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Oxime-catalyzed formation of functionalized 1,3-oxathiolanes from aryl isothiocyanates and oxiranes

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Oxime-catalyzed formation of functionalized 1,3-oxathiolanes from aryl isothiocyanates and oxiranes

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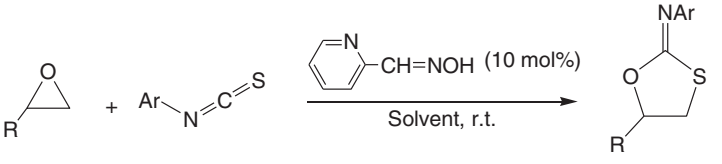
An efficient synthesis of *N*-(5-alkyl-1,3-oxathiolan-2-ylidene)arylamines *via* a one-pot reaction between arylisothiocyanates and substituted oxiranes in the presence of catalytic amount of pyridine-2-carbaldehyde oxime is described.



Keywords: 1,3-oxathiolane; oxirane; oxime; one-pot reaction; aryl isothiocyanate

1. Introduction

Because of the strain induced by the presence of a three-membered ring,[1] epoxides are significantly more reactive than other cyclic ethers. Synthetic procedures for opening epoxide ring can be based on nucleophilic or protic/Lewis acid-mediated ring opening.[2] A number of procedures, which feature the oxyphilic Lewis character of metal ions and non-metallic Lewis acids, have been developed.[2–7] Suitable epoxide opening catalysts include Lewis acids, Lewis bases, Bronsted acids and porphyrin complexes.

Compounds containing an imine group are important in organic synthesis.[8–11] The 1,3-oxathiolane-2-imine structure includes an exocyclic imine group and can be used in the preparation of biologically active compounds.

As part of our current studies on the development of new routes in heterocyclic synthesis, [12–14] we report on the formation of *N*-(5-alkyl-1,3-oxathiolan-2-ylidene)arylamines *via* a one-pot reaction between arylisothiocyanates and substituted oxiranes.

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2. Results and discussion

The reaction of epoxides **1** and aryl isothiocyanates **2** in the presence of catalytic amounts of pyridine-2-carbaldehyde oxime at room temperature proceeds smoothly and affords 1,3-oxathiolanes **3** in good yields (Table 1).

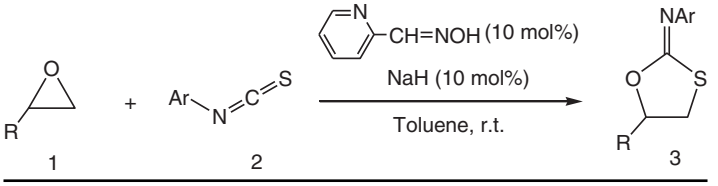
In a preliminary study, hydroxide and methoxide ions were employed as a catalyst in this reaction, but the yields and regioselectivity were poor. Then, we turned to oximes as a catalyst and found that the carbaldehyde oxime anions are better catalysts for cyclocondensation of epoxides and arylisothiocyanates.

To investigate the effects of media, we carried out the condensation reaction of methyloxirane with phenylisothiocyanate in various organic solvents while using 10 mol% of carbaldehyde oximes as the catalyst (Table 2). The use of solvents such as DMSO, THF, 1,4-dioxane, MeCN, Et_2O, or CH_2Cl_2 decreased the product yields (Table 2, Entries 1–6). In evaluating the effects of the catalyst, we found that pyridine-2-carbaldehyde oxime is much more effective compared with benzaldehyde oxime (Table 2, Entries of 8–10). Acetaldehyde oxime did not catalyze the reaction to an appreciable extent (Table 2, Entries 11 and 12). Increasing the catalyst concentration to 20 mol% did not improve the yield of **3a** to a significant extent.

Structures of compounds **3a–3k** were assigned by IR, ^{1}H NMR, ^{13}C NMR, and mass spectral data. For example, the ^{1}H NMR spectrum of **3a** exhibited characteristic multiplets for the CH_2–CH protons, together with signals for the methyl and phenyl groups. The ^{13}C NMR spectrum of **3a** exhibits 10 signals in agreement with the proposed structure. The mass spectrum of **3a** displayed the molecular ion peak at $m/z = 193$. The ^{1}H- and ^{13}C NMR spectra of compounds **3b-3k** are similar to those of **3a** except for the alkyl and aryl groups, which show, in each case, characteristic peaks in appropriate regions of the spectra.

