Supporting Information for

Low-molecular weight and branched polyethylenes via ethylene polymerization by 9-(arylimino)-5,6,7,8-tetrahydrocycloheptapyridylnickel precatalysts

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Table of contents

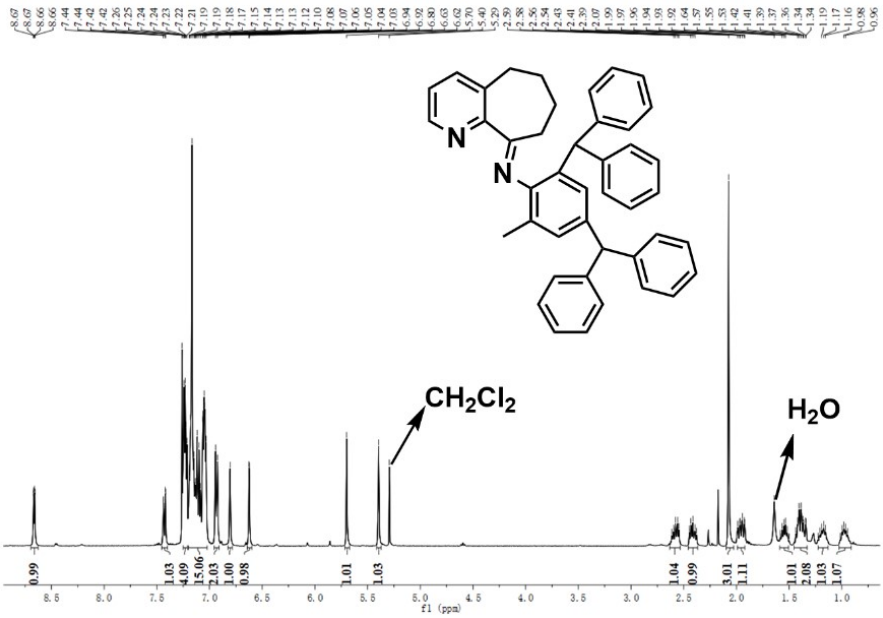

Figure S1. ^{1}H NMR spectrum of **L1**

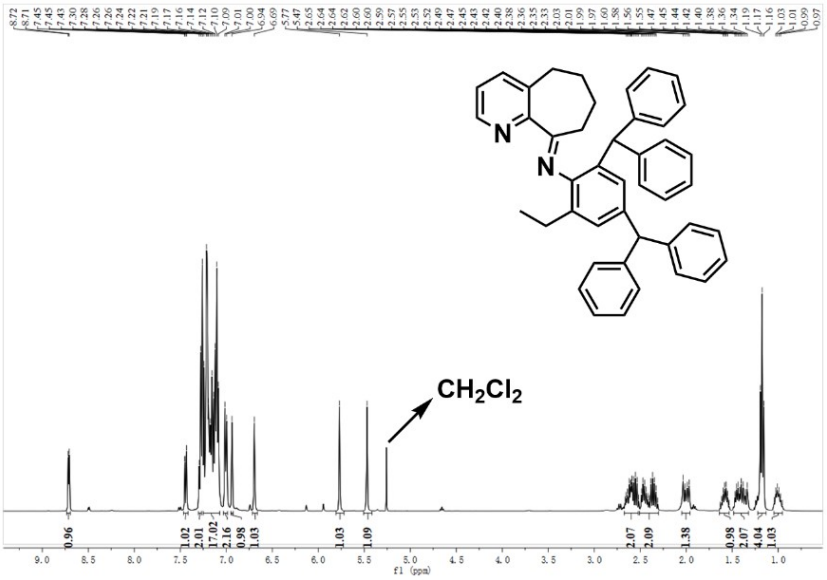

Figure S2. ^{1}H NMR spectrum of **L2**

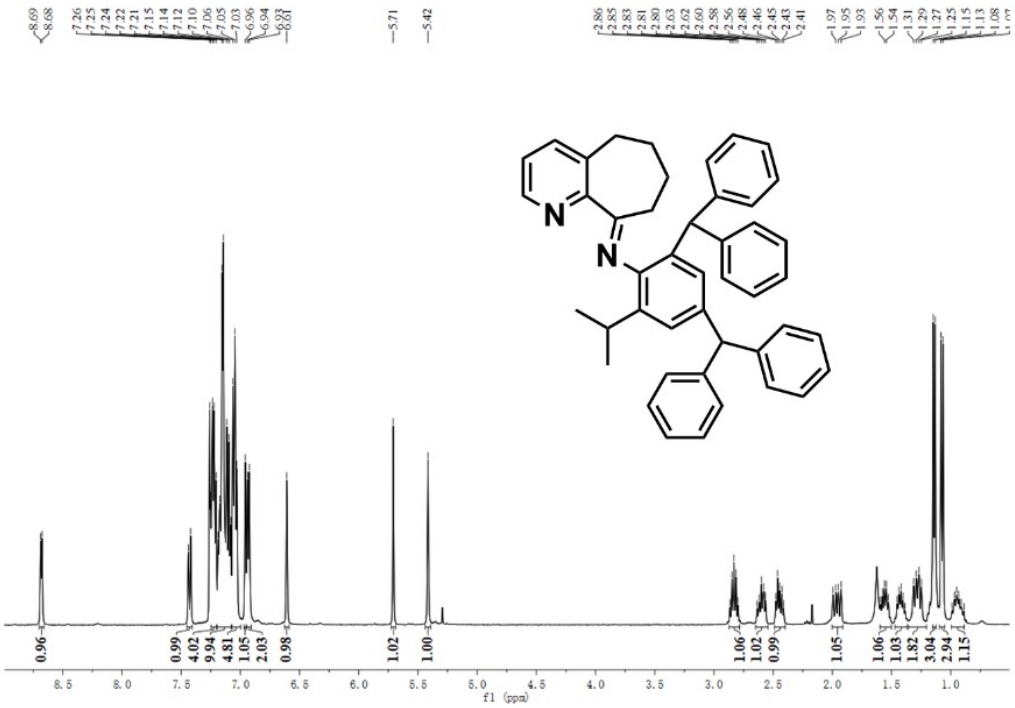

Figure S3. ^{1}H NMR spectrum of **L3**

