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# Palladium-Catalyzed C−C Bond Activation of Cyclopropenone: Modular Access to Trisubstituted α,β-Unsaturated Esters and Amides

Tanmayee Nanda, Pragati Biswal, Bedadyuti Vedvyas Pati, Shyam Kumar Banjare, and Ponneri Chandrababu Ravikumar*

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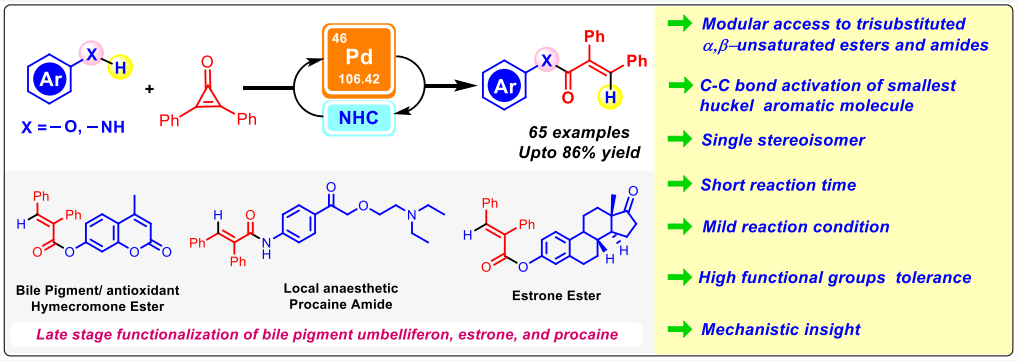


**ABSTRACT:** Strain-driven palladium/*N*-heterocyclic carbene-catalyzed C−C bond activation of diphenylcyclopropenone (DPC) has been explored for one-step access to trisubstituted α,β-unsaturated esters and amides. The designed transformation works under mild conditions providing exclusively a single stereoisomer. Mechanistic studies support the oxidative addition of the C−C bond of cyclopropenone to in-situ-generated Pd(0) intermediate. We have proved that vinylic hydrogen in the product is coming from phenol/aniline through deuterium-labeling studies. Late-stage functionalization of bioactive molecules such as procaine, estrone, and hymecromone demonstrates the robustness of this protocol.

## INTRODUCTION

Transition-metal-catalyzed carbon−carbon (C−C) bond activation has attracted both organometallic chemists and organic chemists due to its fundamental scientific importance and potential utility in organic synthesis.[1] Owing to the C−C bond's statistical abundance and inertness, selective activation of the C−C bond is quite challenging and remains underdeveloped.[2] Over the past few years, significant breakthroughs have been achieved by Murakami et al.,[3] Dong et al.,[4] and Bower et al.[5] among others,[6] and these reports mainly focused on C−C bond activation of the strained ring system due to thermodynamic advantage in breaking strained systems. Thus, the C−C bond activation arena driven by the ring strain of three- and four-membered carbocycles has undergone dramatic expansion over the years, resulting in a straightforward route to construct complex value-added scaffolds.[7] There are two primary modes of C−C bond activation pathways: (i) oxidative addition of C−C bonds to transition metals and (ii) β-carbon elimination. Recently, through the β-carbon elimination pathway, we have demonstrated C−C bond activation of cyclopropanol to achieve 1,6-diketone derivatives.[8] In this vein, the smallest Huckel aromatic system cyclopropenone is less investigated.[9] Although, Rh-, Pt-, and Ni-catalyzed ring opening of cyclopropenone was reported before,[9] limited scope and lack of mechanistic evidence offers a multitude of scopes to explore the C−C bond activation of cyclopropenone.

α,β-Unsaturated esters and amides are common structural motifs present in drugs and natural products. For instance, these molecule series show antifungal, 17β-HSDCl inhibitory, analgesic, antioxidant, anti-inflammatory, antitumor, antiviral, and MMP-2/9 inhibitory activity.[10,11] Thus, ester and amide bond formation reactions are considered as the most significant transformations in the pharmaceutical industry. However, only limited methods are known to synthesize these molecules like aldol condensation,[12] Wittig reaction,[13] Horner−Wadsworth−Emmons reactions,[14] and nucleophilic substitution of activated carboxylic acid derivatives.[15] Nevertheless, some starting

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materials are not easy to access, and sensitive functional groups are not tolerated. Moreover, to synthesize highly substituted conjugated esters and amides, strategies like hydroxy-carbonylation,[16] and amino-carbonylation[17] of alkynes have been employed. Furthermore, Rahaim and co-worker synthesized conjugated amides by coupling of alkynes with Weinreb amides,[18a] and Tsuji et al. reported the synthesis of conjugated esters by hydroesterification of carboxylic acid derivatives[18b] (Figure 1). While these new approaches have enabled the

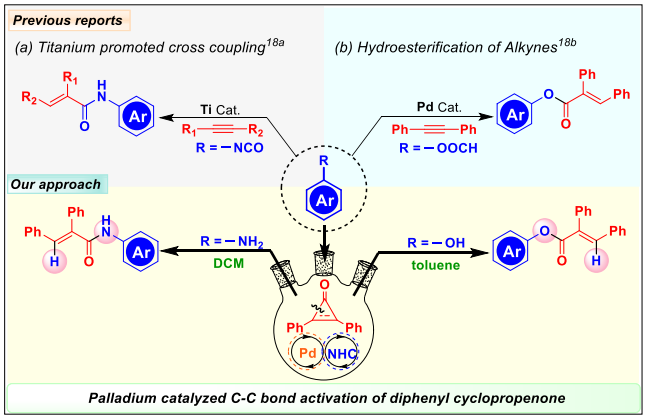



**Figure 1.** (a) Titanium-promoted conjugated amide synthesis. (b) Hydroesterification of alkynes. (c) C−C bond activation of diphenyl cyclopropenone leading to conjugated ester and amide.

synthesis of trisubstituted conjugated esters and amides, stereoselectivity challenges and tedious operational conditions necessitate the development of modified methods. Thus, it is an important objective to construct $\alpha,\beta$-unsaturated esters and amides directly and selectively.

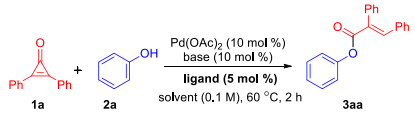
We recently illustrated the catalytic C−C bond activation of cyclopropenone in the presence of a palladium catalyst resulting in highly functionalized maleimide wherein cyclopropenone was shown to behave as carbon monoxide surrogate.[19] Thus, the above successful approach and our continuous interest encouraged us to explore an expeditious strategy to prepare conjugated esters and amides through Pd(0)-catalyzed C−C bond activation of diphenylcyclopropenone in the presence of commercially available phenol and aniline moieties. In this protocol, the NHC ligand plays a vital role in generating Pd(0) catalyst in the presence of a catalytic amount of base. Notable features of our strategy include (i) palladium-catalyzed C−C bond activation of cyclopropenone, (ii) high stereoselectivity, (iii) a wide range of functional group tolerance, (iv) short reaction times, and (v) late-stage functionalization of bioactive molecules and drugs like umbelliferon, estrone, and procaine. Herein, we disclosed palladium-catalyzed ligand-controlled C−C bond activation of cyclopropenone to give unsaturated esters and amides in a stereoselective manner.

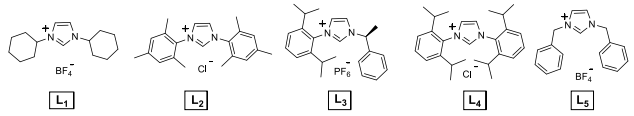
## RESULTS AND DISCUSSION

We began our investigation by examining various parameters for reaction of the diphenylcyclopropenone **1a** with phenol **2a** in the presence of $Pd(OAc)_2$ as a catalyst. First, we screened different *N*-heterocyclic carbene ligands using $Cs_2CO_3$ as a base in 1,4-dioxane solvent, as they are known to generate Pd(0) catalyst in situ.[20]

The screening started with less sterically hindered imidazolinium salts ICy·$HBF_4$ ($\mathbf{L_1}$) as ligand, and an 11% yield of the respective $\alpha,\beta$-unsaturated ester was observed (Table 1, entry 1). Further, to explore the steric effect of the ligand, other NHC

**Table 1. Optimization of Reaction Conditions**[a]



| entry | ligand | solvent | base | yield[b] |
|---|---|---|---|---|
| 1 | $\mathbf{L_1}$ | 1,4-dioxane | $Cs_2CO_3$ | 11%[c] |
| 2 | $\mathbf{L_2}$ | 1,4-dioxane | $Cs_2CO_3$ | 13%[c] |
| 3 | $\mathbf{L_3}$ | 1,4-dioxane | $Cs_2CO_3$ | 25%[c] |
| 4 | $\mathbf{L_4}$ | 1,4-dioxane | $Cs_2CO_3$ | 30%[c] |
| 5 | $\mathbf{L_5}$ | 1,4-dioxane | $Cs_2CO_3$ | 16%[c] |
| 6 | $\mathbf{L_4}$ | THF | $Cs_2CO_3$ | 23%[c] |
| 7 | $\mathbf{L_4}$ | benzene | $Cs_2CO_3$ | 25%[c] |
| 8 | $\mathbf{L_4}$ | cyclohexane | $Cs_2CO_3$ | 38%[c] |
| 9 | $\mathbf{L_4}$ | toluene | $Cs_2CO_3$ | 78% |
| 10 | $\mathbf{L_4}$ | toluene | $Li_2CO_3$ | 37%[c] |
| 11 | $\mathbf{L_4}$ | toluene | $Na_2CO_3$ | 77% |
| **12** | $\mathbf{L_4}$ | **toluene** | $\mathbf{K_2CO_3}$ | **83%** |
| 13 | $\mathbf{L_4}$ | toluene | $NaHCO_3$ | 38%[c] |
| 14 | $\mathbf{L_4}$ | toluene | LiOAc | 13%[c] |
| 15 | $\mathbf{L_4}$ | toluene | NaOAc | <10%[c] |
| 16 | $\mathbf{L_4}$ | toluene | KOAc | 6%[c] |
| 17 | | toluene | $K_2CO_3$ | nd |
| 18 | $\mathbf{L_4}$ | toluene | $K_2CO_3$, without catalyst | nd |

[a]Conditions: **1a** (1 equiv), **2a** (1 equiv), $Pd(OAc)_2$ (10 mol %), base (10 mol %), ligand (5 mol %), solvent (0.1 M), temperature (60 °C). [b]Isolated yields [c]GC yield (dodecane was taken as internal standard for GC).

ligands were screened. By increasing the sterics in the ligand, the yield enhanced to 30% (Table 1, entries 2−4), and decreasing the sterics further led to inferior results (Table 1, entry 5), which implies that IPr·HCl ($\mathbf{L_4}$) is providing the optimal stereoelectronics for the entitled transformation. Intrigued by this result, we screened different nonpolar solvents. Interestingly, after extensive screening of various solvents, it was found that performing the reaction in toluene led to an improved yield of $\alpha,\beta$-unsaturated ester (Table 1, entries 6−9). Aiming to further improve the yield, we performed the reaction with different bases. As $Cs_2CO_3$ has a positive impact on the reaction, various carbonates such as $Li_2CO_3$, $Na_2CO_3$, and $K_2CO_3$ (Table 1, entries 10−12) were screened. Among them, $K_2CO_3$ enhanced the desired product's yield to 83% (Table 1, entry 12). Furthermore, changing the base to bicarbonate and acetates did not show any fruitful results (Table 1, entries 13−16).

Besides, when the reaction was performed in the absence of ligand and catalyst, no product was obtained (Table 1, entries 17−18). This implies that the ligand and catalyst were working synergistically for the above transformation.

