Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information: Part-1

Highly chemo- and regio-selective allylic substitution with tautomerizable heteroarenes

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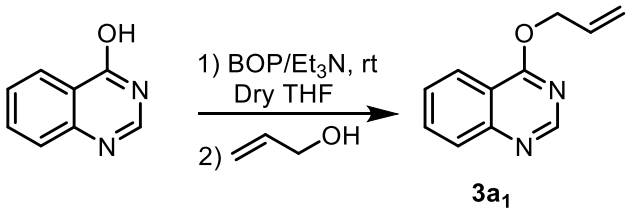
1) General Methods

All commercially obtained reagents/solvents were purchased from Alfa Aesar®, Sigma-Aldrich®, Acros®, TCI America®, Mallinckrodt®, and Oakwood® Products, and used as received without further purification. Unless stated otherwise, reactions were conducted in oven-dried glassware under nitrogen atmosphere in glove box. Glassware was oven-dried for at least 1 h prior to use. Thin layer chromatography (TLC) was performed on silica gel Whatman-60F glass plates, and components were visualized by illumination with UV light or by staining with potassium permanganate solution. Chromatography was performed using silica E. Merck silica gel 60 (230-400 mesh). ^{1}NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz and 100 MHz spectrometers respectively using TMS as an internal standard. Both ^{1}H and ^{13}C NMR chemical shifts were reported in parts per million downfield from tetramethylsilane (δ = 0). Data for ^{1} H NMR are reported as chemical shift (δ ppm) with the corresponding integration values. Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), br (broad), d (doublet), t (triplet), q (quartet) and m (multiplet). Data for ^{13}C NMR spectra are reported in terms of chemical shift (δ ppm). GC-MS analyses were performed on Agilent technologies GC coupled with ELSI mass spectrometer. High-resolution mass spectra were obtained at a Bruker Daltronics BioTOF HRMS spectrometer in positive (ESI^{+}) ion mode.

2) Synthesis of of authentic sample of $3a_1$, $3a_2$, and $3a_3$

2a) Synthesis of 4-(allyloxy) quinazoline ($3a_1$) [1]

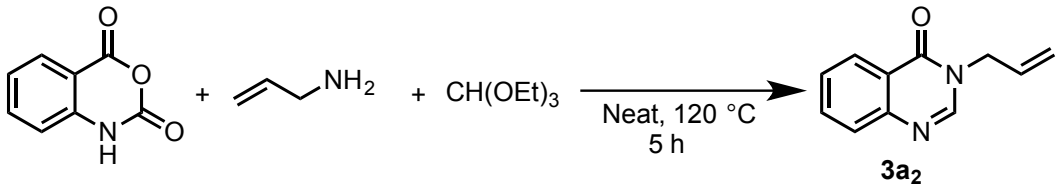


$3a_1$

Experimental procedure: In a glove box, to an oven dried 4 mL glass vial equipped with a stir bar, 4-hydroxy quinazoline **1a** (0.146 g, 1 mmol), BOP [(1-Benzotriazol-1-yloxy) tris (dimethylamino) phosphonium hexafluorophosphate] (0.885 g, 2 mmol, 2 equiv), Cs_2CO_3 (0.652 g, 2 mmol, 2 equiv) followed by dry THF (3 mL) was added and the reaction mixture was stirred at rt for 60 min. The resulting mixture was evaporated under reduced pressure, Cs_2CO_3 (0.652 g, 2 mmol, 2 equiv) and allyl alcohol **2d** (1.16 g, 20 mmol, 20 equiv) were added followed by stirring at rt until TLC (5 h) indicated complete reaction. The reaction mixture was diluted with water (10 mL) and extracted with EtOAc (3 x 10 mL). The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude products were adsorbed on silica gel and pass through the column (eluent: Hexane/EtOAc) to get analytically pure product **$3a_1$** (0.130 g, 70%) as yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, J = 2.9 Hz, 1H), 8.16 (t, J = 2.3 Hz, 1H), 7.92 (t, J = 3.7 Hz, 1H), 7.82-7.79 (m, 1H), 7.55-7.51 (m, 1H), 6.19-6.12 (m, 1H), 5.48 (dd, J = 17.2, 1.5 Hz), 5.34-5.31 (m, 1H),

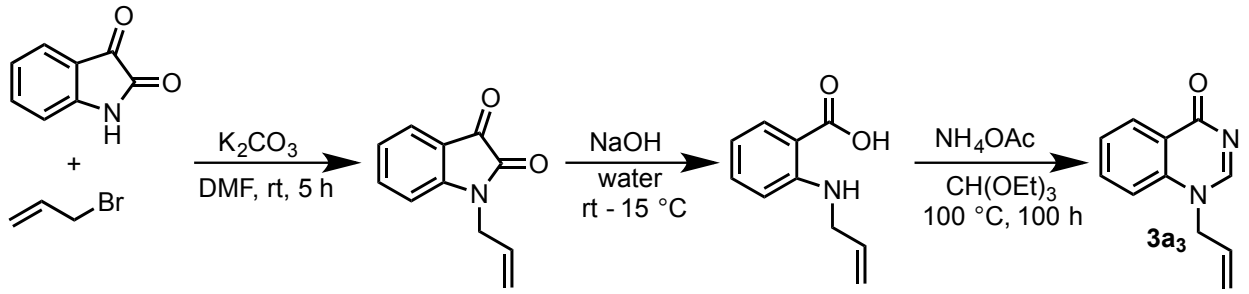
5.09 (d, J = 0.9 Hz, 1Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 154.3, 151.0, 133.5, 132.3, 127.7, 127.0, 123.5, 118.4, 116.6, 67.5; MS (ESI) *m/z*: 186.1 M^+.

2b) Synthesis of 3-allylquinazolin-4(3*H*)-one ($3a_2$)[2]



Experimental procedure: A mixture of isatoic anhydride (0.163 g, 1 mmol), allylamine (0.086 g, 1.5 mmol, 1.5 equiv), and triethyl orthoformate 3 (0.41 g, 2.5 mmol) were stirred magnetically at 120 °C (oil bath temp). After completion of the reaction (TLC, 5 h), the crude reaction mixture was recrystallized from EtOH to obtain analytically pure **3b** (0.134 g, 72%) as white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, J = 8.0 Hz, 1H), 8.04 (s, 1H), 7.80-7.72 (m, 2H), 7.55-7.50 (m, 1H), 6.07- 5.97 (m, 1H), 5.31 (t, J =10.1 Hz, 2H), 4.66 (d, J = 5.7 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 160.8, 148.1, 146.2, 134.3, 131.9, 127.5, 127.3, 126.8, 122.1, 118.9, 48.3; MS (ESI) *m/z*: 186.1 M^+.

2c) Synthesis of 1-allylquinazolin-4(1*H*)-one ($3a_3$)[3]



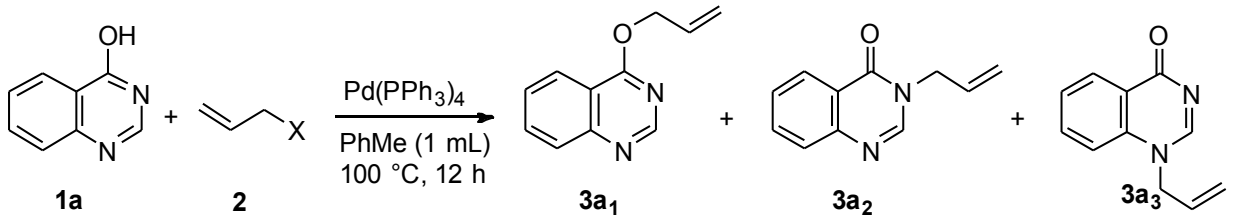
Experimental procedure: Step 1: To a solution of isatin (1.47 g, 10 mmol) in DMF (10 mL), potassium carbonate (1.65 g, 12 mmol, 1.2 equiv) and allyl bromide (3.62 g, 30 mmol, 3 equiv) were added. After reacting at rt for 5 h (monitored by TLC), the mixture was poured into ice water. The precipitate formed was filtered, dried and used as such without further purification.

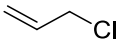
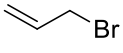
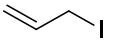
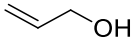
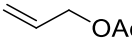
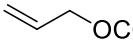
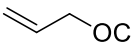
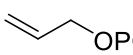
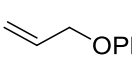
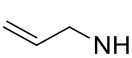
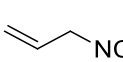
Step 2: A solution of sodium hydroxide (0.84 g, 21 mmol) in water (10 mL) was cooled in an ice-water bath. N-allyl isatin (10 mmol) was then added and dissolved. While maintaining the temperature of below 15 °C, a 30% aqueous solution of hydrogen peroxide (1.8 g, 52.8 mmol) was added dropwise. Stirring was continued at 15–20 °C for 2 h (monitored by TLC). The mixture was cooled in an ice bath and pH was adjusted to 5–6 with glacial acetic acid. After several hours of standing in refrigerator, the precipitate formed was collected by filtration, washed with ice water three times, and dried in air to give the 2-(*N*-allyl amino) benzoic acid.

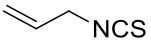
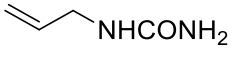
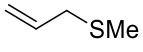
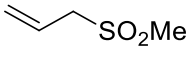
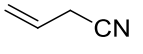
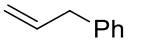
Step 3: A mixture of 2-(*N*-allyl amino) benzoic acid (0.53 g, 3 mmol), ammonium acetate (0.69 g, 9 mmol) and triethyl orthoformate (2.22 g, 15 mmol) was stirred at 100 °C for 10 h (monitored by TLC). Excess triethyl orthoformate was removed by rotary evaporation, and the residue was applied to a silica-gel column and eluted with DCM: MeOH (95:5) to give analytically pure **3c** (0.379 g, 68%) as white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24-8.22 (m, 2H), 7.67-7.62 (m, 1H), 7.41-7.37 (m, 1H), 7.29 (d, J = 8.4 Hz 1H), 6.00 - 5.90 (m, 1H), 5.31-5.28 (m, 1H), 5.19-5.15 (m, 1H), 4.74 (d, J = 4.9 Hz 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 153.3, 139.2, 133.8,130.6, 128.7, 124.4, 120.4, 119.3, 115.4, 52.2; MS(ESI) *m/z*: 186.1 M^+.

3) Investigation of allylating reagents for selectivity control under base free condition

Table 1: Reaction of **1a** with different allylating reagents **2** in presence of $Pd(PPh_3)_4$ under base-free condition .[A]



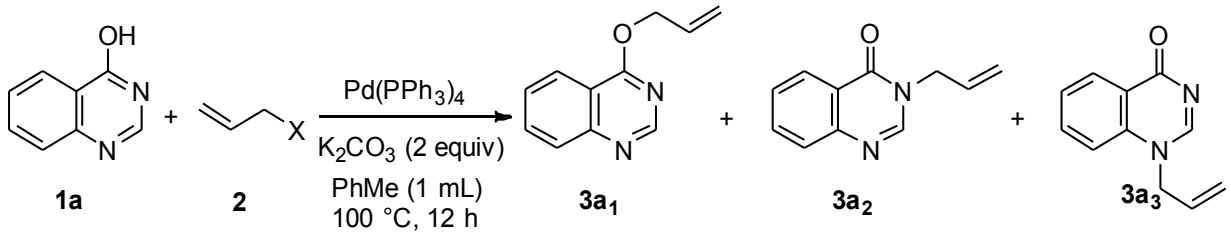
Entry	Allylating agent	% Conversion[b]			Selectivity	Yield (%)[c]
		3a$_1$	**3a$_2$**	**3a$_3$**	**3a$_1$: 3a$_2$: 3a$_3$**	**3a$_2$**
1	**2a**; 	0	0	0	N/A	0
2	**2b**; 	0	76	0	00 : 100 : 00	62[d]
3	**2c**; 	0	81	0	00 : 100 : 00	68[d]
4	**2d**; 	0	82	0	00 : 100 : 00	70[d]
5	**2e**; 	0	85	0	00 : 100 : 00	71[d]
6	**2f**; 	3	85	0	03 : 97 : 00	72[d]
7	**2g**; 	0	95	0	00 : 100 : 00	88[d]
8	**2h**; 	0	100	0	00 : 100 : 00	86[d]
9	**2i**; 	0	0	0	N/A	0
10	**2j**; 	0	0	0	N/A	0
11	**2k**; 	4	65	0	06 : 94 : 00	52[d]

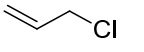
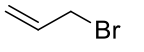
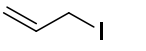
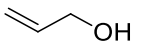
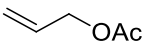
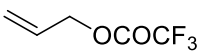
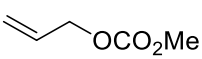
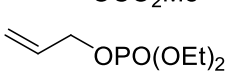
12	**2l**; 	0	0	0	N/A	0
13	**2m**; 	6	60	0	10 : 90 : 00	49[d]
14	**2n**; 	0	26	0	00 : 100 : 00	15[d]
15	**2o**; 	0	38	0	00 : 25 : 00	25[d]
16	**2p**; 	0	0	0	N/A	0
17	**2q**; 	0	0	0	N/A	0

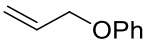
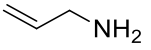
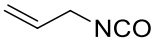
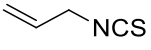
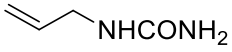
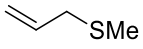
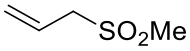
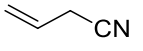
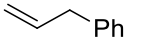
[a]**1a** (0.5 mmol) was treated with different allylating reagents **2** (2 equiv, 1 mmol) in PhMe (1 mL) at 100 °C in presence of $Pd(PPh_3)_4$ (10 mol %) for 12 h. [b]Based on GC-MS. [c]Isolated yield of **3a₂**. [d]No product formation was observed (**1a** was found intact) in absence of catalyst.

