Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information

Selective ethylene oligomerisation using supported tungsten mono-imido catalysts

Christopher M. R. Wright, Thomas Williams, Zoë R. Turner, Jean-Charles Buffet and Dermot O'Hare*

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1. X-ray Crystallography

Table S1. Selected experimental crystallographic data.

Crystal data		
Compound **CCDC number** **Chemical formula**	$W\{N(C_6H_5)\}Cl_4(THF)$ (**1.1**) 1518771 $C_{10}H_{13}Cl_4NOW$	$W\{N(2,6\text{-}Me\text{-}C_6H_3)\}Cl_4(THF)$ (**1.2**) 1518770 $C_{12}H_{17}Cl_4NOW$
Mr	488.86	516.92
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P1$
Temperature (K)	150	150
***a, b, c* (Å)**	14.7317(3), 7.1889(1), 13.9923(3)	7.9869(2), 8.7291(2), 12.9648(4)
α, β, γ (°)	90, 102.120(1), 90	85.609(1), 89.995(1), 64.329(1)
***V* (Å^3)**	1448.82(5)	811.73(4)
Z	4	2
μ (mm^{-1})	8.69	7.76
Crystal size (mm)	0.30 × 0.20 × 0.20	0.20 × 0.15 × 0.10
Data collection		
Diffractometer	Nonius KappaCCD diffractometer	Nonius KappaCCD diffractometer
Absorption correction	Multi-scan *SADABS*	Multi-scan *SADABS*
T_{min}, T_{max}	0.67, 1	0.74, 1.00
No. of measured, independent and observed [*I* > 2*s*(*I*)] reflections	6016, 3314, 2812	6820, 3709, 2978
R_{int}	0.030	0.051
(sin θ/λ)$_{max}$ (Å^{-1})	0.650	0.649
Refinement		
R*[F^2 > 2*s*(F^2)], *wR*(F^2), *S	0.031, 0.074, 1.09	0.039, 0.087, 1.01
No. of reflections	3314	3709
No. of parameters	154	174
No. of restraints	0	0
H-atom treatment	Constrained	Constrained
(Δ/σ)$_{max}$	0.001	0.001
Δρ$_{max}$, Δρ$_{min}$ (e Å^{-3})	2.24, −1.45	1.95, −1.95
Absolute structure	-	-
Absolute structure parameter	-	-
Computer programs: Collect (Nonius BV, 1997-2000), *HKL SCALEPACK* (Otwinowski & Minor 1997), *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor 1997), Palatinus, L.; Chapuis, G. J. Appl. Cryst. 2007, 40, 786-790., *SHELXL2014* (Sheldrick, 2014), *ORTEP-3 for Windows* (Farrugia, 1997), *WinGX* publication routines (Farrugia, 1999).		

Crystal data		
Compound **CCDC number** **Chemical formula**	W{N(3,5-Me-C_6H_3)}Cl_4(THF) (**1.3**) 1518775 $C_{12}H_{17}Cl_4NOW$	W{N(2,4,6-Me-C_6H_2)}Cl_4(THF) (**1.4**) 1518769 $C_{13}H_{19}Cl_4NOW$
Mr	516.92	530.94
Crystal system, space group	Triclinic, *P*1	Triclinic, *P*1
Temperature (K)	150	150
***a, b, c* (Å)**	8.6354(1), 9.6261(2), 10.9204(2)	7.8367(1), 8.7690(2), 14.2277(3)
α, β, γ (°)	101.470(1), 95.240(1), 107.534(1)	78.940(1), 89.844(1), 63.883(1)
***V* (Å^3)**	837.11(3)	857.88(3)
Z	2	2
μ (mm^{-1})	7.53	7.35
Crystal size (mm)	0.20 × 0.15 × 0.10	0.40 × 0.20 × 0.02
Data collection		
Diffractometer	Nonius KappaCCD diffractometer	Nonius KappaCCD diffractometer
Absorption correction	Multi-scan *SADABS*	Multi-scan *DENZO/SCALEPACK* (Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.69, 1	0.744, 1.000
No. of measured, independent and observed [*I* > 2*s*(*I*)] reflections	7196, 3819, 3471	7214, 3936, 3594
R_{int}	0.025	0.028
(sin θ/λ)$_{max}$ (Å^{-1})	0.650	0.651
Refinement		
R*[F^2 > 2*s*(F^2)], *wR*(F^2), *S	0.028, 0.065, 1.13	0.028, 0.068, 1.08
No. of reflections	3819	3936
No. of parameters	175	184
No. of restraints	5	0
H-atom treatment	Constrained	Constrained
(Δ/σ)$_{max}$	0.001	0.001
Δρ_{max}, Δρ_{min} (e Å^{-3})	1.62, −1.41	1.71, −1.71
Absolute structure	-	-
Absolute structure parameter	-	-
Computer programs: Collect (Nonius BV, 1997-2000), *HKL SCALEPACK* (Otwinowski & Minor 1997), *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor 1997), Palatinus, L.; Chapuis, G. J. Appl. Cryst. 2007, 40, 786-790., *SHELXL2014* (Sheldrick, 2014), *ORTEP-3 for Windows* (Farrugia, 1997), *WinGX* publication routines (Farrugia, 1999).		

Crystal data		
Compound **CCDC number** **Chemical formula**	W{N(4-OMe-C_6H_4)}Cl_4(THF) (**1.5**) 1518774 $C_{11}H_{15}Cl_4NO_2W$	W{N(2,6-F-C_6H_3)}Cl_4(THF) (**1.6**) 1518772 $C_{10}H_{11}Cl_4F_2NOW$
Mr	518.89	524.85
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P1$
Temperature (K)	150	150
***a, b, c* (Å)**	13.2115(2), 8.0822(1), 15.7475(2)	8.1651(2), 9.4012(3), 9.9731(3)
α, β, γ (°)	90, 109.109(1), 90	87.462(2), 86.122(2), 79.773(2)
***V* (Å^3)**	1588.83(4)	751.26(4)
Z	4	2
μ (mm^{-1})	7.94	8.41
Crystal size (mm)	0.20 × 0.12 × 0.10	0.21 × 0.16 × 0.10
Data collection		
Diffractometer	Nonius KappaCCD diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer
Absorption correction	Multi-scan Multi-scan from symmetry-related measurements using *SORTAV* (Blessing 1995)	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.735, 1.000	0.555, 1.000
No. of measured, independent and observed [*I* > 2*s*(*I*)] reflections	7374, 3921, 3396	15868, 3447, 3325
R_{int}	0.027	0.040
(sin θ/λ)$_{max}$ (Å^{-1})	0.666	0.649
Refinement		
R*[F^2 > 2*s*(F^2)], *wR*(F^2), *S	0.029, 0.075, 1.10	0.016, 0.039, 1.00
No. of reflections	3921	3447
No. of parameters	173	172
No. of restraints	0	0
H-atom treatment	Constrained	Constrained
(Δ/σ)$_{max}$	0.001	0.001
Δρ_{max}, Δρ_{min} (e Å^{-3})	1.74, −1.67	0.61, −0.88
Absolute structure	-	-
Absolute structure parameter	-	-
Computer programs: Collect (Nonius BV, 1997-2000), *HKL SCALEPACK* (Otwinowski & Minor 1997), *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor 1997), Palatinus, L.; Chapuis, G. J. Appl. Cryst. 2007, 40, 786-790., *SHELXL2014* (Sheldrick, 2014), *CrysAlis PRO* (Agilent (2014). Agilent Technologies Ltd, Yarnton, Oxfordshire, England.), *ORTEP-3 for Windows* (Farrugia, 1997), *WinGX* publication routines (Farrugia, 1999).		

Crystal data		
Compound **CCDC number** **Chemical formula**	W{N(3,5-CF_3-C_6H_3)}Cl_4(THF) (**1.7**) 1518773 $C_{12}H_{11}Cl_4F_6NOW$	W{N(C_6H_5)}Me_3Cl (**2.1**) 1518777 $C_9H_{14}ClNW$
Mr	624.87	355.51
Crystal system, space group	Triclinic, *P*1	Monoclinic, $P2_1/m$
Temperature (K)	150	150
***a, b, c* (Å)**	8.9918(1), 10.3714(1), 10.9720(1)	6.3636(2), 7.2907(2), 11.9698(3)
α, β, γ (°)	63.427(1), 86.047(1), 89.359(1)	90, 93.495(2), 90
***V* (Å^3)**	912.74 (2)	554.31(3)
Z	2	2
μ (mm^{-1})	6.97	10.61
Crystal size (mm)	0.20 × 0.15 × 0.10	0.20 × 0.15 × 0.10
Data collection		
Diffractometer	Nonius KappaCCD diffractometer	Nonius KappaCCD diffractometer
Absorption correction	Multi-scan Multi-scan from symmetry-related measurements using *SORTAV* (Blessing 1995)	Multi-scan Multi-scan from symmetry-related measurements using *SORTAV* (Blessing 1995)
T_{min}, T_{max}	0.714, 1.000	0.695, 1.000
No. of measured, independent and observed [*I* > 2*s*(*I*)] reflections	7916, 4161, 3919	2527, 1367, 1208
R_{int}	0.019	0.045
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650	0.650
Refinement		
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, *S*	0.024, 0.058, 1.10	0.038, 0.094, 1.03
No. of reflections	4161	1367
No. of parameters	226	77
No. of restraints	0	0
H-atom treatment	Constrained	Constrained
$(\Delta/\sigma)_{max}$	0.001	<0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.58, −1.24	1.90, −2.13
Absolute structure	-	-
Absolute structure parameter	-	-
Computer programs: Collect (Nonius BV, 1997-2000), *HKL SCALEPACK* (Otwinowski & Minor 1997), *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor 1997), Palatinus, L.; Chapuis, G. J. Appl. Cryst. 2007, 40, 786-790., *SHELXL2014* (Sheldrick, 2014), *ORTEP-3 for Windows* (Farrugia, 1997), *WinGX* publication routines (Farrugia, 1999).		

Crystal data		
Compound **CCDC number** **Chemical formula**	W{N(2,6-Me-C_6H_3)}Me_3Cl (**2.2**) 1518776 $C_{11}H_{18}ClNW$	W{N(3,5-Me-C_6H_3)}Me_3Cl (**2.3**) 1543007 $C_{11}H_{18}ClNW$
Mr	383.56	383.56
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, *Pnma*
Temperature (K)	150	150
***a, b, c* (Å)**	10.4810(2), 10.8951(3), 12.1474(3)	21.1055(3), 7.2526(1), 17.4808(3)
α, β, γ (°)	90, 110.473(1), 90	90
***V* (Å^3)**	1299.51(5)	2675.78(7)
Z	4	8
μ (mm^{-1})	9.06	17.55
Crystal size (mm)	0.10 × 0.07 × 0.05	0.30 × 0.23 × 0.15
Data collection		
Diffractometer	Nonius KappaCCD diffractometer	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Multi-scan Multi-scan from symmetry-related measurements using *SORTAV* (Blessing 1995)	Multi-scan CrysAlis PRO 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.708, 1.000	0.106, 1.000
No. of measured, independent and observed [*I* > 2*s*(*I*)] reflections	5749, 2964, 2473	8777, 2949, 2795
R_{int}	0.027	0.054
(sin θ/λ)$_{max}$ (Å^{-1})	0.650	0.625
Refinement		
R*[F^2 > 2*s*(F^2)], *wR*(F^2), *S	0.032, 0.079, 1.06	0.043, 0.122, 1.10
No. of reflections	2964	2949
No. of parameters	132	158
No. of restraints	0	0
H-atom treatment	Constrained	Constrained
(Δ/σ)$_{max}$	0.001	0.001
Δρ_{max}, Δρ_{min} (e Å^{-3})	2.28, −1.69	2.52, −1.75
Absolute structure	-	-
Absolute structure parameter	-	-
Computer programs: Collect (Nonius BV, 1997-2000), *HKL SCALEPACK* (Otwinowski & Minor 1997), *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor 1997), Palatinus, L.; Chapuis, G. J. Appl. Cryst. 2007, 40, 786-790., *SHELXL2014* (Sheldrick, 2014), *CrysAlis PRO* (Agilent (2014). Agilent Technologies Ltd, Yarnton, Oxfordshire, England.), *ORTEP-3 for Windows* (Farrugia, 1997), *WinGX* publication routines (Farrugia, 1999).		

Crystal data		
Compound **CCDC number** **Chemical formula**	W{N(4-OMe-C_6H_4)}Me_3Cl (**2.5**) 1518779 $C_{10}H_{16}ClNOW$	W{N(2,6-F-C_6H_3)}Me_3Cl (**2.6**) 1518778 $C_9H_{12}ClF_2NW$
Mr	385.54	391.50
Crystal system, space group	Monoclinic, $P2_1$	Triclinic, $P\bar{1}$
Temperature (K)	150	150
***a, b, c* (Å)**	6.0476(3), 7.3129(3), 14.2223(6)	7.3092(1), 7.5096(1), 11.8873(2)
α, β, γ (°)	90, 97.885(4), 90	90.124(1), 95.770(1), 118.542(1)
***V* (Å^3)**	623.04(5)	569.34(2)
Z	2	2
μ (mm^{-1})	18.92	10.37
Crystal size (mm)	0.06 × 0.05 × 0.04	0.15 × 0.12 × 0.10
Data collection		
Diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer	Nonius KappaCCD diffractometer
Absorption correction	Multi-scan *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan Multi-scan from symmetry-related measurements using *SORTAV* (Blessing 1995)
T_{min}, T_{max}	0.736, 1.000	0.728, 1.000
No. of measured, independent and observed [*I* > 2*s*(*I*)] reflections	3247, 3247, 3164	4939, 2615, 2426
R_{int}	-	0.036
(sin θ/λ)$_{max}$ (Å^{-1})	0.629	0.651
Refinement		
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.039, 0.108, 1.10	0.031, 0.080, 1.04
No. of reflections	3247	2615
No. of parameters	119	130
No. of restraints	5	0
H-atom treatment	Constrained	Constrained
(Δ/σ)$_{max}$	0.001	<0.001
Δρ_{max}, Δρ_{min} (e Å^{-3})	1.39, −1.65	2.13, −3.00
Absolute structure	Classical Flack method preferred over Parsons because s.u. lower.	-
Absolute structure parameter	0.56(3)	-
Computer programs: Collect (Nonius BV, 1997-2000), *HKL SCALEPACK* (Otwinowski & Minor 1997), *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor 1997), Palatinus, L.; Chapuis, G. J. Appl. Cryst. 2007, 40, 786-790., *SHELXL2014* (Sheldrick, 2014), *CrysAlis PRO* (Agilent (2014). Agilent Technologies Ltd, Yarnton, Oxfordshire, England.), *ORTEP-3 for Windows* (Farrugia, 1997), *WinGX* publication routines (Farrugia, 1999).		

Table S2. Comparison of pKa values for the parent anilines,[1,2] imido ligand volumes (Å^3)[3] and steric parameters of the imido ligands (Å).

Complex	R	pK_a[1,2]	Ligand volume[3]	Steric parameters	
				x	y
B	4-Me-C_6H_4[4]	31.7	155.78	4.287	1.763
C[a]	4-I-C_6H_4[5]	29.1[b]	156.57	3.983	2.779
1.a	2,6-^{i}Pr-C_6H_3[6]	-	273.60	8.481	4.090
1.1	C_6H_5	30.6	123.52	4.062	1.394
1.2	2,6-Me-C_6H_3	-	173.71	6.540	1.600
1.3	3,5-Me-C_6H_3	31.0[d]	177.30	6.116	1.601
1.4	2,4,6-Me-C_6H_2	-	198.03	6.541	1.566
1.5	4-OMe-C_6H_4	32.5	161.97	4.070	1.601
1.6	2,6-F-C_6H_3	24.8[c]	128.85	4.679	1.384
1.7	3,5-CF_3-C_6H_3	25.75	189.50	7.018	2.130

[a] Coordinating solvent NCMe. [b] 4-Br aniline. [c] 2,6-Cl aniline. [d] 3-Me aniline.

2. Solid Angle calculations and spacefilled models

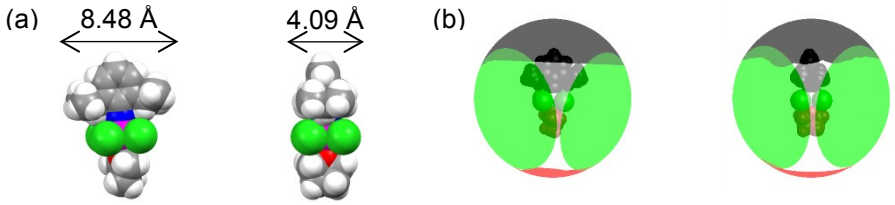

Figure S1. Spacefilled molecular structure of W{N(2,6-^{i}Pr-C_6H_3)}Cl_4(THF) (**1.a**) showing the imido group from the front (left) and side on (right). (b) Solid-G^3 calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and THF (red) from the front of the imido group (left) and side on (right).

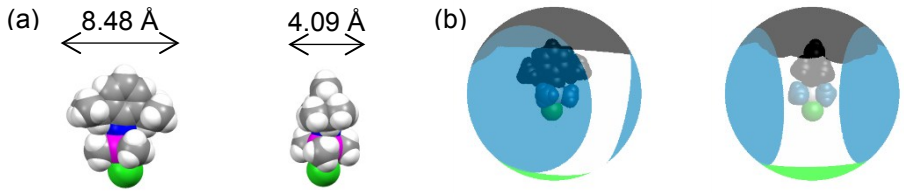

Figure S2. (a) Spacefilled molecular structure of W{N(2,6-^{i}Pr-C_6H_3)}Me_3Cl (**2.a**) showing the imido group from the front (left) and side on (right). (b) Solid-G^3 calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and methyl groups (blue) from the front of the imido group (left) and side on (right).

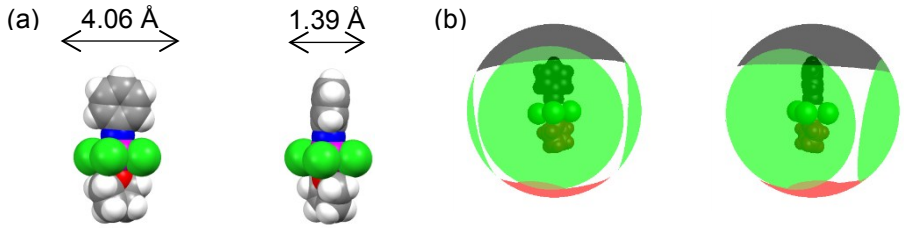

Figure S3. (a) Spacefilled molecular structure of W{N(C_6H_5)}Cl_4(THF) (**1.1**) showing the imido group from the front (left) and side on (right). (b) Solid-G^3 calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and THF (red) from the front of the imido group (left) and side on (right).

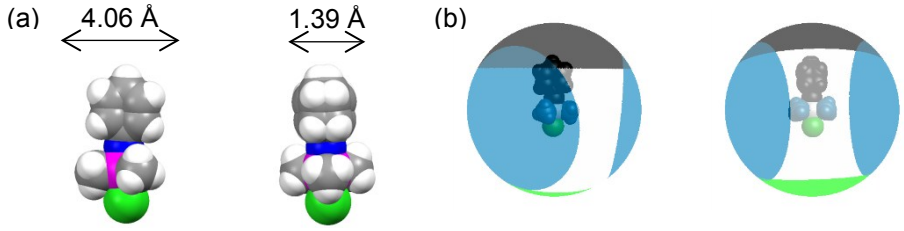

Figure S4. (a) Spacefilled molecular structure of W{N(C_6H_5)}Me_3Cl (**2.1**) showing the imido group from the front (left) and side on (right). (b) Solid-G^3 calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and methyl groups (blue) from the front of the imido group (left) and side on (right).

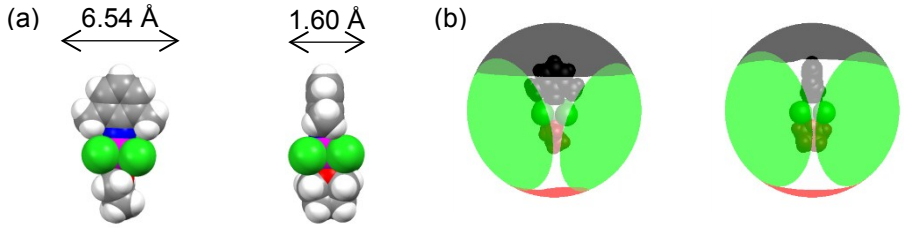

Figure S5. (a) Spacefilled molecular structure of W{N(2,6-Me-C_6H_3)}Cl_4(THF) (**1.2**) showing the imido group from the front (left) and side on (right). (b) Solid-G^3 calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and THF (red) from the front of the imido group (left) and side on (right).

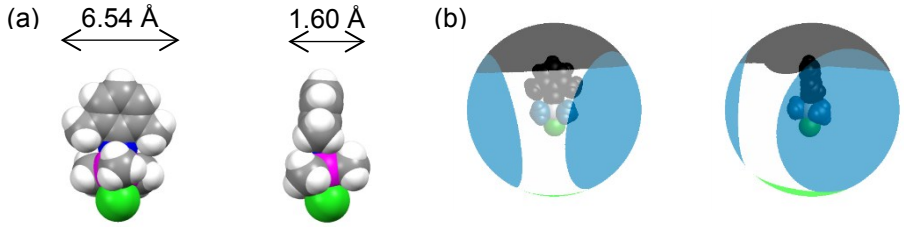

Figure S6. (a) Spacefilled molecular structure of W{N(2,6-Me-C_6H_3)}Me_3Cl (**2.2**) showing the imido group from the front (left) and side on (right). (b) Solid-G^3 calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and methyl groups (blue) from the front of the imido group (left) and side on (right).

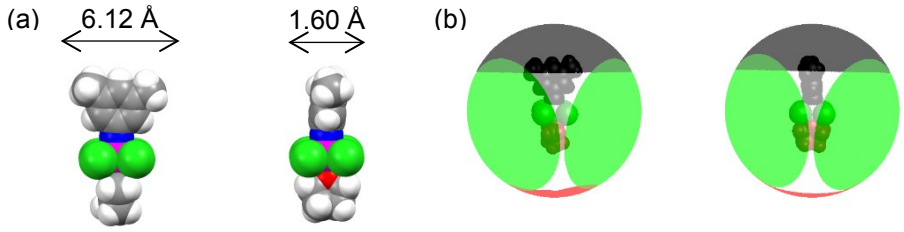

Figure S7. (a) Spacefilled molecular structure of W{N(3,5-Me-C_6H_3)}Cl_4(THF) (**1.3**) showing the imido group from the front (left) and side on (right). (b) Solid-G^3 calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and THF (red) from the front of the imido group (left) and side on (right).

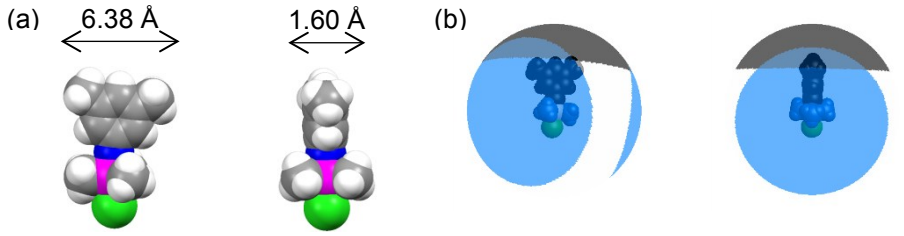

Figure S8. (a) Spacefilled molecular structure of W{N(3,5-Me-C_6H_3)}Me_3Cl (**2.3**) showing the imido group from the front (left) and side on (right). (b) Solid-G calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and methyl groups (blue) from the front of the imido group (left) and side on (right).

