Use of Group 4 Bis(sulfonamido) Complexes in the Hydroamination of Alkynes and Allenes

* Prof. R. G. Bergman, Dr. L. Ackermann, Rebecca N. Loy

Department of Chemistry and Center for New Directions in Organic Synthesis

University of California

Berkeley, CA 94720-1460 (USA)

Fax: (+1)510-642-7714

E-mail: bergman@cchem.berkeley.edu

Supporting Information

Lutz Ackermann, Robert G. Bergman*, Rebecca N. Loy

Experimental Section:

General: All syntheses were carried out under N₂ using pre-dried glassware. All hydroamination reactions and complex synthesis were performed in a N₂-filled Vacuum Atmospheres inert atmosphere box. Et₂O, pyridine, THF, and d₆-benzene were dried by distillation over Na and transferred under N₂. CH₂Cl₂, benzene, n-pentane, and toluene were dried by passing through a single column of activated alumina.^{1,2} Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on Bruker AMX300 or AMX400 spectrometers in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. 1,3,5-Trimethoxybenzene (Aldrich) was employed as an internal standard in NMR tube reactions. All cyclization products were > 95% pure by ¹H-NMR and GC/MS. (The purity of some compounds was estimated by ¹H-NMR integrating well-resolved resonances.) IR: Mattson Galaxy FTIR 3000, wavenumbers in cm⁻¹; only selected data are reported. Mass spectra were performed by the University of California, Berkeley Micro-Mass Facility. Compounds **1**³, **2**⁴, **6**⁵, **7**⁶, **10**⁷, **13**⁸, **15**⁸, were prepared as described in the literature. The spectroscopic

data for **11**⁷, **12**⁷, **29**⁹ γ -Conicein¹⁰, and 6-butyl-2,3,4,5-tetrahydro-pyridine¹¹ are consistent with the reported data.

Typical Procedure A for the Synthesis of Imines.¹²

2,4-Dichlorobenzylamine (1.65 g, 9.38 mmol), 2,4-dichlorobenzaldehyde (1.65 g, 9.40 mmol) and K₂CO₃ (0.65 g, 4.70 mmol) in benzene (80 mL) containing crushed 4-Å molecular sieves were stirred overnight at room temperature. The solution was filtered through a plug of Celite[®] using CH₂Cl₂ (200 mL) as eluent. The filtrate was concentrated in *vacuo* to yield (2,4-dichloro-benzyl)-(2,4-dichloro-benzylidene)-amine (2.98 g, 95%) as a pale yellow oil with a purity of > 95% by NMR.

(2,4-Dichloro-benzyl)-(2,4-dichloro-benzylidene)-amine. ¹H NMR (CD₂Cl₂, 300 MHz): δ 8.81 (1H, s), 8.06 (1H, d, J = 8.5 Hz), 7.44 (1H, d, J = 2.1 Hz), 7.43 (1H, d, J = 2.1 Hz), 7.39 (1H, d, J = 8.4 Hz), 7.32 (1H, dd, J = 8.5, 2.1 Hz), 7.27 (1H, dd, J = 8.4, 2.1 Hz), 4.87 (2H, s). MS (EI) m/z (relative intensity) 335 (13) [M^+ , ³⁷Cl₃³⁵Cl₁], 333 (26) [M^+ , ³⁷Cl₁³⁵Cl₃], 163 (10), 161 (64), 160 (10), 159 (100), 123 (14). HR-MS (EI) m/z calcd for C₁₄H₉Cl₄N 332.9460, found 332.9458.

Following the typical procedure A, (4-fluoro-benzyl)-(4-fluoro-benzylidene)-amine (> 99 %) was obtained as a pale yellow oil with a purity > 90% by NMR.

(4-Fluoro-benzyl)-(4-fluoro-benzylidene)-amine. ¹H NMR (C₆D₆, 300 MHz): δ 7.77 (1H, s), 7.50 (2H, tm, J = 7.2 Hz), 7.04 (2H, tm, J = 7.1 Hz), 6.86 (2H, tm, J = 8.7 Hz), 6.75 (2H, tm, J = 8.7 Hz), 4.40 (2H, s). MS (EI) m/z (relative intensity) 231 (29) [M^+], 135 (6), 110 (11), 109 (100), 83 (11). HR-MS (EI) m/z calcd for C₁₄H₁₁F₂N 231.0860, found 231.0857.

Typical Procedure B for the Synthesis of Alkynyl- and Allenylamines.¹³

A solution of *N*-4-methyl-benzyliden-4-methyl-benzylamine (415 mg, 1.86 mmol) in THF (20 mL) was cooled to -78 °C and treated with LDA [prepared from *n*-BuLi (1.6 M in *n*-hexane; 1.0 mL, 2.1 mmol) and diisopropylamine (0.3 mL, 2.1 mmol) in THF (5 mL)] according to the literature.¹⁴ The resulting deep red solution was stirred for 2 h after

which 5-bromopenta-1,2-diene (330 mg, 2.24 mmol) was added and the solution was allowed to warm to room temperature overnight. Saturated aqueous NH_4Cl (10 mL) was added together with sufficient water to dissolve the solids and the product was extracted with Et_2O (3 x 70 mL). The combined extracts were then stirred vigorously with aqueous HCl (2 M, 75 mL) for 3 h. The organic phase was extracted with aqueous HCl (2M, 3 x 50 mL) and the combined aqueous extracts were treated with NaOH at 0 °C until basic. The product was then extracted with Et_2O (3 x 75 mL) and the combined extracts were dried (MgSO_4). Concentration in vacuo and purification of the residue by flash chromatography ($\text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2/\text{MeOH}$ 20/1) afforded 1-(4-methyl-phenyl)-hexa-4,5-dienyl-1-amine (227 mg, 65%) as a pale yellow oil with a purity of 98% by NMR.

1-(4-Methyl-phenyl)-hexa-4,5-dienyl-1-amine. ^1H NMR (CD_2Cl_2 , 300 MHz): δ 7.19 (2H, d, $J = 7.9$ Hz), 7.13 (2H, d, $J = 7.9$ Hz), 5.11 (1H, quint, $J = 6.7$ Hz), 4.67 (2H, dt, $J = 6.7, 3.3$ Hz), 3.87 (1H, t, $J = 6.9$ Hz), 2.32 (3H, s), 2.05-1.80 (2H, m), 1.80-1.65 (2H, m), 1.51 (2H, brs). ^{13}C NMR (C_6D_6 , 100 MHz): δ 208.5, 143.8, 136.4, 129.0, 126.3, 89.6, 74.7, 55.2, 38.9, 25.2, 20.8. IR (CH_2Cl_2): 3379, 1955, 1585 cm^{-1} . MS (EI) m/z (relative intensity) 187 (1) [M^+], 186 (2), 121 (9), 120 (100), 118 (12), 93 (13), 91 (16), 69 (20). HR-MS (EI) m/z calcd for $\text{C}_{13}\text{H}_{18}\text{N}$ 188.1439, found 188.1445.

Following the typical procedure B, **4** (65%) was obtained as a pale yellow oil with a purity of > 95% by NMR.

1-(4-Methyl-phenyl)-hex-5-ynyl-1-amine (4). ^1H NMR (C_6D_6 , 300 MHz): δ 7.11 (2H, d, $J = 8.0$ Hz), 7.01 (2H, d, $J = 7.9$ Hz), 3.58 (2H, t, $J = 6.8$ Hz), 2.18 (3H, s), 1.91 (2H, td, $J = 7.0, 2.7$ Hz), 1.77 (1H, t, $J = 5.3$ Hz), 1.60-1.50 (2H, m), 1.45-1.20 (2H, m), 1.02 (2H, brs). ^{13}C NMR (C_6D_6 , 100 MHz): δ 144.4, 136.2, 129.2, 126.6, 84.3, 69.0, 55.8, 39.1, 25.7, 21.0, 18.6. IR (neat): 3300 cm^{-1} . MS (EI) m/z (relative intensity) 187 (2) [M^+], 186 (2), 172 (2), 171 (3), 121 (32), 120 (100), 93 (34), 91 (30). HR-MS (EI) m/z calcd for $\text{C}_{13}\text{H}_{17}\text{N}$ 187.1361, found 187.1358.

Following the typical procedure B, 1-phenyl-hexa-4,5-dienyl-1-amine (81%) was obtained as a pale yellow oil with a purity of 98 % by NMR.

1-Phenyl-hexa-4,5-dienyl-1-amine. ^1H NMR (C_6D_6 , 300 MHz): δ 7.20-6.95 (5H, m), 4.96 (1H, quint, $J = 6.7$ Hz), 4.55 (2H, dt, $J = 6.7$, 3.3 Hz), 3.62 (1H, t, $J = 6.8$ Hz), 2.00-1.75 (2H, m), 1.65-1.50 (2H, m), 0.86 (2H, brs). ^{13}C NMR (C_6D_6 , 100 MHz): δ 208.9, 147.2, 128.5, 127.0, 126.7, 90.1, 75.1, 55.8, 39.3, 25.4. IR (CH_2Cl_2): 3380, 1955, 1603 cm^{-1} . MS (EI) m/z (relative intensity) 174 (7) [M^+], 119 (11), 106 (100), 104 (15), 79 (25), 77 (20), 69 (38). HR-MS (EI) m/z calcd for $\text{C}_{12}\text{H}_{16}\text{N}$ 174.1283, found 174.1287.

Following the typical procedure B, 1-(4-methoxy-phenyl)-hexa-4,5-dienyl-1-amine (13%) was obtained as a colorless oil with a purity of 98 % by NMR.