4) Investigation of allylating reagents for selectivity control under basic condition

Table 2: Reaction of **1a** with different allylating reagents **2** in presence of $Pd(PPh_3)_4$ in the under basic condition.[a]



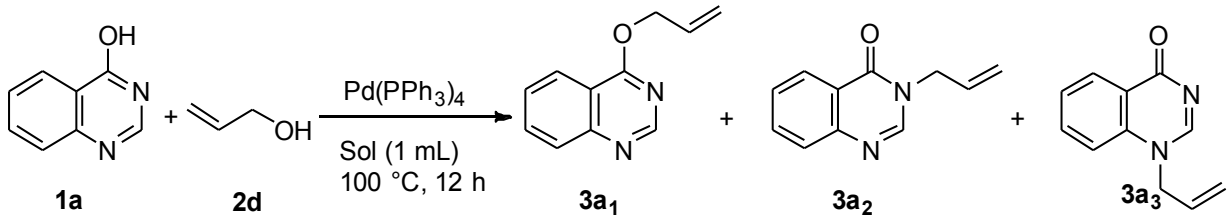
Entry	Allylating agent	% Conversion[b]			Selectivity	Yield (%)[c]
		3a₁	**3a₂**	**3a₃**	**3a₁ : 3a₂ : 3a₃**	**3a₂**
1	**2a**; 	0	73	0	00 : 100 : 00	60
2	**2b**; 	0	100	0	00 : 100 : 00	89
3	**2c**; 	0	100	0	00 : 100 : 00	88
4	**2d**; 	0	92	0	00 : 100 : 00	79[d]
5	**2e**; 	0	85	0	00 : 100 : 00	73[d]
6	**2f**; 	3	92	0	03 : 97 : 00	79[d]
7	**2g**; 	0	100	0	00 : 100 : 00	90[d]
8	**2h**; 	0	100	0	00 : 100 : 00	91[d]

9	**2i**; 	6	88	0	06 : 94 : 00	74[d]
10	**2j**; 	0	25	0	00 : 100 : 00	12[d]
11	**2k**; 	10	85	0	11 : 89 : 00	73[d]
12	**2l**; 	0	97	0	00 : 100 : 00	81[d]
13	**2m**; 	6	45	0	12 : 88 : 00	27[d]
14	**2n**; 	0	38	0	00 : 100 : 00	24[d]
15	**2o**; 	0	51	0	00 : 100 : 00	37[d]
16	**2p**; 	0	0	0	N/A	0
17	**2q**; 	0	0	0	N/A	0

[a]**1a** (0.5 mmol) was treated with different allylating reagents **2** (2 equiv, 1 mmol) in PhMe (1 mL) at 100 °C in presence of $Pd(PPh_3)_4$ (10 mol %) and K_2CO_3 (2 equiv, 1 mmol) for 12 h. [b]Based on GC-MS. [c]Isolated yield of **3a₂**. [d]No product formation was observed (**1a** was found intact) in absence of catalyst except for entry 1-3 where mixture of **3a₁** and **3a₂** was **f**ormed.

5) Effect of solvents on the selectivity control

Table 3: Reaction of **1a** with allyl alcohol **2d** in different solvents under $Pd(PPh_3)_4$ catalysis.[a]



1a **2d** **3a₁** **3a₂** **3a₃**

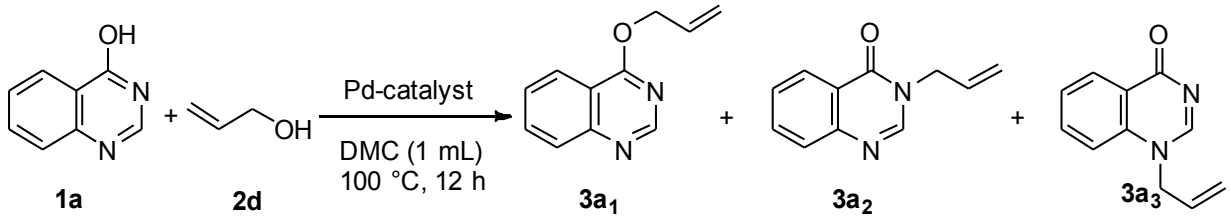
Entry	Solvent	% Conversion[b]			Selectivity	Yield (%)[c]
		3a₁	**3a₂**	**3a₃**	**3a₁ : 3a₂ : 3a₃**	**3a₂**
1	MeOH	9	60	0	13 : 87 : 00	47
2	EtOH	5	90	0	05 : 95 : 00	78
3	TFE	2	97	0	02 : 98 : 00	81
4	1,4-Dioxane	0	97	0	00 : 100 : 00	84
5	THF	0	37	0	00 : 86 : 00	25
6	DMF	0	93	0	00 : 100 : 00	82
7	DMSO	0	96	0	00 : 100 : 00	85

8	PhMe	0	83	0	00 : 100 : 00	70
9	PhH	0	89	0	00 : 100 : 00	75
10	DCE	0	79	0	00 : 100 : 00	67
11	DMC	0	100	0	00 : 100 : 00	92
12	$MeNO_2$	5	46	0	09 : 91 : 00	29
13	MeCN	0	93	0	00 : 96 : 00	80

[a]**1a** (0.5 mmol) was treated with **2d** (2 equiv, 1 mmol) in various solvents (1 mL) at 100 °C in presence of $Pd(PPh_3)_4$ (10 mol%) for 12 h. [b]Based on GC-MS. [c]Isolated yield of **3a₂**.

6) Effect of different Pd-catalysts on the selectivity control

Table 4: Reaction of **1a** with allyl alcohol (**2d**) in presence of different Pd-catalysts using DMC as solvent.[a]

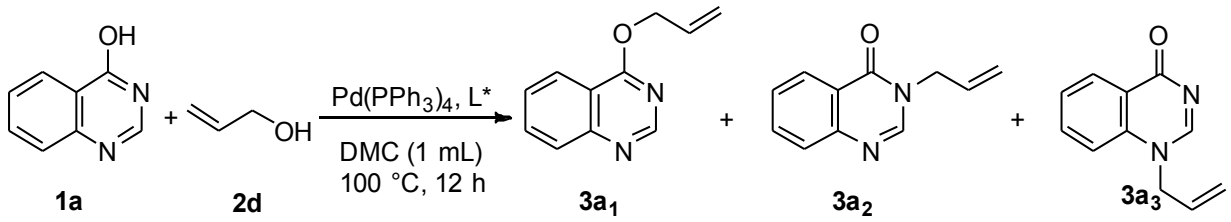


Entry	Catalyst	% Conversion[b]			Selectivity	Yield (%)[c]
		3a₁	**3a₂**	**3a₃**	**3a₁ : 3a₂ : 3a₃**	**3a₂**
1	$PdCl_2$	0	21	0	00 : 100 : 00	12
2	$Pd(OAc)_2$	0	18	0	00 : 100 : 00	10
3	$(PPh_3)_4Pd$	0	100	0	00 : 100 : 00	91
4	$(PPh_3)_2PdCl_2$	0	8	0	00 : 100 : 00	traces
5	$(TFA)_2Pd$	0	41	0	00 : 100 : 00	28
6	$[PdCl(C_3H_5)]_2$	0	40	0	00 : 100 : 00	28
7	$(C_6H_5CN)_2PdCl_2$	0	13	0	00 : 100 : 00	traces
8	$Pd_2(dba)_3$	0	12	0	00 : 100 : 00	traces
9	$Pd(dppf)Cl_2$	0	5	0	00 : 100 : 00	traces

[a]**1a** (0.5 mmol) was treated with **2d** (2 equiv, 1 mmol) in DMC (1 mL) at 100 °C in presence of different Pd-catalysts (10 mol%) for 12 h. [b]Based on GC-MS. [c]Isolated yield of **3a₂**.

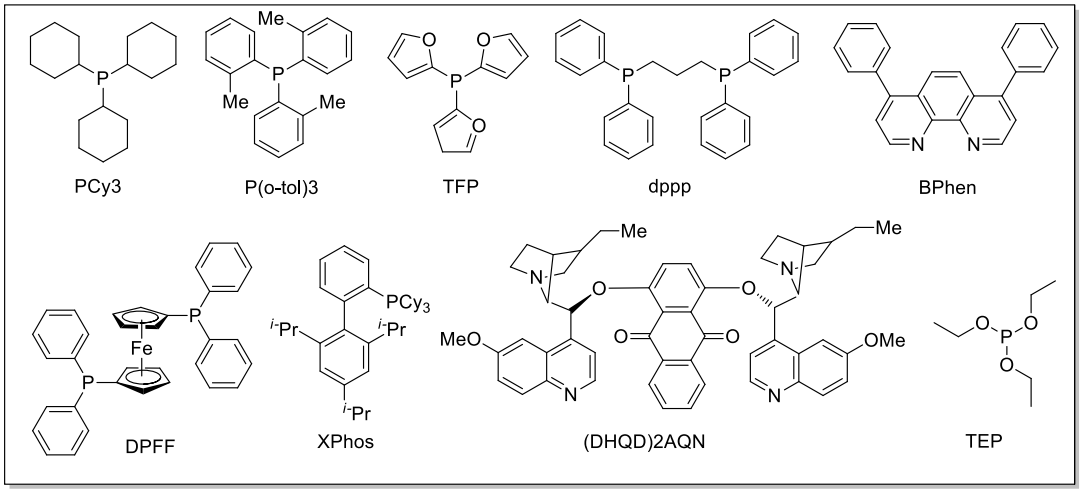
7) Effect of ligands on the selectivity control

Table 5: Reaction of **1a** with allyl alcohol **2d** in presence of different ligands under $(PPh_3)_4Pd$ catalysis using DMC as solvent.[a]



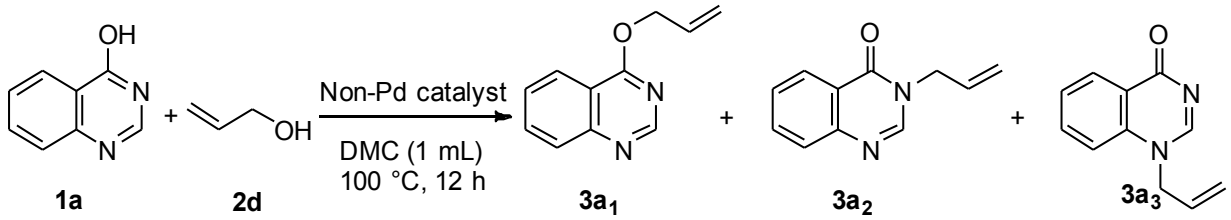
Entry	Ligand	% Conversion[b]			Selectivity	Yield (%)[c]
		$3a_1$	**$3a_2$**	**$3a_3$**	**$3a_1 : 3a_2 : 3a_3$**	**$3a_2$**
1	PCy_3	0	96	0	00 : 100 : 00	85
2	P(*o*-tol)$_3$	0	87	0	00 : 100 : 00	76
3	TFP	0	91	0	00 : 100 : 00	78
4	dppp	3	70	0	04 : 96 : 00	67
5	BPhen	4	88	0	04 : 96 : 00	92
6	DPFF	0	95	0	00 : 100 : 00	83
7	XPhos	0	86	0	00 : 100 : 00	72
8	$(DHQD)_2AQN$	5	93	0	05 : 95 : 00	84
9	TEP	5	82	0	06 : 94 : 00	70

[a]**1a** (0.5 mmol) was treated with **2d** (2 equiv, 1 mmol) in dimethyl carbonate (1 mL) at 100 °C in presence of $Pd(PPh_3)_4$ (10 mol%) and different ligands (20 mol%) for 12 h. [b]Based on GC-MS. [c]Isolated yield of **$3a_2$**.



