



## Synthesis and Structural Characterization of New Benzimidazole Compounds Derived from Electron-Rich Olefins Bearing 1,4-Bisbenzimidazole with CS<sub>2</sub>, PhNCS, and Chalcogens

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**Abstract:** In this work, 1,4-bis(3-isopropylbenzimidazolidine-2-ylidene-1-yl)butane (**1**) and 1,4-bis(3,5(6)-dimethylbenzimidazolidine-2-ylidene-1-yl)butane (**2**) were reacted with oxygen, sulfur, selenium, tellurium, phenyl isothiocyanate, and carbon disulfide. New zwitterionic compounds (**9-12**) and cyclic urea derivatives of benzimidazole as one (**3**), thione (**4,6**), selenone (**5,7**), tellurone (**8**) were prepared from enetetramines. The chemical structures of novel benzimidazole compounds were determined by FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR spectroscopic methods and elemental analysis.

**Keywords:** Bisbenzimidazole, electron-rich olefin, strong nucleophiles, urea derivatives, zwitterion.

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### INTRODUCTION

Benzimidazoles and their derivatives possess antibacterial, antitumor, antineoplastic, antihistaminic, local analgesic, vasodilative, hypotensive, antifungal, antihelmintic, spasmolytic and antimicrobial pharmacological activities (1-6). In recent years, principally bisbenzimidazole derivatives have become of interest due to their possible use in cancer cure by immobilization of DNA binding (7,8). Benzimidazole derivatives, especially 2-substituted benzimidazoles (9), generally show physiological activity and even inhibitory effect on production of viruses in tissue cultures (10). Enetetramines, in other words, electron-rich olefins, have four electron donating substituents and are strong nucleophiles and highly reactive (11-15). They act as vigorous reducing agents and are organic ligands to transition-metal carbene complex precursors as well as catalysts for acyloin type C-C pairing reactions (16-23). Moreover enetetramines react with proton-active compounds give insertion products of nucleophilic carbenes due to the separation of the main C=C double bond (24,25). Electron-rich olefins are reducing factors and its known that the oxidation

product of electron rich olefins have been synthesized with oxygen in air, sulfur, selenium, and tellurium (26).

Here we present the synthesis of new electron rich olefins from 1,4-bisbenzimidazolium salts and the synthesis of new cyclic urea compounds incorporating oxygen, its group elements, and dipolar derivatives containing sulfur.

### EXPERIMENTAL SECTION

The experiments were carried out under argon using dry solvents. NMR (<sup>1</sup>H-NMR, 300 MHz; <sup>13</sup>C-NMR, 75 MHz) spectra were defined using Bruker Avance 300 MHz Ultrashield FT NMR spectrometer. Infrared spectra were identified in the range 4000-650 cm<sup>-1</sup> on a Perkin-Elmer Spectrum One FT-IR spectrometer by ATR. Elemental analyses were identified with a LECO CHNS-932 elemental analyzer. Melting points were specified using an electrothermal-9200 melting point apparatus. Compounds **I** and **II** were synthesized according to the literature (27).

**Synthesis of 1,4-bis(3-isopropylbenzimidazolidine-2-ylidene-1-yl)butane (1)**

A blend of **1** (5.00 g, 7.94 mmol) and NaH (0.39 g, 16.25 mmol) in THF (40 mL) was stirred for 12 hours at room temperature. The solvent was removed from the medium and oily part was extracted with hot toluene (20 mL) and the extract was filtered when hot. The yellow filtrate was condensed (10 mL), n-hexane (10 mL) was put in and the solution was cooled to -20 °C to yield a yellow compound (**1**). Yield: 2.15 g (72 %). <sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, δ, ppm): 1.32 (8H, d, J = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.58 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.29 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 4.15 (2H, sept, J = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 6.29-6.32 (2H, m, Ar-H), 6.75-6.86 (6H, m, Ar-H). Compound **2** was synthesized with a similar process from related benzimidazolium salt (**1**).

