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Supporting Information

A nanoscale iron catalyst for heterogeneous direct N- and C-alkylations of anilines and ketones using alcohols via hydrogen autotransfer conditions

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1. General Information:

Commercially available materials purchased from Alfa Aesar, Merck, Loba Chemie, Sigma-Aldrich, TCI and Combi-Blocks were used as received. Iron(III) oxide, 544884-25g, nanopowder, < 50 nm particle size (BET), p.code:1002329579 purchased from Sigma-Aldrich was used as received. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker BBFO (500 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ = 7.26, singlet). ¹H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets), m (multiplets) etc. Carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on a Bruker BBFO (126 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on LC/MS, 6230B Time of Flight (TOF), Agilent Technologies. Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plates (0.2 mm thickness).

2. Experiment procedures

la la	OH + 2a	H ₂ Cond	itions	H + C	N 3a'
Entry	Catalyst	Base	Solvent	3a (%) ^b	3a' (%) ^b
1	Fe ₂ O ₃	КОН	toluene	41	-
2°	Fe ₂ O ₃	КОН	toluene	43	7
3 ^d	Fe ₂ O ₃	КОН	toluene	47	6
4e	Fe ₂ O ₃	КОН	toluene	44	9
5	Fe ₂ O ₃	tBuOK	toluene	34	4
6	Fe ₂ O ₃	tBuONa	toluene	26	7
7	Fe ₂ O ₃	Cs ₂ CO ₃	toluene	14	5
8	Fe ₂ O ₃	K ₂ CO ₃	toluene	7	8
9	Fe ₂ O ₃	КОН	m-xylene	21	6
10	Fe ₂ O ₃	КОН	DMSO	9	11
11	Fe ₂ O ₃	КОН	i-PrOH	17	13

a. Table S1.	Optimization of N-Alkylation of anilines with bulk Fe ₂ O ₃
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^aReaction Conditions: Benzyl alcohol (1 eq, 0.9 mmol), Aniline (1.5 eq, 1.38 mmol), catalyst (bulk-Fe₂O₃, 30 mol%), base (0.3 eq, 0.27 mmol) and solvent 1 ml, under Argon atmosphere in a pressure tube at 135 °C for 24 h. ^bGC yield. ^cAt 140 °C. ^d60 mmol of catalyst was used. ^eReaction time 36 h.

b. General procedure for the N-Alkylation with nano-Fe₂O₃:



Benzyl alcohol (100 mg, 0.9 mmol), was added to a oven-dried 15 ml pressure reaction tube followed by aniline (129 mg, 1.38 mmol), 30 mol% (44 mg) of the nano-Fe₂O₃ catalyst with respect to benzyl alcohol and KOH (15.5 mg, 0.27 mmol). 1 ml of Toluene as solvent was added to the pressure tube which was then flushed with Ar-gas for 1-2 min, and then closed with a PTFE cap. The reaction tube was placed in an oil bath which was preheated to 135 °C and the reaction was stirred for the required time. After the completion of the reaction, the reaction tube was cooled to room temperature, the solid catalyst was filtered off and washed thoroughly with ethyl acetate. The corresponding N-alkylation product was purified by column chromatography (silica 100-200 mesh; n-hexane-ethyl acetate mixture, 98:2) and characterized by NMR spectral analysis. Following the procedure above, **N**-benzylaniline (**3a**) was obtained (0.141g, isolated yield = 83%).





The reaction was stopped at 18 hours and solvent was removed by rotary evaporator and the residue was submitted for ¹H-NMR analysis.

c. C-Alkylation of ketones with alcohols:



Acetophenone (120 mg, 1 mmol) was added a oven-dried 15 ml pressure reaction tube followed by benzyl alcohol (162 mg, 1.5 mmol), 30 mol% (48 mg) of catalyst and t-BuOK (33.6 mg, 0.3 mmol). 1 ml of toluene were added as the solvent and the tube was flushed with Ar gas for 1-2 min, and closed with a PTFE cap. The reaction tube was placed in an oil bath which was pre heated to 135 °C and the reaction was stirred for the required time. After the completion of the reaction, the reaction tube was cooled to room temperature and the solid catalyst was filtered off and washed thoroughly with ethyl acetate. The corresponding C-Alkylation product was purified by column chromatography (silica 100-200 mesh ; n-hexane-ethyl acetate mixture, 99:1) and characterized by NMR spectral analysis. Following the procedure above, 1,3-diphenylpropan-1-one (**5a**) was obtained (203 mg, isolated yield = 97%).

Scheme S1.



^aReaction conditions: 4- methylacetophenone (134 mg, 1 mmol), benzyl alcohol (162 mg, 1.5 mmol), catalyst (48 mg 30 mol%) , tBuOK (33.6 mg, 0.3 mmol) and toluene 1ml, under argon atmosphere in pressure tube at 135 °C for 18 h.

Crude ¹H-NMR of Scheme S1.





d. General procedure for quinoline synthesis:

Acetophenone (120 mg, 1 mmol), was added into a oven-dried 15 ml pressure reaction tube followed by 2-Amino benzyl alcohol (185 mg, 1.5 mmol), 30 mol% (48 mg) of catalyst and tBuOK (36.3 mg, 0.3 mmol). 1 ml of toluene was added as a solvent and the tube was flushed with Ar gas for 1-2 min, and closed with a PTFE cap. The reaction tube was placed in an oil bath which was pre-heated to 135 °C for 15 h. After completion of the reaction, the reaction tube was cooled to room temperature. The solid catalyst was filtered off and washed thoroughly with ethyl acetate. The corresponding quinoline products were purified by column chromatography (silica 100-200 mesh; n-hexane-ethyl acetate mixture 97:3) and characterized by NMR spectral analysis. Following the procedure above, 2-phenylquinoline (**8a**) was obtained (195 mg, isolated yield = 95%).



e. Deuterium labeling studies:

Procedure for Deuterium Labelling experiment : Deuterated benzyl alcohol [D2]-1a (110 mg, 1 mmol), was added to a oven-dried 15 ml pressure reaction tube followed by aniline (139 mg, 1.5 mmol), 30 mol% (48 mg) of catalyst and KOH (16.8 mg, 0.3 mmol). 1 ml of toluene as solvent was added to the pressure tube which was then flushed with Ar gas for 1-2 min, and then closed with a PTFE cap . The reaction tube was placed in an oil bath which was preheated to 135 °C and the reaction was stirred for 24 h. After the completion of the reaction, the reaction tube was cooled to room temperature. The solid catalyst was filtered off and washed thoroughly with ethyl acetate. The corresponding N-Alkylation product was purified by column chromatography (silica 100-200 mesh ; n-hexane-ethyl acetate mixture 98:2) and characterized by NMR spectral analysis. Following the procedure above, product was obtained (0.148g, isolated yield = 80%).





