Electronic Supplementary Information for

New tetradentate *N,N,N,N*-chelating α-diimine ligands and their corresponding zinc and nickel complexes: synthesis, characterisation and testing as olefin polymerisation catalysts

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Structure of *N*-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)phenyl)acetamide (byproduct 3a)

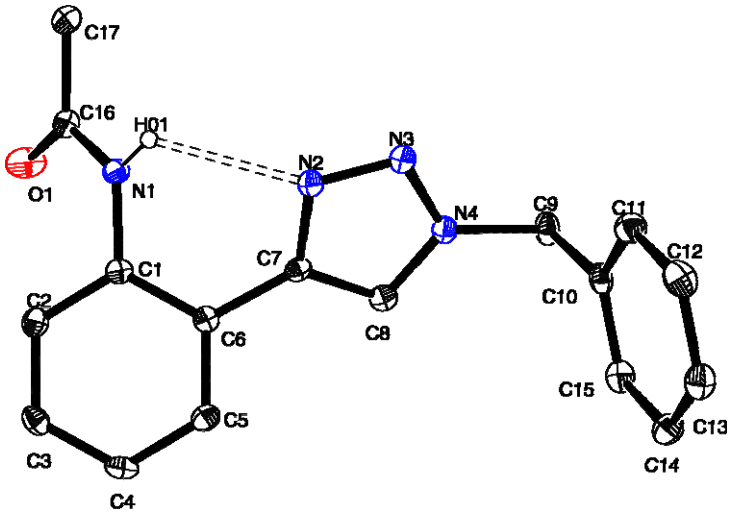

Fig. S1 ORTEP diagram of compound **3a** with 50% probability ellipsoid displacement. All the hydrogen atoms are omitted for clarity.

Crystals of the amide **3a** were obtained by crystallisation in a dilute diethyl ether solution, at -20 ^{o}C. This compound crystallised in the monoclinic system, space group $P2_1/c$, each unit cell containing four molecules. The corresponding molecular structure is represented in Fig. S1, its bond distances and angles being comparable with those of **1a** and **1c** (Table 1 of the article and Table S1). As in compound **1c**, the phenyl and triazolyl rings form a dihedral angle of 31.28(10)º and the C6−C7 bond (1.476(3) Å) connecting both rings is also typical of a C-C single bond.

Table S1 Selected bond distances (Å), angles (º) and torsion angles (º) for compound **3a**.

Distances		*Angles*	
C1−N1	1.418(2)	C7−C8−N4	104.98(17)
C6−C7	1.476(3)	C8−N4−N3	111.37(16)
C7−C8	1.372(3)	N4−N3−N2	106.76(15)
C7−N2	1.363(2)	N3−N2−C7	108.85(16)
C8−N4	1.342(2)	N2−C7−C8	108.04(17)
C9−N4	1.471(2)	N1−H01···N2	121(2)
N2−N3	1.325(2)	N1−C1−C6−C7	2.0(3)
N3−N4	1.342(2)	C1−C6−C7−C8	-150.2(2)
N1···N2	2.861(2)	C1−C6−C7−N2	32.8(3)
N1−H01	0.81(2)	C1−N1−H01···N2	43(3)
H01···N2	2.36(2)		