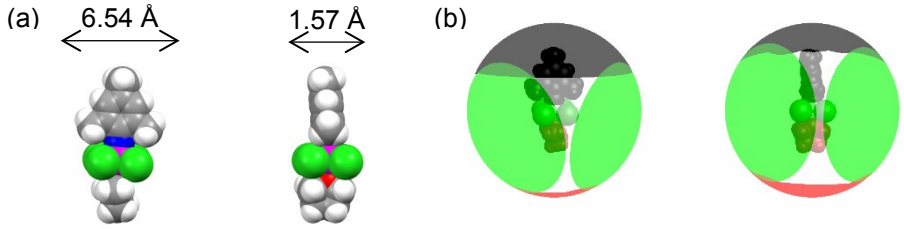

Figure S9. (a) Spacefilled molecular structure of W{N(2,4,6-Me-C_6H_2)}Cl_4(THF) (**1.4**) showing the imido group from the front (left) and side on (right). (b) Solid-G^3 calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and THF (red) from the front of the imido group (left) and side on (right).

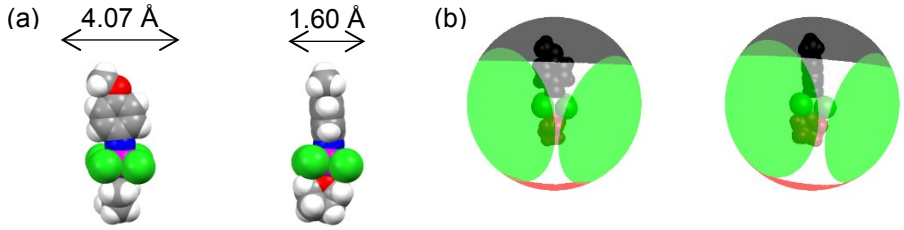

Figure S10. (a) Spacefilled molecular structure of W{N(4-OMe-C_6H_4)}Cl_4(THF) (**1.5**) showing the imido group from the front (left) and side on (right). (b) Solid-G^3 calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and THF (red) from the front of the imido group (left) and side on (right).

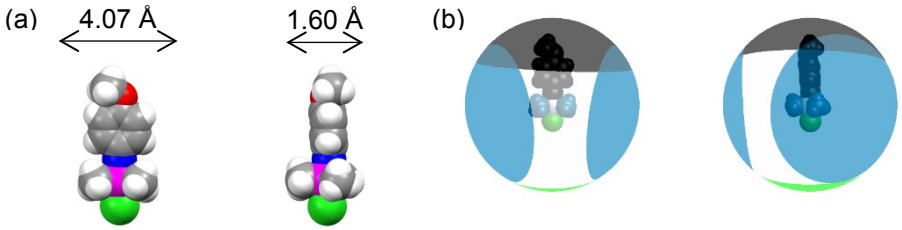

Figure S11. (a) Spacefilled molecular structure of W{N(4-OMe-C_6H_4)}Me_3Cl (**2.5**) showing the imido group from the front (left) and side on (right). (b) Solid-G^3 calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and methyl groups (blue) from the front of the imido group (left) and side on (right).

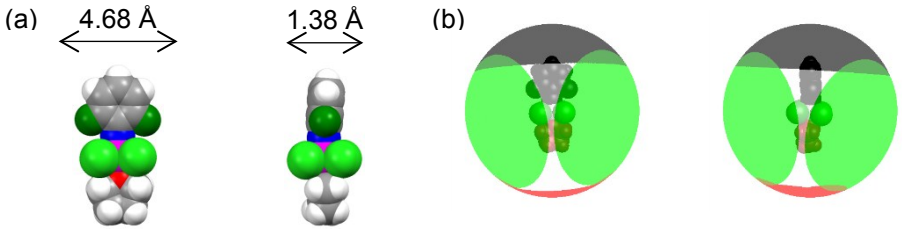

Figure S12. (a) Spacefilled molecular structure of W{N(2,6-F-C_6H_3)}Cl_4(THF) (**1.6**) showing the imido group from the front (left) and side on (right). (b) Solid-G^3 calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and THF (red) from the front of the imido group (left) and side on (right).

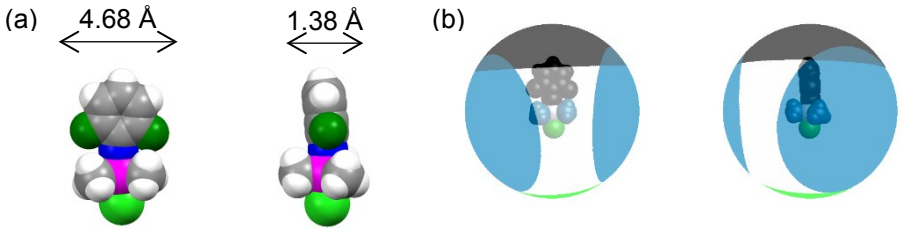

Figure S13. (a) Spacefilled molecular structure of W{N(2,6-F-C_6H_3)}Me_3Cl (**2.6**) showing the imido group from the front (left) and side on (right). (b) Solid-G^3 calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and methyl groups (blue) from the front of the imido group (left) and side on (right).

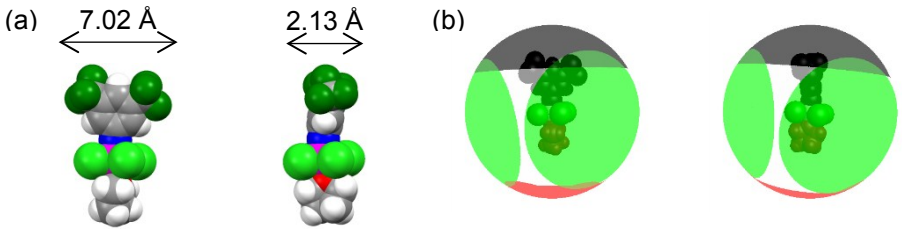

Figure S14. (a) Spacefilled molecular structure of W{N(3,5-CF_3-C_6H_3)}Cl_4(THF) (**1.7**) showing the imido group from the front (left) and side on (right). (b) Solid-G^3 calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and THF (red) from the front of the imido group (left) and side on (right).

3. Characterisation of the homogeneous catalysts

NMR spectroscopy

$W(NR)Cl_4(THF)$ complexes

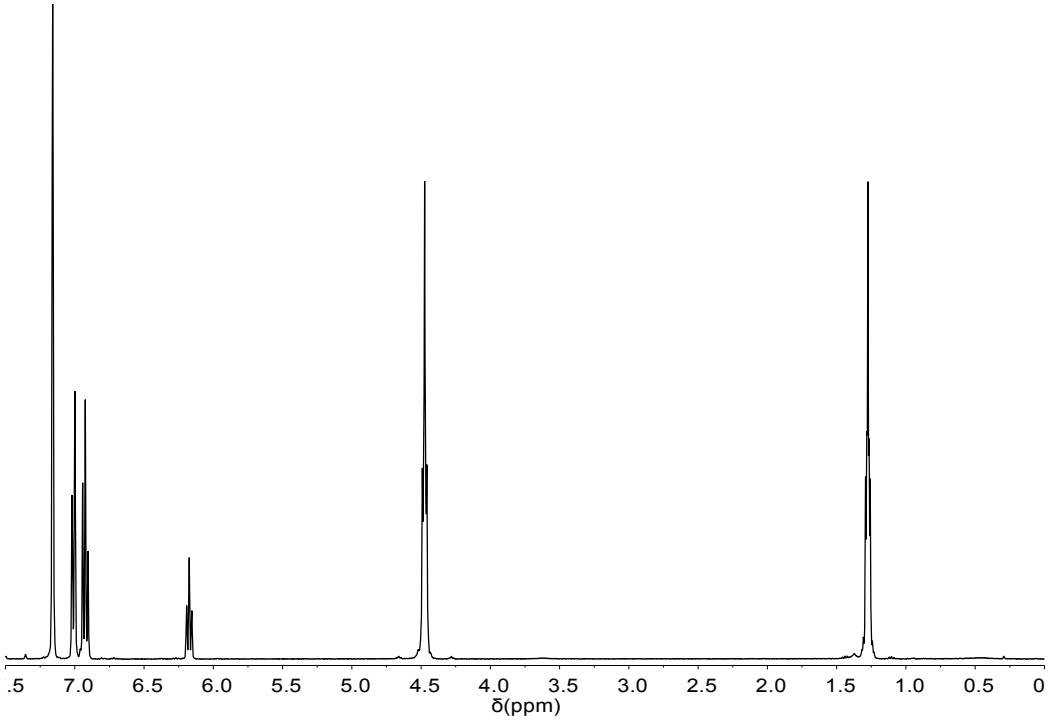

Figure S16. ^{1}H NMR spectrum of **1.1** in d_6-benzene (7.16 ppm).

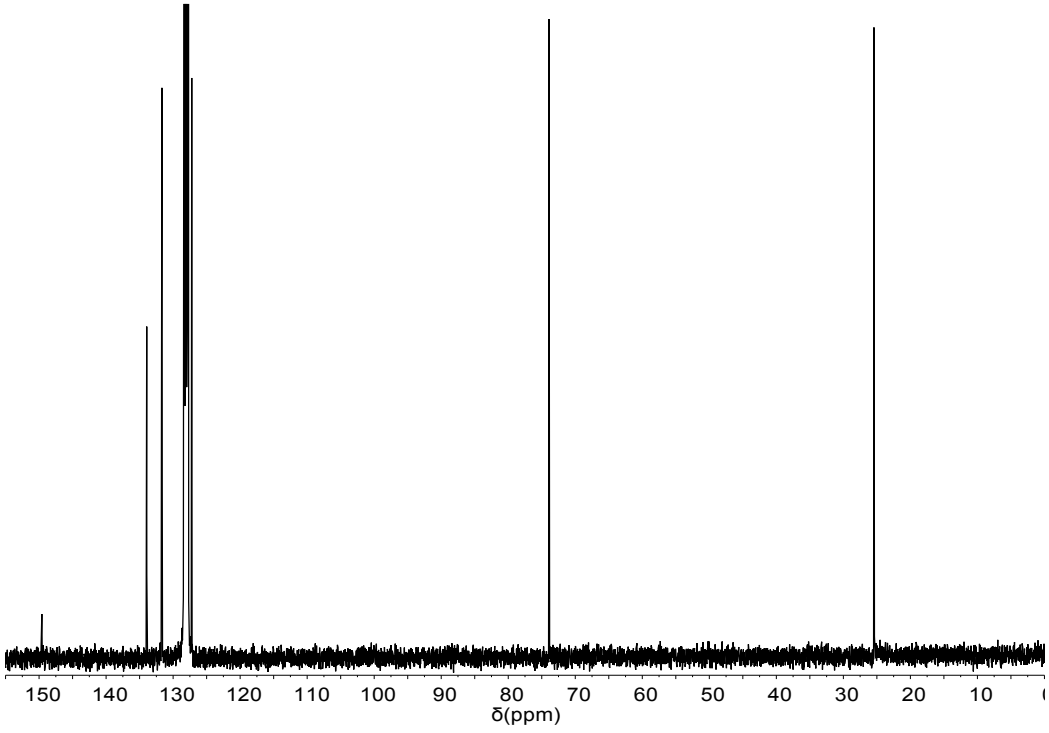

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **1.1** in d_6-benzene (128.06 ppm).

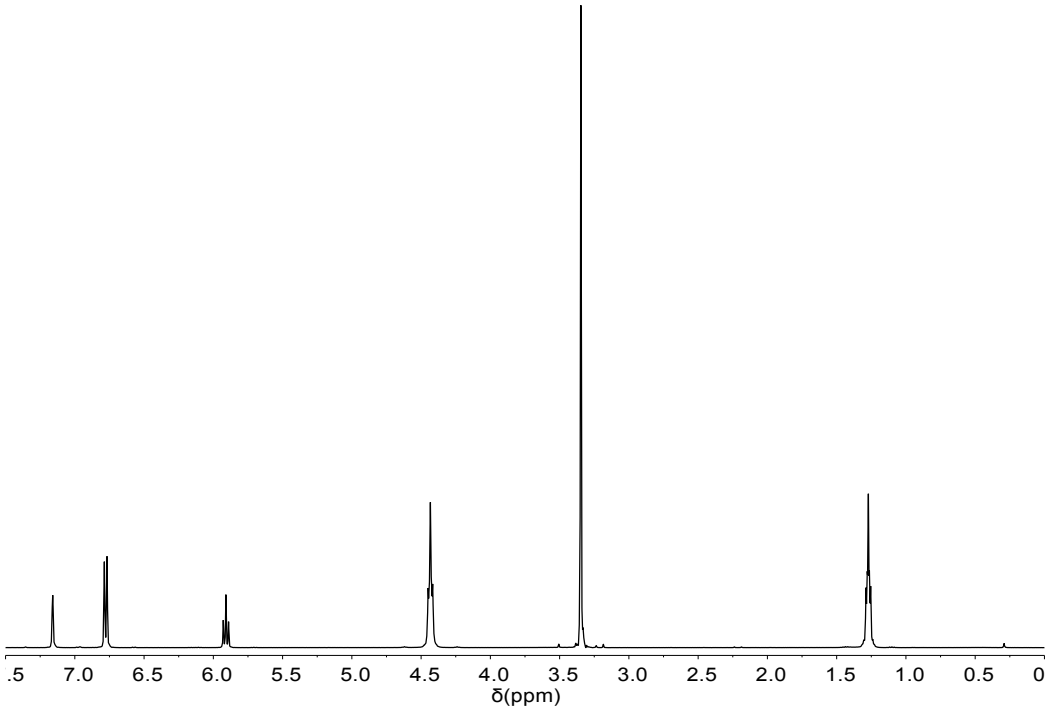

Figure S18. ^{1}H NMR spectrum of **1.2** in d_6-benzene (7.16 ppm).

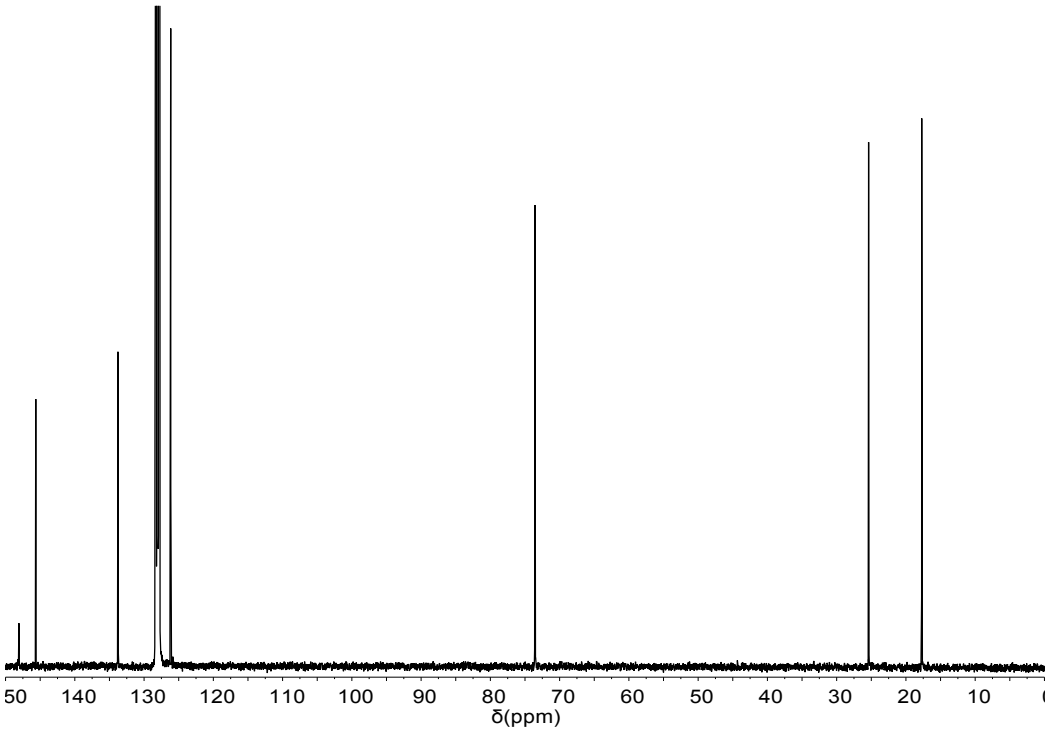

Figure S19. ^{13}C{^{1}H} NMR spectrum of **1.2** in d_6-benzene (128.06 ppm).

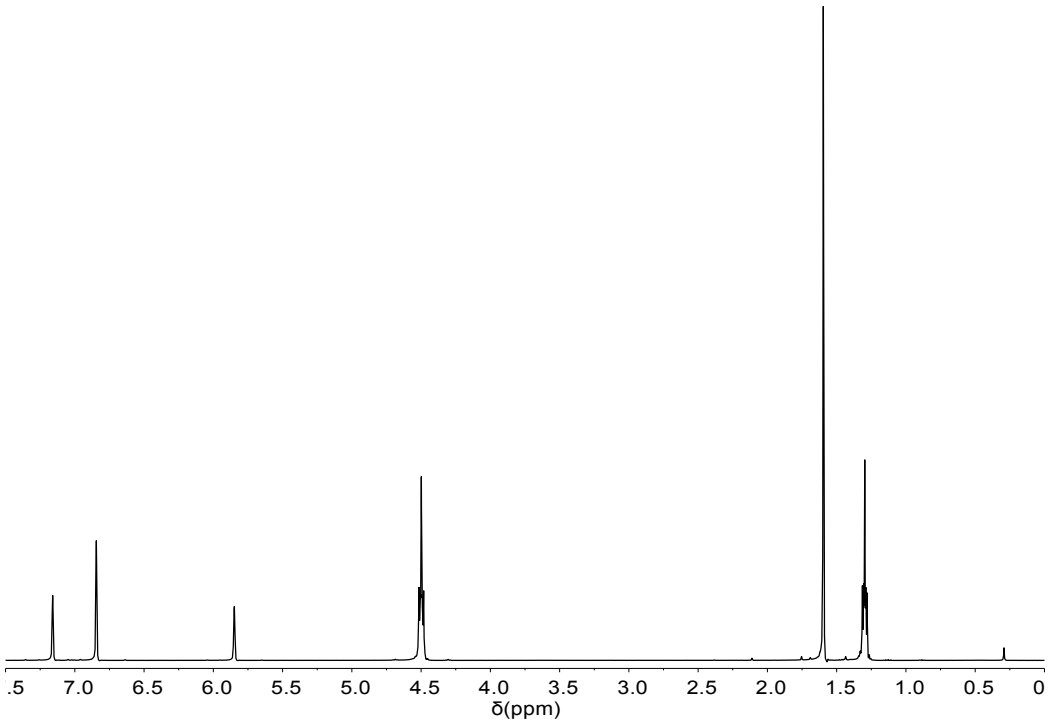

Figure S20. ^{1}H NMR spectrum of **1.3** in d_6-benzene (7.16 ppm).

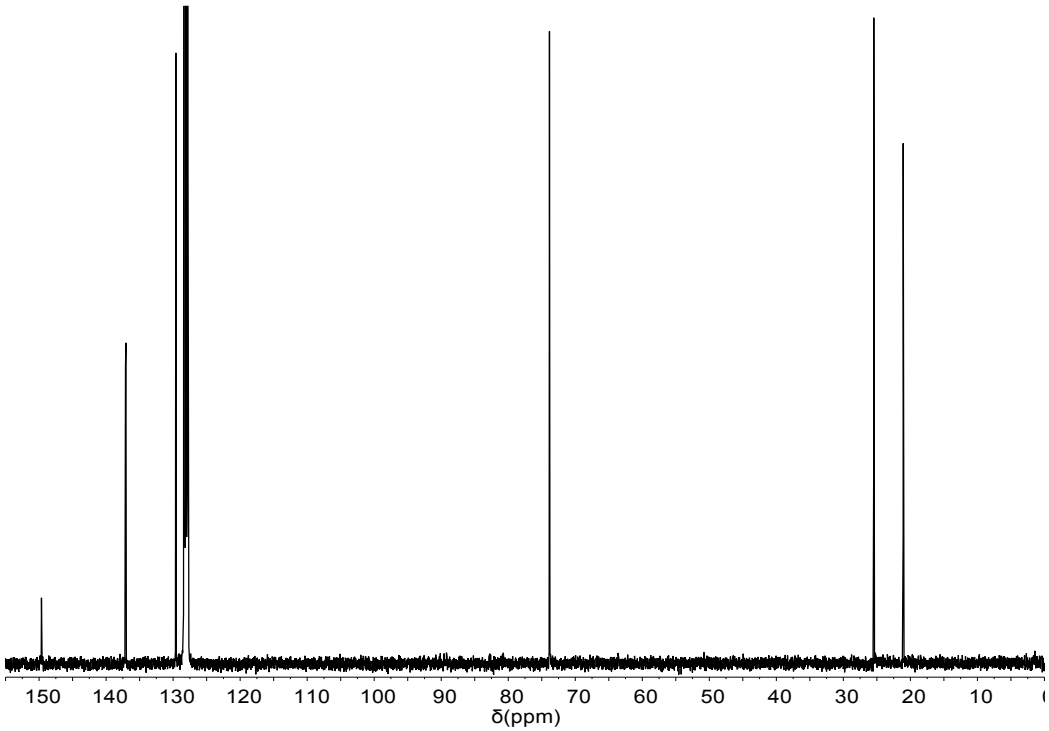

Figure S21. ^{13}C{^{1}H} NMR spectrum of **1.3** in d_6-benzene (128.06 ppm).

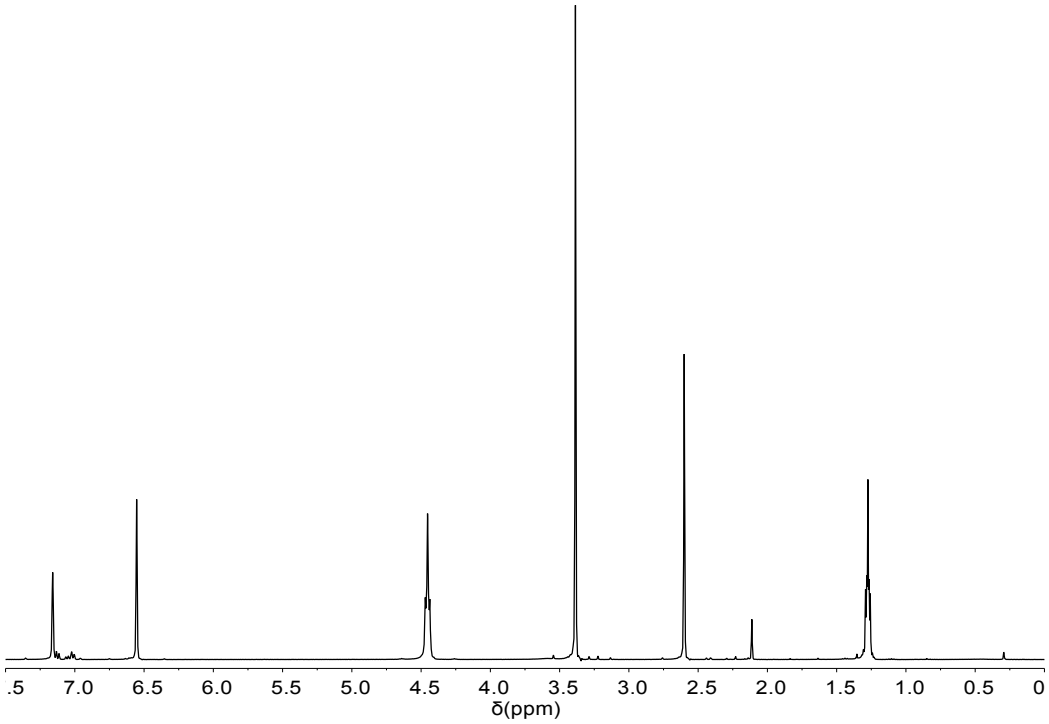

Figure S22. ^{1}H NMR spectrum of **1.4** in d_6-benzene (7.16 ppm).

