SUPPORTING INFORMATION

(12 pages including this cover page)

Synthesis and Diels-Alder Reactions of 4-Vinylimidazoles

Carl J. Lovely,* Hongwang Du, H.V. Rasika Dias

Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington, TX 76019.

Table of Contents

Experimental and Characterization Data for Compounds **15-17**, **18b**, **19a-c**, **21b**, **22a-c**

Table S1. Crystal, data collection, and refinement parameters

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for **22a**.

Table S3. Bond lengths and angles for **22a**.

Table S4. Anisotropic displacement parameters for **22a**.

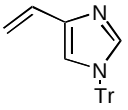
Table S5. Hydrogen coordinates and isotropic displacement parameters for **22a**.

Figure S1. ORTEP drawing (30% probability ellipsoids) of **22a**, showing atom numbering.

Experimental:

General: All chemicals and solvents were purchased from commercial vendors and were used as received unless indicated otherwise. All reactions involving air- or water-sensitive compounds were conducted in oven-dried glassware under an atmosphere of dry argon or nitrogen. Tetrahydrofuran and CH_2Cl_2 were distilled from sodium/benzophenone ketyl and from CaH_2 respectively under a nitrogen atmosphere. NMR spectra were obtained on a JEOL Eclipse+ 500 MHz spectrometer. ^{1}H NMR spectra were recorded in deuteriochloroform (unless otherwise indicated) at a spectrometer frequency of 500.16 MHz, residual protiochloroform was used as reference. The ^{13}C NMR spectra were obtained in deuteriochloroform (unless otherwise indicated) at 125.79 MHz, using $^{13}CDCl_3$ (δ = 77.0) as internal reference. Infrared (IR) spectra were obtained either on a BioRad 3240-SPC or a Bruker Vector 22 FT-IR spectrometer, using KBr pressed pellets for solids or neat films between NaCl plates for liquids and oils, and are reported in cm^{-1}. Mass spectra were recorded by electron impact (at 70 eV) on a Finnigan MAT TSQ-70 spectrometer or a Bear Instruments, Kodiak 1200 spectrometer. Elemental analyses were performed on a Perkin Elmer 2400 CHN Elemental Analyzer or determined by Quantitative Technologies Inc. (QTI), Whitehouse, New Jersey. Melting points were recorded on a Thomas Hoover Scientific capillary tube melting point apparatus and are uncorrected. Analytical thin layer chromatography (TLC) was performed on silica gel $60F_{254}$ aluminum backed precoated plates (0.25 mm layer).

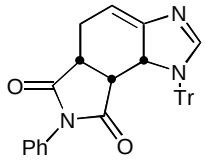
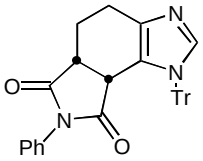
4,5-diiodoimidazole[1] was prepared according to the procedure of Lindell.



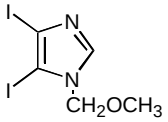
4-Ethenyl-1-triphenylmethylimidazole 15: A solution containing 1-triphenylmethyl-4-iodoimidazole **14**[2] (5.00 g, 11.5 mmol), Pd_2dba_3 (332 mg, 0.36 mmol), PPh_3 (378 mg, 1.44 mmol) and tributylvinyltin (6.7 mL, 22.9 mmol) in DMF (62 mL) was heated at 90 °C overnight. After cooling to room temperature, the mixture was diluted with EtOAc and filtered through Celite. The filtrate was washed with water (4x100 mL), dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (hexanes/EtOAc, 9:1→3:2) to afford **15** (3.08 g, 80%) as a colorless solid, contaminated with *ca.* 2-3% tin residues. This material can be used as is or further purified by recrystallization from benzene/hexanes. mp: 210-212 °C (Lit. 205-207, 206-208 °C).[3] ^{1}H NMR δ = 7.41 (s, 1H), 7.4-7.3 (m, 9H), 7.2-7.1 (m, 6H), 6.77 (s, 1H), 6.54 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.84 (dd, *J* = 17.5, 1.7 Hz, 1H), 5.12 (dd, *J* = 10.9, 1.7 Hz, 1H); ^{13}C NMR δ = 142.3, 139.5, 139.2, 128.8, 128.6, 128.4, 128.2, 119.4, 112.4, 75.5.

