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SYNTHESIS AND CHARACTERISATION OF *N*-FUNCTIONALIZED ENETETRAMINES, AND THEIR PROPERTIES

Yetkin Gök,[a]* Engin Çetinkaya,[b] İsmail Özdemir,[a] Bekir Çetinkaya,[b] and Michael F. Lappert[c]

[a] *Inönü University, Faculty Science and Art, Department of Chemistry, 44069 Malatya,Türkiye*
[b] *Ege University, Department of Chemistry, 35100 Bornova-İzmir, Türkiye*
[c] *University of Sussex, Chem Lab., Brighton 9QJ, E Sussex, England*

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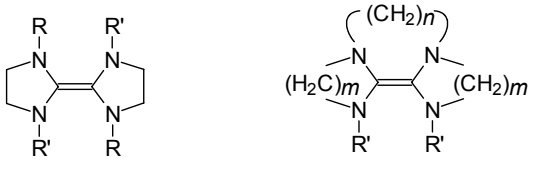
Abstract

Two general routes are described for the synthesis of the title compounds from the reaction of, either the dimethyl acetal of *N,N'*-dimethylformamide and an appropriate *N,N*'bis(secondary amine), or sodium hydride (or potassium *tert*-butoxide) and 4,5-dihydroimidazolium salts. *N*-Functionalized enetetramines (**3**, **8**) having 2-methoxyethyl or allyl substituent on the *N*-atom have been made. The reaction of this enetetramines with S_8 and Se, gave the corresponding cyclic chalcogeno ureas derivatives (**4**, **5**). Treatment of potassium *tert*-butoxide with 1,1'-ethylene-3,3'-diallyldiimidazolidinium dibromide (**7**) afforded, either the enetetramine (**8**), or, alternatively, the amino-Claisen isomer (**9**). All new compounds were identified by ^{1}H, ^{13}C NMR, FT-IR and micro analysis.

Key words: enetetramines, imidazole, amino-Claisen rearrangement

Introduction

The chemical behavior of the carbon-carbon double bond in tetrasubstituted ethylene derivatives is greatly influenced by the electron-donating or withdrawing power of its four substituents. Alkenes with four electron-donating substituents react as strong nucleophiles and this trend is particularly pronounced in tetraaminoethylenes. These compounds are referred to as enetetramines (electron-rich olefins).[1,2] Although an extensive chemistry of enetetramines of the type **I** (R = R' or R ≠ R') and **II** (Figure 1) has been developed,[3] relatively little is known of chemistry of analogues.



I **II**

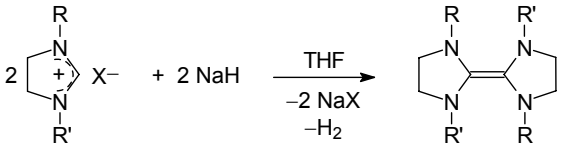
Figure 1. Exobicyclic and endotricyclic enetetramines.

The general route to compound **I** involves interaction of the appropriate *N,N'*-disubstituted-1,2-diaminoetane, $NH(R)(CH_2)_2NRH$ (R=a primary alkyl or an unhindered aryl group) with the dimethyl acetal of *N,N*-dimethylformamide (DMFDMA) in an inert atmospher, eqn 1.

$$2HN(R)(CH_2)_2N(R)H + 2CH(NMe_2)(OMe)_2 \rightleftharpoons \mathbf{I}\,(R=R') + 2Me_2NH + 4MeOH \qquad (1)$$

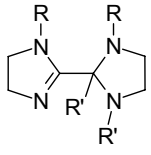
The equilibrium is driven to the right by continuous removal by distillation of MeOH and Me_2NH. The reaction has been extended to (i) six-membered bicyclic analogues of **I** and (ii) compounds **II**.[5,6] Symmetrical tetraarylenetetramines (**I**, R= an unhindered aryl group, eg. R= Ph) have been prepared by a similar procedure (EtOH elimination) from the orthoester $CH(OEt)_3$ and $HN(R)(CH_2)_2NRH$ or by heating $PhN(CH_2)_2N(Ph)C(H)CCl_3$ ($CHCl_3$ elimination).[7]

Our group described a useful alternative method for preparing compounds **I** and **II** from sodium hydride and a 4,5-dihydroimidazolium halide, eqn. (2) [e.g. For **I** or **II**, *n*=*m*= 2, R= CH_2Ph].[6]



(2)

This procedure has the advantages that it requires extremely mild conditions, affords the products in high yield and is particularly suitable for unsymmetrical enetetramines, e.g. **I** and **II** (R ≠ R').