1-(4-Methoxy-phenyl)-hexa-4,5-dienyl-1-amine. ^1H NMR (CD_2Cl_2 , 300 MHz): δ 7.24 (2H, d, $J = 6.6$ Hz), 6.84 (2H, d, $J = 6.6$ Hz), 5.10 (1H, quint, $J = 6.7$ Hz), 4.66 (2H, dt, $J = 6.7$, 3.3 Hz), 3.86 (1H, t, $J = 6.9$ Hz), 3.77 (3H, s), 2.00-1.85 (2H, m), 1.75-1.65 (2H, m), 1.43 (2H, brs). ^{13}C NMR (C_6D_6 , 100 MHz): δ 208.4, 158.5, 138.9, 127.4, 113.6, 89.6, 74.7, 55.2, 54.9, 39.0, 25.2. IR (CH_2Cl_2): 3371, 1955, 1611 cm^{-1} . MS (EI) m/z (relative intensity) 203 (4) [M^+], 186 (3), 137 (9), 136 (100), 134 (26), 109 (7). HR-MS (EI) m/z calcd for $\text{C}_{13}\text{H}_{17}\text{NO}$ 203.1310, found 203.1313.

Following the typical procedure B, 1-(4-fluoro-phenyl)-hexa-4,5-dienyl-1-amine (70%) was obtained as a pale yellow oil with a purity of > 95% by NMR.

1-(4-Fluoro-phenyl)-hexa-4,5-dienyl-1-amine. ^1H NMR (C_6D_6 , 300 MHz): δ 6.96 (2H, tm, $J = 7.1$ Hz), 6.82 (2H, tm, $J = 8.7$ Hz), 5.00 (1H, quint, $J = 6.7$ Hz), 4.61 (2H, dt, $J = 6.7$, 3.3 Hz), 3.55 (1H, t, $J = 6.8$ Hz), 1.90-1.70 (2H, m), 1.60-1.40 (2H, m), 0.85 (2H, brs). ^{13}C NMR (CD_2Cl_2 , 100 MHz): δ 208.5, 128.0, 128.0, 115.0, 114.8, 89.5, 74.8, 54.8, 39.0, 25.1. IR (CH_2Cl_2): 3380, 1955, 1603 cm^{-1} . MS (EI) m/z (relative intensity) 192 (9) [$\text{M}^+ + \text{H}$], 175 (8), 137 (9), 124 (100), 122 (12), 97 (15), 69 (32). HR-MS (EI) m/z calcd for $\text{C}_{12}\text{H}_{14}\text{NF}$ 192.1189, found 192.1184.

Following the typical procedure B, 1-(2,4-dichloro-phenyl)-hexa-4,5-dienyl-1-amine (72%) was obtained as a colorless oil with a purity of > 95% by NMR.

1-(2,4-Dichloro-phenyl)-hexa-4,5-dienyl-1-amine. ^1H NMR (CD_2Cl_2 , 300 MHz): δ 7.48 (1H, d, J = 8.4 Hz), 7.36 (1H, d, J = 2.1 Hz), 7.28 (1H, dd, J = 8.4, 2.1 Hz), 5.13 (1H, quint, J = 6.7 Hz), 4.67 (2H, dt, J = 6.7, 3.3 Hz), 4.38 (1H, dd, J = 7.7, 5.6 Hz), 2.25-1.95 (2H, m), 1.85-1.60 (2H, m), 1.45 (2H, brs). ^{13}C NMR (C_6D_6 , 100 MHz): δ 208.5, 142.7, 133.4, 132.5, 129.0, 128.5, 127.4, 89.3, 74.9, 51.0, 37.2, 25.0. IR (CH_2Cl_2): 1955 cm^{-1} . MS (EI) m/z (relative intensity) 242 (1) [M^+H , $^{35}\text{Cl}_2$], 226 (1), 224 (2), 206 (2), 176 (63), 174 (100). HR-MS (EI) m/z calcd for $\text{C}_{12}\text{H}_{12}\text{N}^{35}\text{Cl}^{37}\text{Cl}$ 242.0317, found 242.0313.

Following the typical procedure B, 1-(4-methyl-phenyl)-hepta-5,6-dienyl-1-amine (67%) was obtained as a colorless oil with a purity of 98% by NMR.

1-(4-Methyl-phenyl)-hepta-5,6-dienyl-1-amine. ^1H NMR (C_6D_6 , 300 MHz): δ 7.17 (2H, d, J = 7.8 Hz), 7.03 (2H, d, J = 7.9 Hz), 4.99 (1H, quint, J = 6.7 Hz), 4.59 (2H, dt, J = 6.7, 3.3 Hz), 3.64 (1H, t, J = 6.8 Hz), 2.16 (3H, s), 1.95-1.80 (2H, m), 1.65-1.45 (2H, m), 1.43-1.20 (2H, m), 0.95 (2H, brs). ^{13}C NMR (C_6D_6 , 100 MHz): δ 208.9, 144.6, 136.1, 129.2, 126.7, 90.2, 74.8, 56.1, 39.7, 28.6, 26.4, 21.1. IR (CH_2Cl_2): 3380, 1955, 1590 cm^{-1} . MS (EI) m/z (relative intensity) 202 (7) [M^+H], 186 (8), 185 (10), 121 (13), 120 (100), 93 (13), 91 (10). HR-MS (EI) m/z calcd for $\text{C}_{14}\text{H}_{20}\text{N}$ 202.1596, found 202.1598.

Following the typical procedure B, 1-(4-methyl-phenyl)-hepta-4,5-dienyl-1-amine (84%) was obtained as a colorless oil with a purity of > 95% by NMR.

1-(4-Methyl-phenyl)-hepta-4,5-dienyl-1-amine. ^1H NMR (CD_2Cl_2 , 300 MHz): δ 7.21 (2H, d, J = 8.0 Hz), 7.13 (2H, d, J = 8.0 Hz), 5.15-5.00 (2H, m), 3.88 (1H, t, J = 6.9 Hz), 2.32 (3H, s), 2.05-1.85 (2H, m), 1.71 (2H, t, J = 7.2 Hz), 1.68-1.55 (3H, m), 1.46 (2H, brs). ^{13}C NMR (CD_2Cl_2 , 100 MHz): δ 204.6, 143.9, 136.4, 129.0, 126.3, 89.9, 85.8, 55.2, 39.0, 25.9, 20.8, 14.4. IR (neat): 3369, 1964, 1583 cm^{-1} . MS (EI) m/z (relative intensity) 201

(0.4) $[M^+]$, 200 (1), 186 (2), 185 (2), 169 (1), 158 (2), 133 (20), 120 (100), 91 (12), 83 (30). HR-MS (EI) m/z calcd for $C_{14}H_{19}N$ 201.1518, found 201.1505.

Following the typical procedure B, 1-(4-methyl-phenyl)-octa-4,5-dienyl-1-amine (45%) was obtained as a pale yellow oil with a purity of > 95% by NMR.

1-(4-Methyl-phenyl)-octa-4,5-dienyl-1-amine. 1H NMR (C_6H_6 , 300 MHz): δ 7.18 (2H, d, $J = 7.9$ Hz), 7.02 (2H, d, $J = 7.9$ Hz), 5.20-5.00 (2H, m), 3.75 (Diastereomer I, 1H, t, $J = 6.8$ Hz), 3.75 (Diastereomer II, 1H, t, $J = 6.8$ Hz), 2.21 (3H, s), 2.10-1.85 (4H, m), 1.80-1.65 (2H, m), 1.00 (2H, brs), 0.96 (3H, t, $J = 7.4$ Hz). ^{13}C NMR (CD_2Cl_2 , 100 MHz): δ 204.0, 144.5, 136.2, 129.2, 126.7, 93.2, 91.8, 55.6 (Diastereomer I), 55.6 (Diastereomer II), 39.7, 26.3, 22.4, 21.0, 13.7 (Diastereomer I), 13.6 (Diastereomer I). IR (neat): 3366, 1962 cm^{-1} . MS (EI) m/z (relative intensity) 215 (0.8) $[M^+]$, 214 (2), 200 (1), 199 (1), 186 (5), 133 (48), 120 (100), 97 (53), 93 (26), 91 (22), 77 (17). HR-MS (EI) m/z calcd for $C_{15}H_{22}N$ 216.1752, found 216.1747.

Following the typical procedure B, 1-(4-methyl-phenyl)-6-methyl-octa-4,5-dienyl-1-amine (15 %) was obtained as a colorless oil with a purity of 90% by NMR.

1-(4-Methyl-phenyl)-6-methyl-octa-4,5-dienyl-1-amine. 1H NMR (CD_2Cl_2 , 300 MHz): δ 7.23 (2H, d, $J = 8.0$ Hz), 7.12 (2H, d, $J = 7.9$ Hz), 5.10-5.00 (1H, m), 3.88 (1H, t, $J = 6.9$ Hz), 2.34 (3H, s), 2.00-1.80 (4H, m), 1.75-1.60 (m, 5H), 1.52 (2H, brs), 0.98 (Diastereomer I, 3H, t, $J = 7.4$ Hz), 0.98 (Diastereomer II, 3H, t, $J = 7.4$ Hz). ^{13}C NMR (CD_2Cl_2 , 100 MHz): δ 200.9, 144.0, 136.3, 129.0, 126.3, 90.4 (I), 90.4 (II), 70.8 (I), 70.8 (II), 55.3 (I), 55.2 (II), 39.2, 27.0, 26.4, 20.8, 19.1, 12.2 (I), 12.2 (II). IR (neat): 3357, 1964 cm^{-1} . MS (EI) m/z (relative intensity) 229 (0.7) $[M^+]$, 214 (1), 212 (5), 200 (1), 197 (2), 183 (3), 132 (45), 120 (100), 111 (36), 96 (23), 77 (15). HR-MS (EI) m/z calcd for $C_{16}H_{23}N$ 229.1831, found 229.1829.

General procedure for the synthesis of toluene-4-sulfonic acid dienyl ester:

To an ice-cold solution of the respective alcohol (10 mmol) in pyridine (6 mL) was added tosyl chlorid (13 mmol). After 90 minutes, the mixture was allowed to warm to room

temperature and stirred for one hour, followed by storage at $-35\text{ }^{\circ}\text{C}$ overnight. The mixture was diluted with Et_2O (50 mL), and washed with aqueous HCl (2N, 3 x 20 mL). The aqueous washings were extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with brine and dried (MgSO_4). Evaporation of the solvent in vacuo yielded the corresponding tosylate in quantitative yield, which was used without further purification.

