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Note

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Employing Arynes for the Generation of Aryl Anion Equivalents and Subsequent Reaction with Aldehydes

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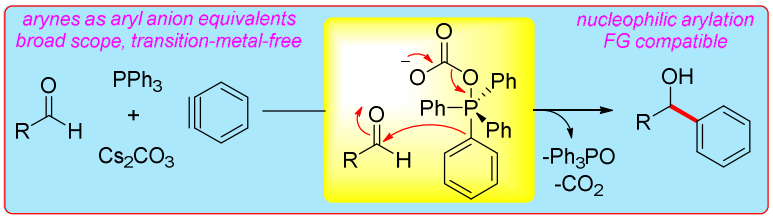
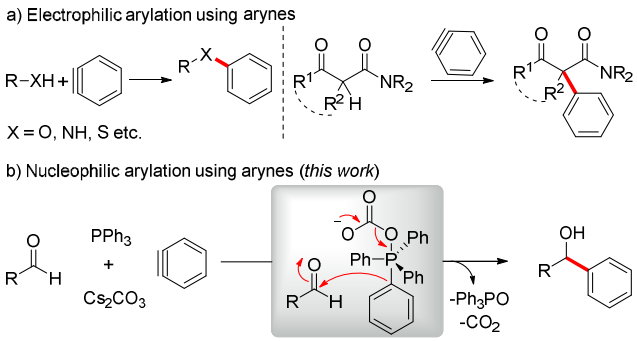


ABSTRACT: Arynes are highly reactive intermediates, which are utilized for the electrophilic arylation of various X-H bonds (X = O, N, S etc.). Herein, a new synthetic strategy is demonstrated, where arynes are converted into aryl anion equivalents by treating with phosphines and a base. The addition of phosphines to arynes form the phosphonium salts, which in the presence of a carbonate base generates the aryl anion equivalent. Subsequent addition of the aryl anions with aldehydes afforded the secondary alcohols.

Ever since the seminal discovery of 2-trimethylsilylaryl triflates as a precursor for the mild and convenient generation of arynes,[1] the chemistry of this highly reactive intermediate has witnessed a resurgence of interest in the last three decades.[2] The inherent strain in the C-C triple bond of aryne has been exploited in various pericyclic reactions,[3] insertion reactions,[4] multicomponent reactions,[5] molecular rearrangements,[6] and transition-metal-catalyzed reactions.[7] Moreover arynes are widely employed for the electrophilic arylation of X-H bonds (X = O, N, S etc.)[2l] and even for the activated C-H bonds (Scheme 1a).[8] Interestingly, however, the use of arynes for the generation of aryl anions, and thereby for the nucleophilic arylation reactions, to the best of our knowledge is not reported. This will be interesting as this method

will obviate the use of aryl organometallic reagents for the arylation reactions. Herein, we demonstrate the use of arynes for the generation of aryl anion equivalents and subsequent interception with aldehydes for the synthesis of secondary alcohols (Scheme 1b). For this, arynes are initially treated with phosphines for the in situ generation of phosphonium salts,[9] which in the presence of a carbonate base generates the aryl anion equivalent. It may be noted in this context that the nucleophile-triggered generation of aryl anion intermediates from arynes followed by their interception with a third-component is known in the literature.[2d]

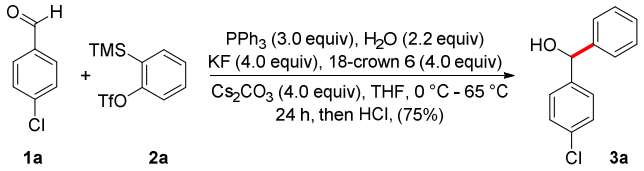
Scheme 1. Transition-Metal-Free Arylation Using Arynes



We have recently reported the aryne multicomponent coupling triggered by phosphines using aldehydes/activated ketones as the third-component for the synthesis of stable pentacovalent phosphoranes based on the benzooxaphosphole system.[10] In this reaction, the initial 1,3-zwitterionic intermediate generated from phosphine and aryne was intercepted with the carbonyl moiety in a formal [3+2] cycloaddition allowing the synthesis of phosphorous heterocycles.[11,12] In this context, we envisioned that if the initially formed 1,3-diplole is protonated by water to generate the phosphonium salt, followed by the addition of a carbonate base to the phosphonium salt could eventually generate the aryl anion, which could intercept the aldehyde to form the secondary alcohol. Related aryl anion generation from tetraaryl phosphonium salt was recently uncovered by Xiao and co-workers[13a] and McNally and co-workers.[14]

The present study was initiated by the treatment of PPh_3 with aryne generated from 2-(trimethylsilyl) aryl triflate **2a**[1] (using KF and 18-crown-6) for the in situ formation of the tetraphenyl phosphonium salt followed by the reaction with 4-chlorobenzaldehyde **1a** in the presence of Cs_2CO_3.[15] Interestingly, under these conditions, the reaction afforded the benzhydrol derivative **3a** in 75% yield (Scheme 2).[16,17] Notably, the benzooxaphosphole derivative (multicomponent adduct)[10] was not observed under these conditions. The addition of water was necessary for the smooth formation of the phosphonium salt, and Cs_2CO_3 was found to be the best carbonate base source for the reaction (over other bases including $SrCO_3$ and K_2CO_3) probably due to the better solubility in THF. The high affinity between oxygen and phosphorus (for the release of $Ph_3P=O$) may be the driving force for the smooth generation of the aryl anion intermediate and subsequent interception with aldehyde.

