Supporting information for

The effect of outer-sphere anions on the spectroscopic response of metal-binding chemosensors

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X-ray crystal packing

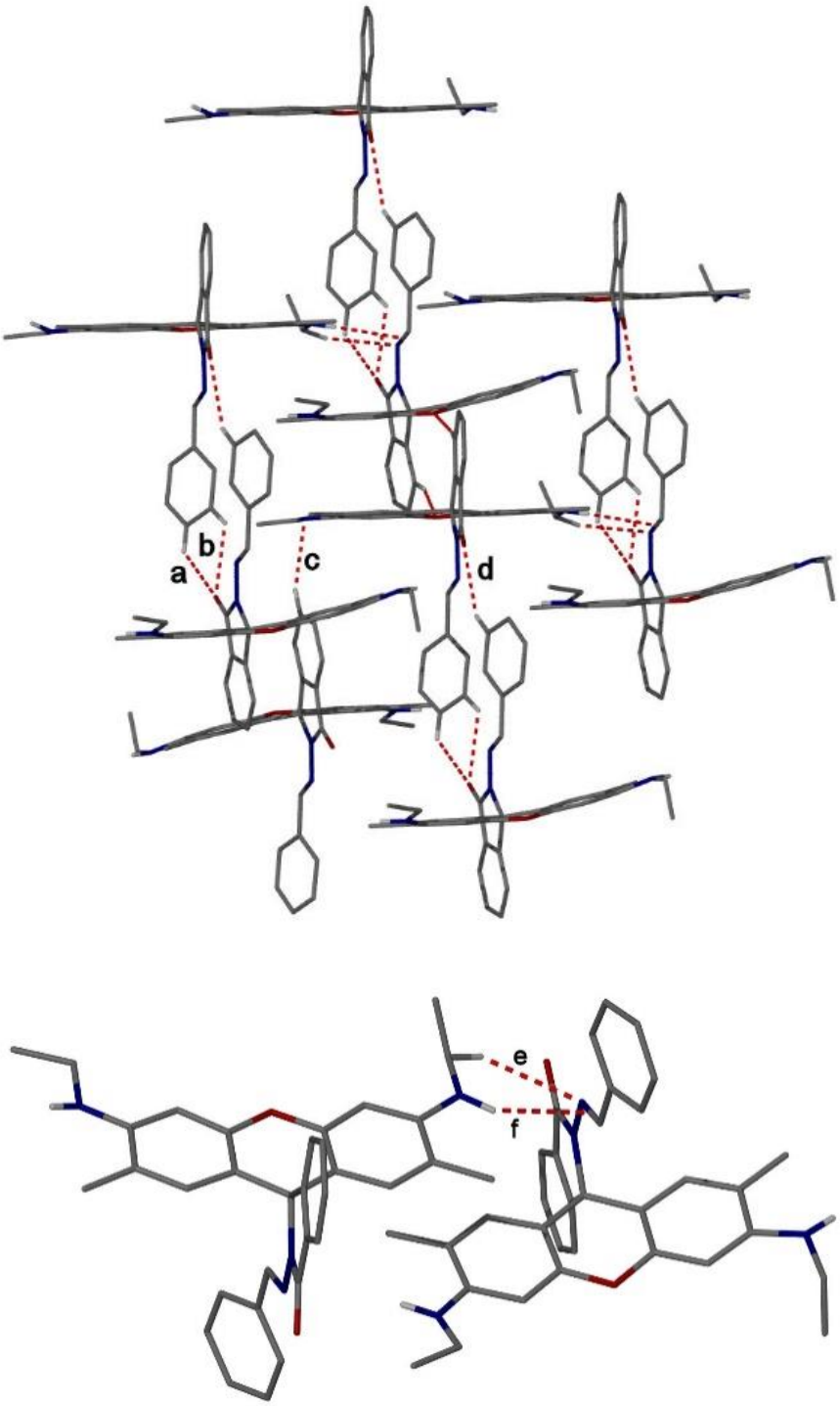

Figure S1 Top: Crystal packing of **Rh Benz**, highlighting the array of hydrogen bonding interactions responsible for the packing. Hydrogen bond distances (D···A) (a) C24-H24···O4 = 3.276(3) Å; (b) C25-H25···O4 = 3.247(3) Å; (c) C51-H51···N3 = 3.456(3) Å (d) C57-H57···O2 = 3.384(3) Å. Bottom: a closer view of the crystal packing highlighting hydrogen bonds (e) C32-H32B···N6 = 3.467(3) and (f) N4-H4N···N6 = 3.365(2).

Metal titration spectra

UV-vis absorbance titrations

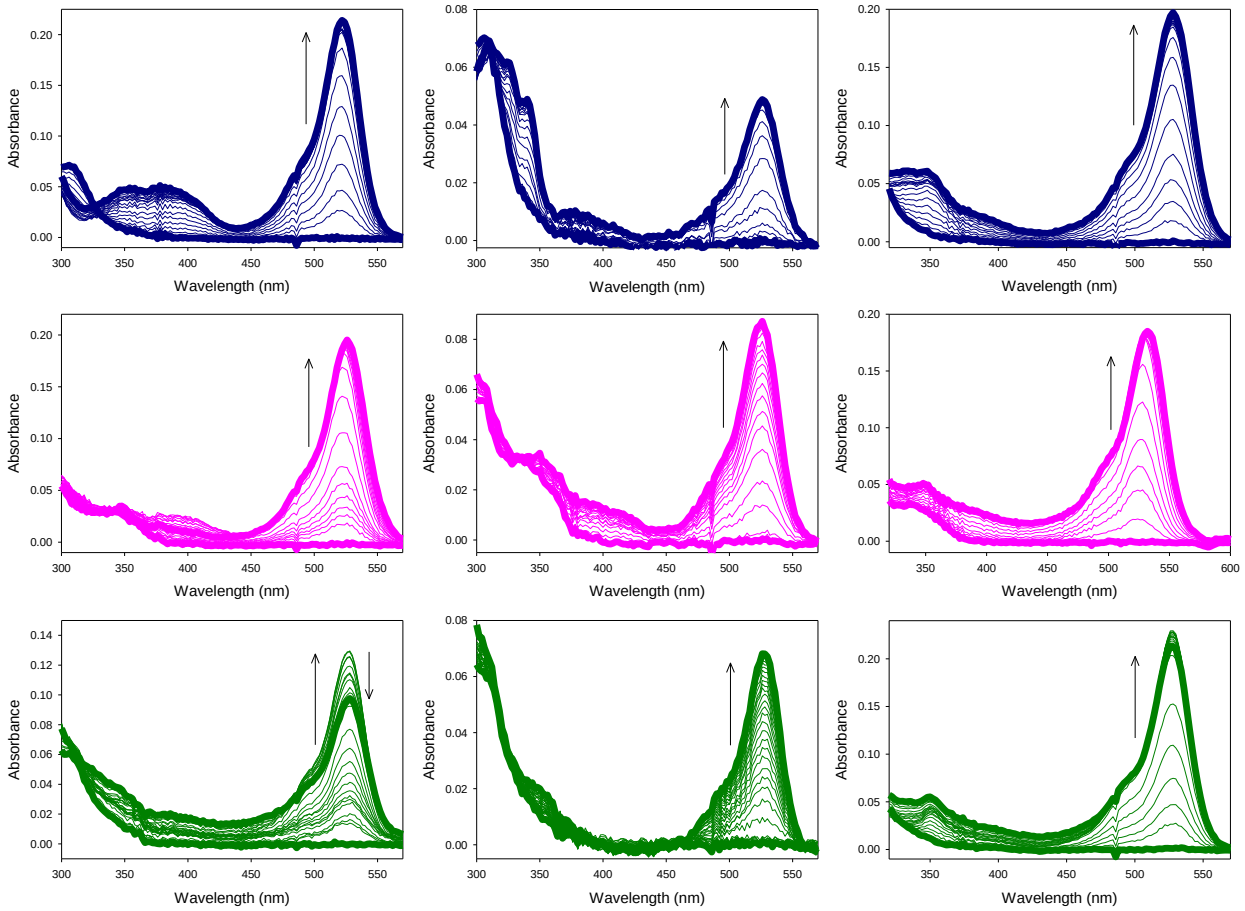

Figure S2. Absorbance spectra of **Rh-pyr** (top row, blue spectra), **Rh-phen** (pink, middle row), and **Rh-benz** (green, bottom row) upon the addition of $Cu(OTf)_2$ (left column), $Zn(OTf)_2$ (middle column), and $Fe(OTf)_3$ (right column). The first and last spectrum of each titration are highlighted with a bold line. All titrations were conducted in acetonitrile ([dye] = 2.5 μM, [metal] = 0-23.3 μM).

