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Supporting information

Well-defined Phosphino-phenolate Neutral Nickel(II) Catalysts for Efficient (Co)polymerization of Norbornene and Ethylene

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Table S1. Crystal data and structure refinements of complexes **1**, **2**, **4**, **5**, **3-OH** and **3-Bis**.

	1	**2**	**4**	**5**	**3-OH**	**3-Bis**
Formula	$C_{28}H_{30}NNiOP$	$C_{30}H_{21}NONiPF_5$	$C_{51}H_{52}NiO_2P_2$	$C_{29}H_{38}N_2ONi$	$C_{25}H_{32}NO_2NiP$	$C_{40}H_{52}NiO_2P_2$
Formula weight	486.21	596.16	817.58	489.32	468.20	685.47
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	P_{21}/n	P_{21}/n	P2/C	P^{-1}	C_2/c	P^{-1}
a (Å)	10.4122(7)	14.0396(13)	13.2453(9)	8.7278(6)	31.683(3)	12.9127(13)
b (Å)	39.269(2)	13.6829(13)	11.7477(8)	11.8643(9)	10.7807(10)	13.303(2)
c (Å)	12.1425(8)	14.8362(14)	15.6869(8)	13.9859(10)	16.0669(15)	13.3881(13)
α (°)	90.00	90.00	90.00	94.9720(10)	90.00	98.806(2)
β (°)	90.9940(10)	111.474(2)	119.710(4)	99.1800(10)	115.753(2)	114.932(2)
γ (°)	90.00	90.00	90.00	108.4000(10)	90.00	107.871(2)
V ($Å^3$), Z	4964.1(6), 8	2652.2(4), 4	2120.0(2), 2	1342.00(17), 2	4942.8(8), 8	1875.6(4), 2
Density (Mg/m^3)	1.301	1.493	1.281	1.211	1.258	1.214
Absorpt. Coeff. (mm^{-1})	0.866	0.852	0.573	0.745	0.869	0.634
F (000)	2048	1216	864	524	1984	732
θ range (°)	1.76 to 25.04	1.71 to 26.03	1.73 to 26.04	1.49 to 26.03	2.02 to 25.05	1.70 to 26.03
Reflect. collected	28142	13917	15776	7238	13806	10458
Independ. Reflect.	8765(R_{int}= 0.0579)	5207 (R_{int}= 0.0303)	4170[Rint = 0.0172]	5145 (R_{int}= 0.0222)	4355 (R_{int}= 0.0701)	7291 [Rint = 0.0542]
Data/restraints/ parameters	8765/0/577	5207/0/352	4170/0/259	5145/0/298	4355/0/281	7291/0/418
Goof on F^2	1.039	1.054	1.024	1.091	1.000	0.973
R_1, wR_2	0.0572, 0.1293	0.0527, 0.1365	0.0404, 0.0936	0.0582, 0.1509	0.0521, 0.1053	0.0632, 0.1168
diff. Peak/hole (e $Å^{-3}$)	0.574/-0.476	0.761/-0.384	0.470/-0.207	0.492/-0.366	0.492/-0.278	0.479/-0.466

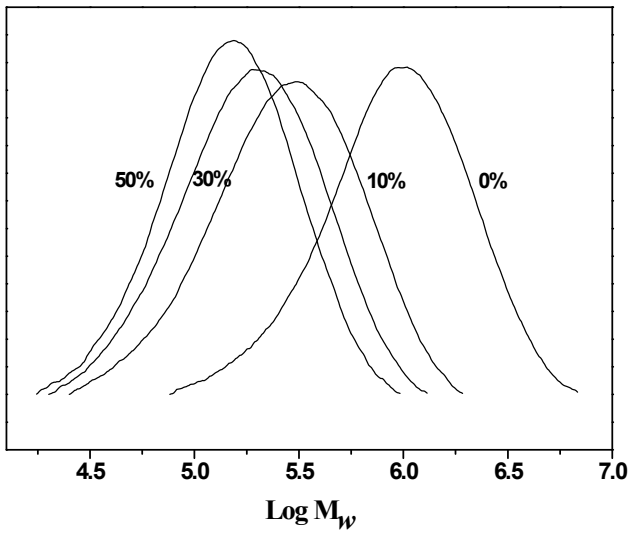

Figure S1. GPC spectrum of NB/NBC copolymers obtained (Entry 4-6 in Table 4 and Entry 3 in Table 1) by complex **2**

