1-AZADIENES AS A SYNTON FOR HETEROCYCLIC SYNTHESIS

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Abstract — 1-Azabutadienes 1 were found to be a good building block for three- to five-membered heterocycles having a functional group. Oxidation of 1 with mCPBA afforded 3-alkenyloxaziridines 2. Cycloaddition of 1 with ketenes gave the 4-alkenylazetidinones 6. Addition of a nitrile imine occurred across the C=N bond to give the 3-alkenyltriazoline 8, while that of a nitrile ylide occurred on the C=C bond to give the 3-formylpyrrole 14 formed by hydrolysis of the C=N bond.

Much attention has come to be paid to 1-azabutadienes as precursors of some alkaloids,¹ and this class of compounds are also expected to be good synthetic building blocks for functionalized three- to five-membered heterocyclic compounds via cycloaddition reactions. However, such types of cycloadditions have been less studied.²⁻⁵ Here we wish to report several reactions of 1-azabutadienes to clarify the usefulness of the dienes in heterocyclic synthesis.⁶

Selective oxidation of the imino function of the azadienes 1 leading to 3-alkenyloxaziridines 2 was observed upon treatment with m-chloroperbenzoic acid.

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<tr>
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<th>Yield (%)</th>
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<tr>
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<tr>
<td>Ph</td>
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<td>[90 : 10]</td>
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<tr>
<td>Ph</td>
<td>Me</td>
<td>20</td>
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When the N-substituent was isopropyl or methyl group (1c or 1d), the product 2 was a mixture of trans- (major product) and cis-isomers, and exclusive formation of the trans-isomers 2a and 2b was caused by the bulky tert-butyl substituent. Although the oxaziridines 2 were thermally unstable, they could be subjected to further reactions without isolation. After the usual workup, for example, the crude oxaziridine 2a was treated with phenyl isocyanate to give the oxadiazolidin-one 3 in 72% yield. The oxaziridine 2a rearranged into the nitrone 4 quantitatively in refluxing acetonitrile, and 3 was also obtained from 4 and the isocyanate.

\[
\text{PhNCO/\text{Et}_2\text{O}, reflux 0.5 h} \quad \xrightarrow{72\%} \quad 3
\]

\[
\text{MeCN, reflux 2 h} \quad \xrightarrow{\text{quantitatively}} \quad 4
\]

As oxaziridines are known to form various heterocyclic compounds by cycloaddition reactions, this new class of oxaziridines seems to be useful as a building block for heterocycles having an alkenyl group. Oxidation of 1a with hydrogen peroxide in basic media, on the other hand, gave rise to the unstable imidoyloxirane 5, whose formation was only detected by NMR.

\[
\text{1a} \quad \xrightarrow{\text{H}_2\text{O}_2/\text{OH}^-/\text{EtOH}} \quad \text{rt 12 h} \quad 5
\]

While several 1,4-cycloadditions of 1-azabutadienes with ketenes forming 6-lactams (pyridone derivatives) are known, 1,2-cycloadditions leading to 6-lactams are also reported. Here we further exemplified the tendency of alkenyl-6-lactam formation of the azadienes.

When the azadiene 1a was treated with phenylacetyl chloride in the presence of _
triethylamine, the cis-β-lactam 6a was exclusively obtained without any formation of the trans-isomer. In this case, the chloride was added very slowly to a refluxing benzene solution of 1a and the amine. On reverse addition of triethylamine and the chloride, stereoselectivity was reduced and a small amount of the pyridone derivative 7 was isolated. The higher stereoselectivity in the former case might be attributed to concerted cycloaddition of 1a to phenylketene generated in situ. The structures of cis- and trans-isomers were clarified by the coupling constants between the vicinal methine protons. Treatment of the cis-isomer with sodium ethoxide in ethanol caused ready rearrangement into the trans-isomer, which supported the structural assignment.

