Supporting Information

Aerobic Oxidative Amination of Unactivated Alkenes Catalyzed by Palladium

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General Considerations.

All commercially available compounds were used as received, and were purchased from Aldrich except $\text{Pd}(\text{OAc})_2$ and PdCl_2 (DuPont), $\text{Pd}(\text{O}_2\text{CCF}_3)_2$ and CuCl_2 (Strem). ^1H , ^{13}C , and ^{31}P NMR spectra were recorded on Bruker AC-300 MHz spectrometers, and CDCl_3 was purchased from Cambridge Isotope Laboratories, Inc. and Aldrich. The chemical shifts (δ) are given in part per million relative to internal TMS (0 ppm for ^1H), CDCl_3 (77.23 ppm for ^{13}C), and external standard 85 % H_3PO_4 (0 ppm for ^{31}P). Gas chromatography was performed with a Shimadzu GC-17A gas chromatograph equipped with a 15 m RTX-5 capillary column (Restek). Flash chromatography was performed on silica gel 60 (particle size 0.040-0.063mm, 230-400 mesh ASTM, purchased from Sorbent Technology) with hexanes/diethylether or methylene chloride.

General Procedure for Catalyst Screening.

In a disposable culture tube, phthalimide (0.5 mmol, 73.6 mg), catalyst (0.025 mmol), additive (0.025 mmol) and PhCN (0.667 mL) were combined. The reaction tubes were placed into a custom 48-well parallel reactor mounted on a Large Capacity Mixer (Glas-Col) and the headspace was purged with molecular oxygen for ca. 15 min. After warming to 60 °C, 1-octene (3.0 mmol, 0.47 mL) was added to each tube to initiate the reactions. The reactions were vortexed for 24 h under 1 atm molecular oxygen. Upon cooling, 1,3,5-trimethoxybenzene (0.056 mmol, 9.4 mg) internal standard was added to each reaction mixture. Terminal enamide product yield was evaluated by ^1H NMR spectroscopy relative to the internal standard. Yield of additional amination products was established by gas chromatography. Determination of percent conversion phthalimide was hindered by poor solubility and low detector (FID) response.

General Procedure for the Palladium-Catalyzed Oxidative Amination of Aryl and Alkyl Olefins.

A typical procedure is given for the reaction of 1-octene with phthalimide, $\text{Pd}(\text{OAc})_2$ (0.025 mmol, 5.6 mg) and phthalimide (0.50 mmol, 73.6 mg) were suspended in PhCN (0.667 mL) in 13x100 mm disposable culture tubes. The reaction tubes were placed into a custom 48-well parallel reactor mounted on a Large Capacity Mixer (Glas-Col) and the headspace was purged with molecular oxygen for ca. 15 min. After warming to 60 °C, octene (3.0 mmol, 0.47 mL) was added to each tube to initiate the reactions. The reactions were carried out for 24 h under an oxygen atmosphere (1 atm). For product purification, four individual reactions were combined and adsorbed onto silica gel. The product was isolated by eluting with ether/hexanes to give a 87 % yield

(447 mg) of 2-(1-hexylvinyl)-isoindol-1,3-dione. Performing this reaction in a 25 mL round-bottom flask equipped with a magnetic stir bar under an oxygen balloon resulted in comparable yield, 76 % yield (391 mg).

General Procedure for the Palladium-Catalyzed Oxidative Amination of Volatile Alkyl Olefins Performed in a Sealed Flask (1-Hexene, Cyclopentene).

A typical procedure is given for the reaction of cyclopentene with phthalimide. To a bomb flask with a Kontes valve equipped with a magnetic stir bar were added *p*-toluenesulfonamide (2 mmol, 342 mg), Pd(OAc)₂ (0.1 mmol, 22.4 mg), cyclopentene (12 mmol, 1.058 mL), and PhCN (2.67 mL). The flask was sealed, cooled with liquid nitrogen, and evacuated. Pressure was monitored by a mercury monometer while oxygen (3.5 atm at room temperature) was condensed into the flask. The reaction was heated to 60 °C in an oil bath and stirred for 48 hours. Upon completion, the reaction mixture was allowed to cool before opening and loaded directly onto a chromatography column (elution solvent: methylene chloride) to give 64 % yield (301 mg).

