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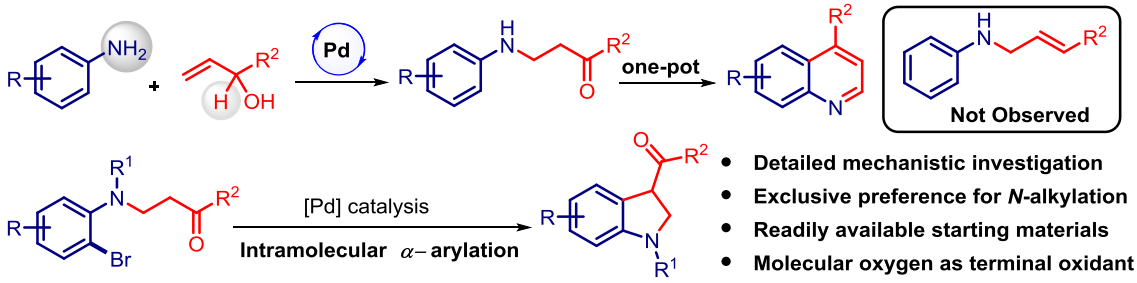
Palladium-Catalyzed Aerobic Oxidative Coupling of Allylic Alcohols with Anilines in the Synthesis of Nitrogen Heterocycles

Gangam Srikanth Kumar, Diksha Singh, Manish Kumar and Manmohan Kapur*

Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhopal Bypass Road, Bhauri, Bhopal 462066, MP, India

E-mail: mk@iiserb.ac.in

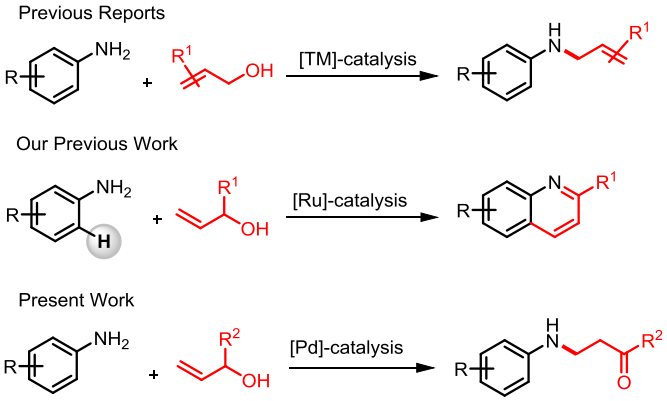


ABSTRACT: We report herein, an unprecedented and expedient Pd-catalyzed oxidative coupling of allyl alcohols with anilines to afford *β*–amino ketones which are converted into substituted quinolines in a one-pot fashion. The exclusive preference for *N*-alkylation over *N*-allylation makes this approach unique, when compared to those reported in literature. Detailed mechanistic investigations reveal that the conjugate addition pathway was the predominant one over the allylic amination pathway. The notable aspects of the present approach are the use of readily available, bench-stable, allyl alcohols and molecular oxygen as the terminal oxidant, in the process dispensing the need for unstable and costly enones. Further, we explored the synthetic utility of *β*–amino ketones through an intramolecular *α*–arylation methodology and a one-pot domino annulation thereby providing rapid access to indolines and quinolines.

INTRODUCTION

Allylic alcohols, which possess unique reactivity, have emerged as valuable building blocks for organic synthesis in the construction of complex entities.[1] This is due to the fact that allyl alcohols can react as allylating as well as alkylating agents to afford diverse products. Allyl alcohols often function as an alternative to *α, β*–unsaturated carbonyl compounds and preactivated allylating agents.[2] The palladium-catalyzed Mizoroki-Heck reaction has also been extended to non-biased olefins and allylic alcohols as coupling partners, and the cross-coupling of various arylating agents with allylic alcohols have been extensively studied.[3] This

method has advantages in accessing *β*–aryl carbonyl compounds since it avoids the use of highly electrophilic agents such as vinyl ketones and alkyl halides. Notable works by the groups of Sigman, Jiang, Lei and Kommu, among others, have made considerable contributions to this field.[4-6] Transition metal-mediated oxidation of alcohols to carbonyl compounds has revolutionized the approaches in the organic chemistry, thereby making alcohols important building blocks in synthesis.[7] Palladium-catalyzed oxidation of alcohols has witnessed important advancements and alcohols are now widely used as efficient alternatives to carbonyl compounds. In this context, the metal-catalyzed oxidative coupling of allylic alcohols with anilines would be a straightforward approach to access *β*–amino carbonyl compounds. To the best of our knowledge, the palladium-mediated oxidative coupling of allyl alcohols with anilines to directly afford *β*–amino ketones in one step has not been studied. The direct coupling of amines and allylic alcohols provides *N*-allylated products *via* allylic amination reaction (Scheme 1),[8] which is the reason why allylic alcohols have not been used in the synthesis of *β*–aminoketones. With advancements in the Tsuji-Trost allylation,[1c] direct activation of allylic alcohols leading to the electrophilic *π*–allyl intermediates, is a significant advancement in the area of nucleophilic allylation reactions. Moreover, considerable progress has been achieved in the transition metal catalyzed direct coupling of anilines with allyl alcohols to afford quinolines as the products.[9] Very recently, we reported a ruthenium-catalyzed [3+3] annulation of anilines with allyl alcohols for the synthesis of substituted quinolines (Scheme 1).[10] With our continued interest in exploring the reactivity of allyl alcohols,[10, 11] we report herein, an efficient and unprecedented palladium-catalyzed oxidative coupling of allyl alcohols with anilines to directly access *β*–amino ketones. We also extended the synthetic utility of *β*–amino ketones *via* an intramolecular *α*–arylation methodology and a one-pot domino annulation thereby providing rapid access to indolines and quinolines.



Scheme 1: Palladium catalyzed aerobic oxidative coupling of allylic alcohols with amines.

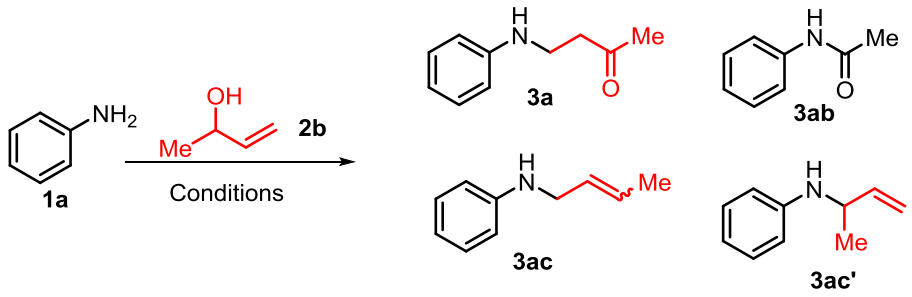
The synthesis of β–aminocarbonyl compounds have attracted great attention of chemists due to their pervasiveness as fundamental building blocks for biologically essential scaffolds. In particular, β–amino ketones serve as the critical intermediates for the synthesis of β–amino acids, β–lactam antibiotics and diverse nitrogen heterocycles.[12] The aza-Michael reaction is one of the most utilized approach for the synthesis of the β–aminocarbonyl compounds which involves a conjugate addition of amines on to α, β–unsaturated olefins.[13-17] Numerous protocols, using stoichiometric or catalytic amounts of Lewis acids[15] and transition metal catalysts[16] as well as organocatalysts[17] have been reported. Despite significant advances, there are still limitations for these approaches as the most of these methods often involve the use of strongly acidic or basic conditions which can cause polymerization of labile α, β–unsaturated carbonyl compounds in addition to long reaction times. To circumvent these challenges, the development of simple, convenient approaches for the synthesis of β–aminoketones is highly desirable. In this regard, use of allyl alcohols as an alternative to the labile vinyl ketones can be a highly user-friendly approach for the synthesis of β–aminoketones. During the preparation of our manuscript, Jiang and co-workers reported a novel Pd-catalyzed oxidative amination of homoallylic alcohols to afford β-amino ketones by using TBHP as the terminal oxidant, but the scope of this methodology was limited to only a single homoallylic alcohol.[18] The mechanism proposed involved the TBHP mediated Wacker-type oxidation of homoallylic alcohol to form 4-hydroxybutan-2-one and followed by β–hydride elimination and condensation reaction with amine to afford the product.

RESULTS AND DISCUSSION

We began our optimization studies by choosing aniline and but-3-en-2-ol as the benchmark substrates for the transformation. The most important results are summarized in Table 1 (for detailed optimization studies, see the Supporting Information (SI)). Various catalytic systems were screened, in which an initial success was obtained (20% yield, Table 1, entry 4), under palladium catalysis. Increasing the loading of $Cu(OAc)_2$ did not result in any significant increment in the yield (Table 1, entry 5). The desired product was obtained in 30% yield when the acetate source was changed (Table 1, entry 7). Of all the additives scanned, NaOAc worked the best (see the Supporting Information (SI) for details). Interestingly, use of protic conditions led to a considerable increase in the yield (Table 1, entry 8). While screening various Brønsted-acids, AcOH was found to be the best for the transformation. The use of TFA yielded the mixture *N*-allylated products **3ac** and **3ac'** (Table 1, entries 8-12). Increasing

the catalyst loading to an optimum of 10 mol% improved the transformation considerably (Table 1, entry 9).

