Supporting Information for

Synthesis of Tungsten Imido Alkylidene Complexes that Contain an Electron-Withdrawing

Imido Ligand

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Figure S1. Thermal ellipsoid drawing (50%) of W(NAr^Cl3)(CHCMe$_3$)(OTf)$_2$(dme) (**3a**). Hydrogen atoms have been omitted for clarity. Select bond distances (Å) and angles (°): W1-N1 = 1.736(11), W1-C1 = 1.1983(15), W1-O1 = 2.3122(10), W1-O2 = 2.1031(10), W1-O13 = 2.0561(10), W1-O23 = 2.1710(10); W1-N1-C31 = 170.71(11), W1-C1-C2 = 141.39(11), N1-W1-C1 = 100.41(6).

X-ray crystal structure determination details.

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart APEX2 CCD detector with Mo Kα radiation ($\lambda = 0.71073$ Å) from an IμS micro-source for the structures of compounds **3a** and **4a**, and on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) for the structure of compound **2d**. Absorption and other corrections were applied using SADABS [Reference 1]. All structures were solved by direct methods using SHELXS [Reference 2] and refined against F^2 on all data by full-matrix least squares with SHELXL-97 (structure of **X8_3a**) or SHELXL-2013 [Reference 3] (structures of **4a** and **2d**) using established refinement approaches [Reference 4]. Coordinates for hydrogen atoms bound to carbon directly attached to the central metal atoms were taken from the difference Fourier synthesis and those hydrogen atoms were subsequently refined semi-freely with the help of distance restraints. All other hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U_{eq} value of the atoms they are linked to (1.5 times for methyl groups).

Compound **3a** crystallizes in the monoclinic centrosymmetric space group $P2_1/n$ with one molecule of **3a** and one molecule of dichloromethane per asymmetric unit. There is no disorder and except for the C1—H1 distance restraint, no restraints were applied. Compound **4a** crystallizes in the triclinic centrosymmetric space group $P\bar{1}$ with one molecule of **4a** and one half Et$_2$O molecule per asymmetric unit. The half Et$_2$O molecule is located near a crystallographic inversion center and was refined as over two independent sites, resulting in a four-fold disorder of the full Et$_2$O molecule in the unit cell with two of the four disorder components pairwise related to the other two by the crystallographic inversion center. In addition, the alkylidene ligand was found to be disordered over two positions, approximately corresponding to a slight rotation about the W1—C1 and a stronger rotation about the C1—C2 bond. Those disorders were refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The circumstance that the structure contains only half a molecule of diethyl ether for every full molecule of **4a** results in a non-integer number for the element oxygen in the empirical Formula in Table S3.

Compound **2d** crystallizes in the monoclinic centrosymmetric space group $P2_1/n$ with one half molecule of **2d** per asymmetric unit. The other half of the molecule is generated by a crystallographic inversion center. Two of the four crystallographically independent CF3 groups were refined as disordered over two positions, corresponding to a rotation about the respective C—C bonds. All C—F bonds and all F—C—F angles in the structure were refined to be equivalent. For one of the two disordered CF$_3$ groups the disorder was found to correspond to a rotation of approximately 60° about the C—C bond and fluorine atoms located on opposite sides of the disorder axis were pairwise constrained to have identical anisotropic displacement parameters as described in section 4.2 in reference 4. In addition, similarity and rigid bond restraints were applied to the anisotropic displacement parameters of all atoms involved in the disorders.

Table S1. Crystal data and structure refinement for **3a**

Identification code	x12199
Empirical formula	C18 H24 Cl5 F6 N O8 S2 W
Formula weight	921.60
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 9.7487(7) Å α= 90°
	b = 20.1371(14) Å β= 92.5210(10)°
	c = 15.5354(11) Å γ = 90°
Volume	3046.8(4) Å^3
Z	4
Density (calculated)	2.009 Mg/m^3
Absorption coefficient	4.446 mm^{-1}
F(000)	1792
Crystal size	0.21 x 0.16 x 0.14 mm^3
Theta range for data collection	1.66 to 31.50°.
Index ranges	-14<=h<=14, -29<=k<=29, -22<=l<=22
Reflections collected	212424
Independent reflections	10153 [R(int) = 0.0414]
Completeness to theta = 31.50°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5749 and 0.4553
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10153 / 1 / 378
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0148, wR2 = 0.0345
R indices (all data)	R1 = 0.0164, wR2 = 0.0350
Largest diff. peak and hole	1.548 and -0.685 e.Å^{-3}

Table S2. Crystal data and structure refinement for **2d**.

Identification code	14011
Empirical formula	C52 H56 F24 N4 W2
Formula weight	1560.70
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2_1/n
Unit cell dimensions	a = 13.8640(19) Å α= 90°
	b = 14.775(2) Å β= 97.329(2)°
	c = 14.478(2) Å γ = 90°
Volume	2941.6(7) Å^3
Z	2
Density (calculated)	1.762 Mg/m^3
Absorption coefficient	4.022 mm^{-1}
F(000)	1520
Crystal size	0.460 x 0.440 x 0.130 mm^3
Theta range for data collection	1.915 to 30.505°.
Index ranges	-19<=h<=19, -21<=k<=21, -20<=l<=20
Reflections collected	82838
Independent reflections	8967 [R(int) = 0.0376]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8967 / 617 / 422
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0195, wR2 = 0.0462
R indices (all data)	R1 = 0.0228, wR2 = 0.0482
Extinction coefficient	n/a
Largest diff. peak and hole	1.069 and -0.774 e.Å^{-3}

Table S3. Crystal data and structure refinement for **4a**.

