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# One-Pot Regioselective Synthesis of Nitrophenyloxazolinyl Styrene Oxides by the Darzens Reaction of Vicarious Nucleophilic Substitution-Formed Carbanions of 2-Dichloromethyl-4,4-dimethyloxazoline

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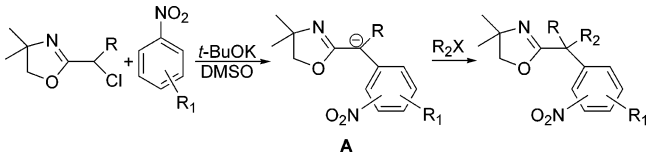
The vicarious nucleophilic substitution reaction of dichloromethyloxazoline **2** with nitrobenzene has been investigated. Treatment of **2** with *t*-BuOK followed by the addition of nitrobenzene leads to benzylic carbanions **4** or **9** depending upon the solvent used (DMSO, DMF, or THF). Subsequent treatment of **4** or **9** with aldehydes, in a Darzens-like reaction, furnishes very good yields of nitrophenyl oxazolinyloxiranes **8** and **11**. 1,2-Dioxazolinyl-1,2-dinitrophenylethene **7** forms quantitatively when carbanion **4** is allowed to warm to room temperature in the absence of external electrophiles.

## Introduction

Direct replacement of hydrogen in electron-deficient aromatic rings by vicarious nucleophilic substitution (VNS) has become a useful methodology for the introduction of functional groups into aromatic and heterocyclic rings.[1] In the classic VNS reaction an auxiliary good α-leaving group on the nucleophilic center that promotes *β*-elimination for the rearomatization of the initially formed $\sigma^H$ adduct is needed. However, examples of direct nucleophilic substitution of hydrogen in aromatic rings by nucleophiles that do not require any α-leaving group have been also reported.[2]

In previous papers, we reported that chloroalkyloxazolines and other chloroalkylheterocycles under basic conditions react with nitroarenes leading to VNS products.[3] The intermediacy of the benzylic VNS carbanion **A** could be proved by its trapping with electrophiles (Scheme 1).

**SCHEME 1**




However, the capture with aldehydes did not take place, so that the aldol-type product did not form, likely due to a retroaldol reaction.[3,4a] With reference to this we envisaged that the presence of a second leaving group on the nucleophilic center might drive the reaction toward the aldol-type product.

In this paper, we report on the regioselective reaction of dichloromethyloxazoline **2** with nitrobenzene under basic conditions for *t*-BuOK followed by trapping with carbonyl compounds.

## Results and Discussion

2-Dichloromethyl-4,4-dimethyl-2-oxazoline **2** was prepared by chlorination (*tert*-butylhypochlorite) of commercially available oxazoline **1**. The addition of a mixture of nitrobenzene (1.1 equiv) and oxazoline **2** (1 equiv) to a suspension of potassium *tert*-butoxide (*t*-BuOK) (3 equiv) in dimethylformamide (DMF) at −50 °C produced a dark red solution, presumably containing the carbanion **4**,

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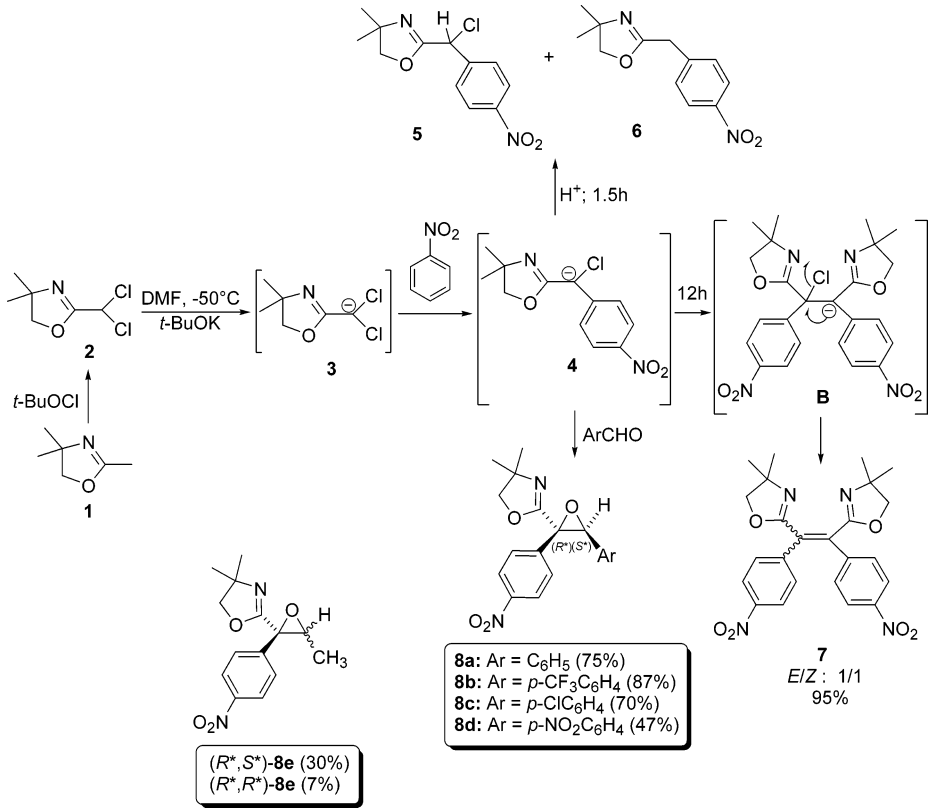
**SCHEME 2**