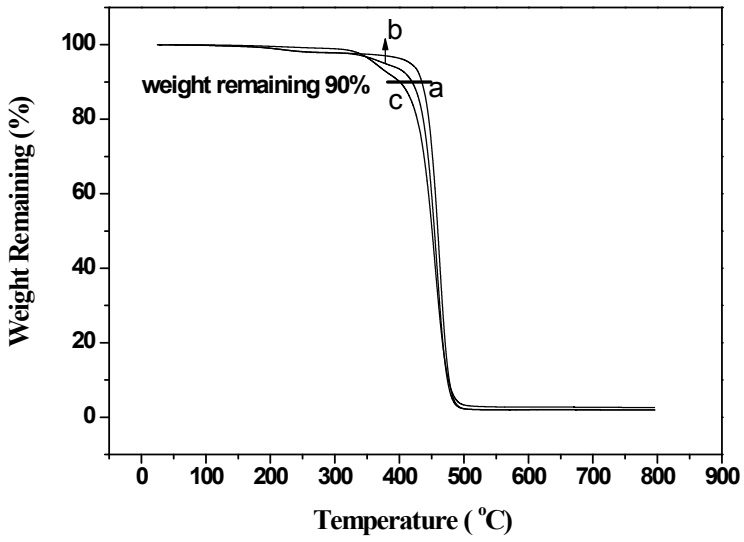

Figure S2. TGA curves of NB/NBA copolymers obtained (a: entry 3, Table 1, b: entry 3, Table 5, c: entry 4, Table 5) by complex **2**

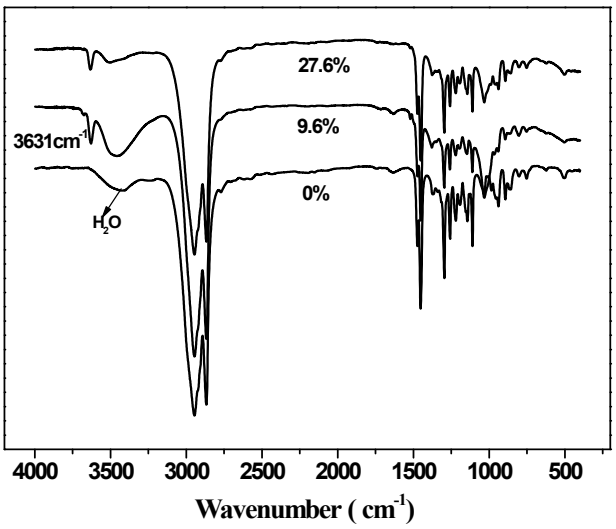

Figure S3. FTIR Spectra of NB/NBM copolymers obtained (entry 3,4 in Table 6 and entry 3 in Table 1) by complex **2**