Identification code	x13201
Empirical formula	C79 H71 Cl3 N O2.50 W
Formula weight	1364.56
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P$\bar{1}$
Unit cell dimensions	a = 12.8493(18) Å α= 87.484(3)°
	b = 13.6749(19) Å β= 88.749(3)°
	c = 20.269(3) Å γ = 69.065(3)°
Volume	3323.2(8) Å^3
Z	2
Density (calculated)	1.364 Mg/m^3
Absorption coefficient	1.907 mm^{-1}
F(000)	1394
Crystal size	0.060 x 0.050 x 0.015 mm^3
Theta range for data collection	1.596 to 30.508°
Index ranges	-18<=h<=18, -19<=k<=19, -28<=l<=28
Reflections collected	108220
Independent reflections	20238 [R(int) = 0.0787]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	20238 / 358 / 887
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0367, wR2 = 0.0686
R indices (all data)	R1 = 0.0553, wR2 = 0.0750
Extinction coefficient	n/a
Largest diff. peak and hole	2.112 and -1.159 e.Å^{-3}
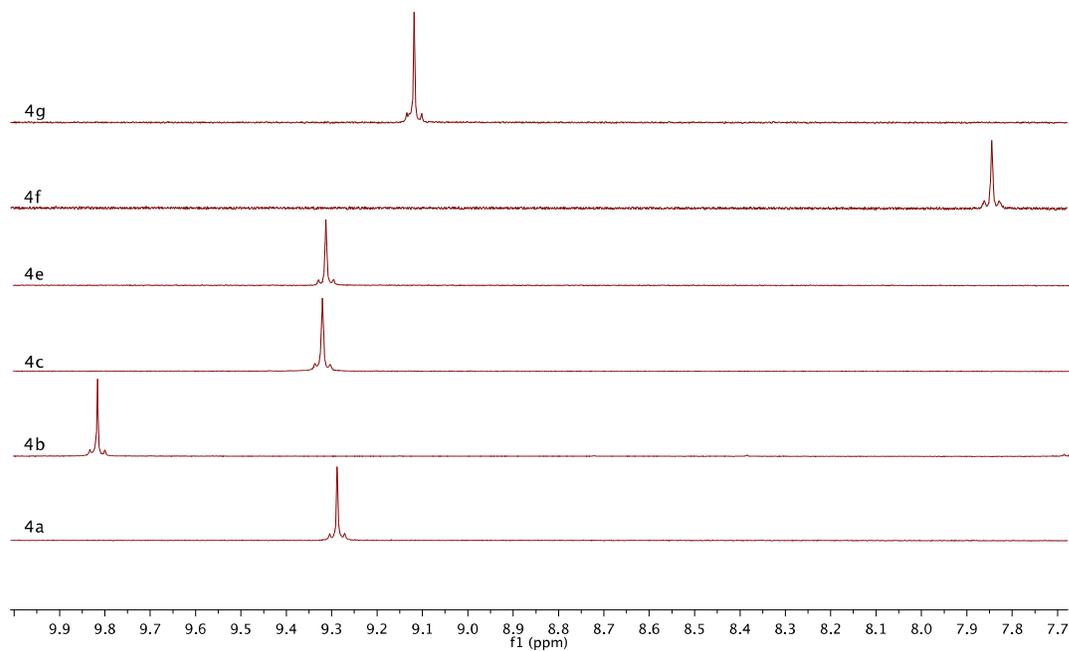
Figure S2. ^{1}H NMR (500 MHz) spectra of the alkylidene region of **4a-4c**, **4e-4g** in CD$_2$Cl$_2$. The alkylidene peaks of **4d** and **4h** are obscured by peaks in the phenyl region of the ODBMP ligands.
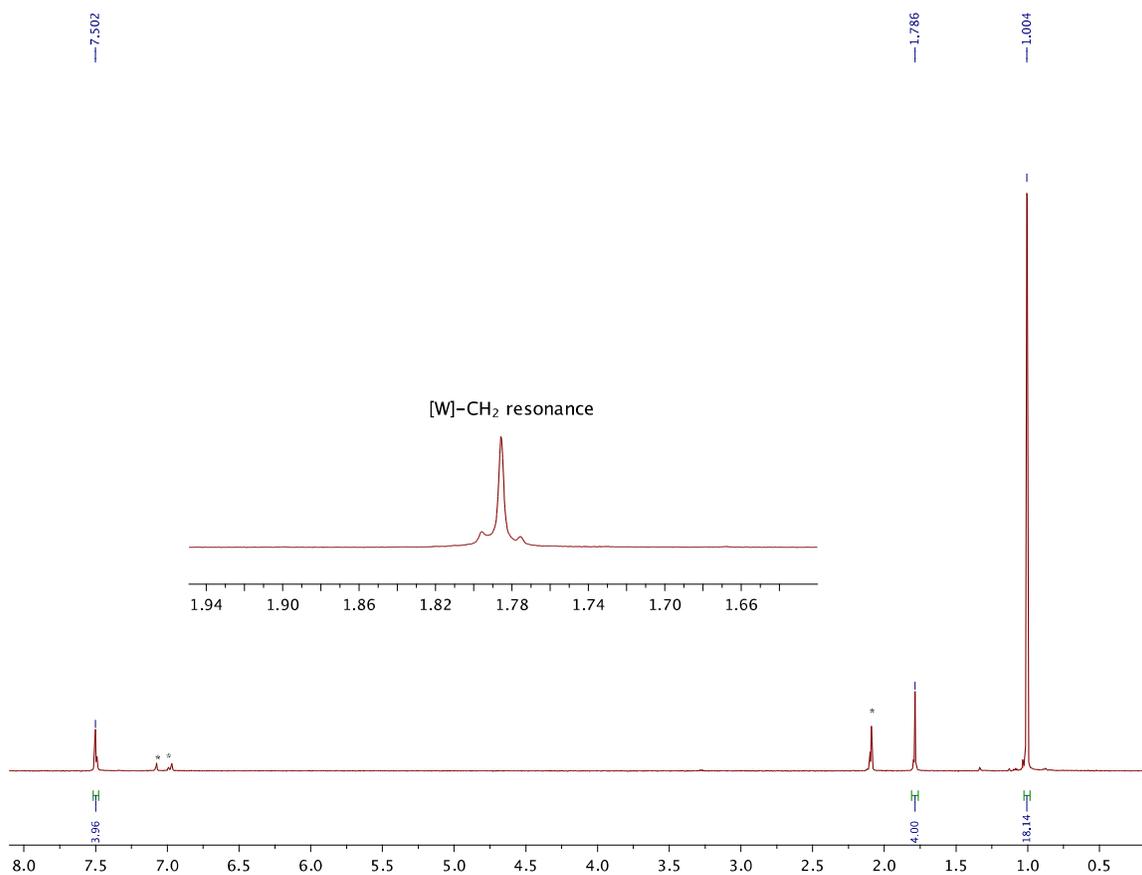
Figure S3. ^{1}H NMR (500 MHz) spectrum of **2d** at 70˚C in C$_7$D$_8$. Heating **2d** pushes the