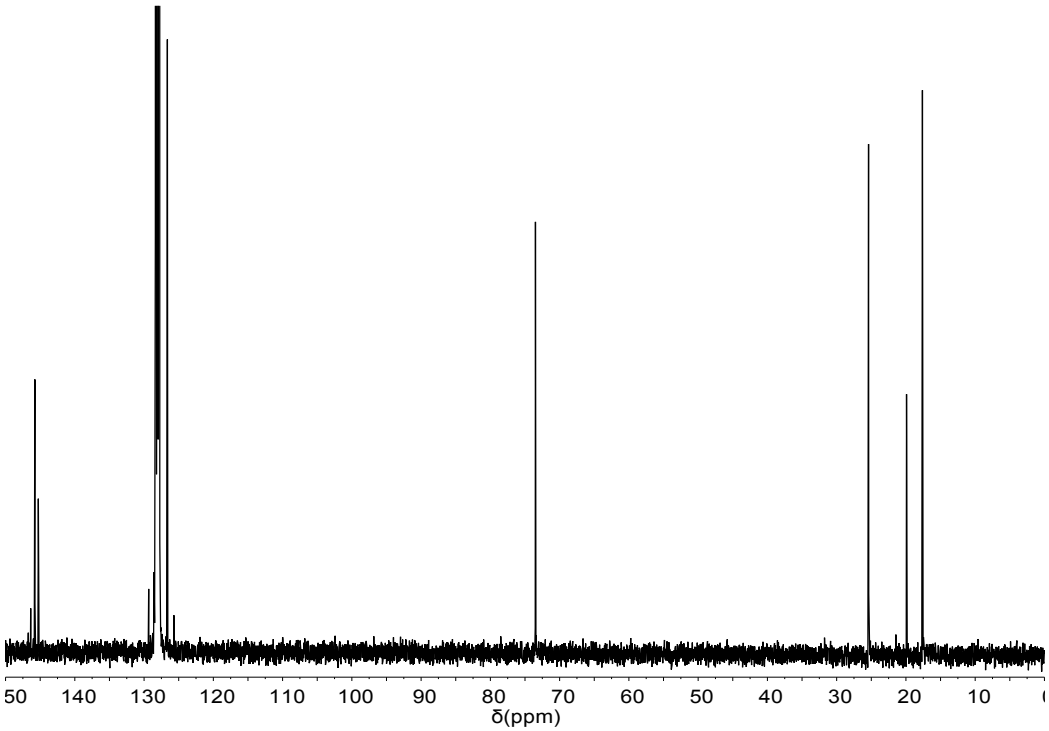

Figure S23. ^{13}C{^{1}H} NMR spectrum of **1.4** in d_6-benzene (128.06 ppm).

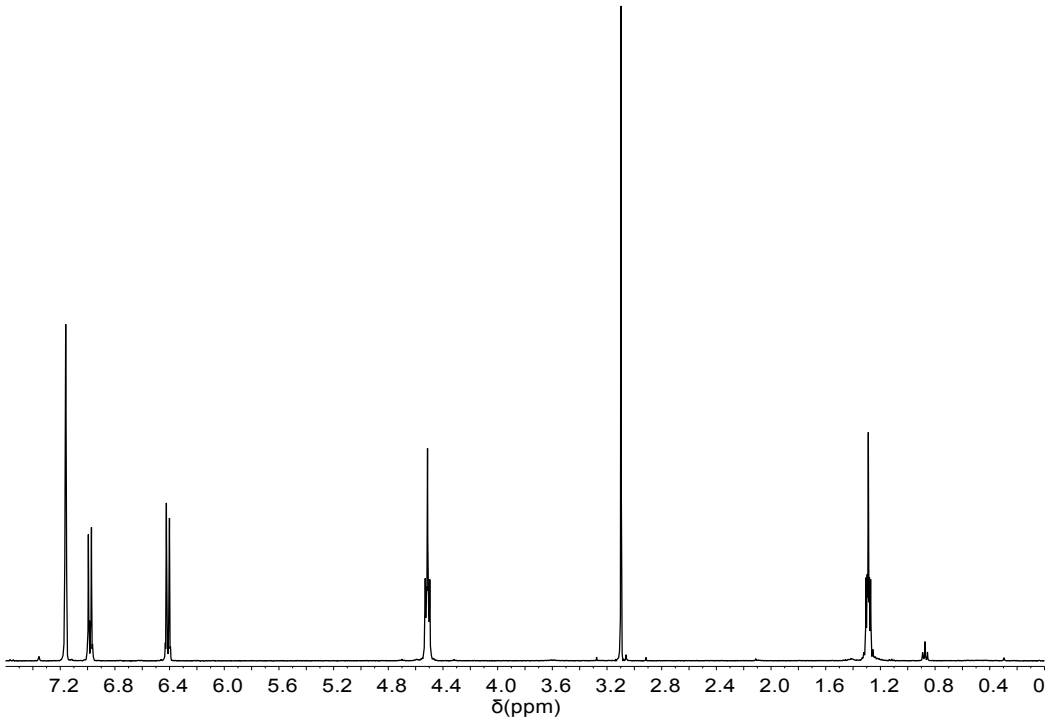

Figure S24. ^{1}H NMR spectrum of **1.5** in d_6-benzene (7.16 ppm).

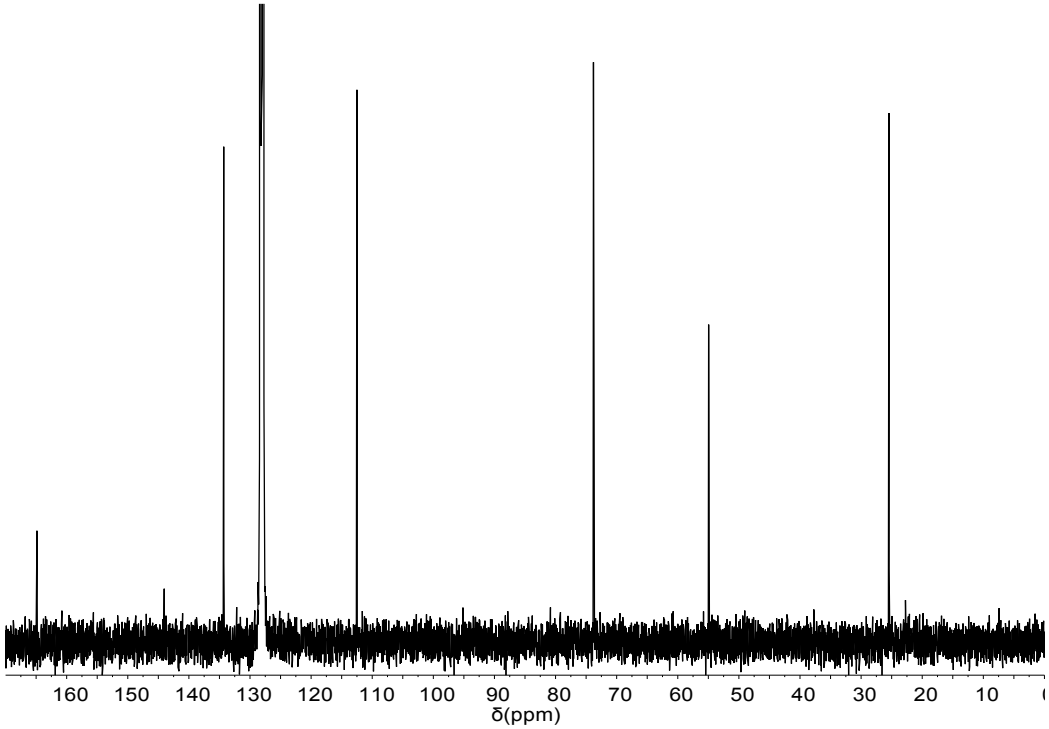

Figure S25. ^{13}C{^{1}H} NMR spectrum of **1.5** in d_6-benzene (128.06 ppm).

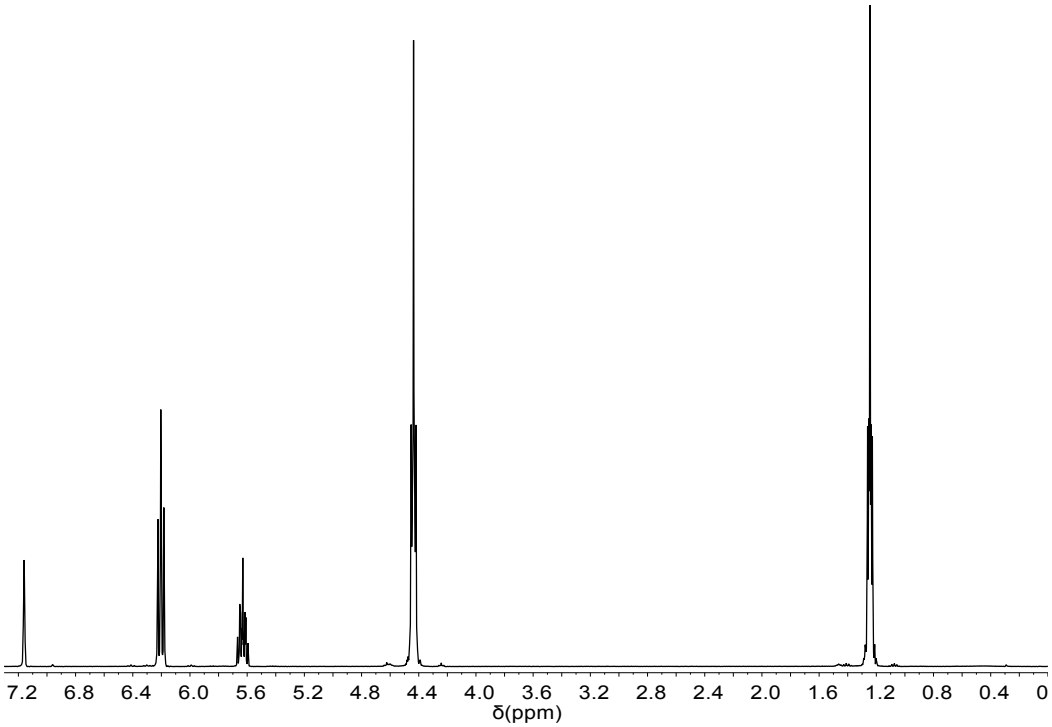

Figure S26. ^{1}H NMR spectrum of **1.6** in d_6-benzene (7.16 ppm).

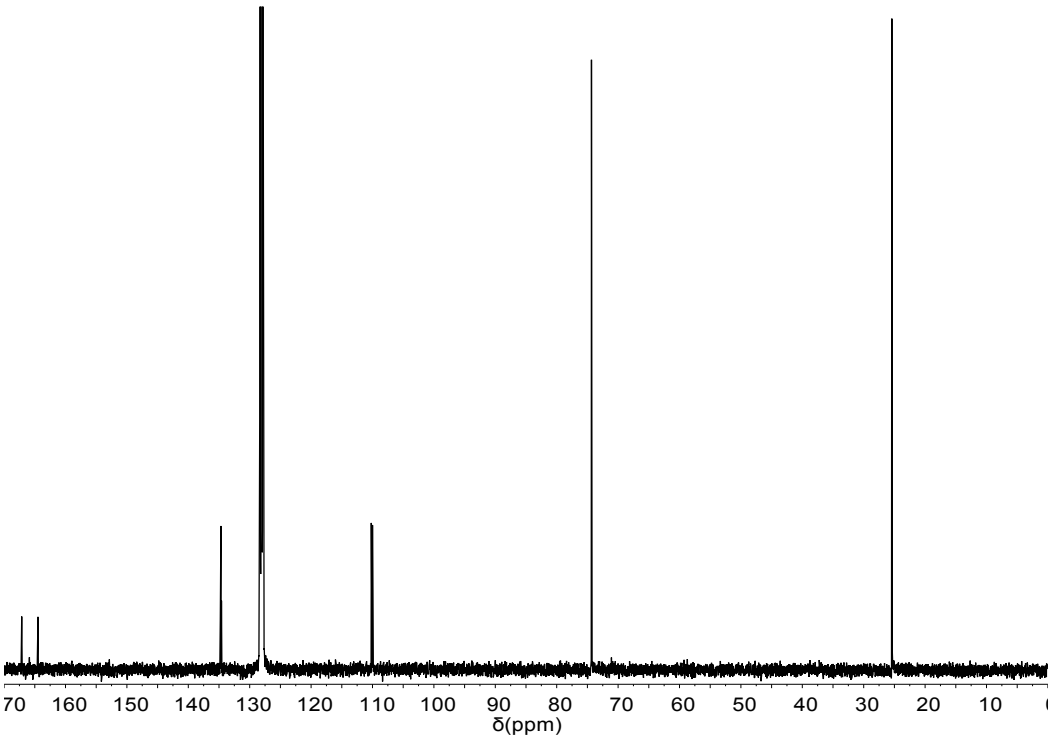

Figure S27. ^{13}C{^{1}H} NMR spectrum of **1.6** in d_6-benzene (128.06 ppm).

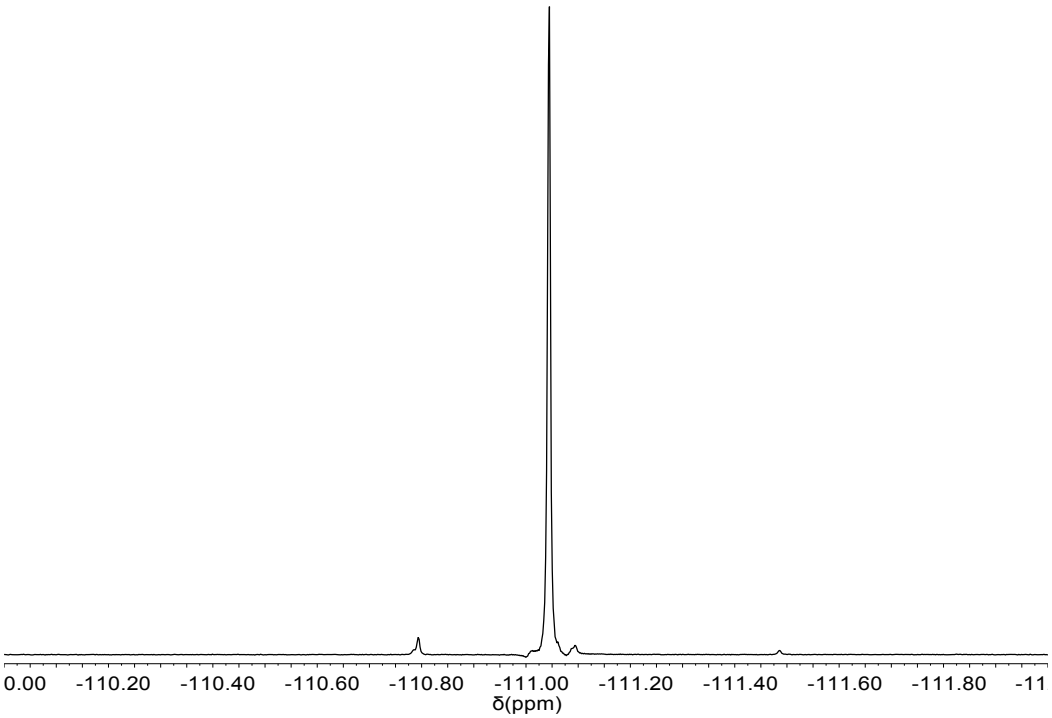

Figure S28. $^{19}F\{^{1}H\}$ NMR spectra of **1.6** in d_6-benzene.

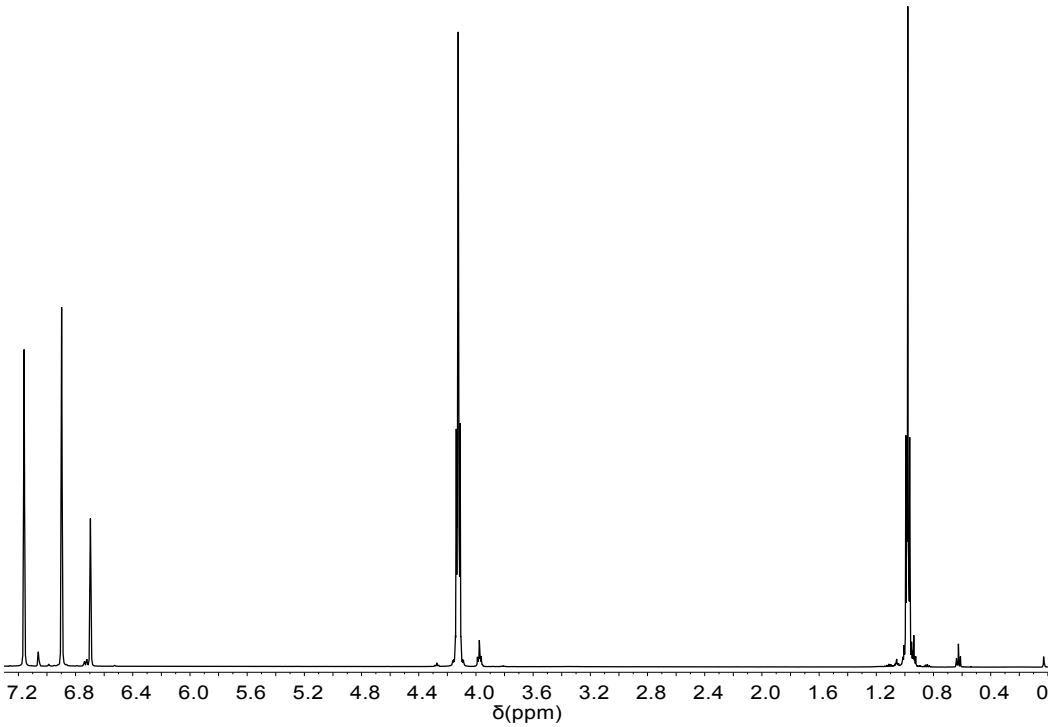

Figure S29. ^{1}H NMR spectrum of **1.7** in d_6-benzene (7.16 ppm).

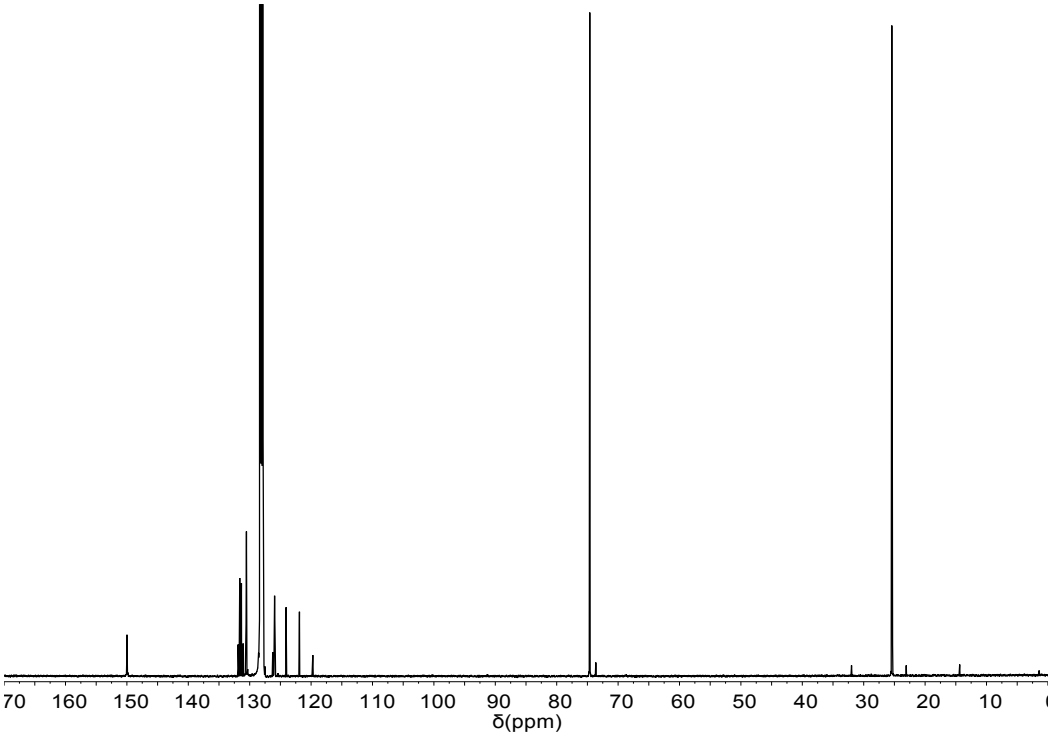

Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of **1.7** in d_6-benzene (128.06 ppm).

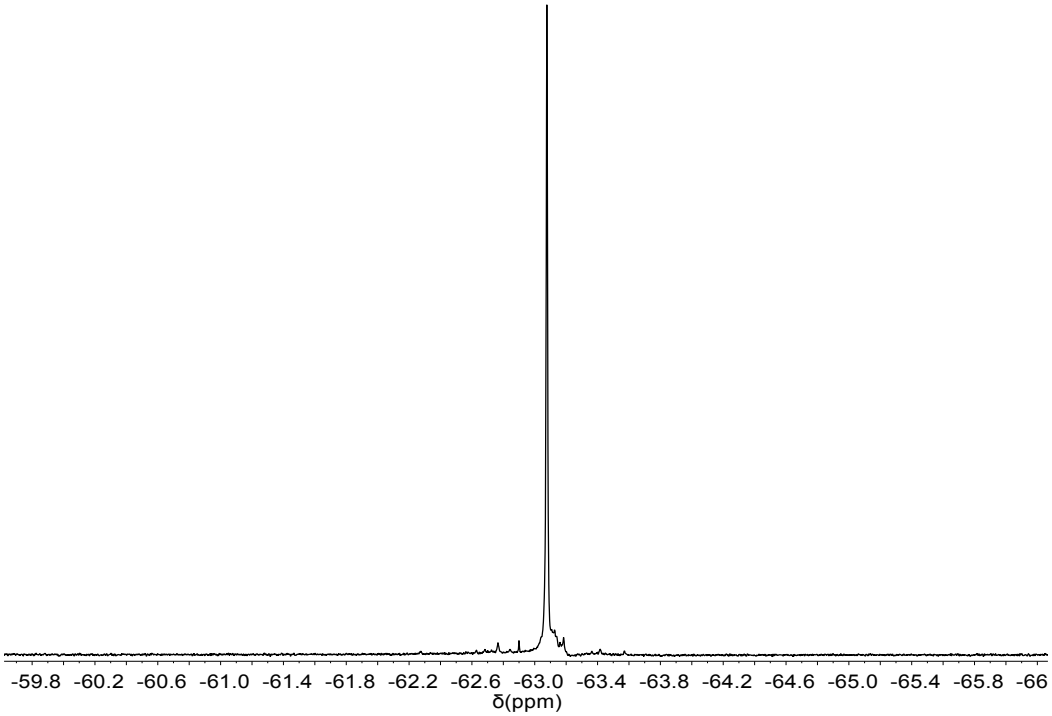

Figure S31. $^{19}F\{^{1}H\}$ NMR spectra of **1.7** in d_6-benzene.

