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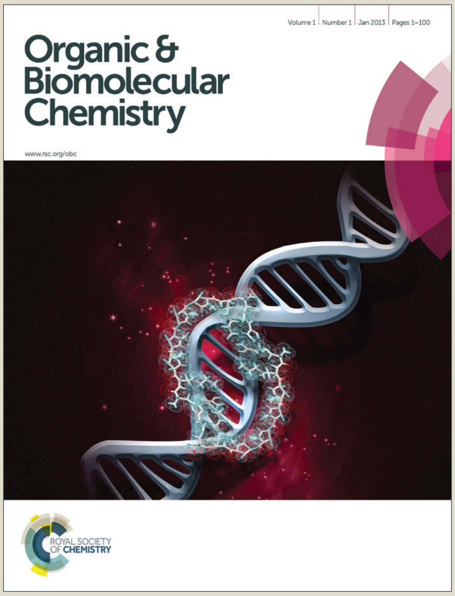

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# Molecular Iodine-Mediated Reaction of 2-(2-phenylethynyl)-Morita-Baylis-Hillman Adducts: An Easy Route to Naphthyl ketones and Iodo-Substituted Isochromenes †

Donala Janreddy, Veerababurao Kavala, Trimurtulu Kotipalli, Rajawinslin. R. R, Chun-Wei Kuo, Wen-Chang Huang, and Ching-Fa Yao *[a]

The molecular iodine-promoted reaction of 2-(2-phenylethynyl)-Morita-Baylis-Hillman adducts is reported. In the presence of $I_2$, naphthyl ketone derivatives are produced, whereas, in the presence of $I_2/K_3PO_4$, iodo-substituted isochromenes derivatives are produced.

## Introduction

The development of aromatic compounds and new methods for their construction has been of great interest, due to the fact that such moieties are present in various drugs and in devices used in the field of material science.[1] Among such aromatic compounds, naphthalene derivatives have enjoyed widespread use in the field of chiral catalysts, biologically active compounds, synthetic intermediates and advanced functional materials.[2] Hence, the development of new and efficient methods for the synthesis of polysubstituted naphthalene derivatives is of great importance. Traditional methods used in the construction of naphthalene derivatives involve electrophilic substitution or coupling reactions, in conjunction with multistep procedures.[3] However, over the past several years, the Lewis acid-catalyzed benzannulation of *o*-alkynyl-substituted carbonyl compounds with alkynes, alkenes, and enols, has proved to be one of the most powerful and reliable approaches for the construction of naphthalene derivatives.[4,5] In contrast, the electrophilic cyclization of alkynes has been extensively explored by Barluenga, Larock and others. Among the various electrophiles, the iodine-activated cyclization of ortho substituted aryl alkynes is one of the more interesting technique for the construction of iodine containing fused heterocyclic derivatives.[6] Nachtsheim *et.al.* recently reported on the synthesis of 1-naphthalenone derivatives by the iodocyclization reaction of *o*-alkynylphenyl carboxaldehyde with styrenes in the presence of tetrabutylammonium iodide (TBAI), Oxone and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as a solvent.[7] Kim *et.al.* reported on the synthesis of naphthalene derivatives from Morita-Baylis-Hillman (MBH) adducts using a copper catalyst (Figure 1).[8] However, to the best of our knowledge, the synthesis of naphthyl ketone derivatives starting from 2-(2-phenylethynyl)-Morita-Baylis-Hilman adducts using molecular iodine has not been reported in the literature. In fact, in recent years, we reported on some iodine-mediated reactions for the synthesis of a variety of heterocyclic compounds.[9] In a continuation of these studies, we wish to report herein, on the molecular iodine mediated cyclization reaction of 2-(2-phenylethynyl)-MBH adducts to give naphthyl ketones, and iodo-substituted 1*H*-isochromene derivatives.

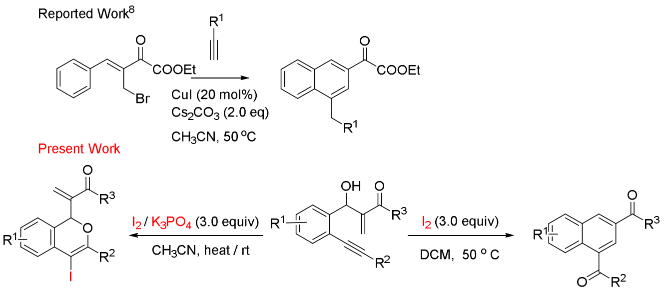

**Fig 1.** Previous and present report on the synthesis of naphthalenes from Morita-Baylis-Hillman adducts.

## Results and discussion

To pursue our goal, compound **1a** was treated with molecular iodine (3.0 equiv) in acetonitrile at 50 °C for 3 h. Under these conditions, three products were produced. From $^1H$ and $^{13}C$ NMR spectral analyses, the major product was determined to be methyl 2-(acetamidomethyl)-3-(2-

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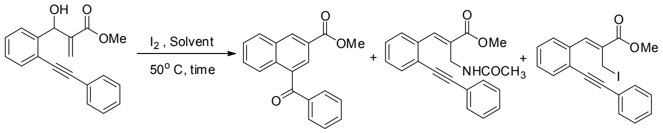
†Electronic Supplementary Information (ESI) available: Detailed experimental procedures and the $^1H$ and $^{13}C$ NMR spectra for relevant compounds. See DOI: 10.1039/b000000x

(phenylethynyl)phenyl)acrylate (**1c**) which was further confirmed by single crystal X-ray analysis (supporting information). Spectral data for the minor product suggested that it was methyl 4-benzoyl-2-naphthoate (**1b**) and the structure was further confirmed by a single crystal X-ray analysis (Figure 2). And another minor product was methyl 2-(iodomethyl)-3-(2-(phenylethynyl)phenyl)acrylate (**1d**). The structure of compound **1d** was confirmed by single crystal X-ray analysis (supporting information). The formation of **1c** may be occured through Ritter reaction. From these experimental results, it quite clear that acetonitrile functions both as a nucleophile and a solvent in the present reaction provide the methyl 2-(acetamidomethyl)-3-(2-(phenylethynyl)phenyl)acrylate derivative (**1c**). Hence, the same reaction was conducted in dichloromethane as the solvent. In this case, the reaction furnished methyl 4-benzoyl-2-naphthoate (**1b**) in 50% isolated yield. Encouraged by these results, we further screened a variety of other solvents, including toluene, tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), 1,2-dichloroethane (DCE). To our disappointment, using toluene or THF as solvents, resulted in the production of the iodosubstituted product **1d** as a sole product (entries 3 and 4) and no trace of the desired product was observed. When DCE was used as the solvent, the expected product **1b** was obtained in 40% isolated yield (entry 5) and trace amounts of the desired product were observed when DMF was used as the solvent (entry 6). From the results, it is quite clear that DCM is the optimal solvent for this transformation. We screened some additional iodine reagents, such as NIS and ICl (entries 7 and 8) for he reation. Among the tested iodine sources, molecular iodine proved to be the best choice. Thus, the optimum conditions for the reaction include molecular iodine (3 equiv) in DCM at a temperature of 50 °C.

