Supporting Information

1,4-Bis(4-nitrosophenyl)piperazine: Novel bridging ligand in dinuclear complexes of rhodium (III) and iridium(III)

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Table 4 ^{13}C Solid state NMR data [ppm] of **4** and its resulting complexes **7a**−**c** and **8a**.

	C_4 C (NO)	C_1 C (N pip.)	C_3 CH (*anti*-O)	$C_2 + C_5 + C_6$ CH (aromatic)	$C_7 + C_8$ CH_2 (pip.)	C_q (C_5Me_5)	Me (C_5Me_5)
4	163.8, 162.2	154.6	142.5	112.7, 112.2 110.1, 110.0	46.3, 45.0 43.9, 38.6	–	–
7a	167.2, 165.4	155.6, 153.9	140.5	122.7, 113.0, 111.0	48.1, 45.2	88.6	8.9
7b	168.2, 165.0 164.9	156.8, 154.8 154.8	140.6, 137.4	121.0 120.4, 112.3 110.8, 110.5	46.5, 46.3, 44.8	89.3, 88.8	9.7
7c	166.2	155.2	140.8	123.8, 111.3	45.5	90.3	12.5
8a	163.0, 162.3	156.4, 153.5	139.3, 137.6	122.6, 114.8, 110.4, 107.9	48.0, 44.6, 43.5	98.8, 94.3	10.4

Table 5 Selected distances [Å] and angles [°] between the planes of the η^5-Cp*-ring and the aromatic system of the nitroso ligand.

	distance plane C_5Me_5 metal center	distance plane C_5Me_5 (1) plane C_5Me_5 (2)	angle plane C_5Me_5 (1) plane C_5Me_5 (2)	angle plane C_5Me_5 plane NO lig.	distance plane(1) NO lig. plane(2) NO lig.	angle plane(1) NO lig. plane(2) NO lig.
7a (chair)	1.786	12.622	–	38.15	1.711	–
7a'(boat)*	1.790	–	23.62	16.75	–	62.43
	1.789	–	23.62	27.78	–	62.43
7b (chair)	1.797	13.025	–	40.82	1.655	–
7c (boat)	1.824	–	84.29	28.22	–	55.00
8a (chair)	1.786	12.611	–	37.61	1.681	–

* If more than one complex molecule in similar conformation was present in the asymmetric unit, only the data for one unit are listed.

Table 6 Hydrogen bonds to the piperazine ring for **7a**, **7b** and **8a** [Å and °].

	D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
7a	C(8)-H(8B)...O(2)#1	0.99	2.38	3.335(6)	162.8
7b	C(8)-H(8B)...O(2)#2	0.99	2.33	3.288(11)	161.4
8a	C(8)-H(8B)...O(2)#3	0.99	2.39	3.342(4)	160.7

Symmetry transformations used to generate equivalent atoms: #1 –x+1, –y+1, –z; #2 x, –y+1/2,z–1/2; #3 –x, –y+1, –z+1