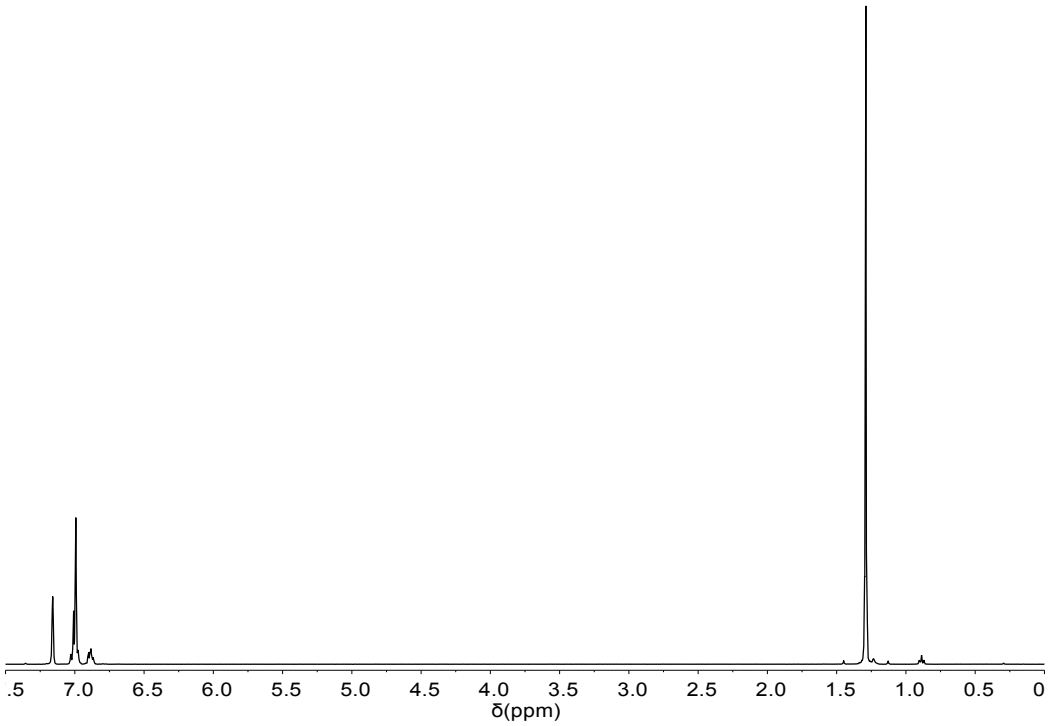

Figure S32. ^{1}H NMR spectrum of **2.1** in d_6-benzene (7.16 ppm).

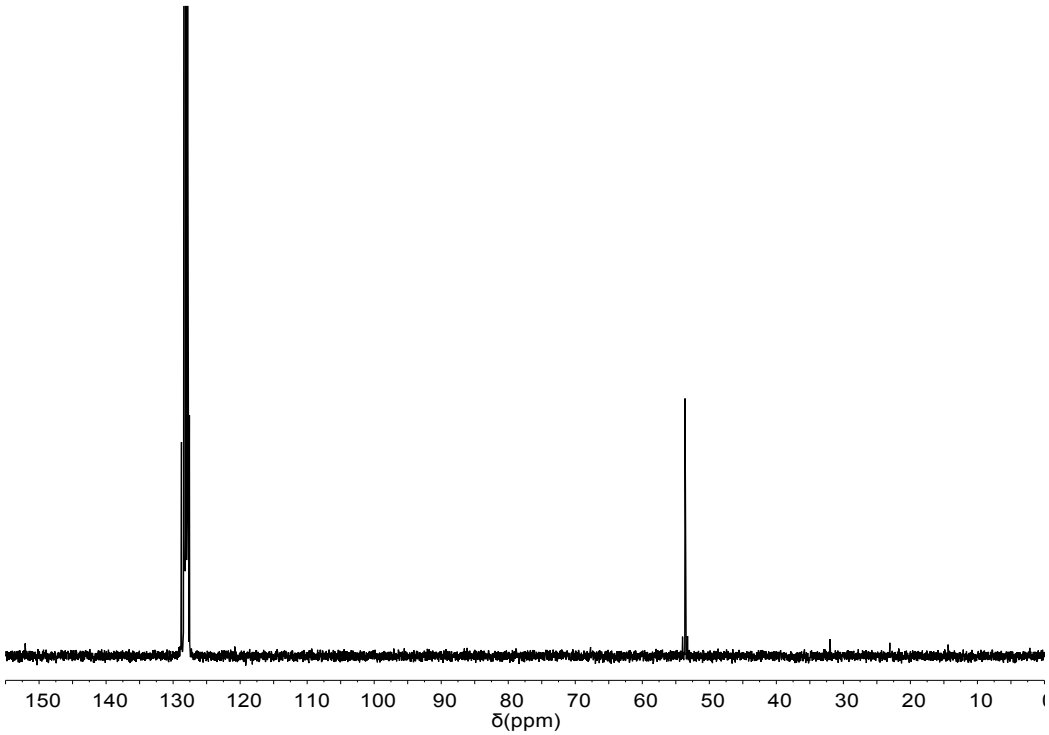

Figure S33. ^{13}C{^{1}H} NMR spectrum of **2.1** in d_6-benzene (128.06 ppm).

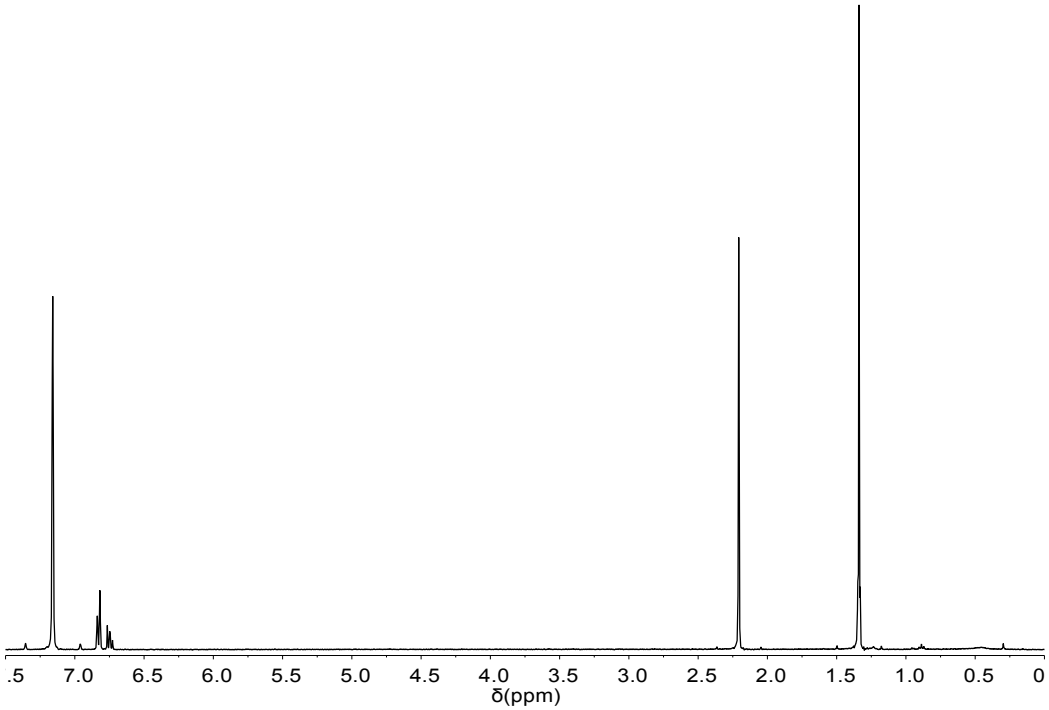

Figure S34. ^{1}H NMR spectrum of **2.2** in d_6-benzene (7.16 ppm).

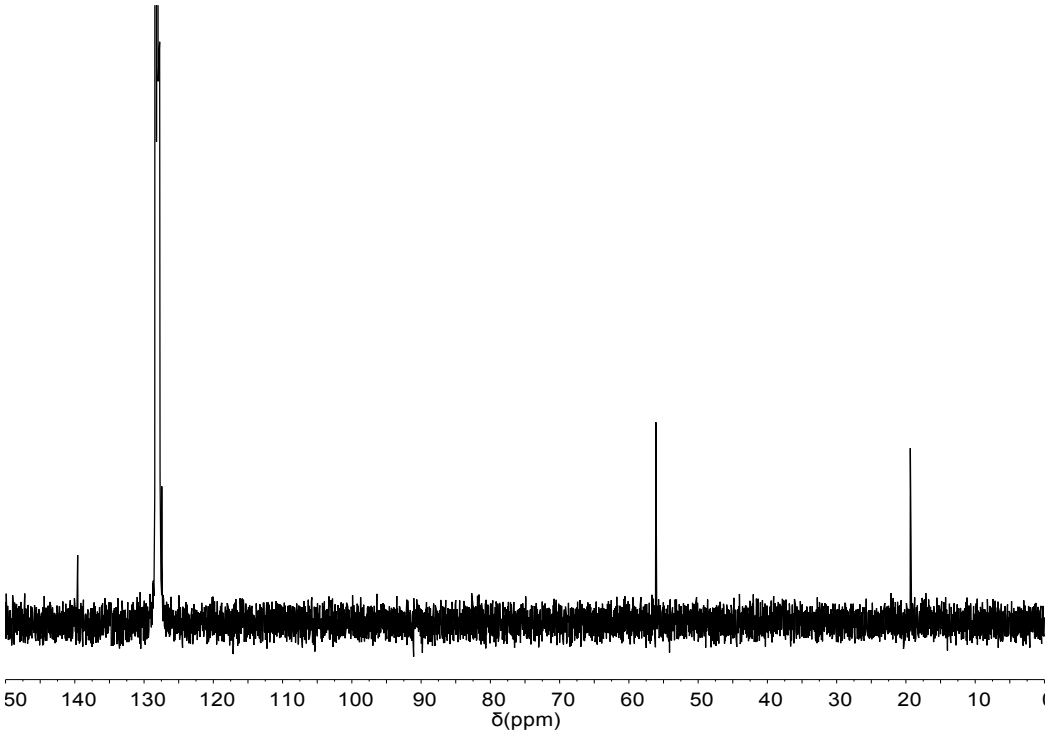

Figure S35. ^{13}C{^{1}H} NMR spectrum of **2.2** in d_6-benzene (128.06 ppm).

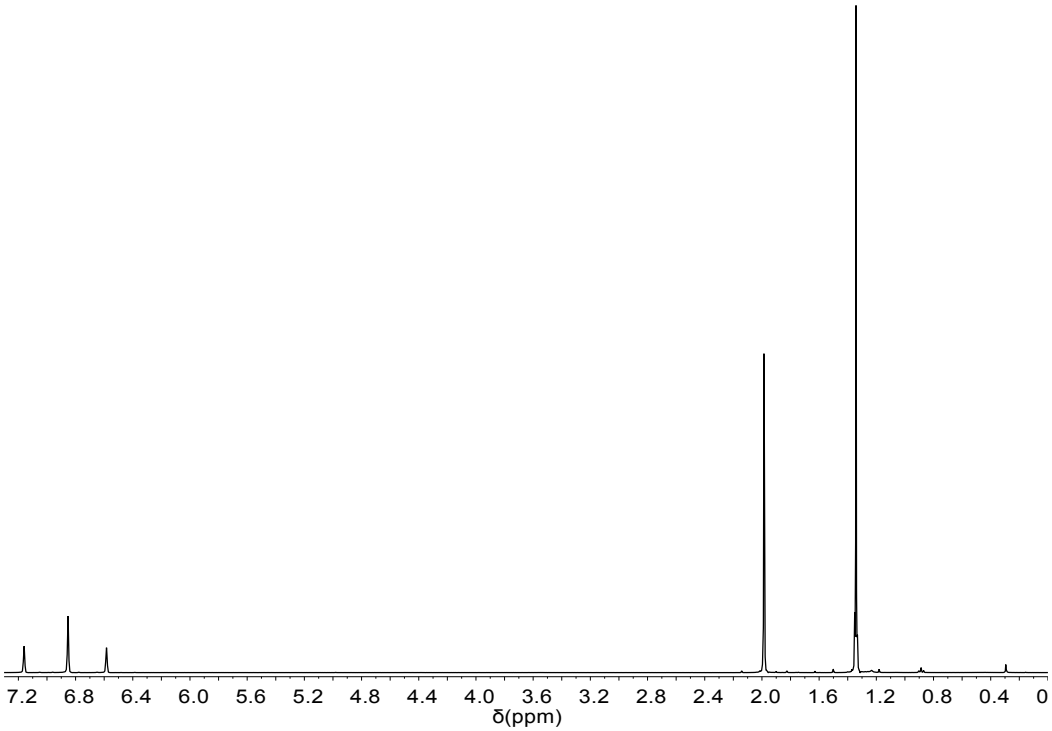

Figure S36. ^{1}H NMR spectrum of **2.3** in d_6-benzene (7.16 ppm).

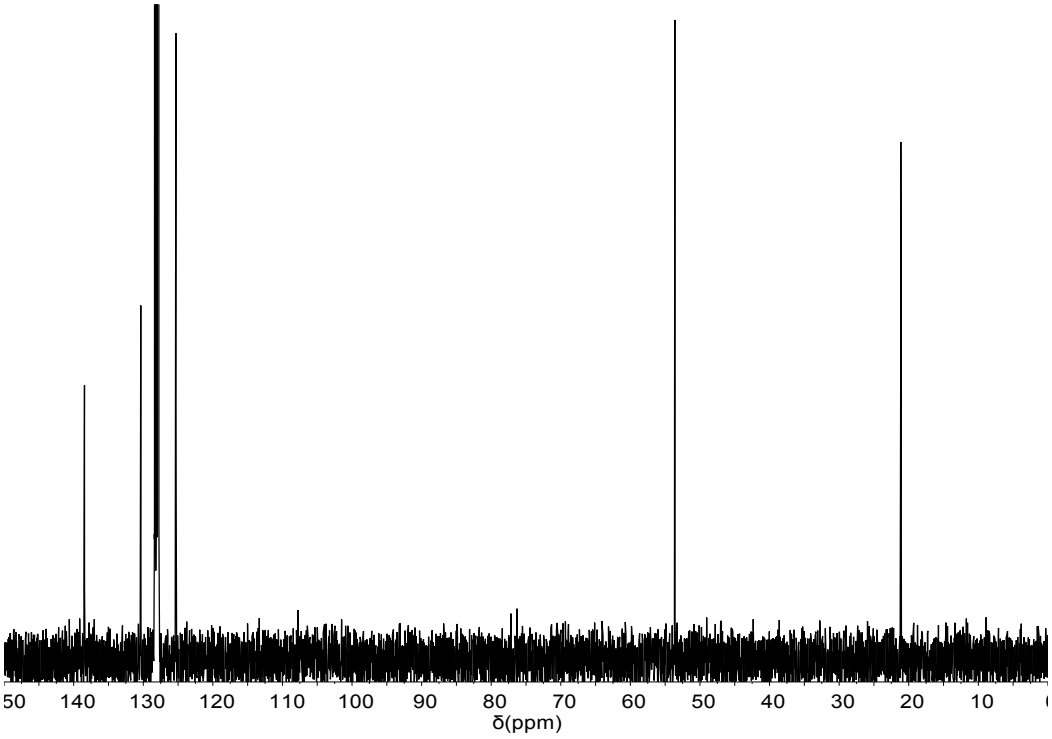

Figure S37. ^{13}C{^{1}H} NMR spectrum of **2.3** in d_6-benzene (128.06 ppm).

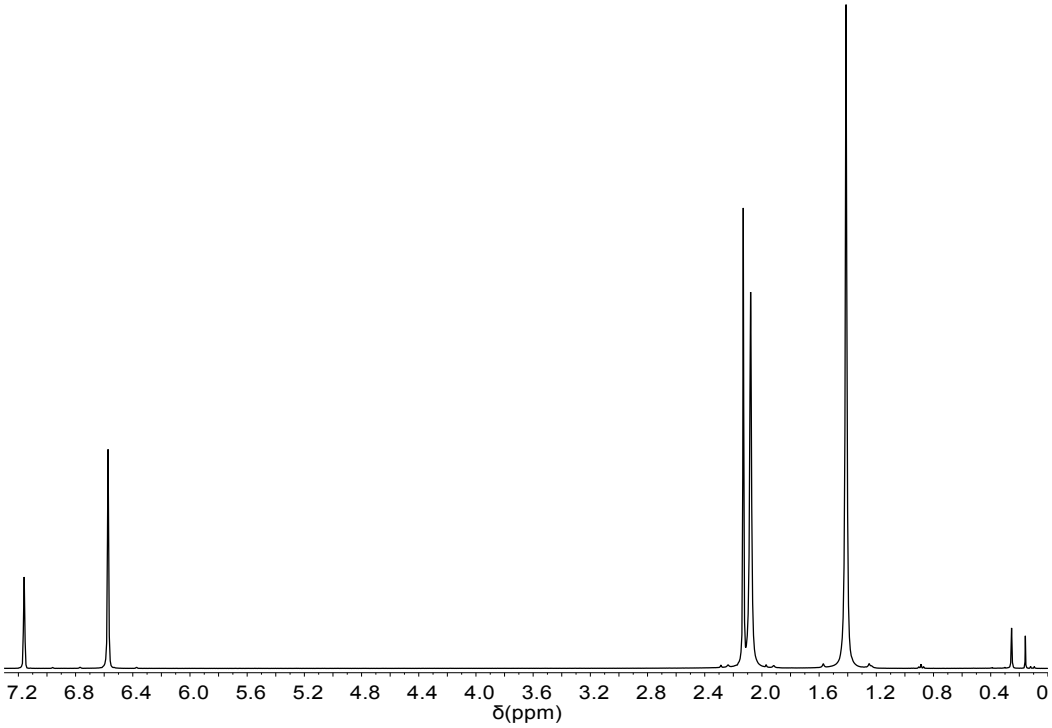

Figure S38. ^{1}H NMR spectrum of **2.4** in d_6-benzene (7.16 ppm).

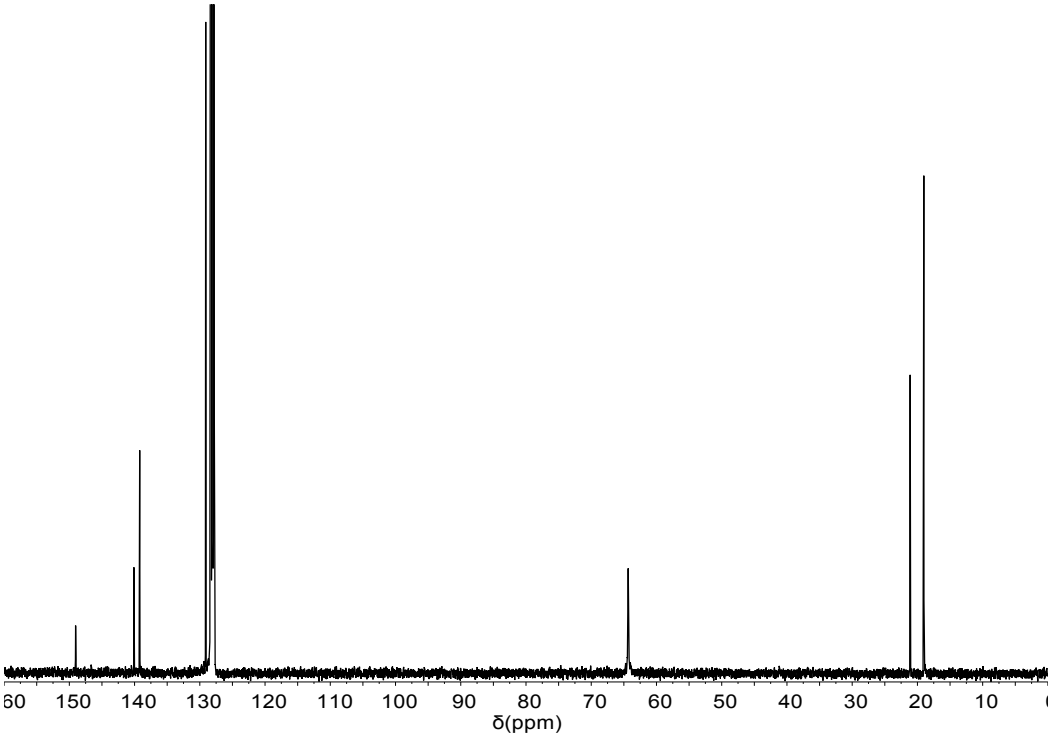

Figure S39. ^{13}C{^{1}H} NMR spectrum of **2.4** in d_6-benzene (128.06 ppm).

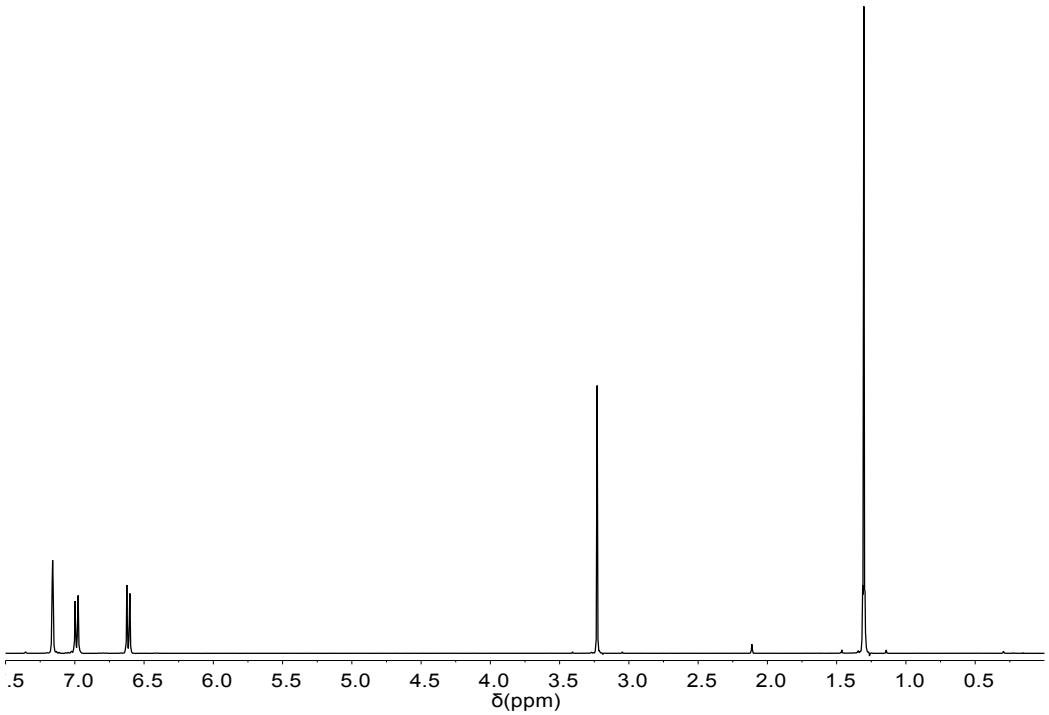

Figure S40. ^{1}H NMR spectrum of **2.5** in d_6-benzene (7.16 ppm).

