### Synthesis and Characterization of Regioselective Substituted Tetrapyridophenazine Ligands and their Ru(II) Complexes

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#### Notes

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#### **Supporting information**



Fig. S1 General <sup>1</sup>H-NMR numbering scheme for the described different tetrapyridophenazine ligands 1-4 and the ruthenium complexes 5-7. The position of the protons of the tpphzRn ligands are marked with small letters and the protons of 4,4<sup>2</sup>-di-tert.-butyl-2,2<sup>2</sup>-bipyridine (tbbpy) are labeled with roman numerals.



Fig. S2 <sup>1</sup>H-NMR spectra of [(tbbpy)<sub>2</sub>Ru(Br<sub>2</sub>tpphz)](PF<sub>6</sub>)<sub>2</sub> 7 at 400 MHz in CD<sub>3</sub>CN and the assignment of the according NMR values.



Fig. S3 Mass spectra (ESI): measured (top) and calculated (bottom) isotopic pattern of the  $[M-1PF_6]$ -Peak of  $[(tbbpy)_2Ru(Br_2tpphz)](PF_6)_2$  6 (left) and  $[(tbbpy)_2Ru(tpphzBr_2)](PF_6)_2$  7 (right).

Reactivity and structural motifs of the decomposition products of [(tbbpy)<sub>2</sub>Ru(phenBr<sub>2</sub>O<sub>2</sub>)](PF<sub>6</sub>)<sub>2</sub>

![](_page_2_Figure_2.jpeg)

**Fig. S4** Overview and detailed reaction scheme of the behavior of  $[(tbpy)_2Ru(phenBr_2O_2)](PF_6)_2$  in an acetone containing solution. Several species (A= **6.1** and B=**6.2**) are probably, which can be investigated by MS(ESI) (Fig. S6) and <sup>1</sup>H-NMR spectroscopy (Fig. S7), as well as X-ray analysis (Fig. S5).

In the case of  $[(tbbpy)_2Ru(phenBr_2O_2)](PF_6)_2$  it seems likely that an aldol kind reaction between the dione sphere and acetone solvent molecules can occur (Fig. S4). This behavior could be affirmed by X-ray analysis of crystals obtained from an acetone solution (Fig. S5). Within the crystal structure the presence of different products could be verified. On one hand the position of significant electron density maxima in the region of the phenBr<sub>2</sub>O<sub>2</sub> moiety suggests that addition of an acetone molecule under formation of a new C-C bond takes place, Fig. S5. This interpretation is further supported by the ESI-MS analysis and by the instability of  $[(tbbpy)_2Ru(phenBr_2O_2)](PF_6)_2$  in acetone as verified by the <sup>1</sup>H-NMR in acetone (d<sub>6</sub>) (Fig. S7). On the other hand, the identification of remaining electron density maxima indicates that the destruction of the C5-C6 bond of the 1,10phenanthroline framework, with the formation of 5,5'dibromo-3'-mehtyl-2,2'-bipyridine-3-carboxylic acid as intermediate, is likely to happen (Fig. S5). Thus this observed reactivity and the instability of phenBr<sub>2</sub>O<sub>2</sub> is a persuasive explanation for the relatively moderate yields for the synthesis of the targeted mononuclear tetrapyridophenazine complex  $[(tbbpy)_2Ru(Br_2tpphz)](PF_6)_2 6$ .

![](_page_3_Figure_1.jpeg)

**Fig.S5** Molecular structure motifs **6.1** (top) and **6.2** (bottom) of the decomposition products of  $[(tbbpy)_2Ru(phenBr_2O_2)](PF_6)_2$ , observed in acetone solution (H-atoms and PF<sub>6</sub>-anions are omitted for clarity)