monomer/dimer equilibrium toward monomer, resulting in a sharpening of the W-CH$_2$ resonance and the observation of $^2J_{WH}$ satellites. * Toluene-d^8
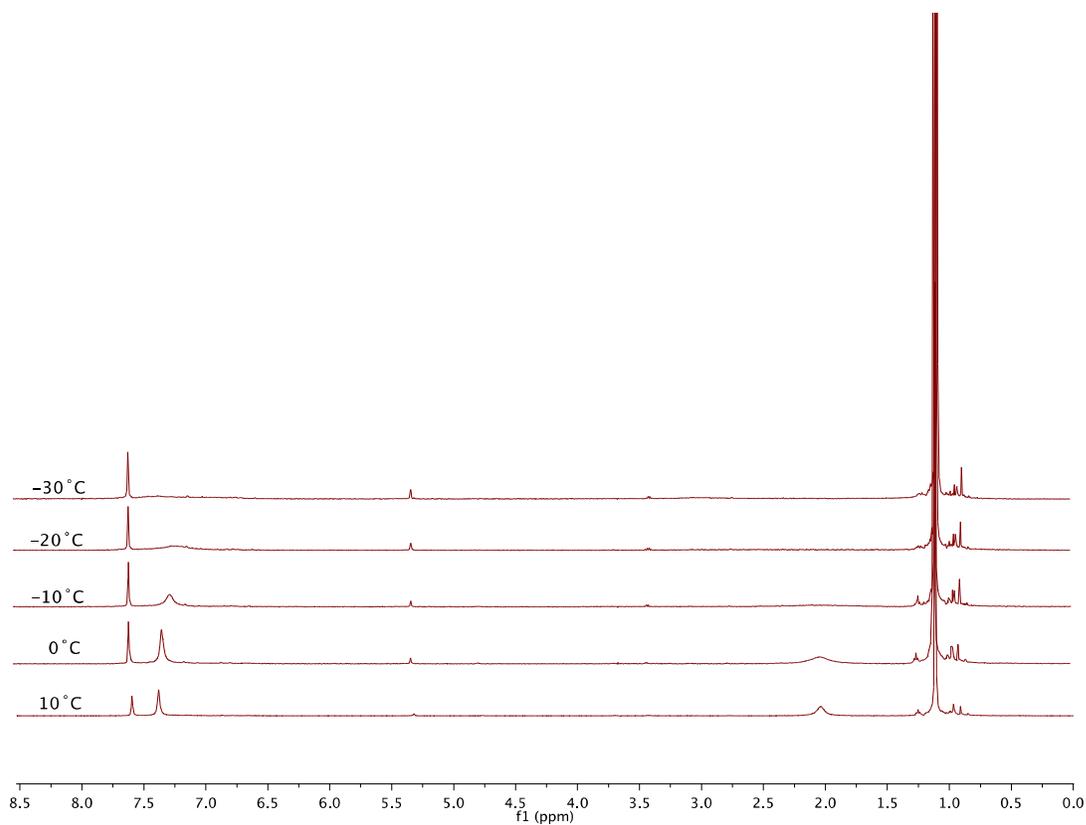
Figure S4. Low temperature ^{1}H NMR (500 MHz) of **2d** in CD_2Cl_2. Cooling **2d** results in the broadening of the W-CH$_2$ resonance, in addition to that for the 2- and 6- proton substituents on the arylimido ring. Below -30°C **2d** begins to precipitate from solution.
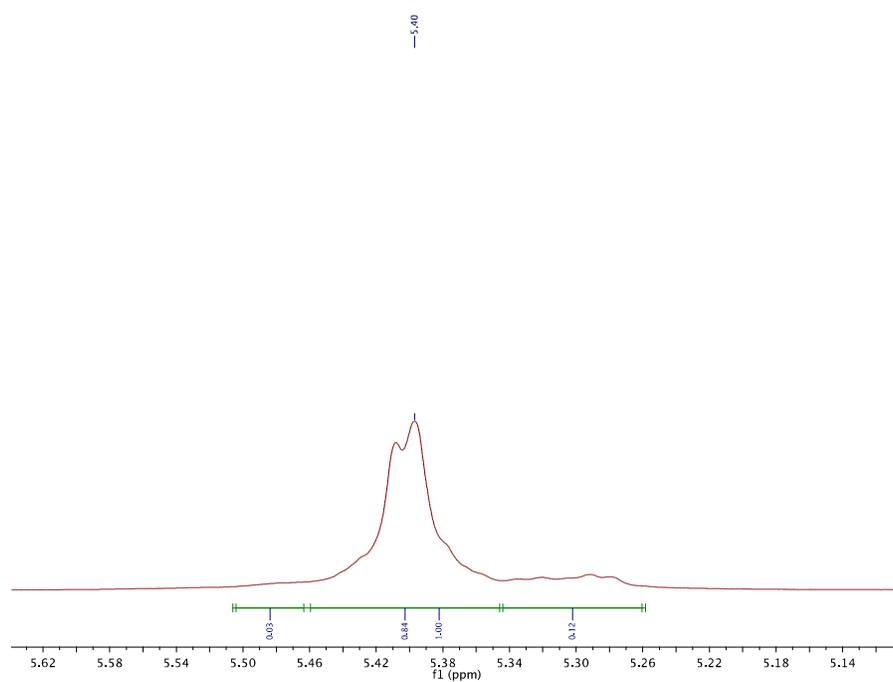
Figure S5. ^{1}H NMR (500 MHz) of poly(DCMNBD) generated by **4a**.
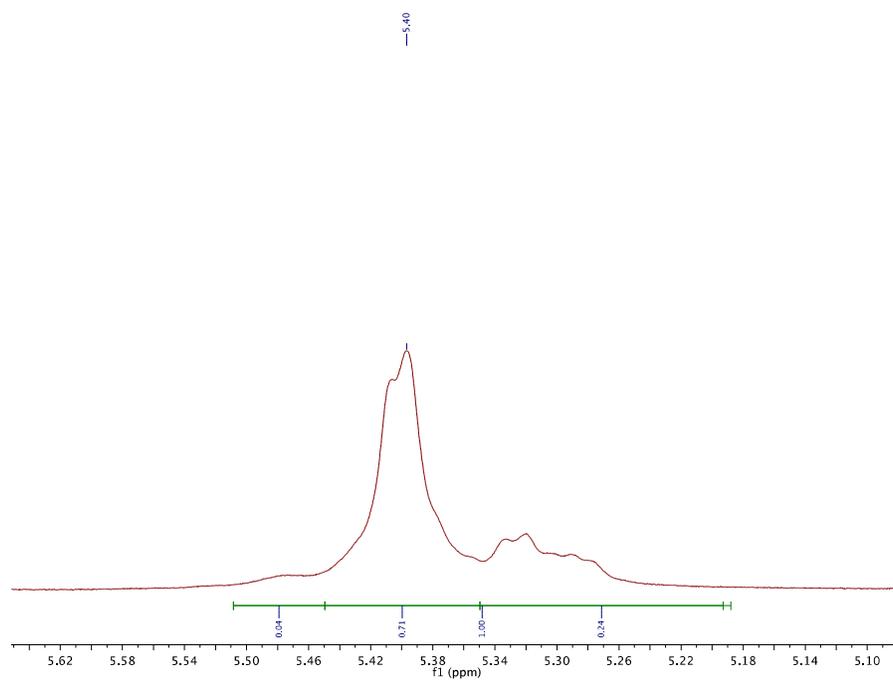