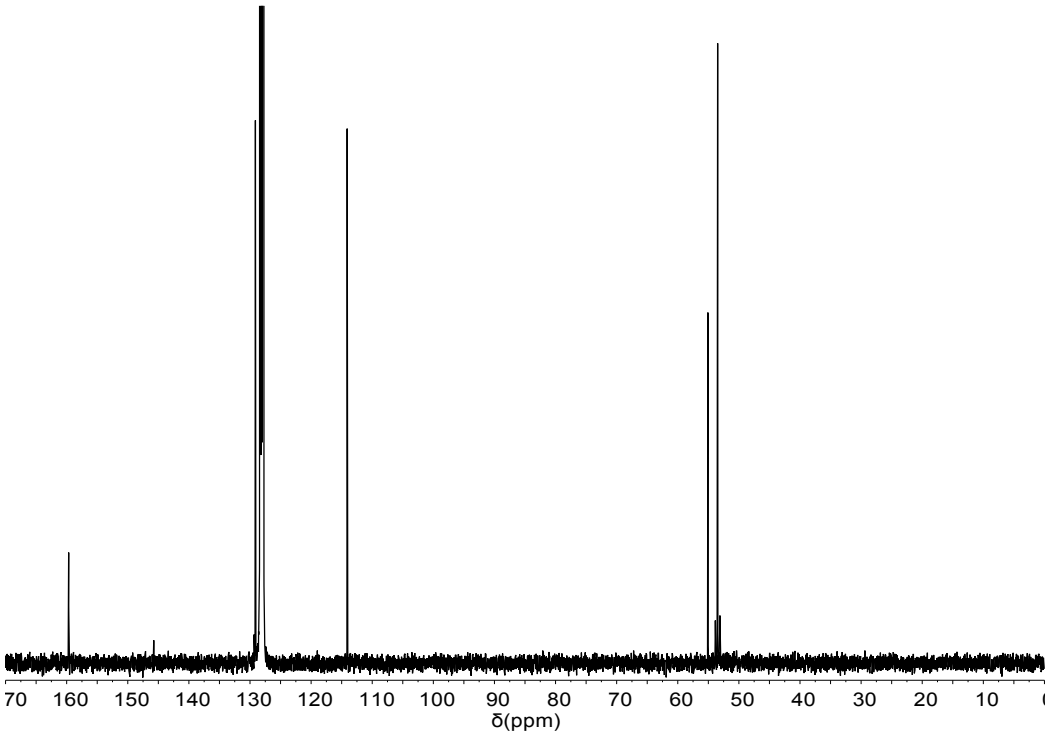

Figure S41. ^{13}C{^{1}H} NMR spectrum of **2.5** in d_6-benzene (128.06 ppm).

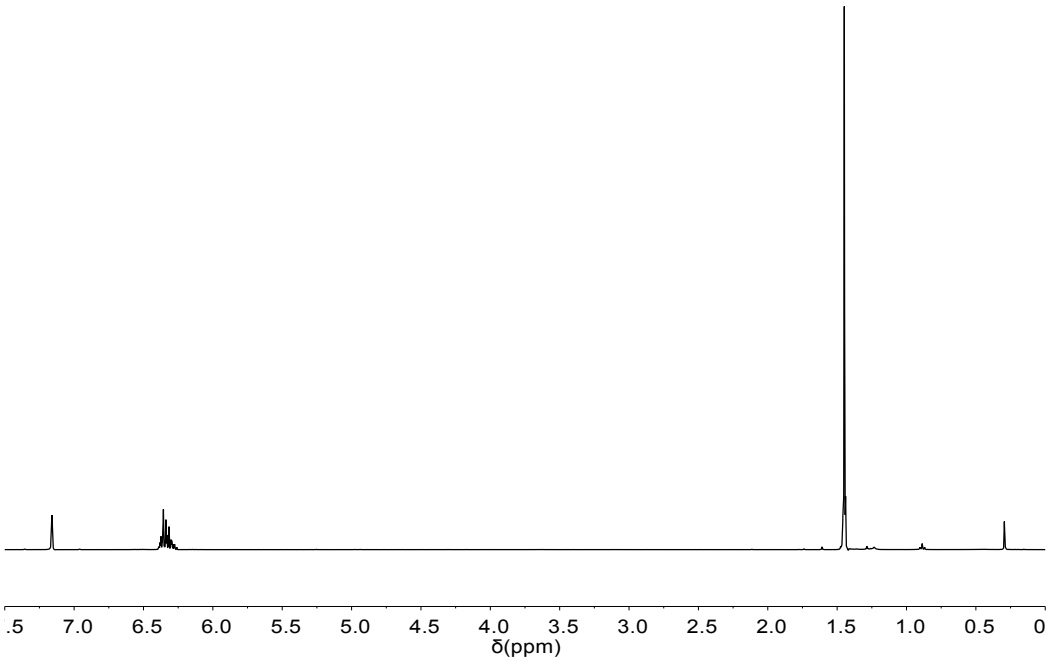

Figure S42. ^{1}H NMR spectrum of **2.6** in d_6-benzene (7.16 ppm).

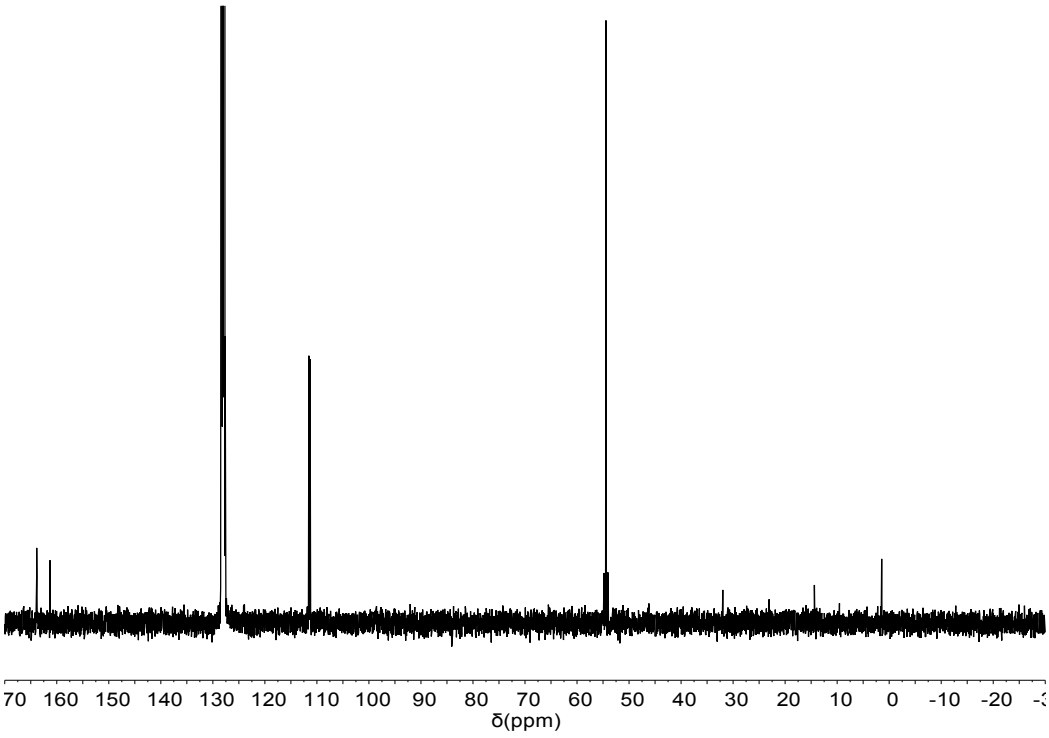

Figure S43. ^{13}C{^{1}H} NMR spectrum of **2.6** in d_6-benzene (128.06 ppm).

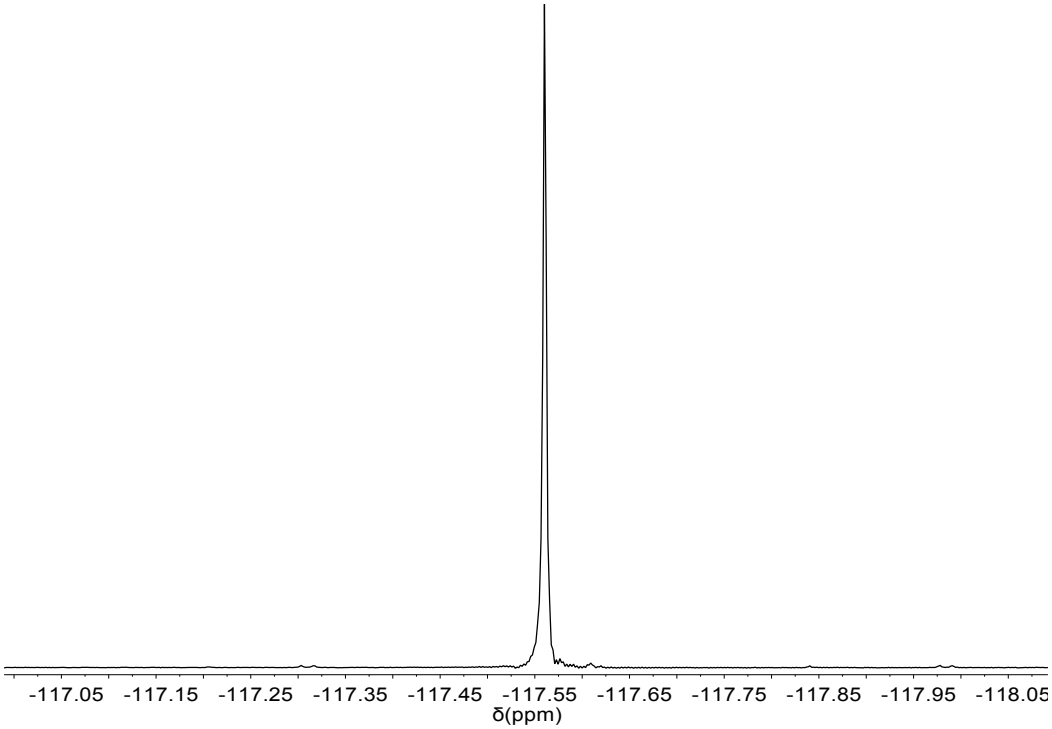

Figure S44. $^{19}F\{^{1}H\}$ NMR spectra of **2.6** in d_6-benzene.

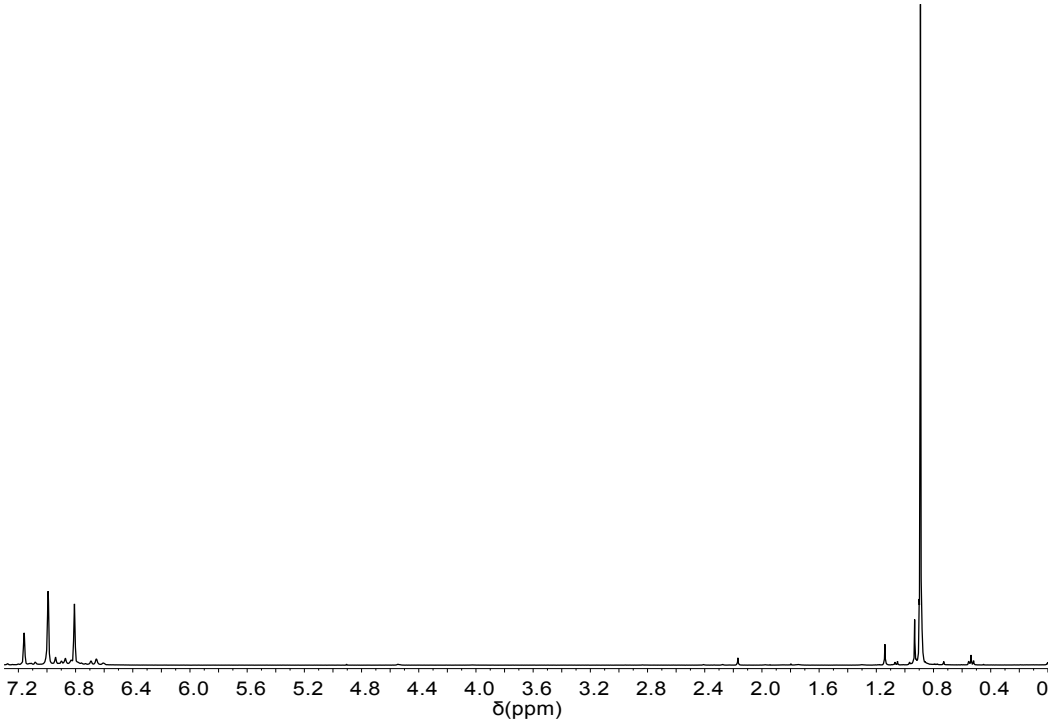

Figure S45. ^{1}H NMR spectrum of **2.7** in d_6-benzene (7.16 ppm).

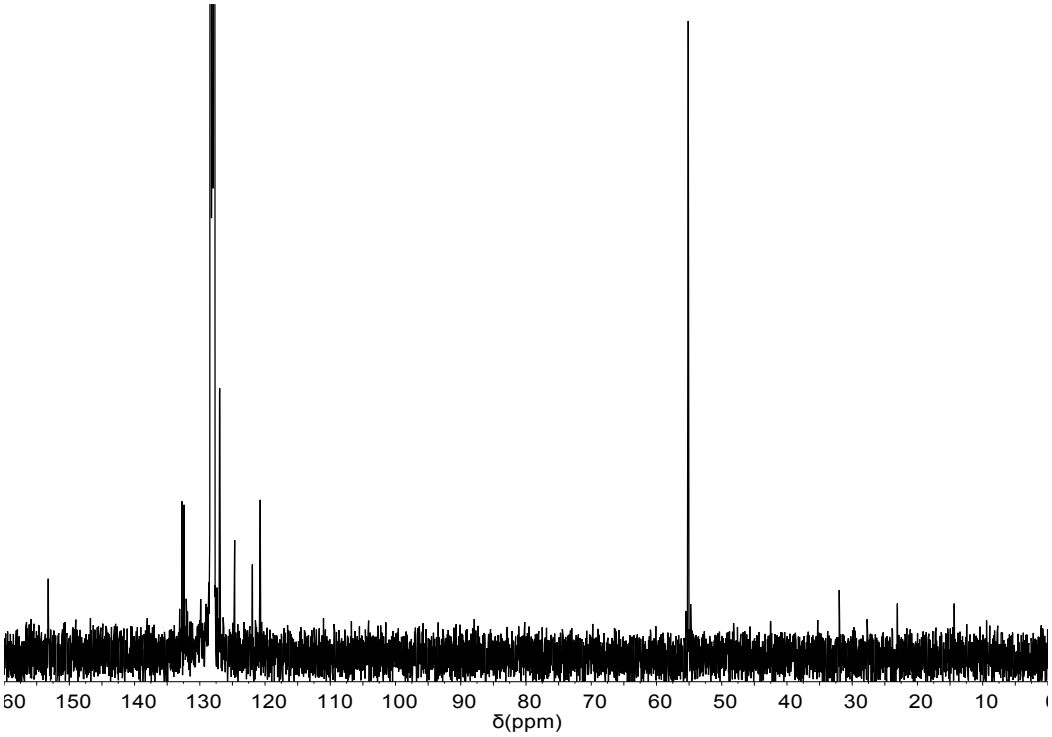

Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum of **2.8** in d_6-benzene (128.06 ppm).

Fourier transform infrared (FTIR) spectroscopy

$W(NR)Cl_4(THF)$ complexes

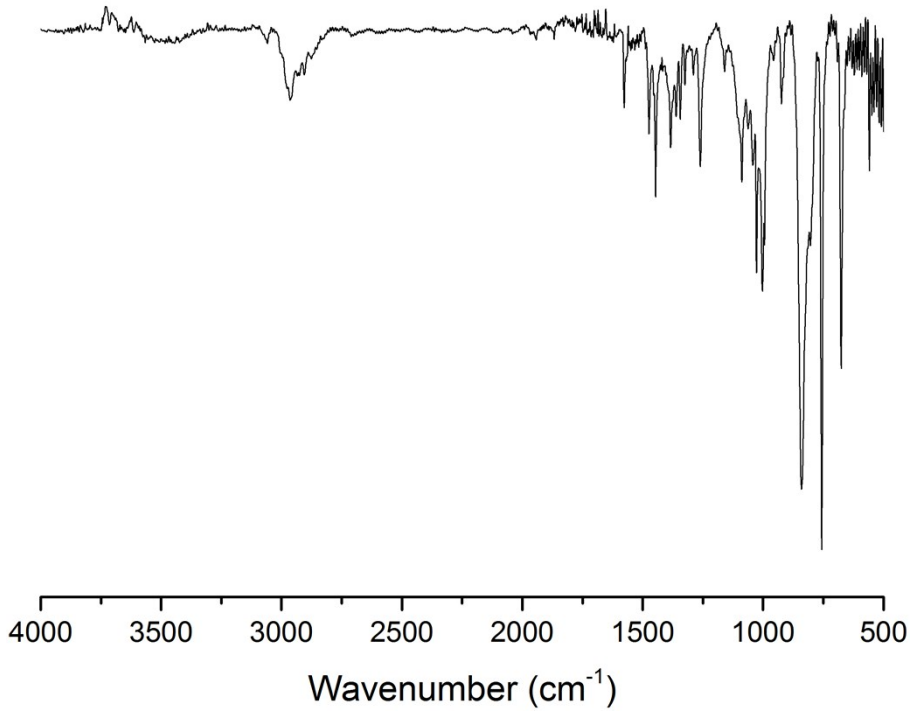

Figure S47. FTIR spectrum of **1.1**.

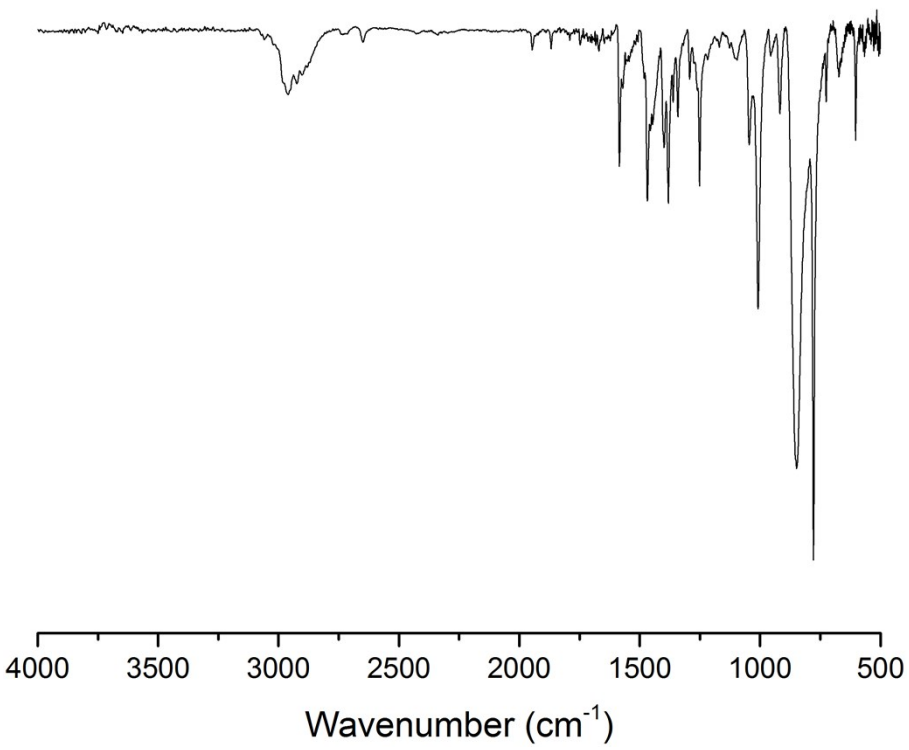

Figure S48. FTIR spectrum of **1.2**.

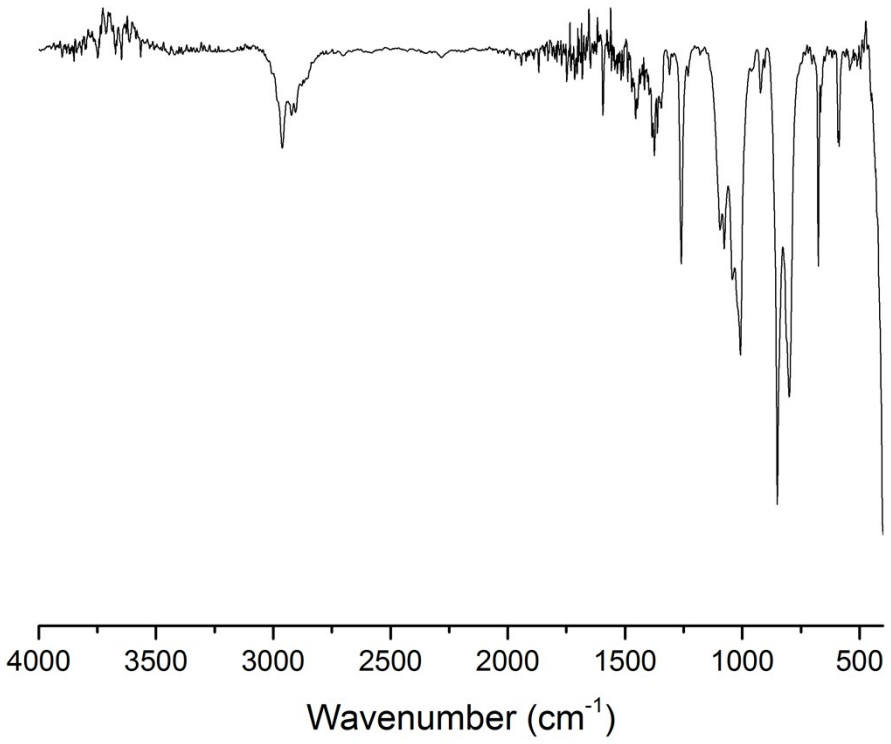

Figure S49. FTIR spectrum of **1.3**.