After establishing the condition, we initiated our studies to explore the scope of the reaction. As expected, a variety of substituted phenols could participate in the current C−C activation reaction regardless of the electronic nature of the substituents incorporated in the phenyl ring. A series of electron-


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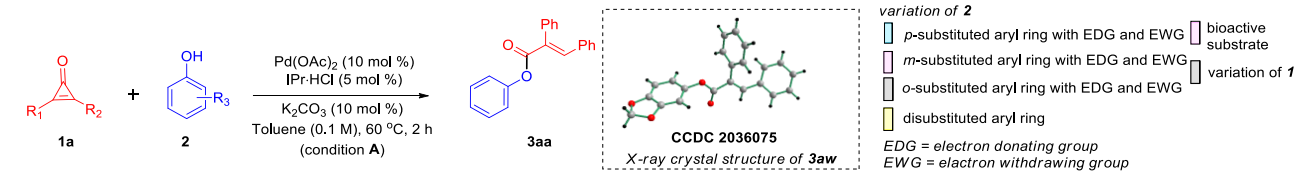
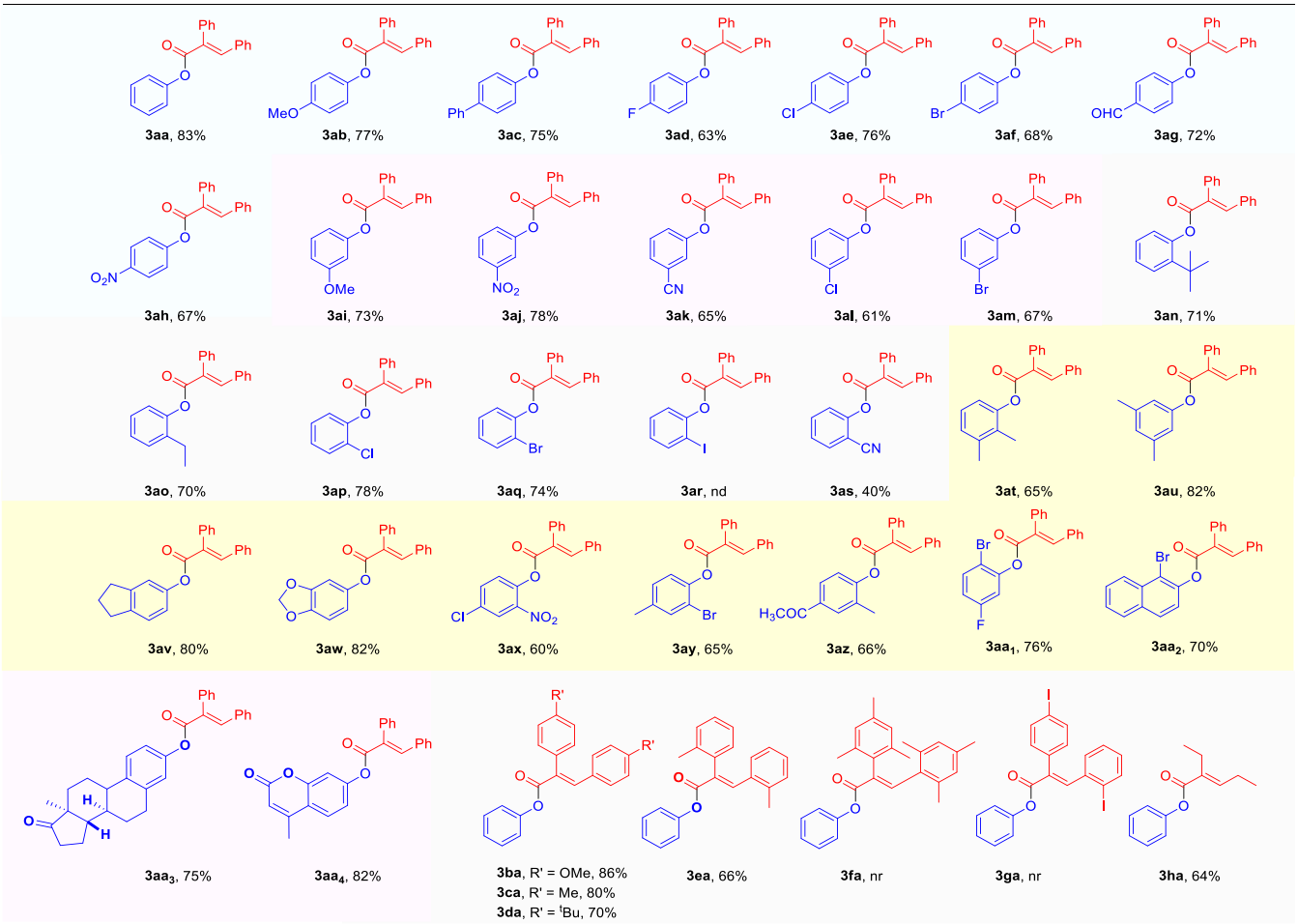
**Table 2. Scope of Phenols for the Synthesis of Acrylate Derivatives**[a]




[a]Conditions: **1a** (1 equiv), **2a** (1 equiv), $Pd(OAc)_2$ (10 mol %), $K_2CO_3$ (10 mol %), IPr·HCl (5 mol %), toluene (0.1 M), 60 °C, 2 h.

donating, aryl, and electron-withdrawing para-substituted phenols was subjected to the reaction, which gave 67−77% (Table 2, **3ab**−**3ah**) yield. Further, the meta-substituted phenol delivered the unsaturated ester in good yields (Table 2, **3ai**−**3am**). In this case, *m*-nitro-substituted phenol showed superior reactivity, giving a 78% yield of the respective product (Table 2, **3aj**). Switching the substituent position from meta to ortho did not change the reactivity much. The compatibility of ortho $^t$Bu and ethyl phenol suggests that the reaction is relatively robust toward steric hindrance (Table 2, **3an**−**3ao**). When *o*-Cl and *o*-Br phenol were subjected to the standard conditions, 78% and 74% yields (Table 2, **3ap** and **3aq**) of the corresponding esters were obtained, respectively. The tolerance of halo-substituted phenols under palladium-catalyzed reaction conditions provides an excellent opportunity to do various late-stage functionalizations with the products. However, *o*-iodophenol failed to give the desired unsaturated ester, leading to several uncharacterizable products (Table 2, **3ar**). Furthermore, *o*-CN phenol also provided the desired product **3as** in 40% yield. The variation concerning phenol was not limited to only monosubstituted derivatives. To check the viability of the developed methodology, we chose disubstituted phenol, giving rise to a highly substituted benzene system in the product moiety (Table 2, **3at**−**3aa$_1$**). In addition, 2-bromo naphthol shows good reactivity, giving a 70% yield of the desired product (Table 2, **3aa$_2$**). Construction of a biologically important skeleton around another bioactive molecule assumes significance. With this thought, estrone **2a$_3$**, 4-methylumbelliferone **2a$_4$** was chosen (commonly known as hymecromone, which is used as a drug in bile therapy), and the respective derivatized unsaturated ester were synthesized in good yields (Table 2, **3aa$_3$**−**3aa$_4$**). Further, the scope of the reaction was extended to different aryl- and alkyl-substituted cyclopropenones (Table 2, **3ba**−**3ha**). While various electron-rich aryl substituents in the cyclopropenone ring gave the desired product in very good yield (Table 2, **3ba**−**3da**), sterically hindered substrates showed retarded reactivity, resulting in a lower yield or even no reaction (Table 2, **3ea**−**3ga**). Furthermore, dialkyl-substituted cyclopropenone was also subjected to the standard condition, giving a 64% yield of the desired unsaturated ester **3ha**.



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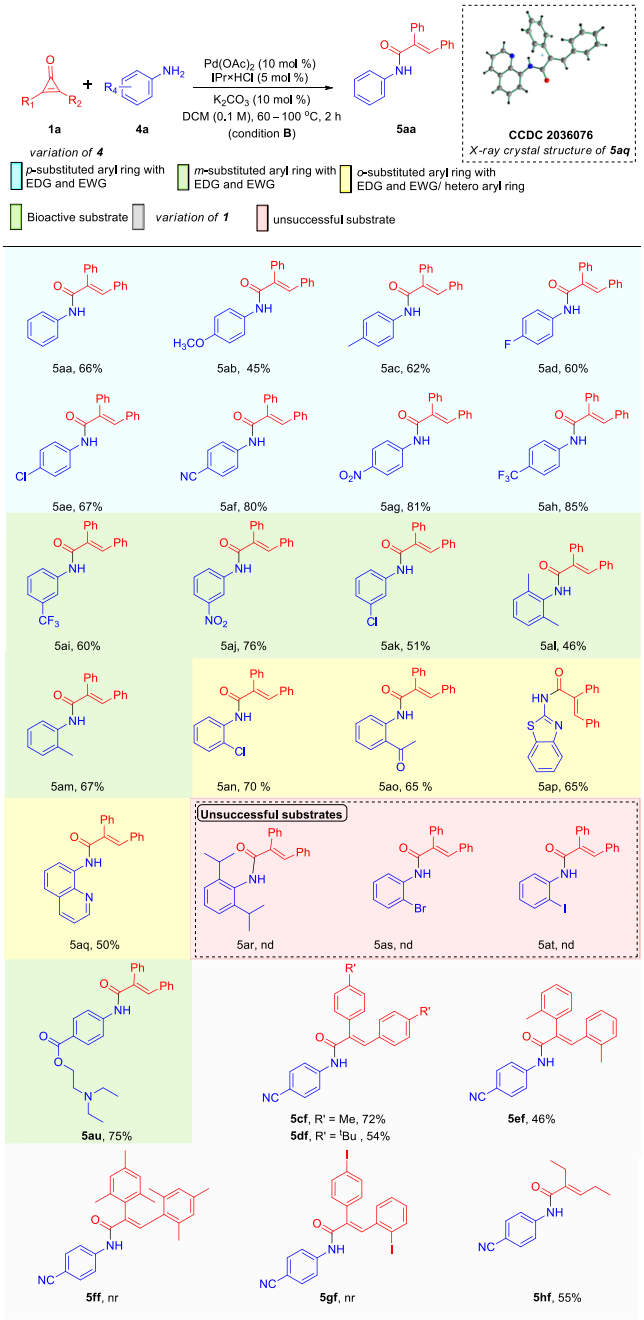
As the current methodology is compatible with a series of phenol moieties, aniline was chosen as the substrate to show the developed protocol's diversity. As $\alpha,\beta$-unsaturated amide is present in several biologically active molecules, developing a one-step protocol is essential. With this motivation, when condition A was directly applied to the reaction of aniline **4a** with diphenyl cyclopropenone **1a**, we got only a 45% yield of the desired product **5aa**. After several solvent optimizations, delightfully, DCM was found to be working well, giving a 66% (Table 3, **5aa**) yield of the unsaturated amide. A wide variety of substituted anilines were next evaluated under the optimized reaction conditions, as demonstrated in Table 3. Substitution of aniline in the para position with electron-releasing groups such as methoxy and methyl were found to be compatible, giving 45% and 62% yields, respectively (Table 3, **5ab** and **5ac**). Further, modifiable halo substituents in the para position of aniline worked well, giving good yields of the desired unsaturated amides (Table 3, **5ad** and **5ae**). An enhanced yield was observed in the case of electron-withdrawing groups like −CN-, $-NO_2$-, and $-CF_3$-substituted aniline delivering 80−85% yields of the desired product (Table 3, **5af**−**5ah**). Further, reaction of meta-substituted aniline resulted in good yields of unsaturated amides (Table 3, **5ai**−**5ak**).

When *o*-2,6-dimethyl aniline (Table 3, **5al**) was taken as the substrate, a detrimental effect on the reaction yield was observed; otherwise, *o*-Me, *o*-Cl, and *o*-acetyl anilines delivered quantitative amounts of the desired products (Table 3, **5am**−**5ao**). Furthermore, when 2-aminobenzothiazole and 8-amino-quinoline were taken as the substrates, the desired unsaturated amide was obtained in 65% and 50% yields, respectively (Table 3, **5ap** and **5aq**). However, ortho-substituted diisopropyl, bromo, and iodo aniline failed to give their respective products (Table 3, **5ar**−**5at**), which implies that steric bulk in the substrate might be retarding the reaction. While screening electronically divergent anilines, procaine **4u** (local anesthetic) was also subjected to the standard reaction conditions; it was found to be compatible, delivering a 75% yield of the desired unsaturated amide **5au**. In essence, the developed methodology provides a rapid and modular approach to access several bioactive compounds.

Furthermore, the scope of $\alpha,\beta$-unsaturated amide was expanded to different diaryl-substituted cyclopropenones, delivering the desired product in good to moderate yield (Table 3, **5cf**−**5ef**). Sterically hindered diaryl cyclopropenone failed to give any product, leaving unreacted starting materials (Table 3, **5ff**−**5gf**). We also screened diethyl-substituted cyclopropenone; it gave the respective unsaturated amide **5hf** in 55% yield. The X-ray data of **3aw** and **5aq** unambiguously justify the structure of demonstrated products. Moreover, the survival of a wide range of sensitive functional groups under the reaction conditions without interference indicates notable innate chemoselectivity.

