

**Table S1** Proton,  $^{13}\text{C}$ - $\{^1\text{H}\}$  and  $^{19}\text{F}$  NMR spectroscopic data for  $[\text{MX}^1\text{X}^2(\eta\text{-RC}\equiv\text{CR})\text{Tp}'][\text{Y}]^{\text{a}}$

Complex	$^1\text{H}$	$^{13}\text{C}$ - $\{^1\text{H}\}$	$^{19}\text{F}$
$[\text{WF}_2(\eta\text{-MeC}\equiv\text{CMe})\text{Tp}'][\text{BF}_4]^-$ $1^+[\text{BF}_4]^-$	1.84 (6H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.22 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.37 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.41 (6H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 3.34 (3H, s, $\text{MeC}_2\text{Me}$ ), 4.44 (3H, s, $\text{MeC}_2\text{Me}$ ), 5.96 (2H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 6.10 (2H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ )	12.1, 12.5, 12.6, 14.2 (s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 24.1, 27.0 (s, $\text{MeC}_2\text{Me}$ ), 109.0, 110.8 (s, 4- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 148.2, 148.9, 153.2, 153.5 (s, 3,5- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 217.1, 254.6 (s, $\text{PhC}\equiv\text{CPh}$ )	178.6, $J(^{19}\text{F}^{183}\text{W})$ 45
$[\text{WF}_2(\eta\text{-PhC}\equiv\text{CPh})\text{Tp}'][\text{BF}_4]^-$ $2^+[\text{BF}_4]^-$	1.53 (6H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.42 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.44 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.51 (6H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 5.97 (2H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 6.03 (1H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 6.76 (2H, m, <i>o</i> - $\text{PhC}_2\text{Ph}$ ), 7.46 (3H, m, <i>m</i> - and <i>p</i> - $\text{PhC}_2\text{Ph}$ ), 7.76 (1H, t, $^1J_{\text{HH}}$ 8, <i>p</i> - $\text{PhC}_2\text{Ph}$ ), 7.88 (2H, t, $^1J_{\text{HH}}$ 8, <i>m</i> - $\text{PhC}_2\text{Ph}$ ), 8.07 (2H, t, $^1J_{\text{HH}}$ 8, <i>o</i> - $\text{PhC}_2\text{Ph}$ )	12.2, 12.8, 13.2, 14.2 (s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 109.0, 110.9 (s, 4- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 130.2, 130.3, 133.3, 134.6, 135.2, 135.7, 136.0, 136.7 (s, $\text{PhC}\equiv\text{CPh}$ ), 147.9, 149.6, 153.2, 154.4 (s, 3,5- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 217.1, 254.6 (s, $\text{PhC}\equiv\text{CPh}$ )	166.5, $J(^{19}\text{F}^{183}\text{W})$ 45
	1.51 (6H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.46 (6H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.53 (6H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 5.50 (1H, m, <i>o</i> - $\text{PhC}_2\text{Ph}$ ), 6.01 (2H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 6.09 (1H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 7.24 (1H, m, <i>m</i> - $\text{PhC}_2\text{Ph}$ ), 7.56 (1H, t, $^1J_{\text{HH}}$ 8, <i>p</i> - $\text{PhC}_2\text{Ph}$ ), 7.80 (2H, m, <i>m</i> - $\text{PhC}_2\text{Ph}$ and <i>p</i> - $\text{PhC}_2\text{Ph}$ ). 7.94 (2H, t, $^1J_{\text{HH}}$ 8, <i>m</i> - $\text{PhC}_2\text{Ph}$ ), 8.12 (3H, m, <i>o</i> - $\text{PhC}_2\text{Ph}$ and <i>o</i> - $\text{PhC}_2\text{Ph}$ ) <sup>b</sup>	-	-
$[\text{WFC}l(\eta\text{-PhC}\equiv\text{CPh})\text{Tp}'][\text{SbCl}_6]^-$ $3^+[\text{SbCl}_6]^-$	1.50 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 1.57 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.52 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.55 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.58 (6H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.59 (6H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 6.00 (1H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 6.07 (1H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 6.18 (1H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 6.76 (2H, m, <i>o</i> - $\text{PhC}_2\text{Ph}$ ), 7.55 (3H, m, <i>m</i> - and <i>p</i> - $\text{PhC}_2\text{Ph}$ ), 7.84 (1H, m, <i>p</i> - $\text{PhC}_2\text{Ph}$ ), 7.98 (2H, m, <i>m</i> - $\text{PhC}_2\text{Ph}$ ), 8.14 (2H, m, <i>o</i> - $\text{PhC}_2\text{Ph}$ )	11.6, 12.1, 12.4, 13.4, 13.8, 15.2 (s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 109.1, 110.2, 110.4 (s, 4- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 129.2, 129.6, 132.2, 134.3, 134.8, 135.7, 136.3, 136.6 (s, $\text{PhC}\equiv\text{CPh}$ ), 147.0, 148.4, 149.0, 153.7, 154.0, 154.1 (s, 3,5- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 225.5, 262.7 (s, $\text{PhC}\equiv\text{CPh}$ )	182.6, $J(^{19}\text{F}^{183}\text{W})$ 21