I'

Figure 2. The rearrangement of **I**.

The biimidazolidinylidene I (R=R'= allyl) was not accessible using the procedure of eqn. (1) and, if formed, spontaneously rearranged to the isomer I' (R=R'= allyl) (Figure 2).[8] This thermal amino-Claisen rearrangement was believed to be [3,3]-sigmatropic, because the corresponding thermal transformation of the tetracrotyl analogue **I** (R=R'= $CH_2CH=CHMe$) regiospecifically yielded **I'** [R= $CH_2CH=CHMe$, R'= $CH(Me)CH=CH_2$], while its photochemical isomerisation gave, not only the latter,

but also the isomer I' (R=R'= crotyl). In a preliminary publication we noted, that a similar **I→I'** isomerisation (**8→9**, iii in Scheme 2) occured for the case of R= -CH_2CH_2-, R'= $CH_2CH{=}CH_2$.

For some years we have used to enetetramines (electron-rich olefins) such as **I** as a sources of carbenetransition metal complexes.[9] In this paper we report straightforward preparation of a series (i) *N*-functionalized enetetramines (**3**, **8**) having 2-methoxyethyl or allyl substituent on the *N*-atom, (ii) the cyclic chalcogeno ureas (**4**, **5**) and (iii) the thermal degradation product **9** of the enetetramine **8**.

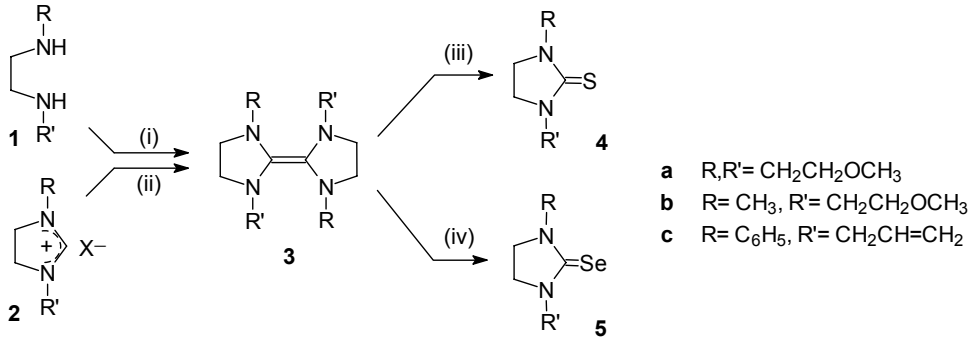
Results and Discussion

The enetetramines **3** can be prepared from the interaction of the DMFDMA with the appropriate secondary diamine (eqn. 1) or sodium hydride (or potassium *tert*-butoxide) with 4,5-dihydroimidazolium salts in an inert atmospher (eqn. 2). These methods are illustrated in Scheme 1 and Scheme 2 for the case of the *N*-functionalized enetetramines (**3a**, R=R'= CH_2CH_2OMe; **3b**, R= $CH_2CH_2OCH_3$, R'= CH_3; **3c**, R= Ph, R'= $CH_2CH{=}CH_2$; **8**, R= -CH_2CH_2-, R'= $CH_2CH{=}CH_2$). The identify of these compounds has been confirmed by CHN analyses, FT-IR, ^{1}H and ^{13}C NMR spektroscopy.

The starting materials for the enetetramine **3a** was made by the literature procedure from $ClCH_2CH_2OCH_3$ and $H_2N(CH_2)_2NH_2$.[9] The enetetramine **3a** was prepared from DMFDMA and $H_3CO(CH_2)_2HN(CH_2)_2NH(CH_2)_2OCH_3$, as for eqn. (1).[4] The starting materials (**2b**, **2c**, **7**) for enetetramines **3b**, **3c** and **8** readily prepared from appropriate alkyl halide. The hydrogen atom attached to $C_{(2)}$ of imidazolium salt has considerable protic character (as evident from ^{1}H NMR data) and hence the high reactivity to the base-induced protic acid elimination is not surprising. Thus, they reacted smoothly and good yield with an excess (*ca*. 20%) sodium hydride or potassium *tert*-butoxide in tetrahyrofuran at ambient temperature within 9-18h.

