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ARTICLE

Designed pincer ligands supported Co(II)-based catalysts for dehydrogenative activation of alcohols: Studies on *N*-alkylation of amines, α-alkylation of ketones and synthesis of quinolines

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Base-metal catalysts **Co1**, **Co2** and **Co3** were synthesized from designed pincer ligands L^1, L^2 and L^3 having NNN donor atoms respectively. **Co1**, **Co2** and **Co3** were characterized by IR, UV–Vis. and ESI-MS spectroscopic studies. Single crystal X-ray diffraction studies were investigated to authenticate the molecular structures of **Co1** and **Co3**. Catalysts **Co1**, **Co2** and **Co3** were utilized to study the dehydrogenative activation of alcohols for *N*-alkylation of amines, α-alkylation of ketones and synthesis of quinolines. Under optimized reaction conditions a broad range of substrates including alcohols, anilines and ketones were exploited. A series of controlled experiments for *N*-alkylation of amines, α-alkylation of ketones and synthesis of quinolines were examined to understand the reaction pathway. ESI-MS spectral studies were investigated to characterize cobalt-alkoxide and cobalt-hydride intermediates. Reduction of styrene by evolved hydrogen gas during the reaction was investigated to authenticate the dehydrogenative nature of the catalysts. Probable reaction pathways were proposed for *N*-alkylation of amines, α-alkylation of ketones and synthesis of quinolines on the basis of controlled experiments and detection of reaction intermediates.

Introduction

Pincer ligands are meridional tridentate ligands which could binds to the coplanar sites of a metal center.[1] Transition metal based catalysts derived from pincer ligands received considerable current interest.[2] However, catalysts supported by pincer ligands containing NNN donors received special attention for the dehydrogenative activation of alcohols and organic transformations.[3] Earth abundant transition metals not only offer potential environment but also provide chances to explore base-metal catalysts and eventually new avenues for innovations in chemical research.[4] In this regard electronic structures of base-metal complexes are significantly important for their catalytic performance.[5] Development of reliable, readily available base-metal catalysts having effective, atom economical, greener choice and selective method for C–N and C–C bond formation have been exciting endeavour and are vital for organic synthesis with various functional groups.[6] Amines are valuable building blocks for different fungicides, pesticides, pharmaceuticals, fine chemicals additives and agrochemicals[7] (Scheme 1). Moreover, it is well known that nitrogen functionality occurs in various biologically active molecules and different pharmaceuticals compounds.[8] Hence, synthesis of amines and development of base-metal catalysts were found to be an important area in chemical research.[9] There are reports on Fe,[10] Mn,[11] and Ni[12]-based catalysts. Although, Co[9a,13]-based catalysts are significantly important for *N*-alkylation reactions. On the other hand, α-alkylation of ketones *via* dehydrogenative activation of alcohols are extremely important in organic syntheses and synthetic chemistry. Several biologically active compounds and drug molecules involved in anti-inflammatory, analgesic, anti-diabetic, antitumor and antibacterial activity were synthesized utilizing this process (Scheme 1).[14] Hence, development of new methodology and catalysts are important areas of chemical research. Excluding platinum metal-based catalysts recently, α-alkylation of ketones has been performed by manganese,[15] iron,[16] copper[17] and cobalt[18] based base-metal catalysts.

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Electronic supplementary information (ESI) available: NMR, ESI-MS, and UV-visible spectral data and information on X-ray crystal structure data have been deposited in the Cambridge Crystallographic Data Centre and the deposition number for Complex **Co1** is CCDC, **2012672** and Complex **Co3** is CCDC **2012671** See DOI: 10.1039/x0xx00000x

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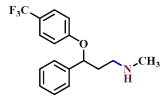
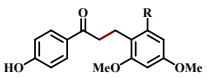
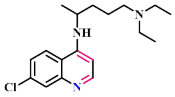
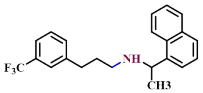
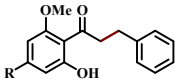
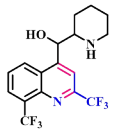
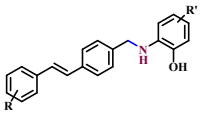
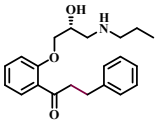
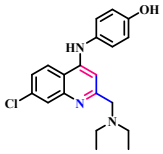
N-alkylated compounds	Alpha-alkylated compounds	Quinoline derivatives
		
Fluoxetine	R= H, Loureirin A R= OMe Loureirin B	Chloroquine
		
Cinacalcet	R= H, Uvangoletin R= Me Myriggalone H	Mefloquine
		
Resveratrol derivatives	(R)-Propafenone	Amodiaquine

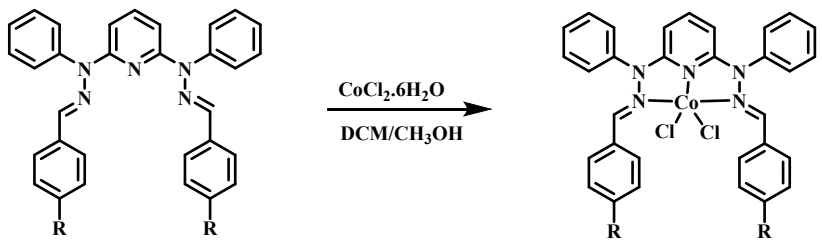
Scheme 1. Selected biologically active molecules contained alkylated amine, 1,4 diaryl ketone moiety and quinoline motif.

Dehydrogenative activation of alcohols could give rise to innovative synthetic methodology for the synthesis of different N-heterocycle *via* cyclization reaction. Quinoline derivatives are such molecules and these derivatives could be synthesized by this method. In fact some related motifs were employed for pharmaceuticals, dyes, pigments, sensors and polymeric materials.[19] Therefore, straight forward method for the synthesis of *N*-heterocycles such as pyrimidines, pyrroles and quinolines from easily available reagents still remains challenging.[20] Over the past few years, dehydrogenative cyclization reaction has become an well-designed protocol which generates water as a by-product for the synthesis of quinoline.[21] For instance, the transition metal complexes of mainly Ru,[22] Ir[23] and Re[24] were utilized for quinoline synthesis. Now-a-days base-metal complexes such as Mn,[20c] Co[25] and Ni[20b] complexes were exploited as catalysts for synthesis of *N*-heterocycles. These methods described above for *N*-alkylation, α-alkylation and quinoline synthesis exhibit disadvantages of high catalyst loading, phosphorous based ligands and harsh reaction conditions.

In recent years there is an upsurge of interest for the reactivity of cobalt complexes derived from pincer ligands having NNN donor atoms.[3,26,27] Cobalt complexes derived from pincer ligands were utilized for hydroboration,[27a] hydrogenation reaction,[27b] isomerization of styrene,[27c] polymerization reaction,[27d] water reduction[28] and hydrosilylation reaction.[29] Further, cobalt complexes derived from pincer ligands are important in terms of structural and electronic properties.[30]

Investigation of literature revealed that Balaraman and co-workers synthesized phosphine free NNN Co(II) complexes which catalyzed direct *N*-alkylation of anilines with alcohols *via* hydrogen autotransfer.[13a] Kundu and co-workers synthesized phosphine free NNN Co(II) complexes which catalyzed for dehydrogenative synthesis of quinolines.[25b] To the best of our knowledge, phosphine free cobalt complexes derived from NNN donors ligands were never been utilized for the α-alkylation of ketones.

Recently, our group reported organoruthenium complexes supported on NN-based bidentate ligands, for α-alkylation of ketones with alcohols and synthesis of quinolines.[31] As part of our interest, we are trying to explore base-metal Co(II) based catalysts supported by pincer ligands for *N*-alkylation of amines, α-alkylation of ketones and synthesis of quinolines.



R= OCH_2CH_3, L^1
R= NEt_2, L^2
R=NMe_2, L^3

R= OCH_2CH_3, Co1
R= NEt_2, Co2
R=NMe_2, Co3

Scheme 2. Schematic drawing for synthesis of complexes (**Co1-Co3**).

This prompted us to study the phosphine free base-metal cobalt complexes having pincer ligands. In the present study we have designed and synthesized a new family of base-metal cobalt complexes **Co1**, **Co2** and **Co3** supported by pincer ligands L^1, L^2 and L^3 (where L^1=2,6-bis(2(4-ethoxybenzylidene)-1-phenylhydrazineyl) pyridine, L^2=4,4'-((pyridine-2,6-diylbis (2-phenylhydra zin-2-yl-1-ylid ene)) bis (methaneyl ylidene)) bis(N,N-diethylaniline) and L^3=4,4'-((pyridine-2,6-diylbis(2-phenyl hydrazine-2-yl-1-ylidene)) bis methaneylylidene)) bis (N,N-diethyl aniline)) respectively (shown in Scheme 2). These complexes were characterized by different spectroscopic methods such as UV–Vis., IR and ESI-MS analysis. Molecular structures of **Co1** and **Co3** were determined by X-ray crystallography. We have investigated *N*-alkylation of amines, α-alkylation of ketones as well as quinoline synthesis by these cobalt based catalysts. Based on the evidences i.e. characterization of intermediate species, control experiments and literature studies, possible reaction pathways will be scrutinized.

Results and discussion

Synthesis and characterization of ligands

Tridentate meridional ligands (L^1-L^3) having two imines and one pyridine donors. Ligands L^1-L^3 were synthesized by condensation of 2,6-bis(1-phenylhydrazineyl)pyridine[32] with 4-ethoxy benzaldehyde, 4-(diethylamino) benzaldehyde and 4-(dimethylamino) benzaldehyde respectively in methanol. Ligands were characterized by NMR, ESI-MS, UV-Vis. and IR spectroscopic studies and the data were consistent with our previous report.[32a] The ^{1}H NMR and ^{13}C NMR spectra of ligands (L^1-L^3) were observed in $CDCl_3$ and d^6-DMSO solution (Shown in Figures S1-S6). The ^{1}H NMR signal of ligands L^1 showed one singlet around ~7.49 ppm for imine proton however, one quartet around ~4.2 ppm due to the methylene proton of -OCH_2CH_3 proton and one triplet around ~1.4 ppm for -CH_3 group. In L^2 we have found that one singlet peak at ~7.44 ppm for imine proton however, one quartet around ~3.3 ppm due to the methylene proton of -NCH_2CH_3 group and one triplet around ~1.1 ppm for -CH_3 group. L^3 showed one singlet peak around ~7.47 ppm for imine proton however, one singlet around ~2.9 ppm due to the methyl proton of -NCH_3 group which clearly indicated the formation of ligands. The electronic spectral data for (L^1-L^3) were shown in supplementary information, (Table S1) and spectra were shown in supplementary information (Figure S7). In IR, azomethine (-HC=N-) characteristic band in free ligands (L^1-L^3) was observed near 1565–1580 cm^{-1} (Shown in Supporting Information, Figures S15-S17). The ESI-MS analysis was performed for all the ligands (L^1-L^3) in the acetonitrile solution. Ligands L^1-L^3 provided peaks at m/z = 556.2775, 610.3701 and 554.3078 for $(L^{1\text{-}3}+H^+)^+$ ions respectively which authenticate the formation of Schiff bases. (Shown in Supporting Information, Figures S9-S11)

Synthesis and characterization of cobalt complexes Co1, Co2 and Co3

Cobalt complexes were prepared by the reaction of $CoCl_2{\cdot}6H_2O$ and ligand (L^1-L^3) in 1:1 molar ratio in CH_2Cl_2/CH_3OH. (shown in Scheme 2) After 6 h of stirring, red coloured solid of complexes **Co1, Co2** and **Co3** were formed with a good yield (~60%). Coordination of ligand to the metal centre was characterized by UV-Vis., IR and ESI-MS spectral studies. The absorption spectra of complexes **Co1, Co2** and **Co3** were recorded in dichloromethane solution at room temperature. The electronic spectral data were shown in (Supplementary Information, Table S2) and spectra were shown in (Supplementary Information, Figure S8). The transition band near 330-460 nm for complexes **Co1, Co2** and **Co3** was assigned as charge transfer transition.[33] In IR, stretching frequencies for $\nu_{C=N}$ in complexes **Co1**, **Co2** and **Co3** were found to be in the range 1560-1605 cm^{-1} which clearly indicated the ligation of azomethine nitrogen to metal centre[33a] (Shown in SI, Figures S18-S20). ^{1}H NMR spectra of all the complexes **Co1**, **Co2** and **Co3** were recorded in $CDCl_3$ solution and were represented in supporting information (Figures S21-S23). ESI-MS analysis was performed for all the complexes **Co1**, **Co2** and **Co3** in acetonitrile solution. Complexes **Co1**, **Co2** and **Co3** provided peaks at m/z = 649.1600, 703.2652 and 647.2095 for (**Co1-Co3**-Cl^-)$^+$ ions which clearly expressed the formation of complexes **Co1, Co2** and **Co3** (Shown in Supporting Information, Figures S12-S14).

Description of crystal structures

Single crystal of cobalt complexes **Co1** and **Co3** suitable for X-ray diffraction analysis was obtained by slow evaporation of the cobalt complexes in CH_2Cl_2/CH_3CN solution. The crystal structure data and refinement parameters for complexes **Co1** and **Co3** are depicted in Supplementary Information (Table S3). Selected bond distances and bond angles are shown in Supporting Information (Tables S4-S5). The single-crystal XRD studies of **Co1** and **Co3** revealed five coordinate geometry with the pincer ligands (L^1 and L^3).