As the two compounds 6.1 and 6.2 represents the decomposition products of  $[(tbbpy)_2Ru(phenBr_2O_2)](PF_6)_2$  it shows severe disorder in the phenBr<sub>2</sub>O<sub>2</sub> moiety, where two reasonable structure motifs could be identified that are occupied by 65(2) and 35(2) %. Two of the PF<sub>6</sub>-anions are situated on crystallographic inversion centers representing half an anion each. The second PF<sub>6</sub>-anion is situated on a general position. Two of the anions are subjected to disorder with two alternative positions being refined in each case. These alternative positions were occupied by 51(4) and 49(4)% for the affected atoms F21, F22 and F21A, F22A and by 75.1(6) and 24.9(6) % for the atoms P3 - F36 and P3A - F36A, respectively. Two of the tert.Butyl groups of the complex cation are disordered. Two alternative sites were refined that resulted in occupancies of 79(2) and 21(2) % for atoms C24 -C26 and C24A - C26A and of 70(2) and 30(2) % for atoms C46 - C48 and C46A - C48A, respectively. Crystal data for **6.1** and **6.2**:  $C_{49,94}H_{55,88}Br_2F_{12}N_6O_3P_2Ru$ ,  $M_r = 1338.99$  gmol<sup>-1</sup>, red fragment, size 0.23 x 0.14 x 0.07 mm<sup>3</sup>, triclinic, space group  $P\bar{i}$ , a = 11.2440(7), b = 16.7226(17), c = 16.7455(14) Å,  $\alpha = 72.255(7), \beta = 87.076(5), \gamma = 71.488(7)^{\circ}, V = 2840.0(4)$ Å<sup>3</sup>, T = 150 K, Z = 2,  $\rho_{calcd.} = 1.566$  gcm<sup>-3</sup>,  $\mu(MoK\alpha) = 1.824$  $\text{cm}^{-1}$ , F(000) = 1347, 66504 reflections in h(-13/13), k(-20/20), l(-20/20), measured in the range  $3.23 \leq \Theta \leq 25.68^{\circ}$ , completeness  $\Theta_{max} = 99.8\%$ , 10765 independent reflections,  $R_{\text{int}} = 0.1129$ , 7198 observed reflections  $[I > 2\sigma(I)]$ , 856 parameters, 558 restraints,  $R_1 [I > 2\sigma(I)] = 0.0893$ ,  $wR_2$  (all data) = 0.2500, GooF on  $F^2$  = 1.110, largest difference peak and hole: 1.601 / -1.229 e Å<sup>-3</sup>.

The data deposited at the Cambridge Crystallographic Data Centre under CCDC-730641 (for **6.1** and **6.2**) contain the supplementary crystallographic data excluding structure factors. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK, phone: (+44) 01223-762-910, fax: (+44) 1223-336-033, or via mail: deposit@ccdc.cam.ac.uk)

![](_page_4_Figure_0.jpeg)

Fig. S6 Mass spectra (ESI in acetone): measured (top) and calculated (bottom) isotopic pattern of the [M-1PF<sub>6</sub>]-Peak of the most likely decomposition species

 $A = 6.1 = [(tbbpy)_2Ru(phenBr_2(OH)_2(C_3H_5O)_2)](PF_6)_2 (left) and the species$ 

 $B = 6.2 = [(tbbpy)_2Ru(bpyBr_2CH_3(COOH))](PF_6)_2 (right).$ 

The two matching isotopic pattern support the existence of several decomposition species of [(tbbpy)<sub>2</sub>Ru(phenBr<sub>2</sub>O<sub>2</sub>)](PF<sub>6</sub>)<sub>2</sub> generated through given reactivity in acetone solution.

![](_page_5_Figure_0.jpeg)

**Fig. S7** <sup>1</sup>H-NMR spectra of [(tbbpy)<sub>2</sub>Ru(phenBr<sub>2</sub>O<sub>2</sub>)](PF<sub>6</sub>)<sub>2</sub> at 400 MHz (300 K) in different deuterated solvents (CD<sub>3</sub>CN, CD<sub>3</sub>CD and CF<sub>3</sub>COOD as well as acetone-D6) and the assignment of the according NMR values. A clearly decomposition reaction, as depicted in the reaction scheme above, in acetone solution is apparent. The two last proton NMR spectra in acetone-D6, with a proceeding conversion, are measured at two different times after 2 h and 72 h respectively. In contrast the addition of 10% of deuterated trifluoroacetic acid (CF<sub>3</sub>COOD) does not lead to novel proton signals or significant shifts. Instead of that the both phenanthroline based signals, marked with a and c, becomes more clearly (sharp doublets).

