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# Ag₂O nanoparticle-catalyzed substrate-controlled regioselectivities: direct access to 3-ylidenephthalides and isocoumarins†

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Herein, we disclose the first example of an efficient, silver oxide nanoparticle-catalyzed, direct regioselective synthesis of 3-ylidenephthalides 11–16 and isocoumarins 17–20 *via* sonogashira type coupling followed by substrate-controlled 5-*exo*-dig or 6-*endo*-dig cyclization reaction, respectively. This one pot coupling involves reaction of substituted 2-halobenzoic acid with *meta*/*para*-substituted and *ortho*-substituted terminal alkynes, which proceeded in a regioselective manner resulting in the formation of 3-ylidenephthalides or isocoumarins, respectively, in excellent yields (up to 95%) with complete Z-selectivity. This protocol features relatively broad substrate scope, mild conditions, operational simplicity, and is favourable with aromatic/alicyclic terminal alkynes. The competition experiments and gram-scale synthesis further highlight the importance and versatility of the methodology. The proposed mechanistic pathways illustrate that the regioselectivity is substantially being controlled by the substituent(s) present on the acetylenic phenyl ring.

## Introduction

Phthalide (isobenzofuran-1(3*H*)-one) is an important building block present in many natural products, pharmaceuticals, and biological materials, and shows a wide range of biological activities, such as anti-HIV, antidiabetic, antispasmodic, anti-allergic, antifungal, pesticidal, herbicidal, insecticidal, and anticancer activity.[1a–d] It has been used as an intermediate for the synthesis of various phthalide-based natural products and therapeutics.[2] Similarly, an inverted δ-lactone moiety, *i.e.*, iso-coumarin (1*H*-2-benzopyran-1-one), also displays astounding bio-activities, namely antitumor, antiallergenic, antimicrobial, anti-inflammatory, antidiabetic, phytotoxic, anti-HIV and immunomodulatery responses.[3,1b]

Consequently, a number of methods have been reported to construct 3-ylidenephthalides and isocoumarins *via* traditional methods as well as C–H bond functionalization.[4] It has been reported that 3-ylidenephthalides and isocoumarins can be easily prepared, respectively, from metal-catalyzed 5-*exo*-dig and 6-*endo*-dig cyclization of 2-alkynylbenzoic acid/esters, which can be generated *in situ* from the Sonogashira-type coupling reaction of 2-halobenzoic acids with terminal alkynes.[5] However,
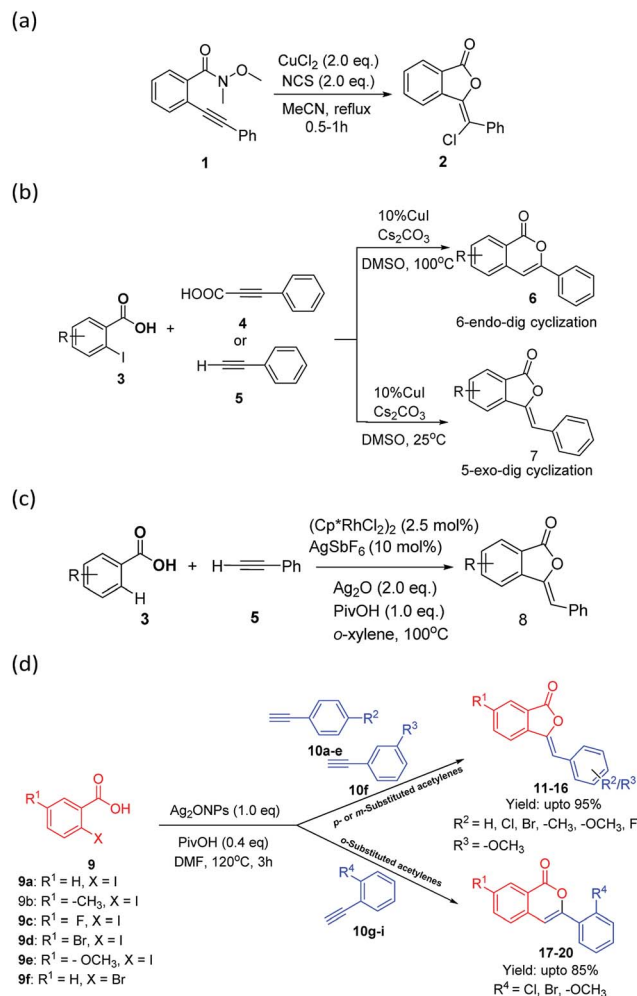
earlier methods suffer from low regioselectivities affording mixture of phthalides and isocoumarins.[6a,b]

The controlled regioselectivity is an important concept for the synthesis of pharmaceutically important molecules with definite regio- and stereo-selectivities. Pertaining to the present study that is the regioselective synthesis of 5-*exo*-dig and 6-*endo*-dig cyclization; only a few regioselective methods, *i.e.*, Cu²⁺-NCS catalyzed (Scheme 1a),[7] acid–base controlled,[8] and temperature controlled synthesis (Scheme 1b),[9] have been reported to synthesize 3-ylidenephthalides 2 and 7 as well as isocoumarins 6 *via* C–C and C–O bond formations. Recently, Rh-catalyzed oxidative coupling/annulation of benzoic acids with terminal alkynes has been reported to construct 3-ylidenephthalides 8 with complete Z-selectively *via* C–H bond activation concept (Scheme 1c).[10]

In general, transition metal-catalyzed cross coupling reactions have been conveniently established for carrying out C–H bond activation *via* new systems that exhibit extremely high catalytic activity and/or unique reactivity. In recent years, the use of metal catalysts of Cu, Mn, Co, and Fe in C–H bond activation has gained significant attention over Pd and Ni catalysts. Since, Ag(ɪ) salt have been reported to show exceptional potential to explicit tremendous affinity especially towards terminal alkynes[11] and several Ag-catalyzed C–C coupling reaction have been well reported in the literature;[12] we envisaged that if terminal alkynes with electron rich substituents at *o*-, *m*-, or *p*-position be chosen as starting material for the reaction with 2-iodobenzoic acid, then Ag(ɪ) may coordinate simultaneously with triple bond as well as with electron-rich

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† Electronic supplementary information (ESI) available: ¹H NMR and ¹³C NMR spectra of all synthesized compounds **11–16**, **17–20**, **21**, **22a–c**. See DOI: 10.1039/c8ra03926g

## Results and discussions

In our endeavors in search for potent bioactive compounds;[13] we were interested in the synthesis of 3-ylidenephthalides **11a** and isocoumarins **11aa′** regioselectively (Table 1).

Consequently, we started our synthetic investigation *via* the reaction of 2-iodobenzoic acid **9a** with phenylacetylene **5** as model reaction for the optimization study of the reaction. We initiated our investigation by carrying out the reaction using CuI in DMF which furnished the desired 3-ylidenephthalide **11a** in 10% yield only (Table 1, entry 1). Since [Ag] salts have high affinity towards terminal alkynes; we used $Ag_2O$ to carry out our model reaction. To our surprise, we obtained only **11a** in 45% yield (Table 1, entry 2) and **11aa′** was not detected at all. The structure of the desired compound was well characterized *via* ^{1}H NMR, ^{13}C NMR, FT-IR and HRMS analysis and it demonstrated complete Z-selectivity. Then, the same reaction has been carried out in the presence of pivalic acid as an additive which furnished **11a** in 75% yield (Table 1, entry 3). Once realizing the unique nature of $Ag_2O$; we also screened various other salts of silver, *i.e.*, acetate, chloride, and nitrate. Among them, only silver acetate/pivalic acid combination furnished **11a** in 43% yields (Table 1, entry 4–6). In addition, screening of metal oxides of Zn, Cu, Cd, Pb, Al, Cr, Ni, Mn, Fe, *etc.* were carried out. Either reaction does not occur at all or **11a** was obtained in traces (see ESI†).

It has been known that nanoparticle leveraged C–H activation has been identified as an efficient sustainable approach for industrial applications by transforming unactivated $C(sp^3)$–H



**Scheme 1** Present study *versus* previous representative approaches for the regioselective synthesis of 3-ylidenephthalides and iso-coumarins. (a) Miyata *et al.,* (b) Manian *et al.,* (c) Liu *et al.,* (d) present work.

substituents (more likely with *o*- as compared to *m*- and *p*-position) *e.g.*, Cl, Br, OMe *etc.* which could undergo 5-*exo*-dig or 6-*endo*-dig cyclisation in a regioselective manner (Fig. 1).

