

**Catalyst-free room-temperature iClick reaction  
of molybdenum(II) and tungsten(II) azide complexes  
with electron-poor alkynes: Structural preferences and  
kinetic studies**

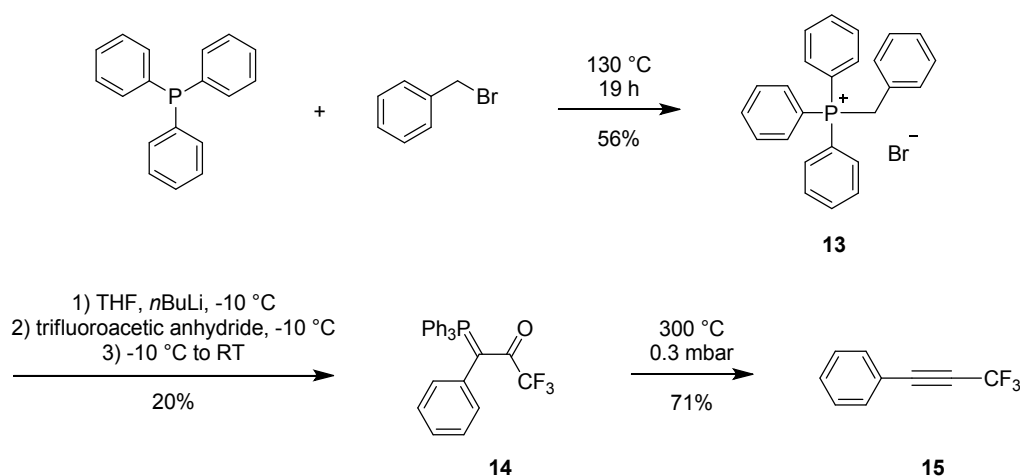
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**Supporting Information**

## Synthesis of ligands and precursors



**Scheme S1.** Three-step synthesis of phenyltrifluoromethylacetylene **15** from benzylbromide and triphenylphosphine (Y. Kobayashi, T. Yamashita, K. Takahashi, H. Kuroda and I. Kumadaki, *Chem. Pharm. Bull.* **1984**, 32, 4402).

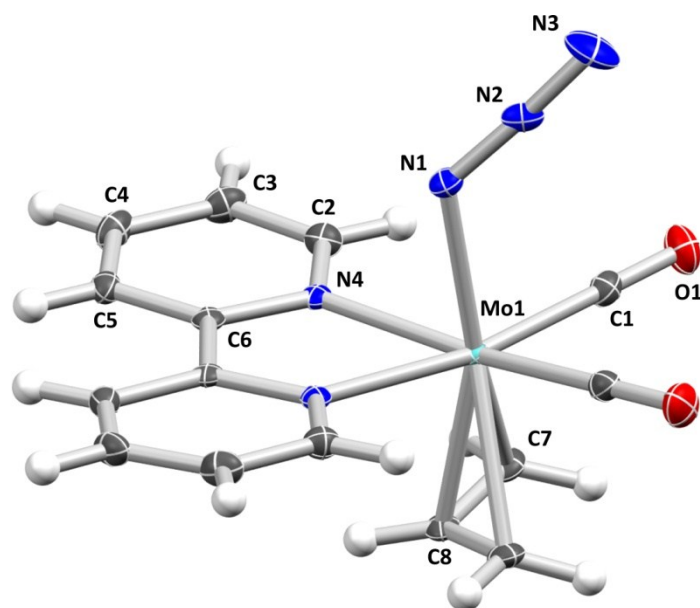
**Synthesis of benzyltriphenylphosphonium bromide (13).** Solid triphenylphosphine (15.3 g, 58.5 mmol) was mixed under argon with benzyl bromide (7.6 mL, 11.0 g, 64.3 mmol) and heated to 130 °C for 19 h. The yellow crude product was then purified by column chromatography on silica using dichloromethane/methanol (9:1 v/v) as the eluent to obtain a colorless solid. Yield: 56% (14.2 g, 32.8 mmol). Elemental analysis (%): calc. C<sub>25</sub>H<sub>22</sub>BrP: C 69.30, H 5.12, found: C 69.19, H 5.10; IR (ATR, cm<sup>-1</sup>): 3055 (m), 2982 (m), 2773 (m), 1438 (s), 1111 (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500.13 MHz, ppm): δ 7.65–7.77 (m, 9H, C<sub>6</sub>H<sub>5</sub>), 7.56–7.63 (m, 6H, C<sub>6</sub>H<sub>5</sub>), 7.16–7.21 (m, 1H, C<sub>6</sub>H<sub>5</sub>), 7.04–7.10 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 5.33 (d, 2H, <sup>2</sup>J<sub>H,P</sub> = 14.4 Hz, CH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.76 MHz, ppm): δ 135.08 (phenyl-C), 133.44 (phenyl-C), 131.57 (phenyl-C), 130.23 (phenyl-C), 128.89 (phenyl-C), 128.47 (phenyl-C), 127.18 (phenyl-C), 117.82 (phenyl-C), 30.92 (CH<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 202.46 MHz, ppm): δ 23.15 (s).

