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Microwave-assisted synthesis of pyrazolo[3,4-*b*]pyridine-spirocycloalkanediones by three-component reaction of 5-aminopyrazole derivatives, paraformaldehyde and cyclic β-diketones

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ABSTRACT

New pyrazolo[3,4-*b*]pyridine-5-spirocycloalkanedione derivatives were prepared via three-component reaction between 5-(4-*R*-benzylamino)pyrazoles, cyclic β-diketones and paraformaldehyde. The use of indandione as β-diketone resulted in the formation of two products, the pyrazolo[3,4-*b*]pyridine-5-spiroindanediones and 3-*tert*-butyl-1-phenylindeno[2,3-*e*]pyrazolo[3,4-*b*]pyridine. The structures of the pyrazolo[3,4-*b*]pyridine-5-spirocycloalkanedione were confirmed by single-crystal X-ray diffraction. This protocol provides a simple one-step synthetic methodology with the advantages of easy work-up, mild reaction conditions and environmentally benign.

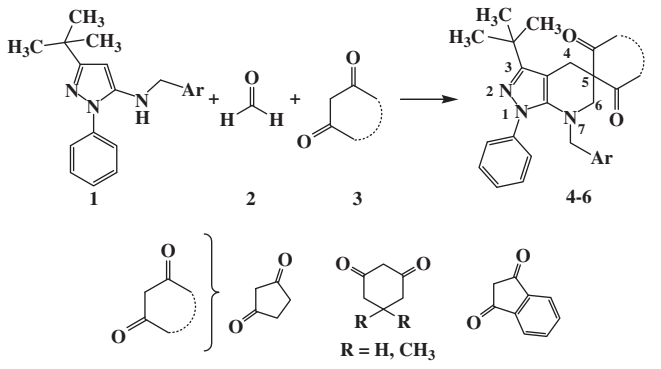
Compounds with spiro skeletons not only constitute subunits in numerous alkaloids, but are also templates for drug discovery and have been used as scaffolds for combinatorial libraries.[1–3] The synthesis of spiro-compounds has been performed by conventional methods and procedures based on the three-component one-pot synthesis.[4,5]

On the other hand, microwave irradiation (MWI) is also emerging as a powerful tool for high-throughput organic synthesis. It has been demonstrated that the use of microwave irradiation can dramatically shorten reaction times, increase product purities and yields, and allow precise control of reaction parameters.[6]

In our interest in the development of synthetic strategies to obtain functionalized heterocycles,[7] we have concentrated much of our recent efforts in the preparation of such bioactive nitrogen-containing heterocycles, and have already reported simple and efficient procedures to reach interesting molecules such as pyrazolo[3,4-*b*]pyridines with biological properties.[8,9]

Herein, we wish to report a simple method for the synthesis of pyrazolopyridine-5-spirocyclodiketones derivatives **4–6** via one-pot condensation of 5-aminopyrazoles derivatives **1**,[10] formaldehyde (**2** as paraformaldehyde) and cyclic β-diketones **3** (Scheme 1).[11]

In a general experimental procedure equimolar amounts of starting compounds **1** and **3** with an excess of formaldehyde (**2** as paraformadehyde 30 mol %) were exposed to MWI using a focused microwave reactor (CEM Discover TM) at 200 °C with a maximum power of 300 W for 25 min to give compounds **4–6** that were isolated in good yields, after purification by simple crystallization of



Scheme 1.

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E-mail addresses: jaiquir@univalle.edu.co (J. Quiroga), jorgetrilleras@mail.uniatlantico.edu.co (J. Trilleras), mmontiel@ujaen.es (M. Nogueras) .