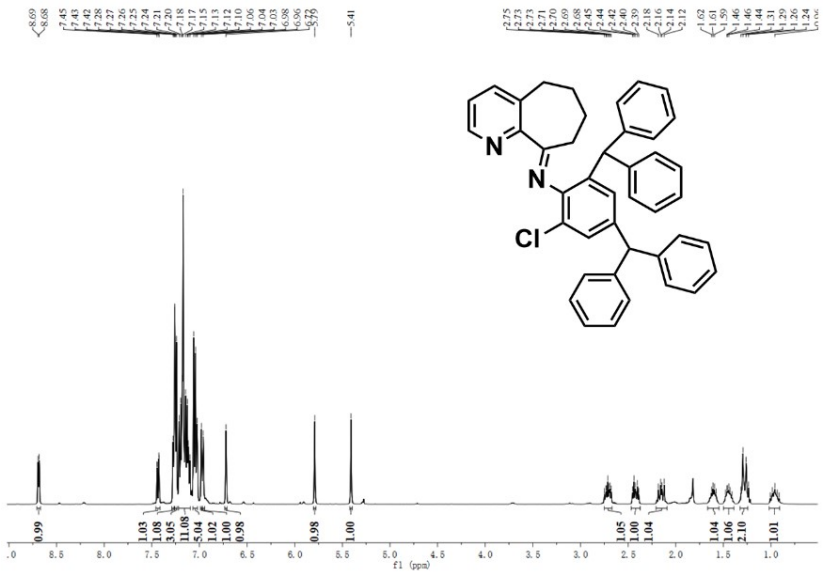

Figure S4. ^{1}H NMR spectrum of **L4**

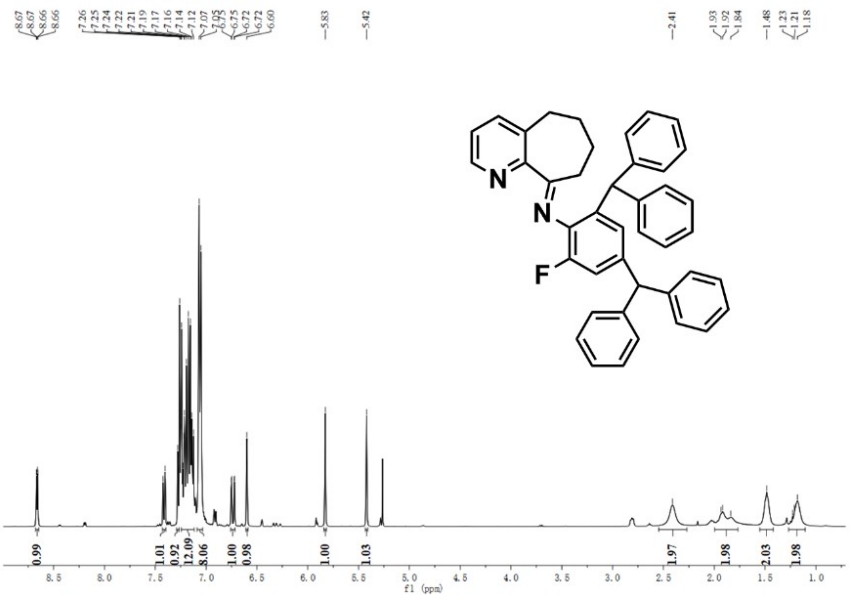

Figure S5. ^{1}H NMR spectrum of **L5**

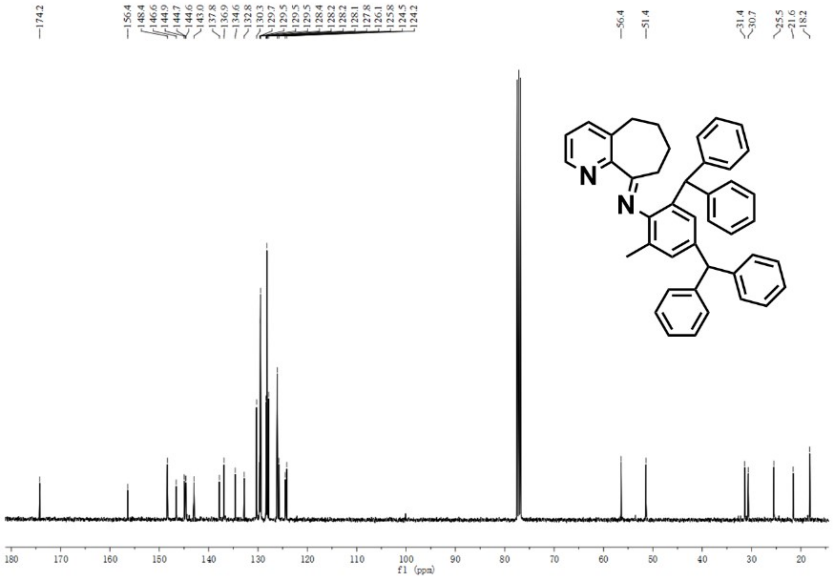

Figure S6. ^{13}C NMR spectrum of **L1**

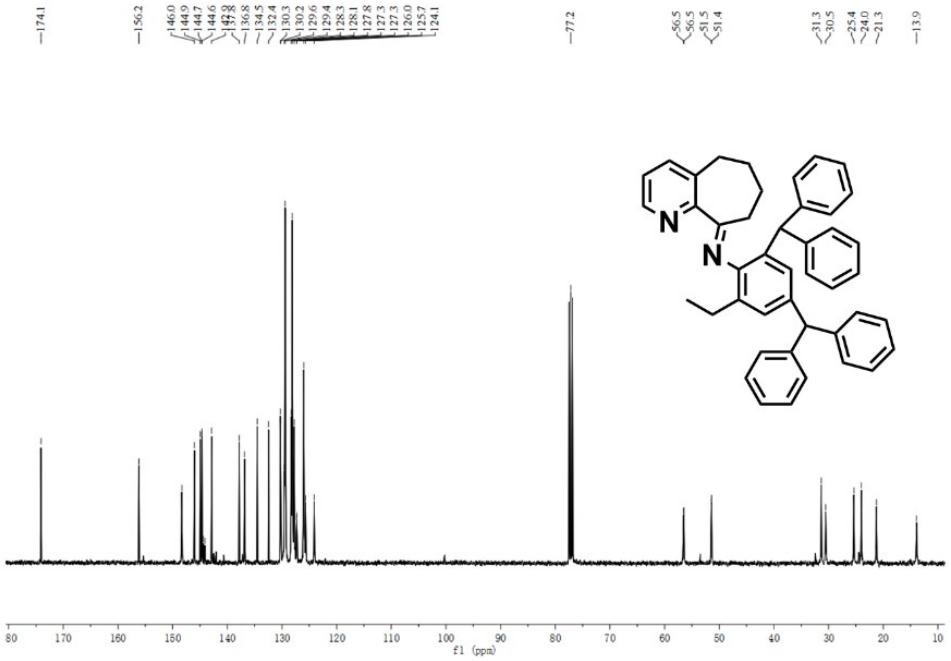

Figure S7. ^{13}C NMR spectrum of **L2**

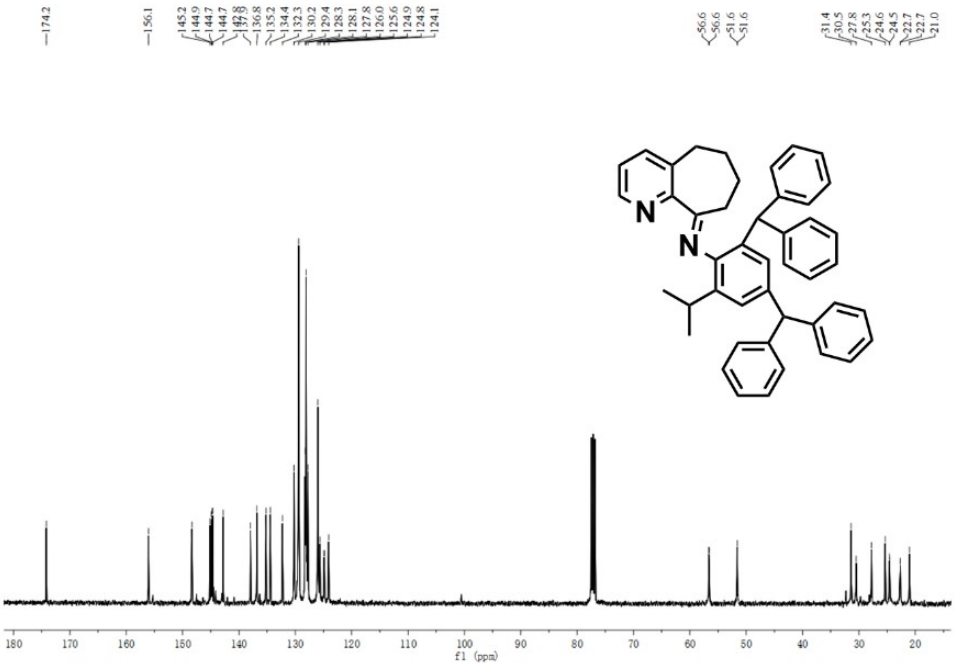

Figure S8. ^{13}C NMR spectrum of **L3**

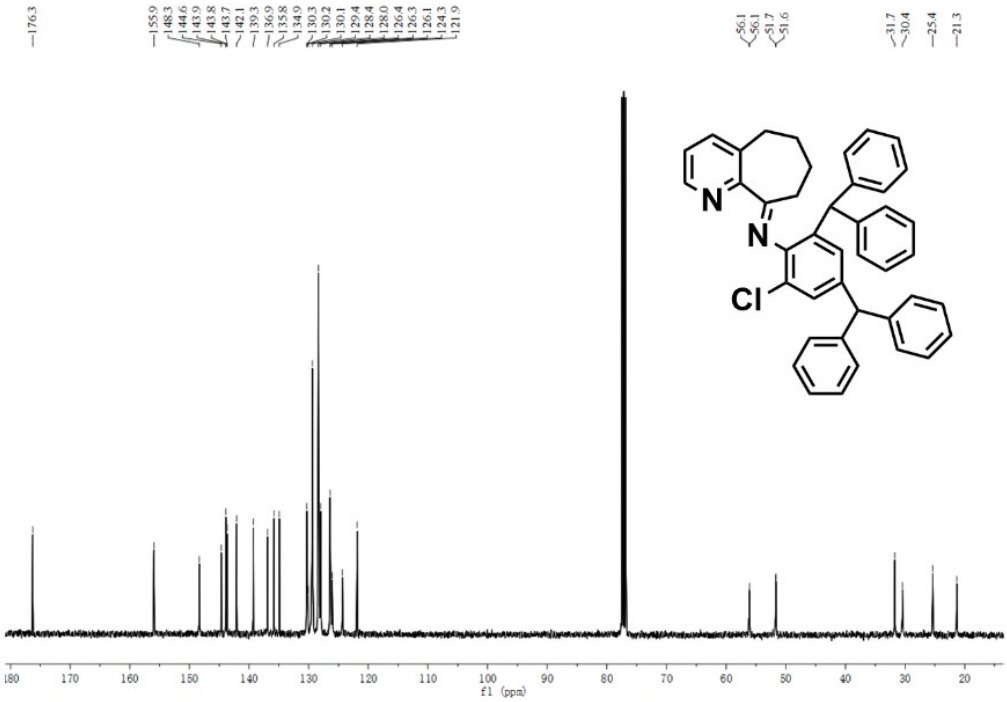