**Synthesis of triphenylphosphonium- $\alpha$ -(trifluoroacetyl)benzylide (14).** Benzyltriphenylphosphonium bromide (**13**, 500 mg, 1.15 mmol) was dissolved under argon in anhydrous tetrahydrofuran (10 mL) and the white suspension cooled to  $-10\text{ }^{\circ}\text{C}$  using a mixture of ice and sodium chloride. Then, over a period of 45 min, 1.6 M *n*-butyllithium in *n*-hexane (1.44 mL, 148 mg, 2.31 mmol) was added, followed by stirring at  $-10\text{ }^{\circ}\text{C}$  for 1 h. Afterwards, trifluoroacetic anhydride (162  $\mu\text{L}$ , 242 mg, 1.15 mmol) was added dropwise over a period of 10 min at  $-10\text{ }^{\circ}\text{C}$  and the mixture then stirred for 1 h at room temperature. After addition of isopropanol (3 mL), the solvent was removed under reduced pressure. The crude brown product was purified by column chromatography on silica using dichloromethane/methanol (49:1 v/v) as the eluent. The resulting yellow material was washed with diethyl ether (10 mL) to obtain a colorless solid. Yield: 20% (101 mg, 0.23 mmol). Elemental analysis (%): calc.  $\text{C}_{27}\text{H}_{20}\text{F}_3\text{OP}$ : C 72.32, H 4.50, found: 72.44, H 4.60; IR (ATR,  $\text{cm}^{-1}$ ): 3056 (w), 1553 (s), 1159 (s), 1104 (s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500.13 MHz, ppm):  $\delta$  7.56–7.49 (m, 9H,  $\text{PC}_6\text{H}_5$ ), 7.43–7.37 (m, 6H,  $\text{PC}_6\text{H}_5$ ), 7.05–6.97 (m, 5H,  $\text{CC}_6\text{H}_5$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125.76 MHz, ppm):  $\delta$  170.39 (dq,  $^2J_{\text{C,F}} = 30.1\text{ Hz}$ ,  $^2J_{\text{C,P}} = 8.6\text{ Hz}$ , C=O), 135.13 (d,  $^3J_{\text{C,P}} = 4.7\text{ Hz}$ , phenyl-C), 134.14 (d,  $^2J_{\text{C,P}} = 8.1\text{ Hz}$ , phenyl-C), 133.77 (d,  $^3J_{\text{C,P}} = 9.7\text{ Hz}$ , phenyl-C), 132.38 (d,  $^4J_{\text{C,P}} = 2.4\text{ Hz}$ , phenyl-C), 128.91 (d,  $^2J_{\text{C,P}} = 12.4\text{ Hz}$ , phenyl-C), 127.55 (d,  $^4J_{\text{C,P}} = 2.4\text{ Hz}$ , phenyl-C), 126.54 (d,  $^5J_{\text{C,P}} = 3.0\text{ Hz}$ , phenyl-C), 124.59 (d,  $^1J_{\text{C,P}} = 90.8\text{ Hz}$ , C-P), 119.41 (dq,  $^1J_{\text{C,F}} = 291.0\text{ Hz}$ ,  $^3J_{\text{C,P}} = 20.1\text{ Hz}$ ,  $\text{CF}_3$ ), signal for C=P carbon atom observed;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 202.46 MHz, ppm):  $\delta$  19.70 (s,  $\text{PPh}_3$ );  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 470.59 MHz, ppm):  $\delta$  -68.36 (d,  $^4J_{\text{F,P}} = 2.6\text{ Hz}$ ,  $\text{CF}_3$ ).