(5a*S, 8a*S**, 8b*S**)-1,5,5a,6,7,8,8a,8b-Tetrahydro-6,8-dioxo-7-phenyl-1-triphenylmethyl-pyrrolo[3,4-*g*]benzimidazole 16 and (5a*S**, 8a*S**)-1,4,5,5a,6,7,8,8a-Tetrahydro-6,8-dioxo-7-phenyl-1-triphenylmethylpyrrolo[3,4-*g*]benzimidazole 17:** A solution containing vinylimidazole **15** (100 mg, 0.30 mmol) and *N*-phenylmaleimide (130 mg, 0.75 mmol) in the appropriate solvent (3 mL, see Table 1) was heated at reflux until all of the diene was

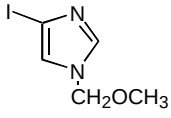
1. Carver, D. S.; Lindell, S. D.; Saville-Stones, E. A. *Tetrahedron* **1997**, *53*, 14481.
2. Kirk, K. L. *J. Heterocycl. Chem.* **1985**, *57*, 57.
3. (a) Altman, J.; Wilchek, M. *J. Heterocycl. Chem.* **1988**, *25*, 915. (b) Kokosa, J. M.; Szafasz, R. A.; Tagupa, E. *J. Org. Chem.* **1983**, *48*, 3605.

consumned (tlc analysis). After cooling the reaction mixture to room temperature, the solvent was removed by rotary evaporation and the residue was purified by column chromatography (hexanes/EtOAc, 1:1) to provide **16** as a foam.^{1}H NMR: δ = 7.59-7.57 (2H, m), 7.44-7.33 (13H, m), 7.11-7.10 (6H, m), 5.62 (ddd, *J* = 7.6, 3.7, 3.5 Hz, 1H), 4.34 (ddd, *J* = 6.2, 3.5, 3.0 Hz, 1H), 2.95 (ddd, *J* = 15.3, 7.6, 1.2 Hz, 1H), 2.75 (ddd, *J* = 8.6, 8.4, 1.2 Hz, 1H), 2.04-1.87 (m, 1H), 1.98 (dd, *J* = 8.6, 6.2 Hz, 1H); ^{13}C NMR: δ = 178.1, 174.2, 162.3, 155.8, 142.3, 131.8, 130.6, 129.2, 128.8, 128.3, 126.8, 102.3, 75.1, 59.1, 42.1, 36.9, 26.4; IR (KBr) 3058, 1712, 1661, 1598, 1383, 1186, 1158 cm^{1}. Further elution provided the aromatized product **17** as a colorless solid. mp: 241-242 ° (dec.) ^{1}H NMR: δ = 7.42-7.48 (m, 2H), 7.28-40 (m, 11H), 7.03-7.21 (m, 8H), 4.26 (d, *J* = 8.4 Hz, 1H), 3.37 (ddd, *J* = 8.4, 4.7, 4.7 Hz, 1H), 2.16 (m, 1H), 1.78 (ddd, *J* = 16.2, 4.7, 4.2 Hz, 1H), 1.68 (m, 1H), 1.49 (ddd, *J* = 16.2, 10.7, 4.7 Hz, 1H); ^{13}C NMR: δ = 177.6, 174.8, 141.5, 139.1, 132.1, 131.7, 129.9, 129.4, 129.1, 128.5, 128.3, 128.2, 126.4, 75.0, 41.6, 40.3, 22.5, 20.9; IR (KBr) 3059, 1714, 1493, 1445, 1382, 1179, 1166, 758 cm^{-1}.

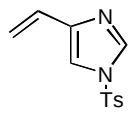


4,5-Diiodo-1-methoxymethylimidazole 21b: Sodium hydride (60% dispersion in mineral oil, 1.32 g, 33.0 mmol) was added in portions to a stirred solution of 4,5-diiodoimidazole (9.60 g, 30.0 mmol) in dry THF (240 mL) with cooling (ice/water) over 10 min. After a further 10 min the reaction mixture was allowed to warm to room temperature and stirred for 2 h. The solution was then re-cooled (ice/water) and MOMCl (2.5 mL, 33.0 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred for a further 16 h. The reaction was quenched by the addition of water (50 mL) and then diluted with CH_2Cl_2 (100 mL). The layers were separated and the aqueous solution was extracted with CH_2Cl_2 (3×30 mL). The combined organic extracts were washed with saturated brine, dried ($MgSO_4$) and concentrated. The crude product was triturated with hexanes (3×30 mL) to yield the title compound as a colorless solid (9.80 g, 89 %). mp: 124.5-125.5 °C. ^{1}H NMR: δ = 7.72 (s, 1H), 5.26 (s, 2H), 3.29 (s, 3H); ^{13}C NMR: δ = 141.8**,** 97.3, 82.1, 79.5, 56.5; IR (KBr): 3104, 2996, 2938, 2827, 1474, 1387, 1213, 1098 cm^{-1}; MS (*m/z*) 363.9 (M^{+}, 100%). Anal. Calcd. for $C_5H_6I_2N_2O$: C, 16.50; H, 1.66; N, 7.70. Found: C, 16.76; H, 1.62; N, 7.97.

