Supporting Information

Ruthenium pincer complex catalyzed efficient synthesis of quinoline, 2styrylquinoline and quinazoline derivatives *via* acceptorless dehydrogenative coupling reactions

Dipanjan Bhattacharyya,^a Priyanka Adhikari,^a Kritartha Deori,^a and Animesh Das^{*a,b}

^aDepartment of Chemistry, Indian Institute of Technology Guwahati, Guwahati- 781039, Assam, India

^bCentre for Sustainable Polymers, Indian Institute of Technology Guwahati, Guwahati-781039, Assam, India.

Email: <u>adas@iitg.ac.in</u>

Table of contents

			Page No.
1.	General information		S2
2.	Synthetic scope of ADC	reactions	
3.	Procedure for the calcu	lation of TON and TOF for quinoline	and qunazolineS5
4.	Mechanistic		
	studies	•••••••••••••••••••••••••••••••••••••••	S6
5.	Deuterium	incorporation	experiments
	•••••••••••••••••••••••••••••••••••••••	S10	
6.	Calculation of green me	etrics	S13
7.	Spectroscopic characte	rization of ruthenium complex	S14
8.	Analytical data of the p	roducts	S16
9.	¹ H, ¹³ C, and ¹⁹ F NMR s	pectra of the products	
10	. References		

1. General information

All the reagents and chemicals were purchased from common commercial suppliers like Sigma-Aldrich, Alfa Aesar, Merck, Spectrochem, Avra Synthesis Pvt. Ltd., Finar Chemicals and directly used as received without any further purification unless otherwise mentioned. 1-([1,1'-biphenyl]-4-yl)ethan-1-ol,^{1,2} 1-(4-(phenylethynyl)phenyl)ethan-1-ol,^{3,4} 4-(allvloxy) benzyl alcohol⁵ were prepared according to the reported literature.¹H, ¹³C, and ¹⁹F NMR spectra of the compounds were measured in $CDCl_3$, DMSO- d_6 , CD₃OD as a solvent by using TMS as an internal standard. Chemical shifts, δ (in ppm), are reported relative to TMS δ ⁽¹H) 0.0 ppm, δ (¹³C) 0.0 ppm, which was used as the internal reference. Otherwise the solvents residual proton resonance and carbon resonance (CHCl₃, δ (¹H) 7.26ppm, δ (¹³C) 77.16 ppm; DMSO- d_6 , (¹H) 2.50 ppm, δ (¹³C) 39.52 ppm; CD₃OD, δ (¹H) 3.31ppm, δ (¹³C) 49 ppm) were also used forcalibration. Bruker Avance III 600 and 400 spectrometers were used to record the NMR spectra. Chemical shifts (δ) values were reported in ppm and spin-spin coupling constant (J) were expressed in Hz, and other data were reported as follows: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, m = multiplet, q = quartet, sext = sextet, br = broad, and brs = broad singlet. IR spectra were recorded on Perkin Elmer Instrument at normal temperature making KBr pellet grinding the sample with KBr (IR Grade). MS (ESI-HRMS): Mass spectra were recorded on an Agilent Accurate-Mass Q-TOF LC/MS 6520. Merck silica gel 60-120 was used for column chromatography.GC analyses were performed on a Perkinelmer-Clarus 590 GC instrument fitted with Elite-1 column (30 m length, 0.32 mm ID) using the following method: Injection volume: 1 µL, inlet temperature: 280 °C, FID detector temperature: 280 °C, oven temperature: start at 60 °C hold time 1 min, ramp: 12 °C /min, upto 320 °C, Flow rate (carrier): 25 mL/min (N₂).

2. Synthetic scope of ADC reactions

2.1. Optimization studies

Table S1: Screening of reaction conditions for synthesis of 2-styrylquinoline^{*a,b*}

	+ HO ^{Ph}	1f, 0.1 mol% KO'Bu (x mol%) 120 °C toluene		+ H ₂ O + H ₂ ↑
4q	5a	time, air	6a	
entry	mol% 1f	base (mol%)	time (h)	yield $(\%)^c$
1	0.1	$KO^{t}Bu(1)$	6	55
2	0.1	$KO^{t}Bu(5)$	6	68
3	0.1	$KO^{t}Bu(10)$	6	81
4	0.1	$KO^{t}Bu(10)$	12	95
5	-	KO ^{<i>t</i>} Bu (10)	12	trace
6	0.1	$KO^{t}Bu(0)$	12	0

^{*a*}Reaction conditions: 2-methylquinoline (1 mmol), benzylalcohol (1.2 equiv.), **1f** (0.1 mol%), base (x mol%) and toluene (2 mL) were heated for x h at 120 °C in the closed reaction tube. ^{*b*}Isolated yield.

Table S2: Screening of reaction conditions for synthesis of quinazoline^{*a,b*}

		NH2 OH		$\frac{1f(x \text{ mol}\%)}{KO'Bu(x \text{ mol}\%)}$			
		2a	7a	120 °C, toluene time, air	8a		
entry	mol% 1f	base (mol%)	time (h)	conv. $(\%)^b$	yield (%) ^c	TON	TOF
1	2	KO ^{<i>t</i>} Bu (20)	12	> 99	98 (95)	49	4
2	1	KO ^{<i>t</i>} Bu (10)	12	> 99	97	97	8
3	0.5	KO ^{<i>t</i>} Bu (10)	12	> 99	97	194	16
4	0.2	KO ^{<i>t</i>} Bu (10)	12	> 99	97	485	40
5	0.1	KO'Bu (10)	12	> 99	96	960	80
6	0.1	$KO^{t}Bu(1)$	12	> 99	95 (92)	950	79
7	0.1	$KO^{t}Bu(1)$	6	> 99	94 (92)	940	156
8	0.05	$KO^{t}Bu(1)$	6	85	80 (78)	1600	266
9	0.01	$KO^{t}Bu(1)$	6	70	43 (41)	430	71
10 ^d	_	$KO^{t}Bu(1)$	6	18	n.d.	_	—
11	0.1	_	6	12	n.d.	_	_
12	0.01	$KO^{t}Bu(1)$	12	84	65	6,500	541
13	0.0001	$KO^{t}Bu(1)$	10	61	24	2,40,000	24,000
1 <u>1</u> e	0.0001	$KO^{t}Bu(1)$	12	67	29	2 90 000	24 166

^{*a*}Reaction conditions: 2-aminobenzylalcohol (3 mmol), benzonitrile (3 mmol), **1f** (x mol%), KO'Bu (x mol%) and toluene (2 mL) were heated under air for x h at 120 °C. ^{*b*}Conversion of 2-aminobenzylalcohol was determined by GC analysis using benzene as internal standard. 'Yields were calculated from GC analysis of the reaction mixture using benzene as an internal standard; isolated yields are given within parentheses. ^{*d*}With RuCl₃•xH₂O (0.1 mol%). ^{*e*}The same has been repeated three times, average data is given.

2.2. General procedure for the synthesis of N-heteroaromatic compounds

2.2.1. General procedure for synthesis of quinoline (GP-1):

The required amount of catalyst **1f** stock solution, synthesized in CH₃OH (0.1 mol%), was added to a reaction tube and the volatiles were removed in high vacuum. To this, 2-aminobenzyl alcohol (3 mmol, 1 equiv), secondary alcohol (3 mmol, 1 equiv), KO'Bu (1 mol%) and toluene (2 mL) were added. The reaction tube was then closed without exclusion of air and placed it in a preheated oil bath (bath temperature 120 °C), kept for 6 hours. The resulting mixture was then passed through a bed of celite, the filtrate was collected and concentrated under reduced pressure. Analytically pure product was obtained by column chromatography over silica gel using ethyl acetate / petroleum ether mixture as an eluent.

2.2.2. General procedure for synthesis of 2-styrylquinoline (GP-2):

The required amount of catalyst **1f** stock solution, synthesized in CH₃OH (0.1 mol%), was added to a reaction tube and the volatiles were removed in high vacuum. To this, 2-methylquinoline (1 mmol, 1 equiv), primary alcohol (1.2 equiv), KO'Bu (10 mol%) and toluene (2 mL) was added. The reaction tube was properly closed without exclusion of air and placed it in a preheated oil bath (bath temperature 120 °C), kept for 12 hours. The resulting mixture was then passed through a bed of celite, the filtrate was collected and concentrated under reduced pressure. Analytically pure product was obtained by column chromatography over silica gel using ethyl acetate / petroleum ether mixture as an eluent.

2.2.3. General procedure for one-pot synthesis of 4-(benzyloxy)-2-styrylquinoline (GP-3):

The required amount of catalyst **1f** stock solution, synthesized in CH₃OH (0.1 mol%), was added to a reaction tube and the volatiles were removed in high vacuum. To this, 4-chloro-2-methylquinoline (1 mmol, 1 equiv), primary alcohol (2.2 equiv), KO'Bu (10 mol%) and toluene (2 mL) was added. The reaction tube was properly closed without exclusion of air and placed it in a preheated oil bath (bath temperature 120 °C), kept for 12 hours. The resulting mixture was then passed through a bed of celite, the filtrate was collected and concentrated under reduced pressure. Analytically pure product was obtained by column chromatography over silica gel using ethyl acetate / petroleum ether mixture as an eluent.

2.2.4. General procedure for one-pot synthesis of 2-styrylquinoline from 2-amino benzylalcohol (GP-4):

The required amount of catalyst **1f** stock solution, synthesized in CH₃OH (0.1 mol%), was added to a reaction tube and the volatiles were removed in high vacuum. To this, 2-aminobenzyl alcohol (1 mmol, 1 equiv), isopropanol (6 mmol, 6 equiv), KO'Bu (10 mol%) and toluene (2 mL) was added. The reaction tube was properly closed without exclusion of air and placed it in a preheated oil bath (bath temperature 120 °C), kept for 6 hours. The reaction mixture was then cooled down to room temperature and subsequently primary alcohol (1.2 mmol, 1.2 equiv.) was added under air. Then the reaction mixture was then passed through a bed of celite, the filtrate was collected and concentrated under reduced pressure. Analytically pure product was obtained by column chromatography over silica gel using ethyl acetate / petroleum ether mixture as an eluent.

