

Supporting Information
for
Efficient catalytic alkyne metathesis with a fluoroalkoxy-
supported ditungsten(III) complex

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Experimental section, NMR spectra, catalysis procedure and
product characterization, crystallographic details for
W₂F₃·(NHMe₂), W₂F₃ and WPhF₃

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Experimental section

General experimental considerations

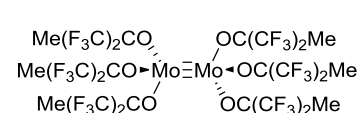
All operations with air and moisture sensitive compounds were conducted in a glove box (MBraun 200B) under dry and oxygen-free argon atmosphere or on a Schlenk line using standard Schlenk techniques. Solvents were purified and dried by a MBraun GmbH solvent purification system and stored over molecular sieve (3–4 Å). **Mo2F6**^[1], [W₂(NMe₂)₆]^[2], NaOC(CF₃)₂Me^[3] and catalysis substrates 3-pentynyl benzyl ether^[4], 3-pentynyl benzyl ester^[4], 3-butynyl benzyl ether^[5], 3-butynyl benzyl ester^[5], *m*-xylene-di(oxapent-3-yne)^[5], *o*-xylylene-di(oxapent-3-yne)^[6] were synthesized according to literature methods. The syntheses of *para*-substituted phenylpropynes were based on the literature procedure by Y. Tsuji^[7]. All other compounds were obtained from commercial sources (Sigma-Aldrich, abcr, Acros, TCI, Alfa Aesar, flurochem) and were used without further purification. Molecular sieves MS 5 Å (Sigma-Aldrich, powder <50 micrometer) for metathesis reactions were dried for 24 h at 180 °C under vacuum prior to use. 1-Phenyl-1-propyne was distilled over CaH₂ and filtered through alumina (Al₂O₃) at least three times and additionally prior to use in catalysis.

Analytical methods

¹H, ¹⁹F and ¹³C NMR spectra were recorded on Bruker AVIIIHD-300, AVIII-400 and AVII-600 instruments at room temperature. Chemical shifts (δ) are expressed in ppm (parts per million). ¹H and ¹³C NMR spectra are referenced to residual solvent signals (C₆D₆: δ(H) 7.16 ppm, δ(C) 128.06 ppm; CDCl₃: δ(H) 7.26 ppm, δ(C) 77.16 ppm; CD₂Cl₂: δ(H) 5.32 ppm, δ(C) 53.84 ppm). For ¹⁹F NMR, an external calibration with CFC₃ was used. Coupling constants (*J*) are reported in Hertz (Hz). Multiplicities are expressed with s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H. When necessary, signal assignment was confirmed by two-dimensional H,C-HSQC NMR and H,C-HMBC NMR experiments. Elemental analyses were performed by combustion and gas chromatographic analysis using a VarioMICRO Tube and WLD detection. Gas chromatography (GC) was executed on a Hewlett Packard 5890 SERIES II using a DB5-HT column and FID detection. For calibration *n*-decane was used as an internal standard.

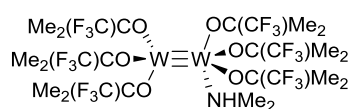
Experimental procedures

[Mo₂{OC(CF₃)₂Me}₆] (**Mo2F6**)^[1]

 A solution of 400 mg (0.68 mmol) [Mo₂Cl₆(dme)₂]^[1] in 25 mL CH₂Cl₂ was treated with 933 mg (4.08 mmol) NaOC(CF₃)₂Me over a period of 15 minutes. The reaction mixture was stirred for 30 hours. Afterwards the solvent was removed under reduced pressure and the residue was extracted with Et₂O (1 × 20 mL, 2 × 10 mL). The combined extracts were filtered over a patch of Celite[®]. The saturated ether solution was stored at –25 °C whereupon the product crystallized as red crystals (243 mg, 0.19 mmol, 28%).

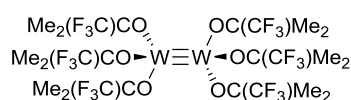
¹H-NMR (300.3 MHz, C₆D₆, 300 K): δ [ppm] = 1.44 [s, C(CF₃)₂(CH₃)]. **¹⁹F{¹H}-NMR** (282.5 MHz, C₆D₆, 300 K): δ [ppm] = -77.5 [s, CF₃]. Anal. Calcd. for C₂₄H₁₈F₃₆O₆Mo₂: C 22.55, H 1.42. Found: C 22.51, H 1.44.

[W₂{OC(CF₃)Me₂}₆(NHMe₂)] (W2F3·NHMe₂)



A solution of 494 mg (0.78 mmol) [W₂(NMe₂)₆] in 20 mL hexane was treated with 2.0 g (15.6 mmol) HOC(CF₃)Me₂. Upon addition of the alcohol the reaction mixture turned dark brown. After three days, the solvent was removed under reduced pressure. The dark residue was treated with CHCl₃ (30 mL) and the resulting suspension was filtered over a patch of Celite®. The filtrate was concentrated and stored at -25 °C whereupon the product crystallized as dark brown crystals (595 mg, 0.506 mmol, 65%).
Anal. Calcd. for C₂₆H₄₃F₁₈NO₆W₂: C 26.57, H 3.69, N 1.19. Found: C 26.57, H 3.11, N 1.33.

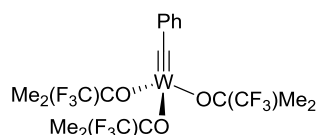
[W₂{OC(CF₃)Me₂}₆] (W2F3)



100 mg (0.085 mmol) **W2F3·NHMe₂** were dissolved in pentane (7 mL). The solution was stirred for 24 h at room temperature and the amine-free product crystallized from the saturated solution at -25 °C as bright red crystals (70 mg, 0.062 mmol, 73%).

¹H-NMR (300.3 MHz, C₆D₆, 300 K): δ [ppm] = 1.51 [s, C(CF₃)(CH₃)₂]. **¹³C{¹H}-NMR** (75.5 MHz, C₆D₆, 300 K): δ [ppm] = 126.9 [q, ¹J_{CF} = 285 Hz, C(CF₃)(CH₃)₂], 83.0 [q, ²J_{CF} = 29 Hz, C(CF₃)(CH₃)₂], 25.3 [s, C(CF₃)(CH₃)₂]. **¹⁹F{¹H}-NMR** (282.5 MHz, C₆D₆, 300 K): δ [ppm] = -82.7 [s, CF₃]. Anal. Calcd. for C₂₄H₃₆F₁₈O₆W₂: C 25.51, H 3.21. Found: C 25.19, H 3.12.

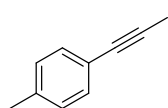
[PhC≡W{OC(CF₃)Me₂}₃] (W^{Ph}F3)



A solution of 170 mg (0.15 mmol) **W2F3** in 10 mL toluene was treated with 35 mg (0.30 mmol) 1-phenyl-1-propyne. The solution was stirred for 4 h at room temperature and afterwards the solvent was removed under reduced pressure. The light brown residue was taken up in pentane and filtered over a short patch of Celite®. Cooling of a saturated solution to -25 °C lead to the formation of light yellow crystals (113 mg, 0.17 mmol, 58%).

