

## Supplementary Information

for

### Photo-release of acetonitrile in Ruthenium (II) complexes with various substituted terpyridine ligands.

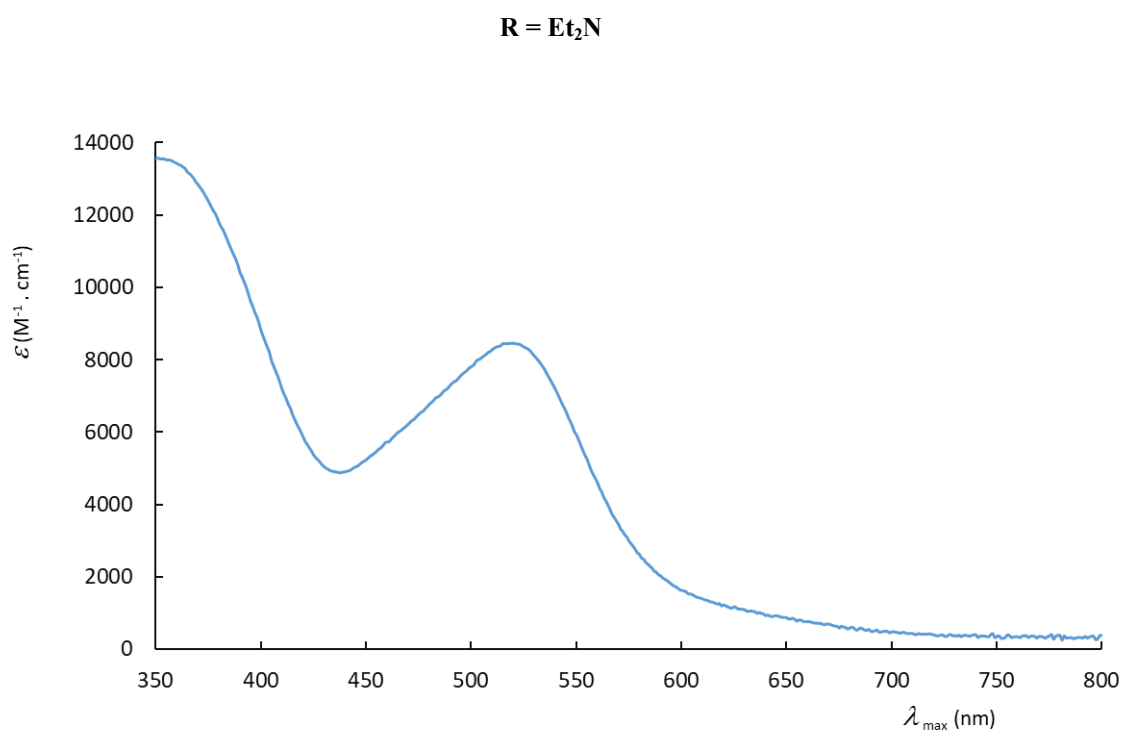
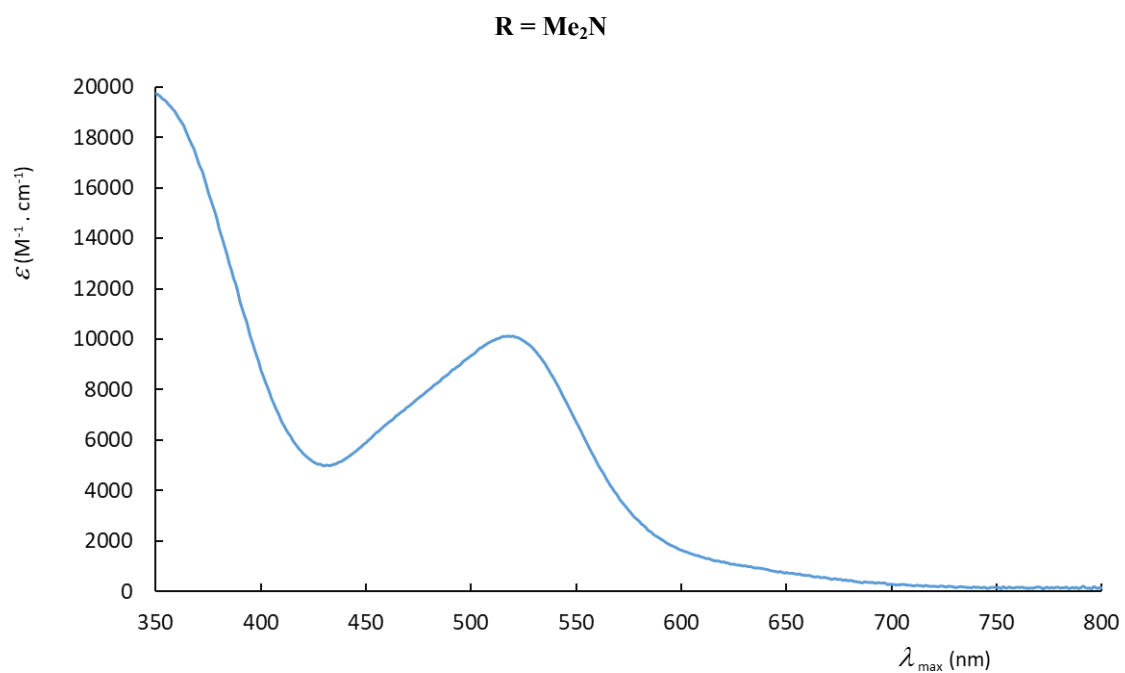
by

Vladyslav Mudrak, Pascal G. Lacroix, Pablo Labra-Vázquez, Marine Tassé, Sonia Mallet-Ladeira, Isabelle Malfant

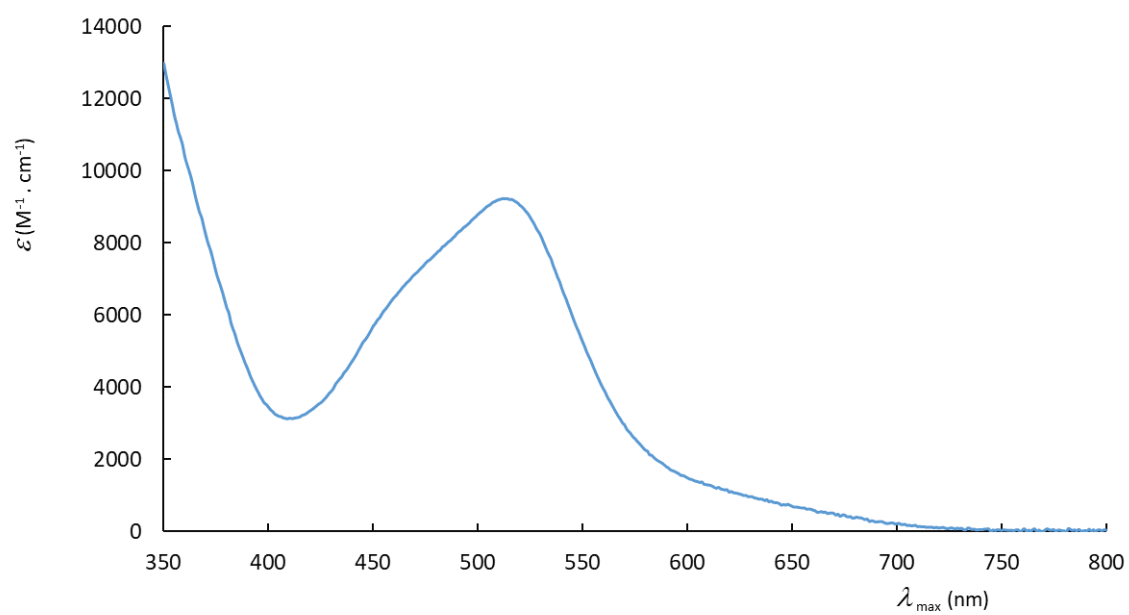
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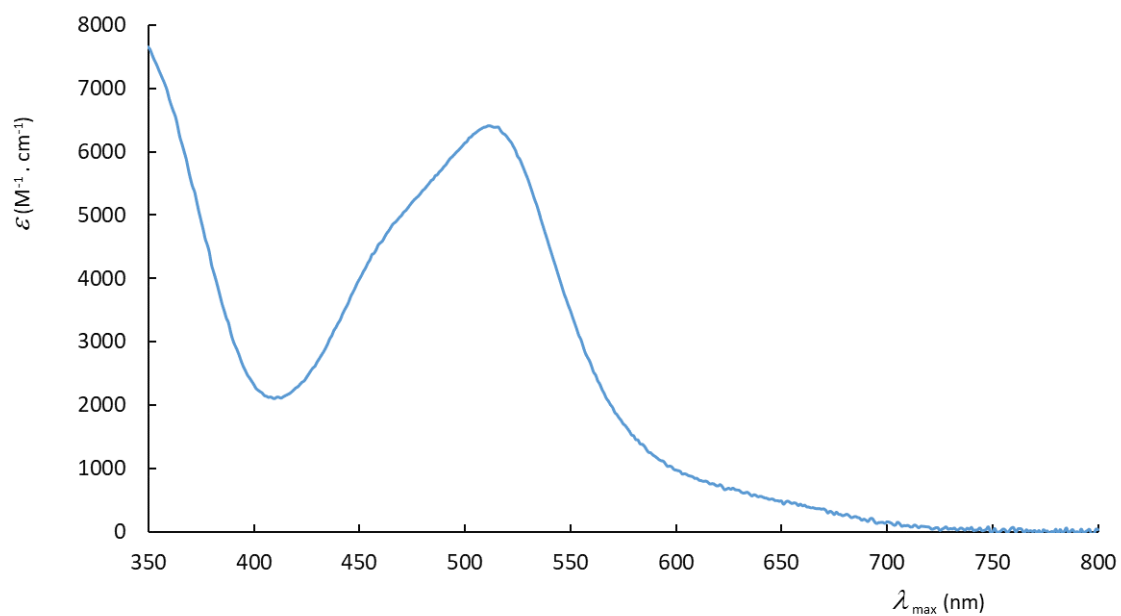
**Figure S1** UV-visible spectra recorded in water for  $[\text{Ru}(\text{R-phtpy})(\text{acac})(\text{MeCN})](\text{PF}_6)$ .



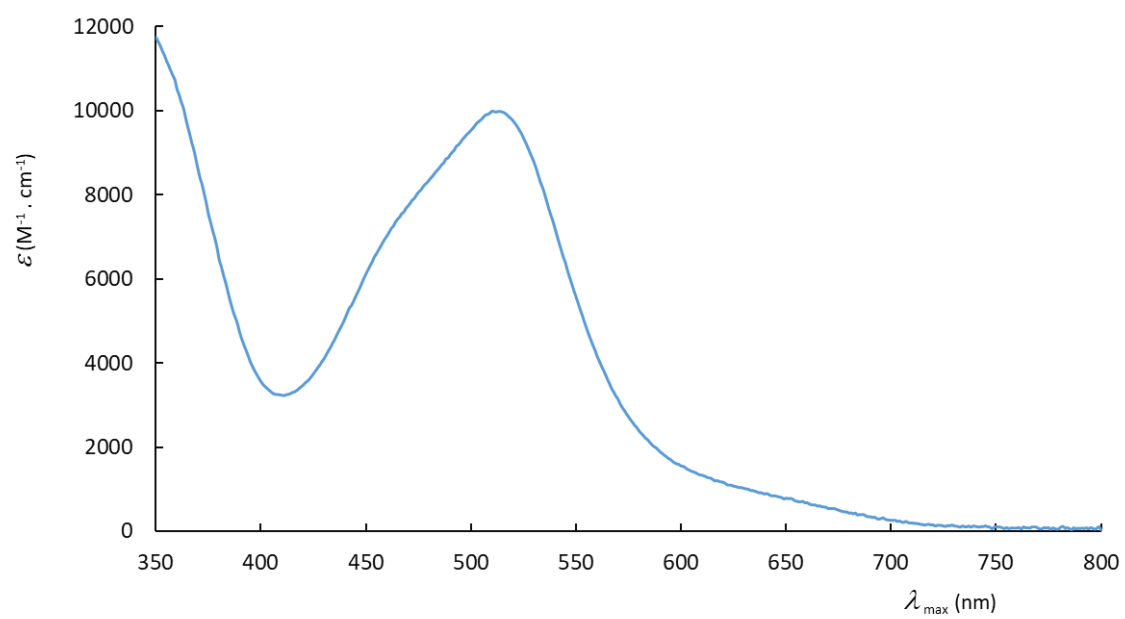
**R = MeO**



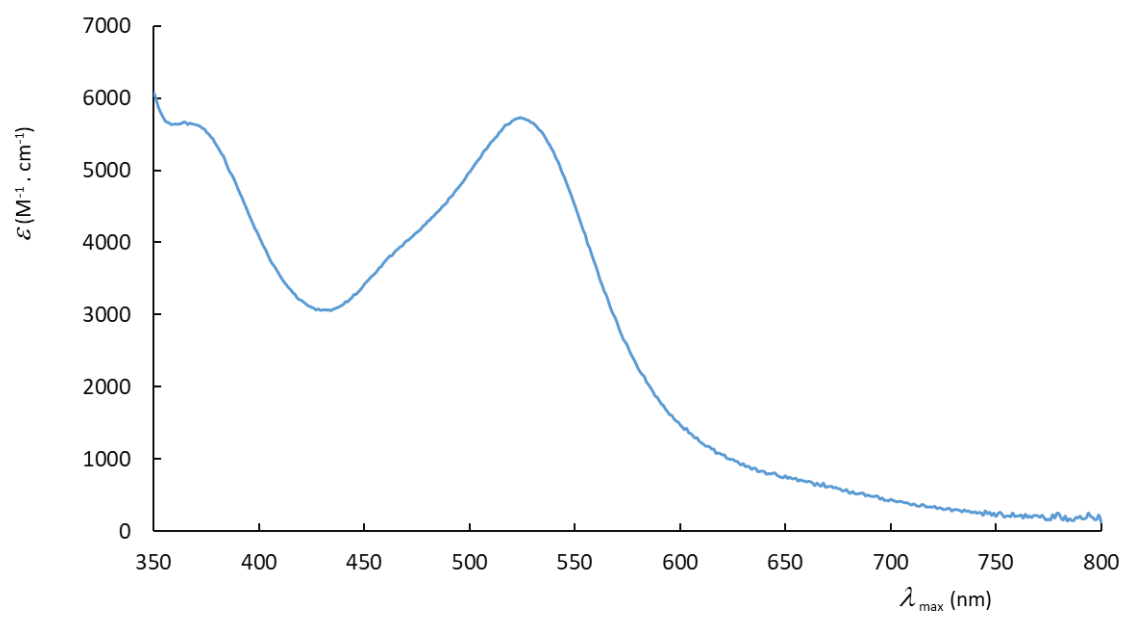
**R = H**



**R = Me**

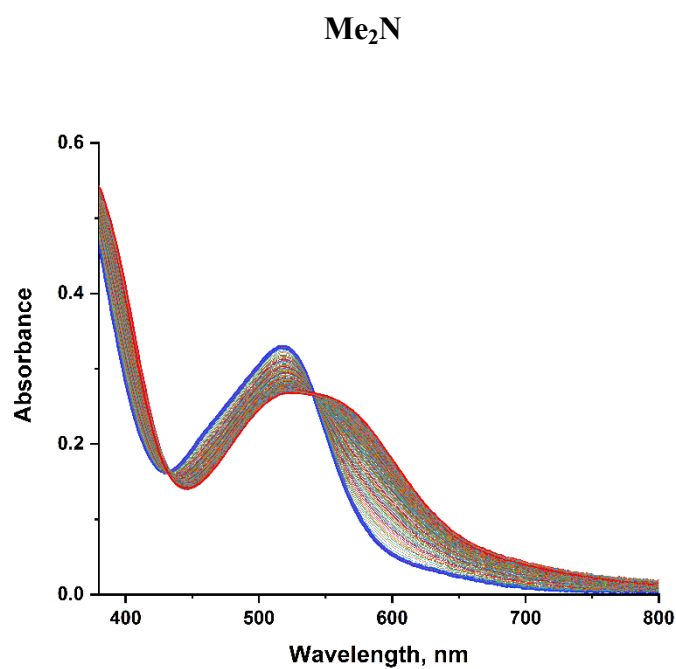
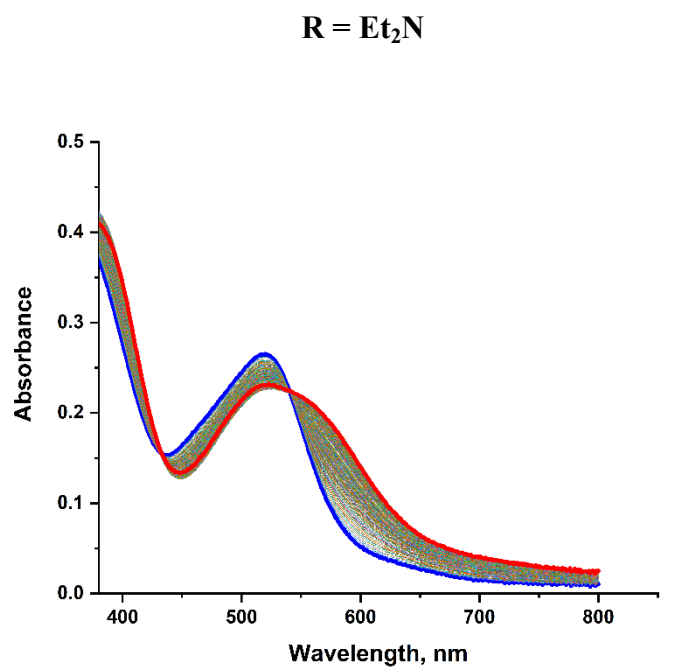


**R = NO<sub>2</sub>**

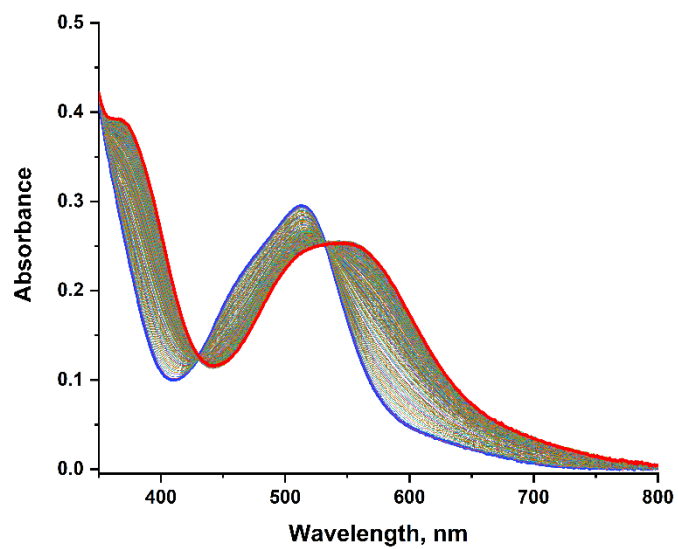


**Figure S2**

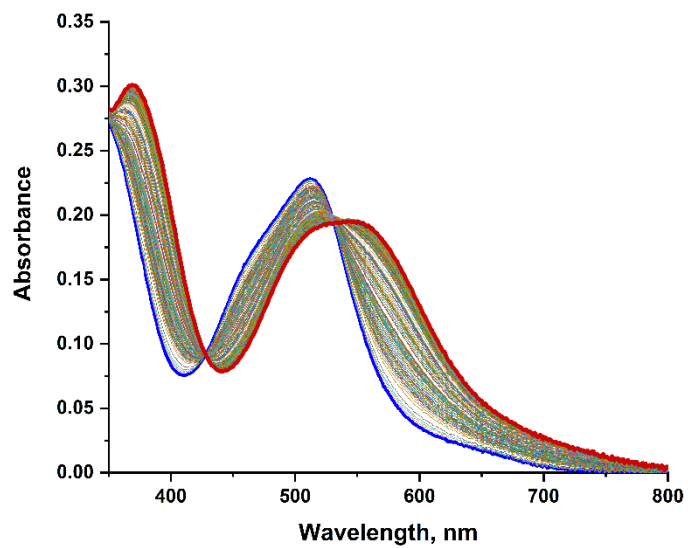
Photorelease experiments in water for  $[\text{Ru}(\text{R-phtpy})(\text{acac})(\text{MeCN})](\text{PF}_6)$ , under irradiation at  $\lambda_{\text{irr}} = 455 \text{ nm}$ . Blue: starting complexes. Red : photo-products. (Note: no photorelease is observed for  $\text{R} = \text{NO}_2$ ).



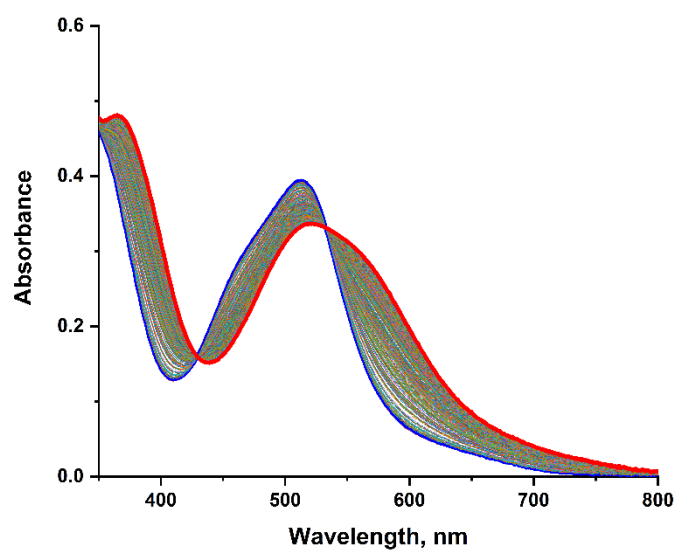
**R = MeO**



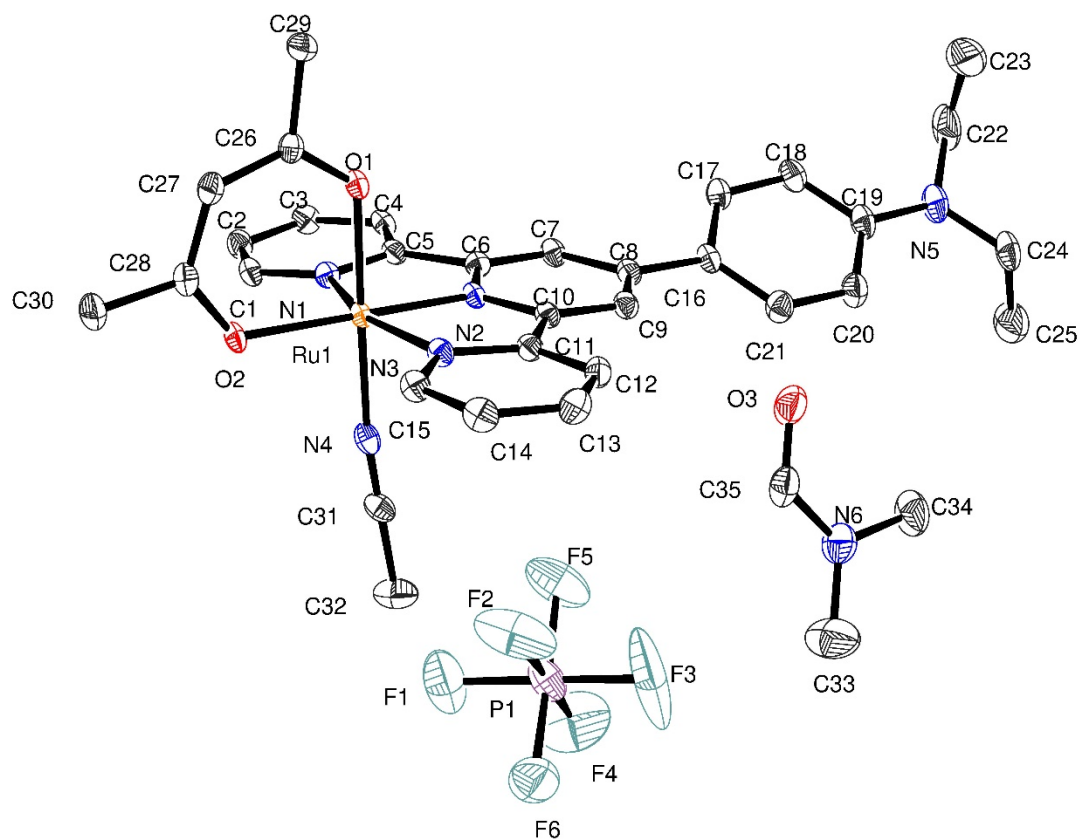
**R = H**



**R = Me**



**Figure S3** Asymmetric unit for [Ru(Et<sub>2</sub>N-phtpy)(acac)(MeCN)](PF<sub>6</sub>)



**Table S1.** Crystal data and structure refinement for [Ru(Et<sub>2</sub>N-phtpy)(acac)(MeCN)](PF<sub>6</sub>)

|                             |                                                                                   |         |
|-----------------------------|-----------------------------------------------------------------------------------|---------|
| Identification code         | VM-PLV-29                                                                         |         |
| Empirical formula           | C <sub>35</sub> H <sub>41</sub> F <sub>6</sub> N <sub>6</sub> O <sub>3</sub> P Ru |         |
| Formula weight              | 839.78                                                                            |         |
| Temperature                 | 100 (2) K                                                                         |         |
| Wavelength                  | 1.54184 Å                                                                         |         |
| Crystal system, space group | Triclinic, P -1                                                                   |         |
| Unit cell dimensions        | a = 8.32390(10) Å                                                                 | alpha = |
| 77.6210(10) deg.            | b = 14.8029(2) Å                                                                  | beta =  |
| 82.4720(10) deg.            |                                                                                   |         |



|                                   |                                             |
|-----------------------------------|---------------------------------------------|
| 82.5980(10) deg.                  | c = 15.4530(2) A    gamma =                 |
| Volume                            | 1833.78(4) A <sup>3</sup>                   |
| Z, Calculated density             | 2, 1.521 Mg/m <sup>3</sup>                  |
| Absorption coefficient            | 4.525 mm <sup>-1</sup>                      |
| F(000)                            | 860                                         |
| Crystal size                      | 0.20 x 0.20 x 0.04 mm                       |
| Theta range for data collection   | 2.945 to 77.335 deg.                        |
| Limiting indices                  | -7<=h<=10, -18<=k<=18, -19<=l<=18           |
| Reflections collected / unique    | 68219 / 7294 [R(int) = 0.0794]              |
| Completeness to theta = 67.684    | 99.8 %                                      |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup> |
| Data / restraints / parameters    | 7294 / 0 / 476                              |
| Goodness-of-fit on F <sup>2</sup> | 1.052                                       |
| Final R indices [I>2sigma(I)]     | R1 = 0.0402, wR2 = 0.1072                   |
| R indices (all data)              | R1 = 0.0415, wR2 = 0.1082                   |
| Largest diff. peak and hole       | 0.963 and -1.236 e.A <sup>-3</sup>          |