Definition of the parameter τ in five-coordinate complexes

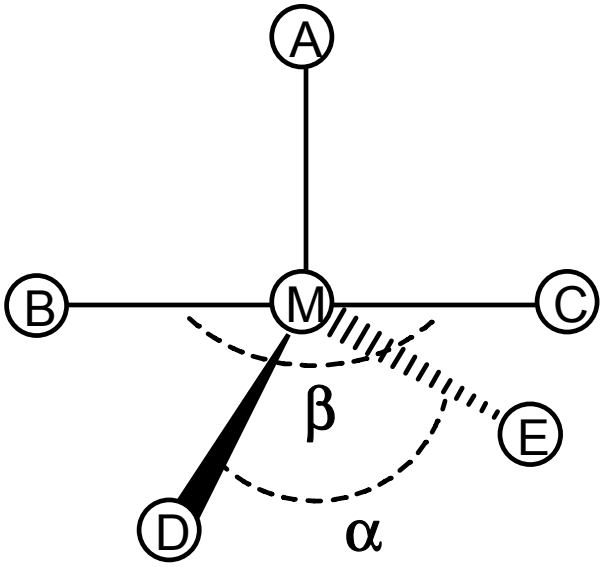

Fig. S2 In a penta-coordinated structure, the τ parameter, $\tau = (\beta - \alpha)/60$, measures the degree of distortion within the structural continuum between trigonal bipyramidal and square pyramidal geometries (τ=1 for an ideal trigonal bipyramid and τ=0 for an ideal square pyramid).[1] Angle α (∠ DME) is defined as the angle formed between the bonds of the donor atoms D and E to the central metal atom M. Angle β (∠ BMC) is defined as the angle formed between the bonds of the donor atoms B and C to the central metal atom M.

[1] (*a*) A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* 1984, 1349-1356; (*b*) C. O'Sullivan, G. Murphy, B. Murphy, B. Hathaway, *J. Chem. Soc., Dalton Trans.* 1999, 1835-1844.

Structure of $\{[ZnCl(ArN{=}C(An){-}C(An){=}NAr)]^{+}\}_2[Zn_2Cl_6]^{2-}$

(Ar = 2-(1-(1-phenylethyl)-1*H*-1,2,3-triazol-4-yl)phenyl) (2b)