Toluene-4-sulfonic acid hepta-3,4-dienyl ester. ^1H NMR (CD_2Cl_2 , 300 MHz): δ 7.76 (2H, d, $J = 8.3$ Hz), 7.36 (2H, d, $J = 8.4$ Hz), 5.25-5.15 (1H, m), 5.10-5.00 (1H, m), 4.06 (2H, t, $J = 6.7$ Hz), 2.44 (3H, s), 2.32 (2H, dq, $J = 6.6, 2.9$ Hz), 2.00-1.90 (2H, m), 0.95 (3H, t, $J = 7.4$ Hz). ^{13}C NMR (CD_2Cl_2 , 100 MHz): δ 204.2, 145.0, 133.1, 129.9, 127.8, 93.9, 68.3, 69.7, 28.6, 21.7, 21.4, 13.0. IR (neat): 1964 cm^{-1} .

Toluene-4-sulfonic acid octa-3,4-dienyl ester. ^1H NMR (CD_2Cl_2 , 300 MHz): δ 7.61 (2H, d, $J = 8.4$ Hz), 7.37 (2H, d, $J = 8.4$ Hz), 5.15-5.10 (1H, m), 5.05-4.95 (1H, m), 4.05 (2H, t, $J = 6.8$ Hz), 2.45 (3H, s), 2.30 (2H, dq, $J = 6.7, 2.9$ Hz), 1.91 (2H, dq, $J = 7.3, 2.9$ Hz), 1.37 (2H, m), 0.89 (3H, t, $J = 7.3$ Hz). ^{13}C NMR (CD_2Cl_2 , 100 MHz): δ 204.7, 145.0, 133.1, 129.9, 127.9, 92.0, 85.5, 69.8, 30.7, 28.6, 22.3, 21.4, 13.4.

Toluene-4-sulfonic acid 5-methyl-hepta-3,4-dienyl ester. ^1H NMR (CD_2Cl_2 , 300 MHz): δ 7.77 (2H, d, $J = 8.4$ Hz), 7.38 (2H, d, $J = 8.4$ Hz), 5.00-4.90 (1H, m), 4.03 (2H, t, $J = 6.8$ Hz), 2.43 (3H, s), 2.23 (2H, q, $J = 6.7$ Hz), 1.88 (dq, 2H, $J = 7.3, 3.2$ Hz), 1.63 (3H, d, $J = 2.8$ Hz), 0.92 (3H, t, $J = 7.3$ Hz). ^{13}C NMR (CD_2Cl_2 , 100 MHz): δ 201.7, 147.5, 145.0, 129.9, 127.8, 85.4, 70.0, 65.7, 29.0, 26.8, 18.8, 15.2, 12.0.

Typical procedure C for the synthesis of the dienitriles:

Toluene-4-sulfonic acid hepta-3,4-dienyl ester (2.13 g, 8.0 mmol) was dissolved in dry DMSO (5 mL) and NaCN (1.16 g, 23.7 mmol) was added to the solution. The mixture was stirred for 18 h at room temperature under nitrogen, diluted with water (10 mL), and

extracted with Et₂O (4 x 25 mL). The combined extracts were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo. Purification by column chromatography (silica gel, *n*-pentane/Et₂O 15/1→10/1→6/1→4/1) yielded 0.87 g octa-4,5-dienitrile (89%) as a colorless oil with a purity of 98% by NMR.

Octa-4,5-dienitrile. ¹H NMR (CD₂Cl₂, 300 MHz): δ 5.40-5.30 (1H, m), 5.25-5.15 (1H, m), 2.42 (2H, t, *J* = 7.2 Hz), 2.35-2.25 (2H, m), 2.10-1.95 (2H, m), 1.01 (3H, t, *J* = 7.4 Hz). ¹³C NMR (CD₂Cl₂, 100 MHz): δ 203.5, 119.5, 95.4, 88.7, 24.7, 21.9, 16.5, 13.1. IR (neat): 2246, 1964 cm⁻¹. MS (EI) *m/z* (relative intensity) 121 (15) [M⁺], 120 (83), 106 (100), 91 (22), 81 (94), 79 (100), 67 (54). HR-MS (EI) *m/z* calcd for C₈H₁₀N 120.0813, found 120.0813.

Prepared from Toluene-4-sulfonic acid octa-3,4-dienyl ester in 97% yield following the typical procedure C.

Nona-4,5-dienitrile. ¹H NMR (CD₂Cl₂, 400 MHz): δ 5.30-5.20 (1H, m), 5.20-5.10 (1H, m), 2.43 (2H, t, *J* = 7.0 Hz), 2.35-2.25 (2H, m), 2.10-1.90 (2H, m), 1.43 (2H, sextett, *J* = 7.4 Hz), 0.93 (3H, t, *J* = 7.4 Hz). ¹³C NMR (CD₂Cl₂, 100 MHz): δ 204.0, 119.5, 93.5, 87.9, 30.9, 24.8, 22.4, 16.6, 13.5. IR (neat): 2247, 1964 cm⁻¹. MS (EI) *m/z* (relative intensity) 135 (4) [M⁺], 134 (24), 120 (45), 107 (30), 106 (100), 95 (37), 79 (79), 77 (41), 67 (81). HR-MS (EI) *m/z* calcd for C₉H₁₂N 134.0970, found 134.0974. C₉H₁₂N (135.21) Anal. Calcd C, 79.95; H, 9.69; N, 10.36. Found C, 79.68; H, 9.77; N, 10.66.

Prepared from Toluene-4-sulfonic acid 5-methyl-hepta-3,4-dienyl ester in 38% yield with a purity of 95% by NMR, following the typical procedure C.

6-Methyl-octa-4,5-dienitrile. ¹H NMR (CD₂Cl₂, 300 MHz): δ 5.15-5.10 (1H, m), 2.45-2.35 (2H, m), 2.30-2.25 (2H, m), 2.00-1.90 (2H, m), 1.71 (3H, d, *J* = 2.8 Hz), 1.00 (3H, t, *J* = 7.4 Hz). ¹³C NMR (CD₂Cl₂, 100 MHz): δ 200.9, 119.7, 104.4, 87.9, 26.9, 25.2, 18.8, 16.6, 12.1. IR (neat): 2246, 1966 cm⁻¹. MS (EI) *m/z* (relative intensity) 135 (7) [M⁺], 134 (30), 120 (100), 106 (53), 95 (22), 93 (22), 79 (46). HR-MS (EI) *m/z* calcd for C₉H₁₂N 134.0970, found 134.0972.

Typical procedure D for the synthesis of the dienylamines:

To an ice-cold suspension of LiAlH_4 (0.57 g, 14.9 mmol) in Et_2O (50 mL) under N_2 was added octa-4,5-dienitrile (0.82 g, 6.8 mmol) in Et_2O (7 mL) over 5 minutes. After 30 minutes, the mixture was allowed to warm to room temperature and was stirred for additional 15 minutes at this temperature. At 0 °C, the mixture was diluted with CH_2Cl_2 (30 mL), and quenched by the dropwise addition of saturated aqueous Na_2SO_4 (50 mL). Et_2O (100 mL) was added. The separated aqueous phase was extracted with Et_2O (3 x 50 mL). The combined organic phases were dried (MgSO_4) and concentrated in vacuo to yield 0.68 mg (80%) octa-4,5-dienylamine as a pale yellow oil with a purity of >95% by NMR.

Octa-4,5-dienylamine. ^1H NMR (CD_2Cl_2 , 300 MHz): δ 5.20-5.05 (2H, m), 2.67 (2H, t, $J = 7.0$ Hz), 2.05-1.95 (4H, m), 1.55-1.45 (2H, m), 1.15 (2H, brs), 0.99 (3H, t, $J = 7.4$ Hz). ^{13}C NMR (CD_2Cl_2 , 100 MHz): δ 203.5, 92.5, 91.4, 41.7, 33.4, 26.4, 22.1, 13.3. IR (neat): 3305, 1962 cm^{-1} . MS (EI) m/z (relative intensity) 125 (15) [M^+], 110 (100), 96 (31), 82 (95), 79 (49), 77 (38), 67 (87). HR-MS (EI) m/z calcd for $\text{C}_8\text{H}_{15}\text{N}$ 125.1205, found 125.1202.

Following the typical procedure D, nona-4,5-dienylamine (54%) was obtained as a colorless oil with a purity of 98% by NMR.

Nona-4,5-dienylamine. ^1H NMR (CD_2Cl_2 , 300 MHz): δ 5.15-5.00 (2H, m), 2.66 (2H, t, $J = 7.0$ Hz), 2.05-1.90 (4H, m), 1.55-1.35 (4H, m), 1.02 (2H, brs), 0.92 (3H, t, $J = 7.3$ Hz). ^{13}C NMR (CD_2Cl_2 , 75 MHz): δ 204.0, 90.9, 90.4, 41.7, 33.4, 31.2, 26.4, 22.5, 13.5. IR (neat): 3362, 1962 cm^{-1} . MS (EI) m/z (relative intensity) 139 (2) [M^+], 111 (18), 110 (100), 96 (24), 82 (93), 79 (37). HR-MS (EI) m/z calcd for $\text{C}_9\text{H}_{17}\text{N}$ 124.1266, found 124.1267.

Following the typical procedure D, 6-methyl-octa-4,5-dienylamine (51%) was obtained as a colorless oil with a purity of > 95% by NMR.

6-Methyl-octa-4,5-dienylamine. ^1H NMR (CD_2Cl_2 , 300 MHz): δ 5.10-5.00 (1H, m), 2.66 (2H, t, $J = 7.1$ Hz), 2.00-1.95 (4H, m), 1.92 (2H, dq, $J = 7.4, 3.2$

Hz), 1.66 (3H, d, $J = 2.9$ Hz), 1.09 (2H, brs), 0.97 (3H, t, $J = 7.4$ Hz). ^{13}C NMR (CD_2Cl_2 , 100 MHz): δ 200.8, 101.3, 90.4, 41.8, 33.5, 27.0, 26.8, 19.0, 12.2. IR (neat): 3357, 1964 cm^{-1} . MS (EI) m/z (relative intensity) 139 (17) [M^+], 124 (60), 110 (13), 96 (64), 81 (100), 79 (40). HR-MS (EI) m/z calcd for $\text{C}_9\text{H}_{17}\text{N}$ 139.1361, found 139.1362.

