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Article

N-Alkylated Sulfamic Acid Derivatives as Organocatalyst in Multicomponent Synthesis of Fatty Dihydropyrimidinones

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In this work, *N*-alkylated sulfamic acid derivatives are introduced as promising acidic organocatalysts with convenient acidity and easy synthesis. The new organocatalysts derived from different nitrogenated compounds (amines, chitosan, urea and thiourea) were applied in multicomponent reactions to synthesize several dihydropyrimidinones (DHPMs). All tested organocatalysts resulted in good DHPM yields, using classic 1,3-dicarbonyl compounds and long-chain 1,3-dicarbonyl derivatives, demonstrating catalytic efficiency. *N*-Alkylated sulfamic acid derived from benzylamine showed good results (ca. 80% yields). In addition, excellent results were obtained with organocatalysts based on sulfamic acid and thiourea (ca. 80-97% yields), demonstrating the catalytic efficiency of new derivatives of thiourea organosulfamic catalysts.

Keywords: sulfamic acid, organocatalysts, Biginelli reaction, multicomponent reaction, fatty derivatives

Introduction

Organocatalysis is a field of organic chemistry in constant growing and several organocatalysts have been developed for different organic reactions. The first mention date to back the second decade of 20th century from the Bredig and Fiske's report[1] using some alkaloids as catalysts in the addition reaction of hydrocyanic acid to benzaldehyde. Organocatalytic methods has been currently widely applied in the synthesis of various bioactive compounds including large-scale intermediates in the pharmaceutical industry.[2] The main advantage is due to avoiding contamination risk by metals.[3] In addition, the organocatalysts are generally cheap, stable in atmospheric conditions, allow reproducible results and require simple reaction conditions.[4]

Sulfamic acid (SA, H_2NSO_3H) has emerged as a substitute for conventional Bronsted and Lewis acid catalysts in organic synthesis.[5] It is a relatively stable, white crystalline and odorless solid, non-volatile, non-hygroscopic, non-corrosive, and inexpensive.[6] In addition, it is a heterogeneous catalyst, and can be recovered by simple filtration and is considered an efficient green catalyst.[7,8] It has been used in acid catalyzed reactions, for functional group protections[8] and deprotections,[9] and some important organic transformations, such as the Beckmann rearrangement,[10] Michael addition,[11] imino Diels-Alder,[12] Pechmann reaction,[13] esterifications,[14] transesterification,[15] Hantzsch reaction[16] and Biginelli condensations.[17] According to a previous study,[18] the pK_a of SA in water is 1.19. As would be expected, the aliphatic derivatives of SA are weaker acids than SA itself. For example: the pK_a value for cyclohexylsulfamic acid was found to be 1.90.[19] Dupont *et al.*[20] synthesized recently different *N*-alkylated sulfamic acid (NSA) as acidic metal extractants (pK_a ca. 2). Other species such as *N*-alkylated sulfamic acid ionic liquids ($[R_2NH–SO_3H][Tf_2N]$) were presented as a new and safe to handle class of super acids (pK_a value < -7).[20] The *N*-alkylated sulfamic acid derivatives

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showed a good miscibility in various organic solvents such as methanol, ethanol and acetone. This fact turns its use in organic media compatible and interesting to apply as a promoter in organic reactions.

In the present work, we describe the synthesis of new *N*-alkylated sulfamic acid derivatives and their uses as organocatalysts in multicomponent Biginelli reactions to achieve the synthesis of dihidropirimidin-2-ones and their respective fatty derivatives following up the research previously developed in our research group.[21]