To the best of our knowledge, there is no report on the silver-catalyzed substrate-controlled regioselectivities on 5-*exo*-dig or 6-*endo*-dig cyclization reaction of 2-iodobenzoic acid with *o*-, *m*-, or *p*-substituted terminal alkynes. Herein, we report an efficient, one-pot, silver oxide nanoparticle (Ag₂ONPs) catalyzed substrate-controlled synthesis of 3-ylidenephthalides and iso-coumarins in a regioselective manner upto 95% yields (Scheme 1d).
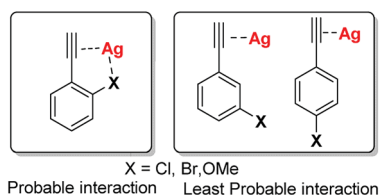


**Fig. 1** Structures depicting the probable interaction between Ag(I) compounds with terminal alkynes and electron rich substituents.

**Table 1** Optimization study: synthesis of 3-ylidene-phthalides from the coupling reaction of 2-iodobenzoic acid **9a** with phenyl acetylene **5**[a]



| Entry | Metal | Add. | Solvent | Temp. | Time (h) | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | CuI | — | DMF | 80 °C | 3 | 10[b] |
| 2 | Ag₂O | — | DMF | 80 °C | 3 | 45 |
| 3 | Ag₂O | PivOH | DMF | 80 °C | 3 | 75 |
| 4 | AgOAc | PivOH | DMF | 80 °C | 3 | 43 |
| 5 | AgCl | PivOH | DMF | 80 °C | 3 | Nil |
| 6 | AgNO₃ | PivOH | DMF | 80 °C | 3 | Nil |
| 7 | Ag₂ONPs | PivOH | DMF | 80 °C | 3 | 83 |
| 8 | Ag₂ONPs | AcOH | DMF | 80 °C | 3 | 46 |
| 9 | Ag₂ONPs | PivOH | DMF | 80 °C | 24 | 59 |
| 10 | Ag₂ONPs | PivOH | DMF | 100 °C | 3 | 90 |
| 11 | Ag₂ONPs | PivOH | DMF | 120 °C | 3 | 95 |
| 12 | Ag₂ONPs | PivOH | DMF | 130 °C | 3 | 88 |
| 13 | Ag₂ONPs | PivOH | DMF | 120 °C | 1.5 | 88 |
| 14 | Ag₂ONPs | PivOH | DMF | 120 °C | 2 | 88 |
| 15 | — | PivOH | DMF | 120 °C | 3 | No reaction |

[a] Reaction conditions: **9a** (1 eq.), **5** (1 eq.), Ag₂ONPs (1 eq.), pivalic acid (0.4 eq.), 120 °C, 3 h. [b] Isocoumarin **11aa′** was also obtained in 5% yield in this reaction.

and $C(sp^2)$–H bonds present in feedstock into important bioactive molecules.[14] We anticipated that silver oxide nanoparticles ($Ag_2ONPs$), having larger surface area, may results in high yield of our desired products.[15] Thus, the model reaction was carried out using $Ag_2ONPs$/pivalic acid in DMF which, to our expectation, furnished the desired **11a** in 83% yields (Table 1, entry 7). Decrease in catalytic loading of $Ag_2ONPs$ leads to decrease in yield of the reaction (see ESI†). The model reaction has been also carried out using $Ag_2ONPs$/acetic acid in DMF which furnished **11a** in only 46% yield (Table 1, entry 8). Extending the reaction for 24 h at the same temperature leads to decrease in reaction yield (Table 1, entry 9). Further examination of variation in temperature and time interval were carried out. Increasing the temperature from 80 °C to 100 °C furnished **11a** in 90% yield (Table 1, entry 10). Interestingly, we further increase the temperature to 120 °C for 3 h which furnished the desired product **11a** in excellent (95%) yield (Table 1, entry 11). Further increase in temperature or decrease in time interval do not have much beneficial effects on the yield of the reaction (Table 1, entry 12–14). While the reaction in other solvents such as DMSO, 1,4-dioxane, toluene, o-xylene, diminishes the catalytic activity; the reaction in PEG and water did not occur at all (see ESI†). Further, change in the nature of additives such as $Na_2CO_3$, $Cs_2CO_3$, NaOH, 1,10-phenanthroline *etc.* do not furnished the desired product **11a** or **11aa′** (see ESI†). This infer us that our model reaction facilitates under acidic conditions. It has been also observed that no reaction occur when $Ag_2ONPs$ is not added to the optimized reaction conditions (Table 1, entry 15). Overall, $Ag_2ONPs$/pivalic acid in DMF at 120 °C for 3 h was found to be the best optimized reaction conditions for this regioselective reaction.

To explore the substrate scope and generality of the present methodology, various substituted 2-iodobenzoic acids **9a–f** were reacted with several o-/m-/p-substituted alkynes **10a–i** under optimized reaction conditions. Thus, **9a–f** were reacted with *para*- and *meta*-substituted alkynes **10a–f** under optimized reaction conditions, which undergoes substrate-controlled 5-*exo*-dig cyclization to furnish 3-ylidenephthalides **11–16** upto 95% yields in a highly regioselective manner (Scheme 2).

Then, **9a** was reacted with **10g** under optimized conditions. As envisioned in the case of *ortho*-substitutent in acetylenic phenyl ring, instead of getting 3-ylidenephthalides; we obtained only isocoumarin **17a** in 42% yield. This encourage us to investigate this unusual observation in details to understand the cause of regioselectivity. Since chlorine having lone pair of electrons at *ortho*-position of the acetylenic phenyl ring displayed different behaviour, we analyzed other groups containing lone pair of electrons such as Br, OMe at *ortho*-position of phenyl acetylenes. Thus, substituted 2-iodobenzoic acid **9a–c** were reacted with *ortho*-substituted alkynes **10g–j** under optimized reaction conditions which furnished isocoumarins **17–20** upto 85% yields *via* substrate-controlled 6-*endo*-dig cyclization reaction (Scheme 3). These groups also furnished isocoumarins regioselectively.

The generality of the reaction was demonstrated by carrying out gram-scale synthesis of 3-ylidinephthalides **11a** as well as isocoumarins **17b** which were obtained in 89% and 80% yields,
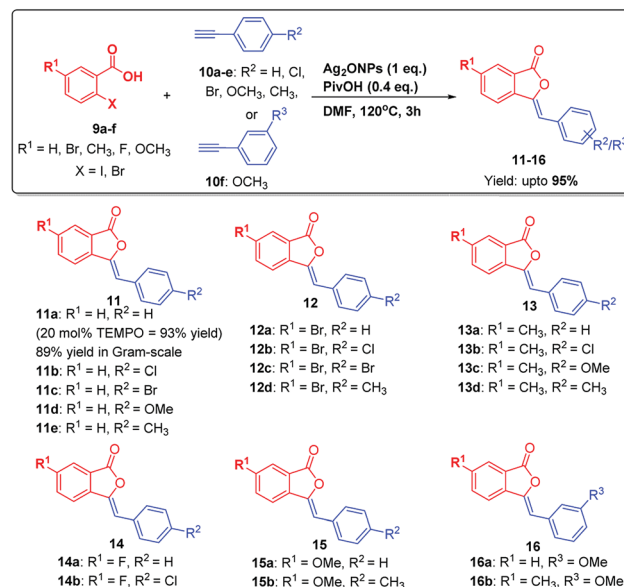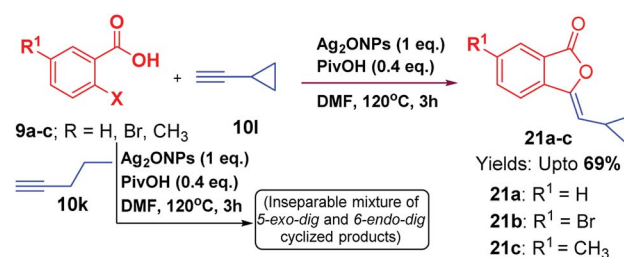