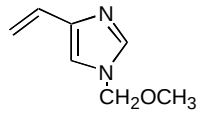


4-Iodo-1-methoxymethylimidazole 18b: A solution of EtMgBr in Et_2O (3.0 M, 13.1 mL, 1.1 eq., 39.3 mmol) was added by syringe to a solution of 4,5-diiodo-1-methoxymethylimidazole **21b** (13.00 g, 35.7 mmol) in dry THF (140 mL) at room temperature. The resulting suspension was stirred at r.t. for 1 h, then quenched with water (3 mL). After stirring for a further 2 h the mixture was diluted with CH_2Cl_2 (70 mL). The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2×30 mL). The combined organic extracts was dried ($MgSO_4$) and evaporated. The residue was purified by flash chromatography (EtOAc/hexaness: 1:2→3:1) to yield the title compound as an opaque liquid (7.70g, 90%). ^{1}H NMR: δ = 7.49 (d, *J* = 1.4 Hz, 1H), 7.13 (d, *J* = 1.4 Hz, 1H), 5.19 (s, 2H), 3.27 (s, 3H); ^{13}C NMR: δ = 138.9, 124,6, 82.9, 77.8, 56.5; IR (neat): 3109, 2994, 2933, 2828, 1643, 1498, 1460, 1392, 1216, 1102 cm^{-1}; MS (*m/z*):

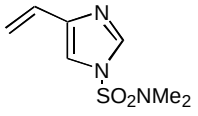
237.9 (M^+, 100%). Anal. Calcd. for $C_5H_7N_2O$: C, 25.23; H, 2.96; N, 11.77. Found: C, 24.93; H, 2.62; N, 11.67.



4-Ethenyl-1-(4-toluenesulfonyl)imidazole 19a: Using the Stille coupling procedure described above for the synthesis of **15**. 4-iodo-1-(4-toluenesulfonyl)imidazole **18a**[4] (696 mg, 2.00 mmol), and tributylvinylstannane (1.1 mL, 4.00 mmol), $Pd_2(dba)_3$ (56 mg, 0.06 mmol), PPh_3 (66 mg, 0.25 mmol) and DMF (10 mL), heating for 27 h. Purification by column chromatography (hexanes/Et_2O, 4:1→1:2) gave the title compound **22a** as a white solid (460 mg, 92%). mp: 105.0-106.0 °C (Lit. 105 °C).[5] ^{1}H NMR: δ = 7.96 (d, *J* = 0.7 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 0.7 Hz, 1H), 6.48 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.92 (d, *J* = 17.4, 1.4 Hz, 1H), 5.27 (d, *J* = 10.9, 1.4 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR: δ = 146.5, 142.7, 136.8, 134.9, 130.5, 127.4, 126.9, 116.0, 113.9, 21.8.



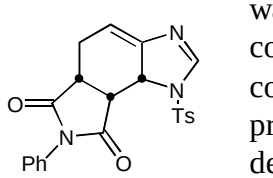
4-Ethenyl-1-methoxymethylimidazole 19b: Using the Stille coupling procedure described above for the synthesis of **15**. A mixture of 4-iodo-1-methoxymethylimidazole (1.00 g, 4.2 mmol), tributylvinylstannane (2.5 mL, 8.4 mmol), triphenylphosphine (138 mg, 0.52 mmol), $Pd_2(dba)_3$ (120 mg, 0.13 mmol) was heated at 90 °C in DMF (22 mL) for 21 h. Purification by column chromatography (Et_2O/EtOAc 2/1→1/2→Et_2O/EtOAc/CH_3OH→5/10/1) gave pure product **19b** as a colorless liquid (0.40 g, 56%). ^{1}H NMR ($CDCl_3$) δ 7.59 (s, 1H), 6.97 (s, 1H), 6.58 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.86 (dd, *J* = 17.4, 1.6 Hz, 1H), 5.18 (s, 2H), 5.16 (dd, *J* = 10.9, 1.6 Hz, 1H), 3.26 (s, 3H); ^{13}C NMR: 141.7, 137.7, 128.4, 116.4, 112.8, 77.8, 56.2; IR (neat): 3107, 2997, 2939, 2827, 1686, 1640, 1495, 1398, 1348, 1230, 1190, 1152, 1110 cm^{-1}; MS (*m/z*) 138.1 (M^+, 49%), 27.8 (100%).

