Supplementary Material

Synthesis of novel C-2 substituted imidazoline derivatives having the norbornene/dibenzobarrelene skeletons

İrfan Çapan\textsuperscript{a} and Süleyman Servi\textsuperscript{b}

\textsuperscript{a}Gazi University, Technical Sciences Vocational College, Department of Polymer Technology, 06560 Ankara, Turkey
\textsuperscript{b}Fırat University, Faculty of Science, Department of Chemistry, 23169 Elazığ, Turkey

\textit{E-mail: sservi@firat.edu.tr}

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The synthesis of Bicyclo [2.2.1] hepta-5-ene-2,3-dicarbonitrile (1)

The dicyclopentadiene was converted into cyclopentadiene by heating in an oil bath at 180 °C. 240 mmol cyclopentadiene (15.86 g) was dissolved in methanol (100 mL) and the solution was cooled to 0 °C. To this solution, 120 mmol fumaronitrile (9.37 g) was added and stirred at 0 °C for 1 hour. After stirring for 24 hours at 25 °C, the solvent was removed under reduced pressure. The resulting solid was crystallized with ethanol.

Colorless powder; yield: 17.10 g, 118 mmol (99%); mp: 90-91 °C, (Ref [24]: 94-95 °C) 17.10 g. IR (KBr) (νmax, cm⁻¹): 3073, 2999, 2960, 2886, 2241, 1461, 1332, 729; ¹H NMR (400 MHz, CDCl₃): δH = 6.39 (2H, s), 3.46 (2H, d, J = 12.8 Hz), 3.19 (1H, m), 2.52 (1H, m), 1.79 (1H, dd, A part of AB system, J = 2.0 Hz), 1.96 (1H, dd, B part of AB system, J = 5.9, 3.4 Hz); ¹³C NMR (100 MHz, CDCl₃): δC = 137.7, 137.2 (=CH), 119.9, 119.5 (CN), 48.4, 46.3 (CH), 47.3 (CH₂), 34.8, 34.6 (CH); Anal. calc. for C₉H₈N₂ (144.18): C, 74.98; H, 5.59; N, 19.43; found C, 75.04; H, 5.73; N, 19.61 %.

The synthesis of 9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarbonitrile (2)

The mixture of anthracene (1.00 g, 5.61 mmol) and of fumaronitrile (0.44 g, 5.61 mmol) in benzene (30 mL) was refluxed for 24 hours. After the removal of the solvent in vacuo, the residue was crystallized from benzene.

Colorless powder; yield: 1.29 g, 5.03 mmol (90%); mp: 269-270 °C {Ref [24]: 259 °C}; IR (KBr) (νmax, cm⁻¹): 3082, 3046, 3026, 2943, 2241, 1460, 1201, 1171, 760, 747; ¹H NMR (400 MHz, CDCl₃): δH = 7.52-7.49 (2H, dd, J = 6.4, 2.2 Hz), 7.42-7.40 (2H, m), 7.33-7.29 (4H, m), 4.69 (2H, s), 3.18 (2H, s); ¹³C NMR (100 MHz, CDCl₃): δC = 139.3, 137.4 (Ar-Cipso), 128.0, 127.9, 125.8, 124.3 (Ar. CH), 118.6 (CN), 46.4 (CHbridgehead), 35.5 (CH); Anal. calc. for C₁₈H₁₂N₂ (256.31): C, 84.35; H, 4.72; N, 10.93; found C, 84.52; H, 4.87; N, 11.13 %.

The synthesis of Bicyclo [2.2.1] hept-5-ene-2,3 dicarboxylic acid (13)

This compound was prepared according a reported procedure. 15.1 mmol cyclopentadiene, which was obtained by cleavage of dicyclopentadiene at 180 °C, and 12.6 mmol fumaric acid were dissolved in the mixture of acetone-water (50 mL, 10 :1) and stirred at 50 °C for 24 hours. The solvent was removed under reduced pressure. The resulting solid was crystallized from the mixture of acetone-water (10: 1). Compound 13 was obtained with quantitative yields as colorless powder 2.30 grams. Its melting point corresponds well with the reported one. Colorless powder; yield: 2.30 g, 12.63 mmol (100%); mp: 174 °C (Ref [25]: 167-173 °C); IR (KBr) (νmax, cm⁻¹): 3078, 2997, 2984, 2876, 1682, 1422, 1275, 1216, 925, 729, 687; ¹H NMR (400 MHz, CDCl₃): δH = 12.32 (2H, s), 6.30 (1H, dd, J = 5.6, 3.1 Hz), 6.07 (1H, dd, J = 5.6, 2.5 Hz), 3.19-3.17 (2H, m), 3.04 (1H, s), 2.43 (1H, dd, J = 4.1, 1.3 Hz), 1.51 (1H, d, A part of AB system, J = 8.5 Hz), 1.34 (1H, dd, B part of AB system, J = 8.5, 1.5 Hz). ¹³C NMR (100 MHz, CDCl₃): δC = 175.8, 174.6 (C=O), 138.0, 135.4 (C=C), 47.5 (CH₂), 47.9, 47.4 (CH), 47.2, 45.4 (CHbridgehead); Anal. calc. for C₉H₁₀O₄ (182,18): C, 59.34; H, 5.53; found C, 59.56; H, 5.70 %.
General synthesis of C-2 aromatic-heteroaromatic substituted imidazolines 6-10