**Scheme 2** Substrate scope: synthesis of 3-ylidenephthalides **11–16**.
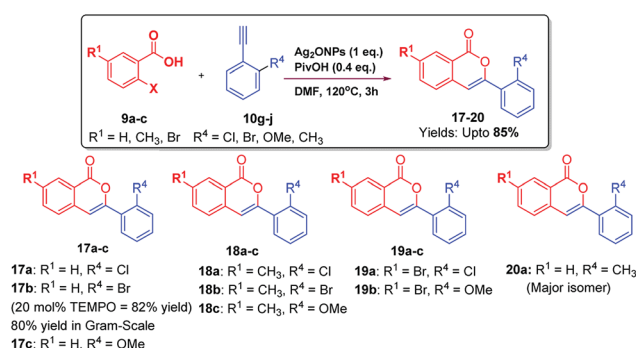


**Scheme 3** Substrate scope: synthesis of isocoumarins **17–20**.

respectively. In order to check the competition between 5-*exo*-dig and 6-*endo*-dig cyclization reaction, reaction of **9a** with an equimolar ratio of **10f** and **10i** was carried out which furnished **17c/16a** in 1.1 : 1 ratio. This infer us that the 5-*exo*-dig and 6-*endo*-dig cyclization occurs in almost equal proportion under optimized reaction conditions. Furthermore, competition reaction between **9a** with an equimolar ratio of **10d** and **10f** furnished **11d/16a** in 1.2 : 1 ratio which indicates that *m*- and *p*-



**Scheme 4** Substrate scope: Synthesis of alicyclic 3-ylidenephthalides **21a–c**.
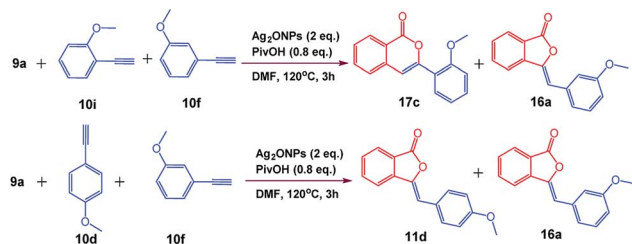
**Scheme 5** Intermolecular competition experiments.

substituted phenylacetylenes undergoes 5-*exo*-dig cyclization in almost equal proportion (Scheme 5).

Like aromatic terminal alkynes, aliphatic terminal alkyne **10k** was also attempted to perform this reaction under optimized reaction conditions; however, we obtained an inseparable mixture of 5-*exo*-dig and 6-*endo*-dig cyclized products. Hence, it may be inferred that the regioselectively of this reaction is favourable with aromatic alkynes as compared to aliphatic alkynes. In addition, when alicyclic acetylene **10l**, was subjected to optimized reaction conditions; cyclopropyl-based 3-ylidenephthalides **21a–c** were obtained favouring 5-*exo*-dig product regioselectively (Scheme 4).

In consideration of the unique features of the Ag$_2$ONPs-catalyzed substrate-controlled regioselective 5-*exo*-dig or 6-*endo*-dig cyclization reaction, we were interested in delineating the tentative mechanism of this reaction. The evidence for the occurrence of the Sonogashira type C–H activation followed by oxycation-mediated cyclization was gathered by carrying out reactions in the presence of typical free-radical scavenger such as 2,2,6,6,-tetramethylpiperidine-*N*-oxyl (TEMPO, 20 mole%) under the same optimized conditions. The occurrence of **11a** in 93% yields and **17b** in 82% yields, respectively, indicates

that the reaction involves cationic mechanism rather than free-radical process.

To study the mechanistic role of groups having lone pair of electrons at *ortho*-position of acetylenic phenyl ring; we were also interested to depict the role of group(s) without having lone pair of electrons at *ortho*-position. Thus, isocoumarin **20a** was obtained as major isomer along with 3-ylidenephthalides (minor) *via* reaction of **9a** with **10j** which infer us that *ortho*-group having lone pair of electrons furnish isocoumarins exclusively; this regioselective methodology is also applicable with *ortho*-group without having lone pair of electrons. Presumably, the formation of **20a** was due to the coordinated association of electron clouds of CH$_3$ group with [Ag] complex which facilitates oxyanion attacks at C-2 position of acetylenic bond *via* 6-*endo*-dig cyclization more favourably than 5-*exo*-dig cyclization which generated 3-ylidenephthalides **20b** as minor product (see ESI†).

Thus, the tentative mechanism of this heterogeneous reaction may be proposed based on previous similar studies (Fig. 2).[16] It involves deprotonation of **5** which furnishes the silver phenylacetylide *in situ*.[17] Due to the ligand to metal charge transfer (LMCT),[18] partial positive charge developed at the acetylene site which favour the attack of **9a** and gives 2-(phenylethynyl)benzoic acid on which residual Ag$_2$ONPs could coordinate with electron rich alkynyl bond as well as with the carboxylate oxyanion [**I**].[19] In the case of *m*-/*p*-substituted terminal alkynes as in intermediate [**I**] (path A), no interaction of lone pair electrons or electron cloud between [Ag] and *m*-/*p*-substituent on acetylenic phenyl ring occurs and hence, carboxylate oxyanion undergoes attack at C-1 position of acetylenic bond *via* 5-*exo*-dig cyclization to give intermediate [**II**], which is further converted into 3-ylidenephthalides upon protonation with PivOH. However, in the case *o*-substituted terminal alkynes as in intermediate [**III**] (path B), there is
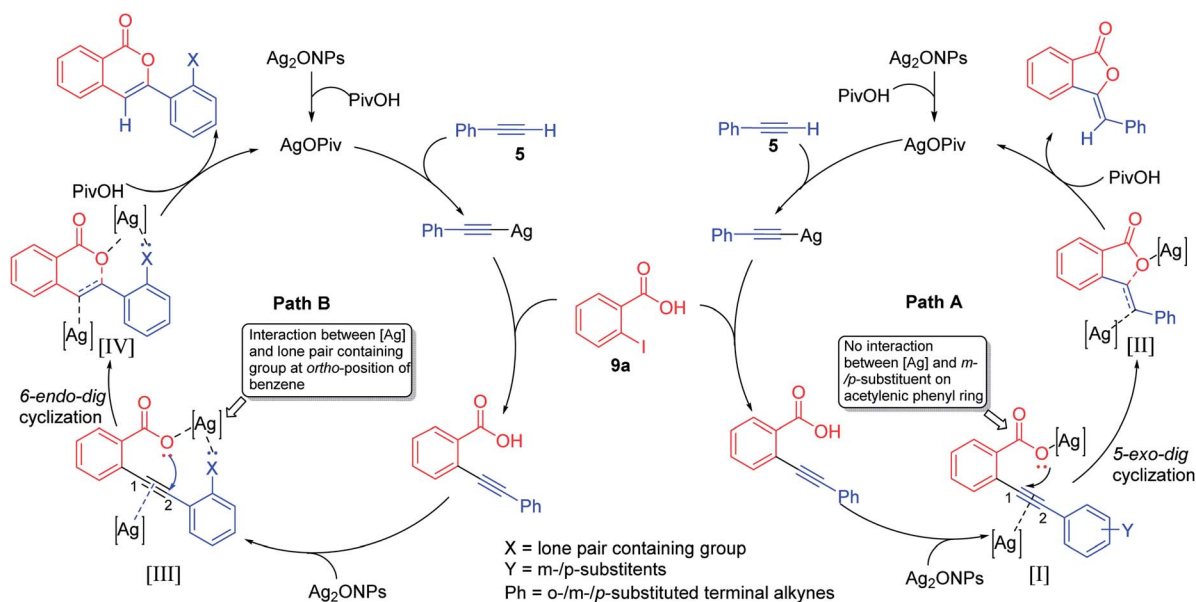


**Fig. 2** Plausible mechanism

significant electronic interaction between the [Ag] and the electronic lobe or lone pair of electrons containing group at *o*-substituted acetylenic phenyl ring. Consequently, oxyanion attacks at C-2 position of acetylenic bond *via* 6-*endo*-dig cyclization to give intermediate [**IV**], which is further converted into isocoumarins upon protonation with PivOH.

## Conclusions

For the first time, we have developed a highly efficient and straightforward route to access two bioactive moieties, 3-ylidinephthalides and isocoumarins, *via* Ag$_2$O nanoparticle-catalyzed Sonogashira type coupling followed by substrate-controlled 5-*exo*-dig or 6-*endo*-dig cyclization in a highly regioselective manner, respectively, with complete Z-selectivity. This protocol features relatively broad substrate scope, mild conditions, operationally simple, and is more favorable with aromatic/alicyclic terminal alkynes as compared to aliphatic terminal alkynes. The intermolecular competition experiments and gram-scale synthesis further highlights the importance and versatility of the newly developed methodology. The proposed mechanistic pathways interprets that the regioselectivity is substantially being controlled by the substituent(s) present on the acetylenic phenyl ring.

