

Supporting Information for

**Synthesis and characterisation of luminescent rhenium
tricarbonyl complexes with axially coordinated 1,2,3-triazole
ligands**

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Figure S1 Comparative UV-vis absorption spectra for complexes	S2
Comparison of X-ray crystal structure of 2a and 2b.	S2
Figure S2 ORTEP plot of the single-crystal X-ray structure of 2a	S2
Figure S3 ORTEP plot of the single-crystal X-ray structure of 2b	S3
Table S1 Selected bond lengths and angles for single-crystal X-ray structures	S3
Figure S1 ¹ H NMR spectrum of 1-methyl-4-phenyl-1,2,3-triazole (1a)	S6
Figure S2 ¹³ C NMR spectrum of 1-methyl-4-phenyl-1,2,3-triazole (1a)	S6
Figure S3 ¹ H NMR spectrum of 4-phenyl-1-propyl-1,2,3-triazole (1b)	S7
Figure S4 ¹³ C NMR spectrum of 4-phenyl-1-propyl-1,2,3-triazole (1b)	S7
Figure S5 ¹ H NMR spectrum of 1-benzyl-4-phenyl-1,2,3-triazole (1c)	S8
Figure S6 ¹³ C NMR spectrum of 1-benzyl-4-phenyl-1,2,3-triazole (1c)	S8
Figure S7 ¹ H NMR spectrum of 1-propyl-4-tolyl-1,2,3-triazole (1d)	S9
Figure S8 ¹³ C NMR spectrum of 1-propyl-4-tolyl-1,2,3-triazole (1d)	S9
Figure S9 ¹ H NMR spectrum of [Re(bpy)(CO) ₃ (1a)]PF ₆ (2b)	S10
Figure S10 ¹³ C NMR spectrum of [Re(bpy)(CO) ₃ (1a)]PF ₆ (2b)	S10
Figure S11 ¹ H NMR spectrum of [Re(bpy)(CO) ₃ (1b)]PF ₆ (2b)	S11
Figure S12 ¹³ C NMR spectrum of [Re(bpy)(CO) ₃ (1b)]PF ₆ (2b)	S11
Figure S13 ¹ H NMR spectrum of [Re(bpy)(CO) ₃ (1c)]PF ₆ (2b)	S12
Figure S14 ¹³ C NMR spectrum of [Re(bpy)(CO) ₃ (1c)]PF ₆ (2b)	S12
Figure S15 ¹ H NMR spectrum of [Re(bpy)(CO) ₃ (1d)]PF ₆ (2b)	S13
Figure S16 ¹³ C NMR spectrum of [Re(bpy)(CO) ₃ (1d)]PF ₆ (2b)	S13

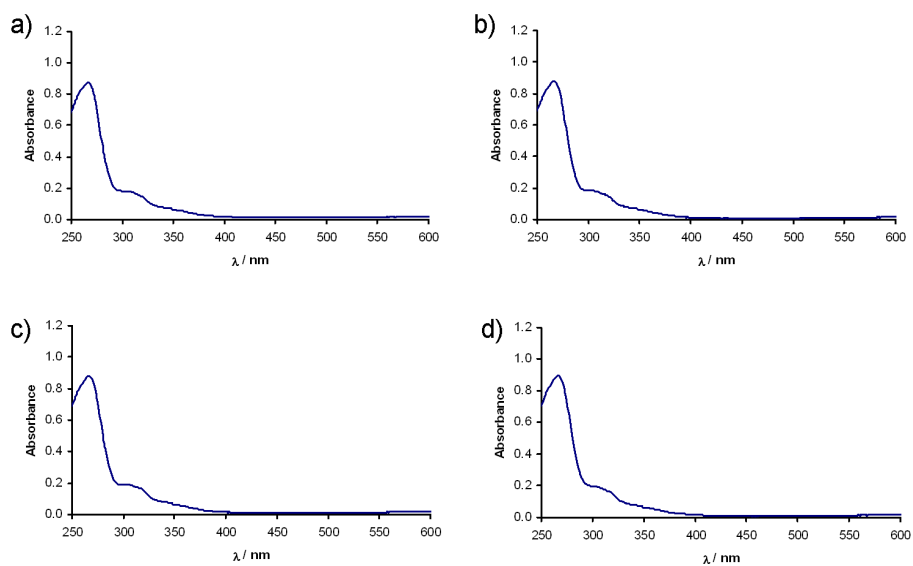


Fig. S1 Comparative UV-vis absorption spectra for complexes, a) $[\text{Re}(\text{bpy})(\text{CO})_3(\mathbf{1a})]\text{PF}_6$, b) $[\text{Re}(\text{bpy})(\text{CO})_3(\mathbf{1b})]\text{PF}_6$, c) $[\text{Re}(\text{bpy})(\text{CO})_3(\mathbf{1c})]\text{PF}_6$, d) $[\text{Re}(\text{bpy})(\text{CO})_3(\mathbf{1d})]\text{PF}_6$.

Comparison of X-ray crystal structure of 2a and 2b.