Figure S9. ^{13}C NMR spectrum of **L4**

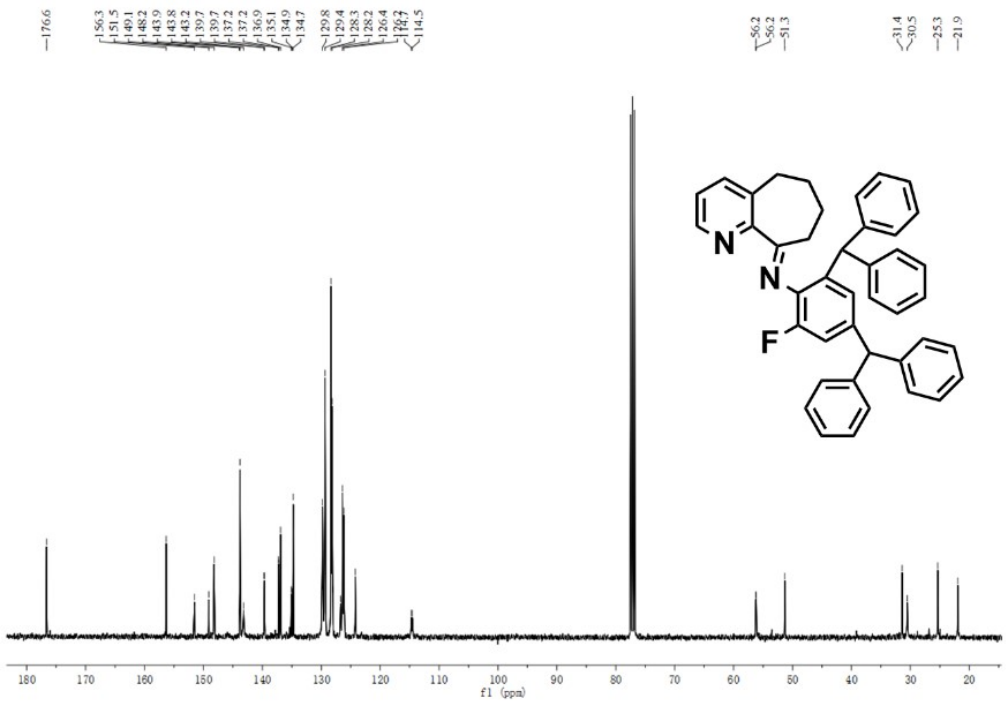

Figure S10. ^{13}C NMR spectrum of **L5**

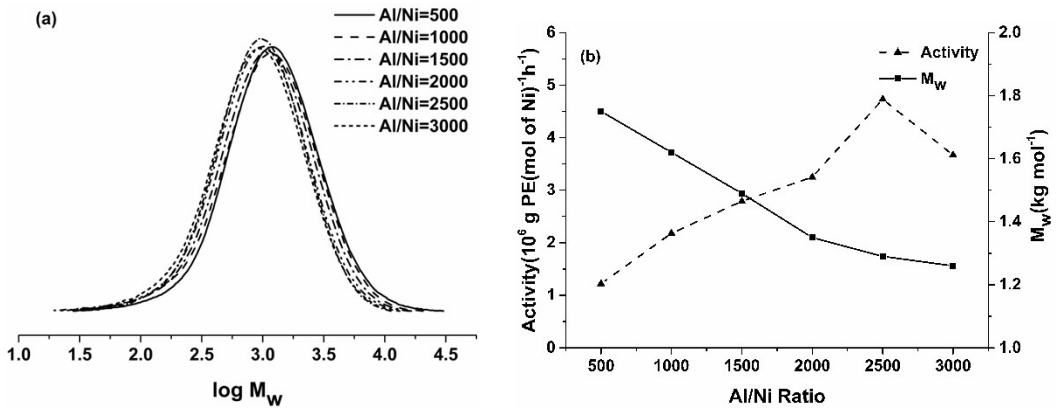

Figure S11. (a) GPC curves of the polyethylene produced using **Ni5**/MAO at different Al:Ni molar ratios; (b) the effects of Al/Ni molar ratios on catalytic activity and molecular weight of polyethylene (entries 1-6, Table 5).

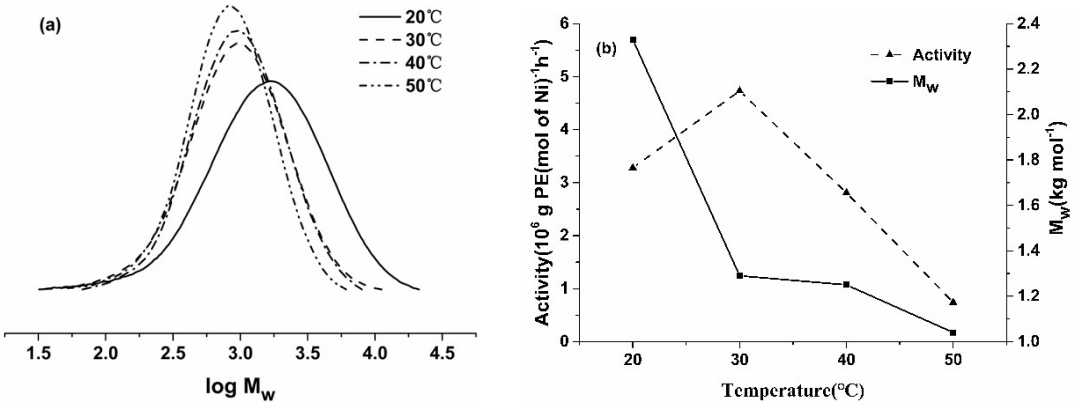

