Microwave-Assisted Base-Catalysed Rearrangement of 3-Aryl(arylalkyl)-4-iminooxazolidin-2-ones into 4-Arylimino- and 4-Arylalkyliminooxazolidin-2-ones

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Abstract: The microwave-assisted base-catalysed Dimroth rearrangement of 3-aryl(arylalkyl)-4-iminooxazolidin-2-ones into 4-arylimino- and 4-arylalkyliminooxazolidin-2-ones is described.

Key words: heterocycles, ring closure, rearrangements, amidines, microwave chemistry

The structural modification of bioactive heterocycles using microwave-assisted chemistry represents an important challenge for organic and medicinal chemists.[1] 4-Arylimino- and 4-arylalkyliminooxazolidin-2-ones **I** (Figure 1) are regioisomers of N-substituted 4-iminooxazolidin-2-ones **II**, a class of compounds that attracted interest in agricultural chemistry, especially due to their fungicidal activity.[2] Compounds **II** (Figure 1) are commonly prepared by reactions of cyanohydrins with isocyanates via α-cyanocarbamates in the presence of a base.[2]

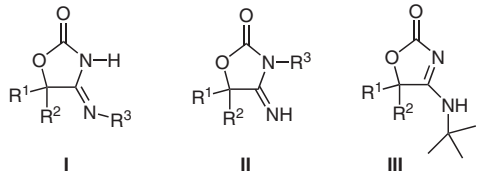

Figure 1

To the best of our knowledge only a few examples of the title compounds **I** are known and no general synthetic method has yet been established for their preparation. Kauffman reported the synthesis of two 4-(*p*-tolylimino)oxazolidin-2-ones by mild acidic hydrolysis of 2-ethoxy-4-(*p*-tolylimino)-2-oxazolines.[3] Stronger acidic reaction conditions afforded the corresponding oxazolidin-2,4-diones. Wu described one example of **I** in the course of the structural modification of α-benzoxazolylcarbamates with herbicidal activity.[4] L'abbé suggested a tautomeric structure **III** for the title compounds (**I**).[5] Again, the acidic hydrolysis of **III** (Figure 1) led to the corresponding oxazolidin-2,4-diones.

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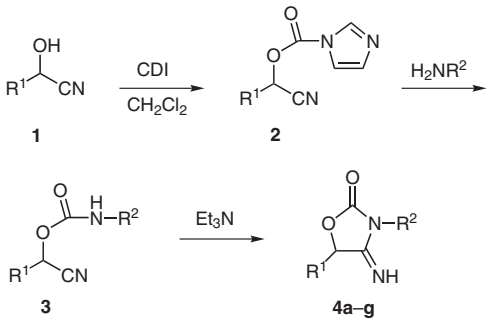
We now describe the microwave-assisted synthesis of 4-arylimino- and 4-arylalkyliminooxazolidin-2-ones starting from 3-substituted 4-iminooxazolidin-2-ones **4**.

Substrates **4** have been prepared in a novel one-pot reaction by stepwise treatment of cyanohydrins **1** with 1,1′-carbonyldiimidazole (CDI) and primary amines via the open chained intermediates **2** and **3** (Scheme 1, Table 1). The formation of compounds **4** was readily monitored by IR spectroscopy. 4-Iminooxazolidin-2-ones **4** are characterised by two sharp IR absorption bands at 1670–1685 (C=N) cm^{-1} and 1760–1791 (C=O) cm^{-1}.



Scheme 1 Synthesis of 3-substituted 4-iminooxazolidin-2-ones **4**.