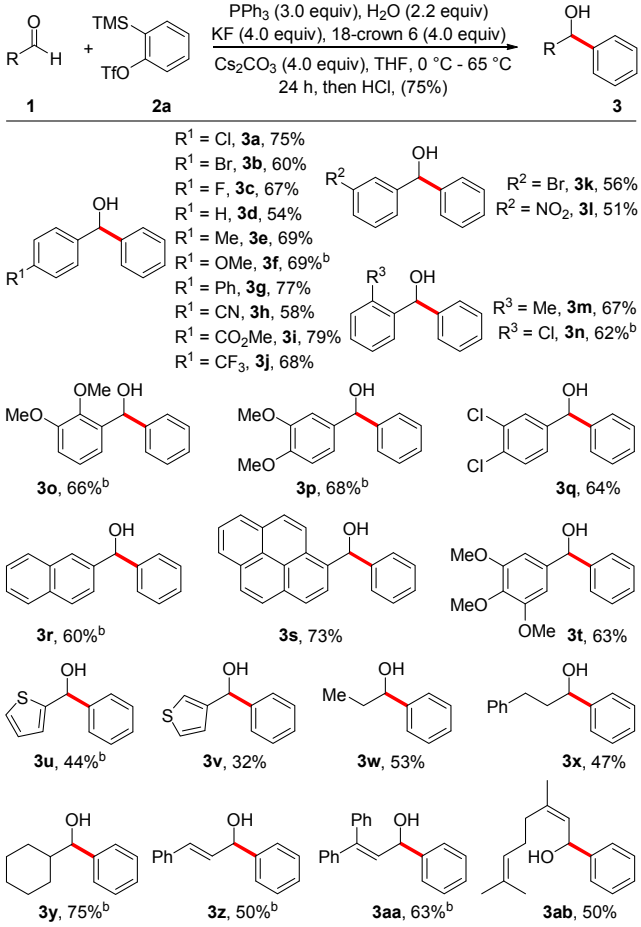
Scheme 2. Nucleophilic Arylation of Aldehydes Using Arynes



With the optimized reaction conditions in hand, we then examined the scope and limitations of the present arylation method (Scheme 3). The in situ generated aryl anion was smoothly added to a range of aromatic aldehydes bearing halogens, electron-releasing, neutral and –withdrawing groups at the 4-position of the ring thereby affording diverse benzhydrol derivatives in moderate to good yield (**3a-3j**). This indicates that the electronic nature of the aldehydes did not significantly influence the outcome of this nucleophilic arylation. Moreover, this nucleophilic arylation was well tolerated by aldehydes having substituents at the 3-position, 2-position as well as di- and tri-substitution to furnish the desired products in moderate to good

yields (**3k-3t**). In addition, heterocyclic aldehydes are found to be good coupling partner for arylation using arynes to afford the aryl heteroaryl methanol derivatives in moderate yield (**3u, 3v**). Interestingly, linear and branched aliphatic aldehydes and α,β-unsaturated aldehydes underwent smooth nucleophilic arylation thus expanding the scope of this reaction (**3w-3ab**). Notably, the reaction using geranial afforded the corresponding alcohol in 50% yield. The enolizable aldehydes did not undergo the aldol condensation or direct addition to arynes under the present reaction conditions.

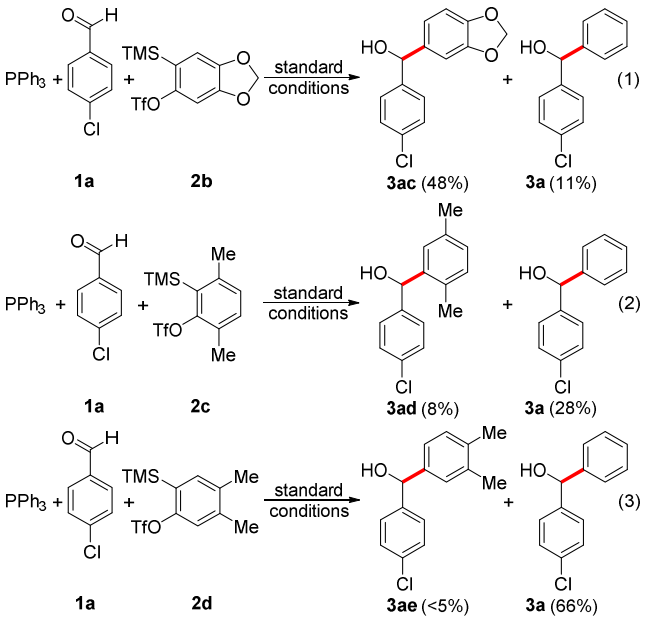
Scheme 3. Substrate Scope of the Reaction[a]



[a] All reactions are performed on 0.25 mmol scale of **1** otherwise indicated. For details on experimental procedure, see the Supporting Information. [b] Reactions performed on 0.5 mmol scale.

Next, we focused our attention on tolerance of the present method with substituents on arynes as well as on phosphines. Performing the reaction under the standard conditions using aryne generated from **2b** afforded the alcohol **3ac** in 48% along with **3a** in 11% (Scheme 4, eq 1). The alcohol **3ac** was formed from the aryl anion generated from the sesamol-derived aryne (formed from **2b**) and the generation of unsubstituted aryl anion from the phosphonium salt upon interception with **1a** could result in the formation of **3a**. The preferential formation of **3ac** in this case could be due to the stabilization of the aryl anion generated from **2b** due to the inductive effect of the two oxygen atoms. Moreover, when the reaction was carried out using aryne generated from **2c**, the alcohol **3ad** was formed in 8% and **3a** in 28% (eq 2). In addition, employing the aryne generated from **2d** in the present arylation reaction afforded the alcohol (generated from the aryne moiety) in traces, and the product **3a** was formed in 66% (eq 3). The

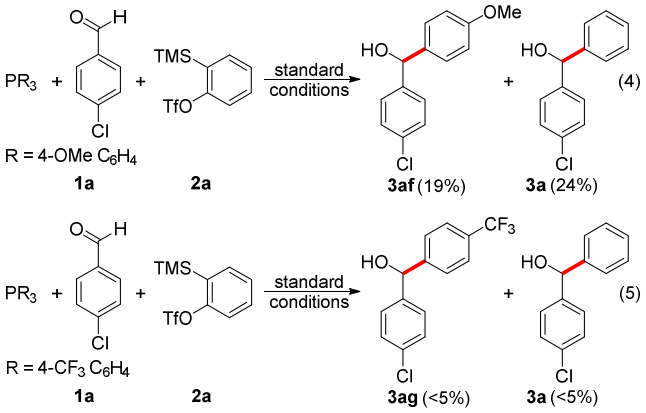
Scheme 4. Variation of Arynes



low reactivity of the aryl anion generated from **2c** and **2d** may be due to the presence of electron-releasing groups, which makes the anion less stable and may readily abstract a proton from the trace water present in the medium.