## Experimental section

All glass apparatus were oven dried prior to use. High quality reagents were purchased from Sigma Aldrich (USA), TCI Chemicals (Tokyo, Japan) and Spectrochem (India) and were used without further purification. Laboratory grade commercial reagents and solvents were purified by standard procedures prior to use. Infrared spectra were recorded on a FT-IR Spectrum 2 (Perkin-Elmer) spectrophotometer. NMR spectra were obtained on a Jeol resonance ECS 400 MHz spectrometer (operating at 400 MHz respectively for $^1$H; 100 MHz respectively for $^{13}$C). The $^1$H-NMR (400 MHz) chemical shifts were measured relative to CDCl$_3$ or DMSO-d$_6$ as the internal reference (CDCl$_3$: $\delta$ = 7.249 ppm; DMSO-d$_6$: $\delta$ = 2.50 ppm). The $^{13}$C-NMR (100 MHz) chemical shifts were given using CDCl$_3$ or DMSO-d$_6$ as the internal standard (CDCl$_3$: $\delta$ = 77.16 ppm; DMSO-d$_6$: $\delta$ = 39.52 ppm). Tetramethylsilane ($\delta$ = 0.00 ppm) served as an internal standard in $^1$H-NMRand CDCl$_3$ ($\delta$ 77.16 ppm) in $^{13}$C NMR. Chemical shifts are reported in parts per million. Splitting patterns are described as singlet (s), doublet (d), triplet (t) and multiplet (m). Electrospray emission mass spectrometry (ESI-MS) and high resolution mass spectra (HRMS) were obtained with a Gevo G-2 S Q-TOF (Waters). Melting points were taken in open capillaries on Complab melting point apparatus and are presented uncorrected. Unless otherwise noted, column chromatography was performed over Rankem silica gel (particle size: 100–200 mesh) procured from Rankem™ (India).

## General procedure (GP) for the synthesis of 3-ylidenephthalides 11–16

To a stirred mixture of substituted halo-aromatic carboxylic acid **9a–f** (1.209 mmol, 1.0 eq.), terminal alkynes **10a–e/10f** (1.209 mmol, 1.0 eq.), Ag$_2$ONPs (1.209 mmol, 1.0 eq.), and PivOH (0.484 mmol, 0.4 eq.) in dry DMF (2 mL) at 120 °C for 3 h. The reaction mixture was then cooled to ambient temperature; diluted with ethyl acetate (10 mL), filtered through a celite pad and washed further with ethyl acetate (15 mL). The combined organic solvents were extracted with ethyl acetate (3 × 10 mL), washed with distilled water (2 × 20 mL) and then with brine solution (20 mL). The combined organic layer was dried over anhyd. Na$_2$SO$_4$ & concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (100–200 mesh size) using 2% ethyl acetate: hexane as eluant to furnish **11–16**.

**(Z)-3-Benzylideneisobenzofuran-1(3H)-one (11a).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as white solid having mp 92–94 °C in 95% yield. IR (Neat, cm$^{-1}$): 1760, 1660, 1607, 1469, 1447, 1270, 754, 682; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J$ = 7.76 Hz, 1H), 7.85 (d, $J$ = 7.28 Hz, 2H), 7.79–7.70 (m, 2H), 7.55 (t, $J$ = 7.40 Hz, 1H), 7.41 (t, $J$ = 7.36 Hz, 2H), 7.33–7.29 (m, 1H), 6.43 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.16, 144.67, 140.71, 134.57, 133.17, 130.21, 129.87, 128.87, 128.52, 125.69, 123.53, 119.90, 107.15; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{15}$H$_{12}$O$_2$]$^+$: 223.0754, found: 223.0755.

**(Z)-3-(4-Chlorobenzylidene)isobenzofuran-1(3H)-one (11b).** This compound was prepared according to the GP and was obtained in 2% EtOAc/hexane solution as white solid having mp 142–146 °C in 70% yield. IR (Neat, cm$^{-1}$): 1790, 1655, 1488, 1470, 1268, 686; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J$ = 7.6 Hz, 1H), 7.78–7.70 (m, 4H), 7.57–7.53 (m, 1H), 7.38–7.34 (m, 2H), 6.36 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.93, 145.00, 140.46, 134.70, 134.30, 131.69, 131.33, 130.08, 129.05, 125.79, 123.49, 119.93, 105.83 ppm; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{15}$H$_{10}$ClO$_2$]$^+$: 257.0314, found 257.0366.

**(Z)-3-(4-Bromobenzylidene)isobenzofuran-1(3H)-one (11c).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as white solid having mp 174–176 °C in 67% yield. IR (Neat, cm$^{-1}$) 1791, 1631, 1487, 1470, 1269, 515; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J$ = 7.68 Hz, 1H), 7.78–7.69 (m, 4H), 7.58–7.51 (m, 3H), 6.35 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.87, 145.13, 140.46, 134.69, 132.12, 132.04, 131.56, 130.13, 125.80, 123.53, 122.63, 119.95, 105.85; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{15}$H$_{10}$BrO$_2$]$^+$: 300.9859, found 300.9860.

**(Z)-3-(4-Methoxybenzylidene)isobenzofuran-1(3H)-one (11d).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as slight greenish blue solid having mp 136–140 °C is 70% yield. IR (Neat, cm$^{-1}$): 2927, 2844, 1780, 1650, 1601, 1511, 1471, 1258; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92 (d, $J$ = 7.08 Hz, 1H), 7.81–7.67 (m, 4H), 7.52–7.48 m, 1H), 6.95–6.92 (m, 2H), 6.38 (s, 1H), 3.84 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.36, 159.89, 143.17, 140.89, 134.44, 131.79, 129.38, 125.97, 125.64, 123.21, 119.60, 114.38, 107.04, 55.43; HRMS

(ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [for C$_{16}$H$_{13}$O$_3$]$^+$: 253.0859, found 253.0860.

**(4-Methyl-benzylidene)-3$H$-isobenzofuran-1-one (11e).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as off-white solid having mp 140–144 °C in 59% yield. IR (Neat, cm$^{-1}$): 2922, 1765, 1660, 1604, 1510, 1471, 1269, 856, 814; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, $J$ = 7.32 Hz, 2H), 7.70–7.50 (m, 3H), 7.41–7.37 (m, 2H), 7.31–7.27 (m, 1H), 6.34 (s, 1H), 2.48 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.27, 144.05, 140.82, 138.76, 134.48, 130.37, 130.19, 129.63, 125.64, 125.28, 123.41, 119.76, 107.29, 21.51; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{16}$H$_{13}$O$_2$]$^+$: 237.0910, found 237.0913.

**(Z)-3-Benzylidene-6-bromoisobenzofuran-1(3$H$)-one (12a).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as white solid having mp 176–178 °C in 63% yield. IR (Neat, cm$^{-1}$): 1773, 1665, 1491, 1461, 1250, 522; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.06–8.05 (m, 1H), 7.83–7.81 (m, 3H), 7.64 (d, $J$ = 8.28 Hz, 1H), 7.43–7.39 (m, 2H), 7.35–7.31 (m, 1H), 6.42 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.62, 145.96, 143.90, 139.31, 137.71, 132.83, 130.30, 128.95, 128.60, 125.19, 123.78, 121.32, 108.08; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for C$_{15}$H$_9$BrO$_2$ [C$_{15}$H$_{10}$BrO$_2$]$^+$: 300.9859, found 300.9861.

**(Z)-6-Bromo-3-(4-chlorobenzylidene)-isobenzofuran-1(3$H$)-one (12b).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as off-white solid having mp 194–196 °C in 61% yield. IR (Neat, cm$^{-1}$): 1779, 1684, 1491, 1463, 1249, 622, 520; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.06–8.05 (m, 1H), 7.84–7.81 (m, 1H), 7.77–7.74 (m, 2H), 7.64–7.61 (m, 1H), 7.38–7.35 (m, 2H), 6.36 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.37, 144.23, 139.06, 137.83, 134.68, 131.42, 131.36, 129.18, 128.70, 125.18, 124.05, 121.34, 106.71; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{15}$H$_9$BrClO$_2$]$^+$: 334.9469, found 334.9470.

**(Z)-6-Bromo-3-(4-bromobenzylidene)isobenzofuran-1(3$H$)-one (12c).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as slight greenish white solid having mp 210–212 °C in 62% yield. IR (Neat, cm$^{-1}$): 1767, 1667, 1581, 1459, 1408, 1246, 1065, 972, 823, 518; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.07–8.06 (m, 1H), 7.85–7.82 (m, 1H), 7.70–7.68 (m, 2H), 7.63 (d, $J$ = 8.28 Hz, 1H), 7.53 (d, $J$ = 8.6 Hz, 2H), 6.35 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.35, 144.46, 139.06, 137.85, 132.15, 131.78, 131.64, 128.73, 125.21, 124.09, 123.04, 121.35, 106.77; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{15}$H$_9$Br$_2$O$_2$]$^+$: 378.8964, found 378.8962.

