenyl)-1-(4-ethylphenyl)propan-1-ol **4l** (104.5 mg, 0.3 mmol), 1-ethynyl-4-methoxybenzene **6d** (59.4 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 88:12 to 85:15) furnished the product **7aa** (91.0 mg, 82%) as a brown liquid. TLC (petroleum ether/ethyl acetate 85:15, R_f(**4l**) = 0.50, R_f(**6d**) = 0.95, R_f(**7aa**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3741, 2962, 1602, 1510, 1248, 1034, 832 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45−7.41 (m, 2H, Ar-H), 7.26−7.24 (m, 2H, Ar-H), 7.14 (dd, J = 8.3 and 3.6 Hz, 3H, Ar-H), 7.02 (d, 1H, Ar-H), 6.90−6.86 (m, 2H, Ar-H), 6.82 (dd, J = 8.5 and 2.8 Hz, 1H, Ar-H), 4.73−4.65 (m, 1H, ArC*H*(OH)), 3.84 (s, 3H, $ArOCH_3$), 3.80 (s, 3H, $ArOCH_3$), 2.98−2.79 (m, 2H, CH_2), 2.63 (q, J = 7.6 Hz, 2H, C*H*$_2$CH$_3$), 2.25−2.03 (m, 2H, CH_2), 1.97 (s, 1H, OH), 1.22 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.6, 157.4, 143.5, 141.8, 136.0, 132.9 (2 × CH), 129.9, 127.9 (2 × CH), 125.9 (2 × CH), 123.5, 116.3, 115.3, 114.9, 114.0 (2 × CH), 92.7, 86.8, 73.8, 55.3 (2 × OCH_3), 40.1, 30.1, 28.5, 15.5 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{27}H_{27}O_2$ 383.2005; Found 383.1989.

3-(5-Fluoro-2-(phenylethynyl)phenyl)-1-(*p*-tolyl)propan-1-ol (7ab). GP-3 was carried out with 3-(2-bromo-5-fluorophenyl)-1-(*p*-tolyl)propan-1-ol **4m** (96.6 mg, 0.3 mmol), ethynylbenzene **6a** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 93:07 to 90:10) furnished the product **7ab** (84.6 mg, 82%) as a brown liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**4m**) = 0.50, R_f(**6a**) = 0.95, R_f(**7ab**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3385, 2921, 1580, 1596, 1497, 1273, 1227, 959, 818 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.53−7.49 (m, 3H, Ar-H), 7.41−7.34 (m, 3H, Ar-H), 7.27 (d, J = 7.9 Hz, 2H, Ar-H), 7.15 (d, J = 7.9 Hz, 2H, Ar-H), 7.07−6.88 (m, 2H, Ar-H), 4.73−4.70 (m, 1H, ArC*H*(OH)), 3.10−2.83 (m, 2H, CH_2), 2.36 (s, 3H, $ArCH_3$), 2.22−1.95 (m, 3H, CH_2 and OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.5 (J_{C-F} = 248 Hz), 146.8 (J_{C-F} = 8 Hz), 141.4, 137.3, 134.0 (J_{C-F} = 8 Hz), 131.5 (2 × CH), 129.2 (2 × CH), 128.4 (2 × CH), 128.3, 125.9 (2 × CH), 123.3, 118.7 (J_{C-F} = 4 Hz), 115.9 (J_{C-F} = 22 Hz), 113.2 (J_{C-F} = 22 Hz), 92.7, 88.2, 74.0, 55.4, 40.1, 30.1 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{24}H_{20}F$ 327.1543; Found 327.1529.

2-Phenyl-4-(2-(phenylethynyl)phenyl)butan-2-ol (8a). GP-3 was carried out with 4-(2-bromophenyl)-2-phenylbutan-2-ol **5a** (91.2 mg, 0.3 mmol), ethynylbenzene **6a** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:05 to 93:07) furnished the product **8a** (87.0 mg, 89%) as a brown liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**5a**) = 0.50, R_f(**6a**) = 0.95, R_f(**8a**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3566, 3435, 2967, 2213, 1492, 1445, 1370, 1026, 755, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) ^1H NMR (400 MHz, $CDCl_3$) δ 7.49−7.44 (m, 5H, Ar-H), 7.37−7.32 (m, 3H, Ar-H), 7.30−7.25 (m, 2H, Ar-H), 7.23−7.18 (m, 2H, Ar-H), 7.16−7.11 (m, 2H, Ar-H), 2.86 (td, J = 12.4 and 5.2 Hz, 1H, CH), 2.73−2.64 (m, 1H, CH), 2.16 (qdd, J = 13.7, 11.9, and 5.1 Hz, 2H, ArC(CH_3)-(OH)CH_2C*H*$_2$), 1.87 (s, 1H, OH), 1.59 (s, 3H, ArC*H*$_3$(OH)) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.5, 144.3, 132.2, 131.5 (2 × CH), 128.7, 128.5, 128.3 (2 × CH), 128.2 (3 × CH), 126.5, 125.8, 124.8 (2 × CH), 123.3, 122.4, 92.8, 88.0, 74.6, 45.2, 30.4, 29.5 ppm. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{22}ONa$ 349.1563; Found 349.1565.

4-(2-((4-Methoxyphenyl)ethynyl)phenyl)-2-phenylbutan-2-ol (8b). GP-3 was carried out with 4-(2-bromophenyl)-2-phenylbutan-2-ol **5a** (91.2 mg, 0.3 mmol), 1-ethynyl-4-methoxybenzene **6d** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 93:07 to 90:10) furnished the product **8b** (84.4 mg, 79%) as a brown liquid. TLC (petroleum ether/ethyl acetate 85:15, R_f(**5a**) = 0.50, R_f(**6d**) = 0.90, R_f(**8b**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3503, 2972, 1731, 1243, 1040, 913, 734 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48−7.44 (m, 3H, Ar-H), 7.43−7.38 (m, 2H, Ar-H), 7.30−7.26 (m, 2H, Ar-H), 7.26−7.20 (m, 2H, Ar-H), 7.17−7.13 (ddd, J = 7.1, 4.0, and 1.4 Hz, 2H, Ar-H), 6.94−6.87 (m, 2H, Ar-H), 3.85 (s, 3H, $ArOCH_3$), 2.88−2.81 (m, 1H, CH), 2.71−2.64 (m, 1H, CH), 2.19 (ddt, J = 13.8, 12.0, and 8.6 Hz, 2H, CH_2), 1.63 (s, 3H, $ArCH_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.6, 147.6,

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J. Org. Chem. 2021, 86, 8706−8725

144.1, 133.0 (2 × CH), 132.1, 128.7, 128.2 (3 × CH), 126.5, 125.8, 124.8 (2 × CH), 122.8, 115.5, 114.0 (2 × CH), 92.9, 86.7, 74.6, 55.3, 45.2, 30.5, 29.6 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{25}H_{23}O$ 339.1743; Found 339.1747.

4-(2-((3,5-Dimethoxyphenyl)ethynyl)phenyl)-2-phenylbutan-2-ol (8c). GP-3 was carried out with 4-(2-bromophenyl)-2-phenylbutan-2-ol **5a** (91.2 mg, 0.3 mmol), 1-ethynyl-3,5-dimethoxybenzene **2f** (72.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 85:15 to 80:20) furnished the product **8c** (92.6 mg, 80%) as a brown liquid. TLC (petroleum ether/ethyl acetate 75:25, R_f(**5a**) = 0.50, R_f(**6a**) = 0.98, R_f(**8c**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3477, 2934, 1589, 1453, 1420, 1205, 1156, 1064, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (dt, J = 7.6 and 1.4 Hz, 3H, Ar-H), 7.32−7.24 (m, 2H, Ar-H), 7.24−7.17 (m, 2H, Ar-H), 7.14 (dd, J = 10.7 and 4.5 Hz, 2H, Ar-H), 6.68 (d, J = 2.3 Hz, 2H, Ar-H), 6.50 (t, J = 2.3 Hz, 1H, Ar-H), 3.83 (s, 6H, 2 × $ArOCH_3$), 2.93−2.86 (m, 1H, CH), 2.74−2.65 (m, 1H, CH), 2.23−2.16 (m, 2H, CH_2), 1.83 (s, 1H, OH), 1.62 (s, 3H, $ArC(CH_3)OH$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.5 (2 × C), 147.5, 144.4, 132.3, 128.1, 128.6, 128.2 (2 × CH), 126.6, 125.8, 124.7 (2 × CH), 124.6, 122.3, 109.4 (2 × CH), 101.7, 92.9, 86.7, 74.6, 55.4 (2 × OCH_3), 45.2, 30.4, 29.6 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{26}H_{25}O_2$ 369.1849; Found 369.1842.

1,1-Diphenyl-3-(2-(phenylethynyl)phenyl)propan-1-ol (8d). GP-3 was carried out with 3-(2-bromophenyl)-1,1-diphenylpropan-1-ol **5b** (109.4 mg, 0.3 mmol), ethynylbenzene **6a** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:05 to 93:07) furnished the product **8d** (82.6 mg, 71%) as a brown liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**5b**) = 0.50, R_f(**6a**) = 0.95, R_f(**8d**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3724, 2923, 1681, 1597, 1455, 1248, 1026, 758 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42−7.32 (m, 7H, Ar-H), 7.26−7.20 (m, 3H, Ar-H), 7.17−7.11 (m, 5H, Ar-H), 7.11−7.03 (m, 4H, Ar-H), 2.81−2.72 (m, 2H, CH_2), 2.59−2.51 (m, 2H, CH_2), 2.14 (s, 1H, OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.8 (2 × C), 144.5, 132.3, 131.4 (2 × CH), 128.9, 128.6, 128.3 (2 × CH), 128.2, 128.2 (4 × CH), 126.8 (2 × CH), 126.0 (4 × CH), 125.9, 123.3, 122.5, 92.9, 88.1, 78.1, 43.2, 29.3 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{29}H_{23}$ 371.1794; Found 371.1805.

