Supporting Information

Magnitude and consequence of OR ligand σ-donation on alkene metathesis activity in d^0 silica supported (≡SiO)W(NAr)(=CHtBu)(OR) catalysts

Victor Mougel[a], Christophe Copéret[a]*

[a] Department of Chemistry and Applied Biosciences, Vladimir Prelog Weg 2, ETH Zürich, CH-8093 Zürich, Switzerland
E-mail: ccoperet@ethz.ch

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A) General procedures

All experiments were carried out under dry and oxygen free argon atmosphere using either standard Schlenk or glove-box techniques for organometallic synthesis. For the syntheses, reactions were carried out using high vacuum lines (10^{-5} mBar) and glove-box techniques. Pentane, toluene and diethyl ether were purified using double MBraun SPS alumina column, and were degassed using three freeze-pump-thaw cycles before being used. DME and THF were distilled from Na/Benzophenone. Silica (Aerosil Degussa, 200 m^2g^{-1}) was compacted with distilled water, calcined at 500°C under air for 4 h and treated under vacuum (10^{-5} mBar) at 500°C for 12 h and then at 700°C for 12 h (support referred to as $SiO_{2-(700)}$) and contained 0.26 mmol of OH per g as measured by titration with MeMgCl. All infrared (IR) spectra were recorded using a Bruker spectrometer placed in the glovebox, equipped with OPUS software. A typical experiment consisted in the measurement of transmission in 32 scans in the region from 4000 to 400 cm^{-1}. The solutions ^1H and ^{13}C-NMR spectra were obtained on Bruker DRX 300, DRX 250 or DRX 500 spectrometers. The solution spectra were recorded in C_6D_6 at room temperature. The ^1H and ^{13}C chemical shifts are referenced relative to the residual solvent peak. Solid-state NMR spectra were recorded under MAS on Bruker Advance 400 and 700 MHz spectrometers with a conventional triple resonance 4 mm CP-MAS probe. The MAS frequency was set to 10 kHz for all of the experiments reported here. The samples were introduced in a 4 mm zirconia rotor in the glovebox and tightly closed. Compound $[(\equiv SiO)Mo(NAr)(CHCMe_3)(OtBu_{F6})]$[1] was synthesized according to literature procedures.

B) Syntheses

Synthesis of the molecular precursors:

Compounds $[W(NAr)(CHCMe_3)(OtBu)_2]$,[3] $[W(NAr)(CHCMe_3)(OtBu_{F3})_2]$,[3] and $[W(NAr)(CHCMe_3)(OtBu_{F6})_2]$[3] were synthesized according to literature procedures.

Synthesis of $[W(NAr)(CHCMe_3)(OtBu_{F9})_2]$, Ar = 2,6-$iPr_2C_6H_3$

A cold (-40 °C) suspension of $(CF_3)_3COLi$ (148 mg, 0.61 mmol, 2 equiv.) in diethyl ether (2 mL) was added to a solution of 250 mg of $[W(NAr)(CHCMe_3)(OTf)_2(DME)]$ (0.305 mmol, 1.05 equiv.) in cold diethyl ether (6 mL, -40 °C) while stirring. The dark red solution was stirred for 2h at room temperature, and the volatiles were removed under reduced pressure. The dark red solid was suspended in pentane (4 mL) and filtered on Celite® to afford a clear orange solution. The filtrate was taken to dryness *in vacuo,* and the orange powder dissolved back in pentane (2 mL). This drying/dissolution cycle was repeated four consecutive times, in order to remove all the coordinated DME molecules. Finally, the orange powder was solubilized in a minimum amount of pentane, and stored at -40 °C to give orange crystals, that were washed with cold (-40 °C) pentane, affording after drying *in vacuo* 218 mg of $[W(NAr)(CHCMe_3)(OtBu_{F9})_2]$ (0.21 mmol, 69%). ^{1}H NMR (200 MHz, C_6D_6) δ (ppm) 9.45 (s, 1H, C*H*CMe_3), 7.04-6.94 (m, 3H, Ar), 3.46 (2H, septet, C*H*Me_2), 1.15 (d, 12H, CH*Me*$_2$), 1.06 (s, 9H, CHC*Me*$_3$). ^{13}C NMR (300 MHz, C_6D_6) δ (ppm) 258.32 (*C*HCMe_3), 151.6 (C_{ipso}), 147.2 (C_o), 128.6 (C_p), 123.0 (C_m), 118.7 (q, OC(*C*F_3)$_3$), 83.6 (m, O*C*$(CF_3)_3$), 34.2 (CH*C*Me_3), 28.3 (*C*HMe_2), 24.1 (CH*Me*$_2$). ^{19}F NMR (200 MHz, C_6D_6) δ (ppm) -73.1 (s, 18F, C(C*F*$_3$)). Elemental Analysis: C 33.14 % (expected 33.39 %), H 3.08 % (exp. 3.03 %), N 0.79 % (exp. 1.56 %), F 38.60 % (exp. 38.03 %).

Synthesis of $[W(NAr)(CHCMe_3)(OSi(OtBu)_3)_2]$, Ar = 2,6-$iPr_2C_6H_3$

A cold (-40 °C) solution of $KOSi(OtBu)_3$ (158 mg, 0.49 mmol, 2 equiv.) in toluene (10 mL) was added to a solution of 200 mg of $[W(NAr)(CHCMe_3)(OTf)_2(DME)]$ (0.24 mmol, 1 equiv.) in cold toluene (10 mL, -40 °C) while stirring. The yellow solution was stirred for 12h at room temperature, resulting in the formation of an off-white precipitate. The precipitate was filtered over Celite® to afford a clear yellow solution and the volatiles were removed under reduced pressure, yielding a yellow solid. The yellow solid was dissolved in pentane (2 mL) and filtered on Celite®. The filtrate was taken to dryness *in vacuo* affording 206 mg of $[W(NAr)(CHCMe_3)(OtBu_{F9})_2]$ (0.22 mmol, 88%) as a yellow powder.

Due to its extreme solubility, this compound could not be recrystallized in toluene and pentane, but is analytically pure, and was used as it is. ^{1}H NMR (200 MHz, C_6D_6) δ (ppm) 8.18 (s, 1H, C*H*CMe$_3$), 7.19-7.03 (m, 3H, Ar), 4.07 (2H, septet, C*H*Me$_2$), 1.43 (br s, 54H, OSiO(*tBu*)$_3$), 1.40 (br d, 12H, CH*Me$_2$*), 1.37 (s, 9H, CHC*Me$_3$*). ^{13}C NMR (300 MHz, C_6D_6) δ (ppm) 236.54 (*C*HCMe$_3$), 151.7 (C_{ipso}), 145.2 (C_o), 126.0 (C_p), 122.9 (C_m), 72.8 (OSi(O*C*Me$_3$)$_3$), 44.8 (CH*C*Me$_3$), 34.6 (CH*C*Me$_3$), 31.8 (OSi(OC*Me$_3$*)$_3$), 27.9 (*C*HMe$_2$), 24.3 (CH*Me$_2$*). Elemental Analysis: C 51.25 % (expected 51.51 %), H 8.64 % (exp. 8.54 %), N 1.74 % (exp 1.46 %).

Synthesis of the grafted catalysts

Representative procedure: Synthesis of [(≡SiO)W(NAr)(CHCMe$_3$)(OtBu$_{F9}$)] (Ar = 2,6-iPr$_2$C$_6$H$_3$, tBu$_{F9}$OH = (CF$_3$)$_3$COH), 1.

A solution of 185.9 mg of [W(NAr)(CHCMe$_3$)(OtBu$_{F9}$)$_2$] (0.21 mmol, 1.05 equiv.) in benzene (4 mL) was added to a suspension of $SiO_{2-(700)}$ (790 mg, 0.20 mmol) in benzene (3 mL) at room temperature. The suspension was slowly stirred at room temperature for 12h, resulting in a fading of the color of the solution and a coloration of the silica to orange. The orange solid was collected by filtration, and was washed by four suspension/filtration cycles in benzene (4 x 2 mL). The resulting orange solid was dried thoroughly under high vacuum (10^{-5} mBar) at room temperature for 3h to afford 857 mg of the title compound. All the filtrate solutions were collected and analyzed by ^{19}F NMR spectroscopy in C_6D_6 using fluorobenzene as internal standard (11.5 mg, 11.3µL, 1 equiv.), indicating that 0.16 mmol of tBu$_{F9}$OH were released upon grafting (0.76 tBu$_{F9}$OH/W$_{surf}$).Elemental Analysis: W 3.47%, C 4.84%, H 0.51%, N 0.38%, F 3.14% corresponding to 21.3 C/W (21 expected), 26.8 H/W (27 expected), 1.4 N (1 expected), 8.8 F (9 expected).

Synthesis of [(≡SiO)W(NAr)(CHCMe$_3$)(OtBu$_{F6}$)] (Ar = 2,6-iPr$_2$C$_6$H$_3$, tBu$_{F6}$OH = (CF$_3$)$_2$MeCOH), 2.

From a solution of 100 mg of [W(NAr)(CHCMe$_3$)(OtBu$_{F6}$)$_2$] (0.13 mmol, 1.05 equiv.) in benzene (3 mL) and a suspension of $SiO_{2-(700)}$ (500 mg, 0.12 mmol) in benzene (2 mL), 512 mg of a light orange solid were isolated. All the filtrate solutions were collected and analyzed by ^{1}H NMR spectroscopy in C_6D_6 using ferrocene as internal standard (11.8 mg, 0.5 equiv.), indicating that 0.10 mmol of tBu$_{F6}$OH were released upon grafting (0.8 tBu$_{F6}$OH/W$_{surf}$). Elemental Analysis: W 3.88%, C 5.39%, H 0.65%, N 0.37%, F 2.05% corresponding to 21.3 C/W (21 expected), 30.6 H/W (30 expected), 1.3 N (1 expected), 5.1 F (6 expected).

Synthesis of [(≡SiO)W(NAr)(CHCMe$_3$)(OtBu$_{F3}$)] (Ar = 2,6-iPr$_2$C$_6$H$_3$, tBu$_{F3}$OH = (CF$_3$)Me$_2$COH), 3.

A solution of (CF$_3$Me$_2$)COLi (46 mg, 0.34 mmol, 2 equiv.) in C$_6$D$_6$ (1.5 mL) was added to a solution of 139 mg of [W(NAr)(CHCMe$_3$)(OTf)$_2$(DME)] (0.17 mmol, 1 equiv.) in C$_6$D$_6$ (1.5 mL) while it was stirred. The light yellow solution was stirred for 2h at room temperature, resulting in the formation of an off white precipitate. The suspension was filtered on a small celite plug that was rinced with C$_6$D$_6$ (2 x 1 mL) to afford a clear yellow solution. ^{1}H NMR of this solution confirmed the presence of [W(NAr)(CHCMe$_2$Ph)(OtBu$_{F3}$)$_2$(DME)] with no significant byproduct (≥ 95% purity). ^{1}H NMR (200 MHz, C$_6$D$_6$) δ (ppm) 8.37 (s, 1H, C*H*CMe$_3$), 7.06-6.97 (m, 3H, Ar), 3.69 (2H, septet, C*H*Me$_2$), 3.32 (br s, DME), 3.08 (br s, DME), 1.31 (s, 6H, C*Me$_2$*CF$_3$), 1.24 (s, 6H, C*Me$_2$*CF$_3$), 1.20 (d, 12H, CH*Me$_2$*), 1.13 (s, 9H, CHC*Me$_3$*) ^{19}F NMR (200 MHz, C$_6$D$_6$) δ (ppm) -80.1 (s, 6H, CMe$_2$*CF$_3$*)

From a solution of [W(NAr)(CHCMe$_3$)(OtBu$_{F3}$)$_2$(DME)] (prepared as described above 0.17 mmol assuming a quantitative reaction, 1,3 equiv.) and a suspension of SiO$_{2-(700)}$ (500 mg, 0.13 mmol) in benzene (2 mL) 552 mg of a yellow solid were isolated. All the filtrate solutions were collected and analyzed by ^{1}H NMR spectroscopy in C$_6$D$_6$ using ferrocene as internal standard (11 mg, 1 equiv.), indicating that 0.11 mmol of tBu$_{F3}$OH were released upon grafting (0.85 tBu$_{F3}$OH/W$_{surf}$). Elemental Analysis: W 3.71%, C 5.18%, H 0.72%, N 0.38% F 1.09% corresponding to 21.4 C/W (21 expected), 35.4 H/W (33 expected), 1.3 N (1 expected), 2.8 F (3 expected).

Synthesis of [(≡SiO)W(NAr)(CHCMe$_3$)(OtBu)] (Ar = 2,6-iPr$_2$C$_6$H$_3$), 4.

A solution of 80.6 mg of [W(NAr)(CHCMe$_3$)(OtBu)$_2$] (0.140 mmol, 1.05 equiv.) in benzene (8 mL, -40°C) was added dropwise to a suspension of SiO$_{2-(700)}$ (512 mg, 0.133 mmol) in benzene (2 mL, -40°C). The suspension was slowly stirred at room temperature for 30 minutes, resulting in a fading of the color of the solution and a coloration of the silica to yellow. The yellow solid was collected by filtration, and was washed by four suspension/filtration cycles in benzene (4 x 2 mL). The resulting yellow solid was dried thoroughly under high vacuum (10^{-5} mBar) at room temperature for 3h to afford 475 mg of the title compound. All the filtrate solutions were collected and analyzed by ^{1}H NMR spectroscopy in C$_6$D$_6$ using ferrocene as internal standard (24.7 mg, 1.05 equiv.), indicating that 0.08 mmol of tBuOH were released upon grafting (0.6 tBuOH/W$_{surf}$). Elemental Analysis: W 3.32%, C 4,78%, H 0.68%, N 0.48% corresponding to 22.0 C/W (21 expected), 37.4 H/W (36 expected), 1.9 N (1 expected).

Grafting of [(≡SiO)W(NAr)(CHCMe$_3$)(OtBu)] at room temperature (Ar = 2,6-iPr$_2$C$_6$H$_3$).

A solution of 104 mg of [W(NAr)(CHCMe$_3$)(OtBu)$_2$] (0.181 mmol, 1.05 equiv.) in benzene (2 mL) was added to a suspension of $SiO_{2-(700)}$ (673 mg, 0.17 mmol) in benzene (2 mL) at room temperature. The suspension was slowly stirred at room temperature for 12h, resulting in a fading of the color of the solution and a coloration of the silica to yellow. The yellow solid was collected by filtration, and was washed by four suspension/filtration cycles in benzene (4 x 2 mL). The resulting yellow solid was dried thoroughly under high vacuum (10^{-5} mBar) at room temperature for 3h to afford 672 mg of the title compound. All the filtrate solutions were collected and analyzed by ^{1}H NMR spectroscopy in C_6D_6 using ferrocene as internal standard (33.7 mg, 1.05 equiv.), indicating that 0.07 mmol of tBuOH were released upon grafting (0.4 tBuOH/W_{surf}).

Synthesis of [(≡SiO)W(NAr)(CHCMe$_3$)(OSi(OtBu)$_3$)] (Ar = 2,6-iPr$_2$C$_6$H$_3$), 5.