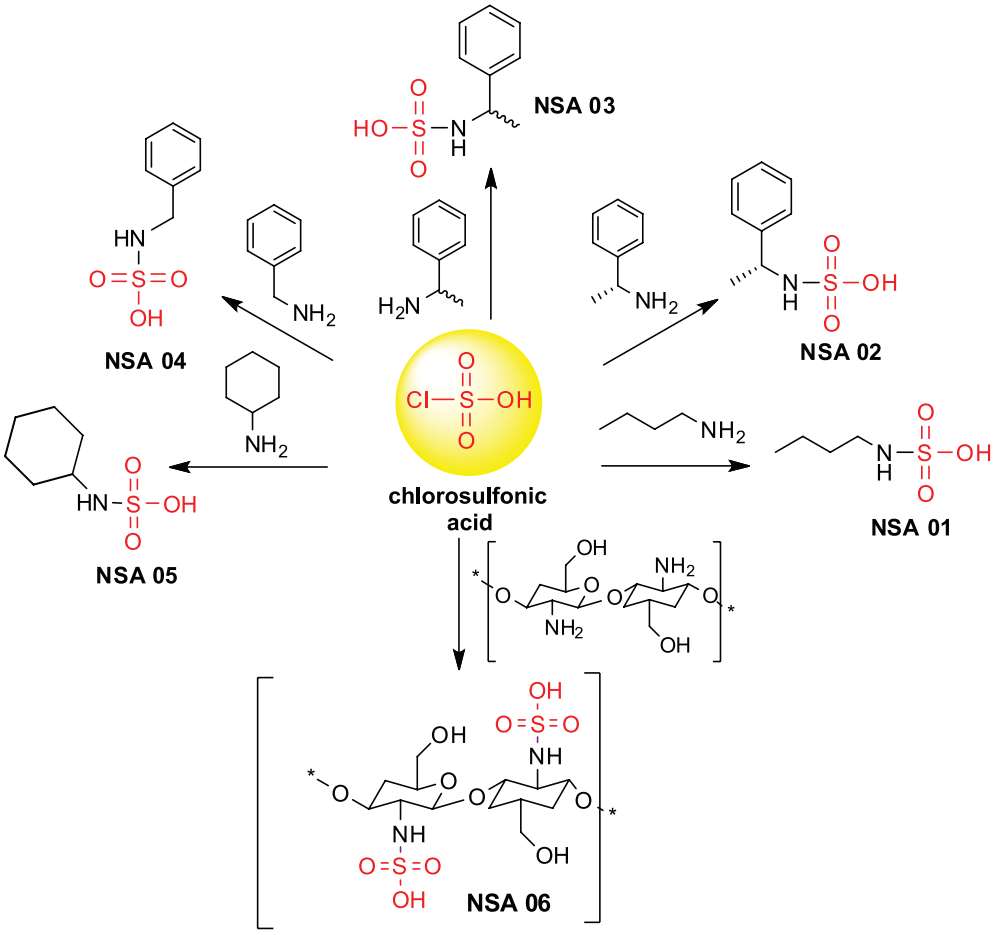
Results and Discussion

A series of *N*-alkylated sulfamic acid derivatives **NSA 01-06** was synthesized using a set of primary amines and chlorosulfonic acid, according to a procedure described in the literature (Scheme 1).[22] The **NSA 01-06** organocatalysts were characterized by melting point, and infrared (IR), nuclear magnetic resonance (NMR), and high resolution mass spectrometries (HRMS).

Initially, the Biginelli reaction was carried out reacting methyl acetoacetate, benzaldehyde and urea in the presence of 10 mol% of SA as pattern, under reflux of methanol.[23] The reaction was monitored by thin-layer chromatography (TLC) and the aldehyde consumption was observed after 4 h. In this case, the dihydropyrimidinone **1** was formed in 84% yield. The result is shown in Table 1 (entry 2).

Next, we examined the ability of NSA's as organocatalysts to promote the Biginelli reaction. The loading of 10 or 20 mol% of **NSA 01-06** were investigated under the same experimental conditions (Scheme 2). The dihydropyrimidinone **1** was formed in good yields in all examined cases (Table 1, entries 3-14). The best catalytic behavior was observed when 20 mol% of organocatalyst **NSA 04** was employed (Table 1, entry 10).

As a part of our ongoing efforts to synthesize new fatty hybrid molecules, we applied this protocol to the synthesis of hybrid fatty dihydropyrimidinones (fatty-DHPMs).[16,21,24] Thus, the multicomponent Biginelli reaction was performed in the presence of long-chain octadecyl acetoacetate **2c**,[24] benzaldehyde, urea and 20 mol% of **NSA 01-06** under reflux of methanol. In these cases, 24 h were necessary to complete the reactions (Scheme 3). The crude product was purified by column chromatography and characterized by



Scheme 1. Synthesis of *N*-alkylated sulfamic acid organocatalysts **NSA 01-06**.

Table 1. Multicomponent synthesis of DHPM **1** using SA and organocatalysts **NSA 01-06**

entry	Catalyst	Catalyst / mol%	**1**, Yield / %
1	–	–	9
2	NH_2SO_3H	10	84
3	**NSA 01**	10	57
4	**NSA 01**	20	75
5	**NSA 02**	10	49
6	**NSA 02**	20	68
7	**NSA 03**	10	54
8	**NSA 03**	20	67
9	**NSA 04**	10	63
10	**NSA 04**	20	79
11	**NSA 05**	10	45
12	**NSA 05**	20	65
13	**NSA 06**	10	59
14	**NSA 06**	20	67

IR, ^{1}H and ^{13}C NMR spectroscopies.[23,24] The results are showed in Table 2. The fatty-DHPM **1c** was formed in good yields, with **NSA 04** and **NSA 01** catalysts showing the most relevant results (Table 2, entries 2 and 5, respectively).