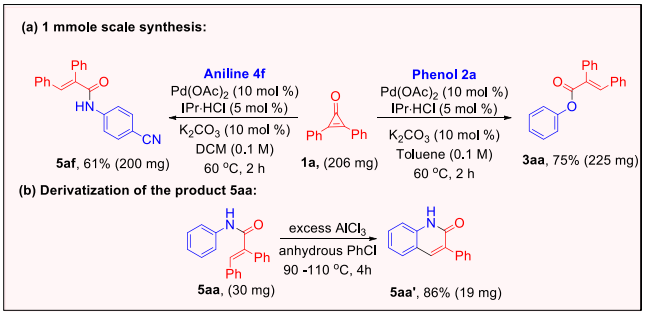
The scale-up experiment and synthetic transformation reactions were carried out to explore the efficiency and practical utility of this method. When a 1 mmol scale reaction was conducted, $\alpha,\beta$-unsaturated ester **3aa** and amide **5af** were isolated in 75% and 61% yields, respectively (Scheme 1a). Also, product applicability was shown in Scheme 2b, where substrate **5aa** was subjected to Lewis acid-catalyzed conditions.[20] In the presence of excess $AlCl_3$, we isolated 3-phenyl carbostyril **5aa′** as

**Table 3. Scope of Anilines for the Synthesis of Acrylamide Derivatives**[a]




[a]Conditions: **1a** (1 equiv), **4a** (1 equiv), $Pd(OAc)_2$ (10 mol %), $K_2CO_3$ (10 mol %), IPr·HCl (5 mol %), DCM (0.1 M), 60 °C.

**Scheme 1. Synthetic Application**



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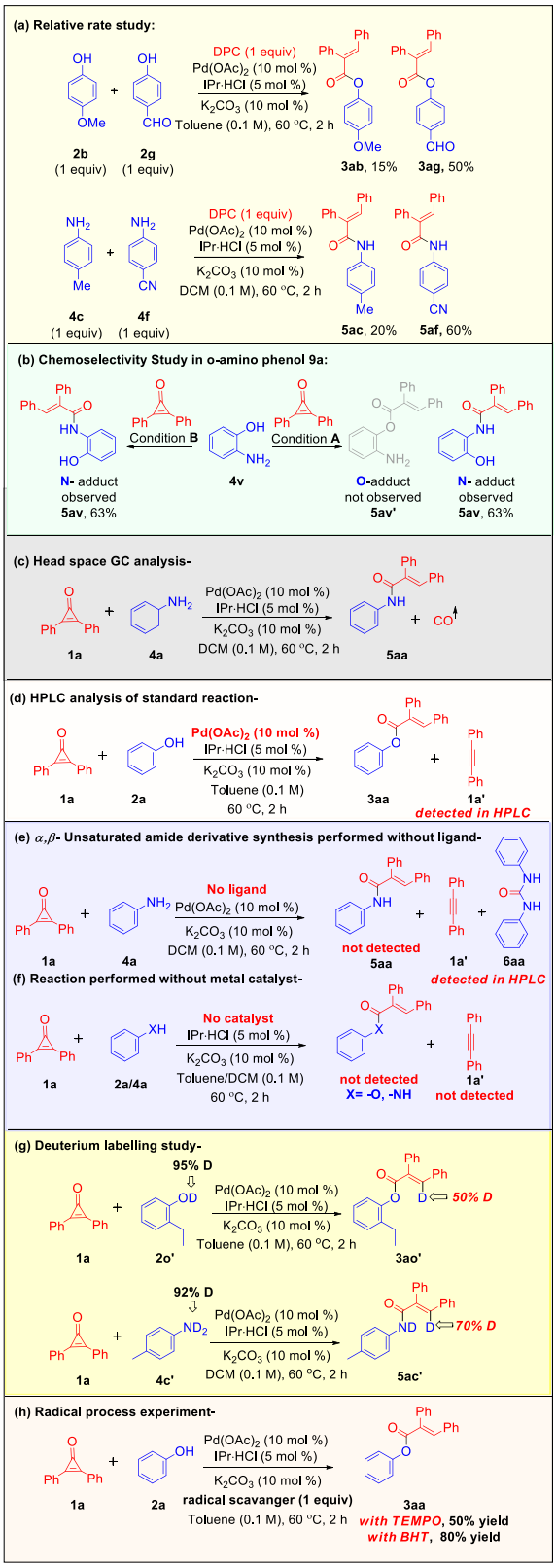
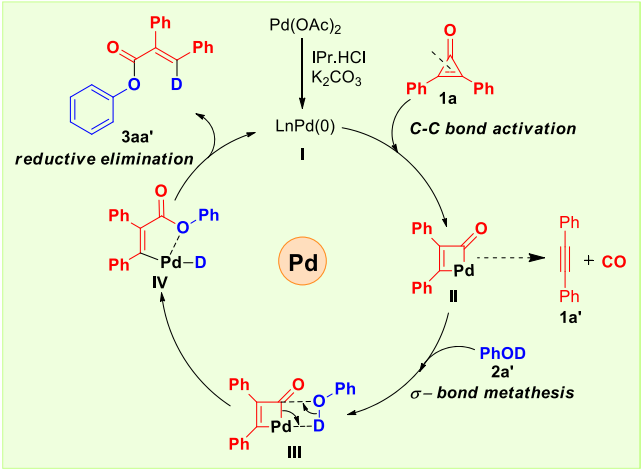
**Scheme 2. Mechanistic Study**




the product in 86% yield (Scheme 1b). In this process one phenyl ring got eliminated, which was supported by the result disclosed by Ramakrishnan et al.[20a] Next, we examined the effect of electronics on the reaction rate. When a competition reaction was carried out between electron-rich and -deficient substrate, the rate of the reaction was found to be accelerated by electron-deficient substrate (Scheme 2a). When *o*-aminophenol **4v** was subjected to optimized reaction conditions **A** and **B**, we observed that amide formation is highly selective though another reactive phenolic site was available. This suggests that the reaction is highly chemoselective (Scheme 2b). For a better understanding of this reaction, several control experiments were conducted. When the reaction was monitored by gas chromatography, we observed a carbon monoxide (CO) peak in the GC (Scheme 2c). Under the standard reaction conditions, diphenylacetylene was formed as a side product (Scheme 2d) (confirmed through HPLC, see Supporting Information). The fact that in the presence of metal catalyst diphenyl acetylene is forming along with extrusion of carbon monoxide signifies the presence of a four-membered palladacycle intermediate (Scheme 3) in the catalytic cycle as described in our previous report.[19] Thus, to substantiate the formation of a four-membered palladacycle from which diphenylacetylene **1a′** and CO is forming, the reaction was carried out without ligand where no product was observed, but tolane **1a′** (diphenylacetylene) was detected as the byproduct along with diphenyl urea **6aa** (Scheme 2e) (confirmed through HPLC). Also, when the standard reaction was performed without metal catalyst there was no reaction (Scheme 2f) (confirmed through crude NMR). Furthermore, to get additional information about the origin of the vinylic hydrogen in the product, we performed a deuterium exchange experiment. The deuterated phenol **2o′** (95% D) and aniline **4c′** (92% D) were subjected to the optimized reaction conditions, giving **3ao′** and **5ac′** in 50% and 70% deuterium-exchanged products, respectively (Scheme 2g). To check the nature of the intermediate, a radical process experiment was performed. In the presence of 1 equiv of a radical scavenger like TEMPO and BHT, we observed decent reactivity, giving 50% and 80% of the desired product **3aa** (Scheme 2h), indicating that the reaction was proceeding through a nonradical pathway.

**Scheme 3. Proposed Catalytic Cycle**




On the basis of the above experiments and literature precedence,[20] a plausible catalytic cycle has been proposed (Scheme 3). Formation of Pd(0) in the presence of imidazolinium salt and a catalytic amount of base was well explored.[20] Taking this into account, we presumed formation of Pd(0) intermediate **I** which is undergoing oxidative addition with the C−C bond of diphenyl cyclopropenone to give intermediate **II**. Intermediate **II** undergoes σ-bond metathesis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with phenol-D, across the C−Pd bond to form intermediate **IV** (supported by experiments in Scheme 2a and 2g). Then intermediate **IV** undergoes reductive elimination to deliver the desired product **3aa′**, regenerating the active Pd(0) catalyst for the next catalytic cycle.

## CONCLUSION

In summary, we established a palladium-catalyzed C−C bond activation strategy of the smallest Huckel aromatic system for the synthesis of $\alpha,\beta$-unsaturated esters and amides in a highly stereo- and chemoselective manner. The current protocol is quite general and covers a broad range of substrates. Further, we demonstrated this strategy's general application for late-stage functionalization of bioactive molecules. In addition, conversion of the $\alpha,\beta$-unsaturated amide into a biologically important quinolone motif provides a unique opportunity to extend the developed protocol.

## EXPERIMENTAL SECTION

**General Information.**[21] Reactions were performed using a borosil Schlenk tube vial under $N_2$ atmosphere. Column chromatography was done using 100−200 and 230−400 mesh size silica gel from Acme Chemicals. Gradient elution was performed using distilled petroleum ether and ethyl acetate. TLC plates were detected under UV light at 254 nm. $^1$H NMR and $^{13}$C NMR data were recorded on Bruker AV 400 and 700 MHz spectrometers using $CDCl_3$ as the internal standard; the residual $CHCl_3$ for $^1$H NMR ($\delta$ = 7.26 ppm) and the deuterated solvent signal for $^{13}$C NMR ($\delta$ = 77.36 ppm) were used as the reference.[21b] Multiplicity (s = single, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet), integration, and coupling constants ($J$) in hertz (Hz) were determined. HRMS signal analysis was performed using a micro TOF Q-II mass spectrometer. X-ray analysis was conducted using a Rigaku Smartlab X-ray diffractometer at SCS, NISER. Reagents and starting materials were purchased from Sigma-Aldrich, Alfa Aesar, TCI, Avra, Spectrochem, and other commercially available sources and used without further purification unless otherwise noted.

*General Procedure 1 for Synthesis of Cyclopropenones (Method A).*[19,22] To a suspension of tetrachlorocyclopropene (0.64 mmol, 1 equiv) and anhydrous $AlCl_3$ (1.35 mmol, 1.05 equiv) in $CH_2Cl_2$ (0.06 M, 10 mL) was added dropwise a solution of benzene (1.28 mmol, 2 equiv) in $CH_2Cl_2$ (1.2 M, 1 mL) at −78 °C. The mixture was stirred for 2 h, warmed to room temperature, and stirred for another 2 h. After completion of the reaction as monitored by TLC analysis, the resulting mixture was quenched with water, diluted with $CH_2Cl_2$, and washed with water (2 × 50 mL) and brine (2 × 50 mL). The organic layers were dried over anhydrous $Na_2SO_4$, filtered, and concentrated under reduced pressure to yield the crude residue as an orange oil. The crude residue was then purified by flash column chromatography on silica gel (20% EtOAc in hexanes) to afford diarylcyclopropenone (175 mg, 85% yield) as a white solid.

*General Procedure 1 for Synthesis of Cyclopropenones (Method B).*[22] *n*-Butyllithium (2.2 mmol, 2.2 equiv) was added dropwise over a period of 60 min to a stirring solution of chloroform (0.20 mL, 2.5 mmol) and alkyne (1.0 mmol, 1 equiv) in THF (20 mL, 0.05 M) under a $N_2$ atmosphere at −78 °C. The resulting mixture was stirred for an additional 4 h at −78 °C before concentrated hydrochloric acid (1 mL, 1 M) was added dropwise over 10 min. The cooling bath was removed, and the mixture was stirred for 10 min without external cooling before water (20 mL) was added. The mixture was extracted with dichloromethane (5 × 20 mL), and the combined organic extracts were dried ($MgSO_4$) and evaporated in vacuo. The products were isolated by flash chromatography.

*General Procedure 2 for Synthesis of Highly Substituted Acrylates **3** (Condition A).* To a 25 mL Schlenk tube under $N_2$ atmosphere, diphenyl cyclopropenone **1a** (0.1 mmol, 1 equiv) in toluene (0.1 M, 1 mL), $Pd(OAc)_2$ (10 mol %, 0.1 equiv), IPr·HCl (5 mol %, 0.05 equiv), $K_2CO_3$ (10 mol %, 0.1 equiv), and phenol **2** (0.1 mmol, 1 equiv) were added and stirred vigorously (750 rpm) in a preheated aluminum block at 60 °C for 2 h. After completion of the reaction (in 2 h) as monitored by TLC analysis, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/hexane) to give the pure product **3**.