**Table S2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Ru}(\text{Et}_2\text{N-phtpy})(\text{acac})(\text{MeCN})](\text{PF}_6)$ .  
 $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

|        | x         | y         | z         | U (eq)  |
|--------|-----------|-----------|-----------|---------|
| C (1)  | 3341 (3)  | 7264 (2)  | 3807 (2)  | 19 (1)  |
| C (2)  | 1947 (4)  | 6852 (2)  | 3776 (2)  | 22 (1)  |
| C (3)  | 1594 (3)  | 6074 (2)  | 4411 (2)  | 22 (1)  |
| C (4)  | 2614 (3)  | 5737 (2)  | 5078 (2)  | 19 (1)  |
| C (5)  | 3966 (3)  | 6189 (2)  | 5087 (2)  | 17 (1)  |
| C (6)  | 5065 (3)  | 5929 (2)  | 5805 (2)  | 17 (1)  |
| C (7)  | 4911 (3)  | 5252 (2)  | 6571 (2)  | 19 (1)  |
| C (8)  | 6023 (3)  | 5132 (2)  | 7211 (2)  | 19 (1)  |
| C (9)  | 7274 (3)  | 5720 (2)  | 7035 (2)  | 18 (1)  |
| C (10) | 7410 (3)  | 6369 (2)  | 6254 (2)  | 17 (1)  |
| C (11) | 8688 (3)  | 7014 (2)  | 5949 (2)  | 17 (1)  |
| C (12) | 9979 (3)  | 7033 (2)  | 6428 (2)  | 20 (1)  |
| C (13) | 11093 (4) | 7670 (2)  | 6094 (2)  | 24 (1)  |
| C (14) | 10896 (4) | 8282 (2)  | 5293 (2)  | 23 (1)  |
| C (15) | 9602 (3)  | 8227 (2)  | 4833 (2)  | 20 (1)  |
| C (16) | 5918 (3)  | 4402 (2)  | 8026 (2)  | 19 (1)  |
| C (17) | 5346 (4)  | 3551 (2)  | 8033 (2)  | 22 (1)  |
| C (18) | 5419 (4)  | 2821 (2)  | 8756 (2)  | 26 (1)  |
| C (19) | 6004 (4)  | 2910 (2)  | 9549 (2)  | 26 (1)  |
| C (20) | 6486 (4)  | 3789 (2)  | 9564 (2)  | 28 (1)  |
| C (21) | 6478 (4)  | 4497 (2)  | 8815 (2)  | 24 (1)  |
| C (22) | 5903 (5)  | 1235 (2)  | 10192 (3) | 45 (1)  |
| C (23) | 7435 (7)  | 758 (3)   | 9786 (3)  | 58 (1)  |
| C (24) | 6688 (4)  | 2284 (2)  | 11085 (2) | 34 (1)  |
| C (25) | 5367 (5)  | 2684 (3)  | 11719 (2) | 47 (1)  |
| C (26) | 8289 (3)  | 6654 (2)  | 3081 (2)  | 17 (1)  |
| C (27) | 8161 (4)  | 7511 (2)  | 2502 (2)  | 22 (1)  |
| C (28) | 7377 (3)  | 8359 (2)  | 2691 (2)  | 20 (1)  |
| C (29) | 9179 (4)  | 5830 (2)  | 2713 (2)  | 22 (1)  |
| C (30) | 7365 (4)  | 9211 (2)  | 1963 (2)  | 29 (1)  |
| C (31) | 4682 (4)  | 8853 (2)  | 5742 (2)  | 22 (1)  |
| C (32) | 3904 (4)  | 9459 (2)  | 6338 (2)  | 36 (1)  |
| C (33) | 8747 (7)  | 7747 (3)  | 9848 (3)  | 59 (1)  |
| C (34) | 8673 (5)  | 6041 (3)  | 10312 (2) | 42 (1)  |
| C (35) | 9294 (4)  | 6752 (2)  | 8762 (2)  | 31 (1)  |
| N (1)  | 4353 (3)  | 6936 (2)  | 4438 (2)  | 17 (1)  |
| N (2)  | 6305 (3)  | 6472 (2)  | 5662 (1)  | 15 (1)  |
| N (3)  | 8517 (3)  | 7600 (2)  | 5144 (2)  | 17 (1)  |
| N (5)  | 6078 (4)  | 2186 (2)  | 10273 (2) | 34 (1)  |
| N (4)  | 5276 (3)  | 8368 (2)  | 5277 (2)  | 19 (1)  |
| N (6)  | 8873 (4)  | 6848 (2)  | 9601 (2)  | 35 (1)  |
| O (1)  | 7741 (2)  | 6466 (1)  | 3904 (1)  | 18 (1)  |
| O (2)  | 6660 (2)  | 8471 (1)  | 3444 (1)  | 18 (1)  |
| O (3)  | 9546 (3)  | 6008 (2)  | 8514 (2)  | 37 (1)  |
| F (1)  | 7182 (3)  | 10327 (2) | 6505 (2)  | 69 (1)  |
| F (2)  | 9807 (3)  | 9805 (2)  | 6498 (2)  | 79 (1)  |
| F (3)  | 9455 (5)  | 9345 (2)  | 7986 (3)  | 124 (2) |
| F (4)  | 6800 (4)  | 9859 (3)  | 7973 (2)  | 87 (1)  |
| F (5)  | 7875 (3)  | 8843 (2)  | 7140 (2)  | 67 (1)  |
| F (6)  | 8756 (3)  | 10819 (2) | 7341 (2)  | 55 (1)  |
| P (1)  | 8316 (1)  | 9824 (1)  | 7252 (1)  | 33 (1)  |
| Ru (1) | 6476 (1)  | 7437 (1)  | 4588 (1)  | 14 (1)  |

**Table S3.** Bond lengths [Å] and angles [deg] for [Ru(Et<sub>2</sub>N-phtpy)(acac)(MeCN)](PF<sub>6</sub>).

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|                 |           |
|-----------------|-----------|
| C (1) -N (1)    | 1.342 (3) |
| C (1) -C (2)    | 1.388 (4) |
| C (1) -H (1)    | 0.9500    |
| C (2) -C (3)    | 1.380 (4) |
| C (2) -H (2)    | 0.9500    |
| C (3) -C (4)    | 1.390 (4) |
| C (3) -H (3)    | 0.9500    |
| C (4) -C (5)    | 1.384 (4) |
| C (4) -H (4)    | 0.9500    |
| C (5) -N (1)    | 1.366 (3) |
| C (5) -C (6)    | 1.486 (4) |
| C (6) -N (2)    | 1.355 (3) |
| C (6) -C (7)    | 1.381 (4) |
| C (7) -C (8)    | 1.411 (4) |
| C (7) -H (7)    | 0.9500    |
| C (8) -C (9)    | 1.405 (4) |
| C (8) -C (16)   | 1.474 (4) |
| C (9) -C (10)   | 1.373 (4) |
| C (9) -H (9)    | 0.9500    |
| C (10) -N (2)   | 1.353 (3) |
| C (10) -C (11)  | 1.485 (4) |
| C (11) -N (3)   | 1.369 (3) |
| C (11) -C (12)  | 1.388 (4) |
| C (12) -C (13)  | 1.381 (4) |
| C (12) -H (12)  | 0.9500    |
| C (13) -C (14)  | 1.384 (4) |
| C (13) -H (13)  | 0.9500    |
| C (14) -C (15)  | 1.386 (4) |
| C (14) -H (14)  | 0.9500    |
| C (15) -N (3)   | 1.349 (3) |
| C (15) -H (15)  | 0.9500    |
| C (16) -C (17)  | 1.401 (4) |
| C (16) -C (21)  | 1.401 (4) |
| C (17) -C (18)  | 1.380 (4) |
| C (17) -H (17)  | 0.9500    |
| C (18) -C (19)  | 1.413 (4) |
| C (18) -H (18)  | 0.9500    |
| C (19) -N (5)   | 1.376 (4) |
| C (19) -C (20)  | 1.416 (4) |
| C (20) -C (21)  | 1.385 (4) |
| C (20) -H (20)  | 0.9500    |
| C (21) -H (21)  | 0.9500    |
| C (22) -N (5)   | 1.466 (5) |
| C (22) -C (23)  | 1.505 (6) |
| C (22) -H (22A) | 0.9900    |
| C (22) -H (22B) | 0.9900    |
| C (23) -H (23A) | 0.9800    |
| C (23) -H (23B) | 0.9800    |
| C (23) -H (23C) | 0.9800    |
| C (24) -N (5)   | 1.454 (4) |
| C (24) -C (25)  | 1.523 (5) |
| C (24) -H (24A) | 0.9900    |
| C (24) -H (24B) | 0.9900    |
| C (25) -H (25A) | 0.9800    |
| C (25) -H (25B) | 0.9800    |
| C (25) -H (25C) | 0.9800    |
| C (26) -O (1)   | 1.277 (3) |
| C (26) -C (27)  | 1.388 (4) |

|                     |             |
|---------------------|-------------|
| C (26) -C (29)      | 1.521 (4)   |
| C (27) -C (28)      | 1.408 (4)   |
| C (27) -H (27)      | 0.9500      |
| C (28) -O (2)       | 1.270 (3)   |
| C (28) -C (30)      | 1.499 (4)   |
| C (29) -H (29A)     | 0.9800      |
| C (29) -H (29B)     | 0.9800      |
| C (29) -H (29C)     | 0.9800      |
| C (30) -H (30A)     | 0.9800      |
| C (30) -H (30B)     | 0.9800      |
| C (30) -H (30C)     | 0.9800      |
| C (31) -N (4)       | 1.144 (4)   |
| C (31) -C (32)      | 1.457 (4)   |
| C (32) -H (32A)     | 0.9800      |
| C (32) -H (32B)     | 0.9800      |
| C (32) -H (32C)     | 0.9800      |
| C (33) -N (6)       | 1.451 (5)   |
| C (33) -H (33A)     | 0.9800      |
| C (33) -H (33B)     | 0.9800      |
| C (33) -H (33C)     | 0.9800      |
| C (34) -N (6)       | 1.450 (4)   |
| C (34) -H (34A)     | 0.9800      |
| C (34) -H (34B)     | 0.9800      |
| C (34) -H (34C)     | 0.9800      |
| C (35) -O (3)       | 1.227 (4)   |
| C (35) -N (6)       | 1.329 (4)   |
| C (35) -H (35)      | 0.9500      |
| N (1) -Ru (1)       | 2.060 (2)   |
| N (2) -Ru (1)       | 1.946 (2)   |
| N (3) -Ru (1)       | 2.064 (2)   |
| N (4) -Ru (1)       | 2.007 (2)   |
| O (1) -Ru (1)       | 2.0649 (18) |
| O (2) -Ru (1)       | 2.0795 (18) |
| F (1) -P (1)        | 1.585 (3)   |
| F (2) -P (1)        | 1.589 (3)   |
| F (3) -P (1)        | 1.566 (3)   |
| F (4) -P (1)        | 1.573 (3)   |
| F (5) -P (1)        | 1.593 (2)   |
| F (6) -P (1)        | 1.599 (2)   |
|                     |             |
| N (1) -C (1) -C (2) | 122.4 (2)   |
| N (1) -C (1) -H (1) | 118.8       |
| C (2) -C (1) -H (1) | 118.8       |
| C (3) -C (2) -C (1) | 118.9 (3)   |
| C (3) -C (2) -H (2) | 120.5       |
| C (1) -C (2) -H (2) | 120.5       |
| C (2) -C (3) -C (4) | 119.4 (3)   |
| C (2) -C (3) -H (3) | 120.3       |
| C (4) -C (3) -H (3) | 120.3       |
| C (5) -C (4) -C (3) | 119.1 (2)   |
| C (5) -C (4) -H (4) | 120.4       |
| C (3) -C (4) -H (4) | 120.4       |
| N (1) -C (5) -C (4) | 121.5 (2)   |
| N (1) -C (5) -C (6) | 115.0 (2)   |
| C (4) -C (5) -C (6) | 123.5 (2)   |
| N (2) -C (6) -C (7) | 119.8 (2)   |
| N (2) -C (6) -C (5) | 112.4 (2)   |
| C (7) -C (6) -C (5) | 127.7 (2)   |
| C (6) -C (7) -C (8) | 120.3 (2)   |
| C (6) -C (7) -H (7) | 119.9       |
| C (8) -C (7) -H (7) | 119.9       |

|                     |          |
|---------------------|----------|
| C(9)-C(8)-C(7)      | 117.6(2) |
| C(9)-C(8)-C(16)     | 120.7(2) |
| C(7)-C(8)-C(16)     | 121.7(2) |
| C(10)-C(9)-C(8)     | 120.3(3) |
| C(10)-C(9)-H(9)     | 119.9    |
| C(8)-C(9)-H(9)      | 119.9    |
| N(2)-C(10)-C(9)     | 120.3(2) |
| N(2)-C(10)-C(11)    | 112.5(2) |
| C(9)-C(10)-C(11)    | 127.2(2) |
| N(3)-C(11)-C(12)    | 121.4(2) |
| N(3)-C(11)-C(10)    | 114.9(2) |
| C(12)-C(11)-C(10)   | 123.6(2) |
| C(13)-C(12)-C(11)   | 119.3(3) |
| C(13)-C(12)-H(12)   | 120.4    |
| C(11)-C(12)-H(12)   | 120.4    |
| C(12)-C(13)-C(14)   | 119.5(3) |
| C(12)-C(13)-H(13)   | 120.3    |
| C(14)-C(13)-H(13)   | 120.3    |
| C(13)-C(14)-C(15)   | 119.1(3) |
| C(13)-C(14)-H(14)   | 120.5    |
| C(15)-C(14)-H(14)   | 120.5    |
| N(3)-C(15)-C(14)    | 122.2(3) |
| N(3)-C(15)-H(15)    | 118.9    |
| C(14)-C(15)-H(15)   | 118.9    |
| C(17)-C(16)-C(21)   | 116.5(2) |
| C(17)-C(16)-C(8)    | 121.4(3) |
| C(21)-C(16)-C(8)    | 121.9(2) |
| C(18)-C(17)-C(16)   | 122.1(3) |
| C(18)-C(17)-H(17)   | 119.0    |
| C(16)-C(17)-H(17)   | 119.0    |
| C(17)-C(18)-C(19)   | 121.5(3) |
| C(17)-C(18)-H(18)   | 119.3    |
| C(19)-C(18)-H(18)   | 119.3    |
| N(5)-C(19)-C(18)    | 121.8(3) |
| N(5)-C(19)-C(20)    | 121.7(3) |
| C(18)-C(19)-C(20)   | 116.5(3) |
| C(21)-C(20)-C(19)   | 121.0(3) |
| C(21)-C(20)-H(20)   | 119.5    |
| C(19)-C(20)-H(20)   | 119.5    |
| C(20)-C(21)-C(16)   | 122.3(3) |
| C(20)-C(21)-H(21)   | 118.9    |
| C(16)-C(21)-H(21)   | 118.9    |
| N(5)-C(22)-C(23)    | 113.2(3) |
| N(5)-C(22)-H(22A)   | 108.9    |
| C(23)-C(22)-H(22A)  | 108.9    |
| N(5)-C(22)-H(22B)   | 108.9    |
| C(23)-C(22)-H(22B)  | 108.9    |
| H(22A)-C(22)-H(22B) | 107.8    |
| C(22)-C(23)-H(23A)  | 109.5    |
| C(22)-C(23)-H(23B)  | 109.5    |
| H(23A)-C(23)-H(23B) | 109.5    |
| C(22)-C(23)-H(23C)  | 109.5    |
| H(23A)-C(23)-H(23C) | 109.5    |
| H(23B)-C(23)-H(23C) | 109.5    |
| N(5)-C(24)-C(25)    | 112.6(3) |
| N(5)-C(24)-H(24A)   | 109.1    |
| C(25)-C(24)-H(24A)  | 109.1    |
| N(5)-C(24)-H(24B)   | 109.1    |
| C(25)-C(24)-H(24B)  | 109.1    |
| H(24A)-C(24)-H(24B) | 107.8    |
| C(24)-C(25)-H(25A)  | 109.5    |

|                          |             |
|--------------------------|-------------|
| C (24) -C (25) -H (25B)  | 109.5       |
| H (25A) -C (25) -H (25B) | 109.5       |
| C (24) -C (25) -H (25C)  | 109.5       |
| H (25A) -C (25) -H (25C) | 109.5       |
| H (25B) -C (25) -H (25C) | 109.5       |
| O (1) -C (26) -C (27)    | 127.5 (3)   |
| O (1) -C (26) -C (29)    | 114.9 (2)   |
| C (27) -C (26) -C (29)   | 117.6 (2)   |
| C (26) -C (27) -C (28)   | 127.4 (3)   |
| C (26) -C (27) -H (27)   | 116.3       |
| C (28) -C (27) -H (27)   | 116.3       |
| O (2) -C (28) -C (27)    | 125.1 (2)   |
| O (2) -C (28) -C (30)    | 115.8 (2)   |
| C (27) -C (28) -C (30)   | 119.1 (3)   |
| C (26) -C (29) -H (29A)  | 109.5       |
| C (26) -C (29) -H (29B)  | 109.5       |
| H (29A) -C (29) -H (29B) | 109.5       |
| C (26) -C (29) -H (29C)  | 109.5       |
| H (29A) -C (29) -H (29C) | 109.5       |
| H (29B) -C (29) -H (29C) | 109.5       |
| C (28) -C (30) -H (30A)  | 109.5       |
| C (28) -C (30) -H (30B)  | 109.5       |
| H (30A) -C (30) -H (30B) | 109.5       |
| C (28) -C (30) -H (30C)  | 109.5       |
| H (30A) -C (30) -H (30C) | 109.5       |
| H (30B) -C (30) -H (30C) | 109.5       |
| N (4) -C (31) -C (32)    | 179.0 (3)   |
| C (31) -C (32) -H (32A)  | 109.5       |
| C (31) -C (32) -H (32B)  | 109.5       |
| H (32A) -C (32) -H (32B) | 109.5       |
| C (31) -C (32) -H (32C)  | 109.5       |
| H (32A) -C (32) -H (32C) | 109.5       |
| H (32B) -C (32) -H (32C) | 109.5       |
| N (6) -C (33) -H (33A)   | 109.5       |
| N (6) -C (33) -H (33B)   | 109.5       |
| H (33A) -C (33) -H (33B) | 109.5       |
| N (6) -C (33) -H (33C)   | 109.5       |
| H (33A) -C (33) -H (33C) | 109.5       |
| H (33B) -C (33) -H (33C) | 109.5       |
| N (6) -C (34) -H (34A)   | 109.5       |
| N (6) -C (34) -H (34B)   | 109.5       |
| H (34A) -C (34) -H (34B) | 109.5       |
| N (6) -C (34) -H (34C)   | 109.5       |
| H (34A) -C (34) -H (34C) | 109.5       |
| H (34B) -C (34) -H (34C) | 109.5       |
| O (3) -C (35) -N (6)     | 125.0 (3)   |
| O (3) -C (35) -H (35)    | 117.5       |
| N (6) -C (35) -H (35)    | 117.5       |
| C (1) -N (1) -C (5)      | 118.6 (2)   |
| C (1) -N (1) -Ru (1)     | 128.18 (18) |
| C (5) -N (1) -Ru (1)     | 113.24 (17) |
| C (10) -N (2) -C (6)     | 121.6 (2)   |
| C (10) -N (2) -Ru (1)    | 119.26 (18) |
| C (6) -N (2) -Ru (1)     | 119.10 (18) |
| C (15) -N (3) -C (11)    | 118.6 (2)   |
| C (15) -N (3) -Ru (1)    | 128.10 (19) |
| C (11) -N (3) -Ru (1)    | 113.25 (17) |
| C (19) -N (5) -C (24)    | 121.3 (3)   |
| C (19) -N (5) -C (22)    | 120.9 (3)   |
| C (24) -N (5) -C (22)    | 116.3 (3)   |
| C (31) -N (4) -Ru (1)    | 172.9 (2)   |

|                       |             |
|-----------------------|-------------|
| C (35) -N (6) -C (34) | 120.9 (3)   |
| C (35) -N (6) -C (33) | 121.4 (3)   |
| C (34) -N (6) -C (33) | 117.5 (3)   |
| C (26) -O (1) -Ru (1) | 123.82 (17) |
| C (28) -O (2) -Ru (1) | 125.40 (17) |
| F (3) -P (1) -F (4)   | 91.3 (2)    |
| F (3) -P (1) -F (1)   | 178.87 (15) |
| F (4) -P (1) -F (1)   | 89.20 (19)  |
| F (3) -P (1) -F (2)   | 90.7 (2)    |
| F (4) -P (1) -F (2)   | 178.0 (2)   |
| F (1) -P (1) -F (2)   | 88.82 (19)  |
| F (3) -P (1) -F (5)   | 91.35 (19)  |
| F (4) -P (1) -F (5)   | 88.76 (16)  |
| F (1) -P (1) -F (5)   | 89.68 (15)  |
| F (2) -P (1) -F (5)   | 91.15 (15)  |
| F (3) -P (1) -F (6)   | 89.72 (17)  |
| F (4) -P (1) -F (6)   | 91.97 (16)  |
| F (1) -P (1) -F (6)   | 89.24 (14)  |
| F (2) -P (1) -F (6)   | 88.09 (14)  |
| F (5) -P (1) -F (6)   | 178.69 (16) |
| N (2) -Ru (1) -N (4)  | 89.63 (9)   |
| N (2) -Ru (1) -N (1)  | 80.09 (9)   |
| N (4) -Ru (1) -N (1)  | 92.45 (9)   |
| N (2) -Ru (1) -N (3)  | 80.00 (9)   |
| N (4) -Ru (1) -N (3)  | 86.48 (9)   |
| N (1) -Ru (1) -N (3)  | 160.08 (9)  |
| N (2) -Ru (1) -O (1)  | 89.41 (8)   |
| N (4) -Ru (1) -O (1)  | 178.68 (8)  |
| N (1) -Ru (1) -O (1)  | 88.27 (8)   |
| N (3) -Ru (1) -O (1)  | 92.47 (8)   |
| N (2) -Ru (1) -O (2)  | 179.79 (8)  |
| N (4) -Ru (1) -O (2)  | 90.22 (8)   |
| N (1) -Ru (1) -O (2)  | 100.05 (8)  |
| N (3) -Ru (1) -O (2)  | 99.85 (8)   |
| O (1) -Ru (1) -O (2)  | 90.75 (7)   |

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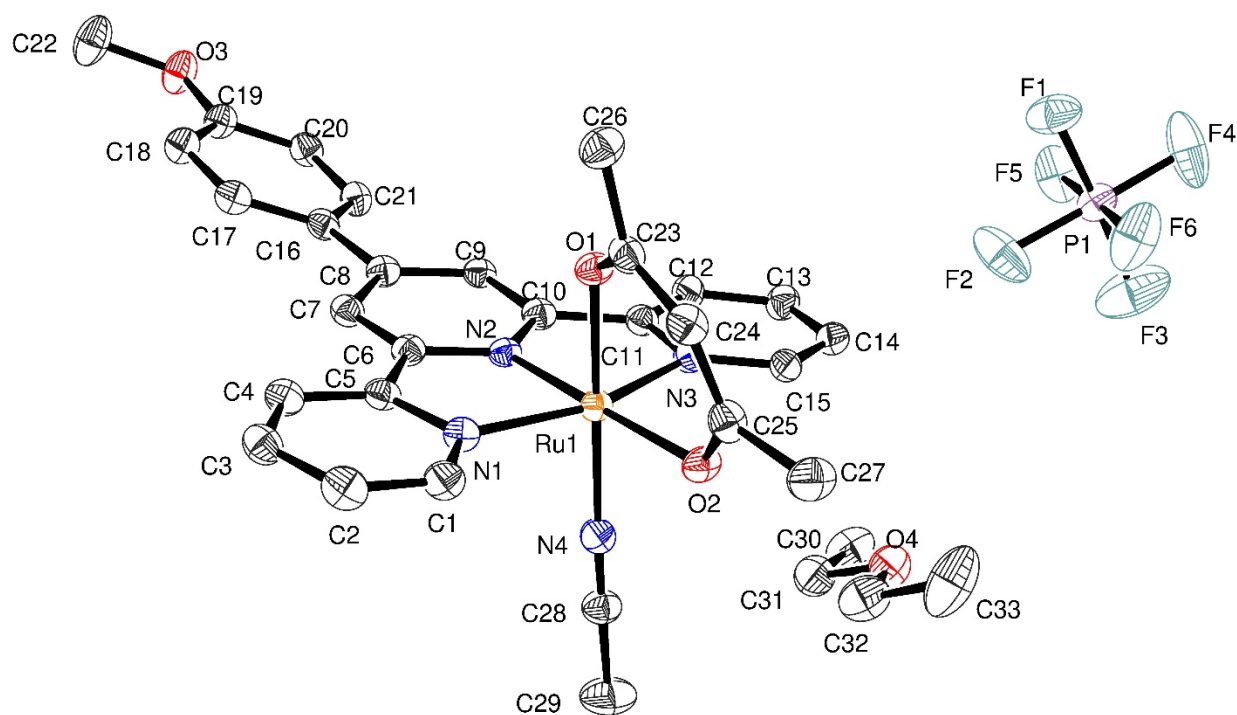
Symmetry transformations used to generate equivalent atoms:

**Table S4.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Ru}(\text{Et}_2\text{N-phtpy})(\text{acac})(\text{MeCN})](\text{PF}_6)$   
The anisotropic displacement factor exponent takes the form:  
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

|        | U11     | U22     | U33     | U23     | U13     | U12     |
|--------|---------|---------|---------|---------|---------|---------|
| C (1)  | 19 (1)  | 17 (1)  | 20 (1)  | 1 (1)   | -4 (1)  | 1 (1)   |
| C (2)  | 19 (1)  | 24 (1)  | 23 (1)  | -3 (1)  | -7 (1)  | 3 (1)   |
| C (3)  | 16 (1)  | 24 (1)  | 27 (1)  | -5 (1)  | -4 (1)  | -3 (1)  |
| C (4)  | 18 (1)  | 14 (1)  | 21 (1)  | 1 (1)   | -1 (1)  | 0 (1)   |
| C (5)  | 17 (1)  | 15 (1)  | 18 (1)  | -2 (1)  | -1 (1)  | 1 (1)   |
| C (6)  | 15 (1)  | 18 (1)  | 17 (1)  | -3 (1)  | 0 (1)   | -1 (1)  |
| C (7)  | 14 (1)  | 19 (1)  | 21 (1)  | -1 (1)  | -2 (1)  | 1 (1)   |
| C (8)  | 18 (1)  | 17 (1)  | 18 (1)  | -1 (1)  | -2 (1)  | 1 (1)   |
| C (9)  | 16 (1)  | 19 (1)  | 18 (1)  | -2 (1)  | -2 (1)  | 2 (1)   |
| C (10) | 15 (1)  | 16 (1)  | 18 (1)  | -3 (1)  | -2 (1)  | 1 (1)   |
| C (11) | 17 (1)  | 17 (1)  | 16 (1)  | -2 (1)  | 0 (1)   | -1 (1)  |
| C (12) | 20 (1)  | 21 (1)  | 17 (1)  | -2 (1)  | -2 (1)  | 0 (1)   |
| C (13) | 20 (1)  | 29 (2)  | 22 (1)  | -5 (1)  | -3 (1)  | -6 (1)  |
| C (14) | 20 (1)  | 23 (1)  | 26 (2)  | -3 (1)  | 2 (1)   | -6 (1)  |
| C (15) | 18 (1)  | 20 (1)  | 21 (1)  | -2 (1)  | 0 (1)   | -3 (1)  |
| C (16) | 17 (1)  | 18 (1)  | 19 (1)  | 2 (1)   | -1 (1)  | 1 (1)   |
| C (17) | 22 (1)  | 23 (1)  | 20 (1)  | 2 (1)   | -3 (1)  | -3 (1)  |
| C (18) | 29 (2)  | 20 (1)  | 27 (2)  | 3 (1)   | -4 (1)  | -3 (1)  |
| C (19) | 28 (2)  | 25 (1)  | 21 (1)  | 6 (1)   | -3 (1)  | -1 (1)  |
| C (20) | 31 (2)  | 27 (2)  | 22 (1)  | 2 (1)   | -6 (1)  | -4 (1)  |
| C (21) | 28 (2)  | 23 (1)  | 21 (1)  | 1 (1)   | -2 (1)  | -7 (1)  |
| C (22) | 61 (3)  | 31 (2)  | 39 (2)  | 16 (2)  | -20 (2) | -14 (2) |
| C (23) | 101 (4) | 26 (2)  | 41 (2)  | 3 (2)   | -9 (2)  | 1 (2)   |
| C (24) | 39 (2)  | 32 (2)  | 24 (2)  | 10 (1)  | -7 (1)  | 1 (1)   |
| C (25) | 55 (3)  | 47 (2)  | 32 (2)  | 0 (2)   | -1 (2)  | 4 (2)   |
| C (26) | 13 (1)  | 21 (1)  | 17 (1)  | -2 (1)  | -5 (1)  | -2 (1)  |
| C (27) | 26 (2)  | 23 (1)  | 15 (1)  | 0 (1)   | 0 (1)   | -3 (1)  |
| C (28) | 20 (1)  | 21 (1)  | 18 (1)  | 1 (1)   | -5 (1)  | -2 (1)  |
| C (29) | 25 (2)  | 20 (1)  | 21 (1)  | -4 (1)  | 0 (1)   | 1 (1)   |
| C (30) | 39 (2)  | 24 (2)  | 20 (1)  | 4 (1)   | -3 (1)  | 1 (1)   |
| C (31) | 22 (1)  | 15 (1)  | 27 (1)  | -1 (1)  | 0 (1)   | -4 (1)  |
| C (32) | 36 (2)  | 30 (2)  | 43 (2)  | -16 (2) | 8 (2)   | -7 (1)  |
| C (33) | 91 (4)  | 42 (2)  | 39 (2)  | -11 (2) | 20 (2)  | -12 (2) |
| C (34) | 49 (2)  | 46 (2)  | 24 (2)  | 5 (2)   | 2 (2)   | 3 (2)   |
| C (35) | 35 (2)  | 35 (2)  | 22 (2)  | 1 (1)   | -8 (1)  | -10 (1) |
| N (1)  | 14 (1)  | 18 (1)  | 18 (1)  | -3 (1)  | -2 (1)  | -1 (1)  |
| N (2)  | 15 (1)  | 13 (1)  | 15 (1)  | 1 (1)   | -1 (1)  | 0 (1)   |
| N (3)  | 17 (1)  | 16 (1)  | 17 (1)  | 0 (1)   | 1 (1)   | -2 (1)  |
| N (5)  | 44 (2)  | 28 (1)  | 23 (1)  | 10 (1)  | -6 (1)  | -4 (1)  |
| N (4)  | 16 (1)  | 17 (1)  | 21 (1)  | 3 (1)   | -1 (1)  | -4 (1)  |
| N (6)  | 41 (2)  | 37 (2)  | 23 (1)  | -1 (1)  | 0 (1)   | -6 (1)  |
| O (1)  | 18 (1)  | 16 (1)  | 16 (1)  | 2 (1)   | -2 (1)  | 0 (1)   |
| O (2)  | 21 (1)  | 14 (1)  | 16 (1)  | 4 (1)   | -2 (1)  | -1 (1)  |
| O (3)  | 54 (2)  | 33 (1)  | 24 (1)  | -1 (1)  | -10 (1) | -11 (1) |
| F (1)  | 71 (2)  | 56 (2)  | 78 (2)  | 19 (1)  | -37 (2) | -23 (1) |
| F (2)  | 62 (2)  | 44 (1)  | 121 (3) | -23 (2) | 51 (2)  | -16 (1) |
| F (3)  | 103 (3) | 95 (2)  | 157 (3) | 92 (2)  | -94 (3) | -60 (2) |
| F (4)  | 78 (2)  | 110 (3) | 72 (2)  | -31 (2) | 44 (2)  | -40 (2) |
| F (5)  | 57 (2)  | 31 (1)  | 108 (2) | -4 (1)  | 7 (2)   | -16 (1) |
| F (6)  | 72 (2)  | 44 (1)  | 52 (1)  | -8 (1)  | -6 (1)  | -19 (1) |
| P (1)  | 24 (1)  | 27 (1)  | 40 (1)  | 6 (1)   | 2 (1)   | -4 (1)  |
| Ru (1) | 14 (1)  | 13 (1)  | 14 (1)  | 1 (1)   | -1 (1)  | -1 (1)  |



**Figure S4** Asymmetric unit for [Ru(MeO-phtpy)(acac)(MeCN)](PF<sub>6</sub>)



**Table S5.** Crystal data and structure refinement for [Ru(MeO-phtpy)(acac)(MeCN)](PF<sub>6</sub>)

|                             |                                                                                                                            |
|-----------------------------|----------------------------------------------------------------------------------------------------------------------------|
| Identification code         | VM-PLV-26plate                                                                                                             |
| Empirical formula           | C <sub>29</sub> H <sub>27</sub> N <sub>4</sub> O <sub>3</sub> Ru, F <sub>6</sub> P, 0.5 (C <sub>4</sub> H <sub>10</sub> O) |
| Formula weight              | 762.64                                                                                                                     |
| Temperature                 | 100 (2) K                                                                                                                  |
| Wavelength                  | 1.54184 Å                                                                                                                  |
| Crystal system, space group | Triclinic, P -1                                                                                                            |

|                                   |                                             |         |
|-----------------------------------|---------------------------------------------|---------|
| Unit cell dimensions              | a = 11.0282(3) Å                            | alpha = |
| 82.448(2) deg.                    | b = 11.3656(3) Å                            | beta =  |
| 76.204(2) deg.                    | c = 13.5530(3) Å                            | gamma = |
| 75.467(2) deg.                    |                                             |         |
| Volume                            | 1592.33(7) Å <sup>3</sup>                   |         |
| Z, Calculated density             | 2, 1.591 Mg/m <sup>3</sup>                  |         |
| Absorption coefficient            | 5.141 mm <sup>-1</sup>                      |         |
| F(000)                            | 774                                         |         |
| Crystal size                      | 0.24 x 0.18 x 0.04 mm                       |         |
| Theta range for data collection   | 3.368 to 76.596 deg.                        |         |
| Limiting indices                  | -13<=h<=13, -7<=k<=13, -16<=l<=16           |         |
| Reflections collected / unique    | 20459 / 6267 [R(int) = 0.0590]              |         |
| Completeness to theta = 67.684    | 99.4 %                                      |         |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup> |         |
| Data / restraints / parameters    | 6267 / 34 / 449                             |         |
| Goodness-of-fit on F <sup>2</sup> | 1.085                                       |         |
| Final R indices [I>2sigma(I)]     | R1 = 0.0473, wR2 = 0.1253                   |         |
| R indices (all data)              | R1 = 0.0520, wR2 = 0.1281                   |         |
| Largest diff. peak and hole       | 1.106 and -1.267 e.Å <sup>-3</sup>          |         |

**Table S6.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Ru}(\text{MeO-phtpy})(\text{acac})(\text{MeCN})](\text{PF}_6)$

U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

|        | x        | y         | z         | U (eq) |
|--------|----------|-----------|-----------|--------|
| C (1)  | 484 (4)  | 2906 (3)  | 7624 (3)  | 27 (1) |
| C (2)  | -164 (4) | 2144 (3)  | 7353 (3)  | 30 (1) |
| C (3)  | 435 (4)  | 1440 (3)  | 6538 (3)  | 28 (1) |
| C (4)  | 1668 (3) | 1513 (3)  | 6024 (3)  | 25 (1) |
| C (5)  | 2272 (3) | 2281 (3)  | 6336 (3)  | 22 (1) |
| C (6)  | 3580 (3) | 2413 (3)  | 5847 (3)  | 21 (1) |
| C (7)  | 4408 (3) | 1796 (3)  | 5050 (3)  | 23 (1) |
| C (8)  | 5610 (3) | 2066 (3)  | 4632 (3)  | 22 (1) |
| C (9)  | 5924 (3) | 2980 (3)  | 5063 (3)  | 21 (1) |
| C (10) | 5083 (3) | 3554 (3)  | 5881 (3)  | 23 (1) |
| C (11) | 5274 (3) | 4534 (3)  | 6406 (3)  | 22 (1) |
| C (12) | 6401 (4) | 4932 (3)  | 6196 (3)  | 25 (1) |
| C (13) | 6485 (4) | 5849 (3)  | 6748 (3)  | 27 (1) |
| C (14) | 5441 (4) | 6352 (3)  | 7474 (3)  | 27 (1) |
| C (15) | 4332 (4) | 5937 (3)  | 7641 (3)  | 24 (1) |
| C (16) | 6469 (3) | 1495 (3)  | 3721 (3)  | 22 (1) |
| C (17) | 6022 (3) | 876 (3)   | 3109 (3)  | 25 (1) |
| C (18) | 6760 (4) | 459 (3)   | 2190 (3)  | 27 (1) |
| C (19) | 7997 (4) | 649 (3)   | 1856 (3)  | 25 (1) |
| C (20) | 8484 (4) | 1234 (3)  | 2474 (3)  | 26 (1) |
| C (21) | 7738 (3) | 1640 (3)  | 3381 (3)  | 24 (1) |
| C (22) | 8316 (4) | -267 (5)  | 309 (4)   | 43 (1) |
| C (23) | 779 (3)  | 6008 (3)  | 6442 (3)  | 24 (1) |
| C (24) | 52 (4)   | 6310 (3)  | 7406 (3)  | 27 (1) |
| C (25) | 423 (4)  | 5971 (3)  | 8349 (3)  | 27 (1) |
| C (26) | 251 (4)  | 6594 (4)  | 5522 (3)  | 31 (1) |
| C (27) | -398 (4) | 6593 (4)  | 9282 (3)  | 36 (1) |
| C (28) | 3888 (4) | 2483 (3)  | 9070 (3)  | 27 (1) |
| C (29) | 4441 (5) | 1738 (4)  | 9886 (4)  | 47 (1) |
| C (30) | 7216 (7) | 4578 (9)  | 9420 (7)  | 44 (2) |
| C (31) | 5902 (8) | 4336 (6)  | 9616 (7)  | 37 (2) |
| O (4)  | 4993 (4) | 5419 (5)  | 9957 (5)  | 36 (1) |
| C (32) | 3703 (7) | 5269 (8)  | 10224 (8) | 44 (2) |
| C (33) | 2839 (9) | 6470 (11) | 10523 (9) | 65 (3) |
| N (1)  | 1668 (3) | 2986 (2)  | 7137 (2)  | 22 (1) |
| N (2)  | 3937 (3) | 3268 (2)  | 6259 (2)  | 19 (1) |
| N (3)  | 4227 (3) | 5042 (2)  | 7126 (2)  | 22 (1) |
| N (4)  | 3460 (3) | 3075 (3)  | 8443 (2)  | 24 (1) |
| O (1)  | 1901 (2) | 5304 (2)  | 6240 (2)  | 23 (1) |
| O (2)  | 1421 (2) | 5177 (2)  | 8492 (2)  | 24 (1) |
| O (3)  | 8794 (3) | 304 (3)   | 960 (2)   | 34 (1) |
| F (1)  | 6738 (3) | 10070 (3) | 6218 (2)  | 50 (1) |
| F (2)  | 7117 (3) | 8428 (2)  | 7280 (3)  | 62 (1) |
| F (3)  | 7889 (4) | 9446 (4)  | 8213 (3)  | 84 (1) |
| F (4)  | 7480 (3) | 11147 (3) | 7125 (3)  | 69 (1) |
| F (5)  | 8706 (2) | 9380 (2)  | 6552 (3)  | 51 (1) |
| F (6)  | 5893 (3) | 10166 (3) | 7906 (3)  | 63 (1) |
| P (1)  | 7293 (1) | 9805 (1)  | 7218 (1)  | 31 (1) |
| Ru (1) | 2722 (1) | 4175 (1)  | 7342 (1)  | 20 (1) |

**Table S7.** Bond lengths [Å] and angles [deg] for [Ru(MeO-phtpy)(acac)(MeCN)](PF<sub>6</sub>)

---

|                 |           |
|-----------------|-----------|
| C (1) -N (1)    | 1.335 (5) |
| C (1) -C (2)    | 1.383 (5) |
| C (1) -H (1)    | 0.9500    |
| C (2) -C (3)    | 1.384 (6) |
| C (2) -H (2)    | 0.9500    |
| C (3) -C (4)    | 1.390 (5) |
| C (3) -H (3)    | 0.9500    |
| C (4) -C (5)    | 1.382 (5) |
| C (4) -H (4)    | 0.9500    |
| C (5) -N (1)    | 1.371 (5) |
| C (5) -C (6)    | 1.473 (5) |
| C (6) -N (2)    | 1.361 (4) |
| C (6) -C (7)    | 1.378 (5) |
| C (7) -C (8)    | 1.405 (5) |
| C (7) -H (7)    | 0.9500    |
| C (8) -C (9)    | 1.406 (5) |
| C (8) -C (16)   | 1.480 (5) |
| C (9) -C (10)   | 1.381 (5) |
| C (9) -H (9)    | 0.9500    |
| C (10) -N (2)   | 1.349 (5) |
| C (10) -C (11)  | 1.478 (5) |
| C (11) -N (3)   | 1.377 (5) |
| C (11) -C (12)  | 1.382 (5) |
| C (12) -C (13)  | 1.392 (5) |
| C (12) -H (12)  | 0.9500    |
| C (13) -C (14)  | 1.378 (6) |
| C (13) -H (13)  | 0.9500    |
| C (14) -C (15)  | 1.378 (5) |
| C (14) -H (14)  | 0.9500    |
| C (15) -N (3)   | 1.349 (4) |
| C (15) -H (15)  | 0.9500    |
| C (16) -C (17)  | 1.396 (5) |
| C (16) -C (21)  | 1.409 (5) |
| C (17) -C (18)  | 1.384 (5) |
| C (17) -H (17)  | 0.9500    |
| C (18) -C (19)  | 1.393 (5) |
| C (18) -H (18)  | 0.9500    |
| C (19) -O (3)   | 1.359 (4) |
| C (19) -C (20)  | 1.405 (5) |
| C (20) -C (21)  | 1.369 (5) |
| C (20) -H (20)  | 0.9500    |
| C (21) -H (21)  | 0.9500    |
| C (22) -O (3)   | 1.421 (5) |
| C (22) -H (22A) | 0.9800    |
| C (22) -H (22B) | 0.9800    |
| C (22) -H (22C) | 0.9800    |
| C (23) -O (1)   | 1.282 (4) |
| C (23) -C (24)  | 1.395 (5) |
| C (23) -C (26)  | 1.507 (5) |
| C (24) -C (25)  | 1.410 (5) |
| C (24) -H (24)  | 0.9500    |
| C (25) -O (2)   | 1.273 (5) |
| C (25) -C (27)  | 1.512 (5) |
| C (26) -H (26A) | 0.9800    |
| C (26) -H (26B) | 0.9800    |
| C (26) -H (26C) | 0.9800    |

|                      |           |
|----------------------|-----------|
| C (27) -H (27A)      | 0.9800    |
| C (27) -H (27B)      | 0.9800    |
| C (27) -H (27C)      | 0.9800    |
| C (28) -N (4)        | 1.132 (5) |
| C (28) -C (29)       | 1.459 (6) |
| C (29) -H (29A)      | 0.9800    |
| C (29) -H (29B)      | 0.9800    |
| C (29) -H (29C)      | 0.9800    |
| C (30) -C (31)       | 1.498 (9) |
| C (30) -H (30A)      | 0.9800    |
| C (30) -H (30B)      | 0.9800    |
| C (30) -H (30C)      | 0.9800    |
| C (31) -O (4)        | 1.429 (7) |
| C (31) -H (31A)      | 0.9900    |
| C (31) -H (31B)      | 0.9900    |
| O (4) -C (32)        | 1.429 (7) |
| C (32) -C (33)       | 1.498 (9) |
| C (32) -H (32A)      | 0.9900    |
| C (32) -H (32B)      | 0.9900    |
| C (33) -H (33A)      | 0.9800    |
| C (33) -H (33B)      | 0.9800    |
| C (33) -H (33C)      | 0.9800    |
| N (1) -Ru (1)        | 2.072 (3) |
| N (2) -Ru (1)        | 1.943 (3) |
| N (3) -Ru (1)        | 2.079 (3) |
| N (4) -Ru (1)        | 2.008 (3) |
| O (1) -Ru (1)        | 2.062 (2) |
| O (2) -Ru (1)        | 2.089 (2) |
| F (1) -P (1)         | 1.579 (3) |
| F (2) -P (1)         | 1.613 (3) |
| F (3) -P (1)         | 1.601 (3) |
| F (4) -P (1)         | 1.575 (3) |
| F (5) -P (1)         | 1.594 (3) |
| F (6) -P (1)         | 1.587 (3) |
|                      |           |
| N (1) -C (1) -C (2)  | 122.8 (3) |
| N (1) -C (1) -H (1)  | 118.6     |
| C (2) -C (1) -H (1)  | 118.6     |
| C (1) -C (2) -C (3)  | 118.8 (4) |
| C (1) -C (2) -H (2)  | 120.6     |
| C (3) -C (2) -H (2)  | 120.6     |
| C (2) -C (3) -C (4)  | 119.1 (3) |
| C (2) -C (3) -H (3)  | 120.5     |
| C (4) -C (3) -H (3)  | 120.5     |
| C (5) -C (4) -C (3)  | 119.5 (3) |
| C (5) -C (4) -H (4)  | 120.2     |
| C (3) -C (4) -H (4)  | 120.2     |
| N (1) -C (5) -C (4)  | 121.1 (3) |
| N (1) -C (5) -C (6)  | 115.3 (3) |
| C (4) -C (5) -C (6)  | 123.5 (3) |
| N (2) -C (6) -C (7)  | 120.1 (3) |
| N (2) -C (6) -C (5)  | 112.5 (3) |
| C (7) -C (6) -C (5)  | 127.4 (3) |
| C (6) -C (7) -C (8)  | 120.7 (3) |
| C (6) -C (7) -H (7)  | 119.6     |
| C (8) -C (7) -H (7)  | 119.6     |
| C (7) -C (8) -C (9)  | 117.2 (3) |
| C (7) -C (8) -C (16) | 121.8 (3) |
| C (9) -C (8) -C (16) | 120.9 (3) |
| C (10) -C (9) -C (8) | 120.4 (3) |
| C (10) -C (9) -H (9) | 119.8     |

|                     |          |
|---------------------|----------|
| C(8)-C(9)-H(9)      | 119.8    |
| N(2)-C(10)-C(9)     | 120.5(3) |
| N(2)-C(10)-C(11)    | 112.9(3) |
| C(9)-C(10)-C(11)    | 126.6(3) |
| N(3)-C(11)-C(12)    | 121.6(3) |
| N(3)-C(11)-C(10)    | 114.7(3) |
| C(12)-C(11)-C(10)   | 123.6(3) |
| C(11)-C(12)-C(13)   | 118.9(3) |
| C(11)-C(12)-H(12)   | 120.5    |
| C(13)-C(12)-H(12)   | 120.5    |
| C(14)-C(13)-C(12)   | 119.5(3) |
| C(14)-C(13)-H(13)   | 120.2    |
| C(12)-C(13)-H(13)   | 120.2    |
| C(13)-C(14)-C(15)   | 119.3(3) |
| C(13)-C(14)-H(14)   | 120.4    |
| C(15)-C(14)-H(14)   | 120.4    |
| N(3)-C(15)-C(14)    | 122.5(3) |
| N(3)-C(15)-H(15)    | 118.7    |
| C(14)-C(15)-H(15)   | 118.7    |
| C(17)-C(16)-C(21)   | 116.9(3) |
| C(17)-C(16)-C(8)    | 121.2(3) |
| C(21)-C(16)-C(8)    | 121.7(3) |
| C(18)-C(17)-C(16)   | 122.3(3) |
| C(18)-C(17)-H(17)   | 118.9    |
| C(16)-C(17)-H(17)   | 118.9    |
| C(17)-C(18)-C(19)   | 119.6(3) |
| C(17)-C(18)-H(18)   | 120.2    |
| C(19)-C(18)-H(18)   | 120.2    |
| O(3)-C(19)-C(18)    | 124.7(3) |
| O(3)-C(19)-C(20)    | 116.2(3) |
| C(18)-C(19)-C(20)   | 119.2(3) |
| C(21)-C(20)-C(19)   | 120.3(3) |
| C(21)-C(20)-H(20)   | 119.9    |
| C(19)-C(20)-H(20)   | 119.9    |
| C(20)-C(21)-C(16)   | 121.7(3) |
| C(20)-C(21)-H(21)   | 119.2    |
| C(16)-C(21)-H(21)   | 119.2    |
| O(3)-C(22)-H(22A)   | 109.5    |
| O(3)-C(22)-H(22B)   | 109.5    |
| H(22A)-C(22)-H(22B) | 109.5    |
| O(3)-C(22)-H(22C)   | 109.5    |
| H(22A)-C(22)-H(22C) | 109.5    |
| H(22B)-C(22)-H(22C) | 109.5    |
| O(1)-C(23)-C(24)    | 126.7(3) |
| O(1)-C(23)-C(26)    | 114.8(3) |
| C(24)-C(23)-C(26)   | 118.5(3) |
| C(23)-C(24)-C(25)   | 127.5(3) |
| C(23)-C(24)-H(24)   | 116.3    |
| C(25)-C(24)-H(24)   | 116.3    |
| O(2)-C(25)-C(24)    | 125.3(3) |
| O(2)-C(25)-C(27)    | 115.6(3) |
| C(24)-C(25)-C(27)   | 119.1(3) |
| C(23)-C(26)-H(26A)  | 109.5    |
| C(23)-C(26)-H(26B)  | 109.5    |
| H(26A)-C(26)-H(26B) | 109.5    |
| C(23)-C(26)-H(26C)  | 109.5    |
| H(26A)-C(26)-H(26C) | 109.5    |
| H(26B)-C(26)-H(26C) | 109.5    |
| C(25)-C(27)-H(27A)  | 109.5    |
| C(25)-C(27)-H(27B)  | 109.5    |
| H(27A)-C(27)-H(27B) | 109.5    |

|                          |            |
|--------------------------|------------|
| C (25) -C (27) -H (27C)  | 109.5      |
| H (27A) -C (27) -H (27C) | 109.5      |
| H (27B) -C (27) -H (27C) | 109.5      |
| N (4) -C (28) -C (29)    | 179.1 (4)  |
| C (28) -C (29) -H (29A)  | 109.5      |
| C (28) -C (29) -H (29B)  | 109.5      |
| H (29A) -C (29) -H (29B) | 109.5      |
| C (28) -C (29) -H (29C)  | 109.5      |
| H (29A) -C (29) -H (29C) | 109.5      |
| H (29B) -C (29) -H (29C) | 109.5      |
| C (31) -C (30) -H (30A)  | 109.5      |
| C (31) -C (30) -H (30B)  | 109.5      |
| H (30A) -C (30) -H (30B) | 109.5      |
| C (31) -C (30) -H (30C)  | 109.5      |
| H (30A) -C (30) -H (30C) | 109.5      |
| H (30B) -C (30) -H (30C) | 109.5      |
| O (4) -C (31) -C (30)    | 108.0 (5)  |
| O (4) -C (31) -H (31A)   | 110.1      |
| C (30) -C (31) -H (31A)  | 110.1      |
| O (4) -C (31) -H (31B)   | 110.1      |
| C (30) -C (31) -H (31B)  | 110.1      |
| H (31A) -C (31) -H (31B) | 108.4      |
| C (31) -O (4) -C (32)    | 112.8 (6)  |
| O (4) -C (32) -C (33)    | 108.0 (5)  |
| O (4) -C (32) -H (32A)   | 110.1      |
| C (33) -C (32) -H (32A)  | 110.1      |
| O (4) -C (32) -H (32B)   | 110.1      |
| C (33) -C (32) -H (32B)  | 110.1      |
| H (32A) -C (32) -H (32B) | 108.4      |
| C (32) -C (33) -H (33A)  | 109.5      |
| C (32) -C (33) -H (33B)  | 109.5      |
| H (33A) -C (33) -H (33B) | 109.5      |
| C (32) -C (33) -H (33C)  | 109.5      |
| H (33A) -C (33) -H (33C) | 109.5      |
| H (33B) -C (33) -H (33C) | 109.5      |
| C (1) -N (1) -C (5)      | 118.7 (3)  |
| C (1) -N (1) -Ru (1)     | 128.4 (2)  |
| C (5) -N (1) -Ru (1)     | 112.7 (2)  |
| C (10) -N (2) -C (6)     | 121.0 (3)  |
| C (10) -N (2) -Ru (1)    | 119.6 (2)  |
| C (6) -N (2) -Ru (1)     | 119.2 (2)  |
| C (15) -N (3) -C (11)    | 118.1 (3)  |
| C (15) -N (3) -Ru (1)    | 128.9 (2)  |
| C (11) -N (3) -Ru (1)    | 112.7 (2)  |
| C (28) -N (4) -Ru (1)    | 178.0 (3)  |
| C (23) -O (1) -Ru (1)    | 122.7 (2)  |
| C (25) -O (2) -Ru (1)    | 123.8 (2)  |
| C (19) -O (3) -C (22)    | 117.4 (3)  |
| F (4) -P (1) -F (1)      | 90.94 (19) |
| F (4) -P (1) -F (6)      | 92.44 (18) |
| F (1) -P (1) -F (6)      | 91.15 (18) |
| F (4) -P (1) -F (5)      | 89.88 (16) |
| F (1) -P (1) -F (5)      | 90.15 (17) |
| F (6) -P (1) -F (5)      | 177.3 (2)  |
| F (4) -P (1) -F (3)      | 92.3 (2)   |
| F (1) -P (1) -F (3)      | 176.3 (2)  |
| F (6) -P (1) -F (3)      | 90.6 (2)   |
| F (5) -P (1) -F (3)      | 88.0 (2)   |
| F (4) -P (1) -F (2)      | 178.5 (2)  |
| F (1) -P (1) -F (2)      | 87.97 (17) |
| F (6) -P (1) -F (2)      | 88.68 (18) |

|                 |            |
|-----------------|------------|
| F(5)-P(1)-F(2)  | 89.03(16)  |
| F(3)-P(1)-F(2)  | 88.8(2)    |
| N(2)-Ru(1)-N(4) | 93.08(12)  |
| N(2)-Ru(1)-O(1) | 88.37(11)  |
| N(4)-Ru(1)-O(1) | 178.00(10) |
| N(2)-Ru(1)-N(1) | 79.93(11)  |
| N(4)-Ru(1)-N(1) | 93.68(11)  |
| O(1)-Ru(1)-N(1) | 85.22(10)  |
| N(2)-Ru(1)-N(3) | 79.81(11)  |
| N(4)-Ru(1)-N(3) | 88.09(12)  |
| O(1)-Ru(1)-N(3) | 93.52(10)  |
| N(1)-Ru(1)-N(3) | 159.72(12) |
| N(2)-Ru(1)-O(2) | 179.04(10) |
| N(4)-Ru(1)-O(2) | 87.59(11)  |
| O(1)-Ru(1)-O(2) | 90.97(10)  |
| N(1)-Ru(1)-O(2) | 100.73(11) |
| N(3)-Ru(1)-O(2) | 99.53(10)  |