A solution of 130 mg of [W(NAr)(CHCMe$_3$)(OSi(OtBu)$_3$)$_2$] (0.136 mmol, 1.05 equiv.) in benzene (3 mL) was added to a suspension of $SiO_{2-(700)}$ (500 mg, 0.129 mmol) in benzene (3 mL) at room temperature. The suspension was slowly stirred at room temperature for 12h, resulting in a fading of the color of the solution and a coloration of the silica to yellow. The yellow solid was collected by filtration, and was washed by four suspension/filtration cycles in benzene (4 x 2 mL). The resulting orange solid was dried thoroughly under high vacuum (10^{-5} mBar) at room temperature for 3h to afford 558 mg of the title compound. All the filtrate solutions were collected and analyzed by ^{1}H NMR spectroscopy in C_6D_6 using ferrocene as internal standard (24 mg, 1.05 equiv.), indicating that 0.06 mmol of (tBuO)$_3$SiOH were released upon grafting (0.54 (tBuO)$_3$SiOH/W_{surf}). Elemental Analysis: W 2.48 %, C 4.72 %, H 0.76 %, N 0.29 % corresponding to 29.1 C/W (29 expected), 55.9 H/W (54 expected), 1.5 N (1 expected).

Reaction with ^{13}C dilabeled ethylene

General procedure:

100 mg of catalyst **1-5** (≈ 26 µmol, 1 equiv.) were loaded in a glass reactor and evacuated under high vacuum (10^{-5} mBar). ≈ 280 µmol of ^{13}C dilabeled ethylene (15 equiv.) were vacuum transferred on the grafted complex at -196 °C. After standing 1h at room temperature, the volatiles were vacuum transferred and collected for analysis by GC-MS. The solid was dried under high vacuum (10^{-5} mbar) at room temperature for 1h30, and stored at -40 °C. The solid was analyzed by magic angle spinning solid state proton and carbon NMR in a 4-mm zirconia rotor within one day after exposure to ethylene. The ratio between the trigonal bipyramid (TBP) and square based pyramid (SP) geometry of the metallacycles formed upon exposure to ^{13}C dilabeled ethylene was determined by integration of the α-carbon signal of the TBP (ca 100 ppm) and the SP (ca 50 ppm) metallacyclobutane given by a CP MAS experiment measured on a Bruker Avance II 700 MHz spectrometer, according to methods described in the literature[4]. The MAS frequency was set to 10 kHz, and a contact time of 250 µs. The signals of the α-carbon of the SP metallacyclobutane and the spinning side band of the α-carbon of the TBP metallacyclobutane overlap; the two signals were deconvoluted using the solid state NMR fit tool of the Bruker-TOPSPIN® 3.1 software ("sola" module) to take the spinning side bands into account prior to integration of the signals.

Reaction of ^{13}C dilabeled ethylene with 1: 100 mg of **1** (18.9 µmol according to elemental analysis of W, 1 equiv.) were exposed to 280 µmol of ^{13}C dilabeled ethylene (14.8 equiv.). Analysis of the volatiles by GC indicated the formation of 13.7 µmol of 3,3-dimethylbutene (0.73 equiv.)

TBP/SP ratio: 83% / 17%

Reaction of ^{13}C dilabeled ethylene with 2: 100 mg of **2** (21.1 µmol according to elemental analysis of W, 1 equiv.) were exposed to 280 µmol of ^{13}C dilabeled ethylene (13.3 equiv.). Analysis of the volatiles by GC indicated the formation of 16.0 µmol of 3,3-dimethylbutene (0.76 equiv.)

TBP/SP ratio: 43% / 57%

Reaction of ^{13}C dilabeled ethylene with 3: 100 mg of **3** (20.2 µmol according to elemental analysis of W, 1 equiv.) were exposed to 280 µmol of ^{13}C dilabeled ethylene (13.9 equiv.). Analysis of the volatiles by GC indicated the formation of 14.8 µmol of 3,3-dimethylbutene (0.73 equiv.)

TBP/SP ratio: 9% / 91%

Reaction of ^{13}C dilabeled ethylene with 4: 100 mg of **4** (18 µmol according to elemental analysis of W, 1 equiv.) were exposed to 280 µmol of ^{13}C dilabeled ethylene (15.5 equiv.). Analysis of the volatiles by GC indicated the formation of 3.8 µmol of 3,3-dimethylbutene (0.21 equiv.)

TBP/SP ratio: 0% / 100%

Reaction of ^{13}C dilabeled ethylene with 5: 100 mg of **5** (13.4 µmol according to elemental analysis of W, 1 equiv.) were exposed to 280 µmol of ^{13}C dilabeled ethylene (20.1 equiv.). Analysis of the volatiles by GC indicated the formation of 10.2 µmol of 3,3-dimethylbutene (0.76 equiv.)

TBP/SP ratio: 22% / 78%

C) XRD crystallography.

Figure S1. Thermal ellipsoid plot at the 50% probability of **[W(NAr)(CHCMe$_3$)(OtBu$_{F9}$)$_2$].** Hydrogen atoms have been omitted and only one of the three independent molecules in the asymmetric unit have been represented for clarity.

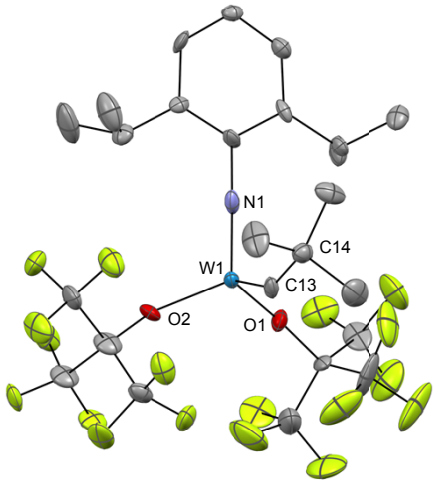


Table S1. Selected bonds for **[W(NAr)(CHCMe$_3$)(OtBu$_{F9}$)$_2$]** (distances are given in Å)

Structural parameters	**[W(NAr)(CHCMe$_3$)(OtBu$_{F9}$)$_2$]**
W1 – C13	1.870(8)
W1 – N1	1.712(7)
W1 – O1	1.929(6)
W1 – O2	1.929(5)
C13 – C14	1.535(11)

Table S2. Selected angles for **[W(NAr)(CHCMe$_3$)(OtBu$_{F9}$)$_2$]** (given in °)

Structural parameters	**[W(NAr)(CHCMe$_3$)(OtBu$_{F9}$)$_2$]**
O1 – W1 – O2	112.6(2)
O1 – W1 – N1	111.0(3)
O1 – W1 – C13	108.6(3)
O2 – W1 – N1	113.0(3)
O2 – W1 – C13	108.8(3)
C13 – W1 – N1	102.2(3)

Table S3. Crystallographic data for **[W(NAr)(CHCMe$_3$)(OtBu$_{F9}$)$_2$]**

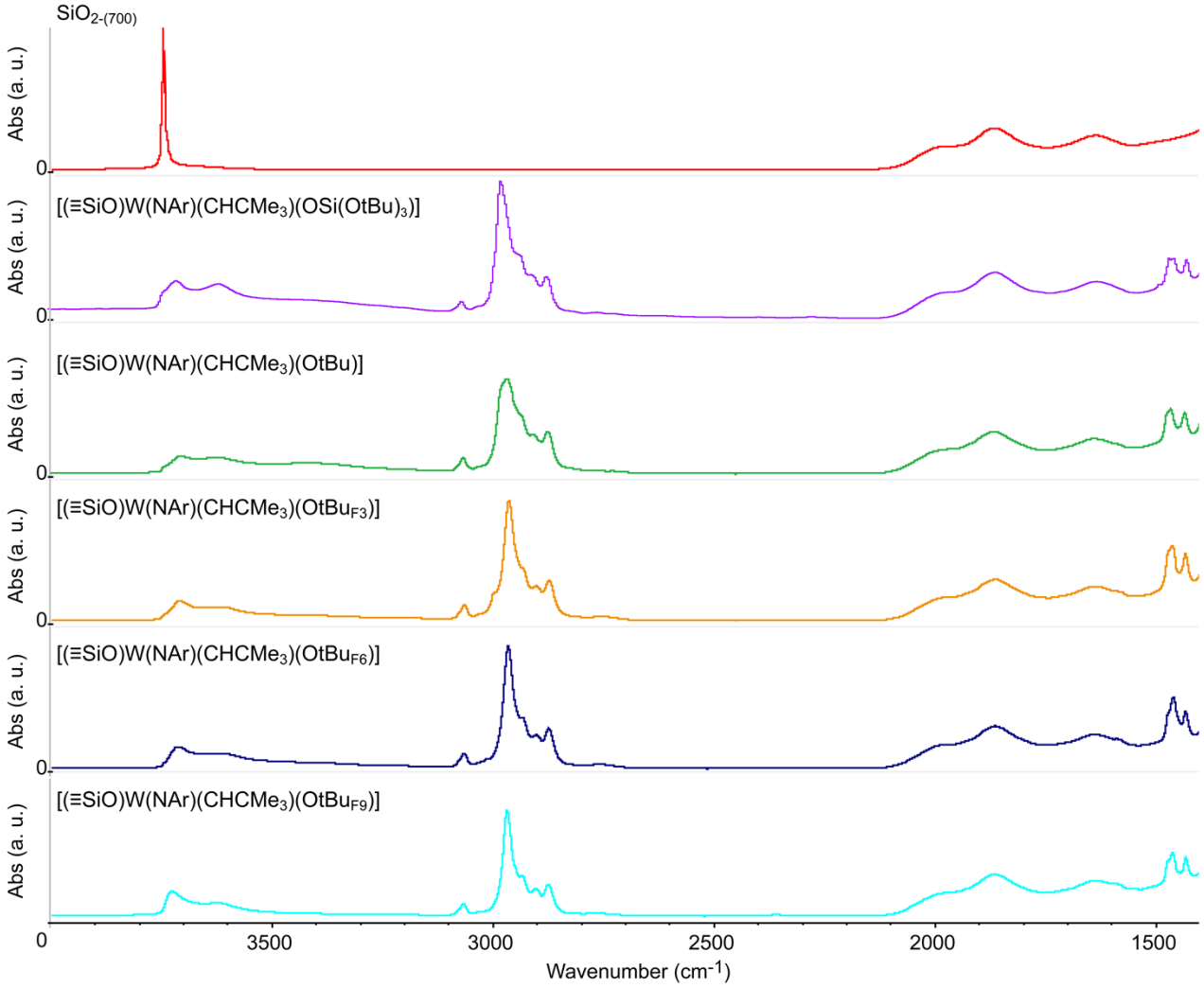
	[W(NAr)(CHCMe$_3$)(OtBu$_{F9}$)$_2$]
Formula	$C_{25}H_{27}F_{18}NO_2W$
Crystal size (mm)	0.24 × 0.15 × 0.12
cryst syst	Triclinic
space group	P-1
volume (Å^3)	4728.0(3)
a (Å)	15.3435(4)
b (Å)	17.6683(5)
c (Å)	21.0020(5)
α (deg)	65.712(3)
β (deg)	71.109(3)
γ (deg)	68.540(3)
Z	6
formula weight (g/mol)	899.32
density (g cm^{-3})	1.895
F(000)	1868.0
temp (K)	100.0(3)
total no. reflections	95484
unique reflections [R(int)]	25449 [0.0826]
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0521, wR_2 = 0.1216
Largest diff. peak and hole (e.A^{-3})	2.62/-3.91
GOF	0.983

Table S4. Buried volume $\%V_{Bur}$ of $OtBuF_9$, $OtBuF_6$, $OtBuF_3$, OtBu, and $OSi(OtBu)_3$ was calculated using *SambVca* tool[9]. Crystallographic data for the ligands were obtained from the crystal structures of the molecular precursors **[W(NAr)(CHCMe$_3$)(OtBu$_{F9}$)$_2$]**, **[W(NAr)(CHPh)(OtBu$_{F6}$)$_2$]**[6], **[W(NAr)(CHCMe$_3$)(OtBu$_{F3}$)$_2$]**[7], **[W(NAr)(CHCMe$_3$)(OtBu)$_2$]**[3] and **[WO$_2$(OSi(OtBu)$_4$(DME)]**. For the calculation, the metal-ligand distance d was taken from the crystal structures cited above and the radius R and the mesh spacing s were set constant to 3.5 Å and 0.05 Å respectively.

Ligand	**W-O**	**$\%V_{Bur}$**
$OtBu_{F9}$	1.930 Å	23.9
$OtBu_{F6}$	1.902 Å	23.1
$OtBu_{F3}$	1.888 Å	22.3
OtBu	1.866 Å	20.6
$OSi(OtBu)_3$	1.851 Å	23.4

D) IR spectra.

Figure S2. FTIR transmission spectra of **1-5** and **$SiO_{2-(700)}$**



E) NMR spectra.

Figure S3. ^{1}H NMR spectrum (400 MHz, spinning rate 10 kHz, ns = 128) of **1** (*: spinning side bands).

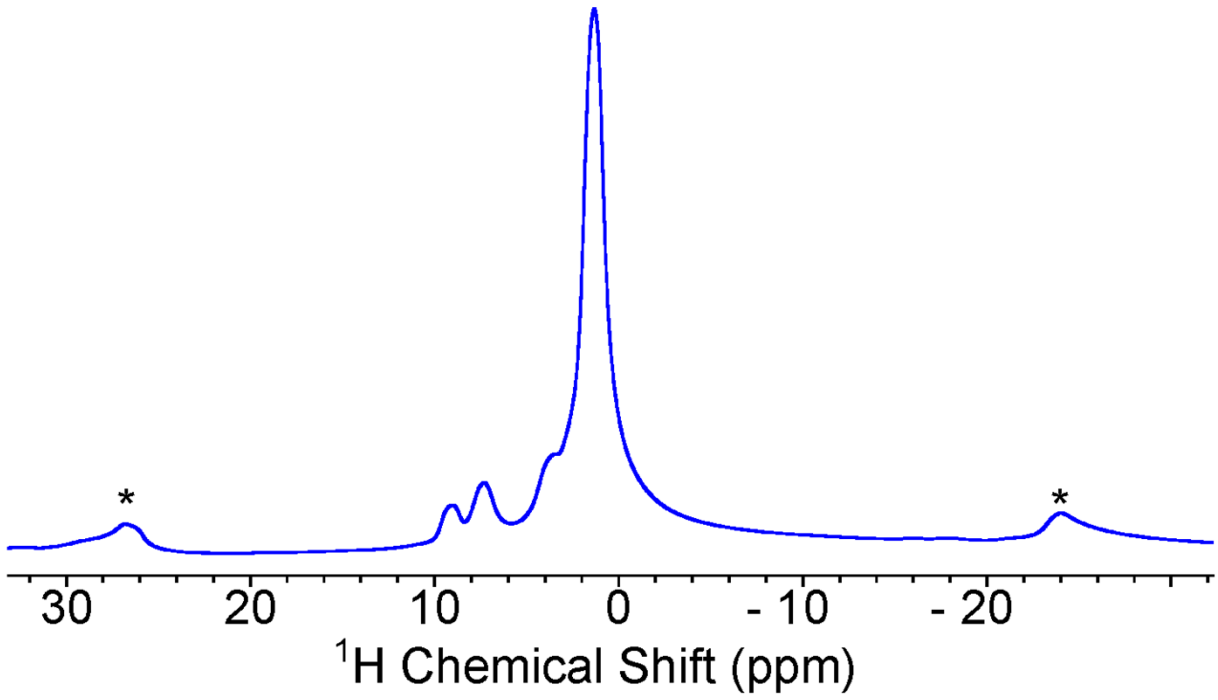


Figure S4. ^{13}C NMR spectrum (400 MHz, spinning rate 10 kHz, contact Time = 3 ms, recycle delay = 2 sec, ns = 50k) of **1**.