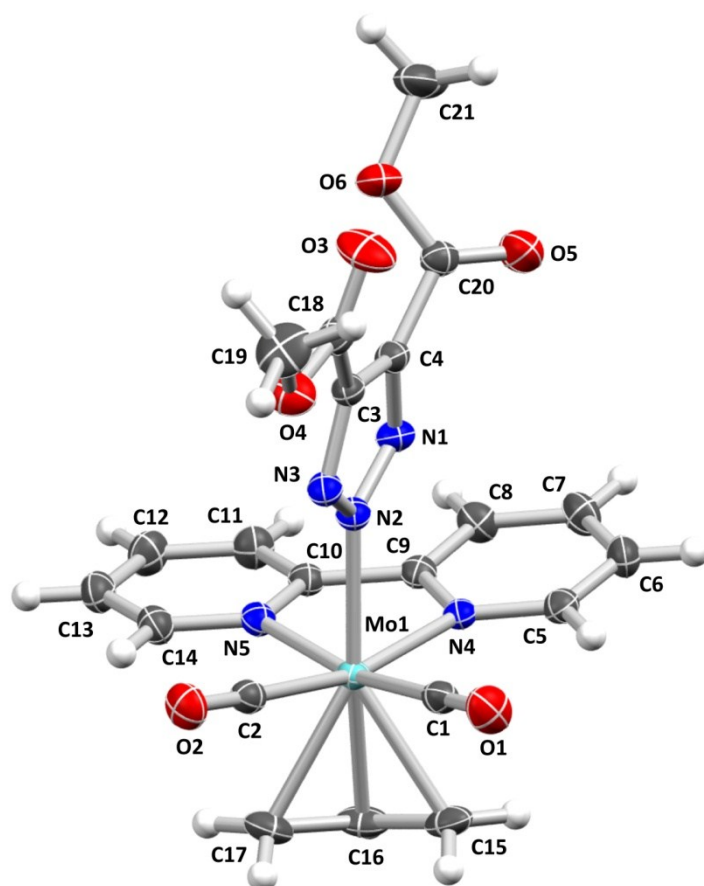
**Synthesis of phenyltrifluoromethylacetylene (15).** A one-neck round-bottom flask filled with triphenylphosphonium- $\alpha$ -(trifluoroacetyl)benzylide (**14**, 2.75 g, 6.14 mmol) was connected *via* a long glass tube to a Schlenk flask immersed in liquid dinitrogen, which was heated to  $300\text{ }^{\circ}\text{C}$  under vacuum ( $3 \cdot 10^{-1}$  mbar) for 2 h with a heat gun. The collection flask was allowed to reach room temperature and the product collected as a clear colorless liquid. Yield: 71% (740 mg, 4.35 mmol). Elemental analysis (%): calc.  $\text{C}_9\text{H}_5\text{F}_3$ : C 63.54, H 2.96, found: C 63.39, H 2.97; IR (ATR,  $\text{cm}^{-1}$ ): 2254 (s), 1493 (m), 1309 (vs), 1124 (vs);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.40 MHz, ppm):  $\delta$  7.60–7.54 (m, 2H,  $\text{C}_6\text{H}_5$ ), 7.51–7.45 (m, 1H,  $\text{C}_6\text{H}_5$ ), 7.44–7.37 (m, 2H,  $\text{C}_6\text{H}_5$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.68 MHz, ppm):  $\delta$  132.59 (q,  $^5J_{\text{C,F}} = 1.6\text{ Hz}$ , phenyl-C), 131.02 (s, phenyl-C), 128.80 (s, phenyl-C), 118.68 (q,  $^4J_{\text{C,F}} = 1.8\text{ Hz}$ ,  $\text{C}\equiv\text{C}-\text{CF}_3$ ), 115.00 (q,  $^1J_{\text{C,F}} = 257.0\text{ Hz}$ ,  $\text{CF}_3$ ), 86.67 (q,  $^3J_{\text{C,F}} = 6.5\text{ Hz}$ , phenyl-C), 75.85 (q,  $^2J_{\text{C,F}} = 52.5\text{ Hz}$ ,  $\text{C}\equiv\text{C}-\text{CF}_3$ );  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376.75 MHz, ppm):  $\delta$  -49.80 (s,  $\text{CF}_3$ ).

**Synthesis of [W(bpy)(CO)<sub>4</sub>] (7).** Tungsten hexacarbonyl (1.00 g, 2.84 mmol) was suspended under argon in degassed benzene (25 mL). Then, under efficient stirring, a solution of trimethylamine-*N*-oxide dihydrate (TMAO, 679 mg, 6.11 mmol) in degassed methanol (10 mL) was added, which resulted in the solution to turn yellow immediately. Then, solid 2,2'-bipyridine (470 mg, 3.01 mmol) was added, upon which the solution turned red over the course of 1 h. Stirring was continued at room temperature for 2 d. The resulting red-brown solid which had precipitated was filtered off and recrystallized from acetonitrile (100 mL). Finally, the product was washed with *n*-hexane (50 mL) and dried under vacuum overnight, resulting in a dark violet crystalline solid. Yield: 31% (399 mg, 0.88 mmol). Elemental analysis (%): calc. C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>W: C 37.20, H 1.78, N 6.20, found: C 37.16, H 1.96, N 6.17; IR (ATR, cm<sup>-1</sup>): 2001 (m), 1902 (m), 1821 (s), 1787 (s), 1599 (s), 1467 (s), 1437 (m), 759 (m); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500.13 MHz, ppm): δ 9.09 (ddd, 2H, <sup>3</sup>J<sub>H6,H5</sub> = 5.5 Hz, <sup>4</sup>J<sub>H6,H4</sub> = 1.6 Hz, <sup>5</sup>J<sub>H6,H3</sub> = 0.8 Hz, bpy-H6), 8.71 (dt, 2H, <sup>3</sup>J<sub>H3,H4</sub> = 8.3 Hz, <sup>4</sup>J<sub>H3,H5</sub> = 1.0 Hz, bpy-H3), 8.24 (ddd, 2H, <sup>3</sup>J<sub>H4,H3</sub> = 8.1 Hz, <sup>3</sup>J<sub>H4,H5</sub> = 7.6 Hz, <sup>4</sup>J<sub>H4,H6</sub> = 1.6 Hz, bpy-H4), 7.67 (ddd, 2H, <sup>3</sup>J<sub>H5,H4</sub> = 7.5 Hz, <sup>3</sup>J<sub>H5,H6</sub> = 5.5 Hz, <sup>4</sup>J<sub>H5,H3</sub> = 1.3 Hz, bpy-H5); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125.76 MHz, ppm): δ 214.80 (C≡O), 201.64 (C≡O), 155.22 (bpy-C2), 152.41 (bpy-C6), 138.84 (bpy-C4), 127.04 (bpy-C5), 124.05 (bpy-C3).