**(Z)-6-Bromo-3-(4-methylbenzylidene)-isobenzofuran-1(3$H$)-one (12d).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as slight greenish white solid having mp 162–164 °C in 46% yield. IR (Neat, cm$^{-1}$): 2917, 2830, 1764, 1668, 1606, 1509, 1459, 1286, 525; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05–8.04 (m, 1H), 7.80 (dd, $J$ = 8.24, 1.72 Hz, 1H), 7.72 (d, $J$ = 8.12 Hz, 2H), 7.62 (d, $J$ = 8.36 Hz, 1H), 7.21 (d, $J$ = 8.04 Hz, 2H), 6.40 (s, 1H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.75, 143.28, 139.43, 139.19, 137.62, 130.29, 130.05, 129.72, 128.55, 125.08, 123.47, 121.19, 108.23, 21.57; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{16}$H$_{12}$BrO$_2$]$^+$: 315.0015, found 315.0013.

**(Z)-3-Benzylidene-6-methylisobenzofuran-1(3$H$)-one (13a).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as off-white solid having mp 140–144 °C in 63% yield. IR (Neat, cm$^{-1}$): 2920, 2852, 1776, 1600, 1492, 1447, 1272; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, $J$ = 7.32 Hz, 2H), 7.70 (s, 1H), 7.64 (d, $J$ = 8.0 Hz, 1H), 7.52 (d, $J$ = 8 Hz, 1H), 7.41–7.37 (m, 2H), 7.30–7.27 (m, 1H), 6.37 (s, 1H), 2.47 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.32, 144.82, 140.56, 138.33, 135.90, 133.35, 130.09, 128.83, 128.29, 125.32, 123.75, 119.71, 106.33, 21.65; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{16}$H$_{13}$O$_2$]$^+$: 237.0910, found 237.0911.

**(Z)-3-(4-Chlorobenzylidene)-6-methylisobenzofuran-1(3$H$)-one (13b).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as white solid having mp 182–184 °C in 60% yield. IR (Neat, cm$^{-1}$): 2922, 2840, 1756, 1666, 1490, 1250, 675; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.74–7.69 (m, 3H), 7.63 (d, $J$ = 7.92 Hz, 1H), 7.52 (d, $J$ = 8.0 Hz, 1H), 7.35–7.32 (m, 2H), 6.27 (s, 1H), 2.48 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.04, 145.15, 140.84, 138.08, 135.97, 134.02, 131.88, 131.19, 128.99, 125.62, 123.75, 119.72, 104.98, 21.63; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{16}$H$_{12}$ClO$_2$]$^+$: 271.0521, found 271.0520.

**(Z)-3-(4-Methoxybenzylidene)-6-methylisobenzofuran-1(3$H$)-one (13c).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as slight greenish white solid having mp 152–154 °C in 67% yield. IR (Neat, cm$^{-1}$): 2927, 2840, 1761, 1663, 1603, 1509, 1255; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.78 (d, $J$ = 8.8 Hz, 2H), 7.69 (s, 1H), 7.62 (d, $J$ = 8.0 Hz, 1H), 7.50 (d, $J$ = 8.0 Hz, 1H), 6.93 (d, $J$ = 8.88 Hz, 2H), 6.30 (s, 1H), 3.83 (s, 3H), 2.47 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.53, 159.68, 143.34, 140.00, 138.52, 131.62, 126.75, 126.14, 125.54, 123.46, 119.41, 118.33, 106.20, 55.42, 21.60; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{17}$H$_{14}$O$_3$]$^+$: 267.1016, found 267.1015.

**(Z)-6-Methyl-3-(4-methylbenzylidene)-isobenzofuran-1(3$H$)-one (13d).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as white solid having mp 170–172 °C in 60% yield. IR (Neat, cm$^{-1}$): 2921, 1762, 1663, 1487, 1270; $^1$H NMR (400 MHz, CDCl) δ 7.72–7.69 (m, 3H), 7.62 (d, $J$ = 8.0 Hz, 1H), 7.51 (d, $J$ = 8.0 Hz, 1H), 7.20 (d, $J$ = 8.08 Hz, 2H), 6.31 (s, 1H), 2.47 (s, 3H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.46, 144.49, 140.27, 138.49, 138.45, 135.82, 130.54, 130.06, 129.63, 125.47, 123.64, 119.54, 106.47, 21.61, 21.49; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{17}$H$_{15}$O$_2$]$^+$ 251.1067, found 251.1068.

**(Z)-3-Benzylidene-6-fluoroisobenzofuran-1(3$H$)-one (14a).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as white solid having mp 172–174 °C in 61% yield. IR (Neat, cm$^{-1}$): 1763, 1668, 1610, 1478, 1256, 1063, 982, 919, 681, 529; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, $J$ = 7.44 Hz, 2H), 7.77–7.74 (m, 1H), 7.58 (dd, $J$ = 7.04, 2.28 Hz, 1H), 7.47–7.39 (m, 3H), 7.32 (t, $J$ = 7.32 Hz, 1H), 6.38 (s, 1H); $^{13}$C NMR (100 MHz, CDCl) δ 165.98, 164.78, ($J_{C-F}$ = 251 Hz), 143.89, 136.71, 132.94, 130.16, 128.92, 128.68, 125.36, ($J_{C-F}$ = 9 Hz), 123.00, ($J_{C-F}$ = 25 Hz), 121.85, ($J_{C-F}$ = 9 Hz), 111.87, ($J_{C-F}$ = 24 Hz), 107.29; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{15}$H$_{10}$FO$_2$]$^+$: 241.0659, found 241.0662.

**(Z)-3-(4-Chlorobenzylidene)-6-fluoroisobenzofuran-1(3H)-one (14b).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as yellow solid having mp 166–168 °C in 44% yield. IR (Neat, cm$^{-1}$): 1764, 1665, 1597, 1481, 1261, 1071, 984, 922, 824, 681, 530; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76–7.72 (m, 3H), 7.58 (dd, $J$ = 7 Hz, 2.28 Hz, 1H), 7.47–7.42 (m, 1H), 7.38–7.36 (m, 2H), 6.32 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.68, 163.63, ($J_{C-F}$ = 251 Hz), 144.21, 136.46 ($J_{C-F}$ = 1 Hz), 134.48, 131.46, 131.28, 129.14, 125.37, ($J_{C-F}$ = 9 Hz), 123.12, ($J_{C-F}$ = 24 Hz), 121.91, ($J_{C-F}$ = 9 Hz), 112.00, ($J_{C-F}$ = 24 Hz), 105.96; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{15}$H$_9$ClFO$_2$]$^+$: 275.0270, found 275.0270.

**(Z)-3-Benzylidene-6-methoxyisobenzofuran-1(3H)-one (15a).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as white solid having mp 146–150 °C in 72% yield. IR (Neat, cm$^{-1}$): 2935, 2841, 1759, 1658, 1605, 1448, 1486, 1283, 1071, 975, 781, 687, 544; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82–7.79 (m, 2H), 7.66 (d, $J$ = 8.48 Hz, 1H), 7.41–7.37 (m, 2H), 7.33 (d, $J$ = 2.28 Hz, 1H), 7.30–7.26 (m, 2H), 6.28 (s, 1H), 3.89 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.25, 161.45, 144.68, 133.72, 133.44, 129.95, 128.83, 128.16, 125.06, 124.12, 121.18, 106.86, 105.73, 55.99; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{16}$H$_{13}$O$_3$]$^+$: 253.0859, found 253.0861.

**(Z)-6-Methoxy-3-(4-methylbenzylidene)isobenzofuran-1(3H)-one (15b).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as greenish white solid having mp 178–180 °C in 50% yield. IR (Neat, cm$^{-1}$): 2922, 2837, 1755, 1615, 1487, 1229, 1019, 978, 815, 539, 495; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J$ = 8.16 Hz, 2H), 7.63 (d, $J$ = 8.6 Hz, 1H), 7.32 (d, $J$ = 2.24 Hz, 1H), 7.28–7.25 (m, 1H), 7.20 (d, $J$ = 8.04 Hz, 2H), 6.26 (s, 1H), 3.89 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 167.36, 161.27, 144.05, 138.33, 133.87, 130.62, 129.91, 129.58, 124.91, 124.10, 121.04, 106.76, 105.85, 55.88, 21.49; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{17}$H$_{15}$O$_3$]$^+$: 267.1016, found 267.1018.