which results from the regioselective attack of the anion **3** to the para position of nitrobenzene, likely for steric reasons. Acidic quenching (aq satd $NH_4Cl$) after 1.5 h gave the expected VNS product **5** jointly with nitrobenzyloxazoline **6**, which probably originates from **5** by dechlorination (Scheme 2). The dehalogenation is a rather common process in the VNS reaction of halocarbanions.[3,4b] After 24 h, the same reaction mixture, spontaneously, without addition of any electrophile, furnished in high yield (95%) a mixture of *E* and *Z* 1,2-dioxazolinyl-1,2-di-*p*-nitrophenylethene **7** (1:1 ratio).[5] The formation of compound **7** could be tentatively explained with the carbenoidic character of **4**, which undergoes a homocoupling reaction to give **B**. $Cl^-$ elimination would generate **7**. However, at least at present, we cannot rule out a radical pathway of the kind of that suggested in ref 4. To prove the intermediacy of the above chlorobenzylic carbanion **4** benzaldehyde was added to the reaction mixture immediately after mixing the reagents. After 12 h (1 h at −50 °C and warming up to room temperature), usual workup furnished stereoselectively a very good yield of oxazolinyldiaryloxirane (*R**,*S**)-**8a** as a single diastereomer. It is worth noting that, as reported, the VNS benzylic carbanion from chloromethyloxazoline,[3] ethylchloropropionate, chloroethyl sulfones, and chloromethyl phosphinoxides do not react with benzaldehydes probably because of the reversibility of the aldol-type reaction.[6] The reaction of **4** with benzaldehyde carried out at room temperature in DMF or DMSO afforded epoxide **8a** in a much lower yield together with compound **7** in a 4:1 ratio, approximatively. Equally stereoselective and high yielding were the reactions of **4** with other aromatic aldehydes ending up with the formation of epoxides **8b**−**d** (Scheme 1), while the reaction with acetaldehyde proceeded less stereoselectively affording oxazolinyloxiranes (*R**,*S**)-**8e** and (*R**,*R**)-**8e** (*R**,*S**/*R**,*R** = 8:2), together with compound **7** in a 2:1 ratio, approximatively. Attempts to trap carbanion **4** with ketones and imines failed: all these reactions furnished the ethene **7**.

The stereochemistry of all compounds was determined by $^1H$ NMR spectroscopy on the basis of the chemical shifts of the oxazoline methylene and methyl protons. In a trans arrangement with the aryl group, these protons are downfield shifted.[7] The *R**,*S** relative configuration of **8a** was later confirmed by X-ray analysis.[8]

There are precedents of the VNS reaction with dichloro and trichloro carbanions.[9] None of these, however, was subsequently used in a Darzens reaction.

The observed (*R**,*S**) high diastereoselectivity could tentatively be explained in terms of transition-state

(5) Alkene **7** formed as a separable *E*/*Z* mixture (1:1); the configuration was assigned on the basis of the $^1H$ NMR spectra; in the *E*-configurated alkene the oxazoline methylene and methyl protons are more shielded from the phenyl ring with respect to the *Z*-configurated alkene. Also in the UV spectra, where a better conjugation for the *E*-isomer was expected, a red shift was observed for the *E* isomer ($\lambda_{max}$ = 302, $CHCl_3$ $10^{-5}$) with respect to the *Z* isomer ($\lambda_{max}$ = 285, $CHCl_3$ $10^{-5}$).