2-(4-Chlorophenyl)-4-(2-(phenylethynyl)phenyl)butan-2-ol (8e). GP-3 was carried out with 4-(2-bromophenyl)-2-(4-chlorophenyl)butan-2-ol **5c** (101.4 mg, 0.3 mmol), ethynylbenzene **6a** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:05 to 93:07) furnished the product **8e** (82.1 mg, 76%) as a brown liquid. TLC (petroleum ether/ethyl acetate 93:07, R_f(**5c**) = 0.50, R_f(**6a**) = 0.95, R_f(**8e**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3448, 2930, 1599, 1493, 1444, 1280, 1067, 755 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51−7.45 (m, 2H, Ar-H), 7.45−7.41 (m, 2H, Ar-H), 7.41−7.32 (m, 4H, Ar-H), 7.25−7.20 (m, 3H, Ar-H), 7.18 (dd, J = 10.9 and 4.4 Hz, 2H, Ar-H), 2.87 (td, J = 12.4 and 5.1 Hz, 1H, CH), 2.67 (td, J = 12.4 and 5.2 Hz, 1H, CH), 2.25−2.04 (m, 2H, CH_2), 1.83 (s, 1H, OH), 1.60 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.9, 144.0 (2 × C), 132.3, 131.4 (2 × CH), 128.8, 128.6, 128.4 (2 × CH), 128.3 (3 × CH), 125.4 (2 × CH), 125.9, 123.2, 122.4, 92.9, 87.9, 74.4, 45.4, 30.7, 29.4 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{24}H_{20}Cl$ 343.1248; Found 343.1235.

2-(Benzo[*d*][1,3]dioxol-5-yl)-4-(2-(phenylethynyl)phenyl)-butan-2-ol (8f). GP-3 was carried out with 2-(benzo[*d*][1,3]dioxol-5-yl)-4-(2-bromophenyl)butan-2-ol **5d** (104.4 mg, 0.3 mmol), ethynylbenzene **6a** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 88:12) furnished the product **8f** (91.0 mg, 82%) as a brown liquid. TLC (petroleum ether/ethyl acetate 85:15, R_f(**5d**) = 0.50, R_f(**6a**) = 0.95, R_f(**8f**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2953, 1718, 1357, 1219, 1032 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (ddd, J = 6.5 Hz, 3.7 and 2.4 Hz, 3H, Ar-H), 7.40−7.30 (m, 3H, Ar-H), 7.25−7.20 (m, 1H, Ar-H), 7.14 (dd, J = 11.6 and 4.3 Hz, 2H, Ar-H), 7.00 (d, J = 1.8 Hz, 1H, Ar-H), 6.93 (dd, J = 8.1 and 1.8 Hz, 1H, Ar-H), 6.69 (d, J = 8.1 Hz, 1H, Ar-H), 5.88 (d, J = 1.5 Hz, 1H, $-OCH_aCH_b-$, 5.87 (d, J = 1.5 Hz, 1H, $-OCH_aCH_b-$), 2.91−2.81 (m, 1H, CH), 2.71 (m, 1H, CH), 2.21−2.04 (m, 2H, CH_2), 1.84 (s, 1H, OH), 1.57 (s, 3H, $ArCH_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.5, 146.0, 144.2, 141.7, 132.4, 131.4 (2 × CH), 128.8, 128.5, 128.3 (2 × CH), 128.2, 125.8, 123.3, 122.4, 117.8, 107.8, 105.9, 100.9, 92.8, 88.0, 74.5, 45.4, 30.6, 29.5 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{25}H_{21}O_2$ 353.1536; Found 353.1520.

3-(4-Chlorophenyl)-1-(2-((4-methoxyphenyl)ethynyl)-phenyl)pentan-3-ol (8g). GP-3 was carried out with 1-(2-bromophenyl)-3-(4-chlorophenyl)pentan-3-ol **5e** (105.6 mg, 0.3 mmol), 1-ethynyl-4-methoxybenzene **6d** (45.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:05 to 93:07) furnished the product **8g** (88.6 mg, 79%) as a brown liquid. TLC (petroleum ether/ethyl acetate 90:10, R_f(**5e**) = 0.50, R_f(**6d**) = 0.95, R_f(**8g**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3448, 2930, 1599, 1493, 1444, 1280, 1067, 755 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48−7.44 (m, 1H, Ar-H), 7.40−7.34 (m, 4H, Ar-H), 7.25−7.19 (m, 3H, Ar-H), 7.18−7.12 (m, 2H, Ar-H), 6.95 (m, 2H, Ar-H), 3.86 (s, 3H, $ArOCH_3$), 2.85 (td, J = 12.5 and 4.8 Hz, 1H, CH), 2.58−2.30 (m, 1H, CH), 2.20−2.10 (m, 2H, CH_2), 1.91−1.76 (m, 2H, CH_2CH_3), 1.75 (s, 1H, OH), 0.77 (t, J = 7.4 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.6, 143.9 (2 × C), 132.9 (2 × CH), 132.1, 132.1, 128.8, 128.3, 128.2 (2 × CH), 126.9 (2 × CH), 125.8, 122.7, 115.3, 114.1 (2 × CH), 92.8, 86.7, 77.0, 55.3, 43.8, 35.8, 29.1, 7.67 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{26}H_{24}ClO$ 387.1510; Found 387.1482.

3-(Benzo[*d*][1,3]dioxol-5-yl)-1-(2-((3,4-dimethoxyphenyl)-ethynyl)phenyl)pentan-3-ol (8h). GP-3 was carried out with 1-(2-bromophenyl)-3-(4-chlorophenyl)pentan-3-ol **5f** (108.6 mg, 0.3 mmol), 4-ethynyl-1,2-dimethoxybenzene **6e** (72.9 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 85:15) furnished the product **8h** (107.8 mg, 81%) as a brown liquid. TLC (petroleum ether/ethyl acetate 80:20, R_f(**5f**) = 0.50, R_f(**6e**) = 0.90, R_f(**8h**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3536, 3060, 2963, 2934, 2835, 1486, 1439, 1326, 1248, 1133, 1038, 930 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51−7.42 (m, 1H, Ar-H), 7.25−7.18 (m, 1H, Ar-H), 7.19−7.02 (m, 4H, Ar-H), 6.95 (d, J = 1.7 Hz, 1H, Ar-H), 6.93−6.83 (m, 2H, Ar-H), 6.71 (d, J = 8.1 Hz, 1H, Ar-H), 5.90 (dd, J = 8.6, 1.4 Hz, 2H, OCH_2), 3.92 (d, J = 0.9 Hz, 6H, $ArOCH_3$), 2.90 (ddd, J = 13.0, 10.4, and 6.6 Hz, 1H, CH_2), 2.76−2.51 (m, 1H, CH), 2.42−2.06 (m, 2H, CH_2), 1.96−1.70 (m, 3H, CH_2 and OH), 0.77 (t, J = 7.4 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.5, 148.7, 147.6, 145.9, 144.3, 139.8, 132.1, 128.9, 128.3, 125.9, 124.8, 122.6, 118.5, 115.6, 114.2, 111.1, 107.8, 106.4, 100.9, 93.1, 86.7, 76.8, 55.9, 55.8, 43.7, 35.8, 29.1, 7.67 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{28}H_{27}O_4$ 427.1904; Found 427.1878.

3-(2-((3-Aminophenyl)ethynyl)phenyl)-1-(*p*-tolyl)propan-1-ol (7ac). GP-3 was carried out with 3-(2-bromophenyl)-1-(*p*-tolyl)propan-1-ol **4b** (91.2 mg, 0.3 mmol), 3-ethynylaniline **6i** (52.6 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 3 mol %), PPh_3 (4.7 mg, 6 mol %), Cs_2CO_3 (146.3 mg, 0.45 mmol), and DMF (2 mL) at 100 °C for 12 h. Purification of the crude material by silica gel column

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chromatography (petroleum ether/ethyl acetate 90:10 to 95:15) furnished the product **7ac** (107.8 mg, 81%) as a brown liquid. TLC (petroleum ether/ethyl acetate 80:20, R_f(**4b**) = 0.50, R_f(**7ac**) = 0.45, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3536, 3432, 3360, 2934, 2835, 1486, 1439, 1326, 1248, 1133, 1038, 930 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.7 Hz, 2H, Ar-H), 7.28−7.22 (m, 2H, Ar-H), 7.17 (ddd, J = 8.9 Hz, 6.0 and 3.0 Hz, 2H, Ar-H), 7.14−7.10 (m, 3H, Ar-H), 6.90 (d, J = 7.6 Hz, 1H, Ar-H), 6.81−6.78 (m, 1H, Ar-H), 6.63 (ddd, J = 8.1 Hz, 2.4 and 0.9 Hz, 1H, Ar-H), 4.93 (t, J = 6.3 Hz, 1H, ArC*H*(OH)), 3.72 (br. s, 2H, $ArNH_2$), 3.06−3.03 (m, 2H, CH_2), 2.16 (s, 3H, $ArCH_3$), 2.16−2.02 (m, 3H, CH_2 and OH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.2, 143.9, 142.7, 134.4, 132.4, 130.1, 129.2, 128.9, 128.4, 127.3, 126.9, 125.9, 125.0, 123.9, 122.6, 121.9, 117.7, 115.3, 93.2, 87.6, 69.2, 38.8, 31.9, 18.7 ppm. HRMS (ESI) m/z: $[(M + H) + (-H_2O)]^+$ Calcd for $C_{24}H_{22}N$ 310.1590; Found:--- .

11-Phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluorene (9a). GP-4 was carried out with 1-phenyl-3-(2-(phenylethynyl)phenyl)propan-1-ol **7a** (62.4 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.9 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate/hexane to 99:1) furnished the product **9a** (46.4 mg, 79%) as colorless liquid.

1.35 mmol Scale-up Reaction of 9a. GP-4 was carried out with 1-phenyl-3-(2-(phenylethynyl)phenyl)propan-1-ol **7a** (422 mg, 1.35 mmol), $BF_3{\cdot}OEt_2$ (114 mg, 30 mol %) in dry DCE (10 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate/hexane to 99:1) furnished the product **9a** (262 mg, 63%) as a colorless liquid. TLC (petroleum ether/ethyl acetate 99:1, R_f(**7a**) = 0.20, R_f(**9a**) = 0.9, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 2921, 2363, 1488, 1240, 1039, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.52 (d, J = 6.8 Hz, 1H, Ar-H), 7.48−7.42 (m, 2H, Ar-H), 7.38 (t, J = 6.8 Hz, 3H, Ar-H), 7.26−7.13 (m, 4H, Ar-H), 7.09−7.06 (m, 2H, Ar-H), 6.87 (t, J = 7.6 Hz, 1H, Ar-H), 3.61 (dd, J = 13.5 and 4.3 Hz, 1H, CH), 3.20−3.05 (m, 2H, CH_2), 2.72−2.66 (m, 1H, CH), 1.67−1.52 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 147.2, 145.8, 142.1, 137.6, 136.4, 136.2, 132.2, 129.3 (2 × CH), 129.0, 128.9 (2 × CH), 127.4, 127.1, 126.9 (2 × CH), 125.5, 124.8, 122.5, 120.2, 42.2, 30.6, 28.4 ppm. HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{23}H_{18}$ 294.1403; Found 294.1399.