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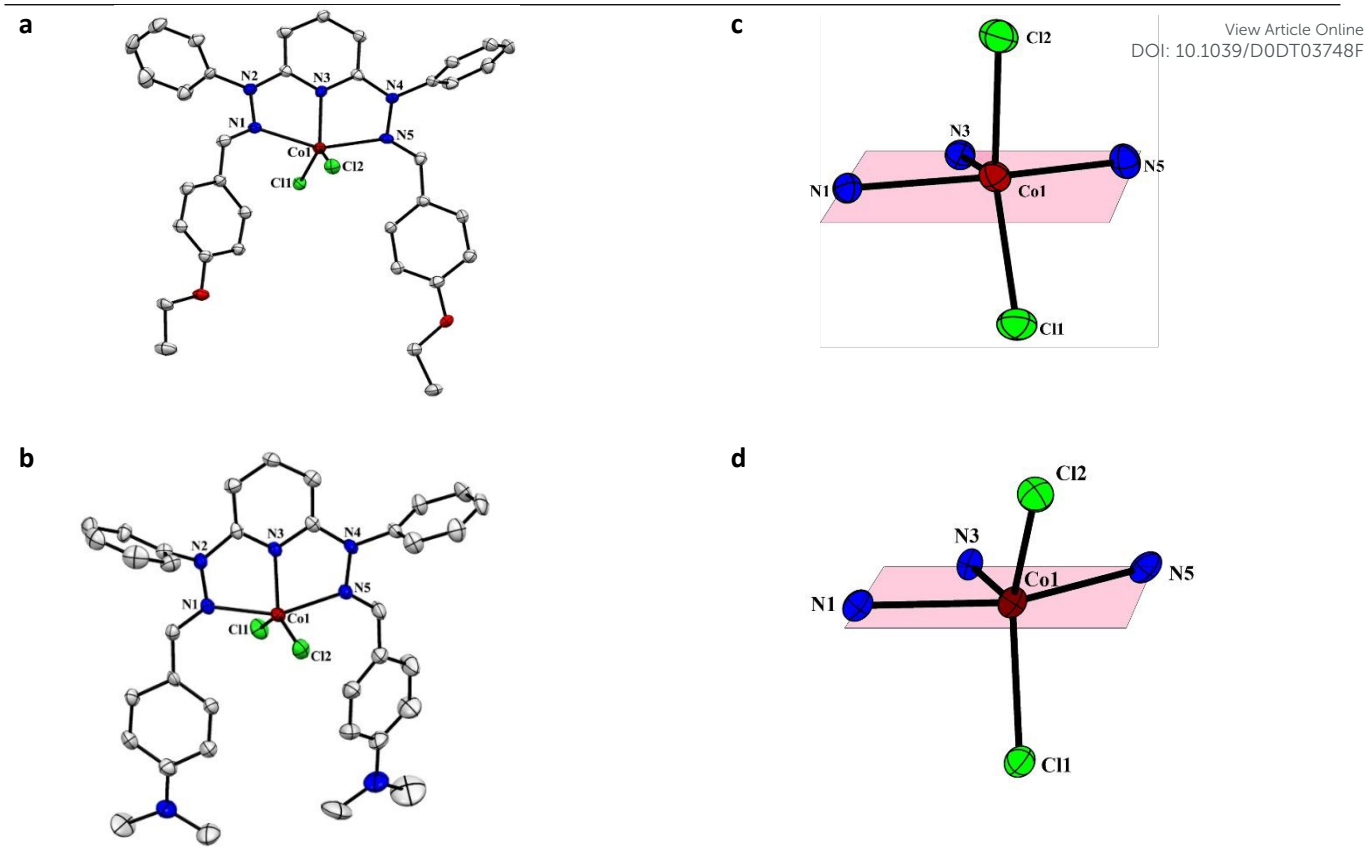

Figure 1. (a, b) ORTEP diagram (30% probability level) of complexes **Co1** and **Co3.** All hydrogen atoms and solvent molecules are omitted for clarity. (c, d) Distorted trigonal bipyramidal structure around the cobalt atom of complexes **Co1** and **Co3**.

In complexes **Co1** and **Co3,** distorted trigonal bipyramidal geometry were observed with in plane coordination of one pyridine nitrogen along with two azomethine nitrogen atoms. Two Cl atoms were observed as axial ligands for both the complexes (Cl2— Co1— Cl1) angles were 132° for **Co1** and 143° for **Co3**. Geometry of cobalt ion for **Co1** and **Co3** were also calculated by trigonality index (τ value).[32a,32c] τ value was found to be 0.361 [τ= (β-α) /60°, where β = N1— Co1—N5 =153.49(12) and α= Cl2— Co1— Cl1 = 131.83(5)] for Co1 and for Co3 0.211 [τ= (β-α) /60°, where β = N1— Co1—N5 =155.3(2) and α= Cl2— Co1— Cl1 = 142.63(9)] Thus, the coordination environment around the metal centre was described as distorted trigonal bipyramidal for complexes **Co1** and **Co3**.[34] ORTEP diagram of cobalt complexes **Co1** and **Co3** are shown in Figure 1. Co1—N_{py} bond lengths for complexes **Co1** and **Co3** were found to be 1.982(5) Å and 1.988(3) Å respectively. This bond length was smaller than the values reported in the literature. [33,35] The bond length Co1—N_{im} for both the complexes **Co1** and **Co3** are in the range of 2.169 Å–2.236 Å. These bond distances were found to be smaller than the values reported by Batisha and co-workers[36] and larger than the values reported by our previous reports[33a] and the report by Zhang and co-workers.[37] Co–Cl bond length for both complexes **Co1** and **Co3** are in the range of 2.249 Å–2.299 Å. These distances were larger than the values communicated by our previous report[33a] and some reports in the literature.[38] However, these values were smaller than the values reported by Zhang and co-workers.[37a] These bond lengths clearly indicate that Co(II) high-spin centre was stabilized in presence of meridional ligands having NNN donors and two Cl atoms.[33a]

***N*-alkylation of anilines with primary alcohols**

Our initial investigation focused on the *N*-alkylation of anilines, reaction was carried out with aniline (**1a**), benzyl alcohol (**2a**) as substrates and **Co1** as catalyst (Shown in Table 1). A series of reactions were performed to optimize various parameters such as solvent, temperature, base and time (Shown in SI Figure S24). Formation of N-benzylaniline **3aa** with yield of 82% after 24 h was observed when the reaction was carried out in presence of **Co1** (4 mol%) with aniline (1 mmol) and benzyl alcohol (1 mmol) at 110 °C in toluene solution (Table 1, Entry 5). 54% yield of desired product **3aa** was obtained when the reaction was carried out with 3 mol% of

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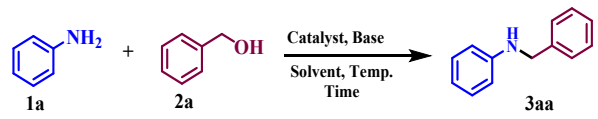
catalyst **Co1** (Table 1, Entry 13). We have performed the reaction in presence of 5 eq. PPh_3 and we observed no change in the catalytic outcome which clearly indicated the homogeneous nature of the reaction (Table 1, Entry 14). To examine the role of solvent the reaction was performed in various solvents (Table 1, Entry 6-13) and toluene was observed to be best solvent resulting in yield of 82%. KO^tBu was found to be the best base for this purpose compared to other bases like KOH, NaOH, K_2CO_3 Na_2CO_3, Et_3N, CH_3COOK and K_3PO_4 (Shown in SI, Figure S24). The optimum reaction temperature was found to be 110 °C (shown in supporting information, Figure S24). Further, the effect of time was also investigated and the maximum yield of the formation of product at 24 h (Shown in SI, Figure S24). Control experiments were performed in the absence of catalyst **Co1,** only ligand L^1, in-situ generated catalyst system (1:1, L^1 and $CoCl_2.6H_2O$), and in absence of base KO^tBu. (Table1, Entry 1, 2 and 4). In all those control experiments no detectable desired product was obtained. Moreover, commercially available cobalt sources like $CoCl_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ also examined (Table1, Entry 3). These observations clearly depicted that the assembled i.e. coordination complex was important for the catalytic activity. Thus, the optimized reaction condition was found to be 4 mol% catalyst loading of catalyst **Co1**, 0.5 mmol of base KO^tBu in toluene at 110 °C for 24 h.

We next set out to investigate the reaction scope for N-alkynation reaction and then, the reaction of benzyl alcohol with structurally diverse amines were investigated (Table 2) Anilines bearing electron-donating substituents such as **-OCH_3** (Table 2, **3ba**) on para position, **-OCH_3** (Table 2, **3ca**) on ortho position, **-CH_3** (Table 2, **3da** and **3db**) on para position with different benzyl alcohols results good (>75%) to excellent yield (>80%) of *N*-alkylated products. Electron deficient substituent bearing i.e. **-Cl**, on para position smoothly reacted with benzyl alcohol derivatives to afford products **3ea** and **3eb** with 70% to 78% yield. Heterocyclic amine such as 2-amino pyridine could be transformed into the desired products (Table 2, **3fa**) in moderate yield (>65%) due to the electronic effect. Next, the scope of different benzyl alcohol derivatives was investigated.

Table 1. Optimization reaction condition for the *N*-alkylation of anilines.

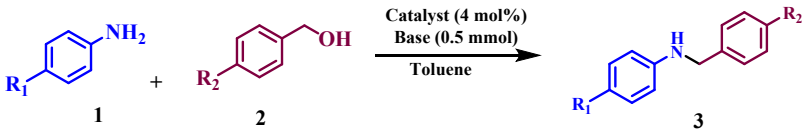


1a 2a 3aa

Entry	Cat.	Cat. loading (mol%)	Solvent	Temp (°C)	Time (h)	% Yield
1	–	–	Toluene	110	24	0
2	Ligand L^2	4	Toluene	110	24	0
3	$CoCl_2.6H_2O$/ $Co(NO_3)_2.6H_2O$	4	Toluene	110	24	Trace
4	L^2+$CoCl_2$. $6H_2O$	4	Toluene	110	24	Trace
5	**Co1**	4	Toluene	110	24	82
6	**Co1**	4	DMSO	110	24	35
7	**Co1**	4	DMF	110	24	30
8	**Co1**	4	Benzene	110	24	50
9	**Co1**	4	Xylene	110	24	52
10	**Co1**	4	EtOH	110	24	Trace
11	**Co1**	4	THF	110	24	Trace
12	**Co1**	4	ACN	110	24	Trace
13	**Co1**	3	Toluene	110	24	54
14	**Co1**	4	[a]Toluene	110	24	78

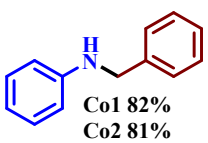
Reaction Condition: Aniline (1 mmol), Benzyl alcohol (1 mmol), Catalyst (4 mol%), KO^tBu (0.5 mmol), Toluene 2 ml, Temperature 110 °C for 24 h. [a] In presence of 5 eq. of PPh_3. Isolated yields.

Table 2. Substrate scope of *N*-alkylation of anilines

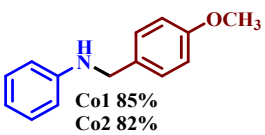


1 2 3

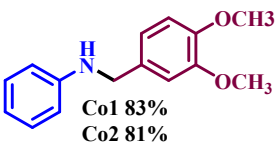
R_1, R_2= H , OCH_3, CH_3, Cl



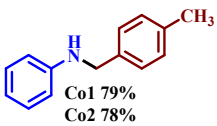
Co1 82%
Co2 81%
Co3 78%
3aa



Co1 85%
Co2 82%
Co3 80%
3ab



Co1 83%
Co2 81%
Co3 78%
3ac



Co1 79%
Co2 78%
Co3 77%
3ad

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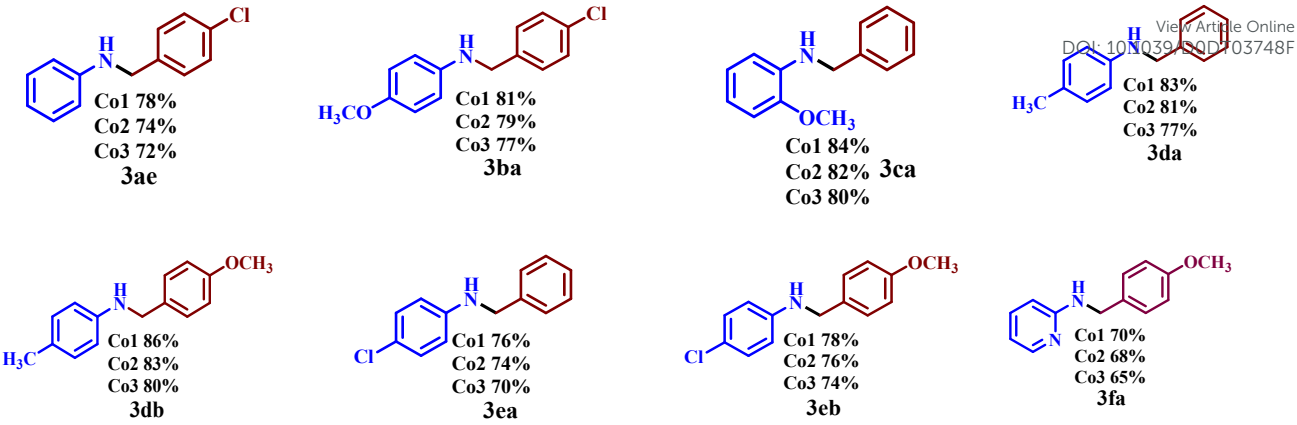


Reaction Condition: Aniline (1 mmol), Benzyl alcohol (1 mmol), cat. (4 mol%), KO^{t}Bu (0.5 mmol), Toluene 2 ml heated at 110 °C for 24 h. Isolated yields.

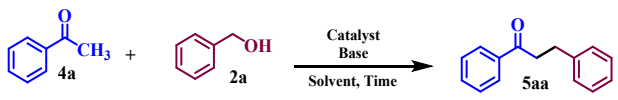
Alcohols containing electron-donating **4-OCH$_3$**, **3,4-OCH$_3$** and **4-CH$_3$** as well as electron deficient **4-Cl** reacted with anilines afforded desired products (**3ab-3ae**) with 72% to 85% yield. However, efforts at the alkylation of electron deficient **-NO$_2$** containing amines with alcohols did not provide the desired products. Acidity, nucleophilicity and steric effects of anilines play important roles for N-alkylation reactions. We have also performed the alkylation of aliphatic amines with alcohols, however we observed that the catalysts were ineffective and a trace amount of desired products were formed. The catalysts were also ineffective for the alkylation of amines with heterocyclic alcohols.

We have tried to compare our results, for catalytic activity of **Co1-Co3** for *N*-alkylation reaction of anilines with benzyl alcohols to produce the *N*-alkylated products, with previous literature reports. The optimum loading of catalysts (**Co1-Co3**) for catalytic activity (4 mol%) of *N*-alkylation of anilines is lower than the values reported by Midya *et al.* (catalyst loading 5 mol%) by cobalt complexes supported by ligands having NNN donors.[13a] The data reported by us is comparable with the data reported by Midya *et al.* for all the catalysts (**Co1-Co3**). Air and moisture insensitivity of our catalysts as well as phosphorous free complexes are additional advantages.

α-Alkylation of Ketones with Primary Alcohols

In order to demonstrate the potential of catalysts we have examined α-alkylation of ketones. Initially, α-alkylation of acetophenone (**4a**) and benzyl alcohol (**2a**) was investigated in presence of catalyst loading (2 mol%) of **Co1** at 110°C in toluene which resulted in the formation of 1,3-diphenylpropan-1-one **5aa** with 91% yield after 24 h (Table 1, Entry 13). To our delight other parameters such as temperature, solvent, time and base were optimised and measured (shown in SI, Figures S49).