Figure S12. (a) GPC curves of the polyethylene produced using **Ni5**/MAO at different reaction temperatures; (b) the effects of reaction temperatures on catalytic activity and molecular weight of polyethylene (entries 5 and 7-9, Table 5).

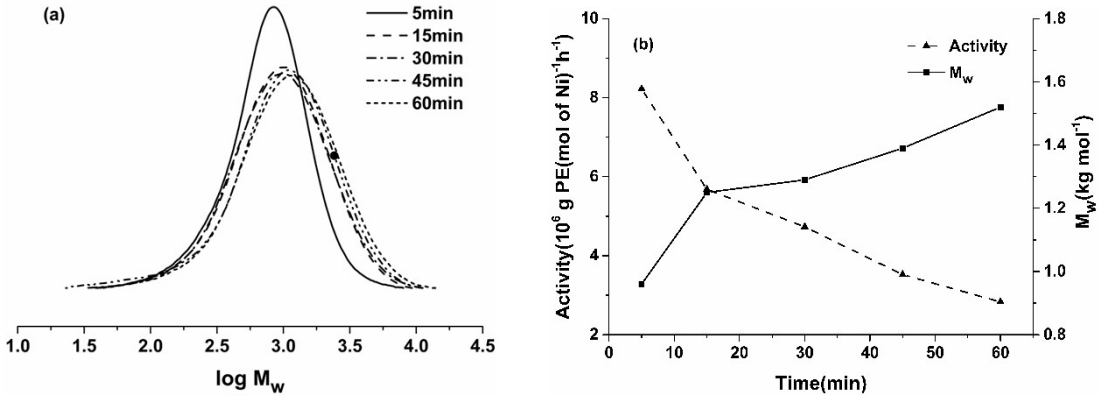

Figure S13. (a) GPC curves of the polyethylene produced using **Ni5**/MAO over different reaction times; (b) the effects of reaction times on catalytic activity and molecular weight of polyethylene (entries 5 and 10-13, Table 5).