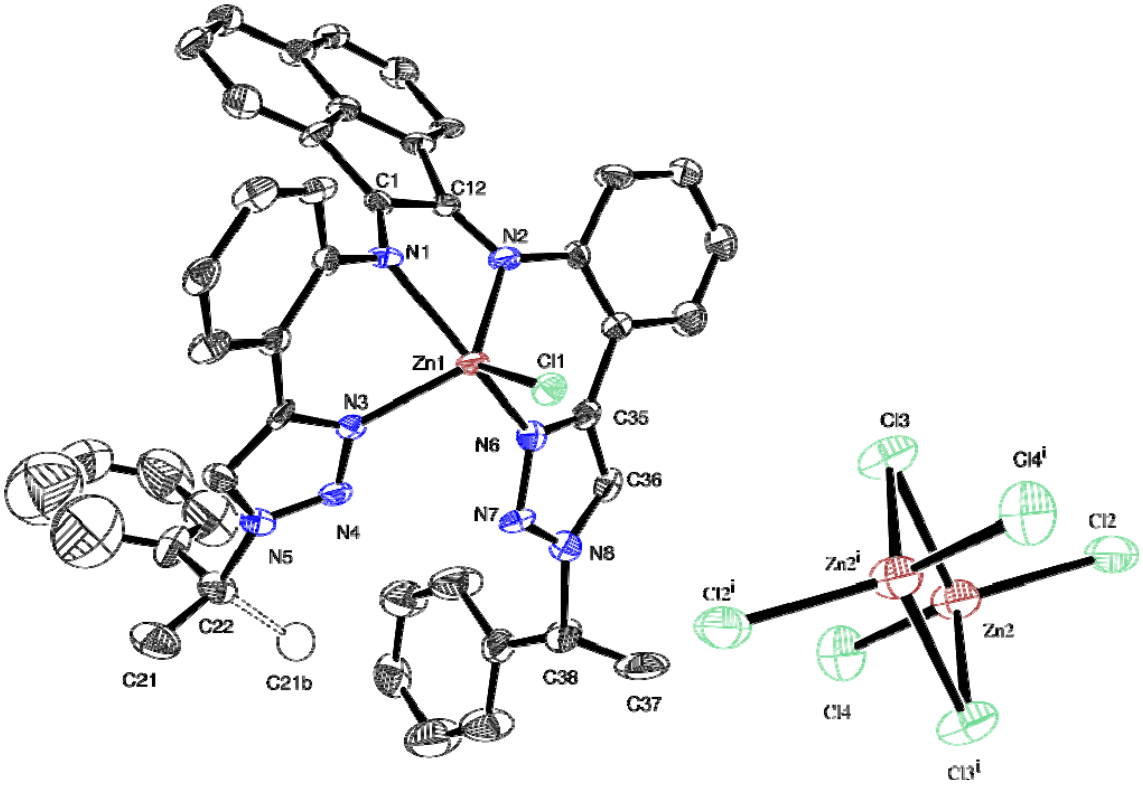

Fig. S3 ORTEP diagram of compound **2b** with 50% probability ellipsoid displacement. The remaining Zn cationic moiety, CH_2Cl_2 solvent molecules and all the hydrogen atoms are omitted for clarity.

Structure of $[ZnCl(ArN{=}C(An)\text{-}C(An){=}NAr)]^{+}[ZnCl_3{\cdot}CH_3CN]^{-}$

(Ar = 2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)phenyl) (4a)

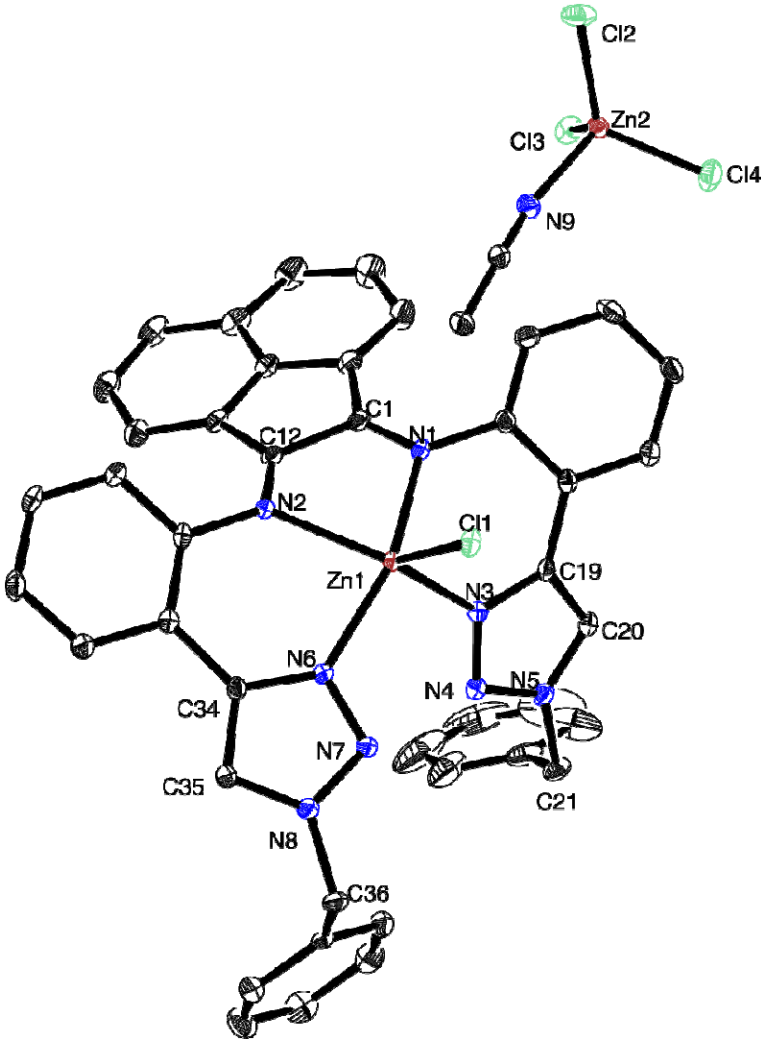

Fig. S4 ORTEP diagram of compound **4a** with 50% probability ellipsoid displacement. Two acetonitrile solvent molecules and all the hydrogen atoms are omitted for clarity.

