Supporting information

Ultra-high molecular weight elastomeric polyethylene using an electronically and sterically enhanced nickel catalyst

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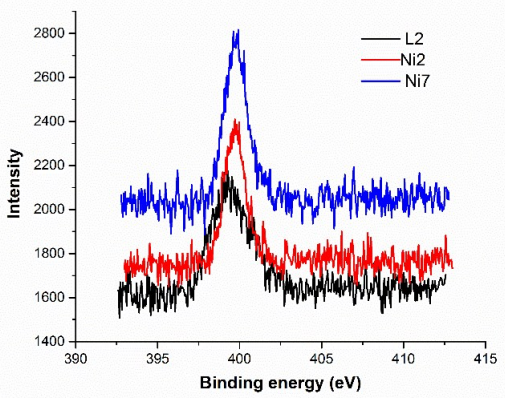


Figure S1. N (1s) core level spectra for **L2**, **Ni2** and **Ni7**

Table S1. Binding energies of the N (1s) and Ni (2p) levels in ligands and nickel complexes

	Binding energy (eV)	
	N (1s)	Ni (2p)
L1	398.67	–
Ni1	399.6	855.52
Ni6	399.72	855.66
L2	399.38	–
Ni2	399.72	856.02
Ni7	399.79	855.67
L3	399.28	–
Ni3	399.89	856.13
Ni8	399.74	856.39
L4	399.39	–
Ni4	399.88	856.23
Ni9	399.64	856.79
L5	399.39	–
Ni5	399.88	855.87
Ni10	399.54	856.23

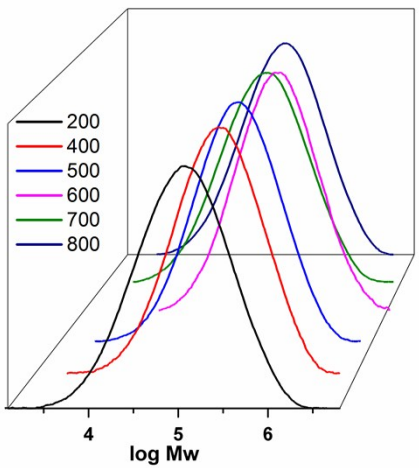


Figure S2. GPC curves of the polyethylenes obtained using **Ni1**/Et_2AlCl with different Al/Ni ratios (entries 4 in Table 2; 1–5 in Table 3).

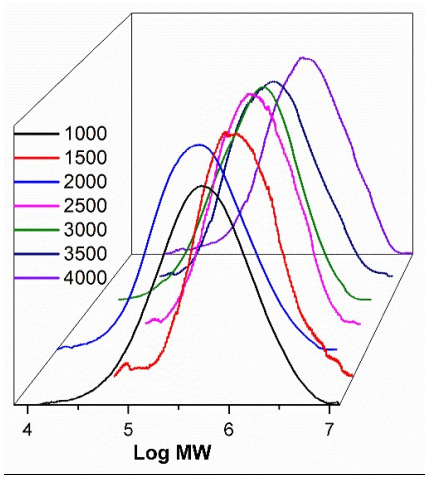


Figure S3. GPC curves of the polyethylenes obtained using **Ni1**/MMAO with different Al/Ni ratios (entry 2, Table 2; 1 – 6, Table 4).

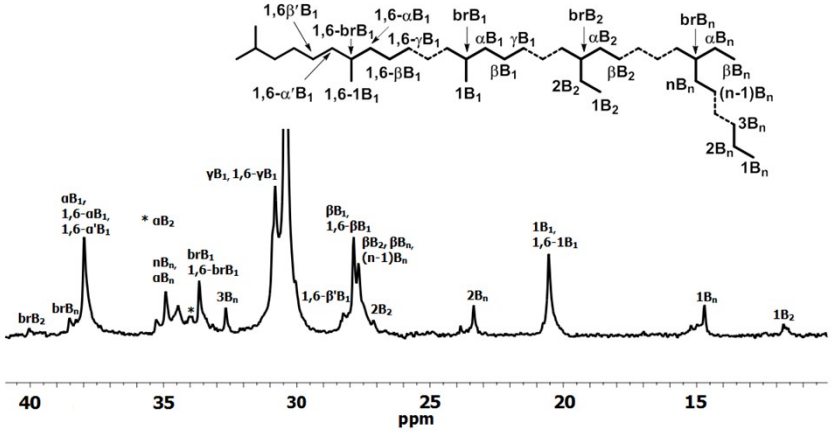


Figure S4. ^{13}C NMR spectrum of the polyethylene obtained using **Ni1**/MMAO at 50 °C (entry 9, Table 4).

Table S2. Branching analysis of the polyethylene sample obtained using **Ni1**/Et_2AlCl at 30 °C (entry 3, Table 3)

Peaks	Chemical shift	Integral exp.	Branching content		Relative Percentage
$1B_2$	11.31	1	N_M	9.46	54.67%
$1B_4$, $1B_5$, $1B_n$	14.27	3	N_E	1.05	6.09%
$1B_3$	14.77	0.77	N_P	0.84	4.85%
$1B_1$, 1,61B_1	19.86	9.96	N_B	1.58	9.13%
$2B_3$	20.33	1.23	N_A	0.84	4.85%
$2B_5$, $2B_n$	22.93	2.39	$N_{M(1,6)}$	1.46	8.44%
$2B_4$	23.42	0.57	N_L	2.07	11.96%
$2B_2$	26.69	1.12			
βB_2, βB_3, βB_4, βB_5, βB_n, (n-1)B_n	27.25	8.07	[E]	45.42	
βB_1, 1,6-βB_1, $4B_5$	27.44	11.34	[R]	17.35	100%
1,6β'B_1	27.83	2.92			
$3B_4$	29.53	2.56	Total Branches/1000C =		
4Bn	29.61	2.48	138		
δB_{1-n}	30.00	92.90			
γB_1, 1,6-γB_1	30.38	22.98			
$3B_n$	32.23	2.07			
$3B_5$	32.72	0.84			
brB_1, 1,6-brB_1	33.22	6.31			
αB_2	33.83	2.55			
$4B_4$	34.01	2.59			
αB_3, αB_4, $5B_5$, nB_n, αB_5, αB_n	34.49	7.49			
$3B_3$	36.94	0.84			
αB_1, 1,6-αB_1, 1,6-α'B_1	37.55	13.17			
brB_3	37.86	1.45			
$brB_{4,5,n}$	38.07	2.56			
brB_2	39.61	0.77			