The formation of β-lactams was also observed for the reactions of the 3-substituted 1-azadienes 1e and 1f and diphenylketene.
With 1,3-dipoles, the azadienes 1 are expected to form functionalized 5-membered heterocycles, one of which is known as formation of 5-styryl-1,2,4-oxadiazoline derivative from cinnamylideneaniline and benzonitrile oxide. In the case with N-phenylbenzonitrile imine, which was generated in situ, cycloaddition across the C=N bond of 1 was observed along with a minor reaction across the C=C bond. The major product was isolated as the triazoline 8a after chromatographic treatment on an Al₂O₃ column, but exclusive aromatization of 8a to the triazole 9a by de-tert-butylation was observed on a SiO₂ column. Oxidative aromatization was also observed for the minor adduct 10a which was isolated as the hydrolyzed product, the 4-formylpyrazole 11a. Acidic hydrolysis of the triazoline 8a gave the triazole 9a along with the hydrolyzed products. Oxidation of 9a with ozone followed by treatment with triphenylphosphine gave the 3-formyltriazole 12. However, the reaction of the azadiene 1b with the nitrile imine afforded only the corresponding triazole 9b in 22% yield.

\[
1a + \text{PhN}=C\text{Ph} \xrightarrow{\text{C=N addition}} \xrightarrow{\text{C=C addition}} 8a + 9a
\]

Separated on

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<td>56%</td>
<td>3%</td>
</tr>
<tr>
<td>SiO₂</td>
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</table>

\[
\text{9a} \xrightarrow{\text{H}^+/\text{H}_2\text{O-EtOH rt 4 h}} \xrightarrow{1) \text{O}_3/\text{CCl}_4 2) \text{PPh}_3} \text{OHC} \xrightarrow{\text{on Al}_2\text{O}_3} \text{11a} \xrightarrow{\text{on SiO}_2} \text{12}
\]

*{the other products: PhCH=CHCHO (37%), PhCONHBut (38%), and PhNHNNH₂ (42%)}
Benzonitrile p-nitrobenzylide was allowed to react with the azadiene 1\text{a} to give the formylpyrrole 1\text{4}, which was formed by oxidative aromatization and hydrolysis of the C=C addition product 1\text{3}, in 25% yield. No C=N addition (formation of styrylimidazole or styrylimidazoline) was detected and 40% of 1\text{a} was recovered.

\[
\begin{align*}
1\text{a} + \text{PhC} &= \text{N} - \text{CHAr} & \text{PhH} \text{ reflux 5 h} \\
&\rightarrow \begin{array}{c}
\text{Ph} \\
\text{N-Bu}^\text{t} \\
\text{Ar} \\
\text{Ph}
\end{array} \\
&\rightarrow \begin{array}{c}
\text{Ph} \\
\text{CHO} \\
\text{Ar} \\
\text{Ph}
\end{array}
\end{align*}
\]

Thus 1-azabutadienes are shown to be a good building block for the three- to five-membered heterocycles having an alkenyl or a formyl substituent, which would provide them with possibility of a variety of further transformations.

**EXPERIMENTAL**

Melting points were determined on a Yanagimoto micro melting point apparatus and were uncorrected. $^1$H and $^{13}$C NMR spectra were obtained with JEOL JNM PMX-60 and JNM FX-90Q spectrometers in CDCl$_3$, unless otherwise noted, using TMS as an internal standard. IR spectra were taken on a JASCO IRA-1 spectrophotometer in Nujol mull. Mass spectrometry was performed on a Hitachi RMU-6E spectrometer at an ionizing voltage of 70 eV.

**Materials.** The azadienes 1\text{a}-d,f were prepared by condensation of the corresponding $\alpha,\beta$-unsaturated aldehydes and primary amines, and 1\text{e} was prepared according to our method.\textsuperscript{15} Diphenylketene,\textsuperscript{16} N-phenylbenzhydrazidoyl chloride,\textsuperscript{17} and N-p-nitrobenzylbenzimidoyl chloride\textsuperscript{18} were prepared by the known methods. Phenyl isocyanate was obtained from a commercial source and distilled prior to use. Commercially available m-chloroperbenzoic acid (mCPBA) was used without purification.