¹H-NMR (600.1 MHz, CD₂Cl₂, 300 K): δ [ppm] = 7.35–7.37 [m, 2H, CH], 7.04 [d, 2H, ³J_{HH} = 7.4 Hz, CH], 7.02 [t, 1H, ³J_{HH} = 7.4 Hz CH], 1.65 [s, 18H, CH₃]. **¹³C{¹H}-NMR** (150.9 MHz, CD₂Cl₂, 300 K): δ [ppm] = 266.9 [s, W≡C], 146.2 [s, *ipso*-C], 132.6 [s, PhC], 127.9 [s, PhC], 127.9 [s, *para*-C], 127.0 [q, ¹J_{CF} = 285 Hz, C(CF₃)Me₂], 83.2 [q, ²J_{CF} = 29 Hz, C(CF₃)Me₂], 25.5 [s, CH₃]. **¹⁹F{¹H}-NMR** (282.5 MHz, C₆D₆, 300 K): δ [ppm] = -82.4 [s, CF₃]. Anal. Calcd. for C₁₉H₂₃F₉O₃W: C 34.88, H 3.54. Found: C 34.41, H 3.54.

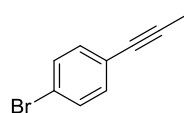
4-Methyl-1-propynylbenzene^[7]



4.65 g (40 mmol) 1-Methyl-4-ethynylbenzene dissolved in 140 mL THF were treated with 50 mL (80 mmol, 1.6 M in hexane) *n*-BuLi at $-20\text{ }^{\circ}\text{C}$. The reaction mixture was stirred for one hour at low temperature and 7.2 mL (14.2 g, 100 mmol) methyl iodide were added dropwise at $-20\text{ }^{\circ}\text{C}$. The solution was warmed to room temperature and stirred for six hours. The reaction was quenched with a saturated NH_4Cl solution (100 mL) and the aqueous phase was extracted with ethyl acetate ($3 \times 100\text{ mL}$). The combined organic phases were dried over Na_2SO_4 and the solvent was removed in vacuo. The colorless liquid was distilled at 3 mbar and $65\text{ }^{\circ}\text{C}$ (3.38 g, 26 mmol, 65%).

$^1\text{H-NMR}$ (300.1 MHz, CDCl_3 , 300 K): δ [ppm] = 7.27–7.30 [m, 2H, Ar-CH], 7.07–7.10 [m, 2H, Ar-CH], 2.33 [s, 3H, PhCH_3], 2.04 [s, 3H, $\text{C}\equiv\text{CH}_3$]. $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (75.5 MHz, CDCl_3 , 300 K): δ [ppm] = 137.6 [s, Ar-C], 131.5 [s, Ar-CH], 129.1 [s, Ar-CH], 121.1 [s, Ar-C], 85.1 [s, $\text{C}\equiv\text{CCH}_3$], 79.9 [s, $\text{C}\equiv\text{CCH}_3$], 21.5 [s, PhCH_3], 4.5 [s, $\text{C}\equiv\text{CCH}_3$].

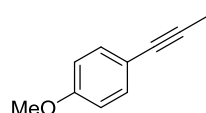
4-Bromo-1-propynylbenzene^[7]



2.0 g (11.1 mmol) 1-Bromo-4-ethynylbenzene dissolved in 60 mL THF were treated with 6.9 mL (11.1 mmol, 1.6 M in hexane) *n*-BuLi at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred for one hour at low temperature and 1.6 mL (3.14 g, 22.1 mmol) methyl iodide were added dropwise at $-78\text{ }^{\circ}\text{C}$. The solution was warmed to room temperature and stirred for three hours. The reaction was quenched with a saturated NH_4Cl solution (50 mL) and the aqueous phase was extracted with CH_2Cl_2 ($3 \times 80\text{ mL}$). The combined organic phases were dried over MgSO_4 and the solvent was removed in vacuo. After flash chromatography (hexane) the product was isolated as a colorless oil (1.53 g, 7.8 mmol, 71%).

$^1\text{H-NMR}$ (600.1 MHz, CDCl_3 , 300 K): δ [ppm] = 7.38–7.43 [m, 2H, Ar-CH], 7.21–7.26 [m, 2H, Ar-CH], 2.03 [s, 3H, $\text{C}\equiv\text{CH}_3$]. $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (150.9 MHz, CDCl_3 , 300 K): δ [ppm] = 133.1 [s, Ar-CH], 131.6 [s, Ar-CH], 123.1 [s, Ar-C], 121.7 [s, Ar-C], 87.3 [s, $\text{C}\equiv\text{CCH}_3$], 78.9 [s, $\text{C}\equiv\text{CCH}_3$], 4.5 [s, $\text{C}\equiv\text{CCH}_3$].

4-Methoxy-1-propynylbenzene^[7]



500 mg (3.78 mmol) 1-Methoxy-4-ethynylbenzene dissolved in 15 mL THF were treated with 2.4 mL (3.78 mmol, 1.6 M in hexane) *n*-BuLi at $-20\text{ }^{\circ}\text{C}$. The reaction mixture was stirred for one hour at low temperature and 0.6 mL (7.56 mmol) methyl iodide were added dropwise at $-20\text{ }^{\circ}\text{C}$. The solution was warmed to room temperature and stirred for 16 hours. The reaction was quenched with a saturated NH_4Cl solution (30 mL) and the aqueous phase was extracted with CH_2Cl_2 ($3 \times 70\text{ mL}$). The combined organic phases were dried over MgSO_4 and the solvent was removed in vacuo. After flash chromatography (hexane) the product was isolated as a colorless oil (475 mg, 3.25 mmol, 86%).

^1H -NMR (400.4 MHz, CDCl_3 , 300 K): δ [ppm] = 7.31–7.34 [m, 2H, Ar-CH], 6.79–6.83 [m, 2H, Ar-CH], 3.79 [s, 3H, OCH_3], 2.03 [s, 3H, $\text{C}\equiv\text{CH}_3$]. **$^{13}\text{C}\{^1\text{H}\}$ -NMR** (100.7 MHz, CDCl_3 , 300 K): δ [ppm] = 159.1 [s, Ar-C], 132.9 [s, Ar-CH], 116.3 [s, Ar-C], 114.0 [s, Ar-CH], 84.2 [s, $\text{C}\equiv\text{CCH}_3$], 79.6 [s, $\text{C}\equiv\text{CCH}_3$], 55.4 [s, OCH_3], 4.40 [s, $\text{C}\equiv\text{CH}_3$].

NMR Spectra

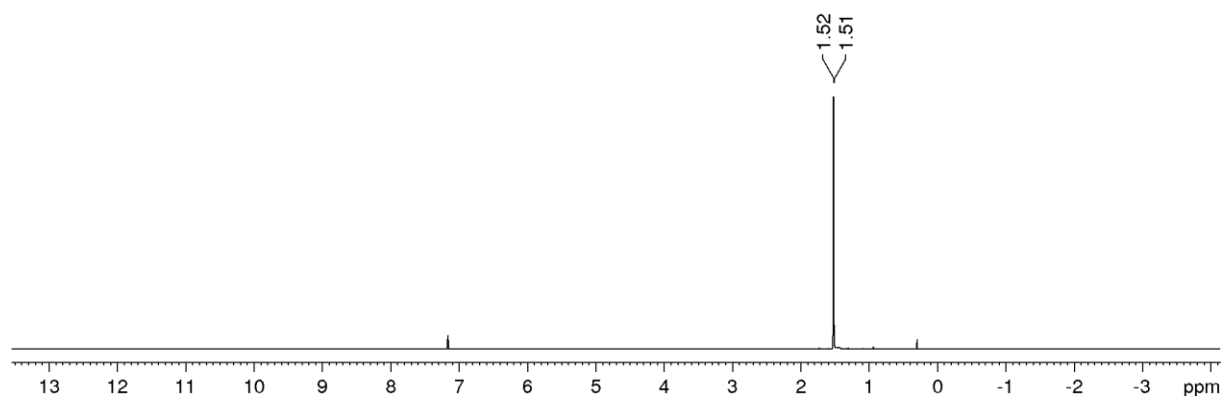


Figure S1: ^1H NMR (C_6D_6 , 300.3 MHz, 300 K) of **W2F3**.