Figure S6. ^{1}H NMR (500 MHz) of poly(DCMNBD) generated by **4b**.
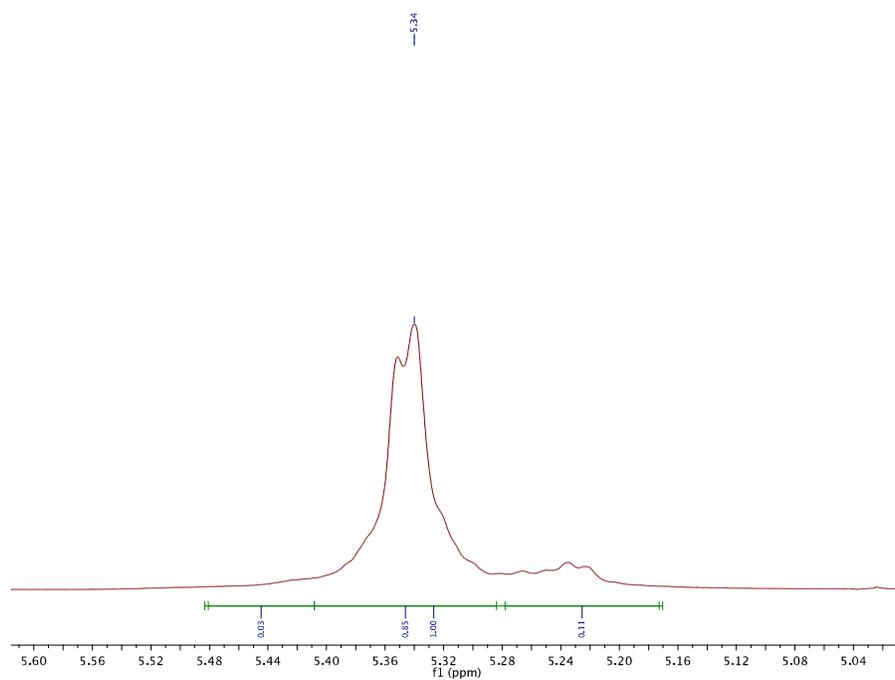
Figure S7. ^{1}H NMR (500 MHz) of poly(DCMNBD) generated by **4c**. Polymer peaks are slightly shifted due to presence of residual methanol.
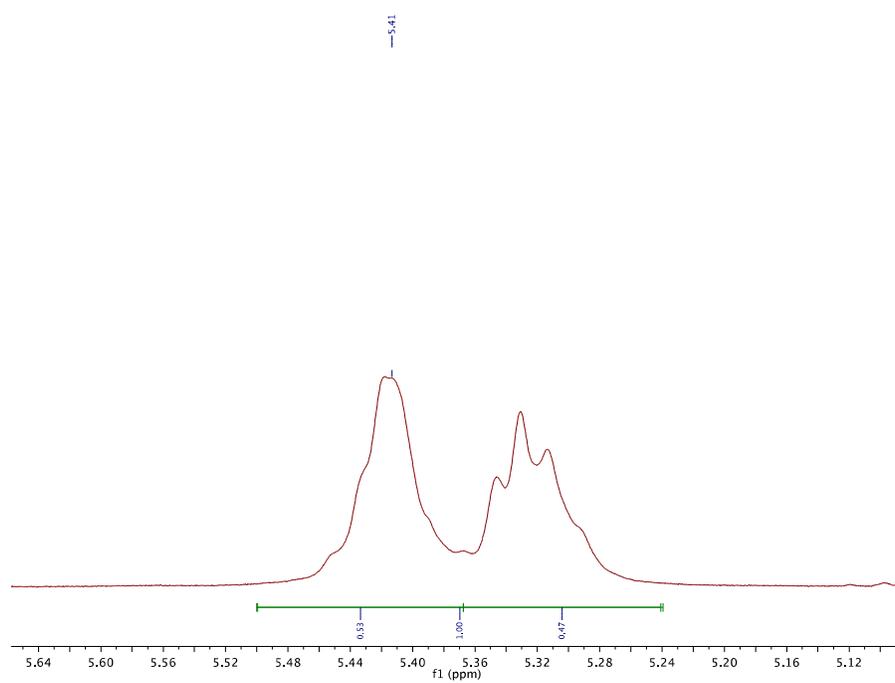
Figure S8. ^{1}H NMR (500 MHz) of poly(DCMNBD) generated by **4d**.
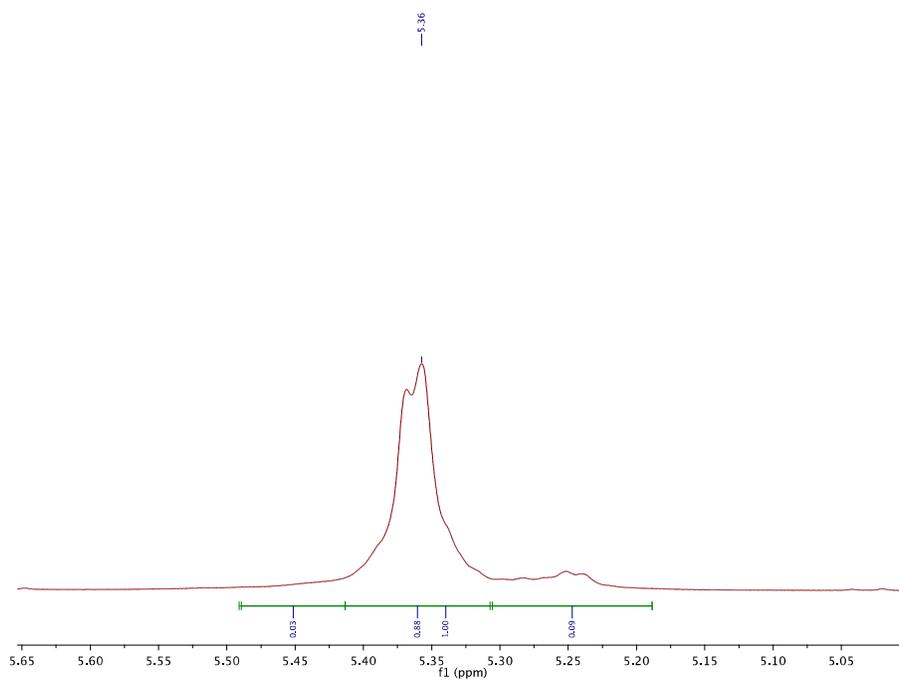
Figure S9. ^{1}H NMR (500 MHz) of poly(DCMNBD) generated by **4e**. Polymer peaks are slightly shifted due to presence of residual methanol.
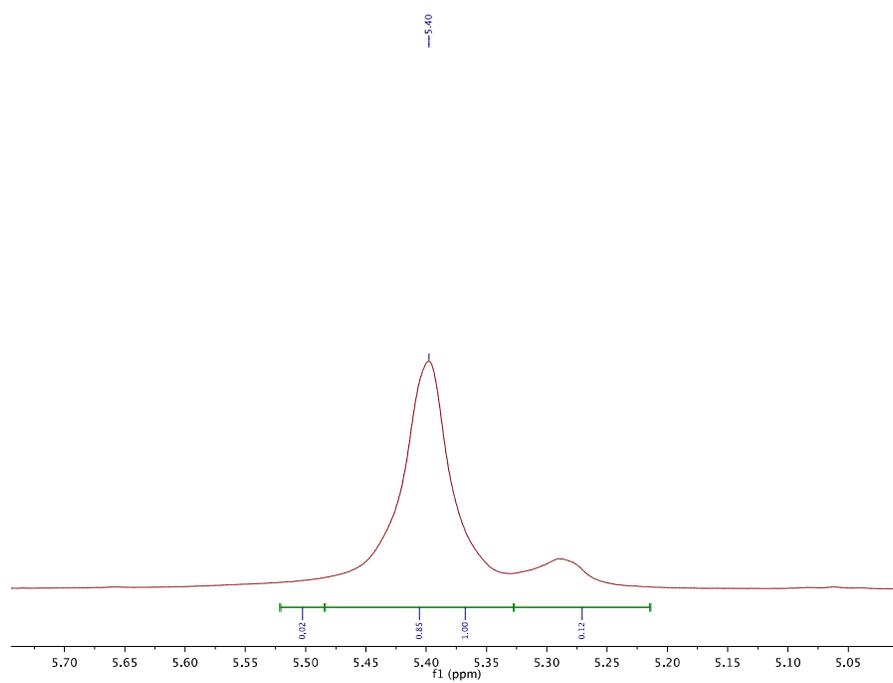
Figure S10. ^{1}H NMR (500 MHz) of poly(DCMNBD) generated by **4f**.

