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MICROWAVE-ASSISTED SYNTHESIS OF BENZOFURAN/ BENZOTHIOPHENE-FUSED NAPHTHYRIDINES VIA THORPE-ZIEGLER TYPE HETEROCYCLIZATION

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Abstract – An efficient one-pot domino protocol for the synthesis of novel benzofuran/benzothiophene-fused naphthyridines, benzofuro- and benzothieno-[3,2-*h*]benzo[*b*][1,6]naphthyridin-5(6*H*)-one derivatives **4**, was developed, starting from 2-chloromethylquinoline-3-carboxylates (**1**) with salicylonitriles (**2**) or 2-mercaptobenzonitrile (**3**) by microwave-assisted Thorpe-Ziegler type heterocyclization in the presence of cesium carbonate with good yields.

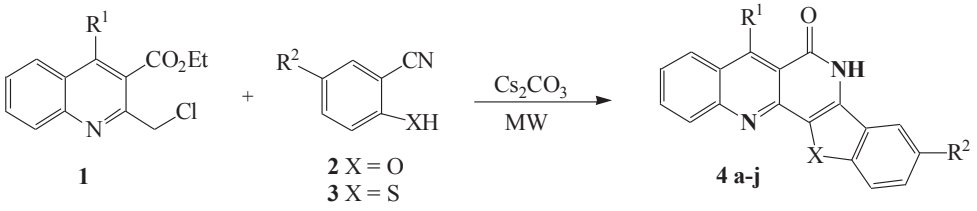
INTRODUCTION

Naphthyridines and their polycyclic derivatives are an important pharmacophore present in many natural and designed synthetic products of therapeutic applications.[1] Among them, [1,6]naphthyridines and their benzo/hetero-fused analogues have displayed a wide range of physiological activities, such as anticancer,[2] anti HIV-1,[3] antimicrobial[4] and cytotoxic activities.[5] Consequently, various methods have been reported for the synthesis of these compounds including multi component reactions,[6] metal-catalyzed reactions,[7] cycloaddition reactions[8] and other approaches.[9]

On the other hand, compounds with the core of benzofuran or benzothiophene are an important class of heterocycles, which are frequently present in biologically active molecules and natural products.[10] Thus a molecular scaffold containing both naphthyridine and benzofuran or benzothiophene unit may be of great interest from biological and molecular diversity viewpoint.

Microwave irradiation, because of its significant enhancement in reaction rates and yields, has emerged as a powerful technique for promoting a variety of chemical reactions.[11] As part of our continuing interest on

the development of new synthetic methods for heterocyclic compounds,[12] we herein report an efficient synthesis of benzofuro- and benzothieno[3,2-*h*]benzo[*b*][1,6]naphthyridin-5(6*H*)-ones by microwave-assisted Thorpe-Ziegler type heterocyclization of 2-chloromethylquinoline-3-carboxylates (**1**) with salicylonitriles (**2**) or 2-mercaptobenzonitrile (**3**) (Scheme 1).



Scheme 1. Synthesis of new fused [1,6]naphthyridin-5(6*H*)-ones

RESULTS AND DISCUSSION

The carbon-carbon and carbon-heteroatom bond-forming reactions are crucial to organic synthesis. Domino processes are important for generating high levels of diversity and complexity giving rise to complex structures by simultaneous formation of two or more bonds from simple substrates. These advantages are of particular interest in pharmaceutical research for the construction of libraries of biologically active compounds. Thus, developing new, environmentally benign domino reactions is an important topic of green chemistry.[13] In this study we describe a new one-pot method of synthesis of new fused [1,6]naphthyridines using Thorpee-Ziegler type heterocyclization domino reaction.[14]

Thorpe-Ziegler cyclization generally proceeds smoothly in the presence of bases in aprotic solvents to give the corresponding intramolecular condensation products in poor to moderate yields. Therefore, we first investigated the effect of modifying the base, solvent, temperature, and reaction time under microwave irradiation. The reaction of ethyl 2-chloromethyl-4-methylquinoline-3-carboxylate (**1a**) with salicylonitrile (**2a**) was chosen as a model to optimize the reaction conditions (Table 1).