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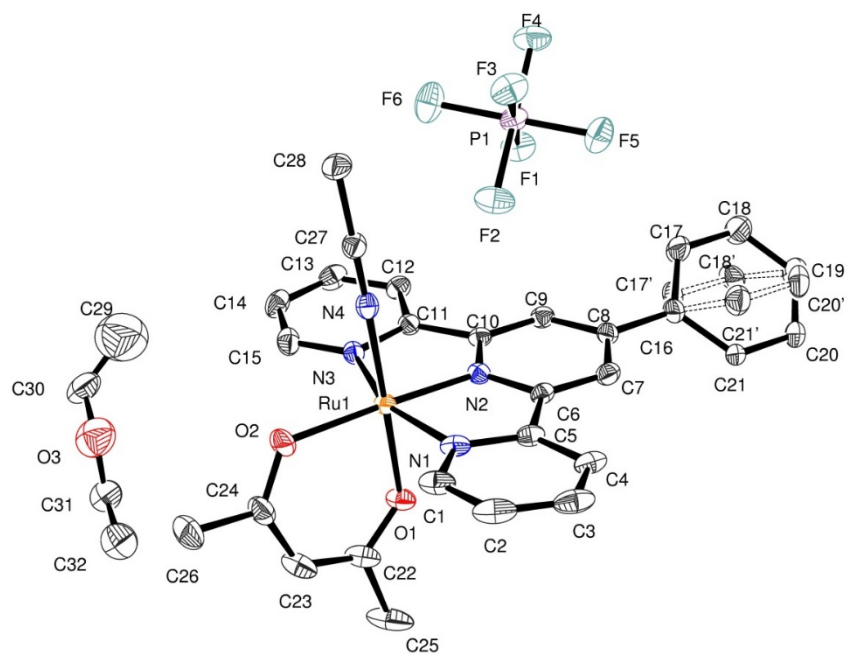
Symmetry transformations used to generate equivalent atoms:



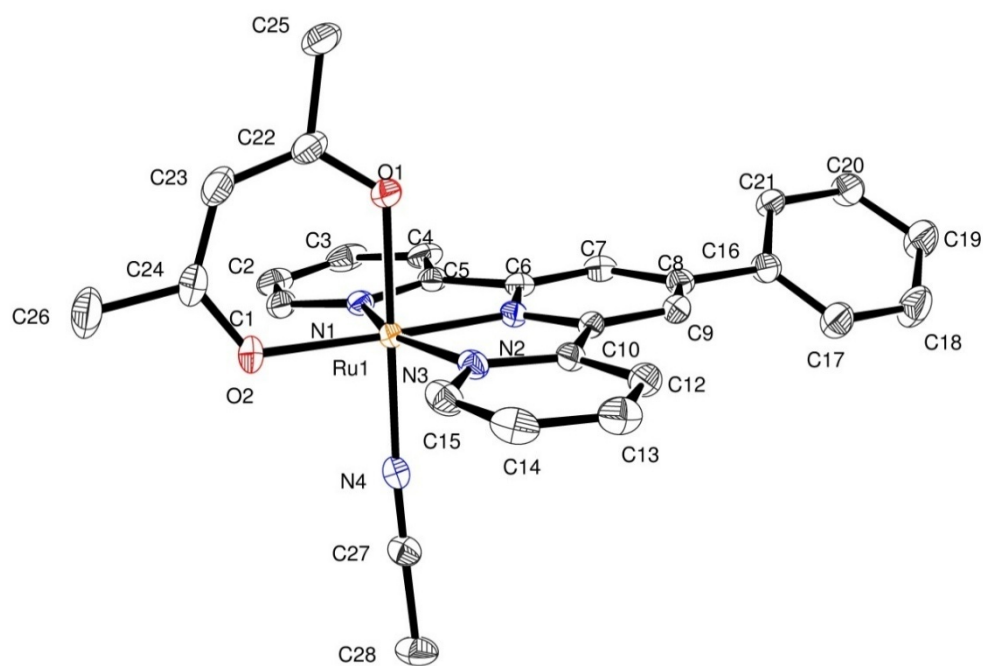
**Table S8.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Ru}(\text{MeO-phtpy})(\text{acac})(\text{MeCN})](\text{PF}_6)$   
The anisotropic displacement factor exponent takes the form:  
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

|        | U11    | U22     | U33     | U23     | U13     | U12     |
|--------|--------|---------|---------|---------|---------|---------|
| C (1)  | 24 (2) | 30 (2)  | 25 (2)  | -4 (1)  | 2 (2)   | -6 (1)  |
| C (2)  | 20 (2) | 34 (2)  | 34 (2)  | -2 (2)  | 0 (2)   | -6 (1)  |
| C (3)  | 25 (2) | 25 (2)  | 33 (2)  | 1 (1)   | -7 (2)  | -7 (1)  |
| C (4)  | 23 (2) | 23 (2)  | 28 (2)  | 0 (1)   | -6 (2)  | -2 (1)  |
| C (5)  | 23 (2) | 20 (2)  | 21 (2)  | 1 (1)   | -3 (1)  | -3 (1)  |
| C (6)  | 21 (2) | 21 (2)  | 21 (2)  | 0 (1)   | -7 (1)  | -2 (1)  |
| C (7)  | 23 (2) | 21 (2)  | 25 (2)  | 0 (1)   | -7 (1)  | -4 (1)  |
| C (8)  | 20 (2) | 22 (2)  | 24 (2)  | 0 (1)   | -6 (1)  | -1 (1)  |
| C (9)  | 21 (2) | 21 (2)  | 20 (2)  | 0 (1)   | -3 (1)  | -4 (1)  |
| C (10) | 22 (2) | 21 (2)  | 24 (2)  | 0 (1)   | -7 (1)  | -1 (1)  |
| C (11) | 23 (2) | 21 (2)  | 22 (2)  | 0 (1)   | -4 (1)  | -4 (1)  |
| C (12) | 25 (2) | 24 (2)  | 25 (2)  | -5 (1)  | -2 (1)  | -3 (1)  |
| C (13) | 27 (2) | 30 (2)  | 27 (2)  | -3 (1)  | -8 (2)  | -9 (1)  |
| C (14) | 35 (2) | 24 (2)  | 24 (2)  | -1 (1)  | -10 (2) | -5 (1)  |
| C (15) | 29 (2) | 18 (2)  | 24 (2)  | -2 (1)  | -9 (2)  | -1 (1)  |
| C (16) | 22 (2) | 18 (2)  | 25 (2)  | -1 (1)  | -5 (1)  | -1 (1)  |
| C (17) | 19 (2) | 26 (2)  | 26 (2)  | -1 (1)  | -1 (1)  | -4 (1)  |
| C (18) | 23 (2) | 32 (2)  | 26 (2)  | -5 (1)  | -2 (2)  | -7 (1)  |
| C (19) | 23 (2) | 27 (2)  | 23 (2)  | -6 (1)  | 0 (1)   | -3 (1)  |
| C (20) | 24 (2) | 26 (2)  | 27 (2)  | -3 (1)  | 0 (2)   | -7 (1)  |
| C (21) | 21 (2) | 22 (2)  | 29 (2)  | -4 (1)  | -6 (1)  | -2 (1)  |
| C (22) | 32 (2) | 63 (3)  | 36 (2)  | -24 (2) | 2 (2)   | -14 (2) |
| C (23) | 24 (2) | 22 (2)  | 29 (2)  | 0 (1)   | -7 (2)  | -7 (1)  |
| C (24) | 22 (2) | 24 (2)  | 30 (2)  | -2 (1)  | -2 (2)  | -1 (1)  |
| C (25) | 23 (2) | 24 (2)  | 31 (2)  | -5 (1)  | -2 (2)  | -3 (1)  |
| C (26) | 29 (2) | 35 (2)  | 28 (2)  | -4 (2)  | -8 (2)  | -2 (2)  |
| C (27) | 34 (2) | 33 (2)  | 30 (2)  | -4 (2)  | 0 (2)   | 5 (2)   |
| C (28) | 26 (2) | 27 (2)  | 25 (2)  | 0 (1)   | -5 (2)  | -2 (1)  |
| C (29) | 47 (3) | 49 (3)  | 38 (3)  | 12 (2)  | -13 (2) | 0 (2)   |
| C (30) | 34 (4) | 57 (5)  | 35 (5)  | -6 (4)  | -9 (4)  | 1 (4)   |
| C (31) | 38 (4) | 36 (4)  | 37 (4)  | -3 (3)  | -10 (4) | -4 (3)  |
| O (4)  | 29 (3) | 41 (3)  | 35 (3)  | -8 (3)  | -3 (2)  | -3 (3)  |
| C (32) | 32 (4) | 58 (5)  | 37 (5)  | -4 (4)  | -1 (4)  | -11 (4) |
| C (33) | 35 (5) | 97 (8)  | 60 (7)  | -44 (6) | 2 (5)   | -2 (5)  |
| N (1)  | 18 (1) | 23 (1)  | 22 (2)  | -1 (1)  | -3 (1)  | -4 (1)  |
| N (2)  | 20 (1) | 20 (1)  | 16 (1)  | -1 (1)  | -2 (1)  | -3 (1)  |
| N (3)  | 24 (2) | 20 (1)  | 20 (2)  | -2 (1)  | -5 (1)  | -2 (1)  |
| N (4)  | 22 (2) | 24 (1)  | 24 (2)  | -3 (1)  | 0 (1)   | -5 (1)  |
| O (1)  | 21 (1) | 24 (1)  | 20 (1)  | -1 (1)  | -4 (1)  | -2 (1)  |
| O (2)  | 21 (1) | 26 (1)  | 20 (1)  | -5 (1)  | 2 (1)   | 1 (1)   |
| O (3)  | 26 (1) | 46 (2)  | 29 (2)  | -16 (1) | 3 (1)   | -10 (1) |
| F (1)  | 48 (2) | 71 (2)  | 39 (2)  | 10 (1)  | -20 (1) | -26 (1) |
| F (2)  | 42 (2) | 39 (1)  | 108 (3) | 17 (2)  | -30 (2) | -15 (1) |
| F (3)  | 63 (2) | 153 (4) | 52 (2)  | 5 (2)   | -32 (2) | -42 (2) |
| F (4)  | 34 (2) | 41 (2)  | 138 (3) | -33 (2) | -16 (2) | -8 (1)  |
| F (5)  | 26 (1) | 47 (1)  | 80 (2)  | -14 (1) | -2 (1)  | -8 (1)  |
| F (6)  | 32 (1) | 96 (2)  | 64 (2)  | -41 (2) | 8 (1)   | -20 (2) |
| P (1)  | 24 (1) | 41 (1)  | 30 (1)  | -3 (1)  | -8 (1)  | -10 (1) |
| Ru (1) | 18 (1) | 20 (1)  | 19 (1)  | -2 (1)  | -2 (1)  | -2 (1)  |

**Figure S5** Asymmetric unit for [Ru(H-phtpy)(acac)(MeCN)](PF<sub>6</sub>)



**Asymmetric Unit**



Compound

**Table S9.** Crystal data and structure refinement for [Ru(H-phtpy)(acac)(MeCN)](PF<sub>6</sub>)

|                                   |                                                                                                                                  |
|-----------------------------------|----------------------------------------------------------------------------------------------------------------------------------|
| Identification code               | VM-PLV-28                                                                                                                        |
| Empirical formula                 | C <sub>28</sub> H <sub>25</sub> N <sub>4</sub> O <sub>2</sub> Ru, F <sub>6</sub> P, 0.5 (C <sub>4</sub> H <sub>10</sub> O)       |
| Formula weight                    | 732.62                                                                                                                           |
| Temperature                       | 100 (2) K                                                                                                                        |
| Wavelength                        | 1.54184 Å                                                                                                                        |
| Crystal system, space group       | Monoclinic, P 2 <sub>1</sub> /c                                                                                                  |
| Unit cell dimensions              | a = 13.44010 (10) Å    alpha = 90 deg.<br>b = 23.9107 (2) Å    beta = 97.3060 (10) deg.<br>c = 9.60110 (10) Å    gamma = 90 deg. |
| Volume                            | 3060.38 (5) Å <sup>3</sup>                                                                                                       |
| Z, Calculated density             | 4, 1.590 Mg/m <sup>3</sup>                                                                                                       |
| Absorption coefficient            | 5.298 mm <sup>-1</sup>                                                                                                           |
| F(000)                            | 1484                                                                                                                             |
| Crystal size                      | 0.2 x 0.2 x 0.04 mm                                                                                                              |
| Theta range for data collection   | 3.315 to 76.889 deg.                                                                                                             |
| Limiting indices                  | -13 ≤ h ≤ 16, -28 ≤ k ≤ 30,<br>-12 ≤ l ≤ 10                                                                                      |
| Reflections collected / unique    | 56490 / 6353 [R(int) = 0.0619]                                                                                                   |
| Completeness to theta = 67.684    | 100.0 %                                                                                                                          |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>                                                                                      |
| Data / restraints / parameters    | 6353 / 134 / 465                                                                                                                 |
| Goodness-of-fit on F <sup>2</sup> | 1.051                                                                                                                            |
| Final R indices [I > 2sigma(I)]   | R <sub>1</sub> = 0.0406, wR <sub>2</sub> = 0.1113                                                                                |
| R indices (all data)              | R <sub>1</sub> = 0.0413, wR <sub>2</sub> = 0.1120                                                                                |
| Largest diff. peak and hole       | 1.331 and -1.309 e.Å <sup>-3</sup>                                                                                               |

**Table S10.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Ru}(\text{H-phtpy})(\text{acac})(\text{MeCN})](\text{PF}_6)$

$U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

|         | x         | y        | z         | $U(\text{eq})$ |
|---------|-----------|----------|-----------|----------------|
| C (1)   | 9195 (2)  | 3898 (2) | 3934 (3)  | 26 (1)         |
| C (2)   | 9967 (2)  | 4099 (2) | 3257 (3)  | 31 (1)         |
| C (3)   | 10019 (2) | 4665 (2) | 2969 (3)  | 31 (1)         |
| C (4)   | 9301 (2)  | 5021 (1) | 3393 (3)  | 25 (1)         |
| C (5)   | 8549 (2)  | 4801 (1) | 4098 (3)  | 20 (1)         |
| C (6)   | 7783 (2)  | 5150 (1) | 4667 (3)  | 18 (1)         |
| C (7)   | 7697 (2)  | 5723 (1) | 4615 (3)  | 21 (1)         |
| C (8)   | 6956 (3)  | 5991 (1) | 5280 (3)  | 21 (1)         |
| C (9)   | 6294 (2)  | 5656 (1) | 5928 (3)  | 20 (1)         |
| C (10)  | 6400 (2)  | 5085 (1) | 5943 (3)  | 17 (1)         |
| C (11)  | 5776 (2)  | 4672 (1) | 6576 (3)  | 18 (1)         |
| C (12)  | 4994 (2)  | 4823 (1) | 7313 (3)  | 22 (1)         |
| C (13)  | 4455 (2)  | 4410 (1) | 7903 (3)  | 27 (1)         |
| C (14)  | 4713 (2)  | 3856 (2) | 7730 (3)  | 27 (1)         |
| C (15)  | 5491 (2)  | 3729 (1) | 6967 (3)  | 24 (1)         |
| C (16)  | 6868 (2)  | 6610 (1) | 5282 (3)  | 24 (1)         |
| C (19)  | 6682 (3)  | 7775 (1) | 5241 (4)  | 37 (1)         |
| C (17)  | 6618 (6)  | 6886 (3) | 6408 (7)  | 33 (2)         |
| C (18)  | 6535 (7)  | 7463 (3) | 6404 (7)  | 40 (2)         |
| C (20)  | 7012 (5)  | 7500 (2) | 4086 (6)  | 28 (1)         |
| C (21)  | 7123 (5)  | 6923 (2) | 4099 (6)  | 21 (1)         |
| C (17') | 5934 (5)  | 6867 (2) | 5506 (7)  | 24 (1)         |
| C (18') | 5834 (5)  | 7448 (2) | 5462 (7)  | 27 (1)         |
| C (20') | 7569 (5)  | 7539 (3) | 5132 (8)  | 34 (2)         |
| C (21') | 7673 (5)  | 6960 (3) | 5166 (7)  | 30 (2)         |
| C (22)  | 6305 (2)  | 3614 (2) | 2624 (3)  | 28 (1)         |
| C (23)  | 6655 (3)  | 3075 (2) | 2921 (4)  | 32 (1)         |
| C (24)  | 7166 (3)  | 2875 (1) | 4192 (4)  | 28 (1)         |
| C (25)  | 5733 (3)  | 3739 (2) | 1197 (4)  | 45 (1)         |
| C (26)  | 7475 (3)  | 2269 (2) | 4285 (4)  | 41 (1)         |
| C (27)  | 8440 (2)  | 4019 (1) | 8411 (3)  | 21 (1)         |
| C (28)  | 8875 (3)  | 4020 (1) | 9884 (3)  | 29 (1)         |
| C (29)  | 196 (14)  | 3029 (7) | 7957 (15) | 132 (4)        |
| C (30)  | -182 (7)  | 2594 (4) | 7112 (8)  | 57 (2)         |
| O (3)   | 327 (6)   | 2505 (3) | 5996 (5)  | 72 (2)         |
| C (31)  | -130 (5)  | 2466 (4) | 4653 (7)  | 43 (2)         |
| C (32)  | 525 (7)   | 2390 (4) | 3679 (10) | 57 (2)         |
| N (1)   | 8482 (2)  | 4239 (1) | 4352 (2)  | 20 (1)         |
| N (2)   | 7147 (2)  | 4840 (1) | 5346 (2)  | 17 (1)         |
| N (3)   | 6021 (2)  | 4124 (1) | 6391 (3)  | 18 (1)         |
| N (4)   | 8078 (2)  | 4020 (1) | 7271 (3)  | 19 (1)         |
| O (1)   | 6405 (2)  | 4036 (1) | 3439 (2)  | 24 (1)         |
| O (2)   | 7415 (2)  | 3163 (1) | 5293 (2)  | 27 (1)         |
| F (1)   | 6787 (1)  | 5842 (1) | 9333 (2)  | 32 (1)         |
| F (2)   | 7918 (2)  | 5277 (1) | 8454 (2)  | 36 (1)         |
| F (3)   | 9048 (1)  | 5450 (1) | 10346 (2) | 34 (1)         |
| F (4)   | 7920 (2)  | 6012 (1) | 11237 (2) | 39 (1)         |
| F (5)   | 8333 (2)  | 6171 (1) | 9058 (2)  | 38 (1)         |
| F (6)   | 7510 (2)  | 5121 (1) | 10631 (2) | 38 (1)         |
| P (1)   | 7917 (1)  | 5647 (1) | 9837 (1)  | 22 (1)         |
| Ru (1)  | 7270 (1)  | 4032 (1) | 5358 (1)  | 16 (1)         |

**Table S11.** Bond lengths [Å] and angles [deg] for [Ru(H-phtpy)(acac)(MeCN)](PF<sub>6</sub>)

---

|                  |           |
|------------------|-----------|
| C (1) -N (1)     | 1.357 (4) |
| C (1) -C (2)     | 1.379 (5) |
| C (1) -H (1)     | 0.9500    |
| C (2) -C (3)     | 1.384 (5) |
| C (2) -H (2)     | 0.9500    |
| C (3) -C (4)     | 1.387 (5) |
| C (3) -H (3)     | 0.9500    |
| C (4) -C (5)     | 1.389 (4) |
| C (4) -H (4)     | 0.9500    |
| C (5) -N (1)     | 1.370 (4) |
| C (5) -C (6)     | 1.483 (4) |
| C (6) -N (2)     | 1.359 (4) |
| C (6) -C (7)     | 1.376 (4) |
| C (7) -C (8)     | 1.404 (4) |
| C (7) -H (7)     | 0.9500    |
| C (8) -C (9)     | 1.401 (4) |
| C (8) -C (16)    | 1.483 (4) |
| C (9) -C (10)    | 1.374 (4) |
| C (9) -H (9)     | 0.9500    |
| C (10) -N (2)    | 1.352 (4) |
| C (10) -C (11)   | 1.474 (4) |
| C (11) -N (3)    | 1.369 (4) |
| C (11) -C (12)   | 1.388 (4) |
| C (12) -C (13)   | 1.387 (4) |
| C (12) -H (12)   | 0.9500    |
| C (13) -C (14)   | 1.385 (5) |
| C (13) -H (13)   | 0.9500    |
| C (14) -C (15)   | 1.385 (5) |
| C (14) -H (14)   | 0.9500    |
| C (15) -N (3)    | 1.343 (4) |
| C (15) -H (15)   | 0.9500    |
| C (16) -C (17)   | 1.346 (7) |
| C (16) -C (21')  | 1.384 (7) |
| C (16) -C (21)   | 1.438 (6) |
| C (16) -C (17')  | 1.439 (7) |
| C (19) -C (20')  | 1.333 (8) |
| C (19) -C (18)   | 1.377 (7) |
| C (19) -C (20)   | 1.408 (7) |
| C (19) -C (18')  | 1.421 (7) |
| C (19) -H (19)   | 0.9500    |
| C (17) -C (18)   | 1.385 (8) |
| C (17) -H (17)   | 0.9500    |
| C (18) -H (18)   | 0.9500    |
| C (20) -C (21)   | 1.388 (8) |
| C (20) -H (20)   | 0.9500    |
| C (21) -H (21)   | 0.9500    |
| C (17') -C (18') | 1.394 (8) |
| C (17') -H (17') | 0.9500    |
| C (18') -H (18') | 0.9500    |
| C (20') -C (21') | 1.392 (9) |
| C (20') -H (20') | 0.9500    |
| C (21') -H (21') | 0.9500    |
| C (22) -O (1)    | 1.274 (4) |
| C (22) -C (23)   | 1.390 (5) |
| C (22) -C (25)   | 1.512 (4) |
| C (23) -C (24)   | 1.406 (5) |

|                     |             |
|---------------------|-------------|
| C (23) -H (23)      | 0.9500      |
| C (24) -O (2)       | 1.271 (4)   |
| C (24) -C (26)      | 1.505 (5)   |
| C (25) -H (25A)     | 0.9800      |
| C (25) -H (25B)     | 0.9800      |
| C (25) -H (25C)     | 0.9800      |
| C (26) -H (26A)     | 0.9800      |
| C (26) -H (26B)     | 0.9800      |
| C (26) -H (26C)     | 0.9800      |
| C (27) -N (4)       | 1.140 (4)   |
| C (27) -C (28)      | 1.460 (4)   |
| C (28) -H (28A)     | 0.9800      |
| C (28) -H (28B)     | 0.9800      |
| C (28) -H (28C)     | 0.9800      |
| C (29) -C (30)      | 1.376 (10)  |
| C (29) -H (29A)     | 0.9800      |
| C (29) -H (29B)     | 0.9800      |
| C (29) -H (29C)     | 0.9800      |
| C (30) -O (3)       | 1.360 (7)   |
| C (30) -H (30A)     | 0.9900      |
| C (30) -H (30B)     | 0.9900      |
| O (3) -C (31)       | 1.359 (7)   |
| C (31) -C (32)      | 1.376 (10)  |
| C (31) -H (31A)     | 0.9900      |
| C (31) -H (31B)     | 0.9900      |
| C (32) -H (32A)     | 0.9800      |
| C (32) -H (32B)     | 0.9800      |
| C (32) -H (32C)     | 0.9800      |
| N (1) -Ru (1)       | 2.057 (2)   |
| N (2) -Ru (1)       | 1.937 (2)   |
| N (3) -Ru (1)       | 2.067 (3)   |
| N (4) -Ru (1)       | 2.011 (3)   |
| O (1) -Ru (1)       | 2.050 (2)   |
| O (2) -Ru (1)       | 2.089 (2)   |
| F (1) -P (1)        | 1.604 (2)   |
| F (2) -P (1)        | 1.595 (2)   |
| F (3) -P (1)        | 1.6065 (19) |
| F (4) -P (1)        | 1.603 (2)   |
| F (5) -P (1)        | 1.596 (2)   |
| F (6) -P (1)        | 1.601 (2)   |
|                     |             |
| N (1) -C (1) -C (2) | 122.1 (3)   |
| N (1) -C (1) -H (1) | 118.9       |
| C (2) -C (1) -H (1) | 118.9       |
| C (1) -C (2) -C (3) | 119.6 (3)   |
| C (1) -C (2) -H (2) | 120.2       |
| C (3) -C (2) -H (2) | 120.2       |
| C (2) -C (3) -C (4) | 119.2 (3)   |
| C (2) -C (3) -H (3) | 120.4       |
| C (4) -C (3) -H (3) | 120.4       |
| C (3) -C (4) -C (5) | 119.1 (3)   |
| C (3) -C (4) -H (4) | 120.5       |
| C (5) -C (4) -H (4) | 120.5       |
| N (1) -C (5) -C (4) | 121.8 (3)   |
| N (1) -C (5) -C (6) | 114.9 (2)   |
| C (4) -C (5) -C (6) | 123.3 (3)   |
| N (2) -C (6) -C (7) | 120.4 (2)   |
| N (2) -C (6) -C (5) | 112.2 (3)   |
| C (7) -C (6) -C (5) | 127.3 (3)   |
| C (6) -C (7) -C (8) | 120.0 (3)   |
| C (6) -C (7) -H (7) | 120.0       |