**Table 1**. Optimization studies for producing naphthyl ketone derivatives from a 2-(2-phenylethynyl)-Morita-Baylis-Hillman adduct

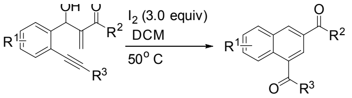


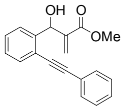
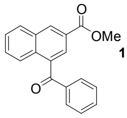
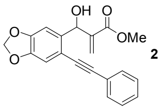
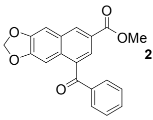
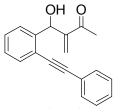
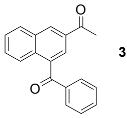
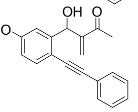
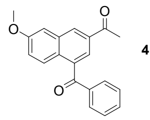
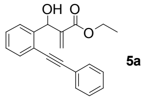
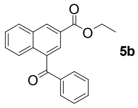
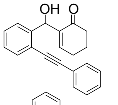
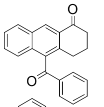
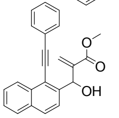
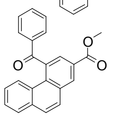
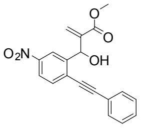
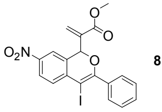
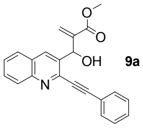
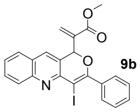
**1a** **1b** **1c** **1d**

| Entry[a] | Solvent | Iodine Source (3 equiv) | Temp (°C) | Time (h) | Isolated yield(s) (%)[b] | | |
|---|---|---|---|---|---|---|---|
| | | | | | **1b** | **1c** | **1d** |
| 1 | $CH_3CN$ | $I_2$ | 50 | 3 | 20 | 50 | 10 |
| 2 | **DCM** | $I_2$ | **50** | **4** | **50** | **-** | **20** |
| 2[c] | DCM | $I_2$ | 50 | 5 | 30 | - | 35 |
| 3 | Toluene | $I_2$ | 50 | 4 | - | - | 50 |
| 4 | THF | $I_2$ | 50 | 4 | - | - | 45 |
| 5 | DCE | $I_2$ | 50 | 4 | 40 | - | 25 |
| 6 | DMF | $I_2$ | 50 | 12 | trace | - | - |
| 7[d] | DCM | NIS | 50 | 3 | 20 | - | - |
| 8 | DCM | ICl | 50 | 3 | 20 | - | - |

[a] All reactions were conducted on a 1 mmol scale. [b] Isolated yields. [c] 1.5 Equiv of iodine was used. [d] a mixture of iodo-substituted isochromene and dihydroisobenzofuran derivatives was produced.

**Table 2**. Formation of naphthyl ketone derivatives *via* the iodine-mediated reaction of 2-(2-phenylethynyl)-Morita-Baylis-Hillman adducts.



| Entry[a] | Substrate | Time (h) | Product | yield(%)[b,c] |
|---|---|---|---|---|
| 1 |  **1a** | 3 |  **1b** | 50 |
| 2 |  **2a** | 3 |  **2b** | 52 |
| 3 |  **3a** | 3 |  **3b** | 55 |
| 4 |  **4a** | 4 |  **4b** | 51 |
| 5 |  **5a** | 2 |  **5b** | 70 |
| 6 |  **6a** | 2 |  **6b** | 50 |
| 7 |  **7a** | 6 |  **7b** | 60 |
| 8 |  **8a** | 12 |  **8b** | 70 |
| 9 |  **9a** | 12 |  **9b** | 75 |

[a] All reactions were conducted on s 1 mmol scale. [b] Isolated yields. From entries **1**-**7**, about 10-20% of **1d** type 2-(iodomethyl derivatives were observed as side reaction products.

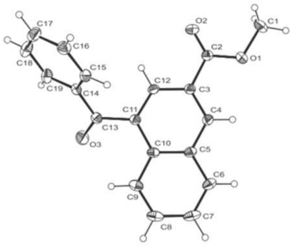


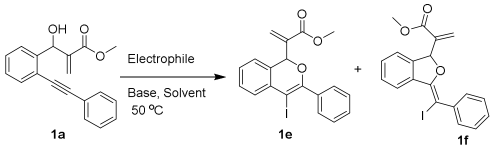
**Fig 2**. ORTEP diagram of the single-crystal X-ray structure of **1b**. [12]

With the optimized reaction conditions for the formation of naphthyl ketone derivative in hand, we next explored the scope and limitations of the methodology. In this regard, we investigated the reaction using a variety of 2-(2-phenylethynyl)-MBH adducts under the optimal reaction conditions and the results are summarized in Table 2. We initially examined the reactions with the 2-(2-phenylethynyl)-MBH substrate **1a** and **2a** derived from methyl acrylate (Table 2, entries 1 and 2). In the case of compound **1a** (entry 1), the desired product **1b**, was obtained in 50% isolated yield. Under the optimized reaction conditions, the dioxaole substituted substrate **2a** (entry 2) produced the corresponding naphthyl ketone derivatives in moderate yield. A similar trend was observed, in the case of reactions with MBH-compounds **3a** and **4a** derived from methyl vinyl ketone, in which the expected products were obtained in 55% and 51% yields, respectively (Table 2, entries 3 and 4). The scope of the methodology was further evaluated by examining the production of substrates **5a**, and **6a**, ethyl acrylate and 2-cyclohexenone MBH adducts under the optimal conditions. The corresponding naphthyl ketone derivatives were produced in moderate-to-good yields (Table 2, entries 5 and 6). Consequently, whenwe examined the reaction with compound **7a**, the expected naphthyl ketone derivative was obtained in good yield (entry 7). To introduce more variation into our protocol, we used the 4-nitro and quinoline substituted compounds **8a** and **9a** as substrates under the present reaction conditions. These substrates underwent iodocyclization instead of naphthyl ketone derivative formation, with iodo-substituted isochromene derivatives being produced in 70% and 75% yields, respectively (entries 8 and 9).

On the other hand, during our attempts to optimize the reaction conditions for increasing the yield of naphthyl ketone derivative **1b**, we conducted the reaction with **1a** in the presence of molecular iodine (3.0 equiv) and $K_3PO_4$ as a base (3.0 equiv) in acetonitrile as the solvent at 50 °C. Under these conditions, the reaction produced the iodo-substituted isochromene derivative **1e** as the sole product in 75% yield and the structure was confirmed by $^1$H NMR, $^{13}$C NMR, LRMS and HRMS (Table 3, entry 1). In fact, the use of various iodine reagents in the synthesis of iodo substituted 1*H*-isochromene derivatives has been reported in the literature, to our knowledge, the use of 2-(2-phenylethynyl)-MBH adducts in the synthesis of iodo-substituted isochromene derivatives has not been reported previously. This fact prompted us to further investigate this reaction in more detail.

To determine the optimum conditions for this reaction, we evaluated various iodine reagents, bases and solvents. We first examined the use of various iodine reagents such as, $I_2$, NIS, and ICl (Table 3, entries 1-3). The reaction with NIS produces desired iodo-substituted isochromene along with iodo-substituted dihydroisobenzofuran. However, in the presence of ICl, the reaction was incomplete and furnished a trace amount of the iodo-substituted isochromene derivative after 24 h. We further examined the reaction with a series of bases including $K_3PO_4$, $Et_3N$, $K_2CO_3$, and $NaHCO_3$ (entries 1, 4, 5, and 6). Among the bases tested, $K_3PO_4$ gave the best yield of the desired product. We next investigated the effect of the solvent on the reaction by carrying out the reactions in different solvents such as $CH_3CN$, $CH_2Cl_2$, $CHCl_3$, DMSO and toluene (entries 7-10). Solvents other than $CH_3CN$ produced a mixture of iodo-substituted isochromene and dihydroisobenzofuran derivatives under the present reaction conditions. Hence, the best result was obtained, when the reaction was performed in the presence of $I_2$ (3.0 equiv), $K_3PO_4$ (3.0 equiv) in acetonitrile as the solvent at 50 °C.