To a solution of the requisite aldehyde (0.87 mmol) in CH₂Cl₂ (30 mL), ethylenediamine (1.05 mmol) was added and stirred at 0 °C in an argon atmosphere for 2 hours. N-bromosuccinimide (NBS, 1.05 mmol) was slowly added to the mixture. After stirring at room temperature overnight, % NaOH solution was added until pH 8-10. The mixture was extracted with CH₂Cl₂. The organic phase was dried with Na₂SO₄ and the solvent was removed under reduced pressure. The crude products were crystallized from methanol-ethyl acetate 1:1 solvent mixture.

2-Phenyl-4,5-dihydro-1H-imidazole (6) Yield 96% (1.32 g, 9.03 mmol), m.p.: 98-100 °C, [Ref. 35: 100-101 °C]; IR (ATR) (νmax, cm⁻¹): 3197, 3064, 2970, 2929, 2868, 1636, 1610, 1598, 1573, 1508, 1468, 1269, 981. ¹H NMR (400 MHz, CDCl₃) δH: 7.80-7.78 (2H, m), 7.45-7.38 (3H, m), 4.82 (1H, br), 3.77 (4H, s). ¹³C NMR (100 MHz, CDCl₃) δC: 164.9 (C=N), 130.7, 128.5, 127.0 (CHAr), 130.3 (CAr-ipso), 50.3 (CH₂). Anal. calc. for C₉H₁₀N₂ (146,19): C, 73.94; H, 6.89; N, 19.16; found C, 74.06; H, 7.11; N, 19.48.

2-(3-Chlorophenyl)-4,5-dihydro-1H-imidazole (7) Yield 94% (1.26 g, 6.98 mmol), m. p.: 137-138 °C, [Ref. 35: 138-139 °C]; IR (KBr) (νmax, cm⁻¹): 3145, 3075, 2964, 2924, 2857, 1608, 1597, 1563, 1271, 757. ¹H NMR (400 MHz, CDCl₃) δH: 7.86 (1H, d, J = 1.2), 7.81 (1H, dd, J = 7.6, 1.2), 7.55-7.53 (1H, m), 7.08 (1H, br), 3.63 (4H, s). ¹³C NMR (100 MHz, CDCl₃) δC: 162.8 (C=N), 133.5, 133.1 (CAr-ipso), 130.7, 130.5, 127.3, 126.2 (CHAr), 50.2 (CH₂). Anal. calc. for C₉H₉ClN₂ (180,64): C, 59.84; H, 5.02; Cl, 19.63; N, 15.51; found C, 59.75; H, 5.26; N, 15.86.

2-(4-Methoxyphenyl)-4,5-dihydro-1H-imidazole (8) Yields 90% (1.16 g, 6.58 mmol), m. p.: 138-139 °C, [Ref. 35: 138-139 °C]; IR (KBr) (νmax, cm⁻¹): 3111, 3011, 2929, 2870, 2835, 1612, 1523, 1491, 1252, 1172, 1032, 841. ¹H NMR (400 MHz, CDCl₃) δH: 7.73-7.70 (2H, m), 6.89-6.88 (2H, m), 4.91 (1H, br), 3.82-3.80 (3H, d, J = 5.2), 3.73 (4H, s). ¹³C NMR (100 MHz, CDCl₃) δC: 161.5 (C=N), 161.4, 123.0 (CAr-ipso), 128.5, 113.7 (CHAr), 55.3 (CH₃). Anal. calc. for C₁₀H₁₂N₂O (176,22): C, 68.16; H, 6.86; N, 15.90; found C, 68.41; H, 7.13; N, 16.07.

