Note

Transition-Metal Free Arylation and Alkylation of Diarylmethyl p-Tolyl Sulfones with Zinc Reagents

Maozhong Miao, Wenguang Yin, Lei Wang, Zhengkai Chen, Jianfeng Xu, and Hongjun Ren

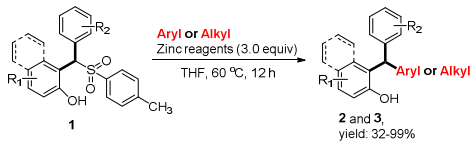
J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b01428 • Publication Date (Web): 01 Aug 2018

Transition-Metal Free Arylation and Alkylation of Diarylmethyl *p*-Tolyl Sulfones with Zinc Reagents

Maozhong Miao, Wenguang Yin, Lei Wang, Zhengkai Chen, Jianfeng Xu, and Hongjun Ren**

Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, Zhejiang 310018 (P. R. China)

mmzok@zstu.edu.cn；renhj@zstu.edu.cn



Abstract: The transition-metal free synthesis of unsymmetrical and highly functionalized triarylmethanes through arylation of the situ generated *o*-QMs from diarylmethyl *p*-tolyl sulfones with aryl zinc reagents is described. Alkyl zinc reagents are also well tolerated in this reaction. Additionally, the straightforward synthesis of the analogue of the anti-tuberculosis agent **A** and the key precursor of the anti-breast cancer agent **B** are achieved by this strategy.

The triarylmethanes, a class of structurally unique molecules, are widespread in material science and medicinal chemistry.[1] For example, several triarylmethane compounds have been utilized as pharmacological agents for treating bacterial infection (**A**, **Chart 1**),[2] breast cancer (**B**)[3] and diabetes (**C**).[4] Triarylmethane dyes are synthetic organic compounds containing triphenylmethane backbones, which have been widely used in material sciences due to their special photochemical and photophysical properties.[5] Although quite rare, the triarylmethane units have been found in natural products such as cassigarol B and muchimangin B (**D**).[6]

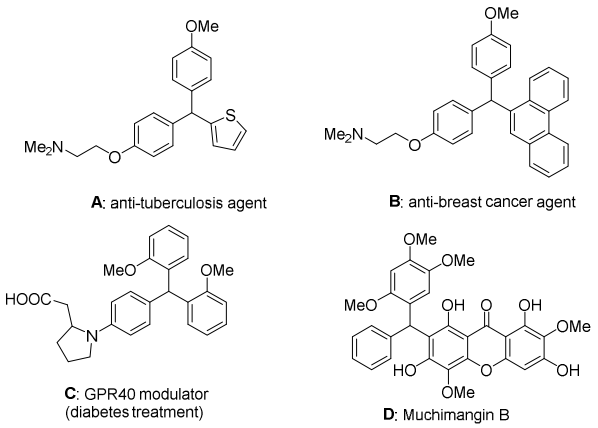
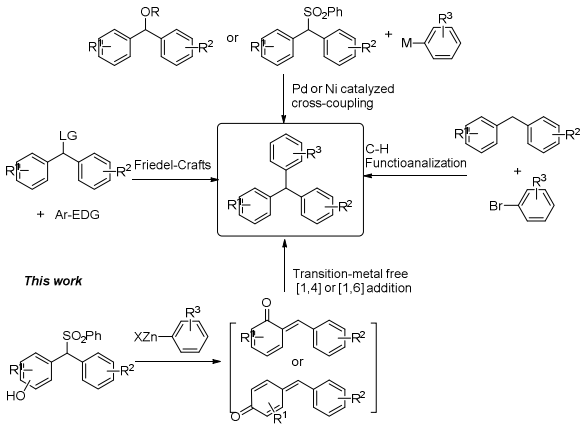


Chart 1. Biologically pertinent triarylmethanes.

The synthesis of unsymmetrical triarylmethanes is a challenge because of their unique structures with three aryl groups attached to the central sp^3-hybridized methide carbon. Conventionally, triarylmethanes are prepared through typical Friedel–Crafts alkylation of diarylcarbinols in the presence of either Brönsted or Lewis acids (**Scheme 1**),[7] however, these reactions are limited to electron-rich arenes and have poor regioselectivies. Despite the cross coupling and C-H activation based strategies addressing these synthesis most require expensive palladium salts and ligands (**Scheme 1**).[8] Hence, the development of environmentally benign, practical, transition-metal free protocols for the efficient synthesis of unsymmetrically functionalized triarylmethanes are highly desired. [9]

Ortho-quinone methides (*o*-QMs), are useful building blocks in modern chemical transformations.[11] Pioneering synthesis are availuable for generating *o*-QMs *in situ* from the corresponding substituted benzylsulfones.[12] We envisaged that the appropriately substituted benzylsulfones might undergo elimination to form transient *o*-QMs with the assistance of aryl zinc reagents,[13] the resulting *o*-QMs could be trapped by the excess aryl zinc reagents to afford the triarylmethanes. In this process, the zinc reagents play dual roles, as bases generating *o*-QM intermediates and attacking the *o*-QMs as nucleophiles (**Scheme 1**).

Scheme 1. Synthetic Approaches to Triarylmethanes

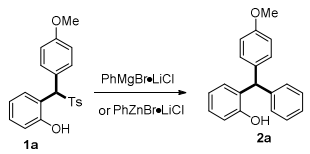


a) Friedel–Crafts reaction, b) Pd or Ni catalyzed cross-coupling reaction, c) transition-metal catalyzed C-H functionalization. d) This work: transition-metal free [1,4] or [1,6] addition (R^1, R^2, R^3 = substituted groups, EDG = Electron-Donating Group, LG = Leaving Group).

With this idea in mind, we started our investigation by using 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** as a model substrate which was prepared according to a modified literature method.[11a] The typical results are summarized in **Table 1**. The reaction of **1a** with phenyl Grignard reagent (Knochel type Grignard with LiCl) catalyzed by CuI (5 mol %) in tetrahydrofuran (THF) at -78 ^{o}C for 12 hours detected the desired arylation product **2a** in trace amount (**Table 1**, entry 1). Elevating the temperature to 0 ^{o}C gave only trace product (entry 2). When the phenyl zinc reagent was employed, the desired arylation product **2a** was isolated in 22% yield (entry 3). To our delight, after some experimentation, we found that the arylation product **2a** could be obtained in 20 % yield in the absence of CuI at 0 ^{o}C (entry 4). Decreasing the temperature to - 30 ^{o}C decreased the yield (entry 5) but the yield was dramatically improved when the reaction temperature was raised to 60 ^{o}C (entry 6). By contrast, the phenyl Grignard reagent gave a poor result at 60 ^{o}C (entry 7). Under optimal conditions using 3.0 equivalent of phenyl zinc reagent at 60 ^{o}C for 12 hours, the yield was further improved to 82% (entry 8). Furthermore, the reaction was carried out using 1

equivalent of bases such as K_2CO_3 and Et_3N together with 1 equivalent of zinc reagent at 60 ^oC, however, poor results were obtained (entries 9 and 10). These results indicated that excess zinc reagents were necessary.

Table 1. Optimization of the Reaction Conditions[a]



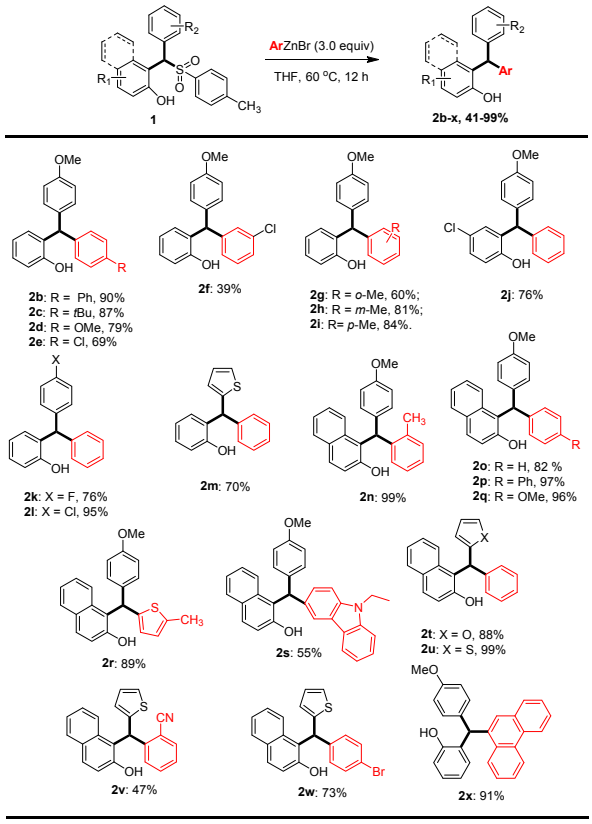
entry	reagent (equiv)	catalyst	temp. (^oC)	yield (%)[b]
1	PhMgBr·LiCl (2.5)	CuI	-78	trace
2	PhMgBr·LiCl (2.5)	CuI	0	trace
3	PhZnBr·LiCl (2.5)	CuI	0	22
4	PhZnBr·LiCl (2.5)	/	0	20
5	PhZnBr·LiCl (2.5)	/	-30	trace
6	PhZnBr·LiCl (2.5)	/	60	78
7	PhMgBr·LiCl (2.5)	/	60	trace
8	**PhZnBr·LiCl (3.0)**	**/**	**60**	**82**
9	PhZnBr·LiCl (1.0)[c]	/	60	0
10	PhZnBr·LiCl (1.0)[d]	/	60	trace

[a]Conditions: **1a** (0.5 mmol), PhMgBr·LiCl (2.5 equiv) or PhZnBr·LiCl (2.5 or 3.0 equiv), in solvent of THF under N_2. [b] Isolated yield. [c] K_2CO_3 (1 equiv) was used. [d] Et_3N (1 equiv) was used. (THF = tetrahydrofuran).

With the optimized conditions, the generality of arylation reaction for the synthesis of triarylmethane derivatives **2** from various tosylmethyl phenols **1** and functionalized aryl zinc reagents was next investigated (**2b**−**x**, **Scheme 2**). *para*-Substituted aryl zinc reagents with groups such as *p*-phenyl, *p*-*t*-Bu, *p*-OMe, and *p*-chloro reacted with 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** to afford the corresponding desulfonylation arylation products **2b**−**e** in good yields (69-90%). *para*-, *meta*- and *ortho*- Methyl substituted phenyl zinc reagents were well tolerated, whereas *o*-methyl phenyl zinc reagent gave the slightly lower yield presumably because of steric effect (**2g**−**i**). With respect to tosylmethyl phenols **1**, products (**2j**−**l)** were isolated in up to 95% yield. Furthermore, heterocycles such as thiophene could be tolerated in this reaction (**2m**). In the case of β-naphthol substrates, the desulfonylation products were obtained in good to excellent yields (**2n**−**s**). In particular, heterocyclic zinc reagents such as thiophenyl and

carbazolyl zinc reagents could be used in this transformation to provide the unsymmetrical triarylmethanes containing heterocycles with high potential in material science (**2r**−**s**). Tosylmethyl naphthols with heterocyclic structures were also compatible with the desulfonylation arylation method (**2t**−**u**). Functionalized zinc reagents with CN and Br substitutents at *ortho*- and *para*-position of benzene ring were suitable substrates to affording triarylmethanes in reasonable yield (**2v**−**w**). However, the zinc reagent with strong electron-withdrawing group -COOEt at *para*-position of benzene ring failed to give the desired product. The bulky zinc reagent phenanthren-9-ylzinc(II) bromide reacted with 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** to provide the arylation product **2x** in 91% yield, which is an analogue of the anti-breast-cancer agent **B**.

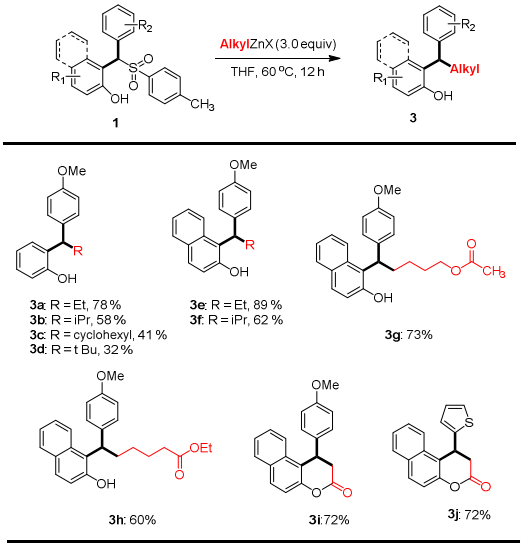
Scheme 2. Generality of the Reaction with Aryl Zinc Reagents[a,b]



[a] Conditions: **1** (0.5 mmol), Zinc reagents (3.0 equiv), in THF at 60 °C in under N_2. [b] Isolated yield.