As shown in Table 1, the reaction of **1a** with **2a** proceeded smoothly with 68% yield in the presence of K_2CO_3 at 120 °C in DMF for 10 min (entry 1). Then, a series of bases was screened for this reaction, such as Cs_2CO_3, KOH, NaH and *t*-BuOK (entries 2-5), and the desired product **4a** was obtained in 54% to 86% yields. Excellent improvement in the yield of **4a** was observed by replacing Cs_2CO_3 (entries 2, 6 and 7). Moreover, several solvents (such as DMF, NMP, and DMSO) were tested, and DMF was proved to be the most effective solvent. Increasing or decreasing the temperature of the reaction did not lead to any further improvements in the yield (entries 8 and 9). On the other hand, the yields increased with time, from 78% (5 min) to a maximum of 86% (10 min) (entries 2, 10, and 11). Extending the reaction time longer than 10 min did not change the yield significantly. Taken together, we concluded that under microwave irradiation, the optimal conditions were 120 °C, 10 min, and Cs_2CO_3 in DMF.

Table 1. Optimization of microwave-assisted reaction conditions on the synthesis of **4a***

Entry	Base	Solvent	Temp (°C)	Time (min)	Yield (%)
1	K_2CO_3	DMF	120	10	68
2	Cs_2CO_3	DMF	120	10	86
3	KOH	DMF	120	10	54
4	NaH	DMF	120	10	58
5	*t*-BuOK	DMF	120	10	80
6	Cs_2CO_3	NMP	120	10	75
7	Cs_2CO_3	DMSO	120	10	70
8	Cs_2CO_3	DMF	140	10	82
9	Cs_2CO_3	DMF	100	10	73
10	Cs_2CO_3	DMF	120	5	78
11	Cs_2CO_3	DMF	120	15	84

* Reaction conditions: **1** (1.0 mmol), salicylonitrile (**2a**, 1.0 mmol), base (3.0 mmol), solvent (15 mL).

With the optimized conditions in hand, the scope and generality of this novel synthesis of benzofuro[3,2-*h*]benzo[*b*][1,6]naphthyridin-5(6*H*)-ones (**4a-h**) were studied. The results, together with those obtained under the conventional method for comparison, are shown in Table 2.

The results in Table 2 indicate that moderate to good isolated yields (72-83%) could be achieved under the conventional method after a long reaction time (5-8 h), and the results were highly dependent on the starting materials that were used. Prolonging the reaction time or adding excess salicylonitriles **2** did not significantly improve the yield. In contrast, under microwave irradiation, the reactions were completed in 10 min and benzofuro[3,2-*h*]benzo[*b*][1,6]naphthyridin-5(6*H*)-ones were isolated in good yields (79-88%). Thus, microwave irradiation increased the yield by 4-15%. Note that substituents on the aromatic ring, such as Me, Ph, OMe, Cl, and Br, have practically no obvious effect on the yield under both conventional and microwave conditions.

To expand the scope of the current method, 2-mercaptobenzonitrile was examined as a replacement for salicylonitrile to synthesize benzothieno[3,2-*h*]benzo[*b*][1,6]naphthyridin-5(6*H*)-ones. The desired products (**4i, 4j**) were also successfully obtained with good yields (Table 2, entries 9 and 10).

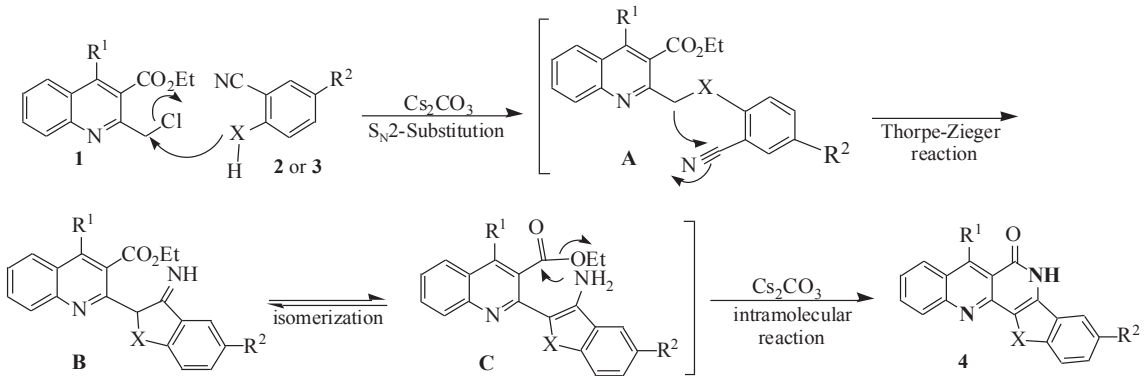
All the products were characterized by IR, ^{1}H NMR, ^{13}C NMR and elemental analysis. And all the data is consistent with the desired structures.