¹H NMR of 3a + 3a[D1] + 3a[D2]



¹H NMR of 3a



HRMS Spectra of 3a + 3a[D1] + 3a[D2]

	3a + [D1]-3a	3a	[D1]-3a	[D2]-3a
Signal δ	6.61 [para-H, (1H)]	4.21 [benzyl-H (2H)]	4.23 [benzyl-H(1H)]	-
Integral Value	1.00	0.01/2.12=0.0047	0.08	
Calculated ratio		0.5%	8.0%	91.5%
HRMS ratio		0.0%	8.0%	92.0%



Procedure for competition experiment : Deuterated benzyl alcohol [D2]-1a (55 mg, 0.5 m.mol) and benzyl alcohol 1a (54 mg, 0.5 m.mol) were added to a oven-dried 15 ml pressure reaction tube followed by aniline (139mg, 1.5 mmol), 30 mol% (48 mg) of catalyst and 0.3 mmol KOH (16.8 mg). 1 ml of toluene as solvent was added to the pressure tube which was then flushed with Ar gas for 1-2 min, and then closed with a PTFE cap. The reaction tube was placed in an oil bath which was preheated to 135 °C and the reaction was stirred for 24 h. After the completion of the reaction, the reaction tube was cooled to room temperature. The solid catalyst was filtered off and washed thoroughly with ethyl acetate. The corresponding N-Alkylation products was purified by column chromatography (silica 100-200 mesh ; n-

hexane-ethyl acetate mixture, 98:2) and characterized by NMR spectral analysis. Following the procedure above, product was obtained (0.143g, isolated yield = 78%).



¹H NMR of 3a



HRMS Spectra of 3a + 3a[D1] + 3a[D2]

	3a + [D1]-3a	3a	[D1]-3a	[D2]-3a
Signal δ	6.62 [para-H, (1H)]	4.21 [benzyl-H (2H)]	4.23 [benzyl-H(1H)]	-
Integral Value	1.00	1.17/2.12=0.55	0.32	
Calculated ratio		55%	32%	13%
HRMS ratio		55%	32%	13%
KIE		$K_{CHH}/K_{CDH} = 1.72$		



f. Catalyst Recyclability Test

After completing the first run of the N-alkylation reaction under standard conditions, the catalyst was filtered and washed with EtOAc and water. Then it was oven dried at 100 °C for 3 h before being used for the next run. This process was repeated over five cycles. The recovered catalyst retained its catalytic activity and the desired product was obtained above 75% yield (Table S2, entry 5).

Table S2

Number of	1	2	3	4	5
runs					
Isolated Yield	83	82	79	77	75

g. Hot Filtration Test

The standard N-alkylation reaction between anilines and benzylalcohols was carried out at 135 °C for 14 h. The iron catalyst was filtered from the hot reaction mixture and the filtrate was further heated at 135 °C for additional 10 h. The obtained results indicate that there was no appreciable leaching of metal ions under the present reaction conditions.

Table S3

Catalyst	Time	GC Yield(%)
nano-Fe2O3	14 h	43
-	14 + 10 h	44

h. Gram Scale Reactions

Table S4

N-Alkylation	NH2 Nano-Fe2O3 (30 mol%) KOH (0.3 equiv) KOH (0.3 equiv) Toluene (5 mL), 135 °C Nano-Fe2O3 (30 mol%) Ar atmosphere, 24 h Nano-Fe2O3 (30 mol%) 1.08 g, 10 mmol 1.39 g, 15 mmol
C-Alkylation	Mano-Fe ₂ O ₃ (30 mol%) tBuOK (0.3 equiv) 1a 4a 1.62 g, 15 mmol 1.2 g, 10 mmol
Quinoline Synthesis	OH + OH Nano-Fe2O3 (30 mol%) NH2 + Image: Nano-Fe2O3 (30 mol%) Nano-Fe2O3 (30 mol%) 6 7 Toluene (5 mL), 135 °C N 1.85 g, 15 mmol 1.2 g, 10 mmol Toluene (5 mL), 135 °C N 8 1.88 g, 92% 1.88 g, 92%

3. Characterization Data:

1		N-benzylaniline ¹ (3a): Yellow oil (0.141g, 83% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.34 – 7.19 (m, 5H), 7.13 (t, J = 7.9 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 7.8 Hz, 2H), 4.23 (s, 2H), 3.91 (br, 1H).
		127.50, 127.21, 117.51, 112.86, 48.21.
2		N-benzyl-2-methoxyaniline ² (3b): Yellow oil (0.167 g, 85% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.73 – 7.54 (m, 5H), 7.19 (td, <i>J</i> = 7.6, 1.5 Hz, 1H), 7.09 (dd, <i>J</i> = 7.9, 1.4 Hz, 1H), 7.07 – 7.00 (m, 1H), 6.94 (dd, <i>J</i> = 7.8, 1.4 Hz, 1H), 4.99 (br, 1H), 4.63 (s, 1H), 4.08 (s, 3H).
		¹³ C NMR (126 MHz, CDCl ₃) δ 146.88, 139.71, 138.24, 128.66, 127.58, 127.19, 121.39, 116.71, 113.42, 110.17, 109.50, 55.45, 48.10.
3	N N N N N N N N N N N N N N N N N N N	N-benzyl-4-methoxyaniline ² (3c): Brown solid (0.169 g, 86% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.31 – 7.17 (m, 5H), 6.73 – 6.69 (m, 2H), 6.53 – 6.48 (m, 2H), 4.17 (s, 2H), 3.71 (br, 1H), 3.63 (s, 3H).
		¹³ C NMR (126 MHz, CDCl ₃) δ 152.41, 142.58, 139.82, 128.78, 127.75, 127.36, 115.10, 114.34, 56.00, 49.47.
4		N-benzyl-3,4-dimethoxyaniline³ (3d): black solid (0.180 g, 80% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.30 – 7.14 (m, 5H), 6.63 (d, <i>J</i> = 8.5 Hz, 1H), 6.17 (d, <i>J</i> = 2.5 Hz, 1H), 6.07 (dd, <i>J</i> = 8.5, 2.5 Hz, 1H), 4.18 (s, 2H), 3.68 (s, 3H), 3.69 (s, 3H).
		¹³ C NMR (126 MHz, CDCl ₃) δ 150.19, 143.26, 141.87, 139.72, 128.79, 127.76, 127.41, 113.45, 103.81, 99.20, 56.89, 55.88, 49.39.
5		N-benzyl-3,4,5-trimethoxyaniline (3e): pale green crystals (0.199g, 79% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.37-7.26 (m, 5H), 5.86 (s, 2H), 4.27 (s, 2H), 4.00 (br, 1H), 3.75 (s, 9H).
	Ϋ́ΥΫ́ΥΫ́ΥΫ́ΥΫ́ΥΫ́ΥΫ́ΥΫ́ΥΫ́ΥΫ́	${}^{13}C NMR (126 MHz, CDCl_3) \delta 154.14, 145.14, 139.47, 128.85, 127.78, 127.53, 90.67, 61.27, 56.09, 49.09, HRMS for C_{16}H_{19}NO_3 [M+H] Calculated: 274.1444, Found: 274.1430.$