2.2.5. General procedure for synthesis of quinazoline (GP-5):

The required amount of catalyst **1f** stock solution, synthesized in CH₃OH (0.1 mol%), was added to a reaction tube and the volatiles were removed in high vacuum. To this, 2-aminobenzyl alcohol (3 mmol, 1 equiv.), aryl nitrile (1 equiv.), KO'Bu (1 mol%) and toluene (2 mL) was added. The reaction tube was properly closed without exclusion of air and placed it in a preheated oil bath at 120 °C for 6 hours. The resulting mixture was then passed through a bed of celite, the filtrate was collected and concentrated under reduced pressure. Analytically pure product was obtained by column chromatography over silica gel using ethyl acetate / petroleum ether mixture as an eluent.

2.3. Experimental procedure for gram-scale reactions



For quinolines: A mixture of 2-aminobenzyl alcohol (1 g, 8.1 mmol, 1 equiv), 1-(4-methoxyphenyl) ethan-1-ol (1.231 g, 8.1 mmol, 1 equiv), 1f(0.1 mol%), KO/Bu (1 mol%) and toluene (2 mL) was added into a reaction tube (50 mL) equipped with stirring bar. The reaction tube was properly closed without exclusion of air and kept it in a preheated oil bath at 120 °C with continuous stirring for 6 hours. The resulting mixture was then passed through a bed of celite, the filtrate was collected and concentrated under reduced pressure. The residue was

purified by column chromatography over silica gel (60-120 mesh) with pet-ether/ethyl acetate mixture as eluent to get 88% yield of the product (1.675 g).



For quinazolines: A mixture of 2-aminobenzyl alcohol (1 g, 8.1 mmol, 1 equiv), benzonitrile (0.84 g, 8.1 mmol, 1 equiv), **1f** (0.1 mol%), KO/Bu (1 mol%) and toluene (2 mL) was added into a reaction tube (50 mL) equipped with stirring bar. The reaction tube was then properly closed without exclusion of air and kept it in a preheated oil bath at 120 °C with continuous stirring for 6 hours. After completion of the reaction, the resulting mixture was passed through a bed of celite, the filtrate was collected and concentrated under reduced pressure. The residue was purified by column chromatography over silica gel (60-120 mesh) with pet-ether/ethyl acetate mixture as eluent to get 83% yield of the product (1.384 g).



For 2-styrylquinolines: A mixture of 2-methylquinoline (1 g, 6.98 mmol, 1 equiv), benzyl alcohol (0.907 g, 8.4 mmol, 1.2 equiv), **1f** (0.1 mol%), KO'Bu (10 mol%) and toluene (2 mL) was added into a reaction tube (50 mL) equipped with stirring bar. The reaction tube was then properly closed without exclusion of air and kept it in a preheated oil bath at 120 °C with continuous stirring for 12 hours. After completion of the reaction, the resulting mixture was passed through a bed of celite, the filtrate was collected and concentrated under reduced pressure. The residue was purified by column chromatography over silica gel (60-120 mesh) with pet-ether/ethyl acetate mixture as eluent to get 87% yield of the product (1.406 g).

3. Procedure for the calculation of TON and TOF for quinoline and qunazoline

The catalyst stock solution was prepared by dissolving **1f** in CH₃OH. A reaction tube was charged with a required amount of **1f** (0.0001 mol%) stock solution and all the volatiles were removed in vacuum. To this, 2-aminobenzyl alcohol (3 mmol, 1 equiv), secondary alcohol (3 mmol, 1 equiv), and KO'Bu (1 mol%) followed by toluene (2 mL) was added. The reaction tube was closed without exclusion of air and placed it in a preheated oil bath at 120 °C for 12 hours. After that the reaction mixture was cooled to room temperature and subjected to GC-MS analysis. The average data based on the GC-MS analysis shows the 44% formation of **4a** which provides TON of 4,40,000. Under the same reaction conditions by using benzonitrile (1 equiv), 29% formation of **8a** in GC-MS indicating TON of 2,90,000.

4. Mechanistic studies

4.1. Mercury drop test

To establish the homogeneity of current catalytic reaction, mercury drop experiment was carried out.



For quinoline: In this test, the reaction tube was charged with 2-aminobenzyl alcohol (3 mmol, 369 mg), 1-(4-methoxyphenyl)ethan-1-ol (3 mmol, 456 mg), mercury (1.5 mmol, 300 mg), KO'Bu (1 mol%) and complex **1f** (0.1 mol%). To this reaction mixture, 2 mL of toluene was added and heated at 120 °C for 6 h. The desired product was obtained in 92% yield, indicating the homogenous behaviour of the reaction.



For quinazoline: In this test, the reaction tube was charged with 2-aminobenzyl alcohol (3 mmol, 369 mg), benzonitrile (3 mmol, 309 mg), mercury (1.5 mmol, 300 mg), KO'Bu (1 mol%) and complex **1f** (0.1 mol%). To this reaction mixture, 2 mL of toluene was added and heated at 120 °C for 6 h. The desired product was obtained in 90% yield, suggesting the homogenous behaviour of the catalytic process.

 $\begin{array}{c|c} & \mathbf{If}, 0.1 \text{ mol}\% \\ \hline \mathbf{KO'Bu}, 10 \text{ mol}\% \\ \hline \mathbf{Hg}, 50 \text{ mol}\%, \\ 120 \text{ °C}, \text{ toluene} \\ 12 \text{ h} \end{array} + H_2O$

For 2-styrylquinolines: In this test, the reaction tube was charged with 1 mmol (143 mg) of 2-methylquinoline, 1.2 mmol (129 mg) of benzyl alcohol, 0.5 mmol (100 mg) of mercury, 0.1 mmol of KO/Bu and 0.001 mmol of complex **1f**. To this reaction mixture 2 mL of toluene was added and heated at 120 °C for 12 h. The expected product was obtained in 93% of yield, demonstrating the homogenous behavior of the catalytic process.

4.2. Proof for the formation of intermediate 2-amino benzaldehyde, ketone in quinoline synthesis:

4.2.1. Reaction of 2-aminobenzyl alcohol and acetophenone



Method: A mixture of **2a** (3 mmol, 1 equiv.), **3a'** (3 mmol, 1 equiv.), **1f** (0.1 mol%), KO'Bu (1 mol%) and toluene (2 mL) was loaded into the reaction tube and heated at 120 °C for 6 h. The product **4a** was isolated in 95% of yield.

4.2.2. Reaction of 2-aminobenzaldehyde and 1-phenylethanol



Method: A mixture of **2a'** (3 mmol, 1 equiv.), **3a** (3 mmol, 1 equiv.), **1f** (0.1 mol%), KO'Bu (1 mol%) and toluene (2 mL) was loaded into the reaction tube and heated at 120 °C for 6 h. The product **4a** was isolated in 77% of yield.

4.3. Proof for the formation of intermediate 2-aminobenzaldehyde and benzamide in quinazoline synthesis:

4.3.1. Reaction of 2-aminobenzaldehyde and benzonitrile



A mixture of **2a'** (3 mmol, 1 equiv.), **7a** (3 mmol, 1 equiv.), **1f** (0.1 mol%), KO'Bu (1 mol%) and toluene (2 mL) was loaded into the reaction tube and heated at 120 °C for 6 h. The product **8a** was isolated in 89% of yield.

4.3.2. Formation of benzamide under the reaction conditions



A mixture of **7a** (3 mmol, 1 equiv.), **1f** (0.1 mol%), KO'Bu (1 mol%) and toluene (2 mL) was loaded into the reaction tube under air and heated at 120 °C for 6 h. The product **7a-I** was isolated in 34% of yield. In the presence of H₂O (2 equiv.), the yield of **7a-I** was obtained in 80% yield.

4.3.3. Reaction of 2-aminobenzaldehyde and benzamide



A mixture of **2a'** (3 mmol, 1 equiv.), **7a-I** (3 mmol, 1 equiv.), **1f** (0.1 mol%), KO'Bu (1 mol%) and toluene (2 mL) was loaded into the reaction tube and heated at 120 °C for 6 h. The product **8a** was isolated in 90% of yield.

4.4. Evidence of intermediate in 2-styrylquinoline and 4-benzyloxy-2-styrylquinoline synthesis:

4.4.1. Reaction of 2-methylquinoline and benzaldehyde



A mixture of 2-methylquinoline 4q (1 mmol, 1 equiv.), benzaldehyde 5a (1.2 mmol, 1.2 equiv.), 1f (0.1 mol%), KO/Bu (1 mol%) and toluene (2 mL) was loaded into the reaction tube and heated at 120 °C for 12 h. The product 6a was isolated in 92% of yield.

4.4.2. Reaction of 2-aminochalcone under the standard reaction condition



Method: A mixture of **9** (1 mmol, 1 equiv.), **1f** (0.1 mol%), KO'Bu (1 mol%) and toluene (2 mL) was loaded into the reaction tube under air and heated at 120 °C for 6 h. The product **4a** was isolated in 89% of yield.

4.4.3. Reaction of 4-chloro-2-methylquinoline and benzylalcohol



A mixture of 4-chloro-2-methylquinoline (1 mmol, 1 equiv.), benzylalcohol (1 mmol, 1 equiv.), KO'Bu (10 mol%), **1f** (0.1 mol%) and toluene (2 mL) was loaded into the reaction tube and heated at 120 °C for 4 h. The product **6l** (30%), **10** (31%), and **11** (10%) was isolated.

4.4.4. Reaction of 4-benzyloxy-2-methylquinoline and benzylalcohol



A mixture of 4-benzyloxy-2-methylquinoline 10 (1 mmol, 1 equiv.), benzylalcohol (1 mmol, 1 equiv.), KO'Bu (10 mol%), 1f (0.1 mol%) and toluene (2 mL) was loaded into the reaction tube and heated at 120 °C for 12 h. The product 6l was isolated in 91% of yield.

4.4.4. Reaction of 4-chloro-2-styrylquinoline and benzylalcohol



A mixture of 4-chloro-2-styrylquinoline 11 (1 mmol, 1 equiv.), benzylalcohol (1 mmol, 1 equiv.), KO'Bu (10 mol%), 1f (0.1 mol%) and toluene (2 mL) was loaded into the reaction tube and heated at 120 °C for 12 h. The product 6l was isolated in 90% of yield, and in the absence of 1f, yielded 29% of 6l.