We extended the above protocol using alkyl zinc reagents. Under the standard reaction condition, the substrate of 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** was treated with various simple alkyl zinc reagents, such as ethyl, *i*-propyl, and *t*-butyl zinc reagents to afford the corresponding functionalized diaryl compounds in 32−78% yields. More sterically crowded reagents afforded the products in lower yields (**Scheme 3**, **3a**−**d**). In the case of tosylmethyl naphthol substrates, the ethylation and isopropylation went well to provide the corresponding products in 89% and 72% yields, respectively (**3e**−**f**). Functionalized alkyl zinc reagents, such as (4-acetoxybutyl)zinc(II) bromide and (5-ethoxy-5-oxopentyl)zinc(II) bromide were also suitable to this transformation and provided the products in yield of 73% and 60%, respectively (**3g**−**h**). Interestingly, when Reformatsky enolate was introduced, both the intermolecular desulfonylation alkylation and the intramolecular esterification occurred to furnish the 1,2-dihydro benzo[*f*]chromen-3-one derivatives in good yields (**3i**−**j**).

Scheme 3. Generality of the Reaction with Alkyl Zinc Reagents[a,b]

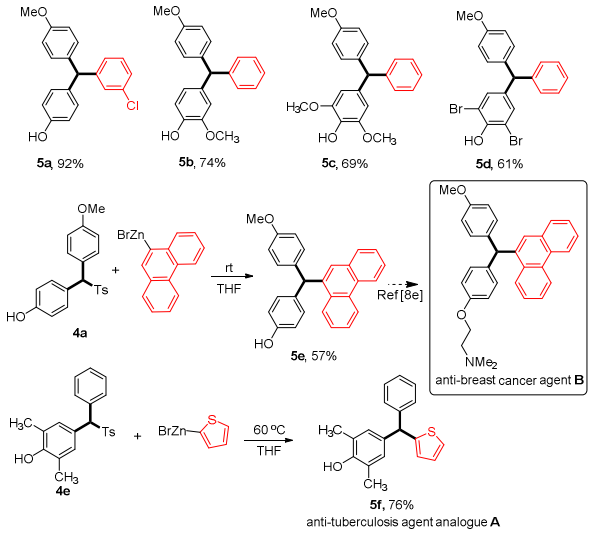


[a] Conditions: **1** (0.5 mmol), Zinc reagents (3.0 equiv), in THF at 60 °C in under N_2. [b] Isolated yield.

To show the utility of the modular approach to unsymmetrically functionalized triarylmethanes, the applications for the synthesis of anti-tuberculosis agent **A** and anti-breast-cancer agent **B**

analogues were carried out (**Scheme 4**). Gratifying, the desulfonylation arylation proceed smoothly when substrate *para*-phenol sulfone **4a** was utilized instead of *ortho*-phenol sulfone **1a**. Treatment of *para*-phenol sulfone **4a** with (3-chlorophenyl)zinc(II) bromide at 60 ^{o}C gave the desulfonylation arylation product **5a** in 92% yield. Various tosylmethyl phenols **4** with different substituents were well tolerated in this reaction to afford **5b**−**d** in high yields. Moreover, switching to phenanthren-9-ylzinc(II) bromide led to the key precursor of anti-breast-cancer agent **B** in 57% yield (**Scheme 4**). The reaction of 2,6-dimethyl-4-(phenyl(tosyl)methyl)phenol **4f** and thiophen-2-ylzinc(II) bromide furnished **5f**, an analogue of the anti-tuberculosis agent **A**, in 76% yield (**Scheme 4**).

Scheme 4. Synthesis of the Anti-tuberculosis Agent Analogue A and the Key Precursor of the Anti-breast-cancer Agent B.



In summary, we have realized the first arylation of an *ortho*-quinone methides (*o*-QMs) from the readily available 2-tosylalylphenol with functionalized zinc reagents, providing several types of unsymmetrical and functionalized triarylmethanes, including those are difficult to access *via* transition metal-catalyzed reactions, in good to excellent yields. This strategy can be applied to prepare the key precursor of the anti-breast-cancer agent **B** and the analogues of the anti-tuberculosis

agent **A** in a straightforward manner. In particular, the alkylation with functionalized alkyl zinc reagents also successfully lead to the functionalized diaryl compounds. Moreover, the reaction of Reformatsky enolate gave 1,2-dihydro benzo[*f*]chromen-3-one derivatives in good yields.

EXPERIMENTAL SECTION

1. General Methods.

The ^{1}H NMR (400 MHz) chemical shifts were reported in parts per million (δ) relative to internal standard TMS (7.26 ppm). The coupling constants, *J* values are reported in Hertz (Hz). The ^{13}C NMR (100 MHz) chemical shifts were referenced to the internal solvent signals (central peak is 77.0 ppm in $CDCl_3$). High-resolution mass spectra (HRMS) were recorded by ESI ionization. Infrared spectra (IR) were recorded by an ATR module and absorption bands are given in wavenumbers (cm^{-1}). Melting points were not corrected. All commercial reagents were used without additional purification and solvents were dried by standard methods when necessary. Petroleum ether refers to the fraction with boiling point in the range 60−90 °C. All reactions were monitored by TLC with GF 254 silica gel coated plates. Flash column chromatography was carried out using 200−300 mesh silica gel. The substrates **1**[11a, 12c] were prepared according to the literature procedure.

2. Procedure and experiment data for triarylmethanes 2

(1) General procedure for the synthesis of triarylmethanes ***2***

Method A: In a 25 mL Schlenk tube, aryl Grignard reagent in THF (3.0 equiv) was added to a solution of $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv) at 0 ^{o}C under N_2 atmosphere. After 15 min, the mixture was treated with substrate **1** (0.5 mmol, 1.0 equiv) at room temperature. After the addition

was completed, the reaction mixture was stirred at 60 °C for 12 h. Then the mixture was quenched by adding 5 mL of NH_4Cl and extracted with EtOAc (3×10 mL). The combined organic phase was washed with H_2O (3×10 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash silica gel chromatography to afford **2**.

Method B: In a 25 mL Schlenk tube, aryl halides (3.0 equiv) in dry THF (2 mL) was added dropwise *n*-BuLi (0.6 mL, 3.0 equiv, 2.5 M in hexane) at 0 ^oC under N_2 atmosphere. The reaction mixture was stirred for 1-2 h. Suspension of $ZnBr_2$ solution (1.5 mL, 1.0 M in THF, 3.0 equiv) was added, After 15 min at 0°C, the mixture was treated with substrate **1** (0.5 mmol, 1.0 equiv) at room temperature. After the addition was completed, the reaction mixture was stirred at 60 °C for 12 h. After completion of the reaction, the mixture was quenched by adding 5 mL of NH_4Cl and extracted with EtOAc (3×10 mL). The combined organic phase was washed with H_2O (3×10 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash silica gel chromatography to afford **2**.

Method C: In a 25 mL Schlenk tube, aryl halides in dry THF (2 mL) was added dropwise isopropylmagnesium chloride (3.0 equiv, 2.5 M in THF, 0.6 mL) at -30°C under N_2 atmosphere. The reaction mixture was stirred for 3.5 h. Suspension of $ZnBr_2$ solution (1.5 mL, 1.0 M in THF, 3.0 equiv) was added, After 15 min stir at 0 °C, the mixture was treated with substrate **1** (0.5 mmol, 1.0 equiv) at room temperature. After the addition was completed, the reaction mixture was stirred at 60 °C for 12 h. After completion of the reaction, the mixture was quenched by adding 5 mL of NH_4Cl and extracted with EtOAc (3×10 mL). The combined organic phase was washed with H_2O (3×10 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash silica gel chromatography to afford **2**.

Experiment data

2-((4-methoxyphenyl)(phenyl)methyl)phenol (2a)

According to Method A with phenylmagnesium bromide (1.5 mmol, 1.74 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 °C for 12 h. Purification by flash column chromatography provided ***2a*** (118.9 mg, 91%) as yellow oil; R*f* = 0.51 (Petroleum ether/EtOAc = 3/1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, *J* =7.2 Hz, 2H), 7.22-7.24 (m, 1H), 7.17-7.12 (m, 3H), 7.05 (d, *J* =8.4 Hz, 2H), 6.86-6.80 (m, 5H), 5.67 (s, 1H), 4.74 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3,

153.4, 142.7, 134.4, 130.5, 130.4, 130.3, 129.3, 128.5, 127.8, 126.6, 120.7, 116.0, 113.9, 55.2, 50.1; HRMS (ES^+-TOF) calcd for $C_{20}H_{19}O_2$ ($[M+H]^+$): 291.1380, found 291.1375. IR: 3405, 1589, 1507, 1454, 1236, 1180, 1091, 1027, 841, 807, 752.

2-([1,1'-biphenyl]-4-yl(4-methoxyphenyl)methyl)phenol *(2b)*

According to Method A with [1,1'-biphenyl]-4-ylmagnesium bromide (1.5 mmol, 0.66 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 °C for 12 h. Purification by flash column chromatography provided **2b** (164.7 mg, 90%) as white solid; m.p 70-71 °C (Petroleum ether/EtOAc); R*f* = 0.64 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.56 (m, 4H), 7.47-7.43 (m, 3H), 7.36-7.26 (m, 1H), 7.24-7.22 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.91-6.79 (m, 5H), 5.77 (s, 1H), 4.95 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 153.4, 142.0, 140.7, 139.3, 134.5, 130.5, 130.4, 130.3, 129.6, 128.7, 128.3, 127.9, 127.1, 127.0, 126.7, 126.6, 120.7, 116.0, 115.6, 114.0, 55.2, 49.7; HRMS (ES^+-TOF) calcd for $C_{26}H_{22}O_2Na$($[M+Na]^+$): 389.1512, found 389.1516. IR: 3416, 1608, 1508, 1486, 1454, 1245, 1177, 1034, 834, 757, 697.

2-((4-(tert-butyl)phenyl)(4-methoxyphenyl)methyl)phenol (2c)

According to Method A with (4-(*tert*-butyl)phenyl)magnesium bromide (1.5 mmol, 0.65 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 °C for 12 h. Purification by flash column chromatography provided ***2c*** (150.5, 62%) as yellow oil; R*f* = 0.73 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.31 (m, 2H), 7.16-7.05 (m, 5H), 6.86-6.81 (m, 5H), 5.62 (s, 1H), 4.76 (s, 1H), 3.79 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 153.5, 149.4, 139.4, 134.5, 130.7, 130.3, 130.2, 128.8, 127.8, 125.5, 120.7, 116.2, 113.9, 55.2, 49.8, 34.4, 31.3; HRMS (ES^+-TOF) calcd for $C_{24}H_{27}O_2$ ($[M+H]^+$): 347.2006, found 347.2010. IR: 3425, 1595, 1512, 1454, 1238, 1178, 1088, 1027, 841, 810, 753.

2-(bis(4-methoxyphenyl)methyl)phenol (2d)

According to Method A with (4-methoxyphenyl)magnesium bromide (1.5 mmol, 1.4 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 °C for 12 h. Purification by flash column chromatography provided **2d** (126.4 mg, 79%) as yellow oil; R*f* = 0.54 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.14 (m, 1H), 7.06 (d, *J* = 8.8 Hz, 4H), 6.88-6.80 (m, 7H), 5.62 (s, 1H), 4.92 (s,

1H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 153.4, 134.8, 130.8, 130.24, 130.20, 127.8, 120.6, 116.0, 113.9, 55.2, 49.3; HRMS (ES^+-TOF) calcd for $C_{21}H_{20}O_3Na$ ($[M+Na]^+$): 343.1305, found 343.1321. IR: 3418, 1608, 1508, 1454, 1245, 1176, 1033, 833, 755.

2-((4-chlorophenyl)(4-methoxyphenyl)methyl)phenol (2e)

According to Method A with (4-chlorophenyl)magnesium bromide (1.5 mmol, 0.55 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 °C for 12 h. Purification by flash column chromatography provided **2e** (111.8 mg, 69%) as yellow oil; R*f* = 0.69 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.20 (m, 2H), 7.18-7.14 (m, 2H), 7.07-7.03 (m, 3H), 6.90-6.86 (m, 3H), 6.81-6.78 (m, 2H), 5.72 (s, 1H) 5.00 (s, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 153.2, 145.4, 134.3, 133.9, 130.3, 130.2, 130.0, 129.6, 129.3, 128.0, 127.5, 126.6, 120.8, 115.9, 114.0, 55.2, 49.4; HRMS (ES^+-TOF) calcd for $C_{20}H_{18}ClO_2$ ($[M+H]^+$): 325.0990, found 325.0995. IR: 3404, 1592, 1509, 1454, 1246, 1178, 1033, 788.