Table 3. Optimization conditions for iodo-substituted isochromene derivative **1e**



| Entry[a] | Electrophile (equiv) | Base (equiv) | Solvent | Time (h) | Product(s) (%)[b] 1e | 1f |
|---|---|---|---|---|---|---|
| 1 | $I_2$ (3.0) | $K_3PO_4$ (3.0) | $CH_3CN$ | 8 | 75 | - |
| 2 | NIS (3.0) | $K_3PO_4$ (3.0) | $CH_3CN$ | 12 | 45 | 40 |
| 3 | ICl (3.0) | $K_3PO_4$ (3.0) | $CH_3CN$ | 24 | 10 | - |
| 4 | $I_2$ (3.0) | $NaHCO_3$(3.0) | $CH_3CN$ | 12 | 60 | 35 |
| 5[c] | $I_2$ (3.0) | $K_2CO_3$(3.0) | $CH_3CN$ | 24 | 40 | 30 |
| 6[c] | $I_2$ (3.0) | $Et_3N$ (3.0) | $CH_3CN$ | 24 | - | - |
| 7[c] | $I_2$ (3.0) | $K_3PO_4$ (3.0) | $CHCl_3$ | 24 | 50 | 30 |
| 8[d] | $I_2$ (3.0) | $K_3PO_4$ (3.0) | $CH_2Cl_2$ | 24 | 30 | - |
| 9[c] | $I_2$ (3.0) | $K_3PO_4$ (3.0) | Toluene | 24 | 35 | 25 |
| 10[c] | $I_2$ (3.0.) | $K_3PO_4$ (3.0) | DMSO | 24 | 30 | 20 |

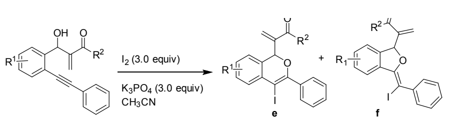
[a] Unless otherwise noted, all the reactions were carried out on a 1 mmol scale. [b] NMR yields ($CH_2Br_2$ as internal standard). [c] Unreacted starting material was recovered. [d] 20% Of **1b** compound was observed.

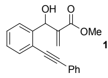
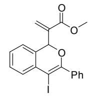
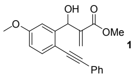
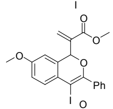
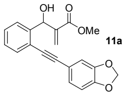
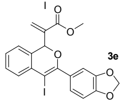
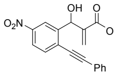
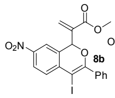
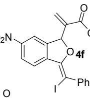
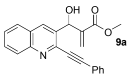
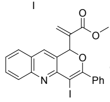
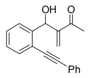
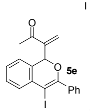
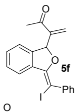
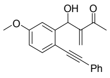
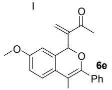
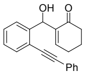
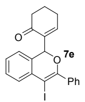
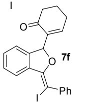
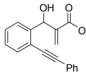
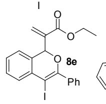
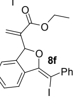
With these optimized conditions in hand, the scope of the present protocol was investigated (Table 4). As shown in Table 4, electron-neutral, electron-deficient and electron-rich groups on 2-(2-phenylethynyl)-MBH adducts were all well tolerated and the desired products were obtained in moderate-to-good yields (Table 4). The regioselectivity of the reaction depends on the substitution pattern of the substrate.

The presence of an electron-withdrawing group on the phenyl ring of the 2-(2-phenylethyny)-MBH adduct **8a** led to mixture of isochromene and dihydrobenzofuran derivatives (Table 4, entry 4). Moreover, when an electron-donating group was present on the phenyl ring of 2-(2-phenylethynyl)-MBH adducts, such as **10a** and **2a**, the isochromene derivative was preferentially formed (Table 4, entries 2 and 7). Furthermore, reactions with compound **3a** and **6a** derived from methyl vinyl ketone and cyclohexenone respectively, produced a mixture of the iodo-substituted isochromene and dihydroisobenzofuran derivatives in good yields (entries 6 and 8). Finally, we conducted the reaction with the ethyl acrylate derivative of the

2-(2-phenylethynyl)-MBH adduct **5a** under standard reaction conditions. An inseparable mixture of iodo-substituted isochromene and dihydrobenzofuran derivatives was produced in 80% isolated yield (entry 9).

Table 4. Synthesis of various iodo-substituted isochromene and dihydroisobenzofuran derivatives from 2-(2-phenylethynyl)-Morita-Baylis-Hillman adducts



| Entry$^a$ | Substrate | Temp (°C) | Time (h) | Products | Yield(s) (%)$^b$ (**e**) or (**e, f**) |
|---|---|---|---|---|---|
| 1 |  **1a** | 50 | 8 |  **1e** | 62 |
| 2 |  **10a** | rt | 5 |  **2e** | 58 |
| 3 |  **11a** | rt | 24 |  **3e** | 65 |
| 4 |  **8a** | rt | 24 |  **8b**  **4f** | (40,30) |
| 5 |  **9a** | rt | 24 |  **9b** | 70 |
| 6 |  **3a** | rt | 3 |  **5e**  **5f** | (30, 35) |
| 7 |  **4a** | rt | 24 |  **6e** | 60 |
| 8 |  **6a** | 40 | 24 |  **7e**  **7f** | (60, 15) |
| 9 |  **5a** | 40 | 24 |  **8e**  **8f** | 80$^c$ |

$^a$ Unless otherwise noted, all the reactions were carried out on a 1.0 mmol scale. $^b$ Isolated yield. $^c$ An inseparable mixture of the two regioisomers was obtained from column chromatography and the mixture was decomposing.

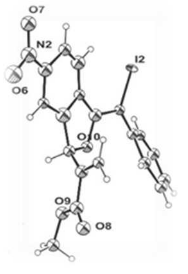
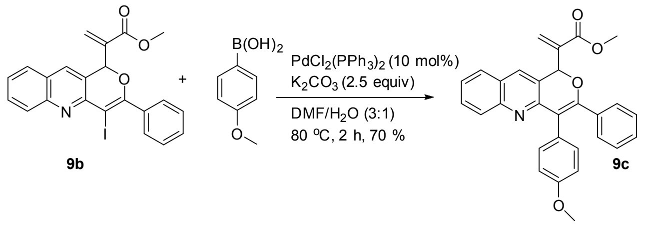


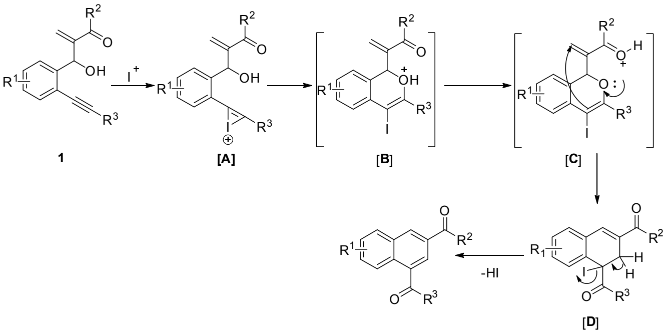
**Fig 3**. ORTEP diagram of the single-crystal X-ray structure of **4f.** [12]

To demonstrate the utility of this method, the presence of an iodo group in the isochromene system can be further elaborated by using a palladium-catalyzed C-C bond coupling reaction (Scheme 1). Compound **9b** was treated with 4-methoxy phenyl boronic acid under Suzuki reaction conditions to afford compound **9c** in 70% yield.