**(Z)-3-(3-Methoxybenzylidene)isobenzofuran-1(3H)-one (16a).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution off-white solid having mp 118–120 °C in 71% yield. IR (Neat, cm$^{-1}$): 2923, 2861, 1765, 1665, 1600, 1570, 1472, 1453, 1434, 1276, 1047, 970, 756, 685, 634, 476; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J$ = 8.44 Hz, 1H), 7.77–7.69 (m, 2H), 7.55–7.52 (m, 1H), 7.41–7.40 (m, 2H), 7.33–7.29 (m, 1H), 6.88–6.86 (m, 1H), 6.38 (s, 1H), 3.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.04, 159.86, 144.82, 140.66, 134.57, 134.42, 129.92, 129.79, 125.70, 123.53, 122.91, 119.92, 115.09, 114.58, 107.58, 55.43; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{16}$H$_{13}$O$_3$]$^+$: 253.0859, found 253.0862.

**(Z)-3-(3-Methoxybenzylidene)-6-methylisobenzofuran-1(3H)-one (16b).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as white solid having mp 128–130 °C in 80% yield. IR (Neat, cm$^{-1}$): 3073, 3001, 2913, 2830, 1758, 1661, 1567, 1465, 1277, 969, 890, 779, 690, 494; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.70 (s, 1H), 7.64 (d, $J$ = 8.0 Hz, 1H), 7.52 (d, $J$ = 8.36 Hz, 1H), 7.40–7.39 (m, 2H), 7.32–7.28 (m, 1H), 6.87–6.84 (m, 1H), 6.31 (s, 1H), 3.85 (s, 3H), 2.48 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.18, 159.84,

144.98, 140.61, 138.29, 135.88, 134.61, 129.74, 125.54, 123.80, 122.79, 119.72, 114.94, 114.37, 106.21, 55.42, 21.64; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{17}$H$_{15}$O$_3$]$^+$: 267.1016, found 267.1017.

## General procedure (GP) for the synthesis of isocoumarins 17–20

To a stirred mixture of substituted halo aromatic carboxylic acid **9a–c** (1.209 mmol, 1.0 eq.), terminal alkynes **10g–j** (1.209 mmol, 1.0 eq.), Ag$_2$ONPs (1.209 mmol, 1.0 eq.), and PivOH (0.484 mmol, 0.4eq.) in dry DMF (2 mL) at 120 °C for 3 h. The reaction mixture was then cooled to ambient temperature; diluted with ethyl acetate (10 mL), filtered through a celite pad and washed further with ethyl acetate (15 mL). The combined organic solvents were extracted with ethyl acetate (3 × 10 mL), washed with distilled water (2 × 20 mL) and then with brine solution (20 mL). The combined organic layer was dried over anhyd. Na$_2$SO$_4$ & concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (100–200 mesh size) using 2% ethyl acetate: hexane as eluant to furnish **17–20**.

**3-(2-Chlorophenyl)-1H-isochromen-1-one (17a).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as off-white solid having mp 176–178 °C in 42% yield. IR (Neat, cm$^{-1}$): 1769, 1654, 1601, 1465, 1267, 1074, 949, 746, 681, 523; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.32–8.30 (m, 1H), 7.95 (d, $J$ = 7.72 Hz, 1H), 7.86 (d, $J$ = 7.88 Hz, 1H), 7.78–7.74 (m, 1H), 7.60–7.56 (m, 1H), 7.43 (dd, $J$ = 8.04 Hz, 1.16 Hz, 1H), 7.36–7.32 (m, 1H), 7.24–7.22 (m, 1H), 6.91 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.99, 145.90, 140.57, 134.77, 133.90, 131.85, 131.03, 130.35, 129.71, 129.41, 127.32, 125.73, 123.59, 120.41, 102.39; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{15}$H$_{10}$ClO$_2$]$^+$: 257.0364, found 257.0365.

**3-(2-Bromophenyl)-1H-isochromen-1-one (17b).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as off-white solid having mp 160–162 °C in 85% yield. IR (Neat, cm$^{-1}$): 1768, 1652, 1601, 1463, 1357, 1266, 1075, 945, 746, 678, 522; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.29 (d, $J$ = 7.92 Hz, 1H), 7.95 (d, $J$ = 7.72 Hz, 1H), 7.87 (d, $J$ = 7.8 Hz, 1H), 7.77–7.73 (m, 1H), 7.63–7.56 (m, 2H), 7.39–7.36 (m, 1H), 7.17–7.13 (m, 1H), 6.87 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.96, 145.76, 140.52, 134.78, 133.05, 132.65, 131.98, 130.37, 129.62, 127.92, 125.72, 124.71, 123.56, 120.41, 105.15; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{15}$H$_{10}$BrO$_2$]$^+$: 300.9859, found 300.9861.

**3-(2-Methoxyphenyl)-1H-isochromen-1-one (17c).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as yellowish green solid having mp 158–160 °C in 60% yield. IR (Neat, cm$^{-1}$): 2922, 2851, 1761, 1596, 1462, 1241, 1076, 966, 740, 684; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.28–8.25 (m, 1H), 7.92 (d, $J$ = 7.72 Hz, 1H), 7.83 (d, $J$ = 7.8 Hz, 1H), 7.72–7.68 (m, 1H), 7.54–7.50 (m, 1H), 7.31–7.27 (m, 1H), 7.05–7.01 (m, 1H), 6.96 (s, 1H), 6.91 (d, $J$ = 8.28 Hz, 1H), 3.90 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.45, 151.11, 144.56, 141.08, 134.44, 131.43, 129.85, 129.57, 125.53, 123.26, 122.04, 121.18, 120.14, 110.53, 100.91, 55.70; HRMS (ESI/QTOF)

$m/z$ [M + H]$^+$ calculated for [C$_{16}$H$_{13}$O$_3$]$^+$: 253.0859, found 253.0861.

**3-(2-Chlorophenyl)-7-methyl-1H-isochromen-1-one (18a).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as off-white solid having mp 186–188 °C in 66% yield. IR (Neat, cm$^{-1}$): 2920, 1776, 1654, 1482, 1437, 1280, 1105, 964, 756, 538, 486; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.31–8.28 (m, 1H), 7.74 (d, $J$ = 7.84 Hz, 2H), 7.56–7.54 (m, 1H), 7.41 (dd, $J$ = 7.96 Hz, 1.24 Hz, 1H), 7.34–7.30 (m, 1H), 7.24–7.19 (m, 1H), 6.82 (s, 1H), 2.50 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.12, 146.07, 141.11, 138.20, 136.05, 133.75, 131.76, 131.20, 129.67, 129.18, 127.27, 125.58, 123.86, 120.19, 101.55, 21.71; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{16}$H$_{12}$ClO$_2$]$^+$: 271.0521, found 271.0523.

**3-(2-Bromophenyl)-7-methyl-1H-isochromen-1-one (18b).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as white solid having mp 182–184 °C in 67% yield. IR (Neat, cm$^{-1}$): 2916, 2857, 1776, 1654, 1486, 1433, 1281, 1103, 964, 755, 534, 483; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.27 (dd, $J$ = 7.96 Hz, 1.56 Hz, 1H), 7.74 (d, $J$ = 8.28 Hz, 2H), 7.61–7.59 (m, 1H), 7.56–7.54 (m, 1H), 7.38–7.34 (m, 1H), 7.15–7.11 (m, 1H), 6.79 (s, 1H), 2.49 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.08, 146.02, 141.13, 138.15, 136.04, 133.06, 132.87, 131.90, 129.39, 127.88, 125.58, 124.58, 123.85, 120.19, 104.31, 21.70; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{16}$H$_{12}$BrO$_2$]$^+$: 315.0015, found 315.0018.

**3-(2-Methoxyphenyl)-7-methyl-1H-isochromen-1-one (18c).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as yellowish green solid having mp 156–158 °C in 80% yield. IR (Neat, cm$^{-1}$): 2920, 2847, 1755, 1588, 1471, 1237, 969, 808, 740, 501; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.25 (dd, $J$ = 7.8 Hz, 1.2 Hz, 1H), 7.71 (d, $J$ = 7.6 Hz, 2H), 7.51 (d, $J$ = 8.24 Hz, 1H), 7.29–7.27 (m, 1H), 7.15 (t, $J$ = 7.56 Hz, 1H), 6.90–6.88 (m, 2H), 3.89 (s, 3H), 2.48 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.57, 157.00, 144.73, 140.20, 138.73, 135.77, 131.34, 129.59, 125.36, 123.67, 122.21, 121.16, 119.93, 110.50, 100.02, 55.69, 21.64; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{17}$H$_{15}$O$_3$]$^+$: 267.1016, found 267.1018.