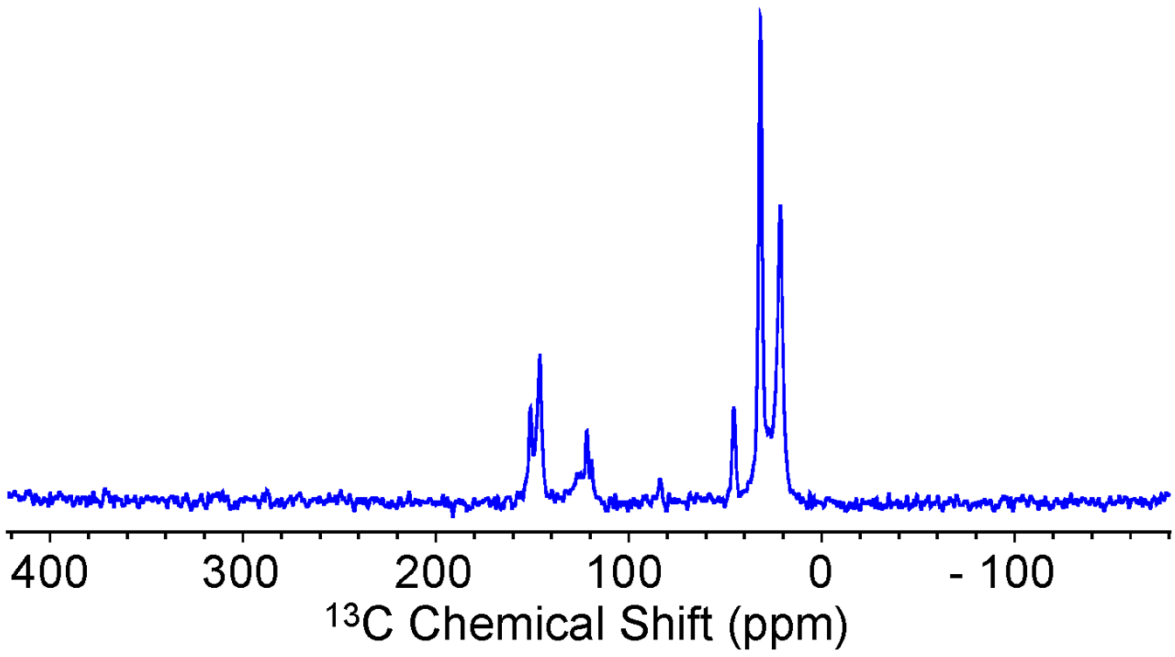


Figure S5. ^{1}H NMR spectrum (400 MHz, spinning rate 10 kHz, ns = 128) of **2** (*: spinning side bands).

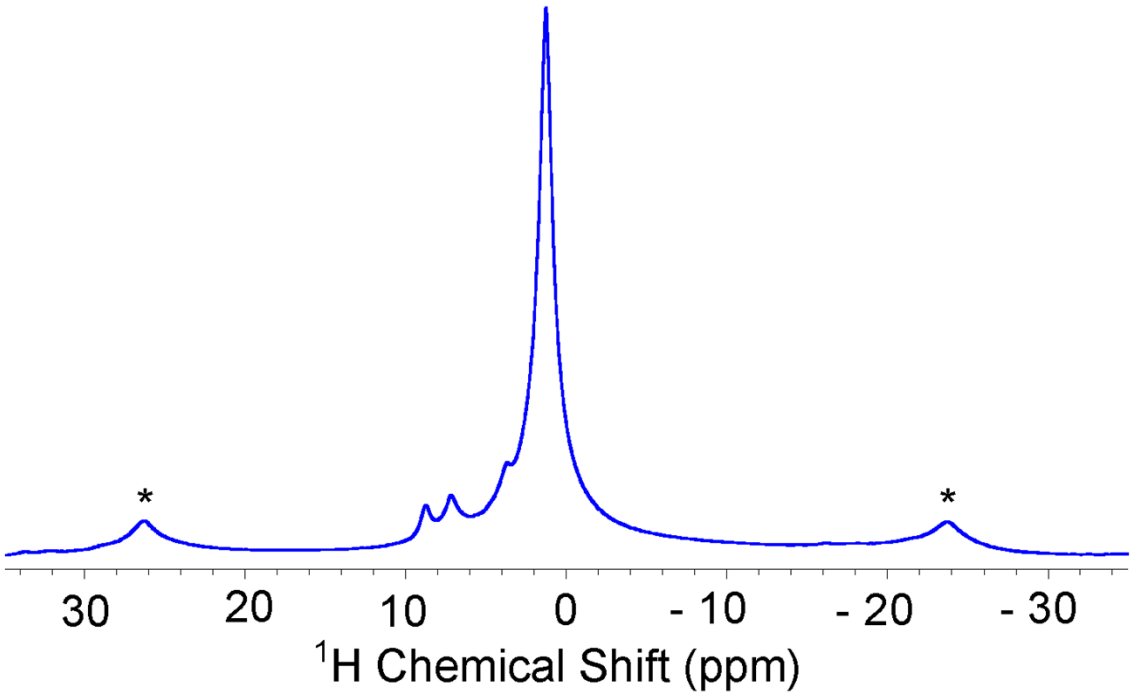


Figure S6. ^{13}C NMR spectrum (400 MHz, spinning rate 10 kHz, contact Time = 3 ms, recycle delay = 2 sec, ns = 50k) of **2**.

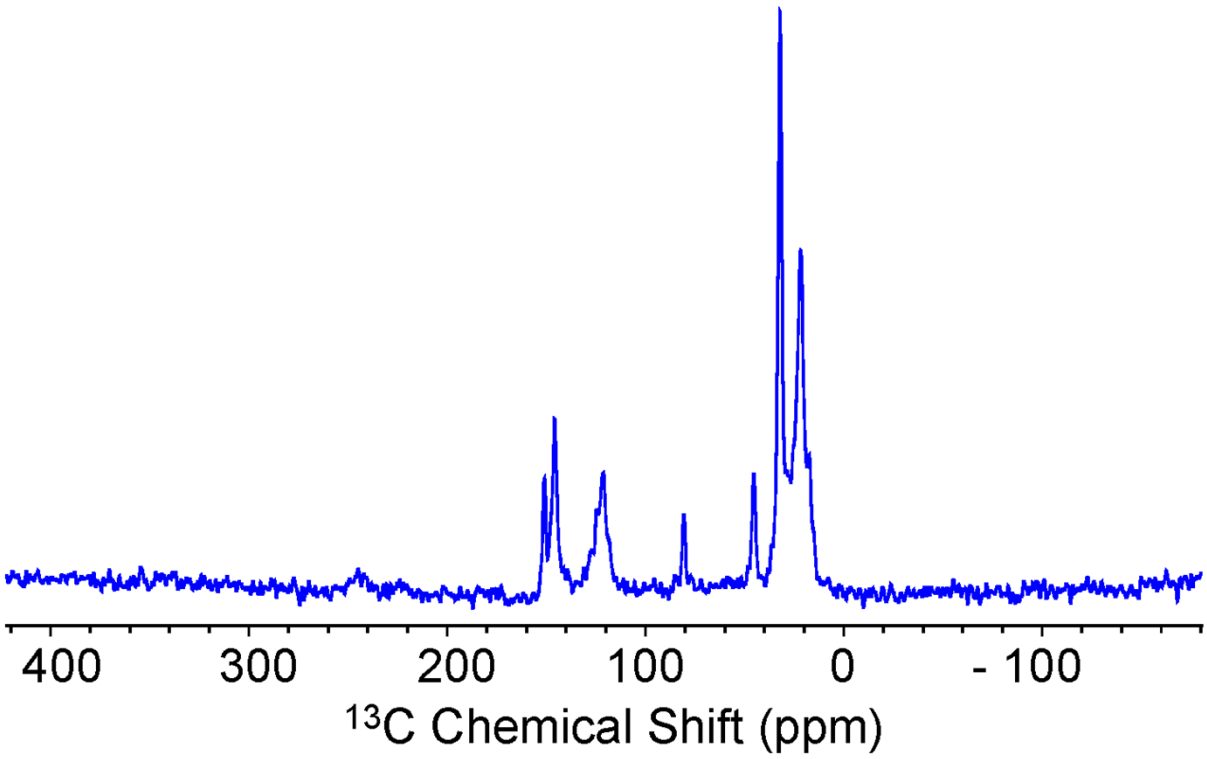


Figure S7. ^{1}H NMR spectrum (400 MHz, spinning rate 10 kHz, ns = 128) of **3** (*: spinning side bands).

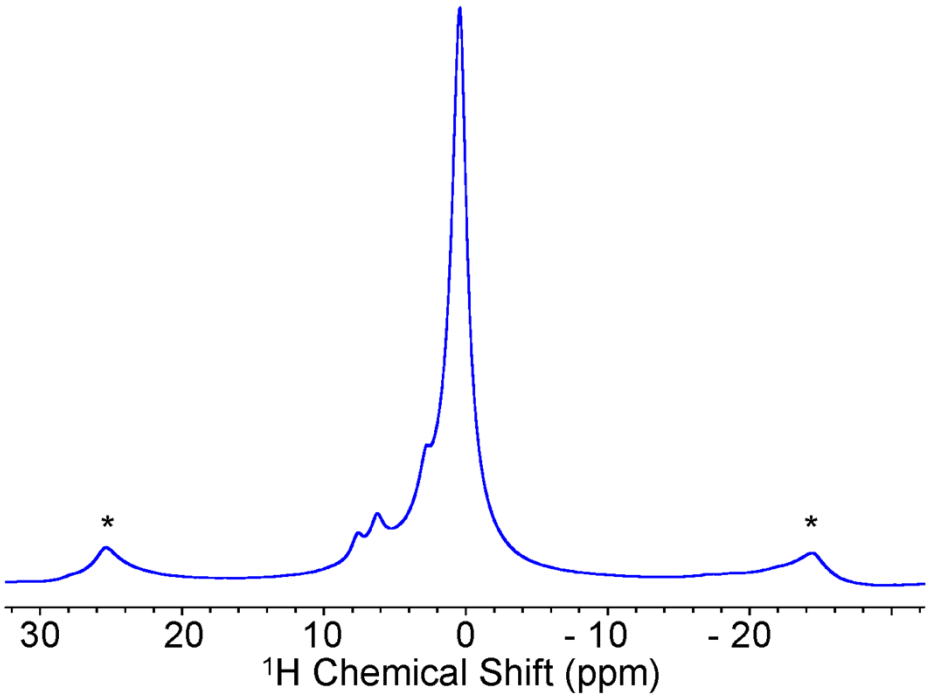


Figure S8. ^{13}C NMR spectrum (400 MHz, spinning rate 10 kHz, contact Time = 3 ms, recycle delay = 2 sec, ns = 50k) of **3** (*: spinning side bands).

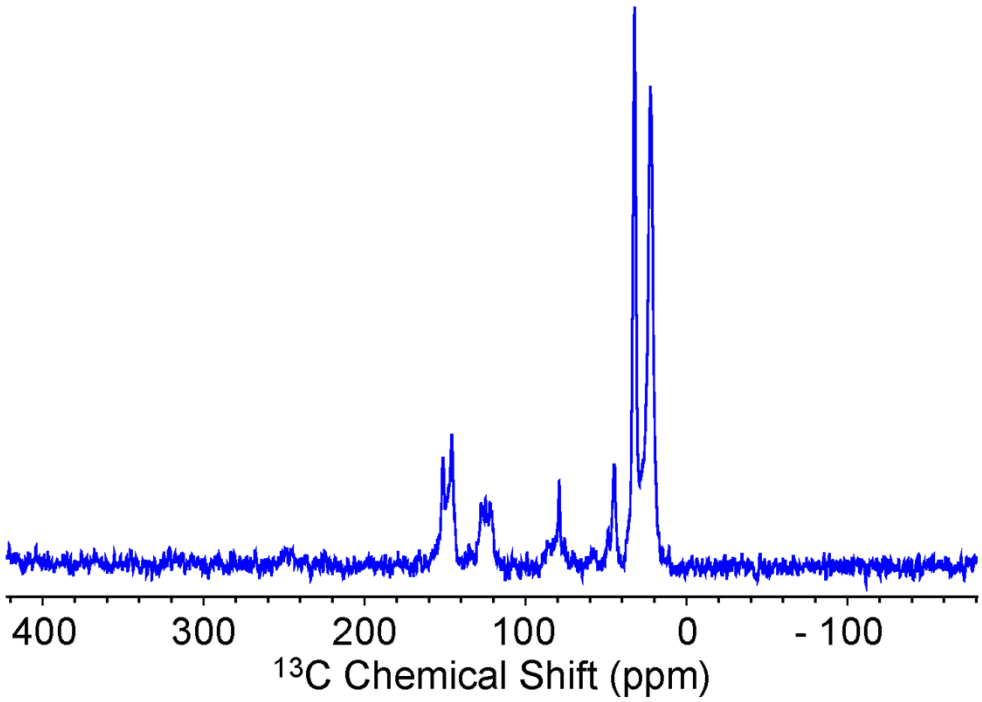


Figure S9. ^{1}H NMR spectrum (400 MHz, spinning rate 10 kHz, ns = 128) of **4** (*: spinning side bands).

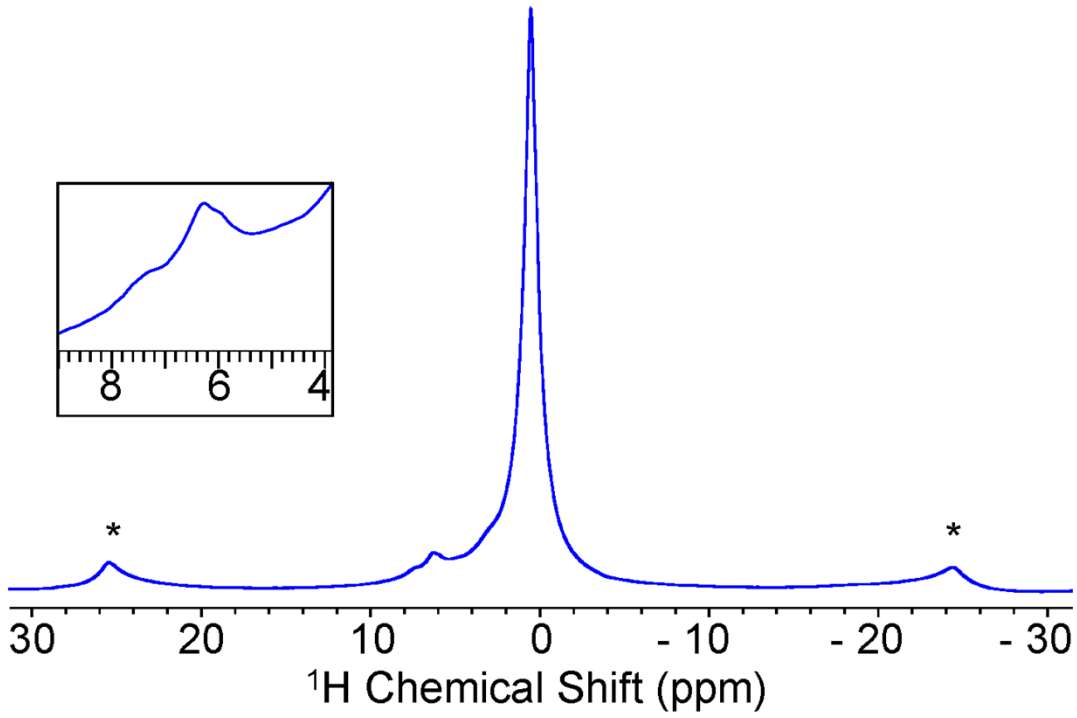


Figure S10. ^{13}C NMR spectrum (400 MHz, spinning rate 10 kHz, contact Time = 3 ms, recycle delay = 2 sec, ns = 40k) of **4**.