Although the yield of reactions involving the **NSA 06** catalyst, derived from chitosan, were modest (Table 1, entries 13-14 and Table 2, entry 7), they could be considered relevant, since the chitosan is easily obtained from natural resources and is a low-cost material.[25]

To increase the scope of products obtained through this process, we utilized long-chain alkyl acetoacetates derived from fatty alcohols, combined with urea or thiourea and

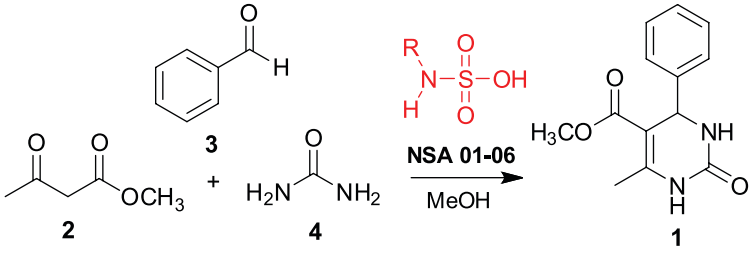
Table 2. Synthesis of fatty DHPM **1c** using SA and organocatalysts **NSA 01-06**

entry	Catalyst	Catalyst / mol%	**1c**, Yield / %
1	NH_2SO_3H	20	74
2	**NSA 01**	20	79
3	**NSA 02**	20	56
4	**NSA 03**	20	53
5	**NSA 04**	20	80
6	**NSA 05**	20	72
7	**NSA 06**	20	53

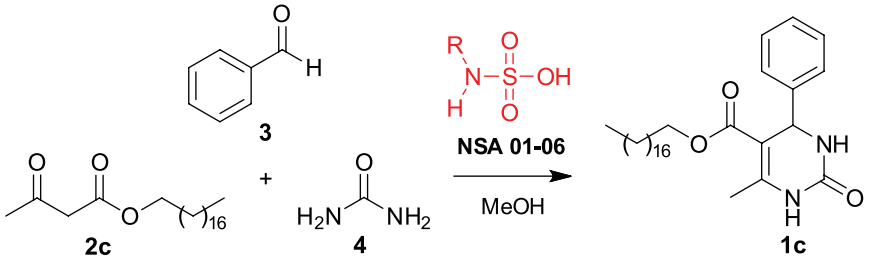
several aromatic aldehydes. After reactions using 20 mol% of catalyst **NSA 04**, the fatty dihydropyrimidinones **1-6a-d** were obtained (Scheme 4). All tested examples resulted in good fatty dihydropyrimidinones yields, demonstrating the catalytic efficiency of the new aminosulfamic organocatalysts **NSA 04** derived from benzylamine in the multicomponent Biginelli reaction (Table 3).

In recent decades, interest has arisen in the development of organocatalysts based on mono or bifunctional urea or thiourea capable of double hydrogen bonding. A broad variety of monofunctional and bifunctional achiral double hydrogen-bonding thiourea organocatalysts have been developed to accelerate various synthetically useful organic transformations employing H-bond-accepting substrates (Figure 1).[26]

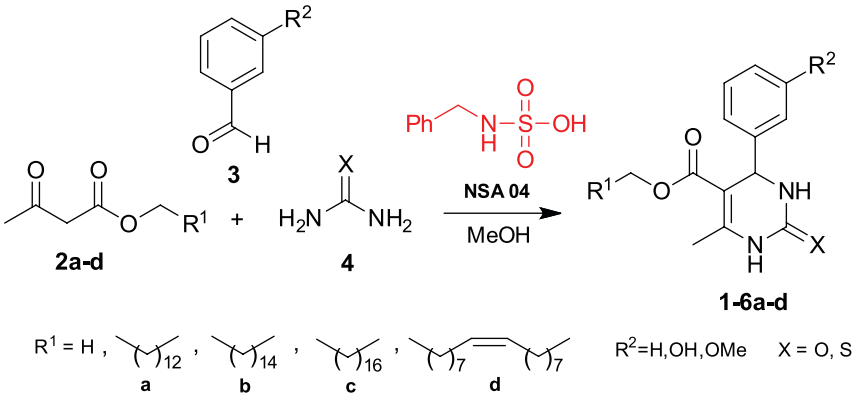
A recent report of Puripat *et al.*[27] based on computational calculations, suggested that urea would be a good catalyst for the synthesis of 3,4-dihydropyrimidinones via Biginelli reaction. Taking this into account, we decided to investigate



Scheme 2. Synthesis of DHPM **1** using aminosulfamic organocatalysts **NSA 01-06**.



Scheme 3. Synthesis of fatty DHPM **1c** under catalysis with **NSA 01-06**.



Scheme 4. Synthesis of long chain DHPMs **1-6a-d** under catalysis with **NSA 04**.

