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Short Report

Microwave-Assisted Synthesis under Solvent-Free Conditions of (*E*)-2-(Benzo[*d*]thiazol-2-yl)-3-arylacrylonitriles

Jorge E. Trilleras,*,[a] Kelly J. Velasquez,[a] Dency J. Pacheco,[a] Jairo Quiroga[b] and Alejandro Ortíz[b]

[a]Grupo de Investigación en Compuestos Heterocíclicos, Programa de Química, Facultad de Ciencias Básicas, Universidad del Atlántico, Km 7 Antigua vía Puerto Colombia, Barranquilla-Atlántico, Colombia

[b]Grupo de Investigación de Compuestos Heterocíclicos, Departamento de Química, Universidad del Valle, A. A 25360 Cali, Colombia

Uma série de (*E*)-2-(benzo[*d*]tiazol-2-il)-3-arilacrilonitrilas foi sintetizada pela condensação de Knoevenagel assistida por microondas, na ausência de solvente, partindo do correspondente 2-(benzo[*d*]tiazo-2-il)acetonitrila e aldeídos aromáticos, contendo tanto grupos doadores de elétrons, como retiradores. Os tempos de reação foram consideravelmente curtos e os produtos, obtidos em rendimentos moderados (50-75%) e boa pureza. A configuração da dupla ligação da acrilonitrila não pôde ser estabelecida por métodos comuns de RMN. No entanto, estudos teóricos sugerem que nesses compostos o isômero *E* é mais estável do que o *Z*, o que está de acordo com algumas evidências experimentais.

A series of (*E*)-2-(benzo[*d*]thiazol-2-yl)-3-arylacrylonitriles was synthesized by microwave assisted Knoevenagel condensation under solvent-free conditions from the corresponding 2-(benzo[*d*]thiazol-2-yl)acetonitrile and aromatic aldehydes with electrondonating/electron-withdrawing groups. The reaction times were considerably short and the products obtained in moderate yields (50 to 75%) and good purity. The configuration of the acrylonitrile double bond could not be established by regular NMR methods. However, theoretical studies suggest that the *E* isomer is more stable than *Z*, which is in good agreement with some experimental evidences.

Keywords: acrylonitriles, 2-(benzo[*d*]thiazol-2-yl)acetonitrile, solvent-free reaction, irradiation microwave, Knoevenagel condensation, benzaldehydes

Introduction

Acetonitrile derivatives are convenient precursors which have been extensively utilized in heterocyclic synthesis. Several reactions were developed in the last decades for which the reactivity of hetarylacetonitriles towards diverse reagents was exploited for the synthesis of nitrogen bridged heterocycles.[1-3] From the point of view for biological activities, acetonitrile derivatives are useful intermediates and subunits for the development of molecules having pharmaceutical or biological interests.[4-6] Nitrogen containing heteroaromatic compounds have received considerable attention in the literature over the years. From the synthetic point of the view, it is known that heteroaromatic acetonitrile derivatives undergo Knoevenagel condensation reactions with arylaldehydes to yield 3-aryl-2hetarylacrylonitriles.[1-3,5-9] Substituted acrylonitriles have been found to possess interesting biological properties, among them, antifungal and antitumor activities.[7,10,11] Although acrylonitrile derivatives are an-easy-to synthesize template, a great diversity of the methods is available in literature that describe their synthesis under different conditions making use of conventional thermal energy and microwave irradiation conditions.[1-3,12-17] Typically, Knoevenagel adducts have been obtained under conventional heating conditions for extended periods of reaction in the presence of catalytic amounts of base, obtaining generally from good to very low yields.[18-23] Condensation reactions leading to heterocyclic systems have been performed with great success under

*e-mail: jorgetrilleras@mail.uniatlantico.edu.co

microwave irradiation in "dry media" reducing substantially the reaction times and increasing product yields.[24-26] Because of the advantages that microwave irradiation has over conventional reflux methods, we present, herein, the Knoevenagel synthesis of 3-arylacrylonitriles by the reaction of 2-(benzo[*d*]thiazol-2-yl)acetonitrile with different substituted arylaldehydes. The synthesis has been assisted by microwave irradiation and under solvent-free conditions. When compared with other methods, this one has better yields, milder reaction conditions and easy work-up, in addition to inexpensive reagents, and an environmentally friendly procedure.