**Oxidation of the Azadienes 1.** To an ethereal solution (10 ml) of 1 (5-20 mmol) was added dropwise 1.3 equiv of mCPBA in ether (10-30 ml) under cooling with an ice
bath. The solution was gradually warmed to room temperature and was stirred for 1 h. The reaction mixture was then washed with sodium carbonate solution containing crushed ice and extracted (Et₂O). The extract was dried (Na₂SO₄), and concentrated in vacuo to give an oily residue which was subjected to spectral analysis or to further reactions.

trans-2-tert-Butyl-3-(E)-styryloxaziridine (2a); NMR δ 1.13 (s, 9H, tBu), 4.23 (d, J = 7.6 Hz, 1H, CH), 5.83 (dd, J = 7.6 and 16.0 Hz, 1H, =CH), 6.83 (d, J = 16.0 Hz, 1H, PhCH=), 7.0-7.5 (m, 5H, Ph); MS m/z 203 (M⁺).

trans-2-tert-Butyl-3-(1-propenyl)oxaziridine (2b); NMR δ 1.13 (s, 9H, tBu), 1.77 (dd, J = 6.0 and 1.2 Hz, 3H, Me), 4.13 (d, J = 7.0 Hz, 1H, CH), 5.27 (ddq, J = 7.0, 15.6 and 1.2 Hz, 1H, =CH), 6.97 (d, J = 16.2 Hz, 1H, PhCH=), 7.2-7.5 (m, 5H, Ph); the cis-isomer of 2b was characterized by a doublet at δ 4.65 (J = 7.2 Hz) and the ratio of trans : cis = 9.2 : 1.

trans-2-Methyl-3-(E)-styryloxaziridine (2d); NMR δ 2.80 (s, 3H, Me), 4.10 (d, J = 7.2 Hz, 1H, CH), 5.87 (dd, J = 7.2 and 16.0 Hz, 1H, =CH), 6.97 (d, J = 16.0 Hz, 1H, PhCH=), 7.1-7.5 (m, 5H, Ph); the cis-isomer was characterized by a doublet at δ 4.62 (J = 7.2 Hz) and a doublet of doublets at δ 6.17 (J = 7.2 and 16.0 Hz) and the ratio of trans : cis = 4.4 : 1.

Oxidation of 1a under basic conditions was performed as follows: to a solution of potassium hydroxide (400 mg) and hydrogen peroxide (30% solution, 2 ml) in EtOH (10 ml) was added 1a (1.87 g, 10 mmol) and the mixture was allowed to stand for 12 h at room temperature. The reaction mixture was extracted (Et₂O-saturated NaCl solution) and an oily material, obtained by concentration of the ethereal layer, was proved to contain 1-N-tert-butylimidoyl-2-phenyloxirane (5) by NMR (yield 15%): NMR δ 1.30 (s, 9H, tBu), 3.55 (dd, J = 2.0 and 7.0 Hz, 1H, CH), 3.93 (d, J = 2.0 Hz, 1H, CH), 7.0-7.6 (m, 6H, Ph and =CH).

The Reaction of the Oxaziridine 2a with Phenyl Isocyanate. To an ethereal solution (10 ml) containing 2a (2.64 g, 13 mmol determined by NMR) was added dropwise the isocyanate (3.7 g, 31 mmol) in ether (10 ml) at room temperature and the mixture was refluxed for 0.5 h. Concentration of the reaction mixture gave a crystalline solid, whose CH₂Cl₂-soluble part gave 3.0 g (72%) of 2-tert-butyl-4-phenyl-3-(E)-styryl-1,2,4-oxadiazolidin-5-one (3) as colorless columns: mp 164-165
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°C, IR 1720 cm⁻¹ (C=O); NMR δ 1.27 (s, 9H, tBu), 5.53 (d, J = 6.0 Hz, 1H, CH), 6.18 (dd, J = 6.0 and 16.0 Hz, 1H, =CH), 6.70 (d, J = 16.0 Hz, 1H, PhCH=), 6.9-7.9 (m, 10H, 2Ph); MS m/e 322 (M⁺).

Anal. Calcd for C₂₀H₂₂N₂O₂: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.26; H, 6.88; N, 8.73.