Table S3. Branching analysis of the polyethylene sample obtained using **Ni1**/MMAO at 30 °C (entry 4, Table 4)

Peaks	Chemical shift	Integral exp.	Branching content		Relative Percentage
$1B_2$	11.31	1	N_M	7.35	52.57%
$1B_4$, $1B_n$	14.27	3.35	N_E	0.98	7.02%
$1B_1$, 1,6B_1	19.86	8.37	N_B	1.62	11.57%
$2B_n$	22.93	2.74	$N_{M(1,6)}$	1.56	11.16%
$2B_4$	23.42	0.73	N_L	2.47	17.67%
$2B_2$	26.69	1.01			
βB_2, βB_4,βB_n, (n-1)B_n	27.25	7.3	[E]	26.43	
βB_1, 1,6-βB_1,	27.44	8.91	[R]	13.98	100%
1,6β'B_1	27.83	3.12			
$3B_4$	29.53	4.6	Total Branches/1000C =		
δB_{1-n}	30.00	55.32	173		
γB_1, 1,6-γB_1	30.38	7.52			
γB_2, γB_4, γB_n	30.48	9.06			
$3B_n$	32.23	2.47			
brB_1, 1,6-brB_1	33.22	4.92			
αB_2	33.83	2.31			
$4B_4$	34.01	2.51			

αB_4, nB_n, αB_n	34.49	7.13
αB_1, 1,6-αB_1, 1,6-$\alpha' B_1$	37.55	11.0
$brB_{4,n}$	38.07	2.71
brB_2	39.61	0.78

Table S4. Branching analysis of the polyethylene sample obtained using **Ni1**/MMAO at 50 °C (entry 9, Table 4)

Peaks	Chemical shift	Integral exp.	Branching content		Relative Percentage
$1B_2$	11.31	1	N_M	6.45	62.54%
$1B_n$	14.27	2.31	N_E	1.00	9.75%
$1B_1$, $1,6B_1$	19.86	8.08	$N_{M(1,6)}$	0.96	9.27%
$2B_n$,	22.93	2.22	N_L	1.9	18.44%
$2B_2$	26.69	1.44			
βB_2, βB_n, $(n-1)B_n$	27.25	6.65	[E]	25.73	
βB_1, 1,6-βB_1	27.44	7.4	[R]	10.31	100%
$1,6\beta' B_1$	27.83	1.91			
δB_{1-n}	30.00	53.36	Total Branches/1000C =		
γB_1, 1,6-γB_1	30.38	19.57	142		
$3B_n$	32.23	1.90			
brB_1, 1,6-brB_1	33.22	4.86			
αB_2	33.83	2.29			
nB_n, αB_n	34.49	4.28			
αB_1, 1,6-αB_1, 1,6-$\alpha' B_1$	37.55	11.43			
brB_n	38.07	1.29			
brB_2	39.61	0.41			

Table S5 Selected data for various types of polyethylene and polypropylene

Polymer type	T_m (°C)	X_c (%)	M_w	Stress (MPa)	Strain (%)	Reference
PE-$30_{M/Ni3}$	53.4	10.7	30.8	13.22	843.9	This work
CPOE	80.7	14	1.15	13.62	845	*Polymer, 2015,* 80, 109.
LLDPE	120-125	40-60	-	30	500	*Prog. Polym. Sci.*, 2008, 33, 797.
LDPE	106-120	65-80	-	12-15	600	*Prog. Polym. Sci.*, 2008, 33, 797.
PP	90-130	10-16		16-25	400-800	*Coord. Chem. Rev.,* 2006, 250, 189 *Polymer Testing, 2005, 24,468–473*

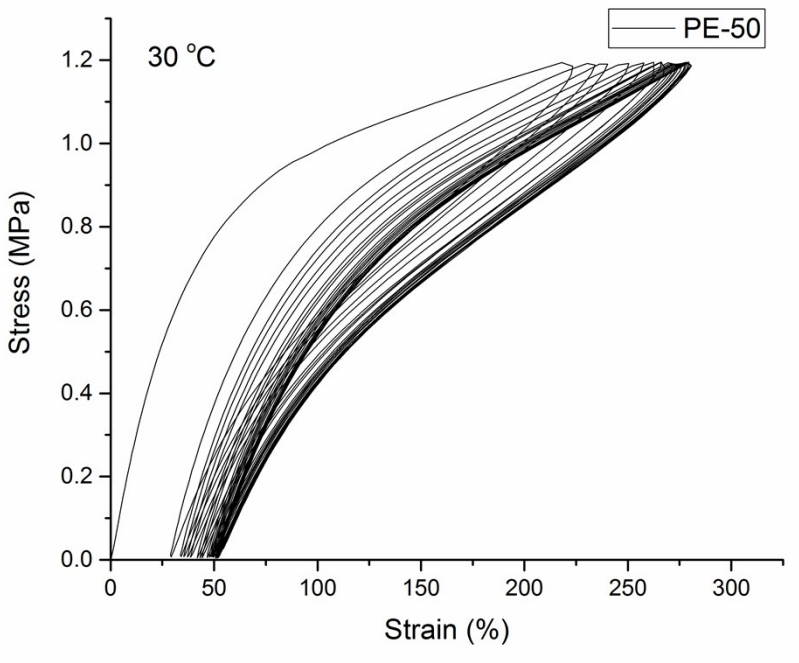


Figure S5. Elastic recovery curves for PE-50 performed at 30 °C (20 cycles)