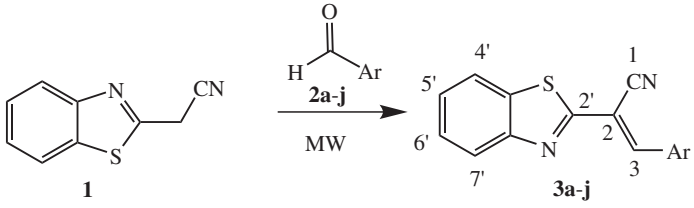
Results and Discussion

Microwave enhanced synthesis of (*E*)-2-(benzo[*d*] thiazol-2-yl)-3-arylacrylonitriles **3a**-**j** was carried out under solvent-free conditions using different substituted arylaldehydes **2** as shown in Scheme 1 and Table 1.

The reactions proceeded quite well with different substituted aldehydes with electrondonating/electron-withdrawing groups giving moderate yields (50 to 75%).

The condensation between 2-(benzo[*d*]thiazol-2-yl) acetonitrile **1** and different substituted arylaldehydes **2** yields (*E*)-2-(benzo[*d*]thiazol-2-yl)-3-arylacrylonitriles **3** in "dry media" conditions in excellent purities and moderate yields. Reaction times were reduced to minutes rather than hours when compared with conventional thermal synthesis.[18-23] This type of condensation reaction represents a great potential for the synthesis of heterocyclic compounds with possible biological activity. The fast reaction times, combined with the easy purification and improved yields make this method highly suitable. The synthesis of products consists in irradiating the heterogeneous mixture of 2-(benzo[*d*]thiazol-2-yl)acetonitrile **1** with different substituted arylaldehydes **2** through reactions that are conducted with neat solid reagents without catalysts; elevation of the temperature had some positive effects and improved the yield of the target product. Due to the dipolar polarization phenomenon, the greater the polarity of a molecule the more pronounced the microwave effect when the rise in temperature is considered. In terms of reactivity, the specific effect has therefore to be considered according to the reaction mechanism and particularly with regard to how the polarity of the system is altered during the progress of the reaction.[12]

In initial attempts, we carried out the reaction under solvent-free conditions during 15-20 min of microwave irradiation in a commercial domestic oven, and then the reactions conditions were optimized in a focused microwaves reactor (CEM Discover TM) twice. In order to improve our initial attempts, different reaction times, power and temperatures were studied for the preparation of (*E*)-2-(benzo[*d*]thiazol-2-yl)-3-arylacrylonitriles **3**. The reaction



Scheme 1. Microwave irradiation synthesis under solvent-free conditions of (*E*)-2-(benzo[*d*]thiazol-2-yl)-3-arylacrylonitriles **3a**-**j**.

Table 1. Knoevenagel reaction between 2-(benzo[*d*]thiazol-2-yl)acetonitrile (**1**) and aromatic aldehydes (**2a**-**j**)

	Ar	Data reported in literature for compounds **3a**-**j**[18-23]		
		time reaction / min	yield / (%)	mp / (ºC)
a	C_6H_5	15/180	70/46	116-118/121-123
b	4-H_3C-C_6H_4	15/180	70/54	140-142/147-148
c	4-O_2N-C_6H_4	20/240	50/50	170-172/177-180
d	4-Cl-C_6H_4	20/240	75/51	144-148/148-150
e	4-Br-C_6H_4	20/180	50/54	138-140/143-145
f	4-F-C_6H_4	10	50	150-152
g	4-F_3C-C_6H_4	10/180	75/56	122-124/128-133
h	4-$H_3COC_6H_4$	15/180	50/62	130-dec./143-144
i	3,4,5-*tri*-H_3CO-C_6H_2	15	55	140-142
j	3,4-OCH_2O-C_6H_3	15/180	50/40	192-194/200-205

carried under the maximum power 150W during 10-20 min at a controlled temperature of 473 K and 250 psi proved to be the most satisfactory. An increase in the irradiation time did not affect the yields.

