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# Recyclable bismuth complex catalyzed 1,6-conjugate addition of various nucleophiles to *para*-quinone methides: expedient access to unsymmetrical diaryl- and triarylmethanes

Xianghao Liang,[†] Haiyan Xu,[†]* Hanlin Li, Lizhuang Chen and Hongfei Lu*

**Abstract:** An efficient method for the 1,6-conjugate addition of *para*-quinone methides with readily available nucleophiles was developed. This protocol provides straightforward access to a class of diaryl and triarylmethane derivatives with good to excellent yields in the presence of $(C_4H_{12}N_2)_2[BiCl_6]Cl{\cdot}H_2O$. Moreover, this bismuth catalyst can be recycled for several times.

## Introduction

*Para*-quinone methides (*p*-QMs) are prevalent structural skeletons in a broad array of synthetic bioactive molecules, natural products and pharmaceuticals. Moreover, the *p*-QMs have been widely studied as an important and readily available class of synthetic intermediates, owing to their unique structural features.[1] The *p*-QMs have the zwitterionic resonance structure of a cyclohexadiene moiety in *para*-conjugation with a carbonyl group, which enable them to be a good candidate for 1,6-conjugate addition, [4+1]-cycloaddition,[2] [4+2]-cycloaddition,[3] [3+2]-cycloaddition[4] and so on. In recent years, various catalytic system have been designed for 1,6-conjugate addition of *p*-QMs, such as $BF_3{\cdot}OEt$,[5] $B(C_6F_5)_3$,[6] Phosphine,[7] copper salts,[8] $Fe(acac)_3$,[9] $Fe(OTf)_3$,[10] $Bi(OTf)_3$,[11] as well as some chiral catalysts[12]. However, all these catalysts have limited substrates scope and are difficulty in recycling. Therefore, the development of high efficient strategies for the synthesis of diaryl and triarylmethane derivatives in a green manner through 1,6-conjugate addition of *p*-QMs has attracted considerable attention.[13]

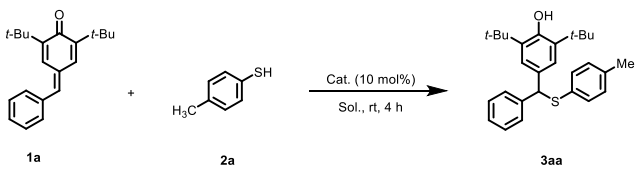
Bismuth is known as a low cost, environmentally benign, easy handle element and its bismuth(III) salts has been widely used as Lewis acid catalysts in organic chemistry. Very recently, Li Xin group have reported $Bi(OTf)_3$ catalyzed 1,6-conjugate addition of *p*-QMs with 3-propenyl-2-silyloxyindoles and allylboronic acid pinacol ester to synthesize diphenylmethane type compounds.[11a] Anand group has reported $Bi(OTf)_3$ catalyzed intermolecular 1,6-hydroolefination of *p*-QMs with styrenes.[11b] However, the $Bi(OTf)_3$ is difficult to be separated from the reaction and be reused. A novel heterogeneous bismuth complex formed by $BiCl_3$ and piperazine has been designed, synthesized and characterized in our group and been used as an efficient and recyclable catalyst for three-component Mannich.[14] and ring opening of epoxides reactions.[15] Notably, this bismuth complex is easy-to-prepare and stable storage. Related bismuth complex $\{(C_5H_6N_4O)(C_5H_4N_4)_3(C_5H_4N_4O)[Bi_2Cl_{11}]Cl_2\}$ also has been designed and successfully applied in the one pot three-component Biginelli reaction.[16]

In continuation of our research interests,[14-16] we assumed that using a green and reusable heterogeneous bismuth complex as a catalyst for the synthesis of functionalized diaryl and triarylmethane derivatives through 1,6-conjugate addition of *p*-QMs. To our surprise, we disclose that the air-stable and recoverable bismuth complex $\{(C_4H_{12}N_2)_2[BiCl_6]Cl{\cdot}H_2O\}$ showed high catalytic activities in the 1,6-conjugate addition of *p*-QMs under the mild reaction conditions. This methodology was compatible with several functional nucleophiles and afforded the corresponding products with good to excellent yields. Notably, this novel bismuth complex can be recycled six times by simple isolation procedures and without catalytic activities decreasing. Herein, we report our results.

## Results and Discussion

For the initial study, *p*-QM (**1a**) and *p*-methylbenzenethiol **2a** were selected as model substrates to optimize the reaction conditions (Table 1). As expected, the model reaction did not occur without the catalyst (Table 1, entry 1). To our delight, it was found that the 10 mol% $(C_4H_{12}N_2)_2[BiCl_6]Cl{\cdot}H_2O$ could be efficient to promote the model reaction and afforded the desired product **3aa** in excellent yield (98%) within 4 h. While other commercial available bismuth salts, such as $BiCl_3$ and $Bi(OTf)_3$, were examined on the same reaction conditions, the yields of the product were obtained in 76% and 72%, respectively (Table 1, entries 3 and 4 ). We also screened other commonly utilized Lewis acid catalysts, such as $FeCl_3$, $Fe(OTf)_3$, $Cu(OTf)_2$, $Ni(OTf)_2$, $Sc(OTf)_3$ and $AlCl_3$, no better results were obtained (Table 1, entries 5-10). We subsequently investigated the solvent effect by employing different solvents including MeOH, 1,4-dioxane, toluene and chloroform ($CHCl_3$) , but less than 98% yield was observed (Table 1, entries 11-14). Reducing the catalyst loading from 10 mol% to 5 mol% or 8 mol% results in lower yields of the desired product (36% and 75%), respectively (Table 1, entries 15 and 16).

**Table 1** Conditions screening[a]

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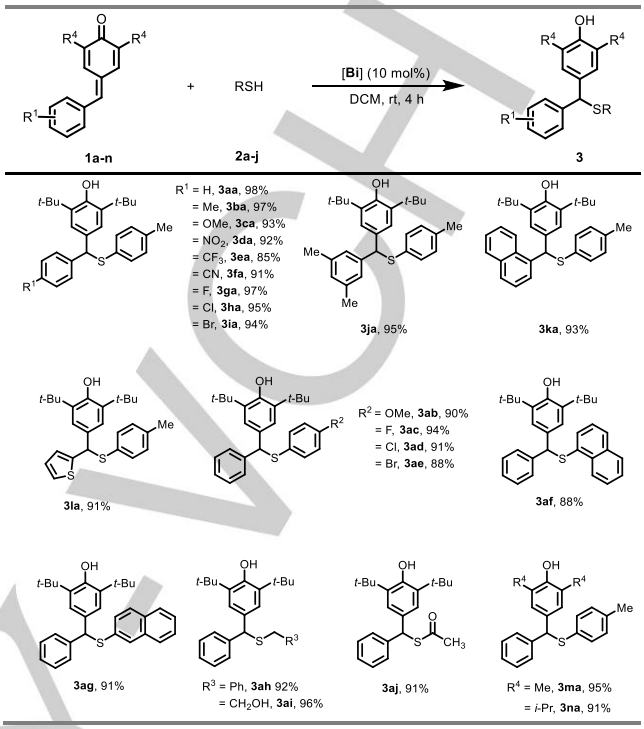
| Entry | Catalyst | Solvent | Yield (%)[b] |
|---|---|---|---|
| 1 | - | DCM | 0 |
| 2[c] | [Bi] | DCM | 98 |
| 3 | $BiCl_3$ | DCM | 76 |
| 4 | $Bi(OTf)_3$ | DCM | 72 |
| 5 | $FeCl_3$ | DCM | 53 |
| 6 | $Fe(OTf)_3$ | DCM | 85 |
| 7 | $Cu(OTf)_2$ | DCM | 83 |
| 8 | $Ni(OTf)_2$ | DCM | 70 |
| 9 | $Sc(OTf)_3$ | DCM | 79 |
| 10 | $AlCl_3$ | DCM | 55 |
| 11 | [Bi] | MeOH | 47 |
| 12 | [Bi] | 1,4-Dioxane | 83 |
| 13 | [Bi] | Toluene | 84 |
| 14 | [Bi] | $CHCl_3$ | 87 |
| 15 | [Bi] (5 mol%) | DCM | 36 |
| 16 | [Bi] (8 mol%) | DCM | 75 |

[a] Reaction conditions: *p*-QM (**1a**) (0.5 mmol), 4-methylbenzenethiol (**2a**) (1 mmol), Solvent (2 mL). [b] Isolated yield based on *p*-QM as limiting reagent. [c]The bismuth complex [Bi] refers to $(C_4H_{12}N_2)_2[BiCl_6]Cl{\cdot}H_2O$.