8) Effect of non-Pd transition metal catalysts on the selectivity control

Table 6: Reaction of **1a** with allyl alcohol **2d** in presence of different non-palladium transition metal catalysts under ligand and base free condition.[a]

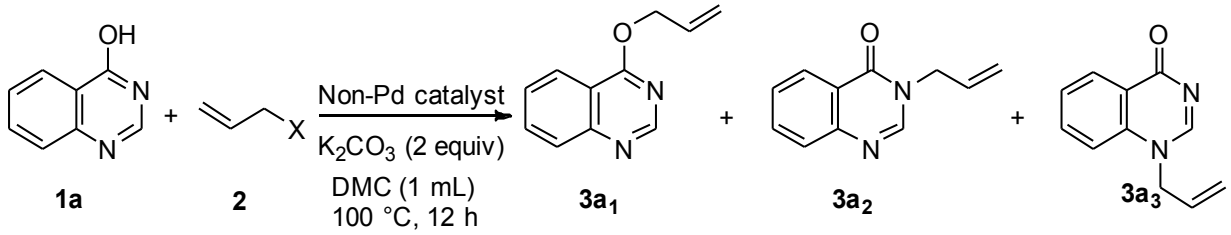


1a **2d** **3a$_1$** **3a$_2$** **3a$_3$**

Entry	Catalyst	% Conversion[b]			Selectivity	Yield (%)[c]
		3a$_1$	**3a$_2$**	**3a$_3$**	**3a$_1$: 3a$_2$: 3a$_3$**	**3a$_2$**
1	$[Ir(1,5\text{-cod})Cl]_2$	0	32	0	00 : 100 : 00	20
2	$RhCl(PPh_3)_3$	0	14	0	00 : 100 : 00	traces
3	$Ni(PPh_3)_4$	0	15	0	00 : 100 : 00	traces
4	$[Ru(p\text{-cymene})Cl_2]_2$	0	0	0	N/A	0
5	$Fe(acac)_3$	0	0	0	N/A	0
6	$(Ph_3P)AuCl$	0	0	0	N/A	0
7	CuI(I)	0	0	0	N/A	0
8	Zirconocene dichloride	0	0	0	N/A	0

[a]**1a** (0.5 mmol) was treated with **2d** (2 equiv, 1 mmol) in DMC (1 mL) at 100 °C in presence of different non-palladium transition metal catalysts (10 mol%) for 12 h. [b]Based on GC-MS. [c]Isolated yield of **3a$_2$**.

Table 7: Reaction of **1a** with allyl alcohol **2d** in presence of different non-palladium transition metal catalysts under basic condition.[a]

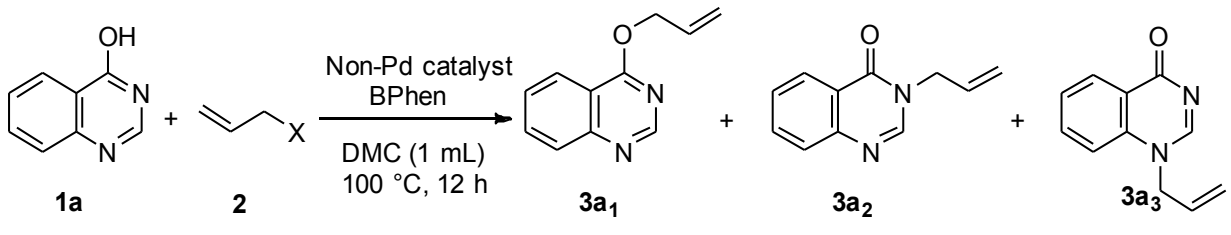


1a **2** **3a$_1$** **3a$_2$** **3a$_3$**

Entry	Catalyst	% Conversion[b]			Selectivity	Yield (%)[c]
		3a$_1$	**3a$_2$**	**3a$_3$**	**3a$_1$: 3a$_2$: 3a$_3$**	**3a$_2$**
1	$[Ir(1,5\text{-cod})Cl]_2$	0	30	0	00 : 100 : 00	17
2	$RhCl(PPh_3)_3$	0	12	0	00 : 100 : 00	traces
3	$Ni(PPh_3)_4$	0	52	0	00 : 100 : 00	36
4	$[Ru(p\text{-cymene})Cl_2]_2$	0	23	0	00 : 100 : 00	12
5	$Fe(acac)_3$	0	22	0	00 : 100 : 00	10
6	$(Ph_3P)AuCl$	0	19	0	00 : 100 : 00	10
7	CuI(I)	0	27	0	00 : 100 : 00	15
8	Zirconocene dichloride	0	0	0	N/A	0

[a]**1a** (0.5 mmol) was treated with **2d** (2 equiv, 1 mmol) in dimethyl carbonate (1 mL) at 100 °C in presence of different non-palladium transition metal catalysts (10 mol%) and K_2CO_3 (2 equiv) for 12 h. [b]Based on GC-MS. [c]Isolated yield of **3a$_2$**.

Table 8: Reaction of **1a** with allyl alcohol **2d** under non-palladium transition metal catalysis in presence of bathophenanthroline (Bhpen).[a]



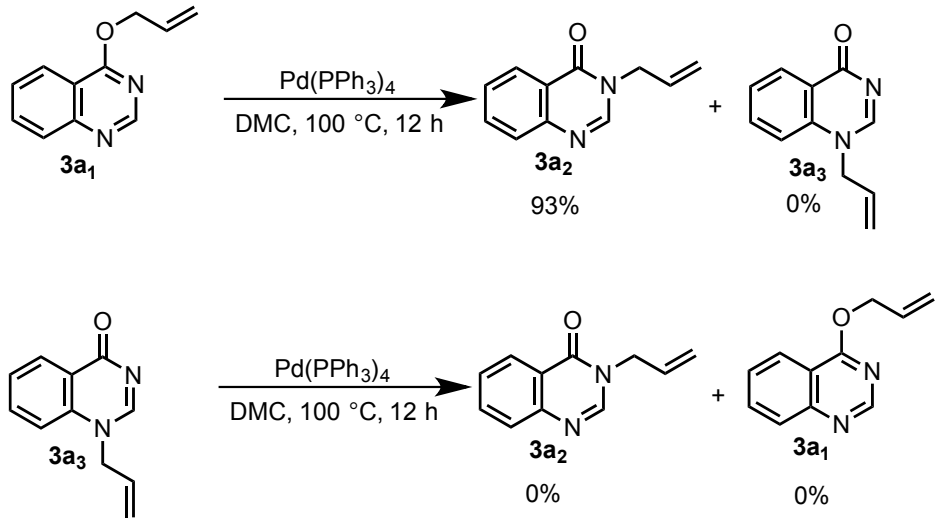
1a **2** **3a$_1$** **3a$_2$** **3a$_3$**

Entry	Catalyst	% Conversion[b]			Selectivity	Yield (%)[c]
		3a$_1$	**3a$_2$**	**3a$_3$**	**3a$_1$: 3a$_2$: 3a$_3$**	**3a$_2$**
1	$[Ir(1,5\text{-cod})Cl]_2$	0	36	0	00 : 100 : 00	24

2	$RhCl(PPh_3)_3$	0	25	0	00 : 100 : 00	18
3	$Ni(PPh_3)_4$	0	32	0	00 : 100 : 00	21
4	$[Ru(p\text{-cymene})Cl_2]_2$	0	0	0	N/A	0
5	$Fe(acac)_3$	0	0	0	N/A	0
6	$(Ph_3P)AuCl$	0	0	0	N/A	0
7	CuI(I)	0	0	0	N/A	0
8	Zirconocene dichloride	0	0	0	N/A	0

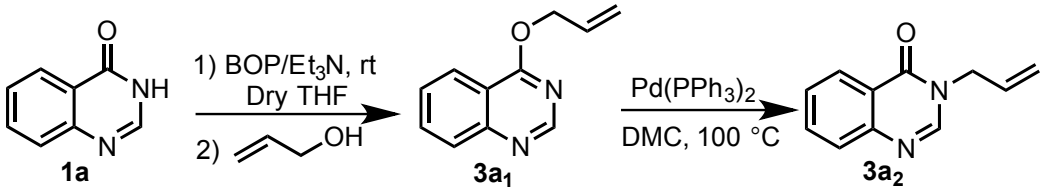
[a]**1a** (0.5 mmol) was treated with **2d** (2 equiv, 1 mmol) in DMC (1 mL) at 100 °C in presence of different non-palladium transition metal catalysts (10 mol%) and BPhen (20 mol%) for 12 h. [b]Based on GC-MS. [c]Isolated yield of $\mathbf{3a_2}$.

9) Investigation of allylic disposition under reaction condition



Representative experimental procedure: In a glove box, to an oven dried 4 mL glass vial equipped with a stirring bar, $\mathbf{3a_1}$ (0.093 g, 0.5 mmol), $Pd(PPh_3)_4$ (0.578 g, 0.05 mmol, 10 mol%), followed by DMC (1 mL) was added and the reaction mixture was stirred at 100 °C for 12 h. Then the reaction mixture was cooled to rt, diluted with MeOH (2 x 10 mL) and passed through bed of celite to remove catalyst. An aliquot portion (100 μL) of the organic layer was taken out, diluted with MeOH and subjected to GCMS to observe the selectivity. The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude products were adsorbed on to silica gel and passed through the column (eluent: Hexane/EtOAc) to get analytically pure product $\mathbf{3a_2}$ as white solid (0.086 g, 93%).

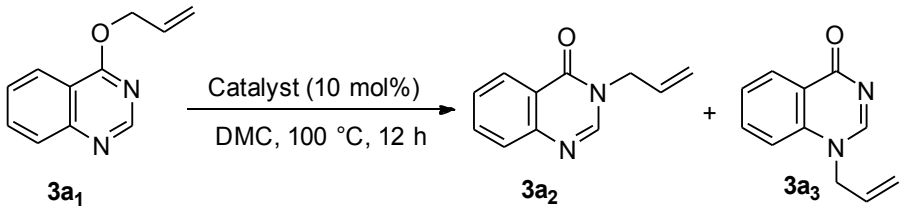
10) Investigation of allylic disposition from in-situ generated $3a_1$



Representative experimental procedure: In a glove box, to an oven dried 4 mL glass vial equipped with a stirring bar, **1a** (0.731 g, 0.5 mmol), BOP reagent (0.442 g, 1 mmol, 2 equiv), Cs_2CO_3 (0.326 g, 1 mmol, 2 equiv) followed by dry Dioxane (2 mL) was added and the reaction mixture was stirred at rt for 60 min. The resulting mixture was evaporated under reduced pressure, Cs_2CO_3 (0.326 g, 1 mmol, 2 equiv) and allyl alcohol **2d** (10 mmol, 20 equiv) were added followed by stirring at rt until TLC (5 h) indicated complete reaction. To the above resulting reaction mixture, $Pd(PPh_3)_4$ (0.578 g, 0.05 mmol, 10 mol%) followed by DMC (1 mL) was added and the resultant reaction mixture was stirred at 100 °C for 12 h. After stipulated time period, the reaction mixture was cooled to rt, diluted with water (10 mL) and extracted with EtOAc (3 x 10 mL). The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude products were adsorbed on to silica gel and passed through the column (eluent: Hexane/EtOAc) to get analytically pure product **$3a_2$** as white solid (0.067 g, 72%).