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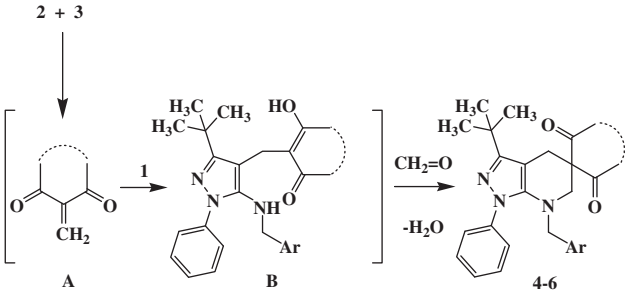
the reaction mixture from ethanol. We have also carried out this three-component reaction under conventional heating in refluxing absolute ethanol and again spiro-compounds were isolated in good yields. This three-component reaction can easily be carried out by microwave irradiation or conventional heating in ethanol. In both cases the reaction gave the same products **4–6**. The only difference between these two methods is that by MWI the reaction times are much shorter than by refluxing ethanol, 25 min versus 24 h, respectively. The results are summarized in Table 1, entries 1–33.

A possible mechanism for the reported condensation is outlined in Scheme 2. Presumably, the reaction starts with the formation of Knoevenagel adduct intermediate **A**, which then suffers a Michael-type addition reaction of the nucleophilic C-4 at 5-aminopyrazole **1** leading to the formation of intermediate **B**. Finally, the intermediate **B** undergoes cyclocondensation with another molecule of formaldehyde yielding **4–6**.[9a,12]

In the case of reaction with indandione, the formation of two products was observed, and after separation by column chromatography using chloroform as eluent, they were characterized by spectroscopic and analytical data as pyrazolo[3,4-*b*]pyridine-5-spiroindanediones **6** and 3-*tert*-butyl-1-phenylindeno[2,3-*e*]pyrazolo[3,4-*b*]pyridine **7** (Fig. 1).[13]

The formation of compound **7** occurred with the loss of a benzyl fragment. We have previously reported the synthesis of analogues to compound **7** via the three-component reaction between 5-amino-3-methyl-1-phenylpyrazole, indandione and aromatic aldehydes.[8d] Compound **7** can be easily identified because of it is high luminescence both in the solid and in the solution state. The



Scheme 2.

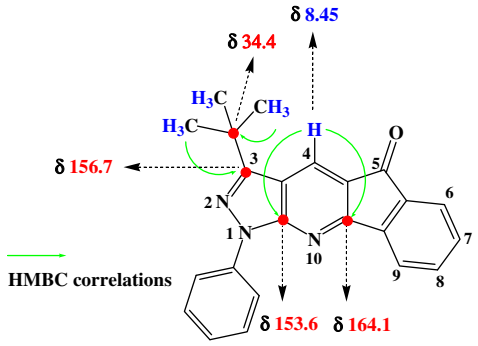
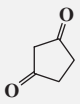
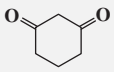
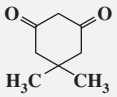
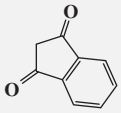


Figure 1. Structural determination of compounds **7**.

Table 1
One-pot condensation of 5-aminopyrazoles, formaldehyde and cyclic β-diketones—synthesis of pyrazolo[3,4-*b*]pyridine-5-spirocycloalkanedione derivatives **4–6**