Typical procedure for the hydroamination/cyclization reaction:

A solution of **18** (121 mg, 0.63 mmol) and **11** (18 mg, 0.03 mmol) in benzene (3 mL) was heated for 10 h to 75 °C. The solution was cooled and treated with 20 drops of methanolic NaOH (10 %). The mixture was stirred for 0.5 h at room temperature and concentrated in vacuo. The remaining residue was extracted with *n*-hexane (30 mL) and filtered through K_2CO_3 to afford 2-(4-fluoro-phenyl)-6-methyl-2,3,4,5-tetrahydro-pyridine (112 mg, 93%) as a pale yellow oil with a purity of > 95% by NMR.

2-(4-Fluoro-phenyl)-6-methyl-2,3,4,5-tetrahydro-pyridine. ^1H NMR (CD_2Cl_2 , 300 MHz): δ 7.23 (m, 2H), 7.01 (tm, 2H, $J = 8.9$ Hz), 4.43 (m, 1H), 2.30-2.10 (m, 2H), 1.98 (d, 3H, $J = 2.0$ Hz), 1.95-1.60 (m, 3H), 1.40-1.20 (m, 1H). ^{13}C NMR (CD_2Cl_2 , 100 MHz): δ 168.6, 128.4, 128.3, 114.8, 114.5, 60.8, 30.6, 29.9, 27.3, 19.0. MS (EI) m/z (relative intensity) 191 (81) [M^+], 163 (14), 162 (14), 148 (11), 121 (100), 109 (10). HR-MS (EI) m/z calcd for $\text{C}_{12}\text{H}_{14}\text{FN}$ 191.1110, found 191.1109.

2-Phenyl-6-methyl-2,3,4,5-tetrahydro-pyridine. ^1H NMR (CD_2Cl_2 , 400 MHz): δ 7.32 (2H, tm, $J = 6.4$ Hz), 7.28-7.15 (3H, m), 4.47 (1H, m), 2.30-2.10 (2H, m), 2.00 (3H, d, $J = 2.0$ Hz), 1.85-1.30 (4H, m). ^{13}C NMR (CD_2Cl_2 , 100 MHz): δ 168.4, 146.1, 128.1, 126.8, 126.2, 61.5, 30.6, 29.9, 27.3, 19.0. MS (EI) m/z (relative intensity) 173 (86) [M^+], 145 (13), 144 (17), 130 (11), 105 (10), 104 (100), 103 (12), 91 (10), 77 (11). HR-MS (EI) m/z calcd for $\text{C}_{12}\text{H}_{15}\text{N}$ 173.1205, found 173.1205.

The analytical data are consistent with the reported data.¹⁵

2-(4-Methyl-phenyl)-6-methyl-2,3,4,5-tetrahydro-pyridine. ^1H NMR (C_6D_6 , 400 MHz): δ 7.34 (2H, d, $J = 8.1$ Hz), 7.12 (2H, d, $J = 8.0$ Hz),

4.51 (1H, m), 2.18 (3H, s), 1.87 (3H, d, $J = 1.9$ Hz), 1.85-1.72 (1H, m), 1.70-1.55 (2H, m), 1.45-1.20 (3H, m). ^{13}C NMR (CD_2Cl_2 , 100 MHz): δ 163.5, 143.7, 135.4, 129.0, 127.2, 61.1, 30.8, 29.7, 27.5, 21.1, 19.2. IR (CH_2Cl_2): 1661 cm^{-1} . MS (EI) m/z (relative intensity) 187 (100) [M^+], 186 (27), 144 (31), 118 (51), 117 (16). HR-MS (EI) m/z calcd for $\text{C}_{13}\text{H}_{17}\text{N}$ 187.1361, found 187.1361.

2-(4-Methoxy-phenyl)-6-methyl-2,3,4,5-tetrahydro-pyridine.

^1H NMR (C_6D_6 , 300 MHz): δ 7.30 (2H, d, $J = 8.7$ Hz), 6.83 (2H, d, $J = 8.7$ Hz), 4.47 (1H, m), 3.34 (3H, s), 1.87 (3H, d, $J = 1.9$ Hz), 1.80-1.55 (3H, m), 1.50-1.15 (3H, m). ^{13}C NMR (C_6D_6 , 100 MHz): δ 166.9, 158.8, 138.5, 128.1, 113.5, 60.7, 54.8, 30.8, 29.7, 27.4, 19.0. MS (EI) m/z (relative intensity) 203 (93) [M^+], 188 (19), 160 (20), 134 (100), 121 (16), 119 (11), 91 (14), 86 (50), 84 (78), 51 (35). HR-MS (EI) m/z calcd for $\text{C}_{13}\text{H}_{17}\text{NO}$ 203.1310, found 203.1309.

2-(2,4-Dichloro-phenyl)-6-methyl-2,3,4,5-tetrahydro-pyridine.

^1H NMR (CD_2Cl_2 , 300 MHz): δ 7.37 (1H, d, $J = 2.1$ Hz), 7.25 (1H, dd, $J = 8.4, 2.1$ Hz), 7.15 (1H, d, $J = 8.4$ Hz), 4.78 (1H, m), 2.30-2.15 (2H, m), 2.10-2.00 (1H, m), 2.01 (3H, d, $J = 2.0$ Hz), 1.80-1.65 (2H, m), 1.25-1.10 (1H, m). ^{13}C NMR (CD_2Cl_2 , 100 MHz): δ 169.7, 142.0, 133.0, 132.3, 129.7, 128.7, 127.1, 58.3, 29.9, 28.5, 27.3, 19.0. MS (EI) m/z (relative intensity) 243 (11) [M^+ , $^{35}\text{Cl}^{37}\text{Cl}$], 241 (88) [M^+ , $^{35}\text{Cl}_2$], 213 (14), 208 (22), 206 (72), 178 (74), 174 (70), 172 (100), 137 (17), 123 (20). HR-MS (EI) m/z calcd for $\text{C}_{12}\text{H}_{13}\text{Cl}_2\text{N}$ 243.0396, found 243.0400.

2-(4-Methyl-phenyl)-6-ethyl-2,3,4,5-tetrahydro-pyridine.

^1H NMR (CD_2Cl_2 , 300 MHz): δ 7.13-7.12 (4H, m), 4.44 (1H, m), 2.33 (3H, s), 2.25 (2H, q, $J = 7.6$ Hz), 2.20-2.10 (1H, m), 2.00-1.90 (1H, m), 1.80-1.60 (2H, m), 1.45-1.25 (2H, m), 1.12 (3H, t, $J = 7.6$ Hz). ^{13}C NMR (CD_2Cl_2 , 100 MHz): δ 171.8, 143.2, 135.7, 128.7, 126.8, 60.9, 33.7, 31.1, 28.6, 20.8, 18.9, 10.6. MS (EI) m/z (relative intensity) 202 (21) [$\text{M}^+ + \text{H}$], 201 (100) [M^+], 200 (29), 186 (28), 158 (19), 118 (61), 105 (14), 91 (12). HR-MS (EI) m/z calcd for $\text{C}_{14}\text{H}_{19}\text{N}$ 201.1518, found 201.1523.

2-(4-Methyl-phenyl)-6-*n*-propyl-2,3,4,5-tetrahydro-pyridine.

^1H NMR (C_6D_6 , 400 MHz): δ 7.34 (2H, d, $J = 8.0$ Hz), 7.12 (2H, d, $J = 8.0$ Hz), 4.53 (1H, m), 2.19 (3H, s), 2.15-2.05 (2H, m), 1.85-1.65 (4H, m), 1.45-1.20 (4H, m), 0.95 (3H, t, $J = 7.4$ Hz). ^{13}C NMR (C_6D_6 , 100 MHz): δ 169.4, 143.8, 135.5, 129.0, 127.1, 60.9, 42.8, 31.3, 21.1, 19.8, 19.2, 14.2. MS (EI) m/z (relative intensity) 215 (77) [M^+], 200 (32), 187 (100), 186 (51), 172 (16), 144 (23), 118 (63). HR-MS (EI) m/z calcd for $\text{C}_{15}\text{H}_{21}\text{N}$ 215.1674, found 215.1678.

General procedure for formation of trifluoro acetamide derivatives:

Volatile allylamines were isolated as the corresponding trifluoro acetamides: CH_2Cl_2 (5 mL) was added to the crude reaction mixture. Thereafter, $(\text{F}_3\text{CCO})_2\text{O}$ (0.05 mL) was added and the mixture was stirred overnight at room temperature. H_2O (5 mL) was added. The separated aqueous phase was washed with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried (MgSO_4) and concentrated in vacuo.

(Z)-2But-1-enyl-pyrrolidine. ^1H NMR (C_6D_6 , 300 MHz): δ 5.45 (2H, m), 3.71 (1H, q, $J = 7.2$ Hz), 2.88 (1H, m), 2.66 (1H, m), 1.95 (1H, m), 1.80-1.65 (2H, m), 1.60-1.40 (2H, m), 1.33 (1H, m), 1.05 (1H, brs), 0.92 (3H, t, $J = 7.5$ Hz). ^{13}C NMR (C_6D_6 , 100 MHz): δ 133.7, 131.9, 55.9, 46.9, 33.3, 25.9, 21.3, 14.8.

(Z)-2,2,2-Trifluoro-1-(2-but-1-enyl-pyrrolidin-1-yl)-ethanone. ^1H NMR (CD_2Cl_2 , 400 MHz): δ 5.49 (1H, dt, $J = 10.8, 7.3$ Hz), 5.20 (1H, dd, $J = 10.7, 9.1$ Hz), 4.82 (1H, m), 3.65 (2H, t, $J = 6.7$ Hz), 2.30-1.85 (3H, m), 1.70 (1H, m), 1.50-1.20 (2H, m), 0.93 (3H, t, $J = 7.3$ Hz). IR (neat): 1642 cm^{-1} . MS (GC/MS) m/z (relative intensity) 221 (2) [M^+], 206 (4), 192 (46), 166 (100), 152 (43), 69 (18), 55 (6). $\text{C}_{10}\text{H}_{14}\text{F}_3\text{NO}$ (221.22) calcd C, 54.29; H, 6.38; N, 6.33; found C, 54.03; H, 6.56; N, 6.46.