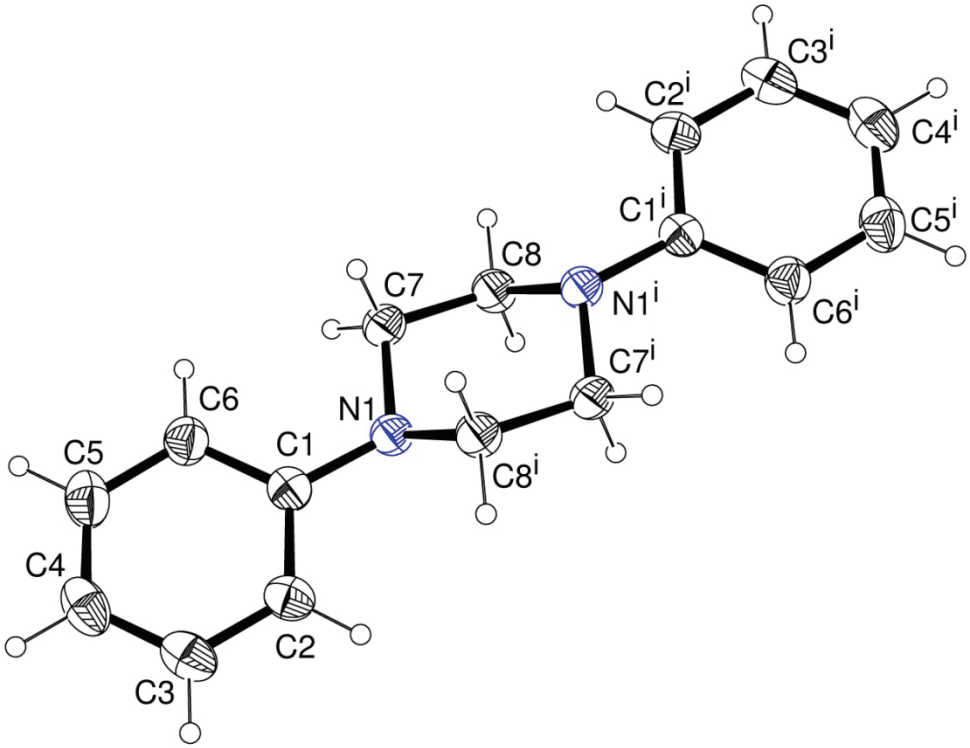


Figure 6 Molecular structure of 1,4-diphenylpiperazine (**3**). Displacement ellipsoids are drawn at 30% probability level.

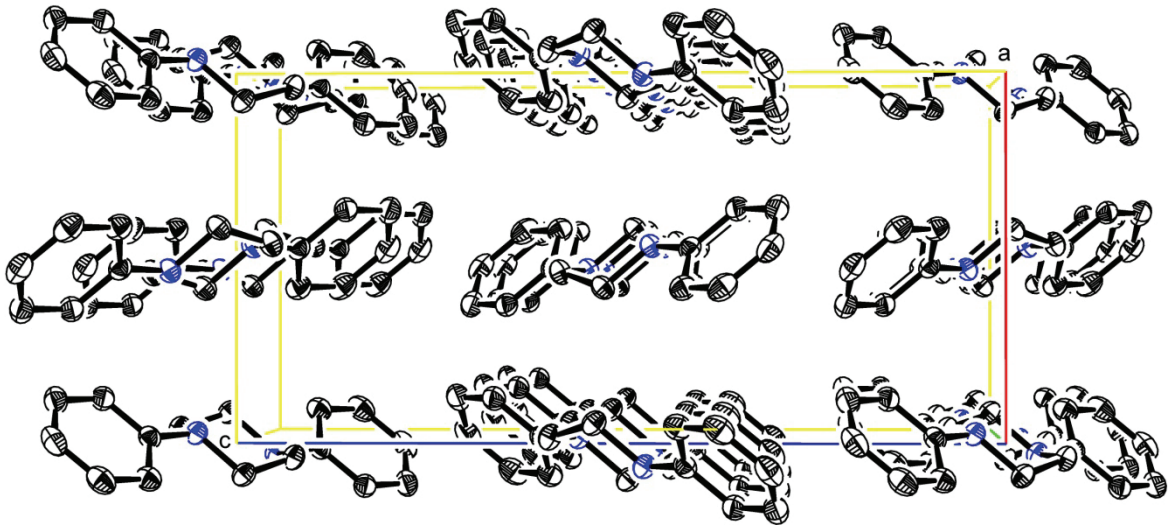


Figure 7 Molecular packing of 1,4-diphenylpiperazine (**3**) (view along b-axis). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at 30% probability level.