Structure of $[ZnCl(ArN{=}C(An)\text{-}C(An){=}NAr)]^{+}[ZnCl_3{\cdot}CH_3CN]^{-}$

(Ar = 2-(1-phenyl-1*H*-1,2,3-triazol-4-yl)phenyl) (4c)

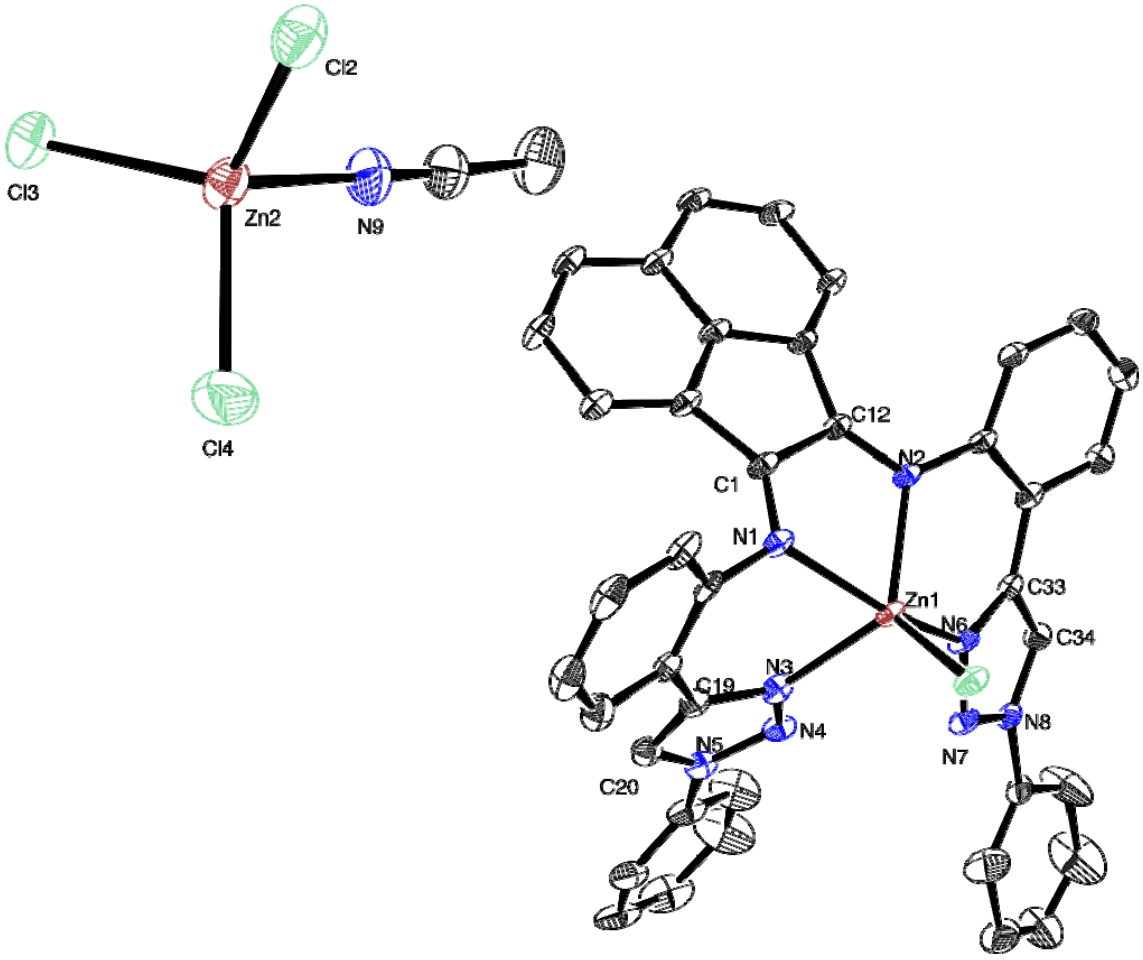

Fig. S5 ORTEP diagram of compound **4c** with 50% probability ellipsoid displacement. All the hydrogen atoms are omitted for clarity.