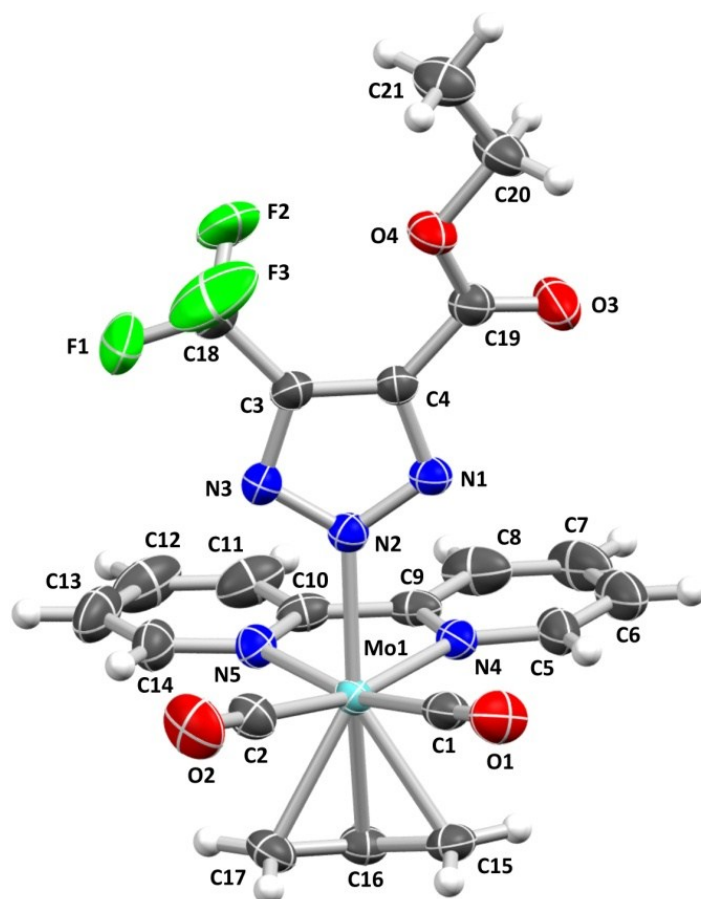
**Synthesis of [W(bpy)(CO)<sub>3</sub>(py)] (8).** Pyridine (1 mL, 0.98 g, 12.4 mmol) was dissolved in degassed xylene (10 mL), solid [W(bpy)(CO)<sub>4</sub>] (7, 250 mg, 0.55 mmol) added, and the reaction mixture heated to reflux for 18 h. The resulting black precipitate was filtered from the yellow-red solution, washed with toluene (50 mL) and methanol (20 mL) and dried under vacuum overnight. Yield: 76% (213 mg, 0.42 mmol). Elemental analysis (%): calc. C<sub>18</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub>W: C 42.97, H 2.60, N 8.35, found: C 40.37, H 2.70, N 7.40; IR (ATR, cm<sup>-1</sup>): 1874 (s) 1745 (s), 1600 (w), 1466 (w), 1440 (m), 763 (m); since the pyridine ligand rapidly exchanged with solvent, for example in DMSO, no NMR assignment was made.



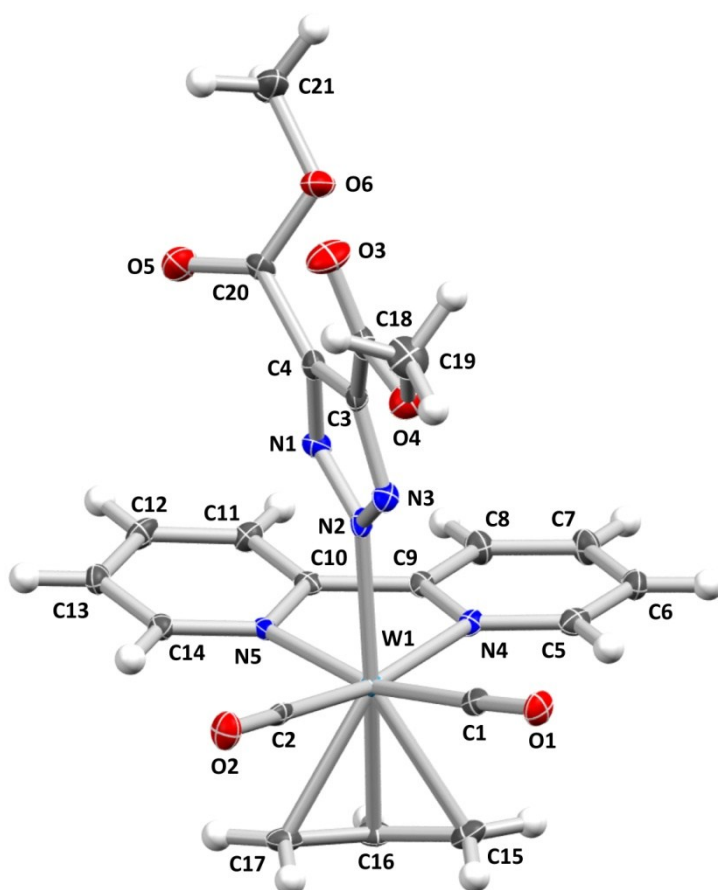
**Fig. S1** Molecular structure of  $[\text{Mo}(\eta^3\text{-allyl})(\text{N}_3)(\text{bpy})(\text{CO})_2]$  (**2**) with thermal ellipsoids displayed at the 50% probability level. The asymmetric unit contains only one half of the molecule with the other one related to it by a mirror plane. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **2**: Mo1–C1 1.956(2), Mo1–N1 2.180(3), Mo1–N4 2.240(2), Mo1–(allyl centroid) 2.044(2), C1–O1 1.163(3), C7–C8 1.409(3), N1–N2 1.201(4), N2–N3 1.152(4), C1–Mo1–C1a 81.4(1), N4–Mo1–N4a 72.3(1), C1–Mo1–N4 102.53(9), N1–Mo1–(allyl centroid) 174.24(9), C7–C8–C7a 114.8(3), Mo1–N1–N2 124.9(2), N1–N2–N3 176.7(4).



