

Coordination chemistry-assembled porphyrinic catenanes

Maryline Beyler, Valérie Heitz*, Jean-Pierre Sauvage*

Laboratoire de Chimie Organo-Minérale, Institut de Chimie, Université de Strasbourg-

CNRS/UMR 7177, 4, rue Blaise Pascal, 67070 Strasbourg-Cedex, France

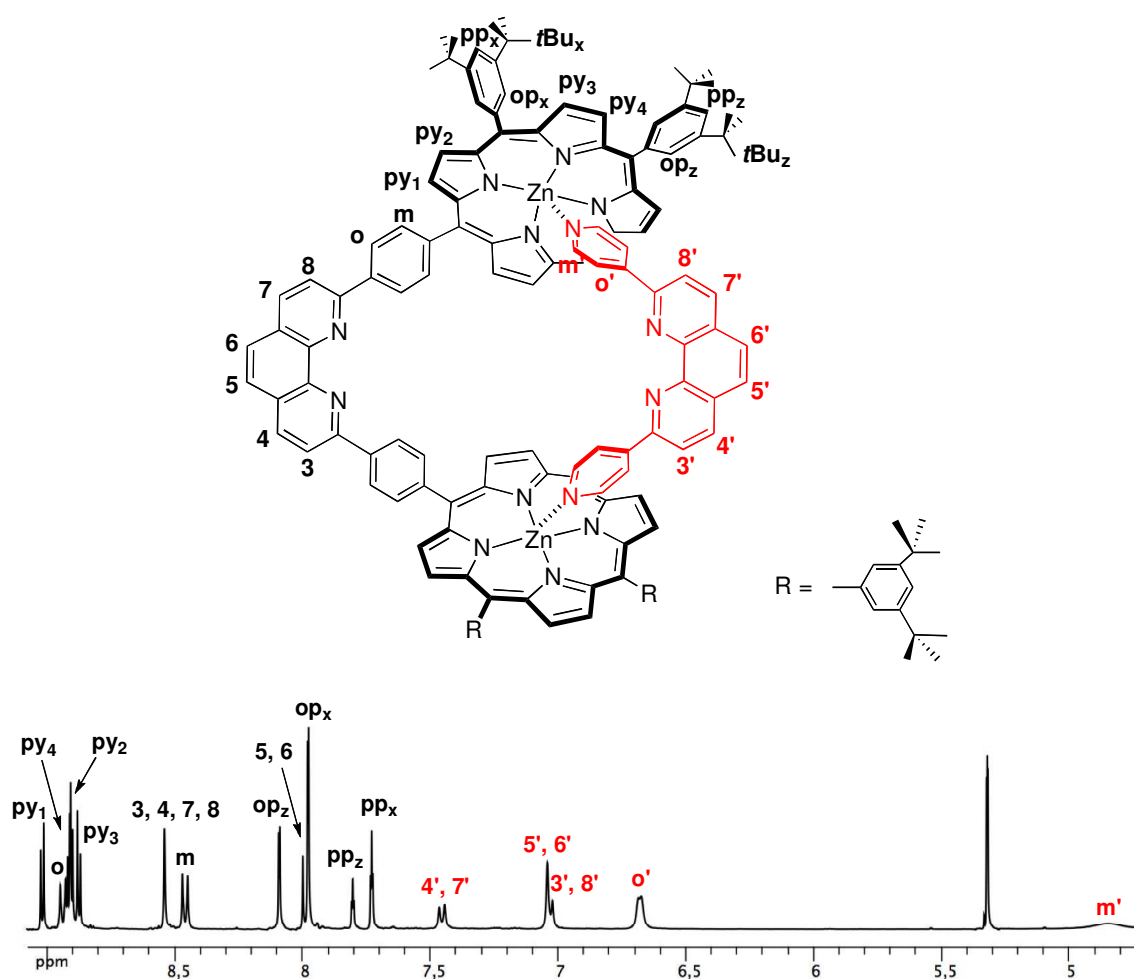
sauvage@chimie.u-strasbg.fr; heitz@chimie.u-strasbg.frNMR data of **8**

Fig SI-1. (top) Proton number assignment for **8** and (bottom) ¹H NMR spectrum (5-9 ppm range).

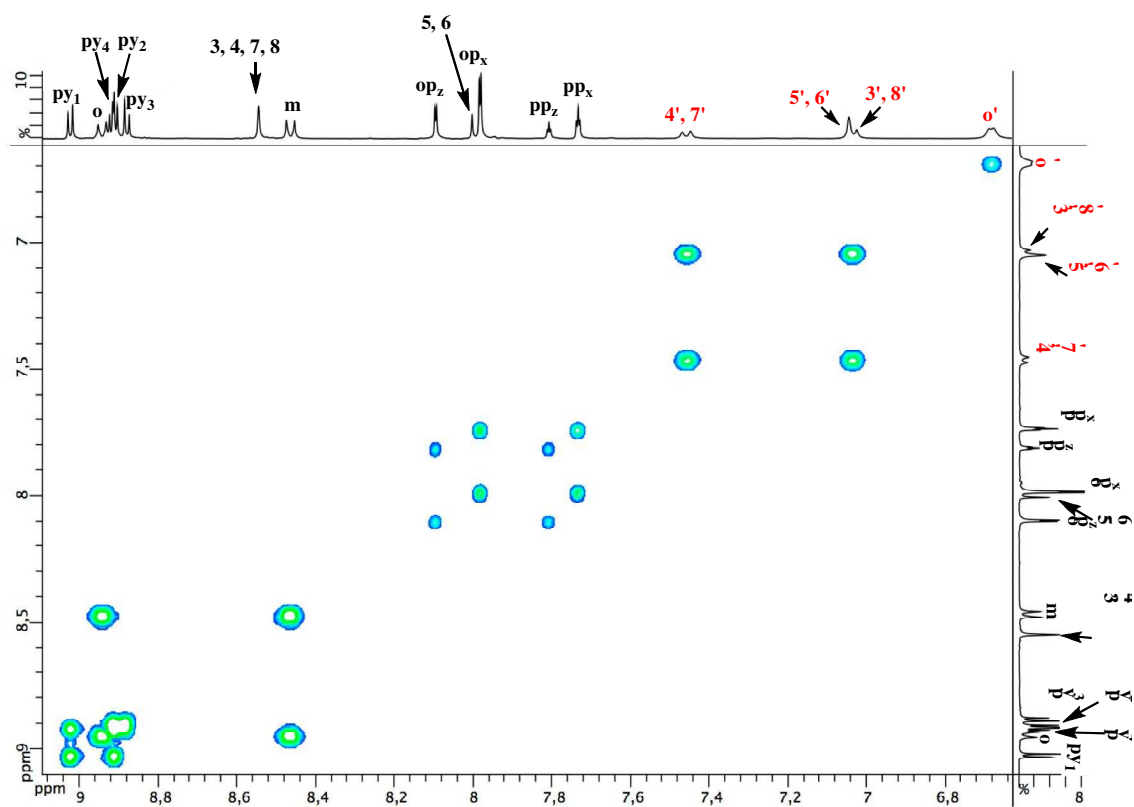


Fig SI-2. COSY spectrum of **8** showing scalar couplings in the 6.8-9 ppm range.

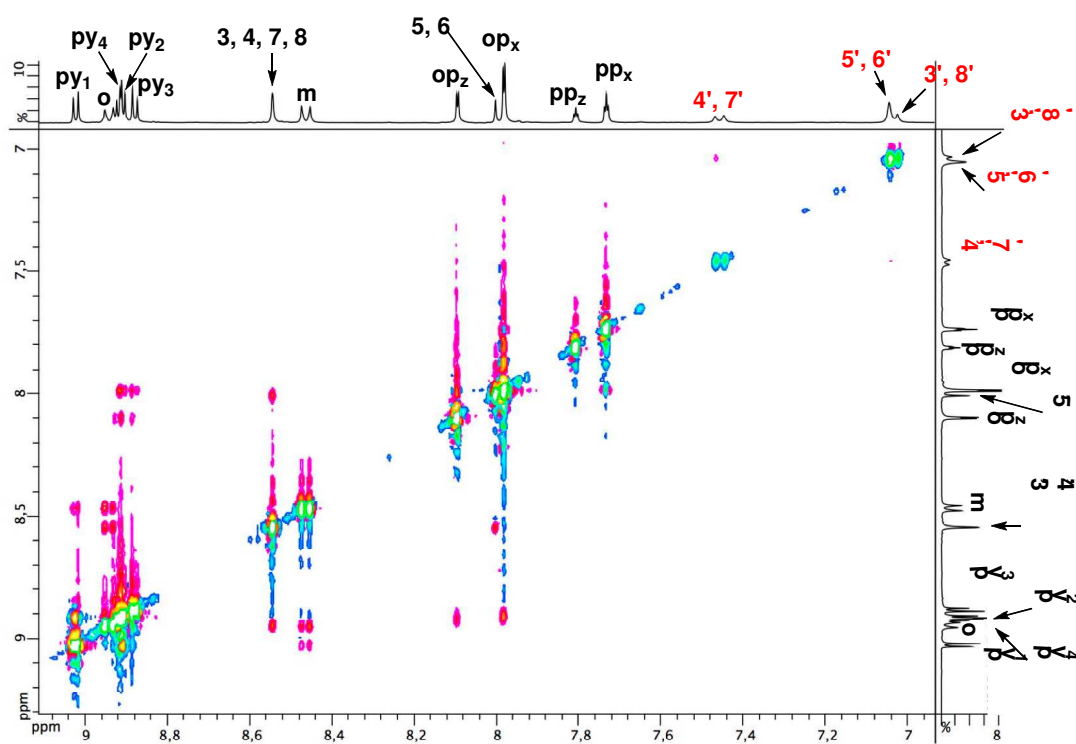


Fig SI-3(a). ROESY spectrum of **8** showing dipolar couplings in the 7-9 ppm range.