Discussion of the structures of the anionic counterparts of compounds 2b, 4a and 4c

The zinc anionic counterparts of compounds **2b**, **4a** and **4c** display tetrahedral geometries around Zn2 atoms (Figs. S3-S5). The $ZnCl_3^-$ anion exists in **2b** (and also in **2a** and **2c**) as a dinegative dimer ($[Zn_2Cl_6]^{2-}$) containing two bridging chlorine atoms, whereas in **4a** and **4c** (and also in **4b**) this dimeric nature is broken by the coordination of an acetonitrile molecule giving rise to the monoanionic species $[ZnCl_3(NCCH_3)]^-$). In both type of anions the corresponding bond distances and angles are comparable, being also similar to the values reported in the literature for these two types of anions.[2,3]

[2] (*a*) K. M. Doxsee, J. R. Hagadorn, T. J. R. Weakley, *Inorg.Chem.*, 1994, **33**, 2600-2606; (*b*) V. K. Bel'sky, N. R. Streltsova, B. M. Bulychev, P. A. Storozhenko, L. V. Ivankina, A.I. Gorbunov, *Inorg. Chim. Acta*, 1989, **164**, 211-220; (*c*) L. V. Ivakina, V. K. Belskii, N. R. Streltsova, P. A. Storozhenko, B. M. Bulychev, *J. Struct. Chem.*, 1989, **30**, 502-504; (*d*) J. Bremer, R. Wegner, B. Krebs, *Z. Anorg. Allg. Chem.*, 1995, **621**, 1123-1132; (*e*) M. Enders, G. Kohl, H. Pritzkow, *Organometallics*, 2002, **21**, 1111-1117; (*f*) A. Schneider, H. Vahrenkamp, *Z. Anorg. Allg. Chem.*, 2003, **629**, 2122-2126; (*g*) F. B. Johansson, A. D. Bond, C. J. McKenzie, *Inorg. Chem.*, 2007, **46**, 2224-2236.

[3] K. Yoshioka, H. Kikuchi, J. Mizutani, K. Matsumoto, *Inorg. Chem.*, 2001, **40**, 2234-2239.

Table S2. Crystal data and structure refinements for compounds **1a**, **1c**, **2b**, **3a, 4a**, **4c**, **5a**, **5c**, **6a** and **7a**.