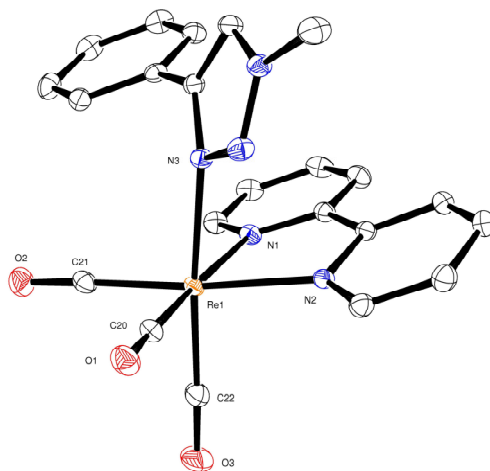


Fig. S2 ORTEP plot of the single-crystal X-ray structure of $[\text{Re}(\text{bpy})(\text{CO})_3(\mathbf{1a})]\text{PF}_6$ (hydrogen atoms and PF_6^- counterion omitted for clarity, ellipsoids at 50 % probability).

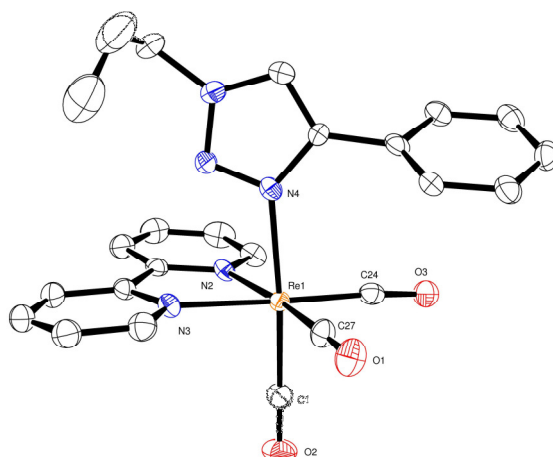


Fig. S3 ORTEP plot of the single-crystal X-ray structure of $[\text{Re}(\text{bpy})(\text{CO})_3(\mathbf{1b})]\text{PF}_6$ (hydrogen atoms and PF_6^- counterion omitted for clarity, ellipsoids at 50 % probability).

Table 2 Selected bond lengths (Å) and angles (°) for single-crystal X-ray structures of $[\text{Re}(\text{bpy})(\text{CO})_3(\mathbf{1b})]\text{PF}_6$ (**2a**) and $[\text{Re}(\text{bpy})(\text{CO})_3(\mathbf{1b})]\text{PF}_6$ (**2b**).

$[\text{Re}(\text{bpy})(\text{CO})_3(\mathbf{1a})]\text{PF}_6$			
Re-N1	2.1730(13)	Re-C22	1.9176(18)
Re-N2	2.1711(14)	C20-O1	1.150(2)
Re-N3	2.2186(14)	C21-O2	1.154(2)
Re-C20	1.9319(17)	C22-O3	1.152(2)
Re-C21	1.9221(18)		
N1-Re-N2	74.80(5)	C22-Re-C21	87.69(8)
N1-Re-N3	83.92(5)	C20-Re-C21	88.56(7)
N2-Re-N3	78.82(5)	C20-Re-C22	89.16(7)
C22-Re-N3	174.82(7)		
$[\text{Re}(\text{bpy})(\text{CO})_3(\mathbf{1b})]\text{PF}_6$			
Re-N2	2.164(4)	Re-C27	1.922(5)
Re-N3	2.170(4)	C1-O2	1.150(6)
Re-N4	2.198(4)	C24-O3	1.155(6)
Re-C1	1.915(5)	C27-O1	1.145(6)
Re-C24	1.930(5)		
N2-Re-N3	75.07(14)	C1-Re-C24	88.2(2)
N2-Re-N4	82.70(14)	C1-Re-C27	88.1(2)
N3-Re-N4	83.90(14)	C24-Re-C27	86.9(2)
C1-Re-N4	174.50(18)		

[Re(bpy)(CO)₃(**1a**)]PF₆ crystallised in the space group C2/c whereas [Re(bpy)(CO)₃(**1b**)]PF₆ crystallises in the space group Pbc_a. As can be seen from Figures S1 and S2, both complexes adopt a distorted octahedral geometry with a facial arrangement of the carbonyl ligands. The triazole ligands are coordinated to the metal through the N3 position of the ring which would be expected to be the more basic of the two potential N-donor atoms. The Re-N bonds to bpy are approximately 2.17 Å. The Re-N bond lengths to the axial triazole ligands in **2a** and **2b** are 2.2186(14) and 2.198(4) Å. C-O bond lengths are unremarkable for both complexes varying from 1.145 to 1.155 Å. The Re-C and C-O bond lengths *trans* to the triazole ligands are indistinguishable to those *trans* to bpy within experimental error.