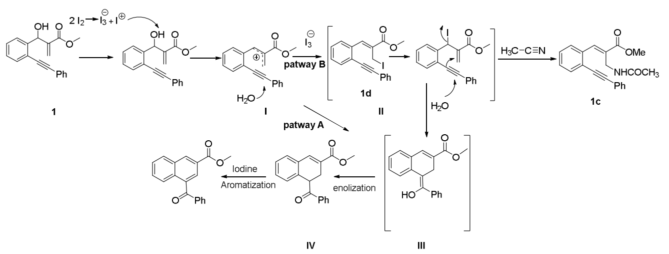
**Scheme 1**. Synthetic applications of iodo-substituted isochromene derivative.

Based on the experimental results and previous literature reports[10, 11] We propose two plausible mechanistic routes for the molecular $I_2$ mediated reactions of 2-(2-phenylethynyl)-MBH to naphthyl ketones is shown in scheme 2 and scheme 3. Firstly, we propose that the reaction proceeds via the formation of the 2-(2-phenylethynyl)-MBH adduct **1** in presence of $I_2$, the $I^+$ ion co-ordinates with the triple bond of the MBH-alkyne, which leads to the generation of the iodonium intermediate **A.** The subsequent nucleophilic attack of the hydroxyl group then produces the unstable charged species **B** *via* 6-*endo-dig* cyclization. Further, the proton transfer to the carbonyl oxygen, thus generate intermediate **C**. The intermediate **C** leading to the formation of the intermediate **D**. Subsequently, intermediate **D** is produced naphthyl ketone derivative by the loss of an HI molecule, respectively (Scheme 2`).



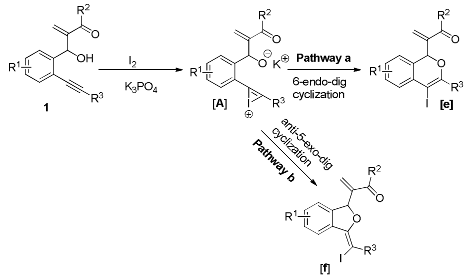
**Scheme 2**. Plausible mechanism for the formation of naphthyl ketones via the iodine-mediated reaction of 2-(2-phenylethynyl)-Morita-Baylis-Hillman adducts.

Alternatively, we propose another mechanism in which the reaction initiates by the formation of allylic carbocation intermediate (**I**) from the reaction of the 2-(2-phenylethynyl)-MBH adduct **1** in the presence of $I_2$. The intermediate (**I**) may be afford intermediate **III** through **path A** or **path B**. Further, the intermediate **III** undergoes enolization to produce the intermediate **IV**. Finally, the intermediate **IV** upon aromatization in the presence of iodine leads to the formation of the desired naphthyl ketone derivative (Scheme 3). The experimental results such as the formation of allyliodide derivative (**1d**) and the formation Ritter compound (**1c**) supports the mechanistic route 2 (Scheme 3).



**Scheme 3**. Plausible mechanism for the formation of naphthyl ketones via the iodine-mediated reaction of 2-(2-phenylethynyl)-Morita-Baylis-Hillman adducts.

On the other hand, the formation of the iodo-substituted isochromene derivative (**e**) or the dihydroisobenzofuran derivative (**f**) via 6-*endo-dig* cyclization (**pathway a**) or anti-5-*exo-dig*, cyclization (**pathway b**) from the iodonium alkoxide intermediate **A.** which is generated from the reaction of 2-(2-phenylethynyl)-MBH adduct **1** in presence of $I_2$ and base (**Scheme 4**).



**Scheme 4**. Plausible mechanistic pathway for the formation of iodo-substituted isochromene derivatives in the presence of iodine and base.

The failure to form naphthyl ketones in the presence of iodine from the reactions of substrates containing nitro and pyridyl groups of MBH-adducts (Table 2, entry 8 and 9) can be explained by the proposed reaction mechanism. In both cases, after the formation of intermediate **B**, the intermediate **C** would not be formed **(Scheme 2**). In the former case due to the electronic effect of nitro group on the phenyl ring of the MBH-adduct whereas in the latter case a pyridine moiety on the MBH-adduct would act as a base and neutralize intermediate **B**, leading to the formation of the iodo-substituted isochromene derivative.

## Conclusions

In conclusion, we report on the molecular iodine mediated reaction of 2-(2-phenylethynyl)-MBH adducts using $I_2$ and $I_2/K_3PO_4$ systems. The presence of $I_2$, naphthyl ketone derivatives are formed, whereas in the case of the $I_2/K_3PO_4$ system. iodo-substituted 1*H*-isochromene derivatives are formed, which can be further used in C-C bond forming reactions (Heck, Sonogashira and Suzuki reactions). Furthermore, the conventional molecular iodine system is much more cost effective than existing methods that involve the use of transition metals for the synthesis of naphthyl ketone derivatives. We believe that this protocol provides a simple, efficient and convenient alternative to the existing methodologies for producing a variety of substituted naphthyl ketones and 1*H*-isochromene derivatives from same starting materials in good-to-moderate yields.

## Experimental Section

### General Information

Reagents and solvents were purchased from various commercial sources and were used directly without any further purification, unless otherwise stated. Column chromatography was performed on 63-200 mesh silica gel. $^1H$ and $^{13}C$ NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts are reported in parts per million (δ) using $CDCl_3$ as an internal standard and coupling constants are expressed in hertz. IR spectra were recorded on an FT-IR spectrometer and are reported in $cm^{-1}$. Melting points were recorded using an Electro Thermal capillary melting point apparatus and are uncorrected. HRMS spectra were recorded using ESI-TOF or $EI^+$ mode.

### Procedure for the synthesis of naphthyl ketone derivatives (Table 2, entries 1- 9)

Molecular iodine (3.0 equiv) was added to a stirred solution of the 2-(2-phenylethynyl)-MBH adduct (1.0 mmol) in dichloromethane (8.0 mL) at room temperature, and the reaction mixture was then heated to 50 $^oC$ under a closed system and monitored by TLC. After completion of the reaction, the solution was cooled to room temperature and the solvent removed under reduced pressure. Water was then added To the reaction mixture and the resulting solution was extracted with DCM (20 mL × 3). The combined organic layer was washed with a saturated $Na_2S_2O_3$ aqueous solution to remove the excess iodine, dried over magnesium sulfate and filtered. The solvent was evaporated at reduced pressure and the resulting residue was further purified by column chromatography.

### Procedure for the synthesis of iodo-substituted isochromes, and dihydroisobenzofurans (Table 4, entries 1-9)

Molecular iodine (3.0 equiv) and potasium phosphate tribasic ($K_3PO_4$, 3.0 equiv) were added to a stirred solution of 2-(2-phenylethynyl)-MBH adduct (1.0 mmol) in acetonitrile (8.0 mL) at room temperature and the progress of the reaction was was monitored by TLC (reaction temperature was mentioned in the Table). After completion of the reaction, water was added and the resulting solution was extracted with dichloromethane (20 mL × 3). The combined organic phase was washed with aq. $Na_2S_2O_3$ solution to remove excess iodine, dried over magnesium sulfate and filtered. The solvent was removed by evaporation at reduced pressure. The resulting residue was further purified by column chromatography.