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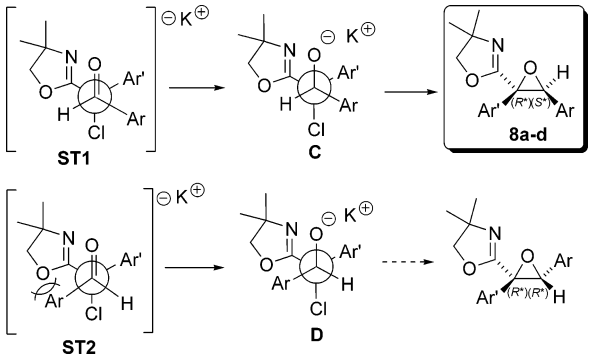
(8) CCDC 234941 and 234942 contains the supplementary crystallographic data for compounds **8a** and **11c**, respectively. These data can be obtained free of charge at www.ccdc.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; Fax: (int) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

**SCHEME 3**




energy. $\mathbf{ST_1}$, resulting from the interaction between carbanion **3** and aldehyde and leading to chloroalkoxide **C** (which, on the basis of PM3 semiempirical calculations, is of lower energy with respect to the diastereomeric chloroalkoxide **D** of about 3 kcal/mol) and then to oxazolinyloxiranes **8a**−**d**, is of lower energy with respect to $\mathbf{ST_2}$, leading to the (*R**,*R**)-configurated oxazolinyloxiranes, for experiencing weaker steric interactions (Scheme 3).

To investigate the solvent effect we decided to study the reaction of carbanion **3** with nitrobenzene in a less polar solvent such as THF at −80 °C. We were happy to find that, in this solvent, the reaction was completely ortho regioselective affording benzylic carbanion **9** (Scheme 4), which gave the VNS product **10** after acidic quenching (aq satd $NH_4Cl$, 1.5 h) while the capture with benzaldehyde led after 2.5 h stereoselectively and in high yield to (*R**,*S**)-*o*-nitrophenylphenyloxazolinyloxirane **11a**. Quite comparable results were obtained when carbanion **9** was reacted with other aromatic aldehydes to give epoxides **11b**−**f**. The configuration to compounds **11** was assigned by $^1$HNMR and by an X-ray analysis in the case of **11c**.[8]

The contrasting regioselectivity of the VNS reaction of carbanion **3** with nitrobenzene from para to ortho on going from a very polar solvent such as DMF (or DMSO) to the much less polar THF is particularly interesting and synthetically useful. Usually, VNS reactions are very sensitive to steric hindrance in polar solvents: bulky tertiary carbanions usually replace exclusively para hydrogen atoms.[10] Accordingly, carbanion **3** in DMF or DMSO attacks exclusively the para position of nitrobenzene giving oxiranes **8**. On the other hand, it is known that the regiochemistry of the VNS reaction can be affected by the aggregation state of the carbanion in the medium.[11a] In THF, the potassium counterion and the carbanions likely exist as tight ion pairs or high molecular weight aggregates, and in their interaction with the nitrobenzene the negatively charged oxygen atoms of the nitro group attract the potassium cation so that the associated carbanion is driven to the close ortho position.[12] In line with this consideration, we assume that carbanion **3**, in THF, forms a preliminary complex in which the potassium cation is coordinated by the negatively charged oxygen of the nitro group so that the associated carbanion is forced to attack the ortho position of nitrobenzene to give the VNS product **10** after acidic quenching and epoxides **11** upon trapping with aldehydes, although **3** is a sterically hindered carbanion and should facilitate the attainment of the least hindered intermediate (Scheme 5).[11a−c]

In conclusion, in the present paper we have demonstrated that the carbanion of dichloromethyloxazoline **2** is a very good VNS reagent and the benzylic carbanions **4** and **9**, easily obtainable by the regioselective reaction with nitrobenzene (in DMF or THF, respectively), can be easily trapped with aldehydes, in a Darzens-like reaction, to give novel and useful nitrophenyl aryl oxazolinyloxiranes **8** and **11**. The interest for this kind of epoxides resides in their availability to be further functionalized to tetrasubstituted oxiranes by using the oxiranyl anion methodology.[13]

## Experimental Section

General procedures are reported in the Supporting Information.

