Study of the Synthesis of Some Biginelli-type Products Catalyzed by Nano-ZrO_2

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Nanoparticles of zirconium(IV) oxide catalyze the three-component coupling of aromatic aldehydes, β-diketones and urea to afford the corresponding 3,4-dihydropyrimidinones (Biginelli compounds) in moderate to good yields under mild conditions.

Key words: Nanoparticles Zirconium (IV) Oxide, 3,4-Dihydropyrimidinones, Biginelli Compounds, Catalyst, Mild Conditions

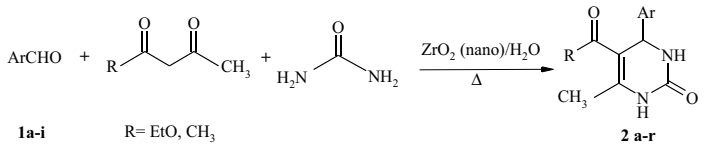
Introduction

The synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones (DHPMs), also called Biginelli compounds, has gained significant attention because they exhibit diverse biological and medical activities. These compounds have potential therapeutic and biological activities, *e. g.* as antihypertensive agents and α_{1a}-adrenoceptor selective antagonists, and are valuable new leads for cancer and AIDS therapy. They also exhibit antibacterial, antifungal, antiviral, and anti-inflammatory effects [1]. While the biological interest in DHPMs exploded, many methods for preparing DHPMs have been developed during the last two decades. Furthermore, dehydrogenation of 3,4-dihydropyrimidin-2(1*H*)-ones (DHPMs) is an important method for the preparation of pyrimidine derivatives. Pyrimidine cores with extended π systems have interesting fluorescence properties, and similar compounds are useful in the development of advanced electronic and photonic materials [2]. Although various methods for the dehydrogenation of specific 1,4-dihydropyridines have been reported in the literature [3], 3,4-dihydropyrimidin-2(1*H*)-ones are highly stable toward mild and powerful oxidizing reagents. Recently, Memarian and coworkers have developed the best methods for the oxidation of these compounds [4 – 10].

Originally, the Italian chemist Pietro Biginelli reported a ternary condensation of ethyl acetoacetate, aromatic aldehyde and urea under strongly acidic conditions for the synthesis of the heterocyclic system of dihdropyrimidinones (DHPMs) [11]. It was found that not only protic acids but also various reagents could be utilized as catalysts for the Biginelli reaction. The design of promising Lewis acid catalysts has attracted considerable interest in organic synthesis because of their unique catalytic performances in organic reactions [12].

Angeles-Beltrán *et al.* reported a new catalyst for the synthesis of dihdropyrimidinones. They prepared sulfated zirconia (SO_4^{2-}/ZrO_2) by a multistep procedure and applied it as an acid catalyst replacement for common acid substances in the Biginelli reaction [13]. In this method a mixture of catalyst (50 mg, 0.26 mmol *vis.* 1 mmol ethyl acetoacetate) and other components was blended and stirred at 60 °C for 4 hours to give dihydropyrimidinones in the yields of 80 % – 98 %. Even though DHPMs were obtained in high yields, the stages of the catalyst preparation and identification that include examination by X-ray diffraction, BET surface area, and ammonia-TPD techniques might be considered as disadvantages.

ZrO_2 nanoparticles are commercially available, inexpensive and a mild but very good Lewis acid [14]. Moreover ZrO_2-pillared clay was used to synthesize some dihydropyrimidinones under microwave irradiation [15]. Furthermore, these particles have numerous applications such as solid oxide electrolytes [16], drug delivery [17], gate dielectrics [18] and solar cells [19]. In view of this, we used ZrO_2 nanoparticles as an ef-



R = EtO (EDHPMs) and R = CH_3 (ADHPMs)

Scheme 1.

ficient Lewis acid for the one-pot synthesis of some 3,4-dihydropyrimidin-2(1*H*)-ones (DHPMs). Our procedure is simple but effective for the synthesis of the some DHPMs. Comparison of these data with the data of SO_4^{2-}/ZrO_2 shows that using the nano-ZrO_2 is a simple and mild method which has advantages such as excellent yields, short reaction times and low cost.