6	O ^{-Ph} H	N-benzyl-3-phenoxyaniline ⁴ (3f): Yellow oil (0.217 g, 85% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.33 – 7.19 (m, 3H), 7.17 – 6.80 (m, 8H), 6.73 – 6.52 (m, 3H), 4.23 (s, 2H), 4.00 (br, 1H). ¹³ C NMR (126 MHz, CDCl ₃) δ 158.53, 157.31, 149.81, 139.18, 130.34, 129.72, 128.75, 127.63, 127.39, 123.13, 119.09, 108.13, 107.90, 103.43, 48.31.
7	N N	N-benzyl-4-butylaniline⁵ (3g): Orange liquid (0.181 g, 82% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.12-7.33 (m, 5H), 6.98 (d, J = 7.9 Hz, 2H), 6.56 (d, J = 8.2 Hz, 2H), 4.28 (s, 2H), 3.87 (br, 1H), 2.49 (t, J = 7.7 Hz, 2H), 1.59 – 1.47 (m, 2H), 1.33 (dd, J = 14.8, 7.4 Hz, 2H), 0.90 (t, J = 7.3 Hz, 3H).
		128.66, 127.62, 127.23, 112.96, 48.72, 34.80, 34.09, 22.42, 14.09.
8	CI N	N-benzyl-4-chloroaniline ^{6, 7} (3h): Yellow oil (0.161 g, 80% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.59 – 7.45 (m, 5H), 7.30 (d, <i>J</i> = 8.0 Hz, 2H), 6.67 (d, <i>J</i> = 8.0 Hz, 2H), 4.41 (s, 2H), 4.18 (br, 1H).
		¹³ C NMR (126 MHz, CDCl ₃) δ 146.83, 139.11, 129.25, 128.88, 127.59, 127.55, 122.29, 114.10, 48.53.
9	F	N-benzyl-3-fluoroaniline⁸ (3i): Yellow oil (0.143 g, 77% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.61 – 7.44 (m, 5H), 7.37 – 7.19 (m, 1H), 6.69 – 6.45 (m, 3H), 4.43 (s, 1H), 4.27 (br, 1H).
	H I	¹³ C NMR (126 MHz, CDCl ₃) δ 164.19 (d, <i>J</i> = 242.8 Hz), 149.97 (d, <i>J</i> = 10.7 Hz), 138.90, 130.36 (d, <i>J</i> = 10.2 Hz), 128.78, 127.52, 127.47, 108.78, 103.99 (d, <i>J</i> = 21.5 Hz), 99.58 (d, <i>J</i> = 25.4 Hz). 48.21.
10	CI	N-benzyl-2,3-dichloroaniline (3j): Yellow oil (0.203g, 87% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) & 7.37 – 7.25 (m, 5H), 6.98 (t, <i>J</i> = 8.1 Hz, 1H), 6.78 (dd, <i>J</i> = 8.0, 1.2 Hz, 1H), 6.49 (d, <i>J</i> = 8.3 Hz, 1H), 4.89 (br, 1H), 4.38 (d, <i>J</i> = 5.5 Hz, 1H).
		¹³ C NMR (126 MHz, CDCl ₃) δ 145.42, 138.38, 132.99, 128.94, 127.88, 127.64, 127.34, 118.25, 117.26, 109.52, 48.08. HRMS for C ₁₃ H ₁₁ Cl ₂ N [M+H] Calculated: 252.0348, Found: 252.0340.

11		 N-benzyl-2,4-dichloroaniline⁹ (3k): Yellow oil (0.189 g, 81% yield); ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS) δ 7.37 – 7.22 (m, 6H), 7.01 (dd, <i>J</i> = 8.7, 2.3 Hz, 1H), 6.49 (d, <i>J</i> = 8.7 Hz, 1H), 4.71 (br, 1H), 4.34 (d, <i>J</i> = 5.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃, 25°C, TMS) δ 142.67, 138.36, 128.93, 128.82, 127.87, 127.80, 127.64, 127.32, 121.46, 119.47, 112.18, 47.96.
12	N N H	N-benzylpyridin-2-amine¹⁰ (3l): Colourless crystals (0.153 g, 90% yield); ¹ H-NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 8.05-8.04 (m, 1H), 7.37-7.29 (m, 5H), 7.25-7.22 (m, 1H), 6.56-6.53 (m, 1H), 6.33(d, J=8.3Hz, 1H), 5.19 (br, 1H), 4.47 (d, J=6.1 Hz, 2H).
		¹³ C NMR (126 MHz, CDCl ₃) δ 158.82, 148.42, 139.36, 137.67, 128.83, 127.60, 127.44, 113.39, 107.01, 46.53.
13		N-benzylpyrimidin-2-amine⁹ (3m): Colourless crystals (0.150g, 88% yield); ¹ H-NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 8.25 (d, $J = 3.5$ Hz, 2H), 7.39 – 7.23 (m, 5H), 6.53 (t, $J = 4.8$ Hz, 1H), 5.69 (br, 1H), 4.64 (d, $J = 5.9$ Hz, 2H).
		¹³ C NMR (126 MHz, CDCl ₃) δ 162.52, 158.27, 139.26, 128.79, 127.67, 127.43, 111.03, 45.63.
14		N-benzylpyrazin-2-amine¹¹ (3n): Colourless crystals (0.147 g, 86% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.98 (dd, $J = 2.5$, 1.4 Hz, 1H), 7.88 (d, $J = 1.3$ Hz, 1H), 7.81 (d, $J = 2.8$ Hz, 1H), 7.34 (d, $J = 4.4$ Hz, 4H), 7.32 – 7.23 (m, 1H), 5.07 (br, 1H), 4.55 (d, $J = 5.8$ Hz, 2H).
		¹³ C NMR (126 MHz, CDCl ₃) δ 154.62, 142.14, 142.11, 138.62, 133.27, 132.25, 128.91, 127.73, 127.70, 45.71.
15	N O O	N-benzylbenzo[d][1,3]dioxol-5-amine¹² (30): Black solid (0.168 g, 80% yield); ¹ H-NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.25-7.15 (m, 5H), 6.54 (d, J=8.3Hz, 1H), 6.15 (d, J=2.3Hz, 1H), 5.95 (dd, J=8.3Hz, 2.4Hz, 1H), 5.71 (s, 2H), 4.13 (s, 2H), 3.71 (br, 1H).
		¹³ C NMR (126 MHz, CDCl ₃) δ 148.51, 144.12, 139.88, 139.58, 128.81, 127.71, 127.43, 108.81, 104.61, 100.76, 96.19, 49.45.
16		N-(4-methoxybenzyl)aniline ¹ (3p): Brown oil (0.165 g, 86% yield); ¹ H-NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.18-7.17 (m, 2H), 7.09-7.05 (m, 2H), 6.78-6.76 (m, 2H), 6.63 -6.60 (m, 1H), 6.53-6.51 (m, 2H), 4.13 (s, 2H), 3.68 (s, 3H).
	<u>`0´ `∕′</u>	13C NMD (126 MHz, CDCL) \$ 150.05, 149.26, 121.59, 120.42