Product Characterization Data.

2-(1-Phenyl-vinyl)-isoindole-1,3-dione. 80 % (399 mg), white solid. Characterization data matches literature report. (*1*)

2-[1-(4-Methyl-phenyl)-vinyl]-isoindole-1,3-dione. 78 % (410 mg), yellow solid. ¹H NMR (300 MHz, CDCl₃) δ 7.93 (m, 2H), δ 7.78 (m, 2H), δ 7.27 (d, J = 8.4 Hz, 2H), δ 7.13 (d, J = 8.4 Hz, 2H), δ 5.96 (s, 1H), δ 5.39 (s, 1H), δ 2.33 (s, 3H); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 167.1, 138.8, 137.1, 134.5, 132.5, 131.8, 129.3, 125.3, 123.7, 115.1, 21.2; HRMS: m/z (EI) calculated [M]⁺ = 263.0946, measured 263.0941.

2-[1-(3-Methoxy-phenyl)-vinyl]-isoindole-1,3-dione. Column chromatography (Et₂O/hexanes, 1:2) afforded a yellow solid, 80 % (446 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.94 (m, 2H), δ 7.78 (m, 2H), δ 7.26 (m, 1H), δ 6.95 (m, 3H), δ 6.00 (s, 1H), δ 5.45 (s, 1H), δ 3.79 (s, 3H); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 167.2, 159.9, 137.2, 137.0, 134.6, 131.9, 129.8, 123.9, 118.0, 116.5, 114.2, 111.7, 55.4; HRMS: m/z (EI) calculated [M]⁺ = 279.0895, measured 279.0888.

***N*-(1-Phenyl-ethylidene)-4-Methyl-benzenesulfonamide.** 82 % (448 mg), mustard color solid. Characterization data matches literature report. (1)

2-(1-Methylene-pentyl)-isoindole-1,3-dione. Column chromatography (Et₂O/hexanes, 1:4) afforded yellow oil, 90 % (412 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.9-7.6 (m, 4H), δ 5.40 (s, 1H), δ 5.14 (s, 1H), δ 2.48 (t, J = 7.1 Hz, 2H), δ 1.63-1.33 (m, 4H), δ 0.97 (m, 3H) [internal isomer (tri-substituted olefin) δ 7.9-7.6 (m, 0.4H), δ 5.53 (tt, J = 7.5, 1.1 Hz, 0.1H), δ 2.21 (q, J = 7.4 Hz, 0.2H), δ 1.98 (s, 0.3H), δ 1.63-1.33 (m, 0.2H), δ 0.99 (m, 0.3H)]; ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 167.048, 138.940, 133.955, 131.813, 123.320, 114.557, 33.380, 28.662, 21.841, 13.617; HRMS: m/z (ESI) calculated [M+Na+CH₃OH]⁺ = 284.1263, measured 284.1277.

2-(1-Methylene-heptyl)-isoindole-1,3-dione. Column chromatography (Et₂O/hexanes, 1:4) afforded yellow oil, 87% (447 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.9-7.6 (m, 4H), δ 5.4 (s, 1H), δ 5.2 (s, 1H), δ 2.46 (t, J = 7.4 Hz, 2H), δ 1.4-0.9 (m, 7H), 0.87 (t, J = 6.9 Hz, 3H) [internal isomer (tri-substituted olefin) δ 7.9-7.6 (m, 0.24H), δ 5.54 (t, J = 7.2 Hz, 0.8H), δ 2.22 (q, J = 7.2 Hz, 0.16H), 1.97 (s, 0.28H), and δ 1.4-0.9 (m, 0.8H)] ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 167.059, 138.995, 133.955, 131.630, 123.326, 114.547, 33.693, 31.350, 28.418, 26.526, 22.314, and 13.828; HRMS: m/z (ESI) calculated [M+Na+CH₃OH]⁺ = 312.1576, measured 312.1569.