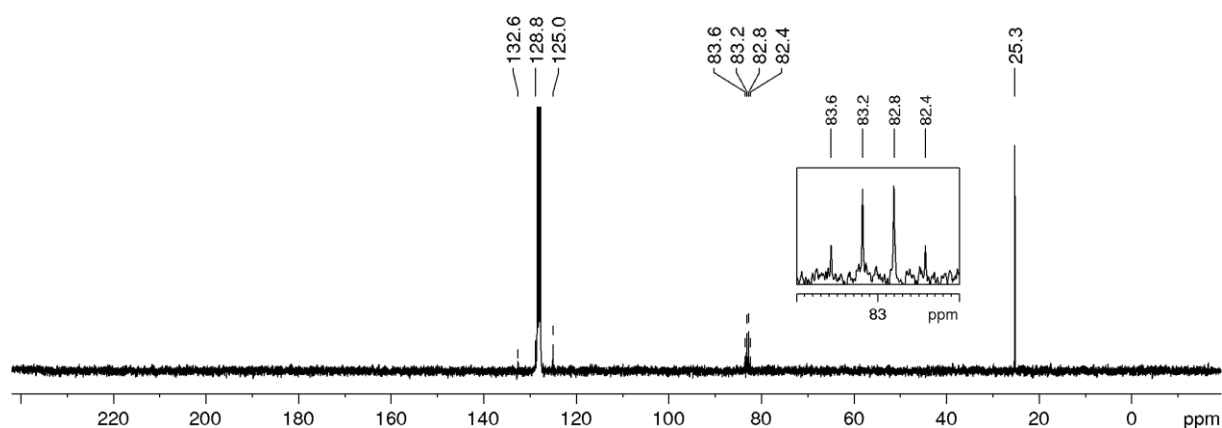


Figure S2: ^{13}C NMR (C_6D_6 , 75.5 MHz, 300 K) of **W2F3**.

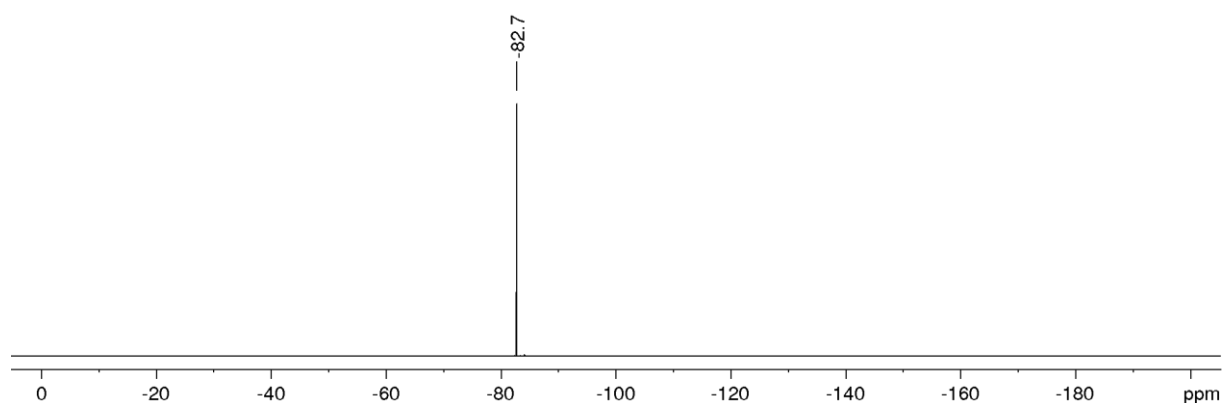


Figure S3: ^{19}F NMR (C_6D_6 , 282.5 MHz, 300 K) of **W2F3**.

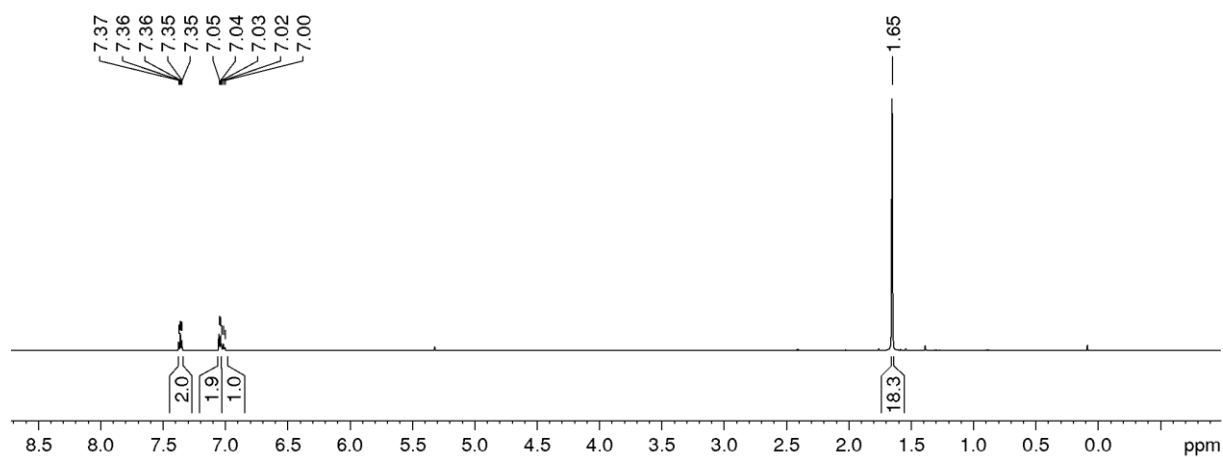


Figure S4: ¹H NMR (CD₂Cl₂, 600.1 MHz, 300 K) of **W^{Ph}F3**.

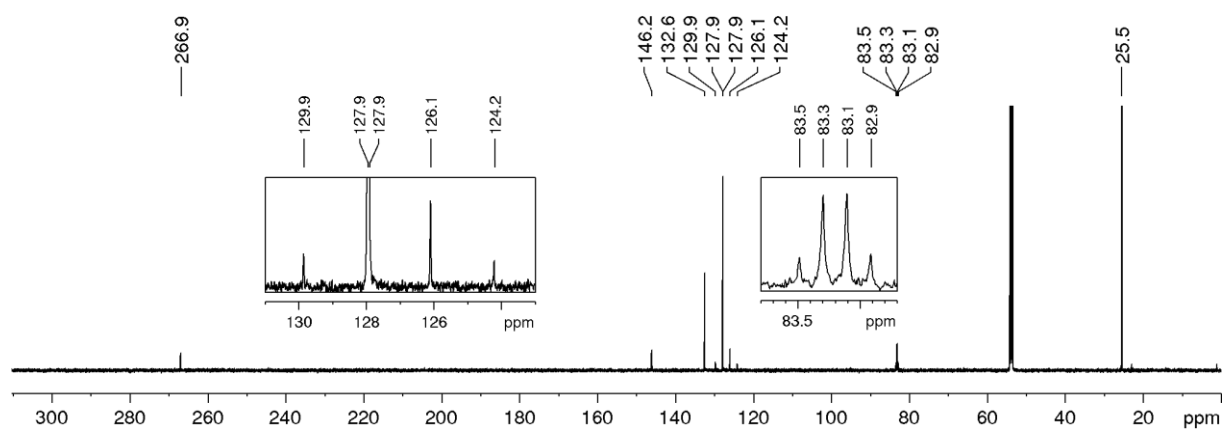


Figure S5: ¹³C NMR (CD₂Cl₂, 150.9 MHz, 300 K) of **W^{Ph}F3**.