4.4.5. Reaction of 4-chloro-2-methylquinoline and benzylalcohol



A mixture of 4-chloro-2-methylquinoline (1 mmol, 1 equiv.), benzylalcohol (1 mmol, 1 equiv.), KO'Bu (10 mol%) and toluene (2 mL) was loaded into the reaction tube and heated at 120 °C for 12 h. The product **10** was isolated in 30% of yield.

4.5. Hydrogenation of styrene by evolved hydrogen during synthesis of quinoline and quinazoline

For 4a:



An oven dried H-shaped bridged tube was equipped with a magnetic stir bar. Under Ar atmosphere, chamber one charged with catalyst **1f** (0.1 mol%), 3 mmol of **2a**, 3 mmol of **3a**, KO'Bu (1 mol%), and toluene (2 mL) and chamber two in which styrene (3 mmol), Pd/C (12 mg) were placed in 'AmOH (2 mL). Both chambers were closed with cap. The sealed bridged tube was placed in preheated oil bath at 120 °C for 6 h. After completion of the reaction, small portion of aliquot taken from chamber two for GC analysis, revealed conversion of styrene to ethyl benzene (38%).

For 8a:



Similarly, the following experiment was performed for 8a using catalyst 1f(0.1 mol%), KO/Bu (1 mol%), 3 mmol of 2a, and 3 mmol of 7a in toluene (2 mL). the conversion of styrene to ethyl benzene was observed in 27%.

4.6. The impact of the NH functionality in ruthenium complex



Scheme S19. The influence of the -NH functionality in catalysis

For 4a: Using the *N*-methylated catalyst $1f^{Me}$ instead of 1f and the following the general procedure GP-1 the title compound 4a was obtained in 48% yield.

For 6a: Using the *N*-methylated catalyst $1f^{Me}$ instead of 1f and the following the general procedure GP-2 the title compound 6a was obtained in 35% yield.

For 8a: Using the *N*-methylated catalyst $1f^{Me}$ instead of 1f and the following the general procedure GP-5 the title compound 8a was obtained in 22% yield.

5. Deuterium incorporation experiments:

(a) Deuterium incorporation at the α -position of 6a:



Scheme S20. Deuterium incorporation at the α -position of 6a

Procedure for 6a-\alpha-d1: A mixture of deuterated quinaldine **4q-d3** (146 mg, 1 mmol, 1 equiv), benzyl alcohol (130 mg, 1.2 mmol, 1.2 equiv), **1f** (0.1 mol%), KO/Bu (10 mol%) and toluene (2 mL) was added into a reaction tube (50 mL) equipped with stirring bar. The reaction tube was then properly closed without exclusion of air and kept it in a preheated oil bath at 120 °C with continuous stirring for 12 hours. After completion of the reaction, the resulting mixture was passed through a bed of celite, the filtrate was collected and concentrated under reduced pressure. The residue was purified by column chromatography over silica gel (60-120 mesh) with pet-ether/ethyl acetate mixture as eluent to get 81% yield of the product.



Based on nOe, HSQC, and ¹H-¹H COSY NMR, α -H in **6a-\alpha-d1** is assigned at 7.42 ppm. Deuterium incorporation in the α -position of **6a-\alpha-d1**: 34%

(b) Deuterium incorporation at the β -position of 6a:



Scheme S20. Deuterium incorporation at the β -position of 6a

Procedure for 6a-\beta-d1: A mixture of 2-methylquinoline (146 mg, 1 mmol, 1 equiv), deuterated benzyl alcohol **5a-d2** (130 mg, 1.2 mmol, 1.2 equiv), **1f** (0.1 mol%), KO/Bu (10 mol%) and toluene (2 mL) was added into a reaction tube (50 mL) equipped with stirring bar. The reaction tube was then properly closed without exclusion of air and kept it in a preheated oil bath at 120 °C with continuous stirring for 12 hours. After completion of the reaction, the resulting mixture was passed through a bed of celite, the filtrate was collected and concentrated under reduced pressure. The residue was purified by column chromatography over silica gel (60-120 mesh) with pet-ether/ethyl acetate mixture as eluent to get 75% yield of the product.



Based on nOe, HSQC, and ¹H-¹H COSY NMR, β-H in **6a-β-d1** is assigned at 7.67 ppm.

Deuterium incorporation in the α -position of **6a- \beta-d1:** 22%

(c) Evidence for the enamine intermediate 4q'



Scheme S21. Evidence for the enamine intermediate 4q'

Procedure: 2-methylquinoline **4q** (0.25 mmol), D_2O (0.2 mL), *t*-BuOK (0.5 mmol) and toluene (1.0 mL) were added in the reaction tube. The reaction mixture was heated at 120 °C oil bath for 12 h. The resulting mixture was then cooled to room temperature and removed the

volatiles. Check the ¹H NMR spectra of crude compound in CDCl₃. The result suggests that 10% D in 4q-d1.



6. Calculation of green metrics for quinoline synthesis:

For quinoline synthesis:



Reactant 1	2-aminobenzyl alcohol	1 g	F.W 123.16
Reactant 2	1-(4-methoxyphenyl)ethan-1-ol	1.23 g	F.W 152.19
Base	Potassium tert-butoxide	9.1 mg	F.W 112.21
Solvent	Toluene	1.73 g	F.W 92.14
Auxillary	-	-	-
Product	2-(4-methoxyphenyl)quinoline	1.68 g	F.W 235.29
Byproduct 1	Water	257.4 mg	F.W 18.01
Byproduct 2	Hydrogen	28.8 mg	F.W 2.02

Product yield = 88%

Atom economy: 235.29/275.35 = 85.4%

Atom efficiency: $88 \times (85.4/100) = 75.2\%$

Carbon efficiency: $(16/16) \times 100 = 100\%$

Reaction mass efficiency: $[1.68 \text{ g} / (1 \text{ g} + 1.23 \text{ g})] \times 100 = 75.3\%$

For quinazoline synthesis:



Reactant 1	2-aminobenzyl alcohol	1 g	F.W 123.16
Reactant 2	Benzonitrile	1 g	F.W 103.12
Base	Potassium tert-butoxide	9.1 mg	F.W 112.21
Solvent	Toluene	1.73 g	F.W 92.14
Auxillary	-	-	-
Product	2-phenylquinazoline	1.38 g	F.W 206.25
Byproduct 1	Water	257.4 mg	F.W 18.01
Byproduct 2	Hydrogen	28.8 mg	F.W 2.02

Product yield = 83%

Atom economy: 206.25/226.28 = 91.1%

Atom efficiency: $83 \times (91.1/100) = 75.6\%$

Carbon efficiency: $(14/14) \times 100 = 100\%$

Reaction mass efficiency: $[1.38 \text{ g} / (1 \text{ g} + 1 \text{ g})] \times 100 = 69\%$

7. Spectroscopic characterization of ruthenium complex



Spectroscopic characterization for active catalyst I



Figure S1. ¹H NMR spectrum of active species I (CD₃OD, 400 MHz, 298 K)

Procedure: The reaction tube was equipped with a stir bar, complex **1f** (30 mg, 0.05 mmol, 1 equiv) KO'Bu (4 equiv), and toluene (1.5 mL). The reaction mixture was stirred at 120 °C for 12 h. The resulting solution was then cooled to room temperature; all the volatile was removed under reduced pressure. The obtained residue was dissolved in methanol- d_4 and subjected for NMR analysis at room temperature. The above brown residue was dissolved in equimolar ratio of acetonitrile and water, and analyze the ESI-HRMS.



Figure S2. HRMS (ESI) spectra of active species I.

HRMS spectra for ruthenium hydride species (II):



Procedure: The reaction tube was equipped with a stir bar, complex **1f** (30 mg, 0.05 mmol, 0.15 equiv), **3b** (50 mg, 0.33 mmol, 1 equiv), and KO'Bu (23 mg, 0.20 mmol, 0.6 equiv). To the reaction mixture, 1.5 mL of toluene was added and stirred at 120 °C for 12 h. The resulting solution was cooled to room temperature, then 0.2 ml of solution was taken out by using syringe and mixed in equimolar ratio of HPLC grade acetonitrile and water (1 mL) mixture and analyzed the mass spectrometry.



Figure S3. HRMS (ESI) spectra for intermediate II species.

8. Analytical data of the products:

2-phenylquinoline (4a)⁶



Following the general procedure **GP-1** the title compound **4a** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 50/1, R_f = 0.5) in 92% yield (0.565 g). ¹H NMR (600 MHz, Chloroform-*d*): δ 8.23 – 8.17 (m, 4H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.56 – 7.52 (m, 3H), 7.49 – 7.47

(m, 1H). ¹³C NMR (151 MHz, CDCl₃): δ 157.5, 148.4, 139.8, 136.9, 129.8, 129.8, 129.4, 129.0, 127.7, 127.6, 127.3, 126.4, 119.1. Spectral data is in accordance to the reported literature.

2-(4-methoxyphenyl)quinoline (4b)⁶



Following the general procedure **GP-1** the title compound **4b** was isolated as light yellow solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.5) in 96% yield (0.675 g). ¹H NMR (600 MHz, CDCl₃): δ 8.19 (d, J = 6 Hz, 1H), 8.16 – 8.12 (m, 3H), 7.84 (d, J = 6 Hz, 1H), 7.82 – 7.80 (m, 1H), 7.72 – 7.70 (m, 1H), 7.51 – 7.49 (m, 1H), 7.07 – 7.04 (m, 2H), 3.89 (s, 3H). ¹³C NMR (151 MHz, CDCl₃): δ 160.9, 157.1, 148.4, 136.8, 132.4, 129.7, 129.6, 129.0, 127.6, 127, 126.1, 118.7, 114.4, 55.6. Spectral data is in accordance to the reported literature.