11) Investigation of allylic migration from $3a_1$ in the presence of different catalysts under reaction conditions

Table 9: Treatment of **$3a_1$** in the presence of different catalysts under reaction conditions.[a]



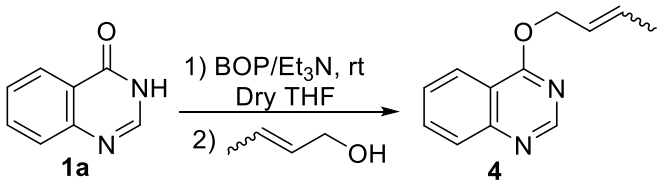
Entry	Catalyst	% Conversion[b]		Selectivity[b]	Yield (%)[c]
		$3a_2$	**$3a_3$**	**$3a_2$: $3a_3$**	**$3a_2$**
1	None	0	0	N/A	0
2	K_2CO_3	0	0	N/A	0
3	$In(OTf)_3$	0	0	N/A	0
4	$(PPh_3)_4Pd$	100	0	100 : 00	93

[a]**3a$_1$** (0.5 mmol) was subjected to under reaction condition in presence of different catalysts/additives in DMC (1 mL) at 100 °C for 12 h. [b] Based on GC-MS. [b] Isolated yield of **3a$_2$**.

Representative experimental procedure: In a glove box, to an oven dried 4 mL glass vial equipped with a stirring bar, **3a$_1$** (0.093 g, 0.5 mmol), $Pd(PPh_3)_4$ (0.578 g, 0.05 mmol, 10 mol%) followed by DMC (1 mL) was added and the reaction mixture was stirred at 100 °C for 12 h. After stipulated time period, the reaction mixture was cooled to rt, diluted with MeOH (2 x 10 mL) and passed through bed of celite to remove catalyst. An aliquot portion (100 μL) of the organic layer was taken out, diluted with MeOH and subjected to GCMS to observe the selectivity. The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude products were adsorbed on silica gel and passed through the column (eluent: Hexane/EtOAc) to get analytically pure product **3a$_2$** as white solid (0.086 g, 93%).

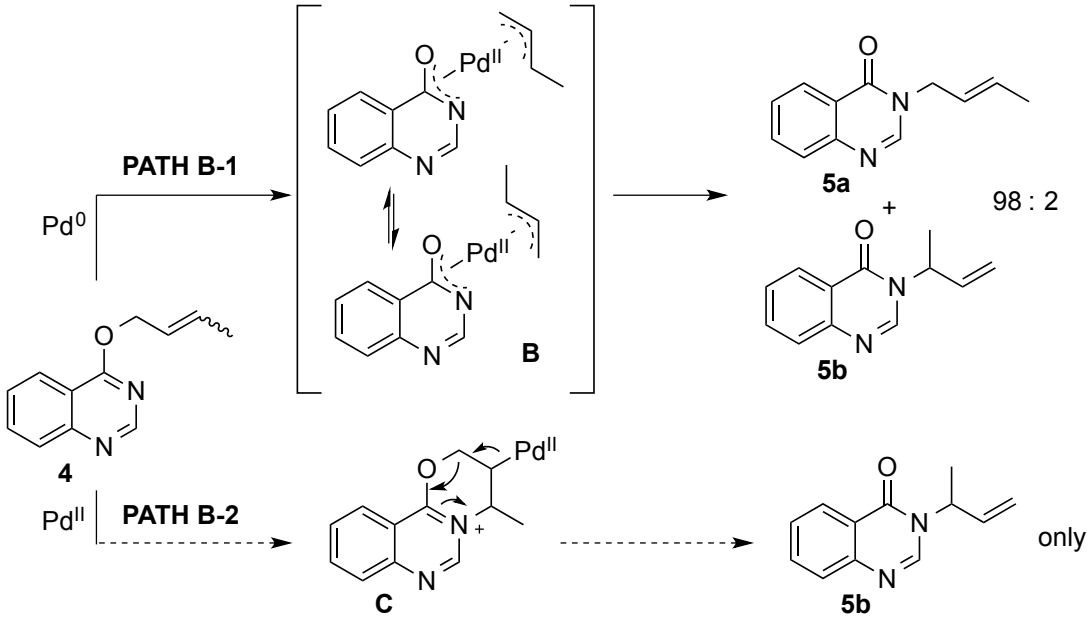
12) Validation of route B-1 / B-2: Investigation of allylic migration from 4

12a) Synthesis of (E)-4-(but-2-en-1-yloxy)quinazoline (4)[1]



Experimental procedure: In a glove box, to an oven dried 10 mL glass vial equipped with a stirring bar, 4-hydroxy quinazoline **1a** (0.292 g, 2 mmol), BOP reagent (1.77 g, 4 mmol, 2 equiv), Cs_2CO_3 (1.304 g, 2 mmol, 2 equiv) followed by dry Dioxane (6 mL) was added and the reaction mixture was stirred at rt for 60 min. The resulting mixture was evaporated under reduced pressure, Cs_2CO_3 (1.304 g, 4 mmol, 2 equiv) and 2-buten-1-ol (2.88 g, 40 mmol, 20 equiv) were added followed by stirring at the rt until TLC (5 h) indicated reaction completion. After stipulated time period, the reaction mixture was diluted with water (15 mL) and extracted with EtOAc (3 x 15 mL). The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude products were adsorbed on to silica gel and passed through the column (eluent: Hexane/EtOAc) to get analytically pure product **4** (0.288 g, 72%) as yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 1H), 8.19 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.84-7.80 (m, 1H), 7.57-7.53 (m, 1H), 5.99-7.89 (m, 1H), 5.87-7.83 (m, 1H), 5.03 (dd, *J* = 6.2, 0.9 Hz, 1H), 1.78 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.5, 154.4, 150.9, 133.4, 131.6, 127.6, 126.9, 125.2, 123.6, 116.7, 67.6, 17.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{13}N_2O$ 201.1028, Found 201.1031.

12b) Representative experimental procedure for the validation of route B-1 / B-2:

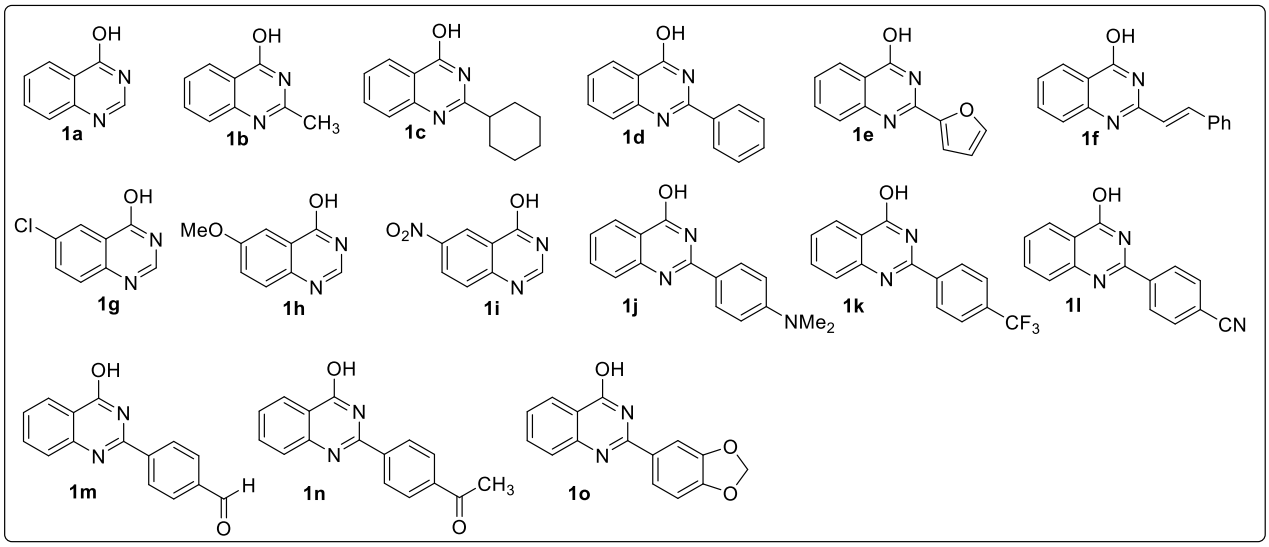


In a glove box, to an oven dried 4 mL glass vial equipped with a stirring bar, **4** (0.1 g, 0.5 mmol), $Pd(PPh_3)_4$ (0.578 g, 0.05 mmol, 10 mol%) followed by DMC (1 mL) was added and the reaction mixture was stirred at 100 °C for 12 h. After stipulated time period, the reaction mixture was cooled to rt, diluted with MeOH (2 x 10 mL) and passed through bed of celite to remove catalyst. An aliquot portion (100 µL) of the organic layer was taken out, diluted with MeOH and subjected to GCMS to observe the selectivity. The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude products were adsorbed on silica gel and passed through the column (eluent: Hexane/EtOAc) to get analytically pure product **5a** as white solid (0.074 g, 74%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (td, J = 8.1, 1.4 Hz, 1H), 7.98 (s, 1H), 7.67-7.62 (m, 2H), 7.44-7.39 (m, 1H), 5.76-5.70 (m, 1H), 5.61-5.57 (m, 1H), 4.50 (td, J = 7.4, 2.3 Hz, 2H), 1.67-1.65 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 160.7, 148.0, 146.2, 146.1, 134.0, 131.0, 130.0, 127.3, 127.12, 127.10, 126.7, 126.6, 124.8, 123.9, 122.1, 47.8, 42.7, 17.6, 13.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{13}N_2O$ 201.1028, Found 201.1030.

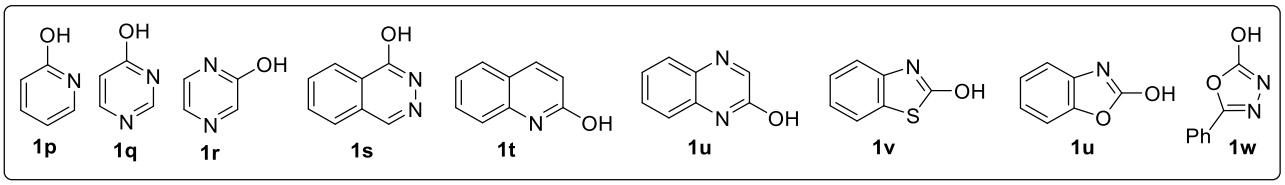
13) Preparation of substrates

1a and **1p-1w** were purchased from Sigma-Aldrich and Alfa Aesar. Compounds **1b-1o** and **1x** were prepared according to literature report. All allyl alcohols were purchased from Sigma-Aldrich and used as such.