Despite the seemingly simple difference between the two complexes in terms of the methyl versus propyl substituents of the triazole ring, these ligands are oriented quite differently in the solid state for the two complexes. For the propyltriazole complex **2b** the Re-N4 bond length is 2.198(4) Å and the triazole ligand is oriented such that the phenyl group lies above the carbonyl ligands. For the methyltriazole **2a** complex the Re-N3 bond length is longer at 2.2186(14) Å and the triazole ligand is oriented such that it brings the phenyl ring over one of the pyridyl rings of the bpy ligand. The planes of the phenyl and pyridyl rings are almost parallel and are separated by a distance of approximately 3.3 Å indicative of a π -stacking interaction. The formation of this π -stacking interaction in **2a** leads to significant twisting of the bpy ligand and a tilting of the triazole ligand. The plane of the triazole ring is tilted by 13 ° with respect to the N3-Re bond which compares to a much smaller tilt of 7.1 ° for the propyl-substituted ligand. As a result of the π -stacking interaction with the phenyl ring of the ligand **1a** the participating pyridyl ring is twisted such that it is inclined by 3.4 ° with respect to the N1-Re bond and is twisted by 14.9 ° with respect to the plane defined by the Re atom and the carbonyl carbon atoms *trans* to bpy. This twisting results in an angle of 8.8 ° between the planes of the two pyridyl rings and a more severe deviation from coplanarity of the second pyridyl ring with respect to the square plane about the Re centre. Here the ring has an inclination of the 15 ° with respect to the N2-Re bond and a twist of 22.5 ° relative to the same plane defined by the Re atom and carbonyl ligands. In comparison, the propyl triazole complex experiences

much less distortion. The twist between rings in the bpy ligand is only 6.1 °, the rings have inclinations with respect to their Re-N bonds of only 1.7 and 4.1 ° and are twisted relative to the plane of the Re atom and the *trans* carbonyl carbon atoms by 2.7 and 3.5 °.

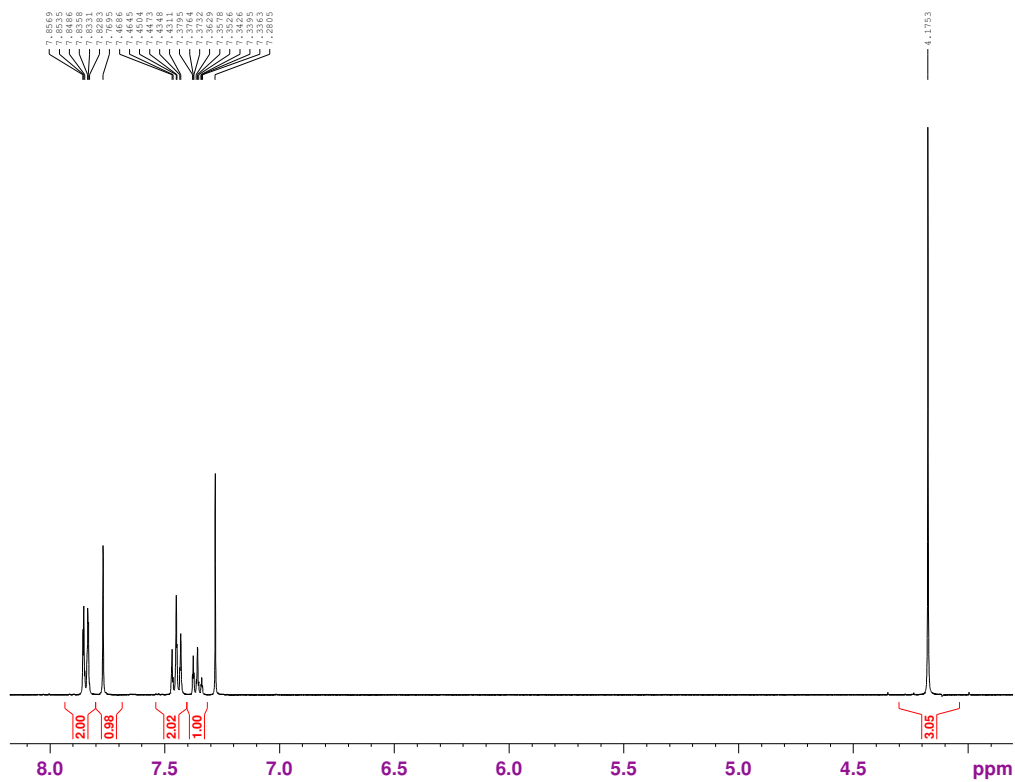


Figure S4 ^1H NMR spectrum of 1-methyl-4-phenyl-1,2,3-triazole (**1a**) (CDCl_3).