—5.41
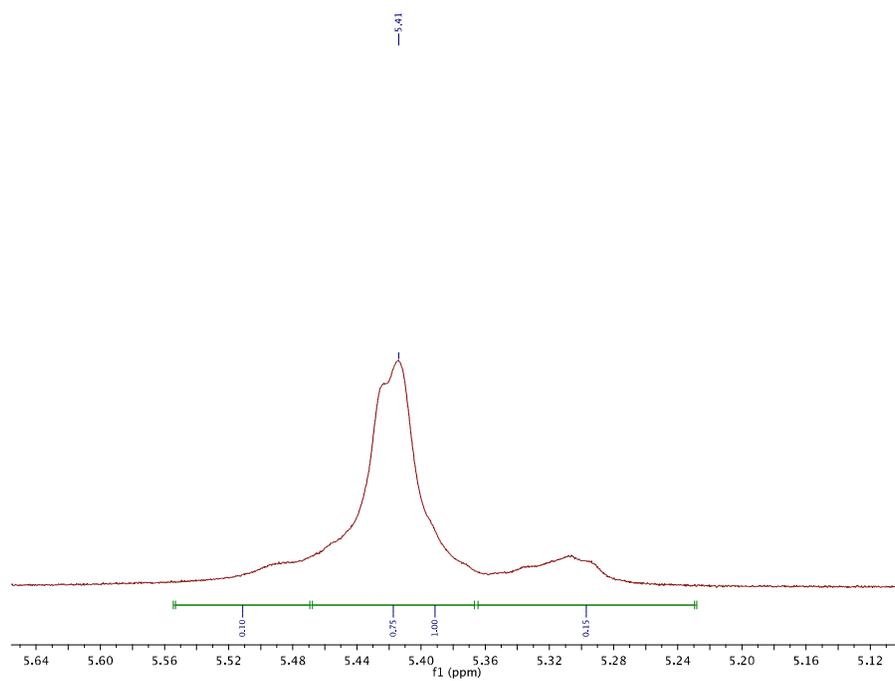
Figure S11. ^{1}H NMR (500 MHz) of poly(DCMNBD) generated by **4g**.