The analytical data are consistent with the reported data.¹⁶

(Z)-2Pent-1-enyl-pyrrolidine. ^1H NMR (C_6D_6 , 300 MHz): δ 5.50-5.30 (2H, m), 3.72 (1H, m), 2.90 (1H, m), 2.73 (1H, m), 2.03 (2H, m), 1.80-1.45 (2H, m), 1.40-1.20 (4H, m), 1.05 (1H, brs), 0.86 (3H, t, $J = 7.3$ Hz). ^{13}C NMR (C_6D_6 , 100 MHz): δ 134.5, 130.0, 55.9, 46.9, 33.3, 30.0, 25.9, 23.4, 13.9. **(Z)-2,2,2-Trifluoro-1-(2-pent-1-enyl-pyrrolidin-1-yl)-ethanone.** ^1H NMR (CD_2Cl_2 , 400 MHz): δ

5.49 (1H, dtd, $J = 10.8, 7.4, 1.0$ Hz), 5.23 (1H, ddt, $J = 10.8, 9.1, 1.5$ Hz), 4.82 (1H, m), 3.66 (2H, t, $J = 6.7$ Hz), 2.30-1.90 (4H, m), 1.70 (1H, m), 1.50-1.20 (3H, m), 0.93 (3H, t, $J = 7.3$ Hz). IR (neat): 1642 cm^{-1} . MS (EI) m/z (relative intensity) 235 (13) [M^+], 220 (13), 206 (14), 205 (18), 192 (33), 166 (100), 149 (7), 124 (6). HR-MS (EI) m/z calcd for $C_{11}H_{16}F_3NO$ 235.1184, found 235.1183.

(*E/Z*)-2-(2-Methyl-but-1-enyl)-pyrrolidine. ^1H NMR (C_6D_6 , 300 MHz): δ 5.23 (1H, dq, $J = 8.2, 1.2$ Hz, *E*-Isomer), 5.17 (1H, d, $J = 8.5$ Hz, *Z*-Isomer), 3.65 (1H, m), 2.92 (1H, m), 2.69 (1H, m), 2.10-1.70 (4H, m), 1.64 (3H, d, $J = 1.4$ Hz, *Z*-Isomer), 1.61 (3H, d, $J = 1.2$ Hz, *E*-Isomer), 1.60-1.50 (2H, m), 1.25 (1H, m), 0.97 (3H, t, $J = 7.4$ Hz, *E*-Isomer), 0.94 (3H, t, $J = 7.7$ Hz, *Z*-Isomer). ^{13}C NMR (C_6D_6 , 100 MHz): δ 138.0, 137.6, 129.3, 128.1, 57.0, 56.6, 47.0, 38.9, 33.6, 33.3, 32.6, 26.0, 26.0, 25.6, 23.0, 16.4, 13.6, 12.8. **(*E/Z*)-2,2,2-Trifluoro-1-[2-(2-methyl-but-1-enyl)-pyrrolidin-1-yl]-ethanone.** IR (CH_2Cl_2): 1691 cm^{-1} . MS (EI) m/z (relative intensity) 235 (1) [M^+], 220 (3), 206 (25), 167 (8), 166 (100). HR-MS (EI) m/z calcd for $C_{11}H_{16}F_3NO$ 235.1184, found 235.1187.

General procedure E for the synthesis of titanium and zirconium complexes.⁸

Under an N_2 -atmosphere, the appropriate ligand (1 mmol) was stirred in Et_2O (10 mL) at room temperature. To this mixture was added $Ti(NMe_2)_4$ (1mmol) as a solution in Et_2O (1 mL) in one portion. On addition of the titanium complex, the mixture turned red-brown and the ligand dissolved to give a clear solution. If necessary, the solution was filtered after the ligand had dissolved. When no undissolved ligand remained, stirring was discontinued and the solution was cooled to $-35\text{ }^\circ\text{C}$. The solution was decanted, washed with cold Et_2O (1 mL, $-35\text{ }^\circ\text{C}$), and the product was dried in vacuo.

Following the general procedure E, **8** was obtained as red crystals in 55 % yield.

^1H NMR (C_6D_6 , 300 MHz): δ 7.81 (2H, d, $J = 8.0$ Hz), 7.59 (2H, d, $J = 8.8$ Hz), 7.38 (2H, d, $J = 8.5$ Hz), 7.23 (2H, dd, $J = 7.4, 7.4$ Hz), 6.99 (2H, dd, $J = 8.4, 8.1$ Hz), 6.80 (2H, d, $J = 8.7$ Hz), 2.91 (12 H, s). ^{13}C NMR (C_6D_6 , 100 MHz): δ 160.2,

134.1, 130.1, 129.4, 128.5, 127.6, 125.9, 123.5, 121.0, 119.1, 46.2. IR (CH₂Cl₂): 3063, 3045, 2950, 2863, 2774, 1590, 1503, 1462, 1331, 1241, 1150, 1073, 995, 952 cm⁻¹. C₂₄H₂₄N₂O₂Ti (512.33) Anal. Calcd C, 68.58; H, 5.75; N, 6.66. Found C, 68.26; H, 5.82; N, 6.44.

Following the general procedure E, **16** was obtained as red crystals in 69% yield.

Following the general procedure E, **17** was obtained as red crystals in 47 % yield.

Following the general procedure E, **21** was obtained as white crystals in 99 % yield.

A solution of **13** (81 mg, 0.13 mmol), 2,6-dimethylaniline (32 mg, 0.26 mmol), and pyridine (0.16 mg, 0.20 mmol) in toluene (4 mL) was heated to 85 °C for 24 h. The solvent was removed in vacuo to afford a red oil. Benzene (5 mL) was added and the mixture was filtered. The solution was concentrated in vacuo to yield a red foam. Washing with n-pentane (4 x 2 mL) and drying in vacuo afforded 60 mg **27** (63%) as a brick-red powder. It was not possible to completely remove the excess of free amine.

^1H NMR (C_6D_6 , 400 MHz): δ 9.23 (2H, d, $J = 4.9$ Hz, *o*-py), 6.91 (2H, d, $J = 7.5$ Hz, *m*-imido), 6.76 (1H, t, $J = 7.6$ Hz, *p*-py), 6.69 (1H, t, $J = 7.4$ Hz, *p*-imido), 6.61 (2H, s, *Mes*), 6.56 (2H, s, *Mes*), 6.48 (2H, t, $J = 7.0$ Hz, *m*-py), 4.32 (1H, m, NCH), 3.77 (1H, m, NCH), 3.00 (6H, s, *o*-Me-imido), 2.64 (6H, s, *o*-Me-Mes), 2.60 (6H, s, *o*-Me-Mes), 2.25-2.15 (2H, m, Cy), 1.90 (3H, s, *p*-Me-Mes), 1.87 (3H, s, *p*-Me-Mes), 1.60-1.50 (2H, m, Cy), 1.25-0.95 (4H, m, Cy). ^{13}C NMR (C_6D_6 , 100 MHz): δ 159.4, 150.7, 140.9, 138.3, 138.2, 132.8, 131.6, 128.0, 127.0, 123.7, 120.7, 46.4, 33.3, 24.8, 23.3, 23.2, 20.3, 20.2, 19.5. IR (CH_2Cl_2): 3029, 2978, 2938, 2860, 1604, 1564, 1469, 1447, 1405, 1310, 1241, 1156, 1070, 1035, 982, 900 cm^{-1} . $\text{C}_{37}\text{H}_{46}\text{N}_4\text{O}_4\text{S}_2\text{Ti}$ (722.81) Anal. Calcd C, 61.48; H, 6.41; N, 7.75. Found C, 60.98; H, 6.99; N, 7.10.

Figure S-1. ORTEP diagram of **20**. Thermal ellipsoids are shown at 50% probability.

Table S-1. Crystal and Data Collection Parameters for **20**.

a. Crystal Data

Empirical Formula	$\text{ZrS}_2\text{O}_4\text{N}_5\text{C}_{26}\text{H}_{43}$
Formula Weight	645.00
Crystal Color, Habit	colorless, bladelike
Crystal Dimensions (mm)	0.19 X 0.22 X 0.28
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	$a = 17.6761(6) \text{ \AA}$ $b = 9.1902(3) \text{ \AA}$ $c = 19.6839(7) \text{ \AA}$ $\beta = 103.483(1)^\circ$ $V = 3109.5(2) \text{ \AA}^3$
Space Group	$P2_1$ (No. 4)
Z value	4
D_{calc}	1.378 g/cm^3
F_{000}	1352.00
$\mu(\text{MoK}_\alpha)$	5.26 cm^{-1}

b. Intensity Measurements

Diffractometer	Bruker SMART CCD
Radiation	MoK_α ($\lambda = 0.71069 \text{ \AA}$) graphite monochromated
Detector Position	60.00 mm
Scan Type	ω (0.3 degrees per frame)
$2\theta_{\text{max}}$	49.3°

No. of Reflections Measured	Total: 13822 Unique: 9170 ($R_{int} = 0.039$)
Corrections	Lorentz-polarization Absorption ($T_{max} = 1.00$, $T_{min} = 0.57$)
c. Structure Solution and Refinement	
Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares
Function Minimized	$\sum w(F_o - F_c)^2$
Least Squares Weights	$w = 1/\sigma^2(F_o)$
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 3.00\sigma(I)$)	7733
No. Variables	684
Reflection/Parameter Ratio	11.31
Residuals: R; R_w , R_{all}	0.040; 0.045; 0.051
<i>Goodness of Fit Indicator</i>	<i>1.24</i>
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	$0.51 \text{ e}^-/\text{\AA}^3$
Minimum peak in Final Diff. Map	$-1.15 \text{ e}^-/\text{\AA}^3$