Fluorescence emission titrations

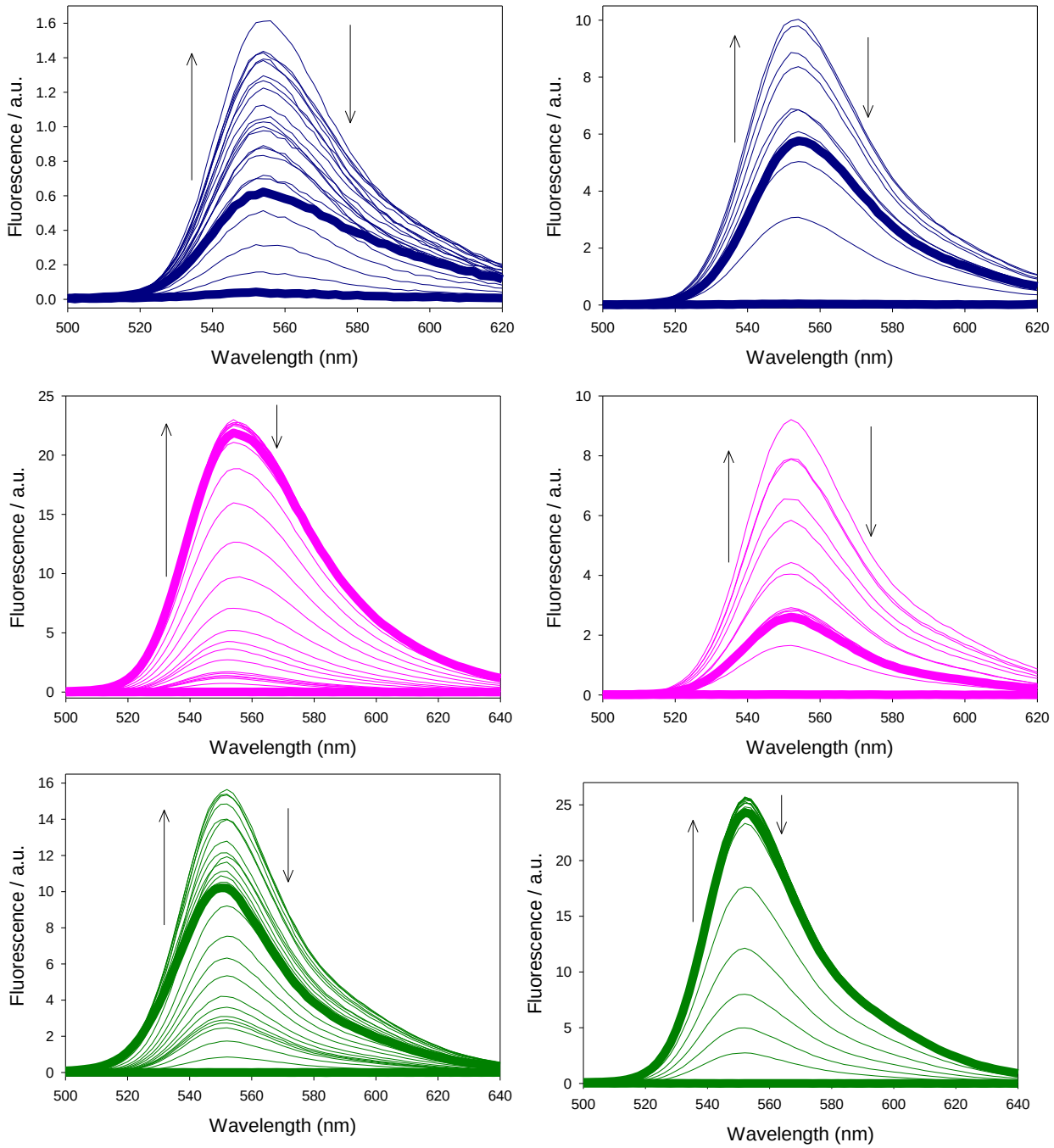

Figure S3. Steady-state fluorescence spectra of **Rh-pyr** (top row, blue spectra, $\lambda_{exc.}$ = 314-330 nm), **Rh-phen** (middle row, pink, $\lambda_{exc.}$ = 350 nm), and **Rh-benz** (bottom row, green, $\lambda_{exc.}$ = 450 nm), upon the addition of $Cu(OTf)_2$ (left column) and $Fe(OTf)_3$ (right column). The first and last spectrum of each titration are highlighted with a bold line. All titrations were conducted in acetonitrile ([dye] = 2.5 μM, [metal] = 0-22.7 μM).

Metal binding constant determination

$$K_{11} = \frac{[\mathrm{Zn{\cdot}sensor}]}{[\mathrm{Zn}][\mathrm{sensor}]} \qquad K_{21} = \frac{[\mathrm{Zn_2sensor}]}{[\mathrm{Zn{\cdot}sensor}][\mathrm{Zn}]}; \qquad \beta = \frac{[\mathrm{Zn_2sensor}]}{[\mathrm{Zn}]^2[\mathrm{sensor}]}$$

In the following pages, we present plots of representative results obtained upon the addition of $Zn(OTf)_2$ to solutions of **Rh-benz** (Figures S4 and S5), **Rh-phen** (Figures S6 and S7), and **Rh-pyr** (Figure S8 and S9) in acetonitrile at 25°C, together with the respective results from nonlinear fitting of these titration profiles to the binding models shown above.

Table S1 Formation constants for representative results obtained from the complexation of Zn(II) triflate to the three sensors. The concentration of the sensor molecule was maintained constant at 2.5×10^{-6} M. Experiments were run in acetonitrile at 25 °C.

		From absorbance data			From fluorescence data		
		log K_{11}	log K_{21}	log β	log K_{11}	log K_{21}	log β
Rh-benz	$Zn(OTf)_2$	5.63(4)	5.3(2)	11.0(3)	6.1(1)	5.3(2)	11.4(1)
Rh-pyr	$Zn(OTf)_2$	6.81(9)	–	–	7.34(3)	–	–
Rh-phen	$Zn(OTf)_2$	7.57(2)	6.15(8) 5.42(2)[a]	13.72(7) 13.00(2)[a]	6.45(1)	–	–

K_{21} refers to the formation constant for the species containing 2 probe molecules per metal ion. In cases indicated with (a), a species containing 2 metal ions per sensor was observed; this corresponds to a K_{12} formation constant.

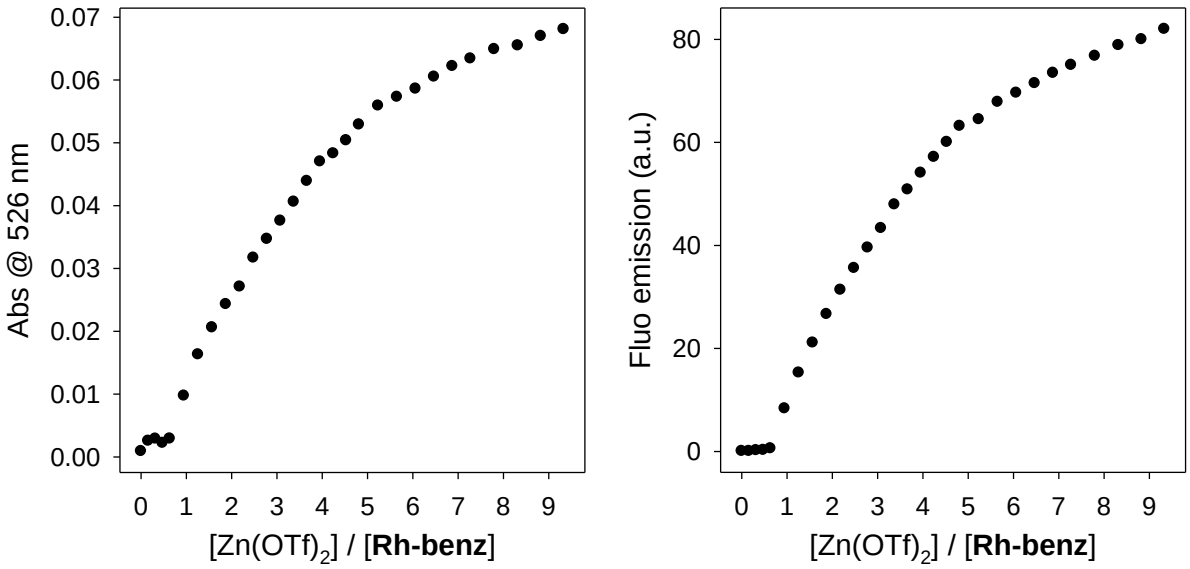

Figure S4 Binding isotherms obtained from the absorbance (left) and fluorescence (right) titrations of $Zn(OTf)_2$ into **Rh-benz** ([ligand] = 2.5×10^{-6} M in acetonitrile at 25°C). Binding constants were obtained by non-linear model fitting, as shown below.

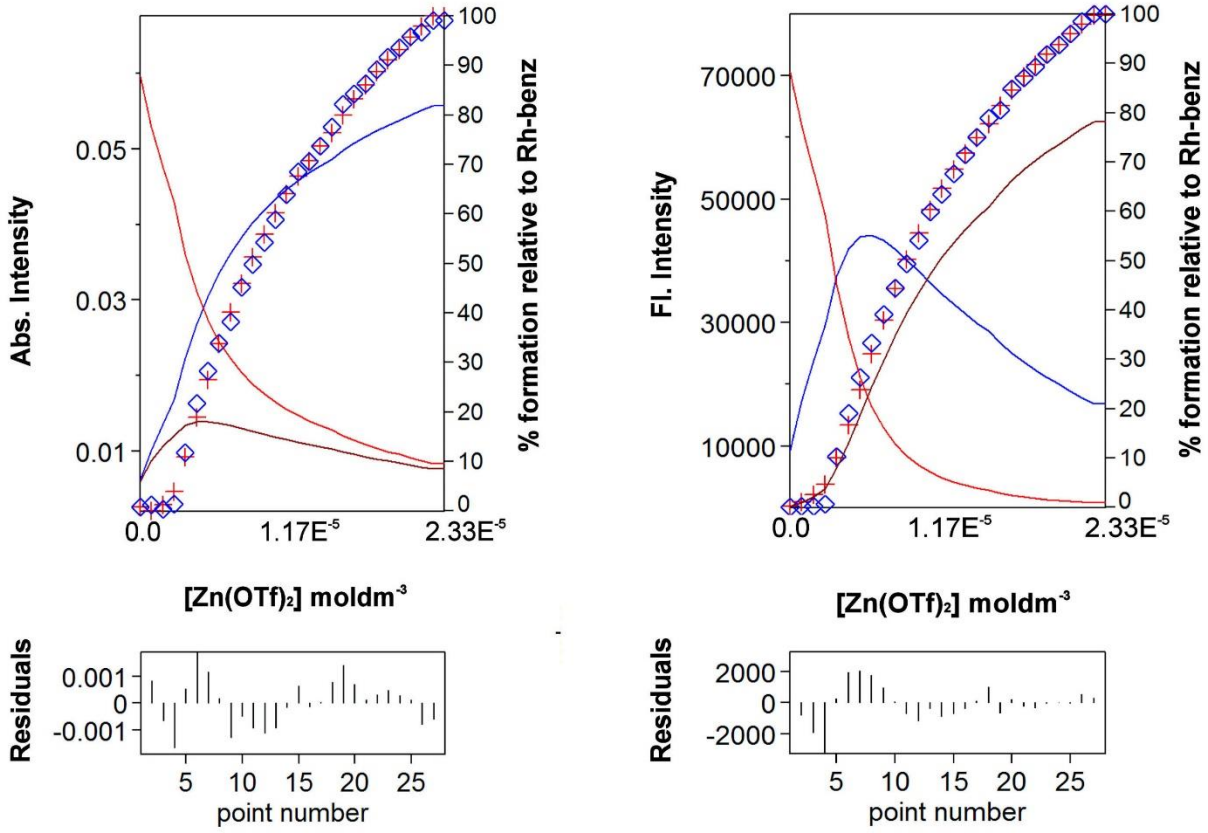

Figure S5 Nonlinear least-squares fit for the titration of **Rh-benz** (2.5×10^{-6} M solution in acetonitrile) with $Zn(OTf)_2$. Blue diamonds correspond to the experimental data; red crosses to the calculated fit; and solid lines represent the % speciation (left: absorbance data, right: fluorescence emission data).

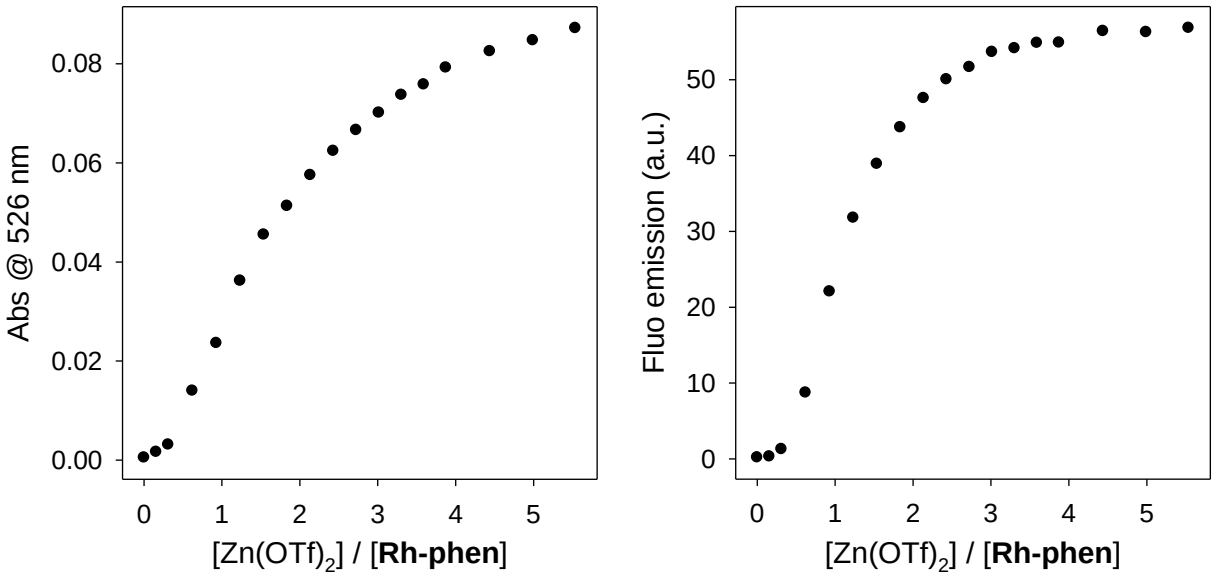

Figure S6 Binding isotherms obtained from the absorbance (left) and fluorescence (right) titrations of $Zn(Otf)_2$ into **Rh-phen** ([ligand] = 2.5×10^{-6} M in acetonitrile at 25°C). Binding constants were obtained by non-linear model fitting, as shown below.