### Preparation of 1-(3-methoxybuta-1,3-dien-2-yl)-4-(4-methoxyphenyl)-3-phenyl-1*H*-pyrano[4,3-b]quinoline (3c)

Into 5.0 mL of a 3:1 ratio of DMF/$H_2O$ solution containing compound **9e** (0.5 mmol) and 4-methoxyphenylboronic acid (0.6 mmol), $PdCl_2(PPh_3)_2$ (5 mol%) was added and the reaction mixture was stirred for 10 min. $K_2CO_3$ (2.5 equiv) was then added and the solution stirred at 80 °C for 2 h under a nitrogen atmosphere. The resulting reaction mixture was extracted with ethyl acetate (2 x 10 ml). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under a vacuum. The crude compound was then purified by column chromatography to afford **3a** as a yellow solid.

## Spectral Data of Compounds

### Methyl 4-benzoylnaphthalene-2-carboxylate (1b)

Purified by column chromatography (EtOAc:hexane 10:90). Yield: 145 mg (50%), starting from 292 mg of **1a** (Table 2, entry 1). Yellow solid; mp: 118-119 °C. FT-IR (KBr) **(**ν/$cm^{-1}$): 1721, 1662. $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ (ppm): 8.76 (s, 1H), 8.16 (d, *J* = 1.64 Hz, 1H), 8.12-8.09 (m, 1H), 8.05-8.03 (m, 1H), 7.89-7.86 (m, 2H), 7.64-7.60 (m, 3H), 7.48 (t, *J* = 7.74 Hz, 2H), 3.97 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$ (ppm): 197.3, 166.6, 138.0, 137.0, 133.9, 133.7, 133.2, 133.1, 130.6, 130.0, 129.7, 128.8, 127.4, 126.7, 126.3, 125.9, 52.6. LRMS (EI) (*m/z*) (relative intensity): 290 ($M^+$, 100), 213 (80), 105 (74). HRMS calcd for $C_{19}H_{14}O_3$ ($M^+$): 290.0943, found 290.0948.

### Methyl 8-benzoyl-2*H*-naphtho[2,3-*d*][1,3]dioxole-6-carboxylate (2b)

Purified by column chromatography (EtOAc:hexane 10:90). Yield: 174 mg (52%), starting from 336 mg of **2a** (Table 2, entry 2). White solid; mp: 179-180 °C. FT-IR (KBr) (ν/$cm^{-1}$): 1714, 1651. $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ (ppm): 8.53 (s, 1H), 8.01 (d, *J* = 1.44 Hz, 1H), 7.85-7.83 (m, 2H), 7.61 (t, *J* = 7.38 Hz, 1H), 7.49-7.45 (m, 3H), 7.27-7.26 (m, 1H), 6.08 (s, 2H), 3.93 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$ (ppm): 197.5, 166.8, 151.1, 148.7, 138.1, 135.6, 133.6, 132.6, 131.2, 130.8, 130.6, 128.7, 126.1, 124.8, 105.5, 102.6, 102.0, 52.5. LRMS (FAB) (*m/z*) (relative intensity): 335 ($M^+$, 100), 259 (36), 219 (35), 105 (50). HRMS (FAB) calcd for $C_{20}H_{15}O_5$ ($M^+$): 335.0919, found 335.0916.

### 1-(4-Benzoylnaphthalen-2-yl)ethan-1-one (3b)

Purified by column chromatography (EtOAc:hexane 10:90). Yield: 150 mg (55%), starting from 276 mg of **3a** (Table 2, entry 3). White solid. mp: 117-118 °C. FT-IR (KBr) (ν/$cm^{-1}$): 1680, 1661, 1619. $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ (ppm): 8.61 (s, 1H), 8.13 (d, *J* = 1.6 Hz, 1H), 8.10-8.05 (m, 2H), 7.88-7.86 (m, 2H), 7.65-7.61 (m, 3H), 7.48 (t, J = 7.76 Hz, 2H), 2.74 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$ (ppm): 197.5, 197.3, 137.9, 137.3, 133.8, 133.3, 133.2, 133.2, 132.9, 130.6, 130.3, 129.9, 128.8, 127.6, 126.0, 125.4, 26.8. LRMS (EI) (*m/z*) (relative intensity): 274 ($M^+$, 100 ), 259.0 (90), 197 (65), 105 (75). HRMS calcd for $C_{19}H_{14}O_2$ ($M^+$): 274.0994, found 274.0992.

### 1-(4-Benzoyl-7-methoxynaphthalen-2-yl)ethan-1-one (4b)

Purified by column chromatography (EtOAc:hexane 10:90). Yield: 155 mg (51%), starting from 306 mg of **4a** (Table 2, entry 4). White solid; mp: 133-134 °C. FT-IR (KBr) (ν/$cm^{-1}$): 1680, 1619, 1592. $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ (ppm): 8.51 (s, 1H), 8.01-7.96 (m, 2H), 7.87-7.85 (m, 2H), 7.62-7.60 (m, 1H), 7.47 (t, *J* = 7.72 Hz, 2H), 7.34 (d, *J* = 2.56 Hz, 1H), 7.29-7.26 (m, 1H), 3.97 (s, 3H), 2.72 (s, 3H). $^{13}$C NMR (100 MHz, CDCl3) δC (ppm): 197.6, 197.5, 158.7, 138.0, 137.2, 134.8, 133.8, 133.7, 131.5, 130.6, 128.8, 128.6, 127.4, 123.4, 122.6, 107.9, 55.6, 26.9. LRMS (EI) (*m/z*) (relative intensity): 304 ($M^+$, 100), 289 (44), 227 (22). HRMS calcd for $C_{20}H_{16}O_3$ ($M^+$): 304.1099, found 304.1106.

### Ethyl 4-benzoylnaphthalene-2-carboxylate (5b)

Purified by column chromatography (EtOAc:hexane 10:90). Yield: 213 mg (70%), starting from 306 mg of **5a** (Table 2, entry 5). White solid; mp: 82-83 °C. FT-IR (KBr) (ν/$cm^{-1}$): 1717, 1662, 1596. $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ (ppm): 8.75 (s, 1H), 8.16 (d, *J* = 1.36 Hz, 1H), 8.08-8.02 (m, 2H), 7.88-7.86 (m, 2H), 7.63-7.58 (m, 3H), 7.47 (t, *J* = 7.72 Hz, 2H), 4.44 (q, *J* = 7.12 Hz, 2H), 1.42 (t, *J* = 7.12 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$ (ppm): 197.5, 166.2, 138.0, 137.1, 133.8, 133.7, 133.2, 133.1, 130.6, 130.0, 129.6, 128.8, 127.4, 126.8, 126.7, 125.9, 61.6, 14.5. LRMS (FAB) (*m/z*) (relative intensity): 305 ($M^+$+H, 100), 259 (15), 105 (33). HRMS (FAB) calcd for $C_{20}H_{17}O_3$ ($M^+$+H): 305.1178, found 305.1174.

