## Electronic Supplementary Information

# Catalyst and solvent switched divergent C-H functionalization: oxidative annulation of N-aryl substituted quinazolin-4-amine with alkynes

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## 1. Table S1. Selected Screening Results



Entry	Catalyst (mol%)	Oxidant	Additive	Solvent	Yield <sup>b</sup>	
					(7 3ea	'o) 4ea
1	$Pd(OAc)_2$ (10)	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBAB	DMF	38	0
2	$Pd(OAc)_2(10)$	Ag <sub>2</sub> CO <sub>3</sub>	TBAB	DMF	45	0
3	$Pd(OAc)_2(10)$	AgNO <sub>3</sub>	TBAB	DMF	48	0
4	$Pd(OAc)_2(10)$	Cu(OAc) <sub>2</sub>	TBAB	1,4-dioxane	52	0
5	$Pd(OAc)_2(10)$	Cu(OAc) <sub>2</sub>	TBAB	toluene	33	0
6	$Pd(OAc)_2(10)$	Cu(OAc) <sub>2</sub>	TBAB	DCE	30	0
7	$Pd(OAc)_2(10)$	Cu(OAc) <sub>2</sub>	TBAB	PEG-400	58	0
8	$Pd(OAc)_2(10)$	Cu(OAc) <sub>2</sub>	TBAB	H <sub>2</sub> O	55	0
9c	$Pd(OAc)_2(10)$	Cu(OAc) <sub>2</sub>	TBAB	DMF	55	0
10 <sup>d</sup>	$Pd(OAc)_2 (10)$	Cu(OAc) <sub>2</sub>	TBAB	DMF	63	0
11	$Pd(OAc)_2(5)$	Cu(OAc) <sub>2</sub>	TBAB	DMF	35	0
12	PdCl <sub>2</sub> (10)	Cu(OAc) <sub>2</sub>	TBAB	DMF	10	0
13	$[RuCl_2(p-cymene)]_2(5)$	Cu(OAc) <sub>2</sub>	-	1,4-dioxane	15	20
14	$[RuCl_2(p-cymene)]_2(5)$	Cu(OAc) <sub>2</sub>	-	toluene	18	25
15	$[RuCl_2(p-cymene)]_2(5)$	Cu(OAc) <sub>2</sub>	-	DCE	12	18
16	$[RuCl_2(p-cymene)]_2(5)$	AgOAc	-	PEG-400	-	40
17	$[RuCl_2(p-cymene)]_2 (5)$	Ag <sub>2</sub> CO <sub>3</sub>	-	PEG-400	-	38
18	$[RuCl_2(p-cymene)]_2 (5)$	AgNO <sub>3</sub>	-	PEG-400	-	40
19	$[RuCl_2(p-cymene)]_2(7.5)$	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	-	PEG-400	-	62
20	$[RuCl_2(p-cymene)]_2 (2.5)$	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	-	PEG-400	-	32
21°	$[RuCl_2(p-cymene)]_2(5)$	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	-	PEG-400	-	40
22 <sup>d</sup>	$[\operatorname{RuCl}_2(p-cymene)]_2(5)$	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	-	PEG-400	-	60
23 <sup>e</sup>	$[RuCl_2(p-cymene)]_2(5)$	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	-	PEG-400	-	56
	$[\mathbf{D}\mathbf{u}\mathbf{C}]$ (n					

24 <sup>f</sup>	cymene)] <sub>2</sub> (5)	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	-	PEG-400	-	62

Reaction conditions: **1e** (0.452 mmol), **2a** (0.452 mmol), catalyst, oxidant (0.3 equiv.), TBAB (0.452 mmol), solvent (3 mL), 100 °C, 12 h. <sup>b</sup>Yields of isolated products are given. <sup>c</sup>The reaction was performed at 80 °C. <sup>d</sup>The reaction was performed at 120 °C. <sup>e</sup>The reaction was performed for 10 h. <sup>f</sup>The reaction was performed for 15 h.

#### 2. X-Ray Structure Determination:

X-ray intensity data measurements were carried out on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer equipped with Incoatech multilayer mirrors optics. The intensity measurements were carried out with Mo micro-focus sealed tube diffraction source (Cu-K $\alpha$  = 0.72 Å) at 100(2) K temperature. The X-ray generator was operated at 50 kV and 1.4 mA. A preliminary set of cell constants and an orientation matrix were calculated from two sets of 20 frames. Data were collected with  $\omega$  scan width of 0.5° at different settings of  $\varphi$  and 2 $\Theta$  with a frame time of 40 seconds keeping the sample–to-detector distance fixed at 4.00 cm. The X-ray data collection was monitored by APEX3 program (Bruker, 2016). All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2016). SHELX-97 was used for structure solution and full matrix least-squares refinement on F<sup>2</sup>. Molecular diagrams were generated using ORTEP-33 and Mercury programs. Geometrical calculations were performed using SHELXTL and PLATON. All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms. An ORTEP III view of both compounds were drawn with 50% probability displacement ellipsoids and H–atoms are shown as small spheres of arbitrary radious.

**Crystal Data of (3aa)**: CCDC 1949446, Single crystals suitable for X-ray diffraction of **3aa** EtOAc. Molecular formula =  $C_{28}H_{19}N_3$ , Formula weight = 397.46, Crystal system = Monoclinic, space group = P 21/n, a=9.9378(3) Å, b =11.6946(4) Å, c = 18.4106(7) Å, V = 2123.19(13) Å3, T = 296(2) K, Z = 4, Dc = 1.243 Mg/m3, 16746 Reflections collected, 4175 [R(int) = 0.0443] independent reflections, Goodness of fit = 0.951.



**Crystal Data of (4ea)**: CCDC 1949441, Single crystals suitable for X-ray diffraction of **4ea** DCM: EtOAc (1:1). Molecular formula =  $C_{29}$  H<sub>21</sub> N<sub>3</sub> O, Formula weight = 427.49, Crystal system = Triclinic, space group = P -1, a= 9.707(9) Å, b = 11.145(10) Å, c = 21.590(16) Å, V = 2247(3) Å3, T = 293(2) K, Z = 4, Dc = 1.264 Mg/m<sup>3</sup>, 51342 Reflections collected, 7907 [R(int) = 0.0921] independent reflections, Goodness of fit = 0.991.



#### **3. Experimental Section**

Unless stated otherwise, solvents and chemicals were obtained from commercial sources and were used without further purification. Reactions were monitored by thin layer chromatography (TLC) on silica gel plates (60 F254), visualizing with ultraviolet light or iodine spray. Flash chromatography was performed on silica gel (100-200 mesh) using hexane and ethyl acetate. Melting points were recorded on a DBK digital melting point apparatus and were uncorrected. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a 400 MHz Bruker BiospinAvance III FT-NMR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were determined in CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> solutions by using 400 or 126 or 100 MHz spectrometers, respectively. Proton chemical shifts ( $\delta$ ) are relative to tetramethylsilane (TMS,  $\delta$  = 0.00) as internal standard and expressed in ppm. Spin multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet). Coupling constants (*J*) are given in hertz. High-resolution mass spectra were recorded on a Bruker maxis-TOF mass spectrometer.

4. General Procedure for the Synthesis of N-Arylquinazolin-4-amine Derivatives (1)<sup>1,2</sup>



A mixture of 2-Aminobenzonitrile (S1, 500 mg, 4.237 mmol) and DMF-DMA (S2, 8.5 mL, 63.559 mmol) in DMF (5 mL) was heated to 90 °C for 4 h. After completion of the reaction the mixture was cooled to room temp, diluted with water (25 mL) and extracted with ethyl acetate ( $3 \times 20$  mL). The organic layers were collected, combined, washed with brine solution (20 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. providing a colorless solid as *N'*-(2-cyanophenyl)-*N*,*N*-dimethylformimidamide (S3). The crude compound were used directly in the next step without further purification.

To the solution of the above-made solid in a stirred solution of N'-(2-cyanophenyl)-N,N-dimethylformimidamide (**S3**, 500 mg, 2.890 mmol), aniline (**S4**, 269 mg, 2.890 mmol), in AcOH (2.5 mL, 43.352 mmol) and refluxed for 3 h. After completion of the reaction. The reaction mixture was poured into ice water and stirred for 10 min then extracted with ethyl acetate. The ethyl acetate layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude compounds were purified by column chromatography using ethyl acetate and *n*-hexane to give the desired product (**1**).

#### 5. Analytical data of N-Arylquinazolin-4-amine Derivatives

N-Phenylquinazolin-4-amine (1a)



Off white solid; Yield: 81%; mp: 249-252 °C (lit<sup>3</sup> 251-253 °C);  $R_f = 0.2$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.74 (s, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.81 (t, J = 7.6 Hz, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 8.0 Hz, 1H), 7.42 (t, J = 8.0 Hz, 2H), 7.20 (t, J = 8.0 Hz, 1H).

#### *N*-(*p*-Tolyl)quinazolin-4-amine (1b)



Off white solid; Yield: 76%; mp: 168-172 °C;  $R_f = 0.5$  (30% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.72 (s, 1H), 8.54

(s, 1H), 8.52 (d, J = 8.0 Hz, 1H), 7.83 (t, J = 8.0 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.61 (t, J = 6.0 Hz, 1H), 7.19 (d, J = 8.4 Hz, 2H), 2.30 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.0, 155.1, 149.9, 135.5, 134.6, 132.8, 129.6 (2C), 128.7, 126.4, 122.6 (2C), 120.8, 115.2, 20.9; HRMS (ESI): m/z calcd for C<sub>15</sub>H<sub>14</sub>N<sub>3</sub>([M + H]<sup>+</sup>) 236.1187, found 236.1188.

*N*-(*m*-Tolyl)quinazolin-4-amine (1c)



White solid; Yield: 84%; mp: 195-197 °C (lit<sup>4</sup> 196-197 °C); R<sub>f</sub>= 0.2 (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.76 (s, 1H), 7.95-7.89 (m, 2H), 7.80-7.76 (m, 1H), 7.73 (bs, 1H), 7.55-7.51 (m, 3H), 7.29 (t, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 2.38 (s, 3H).