2-(4-chlorophenyl)quinoline (4c)⁷



Following the general procedure **GP-1** the title compound **4c** was isolated as yellow solid using silica gel column chromatography with pet-ether/ ethylacetate (v/v = 50/1, R_f = 0.5) in 85% yield (0.61 g). ¹H NMR (600 MHz, CDCl₃): δ 8.19 (d, J = 6.0 Hz, 1H), 8.16 (d, J = 6.0 Hz, 1H), 8.11 (d, J = 6.0 Hz, 2H), 7.82 – 7.80 (m, 2H), 7.75 – 7.72 (m, 1H), 7.53 (t, J = 6.0 Hz, 1H), 7.50 – 7.48 (m, 2H). ¹³C NMR (151 MHz, CDCl₃): δ 156.1, 148.3, 138.1, 137.0, 135.6, 129.9, 129.8, 129.1, 128.9, 127.6, 127.3, 126.6, 118.6.

2-(4-(benzyloxy)phenyl)quinoline (4d)



Following the general procedure **GP-1** the title compound **4d** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 20/1, R_f = 0.5) in 96% yield (0.89 g). ¹H NMR (600 MHz, CDCl₃): δ 8.18 (d, J = 8.6 Hz, 1H), 8.15 – 8.13 (m, 3H), 7.83 (d, J = 6.0 Hz, 1H), 7.81 (d, J = 6.0 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.51 – 7.47 (m, 3H), 7.41 (t, J = 6.0 Hz, 2H), 7.36 – 7.33 (m, 1H), 7.14 – 7.12 (m, 2H), 5.16 (s, 2H). ¹³C NMR (151 MHz, CDCl₃): δ 160.1, 157.0, 148.4, 136.9, 136.8, 132.6, 129.72, 129.7, 129.0, 128.8, 128.2, 127.6, 127.6, 127.1, 126.1, 118.7, 115.3, 70.2. HRMS (ESI) *m/z*: [M+H]⁺ calculated for C₂₂H₁₇NO 312.1383; found: 312.1386.

2-(4-(allyloxy)phenylquinoline (4e)



Following the general procedure **GP-1** the title compound **4e** was isolated as colourless oil using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 50/1, R_f = 0.5) in 84% yield (0.66 g). ¹H NMR (600 MHz, CDCl₃): δ 8.18 (d, J = 8.6 Hz, 1H), 8.15 – 8.11 (m, 3H), 7.83 (d, J = 8.6 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 8.6 Hz, 2H), 6.12 – 6.07 (m, 1H), 5.46 (dd, J = 0.8, 16.4, Hz, 1H), 5.33 (d, J = 10.4 Hz, 1H), 4.62 (d, J = 5.1 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃): δ 159.9, 157.0, 148.4, 136.8, 133.2, 132.52, 129.7, 129.6, 129.0, 127.6, 127.0, 126.1, 118.7, 118.0, 115.1, 69.0. HRMS (ESI) *m/z*: [M+H]⁺ calculated for C₁₈H₁₅NO 262.1227; found: 262.1220.

2-([1,1'-biphenyl]-4-yl)quinoline (4f)⁸



Following the general procedure **GP-1** the title compound **4f** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethylacetate (v/v = 50/1, R_f = 0.5) in 92% yield (0.77 g). ¹H NMR (600 MHz, CDCl₃): δ 8.28 (d, J = 8.2 Hz, 2H), 8.22 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.79 – 7.74 (m, 3H), 7.70 (d, J = 7.8 Hz, 2H), 7.57 – 7.53 (m, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.42 – 7.39 (m, 1H). ¹³C NMR (151 MHz, CDCl₃): δ 157.0, 148.5, 142.2, 140.7, 138.6, 136.9, 129.9, 129.8, 129.0, 128.1, 127.7, 127.7, 127.6, 127.3, 126.4, 119.0.

2-(4-(phenylethynyl)phenyl)quinoline (4g)⁹



Following the general procedure **GP-1** the title compound **4g** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 20/1, $R_f = 0.5$) in 80% yield (0.73 g). ¹H NMR (600 MHz, CDCl₃): δ 8.24 (d, J = 8.4 Hz, 1H), 8.20 – 8.17 (m, 3H), 7.91 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.75 (t, J = 7.5 Hz, 1H), 7.70 (d, J = 8.1 Hz, 2H), 7.58 – 7.55 (m, 3H), 7.38 – 7.36 (m, 3H). ¹³C NMR (151 MHz, CDCl₃): δ 156.5, 148.4, 139.4, 137.0, 132.2, 131.8, 130.0, 129.9, 128.5, 127.6, 127.6, 127.4, 126.6, 124.4, 123.3, 118.9, 91.0, 89.5.

4-(quinolin-2-yl)benzonitrile (4h)¹⁰



Following the general procedure **GP-1** the title compound **4h** was isolated as off white solid using silica gel column chromatography with pet-ether/ethylacetate (v/v = 50/1, R_f = 0.5) in 86% yield (0.59 g).¹H NMR (600 MHz, CDCl₃): δ 8.31 – 8.28 (m, 3H), 8.18 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 7.4 Hz, 2H), 7.79 – 7.76 (m, 1H), 7.60 – 7.58 (m, 1H). ¹³C NMR (151 MHz, CDCl₃): δ 155.1, 148.4, 143.9, 137.4, 132.8, 130.3, 130.1, 128.2, 127.7, 127.7, 127.3, 119.0, 118.8, 112.9.

6-chloro-2-(4-methoxyphenyl)quinoline (4i)¹¹



Following the general procedure **GP-1** the title compound **4i** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 20/1, $R_f = 0.5$) in 86% yield (0.66 g). ¹H NMR (400 MHz, CDCl₃): δ 8.14 – 8.05 (m, 4H), 7.86 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 3.5 Hz, 1H), 7.64 (dd, J = 13.4, 3.5 Hz, 1H), 7.06 – 7.04 (m, 2H), 3.93 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 161.1, 157.3, 146.8, 135.9, 131.9, 131.6, 131.2, 130.6, 129.0, 127.6, 126.3, 119.5, 114.4, 55.6.

2-(3-methoxyphenyl)quinoline (4j)¹²



Following the general procedure **GP-1** the title compound **4j** was isolated as yellow solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 100/1, R_f = 0.5) in 89% yield (0.63 g). ¹H NMR (600 MHz, CDCl₃): δ 8.21 – 8.18 (m, 2H), 7.86 – 7.79 (m, 3H), 7.75 – 7.71 (m, 2H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.03 (dd, *J* = 2, 8.2 Hz, 1H), 3.96 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 160.2, 157.2, 148.3, 141.2, 136.9, 129.9, 129.8, 129.8, 127.6, 127.3, 126.4, 120.1, 119.2, 115.5, 112.8, 55.5.

2-(2-methoxyphenyl)quinoline (4k)⁶



Following the general procedure **GP-1** the title compound **4k** was isolated as light yellow liquid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 100/1, R_f = 0.5) in 84% yield (0.59 g). ¹H NMR (600 MHz, CDCl₃): δ 8.18 – 8.14 (m, 2H), 7.89 (d, J = 8.4 Hz, 1H), 7.84 (t, J = 8.2 Hz, 2H), 7.71 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.4

Hz, 1H), 7.14 (t, J = 7.4 Hz, 1H), 7.04 (d, J = 8.2 Hz, 1H), 3.87 (s, 3H).¹³C NMR (151 MHz, CDCl₃): δ 157.3, 157.3, 148.4, 135.2, 131.6, 130.4, 129.9, 129.8, 129.3, 127.5, 127.2, 126.3, 123.6, 121.4, 111.5, 55.8.

3-methyl-2-phenylquinoline (4l)⁶



Following the general procedure **GP-1** the title compound **41** was isolated as light yellow liquid using pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.5) in 90% yield (0.60 g). ¹H NMR (400 MHz, CDCl₃): δ 8.14 (d, J = 8.4 Hz, 1H), 8.02 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.61 – 7.59 (m, 2H), 7.55 – 7.42 (m, 4H), 2.47 (s, 3H). ¹³C NMR (151 MHz, CDCl₃): δ 160.5, 146.6, 140.9, 136.8, 129.3, 129.2, 128.9, 128.8, 128.3, 128.3, 128.2, 127.6, 126.7, 126.4, 20.6. Spectral data is in accordance to the reported literature.

2-(pyridin-2-yl)quinoline (4m)¹³



Following the general procedure **GP-1** the title compound **4m** was isolated as yellow solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 20/1, R_f = 0.5) in 91% yield (0.56 g). ¹H NMR (600 MHz, CDCl₃): δ 8.74 – 8.73 (m, 1H), 8.65 (d, J = 7.9 Hz, 1H), 8.56 (d, J = 8.6 Hz, 1H), 8.28 (d, J = 8.6 Hz, 1H), 8.18 (d, J = 8.6 Hz, 1H), 7.88 – 7.84 (m, 2H), 7.75 – 7.72 (m, 1H), 7.56 – 7.53 (m, 1H), 7.36 – 7.34 (m, 1H). ¹³C NMR (151 MHz, CDCl₃): δ 156.4, 156.3, 149.3, 148.0, 137.1, 136.9, 129.9, 129.7, 128.3, 127.7, 126.9, 124.1, 121.9, 119.1.

2-(pyridin-3-yl)quinoline (4n)⁶



Following the general procedure **GP-1** the title compound **4n** was isolated as off yellow solid using silica gel column chromatography with pet-ether/ethyl acetate (v/v= 20/1, $R_f = 0.5$) in 92% yield (0.57 g). ¹H NMR (600 MHz, CDCl₃): δ 9.35 (d, J = 1.8 Hz, 1H), 8.70 (dd, J = 1.6, 4.8 Hz, 1H), 8.52 (dt, J = 2, 8 Hz, 1H), 8.29 (d, J = 8.0 Hz, 1H), 8.18 (d, 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.78 – 7.75 (m, 1H), 7.59 – 7.56 (m, 1H), 7.48 – 7.46 (m, 1H). ¹³C NMR (151 MHz, CDCl₃): δ 154.8, 150.4, 149.0, 148.5, 137.4, 135.3, 135.1, 130.2, 129.9, 127.7, 127.5, 127.0, 123.9, 118.7.