A plausible rationalization[1] may be advanced to explain the product formation (Scheme 1). Presumably, the reaction involves regiospecific nucleophilic substitution reaction of the nitrogen atom of oxime anion **4** [15–19]) on epoxide **1** to generate alkoxide **5**. Then, alkoxide addition to the isothiocyanate **2** produce intermediate **6**, which undergoes a cyclization reaction to afford product **3**.

Table 1. One-Pot Synthesis of 1,3-Oxathiolanes **3**.

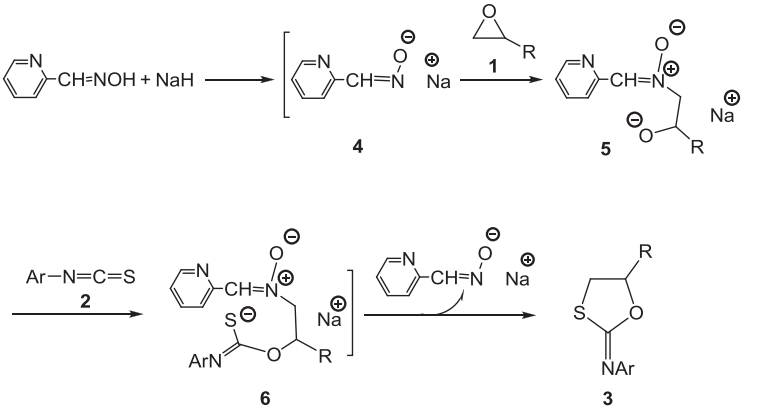


1 2 3

Entry	R	Ar	Product	Yield (%)
1	Me	Ph	**3a**	87
2	Me	*p*-Tol	**3b**	85
3	Me	4-MeO-C_6H_4	**3c**	86
4	*n*-Pr	*p*-Tol	**3d**	86
5	*n*-Pr	4-MeO-C_6H_4	**3e**	87
6	$PhOCH_2$	Ph	**3f**	90
7	$PhOCH_2$	*p*-Tol	**3g**	92
8	$PhOCH_2$	4-MeO-C_6H_4	**3h**	88
9	*i*-Pr-O-CH_2	Ph	**3i**	89
10	*i*-Pr-O-CH_2	*p*-Tol	**3j**	89
11	*i*-Pr-O-CH_2	4-MeO-C_6H_4	**3k**	87

Table 2. Optimization of the oxime-catalized model reaction for the synthesis of *N*-(5-Methyl-1,3-oxathiolan-2-ylidene)benzeneamine (**3a**).

Entry	Catalyst	Solvent	Yield (%)
1	Pyridine-2-carbaldehyde oxime	DMSO	10
2	Pyridine-2-carbaldehyde oxime	THF	47
3	Pyridine-2-carbaldehyde oxime	1,4-Dioxane	27
4	Pyridine-2-carbaldehyde oxime	CH_2Cl_2	42
5	Pyridine-2-carbaldehyde oxime	MeCN	65
6	Pyridine-2-carbaldehyde oxime	Et_2O	25
7	Pyridine-2-carbaldehyde oxime	Toluene	92
8	Benzaldehyde oxime	Toluene	64
9	Benzaldehyde oxime	MeCN	38
10	Benzaldehyde oxime	CH_2Cl_2	23
11	Acetaldehyde oxime	Toluene	trace
12	Acetaldehyde oxime	MeCN	trace



Scheme 1. Proposed mechanism for the formation of products **3**.

3. Conclusions

In conclusion, we have described a convenient route to functionalized *N*-(5-alkyl-1,3-oxathiolan-2-ylidene)arylamines from carbaldehyde oxime-catalyzed ring-opening reaction of epoxides with aryl isothiocyanates. This method offers advantages such as high yields, a simple work-up procedure, and ease of separation.

