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Ethylene oligomerization studies by nickel(II) complexes chelated by (amino)pyridine ligands: Experimental and density functional theory studies

Supporting information

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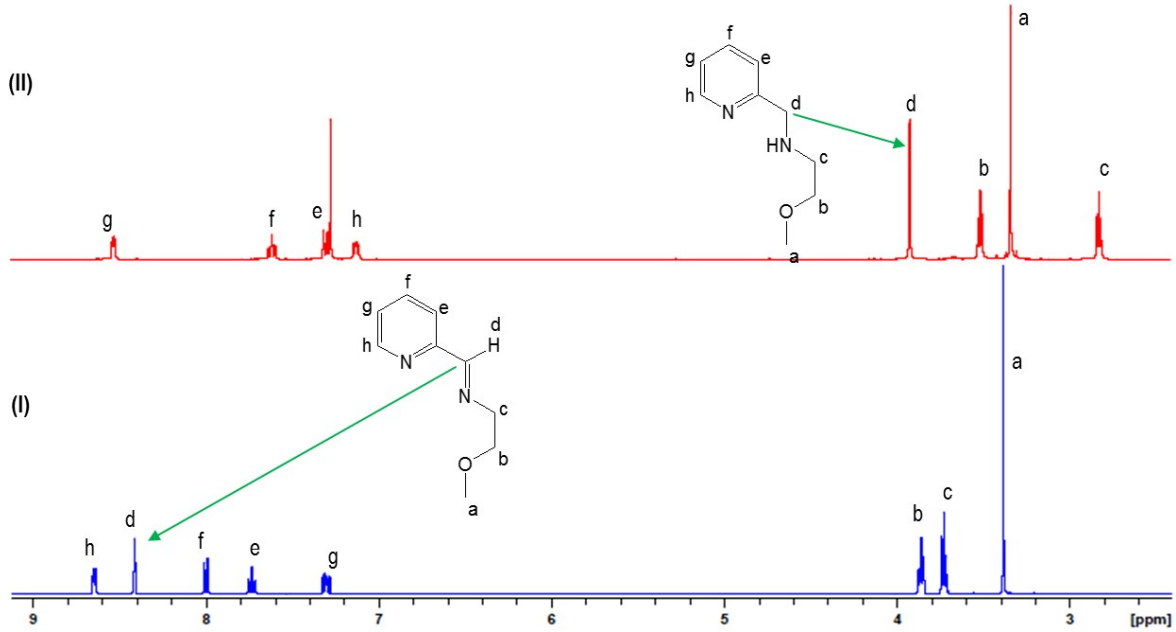

Fig. S1: ^{1}H NMR spectrum of **L2 (I)** and **L2a (II)** showing the shift of signature peaks upon reduction of ligand **L2** to **L2a**.

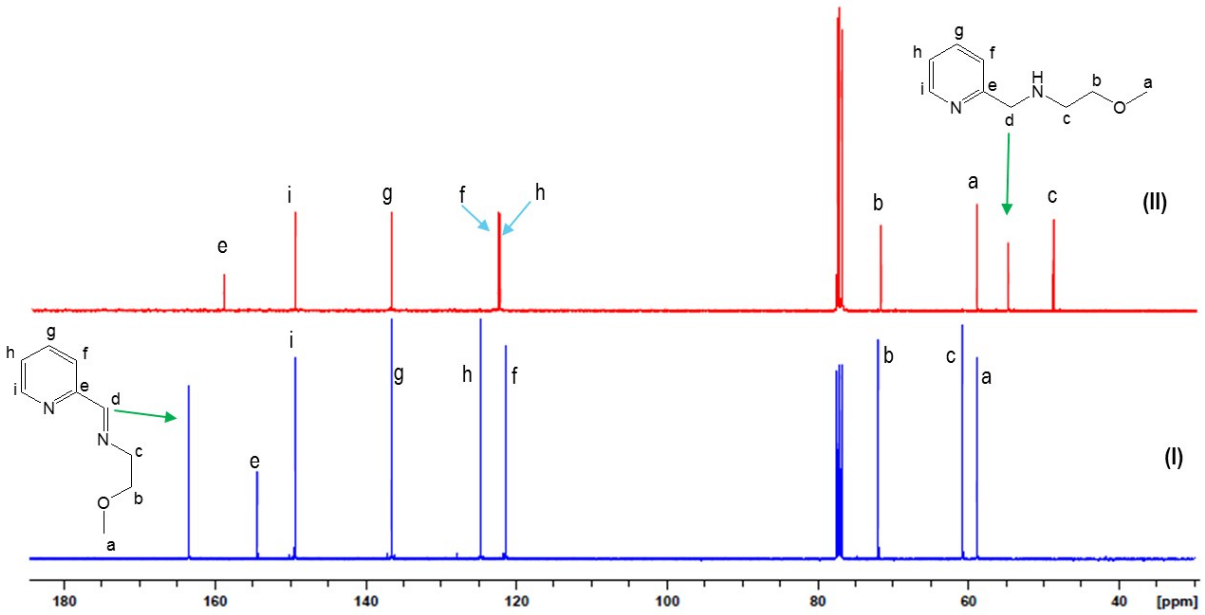

Fig. S2: ^{13}C-NMR spectrum of ligands **L2 (I)** and **L2a (II)** showing the shift of signature peaks upon reduction of ligand **L2** to **L2a**.