2-pentylquinoline (40)¹⁴



Following the general procedure **GP-1** the title compound **40** was isolated as oily colourless liquid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 100/1, R_f = 0.5) in 76% yield (0.45 g). ¹H NMR (600 MHz, CDCl₃): δ 8.05 (t, J = 8.4 Hz, 2H), 7.77 (d, J = 8.0 Hz, 1H), 7.69 – 7.66 (m, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.30 (d, J = 8.4 Hz, 1H), 2.99 – 2.95 (m, 2H), 1.83 – 1.78 (m, 2H), 1.41 – 1.35 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H).¹³C NMR (151 MHz, CDCl₃): δ 163.3, 148.0, 136.3, 129.5, 128.9, 127.6, 126.8, 125.8, 121.5, 39.5, 31.9, 29.9, 22.7, 14.2.

2-isopropylquinoline (4p)¹⁵



Following the general procedure **GP-1** the title compound **4p** was isolated as light yellow liquid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 100/1, R_f = 0.5) in 78% yield (0.4 g). ¹H NMR (600 MHz, CDCl₃): δ 8.07 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.6 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.67–7.64 (m, 1H), 7.45 (t, J = 7.0 Hz, 1H), 7.30 (d, J = 8.6 Hz, 1H), 3.27 (hept, J = 7.0 Hz, 1H), 1.40 (d, J = 7.0 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃): δ 167.7, 147.8, 136.4, 129.3, 129.0, 127.5, 127.0, 125.7, 119.2, 37.3, 22.6.

2-methylquinoline (4q)¹⁶



Following the general procedure **GP-1** the title compound **4q** was isolated as light yellow oil using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 95/5, $R_f = 0.5$) in 62% yield (0.57 g). ¹H NMR (600 MHz, CDCl₃) δ 7.99 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 8.4 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.16 (d, J = 8.4 Hz, 1H), 2.67 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 158.9, 158.9, 147.8, 136.1, 129.3, 128.5, 127.4, 126.4, 125.6, 121.9, 25.3.

(E)-2-styrylquinoline (6a)¹⁷



Following the general procedure **GP-2** the title compound **6a** was isolated as off-white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.5) in 95% yield (0.219 g). ¹H NMR (600 MHz, CDCl₃): δ 8.13 (d, J = 8.5 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.73 – 7.67 (m, 3H), 7.65 (d, J = 7.3 Hz, 2H), 7.51 – 7.49 (m, 1H), 7.45 – 7.38 (m, 3H), 7.33 (t, J = 7.3 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃): δ 156.1, 148.4, 136.7, 136.5, 134.6, 129.9, 129.3, 129.2, 128.9, 128.8, 127.6, 127.5, 127.4, 126.3, 119.4.

(*E*)-2-(4-methoxystyryl)quinoline (6b)¹⁷



Following the general procedure **GP-2** the title compound **6b** was isolated as off-white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.5) in 96% yield (0.250 g). ¹H NMR (600 MHz, CDCl₃) δ 8.10 (d, J = 8.5 Hz, 1H), 8.07 (d, J = 8.5 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.71 – 7.68 (m, 1H), 7.66 – 7.62 (m, 2H), 7.59 (d, J = 8.6 Hz, 2H), 7.49 – 7.47 (m, 1H), 7.29 (d, J = 16.2 Hz, 1H), 6.94 (d, J = 8.7 Hz, 2H), 3.85 (s, 3H). ¹³C NMR (151 MHz, CDCl₃): δ 160.3, 156.5, 148.4, 136.4, 134.2, 129.8, 129.4, 129.2, 128.8, 127.6, 127.4, 127.0, 126.1, 119.3, 114.4, 55.5.

(E)-2-(4-bromostyryl)quinoline (6c)¹⁷



Following the general procedure **GP-2** the title compound **6c** was isolated as off-white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.5) in 93% yield (0.288 g). ¹H NMR (600 MHz, CDCl₃) δ 8.14 (d, J = 8.5 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.74 – 7.70 (m, 1H), 7.67 – 7.62 (m, 2H), 7.55 – 7.48 (m, 5H), 7.39 (d, J = 16.3 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃): δ 155.7, 148.4, 136.6, 135.6, 133.2, 132.1, 130.0, 129.8, 129.4, 128.8, 127.7, 127.6, 126.5, 122.7, 119.5.

(E)-2-(4-nitrostyryl)quinoline (6d)¹⁸



Following the general procedure **GP-2** the title compound **6d** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 25/1, R_f = 0.5) in 67% yield (0.185 g). ¹H NMR (600 MHz, CDCl₃) δ 8.26 (d, J = 8.7 Hz, 2H), 8.18 (d, J = 8.5 Hz, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.78 – 7.72 (m, 4H), 7.66 (d, J = 8.5 Hz, 1H), 7.56 – 7.50 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 154.8, 148.4, 147.5, 143.1, 136.9, 133.3, 131.8, 130.2, 129.5, 127.8, 127.7, 126.9, 124.3, 119.9.

(E)-2-(4-(trifluoromethyl)styryl)quinoline (6e)¹⁷



Following the general procedure **GP-2** the title compound **6e** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 25/1, R_f = 0.5) in 83% yield (0.248 g). ¹H NMR (600 MHz, CDCl₃) δ 8.17 (d, J = 8.5 Hz, 1H), 8.11 – 8.07 (m,

1H), 7.83 – 7.80 (m, 1H), 7.75 – 7.71 (m, 4H), 7.69 – 7.64 (m, 3H), 7.55 – 7.51 (m, 1H), 7.49 – 7.46 (m, 1H). ¹³C NMR (151 MHz, CDCl₃): *δ* 155.4, 148.4, 140.1, 136.7, 132.8, 131.5, 130.1, 129.5, 127.7, 127.7, 127.5, 126.7, 125.9 (q, *J* = 2.6 Hz, CF₃), 119.7.

(E)-4-(2-(quinolin-2-yl)vinyl)phenyl acetate (6f)¹⁹



Following the general procedure **GP-2** the title compound **6f** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 50/1, R_f = 0.5) in 92% yield (0.265 g). ¹H NMR (600 MHz, CDCl₃): δ 8.13 (d, J = 8.5 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 8 Hz, 1H), 7.72 – 7.61 (m, 5H), 7.50 (t, J = 7.5 Hz, 1H), 7.36 (d, J = 16.2 Hz, 1H), 7.14 (d, J = 8.4 Hz, 2H), 2.32 (s, 3H). ¹³C NMR (151 MHz, CDCl₃): δ 169.5, 155.9, 151.0, 148.4, 136.6, 134.5, 133.5, 129.9, 129.3, 128.4, 128.4, 127.6, 127.5, 126.4, 122.1, 119.4, 21.3. HRMS (ESI) m/z: [M+H]⁺ calculated for C₁₉H₁₅NO 290.1176; found: 290.1188

(*E*)-2-(2-methylstyryl)quinoline (6g)¹⁸



Following the general procedure **GP-2** the title compound **6g** was isolated as colourless liquid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 100/1, R_f = 0.5) in 71% yield (0.174 g). ¹H NMR (600 MHz, Chloroform-*d*): δ 8.13 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 16.2 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.76 – 7.67 (m, 3H), 7.53 – 7.47 (m, 1H), 7.32 (d, J = 16.2 Hz, 1H), 7.28 – 7.20 (m, 3H), 2.52 (s, 3H).¹³C NMR (151 MHz, CDCl₃): δ 156.4, 148.4, 136.7, 136.5, 135.7, 132.3, 130.7, 130.3, 129.9, 129.4, 128.6, 127.6, 127.5, 126.5, 126.3, 126.0, 119.5, 20.2.

(E)-2-(2-(naphthalen-1-yl)vinyl)quinoline (6h)¹⁸



Following the general procedure **GP-2** the title compound **6h** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 50/1, R_f = 0.5) in 90% yield (0.253 g). ¹H NMR (600 MHz, Chloroform-*d*): δ 8.16 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 8.01 (brs, 1H), 7.88 – 7.83 (m, 5H), 7.80 (d, J = 8.0 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.57 – 7.47 (m, 4H). ¹³C NMR (151 MHz, CDCl₃): δ 156.2, 148.5, 136.5, 134.7, 134.2, 133.8, 133.7, 129.9, 129.5, 129.4, 128.7, 128.4, 128.3, 127.9, 127.7, 127.5, 126.6, 126.6, 126.3, 123.8, 119.5.

2-(2-(pyren-1-yl)ethyl)quinoline (6i)



Following the general procedure **GP-2** the title compound **6i** was isolated as fluorescent yellow solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.5) in 85% yield (0.305 g). ¹H NMR (500 MHz, Chloroform-*d*): δ 8.40 (d, J = 9.2 Hz, 1H), 8.20 – 8.14 (m, 3H), 8.13 – 8.07 (m, 2H), 8.05 – 7.97 (m, 4H), 7.88 (d, J = 7.7 Hz, 1H), 7.81 – 7.72 (m, 2H), 7.55 – 7.50 (m, 1H), 7.16 (d, J = 8.3 Hz, 1H), 3.96 – 3.88 (m, 2H), 3.58 – 3.51 (m, 2H). ¹³C NMR (126 MHz, CDCl₃): δ 161.9, 148.3, 136.3, 135.9, 131.6, 131.1, 130.1, 129.6, 129.2, 128.9, 127.7, 127.7, 127.5, 127.5, 127.0, 126.8, 126.0, 125.3, 125.2, 125.1, 125.0, 124.9, 123.5, 121.8, 41.2, 33.6. HRMS (ESI) *m/z*: [M+H]⁺ calculated for C₂₇H₂₀N 358.1591; found: 358.1589.

(E)-2-(2-(thiophen-2-yl)vinyl)quinoline (6j)²⁰



Following the general procedure **GP-2** the title compound **6j** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 50/1, R_f = 0.5) in 89% yield (0.211 g). ¹H NMR (600 MHz, CDCl₃): δ 8.11 – 8.04 (m, 2H), 7.84 (d, J = 16.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.71 – 7.68 (m, 1H), 7.57 (d, J = 8.5 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.29 (d, J = 5.0 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.07 – 7.03 (m, 1H). ¹³C NMR (151 MHz, CDCl₃): δ 155.7, 148.4, 142.2, 136.5, 129.9, 129.3, 128.3, 128.2, 128.0, 127.6, 127.4, 126.2, 126.1, 119.5.