9-Methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluorene (9b). GP-4 was carried out with 3-(2-(phenylethynyl)phenyl)-1-(*p*-tolyl)propan-1-ol **7b** (65.2 mg, 0.2 mmol) and $BF_3{\cdot}OEt_2$ (16.9 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate/exane to 99:1) furnished the product **9b** (43.1 mg, 70%) as a colorless liquid. TLC (petroleum ether/ethyl acetate 99:1, R_f(**7b**) = 0.20, R_f(**9b**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3535, 3054, 2924, 2853, 1452, 746 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, J = 7.2 Hz, 2H, Ar-H), 7.47−7.37 (m, 4H, Ar-H), 7.22 (d, J = 7.6 Hz, 1H, Ar-H), 7.15−7.07 (m, 3H, Ar-H), 6.92−6.89 (m, 2H, Ar-H), 3.62 (dd, J = 13.5 and 4.3 Hz, 1H, CH), 3.30−3.16 (m, 2H, CH_2), 2.77−2.65 (m, 1H, CH), 2.36 (s, 3H, $ArCH_3$), 1.67−1.57 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 147.3, 143.0, 142.4, 137.6, 136.7, 136.5, 136.2, 132.3, 129.3 (2 × CH), 129.0, 128.9 (2 × CH), 127.4, 127.1, 126.9, 125.7, 125.4, 122.2, 120.9, 48.9, 30.6, 28.5, 21.5 ppm. HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{24}H_{20}$ 308.1560; Found 308.1568.

9-Ethyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluorene (9c). GP-4 was carried out with 1-(4-ethylphenyl)-3-(2-(phenylethynyl)-phenyl)propan-1-ol **7c** (68.0 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate/hexane to 99:1) furnished the product **9c** (41.9 mg, 65%) as colorless liquid. TLC (petroleum ether/ethyl acetate 99:1, R_f(**7c**) = 0.20, R_f(**9c**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2923, 1597, 1492, 1443, 1090, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55−7.43 (m, 6H, Ar-H), 7.24 (d, J = 7.3 Hz, 1H, Ar-H), 7.17−7.11 (m, 3H, Ar-H), 6.97 (d, J = 0.8 Hz, 1H, Ar-H), 6.92 (t, J = 7.6 Hz, 1H, Ar-H), 3.64 (dd, J = 13.5 and 4.3 Hz, 1H, CH), 3.24−3.17 (m, 2H, CH_2), 2.74−2.68 (m, 1H, CH), 2.67 (q, J = 7.7 Hz, CH_2CH_3), 1.69−1.64 (m, 1H, CH), 1.25 (t, J = 7.7 Hz, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 147.4, 143.3, 143.2, 142.4, 137.6, 136.5, 136.3, 132.3, 129.3 (2 × CH), 129.0, 128.9 (2 × CH), 127.3, 127.0, 126.8, 125.4, 124.5, 122.3, 119.7, 48.9, 30.6, 29.0, 28.5, 16.0 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}$ 323.1794; Found 323.1797.

9-Isopropyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluorene (9d). GP-4 was carried out with 1-(4-isopropylphenyl)-3-(2-(phenylethynyl)phenyl)propan-1-ol **7d** (70.8 mg, 0.2 mmol) and $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate/hexane to 99:1) furnished the product **9d** (45.7 mg, 68%) as a yellow liquid. TLC (petroleum ether/ethyl acetate 99:1, R_f(**7d**) = 0.20, R_f(**9d**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3054, 2925, 2958, 1608, 1469, 814, 745 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ ^1H NMR (400 MHz, $CDCl_3$) δ 7.57−7.25 (m, 6H, Ar-H), 7.22 (d, J = 7.6 Hz, 1H, Ar-H), 7.18−7.06 (m, 3H, Ar-H), 6.96 (d, J = 1.4 Hz, 1H, Ar-H), 6.90 (t, J = 7.5 Hz, 1H, Ar-H), 3.61 (dd, J = 13.5, 4.3 Hz, 1H, CH), 3.34−3.05 (m, 2H, CH_2), 2.91 (dt, J = 13.8, 6.9 Hz, 1H, ArC*H*$(CH_3)_2$), 2.83−2.57 (m, 1H, CH), 1.80−1.59 (m, 1H, CH), 1.24 (dd, J = 6.9 and 1.6 Hz, 6H, ArCH$(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 147.9, 147.2, 143.5, 142.4, 137.6, 136.5, 136.3, 132.3, 129.4 (2 × CH), 129.0, 128.9 (2 × CH), 127.3, 127.0, 126.8, 125.4, 122.9, 122.3, 118.4, 48.9, 34.3, 30.6, 28.4, 24.3, 24.2 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}$ 337.1951; Found 337.1930.

8,9-Dimethoxy-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]-fluorene (9e). GP-4 was carried out with 1-(3,4-dimethoxyphenyl)-3-(2-(phenylethynyl)phenyl)propan-1-ol **7e** (74.4 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 97:3−95:5) furnished the product **9e** (48.1 mg, 68%) as a brown liquid. TLC (petroleum ether/ethyl acetate 95:05, R_f(**7e**) = 0.20, R_f(**9e**) = 0.85, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3446, 3060, 2924, 2854, 1673, 1271, 1118, 1071 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.50 (t, J = 7.2 Hz, 2H, Ar-H), 7.46−7.38 (m, 3H, Ar-H), 7.21−7.20 (m, 1H, Ar-H), 7.14 (s, 1H, Ar-H), 7.10−7.06 (m, 2H, Ar-H), 6.89 (t, J = 7.6 Hz, 1H, Ar-H), 6.64 (s, 1H, Ar-H), 3.96 (s, 3H, $ArOCH_3$), 3.81 (s, 3H, $ArOCH_3$), 3.58 (dd, J = 13.5 and 4.2 Hz, 1H, CH), 3.20−3.15 (m, 2H, CH_2), 2.72−2.66 (m, 1H, CH), 1.67−1.57 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 148.8, 147.6, 141.0, 139.8, 138.5, 137.1, 136.6, 136.1, 132.3, 129.3 (2 × CH), 129.0 (3 × CH), 127.4, 126.7, 126.4, 125.5, 106.8, 103.9, 56.4, 56.1, 48.9, 30.6, 28.8 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}O_2$ 355.1698; Found 355.1693.

8,10-Dimethoxy-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]-fluorene (9f). GP-4 was carried out with 1-(3,5-dimethoxyphenyl)-3-(2-(phenylethynyl)phenyl)propan-1-ol **7f** (74.4 mg, 0.2 mmol) and $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 97:3−95:5) furnished the product **9f** (50.2 mg, 71%) as lightyellow liquid.

TLC (petroleum ether/ethyl acetate 95:05, R_f(**7f**) = 0.20, R_f(**9f**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 2936, 2836, 1596, 1493, 1204, 1154, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.50−7.30 (m, 4H, Ar-H), 7.19−7.16 (m, 2H, Ar-H), 7.04 (td, J = 7.4 Hz, and 1.4 Hz, 1H, Ar-H), 6.89 (dd, J = 8.0 Hz, and 1.2 Hz, 1H, Ar-H), 6.82 (t, J = 7.5 Hz, 1H, Ar-H), 6.77 (dd, J = 2.0 and 0.8 Hz, 1H, Ar-H), 6.38 (d, J = 2.0 Hz, 1H, Ar-H), 3.87 (s, 3H, $ArOCH_3$), 3.57 (dd, J = 13.4 and 4.3 Hz, 1H, CH), 3.49 (s, 3H, $ArOCH_3$), 3.19−3.08 (m, 2H, CH_2), 2.72−2.59 (m, 1H, CH), 1.73−1.58 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 159.4, 155.2, 149.5, 139.1, 138.7, 137.0, 135.8, 132.7, 128.9, 127.9, 127.6, 126.6 (2 × CH), 126.5 (2 × CH), 126.3 (2 × CH), 125.4, 100.6, 98.2, 55.6, 55.6, 49.5, 30.6, 28.8 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}O_2$ 355.1698; Found 355.1692.

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J. Org. Chem. 2021, 86, 8706−8725

12-Phenyl-6,6a-dihydro-5*H*-benzo[7,8]fluoreno[2,3-*d*][1,3]-dioxole (9g). GP-4 was carried out with 1-(benzo[*d*][1,3]dioxol-5-yl)-3-(2-(phenylethynyl)phenyl)propan-1-ol **7g** (71.2 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 97:3−95:5) furnished the product **9g** (49.3 mg, 73%) as a brown liquid.

TLC (petroleum ether/ethyl acetate 95:05, R_f(**7g**) = 0.20, R_f(**9g**) = 0.85, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3057, 2146, 2073, 1687, 1372, 1263, 730 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.2 Hz, 2H, Ar-H), 7.41−7.34 (m, 3H, Ar-H), 7.17 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.06 (ddd, *J* = 8.8, 7.2, and 3.4 Hz, 2H, Ar-H), 7.02 (s, 1H, Ar-H), 6.86 (t, *J* = 7.6 Hz, 1H, Ar-H), 6.56 (s, 1H, Ar-H), 5.94 (d, *J* = 1.5 Hz, 1H, -OCH_aCH_bO−), 5.92 (d, *J* = 1.5 Hz, 1H, -OCH_aCH_bO−), 3.51 (dd, *J* = 13.5 and 4.2 Hz, 1H, CH), 3.20−3.08 (m, 2H, CH_2), 2.70−2.59 (m, 1H, CH), 1.65−1.56 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 147.0, 145.9, 141.1, 141.1, 139.9, 137.1, 136.3, 136.0, 132.2, 129.2 (2 × CH), 129.0, 128.9 (2 × CH), 127.4, 126.7, 126.4, 125.5, 104.0, 101.4, 100.9, 48.9, 30.6, 28.7 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{24}H_{19}O_2$ 339.1385; Found 339.1381.