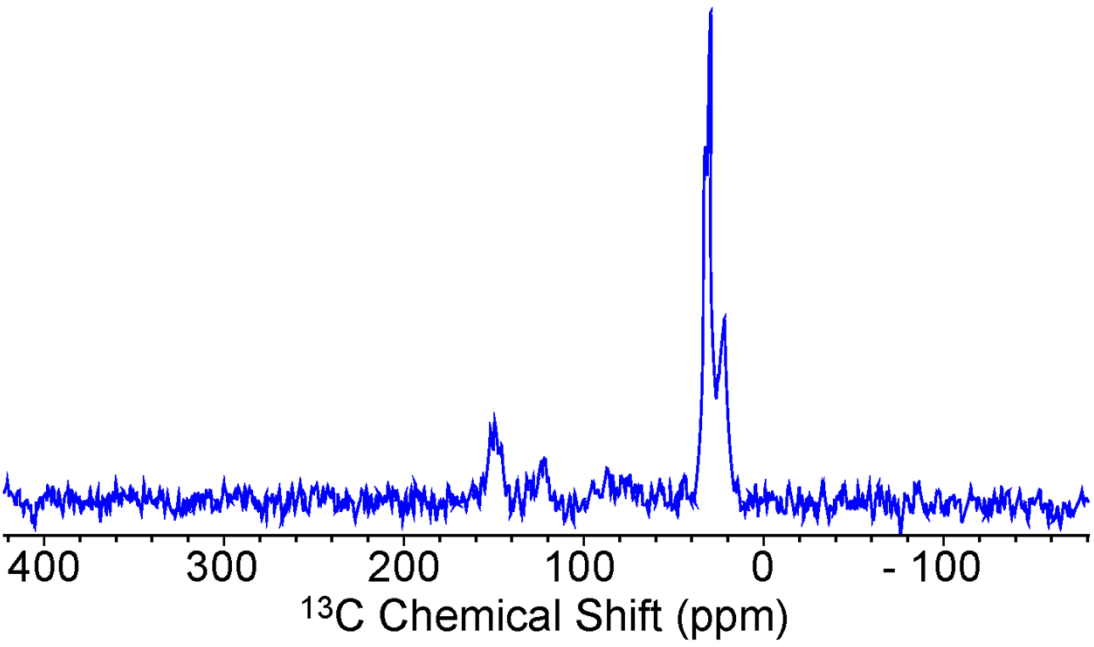


Figure S11. ^{1}H NMR spectrum (400 MHz, spinning rate 10 kHz, ns = 128) of **5** (*: spinning side bands).

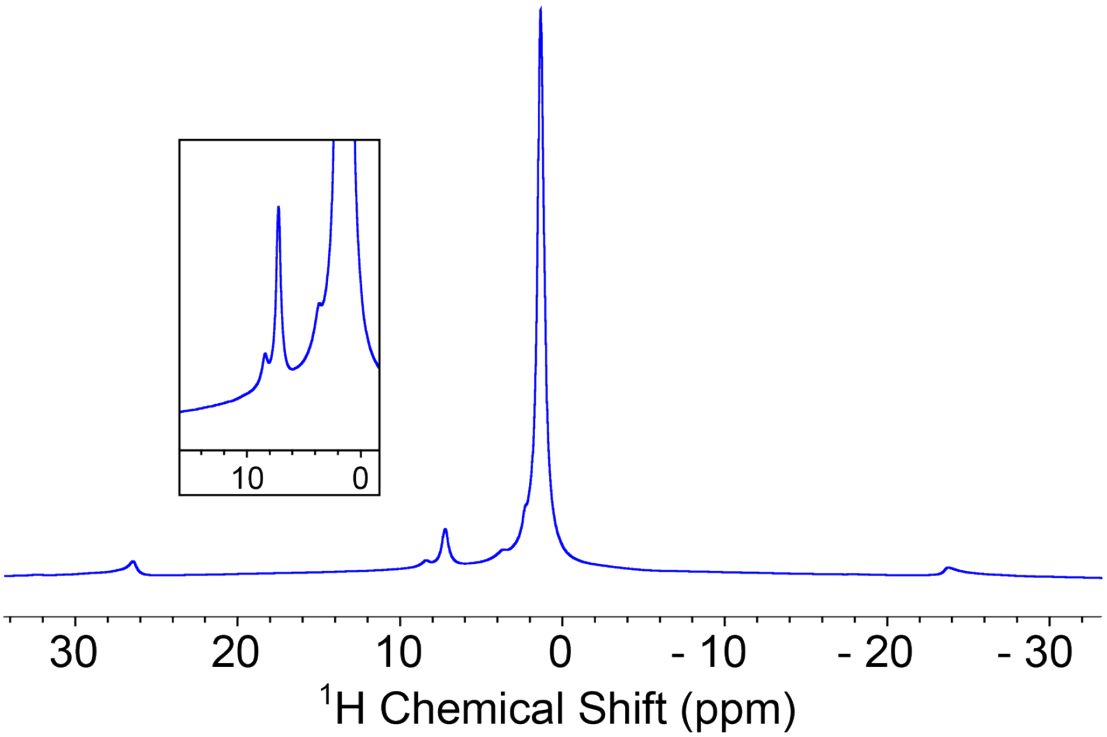


Figure S12. ^{13}C NMR spectrum (400 MHz, spinning rate 10 kHz, contact Time = 3 ms, recycle delay = 2 sec, ns = 40k) of **5**.

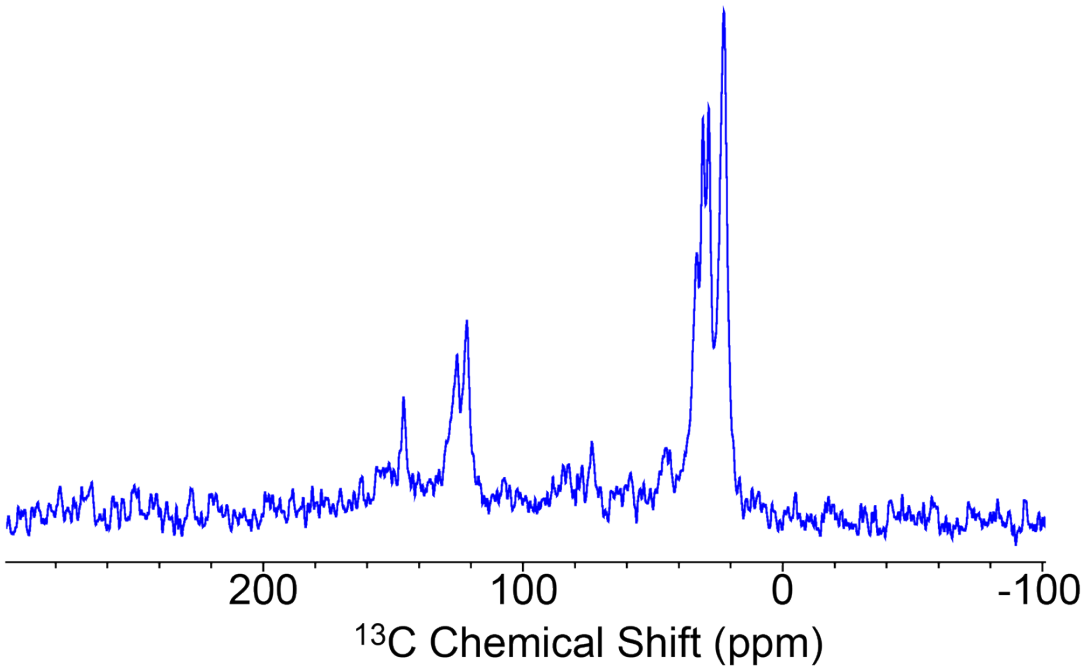


Figure S13. ^{1}H NMR spectrum (700 MHz, spinning rate 10 kHz, ns = 128) of **1** before (blue) and after exposure to ^{13}C dilabeled ethylene (red).

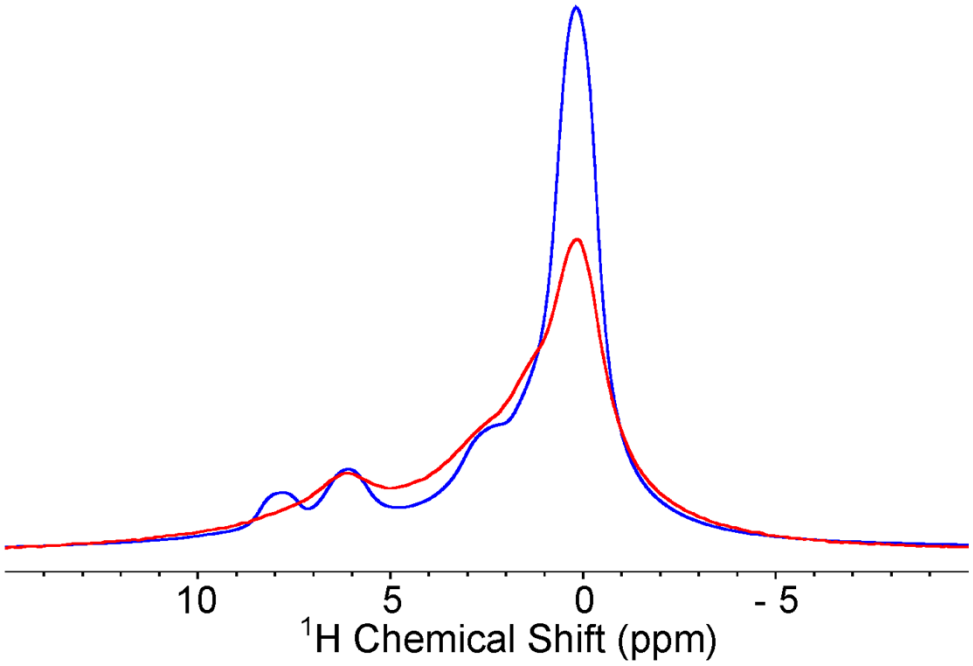


Figure S14. ^{13}C NMR spectrum (700 MHz, spinning rate 10 kHz, contact Time = 250 μs, recycle delay = 1 sec, ns = 10k) of **1** before (blue) and after exposure to ^{13}C dilabeled ethylene (red) (*: spinning side bands).

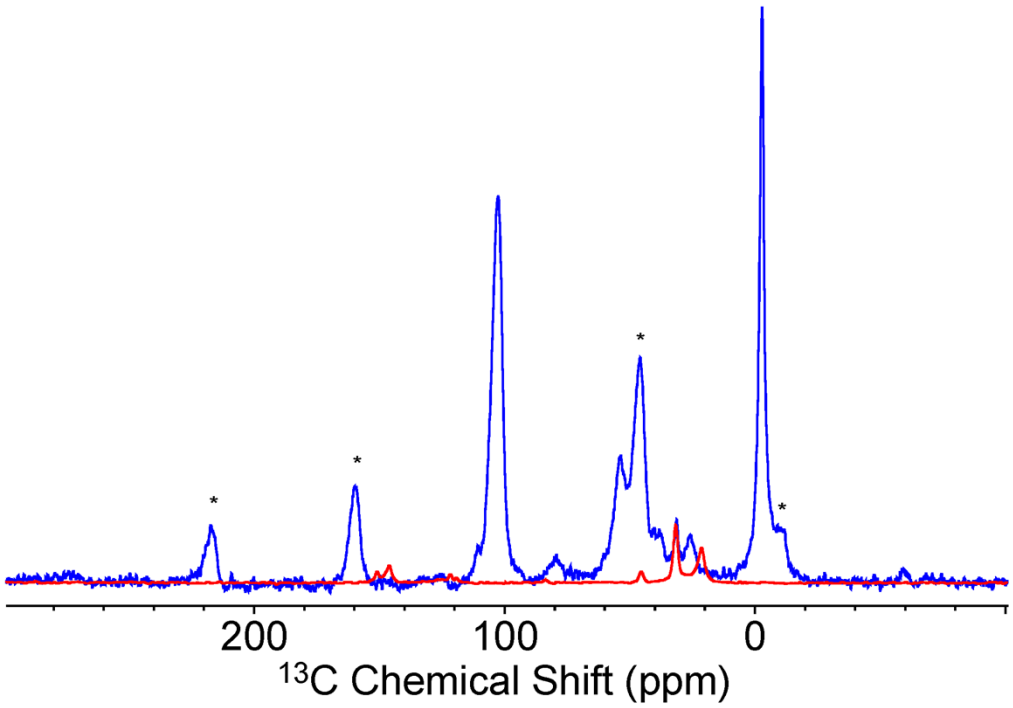


Figure S15. ^{1}H NMR spectrum (700 MHz, spinning rate 10 kHz, ns = 128) of **2** before (blue) and after exposure to ^{13}C dilabeled ethylene (red).

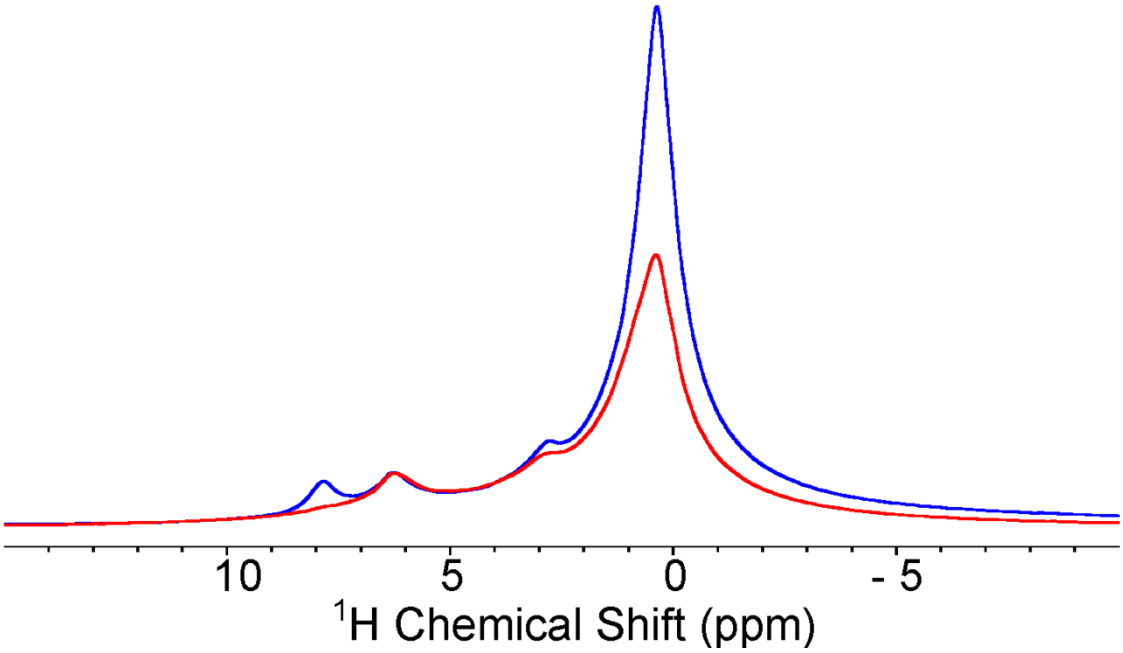


Figure S16. ^{13}C NMR spectrum (700 MHz, spinning rate 10 kHz, contact Time = 250 µs, recycle delay = 1 sec, ns = 30k) of **2** before (blue) and after exposure to ^{13}C dilabeled ethylene (red) (*: spinning side bands).

