

Table S1 ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectroscopic data for $[\text{M}(\text{SR})\text{L}(\eta\text{-R}'\text{C}\equiv\text{CR}')\text{L}']^{\text{a}}$

Complex	^1H	$^{13}\text{C}\{-^1\text{H}\}$	^{31}P
$[\text{Mo}(\text{SMe})(\text{CO})(\eta\text{-MeC}\equiv\text{CMe})(\eta\text{-C}_5\text{H}_5)]$ 1	2.40 (s, 3H, <i>SMe</i>), 2.88 (s, 3H, <i>MeC}\equiv\text{CMe}</i>), 3.30 (s, 3H, <i>MeC}\equiv\text{CMe}</i>), 5.42 (s, 5H, <i>C}_5\text{H}_5</i>).	16.73 (s, <i>MeC}\equiv\text{CMe}</i>), 20.16 (s, <i>MeC}\equiv\text{CMe}</i>), 28.17 (s, <i>SMe</i>), 95.48 (s, <i>C}_5\text{H}_5</i>), 175.02 (s, <i>MeC}\equiv\text{CMe}</i>), 178.29 (s, <i>MeC}\equiv\text{CMe}</i>), 235.47 (s, CO).	-
$[\text{Mo}(\text{SPh})(\text{CO})(\eta\text{-MeC}\equiv\text{CMe})(\eta\text{-C}_5\text{H}_5)]$ 2	2.86 (s, 3H, <i>MeC}\equiv\text{CMe}</i>), 3.09 (s, 3H, <i>MeC}\equiv\text{CMe}</i>), 5.14 (s, 5H, <i>C}_5\text{H}_5</i>), 6.90-7.10 (m, 5H, <i>SPh</i>).	17.18 (s, <i>MeC}\equiv\text{CMe}</i>), 20.70 (s, <i>MeC}\equiv\text{CMe}</i>), 96.65 (s, <i>C}_5\text{H}_5</i>), 124.76 (s, <i>p-SPh</i>), 127.50 (s, <i>m-SPh</i>), 131.63 (s, <i>o-SPh</i>), 151.81 (s, <i>ipso-SPh</i>), 179.43 (s, <i>MeC}\equiv\text{CMe}</i>), 181.34 (s, <i>MeC}\equiv\text{CMe}</i>), 234.79 (s, CO).	-
$[\text{Mo}(\text{SMe})(\text{CO})(\eta\text{-PhC}\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)]$ 3	2.57 (s, 3H, <i>SMe</i>), 5.44 (s, 5H, <i>C}_5\text{H}_5</i>), 7.20-7.80 (m, 10H, (<i>PhC}\equiv\text{CPh}</i>)).	29.99 (s, <i>SMe</i>), 95.38 (s, <i>C}_5\text{H}_5</i>), 127.31, 128.12, 128.52, 128.85, 129.42, 130.15 (<i>PhC}\equiv\text{CPh}</i>), 136.33 (s, <i>ipso-PhC}\equiv\text{CPh}</i>), 137.93 (s, <i>ipso-PhC}\equiv\text{CPh}</i>), 180.40 (s, <i>PhC}\equiv\text{CPh}</i>), 180.74 (s, <i>PhC}\equiv\text{CPh}</i>), 235.47 (s, CO).	-

[Mo(SPh)(CO)(η -PhC $\equiv$ CPh)(η -C ₅ H ₅)] 4	5.29 (s, 5H, C ₅ H ₅), 7.00-7.15 (m, 5H, SPh), 7.25-7.77 (m, 10H, (PhC $\equiv$ CPh).	96.46 (s, C ₅ H ₅), 125.36 (s, <i>p</i> -SPh) 126.84 (s, <i>m</i> -SPh), 127.55, 128.14, 128.59, 128.98, 129.89, 130.56 (PhC $\equiv$ CPh), 132.56 (s, <i>o</i> -SPh), 135.07 (s, <i>ipso</i> -PhC $\equiv$ CPh), 138.80 (s, <i>ipso</i> -PhC $\equiv$ CPh), 152.50 (s, <i>ipso</i> -SPh), 234.99 (s, CO).
[W(SMe)(CO)(η -MeC $\equiv$ CMe)(η -C ₅ H ₅)] 5	2.36 (s, 3H, SMe), 2.93 (s, 3H, MeC $\equiv$ CMe), 3.06 (s, 3H, MeC $\equiv$ CMe), 5.50 (s, 5H, C ₅ H ₅).	17.28 (s, MeC $\equiv$ CMe), 20.44 (s, MeC $\equiv$ CMe), 30.93 (s, SMe), 93.87 (s, C ₅ H ₅), 178.78 (s, MeC $\equiv$ CMe), 179.21 (s, MeC $\equiv$ CMe), 229.25 (s, CO).
[W(SPh)(CO)(η -MeC $\equiv$ CMe)(η -C ₅ H ₅)] 6	3.04 (s, 3H, MeC $\equiv$ CMe), 3.23 (s, 3H, MeC $\equiv$ CMe), 5.78 (s, 5H, C ₅ H ₅), 6.90-7.80 (m, 5H, SPh).	17.61 (s, MeC $\equiv$ CMe), 20.79 (s, MeC $\equiv$ CMe), 94.99 (s, C ₅ H ₅), 124.74 (s, <i>p</i> -SPh), 127.56 (s, <i>m</i> -SPh) 131.80 (s, <i>o</i> -SPh), 153.04 (s, <i>ipso</i> -SPh), 180.91(s, MeC $\equiv$ CMe), 181.90 (s, MeC $\equiv$ CMe), 227.65 (s, CO).
[Mo(SMe){P(OMe) ₃ }(η -MeC $\equiv$ CMe)(η -C ₅ H ₅)] 7	2.17 (brd. s, 3H, SMe), 2.80 (s, 6H, MeC $\equiv$ CMe), 3.66 {d, J _{HP} 11 Hz, 9H, P(OMe) ₃ }, 5.17 (s, 5H, C ₅ H ₅).	29.99 (s, SMe), 31.59 (s, MeC $\equiv$ CMe), 51.30 196.53 {s, {d J _{CP} 4 Hz, P(OMe) ₃ }, 92.73 (s, C ₅ H ₅). P(OMe) ₃ }