Table 1. Optimization studies[a]



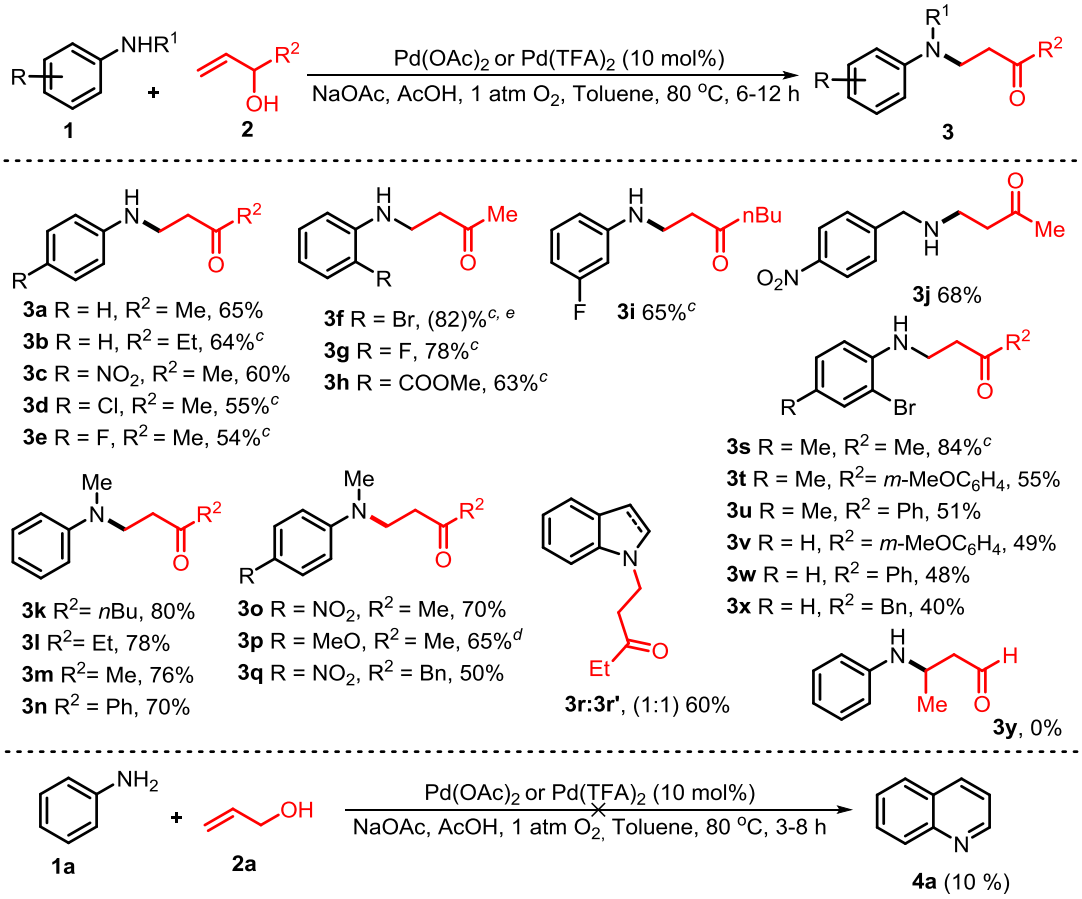
entry	catalyst	additive/oxidant	acid/base	(%) yield of **3a**
1	$Co(OAc)_2$	NaOAc (1 equiv.)	AcOH	0
2	$CoBr_2$	NaOAc (1 equiv.)	AcOH	0
3	$PdCl_2$	NaOAc (1 equiv.)	AcOH	0
4	$Pd(OAc)_2$	$Cu(OAc)_2$ (0.2 equiv.)	K_2CO_3	20[b,c]
5	$Pd(OAc)_2$	$Cu(OAc_{)2}$ (1 equiv.)	K_2CO_3	10[b,c]
6	$Pd(OAc)_2$	CsOAc (1 equiv.)	K_2CO_3	0
7	$Pd(OAc)_2$	NaOAc (2 equiv.)	K_2CO_3	30[c]
8	$Pd(OAc)_2$	NaOAc (2 equiv.)	AcOH	44[c]
9	$Pd(OAc)_2$	NaOAc (1 equiv.)	AcOH	65
10	$Pd(TFA)_2$	NaOAc (1 equiv.)	AcOH	63
11	$Pd(OAc)_2$	NaOAc (1 equiv.)	PivOH	30
12	$Pd(OAc)_2$	NaOAc (1 equiv.)	TFA	**3ab**(10)[b] /**3ac:3ac'**(20)
13	$Pd(OAc)_2$	TBHP (2 equiv.)	-	30[c,d]
14	$Pd(OAc)_2$	NaOAc (1 equiv.)	AcOH	3b(50)[e]

[a]Reaction conditions: unless otherwise mentioned all reactions performed with **1a** (0.3 mmol), **2a** (0.6 mmol), catalyst (0.03 mmol), 2 equiv. acid/base, O_2 (1 atm) and 1.5 mL Toluene; [b]GC yield; [c]0.015 mmol catalyst is used; [d]MeCN as solvent and under air; [e]AcOH as solvent.

Of the numerous solvents screened, toluene was found to be the optimal solvent for the transformation (see the Supporting Information (SI)). The use of AcOH as the solvent led to the exclusive formation of **3ab**. As expected, a control reaction carried out in the absence of the palladium catalyst and O_2, did not yield the desired product (see the Supporting Information (SI)).

With the optimal reaction conditions in hand, we then explored the substrate scope for the transformation. As it is evident from Scheme 2, the substrate scope as well as functional group tolerance was found to be broad enough to be a practical method. The reaction worked well with most of the anilines and allyl alcohols screened. Electronic factors were well-tolerated on the aniline (**3a-3i**, Scheme 2). Further, benzylamine was also successfully transformed into the desired product (**3j**, Scheme 2). The reaction was also compatible with 2^o amines to afford the desired products in moderate yields (**3k-3q**, Scheme 2). Interestingly, electron-rich anilines were found to be highly reactive leading to complex mixtures under the standard conditions. In such cases, decreasing the catalyst loading as well as the reaction temperature, led to the formation of the desired product (**3p**, Scheme 2). Unfortunately this compound was extremely susceptible to retro aza-Michael reaction, thereby reverting back to the parent aniline during silica gel column chromatography. Interestingly, the use of indoline led to the formation of mixture of products (**3r: 3r'** 1:1 ratio) and the crude mixture was subjected to aromatization to afford *N*-alkylated indole (see the Supporting Information (SI)). Except benzyl amine, other alkyl amines were not suitable partners for this reaction.

Notably, halogen substituted anilines were easily transformed into desired products in moderate yields, increasing the scope for further post-functionalization of the C–X bonds (**3f, 3s-3x,** Scheme 4). In all cases, the reaction showed excellent selectivity (*N*-alkylation *versus* *N*-allylation) and majority of the substrates gave monoalkylated products. A notable exception was also observed when crotyl alcohol failed to yield the desired product (**3y,** Scheme 2). Surprisingly, the unsubstituted allyl alcohol yielded a complex mixture and the formation of the quinoline product was observed in low yield (**4a,** Scheme 2). This can be explained by the fact that the product 3-(phenylamino)propanal is highly reactive and undergoes facile cyclization to form quinoline (**4a,** Scheme 2). This intriguing nature of cyclization led us to develop a one-pot domino synthesis of quinolines as these are one of the most sought *N*-heterocycles in synthetic chemistry owing to their biological prevalence and attractive applications (Scheme 3).[19]

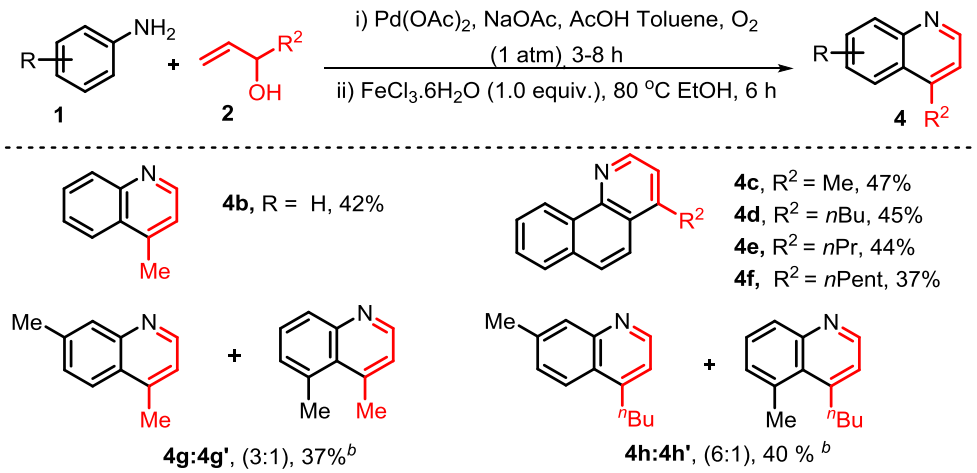


Scheme 2: Substrate Scope for Pd-catalyzed aerobic oxidative coupling of allylic alcohols with amines[a,b].

[a]Unless otherwise mentioned all reactions were performed with **1a** (0.3 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ or $Pd(TFA)_2$ (0.03 mmol), NaOAc (0.3 mmol), AcOH (0.6 mmol) and 1.5 mL Toluene under 1 atm O_2; [b]All yields are isolated yields; [c]$Pd(TFA)_2$ used as catalyst; [d]0.015 mmol $Pd(OAc)_2$ is used and crude yield. [e]Reaction performed on 1 mmol scale.

The *β*–aminoketones, obtained in the first step, were subjected to Lewis acid-catalyzed electrophilic annulation in a one-pot fashion using $FeCl_3$, to afford 4-substituted quinolines (Scheme 3). Interestingly, these observations are completely opposite to our previous report on ruthenium-catalyzed [3+3] annulation of anilines with allyl alcohols where we observed the formation of 2-substituted quinolines (Scheme 1).[10] In that case, we had synthesized 2-substituted quinolines *via* nucleophilic attack of aniline onto the carbonyl moiety, whereas in the present case, aromatic electrophilic substitution reaction (S_EAr mechanism) of

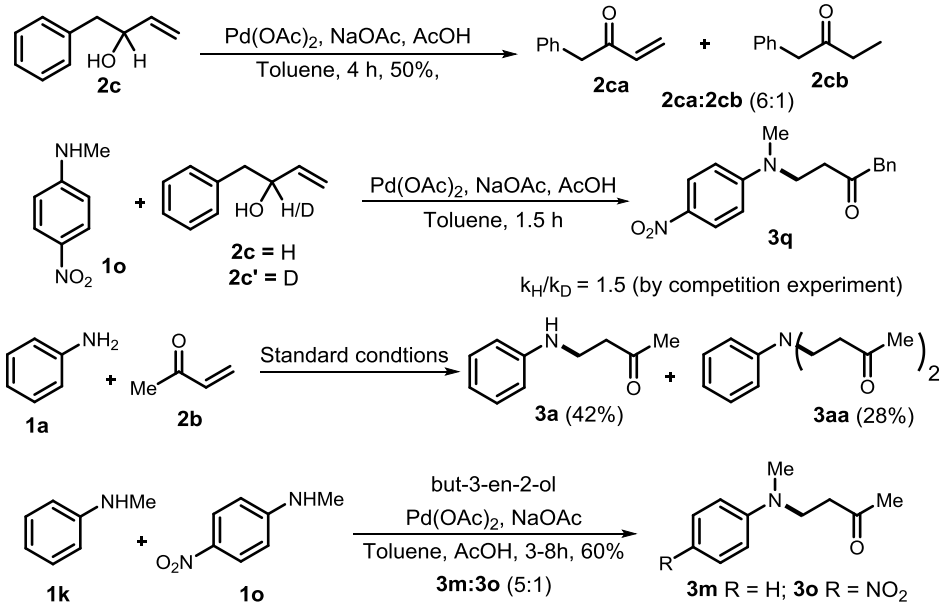
β–aminoketones is involved. As expected, *α*–naphthyl substituted anilines afforded benzo[h]quinolines in moderate yields (**4b-e**, Scheme 3) and *meta*-substituted anilines afforded a mixture of regioisomers (**4g**, **4h**, Scheme 3).