Thermal Rearrangement of 2a. The crude oxaziridine 2a (8 mol by NMR) in acetonitrile (20 ml) was heated at reflux for 2 h. Concentration of the reaction mixture gave cinnamylidene-N-tert-butylamine N-oxide (4) quantitatively: mp 84.5-85 °C (colorless needles from ether-hexane); ¹H NMR δ 1.30 (s, 9H, tBu), 6.80 (d, J = 16.2 Hz, 1H, PhCl=), 7.0-7.5 (m, 6H, Ph and CH=N), 7.83 (dd, J = 16.2 and 9.0 Hz, 1H, =CH); ¹³C NMR (CDCl₃) ppm: 28.0 (q), 68.8 (s), 119.6 (d), 126.8 (d), 128.5 (d), 131.0 (d), 136.4 (s), 136.9 (d), 151.7 (d); MS m/e 203 (M⁺).

Reaction of the Nitrone 4 and Phenyl Isocyanate. To a solution of 4 (1.0 g, 5 mmol) in benzene (10 ml) was added the isocyanate (0.6 g, 5 mmol) in benzene (10 ml) and the solution was heated at reflux for 5 h to give the oxadiazolidinone 7 in 77% yield.

Reaction of the Azadiene 1a with Phenylketene. To a solution of 1a (950 mg, 5.1 mmol) and triethylamine (1.11 g, 11.0 mol) in benzene (15 ml) was added dropwise phenylacetyl chloride (1.55 g, 10.0 mmol) in benzene (10 ml) under reflux and was heated for 5 h. The reaction mixture was washed (H₂O) and extracted (benzene). The extract was dried (Na₂SO₄) and chromatographed (SiO₂ /a 1:1 mixture of benzene-CHCl₃) to give 680 mg (45%) of cis-1-tert-butyl-3-phenyl-4-(E)-styrylazetidin-2-one (6a). When the amine (1.0 g, 9.9 mmol) in benzene (10 ml) was added to a refluxing solution (15 ml) of 1a (940 mg, 5.0 mmol) and the acetyl chloride (1.55 g, 10.0 mmol), 500 mg (33%) of cis-6a (eluted with benzene) and 440 mg (29%) of trans-6a (eluted with CHCl₃) were obtained after the same workup as above. The fraction eluted with a 1:1 mixture of benzene-hexane was subjected to preparative TLC to afford 61 mg (4%) of 1-tert-butyl-3,4-diphenyl-2-pyridone (7), which was identified with an authentic sample.

The cis-6-lactam 6a: mp 108-109 °C (colorless needles from benzene-hexane); IR 1720 (C=O) and 1640 cm⁻¹ (C=C); NMR (C₆D₆) δ 1.30 (s, 9H, tBu), 4.20 (dd, J = 8.4 and 4.6 Hz, 1H, α-CH), 4.38 (d, J = 4.6 Hz, 1H, β-CH), 5.73 (dd, J = 8.4 and 15.8 Hz, 1H, =CH), 6.42 (d, J = 15.8 Hz, 1H, =CH(Ph)), 6.9-7.5 (m, 10H, 2 Ph); MS m/e 305 (M⁺).

Anal. Calcd for C₂₁H₂₃NO: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.29; H, 7.56; N, 4.58.
The trans-6-lactam 6a: mp 165-168°C (colorless needles from EtOH); IR 1720 (C=O) and 1640 cm⁻¹ (C=C); NMR δ 1.37 (s, 9H, tBu), 3.87 (d, J = 2.0 Hz, 1H, α-CH), 4.10 (dd, J = 2.0 and 8.0 Hz, 1H, β-CH), 6.23 (dd, J = 8.0 and 16.0 Hz, 1H, =CH), 6.60 (d, J = 16.0 Hz, 1H, PhCH=); MS m/e 305 (M⁺).

Anal. Calcd for C₂₁H₂₃NO: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.29; H, 7.64; N, 4.56.

Treatment of the cis-6-lactam 6a with Sodium Ethoxide. The cis-isomer 6a (254 mg, 0.83 mmol), was added to a solution of sodium ethoxide (0.92 g) in EtOH (10 ml) and the mixture was stirred for 3 h at room temperature. Then the mixture was poured onto ice-water to afford the crystalline material (260 mg), which was proved to be a mixture of the cis- and trans-6-lactams 6a (1:9 by NMR).