Acetic acid 5-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-hex-5-enyl ester. Column chromatography (Et₂O/hexanes, 1:4 to 100% ether) produced a white solid, 86 % (493 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.9-7.7 (m, 4H), δ 5.41 (s, 1H) δ 5.18 (s, 1H), δ 4.04 (t, J = 6.5 Hz, 2H), δ 2.50 (t, J = 7.5 Hz, 2H), δ 2.00 (s, 3H), δ 1.7-1.4 (m, 4H); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 170.8, 167.0, 138.2, 134.0, 131.6, 123.3, 115.0, 63.8, 33.2, 27.6, 22.9, 20.7; HRMS: m/z (ESI) calculated [MNa]⁺ = 310.1055, measured 310.1052.

2-Cyclooct-2-enyl-isoindole-1,3-dione. Column chromatography (Et₂O/hexanes, 1:4) afforded a white solid, 60 % (306 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.9-7.6 (m, 4H), δ 6.03 (t, J = 11.4 Hz, 1H), δ 5.78 (q, J = 10.8 Hz, 1H), δ 5.25 (m, 1H), δ 2.6-2.0 (m, 4H), and δ 1.9-1.2 (m, 6H). [homoallylic isomer (integrations reported relative to a single proton integral of the major isomer) δ 7.9-7.6 (m, 0.60H) δ 5.9-5.6 (m, 0.29H); δ 4.30 (m, 0.14), δ 3.25 (m, 0.25H), δ 2.6-2.0 (m, 0.7H), δ 1.9-1.2 (m, 0.9.3H)], [bishomoallylic isomer δ 7.9-7.6 (m, 0.94H), δ 5.9-5.6 (m, 0.48), δ 4.15 (m, 0.24H), δ 2.6-2.0 (m, 0.94H), and δ 1.9-1.2 (m, 1.47H)]; ¹³C{¹H} NMR (major product) (75 MHz, CDCl₃) δ 167.9, 133.5, 131.9, 131.3, 127.5, 122.8, 48.5, 33.9, 28.9, 25.9, 25.8, 24.6; HRMS: m/z (EI) calculated [M]⁺ = 255.1259, measured 255.1258.

2-Cyclopent-2-enyl-isoindole-1,3-dione. 80 % (341 mg), white solid. Characterization data matches literature report. (2)

N-Cyclopent-2-enyl-4-methyl-benzenesulfonamide. 64 % (303 mg), white solid. Characterization data matches literature report. (3)

N-(1-Cyclohexyl-ethylidene)-4-methyl-benzenesulfonamide. 63 % (352 mg), yellow solid. ¹H NMR (300 MHz, CDCl₃) δ 7.85 (d, J = 8.4 Hz, 2H), δ 7.31 (d, J = 8.1 Hz, 2H), δ 2.53 (s, 3H), δ 2.43 (s, 3H), δ 2.29 (m, 1H), δ 1.81 (m, 4H), δ 1.67 (d, J = 10.8 Hz, 1H), δ 1.26 (m, 5H); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 192.8, 143.1, 138.4, 129.2, 126.7, 51.1, 29.4, 25.4, 22.3, 21.3; HRMS: m/z (ESI) calculated [MH]⁺ = 280.1371, measured 280.1364.

N-(1-Cyclohexyl-vinyl)-4,N-dimethyl-benzenesulfonamide. Column chromatography (Et₂O/hexanes, 1:4) afforded pale yellow solid, 59 % (347 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.66 (d, J = 8.1 Hz, 2H), δ 7.28 (d, J = 8.1 Hz, 2H), δ 4.88 (s, 1H), δ 4.36 (s, 1H), δ 2.91 (s, 3H), δ 2.43 (s, 3H), δ 2.05 (m, 2H), δ 1.75 (m, 3H), δ 1.4-1.0 (m, 6H); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 156.2, 143.6, 133.6, 129.1, 128.1, 109.0,

44.3, 39.3, 31.7, 26.3, 21.5; HRMS: m/z (EI) calculated $[MH]^+ = 294.1528$, measured 294.1527.

2-(1-cyclohexyl-vinyl)-isoindole-1,3-dione. Column chromatography (Et₂O/hexanes, 1:4) afforded a white solid, 92 % (469 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.9-7.6 (m, 4H), δ 5.41 (s, 1H), δ 5.12 (s, 1H), δ 2.42 (m, 1H), δ 1.9-1.6 (m, 5H), δ 1.3-1.1 (m, 5H); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 167.8, 144.3, 134.3, 132.0, 123.7, 114.1, 41.4, 31.1, 26.3; HRMS: m/z (ESI) calculated $[M+Na+CH_3OH]^+ = 278.1157$, measured 278.1166.