4. Experimental

4.1. *General*

Epoxides **1**, aryl isothiocyanates **2**, and oximes were obtained from *Merck*and were used without further purification. M.p.: *Electrothermal-9100* apparatus. IR spectra (KBr, cm^{-1}): *Shimadzu IR-460* spectrometer, in cm^{-1}. ^1H and ^{13}C NMR spectra: *Bruker DRX-500 Advance* instrument, in $CDCl_3$ at 500.1 and 125.7 MHz, respectively; δ in ppm and J in Hz. MS: *Finnigan-MAT-8430* mass spectrometer, at 70 eV, in m/z (rel. %). Elemental analyses (C, H, N): *HeraeusCHN-O-Rapid* analyzer.

4.2. *General procedure for the preparation of compounds 3*

A solution of aryl isothiocyanate **2** (2 mmol) in toluene (3 mL) was added to a stirred mixture of sodium hydride (10 mol%) and carbaldehyde oxime (10 mol%) in toluene (5 mL). Then, oxirane **1** (2 mmol) was added. After completion of the reaction (0.5–1 h, monitored by TLC), the solvent was removed under reduced pressure, and the residue was purified by column chromatography (SiO_2; hexane/AcOEt 9:1) to afford product **3**.

4.2.1. *N-(5-methyl-1,3-oxathiolan-2-ylidene)benzenamine (**3a**)*

Pale yellow powder, yield: 0.34 g (87%). IR (KBr) (ν_{max}/cm^{-1}): 1626, 1590, 1341, 1161, 1085 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.52$ (d, 3 H, $^3J = 6.2$, Me), 3.01–3.05 (m, 1 H, CH), 3.33–3.37 (m, 1 H, CH), 4.71–4.75 (m, 1 H, CH), 6.97 (d, 2 H, $^3J = 7.3$, 2 CH), 7.10 (t, 1 H, $^3J = 7.2$, CH), 7.30 (t, 2 H, $^3J = 7.2$, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 19.4$ (Me), 37.1 (CH_2), 78.7 (CH), 119.5 (2 CH), 125.2 (CH), 129.1 (2 CH), 137.1 (C), 149.1 (C), 151.1 (C), 163.6 (C). EI-MS: 371 (M^+, 15), 193 (100), 225 (66), 292 (64), 275 (85), 84 (100), 45 (84). Anal. Calcd (%) for $C_{10}H_{11}NOS$ (193.26): C, 62.15, H, 5.74, N, 7.25. Found: C, 61.98, H, 5.62, N, 7.14.

4.2.2. *4-Methyl-N-(5-methyl-1,3-oxathiolan-2-ylidene)benzenamine (**3b**)*

Pale yellow powder, yield: 0.35 g (85%). IR (KBr) (ν_{max}/cm^{-1}): 1632, 1592, 1367, 1174, 1118 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.52$ (d, 3 H, $^3J = 6.2$, Me), 2.29 (s, 3 H, Me), 3.03–3.08 (m, 1 H, CH), 3.36–3.39 (m, 1 H, CH), 4.73–4.76 (m, 1 H, CH), 7.22 (d, 2 H, $^3J = 8.5$, 2 CH), 7.27 (d, 2 H, $^3J = 8.5$, CH). ^{13}C NMR (125.7M MHz, $CDCl_3$): $\delta = 19.5$ (Me), 20.7 (Me), 37.8 (CH_2), 78.5 (CH), 119.1 (2 CH), 129.6 (2 CH), 134.6 (C), 137.0 (C), 146.5 (C), 163.3 (C). EI-MS: 472 (M^+, 5), 399 (35), 397 (35), 340 (60), 337 (85), 135 (100), 31 (54). Anal. Calcd (%) for $C_{11}H_{13}NOS$ (207.29): C, 63.74, H, 6.32, N, 6.76. Found: C, 63.67, H, 6.26, N, 6.67.