—5.38
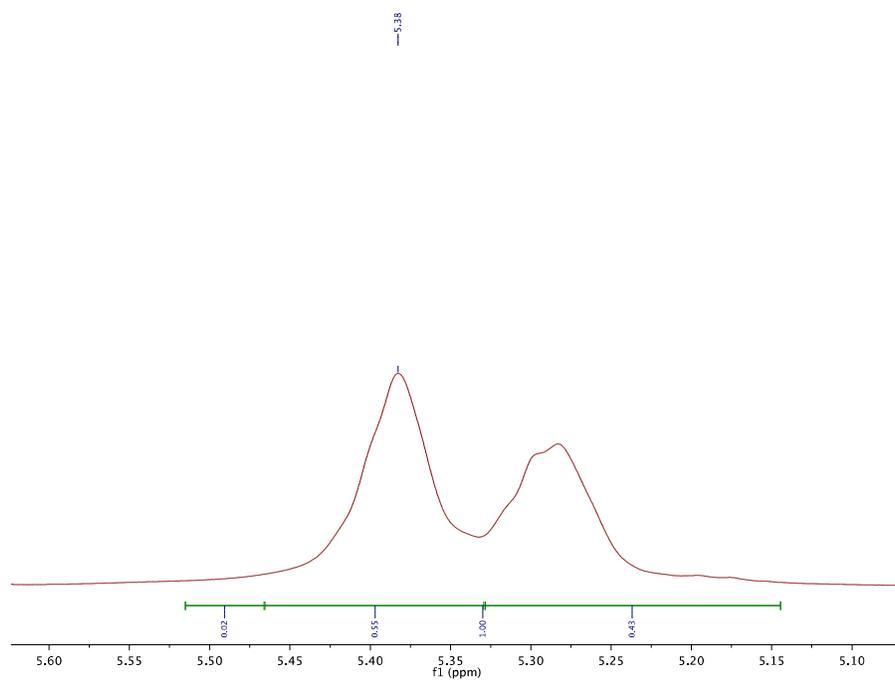
Figure S12. ^{1}H NMR (500 MHz) of poly(DCMNBD) generated by **4h**. Polymer peaks are slightly shifted due to presence of residual methanol.
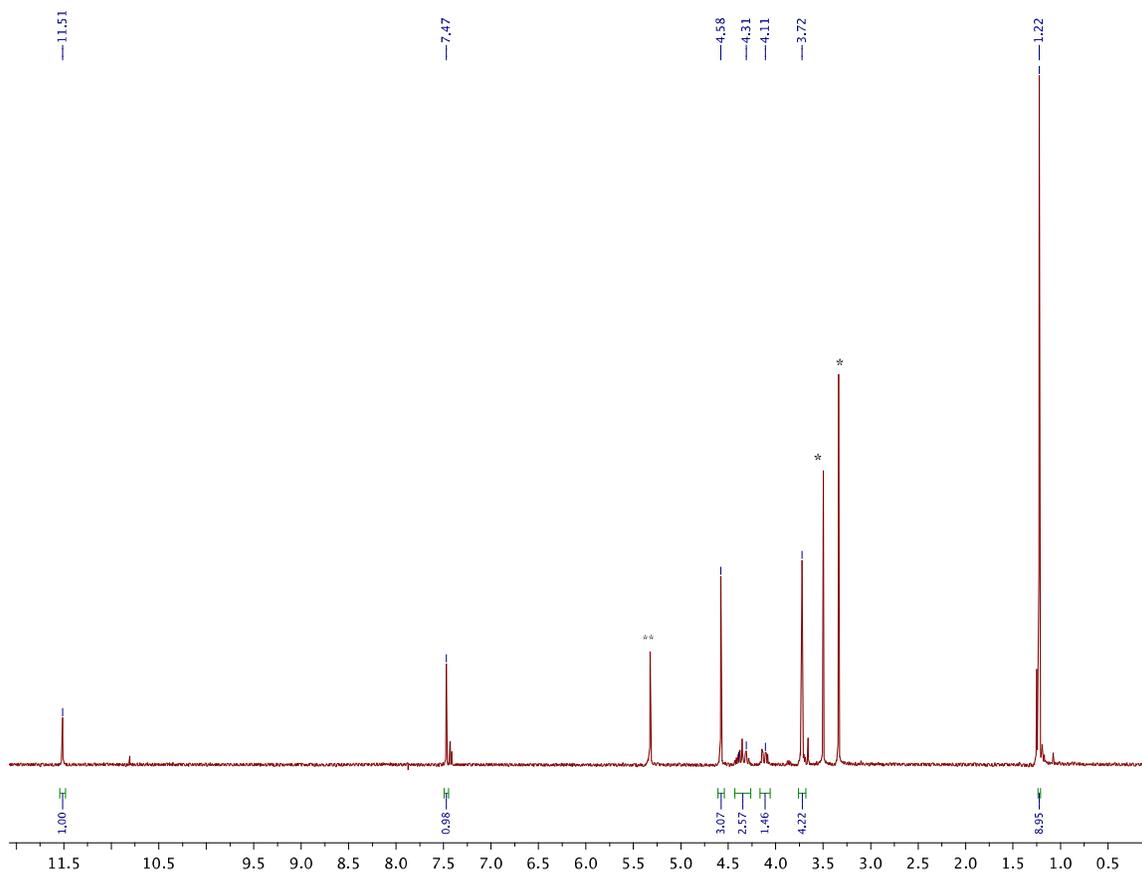
Figure S13. ^{1}H NMR (500 MHz) spectrum of **3a** in CD$_2$Cl$_2$. * Free residual DME; ** CD$_2$Cl$_2$
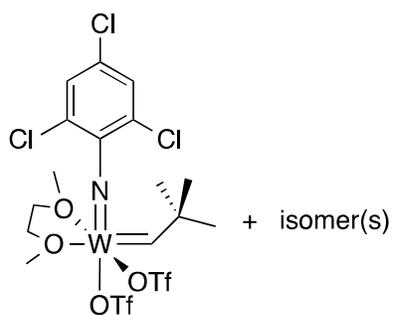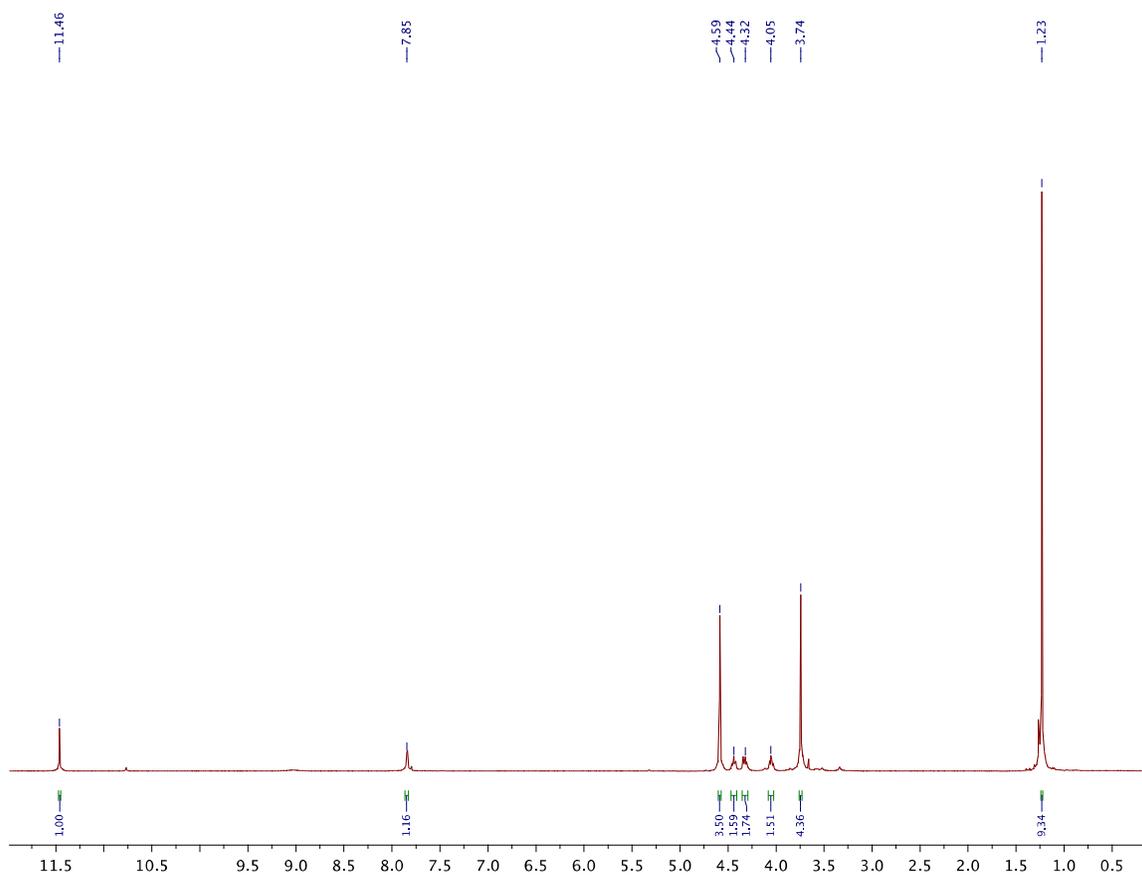
Figure S14. ^{1}H NMR (500 MHz) spectrum of **3b** in CD$_2$Cl$_2$.