2-1-(Cyclohex-3-enyl)-vinyl-isoindole-1,3-dione. Column chromatography (Et₂O/hexanes, 1:4) produced a white solid, 56 % (283 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.9-7.6 (m, 4H), δ 5.67 (m, 2H), δ 5.45 (s, 1H), δ 5.18 (s, 1H), δ 2.75 (m, 1H), δ 2.3-1.8 (m, 5H), δ 1.50 (m, 1H); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 167.3, 143.0, 133.9, 131.6, 126.6, 125.2, 123.4, 114.1, 37.2, 29.5, 26.2, 24.8; HRMS: m/z (ESI) calculated $[M+Na]^+ = 275.110$, measured = 276.0998.

3-(Toluene-4-sulfonyl)-3-aza-pentacyclo[9.2.1.1^{5,8}.0^{2,10}.0^{4,9}]pentadecane (Dinorbornyl Pyrrolidine Complex). Column chromatography (Et₂O/hexanes, 1:4) afforded a white solid, 80 % (572 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.66 (d, J= 7.7 Hz, 2H), δ 7.28 (d, J= 7.3 Hz, 2H), δ 3.52 (d, J= 7.0 Hz, 2H), δ 2.74 (s, 2H), δ 2.41 (s, 3H), δ 2.02 (s, 2H), δ 1.71 (d, J= 7.0 Hz, 2H) δ 1.4-0.88 (m, 14H); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 142.7, 139.2, 129.5, 127.2, 76.7, 70.9, 54.6, 43.2, 41.6, 32.6, 27.9, 24.9, 21.6; HRMS: m/z (EI) calculated $[M]^+ = 357.1763$, measured 357.1766.

Crystallographic Experimental Section

Data Collection

A colorless crystal with approximate dimensions $0.47 \times 0.18 \times 0.15 \text{ mm}^3$ was selected under oil under ambient conditions and attached to the tip of a nylon loop. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K_α ($\lambda = 0.71073 \text{ \AA}$) radiation and the diffractometer to crystal distance of 4.9 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about ω with the exposure time of 30 seconds per frame. A total of 53 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 2689 strong reflections from the actual data collection.

The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of a full sphere to a resolution of $0.80 \text{ \AA}$. A total of 7037 data were harvested by collecting three sets of frames with 0.25° scans in ω with an exposure time 75 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. (4)

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups $P\bar{1}$ and $P1$. The E -statistics strongly suggested the centrosymmetric space group $P\bar{1}$ that yielded chemically reasonable and computationally stable results of refinement (4).

A successful solution by the direct methods provided most non-hydrogen atoms from the E -map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Atoms C2 and C3 are equally disordered over two positions and the phenyl ring was refined with soft constraints.

The final least-squares refinement of 245 parameters against 3542 data resulted in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all data) of 0.0710 and 0.1661, respectively. The final difference Fourier map was featureless.

The ORTEP diagram is drawn with 50% probability ellipsoids.

Table 1. Crystal data and structure refinement for stahl20.