**(*Z*)-1,2-Dioxazolinyl-1,2-di-*p*-nitrophenylethene (7):** $R_f$ 0.3; yield 47%; white solid; mp 227−228 °C; $^1$H NMR (500 MHz) $\delta$ 1.35 (s, 12 H), 4.04 (s, 4 H), 7.25 (d, $J$ = 8.4 Hz, 4 H), 8.03 (d, $J$ = 8.4 Hz, 4 H); $^{13}$C NMR (125 MHz) $\delta$ 27.8, 27.8$_4$, 68.2, 79.4, 109.9, 123.5, 130.8, 134.7, 142.4, 147.4, 161.1; GC MS (70 eV) *m*/*z* 464 (29) [M$^+$], 463 (100), 433 (14), 407 (11), 377 (8); FT-IR (film) cm$^{-1}$ 2960, 1720, 1650, 1600, 1515, 1355, 1300. Anal. Calcd for $C_{24}H_{24}N_4O_6$: C, 62.06; H, 5.21; N, 12.06. Found: C, 62.36; H, 5.54; N, 12.35.

**(*E*)-1,2-Dioxazolinyl-1,2-di-*p*-nitrophenylethene (7):** $R_f$ 0.55; yield 48%; yellow solid; mp 224−225 °C; $^1$H NMR (500 MHz) $\delta$ 1.13 (s, 12 H), 3.76 (s, 4 H), 7.50 (d, $J$ = 8.5 Hz, 4 H), 8.20 (d, $J$ = 8.5 Hz, 4 H); $^{13}$C NMR (125 MHz) $\delta$ 27.4, 68.0, 79.2, 109.9, 123.3, 129.5, 135.2, 143.3, 147.7, 160.6; GC MS (70 eV) *m*/*z* 464 (28) [M$^+$], 463 (100) [M$^+$ − 1], 433 (14), 407 (11), 377 (8); FT-IR (film) cm$^{-1}$ 2974, 1649, 1599, 1517, 1347, 1289, 980, 739. Anal. Calcd for $C_{24}H_{24}N_4O_6$: C, 62.06; H, 5.21; N, 12.06. Found: C, 62.26; H, 5.58; N, 12.27.

**(2*R**,3*S**)-4,4-Dimethyl-2-[2-(4-nitrophenyl)-3-phenyloxiran-2-yl]-4,5-dihydro-1,3-oxazole (8a):** 253 mg; yield 75%; white solid; mp 157−159 °C (petroleum ether); $^1$H NMR (400 MHz) $\delta$ 1.30 (s, 3 H), 1.32 (s, 3 H), 4.05 (s, 2 H), 4.81 (s, 1 H), 7.12−7.13 (m, 5 H), 7.49 (d, $J$ = 8.4 Hz, 2 H), 8.04 (d, $J$ = 8.4 Hz, 2 H); $^{13}$C NMR (100 MHz) $\delta$ 28.0, 61.9, 64.0, 68.0, 79.7, 122.8, 126.4, 127.9, 128.3, 129.3, 132.4, 139.6, 147.5, 161.8; GC MS (70 eV) *m*/*z* 338 (3) [M$^+$], 321 (4), 283 (4), 266 (15), 165 (14), 150 (60), 132 (100); FT-IR (film) cm$^{-1}$ 3060, 2960, 1650 (C=N), 1520, 1350, 995. Anal. Calcd for $C_{19}H_{18}N_2O_4$: C, 67.44; H, 5.36; N, 8.28. Found: C, 67.83; H, 5.48; N, 8.42.

**(2*R**,3*S**)-4,4-Dimethyl-2-[2-(4-nitrophenyl)-3-(4-trifluoromethyl)phenyloxiran-2-yl]-4,5-dihydro-1,3-oxazole (8b):** 353 mg; yield (87%); oil; $^1$H NMR (400 MHz) $\delta$ 1.31 (s, 3 H), 1.33 (s, 3 H), 4.07 (s, 2 H), 4.87 (s, 1 H), 7.24 (d, $J$ = 8.2 Hz, 2 H), 7.42 (d, $J$ = 8.2 Hz, 2 H), 7.51 (d, $J$ = 8.8 Hz, 2 H), 8.07 (d, $J$ = 8.8 Hz, 2 H); $^{13}$C NMR (100 MHz) $\delta$ 27.9, 62.2, 63.3, 68.1, 79.9, 123.0, 125.0, 126.8, 129.2, 136.5, 138.9, 147.7,