[Mo(SPh){P(OMe) ₃ }(η-MeC≡CMe)(η-C ₅ H ₅)] 8	2.88 (brd. s, 6H, <i>MeC≡CMe</i>), 3.59 {d, J _{HP} 11 Hz, 9H, P(OMe) ₃ }, 4.86 (s, 5H, C ₅ H ₅), 6.90 (t, 1H, <i>p-SPh</i>), 7.05 (t, 2H, <i>m-SPh</i>), 7.15 (d, 2H, <i>o-SPh</i>).	31.59 (s, <i>MeC≡CMe</i>), 51.97 {d, J _{CP} 4 Hz, P(OMe) ₃ }, 94.22 (s, C ₅ H ₅), 123.44 (s, <i>p-SPh</i>), 127.06 (s, <i>m-SPh</i>), 131.60 (s, <i>o-SPh</i>), 153.74 (s, <i>ipso-SPh</i>), 204.52 (s, <i>MeC≡CMe</i>).	195.14 {s, P(OMe) ₃ }
[Mo(SMe){P(OMe) ₃ }(η-PhC≡CPh)(η-C ₅ H ₅)] 9	2.40 (s, 3H, <i>SMe</i>), 3.44 {d J _{HP} 11 Hz, 9H, P(OMe) ₃ }, 5.15 (s, 5H, C ₅ H ₅), 7.00-7.50 (m, 10H, (<i>PhC≡CPh</i>)).	32.50 (s, <i>SMe</i>), 51.68 {d, J _{CP} 4 Hz, P(OMe) ₃ }, 92.76 (s, C ₅ H ₅), 127.85 128.38 128.46, 131.54 (<i>PhC≡CPh</i>).	188.54 {s, P(OMe) ₃ }
[Mo(SPh){P(OMe) ₃ }(η-PhC≡CPh)(η-C ₅ H ₅)] 10	3.49 {d, J _{HP} 11 Hz, 9H, P(OMe) ₃ }, 5.02 (s, 5H, C ₅ H ₅), 6.90-7.90 (m, 15H, <i>SPh</i> and (<i>PhC≡CPh</i>)).	51.88 {d, J _{CP} 5 Hz, P(OMe) ₃ }, 94.29 (s, C ₅ H ₅), 124.00 (s, <i>p-SPh</i>), 128.10 (s, <i>m-SPh</i>), 133.00 (s, <i>o-SPh</i>), 148.00 (s, <i>ipso-SPh</i>), 126.50, 129.00, 130.50, 131.50 (<i>PhC≡CPh</i>).	186.23 {s, P(OMe) ₃ }
[W(SPh){P(OMe) ₃ }(η-MeC≡CMe)(η-C ₅ H ₅)] 11	2.93 (brd. s, 6H, <i>MeC≡CMe</i>), 3.57 {d, J _{HP} 11 Hz, 9H, P(OMe) ₃ }, 4.90 (s, 5H, C ₅ H ₅), 6.87 (t, 1H, <i>p-SPh</i>), 7.09 (t, 2H, <i>m-SPh</i>), 7.18 (d, 2H, <i>o-SPh</i>).	15.14 (s, <i>MeC≡CMe</i>), 52.40 {d J _{CP} 6 Hz, P(OMe) ₃ }, 92.04 (s, C ₅ H ₅), 123.51 (s, <i>p-SPh</i>) 127.29 (s, <i>m-SPh</i>), 131.65 (s, <i>o-SPh</i>), 156.50 (s, <i>ipso-SPh</i>).	159.60 {s, P(OMe) ₃ } ^b