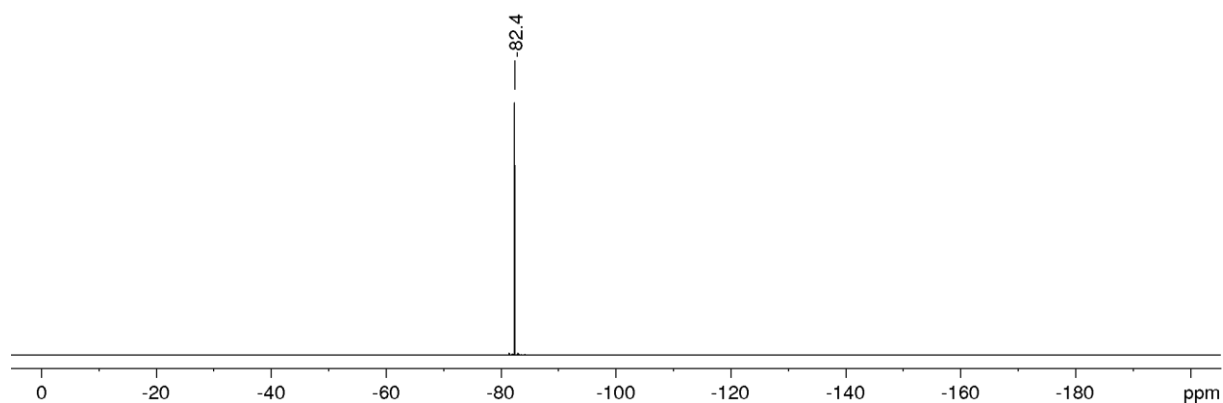


Figure S6: ¹⁹F NMR (CD₂Cl₂, 282.5 MHz, 300 K) of **W^{Ph}F3**.

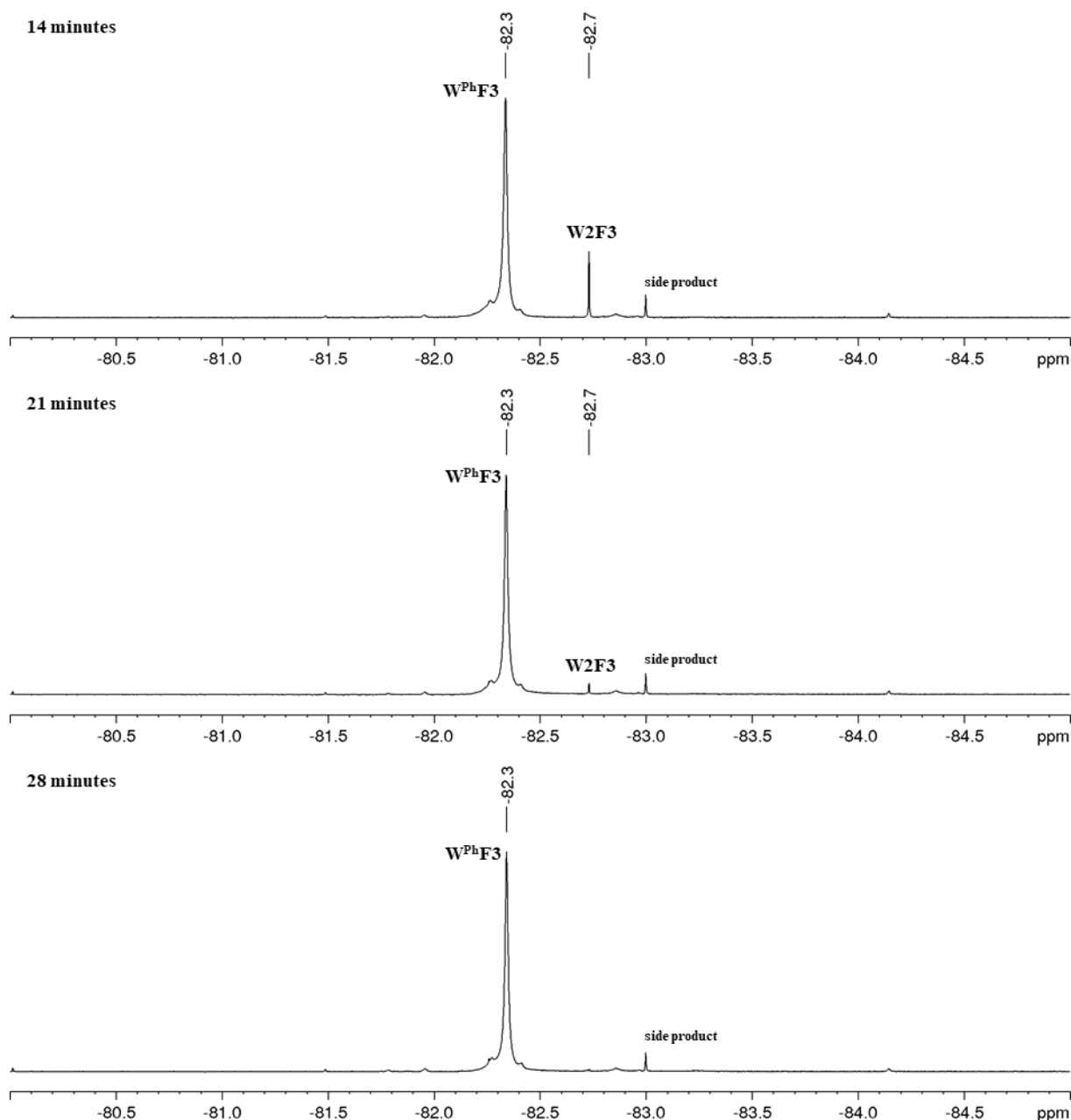


Figure S7: ^{19}F NMR (C_6D_6 , 282.5 MHz, 300 K) of the stoichiometric reaction of **W2F3** (5.0 mg, 4.4 μmol) with two equivalents of 1-phenyl-1-propyne (1.0 mg, 8.8 μmol) to **W^{Ph}F3**.

Catalytic studies

Comparison of catalytic activities. Under an argon atmosphere, a flask was charged with the substrate (0.25 mmol), molecular sieves 5 Å (250 mg), 0.05 mL *n*-decane and toluene (internal alkynes: 1.25 mL, terminal alkynes: 12 mL). Then the catalyst (0.5 mol % **W2F3**, 1 mol % **Mo2F6**, 1 mol % **W^{Ph}F3**) was added and samples (internal alkynes: 0.05 mL, terminal alkynes: 0.25 mL) were taken for gas chromatographic analysis in certain intervals. The samples were filtered through a small patch of alumina and washed with diethyl ether.

General procedure for self-metathesis. Under an argon atmosphere, a flask was charged with the substrate (0.5 mmol), molecular sieves 5 Å (500 mg) and toluene (internal alkynes: 2.5 mL, terminal alkynes: 24 mL). Then the catalyst (0.5 mol % **W2F3**, 1 mol % **W^{Ph}F3**) was added and the mixture was stirred for 2 h at room temperature. The catalyst and the molecular sieves were removed by filtration through alumina and the solvent was evaporated. The crude reaction product was purified by flash chromatography on silica gel with ethyl acetate-hexane (1:8).

General procedure for RCAM. Under an argon atmosphere, a flask was charged with the substrate (0.5 mmol), molecular sieves 5 Å (1.0 g) and toluene (24 mL). Then the catalyst (1 mol % **W2F3**, 2 mol % **W^{Ph}F3**) was added and the mixture was stirred for 2 h at room temperature. The catalyst and the molecular sieves were removed by filtration through alumina and the solvent was evaporated. The crude reaction product was purified by flash chromatography on silica gel with ethyl acetate-hexane (1:8).