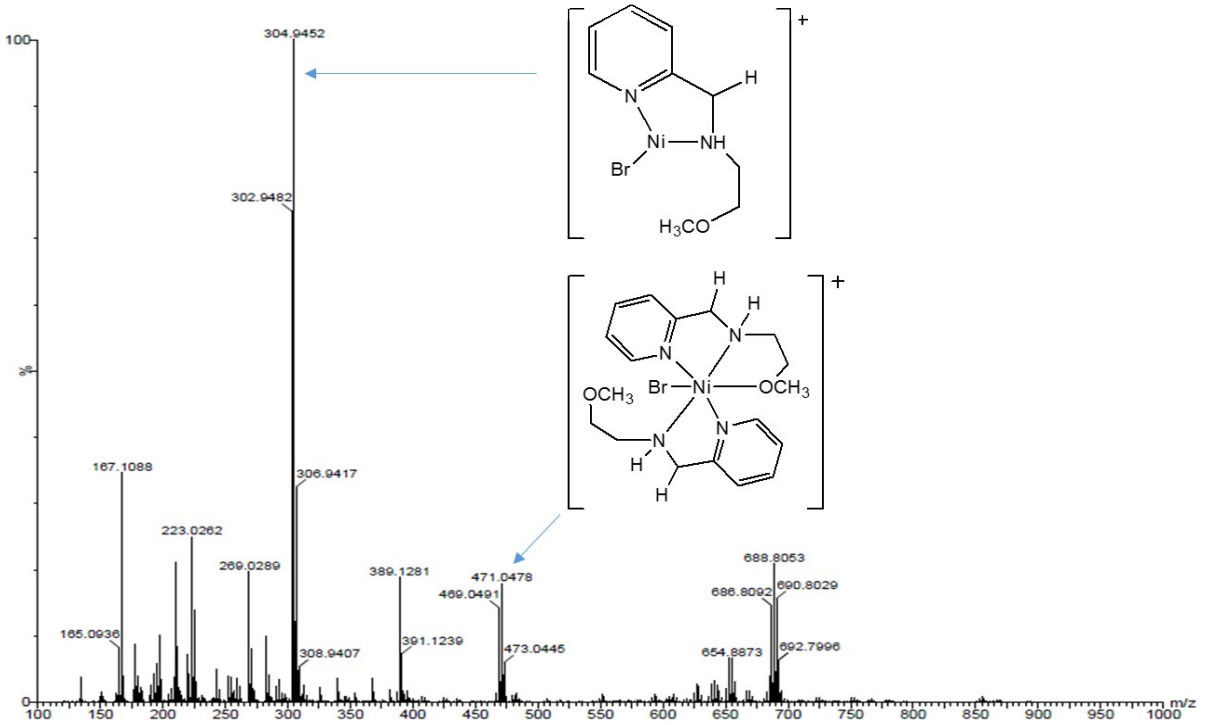

Fig. S3: ESI-MS spectrum of complex **2** showing base peak at m/z = 304 containing one ligand unit.