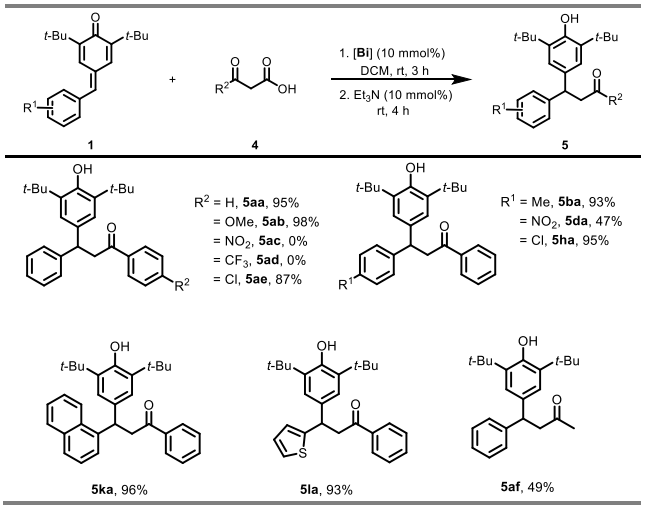
With optimized reaction conditions in hand, we examined the substrate scope of this addition reaction by using various *p*-QMs (**1**) and related thiols (**2**). As illustrated in Scheme 1, the 1,6-conjugate addition of *p*-QMs with a variety of thiols performed well in the presence of bismuth complex as catalysis. The *p*-QMs with electron-donating groups, such as methyl and methoxy, reacted well with 4-methylbenzenethiol (**2a**) to provide the expected products **3ba** and **3ca** in yields of 97% and 93% within 4 h, respectively. The *p*-QMs (**1d-f**) containing a strong electron-withdrawing group were also amenable to this protocol, providing the desired products (**3da-3fa**) in good yield. The *p*-QMs derived from the halo-substituted aromatic aldehydes (**1g-i**) exhibited high relativity under the standard conditions, and the corresponding products (**3ga-3ia**) were produced in yields ranging from 94-97%. The reaction reacted smoothly in case of *p*-QMs derived from other electron-rich arenes, such as 1-naphthaldehyde (**1k**) and thiophene-2-carbaldehyde (**1l**), gave the adduct **3ka** and **3la** in 93% and 91% yield, respectively. Moreover, the scope of this protocol was extended to a wide variety of aromatic and aliphatic thiols under the optimized reaction conditions. As expected, the reaction worked quite well utilizing electron-rich thiophenols substrates (**2b-f**), and affording the related products in good to excellent yields (88-94%). Additional, the efficacy of this protocol was also examined with naphthalene-2-thiol, and in this case, the product (**3ag**) was obtained in 91% isolated yield. Furthermore, the aliphatic thiols, such as phenylmethanethiol (**2h**) and 2-mercaptoethanol (**2i**), were also proved to be effective candidates for the 1,6-conjugate addition of *p*-QM, leading to excellent yield of the products **3ah** and **3ai**. It should be pointed out that our method also allows for the 1,6-conjugate addition of *p*-QMs with thiolacetic acid (**2j**). Additionally, when the methyl (isopropyl) group was modified on the $\alpha$– and $\alpha$'- position in *p*-QM, the corresponding products **3ma** and **3na** were obtain in 95% and 91% yield, respectively.




**Scheme 1.** Bismuth complex [Bi] catalyzed 1,6-conjugate addition of *p*-QMs with a variety of thiols. The yield given in each case is the isolated product of a reaction carried out on a 0.5 mmol scale at standard conditions.

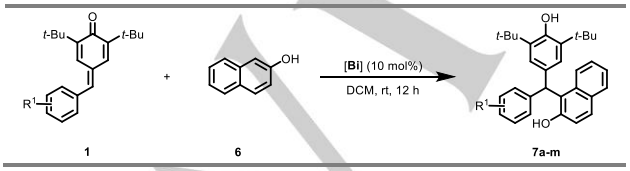
Encouraged by the above successful access to diarylmethyl thioethers and based on our previous results[17], we were eager to know if this method was suitable for the decarboxylative addition of *β*-ketoacids to *p*-QMs. To our delight, a variety of *β*-ketoacids were also subjected to this protocol (Scheme 2). However, electronic effects of the aryl substituents in *β*-ketoacids have a significant effect on the results of this reaction. The *β*-ketoacids with electron-rich group, such as methoxy, gave the desired product (**5ab**) in 98% yield. While the presence of a strong electron-withdrawing group ($NO_2$ or $CF_3$) at the *para* position of 3-oxo-3-phenylpropanoic acid, namely 3-(4-nitrophenyl)-3-oxopropanoic acid (**4c**) and 3-oxo-3-(4-(trifluoromethyl)phenyl)propanoic acid (**4d**), the reactions did not work, presumably owing to their lability.[18] The presence of a weak electron-withdrawing group such as chloride at *para* position of 3-oxo-3-phenylpropanoic acid obviously decreased the reactivity, the expected product (**5ae**) was obtained with 87% yield. After the examination of the substrate scope of *β*-ketoacids, we then explored the scope of *p*-QMs. It is evident from the Scheme 2 that a series of *para*-substituted electron-rich and deficient *p*-QMs could work quite well under standard reaction conditions, leading to the expected products in the yield ranging from 47% to 96%. Notably, this protocol could be applicable to the aliphatic (methyl) *β*-ketoacid (**4f**), in which the desired product **5af** was obtained in moderate yield (49%). Furthermore, some control experiments were performed to gain insight of the reaction mechanism (Scheme S1), and the experiment results indicate that 1,6-addition step takes place

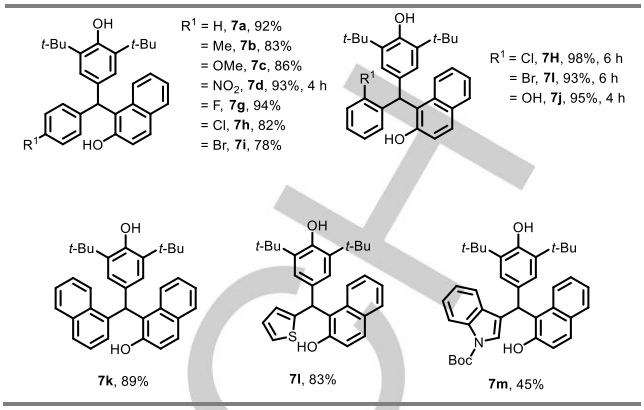
prior to the decarboxylation step in this decarboxylative addition process (Scheme S2).




**Scheme 2**. Bismuth complex [Bi] catalyzed 1,6-conjugate addition of *p*-QMs with various *β*-ketoacids. The reactions were carried out with **1** (0.25 mmol), **4** (0.5 mmol) and 10 mol% [Bi] catalyst in dichloromethane (2.0 ml) at room temperature for 3 hours (the conversion of **1** was completed), then 10 mol% $Et_3N$ was added into the reaction mixture.

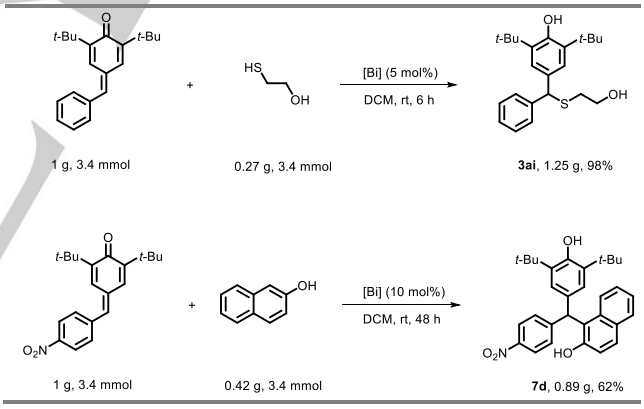
On the other hand, the triarylmethane framework represent an important structural motif widely found in natural products and used in pharmaceuticals.[19] We thus considered to investigate the 1,6-conjugate addition of *p*-QMs with naphthol to construct diversely unsymmetrical triarylmethanes with this standard reaction conditions. Gratifyingly, this protocol was found to be amenable for naphthol (**6**). As represented in Scheme 3, a series of *p*-QMs that bear electron-donating and electron-deficient aromatic moieties performed quite well with naphthalen-2-ol to afford triarylmethane derivatives in good to excellent yields (up to 98%). It is notable that the *p*-QMs bearing a strong electron-withdrawing group, such as 2,6-di-*tert*-butyl-4-(4-nitrobenzylidene)cyclohexa-2,5-dien-1-one (**1d**), was converted into corresponding product (**7d**) in 93% yield within a very short time (4 h). Meanwhile, the *p*-QMs (**1H, 1l and 1j**) with a halogen (or hydroxyl) substituent at 2-position demonstrated much higher efficient to give the desired products (**7H, 7l and 7j**) in excellent yields (up to 98%), presumably owing to the effect of hydrogen bonding. This transformation was also effective for the synthesis of naphthalene-, thiophen-, and indole-substituted triarylmethane products **7k**, **7l**, and **7m** from the related *p*-QMs.




**Scheme 3**. Bismuth complex [Bi] catalyzed 1,6-conjugate addition of *p*-QMs with naphthalen-2-ol. The yield given in each case is the isolated product of a reaction carried out on a 0.25 mmol scale at the standard conditions.

