Supplementary Material

An expeditious synthesis of novel pyranopyridine derivatives involving chromenes under controlled microwave irradiation

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An efficient synthesis of novel pyrano[2,3-*b*]pyridine derivatives has been achieved by aluminium chloride catalyzed cyclocondensation of 2-amino-3-cyano-4*H*-chromenes and cyclohexanone under controlled microwave irradiation. The experimental conditions have been thoroughly optimized and established, allowing significant rate enhancements and excellent yields. The starting 4*H*-chromenes were obtained using one pot DBU-catalysed microwave induced multicomponent condensation of resorcinol, malononitrile and aromatic aldehydes.

Table S1. Optimization of reaction conditions for the multi-component synthesis of **4a**

Entry	Catalyst	Microwave				Conventional		
		MW (Watt)	Temp. (ºC)	Time (min.)	Yield (%)[a]	Temp. (ºC)	Time (min.)	Yield (%)[a]
1	-	80	50	20	25	RT	120	-
2	-	100	50	10	42	Reflux	120	38
3	PTSA	80	50	10	20	RT	120	Trace
4	PTSA	100	50	10	32	50	90	12
5	TBAB	80	50	15	28	RT	120	-
6	TBAB	100	50	10	44	50	120	20
7	$NaHCO_3$	80	50	10	68	RT	120	25
8	$NaHCO_3$	100	50	15	79	50	90	56
9	Guanidine	80	50	15	35	RT	120	-
10	Guanidine	100	50	10	48	50	120	15
11	KF/Al_2O_3	80	50	15	68	RT	120	30
12	KF/Al_2O_3	100	50	10	75	50	120	62
13	DBU	80	50	10	85	RT	60	45
14	**DBU**	**100**	**50**	**03**	**94**	**50**	**40**	**76**
15	DBU	150	50	05	90	Reflux	30	78
16	DBU	150	80	05	87	-	-	-

[a] Isolated mass yield based on resorcinol

Table S2. Synthesis of 2-amino-4*H*-chromenes **4a-l**

Product	R	Microwave (100W, 50 ºC)		DBU, 50 ºC	
		Time (min.)	Yield (%)[a]	Time(min.)	Yield (%)[a]
4a	Ph	3	94	40	76
4b	4-FC_6H_4	2	89	35	62
4c	4-BrC_6H_4	3	93	35	74
4d	4-$MeOC_6H_4$	3	90	35	60
4e	2-furyl	2	92	45	63
4f	4-MeC_6H_4	4	91	50	65
4g	3,4,5-$(MeO)_3C_6H_2$	4	90	45	60
4h	4-$N(Me)_2C_6H_4$	4	88	45	62
4i	2-thienyl	3	96	45	70
4j	3-$NO_2C_6H_4$	3	87	40	72
4k	2-$NO_2C_6H_4$	4	89	30	62
4l	2-FC_6H_4	3	87	35	72

[a] Isolated mass yield based on resorcinol

Table S3. Optimization of the reaction conditions using compound **4a** as reference

Entry	Lewis Acid	Reaction Condition			
		Reflux		MW[a]	
		Time (h)	Yield (%)	Time (min)	Yield (%)
1	**$AlCl_3$ (1.2 equiv)**	**2.0**	**58**	**8**	**91**
2	$AlCl_3$ (0.5 equiv)	2.0	15	10	25
3	$AlCl_3$ (1.0 equiv)	2.0	45	10	78
4	$AlCl_3$ (1.5 equiv)	2.0	57	8	91
5	$AlCl_3$ (1.2equiv)[b]	2.5	-	10	Trace
6	$AlCl_3$ (1.2 equiv)[c]	2.5	-	10	Trace
7	$AlCl_3$ (1.2 equiv)[d]	2.5	-	10	-
8	$FeCl_3$(1.5 equiv)	1.5	-	8	-
9	$ZnCl_2$(1.5 equiv)	2.0	-	8	-
10	$Sc(OTf)_3$	2.5	-	10	-
11	$Yb(OTf)_3$	2.0	-	8	-
12	$InCl_3$	2.0	-	8	-
13	I_2	2.5	-	10	-
14	MontmorilloniteK10	2.0	-	10	-

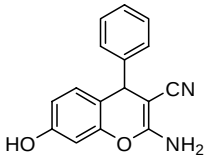
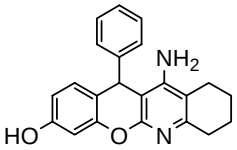
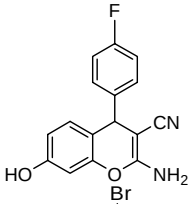
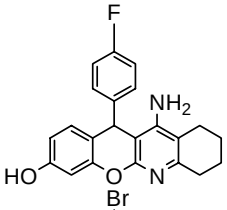
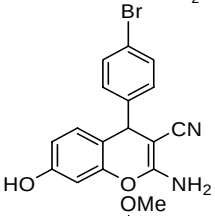
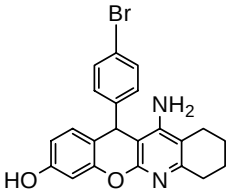
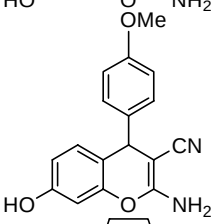
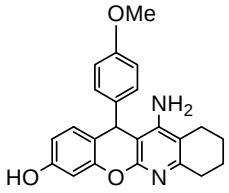
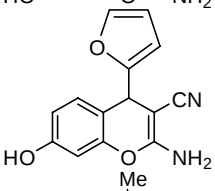
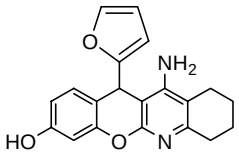
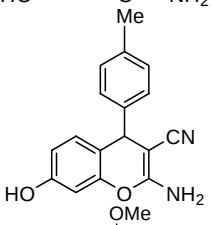
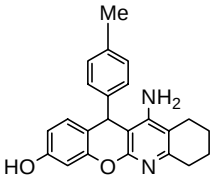
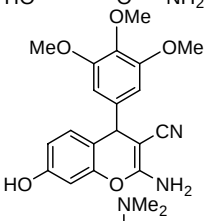
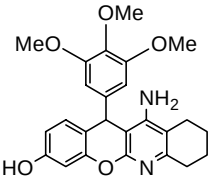
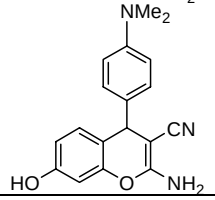
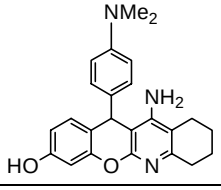
[a]MW heating performed on 150 Watt power and 45°C temperature

[b]Reaction was carried out in ethanol

[c]Reaction was carried out in methanol

[d]Reaction was carried out in acetonitrile

Table S4. Microwave assisted synthesis[a] of pyrano[2,3-*b*]pyridine **6a-h**

Entry	Reactant **4**	Product **6**	Time (min.)	Yield (%)[b]	Mp (°C)
a			8	91	313-315
b			7	89	292-294
c			8	93	281-282
d			6	92	295-297
e			8	89	318-320
f			7	90	282-284
g			8	87	285-287
h			8	85	>320

[a] Microwave heating performed on 150 Watt power and 45 ºC temperature

[b] Isolated mass yield based on chromenes