Scheme 3. One-pot synthesis of 4-substituted quinolines[a]

[a]All yields are isolated yields; [b]ratio determined by ^{1}H NMR of the crude reaction mixture.

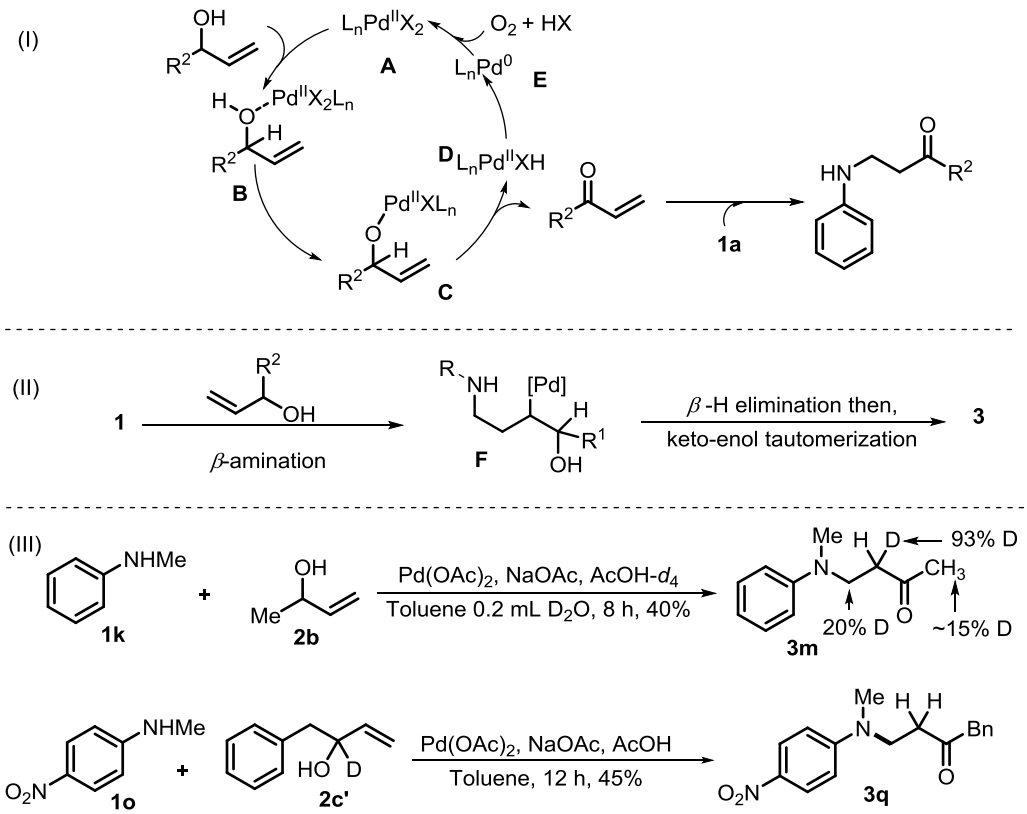
To get more insight into the reaction pathway, control studies were carried out. Critical information was obtained when 1-phenyl but-3-en-2-ol (**2c**) was reacted under standard conditions (Scheme 4). Ketones **2ca** and **2cb** were detected and isolated, suggesting that the oxidation of the allylic alcohol may be the initial step in the reaction.



Scheme 4: Control reactions

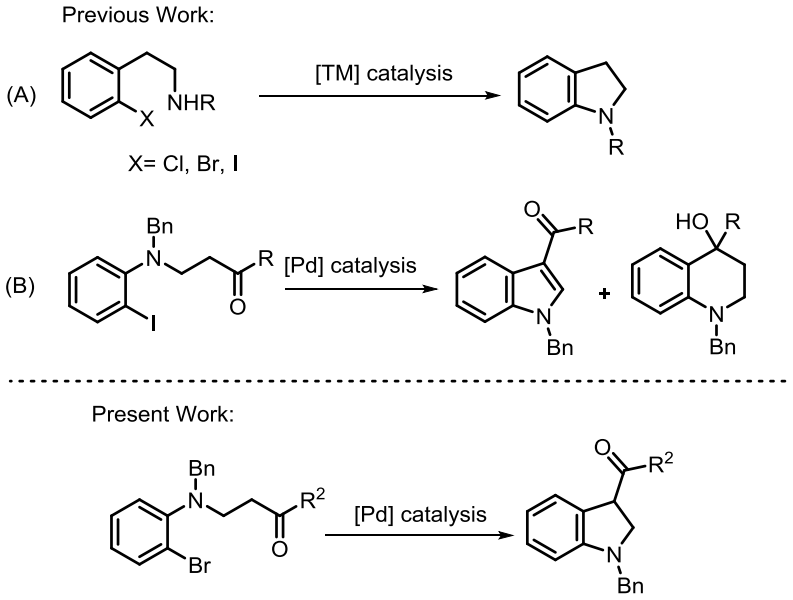
A moderate value of kinetic isotope effect (k_H/k_D = 1.50) was obtained for the competitive experiment performed with **2c** and **2c'** thereby suggesting that the cleavage of the allylic C-H bond may be involved in the rate-limiting step (Scheme 4). The use of methyl vinyl ketone instead of but-3-en-2-ol resulted mixture of mono- and di-*N*-alkylated products. In addition, a competitive experiment conducted between electronically biased anilines and but-3-en-2-ol under optimized conditions (**1k**, **1o** Scheme 4), resulted in the formation of corresponding products in **3m**: **3o** 5:1 ratios, as shown in Scheme 4. This evidence supports the pathway involving conjugate addition of amines onto the *in situ* formed enones.

Based on the previous reports and our observations,[4, 5] a plausible reaction pathway is proposed in Scheme 5, which involves the initial oxidation of allyl alcohols to enones, followed by aza-Michael addition to afford the desired products. Coordination of the allylic alcohol to the catalyst to form complex **B** is followed by deprotonation to form Pd–alkoxide complex **C** and a β–hydride elimination to form the enone. It is possible that Pd-catalyzed amination with the allylic alcohol may also result in **F** which upon β–H elimination and keto-enol tautomerization could lead to the product (Scheme 5, Pathway II). However, when the reaction was carried out with AcOH-d_4 and D_2O, considerable deuterium incorporation was observed at the α–position of the carbonyl group (Scheme 5).