2-((3-chlorophenyl)(4-methoxyphenyl)methyl)phenol (2f)

According to Method A with (3-methoxyphenyl)magnesium bromide (1.5 mmol, 0.65 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 °C for 12 h. Purification by flash column chromatography provided **2f** (63.2 mg, 39%) as yellow oil; R*f* = 0.58 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.22 (m, 2H), 7.17-7.13 (m, 2H), 7.06-7.02 (m, 3H), 6.89-6.86 (m, 3H), 6.82-6.78 (m, 2H), 5.71 (s, 1H), 4.94 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 153.2, 141.7, 134.3, 132.1, 130.6, 130.3, 130.2, 129.4, 128.7, 128.5, 127.9, 127.8, 120.7, 116.6, 115.8, 114.0, 113.9, 55.2, 49.0; HRMS (ES^+-TOF) calcd for $C_{20}H_{17}ClO_2Na$($[M+Na]^+$): 347.0809, found 347.0817. IR: 3396, 1608, 1509, 1454, 1245, 1178, 1089, 1014, 831, 755.

2-((4-methoxyphenyl)(o-tolyl)methyl)phenol (2g)

According to Method A with *o*-tolylmagnesium bromide (1.5 mmol, 0.76 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 °C for 12 h. Purification by flash column chromatography provided **2g** (91.2 mg, 60%) as yellow oil; R*f* = 0.71 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.17 (m, 4H), 7.04-7.02 (m, 2H), 6.87-6.85 (m, 4H), 6.82-6.79 (m, 1H), 6.75-6.73 (m, 1H), 5.78 (s, 1H), 4.86 (s, 1H), 3.81 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2,

153.4, 141.2, 136.8, 133.9, 130.6, 130.5, 130.2, 130.1, 128.8, 127.7, 126.7, 125.9, 120.7, 115.9, 113.9, 55.2, 46.7, 19.6; HRMS (ES^+-TOF) calcd for $C_{21}H_{20}O_2Na$([M+Na]$^+$): 327.1356, found 327.1357. IR: 3415, 1608, 1509, 1454, 1245, 1178, 1034, 836, 751.

2-((4-methoxyphenyl)(m-tolyl)methyl)phenol (2h)

According to Method A with *m*-tolylmagnesium bromide (1.5 mmol, 0.53 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 ^oC for 12 h. Purification by flash column chromatography provided **2h** (123.2 mg, 81%) as yellow oil; R*f* = 0.70 (Petroleum ether/EtOAc = 3/1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.25-7.15 (m, 2H), 7.10-7.08 (m, 3H), 7.01 (s, 1H), 6.97-6.81 (m, 6H), 5.68 (s, 1H), 4.95 (s, 1H), 3.82 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 153.4, 142.7, 138.1, 134.5, 130.6, 130.4, 130.3, 130.0, 128.4, 127.8, 127.4, 126.3, 120.6, 116.0, 113.9, 55.2, 50.0, 21.4; HRMS (ES^+-TOF) calcd for $C_{21}H_{20}O_2Na$ ([M+Na]$^+$): 305.1536, found 305.1529. IR: 3426, 1610, 1516, 1454, 1255, 1172, 1036, 840, 752.

2-((4-methoxyphenyl)(p-tolyl)methyl)phenol (2i)

According to Method A with *p*-tolylmagnesium bromide (1.5 mmol, 0.85 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 ^oC for 12 h. Purification by flash column chromatography provided **2i** (127.7 mg, 84%) as yellow solid; m.p. 121-122^oC (Petroleum ether/EtOAc); R*f* = 0.65 (Petroleum ether/EtOAc = 3/1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.13-7.07 (m, 3H), 7.14-7.09 (m, 4H), 6.99-6.92 (m, 4H), 6.83 (d, *J* =7.6 Hz, 1H), 5.72 (s, 1H), 5.08 (s, 1H), 3.83 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 153.4, 139.8, 136.1, 134.7, 130.7, 130.3, 130.2, 129.2, 129.1, 127.7, 120.6, 116.0, 113.9, 55.2, 49.6, 21.0; HRMS (ES^+-TOF) calcd for $C_{21}H_{21}O_2$ ([M+H]$^+$): 305.1536, found 305.1539. IR: 3405, 1589, 1507, 1454, 1236, 1180, 1091, 1027, 841, 807, 752.

4-chloro-2-((4-methoxyphenyl)(phenyl)methyl)phenol (2j)

According to Method A with phenylmagnesium bromide (1.5 mmol, 1.74 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 4-chloro-2-((4-methoxyphenyl)(tosyl)methyl)phenol **1b** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 ^oC for 12 h. Purification by flash column chromatography provided **2j** (123.3 mg, 76%) as yellow oil; R*f* = 0.51 (Petroleum ether/EtOAc = 3/1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.33 (t, *J* = 8.4 Hz, 2H), 7.27-7.28 (m, 1H), 7.13-7.08 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.88-6.85 (m, 2H), 6.78 (d, *J* = 2.0 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 5.63

(s, 1H), 5.05 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 152.1, 142.0, 133.7, 132.5, 130.2, 130.0, 129.1, 128.7, 127.7, 126.8, 125.6, 117.3, 114.1, 55.2, 50.0; HRMS (ES^+-TOF) calcd for $C_{20}H_{17}ClO_2Na$([M+Na]$^+$): 347.0809, found 347.0802. IR: 3404, 1608, 1509, 1412, 1247, 1177, 1109, 1031, 806, 700, 650.

2-((4-fluorophenyl)(phenyl)methyl)phenol (2k)

According to Method A with phenylmagnesium bromide (1.5 mmol, 1.74 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 2-((4-fluorophenyl)(tosyl)methyl)phenol **1c** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 ^{o}C for 12 h. Purification by flash column chromatography provided **2k** (105.7 mg, 76%) as white solid; m.p. 75-76 ^{o}C (Petroleum ether/EtOAc); R*f* = 0.74 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.25 (m, 3H), 7.19-7.09 (m, 5H), 7.00 (t, *J* = 8.6 Hz, 2H), 6.90-6.86 (m, 1H), 6.80 (d, *J* = 8.4 Hz, 2H), 5.77(s, 1H), 4.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 160.3, 153.2, 142.5, 138.4, 138.3, 130.8 (d, *J* = 7.3 Hz), 130.4, 130.2, 129.2, 129.1, 128.6, 128.5, 128.0, 126.7, 120.8, 115.9, 115.4, 115.1, 49.8; HRMS (ES^+-TOF) calcd for $C_{19}H_{15}FONa$ ([M+Na]$^+$): 301.0999, found 301.0992. IR: 3524, 1604, 1505, 1452, 1329, 1222, 1156, 1087, 837, 748, 700.

2-((4-chlorophenyl)(phenyl)methyl)phenol (2l)

According to Method A with phenylmagnesium bromide (1.5 mmol, 1.74 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 2-((4-chlorophenyl)(tosyl)methyl)phenol **1d** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 ^{o}C for 12 h. Purification by flash column chromatography provided ***2l*** (154.7 mg, 95%) as yellow oil; R*f* = 0.62 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.26 (m, 5H), 7.17-7.06 (m, 5H), 6.89-6.85 (m, 1H), 6.79 (d, *J* = 8.8 Hz, 2H) 5.75 (s, 1H), 4.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 142.2, 141.4, 132.3, 130.7, 130.4, 129.9, 129.3, 128.6, 128.5, 128.0, 126.7, 120.8, 115.9, 44.9; HRMS (ES^+-TOF) calcd for $C_{19}H_{16}ClO$ ([M+H]$^+$): 295.0884, found 295.0891. IR: 3416, 1597, 1488, 1453, 1234, 1089, 1014, 754, 700.

2-(phenyl(thiophen-2-yl)methyl)phenol (2m)

According to Method A with phenylmagnesium bromide (1.5 mmol, 1.74 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 2-(thiophen-2-yl(tosyl)methyl)phenol **1e** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 ^{o}C for 12 h. Purification by flash column chromatography provided **2m** (93.1 mg, 70%) as yellow solid; m.p. 77-78 ^{o}C (Petroleum ether/EtOAc); R*f* = 0.28 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.37-7.34 (m, 2H), 7.31-7.27 (m, 4H), 7.19-7.17

(m, 1H), 7.02-6.98 (m, 2H), 6.91 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 2.4 Hz, 1H), 5.98 (s, 1H), 4.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 146.6, 142.6, 130.3, 129.8, 128.7, 128.5, 128.1, 126.9, 126.7, 126.5, 124.8, 120.8, 116.0, 45.9; HRMS (ES^+-TOF) calcd for $C_{17}H_{14}OSNa$ ($[M+Na]^+$): 289.0658, found 289.0663. IR: 3507, 1594, 1497, 1452, 1325, 1273, 1183, 1086, 757, 700.

1-((4-methoxyphenyl)(o-tolyl)methyl)naphthalen-2-ol (2n)

According to Method A with *o*-tolylmagnesium bromide (1.5 mmol, 0.76 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 1-((4-methoxyphenyl)(tosyl)methyl)naphthalen-2-ol **1f** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 ^{o}C for 12 h. Purification by flash column chromatography provided ***2n*** (175.2 mg, 99%) as yellow oil; R*f* = 0.61 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 14.4 Hz, 1H), 7.25-7.19 (m, 2H), 7.15-7.09 (m, 3H), 7.05-6.99 (m, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.30 (s, 1H), 5.38 (s, 1H), 3.79 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 153.4, 140.2, 137.3 , 133.2, 133.0, 131.1, 130.0, 129.6, 129.5, 128.7, 128.5, 127.4, 126.9, 123.1, 122.5, 119.8, 118.9, 114.7, 55.2, 46.1, 19.7; HRMS (ES^+-TOF) calcd for $C_{25}H_{23}O_2$ ($[M+H]^+$): 355.1693, found 355.1682. IR: 3475, 1621, 1508, 1250, 1176, 1032, 815, 744.

1-((4-methoxyphenyl)(phenyl)methyl)naphthalen-2-ol (2o)

According to Method A with phenylmagnesium bromide (1.5 mmol, 1.74 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 1-((4-methoxyphenyl)(tosyl)methyl)naphthalen-2-ol **1f** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 ^{o}C for 12 h. Purification by flash column chromatography provided ***2o*** (139.4 mg, 82%) as yellow oil; R*f* = 0.72 (Petroleum ether/EtOAc =3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.41-7.32 (m, 6H), 7.26-7.23 (m, 2H), 7.15 (d, *J* = 8.8 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.44 (s, 1H), 5.45 (s, 1H), 3.81 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 152.7, 141.9, 133.34, 133.30, 130.0, 129.5, 129.0, 128.9, 128.6, 127.0, 126.7, 123.1, 122.8, 120.2, 119.7, 115.2, 114.4, 55.1, 47.7; HRMS (ES^+-TOF) calcd for $C_{24}H_{20}O_2Na$($[M+Na]^+$): 363.1356, found 363.1342. IR: 3473, 1621, 1508, 1249, 1177, 1031, 812, 700.

1-([1,1'-biphenyl]-4-yl(4-methoxyphenyl)methyl)naphthalen-2-ol (2p)

According to Method A with [1,1'-biphenyl]-4-ylmagnesium bromide (1.5 mmol, 0.66 M in THF, 3.0

equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 1-((4-methoxyphenyl)(tosyl)methyl)naphthalen-2-ol **1f** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 ^oC for 12 h. Purification by flash column chromatography provided ***2p*** (199.7 mg, 96%) as yellow solid; m.p. 68-69^oC (Petroleum ether/EtOAc); R*f* = 0.57 (Petroleum ether/EtOAc = 3/1); ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.63-7.60 (m, 4H), 7.44-7.41 (m, 3H), 7.40-7.37 (m, 4H), 7.21 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.40 (s, 1H), 5.33 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 152.8, 140.8, 140.5, 139.9, 133.33, 133.29, 130.0, 129.65, 129.6, 129.4, 128.7, 127.7, 127.3, 127.0, 126.8, 123.2, 122.7, 120.1, 119.8, 115.4, 114.6, 55.3, 47.5; HRMS (ES^+-TOF) calcd for $C_{30}H_{24}O_2Na([M+Na]^+)$: 439.1669, found 439.1670. IR: 3470, 1599, 1508, 1487, 1247, 1178, 833, 757, 697.

1-(bis(4-methoxyphenyl)methyl)naphthalen-2-ol (2q)

According to Method A with (4-methoxyphenyl)magnesium bromide (1.5 mmol, 1.40 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 1-((4-methoxyphenyl)(tosyl)methyl)naphthalen-2-ol **1f** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 ^oC for 12 h. Purification by flash column chromatography provided ***2q*** (177.6 mg, 96%) as yellow solid; m.p. 94-95 ^oC (Petroleum ether/EtOAc); R*f* = 0.63 (Petroleum ether/EtOAc = 3/1); ^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 4H), 7.09 (d, *J* = 8.8 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 4H), 6.31 (s, 1H), 5.39 (s, 1H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 152.7, 133.6, 133.3, 129.9, 129.5, 128.7, 123.1, 122.7, 120.3, 119.8, 115.9, 114.5, 55.2,46.9; HRMS (ES^+-TOF) calcd for $C_{25}H_{23}O_3$ ($[M+H]^+$): 371.1642, found 371.1634. IR: 3420, 1604, 1508, 1438, 1246, 1176, 1034, 810, 751.