4.2.3. *4-Methoxy-N-(5-methyl-1,3-oxathiolan-2-ylidene)benzenamine (**3c**)*

Pale yellow powder, yield: 0.38 g (86%). IR (KBr) (ν_{max}/cm^{-1}): 1646, 1591, 1362, 1172, 1122 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.54$ (d, 3 H, $^3J = 6.2$, Me), 3.04–3.08 (m, 1 H, CH), 3.36–3.39 (m, 1 H, CH), 3.79 (s, 3 H, MeO), 4.73–4.75 (m, 1 H, CH), 6.86 (d, 2 H, $^3J = 8.5$, 2 CH), 6.92 (d, 2 H, $^3J = 8.5$, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 19.6$ (Me), 37.8 (CH_2), 55.4 (MeO), 78.5 (CH), 114.3 (2 CH), 122.3 (2 CH), 127.7 (C), 142.4 (C), 156.5 (C), 163.3 (C). EI-MS: 500 (M^+, 5), 427 (35), 425 (35), 365 (78), 135 (100), 73 (54), 45 (80). Anal. Calcd (%) for $C_{11}H_{13}NO_2S$ (223.29): C, 59.17, H, 5.87, N, 6.27. Found: C, 59.25, H, 5.92, N, 6.34.

4.2.4. *4-Methyl-N-(5-propyl-1,3-oxathiolan-2-ylidene)benzenamine (**3d**)*

Pale yellow powder, yield: 0.40 g (86%). IR (KBr) (ν_{max}/cm^{-1} 1655, 1359, 1171, 1084 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.10$ (t, 3 H, $^3J = 7.4$, Me), 1.77–1.82 (m, 2 H, CH_2), 1.93–1.99 (m, 2 H, CH_2), 2.32 (s, 3 H, Me), 3.07–3.11 (m, 1 H, CH), 3.33–3.37 (m, 1 H, CH), 4.52–4.56 (m, 1 H, CH), 6.88 (d, 2 H, $^3J = 8.2$, 2 CH), 7.12 (d, 2 H, $^3J = 8.2$, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 10.9$ (Me), 21.6 (CH_2), 21.9 (Me), 27.8 (CH_2), 36.8 (CH_2), 84.5 (CH), 121.7 (2 CH), 129.4 (2 CH), 134.5 (C), 147.4 (C), 164.3 (C). EI-MS: 358 (M^+, 15), 327 (54), 300 (47), 281 (68), 77 (100), 31 (62). Anal. Calcd (%) for $C_{13}H_{17}NOS$ (235.34): C, 66.35, H, 7.28, N, 5.95. Found: C, 66.28, H, 7.19, N, 5.87.

4.2.5. *4-Methoxy-N-(5-propyl-1,3-oxathiolan-2-ylidene)benzenamine (**3e**)*

Pale yellow powder, yield: 0.44 g (87%). IR (KBr) (ν_{max}/cm^{-1}): 1631, 1592, 1367, 1173, 1082 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.11$ (t, 3 H, $^3J = 7.4$, Me), 1.77–1.82 (m, 2 H, CH_2), 1.93–1.99 (m, 2 H, CH_2), 3.08–3.12 (m, 1 H, CH), 3.34–3.37 (m, 1 H, CH), 3.81 (s, 3 H, MeO), 4.52–4.55 (m, 1 H, CH), 6.85 (d, 2 H, $^3J = 8.2$, 2 CH), 6.92 (d, 2 H, $^3J = 8.2$, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 10.8$ (Me), 28.1 (CH_2), 30.4 (CH_2), 36.9 (CH_2), 56.4 (MeO), 84.5 (CH), 115.2 (2 CH), 123.6 (2 CH), 143.3 (C), 157.3 (C), 164.3 (C). EI-MS: 358 (M^+, 15), 327 (54), 300 (47), 281 (68), 77 (100), 31 (62). Anal. Calcd (%) for $C_{13}H_{17}NO_2S$ (251.34): C, 62.12, H, 6.82, N, 5.57. Found: C, 61.97, H, 6.73, N, 5.48.