Reactions of 1-Azadienes 1e and 1f with Diphenylketene. To a solution of 1-tert-butyl-3-ethyl-1-aza-1,3-butadiene (1e, 1.04 g, 7.5 mmol) in benzene (10 ml) was added dropwise diphenylketene (3.03 g, 15.6 mmol) in benzene (10 ml) and the mixture was refluxed for 9 h. After removal of the solvent, the residue was chromatographed (SiO₂-a 1:1 mixture of benzene and hexane) to give 1.12 g (45%) of 4-(but-1-en-2-yl)-1-tert-butyl-3,3-diphenylazetidin-2-one (6e): mp 119-120°C (colorless plates from hexane); IR 1720 (C=O) and 1600 cm⁻¹ (C=C); NMR δ 0.77 (t, 3H, Me), 1.33 (s, 9H, tBu), 1.76 (q, 2H, CH₂), 4.85 (s, 1H, CH), 4.92 (br s, 1H, =CHH), 5.20 (br s, 1H, =CHH), 7.0-7.7 (m, 10H, Ph); MS m/e 333 (M⁺).

Anal. Calcd for C₂₃H₂₇NO: C, 82.84; H, 8.16; N, 4.20. Found: C, 82.67; H, 8.19; N, 4.11.

Similarly, fractional recrystallization of the reaction mixture of 1-tert-butyl-3-ethyl-4-phenyl-1-aza-1,3-diene (1f, 2.33 g, 10.8 mmol) and the ketene (2.19 g, 10.8 mmol) gave 795 mg (18%) of 1-tert-butyl-3,3-diphenyl-4-(1-phenyl-but-1-en-2-yl)azetidin-2-one (6f): mp 135-136°C (colorless plates from hexane); IR 1720 (C=O) and 1600 cm⁻¹ (C=C); NMR δ 1.07 (t, 3H, Me), 1.43 (s, 9H, tBu), 2.1 (m, 2H, CH₂), 4.97 (s, 1H, CH), 6.43 (s, 1H, =CH), 6.6-7.7 (m, 15H, Ph); MS m/e 409 (M⁺).


