Supplementary Information

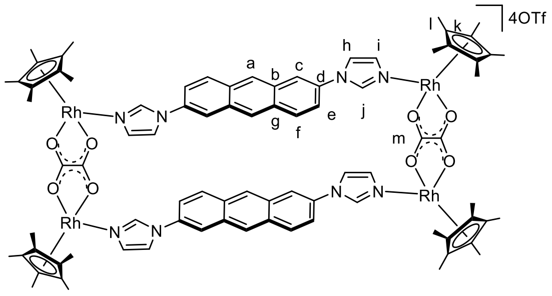
Table of Contents

1. Material and Methods

All starting materials were used as received from commercial sources unless otherwise stated. 2,6-di(1*H*-imidazol-1-yl)anthracene (**La**)[1], 2,7-di(pyridin-4-yl)anthracene (**Lb**)[2] and half-sandwich organometallic [$Cp^*_2Rh_2(\mu\text{-}\eta^4\text{-}C_2O_4)Cl_2$][3] were synthesized according to published procedures. The ^1H, $^{13}C\{^1H\}$ and 2D NMR spectra were recorded on Bruker AVANCE III 400, and JEOL ECZ400R spectrometers. Chemical shifts (*δ*) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard. All coupling constants are expressed in Hertz. Mass spectrum were obtained with a Bruker microTOF-Q II mass spectrometer (Bruker Daltonics USA) in the electrospray ionisation (ESI) mode. The UV/Vis experiments were conducted on an Agilent Cary-100 spectrophotometer. The photochemical [4+4] cycloadditions were conducted on a PL-LED100 lamp.

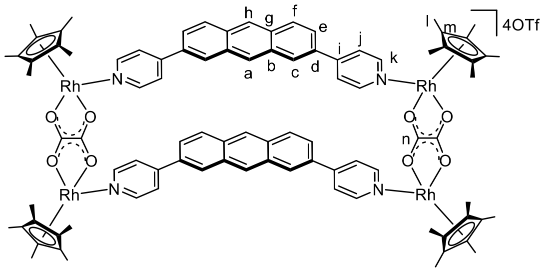
2. Synthesis of Anthracene-Based Tetranuclear Metallarectangles

2.1 Synthesis of Metallarectangle 1a



AgOTf (51.4 mg, 0.2 mmol) was added into a methanol solution (6 mL) of $[Cp^*_2Rh_2(\mu\text{-}\eta^4\text{-}C_2O_4)Cl_2]$ (31.8 mg, 0.05 mmol) and stirred for 6 hours protected from light. After centrifuging to remove AgCl, ligand **La** (15.5 mg, 0.05 mmol) and methanol (6 mL) were added into the clear solution and stirred overnight. The solution was filtered through a filter membrane, and the filtrate was crystallized by diethyl ether diffusion to obtain the tetranuclear metallarectangle **1a**, which was washed with diethyl ether and dried under vacuum. Yield: 49.8 mg, 85%. ^1H NMR (400 MHz, CD_3CN): $\delta = 8.06$ (t, $J = 1.4$ Hz, 4H, H_j), 7.90 (s, 4H, H_a), 7.74 (d, $J = 9.1$ Hz, 4H, H_f), 7.68 (t, $J = 1.6$ Hz, 4H, H_h), 7.65 (d, $J = 2.2$ Hz, 4H, H_c), 7.31 (dd, $J = 9.1, 2.3$ Hz, 4H, H_e), 6.80 (t, $J = 1.4$ Hz, 4H, H_i), 1.63 (s, 60H, H_l) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): $\delta = 171.5$ (C_m), 137.2 (C_h), 133.1 (C_g), 131.4 (C_c), 131.3 (C_b), 130.9 (C_e), 130.0 (C_a), 127.5 (C_j), 121.2 (C_i), 120.0 (C_d), 118.8 (C_f), 96.1 (C_k), 96.1 (C_k), 9.1(C_l) ppm. HRMS (ESI, positive ions): $m/z = 437.1020$ (calcd for $[\mathbf{1a}\text{-}4OTf]^{4+}$ 437.0731), $m/z = 632.4527$ (calcd for $[\mathbf{1a}\text{-}3OTf]^{3+}$ 632.4150), $m/z = 1023.1421$ (calcd for $[\mathbf{1a}\text{-}2OTf]^{2+}$ 1023.0987).

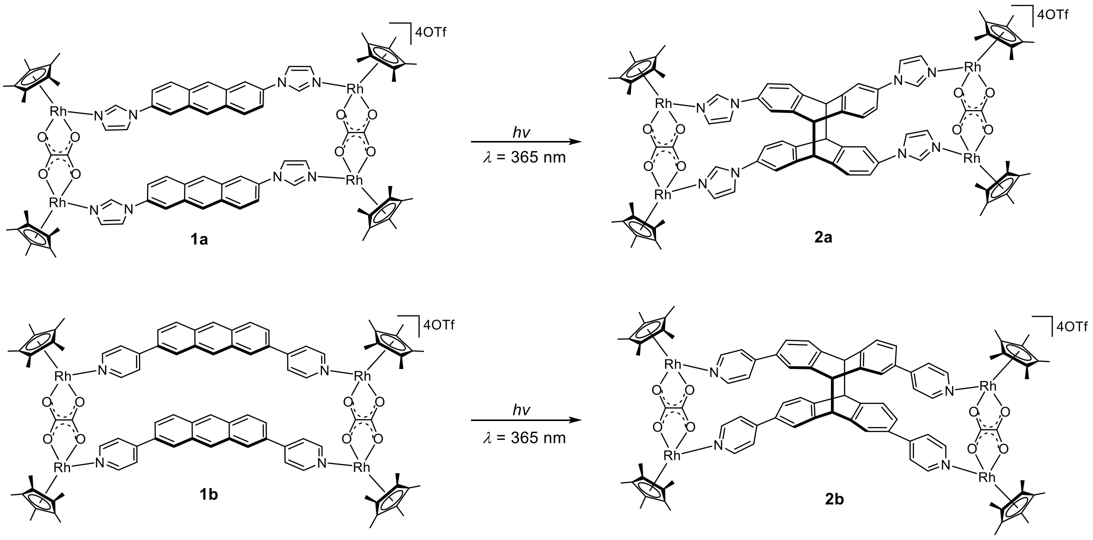
2.2 Synthesis of Metallarectangle 1b



AgOTf (51.4 mg, 0.2 mmol) was added into a methanol solution (6 mL) of $[Cp^*_2Rh_2(\mu\text{-}\eta^4\text{-}C_2O_4)Cl_2]$ (31.8 mg, 0.05 mmol) and stirred for 6 hours protected from light. After centrifuging to remove AgCl, ligand **Lb** (16.6 mg, 0.05 mmol) and methanol (6 mL) were added into the clear solution and stirred overnight. The solution was filtered through a filter membrane, and the filtrate was crystallized by diethyl ether diffusion to obtain the tetranuclear metallarectangle **2a**, which was washed with diethyl ether and dried under vacuum. Yield: 50.2 mg, 84%. ^1H NMR (400 MHz, CD_3CN): $\delta = 8.11$ (s, 2H, H_a), 8.04 (d, $J = 5.2$

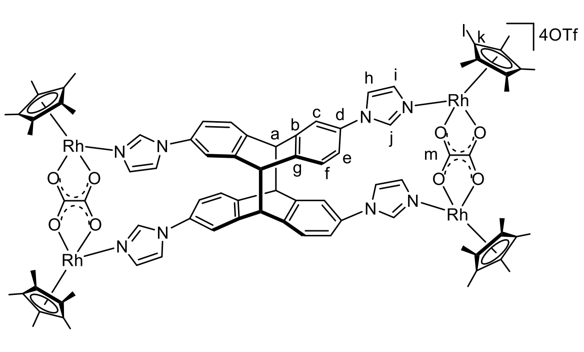
Hz, 8H, H_k), 8.02 (s, 4H, H_c), 7.91 (s, 2H, H_h), 7.75 (d, J = 6.1 Hz, 8H, H_j), 7.69 (d, J = 8.9 Hz, 4H, H_i), 7.37 (d, J = 8.6 Hz, 4H, H_e), 1.59 (s, 60H, H_m) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 171.4 (C_n), 151.9 (C_k), 151.3 (C_d), 132.4 (C_i), 132.3 (C_b), 131.4 (C_g), 130.5 (C_c), 130.1 (C_a), 128.8 (C_f), 126.7 (C_h), 124.9 (C_j), 124.2 (C_e), 96.5 (C_l), 96.4 (C_l), 8.9 (C_m) ppm. HRMS (ESI, positive ions): *m/z* = 448.1054 (calcd for [**1b**-4OTf]$^{4+}$ 448.0778), *m/z* = 647.1122 (calcd for [**1b**-3OTf]$^{3+}$ 647.0880).

3. Photochemical [4+4] Cycloadditions of Anthracene-Based Tetranuclear Metallarectangles



Scheme S1. Photochemical [4+4] cycloadditions of metallarectangles **2a** and **2b**.

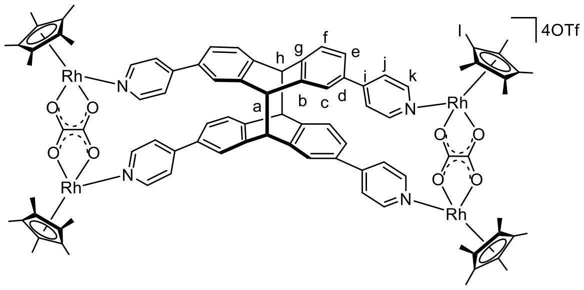
3.1 Synthesis of Complex 2a



A solution of **1a** (11.7 mg , 0.005 mmol) in CD_3CN (0.5 mL, c = 10 mM) in an NMR tube was irradiated with a LED lamp (λ = 365 nm) at ambient temperature for 2 h. Over this time the initially yellow solution turned brown. The conversion to **2a** was quantitative as judged by ^1H NMR spectroscopy. ^1H NMR (400 MHz, CD_3CN): δ = 7.66 (s, 4H, H_j), 7.50 (t, J = 1.5 Hz, 4H, H_h), 7.17 (d, J = 1.9 Hz, 4H, H_f), 7.10 (m, 8H, $H_{c,e}$), 7.06 (t, J = 1.5 Hz, 4H, H_i), 4.76 (s, 4H, H_a), 1.64 (s, 60H, H_l) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 170.8, 170.5, 145.7, 143.0, 136.3, 134.5, 130.1, 121.0, 96.2, 96.1, 52.9, 9.0 ppm. HRMS (ESI, positive ions): *m/z* =

437.0987 (calcd for [**2a**-4OTf]$^{4+}$ 437.0731), *m/z* = 632.4444 (calcd for [**2a**-3OTf]$^{3+}$ 632.4150), *m/z* = 1023.1323 (calcd for [**2a**-2OTf]$^{2+}$ 1023.0987).

3.2 Synthesis of Complex 2b



A solution of **1b** (12.0 mg , 0.005 mmol) in CD_3CN (0.5 mL, *c* = 10 mM) in an NMR tube was irradiated with a LED lamp ($\lambda = 365$ nm) at ambient temperature under a nitrogen atmosphere for 3 h. Over this time the initially yellow solution turned brown. The conversion to **2b** was quantitative as judged by ^1H NMR spectroscopy. ^1H NMR (400 MHz, CD_3CN): δ = 8.03 (d, *J* = 6.6 Hz, 8H, H_k), 7.64 (d, *J* = 6.7 Hz, 8H, H_j), 7.53 (d, *J* = 1.8 Hz, 4H, H_c), 7.37 (dd, *J* = 7.9, 1.9 Hz, 4H, H_e), 7.10 (d, *J* = 7.9 Hz, 4H, H_f), 4.88 (s, 2H, H_a), 4.73 (s, 2H, H_h), 1.60 (s, 60H, H_l) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 169.8, 169.7, 150.7, 149.6, 145.3, 143.9, 131.9, 129.2, 127.4, 124.2, 122.6, 95.7, 95.6, 52.78, 52.76, 8.0 ppm. HRMS (ESI, positive ions): *m/z* = 448.0992 (calcd for [**1b**-4OTf]$^{4+}$ 448.0778), *m/z* = 647.0859 (calcd for [**1b**-3OTf]$^{3+}$ 647.4224).