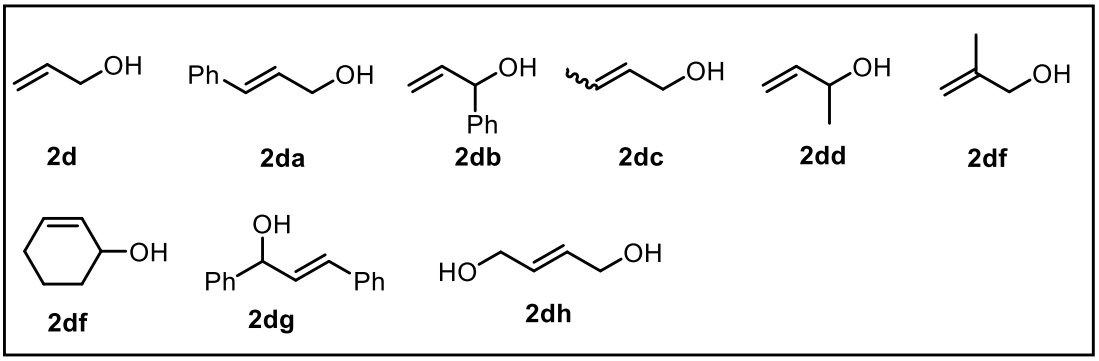
4-Hydroxy quinazolines:



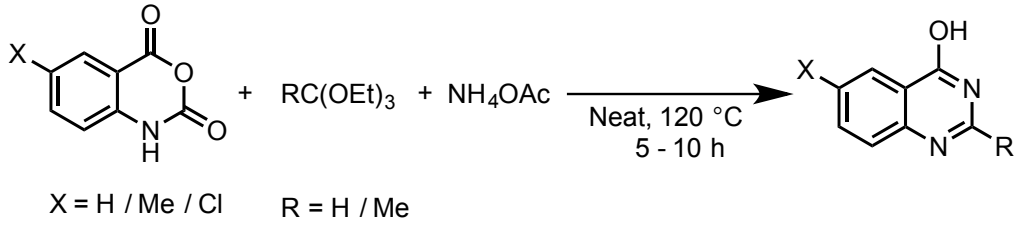
Other tautomerizable heterocycles:



Allyl alcohols

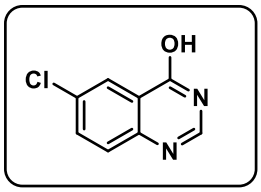


(a) Representative experimental procedure for the synthesis of 1b, 1g, 1h[2]:



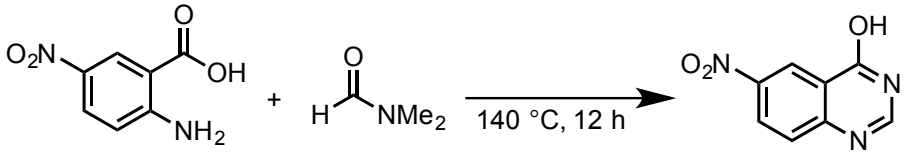
A mixture of isatoic anhydride (0.815 g, 5 mmol), ammonium acetate (0.578 g, 7.5 mmol, 1.5 equiv), and triethyl orthoacetate (1.22 g, 7.5 mmol, 1.5 equiv) were stirred magnetically at 120 °C (oil bath temp). After completion of the reaction (TLC, 5 h), the crude reaction mixture was recrystallized from EtOH to obtain analytically pure **1b** (0.640 g, 80%) as white solid;[2] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (dd, J = 7.5, 1.2 Hz, 1H), 7.80-7.78 (m, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.52-7.48 (m, 1H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 153.7, 149.8, 135.5, 127.3, 127.0, 126.5, 120.6, 22.6.

6-Chloro-quinazolin-4-ol



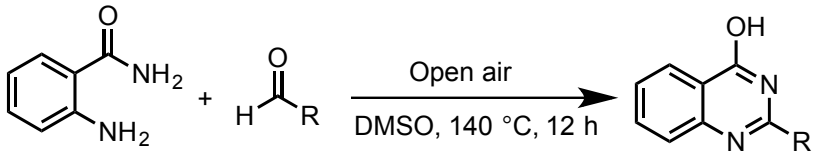
1g; White solid (0.659 g, 73%); ^{1}H NMR (400 MHz, DMSO): δ 12.47 (s, bd, 1H), 8.12 (s, 1H), 8.03 (d, J = 2.4 Hz, 1H), 7.82-7.79 (m, 1H), 7.67 (d, J = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO): δ 160.2, 147.9, 146.4, 134.8, 131.5, 129.9, 125.3, 124.3.

(b) Experimental procedure for the synthesis of 1i[4]:



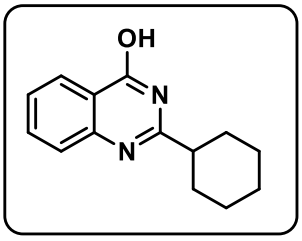
A solution of 2-amino-5-nitrobenzoic acid (1g, mmol) in formamide (1.7 mol) was heated under reflux at 140 °C for 4 h. Solvent was removed under reduced pressure and the crude solid was recrystallized from EtOH to yield analytically pure 1**q** (0.831 g, 87 %); Yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.76 (br, 1H), 8.80 (d, J = 1.6 Hz, 1H), 8.56-8.53 (m, 1H), 8.32 (s, 1H), 7.86 (d, J = 8.9 Hz, 1H).

(c) Representative experimental procedure for the synthesis 1c, 1d, 1e, 1f, 1j-1o[5]:



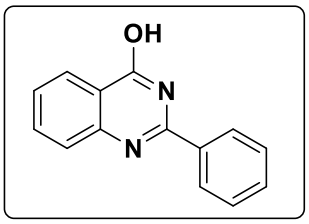
Anthranilamide (5.0 mmol) and an aldehyde (6 mmol, 1.2 equiv) were dissolved in DMSO (10 mL). Then, the reaction mixture was stirred at 100 °C in an open flask and monitored by TLC. After complete consumption of the starting materials (12-36 h), the reaction mixture was cooled to rt. When water (100 mL) was added to the reaction mixture, the precipitate was formed and collected by filtration. Recrystallization in ethanol afforded 4-hydroxy quinazolines.

2-Cyclohexyl-quinazolin-4-ol



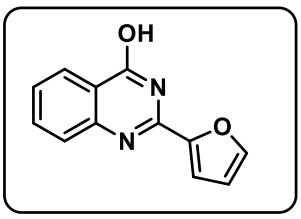
1c; White solid (0.913 g, 80%); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.72 (br, 1H), 8.08 (d, J = 7.5 Hz, 1H), 7.76 (t, J = 7.1 Hz, 1H), 7.59 (d, J = 8.1 Hz, 1H), 7.45 (t, J = 7.4Hz, 1H), 2.61-2.51 (m, 2H), 1.92-1.77 (m, 4H), 1.69-1.54 (m, 3H), 1.34-1.20 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.4; 161.26, 149.29, 134.7, 127.3, 126.4, 126.1, 121.4, 43.3, 30.6, 25.9, 25.8.

2-Phenyl-quinazolin-4-ol



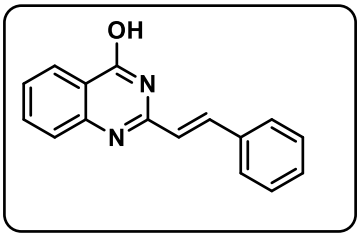
1d; white solid (0.911 g, 82%); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.51 (br, 1H), 8.16 (d, J = 7.5 Hz, 3H), 7.85 (t, J = 7.3 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.66-7.55 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.5, 152.4, 148.6, 134.7, 132.6, 131.4, 128.8, 127.5, 127.4, 126.7, 125.7, 120.7.

2-Furan-2-yl-quinazolin-4-ol



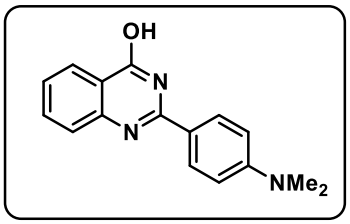
1e; White solid (0.859 g, 81%); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.50 (br, 1H), 8.13 (d, J = 7.4 Hz, 1H), 8.01-7.80 (m, 2H), 7.70-7.64 (m, 2H), 7.50 (t, J = 7.4 Hz, 1H), 6.76 (q, J = 1.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.0, 149.1, 147.1, 146.6, 144.5, 135.1, 127.7, 126.9, 126.4, 121.6, 114.9, 112.9.

2-Styryl-quinazolin-4-ol



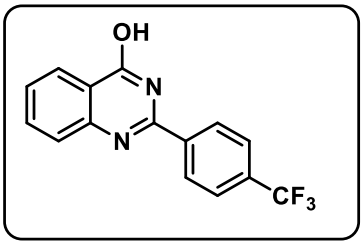
1f; white solid; (0.307 g, 62%); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.32 (d, J = 7.9 Hz, 1H), 7.99 (d, J = 15.3 Hz, 1H), 7.82 (d, J = 3.5 Hz, 2H) 7.64-7.55 (m, 3H), 7.52-7.49 (m, 1H), 7.35-7.29 (m, 7H), 6.40 (d, J = 15.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO): δ 162.7, 152.3, 149.7, 138.9, 135.6, 135.1, 130.4, 129.6, 128.2, 127.7, 126.7, 126.5, 121.8.

2-(4-Dimethylamino-phenyl)-quinazolin-4-ol



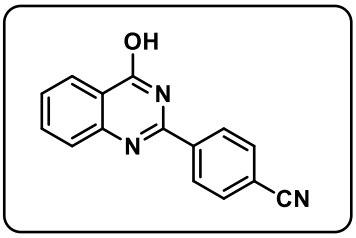
1j; Brown solid (0.968 g, 73%); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.18 (br, 1H), 8.09-8.14 (m, 3H), 7.75-7.79 (m, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.40-7.44 (m, 1H), 6.78 (d, J = 9.1 Hz, 2H), 3.00 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.9, 152.71, 152.70, 149.8, 134.9, 129.3, 127.5, 126.3, 125.8, 120.9, 119.3, 111.7, 66.5, 40.1.

2-(4-Trifluoromethyl-phenyl)-quinazolin-4-ol



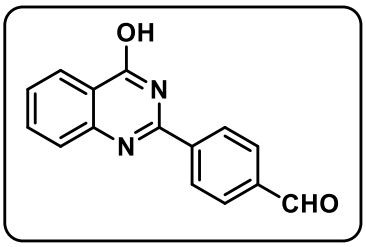
1k; White solid (1.16 g, 80%); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.75 (br, 1H), 8.38 (d, J = 8.1 Hz, 1H), 8.18 (dd, J = 7.9, 1.2 Hz, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.85-7.89 (m, 1H), 7.78 (dd, J = 8.1 0.6 Hz, 1H), 7.54-7.59 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.6, 151.6, 148.9, 137.1, 135.2, 131.6 (q, J = 1.33 Hz), 129.2, 128.2, 127.6, 126.4, 125.9 (q, J = 14.8), 123.1, 121.7.

4-(4-Hydroxy-quinazolin-2-yl)-benzonitrile



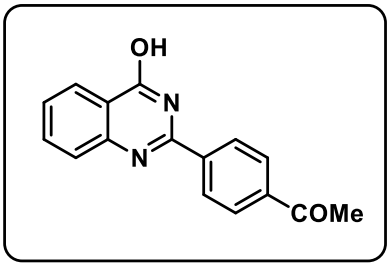
1l; White solid (0.964 g, 78%); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.7 (br, 1H), 7.35 (d, J = 7.0 Hz, 2H), 8.18 (d, J = 7.7 Hz, 1H), 8.05 (d, J = 6.7 Hz, 2H), 7.86 (t, J = 7.5 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.58 (dd, J = 7.5, 7.1 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.5, 160.2, 148.5, 136.9, 135.2, 132.8, 128.9, 127.7, 127.5, 126.2, 121.5, 118.6, 113.8.

4-(4-Hydroxy-quinazolin-2-yl)-benzaldehyde



1m; White solid (0.950 g, 76%); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.72 (br, 1H), 10.12 (s, 1H), 8.38 (d, J = 8.3 Hz, 1H), 8.18 (dd, J = 7.9, 1.0 Hz, 1H), 8.07 (d, J = 8.3 Hz, 2H), 7.89-7.85 (m, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.58-7.55 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 193.3, 162.6, 151.9, 148.9, 138.25, 138.19, 135.2, 129.9, 129.0, 129.2, 127.6, 126.4, 121.7.

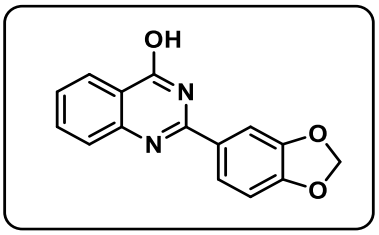
1-[4-(4-Hydroxy-quinazolin-2-yl)-phenyl]-ethanone



1n; White solid (0.924 g, 70%); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.69 (br, 1H), 8.32 (d, J = 8.5 Hz, 2H), 8.18 (dd, J = 7.9, 1.1 Hz, 1H), 8.10 (d, J = 8.4 Hz, 2H), 7.85-7.89 (m, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.54-7.59 (m, 1H), 2.66 (s, 3H); ^{13}C NMR

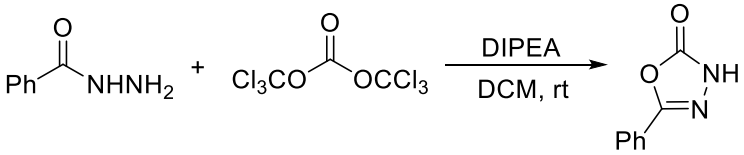
(100 MHz, DMSO-d_6): δ 198.1, 162.6, 151.9, 149.0, 139.0, 137.0, 135.2, 128.8, 128.6, 128.2, 127.5, 121.6, 27.4.