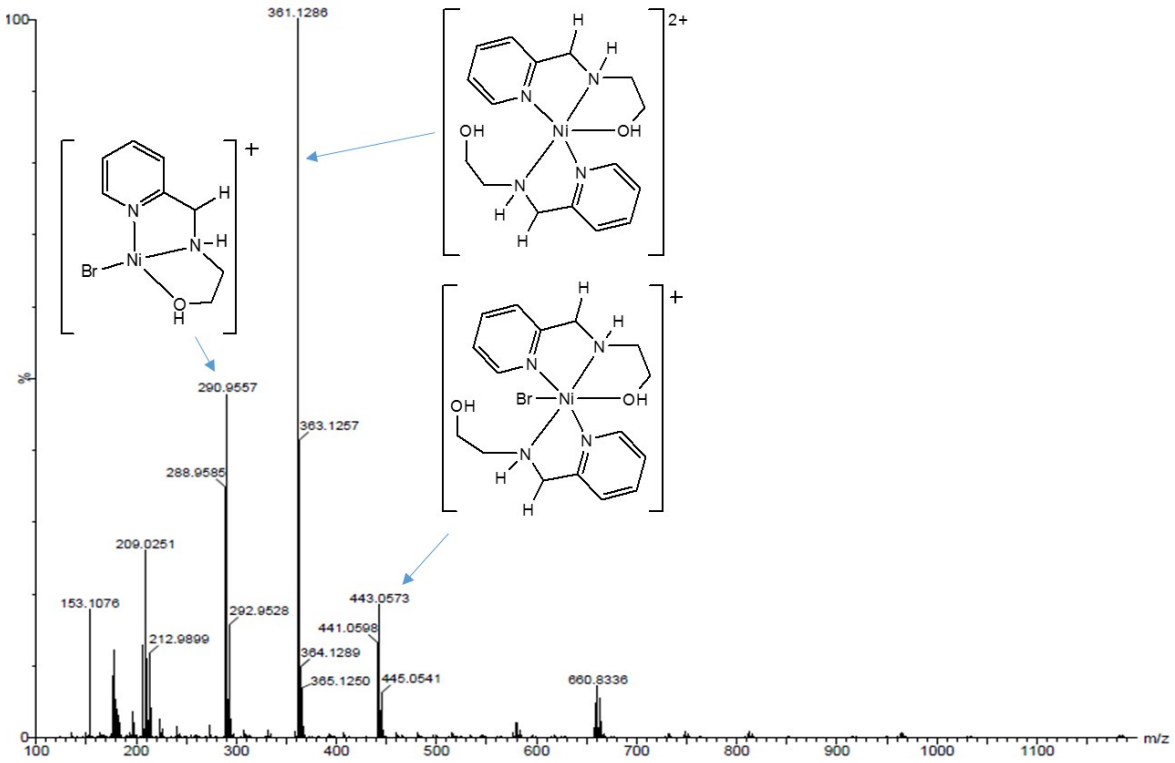

Fig. S4: MS spectrum of complex **4** showing a fragment, m/z = 361, associated with the bis(chelate) and m/z = 290 which is attributed to one ligand unit.

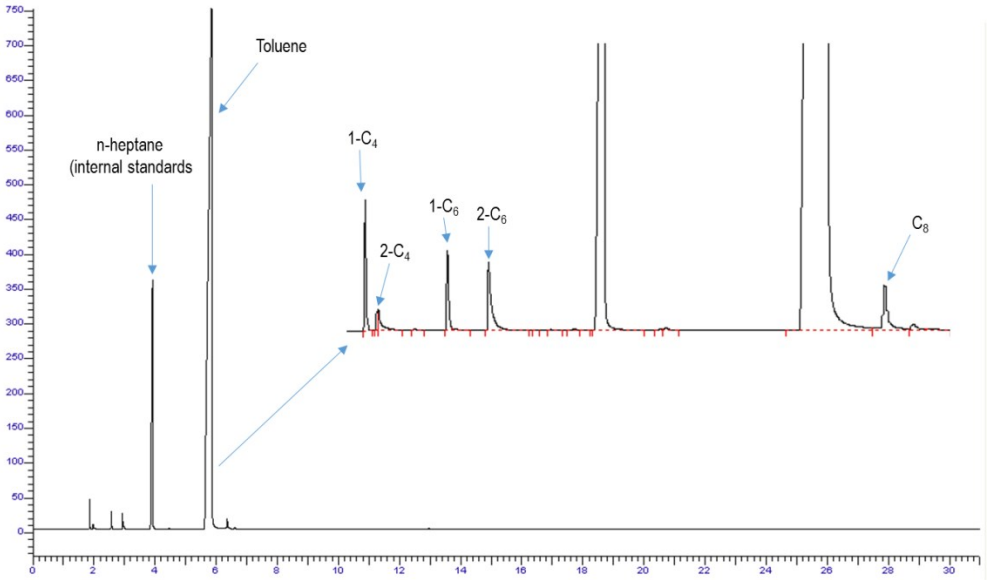

Fig. S5: GC chromatogram of products obtained by catalyst **3**, Al:Ni ratio of 200:1, temperature = 30 °C, pressure = 10 bar, time = 1 h, solvent = toluene and n-heptane as internal standard, showing isomerization of C_4 and C_6 to internal olefins.

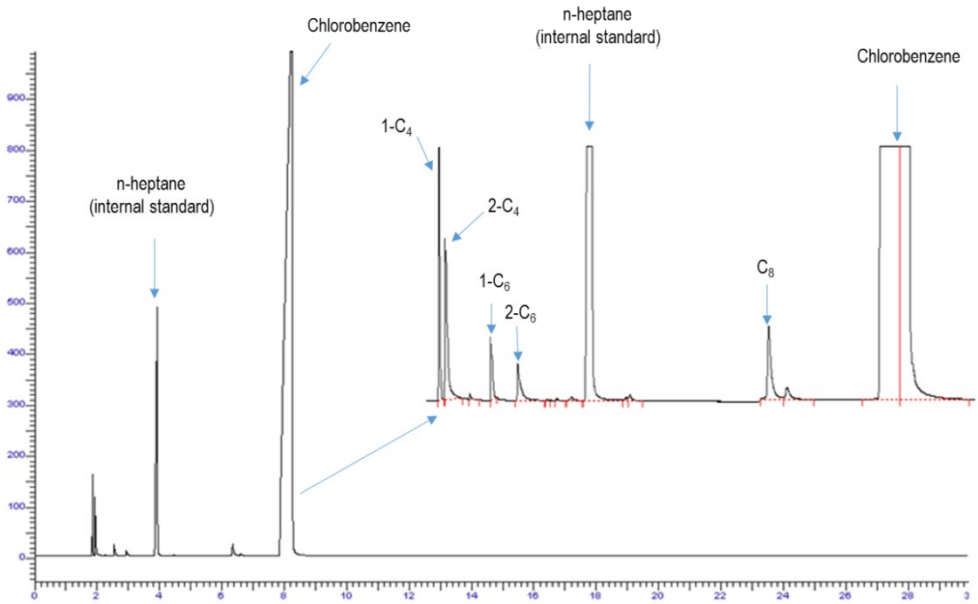

Fig. S6: GC chromatogram of products obtained by catalyst **2**, Al:Ni ratio of 200:1, temperature = 30 °C, pressure = 10 bar, time = 1 h, solvent = chlorobenzene and n-heptane as internal standard, showing isomerization of C_4 and C_6 to internal olefins.