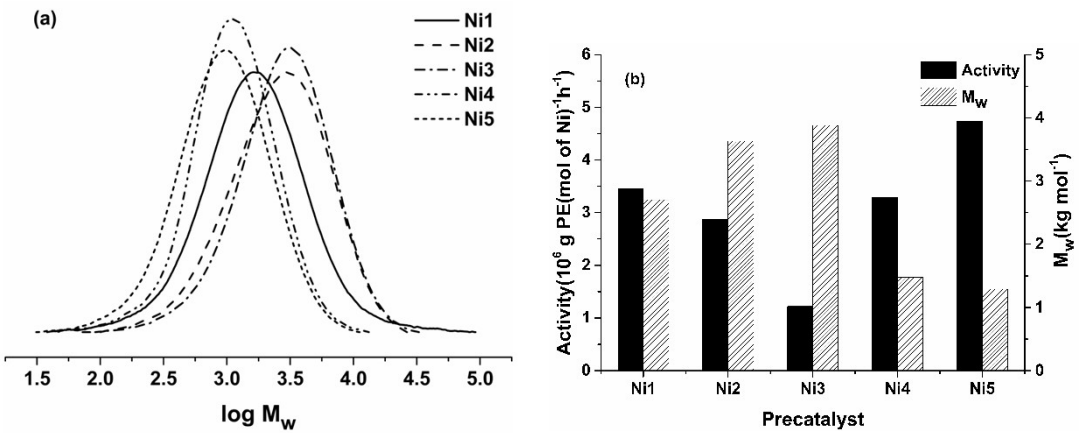

Figure S14. (a) GPC curves of the polyethylene; (b) the comparison trend of catalytic activity and molecular weight of polyethylene produced using **Ni1**-**Ni5** with MAO as the co-catalyst (entries 1-5, Table 6).

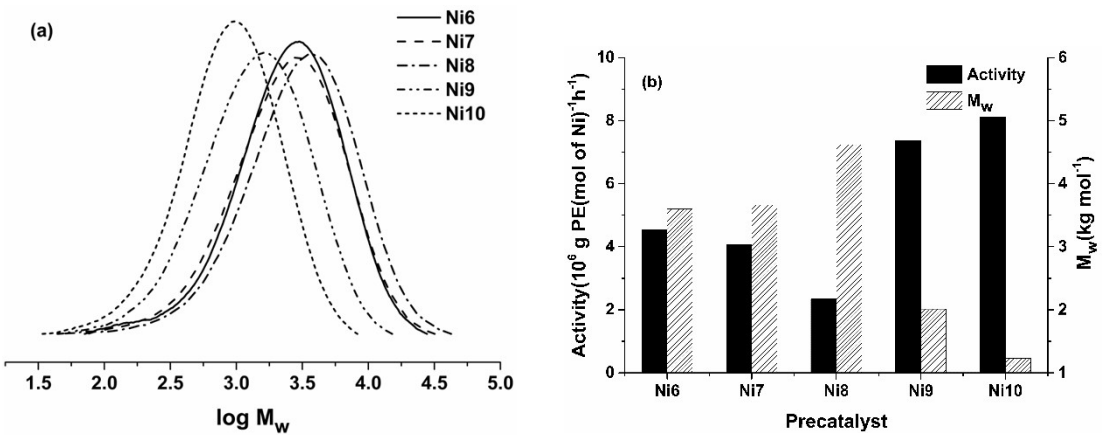

Figure S15. (a) GPC curves of the polyethylene; (b) the comparison trend of catalytic activity and molecular weight of polyethylene produced using **Ni6**-**Ni10** with MAO as the co-catalyst (entries 6-10, Table 6).

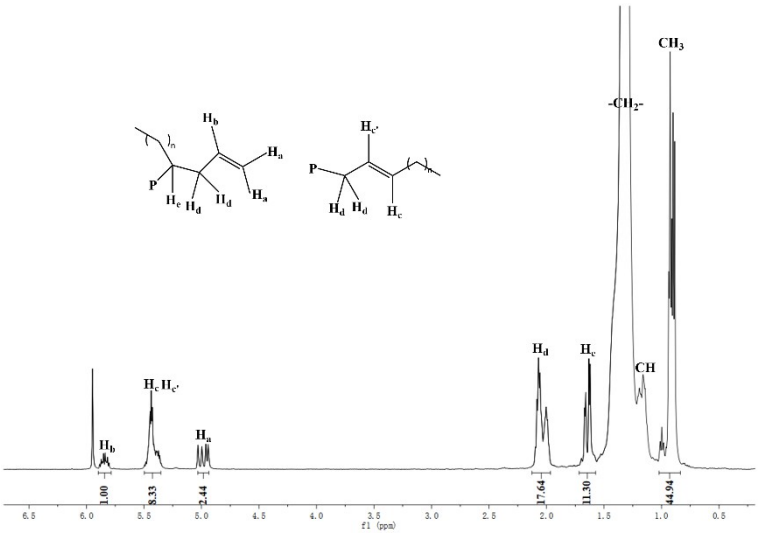

Figure S16. ^{1}H NMR spectrum of the polyethylene sample produced using **Ni5**/MAO at 30 °C (entry 5, Table 6), recorded at 110 °C in 1,1,2,2-tetrachloroethane-d_2.