Table 1 Synthesis of 3-Substituted 4-Iminooxazolidin-2-ones **4**

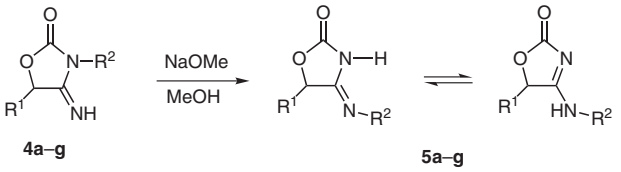
4	R^1	R^2	Yield (%)
a	1-Naphthyl	3-FPh	65
b	Cyclopropyl	4-CNPh	72
c	1-Naphthyl	4-CNPh	70
d	2-Naphthyl	4-FPh	68
e	CH_3	4-CH_3Bn	75
f	CH_3	4-FBn	73
g	Ph	2-ClBn	50

In two previous publications we described the sodium methoxide supported decarbonylation of O-substituted 3-hydroxy-4-iminooxazolidin-2-ones into α-hydroxyamidoximes as well as their triethylamine-catalysed Dimroth rearrangement into 4-alkoxy(aralkoxy)iminooxazolidin-2-ones.[6,7] These results encouraged us to investigate the behaviour of compounds **4** under similar reaction condi-

tions. However, when compound **4a** was heated to reflux with either triethylamine–dichloromethane or with sodium methoxide (0.2 equiv) in methanol the starting material was recovered unchanged.

Interestingly, the reaction of **4a** with equimolar amounts of sodium methoxide in refluxing methanol furnished the rearranged 4-(3-fluorophenylimino)-5-(1-naphthyl)oxazolidin-2-one (**5a**) in 52% yield after three hours. Discrimination between the structures of compounds **4a** and **5a** was accomplished by IR, ^{1}H and ^{13}C NMR spectroscopy. While the IR spectrum of **4a** showed two characteristic absorption bands at 1789 (C=O) cm^{-1} and 1676 (C=N) cm^{-1}, the spectrum of **5a** showed two bathochromic-shifted absorption bands at 1747 (C=O) cm^{-1} and 1630 (C=N) cm^{-1}.

Next we turned our attention to the microwave-assisted synthesis of compounds **5**. Indeed, treatment of compounds **4a–e** with equimolar amounts of sodium methoxide in methanol led to 4-aryl(arylalkyl)iminooxazolidin-2-ones **5a–e** in only 5–20.5 minutes (Scheme 2, Table 2, parameters a). However, the microwave-assisted rearrangement of 4-fluorobenzyl and 2-chlorobenzyl substituted 4-iminooxazolidin-2-ones **4f,g** into **5f,g** required somewhat harsher reaction conditions (parameters b). A simple standard work-up procedure followed by recrystallisation from an appropriate solvent afforded the target compounds **5a–g** in 51–72% yield.[8]



Scheme 2 Synthesis of 4-arylimino- and 4-arylalkyliminooxazolidin-2-ones **5**.

Table 2 Synthesis of 4-Arylimino- and 4-Arylalkyliminooxazolidin-2-ones **5**

5	R^1	R^2	Yield (%)	Hold time (min)[a]
a	1-Naphthyl	3-FPh	64	4.5[b]
b	Cyclopropyl	4-CNPh	60	8.5[b]
c	1-Naphthyl	4-CNPh	63	5.5[b]
d	2-Naphthyl	4-FPh	69	5.5[b]
e	CH_3	4-CH_3Bn	72	20[b]
f	CH_3	4-FBn	61	10[c]
g	Ph	2-ClBn	51	3.5[b]

[a] Hold time + ramp time = 0.5 min.
[b] See 'Parameters a' in the experimental part for more detailed conditions.
[c] See 'Parameters b' in the experimental part for more detailed conditions.

The structures of compounds **4** and **5** were elucidated by IR, ^{1}H, ^{13}C NMR spectroscopy and elemental analysis.

In conclusion, we have established a novel one-pot reaction for the synthesis of N-substituted 4-iminooxazolidin-2-ones by reacting cyanohydrins **1** stepwise with 1,1′-carbonyldiimidazole and primary amines. Furthermore, we describe the microwave-assisted, base-catalysed rearrangement of N-substituted 4-iminooxazolidin-2-ones **4** into the target compounds **5**.