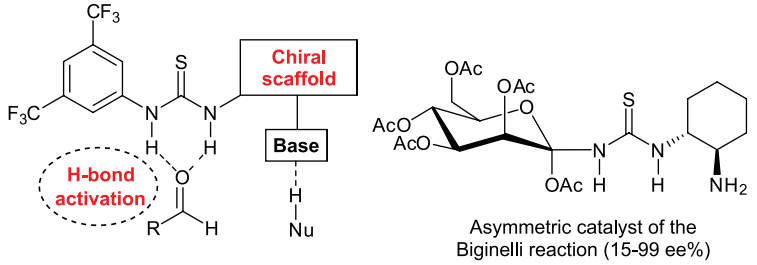
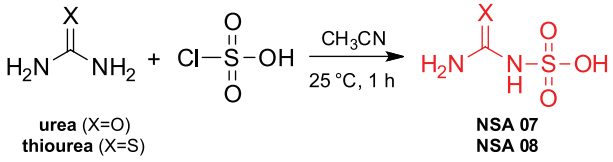


Figure 1. Bifunctional organocatalysts based on thiourea.

Table 3. Synthesis of fatty DHPMs **1-6a-d** using organocatalyst **NSA 04**

entry	R^1	R^2	X	Yield / %
1		H	O	**1a**, 89
2	$(CH_2)_{12}$	OH	O	**2a**, 86
3		OMe	O	**3a**, 80
4		H	O	**1b**, 70
5	$(CH_2)_{14}$	OH	O	**2b**, 87
6		OMe	O	**3b**, 82
7		H	O	**1c**, 80
8	$(CH_2)_{16}$	OH	O	**2c**, 68
9		OMe	O	**3c**, 81
10		H	O	**1d**, 87
11	$(CH_2)_7CH{=}CH(CH_2)_7$	OH	O	**2d**, 84
12		OMe	O	**3d**, 83
13		H	S	**4a**, 82
14	$(CH_2)_{12}$	OH	S	**5a**, 84
15		OMe	S	**6a**, 76
16		H	S	**4b**, 87
17	$(CH_2)_{14}$	OH	S	**5b**, 65
18		OMe	S	**6b**, 62
19		H	S	**4c**, 81
20	$(CH_2)_{16}$	OH	S	**5c**, 61
21		OMe	S	**6c**, 65
22		H	S	**4d**, 70
23	$(CH_2)_7CH{=}CH(CH_2)_7$	OH	S	**5d**, 76
24		OMe	S	**6d**, 66

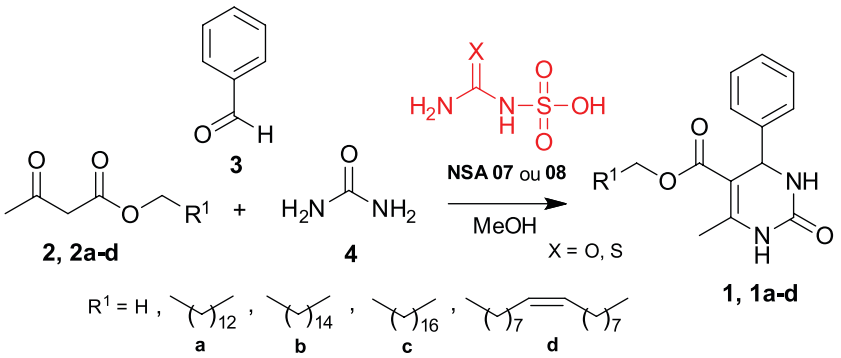
N-substituted sulfamic acid derivatives based on the structure of sulfamic acid and urea (**NSA 07**), as well as thiourea (**NSA 08**) as organocatalysts. The procedure used to obtain compounds **NSA 07** and **NSA 08** (Scheme 5) was the same to **NSA 01-06**.



Scheme 5. Synthesis of organosulfamic catalysts **NSA 07** and **NSA 08**.

NSA 07 and **NSA 08** were obtained at satisfactory yields (82 and 81%, respectively), after removing hydrochloric acid. Then these catalysts were submitted to a Biginelli reaction, using them individually with benzaldehyde, urea and acetoacetates (Scheme 6). Different times and two concentrations of **NSA 07** and **NSA 08** (10 and 20 mol%) in the presence of methanol were evaluated in this reaction. The results are shown in Table 4.

In general, both **NSA 07** and **NSA 08** were able to catalyze the multicomponent reaction in reasonable to good yields, with the latter showing superior catalytic ability when used at 20 mol%, leading to excellent yields of 81-97%. In addition, higher yields were obtained with **NSA 08** (Table 4, entries 11-20) compared to that



Scheme 6. Organocatalytic properties of **NSA 07** and **NSA 08** in Biginelli reaction.