1-((4-methoxyphenyl)(5-methylthiophen-2-yl)methyl)naphthalen-2-ol (2r)

According to Method B: In a 25 mL Schlenk tube, 2,5-dimethylthiophene (1.5 mmol, 3.0 equiv) in dry THF (2 mL) was added dropwise *n*-BuLi (0.6 mL, 3.0 equiv, 2.5 M in hexane) at 0 °C under N_2 atmosphere. The reaction mixture was stirred for 1 h. Suspension of $ZnBr_2$ solution (1.5 mL, 1.0 M in THF, 3.0 equiv) was added, After 15 min stir at 0°C, the mixture was treated with substrate **1f** (0.5 mmol, 1.0 equiv) at room temperature. After the addition was completed, the reaction mixture was stirred at 60 °C for 12 h. Purification by flash column chromatography provided ***2r*** (160.2 mg, 89%)

as yellow solid; m.p. 129-130 °C (Petroleum ether/EtOAc); R*f* = 0.65 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H),7.44 (t, *J* = 7.6 Hz, 1H), 7.35-7.28 (m, 3H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.60 (s, 2H), 6.41 (s, 1H), 5.77 (s, 1H), 3.79 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 152.9, 143.9, 140.7, 133.0, 132.7, 129.7, 129.5, 129.4, 128.7, 126.8, 126.78, 124.8, 123.2, 122.4, 119.8, 119.7, 114.3, 55.2, 43.3, 15.4; HRMS (ES^+-TOF) calcd for $C_{23}H_{21}O_2S$ ($[M+H]^+$): 361.1257, found 361.1224. IR: 3450, 1600, 1510, 1463, 1249, 1177, 1033, 812, 739.

1-((9-ethyl-9H-carbazol-3-yl)(4-methoxyphenyl)methyl)naphthalen-2-ol (2s)

According to Method B: In a 25 ml Schlenk tube, 2-Bromoindazole (1.5 mmol, 3.0 equiv) in dry THF (2 mL) was added dropwise *n*-BuLi (0.6 mL, 3.0 equiv, 2.5 M in hexane) at -78 °C under N_2 atmosphere. The reaction mixture was stirred for 2 h. Suspension of $ZnBr_2$ solution (1.5 mL, 1.0 M in THF, 3.0 equiv) was added, After 15 min stir at 0°C, the mixture was treated with substrate **1f** (0.5 mmol, 1.0 equiv) at room temperature. After the addition was completed, the reaction mixture was stirred at 60 °C for 12 h. Purification by flash column chromatography provided ***2s*** (125.7 mg, 55%) as brown solid; m.p. 81-82 °C (Petroleum ether/EtOAc); R*f* = 0.55 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.93 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 9.2 Hz, 1H), 7.46-7.38 (m, 3H), 7.37-7.31 (m, 3H), 7.26-7.23 (m, 3H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.55 (s, 1H), 5.49 (s, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 1.43 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 153.0, 140.3, 139.0, 133.9 133.4, 132.0, 130.2, 129.5, 128.7, 126.8, 126.5, 125.9, 123.4, 123.1, 122.7, 122.5, 120.63, 120.60, 120.5, 120.0, 118.8, 114.5, 109.2, 108.5, 55.2, 47.9, 37.6, 13.8; HRMS (ES^+-TOF) calcd for $C_{32}H_{27}NO_2Na$ ($[M+Na]^+$):480.1934, found 480.1932**.** IR: 3458, 1600, 1508, 1469, 1384, 1331, 1249, 1177, 1032, 814, 746.

1-(furan-2-yl(phenyl)methyl)naphthalen-2-ol (2t)

According to Method A with phenylmagnesium bromide (1.5 mmol, 1.74 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 1-(furan-2-yl(tosyl)methyl)naphthalen-2-ol **1g** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 °C for 12 h. Purification by flash column chromatography provided ***2t*** (132.0 mg , 88%) ; as brown oil; (Petroleum ether/EtOAc); R*f* = 0.63 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 9.2 Hz, 1H), 7.43-7.39 (m, 2H), 7.33-7.28 (m, 4H), 7.24-7.21 (m, 3H), 7.09 (d, *J* = 8.8 Hz, 1H), 6.40

(s, 1H), 6.33-6.32 (m, 1H), 6.09 (d, *J* = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 152.8, 142.7, 139.9, 133.0, 129.8, 129.5, 128.9, 128.7, 128.1, 127.2, 126.8, 123.1, 122.6, 119.4, 117.7, 110.4, 108.9, 42.1; HRMS (ES^+-TOF) calcd for $C_{21}H_{17}O_2$ ($[M+H]^+$): 301.1223, found 301.1211. IR: 3499, 1621, 1491, 1432, 1256, 1034, 964, 810, 752, 696.

1-(phenyl(thiophen-2-yl)methyl)naphthalen-2-ol (2u)

According to Method A with phenylmagnesium bromide (1.5 mmol, 1.74 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 1-(thiophen-2-yl(tosyl)methyl)naphthalen-2-ol **1h** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 °C for 12 h. Purification by flash column chromatography provided ***2u*** (156.4 mg , 99%) ; as brown oil; (Petroleum ether/EtOAc); R*f* = 0.62 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 9.2 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.39-7.33 (m, 5H), 7.31-7.29 (m, 2H), 7.11 (d, *J* = 8.8 Hz, 1H), 6.98-6.96 (m, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.58 (s, 1H), 5.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 145.9, 141.4, 132.8, 129.9, 129.5, 129.0, 128.8, 128.4, 127.4, 127.0, 126.9, 126.8, 126.0, 123.3, 122.5, 119.9, 119.8, 43.9; HRMS (ES^+-TOF) calcd for $C_{21}H_{16}OSNa$ ($[M+Na]^+$): 339.0814, found 339.0815. IR: 3496, 1623, 1491, 1434, 1253, 1034, 964, 803, 755, 710.

2-((2-hydroxynaphthalen-1-yl)(thiophen-2-yl)methyl)benzonitrile (2v)

According to Method C with 2-iodobenzonitrile(1.5 mmol, 3.0 equiv), isopropylmagnesium chloride (0.82 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 1-(thiophen-2-yl(tosyl)methyl)naphthalen-2-ol **1h** in 2mL of THF at 60 °C for 12 h. Purification by flash column chromatography provided ***2v*** (80.2 mg, 47%); as yellow solid; m.p. 212-213°C (Petroleum ether/EtOAc); R*f* = 0.30 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.79 (t, *J* = 6.4 Hz, 2H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.54-7.43 (m, 3H), 7.41-7.33 (m, 3H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.99-6.97 (m, 1H), 6.89 (s, 1H), 6.68 (d, *J* = 3.6 Hz, 1H), 5.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 145.4, 144.7, 133.4, 133.3, 132.6, 130.6, 129.6, 129.5, 128.9, 127.8, 127.3, 127.0, 123.6, 122.3, 119.6, 118.2, 117.4, 113.0, 42.8; HRMS (ES^+-TOF) calcd for $C_{22}H_{16}NOS$ ($[M+H]^+$): 342.0947, found 342.0956. IR: 3403, 2225, 1626, 1515, 1438, 1284, 968, 812, 766, 744, 697.

1-((4-bromophenyl)(thiophen-2-yl)methyl)naphthalen-2-ol (2w)

According to Method C with 1-bromo-4-iodobenzene (1.5 mmol, 3.0 equiv), isopropylmagnesium chloride (0.82 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv),

1-(thiophen-2-yl(tosyl)methyl)naphthalen-2-ol **1h** in 2 mL of THF at 60 °C for 12 h. Purification by flash column chromatography provided ***2w*** (143.8 mg, 73%); as yellow solid; m.p. 112-113°C (Petroleum ether/EtOAc); R*f* = 0.65 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.8 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 4.49-7.44 (m, 3H), 7.39-7.33 (m, 2H), 7.29-7.28 (m, 2H), 7.14-7.11 (d, *J* = 8.8 Hz, 1H), 6.99 (t, *J* = 4.4 Hz, 1H), 6.86-6.85 (m, 1H), 6.55 (s, 1H), 5.46 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 145.6, 140.5, 132.6, 132.0, 130.2, 130.1, 129.6, 128.9, 127.0, 126.9, 126.3, 123.4, 122.5, 121.2, 119.6, 119.4, 43.3; HRMS (ES^+-TOF) calcd for $C_{21}H_{16}BrOS$ ($[M+H]^+$): 395.0100, found 395.0090. IR: 3532, 1622, 1508, 1486, 1260, 1010, 819, 751, 702.

2-((4-methoxyphenyl)(phenanthren-9-yl)methyl)phenol (2x)

According to Method A withphenanthren-9-ylmagnesium bromide (3.7 mL, 0.41 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** in 2 mL of THF at 60 °C for 12 h. Purification by flash column chromatography provided ***2x*** (193.1 mg, 99%); as white solid; m.p.85-86 °C (Petroleum ether/EtOAc); R*f* = 0.68 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ8.74 (d, *J* = 8.0 Hz, 1H), 8.67 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.64-7.61 (m, 2H), 7.53 (q, *J* = 8.1 Hz, 2H), 7.23 (s, 1H), 7.20-7.13 (s, 3H), 6.88-6.85 (m, 3H), 6.83-6.82 (m, 2H) 6.39 (s, 1H), 4.81 (s, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 153.1, 137.3, 134.0, 131.4, 131.0, 130.9, 130.6, 130.2, 129.9, 128.7, 128.0, 127.9, 126.8, 126.6, 126.5, 126.3, 125.1, 123.0, 122,4, 120.9, 116.1, 114.1, 55.2, 46.5; HRMS (ES^+-TOF) calcd for $C_{28}H_{23}O_2$ ($[M+H]^+$):391.1693, found. 391.1685**.** IR: 3419, 1607, 1508, 1454, 1245, 1177, 1090, 1033, 748.

3. Synthesis of *diarylmethanes* 3 from 1

Method A: In a 25 ml Schlenk tube, alkyl Grignard reagent (3.0 equiv) was added to a solution of $ZnBr_2$ (1.5 mL, 1.0 M, 3.0 equiv) at 0 °C under N_2 atmosphere. After 15 min stir, the mixture was treated with substrate **1** (0.5 mmol, 1.0 equiv) at room temperature. After the addition was completed, the reaction mixture was stirred at 60℃ for 12 h. After completion of the reaction, the mixture was quenched by adding 5 mL of NH_4Cl and extracted with EtOAc (3×10 mL). The combined organic phase was washed with H_2O (3×10 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified with flash silica gel chromatography to afford **3**.

Method D: Zinc powder (156 mg, 2.4 mmol, 1.2 equiv) was suspended in anhydrous THF (3 mL)

under N_2, and then 1,2-dibromoethane (22 μL, 0.3 mmol, 15 mol%) was added. The mixture was heated at 65 °C for 10 min. After the mixture was cooled to room temperature, TMSCl (13 μL, 0.1 mmol, 5 mol%) was added, and the mixture was stirred for another 15 min before a solution of Halogenated hydrocarbons (2 mmol, 1.0 equiv) in anhydrous THF (5 mL) was added dropwise. The resulting mixture was stirred for 24 h at 40 °C. In another 25 mL Schlenk tube, substrate **1** (0.5 mmol, 1.0 equiv) was dissolved in 2 mL of dry THF under N_2 atmosphere. Then formed RZnX (2 mmol, 4.0 equiv) were added to this mixture was heated at 60 °C for 12 h.. After completion of the reaction, the mixture was quenched by adding 5 mL of NH_4Cl and extracted with EtOAc (3×10 mL). The combined organic phase was washed with H_2O (3×10 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified with flash silica gel chromatography to afford **3**.

2-(1-(4-methoxyphenyl)propyl)phenol (3a)

According to Method A with ethylmagnesium bromide (1.5 mmol, 0.69 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 ^oC for 12 h. Purification by flash column chromatography provided ***3a*** (94.4 mg, 78%) as colorless oil; (Petroleum ether/EtOAc); R*f* = 0.75 (Petroleum ether/EtOAc = 3/1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.13-7.08 (m, 1H), 6.97-6.93 (m, 1H), 6.86 (d, *J* = 11.6 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 4.88 (s, 1H), 4.04 (t, *J* = 15.2 Hz, 1H), 3.79 (s, 3H), 2.14-1.73 (m, 2H), 0.94 (t, *J* = 14.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 153.4, 136.1, 131.2, 129.0, 127.8, 127.2, 120.7, 115.9, 113.9, 55.2, 45.3, 27.7, 12.6; HRMS (ES^+-TOF) calcd for $C_{16}H_{18}O_2Na([M+Na]^+)$: 265.1199, found 265.1199. IR: 3403, 1600, 1514, 1462, 1383, 1232, 1126, 1023, 833, 752.

