**Supporting Information for:**

**Rotaxane synthesis exploiting the M(I)/M(III) redox couple**

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1. NMR spectra of isolated compounds

1.1 Rhodium [2]rotaxane 1a

Figure S-1: $^1$H NMR spectrum of 1a (CD$_2$Cl$_2$, 500 MHz).

Figure S-2: $^{13}$C($^1$H) APT NMR spectrum of 1a (CD$_2$Cl$_2$, 126 MHz).

Figure S-3: $^{31}$P($^1$H) NMR spectrum of 1a (CD$_2$Cl$_2$, 202 MHz).
1.2 Iridium [2]rotaxane 1b

Figure S-4: $^1$H NMR spectrum of 1b (CD$_2$Cl$_2$, 500 MHz).

Figure S-5: $^{13}$C($^1$H) APT NMR spectrum of 1b (CD$_2$Cl$_2$, 126 MHz).

Figure S-6: $^{31}$P($^1$H) NMR spectrum of 1b (CD$_2$Cl$_2$, 202 MHz).
1.3 \([\text{Rh(COD)(PPh}_3)_2][\text{BAR}^7_2] \) 2a

Figure S-7: $^1$H NMR spectrum of 2a (CD$_2$Cl$_2$, 500 MHz).

Figure S-8: $^{13}$C($^1$H) APT NMR spectrum of 2a (CD$_2$Cl$_2$, 126 MHz).

Figure S-9: $^{31}$P($^1$H) NMR spectrum of 2a (CD$_2$Cl$_2$, 162 MHz).
1.4 \([\text{Ir(COD)(PPh}_3)_2][\text{BARF}_4]\) 2b

![Figure S-10: $^1\text{H}$ NMR spectrum of 2b (CD$_2$Cl$_2$, 400 MHz).](image)

1.5 Ammonium salt 3

![Figure S-12: $^1\text{H}$ NMR spectrum of 3 (CD$_2$Cl$_2$, 500 MHz).](image)
1.6 Pseudo[2]rotaxane 3-db24c8

Figure S-13: $^{13}$C($^1$H) APT NMR spectrum of 3 (CD$_2$Cl$_2$, 126 MHz).

Figure S-14: $^1$H NMR spectrum of 3-db24c8 (CD$_2$Cl$_2$, 500 MHz).

Figure S-15: $^{13}$C($^1$H) APT NMR spectrum of 3-db24c8 (CD$_2$Cl$_2$, 126 MHz).
1.7 Stack plot of $^1$H NMR spectra of 1a, 1b, 3-db24c8 and 3

Figure S-16: $^1$H NMR spectra of 1a, 1b, 3-db24c8 and 3.

1.8 $[\text{Rh(bipy)}H_2(PPh_3)_2][\text{BAR}^f_4]$ 4a[BAR$^f_4$

Figure S-17: $^1$H NMR spectrum of 4a[BAR$^f_4$] (CD$_2$Cl$_2$, 500 MHz).
Figure S-18: $^{13}\text{C}\{^1\text{H}\}$ APT NMR spectrum of 4a[Bar$^4$] (CD$_2$Cl$_2$, 126 MHz).

Figure S-19: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 4a[Bar$^4$] (CD$_2$Cl$_2$, 162 MHz).

1.9  [Ir(bipy)H$_2$(PPh$_3$)$_2$][Bar$^4$]  4b[Bar$^4$]

Figure S-20: $^1\text{H}$ NMR spectrum of 4b[Bar$^4$] (CD$_2$Cl$_2$, 500 MHz).
1.10  [Rh(bipy)(COD)(PPh$_3$)][BAr$_4$]  5a
Figure S-24: $^{13}$C{\text{[H]} APT NMR spectrum of 5a (CD$_2$Cl$_2$, 126 MHz).

Figure S-25: $^{31}$P{\text{[H]} NMR spectrum of 5a (CD$_2$Cl$_2$, 162 MHz).

1.11 [Ir(bipy)(COD)(PPh$_3$)][BF$_4$] $\mathbf{5b}$

Figure S-26: $^1$H NMR spectrum of $\mathbf{5b}$ (CD$_2$Cl$_2$, 500 MHz).
Figure S-27: $^{13}\text{C}[^1\text{H}]$ APT NMR spectrum of 5b (CD$_2$Cl$_2$, 126 MHz).