Table 4. Synthesis of DHPM **1**, **1a-d** under catalysis of **NSA 07** and **NSA 08**

entry	R^1	Catalyst	Catalyst / mol%	time / h	Yield / %
1	$-CH_3$		10	5	**1**, 47
2	$-CH_3$		20	5	**1**, 54
3	$-CH_3$		10	6	**1**, 52
4	$-CH_3$		20	6	**1**, 65
5	$-CH_3$		10	8	**1**, 57
6	$-CH_3$		20	8	**1**, 67
7	$-(CH_2)_{12}-$		20	24	**1a**, 51
8	$-(CH_2)_{14}-$	**NSA 07**	20	24	**1b**, 57
9	$-(CH_2)_{16}-$		20	24	**1c**, 61
10	$-(CH_2)_7-CH=CH-(CH_2)_7-$		20	24	**1d**, 65
11	$-CH_3$		10	5	**1**, 74
12	$-CH_3$		20	5	**1**, 87
13	$-CH_3$		10	6	**1**, 80
14	$-CH_3$		20	6	**1**, 81
15	$-CH_3$		10	8	**1**, 84
16	$-CH_3$		20	8	**1**, 88
17	$-(CH_2)_{12}-$		20	24	**1a**, 97
18	$-(CH_2)_{14}-$	**NSA 08**	20	24	**1b**, 91
19	$-(CH_2)_{16}-$		20	24	**1c**, 82
20	$-(CH_2)_7-CH=CH-(CH_2)_7-$		20	24	**1d**, 93

with organocatalysts **NSA 07** and **NSA 01-06** (Table 2, entries 2-7).

Figure 2 shows the ^{1}H NMR spectra of new sulfamic organocatalysts **NSA 08** and thiourea precursor. The spectrum of **NSA 08** indicates the disappearance of singlet in 7.05 ppm from NH_2 of thiourea and the appearance of a singlet in 1.78 ppm, attributed to OH and NH hydrogens present in the catalyst structure. In addition, two broad singlets are observed, referent to hydrogens NH_2 and NH_2^+ from neutral and zwitterionic forms, with δ 9.07 and 5.92 ppm, respectively (Figure 2b).

The literature suggests that the catalytic behavior of sulfamic acid and derivatives is associated to the presence of zwitterion.[20,28] Thus, according to ^{1}H NMR spectra (Figure 2b), the results obtained with **NSA 08** could be related to the presence of zwitterion in approximately 70%, showing superior catalytic activity.

Conclusions

In this work, *N*-alkylated sulfamic acid (NSA) derivatives are introduced as promising acidic organocatalysts with

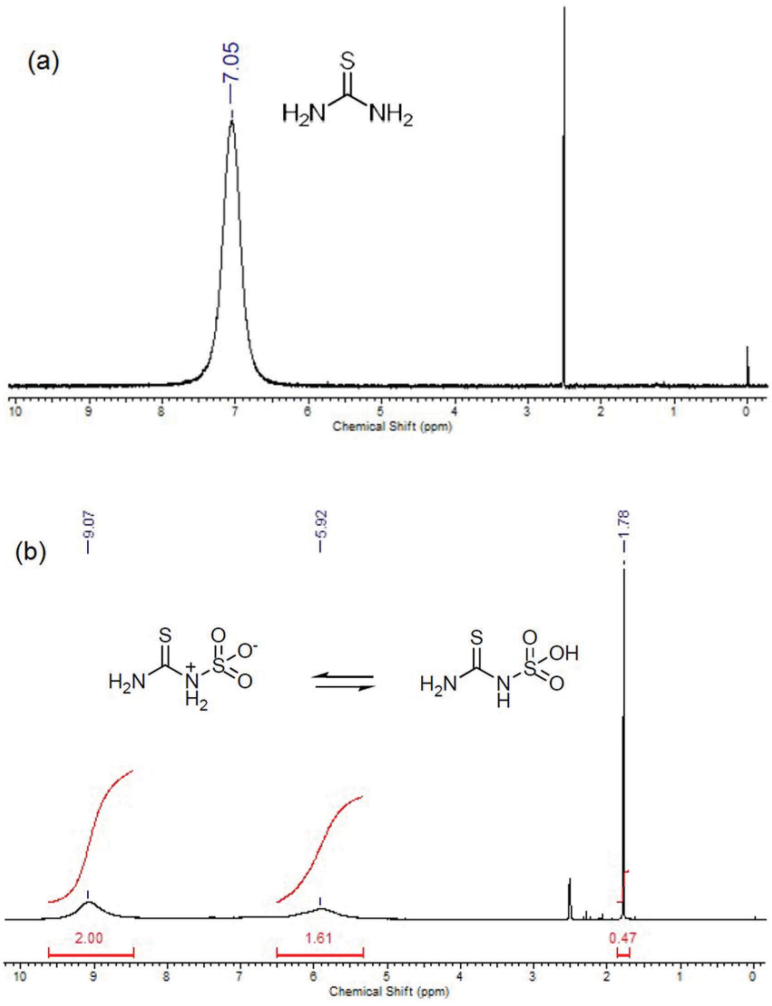


Figure 2. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of thiourea (a) and **NSA 08** (b).

convenient acidity and easy synthesis. These organocatalysts could successfully be applied in multicomponent Biginelli reaction, and good yields were observed in the synthesis of DHPMs using classic 1,3-dicarbonyl compounds and long-chain 1,3-dicarbonyl derivatives.