2-Benzo[1,3]dioxol-5-yl-quinazolin-4-ol



1o; Gray solid (1.13 g, 85%); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.36 (br, 1H), 8.16 (d, J = 7.6 Hz, 1H), 7.85-7.72 (m, 4H), 7.53 (t, J = 7.8 Hz, 1H), 7.12 (d, J = 8.6 Hz, 1H), 6.18 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.7, 147.9, 147.5, 135.8, 134.8, 133.5, 127.6, 125.9, 123.2, 120.5, 177.4, 114.5, 108.2, 107.7, 101.9.

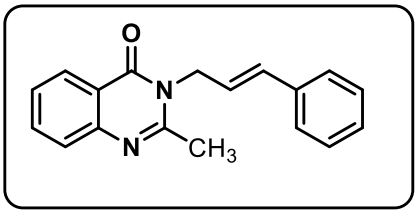
(d) Experimental procedure for the synthesis of 1x[6]:



To a round bottom flask containing a magnetic stir bar was added benzhydrazide (2.0 g, 14.7 mmol), CH_2Cl_2 (300 mL) and DIPEA (5.1 mL, 29 mmol, 2 equiv). The flask was fitted with a rubber septum containing two needles: one connected to a positive pressure N_2 line, the other open to air. Triphosgene (1.75 g, 5.9 mmol, 0.4 equiv) and CH_2Cl_2 (10 mL) were added to a 40 mL vial; the vial was sonicated until the triphosgene had dissolved. Using a syringe, the triphosgene/CH_2Cl_2 solution was added drop wise to the stirred solution of benzhydrazide. The solution was stirred at room temperature; by TLC analysis, the reaction was nearly complete within 20 minutes (hexanes/EtOAc). The reaction mixture was concentrated by rotary evaporation; the crude product was purified by chromatography on silica (gradient elution from hexanes to EtOAc) affording **1x** (0.689 g, 72%) as a white solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.51 (br, 1H), 7.85-7.73 (m, 2H), 7.62-7.53 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.7, 154.1, 131.6, 129.5, 125.5, 124.2.

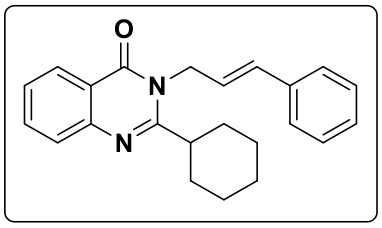
14) Spectra data of products (Table 6 & 7)

3-Cinnamyl-2-methylquinazolin-4(3*H*)-one (3c; Entry 2, Table 6)



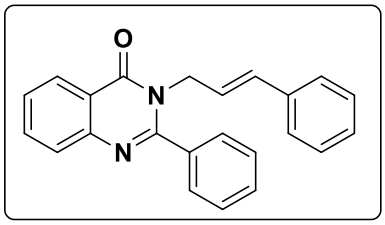
White solid (0.126 g, 91%); MP 127-128 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 - 8.28 (m, 1H), 7.74 - 7.62 (m, 2H), 7.47 – 7.45 (m, 1H), 7.43 - 7.21 (m, 5H), 6.55 (dt, *J* = 16.0, 1.6 Hz, 1H), 6.30 (dt, *J* = 16.0, 5.8 Hz, 1H), 4.92 (dd, J = 5.9, 1.6 Hz, 2H), 2.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.9, 154.3, 147.4, 136.0, 134.3, 132.9, 128.6, 128.1, 126.9, 126.7, 126.49, 126.47, 122.9, 120.5, 45.9, 23.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}N_2O$ 277.1341, Found 277.1339.

3-Cinnamyl-2-cyclohexylquinazolin-4(3*H*)-one (3d; Entry 3, Table 6)



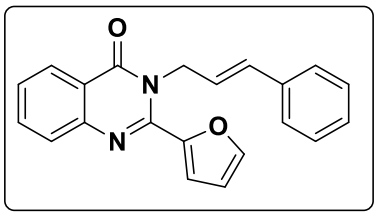
Colorless viscous liquid (0.146 g, 85%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 - 8.31 (m, 1H), 7.74 -7.69 (m, 2H), 7.47 - 7.42 (m, 1H), 7.39 - 7.25 (m, 5H), 6.53 (dt, *J* = 16.0, 1.6 Hz, 1H), 6.35 (dt, *J* = 16.0, 5.5 Hz, 1H), 5.01 (dd, *J* = 5.6, 1.7 Hz, 2H), 2.93 – 2.86 (m, 1H), 1.98 - 1.79 (m, 7H), 1.43 - 1.38 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.4, 160.6, 147.66, 136.2, 134.1, 132.4, 128.6, 127.9, 127.2, 126.9, 126.5, 126.2, 124.08, 120.4, 44.7, 42.3, 31.7, 26.2, 25.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{25}N_2O$ 345.1967, Found 345.1962.

3-Cinnamyl-2-phenylquinazolin-4(3*H*)-one (3e; Entry 4, Table 6)



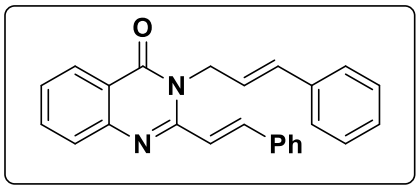
White solid (0.149 g, 88%); MP 105-106 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 - 8.36 (m, 1H), 7.85 - 7.75 (m, 2H), 7.63 - 7.49 (m, 6H), 7.37 - 7.19 (m, 5H), 6.30 - 6.14 (m, 2H), 4.79 (d, *J* = 5.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.1, 156.2, 147.3, 136.2, 135.4, 134.5, 133.6, 130.0, 128.7, 128.5, 128.1, 127.9, 127.6, 127.1, 126.9, 126.5, 123.3, 120.9, 47.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}N_2O$ 339.1497, Found 339.1497.

3-Cinnamyl-2-(furan-2-yl)quinazolin-4(3*H*)-one (3f; Entry 5, Table 6)



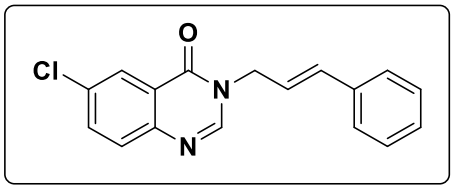
Light yellow solid (0.138 g, 84%); MP 98-100 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.83 - 7.73 (m, 2H), 7.67 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.38 - 7.11 (m, 6H), 6.64 - 6.42 (m, 2H), 6.33 (dt, *J* = 15.9, 5.9 Hz, 1H), 5.11 (dd, *J* = 5.9, 1.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.1, 147.5, 147.4, 146.1, 144.5, 136.3, 134.5, 133.1, 128.5, 127.9, 127.6, 127.2, 127.0, 126.5, 123.69, 120.7, 115.5, 112.0, 46.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}N_2O_2$ 329.1290, Found 329.1295.

3-Cinnamyl-2-((*E*)-styryl)quinazolin-4(3*H*)-one (3g; Entry 6, Table 6)



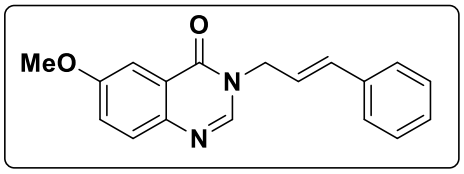
Light yellow solid (0.131 g, 72%); MP 180-182 ^{0}C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (dt, J = 8.0, 1.1 Hz, 1H), 8.02 (d, J = 15.4 Hz, 1H), 7.80 - 7.76 (m, 2H), 7.62 - 7.59 (m, 2H), 7.51 - 7.47 (m, 1H), 7.46 - 7.38 (m, 5H), 7.35 – 7.30 (m, 2H), 7.28 - 7.26 (m, 1H), 7.21 (d, J = 15.4 Hz, 1H), 6.65 (dt, J = 16.0, 1.7 Hz, 1H), 6.41 (dt, J = 16.0, 5.6 Hz, 1H), 5.10 (dd, J = 5.5, 1.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.0, 152.4, 147.7, 141.2, 136.1, 135.5, 134.4, 132.9, 129.8, 128.9, 128.6, 128.6, 128.1, 127.8, 127.4, 127.0, 126.5, 126.5, 126.3, 123.4, 120.6, 119.3, 45.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{20}N_2O$ 365.1654, Found 365.1658.

6-Chloro-3-cinnamylquinazolin-4(3*H*)-one (3h; Entry 7, Table 6)



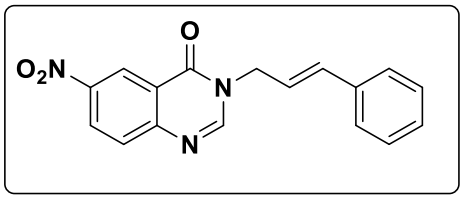
Off white solid (0.133 g, 90%); MP 120-121 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 - 8.28 (m, 1H), 8.10 (s, 1H), 7.72 - 7.66 (m, 2H), 7.40 - 7.25 (m, 5H), 6.69 (dt, J = 16.0, 1.5 Hz, 1H), 6.34 (dt, J = 15.8, 6.5 Hz, 1H), 4.80 (dd, J = 6.5, 1.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.9, 146.6, 146.3, 135.7, 134.9, 134.7, 133.2, 129.2, 128.7, 128.4, 126.6, 126.2, 123.2, 122.4, 48.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}ClN_2O$ 297.0795, Found 297.0792.

3-Cinnamyl-6-methoxyquinazolin-4(3*H*)-one (3i; Entry 8, Table 6)



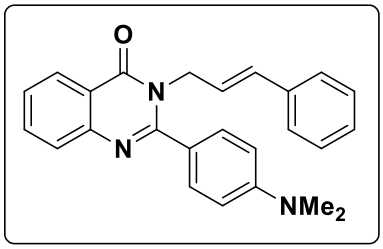
White solid (0.123 g, 84%); MP 172-173 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.71 - 7.63 (m, 2H), 7.39 - 7.33 (m, 3H), 7.31 - 7.26 (m, 3H), 6.67 (dt, J = 15.9, 1.5 Hz, 1H), 6.36 (dt, J = 15.9, 6.4 Hz, 1H), 4.80 (dd, J = 6.5, 1.4 Hz, 2H), 3.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.8, 158.8, 144.0, 142.7, 135.8, 134.4 129.1, 128.6, 128.2, 126.6, 124.5, 123.0, 122.9, 106.1, 55.8, 48.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}N_2O_2$ 293.1290, Found 293.1293.

3-Cinnamyl-6-nitroquinazolin-4(3*H*)-one (3j; Entry 9, Table 6)



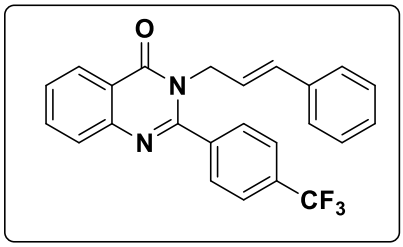
Yellow solid (0.126 g, 82%); MP 145-146 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.22 (d, J = 2.6 Hz, 1H), 8.57 (dd, J = 8.9, 2.6 Hz, 1H), 8.26 (s, 1H), 7.87 (d, J = 8.9 Hz, 1H), 7.42 – 7.29 (m, 5H), 6.71 (d, J = 15.8 Hz, 1H), 6.39 - 6.31 (m, 1H), 4.76 (dd, J = 6.6, 1.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.8, 152.1, 149.0, 146.1, 135.6, 135.4, 129.3, 128.8, 128.6, 128.4, 126.7, 123.5, 122.4, 121.7, 48.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}N_3O_3$ 308.1035, Found 308.1033.