Figure S-28: $^{31}\text{P}[^1\text{H}]$ NMR spectrum of 5b (CD$_2$Cl$_2$, 162 MHz).

1.12 [Rh(bipy)(COD)][BAr$_4^2$] 6a

Figure S-29: $^1\text{H}$ NMR spectrum of 6a (CD$_2$Cl$_2$, 500 MHz).
Figure S-30: $^{13}$C($^1$H) APT NMR spectrum of 6a (CD$_2$Cl$_2$, 126 MHz).

1.13 [Ir(bipy)(COD)][BAr$_{4.3}$] 6b

Figure S-31: $^1$H NMR spectrum of 6b (CD$_2$Cl$_2$, 500 MHz).

Figure S-32: $^{13}$C($^1$H) APT NMR spectrum of 6b (CD$_2$Cl$_2$, 126 MHz).
1.14 \([\text{Rh(bipy)}(\text{PPh}_3)_2][\text{BAR}^1_4]\) \(7\)

Figure S-33: \(^1\text{H}\) NMR spectrum of \(7\) (CD\(_2\)Cl\(_2\), 500 MHz).

Figure S-34: \(^{13}\text{C}\{^1\text{H}\}\) APT NMR spectrum of \(7\) (CD\(_2\)Cl\(_2\), 126 MHz).

Figure S-35: \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of \(7\) (CD\(_2\)Cl\(_2\), 162 MHz).
1.15 [Rh(PPh$_3$)$_2$][BAR$_4$]$_2$ 8

Figure S-36: $^1$H NMR spectrum of 8 (CD$_2$Cl$_2$, 500 MHz).

Figure S-37: $^{13}$C($^1$H) APT NMR spectrum of 8 (CD$_2$Cl$_2$, 126 MHz).

Figure S-38: $^{31}$P($^1$H) NMR spectrum of 8 (CD$_2$Cl$_2$, 162 MHz).
1.16 5-phthalimidomethylbipyridine

Figure S-39: $^1$H NMR spectrum of 5-phthalimidomethylbipyridine (CDCl$_3$, 400 MHz).

Figure S-40: $^{13}$C($^1$H) APT NMR spectrum of 5-phthalimidomethylbipyridine (CDCl$_3$, 101 MHz).

1.17 5-aminomethylbipyridine

Figure S-41: $^1$H NMR spectrum of 5-aminomethylbipyridine ((CD$_3$)$_2$SO, 400 MHz).
1.18 Amine 10

Figure S-42: $^{13}$C($^1$H) APT NMR spectrum of 5-aminomethylbipyridine ((CD$_3$)$_2$SO, 101 MHz).

Figure S-43: $^1$H NMR spectrum of 10 (CD$_2$Cl$_2$, 500 MHz).

Figure S-44: $^{13}$C($^1$H) APT NMR spectrum of 10 (CD$_2$Cl$_2$, 126 MHz).
2. **Selected in situ reaction data**

2.1 Hydrogenation of 2a+bipy @ 50 °C

Figure S-45: Selected $^1$H NMR spectra recorded during the hydrogenation of 2a+bipy (400 MHz, CD$_2$Cl$_2$).

Figure S-46: Selected $^{31}$P($^1$H) NMR spectra recorded during the hydrogenation of 2a+bipy (400 MHz, CD$_2$Cl$_2$).

Figure S-47: Relative concentration of species observed during the hydrogenation of 2a+bipy over 18 h, determined by integration of $^1$H NMR data.
2.2 Hydrogenation of 2b+bipy @ RT

Figure S-48: GC trace obtained following hydrogenation of 2a+bipy.

Figure S-49: $^1$H NMR spectrum obtained following hydrogenation of 2b+bipy (400 MHz, CD$_2$Cl$_2$). Signals belonging to COA and COE integrated.

Figure S-50: $^{31}$P($^1$H) NMR spectrum obtained following hydrogenation of 2b+bipy (162 MHz, CD$_2$Cl$_2$).

Figure S-51: GC trace obtained following hydrogenation of 2b+bipy.
2.3 Reaction between 2a and bipy

Figure S-52: Selected $^1$H NMR spectra recorded during the reaction between 2a with bipy (400 MHz, CD$_2$Cl$_2$).

Figure S-53: Selected $^{31}$P($^1$H) NMR spectra recorded during the reaction between 2a and bipy (162 MHz, CD$_2$Cl$_2$).
2.4 Reaction between 2b and bipy

Figure S-55: Selected $^1$H NMR spectra recorded during the reaction between 2b and bipy (400 MHz, CD$_2$Cl$_2$).