9-Chloro-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluorene (9h). GP-4 was carried out with 1-(4-chlorophenyl)-3-(2-(phenylethynyl)phenyl)propan-1-ol **7h** (71.2 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate/hexane to 99:1) furnished the product **9h** (39.3 mg, 60%) as colorless liquid.

TLC (petroleum ether/ethyl acetate 98:2, R_f(**7h**) = 0.20, R_f(**9h**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3064, 2923, 1722, 1449, 1289, 1073, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.52 (t, *J* = 7.1 Hz, 2H, Ar-H), 7.48−7.37 (m, 4H, Ar-H), 7.28−7.20 (m, 2H, Ar-H), 7.16 (dd, *J* = 14.0 and 7.6 Hz, 2H, Ar-H), 7.08 (d, *J* = 1.6 Hz, 1H, Ar-H), 6.93 (t, *J* = 7.6 Hz, 1H, Ar-H), 3.62 (dd, *J* = 13.5 and 4.4 Hz, 1H, CH), 3.28−3.10 (m, 2H, CH_2), 2.78−2.65 (m, 1H, CH), 1.63 (dd, *J* = 12.8 and 5.9 Hz, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 148.8, 144.0, 143.8, 137.6, 135.6, 135.5, 133.1, 131.9, 129.2 (2 × CH), 129.1 (3 × CH), 127.7, 127.5, 126.9, 125.6, 124.6, 123.4, 120.3, 48.8, 30.4, 28.3 ppm. HRMS (ESI) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{17}Cl$ 328.1013; Found 328.1016.

9-Fluoro-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluorene (9i). GP-4 was carried out with 1-(4-florophenyl)-3-(2-(phenylethynyl)-phenyl)propan-1-ol **7i** (66.1 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate/hexane to 99:1) furnished the product **9i** (36.2 mg, 58%) as colorless liquid.

TLC (petroleum ether/ethyl acetate 98:2, R_f(**7i**) = 0.20, R_f(**9i**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 2922, 1749, 1614, 1465, 1345, 1286, 1129, 1060, 920, 761, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.1 Hz, 2H, Ar-H), 7.48−7.42 (m, 2H, Ar-H), 7.41−7.36 (m, 2H, Ar-H), 7.23 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.20−7.10 (m, 2H, Ar-H), 6.96−6.90 (m, 2H, Ar-H), 6.79 (dd, *J* = 9.3 and 2.4 Hz, 1H, Ar-H), 3.61 (dd, *J* = 13.6 and 4.4 Hz, 1H, CH), 3.29−3.08 (m, 2H, CH_2), 2.78−2.65 (m, 1H, CH), 1.72−1.57 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.8 (J_{C-F} = 241 Hz), 149.0 (J_{C-F} = 8.6 Hz), 144.2, 141.2, 137.6, 135.3, 133.5 (J_{C-F} = 3.2 Hz), 131.8, 129.2 (2 × CH), 129.1, 129.0 (2 × CH), 127.7, 127.5, 126.9, 125.5, 123.2 (J_{C-F} = 9 Hz), 111.4 (J_{C-F} = 22 Hz), 107.3 (J_{C-F} = 23.4 Hz), 48.6, 30.5, 28.5 ppm. HRMS (ESI) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{17}F$ 312.1309; Found 312.1291.

13-(4-Methoxyphenyl)-6,6a-dihydro-5*H*-dibenzo[a,g]-fluorene (9j′). GP-4 was carried out with 1-(naphthalen-1-yl)-3-(2-(phenylethynyl)phenyl)propan-1-ol **7j** (78.4 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 97:3−95:5) furnished the product **9j′** (60.6 mg, 81%) as yellow liquid.

TLC (petroleum ether/ethyl acetate 95:5, R_f(**7j**) = 0.20, R_f(**9j′**) = 0.70, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 2936, 1605, 1507, 1249, 1178, 1031, 1345, 840 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 1H, Ar-H), 7.59 (dd, *J* = 8.1 and 1.9 Hz, 2H, Ar-H), 7.50−7.39 (m, 3H, Ar-H), 7.39−7.32 (m, 1H, Ar-H), 7.29−7.22 (m, 2H, Ar-H), 7.16−6.04 (m, 3H, Ar-H), 6.68−6.61 (m, 2H, Ar-H), 5.63 (s, 1H, CH), 3.63 (s, 3H, $ArOCH_3$), 3.15−3.10 (m, 1H, CH), 2.94−2.91 (m, 2H, CH_2), 2.76−2.69 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 157.9, 139.2, 138.6, 136.7, 134.7, 133.2, 133.0, 132.4, 130.4, 128.0 (2 × CH), 127.3, 127.2, 126.7, 126.6, 126.3, 126.3, 126.1, 125.9, 125.5, 123.9, 120.0, 114.1 (2 × CH), 55.0, 46.3, 28.5, 23.4 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{28}H_{23}O$ 375.1743; Found 375.1728.

11-(3,4-Dimethoxyphenyl)-6,6a-dihydro-5*H*-benzo[*a*]-fluorene (9k). GP-4 was carried out with 1-phenyl-3-(2-(phenylethynyl)phenyl)propan-1-ol **7k** (74.4 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 97:3−95:5) furnished the product **9k** (55.2 mg, 78%) as white solid with M.P = 130−132 °C.

TLC (petroleum ether/ethyl acetate 95:05, R_f(**7k**) = 0.30, R_f(**9k**) = 0.80, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 2923, 2853, 1509, 1460, 1249, 1026, 762 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56−7.54 (m, 1H, Ar-H), 7.32−7.25 (m, 3H, Ar-H), 7.23 (dd, *J* = 6.6 and 2.8 Hz, 1H, Ar-H), 7.16 (ddd, *J* = 4.4 Hz, 2.7 and 0.9 Hz, 1H, Ar-H), 7.12 (dd, *J* = 7.5 and 1.3 Hz, 1H, Ar-H), 7.04−6.98 (m, 2H, Ar-H), 6.98−6.90 (m, 2H, Ar-H), 3.99 (s, 3H, $ArOCH_3$), 3.85 (s, 3H, $ArOCH_3$), 3.64 (dd, *J* = 13.5 and 4.3 Hz, 1H, CH), 3.28−3.10 (m, 2H, CH_2), 2.79−2.67 (m, 1H, CH), 1.72−1.59 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 149.3, 148.3, 147.2, 145.7, 141.9, 137.5, 135.9, 132.2, 129.0, 128.7, 127.1, 126.9 (2 × CH), 125.5, 124.8, 122.5, 121.5, 120.2, 112.2, 111.6, 55.9, 55.8, 49.2, 30.6, 28.2 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{25}H_{23}O_2$ 355.1693; Found 355.1685.

9-Methyl-11-(*p*-tolyl)-6,6a-dihydro-5*H*-benzo[*a*]fluorene (9l). GP-4 was carried out with 1-(*p*-tolyl)-3-(2-(*p*-tolylethynyl)-phenyl)propan-1-ol **7l** (70.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate/hexane to 99:1) furnished the product **9l** (53.8 mg, 80%) as yellow oil.

TLC (petroleum ether/ethyl acetate 99:01, R_f(**7l**) = 0.10, R_f(**9l**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3743, 3005, 2937, 2298, 2252, 1438, 1378, 1038, 748 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.32−7.21 (m, 4H, Ar-H), 7.21−7.13 (m, 2H, Ar-H), 7.10−7.00 (m, 2H, Ar-H), 6.88 (s, 1H, Ar-H), 6.85 (d, *J* = 7.6 Hz, 1H, Ar-H), 3.56 (dd, *J* = 13.5 and 4.2 Hz, 1H, CH), 3.23−3.05 (m, 2H, CH_2), 2.70−2.61 (m, 1H, CH), 2.41 (s, 3H, $ArCH_3$), 2.31 (s, 3H, $ArCH_3$), 1.69−1.51 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 147.4, 143.0, 142.2, 137.5, 136.9, 136.6, 136.2, 133.4, 132.4, 129.6 (2 × CH), 129.2 (2 × CH), 129.0, 126.9, 126.8, 125.6, 125.4, 122.2, 120.9, 48.8, 30.6, 28.5, 21.5, 21.4 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{25}H_{23}$ 323.1794; Found 323.1786.

11-(4-Methoxyphenyl)-9-methyl-6,6a-dihydro-5*H*-benzo[*a*]-fluorene (9m). GP-4 was carried out with 3-(2-((4-methoxyphenyl)-ethynyl)phenyl)-1-(*p*-tolyl)propan-1-ol **7m** (70.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 97:3−95:5) furnished the product **9m** (53.8 mg, 80%) as white solid with melting point = 124−122 °C.

TLC (petroleum ether/ethyl acetate 90:10, R_f(**7m**) = 0.30, R_f(**9m**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3384, 2915, 2825, 2150, 2060, 1361, 1172, 946, 888, 831 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.21 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.12−7.06 (m, 2H, Ar-H), 7.00−6.91 (m, 4H, Ar-H), 6.81 (dd, *J* = 12.5 and 3.9 Hz, 2H, Ar-H), 3.78 (s, 3H, $ArOCH_3$), 3.47 (dd, *J* = 13.5 and 4.3 Hz, 1H, CH), 3.15−2.95 (m, 2H, CH_2), 2.61−2.52 (m, 1H, CH), 2.24 (s, 3H, $ArCH_3$), 1.56−1.41 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 158.9, 147.5, 143.0,

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J. Org. Chem. 2021, 86, 8706−8725

142.3, 137.5, 136.6, 135.8, 132.4, 130.4 (2 × CH), 129.0, 128.5, 126.9, 126.8, 125.6, 125.4, 122.2, 120.8, 114.3 (2 × CH), 55.2, 48.8, 30.6, 28.5, 21.5 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}O$ 339.1743; Found 339.1734.

11-(3,4-Dimethoxyphenyl)-9-methyl-6,6a-dihydro-5*H*-benzo[*a*]fluorene (9n). GP-4 was carried out with 3-(2-((3,4-dimethoxyphenyl)ethynyl)phenyl)-1-(*p*-tolyl)propan-1-ol **7n** (71.2 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:5−93:7) furnished the product **9n** (66.4 mg, 89%) as yellow oily.