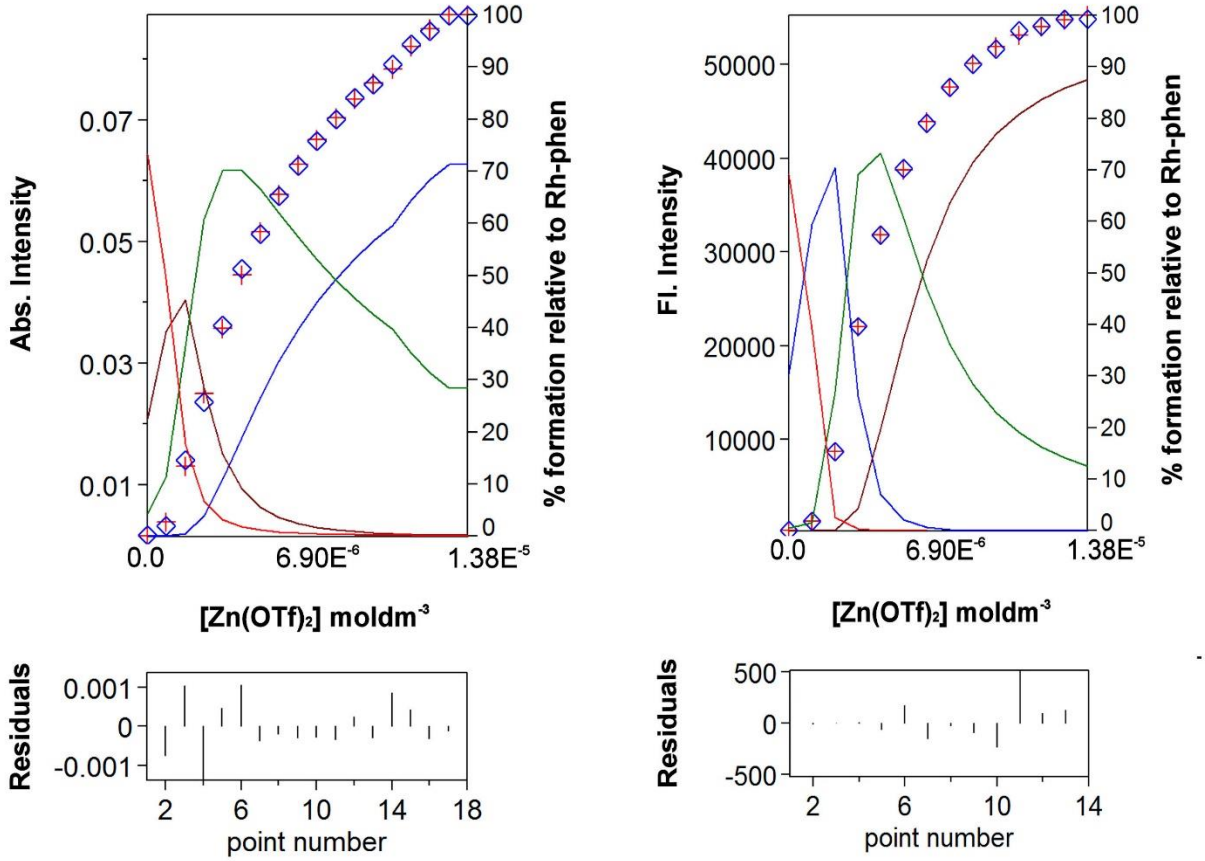

Figure S7 Nonlinear least-squares fit for the titration of **Rh-phen** (2.5×10^{-6} M solution in acetonitrile) with $Zn(Otf)_2$. Blue diamonds correspond to the experimental data; red crosses to the calculated fit; and solid lines represent the % speciation (left: absorbance data, right: fluorescence emission data).

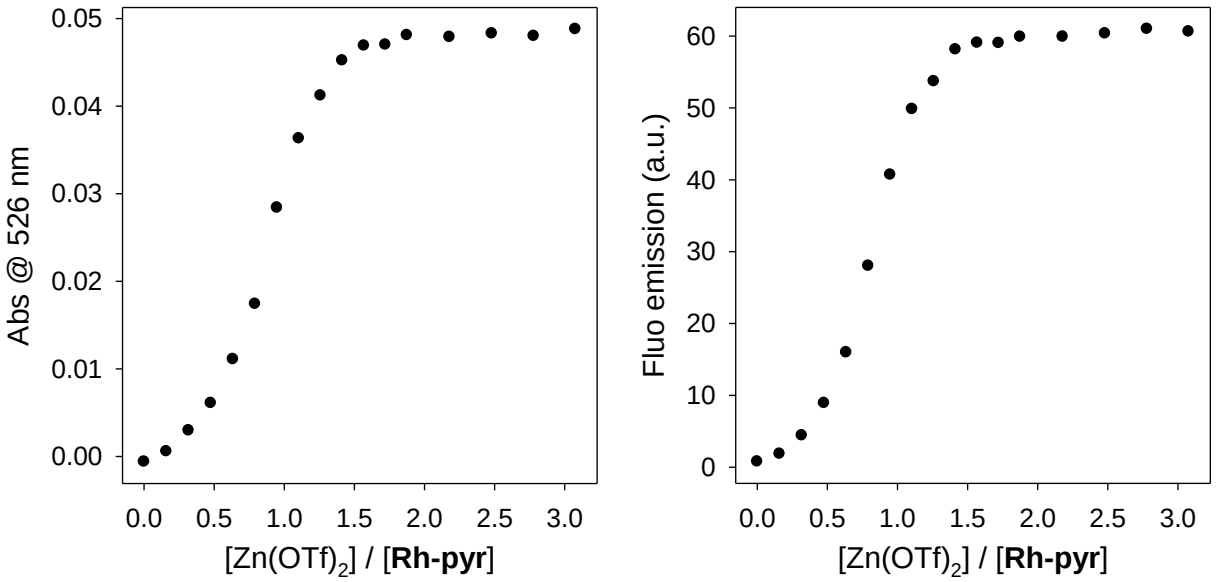

Figure S8 Binding isotherms obtained from the absorbance (left) and fluorescence (right) titrations of $Zn(Otf)_2$ into **Rh-pyr** ([ligand] = 2.5×10^{-6} M in acetonitrile at 25°C). Binding constants were obtained by non-linear model fitting, as shown below.

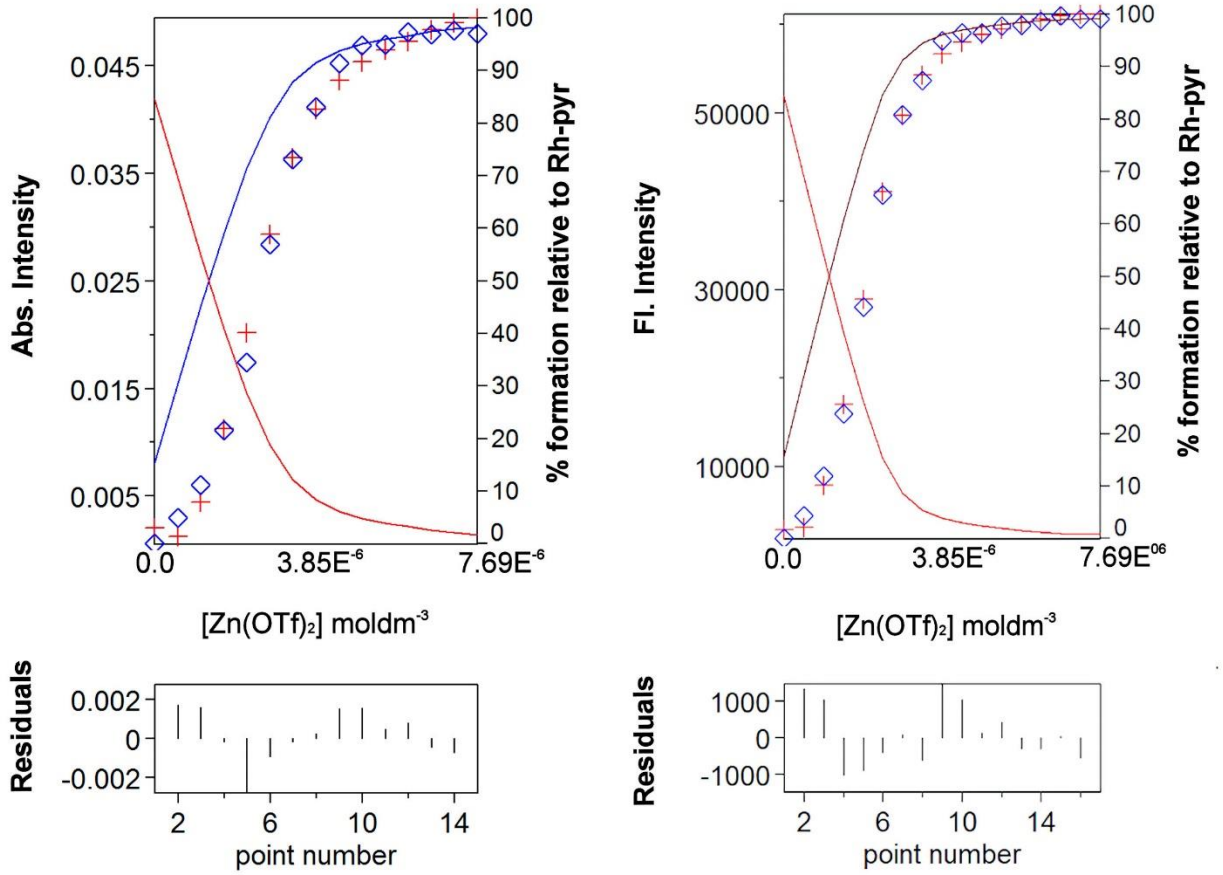

Figure S9 Nonlinear least-squares fit for the titration of **Rh-pyr** (2.5×10^{-6} M solution in acetonitrile) with $Zn(Otf)_2$. Blue diamonds correspond to the experimental data; red crosses to the calculated fit; and solid lines represent the % speciation (left: absorbance data, right: fluorescence emission data).

Multivariate data analysis

Outlier rejection

As a first step towards data analysis, we checked for statistical outliers using principal component analysis (PCA) on each set of metal-anion salt/dye replicate points. Points well outside a 95% confidence interval (CI) were considered outliers and removed from the data set before analysis. As an example, see **Figure S10** for the $ZnCl_2$ sample: in this case, data point 8 (the red point) lies well outside the 95% two-dimensional CI and was removed from the data set before further analysis.