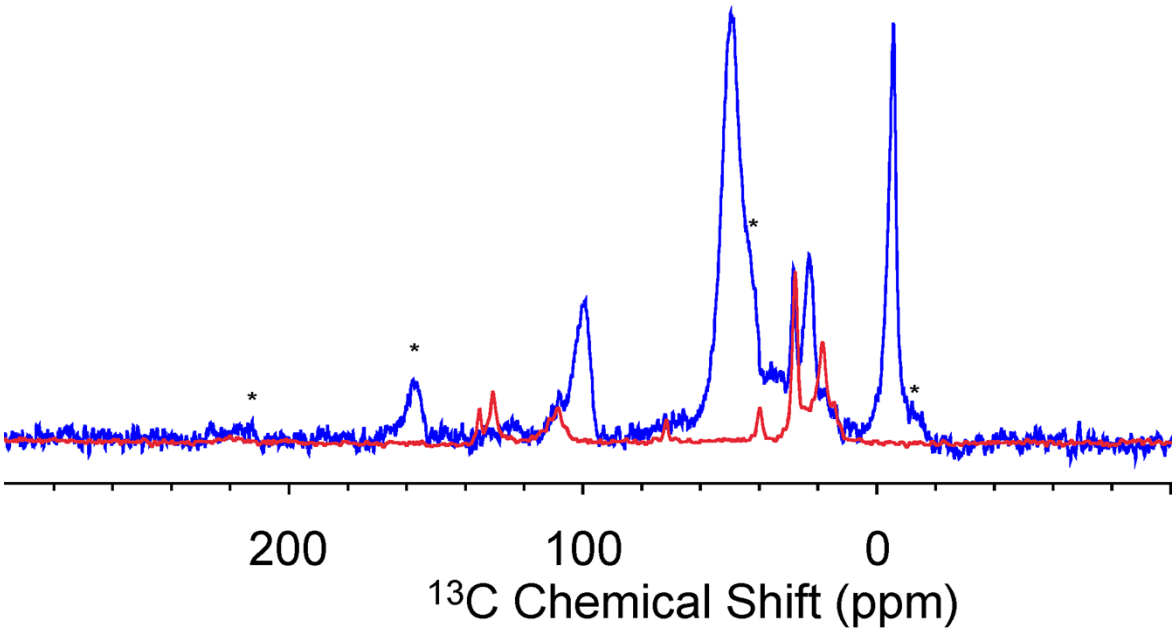


Figure S17. ^{1}H NMR spectrum (700 MHz, spinning rate 10 kHz, ns = 128) of **3** before (blue) and after exposure to ^{13}C dilabeled ethylene (red).

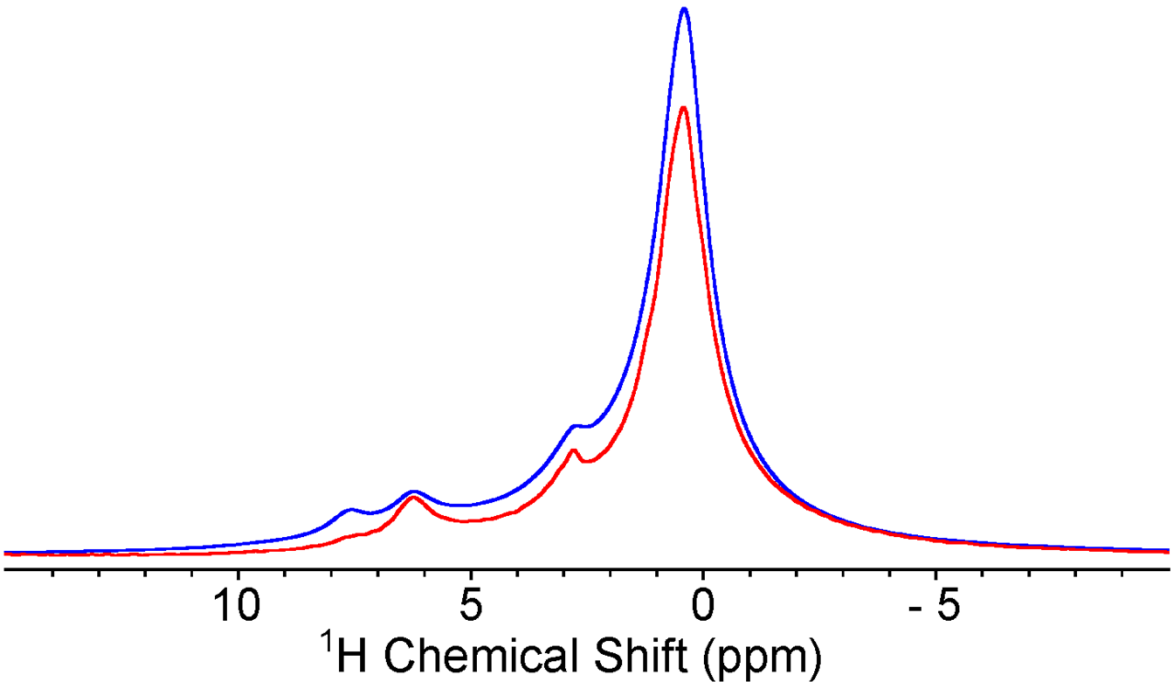


Figure S18. ^{13}C NMR spectrum (700 MHz, spinning rate 10 kHz, contact Time = 250 μs, recycle delay = 1 sec, ns = 25k) of **3** before (blue) and after exposure to ^{13}C dilabeled ethylene (red).

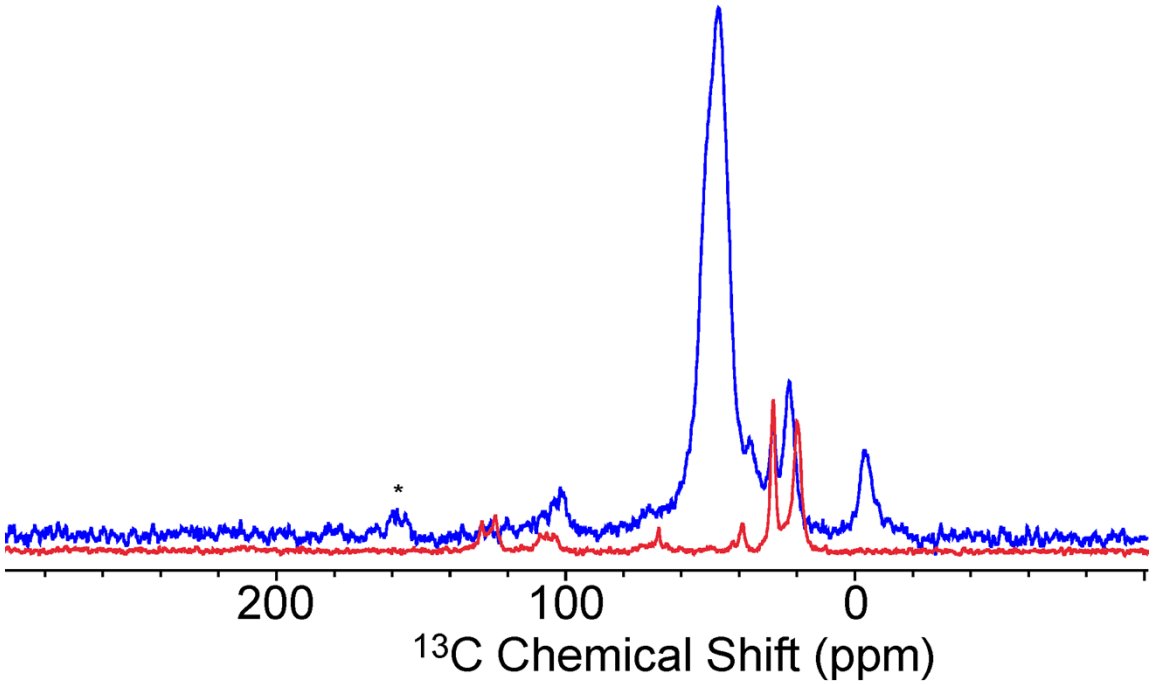


Figure S19. ^{1}H NMR spectrum (700 MHz, spinning rate 10 kHz, ns = 128) of **4** before (blue) and after exposure to ^{13}C dilabeled ethylene (red).

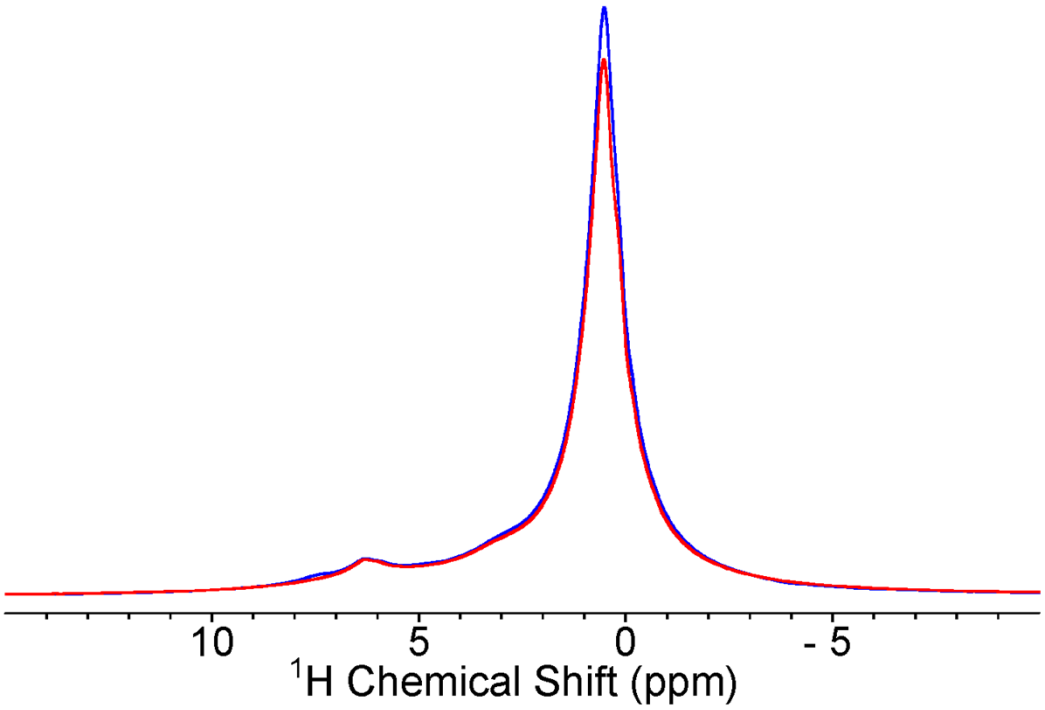


Figure S20. ^{13}C NMR spectrum (700 MHz, spinning rate 10 kHz, contact Time = 250 μs, recycle delay = 1 sec, ns = 20k) of **4** before (blue) and after exposure to ^{13}C dilabeled ethylene (red).

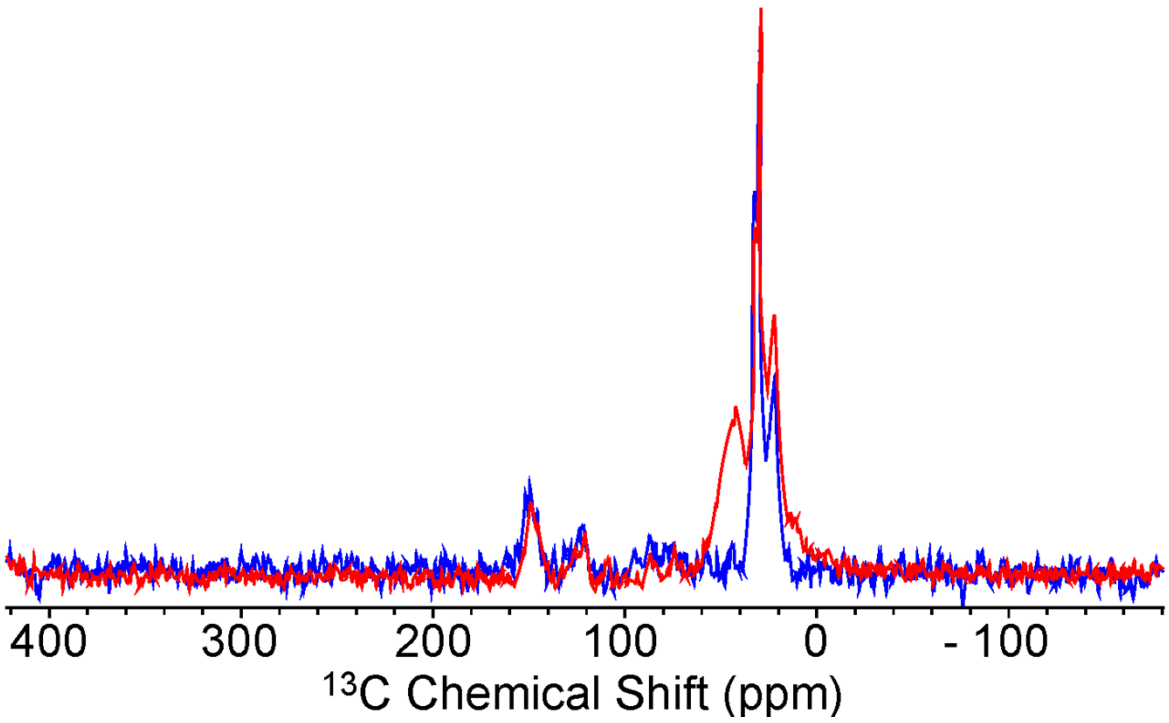


Figure S21. ^{1}H NMR spectrum (700 MHz, spinning rate 10 kHz, ns = 128) of **5** before (blue) and after exposure to ^{13}C dilabeled ethylene (red).

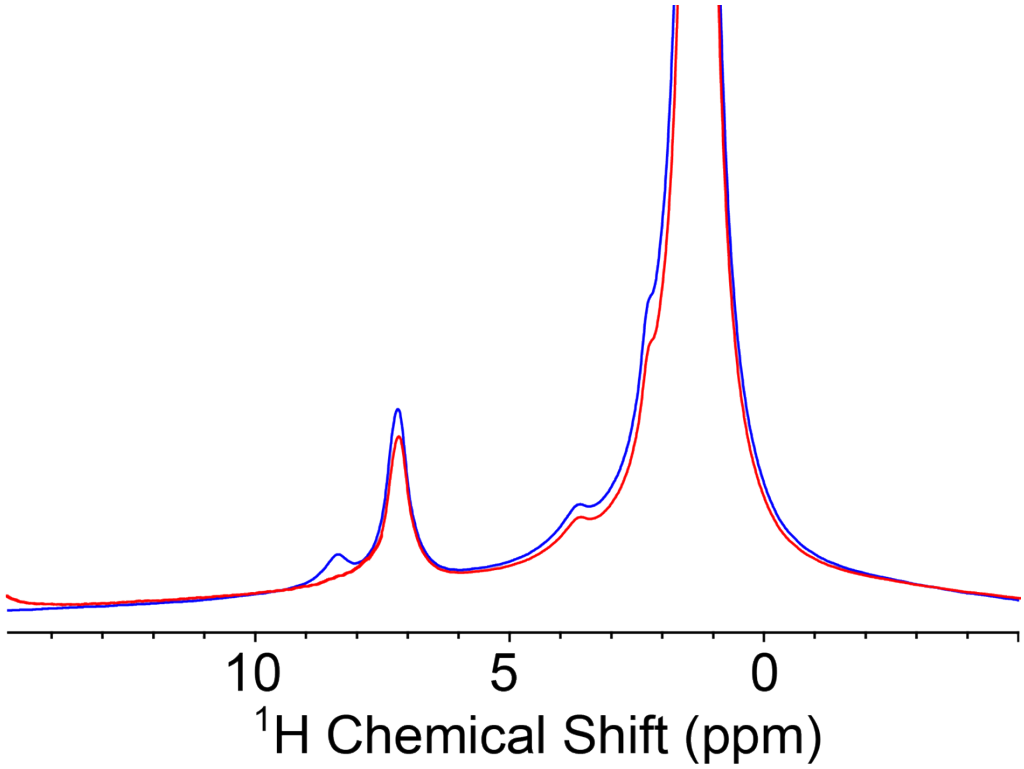


Figure S22. ^{13}C NMR spectrum (700 MHz, spinning rate 10 kHz, contact Time = 250 µs, recycle delay = 1 sec, ns = 80k) of **5** before (blue) and after exposure to ^{13}C dilabeled ethylene (red).