**Fig. S2** Molecular structure of  $[\text{Mo}(\eta^3\text{-allyl})(\text{triazolate}^{\text{COOCH}_3, \text{COOCH}_3})(\text{bpy})(\text{CO})_2]$  (**5**) with thermal ellipsoids displayed at the 50% probability level. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **5**: Mo1–C1 1.978(2), Mo1–C2 1.969(2), Mo1–N2 2.221(2), Mo1–N4 2.255(2), Mo1–N5 2.258(2), Mo1–(allyl centroid) 2.056(2), C1–O1 1.156(3), C2–O2 1.160(3), C15–C16 1.408(4), C16–C17 1.411(3), C1–Mo1–C2 80.47(9), N4–Mo1–N5 72.77(7), C1–Mo1–N4 104.38(8), C2–Mo1–N5 100.25(8), N2–Mo1–(allyl centroid) 177.63(6), C15–C16–C17 116.1(2), (N2–Mo1–C16)–(triazolate) 13.6(3).



**Fig. S3** Molecular structure of  $[\text{Mo}(\eta^3\text{-allyl})(\text{triazolate}^{\text{CF}_3, \text{COOEt}})(\text{bpy})(\text{CO})_2]$  (**6**) with thermal ellipsoids displayed at the 50% probability level. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **6**: Mo1–C1 1.954(3), Mo1–C2 1.964(2), Mo1–N2 2.210(2), Mo1–N4 2.218(2), Mo1–N5 2.234(2), Mo1–(allyl centroid) 2.048(2), C1–O1 1.156(3), C2–O2 1.150(3), C15–C16 1.400(4), C16–C17 1.396(4), C1–Mo1–C2 81.4(1), N4–Mo1–N5 73.11(8), C1–Mo1–N4 101.8(1), C2–Mo1–N5 101.4(1), N2–Mo1–(allyl centroid) 176.37(7), C15–C16–C17 116.4(3), (N2–Mo1–C16)–(triazolate) 80.4(3).