**1,4-Bis(3,5(6)-dimethylbenzimidazolidine-2-ylidene-1-yl)butane (2)**

Yield: 2.16 g (75 %). <sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, δ, ppm): 1.46 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 2.29 (6H, s, Ar-CH<sub>3</sub>), 2.90 (6H, s, N-CH<sub>3</sub>), 3.31 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 6.24-6.53 (6H, m, Ar-H).

**1,4-Bis(3-isopropylbenzimidazolidine-2-one-1-yl)butane (3)**

The compound **1** (0.50 g, 1.34 mmol) was kept in air for 24 hours. Then it was observed that the color of the yellow-colored solid turned to white. The crude product was crystallized from toluene/n-hexane (2:1). Yield: 0.39 g (72 %). M.P.: 180-181 °C, FT-IR ν (cm<sup>-1</sup>): 3375, 2944, 1690 (C=O), 730. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 1.55 (12H, d, J = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.85 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.95 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 4.76 (2H, sept, J = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 7.02-7.17 (8H, m, Ar-H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ 20.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.6 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 40.4 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 44.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 107.8, 109.0, 120.7, 120.8, 128.2, 129.4 (Ar-C), 153.7 (C=O). Anal. Calcd. for C<sub>24</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>: C, 70.91; H, 7.44; N, 13.79. Found: C, 70.29; H, 7.50; N, 13.43.

**1,4-Bis(3-isopropylbenzimidazolidine-2-thione-1-yl)butane (4)**

A blend of **1** (0.42 g, 1.12 mmol) and S<sub>8</sub> (0.08 g, 0.31 mmol) in toluene (5 mL) was boiled under reflux for 2 hours. Then the mixture was filtered to remove non-reacted sulfur and the solvent were removed *in vacuo*. The raw product was crystallized from ethanol /toluene (2:1). Yield: 0.35 g (71 %). M.P.: 177-178 °C, FT-IR ν (cm<sup>-1</sup>): 2975, 1481 (C=S), 1414, 730. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 1.56 (12H, d, J = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.97 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 4.39 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 5.70 (2H, sept, J = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 7.14-7.41 (8H, m, Ar-H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ 20.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.2 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 44.6 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 49.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 109.5, 110.8, 122.4, 122.6, 130.4, 132.4 (Ar-C), 168.6 (C=S). Anal. Calcd.

for C<sub>24</sub>H<sub>30</sub>N<sub>4</sub>S<sub>2</sub>: C, 65.72; H, 6.89; N, 12.77; S, 14.62. Found: C, 65.13; H, 6.21; N, 11.98; S, 14.92. The compounds **5-8** were synthesized in a similar pathway from **1** and **2** olefins and related chalcogens.

**1,4-Bis(3-isopropylbenzimidazolidine-2-selenone-1-yl)butane (5)**

Yield: 0.48 g (75 %). M.P.: 175-176 °C, FT-IR ν (cm<sup>-1</sup>): 3676, 2973, 1483 (C=Se), 747, 730. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 1.45 (12H, d, J = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.76 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.85 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 4.66 (2H, sept, J = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 6.92-7.11 (8H, m, Ar-H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ 19.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.1 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 39.9 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 44.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 107.3, 108.5, 120.2, 120.3, 127.7, 128.9 (Ar-C), 153.2 (C=Se). Anal. Calcd. for C<sub>24</sub>H<sub>30</sub>N<sub>4</sub>Se<sub>2</sub>: C, 54.14; H, 5.68; N, 10.52. Found: C, 54.02; H, 5.70; N, 10.47.