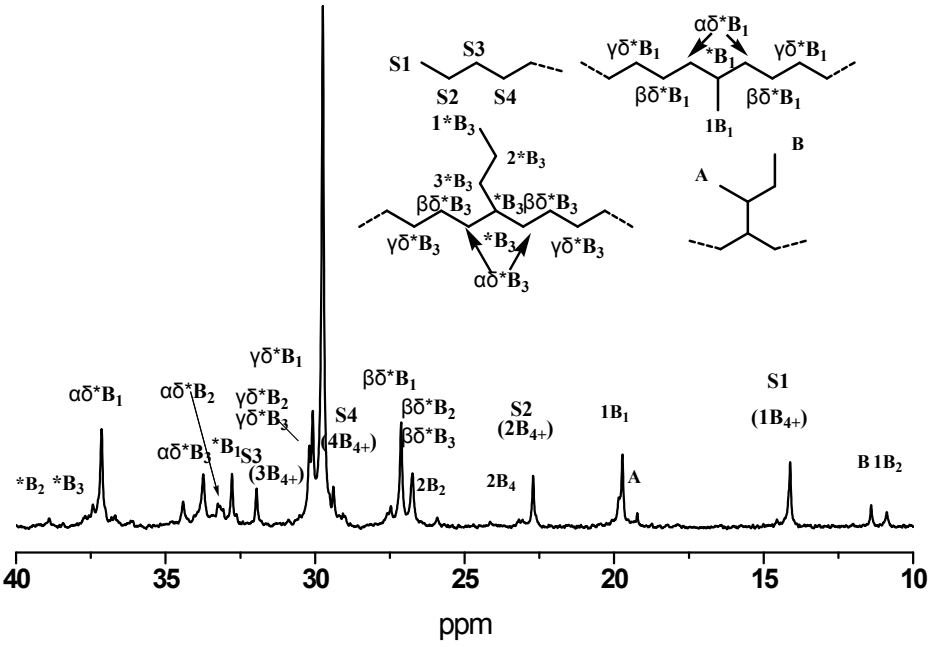

Figure S4. ^{13}C-NMR spectrum of the ethylene oligomers produced by salicylaldimine nickel complex **5**

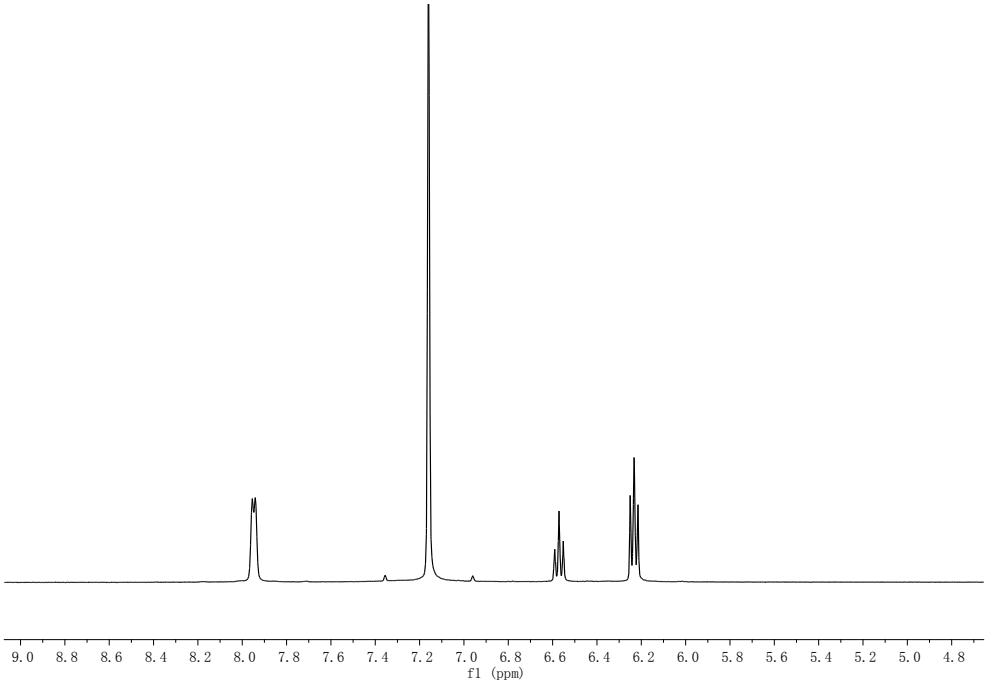

Figure S5. ^{1}H NMR of pyridine/B(C_6F_5)$_3$ adduct in C_6D_6

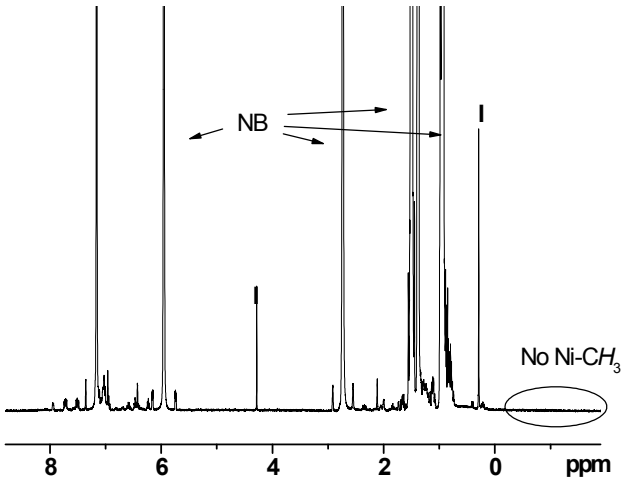

Figure S6. ^{1}H NMR spectrum of the mixture of complex **2** + the first nickel methyl species reacts with 400 equiv norbornene. 'I' signifies impurities dichloromethane and silicon grease.