3-Cinnamyl-2-(4-(dimethylamino)phenyl)quinazolin-4(3*H*)-one (3k; Entry 10, Table 6)



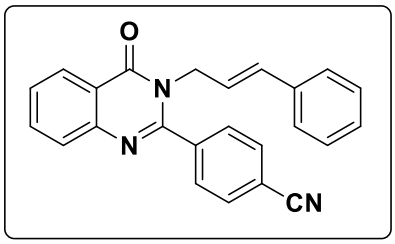
White semisolid (0.162 g, 85%); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.19 - 8.17 (m, 1H), 7.85 - 7.81 (m, 1H), 7.68 - 7.66 (m, 1H), 7.55 - 7.48 (m, 3H), 7.37 - 7.20 (m, 5H), 6.80 - 6.77 (m, 2H), 6.36 - 6.23 (m, 2H), 4.77 - 4.73 (m, 2H), 2.97 (s, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.0, 157.2, 151.5, 147.7, 136.6, 134.9, 131.6, 129.9, 129.0, 128.1, 127.6, 126.9, 126.7, 126.7, 125.3, 122.7, 120.5, 111.5, 48.0, 36.7, 24.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3O$ 382.1919, Found 382.1923.

3-Cinnamyl-2-(4-(trifluoromethyl)phenyl)quinazolin-4(3*H*)-one (3l; Entry 11, Table 6)



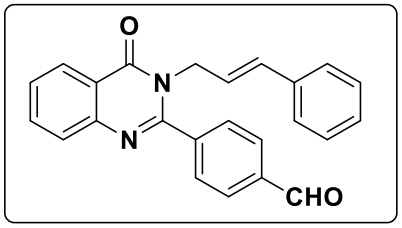
White solid (0.175 g, 86%); MP 138-140 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (dd, J = 8.0, 1.4 Hz, 1H), 7.84 - 7.72 (m, 6H), 7.60 – 7.56 (m, 1H), 7.34 - 7.24 (m, 5H), 6.27 - 6.18 (m, 2H), 4.76 (d, J = 5.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.8, 154.8, 147.1, 138.7 (q, JF-CCCC = 1.33 Hz), 135.8, 134.7, 133.7, 132.14 (q, JF-CC = 33.23 Hz) 128.8, 128.6, 128.2, 127.6, 127.5, 127.0, 126.5, 125.7 (q, JF-CCC = 3.73 Hz) 123.7 (q, JF-C = 272.38 Hz), 122.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{18}F_3N_2O$ 407.1371, Found 407.1368.

4-(3-Cinnamyl-4-oxo-3,4-dihydroquinazolin-2-yl)benzonitrile (3m; Entry 12, Table 6)



White solid (0.154 g, 85%); MP 110-111 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (dd, J = 7.7, 1.5 Hz, 1H), 7.84 - 7.81 (m, 3H), 7.76 - 7.71 (m, 3H), 7.60 - 7.56 (m, 1H), 7.34 - 7.25 (m, 6H), 6.25 - 6.13 (m, 2H), 4.74 (d, J = 5.3 Hz, 2H); 13C NMR (101 MHz, $CDCl_3$): δ 161.7, 154.3, 146.9, 139.4, 135.8, 134.8, 133.6, 132.5, 129.2, 128.7, 128.3, 127.7, 127.6, 127.0, 126.50, 122.8, 120.9, 118.0, 114.0, 48.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{18}N_3O$ 364.1450, Found 364.1443.

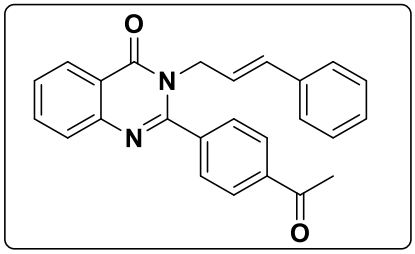
(*E*)-4-(3-Cinnamyl-4-oxo-3,4-dihydroquinazolin-2-yl)benzaldehyde (3n; Entry 13, Table 6)



Colorless liquid (0.165 g, 90%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.2 (s, 1H), 8.40 (dd, J = 8.1, 1.0 Hz, 1H), 8.06 (dd, J = 6.5, 1.8 Hz, 1H), 7.85 - 7.77 (m, 4H), 7.60 - 7.56 (m, 1H), 7.33 - 7.23 (m, 5H), 6.26 - 7.14 (m, 2H), 4.76 (d, J = 5.0 Hz 2H); 13C NMR (101 MHz, $CDCl_3$): δ 191.4, 161.9, 154.9, 147.1, 140.7, 137.2, 135.9, 134.7, 133.7, 129.9, 129.1, 128.6, 128.2,

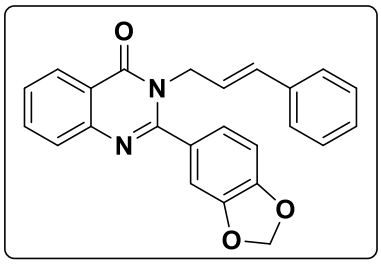
127.63, 127.58, 126.5, 122.9, 120.1, 47.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{19}N_2O_2$ 367.1447, Found 367.1448.

2-(4-Acetylphenyl)-3-cinnamylquinazolin-4(3*H*)-one (3o; Entry 14, Table 6)



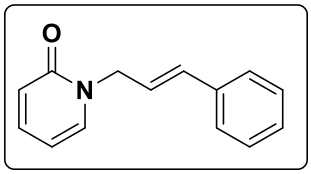
Colorless semisolid (0.162 g, 85%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 - 8.37 (m, 1H), 8.12 - 8.10 (m, 2H), 7.86 - 7.74 (m, 2H), 7.71 – 7.69 (m, 2H), 7.57 - 7.53 (m, 1H), 7.32 - 7.21 (m, 5H), 6.25 - 6.15 (m, 2H), 4.75 (d, J = 4.5 Hz, 2H), 2.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.2, 161.2, 155.2, 147.1, 139.5, 138.1, 135.9, 134.6, 133.6, 128.6, 128.6, 128.6, 128.1, 127.6, 127.5, 126.9, 126.5, 123.0, 120.9, 47.9, 26.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{21}N_2O_2$ 381.1603, Found 381.1610.

2-(Benzo[*d*][1,3]dioxol-5-yl)-3-cinnamylquinazolin-4(3*H*)-one (3p; Entry 15, Table 6)



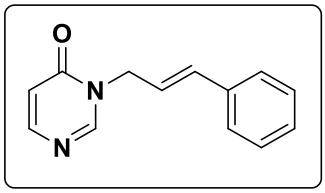
White solid (0.159 g, 83%); MP 142-143 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 - 8.36 (m, 1H), 7.81 - 7.70 (m, 2H), 7.55 – 7.51 (m, 1H), 7.40 - 7.22 (m, 6H), 7.10 - 7.06 (m, 2H), 6.95 (d, J = 7.8 Hz, 1H), 6.33 – 6.22 (m, 2H), 6.08 (s, 2H), 4.82 (d, J = 4.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.2, 155.7, 149.1, 147.9, 147.2, 136.2, 134.5, 133.5, 129.0, 128.6, 127.9, 127.5, 127.1, 126.9, 126.5, 123.4, 122.5, 120.9, 108.8, 108.5, 101.7, 48.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{19}N_2O_3$ 383.1396, Found 383.1401.

1-Cinnamylpyridin-2(1*H*)-one[7] (3q; Entry 16, Table 6)



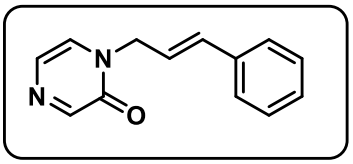
Pale brown liquid (0.085 g, 81%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 - 7.24 (m, 7H), 6.63 - 6.57 (m, 2H), 6.33 (dt, J = 15.9, 6.5 Hz, 1H), 6.19 (td, J = 6.7, 1.4 Hz, 1H), 4.73 (dd, J = 6.5, 1.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.5, 139.5, 136.9, 136.0, 128.63, 128.5, 128.1, 126.6, 123.6, 121.2, 106.2, 50.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{13}NONa$ 234.0895, Found 234.0895.

3-Cinnamylpyrimidin-4(3*H*)-one (3r; Entry 17, Table 6)



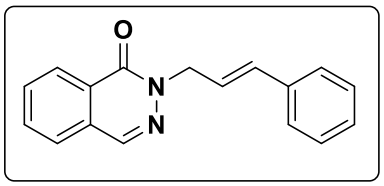
White solid (0.089 g, 84%); MP 138-140 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.92 (d, J = 6.8 Hz, 1H), 7.41 - 7.30 (m, 5H), 6.67 (d, J = 16.0 Hz, 1H), 6.51 (dd, J = 6.4, 0.4 Hz, 1H), 6.36-6.29 (m, 1H), 4.73 (dd, J = 6.8, 1.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.7, 153.4, 150.9, 135.6, 135.2, 128.7, 128.4, 126.7, 122.1, 116.1, 48.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{12}N_2ONa$ 235.0847, Found 235.0845.

1-Cinnamylpyrazine-2(1*H*)-one (3s; Entry 18, Table 6)



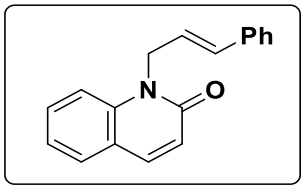
white solid (0.089 g, 84%); MP 59-60 ^{0}C; 1H NMR (400 MHz, CDCl3) δ 8.21 (d, J = 1.2 Hz, 3H), 7.44 – 7.25 (m, 19H), 7.19 (dd, J = 4.4, 1.2 Hz, 3H), 6.68 (dt, J = 15.8, 1.4 Hz, 3H), 6.27 (dt, J = 15.8, 6.7 Hz, 3H), 4.69 (dd, J = 6.7, 1.4 Hz, 6H); ^{13}C NMR (101 MHz, CDCl3) δ 156.0, 149.7, 135.8, 135.5, 128.7, 128.5, 127.8, 126.7, 124.0, 121.6, 50.3. HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C13H12N2ONa 235.0847, Found 235.0844.

2-Cinnamylphthalazin-1(2*H*)-one (3t; Entry 19, Table 6)



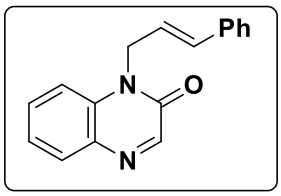
White solid (0.117 g, 89%); MP 64-65 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (dd, J = 7.5, 1.8 Hz, 1H), 8.19 (s, 1H), 7.81 – 7.73 (m, 2H), 7.68 (dd, J = 7.6, 1.6 Hz, 1H), 7.40 - 7.30 (m, 2H), 7.29 - 7.26 (m, 2H), 7.24 - 7.20 (m, 1H), 6.72 (dt, J = 15.8, 1.4 Hz, 1H), 6.47 (dt, J = 15.8, 6.6 Hz, 1H), 5.02 (dd, J = 6.5, 1.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.2, 138.1, 136.5, 133.7, 133.1, 131.7, 129.7, 128.5, 128.0, 127.8, 126.7, 126.6, 126.1, 123.7, 53.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2O$ 263.1184, Found 263.1186.

1-Cinnamylquinolin-2(1*H*)-one (3u; Entry 20, Table 6)



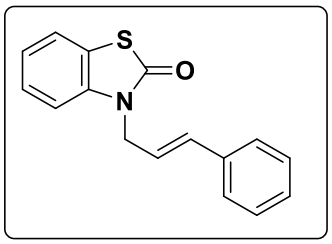
White solid (0.112 g, 86%); MP 45-46 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 9.5 Hz, 1H), 7.65 - 7.51 (m, 2H), 7.45 (d, J = 8.6 Hz, 1H), 7.35 - 7.20 (m, 6H), 6.78 (d, J = 9.5 Hz, 1H), 6.57 (dt, J = 15.9, 1.8 Hz, 1H), 6.34 (dt, J = 16.0, 5.5 Hz, 1H), 5.14 (dd, J = 5.8, 1.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.1, 139.4, 139.4, 136.3, 132.5, 130.7, 128.94, 128.92, 128.6, 128.5, 127.7, 126.4, 123.5, 122.2, 121.7, 120.9, 114.7, 44.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{15}NONa$ 284.1051, Found 284.1047.