**1,4-Bis(3,5(6)-dimethylbenzimidazole-2-thione-1-yl)butane (6)**

Yield: 0.39 g (74 %). M.P.: 173-175 °C, FT-IR ν (cm<sup>-1</sup>): 2936, 1502 (C=S), 1439, 1389, 796. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 1.98 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 2.46 (6H, s, Ar-CH<sub>3</sub>), 3.76 (6H, s, N-CH<sub>3</sub>), 4.380 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 7.05-7.14 (6H, m, Ar-H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ 21.3 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 25.1 (Ar-CH<sub>3</sub>), 32.5 (N-CH<sub>3</sub>), 45.1 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 109.1, 109.3, 109.6, 109.7, 124.2, 125.1, 128.2, 128.7, 130.5, 131.3, 132.6, 133.4 (Ar-C), 164.2 (C=S). Anal. Calcd. for C<sub>22</sub>H<sub>26</sub>N<sub>4</sub>S<sub>2</sub>: C, 64.36; H, 6.38; N, 13.65; S, 15.62. Found: C, 63.79; H, 6.02; N, 13.20; S, 15.75.

**1,4-Bis(3,5(6)-dimethylbenzimidazole-2-selenone-1-yl)butane (7)**

Yield: 0.59 g (78 %). M.P.: 166-167 °C, FT-IR ν (cm<sup>-1</sup>): 2934, 1498 (C=Se), 1439, 1384, 792, 739. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 2.05 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 2.48 (6H, s, Ar-CH<sub>3</sub>), 3.88 (6H, s, N-CH<sub>3</sub>), 4.51 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 7.07-7.30 (6H, m, Ar-H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ 21.5 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 25.2 (Ar-CH<sub>3</sub>), 33.2 (N-CH<sub>3</sub>), 46.2 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 109.1, 109.4, 109.8, 110.0, 124.5, 125.3, 128.2, 129.0, 130.8, 131.6, 132.8, 133.7 (Ar-C), 165.5 (C=Se). Anal. Calcd. for C<sub>22</sub>H<sub>26</sub>N<sub>4</sub>Se<sub>2</sub>: C, 52.39; H, 5.20; N, 11.11. Found: C, 51.98; H, 5.19; N, 11.17.

**1,4-Bis(3,5(6)-dimethylbenzimidazole-2-tellurone-1-yl)butane (8)**

Yield: 0.68 g (65 %). M.P.: 168-169 °C, FT-IR ν (cm<sup>-1</sup>): 2928, 1432 (C=Te), 1313, 800, 788. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 2.09 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 2.50 (s, 6H, Ar-CH<sub>3</sub>), 3.96 (6H, s, N-CH<sub>3</sub>), 4.57 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 7.08-7.34 (6H, m, Ar-H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ 21.5 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 25.6 (Ar-CH<sub>3</sub>), 36.9 (N-CH<sub>3</sub>), 49.3 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 109.9, 110.2, 110.4, 110.7, 125.0, 128.2, 129.0,

131.9, 132.8, 133.8, 134.1, 134.3 (Ar-C), 143.9 (C=Te). Anal. Calcd. for  $C_{22}H_{26}N_4Te_2$ : C, 43.92; H, 4.36; N, 9.31. Found: C, 43.82; H, 4.30; N, 9.30.

#### 1.4-Bis(3-isopropyl-2-dithioatebenzimidazolium-1-yl)butane (9)

A blend of **1** (0.46 g, 1.23 mmol) in toluene (5 mL) was put in  $CS_2$  (0.15 mL, 2.48 mmol). A red precipitate occurring was observed right away. The product was washed with diethyl ether and crystallized from DMF/ethanol (5:1). Yield: 0.63 g (97 %). M.P.: 239-240 °C, FT-IR  $\nu$  ( $cm^{-1}$ ): 2975, 1671, 1469 (C=S), 1049, 748.  $^1H$ -NMR (300 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 1.66 (12H, d, J = 6.9 Hz,  $CH(CH_3)_2$ ), 1.92 (4H, m,  $NCH_2CH_2CH_2CH_2N$ ), 4.27 (4H, m,  $NCH_2CH_2CH_2CH_2N$ ), 4.85 (2H, sept, J = 6.9 Hz,  $CH(CH_3)_2$ ), 7.50-7.58 (4H, m, Ar-H), 7.87-7.92 (2H, m, Ar-H), 8.09 (2H, m, Ar-H).  $^{13}C$ -NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  20.2 ( $CH(CH_3)_2$ ), 26.1 ( $NCH_2CH_2CH_2CH_2N$ ), 44.8 ( $NCH_2CH_2CH_2CH_2N$ ), 51.4 ( $CH(CH_3)_2$ ), 114.0, 115.4, 126.3, 126.4, 128.0, 130.8, 151.6 (Ar-C), 162.8 (NCN), 225.2 (SCS). Anal. Calcd. for  $C_{26}H_{30}N_4S_4$ : C, 59.28; H, 5.74; N, 10.64; S, 24.34. Found: C, 58.91; H, 5.55; N, 10.45; S, 23.92.