Table 3. Optimization reaction condition for the α-alkylation of ketones



Entry	Cat.	Cat. loading (mol%)	Solvent	Temp (°C)	Time (h)	% Yield
1	–	–	Toluene	110	24	0
2	Ligand L^2	2	Toluene	110	24	0
3	$CoCl_2$. $6H_2O$/ $Co(NO_3)_2$. $6H_2O$	2	Toluene	110	24	Trace
4	L^2+$CoCl_2$. $6H_2O$	2	Toluene	110	24	Trace
5	**Co1**	1	Toluene	110	24	48
6	**Co1**	2	DMSO	110	24	42
7	**Co1**	2	DMF	110	24	35
8	**Co1**	2	Benzene	110	24	62
9	**Co1**	2	Xylene	110	24	64
10	**Co1**	2	EtOH	110	24	Trace
11	**Co1**	2	THF	110	24	Trace
12	**Co1**	2	ACN	110	24	Trace
13	**Co1**	2	Toluene	110	24	91
14	**Co1**	2	[a]Toluene	110	24	87

Reaction Condition: Acetophenone (1 mmol), Benzyl alcohol (1 mmol), catalyst (2 mol%), KO^{t}Bu (0.5 mmol) Toluene 2 ml Temperature 110 °C for 24 h. [a]In presence of 5 eq. of PPh_3. Isolated yields.

Lowering the catalyst loading up to 1 mol% decreased the yield by 58% of desired product **5aa**. No retardation of the catalytic cycle was observed due to the addition of 5 eq. PPh_3 to the reaction mixture. These data clearly expressed the homogenous nature of catalysts. (Table 1, Entry 14). Toluene were found to the best solvent compared than other solvents and KO^{t}Bu was found to be the best base utilized for the reaction (Shown in SI Figures S49). Controlled

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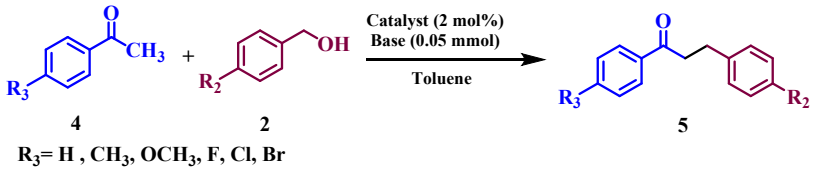
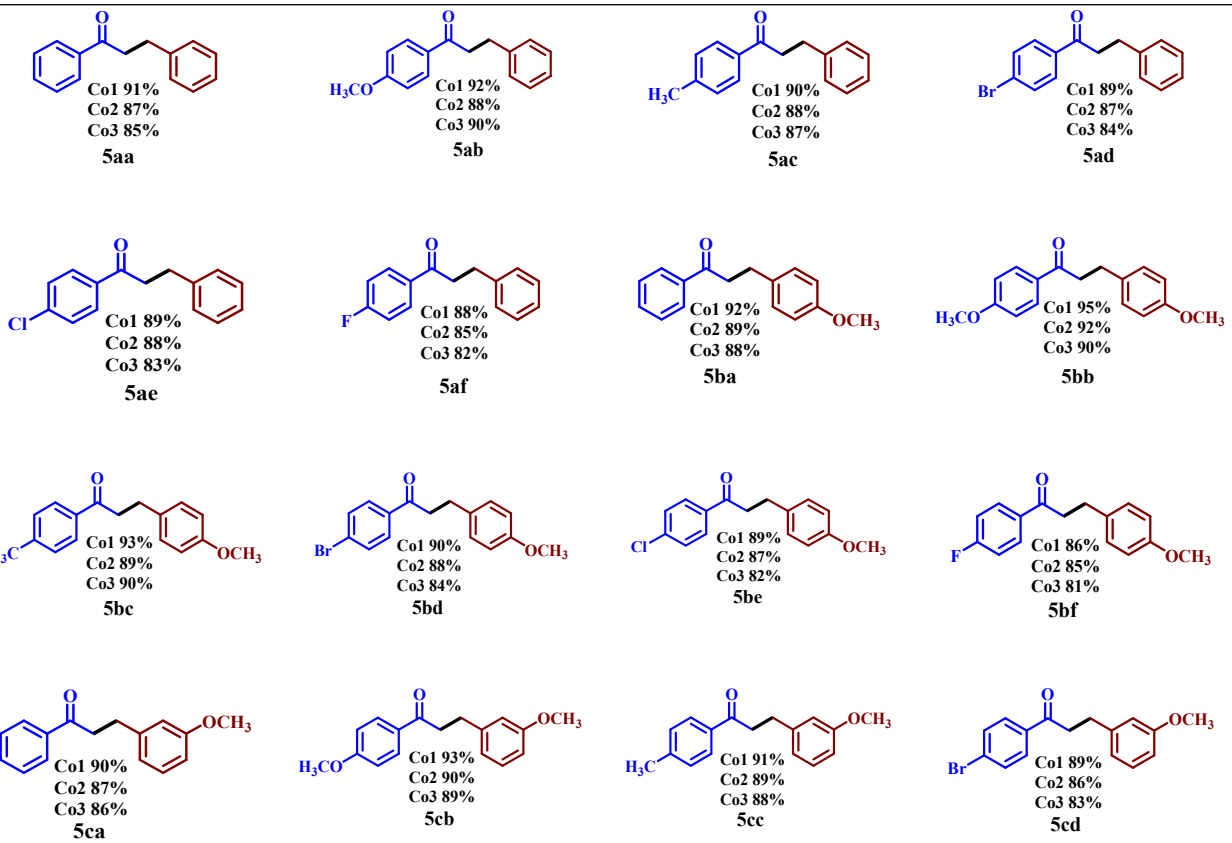
experiments were performed in the absence of catalyst **Co1,** in-situ generated catalyst system (1:1, L^1 and $CoCl_2.6H_2O$), only ligand L^1 and in absence of base KO^tBu. These control experiments resulted in no noticeable formation of desired product **5aa**, signifying the importance of the assembled catalyst i.e. cobalt complex for the catalytic activity. However, commercially available cobalt sources like $CoCl_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ also examined for α- alkylation reaction which provided no significant formation of desired product **5aa** (Table 3, Entry 1-4). Ultimately the optimization reaction performed with 1 mmol of ketone, 1 mmol of alcohol, 2 mol% catalyst loading of catalyst **Co1** and 0.5 mmol base KO^tBu in toluene solvent at 110 °C in 24 h for testing of different substrates. Under the established reaction conditions a series of primary alcohols and ketones were investigated for the substrate and functional group tolerance (Table 4). The reaction of acetophenone and their derivatives containing electron rich and electron deficient with benzyl alcohol showed high conversion of 82% to 91% of the desired products (Table 4, **5aa-5af**). Benzyl alcohols having electron-donating substituents (**4-OCH_3**) reacted with substituted ketones having (**4-OCH_3, 4-CH_3**) groups and halides (**4-Br**, **4-Cl** and **4-F**) groups produced α-alkylated product in high to excellent yields of 81% to 95% (Table 4, **5bb-5bf**). However, reaction of ketones having electron-donating (**4-OCH_3, 4-CH_3**) groups and electron-withdrawing (**4-Br**, **4-Cl** and **4-F**) groups with benzyl alcohol having electron rich substituents (**3-OCH_3**) afforded corresponding substituted 1,3-diphenylpropan-1-one product in high to excellent yields of 81% to 93% (Table 4, **5cb-5cf**).

Table 4. Substrate scope of α-alkylation of ketones



4 2 5

R_3= H , CH_3, OCH_3, F, Cl, Br
R_2= H, OCH_3, CH_3, Cl



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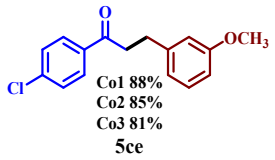
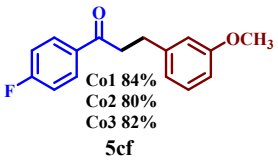


5ce



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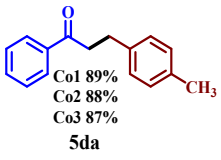

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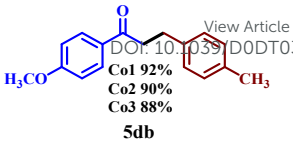
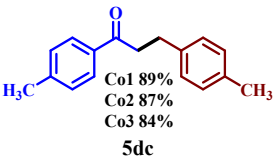


5db



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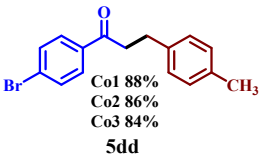

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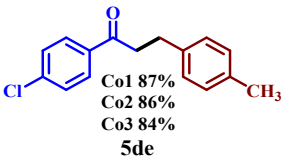

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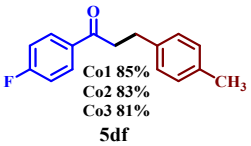

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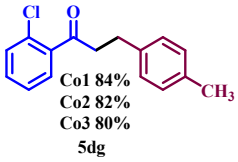

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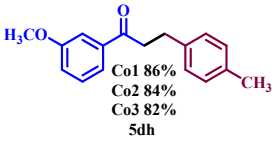

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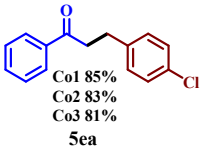

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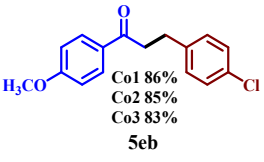

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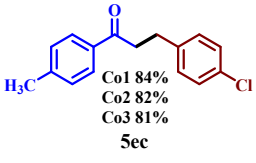

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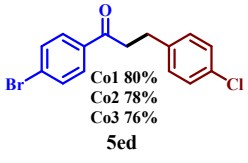

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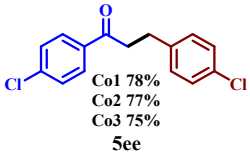

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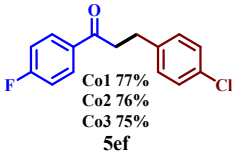

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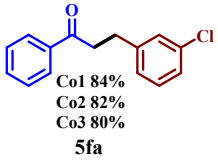

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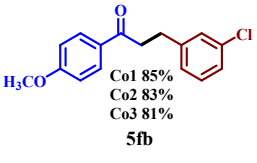

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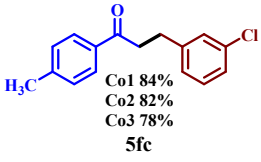

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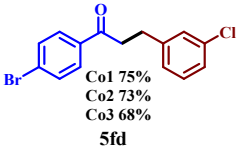

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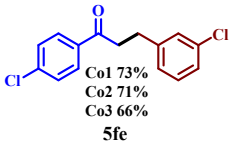

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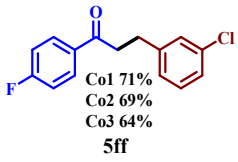

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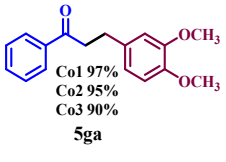

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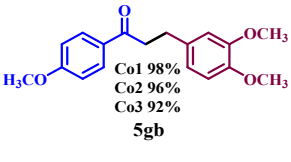

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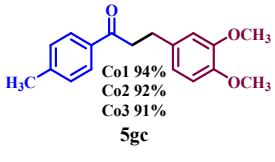

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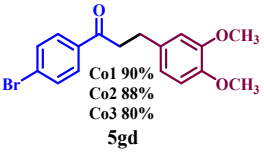

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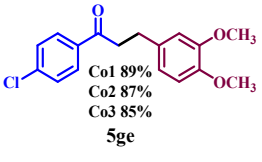

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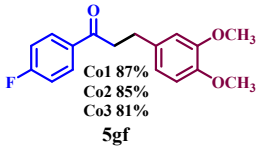

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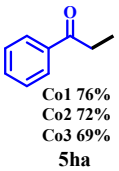
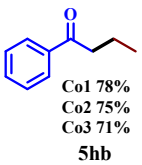


5ha



5hb

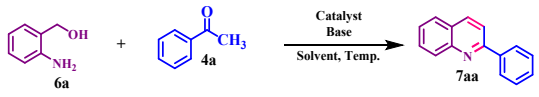
Reaction Condition: Acetophenone derivatives (1 mmol), Benzyl alcohol derivatives (1mmol), catalyst (2 mol%), KO^{t}Bu (0.5 mmol) Toluene 2 ml Temperature 110 °C for 24 h. Isolated yields.

Nevertheless, benzyl alcohols having electron-donating substituents (**4-CH_3**) reacted with substituted ketones having (**4-OCH_3, 4-CH_3**) groups and halides (**4-Br**, **4-Cl** and **4-F**) groups produced desired products **5db-5df** in high to excellent yields of 81% to 92%. The reaction of benzyl alcohols having electron-withdrawing substituents (**4-Cl**) with substituted ketones having (**4-OCH_3, 4-CH_3**) groups and halides (**4-Br**, **4-Cl** and **4-F**) groups formed C-alkylated products in good to high yields of 75% to 86% (Table 4, **5eb-5ef**). Under similar reaction condition, reaction with ketones having electron rich (**4-OCH_3, 4-CH_3**) groups and electron deficient (**4-Br**, **4-Cl** and **4-F**) groups and benzyl alcohol having electron-withdrawing substituents (**3-Cl**) afforded corresponding substituted 1,3-diphenylpropan-1-one in good to high yields 64% to 85% (Table 4, **5fb-5ff**). We also checked the effect of benzyl alcohols having electron-donating group (**3,4-OCH_3**) and substituted ketones having halides (**4-Br**, **4-Cl** and **4-F**) groups and (**4-OCH_3, 4-CH_3**) groups we ended up with the α-alkylated product in high to excellent yields 80% to 98% (Table 4, **5gb-5gf**). Under optimized protocol reaction of acetophenone with substituted alcohols containing electron rich as well as electron deficient afforded desired products **5aa, 5ba, 5ca, 5da, 5ea, 5fa** and **5ga** in high to excellent yield 85% to 97%. Catalytic system also useful in presence of sterically hindered ketone (**2-Cl**) gave rise to α-alkylated products in excellent yield 80% to 84% (Table 4, **5dg**). The reaction of electron rich ketone (**3-OCH_3**) with benzyl alcohols afforded desired product **5dh** in excellent yield of 82% to 86%. We have also explored the reaction of acetophenone with aliphatic alcohols gave rise to desired product **5ha** and **5hb** in good yield of 69% to 78% (shown in SI Figures S169-S172). Significant achievement has been made for α-alkylation of ketones from benzyl alcohols catalyzed by cobalt-based catalysts *via* dehydrogenative coupling. Thus, the present complexes (**Co1-Co3**) may be effective catalysts for α-alkylation reaction along with phosphorous free reaction conditions which would be an additional advantage. However, efforts at the alkylation of ketones with heterocyclic alcohols were not successful.