Melting points were determined on a Mettler FP 62 apparatus and are uncorrected. Elemental analyses were carried out with a Heraeus CHN-O-Rapid instrument. IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AMX 400 spectrometer using tetramethylsilane as an internal standard and DMSO-d_6 as solvent. Microwave chemistry was carried out using a CEM Corporation Focused Microwave System, Model Discover.

Preparation of 4a–g; General Procedure

A solution of cyanohydrin **1** (5 mmol) in anhyd CH_2Cl_2 (5 mL) was added dropwise over a period of 10 min to a suspension of 1,1′-carbonyldiimidazole (851 mg, 5.25 mmol) in anhyd CH_2Cl_2 (5 mL) under ice cooling. After stirring at r.t. for 10 min a solution of the appropriate amine (5 mmol) in anhyd CH_2Cl_2 (5 mL) was added and the reaction mixture was stirred at r.t. for 1 h. Et_3N (3 mL) was added and the reaction mixture was stirred for 6–12 h until two sharp bands in the IR spectra appeared at 1760–1791 cm^{-1} and 1670–1685 cm^{-1}. The solvent was removed under reduced pressure and the residue was dissolved in EtOAc (25 mL). The organic layer was washed with H_2O (3 × 10 mL), dried over $MgSO_4$ and evaporated. Removal of the solvent afforded **4a–g** as solid compounds. Analytically pure products were obtained after recrystallisation from EtOAc–hexane (**4b**,**c**,**e–g**) or THF (**4a**,**d**).

3-(3-Fluorophenyl)-4-imino-5-(1-naphthyl)oxazolidin-2-one (4a)

Yield: 1.04 g (65%); colourless solid; mp 125 °C (THF).

IR (KBr): 1789, 1676 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 6.95 (s, 1 H), 7.20 (t, *J* = 7.1 Hz, 1 H), 7.30–7.40 (m, 2 H), 7.45–7.70 (m, 5 H), 7.95 (t, *J* = 8.9 Hz, 2 H), 8.10 (d, *J* = 7.9 Hz, 1 H), 8.72 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 79.9, 113.4, 113.8, 116.5, 116.6, 122.0, 123.2, 124.8, 125.6, 127.4, 128.0, 129.5, 131.0, 131.1, 131.6, 142.4, 150.8, 160.5.

Anal Calcd for $C_{19}H_{13}N_2O_2$: C, 71.24; H, 4.09; N, 8.75. Found: C, 71.10; H, 4.20; N, 8.80.

3-(4-Cyanophenyl)-5-cyclopropyl-4-iminooxazolidin-2-one (4b)

Yield: 0.86 g (72%); colourless solid; mp 118 °C (EtOAc–hexane).

IR (KBr): 1780, 1685 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 0.45–0.82 (m, 4 H), 1.36–1.46 (m, 1 H), 4.64 (d, *J* = 8.4 Hz, 1 H), 7.75 (d, *J* = 8.7 Hz, 2 H), 7.98 (d, *J* = 8.7 Hz, 2 H), 8.72 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 1.6, 11.2, 79.8, 108.3, 116.7, 125.8, 131.1, 135.4, 152.3, 160.4.

Anal. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.55; H, 4.70; N, 17.60.

3-(4-Cyanophenyl)-4-imino-5-(1-naphthyl)oxazolidin-2-one (4c)

Yield: 1.14 g (70%); colourless solid; mp 150 °C (EtOAc–hexane).