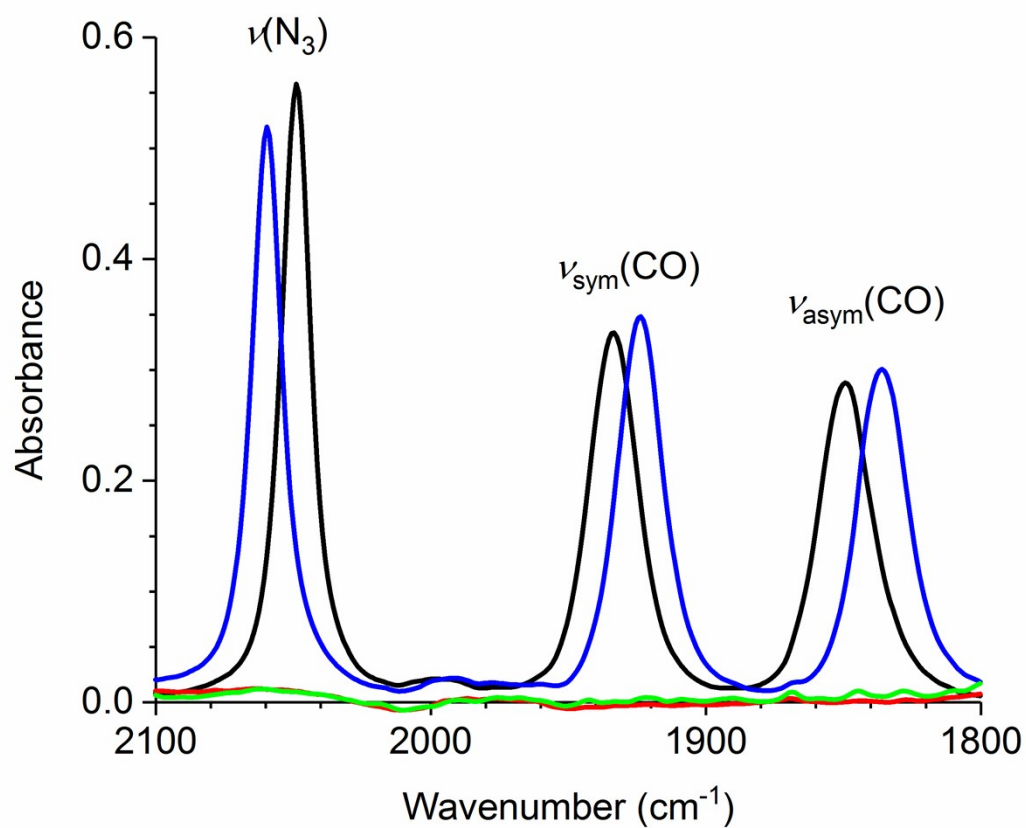
**Fig. S4** Molecular structure of  $[W(\eta^3\text{-allyl})(\text{triazolate}^{\text{COOCH}_3, \text{COOCH}_3})(\text{bpy})(\text{CO})_2]$  (**11**) with thermal ellipsoids displayed at the 50% probability level. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **11**: W1–C1 1.957(4), W1–C2 1.960(4), W1–N2 2.194(3), W1–N4 2.224(3), W1–N5 2.231(3), W1–(allyl centroid) 2.032(2), C1–O1 1.163(4), C2–O2 1.165(5), C15–C16 1.402(6), C16–C17 1.404(6), C1–W1–C2 80.9(2), N4–W1–N5 73.1(1), C1–W1–N4 99.7(1), C2–W1–N5 104.1(1), N2–W1–(allyl centroid) 177.6(1), C15–C16–C17 115.8(3), (N2–W1–C16)–(triazolate) 15.6(5).



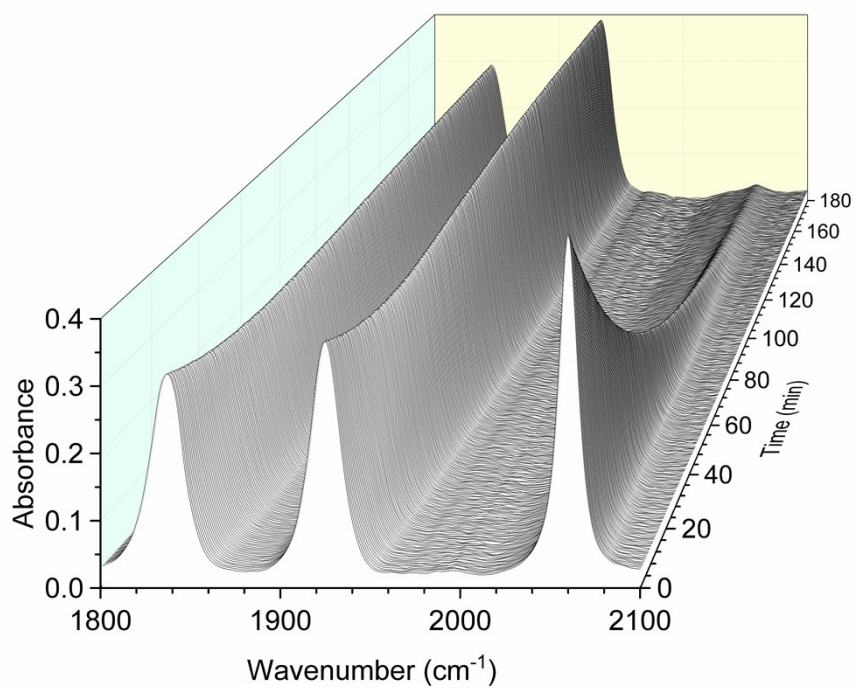
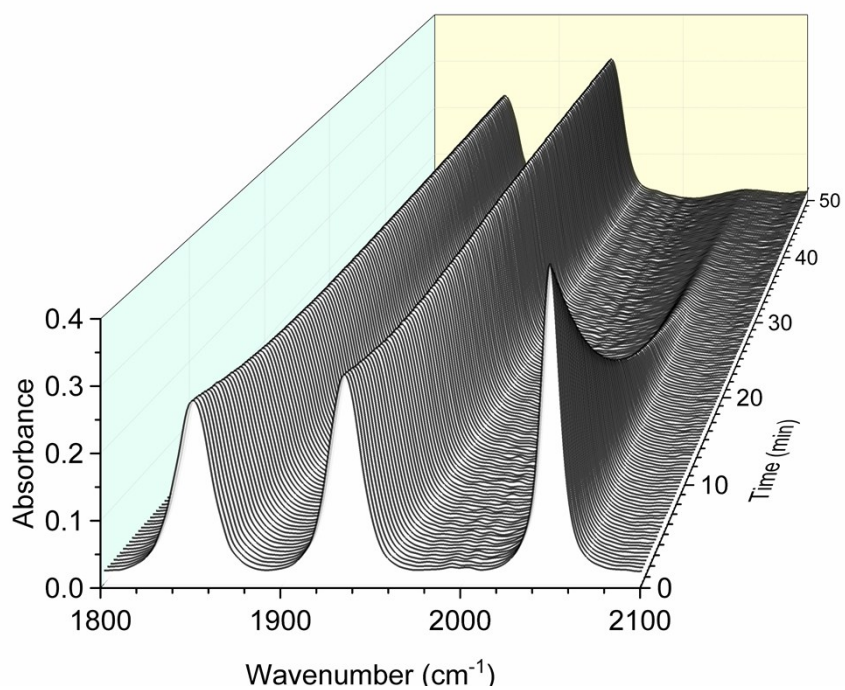
**Table S1** Crystallographic parameters for **2**, **5**, and **6** as well as **10–12**