TLC (petroleum ether/ethyl acetate 85:15, R_f(**7n**) = 0.30, R_f(**9n**) = 0.85, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3024, 2971, 1709, 1542, 1495, 1241, 1157, 1018, 856 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.5 Hz, 1H, Ar-H), 7.23 (dd, J = 10.9 and 4.0 Hz, 2H, Ar-H), 7.14−7.05 (m, 2H, Ar-H), 7.02 (d, J = 8.2 Hz, 1H, Ar-H), 6.98−6.80 (m, 3H, Ar-H), 6.81−6.87 (m, 1H, Ar-H), 3.99 (s, 3H, $ArOCH_3$), 3.83 (s, 3H, $ArOCH_3$), 3.60 (dd, J = 13.5 and 4.3 Hz, 1H, CH), 3.18−3.14 (m, 2H, CH_2), 2.72−2.68 (m, 1H, CH), 2.36 (s, 3H, $ArCH_3$), 1.67−1.56 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 149.3, 148.3, 147.4, 143.0, 142.2, 137.5, 136.7, 135.9, 132.3, 129.0, 128.9, 127.0, 126.9, 125.6, 125.4, 122.2, 121.5, 120.9, 112.3, 111.6, 55.9, 55.8, 48.8, 30.7, 28.4, 21.5 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}O_2$ 369.1849; Found 369.1835.

9-Ethyl-11-(*p*-tolyl)-6,6a-dihydro-5*H*-benzo[*a*]fluorene (9o). GP-4 was carried out with 1-(4-ethylphenyl)-3-(2-(*p*-tolylethynyl)-phenyl)propan-1-ol **7o** (70.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 97:3−95:5) furnished the product **9o** (53.8 mg, 78%) as white liquid.

TLC (petroleum ether/ethyl acetate 99:1, R_f(**7o**) = 0.20, R_f(**9o**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3018, 2924, 1676, 1605, 1360, 1147, 880, 732 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.5 Hz, 1H, Ar-H), 7.32−7.27 (m, 4H, Ar-H), 7.21 (t, J = 7.7 Hz, 2H, Ar-H), 7.13−7.09 (m, 2H, Ar-H), 6.96 (s, 1H, Ar-H), 6.92 (t, J = 7.5 Hz, 1H, Ar-H), 3.61 (dd, J = 13.5 and 4.2 Hz, 1H, CH), 3.25−3.12 (m, 2H, CH_2), 2.73−2.63 (m, 3H, CH and CH_2CH_3), 2.46 (s, 3H, $ArCH_3$), 1.69−1.51 (m, 1H, CH), 1.24 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 147.4, 143.4, 143.2, 142.2, 137.5, 136.9, 136.3, 133.4, 132.4, 129.6 (2 × CH), 129.2 (2 × CH), 129.0, 126.9, 126.9, 125.4, 124.4, 122.3, 119.8, 48.8, 30.7, 29.4, 28.5, 21.5, 16.0 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}$ 337.1951; Found 337.1940.

9-ethyl-11-(4-ethylphenyl)-6,6a-dihydro-5*H*-benzo[*a*]-fluorene (9p). GP-4 was carried out with 1-(4-ethylphenyl)-3-(2-((4-ethylphenyl)ethynyl)phenyl)propan-1-ol **7p** (73.6 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate/hexane to 99:1) furnished the product **9p** (50.4 mg, 72%) as white liquid.

TLC (petroleum ether/ethyl acetate 99:1, R_f(**7p**) = 0.20, R_f(**9p**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2974, 1749, 1614, 1465, 1345, 1286, 1129, 1060, 920, 761, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.46 (d, J = 7.5 Hz, 1H, Ar-H), 7.33−7.32 (m, 4H, Ar-H), 7.24−7.17 (m, 2H, Ar-H), 7.14−7.07 (m, 2H, Ar-H), 6.97 (s, 1H, Ar-H), 6.92 (t, J = 7.4 Hz, 1H, Ar-H), 3.60 (dd, J = 13.5 and 4.3 Hz, 1H, CH), 3.22−3.08 (m, 2H, CH_2), 2.78 (q, J = 7.6 Hz, 2H, CH_2CH_3), 2.75−2.68 (m, 1H, CH), 2.66 (q, J = 7.3 Hz, 2H, CH_2CH_3), 1.69−1.58 (m, 1H, CH), 1.36 (t, J = 7.3 Hz, 3H, CH_2CH_3), 1.24 (t, J = 7.5 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 147.4, 143.3, 143.2 (2 × C), 142.2, 137.5, 136.3, 133.5, 132.4, 129.2 (2 × CH), 129.0, 128.3 (2 × CH), 126.9, 126.8, 125.4, 124.4, 122.3, 119.9, 48.8, 30.6, 29.0, 28.6, 28.4, 16.1, 15.4 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{27}$ 351.2107; Found 351.2112.

9-Ethyl-11-(4-methoxyphenyl)-6,6a-dihydro-5*H*-benzo[*a*]-fluorene (9q). GP-4 was carried out with 1-(4-ethylphenyl)-3-(2-((4-methoxyphenyl)ethynyl)phenyl)propan-1-ol **7q** (74.0 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 97:3−95:5) furnished the product **9q** (52.8 mg, 75%) as colorless liquid.

TLC (petroleum ether/ethyl acetate 93:07, R_f(**7q**) = 0.20, R_f(**9q**) = 0.75, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3010, 2534, 1694, 1508, 1462, 1290, 1245, 1130, 951, 815, 660 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, J = 7.5 Hz, 1H, Ar-H), 7.33 (m, J = 7.9 Hz, 2H, Ar-H), 7.24−7.17 (m, 2H, Ar-H), 7.13−7.07 (m, 2H, Ar-H), 7.04−7.01 (m, 2H, Ar-H), 6.95 (s, 1H, Ar-H), 6.92 (t, J = 7.6 Hz, 1H, Ar-H), 3.91 (s, 3H, $ArOCH_3$), 3.59 (dd, J = 13.5 and 4.3 Hz, 1H, CH), 3.16 (ddd, J = 17.1 Hz, 12.7 and 8.2 Hz, 2H, CH_2), 2.73−2.59 (m, 3H, CH and CH_2CH_3), 1.70−1.56 (m, 1H, CH), 1.23 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 158.9, 147.5, 143.3, 143.2, 142.3, 137.5, 135.9, 132.5, 130.5 (2 × CH), 129.0, 128.5, 126.9, 126.8, 125.4, 124.5, 122.3, 119.7, 114.4 (2 × CH), 55.2, 48.8, 30.9, 29.0, 28.4, 16.1 ppm. HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{26}H_{24}O$ 352.1822; Found 352.1813.

11-(3,5-Dimethoxyphenyl)-9-ethyl-6,6a-dihydro-5*H*-benzo-[*a*]fluorene (9r). GP-4 was carried out with 3-(2-((3,5-dimethoxyphenyl)ethynyl)phenyl)-1-(4-ethylphenyl)propan-1-ol **7r** (80.0 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 97:3−95:5) furnished the product **9r** (60.3 mg, 79%) as yellow oil.

TLC (petroleum ether/ethyl acetate 95:05, R_f(**7r**) = 0.20, R_f(**9r**) = 0.80, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 2923, 2852, 1605, 1486, 1252, 1037, 753, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.5 Hz, 1H, Ar-H), 7.28−7.24 (m, 1H, Ar-H), 7.17 (t, J = 5.5 Hz, 1H, Ar-H), 7.09−7.07 (m, 2H, Ar-H), 6.97 (s, 1H, Ar-H), 6.92 (t, J = 7.4 Hz, 1H, Ar-H), 6.55−6.53 (m, 3H, Ar-H), 3.76 (s, 6H, 2 × $ArOCH_3$), 3.57 (dd, J = 13.5 and 4.3 Hz, 1H, CH), 3.24−3.01 (m, 2H, CH_2), 2.74−2.66 (m, 1H, CH), 2.63 (q, J = 7.6 Hz, 2H, CH_2CH_3), 1.64−1.53 (m, 1H, CH), 1.21 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.2 (2 × C), 147.1, 143.2, 143.1, 142.2, 138.6, 137.5, 136.1, 132.1, 128.9, 127.1, 127.0, 125.5, 124.5, 122.3, 119.8, 106.9, 99.9 (2 × CH), 55.3 (2 × OCH_3), 48.9, 30.6, 29.0, 28.3, 16.1 ppm. HRMS (ESI) m/z: $[M+ H]^+$ Calcd for $C_{27}H_{27}O_2$ 383.2006; Found 383.1997.

9-Ethyl-11-(4-fluorophenyl)-6,6a-dihydro-5*H*-benzo[*a*]-fluorene (9s). GP-4 was carried out with 1-(4-ethylphenyl)-3-(2-((4-fluorophenyl)ethynyl)phenyl)propan-1-ol **7s** (71.6 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate/hexane to 99:1) furnished the product **9s** (46.2 mg, 68%) as colorless liquid.

TLC (petroleum ether/ethyl acetate 99:01, R_f(**7s**) = 0.20, R_f(**9s**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 2923, 2852, 1728, 1605, 1252, 1037, 753 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.53 (d, J = 7.5 Hz, 1H, Ar-H), 7.44−7.26 (m, 2H, Ar-H), 7.27 (dt, J = 8.9 and 6.5 Hz, 3H, Ar-H), 7.19 (ddd, J = 6.7 Hz, 3.3.Hz and 1.4 Hz, 3H, Ar-H), 6.99 (dd, J = 7.4 and 4.2 Hz, 2H, Ar-H), 3.67 (dd, J = 13.5 and 4.3 Hz, 1H, CH), 3.32−3.14 (m, 2H, CH_2), 2.84−2.74 (m, 1H, CH), 2.76−2.66 (m, 2H, CH_2CH_3), 1.76−1.61 (m, 1H, CH), 1.30 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.2 (J_{C-F}= 245 Hz), 147.1, 143.3, 143.3, 142.9, 137.6, 135.1, 132.3 (J = 4 Hz), 132.1, 131.1, 130.1, 129.1, 127.2, 126.7, 125.5, 124.7, 122.4, 119.6, 116.1, 115.9, 48.8, 30.6, 29.0, 28.4, 16.1 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{22}F$ 341.1700; Found 341.1687.