## *N*-(2,4-Dimethylphenyl)quinazolin-4-amine (1d)



Gray solid; Yield: 84%; mp: 155-157 °C;  $R_f = 0.3$  (30% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.66 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 12.0 Hz, 1H), 7.77 (t, J = 6.0 Hz, 1H), 7.61 (bs, 1H), 7.54-7.50 (m, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.10 (s, 1H), 7.07 (d, J = 8.0 Hz, 1H), 2.33 (s, 3H), 2.26 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.7, 155.4, 149.9, 136.4, 133.4, 133.1, 132.8, 131.7, 128.7, 127.5, 126.4, 125.9, 120.9, 115.0, 21.0, 18.1; HRMS (ESI): m/z calcd for C<sub>16</sub>H<sub>16</sub>N<sub>3</sub>([M + H]<sup>+</sup>) 250.1344, found 250.1348.

## *N*-(4-Methoxyphenyl)quinazolin-4-amine (1e)

OCH<sub>3</sub>



Brown solid; Yield: 75%; mp: 150-154 °C;  $R_f = 0.3$  (30% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.71 (s, 1H), 8.49 (d, J = 8.0 Hz, 2H), 7.82 (t, J = 8 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 9.2 Hz, 2H), 7.59 (t, J = 8.0 Hz, 1H), 6.96 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.5, 156.6, 155.1, 149.8, 132.5, 131.5, 128.0, 125.9, 124.9 (2C), 122.2, 115.4, 114.0 (2C), 55.4; HRMS (ESI): m/z calcd for C<sub>15</sub>H<sub>14</sub>N<sub>3</sub>O ([M + H]<sup>+</sup>) 252.1137, found 252.1138.

## N-(4-Chlorophenyl)quinazolin-4-amine (1f)



Yellow solid; Yield: 76%; mp: 155-160 °C (lit<sup>5</sup> 163-164 °C);  $R_f = 0.4$  (30% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.77 (s, 1H), 7.92 (d, J = 8.8 Hz, 2H), 7.80 (t, J = 8.0 Hz, 1H), 7.70 (d, J = 8.0 Hz, 3H), 7.56 (t, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H). *N*-(4-Bromophenyl)quinazolin-4-amine (1g)



Brown solid; Yield: 85%; mp: 161-164 °C (lit<sup>2</sup> 232-234 °C);  $R_f = 0.4$  (30% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.89 (s, 1H), 8.64 (s, 1H), 8.57 (d, J = 8.0 Hz, 1H), 7.92-7.87 (m, 3H), 7.82 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H).

## N-(4-(Trifluoromethyl)phenyl)quinazolin-4-amine (1h)





White solid; Yield: 80%; mp: 195-197 °C;  $R_f = 0.3$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.86 (s, 1H), 8.01-7.94 (m, 4H), 7.90-7.86 (m, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.67-7.62 (m, 1H), 7.61 (bs, 1H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.06; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.0, 155.6, 151.2, 142.5, 134.4, 130.5, 128.3, 127.5, 127.5, 126.7, 122.1 (3C), 121.3, 116.3; HRMS (ESI): m/z calcd for C<sub>15</sub>H<sub>10</sub>N<sub>3</sub>F<sub>3</sub>Na ([M + Na]<sup>+</sup>) 312.0725, found 312.0726.

N-(4-Nitrophenyl)quinazolin-4-amine (1i)



Yellow solid; Yield: 70%; mp: 230-233 °C;  $R_f = 0.3$  (30% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  10.31 (s, 1H), 8.81 (s, 1H), 8.66 (d, *J* = 8.4 Hz, 1H), 8.35-8.29 (m, 3H), 7.97 (t, *J* = 7.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.85 (dd, *J* = 2.0 & 2.0 Hz, 1H), 7.76 (t, *J* = 7.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  157.2, 153.9, 149.9, 145.9, 141.8, 133.5, 127.9, 126.7, 124.5 (2C), 123.0, 120.7 (2C), 115.3; HRMS (ESI): m/z calcd for C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>Na ([M + Na]<sup>+</sup>) 289.0702, found 289.0703.

## 5-Methyl-N-(p-tolyl)quinazolin-4-amine (1j)



Brown solid; Yield: 82%; mp: 138-140 °C;  $R_f = 0.4$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.61 (s, 1H), 7.73 (t, J = 7.6 Hz, 2H), 7.59 (t, J = 7.8 Hz, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 6.4 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.30 (s, 3H), 2.36 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.2, 154.3, 151.9, 135.5, 134.7, 132.2, 132.1, 129.8, 129.6 (2C), 127.3, 122.8 (2C), 115.6, 24.4, 20.9; HRMS (ESI): m/z calcd for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>Na ([M + Na]<sup>+</sup>) 272.1164, found 272.1164.

7-Chloro-N-(p-tolyl)quinazolin-4-amine (1k)



Off white solid; Yield: 82%; mp: 205-208 °C;  $R_f = 0.4$  (30% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.68 (s, 1H), 7.86 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  157.8, 155.9, 150.5, 139.1, 135.1, 135.0, 129.7 (2C), 127.6, 127.3, 122.7 (2C), 122.2, 113.4, 21.0; HRMS (ESI): m/z calcd for C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>Cl ([M + H]<sup>+</sup>) 270.0798, found 270.0796.

N-(4-Bromophenyl)-6,7-dimethoxyquinazolin-4-amine (11)<sup>6</sup>



Brown solid; Yield: 75%; mp: 265-268 °C;  $R_f = 0.3$  (50% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.55 (s, 1H), 8.49 (s, 1H), 7.82 (d, J = 12.0 Hz, 3H), 7.57 (d, J = 12.0 Hz, 2H), 7.20 (s, 1H), 3.97 (s, 3H), 3.94 (s, 3H).

## N-Benzylquinazolin-4-amine (1m)



White solid; Yield: 45%; mp: 143-145 °C (lit<sup>7</sup> 142-145 °C);  $R_f = 0.4$  (50% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.69 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.73 (t, J = 6.0 Hz, 2H), 7.46-7.31 (m, 6H), 6.21 (bs, 1H), 4.87 (d, J = 8.0 Hz, 2H).

*N*-(2,6-Dimethylphenyl)quinazolin-4-amine (1n)

H<sub>3</sub>C



White solid; Yield: 80%; mp: 218-220 °C;  $R_f = 0.3$  (30% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.60 (s, 1H), 8.04 (d, J = 6.8 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.78 (t, J = 8.0 Hz, 1H), 7.59 (bs, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.21-7.14 (m, 3H), 2.23 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.0, 155.7, 149.8, 136.2, 134.8, 132.9 (2C), 128.5 (3C), 127.8, 126.4, 121.2, 114.7, 18.5 (2C); HRMS (ESI): m/z calcd for C<sub>16</sub>H<sub>16</sub>N<sub>3</sub> ([M + H]<sup>+</sup>) 250.1344, found 250.1344.

6. General Procedure for the Synthesis of Indolquinazoline Derivatives (3): To an oven-dried 10 mL round bottom flask were added appropriate quinazolin-4-amine (0.452 mmol), appropriate diphenylacetylene (0.452 mmol),  $Pd(OAc)_2$  (0.045mmol),  $Cu(OAc)_2$  (0.3 equiv.), TBAB (0.452 mmol), and DMF (3.0 mL). The mixture was stirred under open air for 12 h at 100 °C. After the reaction was complete (as indicated by the TLC), the reaction mixture was cooled to room temperature and diluted with ethyl acetate (10 ml).

The mixture was washed with brine (3 x 5 mL), dried over  $Na_2SO_4$ , then concentrated under reduced pressure. The crude compounds were purified by column chromatography using ethyl acetate and *n*-hexane gave the indolquinazoline (**3**).

#### 8. Analytical data of Indolquinazoline Derivatives Derivatives

4-(2,3-Diphenyl-1*H*-indol-1-yl) quinazoline (3aa)



The general procedure was followed by using *N*-phenylquinazolin-4-amine (**1a**) (100 mg, 0.452 mmol), diphenylacetylene (**2a**) (80 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3aa** (117 mg, 65%) as a pale yellow solid; mp: 158-162 °C;  $R_f$ = 0.5 (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.31 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 8.01 (t, *J* = 7.2 Hz, 1H), 7.72-7.61 (m, 3H), 7.40 (d, *J* = 4.0 Hz, 4H), 7.34-7.21 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.07 (bs, 5H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  158.7, 155.0, 152.3, 138.1, 137.6, 135.7, 133.9, 131.2, 130.3 (4C), 129.5, 129.0 (2C), 128.6, 128.5 (2C), 128.3, 128.2, 127.1, 125.4, 124.2, 122.5, 121.9, 119.9, 118.3, 111.6; HRMS (ESI): m/z calcd for C<sub>28</sub>H<sub>20</sub>N<sub>3</sub> ([M + H]<sup>+</sup>) 398.1652, found 398.1673.

4-(2,3-Di-*p*-tolyl-1*H*-indol-1-yl) quinazoline (3ab)



The general procedure was followed by using *N*-phenylquinazolin-4-amine (**1a**) (100 mg, 0.452 mmol), 1,2-di-p-tolylethyne (**2b**) (93 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3ab** (125 mg, 65%) as a brown solid; mp: 130-134 °C;  $R_f$ = 0.5 (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.25 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.88 (t, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 8 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 3H), 7.13 (d, *J* = 8 Hz, 1H), 6.96 (d, *J* = 8 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 2.17 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  160.3, 155.8, 153.4, 139.3, 138.5, 138.4, 137.2, 135.6, 132.3, 131.2 (2C), 131.1 (2C), 130.3 (2C), 130.2, 130.0 (2C), 129.7, 129.6, 129.4, 126.9, 124.7, 123.5, 123.1, 121.3, 120.1, 112.3, 23.3, 23.2; HRMS (ESI): m/z calcd for C<sub>30</sub>H<sub>24</sub>N<sub>3</sub> ([M + H]<sup>+</sup>) 426.1970, found 426.1991.