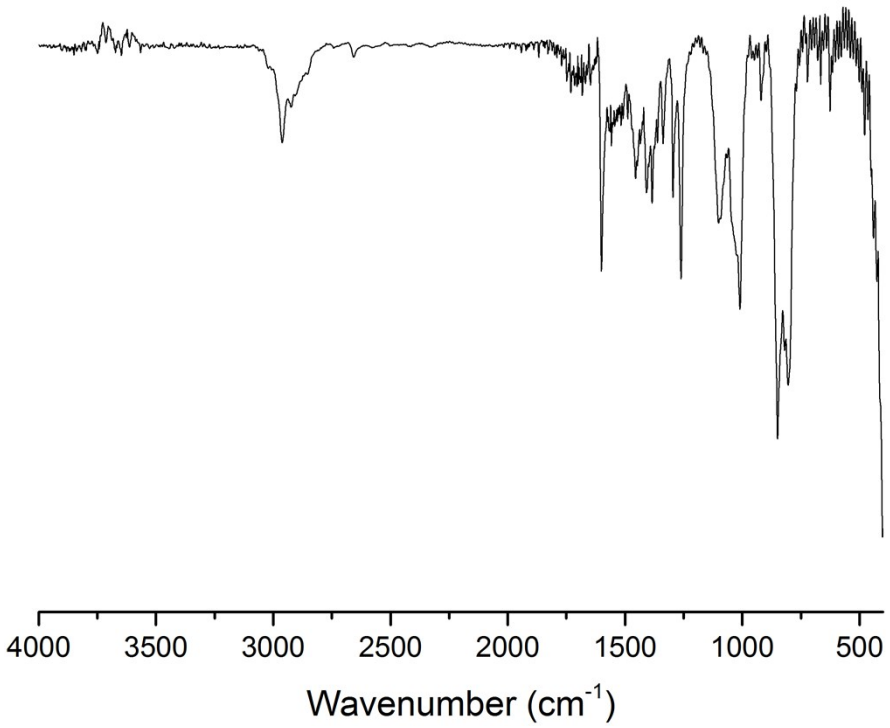

Figure S50. FTIR spectrum of **1.4**.

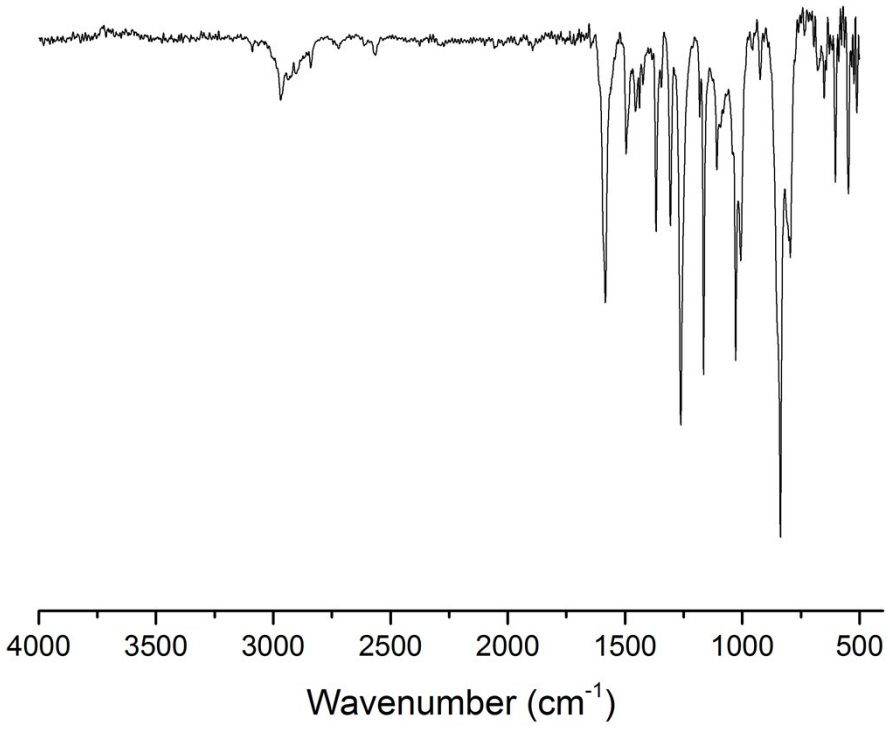

Figure S51. FTIR spectrum of **1.5**.

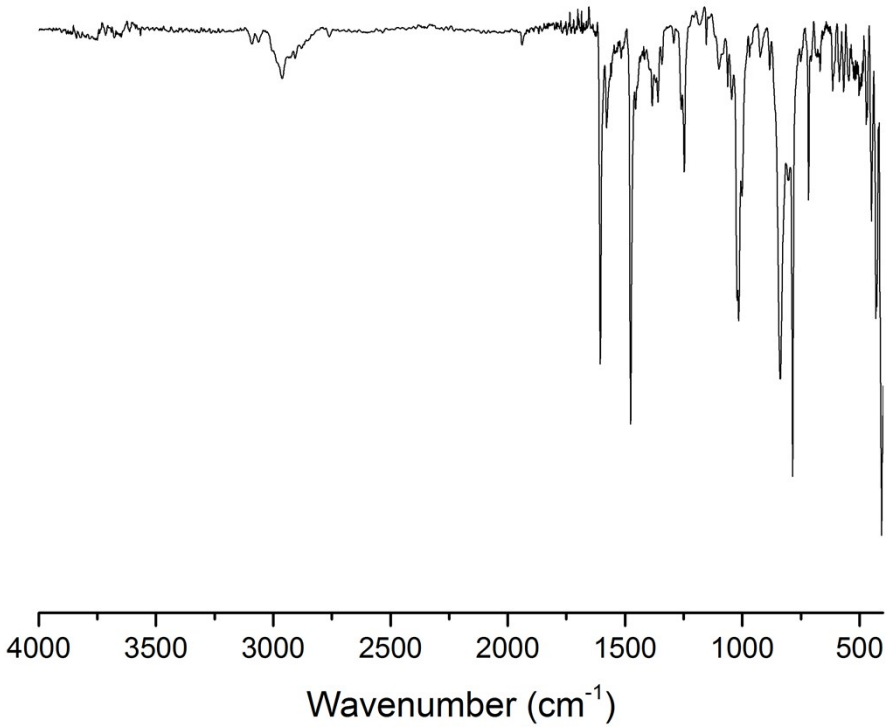

Figure S52. FTIR spectrum of **1.6**.

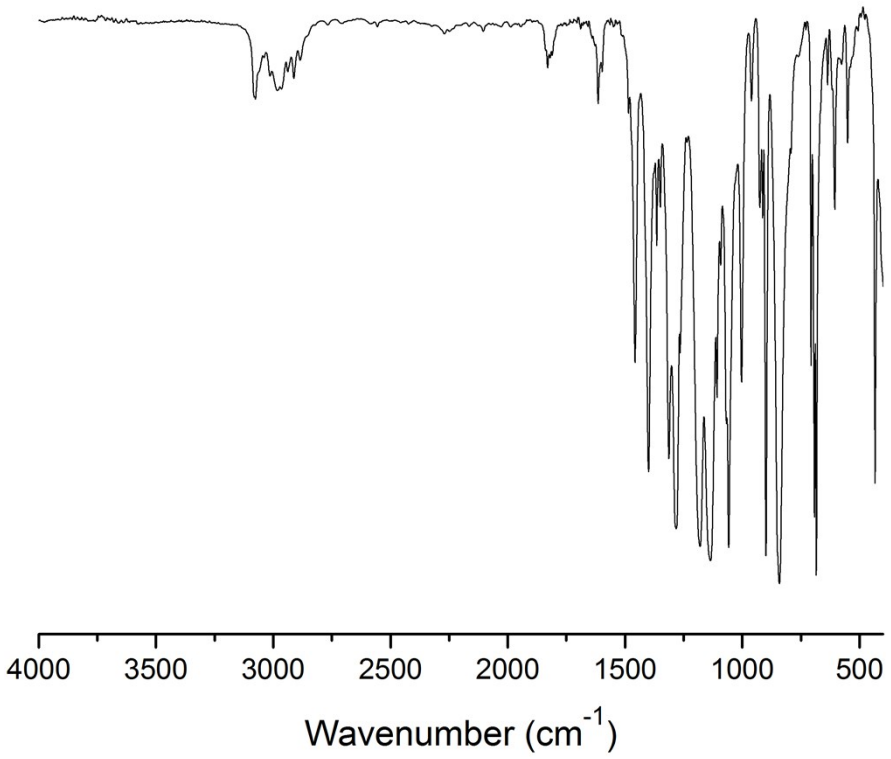

Figure S53. FTIR spectrum of **1.7**.

W(NR)Me_3Cl complexes

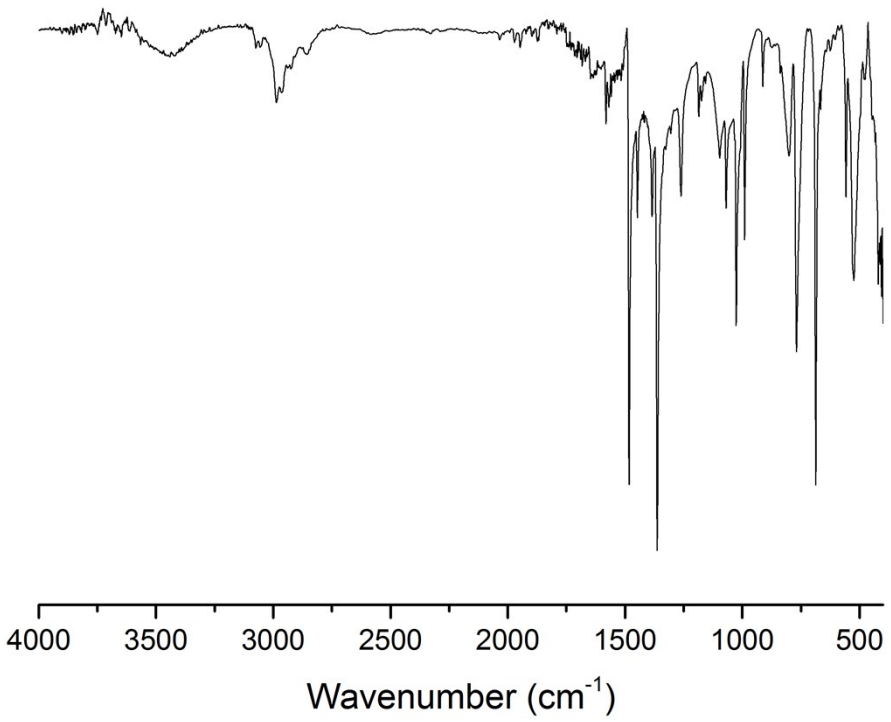

Figure S54. FTIR spectrum of **2.1**.

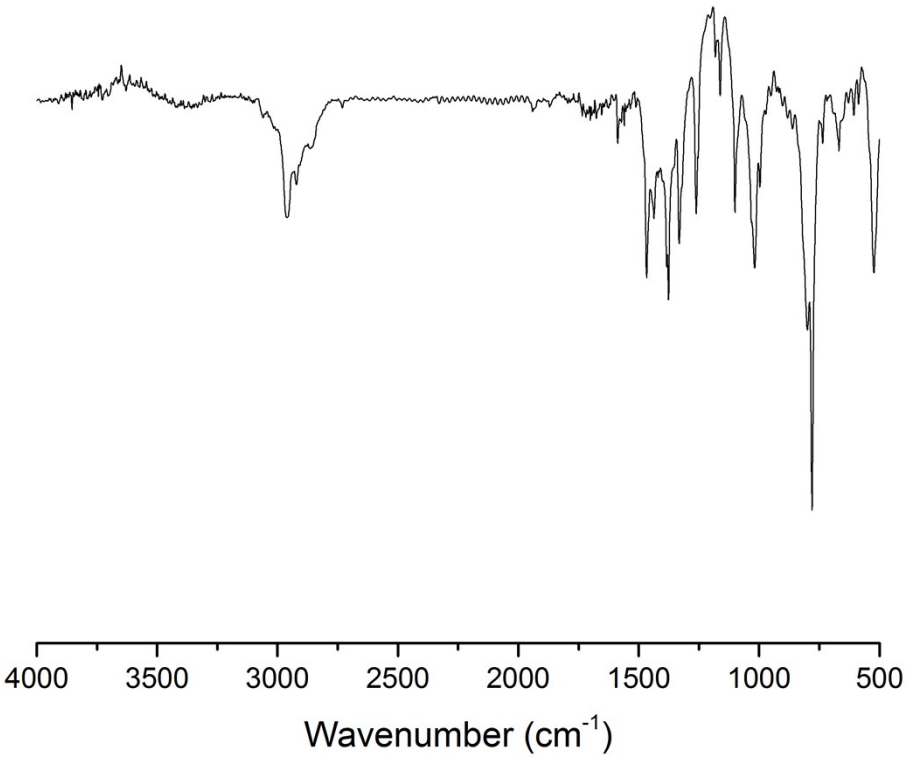

Figure S55. FTIR spectrum of **2.2**.

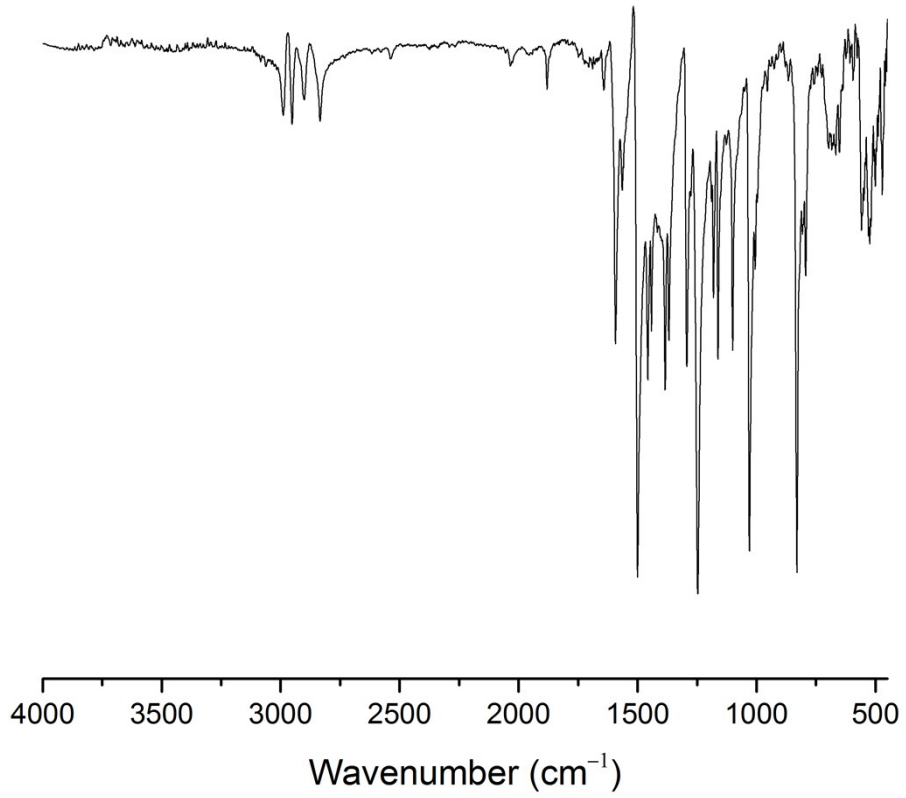

Figure S56. FTIR spectrum of **2.5**.

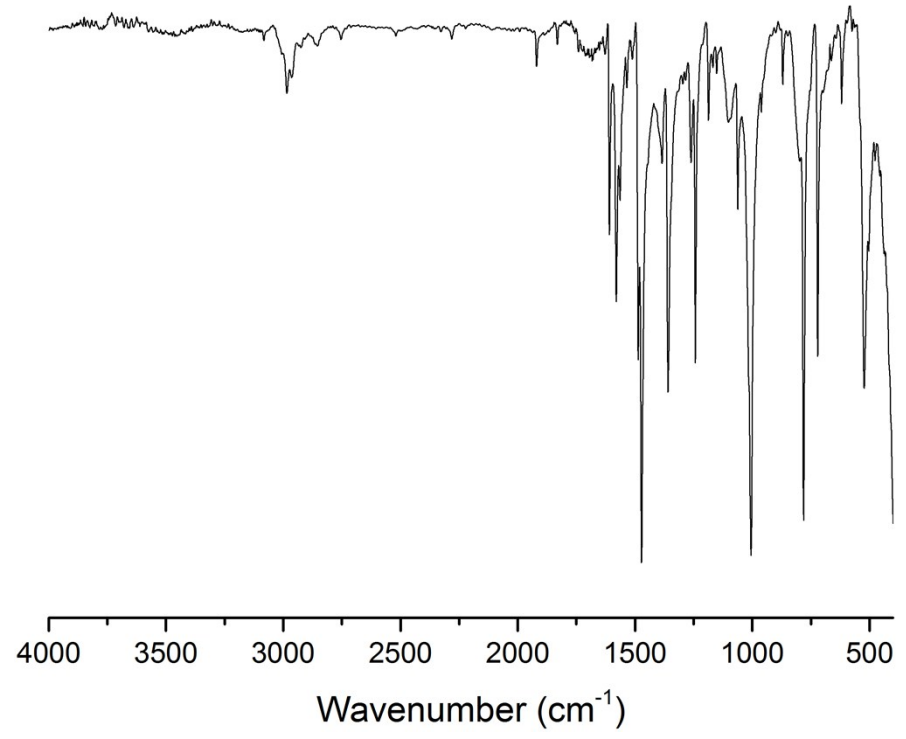

Figure S57. FTIR spectrum of **2.6**.

4. Characterisation of the heterogeneous catalysts

Solid-state NMR spectroscopy

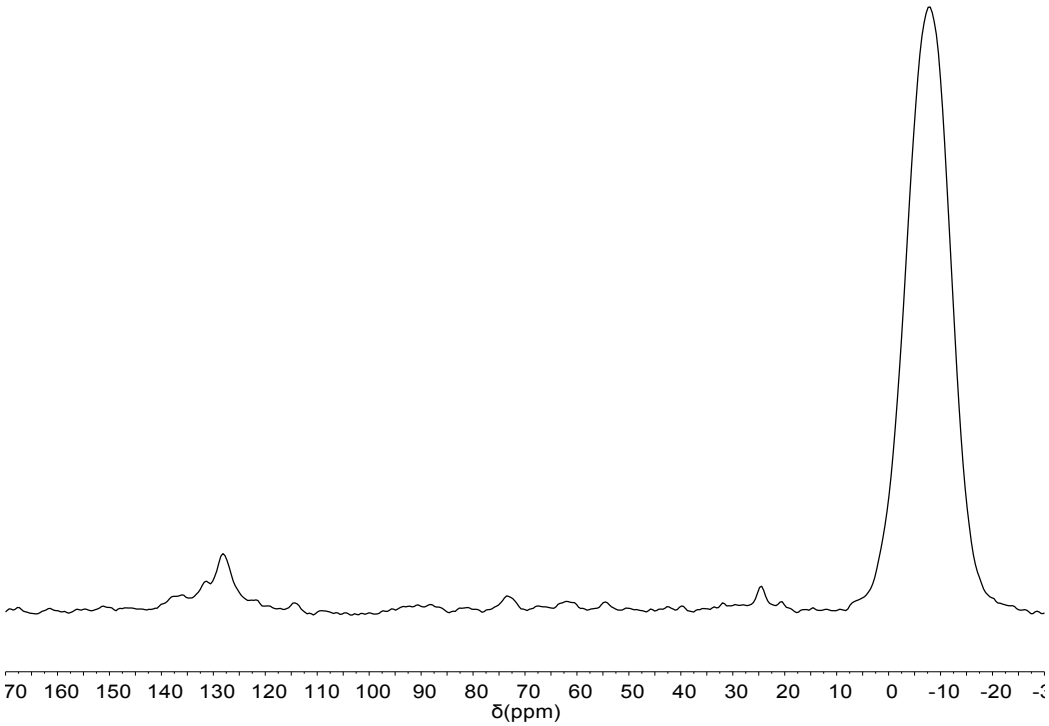

Figure S58. Solid-state ^{13}C-{^{1}H} CP-MAS NMR spectra of sMAO-**1.5**.

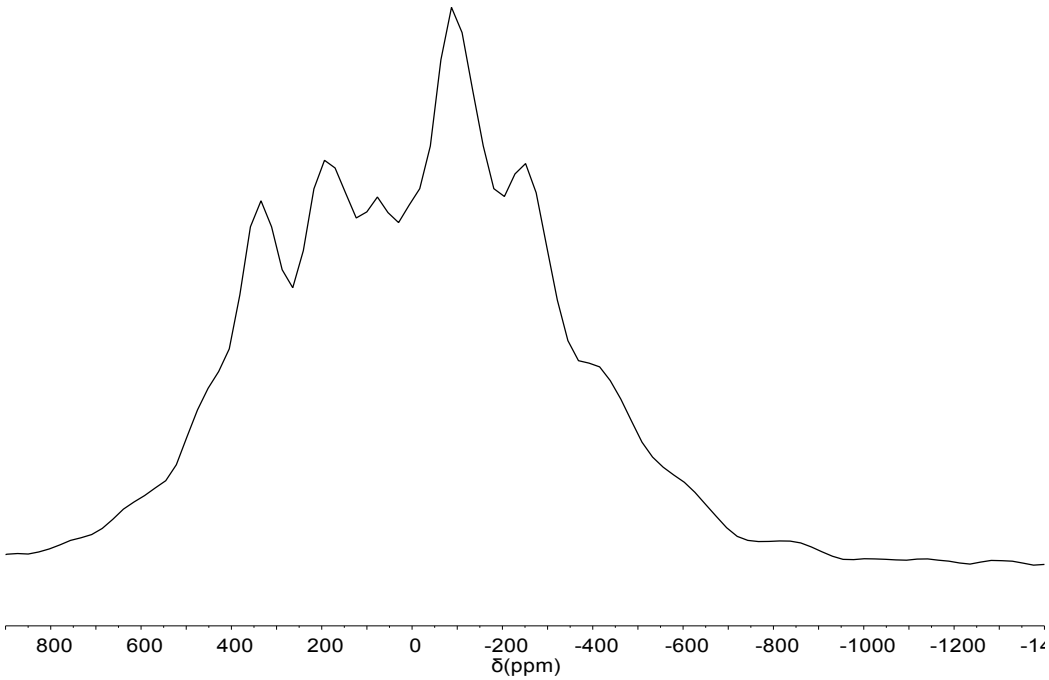

Figure S59. Solid-state ^{27}Al Hahn echo NMR spectra of sMAO-**1.5**.