***Caution:*** *use a mask while using IPr·HCl.*

*General Procedure 3 for Synthesis of Highly Substituted Acrylate **3aa** in 1 mmol Scale.* To a 25 mL Schlenk tube under $N_2$ atmosphere, diphenyl cyclopropenone **1a** (1 mmol, 1 equiv) in toluene (0.1 M, 10 mL), $Pd(OAc)_2$ (10 mol %, 0.1 equiv), IPr·HCl (5 mol %, 0.05 equiv), $K_2CO_3$ (10 mol %, 0.1 equiv), and phenol **2a** (1 mmol, 1 equiv) were added and stirred vigorously (750 rpm) in a preheated aluminum block at 60 °C for 2 h. After completion of the reaction (in 2 h) as monitored by TLC analysis, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/hexane) to give the pure product **3aa**. White solid (225 mg, 75% yield). $R_f$: 0.7 (in 10% EtOAc/hexane).

*General Procedure 4 for Synthesis of Highly Substituted Acrylamide **5** (Condition B).* To a 25 mL Schlenk tube under $N_2$ atmosphere, diphenyl cyclopropenone **1a** (0.1 mmol, 1 equiv) in DCM (0.1 M, 1 mL), $Pd(OAc)_2$ (10 mol %, 0.1 equiv), IPr·HCl (5 mol %, 0.05 equiv), $K_2CO_3$ (10 mol %, 0.1 equiv), and aniline **4** (0.1 mmol, 1 equiv) were added and stirred vigorously (750 rpm) in a preheated aluminum block at 60 °C for 2 h. After completion of the reaction (in 2 h) as monitored by TLC analysis, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/hexane) to give the pure product **5**.

*General Procedure 5 for Synthesis of Highly Substituted Acrylamide **5af** in 1 mmol Scale.* To a 25 mL Schlenk tube under $N_2$ atmosphere, diphenyl cyclopropenone **1a** (1 mmol, 1 equiv) in DCM (0.1 M, 10 mL), $Pd(OAc)_2$ (10 mol %, 0.1 equiv), IPr·HCl (5 mol %, 0.05 equiv), $K_2CO_3$ (10 mol %, 0.1 equiv), and aniline **4f** (1 mmol, 1 equiv) were added and stirred vigorously (750 rpm) in a preheated aluminum block at 60 °C for 2 h. After completion of the reaction (in 2 h) as monitored by TLC analysis, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/hexane) to give the pure product **5af**. White solid (200 mg, 61% yield). $R_f$: 0.4 (in 10% EtOAc/hexane).

*General Procedure 6 for the Competition Reaction between Phenols.* To a 25 mL Schlenk tube under $N_2$ atmosphere, diphenyl cyclopropenone **1a** (0.1 mmol, 1 equiv) in toluene (0.1 M, 1 mL), $Pd(OAc)_2$ (10 mol %, 0.1 equiv), IPr·HCl (5 mol %, 0.05 equiv), $K_2CO_3$ (10 mol %, 0.1 equiv), 4-methoxyphenol **2b** (0.1 mmol, 1 equiv), and 4-hydroxybenzaldehyde **2g** (0.1 mmol, 1 equiv) were added and stirred vigorously (750 rpm) in a preheated aluminum block at 60 °C for 2 h. After completion of the reaction (in 2 h) as monitored by TLC analysis, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/hexane) to give **3ab** in 15% yield and **3ag** in 50% yield.

*General Procedure 7 for Competition Reaction between Anilines.* To a 25 mL Schlenk tube under $N_2$ atmosphere, diphenyl cyclopropenone **1a** (0.1 mmol, 1 equiv) in DCM (0.1 M, 1 mL), $Pd(OAc)_2$ (10 mol %, 0.1 equiv), IPr·HCl (5 mol %, 0.05 equiv), $K_2CO_3$ (10 mol %, 0.1 equiv), 4-methylaniline **4c** (0.1 mmol, 1 equiv), and 4-aminobenzonitrile **4f** (0.1 mmol, 1 equiv) were added and stirred vigorously (750 rpm) in a preheated aluminum block at 60 °C for 2 h. After completion of the reaction (in 2 h) as monitored by TLC analysis, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/hexane) to give **5ac** in 20% yield and **5af** in 60% yield.

*General Procedure 8 for the Radical Process Experiment.* To a 25 mL Schlenk tube under $N_2$ atmosphere, diphenyl cyclopropenone **1a** (0.1 mmol, 1 equiv) in toluene (0.1 M, 1 mL), $Pd(OAc)_2$ (10 mol %, 0.1 equiv), IPr·HCl (5 mol %, 0.05 equiv), $K_2CO_3$ (10 mol %, 0.1 equiv), phenol **2a** (0.1 mmol, 1 equiv), and radical scavenger (0.1 mmol, 1 equiv) were added and purged with nitrogen more than three times. The reaction mixture was stirred vigorously (750 rpm) in a preheated aluminum block at 60 °C for 2 h. After completion of the reaction (in 2 h) as monitored by TLC analysis, the solvent was


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evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/hexane) to give the pure product **3aa** in 50% and 80% yield in the presence of TEMPO and BHT, respectively.

*General Procedure 9 for the Synthesis of 2-Quinolone.*[20g] To a solution of **5aa** (0.1 mmol, 1 equiv) in anhydrous chlorobenzene (260 μL, 0.5 M) was added $AlCl_3$ (0.5 mmol, 5 equiv) portionwise at room temperature. The reaction mixture was stirred at 90 °C for 3 h and then at 110 °C for 1 h. After 4 h, the reaction was quenched with $NaHCO_3$, and then the solvent was evaporated in vacuo. The crude mixture was purified by column chromatography on silica gel (EtOAc/hexane), giving the pure product **5aa′** in 86% (19 mg) yield.

*(E)-Phenyl 2,3-Diphenyl Acrylate (**3aa**).*[18b] **3aa** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white solid compound **3aa** (25 mg) in 83% yield; mp 133−135 °C; $R_f$ = 0.8 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.04 (s, 1H), 7.41−7.32 (m, 7H), 7.25−7.09 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 166.4, 151.1, 142.0, 135.5, 134.4, 131.9, 130.8, 129.8, 129.4, 129.3, 128.7, 128.3, 128.0, 125.7, 121.6; IR (KBr, $cm^{-1}$) 3129, 1723, 1400, 1151; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{21}H_{16}O_2Na$ 323.1043; found 323.1042.

*(E)-4-Methoxyphenyl 2,3-Diphenyl Acrylate (**3ab**).*[18b] **3ab** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving white solid compund **3ab** (25 mg) in 77% yield; mp 130−132 °C; $R_f$ = 0.6 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) δ 7.94 (s, 1H), 7.32−7.24 (m, 5H), 7.18−7.09 (m, 3H), 7.03−6.98 (m, 4H), 6.81 (d, $J$ = 8.0 Hz, 2H), 3.72 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 167.0, 157.5, 144.9, 142.1, 135.8, 134.8, 132.3, 131.1, 130.2, 129.6, 129.0, 128.6, 128.3, 122.6, 114.7, 55.9. IR (KBr, $cm^{-1}$) 3135, 1719, 1400, 1149. HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{22}H_{18}O_3Na$ 353.1148; found 353.1154.

*(E)-[1,1′-Biphenyl]-4-yl 2,3-Diphenyl Acrylate (**3ac**).*[18b] **3ac** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white solid compound **3ac** (28 mg) in 75% yield; mp 184−185 °C; $R_f$ = 0.8 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.06 (s, 1H), 7.58 (t, $J$ = 8.0 Hz, 4H), 7.45−7.34 (m, 8H), 7.25−7.18 (m, 5H), 7.12 (d, $J$ = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 166.7, 150.9, 142.4, 140.7, 139.2, 135.8, 135.2, 134.7, 132.2, 131.1, 130.2, 129.7, 129.1 (2C), 128.6, 128.4, 127.6, 127.4, 122.2; IR (KBr, $cm^{-1}$) 3141, 1720, 1401, 1151; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{27}H_{21}O_2$ 377.1536; found 377.1508.

*(E)-4-Fluorophenyl 2,3-Diphenyl Acrylate (**3ad**).* **3ad** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white solid compound **3ad** (20 mg) in 63% yield; mp 124−126 °C; $R_f$ = 0.7 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) 8.03 (s, 1H), 7.43−7.37 (m, 3H), 7.33−7.31 (m, 2H), 7.26−7.17 (m, 3H), 7.12−7.03 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) 166.7, 160.5 (d, $J_{C-F}$ = 242.0 Hz), 147.2 (d, $J_{C-F}$ = 3.0 Hz), 142.6, 135.7, 134.6, 132.0, 131.1, 130.1, 129.8, 129.1, 128.6, 128.4, 123.3 (d, $J_{C-F}$ = 9.0 Hz), 116.3 (d, $J_{C-F}$ = 24.0 Hz); $^{19}$F NMR ($CDCl_3$, 376 MHz) δ −117.2; IR (KBr, $cm^{-1}$) 3141, 1720, 1502, 1401, 1142; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{21}H_{16}FO_2$ 319.1129; found 319.1127.

*(E)-4-Chlorophenyl 2,3-Diphenyl Acrylate (**3ae**).*[18b] **3ae** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white solid compound **3ae** (25 mg) in 76% yield; mp 140−142 °C; $R_f$ = 0.7 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) 8.02 (s, 1H), 7.43−7.30 (m, 7H), 7.26−7.17 (m, 3H), 7.10−7.08 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 166.4, 149.9, 142.7, 135.6, 134.6, 131.9, 131.4, 131.1, 130.1, 129.9, 129.7, 129.1, 128.6, 128.4, 123.3; IR (KBr, $cm^{-1}$) 3141, 1721, 1486, 1149; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{21}H_{15}ClO_2Na$ 357.0658; found 357.0650.

*(E)-4-Bromophenyl 2,3-Diphenyl Acrylate (**3af**).* **3af**was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white solid compound **3af** (26 mg) in 68% yield; mp 156−158 °C; $R_f$ = 0.8 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.02 (s, 1H), 7.49 (d, $J$ = 8.0 Hz, 2H), 7.40−7.38 (m, 3H), 7.32−7.30 (m, 2H), 7.26−7.17 (m, 3H), 7.09 (br, $J$ = 4.0 Hz, 2H), 7.04 (d, $J$ = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 166.3, 150.5, 142.8, 135.6, 134.6, 132.7, 131.9, 131.1, 130.1, 129.9, 129.1, 128.6, 128.4, 123.7, 119.1; IR (KBr, $cm^{-1}$) 3140, 1721, 1400, 1148; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{21}H_{16}BrO_2$ 379.0328; found 379.0301.

*(E)-4-Formylphenyl 2,3-Diphenyl Acrylate (**3ag**).* **3ag** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white solid compound **3ag** (23 mg) in 72% yield; mp 127−130 °C; $R_f$ = 0.3 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) δ 9.99 (s, 1H), 8.06 (s, 1H), 7.92 (d, $J$ = 8.0 Hz, 2H), 7.44−7.39 (m, 3H), 7.35−7.32 (m, 4H), 7.26−7.18 (m, 3H), 7.11 (d, $J$ = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 191.3, 166.0, 156.2, 143.2, 135.4, 134.5, 134.2, 131.6, 131.4, 131.2, 130.1, 130.0, 129.2, 128.7, 128.5, 122.7; IR (KBr, $cm^{-1}$) 3136, 1720, 1704, 1401, 1146; HRMS (ESI) $m/z$ $[M + K]^+$ calcd for $C_{22}H_{16}O_3K$ 367.0737; found 367.0730.

*(E)-4-Nitrophenyl 2,3-Diphenyl Acrylate (**3ah**).* **3ah** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white crystalline solid **3ah** (23 mg) in 67% yield; mp 167−170 °C; $R_f$ = 0.5 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.27 (s, 1H), 8.06 (s, 1H), 7.45−7.40 (m, 3H), 7.35−7.31 (m, 4H), 7.27−7.18 (m, 3H), 7.11 (d, $J$ = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 165.7, 156.2, 145.6, 143.7, 135.3, 134.3, 131.3, 130.2, 130.0, 129.2, 128.7, 128.6, 125.4, 122.8, 122.0; IR (KBr, $cm^{-1}$) 3114, 1723, 1517, 1155; HRMS (ESI) $m/z$ $[M + K]^+$ calcd for $C_{21}H_{15}NO_4K$ 384.0638; found 384.0633.