All compounds were characterized on the basis of their elemental analyses, mass and NMR spectral data. The whole carbon skeleton was assigned using ^{13}C NMR spectra, (including distortionless enhancement by polarization transfer (DEPT)) and two dimensional HSQC (heteronuclear single quantum correlation), and HMBC (heteronuclear multiple bond correlation) experiments. The (*E*)-2-(benzo[*d*]thiazol-2-yl)-3-arylacrylonitriles **3a**-**j** were were characterized by a very polarized carbon-carbon double bond (C2-C3), which leads to chemical shifts from 102.2 to 109.5 ppm for C2 and 143.2 to 146.9 ppm for C3; the signal of CN at δ values from 115.6 to 117.3 ppm; from ^{1}H NMR, a singlet between 8.12 and 8.30 ppm for H3 (Figure 1).

The ^{13}C NMR spectra of all other compounds of the series retain similar signals, differing only in those corresponding to the aryl ring. Regarding to mass spectra, all products **3** exhibit a similar pattern of fragmentation, showing the molecular peak along with a typical loss of the substituents of each aryl group.

The configuration of the acrylonitrile double bond could not be established by NMR methods. However, studies have shown that for these compounds the *E* isomer is more stable than the *Z*. This result can be explained by the steric and electronic repulsions between the aromatic and heteroaromatic groups.[27] In previous research on these

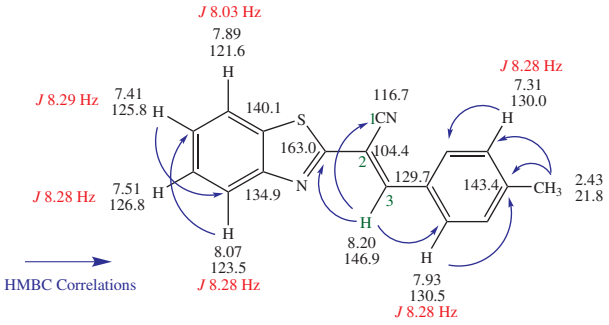


Figure 1. Structural formula of (*E*)-2-(benzo[*d*]thiazol-2-yl)-3-*p*-tolylacrylonitrile **3b**.

3-arylacrylonitrile derivatives it has also been observed preference for the *E* isomer.[7,13-15] Compound (**3a**) and (*E*)-3-phenyl-2-(thiophen-2-yl)acrylonitrile (**4**) previously reported by us,[7] might have a number of conformations due to free rotation around the double bond; the most stable conformations are shown in Figure 2 and apparently the lowest energy structure is favored by planarity of the molecule around the double bond mentioned; this fact was calculated by means theoretical methods like DFT using a B3LYP functional and 3-21G as basis set.

When performing an analysis of net atomic charges of the most stable conformers, it was found that for conformer **3a**, the presence of a hydrogen bond between the H3 and N, is the driving force for greater stability and planarity; these two atoms are at a distance of 2.399 Å, the H3 also presents a net charge of 0.26556e and a valence of 0.73151