Entry	Cyclic β-diketone[a]	Ar	Product	Yield (%)
1		4-$H_3CC_6H_4$	**4a**	84
2		4-$F_3CC_6H_4$	**4b**	73
3		4-FC_6H_4	**4c**	72
4		4-ClC_6H_4	**4d**	66
5		4-BrC_6H_4	**4e**	69
6		4-$H_3COC_6H_4$	**4f**	77
7		C_6H_5	**4g**	75
8		3,4,5-Tri-$H_3COC_6H_2$	**4h**	55
9		3,4-OCH_2O–C_6H_3	**4i**	68
10		4-$O_2NC_6H_4$	**4j**	70
11		4-$F_3CC_6H_4$	**5a**	75
12		4-BrC_6H_4	**5b**	80
13		4-$H_3COC_6H_4$	**5c**	75
14		3,4-OCH_2O-C_6H_3	**5d**	70
15		4-$H_3CC_6H_4$	**5e**	75
16		4-$F_3CC_6H_4$	**5f**	85
17		4-FC_6H_4	**5g**	85
18		4-ClC_6H_4	**5h**	85
19		4-BrC_6H_4	**5i**	77
20		4-$H_3COC_6H_4$	**5j**	75
21		2,4-$DiH_3COC_6H_3$	**5k**	85
22		3,4,5-Tri-$H_3COC_6H_2$	**5l**	71
23		3,4-OCH_2O–C_6H_3	**5m**	70
24		4-$H_3CC_6H_4$	**6a**	50
25		4-$F_3CC_6H_4$	**6b**	50
26		4-FC_6H_4	**6c**	51
27		4-ClC_6H_4	**6d**	59
28		4-BrC_6H_4	**6e**	54
29		4-$H_3COC_6H_4$	**6f**	55
30		C_6H_5	**6g**	52
31		3,4,5-Tri-$H_3COC_6H_2$	**6h**	52
32		3,4-OCH_2O–C_6H_3	**6i**	20
33		4-$O_2NC_6H_4$	**6j**	56

[a] Compounds **5a–d** to pyrazolo[3,4-*b*]pyridine-5-spirocyclohexanedione derivatives and **5e–m** to 4′,4′-dimethyl-pyrazolo[3,4-*b*]pyridine-5-spirocyclohexanedione derivatives.

formation of compound **7** takes place in the reaction of indandione with all 5-benzylaminopyrazoles **1a–m** and isolated in 45% yields.[13]

A plausible rationalization may be advanced to explain the formation of product **7**. Presumably, after the intermediate **B** is formed from Knoevenagel adduct **A**, it can be a competition between cyclocondensation reaction to render **6** and intramolecular cyclocondensation with loss of benzyl alcohol that stabilizes the product by aromatization yielding the lineal derivative **7**. This approach with indandione represents a general method widely used to close both carbocyclic and heterocyclic rings.

We have described multicomponent cyclocondensation reactions (5-aminopyrazoles, cycloalkane-1,3-diones and paraformaldehyde) as a method for spiroannulation of pyrazolo[3,4-*b*]pyridine derivatives in the 5-position, forming four bonds in one-step. The reaction proceeds by Knoevenagel condensation and selective cyclocondensation reaction obtaining spiro derivatives in good purity and yield, showing that the synthetic route allows us to build blocks of 5-spiropyrazolo[3,4-*b*]pyridine derivatives with a wide diversity in substituents. Spiro derivatives with an indandione substituent were obtained in low yields due to the formation of a competitive pyrazolopyridine indeno-fused-derivative. This methodology is simple, practical and is a regioselective alternative synthetic route to obtain good yields spiro derivatives by conventional heating or by microwave irradiation. The latter is much more efficient due to short reaction times and easy work up.