Dehydrogenative cyclization of 2-amino benzyl alcohol

Further, we have examined dehydrogenative cyclization of 2-amino benzyl alcohol **6a** with acetophenone **4a** in presence of **Co1** for the synthesis of 2-phenylquinoline (**7aa**). Several parameters such as temperature, solvent, base and time were optimized (Shown in SI, Figures S138). After investigating the reaction with different base additives, ^{t}BuOK was found to be the best suitable base for dehydrogenative cyclization of 2-amino benzyl alcohol. Among different solvent toluene was effective solvent for the conversion of the desired product **7aa**. On decreasing of catalyst loading (1 mol%) get suppression of desired product (Table 5, Entry 5). No inhibition of the catalytic reaction was observed due to the addition of 5 eq. PPh_3 to the reaction mixture. These data clearly indicated the homogenous nature of catalysts. (Table 1, Entry 14). Control experiments provided following important information. First, reaction attempted with commercially available cobalt sources like $CoCl_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ under optimized conditions gave poor conversion to the desired product (**7aa**). (Table 5, Entry 3) Second, no detectable desired product was obtained in presence of ligand L^1 and base ^{t}BuOK and also in absence of catalyst **Co1**. Third,

Table 5. Optimization reaction condition for the synthesis of quinoline



Entry	Cat.	Cat. loading (mol%)	Solvent	Temp (°C)	Time (h)	% Yield
1	–	–	Toluene	110	24	0
2	Ligand L^1	**2**	Toluene	110	24	0
3	$CoCl_2.6H_2O$/ $Co(NO_3)_2.6H_2O$	**2**	Toluene	110	24	0
4	L^1+$CoCl_2.6H_2O$	**2**	Toluene	110	24	Trace
5	**Co1**	**1**	Toluene	110	24	60
6	**Co1**	**2**	DMSO	110	24	45
7	**Co1**	**2**	DMF	110	24	38
8	**Co1**	**2**	Benzene	110	24	62
9	**Co1**	**2**	Xylene	110	24	64
10	**Co1**	**2**	EtOH	110	24	Trace
11	**Co1**	**2**	THF	110	24	Trace
12	**Co1**	**2**	ACN	110	24	Trace
13	**Co1**	**2**	Toluene	110	24	90
14	**Co1**	**2**	Toluene	110	24	86

Reaction Condition: 2-amino benzyl alcohol (1 mmol), Acetophenone derivatives (1 mmol), catalyst (2 mol%), KO^{t}Bu (0.5 mmol) Toluene 2 ml heated at 110 °C for 24 h. [a]In presence of 5 eq. PPh_3. Isolated yields.

we did not find any desired product when we performed the reaction by in-situ generated catalyst system (1:1, L^1 and $CoCl_2.6H_2O$). (Table 5, Entry 1, 2 and 4). The above control experiments authenticated the role of ligand as well as complexation of ligand with metal in the catalytic activity. Gratifyingly, the optimal results with 90% yield of 2-

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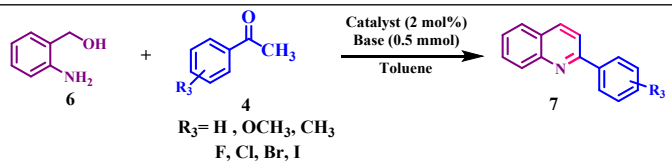
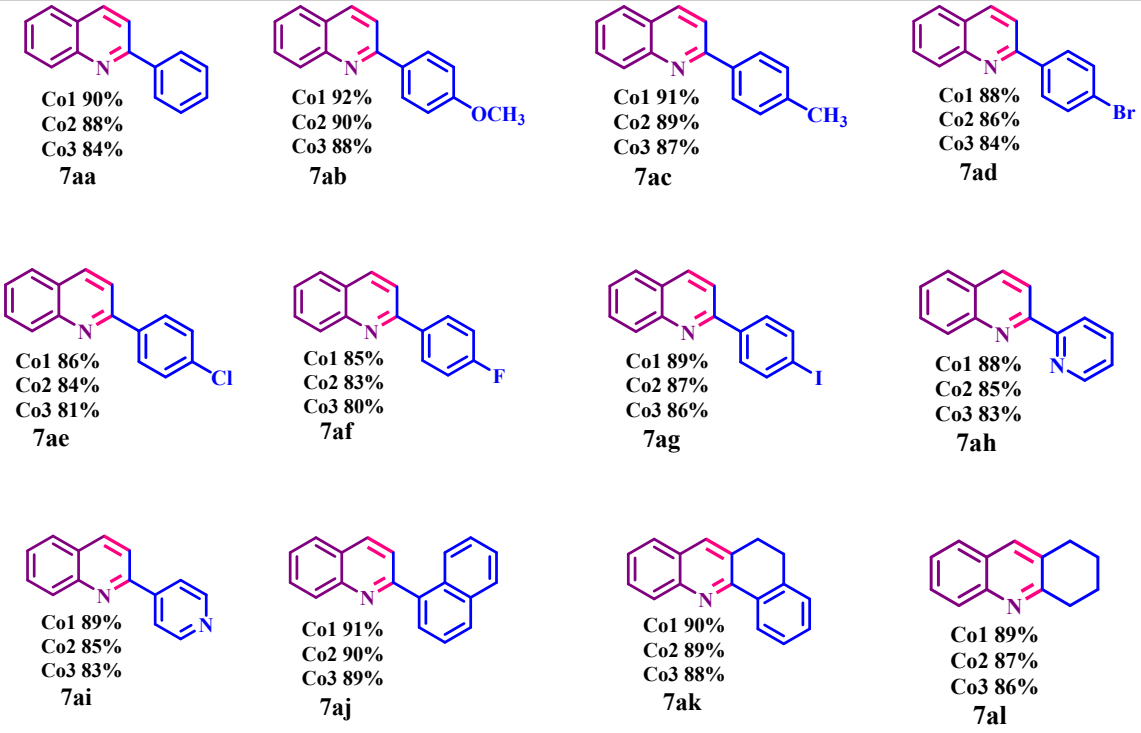
Table 6. Substrate scope for synthesis of quinolines





Reaction Condition: 2-aminobenzyl alcohol (1 mmol), acetophenones derivatives (1 mmol), catalyst (2 mol%), KO^{t}Bu (0.5 mmol) Toluene 2 ml heated at 110 °C for 24 h. Isolated yields.

phenylquinoline (Table 5, Entry 13) were obtained using 2 mol% of catalyst loading for catalyst **Co1**, 0.5 mmol base in toluene at 110 °C for 24 h. With the optimal reaction condition established, we next explored the substrate scope and efficiency of the dehydrogenative cyclization of 2-amino benzyl alcohol. The reaction of substituted acetophenone containing electron-donating groups (**4-OCH$_3$, 4-CH$_3$**) with 2-amino benzyl alcohol afforded corresponding quinoline derivative in good to excellent yield 87% to 91%. (Table 5 **7ab, 7ac**) The transformation of 2-amino benzyl alcohol with electron deficient acetophenones (**4-Br**, **4-Cl**, **4-F** and **4-I**) gave the corresponding quinoline derivatives **7ad, 7ae, 7af** and **7ag** in good to excellent yield 87% to 91%. We also checked the reaction of hetero acetophenones (**2** and **4** acetyl pyridine) with 2-amino benzyl alcohol formed the desired product **7ah, 7ai** in high to excellent yield 83%-89%. The catalytic system also effective with sterically hindered ketone and afforded the corresponding product **7aj** in excellent yield (>89%). The high catalytic activity also observed with alicyclic ketone affording the corresponding product **7ak** with excellent yield (>88%). However, α-tetralone gives the dehydrogenative synthesis of quinoline with 2-amino benzyl alcohol gave rise to corresponding product (Table 5, **7al**) in excellent yield (>86%).

These data obtained from our present study for our catalysts (**Co1-Co3**) for dehydrogenative cyclization of 2-amino benzyl alcohol with ketones were compared with the reports in the literature. The optimum loading of catalysts (**Co1-Co3**) for catalytic activity (2 mol%) for quinoline formation is lower than the values reported by Kundu and co-workers (catalyst loading 5 mol%) and Balaraman and co-workers (catalyst loading 2.5 mol%).[25b,18b] Thus, the catalytic potential of our catalysts may be placed among the best effective catalysts known for dehydrogenative cyclization of 2-amino benzyl alcohol.

Control experiments for *N*-alkylation of anilines and mechanistic investigation

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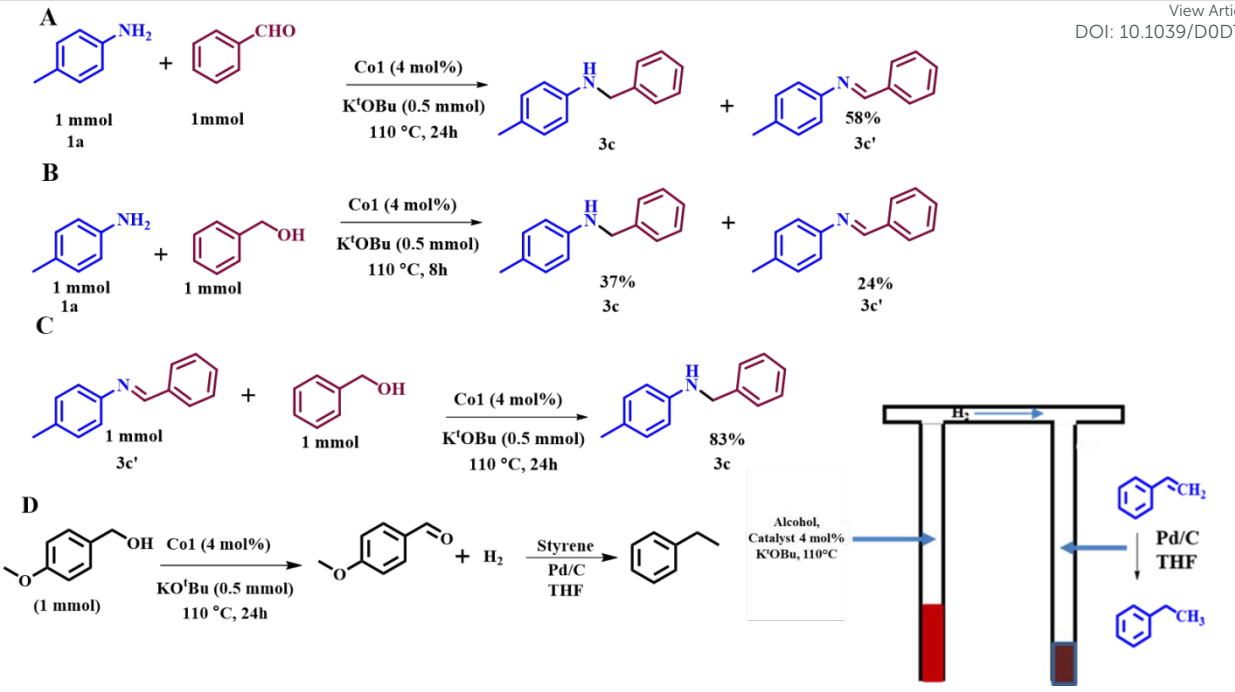


Scheme 3. Control experiment for *N*-alkylation of aniline and reduction of styrene.

To explain the mechanistic pathway, we have performed a series of control experiments under the optimized reaction conditions (Scheme 3). The reaction between *p*-toluidine and benzaldehyde afforded the product 1-phenyl-*N*-(*p*-tolyl)methanimine (**3c'**) with 58% yield. However, *N*-alkylated product was not observed during the reaction (**3c**) (Scheme 3A). We next carried out the reaction between *p*-toluidine and benzyl alcohol after 8h we observed *N*-alkylated product (**3c**) with 37% yield along with 1-phenyl-*N*-(*p*-tolyl)methanimine (**3c'**) (yield 24%) was deposited in Scheme 3B and NMR spectral data are shown in SI (Figures S163 and S164). After that we further utilized 1-phenyl-*N*-(*p*-tolyl)methanimine (**3c'**) as reactant and reacted with benzyl alcohol which gave rise to *N*-alkylated product (**3c**) with 83% yield. To investigate the dehydrogenative nature of catalytic reaction and to authenticate the H_2 evolution during the reaction, we performed the hydrogenation of styrene in presence of Pd/C in THF solution. The H_2 gas liberated in the first-round bottom flask during the acceptorless dehydrogenation of 4-methoxybenzyl alcohol was found to reduce styrene present in the second-round bottom flask. The reaction mixtures were examined and formation of ethylbenzene as hydrogenated product was confirmed.[20d,31] The reaction mixture was analyzed by GC-MS analysis shown in supporting information (Figure S167).

For mechanistic study we have characterized the possible reaction intermediates. Initially, we have performed the ESI-MS upon addition of 4-methoxy benzyl alcohol (5 equivalent) to catalyst **Co1** (0.04 mmol) in toluene for 10 min. A peak was generated at m/z= 786.22 which corresponds to the alkoxide species with the molecular formula $[C_{43}H_{42}ClCoN_5O_4\text{-}Cl^-+H^+]^+$ (shown in Figure S176). The other peak which was observed at m/z= 650.17 corresponds to the [Co–H] species having molecular formula $[C_{35}H_{34}ClCoN_5O_2\text{-}Cl^-]^+$(shown in Figure S177). These data clearly indicated the formation of alkoxide species **II** as well as hydride intermediate **III** generated during the catalytic cycle. We have done the ESI-MS after 12 h and found the peak at m/z= 861.27 which corresponds to the intermediate **IV** with the molecular formula $[C_{49}H_{47}ClCoN_6O_3\text{-}Cl^-]^+$ (shown in Figure S177). This data clearly indicated that the reduction of imine in the complex is not occur during catalytic cycle.[7l,31]

Based on above experimental data and literature reports[11] we propose the possible reaction pathway (Scheme S3). Initially, deprotonated alcohol was bound to the catalyst and generated intermediate **II**. Then the dehydrogenative activation of alkoxide species occurs and produces the benzaldehyde **B** and intermediate **III** was formed. We were successful in characterizing intermediates **II** and **III**. The resulting benzaldehyde **B** condensed with aniline **C** affording imine **D**. After that imine moiety **D** inserted into Co–H bond

afforded intermediate **IV**. Now intermediate **IV** reacted with alcohol to produce the *N*-alkylated product **E** and catalyst was regenerated.