To demonstrate the general application and robustness of this protocol, gram-scale reactions were also investigated as shown in Scheme 4. To our delight, the desired product **3ai** was obtained in 98% yield in the presence of 5 mol% [Bi] catalyst and without need of excessive 2-mercaptoethan-1-ol (**2i**). Furthermore, a large scare reaction of 2,6-di-*tert*-butyl-4-(4-nitrobenzylidene)cyclohexa-2,5-dien-1-one (**1d**) with one equiv. of naphthalen-2-ol (**6**) was carried under the standard reaction conditions. The correspond triarylmethane 1-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(4-nitrophenyl)methyl)naphthalen-2-ol (**7d**) was obtained in 62% yield, albeit with longer reaction time (48 h).




**Scheme 4**. Gram-scale experiments.

To show the high efficiency and utility of this heterogeneous [Bi] catalyst, attempt was made to recycle this catalytic system. The 1,6-conjugate addition of *p*-QM (**1a**) with *p*-methylthiophenol (**2a**) under the optimized reaction conditions described in Table 1 with the [Bi] complex as catalyst was examined. The [Bi] catalyst could be recovered just by simple procedure of filtration, and then washed with DCM after the reaction was completed. As depicted in Figure 1, the easily recovered catalyst can be reused without further process, and showing no significant degrease of catalytic activity in a test of six cycles (up to 90% yield) (Table S1).

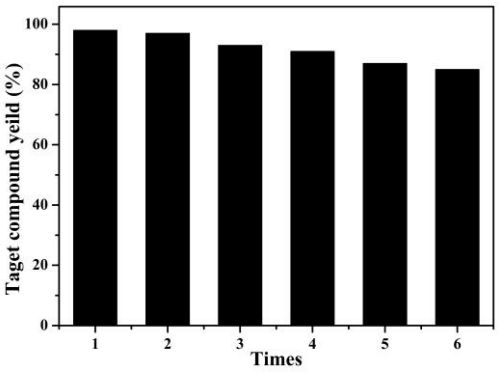



**Figure 1.** Recycling Catalyst $(C_4H_{12}N_2)_2[BiCl_6]Cl{\cdot}H_2O$

## Conclusions

In conclusion, we have developed a highly effective method for the synthesis of diaryl and triarylmethane derivatives through bismuth complex catalyzed 1,6-conjugate addition of commonly utilized nucleophiles to *p*-QMs. The key features of this protocol include broad substrate scope, high yields of products and 100% atom economy. What's more, the bismuth complex is non-toxic, air-stable and can also be efficiently recycled for multi-times as a catalyst. Further studies including the design novel chiral bismuth complexes and an asymmetric version are underway in our laboratory.

## Experimental Section

**General information:** $^1$H NMR spectra were acquired on Bruker 400 MHz spectrometers and chemical shifts were recorded relative to tetramethylsilane (TMS, $\delta$ = 0.00) or residual protiated solvent $CDCl_3$ ($\delta$ = 7.26). $^{13}$C NMR spectra were obtained at 100 MHz instrument and chemical shifts were recorded relative to solvent resonance $CDCl_3$ ($\delta$ = 77.16). Melting points were recorded on RY-51 melting point apparatus. FT-IR spectra were recorded on an iS50 FT-IR spectrometer and are uncorrected. LCMS analysis was conducted on an Agilent 6110 and 6520. Flash column chromatography was performed using silica gel (200–300 mesh) under pressure. Analytical thin layer chromatography (TLC) was carried out using GF254 commercial silica gel plates. Unless otherwise stated, all reagents and solvents were used without further purification.

**General method for the 1,6-conjugate addition reaction of *p*-QMs with thiol (2)**

*p*-QMs (0.5 mmol), $(C_4H_{12}N_2)_2[BiCl_6]Cl{\cdot}H_2O$ (10 mol%) and thiol (1 mmol) were placed into a flask. To the flask, dichloromethane (DCM, 2 mL) was added. Then the mixture was stirred at room temperature, until *p*-QMs was completely consumed as indicated by TLC analysis. After the completion of reaction, the residue was directly purified by flash column chromatography with ethyl acetate and petroleum ether (1:100) as eluents to afford pure product.

**2,6-di-*tert*-butyl-4-[phenyl(*p*-tolylthio)methyl]phenol (3aa):** (204 mg, 98%). Pale yellow solid; m.p. = 101 - 102 °C. $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.51 – 7.45 (m, 2H), 7.34 – 7.28 (m, 2H), 7.25 – 7.19 (m, 1H), 7.14 (d, *J* = 6.9 Hz, 4H), 6.99 (d, *J* = 7.9 Hz, 2H), 5.40 (s, 1H), 5.13 (s, 1H), 2.28 (s, 3H), 1.40 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 152.93, 141.92, 136.91, 135.76, 132.62, 132.19, 131.78, 129.49, 128.54, 128.45, 127.04, 125.27, 58.72, 34.49, 30.39, 21.17. FT-IR (neat): 3633, 2955, 1599, 1491, 1433, 1234, 1153, 802, 699 cm$^{-1}$. MS: Calcd for $C_{28}H_{34}OS$: $[M+H]^+$ 419.2; Found, 419.2.

**2,6-di-*tert*-butyl-4-[*p*-tolyl(*p*-tolylthio)methyl]phenol (3ba):** (105 mg, 97%). Pale yellow solid. m.p. = 104 - 105 °C. The reaction was performed with 77 mg of **1b** (0.25 mmol), dissolved in 2 mL of $CH_2Cl_2$. $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.73 (d, *J* = 7.7 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.16 – 7.09 (m, 6H), 6.99 (d, *J* = 7.9 Hz, 2H), 5.59 (s, 1H), 5.11 (s, 1H), 2.32 (s, 3H), 2.27 (s, 3H), 1.38 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 152.81, 139.84, 136.65, 135.80, 135.66, 131.45, 130.98, 130.50, 129.52, 128.40, 126.96, 126.28, 125.53, 54.83, 34.46, 30.40, 21.16, 19.90. FT-IR (neat): 3634, 2954, 1601, 1490, 1432, 1234, 1152, 801, 735 cm$^{-1}$. MS: Calcd for $C_{29}H_{36}OS$: $[M+H]^+$ 433.2; Found, 433.2.

**2,6-di-*tert*-butyl-4-[(4-methoxyphenyl)(*p*-tolylthio)methyl] phenol (3ca):** (111 mg, 93%). Yellow gummy. The reaction was performed with 81 mg of **1c** (0.25 mmol), dissolved in 2 mL of $CH_2Cl_2$. $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.39 – 7.35 (m, 2H), 7.12 (d, *J* = 8.2 Hz, 4H), 6.98 (d, *J* = 7.6 Hz, 2H), 6.85 – 6.81 (m, 2H), 5.36 (s, 1H), 5.11 (s, 1H), 3.79 (s, 3H), 2.27 (s, 3H), 1.39 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 158.60, 152.86, 135.71, 134.06, 132.10, 132.04, 129.58, 129.47, 125.19, 113.83, 58.05, 55.37, 34.48, 30.39, 21.18. FT-IR (neat): 3592, 2970, 1609, 1512, 1431, 1235, 1111, 1026, 809, 739 cm$^{-1}$. MS: Calcd for $C_{29}H_{36}O_2S$: $[M+H]^+$ 449.2; Found, 449.2.

**2,6-di-*tert*-butyl-4-[(4-nitrophenyl)(*p*-tolylthio)methyl]phenol (3da):** (212 mg, 92%). Yellow gummy. $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 8.15 – 8.11 (m, 2H), 7.60 – 7.56 (m, 2H), 7.14 – 7.10 (m, 2H), 7.09 (s, 2H), 6.99 (d, *J* = 7.8 Hz, 2H), 5.43 (s, 1H), 5.19 (s, 1H), 2.27 (s, 3H), 1.39 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 153.41, 149.75, 146.94, 137.81, 136.29, 132.65, 131.24, 130.16, 129.80, 129.39, 125.10, 123.72, 58.32, 34.55, 30.34, 21.20. FT-IR (neat): 3631, 2956, 1594, 1520, 1434, 1344, 1153, 809, 702 cm$^{-1}$. MS: Calcd for $C_{28}H_{33}NO_3S$: $[M+H]^+$ 464.2; Found, 464.2.

**2,6-di-*tert*-butyl-4-{(*p*-tolylthio)[4-(trifluoromethyl)phenyl] methyl}phenol (3ea):** (103 mg, 85%). Yellow gummy. The reaction was performed with 91 mg of **1e** (0.25 mmol), dissolved in 2 mL of $CH_2Cl_2$. $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.59 – 7.51 (m, 4H), 7.15 – 7.09 (m, 4H), 7.00 (d, *J* = 7.9 Hz, 2H), 5.41 (s, 1H), 5.17 (s, 1H), 2.28 (s, 3H), 1.40 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 153.22, 146.16, 137.43, 136.05, 132.39, 131.82, 130.84, 129.68, 128.84, 125.4, 125.15, 58.37, 34.52, 30.35, 21.20. FT-IR (neat): 3638, 2958, 1434, 1323, 1236, 1123,

1067, 907, 733 $cm^{-1}$. MS: Calcd for $C_{29}H_{33}F_3OS$: $[M+H]^+$ 487.2; Found, 487.2.

