Supporting Information

Experimental Section

General: All reactions were performed under an atmosphere of nitrogen in oven-dried glassware, using syringe/septum cap techniques. Reagents were generally the best quality commercial grade and used without further purification unless otherwise indicated. Et₂O were purified by distillation from sodium before use. CH₂Cl₂ was distilled from calcium hydride before use. Petroleum ether refers to the 40–60 °C boiling fraction. The imines were prepared according to Taguchi’s method. The ¹H and the ¹³C NMR spectra were recorded on a Bruker Avance 400 apparatus (400.13 and 100.62 MHz, for ¹H and ¹³C, respectively) with CDCl₃ as solvent and TMS as internal standard (δ = 7.26 ppm for ¹H spectra; δ = 77.0 ppm for ¹³C spectra). The IR spectra were recorded with an FT–IR spectrophotometer Digilab Scimitar Series FTS 2000. GC–MS analyses were performed with an Agilent Technologies 6850 series II gas chromatograph (5% phenyl-polymethylsiloxane capillary column, 30 m, 0.25 mm i.d.), equipped with a 5973 Network mass-selective detector operating at 70 eV. The electrospray ionization (HR–ESI–MS) experiments were carried out in a hybrid QqTOF mass spectrometer (PE SCIEX–QSTAR) equipped with a ion spray ionization source. MS (+) spectra were acquired by direct infusion (5 µL/min) of a solution containing the appropriate sample (10 pmol/µL), dissolved in a solution 0.1% acetic acid, methanol/water 50:50 at the optimum ion voltage of 4800 V. The nitrogen gas flow was set at 30 psi (pounds per square inch) and the potentials of the orifice, the focusing ring and the skimmer were kept at 30, 50 and 25 V relative to ground, respectively. Melting points were determined using an Electrothermal melting point apparatus and are uncorrected. TLC was performed on Merck silica gel plates with F–254 indicator; viewing was by UV light (254 nm). Column chromatographies were performed on silica gel (63–200 mm) using petroleum ether/diethyl ether (Et₂O) or petroleum ether/ethyl acetate (AcOEt) mixtures as eluents.

General procedure for oxidation of iminic bonds: m-Chloroperbenzoic acid (1.1 or 2.2 mmols) in 3 mL of CH₂Cl₂ was added to a solution of imine (1.0 mmol) dissolved in CH₂Cl₂ (5 mL) under stirring and cooling (0-5 °C). When the reaction was complete (5-6 h), the excess of m-chloroperbenzoic acid was removed by filtration. The filtrate was washed twice with a dilute solution of Na₂SO₃ (5%), then with a solution of Na₂CO₃ (5%), and finally with water. After drying over anhydrous MgSO₄, the mixture was concentrated in vacuo and the crude product was purified by column chromatography (silica gel partly deactivated with triethylamine) petroleum ether : diethyl ether 8:2 for 18c, 19c and petroleum ether : ethyl acetate 9:1, 8:2 and 6:4 for 18c and 18e, 3c and 16c respectively, while every others products were isolated as pure, after filtration of MgSO₄ and evaporation of solvent in vacuo. The spectroscopic data of products deriving from 1–2, 4–7, 15 were in accordance with those already reported. For these compounds melting point data are: 1c: found 82–83 °C; literature data 83–84 °C. 2c: found 85–86 °C; literature data 87–88 °C. 4b and 4c: blue-green oils. 8: found 70–72 °C; literature data 72 °C. 9: found 103–104 °C; literature data 103–104 °C. 10: found 101–102°C; commercial product 102–103 °C. 15c (R₁ = C₆H₅, R₂ = R₃ = H): found 74–75 °C; literature data 74–75 °C. 15d (R₁ = C₆H₅, R₂ = R₃ = H): Z-isomer: found 61–63 °C; literature data 62–63 °C; E-isomer: found 64–65 °C; literature data 65–66 °C.
(E)-1,2-dibutyl diazene 1,2-dioxide (3c). Yield 80.1 mg, 92%, oil; Rf (petroleum ether : ethyl acetate = 6:4) 0.44; 1H NMR (400.13 MHz, CDCl3) δ = 0.95 (3H, d, J 7.4 Hz, CH3CH2), 1.40 (2H, sextet, J 7.4 Hz, CH3CH2CH2), 1.86 (2H, quintet, J 7.4 Hz, CH2CH2CH2), 4.28 (2H, t, J 7.4 Hz, NCH2). 13C NMR (100.62 MHz, CDCl3) δ = 13.3, 19.7, 5.0, 26.9, 58.6. FT-IR (CHCl3) 2980, 2860, 1211 (N=O) cm-1; HRMS (ESI): [M+H]+, found 175.1444. C8H13N2O2 requires 175.1446.