IR (KBr): 1790, 1675 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 6.85 (s, 1 H), 7.40 (d, *J* = 8.7 Hz, 1 H), 7.60 (t, *J* = 7.4 Hz, 1 H), 7.65 (t, *J* = 7.1 Hz, 1 H), 7.71 (t, *J* = 7.4 Hz, 1 H), 7.90 (d, *J* = 8.7 Hz, 2 H), 8.00 (d, *J* = 8.4 Hz, 2 H), 8.10 (t, *J* = 8.7 Hz, 2 H), 8.24 (d, *J* = 8.4 Hz, 1 H), 8.70 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 79.3, 113.8, 115.1, 119.8, 123.5, 125.8, 127.3, 128.6, 128.8, 129.2, 129.8, 130.5, 131.2, 133.5, 152.8, 161.7.

Anal. Calcd for $C_{20}H_{13}N_3O_2$: C, 73.39; H, 4.00; N, 12.84. Found: C, 73.20; H, 4.15; N, 12.70.

3-(4-Fluorophenyl)-4-imino-5-(2-naphthyl)oxazolidin-2-one (4d)
Yield: 1.09 g (68%); colourless solid; mp 169 °C (THF).

IR (KBr): 1773, 1670 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 6.85 (s, 1 H), 7.01 (d, *J* = 7.4 Hz, 2 H), 7.42 (d, *J* = 7.1 Hz, 1 H), 7.60–7.72 (m, 5 H), 8.10 (t, *J* = 7.4 Hz, 2 H), 8.25 (d, *J* = 8.4 Hz, 1 H), 8.70 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 79.2, 113.9, 122.0, 123.3, 125.8, 126.2, 128.0, 128.9, 130.3, 131.6, 133.5, 155.6, 162.8.

Anal. Calcd for $C_{19}H_{13}FN_2O_2$: C, 71.24; H, 4.09; N, 8.75. Found: C, 71.07; H, 4.20; N, 8.60.

4-Imino-5-methyl-3-(4-methylbenzyl)oxazolidin-2-one (4e)
Yield: 0.82 g (75%); colourless solid; mp 75 °C (EtOAc–hexane).

IR (KBr): 1760, 1672 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 1.40 (d, *J* = 7.1 Hz, 3 H), 2.30 (s, 3 H), 4.50 (s, 2 H), 5.05 (q, *J* = 7.1 Hz, 1 H), 7.20 (d, *J* = 7.6 Hz, 2 H), 7.24 (d, *J* = 7.6 Hz, 2 H), 8.70 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 18.2, 20.5, 46.0, 75.9, 127.4, 128.9, 134.3, 136.5, 153.6, 163.0.

Anal. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.04; H, 6.47; N, 12.84. Found: C, 65.85; H, 6.60; N, 12.62.

3-(4-Fluorobenzyl)-4-imino-5-methyloxazolidin-2-one (4f)
Yield: 0.81 g (73%); colourless solid; mp 104 °C (EtOAc–hexane).

IR (KBr): 1761, 1670 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 1.35 (d, *J* = 7.1 Hz, 3 H), 4.55 (s, 2 H), 5.10 (q, *J* = 7.1 Hz, 1 H), 7.20 (d, *J* = 8.9 Hz, 2 H), 7.35 (d, *J* = 8.9 Hz, 2 H), 8.60 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 18.4, 41.9, 75.3, 115.2, 129.3, 129.7, 132.5, 155.7, 163.5.

Anal. Calcd for $C_{11}H_{11}FN_2O_2$: C, 59.46; H, 4.99; N, 12.61. Found: C, 59.30; H, 5.20; N, 12.55.

3-(2-Chlorobenzyl)-4-imino-5-phenyloxazolidin-2-one (4g)
Yield: 0.75 g (50%); colourless solid; mp 85 °C (EtOAc–hexane).

IR (KBr): 1791, 1674 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 4.51 (s, 2 H), 5.60 (s, 1 H), 6.90–7.30 (m, 5 H), 7.51–7.70 (m, 4 H), 9.05 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 41.3, 75.2, 125.5, 127.7, 128.5, 128.9, 129.3, 129.6, 131.8, 133.1, 139.2, 155.5, 162.9.

Anal. Calcd for $C_{16}H_{13}ClN_2O_2$: C, 63.90; H, 4.36; N, 9.31. Found: C, 63.75; H, 4.60; N, 9.21.