2-(1-(4-methoxyphenyl)-2-methylpropyl)phenol (3b)

According to Method A with isopropylmagnesium bromide (1.5 mmol, 0.82 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 ^oC for 12 h. Purification by flash column chromatography provided ***3b*** (74.3 mg, 58%); as red solid; m.p. 103-104 ^oC (Petroleum ether/EtOAc); R*f* = 0.75 (Petroleum ether/EtOAc = 3/1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7..03 (t, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 1H), 4.72 (s, 1H), 3.79 (s, 1H), 3.76 (s, 3H), 2.51-2.45 (m, 1H), 0.94 (d, *J* =6.4 Hz, 3H), 0.87 (d, *J* =6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 153.3, 136.1, 131.2, 129.3, 129.2, 127.9, 126.8,

120.9, 128.0, 115.9, 113.7, 55.2, 51.4, 31.1, 21.7; HRMS (ES^+-TOF) calcd for $C_{17}H_{21}O_2$ ($[M+H]^+$): 257.1536, found 257.1552. IR: 3403, 1608, 1510, 1462, 1383, 1233, 1129, 1023, 833, 753.

2-(1-(4-methoxyphenyl)-2,2-dimethylpropyl)phenol (3c)

According to Method A with *tert*-butylmagnesium bromide (1.5 mmol, 0.99 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 2-((4-methoxyphenyl)(tosyl)methyl)phenol **1a** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 ^oC for 12 h. Purification by flash column chromatography provided ***3c*** (43.2 mg, 32%); as red oil; (Petroleum ether/EtOAc); R*f* = 0.71 (Petroleum ether/EtOAc = 3/1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 1H), 4.77 (s, 1H), 4.27 (s, 1H), 3.77 (s, 3H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 153.4, 134.8, 131.2, 130.4, 129.8, 126.7, 120.3, 115.8, 113.3, 55.1, 52.3, 35.2, 29.2; HRMS (ES^+-TOF) calcd for $C_{18}H_{23}O_2$ ($[M+H]^+$): 271.1693, found 271.1701. IR: 3403, 1610, 1510, 1454, 1380, 1233, 1126, 1023, 831, 750.

1-(1-(4-methoxyphenyl)propyl)naphthalen-2-ol (3d)

According to Method A with ethylmagnesium bromide (1.5 mmol, 0.69 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 1-((4-methoxyphenyl)(tosyl)methyl)naphthalen-2-ol **1f** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 ^oC for 12 h. Purification by flash column chromatography provided ***3d*** (129.9 mg, 89%) as yellow solid; m.p. 65-66^oC (Petroleum ether/EtOAc); R*f* = 0.62 (Petroleum ether/EtOAc = 3/1); ^1H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H),7.68 (d, *J* = 8.8 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.36-7.29 (m, 3H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.04-5.02 (m, 1H), 4.93-4.89 (m, 1H), 3.78 (s, 3H), 2.47-2.39 (m, 1H), 2.28-2.21 (m, 1H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 151.8, 148.1, 134.9, 133.8, 129.6, 128.8, 128.7, 128.5, 126.4, 123.0, 122.5, 119.3, 114.3, 55.2, 41.3, 24.6, 12.7; HRMS (ES^+-TOF) calcd for $C_{20}H_{20}O_2Na$($[M+Na]^+$): 315.1356, found 315.1376. IR: 3398, 1622, 1510, 1465, 1250, 1181, 1030, 801, 748.

1-(1-(4-methoxyphenyl)-2-methylpropyl)naphthalen-2-ol (3e)

According to Method A with isopropylmagnesium bromide (1.5 mmol, 0.82 M in THF, 3.0 equiv), $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv), 1-((4-methoxyphenyl)(tosyl)methyl)naphthalen-2-ol **1f** (0.5 mmol, 1.0 equiv) in 2 mL of THF at 60 ^oC for 12 h. Purification by flash column chromatography provided ***3e*** (79.6 mg, 52%) as yellow solid; m.p. 123-124 ^oC (Petroleum

ether/EtOAc); R*f* = 0.64 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.53-7.49 (m, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 5.22 (s, 1H), 4.58 (d, *J* = 10.4 Hz, 1H), 3.75 (s, 3H), 3.11-3.06 (m, 1H), 1.18 (d, *J* = 6.4 Hz, 3H), 0.80 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7, 151.1, 135.0, 133.9, 129.6, 129.4, 128.8, 128.4, 126.4, 123.4, 123.2, 122.9, 119.0, 113.8, 55.1, 49.0, 28.6, 23.0, 21.5; HRMS (ES^+-TOF) calcd for $C_{21}H_{23}O_2$ ($[M+H]^+$): 307.1693, found 307.1690. IR: 3412, 1621, 1509, 1432, 1263, 1179, 1025, 810, 740, 525.

5-(2-hydroxynaphthalen-1-yl)-5-(4-methoxyphenyl)pentyl acetate (3f)

According to Method D with (5-methoxy-5-oxopentyl)zinc(II) iodide (2 mmol, 4.0 equiv), 1-((4-methoxyphenyl)(tosyl)methyl)naphthalen-2-ol **1f** (0.5 mmol, 1.0 equiv), 2 mL of THF at 60 ^{o}C for 12 h. Purification by flash column chromatography provided **3f** (128.6 mg, 68%) as yellow oil; (Petroleum ether/EtOAc); R*f* = 0.41 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.44 (s, 1H), 7.35-7.28 (m, 3H), 7.02 (d, *J* = 8.8 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.38 (s, 1H), 4.99 (t, *J* = 7.4 Hz, 1H), 3.98 (t, *J* = 6.8 Hz, 1H), 3.77 (m, 3H) , 2.41-2.31 (m, 2H), 1.97 (s, 3H), 1.72-1.60 (m, 2H), 1.43-1.41 (m, 1H), 1.28-1.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 158.0, 151.8, 135.2, 133.6, 129.6, 128.8, 128.6, 128.4, 126.4, 123.1, 122.9, 122.5, 119.0, 114.1, 64.4, 55.2, 39.8, 31.4, 28.7, 24.4, 20.9; HRMS (ES^+-TOF) calcd for $C_{24}H_{26}O_4Na$($[M+Na]^+$): 401.1723, found 401.1724. IR: 3445, 1733, 1610, 1512, 1241, 1177, 1030, 813, 750.

ethyl 6-(2-hydroxynaphthalen-1-yl)-6-(4-methoxyphenyl)hexanoate *(3g)*

According to Method D with (5-ethoxy-5-oxopentyl)zinc(II) iodide (2 mmol, 4.0 equiv), 1-((4-methoxyphenyl)(tosyl)methyl)naphthalen-2-ol **1f** (0.5 mmol, 1.0 equiv), 2 mL of THF at 60 ^{o}C for 12 h. Purification by flash column chromatography provided **3g** (117.6 mg, 60%) as yellow oil; (Petroleum ether/EtOAc); R*f* = 0.46 (Petroleum ether/EtOAc = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.44 (s, 1H), 7.34-7.27 (m, 3H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 5.19 (s, 1H), 4.99-4.96 (m, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 2.37-2.19 (m, 4H); 1.70-1.60 (m, 4H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 158.0, 151.8, 133.5, 129.6, 128.8, 128.6, 128.4, 126.3, 122.9, 122.6, 119.1, 114.1, 60.2, 55.2, 39.7, 34.2, 31.5, 27.6, 25.2, 14.1; HRMS (ES^+-TOF) calcd for $C_{25}H_{28}O_4Na$ ($[M+Na]^+$): 415.1880, found 415.1882. IR: 3445, 1731, 1625, 1510, 1247, 1179, 1033, 813, 747.

1-(4-methoxyphenyl)-1,2-dihydro-3H-benzo[f]chromen-3-one (3h)

According to Method D with Zinc powder (156 mg, 2.4 mmol, 1.2 equiv) was suspended in anhydrous THF (3 mL) under N_2, and then 1,2-dibromoethane (22 μL, 0.3 mmol, 15 mol%) was added. The mixture was heated at 65 °C for 10 min. After the mixture was cooled to room temperature, TMSCl (13 μL, 0.1 mmol, 5 mol%) was added, and the mixture was stirred for another 15 min before a solution of ethyl bromoacetate (2 mmol, 1.0 equiv) in anhydrous THF (5 mL) was added dropwise. The resulting mixture was stirred for 24 h at 40 °C. In another 25 mL Schlenk tube, substrate **1f** (0.5 mmol, 1.0 equiv) was dissolved in 2 mL of dry THF under N_2 atmosphere. Then formed (2-ethoxy-2-oxoethyl)zinc(II) bromide (2 mmol, 4.0 equiv) were added to this mixture was heated at 60 °C for 12 h. Purification by flash column chromatography provided **3h** (109.5 mg, 72%) as white solid; m.p.49.1-50.7 ^{o}C (Petroleum ether/EtOAc); R*f* = 0.43 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.50-7.42 (m, 2H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 4.92-4.91 (m, 1H), 3.73 (s, 3H), 3.18-3.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 158.6, 149.6, 132.5, 131.0, 130.9, 129.8, 128.7, 128.0, 127.4, 125.2, 123.0, 117.9, 117.5, 114.5, 55.2, 37.7, 36.8; HRMS (ES^+-TOF) calcd for $C_{20}H_{17}O_3$([M+H]$^+$): 305.1172, found 305.1181. IR: 3447, 1763, 1611, 1509, 1244, 1176, 1138, 1031, 969, 851, 817, 746.

1-(thiophen-2-yl)-1,2-dihydro-3H-benzo[f]chromen-3-one (3i)

According to Method D with Zinc powder (156 mg, 2.4 mmol, 1.2 equiv) was suspended in anhydrous THF (3 mL) under N_2, and then 1,2-dibromoethane (22 μL, 0.3 mmol, 15 mol%) was added. The mixture was heated at 65 °C for 10 min. After the mixture was cooled to room temperature, TMSCl (13 μL, 0.1 mmol, 5 mol%) was added, and the mixture was stirred for another 15 min before a solution of ethyl bromoacetate (2 mmol, 1.0 equiv) in anhydrous THF (5 mL) was added dropwise. The resulting mixture was stirred for 24 h at 40 °C. In another 25 mL Schlenk tube, substrate **1h** (0.5 mmol, 1.0 equiv) was dissolved in 2 mL of dry THF under N_2 atmosphere. Then formed (2-ethoxy-2-oxoethyl)zinc(II) bromide (2 mmol, 4.0 equiv) were added to this mixture was heated at 60 °C for 12 h. Purification by flash column chromatography provided **3i** (128.8 mg, 92%) as white solid; m.p.78-79 ^{o}C (Petroleum ether/EtOAc); R*f* = 0.52 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.86 (m, 3H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 4.8 Hz, 1H), 6.85 (t, *J* = 8.8 Hz, 1H), 6.68-6.67 (m, 1H), 5.19 (d, *J* =

6.0 Hz, 1H), 3.3 (d, J = 14.8 Hz, 1H), 3.20 (dd, J_1 = 16.0 Hz, J_2 = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 149.3, 143.6, 131.0, 130.6, 130.1, 128.8, 127.6, 127.2, 125.4, 125.0, 124.9, 122.9, 117.9, 117.7, 37.6, 32.8; HRMS (ES^+-TOF) calcd for $C_{17}H_{13}O_2S([M+H]^+)$: 281.0631, found 281.0638. IR: 3446, 1771, 1627, 1516, 1224, 1174, 1109, 819, 710.

4. Application of triarylmethanes derivatives

(S)-4-((3-chlorophenyl)(4-methoxyphenyl)methyl)phenol (5a)

In a 25 mL Schlenk tube, (3-chlorophenyl)magnesium bromide (2.3 mL, 0.65 M in THF, 3.0 equiv) was added to a solution of $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv) at 0 ^oC under N_2 atmosphere. After 15 min, the mixture was treated with 4-((4-methoxyphenyl)(tosyl)methyl)phenol **4a** (0.5 mmol, 1.0 equiv) at room temperature. After the addition was completed, the reaction mixture was stirred at 60 ℃ for 12 h. After completion of the reaction, the mixture was quenched by adding 5 mL of NH_4Cl and extracted with EtOAc (3×10 mL). The combined organic phase was washed with H_2O (3×10 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified with flash silica gel chromatography to afford **5a** (149.6 mg, 92%) as yellow oil; Rf = 0.52 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.26 (m, 2H), 7.07-7.03 (m, 4H), 6.97 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 8.4 Hz, 2H), 5.68 (s, 1H), 5.43 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 154.0, 143.0, 136.0, 135.9, 131.9, 130.6, 130.3, 130.2, 128.3, 115.2, 113.8, 55.2, 54.4; HRMS (ES^+-TOF) calcd for $C_{20}H_{18}ClO_2$ ($[M+H]^+$): 325.0990, found 325.0991. IR: 3404, 1610, 1509, 1471, 1246, 1174, 1034, 830, 706, 580.