Identification code	stahl20	
Empirical formula	C ₂₁ H ₂₇ N O ₂ S	
Formula weight	357.50	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P $\bar{1}$	
Unit cell dimensions	a = 6.2614(10) Å	α = 76.737(3)°
	b = 8.3523(14) Å	β = 88.019(3)°
	c = 17.417(3) Å	γ = 88.673(3)°
Volume	885.9(3) Å ³	
Z	2	
Density (calculated)	1.340 Mg/m ³	
Absorption coefficient	0.198 mm ⁻¹	
F(000)	384	
Crystal size	0.47 x 0.18 x 0.15 mm ³	
Theta range for data collection	1.20 to 26.50°	
Index ranges	-7 ≤ h ≤ 7, -10 ≤ k ≤ 10, -21 ≤ l ≤ 21	
Reflections collected	7037	
Independent reflections	3542 [R(int) = 0.0224]	
Completeness to theta = 26.50°	96.4 %	
Absorption correction	Multi-scan with SADABS	
Max. and min. transmission	0.9710 and 0.9129	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3542 / 6 / 245	
Goodness-of-fit on F ²	1.287	
Final R indices [I > 2σ(I)]	R1 = 0.0710, wR2 = 0.1616	
R indices (all data)	R1 = 0.0830, wR2 = 0.1661	
Largest diff. peak and hole	0.436 and -0.349 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for stahl20. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
S	801(2)	4005(1)	1875(1)	16(1)
O(1)	-1494(4)	4039(3)	1893(2)	22(1)
O(2)	1935(5)	2522(3)	1819(2)	23(1)
N	1550(5)	4489(4)	2670(2)	15(1)
C(1)	1649(5)	5549(5)	1056(2)	17(1)
C(2)	3720(8)	6128(10)	983(5)	20(2)
C(3)	4307(11)	7381(11)	346(4)	24(2)
C(2A)	3746(7)	5542(10)	776(4)	17(2)
C(3A)	4307(11)	6722(9)	105(5)	24(2)
C(4)	2903(7)	7951(6)	-259(2)	33(1)
C(5)	791(7)	7660(5)	-77(3)	29(1)
C(6)	147(7)	6457(6)	576(3)	30(1)
C(7)	3574(10)	9224(8)	-986(3)	58(2)
C(8)	293(6)	5672(4)	3026(2)	15(1)
C(9)	35(6)	7427(5)	2500(2)	19(1)
C(10)	-1433(7)	8393(5)	2960(3)	23(1)
C(11)	14(6)	8716(5)	3612(2)	19(1)
C(12)	2099(6)	7813(4)	3464(2)	16(1)
C(13)	2220(7)	8155(5)	2564(2)	20(1)
C(14)	1692(6)	5953(4)	3702(2)	14(1)
C(15)	3718(6)	4878(4)	3718(2)	14(1)
C(16)	3852(6)	3446(5)	4451(2)	16(1)
C(17)	6089(7)	2656(5)	4455(2)	21(1)
C(18)	6067(7)	1816(5)	3749(2)	21(1)
C(19)	3774(6)	2152(5)	3451(2)	17(1)
C(20)	3640(6)	3977(4)	3024(2)	14(1)
C(21)	2488(6)	2138(5)	4221(2)	18(1)

Table 3. Bond lengths [Å] and angles [°] for stahl20.