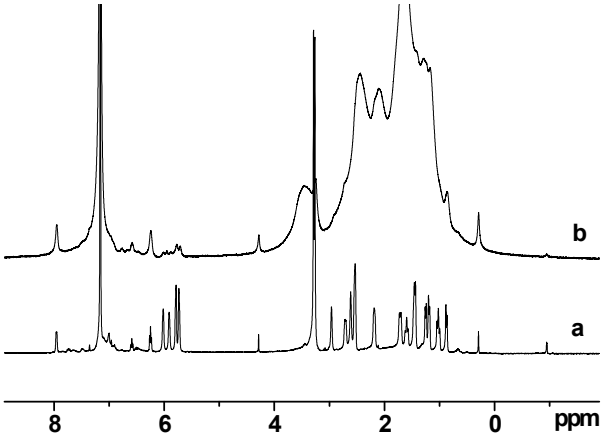

Figure S7. ^{1}H NMR spectra (in C_6D_6 at room temperature) of complex **2** + 4 equiv $B(C_6F_5)_3$ + 20 equiv NBC (a), and (a) + 100 equiv NB after heated at 60 ^{o}C for 15 min (b).

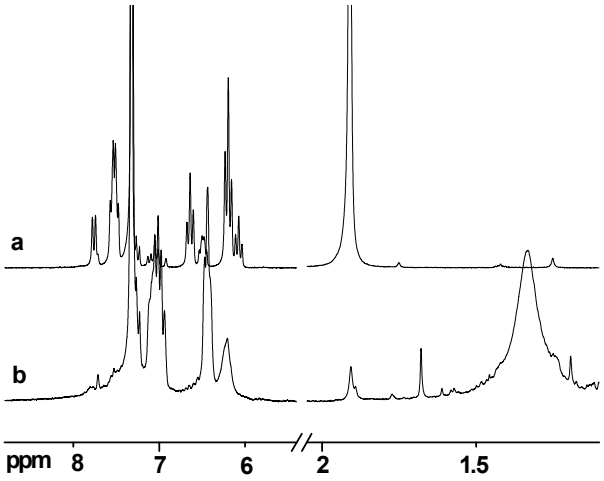

Figure S8. ^{1}H NMR spectra of a mixture of bisligated complex **4** with 6 equiv $B(C_6F_5)_3$ reacted at room temperature for 5 min (a), and heated (a) at 60 ^{o}C for 5 min (b).

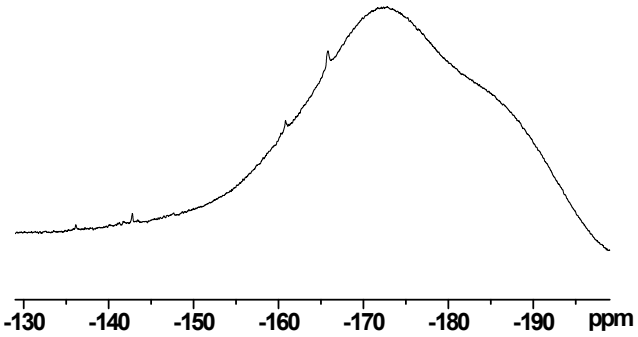

Figure S9. ^{19}F NMR spectrum (in $CDCl_3$ at room temperature, externally referenced to C_6F_6) of the low molecular weight polynorbornene prepared in the presence of ethylene using complex **1**/$B(C_6F_5)_3$ system.

Determination of reactivity ratios of NB and NBC using complex 1 + 4 equiv $B(C_6F_5)_3$

Entry	Cat. (μmol)	B/Ni (mol/mol)	NB/NBC (mol/mol)	time (min)	Incorp. (%)
1	0.5	4	6/4	10	10.7
2	0.5	4	5/5	20	15.9
3	0.5	4	4/6	20	23.1
4	0.5	4	3/7	240	31.5

The activity ratios of NB and NBC were calculated by kelen-tüdös method using catalyst **1** and 4 equiv $B(C_6F_5)_3$, the conditions were controlled to keep the monomer conversion lower than 10%. Activity ratios r_{NB} = 5.84 and r_{NBC} = 0.28 were determined, pointing to a random copolymerization.