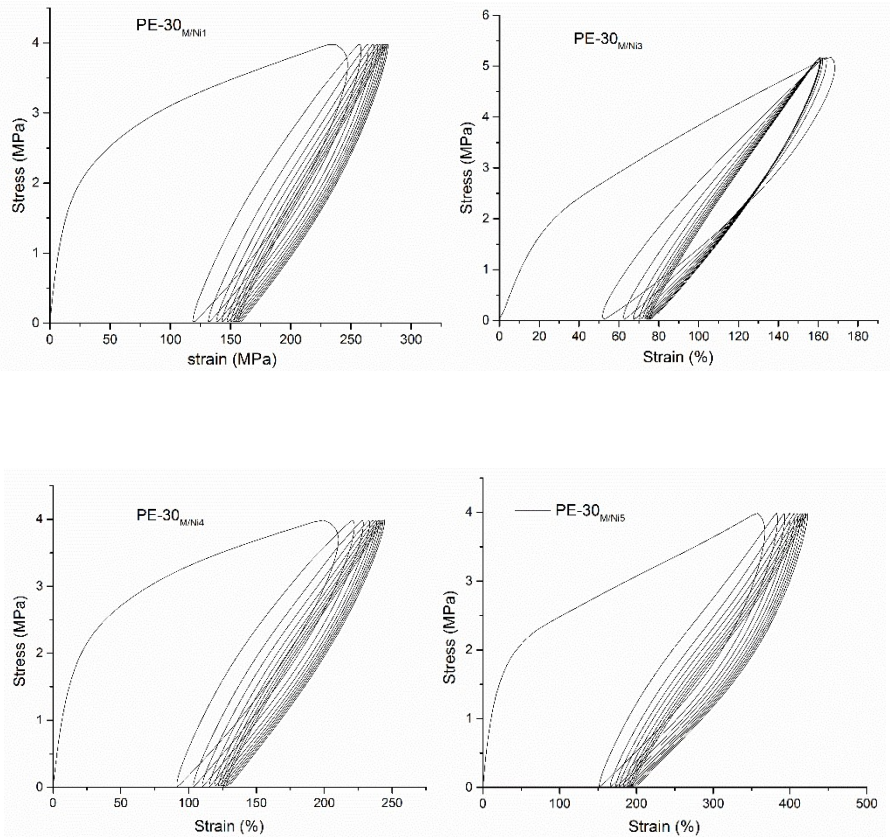
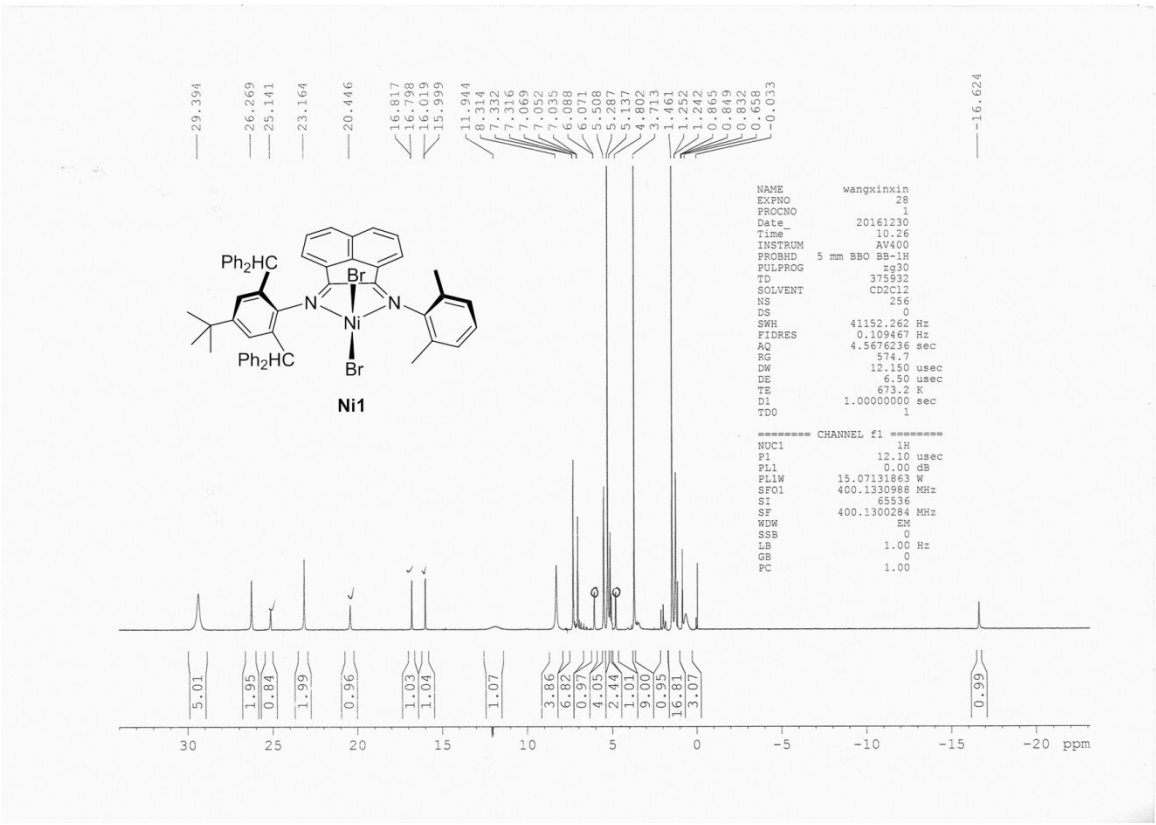