17	S S S S S S S S S S S S S S S S S S S	N-(4-(methylthio)benzyl)aniline ¹³ (3q): Yellow oil (0.186 g, 90% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.11 (dd, J = 22.4, 7.8 Hz, 4H), 7.04 (t, $J = 7.4$ Hz, 2H), 6.59 (t, $J = 7.3$ Hz, 1H), 6.47 (d, $J = 7.9$ Hz, 2H), 4.11 (s, 1H), 3.85 (br, 1H), 2.31 (s, 3H).
		¹³ C NMR (126 MHz, CDCl ₃) δ 148.14, 137.24, 136.51, 129.37, 128.12, 127.05, 117.71, 112.98, 47.89, 16.08.
18	Ph ⁻⁰	N-(3-phenoxybenzyl)aniline ⁵ (3r): Pale yellow crystals (0.208 g, 84% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.39 – 6.96 (m, 10H), 6.95 – 6.67 (m, 2H), 6.61 (t, <i>J</i> = 5.8 Hz, 2H), 4.30 (s, 2H), 4.04 (br, 1H).
		¹³ C NMR (126 MHz, CDCl ₃) δ 157.72, 157.20, 148.08, 141.84, 130.10, 129.95, 129.43, 123.49, 122.31, 119.11, 117.93, 117.80, 117.64, 113.05, 48.14.
19	N N	N-(2-methylbenzyl)aniline ¹⁴ (3s): Yellow oil (0.153 g, 86% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.24 (d, J = 7.1 Hz, 1H), 7.14 – 7.07 (m, 5H), 6.64 (t, J = 7.3 Hz, 1H), 6.55 (d, J = 7.7 Hz, 2H), 4.18 (s, 2H), 3.73 (br, 1H), 2.28 (s, 3H).
	• •	¹³ C NMR (126 MHz, CDCl ₃) δ 148.33, 137.08, 136.55, 130.59, 129.46, 128.47, 127.62, 126.34, 117.75, 112.97, 46.62, 19.11.
20	^	N (A
20	N N	N-(4-methylbenzyl)aniline ¹⁵ (3t): Yellow oil (0.155 g, 87% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.23 (d, $J =$ 7.9 Hz, 2H), 7.18 – 7.11 (m, 4H), 6.69 (t, $J =$ 7.3 Hz, 1H), 6.60 (d, $J =$ 7.8 Hz, 2H), 4.24 (s, 2H), 3.92 (br, 1H), 2.32 (s, 3H).
20	N H	N-(4-methylbenzyl)aniline ¹⁵ (3t): Yellow oil (0.155 g, 87% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.23 (d, $J =$ 7.9 Hz, 2H), 7.18 – 7.11 (m, 4H), 6.69 (t, $J =$ 7.3 Hz, 1H), 6.60 (d, $J =$ 7.8 Hz, 2H), 4.24 (s, 2H), 3.92 (br, 1H), 2.32 (s, 3H). ¹³ C NMR (126 MHz, CDCl ₃) δ 148.33, 137.06, 136.48, 129.48, 129.42, 127.71, 117.71, 113.05, 48.29, 21.27.
20		N-(4-methylbenzyl)aniline ¹⁵ (3t): Yellow oil (0.155 g, 87% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.23 (d, $J =$ 7.9 Hz, 2H), 7.18 – 7.11 (m, 4H), 6.69 (t, $J =$ 7.3 Hz, 1H), 6.60 (d, $J =$ 7.8 Hz, 2H), 4.24 (s, 2H), 3.92 (br, 1H), 2.32 (s, 3H). ¹³ C NMR (126 MHz, CDCl ₃) δ 148.33, 137.06, 136.48, 129.48, 129.42, 127.71, 117.71, 113.05, 48.29, 21.27. N-octylaniline ²⁸ (3u): Yellow oil (0.136 g, 73% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.20 – 7.13 (m, 2H), 6.68 (tt, $J =$ 7.3, 1.0 Hz, 1H), 6.60 (dt, $J =$ 8.8, 1.6 Hz, 2H), 3.59 (br, 1H), 3.10 (t, $J =$ 7.7 Hz, 2H), 1.61 (dt, $J =$ 14.6, 7.1 Hz, 2H), 1.36 – 1.21 (m, 10H), 0.89 (t, $J =$ 7.0 Hz, 3H).
20		N-(4-methylbenzyl)anline ¹⁵ (3t): Yellow oil (0.155 g, 87% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.23 (d, $J = 7.9$ Hz, 2H), 7.18 – 7.11 (m, 4H), 6.69 (t, $J = 7.3$ Hz, 1H), 6.60 (d, $J = 7.8$ Hz, 2H), 4.24 (s, 2H), 3.92 (br, 1H), 2.32 (s, 3H). ¹³ C NMR (126 MHz, CDCl ₃) δ 148.33, 137.06, 136.48, 129.48, 129.42, 127.71, 117.71, 113.05, 48.29, 21.27. N-octylaniline ²⁸ (3u): Yellow oil (0.136 g, 73% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.20 – 7.13 (m, 2H), 6.68 (tt, $J = 7.3$, 1.0 Hz, 1H), 6.60 (dt, $J = 8.8$, 1.6 Hz, 2H), 3.59 (br, 1H), 3.10 (t, $J = 7.7$ Hz, 2H), 1.61 (dt, $J = 14.6$, 7.1 Hz, 2H), 1.36 – 1.21 (m, 10H), 0.89 (t, $J = 7.0$ Hz, 3H). ¹³ C NMR (126 MHz, CDCl ₃) δ 148.71, 129.39, 117.23, 112.84, 44.17, 32.01, 29.75, 29.60, 29.45, 27.37, 22.85, 14.30.
20 21 22 22		N-(4-methylbenzyl)anilne ¹⁵ (3t): Yellow oil (0.155 g, 87% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.23 (d, J = 7.9 Hz, 2H), 7.18 – 7.11 (m, 4H), 6.69 (t, J = 7.3 Hz, 1H), 6.60 (d, J = 7.8 Hz, 2H), 4.24 (s, 2H), 3.92 (br, 1H), 2.32 (s, 3H). ¹³ C NMR (126 MHz, CDCl ₃) δ 148.33, 137.06, 136.48, 129.48, 129.42, 127.71, 117.71, 113.05, 48.29, 21.27. N-octylaniline ²⁸ (3u): Yellow oil (0.136 g, 73% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.20 – 7.13 (m, 2H), 6.68 (tt, J = 7.3, 1.0 Hz, 1H), 6.60 (dt, J = 8.8, 1.6 Hz, 2H), 3.59 (br, 1H), 3.10 (t, J = 7.7 Hz, 2H), 1.61 (dt, J = 14.6, 7.1 Hz, 2H), 1.36 – 1.21 (m, 10H), 0.89 (t, J = 7.0 Hz, 3H). ¹³ C NMR (126 MHz, CDCl ₃) δ 148.71, 129.39, 117.23, 112.84, 44.17, 32.01, 29.75, 29.60, 29.45, 27.37, 22.85, 14.30. N-hexylaniline ²⁹ (3v): Yellow oil (0.108 g, 67% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.13 – 7.03 (m, 2H), 6.60 (tt, J = 7.3, 1.0 Hz, 1H), 6.51 (dt, J = 8.8, 1.6 Hz, 2H), 3.48 (br, 1H), 3.00 (t, J = 7.7 Hz, 2H), 1.52 (dt, J = 14.7, 7.2 Hz, 2H), 1.37 – 1.21 (m, 6H), 0.82 (t, J = 7.0 Hz, 3H).