Table S-2. Atomic Coordinates and *Biso*/*Beq* for **20**.

atom	x	y	z	B(eq)
Zr1	0.75869(3)	0.0343	0.50393(3)	1.32(1)
Zr2	0.77596(3)	0.40556(7)	1.01204(3)	1.56(1)
S1	0.82296(7)	0.0037(1)	0.65680(7)	1.48(3)
S2	0.61647(7)	0.1989(1)	0.43591(7)	1.44(3)
S3	0.83906(8)	0.4271(2)	1.16506(7)	1.94(3)
S4	0.62051(8)	0.2867(1)	0.94116(7)	1.55(3)
O1	0.8382(2)	-0.0873(4)	0.5982(2)	1.54(7)
O2	0.8043(2)	-0.0753(4)	0.7140(2)	1.96(8)
O3	0.6595(2)	0.0882(3)	0.4047(2)	1.57(8)
O4	0.5384(2)	0.1598(4)	0.4401(2)	1.71(8)
O5	0.8632(2)	0.5051(4)	1.1067(2)	2.27(9)
O6	0.8115(2)	0.5173(5)	1.2141(2)	2.30(8)
O7	0.6698(2)	0.3933(4)	0.9133(2)	1.76(7)
O8	0.5399(2)	0.3236(4)	0.9320(2)	1.95(8)
N1	0.7575(2)	0.1017(5)	0.6116(2)	1.37(9)
N2	0.6761(2)	0.2274(5)	0.5078(2)	1.35(9)
N3	0.8417(3)	0.1729(5)	0.4811(2)	1.9(1)
N4	0.7886(3)	-0.1406(5)	0.4499(2)	2.0(1)
N5	0.6430(2)	-0.1174(5)	0.5187(2)	1.77(10)
N6	0.7788(2)	0.3182(5)	1.1214(2)	1.56(9)
N7	0.6698(2)	0.2782(5)	1.0179(2)	1.49(9)
N8	0.8402(3)	0.2328(5)	0.9893(2)	2.2(1)
N9	0.8221(3)	0.5501(6)	0.9514(2)	2.7(1)
N10	0.7003(3)	0.6177(6)	1.0443(4)	5.0(2)
C1	0.7238(3)	0.2377(5)	0.6308(3)	1.4(1)
C2	0.7034(3)	0.2422(6)	0.7022(3)	1.9(1)
C3	0.6647(3)	0.3891(6)	0.7102(3)	2.2(1)
C4	0.5938(3)	0.4189(6)	0.6502(3)	2.2(1)
C5	0.6143(3)	0.4069(6)	0.5788(2)	1.8(1)
C6	0.6505(3)	0.2581(6)	0.5719(3)	1.4(1)
C7	0.9073(3)	0.1072(6)	0.6922(3)	1.5(1)
C8	0.9481(3)	0.1715(7)	0.6490(3)	2.6(1)
C9	1.0118(3)	0.2587(7)	0.6770(3)	2.8(1)
C10	1.0362(3)	0.2817(6)	0.7491(3)	2.4(1)
C11	0.9945(4)	0.2144(7)	0.7908(3)	2.8(1)
C12	0.9306(3)	0.1264(7)	0.7635(3)	2.5(1)
C13	1.1056(3)	0.3757(7)	0.7793(3)	3.1(1)
C14	0.6083(3)	0.3502(5)	0.3797(3)	1.6(1)
C15	0.5396(3)	0.4296(6)	0.3621(3)	2.2(1)
C16	0.5342(3)	0.5470(7)	0.3169(3)	3.0(1)
C17	0.5957(4)	0.5872(6)	0.2899(3)	2.8(1)
C18	0.6647(4)	0.5091(7)	0.3076(3)	2.6(1)
C19	0.6717(3)	0.3897(6)	0.3529(3)	2.0(1)
C20	0.5906(5)	0.7181(8)	0.2408(4)	4.9(2)

atom	x	y	z	B(eq)
C21	0.8460(3)	0.3315(6)	0.4906(3)	2.9(1)
C22	0.9070(4)	0.1285(7)	0.4523(3)	3.2(2)
C23	0.8202(4)	-0.2852(7)	0.4733(3)	3.3(2)
C24	0.7760(4)	-0.1326(7)	0.3740(3)	2.9(1)
C25	0.6538(3)	-0.1937(6)	0.5866(3)	2.3(1)
C26	0.6144(3)	-0.2187(6)	0.4599(3)	2.5(1)
C27	0.7085(3)	0.2656(5)	1.1411(3)	1.6(1)
C28	0.7181(3)	0.1672(6)	1.2058(3)	1.8(1)
C29	0.6380(3)	0.1294(6)	1.2162(3)	2.1(1)
C30	0.5863(3)	0.0577(6)	1.1506(3)	2.2(1)
C31	0.5808(3)	0.1494(6)	1.0842(3)	1.8(1)
C32	0.6618(3)	0.1841(5)	1.0773(3)	1.4(1)
C33	0.9219(3)	0.3328(6)	1.2099(3)	1.9(1)
C34	0.9673(3)	0.2571(7)	1.1711(3)	2.9(1)
C35	1.0297(4)	0.1772(8)	1.2060(3)	3.3(2)
C36	1.0507(3)	0.1687(6)	1.2779(3)	2.4(1)
C37	1.0070(3)	0.2460(6)	1.3162(3)	2.2(1)
C38	0.9428(3)	0.3285(6)	1.2821(3)	2.1(1)
C39	1.1211(4)	0.0794(6)	1.3145(3)	3.3(2)
C40	0.6228(3)	0.1229(5)	0.8945(3)	1.4(1)
C41	0.5603(3)	0.0268(7)	0.8859(3)	2.4(1)
C42	0.5605(3)	-0.0985(7)	0.8473(3)	2.9(1)
C43	0.6207(4)	-0.1317(6)	0.8160(3)	2.4(1)
C44	0.6833(3)	-0.0351(6)	0.8257(3)	2.5(1)
C45	0.6842(3)	0.0917(6)	0.8650(3)	2.4(1)
C46	0.6171(4)	-0.2648(7)	0.7700(3)	3.3(2)
C47	0.8882(4)	0.2303(8)	0.9376(3)	3.8(2)
C48	0.8428(4)	0.0851(6)	1.0193(3)	3.0(1)
C49	0.7893(5)	0.598(1)	0.8803(4)	7.4(3)
C50	0.9007(4)	0.6100(9)	0.9737(4)	4.5(2)
C51	0.7399(4)	0.7580(7)	1.0435(5)	5.8(2)
C52	0.6231(5)	0.6270(9)	1.0331(7)	7.8(3)
H1	0.7588	0.315	0.6285	1.6668
H2	0.6685	0.1652	0.7054	2.329
H3	0.7494	0.2318	0.7381	2.329
H4	0.6485	0.3888	0.7529	2.6264
H5	0.7018	0.4644	0.7111	2.6264
H6	0.5543	0.3501	0.6523	2.6459
H7	0.5752	0.5143	0.6553	2.6459
H8	0.5684	0.418	0.5429	2.1287
H9	0.6504	0.4812	0.5748	2.1287
H10	0.614	0.1855	0.577	1.73
H11	0.9327	0.1565	0.6	3.1366
H12	1.0395	0.3036	0.6466	3.306
H13	1.0097	0.2284	0.84	3.3595
H14	0.9033	0.0799	0.7937	3.0529

atom	x	y	z	B(eq)
H15	1.1446	0.3186	0.8089	3.7757
H16	1.1256	0.4154	0.7426	3.7757
H17	1.0903	0.4524	0.8056	3.7757
H18	0.4966	0.4037	0.3808	2.6228
H19	0.487	0.6003	0.3045	3.5544
H20	0.7075	0.5368	0.2888	3.163
H21	0.719	0.3365	0.3651	2.3765
H22	0.6296	0.7869	0.2606	5.835
H23	0.5982	0.6865	0.1969	5.835
H24	0.5408	0.7621	0.2345	5.835
H25	0.8935	0.3563	0.5222	3.4595
H26	0.8436	0.3772	0.4468	3.4595
H27	0.8036	0.3635	0.5088	3.4595
H28	0.9049	0.0264	0.4445	3.8686
H29	0.9042	0.1775	0.4092	3.8686
H30	0.9544	0.1528	0.4842	3.8686
H31	0.7839	-0.358	0.4527	3.922
H32	0.8677	-0.2997	0.4596	3.922
H33	0.8293	-0.2911	0.5227	3.922
H34	0.7548	-0.0403	0.3582	3.479
H35	0.8242	-0.1453	0.3611	3.479
H36	0.7409	-0.207	0.3531	3.479
H37	0.6055	-0.2336	0.5909	2.7982
H38	0.6907	-0.2698	0.5889	2.7982
H39	0.6721	-0.1268	0.6236	2.7982
H40	0.5665	-0.2601	0.464	2.9508
H41	0.6069	-0.1672	0.417	2.9508
H42	0.6516	-0.2938	0.4608	2.9508
H43	0.6019	-0.0501	0.5174	2.1228
H44	0.679	0.3481	1.1483	1.8697
H45	0.7448	0.0806	1.1989	2.1959
H46	0.747	0.217	1.2458	2.1959
H47	0.6436	0.0639	1.2544	2.5669
H48	0.6134	0.216	1.2264	2.5669
H49	0.6076	-0.0346	1.1439	2.6478
H50	0.5354	0.0453	1.1579	2.6478
H51	0.554	0.0961	1.0445	2.1828
H52	0.5535	0.2372	1.0877	2.1828
H53	0.6877	0.0948	1.0736	1.656
H54	0.9547	0.2617	1.1215	3.4934
H55	1.0597	0.1256	1.1797	3.9689
H56	1.0208	0.2427	1.3658	2.6417
H57	0.9136	0.3816	1.3085	2.4966
H58	1.114	-0.0192	1.2998	3.9487
H59	1.1666	0.117	1.303	3.9487
H60	1.1267	0.0847	1.3637	3.9487

atom	x	y	z	B(eq)
H61	0.5178	0.0475	0.9064	2.8668
H62	0.518	-0.1641	0.8421	3.4782
H63	0.7258	-0.0559	0.8052	3.0389
H64	0.7273	0.1564	0.8715	2.904
H65	0.6139	-0.3498	0.7967	3.9413
H66	0.5725	-0.2589	0.7323	3.9413
H67	0.6626	-0.2692	0.7522	3.9413
H68	0.7118	0.6031	1.0934	5.9406
H69	0.9402	0.2057	0.96	4.5161
H70	0.8681	0.16	0.9026	4.5161
H71	0.8873	0.3236	0.9166	4.5161
H72	0.8115	0.082	1.0525	3.6386
H73	0.8236	0.017	0.9831	3.6386
H74	0.895	0.0613	1.0416	3.6386
H75	0.7878	0.7012	0.8788	8.8291
H76	0.8205	0.5631	0.8505	8.8291
H77	0.738	0.5606	0.865	8.8291
H78	0.923	0.5808	1.0204	5.3863
H79	0.9319	0.5749	0.9439	5.3863
H80	0.8984	0.7132	0.9713	5.3863
H81	0.7946	0.7434	1.0553	6.9568
H82	0.7249	0.7996	0.9981	6.9568
H83	0.7258	0.8219	1.0764	6.9568
H84	0.6098	0.6901	1.0668	9.3438
H85	0.6024	0.6646	0.9876	9.3438
H86	0.602	0.5331	1.037	9.3438