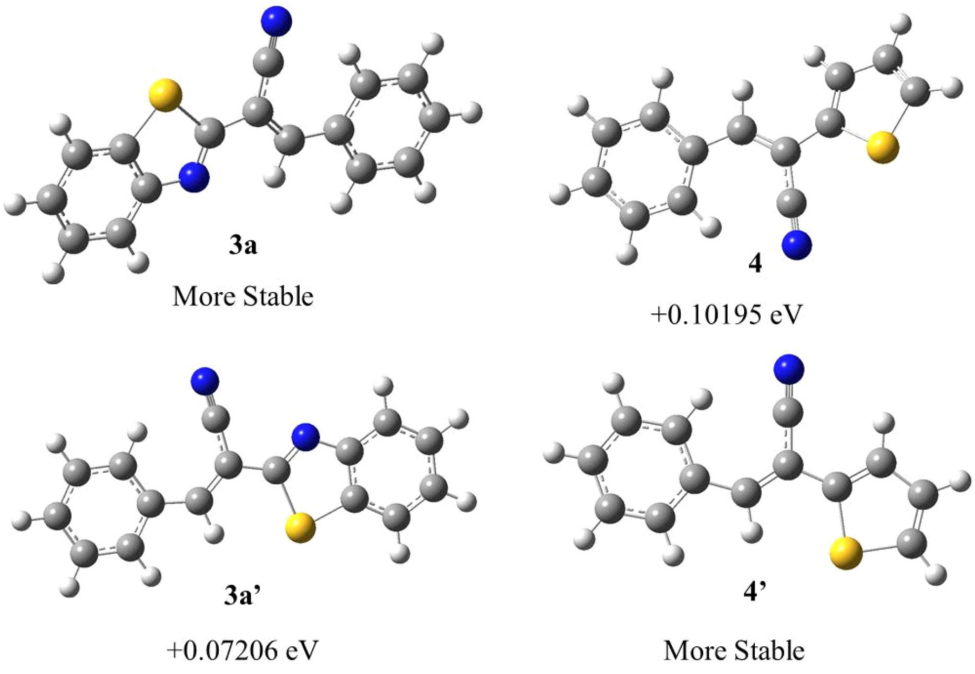
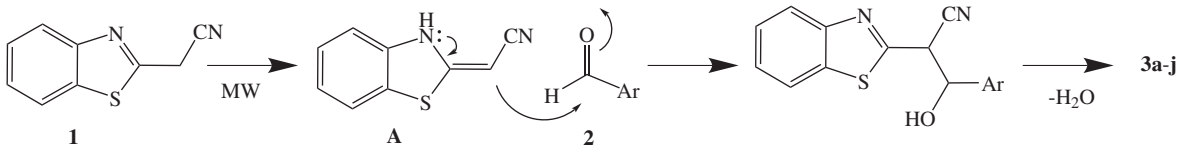


Figure 2. Lowest energy structures calculated for **3a** and **4**.



Scheme 2. Plausible formation of Knoevenagel adducts assisted by microwave irradiation.

versus the average of the other protons in the molecule with net charge 0.24834e and valence of 0.750091. The latter fact is evidenced experimentally in the ^{1}H NMR spectrum for this compound, where the proton H3 is observed at very low field δ 8.25 ppm, because (as presented in this NPA analysis) it is very deshielded compared to the other protons. In the case of NPA analysis for conformer **4'**, all the charges on the protons are in an average; this means that the possibility of hydrogen bonds is low. As a proof of this fact, H3 for this molecule has a net charge 0.24035e and a valence of 0.73710; average values for a proton gave no such address as the deshielding effect, so that its stability can be attributed more to his *E*-type configuration about the double bond.

It seems reasonable to think that microwave irradiation promotes the Knoevenagel reactions through the methylene active component of 2-(benzo[*d*]thiazol-2-yl)acetonitrile **1**. Under the optimized reaction conditions, **1** is likely to be converted to compound **A** containing double bond susceptible to the addition of electrophile **2** (Scheme 2).

Conclusions

We report here an efficient synthetic route to prepare (*E*)-2-(benzo[*d*]thiazol-2-yl)-3-arylacrylonitriles derivatives conducted by microwave irradiation under solvent-free conditions. These conditions allowed us to obtain the compounds in short times and acceptable yields. No relationship was found between them and the nature of the substituents of the aldehydes. Further efforts to expand the scope of the chemistry on these compounds are ongoing subjects in our laboratory.