Results and Discussion

Initially, we studied the Biginelli-type reaction of benzaldehyde (**1a**), ethyl acetoacetate, urea and nano-ZrO_2 (10 – 15 nm) as Lewis acid in different solvents under different conditions (Scheme 1 and Table 1). According to the data presented in Table 1, distilled water as a solvent and oil bath heating at 140 °C were chosen as the best conditions for the synthesis of some 3,4-dihydropyrimidin-2(1*H*)-ones ("green chemistry" condition).

According to the data presented in Table 1 we found that (i) the presence of water was necessary for the reaction since the synthesis of **2a** in dry acetonitrile did not result in the occurrence of any reaction, (ii) the optimized ratio of nano-ZrO_2/ to EAA (1 : 4) indicated that the total disappearance of EAA was dependent on the presence of equimolar amounts of the nano-ZrO_2 and EAA since the reaction was not completed by the ratio of 0.5 : 4 of nano-ZrO_2 to EAA. Using higher amounts of catalyst [nano-ZrO_2 to EAA (1.5 : 4)] did not affect the reaction times and yields (Table 1). Furthermore, with an increase of the catalyst ratio to 1 : 2 of nano-ZrO_2/EAA some by-products were observed, and (iii) heating was necessary for the reaction due to failure of reaction when carried out at room temperature.

Table 1. Nano-ZrO_2-catalyzed synthesis of 1,2,3,4-tetrahydropyrimidin-one (**2a**) under reflux condition in various solvents (EAA = ethyl acetoacetate).

Ratio of nano-ZrO_2 to EAA	Solvent	Time (h)[a]	Yield of **2a** (%)[b]
1 : 2	H_2O	6	45 + byproducts
1.5 : 4	H_2O	6	65
1 : 4	H_2O	6	65
0.5 : 4	H_2O	6	45
1 : 4	EtOH	6	48
1 : 4	CH_3CN (dry)	6	20
1 : 4	Ethyl acetate-*n*-hexane (3 : 1)	6	40
1 : 4	H_2O[c]	24	trace[d]
1 : 4	H_2O[e]	6	54

[a] The times are given after maximum progression of the reaction; [b] isolated yield; [c] the reaction was carried out at room temperature; [d] estimated according to TLC observation; [e] the reaction was carried out at 100 °C.

Table 2. Nano-ZrO_2-catalyzed synthesis of monosubstituted derivatives of 3,4-dihydropyrimidin-2(1*H*)-ones.

	EDHPMs				ADHPMs		
Comp.	Ar	Time (h)	Yield (%)[a]	Comp.	Ar	Time (h)	Yield (%)[a]
2a	Ph	6	65	**2j**	Ph	3	62
2b	4-MeO-C_6H_4-	4	92	**2k**	4-MeO-C_6H_4-	3	80
2c	3-MeO-C_6H_4-	2	90	**2l**	3-MeO-C_6H_4-	1 : 5	85
2d	2-MeO-C_6H_4-	4	65	**2m**	2-MeO-C_6H_4-	2	55
2e	4-Cl-C_6H_4-	4	55	**2n**	4-Cl-C_6H_4-	3	55
2f	3-Cl-C_6H_4-	1	90	**2o**	3-Cl-C_6H_4-	1 : 5	90
2g	2-Cl-C_6H_4-	2	70	**2p**	2-Cl-C_6H_4-	1 : 5	70
2h	4-NO_2-C_6H_4-	3	55	**2q**	4-NO_2-C_6H_4-	3	70
2i	3-NO_2-C_6H_4-	3	75	**2r**	3-NO_2-C_6H_4-	1	70

[a] Isolated yield.

Under the optimized reaction conditions various aldehydes (**1a**–**r**) were converted to the Biginelli-type products in the presence of nano-ZrO_2 in H_2O (1 mL) under thermal conditions (140 °C) as shown in Scheme 1. The results are summarized in Table 2.

The results presented in Table 2 indicate that various aldehydes can be converted to their corresponding 3,4-dihydropyrimidin-2(1*H*)-ones by using nano-ZrO_2 as catalyst in good to excellent yields, comparable with the SO_4^{2-}/ZrO_2 catalyst [13]. Furthermore, the other advantages of this method are the mild reaction conditions, short reaction time, and low cost.