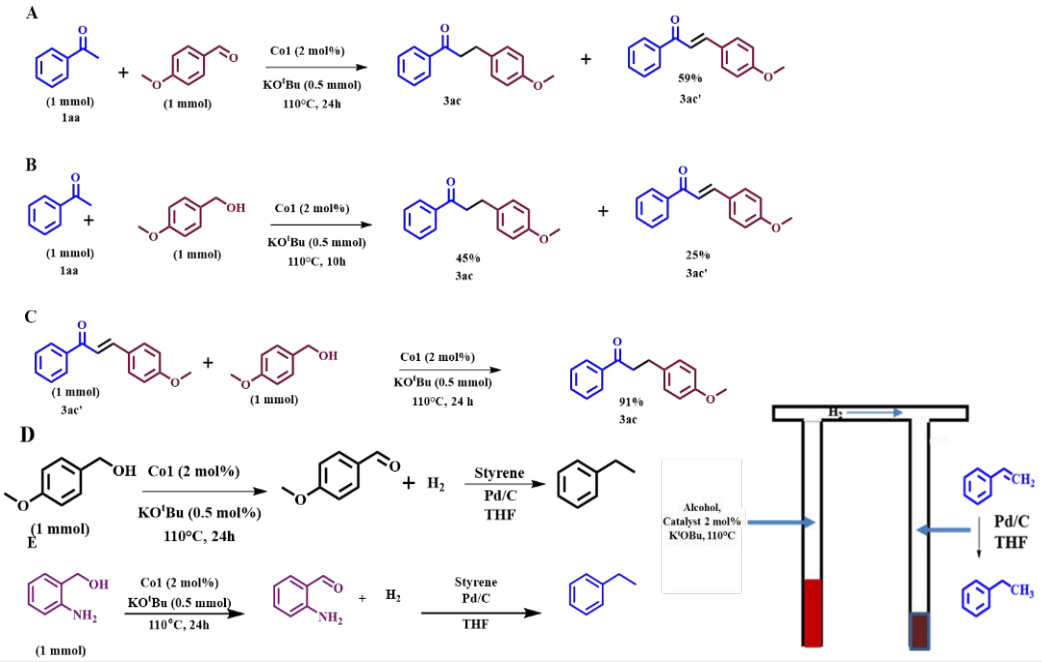
Control experiments for α-alkylation of ketones and mechanistic investigation

To shed light on the mechanism of α-alkylation reaction we set similar-type of control experiments under the optimized reaction conditions (Scheme 4). The reaction between acetophenone and 4-methoxy benzaldehyde afforded the α,β unsaturated ketone (**3ac'**) with 59% yield (Scheme 5A). However, in this case we did not observed α-alkylated product (**3ac**). We had observed that when the reaction was carried out between acetophenone and 4-methoxy benzyl alcohol for 10h, a mixture of α-alkylated product (**3ac**) with 45% yield along with α,β unsaturated ketone (**3ac'**) (shown in SI Scheme 5B, Figures S166 and S165) were obtained. During the reaction with intermediate α,β unsaturated ketone and 4-methoxy benzyl alcohol we have observed the formation of α-alkylated product only (**3ac**) with yield 91%. These reactions clearly dictated the role of alcohol during catalytic reaction. To authenticate the dehydrogenative nature of catalytic reaction and to investigate the H_2 evolution during the reaction we performed the hydrogenation of styrene in presence of Pd/C in THF solution. The H_2 gas liberated in the first-round bottom flask during the acceptorless dehydrogenation of 4-methoxy benzyl alcohol was found to reduce the styrene present in the second-round bottom flask. The reaction mixtures were examined and confirmed the formation of ethylbenzene as hydrogenated product. The reaction mixture was analysed by GC-MS analysis (shown in SI, S165).

On the basis of above experimental findings and previous reports[18b,31] a plausible reaction mechanism was proposed (shown in Scheme S4). Initially, the reaction of cobalt complex and deprotonated alcohol in presence of base generates Co-alkoxide species **II** (shown in Figure 2). Subsequently, β-hydride elimination of intermediate **II** gave rise to cobalt-hydride intermediate (shown in Figure 3) and the aldehyde **B**. In the next step, cross-aldol reaction of ketone **F** and aldehyde afforded α,β unsaturated ketone. Insertion reaction of α, β-unsaturated ketone **G** into Co–H bond afforded intermediate **IV** produced the α-alkylated product **H** and regenerate the catalyst.

Control experiments for dehydrogenative cyclization of 2-amino benzyl alcohol and mechanistic investigation

To explain the mechanistic study, we tried to identify the possible reaction intermediates. Initially, we have performed the ESI-MS generated at m/z= 771.22 which corresponds to the amino-alkoxide species with the molecular formula $[C_{42}H_{41}ClCoN_6O_3\text{-}Cl^-]^+$ (shown in Figure S175).



Scheme 4. Control experiments for α-alkylation of ketones and reduction of styrene.

The other peak which was observed at m/z: 650.17 corresponds to the [Co–H] species having molecular formula $[C_{35}H_{34}ClCoN_5O_2\text{-}Cl^-]^+$ (shown in Figure S176). We performed same procedure mentioned earlier for dehydrogenative nature of 2-aminobenzyl alcohol (shown in scheme 4). We came across the formation of ethylbenzene as hydrogenated product during dehydrogenation of 2-amino benzyl alcohol (shown in SI, S168)

A probable mechanistic pathway was scrutinized (shown in Scheme S5) for the dehydrogenative cyclization of 2-amino benzyl alcohol based on literature reports and our experimental findings.[20b] Initially, the catalyst **I** was reacted with 2-amino benzyl alcohol in presence of base and extraction of one molecule of HCl molecule was proposed giving rise to the formation of intermediate **II** amino-alkoxide species (shown in Figure 4). Dehydrogenative activation of alkoxide species gave rise to species **P** and intermediate **III** (shown in Figure 5). The resulting 2-amino benzaldehyde condense with the ketones **G** afforded aldol product **Q**. Dehydrative cyclization of aldol product **Q** occurred and afforded quinoline moiety **R**. The intermediate **III** reacted with another molecule of **F** regenerated the intermediate **II** with the liberation of dihydrogen.

Conclusions

The following are the major findings and conclusions for the present investigations.

Cobalt complexes **Co1, Co2** and **Co3** derived from pincer ligands L^1, L^2 and L^3 respectively were successfully synthesized and characterized by different spectroscopic methods. Molecular structures of **Co1** and **Co3** were determined by X-ray crystallography. **Co1, Co2** and **Co3** were successfully utilized for C–N bond formation and synthesis of *N*-alkylated products. For the substrate scope a total of 12 entries for *N*-alkylated products were reported. These catalysts were found to be effective for C–C bond formation and we have achieved α-alkylated compounds. To investigate the functional group tolerance, a total of 44 α-alkylated products were synthesized and the formation were authenticated. These catalysts were also found to be efficient in the synthesis of quinoline derivatives. For the substrate scope a total of 12 cyclized quinoline products were synthesized and characterized. Control experiments were examined to get better insight of the reaction pathways. Mechanisms proposed for the reactions were supported by ESI-MS analysis of Co-alkoxide and Co-hydride intermediates. The liberation of molecular hydrogen gas authenticated dehydrogenative nature of catalysts. Reduction of styrene and formation of ethyl benzene clearly expressed the evolution of hydrogen gas. Studies on modification of the ligands and other catalytic activities of these useful cobalt-based catalysts are under progress.

Experimental section

Materials and methods

Analytical grade reagents were used such as phenylhydrazine, (S. D. Fine, Mumbai, India), 2,6 dichloropyridine (Sigma Aldrich, Steinheim, Germany), Derivatives of benzaldehydes (Himedia Laboratories Pvt. Ltd., Mumbai, India), $CoCl_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ (Merck Limited, Mumbai, India). Solvents used for spectroscopic studies were HPLC grade and purified by standard procedures before use. All other chemicals were purchased from commercial suppliers and used as received without further purification. Infrared (IR) measurements were performed (400–4000 cm^{-1}) on a Nicolet FT-IR 6700 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded in CH_2Cl_2 and CH_3OH with an Evolution 600, Thermo Scientific UV–Vis. spectrophotometer using cuvettes of 1 cm path length. C, H, N and O elemental analysis were performed on a Perkin-Elmer 240B elemental analyzer. A Merck 60 F254 silica gel plate (0.25 mm thickness) was used for analytical TLC and Merck 60 silica gel (100–200 mesh) was used for column chromatography. ^1H and ^{13}C NMR spectra were recorded on Bruker D AVANCE III 500 MHz (AV 500) (500 MHz), JEOL (400 MHz) spectrometers in the deuterated solvents. TMS (tetramethylsilane) was used as the internal standard. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). ESI-MS experiments were performed on a Brüker micrOTOFTM-Q-II mass spectrometer.

X-ray Crystallography

Red crystals of complexes **Co1** and **Co3** were obtained by slow evaporation of solution from the complexes in CH_2Cl_2/CH_3CN. The X-ray data collection and processing for complexes were performed on a Bruker Kappa Apex-II CCD diffractometer by using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 150 K for complexes **Co1** and **Co3** at 293(2) K. Crystal structures were solved by direct methods. Structure solutions, refinement and data output were carried out with the SHELXTL program.[39] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. Images were created with the DIAMOND program.[40] The "SQUEEZE"

option in the PLATON program was used to remove a disordered solvent molecule from the overall intensity data for complex **Co1**.[41]

Synthesis of ligands

Synthesis of 2,6-bis(2(4-ethoxybenzylidene)-1-phenylhydrazineyl) pyridine [L^1]

2,6-bis(1-phenylhydrazinyl) pyridine were synthesized by reported procedure.[32] This was used as a reactant (291 mg, 1.00 mmol) with 4-ethoxybenzaldehyde (300.0 mg, 2.00 mmol) and were dissolved in 5 mL of methanol. The reaction mixture was stirred at room temperature in open air. Within 40 minutes off-white solid began to separate out slowly and stirring was continued for another 1 h. Off-white precipitate was filtered, washed thoroughly with methanol, diethyl ether and then dried in vacuum. L^1 was recrystallized from dichloromethane. The compound was characterized by UV-Vis., IR, and NMR spectroscopic studies. Yield: (333 mg, 60%) Selected IR data: (KBr, ν/cm^{-1}): 1566 ($\nu_{C=N}$) UV-Vis. [CH_2Cl_2 (λ_{max}/nm (ε/M^{-1}cm^{-1})]: 364(64100), 473(3680). ^{1}H NMR (400 MHz, CDCl3) δ 7.59 (t, *J* = 8.0 Hz, 1H), 7.49 (s, 2H), 7.47 (s, 2H), 7.27 – 7.08 (m, 7H), 7.20 – 7.16 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.1 Hz, 4H), 6.84 (d, *J* = 8.7 Hz, 3H), 4.03 (q, *J* = 7.0 Hz, 4H), 1.41 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.66, 139.60, 138.83, 138.44, 129.73, 129.22, 127.99, 126.80, 123.33, 111.53, 99.87, 44.50, 12.70. Anal. Calc. $C_{35}H_{33}N_5O_2$: C, 75.65; H, 5.99; N, 12.60 Found C, 75.59; H, 5.95; N, 12.56. HRMS (+ESI) m/z: calcd for [$C_{35}H_{34}N_5O_2$+H$^+$]$^+$: 556.2707; found: 556.2775 for [L^1+H$^+$]$^+$ ion.

Synthesis of 4,4'-((pyridine-2,6-diylbis(2-phenylhydrazin-2-yl-1-ylidene))bis(methaneyl ylidene)) bis(N,N-diethylaniline) [L^2]

L^2 was synthesized in similar manner using 4-(diethylamino) benzaldehyde (234 mg, 2.00 mmol) and 2,6-bis(1-phenylhydrazinyl) pyridine as described above. Yield: 377.58 mg, 62%. Selected IR data: (KBr, ν/cm^{-1}): 1565 ($\nu_{C=N}$) UV-Vis. [CH_2Cl_2 (λ_{max}/nm (ε/M^{-1}cm^{-1}))]: 326(35040), 366(55430). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, *J* = 8.0 Hz, 1H), 7.44 (s, 2H), 7.42 (s, 2H), 7.25 – 7.15 (m, 8H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 3H), 6.62 (d, *J* = 8.9 Hz, 4H), 3.37 (q, *J* = 7.0 Hz, 8H), 1.16 (t, *J* = 7.0 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.66, 148.11, 139.60, 138.83, 138.44, 129.73, 129.22, 127.99, 126.80, 123.33, 111.53, 99.87, 44.50, 12.70. Anal. Calc. $C_{39}H_{43}N_7$: C, 76.81; H, 7.11; N, 16.08 Found C, 76.83; H, 7.08; N, 16.10. HRMS (+ESI) m/z: calcd for [$C_{39}H_{44}N_7$+H$^+$]$^+$: 610.3653; found: 610.3701 for [L^2+H$^+$]$^+$ ion.

Synthesis of 4,4'-((pyridine-2,6-diylbis(2-phenylhydrazin-2-yl-1-ylidene))bis (methaneyl ylidene)) bis(N,N-dimethylaniline) [L^3]

L^3 was synthesized in similar manner using 4-(dimethylamino) benzaldehyde (298 mg, 2.00 mmol) and 2,6-bis(1-phenylhydrazinyl) pyridine as described above. Yield 353.92 mg, 62%. Selected IR data: (KBr, ν/cm^{-1}): 1575 ($\nu_{C=N}$) UV-Vis. [CH_2Cl_2 (λ_{max} /nm (ε/M^{-1}cm^{-1}))]: 365(63500), 471(3400). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, *J* = 8.1 Hz, 1H), 7.47 (s, 2H), 7.45 (s, 2H), 7.26 – 7.18 (m, 8H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 6.7 Hz, 3H), 6.66 (d, *J* = 9.0 Hz, 3H), 2.97 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.62, 150.74, 139.45, 138.86, 138.11, 129.76, 129.27, 128.77, 127.80, 126.92, 124.39, 112.18, 99.93, 40.49. Anal. Calc. $C_{35}H_{35}N_7$: C, 75.92; H, 6.37; N, 17.71 Found C, 75.90; H, 6.34; N, 17.68. HRMS (+ESI) m/z: calcd for [$C_{35}H_{36}N_7$+H$^+$]$^+$: 554.3027; found: = 554.3078 for [L^3+H$^+$]$^+$ ion.

Synthesis of complexes

Synthesis of complex Co1

To a 4 mL of dichloromethane solution of ligand L^1 (555 mg, 1 mmol) a batch of $CoCl_2.6H_2O$ (237 mg, 1 mmol) in 4 mL of methanol was added. The reaction was stirred for 5 h in open air. Red precipitate was filtered and the isolated solid was washed with little amount of methanol. On slow evaporation of CH_2Cl_2/ CH_3CN red coloured crystals are formed. The compound was characterised by IR, UV-Vis. and ESI-MS analysis. Yield: 437.76 mg (64%) Selected IR data: (KBr, *v*/cm^{-1}): 1562 ($\nu_{C=N}$) UV-Vis. [CH_2Cl_2, λ_{max}/nm (ε/M^{-1}cm^{-1})]: 334(35020), 390(11960),420(9220). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (t, *J* = 8.0 Hz, 1H), 7.42 (s, 1H), 7.40 (s, 1H), 7.21 – 7.15 (m, 6H), 7.09 (s, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 6.8 Hz, 4H), 6.77 (d, *J* = 8.5 Hz, 4H), 3.98 (q, *J* = 1 6.9 Hz, 4H), 1.35 (t, *J* = 6.9 Hz, 6H). Anal. Calc. For $C_{35}H_{33}Cl_2CoN_5O_2$; C, 61.32; H, 4.85; N, 10.22. Found: C, 61.16; H, 4.92; N, 10.31. HRMS (+ESI) m/z: calcd for [$C_{35}H_{33}CoClN_5O_2$–Cl$^-$]$^+$: 649.1655; found: = 649.1600 for (**Co1**-Cl$^-$)$^+$ ion.