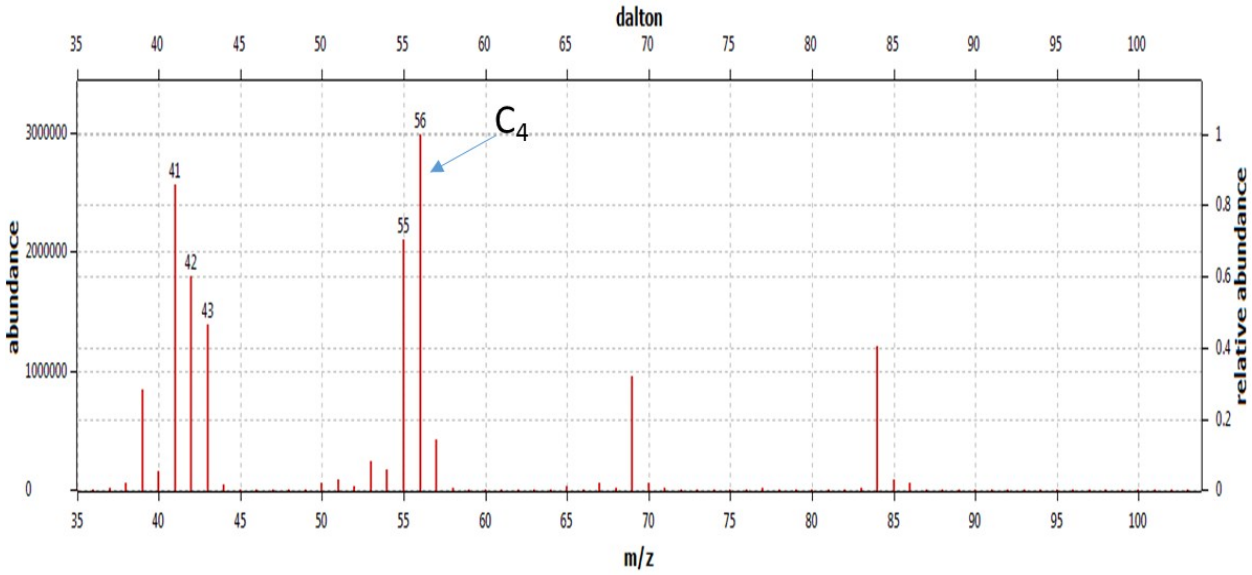

Fig. S7: GC-MS spectrum of the product obtained by catalyst **2**, Al:Ni ratio of 200:1, temperature = 30 °C, pressure = 10 bar, time = 1 h, solvent = chlorobenzene. M^+= 56 corresponds to the molecular ion mass of the C_4 oligomer.

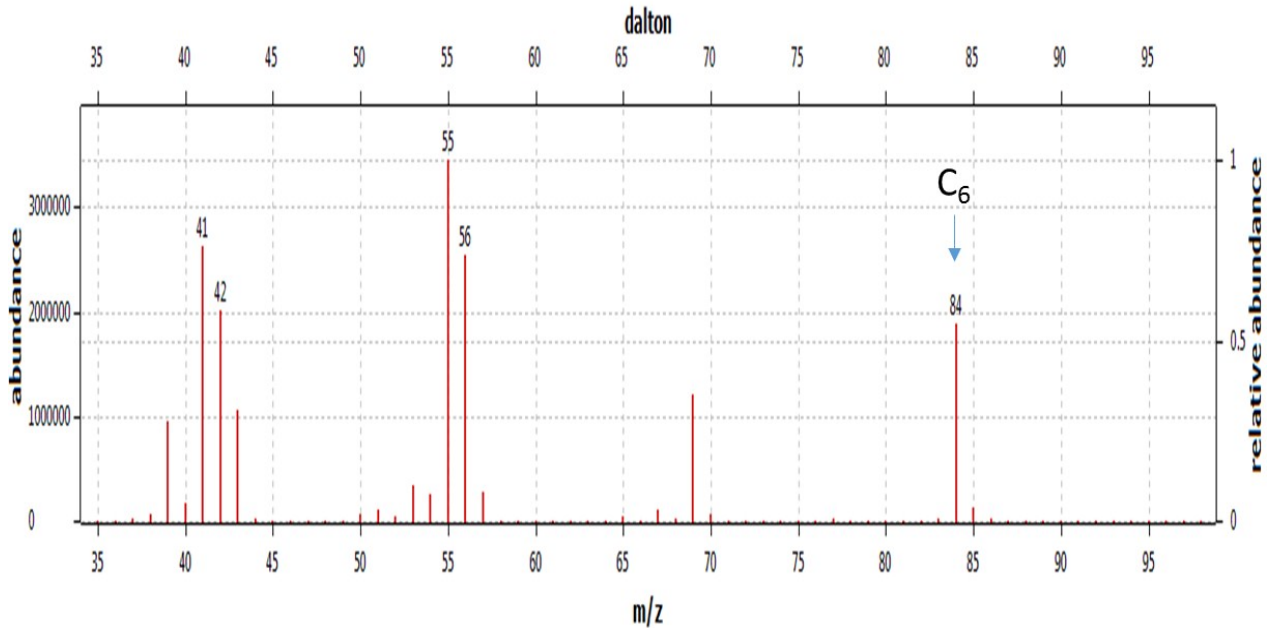

Fig. S8: GC-MS spectrum of the product obtained by catalyst **3**, Al:Ni ratio of 200:1, temperature = 30 °C, pressure = 10 bar, time = 1 h, solvent = toluene. M^+= 84 corresponds to the molecular ion mass of the C_6 oligomer.