#### 1.4-Bis(3,5(6)-dimethyl-2-dithioatebenzimidazolium-1-yl)butane (10)

Yield: 0.54 g (88 %). M.P.: 236-237 °C, FT-IR  $\nu$  ( $cm^{-1}$ ): 2947, 1482 (C=S), 1048, 802.  $^1H$ -NMR (300 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 1.96 (4H, m,  $NCH_2CH_2CH_2CH_2N$ ), 2.51 (6H, s, Ar- $CH_3$ ), 3.79 (6H, s, N- $CH_3$ ), 4.31 (4H, m,  $NCH_2CH_2CH_2CH_2N$ ), 7.39-7.76 (6H, m, Ar-H).  $^{13}C$ -NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  21.7 ( $NCH_2CH_2CH_2CH_2N$ ), 25.6 (Ar- $CH_3$ ), 31.5 (N- $CH_3$ ), 44.88 ( $NCH_2CH_2CH_2CH_2N$ ), 113.1, 114.3, 127.7, 128.7, 129.8, 136.6, 151.9 (Ar-C), 167.9 (NCN), 224.9 (SCS). Anal. Calcd. for  $C_{24}H_{26}N_4S_4$ : C, 57.80; H, 5.25; N, 11.23; S, 25.71. Found: C, 57.13; H, 5.11; N, 10.95; S, 26.29.

#### 1.4-Bis(3-isopropyl-2-mercapto-N-phenylformimidoylbenzimidazolium-1-yl)butane inner salt (11)

A blend of **1** (0.54 g, 1.45 mmol) in toluene (5 mL) was put in PhNCS (0.35 mL, 2.93 mmol). The blend was stirred at room temperature, and an exothermic reaction occurred in seconds. All the liquid part were removed *in vacuo* and yellow raw product was obtained. The product was crystallized from ethanol. Yield: 0.76 g (82 %). M.P.: 214-216 °C, FT-IR  $\nu$  ( $cm^{-1}$ ): 2976, 1497, 1470 (N=C), 747.  $^1H$ -NMR (300 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 1.46 (12H, d, J = 6.9 Hz,  $CH(CH_3)_2$ ), 2.03 (4H, m,  $NCH_2CH_2CH_2CH_2N$ ), 4.44 (4H, m,  $NCH_2CH_2CH_2CH_2N$ ), 5.08 (2H, sept, J = 6.9 Hz,  $CH(CH_3)_2$ ), 6.86-6.91 (2H, m, Ar-H), 7.05-7.18 (8H, m, Ar-H), 7.46-7.50 (4H, m, Ar-H), 7.88-7.91 (2H, m, Ar-H), 8.01-8.04 (2H, m, Ar-H).  $^{13}C$ -NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  20.1 ( $CH(CH_3)_2$ ), 25.9 ( $NCH_2CH_2CH_2CH_2N$ ), 44.6 ( $NCH_2CH_2CH_2CH_2N$ ), 51.2 ( $CH(CH_3)_2$ ), 113.8, 115.6, 122.0, 122.4, 125.7, 125.8, 127.9, 128.0,

130.3, 148.8 (Ar-C), 150.8 (NCN), 166.3 (SCN). Anal. Calcd. for  $C_{38}H_{40}N_6S_2$ : C, 70.77; H, 6.25; N, 13.03; S, 9.94. Found: C, 69.88; H, 6.18; N, 12.95; S, 9.78.