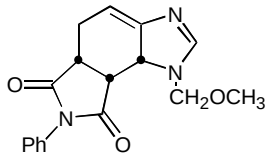


4-Ethenyl-1-(*N*,*N*-dimethylsulfamoyl)imidazole 19c: Using the Stille coupling procedure described above for the synthesis of **15**. 4-Iodo-1-(*N*,*N*-dimethylsulfamoyl)imidazole[6] (1.03 g, 3.4 mmol), and tributylvinylstannane (1.96 mL, 6.8 mmol), $Pd_2(dba)_3$ (98 mg, 0.11 mmol), PPh_3 (115 mg, 0.44 mmol) and DMF (19 mL), heating at 90 °C for 19 h. Purification by column chromatography (hexanes/EtOAc, 1:1) gave the title compound as a white solid (0.54 g, 79%). mp: 76.5-77.5 °C. ^{1}H NMR δ 7.83 (s, 1H), 7.12 (s, 1H), 6.54 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.95 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.28 (dd, *J* = 11.0, 1.4 Hz, 1H), 2.84 (s, 6H); ^{13}C NMR: 141.8, 136.9, 127.0, 115.7, 114.3, 38.3; IR (KBr): 3135, 3021, 2979, 2933, 1640, 1475, 1383, 1270, 1170, 1083 cm^{-1}; MS (*m/z*): 201.1 (M^+, 100%). Anal. Calcd. for $C_7H_{11}N_3O_2S$: C, 41.78; H, 5.51; N, 20.88; Found: C, 42.08; H, 5.31; N, 21.18.

4. Cliff, M. D.; Pyne, S. G. *J. Org. Chem.* **1995**, *60*, 2378.
5. Janin, Y. L.; Aubertin, A.-M.; Chiaroni, A.; Riche, C.; Monneret, C.; Bisagni, E.; Grierson, D. S. *Tetrahedron* **1996**, *52*, 15157.
6. Bhagavatula, L.; Premchandran, R. H.; Plata, D. J.; King, S. A.; Morton, H. E. *Heterocycles* **2000**, *53*, 729.

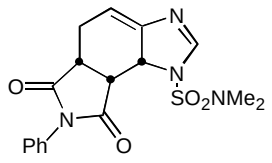
(5a*S, 8a*S**, 8b*S**)-1,5,5a,6,7,8,8a,8b-Tetrahydro-6,8-dioxo-7-phenyl-1-(4-toluenesulfonyl)-pyrrolo[3,4-*g*]benzimidazole 22a:** General procedure for the Diels-Alder reaction. A solution of **19a** (75 mg, 0.30 mmol) and *N*-phenylmaleimide (129 mg, 0.75 mmol) in benzene (3 mL) was heated to reflux. After 27 h, the reaction was complete (all diene was consumed, tlc), the mixture was then cooled, concentrated and purified by column chromatography (hexanes/EtOAc, 2/1→1/2) to give the title product as a colorless solid (101 mg, 80%). Using the procedure described above except that CH_2Cl_2 was used as a solvent, refluxing 48 h, the title compound was obtained (112 mg, 89%). mp: 213-215 °C. ^{1}H NMR: δ = 7.83 (d, *J* = 8.4 Hz, 2H), 7.64 (s, 1H), 7.36 (m, 5H), 7.11 (m, 2H), 5.84 (ddd, *J* = 7.5, 3.5, 3.5 Hz, 1H), 4.27 (ddd, *J* = 6.7, 3.5, 3.3 Hz, 1H), 3.92 (dd, *J* = 8.8, 6.7 Hz, 1H), 3.23 (ddd, *J* = 8.8, 7.3, 1.3 Hz, 1H), 3.06 (ddd, *J* = 15.6, 7.5, 1.3 Hz, 1H), 2.44 (s, 3H), 2.11 (dddd, *J* = 15.6, 7.3, 3.5, 3.3 Hz, 1H); ^{13}C NMR: δ =177.4, 172.5, 152.9, 152.4, 145.6, 134.2, 131.5, 130.4, 129.1, 128.8, 127.6, 126.5, 109.5, 56.7, 42.0, 36.4, 25.9, 21.8; IR (KBr): 3102, 3056, 2954, 2865, 1705, 1548, 1377, 1179, 1090 cm^{-1}; MS (*m/z*): 333.9 (M^+- 87, 100%). Anal. Calcd. for $C_{22}H_{19}N_3O_4S$: C, 62.70; H, 4.54; N, 9.97. Found: C, 62.38; H, 4.51; N, 9.78.