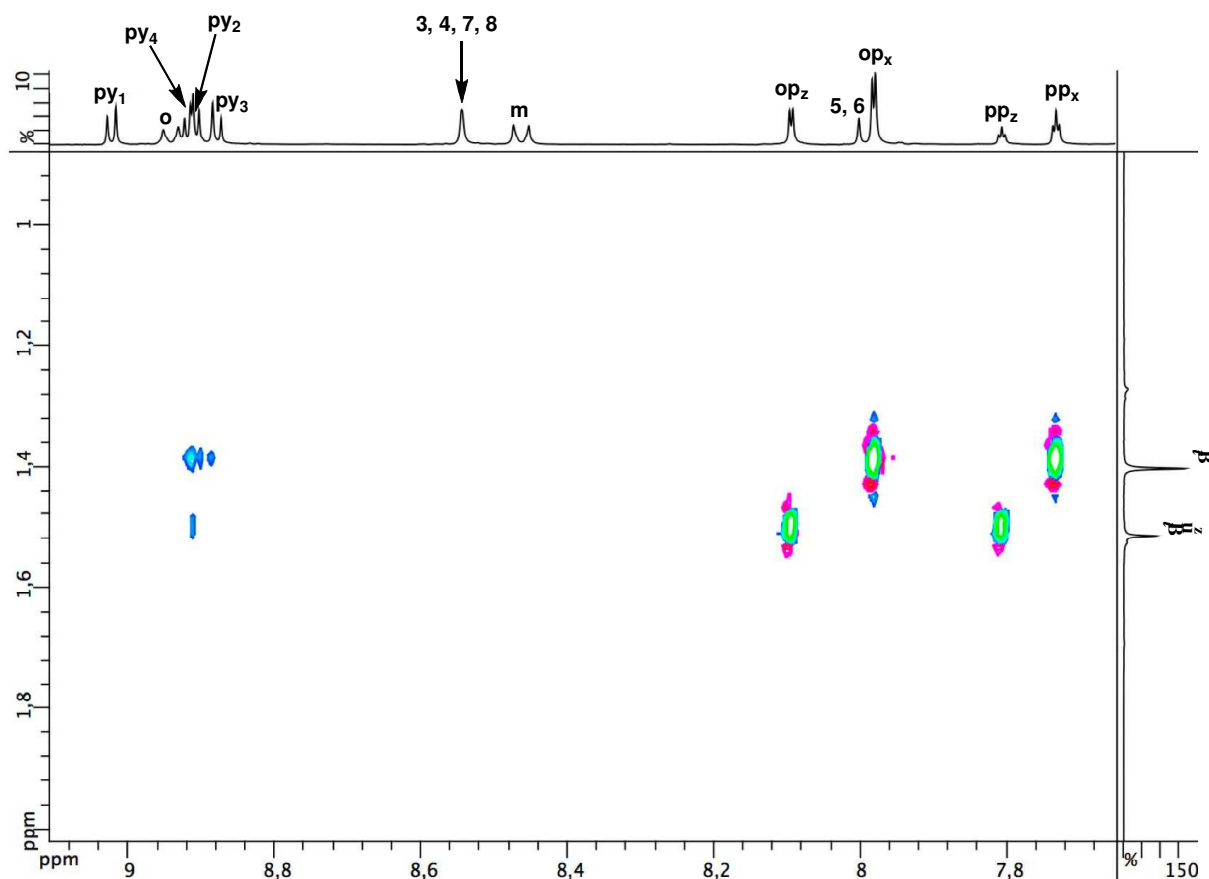


Fig SI-3(b). Zoom of the ROESY spectrum of **8** showing specific dipolar couplings with the *t*Bu groups.

^1H NMR (400 MHz, CD_2Cl_2 , 298 K): δ (ppm) 9.03 (d, 4 H, 3J = 4.7 Hz, py_1), 8.94 (d, 4 H, 3J = 8.7 Hz, o), 8.90 (d, 4 H, 3J = 4.7 Hz, py_4), 8.91 (d, 4 H, 3J = 4.6 Hz, py_2), 8.88 (d, 4 H, 3J = 4.7 Hz, py_3), 8.54 (bs, 4 H, 3, 8 + 4, 7), 8.46 (d, 4 H, 3J = 8.7 Hz, m), 8.10 (d, 4 H, 4J = 1.6 Hz, op_z), 8.00 (s, 2 H, 5, 6), 7.98 (d, 8 H, 4J = 1.6 Hz, op_x), 7.81 (t, 2 H, 4J = 1.7 Hz, pp_z), 7.73 (t, 4 H, 3J = 1.7 Hz, pp_x), 7.46 (bd, 2 H, 3J = 8.2 Hz, 4', 7'), 7.04 (s, 2 H, 5', 6'), 7.03 (bd, 2 H, 3J = 7.6 Hz, 3', 8'), 6.69 (bs, 4 H, o'), 4.85 (vbs, 4 H, m'), 1.51 (s, 36 H, $t\text{Bu}_z$), 1.40 (s, 72 H, $t\text{Bu}_x$).

NMR data of **9**

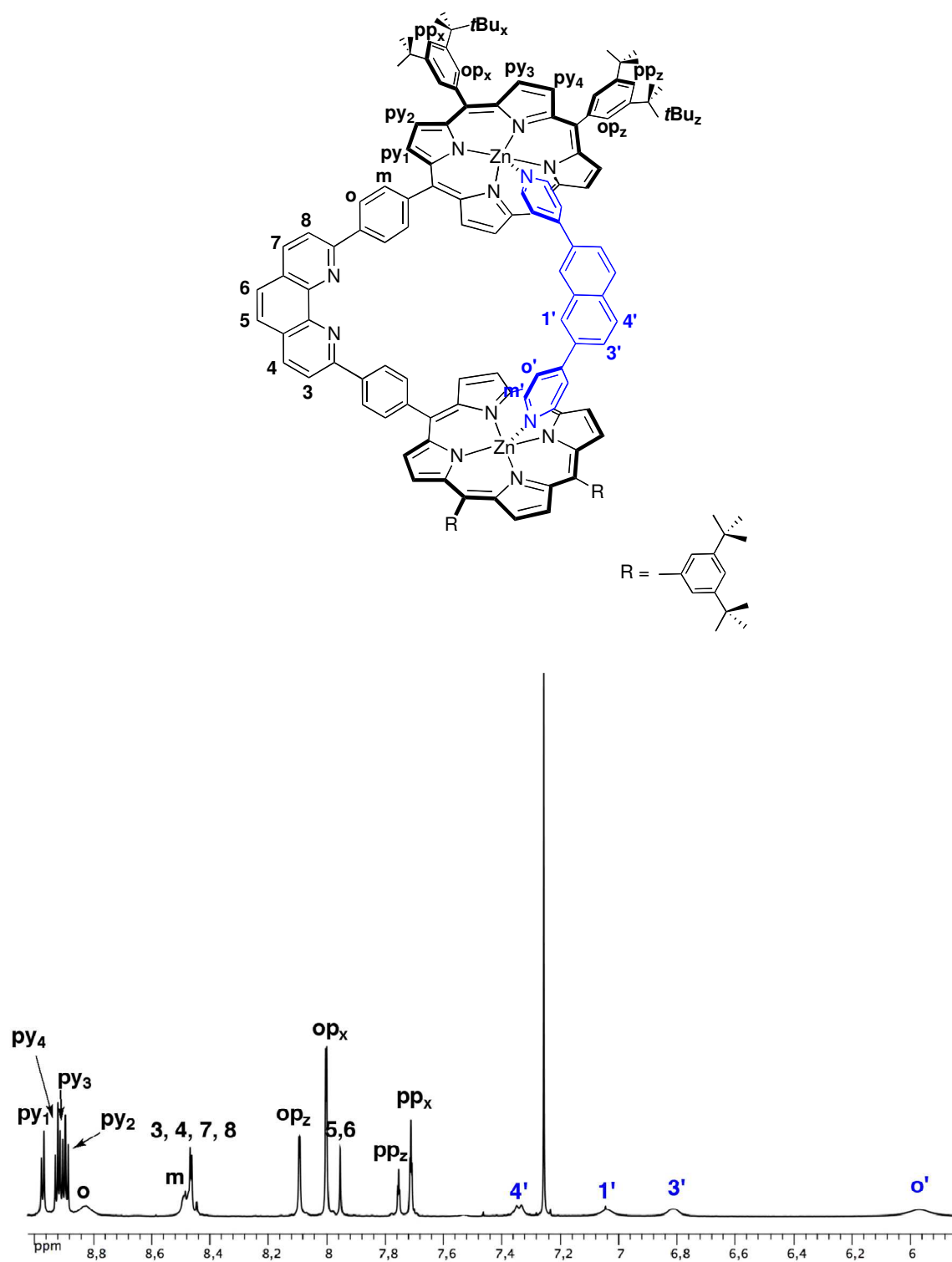


Fig SI-4. (top) Proton number assignment for **9** and (bottom) ^1H NMR spectrum (6-9 ppm range).

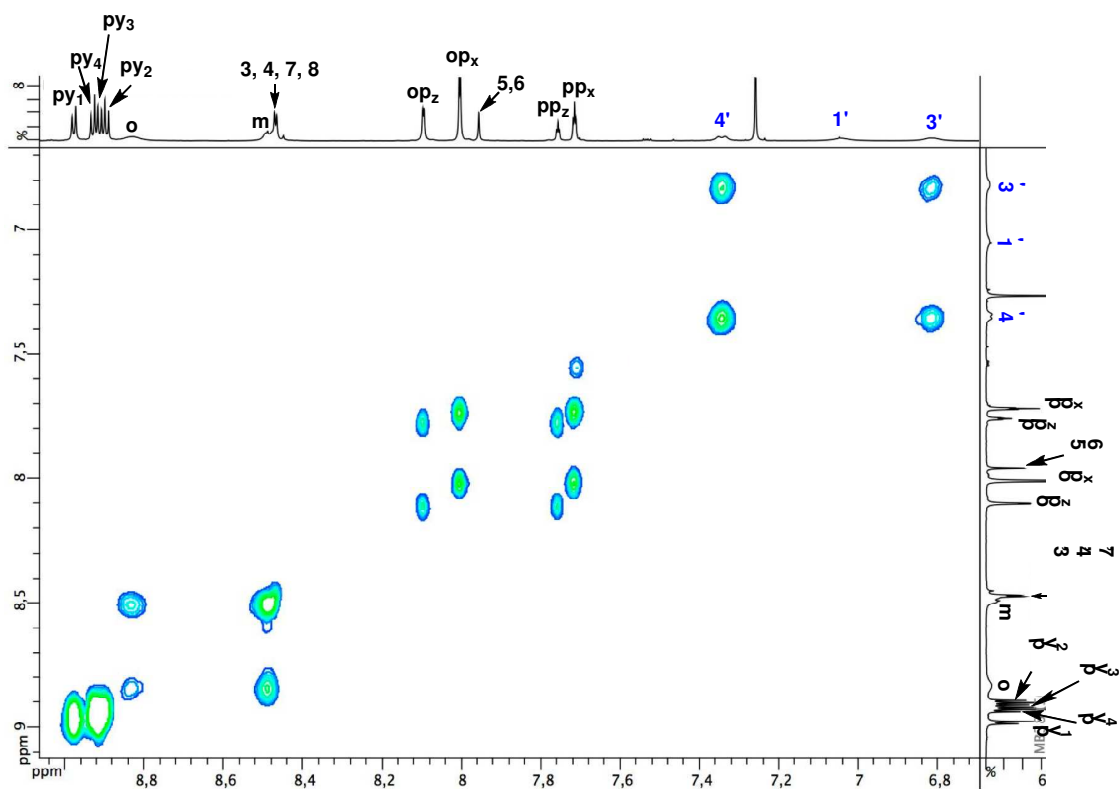


Fig SI-5. COSY spectrum of **9** showing scalar couplings in the 6.8-9 ppm range.