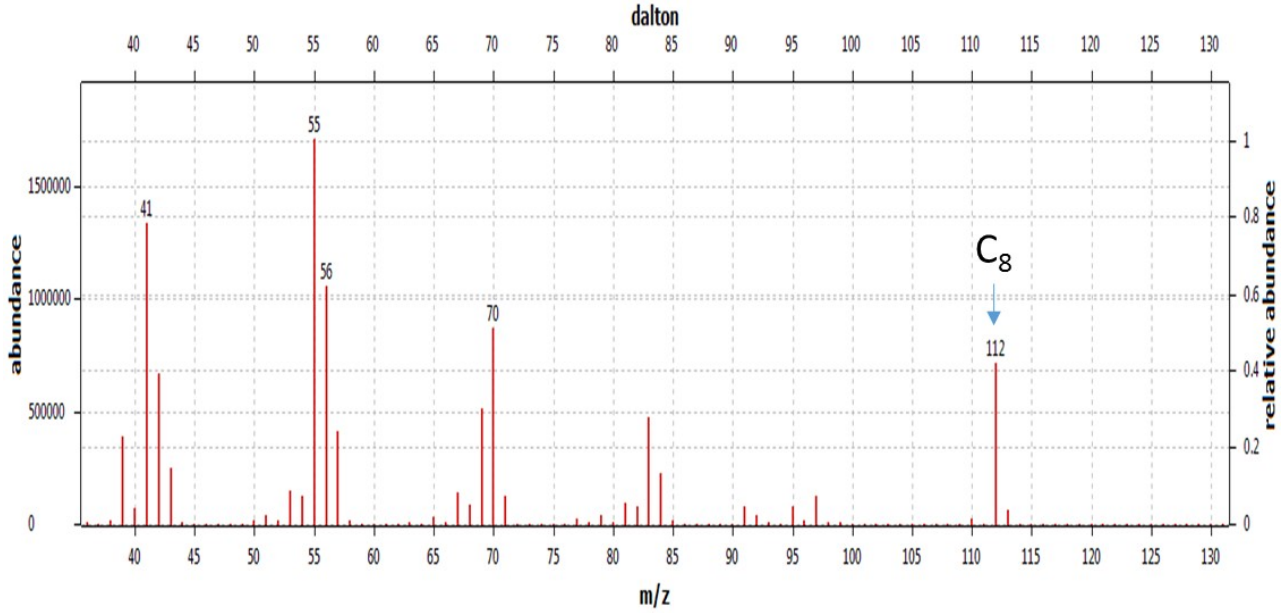

Fig. S9: GC-MS spectrum of the product obtained from catalyst **2**, MAO:Ni ratio of 1000:1, temperature = 30 ˚C, pressure = 10 bar, time = 1 h, solvent = toluene. M^+= 112 corresponds to the molecular ion mass of the C_8 oligomer.

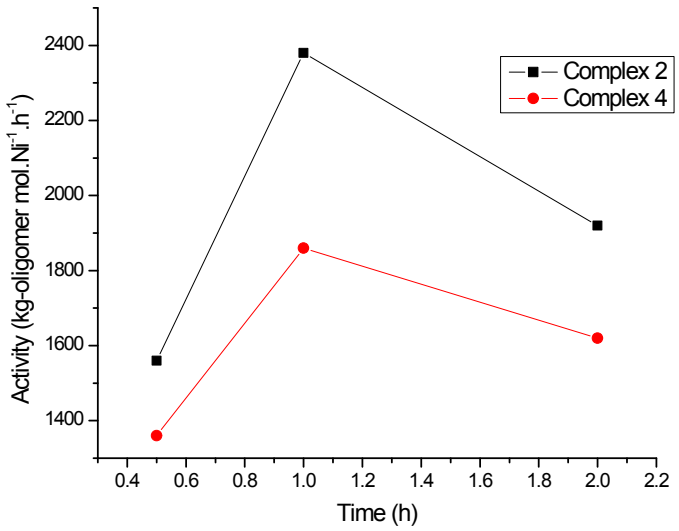

Fig. S10: Plot of activity (kg-oligomer mol.Ni^{-1}.h^{-1}) against time (h), showing fast initiation of complex **2** compared to complex **4** but faster deactivation of **2** compared to **4** indicating that the more active catalyst **2** displayed lower stability compared to the less active **4**.