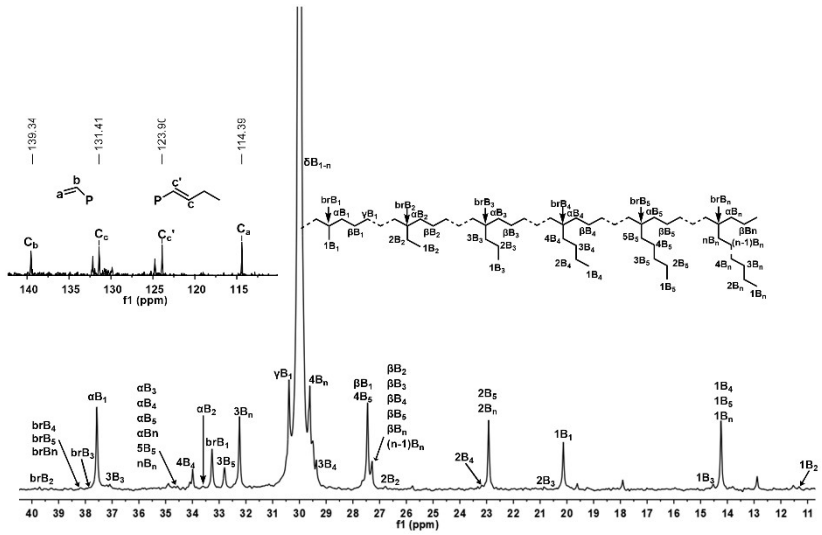

Figure S17. ^{13}C NMR spectrum of the polyethylene sample produced using **Ni5**/MAO at 30 °C (entry 5, Table 6) along with an inset showing the δ 114-140 region and a segment of the assigned polymer backbone, recorded at 110 °C in 1,1,2,2-tetrachloroethane-d_2.

Table S1. Crystal data and structure refinement for **Ni3** and **Ni4**

	Ni3	**Ni4**
Crystal colour	yellow	orange
Empirical formula	$C_{45}H_{42}Br_2N_2Ni$	$C_{43}H_{37}Br_2Cl_3N_2Ni$
Formula weight	829.33	906.62
Temperature/K	169.99(10)	169.99(10)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	I2/a
a/Å	17.1583(5)	24.1230(2)
b/Å	22.9892(6)	10.94452(8)
c/Å	9.3758(3)	30.6237(3)
α/°	90	90
β/°	93.252(3)	107.5690(10)
γ/°	90	90
Volume/Å^3	3692.38(19)	7707.96(12)
Z	4	8
ρ_{calc} g/cm^3	1.492	1.563
μ/mm^{-1}	3.551	5.326
F(000)	1696.0	3664.0
Crystal size/mm^3	0.15 × 0.08 × 0.05	0.25 × 0.2 × 0.18
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range	5.158 to 154.044	6.054 to 154.376
Index ranges	-21 ≤ h ≤ 21	-30 ≤ h ≤ 25
	-12 ≤ k ≤ 28	-13 ≤ k ≤ 13
	-11 ≤ l ≤ 11	-37 ≤ l ≤ 38
No. of rflns collected	25573	52421
No. of unique rflns (R_{int})	7534(0.0496)	8019(0.0439)
Completeness to θ (%)	96.6	98.0
Goodness-of-fit on F^2	1.071	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0515, wR_2 = 0.1039	R_1 = 0.0411, wR_2 = 0.1117
Final R indexes [all data]	R_1 = 0.0633, wR_2 = 0.1085	R_1 = 0.0438, wR_2 = 0.1138
Largest diff. peak/hole / e Å^{-3}	0.74/-0.48	1.62/-1.41

Table S2: Coordinates of the optimized structures: Ni3-R and Ni5-R.

	Ni3-R in Triplet:			Ni3-R in Singlet		
Atomic	Coordinates (Angstroms)			Coordinates (Angstroms)		
Type	X	Y	Z	X	Y	Z
C	-5.681543	0.777013	2.076653	-6.525916	2.069873	1.041942
C	-4.331080	0.443550	2.099888	-5.459567	1.356710	1.578109
N	-3.449885	1.016835	1.282942	-4.217018	1.539171	1.144948
C	-3.881677	1.966652	0.386089	-3.945625	2.425106	0.153752
C	-5.226630	2.323716	0.271207	-4.968818	3.130077	-0.492517
C	-6.123603	1.704119	1.150945	-6.269047	2.936396	-0.004471
C	-2.766129	2.582716	-0.374053	-2.488663	2.562225	-0.130064
C	-2.910083	3.782040	-1.244134	-1.977029	3.612893	-1.056163
C	-3.810993	3.587128	-2.468822	-2.391576	3.462529	-2.525047
C	-5.171964	2.950300	-2.182458	-3.889303	3.284534	-2.764453
C	-5.738923	3.259199	-0.791193	-4.767085	3.978031	-1.718893
N	-1.668848	1.985227	-0.108198	-1.740626	1.751697	0.538733
C	-0.301934	1.850625	0.001101	-0.320685	1.700648	0.507498
C	0.542629	2.825229	0.595626	0.463263	2.694705	1.127358
C	1.816081	2.413390	0.933297	1.843844	2.522012	1.102067
C	2.281747	1.100148	0.725171	2.448246	1.411297	0.506127
C	1.445196	0.174819	0.132918	1.636986	0.424638	-0.038130
C	0.121921	0.496034	-0.221070	0.250009	0.529608	-0.006719
C	3.674829	0.746292	1.208671	3.955361	1.252133	0.587110
C	-0.710296	-0.444025	-1.118189	-0.638113	-0.614580	-0.467917
Ni	-1.604223	0.598211	1.075485	-2.640524	0.422908	1.660377
C	-1.260416	-0.636653	2.478002	-3.092798	-1.042796	2.792607
C	3.743110	0.775718	2.726190	4.405045	0.913044	2.000251
C	4.932473	1.164483	3.344054	5.689404	1.286054	2.401024
C	5.043546	1.175413	4.729477	6.163211	0.960850	3.665572
C	3.961719	0.796606	5.519055	5.356901	0.249816	4.550289
C	2.773798	0.401289	4.913619	4.078982	-0.132498	4.158989
C	2.665344	0.389646	3.525921	3.604189	0.198928	2.892696
C	4.196781	-0.546070	0.610129	4.499987	0.271847	-0.435119
C	4.807757	-0.511523	-0.645186	4.962125	0.741844	-1.664276
C	5.257592	-1.678918	-1.250404	5.413536	-0.140713	-2.640544
C	5.093194	-2.902222	-0.606885	5.396620	-1.510678	-2.401378
C	4.479238	-2.947631	0.640279	4.933645	-1.990681	-1.179511
C	4.034268	-1.776843	1.246754	4.497333	-1.105648	-0.199947
C	-1.102402	0.210845	-2.428516	-1.287444	-0.352623	-1.807317
C	-0.269871	1.111956	-3.095310	-0.549557	0.152048	-2.880538
C	-0.654343	1.660181	-4.315904	-1.150915	0.345848	-4.121089