#### 1.4-Bis(3,5(6)-dimethyl-2-mercapto-N-phenylformimidoylbenzimidazolium-1-yl)butane inner salt (12)

Yield: 0.88 g (85 %). M.P.: 146-147 °C, FT-IR  $\nu$  ( $cm^{-1}$ ): 3024, 1489 (N=C), 995, 770, 693.  $^1H$ -NMR (300 MHz,  $CDCl_3$ ,  $\delta$ , ppm):  $\delta$  2.258 (4H, m,  $NCH_2CH_2CH_2CH_2N$ ), 2.53 (6H, s, Ar- $CH_3$ ), 4.04 (6H, s, N- $CH_3$ ), 4.54 (4H, m,  $NCH_2CH_2CH_2CH_2N$ ), 7.11-7.51 (16H, m, Ar-H).  $^{13}C$ -NMR (75 MHz,  $CDCl_3$ ):  $\delta$  21.8 ( $NCH_2CH_2CH_2CH_2N$ ), 31.7 (N- $CH_3$ ), 45.4 ( $NCH_2CH_2CH_2CH_2N$ ), 111.7, 111.8, 112.4, 112.5, 122.3, 122.4, 124.2, 127.9, 128.1, 128.7, 128.9, 129.4, 130.4, 131.1, 137.1, 137.5, 149.3 (Ar-C), 150.1 (NCN), 167.3 (SCN). Anal. Calcd. for  $C_{36}H_{36}N_6S_2$ : C, 70.10; H, 5.88; N, 13.62; S, 10.39. Found: C, 69.70; H, 5.62; N, 13.29; S, 10.33.

## RESULTS AND DISCUSSION

Enetetramines are strong reducing agents and react with sulfur, selenium, and tellurium to give cyclic thiourea, selenourea and tellurorea derivatives in high yield (28). N-heterocyclic carbenes as a source of electron-rich olefins to react isothiocyanates and carbon disulfide to form stable zwitterionic compounds (29).

In this study, reaction of 1,4-bis(3-isopropylbenzimidazolium-1-yl)butane diiodide and 1,4-bis(3,5-dimethylbenzimidazolium-1-yl)butane diiodide salts (**I** and **II**) with NaH in THF were prepared new electron-rich olefins (**1,2**). These strong nucleophilic compounds were reacted with oxygen, sulfur, selenium, and tellurium and novel cyclic urea benzimidazole derivatives (**3-8**) were synthesized in good yields. The reactions were performed in refluxing dry toluene for 2 h. The products were purified by crystallization from toluene/n-hexane and toluene/ethanol. The electron-rich olefins were reacted also with PhNCS and  $CS_2$  at 20 °C for 5 min. Reactions were very fast and yielded compounds (**9-12**) were purified by crystallization from DMF and ethanol. The synthesis procedure of the novel benzimidazole derivatives (**1-12**) was given in Scheme 1.