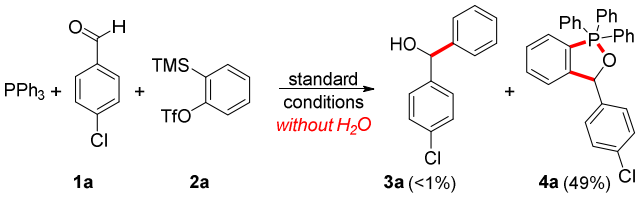
When the reaction was carried out under the standard conditions using tri-*p*-methoxyphenyl phosphine, the reaction furnished a mixture of secondary alcohols **3a** and **3af** in 24% and 19% yield respectively (Scheme 5, eq 4). The formation of **3a** in slightly higher yield may be due to the better leaving group ability of the phenyl group over the *p*-methoxyphenyl group in the initially formed phosphonium salt. Disappointingly, the attempted reaction with the tri-*p*-trifluoromethylphenyl phosphine as the nucleophilic trigger did not afford the expected products **3ag** and **3a** (eq 5). This may be due to the less nucleophilicity of the phosphine for the formation of the tetraaryl phosphonium salt.

Scheme 5. Variation of Phosphines



To demonstrate the role of water in the generation of the tetraaryl phosphonium salt and the aryl anion generation thereof, a reaction was performed in the absence of water. This reaction did not afford the expected alcohol product **3a**, but resulted in the formation of the benzooxaphosphole **4a** in 49% yield (Scheme 6).[10a] In this case, the initially formed 1,3-zwitterion from phosphine and aryne instead of protonation underwent a formal [3+2] annulation with the aldehyde moiety leading to the formation of **4a**.

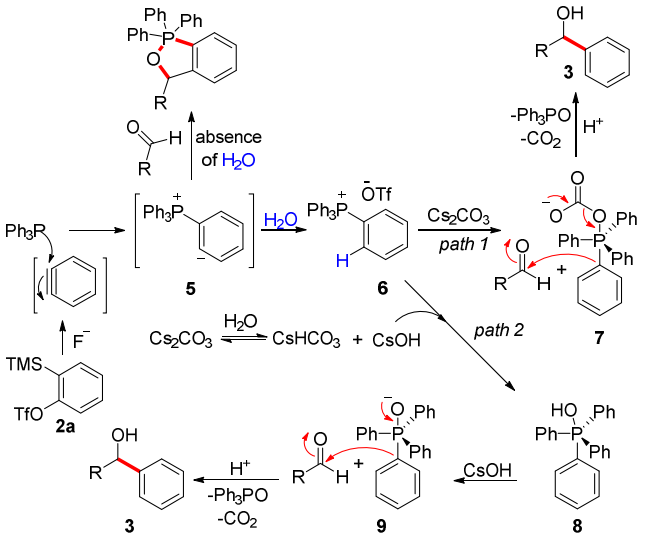
Scheme 6. Reaction in the Absence of H_2O



A proposed mechanism of this nucleophilic arylation using arynes is shown in Scheme 7. The reaction proceeds via the generation of aryne from **2a** using the fluoride source. Nucleophilic addition of phosphine to aryne forms the 1,3-zwitterionic intermediate **5**, which gets protonated in the presence of H_2O to form the tetraaryl phosphonium triflate **6**. In the absence of H_2O, the intermediate **5** undergoes a formal [3+2] annulation with aldehyde to form the benzoxaphosphole derivative. The phosphonium could be converted into the alcohol in two pathways. In pathway 1, the nucleophilic attack of Cs_2CO_3 on the phosphonium cation generates a trigonal bipyramidal tetraaryloxy phosphorane intermediate **7**, where the carbonate and the aryl moiety are in the axial position. Simultaneous decarboxylation and nucleophilic attack of the generated aryl moiety (via the elimination of $Ph_3P{=}O$) on the aldehyde followed by protonation could generate the alcohol **3**. Alternatively, the decomposition of Cs_2CO_3 in presence of H_2O could generate CsOH (pathway 2). The addition of CsOH to the salt **6** could generate the pentavalent phosphorus intermediate **8**, which upon deprotonation in the presence of base generates the oxyanionic phosphorane intermediate **9**. The elimination of aryl anion from **9** (via the elimination of $Ph_3P{=}O$) followed by addition to aldehyde and a subsequent protonation could generate the alcohol **3**. It is reasonable to believe that the elimination of stable $Ph_3P{=}O$ may be the driving force for the generation of aryl anion either from intermediates **7** or **9**. Although the addition of carbonate to **6** generating the intermediate **7** is preferred, the CsOH addition to **6** leading to intermediate **8** cannot be ruled out at this stage because of the presence of H_2O in the reaction medium. Moreover, the reactions performed using substituted arynes (Scheme 4, eqs 1-3), and with phosphine derivative (Scheme 5, eq 4) indicate that the aryl group migration in the

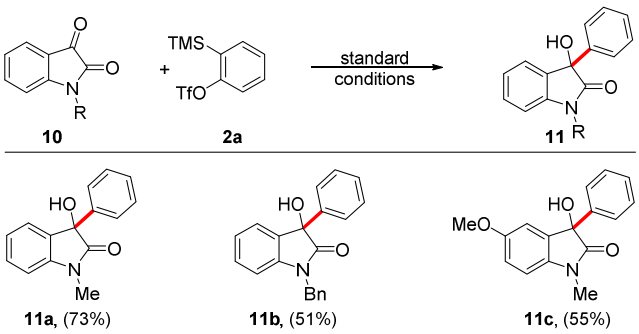
present reaction could be either from the aryne source or from the aryl group attached to the phosphorus.

Scheme 7. Proposed Mechanism of the Reaction



This nucleophilic arylation using arynes was not limited to aldehydes as the electrophiles, but instead activated ketones such as isatins can easily be arylated using this method resulting in the formation tertiary alcohols. For instance, treatment of *N*-methyl isatin **10a** with aryne generated from **2a** under the present reaction conditions afforded the oxindole derivative **11a** in 73% yield (Scheme 8).[18] The reaction afforded moderate yield of desired product with *N*-benzyl isatin and 5-methoxy isatin as substrates under identical reaction conditions.