Compounds	**1a**	**1c**	**2b**·$2CH_2Cl_2$	**3a**	**4a**·$2CH_3CN$	**4c**
Empirical formula	$C_{15}H_{14}N_4$	$C_{14}H_{12}N_4$	$C_{46}H_{37}Cl_8N_8Zn_2$	$C_{17}H_{16}N_4O$	$C_{48}H_{39}Cl_4N_{11}Zn_2$	$C_{42}H_{29}Cl_4N_9Zn_2$
Formula weight	250.30	236.28	1116.18	292.33	1042.44	932.28
Temperature (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	P-1	$P2_1/c$	P-1	P-1
a (Å)	14.720(3)	10.882(2)	13.339(4)	9.1248(13)	11.5240(2)	11.8970(10)
b (Å)	6.1010(10)	9.5745(19)	14.079(2)	19.257(2)	15.4750(3)	13.2519(12)
c (Å)	15.250(3)	11.431(3)	14.760(2)	8.5252(13)	15.8961(3)	15.2286(18)
α (º)	90	90	115.860(7)	90	109.561(2)	64.537(3)
β (º)	99.47(3)	100.539(7)	106.66(1)	100.611(9)	107.565(1)	73.910(6)
γ (º)	90	90	95.185(10)	90	101.401(1)	76.324(4)
V (Å^3)	1350.9(4)	1170.9(4)	2313.9(8)	1472.4(4)	2401.73(8)	2063.7(4)
Z	4	4	2	4	2	2
D_{calc} (Mg Å^{-3})	1.231	1.340	1.602	1.319	1.441	1.500
μ (mm^{-1})	0.077	0.084	1.543	0.086	1.268	1.464
F(000)	528	496	1132	616	1064	944
Crystal size (mm)	0.13×0.09×0.04	0.25×0.12×0.12	0.16×0.16×0.10	0.20×0.18×0.12	0.30×0.26×0.20	0.20×0.16×0.08
θ (º)	2.71-25.67	2.79-25.73	1.66-25.53	2.27-25.67	2.83-26.36	3.02-25.77
Index ranges	$-17 \le h \le 17$, $-7 \le k \le 7$, $-18 \le l \le 18$	$-13 \le h \le 10$, $-11 \le k \le 10$, $-11 \le l \le 13$	$-16 \le h \le 13$, $-16 \le k \le 16$, $-15 \le l \le 17$	$-11 \le h \le 11$, $-23 \le k \le 18$, $-10 \le l \le 10$	$-14 \le h \le 14$, $-19 \le k \le 18$, $-19 \le l \le 18$	$-14 \le h \le 14$, $-16 \le k \le 16$, $-15 \le l \le 18$
Reflections collected	11481	6774	21962	7051	27199	34985
Independent reflections	2539	2215	8406	2769	9760	7792
Reflections observed [$I>2\sigma(I)$]	1462	1143	3168	1820	7694	5682
R_{int}	0.041	0.068	0.126	0.045	0.035	0.047
GOOF	0.987	0.943	0.899	1.002	1.058	1.096
R_1 [$I>2\sigma(I)$]	0.044	0.068	0.085	0.048	0.036	0.051
wR_2 [$I>2\sigma(I)$]	0.105	0.172	0.195	0.098	0.091	0.143
R_1, wR_2 all data	0.094/0.118	0.145/0.203	0.247/0.236	0.085/0.109	0.051/0.087	0.071/0.152

Table S2. (cont.)

Compounds	**5a**	**5c**	**6a**·CH_3CN	**7a**
Empirical formula	$C_{42}H_{30}N_8$	$C_{40}H_{26}N_8$	$C_{44}H_{33}Br_2N_9Ni$	$C_{42}H_{30}Br_2N_8NiO_2$
Formula weight	646.74	618.69	906.32	897.24
Temperature (K)	150(2)	150(2)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	*P*-1	$P2_1/c$	*P*-1	*P*-1
a (Å)	9.264(3)	14.5150(18)	9.9100(12)	16.0297(17)
b (Å)	11.425(3)	11.7900(14)	15.452(2)	16.1944(17)
c (Å)	16.053(5)	18.222(2)	15.745(2)	17.5912(18)
α (º)	79.809(18)	90	109.997(8)	98.066(6)
β (º)	82.010(17)	101.602(5)	103.44(1)	97.010(10)
γ (º)	83.249(19)	90	94.450(8)	105.495(6)
V (Å^3)	1648.5(8)	3054.7(6)	2170.7(5)	4295.7(8)
Z	2	4	2	4
D_{calc} (Mg Å^{-3})	1.303	1.345	1.387	1.387
μ (mm^{-1})	0.080	0.083	2.329	2.355
F(000)	676	1288	916	1808
Crystal size (mm)	0.26×0.06×0.04	0.35×0.10×0.10	0.40×0.40×0.20	0.26×0.12×0.08
θ (º)	2.60-25.03	1.4-26.4	1.43-25.78	1.19-25.74
Index ranges	$-11 \le h \le 11$, $-13 \le k \le 13$, $-19 \le l \le 19$	$-18 \le h \le 18$, $-11 \le k \le 14$, $-22 \le l \le 22$	$-12 \le h \le 11$, $-18 \le k \le 17$, $0 \le l \le 19$	$-19 \le h \le 19$, $-19 \le k \le 19$, $-21 \le l \le 20$
Reflections collected	17711	23540	8154	58414
Independent reflections	5814	6232	8154	16079
Reflections observed [$I>2\sigma(I)$]	2349	3691	4784	9091
R_{int}	0.132	0.056	0.060	0.068
GOOF	0.832	0.947	0.944	0.938
R_1 [$I>2\sigma(I)$]	0.060	0.044	0.063	0.064
wR_2 [$I>2\sigma(I)$]	0.100	0.089	0.155	0.166
R_1, wR_2 all data	0.202/0.124	0.102/0.102	0.116/0.174	0.111/0.183