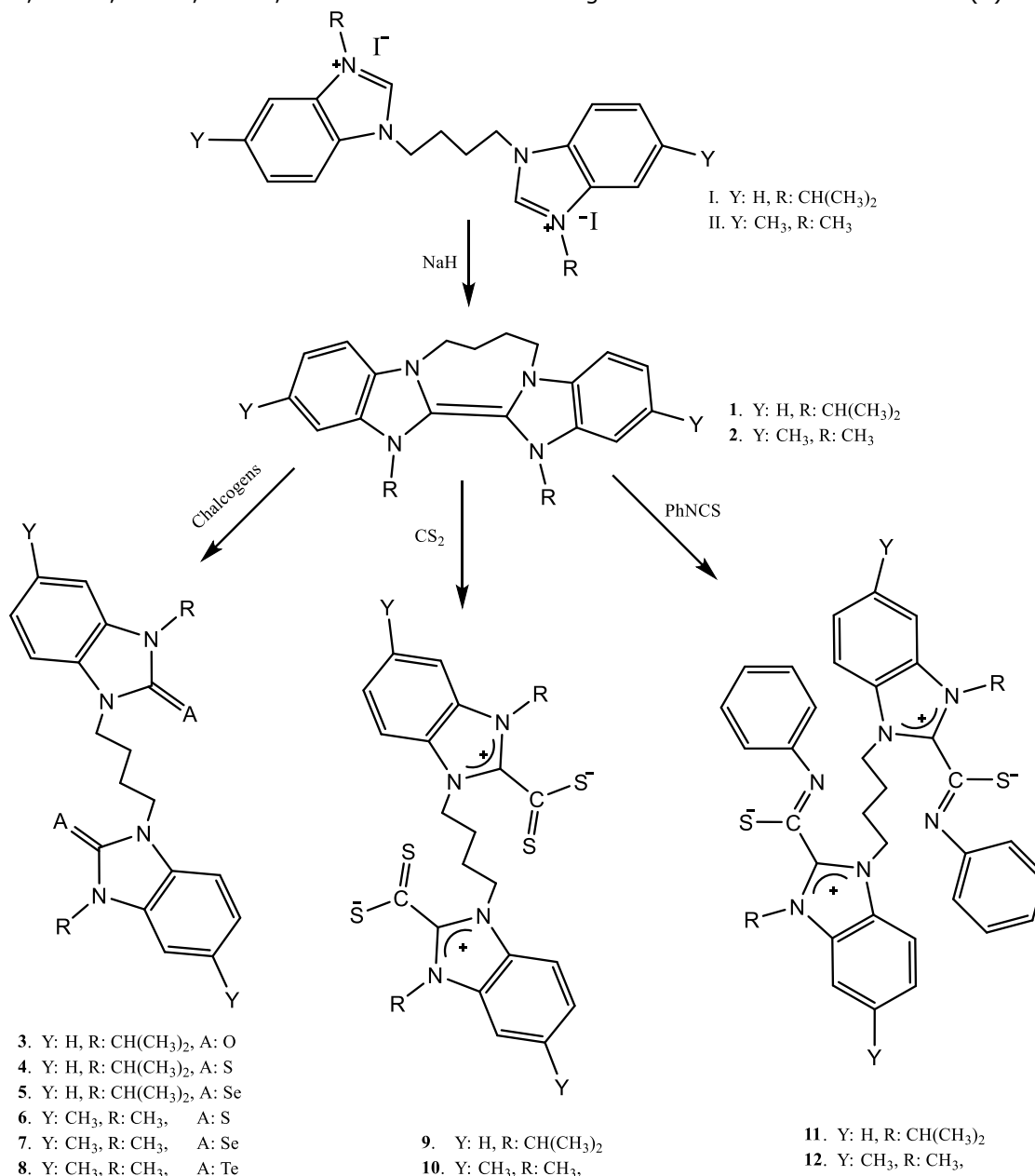
The chemical structures of all novel compounds were elucidated with the  $^1H$  and  $^{13}C$  NMR data as well as from the IR data and elemental analysis. The peaks in the range of 6.24-8.09 ppm are caused by the aromatic protons and aromatic peaks of olefins (**1,2**) were observed at the lowest field compared with their derivatives (**3-12**). The electron-rich olefins are rapidly degrading because they are highly reactive carbene sources. Therefore, only  $^1H$ -NMR analysis of synthesized olefins could be performed (**1,2**).

Benzimidazole contains a hydrogen atom bonded to nitrogen in the 1-position ready to tautomerize. Because of this tautomerism, two tautomer compounds are obtained in the reactions. So, 5-substituted benzimidazole is a tautomer of 6-substituted benzimidazole and both structures are expressed as 5(6)-substituted benzimidazole (30). For this reason, it was observed that 5-methyl substituted benzimidazole derivatives (**6,7,8,10,12**) have aromatic carbon peaks more than expected in the  $^{13}\text{C}$ -NMR spectra.