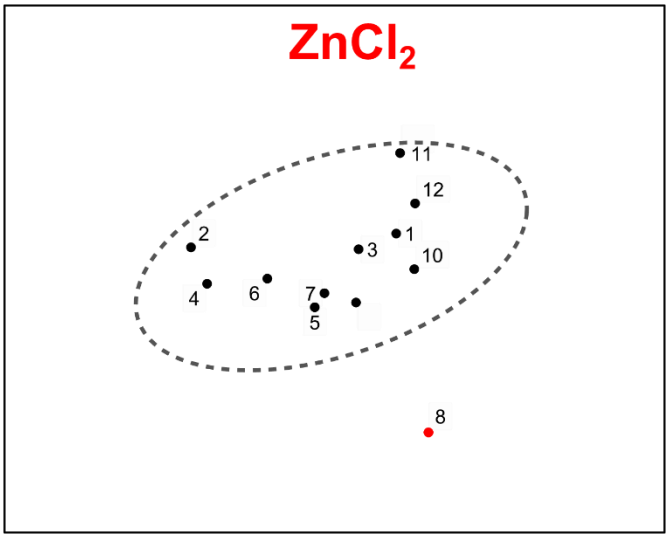

Figure S10. PCA score plot of the zinc(II) chloride replicates in the ion pairs data set, with a calculated 95% confidence ellipsoid shown as a dashed line. Point 8 (indicated in red) is clearly outside the confidence interval and was therefore removed from the data set before further analysis.

Crystal structure data

Computing details

Data collection: Bruker *APEX3*; cell refinement: Bruker *SAINT*; data reduction: Bruker *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2014).

Rh Benz

Crystal data

$C_{33}H_{32}N_4O_2$
$M_r = 516.63$
Triclinic, $P\overline{1}$
$a = 11.3318$ (4) Å
$b = 13.1141$ (5) Å
$c = 18.3687$ (7) Å
$\alpha = 76.736$ (3)°
$\beta = 88.534$ (2)°
$\gamma = 86.056$ (2)°
$V = 2650.46$ (17) Å^3
$Z = 4$
$F(000) = 1096$
$D_x = 1.295$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4566 reflections
$\theta = 2.9$–$29.8°$
$\mu = 0.08$ mm^{-1}
$T = 100$ K
Tablet, colourless
0.23 × 0.22 × 0.13 mm

Data collection

Bruker Kappa APEX-II DUO diffractometer
Radiation source: fine-focus sealed tube
TRIUMPH curved graphite monochromator
φ and ω scans
Absorption correction: multi-scan *SADABS* (Sheldrick, 2004)
$T_{min} = 0.871$, $T_{max} = 0.989$
35735 measured reflections
16408 independent reflections
9532 reflections with $I > 2\sigma(I)$
$R_{int} = 0.060$
$\theta_{max} = 31.0°$, $\theta_{min} = 2.3°$
$h = -16\rightarrow15$
$k = -19\rightarrow19$
$l = -26\rightarrow26$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.202$
$S = 1.03$
16408 reflections
777 parameters
14 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1011P)^2 + 0.1912P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.36055 (12)	0.15348 (11)	0.32374 (8)	0.0243 (3)	

O2	0.21067 (14)	−0.09332 (11)	0.08035 (9)	0.0312 (3)
N1	0.24688 (14)	−0.00742 (12)	0.17435 (9)	0.0197 (3)
N2	0.17820 (13)	−0.07211 (12)	0.22470 (9)	0.0208 (3)
N3	0.69916 (14)	−0.07825 (13)	0.39108 (9)	0.0225 (3)
N4	0.04061 (16)	0.41051 (13)	0.27783 (10)	0.0268 (4)
C1	0.43491 (15)	0.07605 (14)	0.30422 (10)	0.0178 (4)
C2	0.52747 (16)	0.03927 (14)	0.35363 (10)	0.0186 (4)
H2	0.5353	0.0683	0.3960	0.022*
C3	0.60858 (16)	−0.03976 (14)	0.34137 (11)	0.0195 (4)
C4	0.59491 (17)	−0.08224 (16)	0.27780 (12)	0.0245 (4)
C5	0.50221 (16)	−0.04179 (15)	0.22978 (11)	0.0219 (4)
H5	0.4941	−0.0698	0.1870	0.026*
C6	0.41970 (15)	0.03814 (14)	0.24079 (10)	0.0177 (3)
C7	0.31837 (16)	0.07900 (14)	0.18716 (10)	0.0173 (3)
C8	0.24149 (16)	0.16270 (14)	0.21364 (10)	0.0176 (3)
C9	0.14228 (17)	0.21346 (14)	0.17324 (11)	0.0205 (4)
H9	0.1201	0.1899	0.1306	0.025*
C10	0.07518 (17)	0.29577 (15)	0.19209 (11)	0.0223 (4)
C11	0.10637 (17)	0.32979 (14)	0.25700 (11)	0.0217 (4)
C12	0.20272 (17)	0.27882 (15)	0.29867 (11)	0.0218 (4)
H12	0.2240	0.2999	0.3424	0.026*
C13	0.26806 (16)	0.19732 (14)	0.27677 (11)	0.0196 (4)
C14	0.25570 (17)	−0.02444 (15)	0.10244 (11)	0.0224 (4)
C15	0.33000 (16)	0.05806 (15)	0.06001 (11)	0.0213 (4)
C16	0.36379 (18)	0.07843 (18)	−0.01469 (11)	0.0280 (4)
H16	0.3400	0.0363	−0.0468	0.034*
C17	0.4331 (2)	0.16180 (19)	−0.04093 (12)	0.0328 (5)
H17	0.4579	0.1774	−0.0918	0.039*
C18	0.4669 (2)	0.22340 (19)	0.00642 (12)	0.0328 (5)
H18	0.5143	0.2807	−0.0129	0.039*
C19	0.43306 (18)	0.20283 (17)	0.08113 (11)	0.0265 (4)
H19	0.4561	0.2455	0.1130	0.032*
C20	0.36451 (16)	0.11814 (15)	0.10802 (10)	0.0189 (4)
C21	0.18277 (16)	−0.07401 (15)	0.29468 (11)	0.0214 (4)
H21	0.2302	−0.0280	0.3124	0.026*
C22	0.11246 (17)	−0.14958 (15)	0.34672 (11)	0.0223 (4)
C23	0.01550 (17)	−0.19363 (15)	0.32191 (12)	0.0243 (4)
H23	−0.0099	−0.1695	0.2717	0.029*
C24	−0.04359 (18)	−0.27218 (16)	0.37011 (12)	0.0264 (4)
H24	−0.1094	−0.3009	0.3529	0.032*
C25	−0.00606 (19)	−0.30854 (16)	0.44357 (12)	0.0272 (4)
H25	−0.0450	−0.3631	0.4764	0.033*
C26	0.0884 (2)	−0.26477 (18)	0.46855 (13)	0.0317 (5)
H26	0.1140	−0.2894	0.5187	0.038*
C27	0.14656 (19)	−0.18483 (17)	0.42075 (12)	0.0288 (4)
H27	0.2099	−0.1543	0.4390	0.035*
C28	0.6788 (2)	−0.1697 (2)	0.26440 (15)	0.0406 (6)
H28A	0.6553	−0.1911	0.2194	0.061*
H28B	0.6768	−0.2296	0.3075	0.061*
H28C	0.7592	−0.1456	0.2575	0.061*
C29	−0.02983 (19)	0.34872 (17)	0.14598 (12)	0.0291 (5)
H29A	−0.0418	0.3130	0.1056	0.044*

H29B	−0.0151	0.4224	0.1245	0.044*
H29C	−0.1007	0.3451	0.1779	0.044*
C30	0.71797 (17)	−0.03426 (15)	0.45535 (11)	0.0222 (4)
H30A	0.6448	−0.0372	0.4862	0.027*
H30B	0.7359	0.0403	0.4379	0.027*
C31	0.8191 (2)	−0.09414 (18)	0.50258 (13)	0.0310 (5)
H31A	0.8033	−0.1686	0.5177	0.047*
H31B	0.8265	−0.0662	0.5472	0.047*
H31C	0.8929	−0.0863	0.4734	0.047*
C32	0.05745 (18)	0.43956 (17)	0.34879 (13)	0.0282 (4)
H32A	0.0705	0.3747	0.3885	0.034*
H32B	−0.0159	0.4775	0.3616	0.034*
C33	0.1592 (2)	0.5072 (2)	0.34811 (18)	0.0449 (7)
H33A	0.2318	0.4717	0.3333	0.067*
H33B	0.1688	0.5195	0.3982	0.067*
H33C	0.1436	0.5745	0.3124	0.067*
H3N	0.763 (2)	−0.109 (2)	0.3778 (16)	0.054*
H4N	−0.027 (2)	0.432 (2)	0.2549 (16)	0.054*
O3	0.54833 (14)	0.33546 (14)	0.19156 (10)	0.0433 (5)
O4	0.78400 (13)	0.53717 (12)	0.43764 (8)	0.0294 (3)
N5	0.71210 (13)	0.47979 (12)	0.33780 (9)	0.0181 (3)
N6	0.77904 (14)	0.54520 (12)	0.28700 (9)	0.0196 (3)
C34	0.64478 (18)	0.28588 (16)	0.23221 (12)	0.0255 (4)
C35	0.69897 (19)	0.20211 (18)	0.20703 (13)	0.0324 (5)
H35	0.6678	0.1823	0.1652	0.039*
C36	0.79816 (18)	0.14722 (17)	0.24243 (13)	0.0291 (5)
C37	0.84165 (18)	0.17496 (15)	0.30606 (11)	0.0233 (4)
C38	0.78478 (17)	0.25875 (15)	0.32934 (11)	0.0218 (4)
H38	0.8143	0.2778	0.3720	0.026*
C39	0.68634 (16)	0.31691 (14)	0.29363 (10)	0.0187 (4)
C40	0.62510 (16)	0.40675 (14)	0.32229 (10)	0.0172 (3)
C41	0.53176 (16)	0.46419 (15)	0.26752 (10)	0.0200 (4)
C42	0.47751 (17)	0.56071 (15)	0.27468 (11)	0.0236 (4)
H42	0.4975	0.5874	0.3164	0.028*
C43	0.39651 (19)	0.61910 (17)	0.22433 (13)	0.0306 (5)
C44	0.3659 (2)	0.5796 (2)	0.16252 (13)	0.0433 (6)
C45	0.4182 (2)	0.4843 (2)	0.15460 (15)	0.0474 (7)
H45	0.3983	0.4569	0.1132	0.057*
C46	0.49964 (19)	0.42783 (19)	0.20668 (12)	0.0309 (5)
C47	0.71875 (16)	0.48393 (15)	0.41265 (11)	0.0207 (4)
C48	0.63217 (16)	0.41173 (14)	0.45209 (10)	0.0191 (4)
C49	0.60412 (18)	0.38563 (16)	0.52791 (12)	0.0263 (4)
H49	0.6431	0.4149	0.5627	0.032*
C50	0.51724 (19)	0.31529 (17)	0.55096 (12)	0.0284 (4)
H50	0.4962	0.2957	0.6024	0.034*
C51	0.46046 (19)	0.27301 (16)	0.49921 (12)	0.0279 (4)
H51	0.4008	0.2253	0.5161	0.034*
C52	0.48931 (18)	0.29912 (15)	0.42364 (12)	0.0239 (4)
H52	0.4504	0.2701	0.3886	0.029*
C53	0.57664 (16)	0.36874 (14)	0.40089 (10)	0.0182 (4)
C54	0.76981 (17)	0.54778 (15)	0.21723 (11)	0.0213 (4)
H54	0.7189	0.5027	0.2014	0.026*