Mechanism

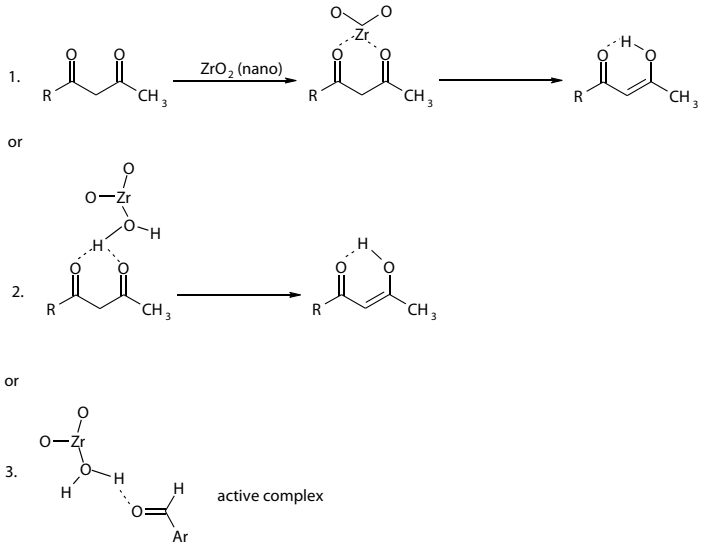
Interaction of water with metal oxides plays an important role in catalysis [20]. The ability to exchange hydrogen and oxygen between water and a catalyst surface affects both acid-base [21] and oxidation-reduction [22] properties of the catalyst. Water can be adsorbed on metal oxide surfaces either molecularly or in a dissociated form [21]. Ignatchenko *et al*. combined an experimental and a computational approach to understand details of the water interaction with zirconia and titania surfaces. They have found that water is adsorbed with its nucleophilic end bound on the surface of both metal oxides [23].

According to the results summarized in Tables 1 and 2, we propose the following mechanism for the synthesis of 3,4-dihydropyrimidinones in the presence of a nano-ZrO_2 catalyst (Scheme 2).

Following the optimized reaction conditions, we extended our study using various aromatic aldehydes containing electron-withdrawing or electron-releasing substituents at the *ortho*-, *meta*- or *para*-positions. According to this proposed mechanism and under these conditions, the yields were significantly increased from 55 up to 92 %, and the reaction time was also shortened. Electron-withdrawing substituents on the phenyl ring of the aromatic aldehyde increased the rate of the reaction by improved activation of the aromatic aldehyde and facilitating the nucleophilic attack. The presence of electron-donating substituents on the phenyl ring of the aromatic aldehydes makes the carbonyl group electron-rich and increases the reaction time by impeding the nucleophilic attack.

Conclusion

In conclusion, we have developed a simple and efficient method for the preparation of a variety of 4-substituted-3,4-dihydropyrimidinones by one-pot three-component reactions of different aromatic aldehydes, β-keto compounds and urea in the presence of a catalytic amount of nano-ZrO_2 catalyst in the



Scheme 2. Interaction between water, nano-ZrO_2 as Lewis acid and β-diketone and aldehyde to generate the enol form or the active complex.

presence of water. More detailed conclusions may be drawn by comparing the performance of the present work with some other recent reports available in the literature [13].

Experimental Section

Melting points were determined on an IA9200 apparatus and are uncorrected. IR spectra were recorded from KBr discs on a Shimadzu apparatus IR 435. ^{1}H NMR spectra were recorded using a Bruker 300 MHz instrument. They are reported as follows: chemical shifts δ in ppm, multiplicity, coupling constants J in Hz, number of protons, and assignment. Mass spectra were obtained on a Platform II spectrometer from Micromass; EI mode at 70 eV. UV spectra (in CH_3CN) were taken with a Shimadzu UV-160 spectrometer. Nano-ZrO_2 (10 – 15 nm) was purchased from TECNAN Ltd., Los Arcos – Navarra/Spain.

General procedure

A mixture of aldehyde (**1a**–**r**, 6 mmol), 1,3-dicarbonyl compound (2 mmol), urea (6 mmol) and nano-ZrO_2 (0.1 mmol) in 1 mL of distilled water was heated to 140 °C, with stirring to complete the reaction (monitored by TLC). TLC monitoring of the reaction using *n*-hexane-ethyl acetate (4 : 1) as eluent was followed until total disappearance of the 1,3-dicarbonyl compounds was observed. The results are reported in Table 2. After cooling to room temperature, the mixture was washed with cold water (10 mL), and then the crude product was recrystallized from ethanol.