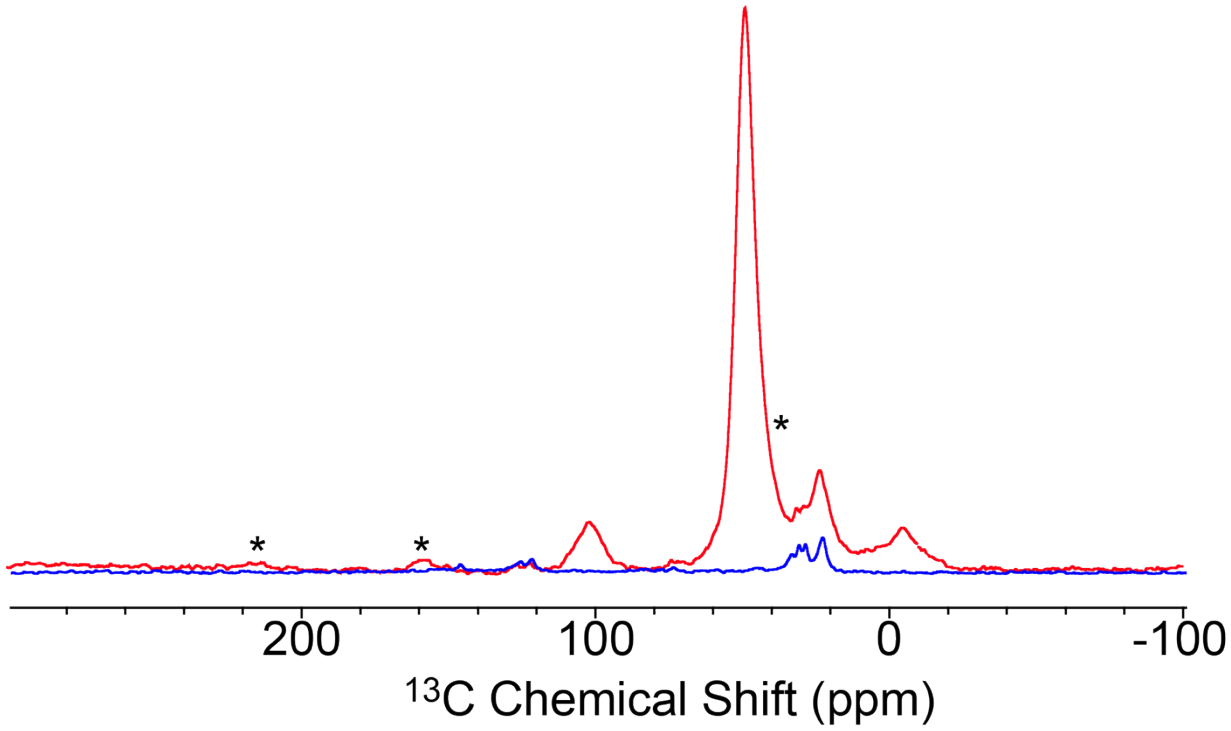


Figure S23. 2D ^{1}H-^{13}C HETCOR solid state NMR spectrum of **1** contacted with ^{13}C dilabeled ethylene (700 MHz, spinning rate 10 kHz). This spectrum was acquired under DUMBO homonuclear decoupling [5]. The contact time for the CP was 250 µs and the recycle delay was 1s. A total of 128 slices with 1024 scans each were collected. Asterisks indicate spinning side bands of the α carbon of the TBP. The ^{13}C CP MAS spectrum (1024 scans) recorded with a CP step of 250µs is indicated above the 2D plot. Blue line indicates the positive signals and green the negative ones.

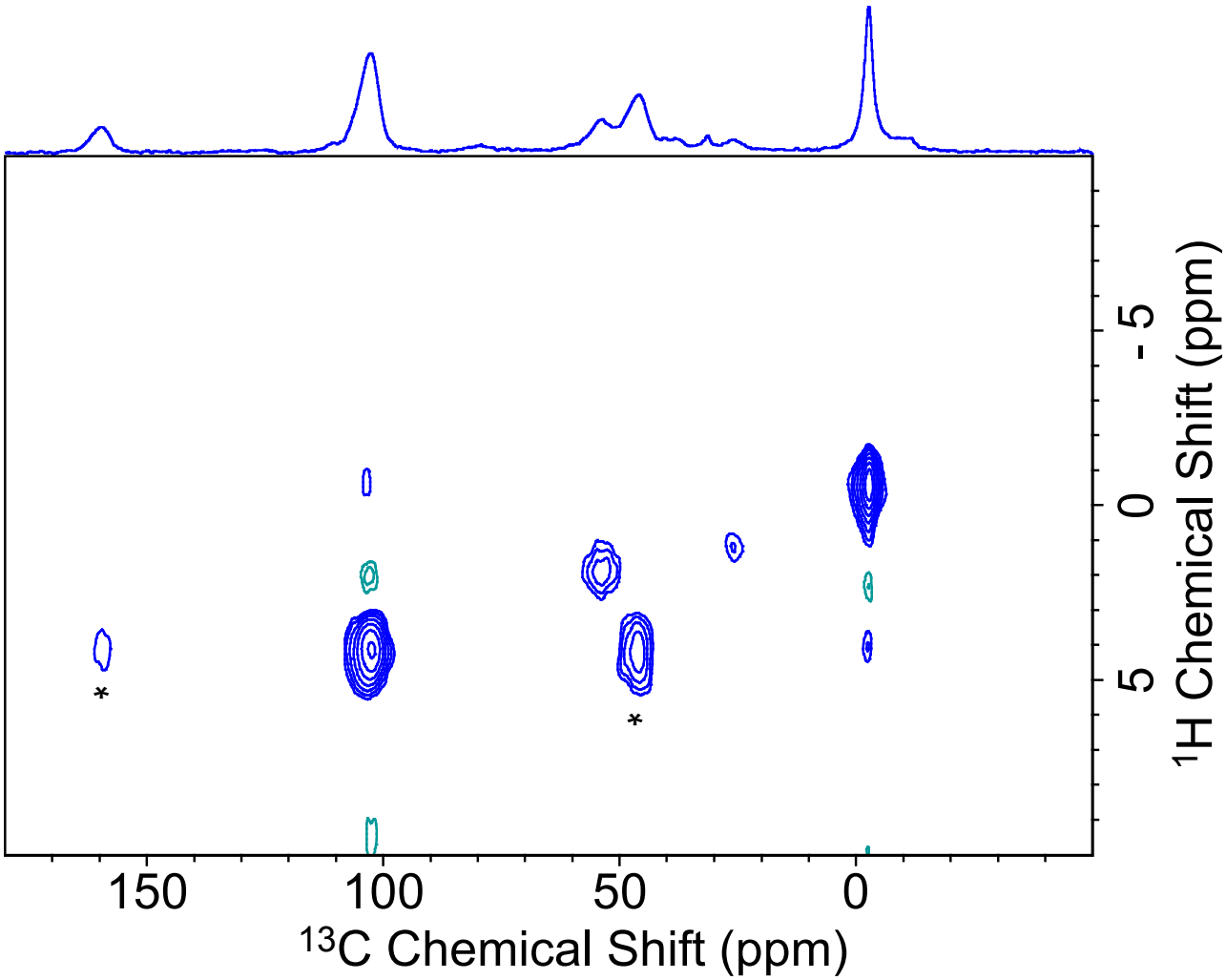


Figure S24. 2D ^{1}H-^{13}C HETCOR solid state NMR spectrum of **2** contacted with ^{13}C dilabeled ethylene (700 MHz, spinning rate 10 kHz). This spectrum was acquired under DUMBO homonuclear decoupling [5]. The contact time for the CP was 250 μs and the recycle delay was 1s. A total of 128 slices with 1024 scans each were collected. Asterisks indicate spinning side bands of the α carbon of the TBP. The ^{13}C CP MAS spectrum (1024 scans) recorded with a CP step of 250μs is indicated above the 2D plot. Blue line indicates the positive signals and green the negative ones.

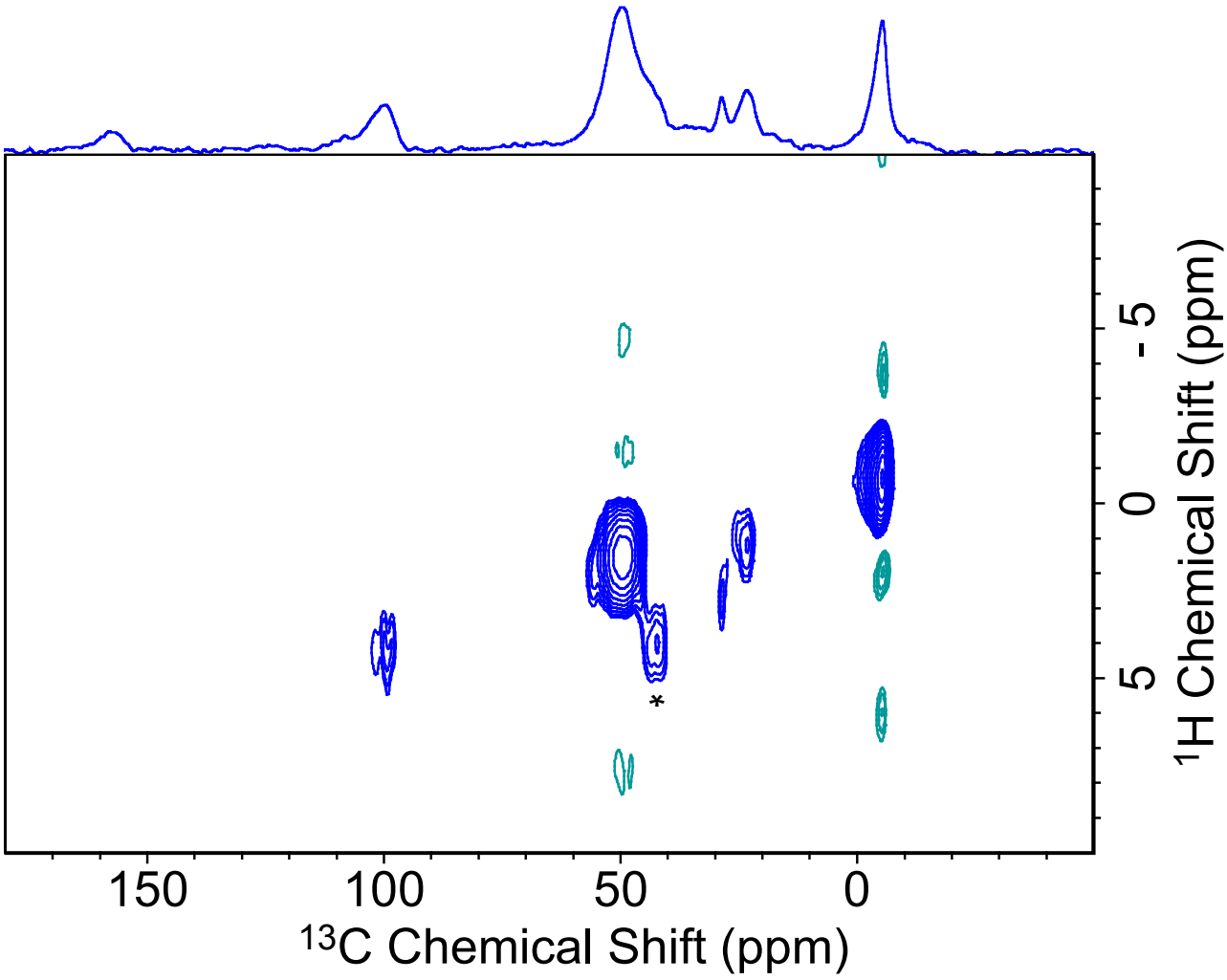


Figure S25. 2D ^{1}H-^{13}C HETCOR solid state NMR spectrum of **3** contacted with ^{13}C dilabeled ethylene (700 MHz, spinning rate 10 kHz). This spectrum was acquired under DUMBO homonuclear decoupling [5]. The contact time for the CP was 250 µs and the recycle delay was 1s. A total of 128 slices with 1024 scans each were collected. Asterisks indicate spinning side bands of the α carbon of the TBP. The ^{13}C CP MAS spectrum (1024 scans) recorded with a CP step of 250µs is indicated above the 2D plot. Blue line indicates the positive signals and green the negative ones.

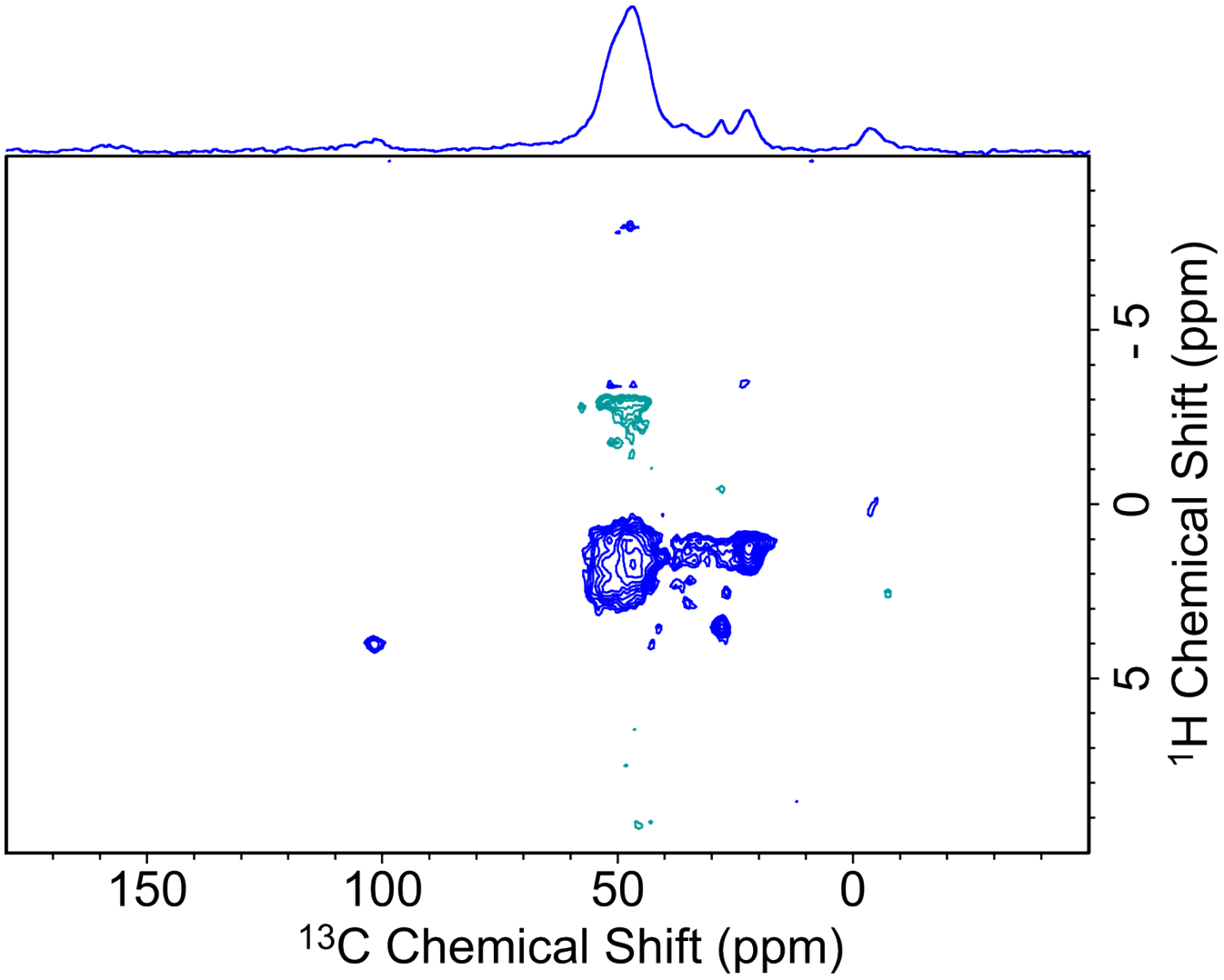


Figure S26. 2D ^{1}H-^{13}C HETCOR solid state NMR spectrum of **4** contacted with ^{13}C dilabeled ethylene (700 MHz, spinning rate 10 kHz). This spectrum was acquired under DUMBO homonuclear decoupling [5]. The contact time for the CP was 250 µs and the recycle delay was 1s. A total of 128 slices with 1024 scans each were collected. The ^{13}C CP MAS spectrum (1024 scans) recorded with a CP step of 250µs is indicated above the 2D plot. Blue line indicates the positive signals and green the negative ones.