Table 2. Synthesis of benzofuro- and benzothieno[3,2-*h*]benzo[*b*][1,6]naphthyridin-5(6*H*)-ones **4**

Entry	Product	R^1	R^2	X	Microwave irradiation[a]		Conventional heating[a]	
					Time (min)	Yield (%)[b]	Time (h)	Yield (%)[b]
1	4a	Me	H	O	10	86	6	73
2	4b	Me	OMe	O	10	88	7	80
3	4c	Me	Cl	O	10	79	7	75
4	4d	Me	Br	O	10	80	8	72
5	4e	Ph	H	O	10	82	6	79
6	4f	Ph	OMe	O	10	83	5	75
7	4g	Ph	Cl	O	10	85	6	70
8	4h	Ph	Br	O	10	80	7	78
9	4i	Me	H	S	10	85	5	81
10	4j	Ph	H	S	10	84	5	78

[a] The reaction was carried out at 120 °C. [b] Isolated yield.

The proposed mechanism of the process is summarized in Scheme 2. The present synthetic sequence was initiated by an alkylation of 2-chloromethylquinoline-3-carboxylates **1** with salicylonitriles (**2**) or 2-mercaptobenzonitrile (**3**) giving rise to the ethers **A**. An intramolecular carbanion addition across the nitrile was brought about by ethers **A** *via* Thorpe-Ziegler reaction, and isomerization, resulting in the formation of 3-amino-2-benzofurans (or 3-amino-2-benzothiophenes) **C**. Next, this then undergoes intramolecular cyclization *via* loss of ethanol leads to yield the pentacyclic products **4**.



Scheme 2. Proposed reaction mechanism for the formation of compound **4**

EXPERIMENTAL

General procedures for conventional preparation: To a solution of 2-chloromethyl-quinoline-3-carboxylate **1**[15] (1.0 mmol) in DMF (15 mL) was added salicylonitrile **2** or 2-mercapto-benzonitrile **3** (1.0 mmol) and cesium carbonate (3.0 mmol). The mixture was heated at 120 °C (monitored by TLC). At the end of the reaction, the reaction mixture was cooled to rt, and solvent was evaporated in vacuo. The crude reaction mixture was recrystallized from HOAc to afford the corresponding products **4a-j**.

General procedures for microwave-assisted preparation: A round bottomed flask charged with 2-chloromethylquinoline-3-carboxylate **1** (1.0 mmol), salicylonitrile **2** or 2-mercaptobenzonitrile **3** (1.0 mmol), and cesium carbonate (3.0 mmol) in DMF (15 mL) was irradiated at 120 °C (150 W, open vessel standard conditions) for 10 min. Reaction flask was then allowed to cool down and solvent was evaporated in vacuo. The crude reaction mixture was purified to afford the desired compounds **4**.

13-Methylbenzofuro[3,2-*h*]benzo[*b*][1,6]naphthyridin-5(6*H*)-one (4a): Red needles. Mp >300 °C; IR (KBr, cm^{-1}): *v* 3410 (NH), 1670 (C=O). ^{1}H NMR (400 MHz, CF_3CO_2D): δ 3.68 (s, 3H), 7.58 (d, J = 7.6 Hz, 1H), 7.75-7.83 (m, 2H), 7.96-8.06 (m, 2H), 8.26-8.29 (m, 2H), 8.71 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, CF_3CO_2D): δ 16.7, 109.2, 112.0, 114.8, 115.7, 117.6, 118.4, 119.9, 125.5, 126.5, 127.2, 128.4, 133.3, 135.1, 136.9, 138.1, 157.7, 162.4, 169.3. *Anal.* Calcd for $C_{19}H_{12}N_2O_2$: C 75.99, H 4.03, N 9.33. Found: C 76.14, H 4.07, N 9.37.

9-Methoxy-13-methylbenzofuro[3,2-*h*]benzo[*b*][1,6]naphthyridin-5(6*H*)-one (4b): Red needles. Mp >300 °C; IR (KBr, cm^{-1}): *v* 3411 (NH), 1680 (C=O). ^{1}H NMR (400 MHz, CF_3CO_2D): δ 3.68 (s, 3H), 4.06 (s, 3H), 7.50 (d, J = 8.4 Hz, 1H), 7.55 (s, 1H), 7.69 (d, J = 9.2 Hz, 1H), 7.97-8.01 (m, 1H), 8.26-8.33 (m, 2H), 8.71 (1H, d, J = 8.8 Hz). ^{13}C NMR (100 MHz, CF_3CO_2D): δ 17.5, 55.8, 102.8, 110.0, 112.2, 116.1, 117.2, 119.2, 126.3, 127.1, 128.9, 129.1, 133.7, 135.8, 137.6, 138.9, 154.2, 156.6, 163.0, 170.0. *Anal.* Calcd for $C_{20}H_{14}N_2O_3$: C 72.72, H 4.27, N 8.48. Found: C 72.89, H 4.30, N 8.52.