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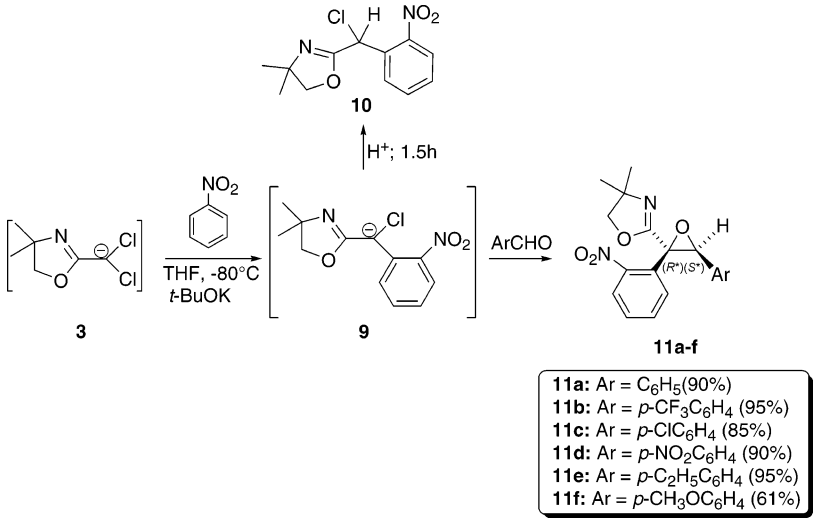
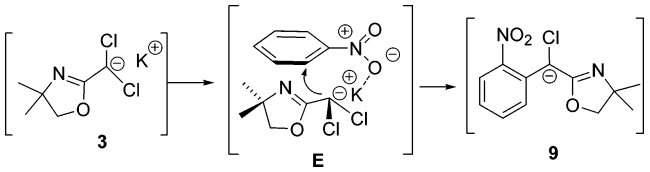
**SCHEME 4**




**SCHEME 5**




161.5; GC MS (70 eV) *m*/*z* 406 (4) [$M^+$], 389 (8), 351 (6), 334 (8), 200 (17), 173 (17), 150 (100); FT-IR (film) $cm^{-1}$ 3060, 2950, 1650 (C═N), 1520, 1350, 1320, 1025. Anal. Calcd for $C_{20}H_{17}F_3N_2O_4$: C, 59.11; H, 4.22; N, 6.89. Found: C, 59.23; H, 4.52; N, 6.69.

**(2*R**,3*S**)-2-[3-(4-Chlorophenyl)-2-(4-nitrophenyl)oxiran-2-yl]-4,4-dimethyl-4,5-dihydro-1,3-oxazole (8c):** 260 mg; yield 70%; oil; $^1$H NMR (400 MHz) $\delta$ 1.30 (s, 3 H), 1.32 (s, 3 H), 4.05 (s, 2 H), 4.78 (s, 1 H), 7.02 (d, $J$ = 8.4 Hz, 2 H), 7.12 (d, $J$ = 8.4 Hz, 2 H), 7.49 (d, $J$ = 8.8 Hz, 2 H), 8.08 (d, $J$ = 8.8 Hz, 2 H); $^{13}$C NMR (100 MHz) $\delta$ 28.0, 62.0, 63.4, 68.1, 79.8, 123.0, 127.8, 128.3, 129.3, 131.0, 134.3, 139.2, 147.6, 161.7; GC MS (70 eV) *m*/*z* 372 (1) [$M^+$], 302 (68), 300 (100), 199 (56), 164 (61), 163 (78); FT-IR (film) $cm^{-1}$ 3060, 2950, 1650 (C═N), 1600, 1520, 1350, 1080. Anal. Calcd for $C_{19}H_{17}ClN_2O_4$: C, 61.21; H, 4.60; N, 7.51. Found: C, 61.33; H, 4.58; N, 7.70.

**(2*R**,3*S**)-2-[2,3-Bis(4-nitrophenyl)oxiran-2-yl]-4,4-dimethyl-4,5-dihydro-1,3-oxazole (8d):** 180 mg; yield 47%; yellow solid; mp 159−161 °C (petroleum ether); $^1$H NMR (400 MHz) $\delta$ 1.31 (s, 3 H), 1.33 (s, 3 H), 4.08 (s, 2 H), 4.92 (s, 1 H), 7.31 (d, $J$ = 8.6 Hz, 2 H), 7.50 (d, $J$ = 8.7 Hz, 2 H), 8.02 (d, $J$ = 8.6 Hz, 2 H), 8.08 (d, $J$ = 8.7 Hz, 2 H); $^{13}$C NMR (100 MHz) $\delta$ 28.0, 62.0, 62.9, 68.2, 79.9, 123.2, 123.3, 123.7, 127.4, 129.1, 129.7, 139.7, 147.8, 161.2; GC MS (70 eV) *m*/*z* 311 (100) [$M^+ - 72$], 281 (20), 163 (40); FT−IR (film) $cm^{-1}$ 3040, 2960, 1650 (C═N), 1600, 1505, 1340, 995. Anal. Calcd for $C_{19}H_{17}N_3O_6$: C, 59.53; H, 4.47; N, 10.96. Found: C, 59.62; H, 4.48; N, 10.80.