C55	0.83765 (18)	0.62008 (16)	0.16204 (12)	0.0263 (4)	
C56	0.9310 (2)	0.67272 (18)	0.18215 (14)	0.0351 (5)	
H56	0.9543	0.6603	0.2329	0.042*	
C57	0.9887 (3)	0.7431 (2)	0.12716 (18)	0.0533 (7)	
H57	1.0519	0.7790	0.1405	0.064*	
C58	0.9554 (3)	0.7615 (3)	0.05330 (19)	0.0670 (10)	
H58	0.9940	0.8115	0.0163	0.080*	
C59	0.8649 (3)	0.7067 (3)	0.03314 (17)	0.0647 (9)	
H59	0.8435	0.7174	−0.0179	0.078*	
C60	0.8067 (2)	0.6370 (2)	0.08742 (14)	0.0428 (6)	
H60	0.7447	0.6002	0.0737	0.051*	
C61	0.9470 (2)	0.11464 (17)	0.34678 (13)	0.0311 (5)	
H61A	1.0174	0.1263	0.3147	0.047*	
H61B	0.9333	0.0396	0.3596	0.047*	
H61C	0.9589	0.1386	0.3927	0.047*	
C62	0.3403 (2)	0.72154 (18)	0.23465 (15)	0.0400 (6)	
H62A	0.3727	0.7382	0.2792	0.060*	
H62B	0.2546	0.7164	0.2409	0.060*	
H62C	0.3568	0.7771	0.1906	0.060*	
N7A	0.8521 (5)	0.0772 (4)	0.2059 (3)	0.0218 (10)	0.558 (6)
H7N	0.9149 (19)	0.0479 (19)	0.2321 (14)	0.026*	
C63A	0.8282 (3)	0.0707 (3)	0.1302 (2)	0.0224 (9)	0.558 (6)
H63A	0.8332	0.1409	0.0963	0.027*	0.558 (6)
H63B	0.7468	0.0488	0.1277	0.027*	0.558 (6)
C64A	0.9147 (3)	−0.0064 (3)	0.1044 (2)	0.0294 (11)	0.558 (6)
H64A	0.8962	−0.0091	0.0530	0.044*	0.558 (6)
H64B	0.9952	0.0159	0.1060	0.044*	0.558 (6)
H64C	0.9088	−0.0762	0.1373	0.044*	0.558 (6)
N7B	0.8554 (6)	0.0477 (5)	0.2323 (4)	0.0233 (13)	0.442 (6)
C63B	0.8341 (4)	0.0149 (4)	0.1650 (3)	0.0261 (12)	0.442 (6)
H63C	0.7477	0.0178	0.1574	0.031*	0.442 (6)
H63D	0.8647	−0.0590	0.1710	0.031*	0.442 (6)
C64B	0.8899 (5)	0.0800 (4)	0.0964 (3)	0.0326 (15)	0.442 (6)
H64D	0.8716	0.0530	0.0527	0.049*	0.442 (6)
H64E	0.8586	0.1531	0.0890	0.049*	0.442 (6)
H64F	0.9758	0.0762	0.1026	0.049*	0.442 (6)
N8A	0.2954 (4)	0.6517 (4)	0.1086 (2)	0.0260 (9)	0.585 (8)
H8N	0.257 (2)	0.7052 (17)	0.1168 (14)	0.031*	
C65A	0.2543 (4)	0.6208 (4)	0.0438 (2)	0.0313 (11)	0.585 (8)
H65A	0.3230	0.5932	0.0181	0.038*	0.585 (8)
H65B	0.2186	0.6836	0.0087	0.038*	0.585 (8)
C66A	0.1651 (5)	0.5390 (3)	0.0618 (3)	0.0345 (11)	0.585 (8)
H66A	0.1408	0.5215	0.0156	0.052*	0.585 (8)
H66B	0.2003	0.4759	0.0956	0.052*	0.585 (8)
H66C	0.0959	0.5663	0.0862	0.052*	0.585 (8)
N8B	0.2674 (7)	0.6087 (7)	0.1159 (4)	0.052 (2)	0.415 (8)
C65B	0.2206 (7)	0.5651 (6)	0.0580 (4)	0.048 (2)	0.415 (8)
H65C	0.1387	0.5951	0.0470	0.057*	0.415 (8)
H65D	0.2173	0.4883	0.0769	0.057*	0.415 (8)
C66B	0.2925 (7)	0.5858 (6)	−0.0134 (4)	0.054 (2)	0.415 (8)
H66D	0.2564	0.5544	−0.0503	0.082*	0.415 (8)
H66E	0.2946	0.6617	−0.0332	0.082*	0.415 (8)

H66F	0.3733	0.5549	−0.0033	0.082*	0.415 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0231 (7)	0.0256 (7)	0.0282 (7)	0.0092 (6)	−0.0116 (6)	−0.0161 (6)
O2	0.0364 (8)	0.0288 (8)	0.0342 (8)	−0.0113 (7)	−0.0077 (7)	−0.0155 (6)
N1	0.0181 (7)	0.0190 (7)	0.0238 (8)	−0.0027 (6)	−0.0044 (6)	−0.0080 (6)
N2	0.0164 (7)	0.0181 (7)	0.0273 (9)	−0.0009 (6)	−0.0035 (6)	−0.0035 (6)
N3	0.0162 (7)	0.0261 (8)	0.0273 (9)	0.0036 (6)	−0.0055 (6)	−0.0112 (7)
N4	0.0256 (9)	0.0242 (8)	0.0325 (10)	0.0079 (7)	−0.0087 (7)	−0.0123 (7)
C1	0.0151 (8)	0.0161 (8)	0.0240 (9)	0.0016 (7)	−0.0018 (7)	−0.0088 (7)
C2	0.0171 (8)	0.0197 (8)	0.0211 (9)	−0.0008 (7)	−0.0028 (7)	−0.0086 (7)
C3	0.0159 (8)	0.0184 (8)	0.0250 (9)	−0.0019 (7)	−0.0028 (7)	−0.0056 (7)
C4	0.0162 (8)	0.0281 (10)	0.0342 (11)	0.0033 (8)	−0.0039 (8)	−0.0184 (9)
C5	0.0178 (8)	0.0270 (9)	0.0256 (10)	0.0002 (7)	−0.0030 (7)	−0.0157 (8)
C6	0.0154 (8)	0.0193 (8)	0.0206 (9)	−0.0027 (7)	−0.0021 (7)	−0.0085 (7)
C7	0.0181 (8)	0.0178 (8)	0.0184 (8)	−0.0021 (7)	−0.0027 (7)	−0.0088 (7)
C8	0.0187 (8)	0.0167 (8)	0.0180 (8)	−0.0001 (7)	−0.0010 (7)	−0.0052 (7)
C9	0.0230 (9)	0.0199 (9)	0.0190 (9)	−0.0004 (7)	−0.0029 (7)	−0.0055 (7)
C10	0.0240 (9)	0.0204 (9)	0.0213 (9)	0.0026 (7)	−0.0045 (7)	−0.0030 (7)
C11	0.0221 (9)	0.0168 (8)	0.0263 (10)	0.0029 (7)	−0.0028 (8)	−0.0063 (7)
C12	0.0221 (9)	0.0202 (9)	0.0255 (10)	0.0015 (7)	−0.0051 (8)	−0.0106 (7)
C13	0.0189 (8)	0.0181 (8)	0.0225 (9)	0.0023 (7)	−0.0058 (7)	−0.0067 (7)
C14	0.0215 (9)	0.0245 (9)	0.0237 (10)	0.0005 (8)	−0.0076 (7)	−0.0102 (8)
C15	0.0187 (8)	0.0269 (10)	0.0213 (9)	−0.0019 (7)	−0.0046 (7)	−0.0113 (8)
C16	0.0282 (10)	0.0386 (12)	0.0224 (10)	−0.0034 (9)	−0.0031 (8)	−0.0171 (9)
C17	0.0316 (11)	0.0490 (13)	0.0202 (10)	−0.0079 (10)	0.0020 (8)	−0.0118 (9)
C18	0.0291 (11)	0.0449 (13)	0.0267 (11)	−0.0170 (10)	0.0024 (9)	−0.0089 (10)
C19	0.0269 (10)	0.0336 (11)	0.0224 (10)	−0.0118 (9)	−0.0014 (8)	−0.0105 (8)
C20	0.0168 (8)	0.0235 (9)	0.0186 (9)	−0.0024 (7)	−0.0030 (7)	−0.0088 (7)
C21	0.0179 (8)	0.0182 (8)	0.0288 (10)	−0.0006 (7)	−0.0040 (7)	−0.0064 (7)
C22	0.0199 (9)	0.0183 (9)	0.0279 (10)	0.0028 (7)	−0.0011 (7)	−0.0050 (7)
C23	0.0236 (9)	0.0206 (9)	0.0288 (10)	−0.0006 (8)	−0.0054 (8)	−0.0057 (8)
C24	0.0246 (10)	0.0218 (9)	0.0339 (11)	−0.0016 (8)	−0.0045 (8)	−0.0082 (8)
C25	0.0282 (10)	0.0230 (10)	0.0305 (11)	−0.0018 (8)	0.0015 (8)	−0.0067 (8)
C26	0.0333 (11)	0.0340 (11)	0.0272 (11)	−0.0018 (9)	−0.0028 (9)	−0.0058 (9)
C27	0.0252 (10)	0.0321 (11)	0.0317 (11)	−0.0050 (9)	−0.0043 (8)	−0.0111 (9)
C28	0.0255 (11)	0.0512 (14)	0.0556 (15)	0.0181 (10)	−0.0167 (10)	−0.0380 (13)
C29	0.0303 (11)	0.0283 (10)	0.0278 (11)	0.0079 (9)	−0.0101 (9)	−0.0063 (8)
C30	0.0205 (9)	0.0237 (9)	0.0232 (9)	−0.0005 (7)	−0.0061 (7)	−0.0064 (8)
C31	0.0293 (11)	0.0334 (11)	0.0301 (11)	0.0034 (9)	−0.0106 (9)	−0.0070 (9)
C32	0.0216 (9)	0.0303 (11)	0.0357 (11)	0.0028 (8)	−0.0020 (8)	−0.0150 (9)
C33	0.0283 (12)	0.0338 (12)	0.081 (2)	−0.0019 (10)	−0.0026 (12)	−0.0304 (13)
O3	0.0341 (9)	0.0571 (11)	0.0519 (11)	0.0115 (8)	−0.0233 (8)	−0.0416 (9)
O4	0.0288 (7)	0.0362 (8)	0.0292 (8)	−0.0147 (7)	−0.0016 (6)	−0.0162 (6)
N5	0.0186 (7)	0.0173 (7)	0.0201 (8)	−0.0044 (6)	−0.0023 (6)	−0.0068 (6)
N6	0.0192 (7)	0.0163 (7)	0.0235 (8)	−0.0002 (6)	−0.0015 (6)	−0.0053 (6)
C34	0.0232 (9)	0.0289 (10)	0.0296 (10)	−0.0050 (8)	−0.0044 (8)	−0.0162 (8)
C35	0.0263 (10)	0.0426 (12)	0.0394 (12)	−0.0091 (9)	0.0027 (9)	−0.0307 (10)
C36	0.0222 (9)	0.0302 (11)	0.0434 (12)	−0.0092 (8)	0.0086 (9)	−0.0247 (10)
C37	0.0256 (9)	0.0174 (9)	0.0268 (10)	−0.0013 (8)	0.0049 (8)	−0.0056 (7)