### Detail assignment of the Raman bands of the ligands 1-4

The Raman band localized at 1269 cm<sup>-1</sup>, labeled as mode 1, in the calculated spectrum of 1 can be assigned to in-plane ring breathing of benzene with an irreducible representation Ag. This modes split into two vibrations if the tpphz ligand is substituted twice. Thus, the modes can be assigned to the unsubstituted moiety, labeled with 1a and the substituted moiety 1b. The wavenumber of the mode 1a does not really differ in comparison to mode 1 of 1 while mode 1 is located at a lower wavenumber. In case of compound 2 and 4 the bands are located at 1253 and 1246 cm<sup>-1</sup>, respectively. The change of the structure also causes a difference in Raman intensity, because the intensities are proportional to the change of the polarizibility. Considering compound 2 the polarizibility and thus the intensity of the mode 1a is divided by two. The situation for the fourfold substituted ligand 3 is different in that there occurs no mode 1 splitting and the calculated Raman band is located at 1249 cm<sup>-1</sup> and the experimental at 1280 cm<sup>-1</sup>. Consequently this molecular vibration is not coupled over the whole molecule.

The vibrational movements of mode 2 can be assigned to the C-N stretch vibrations of the pyridine rings. Hence, with assistance of this Raman band it is possible to characterize the C-N bond strength. The calculated value of 1334 cm<sup>-1</sup> lies between a single and a double C-N bond and in the case of a twofold substitution no change of mode 2a is observed. This means that the C-N bond length does not change on the unsubstituted moiety. On the other hand for compound 2 the second mode is located at 1341 cm<sup>-1</sup> and considering **3** there is only one band located at 1341 cm<sup>-1</sup>. The vibration is uncoupled and the effect of bromine substituents to this vibration is weak, because the -I and the +M-effect are nearly in balance. The situation is different for 4. The phenyl group participates in the conjugated  $\pi$  system and the mode 2b is shifted by 22cm<sup>-1</sup> to 1356cm<sup>-1</sup>. These effects are also detectable in the experimental Raman spectra (Fig. 7).

The mode 3 is located at 1344 cm<sup>-1</sup> in the calculated spectrum of **1** and is coupled over the whole molecule. A mode splitting or a band shift is not detectable by the twofold substitution. The reason is that the movements of the substituted moiety is prevented and only the atoms of the unsubstituted moiety vibrate. A change of the band position occurs if the tpphz frame is substituted at each pyridine ring. Consequently the considered band is located at 1312 and 1310 cm<sup>-1</sup> in the experimental and calculated spectrum for compound **3**, respectively.

The stretch vibration of the benzene ring is labeled with 4 and occurs at 1385 cm<sup>-1</sup> in the calculated spectrum of 1. The behavior of this mode is similar to that of mode 1. A splitting of the mode is observable by the twofold substitution and the Raman activity increases in the order hydrogen (1), bromine (2) and *tert.*-butyl-phenyl (4).

The calculated modes 5 and 6 of **1** are located at 1434 and 1482 cm<sup>-1</sup>. These modes are coupled over the whole molecule. Hence, no mode splitting by substitution is investigated but a Raman band shift to lower wavenumber arises. The dimension of the shift is larger by the fourfold substitution than by the

twofold one. Considering the bromine substituent the Raman bands of mode 6 are located at 1470 cm<sup>-1</sup> (2) and 1460 cm<sup>-1</sup> (3). In the experimental spectra these differences are also detectable at 1493 cm<sup>-1</sup> and 1478 cm<sup>-1</sup>.

Mode 7, the asymmetric valence vibration of the pyrazine rings at 1512 cm<sup>-1</sup> of 1 has the irreducible representation  $B_{1g}$ . This normal coordinates are located at the pyrazine ring and therefore the impact by the substituents at the pyridine rings are very small. Hence, no Raman band splitting is detectable for the ligands 2 and 4 and the shift of the Raman band is only marginal.