9-Isopropyl-11-(*p*-tolyl)-6,6a-dihydro-5*H*-benzo[*a*]fluorene (9t). GP-4 was carried out with 1-(4-isopropylphenyl)-3-(2-(*p*-tolylethynyl)phenyl)propan-1-ol **7t** (73.6 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel

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J. Org. Chem. 2021, 86, 8706−8725

column chromatography (petroleum ether/ethyl acetate/hexane to 99:1) furnished the product **9t** (54.6 mg, 78%) as yellow oil.

TLC (petroleum ether/ethyl acetate 99:1, R_f(**7t**) = 0.20, R_f(**9t**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3049, 2858, 1608, 1469, 1359, 1048, 811, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.5 Hz, 1H, Ar-H), 7.32−7.27 (m, 4H, Ar-H), 7.21−7.16 (t, 2H, Ar-H), 7.15−7.10 (m, 2H, Ar-H), 6.97 (s, 1H, Ar-H), 6.90 (t, J = 7.5 Hz, 1H, Ar-H), 3.58 (dd, J = 13.5 and 4.2 Hz, 1H, CH), 3.17−3.14 (m, 2H, CH_2), 2.90 (dt, J = 13.8 and 6.9 Hz, 1H, CH), 2.76−2.64 (m, 1H, $CH(CH_3)_2$), 2.47 (s, 3H, $ArCH_3$), 1.72−1.52 (m, 1H, CH), 1.24 (dd, J = 6.9 and 1.0 Hz, 6H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 147.9, 147.3, 143.5, 142.2, 137.5, 136.9, 136.4, 133.4, 132.5, 129.6 (2 × CH), 129.2 (2 × CH), 129.0, 126.9, 126.9, 125.4, 122.8, 122.3, 118.5, 48.8, 34.3, 30.7, 28.4, 24.3, 24.2, 21.4 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{27}$ 351.2107; Found 351.2099.

9-Isopropyl-11-(4-methoxyphenyl)-6,6a-dihydro-5*H*-benzo[*a*]fluorene (9u). GP-4 was carried out with 1-(4-isopropylphenyl)-3-(2-((4-methoxyphenyl)ethynyl)phenyl)propan-1-ol **7u** (76.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 98:2−97:3) furnished the product **9u** (59.3 mg, 81%) as yellow oil.

TLC (petroleum ether/ethyl acetate 95:5, R_f(**7u**) = 0.20, R_f(**9u**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 2924, 2958, 1599, 1508, 1244, 1244, 1033, 765 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.6 Hz, 1H, Ar-H), 7.36 (d, J = 7.8 Hz, 2H, Ar-H), 7.25−7.20 (m, 2H, Ar-H), 7.20−7.10 (m, 2H, Ar-H), 7.07 (d, J = 8.6 Hz, 2H, Ar-H), 7.01 (s, 1H, Ar-H), 6.95 (t, J = 7.6 Hz, 1H, Ar-H), 3.94 (s, 3H, $ArOCH_3$), 3.61 (dd, J = 13.5 and 4.3 Hz, 1H, CH), 3.30−3.06 (m, 2H, CH_2), 2.94 (dt, J = 13.8 and 6.9 Hz, 1H, CH), 2.77−2.68 (m, 1H, CH), 1.70−1.59 (m, 1H, $CH(CH_3)_2$), 1.28 (dd, J = 6.9 and 1.1 Hz, 6H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 158.9, 148.0, 147.5, 143.5, 142.3, 137.6, 136.1, 132.5, 130.6 (2 × CH), 129.2, 128.6, 127.0, 126.9, 125.5, 123.0, 122.4, 118.5, 114.4 (2 × CH), 55.3, 48.8, 34.3, 30.7, 28.4, 24.4 (2 × CH_3) ppm. HRMS (ESI) m/z: $[M+H^+]+[-H_2O]$ Calcd for $C_{27}H_{25}$ 349.1950; Found 349.1958.

9-Isopropyl-11-(2-methoxyphenyl)-6,6a-dihydro-5H-benzo[a]fluorene (9v). GP-4 was carried out with 1-(4-isopropylphenyl)-3-(2-((2-methoxyphenyl)ethynyl)phenyl)propan-1-ol **7v** (76.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 98:2−97:3) furnished the product **9v** (48.2 mg, 70%) as yellow oil. TLC (petroleum ether/ethyl acetate 95:5, R_f(**7v**) = 0.20, R_f(**9v**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 2924, 2958, 1599, 1508, 1244, 1244, 1033, 765 cm^{-1}. ^1H NMR according to the major isomer (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 7.6, 3.4 Hz, 2H, Ar-H), 7.27 (d, J = 4.2 Hz, 1H, Ar-H), 7.23−7.16 (m, 4H, Ar-H), 7.07 (d, J = 6.6 Hz, 1H, Ar-H), 6.98 (t, J = 7.3 Hz, 2H, Ar-H), 6.91 (s, 1H, Ar-H), 3.90 (s, 3H, $ArOCH_3$), 3.73 (dd, J = 13.6, 4.4 Hz, 1H, CH), 3.33−3.21 (m, 2H), 3.00 (dd, J = 13.8 and 6.9 Hz, 1H, CH), 2.81−2.76 (m, 1H, CH), 1.74−1.67 (m, 1H, CH), 1.31 (dd, J = 4.2, 2.7 Hz, 6H, 2 × CH_3). ^1H NMR according to the major isomer: $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 158.1, 147.6, 146.8, 143.5, 143.0, 142.9, 137.6, 133.5, 132.6, 131.0, 129.01, 128.9 (2 × CH), 127.0, 125.5, 122.8, 122.2, 121.2, 118.8, 111.3, 55.6, 49.0, 34.3, 30.8, 28.5, 24.5, 24.2 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{27}O$ 367.2056; Found 367.2041.

8,10-dimethoxy-11-(*p*-tolyl)-6,6a-dihydro-5H-benzo[*a*]fluorene (9w). GP-4 was carried out with 1-(3,5-dimethoxyphenyl)-3-(2-(*p*-tolylethynyl)phenyl)propan-1-ol **7w** (73.6 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 97:3−95:5) furnished the product **9w** (44.9 mg, 64%) as yellow oil. TLC (petroleum ether/ethyl acetate 90:10, R_f(**7w**) = 0.20, R_f(**9w**) = 0.80, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3410, 2927, 1691, 1598, 1456, 1257, 1075, 873, 813, 752, 654 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.33−7.12 (m, 5H, Ar-H), 7.03 (td, J = 7.5 and 1.3 Hz, 1H, Ar-H), 6.93 (d, J = 8.0 Hz, 1H, Ar-H), 6.84 (t, J = 7.6 Hz, 1H, Ar-H), 6.76 (dd, J = 2.0 and 0.9 Hz, 1H, Ar-H), 6.39 (d, J = 1.8 Hz, 1H, Ar-H), 3.87 (s, 3H, $ArOCH_3$), 3.55 (dd, J = 13.6 and 4.3 Hz, 1H, CH), 3.51 (s, 3H, $ArOCH_3$), 3.23−3.05 (m, 2H, CH_2), 2.64−2.63 (m, 1H, CH), 2.44 (s, 3H, $ArCH_3$), 1.70−1.57 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.3, 155.2, 149.5, 139.0, 137.0, 136.0, 135.8, 135.5, 132.8, 128.8, 128.6 (2 × CH), 127.7, 126.5 (2 × CH), 126.2 (2 × CH), 125.3, 100.6, 98.3, 55.6, 55.6, 49.5, 30.7, 28.8, 21.4 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}O_2$ 369.1849; Found 369.1834.

8,10-dimethoxy-11-(4-methoxyphenyl)-6,6a-dihydro-5*H*-benzo[*a*]fluorene (9x). GP-4 was carried out with 1-(3,5-dimethoxyphenyl)-3-(2-((4-methoxyphenyl)ethynyl)phenyl)propan-1-ol **7x** (73.6 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 93:7−95:5) furnished the product **9x** (44.9 mg, 64%) as yellow oil.

TLC (petroleum ether/ethyl acetate 90:10, R_f(**7x**) = 0.20, R_f(**9x**) = 0.80, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3410, 2927, 1691, 1598, 1456, 1257, 1075, 873, 813, 752, 654 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44−7.10 (m, 3H, Ar-H), 7.06 (td, J = 7.4 and 1.3 Hz, 1H, Ar-H), 7.02−6.80 (m, 4H, Ar-H), 6.78 (dd, J = 2.1, 0.8 Hz, 1H, Ar-H), 6.41 (d, J = 2.1 Hz, 1H, Ar-H), 3.91 (s, 3H, $ArOCH_3$), 3.89 (s, 3H, $ArOCH_3$), 3.50−3.52 (m, 4H, CH and $ArOCH_3$), 3.26−3.09 (m, 2H, CH_2), 2.76−2.59 (m, 1H, CH), 1.73−1.60 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.3, 158.4, 155.2, 149.5, 139.2, 137.1, 135.5, 132.8, 130.9, 128.9, 127.7, 126.5 (2 × CH), 126.4 (2 × CH), 125.4, 125.3, 113.4, 110.7, 98.3, 55.6 (2 × $ArOCH_3$), 55.2, 49.4, 30.6, 28.8 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}O_3$ 385.1798; Found 385.1784.

9-Chloro-11-(*p*-tolyl)-6,6a-dihydro-5*H*-benzo[*a*]fluorene (9y). GP-4 was carried out with 1-(4-chlorophenyl)-3-(2-(*p*-tolylethynyl)phenyl)propan-1-ol **7y** (72.0 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate/hexane to 99:1) furnished the product **9y** (46.5 mg, 68%) as yellow oil.