C	-1.875512	1.313887	-4.887587	-2.501668	0.055793	-4.298971
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C	-2.327261	-0.126701	-3.008230	-2.640106	-0.642497	-1.995668
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C	1.411191	-4.179685	-1.425415	1.582766	-4.277633	0.014582
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H	-6.368417	0.294366	2.764525	-7.531758	1.922053	1.421711
H	-3.935679	-0.299313	2.788720	-5.595372	0.620389	2.368374
H	-7.180698	1.955477	1.091338	-7.088871	3.474908	-0.476123
H	-1.910079	4.084306	-1.576008	-0.883993	3.629968	-0.992819
H	-3.297629	4.599713	-0.614983	-2.328429	4.583644	-0.672830
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H	-5.108878	1.858539	-2.295457	-4.140075	2.213943	-2.782000
H	-5.885826	3.285984	-2.942467	-4.140284	3.666390	-3.760198
H	-5.536448	4.306197	-0.519317	-4.349799	4.961661	-1.456297
H	-6.831149	3.171670	-0.808596	-5.756806	4.187454	-2.140354
H	2.490767	3.123125	1.411887	2.484212	3.254264	1.592318
H	1.810598	-0.828150	-0.075863	2.088095	-0.472613	-0.456461
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H	5.976925	1.483814	5.194242	7.164620	1.263273	3.962428
H	4.045694	0.808964	6.602780	5.725024	-0.005215	5.540961
H	1.922264	0.100431	5.521540	3.444890	-0.691566	4.843642
H	1.729340	0.072231	3.062369	2.599749	-0.104370	2.594409
H	4.935816	0.447319	-1.148554	4.971231	1.814935	-1.855904
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H	3.566052	-1.818630	2.228927	4.146036	-1.487639	0.758789
H	0.690514	1.385355	-2.656696	0.506275	0.384487	-2.742031
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H	-2.170862	1.737259	-5.844380	-2.969609	0.206550	-5.268698
H	-3.667179	0.135177	-4.669815	-4.299007	-0.680188	-3.366055
H	-2.977228	-0.840209	-2.499653	-3.218064	-1.060193	-1.167647
H	1.069623	-1.226757	-3.068899	0.286216	-2.337722	-2.454812
H	2.336477	-3.344327	-3.180247	1.612103	-4.395881	-2.132554
H	1.976387	-5.107375	-1.472417	2.166169	-5.184479	0.153168

H	0.316507	-4.746682	0.340462	1.371782	-3.898714	2.126855
H	-0.941556	-2.619085	0.462091	0.062629	-1.820315	1.803677
C	-0.002223	4.185089	0.964207	-0.197135	3.799522	1.929755
H	-0.698804	4.494509	0.170222	-1.012255	4.234548	1.330645
C	1.073386	5.257622	1.076459	0.739859	4.938856	2.305773
H	1.727079	5.080886	1.939461	1.509310	4.607865	3.014108
H	1.698624	5.308107	0.178407	1.242876	5.364457	1.430425
H	0.609995	6.238661	1.223609	0.176807	5.740604	2.794981
C	-0.786693	4.082476	2.277942	-0.819849	3.200015	3.195905
H	-1.224683	5.050586	2.546833	-1.320485	3.970408	3.793349
H	-1.595987	3.341253	2.228768	-1.562634	2.422767	2.961209
H	-0.114093	3.777490	3.090529	-0.042293	2.737434	3.817391
C	-1.107601	0.151793	3.772043	-2.728116	-0.393217	4.128563
H	-2.005320	0.763197	3.965749	-3.187619	0.612953	4.214947
H	-0.285023	0.881127	3.669500	-1.639278	-0.224035	4.184829
C	-0.839431	-0.737147	4.980225	-3.164598	-1.214586	5.338118
H	-0.710817	-0.155925	5.901109	-2.889574	-0.732858	6.282400
H	-1.667277	-1.439440	5.140988	-4.251192	-1.360825	5.333919
H	0.065314	-1.340494	4.827561	-2.698686	-2.206111	5.310992

Ni5-R in Triplet:

Ni5-R in Singlet

Atomic	Coordinates (Angstroms)			Coordinates (Angstroms)		
Type	X	Y	Z	X	Y	Z
C	-6.112369	1.906375	1.007546	-6.543201	1.480044	1.134235
C	-5.024320	1.073748	1.231038	-5.445818	0.704957	1.488770
N	-3.793279	1.393342	0.833616	-4.220606	0.998356	1.063087
C	-3.577036	2.577296	0.178059	-3.996981	2.076144	0.265965
C	-4.639098	3.425756	-0.163772	-5.055568	2.870271	-0.192934
C	-5.914725	3.066643	0.284939	-6.336178	2.545522	0.277692
C	-2.145459	2.864516	-0.066844	-2.554668	2.320513	-0.015752
C	-1.694629	4.101420	-0.770543	-2.096252	3.579427	-0.666625
C	-2.225596	4.263364	-2.200326	-2.529730	3.739951	-2.129033
C	-3.746736	4.239690	-2.360299	-4.019545	3.539920	-2.395103
C	-4.499719	4.609971	-1.080475	-4.910646	3.958137	-1.221884
N	-1.367607	1.929731	0.381967	-1.770113	1.376956	0.386002
C	0.035017	1.867597	0.374799	-0.362892	1.377459	0.380360
C	0.908210	2.897357	0.729560	0.382787	2.329439	1.078693
C	2.280662	2.723719	0.731960	1.750546	2.221909	1.226998
C	2.821959	1.490188	0.377421	2.416971	1.134265	0.658825
C	1.955784	0.434508	0.074990	1.678853	0.176405	-0.036534
C	0.582476	0.596728	0.113565	0.298786	0.264522	-0.161174