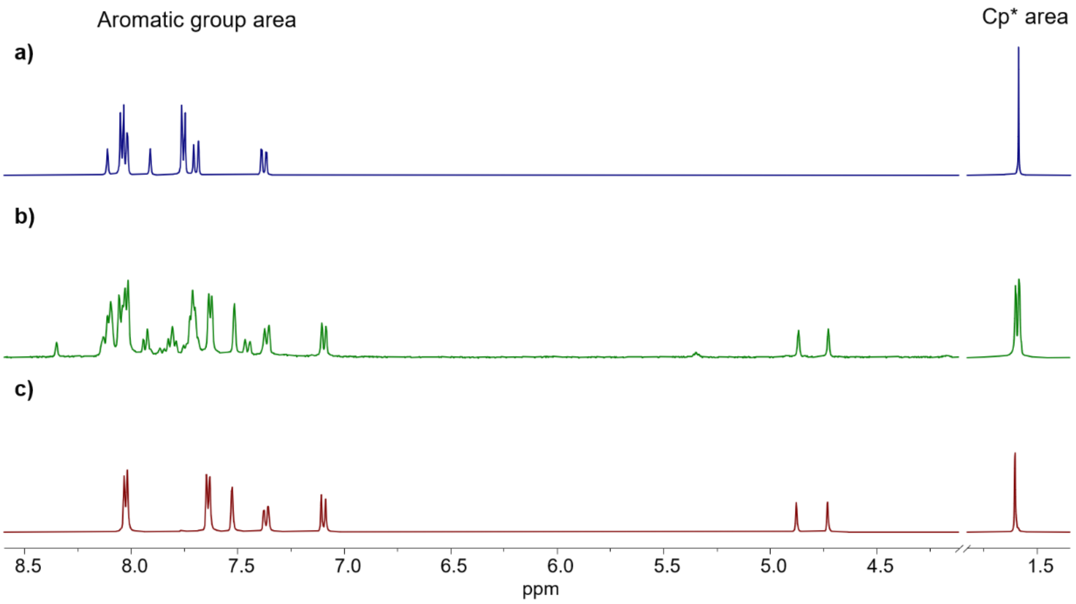


Figure S1. Sections of the ^1H NMR spectra in CD_3CN of complex **1b** a) before, b) after irradiation under an air atmosphere, and c) after irradiation under a nitrogen atmosphere. Noting that the spectra in the Cp* area have been divided by 15 for clarity.

4. Reversibility of Photochemical [4+4] Cycloaddition

The cleavage reactions were monitored by *in situ* ^{1}H NMR analysis. The solution of complexes **2a** and **2b** in CD_3CN (0.5 mL, c = 10 mM) in an NMR tube was irradiated at 254 nm at ambient temperature or heated in an oil bath under sealed conditions, in which **2b** is always maintained in nitrogen atmosphere.

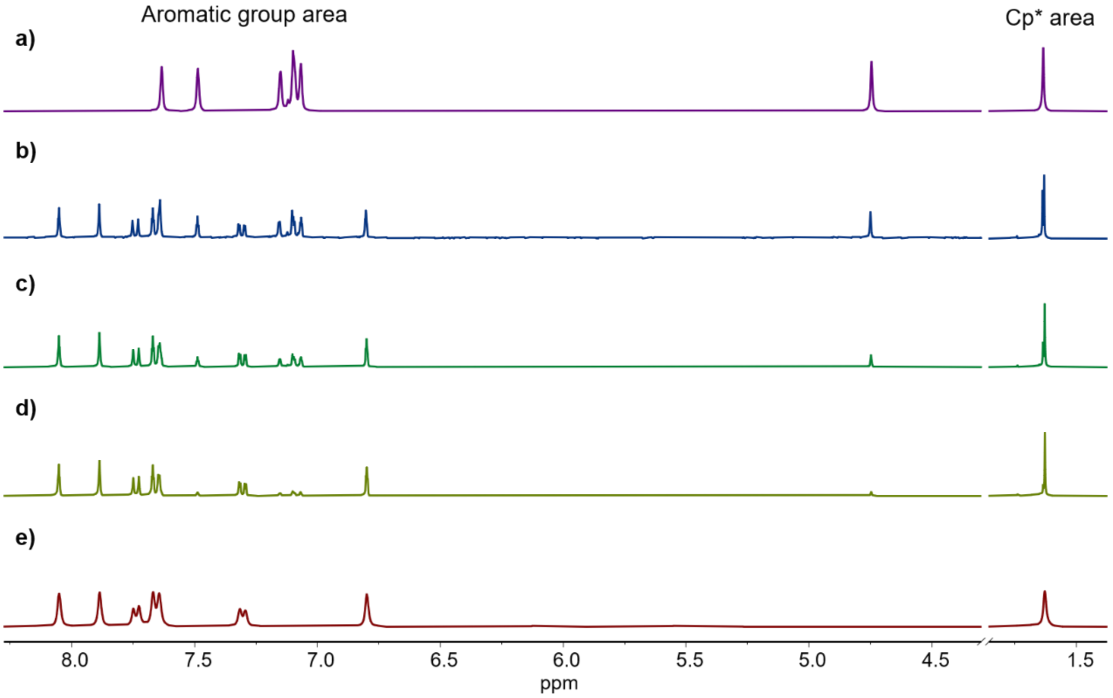


Figure S2. Sections of the ^{1}H NMR spectra in CD_3CN of complex **2a** after heating at 120 °C under air atmosphere for a) 0 h, b) 6 h, c) 20 h, d) 30 h, e) 50 h. Noting that the spectra in the Cp* area have been divided by 15 for clarity.

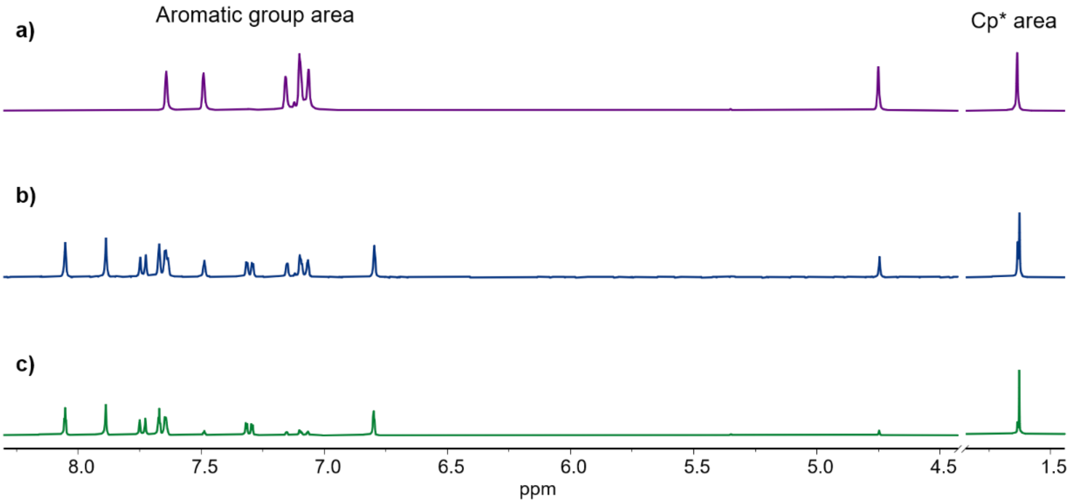


Figure S3. Sections of the ^{1}H NMR spectra in CD_3CN of complex **2a** after irradiation at λ = 254 nm under an air atmosphere for a) 0 h, b) 5 h, c) 15 h. Noting that the spectra in the Cp* area have been divided by 15 for clarity.

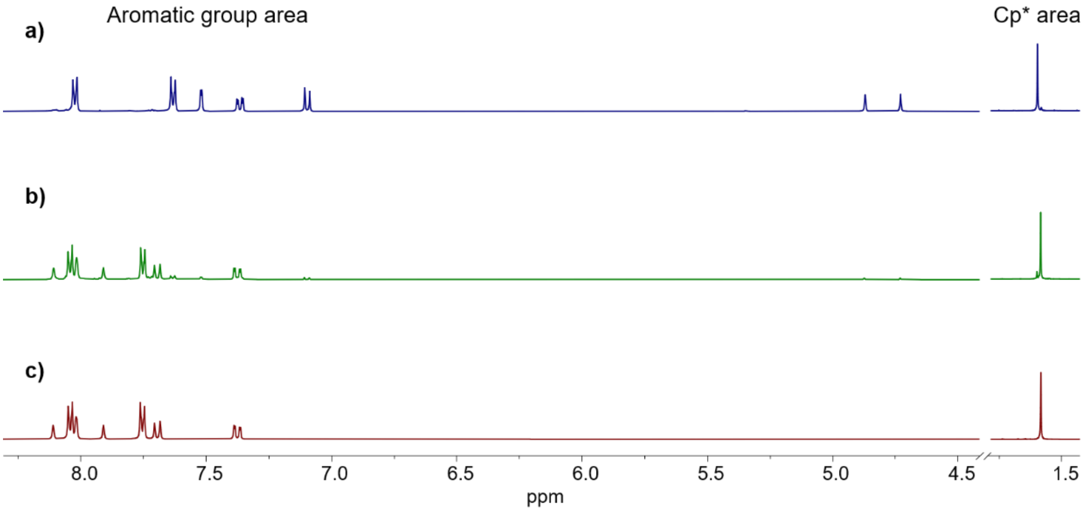


Figure S4. Sections of the ^{1}H NMR spectra in CD_3CN of complex **2b** irradiation at λ = 254 nm under a nitrogen atmosphere for a) 0 h, b) 4 h, c) 6 h. Noting that the spectra in the Cp* area have been divided by 15 for clarity.

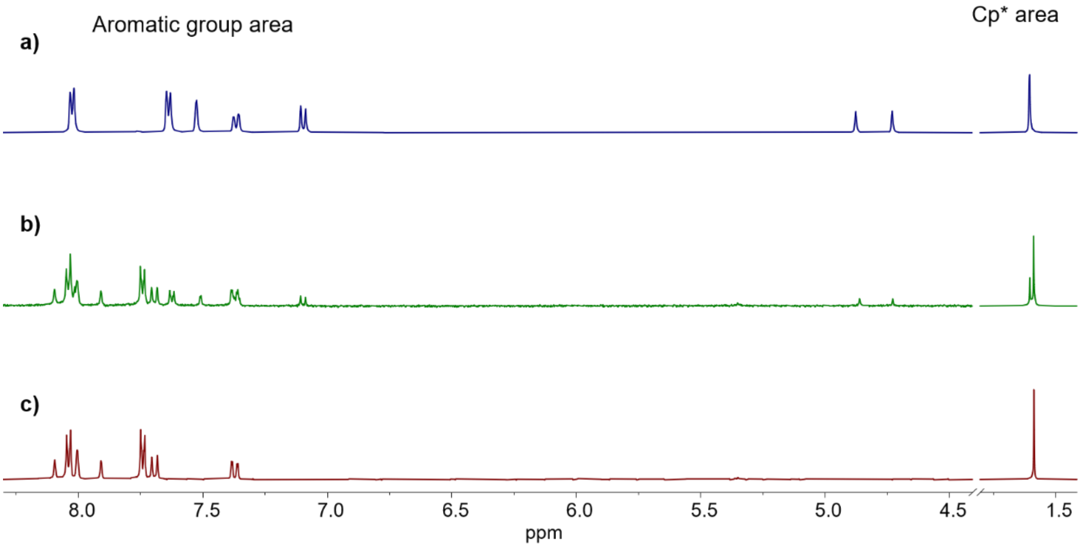


Figure S5. Sections of the ^{1}H NMR spectra in CD_3CN of complex **2b** after heating at 120 °C under a nitrogen atmosphere for a) 0 h, b) 4 h, c) 8 h. Noting that the spectra in the Cp* area have been divided by 15 for clarity.

The reversible conversion was monitored by *in situ* ^{1}H NMR analysis. The solution of complex **1b** in CD_3CN (0.5 mL, c = 10 mM) in an NMR tube was irradiated with LED lamp. Each cycle corresponds to irradiation at 365 nm (3 h), promoting photocyclization, followed by 254 nm (6 h).