A vibration with a special note is the mode 8. This vibration does not exist for **1** and **3**, because in these molecules this movement with a irreducible representation  $B_{3u}$  is Raman forbidden and only IR active. Apart from that the mode, which is coupled over the whole frame, has the same properties like the modes 5 and 6. The calculated Raman bands are located at 1520 cm<sup>-1</sup> (**2**) and 1517 cm<sup>-1</sup> (**4**) and comparable to the experimental results at 1510 (**2**) and 1531 cm<sup>-1</sup> (**4**).

The Raman band with the highest wavenumber is the mode 9 which can be assigned to the symmetric valence vibration of the pyridine rings. By a twofold substitution at these pyridine rings two vibrations located at both moieties, appear again. Similar to mode 1 the Raman band assigned to the substituted moiety, mode 9b, has a lower excitation energy. The considered Raman band shifts by 24 cm<sup>-1</sup> from 1575 cm<sup>-1</sup> (1) to 1551 cm<sup>-1</sup> (2). In the fourfold substituted molecule this vibration occurs at 1552 cm<sup>-1</sup> and possesses no splitting.

![](_page_7_Figure_1.jpeg)

Fig. S8 Normal coordinates of the investigated in-plane vibrations in the range of 1000 to 1700 cm<sup>-1</sup>. The modes can be classified by their position82 to the phenazine unit (mode 7) or to the pyridine and benzene rings, which can be classified into uncoupled (mode 1, 4, 9), coupled (mode 3, 5, 6, 8) and a special C-N-stretch (mode 2) vibrations.

Furthermore Fig. S8 depicts the displacement vectors of these normal coordinates. All these modes can be assigned to in-plane vibrations and can be classified by their position<sup>23a</sup> according to the phenazine unit (mode 7) or to the pyridine and benzene rings, which can be categorized into uncoupled (mode 1,4,9), coupled (mode 3,5,6,8) and a special C-N-stretch (mode 2) vibrations.

## Vibrational mode assignment of the Raman bands of [(tbbpy)<sub>2</sub>Ru(Br<sub>2</sub>tpphz)]<sup>2+</sup> 6

<b>6</b> 1064 nm	6 DFT calculation	vibrational mode assignment <sup>a</sup>				
1616	1590	$v_{ring}$ (tbbpy)*, $v_{ring}$ (phen2)				
1593	1574	v <sub>ring</sub> (phen2)				
	1558	$v_{ring}(phen1)^*$ , $v_{ring}(phen2)$ , $v_{ring}(tbbpy)$				
1541	1536	$v_{ring}(phen 1)^*, v_{ring}(phen 2)^*, v_{ring}(tbbpy)$				
1520	1521	$v_{ring}(phen 1), v_{ring}(phen 2)$				
1497	1493	v <sub>ring</sub> (pyrazine)				
1477	1470	$v_{ring}$ (tbbpy), $v_{ring}$ (phen1), $v_{ring}$ (phen2) $v_{ring}$ (pyrazine)				
	1457	v <sub>ring</sub> (phen2)*, v <sub>ring</sub> (tbbpy)				
1450	1430	v <sub>ring</sub> (phen2)				
1427	1393	$v_{ring}(phen 1), v_{ring}(phen 2)$				
1368	1352	v <sub>ring</sub> (phen2)				
	1336	$v_{ring}(phen 2)^*, v_{ring}(phen 1)$				
1308	1308	$v_{ring}$ (phen1), $v_{ring}$ (phenazine), $\delta$ (C <sub>tbbpy</sub> H)				
1283	1269	$\delta(C_{phenl}H)$				
1252	1248	$\delta(C_{phen1}H)^*, \delta(C_{tbbpy}H)$				
	1223	δ(C <sub>phen2</sub> H)				
1184	1176	$\delta(C_{phen2}H)^*,  \delta(C_{phen1}H)$				
1161	1159	$\delta(C_{phen1}H)^*, \delta(C_{tbbpy}H)$				
	1094	$\delta(C_{phen2}H)^*, \delta(C_{tbbpy}H)$				
1076	1073	$\delta(C_{phen1}H)^*, \delta(C_{phen2}H)$				
1061	1057	$\delta(C_{tbbpy}H)^*, \delta(C_{phen2}H)$				
1038	1020	$v_{ring}(phen 1), v_{ring}(phen 2), v_{ring}(_{tbbpy})$				
	1005	v <sub>ring</sub> (phen1), v <sub>ring</sub> (phen2), v <sub>ring</sub> (pyrazine), v <sub>ring</sub> (tbbpy)				