The carbon peaks of C=A groups were observed at 153.7, 168.6, 153.2, 164.2, 165.5 and 143.9

ppm respectively, in the  $^{13}\text{C}$ -NMR spectrums of related products (**3-8**). Also, SCS and SCN group peaks of dipolar compounds were observed at 225.2, 224.9, 166.3 and 167.3 ppm. The results are in line with the literature (3,26).

The FT-IR spectra of (**3-12**) were given in experimental section. The urea derivative compounds (**3-8**) showed stretching bands at 1690, 1481, 1483, 1502, 1498 and 1432  $\text{cm}^{-1}$  respectively, corresponding to C=A groups. Also, absorbance bands belonging to the C=N and C=S groups of the dipolar compounds (**9-12**) were appeared at 1469, 1482, 1470 and 1489  $\text{cm}^{-1}$  in agreement with the literature data (3).



**Scheme 1.** Synthetic pathways of new benzimidazole derivatives.

## CONCLUSIONS

In brief, we reported the synthesis and structural analysis of novel benzimidazole cyclic urea derivatives and zwitterionic compounds derived

from enetetramines as N-heterocyclic carbene sources. The novel benzimidazole derivatives (**1-12**) were synthesized in good yields.

## REFERENCES

1. Easmon J, Puerstinger G, Roth T, Fiebig HH, Jenny M, Jaeger W, Heinisch G, Hoffmann J. 2-Benzoxazolyl and 2-benzimidazolyl hydrazones derived from 2-acetylpyridine: A novel class of antitumor agents. *Int J Cancer*. 2001;94:89-96.
2. Güneş HS and Cosar G. Synthesis of some hydroxamic acid-derivatives of benzimidazole and their antibacterial and antifungal activities. *Arzneim-Forsch/Drug Res*. 1992;42-2(8):1045-1048.
3. Küçükbay H, Durmaz R, Orhan E, Günel S. Synthesis, antibacterial and antifungal activities of electron-rich olefins derived benzimidazole compounds. *Il Farmaco*. 2003;58:431-437.
4. Yılmaz Ü, Küçükbay H, Şireci N, Akkurt M, Günel S, Durmaz R, Tahir MN. Synthesis, microwave-promoted catalytic activity in Suzuki-Miyaura cross-coupling reactions and antimicrobial properties of novel benzimidazole salts bearing trimethylsilyl group. *Appl Organometal Chem*. 2011;25(5):366-373.
5. Küçükbay H. Part I: Microwave-assisted synthesis of benzimidazoles: An overview (Until 2013). *JOTCSA*. 2017; 4(1):1-22.
6. Buğday N, Küçükbay FZ, Apohan E, Küçükbay H, Serindağ A, Yeşilada Ö. Synthesis and evaluation of novel benzimidazole conjugates incorporating amino acids and dipeptide moieties. *Lett Org Chem*. 2017; 14(3): 198-206.
7. Singh AK and Lown JW. Design, synthesis and antitumor cytotoxicity of novel bis-benzimidazoles. *Anti-Cancer Drug Des*. 2000;15(4):265-275.
8. Soderlind KJ, Gorodetsky B, Singh AK. Bis-benzimidazole anticancer agents: targeting human tumour helicases. *Anti-Cancer Drug Des*. 1999;14(1):19-36.
9. Yılmaz Ü, Küçükbay H. Synthesis and characterization of novel phosphoramidates containing benzimidazole moiety. *Phosphorus Sulfur Silicon Relat Elem*. 2016;191(1):140-143.
10. Thompson RL. The effect of metabolites, metabolite antagonists, and enzyme inhibitors on the growth of vaccinia virus in Maitland type of tissue cultures. *J Immunol*. 1947;55:345-352.
11. Lappert MF. The coordination chemistry of electron-rich alkenes (enetetramines). *J Organomet Chem*. 1988;358(1-3):185-214.