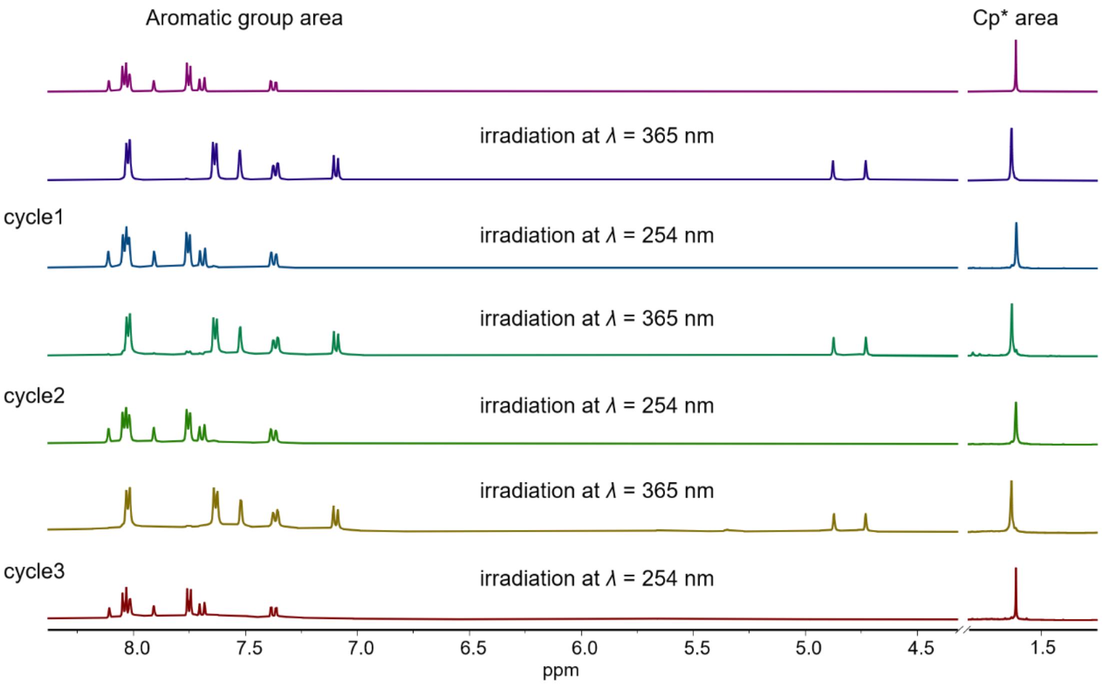
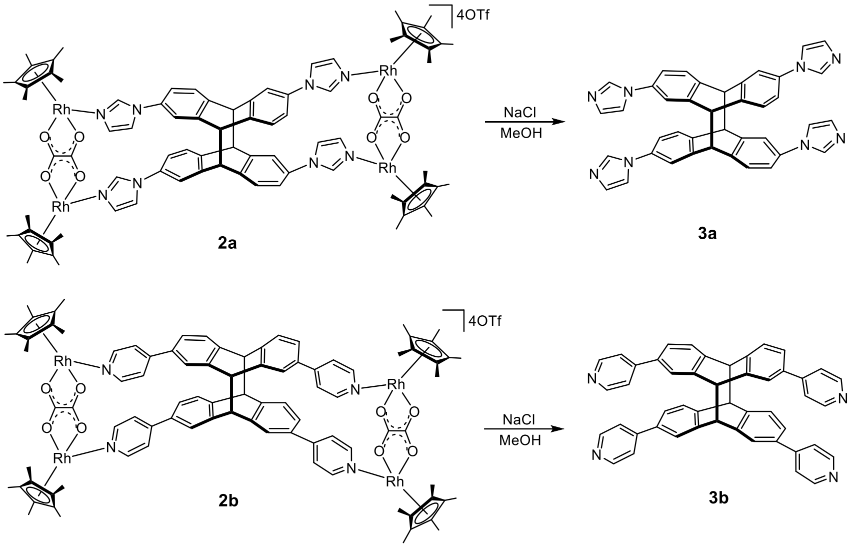


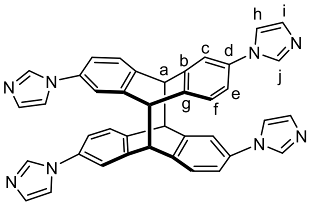
Figure S6. Sections of the ^{1}H NMR spectra of **1b** in CD_3CN upon repeating irradiation for three cycles.

5. Synthesis of Organic Photodimers



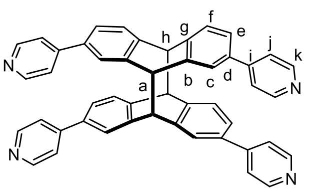
Scheme S2. General synthesis of compounds **3a** and **3b**.

5.1 Synthesis of Compound 3a



Sodium chloride (1.5 mg, 0.025 mmol) was added to the methanol solution (0.5 mL) of **2a** (11.7 mg, 0.005 mmol), and the mixture was stirred for 10 min at room temperature, a brick-red precipitate was obtained immediately. The solids are collected and separated by chromatographic column to obtain yellow solid **3a**. Yield: 2.5 mg, 92%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.10 (s, 4H, H$_j$), 7.58 (s, 4H, H$_f$), 7.36 (s, 4H, H$_c$), 7.18 (d, J = 8.0 Hz, 4H, H$_h$), 7.12 (d, J = 9.4 Hz, 4H, H$_i$), 7.05 (s, 4H, H$_e$), 4.85 (s, 4H, H$_a$) ppm. The NMR characterization of compound **3a** is consistent with that reported in the literature.[1]

5.2 Synthesis of Compound 3b



Sodium chloride (1.5 mg, 0.025 mmol) was added to the methanol solution (0.5 ml) of **2a** (12.0 mg, 0.005 mmol), and and the mixture was stirred for 10 min at room temperature, a brick-red precipitate was obtained immediately. The solids are collected and separated by chromatographic column to obtain yellow solid **3a**. Yield: 3.0 mg, 92%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.51 (d, J = 4.7 Hz, 4H, H$_k$), 7.53 (s, 2H, H$_c$), 7.49 (d, J = 5.7 Hz,4H, H$_j$), 7.26 (d, J = 7.7 Hz, 2H, H$_e$), 7.16 (d, J = 5.7 Hz, 2H, H$_f$), 4.96 (s, 2H, H$_a$), 4.87 (s, 2H, H$_h$) ppm. HRMS (ESI, positive ions): m/z = 665.2485 (calcd for [**3b**+H]$^+$ 665.2700).

6. NMR and MS Spectra

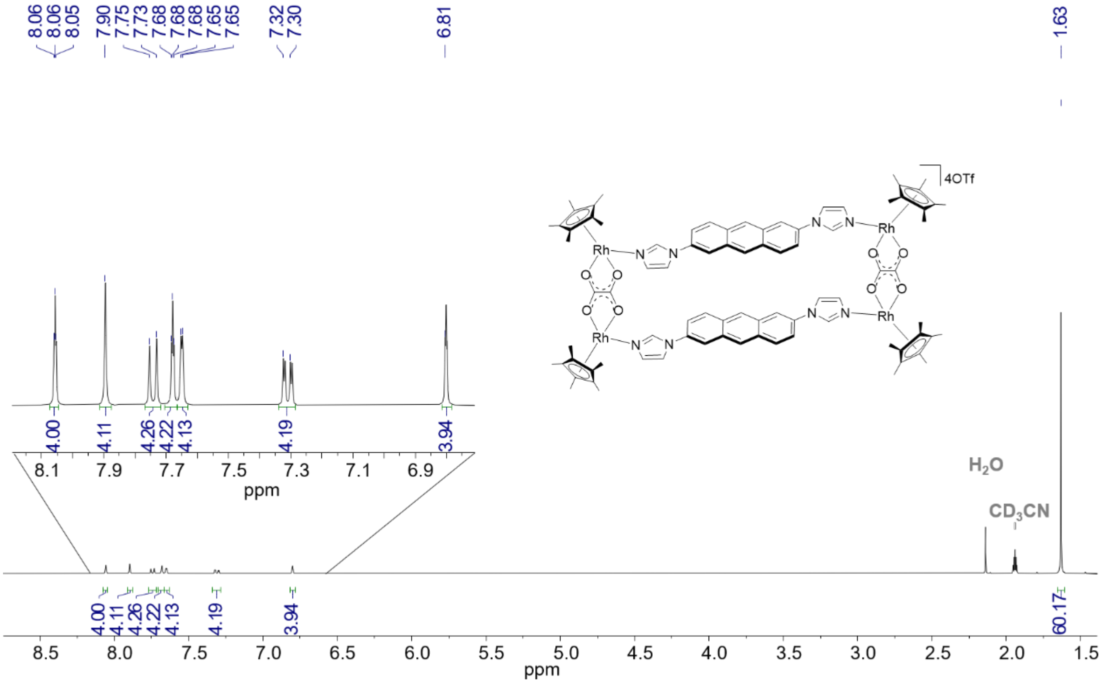


Figure S7. ^{1}H NMR (400 MHz, CD_3CN, ppm) for complex **1a**.

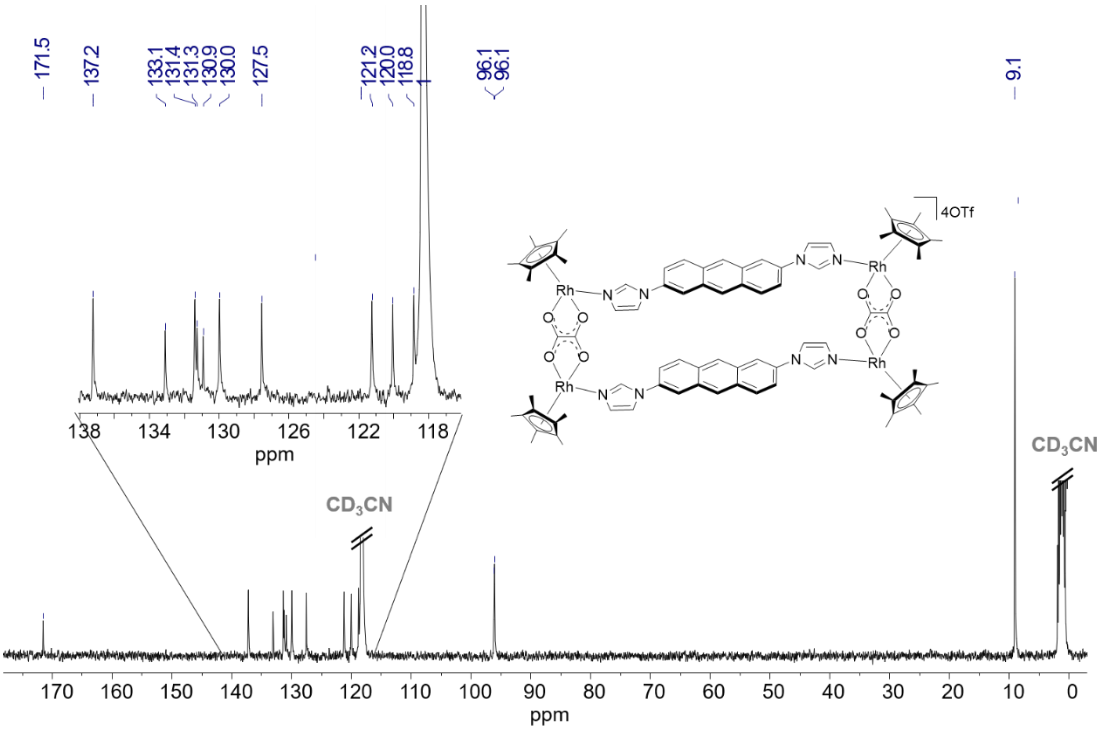


Figure S8. ^{13}C NMR (100 MHz, CD_3CN, ppm) for complex **1a**.