4-(2,3-Bis(4-methoxyphenyl)-1*H*-indol-1-yl)quinazoline (3ac)



The general procedure was followed by using N-phenylquinazolin-4-amine (1a) (100 mg, 0.452 mmol), 1,2-bis(4-

methoxyphenyl)ethyne (**2c**) (108 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3ac** (136 mg, 66%) as a pale yellow solid; mp: 159-162 °C;  $R_f = 0.4$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.26 (s, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.87 (t, J = 8.0 Hz, 1H), 7.77 (t, J = 8.0 Hz, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.25-7.17 (m, 2H), 7.14 (d, J = 8.0 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.55 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 3.65 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.4, 158.8, 158.3, 154.8, 152.5, 138.1, 136.9, 134.5, 131.3 (2C), 131.2 (2C), 129.1, 128.6, 128.2, 126.5, 125.7, 123.8, 123.4, 122.2, 121.9, 119.9, 118.2, 113.9 (2C), 113.6 (2C), 111.0, 55.2, 55.0; HRMS (ESI): m/z calcd for C<sub>30</sub>H<sub>24</sub>N<sub>3</sub>O<sub>2</sub> ([M + H]<sup>+</sup>) 458.1869, found 458.1871.

4-(2,3-Bis(4-fluorophenyl)-1*H*-indol-1-yl)quinazoline (3ad)



The general procedure was followed by using *N*-phenylquinazolin-4-amine (**1a**) (100 mg, 0.452 mmol), 1,2-bis(4-fluorophenyl)ethyne (**2d**) (97 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3ad** (121 mg, 62%) as a brown solid; Yield: 81%; mp: 149-153 °C;  $R_f = 0.6$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.25 (s, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.91 (t, J = 8.4 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 7.2 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.38-7.35 (m, 2H), 7.28 (d, J = 7.2 Hz, 1H), 7.23 (t, J = 6.8 Hz, 1H), 7.14 (d, J = 8 Hz, 1H), 7.08 (t, J = 8.4 Hz, 2H), 7.04-7.01 (m, 2H), 6.74 (t, J = 8.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  163.3 (d, C–F J = 247.0 Hz), 163.0 (d, C–F J = 245.0 Hz), 158.9, 154.8 (2C), 152.6, 138.1, 136.4, 134.6 (2C), 131.9 (d, C–F J = 8.0 Hz), 131.7 (d, C–F J = 8.0 Hz), 129.8 (d, C–F J = 3.0 Hz), 128.8, 128.6, 128.4, 127.3 (d, C–F J = 4.0 Hz), 125.3, 123.9, 122.2, 122.1, 119.8 (2C), 118.4, 115.6 (d, C–F J = 21.0 Hz), 115.4 (d, C–F J = 22.0 Hz), 111.2 (2C); HRMS (ESI): m/z calcd for C<sub>28</sub>H<sub>18</sub>F<sub>2</sub>N<sub>3</sub> ([M + H]<sup>+</sup>) 434.1463, found 434.1459.

4-(2,3-Di(thiophen-2-yl)-1*H*-indol-1-yl)quinazoline (3ae)



The general procedure was followed by using *N*-phenylquinazolin-4-amine (**1a**) (100 mg, 0.452 mmol), 1,2-di(thiophen-2-yl)ethyne (**2e**) (86 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3ae** (111 mg, 60%) as a pale yellow solid; mp: 142-145 °C;  $R_f = 0.4$  (10% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.31 (s, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.94-7.89 (m, 2H), 7.76 (d, J = 8 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.37-7.36 (m, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.23-7.21 (m, 2H), 7.14-7.11 (m, 2H), 7.06 (d, J = 8 Hz, 1H), 6.83 (d, J = 3.2 Hz, 1H), 6.75 (t, J = 4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.6, 154.8, 152.5, 138.0, 134.8, 134.7, 131.4, 131.2, 130.1, 128.7, 128.5, 128.4, 127.8, 127.3, 127.1, 126.8, 125.5, 125.3, 124.3, 122.5, 122.3, 120.4, 113.9, 111.0; HRMS (ESI): m/z calcd for C<sub>24</sub>H<sub>16</sub>N<sub>3</sub>S<sub>2</sub> ([M + H]<sup>+</sup>) 410.0786, found 410.0780. **(S)-4-(2,3-Diethyl-1***H***-indol-1-yl)quinazoline (3af)** 



The general procedure was followed by using *N*-phenylquinazolin-4-amine (**1a**) (100 mg, 0.452 mmol), hex-3-yne (**2f**) (37 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10.0 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3af** (84 mg, 62%) as a yellow semi solid;  $R_f = 0.6$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.35 (s, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.98 (t, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.64-7.57 (m, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.11-3.02 (m, 1H), 2.88-2.83 (m, 2H), 2.74-2.65 (m, 1H), 1.35 (t, *J* = 7.6 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.9, 155.0, 152.7, 139.0, 137.8, 134.5, 129.1, 128.8, 128.3, 126.1, 122.0, 121.6, 120.8, 118.6, 117.9, 110.6, 18.3,

17.6, 15.60, 14.9; HRMS (ESI): m/z calcd for  $C_{20}H_{19}N_3Na$  ([M + Na]<sup>+</sup>) 324.1477, found 324.1478.

4-(5-Methyl-2,3-diphenyl-1*H*-indol-1-yl)quinazoline (3ba)



The general procedure was followed by using *N*-(p-tolyl)quinazolin-4-amine (**1b**) (106 mg, 0.452 mmol), diphenylacetylene (**2a**) (81 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3ba** (119 mg, 64%) as a yellow solid; mp: 138-141 °C;  $R_f$ = 0.6 (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.22 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.87 (t, *J* = 8 Hz, 1H), 7.82 (d, *J* = 8 Hz, 1H), 7.56 (s, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.42-7.36 (m, 4H), 7.30 (t, *J* = 8 Hz, 1H), 7.87 (t, *J* = 8 Hz, 1H), 7.80 (t, *J* = 8 Hz, 1H), 7.86 (s, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.42-7.36 (m, 4H), 7.30 (t, *J* = 8 Hz, 1H), 7.81 (t, *J* = 8 Hz, 1H), 7.80 (t, *J* = 8 Hz, 1H), 7.85 (t, *J* = 8 Hz, 1H), 7.85 (t, *J* = 8 Hz, 1H), 7.86 (t, *J* = 8 Hz, 1H), 7.86 (t, *J* = 8 Hz, 1H), 7.80 (t, *J* = 7.2 Hz, 1H), 7.42-7.36 (m, 4H), 7.30 (t, *J* = 8 Hz, 1H), 7.81 (t, *J* = 8 Hz, 1H), 7.80 (t, *J* = 8 Hz, 1H), 7.85 (t, *J* = 8 Hz, 1H), 7.80 (t, *J* = 8 Hz, 1H), 7.80 (t, *J* = 8 Hz, 1H), 7.80 (t, *J* = 7.2 Hz, 1H), 7.42-7.36 (m, 4H), 7.30 (t, *J* = 8 Hz, 1H), 7.81 (t, *J* = 8 Hz, 1H), 7.80 (t, *J* = 8 Hz, 1H), 7.81 (t, *J* = 8 Hz, 1H), 7.80 (t, *J* = 8 Hz, 1H), 7.80 (t, *J* = 7.2 Hz, 1H), 7.82 (t, *J* = 8 Hz, 1H), 7.80 (t, *J* = 7.2 Hz, 1H), 7.82 (t, *J* = 8 Hz, 1H), 7.80 (t, *J* = 7.2 Hz, 1H), 7.82 (t, *J* = 8 Hz, 1H), 7.80 (t, *J* = 7.2 Hz, 1H), 7.82 (t, *J* = 8 Hz, 1H), 7.80 (t, *J* = 7.2 Hz, 1H), 7.82 (t, *J* = 8 Hz, 1H), 7.80 (t, J = 8 Hz, 1H), 7.80 (t, J

7.2 Hz, 1H), 7.08-6.98 (m, 7H), 2.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.2, 153.7, 151.4, 136.4, 135.7, 133.4, 133.2, 130.5, 130.4, 129.2 (2C), 129.0 (2C), 128.1, 127.5, 127.4 (2C), 127.1, 127.0 (2C), 126.4, 125.5, 124.6, 124.1, 121.1, 118.7, 118.0, 109.8, 20.4; HRMS (ESI): m/z calcd for C<sub>29</sub>H<sub>22</sub>N<sub>3</sub> ([M + H]<sup>+</sup>) 412.1808, found 412.1800.

4-(5-Methyl-2,3-di-*p*-tolyl-1*H*-indol-1-yl)quinazoline (3bb)



The general procedure was followed by using *N*-(p-tolyl)quinazolin-4-amine (**1b**) (106 mg, 0.452 mmol), 1,2-di-p-tolylethyne (**2b**) (93 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3bb** (129 mg, 65%) as a Yellow solid; mp: 125-129 °C;  $R_f$ = 0.6 (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.23 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.87 (t, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.54 (s, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8 Hz, 2H), 7.19 (d, *J* = 8 Hz, 2H), 7.02 (s, 2H), 6.94 (d, *J* = 8 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.40 (s, 3H), 2.16 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.4, 153.8, 151.4, 136.4, 136.1, 135.6, 135.0, 133.3, 130.3 (2C), 129.1 (2C), 128.9 (2C), 128.3, 128.1 (2C), 127.7 (2C), 127.5 (2C), 127.0, 124.7, 123.8, 121.2, 118.6, 117.6, 109.7, 20.4, 20.2, 20.1; HRMS (ESI): m/z calcd for C<sub>31</sub>H<sub>26</sub>N<sub>3</sub> ([M + H]<sup>+</sup>) 440.2121, found 440.2133.