Synthesis of complex Co2

To a 4 mL of dichloromethane solution of ligand L^2 (609 mg, 1 mmol) a batch of $CoCl_2.6H_2O$ (237 mg, 1 mmol) in 4 mL of methanol was added. The reaction was stirred for 5 h in open air. Red precipitate was filtered which was washed with little amount of methanol. The compound was characterised by IR, UV-Vis.and ESI-MS analysis. Yield: 457.56 mg (62%) Selected IR data: (KBr, *v*/cm^{-1}): 1562 ($\nu_{C=N}$) UV-Vis. [CH_2Cl_2, λ_{max}/nm (ε/M^{-1}cm^{-1})]: 356(56290), 418(17060),454(10790). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (t, *J* = 4.5 Hz, 1H), 7.73 (s, 1H), 7.71 (s, H), 7.51 – 7.47 (m, 3H), 7.38 (d, *J* = 15.4 Hz, 4H), 7.07 (d, *J* = 4.9 Hz, 4H), 7.02 – 6.98 (m, 2H), 6.92 – 6.85 (m, 3H), 6.69 (d, *J* = 8.6 Hz, 4H), 3.46 (q, *J* = , 6.8 Hz, 8H), 1.23 (t, *J* = 7.1

Hz, 12H). Anal. Calc. For $C_{39}H_{43}Cl_2CoN_7$; C, 63.33; H, 5.86; N, 13.26. Found: C, 63.30; H, 5.91; N, 13.18. HRMS (+ESI) m/z: calcd for $[C_{39}H_{43}CoClN_7–Cl^-]^+$: 703.2600; found: = 703.2652 for (**Co2**-$Cl^-)^+$ ion.

Synthesis of complex Co3

To a 4 mL of dichloromethane solution of ligand L^3 (553 mg, 1 mmol) a batch of $CoCl_2.6H_2O$ (237 mg, 1 mmol) in 4 mL of methanol was added. The reaction was stirred for 5 h in open air. Red precipitate was filtered which was washed with little amount of methanol. On slow evaporation of CH_2Cl_2/ CH_3CN red coloured crystals are formed. The compound was characterised by IR, UV-Vis. and ESI-MS analysis. Yield: 443.30 mg (65%) Selected IR data: (KBr, ν/cm^{-1}): 1558 ($\nu_{C=N}$) UV-Vis. [CH_2Cl_2, λ_{max}/nm (ε/$M^{-1}cm^{-1}$)]: 369(80400), 419(27440), 456(17240). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.0 Hz, 1H), 7.45 (s, 1H), 7.43 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.14 (m, 4H), 7.13 – 7.08 (m, 2H), 7.01 (d, *J* = 7.9 Hz, 3H), 6.81 (d, *J* = 7.4 Hz, 4H), 6.66 (d, *J* = 8.5 Hz, 1H), 6.60 – 6.55 (m, 3H), 2.91 (s, 12H). Anal. Calc. For $C_{35}H_{35}Cl_2CoN_7$; C, 61.50; H, 5.16; N, 14.34. Found: C, 61.34; H, 5.22; N, 14.43. HRMS (+ESI) m/z: calcd for $[C_{35}H_{35}CoClN_7–Cl^-]^+$: 647.1974; found: = 647.2095 for (**Co3**-$Cl^-)^+$ ion.

General procedure for *N*-alkylation of anilines

The catalytic reaction was performed by following procedure. To a 10mL, clean, oven-dried, screw cap reaction tube containing complexes (0.04 mmol), benzyl alcohols (1 mmol), anilines (1 mmol), KO^tBu (0.5 mmol), and toluene (2 mL) were reacted in argon atmosphere. The reaction mixture was stirred at 110 °C for 24 h. Then, the reaction mixture was diluted with water (5 mL) and extracted with ethyl acetate (3 × 5 mL) and filtered off through Whatman 41 filter paper. The resultant organic layer was dried over anhydrous sodium sulphate and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (100–200 mesh size) using hexane/ethyl acetate as the eluting system. The isolated products were authenticated by ^{1}H and ^{13}C NMR spectra displayed in Supporting Information (Figures S25-S48).

N-benzylaniline (3aa)[13a]: Colourless oil, Yield: **Co1** (150.06 mg, 82%), **Co2** (148.23 mg, 81%), **Co3** (142.74 mg, 78%).^{1}H NMR (400 MHz, $CDCl_3$) δ 744-7.41 (m, 4H), 7.34 (t, *J* = 6.7 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 2H), 4.37 (s, 2H), 4.06 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.32, 139.62, 129.44, 128.80, 127.67, 127.39, 117.72, 113.01, 48.45.

N-(4-methoxybenzyl)aniline (3ab)[42]: Light yellow liquid, Yield: **Co1** (181.05 mg, 85%), **Co2** (174.66 mg, 82%), **Co3** (170.4 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.7 Hz, 2H), 7.25 – 7.21 (m, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 2H), 6.69 (d, *J* = 7.6 Hz, 2H), 4.30 (s, 2H), 4.00 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.94, 148.32, 131.52, 129.33, 128.88, 117.56, 114.10, 112.93, 55.35, 47.84.

1,2-dimethoxy-4-phenethylbenzene (3ac)[43]: Pale yellow liquid, Yield: **Co1** (200.86 mg, 83%), **Co2** (196.02 mg, 81%), **Co3** (188.76 mg, 78%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 10.6, 5.5 Hz, 1H), 7.02 – 6.95 (m, 2H), 6.88 – 6.79 (m, 2H), 6.70 (t, *J* = 7.8 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 4.66 (s, 1H), 4.35 (s, 2H), 3.88 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.96, 146.87, 141.43, 138.21, 129.67, 121.36, 119.86, 116.75, 113.11, 112.64, 110.20, 109.46, 55.50, 55.30, 48.16.

N-(4-methylbenzyl)aniline (3ad)[42]: Light yellow liquid, Yield: **Co1** (155.63 mg, 79%), **Co2** (153.66 mg, 78%), **Co3** (151.69 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.36 – 7.33 (m, 2H), 7.29 (d, *J* = 6.9 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.33 (s, 2H), 3.92 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.03, 139.76, 129.84, 128.70, 127.59, 127.25, 126.85, 113.09, 48.74, 20.49.

N-(4-chlorobenzyl)aniline (3ae)[42]: Colourless liquid, Yield: **Co1** (169.26 mg, 78%), **Co2** (160.08 mg, 74%), **Co3** (156.24 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.38 (d, *J* = 7.0 Hz, 1H), 7.32 (d, *J* = 5.2 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 3H), 6.76 (d, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 6.5 Hz, 2H), 4.36 (s, 2H), 4.04 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.28, 146.86, 138.61, 138.24, 137.87, 134.54, 133.96, 132.83, 131.02, 130.32, 129.50, 128.65, 47.42.

N-(4-chlorobenzyl)-4-methoxyaniline (3ba)[44]: White solid, Yield: **Co1** (200.07 mg, 81%), **Co2** (195.13 mg, 79%), **Co3** (190.19 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 4H), 7.28 (d, *J* = 8.3 Hz, 1H), 6.84 – 6.78 (m, 2H), 6.71 – 6.66 (m, 1H), 6.53 (d, *J* = 7.7 Hz, 1H), 4.65 (s, 1H), 4.33 (s, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.87, 138.25, 137.88, 132.84, 128.78, 121.33, 116.97, 110.20, 109.54, 55.51, 47.43.

N-benzyl-2-methoxyaniline (3ca)[45]: Brownish oil, Yield: **Co1** (178.92 mg, 84%), **Co2** (174.66 mg, 82%), **Co3** (170.4 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 6.9 Hz, 3H), 7.35 (d, *J* = 7.3 Hz, 3H), 7.28 (d, *J* = 6.7 Hz, 1H), 6.81 (d, *J* = 6.6 Hz, 2H), 6.68 (s, 1H), 6.61 (s, 1H), 4.63 (s, 1H), 4.36 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.79, 139.59, 138.15, 128.58, 127.53, 127.20, 121.28, 117.42, 116.63, 111.51, 110.08, 109.40, 55.42, 48.05.

N-benzyl-4-methylaniline (3da)[11]: Colourless oil, Yield: **Co1** (163.51 mg, 83%), **Co2** (159.57 mg, 81%), **Co3** (151.69 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 4H), 7.28 (s, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.33 (s, 2H), 3.92 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.03, 139.76, 129.84, 128.70, 127.59, 127.25, 126.85, 113.09, 48.74, 29.81, 20.49.

N-(4-methoxybenzyl)-4-methylaniline (3db)[46]: White solid, Yield: **Co1** (195.22 mg, 86%), **Co2** (188.41 mg, 83%), **Co3** (181.6 mg, 80%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.7 Hz, 1H), 7.32 (s, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 3H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.25 (s, 2H), 3.89 (s, 1H), 3.82 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.03, 139.76, 129.84, 128.70, 127.59, 127.25, 126.85, 113.09, 48.74, 29.81, 20.49.

N-benzyl-4-chloroaniline (3ea)[44]: Colourless oil, Yield: **Co1** (164.92 mg, 76%), **Co2** (160.58 mg, 74%), **Co3** (151.90 mg, 70%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H), 6.56 (d, *J* = 8.7 Hz, 2H), 4.23 (s, 1H), 3.82 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.05, 146.86, 132.13, 131.03, 128.99, 128.77. 127.4, 122.04, 114.12, 55.41, 47.90.

4-chloro-N-(4-methoxybenzyl)aniline (3eb)[47]: White solid, Yield: **Co1** (192.66 mg, 78%), **Co2** (187.72 mg, 76%), **Co3** (182.78 mg, 74%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.2 Hz, 2H), 6.55 (d, *J* = 8.7 Hz, 2H), 4.22 (s, 2H), 4.02 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.05, 146.86, 132.13, 131.03, 128.99 127.47, 122.04, 114.12, 55.41, 47.90.

N-(4-methoxybenzyl)pyridin-2-amine (3fa)[48]: Colourless oil, Yield: **Co1** (149.82 mg, 70%), **Co2** (145.52 mg, 68%), **Co3** (139.10 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 6.2 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.27 (d, *J* = 6.9 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.58 (d, *J* = 7.2Hz, 1H), 6.36 (d, *J* = 7.4 Hz, 1H), 4.86 (s, 1H), 4.41 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.94, 158.70, 148.22, 137.59, 131.19, 128.78, 114.12, 113.17, 106.88, 55.37, 45.91.

(*E*)-1-phenyl-*N*-(*p*-tolyl)methanimine (3c')[13d]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.18 (m, 3H), 7.16 – 7.11 (m, 2H), 2.38 (s, 3H).

General procedure for α-alkylation of ketones with primary alcohols

The catalytic reactions were performed following a general procedure. To a 10mL, clean, oven-dried, screw cap reaction tube containing 1 mmol of alcohols, 1 mmol ketones in dry toluene (2 mL), solvent was mixed with 2 mol % catalyst, 0.5 mmol KO^{t}Bu were reacted in inert condition. The reaction mixture was heated at 110 °C with constant stirring in a preheated oil bath for 24 h. The resulting solution was then filtered off through Whatman 41 filter paper. The filtrate was dried under reduced pressure, and the organic product was extracted by a solvent extraction technique using a water/ethyl acetate solvent mixture. The organic layer was collected and removed through rotary evaporator. The residue was then purified by 100-200 mesh silica-gel column chromatography to afford the pure product. The isolated products were authenticated by ^{1}H and 13C NMR spectra displayed in Supporting Information (Figure S50-S137) and (Figure S169-S172) .

1,3-diphenylpropan-1-one (5aa)[49]**:** White solid, Yield: **Co1** (191.11 mg, 91%), **Co2** (182.7 mg, 87%), **Co3** (178.50 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 3H), 7.21 (s, 1H), 7.14 (s, 1H), 3.34 (t, *J* = 7.7 Hz, 2H), 3.06 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.33, 141.38, 139.59, 136.94, 133.18, 129.69, 128.14, 126.24, 40.54, 30.21.

1-(4-methoxyphenyl)-3-phenylpropan-1-one (5ab)[49]**:** Yellow oil, Yield: **Co1** (208.84 mg, 92%), **Co2** (204.3 mg, 90%), **Co3** (199.76 mg, 88%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.9 Hz, 2H), 7.28 (m, 4H), 7.21 (t, *J* = 7.0 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 3H), 3.86 (s, 3H), 3.25 (t, *J* = 8.2 Hz, 2H), 3.06 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.91, 163.55, 141.57, 130.40, 130.06, 128.57, 126.18, 113.83, 55.55, 40.20, 30.43.

3-phenyl-1-(p-tolyl)propan-1-one (5ac)[49]**:** Yellow oil, Yield: **Co1** (201.6 mg, 90%), **Co2** (197.12 mg, 88%), **Co3** (194.88 mg, 87%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 2.4 Hz, 2H), 7.25 (s, 1H), 7.22 (t, *J* = 7.1 Hz, 2H), 3.30 (t, *J* = 7.9 Hz, 2H), 3.09(t, *J* = 8.0 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.99, 143.92, 141.49, 134.48, 129.37, 128.56, 128.26, 126.18, 40.43, 30.31, 21.72.

1-(4-bromophenyl)-3-phenylpropan-1-one (5ad)[18b]**:** Off-white solid, Yield: **Co1** (256.32 mg, 89%), **Co2** (250.56 mg, 87%), **Co3** (241.92 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.22 (m, 3H), 3.27 (t, *J* = 7.7 Hz, 2H), 3.10 (t, *J* = 8.0 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 198.24, 141.14 , 135.65, 132.01, 129.67, 128.85, 126.33, 40.49, 30.13.

1-(4-chlorophenyl)-3-phenylpropan-1-one (5ae)[49]**:** Yellow oil, Yield: **Co1** (217.16 mg, 89%), **Co2** (214.72 mg, 88%), **Co3** (202.52 mg, 83%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 3.29 (t, *J*

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= 7.5 Hz, 2H), 3.08 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.60, 139.58, 135.05, 131.98, 130.44, 129.82, 129.43, 128.98, 128.65, 115.00, 40.12, 29.29.