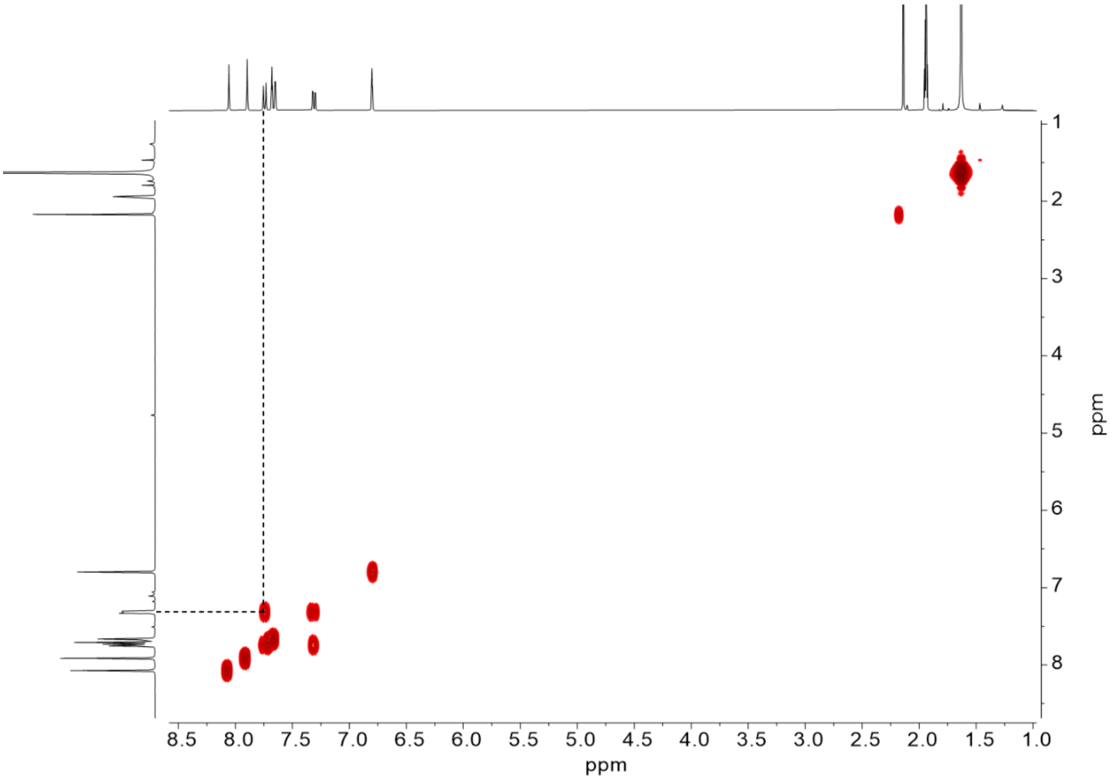


Figure S9. ^{1}H-^{1}H COSY NMR (400 MHz, CD_3CN, ppm) for complex **1a**.

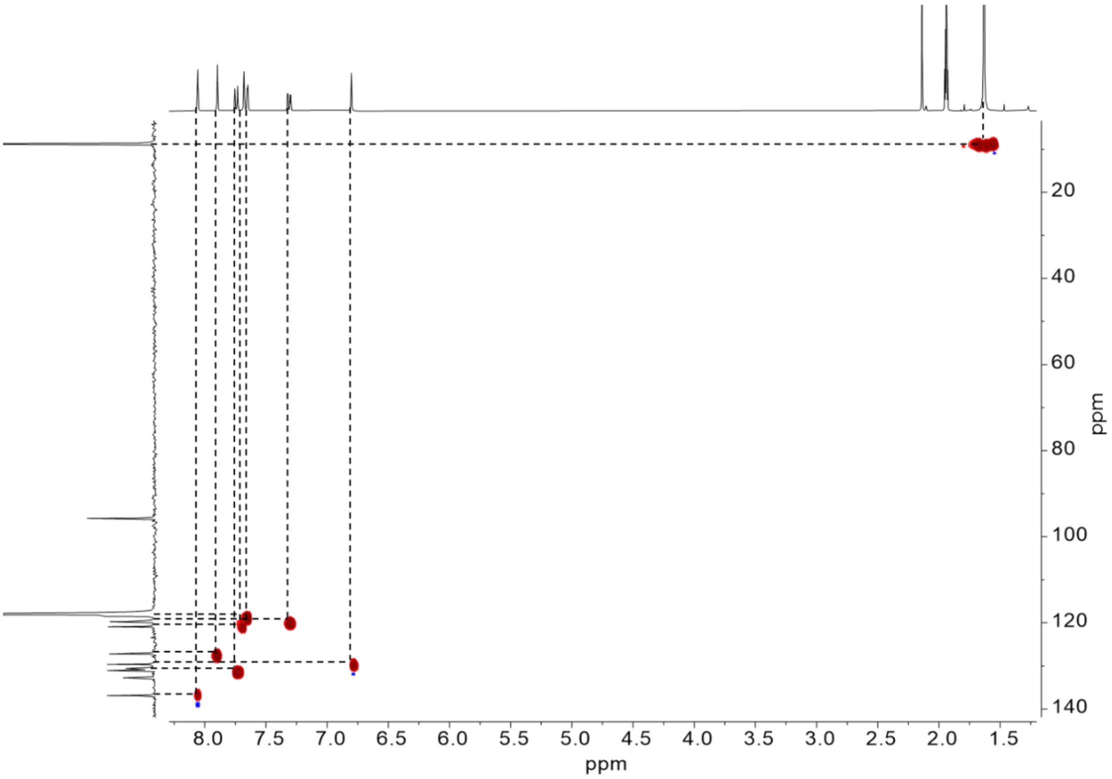


Figure S10. ^{1}H-^{13}C HSQC NMR (400 MHz, CD_3CN, ppm) for complex **1a**.

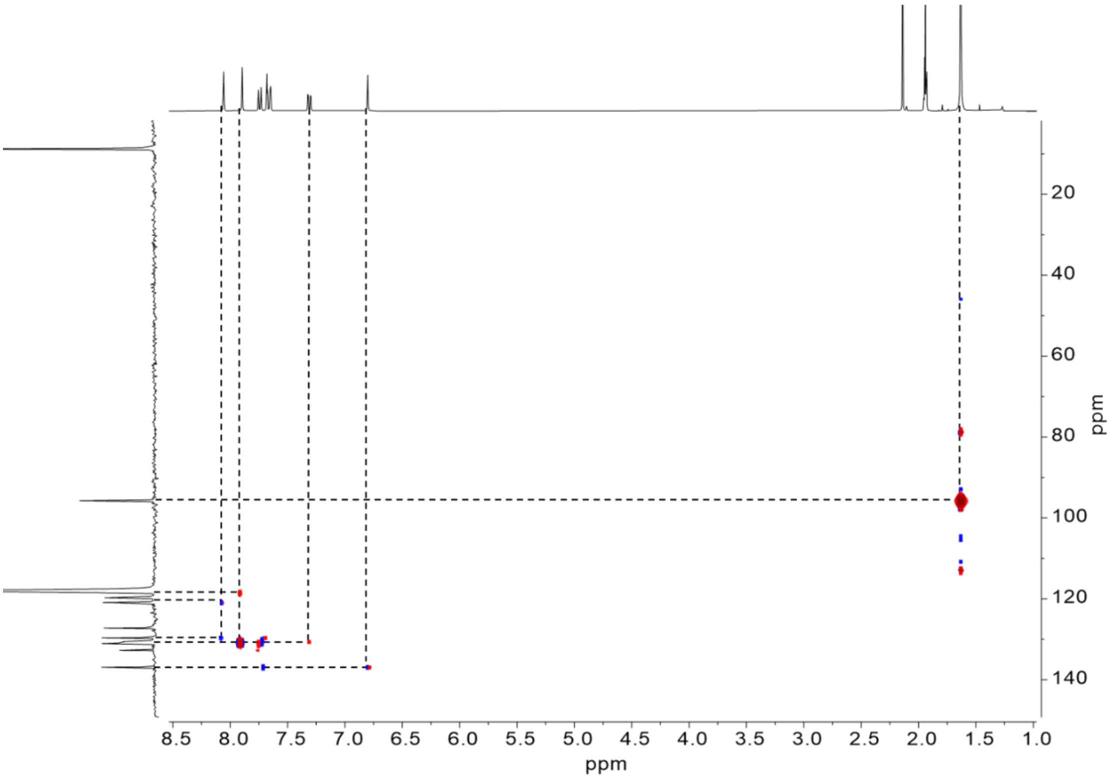


Figure S11. ^{1}H-^{13}C HMBC NMR (400 MHz, CD_3CN, ppm) for complex **1a**.

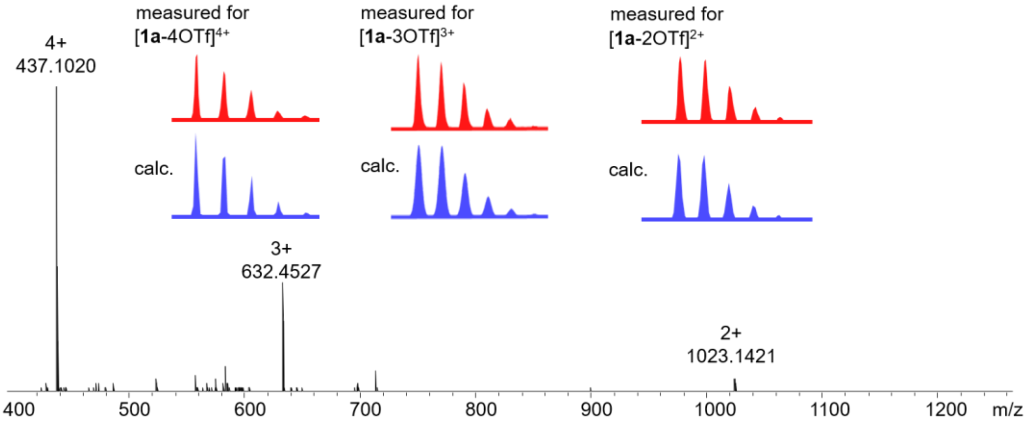


Figure S12. ESI-TOF mass spectrum of complex **1a** with isotope distribution for selected peaks.

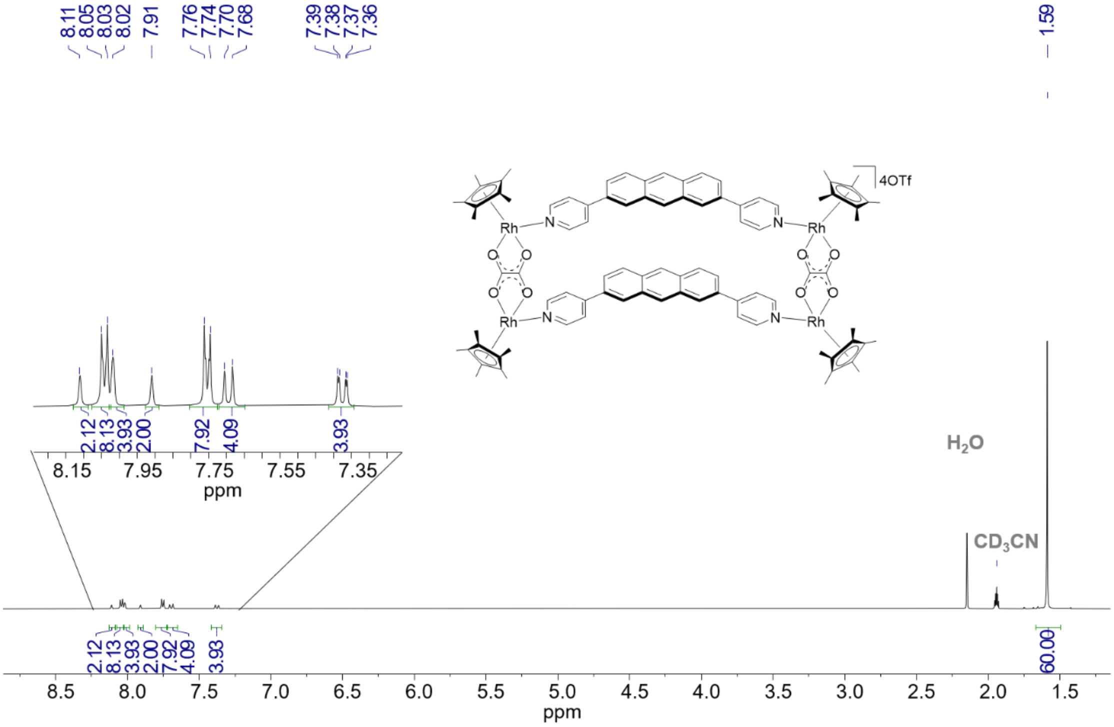


Figure S13. ^{1}H NMR (400 MHz, CD_3CN, ppm) for complex **1b**.