The 1,1'-dimethyl-3,3'-di(2-methoxyethyl)-2,2'-biimidazolidinylidene (**3b**) was obtained as a mixture of *cis/trans*-isomers as evident from the observed two peaks at 129.5 and 129.7 ppm for δ ($^{13}C_{C=C}$) in the ^{13}C NMR spectra of **3b**. 1,1'-Diphenyl-3,3'-diallyl-2,2'-biimidazolidinylidene (**3c**) was similarly obtained as a mixture of *cis/trans*-

isomers. It is clearly notice that δ ($^{13}C_{C=C}$) move to higher field upon attachment of the OMe group.



Scheme 1. Synthesis of *N*-functionalized enetetramines and their cylic chalcogeno urea derivatives. Reaction conditions: (i) $CH(OCH_3)_2N(CH_3)_2$, 100-120 °C; (ii) NaH ($KOBu^t$), THF, 25 °C; (iii) S_8, toluene, 110 °C; (iv) Se, toluene, 110 °C.

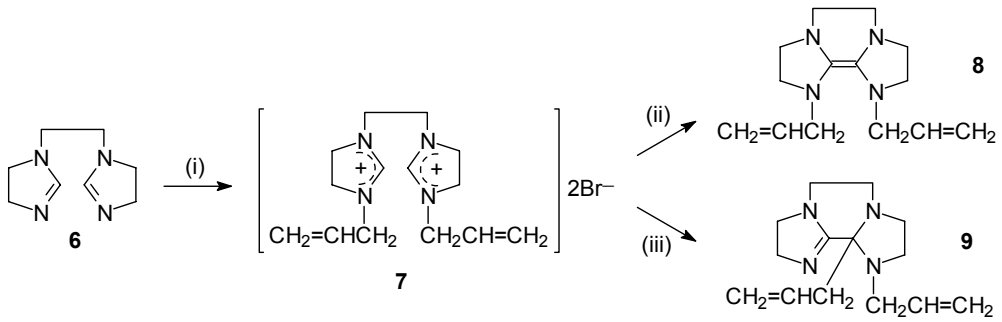
The cyclic chalcogeno ureas were prepared from enetetramines **3** and appropriate Group VI elements in good yields according to the procedure indicated in scheme 1 and described in experimental section. This behavior is typical for reactive enetetramines **I** and **II**.

Both, thio urea and selenourea exhibited a characteristic $\nu_{C=S}$ and $\nu_{C=Se}$ band at 1450-1502 cm^{-1}which corresponded well with 1500 cm^{-1} found for the functionalized derivatives. ^{13}C chemical shifts, which provide a useful diagnostic tool for urea compounds, show that C=S (or C=Se) is substautially deshielded. Values of δ (^{13}C=X, X= S or Se) are in the range 180-184 ppm and similar the those found for non-functionalized derivatives

Treatment of potassium *tert*-butoxide with compound **7** afforded, either the enetetramine **8,** or, alternatively, the isomer **9** depending on the nature of the allyl substituent at nitrogen (Scheme 2). When compound **7** reacted with potassium *tert*-butoxide in THF at ambient temperature within 9 h, the enetetramine **8** was obtained. The enetetramine **8** exhibit a characteristic δ ($^{13}C_{C=C}$) peak at 160.8 ppm. The ^{13}C data showed that (**8**) contained one type of allyl group.

As for eqn. 2, when compound **7** was heated with potassium *tert*-butoxide in THF under reflux for 1 h, a regiospecific rearrangement was observed compound **9** was formed as, the result of a [3,3]-sigmatropic amino-Claisen type rearrangement. The ^{13}C

data were particularly informative, as they showed that (**9**) contained two types of allyl group (Figure 3).



Scheme 2. Synthesis of enetetramines **8** and its thermal degradation product **9**. Reaction conditions: (i)$BrCH_2CH{=}CH_2$, DMF, 25 °C; (ii) $KOBu^t$, Bu^tOH, 25 °C; (iii) $KOBu^t$, THF, 60 °C.