	1.40 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 1.47 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 2.45 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 2.47 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 2.51 (6H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 5.22-5.47 (1H, m, <i>o</i> -PhC <sub>2</sub> Ph), 5.95 (1H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 6.03 (1H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 6.15 (1H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 7.23 (1H, m, <i>m</i> -PhC <sub>2</sub> Ph), 7.51 (1H, m, <i>p</i> -PhC <sub>2</sub> Ph), 7.78 (2H, m, <i>m</i> -PhC <sub>2</sub> Ph and <i>p</i> -PhC <sub>2</sub> Ph). 7.93 (2H, m, <i>m</i> -PhC <sub>2</sub> Ph), 8.10 (3H, m, <i>o</i> -PhC <sub>2</sub> Ph and <i>o</i> -PhC <sub>2</sub> Ph) <sup>c</sup>	-	-
[WCl <sub>2</sub> (η-PhC≡CPh)Tp'] <sup>+</sup> [SbCl <sub>6</sub> ] <sup>-</sup>	1.38 (6H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 2.51 (9H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 2.53 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 5.97 (2H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 6.19 (1H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 6.64 (2H, brd. m, <i>o</i> -PhC <sub>2</sub> Ph), 7.47 (3H, m, <i>m</i> - and <i>p</i> -PhC <sub>2</sub> Ph), 7.79 (1H, t, <sup>1</sup> J <sub>HH</sub> 8, <i>p</i> -PhC <sub>2</sub> Ph), 7.95 (2H, t, <sup>1</sup> J <sub>HH</sub> 8, <i>m</i> -PhC <sub>2</sub> Ph), 8.26 (2H, t, <sup>1</sup> J <sub>HH</sub> 8, <i>o</i> -PhC <sub>2</sub> Ph)	12.7, 13.3, 16.4, 16.5 (s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 110.8, 111.5 (s, 4-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 130.2, 130.4, 133.1, 136.0, 136.1, 137.0, 138.2, 138.4 (s, PhC≡CPh), 147.7, 149.6, 155.6, 155.9 (s, 3,5-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 217.0, 238.8 (s, PhC≡CPh)	-
	1.36 (6H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 2.52 (9H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 2.53 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 5.24 (1H, d, <sup>1</sup> J <sub>HH</sub> 8, <i>o</i> -PhC <sub>2</sub> Ph), 6.01 (2H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 6.24 (1H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 7.26 (1H, m, <i>m</i> -PhC <sub>2</sub> Ph), 7.54 (1H, m, <i>p</i> -PhC <sub>2</sub> Ph), 7.90 (2H, m, <i>m</i> -PhC <sub>2</sub> Ph and <i>p</i> -PhC <sub>2</sub> Ph), 8.01 (2H, t, <sup>1</sup> J <sub>HH</sub> 8, <i>m</i> -PhC <sub>2</sub> Ph), 8.07 (1H, d, <sup>1</sup> J <sub>HH</sub> 8, <i>o</i> -PhC <sub>2</sub> Ph), 8.32 (2H, d, <sup>1</sup> J <sub>HH</sub> 8, <i>o</i> -PhC <sub>2</sub> Ph) <sup>c</sup>	-	-
[MoCl <sub>2</sub> (η-PhC≡CPh)Tp'] <sup>+</sup> [SbCl <sub>6</sub> ] <sup>-</sup>	1.28 (6H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 2.47 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 2.51 (9H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 5.93 (2H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 6.15 (1H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 7.46 (2H, m, <i>m</i> -PhC <sub>2</sub> Ph), 7.60 (1H, m, PhC <sub>2</sub> Ph), 7.95 (3H, m, PhC <sub>2</sub> Ph), 8.35 (2H, m, PhC <sub>2</sub> Ph)		-

<sup>a</sup> Chemical shift ( $\delta$ ) in ppm,  $J$  values in Hz, spectra in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C unless otherwise stated. <sup>b</sup> At -90 °C. <sup>c</sup> At -80 °C.