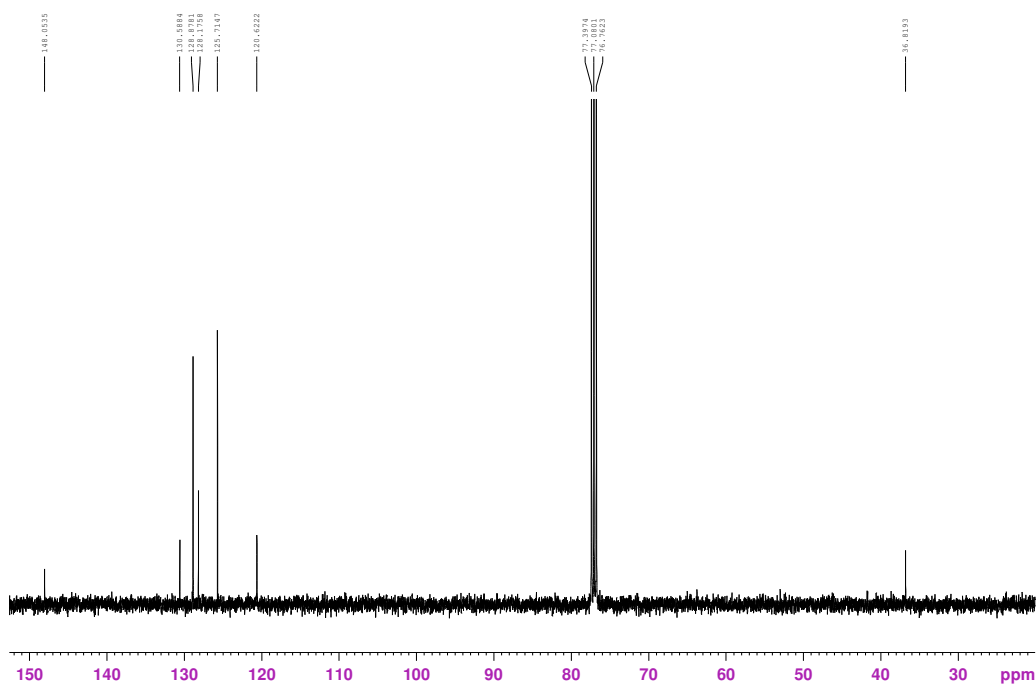


Figure S5 ^{13}C NMR spectrum of 1-methyl-4-phenyl-1,2,3-triazole (**1a**) (CDCl_3).

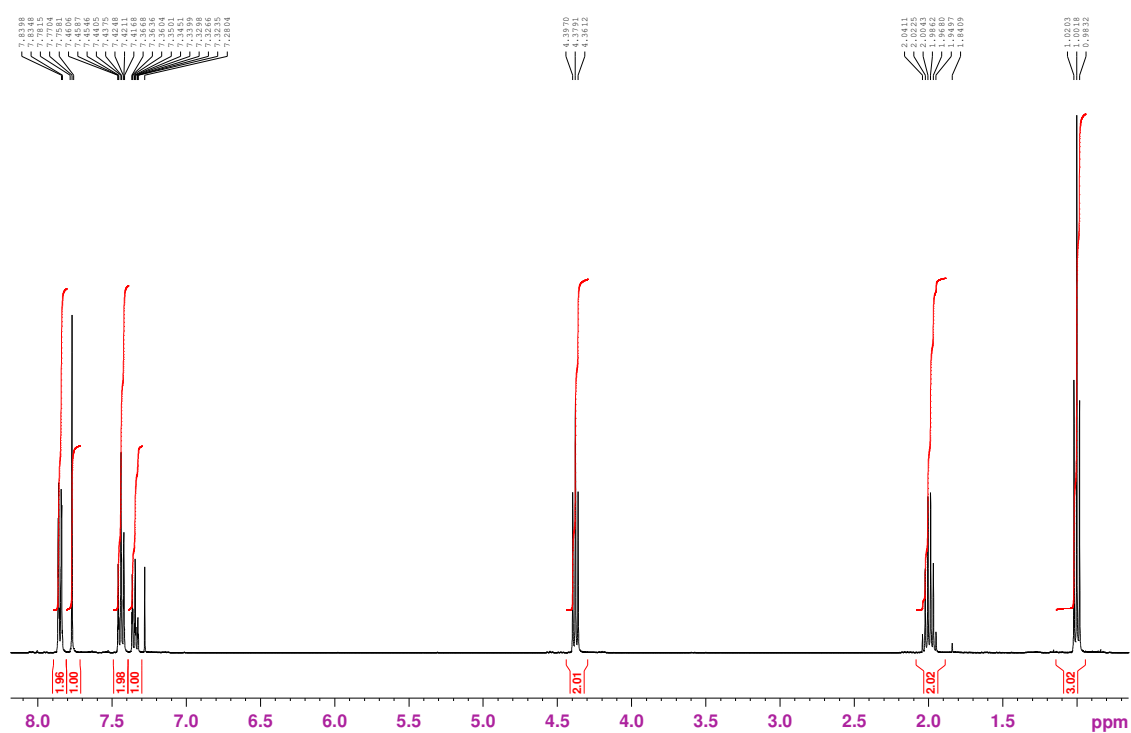


Figure S6 ¹H NMR spectrum of 4-phenyl-1-propyl-1,2,3-triazole (**1b**) (CDCl₃).