C38	0.0264 (9)	0.0209 (9)	0.0194 (9)	0.0010 (8)	−0.0014 (7)	−0.0078 (7)
C39	0.0206 (9)	0.0169 (8)	0.0210 (9)	−0.0034 (7)	−0.0003 (7)	−0.0087 (7)
C40	0.0175 (8)	0.0150 (8)	0.0213 (9)	−0.0032 (7)	−0.0031 (7)	−0.0076 (7)
C41	0.0186 (8)	0.0220 (9)	0.0204 (9)	−0.0023 (7)	−0.0044 (7)	−0.0058 (7)
C42	0.0222 (9)	0.0227 (9)	0.0260 (10)	−0.0006 (8)	−0.0040 (8)	−0.0055 (8)
C43	0.0240 (10)	0.0309 (11)	0.0325 (11)	0.0033 (9)	−0.0019 (9)	0.0006 (9)
C44	0.0278 (11)	0.0701 (18)	0.0273 (12)	0.0158 (12)	−0.0098 (9)	−0.0061 (12)
C45	0.0326 (12)	0.079 (2)	0.0371 (13)	0.0143 (13)	−0.0194 (11)	−0.0299 (13)
C46	0.0238 (10)	0.0425 (12)	0.0320 (11)	0.0028 (9)	−0.0092 (9)	−0.0202 (10)
C47	0.0185 (8)	0.0228 (9)	0.0239 (9)	−0.0004 (7)	−0.0039 (7)	−0.0114 (8)
C48	0.0178 (8)	0.0202 (8)	0.0216 (9)	−0.0016 (7)	−0.0021 (7)	−0.0090 (7)
C49	0.0277 (10)	0.0304 (10)	0.0247 (10)	−0.0040 (8)	−0.0010 (8)	−0.0135 (8)
C50	0.0323 (11)	0.0303 (11)	0.0243 (10)	−0.0064 (9)	0.0038 (8)	−0.0091 (8)
C51	0.0294 (10)	0.0232 (10)	0.0331 (11)	−0.0083 (8)	0.0038 (9)	−0.0088 (8)
C52	0.0251 (9)	0.0199 (9)	0.0292 (10)	−0.0054 (8)	−0.0019 (8)	−0.0091 (8)
C53	0.0180 (8)	0.0166 (8)	0.0219 (9)	0.0008 (7)	−0.0024 (7)	−0.0085 (7)
C54	0.0203 (9)	0.0187 (9)	0.0250 (10)	−0.0004 (7)	−0.0037 (7)	−0.0052 (7)
C55	0.0242 (10)	0.0236 (10)	0.0278 (10)	0.0012 (8)	−0.0009 (8)	0.0000 (8)
C56	0.0332 (11)	0.0303 (11)	0.0392 (13)	−0.0045 (10)	−0.0023 (10)	−0.0018 (10)
C57	0.0411 (14)	0.0431 (15)	0.068 (2)	−0.0130 (12)	0.0011 (14)	0.0064 (14)
C58	0.0545 (18)	0.070 (2)	0.0558 (19)	−0.0129 (16)	0.0027 (15)	0.0295 (16)
C59	0.0537 (18)	0.087 (2)	0.0377 (15)	−0.0127 (17)	−0.0035 (13)	0.0220 (15)
C60	0.0393 (13)	0.0520 (15)	0.0301 (12)	−0.0066 (12)	−0.0052 (10)	0.0068 (11)
C61	0.0331 (11)	0.0237 (10)	0.0348 (12)	0.0074 (9)	0.0043 (9)	−0.0062 (9)
C62	0.0332 (12)	0.0291 (11)	0.0507 (15)	0.0085 (10)	−0.0052 (11)	0.0029 (10)
N7A	0.0218 (18)	0.020 (2)	0.025 (2)	−0.0025 (17)	−0.0009 (19)	−0.0081 (17)
C63A	0.0240 (19)	0.024 (2)	0.023 (2)	0.0041 (15)	−0.0026 (17)	−0.0137 (18)
C64A	0.031 (2)	0.034 (2)	0.0240 (19)	0.0125 (17)	−0.0036 (15)	−0.0136 (16)
N7B	0.020 (2)	0.021 (3)	0.034 (3)	0.001 (2)	0.006 (3)	−0.018 (2)
C63B	0.030 (3)	0.023 (3)	0.028 (3)	−0.001 (2)	0.001 (2)	−0.011 (2)
C64B	0.033 (3)	0.042 (3)	0.026 (3)	−0.007 (2)	−0.002 (2)	−0.016 (2)
N8A	0.0267 (19)	0.022 (2)	0.0281 (18)	0.0005 (15)	−0.0128 (14)	−0.0024 (16)
C65A	0.0277 (19)	0.035 (2)	0.028 (2)	−0.0068 (18)	−0.0115 (16)	0.0019 (17)
C66A	0.035 (3)	0.029 (2)	0.038 (2)	−0.0148 (19)	−0.0120 (19)	−0.0006 (17)
N8B	0.058 (5)	0.043 (4)	0.051 (4)	0.010 (4)	−0.029 (3)	0.000 (4)
C65B	0.042 (4)	0.037 (4)	0.059 (5)	−0.015 (4)	−0.031 (4)	0.005 (3)
C66B	0.068 (5)	0.056 (4)	0.038 (4)	−0.012 (4)	−0.024 (3)	−0.003 (3)

Geometric parameters (Å, º)

O1—C1	1.380 (2)	C34—C39	1.387 (3)
O1—C13	1.382 (2)	C35—C36	1.384 (3)
O2—C14	1.218 (2)	C35—H35	0.9500
N1—N2	1.369 (2)	C36—N7A	1.360 (5)
N1—C14	1.389 (2)	C36—C37	1.411 (3)
N1—C7	1.502 (2)	C36—N7B	1.465 (6)
N2—C21	1.282 (3)	C37—C38	1.382 (3)
N3—C3	1.381 (2)	C37—C61	1.501 (3)
N3—C30	1.454 (2)	C38—C39	1.395 (3)
N3—H3N	0.865 (19)	C38—H38	0.9500
N4—C11	1.373 (2)	C39—C40	1.517 (2)
N4—C32	1.460 (3)	C40—C41	1.515 (2)

N4—H4N	0.884 (18)	C40—C53	1.517 (3)
C1—C6	1.386 (2)	C41—C46	1.378 (3)
C1—C2	1.391 (2)	C41—C42	1.401 (3)
C2—C3	1.391 (3)	C42—C43	1.380 (3)
C2—H2	0.9500	C42—H42	0.9500
C3—C4	1.420 (3)	C43—C44	1.411 (3)
C4—C5	1.385 (3)	C43—C62	1.496 (3)
C4—C28	1.499 (3)	C44—C45	1.383 (4)
C5—C6	1.402 (3)	C44—N8B	1.402 (7)
C5—H5	0.9500	C44—N8A	1.422 (4)
C6—C7	1.519 (2)	C45—C46	1.393 (3)
C7—C8	1.514 (2)	C45—H45	0.9500
C7—C20	1.518 (3)	C47—C48	1.470 (3)
C8—C13	1.386 (3)	C48—C53	1.386 (2)
C8—C9	1.404 (2)	C48—C49	1.390 (3)
C9—C10	1.381 (3)	C49—C50	1.387 (3)
C9—H9	0.9500	C49—H49	0.9500
C10—C11	1.426 (3)	C50—C51	1.395 (3)
C10—C29	1.511 (3)	C50—H50	0.9500
C11—C12	1.390 (3)	C51—C52	1.388 (3)
C12—C13	1.388 (3)	C51—H51	0.9500
C12—H12	0.9500	C52—C53	1.384 (3)
C14—C15	1.480 (3)	C52—H52	0.9500
C15—C16	1.386 (3)	C54—C55	1.462 (3)
C15—C20	1.389 (2)	C54—H54	0.9500
C16—C17	1.379 (3)	C55—C60	1.387 (3)
C16—H16	0.9500	C55—C56	1.403 (3)
C17—C18	1.392 (3)	C56—C57	1.386 (4)
C17—H17	0.9500	C56—H56	0.9500
C18—C19	1.386 (3)	C57—C58	1.380 (5)
C18—H18	0.9500	C57—H57	0.9500
C19—C20	1.389 (3)	C58—C59	1.397 (5)
C19—H19	0.9500	C58—H58	0.9500
C21—C22	1.472 (3)	C59—C60	1.376 (4)
C21—H21	0.9500	C59—H59	0.9500
C22—C27	1.388 (3)	C60—H60	0.9500
C22—C23	1.408 (3)	C61—H61A	0.9800
C23—C24	1.393 (3)	C61—H61B	0.9800
C23—H23	0.9500	C61—H61C	0.9800
C24—C25	1.391 (3)	C62—H62A	0.9800
C24—H24	0.9500	C62—H62B	0.9800
C25—C26	1.385 (3)	C62—H62C	0.9800
C25—H25	0.9500	N7A—C63A	1.446 (6)
C26—C27	1.395 (3)	N7A—H7N	0.883 (17)
C26—H26	0.9500	C63A—C64A	1.506 (5)
C27—H27	0.9500	C63A—H63A	0.9900
C28—H28A	0.9800	C63A—H63B	0.9900
C28—H28B	0.9800	C64A—H64A	0.9800
C28—H28C	0.9800	C64A—H64B	0.9800
C29—H29A	0.9800	C64A—H64C	0.9800
C29—H29B	0.9800	N7B—C63B	1.430 (7)
C29—H29C	0.9800	C63B—C64B	1.502 (7)

C30—C31	1.516 (3)	C63B—H63C	0.9900
C30—H30A	0.9900	C63B—H63D	0.9900
C30—H30B	0.9900	C64B—H64D	0.9800
C31—H31A	0.9800	C64B—H64E	0.9800
C31—H31B	0.9800	C64B—H64F	0.9800
C31—H31C	0.9800	N8A—C65A	1.440 (6)
C32—C33	1.501 (3)	N8A—H8N	0.840 (18)
C32—H32A	0.9900	C65A—C66A	1.500 (7)
C32—H32B	0.9900	C65A—H65A	0.9900
C33—H33A	0.9800	C65A—H65B	0.9900
C33—H33B	0.9800	C66A—H66A	0.9800
C33—H33C	0.9800	C66A—H66B	0.9800
O3—C34	1.377 (3)	C66A—H66C	0.9800
O3—C46	1.380 (3)	N8B—C65B	1.445 (10)
O4—C47	1.217 (2)	C65B—C66B	1.507 (10)
N5—N6	1.367 (2)	C65B—H65C	0.9900
N5—C47	1.393 (2)	C65B—H65D	0.9900
N5—C40	1.497 (2)	C66B—H66D	0.9800
N6—C54	1.281 (2)	C66B—H66E	0.9800
C34—C35	1.387 (3)	C66B—H66F	0.9800