**4-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(*p*-tolylthio)methyl] benzonitrile (3fa):** (101 mg, 91%). Pale yellow solid. m.p. = 111 - 112 °C. The reaction was performed with 80 mg of **1f** (0.25 mmol), dissolved in 2 mL of $CH_2Cl_2$. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.55 (q, *J* = 8.5 Hz, 4H), 7.13 – 7.09 (m, 2H), 7.07 (s, 2H), 6.99 (d, *J* = 7.9 Hz, 2H), 5.39 (s, 1H), 5.19 (s, 1H), 2.28 (s, 3H), 1.39 (s, 18H). $^{13}C$ NMR (100 MHz, Chloroform-*d*) *δ* 153.34, 147.62, 137.69, 136.18, 132.57, 132.28, 131.35, 130.27, 129.74, 129.31, 125.10, 119.01, 110.79, 58.51, 34.52, 30.32, 21.21. FT-IR (neat): 3633, 2957, 1434, 1361, 1236, 907, 810, 730, 555 $cm^{-1}$. MS: Calcd for $C_{29}H_{33}NOS$: $[M+H]^+$ 444.2; Found, 444.2.

**2,6-di-*tert*-butyl-4-[(4-fluorophenyl)(*p*-tolylthio)methyl] phenol (3ga):** (212 mg, 97% ). Pale yellow solid. m.p. = 92 - 93 °C. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.43 – 7.38 (m, 2H), 7.13 – 7.08 (m, 4H), 7.03 – 6.93 (m, 4H), 5.37 (s, 1H), 5.14 (s, 1H), 2.27 (s, 3H), 1.38 (s, 18H). $^{13}C$ NMR (100 MHz, Chloroform-*d*) *δ* 163.10, 160.66, 153.03, 137.73 (137.69), 137.14, 135.89, 132.32, 132.28, 131.54, 130.16, 130.08, 129.57, 125.18, 115.34, 115.13, 57.95, 34.51, 30.38, 21.18. FT-IR (neat): 3634, 2955, 1602, 1505, 1433, 1224, 1155, 1120, 1016, 797, 738 $cm^{-1}$. MS: Calcd for $C_{28}H_{33}FOS$: $[M+H]^+$ 437.2; Found, 437.2.

**2,6-di-*tert*-butyl-4-[(4-chlorophenyl)(*p*-tolylthio)methyl] phenol (3ha):** (214 mg, 95%). Pale yellow solid. m.p. = 123 - 124 °C. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.42 – 7.38 (m, 2H), 7.31 – 7.26 (m, 2H), 7.15 – 7.09 (m, 4H), 7.01 (d, *J* = 7.9 Hz, 2H), 5.37 (s, 1H), 5.16 (s, 1H), 2.29 (s, 3H), 1.40 (s, 18H). $^{13}C$ NMR (100 MHz, Chloroform-*d*) *δ* 153.08, 140.58, 137.20, 135.94, 132.72, 132.29, 132.13, 131.25, 129.91, 129.61, 128.57, 125.14, 58.06, 34.51, 30.38, 21.19. FT-IR (neat): 3633, 2954, 1596, 1488, 1433, 1234, 1152, 1090, 808, 738 $cm^{-1}$. MS: Calcd for $C_{28}H_{33}ClOS$: $[M+H]^+$ 453.2; Found, 453.2.

**4-[(4-bromophenyl)(*p*-tolylthio)methyl]-2,6-di-*tert*-butylphenol (3ia):** (232 mg, 94%). Pale yellow solid. m.p. = 130 - 131 °C. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.43 – 7.37 (m, 2H), 7.34 – 7.30 (m, 2H), 7.13 – 7.06 (m, 4H), 6.99 (d, *J* = 7.9 Hz, 2H), 5.33 (s, 1H), 5.14 (s, 1H), 2.27 (s, 3H), 1.38 (s, 18H). $^{13}C$ NMR (100 MHz, Chloroform-*d*) *δ* 153.09, 141.12, 137.21, 135.96, 132.28, 132.10, 131.52, 131.17, 130.27, 129.61, 125.13, 120.86, 58.12, 34.51, 30.38, 21.19. FT-IR (neat): 3632, 2954, 1597, 1484, 1433, 1234, 1152, 1071, 1010, 808, 738 $cm^{-1}$. MS: Calcd for $C_{28}H_{33}BrOS$: $[M+H]^-$ 497.1; Found, 497.1.

**2,6-di-*tert*-butyl-4-[(3,5-dimethylphenyl)(*p*-tolylthio)methyl] phenol (3ja):** (211 mg, 95%). Pale yellow gummy. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.13 – 7.07 (m, 6H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.85 (s, 1H), 5.28 (s, 1H), 5.09 (s, 1H), 2.28 (s, 6H), 2.27 (s, 3H), 1.38 (s, 18H). $^{13}C$ NMR (100 MHz, Chloroform-*d*) *δ* 152.84, 141.66, 137.86, 136.81, 135.63, 132.87, 132.22, 132.00, 129.43, 128.77, 126.26, 125.27, 58.77, 34.47, 30.39, 21.49, 21.16. FT-IR (neat): 3636, 2954, 1598, 1491, 1433, 1360, 1231, 1152, 811, 736 $cm^{-1}$. MS: Calcd for $C_{30}H_{38}OS$: $[M+H]^+$ 447.2; Found, 447.2.

**2,6-di-*tert*-butyl-4-[naphthalen-2-yl(*p*-tolylthio)methyl]phenol (3ka):** (217 mg, 93%). Yellow solid. m.p. = 134 - 135 °C. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 8.19 – 8.14 (m, 1H), 7.92 – 7.84 (m, 2H), 7.78 – 7.74 (m, 1H), 7.51 – 7.44 (m, 3H), 7.17 (s, 2H), 7.14 – 7.09 (m, 2H), 6.98 – 6.94 (m, 2H), 6.19 (s, 1H), 5.10 (s, 1H), 2.25 (s, 3H), 1.35 (s, 18H). $^{13}C$ NMR (100 MHz, Chloroform-*d*) *δ* 152.91, 136.96, 136.58, 135.73, 134.17, 133.32, 131.44, 131.25, 131.18, 129.56, 128.97, 127.99, 126.58, 126.13, 125.56, 125.53, 123.87, 54.65, 34.47, 30.40, 21.13. FT-IR (neat): 3631, 2956, 1596, 1491, 1433, 1234, 1154, 779, 739 $cm^{-1}$. MS: Calcd for $C_{32}H_{36}OS$: $[M+H]^+$ 469.2; Found, 469.2.

**2,6-di-*tert*-butyl-4-[thiophen-2-yl(*p*-tolylthio)methyl]phenol (3la):** (192 mg, 91% ). Orange gummy. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.21 – 7.19 (m, 1H), 7.16 (d, *J* = 7.7 Hz, 4H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.93 – 6.87 (m, 2H), 5.53 (s, 1H), 5.15 (s, 1H), 2.29 (s, 3H), 1.40 (s, 18H). $^{13}C$ NMR (100 MHz, Chloroform-*d*) *δ* 153.22, 146.54, 137.62, 135.82, 133.28, 131.87, 131.61, 129.52, 126.54, 125.97, 125.12, 125.00, 54.45, 34.49, 30.39, 21.24. FT-IR (neat): 3626, 2954, 1610, 1433, 1238, 1152, 810, 737 $cm^{-1}$. MS: Calcd for $C_{26}H_{32}OS_2$: $[M+H]^+$ 425.1; Found, 425.1.

**2,6-di-*tert*-butyl-4-{[(4-methoxyphenyl)thio](phenyl)methyl} phenol (3ab):** (196 mg, 90%). Pale yellow solid. m.p. = 104 - 105 °C. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.44 – 7.40 (m, 2H), 7.32 – 7.26 (m, 2H), 7.23 – 7.19 (m, 1H), 7.17 – 7.13 (m, 2H), 7.10 (s, 2H), 6.72 – 6.68 (m, 2H), 5.27 (s, 1H), 5.11 (s, 1H), 3.74 (s, 3H), 1.38 (s, 18H). $^{13}C$ NMR (100 MHz, Chloroform-*d*) *δ* 159.43, 152.87, 141.97, 135.70, 135.24, 132.75, 131.81, 128.55, 128.38, 127.00, 125.24, 114.76, 114.28, 59.78, 55.31, 34.46, 30.39. FT-IR (neat): 3627, 2954, 1590, 1491, 1433, 1243, 1171, 1030, 824, 699 $cm^{-1}$. MS: Calcd for $C_{28}H_{34}O_2S$: $[M+H]^+$ 435.2; Found, 435.2.