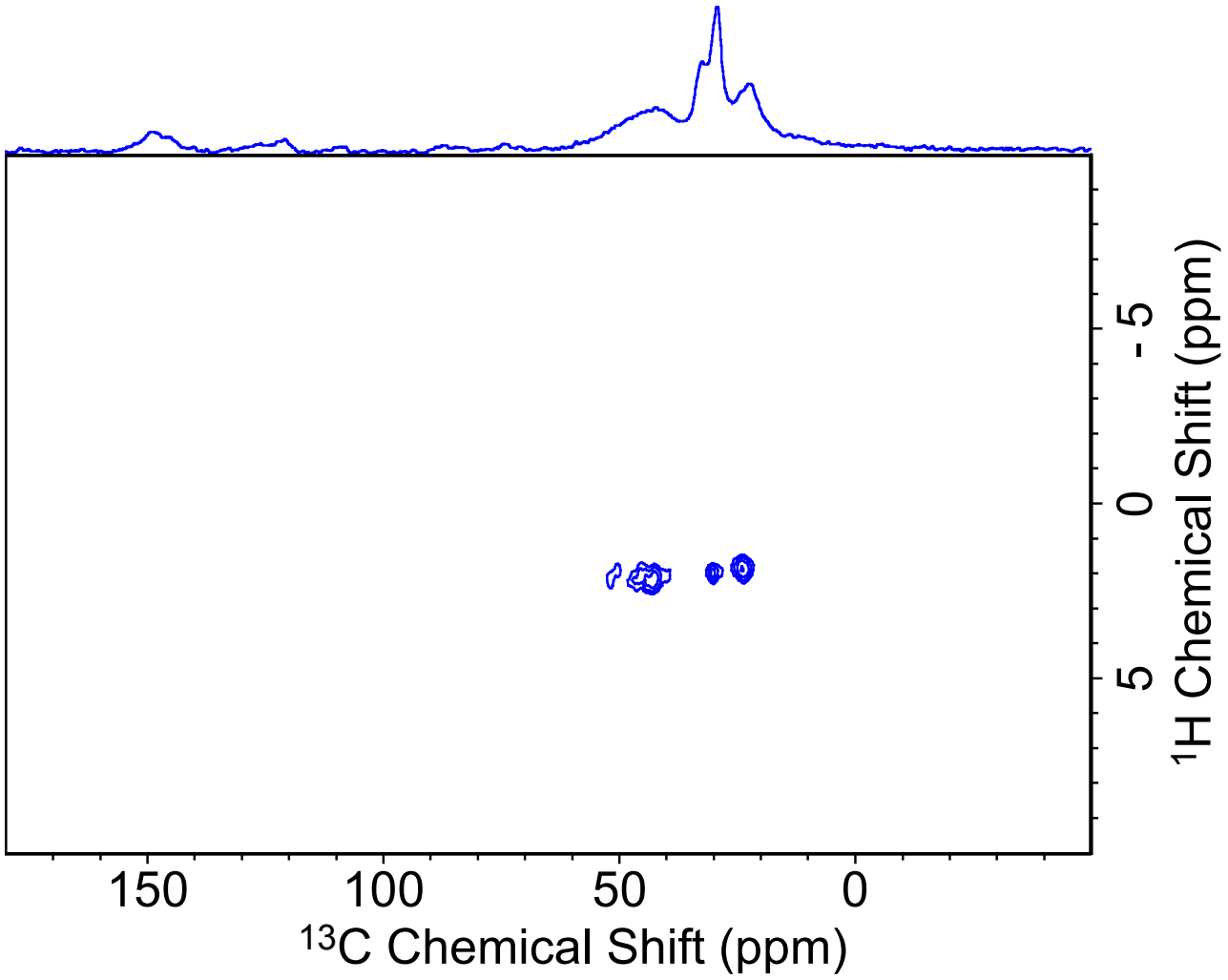
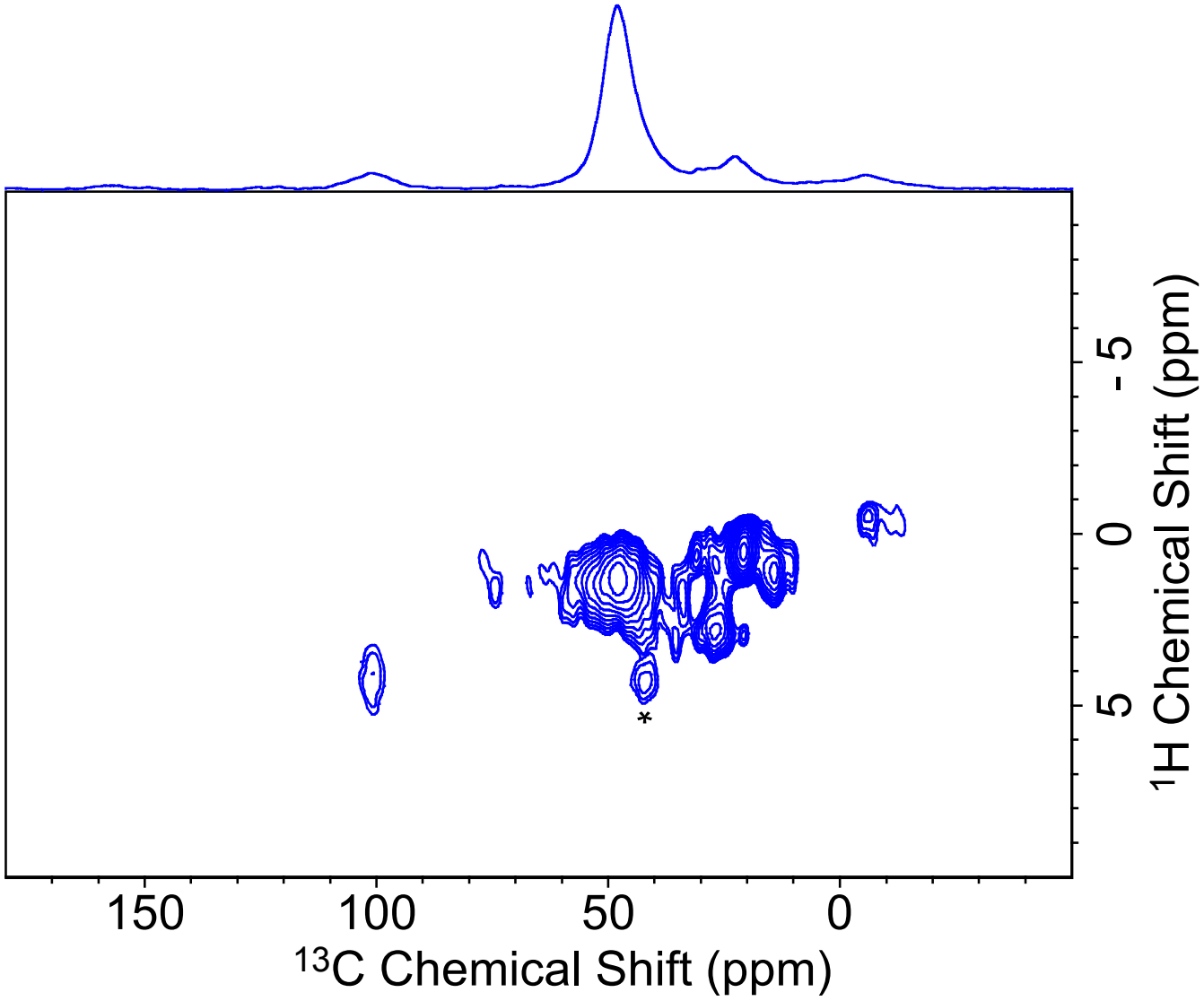


Figure S27. 2D ^{1}H-^{13}C HETCOR solid state NMR spectrum of **5** contacted with ^{13}C dilabeled ethylene (700 MHz, spinning rate 10 kHz). This spectrum was acquired under DUMBO homonuclear decoupling [5]. The contact time for the CP was 250 μs and the recycle delay was 1s. A total of 64 slices with 1024 scans each were collected. Asterisks indicate spinning side bands of the α carbon of the TBP. The ^{13}C CP MAS spectrum (1024 scans) recorded with a CP step of 250μs is indicated above the 2D plot. Blue line indicates the positive signals.



F) Catalytic tests

Metathesis of cis-4-nonene:

A t=0, a 0.8 M solution of cis-4-nonene in toluene containing heptane as internal standard (0.1 M) was added to the catalyst (**1-5**) introduced in a conical base vial containing a wing shaped magnetic stirred, and the reaction mixture was stirred at 600 rpm and kept at 30°C using an aluminum heating block. 10 µL aliquots of the solution were sampled, diluted with pure toluene (100 µL) and quenched by the addition of 1 µL of a 1 M solution of ethyl acetate in toluene. The resulting solution was analyzed by GC/FID (Agilent Technologies 7890 A) equipped with an HP-5 (Agilent Technologies) column. An error of ±10% was estimated for the analysis of a given metathesis reaction based on the reproducibility of data from duplicate and triplicate experiments. Conversion was determined from product formation, that is without taking cis/trans isomerization of the substrate into consideration (eq. 1). In that case, equilibrium conversion is reached at ca. 50%.

$$Product\ conversion_t = \frac{\sum [products]_t}{[substrate]_{ini}} \quad (1)$$

Figure S28. Metathesis of cis-4-nonene by the [W(NAr)(CHMe$_3$)(OR)$_2$] molecular precursors (0.1 mol%, 30°C)

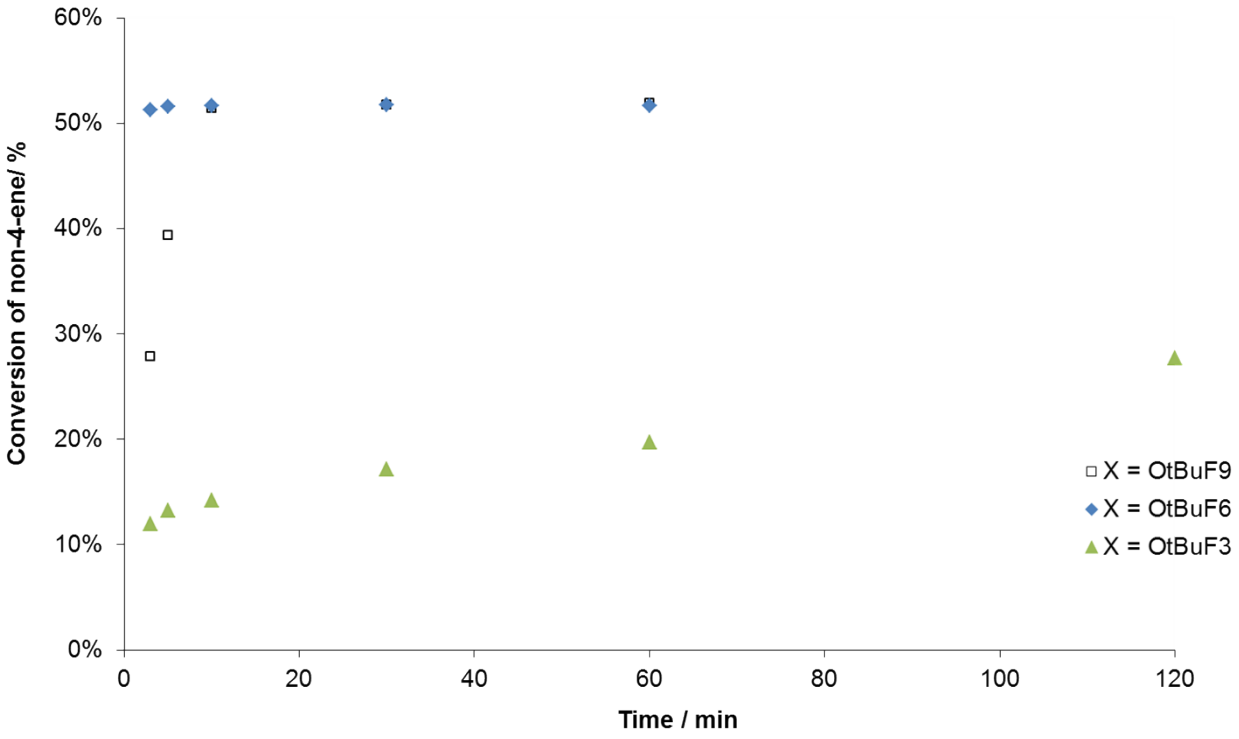


Table S5. Metathesis of cis-4-nonene by the [W(NAr)(CHMe$_3$)(OR)$_2$] molecular precursors (0.1 mol%, 30°C)

OR	TOF (min^{-1})	Time to equilibrium
OtBu	< 1	< 2 % after 24h
$OtBu_{F3}$	61	39% conversion after 24 h
$OtBu_{F6}$	> 166	< 3 min
$OtBu_{F9}$	93	< 10 min
$OSi(OtBu)_3$	< 1	< 1 % after 24h

Supported complexes

Figure S29. Metathesis of cis-4-nonene by complexes **1-5** (0.1 mol%, 30°C)

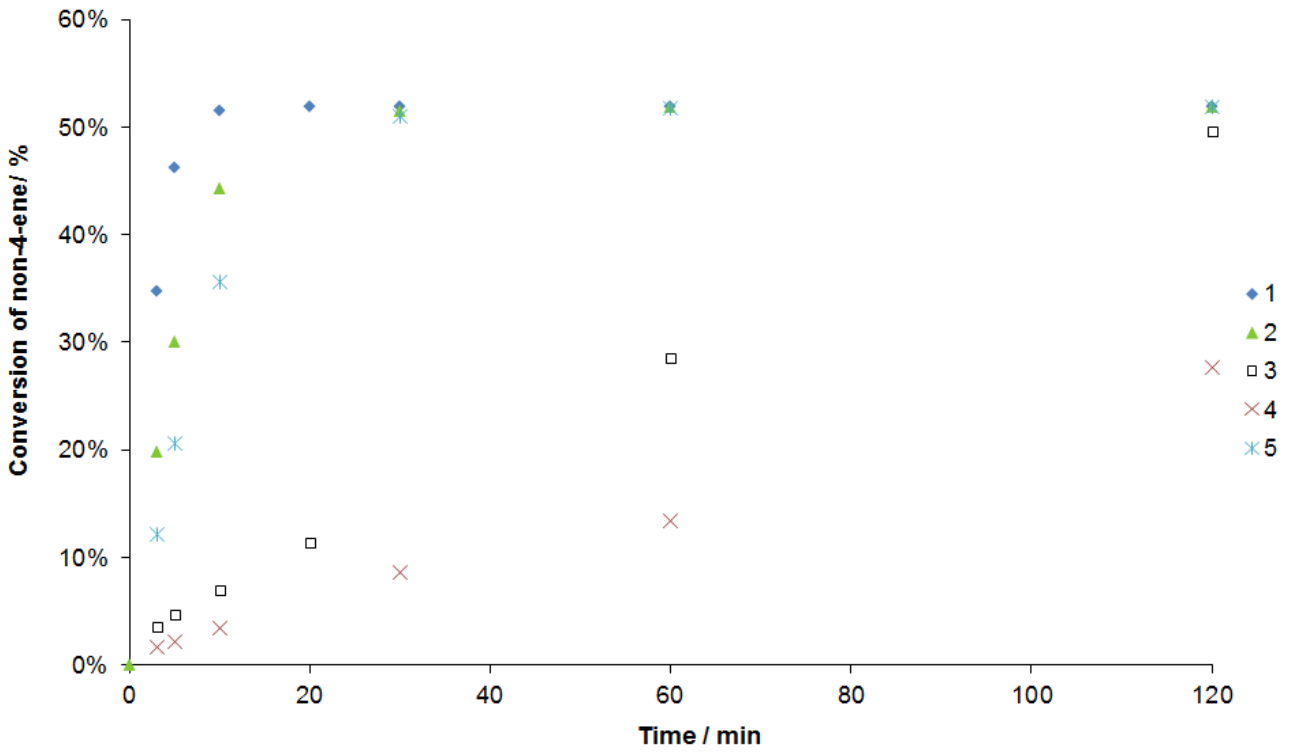


Table S6. Metathesis of cis-4-nonene by complexes **1-5** (0.1 mol%, 30°C)