F	0.403873	4.068996	1.129431	-0.271527	3.345555	1.656849
C	4.325524	1.283995	0.418736	3.908455	0.970881	0.887548
C	-0.387399	-0.572173	-0.048429	-0.521896	-0.796339	-0.872303
Ni	-2.273059	0.283799	0.771538	-2.601515	-0.082281	1.344300
C	-3.076943	-1.261085	1.550324	-1.828138	-0.461816	3.053961
C	4.836164	1.209169	1.846118	4.203962	0.604030	2.331471
C	6.093054	1.736952	2.145073	5.411198	1.015465	2.898398
C	6.613305	1.647711	3.430671	5.741368	0.663981	4.201591
C	5.881248	1.024724	4.436742	4.866546	-0.111299	4.957002
C	4.629351	0.491258	4.148139	3.664545	-0.533388	4.399059
C	4.108855	0.584619	2.861259	3.333761	-0.176560	3.094999
C	4.748398	0.105594	-0.441267	4.531169	0.013379	-0.112958
C	4.819922	0.280140	-1.825358	4.814963	0.475011	-1.400462
C	5.112466	-0.788115	-2.663829	5.298477	-0.387956	-2.376205
C	5.336352	-2.052545	-2.125948	5.502891	-1.731936	-2.075573
C	5.270064	-2.235954	-0.749048	5.225445	-2.200311	-0.795883
C	4.978466	-1.163570	0.089984	4.744177	-1.333293	0.181252
C	-1.296522	-0.466193	-1.275960	-1.146104	-0.254594	-2.142628
C	-1.099613	0.517095	-2.253219	-0.411504	0.535530	-3.029850
C	-1.936597	0.600091	-3.360272	-0.992579	1.009402	-4.203129
C	-2.976628	-0.309604	-3.526680	-2.323894	0.720929	-4.492775
C	-3.146041	-1.329498	-2.595503	-3.068478	-0.053439	-3.606980
C	-2.303271	-1.420211	-1.494279	-2.479545	-0.538305	-2.442745
C	0.326621	-1.907405	0.025345	0.259340	-2.083491	-1.029025
C	0.846829	-2.493429	-1.128769	0.964672	-2.392806	-2.190263
C	1.627334	-3.640069	-1.036645	1.791871	-3.511782	-2.231274
C	1.884827	-4.214146	0.205076	1.914981	-4.334878	-1.117687
C	1.363342	-3.636666	1.358348	1.201656	-4.040410	0.041340
C	0.590921	-2.484455	1.266957	0.380479	-2.921180	0.082101
H	-7.094773	1.621032	1.369568	-7.533215	1.233386	1.503843
H	-5.140307	0.123430	1.743467	-5.541956	-0.168698	2.130814
H	-6.757593	3.711623	0.045067	-7.181333	3.146357	-0.052762
H	-0.605483	4.106025	-0.818230	-1.005853	3.628640	-0.616794
H	-1.966362	4.974098	-0.159567	-2.465328	4.421423	-0.063075
H	-1.772826	3.489532	-2.833986	-1.949238	3.045009	-2.749539
H	-1.828605	5.220235	-2.560650	-2.229731	4.752188	-2.427689
H	-4.077556	3.240715	-2.678286	-4.220420	2.485330	-2.636202
H	-4.037714	4.923898	-3.164632	-4.303800	4.109211	-3.286856
H	-4.017023	5.458770	-0.576207	-4.532169	4.884959	-0.765272
H	-5.509016	4.955627	-1.329931	-5.915502	4.204125	-1.583518
H	2.913258	3.552132	1.045011	2.280925	2.970208	1.812434
H	2.379905	-0.540103	-0.155030	2.188601	-0.681371	-0.468869
H	4.773450	2.185340	-0.030267	4.363068	1.960033	0.712868
H	-0.915565	-0.607194	0.981439	-1.372260	-1.029887	-0.194526

H	-4.075761	-1.466711	1.134004	-2.334684	-1.303763	3.549384
H	-2.476826	-2.159680	1.332266	-0.787223	-0.769614	2.847238
H	6.669439	2.218904	1.355764	6.099596	1.615500	2.303522
H	7.592504	2.067525	3.647725	6.683791	0.997747	4.629033
H	6.285699	0.955500	5.443453	5.121655	-0.385844	5.977515
H	4.053341	0.001496	4.929877	2.979514	-1.145017	4.982083
H	3.127086	0.162303	2.642969	2.388988	-0.514740	2.666186
H	4.640270	1.269726	-2.247024	4.649271	1.526846	-1.636800
H	5.173000	-0.633348	-3.738578	5.522613	-0.010420	-3.371258
H	5.572831	-2.889727	-2.778380	5.885752	-2.409997	-2.834644
H	5.450937	-3.219289	-0.320428	5.389361	-3.247558	-0.551799
H	4.931395	-1.313648	1.167383	4.533327	-1.706617	1.182108
H	-0.285486	1.232691	-2.149458	0.626574	0.775818	-2.799305
H	-1.760063	1.368846	-4.110405	-0.402575	1.609059	-4.892365
H	-3.630813	-0.243190	-4.392103	-2.776644	1.092114	-5.408961
H	-3.926382	-2.073392	-2.733682	-4.105941	-0.292853	-3.830069
H	-2.424204	-2.245659	-0.797738	-3.059476	-1.168963	-1.765790
H	0.654385	-2.038021	-2.099156	0.877512	-1.752568	-3.065956
H	2.038632	-4.084735	-1.939345	2.344681	-3.738287	-3.139696
H	2.490368	-5.114388	0.272918	2.562635	-5.207413	-1.152476
H	1.557326	-4.083295	2.330166	1.285784	-4.683739	0.913709
H	0.197857	-2.021117	2.174182	-0.163226	-2.676575	0.997464
C	-3.115670	-1.056860	3.056309	-1.858969	0.790689	3.913183
H	-3.626174	-0.117195	3.320283	-2.903815	1.055830	4.139697
H	-2.090007	-0.938346	3.440728	-1.448905	1.646574	3.353682
C	-3.794005	-2.213725	3.780589	-1.078399	0.631766	5.211970
H	-3.798938	-2.069621	4.866239	-1.125474	1.535415	5.829130
H	-4.835554	-2.322025	3.451015	-1.469000	-0.203497	5.805331
H	-3.285696	-3.161855	3.568318	-0.021373	0.424198	5.002696