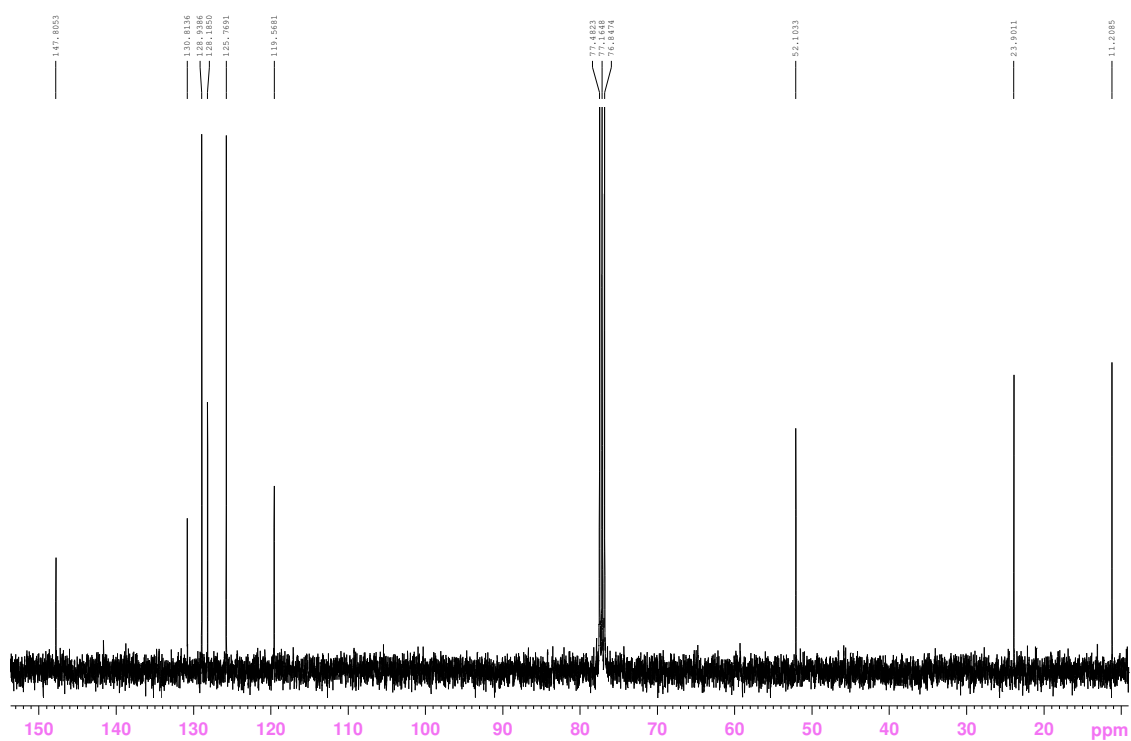


Figure S7 ¹³C NMR spectrum of 4-phenyl-1-propyl-1,2,3-triazole (**1b**) (CDCl₃).