2-((E)-styryl)-4-(((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)quinoline (6k)



Following the general procedure **GP-2** the title compound **6k** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 50/1, R_f = 0.5) in 82% yield (0.540 g). ¹H NMR (600 MHz, Chloroform-*d*): δ 8.42 (d, J = 8.2 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.62 – 7.49 (m, 4H), 7.35 (t, J = 7.2 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.18 (d, J = 16.1 Hz, 1H), 6.43 (d, J = 8.5 Hz, 1H), 2.69 – 2.67 (m, 1H), 2.19 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 1.94 – 1.83 (m, 2H), 1.65 (brs, 2H), 1.53 – 1.49 (m, 2H), 1.44 – 1.35 (m, 4H), 1.35 – 1.17 (m, 10H), 1.17 – 0.95 (m, 6H), 0.94 – 0.81 (m, 12H). ¹³C NMR (151 MHz, CDCl₃): δ 161.8, 157.2, 149.8, 149.5, 142.8, 136.6, 134.1, 130.3, 129.3, 129.0, 128.8, 128.6,

127.8, 127.4, 126.0, 125.6, 123.9, 121.9, 120.4, 118.4, 101.1, 101.0, 75.4, 41.1, 39.5, 39.1, 37.6, 37.6, 37.5, 37.4, 33.0, 32.9, 28.1, 25.0, 24.8, 24.6, 23.2, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 12.9, 12.1. HRMS (ESI) m/z: [M+H]⁺ calculated for C₄₆H₆₁NO₂ 660.4776; found: 660.4751.

(E)-4-(benzyloxy)-2-styrylquinoline (6l)²¹



Following the general procedure **GP-3** the title compound **61** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 50/1, R_f = 0.5) in 91% yield (0.306 g). ¹H NMR (600 MHz, Chloroform-*d*): δ 8.25 – 8.21 (m, 1H), 8.04 – 8.02 (m, 1H), 7.72 – 7.67 (m, 1H), 7.66 – 7.62 (m, 3H), 7.56 (d, J = 7.4 Hz, 2H), 7.46 (t, J = 7.6 Hz, 3H), 7.40 (t, J = 7.6 Hz, 3H), 7.37 – 7.31 (m, 2H), 7.08 (s, 1H), 5.37 (s, 2H). ¹³C NMR (151 MHz, CDCl₃): δ 161.7, 157.2, 149.4, 136.7, 136.0, 134.2, 130.3, 129.7, 129.0, 128.9, 128.7, 128.6, 127.7, 127.4, 125.5, 122.0, 121.0, 99.2, 70.4.

(E)-4-((4-chlorobenzyl)oxy)-2-(4-chlorostyryl)quinoline (6m)



Following the general procedure **GP-3** the title compound **6m** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 20/1, $R_f = 0.5$) in 88% yield (0.357 g). ¹H NMR (500 MHz, Chloroform-*d*): δ 8.23 (d, J = 8.2 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.67 – 7.61 (m, 3H), 7.55 (d, J = 7.0 Hz, 2H), 7.48 – 7.46 (m, 1H), 7.46 – 7.45 (m, 1H), 7.42 – 7.36 (m, 3H), 7.34 – 7.32 (m, 1H), 7.07 (s, 1H), 5.37 (s, 2H). ¹³C NMR (151 MHz, CDCl₃): δ 161.7, 157.2, 149.4, 136.7, 136.0, 134.2, 130.3, 129.7, 129.0, 128.9, 128.9, 128.7, 128.6, 127.7, 127.4, 125.5, 122.0, 121.0, 99.2, 70.4. HRMS (ESI) m/z: [M+H]⁺ calculated for C₂₄H₁₇Cl₂NO 406.0760; found: 406.0762

(E)-4-((4-bromobenzyl)oxy)-2-(4-bromostyryl)quinoline (6n)



Following the general procedure **GP-3** the title compound **6n** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 20/1, $R_f = 0.5$) in 82% yield (0.403 g). ¹H NMR (500 MHz, Chloroform-*d*): δ 8.23 – 8.16 (m, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.61 – 7.56 (m, 3H), 7.54 – 7.46 (m, 5H), 7.42 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 16.3 Hz, 1H), 7.00 (s, 1H), 5.31 (s, 2H). ¹³C NMR (151 MHz, CDCl₃): δ

161.5, 156.7, 149.4, 135.5, 134.9, 133.0, 132.2, 132.1, 130.5, 130.1, 129.3, 128.9, 128.8, 125.8, 122.7, 122.6, 121.9, 120.8, 99.3, 69.7. HRMS (ESI) m/z: [M+H]⁺ calculated for C₂₄H₁₇Br₂NO 495.9730; found: 495.9737.

(E)-4-((4-(trifluoromethyl)benzyl)oxy)-2-(4-(trifluoromethyl)styryl)quinoline (60)



Following the general procedure **GP-3** the title compound **60** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 20/1, $R_f = 0.5$) in 84% yield (0.397 g). ¹H NMR (600 MHz, Chloroform-*d*): δ 8.24 – 8.23 (m, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.79 – 7.62 (m, 10H), 7.54 – 7.49 (m, 1H), 7.40 (d, J = 16.2 Hz, 1H), 7.03 (s, 1H), 5.43 (s, 2H).¹³C NMR (151 MHz, CDCl₃): δ 161.5, 156.3, 149.4, 139.9 (d, J = 27.0 Hz), 132.7, 130.9 (J = 32.4 Hz), 130.6, 130.4 (J = 32.4 Hz), 129.1, 127.6 (J = 27.7 Hz), 126.1-125.9 (m), 125.0 (d, J = 18.4 Hz), 123.2 (J = 20.2 Hz), 121.9, 120.9, 99.5, 69.5. ¹⁹F NMR (471 MHz, Chloroform-*d*): δ -62.60, -62.63. HRMS (ESI) *m/z*: [M+H]⁺ calculated for C₂₆H₁₇F₆NO 474.1288; found: .474.1285

(E)-4-((3-bromobenzyl)oxy)-2-(3-bromostyryl)quinoline (6p)



Following the general procedure **GP-3** the title compound **6p** was isolated as off white solid using silica gel column chromatography with pet-ether/ethyl acetate (v/v = 25/1, R_f = 0.5) in 81% yield (0.402 g). ¹H NMR (600 MHz, CDCl₃): δ 8.21 (d, J = 9.0 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.79 (s, 1H), 7.73 – 7.70 (m, 2H), 7.60 – 7.52 (m, 3H), 7.51 – 7.43 (m, 3H), 7.34 – 7.29 (m, 2H), 7.28 – 7.25 (m, 1H), 6.98 (s, 1H), 5.31 (s, 2H). ¹³C NMR (151 MHz, CDCl₃): δ 161.5, 156.5, 149.4, 138.8, 138.2, 132.7, 131.7, 131.5, 130.8, 130.6, 130.6, 130.5, 130.4, 130.2, 129.0, 128.9, 126.1, 126.0, 125.9, 123.1, 123.0, 121.9, 120.9, 99.4, 69.5. HRMS (ESI) *m/z*: [M+H]⁺ calculated for C₂₄H₁₇Br₂NO 495.9730; found: 495.9739.

2-phenylquinazoline (8a)²²



Following the general procedure **GP-4** the title compound **8a** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethylacetate (v/v= 100/1, R_f = 0.5) in 92% yield (0.57 g). ¹H NMR (600 MHz, CDCl₃): δ 9.48 (s, 1H), 8.62 – 8.61 (m, 2H), 8.10 (d,

J = 8.2 Hz, 1H), 7.94 – 7.90 (m, 2H), 7.64 – 7.61 (m, 1H), 7.56 – 7.51 (m, 3H).¹³C NMR (151 MHz, CDCl₃): δ 161.2, 160.7, 150.9, 138.2, 134.3, 130.8, 128.8, 128.7, 127.4, 127.3, 123.8.

2-(4-methylphenyl)quinazoline (8b)²²



Following the general procedure **GP-4** the title compound **8b** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethylacetate (v/v= 100/1, R_f = 0.5) in 92% yield (0.61 g). ¹H NMR (500 MHz, CDCl₃): δ 9.44 (s, 1H), 8.52 (d, *J* = 9.6 Hz, 2H), 8.07 (d, *J* = 9.6 Hz, 1H), 7.90 – 7.87 (m, 2H), 7.58 (t, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 9.6 Hz, 2H), 2.45 (s, 3H). ¹³C NMR (151 MHz, CDCl₃): δ 161.3, 160.6, 150.9, 141.0, 135.4, 134.2, 129.6, 128.7, 128.6, 127.3, 127.2, 123.6, 21.7.

2-(4-methoxyphenyl)quinazoline (8c)²³



Following the general procedure **GP-4** the title compound **8c** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 100/1, R_f = 0.5) in 96% yield (0.68 g). ¹H NMR (600 MHz, CDCl₃): δ 9.42 (s, 1H), 8.58 (d, J = 8.8 Hz, 2H), 8.04 (d, J = 7.8 Hz, 1H), 7.90 – 7.87 (m, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.05 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H).¹³C NMR (151 MHz, CDCl₃): δ 162.0, 161.0, 160.5, 151.0, 134.2, 130.9, 130.3, 128.6, 127.3, 126.9, 123.5, 114.1, 55.5.

2-(4-chlorophenyl)quinazoline (8d)²³



Following the general procedure **GP-4** the title compound **8d** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 50/1, R_f = 0.5) in 82% yield (0.59 g). ¹H NMR (400 MHz, CDCl₃): δ 9.44 (s, 1H), 8.58 – 8.55 (m, 2H), 8.08 – 8.06 (m, 1H), 7.93 – 7.89 (m, 2H), 7.64 – 7.60 (m, 1H), 7.51 – 7.48 (m, 2H). ¹³C NMR (151 MHz, CDCl₃): δ 160.7, 160.2, 150.8, 137.0, 136.7, 134.4, 130.0, 129.0, 128.7, 127.6, 127.3, 123.8.