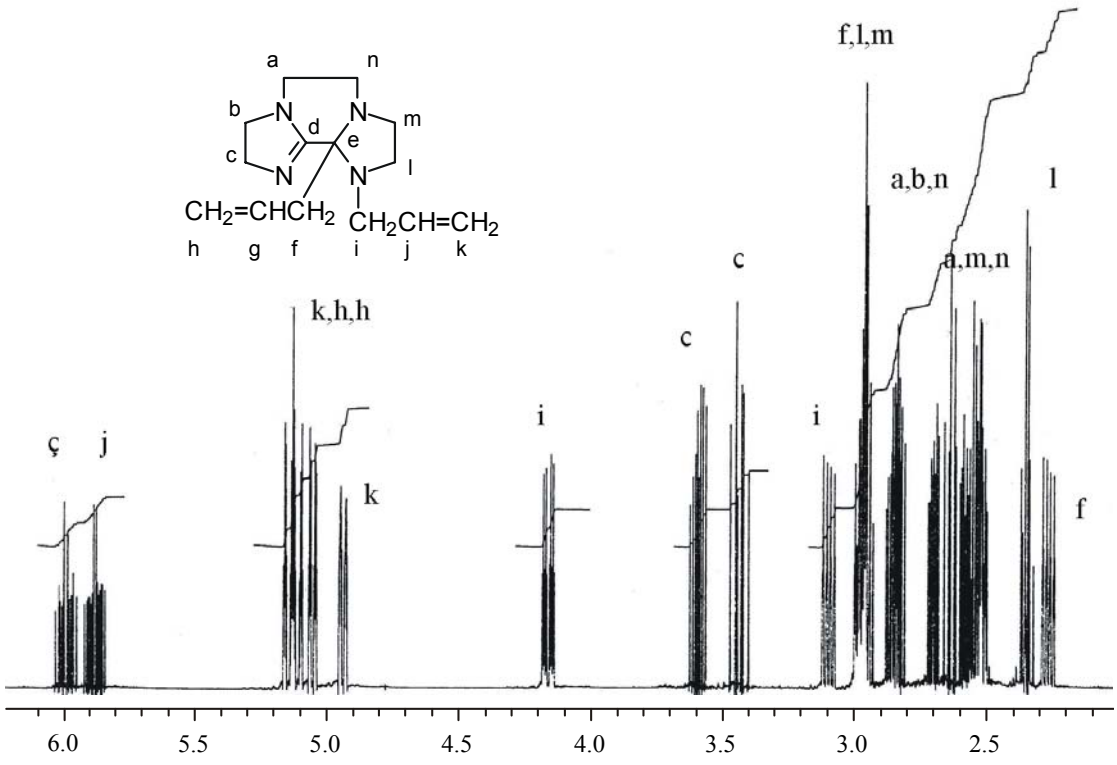


Figure 3. ^{1}H NMR spectrum of compound **9**.

In conclusion from readily available starting materials, such as 1-alkyl-2-imidazoline four new *N*-functionalized enetetramines, six chalcogeno ureas derivatives and one rearanged isomer of 1,1'-ethylen-3,3'di(alyl)-2,2'biimidazolidinylidene have been prepared and characterized.

Experimental

All manipulations of air/or moisture-sensitive compounds were carried out under an argon atmosphere by using standard Schlenk techniques. Solvents were dried and freshly distilled under argon before use. IR absorption spectra were obtained from a Matson 1000-FTIR spectrometer in KBr discs, in the range of 400-4000 cm^{-1}. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were recorded on a Bruker DPX FT NMR spectrometer ($CDCl_3$ or C_6D_6 and TMS as internal standard).

1,3,1',3'-Tetra(2-methoxyethyl)-2,2'-biimidazolidinylidene (3a). A stirred solution of *N,N*-dimethylformamide dimethyl acetal (9.3 mL, 70 mmol) and 1,2-bis(2-methoxyethylamino)etane (11.2 g, 63.6 mmol) in dry toluene (20 mL) was heated for 3 h at 90 °C under an argon atmosphere. The reaction mixture was then heated at 120 °C under distillation conditions, allowing the produced dimethylamine and methanol to be removed. From the resultant product, unreacted starting materials were eliminated by evaporation *in vacuo*. Oily residue was distilled in vacuum (130-140 °C/0.15 mmHg) (6.62 g, 56%). ^{1}H NMR (C_6D_6) δ: 2.48 (s, 6H,CH_3), 2.74 (t, *J* 6.5 Hz, 4H, CH_2CH$_2$OCH$_3$), 2.96 (t, *J* 6.5 Hz, 4H, CH$_2$CH_2OCH$_3$), 3.12 (s, 6H, OCH_3), 3.39 (t, *J* 5.5 Hz, 8H, 4,5-CH$_2$). ^{13}C NMR (C_6D_6) δ: 42.4 (*C*H$_3$), 53.2, 54.9, 74.0 (*C*H$_2$*C*H$_2$O*C*H$_3$), 74.0 (4,5-*C*H$_2$), 129.5, 129.7 (*C*=*C*).