*Ethyl 6-methyl-4-phenyl-1,2,3,4-tetrahydropyrimidin-2-one-5-carboxylate (**2a**)*

M. p. 204 – 206 °C (Lit. [24]: M. p. 201 – 203 °C). – UV/Vis (CH_3CN): λ_{max} (lg ε_{max}) = 274.4 (4.01), 228.6 nm (3.91). – IR (KBr): ν = 1720 ($CO_2C_2H_5$), 1700 (2-CO), 1640 (C=C) cm^{-1}.

*Ethyl 4-(4-methoxyphenyl)-6-methyl-1,2,3,4-tetrahydropyrimidin-2-one-5-carboxylate (**2b**)*

M. p. 203 – 205 °C (Lit. [25]: M. p. 201 – 203 °C). – UV/Vis (CH_3CN): λ_{max} (lg ε_{max}) = 274 (3.47), 230 nm (3.75). – IR (KBr): ν = 1725 ($CO_2C_2H_5$), 1700 (2-CO), 1650 (C=C) cm^{-1}.

*Ethyl 4-(3-methoxyphenyl)-6-methyl-1,2,3,4-tetrahydropyrimidin-2-one-5-carboxylate (**2c**)*

M. p. 209 – 211 °C (Lit. [26]: M. p. 207 – 208 °C). – UV/Vis (CH_3CN): λ_{max} (lg ε_{max}) = 276.5 (3.52), 227 nm (3.36). – IR (KBr): ν = 1700 ($CO_2C_2H_5$), 1645 (2-CO), 1595 (C=C) cm^{-1}.

*Ethyl 4-(2-methoxyphenyl)-6-methyl-1,2,3,4-tetrahydropyrimidin-2-one-5-carboxylate (**2d**)*

M. p. 262 – 263 °C (Lit. [27]: M. p. 259 – 260 °C). – UV/Vis (CH_3CN): λ_{max} (lg ε_{max}) = 276.5 (3.52), 227 nm (3.36). – IR (KBr): ν = 1700 ($CO_2C_2H_5$), 1645 (2-CO), 1595 (C=C) cm^{-1}.

*Ethyl 4-(3-chlorophenyl)-6-methyl-1,2,3,4-tetrahydropyrimidin-2-one-5-carboxylate (**2f**)*

M. p. 197 – 198 °C (Lit. [25]: M. p. 193 – 195 °C). – UV/Vis (CH_3CN): λ_{max} (lg ε_{max}) = 278.5 (3.52), 229 nm (3.36). – IR (KBr): ν = 1710 ($CO_2C_2H_5$), 1690 (2-CO), 1650 (C=C) cm^{-1}.

*Ethyl 4-(2-chlorophenyl)-6-methyl-1,2,3,4-tetrahydropyrimidin-2-one-5-carboxylate (**2g**)*

M. p. 218 – 219 °C (Lit. [25]: M. p. 222 – 224 °C). – UV/Vis (CH_3CN): λ_{max} (lg ε_{max}) = 278.5 (3.52), nm 229 (3.36). – IR (KBr): ν = 1705 ($CO_2C_2H_5$), 1690 (2-CO), 1635 (C=C) cm^{-1}.

*Ethyl 6-methyl-4-(4-nitrophenyl)-1,2,3,4-tetrahydropyrimidin-2-one-5-carboxylate (**2h**)*

M. p. 207 – 208 °C (Lit. [25]: M. p. 207 – 210 °C). – UV/Vis (CH_3CN): λ_{max} (lg ε_{max}) = 264 (3.31), 225 nm (3.17). – IR (KBr): ν = 1725 ($CO_2C_2H_5$), 1700 (2-CO), 1640 (C=C) cm^{-1}.

*5-Acetyl-6-methyl-4-phenyl-1,2,3,4-tetrahydropyrimidin-2-one (**2j**)*

M. p. 232 – 236 °C (Lit. [5]: M. p. 228 – 230 °C). – UV/Vis (CH_3CN): λ_{max} (lg ε_{max}) = 290.5 nm (4.1). – IR (KBr): ν = 1700 (CH_3CO), 1670 (2-CO), 1600 (C=C) cm^{-1}. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.10 (s, 3H, CH_3), 2.28 (s, 3H, CH_3CO), 5.26 (d, J = 3.32 Hz, 1H, 4-H), 7.29 (m$_c$, 5H, H-aromatic), 7.81 (s, 1H, 1-NH), 9.16 (s, 1H, 3-NH).