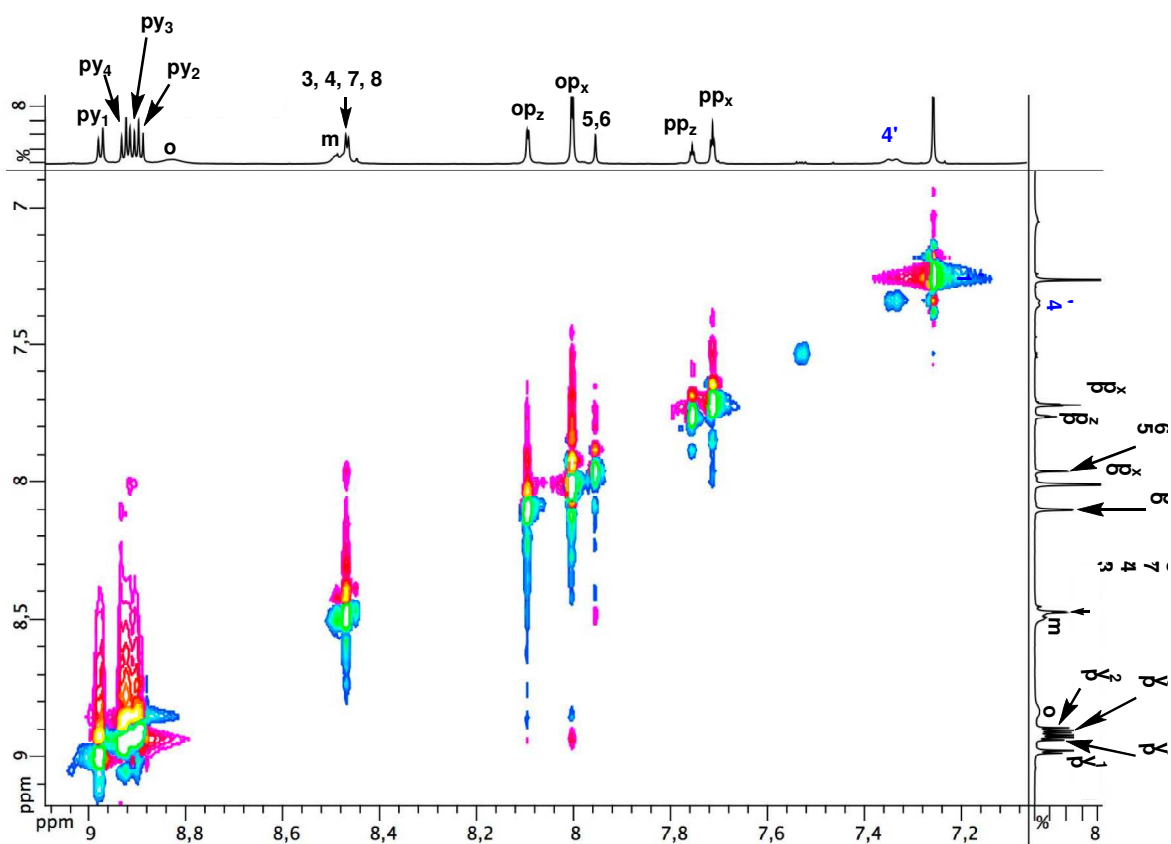


Fig SI-6(a). ROESY spectrum of **9** showing the dipolar couplings in the 7-9 ppm range.

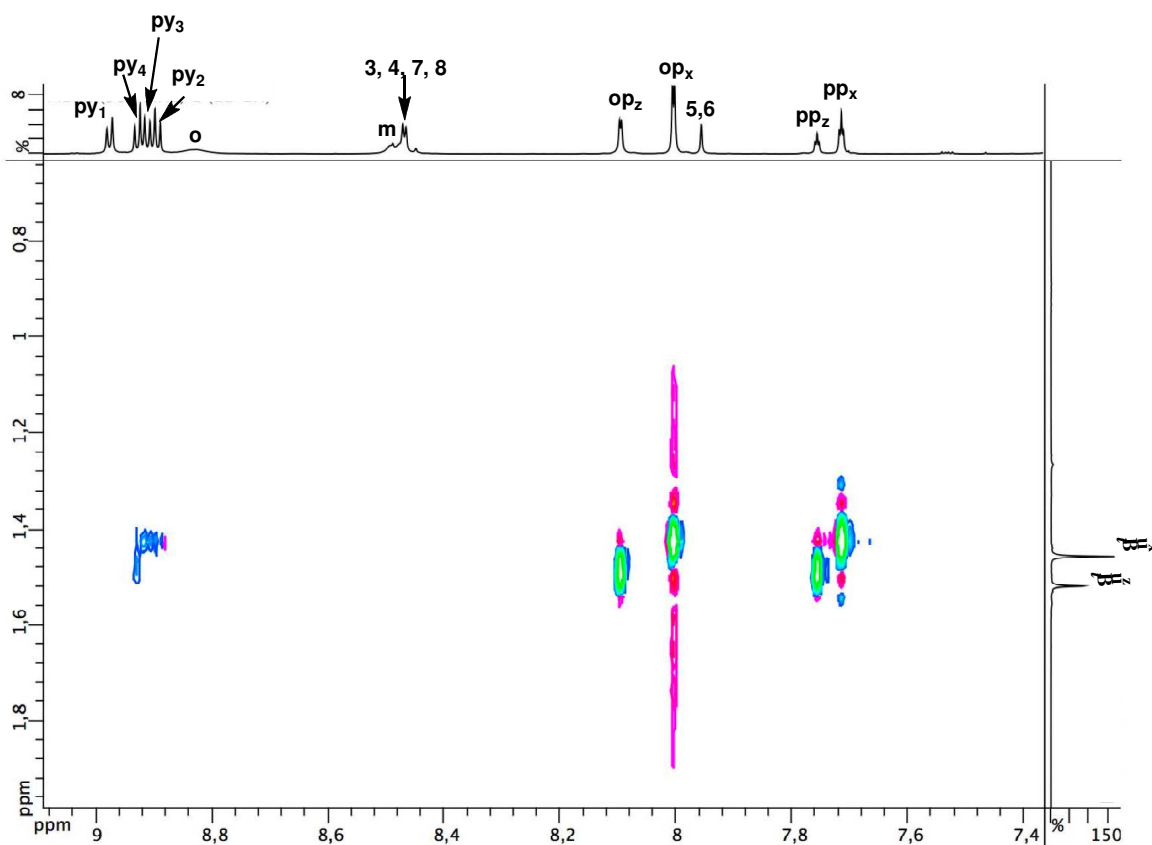


Fig SI-6(b). Zoom of the ROESY spectrum of **9** showing the correlation of the *t*Bu groups with some aromatic protons.

^1H NMR (500 MHz, CDCl_3 , 298 K): δ (ppm) 8.98 (d, 4 H, $^3J = 4.7$ Hz, py_1), 8.93 (d, 4 H, $^3J = 4.7$ Hz, py_4), 8.91 (d, 4 H, $^3J = 4.5$ Hz, py_3), 8.89 (d, 4 H, $^3J = 4.5$ Hz, py_2), 8.83 (d, 4 H, $^3J = 8.7$ Hz, o), 8.48 (d, 4 H, $^3J = 8.6$ Hz, m), 8.47 (bs, 4 H, 3, 8 + 4, 7), 8.09 (d, 4 H, $^4J = 1.7$ Hz, op_z), 8.00 (d, 8 H, $^4J = 1.8$ Hz, op_x), 7.95 (s, 2 H, 5, 6), 7.76 (t, 2 H, $^4J = 1.8$ Hz, pp_z), 7.71 (t, 4 H, $^3J = 1.8$ Hz, pp_x), 7.34 (bd, 2 H, $^3J = 8.3$ Hz, 4'), 7.04 (bd, 2 H, $^4J = 1.8$ Hz, 1'), 6.81 (bd, 2 H, $^3J = 8.7$ Hz, $^4J = 1.8$ Hz, 3'), 5.97 (bs, 4 H, o'), 3.22 (vbs, 4 H, m'), 1.52 (s, 36 H, $t\text{Bu}_z$), 1.45 (s, 72 H, $t\text{Bu}_x$).

NMR and UV-vis data of **12•PF₆** and **13•PF₆**

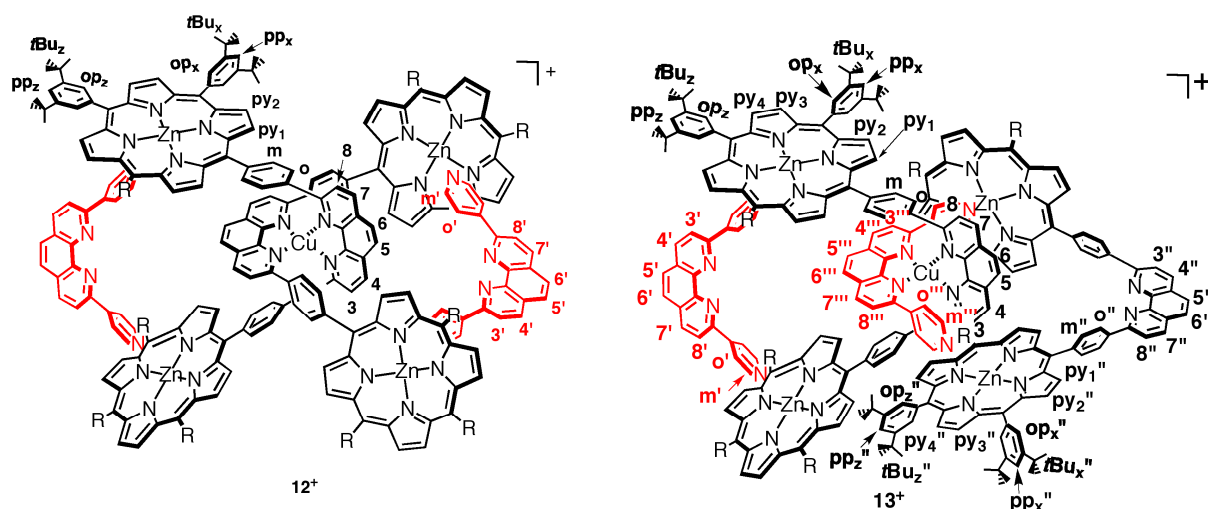


Fig SI-7. Proton number assignment for **12•PF₆** and **13•PF₆**.

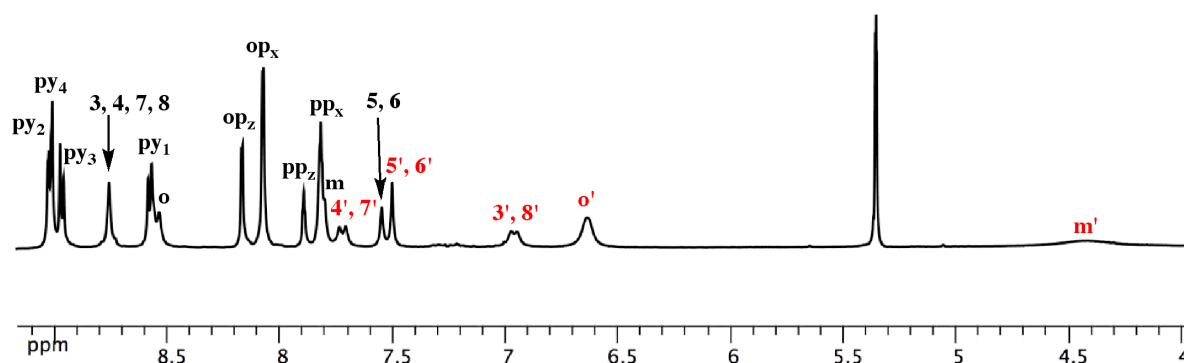


Fig SI-8. ¹H NMR spectrum of **12•PF₆** (4-9 ppm range).