2-(4-bromophenyl)quinazoline (8e)²³



Following the general procedure **GP-4** the title compound **8e** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethylacetate (v/v= 50/1, $R_f = 0.5$) in 86% yield (0.73 g). ¹H NMR (400 MHz, CDCl₃): δ 9.45 (s, 1H), 8.51 – 8.49 (m, 2H), 8.09 – 8.07 (m, 1H), 7.94 – 7.92 (m, 2H), 7.67 – 7.63 (m, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 160.7, 160.3, 150.8, 137.1, 134.4, 131.9, 130.3, 128.7, 127.7, 127.3, 125.6, 123.8.

6-chloro-2-phenylquinazoline (8f)²³



Following the general procedure **GP-4** the title compound **xx** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 95/5, $R_f = 0.5$) in 81% yield (0.57 g). ¹H NMR (600 MHz, CDCl₃): δ 9.41 (s, 1H), 8.61 (dd, J = 1.8, 7.8 Hz, 2H), 8.04 (d, J = 8.9 Hz, 1H), 7.92 (d, J = 1.8 Hz, 1H), 7.84 (dd, J = 2.2, 8.9 Hz, 1H), 7.56 – 7.51 (m, 3H).¹³C NMR (151 MHz, CDCl₃): δ 161.4, 159.7, 149.4, 137.7, 135.3, 132.9, 131.0, 130.5, 128.9, 128.7, 126.0, 124.1.

2-(m-tolyl)quinazoline (8g)²³



Following the general procedure **GP-4** the title compound **8g** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethylacetate (v/v= 100/1, R_f = 0.5) in 85% yield (0.56 g). ¹H NMR (400 MHz, CDCl₃): δ 9.45 (s, 1H), 8.43 – 8.41 (m, 2H), 8.10 – 8.07 (m, 1H), 7.91 – 7.86 (m, 2H), 7.60 – 7.56 (m, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 2.49 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 161.3, 160.5, 150.8, 138.4, 138.1, 134.2, 131.5, 129.2, 128.7, 127.3, 127.2, 125.9, 123.7, 21.6.

2-(3-bromophenyl)quinazoline (8h)²³



Following the general procedure **GP-4** the title compound **8h** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 95/5, R_f = 0.5) in 92% yield (0.57 g). ¹H NMR (600 MHz, CDCl₃): δ 9.46 (s, 1H), 8.79 (t, J = 1.8 Hz, 1H), 8.56 (dt, J = 1.2, 7.8 Hz, 1H), 8.09 (d, J = 6.0 Hz, 1H), 7.94 – 7.91 (m, 2H), 7.65 – 7.62 (m, 2H), 7.40 (t, J = 7.8 Hz, 1H).¹³C NMR (151 MHz, CDCl₃): δ 160.7, 159.7, 150.8, 140.2, 134.5, 133.6, 131.7, 130.3, 128.8, 127.8, 127.3, 127.2, 123.9, 123.1.

2-(o-tolyl)quinazoline (8i)²⁴



Following the general procedure **GP-4** the title compound **8i** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v= 100/1, R_f = 0.5) in 92% yield (0.53 g). ¹H NMR (600 MHz, CDCl₃): δ 9.51 (s, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.95 – 7.93 (m, 1H), 7.90 (d, J = 7.0 Hz, 1H), 7.66 (t, J = 7.0 Hz, 1H), 7.37 – 7.33 (m, 3H), 2.61 (s, 3H). ¹³C NMR (151 MHz, CDCl₃): δ 164.2, 160.2, 150.5, 138.7, 137.5, 134.3, 131.4, 130.8, 129.4, 128.7, 127.7, 127.2, 126.1, 123.1, 21.2.

2-(pyridin-4-yl)quinazoline (8j)²⁵



Following the general procedure **GP-4** the title compound **8j** was isolated as off white solid using silica gel column chromatography with pet-ether/ ethylacetate (v/v = 95/5, R_f = 0.5) in 92% yield (0.57 g). ¹H NMR (600 MHz, CDCl₃): δ 9.52 (s, 1H), 8.82 – 8.81 (m, 2H), 8.47– 8.46 (m, 2H), 8.14 (d, J = 8.4 Hz, 1H), 8.00 – 7.96 (m, 2H), 7.72– 7.69 (m, 1H).¹³C NMR (151 MHz, CDCl₃): δ 160.9, 159.1, 150.7, 150.7, 145.4, 134.7, 129.0, 128.5, 127.4, 124.3, 122.5.

(E)-3-(2-Aminophenyl)-1-phenylprop-2-en-1-one (9)²⁶



¹H NMR (500 MHz, CDCl₃): δ 8.03 (d, J = 7.7 Hz, 2H), 7.99 (d, J = 15.6 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.54 – 7.47 (m, 4H), 7.22 – 7.19 (m, 1H), 6.80 (t, J = 7.5 Hz, 1H), 6.74 – 6.72 (m, 1H), 4.05 (s, 2H).¹³C NMR (126 MHz, CDCl₃): δ 190.4, 146.4, 140.3, 138.5, 132.8, 131.8, 128.7, 128.6, 128.3, 121.9, 120.4, 119.0, 117.0.

4-(benzyloxy)-2-methylquinoline (10)²⁷



¹H NMR (500 MHz, CDCl₃): δ 8.21 (dd, J = 8.4, 1.5 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.68-7.65 (m, 1H), 7.53 – 7.49 (m, 2H), 7.44 (dd, J = 8.3, 6.6 Hz, 3H), 7.41 – 7.37 (m, 1H), 6.71 (s,

1H), 5.27 (s, 2H), 2.70 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ 161.5, 160.2, 149.0, 136.0, 129.9, 128.8, 128.5, 128.2, 127.6, 124.9, 121.9, 120.0, 101.7, 70.2, 26.1. 9. ¹H, ¹³C, and ¹⁹F NMR spectra of the products:



Figure S4: ¹H NMR Spectrum of 4a (CDCl₃, 600 MHz, 298 K)



Figure S5: ¹³C NMR Spectrum of 4a (CDCl₃, 151 MHz, 298 K)



Figure S6: ¹H NMR Spectrum of 4b (CDCl₃, 600 MHz, 298 K)



Figure S7: ¹³C NMR Spectrum of 4b (CDCl₃, 151 MHz, 298 K)



Figure S8: ¹H NMR Spectrum of 4c (CDCl₃, 600 MHz, 298 K)



Figure S9: ¹³C NMR Spectrum of 4c (CDCl₃, 151 MHz, 298 K)



Figure S10: ¹H NMR Spectrum of 4d (CDCl₃, 600 MHz, 298 K)



Figure S11: ¹³C NMR Spectrum of 4d (CDCl₃, 151 MHz, 298 K)



Figure S13: ¹³C NMR Spectrum of 4e (CDCl₃, 151 MHz, 298 K)



Figure S14: ¹H NMR Spectrum of 4f (CDCl₃, 600 MHz, 298 K)



Figure S15: ¹³C NMR Spectrum of 4f (CDCl₃, 151 MHz, 298 K)



Figure S16: ¹H NMR Spectrum of 4g (CDCl₃, 600 MHz, 298 K)



Figure S17: ¹³C NMR Spectrum of 4g (CDCl₃, 151 MHz, 298 K)


Figure S18: ¹H NMR Spectrum of 4h (CDCl₃, 600 MHz, 298 K)



Figure S19: ¹³C NMR Spectrum of 4h (CDCl₃, 151 MHz, 298 K)



Figure S21: ¹³C NMR Spectrum of 4i (CDCl₃, 101 MHz, 298 K)



Figure S22: ¹H NMR Spectrum of 4j (CDCl₃, 600 MHz, 298 K)



Figure S23: ¹³C NMR Spectrum of 4j (CDCl₃, 101 MHz, 298 K)



Figure S24: ¹H NMR Spectrum of 4k (CDCl₃, 600 MHz, 298 K)



Figure S25: ¹³C NMR Spectrum of 4k (CDCl₃, 151 MHz, 298 K)



Figure S27: ¹³C NMR Spectrum of 4l (CDCl₃, 151 MHz, 298 K)



Figure S28: ¹H NMR Spectrum of 4m (CDCl₃, 600 MHz, 298 K)



Figure S29: ¹³C NMR Spectrum of 4m (CDCl₃, 151 MHz, 298 K)



Figure S30: ¹H NMR Spectrum of 4n (CDCl₃, 600 MHz, 298 K)



Figure S31: ¹³C NMR Spectrum of 4n (CDCl₃, 151 MHz, 298 K)



Figure S33: ¹³C NMR Spectrum of 40 (CDCl₃, 151 MHz, 298 K)



Figure S34: ¹H NMR Spectrum of 4p (CDCl₃, 600 MHz, 298 K)



Figure S35: ¹³C NMR Spectrum of 4p (CDCl₃, 151 MHz, 298 K)





Figure S37: ¹³C NMR Spectrum of 4q (CDCl₃, 151 MHz, 298 K)



Figure S38: ¹H NMR Spectrum of 6a (CDCl₃, 600 MHz, 298 K)



Figure S39: ¹³C NMR Spectrum of 6a (CDCl₃, 151 MHz, 298 K)



Figure S41: ¹³C NMR Spectrum of 6b (CDCl₃, 151 MHz, 298 K)



Figure S42: ¹H NMR Spectrum of 6c (CDCl₃, 600 MHz, 298 K)



Figure S43: ¹³C NMR Spectrum of 6c (CDCl₃, 151 MHz, 298 K)



Figure S44: ¹H NMR Spectrum of 6d (CDCl₃, 600 MHz, 298 K)



Figure S45: ¹³C NMR Spectrum of 6d (CDCl₃, 151 MHz, 298 K)



Figure S46: ¹H NMR Spectrum of 6e (CDCl₃, 600 MHz, 298 K)



Figure S47: ¹³C NMR Spectrum of 6e (CDCl₃, 151 MHz, 298 K)



Figure S48: ¹H NMR Spectrum of 6f (CDCl₃, 600 MHz, 298 K)



Figure S49: ¹³C NMR Spectrum of 6f (CDCl₃, 151 MHz, 298 K)



Figure S50: ¹H NMR Spectrum of 6g (CDCl₃, 600 MHz, 298 K)



Figure S51: ¹³C NMR Spectrum of 6g (CDCl₃, 151 MHz, 298 K)



Figure S52: ¹H NMR Spectrum of 6h (CDCl₃, 600 MHz, 298 K)



Figure S53: ¹³C NMR Spectrum of 6h (CDCl₃, 151 MHz, 298 K)



Figure S55: ¹³C NMR Spectrum of 6i (CDCl₃, 126 MHz, 298 K)



Figure S56: ¹H NMR Spectrum of 6j (CDCl₃, 600 MHz, 298 K)



Figure S57: ¹³C NMR Spectrum of 6j (CDCl₃, 151 MHz, 298 K)



Figure S59: ¹³C NMR Spectrum of 6k (CDCl₃, 151 MHz, 298 K)



Figure S61: ¹³C NMR Spectrum of 6l (CDCl₃, 151 MHz, 298 K)



Figure S63: ¹³C NMR Spectrum of 6m (CDCl₃, 151 MHz, 298 K)



Figure S65: ¹³C NMR Spectrum of 6n (CDCl₃, 151 MHz, 298 K)



Figure S67: ¹³C NMR Spectrum of 60 (CDCl₃, 151 MHz, 298 K)





Figure S69: ¹H NMR Spectrum of 6p (CDCl₃, 600 MHz, 298 K)























Figure S81: ¹H NMR Spectrum of 8f (CDCl₃, 600 MHz, 298 K)


















Figure S91: ¹H NMR Spectrum of **9** (CDCl₃, 500 MHz, 298 K).