### 10-Benzoyl-1,2,3,4-tetrahydroanthracen-1-one (6b)

Purified by column chromatography (EtOAc:hexane 10:90). Yield: 150 mg (50%), starting from 302 mg of **6a** (Table 2, entry 6). Yellow gummy solid; FT-IR (KBr) (ν/$cm^{-1}$): 1670, 1615, 1589. $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ (ppm): 8.77 (s, 1H), 8.05-8.02 (m, 1H), 7.84-7.82 (m, 2H) 7.64-7.61 (m, 1H), 7.52-7.45 (m, 5H), 2.77-2.74 (m, 2H), 2.13-2.11 (m, 2H), 1.57-.40 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$ (ppm): 199.5, 198.1, 137.4, 136.1, 135.9, 134.4, 133.0, 131.6, 130.6, 130.5, 130.4, 129.9, 129.6, 129.2, 126.6,125.1, 39.6, 27.7, 23.0. LRMS (EI) (*m/z*) (relative intensity): 300 ($M^+$, 100), 299 (45), 215 (25),105 (35). HRMS calcd for $C_{21}H_{16}O_2$ ($M^+$): 300.1150, found 300.1151.

### Methyl 4-benzoylphenanthrene-2-carboxylate (7b)

Purified by column chromatography (EtOAc:hexane 10:90). Yield: 204 mg (60%), starting from 342 mg of **7a** (Table 2, entry 7).Yellow solid; mp: 150-151 °C. FT-IR (KBr) (ν/$cm^{-1}$): 1721, 1667, 1596. $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ (ppm): 8.73 (d, *J* = 1.76 Hz, 1H), 8.20 (d, *J* = 8.48 Hz, 1H), 8.13 (d, *J* = 1,76 Hz, 1H), 7.91-7.85 (m, 5H), 7.58-7.52 (m, 2H) 7.42-7.33 (m, 3H), 3.98 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$ (ppm): 199.7, 166.5, 138.6, 137.0, 134.2, 134.0, 133.0, 132.6, 131.4, 130.5, 129.2, 129.1, 129.0, 128.6, 128.0, 127.6, 127.3, 126.9, 126.8, 52.6. LRMS (FAB) (*m/z*) (relative intensity): 341 (M$^+$+H, 100), 136 (71), 105 (40). HRMS (FAB) calcd for $C_{23}H_{17}O_3$ (M$^+$): 341.1178, found 341.1173.

**Methyl 2-(4-iodo-7-nitro-3-phenyl-1*H*-isochromen-1-yl)prop-2-enoate (8b)**

Purified by column chromatography (EtOAc:hexane 10:90). Yield: 323 mg (70%), starting from 337 mg **8a** (Table 2, entry 8).Yellow solid; mp: 142-143 °C. FT-IR (KBr) (ν/cm$^{-1}$): 1722, 1607, 1573. $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ (ppm): 8.22 (dd, *J* = 8.64, 2.24 Hz, 1H), 7.82 (d, *J* = 2.08 Hz, 1H), 7.69 (d, *J* = 8.64, Hz, 1H), 7.58-7.55 (m, 2H), 7.43-7.40 (m, 3H), 6.63 (s, 1H), 6.35 (s, 1H), 5.67 (s, 1H), 3.88 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$ (ppm): 165.9, 157.9, 147.1, 139.8, 137.0, 135.7, 131.0, 130.6, 130.5, 130.2, 129.9, 128.2, 124.5, 120.1, 75.7, 70.3, 52.7. LRMS (FAB) (*m/z*) (relative intensity): 463 (M$^+$, 71), 338 (83), 136 (70), 105 (56). HRMS (FAB) calcd for $C_{19}H_{14}O_5N_1$ (M$^+$): 462.9917, found 462.9905.

**Methyl 2-{4-iodo-3-phenyl-1*H*-pyrano[4,3-b]quinolin-1-yl}prop-2-enoate (9b)**

Purified by column chromatography (EtOAc:hexane 10:90). Yield: 352 mg (75%), starting from 343 mg **9a** (Table 2, entry 9).Yellow solid; mp: 112-113 °C. FT-IR (KBr) (ν/cm$^{-1}$): 1723, 1603, 1581. $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ (ppm): 8.17 (d, *J* = 8.44 Hz, 1H), 7.75 (d, *J* = 8.04 Hz, 1H), 7.72-7.66 (m, 3H), 7.64 (s, 1H), 7.48 (t, *J* = 7.52 Hz, 1H), 7.46-7.42 (m, 3H), 6.62 (s, 1H) 6.51 (s, 1H), 5.77 (s, 1H), 3.87 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$ (ppm): 166.13, 160.2, 149.5, 148.4, 138.0, 136.4, 131.8, 130.5, 130.4, 130.3, 130.1, 129.6, 128.0, 127.9, 127.5, 126.6, 124.0, 76.4, 52.6. LRMS (FAB) (*m/z*) (relative intensity): 470 (M$^+$, 100), 469 (32), 105 (28). HRMS (FAB) calcd for $C_{22}H_{17}O_3N_1$ (M$^+$): 470.0253, found 470.0259.

**Methyl 2-(4-iodo-3-phenyl-1*H*-isochromen-1-yl)prop-2-enoate (1e)**

Purified by column chromatography (EtOAc:hexane 5:95). Yield: 258 mg (62%), starting from 292 mg **1a** (Table 4, entry 1). Colorless solid. mp;. 93-94 °C. FT-IR (KBr) (ν/cm$^{-1}$): 1721, 1621. $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ (ppm): 7.56-7.52 (m, 3H), 7.42-7.38 (m, 4H), 7.28-7.25 (m, 1H), 6.94 (d, *J* = 7.36, 1H), 6.55 (m, 1H), 6.31 (s, 1H), 5.50 (s, 1H), 3.88 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$ (ppm): 166.6, 153.7, 138.1, 136.7, 133.5, 130.5, 130.3, 129.7, 129.6, 129.2, 129.1, 128.2, 128.0, 124.8, 75.5, 73.0, 52.5. LRMS (ESI) (*m/z*) (relative intensity): 441 (M$^+$+Na, 30 ), 315 (100), 242 (70). HRMS (ESI) calcd for $C_{19}H_{15}O_3NaI$ (M$^+$+Na): 440.9964, found 440.9961.

**Methyl 2-[(3*E*)-3-[iodo(phenyl)methylidene]-1,3-dihydro-2-benzofuran-1-yl]prop-2-enoate (1f)**

Purified by column chromatography (EtOAc:hexane 5:95) (Table 3). White solid. mp;. 102-103 °C. FT-IR (KBr) (ν/cm$^{-1}$): 1718, 1644. $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ (ppm): 7.45-7.39 (m, 4H), 7.37-7.32 (m, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.62, Hz, 1H), 6.45 (d, *J* = 7.96 Hz, 1H), 6.40 (d, *J*= 5.72 Hz, 2H), 6.07 (s, 1H), 3.85 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$ (ppm): 166.0, 156.1, 144.5, 140.8, 138.9, 130.7, 130.2, 129.3, 129.2, 128.6, 128.4, 126.7, 123.3, 122.7, 81.9, 76.9, 64.4, 52.3. LRMS (ESI) (*m/z*) (relative intensity): 419 (M$^+$+H, 100 ), 293 (11). HRMS (ESI) calcd for $C_{19}H_{16}O_3I$ (M$^+$+H): 419.0144, found 419.0155.