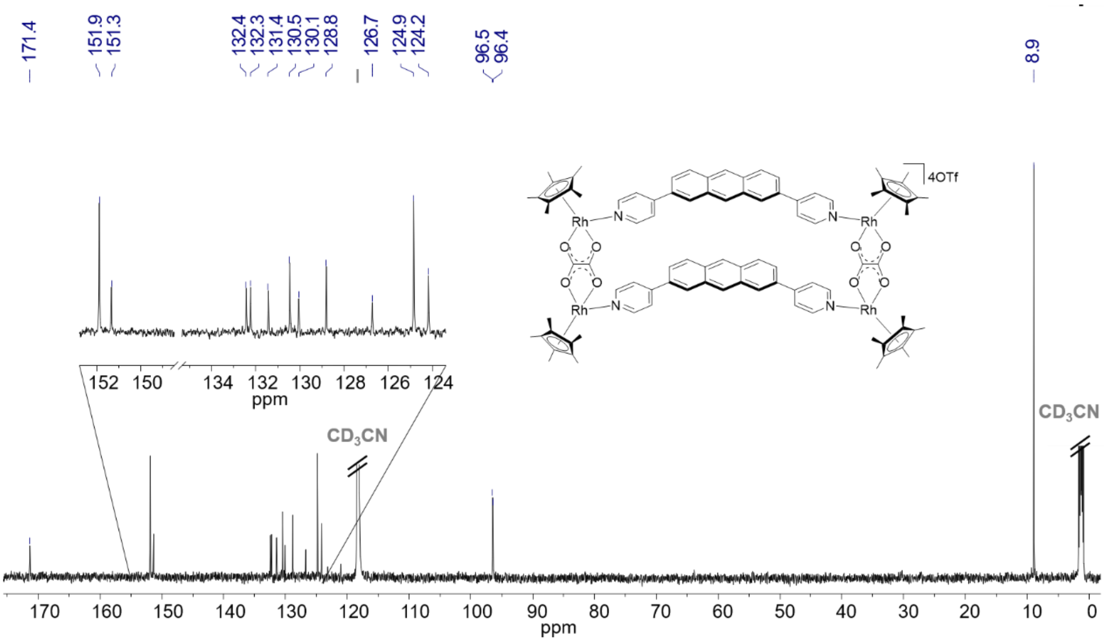


Figure S14. ^{13}C NMR (100 MHz, CD_3CN, ppm) for complex **1b**.

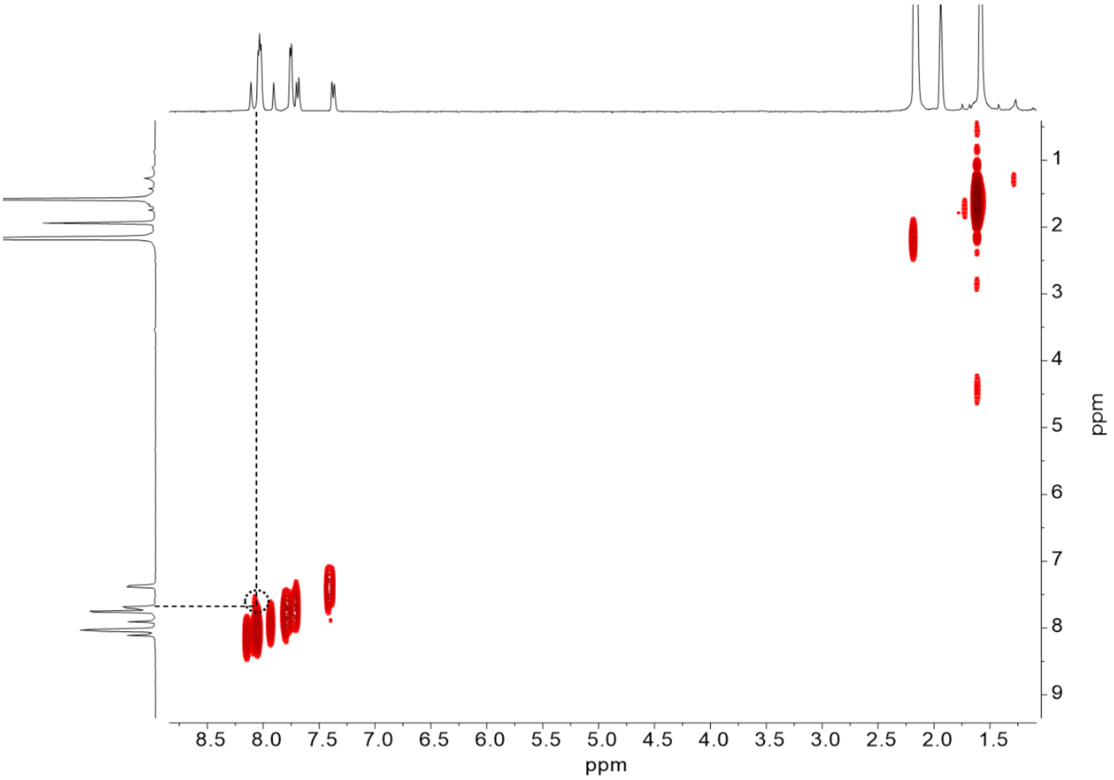


Figure S15. ^{1}H-^{1}H COSY NMR (400 MHz, CD_3CN, ppm) for complex **1b**.

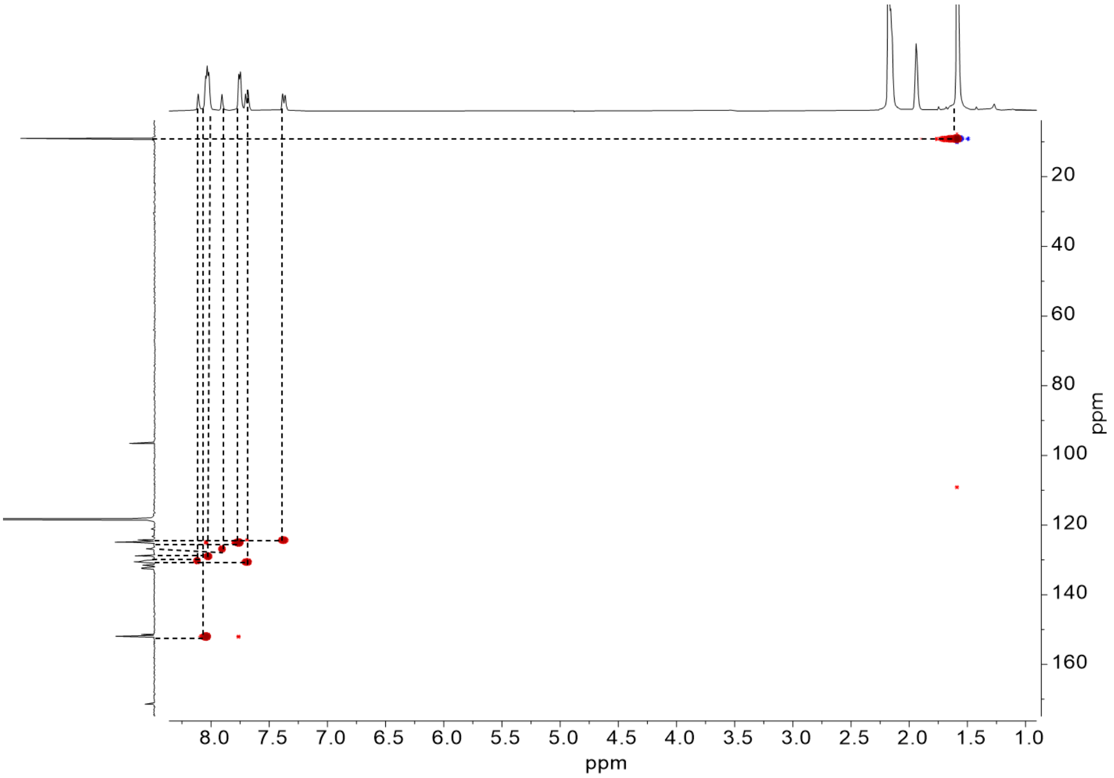


Figure S16. ^{1}H-^{13}C HSQC NMR (400 MHz, CD_3CN, ppm) for complex **1b**.

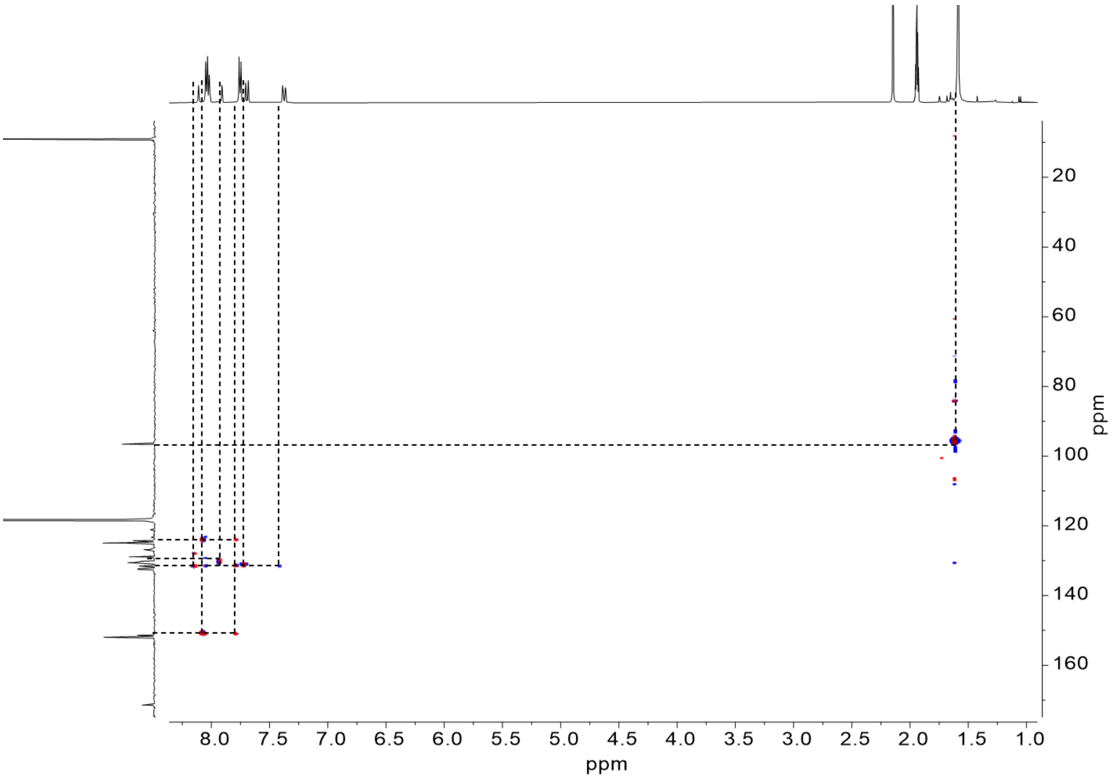


Figure S17. ^{1}H-^{13}C HMBC NMR (400 MHz, CD_3CN, ppm) for complex **1b**.

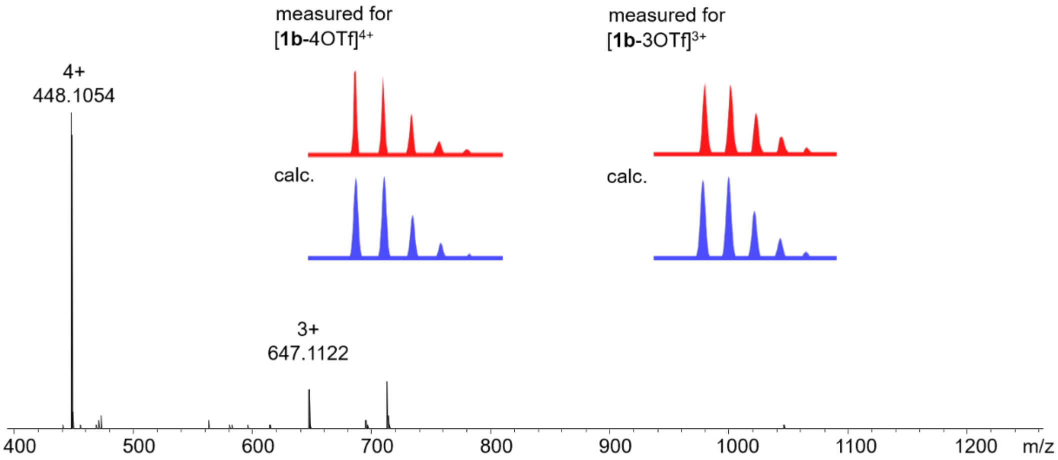


Figure S18. ESI-TOF mass spectrum of complex **1b** with isotope distribution for selected peaks.