*(E)-3-Methoxyphenyl 2,3-Diphenyl Acrylate (**3ai**).* **3ai** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white solid compound **3ai** (24 mg) in 73% yield; mp 104−106 °C; $R_f$ = 0.6 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.03 (s, 1H), 7.42−7.16 (m, 9H), 7.10 (d, $J$ = 8.0 Hz, 2H), 6.79−6.69 (m, 3H), 3.79 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 166.6, 160.7, 152.4, 142.3, 135.7, 134.7, 132.2, 131.1, 130.1, 130.0, 129.7, 129.0, 128.6, 128.3, 114.1, 112.1, 107.8, 55.7; IR (KBr, $cm^{-1}$) 3141, 1725, 1489, 1075; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{22}H_{18}O_3Na$ 353.1148; found 353.1175.

*(E)-3-Nitrophenyl 2,3-Diphenyl Acrylate (**3aj**).* **3aj** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale white solid **3aj** (27 mg) in 78% yield; mp 120−122 °C; $R_f$ = 0.5 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.11 (d, $J$ = 8.0 Hz, 1H), 8.07 (s, 1H), 8.05 (s, 1H), 7.58−7.50 (m, 2H), 7.43−7.40 (m, 3H), 7.34−7.25 (m, 3H), 7.20 (t, $J$ = 8.0 Hz, 2H), 7.11 (d, $J$ = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 166.0, 151.7, 149.1, 143.6, 135.3, 134.4, 131.3, 130.2, 130.1 (2C), 129.2, 128.7, 128.6, 128.5, 128.4, 121.0, 117.8; IR (KBr, $cm^{-1}$) 3123, 1720, 1401, 1155; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{21}H_{15}NO_4Na$ 368.0893; found 368.0879.

*(E)-3-Cyanophenyl 2,3-Diphenyl Acrylate (**3ak**).* **3ak** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white solid compound **3ak** (21 mg) in 65% yield; mp 146−148 °C; $R_f$ = 0.4 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.05 (s, 1H), 7.54−7.47 (m, 3H), 7.45−7.40 (m, 4H), 7.33−7.31 (m, 2H), 7.26−7.25 (m, 1H), 7.20 (t, $J$ = 8.0 Hz, 2H), 7.11 (d, $J$ = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 166.0, 151.5, 143.4, 135.3, 134.4, 131.3, 131.2, 130.6, 130.1, 130.0, 129.7, 129.2, 128.7, 128.6, 127.0, 125.8, 118.2, 113.7; IR (KBr, $cm^{-1}$) 3132, 2230, 1725, 1401, 1148; HRMS (ESI) $m/z$ $[M + K]^+$ calcd for $C_{22}H_{15}NO_2K$ 364.0740; found 364.0739.

*(E)-3-Chlorophenyl 2,3-Diphenyl Acrylate (**3al**).* **3al** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white solid compound **3al** (20 mg) in 61% yield; mp 103−105 °C; $R_f$ = 0.7 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400


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MHz) δ 8.03 (s, 1H), 7.41−7.38 (m, 3H), 7.32−7.17 (m, 8H), 7.11−7.05 (m, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 166.3, 151.9, 142.8, 135.6, 134.9, 134.6, 131.8, 131.2, 130.3, 130.1, 129.9, 129.1, 128.6, 128.4, 126.3, 122.6, 120.4; IR (KBr, $cm^{-1}$) 3140, 1723, 1401, 1148; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{21}H_{15}ClO_2Na$ 357.0653; found 357.0638.

*(E)-3-Bromophenyl 2,3-Diphenyl Acrylate (**3am**).* **3am** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale-yellow solid compound **3am** (25 mg) in 67% yield; mp 102−104 °C; $R_f$ = 0.8 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.02 (s, 1H), 7.41−7.30 (m, 7H), 7.26−7.17 (m, 4H), 7.12−7.09 (m, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 166.3, 151.9, 142.8, 135.5, 134.5, 131.8, 131.2, 130.7, 130.1, 129.9, 129.2, 129.1, 128.6, 128.4, 125.4, 122.6, 120.8; IR (KBr, $cm^{-1}$) 3141, 1723, 1401, 1148; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{21}H_{15}BrO_2Na$ 401.0148; found 401.0118.

*(E)-2-(tert-Butyl)phenyl 2,3-Diphenyl Acrylate (**3an**).* **3an** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a colorless liquid compound **3an** (25 mg) in 71% yield; $R_f$ = 0.7 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.06 (s, 1H), 7.43−7.33 (m, 6H), 7.26−7.07 (m, 8H), 1.20 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 166.9, 149.9, 142.5, 141.4, 135.9, 134.7, 132.7, 131.2, 130.2, 129.8, 129.1, 128.6, 128.3, 127.4, 127.1, 125.9, 124.2, 34.6, 30.2; IR (KBr, $cm^{-1}$) 3053, 1731, 1421; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{25}H_{24}O_2Na$ 379.1669; found 379.1680.

*(E)-2-Ethylphenyl 2,3-Diphenyl Acrylate (**3ao**).* **3ao** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale-yellow compound **3ao** (23 mg) in 70% yield; mp 88−90 °C; $R_f$ = 0.7 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.04 (s, 1H), 7.43−7.33 (m, 5H), 7.24−7.15 (m, 6H), 7.11 (d, $J$ = 8.0 Hz, 3H), 2.50 (q, $J$ = 8.0 Hz, 2H), 1.10 (t, $J$ = 8.0 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 166.6, 149.5, 142.2, 136.1 (2C), 136.0, 134.7, 132.3, 131.2, 130.0, 129.7, 129.1, 128.6, 128.3, 127.0, 126.3, 122.4, 23.8, 14.6; IR (KBr, $cm^{-1}$) 3143, 1724, 1487; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{23}H_{21}O_2$ 329.1536; found 329.1534.

*(E)-2-Chlorophenyl 2,3-Diphenyl Acrylate (**3ap**).* **3ap** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white crystalline solid compound **3ap** (26 mg) in 78% yield; mp 128−130 °C; $R_f$ = 0.7 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.09 (s, 1H), 7.45−7.37 (m, 6H), 7.29−7.15 (m, 6H), 7.12 (d, $J$ = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 165.8, 147.8, 143.0, 135.6, 134.6, 131.6, 131.2, 130.6, 130.2, 129.8, 129.0, 128.6, 128.4, 127.9, 127.3, 127.2, 124.1; IR (KBr, $cm^{-1}$) 3140, 1724, 1476, 1150; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{21}H_{15}ClO_2Na$ 357.0653; found 357.0654.

*(E)-2-Bromophenyl 2,3-Diphenyl Acrylate (**3aq**).* **3aq** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale-yellow solid compound **3aq** (28 mg) in 74% yield; mp 100−102 °C; $R_f$ = 0.7 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.10 (s, 1H), 7.60 (d, $J$ = 8.0 Hz, 1H), 7.43−7.37 (m, 5H), 7.34−7.30 (m, 1H), 7.26−7.17 (m, 4H), 7.12 (d, $J$ = 8.0 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 165.8, 149.0, 143.1, 135.6, 134.6, 133.6, 131.6, 131.2, 130.3, 129.9, 129.0, 128.7, 128.6, 128.4, 127.5, 124.2, 116.5; IR (KBr, $cm^{-1}$) 3141, 1724, 1491, 1150; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{21}H_{15}BrO_2Na$ 401.0148; found 401.0149.

*(E)-2-Cyanophenyl 2,3-Diphenyl Acrylate (**3as**).* **3as** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a colorless liquid compound **3as** (13 mg) in 40% yield; $R_f$ = 0.5 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.13 (s, 1H), 7.68 (d, $J$ = 8 Hz, 1H), 7.63 (t, $J$ = 8 Hz, 2H), 7.42−7.30 (m, 7H), 7.20 (t, $J$ = 8 Hz, 2H), 7.13 (d, $J$ = 8 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 165.6, 153.3, 144.0, 135.2, 134.3, 134.2, 133.5, 131.4, 130.2, 130.1, 129.2, 128.6 (2C), 126.6, 126.4, 123.6, 115.6, 107.4; IR (KBr, $cm^{-1}$) 3131, 2238, 1772, 1729, 1401, 1141; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{22}H_{15}NO_2Na$ 348.0995; found 348.0991.

*(E)-2,3-Dimethylphenyl 2,3-Diphenyl Acrylate (**3at**).* **3at** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white solid **3at** (21 mg) in 65% yield; mp 108−110 °C; $R_f$ = 0.7 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.04 (s, 1H), 7.43−7.34 (m, 5H), 7.24−7.17 (m, 3H), 7.12−7.08 (m, 3H), 7.02 (d, $J$ = 8.0 Hz, 1H), 6.93 (d, $J$ = 8.0 Hz, 1H), 2.28 (s, 3H), 2.06 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 166.6, 149.9, 142.1, 138.7, 136.0, 134.8, 132.3, 131.1, 130.1, 129.7, 129.1, 129.0, 128.6, 128.3, 127.6, 126.3, 119.7, 20.4, 12.8; IR (KBr, $cm^{-1}$) 3145, 1723, 1467, 1156; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{23}H_{20}O_2Na$ 351.1356; found 351.1351.

*(E)-3,5-Dimethylphenyl 2,3-Diphenyl Acrylate (**3au**).* **3au** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white solid compound **3au** (27 mg) in 82% yield; mp 108−110 °C; $R_f$ = 0.8 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.01 (s, 1H), 7.39−7.31 (m, 5H), 7.24−7.16 (m, 3H), 7.10−7.09 (br, $J$ = 4.0 Hz, 2H), 6.85 (s, 1H), 6.76 (s, 2H), 2.30 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 166.9, 151.3, 142.1, 139.5, 135.9, 134.8, 132.4, 131.1, 130.1, 129.6, 129.0, 128.5, 128.2, 127.7, 119.4, 21.5; IR (KBr, $cm^{-1}$) 3133, 1725, 1401, 1155; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{23}H_{20}O_2Na$ 351.1356; found 351.1344.

*(E)-2,3-Dihydro-1H-inden-5-yl 2,3-Diphenyl Acrylate (**3av**).* **3av** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale-yellow solid compound **3av** (27 mg) in 80% yield; mp 102−105 °C; $R_f$ = 0.8 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.01 (s, 1H), 7.41−7.31 (m, 5H), 7.23−7.16 (m, 4H), 7.10 (d, $J$ = 8.0 Hz, 2H), 6.99 (s, 1H), 6.87 (dd, $J$ = 8.0, 4.0 Hz, 1H), 2.89 (q, $J$ = 8.0 Hz, 4H), 2.09 (pent, $J$ = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 167.1, 149.9, 145.9, 142.0, 141.9, 135.9, 134.8, 132.5, 131.1, 130.2, 129.6, 129.0, 128.5, 128.2, 125.0, 119.4, 117.9, 33.2, 32.6, 26.1; IR (KBr, $cm^{-1}$) 3141, 1726, 1401, 1159; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{24}H_{20}O_2Na$ 363.1356; found 363.1353.

*(E)-Benzo[d][1,3]dioxol-5-yl 2,3-Diphenyl Acrylate (**3aw**).* **3aw** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white amorphous solid compound **3aw** (28 mg) in 82% yield; mp 153−155 °C; $R_f$ = 0.5 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.00 (s, 1H), 7.42−7.36 (m, 3H), 7.32−7.30 (m, 2H), 7.23−7.16 (m, 3H), 7.09 (d, $J$ = 8.0 Hz, 2H), 6.77 (d, $J$ = 8.0 Hz, 1H), 6.67 (br, 1H), 6.57 (dd, $J$ = 8.0, 4.0 Hz, 1H), 5.97 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 167.0, 148.2, 145.7, 145.6, 142.3, 135.7, 134.7, 132.1, 131.1, 130.1, 129.7, 129.0, 128.6, 128.3, 114.2, 108.2, 104.1, 101.9; IR (KBr, $cm^{-1}$) 3140, 1721, 1400, 1171; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{22}H_{16}O_4Na$ 367.0941; found 367.0941.

*(E)-4-Chloro-2-nitrophenyl 2,3-Diphenyl Acrylate (**3ax**).* **3ax** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving pale-yellow liquid compound **3ax** (23 mg) in 60% yield; $R_f$ = 0.6 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.10 (d, 1H), 8.06 (s, 1H), 7.60 (dd, $J$ = 8.0, 4.0 Hz, 1H), 7.42−7.35 (m, 5H), 7.26−7.17 (m, 4H), 7.10 (br, $J$ = 4.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 165.7, 144.4, 143.6, 135.2, 135.0, 134.8, 134.3, 132.2, 131.4, 130.8, 130.2, 129.2, 128.7, 128.6, 126.9, 126.8, 126.1; IR (KBr, $cm^{-1}$) 3140, 1777, 1721, 1400, 1107; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{21}H_{14}ClNO_4Na$ 402.0504; found 402.0500.