4-(2,3-Bis(4-methoxyphenyl)-5-methyl-1*H*-indol-1-yl)quinazoline (3bc)



The general procedure was followed by using *N*-(*p*-tolyl)quinazolin-4-amine (**1b**) (106 mg, 0.452 mmol), 1,2-bis(4methoxyphenyl)ethyne (**2c**) (108 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3bc** (128 mg, 60%) as a yellow solid; mp: 177-180 °C;  $R_f$  = 0.5 (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.24 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.86 (t, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.52 (s, 1H), 7.47 (t, *J* = 6.0 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.05-7.02 (m, 2H), 6.98-6.92 (m, 4H), 6.54 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.65 (s, 3H), 2.45 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.5, 158.7, 158.2, 154.8, 152.5, 137.0, 136.5, 134.4, 131.3 (5C), 129.4, 128.5, 128.1, 126.7, 125.8, 124.8, 123.9, 122.2, 119.5, 118.0, 113.9 (2C), 113.6 (2C), 110.7, 55.2, 55.0, 21.5; HRMS (ESI): m/z calcd for C<sub>31</sub>H<sub>26</sub>N<sub>3</sub>O<sub>2</sub> ([M + H]<sup>+</sup>) 472.2025, found 472.2031.

4-(2,3-Bis(4-fluorophenyl)-5-methyl-1*H*-indol-1-yl)quinazoline (3bd)





The general procedure was followed by using *N*-(*p*-tolyl)quinazolin-4-amine (**1b**) (106 mg, 0.452 mmol), 1,2-bis(4-fluorophenyl)ethyne (**2d**) (97 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3bd** (129 mg, 64%) as a brown solid; mp: 192-195 °C;  $R_f = 0.7$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.23 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.90 (t, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 1H), 7.37-7.33 (m, 2H), 7.11-6.99 (m, 6H), 6.73 (t, *J* = 8.8 Hz, 2H), 2.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  163.2 (d, C–F *J* = 247.0 Hz), 160.8 (d, C–F *J* = 244.0 Hz), 158.9, 154.8 (2C), 152.6, 136.6, 136.4, 134.6, 131.8 (3C), 131.7 (d, C–F *J* = 3.0 Hz), 129.9 (d, C–F *J* = 4.0 Hz), 128.9, 128.8 (2C), 128.3, 127.4 (d, C–F *J* = 3.0 Hz), 125.4 (d, C–F *J* = 4.0 Hz), 122.0, 119.5 (2C), 118.2, 115.7 (d, C–F *J* = 21.0 Hz), 115.4 (d, C–F *J* = 22.0 Hz), 110.9 (2C), 21.5; HRMS (ESI): m/z calcd for C<sub>29</sub>H<sub>20</sub>F<sub>2</sub>N<sub>3</sub> ([M + H]<sup>+</sup>) 448.1620, found 448.1635.

4-(5-Methyl-2,3-di(thiophen-2-yl)-1*H*-indol-1-yl)quinazoline (3be)



The general procedure was followed by using *N*-(*p*-tolyl)quinazolin-4-amine (**1b**) (106 mg, 0.452 mmol), 1,2-di(thiophen-2-yl)ethyne (**2e**) (86 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3be** (113 mg, 59%) as a yellow solid; mp: 70-72 °C;  $R_f$ = 0.5 (10% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.30 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.91 (t, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.65 (s, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 5.2 Hz, 1H), 7.20 (d, *J* = 2.4 Hz, 1H), 7.13 (t, *J* = 4.4 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 2.8 Hz, 1H), 6.74 (t, *J* = 4.0 Hz, 1H), 2.47 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.8, 154.8, 152.5, 136.5, 134.9, 134.6, 131.8, 131.6, 131.4, 129.9, 128.7, 128.6, 128.4, 128.1, 127.6, 127.3, 127.1, 126.8, 125.8, 125.5, 125.3, 122.4, 120.0, 110.7, 21.5; HRMS (ESI): m/z calcd for C<sub>25</sub>H<sub>18</sub>N<sub>3</sub>S<sub>2</sub> ([M + H]<sup>+</sup>) 424.0942, found 424.0941.

4-(6-Methyl-2,3-diphenyl-1*H*-indol-1-yl)quinazoline (3ca)



The general procedure was followed by using *N*-(*m*-tolyl)quinazolin-4-amine (**1c**) (106 mg, 0.452 mmol), diphenylacetylene (**2a**) (81 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3ca** (121 mg, 65%) as a yellow solid; mp: 160-162 °C;  $R_f = 0.5$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.27 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 6.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.48-7.41 (m, 3H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 6.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.05-7.00 (m, 6H), 2.38 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.3, 154.8, 152.5, 138.6, 136.7, 134.4, 134.3, 133.8, 131.5, 130.2 (2C), 130.1 (2C), 128.5, 128.4 (2C), 128.2, 128.1 (2C), 127.4, 126.7, 126.5, 125.7, 123.7, 122.2, 119.8, 119.1, 111.0, 21.8; HRMS (ESI): m/z calcd for C<sub>29</sub>H<sub>22</sub>N<sub>3</sub> ([M + H]<sup>+</sup>) 412.1813, found 412.1814.





The general procedure was followed by using *N*-(2,4-dimethylphenyl)quinazolin-4-amine (**1d**) (112 mg, 0.452 mmol), diphenylacetylene (**2a**) (81 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10.0 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3da** (121 mg, 63%) as a pale yellow solid; mp: 158-160 °C;  $R_f$  = 0.6 (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.33 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.80 (s, 1H), 7.49-7.33 (m, 7H), 7.08-6.83 (m, 7H), 2.43 (s, 3H), 1.68 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.5, 154.3, 151.5, 138.7, 135.7, 134.6, 134.4, 131.1, 130.9 (2C), 130.3 (2C), 128.9, 128.7, 128.4, 128.3 (2C), 128.2, 127.8 (2C), 127.7 (2C), 126.2, 124.9, 124.6, 121.3, 117.9, 117.7, 21.3, 19.2; HRMS (ESI): m/z calcd for C<sub>30</sub>H<sub>24</sub>N<sub>3</sub>

 $([M + H]^+)$  426.1970, found 426.1972.

4-(5-Methoxy-2,3-diphenyl-1*H*-indol-1-yl)quinazoline(3ea)



The general procedure was followed by using *N*-(4-methoxyphenyl)quinazolin-4-amine (**1e**) (113 mg, 0.452 mmol), diphenylacetylene (**2a**) (81 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10.0 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3ea** (131 mg, 68%) as a yellow solid; mp: 163-166 °C;  $R_f = 0.5$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.22 (s, 1H), 8.08 (d, J = 8.8 Hz, 1H), 7.86 (t, J = 8.4 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.48 (t, J = 8 Hz, 1H), 7.43-7.36 (m, 4H), 7.33-7.29 (m, 1H), 7.21 (d, J = 2.4 Hz, 1H), 7.09 (d, J = 8.8 Hz, 1H), 7.05-7.00 (m, 5H), 6.86 (dd, J = 9.2 Hz, 1H), 3.85 (s, 3H); <sup>13</sup>C NMR (100

MHz, CDCl<sub>3</sub>):  $\delta$  158.1, 154.8, 153.7, 151.4, 137.0, 133.4, 133.1, 132.3, 130.3, 129.1 (2C), 129.0 (2C), 128.4, 127.5, 127.4 (2C), 127.1, 127.0 (2C), 126.4, 125.5, 124.6, 120.9, 118.2, 112.4, 111.0, 100.8, 54.8; HRMS (ESI): m/z calcd for C<sub>29</sub>H<sub>22</sub>ON<sub>3</sub> ([M + H]<sup>+</sup>) 428.1757, found 428.1742.

4-(5-Methoxy-2,3-di-*p*-tolyl-1*H*-indol-1-yl)quinazoline (3eb)



The general procedure was followed by using *N*-(4-methoxyphenyl)quinazolin-4-amine (**1e**) (113 mg, 0.452 mmol), 1,2-diptolylethyne (**2b**) (93 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10.0 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3eb** (126 mg, 61%) as a yellow solid; mp: 143-147 °C;  $R_f = 0.6$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.22 (s, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.87 (t, J = 7.2 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.49 (t, J = 6.8 Hz, 1H), 7.30 (d, J = 7.6 Hz, 2H), 7.20 (bs, 3H), 7.05 (d, J = 8.8 Hz, 1H), 6.93 (d, J = 7.6 Hz, 2H), 6.84-6.79 (m, 3H), 3.84 (s, 3H), 2.40 (s, 3H), 2.16 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.4, 155.8, 154.8, 152.5, 138.1, 137.2, 136.1, 134.4, 133.4, 131.3, 130.0 (2C), 129.9 (2C), 129.7, 129.3 (2C), 128.8 (2C), 128.5, 128.2, 125.8, 122.1, 118.9, 113.2, 111.9, 106.4, 101.9, 55.9, 21.3, 21.2; HRMS (ESI): m/z calcd for C<sub>31</sub>H<sub>26</sub>N<sub>3</sub>O ([M + H]<sup>+</sup>) 456.2076, found 456.2103.

4-(2,3-Bis(4-fluorophenyl)-5-methoxy-1*H*-indol-1-yl)quinazolin (3ed)



The general procedure was followed by using *N*-(4-methoxyphenyl)quinazolin-4-amine (**1e**) (113 mg, 0.452 mmol), 1,2-bis(4-fluorophenyl)ethyne (**2d**) (97 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10.0 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3ed** (132 mg, 63%) as a yellow solid brown solid; mp: 171-174 °C;  $R_f = 0.6$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.22 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.90 (t, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.35 (dd, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.11-7.06 (m, 3H), 7.00 (dd, *J* = 8.8 Hz, 2H), 6.87 (dd, *J* = 2.4 Hz, 1H), 6.73 (t, *J* = 8.8 Hz, 2H), 3.85 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  163.3 (d, C–F *J* = 247.0 Hz), 160.8 (d, C–F *J* = 245.0 Hz), 158.9, 156.0, 154.8 (2C), 152.6, 137.0, 134.6 (2C), 133.3, 131.8 (d, C–F *J* = 8.0 Hz), 131.7 (d, C–F *J* = 7.0 Hz), 129.9 (d, C–F *J* = 3.0 Hz), 129.3, 128.7, 128.3, 127.3 (d, C–F *J* = 3.0 Hz), 125.4, 121.9, 118.3, 115.7 (d, C–F *J* = 21.0 Hz), 115.5 (d, C–F *J* = 22.0 Hz), 113.6 (2C), 112.1 (2C), 101.7, 55.9; HRMS (ESI): m/z calcd for C<sub>29</sub>H<sub>20</sub>ON<sub>3</sub>F<sub>2</sub> ([M + H]<sup>+</sup>) 464.1569, found 464.1552.