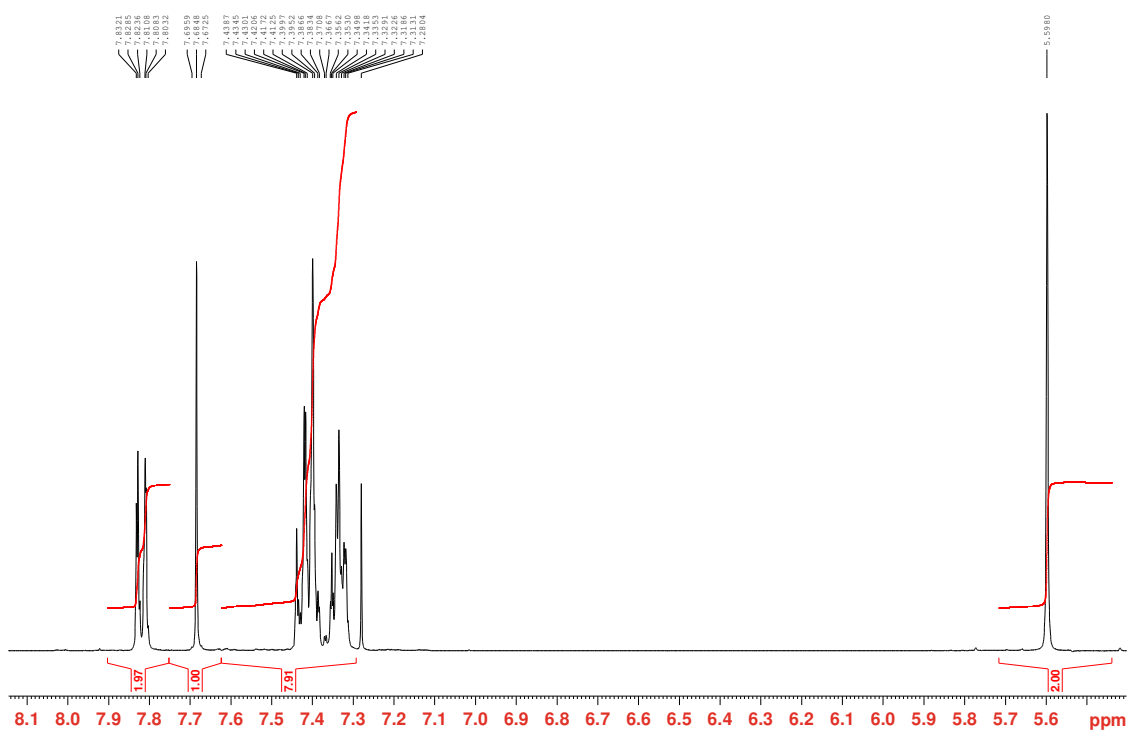


Figure S8 ^1H NMR spectrum of 1-benzyl-4-phenyl-1,2,3-triazole (**1c**) (CDCl_3).

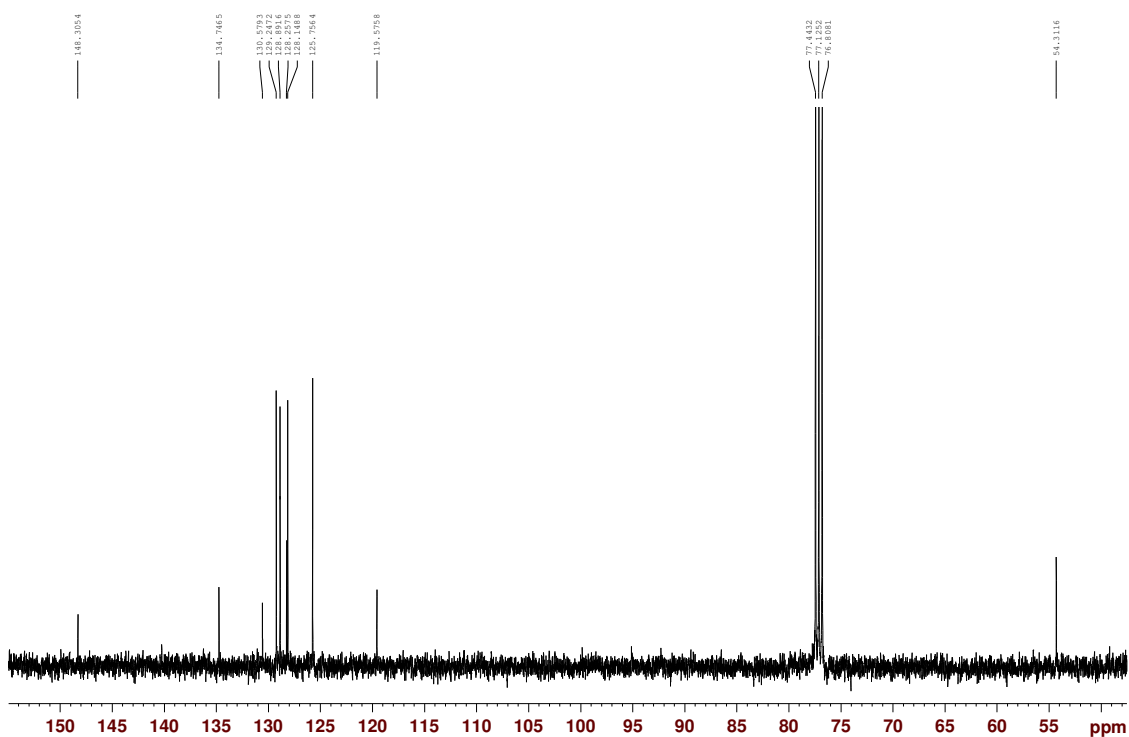


Figure S9 ^{13}C NMR spectrum of 1-benzyl-4-phenyl-1,2,3-triazole (**1c**) (CDCl_3).