TLC (petroleum ether/ethyl acetate 99:1, R_f(**7y**) = 0.20, R_f(**9y**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3410, 2927, 1691, 1598, 1456, 1257, 1075, 873, 813, 752, 654 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.9 Hz, 1H, Ar-H), 7.34−7.25 (m, 4H, Ar-H), 7.20 (dd, J = 6.4 Hz, 5.4 and 4.0 Hz, 3H, Ar-H), 7.13 (td, J = 7.5 and 1.2 Hz, 1H, Ar-H), 7.07 (d, J = 1.9 Hz, 1H, Ar-H), 6.93 (t, J = 7.6 Hz, 1H, Ar-H), 3.59 (dd, J = 13.5 and 4.3 Hz, 1H, CH), 3.28−3.08 (m, 2H, CH_2), 2.75−2.63 (m, 1H, CH), 2.46 (s, 3H, $ArCH_3$), 1.72−1.57 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.0, 144.0, 143.6, 137.6, 137.4, 135.4, 132.9, 132.5, 131.9, 129.8 (2 × CH), 129.0 (3 × CH), 127.4, 127.0, 125.6, 124.6, 123.3, 120.4, 48.8, 30.5, 28.3, 21.4 ppm. HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{24}H_{19}Cl$ 342.1170; Found 342.1173.

2-Methoxy-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluorene (9z). GP-4 was carried out with 3-(4-methoxy-2-(phenylethynyl)-phenyl)-1-phenylpropan-1-ol **7z** (68.4 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate/hexane to 95:5) furnished the product **9z** (51.2 mg, 79%) as yellow oil.

TLC (petroleum ether/ethyl acetate 95:5, R_f(**7z**) = 0.20, R_f(**9z**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3054, 2924, 2853, 1686, 1599, 1452, 1265, 746, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.61−7.51 (m, 3H, Ar-H), 7.50−7.40 (m, 3H, Ar-H), 7.35−7.26 (m, 2H, Ar-H), 7.20−7.09 (m, 2H, Ar-H), 6.75 (dd, J = 4.6 and 1.8 Hz, 2H, Ar-H), 3.66 (dd, J = 13.5 and 4.2 Hz, 1H, CH), 3.39 (s, 3H, $ArOCH_3$), 3.26−3.00 (m, 2H, CH_2), 2.85−2.65 (m, 1H, CH), 1.70−1.48 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 157.0, 146.9, 145.8, 142.4, 136.5 (2 × C), 132.7, 129.8, 129.9, 129.4 (2 × CH), 128.9 (2 × CH), 127.4, 126.9, 124.9, 122.5,

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J. Org. Chem. 2021, 86, 8706−8725

120.2, 115.1, 109.9, 56.4, 49.2, 29.8, 28.5 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{21}O$ 325.1587; Found 325.1565.

9-Ethyl-3-methoxy-11-(4-methoxyphenyl)-6,6a-dihydro-5*H*-benzo[*a*]fluorene (9aa). GP-4 was carried out with 1-(4-ethylphenyl)-3-(4-methoxy-2-((4-methoxyphenyl)ethynyl)phenyl)-propan-1-ol **7aa** (80.0 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 97:3) furnished the product **9aa** (76.4 mg, 68%) as yellow oil.

TLC (petroleum ether/ethyl acetate 95:5, R_f(**7aa**) = 0.20, R_f(**9aa**) = 0.80, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3054, 2924, 2853, 1686, 1599, 1452, 1265, 746, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.36 (d, *J* = 7.7 Hz, 2H, Ar-H), 7.14−7.09 (m, 2H, Ar-H), 7.06 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.97 (d, *J* = 0.9 Hz, 1H, Ar-H), 6.78 (d, *J* = 2.7 Hz, 1H, Ar-H), 6.71 (dd, *J* = 8.4 and 2.7 Hz, 1H, Ar-H), 3.90 (s, 3H, $ArOCH_3$), 3.58 (dd, *J* = 13.5 and 4.2 Hz, 1H, CH), 3.42 (s, 3H, $ArOCH_3$), 3.15−3.01 (m, 2H, CH_2), 2.74−2.61 (m, 3H, CH_2CH_3 and CH), 1.66−1.51 (m, 1H, CH), 1.24 (t, *J* = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 158.9, 157.0, 147.4, 143.3, 143.2, 142.5, 136.2, 133.1, 130.6 (2 × CH), 129.8, 128.6 (2 × C), 124.5, 122.4, 119.7, 114.8, 114.4 (2 × CH), 110.1, 55.3, 54.7, 48.8, 29.9, 29.0, 28.6, 16.1 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{27}O_2$ 383.2006; Found 383.1988.

3-Fluoro-9-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]-fluorene (9ab). GP-4 was carried out with 3-(5-fluoro-2-(phenylethynyl)phenyl)-1-(*p*-tolyl)propan-1-ol **7ab** (68.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 1 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate/hexane to 99:1) furnished the product **9ab** (51.5 mg, 79%) as yellow oil.

TLC (petroleum ether/ethyl acetate 99:1, R_f(**7ab**) = 0.20, R_f(**9ab**) = 0.80, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3054, 2924, 2853, 1686, 1599, 1452, 1265, 746, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.54 (t, *J* = 7.3 Hz, 2H, Ar-H), 7.49−7.41 (m, 4H, Ar-H), 7.15−7.10 (m, 2H, Ar-H), 6.95−6.92 (m, 2H, Ar-H), 6.66−6.61 (m, 1H, Ar-H), 3.61 (dd, *J* = 13.5 and 4.3 Hz, 1H, CH), 3.22−3.13 (m, 2H, CH_2), 2.74−2.70 (m, 1H, CH), 2.39 (s, 3H, $ArCH_3$), 1.73−1.58 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 161.7 (J_{C-F} = 246 Hz), 147.2, 142.8, 141.5, 140.0 (J_{C-F} = 7 Hz), 136.8, 136.4, 135.8, 129.4 (2 × CH), 129.1 (2 × CH), 128.6 (J_{C-F} = 4 Hz), 128.5, 125.8, 122.3, 120.9, 115.4 (J_{C-F} = 21 Hz), 112.8 (J_{C-F} = 21 Hz), 48.8, 30.9, 28.3, 21.6 ppm. HRMS (ESI) *m/z*: $[M]^+$ Calcd for $C_{24}H_{19}F$ 326.1465; Found 326.1454.

6a-Methyl-11-phenyl-6,6a-dihydro-5H-benzo[a]fluorene (10a). GP-4 was carried out with 1-phenyl-3-(2-(phenylethynyl)-phenyl)propan-1-ol **8a** (65.2 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 30 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate/hexane to 99:1) furnished the product **10a** (50.5 mg, 82%) as colorless solid with melting point = 124−126 °C.

TLC (petroleum ether/ethyl acetate 99:1, R_f(**8a**) = 0.20, R_f(**10a**) = 0.90, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3015, 1703, 1596, 1452, 1213, 1150, 1011, 838, 747, 697, 599 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46−7.42 (m, 3H, Ar-H), 7.39−7.36 (m, 3H, Ar-H), 7.25−7.21 (m, 3H, Ar-H), 7.14−7.11 (m, 2H, Ar-H), 7.10−7.07 (m, 1H, Ar-H), 6.90 (t, *J* = 7.5 Hz, 1H, Ar-H), 3.30−3.17 (m, 1H, CH), 3.03 (dd, *J* = 17.7 and 6.4 Hz, 1H, CH), 2.40 (dd, *J* = 13.0 and 5.6 Hz, 1H, CH), 1.70 (td, *J* = 12.7 and 6.5 Hz, 1H, CH), 1.30 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.4, 147.0, 145.0, 136.7, 136.0, 134.4, 131.5, 129.4 (2 × CH), 128.9, 128.7 (2 × CH), 127.8, 127.3, 127.1, 126.8, 125.3, 125.1, 121.3, 120.5, 49.0, 32.5, 26.7, 20.5 ppm. HRMS (ESI) *m/z*: $[M]^+$ Calcd for $C_{24}H_{20}$ 308.1560; Found 308.1555.

11-(4-Methoxyphenyl)-6a-methyl-6,6a-dihydro-5*H*-benzo-[*a*]fluorene (10b). GP-4 was carried out with 4-(2-((4-methoxyphenyl)ethynyl)phenyl)-2-phenylbutan-2-ol **8b** (71.2 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 30 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 98:2−97:3) furnished the product **10b** (52.7 mg, 78%) as white solid with melting point = 108−110 °C.

TLC (petroleum ether/ethyl acetate 95:5, R_f(**8b**) = 0.20, R_f(**10b**) = 0.80, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3009, 2917, 1593, 1501, 1360, 1284, 1169, 1024, 826, 749 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44−7.41 (m, 1H, Ar-H), 7.30 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.25−7.19 (m, 3H, Ar-H), 7.16−7.14 (m, 2H, Ar-H), 7.10 (dd, *J* = 7.5 and 1.4 Hz, 1H, Ar-H), 6.98 (dd, *J* = 7.6 and 1.3 Hz, 2H, Ar-H), 6.92 (t, *J* = 7.3 Hz, 1H, Ar-H), 3.85 (s, 3H, $ArOCH_3$), 3.29−3.15 (m, 1H, CH), 3.02 (dd, *J* = 17.7 and 6.3 Hz, 1H, CH), 2.41−2.36 (m, 1H, CH), 1.67 (td, *J* = 12.7 and 6.5 Hz, 1H, CH), 1.28 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.8, 152.4, 146.8, 145.2, 136.7, 134.0, 131.6, 130.6 (2 × CH), 128.9, 128.0, 127.8, 127.0, 126.7, 125.3, 125.0, 121.2, 120.5, 114.2 (2 × CH), 55.2, 48.9, 32.5, 26.7, 20.6 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{23}O$ 339.1743; Found 339.1730.

11-(3,5-Dimethoxyphenyl)-6a-methyl-6,6a-dihydro-5*H*-benzo[*a*]fluorene (10c). GP-4 was carried out with 4-(2-((3,5-dimethoxyphenyl)ethynyl)phenyl)-2-phenylbutan-2-ol **8c** (77.3 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 30 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 98:2−97:3) furnished the product **10c** (64.8 mg, 80%) as white solid with Melting point = 126−128 °C.