1-(4-fluorophenyl)-3-phenylpropan-1-one (5af)[49]**:** Off-white solid, Yield: **Co1** (200.64 mg, 88%), **Co2** (193.80 mg, 85%), **Co3** (186.96 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (m, 2H), 7.32 – 7.29 (m, 2H), 7.26 (s, 1H), 7.25 – 7.21 (m, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 3.28 (t, *J* = 7.7 Hz, 2H), 3.07 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.70, 167.08, 164.54, 141.22, 133.36, 130.74, 128.57, 126.28, 115.89, 115.67, 40.46, 30.18.

3-(4-methoxyphenyl)-1-phenylpropan-1-one (5ba)[49]**:** Yellow oil, Yield: **Co1** (220.80 mg, 92%), **Co2** (213.60 mg, 89%), **Co3** (211.20 mg, 88%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 3.27 (t, *J* = 8.0 Hz, 2H), 3.05 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.47, 158.10, 137.00, 133.41, 133.13, 129.46, 128.70, 128.14, 114.04, 55.36, 40.79, 29.37.

1,3-bis(4-methoxyphenyl)propan-1-one (5bb)[31]**:** Yellow solid, Yield: **Co1** (256.50 mg, 95%), **Co2** (248.40 mg, 92%), **Co3** (243.00 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 2H), 3.85 (s, 3H), 3.78 (s, 3H), 3.21 (t, *J* = 7.6 Hz, 2H), 3.00 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.93, 163.46, 158.02, 133.51, 130.30, 129.33, 113.95, 113.72, 55.39, 55.22.

3-(4-methoxyphenyl)-1-(p-tolyl)propan-1-one (5bc)[31]**:** Yellow oil, Yield: **Co1** (236.22 mg, 93%), **Co2** (228.60 mg, 90%), **Co3** (226.06 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 3.30 (t, *J* = 7.8 Hz, 2H), 3.06 (t, *J* = 7.7 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.14, 158.07, 143.89, 134.53, 133.52, 129.42, 128.28, 114.02, 55.39, 40.69, 29.47, 21.75.

1-(4-bromophenyl)-3-(4-methoxyphenyl)propan-1-one (5bd)[31]**:** Off-white solid, Yield: **Co1** (286.20 mg, 90%), **Co2** (279.84 mg, 88%), **Co3** (267.12 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.86 – 6.82 (m, 2H), 3.78 (s, 3H), 3.22 (t, *J* = 7.6 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.41, 158.19, 135.74, 133.17, 132.01, 129.69, 129.46, 128.28, 114.10, 55.38, 40.75, 29.31.

1-(4-chlorophenyl)-3-(4-methoxyphenyl)propan-1-one (5be)[31]**:** White solid, Yield: **Co1** (243.86 mg, 89%), **Co2** (238.38 mg, 87%), **Co3** (224.68 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 3.26 (t, *J* = 7.7 Hz, 2H), 2.98 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.24, 158.12, 139.54, 135.27, 133.15, 129.49, 128.99, 114.05, 55.35, 40.77, 29.28.

1-(4-fluorophenyl)-3-(4-methoxyphenyl)propan-1-one (5bf)[31]**:** White solid, Yield: **Co1** (221.88 mg, 86%), **Co2** (219.39 mg, 85%), **Co3** (208.98 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 3.24 (t, *J* = 7.7 Hz, 2H), 3.01 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.86, 167.05, 164.52, 158.12, 133.56, 130.74, 129.43, 115.76, 115.44, 114.04, 55.35, 40.70, 29.34.

3-(3-methoxyphenyl)-1-phenylpropan-1-one (5ca)[31]**:** Yellow oil, Yield: **Co1** (216.0 mg, 90%), **Co2** (208.8 mg, 87%), **Co3** (206.4 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.82 (s, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 3.80 (s, 3H), 3.31 (t, *J*= 7.5, 2H), 3.05 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.29, 159.84, 143.04, 136.93, 133.19, 129.63, 128.72, 128.15, 120.88, 114.34, 111.51, 55.25, 40.46, 30.26.

3-(3-methoxyphenyl)-1-(4-methoxyphenyl)propan-1-one (5cb)[31]**:** Yellow oil, Yield: **Co1** (251.1 mg, 93%), **Co2** (243.0 mg, 90%), **Co3** (240.3 mg, 89%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.9 Hz, 2H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.81 (s, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 3.27 (t, *J* = 7.6 Hz, 2H), 3.06(t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.92, 163.54, 159.79, 143.20, 130.70, 130.41, 129.99, 129.59, 120.87, 114.30, 113.81, 111.44, 55.56, 55.25, 40.13, 30.45.

3-(3-methoxyphenyl)-1-(p-tolyl)propan-1-one (5cc)[31]**:** Yellow oil, Yield: **Co1** (231.14 mg, 91%), **Co2** (226.06 mg, 89%), **Co3** (223.52 mg, 88%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 7.7 Hz, 3H), 7.22 (d, *J* = 7.9 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.82 (s, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 3.80 (s, 3H), 3.26 (t, *J* = 7.1 Hz, 2H), 3.04 (t, *J* = 7.4 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.94, 159.84, 143.92, 143.14, 134.49, 129.44, 128.26, 120.81, 114.25, 111.46, 55.29, 40.33, 30.35, 21.75.

1-(4-bromophenyl)-3-(3-methoxyphenyl)propan-1-one (5cd)[31]**:** Off-white solid, Yield: **Co1** (283.02 mg, 89%), **Co2** (273.48 mg, 86%), **Co3** (263.94 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.80 (s, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 3.80 (s, 3H), 3.27 (t, *J* = 7.6 Hz, 2H), 3.04 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.10, 159.80, 142.69, 135.59, 131.93, 129.58, 128.23, 120.76, 115.00, 114.31, 111.48, 55.18, 40.30, 30.09.

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1-(4-chlorophenyl)-3-(3-methoxyphenyl)propan-1-one (5ce)[31]**:** White solid, Yield: **Co1** (241.12 mg, 88%), **Co2** (232.90 mg, 85%), **Co3** (221.94 mg, 81%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.79 (s, 1H), 6.76 (d, *J* = 8.6 Hz, 1H), 3.80 (s, 3H), 3.29 (t, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.04, 159.83, 142.78, 139.60, 135.21, 129.60, 129.01, 120.83, 114.35, 111.51, 55.26, 40.43, 30.15.

1-(4-fluorophenyl)-3-(3-methoxyphenyl)propan-1-one (5cf)[31]**:** Yellow oil, Yield: **Co1** (216.72 mg, 84%), **Co2** (211.56 mg, 82%), **Co3** (206.4 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.80 (s, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 3.80 (s, 3H), 3.30(t, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.69, 167.08, 164.55, 159.81, 142.86, 133.32, 130.70, 129.70, 120.80, 115.98, 114.36, 111.49, 55.27, 40.36, 30.20.

1-phenyl-3-(p-tolyl)propan-1-one (5da)[50]**:** Yellow oil, Yield: **Co1** (199.36 mg, 89%), **Co2** (197.12 mg, 88%), **Co3** (194.88 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 10.0 Hz, 2H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 4H), 3.33 (t, *J* = 7.7 Hz, 2H), 3.09 (t, *J* = 8.0 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.46, 138.31, 136.98, 135.73, 133.16, 129.46, 128.72, 128.43, 128.16, 40.73, 29.82, 21.14.

1-(4-methoxyphenyl)-3-(p-tolyl)propan-1-one (5db)[51]**:** Yellow oil, Yield: **Co1** (233.68 mg, 92%), **Co2** (228.6 mg, 90%), **Co3** (223.52 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.9 Hz, 2H), 7.19 – 7.11 (m, 4H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 3.27 (t, *J* = 7.5 Hz, 2H), 3.04 (t, *J* = 7.7 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.04, 163.53, 138.48, 135.65, 130.42, 130.08, 129.30, 128.42, 113.82, 55.55, 40.38, 30.02, 21.13.

1,3-di-p-tolylpropan-1-one (5dc)[52]**:** Yellow oil, Yield: **Co1** (211.82 mg, 89%), **Co2** (207.06 mg, 87%), **Co3** (199.92 mg, 84%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.13 (q, *J* = 8.1 Hz, 4H), 3.28 (t, *J* = 7.6 Hz, 2H), 3.05 (t, *J* = 7.4 Hz, 2H), 2.41 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.15, 143.89, 138.38, 135.67, 134.48, 129.32, 128.32, 40.61, 29.88, 21.73, 21.10.

1-(4-bromophenyl)-3-(p-tolyl)propan-1-one (5dd)[53]**:** White soild, Yield: **Co1** (265.76 mg, 88%), **Co2** (259.72 mg, 86%), **Co3** (253.68 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.14 (t, *J* = 6.1 Hz, 4H), 7.03 (d, *J* = 2.0 Hz, 1H), 3.25 (t, *J* = 7.6 Hz, 2H), 3.04 (t, *J* = 7.7 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.38, 138.03, 135.75, 132.00, 129.68, 129.35, 128.39, 40.67, 29.70, 21.13.

1-(4-chlorophenyl)-3-(p-tolyl)propan-1-one (5de)[54]**:** Off-white solid, Yield: **Co1** (224.46 mg, 87%), **Co2** (221.88 mg, 86%), **Co3** (216.72 mg, 84%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 4.3 Hz, 4H), 3.26 (t, *J* = 7.7 Hz, 2H), 3.01 (t, *J* = 7.4 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.19, 139.55, 138.05, 135.82, 135.27, 129.56, 129.35, 129.01, 128.39, 40.68, 29.72, 21.13.

1-(4-fluorophenyl)-3-(p-tolyl)propan-1-one (5df)[52]**:** yellow oil, Yield: **Co1** (205.7 mg, 85%), **Co2** (200.86 mg, 83%), **Co3** (196.02 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 2H), 7.14 (d, *J* = 2.4 Hz, 3H), 7.11 (d, *J* = 9.2 Hz, 3H), 3.24 (t, *J* = 8.1 Hz, 2H), 3.04 (t, *J* = 7.4 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.85, 138.10, 135.80, 133.39, 130.74, 129.31, 128.36, 115.87, 115.65, 40.62, 29.76, 21.09.

1-(2-chlorophenyl)-3-(p-tolyl)propan-1-one (5dg): Off-white solid, Yield: **Co1** (216.72 mg, 84%), **Co2** (211.56 mg, 82%), **Co3** (206.4 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.36 (d, *J* = 8.2Hz, 1H), 7.32 (d, *J* = 1.7 Hz, 1H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.11 (d, *J* = 2.2 Hz, 4H), 3.25 (t, *J* = 7.8 Hz, 2H), 3.04 (t, *J* = 7.5 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.78, 139.47, 137.75, 135.77, 130.99, 129.36, 128.35, 127.09, 44.81, 29.80, 21.10.

1-(3-methoxyphenyl)-3-(p-tolyl)propan-1-one (5dh)[51]**:** Yellow oil, Yield: **Co1** (218.44 mg, 86%), **Co2** (213.36 mg, 84%), **Co3** (208.28 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.50 (s, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.16 (t, *J* = 7.9 Hz, 3H), 7.11 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H), 3.27 (t, *J* = 8.1 Hz, 2H), 3.07 (t, *J* = 7.4 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.27, 159.92, 138.27, 135.76, 132.52, 129.80, 129.50, 128.44, 120.81, 119.71, 112.28, 55.53, 40.84, 29.85, 21.14.

3-(4-chlorophenyl)-1-phenylpropan-1-one (5ea)[31]**:** White solid, Yield: **Co1** (207.4 mg, 85%), **Co2** (202.52 mg, 83%), **Co3** (197.64 mg, 81%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.0 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 3H), 3.28 (t, *J* = 7.6 Hz, 2H), 3.05 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.93, 139.82, 136.84, 133.26, 131.96, 129.91, 128.70, 128.09, 40.22, 29.46.

3-(4-chlorophenyl)-1-(4-methoxyphenyl)propan-1-one (5eb)[31]**:** White solid, Yield: **Co1** (235.64 mg, 86%), **Co2** (232.90 mg, 85%), **Co3** (227.42 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 3.23 (t, *J* = 7.6 Hz, 2H), 3.03 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR

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(126 MHz, $CDCl_3$) δ 197.42, 163.55, 139.93, 131.82, 130.29, 129.83, 128.57, 115.00, 113.78, 55.47, 39.76, 29.58.

3-(4-chlorophenyl)-1-(p-tolyl)propan-1-one (5ec)[31]**:** Off-white solid, Yield: **Co1** (216.72 mg, 84%), **Co2** (211.56 mg, 82%), **Co3** (208.98 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.27 (m, 4H), 7.21 (d, *J* = 8.4 Hz, 2H), 3.28 (t, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 7.4 Hz, 1H), 2.44 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.60, 144.06, 139.94, 134.38, 131.90, 130.44, 129.92, 129.41, 128.66, 128.23, 40.10, 29.55, 21.73.

1-(4-bromophenyl)-3-(4-chlorophenyl)propan-1-one (5ed)[31]**:** Light yellow solid, Yield: **Co1** (256.80 mg, 80%), **Co2** (250.38 mg, 78%), **Co3** (243.96 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 3.25 (t, *J* = 7.1 Hz, 2H), 3.03 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.86, 139.57, 135.52, 132.04, 131.55, 130.81, 130.45, 129.89, 129.61, 128.72, 128.44, 40.18, 29.35.

1,3-bis(4-chlorophenyl)propan-1-one (5ee)[31]**:** Light yellow solid, Yield: **Co1** (216.84 mg, 78%), **Co2** (214.06 mg, 77%), **Co3** (208.5 mg, 75%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 3.29 (t, *J* = 7.5 Hz, 2H), 3.08 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.60, 139.58, 135.05, 131.98, 130.44, 129.82, 129.43, 128.98, 128.65, 115.00, 40.12, 29.29.

3-(4-chlorophenyl)-1-(4-fluorophenyl)propan-1-one (5ef)[31]**:** Off-white solid, Yield: **Co1** (201.74 mg, 77%), **Co2** (199.12 mg, 76%), **Co3** (196.5 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.9 Hz, 2H), 7.26 (d, *J* = 2.7 Hz, 1H), 7.25 (d, *J* = 2.9 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 3.25 (t, *J* = 7.6 Hz, 2H), 3.03 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.34, 167.13, 164.59, 139.66, 133.25, 132.01, 130.73, 129.92, 128.73, 115.99, 40.16, 29.40.

3-(3-chlorophenyl)-1-phenylpropan-1-one (5fa)[31]**:** White solid, Yield: **Co1** (204.96 mg, 84%), **Co2** (200.08 mg, 82%), **Co3** (195.20 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.1 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 3.7 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 8.0Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 3.30 (t, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.79, 143.44, 136.78, 134.31, 133.30, 129.87, 128.71, 128.12, 126.81, 126.43, 40.09, 29.74.