Table S1

 $^{a\,\ast}$  marked the vibrations with the largest intensity to the corresponding Raman band

 $v_{ring}$  ring stretch,  $\delta$  in-plane deformation, phen1 means the phenanthroline part of the tpphz ligand close to the ruthenium center, phen2 means the phenanthroline part further away from the ruthenium center, tbbpy means the 4,4'-tert.-butyl-2,2'-bipyridine

# Vibrational mode assignment of the Raman bands of [(tbbpy)<sub>2</sub>Ru(tpphzBr<sub>2</sub>)]<sup>2+</sup> 7

#### Table S2

<b>7</b> 1064 nm	7 DFT calculation	vibrational mode assignment <sup>a</sup>			
1612	1590	v <sub>ring</sub> (tbbpy)			
1572	1571	$v_{ring}(phen 1)^*, v_{ring}(pyrazine)$			
1539	1552	$v_{ring}$ (phen2), $v_{ring}$ (phen1), $v_{ring}$ (tbbpy)			
	1514	$v_{ring}(phen1), v_{ring}(phen2), v_{ring}(pyrazine)$			
1498	1496	$v_{ring}(pyrazine), v_{ring}(phen 1)$			
1477	1473	$ \begin{array}{ } \nu_{\text{ring}}(phen1), \nu_{\text{ring}}(phen2), \nu_{\text{ring}}(pyrazine), \\ \nu_{\text{ring}}(tbbpy) \end{array} $			
1448	1448	$v_{ring}(phen 2)^*, v_{ring}(tbbpy)$			
1408	1415	$v_{ring}(phen 1), v_{ring}(phen 2), v_{ring}(pyrazine)$			
1364	1375	v <sub>ring</sub> (benzene2)			
	1345	$v_{ring}(phen 1)^*, v_{ring}(phen 2)$			
	1311	$v_{ring}(phen1), v_{ring}(phen2), v_{ring}(pyrazine), \delta(C_{tbbpy}H)$			
1283	1283	$\delta(C_{phen1}H)^*, \delta(C_{tbbpy}H)$			
	1261	$\delta(C_{phen2}H)^*, \delta(C_{tbbpy}H)$			
1190	1178	$\delta(C_{phen1}H)^*, \delta(C_{phen2}H)$			
1169	1157	$\delta(C_{phen2}H)^*, \delta(C_{tbbpy}H)$			
1132	1127	$\delta(C_{phen1}H)$			
1074	1072	$\delta(C_{phen2}H)$			
	1057	$\delta(C_{phen1}H), \delta(C_{tbbpy}H)$			
1039	1036	$v_{ring}$ (phen2), $v_{ring}$ (tbbpy)			
1032	1024	$v_{ring}(phen1), v_{ring}(phen2), v_{ring}(tbbpy)$			
	1014	$v_{ring}(phen1), v_{ring}(phen2), v_{ring}(tbbpy)$			
	1004	$v_{ring}(phen 1), v_{ring}(phen 2), v_{ring}(pyrazine), v_{ring}(tbbpy)$			

 $^{\it a}$  \* marked the vibrations with the largest intensity to the corresponding Raman band

 $v_{ring}$  ring stretch,  $\delta$  in-plane deformation, phen1 means the phenanthroline part of the tpphz ligand close to the ruthenium center, phen2 means the phenanthroline part further away from the ruthenium center, tbbpy means the 4,4'-*tert*.-butyl-2,2'-bipyridine

**Table S3** Distances of the BP86/MARI-J/TZVPP calculated ligands 1-4 and the concerning complexes 5-7 are given in pm, angles and dihedral angles indegrees, \* values of the crystal structures, two values are declared due to the  $C_2$ -axis across the center of the bonds C19-C30 and C24-C25.