*(E)-2-Bromo-4-methylphenyl 2,3-Diphenyl Acrylate (**3ay**).* **3ay** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale-yellow solid compound **3ay** (26 mg) in 65% yield; mp 80−83 °C; $R_f$ = 0.7 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.09 (s, 1H), 7.42−7.37 (m, 6H), 7.25−7.16 (m, 3H), 7.11 (d, $J$ = 8.0 Hz, 3H), 7.06 (d, $J$ = 8.0 Hz, 1H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 166.0, 146.7, 142.9, 137.6, 135.6,


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134.7, 133.9, 131.7, 131.2, 130.3, 129.8, 129.3, 129.0, 128.6, 128.4, 123.6, 116.0, 20.9; IR (KBr, $cm^{-1}$) 3155, 1721, 1401, 1148; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{22}H_{17}BrO_2Na$ 415.0304; found 415.0303

*(E)-4-Acetyl-2-methylphenyl 2,3-Diphenyl Acrylate (**3az**).* **3az** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale white solid compound **3az** (23 mg) in 66% yield; mp 130−131 °C; $R_f$ = 0.2 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 8.05 (s, 1H), 7.84−7.81 (m, 2H), 7.43−7.39 (m, 3H), 7.35−7.33 (m, 2H), 7.24−7.18 (m, 4H), 7.11 (d, $J$ = 8.0 Hz, 2H), 2.58 (s, 3H), 2.21 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 197.6, 165.9, 153.9, 142.9, 135.7, 135.1, 134.5, 131.7, 131.6, 131.2, 131.0, 130.0 (2C), 129.2, 128.7, 128.5, 127.7, 122.4, 26.9, 16.7.; IR (KBr, $cm^{-1}$) 3133, 1719, 1685, 1401, 1152; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{24}H_{20}O_3Na$ 379.1305; found 379.1297.

*(E)-2-Bromo-5-fluorophenyl 2,3-Diphenyl Acrylate (**3aa$_1$**).* **3aa$_1$** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale-yellow solid compound **3aa$_1$** (30 mg) in 76% yield; mp 115−118 °C; $R_f$ = 0.8 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 8.10 (s, 1H), 7.57−7.53 (m, 1H), 7.42−7.38 (m, 5H), 7.27−7.24 (m, 1H), 7.19 (t, $J$ = 8.0 Hz, 2H), 7.12 (d, $J$ = 8.0 Hz, 2H), 7.00 (dd, $J$ = 8.0, 4.0 Hz, 1H), 6.87 (td, $J$ = 8.0 Hz, 4.0 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.3, 162.2 (d, $J_{C-F}$ = 247.0 Hz), 149.7 (d, $J_{C-F}$ = 11.0 Hz), 143.6, 135.3, 134.5, 133.9 (d, $J_{C-F}$ = 9.0 Hz), 131.3, 131.2, 130.2, 130.0, 129.1, 128.6, 128.5, 114.8 (d, $J_{C-F}$ = 22.0 Hz), 112.3 (d, $J_{C-F}$ = 25.0 Hz), 111.1 (d, $J_{C-F}$ = 4.0 Hz); $^{19}F$ NMR ($CDCl_3$, 376 MHz) $\delta$ −112.1; IR (KBr, $cm^{-1}$) 3141, 1736, 1401, 1147; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{21}H_{14}BrFO_2Na$ 419.0053; found 419.0029.

*(E)-1-Bromonaphthalen-2-yl 2,3-Diphenyl Acrylate (**3aa$_2$**).* **3aa$_2$** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white solid compound **3aa$_2$** (30 mg) in 70% yield; mp 166−168 °C; $R_f$ = 0.7 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 8.26 (d, $J$ = 8.0 Hz, 1H), 8.16 (s, 1H), 7.81 (dd, $J$ = 8.0, 4.0 Hz, 2H), 7.59 (t, $J$ = 8.0 Hz, 1H), 7.50 (t, $J$ = 8.0 Hz, 1H), 7.44−7.38 (m, 5H), 7.32 (d, $J$ = 8.0 Hz, 1H), 7.24 (d, $J$ = 8.0 Hz, 1H), 7.19 (t, $J$ = 8.0 Hz, 2H), 7.14 (d, $J$ = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.9, 147.2, 143.1, 135.6, 134.7, 133.0, 132.7, 131.7, 131.2, 130.3, 129.9, 129.1, 129.0, 128.6, 128.5 (2C), 128.0, 127.3, 126.6, 122.3, 115.4; IR (KBr, $cm^{-1}$) 3142, 1719, 1401, 1151; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{25}H_{18}BrO_2$ 429.0485; found 429.0442.

*(E)-(8R,13S,14S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 2,3-Diphenyl Acrylate (**3aa$_3$**).* **3aa$_3$** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale white solid compound **3aa$_3$** (35 mg) in 75% yield; mp 148−150 °C; $R_f$ = 0.2 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 8.01 (s, 1H), 7.39−7.36 (m, 3H), 7.33−7.16 (m, 6H), 7.10 (d, $J$ = 8.0 Hz, 2H), 6.91 (dd, $J$ = 8.0, 4.0 Hz, 1H), 6.87 (br, $J$ = 4.0 Hz, 1H), 2.90 (t, $J$ = 4.0 Hz, 2H), 2.50 (dd, $J$ = 8.0, 4.0 Hz, 1H), 2.39 (s, 1H), 2.17−1.94 (m, 5H), 1.66−1.62 (m, 1H), 1.59−1.45 (m, 7 H), 0.91 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 170.1, 166.9, 149.3, 142.1, 138.2, 137.5, 135.8, 134.8, 132.3, 131.1, 130.2, 129.6, 129.0, 128.6, 128.3, 126.6, 121.8, 119.0, 50.7, 48.2, 44.4, 38.3, 36.1, 31.8, 29.7, 26.6, 26.1, 21.9, 14.1; IR (KBr, $cm^{-1}$) 3139, 1724, 1633, 1401, 1160; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{33}H_{33}O_3$ 477.2424; found 477.2419.

*(E)-4-Methyl-2-oxo-2H-chromen-7-yl 2,3-Diphenyl Acrylate (**3aa$_4$**).* **3aa$_4$** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white solid compound **3aa$_4$** (31 mg) in 82% yield; mp 200−203 °C; $R_f$ = 0.3 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 8.06 (s, 1H), 7.60 (d, $J$ = 8.0 Hz, 1H), 7.44−7.39 (m, 3H), 7.35−7.32 (m, 2H), 7.28−7.10 (m, 7H), 6.26 (s, 1H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 166.0, 160.8, 154.5, 153.9, 152.2, 143.3, 135.4, 134.4, 131.5, 131.2, 130.1, 130.0, 129.2, 128.6, 128.5, 125.5, 118.5, 118.1, 114.8, 110.8, 19.0; IR (KBr, $cm^{-1}$) 3143, 1726, 1624, 1401, 1142; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{25}H_{19}O_4$ 383.1278; found 383.1266.

*(E)-Phenyl 2,3-Bis(4-methoxyphenyl) Acrylate (**3ba**).* **3ba** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale white solid compound **3ba** (31 mg) in 86% yield; mp 120−121 °C; $R_f$ = 0.5 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.95 (s, 1H), 7.37 (t, $J$ = 7.6 Hz, 2H), 7.25 (t, $J$ = 4.4 Hz, 2H), 7.20 (t, $J$ = 7.2 Hz, 1H), 7.13 (d, $J$ = 8.4 Hz, 2H), 7.09 (d, $J$ = 8.8 Hz, 2H), 6.94 (d, $J$ = 8.8 Hz, 2H), 6.72 (d, $J$ = 9.2 Hz, 2H), 3.84 (s, 3H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 167.2, 160.8, 159.5, 151.6, 141.8, 132.9, 131.4, 129.6, 129.3, 128.3, 127.6, 125.9, 122.0, 114.6, 114.1, 55.5; IR (KBr, $cm^{-1}$) 3129, 1716, 1401; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{23}H_{21}O_4$ 361.1434; found 361.1428.

*(E)-Phenyl 2,3-Di-p-tolyl Acrylate (**3ca**).*[18b] **3ca** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale brown solid compound **3ca** (26 mg) in 80% yield; mp 133−134 °C; $R_f$ = 0.5 (5% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.98 (s, 1H), 7.37 (t, $J$ = 7.6 Hz, 2H), 7.22−7.19 (m, 5H), 7.13 (d, $J$ = 8.0 Hz, 2H), 7.03−6.99 (m, 4H), 2.39 (s, 3H), 2.29 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 167.0, 151.5, 142.1, 140.0, 138.0, 132.9, 132.0, 131.1, 130.0, 129.8, 129.6, 129.3, 125.9 (2C), 122.0, 21.7 (2C); IR (KBr, $cm^{-1}$) 3134, 1717, 1603, 1399; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{23}H_{20}O_2Na$ 351.1356; found 351.1331.

*(E)-Phenyl 2,3-Bis(4-(tert-butyl)phenyl) Acrylate (**3da**).* **3da** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a yellow solid compound **3da** (29 mg) in 70% yield; mp 122−123 °C; $R_f$ = 0.6 (5% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.98 (s, 1H), 7.42 (d, $J$ = 8.8 Hz, 2H), 7.36 (t, $J$ = 7.6 Hz, 3H), 7.26 (d, $J$ = 8.4 Hz, 2H), 7.22−7.18 (m, 3H), 7.14 (d, $J$ = 8.4 Hz, 2H), 7.05 (d, $J$ = 8.4 Hz, 2H), 1.36 (s, 9H), 1.26 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 167.1, 153.2, 151.6, 151.2, 142.0, 133.0, 132.0, 131.1, 129.7, 129.6, 126.0, 125.9, 125.6 (2C), 122.0, 35.1, 35.0, 31.7, 31.4; IR (KBr, $cm^{-1}$) 3134, 1720, 1605, 1398, 1195; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{29}H_{33}O_2$ 413.2475; found 413.2469.

*(E)-Phenyl 2,3-Di-o-tolyl Acrylate (**3ea**).* **3ea** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white solid compound **3ea** (22 mg) in 66% yield; mp 132−133 °C; $R_f$ = 0.6 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 8.26 (s, 1H), 7.37−7.35 (m, 2H), 7.23−7.19 (m, 3H), 7.17−7.09 (m, 6H), 6.83 (t, $J$ = 7.6 Hz, 1H), 6.69 (d, $J$ = 7.6 Hz, 1H), 2.46 (s, 3H), 2.24 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 166.8, 151.5, 140.9, 138.4, 137.0, 135.4, 133.9, 132.3, 130.5 (2C), 130.4, 129.6, 129.4, 129.3, 128.4, 126.3, 126.0, 125.8, 121.9, 20.4, 20.0; IR (KBr, $cm^{-1}$) 3131, 1722, 1615, 1401, 1189; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{23}H_{20}O_2Na$ 351.1356; found 351.1343.

*(E)-Phenyl 2-Ethylpent-2-enoate (**3ha**).* **3ha** was prepared according to general procedure 2. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a colorless liquid compound **3ha** (13 mg) in 64% yield; $R_f$ = 0.8 (5% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.40−7.36 (m, 2H), 7.23−7.19 (m, 1H), 7.12−7.09 (m, 2H), 6.96 (t, $J$ = 7.2 Hz, 1H), 2.42 (q, $J$ = 7.6 Hz, 2H), 2.28 (pent, $J$ = 7.6 Hz, 2H), 1.10 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 166.7, 151.5, 146.1, 133.3, 129.6, 125.8, 122.1, 22.2, 20.4, 14.3, 13.7; IR (KBr, $cm^{-1}$) 3146, 1728, 1643, 1401, 1197; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{13}H_{17}O_2$ 205.1223; found 205.1223.

*(E)-N-2,3-Triphenylacrylamide (**5aa**).*[23a] **5aa** was prepared according to general procedure 4. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a yellow solid compound **5aa** (20 mg) in 66% yield; mp 143−145 °C; $R_f$ = 0.5 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.94 (s, 1H), 7.52−7.47 (m, 3H), 7.42 (d, $J$ = 8.0 Hz, 2H), 7.36 (dd, $J$ = 8.0, 1.6 Hz, 2H), 7.28−7.24 (m, 2H), 7.17−7.11 (m, 4H), 7.05 (t, $J$ = 8.0 Hz, 1H), 7.01 (d, $J$ = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.3, 138.6, 138.1, 136.1, 135.1, 134.9, 130.8, 130.4, 130.2, 129.2


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(2C), 129.1, 128.5, 124.7, 120.2; IR (KBr, $cm^{-1}$) 3406, 1677, 1597, 1264.