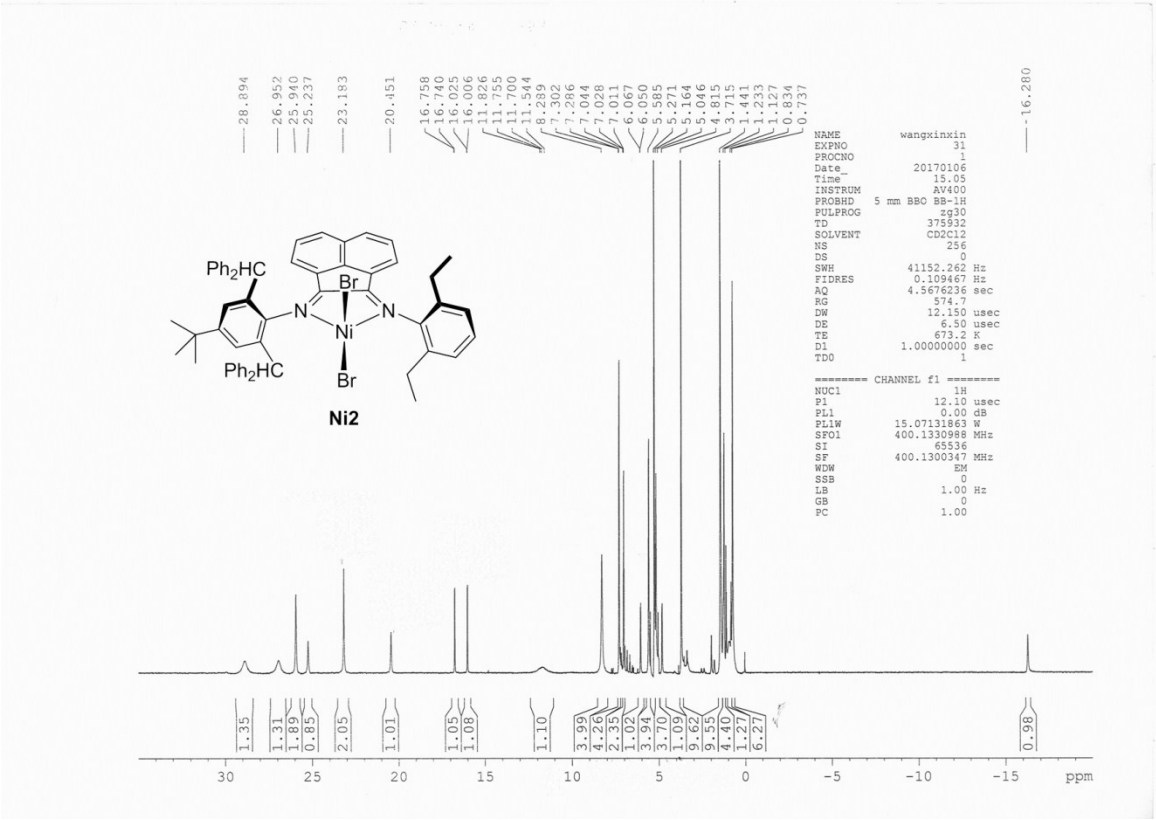
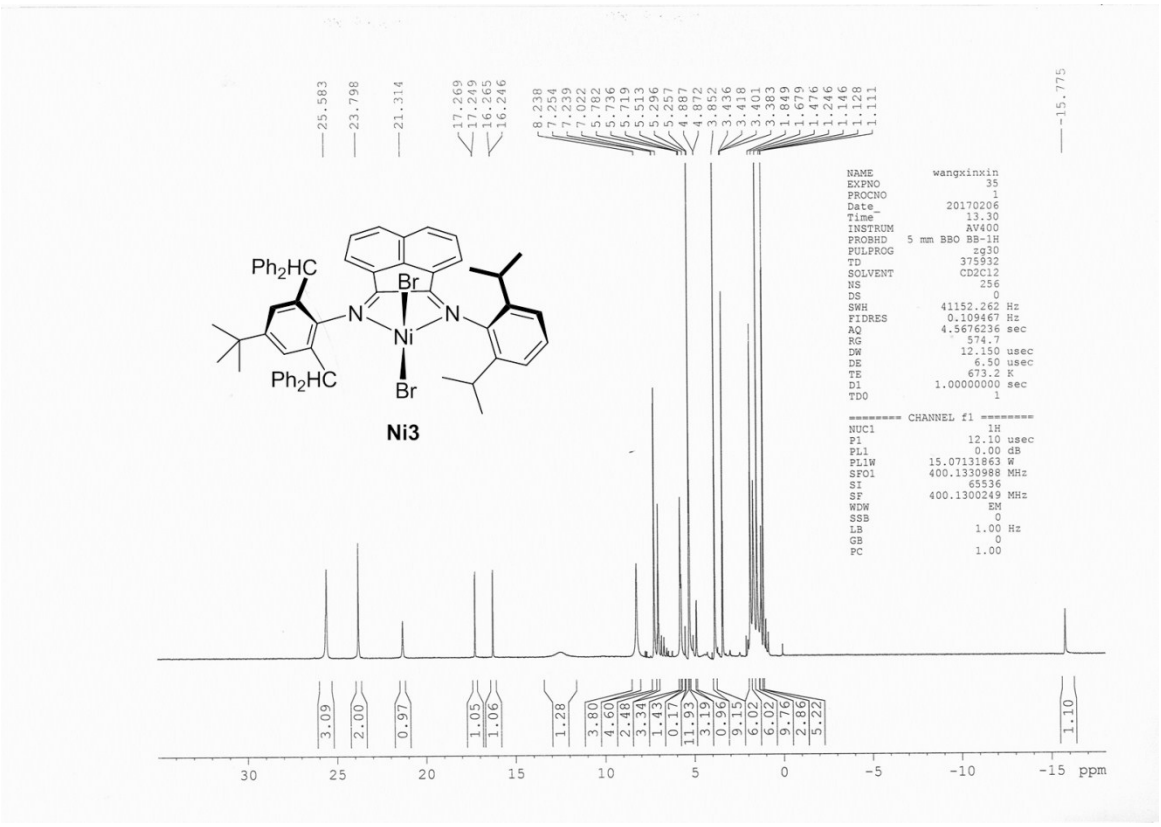