C1—O1—C13	118.38 (14)	C37—C36—N7B	111.3 (3)
N2—N1—C14	117.07 (15)	C38—C37—C36	118.14 (18)
N2—N1—C7	128.26 (15)	C38—C37—C61	121.42 (18)
C14—N1—C7	114.64 (15)	C36—C37—C61	120.44 (18)
C21—N2—N1	120.39 (16)	C37—C38—C39	123.57 (18)
C3—N3—C30	121.82 (15)	C37—C38—H38	118.2
C3—N3—H3N	122 (2)	C39—C38—H38	118.2
C30—N3—H3N	112 (2)	C34—C39—C38	116.56 (17)
C11—N4—C32	122.65 (16)	C34—C39—C40	121.71 (17)
C11—N4—H4N	118 (2)	C38—C39—C40	121.69 (16)
C32—N4—H4N	117 (2)	N5—C40—C41	111.51 (14)
O1—C1—C6	123.27 (16)	N5—C40—C39	111.43 (14)
O1—C1—C2	114.15 (15)	C41—C40—C39	110.18 (15)
C6—C1—C2	122.58 (16)	N5—C40—C53	99.13 (14)
C1—C2—C3	120.39 (17)	C41—C40—C53	113.05 (15)
C1—C2—H2	119.8	C39—C40—C53	111.15 (15)
C3—C2—H2	119.8	C46—C41—C42	116.50 (18)
N3—C3—C2	120.69 (17)	C46—C41—C40	122.53 (17)
N3—C3—C4	120.43 (16)	C42—C41—C40	120.91 (16)
C2—C3—C4	118.85 (16)	C43—C42—C41	123.43 (19)
C5—C4—C3	118.45 (17)	C43—C42—H42	118.3
C5—C4—C28	121.50 (17)	C41—C42—H42	118.3
C3—C4—C28	120.05 (17)	C42—C43—C44	118.6 (2)
C4—C5—C6	123.71 (17)	C42—C43—C62	121.5 (2)
C4—C5—H5	118.1	C44—C43—C62	119.9 (2)
C6—C5—H5	118.1	C45—C44—N8B	110.4 (4)
C1—C6—C5	116.00 (16)	C45—C44—C43	118.9 (2)
C1—C6—C7	122.13 (16)	N8B—C44—C43	128.7 (4)
C5—C6—C7	121.86 (16)	C45—C44—N8A	126.3 (3)
N1—C7—C8	111.60 (14)	C43—C44—N8A	114.2 (3)
N1—C7—C20	98.96 (13)	C44—C45—C46	120.7 (2)

C8—C7—C20	111.98 (15)	C44—C45—H45	119.6
N1—C7—C6	112.39 (14)	C46—C45—H45	119.6
C8—C7—C6	110.62 (14)	C41—C46—O3	122.72 (18)
C20—C7—C6	110.84 (15)	C41—C46—C45	121.9 (2)
C13—C8—C9	116.16 (16)	O3—C46—C45	115.36 (19)
C13—C8—C7	122.15 (16)	O4—C47—N5	125.50 (18)
C9—C8—C7	121.62 (16)	O4—C47—C48	129.22 (18)
C10—C9—C8	123.55 (17)	N5—C47—C48	105.28 (15)
C10—C9—H9	118.2	C53—C48—C49	121.65 (18)
C8—C9—H9	118.2	C53—C48—C47	109.24 (16)
C9—C10—C11	118.48 (17)	C49—C48—C47	129.11 (17)
C9—C10—C29	121.41 (17)	C50—C49—C48	117.67 (18)
C11—C10—C29	120.11 (17)	C50—C49—H49	121.2
N4—C11—C12	121.30 (17)	C48—C49—H49	121.2
N4—C11—C10	119.96 (17)	C49—C50—C51	120.60 (19)
C12—C11—C10	118.74 (17)	C49—C50—H50	119.7
C13—C12—C11	120.47 (17)	C51—C50—H50	119.7
C13—C12—H12	119.8	C52—C51—C50	121.40 (19)
C11—C12—H12	119.8	C52—C51—H51	119.3
O1—C13—C8	123.28 (16)	C50—C51—H51	119.3
O1—C13—C12	114.14 (16)	C53—C52—C51	117.87 (18)
C8—C13—C12	122.57 (16)	C53—C52—H52	121.1
O2—C14—N1	126.19 (19)	C51—C52—H52	121.1
O2—C14—C15	128.35 (19)	C52—C53—C48	120.81 (18)
N1—C14—C15	105.46 (15)	C52—C53—C40	127.48 (17)
C16—C15—C20	122.03 (18)	C48—C53—C40	111.71 (16)
C16—C15—C14	129.30 (17)	N6—C54—C55	120.01 (18)
C20—C15—C14	108.67 (16)	N6—C54—H54	120.0
C17—C16—C15	117.81 (18)	C55—C54—H54	120.0
C17—C16—H16	121.1	C60—C55—C56	119.6 (2)
C15—C16—H16	121.1	C60—C55—C54	118.0 (2)
C16—C17—C18	120.7 (2)	C56—C55—C54	122.37 (19)
C16—C17—H17	119.7	C57—C56—C55	119.3 (2)
C18—C17—H17	119.7	C57—C56—H56	120.4
C19—C18—C17	121.4 (2)	C55—C56—H56	120.4
C19—C18—H18	119.3	C58—C57—C56	120.7 (3)
C17—C18—H18	119.3	C58—C57—H57	119.6
C18—C19—C20	118.12 (18)	C56—C57—H57	119.6
C18—C19—H19	120.9	C57—C58—C59	119.9 (3)
C20—C19—H19	120.9	C57—C58—H58	120.1
C19—C20—C15	119.96 (17)	C59—C58—H58	120.1
C19—C20—C7	127.97 (16)	C60—C59—C58	119.8 (3)
C15—C20—C7	112.07 (16)	C60—C59—H59	120.1
N2—C21—C22	118.05 (17)	C58—C59—H59	120.1
N2—C21—H21	121.0	C59—C60—C55	120.7 (3)
C22—C21—H21	121.0	C59—C60—H60	119.7
C27—C22—C23	118.50 (19)	C55—C60—H60	119.7
C27—C22—C21	119.97 (18)	C37—C61—H61A	109.5
C23—C22—C21	121.35 (18)	C37—C61—H61B	109.5
C24—C23—C22	120.83 (19)	H61A—C61—H61B	109.5
C24—C23—H23	119.6	C37—C61—H61C	109.5
C22—C23—H23	119.6	H61A—C61—H61C	109.5

C25—C24—C23	119.83 (19)	H61B—C61—H61C	109.5
C25—C24—H24	120.1	C43—C62—H62A	109.5
C23—C24—H24	120.1	C43—C62—H62B	109.5
C26—C25—C24	119.6 (2)	H62A—C62—H62B	109.5
C26—C25—H25	120.2	C43—C62—H62C	109.5
C24—C25—H25	120.2	H62A—C62—H62C	109.5
C25—C26—C27	120.7 (2)	H62B—C62—H62C	109.5
C25—C26—H26	119.7	C36—N7A—C63A	125.7 (4)
C27—C26—H26	119.7	C36—N7A—H7N	107.3 (18)
C22—C27—C26	120.49 (19)	C63A—N7A—H7N	125.4 (18)
C22—C27—H27	119.8	N7A—C63A—C64A	111.4 (4)
C26—C27—H27	119.8	N7A—C63A—H63A	109.3
C4—C28—H28A	109.5	C64A—C63A—H63A	109.3
C4—C28—H28B	109.5	N7A—C63A—H63B	109.3
H28A—C28—H28B	109.5	C64A—C63A—H63B	109.3
C4—C28—H28C	109.5	H63A—C63A—H63B	108.0
H28A—C28—H28C	109.5	C63A—C64A—H64A	109.5
H28B—C28—H28C	109.5	C63A—C64A—H64B	109.5
C10—C29—H29A	109.5	H64A—C64A—H64B	109.5
C10—C29—H29B	109.5	C63A—C64A—H64C	109.5
H29A—C29—H29B	109.5	H64A—C64A—H64C	109.5
C10—C29—H29C	109.5	H64B—C64A—H64C	109.5
H29A—C29—H29C	109.5	C63B—N7B—C36	118.7 (5)
H29B—C29—H29C	109.5	N7B—C63B—C64B	114.1 (5)
N3—C30—C31	111.03 (16)	N7B—C63B—H63C	108.7
N3—C30—H30A	109.4	C64B—C63B—H63C	108.7
C31—C30—H30A	109.4	N7B—C63B—H63D	108.7
N3—C30—H30B	109.4	C64B—C63B—H63D	108.7
C31—C30—H30B	109.4	H63C—C63B—H63D	107.6
H30A—C30—H30B	108.0	C63B—C64B—H64D	109.5
C30—C31—H31A	109.5	C63B—C64B—H64E	109.5
C30—C31—H31B	109.5	H64D—C64B—H64E	109.5
H31A—C31—H31B	109.5	C63B—C64B—H64F	109.5
C30—C31—H31C	109.5	H64D—C64B—H64F	109.5
H31A—C31—H31C	109.5	H64E—C64B—H64F	109.5
H31B—C31—H31C	109.5	C44—N8A—C65A	120.2 (4)
N4—C32—C33	113.9 (2)	C44—N8A—H8N	124.4 (18)
N4—C32—H32A	108.8	C65A—N8A—H8N	112.7 (17)
C33—C32—H32A	108.8	N8A—C65A—C66A	113.5 (4)
N4—C32—H32B	108.8	N8A—C65A—H65A	108.9
C33—C32—H32B	108.8	C66A—C65A—H65A	108.9
H32A—C32—H32B	107.7	N8A—C65A—H65B	108.9
C32—C33—H33A	109.5	C66A—C65A—H65B	108.9
C32—C33—H33B	109.5	H65A—C65A—H65B	107.7
H33A—C33—H33B	109.5	C65A—C66A—H66A	109.5
C32—C33—H33C	109.5	C65A—C66A—H66B	109.5
H33A—C33—H33C	109.5	H66A—C66A—H66B	109.5
H33B—C33—H33C	109.5	C65A—C66A—H66C	109.5
C34—O3—C46	118.43 (15)	H66A—C66A—H66C	109.5
N6—N5—C47	117.81 (15)	H66B—C66A—H66C	109.5
N6—N5—C40	127.49 (15)	C44—N8B—C65B	132.8 (6)
C47—N5—C40	114.60 (15)	N8B—C65B—C66B	113.4 (8)

C54—N6—N5	119.38 (16)	N8B—C65B—H65C	108.9
O3—C34—C35	115.09 (17)	C66B—C65B—H65C	108.9
O3—C34—C39	123.12 (18)	N8B—C65B—H65D	108.9
C35—C34—C39	121.78 (19)	C66B—C65B—H65D	108.9
C36—C35—C34	120.51 (19)	H65C—C65B—H65D	107.7
C36—C35—H35	119.7	C65B—C66B—H66D	109.5
C34—C35—H35	119.7	C65B—C66B—H66E	109.5
N7A—C36—C35	114.3 (3)	H66D—C66B—H66E	109.5
N7A—C36—C37	125.9 (3)	C65B—C66B—H66F	109.5
C35—C36—C37	119.40 (18)	H66D—C66B—H66F	109.5
C35—C36—N7B	128.3 (3)	H66E—C66B—H66F	109.5