TLC (petroleum ether/ethyl acetate 90:10, R_f(**8c**) = 0.20, R_f(**10c**) = 0.80, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3055, 2926, 1688, 1357, 1313, 1188, 1145, 940, 748, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44−7.40 (m, 1H, Ar-H), 7.26−7.20 (m, 5H, Ar-H), 7.11 (td, *J* = 7.4 and 1.3 Hz, 1H, Ar-H), 6.94 (t, *J* = 7.4 Hz, 1H, Ar-H), 6.52−6.49 (m, 3H, Ar-H), 3.76 (s, 6H, 2 × $ArOCH_3$), 3.26−3.17 (m, 1H, CH), 3.02 (dd, *J* = 17.7 and 6.2 Hz, 1H, CH), 2.44−2.34 (m, 1H, CH), 1.68 (td, *J* = 12.7 and 6.5 Hz, 1H, CH), 1.29 (s, 3H, $ArCH_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 161.1 (2 × C), 152.3, 146.9, 144.8, 138.0, 136.7, 134.3, 131.3, 128.9, 127.9, 127.2, 126.8, 125.4, 125.1, 121.2, 120.6, 107.1 (2 × CH), 99.9, 55.4 (2 × OCH_3), 49.0, 32.4, 26.4, 20.6 ppm. HRMS (ESI) *m/z*: $[M+K]^+$ Calcd for $C_{26}H_{24}O_2K$ 407.1408; Found 407.1381.

6a,11-Diphenyl-6,6a-dihydro-5*H*-benzo[*a*]fluorene (10d). GP-4 was carried out with 1,1-diphenyl-3-(2-(phenylethynyl)phenyl)-propan-1-ol **8d** (77.6 mg, 0.2 m mol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 30 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate:Hexane to 99:1) furnished the product **10d** (58.5 mg, 79%) as white solid with melting point = 130−132 °C.

TLC (petroleum ether/ethyl acetate 99:1, R_f(**8d**) = 0.20, R_f(**10d**) = 0.80, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3052, 2965, 2923, 1455, 751, 703 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47−7.34 (m, 8H, Ar-H), 7.16−7.11 (m, 4H, Ar-H), 7.10−7.03 (m, 3H, Ar-H), 6.97−6.94 (m, 2H, Ar-H), 6.85−6.81 (m, 1H, Ar-H), 3.16 (ddd, *J* = 13.4, 4.6, and 2.3 Hz, 1H, Ar-H), 2.89 (dt, *J* = 7.4 and 6.9 Hz, 2H, CH_2), 1.99 (ddd, *J* = 13.4, 11.1, and 7.3 Hz, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 151.3, 145.6, 144.6, 140.9, 137.2, 136.9, 135.7, 132.1, 129.4 (2 × CH), 128.8 (2 × CH), 128.7, 128.6 (2 × CH), 127.6, 127.5, 127.2, 126.8, 126.5, 126.3 (2 × CH), 125.5, 125.3, 122.5, 120.7, 57.5, 32.5, 27.1 ppm. HRMS (ESI) *m/z*: $[M+NH_4]^+$ Calcd for $C_{29}H_{26}N$ 388.2060; Found 388.2060.

9-Chloro-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]-fluorene (10e). GP-4 was carried out with 2-(4-chlorophenyl)-4-(2-(phenylethynyl)phenyl)butan-2-ol **8e** (72.0 mg, 0.2 m mol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 30 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate/hexane to 99:1) furnished the product **10e** (56.1 mg, 82%) as yellow oily.

TLC (petroleum ether/ethyl acetate 99:1, R_f(**8e**) = 0.20, R_f(**10e**) = 0.80, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3015, 1703, 1596, 1452, 1213, 1150, 1011, 838, 747, 697, 599 cm^{-1}. ^1H

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J. Org. Chem. 2021, 86, 8706−8725

NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, J = 11.0 and 4.6 Hz, 2H, Ar-H), 7.33 (ddd, J = 6.2 Hz, 3.0 and 1.5 Hz, 1H, Ar-H), 7.27 (dd, J = 11.5 and 3.7 Hz, 3H, Ar-H), 7.18−7.11 (td, J = 7.5 and 1.3 Hz, 2H, Ar-H), 7.07 (td, J = 7.5 and 1.3 Hz, 1H, Ar-H), 7.00 (dd, J = 9.1 and 1.3 Hz, 2H, Ar-H), 6.85 (t, J = 7.5 Hz, 1H, Ar-H), 3.20−3.15 (m, 1H, CH), 3.03−2.94 (dd, J = 17.7 and 6.4 Hz, 1H, CH), 2.34−2.29 (m, 1H, CH), 1.65−1.57 (m, 1H, CH), 1.22 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.6, 148.6, 146.7, 136.7, 135.3, 133.5, 132.7, 131.7, 129.3 (2 × CH), 129.0 (2 × CH), 128.9, 127.8, 127.5, 127.5, 125.4, 124.9, 122.2, 120.6, 48.8, 32.4, 26.5, 20.6 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}Cl$ 343.1248; Found 343.1251.

6a-Methyl-12-phenyl-6,6a-dihydro-5*H*-benzo[7,8]fluoreno-[2,3-*d*][1,3]dioxole (10f). GP-4 was carried out with 2-(benzo[*d*]-[1,3]dioxol-5-yl)-4-(2-(phenylethynyl)phenyl)butan-2-ol **8f** (74.0 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 30 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 97:3) furnished the product **10f** (56.3 mg, 80%) as yellow oil.

TLC (petroleum ether/ethyl acetate 95:5, R_f(**8f**) = 0.20, R_f(**10f**) = 0.80, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3015, 1703, 1596, 1452, 1213, 1150, 1011, 838, 747, 697, 599 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47−7.40 (m, 2H, Ar-H), 7.39−7.35 (m, 3H, Ar-H), 7.22 (d, J = 7.7 Hz, 1H, Ar-H), 7.11 (td, J = 7.5 and 1.3 Hz, 1H, Ar-H), 7.03 (dd, J = 7.9 and 1.0 Hz, 1H, Ar-H), 6.96 (s, 1H, Ar-H), 6.90 (t, J = 7.4 Hz, 1H, Ar-H), 6.61 (s, 1H, Ar-H), 5.95 (dd, J = 9.8 and 1.4 Hz, 2H, -OCH_2O−), 3.25−3.15 (m, 1H, CH), 3.03 (dd, J = 17.7 and 6.4 Hz, 1H, CH), 2.36−2.31 (m, 1H, CH), 1.72−1.64 (m, 1H, CH), 1.27 (s, 3H, Ar-CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.8, 146.8, 146.1, 145.9, 138.8, 136.3, 136.0, 134.2, 131.6, 129.3 (2 × CH), 128.3, 128.8 (2 × CH), 127.4, 127.3, 126.7, 125.3, 102.9, 101.7, 100.9, 48.7, 32.8, 26.7, 20.7 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{21}O_2$ 353.1536; Found 353.1522.

9-Chloro-6a-ethyl-11-(4-methoxyphenyl)-6,6a-dihydro-5*H*-benzo[*a*]fluorene (10g). GP-4 was carried out with 3-(4-chlorophenyl)-1-(2-((4-methoxyphenyl)ethynyl)phenyl)pentan-3-ol **8g** (74.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 30 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 98:2−97:3) furnished the product **10g** (57.7 mg, 82%) as yellow oil.

TLC (petroleum ether/ethyl acetate 95:05, R_f(**8g**) = 0.20, R_f(**10g**) = 0.80, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3015, 1703, 1596, 1452, 1213, 1150, 1011, 838, 747, 697, 599 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28−7.24 (m, 3H, Ar-H), 7.16 (ddd, J = 9.2 Hz, 8.6 and 4.5 Hz, 2H, Ar-H), 7.12−7.07 (m, 3H, Ar-H), 6.96 (d, J = 8.8 Hz, 2H, Ar-H), 6.91 (t, J = 7.5 Hz, 1H, Ar-H), 3.85 (s, $ArOCH_3$), 3.23−3.15 (m, 1H, CH), 2.88 (dd, J = 17.7 and 6.4 Hz, 1H, CH), 2.41 (dd, J = 13.2 and 5.8 Hz, 1H, CH), 1.84−1.59 (m, 3H, CH_2CH_3 and CH), 0.48 (s, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.9, 148.6, 148.2, 146.9, 136.9, 134.2, 132.6, 131.2, 130.4 (2 × CH), 128.9, 127.6, 127.4, 127.3, 125.4, 124.6, 122.4, 120.4, 114.3 (2 × CH), 55.2, 52.6, 31.3, 26.2, 26.1, 8.1 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{24}ClO$ 387.1510; Found 387.1484.

12-(3,4-Dimethoxyphenyl)-6a-ethyl-6,6a-dihydro-5*H*-benzo[7,8]fluoreno[2,3-*d*][1,3]dioxole (10h). GP-4 was carried out with 3-(benzo[*d*][1,3]dioxol-5-yl)-1-(2-((3,4-dimethoxyphenyl)-ethynyl)phenyl)pentan-3-ol **8h** (88.8 mg, 0.2 mmol), and $BF_3{\cdot}OEt_2$ (16.8 mg, 30 mol %) in dry DCE (2 mL) at 0 °C to room temperature for 30 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 98:2−97:3) furnished the product **10h** (68.1 mg, 80%) as yellow oil. TLC (petroleum ether/ethyl acetate 95:5, R_f(**8h**) = 0.20, R_f(**10h**) = 0.80, UV detection. IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 3015, 1703, 1596, 1452, 1213, 1150, 1011, 838, 747, 697, 599 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.23−7.17 (m, 1H, Ar-H), 7.11−7.09 (m, 2H, Ar-H), 6.99−6.90 (m, 4H, Ar-H), 6.83 (s, 1H, Ar-H), 6.65 (s, 1H, Ar-H), 5.95 (dd, J = 11.0 and 1.4 Hz, 2H, -OCH_2O−), 3.96 (s, 3H, $ArOCH_3$), 3.80 (s, 3H, $ArOCH_3$), 3.18−3.14 (m, 1H, CH), 3.00 (dd, J = 17.8 and 6.6 Hz, 1H, CH), 2.39 (dd, J = 13.2 and 5.6 Hz, 1H, CH), 1.82−1.64 (m, 3H, CH_2 and CH), 0.52 (t, J = 7.3 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.1, 148.2, 146.6, 145.8, 144.6, 144.3, 140.2, 136.4, 135.1, 131.6, 128.8, 128.3, 127.2, 126.7, 125.2, 121.6, 112.3, 111.3, 103.2, 101.4, 100.8, 55.8, 55.7, 52.4, 31.7, 26.4, 26.3, 8.1 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{27}O_4$ 427.1904; Found 427.1874.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00525.

Copies of ^1H and $^{13}C\{^1H\}$ NMR spectra for all starting materials and final compounds (PDF)

Accession Codes

CCDC 2063966−2063967 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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