Compound	<b>2</b>	<b>5</b>	<b>6</b>	<b>10</b>	<b>11</b>	<b>12</b>
Empirical formula	C <sub>15</sub> H <sub>13</sub> MoN <sub>5</sub> O <sub>2</sub>	C <sub>21</sub> H <sub>19</sub> MoN <sub>5</sub> O <sub>6</sub>	C <sub>21</sub> H <sub>18</sub> F <sub>3</sub> MoN <sub>5</sub> O <sub>4</sub>	C <sub>15</sub> H <sub>13</sub> N <sub>5</sub> O <sub>2</sub> W	C <sub>21</sub> H <sub>19</sub> N <sub>5</sub> O <sub>6</sub> W	C <sub>21</sub> H <sub>18</sub> F <sub>3</sub> N <sub>5</sub> O <sub>4</sub> W
Formula weight (g·mol <sup>-1</sup> )	391.24	533.35	557.34	479.15	621.26	645.25
Temperature (K)	100(2)	173(2)	273(2)	100(2)	100(2)	100(2)
Radiation, λ (Å)	MoK <sub>α</sub> 0.71073	MoK <sub>α</sub> 0.71073	MoK <sub>α</sub> 0.71073	MoK <sub>α</sub> 0.71073	MoK <sub>α</sub> 0.71073	MoK <sub>α</sub> 0.71073
Crystal system	Orthorhombic	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pnma</i>	<i>P2<sub>1</sub>/c</i>	<i>p</i> $\bar{1}$	<i>Pnma</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>
<i>Unit cell dimensions</i>						
<i>a</i> (Å)	16.96(1)	11.815(8)	10.545(2)	16.83(3)	11.697(6)	11.078(5)
<i>b</i> (Å)	13.755(6)	9.369(6)	10.851(2)	13.77(2)	9.262(6)	9.984(5)
<i>c</i> (Å)	6.589(3)	20.13(1)	11.320(2)	6.602(8)	19.89(1)	19.17(1)
$\alpha$ (°)	90	90	82.745(7)	90	90	90
$\beta$ (°)	90	103.28(1)	63.061(8)	90	103.39(2)	91.10(2)
$\gamma$ (°)	90	90	75.89(2)	90	90	90
Volume (Å <sup>3</sup> )	1537(1)	2169(3)	1119.7(4)	1530(4)	2096(2)	2120(2)
<i>Z</i>	4	4	2	4	4	4
Calculated density (kg·m <sup>-3</sup> )	1.690	1.633	1.653	2.080	1.969	2.022
Absorption coefficient (mm <sup>-1</sup> )	0.870	0.654	0.649	7.566	5.563	5.517
<i>F</i> (000)	784	1080	560	912	1208	1248
Theta range for collection (2 $\theta$ , °)	2.822 to 26.019	1.771 to 26.019	2.216 to 26.843	2.837 to 28.279	2.438 to 26.022	1.839 to 26.022
Reflections collected	9005	17803	15715	9425	15002	24833
Independent reflections	1577	4262	4788	1979	4133	4178
Minimum/maximum transmission	0.6445 / 0.7465	0.5979 / 0.7453	0.8842 / 0.9763	0.5011 / 0.7471	0.4438 / 0.7465	0.5169 / 0.7471
Refinement method	a	a	a	a	a	a
Data / parameters / restraints	1577 / 120 / 0	4262 / 300 / 0	4788 / 325 / 5	1979 / 120 / 0	4133 / 315 / 5	4178 / 323 / 5
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.035	1.060	1.034	1.020	1.026	1.049
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	R <sub>1</sub> = 0.0237 wR <sub>2</sub> = 0.0555	R <sub>1</sub> = 0.0260 wR <sub>2</sub> = 0.0656	R <sub>1</sub> = 0.0330 wR <sub>2</sub> = 0.0634	R <sub>1</sub> = 0.0220 wR <sub>2</sub> = 0.0452	R <sub>1</sub> = 0.0227 wR <sub>2</sub> = 0.0487	R <sub>1</sub> = 0.0155 wR <sub>2</sub> = 0.0345
<i>R</i> indices (all data)	R <sub>1</sub> = 0.0332 wR <sub>2</sub> = 0.0596	R <sub>1</sub> = 0.0292 wR <sub>2</sub> = 0.0676	R <sub>1</sub> = 0.0476 wR <sub>2</sub> = 0.0679	R <sub>1</sub> = 0.0352 wR <sub>2</sub> = 0.0501	R <sub>1</sub> = 0.0299 wR <sub>2</sub> = 0.0511	R <sub>1</sub> = 0.0172 wR <sub>2</sub> = 0.0351
Maximum/minimum residual electron density (e·Å <sup>-3</sup> )	0.512 / -0.461	0.330 / -0.292	0.368 / -0.407	1.380 / -0.764	0.787 / -0.889	0.873 / -0.626