	1		1	1	1	1			1	1
	1	2	3	4	5	6	7	5* 15	6*	7*
N1-C2	133.0	132.6	132.6	132.6	134.6	134.4	134.6	$\begin{array}{c} 133.8 \pm 1.8 \\ 134.5 \pm 1.8 \end{array}$	$\begin{array}{c} 134.6 \pm 3.0 \\ 134.2 \pm 2.7 \end{array}$	$\begin{array}{c} 132.2 \pm 3.0 \\ 133.2 \pm 3.0 \end{array}$
C8-N9	133.0	133.0	132.6	133.0	133.1	133.1	132.6	$\begin{array}{c} 132.4 \pm 2.1 \\ 132.8 \pm 2.4 \end{array}$	$\begin{array}{c} 134.5 \pm 4.2 \\ 130.9 \pm 4.2 \end{array}$	$\begin{array}{c} 130.6 \pm 3.3 \\ 129.6 \pm 3.3 \end{array}$
C2-C3	140.6	140.8	140.9	141.9	140.0	140.5	140.0	$\begin{array}{c} 139.6 \pm 2.1 \\ 139.3 \pm 2.1 \end{array}$	$143.7 \pm 3.6 \\ 138.3 \pm 3.0$	$\begin{array}{c} 139.4 \pm 3.3 \\ 137.1 \pm 3.3 \end{array}$
C7-C8	140.6	140.6	140.9	140.6	140.8	140.8	141.2	$\begin{array}{c} 138.7 \pm 2.7 \\ 139.5 \pm 2.4 \end{array}$	$\begin{array}{c} 135.9 \pm 4.8 \\ 140.5 \pm 4.2 \end{array}$	$\begin{array}{c} 138.5 \pm 3.6 \\ 135.7 \pm 3.9 \end{array}$
C3-C4	138.4	138.2	138.2	139.3	138.7	138.8	138.7	$136.3 \pm 2.4 \\ 137.8 \pm 2.1$	$136.2 \pm 4.2$ $139.7 \pm 3.0$	$\begin{array}{c} 138.0 \pm 3.3 \\ 138.0 \pm 3.3 \end{array}$
C6-C7	138.4	138.3	138.2	138.4	138.2	138.2	138.3	$\begin{array}{c} 138.7 \pm 2.7 \\ 137.7 \pm 2.4 \end{array}$	$139.6 \pm 3.6$ $136.4 \pm 3.9$	$\begin{array}{c} 139.9 \pm 3.3 \\ 136.6 \pm 3.6 \end{array}$
C4-C20	140.8	140.7	140.7	140.4	140.7	140.5	140.7	$\begin{array}{c} 140.0 \pm 2.1 \\ 139.8 \pm 2.1 \end{array}$	$140.1 \pm 3.6$ $138.1 \pm 3.3$	$\begin{array}{c} 137.6 \pm 3.3 \\ 139.7 \pm 3.3 \end{array}$
C6-C23	140.8	140.8	140.7	140.8	141.0	141.0	140.8	$\begin{array}{c} 140.4 \pm 2.1 \\ 140.0 \pm 2.1 \end{array}$	$136.5 \pm 4.2 \\ 137.9 \pm 4.2$	$\begin{array}{c} 137.1 \pm 3.3 \\ 139.5 \pm 3.3 \end{array}$
N1-C19	135.1	135.1	135.1	135.1	137.2	137.1	137.2	$\begin{array}{c} 136.2 \pm 1.8 \\ 136.3 \pm 1.8 \end{array}$	$135.5 \pm 3.0 \\ 136.5 \pm 2.4$	$135.8 \pm 2.7 \\ 138.2 \pm 2.7$