*5-Acetyl-4-(4-methoxyphenyl)-6-methyl-1,2,3,4-tetrahydropyrimidin-2-one (**2k**)*

M. p. 169 – 170 °C (Lit. [28]: M. p. 168 – 170 °C). – UV/Vis (CH_3CN): λ_{max} (lg ε_{max}) = 286.4 nm (3.82). – IR (KBr): ν = 1650 (CH_3CO), 1580 (2-CO), 1430 (C=C) cm^{-1}.

*5-Acetyl-4-(3-methoxyphenyl)-6-methyl-1,2,3,4-tetrahydropyrimidin-2-one (**2l**)*

M. p. 225 – 227 °C (Lit. [5]: M. p. 226 – 228 °C). – UV/Vis (CH_3CN): λ_{max} (lg ε_{max}) = 284.4 (3.88), 239.6 nm (3.43). – IR (KBr): ν = 1670 (CH_3CO), 1590 (2-CO), 1425 (C=C) cm^{-1}.

*5-Acetyl-4-(2-methoxyphenyl)-6-methyl-1,2,3,4-tetrahydropyrimidin-2-one (**2m**)*

M. p. 250 – 252 °C (Lit. [5]: M. p. 250 – 252 °C). – UV/Vis (CH_3CN): λ_{max} (lg ε_{max}) = 283.6 (3.41), 240.2 nm (3.90). – IR (KBr): ν = 1670 (CH_3CO), 1590 (2-CO), 1430 (C=C) cm^{-1}. – ^1H NMR (300 MHz, [D_6]DMSO): δ = 2.00 (s, 3H, CH_3), 2.28 (s, 3H, CH_3CO), 3.81 (s, 3H, CH_3O), 5.56 (s, 1H, 4-H), 7.06 (m_c, 4H, H-aromatic), 7.33 (s, 1H, 1-NH), 9.11 (s, 1H, 3-NH). – MS (EI, 70 eV): m/z (%) = 260 (61) $[M]^+$, 259 (80) $[M–H]^+$, 245 (51) $[M–CH_3]^+$, 229 (92) $[M–CH_3O]^+$, 217 (85) $[M–CH_3CO]^+$, 153 (100) $[M–2\text{-}CH_3COC_6H_4]^+$.

*5-Acetyl-4-(4-chlorophenyl)-6-methyl-1,2,3,4-tetrahydropyrimidin-2-one (**2n**)*

M. p. 220 – 221 °C (Lit. [29]: M. p. 223 – 225 °C). – UV/Vis (CH_3CN): λ_{max} (lg ε_{max}) = 290.6 (4.04), 240.0 nm (3.77). – IR (KBr): ν = 1690 (CH_3CO), 1615 (2-CO), 1420 (C=C) cm^{-1}.

*5-Acetyl-4-(3-chlorophenyl)-6-methyl-1,2,3,4-tetrahydropyrimidin-2-one (**2o**)*

M. p. 282 – 284 °C (Lit. [5]: M. p. 285 – 287 °C). – UV/Vis (CH_3CN): λ_{max} (lg ε_{max}) = 291.4 (3.08), 239.8 nm (2.70). – IR (KBr): ν = 1700 (CH_3CO), 1615 (2-CO), 1525 (C=C) cm^{-1}. – ^1H NMR (300 MHz, [D_6]DMSO): δ = 2.15 (s, 3H, CH_3), 2.30 (s, 3H, CH_3CO), 5.27 (d, J = 3.25 Hz, 1H, 4-H), 7.27 (m_c, 4H, H-aromatic), 7.87 (s, 1H, 1-NH), 9.28 (s, 1H, 3-NH). – MS (EI, 70 eV): m/z (%) = 266 (49) $[M^{37}Cl]^+$, 265 (64) $[M^{37}Cl–H]^+$, 264 (32) $[M^{35}Cl]^+$, 263 (79) $[M^{35}Cl–H]^+$, 249 (80) $[M^{35}Cl–CH_3]^+$, 229 (42) $[M^{35}Cl–{}^{35}Cl]^+$, 223 (28) $[M^{37}Cl–CH_3CO]^+$, 221 (74) $[M^{35}Cl–CH_3CO]^+$, 170 (3) $[2\text{-}{}^{37}ClC_6H_4\text{-}CH{=}NH]^+$, 169 (8) $[2\text{-}{}^{37}ClC_6H_4\text{-}C{=}NH]^+$, 168 (9) $[2\text{-}{}^{35}ClC_6H_4\text{-}CH{=}NH]^+$, 167 (9) $[2\text{-}{}^{35}ClC_6H_4\text{-}C{=}NH]^+$, 153 (100) $[M–2\text{-}ClC_6H_4]^+$.