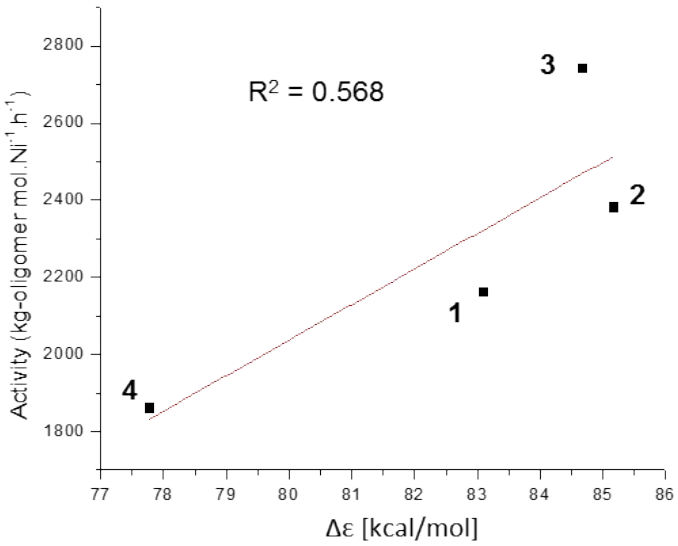

Fig. S11: Plot of activity (kg-oligomer mol.Ni^{-1}.h^{-1}) against HOMO-LUMO energy gap (Δε) [kcal/mol] showing weak relationship between HOMO-LUMO energy gaps (Δε) and catalytic activity.

Table S1: Comparison of selected bond lengths for crystal structures of complexes **2** and **4**, and calculated results

Bond lengths [Å]					
2			**4**		
	Experimental	Theoretical		Experimental	Theoretical
Ni1–Br02	2.5397(9)	ND[a]	Ni1-N1[i]	2.0795 (18)	2.0429
Ni1–O1	2.201(2)	2.6529	Ni1-N1	2.0795 (18)	2.0427
Ni1–N1	2.077 (3)	1.9411	Ni1-N2[i]	2.0818 (19)	2.0475
Ni1–N2	2.116 (2)	2.0214	Ni1-N2	2.0818 (19)	2.0473
Ni1–N3	2.077(3)	1.9477	Ni1-O1[i]	2.1156 (18)	2.5643
Ni1–N4	2.110(3)	2.0038	Ni1-O1	2.1157 (18)	2.5333

[a]The Ni-Br bond length was not determined since the optimized structures were drawn as proposed in Scheme 2, without a bromide ligand; and with both methoxy oxygen atoms coordinated to the Ni atom.

Atomic coordinates of optimized structures

Complex **1**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.596613	-2.142270	0.335349
2	6	0	2.258169	-1.887305	0.250428
3	7	0	1.769595	-0.490701	0.242833
4	6	0	2.591254	0.490200	0.351303
5	6	0	4.117465	0.291591	0.356634
6	6	0	4.597652	-0.971742	0.366961
7	1	0	4.783368	1.129384	0.366639

8	1	0	5.653132	-1.155603	0.404440
9	1	0	3.952088	-3.152112	0.378606
10	1	0	1.564339	-2.699533	0.191755
11	6	0	1.912255	1.833526	0.523521
12	1	0	1.778353	1.981753	1.573637
13	7	0	0.582725	1.776583	-0.120112
14	1	0	0.000448	2.468055	0.313170
15	6	0	0.634011	2.081063	-1.538621
16	1	0	1.225670	2.955707	-1.723665
17	1	0	-0.350291	2.245299	-1.926324
18	6	0	-3.689342	2.060222	-0.187643
19	6	0	-2.348158	1.815652	-0.109062
20	7	0	-1.853168	0.424098	-0.075740
21	6	0	-2.676024	-0.571395	-0.157257
22	6	0	-4.203042	-0.376470	-0.154897
23	6	0	-4.686413	0.883893	-0.193310
24	1	0	-4.866297	-1.217564	-0.136957
25	1	0	-5.742069	1.062657	-0.229364
26	1	0	-4.050849	3.065766	-0.243220
27	1	0	-1.659123	2.631632	-0.073596
28	6	0	-2.004048	-1.932823	-0.306427
29	7	0	-0.644056	-1.843918	0.268131
30	1	0	-2.550567	-2.726809	0.165341
31	1	0	-0.073349	-2.529849	-0.172345
32	6	0	-0.654507	-2.124344	1.701690

33	1	0	-1.225980	-3.004728	1.913900
34	1	0	0.340091	-2.261587	2.067566
35	28	0	-0.038914	-0.033724	0.075775
36	6	0	-1.211212	-0.912407	2.323597
37	1	0	-1.271984	-0.999124	3.388523
38	1	0	-2.190511	-0.704398	1.944821
39	6	0	1.176945	0.870637	-2.161129
40	1	0	2.147647	0.643814	-1.774379
41	1	0	1.253415	0.968431	-3.227148
42	6	0	0.718312	-1.346136	-2.321977
43	6	0	-0.788236	1.313584	2.460513
44	1	0	1.665768	-1.567583	-1.883726
45	1	0	0.034303	-2.135934	-2.122988
46	1	0	-0.111013	2.109306	2.250460
47	1	0	-1.738967	1.525204	2.025555
48	6	0	-1.932507	-2.238412	-1.800970
49	1	0	-1.399641	-1.466607	-2.303210
50	1	0	-1.431937	-3.174608	-1.942720
51	1	0	-2.927741	-2.304147	-2.193379
52	8	0	-0.279882	0.086632	1.940329
53	8	0	0.215505	-0.118223	-1.793528
54	1	0	0.837895	-1.236180	-3.388405
55	1	0	-0.898396	1.210106	3.527117
56	6	0	2.758178	2.984584	-0.075636
57	1	0	2.230881	3.908855	0.017438