4-benzhydryl-2-methoxyphenol (5b)

In a 25 mL Schlenk tube, phenylmagnesium bromide (0.93 mL, 1.61 M in THF, 3.0 equiv) was added to a solution of $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv) at 0 ^oC under N_2 atmosphere. After 15 min, the mixture was treated with 2-methoxy-4-(phenyl(tosyl)methyl)phenol **4b** (0.5 mmol, 1.0

equiv) at room temperature. After the addition was completed, the reaction mixture was stirred at 60°C for 12 h. After completion of the reaction, the mixture was quenched by adding 5 mL of NH_4Cl and extracted with EtOAc (3×10 mL). The combined organic phase was washed with H_2O (3×10 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified with flash silica gel chromatography to afford **5b** (107 mg, 74%) as white solid; m.p.98-99 ^oC (Petroleum ether/EtOAc); R*f* = 0.62 (Petroleum ether/EtOAc = 3/1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.29-7.25 (m, 4H), 7.21 (d, *J* = 6.8 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 4H), 6.82 (d, *J* = 8 Hz, 1H), 6.62 (2, 1H), 6.56 (d, *J* = 8 Hz, 1H), 5.49 (d,*J* = 7.6 Hz, 2H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 144.3, 144.2, 136.0, 129.5, 128.4, 126.4, 122.4, 114.2, 112.2, 56.6, 56.0 ; HRMS (ES^+-TOF) calcd for $C_{20}H_{18}ClO_2$ ($[M+H]^+$): 325.0990, found 325.0991. IR: 2515, 1593, 1509, 1487, 1445, 1425, 1274, 1227, 1025, 807, 713, 689, 535 .

4-benzhydryl-2,6-dimethoxyphenol (5c)

In a 25 mL Schlenk tube, phenylmagnesium bromide (0.93 mL, 1.61 M in THF, 3.0 equiv) was added to a solution of $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv) at 0 ^oC under N_2 atmosphere. After 15 min, the mixture was treated with 2,6-dimethoxy-4-(phenyl(tosyl)methyl)phenol **4c** (0.5 mmol, 1.0 equiv) at room temperature. After the addition was completed, the reaction mixture was stirred at 60 °C for 12 h. After completion of the reaction, the mixture was quenched by adding 5 mL of NH_4Cl and extracted with EtOAc (3×10 mL). The combined organic phase was washed with H_2O (3×10 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified with flash silica gel chromatography to afford **5c** (111 mg, 69%) as yellow solid; m.p.126-127 ^oC (Petroleum ether/EtOAc); R*f* = 0.57 (Petroleum ether/EtOAc = 3/1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.25

(m, 4H), 7.22-7.19 (m, 2H), 7.11 (d, J = 8.4 Hz, 4H), 6.35 (s, 2H), 5.47 (s, 1H), 5.41 (s, 1H), 3.75 (s, 6H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 144.1, 135.1, 133.4, 129.4, 128.4, 126.4, 106.6, 56.9, 56.4 ; HRMS (ES^+-TOF) calcd for $C_{20}H_{18}ClO_2$ ($[M+H]^+$): 325.0990, found 325.0991. IR: 3481, 1618, 1514, 1450, 1422, 1207, 1106, 740, 701.

4-benzhydryl-2,6-dibromophenol (5d)

In a 25 mL Schlenk tube, phenylmagnesium bromide (0.93 mL, 1.61 M in THF, 3.0 equiv) was added to a solution of $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv) at 0 ^{o}C under N_2 atmosphere. After 15 min, the mixture was treated with 2,6-dibromo-4-(phenyl(tosyl)methyl)phenol **4d** (0.5 mmol, 1.0 equiv) at room temperature. After the addition was completed, the reaction mixture was stirred at 60 °C for 12 h. After completion of the reaction, the mixture was quenched by adding 5 mL of NH_4Cl and extracted with EtOAc (3×10 mL). The combined organic phase was washed with H_2O (3×10 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified with flash silica gel chromatography to afford **5d** (127 mg, 61%) as white solid; m.p.120-121 ^{o}C (Petroleum ether/EtOAc); Rf = 0.71 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.28 (m, 4H), 7.24-7.23 (m, 2H), 7.18 (s, 2H), 7.07 (d, J = 7.2 Hz, 4H), 5.79 (s, 1H), 5.42 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 142.8, 138.9,132.8, 132.8, 129.3, 128.7, 126.9, 109.9, 55.6 ; HRMS (ES^+-TOF) calcd for $C_{20}H_{18}ClO_2$ ($[M+H]^+$): 325.0990, found 325.0991. IR: 3491, 1605, 1492, 1472, 1168, 728, 696, 590.

(S)-4-((4-methoxyphenyl)(phenanthren-9-yl)methyl)phenol (5e)

In a 25 mL Schlenk tube, phenanthren-9-ylmagnesium bromide (3.7 mL, 0.41 M in THF, 3.0 equiv) was added to a solution of $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv) at 0 ^{o}C under N_2 atmosphere. After 15 min, the mixture was treated with 4-((4-methoxyphenyl)(tosyl)methyl)phenol **4a** (0.5 mmol, 184.0 mg, 1.0 equiv) at room temperature. After the addition was completed, the reaction mixture

was stirred at room temperature for 18 h. After completion of the reaction, the mixture was quenched by adding 5 mL of NH_4Cl and extracted with EtOAc (3×10 mL). The combined organic phase was washed with H_2O (3×10 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified with flash silica gel chromatography to afford **5e** (103.4 mg, 57%) as white solid; m.p.77-78 ^oC (Petroleum ether/EtOAc); R*f* = 0.52 (Petroleum ether/EtOAc = 3/1); ^1H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 8.4 Hz, 1H), 8.66 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.63-7.59 (m, 2H), 7.55-7.48 (m, 2H), 7.16 (s, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 6.15 (s, 1H), 5.02-4.95 (m, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 154.0, 138.8, 136.0, 135.9, 131.4, 131.2, 130.8, 130.6, 129.8, 128.7, 128.3, 126.6, 126.5, 126.4, 126.1, 125.2, 123.0, 122,3, 115.3, 113.8, 55.2, 51.8; HRMS (ES^+-TOF) calcd for $C_{28}H_{23}O_2$ ($[M+H]^+$):391.1693, found. 391.1687. IR: 3396, 1609, 1508, 1449, 1245, 1172, 1034, 800, 748, 723.

2,6-dimethyl-4-(phenyl(thiophen-2-yl)methyl)phenol (5f)

In a 25 mL Schlenk tube, thiophen-2-ylmagnesium bromide (2.1 mL, 0.72 M in THF, 3.0 equiv) was added to a solution of $ZnBr_2$ (1.5 mL, 1.0 M in THF, 3.0 equiv) at 0 ^oC under N_2 atmosphere. After 15 min, the mixture was treated with 2,6-dimethyl-4-(phenyl(tosyl)methyl)phenol **4f** (0.5 mmol, 183.0 mg, 1.0 equiv) at room temperature. After the addition was completed, the reaction mixture was stirred at 60 °C for 12 h. After completion of the reaction, the mixture was quenched by adding 5 mL of NH_4Cl and extracted with EtOAc (3×10 mL). The combined organic phase was washed with H_2O (3×10 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified with flash silica gel chromatography to afford **5f** (111.7 mg, 76%) as white solid; m.p.105-106 ^oC (Petroleum ether/EtOAc); R*f* = 0.78 (Petroleum ether/EtOAc = 3/1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.30 (m, 2H), 7.26-7.21 (m, 4H), 6.95 (t, *J* = 8.4 Hz, 1H), 6.85 (s, 2H), 6.70 (d, *J* = 3.2 Hz, 1H), 5.57 (s, 1H), 4.58 (s, 1H), 2.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 148..6, 144.2, 135.4, 128.9, 128.7, 128.3, 126.5, 126.4, 126.1, 124.3, 122.8, 51.4, 16.0; HRMS (ES^+-TOF) calcd for $C_{19}H_{18}OSNa$($[M+Na]^+$): 317.0971, found 317.0973. IR: 3580, 1600, 1487, 1300, 1204, 1029, 823, 701.

5. Synthesis of starting materials

General procedure A:

A solution of Grignard reagents **6** (25 mmol) was added to *ortho*-hydroxybenzaldehyde **5** (10.0 mmol) in THF (10 mL) under N_2. After being stirred at room temperature for 3 h, the reaction mixture was quenched by a saturated NH_4Cl (20 mL) and extracted with CH_2Cl_2. The combined organic phases were washed with brine, then dried over Na_2SO_4, filtered and concentrated. The crude mixture was purified through a short silica gel column (hexane/ethyl acetate) to afford 2-(hydroxy(phenyl)methyl)phenols **7**. $TolSO_2Na$ (2.047 g, 11.5 mmol) and TsOH (3.360 g, 17.5 mmol) were placed in a dried Schlenk tube, and dry CH_2Cl_2 (40 mL) was added. The mixture was stirred at room temperature for **5** min. Then, a solution 30 mL of 2-(hydroxy(phenyl)methyl)phenols **7** (10 mmol) in CH_2Cl_2 was added and stirred for 1.5 h, the reaction mixture was quenched and adjusted to pH = 8 by saturated $NaHCO_3$. After extracted with CH_2Cl_2, the combined organic phases were washed with 1N HCl and brine, then dried over Na_2SO_4, filtered and concentrated. The crude mixture was purified through a short silica gel column (hexane/ethyl acetate) to afford 2-(phenyl(tosyl)methyl)phenol **1**.

General procedure B:

At 0 ^oC under N_2, to a flame-dried flask charged with a solution of bromo-hydrocarbons (25 mmol) in dry THF (15 mL) was added *n*-BuLi (25 mmol, 2.5 M in THF, 10 mL) dropwise. The reaction was stirred for 30 min at the same temperature and then a solution of the aldehyde (10 mmol) in THF (6 mL) was added by syringe. The reaction mixture was then warmed to 60 ^oC and stirred overnight. Upon completion, the reaction mixture was cooled to 0 ^oC. A saturated aqueous NH_4Cl solution (20 mL) was added dropwise. The organic layer was separated. The aqueous layer was extracted with Et_2O (3× 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel chromatography to afford the desired alcohol **7**. $TolSO_2Na$ (2.047 g, 11.5 mmol) and TsOH (3.360 g, 17.5 mmol) were placed in a dried Schlenk tube, and dry CH_2Cl_2 (40 mL) was added, and the mixture was stirred at room temperature for **5** min. Then, the solution 30 mL of 2-(hydroxy(phenyl)methyl)phenols **7** (10 mmol) in CH_2Cl_2 was added and stirred for 1.5 h, the reaction mixture was quenched and adjusted to pH = 8 by saturated $NaHCO_3$. After extracted with CH_2Cl_2, the combined organic phases were washed with 1N HCl and brine, then dried over Na_2SO_4, filtered and concentrated. The crude mixture was purified through a short silica gel column (hexane / ethyl acetate) to afford 2-(phenyl(tosyl)methyl)phenol **1**.

2-((4-methoxyphenyl)(tosyl)methyl)phenol (1a)

According to general procedure A: ***1a*** (2.39 g, 65%); as white solid; (Petroleum ether/EtOAc); R*f* = 0.31 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.64 (M , 1H), 7.54 (d, *J* = 8.0 Hz , 2H) , 7.43 (d, *J* = 8.8 Hz , 2H), 7.16-7.09 (m, 3H), 6.90 (t, *J* = 3.6 Hz ,1H), 6.82-6.74 (m, 4H), 5.87 (m, 1H), 3.76 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 154.2, 144.5, 135.0, 131.5, 130.5, 129.9, 129.3, 128.8, 124.2, 121.0, 120.2, 117.4, 114.0, 69.2, 55.2, 21.6.

4-chloro-2-((4-methoxyphenyl)(tosyl)methyl)phenol (1b)

According to general procedure A: ***4e*** (2.17 g, 67%); as white solid; m.p. 164-165^{o}C (Petroleum ether/EtOAc); R*f* = 0.32 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 2.4 Hz , 1H), 7.54 (d, *J* = 8.0 Hz , 2H), 7.44 (d, *J* = 8.8 Hz , 2H), 7.18 (d, *J* = 8.8 Hz , 2H), 7.09-7.06 (m, 1H)， 6.81 (d, *J* = 8.8 Hz , 2H), 6.70 (d, *J* = 8.8 Hz , 1H), 5.79 (s, 1H), 3.77 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 153.0, 144.9, 134.6, 131.4, 130.1, 129.9, 129.4, 128.8, 125.9, 123.6, 121.9, 118.8, 114.1, 69.0, 55.2, 21.6; HRMS(ES^+-TOF) calcd for $C_{21}H_{19}ClO_4SNa$ ([M+Na^+]): 425.0585, found 425.0587. IR: 3415, 1599, 1510, 1416, 1253, 1178, 1140, 1086, 1030, 820, 725, 665, 585, 538.