General procedure for ACM. Under an argon atmosphere, a flask was charged with the substrate (0.5 mmol), TMS-propyne or TMS-acetylene (1.0 mmol), molecular sieves 5 Å (500 mg) and toluene (internal alkynes: 2.5 mL, terminal alkynes: 24 mL). Then the catalyst (1 mol % or 2 mol % **W2F3**) was added and the mixture was stirred for 2 h at room temperature. The catalyst and the molecular sieves were removed by filtration through alumina and the solvent was evaporated. The crude reaction product was purified by flash chromatography on silica gel with ethyl acetate-hexane (1:10).

Catalysis products

1,6-Bis(benzyloxy)hex-3-yne.^[4] colorless oil; ¹H-NMR (200.1 MHz, CDCl₃, 300 K): δ [ppm] = 7.27–7.16 [m, 10H, Ar-CH], 4.46 [s, 4H, OCH₂], 3.48 [t, 4H, ³J = 7.0 Hz, OCH₂], 2.40 [t, 4H, ³J = 7.0 Hz, CH₂]. ¹³C{¹H}-NMR (75.5 MHz, CDCl₃, 300 K): δ [ppm] = 138.2 [s, Ar-C], 128.3 [s, Ar-CH], 127.6 [s, Ar-CH], 127.5 [s, Ar-CH], 77.9 [s, C≡C], 72.9 [s, OCH₂], 68.7 [s, OCH₂], 20.2 [s, CH₂].

1,6-Bis(4-methoxybenzoyloxy)hex-3-yne.^[4] colorless solid; ¹H-NMR (300.1 MHz, CDCl₃, 300 K): δ [ppm] = 7.99 [m, 4H, Ar-CH], 6.89 [m, 4H, Ar-CH], 4.35 [t, 4H, ³J = 6.9 Hz, CH₂], 3.85 [s, 6H, OCH₃], 2.62 [t, 4H, ³J = 6.9 Hz, CH₂]. ¹³C{¹H}-NMR (75.5 MHz, CDCl₃, 300 K): δ [ppm] = 166.2 [s, C=O], 163.5 [s, Ar-C], 131.8 [s, Ar-CH], 122.6 [s, Ar-C], 113.7 [s, Ar-CH], 76.9 [s, C≡C], 62.9 [s, CH₂], 55.6 [s, OCH₃], 19.5 [s, CH₂].

meta-Xylol-cyclophane.^[5] colorless solid; ¹H-NMR (300.1 MHz, CDCl₃, 300 K): δ [ppm] = 8.30 [m, 1H, Ar-CH], 7.21–7.25 [m, 1H, Ar-CH], 6.70–7.03 [m, 1H, Ar-CH], 4.46 [s, 4H, OCH₂], 3.63–6.67 [m, 4H, CH₂], 2.44–2.47 [m, 2H, C≡CCH₂]. ¹³C{¹H}-NMR (75.5 MHz, CDCl₃, 300 K): δ [ppm] = 139.8 [s, Ar-C], 127.7 [s, Ar-CH], 125.1 [s, Ar-CH], 124.5 [s, Ar-CH], 79.6 [s, C≡C], 72.2 [s, OCH₂], 69.0 [s, OCH₂], 21.0 [s, CCH₂].

ortho-[10]Cyclophane.^[5] colorless solid; ¹H-NMR (300.1 MHz, CDCl₃, 300 K): δ [ppm] = 7.67–7.73 [m, 2H, Ar-CH], 7.51–7.60 [m, 2H, Ar-CH], 4.46 [t, 4H, ³J = 5.6 Hz, OCH₂], 2.53–2.57 [m, 4H, ³J = 5.7 Hz, CH₂]. ¹³C{¹H}-NMR (75.5 MHz, CDCl₃, 300 K): δ [ppm] = 167.9 [s, C=O], 133.2 [s, Ar-C], 131.0 [s, Ar-CH], 128.5 [s, Ar-CH], 79.0 [s, C \equiv C], 62.8 [s, OCH₂], 19.8 [s, CH₂].

4-(Benzyloxy)but-1-yn-1-yl)trimethylsilane.^[8] colorless liquid; ¹H-NMR (200.1 MHz, CDCl₃, 300 K): δ [ppm] = 7.29–7.37 [m, 5H, Ar-CH], 4.57 [s, 2H, OCH₂], 3.61 [t, 2H, ³J = 7.1 Hz, OCH₂], 2.56 [t, 2H, ³J = 7.1 Hz, CH₂], 0.16 [s, 9H, Si(CH₃)₃]. ¹³C{¹H}-NMR (75.5 MHz, CDCl₃, 300 K): δ [ppm] = 138.3 [s, Ar-C], 128.5 [s, Ar-CH], 127.8 [s, Ar-CH], 103.9 [s, C \equiv CSi(CH₃)₃], 85.9 [s, C \equiv CSi(CH₃)₃], 73.1 [s, ArCH₂O], 68.5 [s, CH₂], 21.5 [s, CH₂], 0.2 [s, Si(CH₃)₃].

Trimethyl(phenylethynyl)silane.^[9] colorless oil; ¹H-NMR (300.1 MHz, CDCl₃, 300 K): δ [ppm] = 7.27–7.33 [m, 3H, Ar-CH], 7.45–7.48 [m, 2H, Ar-CH], 0.26 [s, 9H, Si(CH₃)₃]. ¹³C{¹H}-NMR (75.5 MHz, CDCl₃, 300 K): δ [ppm] = 132.1 [s, Ar-CH], 128.6 [s, Ar-CH], 128.3 [s, Ar-CH], 123.2 [s, Ar-C], 105.2 [s, C \equiv CSi(CH₃)₃], 94.2 [s, C \equiv CSi(CH₃)₃], 0.1 [s, Si(CH₃)₃].

Tolane.^[10] colorless solid; ¹H-NMR (300.1 MHz, CDCl₃, 300 K): δ [ppm] = 7.52–7.57 [m, 4H, Ar-CH], 7.33–7.39 [m, 6H, Ar-CH]. ¹³C{¹H}-NMR (75.5 MHz, CDCl₃, 300 K): δ [ppm] = 131.8 [s, Ar-CH], 128.5 [s, Ar-CH], 128.4 [s, Ar-CH], 123.4 [s, Ar-C], 89.5 [s, C \equiv C].

1,2-Bis-4-tolyethyne.^[11] colorless solid; ¹H-NMR (300.1 MHz, CDCl₃, 300 K): δ [ppm] = 7.40–7.44 [m, 4H, Ar-CH], 7.13–7.16 [m, 4H, Ar-CH], 2.37 [s, 6H, PhCH₃]. ¹³C{¹H}-NMR (75.5 MHz, CDCl₃, 300 K): δ [ppm] = 138.3 [s, Ar-C], 131.6 [s, Ar-CH], 129.2 [s, Ar-CH], 120.5 [s, Ar-C], 89.0 [s, C \equiv C], 21.6 [s, CH₃].

1,2-Bis(4-bromophenyl)ethyne.^[12] colorless solid; ¹H-NMR (400.4 MHz, CDCl₃, 300 K): δ [ppm] = 7.47–7.50 [m, 4H, Ar-CH], 7.36–7.39 [m, 4H, Ar-CH]. ¹³C{¹H}-NMR (100.7 MHz, CDCl₃, 300 K): δ [ppm] = 133.1 [s, Ar-CH], 131.8 [s, Ar-CH], 122.9 [s, Ar-C], 122.0 [s, Ar-C], 89.6 [s, C \equiv C].