Scheme 8. Nucleophilic Arylation of Isatins Using Arynes[a]



[a] See the Supporting Information for details

In conclusion, we have demonstrated the nucleophilic arylation of aldehydes/isatins by the action of a carbonate base on in situ generated tetraaryl phosphonium salts formed by the addition of phosphines to arynes. Although arynes are widely used for the electrophilic arylation of various element-element bonds, the present method utilizes arynes as aryl anion equivalents for the nucleophilic arylation reactions. The reaction tolerates various functional groups and the desired secondary/tertiary alcohols are formed in moderate to good yields.

Experimental Section

General Information:

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. Reaction temperatures are reported as the temperature of the bath surrounding the reaction vessel. 30 °C corresponds to the room temperature of the lab, when the experiments were carried out. THF was freshly purified by distillation over Na-benzophenone and was transferred under argon. 18-Crown-6 was recrystallized from dry CH_3CN, and KF was dried by heating at 110 °C for 12 h and left to cool under argon. The aldehydes were purchased from commercial sources and were purified either by distillation (for liquids) or washing with $NaHCO_3$ after dissolving in ether or dichloromethane (for solids), prior to use. Phosphines were purchased from commercial sources and used as received. The 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** and the other symmetric and unsymmetric aryne precursors were synthesized following literature procedure.[1b,19] ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ as solvent. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm). HRMS measurements were carried out using

ESI method and ion-trap mass analyzer. Infrared (IR) spectra were recorded on an FT-IR spectrometer as thin films using NaCl plates.

General Procedure for the Reaction involving Phosphine, Aryne and Aldehydes: To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the phosphine (0.197 g, 0.75 mmol), KF (0.058 g, 1.0 mmol) and 18-crown-6 (0.264 g, 1.0 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in THF (4.0 mL) under argon atmosphere and subsequently cooled the reaction mixture to 0 °C and kept stirring for five minutes. To the stirring solution, aryne precursor **2a** (1.0 mmol) was added and continued stirring for another five minutes followed by addition of the water (0.010 g, 10.0 µL, 0.55 mmol). Then the reaction mixture was stirred at 0 °C for 30 minutes. Then aldehyde **1** (0.25 mmol) was added followed by subsequent addition of Cs_2CO_3 (0.326 g, 1.0 mmol) at 0 °C. Then the reaction mixture was slowly warmed to rt and kept stirring for 24 h at 65 °C. After 24 h, the reaction was quenched using 3N HCl (0.25 ml) and subsequent work-up in CH_2Cl_2 (3 x 30 mL). The organic layer dried over Na_2SO_4 and solvent was evaporated, and the crude residue was purified by column chromatography on silica gel (230-400 mesh) (Petroleum ether/EtOAc = 85/15) to afford the corresponding benzhydrol derivatives **3** in moderate to good yields.

General Procedure for the Reaction Involving Phosphine, Aryne and Isatins: To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the phosphine (0.197 g, 0.75 mmol), KF (0.058 g, 1.0 mmol) and 18-crown-6 (0.264 g, 1.0 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in THF (4.0 mL) under argon atmosphere and subsequently cooled the reaction mixture to 0 °C and kept stirring for five minutes. To the stirring solution aryne precursor **2a** (1 mmol) was added and continued stirring for another five minutes followed by addition of the water (0.010 g, 10.0 µL,

0.55 mmol). Then the reaction mixture was stirred at 0 °C for 30 minutes. Then isatin **10** (0.25 mmol) was added followed by the subsequent addition of Cs_2CO_3 (0.326 g, 1.0 mmol) at 0 °C. Then the reaction mixture was slowly warmed to rt and kept stirring for 24 h at 65 °C. After 24 h, the reaction was quenched using 3N HCl (3 mL) and subsequent work-up in CH_2Cl_2 (3 x 30 mL). The organic layer dried over Na_2SO_4 and solvent was evaporated, and the crude residue was purified by column chromatography on silica gel (230-400 mesh) (Petroleum ether/EtOAc = 85/15) to afford the corresponding benzhydrol derivatives **11** in moderate to good yields.

(4-Chlorophenyl)(phenyl)methanol (3a):[20] Pale yellow solid, 0.041 g in 0.25 mmol scale, 75% yield. R_f (Pet. ether /EtOAc = 80/20): 0.53; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31-7.20 (m, 9H), 5.69 (s,1H), 2.46 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.5, 142.3, 133.3, 128.7, 128.7, 128.0, 127.9, 126.6, 75.6. **HRMS (ESI)** calculated $[M\text{-}OH]^+$ for $C_{13}H_{10}Cl$: 201.0466, found: 201.0468. **FTIR (cm^{-1})** 3597, 3411, 3020, 2884, 2402, 1594, 1489, 1216, 1180, 1018, 925.

(4-Bromophenyl)(phenyl)methanol (3b):[21] Pale yellow solid, 0.039 g in 0.25 mmol scale, 60% yield. R_f (Pet. ether /EtOAc = 80/20): 0.53; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 (d, J = 8.2 Hz, 2H), 7.36-2.26 (m, 7H), 5.79 (s, 1H), 2.40 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.5, 142.9, 131.6, 128.8, 128.3, 128.0, 126.6, 121.5, 75.7. **HRMS (ESI)** calculated $[M\text{-}OH]^+$ for $C_{13}H_{10}Br$: 244.9960, found: 244.9965. **FTIR (cm^{-1})** 3600, 3400, 3020, 2402, 1593, 1486, 1410, 1216, 1019, 926.

(4-Fluorophenyl)(phenyl)methanol (3c):[22] Pale yellow solid, 0.034 g in 0.25 mmol scale, 67% yield. R_f (Pet. ether /EtOAc = 80/20): 0.56; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38-7.28 (m, 7H), 7.04 (t, J = 8.7 Hz, 2H), 5.84 (s, 1H), 2.32 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.3 (d, J = 246.7 Hz), 143.8, 139.7 (d, J = 2.9 Hz), 128.7, 128.4 (d, J = 8.6 Hz), 127.9, 126.6, 115.4 (d, J

= 21.4 Hz), 75.7. **HRMS (ESI)** calculated [M-OH] $^{+}$ for $C_{13}H_{10}F$: 185.0761, found: 185.0760. **FTIR (cm^{-1})** 3412, 1601, 1505, 1219, 1167, 1025, 925, 854.