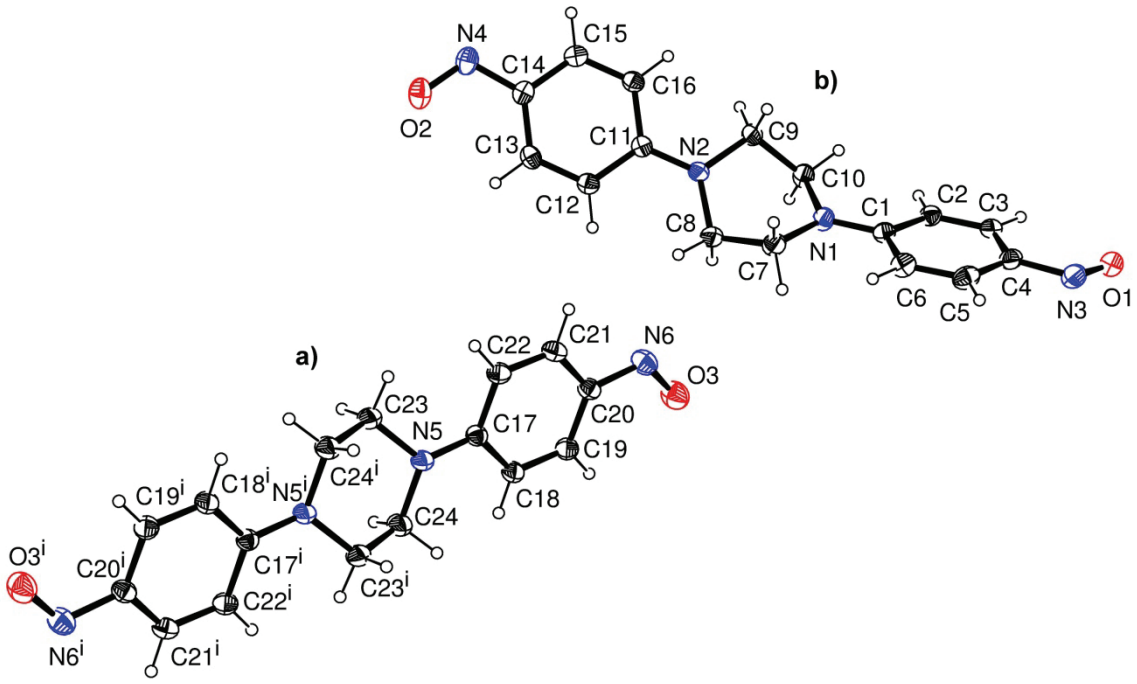


Figure 8 Molecular structure of 1,4-bis(4-nitrosophenyl)piperazine (**4**) in its chair (**a**) and boat (**b**) conformation. Displacement ellipsoids are drawn at 30% probability level.

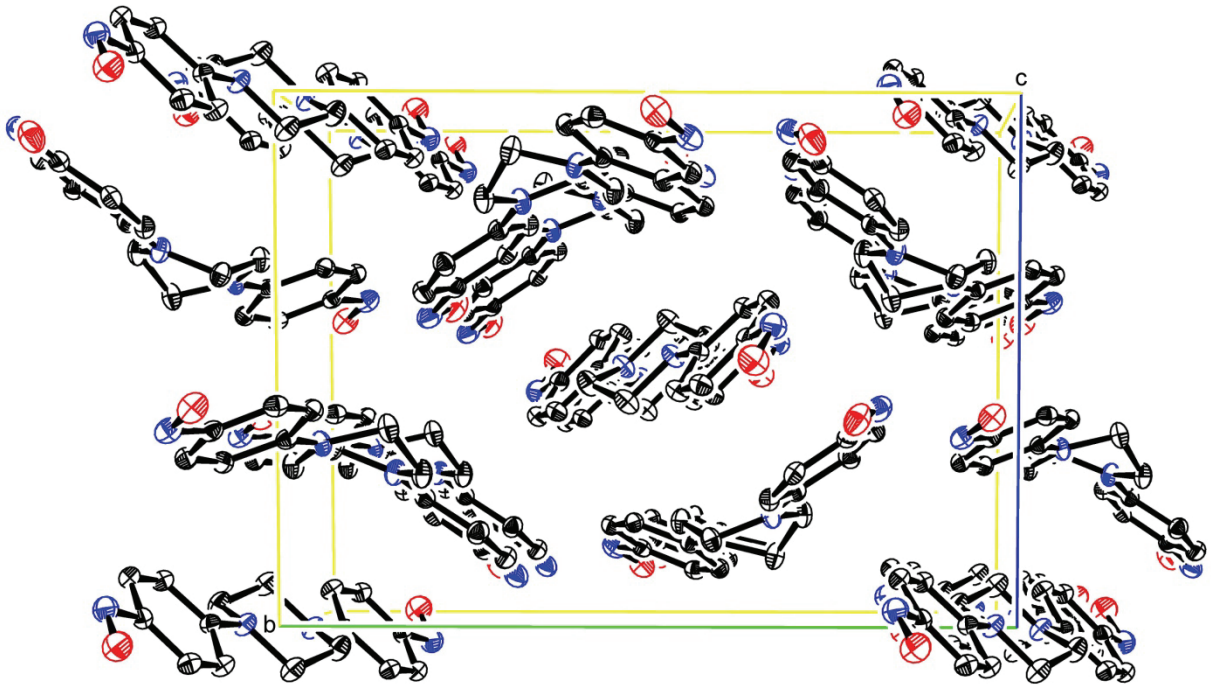
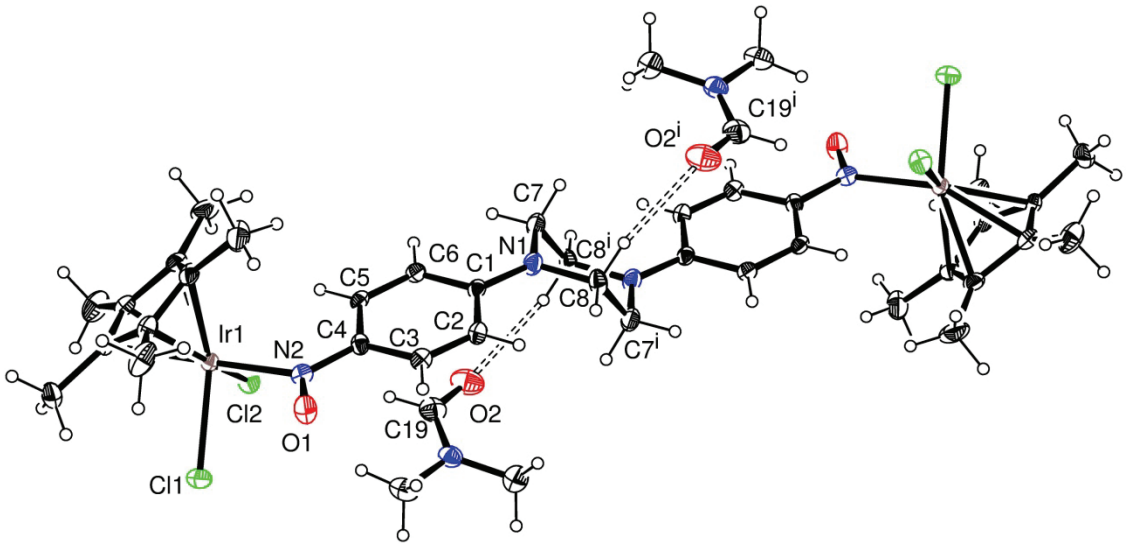