Microwave-Assisted Synthesis of 5a–g; General Procedure
Compound **4a**–**g** (0.5 mmol) and an equimolar amount of NaOMe were weighed in a 10 mL glass pressure microwave tube equipped with a magnetic stirrer bar. MeOH (5 mL) was added, the tube was closed with a silicon septum and the reaction mixture was subjected to microwave irradiation for the indicated time using parameters a or b (Table 2). The reaction mixture was allowed to cool to r.t. and transferred to a round-bottomed flask. The solvent was evaporated, H_2O (0.5 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were dried over $MgSO_4$ and the solution was concentrated. Addition of MeOH (0.5 mL) and Et_2O (3–5 mL) provided **5a**–**g** as solid compounds.

Parameters a for compounds **5a**–**e**: Discover mode; power: 200 W; ramp time: 30 s; hold time: as indicated in Table 2; temperature: 100 °C; pressure: 12 bar; PowerMax-cooling.

Parameters b for compound **5f**,**g**: Discover mode, power: 250 W; ramp time: 30 s; hold time: as indicated in Table 2; temperature: 150 °C; pressure: 15 bar, PowerMax-cooling.

4-(3-Fluorophenylimino)-5-(1-naphthyl)oxazolidin-2-one (5a)
Yield: 0.10 g (64%); colourless solid; mp 180 °C (Et_2O–MeOH).

IR (KBr): 1747, 1630 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 7.01 (s, 1 H), 7.16 (t, *J* = 7.1 Hz, 1 H), 7.31–7.38 (m, 2 H), 7.46–7.68 (m, 5 H), 7.96 (t, *J* = 8.9 Hz, 2 H), 8.10 (d, *J* = 7.9 Hz, 1 H), 11.30 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 78.6, 113.4, 113.7, 116.4, 116.6, 121.4, 123.5, 124.7, 125.6, 127.1, 127.9, 129.5, 130.98, 131.1, 131.5, 142.0, 152.0, 164.0.

Anal. Calcd for $C_{19}H_{13}FN_2O_2$: C, 71.24; H, 4.09; N, 8.75. Found: C, 71.06; H, 4.15; N, 8.76.

4-(4-Cyanophenylimino)-5-cyclopropyloxazolidin-2-one (5b)
Yield: 0.07 g (60%); colourless solid; mp 205 °C (Et_2O–MeOH).

IR (KBr): 1750, 1629 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 0.23–0.30 (m, 1 H), 0.45–0.61 (m, 1 H), 0.63 (d, *J* = 5.9 Hz, 2 H), 1.37 (d, *J* = 5.3 Hz, 1 H), 5.04 (d, *J* = 5.3 Hz, 1 H), 7.87 (d, *J* = 8.7 Hz, 2 H), 7.92 (d, *J* = 8.7 Hz, 2 H), 11.18 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 1.9, 12.2, 79.3, 106.0, 118.8, 120.9, 133.3, 135.2, 150.1, 163.1.

Anal. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.60; H, 4.73; N, 17.30.

4-(4-Cyanophenylimino)-5-(1-naphthyl)oxazolidin-2-one (5c)
Yield: 0.10 g (63%); colourless solid; mp 238 °C (Et_2O–MeOH).

IR (KBr): 1750, 1612 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 7.10 (s, 1 H), 7.39 (d, *J* = 8.65 Hz, 1 H), 7.57 (t, *J* = 7.4 Hz, 1 H), 7.65 (t, *J* = 7.1 Hz, 1 H), 7.71 (t, *J* = 7.4 Hz, 1 H), 7.91 (d, *J* = 8.7 Hz, 2 H), 8.02 (d, *J* = 8.4 Hz, 2 H), 8.08 (t, *J* = 8.7 Hz, 2 H), 8.24 (d, *J* = 8.4 Hz, 1 H), 11.34 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 78.1, 106.6, 118.7, 120.6, 122.9, 125.7, 126.4, 126.5, 127.2, 128.8, 130.5, 131.5, 133.4, 133.5, 142.0, 152.1, 168.4.