**2,6-di-*tert*-butyl-4-{[(4-fluorophenyl)thio](phenyl)methyl} phenol (3ac):** (199 mg, 94%). Pale yellow solid. m.p. = 92 - 93 °C. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.45 – 7.40 (m, 2H), 7.31 – 7.27 (m, 2H), 7.24 – 7.16 (m, 3H), 7.11 (s, 2H), 6.89 – 6.82 (m, 2H), 5.34 (s, 1H), 5.13 (s, 1H), 1.38 (s, 18H). $^{13}C$ NMR (100 MHz, Chloroform-*d*) *δ* 163.59, 161.14, 153.05, 141.54, 135.89, 134.80, 134.72, 131.36, 131.10 (131.07), 128.53, 127.22, 125.26, 115.85, 115.63, 59.32, 34.51, 30.40. FT-IR (neat): 3633, 2956, 1589, 1489, 1434, 1233, 1154, 1120, 827, 700 $cm^{-1}$. MS: Calcd for $C_{27}H_{31}FOS$: $[M+H]^+$ 423.2; Found, 423.2.

**2,6-di-*tert*-butyl-4-{[(4-chlorophenyl)thio](phenyl)methyl} phenol (3ad):** (199 mg, 91%). Pale yellow solid. m.p. = 126 - 127 °C. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.47 – 7.43 (m, 2H), 7.32 – 7.28 (m, 2H), 7.25 – 7.20 (m, 1H), 7.12 (d, *J* = 4.4 Hz, 6H), 5.42 (s, 1H), 5.15 (s, 1H), 1.38 (s, 18H). $^{13}C$ NMR (100 MHz, Chloroform-*d*) *δ* 153.11, 141.25, 135.91, 134.86, 132.85, 132.79, 131.09, 128.83, 128.61, 128.48, 127.31, 125.25, 58.36, 34.50, 30.36. FT-IR (neat): 3633, 2956, 1599, 1475, 1433, 1235, 1153, 1094, 1012, 818, 699 $cm^{-1}$. MS: Calcd for $C_{27}H_{31}ClOS$: $[M+H]^+$ 439.1; Found, 439.1.

**4-{[(4-bromophenyl)thio](phenyl)methyl}-2,6-di-*tert*-butylphenol (3ae):** (211 mg, 88%). Pale yellow solid. m.p. = 130 - 131 °C. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.47 – 7.43 (m, 2H), 7.34 – 7.26 (m, 4H), 7.22 (s, 1H), 7.11 (s, 2H), 7.08 – 7.04 (m, 2H), 5.42 (s, 1H), 5.14 (s, 1H), 1.38 (s, 18H). $^{13}C$ NMR (100 MHz, Chloroform-*d*) *δ* 153.13, 141.19, 135.91, 135.61, 132.83,

131.76, 131.04, 128.63, 128.47, 127.33, 125.24, 120.79, 58.15, 34.50, 30.36. FT-IR (neat): 3632, 2955, 1599, 1471, 1432, 1234, 1152, 1090, 1008, 804, 698 $cm^{-1}$. MS: Calcd for $C_{27}H_{31}BrOS$: $[M+H]^+$ 483.1; Found, 483.1.

**2,6-di-*tert*-butyl-4-[(naphthalen-1-ylthio)(phenyl)methyl] phenol (3af):** (100 mg, 88%). Pale yellow gummy. The reaction was performed with 74 mg of **1a** (0.25 mmol), dissolved in 2 mL of $CH_2Cl_2$. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 8.50 (d, *J* = 8.3 Hz, 1H), 7.83 – 7.80 (m, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.47 (m, 4H), 7.38 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.06 (s, 2H), 5.49 (s, 1H), 5.09 (s, 1H), 1.34 (s, 18H). $^{13}C$ NMR (100 MHz, Chloroform-*d*) *δ* 152.91, 141.58, 135.62, 133.96, 133.23, 131.74, 131.61, 128.55, 128.48, 128.11, 127.15, 126.50, 126.10, 125.64, 125.54, 125.27, 58.28, 34.40, 30.32. FT-IR (neat): 3618, 2948, 1458, 1147, 912, 808, 733 $cm^{-1}$. MS: Calcd for $C_{31}H_{34}OS$: $[M+H]^+$ 455.2; Found, 455.2.

**2,6-di-*tert*-butyl-4-[(naphthalen-2-ylthio)(phenyl)methyl] phenol (3ag):** (103 mg, 91%). Yellow solid. m.p. = 132 - 133 °C. The reaction was performed with 74 mg of **1a** (0.25 mmol), dissolved in 2 mL of $CH_2Cl_2$. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.76 – 7.72 (m, 1H), 7.67 – 7.59 (m, 3H), 7.55 – 7.51 (m, 2H), 7.41 (td, *J* = 6.3, 5.9, 3.3 Hz, 2H), 7.37 – 7.29 (m, 3H), 7.25 – 7.20 (m, 1H), 7.18 (s, 2H), 5.59 (s, 1H), 5.13 (s, 1H), 1.37 (s, 18H). $^{13}C$ NMR (100 MHz, Chloroform-*d*) *δ* 153.03, 141.59, 135.85, 133.93, 133.71, 132.13, 131.47, 129.87, 128.97, 128.58, 128.53, 128.10, 127.70, 127.42, 127.21, 126.36, 125.91, 125.33, 58.07, 34.48, 30.37. FT-IR (neat): 3632, 2955, 1588, 1433, 1234, 1153, 907, 811, 731 $cm^{-1}$. MS: Calcd for $C_{31}H_{34}OS$: $[M+H]^+$ 455.2; Found, 455.2.

**4-[(benzylthio)(phenyl)methyl]-2,6-di-*tert*-butylphenol (3ah):** (96 mg, 92%). Pale yellow solid. m.p. = 96 - 97 °C. The reaction was performed with 74 mg of **1a** (0.25 mmol), dissolved in 2 mL of $CH_2Cl_2$; $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.44 – 7.41 (m, 2H), 7.34 – 7.28 (m, 4H), 7.28 – 7.18 (m, 4H), 7.17 (s, 2H), 5.13 (s, 1H), 4.89 (s, 1H), 3.54 (s, 1H), 1.42 (s, 18H). FT-IR (neat): 3632, 2954, 1600, 1492, 1432, 1234, 1153, 697 $cm^{-1}$. MS (ESI): Calcd for $C_{28}H_{34}OS$: $[M-H]^-$ 417.2; Found, 417.0.

**2,6-di-*tert*-butyl-4-{[(2-hydroxyethyl)thio](phenyl)methyl} phenol (3ai):** (90 mg, 96%). White solid. m.p. = 54 - 55 °C. The reaction was performed with 74 mg of **1a** (0.25 mmol), dissolved in 2 mL of $CH_2Cl_2$. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.52 – 7.47 (m, 2H), 7.38 – 7.34 (m, 2H), 7.25 (s, 3H), 5.19 (s, 1H), 5.16 (s, 1H), 3.67 (t, *J* = 6.2 Hz, 2H), 2.64 (t, *J* = 6.0 Hz, 2H), 2.15 (s, 1H), 1.45 (s, 18H). FT-IR (neat): 3633, 2957, 1433, 1264, 1235, 1055, 890, 733 $cm^{-1}$. MS (ESI): Calcd for $C_{23}H_{32}O_2S$: $[M-H]^-$ 371.2; Found: 371.0.

**S-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl] ethanethioate (3aj):** (169 mg, 91%). Yellow gummy. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.42 – 7.38 (m, 2H), 7.35 – 7.30 (m, 2H), 7.29 – 7.20 (m, 1H), 7.14 (s, 2H), 5.92 (s, 1H), 5.20 (s, 1H), 2.36 (s, 3H), 1.43 (s, 18H). $^{13}C$ NMR (100 MHz, Chloroform-*d*) *δ* 194.29, 153.05, 142.02, 135.98, 131.28, 128.52, 128.35, 127.12, 125.21, 52.24, 34.51, 30.37. FT-IR (neat): 3637, 2957, 1683, 1433, 1235, 905, 726, 632 $cm^{-1}$. MS: Calcd for $C_{23}H_{30}O_2S$: $[M+H]^+$ 371.1; Found, 371.1.

**2,6-dimethyl-4-[phenyl(*p*-tolylthio)methyl]phenol (3ma):** (158 mg, 95%). Pale gray gummy. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.45 – 7.39 (m, 2H), 7.32 – 7.26 (m, 2H), 7.23 – 7.19 (m, 1H), 7.17 – 7.12 (m, 2H), 7.04 – 6.97 (m, 4H), 5.39 (s, 1H), 4.58 (s, 1H), 2.27 (s, 3H), 2.20 (s, 6H). $^{13}C$ NMR (100 MHz, Chloroform-*d*) *δ* 151.42, 141.80, 136.66, 132.82, 131.10, 129.57, 128.60, 128.54, 128.44, 127.09, 123.13, 57.53, 21.15, 16.11. FT-IR (neat): 3586, 2960, 1468, 1283, 1199, 906, 802, 729 $cm^{-1}$. MS: Calcd for $C_{22}H_{22}OS$: $[M+H]^+$ 335.1; Found, 335.1.