Figure 9 Molecular packing of 1,4-bis(4-nitrosophenyl)piperazine (view along a-axis). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at 30% probability level.



7a (chair conformation / crystallized from DMF)

Figure 10 Molecular structure of **7a** crystallized from DMF (chair conformation / structure **7a**) with the nearest interacting DMF molecules. Hydrogen bond data is given in Table 6. Displacement ellipsoids are drawn at 30% probability level.

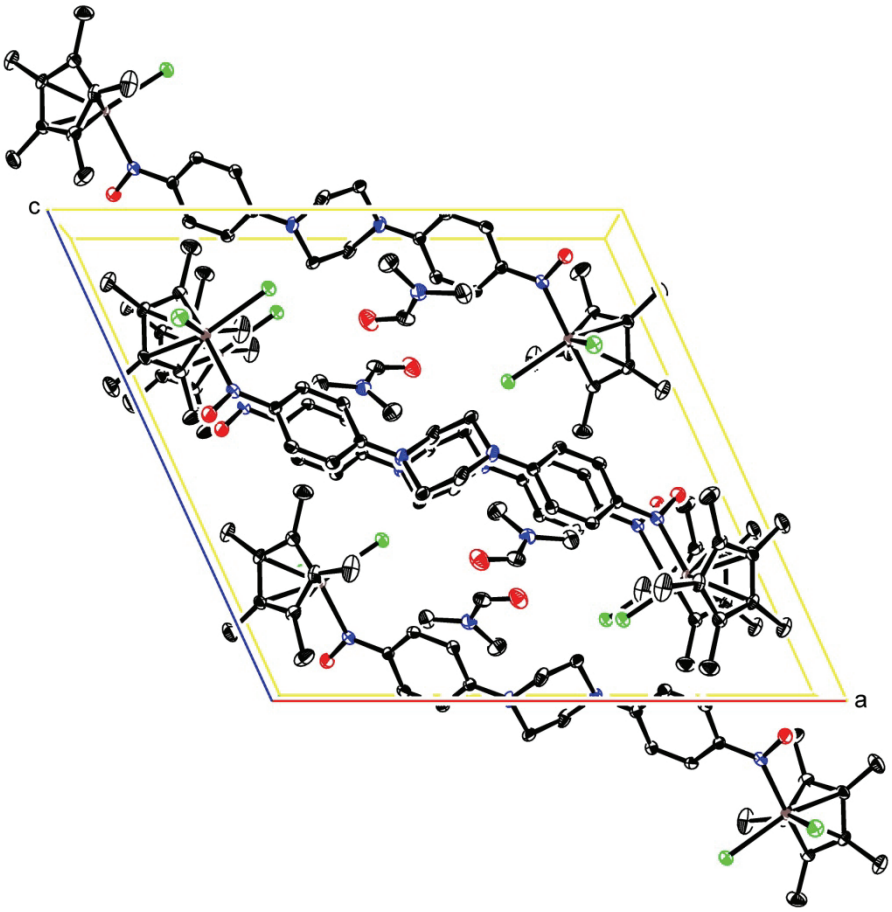
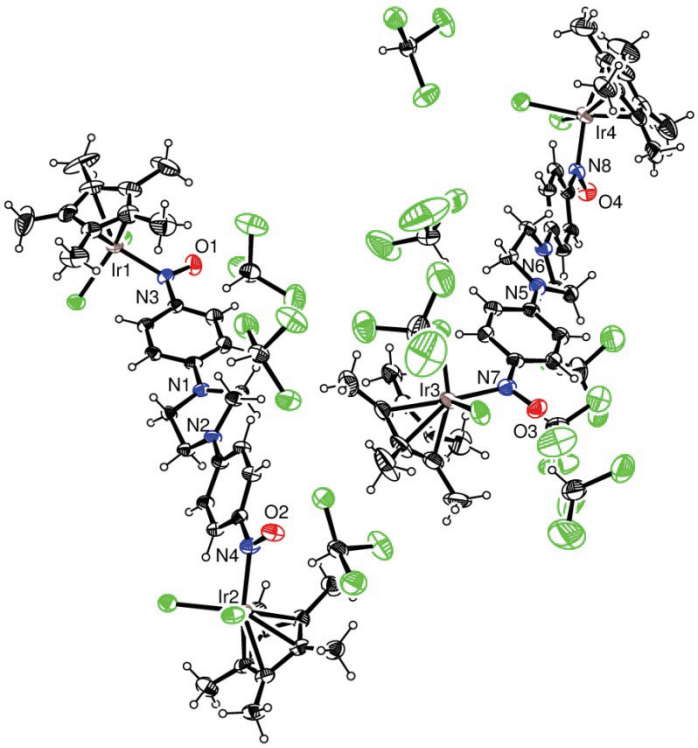