Table S-3. Anisotropic Displacement Parameters for **20**.

atom	U11	U22	U33	U12	U13	U23
Zr1	0.0151(3)	0.0154(3)	0.0184(3)	0.0002(2)	0.0015(2)	-0.0006(2)
Zr2	0.0160(3)	0.0209(3)	0.0208(3)	-0.0005(2)	0.0013(2)	0.0031(2)
S1	0.0161(7)	0.0202(8)	0.0183(7)	0.0025(5)	0.0009(5)	0.0014(6)
S2	0.0178(7)	0.0174(7)	0.0170(7)	0.0003(5)	-0.0010(6)	-0.0012(5)
S3	0.0187(7)	0.0313(9)	0.0221(7)	-0.0063(6)	0.0013(6)	-0.0023(7)
S4	0.0178(7)	0.0204(7)	0.0191(7)	0.0013(6)	0.0008(6)	-0.0015(6)
O1	0.017(2)	0.024(2)	0.018(2)	0.004(2)	0.004(1)	-0.003(2)
O2	0.023(2)	0.028(2)	0.023(2)	0.006(2)	0.003(2)	0.007(2)
O3	0.023(2)	0.014(2)	0.019(2)	0.007(1)	-0.002(2)	-0.006(1)
O4	0.014(2)	0.023(2)	0.025(2)	0.000(2)	0.001(2)	0.002(2)
O5	0.027(2)	0.032(2)	0.024(2)	-0.011(2)	-0.001(2)	0.005(2)
O6	0.023(2)	0.034(2)	0.029(2)	-0.006(2)	0.004(2)	-0.008(2)
O7	0.025(2)	0.019(2)	0.021(2)	-0.002(2)	0.001(2)	0.005(2)
O8	0.019(2)	0.026(2)	0.027(2)	0.003(2)	0.002(2)	-0.005(2)
N1	0.011(2)	0.020(2)	0.019(2)	0.003(2)	-0.003(2)	0.005(2)
N2	0.015(2)	0.021(2)	0.011(2)	0.002(2)	-0.005(2)	-0.001(2)
N3	0.018(3)	0.031(3)	0.027(3)	-0.002(2)	0.007(2)	0.005(2)
N4	0.026(3)	0.021(3)	0.027(3)	0.000(2)	0.002(2)	-0.003(2)
N5	0.022(2)	0.019(2)	0.025(2)	-0.001(2)	0.003(2)	-0.002(2)
N6	0.011(2)	0.030(3)	0.016(2)	-0.004(2)	-0.003(2)	-0.004(2)
N7	0.015(2)	0.026(3)	0.013(2)	-0.001(2)	-0.002(2)	0.002(2)
N8	0.026(3)	0.030(3)	0.027(3)	0.005(2)	0.006(2)	0.003(2)
N9	0.022(3)	0.042(3)	0.036(3)	-0.003(3)	0.000(2)	0.015(3)
N10	0.032(4)	0.025(3)	0.136(6)	-0.005(3)	0.030(4)	-0.019(3)
C1	0.015(3)	0.017(3)	0.019(3)	0.000(2)	0.000(2)	-0.002(2)
C2	0.032(3)	0.021(3)	0.018(3)	0.007(3)	0.001(2)	-0.002(2)
C3	0.037(3)	0.024(3)	0.020(3)	0.009(3)	0.002(2)	0.000(2)
C4	0.030(3)	0.026(3)	0.026(3)	0.011(3)	0.003(2)	-0.004(3)
C5	0.021(3)	0.021(3)	0.024(3)	0.006(3)	0.001(2)	-0.002(2)
C6	0.017(3)	0.022(3)	0.013(3)	-0.001(2)	0.000(2)	-0.001(2)
C7	0.014(3)	0.021(3)	0.021(3)	0.005(2)	0.000(2)	-0.005(2)
C8	0.027(3)	0.045(4)	0.023(3)	-0.002(3)	-0.002(3)	0.003(3)
C9	0.025(3)	0.048(4)	0.030(4)	-0.012(3)	0.001(3)	-0.002(3)
C10	0.020(3)	0.026(3)	0.043(4)	0.003(3)	0.000(3)	-0.004(3)
C11	0.032(4)	0.044(4)	0.025(3)	0.003(3)	-0.004(3)	-0.006(3)
C12	0.023(3)	0.037(4)	0.033(4)	0.002(3)	-0.002(3)	0.004(3)
C13	0.025(3)	0.043(4)	0.044(4)	-0.001(3)	-0.008(3)	-0.012(3)
C14	0.029(3)	0.013(3)	0.017(3)	-0.002(2)	-0.003(2)	0.000(2)
C15	0.023(3)	0.029(3)	0.026(3)	0.002(3)	-0.004(2)	-0.001(3)
C16	0.035(3)	0.025(3)	0.041(4)	0.004(3)	-0.015(3)	0.003(3)
C17	0.052(4)	0.019(3)	0.024(3)	-0.018(3)	-0.011(3)	0.001(2)
C18	0.047(4)	0.034(4)	0.019(3)	-0.017(3)	0.008(3)	-0.007(3)
C19	0.028(3)	0.019(3)	0.027(3)	-0.001(3)	0.005(2)	-0.006(3)
C20	0.076(6)	0.044(4)	0.049(4)	-0.019(4)	-0.017(4)	0.023(4)

atom	U11	U22	U33	U12	U13	U23
C21	0.028(3)	0.033(4)	0.046(4)	-0.013(3)	0.005(3)	0.004(3)
C22	0.036(4)	0.053(4)	0.035(4)	-0.012(3)	0.011(3)	-0.004(3)
C23	0.047(4)	0.031(4)	0.045(4)	0.014(3)	0.007(3)	-0.008(3)
C24	0.036(4)	0.038(4)	0.035(4)	0.001(3)	0.006(3)	-0.008(3)
C25	0.025(3)	0.029(3)	0.035(3)	-0.006(3)	0.007(3)	0.007(3)
C26	0.032(3)	0.025(3)	0.032(3)	-0.012(3)	-0.002(3)	0.000(3)
C27	0.021(3)	0.018(3)	0.019(3)	-0.003(2)	0.003(2)	-0.002(2)
C28	0.024(3)	0.029(3)	0.014(3)	-0.001(3)	0.000(2)	-0.001(2)
C29	0.031(3)	0.029(3)	0.019(3)	-0.009(3)	0.001(3)	0.000(2)
C30	0.033(3)	0.027(3)	0.022(3)	-0.014(3)	0.003(3)	0.000(2)
C31	0.022(3)	0.025(3)	0.021(3)	-0.006(2)	0.004(2)	-0.003(2)
C32	0.015(3)	0.015(3)	0.017(3)	0.002(2)	-0.006(2)	-0.005(2)
C33	0.022(3)	0.028(3)	0.022(3)	-0.007(2)	0.002(3)	0.000(2)
C34	0.029(3)	0.061(4)	0.019(3)	0.007(3)	0.001(3)	-0.008(3)
C35	0.033(4)	0.062(5)	0.030(4)	0.012(3)	0.003(3)	-0.011(3)
C36	0.022(3)	0.034(4)	0.035(4)	-0.007(3)	0.003(3)	0.002(3)
C37	0.027(3)	0.033(3)	0.022(3)	-0.008(3)	0.001(3)	0.004(3)
C38	0.026(3)	0.034(3)	0.020(3)	-0.012(3)	0.007(3)	-0.005(2)
C39	0.033(4)	0.033(4)	0.050(4)	-0.002(3)	-0.009(3)	-0.004(3)
C40	0.019(3)	0.018(3)	0.017(3)	0.002(2)	0.004(2)	0.003(2)
C41	0.027(3)	0.032(3)	0.035(3)	-0.007(3)	0.013(2)	-0.008(3)
C42	0.031(3)	0.032(3)	0.046(4)	-0.013(3)	0.007(3)	-0.009(3)
C43	0.041(4)	0.024(3)	0.025(3)	0.004(3)	0.004(3)	-0.002(2)
C44	0.031(4)	0.030(3)	0.034(4)	0.011(3)	0.006(3)	0.001(3)
C45	0.026(3)	0.030(3)	0.034(4)	0.001(3)	0.004(3)	0.003(3)
C46	0.055(4)	0.034(4)	0.030(3)	0.004(3)	-0.003(3)	-0.005(3)
C47	0.042(4)	0.061(5)	0.045(4)	0.013(4)	0.021(3)	0.004(4)
C48	0.045(4)	0.034(4)	0.038(4)	0.014(3)	0.015(3)	0.003(3)
C49	0.053(5)	0.152(9)	0.059(5)	-0.043(5)	-0.018(4)	0.066(6)
C50	0.033(4)	0.087(6)	0.046(4)	-0.026(4)	0.000(3)	0.021(4)
C51	0.042(4)	0.025(4)	0.154(8)	-0.001(3)	0.022(5)	-0.003(4)
C52	0.043(5)	0.040(5)	0.23(1)	-0.002(4)	0.056(7)	-0.043(6)