Experimental

Equipments

Microwave experiments were carried out using a focused microwave reactor (CEM Discover TM). Melting points were determined in a Buchi melting point apparatus and are reported uncorrected. The ^{1}H and ^{13}C NMR spectrum were measured at RT on a Bruker Avance 400 spectrometer operating at 400 and 100 MHz, respectively, and using $CDCl_3$ as solvent and tetramethylsilane as internal standard. The mass-spectra were scanned on a Hewlett Packard HP Engine-5989 spectrometer (equipped with a direct inlet probe) which was operating at 70 eV. The elemental analyses have been obtained using a LECO CHNS-900 and Thermo Finnigan FlashEA1112 CHNS-O elemental analyzers. Thin layer chromatography was carried out using Merck 0.2 mm silica gel $60F_{254}$ aluminum chromatographic plates.

All theoretical calculations were carried out at the DFT approach using the Gaussian 03 program review C.02.[28] The DFT calculations were determined using three parameters exchange functional of Becke B3LYP and a set of orbital 3-21G basis. The net atomic charges were calculated using NPA analysis included in the algorithm natural bonding orbital (NBO) proposed by Weinhold and co-workers.[29,30]

Reagents

The reagents (2-(benzo[*d*]thiazol-2-yl)acetonitrile and aromatic aldehydes) and solvents used, such as, ethanol, ethyl acetate, hexane and DMF, were acquired commercially.

Synthesis

*General procedure for the preparation of the (E)-2-(benzo[d]thiazol-2-yl)-3-arylacrylonitriles **3a-j***

A mixture of 2-(benzo[*d*]thiazol-2-yl)acetonitrile **1** and aromatic aldehydes **2** with electrondonating/electron-withdrawing groups (1 mmol) were subjected to microwave irradiation (maximum power 150 W during 10-20 min under solvent-free conditions at a controlled temperature of 473 K and 250 psi) using a focused microwave reactor (CEM Discover). The solid products were isolated by simple crystallization of the reaction mixture from ethanol.

*(E)-2-(Benzo[d]thiazol-2-yl)-3-phenylacrylonitrile **3a***

Yellow solid; mp 116-118 °C, 70%. IR (KBr) ν_{max}/cm^{-1}: 2221 (CN), 3060 (–C=H$_{Aromatics}$), 3019 (=C–H), 1590 (C=C). MS (70eV) *m/z* (%): 263(9, M$^+$+1), 262(32, M$^+$), 261(100), 236(13). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.43 (t, 1H, *J* 8.28 Hz, H_p), 7.50-7.56 (m, 4H, H, phenyl), 7.91 (d, 1H, *J* 8.03 Hz, H7'), 8.01-8.04 (m, 2H, H5' and

H6'), 8.08 (d, 1H, *J* 7.76 Hz, H4'), 8.25 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 105.7 (C2), 116.4 (CN), 121.7 (C4'), 123.7 (C7'), 126.0 (C6'), 127.0 (C_p), 129.3 (C_m), 130.4 (C_o), 132.2 (C_i), 135.0 (C7'a), 147.0 (CH), 162.7 (C2'). Anal. calc. for $C_{16}H_{10}N_2S$: C 73.26; H 3.84; N 10.68; found: C 73.16; H 3.83; N 10.65.

(E)-2-(Benzo[d]thiazol-2-yl)-3-p-tolylacrylonitrile ***3b***

Yellow solid; mp 140-142 °C, 70%. IR (KBr) ν_{max}/cm^{-1}: 2223 (CN), 3018 (–C=$H_{Aromatics}$), 2855 (=C–H), 1589 (C=C). MS (70 eV) *m/z* (%): 277(10, M$^+$+1), 276(40, M$^+$), 275(100). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 2.43 (s, 3H, CH_3) 7.31 (d, 2H, *J* 8.28, H_m), 7.41 (t, 1H, *J* 8.29 Hz, H5'), 7.51 (t, 1H, *J* 8.28 Hz, H6'), 7.89 (d, 1H, *J* 8.03 Hz, H4'), 7.93 (d, 2H, *J* 8.28 Hz, H_o), 8.07 (d, 1H, *J* 8.28 Hz, H7'), 8.21 (s, 1H, CH)). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 21.8 (CH_3), 104.4 (C2), 116.7 (CN), 121.6 (C4'), 123.5 (C7'), 125.8 (C5'), 126.8 (C6'), 129.7 (C_i), 130.0 (C_m), 130.5 (C_o), 134.9 (C7'a), 140.1 (C3'a), 143.4 (C_p), 146.9 (CH), 163.0 (C2'). Anal. calc. for $C_{17}H_{12}N_2S$: C 73.88; H 4.38; N 10.14; found: C 73.80; H 4.36; N 10.17.