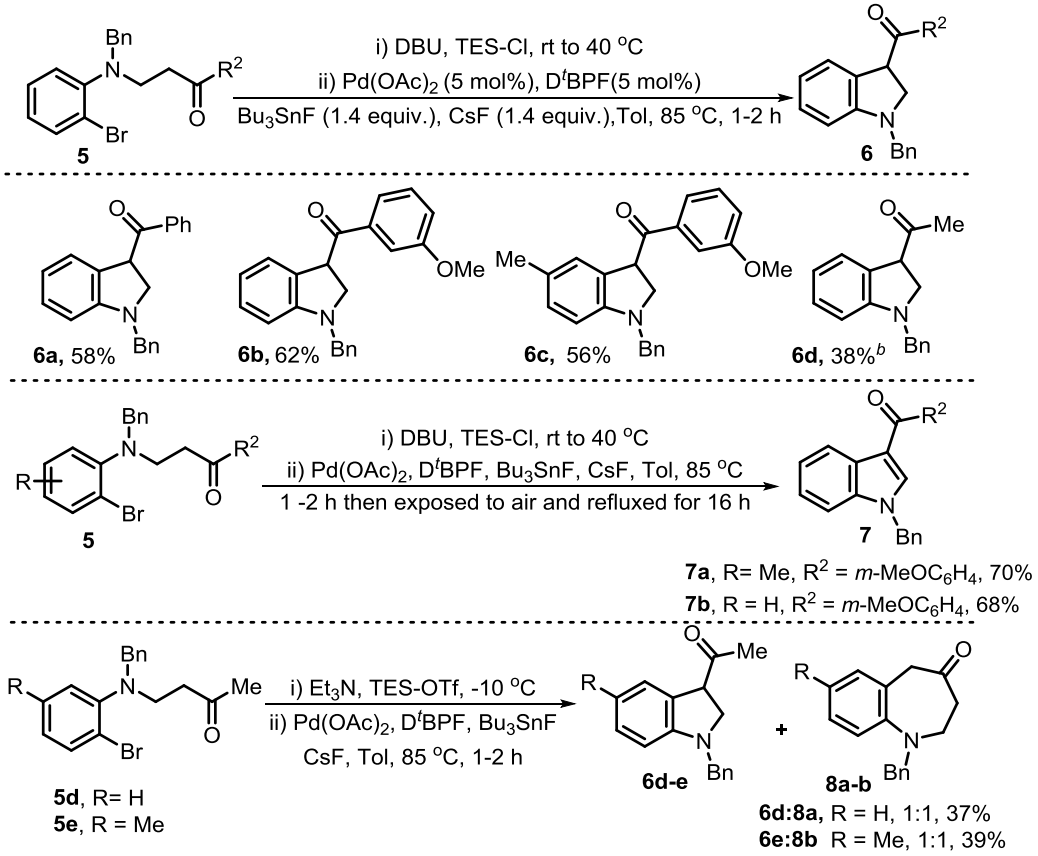
Scheme 5: Plausible Mechanism

A control reaction with 1-phenylbut-3-en-2-d-2-ol (**2c'**) with **1o** did not result in any deuterium incorporation in the corresponding product **3q** (Scheme 5). These experiments clearly indicate that the conjugate addition pathway (Scheme 5, Pathway I) was the predominant one over the allylic amination pathway (Scheme 5, Pathway II). As the halogen functional groups were well-tolerated in the transformation, post-functionalization of C-X bonds can be further utilized to construct important *N*-heterocycles. 3-acyl indolines are important structural motifs as they are ubiquitously present in many natural products and several important pharmaceutically active compounds.[20] The importance of indolines in medicinal chemistry has made them relevant targets in synthetic chemistry. The palladium catalyzed Buchwald–Hartwig carboamination is one of the most widely-utilized strategies for the synthesis of indolines. This approach involves C-N bond coupling between an aryl halide and an amine for the synthesis of the indoline ring through aryl amination (Scheme 6 (A)).[21a] Over the years, this approach has undergone tremendous improvements for the construction of indolines.[21b] However, the synthesis of indolines using sp^2-sp^3 C-C bond coupling is not much explored. In this context, intramolecular α-arylation of (2-bromoanilino)ketones to access indolines and indoles would be a highly appealing approach. Palladium-catalyzed α–arylation of carbonyl compounds stands out as one of the most valuable synthetic tools for the construction of C-C bond.[22] Sole and co-workers carried out an extensive study on the chemoselective Pd-catalyzed cyclization reaction of (2-iodoanilino)carbonyl compounds and provided insights into ketone α–arylation and carbonyl addition dichotomy (Scheme 6 (B)).[23] Intramolecular α-arylation reaction of β–(2-iodoanilino)-ketones using $Pd(PPh_3)_4$ as the catalyst invariably afforded mixtures of products as shown in Scheme 6 (B). The best ratio of α– arylation product was obtained with $[Pd_2(dba)_3]$ as the catalyst, KO^{t}Bu as the base in the presence of an excess of phenol in THF and Xanthphos as the ligand (Scheme 6 (B)).[23b] In this context, we initially made an attempt to synthesize various *N*-heterocycles through a base mediated, palladium-catalyzed α–arylation of β–(2-bromoanilino)-ketones (**5**), however these efforts were unsuccessful. The efforts led to formation of the ketone addition product along with other side products (see the Supporting Information (SI)). Inspired by our previous work on α–arylation of enones,[24] we developed an approach for the synthesis of indolines utilizing an intramolecular α–arylation of silylenol ethers of β–aminoketones (Scheme 7). The formation of silylenol ethers followed by Pd-catalyzed α–arylation led to the formation of the 3-substituted indolines in a highly selective fashion (**6a-6d**, Scheme 7).



Scheme 6: Palladium catalyzed synthesis of Indolines

Trace amounts of 3-substituted indoles were also observed along with the indoline products presumably arising from the oxidation of indolines under the reaction conditions. Extended reaction time led to the exclusive formation of 3-substituted indoles (**7a, 7b,** Scheme 7). The use of Et_3N, TES-OTf for the enolization of **5d** and **5e** led to the formation of azepines and 3-acylindolines as the multiple enolizable positions were accessible (**6d, 8a, 6e, 8b** Scheme 7).



Scheme 7: Intramolecular α–arylation of silylenol ethers of β–aminoketones.[a]

[a]All Pd- catalyzed α–arylation reactions were carried out with $Pd(OAc)_2$ (0.05 mmol), D^tBPF (0.05 mmol), Bu_3SnF (0.42 mmol), CsF (0.42 mmol) in toluene. [b]Trace amounts (~5%) of azepine product (8a) was also observed

Conclusion:

In summary, a simple and unprecedented palladium-catalyzed oxidative coupling of allyl alcohols with anilines to provide a rapid access to β–amino ketones in highly selective fashion has been developed. The transformation is unique since it discloses a new reactivity pattern of allylic alcohols with amines. The highlight of the present approach is the use of readily available, bench-stable allyl alcohols and molecular oxygen as the terminal oxidant. We have also demonstrated new utility for the β–amino ketones in the synthesis of various *N*-heterocycles using a α–arylation methodology and a one-pot domino annulation. For better understanding of the mechanism, detailed mechanistic investigations were carried out and studies revealed that the conjugate addition pathway was the predominant one over the allylic amination pathway.

Experimental Section:

(1) General Methods:

All commercially available compounds were used without purification. Unless otherwise noted, all reactions were performed in oven-dried glassware. All reactions were run under argon or nitrogen atmosphere. All solvents used in the reactions were purified before use. Tetrahydrofuran and toluene were distilled from sodium and benzophenone, whereas dry dichloromethane, dioxane were distilled from CaH_2. [25] Petroleum ether with a boiling range of 40–60 °C was used. Melting points are uncorrected. ^1H, and ^{13}C NMR: Recorded on 400 and 500 MHz NMR Spectrometers; spectra were recorded at 295 K in $CDCl_3$; chemical shifts are calibrated to the residual proton and carbon resonance of the solvent: $CDCl_3$ (^1H δ 7.25; ^{13}C δ 77.0). LC-HRMS: Recorded on a Q-ToF with electron spray ionization (ESI) or Atmospheric pressure chemical ionization (APCI). GC-HRMS: Performed GC-QToF (with Electron Impact (EI), 70eV) using DB-5 column. GC-LRMS: Performed GC-MS (EI 70 eV) using DB-5 column. IR were recorded as thin films between KBr plates.

(2) General procedure for the synthesis of β-aminoketones:

(i) **Synthesis of β-aminoketones (A):** In a Schlenk tube equipped with a stir bar, aniline (0.3 mmol) and allylic alcohol (0.6 mmol) were dissolved in dry toluene (1.5 mL). The reaction mixture was degassed for 5-10 min followed by the addition of $Pd(OAc)_2$ (0.03 mmol), NaOAc (0.3 mmol), and AcOH (0.6 mmol). The tube was attached with an oxygen balloon and the reaction mixture was vigorously stirred at 80 ^oC for 12-16 h during which the reaction was found to be complete (as indicated by TLC). The reaction mixture was then cooled and diluted with EtOAc and washed with $NaHCO_3$ and brine. The organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by a silica gel flash column chromatography to result in the desired product.

2.1. 4-(phenylamino)butan-2-one (3a):[26] Yield: 65% (32 mg); Physical appearance: Yellow oil; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.15 (t, J = 8.0, 2H), 6.69 (t, J = 7.4 Hz, 1H), 6.59 (d, J = 8.0 Hz, 2H), 4.22-3.63 (bs, 1H), 3.40 (t, J = 6.2 Hz, 2H), 2.73 (t, J = 6.2 Hz, 2H), 2.15 (s, 3H); **IR** (KBr, cm^{-1}): 3394, 2918, 1709, 1601, 1504, 750; **GC LR-MS**: 163.1 (30%) $[M]^+$, 145 (10%), 106 (100%).

2.2. 1-(phenylamino)pentan-3-one (3b):[26] Yield: 64% (35 mg); Physical appearance: Pale-yellow oil; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.24 – 7.16 (m, 2H), 6.76 – 6.70 (m, 1H), 6.67 – 6.59 (m, 2H), 4.17 – 3.83 (bs, 1H), 3.45 (t, J = 6.0 Hz, 2H), 2.75 (t, J = 6.0 Hz, 2H), 2.46 (q, J = 7.2Hz, 2H), 1.08 (t, J = 7.2 Hz, 3H); **IR** (KBr, cm^{-1}): 3396, 2915, 1715, 1601, 1505, 748; **ESI-LRMS**: 178.1 $[M+H]^+$.

2.3. 4-((4-nitrophenyl)amino)butan-2-one (3c): Yield: 60% (38 mg); Physical appearance: Yellow Solid; M.p. 88-90 ^oC; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.02 (d, J = 9.0 Hz, 2H), 6.4 (d, J = 9.0 Hz, 2H), 5.10 -4.90 (bs, 1H), 3.47 (t, J = 6.0 Hz, 2H), 2.76 (t, J = 6.0 Hz, 2H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.4, 153.0, 138.0, 126.5, 111.0, 42.1, 37.6, 30.3; **IR** (KBr, cm^{-1}): 3373, 2918, 1707, 1595, 1305, 837; **ESI-HRMS**: Calculated for $C_{10}H_{13}N_2O_3$ $[M+H]^+$ 209.0921, found 209.0908.

2.4. 4-((4-chlorophenyl)amino)butan-2-one (3d):[26] Yield: 55% (32 mg); Physical appearance: Brown solid; M.p. 54-56 ^oC; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.13 (d, J = 8.5 Hz, 2H), 6.54 (d, J = 8.5 Hz, 2H), 4.22-3.94 (bs, 1H), 3.40 (t, J = 6.0 Hz, 2H), 2.75 (t, J = 7.0 Hz, 2H), 2.19 (s, 3H); **IR** (KBr, cm^{-1}): 3382, 2929, 1715, 1596, 841; **GC-LRMS**: 197(40%) $[M]^+$, 180 (10%), 140 (100%).

2.5. 4-((4-fluorophenyl)amino)butan-2-one (3e):[27] Yield: 54% (29 mg); Physical appearance: Brown oil; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.93 – 6.82 (m, 2H), 6.57 – 6.48 (m, 2H), 3.92 (bs, 1H), 3.35 (t, J = 6.0 Hz, 2H),

2.72 (t, *J* = 6.0 Hz, 2H), 2.14 (s, 3H); **IR** (KBr, cm^{-1}): 3390, 2922, 1714, 1505, 822; **GC-LRMS**: 181(50%) $[M]^+$, 138 (10%), 124 (100%).