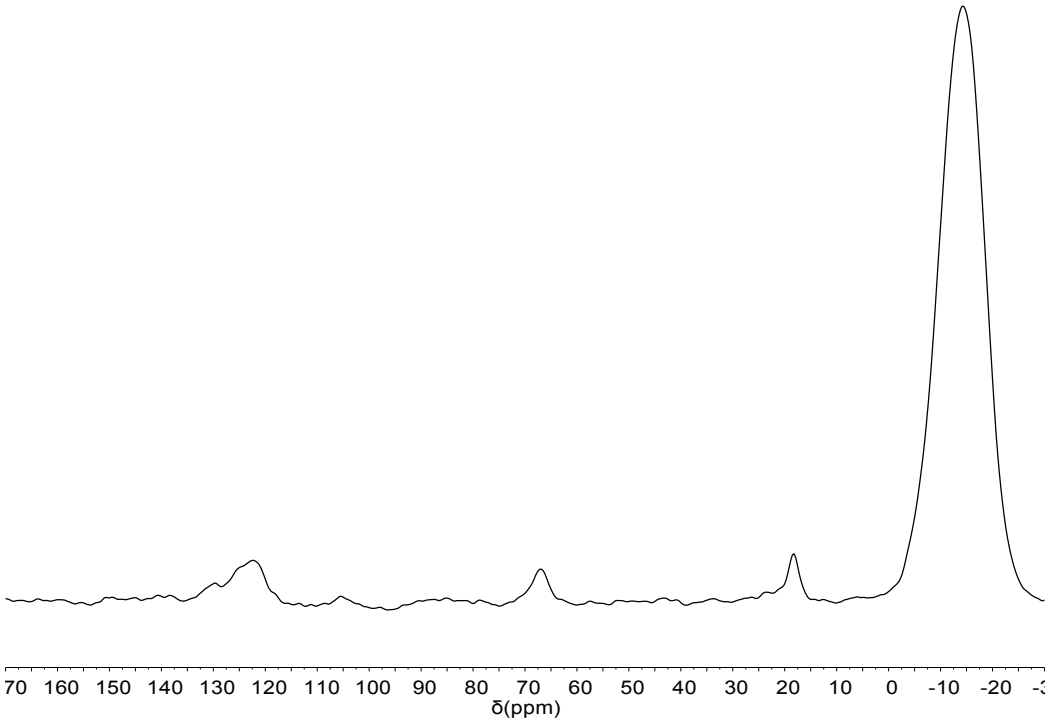

Figure S60. Solid-state ^{13}C-{^{1}H} CP-MAS NMR spectra of sMAO-**1.6**.

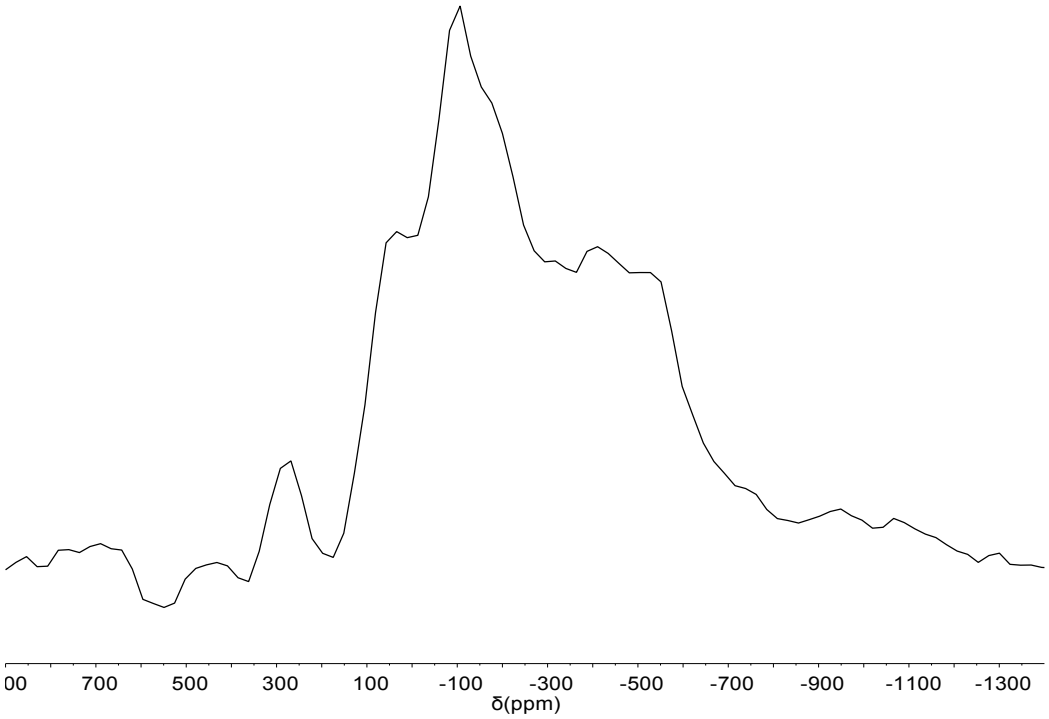

Figure S61. Solid-state ^{27}Al Hahn echo NMR spectra of sMAO-**1.6**.

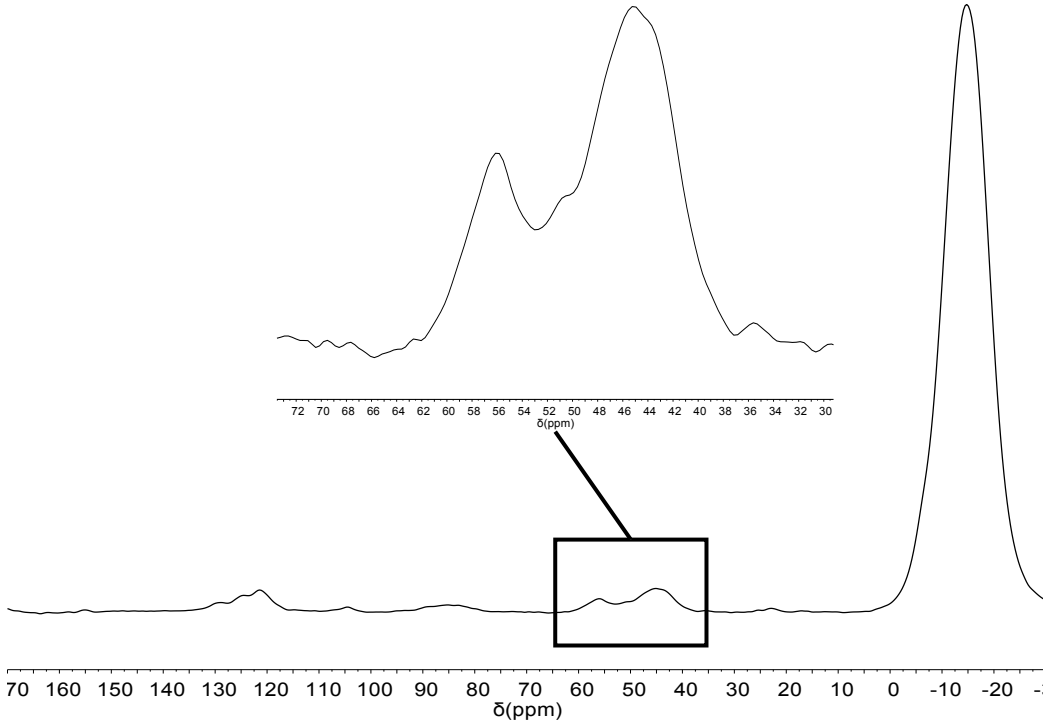

Figure S62. Solid-state ^{13}C-{^{1}H} CPMAS NMR spectra of sMAO-**2.6***. Resonances between 38 and 62 ppm attributed to W(**^{13}C**H_3) groups of the supported complex.

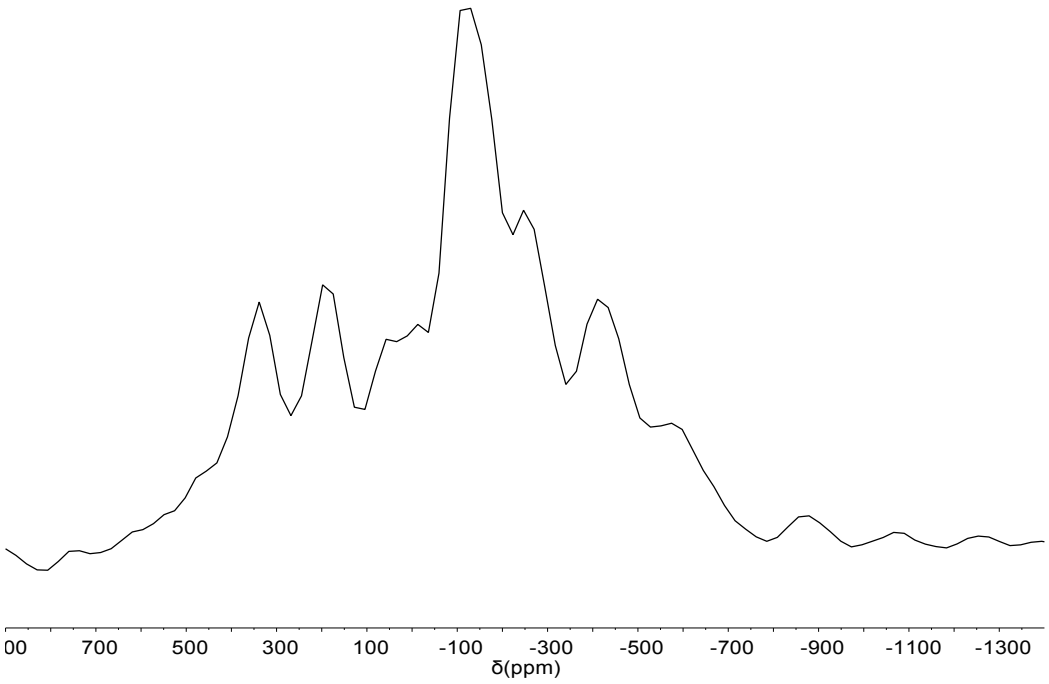

Figure S63. Solid-state ^{27}Al Hahn echo NMR spectra of sMAO-**2.6***.

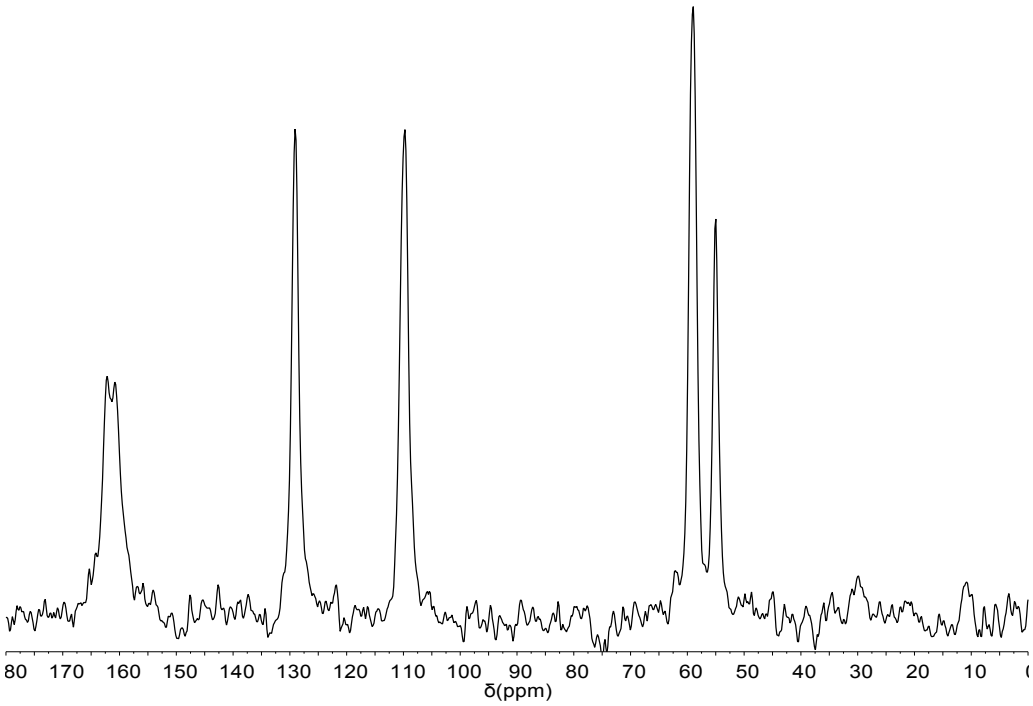

Figure S64. ^{13}C-{^{1}H} CPMAS {^{19}F} decoupled SSNMR spectrum of **2.6**.

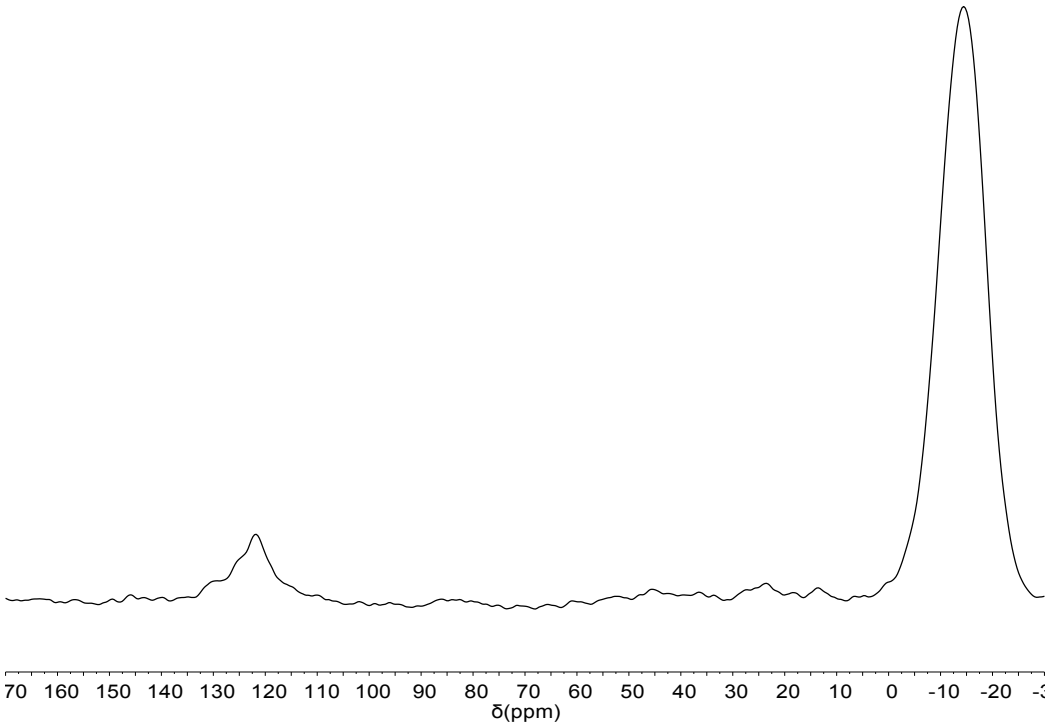

Figure S65. Solid-state ^{13}C-{^{1}H} CP-MAS NMR spectra of sMAO-**1.7**.

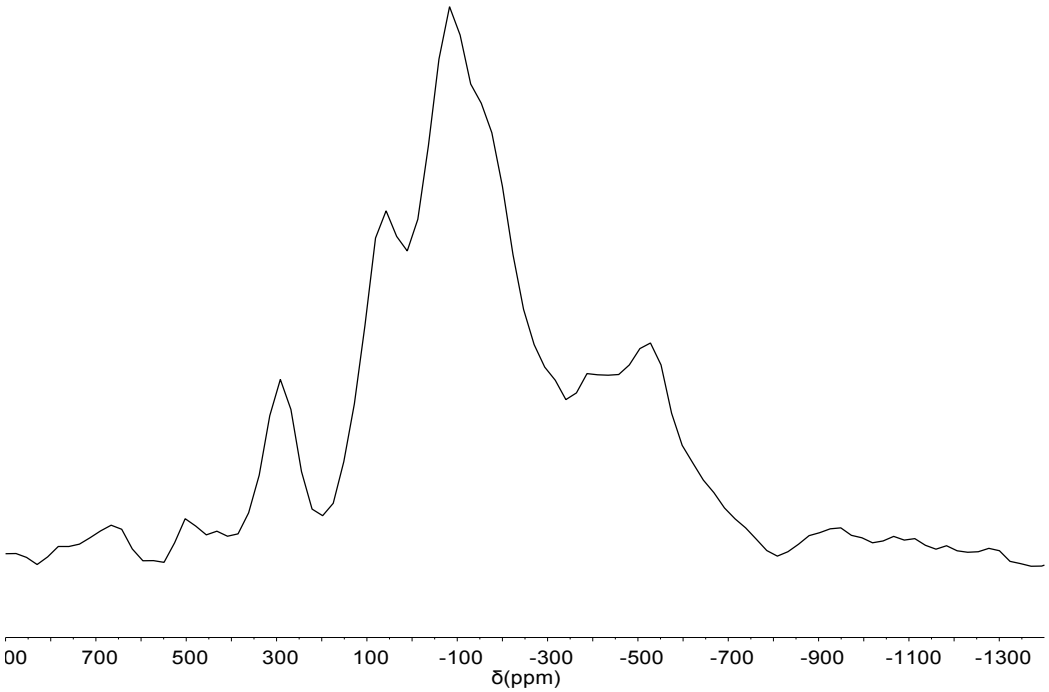

Figure S66. Solid-state ^{27}Al Hahn echo NMR spectra of sMAO-**1.7**.

Fourier transform infrared (FTIR) spectroscopy

sMAO-W(NR)Cl_4(THF) compounds

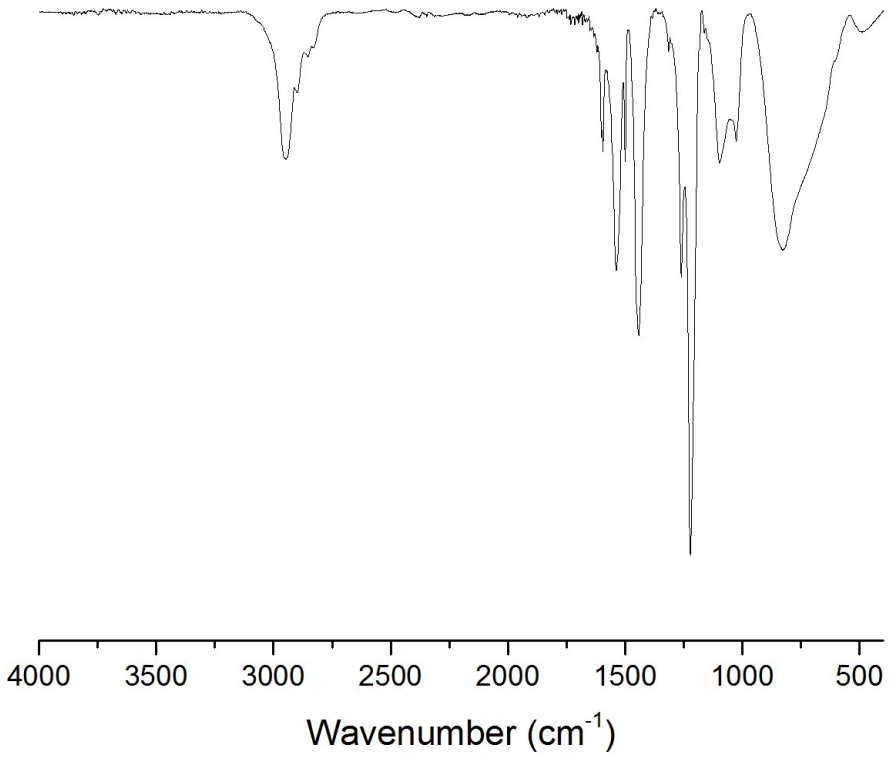

Figure S67. FTIR spectrum of sMAO.

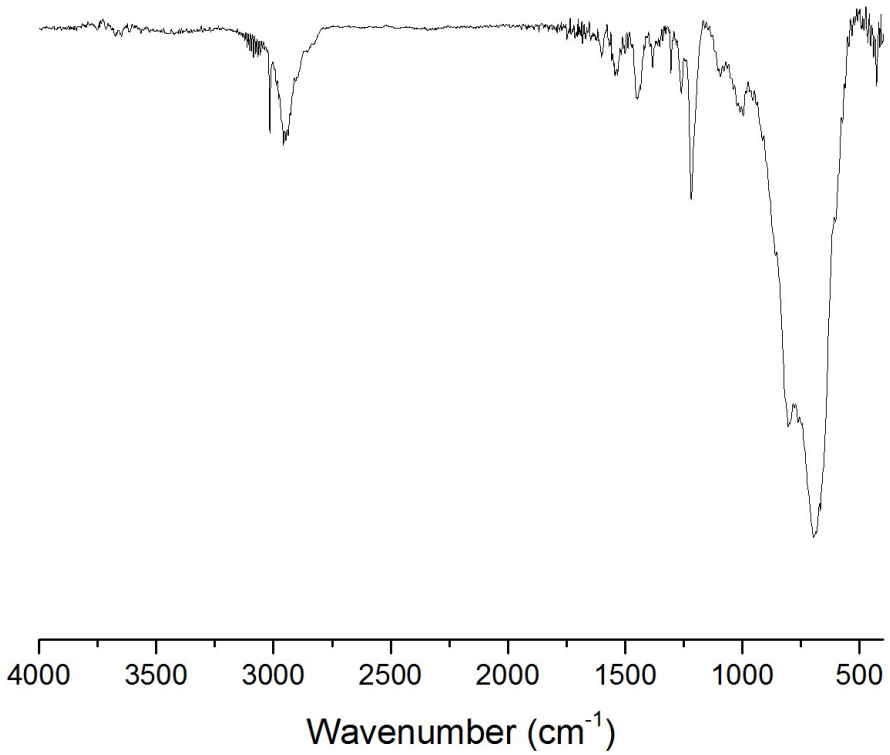

Figure S68. FTIR spectrum of sMAO-**1.1**.

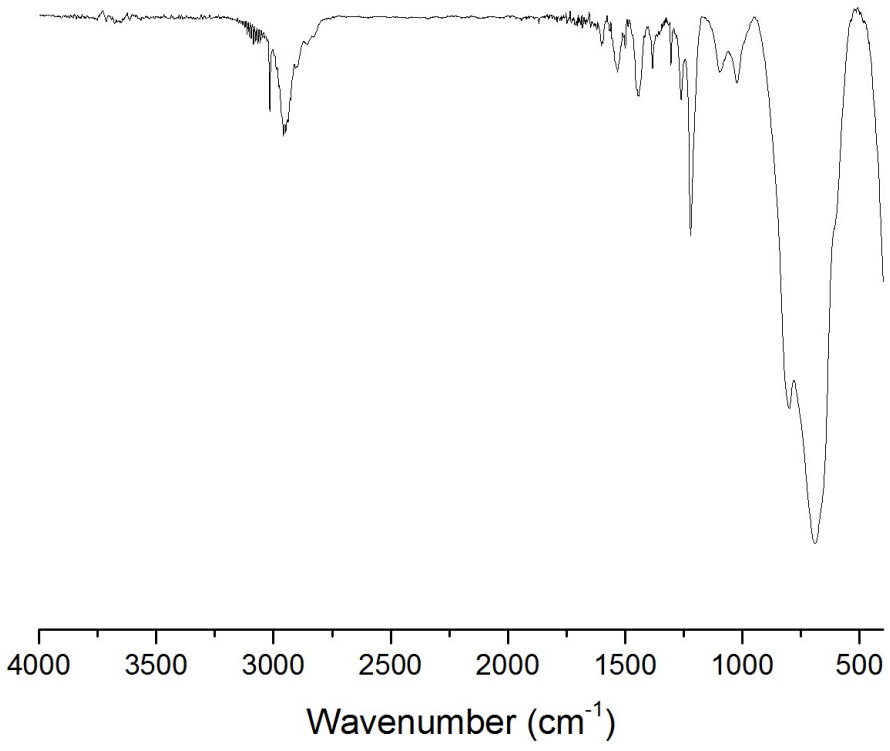

Figure S69. FTIR spectrum of sMAO-**1.2**.