(E)-2-(Benzo[d]thiazol-2-yl)-3-(4-nitrophenyl) acrylonitrile ***3c***

Yellow solid; mp 170-172 °C, 50%. IR (KBr) ν_{max}/cm^{-1}: 2225 (CN), 3031 (–C=H) 2853 (=C–H), 1522 (C=C). MS (70 eV) *m/z* (%): 308(11, M$^+$+1), 307(46, M$^+$), 306(82), 260(100), 261(38). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46 (t, 1H, *J* 7.00 Hz, H5'), 7.55 (t, 1H, *J* 7.00 Hz, H6'), 7.77 (d, 2H, *J* 8.53 Hz, H_m) 7.93 (d, 1H, *J* 8.30 Hz, H4'), 8.10 (d, 3H, *J* 8.78 Hz, H_o, H7'), 8.29 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 108.5 (C2), 116.2 (CN), 122.1 (C4'), 124.1 (C7'), 125.2 (C_i), 126.5 (C5'), 126.7 (C6'), 127.5 (C_m), 130.6 (C_o), 133.3, 133.7 (C7'a), 135.5 (C3'a), 135.9 (C_p), 144.9 (CH), 153.9 (C2'). Anal. calc. for $C_{16}H_9N_3O_2S$: C 62.53; H 2.95; N 13.67; found: C 62.54; H 2.92; N 13.72.

(E)-2-(Benzo[d]thiazol-2-yl)-3-(4-chlorophenyl) acrylonitrile ***3d***

Yellow solid; mp 144-148 °C, 75%. IR (KBr) ν_{max}/cm^{-1}: 2219 (CN), 3060 (–C=$H_{Aromatics}$), 2855 (=C–H), 1584 (C=C). MS (70 eV) *m/z* (%): 298(15, M$^+$+2), 296(42, M$^+$), 295(100), 270(17), 261(11). ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 7.51 (t, 1H, *J* 7.28 Hz, H5'), 7.58 (t, 1H, *J* 7.53 Hz, H6'), 7.66 (d, 2H, *J* 8.79 Hz, H_m,) 8.07 (d, 1H, *J* 7.53 Hz, H4'), 8.09 (d, 2H, *J* 9.03 Hz, H_o), 8.17 (d, 2H, *J* 8.03 Hz, H7'), 8.40 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 106.1 (C2), 115.8 (CN), 122.4 (C4'), 123.1 (C7'), 126.3 (C5'), 127.1 (C6'), 129.3 (C_m), 131.1 (C_i), 131.7 (C_o), 134.3 (C7'a), 136.8 (C3'a), 146.7 (CH), 152.8 (C_p), 162.8 (C2').