**4,4-Dimethyl-2-[3-methyl-2-(4-nitrophenyl)oxiran-2-yl]-4,5-dihydro-1,3-oxazole (8e).** Inseparable diastereomeric mixture of two trans- and cis-configurated oxiranes (dr = 8:2 from $^1$H NMR of the crude reaction mixture): overall yield 97 mg (35%); oil. **Major diastereomer (2*R**,3*S**):** $^1$H NMR (400 MHz) $\delta$ 1.04 (d, $J$ = 5.3 Hz, 3 H), 1.28 (s, 3H), 1.31 (s, 3 H), 3.83 (q, $J$ = 5.3 Hz, 1 H), 4.01 (s, 2 H), 7.67 (d, $J$ = 8.5 Hz, 2 H), 8.24 (d, $J$ = 8.5 Hz, 2 H); GC MS (70 eV) *m*/*z* 276 (3) [$M^+$], 260 (4), 193 (8), 150 (100), 104 (16), 56 (48). **Minor diastereomer (2*R**,3*R**):** $^1$H NMR (400 MHz) $\delta$ 1.36 (s, 3 H), 1.37 (s, 3 H), 1.53 (d, $J$ = 5.2 Hz, 3 H), 3.20 (q, $J$ = 5.2 Hz, 1 H), 4.07 (s, 2 H), 7.76 (d, $J$ = 8.6 Hz, 2 H), 8.20 (d, $J$ = 8.6 Hz, 2 H); GC MS (70 eV) *m*/*z* 276 (2) [$M^+$], 260 (5), 193 (10), 150 (100), 104 (22), 56 (55); $^{13}$C NMR on the inseparable mixture, selected data; $^{13}$C NMR (100 MHz) $\delta$ 13.5, 14.8, 27.9, 59.5, 60.1, 63.1, 67.7, 79.5, 123.1, 123.4, 126.9, 128.7, 140.8 147.7, 162.2; FT-IR (film) $cm^{-1}$ 3040, 2960, 1655, 1600, 1520, 1350.

**4,4-Dimethyl-2-[(2-nitrophenyl)chloromethyl]-4,5-dihydro-1,3-oxazole (10):** 169 mg; yield 63%; white solid; mp 124−126 °C; $^1$H NMR (400 MHz) $\delta$ 1.16 (s, 3 H), 1.18 (s, 3 H), 3.94−3.99 (m, 2 H), 6.23 (s, 1 H), 7.44 (t, $J$ = 8.1 Hz, 1 H), 7.63 (t, $J$ = 8.1 Hz, 1 H), 7.95−7.97 (m, 2 H); $^{13}$C NMR (100 MHz) $\delta$ 27.5, 27.6, 50.5, 67.7, 80.0, 124.8, 129.6, 130.5, 131.0, 133.6, 147.6, 162.0; GC MS (70 eV) *m*/*z* 268 (5) [$M^+$], 253 (15), 233 (90), 222 (69), 136 (82), 84 (100), 77 (60), 55 (73); FT-IR (film) $cm^{-1}$ 3060, 2970, 1600 (C═N), 1515, 1340, 1030, 830, 730, 700.

**(2*R**,3*S**)-4,4-Dimethyl-2-[2-(2-nitrophenyl)-3-phenyloxiran-2-yl]-4,5-dihydro-1,3-oxazole (11a):** 304 mg; yield 90%; mp 145−146 °C (*n*-hexane); $^1$H NMR (400 MHz) $\delta$ 1.23 (s, 3 H), 1.28 (s, 3 H), 3.98 (d, $J$ = 8.1 Hz, 1 H), 4.12 (d, $J$ = 8.1 Hz, 1 H), 5.07 (s, 1 H), 7.06−7.10 (m, 5 H), 7.37 (t, $J$ = 8.3 Hz, 1 H), 7.61 (t, $J$ = 8.3 Hz, 1 H), 7.85 (d, $J$ = 8.3 Hz, 1 H), 7.91 (d, $J$ = 8.3 Hz, 1 H); $^{13}$C NMR (100 MHz) $\delta$ 27.8, 27.9, 62.2, 64.3, 68.2, 79.8, 124.4, 126.5, 127.8, 128.1, 128.4, 129.3, 132.7, 133.0, 133.3, 147.0, 162.9; GC MS (70 eV) *m*/*z* 232 (25) [$M^+ - 106$], 204 (32), 146 (75), 132 (100), 104 (65), 77 (70), 55 (55); FT-IR (KBr) $cm^{-1}$ 3040, 2970, 1650 (C═N), 1530, 1420, 1255. Anal. Calcd for $C_{19}H_{18}N_2O_4$: C, 67.88; H, 5.55; N, 7.99. Found: C, 67.45; H, 5.36; N, 8.28.