S-O(2)	1.435(3)	C(8)-C(14)	1.555(5)
S-O(1)	1.436(3)	C(9)-C(13)	1.528(6)
S-N	1.616(3)	C(9)-C(10)	1.532(5)
S-C(1)	1.765(4)	C(10)-C(11)	1.551(6)
N-C(20)	1.478(5)	C(11)-C(12)	1.536(5)
N-C(8)	1.480(5)	C(12)-C(13)	1.527(5)
C(1)-C(6)	1.375(5)	C(12)-C(14)	1.538(5)
C(1)-C(2A)	1.385(2)	C(14)-C(15)	1.535(5)
C(1)-C(2)	1.386(2)	C(15)-C(16)	1.539(5)
C(2)-C(3)	1.386(2)	C(15)-C(20)	1.565(5)
C(3)-C(4)	1.387(2)	C(16)-C(21)	1.533(5)
C(2A)-C(3A)	1.386(2)	C(16)-C(17)	1.534(5)
C(3A)-C(4)	1.388(2)	C(17)-C(18)	1.550(5)
C(4)-C(5)	1.363(6)	C(18)-C(19)	1.541(5)
C(4)-C(7)	1.509(6)	C(19)-C(20)	1.536(5)
C(5)-C(6)	1.389(6)	C(19)-C(21)	1.538(5)
C(8)-C(9)	1.548(5)		
O(2)-S-O(1)	119.70(18)	C(9)-C(8)-C(14)	102.8(3)
O(2)-S-N	107.10(16)	C(13)-C(9)-C(10)	102.3(3)
O(1)-S-N	107.26(17)	C(13)-C(9)-C(8)	101.7(3)
O(2)-S-C(1)	106.83(17)	C(10)-C(9)-C(8)	106.9(3)
O(1)-S-C(1)	107.02(16)	C(9)-C(10)-C(11)	103.5(3)
N-S-C(1)	108.54(17)	C(12)-C(11)-C(10)	102.4(3)
C(20)-N-C(8)	115.5(3)	C(13)-C(12)-C(11)	101.7(3)
C(20)-N-S	122.9(2)	C(13)-C(12)-C(14)	102.7(3)
C(8)-N-S	121.1(2)	C(11)-C(12)-C(14)	108.0(3)
C(6)-C(1)-C(2A)	118.7(4)	C(12)-C(13)-C(9)	94.2(3)
C(6)-C(1)-C(2)	117.6(4)	C(15)-C(14)-C(12)	114.1(3)
C(2A)-C(1)-C(2)	28.0(4)	C(15)-C(14)-C(8)	107.9(3)
C(6)-C(1)-S	119.3(3)	C(12)-C(14)-C(8)	102.8(3)
C(2A)-C(1)-S	119.6(4)	C(14)-C(15)-C(16)	114.1(3)
C(2)-C(1)-S	121.4(4)	C(14)-C(15)-C(20)	108.2(3)
C(3)-C(2)-C(1)	119.8(6)	C(16)-C(15)-C(20)	103.0(3)
C(2)-C(3)-C(4)	120.4(6)	C(21)-C(16)-C(17)	101.3(3)
C(1)-C(2A)-C(3A)	117.5(6)	C(21)-C(16)-C(15)	102.1(3)
C(2A)-C(3A)-C(4)	122.8(6)	C(17)-C(16)-C(15)	108.3(3)
C(5)-C(4)-C(3)	116.3(5)	C(16)-C(17)-C(18)	103.1(3)
C(5)-C(4)-C(3A)	115.6(5)	C(19)-C(18)-C(17)	103.3(3)
C(3)-C(4)-C(3A)	32.0(4)	C(20)-C(19)-C(21)	101.9(3)
C(5)-C(4)-C(7)	120.3(4)	C(20)-C(19)-C(18)	107.0(3)
C(3)-C(4)-C(7)	121.1(5)	C(21)-C(19)-C(18)	101.9(3)
C(3A)-C(4)-C(7)	121.3(5)	N-C(20)-C(19)	113.9(3)
C(4)-C(5)-C(6)	121.1(4)	N-C(20)-C(15)	103.8(3)
C(1)-C(6)-C(5)	120.0(4)	C(19)-C(20)-C(15)	102.8(3)
N-C(8)-C(9)	115.9(3)	C(16)-C(21)-C(19)	94.4(3)
N-C(8)-C(14)	104.5(3)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for stahl20. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S	18(1)	14(1)	16(1)	-5(1)	-4(1)	1(1)
O(1)	21(2)	24(2)	22(2)	-5(1)	-4(1)	-4(1)
O(2)	35(2)	14(1)	21(2)	-9(1)	-7(1)	5(1)
N	15(2)	14(2)	17(2)	-6(1)	-3(1)	5(1)
C(1)	21(2)	17(2)	13(2)	-6(2)	-3(2)	3(2)
C(2)	25(5)	20(5)	16(5)	-8(4)	-5(3)	7(4)
C(3)	25(5)	23(5)	24(5)	-4(4)	-4(4)	-3(4)
C(2A)	17(4)	24(5)	12(4)	-8(4)	-5(3)	6(4)
C(3A)	18(4)	32(5)	22(5)	-9(4)	1(3)	-8(4)
C(4)	33(3)	37(3)	22(2)	5(2)	0(2)	-1(2)
C(5)	32(3)	24(2)	27(2)	0(2)	-9(2)	9(2)
C(6)	20(2)	36(3)	28(2)	4(2)	-3(2)	3(2)
C(7)	46(3)	68(4)	42(3)	26(3)	-3(3)	-3(3)
C(8)	13(2)	16(2)	16(2)	-6(2)	1(1)	3(2)
C(9)	24(2)	15(2)	18(2)	-5(2)	-7(2)	7(2)
C(10)	21(2)	19(2)	29(2)	-9(2)	-5(2)	7(2)
C(11)	22(2)	14(2)	21(2)	-6(2)	1(2)	3(2)
C(12)	17(2)	14(2)	20(2)	-7(2)	-2(2)	2(2)
C(13)	25(2)	12(2)	22(2)	-2(2)	4(2)	3(2)
C(14)	15(2)	14(2)	14(2)	-3(1)	0(1)	3(1)
C(15)	16(2)	10(2)	16(2)	-4(1)	-1(1)	1(1)
C(16)	21(2)	16(2)	14(2)	-5(2)	-2(2)	3(2)
C(17)	23(2)	18(2)	22(2)	-4(2)	-8(2)	5(2)
C(18)	23(2)	19(2)	20(2)	-3(2)	-2(2)	8(2)
C(19)	19(2)	13(2)	18(2)	-4(2)	-1(2)	4(2)
C(20)	16(2)	13(2)	16(2)	-4(1)	-2(1)	3(1)
C(21)	19(2)	14(2)	19(2)	0(2)	-1(2)	2(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for stahl20.