9-Chloro-13-methylbenzofuro[3,2-*h*]benzo[*b*][1,6]naphthyridin-5(6*H*)-one (4c): Red needles. Mp >300 °C; IR (KBr, cm^{-1}): *v* 3408 (NH), 1679 (C=O). ^{1}H NMR (400 MHz, CF_3CO_2D): δ 3.69 (s, 3H), 7.68-7.77 (m, 2H), 7.99-8.03 (m, 1H), 8.18 (1H, s), 8.28-8.36 (m, 2H), 8.73 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, CF_3CO_2D): δ 17.6, 110.4, 112.2, 113.3, 115.0, 116.0, 117.7, 119.3, 120.1, 120.2, 126.5, 129.4, 132.1, 132.8, 135.9, 137.6, 139.0, 156.5, 170.2. *Anal.* Calcd for $C_{19}H_{11}ClN_2O_2$: C 68.17, H 3.31, N 8.37. Found: C 68.25, H 3.35, N 8.42.

9-Bromo-13-methylbenzofuro[3,2-*h*]benzo[*b*][1,6]naphthyridin-5(6*H*)-one (4d): Red needles. Mp >300 °C; IR (KBr, cm^{-1}): *v* 3415 (NH), 1680 (C=O). ^{1}H NMR (400 MHz, CF_3CO_2D): δ 3.95 (s, 3H), 7.86-7.88 (m, 1H), 7.81-8.83 (m, 1H), 8.28-8.29 (m, 1H), 8.43 (s, 1H), 8.56-8.59 (m, 2H), 9.00 (d, J = 8.4Hz, 1H). ^{13}C NMR (100 MHz, CF_3CO_2D): δ 110.0, 114.3, 115.9, 118.5, 118.8, 119.5, 123.6, 126.8,

127.4, 129.0, 129.7, 132.8, 136.1, 137.9, 139.3, 157.1, 163.1, 170.5. *Anal.* Calcd for $C_{19}H_{11}BrN_2O_2$: C 60.18, H 2.92, N 7.39. Found: C 60.32, H 3.94, N 7.44.

13-Phenylbenzofuro[3,2-*h*]benzo[*b*][1,6]naphthyridin-5(6*H*)-one (4e): Red needles. Mp >300 °C; IR (KBr, cm^{-1}): *v* 3418 (NH), 1679(C=O). ^{1}H NMR (400 MHz, CF_3CO_2D): *δ* 7.29-7.30 (m, 2H), 7.51-7.61 (m, 3H), 7.72-8.01 (m, 3H), 8.26-8.29 (m, 2H), 8.00 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 7.2 Hz, 1H), 8.34 (1H, d, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, CF_3CO_2D): *δ* 111.4, 112.3, 113.4, 115.7, 117.6, 120.0, 124.6, 125.4, 126.1, 127.2, 127.6, 128.1, 128.7, 129.7, 132.4, 132.8, 134.0, 135.3, 137.9, 138.3, 157.7, 167.4. *Anal.* Calcd for $C_{24}H_{14}N_2O_2$: C 79.55, H 3.89, N 7.73. Found: C 79.67, H 3.94, N 7.75.

9-Methoxy-13-phenylbenzofuro[3,2-*h*]benzo[*b*][1,6]naphthyridin-5(6*H*)-one (4f): Red needles. Mp >300 °C; IR (KBr, cm^{-1}): *v* 3380 (NH), 1680 (C=O). ^{1}H NMR(400 MHz, CF_3CO_2D): *δ* 4.03 (3H, s), 7.32-7.33 (m, 2H), 7.48-7.49 (m, 2H), 7.51-7.53 (m, 3H), 7.62-7.70 (m, 1H), 7.71-7.78 (m, 1H), 7.81-7.85 (m, 1H), 8.23-8.27 (m, 1H), 8.35 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, CF_3CO_2D): *δ* 55.1, 102.2, 109.2, 112.2, 113.2, 114.1, 116.5, 117.8, 122.2, 125.5, 126.3, 127.7, 128.3, 128.8, 129.7, 132.8, 133.6, 135.4, 137.9, 138.4, 153.5, 155.8, 167.4. *Anal.* Calcd for $C_{25}H_{16}N_2O_3$: C 76.52, H 4.11, N 7.14. Found: C 76.68, H 4.15, N 7.19.