12. Çetinkaya B, King GH, Krishnamathy SS, Lappert MF, Pedley JB. Photoelectron spectra of electron-rich olefins and an isostructural boron compound; olefins of exceptionally low first ionisation potential *J Chem Soc D*. 1971;1370-1371.
13. Tudose A, Delaude L, Andre B, Demonceau A. Imidazol(in)ium carboxylates as N-heterocyclic carbene ligand precursors for Suzuki-Miyaura. *Tetrahedron Lett*. 2006;47(48):8529-8533.
14. Hahn FE, Paas M., Le Van D, Lugger T. Simple Access to unsymmetrically substituted, saturated N-heterocyclic carbenes. *Angew Chem Int Edit*. 2003;42(42):5243-5246.
15. Kamplain JW, Lynch VM, Bielawski CW. Synthesis and study of differentially substituted dibenzotetraazafulvalenes. *Org Lett*. 2007;9(26):5401-5404.
16. Küçükbay H, Çetinkaya B, Guesmi S, Dixneuf PH. New (Carbene)ruthenium-arene complexes: preparation and uses in catalytic synthesis of furans. *Organometallics*. 1996;15:2434-2439.
17. Vasam CS, and Lin IJB. Silver(I) N-heterocyclic carbenes. *Com Inorg Chem*. 2004;25(3-4):75-129.
18. Tudose A, Demonceau A, Delaude L. Imidazol(in)ium-2-carboxylates as N-heterocyclic carbene precursors in ruthenium-arene catalysts for olefin metathesis and cyclopropanation. *J Organometal Chem*. 2006;691(24-25):5356-5365.
19. Hahn FE, Paas M., Le Van D, Fröhlich R. Spirocyclic diaminocarbenes: Synthesis, coordination chemistry, and investigation of their dimerization behavior. *Chem Eur J*. 2005;11:5080-5085.
20. Khramov DM, Boydston AJ, Bielawski CW. Synthesis and study of janus bis(carbene)s and their transition-metal complexes. *Angew Chem Int Edit*. 2006;45:6186-6189.
21. Lappert MF. Contributions to the chemistry of carbenometal chemistry. *J Organometal Chem*. 2005;690:5467-5473.
22. Çetinkaya E, and Küçükbay H. Effective acyloin condensations catalyzed by electron-rich olefins. *Turk J Chem*. 1995;19:24-30.
23. Lappert MF, Maskell RK. A new class of benzoin condensation catalyst, the bi-(1,3-dialkylimidazolidin-2-ylidenes). *J Chem Soc Chem Commun*. 1982;580-581.
24. Hocker J, and Metren R. Reactions of electron-rich olefins with proton-active compounds. *Angew Chem Int Edit*. 1972;11:964-973.
25. Küçükbay H, Çetinkaya E, Çetinkaya B, Lappert MF. Reactions of electron-rich olefins with proton-active compounds. *Synth Commun*. 1997;27(23):4059-4066.

26. Çetinkaya B, Çetinkaya E, Küçükbay H, Durmaz R. Synthesis and antimicrobial activity of electron rich olefin derived cyclic ureas. *Arzneim-Forsch/Drug Res.* 1996;46(12):1154-1158.

27. Küçükbay H, Durmaz R, Okuyucu N, Günel S, Kazaz C. Synthesis and antibacterial activities of new bis-benzimidazoles. *Arzneim-Forsch/Drug Res.* 2004;54(1):64-68.

28. Küçükbay H, Çetinkaya E, Durmaz R. Synthesis and antimicrobial activity of substituted benzimidazole, benzothiazole and imidazole derivatives. *Arzneim-Forsch/Drug Res.* 1995;45(12):1331-1334.

29. Li J-Q, Liao R-Z, Ding W-J, Cheng Y. Highly efficient and site-selective [3+2] cycloaddition of

carbene-derived ambident dipoles with ketenes for a straightforward synthesis of spiro-pyrrolidons. *J Org Chem.* 2007;72:6266-6269.

30. Wright JB. The chemistry of the benzimidazoles. *Chem Rev.* 1951;48(3):397-541.