*(E)-N-(4-Methoxyphenyl)-2, 3-diphenylacrylamide (**5ab**).*[23c] **5ab** was prepared according to general procedure 4. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale-yellow solid compound **5ab** (14 mg) in 45% yield; mp 136−138 °C; $R_f$ = 0.7 (20% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.96 (s, 1H), 7.51−7.49 (m, 3H), 7.37−7.34 (m, 4H), 7.19−7.13 (m, 3H), 7.11 (br, 1H), 7.02 (d, $J$ = 8.0 Hz, 2H), 6.83 (d, $J$ = 8.0 Hz, 2H), 3.78 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.2, 156.8, 138.2, 136.2, 135.2, 134.9, 131.3, 130.7, 130.3, 130.2, 129.2, 129.0, 128.5, 122.0, 114.4, 55.8; IR (KBr, $cm^{-1}$) 3134, 1670, 1401; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{22}H_{19}NO_2Na$ 352.1308; found 352.1322.

*(E)-2,3-Diphenyl-N-(p-tolyl)acrylamide (**5ac**).*[23d] **5ac** was prepared according to general procedure 4. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale-yellow liquid compound **5ac** (20 mg) in 62% yield; $R_f$ = 0.4 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.96 (s, 1H), 7.53−7.48 (m, 3H), 7.36−7.32 (m, 4H), 7.20−7.13 (m, 4H), 7.09 (d, $J$ = 8.0 Hz, 2H), 7.02 (d, $J$ = 8.0 Hz, 2H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.2, 138.4, 136.2, 135.6, 135.2, 135.0, 134.4, 130.8, 130.3, 130.2, 129.7, 129.2, 129.1, 128.5, 120.2, 21.2; IR (KBr, $cm^{-1}$) 3131, 1667, 1401; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{22}H_{20}NO$ 314.1539; found 314.1526.

*(E)-N-(4-Fluorophenyl)-2,3-diphenylacrylamide (**5ad**).* **5ad** was prepared according to general procedure 4. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white solid compound **5ad** (19 mg) in 60% yield; mp 182−183 °C; $R_f$ = 0.5 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.97 (s, 1H), 7.52−7.49 (m, 3H), 7.43−7.39 (m, 2H), 7.36−7.34 (m, 2H), 7.20−7.13 (m, 4H), 7.03−6.96 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.3, 159.7 (d, $J_{C-F}$ = 243.0 Hz), 138.7, 136.0, 135.0, 134.6, 134.2, 134.1, 130.8, 130.3 (2C), 129.2 (d, $J_{C-F}$ = 11.0 Hz), 128.5, 122.0 (d, $J_{C-F}$ = 7.0 Hz), 115.9 (d, $J_{C-F}$ = 22.0 Hz); $^{19}$F NMR ($CDCl_3$, 376 MHz) $\delta$ −117.7; IR (KBr, $cm^{-1}$) 3140, 1643, 1403; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{21}H_{16}FNONa$ 340.1108; found 340.1123.

*(E)-N-(4-Chlorophenyl)-2,3-diphenylacrylamide (**5ae**).* **5ae** was prepared according to general procedure 4. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a yellow solid compound **5ae** (22 mg) in 67% yield; mp 145−147 °C; $R_f$ = 0.6 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.97 (s, 1H), 7.53−7.51 (m, 3H), 7.43−7.40 (m, 2H), 7.36−7.34 (m, 2H), 7.27−7.24 (m, 2H), 7.19−7.16 (m, 4H), 7.04−7.01 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.3, 138.9, 136.7, 135.9, 135.0, 134.5, 130.8, 130.3 (2C), 129.7, 129.4, 129.3, 129.2, 128.6, 121.4; IR (KBr, $cm^{-1}$) 3122, 1649, 1397; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{21}H_{17}ClNO$ 334.0993; found 334.0998.

*(E)-N-(4-Cyanophenyl)-2,3-diphenylacrylamide (**5af**).* **5af** was prepared according to general procedure 4. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a white solid compound **5af** (26 mg) in 80% yield; mp 175−177 °C; $R_f$ = 0.5 (20% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.99 (s, 1H), 7.58−0.53 (m, 7H), 7.36−7.34 (m, 3H), 7.23−7.15 (m, 3H), 7.03 (d, $J$ = 8.0 Hz, 2H); $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz) $\delta$ 165.5, 142.1, 139.9, 135.6, 134.7, 134.0, 133.5, 130.9, 130.5, 130.2, 129.6 (2C), 128.6, 119.9, 119.1, 107.5; IR (KBr, $cm^{-1}$) 3106, 2224, 1643, 1534; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{22}H_{16}N_2ONa$ 347.1155; found 347.1129.

*(E)-N-(4-Nitrophenyl)-2,3-diphenylacrylamide (**5ag**).* **5ag** was prepared according to general procedure 4. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a yellow solid compound **5ag** (28 mg) in 81% yield; mp 140−142 °C; $R_f$ = 0.6 (20% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.17 (d, $J$ = 8.0 Hz, 2H), 8.01 (s, 1H), 7.62 (d, $J$ = 8.0 Hz, 2H), 7.56−7.54 (m, 3H), 7.47 (br, 1H), 7.38−7.35 (m, 2H), 7.24−7.16 (m, 3H), 7.03 (d, $J$ = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.5, 143.9, 140.2, 135.5, 134.6, 133.9, 131.0, 130.5, 130.3, 129.7 (2C), 128.7, 125.3, 119.5; IR (KBr, $cm^{-1}$) 3121, 1682, 1405; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{21}H_{16}N_2O_3Na$ 367.1053; found 367.1054.

*(E)-2,3-Diphenyl-N-(4-(trifluoromethyl)phenyl)acrylamide (**5ah**).*[23c] **5ah** was prepared according to general procedure 4 with a modified temperature of 80 °C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a colorless liquid compound **5ah** (31 mg) in 85% yield; $R_f$ = 0.6 (20% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.99 (s, 1H), 7.59−7.51 (m, 7H), 7.37−7.35 (m, 2H), 7.33 (br, 1H), 7.22−7.15 (m, 3H), 7.03 (d, $J$ = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.5, 141.2, 139.4, 135.8, 134.8, 134.3, 130.9, 130.4, 130.3, 129.5, 129.4, 128.6, 126.5 (q, $J_{C-F}$ = 4.0 Hz), 126.3, 124.4 (q, $J_{C-F}$ = 269.0 Hz), 119.7; $^{19}$F NMR ($CDCl_3$, 376 MHz) $\delta$ −62.1; IR (KBr, $cm^{-1}$) 3131, 1642, 1401; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{22}H_{16}F_3NONa$ 390.1076; found 390.1080.

*(E)-2,3-Diphenyl-N-(3-(trifluoromethyl)phenyl)acrylamide (**5ai**).* **5ai** was prepared according to general procedure 4 with a modified temperature of 80 °C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a colorless liquid compound **5ai** (22 mg) in 60% yield; $R_f$ = 0.6 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.99 (s, 1H), 7.74 (s, 1H), 7.65 (d, $J$ = 8.0 Hz, 1H), 7.54−7.53 (m, 3H), 7.42−7.33 (m, 4H), 7.30 (br, 1H), 7.22−7.15 (m, 3H), 7.03 (d, $J$ = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.5, 139.3, 138.6, 135.8, 134.9, 134.3, 131.5, 130.9, 130.4, 130.3, 130.1 (q, $J_{C-F}$ = 231.0 Hz), 129.8, 129.5, 129.4, 128.6, 123.3, 121.2 (q, $J_{C-F}$ = 4.0 Hz), 116.9 (q, $J_{C-F}$ = 4.0 Hz); $^{19}$F NMR ($CDCl_3$, 376 MHz) $\delta$ −62.7; IR (KBr, $cm^{-1}$) 3140, 1666, 1400; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{22}H_{16}F_3NONa$ 390.1076; found 390.1067.

*(E)-N-(3-Nitrophenyl)-2,3-diphenylacrylamide (**5aj**).* **5aj** was prepared according to general procedure 4 with a modified temperature of 80 °C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a yellow solid compound **5aj** (26 mg) in 76% yield; mp 136−138 °C; $R_f$ = 0.5 (20% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.24 (s, 1H), 8.01 (s, 1H), 7.93 (d, $J$ = 8.0 Hz, 2H), 7.57−7.54 (m, 3H), 7.49−7.44 (m, 1H), 7.38−7.36 (m, 3H), 7.23−7.15 (m, 3H), 7.03 (d, $J$ = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.6, 148.8, 139.8, 139.3, 135.5, 134.7, 134.0, 130.9, 130.5, 130.2, 130.1, 129.6, 129.5, 128.6, 125.9, 119.3, 114.9; IR (KBr, $cm^{-1}$) 3139, 1670, 1401; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{21}H_{17}N_2O_3$ 345.1234; found 345.1220.

*(E)-N-(3-Chlorophenyl)-2,3-diphenylacrylamide (**5ak**).* **5ak** was prepared according to general procedure 4 with a modified temperature of 80 °C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a yellow liquid compound **5ak** (17 mg) in 51% yield; $R_f$ = 0.8 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.97 (s, 1H), 7.55−7.50 (m, 4H), 7.35−7.30 (m, 3H), 7.22−7.14 (m, 5H), 7.07−7.01 (m, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.3, 139.3, 139.1, 135.8, 134.9 (2C), 134.4, 130.8, 130.3 (2C), 130.2, 129.4, 129.3, 128.6, 124.7, 120.2, 118.1; IR (KBr, $cm^{-1}$) 3123, 1665, 1401; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{21}H_{16}ClNONa$ 356.0813; found 356.0799.

*(E)-N-(2, 6-Dimethylphenyl)-2,3-diphenylacrylamide (**5al**).* **5al** was prepared according to general procedure 4 with a modified temperature 80 °C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a colorless liquid compound **5al** (15 mg) in 46% yield; $R_f$ = 0.5 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.96 (s, 1H), 7.53−7.46 (m, 3H), 7.43−7.41 (m, 2H), 7.20−7.13 (m, 3H), 7.09−7.05 (m, 5H), 6.70 (br, 1H), 2.18 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.6, 138.1, 136.9, 135.5, 135.1, 134.4 (2C), 130.8, 130.2, 130.1, 129.1 (2C), 128.5, 128.4, 127.6, 18.8; IR (KBr, $cm^{-1}$) 3131, 1670, 1401; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{23}H_{22}NO$ 328.1696; found 328.1681.

*(E)-2,3-Diphenyl-N-(o-tolyl)acrylamide (**5am**).*[23e] **5am** was prepared according to general procedure 4. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a yellow solid compound **5am** (21 mg) in 67% yield; mp 92−94 °C; $R_f$ = 0.6 (10% EtOAc/hexane); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.16 (d, $J$ = 8.0 Hz, 1H), 7.99 (s, 1H), 7.55−7.48 (m, 3H), 7.40−7.38 (m, 2H), 7.24−7.15 (m, 5H), 7.08−7.06 (m, 3H), 7.01 (t, $J$


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= 8.0 Hz, 1H), 1.81 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.1, 138.2, 136.5, 136.4, 135.1, 135.0, 130.8, 130.5, 130.3, 130.2, 129.2, 129.1, 128.5, 127.7, 127.2, 124.9, 121.6, 17.3; IR (KBr, $cm^{-1}$) 3125, 1666, 1401; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{22}H_{20}NO$ 314.1539; found 314.1525.

*(E)-N-(2-Chlorophenyl)-2,3-diphenylacrylamide (**5an**).* **5an** was prepared according to general procedure 4. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale-yellow solid compound **5an** (23 mg) in 70% yield; mp 107−109 °C; $R_f$ = 0.6 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 8.56 (dd, $J$ = 8.0, 1.6 Hz, 1H), 8.00 (s, 1H), 7.92 (br, 1H), 7.54−7.48 (m, 3H), 7.38 (dd, $J$ = 8.0, 1.6 Hz, 2H), 7.30−7.25 (m, 2H), 7.21−7.14 (m, 3H), 7.08−7.06 (m, 2H), 6.99 (dt, $J$ = 7.6, 1.2 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.3, 138.8, 135.8, 135.2, 135.0 (2C), 134.9, 130.9, 130.3, 130.2, 129.3, 129.2, 128.6, 128.0, 124.8, 123.2, 121.4; IR (KBr, $cm^{-1}$) 3141, 1687, 1401; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{21}H_{16}ClNONa$ 356.0813; found 356.0805.