Figure 11 Molecular packing of **7a** crystallized from DMF (view along b-axis). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at 30% probability level.



7a' (boat conformation / crystallized from $CHCl_3$)

Figure 12 Molecular structure of **7a** crystallized from $CHCl_3$ (boat conformation / structure **7a'**). One $CHCl_3$ molecule was squeezed during refinement, so only 9 are depicted. Displacement ellipsoids are drawn at 30% probability level.

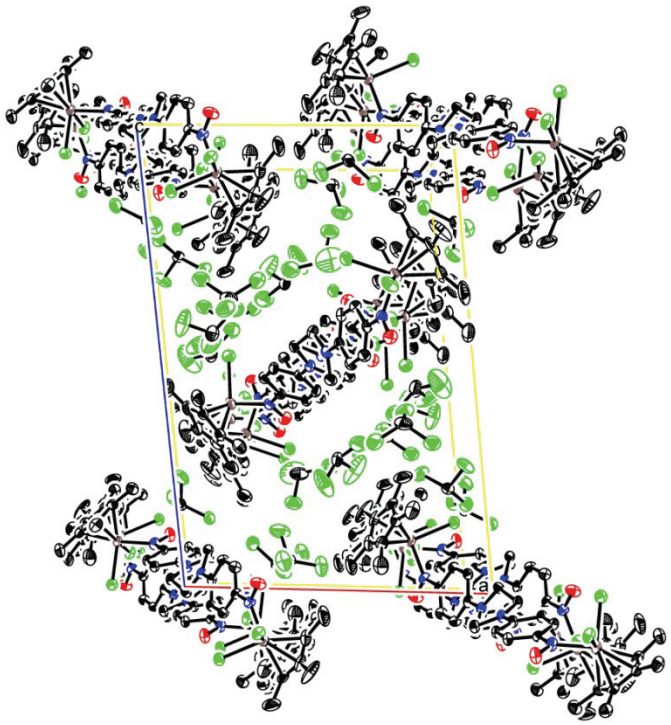
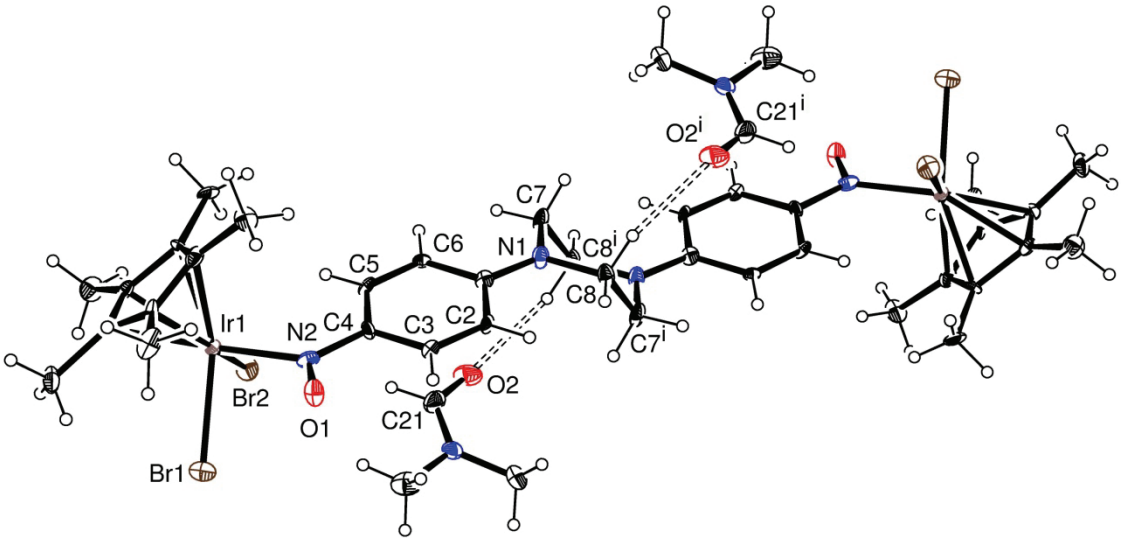


Figure 13 Molecular packing of **7a** crystallized from $CHCl_3$ (view along b-axis). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at 30% probability level.