[W(SMe)(CO)(η -PhC $\equiv$ CPh)Tp'] **12**

1.52 (s, 3H, pz *Me*), 1.63 (s, 3H, pz *Me*), 2.26 (s, 3H, pz *Me*), 2.39 (s, 3H, pz *Me*), 2.48 (s, 3H, pz *Me*), 2.74 (s, 3H, pz *Me*), 3.53 (3H, s, *SMe*), 5.59 (s, 1H, pz *CH*), 5.72 (s, 1H, pz *CH*), 5.78 (s, 1H, pz *CH*), 6.31-6.40 (m, 2H, *o*-PhC $\equiv$ CPh), 6.98-7.04 (m, 3H, *m*- and *p*-PhC $\equiv$ CPh), 7.33-7.40 (m, 1H, *p*-PhC $\equiv$ CPh), 7.43-7.51 (m, 2H, *m*-PhC $\equiv$ CPh), 7.68-7.75 (m, 2H, *o*-PhC $\equiv$ CPh)

12.52 (s, pz *Me*), 12.69 (s, pz *Me*), 15.45 (s, pz *Me*), 15.91 (s, pz *Me*), 16.49 (s, pz *Me*), 30.02 (s, *SMe*), 106.60 (s, pz *CH*), 107.46 (s, pz *CH*), 108.56 (s, pz *CH*), 127.64 (s, PhC $\equiv$ CPh) 128.09 (s, PhC $\equiv$ CPh), 128.74 (s, PhC $\equiv$ CPh), 128.86 (s, PhC $\equiv$ CPh), 130.46 (s, PhC $\equiv$ CPh), 137.03 (s, *ipso*-PhC $\equiv$ CPh), 138.04 (s, *ipso*-PhC $\equiv$ CPh), 144.21 (s, pz CMe), 144.36 (s, pz CMe), 145.19 (s, pz CMe), 150.82 (s, pz CMe), 153.92 (s, pz CMe), 154.18 (s, pz CMe), 183.28 (s, PhC $\equiv$ CPh), 194.08 (s, PhC $\equiv$ CPh), 236.12 (s, CO)

[W(SPh)(CO)(η -PhC $\equiv$ CPh)Tp'] **13**

1.21 (s, 3H, pz CH₃), 1.55 (s, 3H, pz CH₃), 2.35 (s, 3H, pz CH₃), 2.42 (s, 3H, pz CH₃), 2.50 (s, 3H, pz CH₃), 2.69 (s, 3H, pz CH₃), 5.49 (s, 1H, pz *CH*), 5.64 (s, 1H, pz *CH*), 5.80 (s, 1H, pz *CH*), 6.34-6.45 (m, 2H, *o*-PhC $\equiv$ CPh), 6.50-6.70 (m, 2H, *o*-SPh), 6.70-6.90 (m, 3H, *m*- and *p*-SPh),

12.57 (s, pz *Me*), 12.59 (s, pz *Me*), 12.70 (s, pz CH₃), 15.25 (s, pz *Me*), 16.00 (s, pz *Me*), 16.6 (s, pz *Me*), 106.78 (s, pz *CH*), 107.53 (s, pz *CH*), 107.89 (s, pz *CH*), 123.63 (s, *o*-SPh), 127.34 (s, *m*-SPh), 127.95 (s, PhC $\equiv$ CPh), 128.10 (s, PhC $\equiv$ CPh), 128.30 (s, PhC $\equiv$ CPh), 128.73 (s, PhC $\equiv$ CPh), 129.20 (s, PhC $\equiv$ CPh), 130.12 (s, PhC $\equiv$ CPh), 131.72 (s, *p*-SPh),

6.95-7.06 (m, 3H, <i>p</i> -PhC≡CPh),	137.06 (s, <i>ipso</i> -PhC≡CPh), 138.50 (s, <i>ipso</i> -
7.36-7.47 (m, 1H, <i>p</i> -PhC≡CPh), 7.47-	PhC≡CPh), 144.01 (s, pz CMe), 144.56 (s, pz
7.57 (m, 2H, <i>m</i> -PhC≡CPh), 7.75-7.85	CMe), 145.40 (s, pz CMe), 150.70 (s, pz
(m, 2H, <i>o</i> -PhC≡CPh)	CMe), 151.77 (s, <i>ipso</i> -SPh), 153.90 (s, pz
	CMe), 154.44 (s, pz CMe), 187.19 (s,
	PhC≡CPh), 196.80 (s, PhC≡CPh), 233.23 (s,
	CO)

^a Chemical shift (δ) in ppm, spectra in CD₂Cl₂. ^b Tungsten satellites observed: J_{WP} 468 Hz.