*(E)-N-(2-Acetylphenyl)-2,3-diphenylacrylamide (**5ao**).* **5ao** was prepared according to general procedure 4. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale-yellow solid compound **5ao** (22 mg) in 65% yield; mp 141−143 °C; $R_f$ = 0.4 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 11.4 (s, 1H), 8.92 (d, $J$ = 8.0 Hz, 1H), 7.91 (s, 1H), 7.80 (dd, $J$ = 8.0, 1.2 Hz, 1H), 7.58−7.51 (m, 4H), 7.36−7.33 (m, 2H), 7.19−7.13 (m, 3H), 7.11−7.03 (m, 3H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 202.0, 167.4, 141.0, 138.5, 136.4, 135.5, 135.3, 135.0, 131.7, 130.8, 130.5, 129.8, 129.0, 128.5 (2C), 123.0, 122.8, 121.5, 28.7; IR (KBr, $cm^{-1}$) 3152, 1673, 1653, 1401; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{23}H_{19}NO_2Na$ 364.1308; found 364.1325.

*(E)-N-(Benzo[d]thiazol-2-yl)-2,3-diphenylacrylamide (**5ap**).*[23b] **5ap** was prepared according to general procedure 4. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale-yellow solid compound **5ap** (23 mg) in 65% yield; mp 198−200 °C; $R_f$ = 0.5 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 8.74 (br, 1H), 8.10 (s, 1H), 7.84 (d, $J$ = 8.0 Hz, 1H), 7.69 (d, $J$ = 8.0 Hz, 1H), 7.54−7.53 (m, 3H), 7.42 (t, $J$ = 7.6 Hz, 1H), 7.37−7.34 (m, 2H), 7.31 (t, $J$ = 8.0 Hz, 1H), 7.25−7.23 (m, 1H), 7.18 (t, $J$ = 8.0 Hz, 2H), 7.04 (d, $J$ = 7.6 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.2, 158.3, 148.8, 141.5, 134.5, 134.4, 132.7, 132.3, 131.2, 130.7, 130.3, 130.0, 129.9, 128.7, 126.6, 124.3, 121.7, 121.2; IR (KBr, $cm^{-1}$) 3140, 1666, 1401; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{22}H_{17}N_2OS$ 357.1056; found 357.1041.

*(E)-2,3-Diphenyl-N-(quinolin-8-yl)acrylamide (**5aq**).* **5aq** was prepared according to general procedure 4 with a modified temperature of 100 °C and reaction time of 7 h (as monitored by TLC). The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a brownish solid compound **5aq** (18 mg) in 50% yield; mp 168−170 °C; $R_f$ = 0.5 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 10.12 (br, 1H), 8.90 (d, $J$ = 8.0 Hz, 1H), 8.47 (br, $J$ = 4.0 Hz, 1H), 8.06 (d, $J$ = 8.0 Hz, 1H), 8.02 (s, 1H), 7.56−7.53 (m, 4H), 7.47−7.43 (m, 3H), 7.31 (dd, $J$ = 8.0, 4.0 Hz, 1H), 7.21−7.18 (m, 3H), 7.12 (d, $J$ = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.8, 148.3, 139.1, 137.9, 136.3, 136.2, 136.1, 135.3, 135.0, 130.9, 130.4, 130.0, 129.0, 128.8, 128.5, 128.1, 127.7, 121.9, 121.7, 116.6; IR (KBr, $cm^{-1}$) 3140, 1671, 1401; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{24}H_{19}N_2O$ 351.1492; found 351.1480.

*(E)-2-(Diethylamino)ethyl 4-(2,3-Diphenylacrylamido)benzoate (**5au**).* **5au** was prepared according to general procedure 4. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pale-yellow liquid compound **5au** (33 mg) in 75% yield; $R_f$ = 0.3 (100% EtOAc); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.93 (d, $J$ = 8.4 Hz, 3H), 7.52−7.49 (m, 5H), 7.36−7.34 (m, 2H), 7.30 (br, 1H), 7.18−7.12 (m, 3H), 7.99 (d, $J$ = 7.6 Hz, 2H), 4.34 (t, $J$ = 6.4 Hz, 2H), 2.82 (t, $J$ = 6.4 Hz, 2H), 2.62 (q, $J$ = 7.2 Hz, 4H), 1.05 (t, $J$ = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 166.0, 165.0, 142.4, 139.4, 136.1, 135.0, 134.5, 131.1, 130.9, 130.4, 129.4 (2C), 128.6, 126.2, 119.1, 96.5, 63.4, 51.4, 48.1, 12.4; IR (KBr, $cm^{-1}$) 3132, 1717, 1675, 1402; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{28}H_{31}N_2O_3$ 443.2329; found 443.2338.

*(E)-N-(4-Cyanophenyl)-2,3-di-p-tolylacrylamide (**5cf**).* **5cf** was prepared according to general procedure 4 with a modified temperature of 80 °C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a yellow solid compound **5cf** (26 mg) in 72% yield; mp 194−195 °C; $R_f$ = 0.2 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.93 (s, 1H), 7.59−7.54 (m, 4H), 7.40 (br, 1H), 7.33 (d, $J$ = 8.0 Hz, 2H), 7.22 (d, $J$ = 8.0 Hz, 2H), 6.99 (d, $J$ = 8.0 Hz, 2H), 6.93 (d, $J$ = 8.0 Hz, 2H), 2.46 (s, 3H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.9, 142.2, 139.9, 139.7, 139.5, 133.4, 132.9, 132.6, 132.0, 131.2, 130.9, 130.1, 129.4, 119.9, 119.2, 107.3, 21.7, 21.6; IR (KBr, $cm^{-1}$) 3288, 2222, 1643, 1406; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{24}H_{21}N_2O$ 353.1648; found 353.1660.

*(E)-2,3-Bis(4-(tert-butyl)phenyl)-N-(4-cyanophenyl)acrylamide (**5df**).* **5df** was prepared according to general procedure 4. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a yellowish liquid compound **5df** (20 mg) in 54% yield; $R_f$ = 0.4 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.94 (s, 1H), 7.57−7.55 (m, 6H), 7.39 (br, 1H), 7.28−7.26 (m, 2H), 7.18 (d, $J$ = 8.8 Hz, 2H), 6.96 (d, $J$ = 8.4 Hz, 2H), 1.42 (s, 9H), 1.25 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.9, 153.1, 152.8, 142.3, 139.6, 133.4, 132.9, 132.6, 131.9, 130.9, 129.8, 127.4, 125.6, 120.0, 119.2, 107.4, 35.2, 35.0, 31.6, 31.4; IR (KBr, $cm^{-1}$) 3384, 3130, 2962, 2218, 1692, 1404; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{30}H_{33}N_2O$ 437.2587; found 437.2578.

*(E)-N-(4-Cyanophenyl)-2,3-di-o-tolylacrylamide (**5ef**).* **5ef** was prepared according to general procedure 4 with a modified temperature of 80 °C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a yellowish liquid compound **5ef** (16 mg) in 46% yield; $R_f$ = 0.5 (10% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 8.24 (s, 1H), 7.57 (s, 4H), 7.38−7.34 (m, 1H), 7.32−7.26 (m, 3H), 7.20−7.15 (m, 2H), 7.12−7.08 (m, 1H), 6.81 (t, $J$ = 7.6 Hz, 1H), 6.59 (d, $J$ = 7.6 Hz, 1H), 2.47 (s, 3H), 2.16 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 165.6, 142.1, 138.6, 138.2, 137.9, 134.5, 134.0, 133.8, 133.5, 131.6, 130.8, 130.6, 129.7, 129.3, 128.7, 127.5, 125.8, 120.0, 119.1, 107.6, 20.5, 19.9; IR (KBr, $cm^{-1}$) 3130, 2224, 1678, 1404; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{24}H_{21}N_2O$ 353.1648; found 353.1643.

*(E)-N-(4-Cyanophenyl)-2-ethylpent-2-enamide (**5hf**).* **5hf** was prepared according to general procedure 4 with a modified temperature of 100 °C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a yellowish liquid compound **5hf** (12 mg) in 55% yield; $R_f$ = 0.7 (30% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.71−7.69 (m, 3H), 7.61 (d, $J$ = 8.8 Hz, 2H), 6.28 (t, $J$ = 7.6 Hz, 1H), 2.41 (q, $J$ = 7.6 Hz, 2H), 2.24 (pent, $J$ = 7.6 Hz, 2H), 1.08 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 168.1, 142.6, 138.6, 138.2, 133.5, 119.9, 119.2, 107.1, 21.8, 20.7, 14.0, 13.9; IR (KBr, $cm^{-1}$) 3135, 2223, 1659, 1401; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{14}H_{16}N_2ONa$ 251.1155; found 251.1153.

*(E)-N-(2-hydroxyphenyl)-2,3-diphenylacrylamide (**5av**).* **5av** was prepared according to general procedure 4. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a brown solid compound **5av** (20 mg, 63% yield) in both condition A and condition B; mp 175−177 °C; $R_f$ = 0.5 (20% EtOAc/hexane); $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 9.26 (br, 1H), 8.03 (s, 1H), 7.54−7.51 (m, 3H), 7.43 (br, 1H), 7.38−7.36 (m, 2H), 7.23−7.21 (m, 1H), 7.17 (t, $J$ = 8.0 Hz, 2H), 7.11 (dt, $J$ = 8.4, 1.6 Hz, 1H), 7.03 (dd, $J$ = 7.2, 1.6 Hz, 3H), 6.80−6.76 (m, 1H), 6.67 (d, $J$ = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) $\delta$ 167.2, 149.5, 140.3, 135.5, 134.6, 132.9 (2C), 131.0, 130.5, 130.3, 129.6, 128.6, 127.8, 125.7, 122.6, 120.5 (2C); IR (KBr, $cm^{-1}$) 3139, 1653, 1401; HRMS (ESI) $m/z$ $[M + H]^+$ calcd for $C_{21}H_{18}NO_2$ 316.1332; found 316.1311.

*3-Phenylquinolin-2(1H)-one (**5aa′**).*[20g] **5aa′** was prepared according to general procedure 9. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh size), giving a pink solid compound **5aa′** (19 mg) in 86% yield; $R_f$ = 0.2 (20% EtOAc/hexane); mp 275−276 °C; $^1H$ NMR (DMSO-$d_6$, 400 MHz) $\delta$ 11.98 (s,


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1H), 8.13 (s, 1H), 7.80−7.75 (m, 3H), 7.55−7.51 (m, 1H), 7.48−7.45 (m, 2H), 7.42−7.36 (m, 2 H), 7.23 (t, $J$ = 7.2 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (DMSO-$d_6$, 100 MHz) $\delta$ 161.9, 139.3, 138.5, 137.2, 132.4, 131.1, 129.6, 129.0, 128.8, 128.7, 122.8, 120.5, 115.6; IR (KBr, $cm^{-1}$) 3305, 1652, 1567 1400.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02700.

Mechanistic studies and control experiments, NMR spectra ($^{1}$ H, $^{13}$C, and $^{19}$F) of **3aa** −**3ha**, **5aa** −**5hf**, and **5aa′**, and X-ray crystallography data of **3aw** and **5aq** (PDF)

FAIR data, including the primary NMR FID files, for compounds **3aa** −**3ha**, **5aa** −**5hf**, and **5aa′** (ZIP)

### Accession Codes

CCDC 2036075 and 2036076 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

## ■ AUTHOR INFORMATION


### Corresponding Author

**Ponneri Chandrababu Ravikumar** − *School of Chemical Sciences, National Institute of Science Education and Research (NISER), HBNI, Bhubaneswar 752050, India;* orcid.org/0000-0002-5264-820X; Email: pcr@niser.ac.in

### Authors

**Tanmayee Nanda** − *National Institute of Science Education and Research (NISER), HBNI, Bhubaneswar 752050, India;* orcid.org/0000-0001-6875-689X

**Pragati Biswal** − *National Institute of Science Education and Research (NISER), HBNI, Bhubaneswar 752050, India*

**Bedadyuti Vedvyas Pati** − *National Institute of Science Education and Research (NISER), HBNI, Bhubaneswar 752050, India*

**Shyam Kumar Banjare** − *National Institute of Science Education and Research (NISER), HBNI, Bhubaneswar 752050, India*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.0c02700


### Notes

The authors declare no competing financial interest.

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