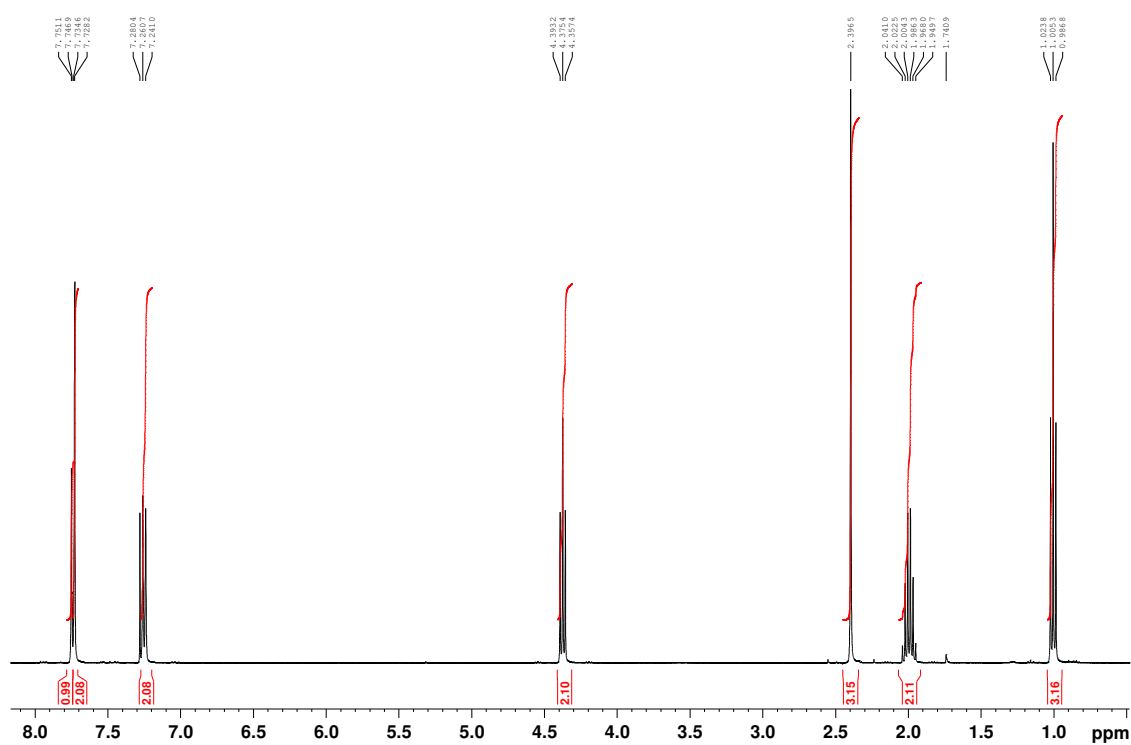


Figure S10 ^1H NMR spectrum of 1-propyl-4-*p*-tolyl-1,2,3-triazole (**1d**) (CDCl_3).

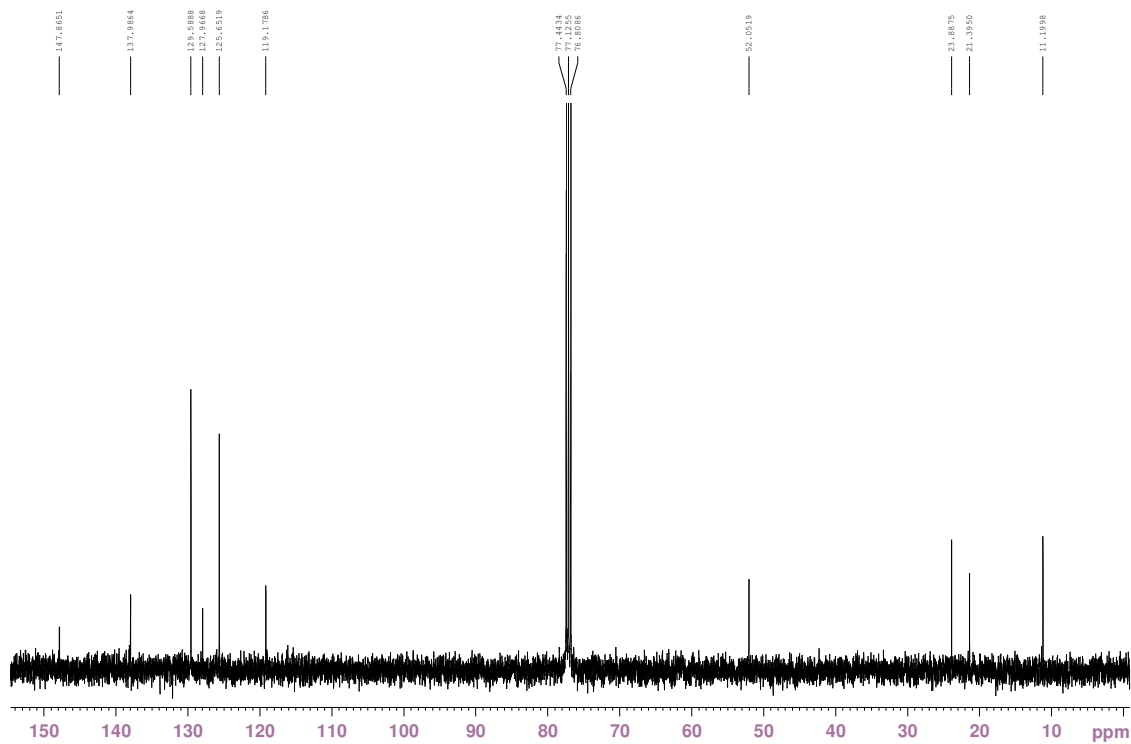


Figure S11 ^{13}C NMR spectrum of 1-propyl-4-*p*-tolyl-1,2,3-triazole (**1d**) (CDCl_3).