2-(Thiophen-2-yl)-4,5-dihydro-1H-imidazole (9) Yield 92% (1.24 g, 8.15 mmol), m. p.: 179-181 °C, [Ref. 35: 180-181 °C]; IR (ATR) (νmax, cm⁻¹): 3146, 3084, 2931, 2856, 1596, 1529, 1495, 1101, 707. ¹H NMR (400 MHz, DMSO-d₆) δH: 7.64-7.63 (1H, d, J = 4 Hz), 7.50-7.49 (1H, d, J = 4 Hz), 7.13-7.11 (1H, dd, J = 4, 0.8 Hz), 6.99 (1H, br), 3.58 (4H, s). ¹³C NMR (100 MHz, DMSO-d₆) δC: 159.5 (C=N), 134.9 (CAr-ipso), 129.4, 128.3, 127.9 (CHAr), 60.9 (CH₂). Anal. calc. for C₇H₈N₂S (152,22): C, 55.24; H, 5.30; N, 18.40; S, 21.06; found C, 55.52; H, 5.63; N, 18.56; S, 21.25.
Spectra of Compound 3

FT-IR Spectrum of Compound 3

$^1$H-$^1$H-NMR Spectrum of Compound 3
$^{13}$CAPT-NMR Spectrum of Compound 3
Spectra of Compound 4

**FT-IR Spectrum of Compound 4**

**1H-1H-NMR Spectrum of Compound 4**
$^{13}$CAPT-NMR Spectrum of Compound 4
Spectra of Compound 5

FT-IR Spectrum of Compound 5

$^1$H-$^1$H-NMR Spectrum of Compound 5
$^{13}$C NMR Spectrum of Compound 5
Spectra of Compound 6

FT-IR Spectrum of Compound 6

1H-NMR Spectrum of Compound 6
$^{13}$CAPT-NMR Spectrum of Compound 6
Spectra of Compound 7

FT-IR Spectrum of Compound 7

1H-NMR Spectrum of Compound 7
$^{13}$CAPT-NMR Spectrum of Compound 7
Spectra of Compound 8

FT-IR Spectrum of Compound 8

$^1$H-NMR Spectrum of Compound 8
$^{13}$CAPT-NMR Spectrum of Compound 8
Spectra of Compound 9

FT-IR Spectrum of Compound 9

1H-NMR Spectrum of Compound 9
$^{13}$APT-NMR Spectrum of Compound 9
Spectra of Compound 10

FT-IR Spectrum of Compound 10

\[ \text{FT-IR Spectrum of Compound 10} \]

\( \text{H-NMR Spectrum of Compound 10} \)
$^{13}$CAPT-NMR Spectrum of Compound 10

X-ray ORTEP diagram of Compound 10
Spectra of Compound 15

FT-IR Spectrum of Compound 15
H-NMR Spectrum of Compound 15

13CAPT-NMR Spectrum of Compound 15
HETCOR-NMR Spectrum of Compound 15
Spectra of Compound 16

FT-IR Spectrum of Compound 16

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$^1$H-NMR Spectrum of Compound 16
$^{13}$CAPT-NMR Spectrum of Compound 16

HETCOR-NMR Spectrum of Compound 16
Spectra of Compound 19

FT-IR Spectrum of Compound 19
$^1$H-NMR Spectrum of Compound 19

$^{13}$CAPT-NMR Spectrum of Compound 19
HETCOR-NMR Spectrum of Compound 19
FT-IR Spectrum of Compound 20
$^1$H-NMR Spectrum of Compound 20
\[^{13}\text{C}]\text{APT-NMR Spectrum of Compound 20}\]

\text{HETCOR-NMR Spectrum of Compound 20}
Spectra of Compound 21

FT-IR Spectrum of Compound 21
$^1$H-NMR Spectrum of Compound 21

$^{13}$CAPT-NMR Spectrum of Compound 21
Spectra of Compound 22

FT-IR Spectrum of Compound 22
$^1$H-NMR Spectrum of Compound 22

$^{13}$CAPT-NMR Spectrum of Compound 22
HETCOR-NMR Spectrum of Compound 22
Spectra of Compound 23

FT-IR Spectrum of Compound 23
$^1$H-NMR Spectrum of Compound 23
$^{13}$CAPT-NMR Spectrum of Compound 23

HETCOR-NMR Spectrum of Compound 23
Spectra of Compound 24

FT-IR Spectrum of Compound 24

$^{1}$H-NMR Spectrum of Compound 24
APT-NMR Spectrum of Compound 24

HETCOR-NMR Spectrum of Compound 24
Spectra of Compound 28

FT-IR Spectrum of Compound 28
$^1$H-NMR Spectrum of Compound 28

$^{13}$CAPT-Spectrum of Compound 28
Spectra of Compound 29

FT-IR Spectrum of Compound 29
$^1$H-NMR Spectrum of Compound 29
$^{13}$CAPT-NMR Spectrum of Compound 29

HETCOR-NMR Spectrum of Compound 29
FT-IR Spectrum of Compound 30
$^{13}$CAPT-NMR Spectrum of Compound 30

$^1$H-NMR Spectrum of Compound 30
HETCOR-NMR Spectrum of Compound 30
Spectra of Compound 31

FT-IR Spectrum of Compound 31

^1H-NMR Spectrum of Compound 31
$^{13}$C$\text{APT}$-NMR Spectrum of Compound 31

HETCOR-NMR Spectrum of Compound 31