2.6. 4-((2-bromophenyl)amino)butan-2-one (3f): Yield: 82% (197 mg) (Reaction performed on 1 mmol scale and excess of but-3-en-2-ol was added after 12 h); Physical appearance: Yellow oil; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.24 – 7.15 (m, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.60–6.55 (m, 1H), 4.72- 4.43 (bs, 1H), 3.48 (t, *J* = 6.4 Hz, 2H), 2.76 (td, *J* = 6.4, 1.5 Hz, 2H), 2.17 (d, *J* = 1.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.4, 144.6, 132.6, 128.5, 118.0, 111.2, 110.1, 42.5, 38.3, 30.4; **IR** (KBr, cm^{-1}): 3394, 2922, 1712, 1594, 740; **ESI-HRMS**: Calculated for $C_{10}H_{12}BrNO$ $[M+Na]^+$ 263.9994 and 265.9974, found 263.9990 and 265.9980.

2.7. 4-((2-fluorophenyl)amino)butan-2-one (3g): Yield: 78% (42 mg); Physical appearance: Yellow oil; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.03 – 6.88 (m, 2H), 6.73 – 6.65 (m, 1H), 6.65 – 6.57 (m, 1H), 4.34 – 4.04 (bs, 1H), 3.42 (t, *J* = 6.4 Hz, 2H), 2.74 (t, *J* = 6.4 Hz, 2H), 2.15 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.5, 151.7 (*J* = 234.8 Hz), 136.2 (11.2 Hz), 124.6 (*J* = 3.4 Hz), 116.9 (*J* = 6.8 Hz), 114.6 (*J* = 18.6 Hz), 112.1 (*J* = 2.3 Hz), 42.7, 38.0, 30.3; **^{19}F NMR** (471 MHz, $CDCl_3$): δ -136.1; **IR** (KBr, cm^{-1}): 3404, 2922, 1712, 1620, 744; **ESI-HRMS**: Calculated for $C_{10}H_{13}FNO$ $[M+H]^+$ 182.0976, found 182.0967.

2.8. Methyl 2-((3-oxobutyl)amino)benzoate (3h): Yield: 63% (42 mg); Physical appearance: Yellow oil; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.92 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.82 – 7.73 (bs, 1H), 7.41 – 7.36 (m, 1H), 6.74 – 6.69 (m, 1H), 6.65 – 6.59 (m, 1H), 3.87 (s, 3H), 3.53 (q, *J* = 6.8 Hz, 2H), 2.83 (t, *J* = 6.8 Hz, 2H), 2.22 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 207.0, 169.0, 150.7, 134.6, 131.8, 114.8, 111.0, 110.3, 51.5, 42.9, 37.4, 30.4; **IR** (KBr, cm^{-1}): 3385, 2900, 1716, 1684, 1280, 767; **ESI-HRMS**: Calculated for $C_{12}H_{15}NO_3Na$ $[M+Na]^+$ 244.0944, found 244.0936.

2.9. 1-((3-fluorophenyl)amino)heptan-3-one (3i): Yield: 65% (44 mg); Physical appearance: Reddish-oil; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.10 – 7.01 (m, 1H), 6.40 – 6.29 (m, 2H), 6.29 – 6.23 (m, 1H), 4.21-4.06 (bs, 1H), 3.37 (t, *J* = 6.0 Hz, 2H), 2.68 (t, *J* = 6.0 Hz, 2H), 2.39 (t, *J* = 7.4 Hz, 2H), 1.59 – 1.49 (m, 2H), 1.35 – 1.22 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 210.4, 165.4, 164.1 (*J* = 242.6 Hz), 149.4 (*J* = 10.6 Hz), 130.3 (d, *J* = 10.4 Hz), 108.8 (*J* = 2.2 Hz), 99.5 (26.5 Hz), 42.9, 41.4, 38.3, 25.8, 22.3, 13.8; **^{19}F NMR** (470 MHz, $CDCl_3$): δ -112.8; **IR** (KBr, cm^{-1}): 3393, 2955, 1703, 1622, 756; **ESI-HRMS**: Calculated for $C_{13}H_{19}NFO$ $[M+H]^+$ 224.1445, found 224.1435.

2.10. 1-((4-nitrobenzyl)amino)propan-2-one (3j): Yield: 68% (46 mg); Physical appearance: Reddish oil; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 5.38 – 4.01 (bs, 1H), 2.77 (t, *J* = 6.8 Hz, 2H), 2.68 (t, *J* = 6.8 Hz, 2H), 2.22 (s, 2H), 2.18 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.6, 147.2, 146.3, 129.5, 123.6, 61.5, 52.0, 41.9, 41.6, 30.1; **IR** (KBr, cm^{-1}): 2922, 1712, 1519, 1265, 737; **ESI-HRMS**: Calculated for $C_{12}H_{17}N_2O_3$ $[M+H]^+$ 237.1234, found 237.1230.

2.11. 1-(methyl(phenyl)amino)heptan-3-one (3k): Yield: 80% (52 mg); Physical appearance: Pale-yellow oil; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29 – 7.18 (m, 2H), 6.75 – 6.64 (m, 3H), 3.64 (t, *J* = 7.0 Hz, 2H), 2.90 (s, 3H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.38 (t, *J* = 7.4 Hz, 2H), 1.62 – 1.43 (m, 2H), 1.34 – 1.19 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 210.5, 148.7, 129.3, 116.6, 112.4, 47.5, 43.3, 39.3, 38.5, 25.8, 22.3, 13.8; **IR** (KBr, cm^{-1}): 2971, 1710, 1600, 1506, 750; **ESI-HRMS**: Calculated for $C_{14}H_{22}NO$ $[M+H]^+$ 220.1696, found 220.1711.

2.12. 1-(methyl(phenyl)amino)pentan-3-one (3l): Yield: 78% (44 mg); Physical appearance: Pale-yellow oil; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29 – 7.20 (m, 2H), 6.80 – 6.66 (m, 3H), 3.65 (t, *J* = 7.0 Hz, 2H), 2.92 (s, 3H), 2.67 (t, *J* = 7.0 Hz, 2H), 2.42 (q, *J* = 7.2 Hz, 2H), 1.06 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 210.7, 148.7, 129.3, 116.6, 112.5, 47.6, 39.0, 38.5, 36.7, 7.7; **IR** (KBr, cm^{-1}): 2975, 1712, 1604, 1510, 750; **ESI-HRMS**: Calculated for $C_{12}H_{18}NO$ $[M+H]^+$ 192.1383, found 192.1371.

2.13. 4-(methyl(phenyl)amino)butan-2-one (3m): Yield: 76% (40 mg); Physical appearance: Pale-yellow oil; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28 – 7.19 (m, 2H), 6.77 – 6.63 (m, 3H), 3.63 (d, *J* = 6.8 Hz, 2H), 2.91 (s, 3H), 2.69(t, *J* = 6.8 Hz, 2H), 2.14 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 208.0, 148.7, 129.3, 116.7, 112.5, 47.3, 40.3, 38.5, 30.6; **IR** (KBr, cm^{-1}): 2921, 1714, 1609, 1505, 751; **ESI-HRMS**: $C_{11}H_{16}NO$ $[M+H]^+$ 178.1226, found 178.1227.

2.14. 3-(methyl(phenyl)amino)-1-phenylpropan-1-one (3n): Yield: 70% (50 mg); Physical appearance: Pale-yellow oil; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99 – 7.94 (m, 2H), 7.63 – 7.55 (m, 1H), 7.52 – 7.45 (m, 2H), 7.33 – 7.25 (m, 2H), 6.83 – 6.72 (m, 3H), 3.88 (d, *J* = 2.0 Hz, 2H), 3.27 (d, *J* = 2.0 Hz, 2H), 3.01 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.5, 148.6, 136.9, 133.2, 129.4, 128.7, 128.1, 116.6, 112.4, 48.0, 38.6, 35.2; **IR** (KBr, cm^{-1}): 2923, 1690, 1598, 1445, 1204, 748; **ESI-HRMS**: Calculated for $C_{16}H_{18}NO$ $[M+H]^+$ 240.1383, found 240.1379.

2.15. 4-(methyl(4-nitrophenyl)amino)butan-2-one (3o): Yield: 70% (47 mg); Physical appearance: Yellow Solid; M.p. 93-95 ^{o}C; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.15 – 8.10 (m, 2H), 6.81 – 6.38 (m, 2H), 3.76 (t, *J* = 6.8 Hz, 2H), 3.11 (s, 3H), 2.80 (t, *J* = 6.8 Hz, 2H), 2.21 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 206.6, 152.9, 137.2, 126.3, 110.3, 46.9, 40.5, 39.0, 30.5; **IR** (KBr, cm^{-1}): 2920, 1705, 1510, 1345, 737; **ESI-HRMS**: Calculated for $C_{11}H_{14}N_2O_3Na$ $[M+Na]^+$ 245.0897, found 245.0917.

2.16. 4-((4-methoxyphenyl)(methyl)amino)butan-2-one (3p): Yield: 65% (40 mg); Physical appearance: Pale-yellow oil; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.84 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 3.76 (s, 3H), 3.55 (d, *J* = 6.8 Hz, 2H), 2.84 (s, 3H), 2.66 (t, *J* = 6.8 Hz, 2H), 2.14 (s, 3H); **^{13}C NMR:**(100 MHz, $CDCl_3$): δ 208.1, 152.1, 143.7, 115.2, 114.8, 55.7, 48.6, 40.2, 39.3, 30.57; **IR** (KBr, cm^{-1}): 2926, 1706, 1243, 1033, 814; **ESI-HRMS**: Calculated for $C_{12}H_{18}NO_2$, $[M+H]^+$ 208.1332, found 208.1303.

2.17. 4-(methyl(4-nitrophenyl)amino)-1-phenylbutan-2-one (3q): Yield: 50% (45 mg); Physical appearance: Yellow Solid; M.p. 57-59 ^{o}C; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.12 – 7.98 (m, 2H), 7.39 – 7.29 (m, 3H), 7.25 – 7.15 (m, 2H), 6.50 (d, *J* = 9.4 Hz, 2H), 3.77 – 3.65 (m, 4H), 3.00 (d, *J* = 1.0 Hz, 3H), 2.79 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 206.5, 152.8, 137.1, 133.4, 129.4, 129.0, 127.4, 126.2, 110.2, 50.9, 47.3, 38.9, 38.5; **IR** (KBr, cm^{-1}): 2918, 1715, 1592, 1305, 823, 744; **ESI-HRMS**: Calculated for $C_{17}H_{19}N_2O_3$ $[M+H]^+$ 299.1390, found 299.1379.