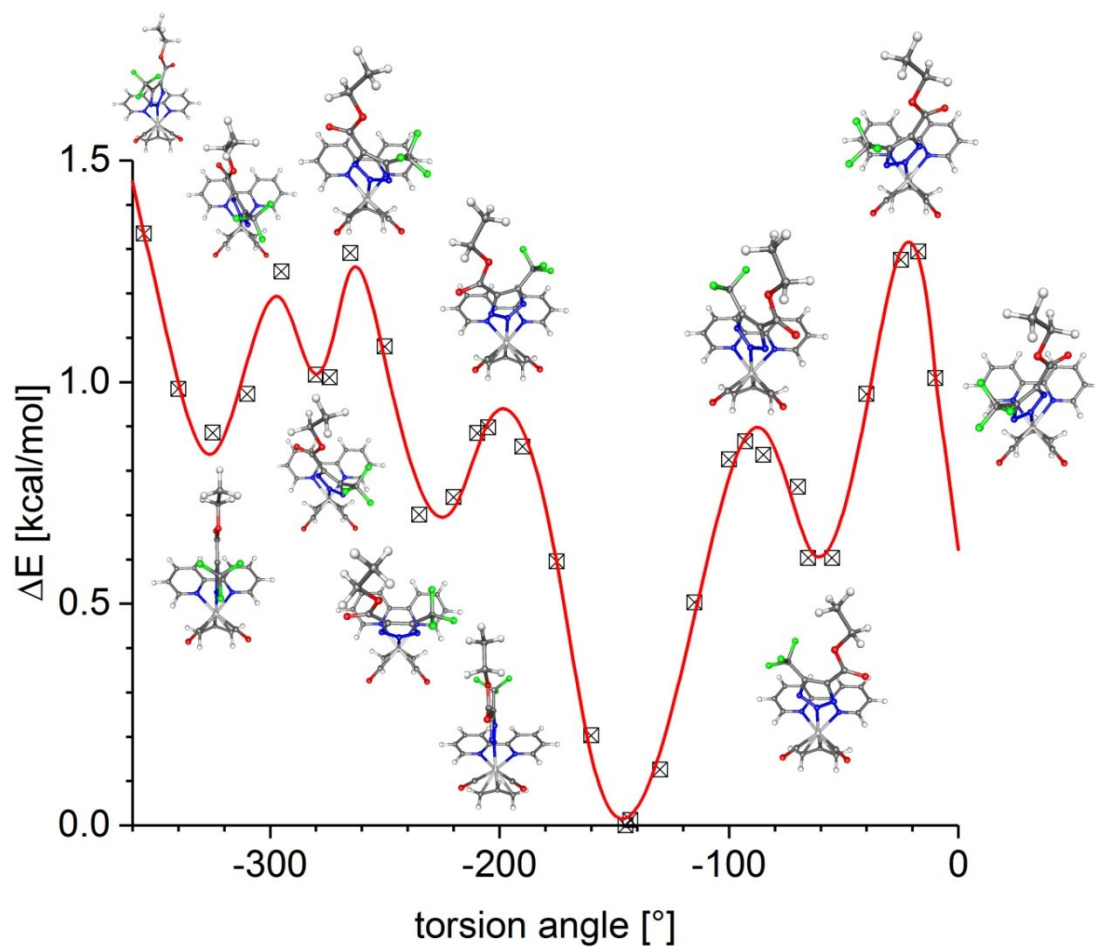
<sup>a</sup> Full-matrix least-squares on *F*<sup>2</sup>.



**Fig. S5** Solution IR spectra of azide complexes **2** (black, 8 mM) and **10** (blue, 8 mM) as well as alkynes **3** (red, 40 mM) and **4** (green, 40 mM) in dimethylsulfoxide.



**Fig. S6** Changes in the 1800–2100  $\text{cm}^{-1}$  spectral range of the IR spectrum of a mixture of **2** (top) or **10** (bottom) in dimethylsulfoxide (8 mM) upon reaction with dimethyl acetylenedicarboxylate (DMAD, **3**, 40 mM) at 26 °C in 20 s intervals for up to 180 min.



**Fig. S7** Conformational energy diagram of **6** for variation of the torsion angle between the triazolite mean plane and the bpy C2–C2' axis calculated with DFT (ORCA 2.8, BP86, RI, TZVP, COSMO in DMSO).