**(2*R**,3*S**)-4,4-Dimethyl-2-[2-(2-nitrophenyl)-3-(4-trifluoromethylphenyl)oxiran-2-yl]-4,5-dihydro-1,3-oxazole (11b):** 386 mg; yield 95%; white solid; mp 103−105 °C (*n*-hexane); $^1$H NMR (400 MHz) $\delta$ 1.22 (s, 3 H), 1.27 (s, 3 H), 3.98 (d, $J$ = 8.1 Hz, 1 H), 4.12 (d, $J$ = 8.1 Hz, 1 H), 5.12 (s, 1 H), 7.23−7.37 (m, 4 H), 7.52−7.60 (m, 2 H), 7.75 (t, $J$ = 8.2 Hz, 1 H), 7.94 (t, $J$ = 8.2 Hz, 1 H); $^{13}$C NMR (100 MHz) $\delta$ 27.7, 27.9, 62.6, 63.7, 68.2, 79.8, 124.6, 124.7, 125.4, 126.8, 128.8, 129.6, 130.7, 133.5, 135.0, 136.8, 148.3, 161.3; GC MS (70 eV) *m*/*z* 341 (3) [$M^+ - 65$], 272 (9), 214 (90), 200 (100), 150 (75), 104 (77), 55 (90); FT-IR (KBr) $cm^{-1}$ 3040 $cm^{-1}$, 2970, 1640 (C═N), 1535, 1420, 1260. Anal. Calcd for $C_{20}H_{17}F_3N_2O_4$: C, 59.11; H, 4.22; N, 6.89. Found: C, 59.24; H, 4.48; N, 6.72.

**(2*R**,3*S**)-2-[3-(4-Chlorophenyl)-2-(2-nitrophenyl)oxiran-2-yl]-4,4-dimethyl-4,5-dihydro-1,3-oxazole (11c):** 316 mg; yield 85%; yellow solid; mp 130−132 °C (petroleum ether); $^1$H NMR (400 MHz) $\delta$ 1.21 (s, 3 H), 1.27 (s, 3 H), 3.97 (d, $J$ = 8.1 Hz, 1 H), 4.10 (d, $J$ = 8.1 Hz, 1 H), 5.07 (s, 1 H), 7.02−7.08 (m, 4 H), 7.41 (t, $J$ = 7.7 Hz, 1 H), 7.63 (t, $J$ = 7.7 Hz, 1 H), 7.83 (d, $J$ = 7.7 Hz, 1 H), 7.95 (d, $J$ = 7.7 Hz, 1 H); $^{13}$C NMR (100 MHz) $\delta$ 27.8, 27.9, 62.6, 63.8, 68.2, 79.8, 124.6, 127.8,

128.0, 128.7, 129.5, 130.8, 131.3, 133.4, 134.0, 147.0, 161.5; GC MS (70 eV) *m*/*z* 232 (10) [$M^+ - 140$], 194 (15), 180 (72), 166 (100), 150 (50), 104 (46), 55 (50); FT-IR (KBr) $cm^{-1}$ 3040, 2970, 1645, 1655, 1520, 1350. Anal. Calcd for $C_{20}H_{17}ClN_2O_4$: C, 61.21; H, 4.60; N, 7.51. Found: C, 61.23; H, 4.55; N, 7.65.

**(2*R**,3*S**)-4,4-Dimethyl-2-[3-(4-nitrophenyl)-2-(2-nitrophenyl)oxiran-2-yl]-4,5-dihydro-1,3-oxazole (11d):** 345 mg; yield 90%; white solid; mp 183−185 °C (*n*-hexane); $^1H$ NMR (400 MHz) $\delta$ 1.22 (s, 3 H), 1.27 (s, 3 H), 3.99 (d, $J = 8.1$ Hz, 1H), 4.12 (d, $J = 8.1$ Hz, 1 H), 5.17 (s, 1H), 7.31 (t, $J = 8.7$ Hz, 2 H), 7.43 (t, $J = 7.7$ Hz, 1 H), 7.65 (t, $J = 7.7$ Hz, 1 H), 7.85 (d, $J = 7.7$ Hz, 1 H), 7.92 (d, $J = 7.7$ Hz, 1 H), 7.96 (d, $J = 8.7$ Hz, 2 H); $^{13}C$ NMR (100 MHz) $\delta$ 27.8, 27.9, 62.7, 63.5, 68.3, 79.9, 123.0, 124.7, 127.4, 128.0, 128.6, 129.8, 130.6, 133.5, 140.1, 147.7, 161.0; GC MS (70 eV) *m*/*z* 232 (35) [$M^+ - 151$], 191 (100), 177 (85), 150 (90), 104 (88), 76 (88), 55 (95); FT-IR (KBr) $cm^{-1}$ 3040, 2960, 1645 (C═N), 1605, 1505, 1340, 995. Anal. Calcd for $C_{19}H_{17}N_3O_6$: C, 59.53; H, 4.47; N, 10.96. Found: C, 59.44; H, 4.56; N, 10.88.