All tested examples resulted in good to reasonable DHPM yields, demonstrating catalytic efficiency. The *N*-alkylated aminosulfamic acid catalysts **NSA 04** and **NSA 01** derived from benzylamine and butylamine, respectively, showed the most relevant results. In addition, excellent results were obtained with organocatalysts **NSA 08** based on the structure of sulfamic acid and thiourea with good yields (80-97%), demonstrating, for the first time, its catalytic efficiency in multicomponent Biginelli reaction.

Experimental

Apparatus and chemistry

The reagents were purchased from Aldrich Chemical Co. and used without further purification. Column chromatography was performed using a silica gel 60A (ACROS Organics, 0.035-0.070 mesh). The reactions were monitored using thin-layer chromatography (TLC) performed with plates containing silica gel (Merck, 60GF245), gradients of hexane:ethyl acetate as eluents, and the spots were visualized using iodine. The melting points were obtained on a Fisatom 430D apparatus and are uncorrected. Infrared (IR) spectra were measured on a Shimadzu PRESTIGIE-21 FT-IR spectrophotometer. Nuclear magnetic resonance experiments for ^{1}H, ^{13}C and ^{15}N nuclei were conducted using a Bruker Ascend 400 MHz spectrometer, equipped with BBO probe with z-axis gradients in $CDCl_3$, DMSO-d_6 or CD_3CN. Chemical shifts are reported in δ (ppm) downfield from the tetramethylsilane (TMS) internal standard or residual solvent. ^{15}N data were acquired from ^{1}H-^{15}N HMBC (heteronuclear multiple bond correlation) experiments at room temperature. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplicities.

General procedure for synthesis of catalysts **NSA 01-05**, **NSA 07** and **NSA 08**

To a round-bottom flask containing nitrogenated compound (1 mmol, amine, urea or thiourea) in dry acetonitrile (3 mL), it was added chlorosulfonic acid (1 mmol) dropwise over a period of 20 min at room temperature. The reactional mixture was stirred for 2 h, and the acetonitrile was removed under vacuum to give the catalysts.

Butylsulfamic acid (**NSA 01**)

153.04 g mol^{-1}; colorless oil; FTIR (KBr) ν / cm^{-1} 3516, 2962, 1597, 1496, 1465, 1220, 1058, 869; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69 (sl, 2H), 2.77 (m, 2H), 1.51 (q, *J* 8 Hz, 2H), 1.32 (q, *J* 8 Hz, 2 H), 0.89 (t, *J* 4 Hz, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.9, 19.5, 29.5, 39.1; HRMS calcd. to $C_4H_{11}NO_3S$ [M$^-$] 152.0381; found 152.0381.

(*R*)-1-Phenylethylsulfamic acid (**NSA 02**)

201.04 g mol^{-1}; yellow viscous liquid; FTIR (KBr) ν / cm^{-1} 3460, 2868, 1764, 1517, 1452, 1087, 887; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.48 (d, *J* 8 Hz, 3H), 4.41 (sl, 9H), 7.45 (m, 5H), 8.30 (sl, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.2, 50.5, 127.2 (2C), 128.9, 129.2 (2C), 139.7; HRMS calcd. to $C_8H_{11}NO_3S$ [M$^-$] 200.0381; found 200.0372.

1-Phenylethylsulfamic acid (**NSA 03**)

201.04 g mol^{-1}; yellow viscous liquid; FTIR (KBr) ν / cm^{-1} 3523, 3062, 1598, 1510, 1292, 887; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.50 (d, *J* 8 Hz, 3H), 4.26 (m, 11H), 7.48 (m, 5H), 8.26 (sl, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.2, 50.5, 127.2 (2C), 129.0, 129.2 (2C), 139.6; HRMS calcd. to $C_8H_{11}NO_3S$ [M$^-$] 200.0381; found 200.0372.

Benzylsulfamic acid (**NSA 04**)

187.03 g mol^{-1}; white solid; mp 69-70 °C; FTIR (KBr) ν / cm^{-1} 3600, 3018, 1591, 1473, 1215, 1050, 887; ^{1}H NMR (400 MHz, CD_3CN) δ 7.39 (m, 7H), 5.42 (sl, 2H), 4.07 (m, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ 134.0, 130.2 (2C), 129.8 (2C), 118.3, 44.5; HRMS calcd. to $C_7H_9NO_3S$ [M$^-$] 186.0225; found 186.0224.

Cyclohexylmethylsulfamic acid (**NSA 05**)

173.01 g mol^{-1}; white solid; mp 163-165 °C; FTIR (KBr) ν / cm^{-1} 3616, 2935, 1597, 1496, 1226, 1066, 887; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.75 (sl, 3H), 4.61 (sl, 7H), 2.93 (m, 1H), 1.88 (m, 2H), 1.72 (m, 2 H), 1.56 (m, 1H), 1.24 (m, 4H), 1.08 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 24.2, 25.0, 30.7, 49.8; HRMS calcd. to $C_6H_7NO_3S$ [M$^-$] 178.0538; found 178.0543.