2.18. 1-(1H-indol-1-yl)pentan-3-one (3r'): Yield: 60% (36 mg); Physical appearance: Brown solid; M.p. 56-58; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69 (m, 1H), 7.40 – 7.33 (t, 1H), 7.28 – 7.22 (m, 1H), 7.17 – 7.10 (t, 2H), 6.50 (dd, *J* = 3.2, 0.8 Hz, 1H), 4.47 (t, *J* = 6.8 Hz, 2H), 2.94 (t, *J* = 6.8 Hz, 2H), 2.37 (d, *J* = 7.2 Hz, 2H), 1.04 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.2, 135.6, 128.7, 128.2, 121.6, 121.1, 119.4, 109.1, 101.4, 42.2, 40.8, 36.6, 7.5; **IR** (KBr, cm^{-1}): 2924, 1710, 1605, 1340, 840; **ESI-HRMS**: Calculated for $C_{13}H_{15}NONa$ $[M+Na]^+$ 224.1046, found 224.1042.

2.19. 4-((2-bromo-4-methylphenyl)amino)butan-2-one (3s): Yield: 84% (64 mg); Physical appearance: Yellow oil; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28 (s, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.59 (d, *J* = 8.2 Hz, 1H), 4.41 (bs, 1H), 3.46 (t, *J* = 4.6 Hz, 2H), 2.79 (t, *J* = 6.4 Hz, 2H), 2.24 (s, 3H), 2.20 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.5, 142.3, 132.9, 129.0, 127.6, 111.3, 110.1, 42.6, 38.6, 30.4, 20.0; **IR** (KBr, cm^{-1}): 3396, 2921, 1710, 1598, 760; **ESI-HRMS**: Calculated for $C_{11}H_{14}BrNONa$ $[M+Na]^+$ 278.0151 and 280.0131, found 278.0126 and 280.0108.

(ii) General procedure for the synthesis of *β*-aminoketones (B):

In a Schlenk tube equipped with a stir bar, 1-phenylprop-2-en-1-ol (0.6 mmol) was dissolved in dry toluene (1.5 mL). The reaction mixture was degassed for 5-10 min followed by the addition of $Pd(OAc)_2$ (0.03 mmol), NaOAc (0.3 mmol), and AcOH (0.6 mmol). The tube was attached with an oxygen balloon and the reaction mixture was vigorously stirred at 80 ^oC for 4-6 h. After cooling to the room temperature, aniline (0.3 mmol) was added and the resulting reaction mixture was allowed to stir at 60 ^oC for 12 – 18 h. This was then diluted with EtOAc and washed with $NaHCO_3$ and brine. The organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography to result in the desired product.

2.20. 3-((2-bromo-4-methylphenyl)amino)-1-(3-methoxyphenyl)propan-1-one (3t): Yield: 55% (57 mg); Physical appearance: Yellow solid; M.p. 64-66 ^oC; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.51 (s, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.28 (s, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 4.55 (bs, 1H), 3.87 (s, 3H), 3.65 (t, *J* = 6.4 Hz, 2H), 3.31 (t, *J* = 6.4 Hz, 2H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.7, 158.9, 142.4, 138.1, 133.0, 129.7, 129.0, 127.6, 120.7, 119.9, 112.2, 111.4, 110.1, 55.5, 39.1, 37.9, 20.0; **IR** (KBr, cm^{-1}): 2910, 1690, 1604, 1249, 749; **ESI-HRMS**: Calculated for $C_{17}H_{19}BrNO_2$ $[M+H]^+$ 348.0594 and 350.0573, found 348.0570 and 350.0553.

2.21. 3-((2-bromo-4-methylphenyl)amino)-1-phenylpropan-1-one (3u): Yield: 51% (48 mg); Physical appearance: Pale-yellow oil; TLC *Rf* 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.64 – 7.55 (m, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.28 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 3.67 (t, *J* = 6.4 Hz, 2H), 3.33 (t, *J* = 6.4 Hz, 2H), 2.22 (s, 3H), 4.73-4.40 (bs, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.9, 142.4, 136.8, 133.4, 133.0, 129.0, 128.7, 128.1, 127.6, 111.4, 110.1, 39.0, 37.7, 20.0; **IR** (KBr, cm^{-1}): 2918, 1734, 1610, 1489, 1267, 739; **ESI-HRMS**: Calculated for $C_{16}H_{17}BrNO$ $[M+H]^+$ 318.0488 and 320.0468, found 318.0464 and 320.0447.

2.22. 3-((2-bromophenyl)amino)-1-(3-methoxyphenyl)propan-1-one (3v): Yield: 49% (49 mg); Physical appearance: Yellow oil; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.52 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.60 (t, *J* = 7.8 Hz, 1H), 4.77 (bs, 1H), 3.87 (s, 3H), 3.68 (t, *J* = 6.4 Hz, 2H), 3.32 (t, *J* = 6.4

Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.6, 159.9, 144.6, 138.0, 132.6, 129.7, 128.5, 120.7, 119.9, 118.0, 112.3, 111.2, 110.1, 55.5, 38.8, 37.8; **IR** (KBr, cm^{-1}): 2909, 1680, 1598, 1256, 739; **ESI-HRMS**: Calculated for $C_{16}H_{16}NBrO_2Na$ $[M+Na]^+$ 356.0257 and 358.0236, found 356.0275 and 358.0256.

2.23. 3-((2-bromo-4-methylphenyl)amino)-1-phenylpropan-1-one (3w):[28] Yield: 48% (43 mg); Physical appearance: Pale-yellow oil; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.49 – 7.37 (m, 3H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.57 (t, *J* = 7.6 Hz, 1H), 4.71 (s, 1H), 3.71-3.56 (m, 2H), 3.29 (t, *J* = 6.4 Hz, 2H); **IR** (KBr, cm^{-1}): 2911, 1716, 1601, 1400, 758; **ESI-LRMS**: 304.2 $[M+H]^+$.

2.24. 4-((2-bromophenyl)amino)-1-phenylbutan-2-one (3x): Yield: 40% (39 mg); Physical appearance: Yellow oil; TLC *Rf* 0.3 (9:1, Petroleum ether: EtOAc); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 6.6 Hz, 1H), 7.42 – 7.29 (m, 3H), 7.27 – 7.14 (m, 3H), 6.70-6.53 (m, 2H), 4.58 (s, 1H), 3.74 (s, 2H), 3.47 (t, *J* = 6.0 Hz, 2H), 2.81 (t, *J* = 6.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.2, 144.5, 133.9, 132.6, 129.5, 128.9, 128.6, 127.2, 118.0, 111.2, 110.1, 50.6, 40.8, 38.4; **IR** (KBr, cm^{-1}): 2923, 1712, 1594, 1452, 1079, 741, 698; **ESI-HRMS:** Calculated for $C_{16}H_{16}NBrONa$ $[M+Na]^+$ 340.0307 and 342.0287, found 340.0280 and 342.0288.

2.25 4,4'-(phenylazanediyl)bis(butan-2-one) (3aa):[12c] Yield: 28% (19 mg); Physical appearance: Yellow oil; TLC *Rf* 0.2 (9:1, Petroleum ether: EtOAc); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 7.24 – 7.18 (m, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 8.2 Hz, 2H), 3.57 (t, *J* = 7.0 Hz, 4H), 2.70 (t, *J* = 7.0 Hz, 4H), 2.14 (s, 6H).

(3) General procedure for the one-pot synthesis of 4-substituted quinolines:

In a Schlenk tube equipped with a stir bar, aniline (0.3 mmol) and allylic alcohol (0.6 mmol) were dissolved dry toluene (1.5 mL). The reaction mixture was degassed for 5-10 min followed by the addition of $Pd(OAc)_2$ (0.03 mmol), NaOAc (0.3 mmol), and AcOH (0.6 mmol). The tube was attached with an oxygen balloon and the mixture was vigorously stirred at 80 ^oC for 6-12 h. After completion of the reaction, $FeCl_3.6H_2O$ (0.3 mmol, 81 mg in 0.5 mL EtOH) was added and the resulting allowed to stir at 60 ^oC for 12 h. Upon cooling to room temperature, the reaction mixture was diluted with EtOAc and washed with 1 N NaOH and brine. The organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by a silica gel flash column chromatography to result in the desired product.

3.1. 4-methylquinoline (4b): Yield: 42% (18 mg); Physical appearance: yellowish oil; TLC R_f 0.40 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 4.2 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.74-7.65 (m,1H), 7.58-7.51(m, 1H), 7.20 (d, *J* = 4.2 Hz, 1H), 2.68 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.2, 148.0, 144.3, 130.0, 129.1, 128.3, 126.3, 123.8, 121.9, 18.6; **IR** (KBr cm^{-1}): 2920, 1596, 1454, 539, 757; **ESI-HRMS**: Calculated for $C_{10}H_{10}N$ $[M+H]^+$ 144.0808, found 144.0823.

3.2. 4-methylbenzo[h]quinolone (4c):[29] Yield: 47% (27 mg); Physical appearance: Brown oil; TLC R_f 0.40 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.33 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.91-7.85 (m,1H), 7.77-7.59 (m, 4H), 7.37 (d, *J* = 8.0 Hz, 1H), 2.83 (s ,3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.8, 146.0, 135.9, 133.7, 131.3, 127.9, 127.7, 127.6, 126.6, 125.2, 124.4, 124.2, 122.2, 25.4; **IR** (KBr cm^{-1}): 2959, 2926, 1596, 1394, 841; **GC-LRMS**: 193 (100%) $[M]^+$, 165 (15%), 143 (10%).