7b (chair conformation / crystallized from DMF)

Figure 14 Molecular structure of **7b** crystallized from DMF (chair conformation) with the nearest interacting DMF molecules. Hydrogen bond data is given in Table 6. Displacement ellipsoids are drawn at 30% probability level.

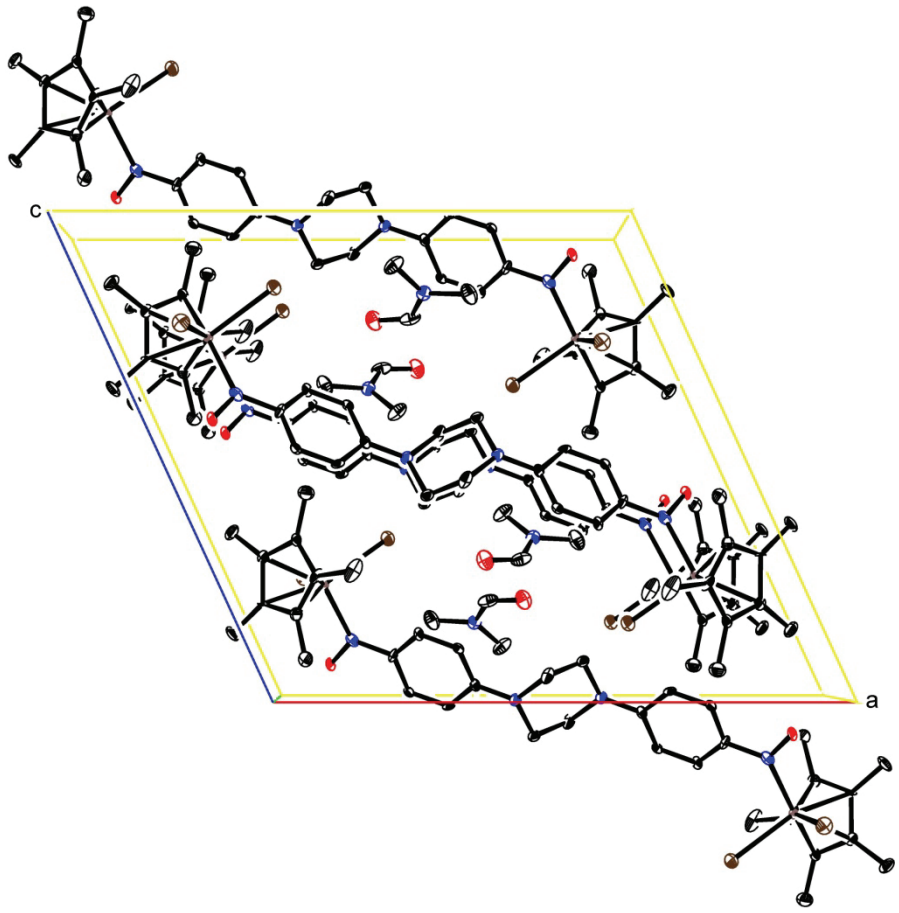
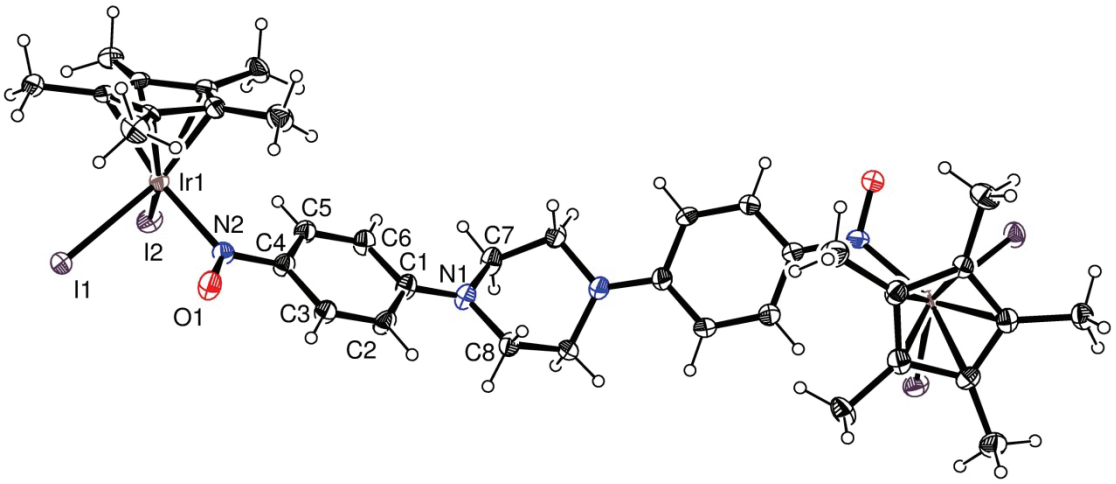


Figure 15 Molecular packing of **7b** crystallized from DMF (view along b-axis). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at 30% probability level.