¹H NMR (300 MHz, CD₂Cl₂, 298 K): δ (ppm) 9.03 (d, 8 H, ³J = 4.7 Hz, py₂), 9.01 (d, 8 H, ³J = 4.8 Hz, py₄), 8.98 (d, 8 H, ³J = 4.7 Hz, py₃), 8.76 (bs, 8 H, 3, 8 + 4, 7), 8.58 (d, 8 H, ³J = 4.7 Hz, py₁), 8.56 (d, 8 H, ³J = 8.7 Hz, o), 8.17 (d, 8 H, ⁴J = 1.6 Hz, op_z), 8.08 (d, 16 H, ⁴J = 1.6 Hz, op_x), 7.90 (t, 4 H, ⁴J = 1.7 Hz, pp_z), 7.83 (m, 16 H, ³J = 1.7 Hz, pp_x + m), 7.73 (bd, 4 H, ³J = 8.2 Hz, 4', 7'), 7.55 (s, 4 H, 5, 6), 7.50 (s, 4 H, 5', 6'), 6.96 (bd, 4 H, ³J = 7.6 Hz, 3', 8'), 6.65 (bs, 8 H, o'), 4.40 (vbs, 8 H, m'), 1.60 (s, 72 H, tBu_z), 1.50 (s, 144 H, tBu_x).

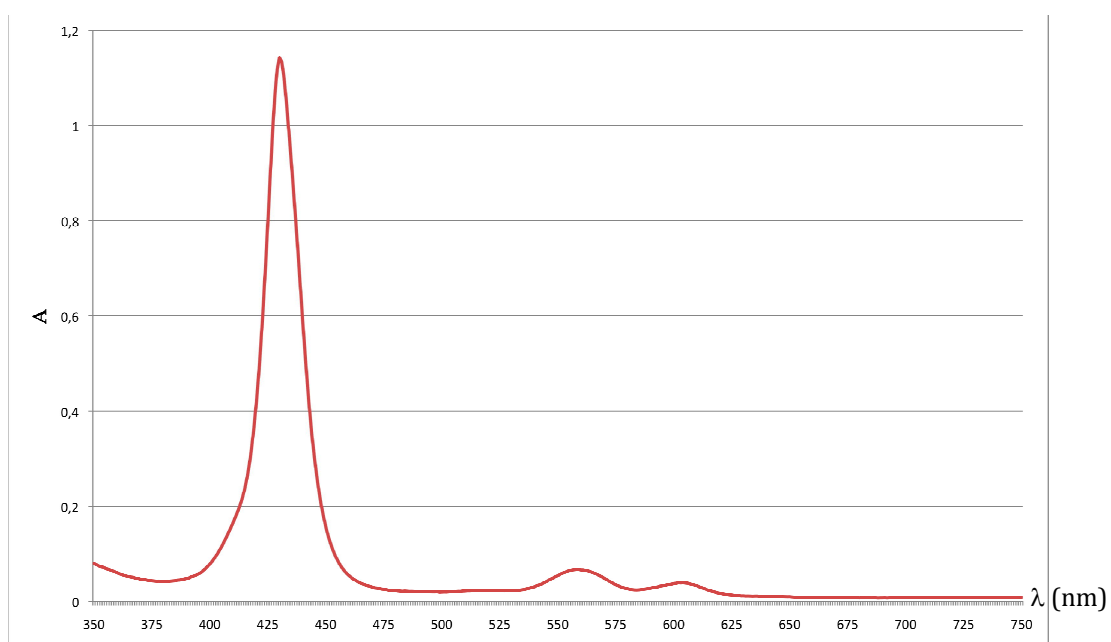


Fig SI-9. UV-vis spectrum of **12•PF₆** (toluene, C= 9.7 x 10⁻⁷ M)

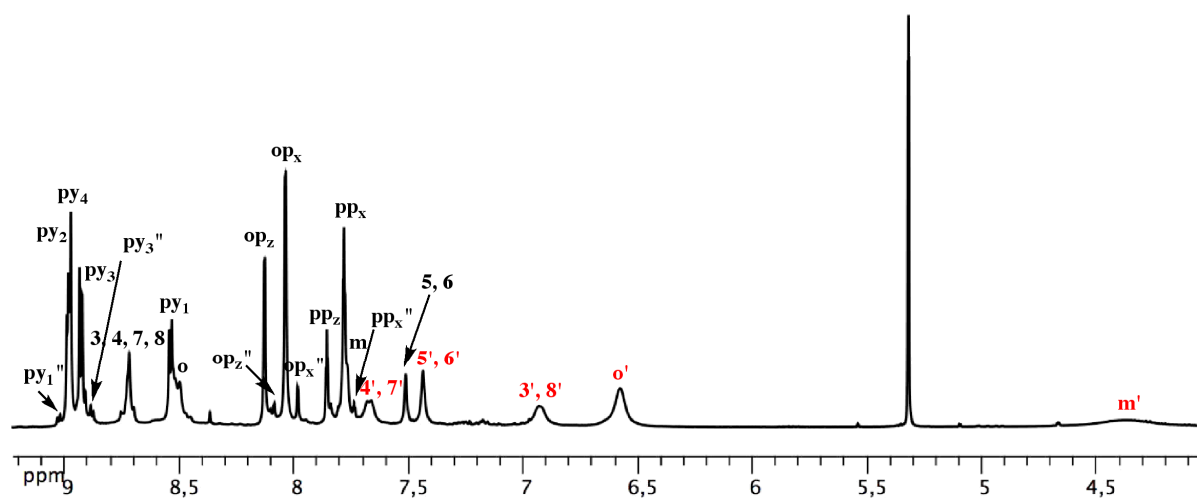


Fig SI-10. ¹H NMR spectrum of a mixture of 80 % of **12•PF₆** and 20 % of **13•PF₆** (4.5-9 ppm range).

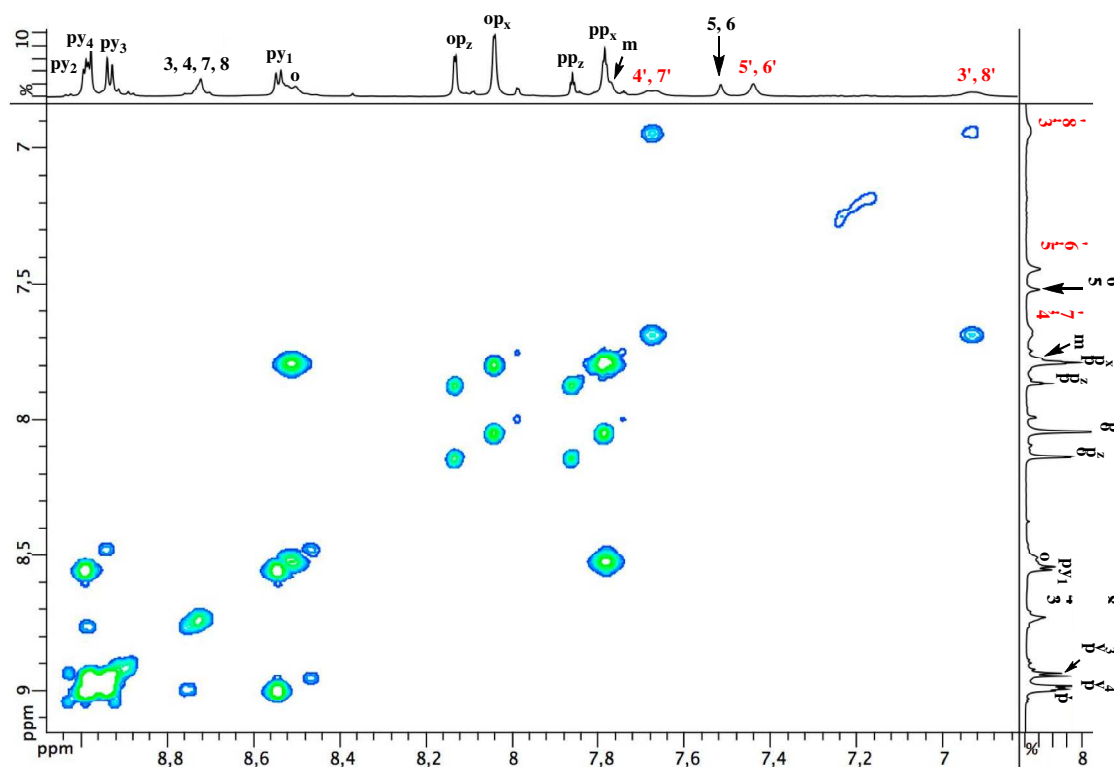


Fig SI-11. COSY Spectrum of mixture of **12•PF₆** showing scalar couplings in the 7-9 ppm range.

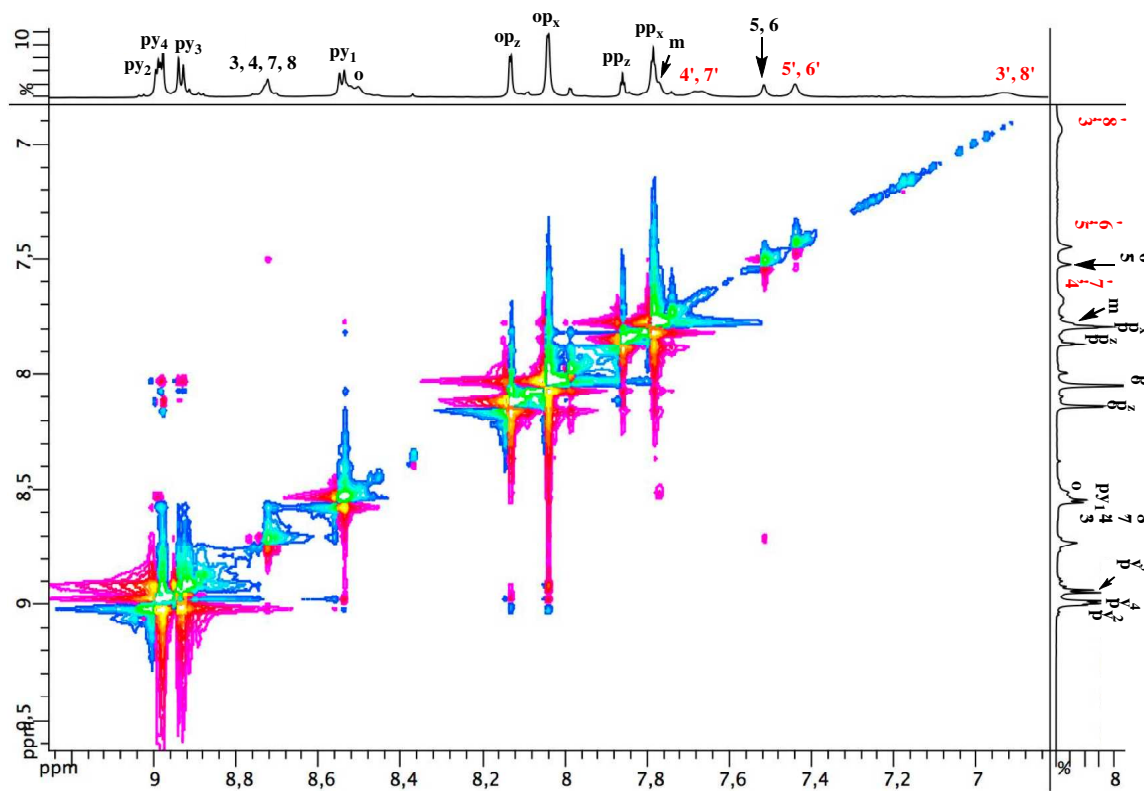


Fig SI-12(a). ROESY spectrum of **12•PF₆** showing the dipolar couplings in the 7-9 ppm range.