3-(3-chlorophenyl)-1-(4-methoxyphenyl)propan-1-one (5fb)[31]**:** Off-white solid Yield: **Co1** (232.90 mg, 85%), **Co2** (227.42 mg, 83%), **Co3** (221.94 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.13 (d, *J* = 7.1 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 2H), 3.85 (s, 3H), 3.22 (t, *J* = 7.7 Hz, 2H), 3.02 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.33, 163.62, 143.65, 134.25, 130.38, 129.87, 128.69, 126.59, 126.34, 113.84, 55.56, 39.70, 29.91.

3-(3-chlorophenyl)-1-(p-tolyl)propan-1-one (5fc)[31]**:** Light yellow solid, Yield: **Co1** (216.72 mg, 84%), **Co2** (211.56 mg, 82%), **Co3** (201.24 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.27 (s, 1H), 7.26 (s, 1H), 7.23 – 7.19 (m, 2H), 7.16 (t, *J* = 7.9 Hz, 2H), 3.27 (t, *J* = 7.6 Hz, 2H), 3.05 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.42, 144.08, 143.58, 134.32, 129.48, 128.83, 128.49, 128.15, 127.02, 126.38, 125.96, 39.95, 29.82, 21.69.

1-(4-bromophenyl)-3-(3-chlorophenyl)propan-1-one (5fd)[31]**:** White solid, Yield: **Co1** (240.75 mg, 75%), **Co2** (234.33 mg, 73%), **Co3** (218.28 mg, 68%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.3 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.38 (d, *J* = 4.8 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 3.25 (t, *J* = 7.5 Hz, 13H), 3.04 (t, *J* = 7.5 Hz, 13H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.62, 143.11, 135.42, 134.29, 131.97, 131.53, 130.77, 129.83, 129.55, 128.58, 128.38, 126.71, 126.45, 39.96, 29.56.

3-(3-chlorophenyl)-1-(4-chlorophenyl)propan-1-one (5fe)[31]**:** White solid, Yield: **Co1** (202.94 mg, 73%), **Co2** (197.38 mg, 71%), **Co3** (183.48 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.43 – 7.41 (m, 1H), 7.23 (d, *J* = 7.0 Hz, 2H), 7.19 (s, 1H), 7.13 (d, *J* = 7.1 Hz, 2H), 3.26 (d, *J* = 8.1 Hz, 2H), 3.05 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.52, 143.20, 139.72, 135.08, 134.35, 129.52, 128.80, 128.51, 126.63, 126.34, 40.05, 29.64.

3-(3-chlorophenyl)-1-(4-fluorophenyl)propan-1-one (5ff)[31]**:** Pale Yellow solid, Yield: **Co1** (186.02 mg, 71%), **Co2** (180.78 mg, 69%), **Co3** (167.68 mg, 64%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 5.4 Hz, 1H), 7.97 (d, *J* = 5.4 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.12 (t, *J* = 8.7 Hz, 2H), 3.26 (t, *J* = 7.7 Hz, 2H), 3.04 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.16, 167.14, 164.60, 143.27, 134.34, 133.23, 130.74, 126.94, 116.22, 39.99, 29.69.

3-(3,4-dimethoxyphenyl)-1-phenylpropan-1-one (5ga)[31]**:** Yellow oil, Yield: **Co1** (261.9 mg, 97%), **Co2** (256.5 mg, 95%), **Co3** (243.0 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 6.78 (d, *J* = 7.9 Hz, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.28 (t, *J* = 7.6 Hz, 2H), 3.02 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.40, 148.93, 147.42, 136.92, 133.93, 133.07, 128.62, 128.05, 120.20, 115.00, 111.89, 111.39, 55.95, 55.85, 40.69, 29.82.

3-(3,4-dimethoxyphenyl)-1-(4-methoxyphenyl)propan-1-one (5gb)[31]**:** Yellow oil, Yield: **Co1** (294.0 mg, 98%), **Co2** (288.0 mg, 96%), **Co3** (276.0 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.79 (t, *J* = 8.1 Hz, 3H), 3.86 (s, 3H), 3.85 (s, 6H), 3.22 (t, *J* = 7.6 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.99, 163.46, 148.90, 147.38, 134.10, 130.32, 130.02, 120.18, 115.00, 113.73, 111.88, 111.36, 55.94, 55.46, 40.35, 30.03.

3-(3,4-dimethoxyphenyl)-1-(p-tolyl)propan-1-one (5gc)[31]**:** Yellow oil, Yield: **Co1** (266.96 mg, 94%), **Co2** (261.28 mg, 92%), **Co3** (258.44 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.77 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 3.23 (t, *J* = 7.6 Hz, 2H), 3.01(t, *J* = 7.4 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.07, 148.97, 147.45, 143.87, 134.51, 134.10, 129.35, 128.23, 120.27, 111.95, 111.44, 55.89, 55.98, 40.60, 29.96, 21.69.

1-(4-bromophenyl)-3-(3,4-dimethoxyphenyl)propan-1-one (5gd)[31]**:** White solid, Yield: **Co1** (313.2 mg, 90%), **Co2** (306.24 mg, 88%), **Co3** (299.28 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 1H), 6.77 (d, *J* = 1.8 Hz, 1H), 6.76 – 6.75 (m, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.23 (t, *J* = 7.6 Hz, 2H), 2.99 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.37, 149.02, 147.56, 135.68, 133.72, 131.97, 129.64, 128.28, 120.25, 111.93, 111.46, 90.06, 56.06, 55.89, 40.72, 29.78.

1-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)propan-1-one (5ge)[31]**:** Off-white solid, Yield: **Co1** (270.56 mg, 89%), **Co2** (264.48 mg, 87%), **Co3** (258.40 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 6.77 – 6.74 (m, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 3.22 (t, *J* = 7.6 Hz, 2H), 2.98 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.14, 148.99, 147.52, 139.50, 135.26, 133.73, 129.52, 129.02, 120.25, 111.90, 111.42, 55.94, 55.86, 40.70, 29.77.

3-(3,4-dimethoxyphenyl)-1-(4-fluorophenyl)propan-1-one (5gf)[31]**:** Yellow liquid, Yield: **Co1** (250.56 mg, 87%), **Co2** (244.80 mg, 85%), **Co3** (233.28 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (m, 2H), 7.11 (t, *J* = 8.6 Hz, 2H), 6.77 (m, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.24 (t, *J* = 8.0 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.85, 167.06, 164.52, 148.98, 147.50, 133.81, 133.40, 130.73, 120.24, 116.04, 115.78, 111.88, 111.38,56.00, 55.91, 40.70, 29.85.

(*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (3ca')[31]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 15.6 Hz, 1H), 7.64 (s, 2H), 7.55 (d, *J* = 15.6 Hz, 1H), 7.41 (m, 3H), 6.99 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H).

Propiophenone (5ha)[31]**:** Yellow liquid, Yield: **Co1** (101.84 mg, 76%), **Co2** (96.48 mg, 72%), **Co3** (92.46 mg, 69%). ^{1}H NMR (500 MHz, CDCl3) δ 7.97 (d, J = 7.1 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.46 (t, J = 7.6 Hz, 2H), 3.01 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 200.81, 136.90, 132.86, 128.53, 127.95, 31.76, 8.23.

1-phenylbutan-1-one (5hb)[31]**:** Yellow liquid, Yield: **Co1** (115.44 mg, 78%), **Co2** (125.80 mg, 75%), **Co3** (105.08 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 2.95 (t, *J* = 7.3 Hz, 2H), 1.78 (dd, *J* = 14.7, 7.4 Hz, 2H), 1.02 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.38, 137.09, 132.85, 128.53, 128.02, 40.49, 17.76, 13.88.

General procedure for dehydrogenative cyclization of 2-amino benzyl alcohols with ketones

To a 10mL, clean, oven-dried, screw cap reaction tube containing 1 mmol of *o*-amino benzyl alcohols, 1 mmol ketones in dry toluene (2 mL) solvent was mixed with 2 mol % catalyst, 0.5 mmol KO^{t}Bu were reacted in inert condition. The reaction mixture was heated at 110 °C with constant stirring in a preheated oil bath for 24 h. The resulting solution was then filtered off through Whatman 41 filter paper. The filtrate was dried under reduced pressure, and the organic product was extracted by a solvent extraction technique using a water/ethyl acetate solvent mixture. The organic layer was collected and removed through rotary evaporator. The residue was then purified by 100-200 mesh column chromatography on silica gel (eluent: hexane /ethyl acetate) to get the derivatives of quinolines. The isolated products were authenticated by ^{1}H and ^{13}C NMR spectra which were displayed in Supporting Information (Figures S139-S162).

2-phenylquinoline (7aa)[20b]**:** White solid, Yield: **Co1** (184.5 mg, 90%), **Co2** (180.4 mg, 88%), **Co 3** (172.2 mg, 84%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.7 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 3H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.84 (d, *J* = 9.9 Hz, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.47 (d, *J* = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.50, 148.36, 139.78, 136.90, 129.77, 129.41, 128.94, 127.62, 127.27, 126.37, 119.14.

2-(4-methoxyphenyl)quinoline (7ab)[20b]**:** White solid, Yield: **Co1** (216.2 mg, 92%), **Co2** (211.5 mg, 90%), **Co 3** (206.8 mg, 88%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.6 Hz, 1H), 8.16 – 8.12 (m, 3H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.05 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.90, 157.01, 148.37, 136.73, 132.34, 129.66, 128.98, 127.52, 126.99, 125.98, 118.66, 114.32, 55.49.

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2-(p-tolyl)quinoline (7ac)[20b]**:** White solid, Yield: **Co1** (199.29 mg, 91%), **Co2** (194.91 mg, 89%), **Co3** (190.53 mg, 87%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.16 (m, 3H), 8.08 – 8.07 (m, 2H), 7.86 (d, *J* = 2.9 Hz, 1H), 7.83 – 7.81 (m, 1H), 7.74 – 7.70 (m, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.33 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.45, 148.36, 139.51, 136.87, 129.72, 127.54, 127.19, 126.17, 118.99, 21.47.

2-(4-bromophenyl)quinoline (7ad)[20b]**:** Off-white solid, Yield: **Co1** (248.16 mg, 88%), **Co2** (242,52 mg, 86%), **Co3** (236.88 mg, 84%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.5 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.08 – 8.04 (m, 2H), 7.85 – 7.82 (m, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.67 – 7.63 (m, 2H), 7.54 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.16, 148.32, 138.59, 137.10, 132.07, 129.87, 129.19, 127.59, 127.33, 126.63, 124.02, 118.63.

2-(4-chlorophenyl)quinoline (7ae)[20b]**:** Off-white solid, Yield: **Co1** (205.54 mg, 86%), **Co2** (200.76 mg, 84%), **Co3** (193.59 mg, 81%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.7 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.14 – 8.08 (m, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.53 – 7.47 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.11, 148.32, 138.14, 137.06, 135.65, 129.86, 129.11, 128.91, 127.58, 127.30, 126.59, 118.66.

2-(4-fluorophenyl)quinoline (7af)[31]**:** Pale-yellow solid, Yield: **Co1** (189.55 mg, 85%), **Co2** (185.09 mg, 83%), **Co3** (178.4 mg, 80%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.7 Hz, 1H), 8.19 – 8.14 (m, 3H), 7.84 (s, 2H), 7.73 (d *J* = 8.4 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.21 (t, *J* = 8.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.13, 162.65, 156.34, 148.30, 137.01, 135.92, 129.65, 127.57, 127.16, 126.42, 118.72, 116.00, 115.70.

2-(4-iodophenyl)quinoline (7ag)[31]**:** White solid, Yield: **Co1** (293.7 mg, 89%), **Co2** (287.1 mg, 87%), **Co3** (283.8 mg, 86%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.6 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.15, 148.32, 138.59, 137.10 , 132.07, 129.97, 129.78, 129.19, 127.59, 127.33, 126.63, 124.02, 118.62.

2-(pyridin-2-yl)quinoline (7ah)[31]**:** Yellow solid, Yield: **Co1** (181.28 mg, 88%), **Co2** (175.1 mg, 85%), **Co3** (170.98 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 5.9 Hz, 1H), 8.66 (d, *J* = 8.5 Hz, 1H), 8.55 (s, 1H), 8.28 (d, *J* = 9.0 Hz, 1H), 8.18 (d, *J* = 4.4 Hz, 1H), 7.86 (d, *J* = 13.5 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.37 – 7.33 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.34, 149.26, 148.01, 137.05, 129.65, 128.34, 127.71, 126.85, 124.07, 121.94, 119.06.

2-(pyridin-4-yl)quinoline (7ai)[31]**:** Yellow solid, Yield: **Co1** (183.34 mg, 89%), **Co2** (175.10 mg, 85%), **Co3** (170.98 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.3 Hz, 1H), 8.64 (d, *J* = 7.9 Hz, 1H), 8.54 (d, *J* = 8.6 Hz, 1H), 8.26 (d, *J* = 8.6 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 2H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.37, 156.19, 149.19, 147.88, 136.89, 129.84, 129.57, 128.27, 127.64, 126.77, 124.04, 121.85, 118.98, 115.00.

2-(naphthalen-1-yl)quinoline (7aj)[20b]**:** White solid, Yield: **Co1** (232.05 mg, 91%), **Co2** (229.50 mg, 90%), **Co3** (226.95 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.38 (d, *J* = 8.6 Hz, 1H), 8.25 (m, 2H), 8.03 (m, 3H), 7.93 – 7.84 (m, 2H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.20, 148.40, 136.91, 133.88, 133.53, 129.75, 128.85, 128.60, 127.74, 127.52, 127.21, 125.09, 119.19.

5,6-dihydrobenzo[c]acridine (7ak)[20b]**:** White solid, Yield: **Co1** (207.90 mg, 90%), **Co2** (205.59 mg, 89%), **Co3** (203.28 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 7.6 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.87 (s, 1H), 7.75 – 7.64 (m, 2H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 6.8 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 3.13 – 3.05 (m, 2H), 3.04 – 2.97 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.51, 147.74, 139.56, 134.82, 133.85, 132.00, 132.00, 129.28, 128.80, 127.99, 127.53, 127.27, 126.16, 28.94, 28.50.

1,2,3,4-tetrahydroacridine (7al)[20b]**:** Colourless oil, Yield: **Co1** (162.87 mg, 89%), **Co2** (159.21 mg, 87%), **Co3** (157.38 mg, 86%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.73 (s, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 3.10 (t, *J* = 6.6 Hz, 2H), 2.92 (t, *J* = 6.3 Hz, 2H), 1.96 (t, *J* = 6.4 Hz, 2H), 1.88 – 1.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.34, 146.64, 135.06, 131.01, 128.43, 128.19, 128.00, 127.11, 125.54, 33.62, 29.30, 23.29.

Conflicts of interest

There are no conflicts to declare.

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