**7-Bromo-3-(2-chlorophenyl)-1H-isochromen-1-one (19a).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as slight yellowish white solid having mp 174–178 °C in 60% yield. IR (Neat, cm$^{-1}$): 1748, 1444, 1364, 1213, 1038, 969, 827, 738, 531; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.29–8.27 (m, 1H), 8.07–8.06 (m, 1H), 7.87–7.83 (m, 1H), 7.74–7.71 (m, 1H), 7.44–7.41 (m, 1H), 7.36–7.31 (m, 1H), 7.27–7.23 (m, 1H), 6.91 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.40, 139.17, 137.88, 134.03, 131.83, 130.72, 129.79, 129.71, 128.64, 127.38, 125.29, 124.32, 121.79, 103.23; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{15}$H$_9$BrClO$_2$]$^+$: 334.9469, found 334.9470.

**7-Bromo-3-(2-methoxyphenyl)-1H-isochromen-1-one (19b).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as green solid having mp 138–140 °C in 65% yield. IR (Neat, cm$^{-1}$): 2920, 2857, 1767, 1588, 1458, 1241, 969, 744, 639, 500; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.24 (dd, $J$ = 7.8 Hz, 1.2 Hz, 1H), 8.04 (m, 1H), 7.81–7.79 (m, 1H), 7.70 (d, $J$ = 8.32 Hz, 1H), 7.32–7.28 (m, 1H), 7.05–7.01 (m, 1H), 6.96 (s, 1H), 6.91 (d, $J$ = 8.28 Hz, 1H), 3.90 (s, 3H); $^{13}$C NMR (100

MHz, CDCl$_3$) δ 165.89, 157.19, 143.78, 139.71, 137.55, 131.04, 130.22, 128.44, 125.01, 123.40, 121.73, 121.56, 121.24, 110.58, 101.85, 55.70; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{16}$H$_{12}$BrO$_3$]$^+$: 330.9965, found 330.9966.

**3-(o-Tolyl)-1H-isochromen-1-one (20a).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as white solid having mp 120–122 °C in 75% yield. IR (Neat, cm$^{-1}$): 3059, 2922, 2851, 1758, 1664, 1608, 1461, 1346, 1269, 1073, 959, 855, 748, 687; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.16 (d, $J$ = 7.68 Hz, 1H), 7.95 (d, $J$ = 7.72 Hz, 1H), 7.82 (d, $J$ = 7.88 Hz, 1H), 7.75–7.71 (m, 1H), 7.57–7.53 (m, 1H), 7.30–7.25 (m, 1H), 7.22–7.20 (m, 2H), 6.63 (s, 1H), 2.47 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.31, 144.82, 140.74, 136.75, 134.54, 131.57, 130.68, 130.41, 129.91, 128.52, 126.59, 125.67, 123.61, 119.96, 104.10, 20.37; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{16}$H$_{13}$O$_2$]$^+$: 237.0910, found 237.0914.

## General procedure for the reaction of 9a with 10k

To a stirred mixture of substituted 2-iodobenzoic acid **9a** (1.209 mmol, 1.0 eq.), 1-pentyne **10k** (1.209 mmol, 1.0 eq.), Ag$_2$ONPs (1.209 mmol, 1.0 eq.), and PivOH (0.484 mmol, 0.4eq.) in dry DMF (2 mL) at 120 °C for 3 h. The reaction mixture was then cooled to ambient temperature; diluted with ethyl acetate (20 mL), filtered through a celite pad and washed further with ethyl acetate (25 mL). The combined organic solvents were extracted with ethyl acetate (3 × 20 mL), washed with distilled water (2 × 20 mL) and then with brine solution (20 mL). The combined organic layer was dried over anhyd. Na$_2$SO$_4$ & concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (100–200 mesh size) using 2% ethyl acetate: hexane as eluant which furnished an inseparable mixture of 5-exo-dig and 6-endo-dig cyclized product in 72% yields.

## General procedures for the synthesis of alicyclic 3-ylidenephthalides 21a–c

To a stirred mixture of substituted halo-aromatic carboxylic acid **9a–c** (1.209 mmol, 1.0 eq.), alicyclic terminal alkyne **10l** (1.209 mmol, 1.0 eq.), Ag$_2$ONPs (1.209 mmol, 1.0 eq.), and PivOH (0.484 mmol, 0.4 eq.) in dry DMF (2 mL) at 120 °C for 3 h. The reaction mixture was then cooled to ambient temperature; diluted with ethyl acetate (10 mL), filtered through a celite pad and washed further with ethyl acetate (15 mL). The combined organic solvents were extracted with ethyl acetate (3 × 10 mL), washed with distilled water (2 × 20 mL) and then with brine solution (20 mL). The combined organic layer was dried over anhyd. Na$_2$SO$_4$ & concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (100–200 mesh size) using 2% ethyl acetate: hexane as eluant to furnish **21a–c** in 61–69% yield range.

**(Z)-3-(Cyclopropylmethylene)isobenzofuran-1(3H)-one (21a).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as white solid having mp 88–90 °C in 69% yield. IR (Neat, cm$^{-1}$): 2925, 2857, 1750, 1689, 1460, 1240, 510; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88–7.86 (m, 1H), 7.65–7.61 (m, 1H), 7.55–7.53 (m, 1H), 7.47–7.43 (m, 1H), 5.08 (d, $J$ =

10.28 Hz, 1H), 2.12–2.03 (m, 1H), 1.02–0.97 (m, 2H), 0.65–0.62 (m, 2H); $^{13}$C NMR (100 MHz, CDCl3) $\delta$ = 167.40, 145.23, 139.43, 134.25, 129.02, 125.36, 123.83, 119.24, 114.57, 9.47, 8.48; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [$C_{12}H_{11}O_2$]$^+$: 187.0754, found 187.0757.

**(Z)-6-Bromo-3-(cyclopropylmethylene)-isobenzofuran-1(3H)-one (21b).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as white solid having mp 84–86 °C in 65% yield. IR (Neat, cm$^{-1}$): 2922, 2853, 1759, 1684, 1459, 1242, 508; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99–7.98 (m, 1H), 7.73 (dd, $J$ = 8.32, 1.72 Hz, 1H), 7.42 (d, $J$ = 8.32 Hz, 1H), 5.10 (d, $J$ = 10.24 Hz, 1H), 2.10–2.02 (m, 1H), 1.04–0.99 (m, 2H), 0.67–0.63 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.83, 144.55, 138.01, 137.38, 128.26, 125.54, 122.76, 120.73, 115.82, 9.69, 8.67; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [$C_{12}H_{10}BrO_2$]$^+$: 264.9859, found 264.9863.

**(Z)-3-(Cyclopropylmethylene)-6-methylisobenzofuran-1(3H)-one (21c).** This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as liquid having in 61% yield. IR (Neat, cm$^{-1}$): 3057, 2920, 2851, 1748, 1680, 1450, 1239, 502; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 (s, 1H), 7.45–7.41 (m, 2H), 5.01 (d, $J$ = 10.2 Hz, 1H), 2.44 (s, 3H) 2.11–2.02 (m, 1H), 1.00–0.95 (m, 2H), 0.63–0.59 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.54, 145.26, 137.32, 136.16, 129.26, 125.23, 124.62, 119.03, 113.50, 21.56, 9.37, 8.23; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [$C_{13}H_{13}O_2$]$^+$: 201.0910, found 201.0911.

### Control experiments

**General synthetic procedure for the intermolecular competition reaction between o- and m-substituted terminal alkynes.** To a stirred mixture of 2-iodobenzoic acid **9a** (2.418 mmol, 2.0 eq.), 2-ethynylanisole **10i** (1.209 mmol, 1.0 eq.), 3-ethynylanisole **10f** (1.209 mmol, 1.0 eq.), Ag$_2$ONPs (2.418 mmol, 2.0 eq.) and PivOH (0.968 mmol, 0.8 eq.), in dry DMF (4 mL) at 120 °C for 3 h. The reaction mixture was then cooled to ambient temperature; diluted with ethyl acetate (10 mL), filtered through a celite pad and washed further with ethyl acetate (15 mL). The combined organic solvents were extracted with ethyl acetate (3 × 20 mL), washed with distilled water (2 × 20 mL) and then with brine solution (20 mL). The combined organic layer was dried over anhyd. Na$_2$SO$_4$ & concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (100–200 mesh size) using 2% ethyl acetate: hexane as eluant furnished **17c** and **16** in 64% and 56% yield, respectively (**17c/16a** ratio = 1.1 : 1).