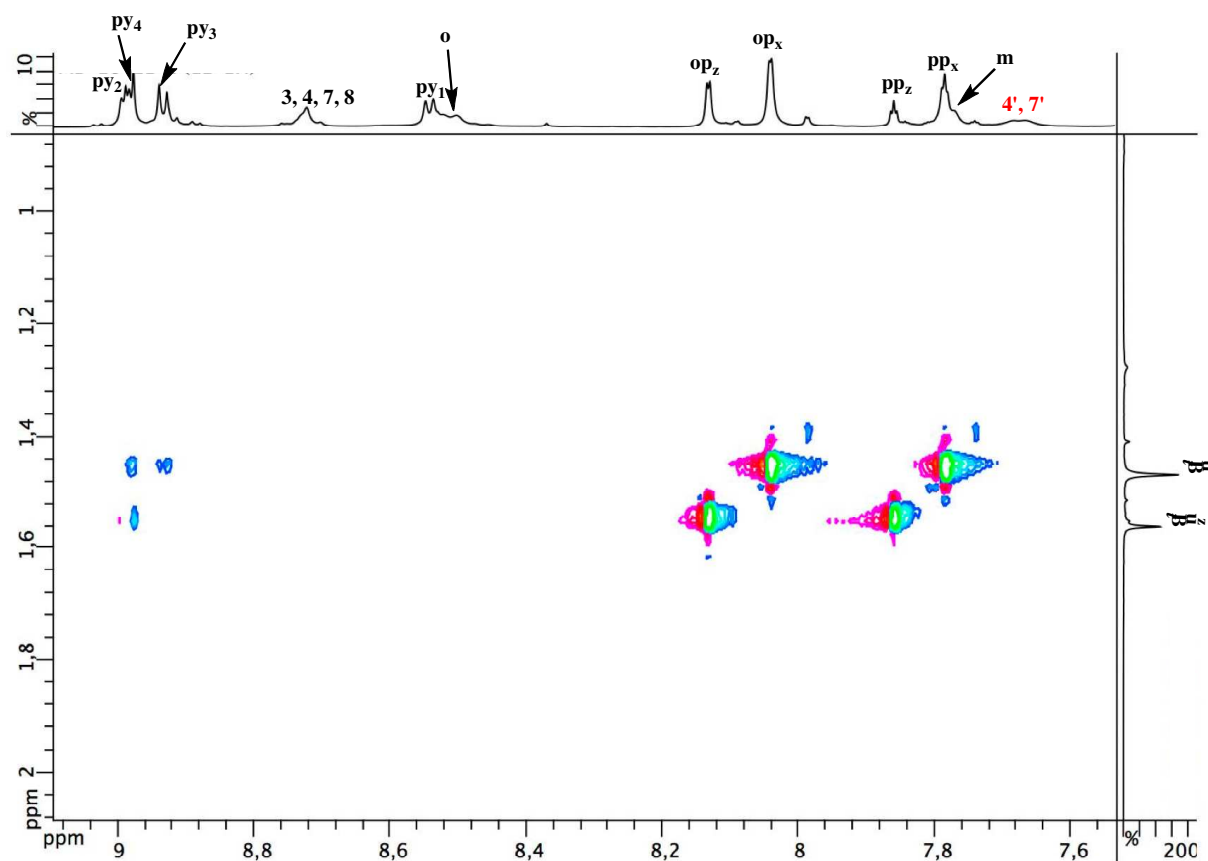


Fig SI-12(b). Zoom of the ROESY spectrum **12•PF₆** showing the correlation of the *t*Bu groups with some aromatic protons.

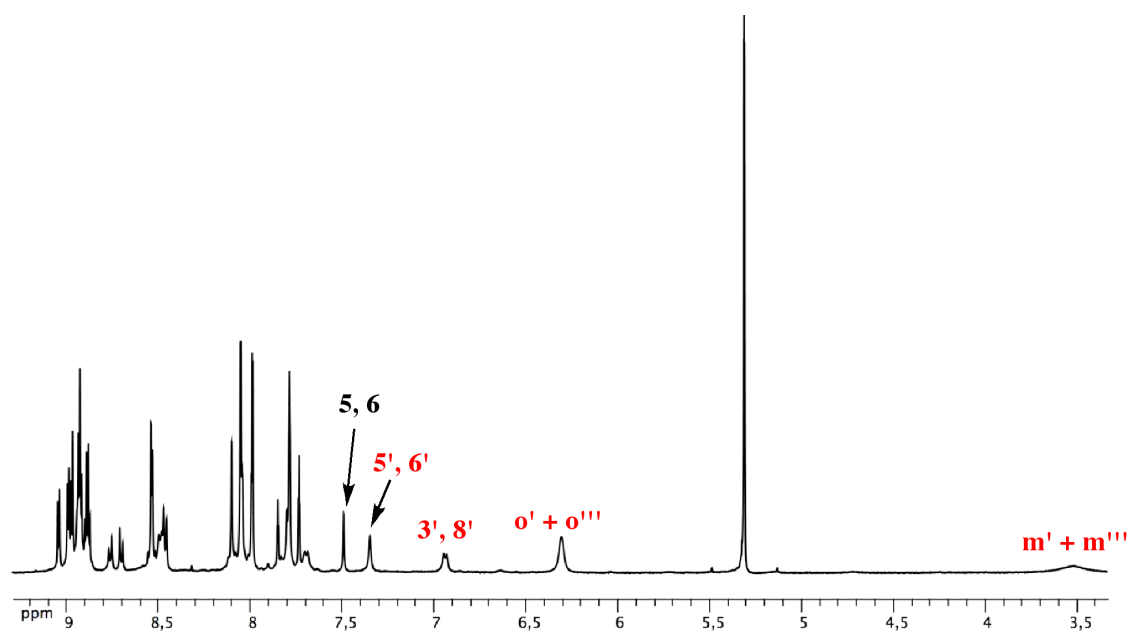


Fig SI-13(a). ¹H NMR spectrum of **13•PF₆** (3.5-9 ppm range).

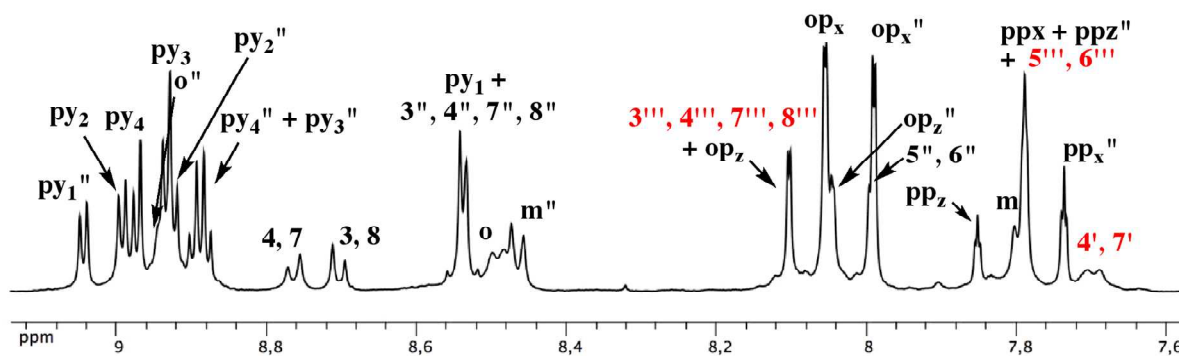


Fig SI-13(b). Zoom of the ^1H NMR spectrum of $13\bullet\text{PF}_6$ (7.6-9 ppm range).

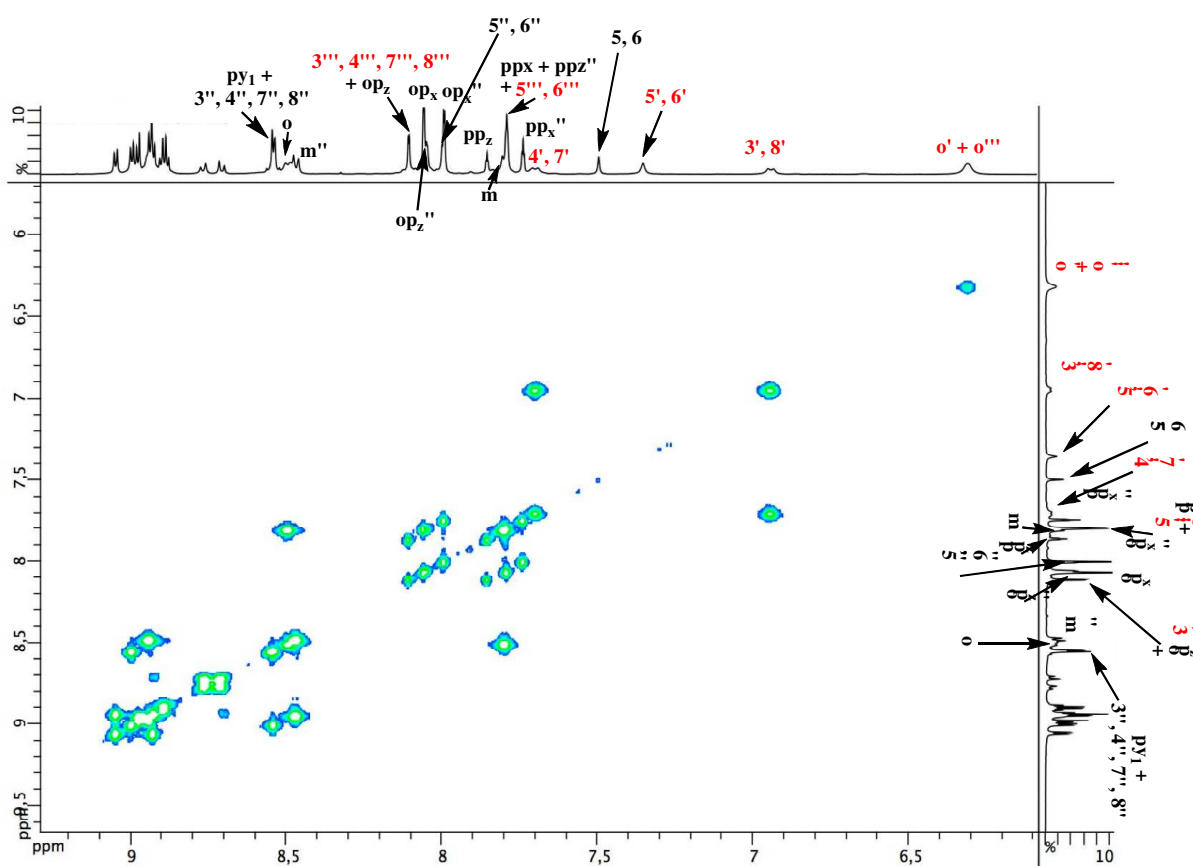


Fig SI-14(a). COSY spectrum of $13\bullet\text{PF}_6$ showing scalar couplings in the 6.5-9 ppm range.