(5a*S, 8a*S**, 8b*S**)-5,5a,8a,8b-Tetrahydro-6,8-dioxo-1-methoxymethyl-7-phenylpyrrolo[3,4-g]benzimidazole 22b:** A solution of **19b** (40 mg, 0.30 mmol) and *N*-phenylmaleimide (129 mg, 0.75 mmol) in benzene (3 mL) was heated to reflux. After 2.5 h, the reaction was complete (all diene was consumed, tlc), the mixture was then cooled, concentrated and purified by column chromatography (Et_2O/EtOAc 2/1→1/2→Et_2O/EtOAc/MeOH→5/10/1) to give the title as a white solid (65 mg, 70%). Using the procedure described above except that CH_2Cl_2 was used as a solvent, refluxing 17 h, the title compound was obtained (80.0 mg, 86%). mp: 193.0-194.0 °C. ^{1}H NMR δ = 7.38 (m, 3H), 7.30 (s, 1H), 7.11 (m, 2H), 5.69 (ddd, *J* = 7.7, 3.9, 3.6 Hz, 1H), 5.18 (d, *J* = 11.5 Hz, 1H), 4.72 (d, *J* = 11.5 Hz, 1H), 4.40 (ddd, *J* = 8.2, 3.9, 3.6 Hz, 1H), 3.78 (dd, *J* = 8.5, 8.2 Hz, 1H), 3.32 (s, 3H), 3.21 (ddd, *J* = 8.5, 6.4, 1.8 Hz, 1H), 3.13 (ddd, *J* = 15.3, 7.7, 1.8 Hz, 1H), 2.06 (dddd, *J* = 15.3, 6.4, 3.6, 3.6 Hz, 1H); ^{13}C NMR δ = 177.7, 173.8, 159.1, 153.7, 131.6, 129.2, 128.9, 126.6, 104.2, 77.5, 55.9, 55.7, 41.0, 36.9, 22.5; IR (KBr): 3110, 3046, 2942, 2818, 1776, 1704, 1546, 1498, 1395, 1204 cm^{-1}; MS (*m/z*): 311.1 (M^+, 24%), 108 (100%). Anal. Calcd. for $C_{17}H_{17}N_3O_3$: C, 65.58; H, 5.50; N, 13.50. Found: C, 65.49; H, 5.54; N, 13.48.

(5a*S, 8a*S**, 8b*S**)-1,5,5a,6,7,8,8a,8b-Tetrahydro-1-(*N*,*N*-dimethylsulfamoyl)-6,8-dioxo-7-phenylpyrrolo[3,4-*g*]benzimidazole 22c:** A solution of **19c** (60 mg, 0.30 mmol) and *N*-phenylmaleimide (129 mg, 0.75 mmol) in benzene (3 mL) was heated to reflux. After 9 h, the reaction was complete (all diene was consumed, tlc), then the mixture was cooled, concentrated and triturated with Et_2O to give pure title product as a white solid (104 mg, 93%). Using the procedure described above except that CH_2Cl_2 was used as a solvent, refluxing 17 h, the title compound was obtained (107 mg, 94%). mp: 198.0-199.0 °C. ^{1}H NMR δ = 7.53 (s, 1H), 7.39 (m, 3H), 7.12 (m, 2H), 5.87 (ddd, *J* = 7.5, 3.7, 3.5 Hz,



1H), 4.62 (ddd, *J* = 6.6, 3.5, 3.5 Hz, 1H), 3.80 (dd, *J* = 8.7, 6.6 Hz, 1H), 3.27 (ddd, *J* = 8.7, 7.2, 1.4 Hz, 1H), 3.09 (ddd, *J* = 15.8, 7.5, 1.4 Hz, 1H), 2.20 (dddd, *J* = 15.8, 7.2, 3.7, 3.5 Hz, 1H); ^{13}C NMR: δ = 177.4, 173.3, 154.4, 152.5, 131.4, 129.3, 129.0, 126.6, 108.4, 57.9, 42.2, 38.0, 36.8, 26.1; IR (KBr): 3065, 2949, 2860, 1772, 1712, 1557, 1499, 1394, 1364, 1202, 1154 cm^{-1}. MS (*m/z*): 333.8 (M^+ - 40.4, 23%), 108.1 (100%). Anal. Calcd. for $C_{17}H_{18}N_4O_4S$: C, 54.54; H, 4.85; N, 14.96. Found: C, 54.73; H, 4.98; N, 15.23.