	x	y	z	U(eq)
H(2)	4733	5668	1370	24
H(3)	5681	7853	323	29
H(2A)	4762	4757	1034	21
H(3A)	5712	6689	-115	28
H(5)	-257	8292	-403	34
H(6)	-1332	6262	690	36
H(7A)	4126	8672	-1393	87
H(7B)	4692	9907	-853	87
H(7C)	2339	9919	-1185	87
H(8)	-1126	5210	3236	18
H(9)	-401	7470	1949	23
H(10A)	-2691	7738	3193	27
H(10B)	-1929	9439	2615	27
H(11A)	247	9907	3552	23
H(11B)	-607	8253	4145	23
H(12)	3381	8166	3706	20
H(13A)	3407	7549	2361	24
H(13B)	2288	9343	2312	24
H(14)	888	5661	4220	17
H(15)	5023	5569	3661	16
H(16)	3391	3738	4958	20
H(17A)	6325	1839	4956	25
H(17B)	7213	3498	4377	25
H(18A)	7134	2307	3334	25
H(18B)	6364	620	3921	25
H(19)	3267	1371	3142	20
H(20)	4852	4295	2634	17
H(21A)	981	2497	4130	22
H(21B)	2558	1062	4604	22

Table 6. Torsion angles [°] for stahl20.