1,1'-Dimethyl-3,3'-di(2-methoxyethyl)-2,2'-biimidazolidinylidene (3b). 1-methyl-3-(2-methoxyethyl)-4,5-dihydroimidazolium iodide (9 g, 33.33 mmol) was added to a suspension of sodium hydride (1.2 g, 50 mmol) in THF (50 mL). The mixture was stirred at 20 °C for 18 h then heated at 60 °C for 1 h, and the volatiles were removed under reduced pressure. Toluene (15 mL) was added to the resultant oily residue and the suspension was filtered. After removal of the solvent from the filtrate, the residue was distilled *in vacuo* (90-100 /0.15 mmHg) (4.16 g; 88%). ^{1}H NMR (C_6D_6) δ: 2.98 (s, 8H, 4,5-CH_2), 3.12 (s, 12H, OCH_3), 3.21 (t, *J* 5.7 Hz, 8H, CH_2CH$_2$OCH$_3$), 3.42 (t, *J* 5.7 Hz, 8H, CH$_2$CH_2OCH$_3$). ^{13}C NMR (C_6D_6) δ: 46.6, 47.9, 52.3 (*C*H$_2$*C*H$_2$O*C*H$_3$), 52.5 (4,5-*C*H$_2$), 128.2 (*C*=*C*).

1,1'-Diphenyl-3,3'-diallyl-2,2'-biimidazolidinylidene (3c). This compound was prepared from 1-phenyl-3-allyl-4,5-dihydroimidazolium iodide (3.3 g, 12.3 mmol) and potassium *tert*-butoxide (42.2 mL, 0.3 M). The compound **3c** was recrystallised from

pentane (5 mL) and Et_2O (7 mL) at –25 °C, yield (1.07 g; 55%), mp 68-69 °C. Anal. Calcd for $C_{24}H_{28}N_4$: C 77.38, H 7.58, N 15.04. Found: C 77.34, H 7.12, N 14.93. ^{1}H NMR (C_6D_6) δ: 2.53 (t, *J* 6.2 Hz, 4H, 4,5-C*H*$_2$), 2.53 (t, *J* 6.2 Hz, 4H, 4,5-C*H*$_2$), 3.70 (d, *J* 6.1 Hz, 4H, CH_2=CHC*H*$_2$), 4.49 (m, 4H, C*H*$_2$=CHCH_2), 5.58 (m, 2H, CH_2=C*H*CH_2), 6.87-7.75 (m, 10H, C_6H_5). ^{13}C NMR (C_6D_6) δ: 48.8, 49.2, 51.4, 54.4 (4,5-*C*H_2), 55.2, 118.3, 136.5 (*C*H_2=*C*H*C*H_2), 116.3, 118.9, 119.4, 121.1, 121.1, 136.2 (*C*$_6$H$_5$), 144.4, 146.1 (*C*=*C*).

Reaction of Group VI Elements (S_8 and Se) With *N*-Functionalized Eneteramines 3. General Procedure for Preparation of Compounds 4 and 5. A mixture of enetetramine **3** (1 mmol) an sulfur, S_8 (2 mmol) in toluene (10 mL) was heated under reflux for 2h. Then, the mixture was filtered to remove unreacted sulfur and all volatiles were removed *in vacuo*. The crude solid was crystallized from toluene/*n*-hexane (1/2) upon cooling to –20 °C.

Using a similar procedure, enetetramine (**3**), (1 mmol) and selenium (2 mmol) afforded 1,3-dialkylimidazolidin-2-selenone (**5**).

