

**Table S1** NMR spectroscopic data for [MnX(CNXyl)(NO)( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] and [M(CN)(CO)(RC $\equiv$ CR)Tp'].

Complex	Chemical shift ( $\delta$ )	
	<sup>1</sup> H	<sup>13</sup> C
[Mn(CN)(CNXyl)(NO)( $\eta$ -C <sub>5</sub> Me <sub>5</sub> )] <b>1</b>	1.88 (15H, s, C <sub>5</sub> Me <sub>5</sub> ), 2.45 (6H, s, C <sub>6</sub> H <sub>3</sub> Me <sub>2</sub> ), 7.1 (3H, m, C <sub>6</sub> H <sub>3</sub> Me <sub>2</sub> )	-
[MnI(CNXyl)(NO)( $\eta$ -C <sub>5</sub> Me <sub>5</sub> )] <b>2</b>	1.85 (15H, s, C <sub>5</sub> Me <sub>5</sub> ), 2.38 (6H, s, C <sub>6</sub> H <sub>3</sub> Me <sub>2</sub> ), 7.09 (3H, s, C <sub>6</sub> H <sub>3</sub> Me <sub>2</sub> )	-
[Mo(CN)(CO)(PhC $\equiv$ CPh)Tp'] <b>5</b>	1.19, 1.29, 2.32 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 2.50 (6H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 2.89 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 5.65, 5.72, 5.82 (1H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 6.77-8.03 (10H, m, $\equiv$ CPh)	12.5, 12.6, 12.8, 14.5, 14.9, 16.0 (s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 106.9, 107.5, 107.6 (s, 4-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 128.6, 129.0, 129.1, 129.4, 130.6, 130.7, 135.2, 137.4 (s, $\equiv$ CPh), 144.8, 145.9, 146.0, 148.0, 152.0, 152.4 (s, 3,5-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 153.8(s, CN), 209.2, 218.9 (s, $\equiv$ CPh), 235.0 (s, CO)
[W(CN)(CO)(PhC $\equiv$ CPh)Tp'] <b>6</b>	1.33, 1.50, 2.30 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 2.49 (6H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 2.86 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 5.74 (2H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 5.85 (1H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 6.71-7.86 (10H, m, $\equiv$ CPh)	12.4, 12.5, 12.7, 15.2, 16.0, 16.5 (s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 107.0, 107.9, 107.9 (s, 4-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 128.7, 129.1, 129.5, 129.8, 130.0, 130.1, 136.5, 138.6 (s, $\equiv$ CPh), 144.7, 146.0, 146.3, 149.4, 152.0, 153.9 (s, 3,5-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 154.6 (s, CN), 206.6, 216.0 (s, $\equiv$ CPh), 233.3 (s, CO)
[W(CN)(CO)(MeC $\equiv$ CMe)Tp'] <b>7</b>	1.33, 2.17, 2.25, 2.34, 2.43, 2.71 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 2.72, 3.25 (3H, s, $\equiv$ CMe), 5.67, 5.79, 6.00 (1H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ),	12.4, 12.5, 12.6, 15.6, 16.1, 16.2 (s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 20.2, 21.5 (s, $\equiv$ CMe), 107.0, 107.7, 107.8 (s, 4-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 144.6, 145.6, 145.9, 149.4, 152.3, 153.5 (s, 3,5-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 154.3 (s, CN), 208.7, 220.1 (s, $\equiv$ CMe), 231.5 (s, CO)