7c (boat conformation / crystallized from dichloromethane)

Figure 16 Molecular structure of **7c** crystallized from dichloromethane (boat conformation). The CH_2Cl_2 molecule was squeezed during refinement, and so is not depicted. Displacement ellipsoids are drawn at 30% probability level.

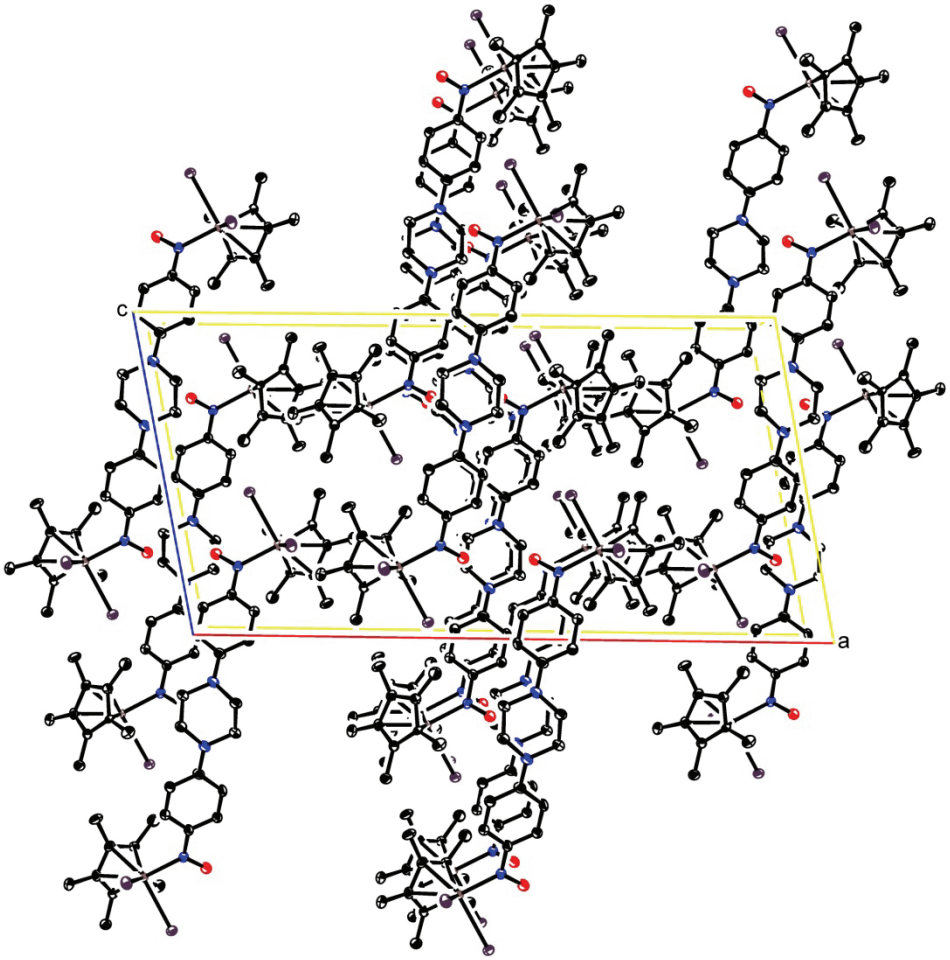
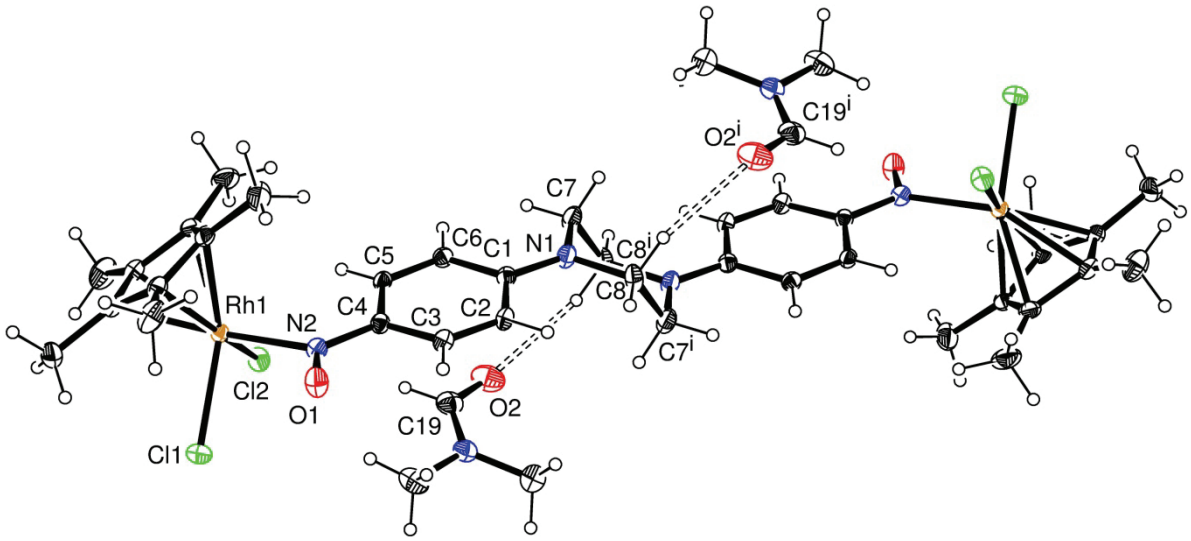