3.3. 4-butylbenzo[h]quinolone (4d): Yield: 45% (32 mg); Physical appearance: Pale-yellow oil; TLC R_f 0.40 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.36 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 7.4 Hz ,1H), 7.78-7.58 (m,4H), 7.39 (d, *J* = 8.2 Hz, 1H), 3.08 (t, *J* = 7.8 Hz, 2H), 1.98-1.84 (m, 2H), 1.54-1.42 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.7, 145.9, 135.8, 133.7, 131.5, 127.9, 127.6, 126.7, 126.6, 125.2, 124.6, 124.3, 121.6, 38.7, 31.9, 22.6, 14.1; **IR** (KBr cm^{-1}): 2955, 1596, 1507, 1395, 843, 751; **ESI-HRMS**: Calculated for $C_{17}H_{18}N$ $[M+H]^+$ 236.1434, found 236.1425.

3.4. 4-propylbenzo[h]quinolone (4e): Yield: 44% (43 mg); Physical appearance: Pale-yellow oil; TLC R_f 0.40 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.35 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.80-7.60 (m, 4H), 7.37 (d, *J* = 8.2 Hz, 1H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.01-1.88 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.5, 146.0, 135.8, 133.7, 131.6, 127.8, 127.6, 126.7, 126.6, 125.2, 124.5, 124.3, 121.7, 41.1, 23.0, 14.0; **IR** (KBr cm^{-1}): 2959, 2926, 1596, 1505, 1394, 841, 752; **ESI-HRMS**: Calculated for $C_{16}H_{16}N$ $[M+H]^+$ 222.1277, found 222.1302.

3.5. 4-pentylbenzo[h]quinolone (4f): Yield: 37% (29 mg); Physical appearance: Yellow oil; TLC R_f 0.40 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.36 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.80-7.59 (m, 4H), 7.38 (d, *J* = 8.4 Hz, 1H), 3.07 (t, *J* = 8.0 Hz, 2H), 1.47-1.37 (m, 4H), 2.0-1.86 (m,2H), 0.92 (t, *J* = 7.0, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.7, 149.4, 135.8, 133.7, 131.5, 127.8, 127.6, 126.7, 126.6, 125.2, 125.5, 124.3, 121.6, 39.1, 31.7, 29.4, 22.6, 14.1; **IR** (KBr cm^{-1}): 2954, 2925, 1596, 1450, 1209, 842; **ESI-HRMS**: Calculated for $C_{18}H_{20}N$ $[M+H]^+$ 250.1590, found 250.1598.

3.6. 4,7-dimethylquinoline and 4,5-dimethylquinoline (4g:4g' (3:1)): Yield: 37% (18 mg); Physical appearance: yellowish oil; TLC R_f 0.40 (9:1, Petroleum ether : EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 4.4 Hz, 1H), 7.89-7.83 (m, 2H), 7.41-734 (m,1H), 7.17-7.14 (m, 1H), 2.67 (s, 3H), 2.55 (s, 3H), 8.66 (d, *J* = 4.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.54-7.48 (m, 1H), 7.31-7.27 (m, 1H), 7.14-7.11 (m, 1H), 2.93-2.88 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.1, 149.4, 148.2, 144.1, 139.3, 129.5, 129.1, 128.9, 128.5, 126.3, 124.0, 123.5, 121.2, 25.6, 25.3, 21.7, 18.6; **IR** (KBr cm^{-1}): 2923, 1586, 1459, 1036, 753; **ESI-HRMS**: Calculated for $C_{11}H_{12}N$ $[M+H]^+$ 158.0964, found 158.0965.

3.7. 4-butyl-7-methylquinoline and 4-butyl-5-methylquinoline (4h:4h' (6:1)): Yield: 40% (26 mg); Physical appearance: Brown liquid; TLC R_f 0.40 (9:1 Petroleum ether: EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.00 (d. *J* = 8.4 Hz, 1H), 7.80 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.34-7.25 (m,1H), 7.21 (d, *J* = 8.2 Hz, 1H), 2.94 (t, *J* = 8.0 Hz, 2H), 2.53 (s, 3H), 1.85-1.70 (m, 2H), 1.48-1.34 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.1, 148.2, 139.5, 135.8, 128.0, 127.8, 127.1, 124.7, 120.5, 39.1, 32.2, 22.7, 21.9, 14.0; **IR** (KBr cm^{-1}): 2914, 1624, 1549, 1405, 1201, 810; **ESI-HRMS**: Calculated for $C_{14}H_{18}N$ $[M+H]^+$ 200.1434, found 200.1433.

(4) General procedure for the *N*-Benzylation of *β*-aminoketones:[23a] To a solution of 4-((2-bromophenyl)amino)butan-2-one (0.12 g, 0.5 mmol) in CH_3CN (3 mL), benzyl bromide (0.3 mL, 2.5 mmol) and K_2CO_3 (0.28 g, 2.0 mmol) were added and the mixture was vigorously stirred at 40 ^oC for 36 -48 h. Upon completion, the reaction mixture was diluted with EtOAc and washed with brine. The organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography to result in the desired product.

4.1. 3-(benzyl(2-bromophenyl)amino)-1-phenylpropan-1-one (5a): Yield: 65% (191 mg); Physical appearance: Pale-yellow oil; TLC R_f 0.3 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.38 (m, 4H), 7.36 – 7.22 (m, 4H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 4.26 (s, 2H), 3.51 (d, *J* = 7.4 Hz, 2H), 3.12 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.2, 148.7, 138.1, 136.8, 134.0, 133.0, 128.6, 128.5, 128.3, 128.0, 127.9, 127.2, 125.3, 124.5, 122.4, 59.0, 47.4, 36.6; **IR** (KBr cm^{-1}): 2924, 1701, 1621, 1410, 762; **ESI-HRMS**: Calculated for $C_{22}H_{20}BrNONa$ $[M+Na]^+$ 416.0620 and 418.0600, found 416.0642 and 418.0615.

4.2. 3-(benzyl(2-bromophenyl)amino)-1-(3-methoxyphenyl)propan-1-one (5b): Yield: 60% (190 mg); Physical appearance: Yellow oil; TLC R_f 0.3 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.36 (m, 4H), 7.35 – 7.23 (m, 5H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 4.26 (s, 2H), 3.02 (s, 3H), 3.51 (t, *J* = 7.4 Hz, 2H), 3.11 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.0, 159.8, 148.7, 138.2, 138.1, 134.0, 129.5, 128.6, 128.3, 127.9, 127.2, 125.3, 124.5, 122.3, 120.7, 119.4, 112.2, 59.0, 55.4, 47.6, 36.7; **IR** (KBr cm^{-1}): 2914, 1686, 1591, 1471, 1254, 755; **ESI-HRMS**: Calculated for $C_{23}H_{23}BrNO_2$, $[M+H]^+$ 424.0907 and 426.0886, found 424.0903 and 426.0887.

4.3. 3-(benzyl(2-bromo-4-methylphenyl)amino)-1-(3-methoxyphenyl)propan-1-one (5c): Yield: 58% (190 mg); Physical appearance: Yellow oil; TLC R_f 0.3 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48 – 7.36 (m, 5H), 7.32 (t, *J* = 7.6 Hz, 3H), 7.29 – 7.21 (m, 1H), 7.12 – 7.02 (m, 3H), 4.21 (s, 2H), 3.84 (s, 3H), 3.47 (t, *J* = 7.4 Hz, 2H), 3.09 (t, *J* = 7.4 Hz, 2H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.1, 159.7, 146.0, 138.3, 138.2, 135.4, 134.3, 129.5, 128.7, 128.6, 128.2, 127.1, 124.2, 122.3, 120.7, 119.5, 112.2, 59.3, 55.4, 47.4, 36.8, 20.4; **IR** (KBr, cm^{-1}): 2921, 1685, 1491, 1259, 1037, 746; **ESI-HRMS**: Calculated for $C_{24}H_{25}BrNO_2$ $[M+H]^+$ 438.1063 and 440.1043, found 438.1090 and 440.1073.

4.4. 4-(benzyl(2-bromophenyl)amino)butan-2-one (5d): Yield: 80% (198 mg); Physical appearance: Yellow oil; TLC R_f 0.3 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.35 – 7.29 (m, 2H), 7.29 – 7.22 (m, 2H), 7.08 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.90 (ddd, *J* = 8.0, 7.4, 1.6 Hz, 1H), 4.18 (s, 2H), 3.32 (t, *J* = 7.2 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.06 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.8, 148.5, 137.9, 134.0, 128.7, 128.2, 127.9, 127.2, 125.4, 124.5, 122.4, 59.0, 46.6, 41.5, 30.2; **IR** (KBr, cm^{-1}): 2914, 1712, 1357, 1024, 752; **ESI-HRMS:** Calculated for $C_{17}H_{19}BrNO$, $[M+H]^+$ 332.0645 and 334.0624, found 332.0638 and 334.0619.

4.5. 4-(benzyl(2-bromo-4-methylphenyl)amino)butan-2-one(5e): Yield: 76% (197 mg); Physical appearance: Yellow oil; TLC R_f 0.3 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (s, 1H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.30 – 7.18 (m, 3H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 4.09 (s, 2H), 3.24 (t, *J* = 7.2 Hz, 2H), 2.50 (t, *J* = 7.2 Hz, 2H), 2.27 (s, 3H), 2.01 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 208.0, 145.8, 138.1, 135.5, 134.3, 128.8, 128.6, 128.2, 127.2, 124.3, 122.4, 59.4, 46.9, 41.6, 30.2, 20.5; **IR** (KBr, cm^{-1}): 2916, 1708, 1624, 1451, 748; **ESI-HRMS**: Calculated for $C_{18}H_{20}BrNONa$ $[M+Na]^+$ 368.0620 and 370.0600, found 368.0645 and 370.0630.

(5) General procedure for α-arylation of β-aminoketones: The α–arylation of TES enol ethers of various β-aminoketones was performed according to procedure in our previous report.[18]

(a) Step I: Synthesis of TES-enol ether of β-aminoketones: TES-Cl (0.05 mL, 0.3 mmol) was added to a stirring solution of β-aminoketones (0.3 mmol) and DBU (0.09 mL, 0.6 mmol) in dry CH_2Cl_2 (5 mL) at room temperature. The reaction mixture was heated to 40 ^oC and allowed to stir at that temperature for 18 h. After completion of the reaction, the solution was poured into saturated aqueous $NaHCO_3$ and extracted with DCM. The organic layer was dried (anhydrous Na_2SO_4), filtered and concentrated. The residue was immediately used for the next step.