|                      |          |
|----------------------|----------|
| C(8)-C(7)-H(7)       | 120.0    |
| C(9)-C(8)-C(7)       | 117.9(3) |
| C(9)-C(8)-C(16)      | 120.9(3) |
| C(7)-C(8)-C(16)      | 121.2(3) |
| C(10)-C(9)-C(8)      | 120.1(3) |
| C(10)-C(9)-H(9)      | 119.9    |
| C(8)-C(9)-H(9)       | 119.9    |
| N(2)-C(10)-C(9)      | 120.6(3) |
| N(2)-C(10)-C(11)     | 112.2(2) |
| C(9)-C(10)-C(11)     | 127.3(3) |
| N(3)-C(11)-C(12)     | 121.6(3) |
| N(3)-C(11)-C(10)     | 115.4(2) |
| C(12)-C(11)-C(10)    | 123.0(3) |
| C(13)-C(12)-C(11)    | 119.5(3) |
| C(13)-C(12)-H(12)    | 120.3    |
| C(11)-C(12)-H(12)    | 120.3    |
| C(14)-C(13)-C(12)    | 118.7(3) |
| C(14)-C(13)-H(13)    | 120.6    |
| C(12)-C(13)-H(13)    | 120.6    |
| C(13)-C(14)-C(15)    | 119.3(3) |
| C(13)-C(14)-H(14)    | 120.3    |
| C(15)-C(14)-H(14)    | 120.3    |
| N(3)-C(15)-C(14)     | 122.6(3) |
| N(3)-C(15)-H(15)     | 118.7    |
| C(14)-C(15)-H(15)    | 118.7    |
| C(17)-C(16)-C(21)    | 119.2(4) |
| C(21')-C(16)-C(17')  | 117.3(4) |
| C(17)-C(16)-C(8)     | 121.2(4) |
| C(21')-C(16)-C(8)    | 122.7(4) |
| C(21)-C(16)-C(8)     | 119.5(3) |
| C(17')-C(16)-C(8)    | 119.9(3) |
| C(18)-C(19)-C(20)    | 118.6(4) |
| C(20')-C(19)-C(18')  | 121.4(4) |
| C(18)-C(19)-H(19)    | 120.7    |
| C(20)-C(19)-H(19)    | 120.7    |
| C(16)-C(17)-C(18)    | 121.0(6) |
| C(16)-C(17)-H(17)    | 119.5    |
| C(18)-C(17)-H(17)    | 119.5    |
| C(19)-C(18)-C(17)    | 121.4(6) |
| C(19)-C(18)-H(18)    | 119.3    |
| C(17)-C(18)-H(18)    | 119.3    |
| C(21)-C(20)-C(19)    | 120.0(5) |
| C(21)-C(20)-H(20)    | 120.0    |
| C(19)-C(20)-H(20)    | 120.0    |
| C(20)-C(21)-C(16)    | 119.3(5) |
| C(20)-C(21)-H(21)    | 120.3    |
| C(16)-C(21)-H(21)    | 120.3    |
| C(18')-C(17')-C(16)  | 120.3(5) |
| C(18')-C(17')-H(17') | 119.9    |
| C(16)-C(17')-H(17')  | 119.9    |
| C(17')-C(18')-C(19)  | 118.4(5) |
| C(17')-C(18')-H(18') | 120.8    |
| C(19)-C(18')-H(18')  | 120.8    |
| C(19)-C(20')-C(21')  | 120.4(6) |
| C(19)-C(20')-H(20')  | 119.8    |
| C(21')-C(20')-H(20') | 119.8    |
| C(16)-C(21')-C(20')  | 121.8(6) |
| C(16)-C(21')-H(21')  | 119.1    |
| C(20')-C(21')-H(21') | 119.1    |
| O(1)-C(22)-C(23)     | 127.0(3) |
| O(1)-C(22)-C(25)     | 113.7(3) |



|                          |             |
|--------------------------|-------------|
| C (23) -C (22) -C (25)   | 119.3 (3)   |
| C (22) -C (23) -C (24)   | 127.6 (3)   |
| C (22) -C (23) -H (23)   | 116.2       |
| C (24) -C (23) -H (23)   | 116.2       |
| O (2) -C (24) -C (23)    | 125.7 (3)   |
| O (2) -C (24) -C (26)    | 115.6 (3)   |
| C (23) -C (24) -C (26)   | 118.7 (3)   |
| C (22) -C (25) -H (25A)  | 109.5       |
| C (22) -C (25) -H (25B)  | 109.5       |
| H (25A) -C (25) -H (25B) | 109.5       |
| C (22) -C (25) -H (25C)  | 109.5       |
| H (25A) -C (25) -H (25C) | 109.5       |
| H (25B) -C (25) -H (25C) | 109.5       |
| C (24) -C (26) -H (26A)  | 109.5       |
| C (24) -C (26) -H (26B)  | 109.5       |
| H (26A) -C (26) -H (26B) | 109.5       |
| C (24) -C (26) -H (26C)  | 109.5       |
| H (26A) -C (26) -H (26C) | 109.5       |
| H (26B) -C (26) -H (26C) | 109.5       |
| N (4) -C (27) -C (28)    | 178.3 (3)   |
| C (27) -C (28) -H (28A)  | 109.5       |
| C (27) -C (28) -H (28B)  | 109.5       |
| H (28A) -C (28) -H (28B) | 109.5       |
| C (27) -C (28) -H (28C)  | 109.5       |
| H (28A) -C (28) -H (28C) | 109.5       |
| H (28B) -C (28) -H (28C) | 109.5       |
| C (30) -C (29) -H (29A)  | 109.5       |
| C (30) -C (29) -H (29B)  | 109.5       |
| H (29A) -C (29) -H (29B) | 109.5       |
| C (30) -C (29) -H (29C)  | 109.5       |
| H (29A) -C (29) -H (29C) | 109.5       |
| H (29B) -C (29) -H (29C) | 109.5       |
| O (3) -C (30) -C (29)    | 113.5 (7)   |
| O (3) -C (30) -H (30A)   | 108.9       |
| C (29) -C (30) -H (30A)  | 108.9       |
| O (3) -C (30) -H (30B)   | 108.9       |
| C (29) -C (30) -H (30B)  | 108.9       |
| H (30A) -C (30) -H (30B) | 107.7       |
| C (31) -O (3) -C (30)    | 123.1 (8)   |
| O (3) -C (31) -C (32)    | 113.7 (7)   |
| O (3) -C (31) -H (31A)   | 108.8       |
| C (32) -C (31) -H (31A)  | 108.8       |
| O (3) -C (31) -H (31B)   | 108.8       |
| C (32) -C (31) -H (31B)  | 108.8       |
| H (31A) -C (31) -H (31B) | 107.7       |
| C (31) -C (32) -H (32A)  | 109.5       |
| C (31) -C (32) -H (32B)  | 109.5       |
| H (32A) -C (32) -H (32B) | 109.5       |
| C (31) -C (32) -H (32C)  | 109.5       |
| H (32A) -C (32) -H (32C) | 109.5       |
| H (32B) -C (32) -H (32C) | 109.5       |
| C (1) -N (1) -C (5)      | 118.1 (3)   |
| C (1) -N (1) -Ru (1)     | 128.7 (2)   |
| C (5) -N (1) -Ru (1)     | 113.14 (18) |
| C (10) -N (2) -C (6)     | 120.9 (3)   |
| C (10) -N (2) -Ru (1)    | 119.78 (19) |
| C (6) -N (2) -Ru (1)     | 119.23 (19) |
| C (15) -N (3) -C (11)    | 118.2 (3)   |
| C (15) -N (3) -Ru (1)    | 128.9 (2)   |
| C (11) -N (3) -Ru (1)    | 112.75 (19) |
| C (27) -N (4) -Ru (1)    | 172.6 (3)   |

|                  |            |
|------------------|------------|
| C(22)-O(1)-Ru(1) | 123.5(2)   |
| C(24)-O(2)-Ru(1) | 123.3(2)   |
| F(2)-P(1)-F(5)   | 90.46(12)  |
| F(2)-P(1)-F(6)   | 89.89(13)  |
| F(5)-P(1)-F(6)   | 179.36(14) |
| F(2)-P(1)-F(4)   | 179.35(13) |
| F(5)-P(1)-F(4)   | 90.04(12)  |
| F(6)-P(1)-F(4)   | 89.60(12)  |
| F(2)-P(1)-F(1)   | 90.65(11)  |
| F(5)-P(1)-F(1)   | 90.28(12)  |
| F(6)-P(1)-F(1)   | 90.25(11)  |
| F(4)-P(1)-F(1)   | 89.76(12)  |
| F(2)-P(1)-F(3)   | 89.44(11)  |
| F(5)-P(1)-F(3)   | 89.91(11)  |
| F(6)-P(1)-F(3)   | 89.55(11)  |
| F(4)-P(1)-F(3)   | 90.15(12)  |
| F(1)-P(1)-F(3)   | 179.79(13) |
| N(2)-Ru(1)-N(4)  | 93.17(9)   |
| N(2)-Ru(1)-O(1)  | 87.24(9)   |
| N(4)-Ru(1)-O(1)  | 178.07(9)  |
| N(2)-Ru(1)-N(1)  | 80.18(10)  |
| N(4)-Ru(1)-N(1)  | 93.67(10)  |
| O(1)-Ru(1)-N(1)  | 88.26(9)   |
| N(2)-Ru(1)-N(3)  | 79.83(9)   |
| N(4)-Ru(1)-N(3)  | 86.59(10)  |
| O(1)-Ru(1)-N(3)  | 91.63(9)   |
| N(1)-Ru(1)-N(3)  | 160.00(10) |
| N(2)-Ru(1)-O(2)  | 177.83(9)  |
| N(4)-Ru(1)-O(2)  | 88.39(9)   |
| O(1)-Ru(1)-O(2)  | 91.26(8)   |
| N(1)-Ru(1)-O(2)  | 98.21(9)   |
| N(3)-Ru(1)-O(2)  | 101.79(9)  |

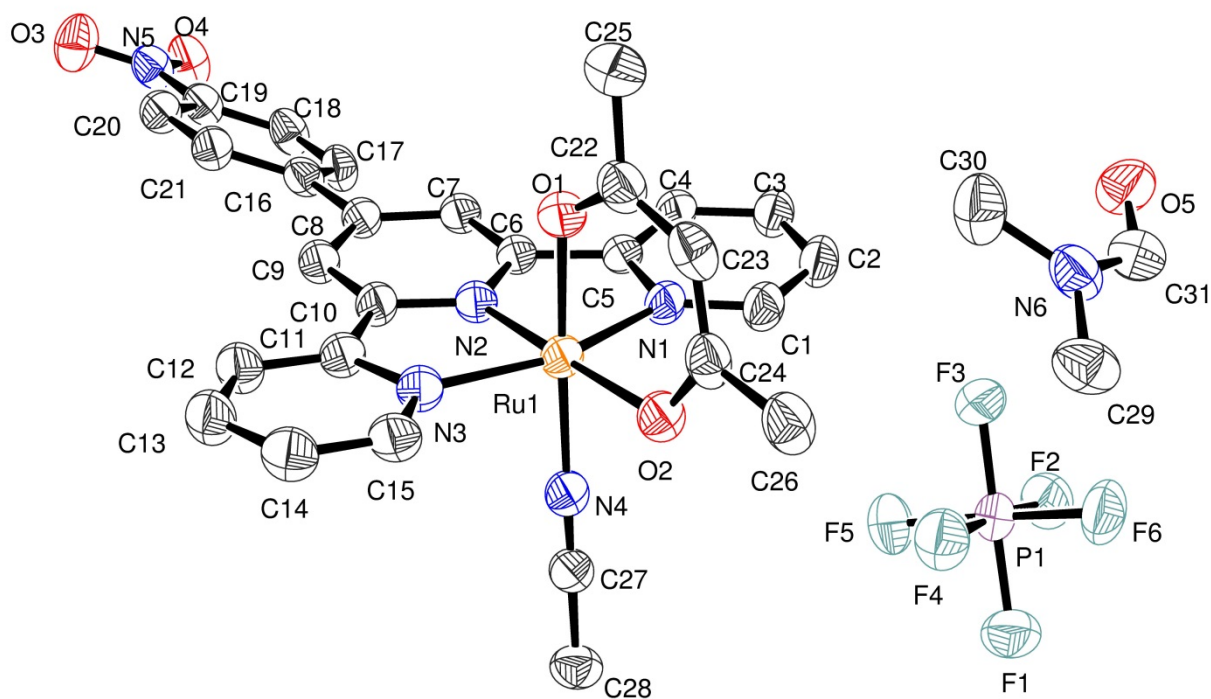
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Symmetry transformations used to generate equivalent atoms:

**Table S12.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Ru}(\text{H-phtpy})(\text{acac})(\text{MeCN})](\text{PF}_6)$   
The anisotropic displacement factor exponent takes the form:  
 $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

|         | U11     | U22     | U33     | U23     | U13     | U12    |
|---------|---------|---------|---------|---------|---------|--------|
| C (1)   | 24 (2)  | 33 (2)  | 20 (1)  | -6 (1)  | -1 (1)  | 13 (1) |
| C (2)   | 19 (2)  | 52 (2)  | 20 (2)  | -9 (1)  | 0 (1)   | 12 (1) |
| C (3)   | 18 (1)  | 57 (2)  | 18 (1)  | -6 (1)  | 4 (1)   | 1 (1)  |
| C (4)   | 22 (1)  | 37 (2)  | 15 (1)  | -1 (1)  | 3 (1)   | 0 (1)  |
| C (5)   | 17 (1)  | 27 (2)  | 15 (1)  | -1 (1)  | 0 (1)   | 3 (1)  |
| C (6)   | 16 (1)  | 22 (1)  | 14 (1)  | 1 (1)   | 1 (1)   | -1 (1) |
| C (7)   | 20 (1)  | 25 (2)  | 17 (1)  | 2 (1)   | 1 (1)   | -3 (1) |
| C (8)   | 28 (2)  | 15 (1)  | 17 (1)  | 1 (1)   | -1 (1)  | 0 (1)  |
| C (9)   | 22 (1)  | 21 (1)  | 17 (1)  | -1 (1)  | 4 (1)   | 3 (1)  |
| C (10)  | 17 (1)  | 19 (1)  | 14 (1)  | -1 (1)  | 2 (1)   | 3 (1)  |
| C (11)  | 19 (1)  | 17 (1)  | 17 (1)  | 0 (1)   | -1 (1)  | 1 (1)  |
| C (12)  | 22 (1)  | 25 (2)  | 20 (1)  | 1 (1)   | 5 (1)   | 2 (1)  |
| C (13)  | 20 (1)  | 38 (2)  | 24 (2)  | 3 (1)   | 6 (1)   | -1 (1) |
| C (14)  | 21 (2)  | 34 (2)  | 26 (2)  | 9 (1)   | 2 (1)   | -8 (1) |
| C (15)  | 23 (1)  | 21 (1)  | 29 (2)  | 4 (1)   | -4 (1)  | -3 (1) |
| C (16)  | 34 (2)  | 15 (1)  | 22 (1)  | 1 (1)   | 0 (1)   | -1 (1) |
| C (19)  | 65 (3)  | 16 (2)  | 31 (2)  | 2 (1)   | 11 (2)  | 1 (2)  |
| C (17)  | 56 (4)  | 18 (3)  | 25 (3)  | 3 (2)   | 10 (3)  | 2 (3)  |
| C (18)  | 70 (5)  | 22 (3)  | 32 (4)  | -2 (3)  | 18 (4)  | 2 (3)  |
| C (20)  | 42 (4)  | 16 (3)  | 25 (3)  | 4 (2)   | 5 (3)   | -4 (2) |
| C (21)  | 30 (3)  | 15 (3)  | 17 (3)  | 0 (2)   | 4 (2)   | -3 (2) |
| C (17') | 28 (3)  | 13 (3)  | 29 (3)  | 0 (2)   | 4 (3)   | 1 (2)  |
| C (18') | 36 (3)  | 16 (3)  | 29 (3)  | -5 (2)  | 3 (3)   | 6 (2)  |
| C (20') | 43 (4)  | 22 (3)  | 38 (4)  | 4 (3)   | 10 (3)  | -9 (3) |
| C (21') | 35 (4)  | 24 (3)  | 32 (3)  | 3 (3)   | 7 (3)   | 0 (3)  |
| C (22)  | 21 (1)  | 38 (2)  | 23 (1)  | -12 (1) | -1 (1)  | 5 (1)  |
| C (23)  | 31 (2)  | 32 (2)  | 32 (2)  | -16 (1) | 0 (1)   | 4 (1)  |
| C (24)  | 32 (2)  | 19 (1)  | 33 (2)  | -7 (1)  | 8 (1)   | 0 (1)  |
| C (25)  | 43 (2)  | 58 (3)  | 28 (2)  | -22 (2) | -13 (2) | 23 (2) |
| C (26)  | 57 (2)  | 21 (2)  | 45 (2)  | -8 (2)  | 14 (2)  | 4 (2)  |
| C (27)  | 19 (1)  | 21 (2)  | 22 (2)  | 2 (1)   | 0 (1)   | -2 (1) |
| C (28)  | 31 (2)  | 33 (2)  | 22 (2)  | 4 (1)   | -7 (1)  | -6 (1) |
| C (29)  | 154 (9) | 126 (9) | 115 (8) | -7 (6)  | 14 (8)  | 21 (8) |
| C (30)  | 84 (5)  | 55 (4)  | 37 (3)  | 13 (3)  | 23 (3)  | 29 (4) |
| O (3)   | 75 (4)  | 73 (3)  | 69 (3)  | 8 (3)   | 6 (3)   | 17 (3) |
| C (31)  | 38 (3)  | 46 (3)  | 45 (3)  | 4 (3)   | 10 (3)  | 17 (3) |
| C (32)  | 50 (4)  | 57 (5)  | 65 (5)  | -4 (4)  | 12 (4)  | 9 (4)  |
| N (1)   | 17 (1)  | 26 (1)  | 15 (1)  | -3 (1)  | -1 (1)  | 7 (1)  |
| N (2)   | 16 (1)  | 17 (1)  | 16 (1)  | 0 (1)   | -1 (1)  | 1 (1)  |
| N (3)   | 18 (1)  | 16 (1)  | 19 (1)  | 1 (1)   | -3 (1)  | -1 (1) |
| N (4)   | 19 (1)  | 16 (1)  | 24 (1)  | 1 (1)   | 3 (1)   | 2 (1)  |
| O (1)   | 24 (1)  | 26 (1)  | 19 (1)  | -5 (1)  | -3 (1)  | 7 (1)  |
| O (2)   | 38 (1)  | 15 (1)  | 28 (1)  | -4 (1)  | 2 (1)   | 6 (1)  |
| F (1)   | 25 (1)  | 40 (1)  | 32 (1)  | -2 (1)  | 5 (1)   | 11 (1) |
| F (2)   | 29 (1)  | 47 (1)  | 31 (1)  | -13 (1) | 3 (1)   | 10 (1) |
| F (3)   | 21 (1)  | 50 (1)  | 31 (1)  | 4 (1)   | 1 (1)   | 4 (1)  |
| F (4)   | 47 (1)  | 46 (1)  | 24 (1)  | -9 (1)  | 5 (1)   | 5 (1)  |
| F (5)   | 42 (1)  | 37 (1)  | 38 (1)  | 10 (1)  | 14 (1)  | -1 (1) |
| F (6)   | 31 (1)  | 37 (1)  | 51 (1)  | 12 (1)  | 18 (1)  | 5 (1)  |
| P (1)   | 19 (1)  | 28 (1)  | 19 (1)  | 0 (1)   | 5 (1)   | 3 (1)  |
| Ru (1)  | 17 (1)  | 15 (1)  | 15 (1)  | -1 (1)  | 0 (1)   | 3 (1)  |

**Figure S6** Asymmetric unit for [Ru(NO<sub>2</sub>-phtpy)(acac)(MeCN)](PF<sub>6</sub>)



### Asymmetric Unit

**Table S13.** Crystal data and structure refinement for [Ru(NO<sub>2</sub>-phtpy)(acac)(MeCN)](PF<sub>6</sub>)

|                     |                                                                                                                       |
|---------------------|-----------------------------------------------------------------------------------------------------------------------|
| Identification code | VM-PLV-27                                                                                                             |
| Empirical formula   | C <sub>28</sub> H <sub>24</sub> N <sub>5</sub> O <sub>4</sub> Ru, F <sub>6</sub> P, C <sub>3</sub> H <sub>7</sub> N O |
| Formula weight      | 813.66                                                                                                                |
| Temperature         | 100 (2) K                                                                                                             |
| Wavelength          | 1.54184 Å                                                                                                             |

|                                   |                                                                                                                            |
|-----------------------------------|----------------------------------------------------------------------------------------------------------------------------|
| Crystal system, space group       | Monoclinic, P 21/c                                                                                                         |
| Unit cell dimensions              | a = 8.41560(10) Å    alpha = 90 deg.<br>b = 19.4068(2) Å    beta = 92.7290(10) deg.<br>c = 21.2910(2) Å    gamma = 90 deg. |
| Volume                            | 3473.30(6) Å <sup>3</sup>                                                                                                  |
| Z, Calculated density             | 4, 1.556 Mg/m <sup>3</sup>                                                                                                 |
| Absorption coefficient            | 4.806 mm <sup>-1</sup>                                                                                                     |
| F(000)                            | 1648                                                                                                                       |
| Crystal size                      | 0.20 x 0.16 x 0.10 mm                                                                                                      |
| Theta range for data collection   | 3.083 to 76.704 deg.                                                                                                       |
| Limiting indices                  | -10<=h<=10, -24<=k<=22,<br>-26<=l<=26                                                                                      |
| Reflections collected / unique    | 64597 / 7089 [R(int) = 0.0655]                                                                                             |
| Completeness to theta = 67.684    | 100.0 %                                                                                                                    |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>                                                                                |
| Data / restraints / parameters    | 7089 / 0 / 456                                                                                                             |
| Goodness-of-fit on F <sup>2</sup> | 1.035                                                                                                                      |
| Final R indices [I>2sigma(I)]     | R1 = 0.0524, wR2 = 0.1414                                                                                                  |
| R indices (all data)              | R1 = 0.0547, wR2 = 0.1432                                                                                                  |
| Largest diff. peak and hole       | 1.061 and -1.821 e.Å <sup>-3</sup>                                                                                         |

**Table S14.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Ru}(\text{NO}_2\text{-phtpy})(\text{acac})(\text{MeCN})](\text{PF}_6)$   
 $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

|        | x        | y         | z        | $U(\text{eq})$ |
|--------|----------|-----------|----------|----------------|
| C (1)  | 2742 (5) | 1531 (2)  | 3138 (2) | 45 (1)         |
| C (2)  | 2109 (6) | 1666 (2)  | 2543 (2) | 49 (1)         |
| C (3)  | 1560 (5) | 2324 (2)  | 2399 (2) | 47 (1)         |
| C (4)  | 1667 (5) | 2826 (2)  | 2863 (2) | 41 (1)         |
| C (5)  | 2322 (4) | 2666 (2)  | 3451 (2) | 36 (1)         |
| C (6)  | 2503 (5) | 3163 (2)  | 3975 (2) | 35 (1)         |
| C (7)  | 2044 (5) | 3847 (2)  | 3964 (2) | 38 (1)         |
| C (8)  | 2343 (5) | 4258 (2)  | 4500 (2) | 37 (1)         |
| C (9)  | 3149 (5) | 3965 (2)  | 5023 (2) | 38 (1)         |
| C (10) | 3587 (5) | 3281 (2)  | 5016 (2) | 38 (1)         |
| C (11) | 4485 (5) | 2897 (2)  | 5516 (2) | 40 (1)         |
| C (12) | 4980 (5) | 3185 (2)  | 6086 (2) | 46 (1)         |
| C (13) | 5862 (6) | 2790 (2)  | 6517 (2) | 51 (1)         |
| C (14) | 6226 (6) | 2114 (2)  | 6368 (2) | 50 (1)         |
| C (15) | 5701 (5) | 1853 (2)  | 5791 (2) | 44 (1)         |
| C (16) | 1840 (5) | 4993 (2)  | 4506 (2) | 37 (1)         |
| C (17) | 574 (5)  | 5222 (2)  | 4112 (2) | 42 (1)         |
| C (18) | 102 (5)  | 5909 (2)  | 4110 (2) | 43 (1)         |
| C (19) | 908 (5)  | 6361 (2)  | 4509 (2) | 39 (1)         |
| C (20) | 2152 (5) | 6156 (2)  | 4918 (2) | 41 (1)         |
| C (21) | 2614 (5) | 5467 (2)  | 4908 (2) | 39 (1)         |
| C (22) | 7022 (5) | 1941 (2)  | 3875 (2) | 47 (1)         |
| C (23) | 7084 (5) | 1221 (2)  | 3890 (2) | 49 (1)         |
| C (24) | 6042 (5) | 769 (2)   | 4168 (2) | 44 (1)         |
| C (25) | 8340 (6) | 2330 (3)  | 3571 (2) | 63 (1)         |
| C (26) | 6348 (6) | 3 (2)     | 4167 (2) | 54 (1)         |
| C (27) | 946 (5)  | 1273 (2)  | 5053 (2) | 39 (1)         |
| C (28) | -409 (5) | 945 (2)   | 5327 (2) | 48 (1)         |
| C (29) | 5590 (6) | -881 (3)  | 2546 (2) | 61 (1)         |
| C (30) | 6118 (7) | 349 (3)   | 2313 (2) | 66 (1)         |
| C (31) | 4615 (6) | -345 (3)  | 1582 (2) | 60 (1)         |
| N (1)  | 2883 (4) | 2015 (2)  | 3589 (2) | 37 (1)         |
| N (2)  | 3224 (4) | 2886 (2)  | 4499 (1) | 37 (1)         |
| N (3)  | 4849 (4) | 2229 (2)  | 5367 (1) | 39 (1)         |
| N (4)  | 2015 (4) | 1532 (2)  | 4841 (2) | 39 (1)         |
| N (5)  | 440 (4)  | 7088 (2)  | 4508 (2) | 44 (1)         |
| N (6)  | 5478 (5) | -315 (2)  | 2105 (2) | 53 (1)         |
| O (1)  | 5955 (3) | 2324 (1)  | 4094 (1) | 44 (1)         |
| O (2)  | 4790 (3) | 941 (1)   | 4438 (1) | 42 (1)         |
| O (3)  | 1171 (4) | 7481 (2)  | 4864 (2) | 59 (1)         |
| O (4)  | -661 (4) | 7269 (2)  | 4144 (1) | 54 (1)         |
| O (5)  | 4361 (5) | 139 (2)   | 1217 (2) | 68 (1)         |
| Ru (1) | 3965 (1) | 1945 (1)  | 4477 (1) | 36 (1)         |
| P (1)  | 904 (1)  | -478 (1)  | 2856 (1) | 45 (1)         |
| F (1)  | -171 (4) | -1032 (2) | 3198 (1) | 70 (1)         |
| F (2)  | -449 (4) | -423 (2)  | 2310 (1) | 63 (1)         |
| F (3)  | 2021 (4) | 47 (1)    | 2525 (1) | 62 (1)         |
| F (4)  | 2258 (3) | -576 (2)  | 3420 (1) | 62 (1)         |
| F (5)  | 141 (3)  | 122 (1)   | 3247 (1) | 59 (1)         |
| F (6)  | 1712 (4) | -1102 (1) | 2486 (1) | 65 (1)         |