C14—N1—N2—C21	167.30 (17)	C34—C35—C36—N7A	−171.0 (3)
C7—N1—N2—C21	−10.6 (3)	C34—C35—C36—C37	2.1 (3)
C13—O1—C1—C6	−1.7 (3)	C34—C35—C36—N7B	169.0 (4)
C13—O1—C1—C2	177.98 (16)	N7A—C36—C37—C38	170.4 (3)
O1—C1—C2—C3	179.26 (17)	C35—C36—C37—C38	−1.9 (3)
C6—C1—C2—C3	−1.1 (3)	N7B—C36—C37—C38	−170.9 (3)
C30—N3—C3—C2	−3.7 (3)	N7A—C36—C37—C61	−9.5 (4)
C30—N3—C3—C4	177.96 (18)	C35—C36—C37—C61	178.2 (2)
C1—C2—C3—N3	−178.56 (17)	N7B—C36—C37—C61	9.2 (4)
C1—C2—C3—C4	−0.2 (3)	C36—C37—C38—C39	0.4 (3)
N3—C3—C4—C5	179.47 (18)	C61—C37—C38—C39	−179.69 (18)
C2—C3—C4—C5	1.1 (3)	O3—C34—C39—C38	179.79 (19)
N3—C3—C4—C28	0.2 (3)	C35—C34—C39—C38	−0.7 (3)
C2—C3—C4—C28	−178.2 (2)	O3—C34—C39—C40	2.1 (3)
C3—C4—C5—C6	−0.9 (3)	C35—C34—C39—C40	−178.40 (19)
C28—C4—C5—C6	178.4 (2)	C37—C38—C39—C34	0.9 (3)
O1—C1—C6—C5	−179.05 (17)	C37—C38—C39—C40	178.58 (18)
C2—C1—C6—C5	1.3 (3)	N6—N5—C40—C41	−55.4 (2)
O1—C1—C6—C7	−0.3 (3)	C47—N5—C40—C41	120.81 (17)
C2—C1—C6—C7	−179.91 (17)	N6—N5—C40—C39	68.2 (2)
C4—C5—C6—C1	−0.3 (3)	C47—N5—C40—C39	−115.61 (17)
C4—C5—C6—C7	−179.12 (18)	N6—N5—C40—C53	−174.71 (16)
N2—N1—C7—C8	−59.5 (2)	C47—N5—C40—C53	1.50 (18)
C14—N1—C7—C8	122.60 (17)	C34—C39—C40—N5	−133.98 (18)
N2—N1—C7—C20	−177.48 (16)	C38—C39—C40—N5	48.4 (2)
C14—N1—C7—C20	4.57 (19)	C34—C39—C40—C41	−9.7 (2)
N2—N1—C7—C6	65.5 (2)	C38—C39—C40—C41	172.75 (17)
C14—N1—C7—C6	−112.46 (17)	C34—C39—C40—C53	116.46 (19)
C1—C6—C7—N1	−125.72 (18)	C38—C39—C40—C53	−61.1 (2)
C5—C6—C7—N1	53.0 (2)	N5—C40—C41—C46	132.4 (2)
C1—C6—C7—C8	−0.2 (2)	C39—C40—C41—C46	8.2 (3)
C5—C6—C7—C8	178.49 (17)	C53—C40—C41—C46	−116.9 (2)
C1—C6—C7—C20	124.59 (18)	N5—C40—C41—C42	−44.5 (2)
C5—C6—C7—C20	−56.7 (2)	C39—C40—C41—C42	−168.75 (17)
N1—C7—C8—C13	128.72 (18)	C53—C40—C41—C42	66.2 (2)
C20—C7—C8—C13	−121.37 (19)	C46—C41—C42—C43	−0.5 (3)
C6—C7—C8—C13	2.8 (2)	C40—C41—C42—C43	176.55 (19)
N1—C7—C8—C9	−54.6 (2)	C41—C42—C43—C44	0.4 (3)
C20—C7—C8—C9	55.3 (2)	C41—C42—C43—C62	179.6 (2)
C6—C7—C8—C9	179.50 (16)	C42—C43—C44—C45	−0.1 (4)

C13—C8—C9—C10	2.1 (3)	C62—C43—C44—C45	−179.4 (2)
C7—C8—C9—C10	−174.76 (18)	C42—C43—C44—N8B	162.1 (6)
C8—C9—C10—C11	−1.5 (3)	C62—C43—C44—N8B	−17.2 (6)
C8—C9—C10—C29	179.10 (19)	C42—C43—C44—N8A	−171.5 (3)
C32—N4—C11—C12	−7.7 (3)	C62—C43—C44—N8A	9.3 (4)
C32—N4—C11—C10	171.36 (19)	N8B—C44—C45—C46	−165.2 (5)
C9—C10—C11—N4	−179.18 (19)	C43—C44—C45—C46	0.1 (4)
C29—C10—C11—N4	0.3 (3)	N8A—C44—C45—C46	170.3 (3)
C9—C10—C11—C12	−0.1 (3)	C42—C41—C46—O3	178.2 (2)
C29—C10—C11—C12	179.36 (19)	C40—C41—C46—O3	1.2 (3)
N4—C11—C12—C13	179.94 (19)	C42—C41—C46—C45	0.5 (3)
C10—C11—C12—C13	0.8 (3)	C40—C41—C46—C45	−176.6 (2)
C1—O1—C13—C8	4.4 (3)	C34—O3—C46—C41	−9.9 (3)
C1—O1—C13—C12	−176.22 (17)	C34—O3—C46—C45	168.0 (2)
C9—C8—C13—O1	178.00 (17)	C44—C45—C46—C41	−0.3 (4)
C7—C8—C13—O1	−5.1 (3)	C44—C45—C46—O3	−178.1 (2)
C9—C8—C13—C12	−1.3 (3)	N6—N5—C47—O4	−4.1 (3)
C7—C8—C13—C12	175.57 (18)	C40—N5—C47—O4	179.34 (18)
C11—C12—C13—O1	−179.49 (17)	N6—N5—C47—C48	176.04 (14)
C11—C12—C13—C8	−0.1 (3)	C40—N5—C47—C48	−0.6 (2)
N2—N1—C14—O2	−2.1 (3)	O4—C47—C48—C53	179.34 (19)
C7—N1—C14—O2	176.08 (18)	N5—C47—C48—C53	−0.8 (2)
N2—N1—C14—C15	177.78 (15)	O4—C47—C48—C49	−0.7 (3)
C7—N1—C14—C15	−4.0 (2)	N5—C47—C48—C49	179.24 (19)
O2—C14—C15—C16	1.7 (3)	C53—C48—C49—C50	−0.6 (3)
N1—C14—C15—C16	−178.2 (2)	C47—C48—C49—C50	179.40 (19)
O2—C14—C15—C20	−178.6 (2)	C48—C49—C50—C51	−0.2 (3)
N1—C14—C15—C20	1.6 (2)	C49—C50—C51—C52	0.4 (3)
C20—C15—C16—C17	−0.5 (3)	C50—C51—C52—C53	0.0 (3)
C14—C15—C16—C17	179.2 (2)	C51—C52—C53—C48	−0.8 (3)
C15—C16—C17—C18	−0.4 (3)	C51—C52—C53—C40	178.39 (18)
C16—C17—C18—C19	0.4 (4)	C49—C48—C53—C52	1.1 (3)
C17—C18—C19—C20	0.4 (3)	C47—C48—C53—C52	−178.91 (17)
C18—C19—C20—C15	−1.2 (3)	C49—C48—C53—C40	−178.21 (18)
C18—C19—C20—C7	178.97 (19)	C47—C48—C53—C40	1.8 (2)
C16—C15—C20—C19	1.3 (3)	N5—C40—C53—C52	178.82 (18)
C14—C15—C20—C19	−178.49 (17)	C41—C40—C53—C52	60.7 (2)
C16—C15—C20—C7	−178.86 (18)	C39—C40—C53—C52	−63.9 (2)
C14—C15—C20—C7	1.4 (2)	N5—C40—C53—C48	−1.95 (18)
N1—C7—C20—C19	176.43 (19)	C41—C40—C53—C48	−120.11 (17)
C8—C7—C20—C19	58.7 (2)	C39—C40—C53—C48	115.37 (17)
C6—C7—C20—C19	−65.4 (2)	N5—N6—C54—C55	177.80 (16)
N1—C7—C20—C15	−3.40 (19)	N6—C54—C55—C60	−166.3 (2)
C8—C7—C20—C15	−121.14 (17)	N6—C54—C55—C56	13.1 (3)
C6—C7—C20—C15	114.80 (17)	C60—C55—C56—C57	1.7 (3)
N1—N2—C21—C22	−176.38 (16)	C54—C55—C56—C57	−177.7 (2)
N2—C21—C22—C27	154.66 (19)	C55—C56—C57—C58	−0.1 (4)
N2—C21—C22—C23	−20.5 (3)	C56—C57—C58—C59	−1.9 (5)
C27—C22—C23—C24	−1.2 (3)	C57—C58—C59—C60	2.1 (5)
C21—C22—C23—C24	174.01 (18)	C58—C59—C60—C55	−0.5 (5)
C22—C23—C24—C25	−0.6 (3)	C56—C55—C60—C59	−1.4 (4)
C23—C24—C25—C26	1.3 (3)	C54—C55—C60—C59	178.0 (3)

C24—C25—C26—C27	−0.2 (3)	C35—C36—N7A—C63A	12.0 (6)
C23—C22—C27—C26	2.3 (3)	C37—C36—N7A—C63A	−160.6 (4)
C21—C22—C27—C26	−172.99 (19)	C36—N7A—C63A—C64A	172.7 (4)
C25—C26—C27—C22	−1.6 (3)	C35—C36—N7B—C63B	20.8 (7)
C3—N3—C30—C31	177.26 (18)	C37—C36—N7B—C63B	−171.4 (4)
C11—N4—C32—C33	80.9 (3)	C36—N7B—C63B—C64B	70.0 (7)
C47—N5—N6—C54	−175.96 (17)	C45—C44—N8A—C65A	11.5 (6)
C40—N5—N6—C54	0.1 (3)	C43—C44—N8A—C65A	−178.0 (3)
C46—O3—C34—C35	−171.3 (2)	C44—N8A—C65A—C66A	67.9 (5)
C46—O3—C34—C39	8.2 (3)	C45—C44—N8B—C65B	−7.5 (12)
O3—C34—C35—C36	178.8 (2)	C43—C44—N8B—C65B	−170.9 (8)
C39—C34—C35—C36	−0.8 (3)	C44—N8B—C65B—C66B	−73.7 (12)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C19—H19···O3	0.95	2.37	3.304 (2)	169
C52—H52···O1	0.95	2.43	3.357 (2)	165
C57—H57···O2^{i}	0.95	2.59	3.384 (3)	141
C51—H51···N3^{ii}	0.95	2.57	3.456 (3)	155
N4—H4*N*···N6^{iii}	0.88 (2)	2.69 (3)	3.365 (2)	134 (2)
C32—H32*B*···N6^{iii}	0.99	2.72	3.467 (3)	133
C24—H24···O4^{iv}	0.95	2.67	3.276 (3)	122
C25—H25···O4^{iv}	0.95	2.61	3.247 (3)	125

Symmetry codes: (i) *x*+1, *y*+1, *z*; (ii) −*x*+1, −*y*, −*z*+1; (iii) *x*−1, *y*, *z*; (iv) *x*−1, *y*−1, *z*.