Table S-4. Bond lengths (Å) for **20**.

atom	atom	distance	atom	atom	distance
ZR1	O1	2.335(3)	S4	O7	1.499(4)
ZR1	O3	2.353(3)	S4	O8	1.435(4)
ZR1	N1	2.213(4)	S4	N7	1.561(4)
ZR1	N2	2.310(4)	S4	C40	1.769(5)
ZR1	N3	2.069(5)	N1	C1	1.470(7)
ZR1	N4	2.063(4)	N2	C6	1.464(7)
ZR1	N5	2.547(4)	N3	C21	1.469(7)
ZR2	O5	2.312(3)	N3	C22	1.458(8)
ZR2	O7	2.369(3)	N4	C23	1.473(7)
ZR2	N6	2.286(4)	N4	C24	1.461(7)
ZR2	N7	2.237(4)	N5	C25	1.483(7)
ZR2	N8	2.061(5)	N5	C26	1.479(7)
ZR2	N9	2.076(5)	N6	C27	1.468(6)
ZR2	N10	2.528(5)	N7	C32	1.486(7)
S1	O1	1.498(4)	N8	C47	1.470(7)
S1	O2	1.441(4)	N8	C48	1.477(7)
S1	N1	1.570(4)	N9	C49	1.453(8)
S1	C7	1.768(5)	N9	C50	1.464(8)
S2	O3	1.487(4)	N10	C51	1.469(8)
S2	O4	1.447(4)	N10	C52	1.334(9)
S2	N2	1.576(4)	C1	C2	1.532(7)
S2	C14	1.762(5)	C1	C6	1.535(7)
S3	O5	1.499(4)	C2	C3	1.537(8)
S3	O6	1.442(4)	C3	C4	1.533(7)
S3	N6	1.564(4)	C4	C5	1.535(7)
S3	C33	1.753(6)	C5	C6	1.530(7)
C7	C8	1.371(8)	C37	C38	1.398(8)
C7	C12	1.380(8)	C40	C41	1.394(7)
C8	C9	1.388(8)	C40	C45	1.375(8)
C9	C10	1.400(8)	C41	C42	1.381(8)
C10	C11	1.373(8)	C42	C43	1.382(8)
C10	C13	1.505(8)	C43	C44	1.397(8)
C11	C12	1.391(8)	C43	C46	1.515(8)
C14	C15	1.389(7)	C44	C45	1.398(8)
C14	C19	1.395(8)			
C15	C16	1.386(8)			
C16	C17	1.367(9)			
C17	C18	1.388(9)			
C17	C20	1.533(8)			
C18	C19	1.401(8)			
C27	C28	1.539(7)			
C27	C32	1.528(6)			
C28	C29	1.518(8)			

atom	atom	distance
C29	C30	1.545(7)
C30	C31	1.539(7)
C31	C32	1.505(7)
C33	C34	1.413(8)
C33	C38	1.384(8)
C34	C35	1.370(8)
C35	C36	1.379(8)
C36	C37	1.394(8)
C36	C39	1.525(8)

Table S-5. Bond angles (°) for **20**.

atom	atom	atom	angle	atom	atom	atom	angle
O1	ZR1	O3	162.6(1)	O5	ZR2	N10	77.6(2)
O1	ZR1	N1	60.7(1)	O7	ZR2	N6	126.6(1)
O1	ZR1	N2	127.5(1)	O7	ZR2	N7	60.3(1)
O1	ZR1	N3	98.1(1)	O7	ZR2	N8	99.0(2)
O1	ZR1	N4	81.8(1)	O7	ZR2	N9	84.3(1)
O1	ZR1	N5	89.9(1)	O7	ZR2	N10	83.0(2)
O3	ZR1	N1	124.4(1)	N6	ZR2	N7	66.6(1)
O3	ZR1	N2	60.8(1)	N6	ZR2	N8	92.4(2)
O3	ZR1	N3	96.8(1)	N6	ZR2	N9	147.2(2)
O3	ZR1	N4	88.1(1)	N6	ZR2	N10	86.1(2)
O3	ZR1	N5	75.4(1)	N7	ZR2	N8	96.8(2)
N1	ZR1	N2	66.8(1)	N7	ZR2	N9	144.3(2)
N1	ZR1	N3	101.6(2)	N7	ZR2	N10	83.8(2)
N1	ZR1	N4	140.6(2)	N8	ZR2	N9	93.3(2)
N1	ZR1	N5	81.8(1)	N8	ZR2	N10	177.9(2)
N2	ZR1	N3	91.1(2)	N9	ZR2	N10	87.3(2)
N2	ZR1	N4	148.8(2)	O1	S1	O2	115.8(2)
N2	ZR1	N5	83.5(2)	O1	S1	N1	97.2(2)
N3	ZR1	N4	95.0(2)	O1	S1	C7	108.5(2)
N3	ZR1	N5	172.0(2)	O2	S1	N1	117.3(2)
N4	ZR1	N5	86.6(2)	O2	S1	C7	106.7(2)
O5	ZR2	O7	158.8(1)	N1	S1	C7	110.9(2)
O5	ZR2	N6	61.1(1)	O3	S2	O4	116.2(2)
O5	ZR2	N7	125.1(1)	O3	S2	N2	100.7(2)
O5	ZR2	N8	100.5(2)	O3	S2	C14	104.8(2)
O5	ZR2	N9	86.1(2)	O4	S2	N2	115.9(2)
O4	S2	C14	107.0(2)	C21	N3	C22	107.7(5)
N2	S2	C14	111.8(2)	ZR1	N4	C23	131.8(4)
O5	S3	O6	116.1(2)	ZR1	N4	C24	119.5(4)
O5	S3	N6	99.4(2)	C23	N4	C24	108.7(4)
O5	S3	C33	105.5(2)	ZR1	N5	C25	115.1(3)
O6	S3	N6	116.3(2)	ZR1	N5	C26	113.1(3)
O6	S3	C33	108.7(2)	C25	N5	C26	110.9(4)
N6	S3	C33	110.0(2)	ZR2	N6	S3	99.0(2)
O7	S4	O8	116.4(2)	ZR2	N6	C27	122.0(3)
O7	S4	N7	98.4(2)	S3	N6	C27	125.1(3)
O7	S4	C40	106.3(2)	ZR2	N7	S4	102.1(2)
O8	S4	N7	116.6(2)	ZR2	N7	C32	125.4(3)
O8	S4	C40	106.1(2)	S4	N7	C32	131.0(3)
N7	S4	C40	112.7(2)	ZR2	N8	C47	126.8(4)
ZR1	O1	S1	99.3(2)	ZR2	N8	C48	126.1(4)
ZR1	O3	S2	98.9(2)	C47	N8	C48	107.0(5)
ZR2	O5	S3	100.0(2)	ZR2	N9	C49	128.7(4)

atom	atom	atom	angle	atom	atom	atom	angle
ZR2	O7	S4	98.5(2)	ZR2	N9	C50	122.8(4)
ZR1	N1	S1	102.2(2)	C49	N9	C50	108.3(5)
ZR1	N1	C1	125.4(3)	ZR2	N10	C51	113.1(4)
S1	N1	C1	129.1(3)	ZR2	N10	C52	126.1(5)
ZR1	N2	S2	97.9(2)	C51	N10	C52	114.4(6)
ZR1	N2	C6	120.0(3)	N1	C1	C2	117.1(4)
S2	N2	C6	122.0(3)	N1	C1	C6	103.4(4)
ZR1	N3	C21	127.0(4)	C2	C1	C6	110.6(4)
ZR1	N3	C22	125.3(4)	C1	C2	C3	108.8(4)
C2	C3	C4	112.4(4)	N6	C27	C28	118.4(4)
C3	C4	C5	111.5(4)	N6	C27	C32	105.8(4)
C4	C5	C6	109.8(4)	C28	C27	C32	109.1(4)
N2	C6	C1	104.6(4)	C27	C28	C29	108.6(4)
N2	C6	C5	118.0(4)	C28	C29	C30	111.9(4)
C1	C6	C5	109.8(4)	C29	C30	C31	112.6(4)
S1	C7	C8	120.3(4)	C30	C31	C32	108.7(4)
S1	C7	C12	119.6(5)	N7	C32	C27	103.2(4)
C8	C7	C12	120.0(5)	N7	C32	C31	117.5(4)
C7	C8	C9	119.9(5)	C27	C32	C31	111.8(4)
C8	C9	C10	121.3(6)	S3	C33	C34	119.0(4)
C9	C10	C11	117.2(5)	S3	C33	C38	121.5(5)
C9	C10	C13	121.2(6)	C34	C33	C38	119.5(5)
C11	C10	C13	121.6(5)	C33	C34	C35	119.0(5)
C10	C11	C12	122.1(5)	C34	C35	C36	122.5(6)
C7	C12	C11	119.4(6)	C35	C36	C37	118.5(5)
S2	C14	C15	120.8(4)	C35	C36	C39	120.7(6)
S2	C14	C19	119.2(4)	C37	C36	C39	120.8(5)
C15	C14	C19	120.0(5)	C36	C37	C38	120.4(5)
C14	C15	C16	119.7(6)	C33	C38	C37	120.1(5)
C15	C16	C17	121.2(5)	S4	C40	C41	119.3(4)
C16	C17	C18	119.7(5)	S4	C40	C45	120.8(4)
C16	C17	C20	121.5(6)	C41	C40	C45	119.9(5)
C18	C17	C20	118.9(6)	C40	C41	C42	119.4(5)
C17	C18	C19	120.4(6)	C41	C42	C43	122.0(5)
C14	C19	C18	119.1(5)	C42	C43	C44	117.9(5)
C42	C43	C46	121.0(6)				
C44	C43	C46	121.1(6)				
C43	C44	C45	120.8(6)				
C40	C45	C44	119.9(6)				

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