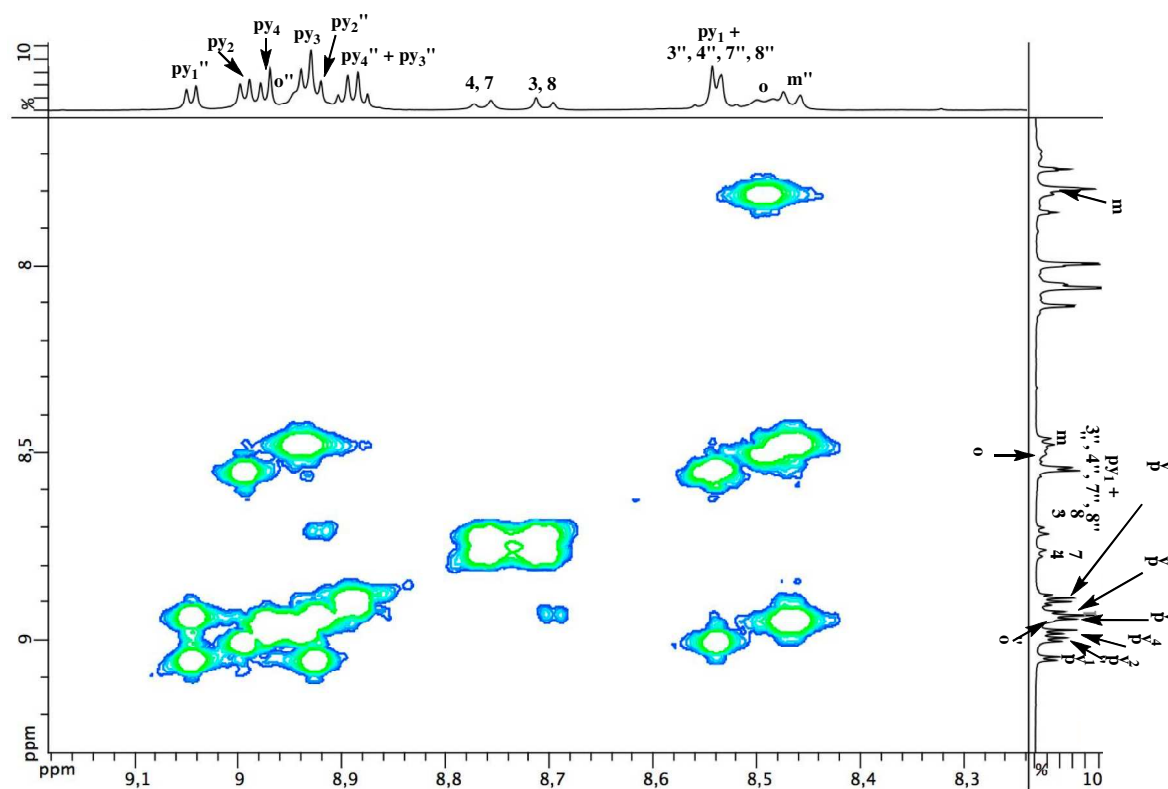


Fig SI-14(b). Zoom of the COSY spectrum of $13 \bullet PF_6$ showing scalar couplings in the 8.3-9 ppm range.

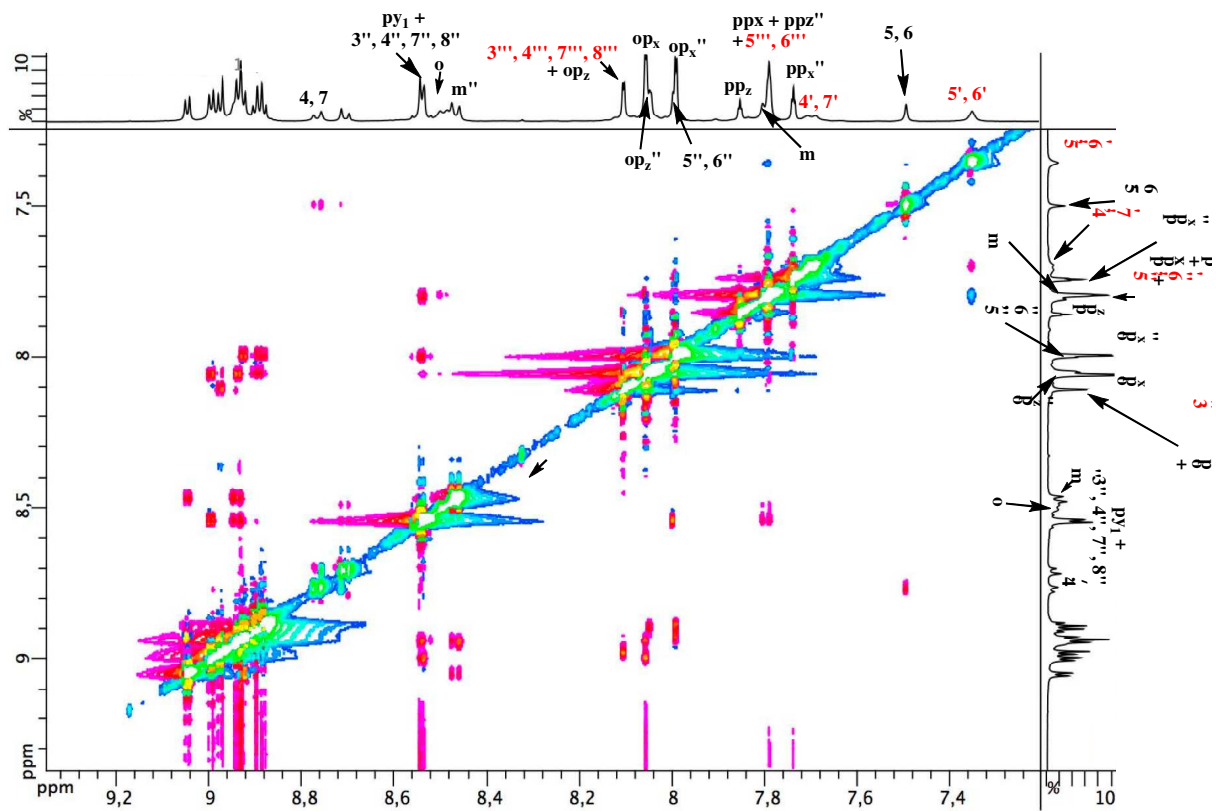


Fig SI-15(a). ROESY spectrum of $13 \bullet PF_6$ showing the dipolar couplings in the 7.4-9.2 ppm range.

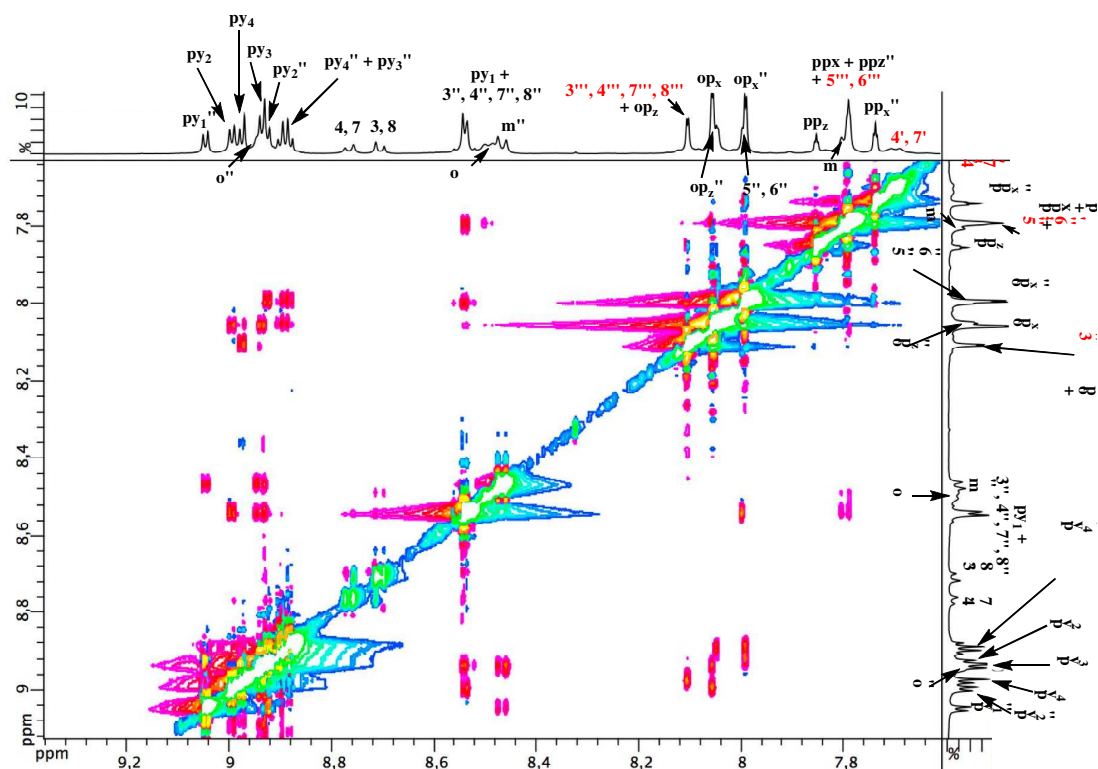


Fig SI-15(b). Zoom of the ROESY spectrum of **13•PF₆** showing the dipolar couplings in the 7.8-9.2 ppm range.