Table S1. Crystal data and structure refinement for 22a

Empirical formula	$C_{22}H_{19}N_3O_4S$	
Formula weight	421.46	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 11.2389(11) Å	α = 90°.
	b = 11.9684(10) Å	β = 90°.
	c = 14.7992(13) Å	γ = 90°.
Volume	1990.7(3) $Å^3$	
Z	4	
Density (calculated)	1.406 Mg/m^3	
Absorption coefficient	0.198 mm^{-1}	
F(000)	880	
Crystal size	0.70 x 0.39 x 0.21 mm^3	
Theta range for data collection	2.19 to 22.49°.	
Index ranges	-1<=h<=12, -1<=k<=12, -1<=l<=15	
Reflections collected	1787	
Independent reflections	1632 [R(int) = 0.0169]	
Completeness to theta = 22.49°	87.3 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8773 and 0.8384	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1632 / 0 / 275	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0319, wR2 = 0.0755	
R indices (all data)	R1 = 0.0374, wR2 = 0.0791	
Absolute structure parameter	0.00(13)	
Largest diff. peak and hole	0.144 and -0.189 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **22a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S	1134(1)	5124(1)	7721(1)	43(1)
O(1)	-4001(3)	7663(3)	9461(2)	72(1)
O(2)	-1702(3)	6336(3)	7173(2)	66(1)
O(3)	1104(3)	4311(2)	7014(2)	61(1)
O(4)	1241(2)	6283(2)	7528(2)	53(1)
N(1)	-135(2)	4966(3)	8267(2)	40(1)
N(2)	-1442(3)	3917(3)	9065(3)	61(1)
N(3)	-3086(3)	6995(3)	8183(2)	41(1)
C(1)	-716(4)	3950(3)	8403(3)	56(1)
C(2)	-1417(3)	4988(4)	9470(3)	46(1)
C(3)	-2074(4)	5397(4)	10126(3)	58(1)
C(4)	-1917(4)	6611(4)	10344(3)	61(1)
C(5)	-1880(3)	7304(4)	9465(2)	48(1)
C(6)	-1111(3)	6826(3)	8705(3)	42(1)
C(7)	-515(3)	5716(3)	8996(3)	40(1)
C(8)	-1928(4)	6668(3)	7924(3)	44(1)
C(9)	-3113(4)	7370(4)	9072(3)	48(1)
C(10)	-4104(3)	6969(3)	7600(2)	45(1)
C(11)	-4350(4)	6027(4)	7104(3)	60(1)
C(12)	-5338(5)	6002(5)	6549(3)	74(2)
C(13)	-6078(4)	6911(5)	6511(3)	75(2)
C(14)	-5838(4)	7851(5)	6993(3)	71(1)
C(15)	-4836(4)	7890(4)	7541(3)	56(1)
C(16)	2243(3)	4753(3)	8495(2)	37(1)
C(17)	3154(3)	5499(3)	8690(3)	47(1)
C(18)	4044(4)	5168(4)	9273(3)	51(1)
C(19)	4046(3)	4120(4)	9672(2)	44(1)
C(20)	3133(3)	3401(3)	9477(3)	46(1)
C(21)	2234(3)	3705(3)	8885(3)	43(1)
C(22)	5023(4)	3791(4)	10315(3)	68(1)

Table S3. Bond lengths [Å] and angles [°] for **22a**.

S-O(4)	1.422(3)	C(5)-C(9)	1.505(5)
S-O(3)	1.429(3)	C(5)-C(6)	1.529(5)
S-N(1)	1.649(3)	C(6)-C(8)	1.489(5)
S-C(16)	1.750(4)	C(6)-C(7)	1.549(5)
O(1)-C(9)	1.204(5)	C(10)-C(11)	1.373(5)
O(2)-C(8)	1.207(4)	C(10)-C(15)	1.379(5)
N(1)-C(1)	1.395(5)	C(11)-C(12)	1.381(6)
N(1)-C(7)	1.467(5)	C(12)-C(13)	1.371(7)
N(2)-C(1)	1.275(5)	C(13)-C(14)	1.359(7)
N(2)-C(2)	1.415(6)	C(14)-C(15)	1.388(6)
N(3)-C(9)	1.389(5)	C(16)-C(21)	1.381(5)
N(3)-C(8)	1.413(5)	C(16)-C(17)	1.389(5)
N(3)-C(10)	1.433(5)	C(17)-C(18)	1.379(5)
C(2)-C(3)	1.314(6)	C(18)-C(19)	1.386(6)
C(2)-C(7)	1.509(5)	C(19)-C(20)	1.370(5)
C(3)-C(4)	1.499(6)	C(19)-C(22)	1.505(5)
C(4)-C(5)	1.543(6)	C(20)-C(21)	1.386(5)