Diphenylmethanol (3d):[23] Yellow solid, 0.025 g in 0.25 mmol scale, 54% yield. R_f (Pet. ether /EtOAc = 80/20): 0.61; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42-7.41 (m, 4H), 7.39-7.36 (m, 4H), 7.32-7.29 (m, 2H), 5.86 (s, 1H), 2.38 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.9, 128.6, 127.7, 126.7, 76.4. **HRMS (ESI)** calculated [M-OH] $^{+}$ for $C_{13}H_{11}$: 167.0855, found: 167.0853. **FTIR (cm^{-1})** 3597, 3414, 3020, 2402, 1597, 1489, 1446, 1216, 1026, 924.

Phenyl(p-tolyl)methanol (3e):[21] Yellow solid, 0.034 g in 0.25 mmol scale, 69% yield. R_f (Pet. ether /EtOAc = 80/20): 0.57; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 3H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.81 (s, 1H), 2.33 (s, 3H), 2.17 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.1, 141.1, 137.4, 129.3, 128.6, 127.6, 126.7, 126.6, 76.2, 21.2. **HRMS (ESI)** calculated [M-OH] $^{+}$ for $C_{14}H_{13}$: 181.1012, found: 181.1015. **FTIR (cm^{-1})** 3596, 3411, 3019, 2924, 1614, 1504, 1216, 1372, 1029, 926.

(4-Methoxyphenyl)(phenyl)methanol(3f):[22] Yellow solid, 0.074 g in 0. 5 mmol scale, 69% yield. R_f (Pet. ether /EtOAc = 80/20): 0.38; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39-7.34 (m, 4H), 7.31-7.29 (m, 3H), 6.89 (d, *J*= 8.3 Hz, 2H), 5.80 (s, 1H), 3.81 (s, 3H), 2.46 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.1, 144.1, 136.3, 128.5, 128.0, 127.5, 126.5, 113.9, 75.8, 55.4. **HRMS (ESI)** calculated [M-OH] $^{+}$ for $C_{14}H_{13}O$: 197.0961, found: 197.0964. **FTIR (cm^{-1})** 3415, 3062, 2954, 2838, 1610, 1508, 1454, 1300, 1176, 1031, 923.

[1,1'-Biphenyl]-4-yl(phenyl)methanol (3g):[21] Yellow solid, 0.050 g in 0.25 mmol scale, 77% yield). R_f (Pet. ether /EtOAc = 80/20): 0.50; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63-7.60 (m, 4H), 7.49-7.45 (m, 6H), 7.42-7.39 (m, 3H), 7.35-7.31 (m, 1H), 5.89 (s, 1H), 2.52 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.9, 142.9, 140.9, 140.5, 128.9, 128.7, 127.7, 127.4, 127.3, 127.2, 127.1,

126.7, 76.1. **HRMS (ESI)** calculated [M-OH] $^{+}$ for $C_{19}H_{15}$: 243.1168, found: 243.1172. **FTIR (cm^{-1})** 3596, 3412, 3020, 2402, 1597, 1486, 1371, 1216, 1032, 923.

4-(Hydroxy(phenyl)methyl)benzonitrile (3h):[24] Yellow solid, 0.030 g in 0.25 mmol scale, 58% yield. R_f (Pet. ether /EtOAc = 80/20): 0.35; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.40-7.32 (m, 5H), 5.88 (s, 1H), 2.53 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.0, 142.9, 132.4, 129.0, 128.4, 127.1, 126.8, 119.0, 111.2, 75.7. **HRMS (ESI)** calculated [M-OH] $^{+}$ for $C_{14}H_{10}N$: 192.0808, found: 192.0806. **FTIR (cm^{-1})** 3435, 2231, 111, 1716, 1495, 1275, 1033, 922, 806, 757.

Methyl 4-(hydroxy(phenyl)methyl)benzoate (3i):[21] Yellow solid, 0.048 g in 0.25 mmol scale, 79% yield. R_f (Pet. ether /EtOAc = 80/20): 0.34; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.35-7.27 (m, 5H), 5.87 (s, 1H), 3.89 (s, 3H), 2.46 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.1, 148.8, 143.4, 129.9, 129.4, 128.8, 128.1, 126.8, 126.5, 76.0, 52.2. **HRMS (ESI)** calculated [M-OH] $^{+}$ for $C_{15}H_{13}O_2$: 225.0910, found: 225.0908. **FTIR (cm^{-1})** 3430, 3020, 1715, 1610, 1442, 1374, 1283, 1184, 1026, 926.

Phenyl(4-(trifluoromethyl)phenyl)methanol (3j):[25] Yellow solid, 0.043 g in 0.25 mmol scale, 68% yield). R_f (Pet. ether /EtOAc = 95/05): 0.53; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.37-7.27 (m, 5H), 5.87 (s, 1H), 2.40 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 147.6, 143.3, 129.8 (d, *J* = 32.2 Hz), 128.9, 128.2, 126.8, 126.8, 125.0 (q, *J* = 3.4 Hz), 75.9. **HRMS (ESI)** calculated [M-OH] $^{+}$ for $C_{14}H_{10}F_3$: 235.0729, found: 235.0727. **FTIR (cm^{-1})** 3597, 3397, 3021, 2926, 2403, 1617, 1489, 1325, 1125, 923.

(3-Bromophenyl)(phenyl)methanol (3k):[26] Yellow solid, 0.037 g in 0.25 mmol scale, 56% yield. R_f (Pet. ether /EtOAc = 80/20): 0.60; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (s, 1H), 7.43-7.30 (m, 7H), 7.24-7.20 (m, 1H), 5.80 (s, 1H), 2.30 (bs, 1H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ

146.1, 143.3, 130.7, 130.2, 129.6, 128.8, 128.6, 128.1, 127.7, 126.7, 125.2, 122.8, 75.7. **HRMS (ESI)** calculated $[M-OH]^+$ for $C_{13}H_{10}Br$: 244.9960, found: 244.9958. **FTIR (cm^{-1})** 3383, 1584, 1217, 1179, 1078, 1029, 913, 758.