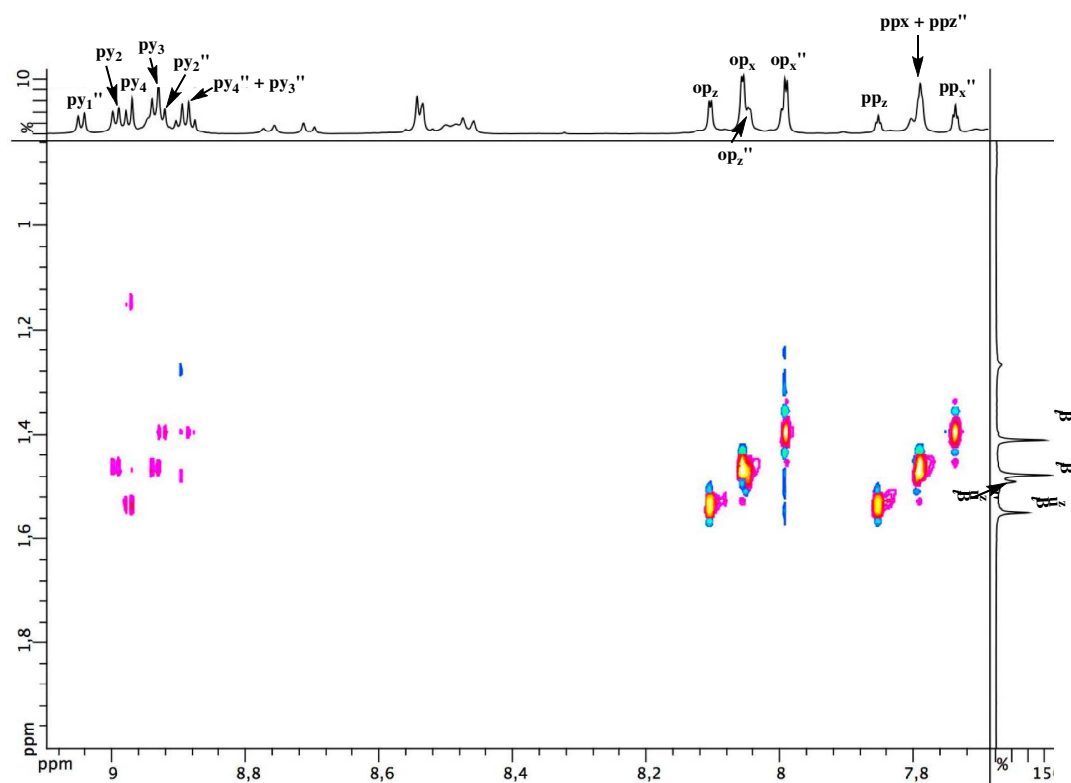


Fig SI-15(c). Zoom of the ROESY spectrum of **13•PF₆** showing the correlation of the *t*Bu groups with some aromatic protons.

^1H NMR (500 MHz, CD_2Cl_2 , 298 K): δ (ppm) 9.05 (d, 4 H, $^3J = 4.6$ Hz, py_1''), 9.00 (d, 4 H, $^3J = 4.6$ Hz, py_2), 8.98 (d, 4 H, $^3J = 4.6$ Hz, py_4), 8.94 (d, 4 H, $^3J = 8.7$ Hz, o''), 8.94 (d, 4 H, $^3J = 4.6$ Hz, py_3), 8.93 (d, 4 H, $^3J = 4.8$ Hz, py_2''), 8.90 (d, 4 H, $^3J = 4.6$ Hz, py_4''), 8.88 (d, 4 H, $^3J = 4.8$ Hz, py_3''), 8.77 (d, 2 H, $^3J = 8.1$ Hz, 4,7), 8.71 (d, 2 H, $^3J = 8.3$ Hz, 3,8), 8.54 (bs, 4 H, 3'',8'' + 4'',7''), 8.54 (d, 4 H, $^3J = 4.4$ Hz, py_1), 8.49 (bd, 4 H, $^3J = 7.7$ Hz, o), 8.47 (d, 4 H, $^3J = 8.3$ Hz, m''), 8.11 (bs, 4 H, 3''',8''' + 4''',7'''), 8.10 (d, 4 H, $^4J = 1.7$ Hz, op_z), 8.06 (d, 8 H, $^4J = 1.7$ Hz, op_x), 8.05 (d, 4 H, $^4J = 1.5$ Hz, op_z''), 8.00 (s, 2 H, 5'',6''), 7.99 (d, 8 H, $^4J = 1.8$ Hz, op_x''), 7.85 (t, 2 H, $^4J = 1.7$ Hz, pp_z), 7.79 (d, 4 H, $^3J = 7.7$ Hz, m), 7.79 (m, 8 H, $\text{pp}_x + \text{pp}_z'' + 5''',6'''$), 7.74 (d, 2 H, $^4J = 1.8$ Hz, pp_x''), 7.70 (bd, 2 H, $^3J = 8.3$ Hz, 4',7'), 7.49 (s, 2 H, 5,6), 7.35 (s, 2 H, 5',6'), 6.94 (bd, 2 H, $^3J = 8.3$ Hz, 3',8'), 6.31 (bs, 8 H, $\text{o}' + \text{o}'''$), 3.52 (vbs, 8 H, $\text{m}' + \text{m}'''$), 1.54 (s, 36 H, $t\text{Bu}_z$), 1.50 (s, 36 H, $t\text{Bu}_z''$), 1.49 (s, 72 H, $t\text{Bu}_x$), 1.41 (s, 72 H, $t\text{Bu}_x''$).

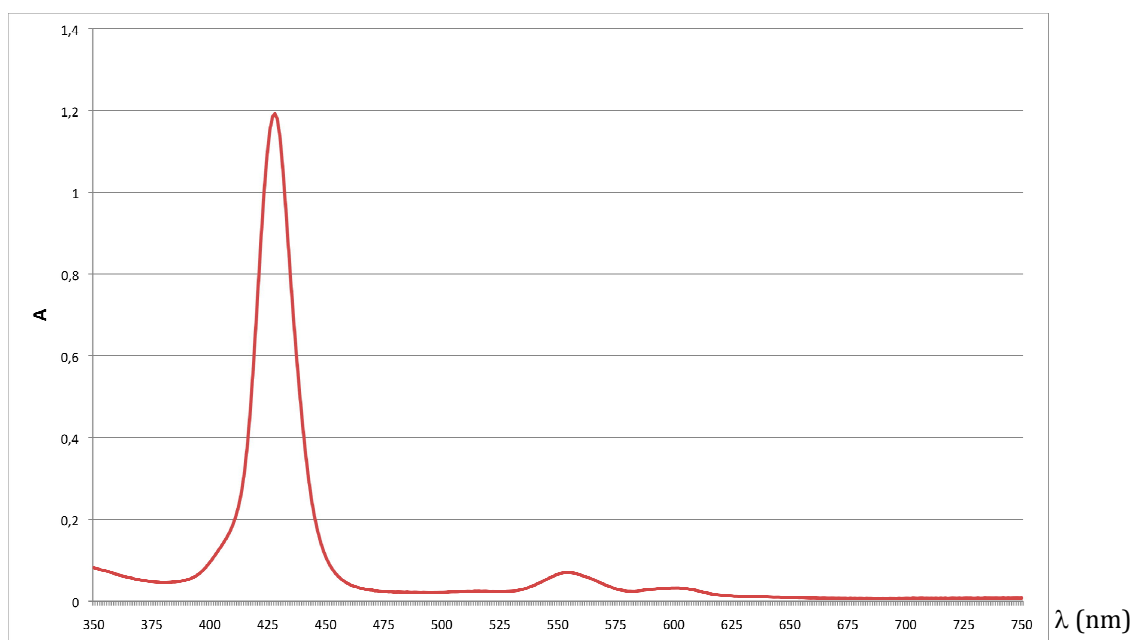
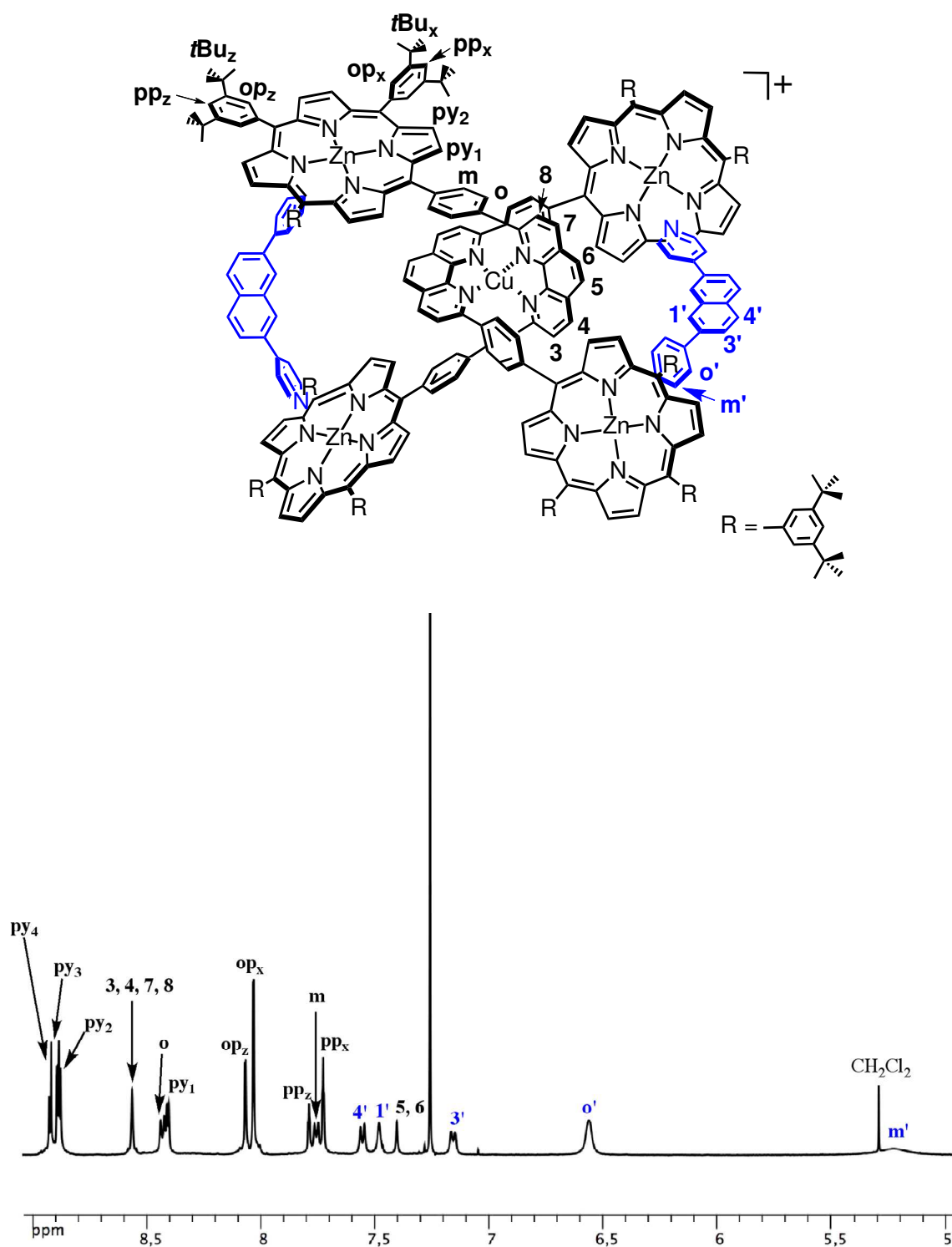


Fig SI-16. UV-vis Spectrum of **13•PF₆** (toluene, $C = 1.0 \times 10^{-6}$ M).