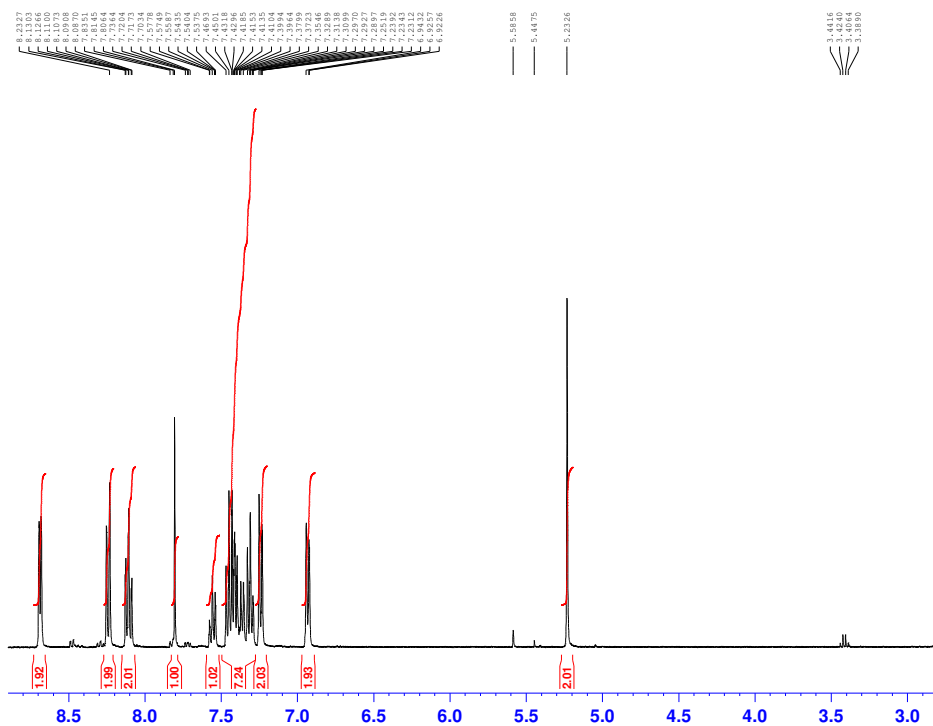


Figure S16 ^1H NMR spectrum of $[\text{Re}(\text{bpy})(\text{CO})_3(\mathbf{1c})]\text{PF}_6$ ($\mathbf{2c}$) (CD_3CN).

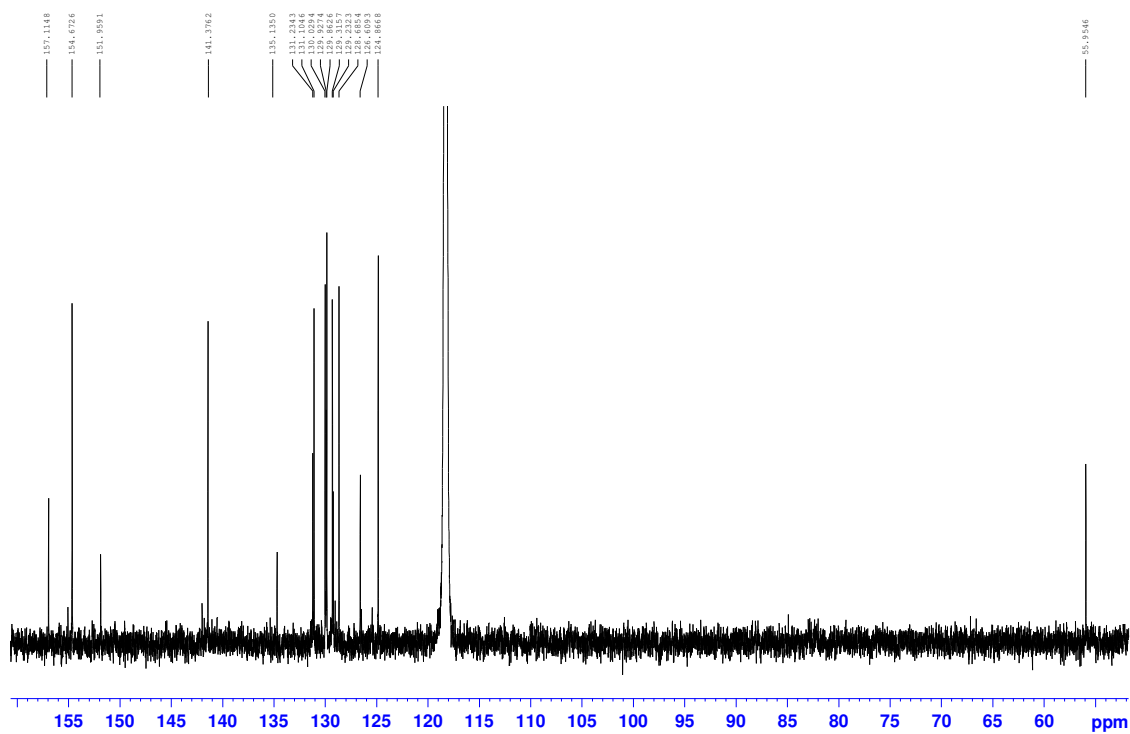


Figure S17 ^{13}C NMR spectrum of $[\text{Re}(\text{bpy})(\text{CO})_3(\mathbf{1c})]\text{PF}_6$ ($\mathbf{2c}$) (CD_3CN).