N9-C24	135.1	135.0	135.1	135.1	134.6	134.6	134.8	$\begin{array}{c} 134.9 \pm 1.8 \\ 134.9 \pm 2.1 \end{array}$	$\begin{array}{c} 135.6 \pm 3.3 \\ 135.5 \pm 3.9 \end{array}$	$\begin{array}{c} 137.2 \pm 3.0 \\ 133.8 \pm 3.0 \end{array}$
C19-C20	142.1	142.0	142.0	142.0	141.2	141.2	141.2	$\begin{array}{c} 139.4 \pm 2.1 \\ 138.7 \pm 2.1 \end{array}$	$141.7 \pm 3.0 \\ 137.9 \pm 3.3$	$\begin{array}{c} 140.8 \pm 3.0 \\ 138.0 \pm 3.0 \end{array}$
C23-C24	142.1	142.1	142.0	142.1	142.2	142.2	142.1	$\begin{array}{c} 140.0 \pm 2.4 \\ 140.6 \pm 2.1 \end{array}$	$141.9 \pm 4.2$ $142.9 \pm 3.6$	$\begin{array}{c} 140.8 \pm 3.3 \\ 141.7 \pm 3.3 \end{array}$
C20-C21	145.7	145.8	145.9	145.8	145.7	145.8	145.8	$\begin{array}{c} 146.0 \pm 2.1 \\ 146.2 \pm 2.1 \end{array}$	$144.2 \pm 3.9$ $148.9 \pm 2.7$	$\begin{array}{c} 146.0 \pm 3.3 \\ 146.2 \pm 3.0 \end{array}$
C22-C23	145.7	145.7	145.9	145.7	145.1	145.1	145.2	$\begin{array}{c} 145.6 \pm 2.1 \\ 144.3 \pm 2.1 \end{array}$	$148.1 \pm 3.3 \\ 146.9 \pm 3.9$	$\begin{array}{c} 146.5 \pm 3.0 \\ 146.4 \pm 3.3 \end{array}$
N5-C21	134.1	134.0	134.0	134.1	134.1	134.0	134.0	$\begin{array}{c} 133.2 \pm 1.8 \\ 132.6 \pm 2.1 \end{array}$	$\begin{array}{c} 135.9 \pm 3.0 \\ 135.5 \pm 3.6 \end{array}$	$\begin{array}{c} 135.3 \pm 2.7 \\ 133.2 \pm 3.0 \end{array}$
N5-C22	134.1	134.0	134.0	134.1	133.9	134.0	133.9	$\begin{array}{c} 134.4 \pm 2.1 \\ 133.5 \pm 2.4 \end{array}$	$\begin{array}{c} 137.0 \pm 3.6 \\ 131.5 \pm 2.7 \end{array}$	$\begin{array}{c} 134.6 \pm 3.0 \\ 134.0 \pm 2.7 \end{array}$
C19-C30	147.2	146,7	146.6	146.7	143.5	143.2	143.6	$145.5 \pm 1.8$	145.1 ± 3.3	$143.8 \pm 3.0$
C21-C28	142.8	142.7	142.7	142.9	142.3	142.3	142.4	$142.6 \pm 2.1$	137.5 ± 3.9	$141.3 \pm 3.0$
C22-C27	142.8	143.0	142.7	142.7	144.6	144.7	144.4	$142.9 \pm 2.1$	$142.9\pm4.2$	$141.5 \pm 3.3$
C24-C25	147.2	147.3	146.6	147.2	147.4	147.4	146.7	$146.4 \pm 2.4$	$146.3 \pm 4.5$	$145.7 \pm 3.6$
N1-N18	274.1	274.4	273.9	275.2	265.1	266.2	265.0	$264.2\pm2.2$	$263.2 \pm 3.5$	$263.8\pm2.9$
N9-N10	274.1	274.0	273.9	274.2	272.6	274.2	273.2	$272.0 \pm 2.1$	$275.5 \pm 3.5$	$273.2 \pm 2.9$