^{1}H NMR spectrum of a typical polynorbornenes obtained in this work

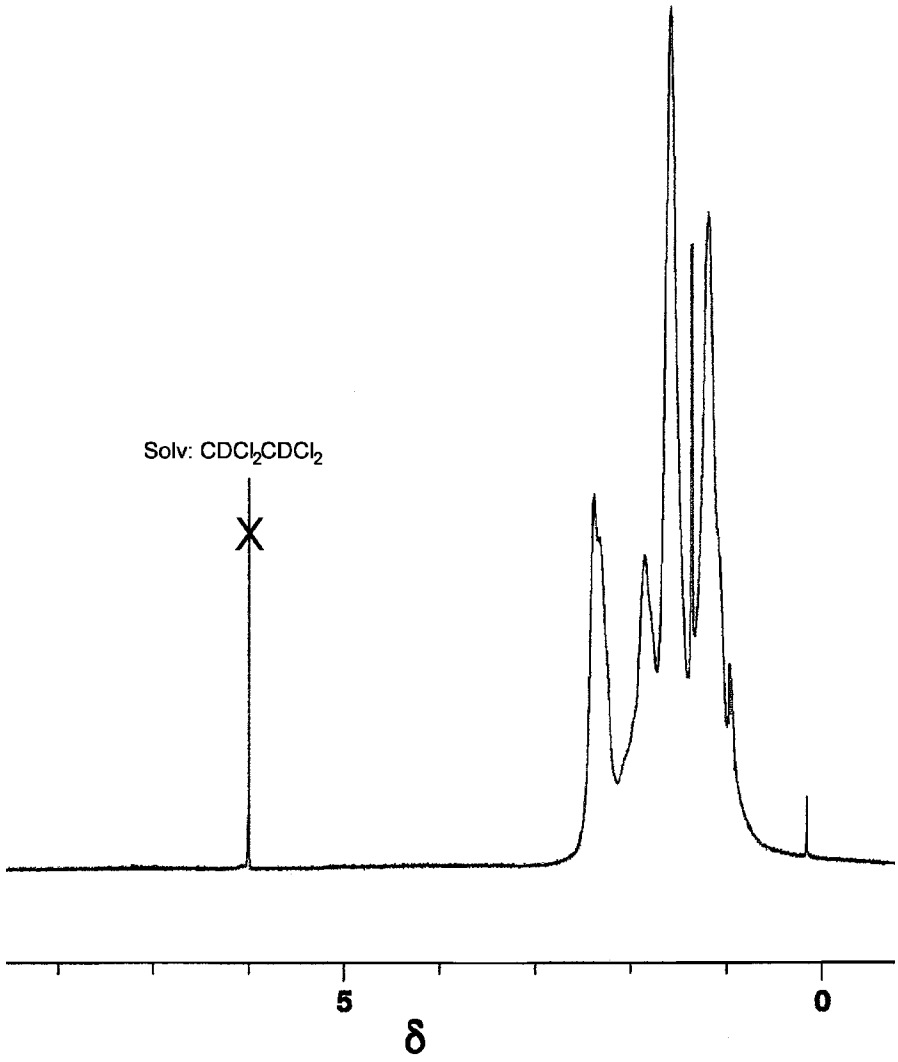

Fig. S6 ^{1}H NMR spectrum of a typical polynorbornene (300 MHz, in 1,1,2,2-tetrachloroethane-d_2, at 110 ºC) obtained in a polymerisation reaction catalysed by **6a-c**/MAO.