(3-Nitrophenyl)(phenyl)methanol (3l):[27] Yellow solid, 0.029 g in 0.25 mmol scale, 51% yield. R_f (Pet. ether /EtOAc = 95/05): 0.51; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.29 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.37-7.30 (m, 5H), 5.91 (s, 1H), 2.56 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.3, 145.9, 142.9, 132.6, 129.5, 129.1, 128.5, 126.8, 122.6, 121.4, 75.5. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{13}H_{11}NO_3Na$: 252.0637, found: 252.0635. **FTIR (cm^{-1})** 3554, 3376, 3068, 2925, 1714, 1528, 1350, 1187, 1032.

Phenyl(*o*-tolyl)methanol (3m):[26] Viscous yellow oil, 0.033 g in 0.25 mmol scale, 67% yield. R_f (Pet. ether /EtOAc = 80/20): 0.63; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.37-7.36 (m, 4H), 7.32-7.17 (m, 4H), 6.02 (s, 1H), 2.28 (s, 3H), 2.20 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.0, 141.6, 135.5, 130.7, 128.6, 127.7, 127.7, 127.2, 126.4, 126.3, 73.5, 19.5. **HRMS (ESI)** calculated $[M-OH]^+$ for $C_{14}H_{13}$: 181.1012, found: 181.1010. **FTIR (cm^{-1})** 3369, 1812, 1593, 1483, 1455, 1377, 1258, 1179, 1020, 919, 755.

(2-Chlorophenyl)(phenyl)methanol (3n):[28] Yellow solid, 0.067 g, in 0.5 mmol scale, 62% yield. R_f (Pet. ether /EtOAc = 80/20): 0.60; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 7.3 Hz, 1H), 7.43-7.41 (m, 2H), 7.38-7.31 (m, 5H), 7.27-7.23 (m, 1H), 6.24 (s, 1H), 2.53 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.3, 141.1, 132.6, 129.7, 128.9, 128.6, 128.1, 127.9, 127.2, 127.0, 72.8. **HRMS (ESI)** calculated $[M-OH]^+$ for $C_{13}H_{10}Cl$: 201.0466, found: 201.0469. **FTIR (cm^{-1})** 3365, 3064, 3030, 2919, 1955, 1584, 1445, 1391, 1184, 1024, 951.

(2,3-Dimethoxyphenyl)(phenyl)methanol (3o):[29] Yellow solid, 0.080 g in 0.5 mmol scale, 66% yield. R_f (Pet. ether /EtOAc = 80/20): 0.48; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 7.5 Hz,

2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.0 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.04 (s, 1H), 3.87 (s, 3H), 3.62 (s, 3H), 3.18 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.7, 146.4, 144.1, 137.7, 128.3, 127.2, 126.4, 124.1, 119.8, 112.0, 72.39, 60.5, 55.8. **HRMS (ESI)** calculated $[M\text{-}OH]^+$ for $C_{15}H_{15}O_2$: 227.1067, found: 227.1064. **FTIR (cm^{-1})** 3419, 3017, 2937, 2839, 2403, 1590, 1478, 1270, 1080, 921.

(3,4-Dimethoxyphenyl)(phenyl)methanol (3p):[30] Yellow oil, 0.083 g in 0.5 mmol scale, 68% yield. ***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.26; **^{1}H NMR (400 MHz, $CDCl_3$)** δ7.38-7.27 (m, 5H), 6.92 (bs, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 5.78 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.43 (s, 1H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.1, 148.5, 144.0, 136.6, 128.5, 127.6, 126.5, 119.0, 111.0, 109.8, 76.0, 56.0, 55.9. **HRMS (ESI)** calculated $[M\text{-}OH]^+$ for $C_{15}H_{15}O_2$: 227.1067, found: 227.1064. **FTIR (cm^{-1})** 3597, 3419, 3019, 2963, 2840, 1596, 1513, 1456, 1259, 1029, 927.

(3,4-Dichlorophenyl)(phenyl)methanol (3q):[31] Yellow oil (0.040 g, 64% yield). ***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.53; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (s, 1H), 7.40-7.31 (m, 6H), 7.19 (d, *J* = 8.0 Hz, 1H), 5.75 (s, 1H), 2.49 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.0, 143.0, 132.6, 131.5, 130.5, 128.9, 128.5, 128.3, 126.7, 125.9, 75.2. **HRMS (ESI)** calculated $[M\text{-}OH]^+$ for $C_{13}H_9Cl_2$: 235.0076, found: 235.0074. **FTIR (cm^{-1})** 3587, 3379, 3020, 2881, 1593, 1464, 1391, 1216, 1185, 1030, 891.

Naphthalen-2-yl(phenyl)methanol (3r):[20] Yellow solid, (0.070 g in 0.25 mmol scale, 60% yield. ***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.50; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (s, 1H), 7.86-7.81 (m, 3H), 7.54-7.49 (m, 2H), 7.46-7.44 (m, 3H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.0 Hz, 1H), 5.98 (s, 1H), 2.60 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.7, 141.2, 133.3, 133.0, 128.6, 128.4, 128.2, 127.8, 127.8, 126.8, 126.3, 126.1, 125.1, 124.9, 76.4. **HRMS (ESI)**

calculated [M-OH] $^{+}$ for $C_{17}H_{13}$: 217.1012, found: 217.1010. **FTIR (cm^{-1})** 3384, 3057, 2874, 1951, 1597, 1497, 1366, 1160, 1028, 957.