**2,6-diisopropyl-4-[phenyl(*p*-tolylthio)methyl]phenol (3na):** (178 mg, 91%). Yellow gummy. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.46 – 7.42 (m, 2H), 7.34 – 7.25 (m, 2H), 7.24 – 7.19 (m, 1H), 7.17 – 7.13 (m, 2H), 7.05 (s, 2H), 6.99 (d, *J* = 7.8 Hz, 2H), 5.43 (s, 1H), 4.75 (s, 1H), 3.10 (p, *J* = 6.8 Hz, 2H), 2.27 (s, 3H), 1.22 (t, *J* = 6.5 Hz, 12H). $^{13}C$ NMR (100 MHz, Chloroform-*d*) *δ* 149.11, 141.84, 136.86, 133.58, 133.01, 132.56, 131.94, 129.50, 128.47, 127.04, 123.80, 58.38, 27.41, 22.79, 21.17. FT-IR (neat): 3566, 2920, 1487, 1195, 1139, 907, 799, 729 $cm^{-1}$. MS: Calcd for $C_{26}H_{30}OS$: $[M+H]^+$ 391.2; Found, 391.2.

**General method for the 1,6-conjugate addition reaction of *p*-QMs with *β*-ketoacid (4)**

*p*-QMs (0.25 mmol), $(C_4H_{12}N_2)_2[BiCl_6]Cl{\cdot}H_2O$ (10 mol%) and *β*-ketoacids (0.5 mmol) were added into a flask. To the flask, dichloromethane (DCM, 2 mL) was added. The mixture was stirred at room temperature for 3 hours (1,6-addition step). Then triethylamine (4 μL, 0.027 mmol) was added into the reaction system and stirred for another 4 hours (decarboxylation step). After the completion of reaction, the residue was directly purified by flash column chromatography with ethyl acetate and petroleum ether (1:150) as eluents to afford pure product.

**3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,3-diphenylpropan-1-one (5aa):** (98 mg, 95%). White solid. m.p. = 139 - 140 °C. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.91 – 7.88 (m, 2H), 7.56 – 7.51 (m, 1H), 7.45 – 7.39 (m, 2H), 7.31 – 7.26 (m, 4H), 7.20 – 7.14 (m, 1H), 7.02 (s, 2H), 5.04 (s, 1H), 4.73 (t, *J* = 7.4 Hz, 1H), 3.75 – 3.62 (m, 2H), 1.37 (s, 18H). FT-IR (neat): 3634, 2955, 1683, 1597, 1434, 1361, 1236, 1153, 739, 699 $cm^{-1}$. MS (ESI): Calcd for $C_{29}H_{34}O_2$: $[M-H]^-$ 413.3; found, 413.3.

**3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-3-phenylpropan-1-one (5ab):** (109 mg, 98%). White solid. m.p. = 122 - 123 °C. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.84 – 7.79 (m, 2H), 7.28 (d, *J* = 2.7 Hz, 4H), 7.24 (s, 1H), 7.22 (s, 1H), 7.19 – 7.14 (m, 1H), 7.03 (s, 2H), 5.04 (s, 1H), 4.73 (t, *J* = 7.4 Hz, 1H), 3.73 – 3.60 (m, 2H), 2.40 (s, 3H), 1.38 (s, 18H). FT-IR (neat): 3636, 2954, 1680, 1606, 1434, 1360, 1235, 1180, 737, 699 $cm^{-1}$. MS (ESI): Calcd for $C_{30}H_{36}O_3$: $[M-H]^-$ 443.2; found, 443.0

**1-(4-chlorophenyl)-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-phenylpropan-1-one (5ae):** (97 mg, 87%). White solid. m.p. = 143 - 144 °C. $^1H$ NMR (400 MHz, Chloroform-*d*) *δ* 7.82 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 4.8 Hz, 4H), 7.21 – 7.14 (m, 1H), 7.01 (s, 2H), 5.05 (s, 1H), 4.70 (t, *J* = 7.4 Hz, 1H), 3.71 – 3.58 (m, 2H), 1.37 (s, 18H). FT-IR (neat): 3636, 2955, 1683, 1588, 1434, 1361, 1235, 1091, 738, 699 $cm^{-1}$. MS (ESI): Calcd for $C_{29}H_{33}ClO_2$: $[M-H]^-$ 447.2; found, 447.2.

**4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4-phenylbutan-2-one (5af):** (43 mg, 49%). Yellow gummy. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 7.30 – 7.27 (m, 2H), 7.26 – 7.22 (m, 2H), 7.20 – 7.15 (m, 1H), 7.01 (s, 2H), 5.06 (s, 1H), 4.52 – 4.46 (m, 1H), 3.22 – 3.06 (m, 2H), 2.07 (s, 3H), 1.40 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 207.52, 152.34, 144.50, 135.92, 134.54, 128.62, 127.83, 126.38, 124.31, 50.63, 46.44, 34.52, 30.80, 30.45. FT-IR (neat): 3638, 2955, 1715, 1435, 1361, 1235, 1157, 700 cm$^{-1}$. MS (ESI): Calcd for $C_{24}H_{32}O_2$: [M-H]$^-$ 351.2; found, 351.1.

**3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-phenyl-3-(*p*-tolyl) propan-1-one (5ba):** (100 mg, 93%). Pale yellow solid. m.p. = 106 - 107 $^o$C. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 7.93 – 7.87 (m, 2H), 7.56 – 7.50 (m, 1H), 7.44 – 7.40 (m, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.10 – 7.06 (m, 2H), 7.03 (s, 2H), 5.03 (s, 1H), 4.69 (t, *J* = 7.4 Hz, 1H), 3.72 – 3.61 (m, 2H), 2.29 (s, 3H), 1.37 (s, 18H). FT-IR (neat): 3636, 2954, 1683, 1597, 1512, 1434, 1360, 1235, 811, 750, 689 cm$^{-1}$. MS (ESI): Calcd for $C_{20}H_{36}O_2$: [M-H]$^-$ 427.2; found, 427.1.

**3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(4-nitrophenyl)-1-phenylpropan-1-one (5da):** (54 mg, 47%). Pale yellow solid. m.p. = 151 - 152 $^o$C. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 8.18 – 8.09 (m, 2H), 7.95 – 7.88 (m, 2H), 7.60 – 7.54 (m, 1H), 7.50 – 7.38 (m, 4H), 6.99 (s, 2H), 5.12 (s, 1H), 4.87 – 4.78 (m, 1H), 3.82 – 3.63 (m, 2H), 1.38 (s, 18H). FT-IR (neat): 3632, 2955, 1683, 1596, 1518, 1434, 1343, 1236, 856, 752, 689 cm$^{-1}$. MS (ESI): Calcd for $C_{29}H_{33}NO_4$: [M-H]$^-$ 458.2; found, 458.0.

**3-(4-chlorophenyl)-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-phenylpropan-1-one (5ha):** (106 mg, 95%) White solid. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 7.92 – 7.87 (m, 2H), 7.57 – 7.52 (m, 1H), 7.46 – 7.41 (m, 2H), 7.25 – 7.18 (m, 4H), 6.98 (s, 2H), 5.07 (s, 1H), 4.73 – 4.67 (m, 1H), 3.72 – 3.59 (m, 2H), 1.37 (s, 18H). FT-IR (neat): 3636, 2954, 1683, 1588, 1361, 1235, 738, 704 cm$^{-1}$. MS (ESI): Calcd for $C_{29}H_{33}ClO_2$: [M-H]$^-$ 447.2; found, 447.0.

**3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(naphthalen-1-yl)-1-phenylpropan-1-one (5ka):** (111 mg, 96%) White solid. m.p. = 151 - 152 $^o$C. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 8.30 (d, *J* = 8.3 Hz, 1H), 7.96 – 7.83 (m, 3H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.36 (m, 7H), 7.09 (s, 2H), 5.62 (t, *J* = 7.2 Hz, 1H), 5.03 (s, 1H), 3.95 – 3.85 (m, 1H), 3.80 – 3.70 (m, 1H), 1.35 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 199.02, 152.25, 140.68, 137.55, 135.81, 134.25, 134.08, 133.04, 131.82, 128.90, 128.64, 128.19, 127.14, 126.15, 125.55, 125.38, 124.70, 124.29, 124.08, 45.60, 41.85, 34.44, 30.40. FT-IR (neat): 3632, 2956, 1682, 1597, 1434, 1360, 1234, 1153, 1021, 734, 689 cm$^{-1}$. MS (ESI): Calcd for $C_{33}H_{36}O_2$ [M-H]$^-$ 463.2; found, 462.9.

**3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-phenyl-3-(thiophen-2-yl)propan-1-one (5la):** (98 mg, 93%). Pale yellow gummy**.** $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 7.95 – 7.87 (m, 2H), 7.57 – 7.51 (m, 1H), 7.47 – 7.40 (m, 2H), 7.12 (d, *J* = 5.3 Hz, 3H), 6.91 – 6.82 (m, 2H), 5.09 (s, 1H), 5.01 – 4.95 (m, 1H), 3.80 – 3.73 (m, 1H), 3.66 – 3.58 (m, 1H), 1.40 (s, 18H). $^{13}$C NMR (100 MHz, $CDCl_3$) *δ* 198.37, 152.59, 149.08, 137.39, 135.94, 134.43, 133.10, 128.65, 128.22, 126.67, 124.39, 124.29, 123.62, 47.19, 42.16, 34.49, 30.43. FT-IR (neat): 3355, 2919, 1688, 1470, 1434, 1264, 737, 704 cm$^{-1}$. MS (ESI): Calcd for $C_{27}H_{32}O_2S$: [M-H]$^-$ 419.2; found, 419.2.