**Methyl 2-(4-iodo-7-methoxy-3-phenyl-1*H*-isochromen-1-yl)prop-2-enoate (2e)**

Purified by column chromatography (EtOAc:hexane 5:95). Yield: 259 mg (58%), starting from 322 mg of **10a** (Table 4, entry 2). Yellow liquid. FT-IR (KBr) (ν/cm$^{-1}$): 1722, 1611. $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ (ppm): 7.53-7.51 (m, 2H), 7.50-7.47 (m, 1H), 7.39-7.35 (m, 3H), 6.91 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.55 (s, 1H), 6.52 (d, *J* = 2.56 Hz, 1H), 6.26 (s, 1H), 5.51 (s, 1H), 3.88 (s, 3H), 3.82 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$ (ppm): 166.6, 159.8, 151.6, 137.8, 136.7, 131.2, 130.5, 130.4, 129.4, 127.9, 126.5, 113.8, 110.7, 75.3, 72.8, 55.7, 52.5. LRMS (ESI) (*m/z*) (relative intensity): 471 (M$^+$+Na, 76 ), 449 (M$^+$, 80). HRMS (ESI) calcd for $C_{20}H_{18}O_4I$ (M$^+$+H): 449.0250, found 449.0240.

**Methyl 2-[3-(2*H*-1,3-benzodioxol-5-yl)-4-iodo-1*H*-isochromen-1-yl]prop-2-enoate (3e)**

Purified by column chromatography (EtOAc:hexane 5:95). Yield: 300 mg (65%), starting from 336 mg of **11a** (Table 4, entry 3). Yellow liquid. FT-IR (KBr) (ν/cm$^{-1}$): 1722, 1623. $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ (ppm): 7.52 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.26-7.22 (m, 1H), 7.08 (dd, *J* = 8.14, 1.62 Hz, 1H), 7.0-6.99 (m, 1H), 6.91 (d, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.12 Hz, 1H), 6.53 (s, 1H), 6.26 (s, 1H), 5.99 (s, 2H), 5.48 (s, 1H), 3.88 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$ (ppm): 166.6, 153.2, 148.7, 147.1, 137.9, 133.7, 130.3, 129.6, 129.2, 129.1, 128.0, 125.3, 124.8, 110.9, 107.8, 101.5, 75.5, 72.3, 52.5. LRMS (FAB) (*m/z*) (relative intensity): 461.9 (M$^+$, 100 ), 149 (50). HRMS (FAB) calcd for $C_{20}H_{15}O_5I$ (M$^+$): 461.9964, found 461.9958.

**Methyl 2-[(3*E*)-3-[iodo(phenyl)methylidene]-6-nitro-1,3-dihydro-2-benzofuran-1-yl]prop-2-enoate (4f)**

Purified by column chromatography (EtOAc:hexane 5:95). Yield: 138 mg (30%), starting from 337 mg of **8a** (Table 4, entry 4). Yellow solid; mp: 136-137 °C. FT-IR (KBr) (ν/cm$^{-1}$): 1717, 1634. $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ (ppm): 8.94 (d, *J* = 8.76 Hz, 1H), 8.32 (dd, *J* = 8.78, 2.02 Hz, 1H), 8.21 (s, 1H), 7.55-7.53 (m, 2H), 7.36 (t, *J* = 7.68 Hz, 2H), 7.26-7.25 (m, 1H), 6.31 (s, 1H), 6.24 (s, 1H), 5.88 (s, 1H), 3.81 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$ (ppm): 165.4, 151.8, 148.7, 146.1, 141.6, 138.8, 137.8, 130.1, 128.3, 128.2, 128.1, 126.6, 123.7, 117.8, 81.8, 68.8, 52.5. LRMS (FAB) (*m/z*) (relative intensity): 463 (M$^+$, 100), 378 (30), 337 (45). HRMS (FAB) calcd for $C_{19}H_{14}O_5N_1I_1$ (M$^+$): 462.9917, found 462.9909.

**3-(4-Iodo-3-phenyl-1*H*-isochromen-1-yl)but-3-en-2-one (5e)**

Purified by column chromatography (EtOAc:hexane 5:95). Yield: 120 mg (30%), starting from 276 mg of **3a** (Table 4, entry 5). Yellow solid; mp: 98-99 °C. FT-IR (KBr) (ν/cm$^{-1}$): 1679, 1592. $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm): 7.55-7.53 (m, 3H), 7.40-7.36 (m, 4H), 7.27-7.22 (m, 1H), 6.84 (d, *J* = 7.48 Hz, 1H), 6.41 (d, *J* = 6.16 Hz ,2H), 5.79 (s, 1H), 2.49 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta_C$ (ppm): 198.3, 154.1, 145.9, 136.6, 133.5, 130.5, 129.8, 129.7, 129.5, 129.0, 128.2, 128.0, 124.7, 74.5, 73.0, 26.6. LRMS (EI) (*m/z*) (relative intensity): 402 (M$^+$, 45), 303 (50), 105 (100). HRMS calcd for $C_{19}H_{15}IO_2$ (M$^+$): 402.0117, found 402.0109.

### 3-[(3*E*)-3-[iodo(phenyl)methylidene]-1,3-dihydro-2-benzofuran-1-yl]but-3-en-2-one (5f)

Purified by column chromatography (EtOAc:hexane 5:95). Yield: 140 mg (35%), starting from 276 mg of **4a** (Table 4, entry 5).Yellow solid; mp: 102-103 °C. FT-IR (KBr) (ν/cm$^{-1}$): 1673, 1645. $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm): 7.45-7.42 (m, 4H), 7.37-7.35 (m, 1H), 7.28-7.25 (m, 1H), 7.19 (t, *J* = 7.48 Hz, 1H), 6.97 (t, *J* = 7.58 Hz, 1H), 6.51 (s, 1H), 6.44 (d, *J* =7.92 Hz, 1H), 6.25 (d, *J* = 7.44 Hz, 2H), 2.43 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta_C$ (ppm): 199.0, 156.2, 147.2, 145.0, 140.8, 130.7, 129.9, 129.4, 129.2, 128.6, 128.3, 126.5, 123.2, 123.0, 81.3, 64.4, 26.5. LRMS (EI) (*m/z*) (relative intensity): 402 (M$^+$, 55), 126 (100). HRMS calcd for $C_{19}H_{15}IO_2$ (M$^+$): 402.0117, found 402.0121.

### 3-(4-Iodo-7-methoxy-3-phenyl-1*H*-isochromen-1-yl)but-3-en-2-one (6e)

Purified by column chromatography (EtOAc:hexane 5:95). Yield: 273 mg (60%), starting from 306 mg of **4a** (Table 4, entry 6). Yellow gummy solid. FT-IR (KBr) (ν/cm$^{-1}$): 1674, 1592. $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm): 7.537.51(m, 2H), 7,47 (d, *J* = 8.56 Hz, 1H), 7.38-7.35 (m, 3H), 6.89 (dd, *J* = 8.56, 2.6 Hz, 1H), 6.44 (d, *J* = 2.56 Hz, 1H), 6.40 (s, 1H), 6.35 (s, 1H), 5.79 (s, 1H), 3.81 (s, 3H), 2.48 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta_C$ (ppm): 198.3, 159.8, 152.0 145.7, 136.7, 131.1, 130.4, 129.8, 129.5, 127.9, 126.6, 113.6, 110.7, 74.3, 72.7, 55.7, 26.6. LRMS (ESI) (*m/z*) (relative intensity): 455 (M$^+$+Na, 35), 433 (M$^+$+H, 65), 266 (100). HRMS (ESI) calcd for $C_{20}H_{17}IO_3Na$ (M$^+$+Na): 455.0120, found 455.0119.