O(4)-S-O(3)	121.27(17)	N(1)-C(7)-C(6)	116.5(3)
O(4)-S-N(1)	106.45(16)	C(2)-C(7)-C(6)	109.5(3)
O(3)-S-N(1)	105.11(18)	O(2)-C(8)-N(3)	122.4(4)
O(4)-S-C(16)	108.57(18)	O(2)-C(8)-C(6)	128.9(4)
O(3)-S-C(16)	108.85(18)	N(3)-C(8)-C(6)	108.8(3)
N(1)-S-C(16)	105.46(15)	O(1)-C(9)-N(3)	124.4(4)
C(1)-N(1)-C(7)	106.9(3)	O(1)-C(9)-C(5)	126.3(3)
C(1)-N(1)-S	125.1(3)	N(3)-C(9)-C(5)	109.2(3)
C(7)-N(1)-S	122.8(2)	C(11)-C(10)-C(15)	120.2(4)
C(1)-N(2)-C(2)	106.5(3)	C(11)-C(10)-N(3)	120.0(4)
C(9)-N(3)-C(8)	111.5(3)	C(15)-C(10)-N(3)	119.8(4)
C(9)-N(3)-C(10)	124.0(3)	C(10)-C(11)-C(12)	119.9(4)
C(8)-N(3)-C(10)	124.4(3)	C(13)-C(12)-C(11)	119.6(5)
N(2)-C(1)-N(1)	115.9(4)	C(14)-C(13)-C(12)	121.0(4)
C(3)-C(2)-N(2)	129.7(4)	C(13)-C(14)-C(15)	119.8(5)
C(3)-C(2)-C(7)	120.4(4)	C(10)-C(15)-C(14)	119.6(4)
N(2)-C(2)-C(7)	109.9(4)	C(21)-C(16)-C(17)	120.2(3)
C(2)-C(3)-C(4)	117.0(4)	C(21)-C(16)-S	119.9(3)
C(3)-C(4)-C(5)	110.0(4)	C(17)-C(16)-S	119.9(3)
C(9)-C(5)-C(6)	104.8(3)	C(18)-C(17)-C(16)	118.7(4)
C(9)-C(5)-C(4)	109.2(3)	C(17)-C(18)-C(19)	121.9(4)
C(6)-C(5)-C(4)	115.7(3)	C(20)-C(19)-C(18)	118.5(3)
C(8)-C(6)-C(5)	105.6(3)	C(20)-C(19)-C(22)	121.0(4)
C(8)-C(6)-C(7)	112.0(3)	C(18)-C(19)-C(22)	120.5(4)
C(5)-C(6)-C(7)	111.2(3)	C(19)-C(20)-C(21)	121.0(4)
N(1)-C(7)-C(2)	100.6(3)	C(16)-C(21)-C(20)	119.8(4)