Figure S6. Elastic recovery curves for PE-$30_{M/Ni1}$, PE-$30_{M/Ni3}$, PE-$30_{M/Ni4}$ and PE-$30_{M/Ni5}$ performed at 30 °C (10 cycles).

^{1}H NMR spectra of **Ni1** - **Ni10** (recorded in CD_2Cl_2 at room temperature)



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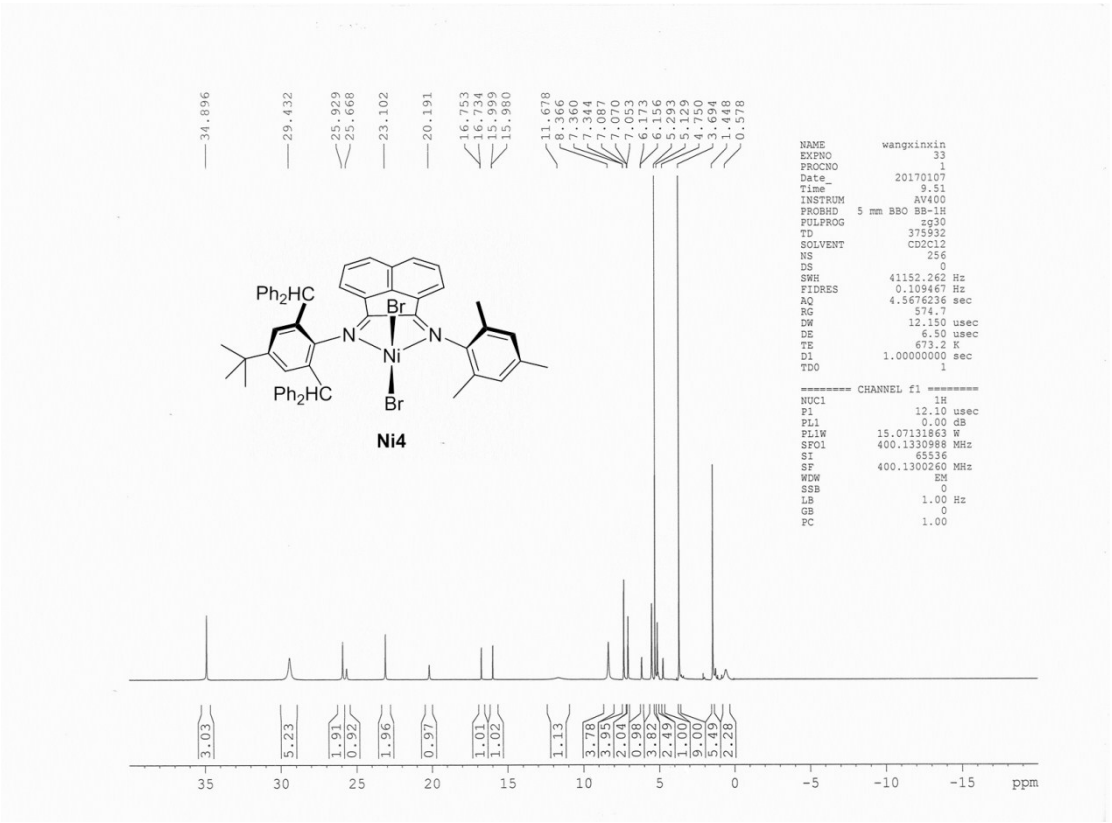