4-(5-Chloro-2,3-diphenyl-1*H*-indol-1-yl)quinazoline (3fa)





The general procedure was followed by using *N*-(4-chlorophenyl)quinazolin-4-amine (**1f**) (115 mg, 0.452 mmol), diphenylacetylene (**2a**) (81 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10.0 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3fa** (127 mg, 65%) as a pale yellow solid; mp: 179-182 °C;  $R_f = 0.6$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.25 (s, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.88 (t, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.50 (t, J = 8.0 Hz, 1H), 7.39-7.38 (m, 4H), 7.35-7.29 (m, 1H), 7.17 (dd, J = 4.0 Hz, 1H), 7.09 (d, J = 8.8 Hz, 1H), 7.06-6.99 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.7, 154.7, 152.6, 138.6, 136.5, 134.6, 133.4, 130.8, 130.1 (4C), 129.9, 128.7, 128.6 (2C), 128.4, 128.2 (2C), 127.9, 127.8, 126.9, 125.2, 123.9, 122.0, 119.6, 118.7, 112.2; HRMS (ESI): m/z calcd for C<sub>28</sub>H<sub>19</sub>N<sub>3</sub>Cl ([M + H]<sup>+</sup>) 432.1262, found 432.1251. **4-(5-Chloro-2,3-di-***p***-tolyl-1***H***-indol-1-yl)quinazoline (<b>3fb**)



The general procedure was followed by using *N*-(4-chlorophenyl)quinazolin-4-amine (**1f**) (115 mg, 0.452 mmol), 1,2-di-*p*-tolylethyne (**2b**) (93 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10.0 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3fb** (131 mg, 63%) as an off white solid; mp: 134-138 °C;  $R_f = 0.6$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.25 (s, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.88 (t, J = 8 Hz, 1H), 7.73 (d, J = 6.8 Hz, 2H), 7.50 (t, J = 7.6 Hz, 1H), 7.27 (d, J = 8 Hz, 2H), 7.19 (d, J = 8 Hz, 2H), 7.14 (d, J = 8.4 Hz, 1H), 7.04 (d, J = 8.8 Hz, 1H), 6.93 (d, J = 7.6 Hz, 2H), 6.81 (d, J = 8 Hz, 2H), 2.39 (s, 3H), 2.16 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.9, 154.8, 152.5, 138.6, 137.7, 136.5, 136.4, 134.6, 130.5, 130.2, 129.9 (4C), 129.3 (2C), 128.9 (2C), 128.7, 128.4, 127.9, 127.6, 125.3, 123.6, 122.0, 119.5, 118.3, 112.1, 21.3, 21.2; HRMS (ESI): m/z calcd for C<sub>30</sub>H<sub>23</sub>ClN<sub>3</sub> ([M + H]<sup>+</sup>) 460.1575, found 460.1563.

4-(5-Bromo-2,3-diphenyl-1*H*-indol-1-yl)quinazoline (3ga)



The general procedure was followed by using *N*-(4-bromophenyl)quinazolin-4-amine (**1g**) (135 mg, 0.452 mmol), diphenylacetylene (**2a**) (81 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10.0 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3ga** (146 mg, 68%) as an off white solid; mp: 157-160 °C;  $R_f = 0.6$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.25 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.89 (t, *J* = 8 Hz, 2H), 7.73 (d, *J* = 8 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.38 (d, *J* = 4.4 Hz, 4H), 7.34-7.29 (m, 2H), 7.06-7.01 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.7, 154.7, 152.6, 138.4, 136.8, 134.7, 133.4, 130.8, 130.5, 130.2 (2C), 130.1 (2C), 128.7, 128.6 (2C), 128.5, 128.2 (2C), 127.9, 126.9, 126.5, 125.2, 122.6, 121.9, 118.6, 115.3, 112.7; HRMS (ESI): m/z calcd for C<sub>28</sub>H<sub>19</sub>N<sub>3</sub>Br ([M + H]<sup>+</sup>) 476.0762, found 476.0754.

4-(5-Bromo-2,3-di-*p*-tolyl-1*H*-indol-1-yl)quinazoline (3gb)



The general procedure was followed by using *N*-(4-bromophenyl)quinazolin-4-amine (**1g**) (135 mg, 0.452 mmol), 1,2-di-*p*-tolylethyne (**2b**) (93 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10.0 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3gb** (152 mg, 67%) as a yellow solid; mp: 161-165 °C;  $R_f$  = 0.6 (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.25 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 10 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 3H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.81 (d, *J* = 7.6 Hz, 2H), 2.39 (s, 3H), 2.16 (s, 3H); <sup>13</sup>C

NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.9, 154.8, 152.5, 138.5, 137.7, 136.8, 136.5, 134.6, 130.7, 130.5, 130.0 (2C), 129.9 (2C), 129.3 (2C), 128.9 (2C), 128.7, 128.5, 127.9, 126.2, 125.3, 122.6, 122.1, 118.2, 115.2, 112.5, 21.3, 21.2; HRMS (ESI): m/z calcd for C<sub>30</sub>H<sub>23</sub>N<sub>3</sub>Br ([M + H]<sup>+</sup>) 504.1075, found 504.1067.

4-(2,3-Diphenyl-5-(trifluoromethyl)-1*H*-indol-1-yl)quinazoline (3ha)



The general procedure was followed by using *N*-(4-(trifluoromethyl)phenyl)quinazolin-4-amine (**1h**) (131 mg, 0.452 mmol), 1,2diphenylethyne (**2a**) (80 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10.0 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3ha** (130 mg, 62%) as a white solid; mp: 175-178 °C;  $R_f = 0.3$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.28 (s, 1H), 8.12 (d, J = 8.4 Hz, 1H), 8.07 (s, 1H), 7.90 (t, J = 7.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 8.8 Hz, 1H), 7.41 (d, J = 4.4 Hz, 4H), 7.37-7.33 (m, 1H), 7.24 (d, J = 10.0 Hz, 1H), 7.07-7.00 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.5, 154.7, 152.6, 139.3, 139.0, 134.7, 133.1, 130.6, 130.2 (2C), 130.1 (2C), 128.8 (d, C-F J = 18.5 Hz), 128.6, 128.3, 128.2, 128.1, 127.1, 126.3, 125.07, 124.6, 124.3, 123.6, 121.9, 120.4 (d, C-F J = 3.4 Hz), 119.4, 117.8 (d, C-F J = 4.2 Hz), 117.7, 111.5; HRMS (ESI): m/z calcd for C<sub>29</sub>H<sub>18</sub>F<sub>3</sub>N<sub>3</sub>Na ([M + Na]<sup>+</sup>) 488.1351, found 488.1352.

4-(5-Nitro-2,3-diphenyl-1*H*-indol-1-yl)quinazoline (3ia)



The general procedure was followed by using *N*-(4-nitrophenyl)quinazolin-4-amine (**1i**) (120 mg, 0.452 mmol), 1,2-diphenylethyne (**2a**) (80 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10.0 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3ia** (110 mg, 55%) as a yellow solid; mp: 165-168 °C;  $R_f = 0.3$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.32 (s, 1H), 8.73 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 2H), 7.92 (t, *J* = 7.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41-7.38 (m, 5H), 7.22 (d, *J* = 9.2 Hz, 1H), 7.07-7.04 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.0, 154.7, 152.7, 143.5, 140.6, 140.2, 134.9, 132.4, 130.1 (3C), 130.0 (3C), 128.9, 128.8 (3C), 128.4, 128.3 (2C), 127.4, 124.7, 121.8, 120.1, 119.1, 117.1, 111.3; HRMS (ESI): m/z calcd for C<sub>28</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>Na ([M + Na]<sup>+</sup>) 465.1328, found 465.1329.

5-Methyl-4-(5-methyl-2,3-diphenyl-1*H*-indol-1-yl)quinazoline (3ja)



The general procedure was followed by using 5-methyl-*N*-(p-tolyl)quinazolin-4-amine (**1j**) (112.5 mg, 0.452 mmol), 1,2-diphenylethyne (**2a**) (80 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10.0 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol), and TBAB (146 mg, 0.452 mmol) to yielded **3ja** (123 mg, 64%) as a orange solid; mp: 235-238 °C;  $R_f = 0.5$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.17 (s, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.76 (t, J = 8.0 Hz, 1H), 7.56 (s, 1H), 7.41 (d, J = 7.2 Hz, 2H), 7.35 (t, J = 7.6 Hz, 3H), 7.27 (t, J = 7.4 Hz, 1H), 7.04-7.00 (m, 6H), 6.80 (d, J = 8.0 Hz, 1H), 2.44 (s, 3H), 2.19 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.2, 154.1, 153.9, 136.9, 136.6, 135.6, 134.4, 134.1, 131.3, 131.2, 131.1, 130.3 (2C), 130.2 (2C), 128.7, 128.4 (2C), 128.0 (2C), 127.5, 127.0, 126.4, 125.3, 123.1, 119.8, 118.8, 110.0, 21.5, 20.4; HRMS (ESI): m/z calcd for C<sub>30</sub>H<sub>23</sub>N<sub>3</sub>Na ([M + Na]<sup>+</sup>) 448.1790, found 448.1792.

7-Chloro-4-(5-methyl-2,3-diphenyl-1*H*-indol-1-yl)quinazoline (3ka)



### 

The general procedure was followed by using 7-Chloro-*N*-(*p*-tolyl)quinazolin-4-amine(**1k**) (121 mg, 0.452 mmol), diphenylacetylene (**2a**) (81 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10.0 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3ka** (131 mg, 65%) as a yellow solid; mp: 190-192 °C;  $R_f = 0.7$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.21 (s, 1H), 8.06 (d, J = 2.0 Hz, 1H), 7.75 (d, J = 8.8 Hz, 1H), 7.55 (s, 1H), 7.42-7.36 (m, 5H), 7.33-7.29 (m, 1H), 7.10-7.01 (m, 7H), 2.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.2, 155.8, 153.0, 140.8, 137.2, 136.5, 134.0, 131.8, 131.2, 130.3 (2C), 130.0 (2C), 129.2, 129.2, 128.5 (2C), 128.2 (2C), 127.7, 127.6, 127.2, 126.7, 125.4, 120.4, 119.8, 119.4, 110.8, 21.5; HRMS (ESI): m/z calcd for C<sub>29</sub>H<sub>21</sub>N<sub>3</sub>ClNa ([M + Na]<sup>+</sup>) 468.1244, found 468.1246.