Figure S-56: Selected $^{31}$P($^1$H) NMR spectra recorded during the reaction between 2b and bipy (162 MHz, CD$_2$Cl$_2$).
2.5 Hydrogenation of 2a

Figure S-57: Selected $^1$H NMR spectra recorded during the hydrogenation of 2a (400 MHz, CD$_2$Cl$_2$).

Figure S-58: Selected $^{31}$P($^1$H) NMR spectra recorded during the hydrogenation of 2a (162 MHz, CD$_2$Cl$_2$).

2.6 Hydrogenation of 2b

Figure S-59: $^1$H NMR spectrum of in situ generated 9 at 298 K (500 MHz, CD$_2$Cl$_2$).
Figure S-60: $^{31}$P{$^1$H} NMR spectrum of *in situ* generated 9 at 298 K (202 MHz, CD$_2$Cl$_2$).

Figure S-61: $^1$H NMR spectrum of *in situ* generated 9 at 185 K (500 MHz, CD$_2$Cl$_2$).

Figure S-62: $^{31}$P{$^1$H} NMR spectrum of *in situ* generated 9 at 185 K (202 MHz, CD$_2$Cl$_2$).
2.7 Reaction between 3 and db24c8

Figure S-65: $^1$H NMR spectra following reaction between 3 and db24c8 (400 MHz, CD$_2$Cl$_2$).
2.8 Attempted hydrogenation of COD mediated by 4a[BArF$_4$]

Figure S-66: GC trace obtained following the reaction of 4a+COD under dihydrogen.

2.9 Reaction between 5a and PPh$_3$

Figure S-67: $^1$H NMR spectra demonstrating reaction between 5a and PPh$_3$ in CD$_2$Cl$_2$: 2a+bipy (400 MHz), 6a+2PPh$_3$ (500 MHz) and, for comparison, isolated 5a (500 MHz).

Figure S-68: $^{31}$P{$^1$H} NMR spectra demonstrating the reaction between 5a and PPh$_3$ in CD$_2$Cl$_2$: from 2a+bipy (162 MHz), 6a+2PPh$_3$ (202 MHz) and, for comparison, isolated 5a (202 MHz).
2.10 Hydrogenation of 7

Figure S-69: $^1$H NMR spectrum obtained following hydrogenation of 7 (400 MHz, CD$_2$Cl$_2$).

2.11 Reaction between 8 and bipy

Figure S-71: $^1$H NMR spectrum obtained following reaction between 8 and bipy (400 MHz, CD$_2$Cl$_2$).
Figure S-72: $^{31}\text{P}^{1\text{H}}$ spectrum obtained following reaction between 8 and bipy (162 MHz, CD$_2$Cl$_2$).
3. HR ESI-MS spectra of new compounds

Figure S-73: HR ESI-MS spectrum of 1a (positive ion, 4 kV).

Figure S-74: HR ESI-MS spectrum of 1b, [M-H]⁺ (positive ion, 4 kV).
Figure S-75: HR ESI-MS spectrum of 1b, [M]$^{2+}$ (positive ion, 4 kV).

Figure S-76: HR ESI-MS spectrum of 2a (positive ion, 4 kV).
Figure S-77: HR ESI-MS spectrum of 3 (positive ion, 4 kV).
Figure S-78: HR ESI-MS spectrum of 4a (positive ion, 4 kV).
Figure S-79: HR ESI-MS spectrum of 4b (positive ion, 4 kV).

Figure S-80: HR ESI-MS spectrum of 5a (positive ion, 4 kV).
Figure S-81: HR ESI-MS spectrum of 5b (positive ion, 4 kV).

Figure S-82: HR ESI-MS spectrum of 6a (positive ion, 4 kV).
Figure S-83: HR ESI-MS spectrum of 6b (positive ion, 4 kV).

Figure S-84: HR ESI-MS spectrum of 7 (positive ion, 4 kV).
Figure S-85: HR ESI-MS spectrum of 8 (positive ion, 4 kV).
Figure S-86: HR ESI-MS spectrum of 5-phthalimidomethylbipyridine (positive ion, 4 kV).

Figure S-87: HR ESI-MS spectrum of 5-aminomethylbipyridine (positive ion, 4 kV).
Figure S-88: HR ESI-MS spectrum of 10 (positive ion, 4 kV).