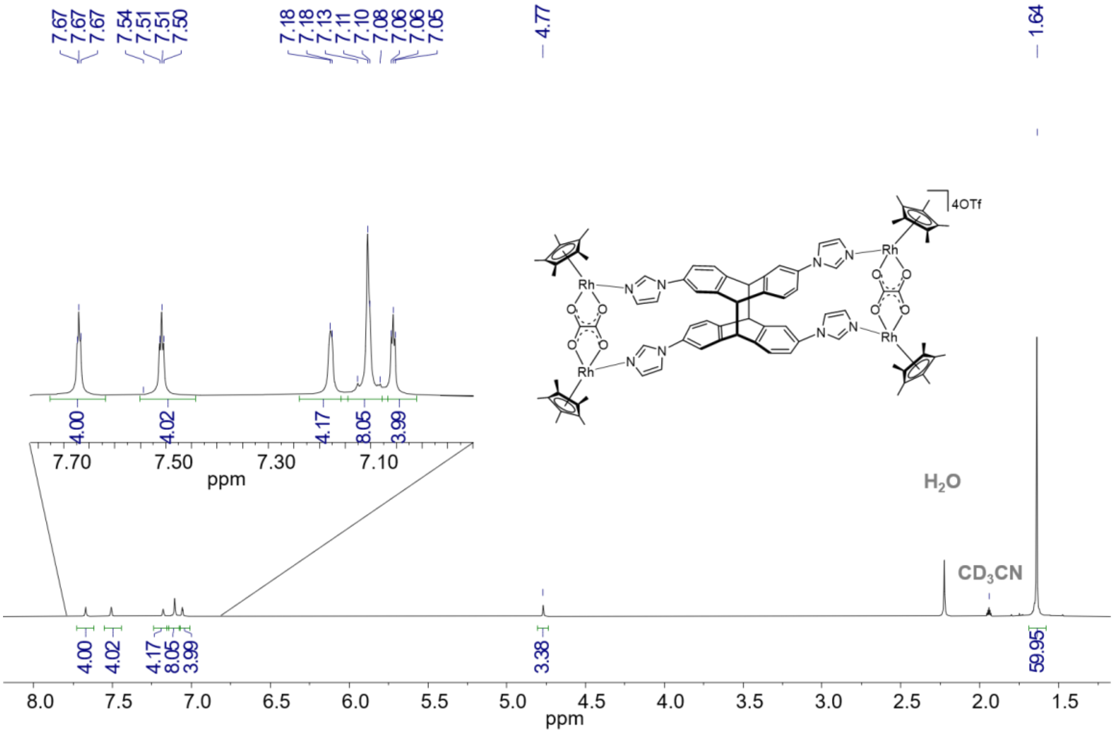


Figure S19. ^{1}H NMR (400 MHz, CD_3CN, ppm) for complex **2a**.

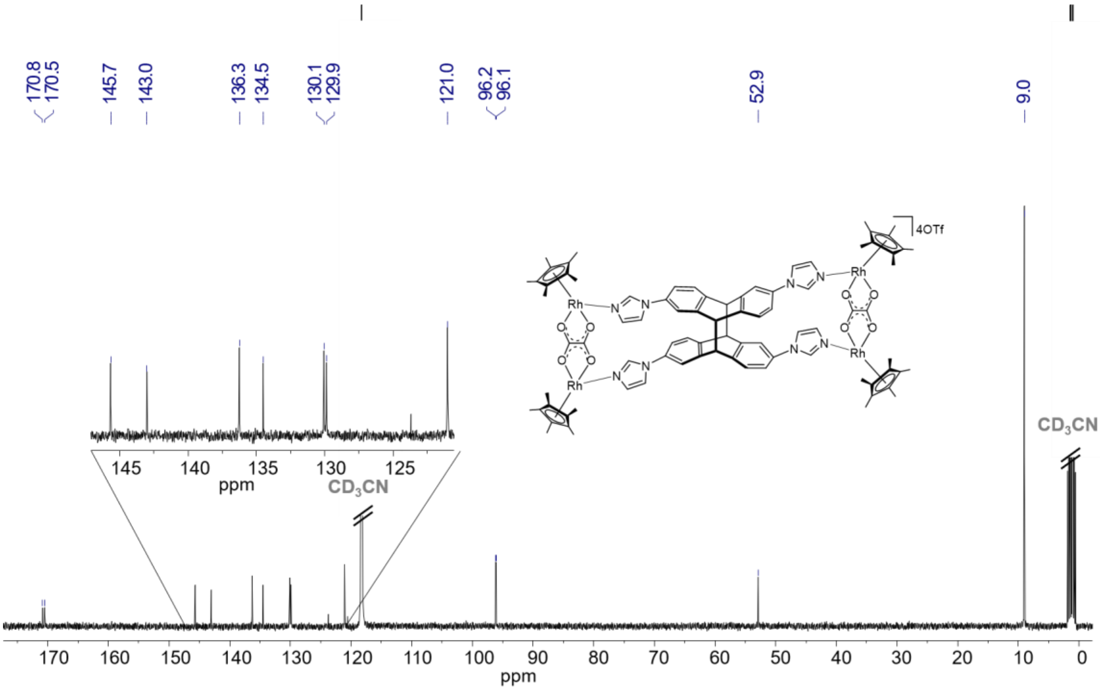


Figure S20. ^{13}C NMR (100 MHz, CD_3CN, ppm) for complex **2a**.

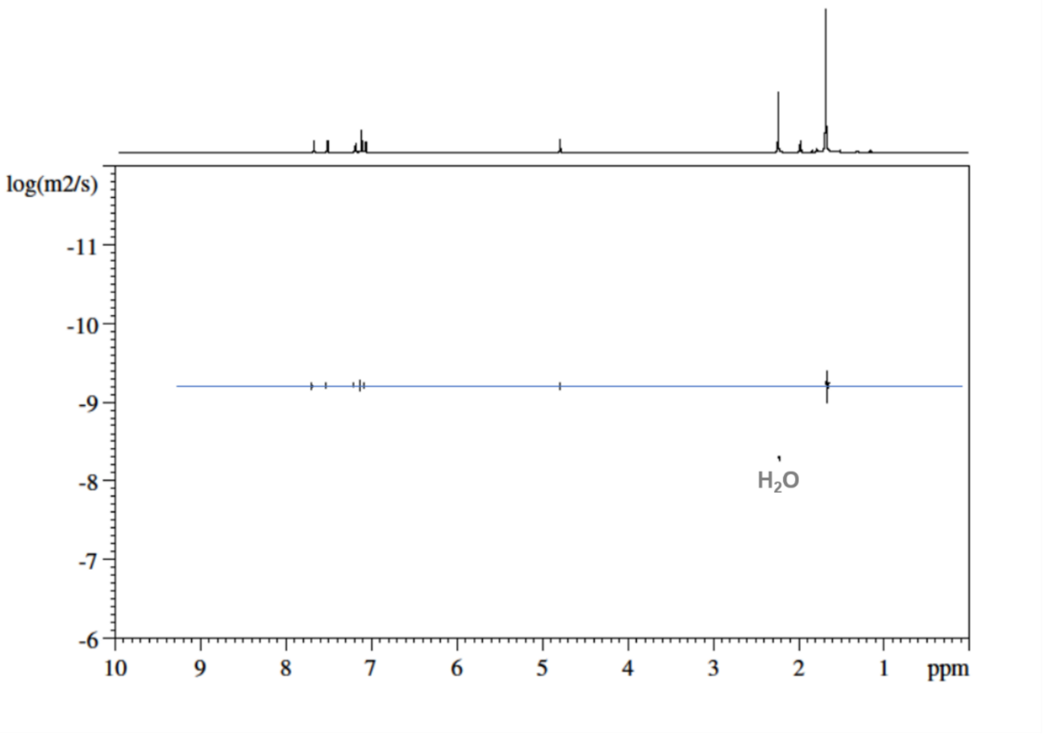


Figure S21. ^{1}H DOSY NMR (400 MHz, CD_3CN, 298 K, *c* = 15 mM) for complex **2a**. ($D = 6.19 \times 10^{-10}$ $m^2 \cdot S^{-1}$, $\log D = -9.21$)

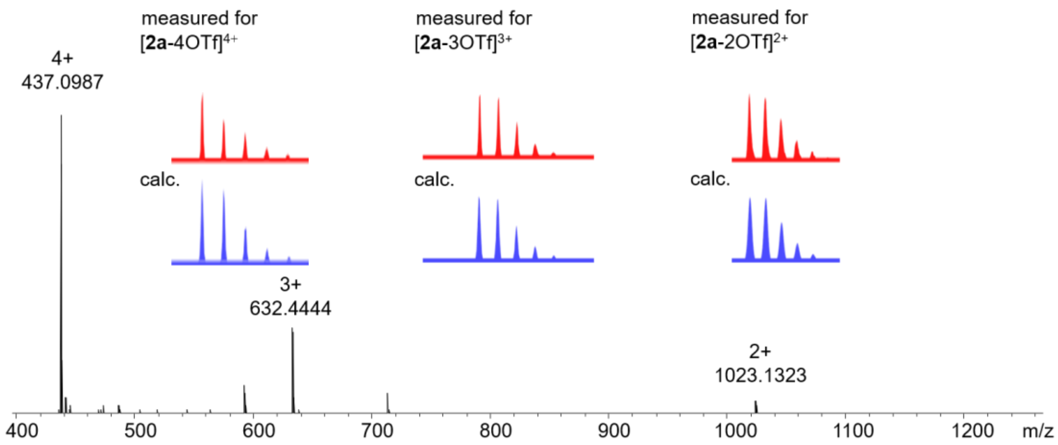


Figure S22. ESI-TOF mass spectrum of compound **2a** with isotope distribution for selected peaks.

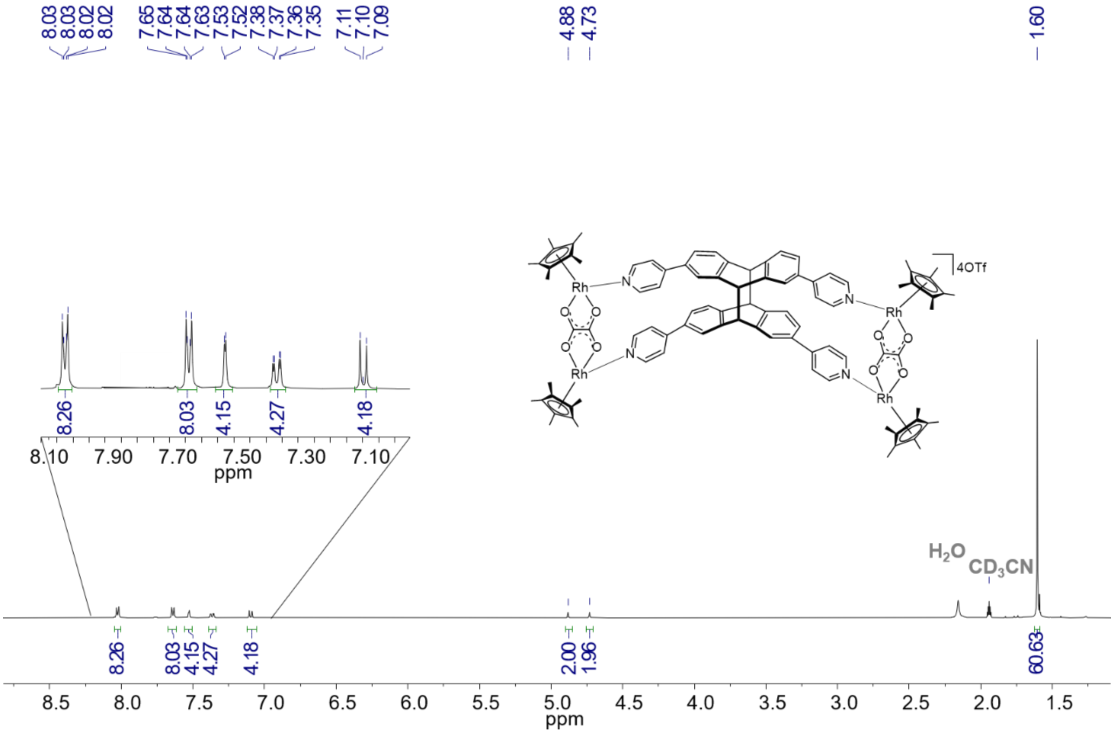


Figure S23. ^{1}H NMR (400 MHz, CD_3CN, ppm) for complex **2b**.