Phenyl(pyren-1-yl)methanol (3s):[32] Yellow solid, 0.056 g in 0.25 mmol scale, 73% yield. R_f (Pet. ether /EtOAc = 80/20): 0.54; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.32 (d, J = 9.2 Hz, 1H), 8.20-8.16 (m, 4H), 8.07-8.0 (m, 4H), 7.48 (d, J = 7.3 Hz, 2H), 7.37-7.28 (m, 3H), 6.87 (s, 1H), 2.62 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.7, 136.7, 131.4, 131.1, 130.7, 128.7, 128.2, 127.9, 127.7, 127.6, 127.1, 126.1, 125.5, 125.3, 125.1, 125.0, 124.9, 124.8, 123.2, 73.7. **HRMS (ESI)** calculated [M-OH] $^{+}$ for $C_{23}H_{15}$: 291.1168, found: 291.1163. **FTIR (cm^{-1})** 3421, 1724, 1595, 1522, 1424, 1216, 1045, 923, 846, 765.

Phenyl(3,4,5-trimethoxyphenyl)methanol (3t):[33] Yellow solid, 0.043 g in 0.25 mmol scale, 63% yield. R_f (Pet. ether /EtOAc = 80/20): 0.26; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41-7.34 (m, 4H), 7.31-7.27 (m, 1H), 6.62 (s, 2H), 5.77 (s, 1H), 3.83 (s, 9H), 3.79 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.3, 143.7, 139.6, 137.2, 128.6, 127.7, 126.6, 103.5, 76.3, 60.9, 56.1. **HRMS (ESI)** calculated [M-OH] $^{+}$ for $C_{16}H_{17}O_3$: 257.1172, found: 257.1167. **FTIR (cm^{-1})** 3490, 1889, 1592, 1501, 1458, 1331, 1231, 1129, 1057, 921, 819.

Phenyl(thiophen-2-yl)methanol (3u):[34] Viscous yellow oil, 0.042 g in 0.5 mmol scale, 44% yield. R_f (Pet. Ether /EtOAc = 80/20): 0.61; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48-7.28 (m, 6H), 6.98-6.91 (m, 2H), 6.06 (s, 1H), 2.62 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.2, 143.2, 128.6, 128.1, 126.8, 126.4, 125.5, 125.0, 72.5. **HRMS (ESI)** calculated [M-OH] $^{+}$ for $C_{11}H_9S$: 173.0419, found: 173.0417. **FTIR (cm^{-1})** 3376, 1594, 1442, 1216, 1038, 759, 703, 703.

Phenyl(thiophen-3-yl)methanol (3v):[35] Viscous yellow oil, 0.015 g in 0.25 mmol scale, 32% yield. R_f (Pet. ether/EtOAc = 80/20): 0.22; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43-7.36 (m, 4H), 7.33-7.28 (m, 2H), 7.21 (s, 1H), 7.03 (d, J = 4.9 Hz, 1H), 5.91 (s, 1H), 2.31 (bs, 1H). **^{13}C NMR**

(100 MHz, $CDCl_3$) δ 145.4, 143.5, 128.7, 127.9, 126.6, 126.5, 126.4, 121.8, 73.0. **HRMS (ESI)** calculated $[M\text{-}OH]^+$ for $C_{11}H_9S$: 173.0419, found: 173.0418. **FTIR (cm^{-1})** 3391, 1647, 1592, 1485, 1452, 1412, 1279, 1224, 1149, 839, 766.

1-Phenylpropan-1-ol (3w):[23] Yellow oil, 0.018 g in 0.25 mmol scale, 53% yield. R_f (Pet. ether /EtOAc = 80/20): 0.48; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40-7.35 (m, 4H), 7.32-7.28 (m, 1H), 4.62 (t, J = 6.6 Hz, 1H), 1.94 (s, 1H), 1.89-1.74 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.7, 128.5, 127.6, 126.1, 76.2, 32.0, 10.3. **HRMS (ESI)** calculated $[M\text{-}OH]^+$ for C_9H_{11}: 119.0855, found: 119.0857. **FTIR (cm^{-1})** 3601, 3412, 3018, 2969, 2930, 1597, 1456, 1217, 1090, 972.

1,3-Diphenylpropan-1-ol (3x):[21] Yellow solid, 0.025 g in 0.25 mmol scale, 47% yield. R_f (Pet. ether /EtOAc = 80/20): 0.60; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38-7.37 (m, 4H), 7.32-7.29 (m, 3H), 7.22-7.21 (m, 3H), 4.70 (dd, ^1J = 5.7 Hz, ^2J = 7.4 Hz, 1H), 2.81-2.65 (m, 2H), 2.20-2.02 (m, 2H), 1.95 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.7, 141.9, 128.6, 128.6, 128.5, 127.8, 126.1, 126.0, 74.0, 40.6, 32.2. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{15}H_{16}ONa$: 235.1093, found: 235.1092. **FTIR (cm^{-1})** 3389, 3019, 2930, 1612, 1491, 1451, 1374, 1318, 1216, 1050, 922.

Cyclohexyl(phenyl)methanol (3y):[24] Colorless oil, 0.071 g in 0.5 mmol scale, 75% yield. R_f (Pet. ether /EtOAc = 80/20): 0.61; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38-7.28 (m, 5H), 4.38 (d, J = 7.2 Hz, 1H), 2.02-1.99 (m, 1H), 1.88 (s, 1H), 1.80-1.77 (m, 1H), 1.67-1.60 (m, 3H), 1.41-1.38 (m, 1H), 1.27-1.02 (m, 4H), 0.99-0.93 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.8, 128.3, 127.5, 126.8, 79.5, 45.1, 29.4, 29.0, 26.6, 26.2, 26.1. **HRMS (ESI)** calculated $[M\text{-}OH]^+$ for $C_{13}H_{17}$: 173.1325, found: 173.1324. **FTIR (cm^{-1})** 3606, 3419, 3019, 2929, 2856, 1587, 1368, 1216, 1067, 922.

1,3-Diphenylprop-2-en-1-ol (3z):[36] Yellow solid (0.053 g, 50% yield). R_f (Pet. ether /EtOAc = 80/20): 0.56; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48-7.47 (m, 2H), 7.43-7.40 (m, 4H), 7.37-7.28 (m, 5H) 6.74 (d, J = 16.0 Hz, 1H), 6.45 (dd, J_1 = 6.5 Hz, J_2 = 15.6 Hz, 1H), 5.42 (d, J = 6.2 Hz, 1H), 2.27 (bs,1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.9, 136.7, 131.7, 130.6, 128.7, 128.7, 127.9, 126.7, 126.5, 75.2. **HRMS (ESI)** calculated [M-OH] $^+$ for $C_{15}H_{13}$: 193.1012, found: 193.1010. **FTIR (cm^{-1})** 3422, 1598, 1487, 1216, 1036, 971, 767.