1,3-Di(2-methoxyethyl)imidazolidin-2-thione (4a). This compound was prepared from 1,3,1',3'-tetra(2-methoxyethyl)-2,2'-biimidazolidinylidene **3a** (0.42 g, 1.12 mmol) and sulfur, S_8 (0.07 g, 2.18 mmol), yield (0.21 g, 41%), mp 46-47 °C. Anal. Calcd for $C_9H_{18}N_2O_2S$: C 49.09, H 9.09, N 12.77. Found C 49.31, H 9.23, N 12.70. IR, ν: 1480 (C=S). ^{1}H NMR ($CDCl_3$) δ: 3.35 (s, 6H, OC*H*$_3$), 3.60 (t, 4H, *J* 5 Hz, C*H*$_2$CH$_2$OCH$_3$), 3.68 (s, 4H, 4,5-C*H*$_2$), 3.81 (t, 4H, *J* 5 Hz, CH$_2$C*H*$_2$OCH$_3$). ^{13}C NMR ($CDCl_3$), δ: 58.8 (4,5-*C*H_2), 47.7, 48.0, 71.4 (*C*H$_2$*C*H$_2$O*C*H$_3$), 182.5 (*C*=S).

1-Methyl-3-(2-methoxyethyl)imidazolidin-2-thione (4b). This compound was prepared from 1,1'-dimethyl-3,3'-di(2-methoxyethyl)-2,2'-biimidazolidinylidene **3b** (0.43 g, 1.36 mmol) and sulfur, S_8 (0.08 g, 2.50 mmol), yield (0.33 g, 68%), mp 38-39 °C. Anal. Calcd for $C_7H_{14}N_2OS$: C 48.25, H 8.11, N 16.09, S 18.37. Found C 48.36, H 8.11, N 15.96, S 18.46. IR, ν: 1502.4 (C=S). ^{1}H NMR ($CDCl_3$) δ: 3.13 (s, 3H, C*H*$_3$), 3.34 (s, 3H, OC*H*$_3$), 3.47-3.82 (m, 4H, C*H*$_2$C*H*$_2$OCH$_3$), 3.47-3.82 (m, 4H, 4,5-C*H*$_2$). ^{13}C NMR ($CDCl_3$) δ: 35.0 (*C*H$_3$), 47.7, 47.8 (4,5-*C*H_2), 49.0, 58.8, 71.4 (*C*H$_2$*C*H$_2$O*C*H$_3$), 182.9 (*C*=S).

1-Phenyl-3-allylimidazolidin-2-thione (4c). This compound was prepared from 1,1'-diphenyl-3,3'-diallyl-2,2'-biimidazolidinylidene **3c** (0.65 g, 1.74 mmol) and sulfur, S_8 (0.11 g, 3.43 mmol), yield (0.12 g, 32%), mp 40-41 °C. Anal. Calcd for $C_{12}H_{14}N_2S$: C 66.05, H 6.42, N 12.84, S 14.67. Found: C 66.01, H 6.31, N 12.73, S 14.44. IR, ν: 1487 (C=S). ^{1}H NMR ($CDCl_3$) δ: 3.65 (t, 2H, *J* 9 Hz, 4,5-CH_2); 3.99 (t, 2H, *J* 9 Hz, 4,5-CH_2), 4.35 (d)-5.87 (m)-5.29 (m) (5H, CH_2CH=CH_2), 7.21-7.60 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$) δ: 46.9, 49.9 (4,5-CH_2), 57.7, 119.6, 126.0 (*C*H_2*C*H=*C*H_2), 127.2, 129.7, 133.2, 142.0 (C_6H_5), 183.3 (*C*=S).

1,3-Di(2-methoxyethyl)imidazolidin-2-selenone (5a). This compound was prepared from 1,3,1',3'-tetra(2-methoxyethyl)-2,2'-biimidazolidinylidene **3a** (0.60 g, 1.61 mmol) and selenium (0.3 g, 3.22 mmol), yield (0.3 g, 60%), mp 49-50 °C. Anal. Calcd for $C_9H_{18}N_2O_2Se$: C 37.83, H 6.35, N 12.61. Found: C 37.69, H 6.11, N 12.71. IR, ν: 1564 (C=Se). ^{1}H NMR ($CDCl_3$) δ: 3.18 (s, 3H, CH_3), 3.29 (s, 3H, OCH_3), 3.50-3.88 (m, 4H, CH_2CH_2OCH$_3$), 3.50-3.88 (m, 4H, 4,5-CH_2). ^{13}C NMR ($CDCl_3$) δ: 37.1 (*C*H$_3$), 49.9, 50.0 (4,5-*C*H$_2$), 49.2, 59.2, 72.0 (*C*H$_2$*C*H$_2$O*C*H$_3$), 181.4 (*C*=Se).