9-Chloro-13-phenylbenzofuro[3,2-*h*]benzo[*b*][1,6]naphthyridin-5(6*H*)-one (4g): Red needles. Mp >300 °C; IR (KBr, cm^{-1}): *v* 3390 (NH), 1680 (C=O). ^{1}H NMR (400 MHz, CF_3CO_2D): *δ* 7.31-7.32 (m, 2H), 7.64-7.65 (m, 3H), 7.74-7.77 (m, 2H), 7.81-7.88 (m, 2H), 8.03-8.04 (m, 1H), 8.27-8.28 (m, 1H), 8.39 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, CF_3CO_2D): *δ* 109.1, 113.1, 115.3, 117.1, 117.9, 119.6, 125.5, 126.5, 127.8, 128.5, 128.9, 129.8, 131.3, 132.6, 132.8, 132.9, 135.5, 138.0, 138.5, 155.8, 160.2, 167.8. *Anal*. Calcd for $C_{24}H_{13}ClN_2O_2$: C 72.64, H 3.30, N 7.06. Found: C 72.76, H 3.35, N 7.10.

9-Bromo-13-phenylbenzofuro[3,2-*h*]benzo[*b*][1,6]naphthyridin-5(6*H*)-one (4h): Red needles. Mp >300 °C; IR (KBr, cm^{-1}): *v* 3400 (NH), 1679 (C=O). ^{1}H NMR (400 MHz, CF_3CO_2D): *δ* 7.64-7.65 (m, 2H), 7.95-7.96 (m, 4H), 8.16-8.18 (m, 3H), 8.52-8.70 (m, 3H). ^{13}C NMR (100 MHz, CF_3CO_2D): *δ* 110.0, 114.4, 115.3, 118.6, 118.9, 119.0, 123.8, 126.6, 127.6, 128.8, 129.2, 129.6, 129.9, 130.8, 133.7, 133.9, 136.3, 136.5, 139.1, 139.6, 157.3, 168.7. *Anal.* Calcd for $C_{24}H_{13}BrN_2O_2$: C 65.32, H 2.97, N 6.35. Found: C 65.41, H 3.02, N 6.39.

13-Methylbenzothieno[3,2-*h*]benzo[*b*][1,6]naphthyridin-5(6*H*)-one (4i): Red needles. Mp >300 °C; IR (KBr, cm^{-1}): *v* 3415 (NH), 1680 (C=O). ^{1}H NMR (400 MHz, CF_3CO_2D): *δ* 3.59 (s, 3H), 7.52-7.59 (m, 2H), 7.80-7.91 (m, 2H), 8.17-8.19 (m, 3H), 8.59-8.60 (m, 1H). ^{13}C NMR (100 MHz, CF_3CO_2D): *δ* 17.8, 107.3, 110.0, 115.7, 119.0, 122.1, 123.1, 126.3, 126.5, 126.9, 129.2, 131.5, 137.8, 138.8, 141.5, 141.6, 143.2, 163.4, 169.5. *Anal.* Calcd for $C_{19}H_{12}N_2OS$: C 72.13, H 3.82, N 8.85. Found: C 72.24, H 3.87, N 8.91.

13-Phenylbenzothieno[3,2-*h*]benzo[*b*][1,6]naphthyridin-5(6*H*)-one (4j): Red needles. Mp >300 °C; IR

(KBr, cm^{-1}): *v* 3419 (NH), 1675 (C=O); ^1H NMR (400 MHz, CF_3CO_2D): *δ* 7.28-7.29 (m, 2H), 7.58-7.59 (m, 4H), 7.68-7.82 (m, 3H), 7.92-7.93 (m, 1H), 8.20-8.27 (m, 3H). ^{13}C NMR (100 MHz, CF_3CO_2D): *δ* 107.5, 115.2, 118.4, 122.3, 123.3, 126.2, 126.5, 127.0, 127.1, 128.3, 128.6, 129.0, 129.4, 129.7, 130.2, 131.7, 133.8, 139.0, 141.9, 142.3, 143.8, 167.8. *Anal.* Calcd for $C_{24}H_{14}N_2OS$: C 76.17, H 3.73, N 7.40. Found: C 76.23, H 3.80, N 7.45.

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