23	1,3-diphenylpropan-1-one ^{16, 21} (5a): Colourless oil (0.203 g, 97% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.93 (d, $J = 7.2$ Hz, 1H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.41 (t, $J = 7.7$ Hz, 1H), 7.31 – 7.16 (m, 3H), 3.26 (t, $J = 7.7$ Hz, 1H), 3.05 (t, $J = 7.7$ Hz, 1H).
	¹³ C NMR (126 MHz, CDCl ₃) δ 199.42, 141.49, 137.07, 133.24, 128.79, 128.72, 128.62, 128.23, 126.32, 40.64, 30.33.
24	3-phenyl-1-(p-tolyl)propan-1-one¹⁶ (5b): Yellow oil (0.204 g, 91% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.86 (d, <i>J</i> = 8.2 Hz, 2H), 7.35 – 7.13 (m, 7H), 3.24 (t, J= 7.7Hz, 2H), 3.05 (t, J= 7.8Hz, 2H), 2.40 (s, 3H).
	¹³ C NMR (126 MHz, CDCl ₃) δ 199.09, 144.01, 141.56, 134.53, 129.44, 128.67, 128.59, 128.33, 126.26, 40.51, 30.37, 21.80.
25	1-(4-ethylphenyl)-3-phenylpropan-1-one ¹⁷ (5c): Yellow oil (0.207 g, 87% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.81 (dd, $J = 8.1$, 1.3 Hz, 2H), 7.25 – 7.16 (m, 6H), 7.16 – 7.09 (m, 1H), 3.20 (t, J= 7.6Hz, 2H), 2.98 (t, $J = 7.7$ Hz, 2H), 2.62 (q, J = 7.6 Hz, 2H), 1.18 (t, $J = 7.6$ Hz, 3H).
	¹³ C NMR (126 MHz, CDCl ₃) δ 198.95, 150.04, 141.43, 134.62, 128.53, 128.44, 128.29, 128.12, 126.11, 40.38, 30.23, 28.94, 15.21.
26	1-(4-isobutylphenyl)-3-phenylpropan-1-one (5d): Yellow oil (0.240 g, 90% yield); ¹ H-NMR (500 MHz, CDCl ₃ , 25°C, TMS) δ 7.88-7.86 (m, 2H), 7.31-7.18 (m, 7H), 3.28 (t, J= 7.8Hz, 2H), 3.06 (t, J= 7.6Hz, 2H), 2.52 (d, J= 7.2Hz, 2H), 1.91-1.86 (m, 1H), 0.90 (d, J=6.5 Hz, 6H).
	¹³ C NMR (126 MHz, CDCl ₃) δ 199.14, 147.74, 141.61, 134.84, 129.50, 128.69, 128.62, 128.22, 126.27, 45.56, 40.54, 30.40, 30.29, 22.51. HRMS for C ₁₉ H ₂₂ O [M+H] Calculated : 267.1750, Found: 267.1745.
27	1-(2,5-dimethylphenyl)-3-phenylpropan-1-one ¹⁸ (5e): Yellow oil (0.197 g, 83% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25°C, TMS) δ 7.30 (s, 1H), 7.21 (t, <i>J</i> = 7.5 Hz, 2H), 7.17 – 7.06 (m, 4H), 7.03 (d, <i>J</i> = 7.8 Hz, 1H), 3.13 (t, <i>J</i> = 7.6 Hz, 2H), 2.95 (t, <i>J</i> = 7.7 Hz, 2H), 2.34 (s, 3H), 2.24 (s, 3H).
	¹³ C NMR (126 MHz, CDCl ₃) δ 203.66, 141.45, 137.98, 135.30, 135.05, 132.11, 132.01, 129.14, 128.66, 128.60, 126.26, 43.40, 30.50, 21.05, 20.92.

28	1-(4-methoxyphenyl)-3-phenylpropan-1-one¹⁶ (5f): White solid (0.205 g, 86% yield); ¹ H-NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.94-7.92 (m, 2H), 7.30-7.17 (m, 5H), 6.92-6.90 (m, 2H), 3.86 (s, 3H), 3.25 (t, J=7.7Hz, 2H), 3.05 (t, J=7.8Hz, 2H). ¹³ C NMR (126 MHz, CDCl ₃) δ 198.03, 163.64, 141.67, 130.50, 128.70, 128.62, 126.27, 113.92, 55.65, 40.31, 30.53.
29	1-(4-ethoxyphenyl)-3-phenylpropan-1-one ¹⁹ (5g): Yellow solid (0.236 g, 93% yield); ¹ H-NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.86-7.84 (m, 2H), 7.23-7.11 (m, 5H), 6.83-6.81 (m, 2H), 4.01(q, J= 7.5 Hz, 2H), 3.16 (t, J=7.5Hz, 2H), 2.97 (t, J= 7.6 Hz, 2H), 1.35 (t, J= 7.7Hz, 3H).
	¹³ C NMR (126 MHz, CDCl ₃) δ 198.02, 163.05, 141.66, 130.48, 129.94, 128.67, 128.60, 126.24, 114.32, 63.91, 40.27, 30.51, 14.84.
30	1-(benzo[d][1,3]dioxol-5-yl)-3-phenylpropan-1-one²⁰ (5h): Yellow oil (0.195 g, 77% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.48 (d, J= 7.8Hz, 1H), 7.36 (d, <i>J</i> = 1.7 Hz, 1H), 7.25 – 7.10 (m, 5H), 6.75 (d, <i>J</i> = 8.2 Hz, 1H), 5.95 (s, 2H), 3.14 (t, J=7.5Hz, 2H), 2.96 (t, J=7.6Hz, 2H).
	¹³ C NMR (126 MHz, CDCl ₃) δ 197.32, 151.73, 148.20, 141.34, 131.77, 128.53, 128.43, 126.13, 124.26, 107.90, 107.87, 101.84, 40.23, 30.36.
31	1-phenyl-3-(o-tolyl)propan-1-one ¹⁷ (5i): Yellow oil (0.204 g, 91% yield); ¹ H-NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.98-7.95 (m, 2H), 7.57-7.53 (m, 1H), 7.46-7.44 (m, 2H), 7.20-7.11 (m, 4H), 3.25 (t, J=7.6Hz, 2H), 3.06 (t, J= 7.5Hz, 2H), 2.35 (s, 3H).
	¹³ C NMR (126 MHz, CDCl ₃) δ 199.56, 139.57, 137.04, 136.18, 133.27, 130.53, 128.92, 128.81, 128.23, 126.51, 126.36, 39.30, 27.70, 19.53.
32	1-phenyl-3-(p-tolyl)propan-1-one ²² (5j) Colourless oil (0.206 g, 92% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.84 (d, $J = 8.2$ Hz, 2H), 7.42 (t, $J = 7.4$ Hz, 1H), 7.32 (t, $J = 7.7$ Hz, 2H), 7.01 (dd, $J = 20.3$, 7.9 Hz, 4H), 3.15 (t, $J = 7.7$ Hz, 2H), 2.92 (t, $J = 7.7$ Hz, 2H), 2.20 (s, 3H).
	¹³ C NMR (126 MHz, CDCl ₃) δ 199.38, 138.28, 136.93, 135.68, 133.12, 129.30, 128.68, 128.39, 128.12, 40.68, 29.78, 21.11.