58	1	0	3.691296	3.051744	0.445225
59	1	0	2.944758	2.783340	-1.113097

Complex **2**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.893146	-1.537311	0.055729
2	6	0	-2.538188	-1.473438	0.148625
3	7	0	-1.845103	-0.210235	-0.161101
4	6	0	-2.485466	0.824339	-0.573462
5	6	0	-4.019406	0.870150	-0.607193
6	6	0	-4.692327	-0.271522	-0.323840
7	1	0	-4.540469	1.769046	-0.860133
8	1	0	-5.760479	-0.298694	-0.368408
9	1	0	-4.401697	-2.460014	0.246599
10	1	0	-1.977449	-2.336711	0.442690
11	6	0	-1.560714	1.929780	-1.068964
12	1	0	-1.381285	1.709304	-2.098469
13	7	0	-0.293556	1.845294	-0.310352
14	1	0	0.414162	2.302958	-0.847013
15	6	0	-0.342956	2.484011	1.010269
16	1	0	-0.790543	3.456318	0.954181

17	1	0	0.641348	2.581353	1.417588
18	6	0	3.902581	1.523579	-0.033107
19	6	0	2.544513	1.469519	-0.123798
20	7	0	1.842908	0.209411	0.162897
21	6	0	2.481473	-0.826309	0.554325
22	6	0	4.018898	-0.890232	0.574834
23	6	0	4.699459	0.248468	0.311783
24	1	0	4.536340	-1.800370	0.803712
25	1	0	5.769447	0.267474	0.349676
26	1	0	4.415912	2.447066	-0.201734
27	1	0	1.989372	2.341455	-0.397125
28	6	0	1.556215	-1.919825	1.046596
29	7	0	0.293317	-1.846654	0.296574
30	1	0	1.982338	-2.897780	0.967879
31	1	0	-0.405197	-2.316125	0.834737
32	6	0	0.323116	-2.474749	-1.026431
33	1	0	0.746146	-3.457386	-0.983261
34	1	0	-0.669805	-2.547995	-1.426686
35	28	0	-0.004120	-0.001045	0.000519
36	6	0	1.095659	-1.533868	-1.869403
37	1	0	1.183524	-1.870919	-2.880577
38	1	0	2.080582	-1.399414	-1.470630
39	6	0	-1.106905	1.534653	1.867252
40	1	0	-2.085818	1.375915	1.474701
41	1	0	-1.196898	1.886350	2.876590

42	6	0	-1.011482	-0.695675	2.483667
43	6	0	1.038792	0.715462	-2.441132
44	1	0	-1.961906	-0.851095	2.025954
45	1	0	-0.439456	-1.597419	2.442569
46	1	0	0.479205	1.623298	-2.379748
47	1	0	1.991723	0.850814	-1.974562
48	8	0	0.323488	-0.331919	-1.787101
49	8	0	-0.318830	0.349060	1.797750
50	1	0	-1.150223	-0.409954	3.510003
51	1	0	1.180894	0.451061	-3.470497
52	1	0	1.356998	-1.692812	2.067244
53	1	0	-1.972313	2.919509	-0.985615

Complex **3**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.806647	-4.053989	1.332792
2	6	0	-0.521627	-2.710099	1.318223
3	7	0	-0.401912	-1.997378	0.195939
4	6	0	-0.577779	-2.618907	-0.966882
5	6	0	-0.873895	-3.968045	-1.050517
6	6	0	-0.985637	-4.700060	0.116370

7	1	0	-1.013239	-4.431179	-2.009093
8	1	0	-1.213250	-5.749148	0.082046
9	1	0	-0.891647	-4.577375	2.265205
10	1	0	-0.391560	-2.187848	2.244491
11	6	0	-0.389091	-1.783041	-2.205180
12	1	0	0.627397	-1.920369	-2.555868
13	7	0	-0.587086	-0.347468	-1.924120
14	1	0	-1.048179	-2.118598	-2.996007
15	1	0	0.039484	0.134898	-2.538851
16	6	0	-1.955010	0.149151	-2.254024
17	1	0	-2.253403	-0.264920	-3.210816
18	1	0	-1.879894	1.218485	-2.384259
19	6	0	0.806263	4.054020	-1.332477
20	6	0	0.520829	2.710207	-1.317740
21	7	0	0.401496	1.997528	-0.195386
22	6	0	0.578225	2.619029	0.967332
23	6	0	0.874784	3.968063	1.050796
24	6	0	0.986114	4.700037	-0.116165
25	1	0	1.014801	4.431180	2.009282
26	1	0	1.214077	5.749052	-0.081949
27	1	0	0.890903	4.577374	-2.264939
28	1	0	0.390091	2.188097	-2.243966
29	6	0	0.390006	1.783134	2.205685
30	1	0	-0.626201	1.920823	2.557062
31	7	0	0.587245	0.347512	1.924409