### 2-(4-Iodo-3-phenyl-1*H*-isochromen-1-yl)cyclohex-2-en-1-one (7e)

Purified by column chromatography (EtOAc:hexane 5:95). Yield: 270 mg (60%), starting from 302 mg of **6a** (Table 4, entry 7). Yellow solid; mp: 141-142 °C. FT-IR (KBr) (ν/cm$^{-1}$): 1673, 1588. $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm): 7.55-7.52 (m, 3H), 7.39-7.35 (m, 4H), 7.72-7.21 (m, 1H), 6.83 (d, *J* = 7.44 Hz, 1H), 6.77 (t, *J* = 4.14 Hz, 1H), 6.39 (s, 1H), 2.64-2.55 (m, 2H), 2.45-2.40 (m, 2H), 2.10-2.04 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta_C$ (ppm): 198.0, 154.3, 150.8, 136.9, 136.7, 133.8, 130.6, 130.1, 129.7, 129.4, 128.8, 128.1, 127.9, 124.6, 73.4, 72.8, 38.6, 26.3, 22.8. LRMS (ESI) (*m/z*) (relative intensity): 429 (M$^+$+H, 100). HRMS (ESI) calcd for $C_{21}H_{17}IO_2Na$ (M$^+$+Na): 451.0171, found 451.0179.

### 2-[(3*E*)-3-[iodo(phenyl)methylidene]-1,3-dihydro-2-benzofuran-1-yl]cyclohex-2-en-1-one (7f)

Purified by column chromatography (EtOAc:hexane 5:95). Yield: 68 mg (15%), starting from 302 mg of **6a** (Table 4, entry 7). Colorless solid; mp: 108-109 °C; FT-IR (KBr): (ν/cm$^{-1}$) 1668, 1596;$^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm): 7.45-7.41 (m, 4H), 7.39-7.36 (m, 1H), 7.35-7.31 (m, 1H), 7.19 (t, *J* = 7.48 Hz, 1H), 7.13-7.11 (m, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.50 (s, 1H), 6.43 (d, *J* = 7.92 Hz, 1H), 2.54-2.45 (m, 3H), 2.42-2.34 (m, 1H), 2.10-2.04 (m, 1H), 2.01-1.93 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta_C$ (ppm): 198.7, 156.3, 146.3, 145.7, 140.9, 138.3, 130.8, 129.8, 129.4, 129.2, 128.6, 128.1, 123.1, 123.1, 80.7, 64.0, 38.6, 25.9, 22.7. LRMS (ESI) (*m/z*) (relative intensity): 451 (M$^+$+Na, 100), 429 (100). HRMS (ESI) calcd for $C_{21}H_{17}IO_2Na$ (M$^+$+Na): 451.0171, found 451.0166.

### Ethyl 2-(4-iodo-3-phenyl-1H-isochromen-1-yl)prop-2-enoate (8e) and ethyl 2-[(3*E*)-3-[iodo(phenyl)methylidene]-1,3-dihydro-2-benzofuran-1-yl]prop-2-enoate (8f)

Purified by column chromatography (EtOAc:hexane 5:95). Yield: 345 mg (80%), starting from 292 mg of **5a** (Table 4, entry 1). Yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm): 8.55-8.53 (m, 2H), 7.46-7.32(m, 9H), 7.27-7.20 (m, 2H), 6.99 (t, *J* =7.58 Hz, 1H), 6.93 (d, *J* = 7.44 Hz, 1H), 6.52 (s, 1H), 6.45 (d, *J* = 7.92 Hz, 1H), 6.41 (s, 2H), 6.31 (s, 1H), 6.05 (s, 1H), 5.46 (s, 1H) 4.38-4.29 (m, 4H), 1.37-1.30 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta_C$ (ppm): 166.1, 166.5, 156.1, 153.7, 144.6,140.9, 139.1, 138.3, 136.7, 133.5, 130.7, 130.5, 130.3, 129.9, 129.7, 129.6, 129.3, 129.2, 129.2, 129.1, 128.6, 128.3, 128.1, 127.9, 126.7, 124.8, 123.2, 122.6, 82.1, 76.9, 75.5, 73.0, 64.3, 61.4,61.2,14.4, 14.4. LRMS (FAB) (*m/z*) (relative intensity): 432 (M$^+$, 100), 333 (36), 306 (62), 105 (32). HRMS (FAB) calcd for $C_{20}H_{17}IO_3$ (M$^+$): 432.0222, found 432.0223.

### Methyl 2-[4-(4-methoxyphenyl)-3-phenyl-1*H*-pyrano[4,3-b]quinolin-1-yl]prop-2-enoate (9c)

Purified by column chromatography (EtOAc:hexane 15:90). Yield: 157 mg (70%), starting from 171 mg of **9b**.Yellow solid; mp: 154-155 °C. FT-IR (KBr) (ν/cm$^{-1}$): 1722, 1609. $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm): 7.99 (d, *J* = 8.4 Hz, 1H), 7.75-7.71 (m, 2H), 7.62-7.58 (m, 1H), 7.44-7.39 (m, 3H), 7.28-7.26 (m, 2H), 7.21-7.17 (m, 2H), 6.89 (d, *J* = 8.72 Hz, 2H), 6.63 (s, 1H) 6.55 (s, 1H), 5.83 (s, 1H), 3.91 (s, 3H), 3.82(s, 3H). $^{13}$C NMR (100 MHz CDCl$_3$) $\delta_C$ (ppm): 166.4, 158.7, 155.8, 151.4, 148.2, 138.6, 135.1, 133.5, 131.7, 130.0, 129.8, 129.7, 129.4, 128.8, 127.8, 127.6, 127.5, 127.1, 125.8, 124.4, 113.5, 75.7, 55.3, 52.5. LRMS (EI) (*m/z*) (relative intensity): 449 (M$^+$, 50), 344 (100), 284 (50), 246 (60), 105 (90). HRMS calcd for $C_{29}H_{23}N_1O_4$ (M$^+$): 449.1627, found 449.1628.

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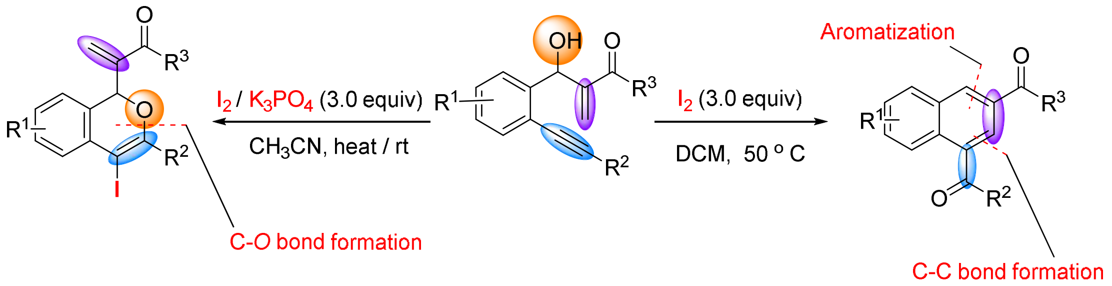
12 CCDC 972525 (**1b**), CCDC 978566 (**1c**), CCDC 973915 (**4f**) and CCDC 1009697 (**1d**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

## Table of Contents Entry



The molecular iodine mediated reaction of 2-(2-phenylethynyl)-MBH adducts is reported. The reaction proceeded smoothly in presence of iodine and an iodine-base system. The corresponding naphthyl ketones and iodo-substituted isochromene derivatives were obtained from same starting material in moderate-to-good yields.