Anal. Calcd for $C_{20}H_{13}N_3O_2$: C, 73.39; H, 4.00; N, 12.84. Found: C, 73.12; H, 4.21; N, 12.76.

4-(4-Fluorophenylimino)-5-(2-naphthyl)oxazolidin-2-one (5d)
Yield: 0.11 g (69%); colourless solid; mp 193 °C (Et_2O–MeOH).

IR (KBr): 1734, 1633 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 6.92 (s, 1 H), 7.00 (d, *J* = 7.4 Hz, 2 H), 7.38 (d, *J* = 7.1 Hz, 1 H), 7.58–7.70 (m, 5 H), 8.05 (t, *J* = 7.4 Hz, 2 H), 8.23 (d, *J* = 8.4 Hz, 1 H), 10.85 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 77.6, 114.0, 121.9, 123.1, 125.7, 126.3, 127.0, 128.7, 130.1, 131.5, 133.4, 156.2, 168.3.

Anal. Calcd for $C_{19}H_{13}FN_2O_2$: C, 71.24; H, 4.09; N, 8.75. Found: C, 70.99; H, 4.24; N, 8.62.

5-Methyl-4-(4-methylbenzylimino)oxazolidin-2-one (5e)
Yield: 0.08 g (72%); colourless solid; mp 116 °C (Et_2O–MeOH).

IR (KBr): 1740, 1630 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 1.41 (d, *J* = 7.12 Hz, 3 H), 2.29 (s, 3 H), 4.48 (s, 2 H), 5.01 (q, *J* = 7.1 Hz, 1 H), 7.17 (d, *J* = 7.6 Hz, 2 H), 7.21 (d, *J* = 7.6 Hz, 2 H), 9.17 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 18.0, 20.6, 45.7, 73.8, 127.4, 128.9, 134.3, 136.5, 156.1, 166.7.

Anal. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.04; H, 6.47; N, 12.84. Found: C, 65.90; H, 6.63; N, 12.60.

4-(4-Fluorobenzylimino)-5-methyloxazolidin-2-one (5f)
Yield: 0.07 g (61%); colourless solid; mp 149 °C (Et_2O–MeOH).

IR (KBr): 1742, 1633 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 1.41 (d, *J* = 7.1 Hz, 3 H), 4.51 (s, 2 H), 5.04 (q, *J* = 7.1 Hz, 1 H), 7.20 (d, *J* = 8.9 Hz, 2 H), 7.36 (d, *J* = 8.9 Hz, 2 H), 9.26 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 17.9, 45.1, 73.8, 115.1, 129.6, 133.5, 152.4, 160.2, 162.6.

Anal. Calcd for $C_{11}H_{11}FN_2O_2$: C, 59.46; H, 4.99; N, 12.61. Found: C, 59.35; H, 5.20; N, 12.53.

4-(2-Chlorobenzylimino)-5-phenyloxazolidin-2-one (5g)
Yield: 0.08 g (51%); colourless solid; mp 128 °C (Et_2O–MeOH).

IR (KBr): 1757, 1616 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 4.58 (s, 2 H), 6.09 (s, 1 H), 7.25–7.35 (m, 5 H), 7.42–7.49 (m, 4 H), 9.25 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 44.5, 79.6, 127.6, 127.9, 129.3, 129.6, 129.7, 132.7, 134.6, 135.2, 152.1, 161.0.

Anal. Calcd for $C_{16}H_{13}ClN_2O_2$: C, 63.90; H, 4.36; N, 9.31. Found: C, 63.77; H, 4.58; N, 9.19.

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(8) Compounds **5** might also appear in a tautomeric form with endocyclic double bond (Scheme 2).