Fig SI-17. (top) Proton number assignation for **15•PF₆** and (bottom) ¹H NMR spectrum (5-8.8 ppm range).



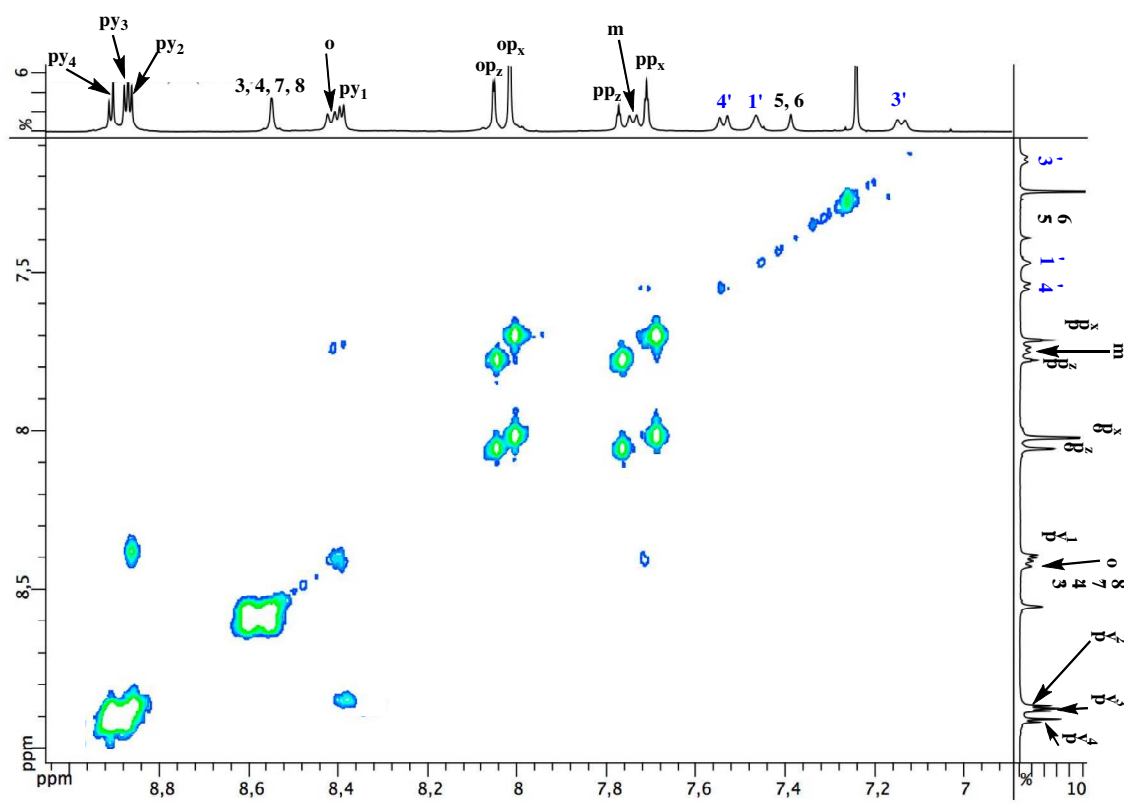


Fig SI-18. COSY spectrum of $15 \bullet \text{PF}_6$ showing scalar couplings in the 7-8.8 ppm range.

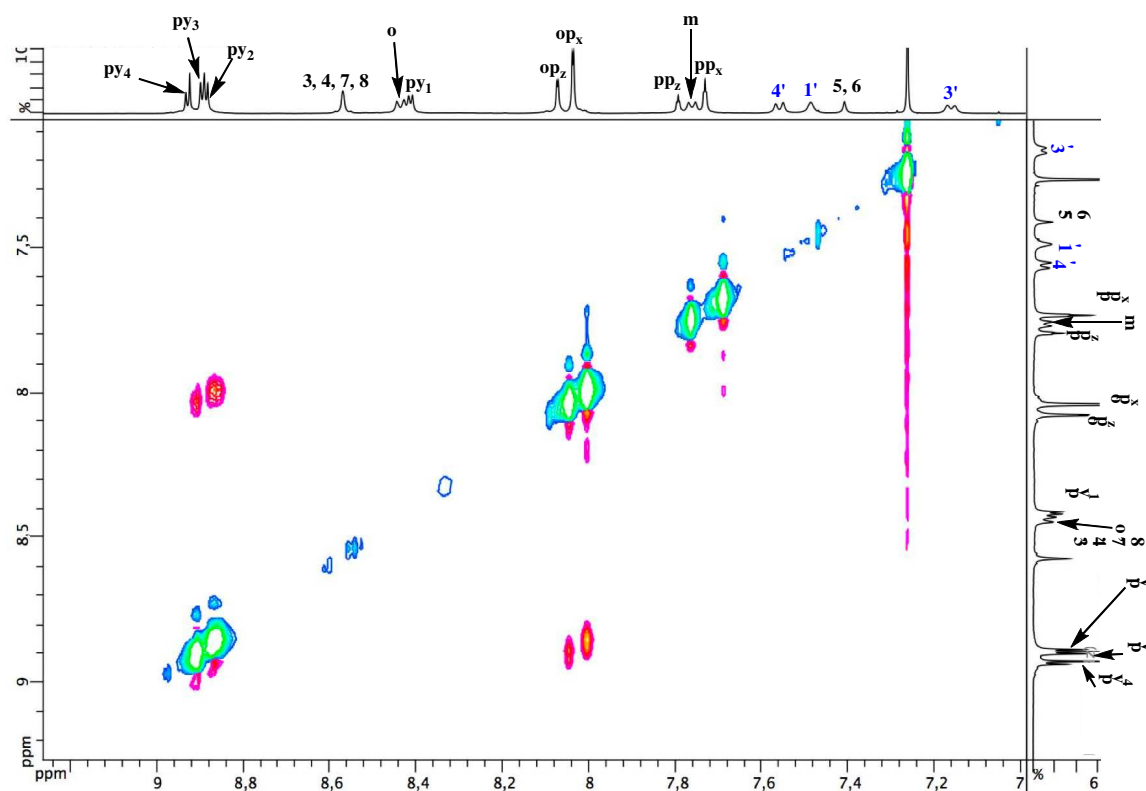


Fig SI-19(a). ROESY spectrum of $15 \bullet \text{PF}_6$ showing the dipolar couplings in the 7-9.2 ppm range.

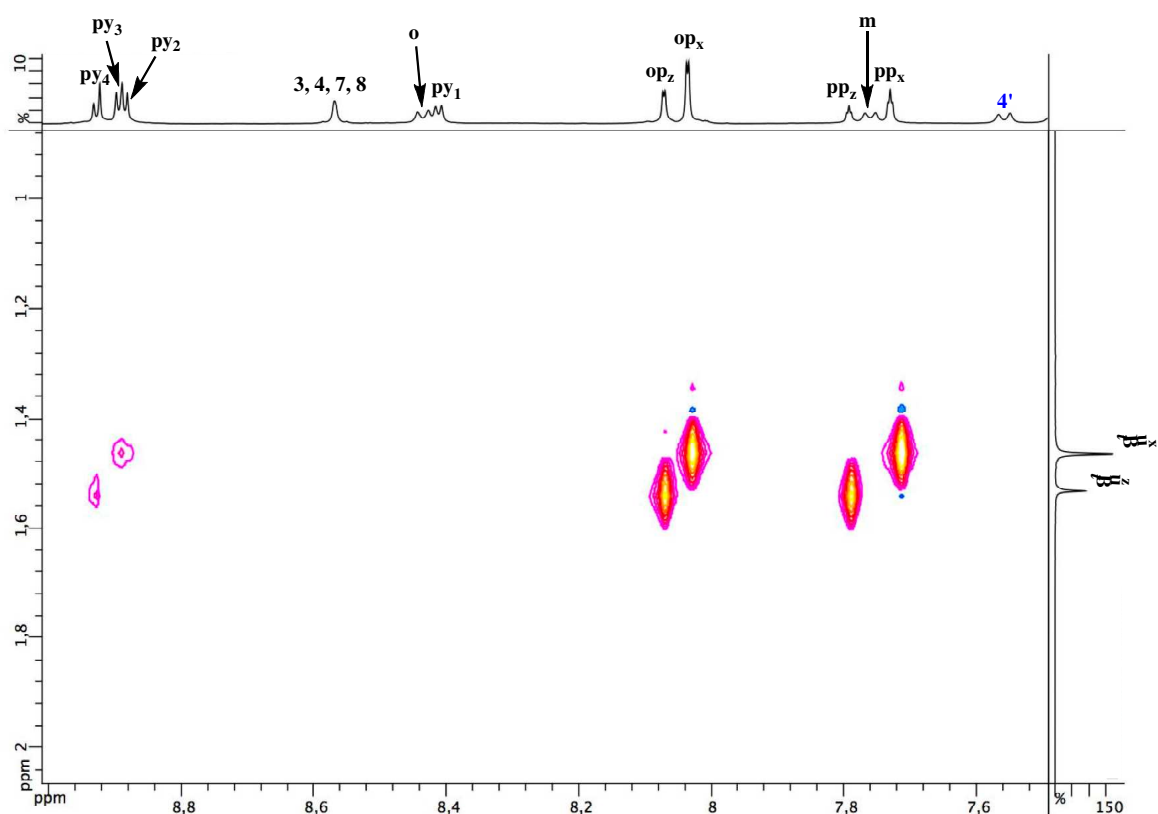


Fig SI-19(b). ROESY spectrum of **15•PF₆** showing the correlation of the *t*Bu groups with some aromatic protons.

¹H NMR (500 MHz, CDCl₃, 298 K): δ (ppm) 8.93 (d, 8 H, ³J= 4.4 Hz, py₄), 8.89 (d, 8 H, ³J= 4.3 Hz, py₃), 8.88 (d, 8 H, ³J= 4.0 Hz, py₂), 8.57 (bs, 8 H, 3, 8 + 4, 7), 8.43 (d, 8 H, ³J= 8.1 Hz, m), 8.41 (d, 8 H, ³J= 4.4 Hz, py₁), 8.07 (d, 8 H, ⁴J= 1.7 Hz, op_z), 8.05 (d, 16 H, ⁴J= 1.7 Hz, op_x), 7.79 (t, 4 H, ⁴J= 1.7 Hz, pp_z), 7.76 (d, 8 H, ³J= 7.9 Hz, m), 7.73 (m, 8 H, ³J= 1.7 Hz, pp_x), 7.56 (bd, 4 H, ³J= 8.7 Hz, 4'), 7.48 (bs, 4 H, 1'), 7.41 (s, 4 H, 5, 6), 7.16 (bd, 4 H, ³J= 8.4 Hz, 3'), 6.56 (bs, 8 H, o'), 5.22 (vbs, 8 H, m'), 1.53 (s, 72 H, *t*Bu_z), 1.46 (s, 144 H, *t*Bu_x).