Carbamoylsulfamic acid (**NSA 07**)

139.99 g mol^{-1}; white solid; mp 58-60 °C; FTIR (KBr) ν / cm^{-1} 1282, 1354, 1550.7, 1728, 3327; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.80 (s), 6.01 (s), 6.96 (s); ^{15}N NMR (40 MHz, DMSO-d_6) δ 22.4, 112.1; CHN calcd. to $CH_4N_2O_3S$: C, 8.57; H, 2.88; N, 19.99%; found: C, 8.65; H, 2.74; N, 19.87%.

Carbamothioylsulfamic acid (**NSA 08**)

155.97 g mol^{-1}; white solid; mp 137-140 °C; FTIR (KBr) ν / cm^{-1} 1217, 1357, 1531.4, 1712.7, 3280; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.78 (s), 5.91 (s), 9.08 (s); ^{15}N NMR (40 MHz, DMSO-d_6) δ 63.3, 86.6; CHN calcd. to $CH_4N_2O_3S_2$: C, 7.69; H, 2.58; N, 17.94%; found: C, 7.96; H, 2.59; N, 17.62%.

Chitosan production

Chitin was extracted from pink shrimp wastes (*Farfantepenaeus brasiliensis*) through chemical treatments, demineralization, deproteination, deodorization and depigmentation. Deacetylation of chitin was carried out with 150 g of chitin and 3 L of concentrated sodium hydroxide solution (45% m/v) at 130 ± 1 °C, under constant agitation of 50 rpm.[25]

Preparation of chitosan sulfonic acid **NSA 06**

To a round-bottom flask containing a mixture of 5.0 g of chitosan and 20 mL of hexane was added dropwise 1.0 g of chlorosulfonic acid (9 mmol), at room temperature and magnetic stirring. After the addition was complete, the mixture was stirred for 1 h. Then the mixture was filtered and washed with 30 mL of acetonitrile, and the solvent was removed under vacuum to afford chitosan sulfonic acid as a pale yellow powder.

Chitosan sulfonic acid (**NSA 06**)

257.0205 g mol^{-1}; pale yellow power; mp > 250 °C; FTIR (KBr) ν / cm^{-1} 3577, 3352, 1637, 1517, 1207, 1182, 1014, 889; HRMS calcd. to $C_6H_{11}NO_8S$ [M$^-$] 256.0491; found 255.2351.

General procedure for synthesis of fatty 3,4-dihydropyrimidin-2(1*H*)-one/thiones (**1-6a-d**)

A mixture of acetoacetate (1 mmol), aldehyde (1 mmol), urea or thiourea (1 mmol) in 3 mL methanol was refluxed

for 24 h in the presence of catalyst (0.2 mmol). The progress of the reaction was monitored by TLC (hexane/ethyl acetate 8:2). After completion of the reaction, the mixture was evaporated under reduced pressure and the crude product was recrystallized from ethyl acetate to obtain pure fatty 3,4-dihydropyrimidin-2(1*H*)-one/thiones according to literature.[23,24]