The Reaction of the Azadienes 1 and the Nitrile Imine. To a solution of the azadiene (1a, 940 mg, 5.0 mmol) and N-phenylbenzhydrazidoyl chloride (1.16 g, 5.0 mmol) in benzene (15 ml) was added triethylamine (530 mg, 5.2 mmol) in benzene (5 ml) and the mixture was heated at reflux for 7 h. The resulting mixture was extracted (benzene), dried (Na₂SO₄), and chromatographed (Al₂O₃-a 1:1 mixture of
benzene-hexane) to give 1.05 g (56%) of 4-tert-butyl-1,3-diphenyl-5-(E)-styryl-
1,2,4-triazoline (8a), 48 mg (3%) of 1,3-diphenyl-5-(E)-styryl-1,2,4-triazole (9a),
and 76 mg (3%) of 4-formyl-1,3,5-triphenylpyrazole (11a) which was purified as 2,4-
dinitrophenylhydrazone. When the separation was done by chromatography on a silica
gel, 840 mg (52%) of 9a and 75 mg (3%) of 11a were isolated.
Similarly, 1,3-diphenyl-5-(E)-(1-propenyl)-1,2,4-triazole (9b) was obtained from the
azadiene 1b (630 mg, 5.0 mmol), the hydrazidoyl chloride (1.16 g, 5.0 mmol), and
triethylamine (520 mg, 5.1 mmol) after column chromatography (SiO2-benzene).
The triazoline 8a: mp 145 °C (dec) (yellow needles from EtOH); IR 1600 cm⁻¹; ¹H NMR
δ 1.17 (s, 9H, tBu), 5.93 (d, J = 5.6 Hz, 1H, CH), 6.17 (dd, J = 5.6 and 16.0 Hz,
1H, =CH), 6.77 (d, J = 16.0 Hz, 1H, PhCH=), 7.1-7.8 (m, 15H, 3 Ph); ¹³C NMR (CDCl₃)
ppm: 153.0 (s, N=C-N), 118.6 (s, PhCH=), 112.8 (s, CH=), 78.4 (d, N-C-N); MS m/e 381 (M⁺).
N, 11.00.
The triazoline 9a: mp 145-147 °C (colorless needles from benzene); IR 1635 cm⁻¹; ¹H
NMR δ 6.83 (d, J = 16.0 Hz, 1H, =CH), 7.03 (d, J = 16.0 Hz, 1H, PhCH=), 7.2-7.4 and
8.2-8.4 (m, 15H, 3 Ph); ¹³C NMR (CDCl₃) ppm: 161.9 (s, N=C-N), 153.3 (s, N=C-N),
111.9 (d, =CH); MS m/e 323 (M⁺).
Anal. Calcd for C₂₂H₁₇N₃: C, 81.71; H, 5.30; N, 13.00. Found: C, 81.72; H, 5.18;
N, 12.90.
The characteristic absorption of the pyrrole 11a is 1675 cm⁻¹ (C=O) in the IR
spectrum and a singlet at δ 9.75 (in CDCl₃) in the NMR spectrum; the 2,4-dinitro-
phenylhydrazone of 11a: mp 293-293.5 °C (reddish orange granules from DMF-
acetonitrile); MS m/e 504 (M⁺).
The triazoline 9b: mp 128-131 °C (colorless needles from benzene); IR 1650 cm⁻¹
(C=C); NMR δ 1.87 (dd, J = 8.0 and 1.4 Hz, 3H, Me), 6.20 (dq, J = 16.0 and 1.4 Hz,
1H, =CH), 6.7-8.3 (m, 11H, 2 Ph and MeC=); MS m/e 261 (M⁺).
Acidic Hydrolysis of the Triazoline 8a. To a solution of 8a (140 mg, 0.38 mmol)
in EtOH (10 ml) was added 5 ml of 1N hydrochloric acid and the mixture was stirred
for 4 h at room temperature. After concentration, the residue was extracted (Et₂O)
to give cinnamaldehyde (37%) and the triazole 9a (37%). The aqueous layer was then
made alkaline with sodium carbonate to afford N-tert-butylbenzamide (34%) and
phenylhydrazine (42%). All the products were identified with authentic samples by GLC and spectral analysis.

**Oxidation of 9a with Ozone.** Into a solution of 9a (160 mg, 0.5 mmol) in CCl₄ (20 ml) was bubbled ozone at 0 °C until 9a disappeared in the NMR spectrum.

Triphenylphosphine (260 mg, 1.0 mmol) was added to the reaction mixture and was concentrated to give 3-formyl-2,5-diphenyl-1,2,4-triazole (12), whose yield was 50% by NMR. An analytical sample was obtained by column chromatography (SiO₂-CHCl₃) to give 45 mg (36%) of the triazole: mp 150-153 °C; IR 1695 cm⁻¹ (C=O); NMR δ 7.0-7.8 (m, 10H, 2 Ph), 9.97 (s, 1H, CHO); MS m/e 249 (M⁺).

**Reaction of the Azadiene 1a with the Nitrile Ylide.** To a solution of 1a (940 mg, 5.0 mmol) and N-p-nitrobenzylbenzimidoyl chloride (1.38 g, 5.0 mmol) in benzene (20 ml) was added dropwise triethylamine (520 mg, 5.1 mmol) in benzene (10 ml) at room temperature and the mixture was stirred at reflux for 5 h. The resulting mixture was washed (H₂O), dried (Na₂SO₄), and chromatographed (Al₂O₃-benzene) to give 280 mg (25% based on the reacted 1a) of 3-formyl-5-p-nitrophenyl-2,3-diphenyl-pyrrole (14): mp 275-276 °C (2,4-dinitrophenylhydrazone: reddish orange granules from DMF-MeCN); IR 1650 cm⁻¹ (C=O); NMR (DMSO-d₆) δ 7.1-8.1 (m, 14H, aromatic H), 9.57 (s, 1H, CHO), 12.1-12.5 (br, 1H, NH); MS m/e 369 (M⁺).

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**REFERENCES**


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