**General synthetic procedure for the intermolecular competition reaction between p- and m-substituted terminal alkynes.** To a stirred mixture of 2-iodobenzoic acid **9a** (2.418 mmol, 2.0 eq.), 4-ethynylanisole **10d** (1.209 mmol, 1.0 eq.), 3-ethynylanisole **10f** (1.209 mmol, 1.0 eq.), Ag$_2$ONPs (2.418 mmol, 2.0 eq.) and PivOH (0.968 mmol, 0.8 eq.), in dry DMF (4 mL) at 120 °C for 3 h. The reaction mixture was then cooled to ambient temperature; diluted with ethyl acetate (10 mL), filtered through a celite pad and washed further with ethyl acetate (15 mL). The combined organic solvents were extracted with ethyl acetate (3 × 30 mL), washed with distilled water (2 × 20 mL) and then

with brine solution (20 mL). The combined organic layer was dried over anhyd. Na$_2$SO$_4$ & concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (100–200 mesh size) using 2% ethyl acetate:hexane as eluant to get **11d** and **16a** in 55% and 50% yield respectively (**11d/16a** ratio = 1.2 : 1).

### Free-radical scavenger experiments

*TEMPO-mediated reaction in the case of 3-ylidenephthalides.* To a stirred mixture of 2-iodo benzoic acid **9a** (1.209 mmol, 1.0 eq.), phenylacetylene **5** (1.209 mmol, 1.0 eq.), Ag$_2$ONPs (1.209 mmol, 1.0 eq.), PivOH (0.484 mmol, 0.4 eq.) and TEMPO (0.242 mmol, 0.2 eq.) in dry DMF (2 mL) at 120 °C for 3 h. The reaction mixture was then cooled to ambient temperature; diluted with ethyl acetate (20 mL), filtered through a celite pad and washed further with ethyl acetate (20 mL). The combined organic solvents were extracted with ethyl acetate (3 × 10 mL), washed with distilled water (2 × 20 mL) and then with brine solution (20 mL). The combined organic layer was dried over anhyd. Na$_2$SO$_4$ & concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (100–200 mesh size) using 2% ethyl acetate: hexane as eluant which furnished **11a** in 93% yield. This illustrates that the mechanism of the reaction do not occur *via* free-radical pathway.

*TEMPO-mediated reaction in the case of isocoumarins.* To a stirred mixture of 2-iodo benzoic acid **9a** (1.209 mmol, 1.0 eq.), 2-bromo phenylacetylene **10h** (1.209 mmol, 1.0 eq.), Ag$_2$ONPs (1.209 mmol, 1.0 eq.), PivOH (0.484 mmol, 0.4 eq.) and TEMPO (0.242 mmol, 0.2 eq.) in dry DMF (2 mL) at 120 °C for 3 h. The reaction mixture was then cooled to ambient temperature; diluted with ethyl acetate (15 mL), filtered through a celite pad and washed further with ethyl acetate (20 mL). The combined organic solvents were extracted with ethyl acetate (3 × 10 mL), washed with distilled water (2 × 20 mL) and then with brine solution (20 mL). The combined organic layer was dried over anhyd. Na$_2$SO$_4$ & concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (100–200 mesh size) using 2% ethyl acetate: hexane as eluant which furnished **17b** in 82% yield. This also illustrates that the mechanism of the reaction do not occur *via* free-radical pathway.

**Gram scale synthesis of 3-ylidenephthalide 11a.** To a stirred mixture of 2-iodobenzoic acid **9a** (2.5 g, 10.0 mmol), phenylacetylene **5** (1.10 mL, 10.0 mmol), Ag$_2$ONPs (2.3 g, 10.0 mmol), and PivOH (0.46 mL, 4.0 mmol.) in dry DMF (16 mL) at 120 °C for 3 h. The reaction mixture was then cooled to ambient temperature; diluted with ethyl acetate (40 mL), filtered through a celite pad and washed further with ethyl acetate (35 mL). The combined organic solvents were extracted with ethyl acetate (3 × 30 mL), washed with distilled water (2 × 30 mL) and then with brine solution (30 mL). The combined organic layer was dried over anhyd. Na$_2$SO$_4$ & concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (100–200 mesh size) using 2% ethyl acetate: hexane as eluant which furnished **11a** as a white solid (2.0 gm, 89% yield).

**Gram scale synthesis of isocoumarin 17b.** To a stirred mixture of 2-iodobenzoic acid **9a** (2.5 gm, 10.0 mmol), 2-bromophenylacetylene **10h** (1.26 mL, 10.0 mmol), Ag$_2$ONPs (2.3 gm, 10.0 mmol), and PivOH (0.46 mL, 4.0 mmol) in dry DMF (16

mL) at 120 °C for 3 h. The reaction mixture was then cooled to ambient temperature; diluted with ethyl acetate (40 mL), filtered through a celite pad and washed further with ethyl acetate (40 mL). The combined organic solvents were extracted with ethyl acetate (3 × 35 mL), washed with distilled water (2 × 30 mL) and then with brine solution (30 mL). The combined organic layer was dried over anhyd. $Na_2SO_4$ & concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (100–200 mesh size) using 2% ethyl acetate: hexane as eluant which furnished **17b** as a white solid (2.48 gm, 82% yield).

**To study the mechanistic role of groups with or without having lone pair of electrons at *ortho*-substituted phenyl-acetylenes: synthesis of 20a (major) and 20b (minor).** To a stirred mixture of 2-iodobenzoic acid **9a** (1.209 mmol, 1.0 eq.), 1-ethynyl-2-methylbenzene **10l** (1.209 mmol, 1.0 eq.), $Ag_2ONPs$ (1.209 mmol, 1.0 eq.) and PivOH (0.484 mmol, 0.4 eq.) in dry DMF (2 mL) at 120 °C for 3 h. The reaction mixture was then cooled to ambient temperature; diluted with ethyl acetate (20 mL), filtered through a celite pad and washed further with ethyl acetate (25 mL). The combined organic solvents were extracted with ethyl acetate (3 × 25 mL), washed with distilled water (2 × 30 mL) and then with brine solution (20 mL). The combined organic layer was dried over anhyd. $Na_2SO_4$ & concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (100–200 mesh size) using 2% ethyl acetate: hexane as eluant which furnished **20a** (major) and **20b** (minor) in 75% and 25% yields, respectively.

*3-(o-Tolyl)-1H-isochromen-1-one (20a).* See spectral data of **20a**.

*(Z)-3-(2-Methylbenzylidene)isobenzofuran-1(3H)-one (20b).* This compound was prepared according to the GP and obtained in 2% EtOAc/hexane solution as light yellow liquid in 25% yield. IR (Neat, cm$^{-1}$): 3067, 2923, 2863, 1727, 1639, 1481, 1331, 1228, 1050, 757, 687; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.33 (d, $J$ = 7.96 Hz, 1H), 7.74–7.70 (m, 1H), 7.53–7.46 (m, 3H), 7.36–7.32 (m, 1H), 7.28 (d, $J$ = 7.4 Hz, 2H), 6.60 (s, 1H), 2.50 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.69, 155.67, 137.58, 136.87, 134.92, 132.85, 131.14, 129.80, 129.28, 128.33, 125.99, 120.42, 106.01, 20.87; HRMS (ESI/QTOF) $m/z$ [M + H]$^+$ calculated for [C$_{16}$H$_{12}$O$_2$]$^+$: 237.0910, found 237.0914.

## Conflicts of interest

All the authors declare no conflict of interest.

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## Notes and references

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17 (*a*) **9a** was reacted with silver phenylacetylide under optimized reaction conditions which furnished the desired **11a** in 35% yield.; (*b*) Following a suggestion from one of the reviewers, the reusability of the silver oxide nanoparticle was checked. It was observed that the reaction diminished tremendously by using recovered residue.

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19 PivOAg was also utilized to underline the tentative mechanism. **9a** was reacted with either **10a** or **10g** under optimized conditions (DMF as solvent at 120 °C for 3 h). The desired 3-ylidinephthalides **11a** and isocoumarins **17a** were obtained in 51% and 35% yield, respectively.