**Table S15.** Bond lengths [Å] and angles [deg] for [Ru(NO<sub>2</sub>phtpy)(acac)(MeCN)](PF<sub>6</sub>)

---

|                 |           |
|-----------------|-----------|
| C (1) -N (1)    | 1.344 (5) |
| C (1) -C (2)    | 1.375 (6) |
| C (1) -H (1)    | 0.9500    |
| C (2) -C (3)    | 1.386 (6) |
| C (2) -H (2)    | 0.9500    |
| C (3) -C (4)    | 1.388 (5) |
| C (3) -H (3)    | 0.9500    |
| C (4) -C (5)    | 1.379 (5) |
| C (4) -H (4)    | 0.9500    |
| C (5) -N (1)    | 1.377 (4) |
| C (5) -C (6)    | 1.477 (5) |
| C (6) -N (2)    | 1.355 (5) |
| C (6) -C (7)    | 1.383 (5) |
| C (7) -C (8)    | 1.406 (5) |
| C (7) -H (7)    | 0.9500    |
| C (8) -C (9)    | 1.396 (5) |
| C (8) -C (16)   | 1.488 (5) |
| C (9) -C (10)   | 1.379 (5) |
| C (9) -H (9)    | 0.9500    |
| C (10) -N (2)   | 1.364 (5) |
| C (10) -C (11)  | 1.477 (5) |
| C (11) -N (3)   | 1.373 (5) |
| C (11) -C (12)  | 1.384 (6) |
| C (12) -C (13)  | 1.384 (6) |
| C (12) -H (12)  | 0.9500    |
| C (13) -C (14)  | 1.388 (6) |
| C (13) -H (13)  | 0.9500    |
| C (14) -C (15)  | 1.381 (6) |
| C (14) -H (14)  | 0.9500    |
| C (15) -N (3)   | 1.342 (5) |
| C (15) -H (15)  | 0.9500    |
| C (16) -C (21)  | 1.395 (5) |
| C (16) -C (17)  | 1.398 (5) |
| C (17) -C (18)  | 1.392 (5) |
| C (17) -H (17)  | 0.9500    |
| C (18) -C (19)  | 1.376 (6) |
| C (18) -H (18)  | 0.9500    |
| C (19) -C (20)  | 1.388 (5) |
| C (19) -N (5)   | 1.465 (5) |
| C (20) -C (21)  | 1.392 (5) |
| C (20) -H (20)  | 0.9500    |
| C (21) -H (21)  | 0.9500    |
| C (22) -O (1)   | 1.271 (5) |
| C (22) -C (23)  | 1.397 (6) |
| C (22) -C (25)  | 1.513 (6) |
| C (23) -C (24)  | 1.392 (6) |
| C (23) -H (23)  | 0.9500    |
| C (24) -O (2)   | 1.270 (5) |
| C (24) -C (26)  | 1.508 (6) |
| C (25) -H (25A) | 0.9800    |
| C (25) -H (25B) | 0.9800    |
| C (25) -H (25C) | 0.9800    |
| C (26) -H (26A) | 0.9800    |
| C (26) -H (26B) | 0.9800    |
| C (26) -H (26C) | 0.9800    |
| C (27) -N (4)   | 1.142 (5) |
| C (27) -C (28)  | 1.452 (6) |
| C (28) -H (28A) | 0.9800    |

|                   |          |
|-------------------|----------|
| C(28)-H(28B)      | 0.9800   |
| C(28)-H(28C)      | 0.9800   |
| C(29)-N(6)        | 1.446(6) |
| C(29)-H(29A)      | 0.9800   |
| C(29)-H(29B)      | 0.9800   |
| C(29)-H(29C)      | 0.9800   |
| C(30)-N(6)        | 1.458(6) |
| C(30)-H(30A)      | 0.9800   |
| C(30)-H(30B)      | 0.9800   |
| C(30)-H(30C)      | 0.9800   |
| C(31)-O(5)        | 1.231(6) |
| C(31)-N(6)        | 1.301(6) |
| C(31)-H(31)       | 0.9500   |
| N(1)-Ru(1)        | 2.062(3) |
| N(2)-Ru(1)        | 1.930(3) |
| N(3)-Ru(1)        | 2.078(3) |
| N(4)-Ru(1)        | 2.014(3) |
| N(5)-O(3)         | 1.220(5) |
| N(5)-O(4)         | 1.230(4) |
| O(1)-Ru(1)        | 2.034(3) |
| O(2)-Ru(1)        | 2.072(3) |
| P(1)-F(3)         | 1.575(3) |
| P(1)-F(5)         | 1.584(3) |
| P(1)-F(2)         | 1.592(3) |
| P(1)-F(1)         | 1.603(3) |
| P(1)-F(6)         | 1.614(3) |
| P(1)-F(4)         | 1.627(3) |
|                   |          |
| N(1)-C(1)-C(2)    | 122.9(4) |
| N(1)-C(1)-H(1)    | 118.5    |
| C(2)-C(1)-H(1)    | 118.5    |
| C(1)-C(2)-C(3)    | 119.2(4) |
| C(1)-C(2)-H(2)    | 120.4    |
| C(3)-C(2)-H(2)    | 120.4    |
| C(2)-C(3)-C(4)    | 118.7(4) |
| C(2)-C(3)-H(3)    | 120.6    |
| C(4)-C(3)-H(3)    | 120.6    |
| C(5)-C(4)-C(3)    | 119.8(4) |
| C(5)-C(4)-H(4)    | 120.1    |
| C(3)-C(4)-H(4)    | 120.1    |
| N(1)-C(5)-C(4)    | 121.3(3) |
| N(1)-C(5)-C(6)    | 114.6(3) |
| C(4)-C(5)-C(6)    | 124.2(3) |
| N(2)-C(6)-C(7)    | 120.6(3) |
| N(2)-C(6)-C(5)    | 112.9(3) |
| C(7)-C(6)-C(5)    | 126.5(3) |
| C(6)-C(7)-C(8)    | 119.5(3) |
| C(6)-C(7)-H(7)    | 120.3    |
| C(8)-C(7)-H(7)    | 120.3    |
| C(9)-C(8)-C(7)    | 118.5(3) |
| C(9)-C(8)-C(16)   | 120.8(3) |
| C(7)-C(8)-C(16)   | 120.7(3) |
| C(10)-C(9)-C(8)   | 120.3(3) |
| C(10)-C(9)-H(9)   | 119.9    |
| C(8)-C(9)-H(9)    | 119.9    |
| N(2)-C(10)-C(9)   | 120.0(3) |
| N(2)-C(10)-C(11)  | 112.7(3) |
| C(9)-C(10)-C(11)  | 127.3(3) |
| N(3)-C(11)-C(12)  | 121.5(3) |
| N(3)-C(11)-C(10)  | 115.0(3) |
| C(12)-C(11)-C(10) | 123.5(3) |
| C(13)-C(12)-C(11) | 119.3(4) |



|                     |          |
|---------------------|----------|
| C(13)-C(12)-H(12)   | 120.4    |
| C(11)-C(12)-H(12)   | 120.4    |
| C(12)-C(13)-C(14)   | 119.2(4) |
| C(12)-C(13)-H(13)   | 120.4    |
| C(14)-C(13)-H(13)   | 120.4    |
| C(15)-C(14)-C(13)   | 119.1(4) |
| C(15)-C(14)-H(14)   | 120.4    |
| C(13)-C(14)-H(14)   | 120.4    |
| N(3)-C(15)-C(14)    | 122.4(4) |
| N(3)-C(15)-H(15)    | 118.8    |
| C(14)-C(15)-H(15)   | 118.8    |
| C(21)-C(16)-C(17)   | 118.7(3) |
| C(21)-C(16)-C(8)    | 120.8(3) |
| C(17)-C(16)-C(8)    | 120.5(3) |
| C(18)-C(17)-C(16)   | 121.0(4) |
| C(18)-C(17)-H(17)   | 119.5    |
| C(16)-C(17)-H(17)   | 119.5    |
| C(19)-C(18)-C(17)   | 118.5(4) |
| C(19)-C(18)-H(18)   | 120.8    |
| C(17)-C(18)-H(18)   | 120.8    |
| C(18)-C(19)-C(20)   | 122.6(3) |
| C(18)-C(19)-N(5)    | 119.2(3) |
| C(20)-C(19)-N(5)    | 118.1(3) |
| C(19)-C(20)-C(21)   | 117.9(4) |
| C(19)-C(20)-H(20)   | 121.0    |
| C(21)-C(20)-H(20)   | 121.0    |
| C(20)-C(21)-C(16)   | 121.3(4) |
| C(20)-C(21)-H(21)   | 119.3    |
| C(16)-C(21)-H(21)   | 119.3    |
| O(1)-C(22)-C(23)    | 127.1(4) |
| O(1)-C(22)-C(25)    | 114.2(4) |
| C(23)-C(22)-C(25)   | 118.7(4) |
| C(24)-C(23)-C(22)   | 128.0(4) |
| C(24)-C(23)-H(23)   | 116.0    |
| C(22)-C(23)-H(23)   | 116.0    |
| O(2)-C(24)-C(23)    | 125.4(4) |
| O(2)-C(24)-C(26)    | 113.9(4) |
| C(23)-C(24)-C(26)   | 120.7(4) |
| C(22)-C(25)-H(25A)  | 109.5    |
| C(22)-C(25)-H(25B)  | 109.5    |
| H(25A)-C(25)-H(25B) | 109.5    |
| C(22)-C(25)-H(25C)  | 109.5    |
| H(25A)-C(25)-H(25C) | 109.5    |
| H(25B)-C(25)-H(25C) | 109.5    |
| C(24)-C(26)-H(26A)  | 109.5    |
| C(24)-C(26)-H(26B)  | 109.5    |
| H(26A)-C(26)-H(26B) | 109.5    |
| C(24)-C(26)-H(26C)  | 109.5    |
| H(26A)-C(26)-H(26C) | 109.5    |
| H(26B)-C(26)-H(26C) | 109.5    |
| N(4)-C(27)-C(28)    | 179.6(5) |
| C(27)-C(28)-H(28A)  | 109.5    |
| C(27)-C(28)-H(28B)  | 109.5    |
| H(28A)-C(28)-H(28B) | 109.5    |
| C(27)-C(28)-H(28C)  | 109.5    |
| H(28A)-C(28)-H(28C) | 109.5    |
| H(28B)-C(28)-H(28C) | 109.5    |
| N(6)-C(29)-H(29A)   | 109.5    |
| N(6)-C(29)-H(29B)   | 109.5    |
| H(29A)-C(29)-H(29B) | 109.5    |
| N(6)-C(29)-H(29C)   | 109.5    |

|                          |             |
|--------------------------|-------------|
| H (29A) -C (29) -H (29C) | 109.5       |
| H (29B) -C (29) -H (29C) | 109.5       |
| N (6) -C (30) -H (30A)   | 109.5       |
| N (6) -C (30) -H (30B)   | 109.5       |
| H (30A) -C (30) -H (30B) | 109.5       |
| N (6) -C (30) -H (30C)   | 109.5       |
| H (30A) -C (30) -H (30C) | 109.5       |
| H (30B) -C (30) -H (30C) | 109.5       |
| O (5) -C (31) -N (6)     | 125.5 (5)   |
| O (5) -C (31) -H (31)    | 117.3       |
| N (6) -C (31) -H (31)    | 117.3       |
| C (1) -N (1) -C (5)      | 118.0 (3)   |
| C (1) -N (1) -Ru (1)     | 129.1 (3)   |
| C (5) -N (1) -Ru (1)     | 112.8 (2)   |
| C (6) -N (2) -C (10)     | 121.0 (3)   |
| C (6) -N (2) -Ru (1)     | 119.2 (2)   |
| C (10) -N (2) -Ru (1)    | 119.4 (2)   |
| C (15) -N (3) -C (11)    | 118.5 (3)   |
| C (15) -N (3) -Ru (1)    | 128.8 (3)   |
| C (11) -N (3) -Ru (1)    | 112.7 (2)   |
| C (27) -N (4) -Ru (1)    | 177.1 (3)   |
| O (3) -N (5) -O (4)      | 123.7 (3)   |
| O (3) -N (5) -C (19)     | 118.3 (3)   |
| O (4) -N (5) -C (19)     | 117.9 (3)   |
| C (31) -N (6) -C (29)    | 122.7 (4)   |
| C (31) -N (6) -C (30)    | 118.8 (4)   |
| C (29) -N (6) -C (30)    | 117.5 (4)   |
| C (22) -O (1) -Ru (1)    | 123.0 (3)   |
| C (24) -O (2) -Ru (1)    | 123.5 (3)   |
| N (2) -Ru (1) -N (4)     | 95.58 (13)  |
| N (2) -Ru (1) -O (1)     | 86.63 (12)  |
| N (4) -Ru (1) -O (1)     | 177.65 (11) |
| N (2) -Ru (1) -N (1)     | 80.32 (12)  |
| N (4) -Ru (1) -N (1)     | 92.70 (13)  |
| O (1) -Ru (1) -N (1)     | 86.88 (12)  |
| N (2) -Ru (1) -O (2)     | 178.82 (12) |
| N (4) -Ru (1) -O (2)     | 85.50 (11)  |
| O (1) -Ru (1) -O (2)     | 92.29 (11)  |
| N (1) -Ru (1) -O (2)     | 99.16 (11)  |
| N (2) -Ru (1) -N (3)     | 80.17 (12)  |
| N (4) -Ru (1) -N (3)     | 90.96 (13)  |
| O (1) -Ru (1) -N (3)     | 90.21 (12)  |
| N (1) -Ru (1) -N (3)     | 160.40 (12) |
| O (2) -Ru (1) -N (3)     | 100.32 (11) |
| F (3) -P (1) -F (5)      | 91.40 (15)  |
| F (3) -P (1) -F (2)      | 92.92 (17)  |
| F (5) -P (1) -F (2)      | 92.30 (16)  |
| F (3) -P (1) -F (1)      | 177.69 (19) |
| F (5) -P (1) -F (1)      | 90.20 (17)  |
| F (2) -P (1) -F (1)      | 88.68 (16)  |
| F (3) -P (1) -F (6)      | 89.59 (15)  |
| F (5) -P (1) -F (6)      | 177.59 (17) |
| F (2) -P (1) -F (6)      | 89.84 (16)  |
| F (1) -P (1) -F (6)      | 88.76 (17)  |
| F (3) -P (1) -F (4)      | 89.68 (17)  |
| F (5) -P (1) -F (4)      | 89.21 (15)  |
| F (2) -P (1) -F (4)      | 176.95 (16) |
| F (1) -P (1) -F (4)      | 88.67 (16)  |
| F (6) -P (1) -F (4)      | 88.60 (15)  |

**Table S16.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Ru}(\text{NO}_2\text{-phtpy})(\text{acac})(\text{MeCN})](\text{PF}_6)$   
The anisotropic displacement factor exponent takes the form:  
 $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

|        | U11     | U22    | U33    | U23     | U13     | U12     |
|--------|---------|--------|--------|---------|---------|---------|
| C (1)  | 61 (2)  | 29 (2) | 43 (2) | -4 (2)  | 2 (2)   | 2 (2)   |
| C (2)  | 72 (3)  | 33 (2) | 41 (2) | -7 (2)  | -1 (2)  | -1 (2)  |
| C (3)  | 67 (3)  | 35 (2) | 38 (2) | -1 (2)  | -3 (2)  | -2 (2)  |
| C (4)  | 59 (2)  | 28 (2) | 37 (2) | 4 (1)   | 4 (2)   | -1 (2)  |
| C (5)  | 47 (2)  | 26 (2) | 34 (2) | 2 (1)   | 5 (1)   | -1 (1)  |
| C (6)  | 46 (2)  | 28 (2) | 32 (2) | 2 (1)   | 4 (1)   | -1 (1)  |
| C (7)  | 51 (2)  | 29 (2) | 33 (2) | 4 (1)   | 4 (2)   | 1 (2)   |
| C (8)  | 52 (2)  | 27 (2) | 34 (2) | 2 (1)   | 5 (2)   | 2 (1)   |
| C (9)  | 51 (2)  | 30 (2) | 33 (2) | 1 (1)   | 1 (2)   | 2 (2)   |
| C (10) | 51 (2)  | 28 (2) | 35 (2) | 1 (1)   | 1 (2)   | 2 (2)   |
| C (11) | 53 (2)  | 28 (2) | 38 (2) | 4 (1)   | 1 (2)   | 3 (2)   |
| C (12) | 66 (3)  | 35 (2) | 36 (2) | 5 (2)   | -2 (2)  | 5 (2)   |
| C (13) | 71 (3)  | 42 (2) | 39 (2) | 4 (2)   | -6 (2)  | 3 (2)   |
| C (14) | 61 (2)  | 45 (2) | 43 (2) | 11 (2)  | -6 (2)  | 6 (2)   |
| C (15) | 55 (2)  | 35 (2) | 41 (2) | 9 (2)   | 0 (2)   | 5 (2)   |
| C (16) | 50 (2)  | 30 (2) | 32 (2) | 3 (1)   | 8 (1)   | 5 (2)   |
| C (17) | 62 (2)  | 34 (2) | 31 (2) | -4 (1)  | 1 (2)   | 7 (2)   |
| C (18) | 56 (2)  | 41 (2) | 33 (2) | 0 (2)   | 2 (2)   | 15 (2)  |
| C (19) | 53 (2)  | 31 (2) | 33 (2) | 2 (1)   | 6 (2)   | 10 (2)  |
| C (20) | 51 (2)  | 32 (2) | 40 (2) | 0 (2)   | 4 (2)   | 3 (2)   |
| C (21) | 51 (2)  | 30 (2) | 36 (2) | 2 (1)   | -1 (2)  | 5 (2)   |
| C (22) | 54 (2)  | 52 (2) | 35 (2) | -1 (2)  | 2 (2)   | 1 (2)   |
| C (23) | 55 (2)  | 54 (2) | 37 (2) | -5 (2)  | 6 (2)   | 13 (2)  |
| C (24) | 58 (2)  | 40 (2) | 34 (2) | -2 (2)  | -2 (2)  | 9 (2)   |
| C (25) | 63 (3)  | 66 (3) | 60 (3) | 0 (2)   | 18 (2)  | -7 (2)  |
| C (26) | 75 (3)  | 43 (2) | 45 (2) | 0 (2)   | 7 (2)   | 20 (2)  |
| C (27) | 50 (2)  | 30 (2) | 38 (2) | 3 (1)   | 5 (2)   | 8 (2)   |
| C (28) | 54 (2)  | 43 (2) | 47 (2) | 10 (2)  | 7 (2)   | 3 (2)   |
| C (29) | 64 (3)  | 61 (3) | 57 (3) | 17 (2)  | 12 (2)  | 15 (2)  |
| C (30) | 84 (3)  | 55 (3) | 57 (3) | -9 (2)  | -7 (2)  | 15 (3)  |
| C (31) | 75 (3)  | 58 (3) | 49 (2) | 4 (2)   | 11 (2)  | -7 (2)  |
| N (1)  | 50 (2)  | 26 (1) | 36 (2) | 1 (1)   | 1 (1)   | 1 (1)   |
| N (2)  | 48 (2)  | 30 (1) | 32 (2) | 4 (1)   | 1 (1)   | 1 (1)   |
| N (3)  | 49 (2)  | 34 (2) | 36 (2) | 4 (1)   | -1 (1)  | 1 (1)   |
| N (4)  | 51 (2)  | 26 (1) | 38 (2) | 3 (1)   | 2 (1)   | 9 (1)   |
| N (5)  | 59 (2)  | 35 (2) | 38 (2) | 1 (1)   | 8 (2)   | 12 (2)  |
| N (6)  | 67 (2)  | 53 (2) | 38 (2) | 3 (2)   | 8 (2)   | 11 (2)  |
| O (1)  | 52 (2)  | 38 (1) | 40 (1) | 2 (1)   | 5 (1)   | -2 (1)  |
| O (2)  | 53 (2)  | 32 (1) | 42 (1) | 2 (1)   | 3 (1)   | 9 (1)   |
| O (3)  | 74 (2)  | 34 (2) | 66 (2) | -9 (1)  | -11 (2) | 10 (1)  |
| O (4)  | 79 (2)  | 43 (2) | 40 (2) | -1 (1)  | -5 (1)  | 24 (2)  |
| O (5)  | 105 (3) | 54 (2) | 42 (2) | 13 (1)  | -11 (2) | -18 (2) |
| Ru (1) | 47 (1)  | 25 (1) | 35 (1) | 2 (1)   | 2 (1)   | 3 (1)   |
| P (1)  | 56 (1)  | 38 (1) | 43 (1) | -9 (1)  | 7 (1)   | -6 (1)  |
| F (1)  | 92 (2)  | 68 (2) | 49 (1) | 9 (1)   | -2 (1)  | -27 (2) |
| F (2)  | 83 (2)  | 60 (2) | 45 (1) | 2 (1)   | -7 (1)  | 0 (1)   |
| F (3)  | 83 (2)  | 39 (1) | 68 (2) | -4 (1)  | 29 (1)  | -10 (1) |
| F (4)  | 70 (2)  | 57 (2) | 59 (2) | -4 (1)  | -2 (1)  | 5 (1)   |
| F (5)  | 64 (2)  | 55 (2) | 58 (2) | -16 (1) | 11 (1)  | 12 (1)  |
| F (6)  | 88 (2)  | 41 (1) | 67 (2) | -16 (1) | 2 (1)   | 6 (1)   |

**Table S17** X-ray relevant interatomic distances (in Å) in Ru(MeCN) and Ru(NO) complexes with terpyridine and acac ligands and averaged values (Avg.) with largest deviation from average (disp.).

Ru(MeCN)

|                              | DEAP       | OMe      | H          | NO <sub>2</sub> | Avg. (disp.)  |
|------------------------------|------------|----------|------------|-----------------|---------------|
| <i>Ru-acac</i>               |            |          |            |                 |               |
| Ru-O <sub>(trans MeCN)</sub> | 2.0649(18) | 2.062(2) | 2.0511(13) | 2.034(3)        | 2.053 (0.6%)9 |
| Ru-O <sub>(cis MeCN)</sub>   | 2.0795(18) | 2.089(2) | 2.0752(13) | 2.072(3)        | 2.079 (0.5%)5 |
| <i>Ru-tpy</i>                |            |          |            |                 |               |
| Ru-N <sub>(lateral)</sub>    | 2.060(2)   | 2.072(3) | 2.0729(15) | 2.062(3)        | 2.066 (0.5%)3 |
| Ru-N <sub>(central)</sub>    | 1.946(2)   | 1.943(3) | 1.9331(15) | 1.930(3)        | 1.938 (0.4%)4 |
| Ru-N <sub>(lateral)</sub>    | 2.064(2)   | 2.079(3) | 2.0678(15) | 2.078(3)        | 2.072 (0.3%)4 |
| <i>Ru-MeCN</i>               |            |          |            |                 |               |
| Ru-N                         | 2.007(2)   | 2.008(3) | 2.0146(15) | 2.014(3)        | 2.011 (0.2%)2 |
| CN                           | 1.144(4)   | 1.132(5) | 1.140(2)   | 1.142(5)        | 1.1395 (0.4%) |

Ru(NO) (values from ref 1)

|                            | DMAP     | OMe      | H        | NO <sub>2</sub> <sup>a</sup> | Avg. (disp.)   |
|----------------------------|----------|----------|----------|------------------------------|----------------|
| <i>Ru-acac</i>             |          |          |          |                              |                |
| Ru-O <sub>(trans NO)</sub> | 1.976(5) | 1.983(3) | 1.986(2) | 1.985(2)                     | 1.9825 (0.2%)3 |
| Ru-O <sub>(cis NO)</sub>   | 2.059(4) | 2.064(3) | 2.055(2) | 2.053(2)                     | 2.058 (0.3%)3  |
| <i>Ru-tpy</i>              |          |          |          |                              |                |
| Ru-N <sub>(lateral)</sub>  | 2.094(5) | 2.098(4) | 2.090(3) | 2.088(2)                     | 2.0925 (0.3%)3 |
| Ru-N <sub>(central)</sub>  | 1.971(5) | 1.978(4) | 1.980(3) | 1.978(2)                     | 1.977 (0.1%)3  |
| Ru-N <sub>(lateral)</sub>  | 2.063(5) | 2.097(4) | 2.091(3) | 2.075(2)                     | 2.0815 (0.7%)9 |
| <i>Ru-NO</i>               |          |          |          |                              |                |
| Ru-N                       | 1.751(6) | 1.762(2) | 1.760(3) | 1.760(2)                     | 1.758 (0.2%)   |
| NO                         | 1.154(7) | 1.136(6) | 1.139(4) | 1.137(3)                     | 1.1415 (1.1%)  |

<sup>a</sup> Averaged values on the two complexes present in the asymmetric unit cell.