4-fluoro-2-((4-methoxyphenyl)(tosyl)methyl)phenol (1c)

According to general procedure A: ***4g*** (2.06 g, 58%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.65 (m , 1H), 7.55-7.49 (m, 4H) , 7.17-7.12 (m , 3H),6.99-6.91 (m , 3H), 6.77-6.75 (m, 1H)，6.55 (s , 1H),5.90 (m , 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.0, 161.5, 154.1, 144.8, 134.9, 132.0 (d, *J* = 9.3 Hz), 130.4, 130.1, 129.4, 128.8, 128.2, 121.2, 119.9, 117.3, 115.7, 115.4, 68.8, 21.6.

2-((4-chlorophenyl)(tosyl)methyl)phenol (1d)

According to general procedure A: ***4f*** (2.75 g, 74%); as white solid; m.p. 183-184^{o}C (Petroleum ether/EtOAc); R*f* = 0.24 (Petroleum ether/EtOAc = 3/1); H NMR (400 MHz, $CDCl_3$): δ 7.60-7.55 (m , 3H), 7.47 (d, *J* = 8.8 Hz, 2H) , 7.29-7.28 (m , 1H), 7.27-7.26 (m, 1H)，7.21-7.17 (m, 3H)，6.93 (t, *J* = 8.0 Hz, 1H)，6.81 (d, , *J* = 8.0 Hz, 1H)，5.85 (s , 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 144.9, 134.9, 134.8, 131.6, 130.9, 130.6, 130.3, 129.4, 128.9, 128.8, 121.4, 119.8, 117.7, 69.3, 21.6; HRMS (ES^+-TOF) calcd for $C_{20}H_{18}ClO_3S$ ([M+H]$^+$): 373.0660, found: 373.0673. IR: 3374, 1596, 1490, 1458, 1312, 1274, 1145, 1085, 1015, 814, 760, 714, 649, 577.

2-(thiophen-2-yl(tosyl)methyl)phenol (1e)

According to general procedure B: 4j (2.82 g, 73%); as purple solid; m.p. 148-149^{o}C (Petroleum ether/EtOAc); R*f* = 0.30 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* =

8.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 5.2 Hz, 1H), 7.25-7.24 (m, 1H), 7.20-7.17 (m, 3H), 6.98-6.96 (m, 1H), 6.93-6.91(m, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.18 (s, 1H), 2.37 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 144.8, 134.2, 133.3, 130.8, 130.4, 129.9, 129.3, 129.1, 127.1, 126.9, 121.2, 119.6, 117.4, 65.3, 21.6; HRMS (ES^+-TOF) calcd for $C_{18}H_{17}O_3S_2$ ($[M+H]^+$): 345.0614, found 345.0630. IR: 3369, 1596, 1458, 1354, 1294, 1134, 1078, 814, 756, 712, 587.

1-((4-methoxyphenyl)(tosyl)methyl)naphthalen-2-ol (1f)

According to general procedure A: ***4i*** (6.41g, 76%) as yellow solid; m.p. 158-159 ^oC (Petroleum ether/EtOAc); R*f* = 0.52 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.58 (m, 7H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.26-7.19 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.44 (s, 1H), 3.77 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 154.4, 145.0, 134.3, 132.9, 131.6, 131.3, 129.3, 128.9, 128.5, 127.1, 123.2, 122.4, 120.9, 120.6, 114.2, 110.8, 69.8, 55.2, 21.5; HRMS (ES^+-TOF) calcd for $C_{25}H_{23}O_4S$ ($[M+H]^+$): 419.1312, found 419.1313. IR: 3318, 1626, 1504, 1437, 1361, 1186, 1138, 1081, 1033, 966, 775, 751, 662, 520.

1-(furan-2-yl(tosyl)methyl)naphthalen-2-ol (1g)

According to general procedure B: ***4d*** (1.74 g, 46%); as green solid; m.p. 114-115 ^oC (Petroleum ether/EtOAc); R*f* = 0.30 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 9.2 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 3H),7.38 (t, *J* = 7.4 Hz, 2H), 7.29-7.27 (m, 1H), 7.29-7.22 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.83 (s, 1H), 6.53 (s, 1H), 3.39-6.38 (m, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.9, 145.3, 144.4, 143.4, 134.2, 132.9. 131.9, 129.5, 129.3, 128.9, 128.7, 127.2, 124.7, 123.3, 120.8, 112.7, 111.2, 108.9, 64.6, 21.4; HRMS (ES^+-TOF) calcd for $C_{22}H_{19}O_4S$ ($[M+H]^+$): 275.1436, found 275.1443. IR: 3406, 1600, 1517, 1439, 1274, 1142, 1085, 1016, 812, 749, 653, 577.

1-(thiophen-2-yl(tosyl)methyl)naphthalen-2-ol (1h)

According to general procedure A: ***4c*** (1.97 g, 50%); as yellow solid; m.p.147-148^oC (Petroleum ether/EtOAc); R*f* = 0.24 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (s, 1H), 7.74 (d, *J* = 9.2 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.55 (s, 1H), 7.35-7.31 (m, 3H), 7.25-7.23 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.99-6.97 (m, 1H), 6.64 (s, 1H), 2.24 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 145.4, 132.6, 132.0, 131.3, 130.1, 129.4, 129.2, 128.9, 128.8, 128.7, 127.7, 127.3, 126.8, 123.3, 121.1, 120.2, 110.6, 66.1, 21.5; HRMS (ES^+-TOF) calcd for $C_{22}H_{18}O_3S_2$ ($[M+H]^+$): 395.0770, found 395.0789. IR: 3360, 1624, 1513, 1438, 1280, 1135, 1078,

822, 756, 709, 648, 579, 527.

4-((4-methoxyphenyl)(tosyl)methyl)phenol (4a)

According to general procedure A: ***4a*** (2.65 g, 72%); as white solid; m.p. 116-117°C; R*f* = 0.30 (Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.2 Hz , 2H), 7.42-7.35 (m, 4H) , 7.16 (d, *J* = 7.2 Hz , 2H), 6.82 (d, *J* = 7.2 Hz , 2H), 6.73 (d, *J* = 7.6 Hz , 2H), 5.17 (s, 1H), 3.77 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 156.3, 144.4, 135.1, 131.2, 131.1, 129.3, 128.9, 125.1, 124.4, 115.7, 114.0, 75.3, 55.2, 21.6; HRMS (ES^+-TOF) calcd for $C_{21}H_{21}O_4S$ ($[M+H]^+$): 369.1155, found 369.1166. IR: 3385, 1610, 1513, 1451, 1253, 1176, 1139, 1081, 1028, 812, 718, 664, 568, 516.

2-methoxy-4-(phenyl(tosyl)methyl)phenol(4b)

According to general procedure A: ***4b*** (4.85 g, 92%); as white solid; m.p. 118-124°C; R*f* = 0.25(Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 10.7 Hz , 4H), 7.15 (d, *J* = 6 Hz , 2H) , 7.10 (s, 1H), 6.91 (d, *J* = 8 Hz , 2H), 6.80 (d, *J* = 8 Hz , 2H), 5.21 (s, 1H), 3.83 (s, 3H), 3.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 145.9, 144.3, 135.3, 133.3, 129.7, 129.2, 128.9, 128.5, 128.4, 124.6, 123.4, 114.3, 112.2, 76.0, 55.9, 21.5 ; HRMS (ES^+-TOF) calcd for $C_{21}H_{21}O_4S$ ($[M+H]^+$): 369.1155, found 369.1166. IR: 3424, 1603, 1524, 1450, 1141, 1079, 1037, 815, 696, 666, 558 .

2,6-dimethoxy-4-(phenyl(tosyl)methyl)phenol(4c)

According to general procedure A: ***4c*** (4.58 g, 93%); as white solid; m.p. 145-155°C; R*f* = 0.22(Petroleum ether/EtOAc = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.49 (m, 4H), 7.31 (d, *J* =4 Hz , 3H) , 7.16 (d, *J* =8 Hz, 2H) , 6.72 (s, 2H) , 5.19 (s, 1H) , 3.81 (s, 6H), 2.36 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 144.5, 135.5, 135.2, 133.3, 129.9, 129.3, 129.1, 128.7, 128.6, 123.9, 100.1, 76.3, 56.42, 21.6 ; HRMS (ES^+-TOF) calcd for $C_{21}H_{21}O_4S$ ($[M+H]^+$): 369.1155, found 369.1166. IR: 3446, 1610, 1519, 1425, 1309, 1212, 1138, 1081, 1028, 822, 703, 600, 553, 491.

2,6-dibromo-4-(phenyl(tosyl)methyl)phenol(4d)

According to general procedure A: ***4d*** (2.47g, 40%); as white solid; m.p. 203-207°C; R*f* = 0.35(Petroleum ether/EtOAc = 3/1);^{1}H NMR (400 MHz, $CDCl_3$): δ7.62 (s, 2H), 7.49 (d, *J* =8 Hz , 2H) , 7.45-7.42 (m, 2H) , 7.33-7.32 (m, 3H) , 7.19 (d, *J* =8 Hz, 2H) , 5.99 (s, 1H), 5.16 (s, 1H), 2.38

(s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 144.9, 134.6, 133.3, 132.3, 129.7, 129.4, 129.0, 128.9, 128.8, 127.4, 109.8, 74.5, 21.6 ; HRMS (ES^+-TOF) calcd for $C_{21}H_{21}O_4S$ ($[M+H]^+$): 369.1155, found 369.1166. IR: 3368, 1602, 1555, 1493, 1485, 1324, 1139, 1081, 1080, 792, 713, 680, 601, 549.

2,6-dimethyl-4-(phenyl(tosyl)methyl)phenol (4f)

According to general procedure A: ***4f*** (2.78 g, 76%); as white solid; m.p. 205-206 ^{o}C (Petroleum ether/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.48 (m , 4H), 7.39-7.27 (m, 3H) , 7.16-7.15 (m, 4H), 5.15 (s, 1H), 2.36 (s, 3H), 2.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 144.2, 135.4, 133.6, 130.1, 129.8, 129.1, 129.0, 128.5,128.3, 124.0, 123.3, 76.0, 21.6, 15.9. HRMS (ES^+-TOF) calcd for $C_{22}H_{22}O_3SNa$ ($[M+Na]^+$): 389.1182, found 389.1183. IR: 3362, 3070, 1608, 1548, 1474, 1408, 1322, 1083, 848, 815, 722.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Copies of ^{1}H and ^{13}C NMR spectra for all new compounds (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: mmzok@zstu.edu.cn; renhj@zstu.edu.cn

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT:

We are grateful to the National Natural Science Foundation of China (21602202, 21602203), the Science Foundation of Zhejiang Sci-Tech University (Grant Nos. 13062121-Y, 1206820-Y and 1206821-Y), the Program for Innovative Research Team of Zhejiang Sci-Tech University (Grant Nos. 13060052-Y) and the Zhejiang Provincial Top Key Academic Discipline of Chemical Engineering and Technology of Zhejiang Sci-Tech University for financial support.

REFERENCES:

(1) For Reviews: (a) Duxbury, D. F. The Photochemistry and Photophysics of Triphenylmethane Dyes in Solid and Liquid Media. *Chem. Rev*. **1993**, *93*, 381. (b) Shchepinov, M. S.; Korshun, V. A. Recent Applications of Bifunctional Trityl Groups. *Chem. Soc. Rev.* **2003**, *32*, 170. (c) Nair, V.; Thomas, S.; Mathew, S. C.; Abhilash, K. G. Recent Advances in the Chemistry of Triaryl- and Triheteroarylmethanes. *Tetrahedron.* **2006**, *62*, 6731.

(2) (a) Parai, M. K.; Panda, G.; Chaturvedi, V.; Manju, Y. K.; Sinha, S. Thiophene Containing Triarylmethanes as Antitubercular Agents. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 289. (b) Panda, G.; Parai, M. K.; Das, S. K.; Shagufta.; Sinha, M.; Chaturvedi, V.; Srivastava, A. K.; Manju, Y. S.; Gaikwad, A. N.; Sinha, S. Effect of Substituents on Diarylmethanes for Antitubercular Activity. *Eur. J. Med. Chem.*, **2007**, *42*, 410. (c) Kashyap, V. Kr.; Gupta, R. K.; Shrivastava, R.; Srivastava, B. S.; Srivastava, R.; Parai, M. K.; Singh, P.; Bera, S.; Panda, G. *In vivo* Activity of Thiophene-containing Trisubstituted Methanes Against Acute and Persistent Infection of Non-tubercular Mycobacterium Fortuitum in a Murine Infection Model. *J. Antimicrob. Chemother.* **2012**, *67*, 1188.