1-Methyl-3-(2-methoxyethyl)imidazolidin-2-selenone (5b). This compound was prepared from 1,1'-dimethyl-3,3'-di(2-methoxyethyl)-2,2'-biimidazolidinylidene **3b** (0.35 g, 1.10 mmol) and selenium (0.18 g, 2.27 mmol), yield (0.44 g, 85%), mp 61-62 °C. *Anal*. Calcd for $C_7H_{14}N_2OSe$: C 40.76, H 6.84, N 10.56. Found: C 40.90, H 6.60, N 10.62. IR, ν: 1514 (C=Se). ^{1}H NMR ($CDCl_3$) δ: 3.35 (s, 6H, OCH_3), 3.64 (t, 4H, *J* 5 Hz, CH_2CH$_2$OCH$_3$), 3.71 (s, 4H, 4,5-CH_2), 3.90 (t, 4H, *J* 5 Hz, CH$_2$CH_2OCH$_3$). ^{13}C NMR ($CDCl_3$) δ: 61.0 (4,5-*C*H$_2$), 51.3, 51.7, 74.0 (*C*H$_2$*C*H$_2$O*C*H$_3$), 182.9 (*C*=Se).

1-Phenyl-3-allylimidazolidin-2-selenone (5c). This compound was prepared from 1,1'-diphenyl-3,3'-diallyl-2,2'-biimidazolidinylidene **3c** (0.44 g, 1.18 mmol) and selenium (0.19 g, 2.40 mmol), yield (0.53 g, 86%), mp 62-63 °C. Anal. Calcd for $C_{12}H_{14}N_2Se$: C 54.34, H 5.32, N 10.56. Found: C 54.45, H 5.08, N 10.53. IR, ν: 1488.9 (C=Se). ^{1}H NMR ($CDCl_3$) δ: 3.63 (t, 2H, *J* 9 Hz, 4,5-CH_2); 3.93 (t, 2H, *J* 9 Hz, 4,5-CH_2), 4.43 (d)-5.85 (m)-5.27 (m) (5H, CH_2CH=CH_2), 7.19-7.49 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$) δ: 47.3, 50.9 (4,5-CH_2), 52.9, 119.3, 126.1 (*C*H_2*C*H=*C*H_2), 127.2, 129.2, 132.3, 141.8 (C_6H_5), 180.8 (*C*=Se).

1,1'-Ethylenediimidazolidine (6). A stirred solution of diethylethane-1,2-diamine **1** (0.44 g, 3.01 mmol) in *N,N*-dimethylformamide dimethyl acetal (0.71 g, 6.07 mmol)

was heated for 3 h at 90 °C under an argon atmosphere. The reaction mixture was then heated at 120 °C under distillation conditions, allowing removal of the produced dimethylamine and methanol. From the resultant product, unreacted starting materials were evaporated *in vacuo*. The yellow precipitate of **6** was recrystallized from toluene and *n*-hexane at -20 °C (0.41 g, 82%). ^{1}H NMR (C_6H_6) δ: 2.38 (s, 4H, CH_2CH_2), 2.55 (t, 4H, *J* 9.3 Hz, 4,5-CH_2), 3.68 (t, 4H, *J* 9.3 Hz, 4,5-CH_2), 6.45 (s, 2H, 2-C*H*). ^{13}C NMR ($CDCl_3$) δ: 46.5 (*C*H_2*C*H_2), 48.8, 55.6 (4,5-*C*H_2), 158.3 (2-*C*H).

3,3'-Diallyl-1,1'-ethylenediimidazolidinium dibromide (7). To a solution of 1,1'-ethylenediimidazoline **6** (5.05 g, 30.4 mmol) in DMF (20 mL) allyl bromide (6 mL, 69.4 mmol) was added and the mixture stirred at room temperature for 1 h. Et_2O (5 mL) was added the reaction mixture. A yellow solid precipitated in this period. The product was filtered, washed twice with dried Et_2O and dried *in vacuo* (12.87 g, 95%), mp 129-130 °C. Anal. Calcd for $C_{14}H_{24}N_4Br_2$: C 41.20, H 5.93, N 13.99. Found: C 41.18, H 5.95, N 13.78. ^{1}H NMR (C_6D_6) δ: 4.03 (t, *J* 3.5 Hz, 4H, 4,5-CH_2), 4.08 (s, 4H, CH_2CH_2), 4.17 (d, *J* 6.4 Hz, 4H, CH_2=CHCH_2), 4.38 (t, *J* 3.5 Hz, 4H, 4,5-CH_2), 5.37 (m, 4H, CH_2=CHCH_2), 5.83 (m, 2H, CH_2=C*H*CH_2), 10.05 (s, 2H, 2-C*H*). ^{13}C NMR (C_6D_6) δ: 48.5 (*C*H_2*C*H_2), 40.8, 49.5 (4,5-*C*H_2), 45.2, 122.2, 129.4 (*C*H_2=*C*H*C*H_2), 158.7 (2-*C*H).