(b) Step II: α-arylation of TES-enol ether of β-aminoketones: The α-arylation of TES enol ethers of various β-aminoketones was performed according to our previous report.[18]

5.1. (1-benzylindolin-3-yl)(phenyl)methanone (6a): Yield: 58% (46 mg); Physical appearance: Yellow oil; TLC R_f 0.3 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.14 – 8.02 (m, 2H), 7.69 – 7.62 (m, 1H), 7.60 – 7.51 (m, 2H), 7.47 – 7.35 (m, 4H), 7.33 – 7.30 (m, 1H), 7.11 (d, J = 7.8 Hz, 1H), 6.90 (d, J = 7.4 Hz, 1H), 6.64 – 6.55 (m, 2H), 5.13 (t, J = 8.8 Hz, 1H), 4.49 (d, J = 15.2 Hz, 1H), 4.29 (d, J = 15.2 Hz, 1H), 3.97 – 3.87 (m, 1H), 3.67 (d, J = 9.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.5, 152.1, 138.0, 136.9, 133.4, 129.1, 128.8, 128.7, 128.6, 127.8, 127.2, 125.0, 117.8, 117.6, 107.4, 55.2, 53.1, 48.3; **IR** (KBr, cm^{-1}): 2914, 1693, 1620, 1520, 1375, 871, 748; **ESI-HRMS**: Calculated for $C_{22}H_{19}NONa$ $[M+Na]^+$ 336.1359, found 336.1382.

5.2. (1-benzylindolin-3-yl)(3-methoxyphenyl)methanone (6b): Yield: 62% (53 mg); Physical appearance: Yellow oil; TLC R_f 0.3 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, J = 7.4 Hz, 1H), 7.56 (s, 1H), 7.48 – 7.22 (m, 6H), 7.16 (d, J = 8.2 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.88 (d, J = 7.4 Hz, 1H), 6.61 – 6.50 (m, 2H), 5.07 (t, J = 8.6 Hz, 1H), 4.45 (d, J = 15.2 Hz, 1H), 4.26 (d, J = 15.2 Hz, 1H), 3.92 – 3.78 (m, 4H), 3.62 (t, J = 9.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.3, 160.0, 152.1, 138.3, 138.0, 129.8, 129.0, 128.7, 128.6, 127.8, 127.2, 125.0, 121.7, 120.0, 117.6, 113.2, 107.4, 55.5, 55.3, 53.1, 48.5; **IR** (KBr, cm^{-1}): 2923, 1653, 1614, 1375, 1173, 1033; **ESI-HRMS**: Calculated for $C_{23}H_{21}NO_2Na$ $[M+Na]^+$ 366.1465, found 366.1468.

5.3. (1-benzyl-5-methylindolin-3-yl)(3-methoxyphenyl)methanone (6c): Yield: 56% (50 mg); Physical appearance: Off-white solid, M.p. 98-100 ^oC; TLC R_f 0.3 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (d, J = 7.6 Hz, 1H), 7.60 (s, 1H), 7.51 –

7.41 (m, 3H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.34 – 7.26 (m, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.75 (s, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 5.07 (t, *J* = 8.8 Hz, 1H), 4.51 – 4.40 (m, 1H), 4.24 (d, *J* = 15.0 Hz, 1H), 3.89 (s, 3H), 3.81 (t, *J* = 8.6 Hz, 1H), 3.63 (t, *J* = 9.2 Hz, 1H), 2.18 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.6, 160.0, 150.1, 138.3, 138.2, 129.8, 129.0, 128.5, 127.9, 127.7, 127.2, 127.1, 125.7, 121.7, 120.0, 113.1, 107.6, 56.0, 55.5, 53.8, 48.6, 20.7; **IR** (KBr, cm^{-1}): 2923, 1618, 1515, 1377, 1178, 787; **ESI-HRMS**: Calculated for $C_{24}H_{24}NO_2$ $[M+H]^+$ 358.1802, found 358.1775.

5.4. 1-(1-benzylindolin-3-yl)ethan-1-one (6d): Yield: 38% (29 mg); Physical appearance: Yellow oil; TLC R_f 0.3 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.39 – 7.30 (m, 5H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.73 (t, *J* = 7.8 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 4.40 (d, *J* = 15.0 Hz, 1H), 4.27 (d, *J* = 15.0 Hz, 1H), 4.10 (dd, *J* = 9.4, 4.8 Hz, 1H), 3.74 (dd, *J* = 9.4, 4.8 Hz, 1H), 3.50 (d, *J* = 9.4 Hz, 1H), 2.23 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 206.4, 152.2, 137.8, 129.0, 128.6, 127.8, 127.3, 126.7, 125.0,117.9, 107.6, 55.0, 54.6, 53.0, 27.3; **IR** (KBr, cm^{-1}): 2921, 1715, 1642, 1526, 1385, 1180, 745; **ESI-HRMS**: Calculated for $C_{17}H_{18}NO$ $[M+H]^+$ 252.1383, found 252.1357.

5.5. (1-benzyl-5-methyl-1H-indol-3-yl)(3-methoxyphenyl)methanone (7a): Yield: 70% (62 mg); Physical appearance: Off-white solid, M.p. 106-108 ^oC; TLC R_f 0.3 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 7.62 (s, 1H), 7.44 – 7.26 (m, 6H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.19 – 7.07 (m, 4H), 5.35 (s, 2H), 3.87 (s, 3H), 2.51 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 190.6, 159.6, 142.3, 137.4, 135.9, 135.5, 132.6, 129.2, 129.0, 128.1, 127.7, 126.8, 125.4, 122.6, 121.3, 117.4, 115.6, 113.5, 109.9, 55.4, 50.8, 21.5; **IR** (KBr, cm^{-1}): 2948, 1620, 1423, 1173, 740; **ESI-HRMS**: Calculated for $C_{24}H_{22}NO_2$ $[M+H]^+$ 356.1645, found 356.1629.

5.6. (1-benzyl-1H-indol-3-yl)(3-methoxyphenyl)methanone (7b): Yield: 68% (58 mg); Physical appearance: Yellow oil; TLC R_f 0.3 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 7.5 Hz, 1H), 7.64 (s, 1H), 7.45 – 7.22 (m, 9H), 7.19 – 7.03 (m, 3H), 5.32 (s, 2H), 3.82 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 190.6, 159.6, 142.2, 137.3, 137.2, 135.9, 129.3, 129.0, 128.2, 127.5, 126.9, 123.8, 122.9, 122.9, 121.3, 117.5, 116.0, 113.5, 110.3, 55.4, 50.8; **IR** (KBr, cm^{-1}): 2953, 1622, 1578, 1463, 1380, 1176, 748; **ESI-HRMS**: Calculated for $C_{23}H_{20}NO_2$ $[M+H]^+$ 342.1489, found 342.1463.

5.7. 1-benzyl-1,2,3,5-tetrahydro-4H-benzo[b]azepin-4-one and 1-(1-benzylindolin-3-yl)ethan-1-one (6d and 8a 1:1):[30] Yield: 37% (29 mg); Physical appearance: Yellow oil; TLC R_f 0.3 (19:1, Petroleum ether: EtOAc); (**Data** for **8a) ^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41 – 7.32 (m, 4H), 7.31 – 7.28 (m, 1H), 7.27 – 7.25 (m, 1H), 7.15 (d, *J* = 6.6 Hz, 1H), 7.10

(d, *J* = 7.8 Hz, 1H), 7.00 (td, *J* = 7.4, 1.0 Hz, 1H), 4.37 (s, 2H), 3.81 (s, 2H), 3.25 (t, *J* = 6.6 Hz, 2H), 2.56 (t, *J* = 6.6 Hz, 2H); **IR** (KBr, cm^{-1}): 2925, 1651, 1601, 1497, 1360, 1166, 748; **ESI-HRMS**: Calculated for $C_{17}H_{18}NO$ $[M+H]^+$ 252.1383, found 252.1373.

5.8. 1-benzyl-7-methyl-1,2,3,5-tetrahydro-4H-benzo[b]azepin-4-one and 1-(1-benzyl-5-methylindolin-3-yl)ethan-1-one (6e and 8b 1:1): Yield: 39% (26 mg); Physical appearance: Yellow oil; TLC R_f 0.3 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 – 7.35 (m, 8H), 7.35 – 7.29 (m, 2H), 7.14 – 7.08 (m, 1H), 7.07 – 7.01 (m, 2H), 7.01 – 6.96 (m, 2H), 6.51 (d, *J* = 8.0 Hz, 1H), 4.38 (d, *J* = 15.0 Hz, 1H), 4.33 (s, 2H), 4.23 (d, *J* = 15.0 Hz, 1H), 4.06 (dd, *J* = 9.4, 4.8 Hz, 1H), 3.78 (s, 2H), 3.69 (dd, *J* = 9.5, 4.8 Hz, 1H), 3.46 (t, *J* = 9.4 Hz, 1H), 3.20 (t, *J* = 6.6 Hz, 2H), 2.54 (d, *J* = 6.6 Hz, 2H), 2.33 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.0, 206.7, 150.2, 146.7, 138.6, 138.0, 132.3, 130.5, 129.8, 129.2, 128.8, 128.6, 128.5, 128.1, 127.8, 127.4, 127.3, 127.2, 127.1, 125.8, 119.4, 107.8, 58.3, 55.5, 54.7, 53.7, 51.4, 48.8, 41.6, 27.3, 20.7, 20.6; **IR** (KBr, cm^{-1}): 2917, 1730, 1557, 1360, 1221, 735; **ESI-HRMS**: Calculated for $C_{18}H_{19}NONa$, $[M+Na]^+$ 288.1359, found 288.1346.

AUTHOR INFORMATION

Corresponding Author

mk@iiserb.ac.in

ORCID Manmohan Kapur: 0000-0003-2592-6726

Notes

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at **http://pubs.acs.org**.

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

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