(3) (a) Panda, G.; Shagufta; Mishra, J. K.; Chaturvedi, V.; Srivastava, A. K.; Srivastava, R.; Srivastava, B. S. Diaryloxy Methano Phenanthrenes: a New Class of Antituberculosis Agents. *Bioorg. Med. Chem.* **2004**, *12,* 5269. (b) Panda, G.; Srivastava, A. K.; Sinha, S. Synthesis and Antitubercular Activity of 2-Hydroxy-aminoalkyl Derivatives of Diaryloxy Methano Phenanthrenes. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 5222. (c) Shagufta, Srivastava, A. K.; Sharma, R.; Mishra, R.; Balapure, A. K.; Murthy, P. S. R.; Panda, G. Substituted Phenanthrenes with Basic Amino Side Chains: A New Series of Anti-breast Cancer Agents. *Bioorg. Med. Chem.* **2006**, *14*, 1497. (d) Palchaudhuri, R.; Nesterenko, V.; Hergenrother, P. J. The Complex Role of the Triphenylmethyl Motif in Anticancer Compounds. *J. Am. Chem. Soc.* **2008**, *130*, 10274.

(4) Ellsworth, B. A.; Ewing, W. R.; Jurica, E. Pyrrolidine GPR40 Modulators[P] U.S. Patent Application 2011/0082165 A1, Apr 7, 2011.

(5) (a) Zollinger, H. Color Chemistry: Syntheses, Properties, and Applications of Organic Dyes and Pigments; Wiley-VCH: Germany, 2003; pp 101−111. (b) R. Muthyala, Chemistry and Applications of Leuco Dyes; Plenum Press: New York, 2002; pp 1−279. (c) Dong, C.; Kodama, S.; Uematsu, A.; Nomoto, A.; Ueshima, M.; A. Ogawa, A. Metal-Free Blue Dye Synthesis: Oxidative Coupling of Benzylamines and N,N-Dimethylanilines to Yield 4,4'-Diaminotriarylmethanes in the Presence of Salicylic Acid as a Co-oxidant. *J. Org. Chem.* **2017**, *82*, 12530. (d) Montagut, A. M.; Gálvez, E.; Shafir, A.; Sebastián, R. M.; Vallribera, A. Triarylmethane Dyes for Artificial Repellent Cotton Fibers.

Chem. Eur. J. **2017**, *23*, 3810. (e) Chhabra, M.; Mishra, S.; Sreekrishnan, T. R. Laccase/Mediator Assisted Degradation of Triarylmethane Dyes in a Continuous Membrane Reactor *J. Biotechnol.*, **2009**, *143*, 69. (f) Mottram, L. F.; Forbes, S.; Ackley, B. D.; Peterson, B. R. Hydrophobic Analogues of Rhodamine B and Rhodamine 101: Potent Fluorescent Probes of Mitochondria in Living C. Elegans. *Beilstein J. Org. Chem.* **2012**, *8,* 2156.

(6) (a) Dibwe, D. F.; Awale, S.; Kadota, S.; Tezuka, Y. Muchimangins A–D: Novel Diphenylmethyl-Substituted Xanthones from Securidaca Longepedunculata. *Tetrahedron Lett.* **2012**, *53*, 6186. (b) Kodama, T.; Ito, T.; Dibwe, D. F.; Woo, S.-Y.; Morita, H. Syntheses of Benzophenone-Xanthone Hybrid Polyketides and Their Antibacterial. *Bioorg. Med. Chem. Lett.* **2017**, *27*, 2397.

(7) (a) Liu, C,-R.; Li, M,-B.; Yang, C,-F.; Tian, S,-K. Catalytic Selective Bis-Arylation of Imines with Anisole, Phenol, Thioanisole and Analogues. *Chem. Commun.* **2008**, *1249*. (b) Nambo, M.; Ariki, Z. T.; Canseco-Gonzalez, D.; Beattie, D. D.; Crudden, C. M. Arylative Desulfonation of Diarylmethyl Phenyl Sulfone with Arenes Catalyzed by Scandium Triflate. *Org. Lett.* **2016**, *18*, 2339.

(8) For selected examples of triarylmethanes formation, see: (a) Esquivias, J.; Arrayas, R. G.; Carretero, J. C. A Copper(II)-Catalyzed Aza-Friedel-Crafts Reaction of N-(2-Pyridyl)sulfonyl Aldimines: Synthesis of Unsymmetrical Diaryl Amines and Triaryl Methanes. *Angew. Chem. Int. Ed*. **2006**, *45*, 629. (b) Xia, Y.; Hu, F.; Liu, Z.; Qu, P.; Ge, R.; Ma, C.; Zhang, Y.; Wang, J. Palladium-Catalyzed Diarylmethyl $C(sp^3)$–$C(sp^2)$ Bond Formation: A New Coupling Approach toward Triarylmethanes. *Org. Lett*. **2013**, *15*, 1784. (c) Nambo, M.; Crudden, C. M. Modular Synthesis of Triarylmethanes through Palladium-Catalyzed Sequential Arylation of Methyl Phenyl Sulfone. *Angew. Chem. Int. Ed.* **2014**, *53*, 742. (d) Taylor, B. L. H.; Harris, M. R.; Jarvo, E. R. Synthesis of Enantioenriched Triarylmethanes by Stereospecific Cross-Coupling Reactions. *Angew. Chem. Int. Ed.* **2012**, *51*, 7790. (e) Zhou, Q.; Srinivas, H. D.; Dasgupta, S.; Watson, M. P. Nickel-Catalyzed Cross-Couplings of Benzylic Pivalates with Arylboroxines: Stereospecific Formation of Diarylalkanes and Triarylmethanes. *J. Am. Chem. Soc*. **2013**, *135*, 3307. (f) Huang, Y.; Hayashi, T. Asymmetric Synthesis of Triarylmethanes by Rhodium-Catalyzed Enantioselective Arylation of Diarylmethylamines with Arylboroxines. *J. Am. Chem. Soc.* **2015**, *137*, 7556. (g) Rygus, J. P. G.; Crudden, C. M. Enantiospecific and Iterative Suzuki–Miyaura Cross-Couplings. *J. Am. Chem. Soc*. **2017**, *139*, 18124 and references cited therein.

(9) Ji, X.; Huang, T.; Wu, W.; Liang, F.; Cao, S. LDA-Mediated Synthesis of Triarylmethanes by Arylation of Diarylmethanes with Fluoroarenes at Room Temperature. *Org. Lett*. **2015**, *17*, 5096.

(10) For recent reviews of *o*- and *p*-quinone methides, see: (a) Willis, N. J.; Bray, C. D. *ortho*-Quinone Methides in Natural Product Synthesis. *Chem. Eur. J.* **2012**, *18*, 9160. (b) Singh, M. S.; Nagaraju, A.; Anand, N.; Chowdhury, S. *ortho*-Quinone Methide (o-QM): a Highly Reactive, Ephemeral and Versatile Intermediate in Organic Synthesis. *RSC Adv*. **2014**, *4*, 55924. (c) Caruana, L.; Fochi, M.; Bernardi, L. The Emergence of Quinone Methides in Asymmetric Organocatalysis. *Molecules.* **2015**, *20,* 11733. (d) Parra, A.; Tortosa, M. *para*-Quinone Methide: a New Player in Asymmetric Catalysis. *ChemCatChem.* **2015**, *7,* 1524. (e) Osipov, D. V.; Osyanin, V. A.; Klimochkin, Y. N. *ortho*-Quinone Methides as Key Intermediates in Cascade Heterocyclizations. *Russ. Chem. Rev.* **2017**, *86,* 625. (f) Bai, W,-J.; David, J. G.; Feng, Z,-G.; Weaver, M. G.; Wu, K,-L.; Pettus, T. R. R. The Domestication of *ortho*-Quinone Methides. *Acc. Chem. Res.* **2014**, *47,* 3655.

(11) (a) Chen, M,-W.; Cao, L,-L.; Ye, Z,-S.; Jiang, G,-F.; Zhou, Y,-G. A Mild Method for Generation of *o*-Quinone Methides under Basic Conditions. The Facile Synthesis of

trans-2,3-Dihydrobenzofurans. *Chem. Commun.* **2013**, *49,* 1660. (b) Jaworski, A. A.; Scheidt, K. A. Emerging Roles of *in Situ* Generated Quinone Methides in Metal-Free Catalysis. *J. Org. Chem.* **2016**, *81,* 10145. (c) Rodriguez, K. X.; Vail, J. D.; Ashfeld, B. L. Phosphorus(III)-Mediated Stereoconvergent Formal [4+1]-Cycloannulation of 1,2-Dicarbonyls and *o*-Quinone Methides: A Multicomponent Assembly of 2,3-Dihydrobenzofurans. *Org. Lett.* **2016**, *18,* 4514. (d) Jarava-Barrera, C.; Parra, A.; López, A.; Cruz-Acosta, F.; Collado-Sanz, D.; Cárdenas, D. J.; Tortosa, M. Copper-Catalyzed Borylative Aromatization of *p*-Quinone Methides: Enantioselective Synthesis of Dibenzylic Boronates. *ACS Catal.* **2016**, *6,* 442. (e) Chu, W,-D.; Zhang, L,-F.; Bao, X.; Zhao, X,-H.; Zeng, C.; Du, J,-Y.; Zhang, G,-B.; Wang, F,-X.; Ma, X.-Y.; Fan, C,-A. Asymmetric Catalytic 1,6-Conjugate Addition/Aromatization of *para*-Quinone Methides: Enantioselective Introduction of Functionalized Diarylmethine Stereogenic Centers. *Angew. Chem. Int. Ed.* **2013**, *52,* 9229. (f) Luan, Y.; Schaus, S. E. Enantioselective Addition of Boronates to *o*-Quinone Methides Catalyzed by Chiral Biphenols. *J. Am. Chem. Soc.* **2012**, *134,* 19965. (g) Osyanin, V. A.; Osipov, D. V.; N. Klimochkin, Y. Reactions of *o*-Quinone Methides with Pyridinium Methylides: A Diastereoselective Synthesis of 1,2-Dihydronaphtho[2,1-b]furans and 2,3-Dihydrobenzofurans. *J. Org. Chem.* **2013**, *78,* 5505.

(12) (a) Guo, W.; Wu, B.;. Zhou, X.; Chen, P.; Wang, X.; Zhou, Y,-G.; Liu, Y.; Li, C. Formal Asymmetric Catalytic Thiolation with a Bifunctional Catalyst at a Water-Oil Interface: Synthesis of Benzyl Thiols. *Angew. Chem. Int. Ed.* **2015,** *54,* 4522. (b) Chen, P.; Wang, K.; Guo, W.; Liu, X.; Liu, Y.; Li, C. Enantioselective Reactions of 2-Sulfonylalkyl Phenols with Allenic Esters: Dynamic Kinetic Resolution and [4+2] Cycloaddition Involving *ortho*-Quinone Methide Intermediates. *Angew. Chem. Int. Ed.* **2017**, *56,* 3689. (c) Xu, J.; Yuan, S.; Peng, J.; Miao, M.; Chen, Z.; Ren, H. Base-Mediated Diastereoselective [4 + 3] Annulation of *in situ* Generated *ortho*-Quinone Methides with C,N-Cyclic Azomethine Imines. *Org. Biomol. Chem*. **2017**, *15,* 7513. (d) Zielke, K.; Waser, M. Formal (4 + 1)-Addition of Allenoates to *o*-Quinone Methides. *Org. Lett.* **2018**, *20*, 768.

(13) For selected examples of zinc reagents in organic synthesis: (a) Chen, Y.-H.; Graßl, S.; Knochel, P. Cobalt-Catalyzed Electrophilic Amination of Aryl- and Heteroarylzinc Pivalates with N-Hydroxylamine Benzoates. *Angew. Chem. Int. Ed.* **2018**, *57,* 1108. (b) Liu, Z.; Dong, N.; Xu, M.; Sun, Z.; Tu, T. Mild Negishi Cross-Coupling Reactions Catalyzed by Acenaphthoimidazolylidene Palladium Complexes at Low Catalyst Loadings. *J. Org. Chem.* **2013**, *78,* 7436. (c) Stathakis, C. I.; Manolikakes, S. M.; Knochel, P. TMPZnOPiv•LiCl: A New Base for the Preparation of Air-Stable Solid Zinc Pivalates of Sensitive Aromatics and Heteroaromatics. *Org. Lett.* **2013**, *15*, 1302. (d) Negishi, E.; Valente. L. F.; Kobayashi, M. Palladium-Catalyzed Cross-Coupling Reaction of Homoallylic or Homopropargylic Organozincs with Alkenyl Halides as a New Selective Route to 1,5-Dienes and 1,5-Enynes. *J. Am. Chem. Soc.* **1980**, *102,* 3298. (e) Erdik, E. Transition Metal Catalyzed Reactions of Organozinc Reagents. *Tetrahedron.* **1992**, *48*, 9577. (f) Buesking, A. W.; Baguley, T. D.; Ellman, J. A. Asymmetric Synthesis of Amines by the Knochel-Type $MgCl_2$-Enhanced Addition of Benzyl Zinc Reagents to N-*tert*-Butanesulfinyl Aldimines. *Org. Lett.* **2011**, *13*, 964.