O(2)-S-N-C(20)	25.4(3)	C(8)-C(9)-C(10)-C(11)	73.6(4)
O(1)-S-N-C(20)	155.1(3)	C(9)-C(10)-C(11)-C(12)	-2.7(4)
C(1)-S-N-C(20)	-89.6(3)	C(10)-C(11)-C(12)-C(13)	37.4(4)
O(2)-S-N-C(8)	-163.1(3)	C(10)-C(11)-C(12)-C(14)	-70.3(4)
O(1)-S-N-C(8)	-33.4(3)	C(11)-C(12)-C(13)-C(9)	-56.5(3)
C(1)-S-N-C(8)	81.9(3)	C(14)-C(12)-C(13)-C(9)	55.3(3)
O(2)-S-C(1)-C(6)	127.5(3)	C(10)-C(9)-C(13)-C(12)	54.6(3)
O(1)-S-C(1)-C(6)	-1.8(4)	C(8)-C(9)-C(13)-C(12)	-55.8(3)
N-S-C(1)-C(6)	-117.3(3)	C(13)-C(12)-C(14)-C(15)	82.6(4)
O(2)-S-C(1)-C(2A)	-34.9(6)	C(11)-C(12)-C(14)-C(15)	-170.4(3)
O(1)-S-C(1)-C(2A)	-164.2(5)	C(13)-C(12)-C(14)-C(8)	-34.0(4)
N-S-C(1)-C(2A)	80.3(5)	C(11)-C(12)-C(14)-C(8)	73.0(3)
O(2)-S-C(1)-C(2)	-67.5(6)	N-C(8)-C(14)-C(15)	-1.0(4)
O(1)-S-C(1)-C(2)	163.2(5)	C(9)-C(8)-C(14)-C(15)	-122.4(3)
N-S-C(1)-C(2)	47.7(6)	N-C(8)-C(14)-C(12)	119.9(3)
C(6)-C(1)-C(2)-C(3)	-12.5(12)	C(9)-C(8)-C(14)-C(12)	-1.4(4)
C(2A)-C(1)-C(2)-C(3)	87.4(13)	C(12)-C(14)-C(15)-C(16)	135.0(3)
S-C(1)-C(2)-C(3)	-177.7(7)	C(8)-C(14)-C(15)-C(16)	-111.5(3)
C(1)-C(2)-C(3)-C(4)	-6.2(15)	C(12)-C(14)-C(15)-C(20)	-111.0(3)
C(6)-C(1)-C(2A)-C(3A)	13.9(11)	C(8)-C(14)-C(15)-C(20)	2.5(4)
C(2)-C(1)-C(2A)-C(3A)	-81.5(12)	C(14)-C(15)-C(16)-C(21)	82.5(4)
S-C(1)-C(2A)-C(3A)	176.5(7)	C(20)-C(15)-C(16)-C(21)	-34.4(3)
C(1)-C(2A)-C(3A)-C(4)	4.2(14)	C(14)-C(15)-C(16)-C(17)	-171.1(3)
C(2)-C(3)-C(4)-C(5)	21.8(12)	C(20)-C(15)-C(16)-C(17)	71.9(4)
C(2)-C(3)-C(4)-C(3A)	-74.9(11)	C(21)-C(16)-C(17)-C(18)	37.5(4)
C(2)-C(3)-C(4)-C(7)	-175.3(8)	C(15)-C(16)-C(17)-C(18)	-69.4(4)
C(2A)-C(3A)-C(4)-C(5)	-19.3(12)	C(16)-C(17)-C(18)-C(19)	-2.8(4)
C(2A)-C(3A)-C(4)-C(3)	80.0(12)	C(17)-C(18)-C(19)-C(20)	73.8(4)
C(2A)-C(3A)-C(4)-C(7)	179.6(8)	C(17)-C(18)-C(19)-C(21)	-32.8(4)
C(3)-C(4)-C(5)-C(6)	-19.1(8)	C(8)-N-C(20)-C(19)	113.6(3)
C(3A)-C(4)-C(5)-C(6)	16.6(8)	S-N-C(20)-C(19)	-74.5(4)
C(7)-C(4)-C(5)-C(6)	177.9(5)	C(8)-N-C(20)-C(15)	2.5(4)
C(2A)-C(1)-C(6)-C(5)	-16.5(8)	S-N-C(20)-C(15)	174.4(2)
C(2)-C(1)-C(6)-C(5)	15.3(8)	C(21)-C(19)-C(20)-N	-75.9(4)
S-C(1)-C(6)-C(5)	-179.1(4)	C(18)-C(19)-C(20)-N	177.5(3)
C(4)-C(5)-C(6)-C(1)	0.7(7)	C(21)-C(19)-C(20)-C(15)	35.7(4)
C(20)-N-C(8)-C(9)	111.3(4)	C(18)-C(19)-C(20)-C(15)	-70.8(4)
S-N-C(8)-C(9)	-60.8(4)	C(14)-C(15)-C(20)-N	-3.0(4)
C(20)-N-C(8)-C(14)	-1.0(4)	C(16)-C(15)-C(20)-N	118.1(3)
S-N-C(8)-C(14)	-173.1(2)	C(14)-C(15)-C(20)-C(19)	-121.9(3)
N-C(8)-C(9)-C(13)	-77.0(4)	C(16)-C(15)-C(20)-C(19)	-0.9(4)
C(14)-C(8)-C(9)-C(13)	36.3(4)	C(17)-C(16)-C(21)-C(19)	-56.5(3)
N-C(8)-C(9)-C(10)	176.2(3)	C(15)-C(16)-C(21)-C(19)	55.2(3)
C(14)-C(8)-C(9)-C(10)	-70.6(4)	C(20)-C(19)-C(21)-C(16)	-55.8(3)
C(13)-C(9)-C(10)-C(11)	-32.9(4)	C(18)-C(19)-C(21)-C(16)	54.7(3)

Symmetry transformations used to generate equivalent atoms:

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