Figure S93: ¹H NMR Spectrum of 10 (CDCl₃, 500 MHz, 298 K).





Figure S95: ¹H NMR Spectrum of 4q-d3 (CDCl₃, 600 MHz, 298 K).



Figure S97: ¹H NMR Spectrum of 5a-d2 (CDCl₃, 600 MHz, 298 K).



8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 f2 (ppm)

Figure S98: ¹H-¹H COSY NMR Spectrum of 6a-α-d1 (CDCl₃, 298 K).



Figure S99: ¹H-¹H COSY NMR Spectrum of 6a-β-d1 (CDCl₃, 298 K).

10. References:

1. Böldl, M.; Fleischer, I., Dehydrative Coupling of Benzylic Alcohols Catalyzed by Brønsted Acid/Lewis Base. *Eur. J. Org. Chem.* **2019**, *2019*, 5856 – 5861.

2. Kourist, R.; González-Sabín, J.; Liz, R.; Rebolledo, F., Kinetic Resolution of 1-Biaryl- and 1-(Pyridylphenyl)alkan-1-ols Catalysed by the Lipase B from Candida antarctica. *Adv. Synth. Catal.* **2005**, *347*, 695 – 702.

3. Dubovtsev, A. Y.; Dar'in, D. V.; Krasavin, M.; Kukushkin, V. Y., Gold-Catalyzed Oxidation of Internal Alkynes into Benzils and its Application for One-Pot Synthesis of Five-, Six-, and Seven-Membered Azaheterocycles. *Eur. J. Org. Chem.* **2019**, *1856* – 1864.

4. Mikhael, M.; Adler, S. A.; Wengryniuk, S. E., Chemoselective Oxidation of Equatorial Alcohols with N-Ligated λ 3-Iodanes. *Org. Lett.* **2019**, *21*, 5889 – 5893.

5. Rao, G. V.; Swamy, B. N.; Chandregowda, V.; Reddy, G. C., Synthesis of (±)Abyssinone I and related compounds: Their anti-oxidant and cytotoxic activities. *Eur. J. Med. Chem.* **2009**, *44*, 2239 – 2245.

6. Chakraborty, G.; Sikari, R.; Das, S.; Mondal, R.; Sinha, S.; Banerjee, S.; Paul, N. D., Dehydrogenative Synthesis of Quinolines, 2-Aminoquinolines, and Quinazolines Using Singlet Diradical Ni(II)-Catalysts. *J. Org. Chem.* **2019**, *84*, 2626 – 2641.

7. Badhani, G.; Joshi, A.; Adimurthy, S., Ionic-Liquid-Catalyzed Synthesis of Imines, Benzimidazoles, Benzothiazoles, Quinoxalines and Quinolines through C-N, C-S, and C-C Bond Formation. *Eur. J. Org. Chem.* **2021**, 6705 – 6716.

8. Guo, B.; Yu, T.-Q.; Li, H.-X.; Zhang, S.-Q.; Braunstein, P.; Young, D. J.; Li, H.-Y.; Lang, J.-P., Phosphine Ligand-Free Ruthenium Complexes as Efficient Catalysts for the Synthesis of Quinolines and Pyridines by Acceptorless Dehydrogenative Coupling Reactions. *ChemCatChem* **2019**, *11*, 2500 – 2510.

9. Li, X.; Tian, J.-J.; Liu, N.; Tu, X.-S.; Zeng, N.-N.; Wang, X.-C., Spiro-Bicyclic Bisborane Catalysts for Metal-Free Chemoselective and Enantioselective Hydrogenation of Quinolines. *Angew. Chem. Int. Ed.* **2019**, *58*, 4664 – 4668.

10. Xu, X.; Ai, Y.; Wang, R.; Liu, L.; Yang, J.; Li, F., Ruthenium-catalyzed acceptorless dehydrogenative coupling of *o*-aminobenzyl alcohols with ketones to quinolines in the presence of carbonate salt. *J. Catal.* **2021**, *395*, 340 – 349.

11. Zhihua Peng, Z.; Yu, C.; Wang, Y.; Wei, D.; Jiang, C., Direct C–H Arylation and Alkylation of Electron-Deficient Heteroaromatic Compounds with Organozinc Reagents. *Organometallics* **2021**, *40*, 21, 3678 – 3688.

12. Xu, J. X.; Pan, N. L.; Chen, J. X.; Zhao, J. W., Visible-Light-Mediated Oxidative Cyclization of 2-Aminobenzyl Alcohols and Secondary Alcohols Enabled by an Organic Photocatalyst. *J. Org. Chem.* **2021**, *86*, 10747 – 10754

13. Wang. Z.; Lin, Q.; Ma, N.; Liu, S.; Han, M.; Yan, X.; Liu, Q.; Solan, A. G.; Sun, W. H., Direct synthesis of ring-fused quinolines and pyridines catalyzed by NN_HY -ligated manganese complexes (Y = NR₂ or SR). *Catal. Sci. Technol.* **2021**, *11*, 8026 – 8036.

14. Cao, F.; Mao, A.; Yang, B.; Ge, C.; Wang, D., The preparation of a $Co@C_3N_4$ catalyst and applications in the synthesis of quinolines from 2-aminobenzyl alcohols with ketones. *New J. Chem.* **2021**, *45*, 6768 – 6772.

15. Ramnathan, M.; Wan, J.; Liu, S. T., Preparation of 3-hydroxyquinolines from direct oxidation of dihydroquinolinium salts. *RSC Adv.* **2018**, *8*, 38166 – 38174.

16. Su, L. L.; Zheng, Y. W.; Wang, W. G.; Chen, B.; Wei, X. Z.; Wu, L. Z.; Tung, C. H., Photocatalytic Synthesis of Quinolines via Povarov Reaction under Oxidant-Free Conditions. *Org. Lett.* **2022**, *24*, 1180 – 1185.

17. Barman, M. K.; Waiba, S.; Maji, B. Manganese-Catalyzed Direct Olefination of Methyl-Substituted Heteroarenes with Primary Alcohols. *Angew. Chem., Int. Ed.* **2018**, *57*, 9126 – 9130.

18. Das, J.; Vellakkaran, M.; Sk, M.; Banerjee, D. Iron-Catalyzed Coupling of Methyl N-Heteroarenes with Primary Alcohols: Direct Access to E-Selective Olefins. *Org. Lett.* **2019**, *21*, 7514–7518.

19. Ferlin, F.; Zangarelli, A.; Lilli, S.; Santoro, S.; Vaccaro, L. Waste-minimized synthesis of C2 functionalized quinolines exploiting iron-catalysed C-H activation. *Green Chem.*, **2021**,*23*, 490-495.

20. Ramalingam, B. M.; Ramakrishna, I.; Baidya, M. Nickel-Catalyzed Direct Alkenylation of Methyl Heteroarenes with Primary Alcohols. *J. Org. Chem.* **2019**, *84*, 9819–9825.

21. Dahatonde, D. J.; Ghosh, A.; Batra, S. Metal-Free Synthesis of Alkenylazaarenes and 2-Aminoquinolines through Base-Mediated Aerobic Oxidative Dehydrogenation of Benzyl Alcohols. *Eur. J. Org. Chem.* **2021**, 2746 – 2751.

22. Yang. J.; Xie, Z.; Jin, L.; Chen, X.; Le, Z., Synthesis of quinazoline by decarboxylation of 2aminobenzylamine and α -keto acid under visible light catalysis. *Org. Biomol. Chem.* **2022**, *20*, 3558 – 3563

23. Das, K.; Mondal, A.; Pal, D.; Srimani, D., Sustainable Synthesis of Quinazoline and 2-Aminoquinoline via Dehydrogenative Coupling of 2-Aminobenzyl Alcohol and Nitrile Catalyzed by Phosphine-Free Manganese Pincer Complex. *Org. Lett.* **2019**, *21*, 3223 – 3227.

24. Yuan, F.; Xie, S.; Zhuo, L.; Wang, L.; Zhu, H., Metal-Free Synthesis of 2-Aryl Quinazolines via Tandem C– H/N– H Bond Functionalization. *ChemistrySelect* **2021**, *6*, 3707 – 3711.

25. Sikari, R.; Chakraborty, G.; Guin, A. K.; Paul, N. D., Nickel-Catalyzed [4+2] Annulation of Nitriles and Benzylamines by C–H/N–H Activation. *J. Org. Chem.* **2021**, *86*, 279 – 290.

26. Filippo, M. D.; Baumann, M. Continuous Flow Synthesis of Quinolines via a Scalable Tandem Photoisomerization-Cyclization Process. *Eur. J. Org. Chem.* **2020**, *2020*, 6199-6211.

27. Todorov, R., A; Wirtanen., T; Helaja, J., Photoreductive removal of O-Benzyl Groups from Oxyarene N-Heterocycles Assisted by O-Pyridine– pyridone Tautomerism. *J. Org. Chem.* **2017**, *82*, 13756–13767.