4-(5-Bromo-2-(4-methoxyphenyl)-3-phenyl-1*H*-indol-1-yl)quinazoline (3gh) and 4-(5-Bromo-3-(4-methoxyphenyl)-2-phenyl-1*H*-indol-1-yl)quinazoline (3gh')



The general procedure was followed by using *N*-(4-bromophenyl)quinazolin-4-amine (**1g**) (135 mg, 0.452 mmol), 1-methoxy-4-(phenylethynyl)benzene (**2h**) (94 mg, 0.452 mmol), Pd(OAc)<sub>2</sub> (10.0 mg, 0.045 mmol), Cu(OAc)<sub>2</sub> (25 mg, 0.135 mmol) and TBAB (146 mg, 0.452 mmol) to yielded **3gh+3gh'** (297 mg, 65%) as a off white solid; mp: 178-180 °C;  $R_f$ = 0.7 (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.26 (d, *J* = 14.0 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.89-7.86 (m, 4H), 7.71 (dd, *J* = 8.4 & 8.0 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 4.0 Hz, 4H), 7.33-7.26 (m, 5H), 7.05-7.01 (m, 7H), 6.97-6.91 (m, 4H), 6.54 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 3.64 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.1, 158.8, 158.7, 158.6, 154.8, 154.7, 152.6, 152.5, 138.4, 138.1, 136.8, 136.7, 134.7, 134.6, 133.6, 131.3 (2C), 131.2 (2C), 130.9, 130.8, 130.5, 130.2, 130.1 (2C), 130.0 (2C), 128.7 (2C), 128.6 (2C), 128.5, 128.4, 128.2 (2C), 127.8, 126.8, 126.4, 126.2, 125.5, 125.3 (2C), 123.0, 122.6, 122.4, 122.0, 121.9, 118.3, 117.8, 115.2, 114.1 (2C), 113.7 (2C), 112.6, 112.5, 55.2, 55.0; HRMS (ESI): m/z calcd for C<sub>29</sub>H<sub>21</sub>BrN<sub>3</sub>O ([M + H]<sup>+</sup>) 506.0868, found 506.0868.

8. General Procedure for the Synthesis of Pyrido[2,3,4-*de*]quinazoline (4): To an oven-dried 10 mL round bottom flask were added appropriate quinazolin-4-amine (0.452 mmol), appropriate diphenylacetylene (0.452 mmol),  $[RuCl_2(p-cymene)]_2$  (0.022 mmol) and  $Cu(OAc)_2.H_2O$  (0.3 equiv.), and PEG-400 (3 mL). The mixture was stirred under open air for 12 h at 100 °C. After the completion of the reaction (as indicated by the TLC), the reaction was cooled to room temperature, the mixture was extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate was concentrated under reduced pressure. The crude product were purified by column chromatography using ethyl acetate and *n*-hexane gave the pyrido[2,3,4-*de*]quinazoline (4).

8. Analytical data of Pyrido[2,3,4-de]quinazoline (4)

4,5,6-Triphenyl-4*H*-pyrido[2,3,4-*de*]quinazoline (4aa)



The general procedure was followed by using *N*-phenylquinazolin-4-amine (**1a**) (100 mg, 0.452 mmol), diphenylacetylene (**2a**) (81 mg, 0.452 mmol),  $[RuCl_2(p-cymene)]_2$  (14 mg, 0.022 mmol) and  $Cu(OAc)_2.H_2O$  (27 mg, 0.135 mmol) to yielded **4aa** (117 mg, 65%) as an off white solid; mp: 290-293 °C;  $R_f = 0.4$  (50% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.24 (s, 1H), 7.69 (t, *J* = 8 Hz, 1H), 7.34 (d, *J* = 8 Hz, 1H), 7.28-7.25 (m, 6H), 7.17-7.15 (m, 4H), 7.10 (d, *J* = 8 Hz, 2H), 6.94-6.89 (m, 3H), 6.54 (d, *J* = 8.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  157.6, 156.5, 151.8, 142.0, 139.1, 138.9, 135.8, 135.7, 134.4, 133.9, 131.0 (2C), 130.5 (2C), 129.8 (2C), 128.7 (2C), 128.5 (2C), 127.7, 127.4, 127.0 (2C), 126.9, 121.3, 119.1, 115.2; HRMS (ESI): m/z calcd for C<sub>28</sub>H<sub>20</sub>N<sub>3</sub> ([M + H]<sup>+</sup>) 398.1657, found 398.1663.

4-Phenyl-5,6-di-p-tolyl-4H-pyrido[2,3,4-de]quinazoline (4ab)

CH3 H<sub>3</sub>C.



The general procedure was followed by using *N*-phenylquinazolin-4-amine (**1a**) (100 mg, 0.452 mmol), 1,2-di-p-tolylethyne (**2b**) (93 mg, 0.452 mmol), [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (14 mg, 0.022 mmol) and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (27 mg, 0.135 mmol) to yielded **4ab** (121 mg, 63%) as a brown solid; mp: 218-220 °C;  $R_f$ = 0.4 (50% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.23 (s, 1H), 7.65 (t, *J* = 6.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.24 (bs, 4H), 7.16 (s, 1H), 7.06 (d, *J* = 8 Hz, 4H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 2H), 6.51 (d, *J* = 8.0 Hz, 1H), 2.22 (s, 3H), 2.01 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  157.6, 156.5, 150.7, 141.9, 139.0, 136.3, 135.9 (2C), 134.3, 132.9, 131.2, 130.8 (2C), 130.3 (2C), 129.8 (2C), 129.2 (2C), 128.7 (2C), 127.6 (4C), 121.3, 119.0, 115.3, 20.7, 20.6; HRMS (ESI): m/z calcd for C<sub>30</sub>H<sub>24</sub>N<sub>3</sub> ([M + H]<sup>+</sup>) 426.1970, found 426.1967.

5,6-Bis(4-methoxyphenyl)-4-phenyl-4*H*-pyrido[2,3,4-*de*]quinazoline (4ac)



The general procedure was followed by using N-phenylquinazolin-4-amine (1a) (100 mg, 0.452 mmol), 1,2-bis(4methoxyphenyl)ethyne (2c) (108 mg, 0.452 mmol), [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (14 mg, 0.022 mmol) and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (27 mg, 0.135 mmol) to yielded 4ac (128 mg, 62%) as a brown solid; mp: 215-217 °C;  $R_f = 0.4$  (70% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  8.26 (s, 1H), 7.68 (s, 1H), 7.27 (s, 1H), 7.24 (s, 2H), 7.18 (d, J = 8.0 Hz, 1H), 7.07 (d, J = 7.6 Hz, 2H), 7.00 (d, J = 8.4Hz, 2H), 6.94 (t, J = 6.4 Hz, 1H), 6.84 (d, J = 8.0 Hz, 2H), 6.63 (t, J = 8.0 Hz, 1H), 6.55 (d, J = 7.2 Hz, 1H), 6.49 (d, J = 8 Hz, 2H), 3.69 (s, 3H), 3.53 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 157.8, 157.5, 156.4, 142.0, 139.1, 136.2, 134.4, 132.2 (2C), 131.6 (2C), 131.4, 129.8 (2C), 128.8 (2C), 128.0, 127.6, 126.4, 121.4, 118.9, 115.4, 115.3, 113.9 (2C), 112.3 (3C), 54.8, 54.7; HRMS (ESI): m/z calcd for  $C_{30}H_{24}N_3O_2$  ([M + H]<sup>+</sup>) 458.1869, found 458.1888.

5,6-Bis(4-fluorophenyl)-4-phenyl-4*H*-pyrido[2,3,4-*de*]quinazoline (4ad)



The general procedure was followed by using N-phenylquinazolin-4-amine (1a) (100 mg, 0.452 mmol), 1,2-bis(4-fluorophenyl)ethyne (2d) (97 mg, 0.452 mmol), [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (14 mg, 0.022 mmol) and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (27 mg, 0.135 mmol) to yielded 4ad (130 mg, 65%) as a pale yellow solid; mp: 228-230 °C;  $R_f = 0.5$  (50% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  8.25 (s, 1H), 7.70 (t, J = 5.6 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 4.0 Hz, 3H), 7.20-7.10 (m, 8H), 6.80 (t, J = 8.0 Hz, 2H), 6.54 (d, J = 8.0 Hz, 1H); <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ ):  $\delta$  162.5 (d, C–F J = 244.0 Hz), 160.5 (d, C–F J = 247.0 Hz), 158.1, 157.0 (2C), 151.2, 141.8, 139.4, 136.1, 135.0 (2C), 133.7 (d, C–F J = 7.5 Hz), 133.1 (d, C–F J = 7.5 Hz), 132.5, 130.9, 130.3 (3C), 129.4 (3C), 128.3, 121.1, 119.9, 117.5, 116.1 (d, C–F J = 21.4 Hz), 115.7, 114.6 (d, C–F J = 22.7 Hz); HRMS (ESI): m/z calcd for C<sub>28</sub>H<sub>18</sub>F<sub>2</sub>N<sub>3</sub> ([M + H]<sup>+</sup>) 434.1469, found 434.1467.