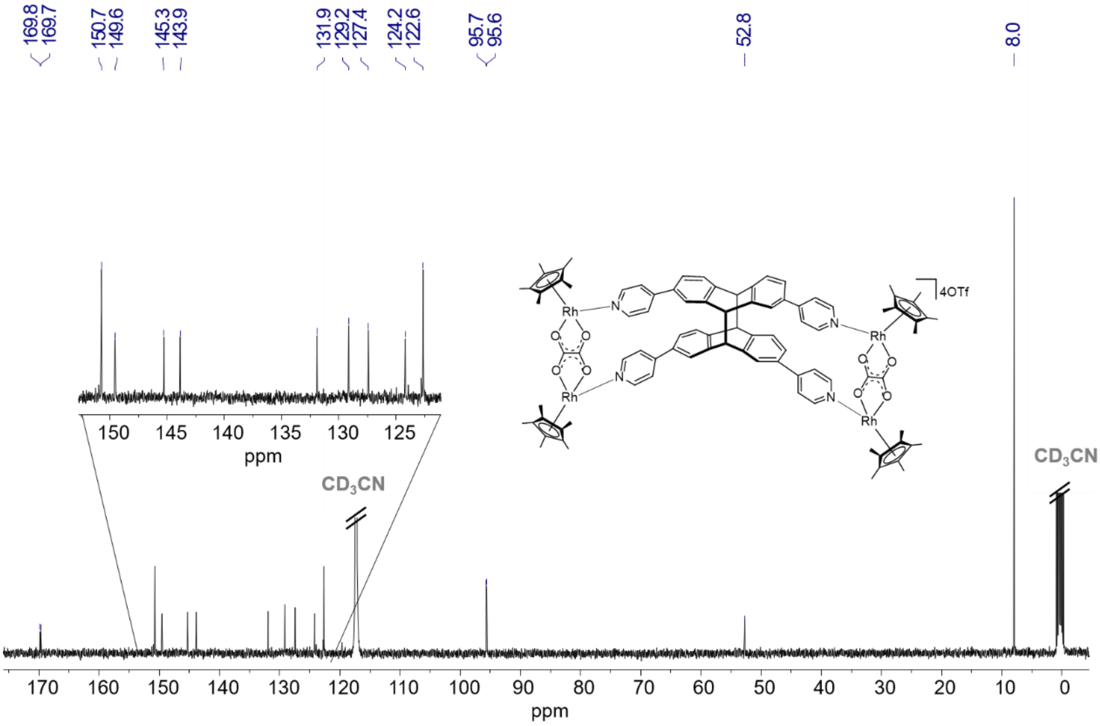


Figure S24. ^{13}C NMR (100 MHz, CD_3CN, ppm) for complex **2b**.

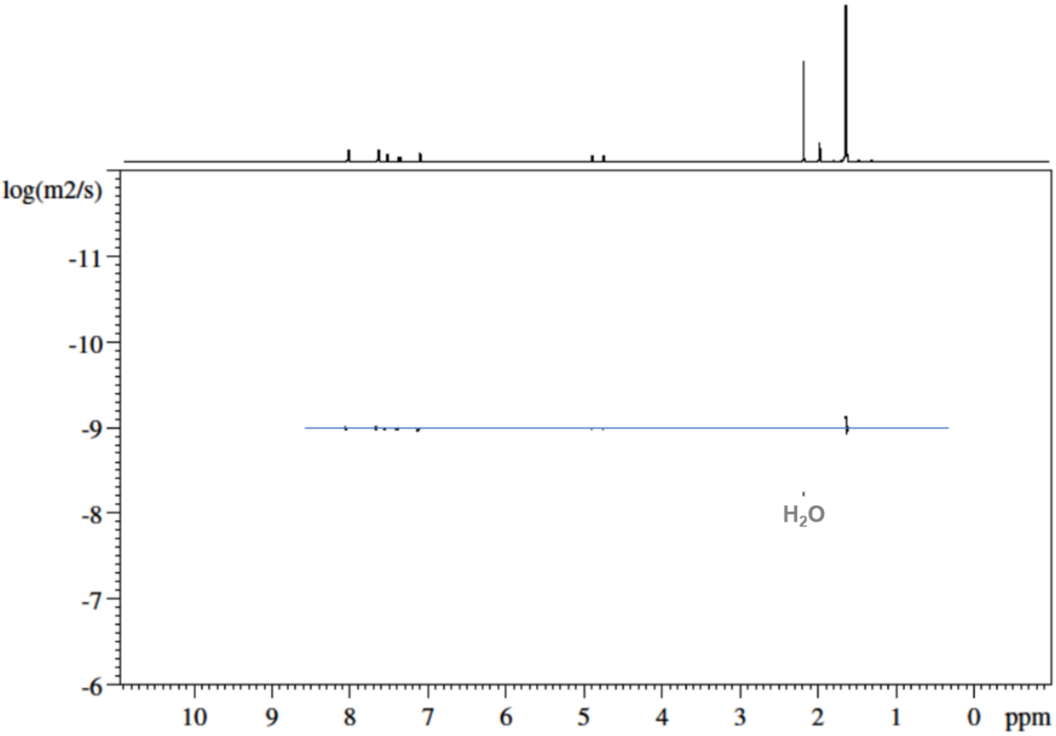


Figure S25. ^{1}H DOSY NMR (400 MHz, CD_3CN, 298 K, *c* = 15 mM) for complex **2b**. ($D = 1.06 \times 10^{-9}$ $m^{2}\cdot S^{-1}$, log D = -8.98)

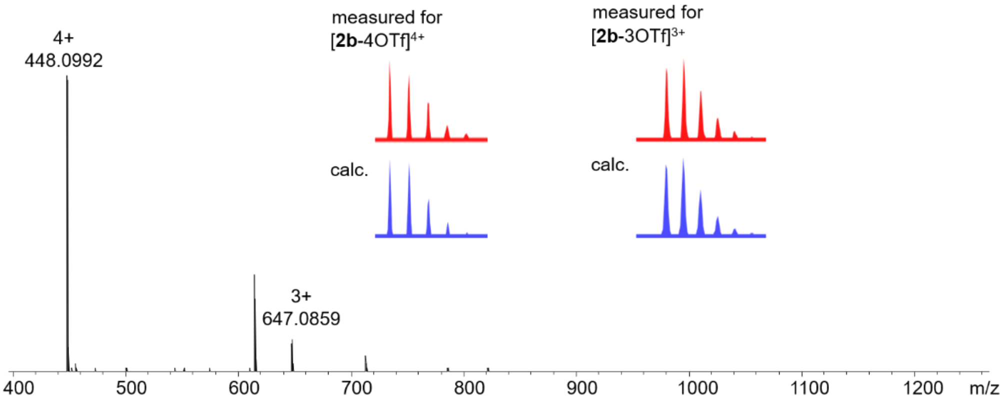


Figure S26. ESI-TOF mass spectrum of complex **2b** with isotope distribution for selected peaks.

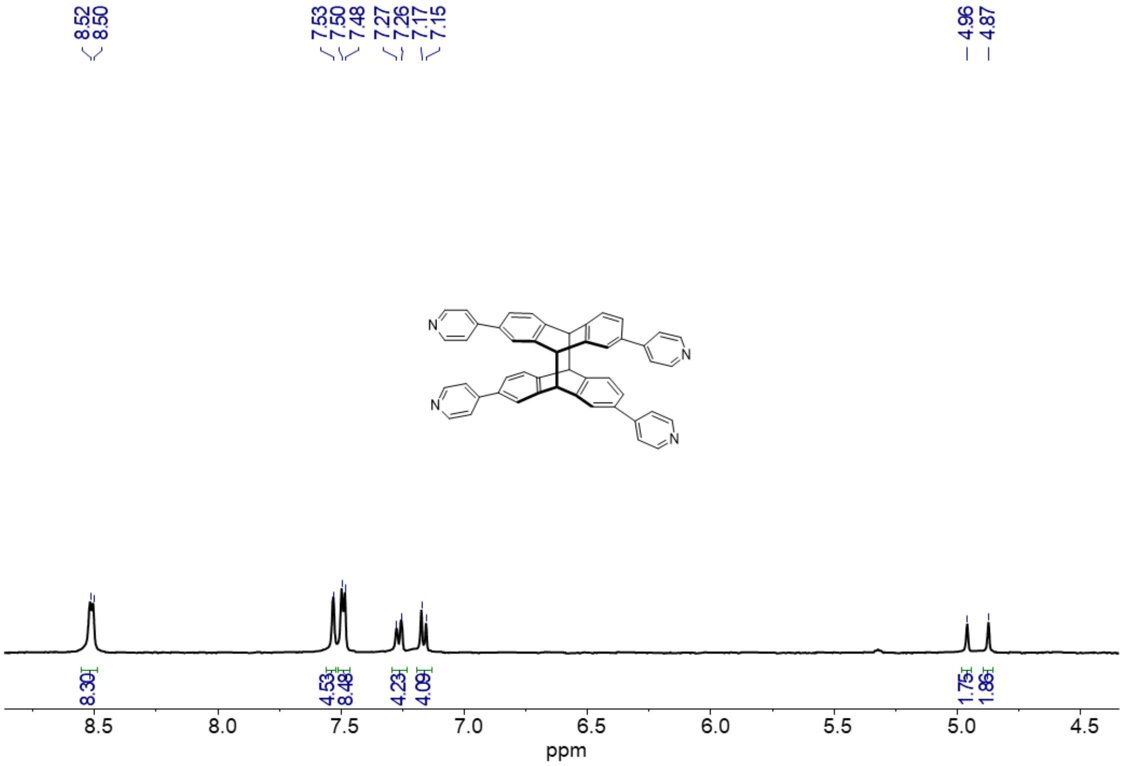


Figure S27. ^{1}H NMR (400 MHz, DMSO-d_6, ppm) for compound **3b**.

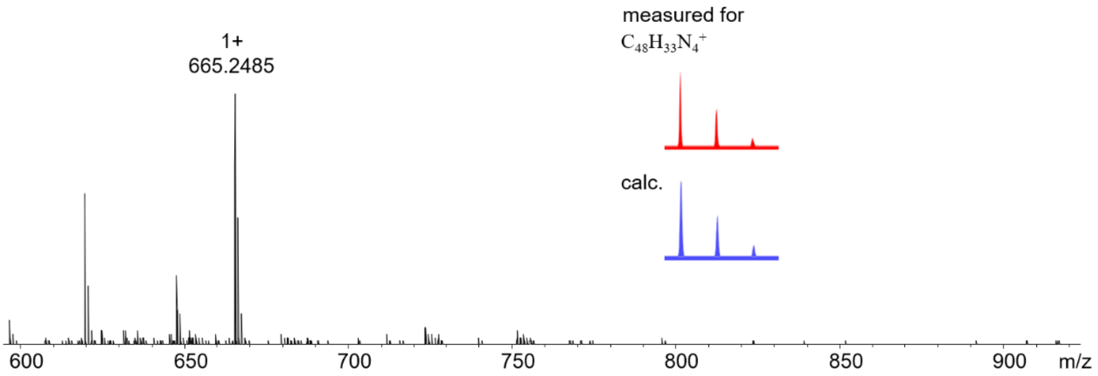


Figure S28. ESI-TOF mass spectrum of compound **3b** with isotope distribution for selected peaks.

7. UV/Vis Spectroscopy

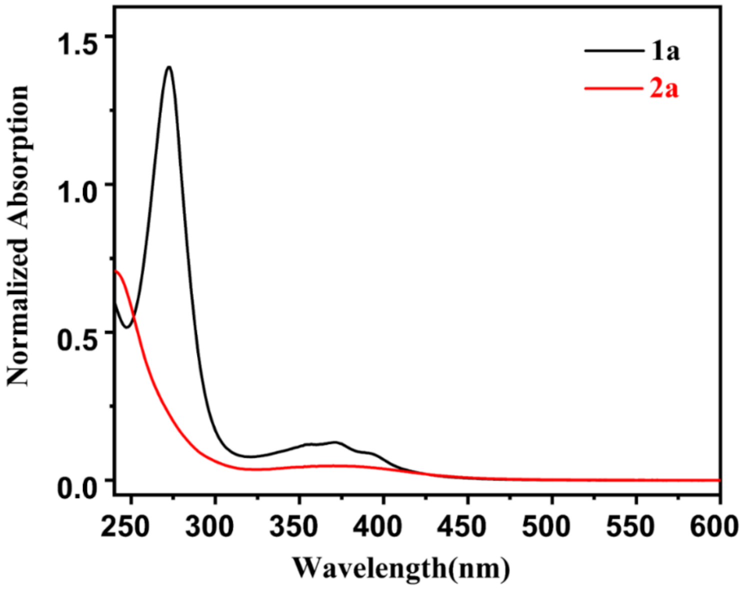


Figure S29. UV/Vis spectrum of complexes **1a** and **2a** in acetonitrile solutions (*T* = 298 K, *c* = 10 μM).