1,2-Bis(4-methoxyphenyl)ethyne.^[10] colorless solid; ¹H-NMR (400.4 MHz, CDCl₃, 300 K): δ [ppm] = 7.43–7.47 [m, 4H, Ar-CH], 6.85–6.89 [m, 4H, Ar-CH], 3.82 [s, 6H, OCH₃]. ¹³C{¹H}-NMR (100.7 MHz, CDCl₃, 300 K): δ [ppm] = 159.3 [s, Ar-C], 133.0 [s, Ar-CH], 115.9 [s, Ar-C], 114.1 [s, Ar-CH], 88.1 [s, C \equiv C], 55.4 [s, OCH₃].

Conversion versus time diagrams

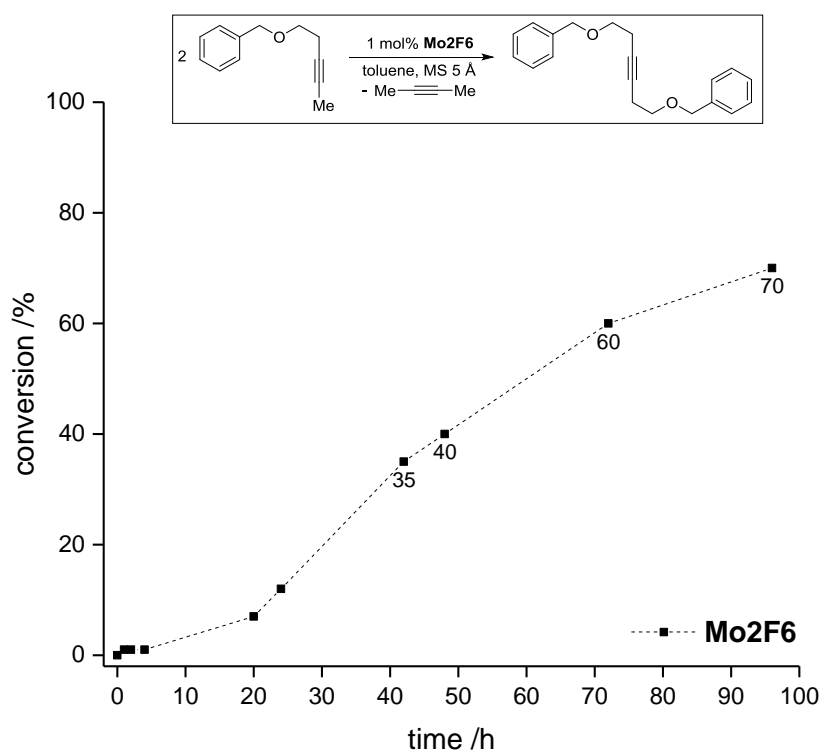


Figure S8: Conversion versus time diagram for self-metathesis of 3-pentynyl benzyl ether with 1 mol % **Mo₂F₆**.

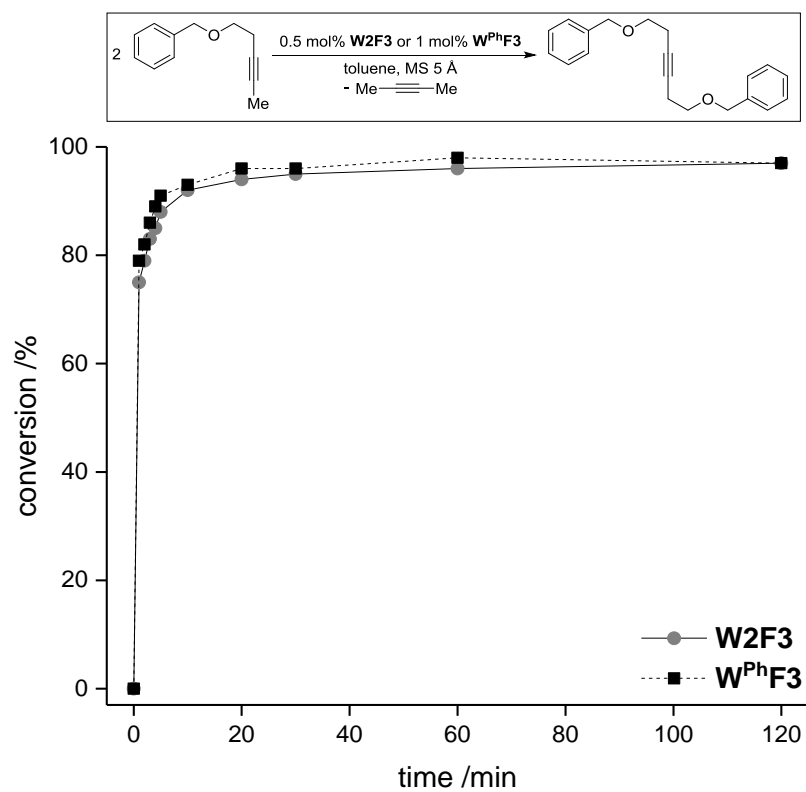


Figure S9: Conversion versus time diagram for self-metathesis of 3-pentynyl benzyl ether with 0.5 mol % **W₂F₃** or 1 mol % **W^{Ph}F₃**.

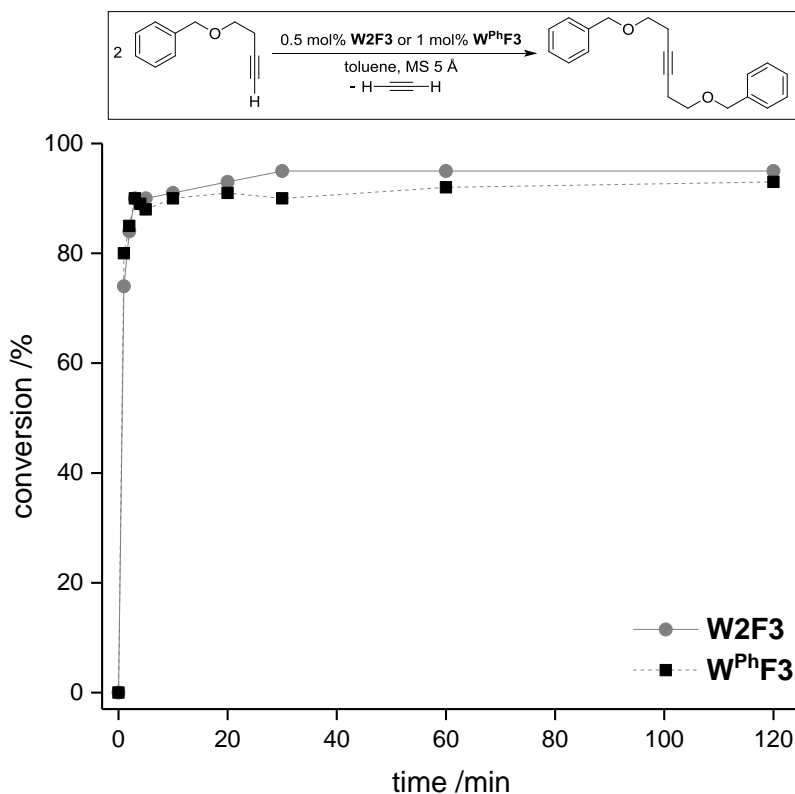


Figure S10: Conversion versus time diagram for self-metathesis of 3-butynyl benzyl ether with 0.5 mol % **W2F3** or 1 mol % **W^{Ph}F3**.