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13. All new compounds gave satisfactory 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR and IR spectral data.
Selected physical data.
Data for 3-tert-butyl-5-spiro-1-phenyl-7-(4-methylbenzyl)-1H-pyrazolo[3,4-b]pyridine-4,5,6,7-tetrahydro-1′-cyclopentano-2,5-dione **4a**. White solid, 84%, mp 224–226 °C. ^{1}H NMR $CDCl_3$ 400 MHz rt δ: 1.42 (s, 9H, CH_3, *t*-Bu), 2.36 (s, 3H, CH_3), 2.80 (m, 4H, C(3′)H_2 and C(4′)H_2), 2.94 (s, 2H, H-4), 3.22 (s, 2H, H-5), 3.94 (s, 2H, N7–CH_2), 7.09 (d, 2H, H_o, aryl J = 8.3 Hz), 7.14 (d, 2H, H_m, aryl, J = 8.2 Hz), 7.19 (t, 1H, H_p, J = 7.5 Hz), 7.36 (t, 2H, H_m, J = 7.9 Hz), 7.72 (d, 2H, H_o, J = 8.0 Hz). ^{13}C NMR $CDCl_3$ 100 MHz rt δ: 21.1 (CH_3), 24.3 (C-4), 29.3 (CH_3, *t*-Bu), 33.4 (Cq, *t*-Bu), 35.3 (C-3′ and C-4′), 51.1 (C-6), 55.2 (N7–CH_2), 55.5 (C-5(1′)), 99.2 (C-3a), 123.4 (C_o), 126.6 (C_p), 128.0 (C_o, aryl), 129.0 (C_m), 129.4 (C_m, aryl), 133.5 (C_i, aryl), 137.5 (C_p, aryl), 140.1 (C_i), 144.6 (C-7a), 157.4 (C-3), 213.4 (C═O). IR (KBr) cm^{-1} 2962 (CH st), 1713–1691 (C═O st). The mass spectrum shows the following peaks: MS (70 eV) *m/z* (%) = 441 (M^+, 100), 336 (29), 280 (86). HR-MS calcd for $C_{28}H_{31}N_3O_2$ 441.2416, found 441.2419. Anal. Calcd for $C_{28}H_{31}N_3O_2$: C, 74.08; H, 7.14; N, 9.26. Found: C, 73.96; H, 6.97; N, 9.37.
Data for 3-tert-butyl-1-phenyl-7-(4-methylbenzyl)-4′,4′-dimethyl-4,5,6,7-tetrahydro-1H-pyrazolo[3,4-b]pyridine-5-spiro-1′-cyclohexane-2′,6′-dione **5e**. White crystalline solid, 75%, mp 199–201 °C. ^{1}H NMR $CDCl_3$ 400 MHz rt δ: 0.86 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 1.41 (s, 9H, CH_3, *t*-Bu), 2.33 (s, 3H, CH_3), 2.45 (d, 2H, CH_2 J = 14.0 Hz), 2.67 (d, 2H, CH_2 J = 14.0 Hz), 3.15 (s, 2H, H-4), 3.35 (s, 2H, H-6), 3.82 (s, 2H, N7–CH_2), 7.09–7.14 (m, 5H, H_p, 4H aryl), 7.29 (t, 2H, H_m, J = 7.5 Hz), 7.63 (d, 2H, H_o, J = 7.5 Hz). ^{13}C NMR $CDCl_3$ 100 MHz rt δ: 21.1 (CH_3), 23.6 (C-4), 26.9 (CH_3), 29.3 (CH_3, *t*-Bu), 29.9 (CH_3), 31.0 (C4′), 33.3 (Cq, *t*-Bu), 51.9 (C3′, C5′), 53.5 (C-6), 55.4 (N7–CH_2), 64.3 (C-5(1′)), 100.7 (C-3a), 123.4 (C_o), 126.5 (C_p), 127.6 (C_m), 129.0 (C_m, aryl), 129.4 (C_o, aryl), 133.5 (C_p, aryl), 137.4 (C_i, aryl), 140.2 (C_i), 144.0 (C-7a), 157.4 (C-3), 206.5 (C═O). IR (KBr) cm^{-1} 2961 (CH *st*), 1722–1690 (C═O *st*). The mass spectrum shows the following peaks: MS (70 eV) *m/z* (%) = 483 (M^+, 100), 378 (76), 322 (57), 276 (22), 252 (19). HR-MS calcd for $C_{31}H_{37}N_3O_2$ 483.2886, found 483.2894. Anal. Calcd for $C_{31}H_{37}N_3O_2$: C, 76.98; H, 7.71; N, 8.69. Found: C, 76.96; H, 7.69; N, 8.72.