**General method for the 1,6-conjugate addition reaction of *p*-QMs with naphthalen-2-ol (6)**

*p*-QMs (0.25 mmol), $(C_4H_{12}N_2)_2[BiCl_6]Cl{\cdot}H_2O$ (10 mol%) and naphthalen-2-ol (0.5 mmol) were placed into a flask. To the flask, dichloromethane (DCM, 2 mL) was added. Then the mixture was stirred at room temperature, until *p*-QMs was completely consumed as indicated by TLC analysis. After the completion of reaction, the residue was directly purified by flash column chromatography with ethyl acetate and petroleum ether (1:100) as eluents to afford pure product.

**1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl] naphthalen-2-ol (7a):** (202 mg, 92%). Pale yellow solid. The reaction was performed with 147 mg of **1a** (0.5 mmol), dissolved in 2 mL of $CH_2Cl_2$. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 8.03 (d, *J* = 14.0 Hz, 1H), 7.79 (d, *J* = 11.4 Hz, 1H), 7.73 (d, *J* = 11.4 Hz, 1H), 7.43 (s, 1H), 7.32 (d, *J* = 10.1 Hz, 1H), 7.28 (s, 3H), 7.23 (d, *J* = 1.6 Hz, 2H), 7.08 (d, *J* = 7.0 Hz, 1H), 7.01 (s, 2H), 6.29 (s, 1H), 5.40 (s, 1H), 5.21 (s, 1H), 1.33 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 153.24, 153.18, 142.22, 136.87, 133.62, 131.92, 129.68, 129.58, 129.58, 129.14, 129.02, 128.80, 127.04, 126.80, 125.79, 123.17, 123.01, 120.38, 120.08, 48.73, 34.57, 30.34. FT-IR (neat): 3633, 3459, 2957, 1601, 1434, 1209, 1141, 906, 730, 649 cm$^{-1}$. MS (ESI): Calcd for $C_{31}H_{34}O_2$: [M-H]$^-$ 437.2; found, 437.2.

**1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(*p*-tolyl)methyl] naphthalen-2-ol (7b):** (94 mg, 83%). Pale yellow solid. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 8.08 – 8.02 (m, 1H), 7.81 – 7.77 (m, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.35 – 7.30 (m, 1H), 7.14 (d, *J* = 1.4 Hz, 4H), 7.10 – 7.04 (m, 3H), 6.27 (s, 1H), 5.44 (s, 1H), 5.21 (s, 1H), 2.33 (s, 3H), 1.35 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 153.16, 153.08, 139.22, 136.75, 136.59, 133.61, 131.92, 129.77, 129.65, 129.47, 128.94, 128.77, 126.77, 125.77, 123.12, 123.00, 120.67, 120.05, 48.30, 34.54, 30.36, 21.20. FT-IR (neat): 3632, 3462, 2956, 1601, 1434, 1264, 1141, 812, 739 cm$^{-1}$. MS (ESI): Calcd for $C_{32}H_{36}O_2$: [M-H]$^-$ 451.2; found, 451.2.

**1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(4-methoxyphenyl) methyl]naphthalen-2-ol (7c):** (101 mg, 86%). Yellow gummy. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 8.05 (t, *J* = 7.1 Hz, 1H), 7.81 (d, *J* = 9.2 Hz, 1H), 7.75 (s, 1H), 7.45 (d, *J* = 6.0 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 1H), 7.20 (s, 2H), 7.11 – 7.08 (m, 1H), 7.06 (s, 2H), 6.88 (s, 2H), 6.27 (s, 1H), 5.47 (s, 1H), 5.22 (s, 1H), 3.79 (s, 3H), 1.36 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 158.54, 153.14, 153.11, 136.82, 134.14, 133.56, 132.18, 130.14, 129.66, 129.47, 128.79, 126.76, 125.70, 123.13, 122.98, 120.64, 120.07, 114.41, 55.36, 47.87, 34.55, 30.36. FT-IR (neat): 3632, 3456, 2956, 1601, 1434, 1247, 1141, 1033, 806, 729 cm$^{-1}$. MS (ESI): Calcd for $C_{32}H_{36}O_3$: [M-H]$^-$ 467.2; found, 467.2.

**1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(4-nitrophenyl)methyl] naphthalen-2-ol (7d):** (224 mg, 93%). Pale yellow solid. m.p. = 190 - 192 $^o$C. The reaction was performed with 164 mg of **1d** (0.5 mmol), dissolved in 2 mL of $CH_2Cl_2$. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 8.17 (d, *J* = 2.0 Hz, 1H), 8.15 (d, *J* = 2.0 Hz, 1H),

7.87 (d, *J* = 8.6 Hz, 1H), 7.82 – 7.79 (m, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 0.6 Hz, 1H), 7.43 (d, *J* = 0.8 Hz, 1H), 7.42 (d, *J* = 1.6 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 6.98 (d, *J* = 0.7 Hz, 2H), 6.40 (s, 1H), 5.33 (s, 1H), 5.28 (s, 1H), 1.33 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 153.52, 153.03, 150.66, 146.79, 137.27, 133.27, 130.69, 130.20, 130.10, 129.84, 129.05, 127.06, 125.69, 123.97, 123.49, 122.82, 119.91, 119.24, 48.51, 34.63, 30.30. FT-IR (neat): 3625, 3458, 2958, 1601, 1516, 1434, 1344, 1210, 1153, 810, 740 cm$^{-1}$. MS (ESI): Calcd for $C_{31}H_{33}NO_4$: [M-H]$^-$ 482.2; found, 482.2.

**1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(4-fluorophenyl)methyl] naphthalen-2-ol (7g):** (215 mg, 94%). Pale yellow solid. m.p. = 163 - 164 $^o$C. The reaction was performed with 156 mg of **1g** (0.5 mmol), dissolved in 2 mL of $CH_2Cl_2$. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 7.98 (d, *J* = 8.5 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.36 – 7.31 (m, 1H), 7.26 – 7.20 (m, 2H), 7.07 (d, *J* = 8.9 Hz, 1H), 7.03 – 6.98 (m, 4H), 6.28 (s, 1H), 5.39 (s, 1H), 5.24 (s, 1H), 1.34 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 163.03, 160.59, 153.31, 153.16, 137.69 (137.66), 137.08, 133.46, 131.94, 130.78, 130.70, 129.73, 128.88, 126.86, 125.64, 123.26, 122.89, 120.14, 120.10, 115.88, 115.67, 47.99, 34.59, 30.33. FT-IR (neat): 3632, 3457, 2958, 1602, 1505, 1434, 1232, 1157, 815, 741 cm$^{-1}$. MS (ESI): Calcd for $C_{31}H_{33}FO_2$: [M-H]$^-$ 456.3; found, 455.5.

**1-[(4-chlorophenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl] naphthalen-2-ol (7h):** (193 mg, 82%). Pale yellow solid. m.p. = 156 - 157 $^o$C. The reaction was performed with 164 mg of **1h** (0.5 mmol), dissolved in 2 mL of $CH_2Cl_2$. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 7.95 (t, *J* = 6.7 Hz, 1H), 7.78 (s, 1H), 7.75 – 7.71 (m, 1H), 7.45 – 7.40 (m, 1H), 7.33 (d, *J* = 6.6 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.20 (d, *J* = 10.5 Hz, 2H), 7.07 (d, *J* = 9.1 Hz, 1H), 6.99 (s, 2H), 6.26 (s, 1H), 5.36 (s, 1H), 5.24 (s, 1H), 1.33 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 153.16, 140.73, 137.09, 133.42, 132.67, 129.81, 129.72, 129.07, 128.89, 126.91, 125.65, 123.30, 122.86, 120.07, 119.85, 48.11, 34.60, 30.32. FT-IR (neat): 3632, 3459, 2959, 1488, 1434, 1209, 1142, 1014, 811, 741 cm$^{-1}$. MS (ESI): Calcd for $C_{31}H_{33}ClO_2$: [M-H]$^-$ 471.2; found, 471.3.

**1-[(4-bromophenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl] naphthalen-2-ol (7i):** (101 mg, 78%). Pale yellow solid. m.p. = 134 - 135 $^o$C. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 7.93 (s, 1H), 7.81 – 7.77 (m, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.36 – 7.30 (m, 1H), 7.17 – 7.12 (m, 2H), 7.06 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 0.8 Hz, 2H), 6.24 (s, 1H), 5.35 (s, 1H), 5.24 (s, 1H), 1.33 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 153.33, 153.12, 141.34, 137.06, 133.40, 131.99, 130.95, 129.81, 129.71, 128.89, 126.89, 125.66, 123.30, 122.88, 120.02, 119.82, 48.14, 34.58, 30.31. FT-IR (neat): 3632, 3454, 2957, 1601, 1433, 1208, 1142, 1010, 904, 727, 649 cm$^{-1}$. MS (ESI): Calcd for $C_{31}H_{33}BrO_2$: [M-H]$^-$ 515.1; found, 515.4.