4.2.6. *N-(5-(Phenoxymethyl)-1,3-oxathiolan-2-ylidene)benzenamine (**3f**)*

Pale yellow powder, yield: 0.51 g (90%). IR (KBr) (ν_{max}/cm^{-1}): 1646, 1591, 1354, 1168, 1098 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.50$–3.59 (m, 2 H, CH_2), 4.24–4.35 (m, 2 H, CH_2), 5.01–5.05 (m, 1 H, CH), 6.96–7.38 (m, 10 H, 10 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 33.5$ (CH_2), 66.9 (CH_2), 78.9 (CH), 114.6 (2 CH), 121.2 (2 CH), 121.7 (CH), 124.4 (CH), 129.1 (2 CH), 129.6 (3 CH), 148.9 (C), 158.0 (C), 162.9 (C). EI-MS: 422 (M^+, 10), 350 (20), 348 (20), 167 (25), 149 (60), 84 (100), 57 (62). Anal. Calcd (%) for $C_{16}H_{15}NO_2S$ (285.36): C, 67.35, H, 5.30, N, 4.91. Found: C, 67.23, H, 5.21, N, 4.85.

4.2.7. *4-Methyl-N-(5-(phenoxymethyl)-1,3-oxathiolan-2-ylidene)benzenamine (**3g**)*

Pale yellow powder, yield: 0.55 g (92%). IR (KBr) (ν_{max}/cm^{-1} 1646, 1591, 1362, 1172, 1122 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.36$ (s, 3 H, Me), 3.49-3.58 (m, 2 H, CH_2), 4.25–4.28 (m, 1 H, CH), 4.32–4.34 (m, 1 H, CH), 4.99–5.04 (m, 1 H, CH), 6.91 (d, 2 H, $^3J = 8.2$ Hz, 2 CH), 6.96 (d, 2 H, $^3J = 8.3$ Hz, 2 CH), 7.02 (t, 1 H, $^3J = 7.3$ Hz, CH), 7.16 (d, 2 H, $^3J = 8.2$, 2 CH), 7.33 (t, 2 H, $^3J = 7.9$ Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 20.9$ (Me), 33.5 (CH_2), 66.9 (CH_2), 78.9 (CH), 114.7 (2 CH), 121.0 (2 CH), 121.7 (CH), 129.6 (2 CH), 129.7 (2 CH), 133.9 (C), 146.4 (C), 158.1 (C), 162.6 (C). EI-MS: 450 (M^+, 5), 377 (24), 375 (24), 370 (68), 231 (45), 229 (45), 84 (100), 73 (60). Anal. Calcd (%) for $C_{17}H_{17}NO_2S$ 299.39): C, 68.20, H, 5.72, N, 4.68. Found: C, 68.25, H, 5.83, N, 4.75.

4.2.8. *4-Methoxy-N-(5-(phenoxymethyl)-1,3-oxathiolan-2-ylidene)benzenamine (**3h**)*

Pale yellow powder, yield: 0.55 g (88%). IR (KBr) (ν_{max}/cm^{-1}): 1643, 1591, 1352, 1170, 1144, 1101 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.47$–3.56 (m, 2 H, CH_2), 3.81 (s, 3 H, MeO), 4.22–4.26 (m, 1 H, CH), 4.29–4.32 (m, 1 H, CH), 4.98–5.01 (m, 1 H, CH), 6.87 (d, 2 H, $^3J = 8.2$ Hz, 2 CH), 6.94 (d, 4 H, $^3J = 8.7$ Hz, 4 CH), 7.02 (t, 1 H, $^3J = 7.2$ Hz, CH), 7.32 (d, 2 H, $^3J = 8.2$, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 33.5$ (CH_2), 55.4 (MeO), 66.9 (CH_2), 78.8 (CH), 114.4 (2 CH), 114.6 (2 CH), 121.6 (CH), 122.2 (2 CH), 129.6 (2 CH), 142.2 (C), 156.6 (C), 158.0 (C), 162.6 (C). EI-MS: 343 (M^+, 10), 270 (85), 306 (66), 292(64), 284 (60), 275 (85), 84 (100), 59 (67). Anal. Calcd (%) for $C_{17}H_{17}NO_3S$ (315.36): C, 64.74, H, 5.43, N, 4.44. Found: C, 64.65, H, 5.38, N, 4.35.