*5-Acetyl-4-(2-chlorophenyl)-6-methyl-1,2,3,4-tetrahydropyrimidin-2-one (**2p**)*

M. p. 263 – 265 °C, (Lit. [5]: M. p. 262 – 264 °C). – UV/Vis (CH_3CN): λ_{max} (lg ε_{max}) = 291.0 (4.00), 240.2 nm (3.62). – IR (KBr): ν = 1700 (CH_3CO), 1615 (2-CO), 1525 (C=C) cm^{-1}. – ^1H NMR (300 MHz, [D_6]DMSO): δ = 2.05 (s, 3H, CH_3), 2.33 (s, 3H, CH_3CO), 5.66 (s, 1H, 4-H), 7.36 (m_c, 4H, H-aromatic), 7.72 (s, 1H, 1-NH), 9.27 (s, 1H, 3-NH). – MS (EI, 70 eV): m/z (%) = 266 (4) $[M^{37}Cl]^+$, 265 (7) $[M^{37}Cl–H]^+$, 264 (10) $[M^{35}Cl]^+$, 263 (16) $[M^{35}Cl–H]^+$, 249 (10) $[M^{35}Cl–CH_3]^+$, 231 (6) $[M^{37}Cl–{}^{37}Cl]^+$, 229 (94) $[M^{35}Cl–{}^{35}Cl]$, 223 (6) $[M^{37}Cl–CH_3CO]^+$, 221 (72) $[M^{35}Cl–CH_3CO]^+$, 170 (14) $[2\text{-}{}^{37}ClC_6H_4\text{-}CH{=}NH]^+$, 169 (18) $[2\text{-}{}^{37}ClC_6H_4\text{-}C{=}NH)^+$, 168 (17) $[2\text{-}{}^{35}ClC_6H_4\text{-}CH{=}NH]^+$, 167 (8) $[2\text{-}{}^{35}ClC_6H_4\text{-}C{=}NH]^+$, 153 (100) $[M–2\text{-}ClC_6H_4]^+$.

*5-Acetyl-6-methyl-4-(4-nitrophenyl)-1,2,3,4-tetrahydropyrimidin-2-one (**2q**)*

M. p. 228 °C (dec.), (Lit. [5]: M. p. 229 – 230 °C (dec.). – UV/Vis (CH_3CN): λ_{max} (lg ε_{max}) = 279.2 nm (4.07). – IR (KBr): ν = 1650 (CH_3CO), 1580 (2-CO), 1520 (C=C) cm^{-1}.

*5-Acetyl-6-methyl-4-(3-nitrophenyl)-1,2,3,4-tetrahydropyrimidin-2-one (**2r**)*

M. p. 286 – 288 °C, (Lit. [5]: M. p. 286 – 288 °C). – UV/Vis (CH_3CN): λ_{max} (lg ε_{max}) = 292.2 (3.98), 239.8 nm (3.70). – IR (KBr): ν = 1650 (CH_3CO), 1585 (2-CO), 1420 (C=C) cm^{-1} . – ^1H NMR (300 MHz, [D_6]DMSO): δ = 2.04 (s, 3H, CH_3), 2.33 (s, 3H, CH_3CO), 5.62 (d, J = 2.85 Hz, 1H, 4-H), 7.39 (m_c, 4H, H-aromatic), 7.69 (brd s, 1H, 1-NH), 9.28 (s, 1H, 3-NH). – MS (EI, 70 eV): m/z (%) = 267 (10) $[M^{81}Br–CH_3CO]^+$, 265 (11) $[M^{79}Br–CH_3CO]^+$, 231 (2) $[M^{81}Br–{}^{81}Br]^+$, 229 (97) $[M^{79}Br–{}^{79}Br]^+$, 214 (13) $[M^{79}Br–{}^{79}Br–CH_3]^+$, 168 (5) $[2\text{-}BrC_6H_4\text{-}CH{=}NH]^+$, 153 (100) $[M–2\text{-}BrC_6H_4]^+$.

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