**(2*R**,3*S**)-2-[3-(4-Ethylphenyl)-2-(2-nitrophenyl)oxiran-2-yl]-4,4-dimethyl-4,5-dihydro-1,3-oxazole (11e):** 345 mg; yield 95%; mp 137−138 °C (petroleum ether); $^1H$ NMR (400 MHz) $\delta$ 1.10 (t, $J = 7.6$ Hz, 3 H), 1.22 (s, 3 H), 1.27 (s, 3 H), 2.49 (q, $J = 7.6$ Hz, 2 H), 3.97 (d, $J = 8.1$ Hz, 1 H), 4.10 (d, $J = 8.1$ Hz, 1 H), 5.04 (s, 1 H), 6.90 (d, $J = 8.1$ Hz, 2 H), 6.97 (d, $J = 8.1$ Hz, 2 H), 7.38 (t, $J = 8.2$ Hz, 1 H), 7.62 (t, $J = 8.2$ Hz, 1 H), 7.80 (d, $J = 8.2$ Hz, 1 H), 7.92 (d, $J = 8.2$ Hz, 1 H); $^{13}C$ NMR (100 MHz) $\delta$ 15.2, 27.8, 27.9, 28.4, 62.5, 64.3, 68.1, 79.7, 124.4, 126.4, 127.2, 129.2, 129.8, 131.0, 133.3, 134.5, 142.8, 144.1, 161.9; GC MS (70 eV) *m*/*z* 232 (40) [$M^+ - 134$], 174 (80), 160 (100), 104 (32), 76 (28), 55 (25); FT-IR (KBr) $cm^{-1}$ 3040, 2970, 2910, 1655 (C═N), 1530, 1420, 1250, 990. Anal. Calcd for $C_{21}H_{22}N_2O_4$: C, 68.84; H,6.05; N, 7.28. Found: C, 69.31; H, 6.13; N, 7.38.

**(2*R**,3*S**)-2-[3-(4-Methoxyphenyl)-2-(2-nitrophenyl)-oxiran-2-yl]-4,4-dimethyl-4,5-dihydro-1,3-oxazole (11f):** 224 mg; yield 61%; white solid; mp 97−99 °C; $^1H$ NMR (400 MHz) $\delta$ 1.21 (s, 3 H), 1.26 (s, 3 H), 3.66 (s, 3 H), 3.96 (d, $J = 8.0$ Hz, 1 H), 4.09 (d, $J = 8.0$ Hz, 1 H), 5.01(s, 1 H), 6.59 (d, $J = 8.2$ Hz, 2 H), 6.97 (d, $J = 8.2$ Hz, 2 H), 7.38 (t, $J = 8.0$ Hz, 1 H), 7.61 (t, $J = 8.0$ Hz, 1 H), 7.85 (d, $J = 8.0$ Hz, 1 H), 7.92 (d, $J = 8.0$ Hz, 1 H); $^{13}C$ NMR (100 MHz) $\delta$ 27.7, 27.8, 54.9, 60.1, 64.1, 67.9, 79.6, 124.4, 124.9, 127.6, 128.5, 129.1, 130.9, 133.2, 147.0, 159.3, 161.8; GC MS (70 eV) *m*/*z* 234 (52) [$M^+ - 134$], 190 (20), 176 (75), 162 (100), 135 (50), 104 (30), 77 (45), 55 (25); FT-IR (film) $cm^{-1}$ 3050, 2970, 1655 (C═N), 1520, 1340, 990. Anal. Calcd for $C_{20}H_{20}N_2O_5$: C, 65.21; H, 5.47; N, 7.60. Found: C, 65.60; H, 5.52; N, 7.63.

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**Supporting Information Available:** Copies of the $^1H$ NMR and $^{13}C$ NMR spectra of compound **7**, **8a**−**e**, **10**, and **11a**−**f** and an ORTEP view of **8a** and **11c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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