33	o Contraction of the second se	3-(4-methoxyphenyl)-1-phenylpropan-1-one ¹⁷ (5k): Yellow solid (0.232 g, 97% yield); ¹ H-NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.99-7.97 (m, 2H), 7.59-7.56 (m, 1H), 7.49-7.46 (m, 2H), 7.20-7.19 (m, 2H), 6.86-6.87 (m, 2H), 3.81 (s, 3H), 3.29 (t, J=7.5Hz, 2H), 3.04 (t, J=7.4Hz, 2H). ¹³ C NMR (126 MHz, CDCl ₃) δ 199.59, 158.17, 137.08, 133.49, 133.21, 129.53, 128.77, 128.22, 114.12, 55.45, 40.88, 29.46.
34	s f	3-(4-(methylthio)phenyl)-1-phenylpropan-1-one¹⁹ (5l): Yellow oil (0.210 g, 82% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.92 (d, <i>J</i> = 8.2 Hz, 2H), 7.50 (t, <i>J</i> = 7.3 Hz, 1H), 7.40 (t, <i>J</i> = 7.6 Hz, 2H), 7.17-7.13 (m, 4H), 3.23 (t, <i>J</i> = 7.6 Hz, 2H), 2.99 (t, <i>J</i> = 7.6 Hz, 2H), 2.40 (s, 3H). ¹³ C NMR (126 MHz, DMSO) δ 198.96, 138.26, 136.71, 135.72, 133.04, 128.96, 128.56, 127.96, 127.05, 40.21, 29.44, 16.11
35		(E)-3-phenyl-1-(p-tolyl)prop-2-en-1-one ³⁰ (5b'): White crystals (0.210 g, 95% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 7.92 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 15.7 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.51 (d, J = 15.7 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.26 – 7.21 (m, 2H), 2.36 (s, 3H).
		¹³ C NMR (126 MHz, CDCl ₃) & 189.73, 144.24, 143.57, 135.53, 134.89, 130.38, 129.29, 128.87, 128.60, 128.37, 121.89, 21.60.
36		2-phenylquinoline ^{22, 23} (8a): White solid (0.195 g, 95% yield); ¹ H-NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 8.18 – 8.06 (m, 4H), 7.81 (d, <i>J</i> = 8.6 Hz, 1H), 7.76 (d, <i>J</i> = 8.1 Hz, 1H), 7.67-7.63 (m, 1H), 7.50 – 7.43 (m, 3H), 7.40-7.37 (m, 1H).
		¹³ C NMR (126 MHz, CDCl ₃) δ 157.58, 148.47, 139.88, 136.98, 129.92, 129.85, 129.51, 129.03, 127.77, 127.65, 127.38, 126.48, 119.22.
37		3-methyl-2-phenylquinoline ²² (8b): White solid (0.213 g, 97% yield); ¹ H-NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 8.01 (d, <i>J</i> = 8.5 Hz, 1H), 7.81 (s, 1H), 7.59 (d, <i>J</i> = 8.1 Hz, 1H), 7.52-7.48 (m, 1H), 7.46-7.44 (m, 2H), 7.35-7.32 (m, 3H), 7.31 – 7.25 (m, 1H), 2.28 (s, 3H).
		¹³ C NMR (126 MHz, CDCl ₃) δ 160.52, 146.68, 140.92, 136.74, 129.30, 129.16, 128.90, 128.75, 128.32, 128.20, 127.61, 126.74, 126.41, 20.63.

38		 2-(p-tolyl)quinoline²⁴ (8C): White solid (0.210 g, 96% yield); ¹H-NMR (500 MHz, CDCl₃, 25 °C, TMS) δ 8.15 (t, <i>J</i> = 8.7 Hz, 2H), 8.06 (d, <i>J</i> = 8.2 Hz, 2H), 7.81 (d, <i>J</i> = 8.6 Hz, 1H), 7.77 (d, <i>J</i> = 8.2 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.51 – 7.45 (m, 1H), 7.31 (d, <i>J</i> = 7.9 Hz, 2H), 2.41 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 157.43, 148.39, 139.52, 136.97, 136.79, 129.75, 129.70, 127.56, 127.21, 126.20, 118.98, 21.49.
39		2-(4-ethylphenyl)quinoline ²⁶ (8d): White solid (0.226 g, 97% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 8.16 (dd, J = 8.4, 0.7 Hz, 1H), 8.09 – 8.03 (m, 2H), 8.00 (d, J = 8.6 Hz, 1H), 7.71 (d, J = 8.6 Hz, 1H), 7.69 – 7.60 (m, 2H), 7.40 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 7.28 (d, J = 8.4 Hz, 2H), 2.66 (q, J = 7.6 Hz, 2H), 1.23 (t, J = 7.6 Hz, 3H).
		¹³ C NMR (126 MHz, CDCl ₃) δ 157.28, 148.31, 145.68, 137.11, 136.60, 129.67, 129.54, 128.41, 128.38, 127.56, 127.46, 127.08, 126.04, 118.81, 28.74, 15.59.
40		2-(2,5-dimethylphenyl)quinoline (8e): Yellow oil (0.226 g, 97% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 8.18 (d, <i>J</i> = 8.4 Hz, 1H), 8.07 (d, <i>J</i> = 8.5 Hz, 1H), 7.74 (d, <i>J</i> = 8.1 Hz, 1H), 7.70 – 7.62 (m, 1H), 7.46 (dd, <i>J</i> = 11.8, 5.5 Hz, 2H), 7.32 (d, <i>J</i> = 1.5 Hz, 1H), 7.17 (d, <i>J</i> = 7.7 Hz, 1H), 7.11 (dd, <i>J</i> = 7.8, 1.7 Hz, 1H), 2.34 (s, 6H).
		¹³ C NMR (126 MHz, CDCl ₃) δ 160.30, 147.84, 140.45, 135.83, 135.31, 132.62, 130.73, 130.25, 129.48, 129.18, 127.42, 126.60, 126.23, 122.31, 20.90, 19.81. HRMS for $C_{17}H_{15}N$ [M+H] Calculated : 234.1283, Found: 234.1289.
41	N F	2-(4-fluoro-3-methylphenyl)quinoline (8f): White solid (0.216 g, 91% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 8.14 (d, <i>J</i> = 8.5 Hz, 1H), 8.09 (d, <i>J</i> = 8.6 Hz, 1H), 7.99 (dd, <i>J</i> = 7.5, 1.6 Hz, 1H), 7.91 – 7.84 (m, 1H), 7.77 – 7.66 (m, 3H), 7.47 (ddd, <i>J</i> = 8.0, 7.0, 1.1 Hz, 1H), 7.10 (t, <i>J</i> = 8.9 Hz, 1H), 2.35 (d, <i>J</i> = 1.6 Hz, 3H).
		¹³ C NMR (126 MHz, CDCl ₃) δ 162.44 (d, J = 247.8 Hz), 156.49, 148.22, 136.84, 135.46 (d, J = 3.4 Hz), 130.88 (d, J = 5.6 Hz), 129.77, 129.60, 127.52, 127.06, 126.69 (d, J = 8.4 Hz), 126.28, 125.33 (d, J = 17.6 Hz), 118.73, 118.54, 115.38 (d, J = 22.7 Hz), 14.79 (d, J = 2.8 Hz). HRMS for C ₁₆ H ₁₂ FN [M+H] Calculated : 238.1033, Found: 238.1032.