Acetic acid 3-[(3-acetoxy-1,1-dimethyl-butyl)-dioxy-diazenyl]-1,3-dimethyl-butyl ester (16c). Total yield 98%, 179.4 mg. (E) yield 89.7 mg, 49%, oil; Rf (petroleum ether : ethyl acetate = 9:1) 0.33; 1H NMR (400.13 MHz, CDCl3) δ = 1.23 (3H, d, J 6.5 Hz, CHCH3), 1.57 (3H, s, CCH3), 1.59 (3H, s, CCH3), 1.96 (3H, s, CCH3), 1.97–2.07 (1H, m, CH4H5CH), 2.47–2.53 (1H, m, CH2CH3), 5.02–5.10 (1H, m, CHCH3); 13C NMR (100.62 MHz, CDCl3) δ = 20.8, 24.5, 27.6, 45.7, 66.8, 86.1, 170.3; FT-IR (CHCl3) 2948, 2845, 1730, (C=O), 1270, (N=O), 1080 cm-1; HRMS (ESI): [M+H]+, found 361.2330. C17H33N2O6 requires 361.2333.

(E)-1,2-bis(2-(N-acetylacetamido)ethyl)diazene 1,2-dioxide (17c). Yield 156.4 mg, 99%, oil. 1H NMR (400.13 MHz, CDCl3) δ = 1.98 (6H, s, COCH3), 3.32–3.38 (4H, m, CH2CH2). 13C NMR (100.62 MHz, CDCl3) δ = 23.1, 40.1, 171.6. FT-IR (CHCl3) 2965, 2825, 1650 (C=O), 1215 (N=O) cm-1; HRMS (ESI): [M+H]+, found 317.1458. C12H21N4O6 requires 317.1461.

(E)-1,2-bis(2-(N-acetyl-N-methylsulfamoyl)-4-chlorophenyl)diazene 1,2-dioxide (18c). Yield 273.2 mg, 99%, mp 138.2–139.9°C (CHCl3). Rf (petroleum ether : diethyl ether = 8:2) 0.52; 1H NMR (400.13 MHz, CDCl3) δ = 2.27 (3H, s, COCH3), 3.28 (3H, s, NCH3), 6.15 (1H, d, J 8.5 Hz, Ph), 7.60 (1H, d, J 8.5 Hz, Ph), 8.44 (1H, s, Ph). 13C NMR (100.62 MHz, CDCl3) δ = 24.7, 32.0, 107.6, 131.3, 133.9, 142.6, 143.3, 155.3, 170.8. FT-IR (CHCl3) 3030, 2975, 2850, 1660 (C=O), 1350 (SO2), 1200 (N=O) cm-1; HRMS (ESI): [M+H]+, found 553.0018. C18H19Cl2N4O8S2 requires 553.0020.

(E)-1,2-bis(4-chloro-2-(2-oxopyrrolidin-1-ylsulfonyl)phenyl)diazene 1,2-dioxide (19c). Yield 285.1 mg, 99%, mp 110–112°C (CHCl3). Rf (petroleum ether : diethyl ether = 8:2) 0.52; 1H NMR (400.13 MHz, CDCl3) δ = 2.06 (2H, q, J 7.0 Hz, CH2CH2CH2), 2.42 (2H, t, J 7.0 Hz, COCH2), 3.96 (2H, t, J 7.0 Hz, NCH2), 6.15 (1H, d, J 8.5 Hz, Ph), 7.59 (1H, d, J 8.5 Hz, Ph), 8.50 (1H, s, Ph). 13C NMR (100.62 MHz, CDCl3) δ = 24.3, 34.1, 125.9, 126.9, 131.5, 133.4, 134.5, 138.8, 170.7. FT-IR (CHCl3) 3030, 2965, 2850, 1660 (C=O), 1355 (SO2), 1205 (N=O) cm-1; HRMS (ESI): [M+H]+, found 577.0018. C20H19Cl2N4O8S2 requires 577.0022.

N-(5-chloro-2-nitrophenylsulfonyl)-N-methylacetamide (18e). Yield 285.1 mg, 99%, mp 110–112°C (CHCl3). Rf (petroleum ether : ethyl acetate = 8:2) 0.52; 1H NMR (400.13 MHz, CDCl3), δ = 2.30 (3H, s, COCH3), 3.42 (3H, s, NCH3), 7.75–7.76 (2H, m, Ph), 8.37 (1H, d, J 2.0 Hz, Ph). 13C NMR (100.62 MHz, CDCl3) δ = 24.3, 34.1, 125.9, 126.9, 131.5, 133.4, 134.5, 138.8, 170.7. FT-IR (CHCl3) 3030, 2962, 2855, 1662 (C=O), 1550 (NO2), 1355 (SO2) cm-1; HRMS (ESI): [M+H]+, found 292.9996. C9H10ClN2O5S requires 292.9999.