32	1	0	1.049741	2.118313	2.996133
33	1	0	-0.039078	-0.134671	2.539550
34	6	0	1.955140	-0.149681	2.253585
35	1	0	2.253856	0.263778	3.210546
36	1	0	1.879739	-1.219061	2.383223
37	28	0	-0.000413	0.000154	0.000277
38	6	0	3.017601	0.186616	1.211829
39	1	0	3.979734	-0.053824	1.656240
40	1	0	3.027073	1.257350	1.047720
41	6	0	-3.017600	-0.186855	-1.212317
42	1	0	-3.027203	-1.257559	-1.048078
43	1	0	-3.979661	0.053644	-1.656864
44	7	0	-2.806877	0.471441	0.069979
45	7	0	2.806886	-0.471549	-0.070553
46	6	0	-3.070184	1.919120	0.064420
47	6	0	3.070345	-1.919212	-0.065182
48	6	0	-4.506527	2.415562	-0.125797
49	6	0	4.506629	-2.415677	0.125483
50	1	0	-4.486681	3.492768	-0.253147
51	1	0	-5.130314	2.206352	0.732775
52	1	0	-4.983397	1.995745	-1.004249
53	1	0	-2.695121	2.310006	1.004487
54	1	0	-2.452820	2.363285	-0.705863
55	1	0	2.452725	-2.363641	0.704743
56	1	0	2.695688	-2.309936	-1.005473

57	1	0	5.130780	-2.206308	-0.732779
58	1	0	4.983159	-1.996044	1.004213
59	1	0	4.486723	-3.492908	0.252620
60	6	0	-3.430518	-0.248261	1.193532
61	6	0	-4.883165	-0.716923	1.053547
62	6	0	3.430347	0.248364	-1.194030
63	6	0	4.883038	0.716933	-1.054141
64	1	0	-2.825080	-1.126839	1.392107
65	1	0	-3.346086	0.391669	2.065552
66	1	0	-5.003812	-1.432243	0.247731
67	1	0	-5.578283	0.093368	0.888655
68	1	0	-5.174607	-1.217531	1.970884
69	1	0	3.345774	-0.391369	-2.066171
70	1	0	2.824907	1.127007	-1.392328
71	1	0	5.174457	1.217588	-1.971460
72	1	0	5.003770	1.432177	-0.248272
73	1	0	5.578095	-0.093430	-0.889336

Complex **4**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.109166	1.001687	0.017717

2	6	0	-2.763073	1.142435	0.019442
3	7	0	-1.909891	-0.044100	-0.105994
4	6	0	-2.379495	-1.184197	-0.260453
5	6	0	-3.884264	-1.442801	-0.240121
6	6	0	-4.715118	-0.392016	-0.105588
7	1	0	-4.268216	-2.437217	-0.334243
8	1	0	-5.775753	-0.530446	-0.085704
9	1	0	-4.742835	1.859225	0.105605
10	1	0	-2.328628	2.110416	0.115773
11	6	0	-1.359171	-2.302882	-0.486283
12	1	0	-1.153092	-3.280206	-0.089145
13	7	0	-0.502953	-1.834036	0.752565
14	1	0	-2.254616	-2.797569	-0.825530
15	1	0	-0.289718	-2.806049	0.621256
16	6	0	0.927123	-1.793551	0.990327
17	1	0	1.302859	-2.606835	1.581113
18	8	0	0.595577	-1.129997	-1.249490
19	1	0	1.137146	-0.879318	1.499059
20	6	0	4.002563	-1.130184	0.387353
21	6	0	2.632321	-1.197978	0.435512
22	7	0	1.826510	0.005148	0.080893
23	6	0	2.402997	1.111762	-0.223915
24	6	0	3.910854	1.249021	-0.336455
25	6	0	4.675491	0.169616	-0.043695
26	1	0	4.353318	2.177427	-0.630712

27	1	0	5.742172	0.225969	-0.110803
28	1	0	4.594030	-1.983137	0.645330
29	1	0	2.138336	-2.120118	0.729251
30	6	0	1.415784	2.224008	-0.420675
31	1	0	1.744322	2.987866	-1.097183
32	7	0	0.149041	1.603098	-0.898320
33	1	0	1.283657	2.651138	0.536924
34	1	0	0.178958	1.451692	-1.888586
35	6	0	-0.925826	2.462795	-0.443675
36	1	0	-0.868657	3.454137	-0.851535
37	8	0	-0.679131	1.010216	1.431978
38	1	0	-1.915508	2.054614	-0.681446
39	28	0	-0.078799	-0.043126	-0.002371
40	6	0	-0.633473	2.416501	1.072927
41	1	0	-1.318528	2.988150	1.667504
42	1	0	0.341409	2.795441	1.233334
43	1	0	-1.593310	0.751210	1.576484
44	1	0	1.001217	-0.725334	-2.021498
45	6	0	1.546274	-1.843331	-0.458540
46	1	0	1.627765	-2.833647	-0.861357
47	1	0	2.536616	-1.397733	-0.454669