4.2.9. *N-(5-Isopropoxymethyl-1,3-oxathiolan-2-ylidene)benzenamine (**3i**)*

Pale yellow powder, yield: 0.45 g (89%). IR (KBr) (ν_{max}/cm^{-1}): 1649, 1581, 1340, 1155, 1144 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.22$ (d, 6 H, $^3J = 6.2$, 2 Me), 3.34-3.42 (m, 2 H,

CH_2), 3.62–3.70 (m, 3 H, 3 CH), 4.76–4.77 (m, 1 H, CH), 6.98 (d, 2 H, $^3J = 7.6$, 2 CH), 7.12 (t, 1 H, $^3J = 7.4$, CH), 7.33 (t, 2 H, $^3J = 7.4$, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 22.3$ (2 Me), 33.9 (CH_2), 67.3 (CH_2), 73.7 (CH), 80.4 (CH), 121.3 (2 CH), 126.8 (CH), 128.9 (2 CH), 149.0 (C), 163.5 (C). EI-MS: 393 (M^+, 10), 334 (68), 320 (65), 258 (66), 135 (100), 74 (85), 31 (62). Anal. Calcd (%) for $C_{13}H_{17}NO_2S$ (251.34): C, 62.12, H, 6.82, N, 5.57. Found: C, 61.97, H, 6.78, N, 5.48.

4.2.10. *N-(5-Isopropoxymethyl-1,3-oxathiolan-2-ylidene)-4-methylbenzenamine (**3j**)*

Pale yellow powder, yield: 0.47 g (89%). IR (KBr) (ν_{max}/cm^{-1}): 1649, 1571, 1342, 1160, 1144 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.15$ (d, 6 H, $^3J = 6.5$, 2 Me), 2.33 (s, 3 H, Me), 3.31–3.38 (m, 2 H, CH_2), 3.59–3.73 (m, 3 H, 3 CH), 4.71–4.73 (m, 1 H, CH), 7.06 (d, 2 H, $^3J = 7.8$, 2 CH), 7.25 (d, 2 H, $^3J = 7.6$, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 21.9$ (Me), 22.1 (2 Me), 33.4 (CH_2), 67.2 (CH_2), 72.7 (CH), 80.3 (CH), 121.1 (2 CH), 129.7 (2 CH), 133.6 (C), 146.5 (C), 163.3 (C). EI-MS: 421 (M^+, 15), 348 (45), 275 (60), 286 (84), 135 (100), 73 (74), 45 (80). Anal. Calcd (%) for $C_{14}H_{19}NO_2S$ (265.37): C, 63.37, H, 7.22, N, 5.28. Found: C, 63.32, H, 7.18, N, 5.20.

4.2.11. *N-(5-Isopropoxymethyl-1,3-oxathiolan-2-ylidene)-4-methoxybenzenamine (**3k**)*

Pale yellow powder, yield: 0.49 g (87%). IR (KBr) (ν_{max}/cm^{-1}): 1652, 1561, 1332, 1150, 1132 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.17$ (d, 6 H, $^3J = 6.5$, 2 Me), 3.32–3.40 (m, 2 H, CH_2), 3.64–3.71 (m, 2 H, CH_2), 3.72–3.75 (m, 1 H, CH), 3.78 (s, 3 H, MeO), 4.69–4.74 (m, 1 H, CH), 6.84 (d, 2 H, $^3J = 8.8$, 2 CH), 6.91 (d, 2 H, $^3J = 8.8$, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 22.0$ (2 Me), 33.5 (CH_2), 55.4 (MeO), 67.3 (CH_2), 72.7 (CH), 80.2 (CH), 114.3 (2 CH), 122.3 (2 CH), 142.3 (C), 156.5 (C), 163.3 (C). EI-MS: 358 (M^+, 15), 327 (54), 300 (47), 281 (68), 77 (100), 31 (62). Anal. Calcd (%) for $C_{14}H_{19}NO_3S$ (281.37): C, 59.76, H, 6.81, N, 4.98. Found: C, 59.65, H, 6.74, N, 4.87.

Note

1. We thank a reviewer of this manuscript for suggesting this plausible mechanism.

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