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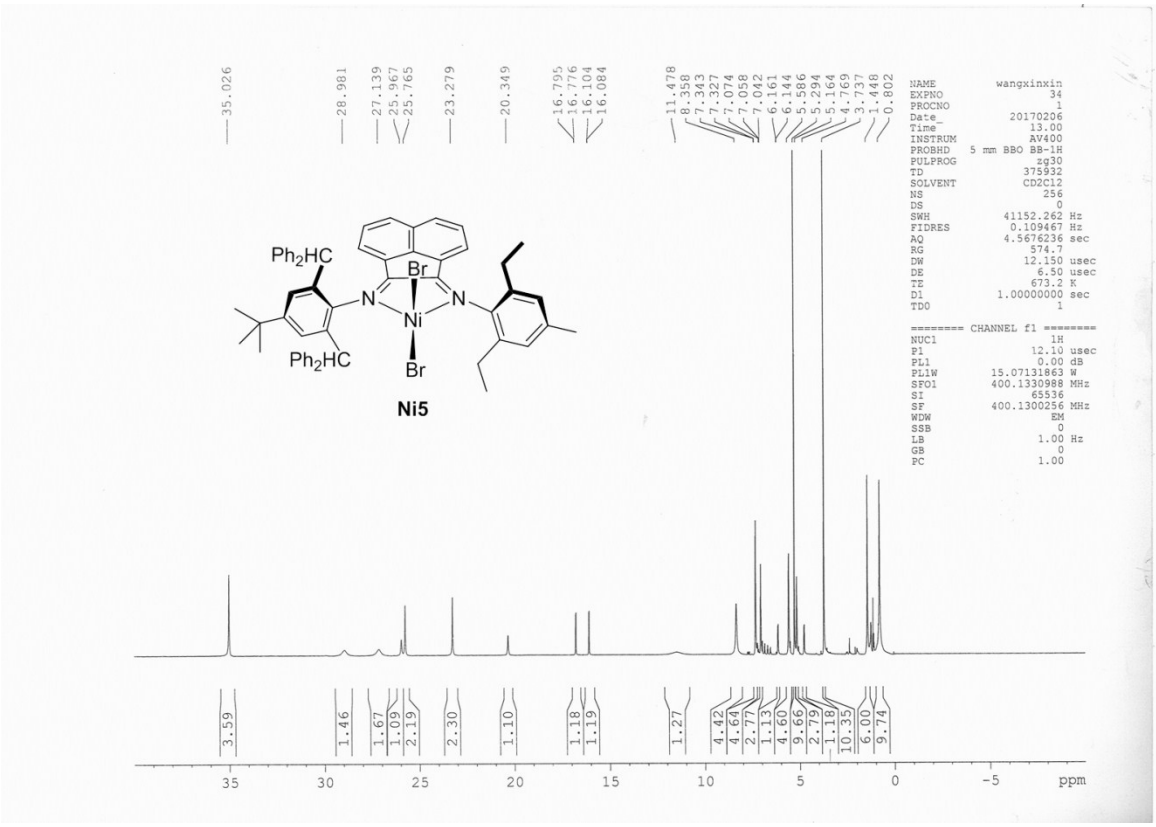
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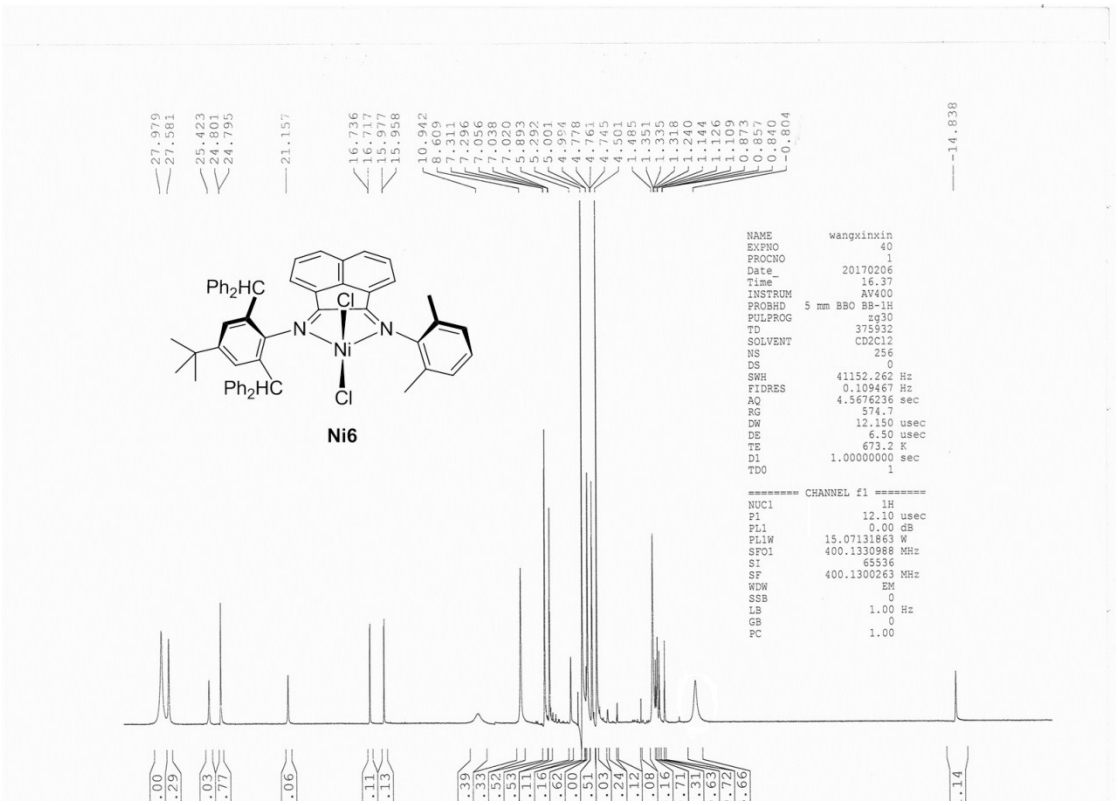
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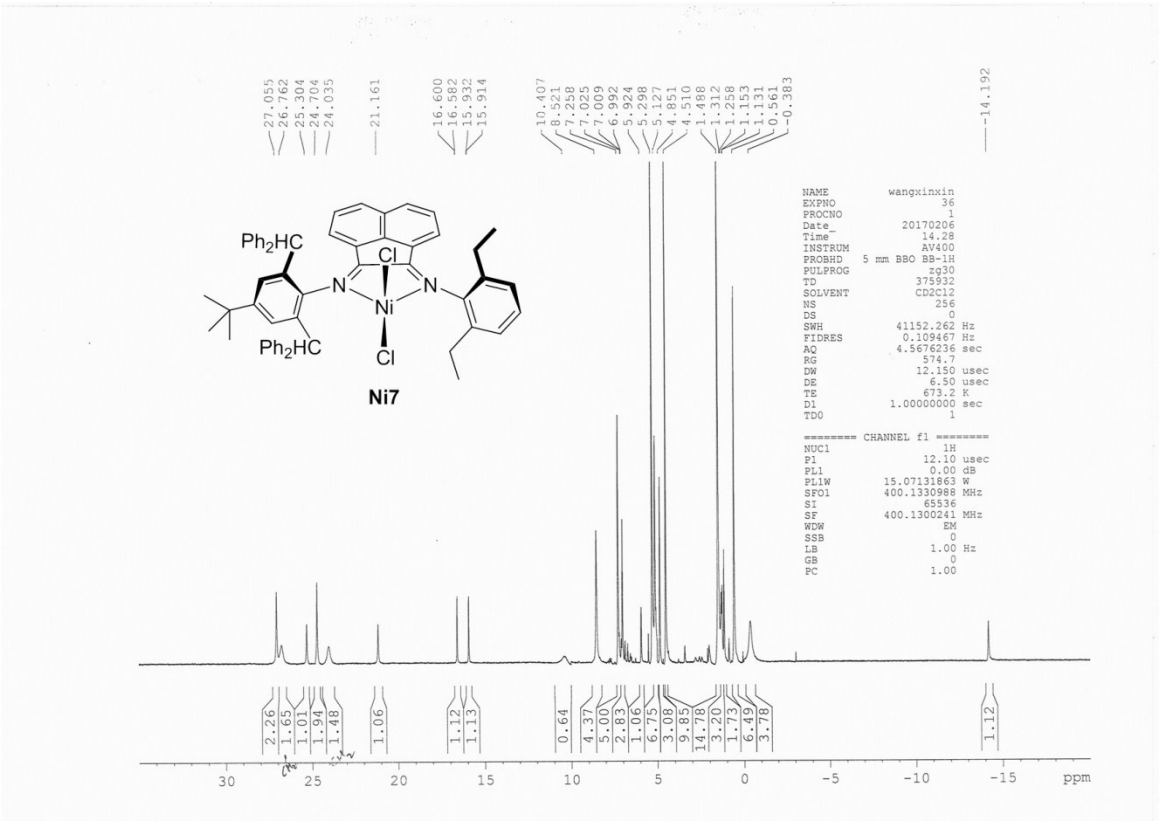