(E)-2-(Benzo[d]thiazol-2-yl)-3-(4-bromophenyl) acrylonitrile ***3e***

Brown solid; mp 138-140 °C, 50%. IR (KBr) ν_{max}/cm^{-1}: 2219 (CN), 3062 (–C=$H_{Aromatics}$), 3020 (=C–H), 1579 (C=C). MS (70 eV) *m/z* (%): 341(17, M$^+$+2), 339(16, M$^+$), 280(40), 279(100), 254(21). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.44 (t, 1H, *J* 7.28 Hz, H5'), 7.54 (t, 1H, *J* 7.03 Hz, H6'), 7.64 (d, 2H, *J* 8.53, H_m), 7.87 (d, 2H, *J* 8.78 Hz, H_o), 7.91 (d, 1H, *J* 8.03 Hz, H4'), 8.08 (d, 1H, *J* 8.04 Hz, H7'), 8.18 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 106.1 (C2), 116.2 (CN), 121.7 (C4'), 123.7 (C7'), 126.1 (C5'), 126.9 (C_i), 127.0 (C6'), 131.5 (C_m), 132.6 (C_o), 135.0 (C7'a), 145.2 (CH), 153.4 (C_p), 162.3 (C2'). Anal. calc. for $C_{16}H_9BrN_2S$: C 56.32; H 2.66; N 8.21; found: C 56.33; H 2.63; N 8.17.

(E)-2-(Benzo[d]thiazol-2-yl)-3-(4-fluorophenyl) acrylonitrile ***3f***

Brown solid; mp 150-152 °C, 50%. IR (KBr) ν_{max}/cm^{-1}: 2224 (CN), 3052 (–C=$H_{Aromatics}$), 1588 (C=C). MS (70 eV) *m/z* (%): 281(10, M$^+$+1), 280(39, M$^+$), 279(100), 254(22). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.19 (t, 2H, *J* 8.53 Hz, H_m), 7.43 (t, 1H, *J* 7.02 Hz, H5') 7.52 (t, 1H, *J* 7.02 Hz, H6'), 7.90 (d, 1H, *J* 8.28 Hz, H4'), 8.02-8.07 (m, 3H, H_o, H7'), 8.20 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 105.2 (C2), 116.4 (CN), 116.7 (C_m), 121.7 (C4'), 123.6 (C7'), 126.0 (C5'), 127.0 (C6'), 128.7 (C_i), 132.7 (C_o), 134.9 (C7'a), 145.3 (CH), 153.6 (C_p), 162.5 (C2').

(E)-2-(Benzo[d]thiazol-2-yl)-3-(4-(trifluoromethyl)phenyl) acrylonitrile ***3g***

Beige solid; mp 122-124 °C, 75%. IR (KBr) ν_{max}/cm^{-1}: 2229 (CN), 3066 (–C=$H_{Aromatics}$), 2942 (=C–H), 1476 (C=C). MS (70 eV) *m/z* (%): 331(10, M$^+$+1), 330(38, M$^+$), 329(100), 304(13), 261(11). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.48 (t, 1H, *J* 7.03 Hz, H5'), 7.56 (t, 1H, *J* 7.03 Hz, H6'), 7.93 (d, 1H, *J* 7.78 Hz, H4') 8.10 (d, 1H, *J* 8.04 Hz, H7'), 8.14 (d, 2H, *J* 8.79 Hz H_o), 8.30 (s, 1H, CH), 8.34 (d, 2H, *J* 8.78 Hz, H_m). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 109.5 (C2), 115.6 (CN), 121.80 (C4'), 124.0 (C7'), 124.3 (C5'), 126.6 (C6'), 127.3 (C_m), 130.8 (C_o), 135.3 (C7'a), 138.0 (C3'a), 143.2 (CH), 161.2 (C2'). Anal. calc. for: C 61.81; H 2.75; N 8.48; found: C 61.82; H 2.71; N 8.49.

(E)-2-(Benzo[d]thiazol-2-yl)-3-(4-methoxyphenyl) acrylonitrile ***3h***

Yellow solid; mp 130 °C (decomposition); 50%. IR (KBr) ν_{max}/cm^{-1}: 2219 (CN), 3007 (–C=$H_{Aromatics}$), 2833 (=C–H), 1589 (C=C). MS (70 eV) *m/z* (%): 293(13, M$^+$+1),