42	CI CI	2-(4-chlorophenyl)quinoline ²² (8g): White solid (0.230 g, 96% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 8.14 (d, <i>J</i> = 8.5 Hz, 2H), 8.07 (d, <i>J</i> = 8.5 Hz, 2H), 7.77-7.74 (m, 2H), 7.73 – 7.67 (m, 1H), 7.53 – 7.43 (m, 3H). ¹³ C NMR (126 MHz, CDCl ₃) δ 156.05, 148.33, 138.13, 137.05, 135.64, 129.95, 129.80, 129.11, 129.02, 128.92, 127.61, 127.32, 126.61, 118.63.
43	F	2-(4-fluorophenyl)quinoline ²⁴ (8h): White solid (0.210 g, 94% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 8.16 – 8.02 (m, 4H), 7.72 (d, <i>J</i> = 8.3 Hz, 2H), 7.64 (t, <i>J</i> = 7.6 Hz, 1H), 7.43 (t, <i>J</i> = 7.5 Hz, 1H), 7.11 (t, <i>J</i> = 8.5 Hz, 2H). ¹³ C NMR (126 MHz, CDCl ₃) δ 163.82 (d, <i>J</i> = 249.0 Hz), 156.25,
		(d, J = 8.5 Hz), 127.51, 127.10, 126.37, 118.64, 115.79 (d, J = 21.6 Hz).
44		2-(4-methoxyphenyl)quinoline ²⁴ (8i): White solid (0.228 g, 97% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 8.14-8.10 (m, 4H), 7.83 – 7.72 (m, 2H), 7.70-7.76 (m, 1H), 7.47-7.44 (m, 1H), 7.07 – 6.96 (m, 2H), 3.84 (s, 3H).
	~~~0~	¹³ C NMR (126 MHz, CDCl ₃ ) δ 160.90, 157.00, 148.37, 136.76, 132.31, 129.70, 129.59, 129.00, 127.56, 127.01, 126.02, 118.66, 114.32, 55.48.
45		<b>2-(4-ethoxyphenyl)quinoline (8j):</b> White solid (0.242 g, 97% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) δ 8.16 – 8.07 (m, 4H), 7.75 (t, <i>J</i> = 8.9 Hz, 2H), 7.68 (ddd, <i>J</i> = 8.3, 6.9, 1.4 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.03 – 6.96 (m, 2H), 4.05 (q, <i>J</i> = 7.0 Hz, 2H), 1.41 (t, <i>J</i> = 7.0 Hz, 3H).
		$^{13}\text{C}$ NMR (126 MHz, CDCl ₃ ) $\delta$ 160.27, 157.00, 148.36, 136.69, 132.09, 129.64, 129.58, 128.95, 127.54, 126.96, 125.95, 118.61, 114.80, 63.61, 14.91. HRMS for C17H15NO [M+H] Calculated : 250.1233, Found: 250.1236.
46		<b>2-(3,4-dimethoxyphenyl)quinoline</b> ²⁷ (8k): White solid (0.252 g, 95% yield); ¹ H NMR (500 MHz, CDCl ₃ , 25 °C, TMS) $\delta$ 8.14 (dd, $J = 11.7, 8.7$ Hz, 2H), 7.88 (d, $J = 2.0$ Hz, 1H), 7.79 (dd, $J = 17.5, 8.4$ Hz, 2H), 7.73 – 7.66 (m, 1H), 7.63 (dd, $J = 8.3, 2.0$ Hz, 1H), 7.51 – 7.44 (m, 1H), 6.96 (d, $J = 8.4$ Hz, 1H), 4.03 (s, 3H), 3.93 (s, 3H).
		¹³ C NMR (126 MHz, CDCl ₃ ) δ 156.88, 150.44, 149.45, 148.28, 136.71, 132.58, 129.69, 129.56, 127.53, 127.05, 126.07, 120.32, 118.68, 111.08, 110.45, 56.09, 56.04.



### 4 References :

- C. M. Wong, R. T. McBurney, S. C. Binding, M. B. Peterson, V. R. Gonçales, J. J. Gooding and B. A. Messerle. Iridium (III) homo- and heterogeneous catalysed hydrogen borrowing C—N bond formation. Green Chemistry, **2017**, 19(13), 3142-3151.
- T. Higuchi, T. Tagawa, A. Iimuro, S. Akiyama, H. Nagae, and K. Mashima. Tunable Ligand Effects on Ruthenium Catalyst Activity for Selectively Preparing Imines or Amides by Dehydrogenative Coupling Reactions of Alcohols and Amines, *Chem. Eur. J.*, 2017, 23(52), 12795-12804.
- 3. E. J. Hennessy, and S. L. Buchwald. Synthesis of Substituted Oxindoles from α-Chloroacetanilides via Palladium-Catalyzed C-H Functionalization, *J. Am. Chem. Soc.*, **2003**, 125, 40, 12084-12085.

- 4. C. Wang, C. Chen, J. Zhang, Y. Yao, and Y. Zhao. Insight into O₂–Promoted Base–Catalyzed N– Alkylation of Amines with Alcohols, *Eur. J. Org. Chem.* **2015**, (13), 2972-2977.
- 5. X. Dai, X. Cui, Y. Deng, and F. Shi. A conjugated ketone as a catalyst in alcohol amination reactions under transition-metal and hetero-atom free conditions, *RSC Adv.*, **2015**, 5, 43589-43593.
- S. Elangovan, J. Neumann, J.B. Sortais, K. Junge, C. Darcel, and M. Beller. Efficient and selective Nalkylation of amines with alcohols catalysed by manganese pincer complexes, *Nat. Commun.* 2016, 7, 12641pp.
- 7. F. Fernandes and B. Royo. Water–Soluble Iridium N–Heterocyclic Carbene Complexes for the Alkylation of Amines with Alcohols, *Chem.Cat.Chem.*, **2017**, 9(20), 3912-3917.
- H. Hikawa, K. Izumi, Y. Ino, S. Kikkawa, Y. Yokoyama and I. Azumaya. Palladium– Catalyzed Benzylic C-H Benzylation via Bis–Benzylpalladium(II) Complexes in Water: An Effective Pathway for the Direct Construction of N–(1,2–Diphenylethyl)anilines, *Adv. Synth. Catal*, **2015**, 357(5), 1037-1048.
- P. Liu, R. Liang, L. Lu, Z. Yu and F. Li. Use of a Cyclometalated Iridium(III) Complex Containing a NACAN-Coordinating Terdentate Ligand as a Catalyst for the α-Alkylation of Ketones and N-Alkylation of Amines with Alcohols, *J. Org. Chem.* **2017**, 82, 4, 1943-1950.
- 10. H. Yang, X. Cui, X. Dai, Y. Deng and F. Shi. Carbon-catalysed reductive hydrogen atom transfer reactions, *Nat. Commun.*, **2015**, 6,6478pp.