Figure 17 Molecular packing of **7c** crystallized from CH_2Cl_2 (view along b-axis). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at 30% probability level.



8a (chair conformation / crystallized from DMF)

Figure 18 Molecular structure of **8a** crystallized from DMF (chair conformation) with the nearest interacting DMF molecules. Hydrogen bond data is given in Table 6. Displacement ellipsoids are drawn at 30% probability level.

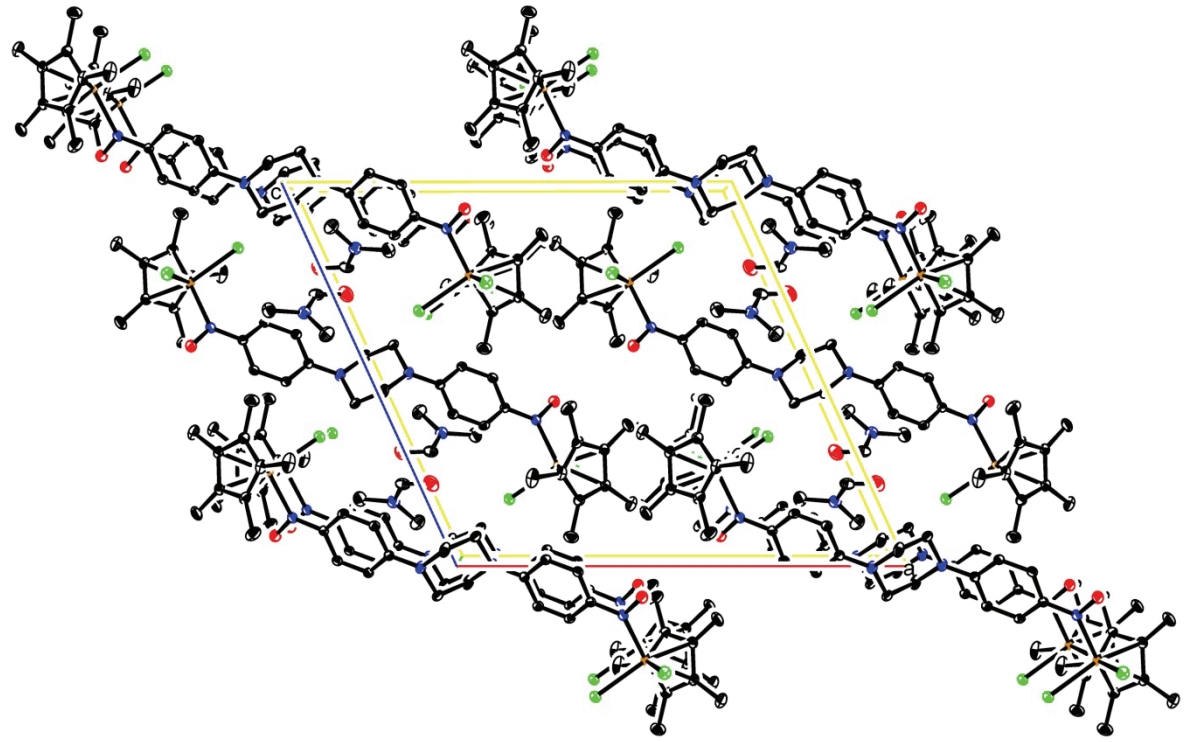


Figure 19 Molecular packing of **8a** crystallized from DMF (view along b-axis). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at 30% probability level.