Figure S15. ^{1}H NMR (500 MHz) spectrum of **3c** in CD$_2$Cl$_2$.
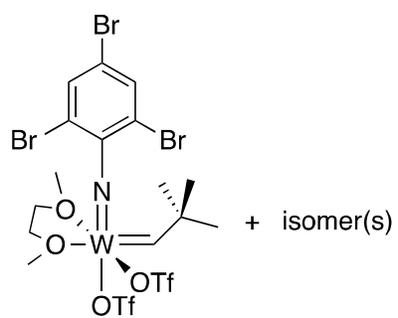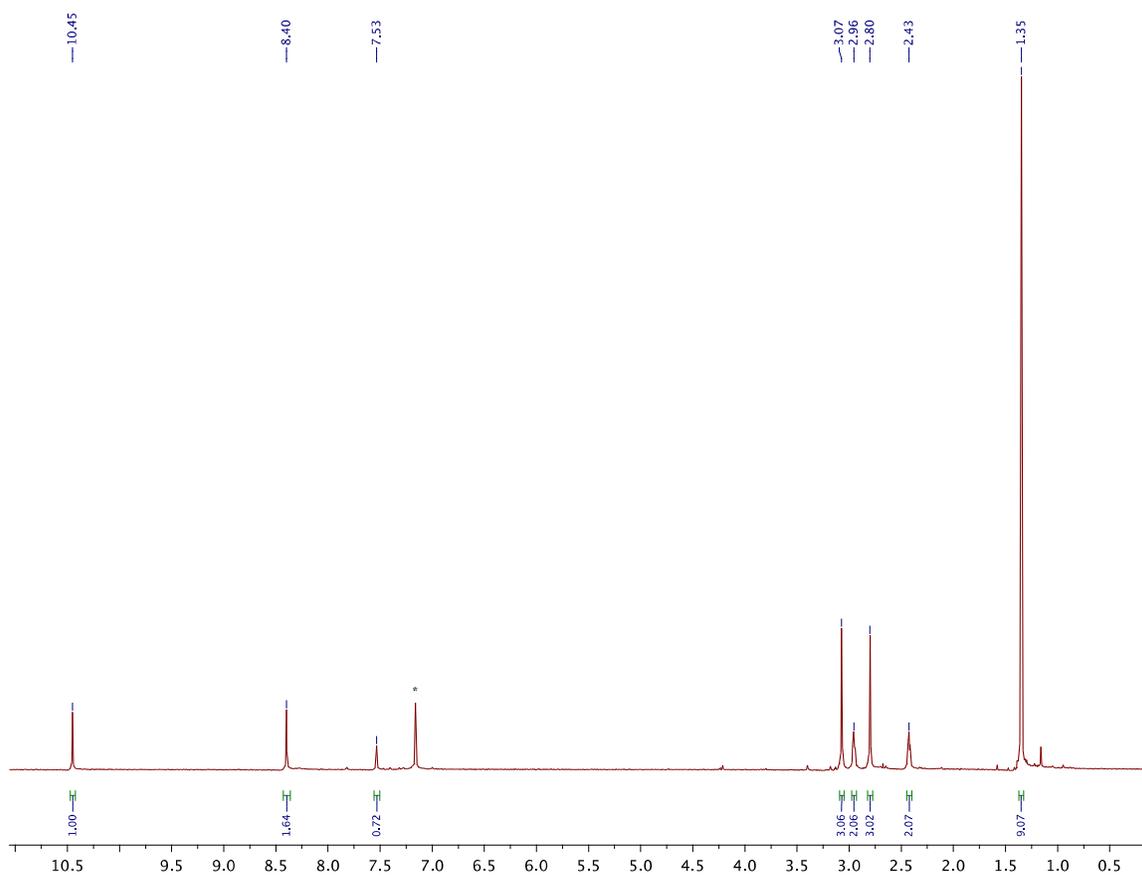
Figure S16. ^{1}H NMR (500 MHz) spectrum of **3d** in C$_6$D$_6$. * C$_6$D$_6$