- 1 P. Labra-Vázquez, V. Mudrak, M. Tassé, S. Mallet-Ladeira, A. Sournia-Saquet, J.-P. Malval, P. G. Lacroix, I. Malfant, *Inorg. Chem.*, 2023, 62, 20349-20363.

**Table S18**Atomic coordinates for [Ru(R-phtpy)(acac)(MeCN)]<sup>+</sup> complexes  
computed by DFT.

---

**R = Me<sub>2</sub>N****Ground state (<sup>1</sup>GS)**

|    |           |           |           |
|----|-----------|-----------|-----------|
| C  | 1.809413  | 1.205486  | -0.032213 |
| C  | 0.422198  | 1.189814  | 0.049944  |
| N  | -0.233122 | 0.015857  | 0.180586  |
| C  | 0.418019  | -1.167233 | 0.210737  |
| C  | 1.805669  | -1.197542 | 0.141299  |
| C  | 2.536639  | 0.000365  | 0.021837  |
| C  | -0.482819 | 2.355943  | -0.016908 |
| C  | -0.490022 | -2.327859 | 0.319677  |
| N  | -1.823616 | -2.027541 | 0.333497  |
| C  | -2.717268 | -3.020324 | 0.432899  |
| C  | -2.344833 | -4.357373 | 0.519073  |
| C  | -0.989583 | -4.675571 | 0.503679  |
| C  | -0.054751 | -3.649169 | 0.403947  |
| C  | -0.043247 | 3.674287  | -0.121562 |
| C  | -0.975071 | 4.706768  | -0.178023 |
| C  | -2.331540 | 4.397737  | -0.125259 |
| C  | -2.708269 | 3.063332  | -0.018288 |
| N  | -1.817456 | 2.064434  | 0.032589  |
| Ru | -2.187287 | 0.020377  | 0.201086  |
| O  | -2.122320 | -0.129820 | -1.851094 |
| C  | -3.150432 | -0.200735 | -2.607932 |
| C  | -2.829158 | -0.314198 | -4.079487 |
| C  | -4.495557 | -0.181916 | -2.207463 |
| C  | -4.990428 | -0.075307 | -0.893312 |
| O  | -4.292344 | 0.017305  | 0.167830  |
| C  | -6.486181 | -0.063494 | -0.678273 |
| H  | 2.333551  | 2.143888  | -0.171756 |
| H  | 2.330823  | -2.143729 | 0.200792  |
| H  | -3.757594 | -2.713471 | 0.441612  |
| H  | -3.107209 | -5.125142 | 0.595869  |
| H  | -0.660407 | -5.707798 | 0.569881  |
| H  | 1.005272  | -3.876679 | 0.393511  |
| H  | 1.017738  | 3.894592  | -0.156500 |
| H  | -0.642748 | 5.736859  | -0.259918 |
| H  | -3.091575 | 5.170628  | -0.164939 |
| H  | -3.749559 | 2.763260  | 0.030067  |
| H  | -2.213929 | -1.204574 | -4.253572 |
| H  | -3.725739 | -0.375343 | -4.700312 |
| H  | -2.237122 | 0.553004  | -4.394276 |
| H  | -5.234069 | -0.253101 | -2.998327 |
| H  | -7.045501 | -0.154917 | -1.612092 |
| H  | -6.768243 | -0.886842 | -0.011899 |
| H  | -6.777952 | 0.868249  | -0.179730 |
| N  | -2.269856 | 0.170165  | 2.199857  |
| C  | -2.332009 | 0.259446  | 3.355088  |
| C  | 4.003780  | -0.007322 | -0.053150 |
| C  | 4.771125  | 1.066733  | 0.432339  |

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | 4.279193  | 1.914333  | 0.903039  |
| C | 6.090201  | -1.103563 | -0.689852 |
| H | 6.574794  | -1.957332 | -1.149573 |
| C | 6.154602  | 1.066397  | 0.372368  |
| C | 4.707750  | -1.088957 | -0.612307 |
| H | 4.162805  | -1.930875 | -1.032005 |
| C | 6.862517  | -0.022888 | -0.194854 |
| H | 6.691899  | 1.915150  | 0.779919  |
| N | 8.229038  | -0.030614 | -0.261118 |
| C | -2.417146 | 0.371137  | 4.800231  |
| H | -3.464630 | 0.344538  | 5.115750  |
| H | -1.882978 | -0.458935 | 5.272448  |
| H | -1.970930 | 1.314261  | 5.130020  |
| C | 8.988180  | 1.098309  | 0.241813  |
| H | 10.051712 | 0.909217  | 0.092653  |
| H | 8.731924  | 2.027543  | -0.284920 |
| H | 8.819657  | 1.255971  | 1.315856  |
| C | 8.923875  | -1.164107 | -0.840656 |
| H | 9.998894  | -0.988259 | -0.790412 |
| H | 8.707257  | -2.094074 | -0.297859 |
| H | 8.653809  | -1.312186 | -1.895227 |

### <sup>3</sup>MLCT

|    |           |           |           |
|----|-----------|-----------|-----------|
| C  | 1.819240  | 1.229258  | -0.095247 |
| C  | 0.437203  | 1.262303  | -0.026581 |
| N  | -0.246023 | 0.081672  | 0.196369  |
| C  | 0.391580  | -1.132731 | 0.299875  |
| C  | 1.764878  | -1.179959 | 0.234352  |
| C  | 2.527183  | 0.012046  | 0.042862  |
| C  | -0.432140 | 2.404526  | -0.210026 |
| C  | -0.523337 | -2.252966 | 0.498212  |
| N  | -1.860359 | -1.926893 | 0.508072  |
| C  | -2.777059 | -2.889504 | 0.700806  |
| C  | -2.437349 | -4.219978 | 0.881358  |
| C  | -1.080517 | -4.571010 | 0.867017  |
| C  | -0.126421 | -3.584209 | 0.677949  |
| C  | 0.002962  | 3.727202  | -0.407759 |
| C  | -0.920341 | 4.744009  | -0.558763 |
| C  | -2.293181 | 4.443742  | -0.507447 |
| C  | -2.673698 | 3.128480  | -0.308792 |
| N  | -1.785533 | 2.129665  | -0.169928 |
| Ru | -2.187962 | 0.119627  | 0.160761  |
| O  | -2.120753 | -0.228508 | -1.817683 |
| C  | -3.086260 | -0.698206 | -2.522124 |
| C  | -2.697507 | -1.093686 | -3.920977 |
| C  | -4.420370 | -0.814404 | -2.109896 |
| C  | -4.947943 | -0.334929 | -0.897893 |
| O  | -4.254155 | 0.166546  | 0.051057  |
| C  | -6.436239 | -0.349540 | -0.673132 |
| H  | 2.362557  | 2.143810  | -0.305090 |
| H  | 2.276330  | -2.127177 | 0.359800  |
| H  | -3.810636 | -2.560686 | 0.709636  |
| H  | -3.214900 | -4.960558 | 1.032693  |
| H  | -0.775291 | -5.603410 | 1.007036  |
| H  | 0.927880  | -3.838669 | 0.670484  |
| H  | 1.065717  | 3.943297  | -0.437382 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | -0.585240 | 5.765247  | -0.712843 |
| H | -3.048046 | 5.214078  | -0.620346 |
| H | -3.717480 | 2.834812  | -0.259454 |
| H | -1.896236 | -1.839995 | -3.882307 |
| H | -3.540019 | -1.499335 | -4.484372 |
| H | -2.301580 | -0.219834 | -4.450928 |
| H | -5.124850 | -1.204710 | -2.835068 |
| H | -6.972154 | -0.858749 | -1.476683 |
| H | -6.660533 | -0.839827 | 0.280388  |
| H | -6.802486 | 0.681401  | -0.601185 |
| N | -2.302441 | 0.523493  | 2.152132  |
| C | -2.380319 | 0.760551  | 3.282495  |
| C | 3.985957  | -0.030520 | -0.024911 |
| C | 4.779016  | 1.095110  | 0.285019  |
| H | 4.305159  | 2.013680  | 0.620905  |
| C | 6.063366  | -1.242690 | -0.480919 |
| H | 6.534616  | -2.166334 | -0.797673 |
| C | 6.160415  | 1.067291  | 0.219853  |
| C | 4.682637  | -1.197013 | -0.406227 |
| H | 4.131218  | -2.089384 | -0.689664 |
| C | 6.853270  | -0.107311 | -0.169325 |
| H | 6.709768  | 1.962626  | 0.488330  |
| N | 8.219432  | -0.143757 | -0.239896 |
| C | -2.484251 | 1.058985  | 4.696742  |
| H | -3.533551 | 1.224263  | 4.959242  |
| H | -2.096675 | 0.219623  | 5.281522  |
| H | -1.908804 | 1.959507  | 4.930057  |
| C | 8.997356  | 1.042061  | 0.064381  |
| H | 10.056057 | 0.821243  | -0.074945 |
| H | 8.735451  | 1.877985  | -0.597835 |
| H | 8.852434  | 1.369166  | 1.103066  |
| C | 8.896165  | -1.369448 | -0.618854 |
| H | 9.973815  | -1.205172 | -0.596682 |
| H | 8.663738  | -2.190137 | 0.072843  |
| H | 8.622023  | -1.688654 | -1.633582 |

### <sup>3</sup>MC

|    |           |           |           |
|----|-----------|-----------|-----------|
| C  | 1.782184  | 1.155174  | -0.369761 |
| C  | 0.395068  | 1.144014  | -0.300321 |
| N  | -0.275934 | -0.008152 | -0.056707 |
| C  | 0.399167  | -1.154931 | 0.202532  |
| C  | 1.786341  | -1.187171 | 0.153091  |
| C  | 2.518068  | -0.026035 | -0.160151 |
| C  | -0.490705 | 2.309150  | -0.423546 |
| C  | -0.481822 | -2.263615 | 0.590399  |
| N  | -1.801221 | -1.926740 | 0.681582  |
| C  | -2.695653 | -2.847796 | 1.076470  |
| C  | -2.327845 | -4.149399 | 1.389235  |
| C  | -0.984724 | -4.508937 | 1.286222  |
| C  | -0.053608 | -3.557297 | 0.884028  |
| C  | -0.067191 | 3.606799  | -0.707114 |
| C  | -1.002824 | 4.634997  | -0.751075 |
| C  | -2.345217 | 4.348172  | -0.507307 |
| C  | -2.707229 | 3.035716  | -0.235003 |
| N  | -1.808844 | 2.038574  | -0.198626 |
| Ru | -2.264324 | -0.023927 | -0.092475 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| O | -2.346547 | -0.459959 | -2.230928 |
| C | -3.432347 | -0.603031 | -2.883100 |
| C | -3.263787 | -0.896077 | -4.356356 |
| C | -4.738313 | -0.513879 | -2.359519 |
| C | -5.107963 | -0.253315 | -1.032684 |
| O | -4.312785 | -0.043084 | -0.046913 |
| C | -6.571902 | -0.203395 | -0.672878 |
| H | 2.298653  | 2.079708  | -0.599388 |
| H | 2.309956  | -2.103773 | 0.397856  |
| H | -3.725894 | -2.512829 | 1.131080  |
| H | -3.082559 | -4.861229 | 1.705036  |
| H | -0.663461 | -5.519483 | 1.518006  |
| H | 0.994593  | -3.820040 | 0.798670  |
| H | 0.980700  | 3.813412  | -0.892719 |
| H | -0.685273 | 5.649417  | -0.970718 |
| H | -3.103174 | 5.123543  | -0.526113 |
| H | -3.736048 | 2.751319  | -0.041828 |
| H | -2.674256 | -1.811748 | -4.480242 |
| H | -4.217680 | -1.013547 | -4.875587 |
| H | -2.698755 | -0.083188 | -4.826839 |
| H | -5.550489 | -0.665350 | -3.061802 |
| H | -7.220108 | -0.395095 | -1.530610 |
| H | -6.783446 | -0.943947 | 0.107023  |
| H | -6.813619 | 0.781272  | -0.256154 |
| N | -2.233675 | 0.853281  | 3.989202  |
| C | -1.716911 | 1.088746  | 5.002015  |
| C | 3.983310  | -0.044312 | -0.235916 |
| C | 4.754689  | 1.094800  | 0.058344  |
| H | 4.268336  | 2.010901  | 0.383713  |
| C | 6.065087  | -1.237105 | -0.687640 |
| H | 6.546370  | -2.157452 | -0.998171 |
| C | 6.137349  | 1.081414  | -0.007598 |
| C | 4.683548  | -1.206623 | -0.607488 |
| H | 4.135887  | -2.106131 | -0.877199 |
| C | 6.841353  | -0.089362 | -0.387130 |
| H | 6.677190  | 1.985150  | 0.250969  |
| N | 8.206602  | -0.111021 | -0.460463 |
| C | -1.071860 | 1.383938  | 6.272283  |
| H | -1.697844 | 1.037709  | 7.099867  |
| H | -0.102365 | 0.880139  | 6.326374  |
| H | -0.916955 | 2.462207  | 6.372206  |
| C | 8.971491  | 1.085671  | -0.165260 |
| H | 10.032113 | 0.876823  | -0.308709 |
| H | 8.697272  | 1.914907  | -0.830810 |
| H | 8.828042  | 1.416970  | 0.872439  |
| C | 8.896611  | -1.335321 | -0.820250 |
| H | 9.972432  | -1.158694 | -0.800910 |
| H | 8.673887  | -2.147997 | -0.115877 |
| H | 8.626691  | -1.673382 | -1.829970 |

---

**R = MeO**

**Ground state (<sup>1</sup>GS)**

|   |          |          |           |
|---|----------|----------|-----------|
| C | 2.027252 | 1.285508 | -0.005900 |
| C | 0.639338 | 1.233472 | 0.064873  |
| N | 0.015720 | 0.040852 | 0.181818  |



|    |           |           |           |
|----|-----------|-----------|-----------|
| C  | 0.696030  | -1.125808 | 0.209026  |
| C  | 2.085387  | -1.118855 | 0.148359  |
| C  | 2.779562  | 0.098898  | 0.043235  |
| C  | -0.295026 | 2.375704  | 0.002734  |
| C  | -0.181556 | -2.310020 | 0.305080  |
| N  | -1.522255 | -2.043989 | 0.314516  |
| C  | -2.390280 | -3.060169 | 0.402082  |
| C  | -1.983322 | -4.387678 | 0.480481  |
| C  | -0.620262 | -4.670813 | 0.469861  |
| C  | 0.288230  | -3.619890 | 0.382291  |
| C  | 0.110600  | 3.705641  | -0.089697 |
| C  | -0.847810 | 4.713695  | -0.142597 |
| C  | -2.195777 | 4.368704  | -0.098729 |
| C  | -2.538122 | 3.024034  | -0.003785 |
| N  | -1.621592 | 2.048581  | 0.043841  |
| Ru | -1.936680 | -0.004880 | 0.195914  |
| O  | -1.866569 | -0.138428 | -1.856304 |
| C  | -2.892045 | -0.226184 | -2.615254 |
| C  | -2.566216 | -0.321423 | -4.086914 |
| C  | -4.237538 | -0.239773 | -2.216275 |
| C  | -4.735013 | -0.155179 | -0.901713 |
| O  | -4.038921 | -0.056522 | 0.160405  |
| C  | -6.230433 | -0.177563 | -0.686596 |
| H  | 2.531086  | 2.237299  | -0.129987 |
| H  | 2.637354  | -2.050078 | 0.202826  |
| H  | -3.438333 | -2.780853 | 0.407996  |
| H  | -2.725934 | -5.175428 | 0.547814  |
| H  | -0.264943 | -5.694645 | 0.530385  |
| H  | 1.353901  | -3.819450 | 0.375879  |
| H  | 1.165463  | 3.954303  | -0.118351 |
| H  | -0.542239 | 5.752713  | -0.214965 |
| H  | -2.975615 | 5.121697  | -0.136126 |
| H  | -3.571463 | 2.696871  | 0.037602  |
| H  | -1.931387 | -1.196787 | -4.266611 |
| H  | -3.460397 | -0.397572 | -4.709506 |
| H  | -1.992884 | 0.560890  | -4.394209 |
| H  | -4.973729 | -0.320350 | -3.008351 |
| H  | -6.787688 | -0.271202 | -1.621394 |
| H  | -6.494740 | -1.013648 | -0.028863 |
| H  | -6.541769 | 0.742484  | -0.178304 |
| N  | -2.027990 | 0.126813  | 2.196936  |
| C  | -2.096371 | 0.204411  | 3.352491  |
| C  | 4.252801  | 0.130987  | -0.021445 |
| C  | 4.981448  | 1.189313  | 0.553248  |
| H  | 4.460392  | 1.985165  | 1.078603  |
| C  | 6.364656  | -0.869189 | -0.724170 |
| H  | 6.880900  | -1.672689 | -1.237378 |
| C  | 6.364742  | 1.220272  | 0.498134  |
| C  | 4.974000  | -0.889771 | -0.655822 |
| H  | 4.445525  | -1.708154 | -1.137527 |
| C  | 7.071824  | 0.190506  | -0.142638 |
| H  | 6.923128  | 2.031699  | 0.955467  |
| C  | -2.189247 | 0.302014  | 4.798071  |
| H  | -3.237022 | 0.248109  | 5.109049  |
| H  | -1.637410 | -0.519309 | 5.265198  |
| H  | -1.766516 | 1.252621  | 5.137138  |
| O  | 8.419016  | 0.311697  | -0.145459 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 9.186044  | -0.706878 | -0.773168 |
| H | 10.228836 | -0.410715 | -0.652626 |
| H | 9.026045  | -1.679570 | -0.293053 |
| H | 8.950606  | -0.782260 | -1.841383 |

### <sup>3</sup>MLCT

|    |           |           |           |
|----|-----------|-----------|-----------|
| C  | 2.039628  | 1.292441  | -0.027880 |
| C  | 0.654278  | 1.247944  | 0.023726  |
| N  | 0.020846  | 0.037123  | 0.109591  |
| C  | 0.716956  | -1.140634 | 0.163456  |
| C  | 2.102492  | -1.118789 | 0.113977  |
| C  | 2.799539  | 0.104282  | 0.012659  |
| C  | -0.260129 | 2.368382  | 0.000837  |
| C  | -0.136593 | -2.300998 | 0.297262  |
| N  | -1.481620 | -2.015566 | 0.390121  |
| C  | -2.372957 | -3.011562 | 0.564737  |
| C  | -1.992983 | -4.337843 | 0.628284  |
| C  | -0.626689 | -4.653141 | 0.514591  |
| C  | 0.294703  | -3.635304 | 0.351716  |
| C  | 0.099924  | 3.720377  | -0.110251 |
| C  | -0.875492 | 4.699668  | -0.083455 |
| C  | -2.225072 | 4.328643  | 0.059767  |
| C  | -2.534314 | 2.986556  | 0.162294  |
| N  | -1.589552 | 2.026166  | 0.121717  |
| Ru | -1.972538 | -0.013440 | 0.137050  |
| O  | -1.884575 | -0.144726 | -1.865168 |
| C  | -2.893636 | -0.230778 | -2.653735 |
| C  | -2.531720 | -0.324229 | -4.111138 |
| C  | -4.243585 | -0.241458 | -2.270295 |
| C  | -4.736069 | -0.155114 | -0.961396 |
| O  | -4.015506 | -0.058422 | 0.098292  |
| C  | -6.219949 | -0.169652 | -0.716278 |
| H  | 2.542013  | 2.249377  | -0.120392 |
| H  | 2.656145  | -2.048318 | 0.190673  |
| H  | -3.411001 | -2.707741 | 0.647881  |
| H  | -2.744098 | -5.107420 | 0.766830  |
| H  | -0.294930 | -5.685802 | 0.559006  |
| H  | 1.352462  | -3.860190 | 0.267281  |
| H  | 1.145421  | 3.989525  | -0.214695 |
| H  | -0.598812 | 5.745993  | -0.167628 |
| H  | -3.017027 | 5.068386  | 0.094466  |
| H  | -3.555245 | 2.638364  | 0.276331  |
| H  | -1.895108 | -1.201089 | -4.274041 |
| H  | -3.412120 | -0.397106 | -4.752358 |
| H  | -1.949205 | 0.557705  | -4.400287 |
| H  | -4.975192 | -0.319054 | -3.065983 |
| H  | -6.792982 | -0.256340 | -1.641381 |
| H  | -6.473357 | -1.007214 | -0.056579 |
| H  | -6.513121 | 0.750272  | -0.197733 |
| N  | -2.088847 | 0.119506  | 2.168942  |
| C  | -2.166645 | 0.194696  | 3.320625  |
| C  | 4.272229  | 0.138828  | -0.035435 |
| C  | 4.998576  | 1.211537  | 0.518469  |
| H  | 4.473047  | 2.020764  | 1.018693  |
| C  | 6.400165  | -0.876006 | -0.683966 |
| H  | 6.922783  | -1.694252 | -1.167238 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 6.383055  | 1.245402  | 0.474916  |
| C | 5.007687  | -0.895262 | -0.633883 |
| H | 4.487607  | -1.727880 | -1.100553 |
| C | 7.100295  | 0.200298  | -0.126865 |
| H | 6.933994  | 2.071577  | 0.915304  |
| C | -2.268469 | 0.288455  | 4.764051  |
| H | -3.318763 | 0.239171  | 5.065756  |
| H | -1.721811 | -0.538171 | 5.227231  |
| H | -1.840692 | 1.236354  | 5.103445  |
| O | 8.450935  | 0.324093  | -0.117879 |
| C | 9.221685  | -0.712643 | -0.706557 |
| H | 10.264453 | -0.416227 | -0.584177 |
| H | 9.054996  | -1.671690 | -0.201045 |
| H | 8.998116  | -0.820367 | -1.774947 |

### <sup>3</sup>MC

|    |           |           |           |
|----|-----------|-----------|-----------|
| C  | 2.025048  | 1.157530  | -0.565183 |
| C  | 0.636833  | 1.122853  | -0.508884 |
| N  | -0.007239 | 0.021988  | -0.049546 |
| C  | 0.689972  | -1.033723 | 0.437922  |
| C  | 2.079286  | -1.037928 | 0.406151  |
| C  | 2.779831  | 0.059158  | -0.122534 |
| C  | -0.275885 | 2.213402  | -0.871144 |
| C  | -0.169889 | -2.068333 | 1.025824  |
| N  | -1.498566 | -1.758762 | 1.029593  |
| C  | -2.376164 | -2.608994 | 1.585988  |
| C  | -1.981160 | -3.811611 | 2.156719  |
| C  | -0.627506 | -4.144897 | 2.146328  |
| C  | 0.286385  | -3.264944 | 1.576126  |
| C  | 0.118561  | 3.447274  | -1.386097 |
| C  | -0.844569 | 4.416648  | -1.645181 |
| C  | -2.184859 | 4.135778  | -1.382747 |
| C  | -2.517507 | 2.887400  | -0.874861 |
| N  | -1.591781 | 1.946189  | -0.628153 |
| Ru | -1.990655 | -0.059363 | -0.124325 |
| O  | -1.990478 | -1.005878 | -2.090079 |
| C  | -3.046060 | -1.326438 | -2.728889 |
| C  | -2.811931 | -1.971311 | -4.075377 |
| C  | -4.372633 | -1.134707 | -2.293327 |
| C  | -4.793251 | -0.563687 | -1.084616 |
| O  | -4.035376 | -0.110285 | -0.152641 |
| C  | -6.269165 | -0.447346 | -0.797624 |
| H  | 2.526296  | 2.030812  | -0.966178 |
| H  | 2.626540  | -1.874824 | 0.824562  |
| H  | -3.415660 | -2.300240 | 1.559294  |
| H  | -2.723273 | -4.468269 | 2.597234  |
| H  | -0.284721 | -5.079267 | 2.579358  |
| H  | 1.342441  | -3.508665 | 1.558478  |
| H  | 1.165046  | 3.650410  | -1.582728 |
| H  | -0.550141 | 5.381566  | -2.045541 |
| H  | -2.963774 | 4.867677  | -1.566007 |
| H  | -3.542809 | 2.609341  | -0.655954 |
| H  | -2.218832 | -2.883590 | -3.943506 |
| H  | -3.741608 | -2.222772 | -4.590957 |
| H  | -2.225129 | -1.294026 | -4.706408 |
| H  | -5.155503 | -1.466943 | -2.965949 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | -6.885353 | -0.826770 | -1.615450 |
| H | -6.509475 | -1.002154 | 0.116796  |
| H | -6.525281 | 0.602432  | -0.614081 |
| N | -2.070533 | 1.682532  | 3.682766  |
| C | -1.822942 | 2.066846  | 4.750061  |
| C | 4.252046  | 0.065409  | -0.188174 |
| C | 4.985196  | 1.256261  | -0.026922 |
| H | 4.469774  | 2.189312  | 0.184143  |
| C | 6.358330  | -1.127088 | -0.496761 |
| H | 6.870352  | -2.062182 | -0.694148 |
| C | 6.368020  | 1.260076  | -0.093086 |
| C | 4.968141  | -1.116963 | -0.420851 |
| H | 4.435287  | -2.050785 | -0.579624 |
| C | 7.070195  | 0.067557  | -0.330961 |
| H | 6.930319  | 2.178643  | 0.045886  |
| C | -1.514802 | 2.549182  | 6.087620  |
| H | -2.429279 | 2.606713  | 6.685151  |
| H | -0.812673 | 1.869194  | 6.578801  |
| H | -1.064318 | 3.544513  | 6.032583  |
| O | 8.416929  | 0.175638  | -0.382116 |
| C | 9.179783  | -1.001322 | -0.612474 |
| H | 10.223521 | -0.684826 | -0.607467 |
| H | 9.019737  | -1.741408 | 0.180462  |
| H | 8.939739  | -1.447813 | -1.584646 |