Data for 3-tert-butyl-5-spiro-1-phenyl-7-(4-methylbenzyl)-1H-pyrazolo[3,4-b]pyridine-4,5,6,7-tetrahydro-2′-indan-1′,3′-dione **6a.** After separating the compound **7** in 45% yield**.** Pale yellow solid, 50%, mp 230–231 °C. ^{1}H NMR $CDCl_3$ 400 MHz rt δ: 1.38 (s, 9H, CH_3, *t*-Bu), 2.25 (s, 3H, CH_3), 3.06 (s, 2H, H-4), 3.33 (s, 2H, H-5), 4.07 (s, 2H, N7–CH_2), 7.00 (s, 4H, H_o, H_m, aryl), 7.17 (t, 1H, H_p, J = 7.5 Hz), 7.33 (t, 2H, H_m, J = 7.9 Hz), 7.75 (d, 2H, H_o, J = 7.5 Hz), 7.84–7.86 (m, 2H, H-5′, H-6′), 7.96–7.98 (m, 2H, H-4′, H-7′). ^{13}C NMR $CDCl_3$ 100 MHz rt δ: 21.0 (CH_3), 26.0 (C-4), 29.30 (CH_3, *t*-Bu), 33.3 (Cq, *t*-Bu), 50.8 (C-5(2′)), 50.9 (C-6) 55.4 (N7–CH_2), 98.7 (C-3a), 123.4 (C-4′ and C-7′), 123.6 (C_o), 126.5 (C_p), 127.9 (C_m, aryl), 129.0 (C_m), 129.1 (C_o, aryl), 133.9 (C_i, aryl), 135.8 (C-5′ and C-6′), 136.9 (C_p, aryl), 140.4 (C_i), 141.0 (C-3′ and C-1′), 145.4 (C-7a), 157.4 (C-3), 202.1(C═O). IR (KBr) cm^{-1} 2963 (CH *st*), 1721–1700 (C═O *st*). The mass spectrum shows the following peaks: MS (70 eV) *m/z* (%) = 489 (M^+, 100), 328 (90), 384 (19). HR-MS calcd for $C_{32}H_{31}N_3O_2$ 489.2416, found 489.2426. Anal. Calcd for $C_{32}H_{31}N_3O_2$: C, 77.66; H, 6.27; N, 8.49. Found C, 77.21; H, 6.43; N, 8.67.
Data for 3-tert-butyl-1-phenyl-1H-indeno[2,3-e]pyrazolo[3,4-b]pyridine-5-one **7**. The product was separated by silica gel chromatography eluting with chloroform. Yellow solid, 45%, mp 192–194 °C. ^{1}H NMR $CDCl_3$ 400 MHz rt δ: 1.56 (s, 9H, CH_3, *t*-Bu), 7.33 (t, 1H, H_p, J = 7.3 Hz), 7.47 (t, 1H, H-7, J = 7.5 Hz), 7.54 (t, 2H, H_m, aryl, J = 7.5 Hz), 7.76 (d, 2H, H_o, J = 7.3 Hz), 7.62 (t, 1H, H-8, J = 7.5 Hz), 7.97 (d, 1H, H-6, J = 7.5 Hz), 8.34 (d, 1H, H-9, J = 8.0 Hz), 8.45 (s, 2H, H-4). ^{13}C NMR $CDCl_3$ 100 MHz rt δ: 29.9 (CH_3), 34.4 (Cq, *t*-Bu), 114.5 (C-3a), 121.5 (C-9), 121.6 (C-6), 123.9 (C_o), 126.2 (C_p), 127.7 (C-4), 129.0 (C_m), 131.4 (C-7), 135.0 (C-8), 137.3 (C-5a), 139.2 (C_i), 143.1 (C-9a), 153.6 (C-10a), 156.7 (C3), 164.1 (C-9b), 190.9 (C═O). IR (KBr) cm^{-1} 2963 (CH *st*), 1715 (C═O *st*). The mass spectrum shows the following peaks: MS (70 eV) *m/z* (%) = 353 (M^+, 39), 339 (22), 338 (100). HR-MS calcd for $C_{23}H_{19}N_3O$ 353.1528, found 353.1529. Anal. Calcd for $C_{23}H_{19}N_3O$: C, 78.16; H, 5.42; N, 11.89. Found: C, 78.10; H, 5.48; N, 11.90.