1,1'-Ethylene-3,3'di(alyl)-2,2'biimidazolidinylidene (8). 3,3'-diallyl-1,1'-ethylenediimidazolidinium dibromide **7** (1.6 g, 3.9 mmol) was added to a suspension of potassium *tert*-butoxide (1 g, 8.9 mmol) in *tert*-butanol (20 mL). The mixture was stirred at 20 °C for 10 h. The volatiles were removed under reduced pressure. Pentane (15 mL) was added to the resultant oily residue and product was precipitated. The crude product was recrystallised from pentane (5 mL) and Et_2O (7 mL) at –25 °C (0.28 g, 30%), mp 73-75 °C. Anal. Calcd for $C_{14}H_{22}N_4$: C 68.26, H 9.00, N, 22.74. Found: C 68.15, H 8.88, N 22.63. ^{1}H NMR (C_6D_6) δ: 2.71 (t, *J* 7.6 Hz, 4H, 4,5-CH_2), 2.98 (t, *J* 7.6 Hz, 4H, 4,5-CH_2), 3.09 (s, 4H, CH_2CH_2), 3.68 (d, *J* 5.9 Hz, 4H, CH_2=CHCH_2), 5.00 (m, 4H, CH_2=CHCH_2), 5.54 (m, 2H, CH_2=C*H*CH_2). ^{13}C NMR (C_6D_6) δ: 41.1, 41.5 (4,5-*C*H_2), 42.3 (*C*H_2*C*H_2), 45.0, 47.3, 116.6, 134.5 (*C*H_2=*C*H*C*H_2), 160.8 (*C*=*C*).

1,1'-Ethylene-2-imidazolinyl-2,3-dialylimidazolidine (9). 3,3'-dialyl-1,1'-ethylenediimidazolidinium dibromide **7** (9.37 g, 22.9 mmol) was added to a suspension of potassium *tert*-butoxide (7 g, 62.3 mmol) in THF (50 mL). The mixture was stirred at 20 °C for 12 h and heated for 1 h at 60 °C. The volatiles were removed under reduced

pressure. The oily residue was distilled *in vacuo* (94-95 °C/0.01 mmHg) (2.99 g, 53%). ^{13}C NMR ($CDCl_3$) δ: 35.9 (^{f}C), 44.9 (^{n}C), 47.8 (^{a}C), 48.2 (^{l}C), 49.7 (^{m}C), 52.1 (^{b}C), 52.5 (^{i}C), 53.0 (^{c}C), 80.4 (^{e}C), 115.0 (^{k}C), 116.3 (^{h}C), 135.7 (^{g}C), 138.3 (^{j}C), 164.3 (^{d}C).

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Povzetek

Opisana sta dva splošna načina sinteze naslovnih spojin iz *N*,*N*'-dimetilformamida dimetil acetala in ustreznega *N*,*N*'-bis(sekundarnega amina), oziroma natrijevega hidrida (ali kalijevega *t*-butoksida) in 4,5-dihidroimidazolijevih soli. Pripravili smo *N*-funkcionalizirane entetramine (**3**, **8**) z 2-metoksietil- ali alil- substituentom na N-atomu. Reakcija teh entetraminov z S_8 in Se so dale ustrezne ciklične halkogeno sečnine (**4**, **5**). Obdelava kalijevega *t*-butoksida z 1,1'-etilen-3,3'-dialildiimidazolidinijevim dibromidom (**7**) je dala entetramin (**8**) oziroma amino-Claisen-ov isomer (**9**). Vse nove spojine so identificirane z ^{1}H, ^{13}C NMR, FT-IR in mikro analizo.