292(58, M^+), 291(100), 277(11), 266(27), 261(13), 248(41). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 3.87 (s, 3H, OCH_3), 6.99 (d, 2H, *J* 8.79 Hz, H_m), 7.39 (t, 1H, *J* 8.03 Hz, H5'), 7.49 (t, 1H, *J* 8.03 Hz, H6'), 7.87 (d, 1H, *J* 8.03 Hz, H4'), 8.00 (d, 2H, *J* 8.79 Hz, H_o), 8.02 (d, 1H, *J* 8.28 Hz, H7'), 8.14 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 55.8 (OCH_3), 102.6 (C2), 115.0 (C_m), 117.3 (CN), 121.9 (C4'), 123.6 (C7'), 125.5 (C_i), 126.0 (C5'), 127.1 (C6'), 133.0 (C_o), 135.1 (C7'a), 146.7 (CH), 153.9 (C_p), 163.2 (C2'). Anal. calc. for $C_{17}H_{12}N_2OS$: C 69.84; H 4.14; N 9.58; found: C 69.86; H 4.15; N 9.55.

(E)-2-(Benzo[d]thiazol-2-yl)-3-(3,4,5-trimethoxyphenyl) acrylonitrile ***3i***

Yellow solid; mp 140-142 °C, 55%. IR (KBr) ν_{max}/cm^{-1}: 2210 (CN), 3055 (–C=$H_{Aromatics}$), 2838 (=C–H), 1573 (C=C). MS (70 eV) *m/z* (%): 353(14, M^++1), 352(53, M^+), 357(37), 151(100). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 3.93 (s, 6H, OCH_3–C_m), 3.95 (s, 3H, OCH_3–C_p), 7.31 (s, 2H, H_o), 7.41 (t, 1H, *J* 7.03 Hz, H5'), 7.51 (t, 1H, *J* 7.03 Hz, H6'), 7.89 (d, 1H, *J* 7.03 Hz, H4'), 8.05 (d, 1H, *J* 7.28 Hz, H7'), 8.15 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 56.3 (OCH_3–C_m), 61.1 (OCH_3–C_p), 104.0 (C2), 107.9 (C_o), 116.9 (CN), 121.6 (C4'), 123.4 (C7'), 125.9 (C5'), 126.9 (6'), 127.5 (C_i), 134.9 (C7'a), 141.9 (C3'a), 146.7 (CH), 153.3 (C_m), 153.6 (C_p), 162.9 (C2'). Anal. calc. for $C_{19}H_{16}N_2O_3S$: C 64.76; H 4.58; N 7.95; found: C 64.74; H 4.59; N 7.91.

(E)-3-(Benzo[d][1,3]dioxol-6-yl)-2-(benzo[d]thiazol-2-yl) acrylonitrile ***3j***

Yellow solid; mp 192-194 °C, 50%. IR (KBr) ν_{max}/cm^{-1}: 2211 (CN), 3065 (–C=$H_{Aromatics}$), 2918 (=C–H), 1570 (C=C). MS (70eV) *m/z* (%): 307(14, M^++1), 306(56, M^+), 305(100), 280(16), 248(16). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 6.11 (s, 2H, CH_2), 6.95 (d, 1H, *J* 8.03 Hz, H5-aryl), 7.43 (t, 1H, *J* 8.28 Hz, H5'), 7.47 (d, 1H, *J* 8.28 Hz, H6-aryl), 7.52 (t, 1H, *J* 8.28 Hz, H6'), 7.71 (s, 1H, H2-aryl), 7.93 (d, 1H, *J* 8.53 Hz, H4'), 8.03 (d, 1H, *J* 8.03 Hz, H7'), 8.12 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 101.5 (CH_2), 102.2 (C2), 107.6 (CH-aryl), 108.2 (CH-aryl), 115.9 (CN), 120.9 (C4'), 122.6 (C7'), 125.1 (C5'), 126.1 (C6'), 127.6 (CH-aryl), 134.0 (C_q), 146.0 (CH), 147.9 (C_q), 150.7 (C_q), 152.8 (C_q), 162.4 (C2'). Anal. calc. for $C_{16}H_9N_3O_2S$: C 62.53; H 2.95; N 13.67; found: C 62.54; H 2.92; N 13.62.

Supplementary Information

Supplementary information (Figures S1-S20) is available free of charge at http://jbcs.sbq.org.br as PDF file.

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