X-ray structure analysis

Numerical data are collected in table S1. Single crystals were mounted on glass fibers (**W2F3**·NHMe₂ and **W^{Ph}F3**) or on top of a human hair (**W2F3**) in perfluorinated inert oil. Measurements were performed on Oxford Diffraction Xcalibur diffractometers using monochromated Mo K α radiation. Absorption corrections were applied on the basis of multi-scans and additional absorption correction based on face indexing and integration on a Gaussian grid. Data reduction was performed with CrysAlisPro.^[13] The structures were solved by intrinsic phasing with SHELXT-2014/5^[14] and refined on F^2 using the program SHELXL-2017/1^[15]. The Hydrogen H1 on the nitrogen atom in **W2F3**·NHMe₂ was refined freely. All other H atoms in all the reported crystal structures were placed in idealized positions and refined using a riding model.

W2F3. Measurement and refinement details: Crystals were mounted on the diffractometer on top of a human hair with inert oil at 250 K. The crystal was then slowly cooled down on the diffractometer to 100 K in the nitrogen gas stream before the data collection was started. The asymmetric unit consists of two halves of two independent molecules. The tungsten atoms are disordered over four positions each resulting in eight positions because of the inversion centre on the tungsten-tungsten bonds. On

both molecules one alkoxide ligand moiety is refined as disordered over two positions each (Occupancies: O3 / O3A: 48.7 % / 51.3 %; O6 / O6A: 63.5 % / 36.5 %). Occupancies as well as bond distances for each tungsten atom are given in Table S1.

Table S1: Occupancies and bond distances for the tungsten atoms.

atom	occupancy	$d_{(W-W)}$ [Å]	$d_{(W-O1 4)}$ [Å]	$d_{(W-O2 5)}$ [Å]	$d_{(W-O3 O6/O3A O6A)}$ [Å]
W1	85.7(2) %	2.3298(7)	1.920(5)	1.879(7)	1.832(11)/1.927(14)
W1A	3.1(2) %	2.293(14)	1.993(9)	2.081(10)	2.021(13)/2.154(16)
W1B	8.6(2) %	2.317(10)	2.043(7)	2.277(7)	2.095(11)/1.908(14)
W1C	2.6(1) %	2.31(2)	1.975(12)	2.128(12)	2.289(15)/2.169(17)
W2	63.4(2) %	2.3294(8)	1.919(7)	1.876(8)	1.888(9)/2.46(3)
W2A	23.6(1) %	2.325(3)	1.856(7)	1.899(7)	2.577(9)/1.87(3)
W2B	2.5(1) %	2.385(19)	2.055(11)	2.075(11)	2.211(13)/2.07(3)
W2C	10.5(1) %	2.315(6)	1.925(7)	2.245(8)	2.035(10)/1.92(4)

This structure only confirms the connectivity of this molecule and discussion of any bond length is not meaningful. This kind of disorder is an inherent problem in M_2X_6 systems resulting from a pseudo octahedral ligand arrangement and an internal flip mechanism for the metal atoms.^[16] The different positions of the metal atoms on the disordered metal-metal vector occupy the edges of an imaginary cuboid.

W^{Ph}F3. Two alkoxide ligands were refined with a disorder model comprising two or three different positions, respectively. The simulated precession images of this dataset (see Figures S11 and S12) show very weak satellite peaks in the 0kl and hk0 planes for low diffraction angles only. Meaningful integration of these peaks was not possible. We assume that these satellite peaks result from a modulation of the crystal structure and that the refined disorder model is the most eligible approximation.

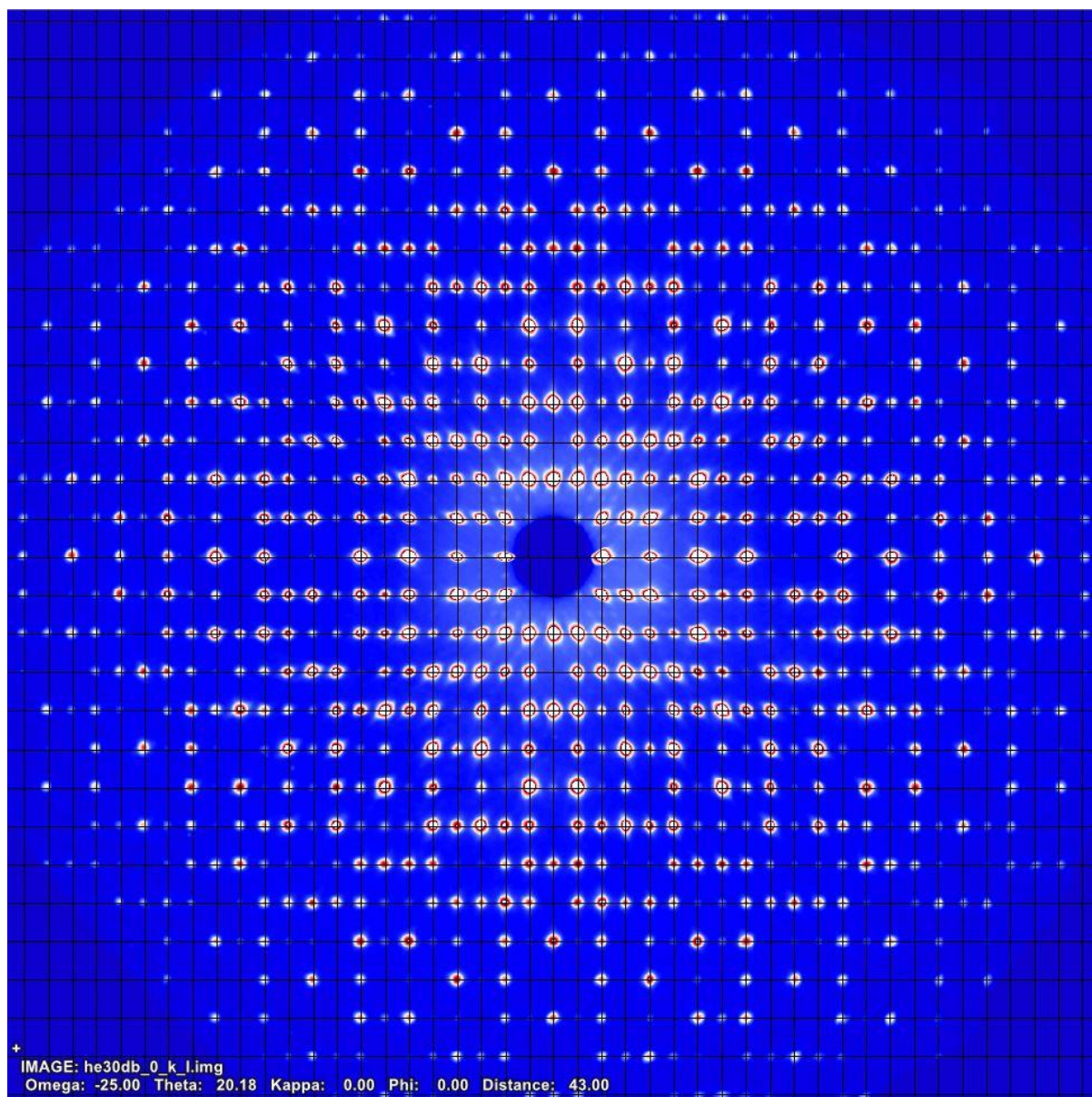


Figure S11: Simulated precession image of the 0kl plane showing weak satellite peaks for small diffraction angles.^[13]