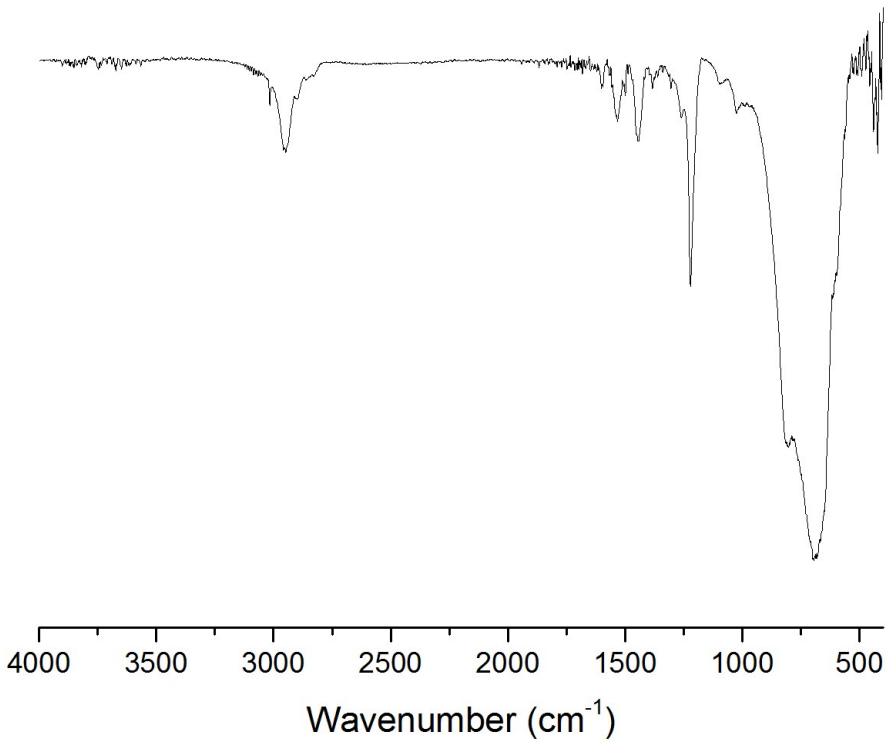

Figure S70. FTIR spectrum of sMAO-**1.3**.

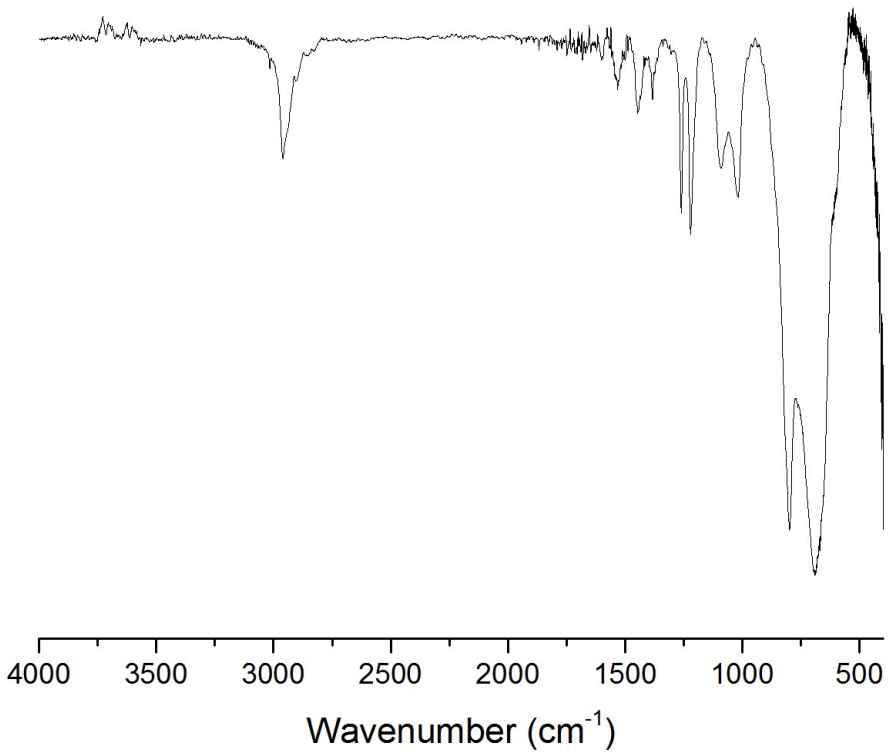

Figure S71. FTIR spectrum of sMAO-**1.4**.

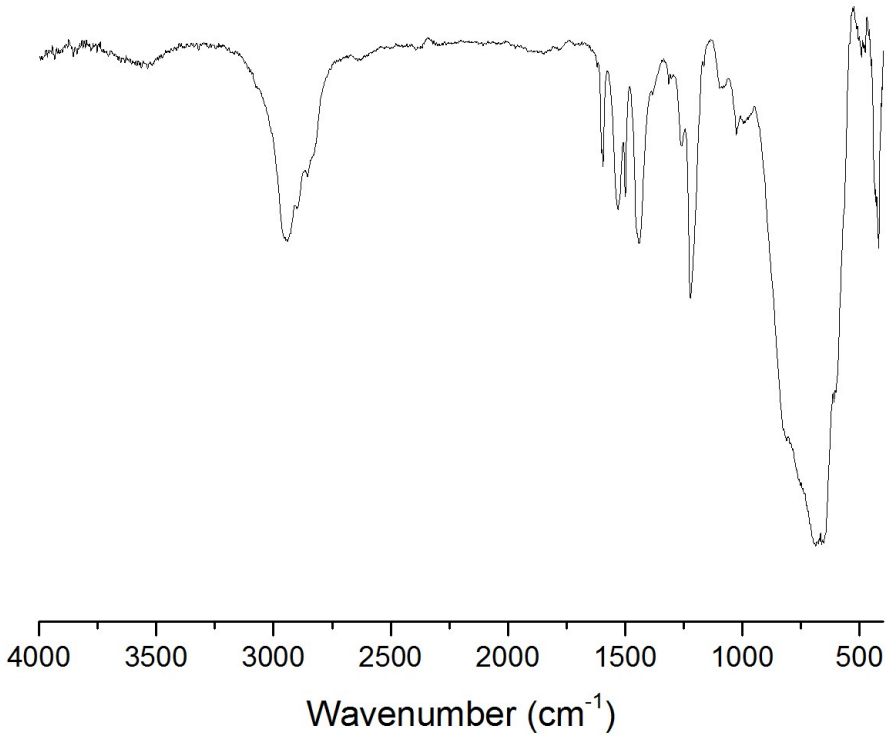

Figure S72. FTIR spectrum of sMAO-**1.5**.

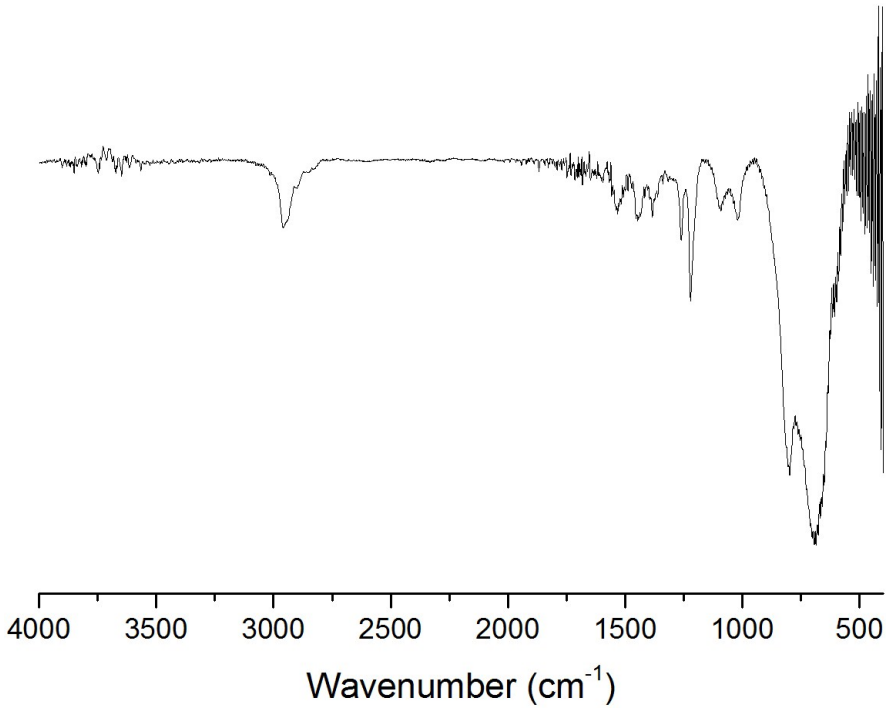

Figure S73. FTIR spectrum of sMAO-**1.6**.

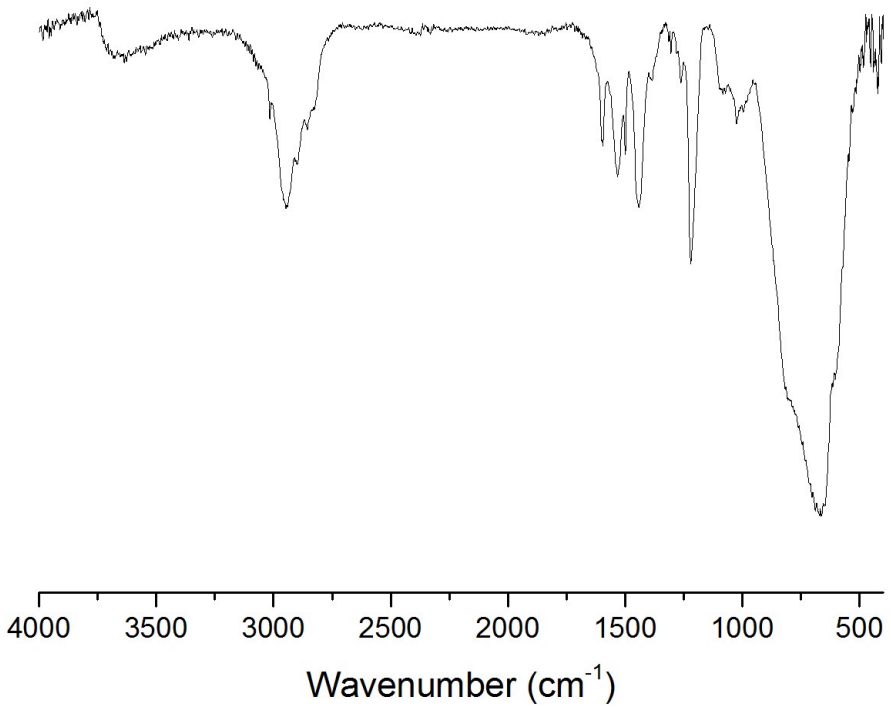

Figure S74. FTIR spectrum of sMAO-**1.7**.

ICP-MS

Table S3. ICP-MS analysis and calculated Al/W ratios and percentage loading for sMAO-**1.4**, sMAO-**1.5** and sMAO-**1.7**.

Sample	Mass (mg)	^{27}Al (mol%)	^{182}W (mol%)	^{184}W (mol%)	^{186}W (mol%)	Mean Al/W	Complex loading (%)
sMAO-**1.4**	10.5	1.32800	286.66745	285.15483	269.35047	280.4	56.8
sMAO-**1.4**	10.9	1.31104	314.49531	313.49390	287.95395	305.3	60.9
sMAO-**1.4**	10.3	1.33036	257.06339	258.16085	260.31382	258.5	66.6
sMAO-**1.5**	10.4	1.23304	271.42338	278.08870	252.42916	267.3	53.5
sMAO-**1.5**	11.9	1.15148	225.52342	236.56812	229.83080	230.6	49.1
sMAO-**1.5**	14.8	1.27063	243.82493	246.54624	228.79860	239.7	58.0
sMAO-**1.7**	10.2	1.16746	267.07904	266.39814	258.44509	264.0	56.1
sMAO-**1.7**	10.9	1.39051	255.20206	245.76385	238.04334	246.3	65.0
sMAO-**1.7**	10.4	1.32003	217.26813	241.42522	216.83394	225.2	62.6

5. Heterogeneous oligomerisation studies

Statistical correlations

Table S4. Pearson correlations for all the $W(NR)Cl_4(THF)$ complex parameters and the turnover frequency (TOF) of the sMAO supported catalysts.

	δ C_{ipso}	**pKa**	**ECA**	**Solid-G**	**Ligand volume**	**W-N**	**W-N-C**
TOF	0.517	−0.581	−0.105	−0.096	0.191	−0.158	−0.308

Table S5. Pearson correlations for the $W(NR)Cl_4(THF)$ (R = C_6H_5, 2,6-Me-C_6H_3, 2,4,6-Me-C_6H_2, 2,6-^{i}Pr-C_6H_3 and 3,5-Me-C_6H_3) complexes parameters and the turnover frequency (TOF) of the sMAO supported catalysts.

	δ C_{ipso}	**pKa**	**ECA**	**Solid-G**	**Ligand volume**	**W-N**	**W-N-C**
TOF	0.806	−0.343	0.181	0.202	0.370	−0.332	−0.205

Table S6. Pearson correlations for the $W(NR)Me_3Cl$ complexes parameters and the turnover frequency (TOF) of the sMAO-supported catalysts.

	W-N	**W-Cl**	**W-N-C**	**δ C_{ipso}**	**δ W-Me**
TOF	0.310	−0.281	−0.242	0.059	0.55

1-Hexene and 1-octene reactions

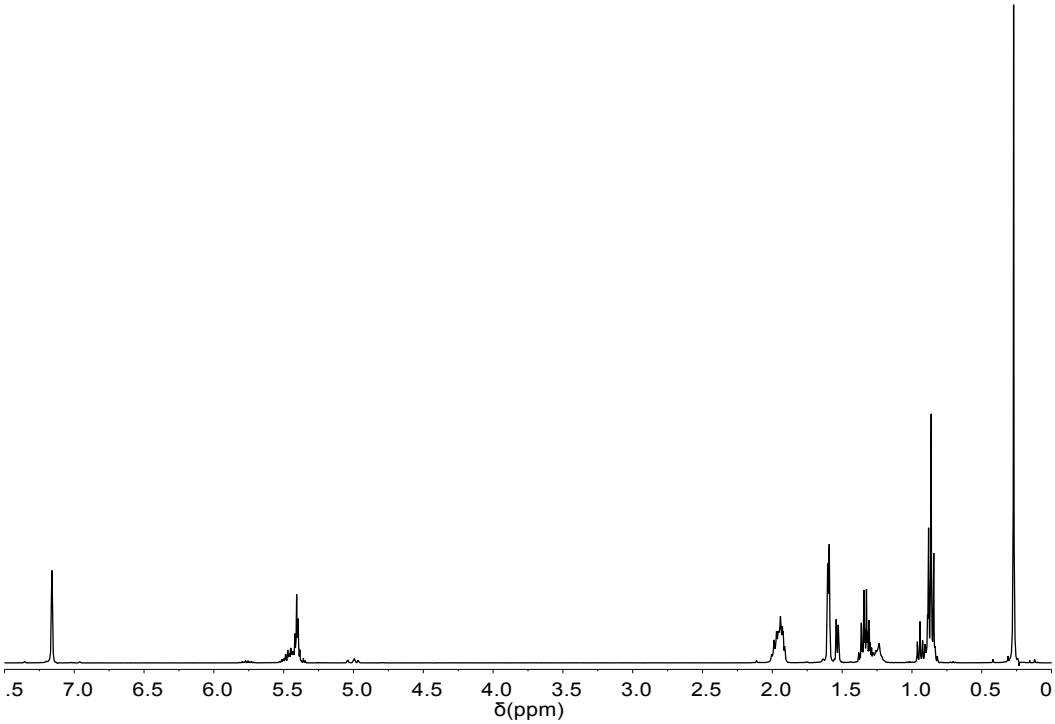

Figure S75. Reaction of sMAO-**1.6** (W:Al = 1:150) with 1-hexene after 4 hours at 75 °C in d_6-benzene (7.16 ppm) containing $Si(SiMe_3)_4$ (0.27 ppm) showing almost complete isomerisation of the *α*-olefin to *cis*- and *trans*-2-hexene.

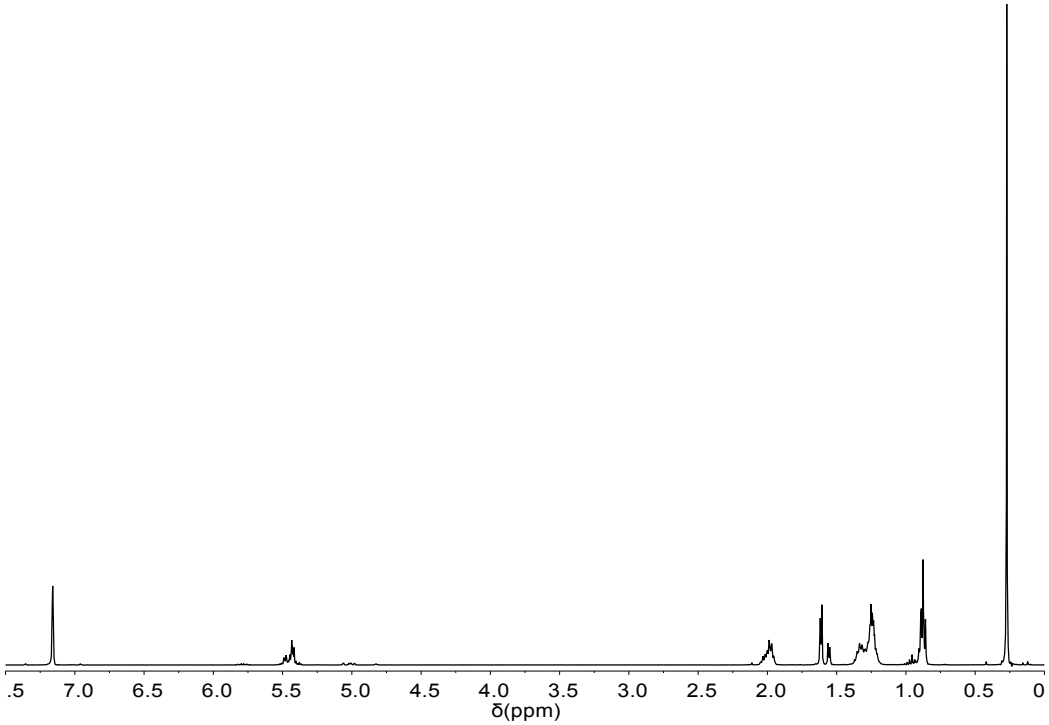

Figure S76. Reaction of sMAO-**1.6** (W:Al = 1:150) with 1-octene after 4 hours at 75 °C in d_6-benzene (7.16 ppm) containing $Si(SiMe_3)_4$ (0.27 ppm) showing almost complete isomerisation of the *α*-olefin to *cis*- and *trans*-2-octene.

Temperature study

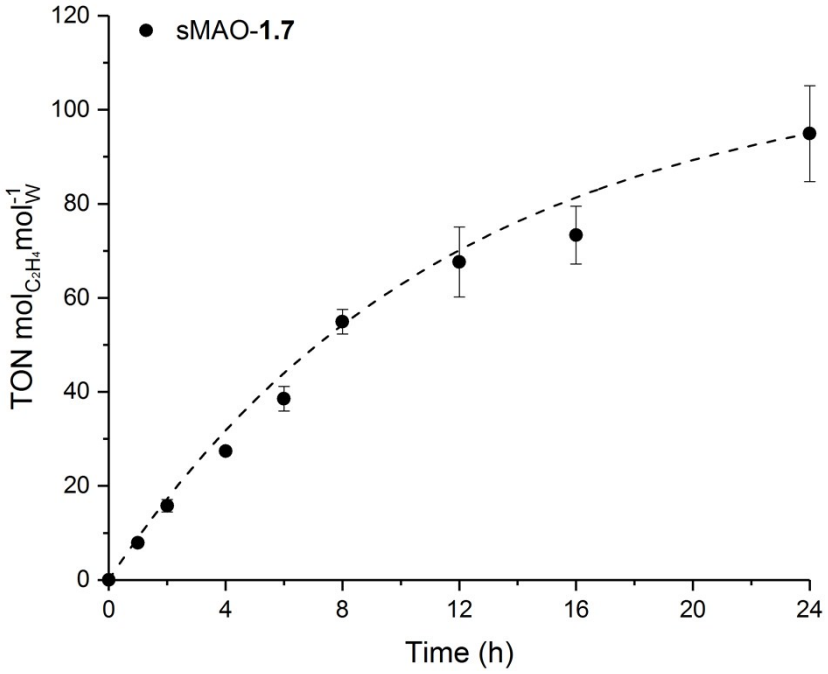

Figure S77. Reaction of sMAO-**1.7** with ethylene (1 bar) at 75 °C in d_6-benzene.

Solvent properties

Table S7. Dielectric constants and donor numbers for solvents used in this study.[7,8]

Solvent	Dielectric Constant (ε)	Donor Number
Octane	Heptane = 1.9	Heptane = 0
Benzene	2.3	0.1
Toluene	2.4	0.1
THF	7.6	20
DCM	8.9	1
Pyridine	12.4	33.1
Chlorobenzene	5.62	3.3
Bromobenzene	5.4	3
1,2-dichlorobenzene	9.9	3
Mesitylene	*p*-Xylene = 2.3	10

Loading study

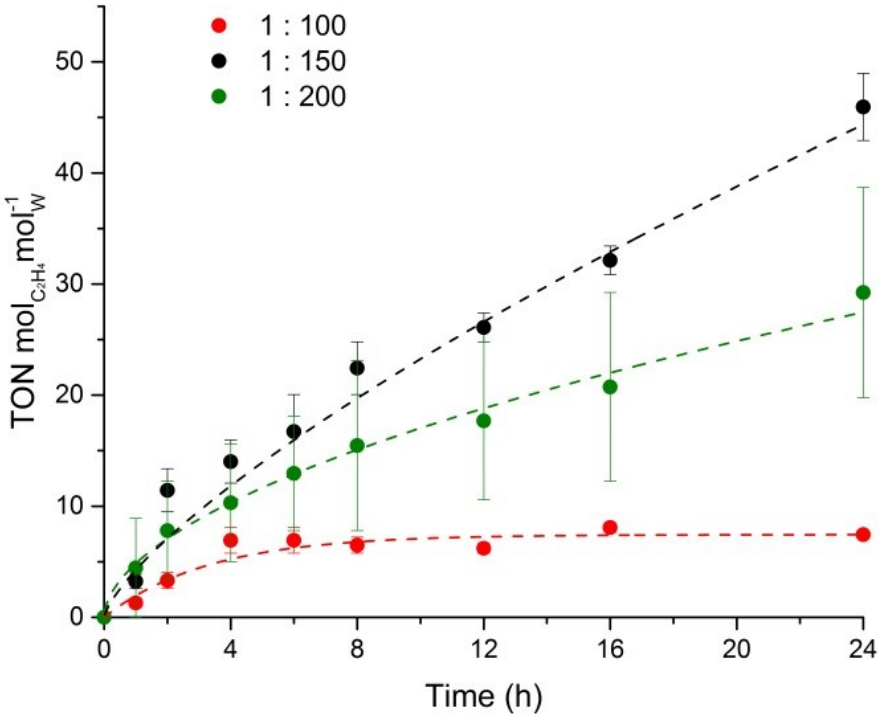

Figure S78. Effect of complex loading on the oligomerisation activity of sMAO-**1.5**. W:Al = 1:100, 1:150 and 1:200. 75 °C, d_6-benzene.

6. References

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