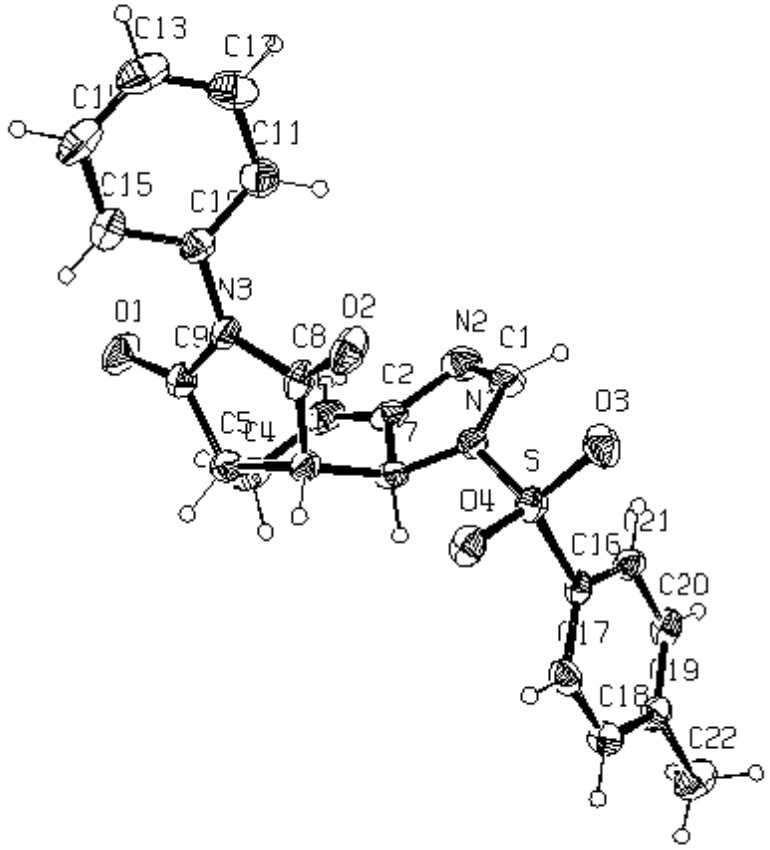
Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **22a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S	44(1)	41(1)	44(1)	4(1)	1(1)	5(1)
O(1)	46(2)	109(3)	61(2)	-26(2)	3(2)	25(2)
O(2)	58(2)	100(2)	41(2)	1(2)	4(2)	32(2)
O(3)	78(2)	62(2)	45(1)	-11(2)	-6(2)	13(2)
O(4)	51(2)	43(2)	64(2)	16(1)	6(2)	4(1)
N(1)	38(2)	30(2)	52(2)	4(2)	-3(2)	-3(2)
N(2)	53(2)	53(3)	75(2)	12(2)	-6(2)	-14(2)
N(3)	32(2)	46(2)	45(2)	-3(2)	1(2)	6(2)
C(1)	51(3)	40(3)	76(3)	-2(3)	-10(3)	-4(2)
C(2)	38(2)	51(3)	49(2)	16(3)	-10(2)	-4(2)
C(3)	41(2)	76(4)	56(3)	23(3)	0(2)	-11(3)
C(4)	39(2)	98(4)	47(2)	-4(3)	-1(2)	-3(3)
C(5)	38(2)	56(3)	50(2)	-13(2)	1(2)	-2(2)
C(6)	31(2)	39(2)	57(2)	3(2)	1(2)	0(2)
C(7)	30(2)	44(2)	47(2)	5(2)	-4(2)	-6(2)
C(8)	42(2)	46(2)	43(2)	14(2)	8(2)	12(2)
C(9)	42(2)	51(3)	51(2)	-8(2)	1(2)	8(2)
C(10)	39(2)	56(3)	39(2)	3(2)	-1(2)	3(2)
C(11)	62(3)	64(3)	53(3)	-2(3)	-6(2)	5(2)
C(12)	77(3)	90(4)	54(3)	-3(3)	-9(3)	-14(3)
C(13)	51(3)	119(5)	53(3)	17(3)	-7(3)	-2(4)
C(14)	48(3)	99(4)	65(3)	24(3)	-4(3)	19(3)
C(15)	50(2)	60(3)	58(3)	7(2)	6(2)	12(2)
C(16)	37(2)	37(2)	38(2)	3(2)	8(2)	6(2)
C(17)	53(3)	34(2)	53(2)	1(2)	4(2)	-3(2)
C(18)	47(2)	52(3)	55(2)	-7(3)	0(2)	-4(2)
C(19)	38(2)	53(3)	42(2)	2(2)	8(2)	5(2)
C(20)	45(2)	40(3)	53(2)	16(2)	9(2)	7(2)
C(21)	35(2)	41(3)	54(2)	5(2)	1(2)	-3(2)
C(22)	52(3)	91(4)	61(3)	11(3)	-6(2)	7(3)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **22a**.

	x	y	z	U(eq)
H(1A)	-582	3334	8034	67
H(4B)	-1183	6717	10678	74
H(4C)	-2571	6863	10720	74
H(5A)	-1605	8061	9607	58
H(6A)	-494	7369	8544	51
H(7A)	155	5870	9401	48
H(11A)	-3853	5408	7141	72
H(12A)	-5500	5371	6203	88
H(13A)	-6754	6885	6150	89
H(14A)	-6342	8465	6956	85
H(15A)	-4661	8534	7867	67
H(17A)	3164	6208	8433	56
H(18A)	4660	5662	9401	62
H(20A)	3116	2699	9745	55
H(21A)	1626	3205	8750	52
H(22A)	5581	4395	10371	102
H(22B)	5424	3141	10088	102
H(22C)	4687	3628	10897	102
H(3)	-2590(40)	4910(40)	10410(30)	65(13)


C13
C12
C14
C11
C15
C10
N3
O1
C9
C8
O2
N2
C1
C2
N1
O3
C5
C4
C7
S
O4
C21
C16
C20
C17
C19
C18
C22