---

**R = H**

**Ground state (<sup>1</sup>GS)**

|    |           |           |           |
|----|-----------|-----------|-----------|
| C  | -1.822571 | 1.220231  | -0.273561 |
| C  | -0.428559 | 1.201163  | -0.308385 |
| N  | 0.220679  | 0.018525  | -0.395204 |
| C  | -0.424291 | -1.169300 | -0.422952 |
| C  | -1.818219 | -1.196642 | -0.390374 |
| C  | -2.512993 | 0.010018  | -0.321010 |
| C  | 0.477412  | 2.364192  | -0.244928 |
| C  | 0.485870  | -2.329753 | -0.471877 |
| N  | 1.818823  | -2.030393 | -0.437314 |
| C  | 2.714015  | -3.025618 | -0.486140 |
| C  | 2.342248  | -4.363528 | -0.564936 |
| C  | 0.987082  | -4.680356 | -0.597413 |
| C  | 0.050817  | -3.651500 | -0.551918 |
| C  | 0.037593  | 3.685930  | -0.197326 |
| C  | 0.970143  | 4.717730  | -0.143053 |
| C  | 2.326444  | 4.404110  | -0.140733 |
| C  | 2.703030  | 3.066180  | -0.191187 |
| N  | 1.811429  | 2.067683  | -0.238921 |
| Ru | 2.174907  | 0.019131  | -0.335298 |
| O  | 2.017453  | -0.080363 | 1.713142  |
| C  | 3.009032  | -0.117389 | 2.519898  |
| C  | 2.619612  | -0.188516 | 3.977194  |
| C  | 4.370754  | -0.098415 | 2.181802  |
| C  | 4.922120  | -0.034977 | 0.887821  |
| O  | 4.269153  | 0.016624  | -0.204863 |
| C  | 6.425133  | -0.025247 | 0.735273  |
| H  | -2.366282 | 2.155338  | -0.203203 |
| H  | -2.358559 | -2.136119 | -0.410656 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | 3.754999  | -2.721902 | -0.460840 |
| H | 3.105720  | -5.133197 | -0.599680 |
| H | 0.659198  | -5.713170 | -0.659950 |
| H | -1.009162 | -3.877375 | -0.581923 |
| H | -1.023192 | 3.909844  | -0.205840 |
| H | 0.638538  | 5.750580  | -0.105865 |
| H | 3.087136  | 5.176277  | -0.100800 |
| H | 3.745101  | 2.765177  | -0.194947 |
| H | 2.007198  | -1.080904 | 4.150744  |
| H | 3.486715  | -0.218750 | 4.640617  |
| H | 2.003573  | 0.680491  | 4.235745  |
| H | 5.073322  | -0.136900 | 3.006888  |
| H | 6.944991  | -0.067937 | 1.695022  |
| H | 6.737638  | -0.879466 | 0.123469  |
| H | 6.734440  | 0.881889  | 0.203283  |
| N | 2.356707  | 0.116589  | -2.333483 |
| C | 2.478345  | 0.173419  | -3.485762 |
| H | -3.597688 | 0.006751  | -0.293833 |
| C | 2.636714  | 0.244825  | -4.927140 |
| H | 3.669178  | 0.007267  | -5.201071 |
| H | 1.966614  | -0.470820 | -5.413031 |
| H | 2.397645  | 1.252493  | -5.280460 |

### <sup>3</sup>MLCT

|    |           |           |           |
|----|-----------|-----------|-----------|
| C  | 2.580251  | 1.206164  | -0.097598 |
| C  | 1.197186  | 1.198860  | -0.000874 |
| N  | 0.533057  | 0.005029  | 0.093983  |
| C  | 1.196542  | -1.193032 | 0.105610  |
| C  | 2.579105  | -1.209318 | 0.005358  |
| C  | 3.305725  | -0.004248 | -0.101757 |
| C  | 0.313465  | 2.344592  | 0.015924  |
| C  | 0.314131  | -2.330817 | 0.248414  |
| N  | -1.019641 | -2.009943 | 0.373166  |
| C  | -1.934431 | -2.982011 | 0.559070  |
| C  | -1.589949 | -4.319020 | 0.603251  |
| C  | -0.236135 | -4.670135 | 0.457347  |
| C  | 0.709572  | -3.676639 | 0.282939  |
| C  | 0.709176  | 3.687513  | -0.078852 |
| C  | -0.238099 | 4.692669  | -0.013668 |
| C  | -1.593548 | 4.356729  | 0.152248  |
| C  | -1.938000 | 3.021796  | 0.238382  |
| N  | -1.021243 | 2.037258  | 0.160141  |
| Ru | -1.459328 | 0.008311  | 0.156621  |
| O  | -1.403824 | -0.098445 | -1.848023 |
| C  | -2.425913 | -0.143424 | -2.623081 |
| C  | -2.087331 | -0.225981 | -4.086649 |
| C  | -3.769959 | -0.120568 | -2.219902 |
| C  | -4.240681 | -0.039762 | -0.902651 |
| O  | -3.502398 | 0.021034  | 0.147619  |
| C  | -5.720526 | -0.016308 | -0.635308 |
| H  | 3.106535  | 2.149566  | -0.195362 |
| H  | 3.109111  | -2.154845 | 0.044218  |
| H  | -2.961475 | -2.650052 | 0.667072  |
| H  | -2.358828 | -5.069002 | 0.751299  |
| H  | 0.068104  | -5.711787 | 0.486438  |
| H  | 1.758615  | -3.930098 | 0.174967  |

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | 1.759457  | 3.929453  | -0.200035 |
| H | 0.065939  | 5.732335  | -0.084970 |
| H | -2.363675 | 5.117218  | 0.216708  |
| H | -2.965555 | 2.699792  | 0.368494  |
| H | -1.480679 | -1.119587 | -4.271415 |
| H | -2.978377 | -0.261764 | -4.716128 |
| H | -1.481572 | 0.641741  | -4.370944 |
| H | -4.515016 | -0.165500 | -3.005568 |
| H | -6.309441 | -0.077847 | -1.552403 |
| H | -5.986756 | -0.853345 | 0.019945  |
| H | -5.980628 | 0.905920  | -0.103345 |
| N | -1.541623 | 0.115247  | 2.191562  |
| C | -1.600680 | 0.175013  | 3.345249  |
| C | 4.777218  | -0.010903 | -0.207772 |
| C | 5.549683  | 1.026914  | 0.344102  |
| H | 5.062555  | 1.833222  | 0.886292  |
| C | 6.837639  | -1.064382 | -0.967624 |
| H | 7.332388  | -1.879959 | -1.488883 |
| C | 6.938214  | 1.019351  | 0.239170  |
| C | 5.448993  | -1.056716 | -0.866310 |
| H | 4.878008  | -1.857496 | -1.329181 |
| C | 7.590437  | -0.026185 | -0.416423 |
| H | 7.513238  | 1.828983  | 0.681324  |
| H | 8.674136  | -0.031861 | -0.496796 |
| C | -1.679343 | 0.249683  | 4.791180  |
| H | -2.725765 | 0.214717  | 5.107897  |
| H | -1.140858 | -0.593173 | 5.234255  |
| H | -1.229595 | 1.184836  | 5.137418  |

### <sup>3</sup>MC

|    |           |           |           |
|----|-----------|-----------|-----------|
| C  | 2.555487  | 1.184475  | -0.294099 |
| C  | 1.172681  | 1.180823  | -0.149216 |
| N  | 0.494843  | 0.012535  | -0.027249 |
| C  | 1.158202  | -1.169267 | 0.028376  |
| C  | 2.540891  | -1.209622 | -0.110026 |
| C  | 3.267940  | -0.023633 | -0.293503 |
| C  | 0.306695  | 2.362256  | -0.066580 |
| C  | 0.279797  | -2.312644 | 0.304034  |
| N  | -1.025936 | -1.978912 | 0.510762  |
| C  | -1.914102 | -2.936048 | 0.820327  |
| C  | -1.553543 | -4.272690 | 0.930162  |
| C  | -0.223853 | -4.627595 | 0.707953  |
| C  | 0.701816  | -3.638547 | 0.392349  |
| C  | 0.743963  | 3.680812  | -0.184942 |
| C  | -0.172947 | 4.717004  | -0.044189 |
| C  | -1.509431 | 4.415596  | 0.214951  |
| C  | -1.885088 | 3.082936  | 0.318381  |
| N  | -1.004816 | 2.079058  | 0.177465  |
| Ru | -1.490337 | 0.031195  | 0.037838  |
| O  | -1.679708 | -0.222850 | -2.134087 |
| C  | -2.791635 | -0.288834 | -2.752062 |
| C  | -2.689025 | -0.477095 | -4.248445 |
| C  | -4.072651 | -0.202901 | -2.169405 |
| C  | -4.375790 | -0.033565 | -0.812024 |
| O  | -3.533031 | 0.069825  | 0.151151  |
| C  | -5.820369 | 0.040205  | -0.384075 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | 3.082796  | 2.123118  | -0.419944 |
| H | 3.064425  | -2.155984 | -0.039336 |
| H | -2.934389 | -2.602571 | 0.976792  |
| H | -2.303083 | -5.014014 | 1.184421  |
| H | 0.091654  | -5.663532 | 0.781299  |
| H | 1.739742  | -3.897556 | 0.216754  |
| H | 1.787307  | 3.896812  | -0.384692 |
| H | 0.154009  | 5.748066  | -0.133822 |
| H | -2.252986 | 5.195617  | 0.336539  |
| H | -2.910541 | 2.788134  | 0.513563  |
| H | -2.137592 | -1.399976 | -4.462131 |
| H | -3.665146 | -0.525203 | -4.736758 |
| H | -2.113495 | 0.349369  | -4.680953 |
| H | -4.917661 | -0.275364 | -2.844965 |
| H | -6.510889 | -0.063522 | -1.223763 |
| H | -6.026887 | -0.749128 | 0.347842  |
| H | -6.006687 | 0.998543  | 0.114461  |
| N | -1.545309 | 0.248785  | 3.119086  |
| C | -0.977071 | 0.284974  | 4.131142  |
| C | 4.737040  | -0.047055 | -0.455216 |
| C | 5.536523  | 0.969646  | 0.090942  |
| H | 5.078641  | 1.770127  | 0.665995  |
| C | 6.742861  | -1.110812 | -1.318842 |
| H | 7.207043  | -1.919185 | -1.877180 |
| C | 6.920074  | 0.943471  | -0.064832 |
| C | 5.359450  | -1.088978 | -1.161174 |
| H | 4.756797  | -1.871660 | -1.614560 |
| C | 7.527814  | -0.095505 | -0.770982 |
| H | 7.524659  | 1.732985  | 0.373162  |
| H | 8.607350  | -0.113881 | -0.893263 |
| C | -0.267959 | 0.330099  | 5.400535  |
| H | -0.982578 | 0.388586  | 6.226687  |
| H | 0.341069  | -0.570515 | 5.521272  |
| H | 0.385083  | 1.207052  | 5.433488  |

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**R = NO<sub>2</sub>**

**Ground state (<sup>1</sup>GS)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 1.883688  | 1.207503  | -0.025816 |
| C | 0.494819  | 1.191929  | 0.050947  |
| N | -0.157601 | 0.014833  | 0.179516  |
| C | 0.490496  | -1.171301 | 0.206926  |
| C | 1.879134  | -1.201268 | 0.129940  |
| C | 2.596795  | -0.000464 | 0.018855  |
| C | -0.409076 | 2.357266  | -0.012874 |
| C | -0.416635 | -2.330976 | 0.314525  |
| N | -1.749139 | -2.027993 | 0.328623  |
| C | -2.644778 | -3.018551 | 0.427756  |
| C | -2.273682 | -4.356245 | 0.512926  |
| C | -0.919140 | -4.676943 | 0.497394  |
| C | 0.017857  | -3.652360 | 0.398405  |
| C | 0.030044  | 3.675666  | -0.115780 |
| C | -0.903640 | 4.706707  | -0.169167 |
| C | -2.259463 | 4.395501  | -0.115493 |
| C | -2.635205 | 3.060413  | -0.010972 |
| N | -1.742675 | 2.063364  | 0.036987  |

|    |           |           |           |
|----|-----------|-----------|-----------|
| Ru | -2.106208 | 0.019507  | 0.199772  |
| O  | -2.044449 | -0.125146 | -1.849652 |
| C  | -3.072756 | -0.192494 | -2.607515 |
| C  | -2.750201 | -0.301526 | -4.078530 |
| C  | -4.417214 | -0.173474 | -2.206442 |
| C  | -4.908649 | -0.071013 | -0.891173 |
| O  | -4.206206 | 0.017359  | 0.168113  |
| C  | -6.402867 | -0.058846 | -0.670073 |
| H  | 2.413638  | 2.144513  | -0.152735 |
| H  | 2.408654  | -2.145805 | 0.176678  |
| H  | -3.684532 | -2.710125 | 0.437228  |
| H  | -3.037169 | -5.122874 | 0.589334  |
| H  | -0.591892 | -5.709713 | 0.563201  |
| H  | 1.077337  | -3.882289 | 0.388896  |
| H  | 1.090509  | 3.898014  | -0.152185 |
| H  | -0.572992 | 5.737356  | -0.249590 |
| H  | -3.020413 | 5.167530  | -0.152933 |
| H  | -3.676003 | 2.759062  | 0.037695  |
| H  | -2.137239 | -1.192971 | -4.254922 |
| H  | -3.646548 | -0.358109 | -4.699992 |
| H  | -2.155582 | 0.565251  | -4.389425 |
| H  | -5.156855 | -0.241129 | -2.996410 |
| H  | -6.965560 | -0.143167 | -1.602440 |
| H  | -6.683013 | -0.886628 | -0.008435 |
| H  | -6.691265 | 0.869676  | -0.163755 |
| N  | -2.195619 | 0.164208  | 2.202742  |
| C  | -2.264898 | 0.249682  | 3.357367  |
| C  | 4.073642  | -0.008162 | -0.059907 |
| C  | 4.826711  | 1.001143  | 0.563257  |
| H  | 4.328164  | 1.780660  | 1.130952  |
| C  | 6.132391  | -1.038280 | -0.836042 |
| H  | 6.656513  | -1.814221 | -1.380907 |
| C  | 6.213153  | 0.999941  | 0.494518  |
| C  | 4.746587  | -1.024860 | -0.758319 |
| H  | 4.183156  | -1.798887 | -1.269981 |
| C  | 6.847656  | -0.022677 | -0.206344 |
| H  | 6.799835  | 1.769865  | 0.981049  |
| N  | 8.305554  | -0.030536 | -0.282841 |
| O  | 8.915835  | 0.878177  | 0.271763  |
| O  | 8.844660  | -0.945438 | -0.897758 |
| C  | -2.358093 | 0.356519  | 4.802043  |
| H  | -3.407149 | 0.320823  | 5.111206  |
| H  | -1.819969 | -0.471104 | 5.273938  |
| H  | -1.920859 | 1.302248  | 5.136190  |

### <sup>3</sup>MLCT

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 1.888210  | 1.212319  | -0.002473 |
| C | 0.509093  | 1.192706  | 0.061046  |
| N | -0.157653 | 0.006044  | 0.144057  |
| C | 0.510746  | -1.182399 | 0.163832  |
| C | 1.889311  | -1.205620 | 0.092427  |
| C | 2.631285  | 0.002321  | 0.006054  |
| C | -0.385105 | 2.346249  | 0.056533  |
| C | -0.380714 | -2.331403 | 0.290449  |
| N | -1.711486 | -2.017992 | 0.360772  |
| C | -2.629464 | -2.986543 | 0.521581  |



|                       |           |           |           |
|-----------------------|-----------|-----------|-----------|
| C                     | -2.278489 | -4.324423 | 0.594660  |
| C                     | -0.925318 | -4.666903 | 0.508938  |
| C                     | 0.024600  | -3.667129 | 0.360112  |
| C                     | 0.017893  | 3.683235  | -0.003721 |
| C                     | -0.934941 | 4.690557  | 0.032485  |
| C                     | -2.288834 | 4.355178  | 0.136420  |
| C                     | -2.637477 | 3.016080  | 0.195131  |
| N                     | -1.716089 | 2.038857  | 0.144077  |
| Ru                    | -2.150801 | 0.004532  | 0.136103  |
| O                     | -2.030419 | -0.108800 | -1.863067 |
| C                     | -3.024356 | -0.152087 | -2.674250 |
| C                     | -2.635831 | -0.239799 | -4.124073 |
| C                     | -4.381230 | -0.123396 | -2.315222 |
| C                     | -4.892407 | -0.040446 | -1.014041 |
| O                     | -4.183668 | 0.016547  | 0.058444  |
| C                     | -6.378124 | -0.010801 | -0.789274 |
| H                     | 2.399941  | 2.162845  | -0.093794 |
| H                     | 2.406075  | -2.156306 | 0.145853  |
| H                     | -3.660998 | -2.658486 | 0.585065  |
| H                     | -3.049252 | -5.076735 | 0.718232  |
| H                     | -0.615517 | -5.705696 | 0.564261  |
| H                     | 1.078044  | -3.916206 | 0.301162  |
| H                     | 1.071770  | 3.927224  | -0.074181 |
| H                     | -0.627271 | 5.730434  | -0.013533 |
| H                     | -3.061795 | 5.114421  | 0.174274  |
| H                     | -3.668680 | 2.692157  | 0.279949  |
| H                     | -2.027201 | -1.136583 | -4.285178 |
| H                     | -3.505092 | -0.273448 | -4.783249 |
| H                     | -2.016767 | 0.624585  | -4.388989 |
| H                     | -5.100772 | -0.166446 | -3.124227 |
| H                     | -6.939659 | -0.061216 | -1.723947 |
| H                     | -6.667654 | -0.852106 | -0.149566 |
| H                     | -6.648196 | 0.908255  | -0.256984 |
| N                     | -2.302556 | 0.114766  | 2.165371  |
| C                     | -2.400711 | 0.176904  | 3.316106  |
| C                     | 4.084336  | -0.000254 | -0.063135 |
| C                     | 4.844040  | 1.140150  | 0.301693  |
| H                     | 4.345460  | 2.028847  | 0.675480  |
| C                     | 6.180143  | -1.153069 | -0.565955 |
| H                     | 6.715465  | -2.028078 | -0.915370 |
| C                     | 6.223146  | 1.142751  | 0.242135  |
| C                     | 4.801443  | -1.143754 | -0.497872 |
| H                     | 4.266033  | -2.029537 | -0.824690 |
| C                     | 6.898539  | -0.007116 | -0.193400 |
| H                     | 6.792670  | 2.015240  | 0.539932  |
| N                     | 8.324040  | -0.011238 | -0.257330 |
| O                     | 8.936159  | 1.019925  | 0.066030  |
| O                     | 8.898686  | -1.046023 | -0.633587 |
| C                     | -2.528266 | 0.254625  | 4.757922  |
| H                     | -3.584663 | 0.212505  | 5.038775  |
| H                     | -1.998442 | -0.583146 | 5.220624  |
| H                     | -2.097206 | 1.194237  | 5.115715  |
| <b><sup>3</sup>MC</b> |           |           |           |
| C                     | 1.900717  | 1.068997  | -0.579190 |
| C                     | 0.510968  | 1.063252  | -0.543075 |

|    |           |           |           |
|----|-----------|-----------|-----------|
| N  | -0.159757 | -0.011447 | -0.057281 |
| C  | 0.507556  | -1.068723 | 0.470355  |
| C  | 1.897033  | -1.105223 | 0.450249  |
| C  | 2.618445  | -0.034540 | -0.097159 |
| C  | -0.374398 | 2.159532  | -0.950476 |
| C  | -0.380058 | -2.067218 | 1.076872  |
| N  | -1.701564 | -1.728386 | 1.055334  |
| C  | -2.604956 | -2.542791 | 1.623893  |
| C  | -2.243195 | -3.737250 | 2.232458  |
| C  | -0.897314 | -4.100425 | 2.248504  |
| C  | 0.043211  | -3.257395 | 1.665968  |
| C  | 0.050688  | 3.366907  | -1.502341 |
| C  | -0.890100 | 4.346650  | -1.801609 |
| C  | -2.237951 | 4.102160  | -1.541984 |
| C  | -2.601210 | 2.878089  | -0.996856 |
| N  | -1.697294 | 1.926991  | -0.711773 |
| Ru | -2.138830 | -0.054652 | -0.147661 |
| O  | -2.156966 | -1.030622 | -2.091253 |
| C  | -3.215783 | -1.340325 | -2.731454 |
| C  | -2.986375 | -2.005077 | -4.068434 |
| C  | -4.539473 | -1.120150 | -2.302710 |
| C  | -4.949881 | -0.528016 | -1.100774 |
| O  | -4.181794 | -0.075185 | -0.176760 |
| C  | -6.422567 | -0.385781 | -0.811364 |
| H  | 2.428397  | 1.919903  | -0.994284 |
| H  | 2.424213  | -1.943516 | 0.890963  |
| H  | -3.636710 | -2.211866 | 1.575316  |
| H  | -3.004907 | -4.364967 | 2.681525  |
| H  | -0.580810 | -5.029580 | 2.711540  |
| H  | 1.093453  | -3.525534 | 1.669457  |
| H  | 1.102542  | 3.541802  | -1.696949 |
| H  | -0.572357 | 5.291565  | -2.230688 |
| H  | -2.999769 | 4.843761  | -1.755424 |
| H  | -3.633880 | 2.629658  | -0.777234 |
| H  | -2.413724 | -2.928129 | -3.922026 |
| H  | -3.917996 | -2.242685 | -4.586947 |
| H  | -2.381221 | -1.347615 | -4.703008 |
| H  | -5.326989 | -1.447481 | -2.972186 |
| H  | -7.046273 | -0.765130 | -1.623430 |
| H  | -6.668655 | -0.926669 | 0.109808  |
| H  | -6.662063 | 0.669761  | -0.639075 |
| N  | -2.170300 | 1.723278  | 3.644797  |
| C  | -2.188999 | 2.209002  | 4.699190  |
| C  | 4.095735  | -0.061861 | -0.143122 |
| C  | 4.842817  | 1.107311  | 0.077547  |
| H  | 4.340224  | 2.039970  | 0.314152  |
| C  | 6.160742  | -1.300777 | -0.460668 |
| H  | 6.689642  | -2.221247 | -0.676699 |
| C  | 6.230038  | 1.083199  | 0.033270  |
| C  | 4.774045  | -1.262652 | -0.411335 |
| H  | 4.214046  | -2.171118 | -0.610676 |
| C  | 6.870335  | -0.123715 | -0.236446 |
| H  | 6.812708  | 1.978750  | 0.212518  |
| N  | 8.329490  | -0.155989 | -0.284914 |
| O  | 8.934994  | 0.892443  | -0.085819 |
| O  | 8.873507  | -1.229897 | -0.522139 |
| C  | -2.212822 | 2.816815  | 6.020841  |

|   |           |          |          |
|---|-----------|----------|----------|
| H | -3.104347 | 3.441164 | 6.130368 |
| H | -2.227832 | 2.039599 | 6.790526 |
| H | -1.324611 | 3.439277 | 6.163234 |

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**R = CHO**

**Ground state (<sup>1</sup>GS)**

|    |           |           |           |
|----|-----------|-----------|-----------|
| C  | 2.137808  | 1.144695  | -0.059097 |
| C  | 0.750409  | 1.155814  | 0.041732  |
| N  | 0.076423  | -0.009167 | 0.165701  |
| C  | 0.701184  | -1.207837 | 0.167280  |
| C  | 2.087613  | -1.264202 | 0.068284  |
| C  | 2.828765  | -0.077139 | -0.041061 |
| C  | -0.130849 | 2.339741  | 0.007160  |
| C  | -0.227612 | -2.350685 | 0.272091  |
| N  | -1.553750 | -2.022158 | 0.308142  |
| C  | -2.467246 | -2.996468 | 0.406625  |
| C  | -2.121467 | -4.342172 | 0.469516  |
| C  | -0.773816 | -4.688788 | 0.431140  |
| C  | 0.181572  | -3.681340 | 0.332491  |
| C  | 0.333762  | 3.650530  | -0.080997 |
| C  | -0.579288 | 4.700896  | -0.107854 |
| C  | -1.940498 | 4.416231  | -0.042822 |
| C  | -2.341930 | 3.087584  | 0.046875  |
| N  | -1.469451 | 2.072021  | 0.069503  |
| Ru | -1.872346 | 0.032978  | 0.210216  |
| O  | -1.833335 | -0.087147 | -1.842043 |
| C  | -2.870434 | -0.123551 | -2.589815 |
| C  | -2.565414 | -0.218401 | -4.065645 |
| C  | -4.210203 | -0.083934 | -2.174552 |
| C  | -4.686703 | 0.008569  | -0.852926 |
| O  | -3.972650 | 0.068939  | 0.200439  |
| C  | -6.178333 | 0.044501  | -0.616776 |
| H  | 2.683866  | 2.072514  | -0.184761 |
| H  | 2.599218  | -2.219390 | 0.094586  |
| H  | -3.500509 | -2.667920 | 0.434128  |
| H  | -2.898734 | -5.094777 | 0.546490  |
| H  | -0.465937 | -5.728505 | 0.478930  |
| H  | 1.236088  | -3.931666 | 0.304902  |
| H  | 1.398183  | 3.851687  | -0.125715 |
| H  | -0.228763 | 5.725821  | -0.176569 |
| H  | -2.686072 | 5.203842  | -0.059923 |
| H  | -3.388020 | 2.806555  | 0.103494  |
| H  | -1.971460 | -1.118769 | -4.260767 |
| H  | -3.469131 | -0.249362 | -4.678178 |
| H  | -1.957612 | 0.641150  | -4.371104 |
| H  | -4.958899 | -0.126286 | -2.957748 |
| H  | -6.751679 | -0.019947 | -1.544248 |
| H  | -6.466395 | -0.785314 | 0.038871  |
| H  | -6.445514 | 0.972428  | -0.097828 |
| N  | -1.936407 | 0.154871  | 2.215172  |
| C  | -1.990455 | 0.228929  | 3.371472  |
| C  | 4.303563  | -0.112839 | -0.147254 |
| C  | 5.088112  | 0.880161  | 0.468870  |
| H  | 4.610228  | 1.663890  | 1.049816  |
| C  | 6.328758  | -1.166872 | -0.963905 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | 6.814494  | -1.958573 | -1.529840 |
| C | 6.470540  | 0.848002  | 0.371163  |
| C | 4.942930  | -1.136773 | -0.864468 |
| H | 4.353328  | -1.896005 | -1.369930 |
| C | 7.102304  | -0.176646 | -0.347422 |
| H | 7.079664  | 1.606825  | 0.853511  |
| C | -2.065006 | 0.322422  | 4.818215  |
| H | -3.111128 | 0.309580  | 5.138900  |
| H | -1.542595 | -0.523293 | 5.275466  |
| H | -1.600624 | 1.253322  | 5.157344  |
| C | 8.572548  | -0.221424 | -0.458968 |
| O | 9.328567  | 0.592060  | 0.043468  |
| H | 8.969193  | -1.072656 | -1.049979 |

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