OR	TOF (min^{-1})	Time to equilibrium
OtBu	5	< 480 min
$OtBu_{F3}$	15	< 120 min
$OtBu_{F6}$	75	< 30 min
$OtBu_{F9}$	115	< 10 min
$OSi(OtBu)_3$	40	< 30 min

Figure S30. Metathesis of cis-4-nonene by complexes **1-5** (0.02 mol%, 30°C)

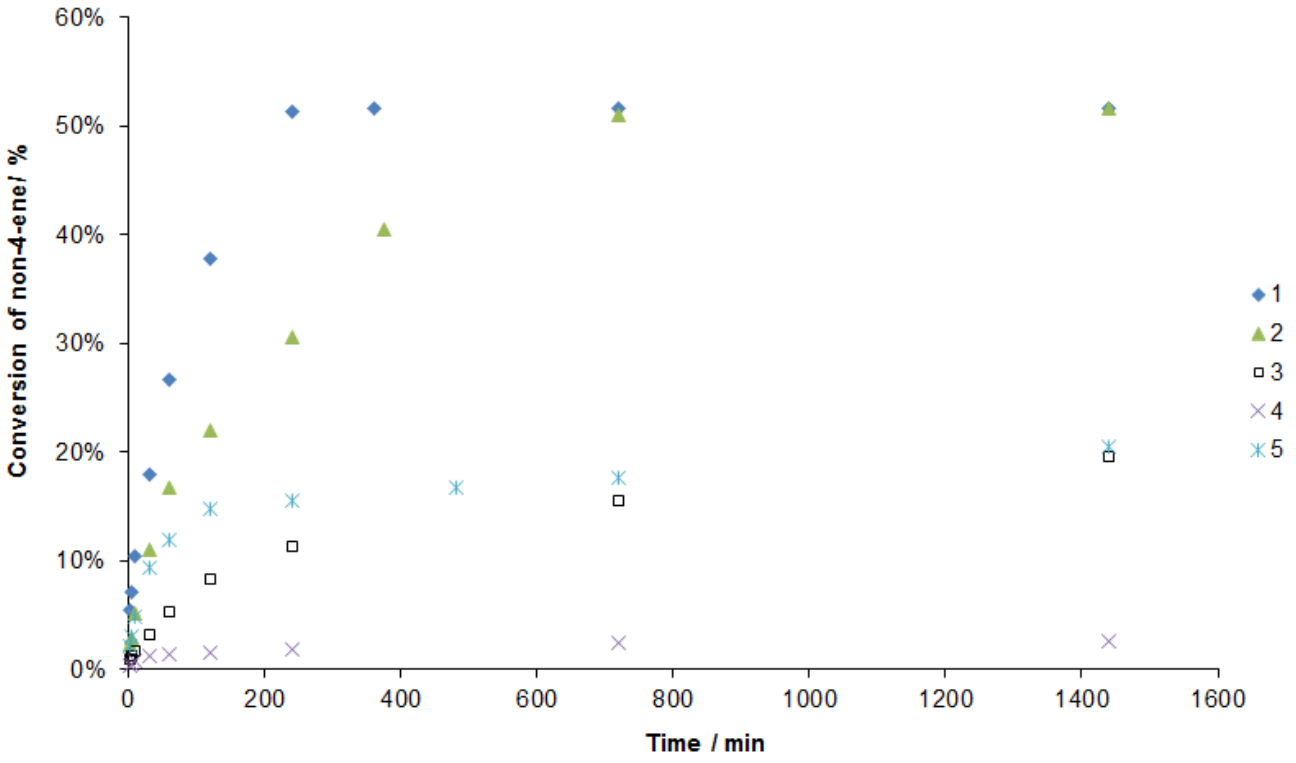


Table S7. Metathesis of cis-4-nonene by complexes **1-5** (0.02 mol%, 30°C)

OR	TOF (min^{-1})	Time to equilibrium
OtBu	5	3% product conversion after 24h
$OtBu_{F3}$	16	20% product conversion after 24h
$OtBu_{F6}$	38	< 12 h
$OtBu_{F9}$	82	210 min
$OSi(OtBu)_3$	37	21% product conversion after 24h

Metallacycles

Figure S31. Metathesis of cis-4-nonene by the metallacycles formed by contact of ^{13}C labeled ethylene on complexes **1-4** according to the general procedure described above (0.1 mol%, 30°C).

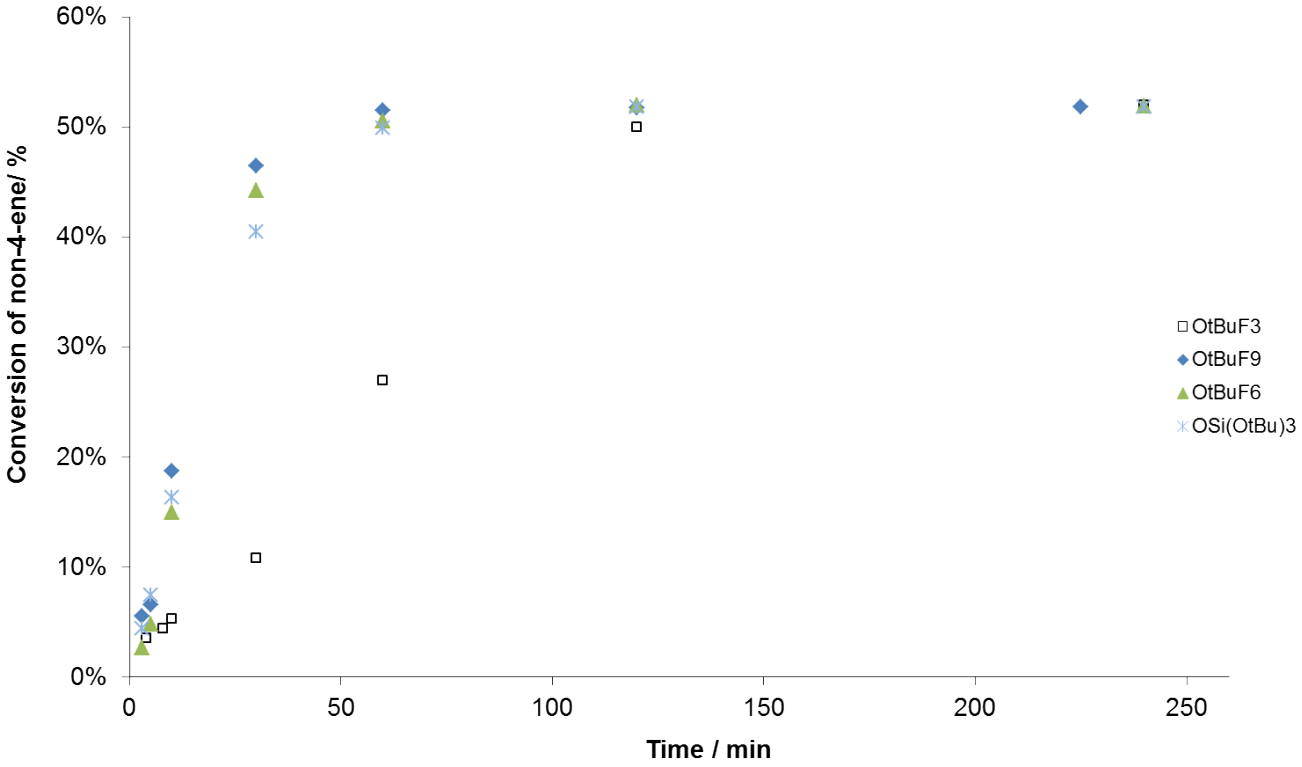


Table S8. Metathesis of cis-4-nonene by the metallacycles formed by contact of ^{13}C labeled ethylene on complexes **1-4** according to the general procedure described above (0.1 mol%, 30°C).

OR	TOF (min^{-1})	Time to equilibrium
OtBu	< 0.1	< 3 % conversion after 24h
$OtBu_{F3}$	11	< 150 min
$OtBu_{F6}$	7	< 80 min
$OtBu_{F9}$	23	< 60 min
$OSi(OtBu)_3$	15	< 60 min

Previously described complexes [1,2]

Figure S32. Metathesis of cis-4-nonene by complex [(≡SiO)Mo(NAr)(CHCMe$_3$)(OtBu$_{F6}$)][5] (black squares) (0.1 mol%, 30°C).

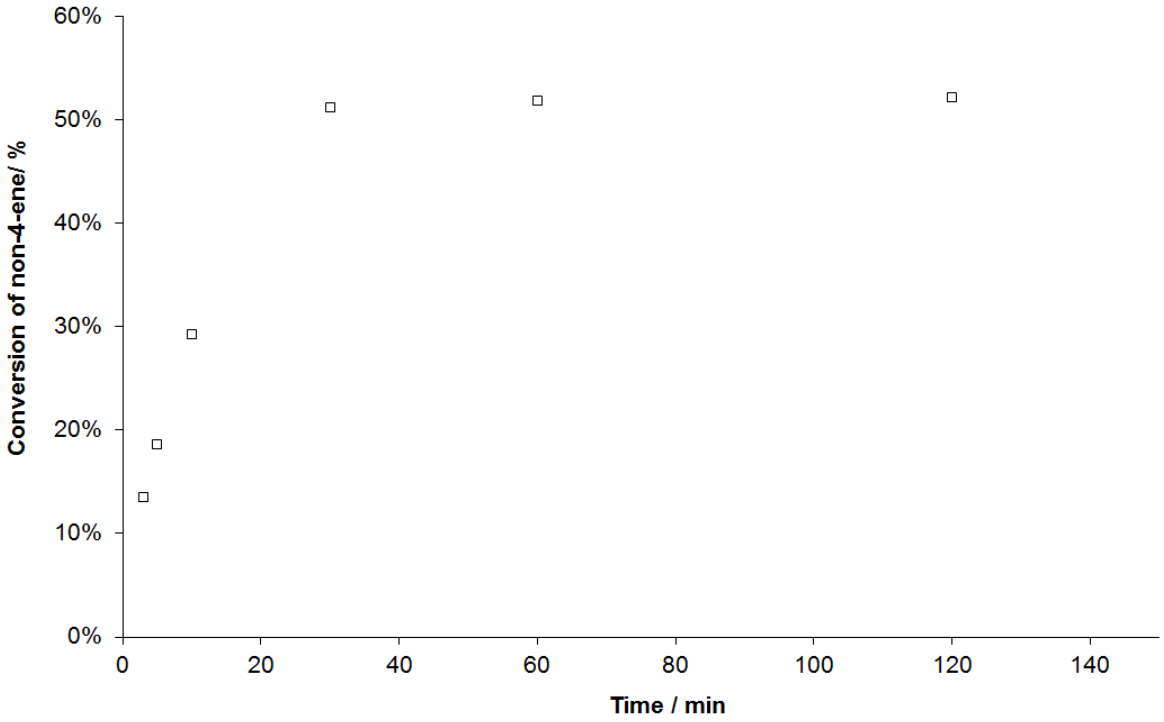


Table S9. Metathesis of cis-4-nonene by complexes [(≡SiO)W(NAr)(CHCMe$_3$)(Me$_2$Pyr)][2] and [(≡SiO)Mo(NAr)(CHCMe$_3$)(OtBu$_{F6}$)][5] (0.1 mol%, 30°C).

complex	**TOF (min^{-1})**	**Time to equilibrium**
[(≡SiO)Mo(NAr)(CHCMe$_3$)(OtBu$_{F6}$)]	46	< 30 min

G) Stability

Exposure to cis-3-hexene

A solution of cis-3-hexene (10.4 µmol, 20 equiv.) in toluene (0.5 mL) was introduced in a conical shaped vial containing a wing shaped magnetic stirrer and catalyst **3** (2.6 mg, 0.52 µmol, 1 equiv.). The resulting suspension was stirred for 2h at room temperature. The solution was then filtered off, and the catalyst was taken to dryness under reduced pressure. Catalytic test on cis-4-nonene (1000 equiv.) as described above was then carried out on that sample, without any noticeable change in activity (same TOF and time to equilibrium conversion).

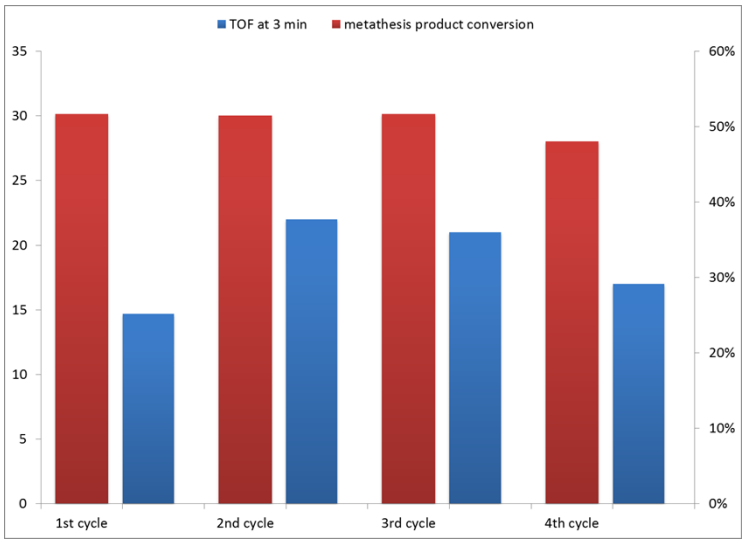
Catalyst recycling

-Step a: A 0.5 M solution of cis-non-4-ene in toluene containing heptane as internal standard (0.1 M) was added to the catalyst **3** (catalyst to substrate ratio 1000) in a conical base vial containing a wing shaped magnetic stirrer.

-Step b: The reaction mixture was stirred at 600 rpm and kept at 30°C using an aluminum heating block for 180 min. After leaving the supported catalyst settling, the olefin mixture was filtered out, and replaced by the same amount of fresh cis-non-4-ene solution, keeping the catalyst to substrate ratio to 1000.

Step b was repeated four times without any noticeable loss of activity of the catalyst (Figure S26).

Figure S33. TOF(min^{-1}) at 3 min and productive conversion (equilibrium conversion correspond to ca 50%) after 180min during the cycles described above for catalyst **3**



H) References

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