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

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References

1. Bredig, G.; Fiske, P. S.; *Biochem. Z.* **1913**, *46*, 7.
2. Jensen, K. L.; Poulsen, P. H.; Donslund, B. S.; Morana, F.; Jørgensen, K. A.; *Org. Lett.* **2012**, *14*, 1516.
3. Baran, R.; Veverková, V.; Škvorcová, A.; Sebesta, R.; *Org. Biomol. Chem.* **2013**, *11*, 7705.
4. Verma, S.; Jain, S. L.; Sain, B.; *Tetrahedron Lett.* **2010**, *51*, 6897.
5. Heravi, M. M.; Baghernejad, B.; Oskooie, H. A.; *Curr. Org. Chem.* **2009**, *13*, 1002.
6. Kaliannan, P.; Vishveswara, S.; Rao, V. S. R.; *Curr. Sci.* **1985**, *54*, 1174; Heravi, M. M.; Ranjbar, L.; Derikvand, F.; Alimadadi, B.; *Mol. Diversity* **2008**, *12*, 191; Rostamniai, A.; Ahmad-Jangi, F.; *Chin. Chem. Lett.* **2011**, *22*, 1029.
7. Yadav, J. S.; Ather, H.; Rao, P. P.; Rao, R. S.; Nagaiah, K.; Prasad, A. R.; *Catal. Commun.* **2006**, *7*, 797.
8. Jin, T. S.; Sun, G.; Li, Y. W.; Li, T. S.; *Green Chem.* **2002**, *4*, 255.
9. Wang, B.; He, J.; Sun, R. C.; *Chin. Chem. Lett.* **2010**, *21*, 794.
10. Li, J. T.; Meng, X.-T.; Yin, Y.; *Synth. Commun.* **2010**, *40*, 1445.
11. An, L.-T.; Zou, J.-P.; Zhang, L.-L.; Zhang, Y.; *Tetrahedron Lett.* **2007**, *48*, 4297.
12. Nagarajan, R.; Magesh, C. J.; Perumal, P. T.; *Synthesis* **2004**, *1*, 69.
13. Sing, P. R.; Singh, D. U.; Samant, S. D.; *Synlett* **2004**, *11*, 1909.
14. D'Oca, M. G. M.; Marinho, R. S.; de Moura, R. R.; Granjão, V. F.; *Fuel* **2012**, *97*, 884; de Oliveira, P. M.; Farias, L. M.; Morón-Villarreyes, J. A.; D'Oca, M. G. M.; *J. Am. Oil Chem. Soc.* **2016**, *93*, 1393.
15. Weber, A. C. H.; Batista, T. C.; Gonçalves, B.; Hack, C. R. L.; Porciuncula, L. M.; Treptow, T. G. M.; D'Oca, C. R. M.; Russowsky, D.; D'Oca, M. G. M.; *J. Am. Oil Chem. Soc.* **2016**, *93*, 1399.
16. Fontecha-Terazona, H. D.; Brinkerhoff, R. C.; Oliveira, P. M.; Rosa, S. B.; Flores, D. C.; D'Oca, C. R. M.; Russowsky, D.; D'Oca, M. G. M.; *RSC Adv.* **2015**, *5*, 59638; Cabrera, D. C.; Rosa, S. B.; de Oliveira, F. S.; Marinho, M. A. G.; D'Oca, C. R. M.; Russowsky, D.; Horn, A. P.; D'Oca, M. G. M.; *Med. Chem. Commun.* **2016**, *7*, 2167.
17. Wang, B.; *Synlett* **2005**, *2005*, 1342; Li, J.-T.; Han, J.-F.; Yang, J.-H.; Li, T.-S.; *Ultrason. Sonochem.* **2003**, *10*, 119; Chen, W. Y.; Qin, S. D.; Jin, J. R.; *Synth. Commun.* **2007**, *37*, 47.
18. Benson, G. A.; Spillane, W. J.; *Chem. Rev.* **1980**, *80*, 151.
19. Kojima, S.; Ichibagase, H.; Iguchi, S.; *Chem. Pharm. Bull.* **1966**, *14*, 965.
20. Dupont, D.; Renders, E.; Raiguel, S.; Binnemans, K.; *Chem. Commun.* **2016**, *52*, 7032.
21. Duarte, R. C.; Ongaratto, R.; Piovesan, L. A.; de Lima, V. R.; Soldi, V.; Merlo, A. A.; D'Oca, M. G. M.; *Tetrahedron Lett.* **2012**, *53*, 2454; Brinkerhoff, R. C.; Fontecha-Terazona, H. D.; de Oliveira, P. M.; Flores, D. C.; D'Oca, C. R. M.; Russowsky, D.; D'Oca, M. G. M.; *RSC Adv.* **2014**, *4*, 49556.
22. Safari, J.; Banitaba, S. H.; Khalili, S. D.; *J. Mol. Catal. A: Chem.* **2011**, *335*, 46.
23. Godoi, M. N.; Costenaro, H. S.; Kramer, E.; Machado, P. S.; D'Oca, M. G. M.; Russowsky, D.; *Quim. Nova* **2005**, *28*, 1010.
24. Treptow, T. G. M.; Figueiró, F.; Jandrey, E. H. F.; Battastini, A. M. O.; Salbego, C. G.; Hoppe, J. B.; Taborda, P. S.; Rosa, S. B.; Piovesan, L. A.; D'Oca, C. R. M.; Russowsky, D.; D'Oca, M. G. M.; *Eur. J. Med. Chem.* **2015**, *95*, 552.
25. Moura, C. M.; Moura, J. M.; Soares, N. M.; Pinto, L. A. A.; *Chem. Eng. Process.* **2011**, *50*, 351; Moura, J. M.; Farias, B. S.; Rodrigues, D. A. S.; Moura, C. M.; Dotto, G. L.; Pinto, L. A. A.; *J. Polym. Environ.* **2015**, *23*, 470.
26. Schreiner, P. R.; Wittkopp, A.; *Org. Lett.* **2002**, *4*, 217; Wang, J.; Li, H.; Yu, X.; Zu, L.; Wang, W.; *Org. Lett.* **2005**, *7*, 4293; Yamaoka, Y.; Miyabe, H.; Takemoto, Y.; *J. Am. Chem. Soc.* **2007**, *129*, 6686.
27. Puripat, M.; Ramozzi, R.; Hatanaka, M.; Parasuk, W.; Parasuk, V.; Morokuma, K.; *J. Org. Chem.* **2015**, *80*, 6959.
28. Spillane, W.; Malaubier, J.-B.; *Chem. Rev*. **2014**, *114*, 2507.

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