1,3,3-Triphenylprop-2-en-1-ol (3aa):[37] Yellow solid, 0.082 g in 0.5 mmol scale, 63% yield. R_f (Pet. ether /EtOAc = 95/05): 0.53; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39-7.29 (m, 7H), 7.23 (s, 8H), 6.27 (d, J = 9.4, 1H), 5.24 (d, J = 9.4, 1H), 2.25 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.5, 143.5, 141.6, 139.2, 130.2, 129.9, 128.7, 128.4, 128.3, 127.8, 127.7, 127.7, 126.3, 71.7. **HRMS (ESI)** calculated [M-OH] $^+$ for $C_{17}H_{17}OS$: 269.1325, found: 269.1327. **FTIR (cm^{-1})** 3557, 3328, 3057, 3027, 2924, 1596, 1492, 1446, 1362, 1072, 1006.

3,7-Dimethyl-1-phenylocta-2,6-dien-1-ol (3ab): Viscous yellow oil, 0.029 g in 0.25 mmol scale, 50% yield. R_f (Pet. ether /EtOAc = 80/20): 0.66; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 (d, J = 7.4 Hz, 2H), 7.34 (t, J = 7.1 Hz, 2H), 7.30-7.23 (m, 1H), 6.64 (d, J = 16.1 Hz, 1H), 6.32 (d, J = 16.1 Hz, 1H), 5.18-5.15 (m, 1H), 2.16-2.05 (m, 2H), 1.70-1.68 (m, 6H), 1.62-1.60 (m, 2H), 1.41 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 137.2, 136.8, 132.3, 128.7, 127.5, 127.3, 126.5, 124.5, 73.7, 42.7, 28.6, 25.9, 23.1, 17.9. **HRMS (ESI)** calculated [M-OH] $^+$ for $C_{16}H_{21}$: 213.1638, found: 213.1635. **FTIR (cm^{-1})** 3444, 1665, 1589, 1460, 1370, 1260, 1215, 1114, 1052, 974, 765.

Benzo[d][1,3]dioxol-5-yl(phenyl)methanol (3ac):[38] Yellow oil, 0.031 g in 0.25 mmol scale, 48% yield. R_f (Pet. ether /EtOAc = 80/20): 0.41; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31-7.26 (m, 4H), 6.80-6.74 (m, 3H), 5.92 (s, 2H), 5.68 (s, 1H), 2.49 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ

148.0, 147.3, 142.3, 137.7, 133.3, 128.7, 127.8, 120.2, 108.3, 107.2, 101.2, 75.4. **FTIR (cm^{-1})** 3359, 2956, 2893, 2778, 1603, 1489, 1245, 1038, 929.

(4-Chlorophenyl)(4-methoxyphenyl)methanol (3af):[39] Yellow oil, 0.012 g in 0.25 mmol scale, 19% yield. R_f (Pet. ether /EtOAc = 80/20): 0.49; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 (s, 4H), 7.25 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.77 (s, 1H), 3.79 (s, 3H), 2.25 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.4, 142.6, 135.9, 133.2, 128.7, 128.1, 127.9, 114.1, 75.3, 55.4. **HRMS (ESI)** calculated $[M-OH]^+$ for $C_{14}H_{12}ClO$: 231.0571, found: 231.0578. **FTIR (cm^{-1})** 3394, 3002, 2928, 2838, 1609, 1511, 1248, 1173, 1032.

Hydroxy-1-methyl-3-phenylindolin-2-one (11a):[40] Pale brown solid, 0.043 g in 0.25 mmol scale, 73% yield. R_f (Pet. ether /EtOAc = 60/40): 0.36; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40-7.28 (m, 7H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 3.92 (s, 1H), 3.24 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.7, 143.6, 140.3, 131.8, 129.9, 128.6, 128.3, 125.5, 125.0, 123.7, 108.8, 78.1, 26.6. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{15}H_{14}O_2N$: 240.1019, found: 240.1020. **FTIR (cm^{-1})** 3684, 3386, 3020, 2402, 1718, 1614, 1477, 1369, 1092, 930.

1-Benzyl-3-hydroxy-3-phenylindolin-2-one (11b):[41] Pale brown solid, 0.040 g in 0.25 mmol scale, 51% yield. R_f (Pet. ether /EtOAc = 60/40): 0.53; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44-7.42 (m, 2H), 7.36-7.22 (m, 10H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 5.05 (d, *J*= 15.6 Hz, 1H), 4.82 (d, *J* = 15.6 Hz, 1H), 3.89 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.8, 142.7, 140.3, 135.5, 131.8, 129.8, 129.0, 128.8, 128.4, 127.9, 127.4, 125.5, 125.1, 123.7, 109.9, 78.1, 44.1. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{21}H_{18}O_2N$: 316.1332, found: 316.1333. **FTIR (cm^{-1})** 3387, 3020, 2402, 1718, 1613, 1479, 1367, 1216, 1075, 930.

3-Hydroxy-5-methoxy-1-methyl-3-phenylindolin-2-one (11c):[42] Pale brown solid, 0.037 g in 0.25 mmol scale, 55% yield. R_f (Pet. ether /EtOAc = 60/40): 0.23; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39-7.28 (m, 5H), 6.90-6.86 (m, 2H), 6.81 (d, *J* = 8.3 Hz, 1H), 3.75 (s, 3H), 3.20 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.6, 156.7, 140.3, 136.8, 133.1, 128.6, 128.3, 125.4, 114.7, 111.8, 109.3, 78.5, 55.9, 26.7. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{16}H_{15}O_3NNa$: 292.0944, found: 292.0947. **FTIR (cm^{-1})** 3380, 3020, 2402, 1713, 1609, 1495, 1434, 1366, 1161, 1103, 933.

Supporting Information

Details on mechanistic experiments, optimization studies, and the copies of ^{1}H and ^{13}C NMR spectra of all products. The Supporting Information is available free of charge on the ACS Publications website.

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