#### 5,6-diethyl-4-phenyl-4H-pyrido[2,3,4-de]quinazoline (4af)



The general procedure was followed by using N-phenylquinazolin-4-amine (1a) (100 mg, 0.452 mmol), hex-3-yne (2f) (37 mg, 0.452 mmol), [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (14 mg, 0.022 mmol) and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (27 mg, 0.135 mmol) to yielded 4af (82 mg, 60%) as a yellow solid; mp: 98-102 °C;  $R_f = 0.3$  (30% EtOAc/n-hexane); <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  8.23 (s, 1H), 7.76 (bs, 1H), 7.58 (t, J = 5.6Hz, 2H), 7.51 (d, J = 5.6 Hz, 1H), 7.35-7.29 (m, 3H), 7.18 (d, J = 6.0 Hz, 1H), 2.65-2.63 (m, 2H), 2.33-2.31 (m, 2H), 1.17 (t, J = 5.2 Hz, 2H), 7.51 (d, J = 5.6 Hz, 1H), 7.35-7.29 (m, 3H), 7.18 (d, J = 6.0 Hz, 1H), 2.65-2.63 (m, 2H), 2.33-2.31 (m, 2H), 1.17 (t, J = 5.2 Hz, 2H), 7.51 (d, J = 5.6 Hz, 2H), Hz, 3H), 0.91 (t, J = 5.4 Hz, 3H); <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ ):  $\delta$  157.7, 156.4, 142.3, 139.3, 134.9, 134.8, 130.2 (3C), 129.7 (3C), 129.1, 118.8, 118.6, 113.6, 22.8, 20.7, 13.9, 13.0; HRMS (ESI): m/z calcd for C<sub>20</sub>H<sub>19</sub>N<sub>3</sub>Na ([M + Na]<sup>+</sup>) 324.1477, found 324.1480.

#### 5,6-Diphenyl-4-(*p*-tolyl)-4*H*-pyrido[2,3,4-*de*]quinazoline (4ba)



The general procedure was followed by using N-(p-tolyl)quinazolin-4-amine (1b) (106 mg, 0.452 mmol), diphenylacetylene (2a) (81 mg, 0.452 mmol), [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (14 mg, 0.022 mmol) and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (27 mg, 0.135 mmol) to yielded **4ba** (121 mg, 65%) as an off white solid; mp: 275-278 °C;  $R_f = 0.5$  (50% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.24 (s, 1H), 7.67 (t, *J* = 8 Hz, 1H), 7.33 (d, J = 8 Hz, 1H), 7.25 (t, J = 6.0 Hz, 2H), 7.16 (t, J = 8.0 Hz, 3H), 7.11 (t, J = 8.0 Hz, 4H), 7.05 (d, J = 8 Hz, 2H), 6.94-6.92 (m, 3H), 6.52 (d, J = 8.0 Hz, 1H), 2.19 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  157.7, 156.6, 156.5, 142.1, 136.9, 136.4, 135.8, 135.7, 134.4, 134.0, 131.1, 130.9 (2C), 130.5 (2C), 129.5 (2C), 129.3 (2C), 128.5 (2C), 127.4, 127.0, 126.9 (2C), 121.3, 119.1, 115.1, 20.6; HRMS (ESI): m/z calcd for C<sub>29</sub>H<sub>22</sub>N<sub>3</sub> ([M + H]<sup>+</sup>) 412.1814, found 412.1820.

5,6-Bis(4-methoxyphenyl)-4-(p-tolyl)-4H-pyrido[2,3,4-de]quinazoline (4bc)



The general procedure was followed by using *N*-(*p*-tolyl)quinazolin-4-amine (**1b**) (106 mg, 0.452 mmol), 1,2-bis(4-methoxyphenyl)ethyne (**2c**) (108 mg, 0.452 mmol), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (14 mg, 0.022 mmol) and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (27 mg, 0.135 mmol) to yielded **4bc** (128 mg, 60%) as a brown solid; mp: 195-198 °C;  $R_f = 0.4$  (70% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.42 (s, 1H), 7.60 (t, *J* = 8 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8 Hz, 2H), 7.02-6.96 (m, 4H), 6.79-6.76 (m, 4H), 6.74 (d, *J* = 8 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 2H), 3.76 (s, 3H), 3.62 (s, 3H), 2.26 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.4, 158.3 (2C), 157.0, 141.9, 137.8, 136.5, 136.2, 134.3, 132.2 (2C), 132.0, 131.7 (2C), 129.9 (2C), 129.1 (2C), 128.6, 128.3, 126.7, 122.6, 119.6, 116.3, 114.0 (2C), 112.7 (2C), 55.1, 54.9, 21.2; HRMS (ESI): m/z calcd for C<sub>31</sub>H<sub>26</sub>N<sub>3</sub>O<sub>2</sub> ([M + H]<sup>+</sup>) 472.2025, found 472.2025. **4-(4-Methoxyphenyl)-5,6-diphenyl-4***H***-pyrido[2,3,4-***de***]quinazoline (4ea)** 



The general procedure was followed by using *N*-(4-methoxyphenyl)quinazolin-4-amine (**1e**) (113 mg, 0.452 mmol), diphenylacetylene (**2a**) (81 mg, 0.452 mmol),  $[RuCl_2(p-cymene)]_2(14$  mg, 0.022 mmol) and  $Cu(OAc)_2.H_2O$  (27 mg, 0.135 mmol) to yielded **4ea** (126 mg, 65%) as a brown solid; mp: 238-240 °C;  $R_f = 0.45$  (80% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.26 (s, 1H), 7.67 (t, *J* = 8 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.16 (t, *J* = 6.4 Hz, 5H), 7.10 (d, *J* = 6.4 Hz, 2H), 6.95-6.93 (m, 3H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.52 (d, *J* = 8 Hz, 1H), 3.66 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  158.1, 157.8, 156.6, 150.8, 142.4, 135.9, 135.7, 134.3, 134.1, 131.6, 130.9 (2C), 130.8 (2C), 130.5 (2C), 128.4 (2C), 127.4, 127.0, 126.9 (2C), 124.4, 121.2, 119.1, 115.1, 113.9 (2C), 55.1; HRMS (ESI): m/z calcd for C<sub>29</sub>H<sub>22</sub>ON<sub>3</sub> ([M + H]<sup>+</sup>) 428.1763, found 428.1780.

4,5,6-Tris(4-methoxyphenyl)-4*H*-pyrido[2,3,4-*de*]quinazoline (4ec)



The general procedure was followed by using *N*-(4-methoxyphenyl)quinazolin-4-amine (**1e**) (113 mg, 0.452 mmol), 1,2-bis(4-methoxyphenyl)ethyne (**2c**) (108 mg, 0.452 mmol),  $[RuCl_2(p-cymene)]_2$  (14 mg, 0.022 mmol) and  $Cu(OAc)_2$ .H<sub>2</sub>O (27 mg, 0.135 mmol) to yielded **4ec** (132 mg, 60%) as a white solid; mp: 158-160 °C;  $R_f$ = 0.3 (80% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.22 (s, 1H), 7.66 (t, *J* = 6.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* 

Hz, 2H), 6.84-6.80 (m, 4H), 6.54-6.51 (m, 3H), 3.70 (s, 3H), 3.69 (s, 3H), 3.56 (s, 3H); <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ ):  $\delta$  158.5, 158.4, 158.3 (2C), 157.0, 151.2, 142.9, 136.7, 134.8, 132.7 (2C), 132.4, 132.1 (2C), 131.3 (2C), 128.6, 127.1, 121.7, 119.3, 117.5, 115.6, 114.4 (4C), 112.9 (2C), 55.6, 55.3, 55.2; HRMS (ESI): m/z calcd for C<sub>31</sub>H<sub>26</sub>N<sub>3</sub>O<sub>3</sub> ([M + H]<sup>+</sup>) 488.1974, found 488.1972. **4-(4-Chlorophenyl)-5,6-diphenyl-4***H***-pyrido[2,3,4-***de***]quinazoline (4fa)** 



The general procedure was followed by using *N*-(4-chlorophenyl)quinazolin-4-amine (**1f**) (115 mg, 0.452 mmol), diphenylacetylene (**2a**) (81 mg, 0.452 mmol),  $[RuCl_2(p-cymene)]_2$  (14 mg, 0.022 mmol) and  $Cu(OAc)_2$ .H<sub>2</sub>O (27 mg, 0.135 mmol) to yielded **4fa** (123

mg, 63%) as an off white solid; mp: 198-200 °C;  $R_f = 0.4$  (30% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.44 (s, 1H), 7.63 (t, J = 8 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.25-7.22 (m, 4H), 7.19-7.16 (m, 1H), 7.10 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.96-6.94 (m, 3H), 6.89-6.87 (m, 2H), 6.75 (d, J = 8.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.2, 156.9, 141.3, 137.5, 135.7, 135.5, 134.5, 133.9, 133.8, 131.0 (2C), 130.9 (2C), 130.6 (2C), 129.5 (2C), 129.0, 128.6 (2C), 127.8, 127.5 (2C), 127.2, 122.9, 120.4, 117.7, 116.6; HRMS (ESI): m/z calcd for C<sub>28</sub>H<sub>19</sub>N<sub>3</sub>Cl ([M + H]<sup>+</sup>) 432.1268, found 432.1269.

4-(4-Chlorophenyl)-5,6-di-p-tolyl-4H-pyrido[2,3,4-de]quinazoline (4fb)



The general procedure was followed by using *N*-(4-chlorophenyl)quinazolin-4-amine (**1f**) (115 mg, 0.452 mmol), 1,2-di-*p*-tolylethyne (**2b**) (93 mg, 0.452 mmol), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (14 mg, 0.022 mmol) and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (27 mg, 0.135 mmol) to yielded **4fb** (127 mg, 61%) as an off white solid; mp: 180-182 °C;  $R_f$  = 0.45 (30% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.42 (s, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.06-7.03 (m, 4H), 6.97 (d, *J* = 8 Hz, 2H), 6.75-6.72 (m, 5H), 2.28 (s, 3H), 2.13 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.2, 156.9, 141.3, 137.7, 137.4, 136.7, 135.8, 134.5, 134.4, 133.8, 132.8, 131.0 (2C), 130.7 (2C), 130.4 (2C), 129.4 (2C), 129.2 (2C), 128.2 (2C), 127.7, 125.5, 120.2, 117.7, 116.6, 21.2, 21.1; HRMS (ESI): m/z calcd for C<sub>30</sub>H<sub>23</sub>ClN<sub>3</sub> ([M + H]<sup>+</sup>) 460.1581, found 460.1586.