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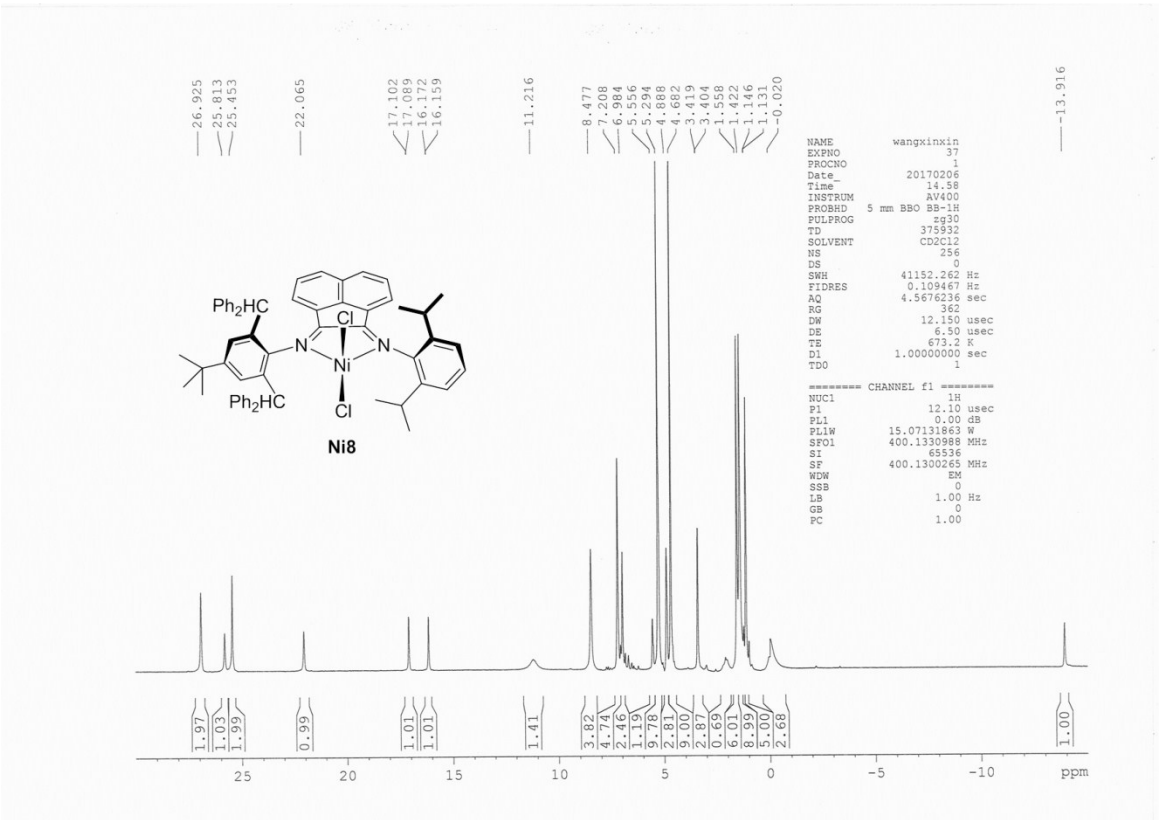
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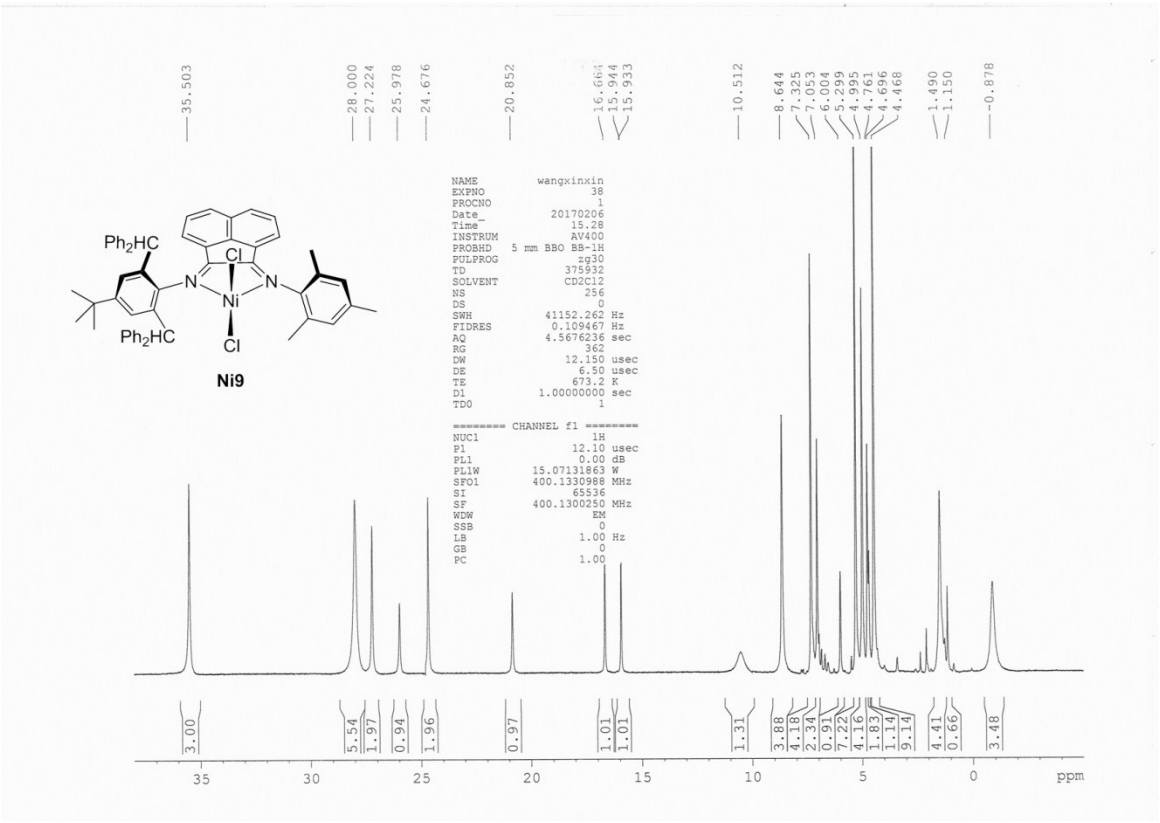
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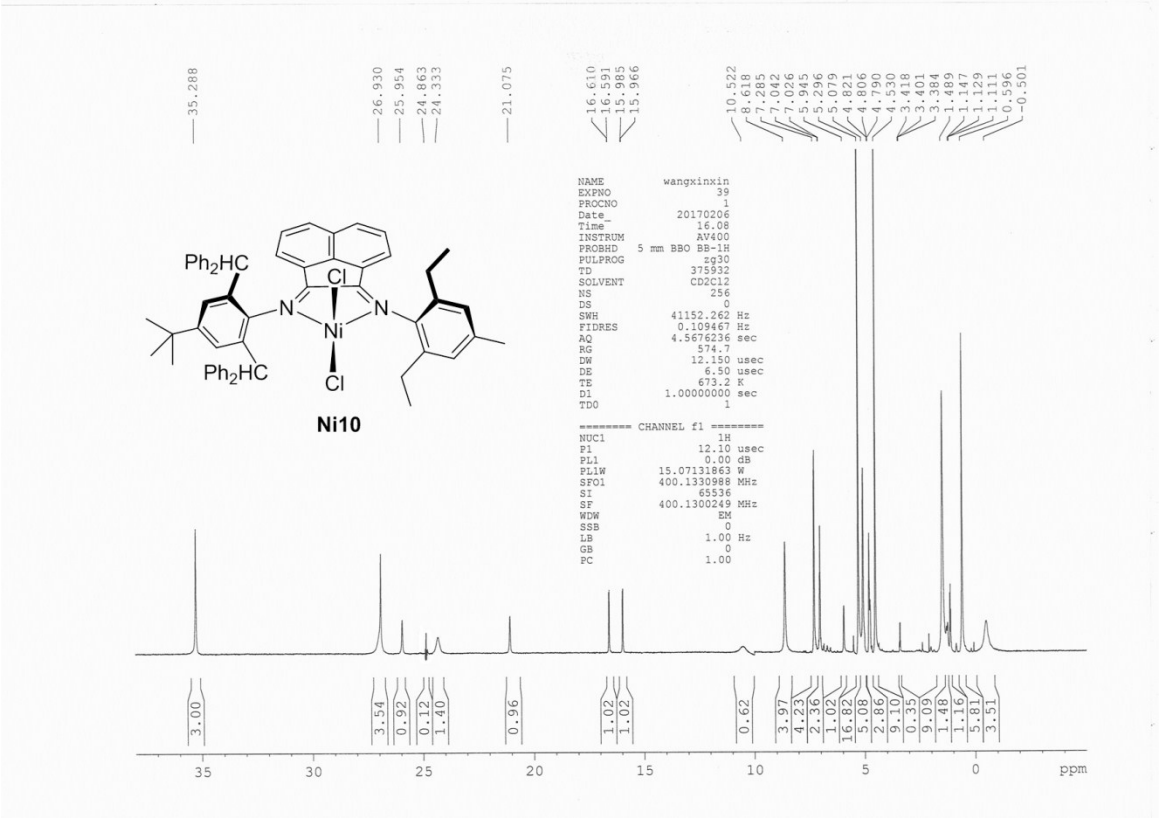
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ppm