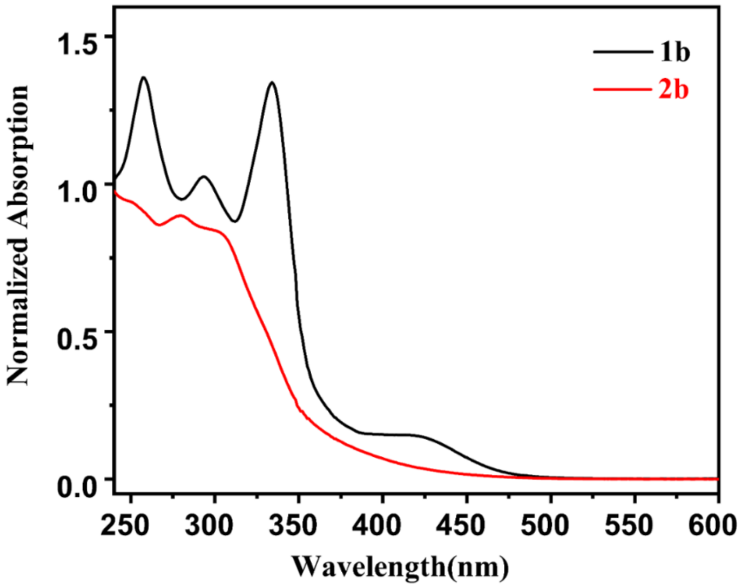


Figure S30. UV/Vis spectrum of complexes **1b** and **2b** in acetonitrile solutions (*T* = 298 K, *c* = 10 μM).

8. X-Ray Crystallography

The single crystals of **1a** were grown by slowly diffusing ethyl ether into the acetonitrile solution of **1a** at ambient temperature. The single crystals of **2a** were grown by slowly diffusing ethyl ether into its acetonitrile solution at ambient temperature. The single crystals of **1b**' with PF_6^- anions was obtained by adding KPF_6 to an acetonitrile solution of **1b** and allowing the solution to stand at ambient temperature for several days. Afterward, ethyl ether was slowly diffused into the acetonitrile solution at ambient temperature to obtain the single crystal. All data for crystal structure determinations were measured on a Bruker D8 Venture diffractometer, using graphite monochromated MoKα radiation (λ = 0.71073 Å). Reduction of data and semiempirical absorption correction were done using SADABS program.[4] The structures were solved by direct methods, which revealed the position of all non-hydrogen atoms. These atoms were refined on F^2 by a full matrix least-squares procedure using anisotropic displacement parameters.[5,6] All hydrogen atoms were assigned to ideal positions and refined using a riding model. A number of disordered solvent molecules could not be restrained properly and were therefore removed using the SQUEEZE route. For **1a**, one trifluoromethanesulfonic anion was disordered and it was divided into two parts.

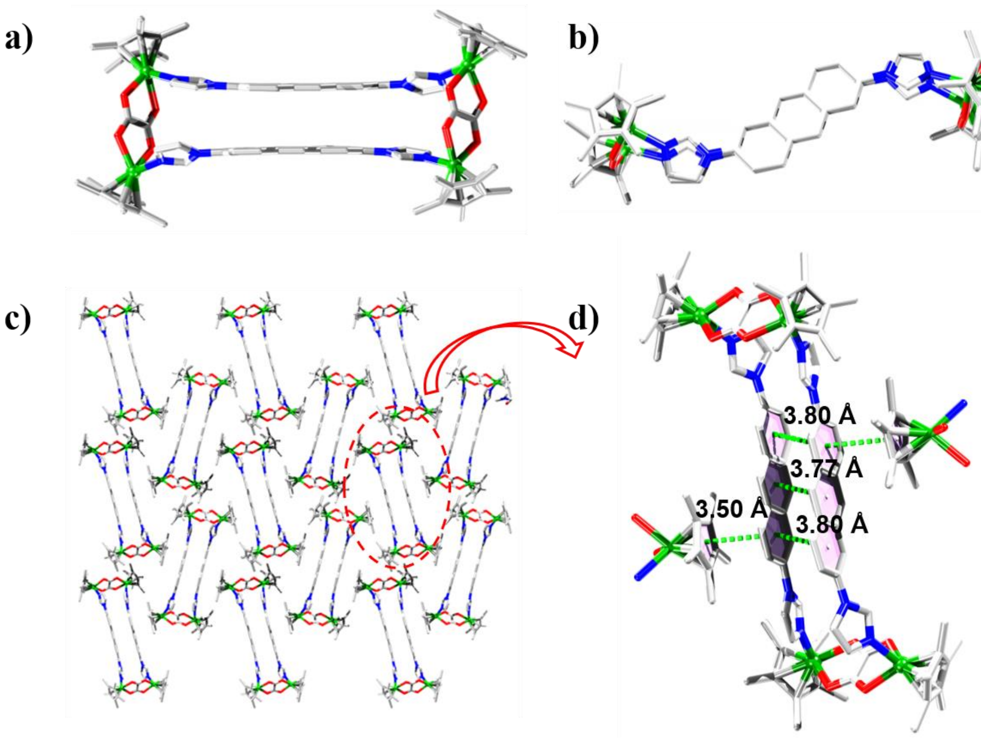


Figure S31. (a) Side and (b) top views of **1a**; (c) stacking of the molecules in crystals of **1a** viewed along the x-axis; (d) the π···π stacking interaction in **1a**. All hydrogen atoms, solvent molecules, and counterions are omitted for clarity. Color code:N, blue; O, red; C, gray; Rh, green.

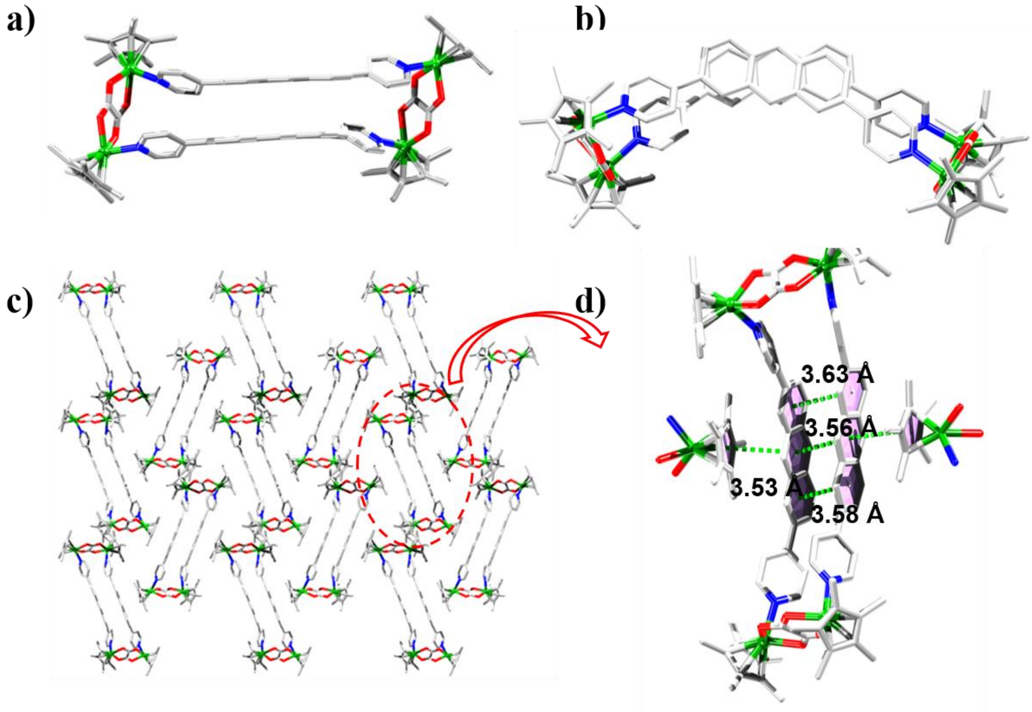


Figure S32. (a) Side and (b) top views of **1b**'; (c) stacking of the molecules in crystals of **1b**' viewed along the y-axis; (d) the π···π stacking interaction in **1b**'. All hydrogen atoms, solvent molecules, and counterions are omitted for clarity. Color code:N, blue; O, red; C, gray; Rh, green.

Table S1. Crystal data of ligand **1a**.

Empirical formula	$C_{94}H_{102}F_{12}N_{10}O_{22}Rh_4S_4$
Formula weight	2491.74
Temperature/K	200.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	23.3105(9)
b/Å	22.2812(8)
c/Å	22.7128(7)
α/°	90
β/°	100.3480(10)
γ/°	90
Volume/Å^3	11604.8(7)
Z	4
ρ_{calc}/(g.cm^{-3})	1.426
μ(mm^{-1})	0.716
F(000) 648.0	5056.0
Crystal size/mm^3	0.18 × 0.17 × 0.15
Radiation	Mo Kα ($\lambda = 0.71073$)
2Θ range for data collection/°	4.322 to 50.732
Index ranges	$-19 \le h \le 28$, $-26 \le k \le 26$, $-27 \le l \le 25$
Reflections collected	103665
Independent reflections	21199 [$R_{int} = 0.0703$]
Data/restraints/parameters	21199/199/1356
Goodness-of-fit on F^2	1.027
Final R indexes [$I \ge 2\sigma(I)$]	$R_1 = 0.0590$, $wR_2 = 0.1475$
Final R indexes [all data]	$R_1 = 0.0964$, $wR_2 = 0.1664$
Largest diff. peak/hole / e Å^{-3}	2.05/-0.86
CCDC	2165005

Table S2. Crystal data of ligand **1b**'.

Empirical formula	$C_{96}H_{98}F_{24}N_6O_8P_4Rh_4$
Formula weight	2455.32
Temperature/K	192.0
Crystal system	Orthorhombic
Space group	*Pbca*
a/Å	24.277(7)
b/Å	22.228(6)
c/Å	41.74(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	22522(18)
Z	8
ρ_{calc}/(g.cm^{-3})	1.448
μ(mm^{-1})	0.724
F(000) 648.0	9888.0
Crystal size/mm^3	0.16 × 0.17 × 0.15
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.478 to 51.37
Index ranges	$-29 \leq h \leq 27$, $-27 \leq k \leq 24$, $-50 \leq l \leq 50$
Reflections collected	145730
Independent reflections	21326 [R_{int} = 0.0750]
Data/restraints/parameters	21326/0/1301
Goodness-of-fit on F^2	1.014
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0596, wR_2 = 0.1558
Final R indexes [all data]	R_1 = 0.1030, wR_2 = 0.1834
Largest diff. peak/hole / e Å^{-3}	1.01/-0.67
CCDC	2165004

Table S3. Crystal data of ligand **2a**.

Empirical formula	$C_{87}H_{88}F_9N_8O_{17}Rh_4S_3$
Formula weight	2196.47
Temperature/K	150.0
Crystal system	Monoclinic
Space group	*C2/c*
a/Å	30.7296(12)
b/Å	19.6924(8)
c/Å	23.9910(8)
α/°	90
β/°	126.9440(10)
γ/°	90
Volume/Å^3	11603.0(8)
Z	4
ρ_{calc}/(g.cm^{-3})	1.257
μ(mm^{-1})	0.682
F(000) 648.0	4444.0
Crystal size/mm^3	0.25 × 0.22 × 0.21
Radiation	Mo Kα ($\lambda = 0.71073$)
2Θ range for data collection/°	4.65 to 50.756
Index ranges	$-36 \leq h \leq 36$, $-23 \leq k \leq 23$, $-28 \leq l \leq 27$
Reflections collected	37812
Independent reflections	10418 [$R_{int} = 0.0380$]
Data/restraints/parameters	10418/278/606
Goodness-of-fit on F^2	1.042
Final R indexes [$I \geq 2\sigma (I)$]	$R_1 = 0.0887$, $wR_2 = 0.2477$
Final R indexes [all data]	$R_1 = 0.1206$, $wR_2 = 0.2812$
Largest diff. peak/hole / e Å^{-3}	1.50/-1.36
CCDC	2165001

9. References

1. S. Bai, L.-L. Ma, T. Yang, F. Wang, L.-F. Wang, F. E. Hahn, Y.-Y. Wang and Y.-F. Han, *Chem. Sci.*, 2021, **12**, 2165–2171.
2. R. Ozawa, K. Yoza, K. Kobayashi, *Chem. Lett.*, **2011**, *40*, 941–943.
3. Y.-F. Han, Y.-J. Lin, W.-G. Jia, L.-H. Weng and G.-X. Jin, *Organometallics*, **2007**, *26*, 5848–5853.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.
5. L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard, H. Puschmann, *Acta Cryst*. 2015, **A71**, 59–75.
6. G. M. Sheldrick, *Acta Cryst*. 2015, **C71**, 3–8.