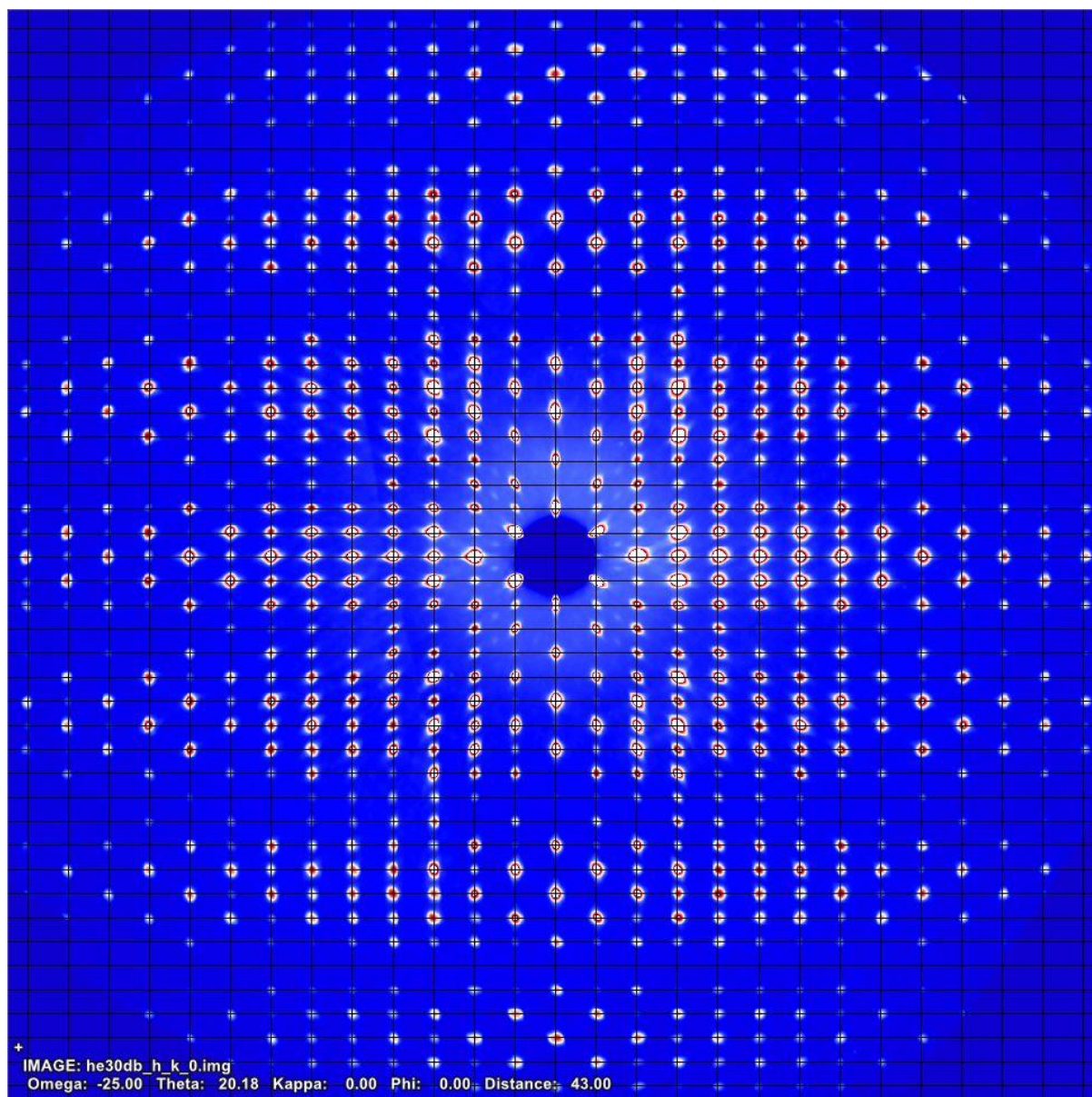


Figure S12: Simulated precession image of the $hk0$ plane showing weak satellite peaks for small diffraction angles.^[13]

Complete data have been deposited with the Cambridge Crystallographic Data Centre under the CCDC numbers 1850924–1850926. These data can be obtained free of charge from <http://www.ccdc.cam.ac.uk/>.

Table S2: Selected crystallographic data for compounds measured by X-ray structure analysis.

	W2F3·NHMe₂	W2F3	W^{Ph}F3
CCDC	1850924	1850925	1850926
Formula	C ₂₆ H ₄₃ F ₁₈ NO ₆ W ₂	C ₂₄ H ₃₆ F ₁₈ O ₆ W ₂	C ₁₉ H ₂₃ F ₉ O ₃ W
M [g mol ⁻¹]	1175.31	1130.23	654.22
T/K	100(2)	100(2)	100(2)
$\lambda/\text{\AA}$	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	10.6380(4)	18.3989(8)	11.2694(2)
<i>b</i> /Å	10.7814(3)	17.5157(6)	18.1575(4)
<i>c</i> /Å	17.1943(6)	11.0958(6)	11.9490(3)
$\alpha/^\circ$	91.326(3)	90	90
$\beta/^\circ$	92.636(3)	97.361(4)	107.613(2)
$\gamma/^\circ$	108.043(3)	90	90
<i>V</i> /Å ³	1871.64(11)	3546.4(3)	2330.43(9)
<i>Z</i>	2	4	4
<i>D_x</i> /g cm ⁻³	2.085	2.117	1.865
μ/mm^{-1}	6.269	6.612	5.045
<i>F</i> (000)	1128	2152	1264
Cryst. habitus	black-brown dichroic prism	red needle	brown, irregular shape
Cryst. size/mm	0.144 x 0.119 x 0.071	0.397 x 0.088 x 0.085	0.328 x 0.258 x 0.194
Theta range/°	2.275 to 28.700°	2.232 to 29.574	2.243–29.129
Reflections collected	96247	120724	106472
Indep. reflections	9663	9947	6261
<i>R</i> (int)	0.0682	0.0784	0.0297
Data / restraints / parameters	9663 / 0 / 496	9947 / 56 / 485	6261 / 61 / 388
GooF	1.041	1.021	1.055
<i>R</i> 1 (<i>F</i> , >4 σ (<i>F</i>))	0.0259	0.0567	0.0151
w <i>R</i> 2 (<i>F</i> ² , all refl.)	0.0554	0.1634	0.0354
max. $\Delta\rho/\text{e \AA}^{-3}$	2.174 and -0.840	4.176 and -1.937	0.728 / -0.452

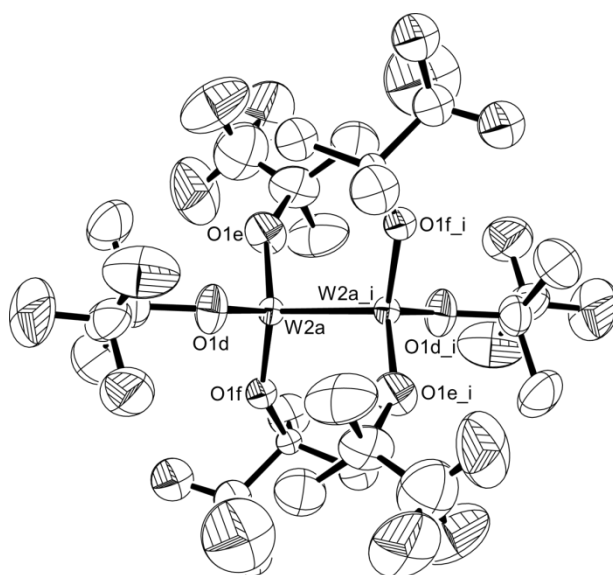


Figure S13: ORTEP diagram of **W2F3**. Hydrogen atoms and disordered tungsten atoms and alkoxides are omitted for clarity.

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