Table S6. Crystal data and structure refinements for **Ni1**, **Ni2** and **Ni6**

	Ni1	**Ni2**	**Ni6**
Empirical formula	$C_{56}H_{48}Br_2N_2Ni$	$C_{58}H_{52}Br_2N_2Ni$	$C_{56}H_{48}Cl_2N_2Ni$
Formula weight	967.45	995.57	878.57
Temperature/K	173(2)	173(2)	173(2)
Wavelength/ Å	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	Trigonal
Space group	P 21/n	$P2_1$	R^{-3}
a/ Å	12.777(3)	10.452(2)	29.579(4)
b/ Å	19.699(4)	19.191(4)	29.579(4)
c/ Å	18.981(4)	12.944(3)	32.113(6)
Alpha/°	90	90	90
Beta/°	106.55(3)	91.09(3)	90
Gamma/°	90	90	120
Volume/ Å^3	4579.5(19)	2595.8(9)	24333(8)
Z	4	2	18
D_{calcd}/(g·cm^{-3})	1.403	1.2736	1.079
μ/mm^{-1}	2.208	1.950	0.491
F(000)	1984.0	1023.9	8280
Crystal size/mm	0.395 × 0.309 × 0.128	0.447 × 0.435 × 0.211	0.3330 x 0.1040 x 0.0520
θ Range (°)	3.92 to 54.96	5.06 to 54.96	1.017 to 27.469
Limiting indices	-16 ≤ h ≤ 16	-13 ≤ h ≤ 13	-38<=h<=38
	-25 ≤ k ≤ 25	-24 ≤ k ≤ 24	-38<=k<=38
	-24 ≤ l ≤ 24	-16 ≤ l ≤ 16	-41<=l<=40
No. of rflns collected	15274	27904	88188
No. unique rflns	10500	11768	12360
R(int)	0.0385	0.0366	0.0667
No. of params	555	623	555
Completeness to θ	99.9	X	99.6
Goodness of fit on F^2	1.139	1.040	1.099
Final R indices [I >2∑(I)]	R1 = 0.0464	R_1 = 0.0447	R1 = 0.0868
	wR2 = 0.1175	wR_2 = 0.1116	wR2 = 0.2477
R indices (all data)	R_1 = 0.0464	R_1 = 0.0491	R1 = 0.1011
	wR_2 = 0.1158	wR_2 = 0.1154	wR2 = 0.2621
Largest diff. peak, and hole/(e Å^{-3})	0.74/-0.46	1.05/-0.45	1.080/-0.893