1-Cinnamylquinoxalin-2(1*H*)-one (3v; Entry 21, Table 6)



Light yellow solid (0.118 g, 90%); MP 91-93 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.93 (dd, J = 8.0, 1.5 Hz, 1H), 7.59 (m, 1H), 7.44 (dd, J = 8.5, 1.2 Hz, 1H), 7.41 - 7.22 (m, 7H), 6.63 (dt, J = 16.1, 1.6 Hz, 1H), 6.29 (dt, J = 16.0, 5.8 Hz, 1H), 5.08 (dd, J = 5.8, 1.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.7, 150.3, 135.9, 133.7, 133.6, 132.5, 131.1, 130.7, 128.6, 128.1, 126.5, 123.8, 121.8, 114.3, 43.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2O$ 263.1184, Found 263.1181.

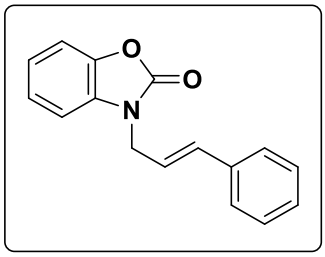
3-Cinnamylbenzo[*d*]thiazol-2(3*H*)-one (3w; Entry 22, Table 6)



Light yellow solid (0.115 g, 86%); MP 46-47 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (dd, J = 7.8, 1.2 Hz, 1H), 7.38 - 7.25 (m, 6H), 7.21 - 7.13 (m, 2H), 6.65 (dt, J = 15.9, 1.6 Hz, 1H), 6.26 (dt, J = 15.9, 6.0 Hz, 1H), 4.76 (dd, J = 6.0, 1.6 Hz, 2H); ^{13}C NMR (101

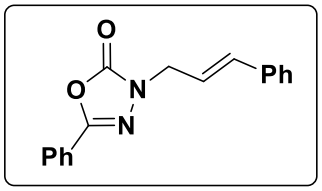
MHz, $CDCl_3$): δ 169.8, 137.0, 136.0, 133.5, 128.7, 128.1, 126.6, 126.4, 123.3, 122.7, 122.1, 111.16, 44.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}NOS$ 268.0796, Found 268.0792.

3-Cinnamylbenzo[*d*]oxazol-2(3*H*)-one (3x; Entry 23, Table 6)



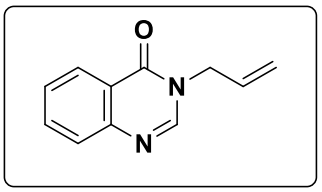
Light brown solid (0.113 g, 90%); MP 100-102 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.48 – 7.00 (m, 10H), 6.71 (dt, *J* = 15.9, 1.6 Hz, 1H), 6.28 (dt, *J* = 15.9, 6.2 Hz, 1H), 4.64 (dd, *J* = 6.2, 1.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 154.4, 142.7, 135.8, 134.2, 131.0, 128.7, 128.3, 126.6, 123.9, 122.5, 121.7, 110.1, 108.9, 44.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}NO_2$ 252.1024, Found 252.1030.

3-Cinnamyl-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (3y; Entry 24, Table 6)



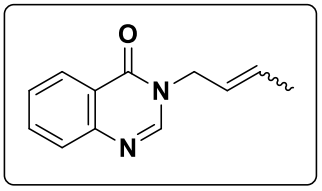
White solid (0.119 g, 86%); MP 49-50 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.90 - 7.64 (m, 2H), 7.54 - 7.42 (m, 5H), 7.37 - 7.27 (m, 3H), 6.74 (dt, *J* = 15.9, 1.4 Hz, 1H), 6.33 (dt, *J* = 15.8, 6.5 Hz, 1H), 4.59 (dd, *J* = 6.6, 1.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 148.7, 148.6, 131.2, 130.0, 126.8, 124.2, 123.9, 123.5, 121.9, 121.0, 119.1, 117.01, 43.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2O_2$ 279.1133, Found 279.1136.

3-Allyl-quinazolin-4(3*H*)-one (3a$_2$; Entry 1, Table 7)



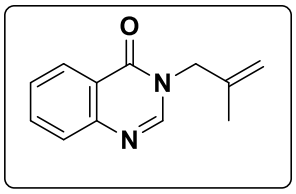
White solid (0.084 g, 91%); MP 65-66 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.34 (d, *J* = 8.0 Hz, 1H), 8.04 (s, 1H), 7.80-7.72 (m, 2H), 7.55-7.50 (m, 1H), 6.07- 5.97 (m, 1H), 5.31 (t, *J* =10.1 Hz, 2H), 4.66 (d, *J* = 5.7 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *δ* 160.8, 148.1, 146.2, 134.3, 131.9, 127.5, 127.3, 126.8, 122.1, 118.9, 48.3; MS (ESI) *m/z*: 186.1 M^+.

3-(1-Methylallyl)quinazolin-4(3*H*)-one (5a; Entry 4, Table 7)



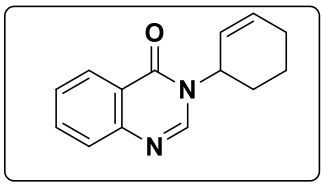
White semi-solid (0.082 g, 82%); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.24 (td, *J* = 8.1, 1.4 Hz, 1H), 7.98 (s, 1H), 7.67-7.62 (m, 2H), 7.44-7.39 (m, 1H), 5.76-5.70 (m, 1H), 5.61-5.57 (m, 1H), 4.50 (td, *J* = 7.4, 2.3 Hz, 2H), 1.67-1.65 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 160.7, 148.0, 146.2, 146.1, 134.0, 131.0, 130.0, 127.3, 127.12, 127.10, 126.7, 126.6, 124.8, 123.9, 122.1, 47.8, 42.7, 17.6, 13.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{13}N_2O$ 201.1028, Found 201.1030.

3-(2-Methylallyl)quinazolin-4(3*H*)-one (6a; Entry 6, Table 7):



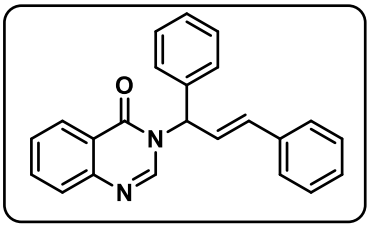
Colorless liquid (0.085 g, 85%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25-8.28 (m, 1H), 7.96 (s, 1H), 7.65-7.72 (m, 2H), 7.43-7.47 (m, 1H), 4.94 (t, *J* = 1.2 Hz, 1H), 4.94 (d, *J* = 0.7 Hz, 1H), 4.53 (s, 2H), 1.74 (d, *J* = 0.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8, 148.0, 146.4, 139.8, 134.2, 127.5, 127.2, 126.8, 122.0, 113.5, 50.9, 20.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{13}N_2O$ 201.1028, Found 201.1031.

3-(Cyclohex-2-en-1-yl)quinazolin-4(3*H*)-one (6b; Entry 7, Table 7):



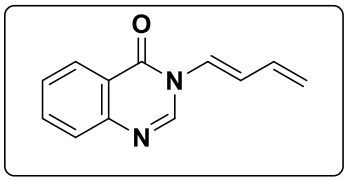
Colorless liquid (0.088 g, 78%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32-8.35 (m, 1H), 8.19 (s, 1H), 7.70-7.76 (m, 2H), 7.49-7.53 (m, 1H), 6.22-6.27 (m, 1H), 5.65-5.69 (m, 1H), 5.55-7.56 (m, 1H), 2.17-2.67 (m, 3H), 1.68-1.82 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 144.7, 134.6, 134.1, 127.4, 127.1, 126.9, 125.2, 121.9, 49.9, 29.8, 24.6, 19.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{14}N_2ONa$ 249.1004, Found 249.1006.

3-(1,3-Diphenyl-allyl)-3*H*-quinazolin-4-one (6c; Entry 8, Table 7):



White solid (0.120g, 71%); MP 100-101 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 – 8.36 (m, 1H), 8.19 (s, 1H), 7.81 – 7.71 (m, 2H), 7.52 (ddd, *J* = 8.2, 5.8, 2.6 Hz, 1H), 7.47 – 7.24 (m, 11H), 6.99 (d, *J* = 5.9 Hz, 1H), 6.76 – 6.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 147.7, 145.2, 138.2, 135.7, 135.4, 134.4, 129.2, 128.8, 128.5, 128.5, 127.9, 127.6, 127.4, 127.2, 126.8, 125.8, 122.0, 58.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{18}N_2ONa$ 361.1317, Found 361.1318.

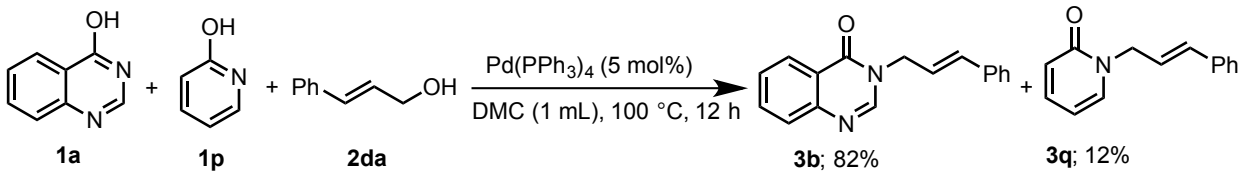
(*E*)-3-(buta-1,3-dien-1-yl)quinazolin-4(3*H*)-one(6d; Entry 9, Table 7):



White solid (0.081g, 82%); MP 92-93 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 7.8 Hz, 1H), 8.28 (s, 1H), 7.72-7.80 (m, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 13.2 Hz, 1H), 6.49-6.57 (m, 2H), 5.45 (d, *J* = 15.9 Hz, 1H), 5.32 (d, *J* = 9.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 159.6, 147.3, 142.5, 134.6, 133.3, 127.76, 127.14, 125.9, 123.1,121.6, 120.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{11}N_2O$ 199.0871, Found 199.0876.

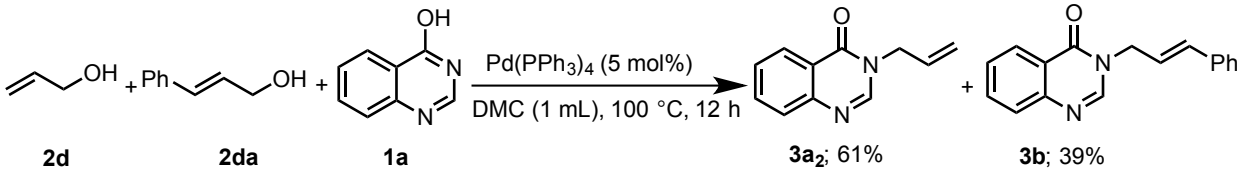
15) Experimental procedure for inter-molecular competition study

Typical procedure for Inter-molecular competition study involving two different tautomerizable heteroarenes:



In a glove box, to an oven dried 4 mL glass vial equipped with a stirring bar, 4-hydroxy quinazoline **1a** (0.036 g, 0.25 mmol), 2-hydroxy pyridine **1p** (0.024 g, 0.25 mmol, 1 equiv), cinnamyl alcohol **2da** (0.034 g, 0.25 mmol, 1 equiv), and $Pd(PPh_3)_4$ (0.015 g, 0.013 mmol, 5 mol%) followed by DMC (1 mL) was added and the resulted reaction mixture was stirred at 100 °C for 12 h. After stipulated time period, the reaction mixture was then cooled to rt, diluted with MeOH (2 x 5 mL) and passed through bed of celite to remove catalyst. An aliquot portion (100 µL) of the organic layer was taken out, diluted with MeOH and subjected to GCMS to observe the selectivity, which reflected an 82:18 selectivity in favor of **1a**.

Typical procedure for Inter-molecular competition study involving two different allyl alcohols



In a glove box, to an oven dried 4 mL glass vial equipped with a stirring bar, 4-hydroxy quinazoline **1a** (0.036 g, 0.25 mmol), allyl alcohal **2d** (0.029 g, 0.5 mmol, 2 equiv), cinnamyl alcohol **2da** (0.067 g, 0.5 mmol, 2 equiv), and $Pd(PPh_3)_4$ (0.015 g, 0.013 mmol, 5 mol%) followed by DMC (1 mL) was added and the resulting reaction mixture was stirred at 100 °C for 12 h. After stipulated time period, the reaction mixture was cooled to rt, diluted with MeOH (2 x 5 mL) and passed through bed of celite to remove catalyst. An aliquot portion (100 µL) of the organic layer was taken out, diluted with MeOH and subjected to GCMS to observe the selectivity, which reflected a 61:39 selectivity in favor of **2d**.

16) References:

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