- S. Sharif, R. P. Rucker, N. Chandrasoma, D. Mitchell, M. J. Rodriguez, R. D. J. Froese and M. G. Organ. Selective Monoarylation of Primary Amines Using the Pd-PEPPSI- IPentCl Precatalyst*, *Angew. Chem. Int. Ed.*, **2015**, 54(33), 9507-9511.
- J. Gao, S. Bhunia, K. Wang, L. Gan, S. Xia, and D. Ma. Discovery of N-(Naphthalen-1-yl)-N'-alkyl Oxalamide Ligands Enables Cu-Catalyzed Aryl Amination with High Turnovers, **2017**, *Org. Lett.* 19, 11, 2809-2812.

- 13. S. Rösler, M. Ertl, T. Irrgang and R. Kempe, Cobalt–Catalyzed Alkylation of Aromatic Amines by Alcohols, *Angew. Chem. Int. Ed.* **2015**, 54(50), 15046-15050.
- F.-L. Yang, Y.-H. Wang, Y.-F. Ni, X. Gao, B. Song, X. Zhu, and X.-Q. Hao. An Efficient Homogenized Ruthenium(II) Pincer Complex for N–Monoalkylation of Amines with Alcohols, *Eur. J. Org. Chem.* 2017, (24), 3481-3486.
- 15. T. Zhang, Y. Zhang, W. Zhang and M. Luo. A Convenient and General Reduction of Amides to Amines with Low–Valent Titanium, *Adv. Synth. Catal.* **2013**, 355, 2775-2780.
- 16. M. Zhang, R. Ruzi, J. Xi, N. Li, Z. Wu, W. Li, S. Yu S. and C. Zhu. Photoredox-Catalyzed Hydroacylation of Olefins Employing Carboxylic Acids and Hydrosilanes, *Org. Lett.*, **2017**, 19, 13, 3430-3433.
- R. Wang, J. Ma, and F. Li. Synthesis of a-Alkylated Ketones via Tandem Acceptorless Dehydrogenation/a-Alkylation from Secondary and Primary Alcohols Catalyzed by Metal–Ligand Bifunctional Iridium Complex [Cp*Ir(2,2'-bpyO)(H₂O)], *J. Org. Chem.* **2015**, 80, 21, 10769-10776.
- Q. Jiang, T. Guo, Q. Wang, P. Wu, and Z. Yu. Rhodium(I)–Catalyzed Arylation of β–Chloro Ketones and Related Derivatives through Domino Dehydrochlorination/ Conjugate Addition, *Adv. Synth. Catal.*, **2013**, 355(9), 1874-1880.
- X. Cui, Y. Zhang, F. Shi, and Y. Deng. Organic Ligand–Free Alkylation of Amines, Carboxamides, Sulfonamides, and Ketones by Using Alcohols Catalyzed by Heterogeneous Ag/Mo Oxides, *Eur. J.*, 2011,17(3),1021-1028, S1021/1-S1021/69.
- P. Colbon, J. Ruan, M. Purdie and J. Xiao. Direct Acylation of Aryl Chlorides with Aldehydes by Palladium– Pyrrolidine Co-catalysis, Org. Lett., 2010, 12, 16, 3670-3673.
- M. J. C. Corrêa, F. M. Nunes and H. R. Bitencourt et.al, Biotransformation of chalcones by the endophytic fungus Aspergillus flavus isolated from Paspalum maritimum Trin. *J Brazilian. Chem., Soc.,* 2011,22(7), 1333-1338.

- 22. G. Zhang, J. Wu, H. Zeng, S. Zhang, Z. Yin, and S. Zheng. Cobalt-Catalyzed α-Alkylation of Ketones with Primary Alcohols, *Org. Lett.*, **2017**, 19, 5, 1080-1083.
- 23. C. J. Evoniuk, G. D. P. Gomes, S. P. Hill, S. Fujita, K. Hanson and I. V. Alabugin. Coupling N–H Deprotonation, C–H Activation, and Oxidation: Metal-Free C(sp3)–H Aminations with Unprotected Anilines, *J. Am. Chem Soc.*, **2017**, 139,45, 16210-16221.
- 24. J. Xu, J. Sun, J, Zhao, B. Huang, X. Li and Y. Sun Palladium-catalyzed synthesis of quinolines from allyl alcohols and anilines, *RSC Adv.*, **2017**,7, 36242-36245.
- 25. S. Sujan, G. Kasturi, J. Kalipada, and K. Sabuj. Cobalt complex catalyzed atom-economical synthesis of quinoxaline, quinoline and 2-alkylaminoquinoline derivatives, *Chem. Commun.*, **2018**, 54, 6883-6886.
- 26. K. Singh, M. Vellakkaran and D. Banerjee. A nitrogen-ligated nickel-catalyst enables selective intermolecular cyclisation of β- and γ-amino alcohols with ketones: access to five and six membered Nheterocycles, *Green Chem.*, **2018**, 20, 2250-2256.
- C. S. Cho, N. Y. Lee, T.-J. Kim and Shim. Consecutive isomerization and cyclization of 3-(2 amino phenyl)-1arylprop-2-yn-1-ols leading to 2-arylquinolines in the presence of potassium hydroxide, *J. Heterocyclic Chem.*, 41, 409 (2004).
- M. Vellakkaran, K. Singh, and D. Banerjee. An Efficient and Selective Nickel-Catalyzed Direct N-Alkylation of Anilines with Alcohols. ACS Catalysis, 2017, 7(12), 8152–8158.
- 29. Y. Yoshida, S. Otsuka, K. Nogi, and H.Yorimitsu. Palladium-Catalyzed Amination of Aryl Sulfoxides, *Organic Letters*, **2018**, 20(4), 1134–1137.
- 30. M. Vellakkaran, M. M. S. Andappan, and K. Nagaiah. Oxygen as single oxidant for two steps: base-free one-pot Pd(ii)-catalyzed alcohol oxidation & arylation to halogen-intact β-aryl α,β-enones. RSC Adv., 2014, 4(85), 45490–45494.



# ¹H NMR and ¹³C NMR Spectra

S26






























































































S50































































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