4-(4-Bromophenyl)-5,6-diphenyl-4H-pyrido[2,3,4-de]quinazoline (4ga)



The general procedure was followed by using *N*-(4-bromophenyl)quinazolin-4-amine (**1g**) (135 mg, 0.452 mmol), diphenylacetylene (**2a**) (81 mg, 0.452 mmol),  $[\text{RuCl}_2(p\text{-cymene})]_2$  (14 mg, 0.022 mmol) and  $\text{Cu}(\text{OAc})_2$ .H<sub>2</sub>O (27 mg, 0.135 mmol) to yielded **4ga** (135 mg, 63%) as a brown solid; mp: 215-217 °C;  $R_f$ = 0.4 (30% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.26 (s, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.46 (d, J = 8 Hz, 2H), 7.36 (d, J = 8 Hz, 1H), 7.28-7.26 (m, 4H), 7.17-7.12 (m, 5H), 6.98-6.96 (m, 3H), 6.54 (d, J = 7.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  157.5, 156.4, 141.5, 138.3, 135.6, 134.5, 133.7, 132.2 (2C), 131.8 (2C), 131.4, 130.9 (2C), 130.4 (2C), 128.5 (2C), 127.7, 127.1 (2C), 121.5, 121.4, 121.0, 120.8, 119.4, 119.3, 115.4; HRMS (ESI): m/z calcd for C<sub>28</sub>H<sub>19</sub>N<sub>3</sub>Br ([M + H]<sup>+</sup>) 476.0762, found 476.0768.

5,6-Diphenyl-4-(4-(trifluoromethyl)phenyl)-4*H*-pyrido[2,3,4-de]quinazoline (4ha)



The general procedure was followed by using *N*-(4-(trifluoromethyl)phenyl)quinazolin-4-amine (**1h**) (130.6 mg, 0.452 mmol), 1,2diphenylethyne (**2a**) (80 mg, 0.452 mmol), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (14 mg, 0.022 mmol) and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (27 mg, 0.135 mmol) to

uphenyleunyle (2a) (30 mg, 0.452 mmor), [Rucl<sub>2</sub>(*p*-cyntenc)]<sub>2</sub> (14 mg, 0.022 mmor) and Cu(OAC)<sub>2</sub>:H<sub>2</sub>O (27 mg, 0.135 mmor) to yielded **4ha** (126 mg, 60%) as a off white solid; mp: 238-240 °C;  $R_f = 0.2$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.45 (s, 1H), 7.65 (bs, 1H), 7.53 (d, *J* = 7.6 Hz, 3H), 7.28-7.16 (m, 5H), 7.12 (d, *J* = 6.8 Hz, 2H), 6.93-6.88 (m, 5H), 6.77 (d, *J* = 7.6 Hz, 1H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.68; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 158.0, 142.1, 140.9, 135.6, 135.4, 134.5, 133.6, 130.9 (2C), 130.6 (2C), 130.3 (2C), 130.2, 129.8, 128.6 (3C), 127.9 (d, C–F *J* = 62.6 Hz), 127.3 (2C), 126.4, 126.3 (d, C–F *J* = 7.1 Hz), 126.2, 124.9, 123.1, 122.2, 120.7, 116.9; HRMS (ESI): m/z calcd for C<sub>29</sub>H<sub>18</sub>N<sub>3</sub>F<sub>3</sub>Na ([M + Na]<sup>+</sup>) 488.1351, found 488.1353. **8-Chloro-5,6-diphenyl-4-(***p***-tolyl)-4***H***-pyrido[2,3,4-***de***]quinazoline (4ka)** 



The general procedure was followed by using 7-chloro-*N*-(*p*-tolyl)quinazolin-4-amine (**1k**) (121 mg, 0.452 mmol), diphenylacetylene (**2a**) (81 mg, 0.452 mmol),  $[RuCl_2(p-cymene)]_2$  (14 mg, 0.022 mmol) and  $Cu(OAc)_2.H_2O$  (27 mg, 0.135 mmol) to yielded **4ka** (129 mg, 64%) as a brown solid; mp: 267-269 °C;  $R_f$ = 0.2 (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.45 (s, 1H), 7.42 (d, *J* = 2.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.20-7.17 (m, 1H), 7.09-7.06 (m, 4H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.94-6.92 (m, 3H), 6.89-6.86 (m, 2H), 6.66 (d, *J* = 4.0 Hz, 1H), 2.25 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.0, 157.9, 152.2, 143.3, 140.8, 138.1, 137.2, 136.0, 135.3, 133.8, 130.8 (2C), 130.6 (2C), 129.9 (2C), 129.1 (2C), 128.7 (2C), 127.7, 127.4, 127.3 (2C), 121.9, 119.5, 116.3, 116.2, 21.2; HRMS (ESI): m/z calcd for C<sub>29</sub>H<sub>21</sub>N<sub>3</sub>ClNa([M + Na]<sup>+</sup>) 468.1244, found 468.1243.

8-Chloro-4,5,6-tri-*p*-tolyl-4*H*-pyrido[2,3,4-*de*]quinazoline (4kb)



The general procedure was followed by using 7-chloro-*N*-(*p*-tolyl)quinazolin-4-amine (**1k**) (121 mg, 0.452 mmol), 1,2-di-*p*-tolylethyne (**2b**) (93 mg, 0.452 mmol), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (14 mg, 0.022 mmol) and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (27 mg, 0.135 mmol) to yielded **4kb** (128 mg, 60%) as a brown solid; mp: 125-130 °C;  $R_f = 0.3$  (20% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.43 (s, 1H), 7.40 (s, 1H), 7.06 (t, *J* = 10.0 Hz, 4H), 6.95 (t, *J* = 6.0 Hz, 4H), 6.75-6.73 (m, 4H), 6.66 (s, 1H), 2.28 (s, 3H), 2.26 (s, 3H), 2.11 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  157.9, 157.8, 151.9, 143.3, 140.9, 138.0, 137.5, 137.3, 136.9, 136.1, 132.3, 130.9, 130.6 (2C), 130.3 (2C), 129.9 (2C), 129.4 (2C), 129.0 (2C), 128.0 (2C), 122.0, 119.1, 116.3, 116.2, 21.2 (2C), 21.2; HRMS (ESI): m/z calcd for C<sub>31</sub>H<sub>25</sub>N<sub>3</sub>Cl ([M + H]<sup>+</sup>) 474.1737, found 474.1727.

4-(4-Bromophenyl)-7,8-dimethoxy-5,6-diphenyl-4*H*-pyrido[2,3,4-*de*]quinazoline (4la)



The general procedure was followed by using *N*-(4-bromophenyl)-6,7-dimethoxyquinazolin-4-amine (**1**I) (163 mg, 0.452 mmol), diphenylacetylene (**2a**) (81 mg, 0.452 mmol),  $[RuCl_2(p-cymene)]_2$  (14 mg, 0.022 mmol) and  $Cu(OAc)_2.H_2O$  (27 mg, 0.135 mmol) to yielded **4la** (133 mg, 55%) as a white solid; mp: 190-194 °C;  $R_f = 0.5$  (40% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.33 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.13-7.03 (m, 6H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.92-6.91 (m, 3H), 6.85-6.82 (m, 2H), 3.96 (s, 3H), 3.04 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.6, 157.3, 156.4, 149.6, 142.7, 139.2, 138.3 (2C), 134.0, 132.3 (2C), 131.5 (2C), 131.1 (2C), 130.7 (2C), 127.5, 127.3 (2C), 126.8 (2C), 126.5, 126.0, 121.9, 119.6, 113.0, 103.2, 60.7, 55.9; HRMS (ESI): m/z calcd for  $C_{30}H_{23}BrN_3O_2([M + H]^+)$  536.0973, found 536.0975.

4-Benzyl-5,6-diphenyl-4*H*-pyrido[2,3,4-*de*]quinazoline (4ma)



 $\sim \sim N^{\prime}$ 

The general procedure was followed by using *N*-benzylquinazolin-4-amine (**1m**) (106 mg, 0.452 mmol), diphenylacetylene (**2a**) (81 mg, 0.452 mmol),  $[RuCl_2(p-cymene)]_2$  (14 mg, 0.022 mmol) and  $Cu(OAc)_2.H_2O$  (27 mg, 0.135 mmol) to yielded **4ma** (117 mg, 63%) as a brown solid; mp: 236-239 °C;  $R_f$ = 0.5 (40% EtOAc/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): $\delta$  8.54 (s, 1H), 7.60 (t, *J* = 6.0 Hz, 1H), 7.47 (bs, 1H), 7.20-7.17 (m, 5H), 7.14-7.11 (m, 2H), 7.07-7.02 (m, 4H), 6.93-6.89 (m, 4H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.26 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  157.5, 157.1, 151.0, 142.1, 136.9, 136.0, 135.6, 134.2, 133.6, 130.6 (3C), 130.5 (2C), 128.4 (3C), 128.3 (2C), 127.7 (2C), 127.1 (2C), 126.7 (2C), 123.3, 119.9, 116.1, 49.3; HRMS (ESI): m/z calcd for C<sub>29</sub>H<sub>22</sub>N<sub>3</sub> ([M + H]<sup>+</sup>) 412.1813,found 412.1815.

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# 12. Copies of <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Products Compound 3aa







# **Compound 3ac**







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**Compound 3ea** 








































www.www.com.com/website/we

90 80 f1 (ppm) 











## Compound 3ka







Compound 3gh and 3gh'













# **Compound 4ab**





### **Compound 4ac**





# **Compound 4ad**





# **Compound 4af**



# **Compound 4ba**





# **Compound 4bc**







# **Compound 4ea**





## **Compound 4ec**



**Compound 4fa** 





S54

**Compound 4fb** 





## **Compound 4ga**



### 157.50 156.42 156.42 138.33 131.55 133.55 1133.55 1135.55 1135.55 1135.55 1135.55 1135.55 1135.55 1135.55 1135.55 1135.55 1135.55 1135.55 1135.55 1155.55 1155.55 1155.55 1155.55 1155





# Compound 4ha





## **Compound 4ka**



En









## **Compound 4la**



# **Compound 4ma**





# **Compound 1a**



## **Compound 1b**

















# **Compound 1e**







# **Compound 1f**









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## Compound-1n