**1-[(2-chlorophenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl] naphthalen-2-ol (7H):** (116 mg, 98%). Pale yellow solid. m.p. = 137 - 138 $^o$C. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 7.93 – 7.89 (m, 1H), 7.80 – 7.72 (m, 2H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.22 – 7.18 (m, 1H), 7.15 (s, 2H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.91 (s, 2H), 6.60 (s, 1H), 5.50 (s, 1H), 5.24 (s, 1H), 1.32 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 153.80, 153.46, 139.43, 137.23, 134.46, 133.63, 130.74, 130.25, 129.87, 129.83, 129.65, 128.77, 128.48, 127.51, 127.08, 125.29, 123.32, 122.88, 120.11, 119.53, 46.11, 34.57, 30.31. FT-IR (neat): 3632, 3456, 2958, 1621, 1518, 1434, 1211, 1142, 814, 744 cm$^{-1}$. MS (ESI): Calcd for $C_{31}H_{33}ClO_2$: [M-H]$^-$ 471.2; found, 471.2.

**1-[(2-bromophenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl] naphthalen-2-ol (7I):** (120 mg, 93%). Pale yellow solid. m.p. = 134 - 135 $^o$C. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 7.89 (d, *J* = 7.2 Hz, 1H), 7.78 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.66 (s, 1H), 7.44 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.19 (s, 1H), 7.15 – 7.09 (m, 2H), 7.07 (s, 1H), 6.89 (s, 2H), 6.54 (s, 1H), 5.50 (s, 1H), 5.23 (s, 1H), 1.31 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 153.77, 153.45, 141.07, 137.23, 133.68, 133.29, 130.88, 130.19, 129.86, 129.66, 128.76, 128.72, 128.15, 127.09, 125.44, 125.42, 123.32, 123.03, 120.11, 48.90, 34.58, 30.32. FT-IR (neat): 3627, 3451, 2956, 1601, 1518, 1433, 1211, 1141, 1023, 814, 741 cm$^{-1}$. MS (ESI): Calcd for $C_{31}H_{33}BrO_2$: [M-H]$^-$ 515.2; found, 515.2

**1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl) methyl]naphthalen-2-ol (7j):** (108 mg, 95%). Pale yellow solid. m.p. = 190 - 191 $^o$C. $^1$H NMR (400 MHz, Chloroform-d) *δ* 8.01 (d, *J* = 8.6 Hz, 1H), 7.80 – 7.71 (m, 2H), 7.45 – 7.40 (m, 1H), 7.35 – 7.30 (m, 1H), 7.19 – 7.14 (m, 1H), 7.08 – 7.00 (m, 4H), 6.89 – 6.83 (m, 2H), 6.46 (s, 1H), 5.58 (s, 1H), 5.22 (s, 1H), 5.02 (s, 1H), 1.33 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 153.67, 153.56, 153.38, 137.08, 133.46, 130.32, 130.09, 129.81, 129.78, 128.82, 128.62, 128.26, 126.95, 125.41, 123.33, 123.08, 121.66, 119.91, 116.27, 42.91, 34.58, 30.33. FT-IR (neat): 3632, 3447, 2957, 1601, 1434, 1398, 1317, 1264, 1142, 810, 738 cm$^{-1}$. MS (ESI): Calcd for $C_{31}H_{34}O_3$: [M-H]$^-$ 453.3; found, 453.3.

**1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(naphthalen-1-yl) methyl]naphthalen-2-ol (7k):** (108 mg, 89%). Pale yellow solid. m.p. = 178 - 179 $^o$C. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 7.95 (s, 1H), 7.91 – 7.86 (m, 2H), 7.80 (d, *J* = 11.3 Hz, 2H), 7.73 (s, 1H), 7.46 (s, 1H), 7.41 – 7.30 (m, 4H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.00 (s, 3H), 6.88 (s, 1H), 5.59 (s, 1H), 5.18 (s, 1H), 1.28 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 154.14, 153.17, 138.49, 136.87, 134.23, 133.42, 131.99, 131.49, 129.73, 129.61, 129.05, 128.85, 128.30, 127.02, 126.98, 126.58, 125.99, 125.94, 125.85, 124.21, 123.18, 122.85, 119.99, 46.04, 34.51, 30.34. FT-IR (neat): 3627, 3461, 2956, 1621, 1518, 1434, 1209, 1141, 788, 739 cm$^{-1}$. MS (ESI): Calcd for $C_{35}H_{36}O_2$: [M-H]$^-$ 487.3; found, 487.3.

**1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(thiophen-2-yl)methyl] naphthalen-2-ol (7l):** (93 mg, 83%). Yellow gummy. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 8.06 (d, *J* = 13.3 Hz, 1H), 7.80 (s, 1H), 7.75 (d, *J* = 11.4 Hz, 1H), 7.47 (d, *J* = 7.1 Hz, 1H), 7.35 (d, *J* = 13.3 Hz, 1H), 7.26 (s, 1H), 7.17 (s, 2H), 7.11 (d, *J* = 10.9 Hz, 1H), 6.95 (s, 1H), 6.83 (s, 1H), 6.49 (s, 1H), 5.59 (s, 1H), 5.22 (s, 1H), 1.37 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 153.32, 153.10, 146.78, 136.69, 133.13, 131.52, 129.84, 129.61, 129.61, 127.02, 126.92, 126.80, 125.66, 125.19, 123.28, 122.70, 120.49, 120.02, 43.74, 34.38, 30.52. FT-IR (neat): 3632, 3460, 2957, 1601, 1434, 1210, 1153, 906, 730, 649 cm$^{-1}$. MS (ESI): Calcd for $C_{29}H_{32}O_2S$: [M-H]$^-$ 443.2; found, 443.3.

***tert*-butyl-3-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxynaphthalen-1-yl)methyl]-1H-indole-1-carboxylate**

**(7m):** (65 mg, 45%). Yellow solid. m.p. = 172 - 173 °C. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 8.12 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 9.4 Hz, 1H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.39 – 7.34 (m, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 1.5 Hz, 2H), 7.16 – 7.04 (m, 4H), 6.37 (s, 1H), 5.97 – 5.87 (m, 1H), 5.19 (s, 1H), 1.64 (s, 9H), 1.35 (s, 18H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 153.57, 152.96, 136.45, 130.18, 129.90, 129.60, 129.49, 128.81, 126.75, 125.22, 125.17, 124.91, 123.06, 122.66, 122.60, 120.00, 119.57, 118.51, 115.33, 83.87, 40.17, 34.42, 30.28, 28.18. FT-IR (neat): 3632, 3461, 2958, 1732, 1451, 1370, 1256, 1154, 1081, 821, 745 cm$^{-1}$. MS (ESI): Calcd for $C_{38}H_{43}NO_4$: $[M-H]^-$ 576.3; found, 576.3.

**General procedure for the recovery of the [Bi] catalyst**

*p*-QMs (0.5 mmol), $(C_4H_{12}N_2)_2[BiCl_6]Cl{\cdot}H_2O$ (10 mol%) and *p*-methylthiophenol (**2a**) (1 mmol) were added into a flask. To the flask, dichloromethane (DCM, 2 mL) was added. Then the mixture was stirred at room temperature, until *p*-QMs was completely consumed as indicated by TLC analysis. After the completion of reaction, the [Bi] catalyst was directly recovered by filtration and washed with DCM. Then, the recovered [Bi] catalyst could be reused without further process.

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**Keywords:** *para*-quinone methides • 1,6-conjugate addition reaction • bismuth complex • triarylmethane derivatives • diarylmethane derivatives

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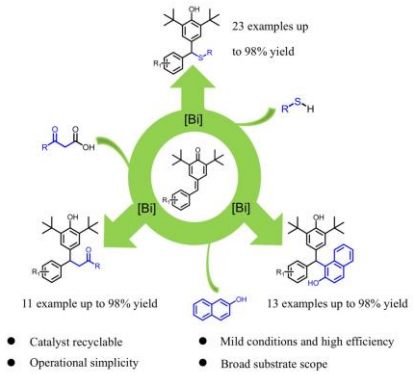
# COMMUNICATION

An efficient method for the 1,6-conjugate addition of *para*-quinone methides with readily available nucleophiles was developed. This protocol provides straightforward access to a class of diaryl and triarylmethane derivatives with good to excellent yields in the presence of $(C_4H_{12}N_2)_2[BiCl_6]Cl{\cdot}H_2O$. Moreover, this bismuth complex can be recycled for several times.

*Recyclable catalyst / diaryl- and triarylmethanes synthesis




**Key Topic***

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**Recyclable bismuth complex catalyzed 1,6-conjugate addition of various nucleophiles to *para*-quinone methides: expedient access to unsymmetrical diaryl- and triarylmethanes**