The Big Impact of a Small Detail: Cobalt nanocrystal polymorphism as a result of precursor addition rate during stock solution preparation.

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Supporting Information

S1. $Co(LA)_2$

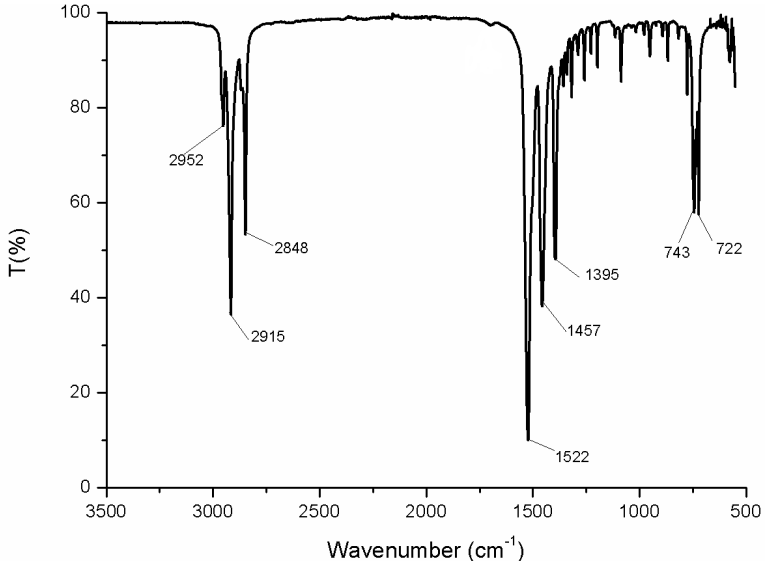


Figure S1a: Fourrier Transform - Infra Rouge (FT-IR) spectrum of the solid [$Co(LA)_2$] obtained by a Thermo-Scientific Nicolet 6700 FT-IR Instrument in a ATR (Attenuated Total Reflectance) mode (diamond window).

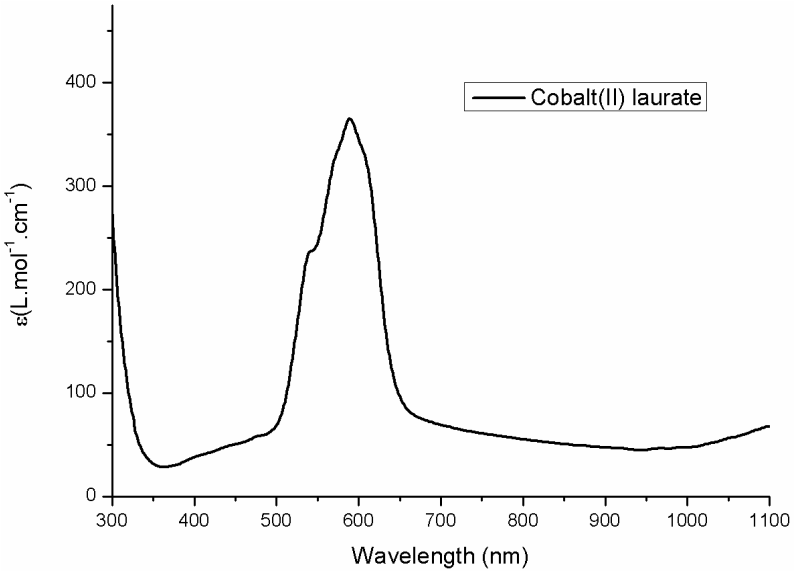


Figure S 1b: UV-Vis spectrum of a $[Co(LA)_2]$ solution in anisole [Co] = 25 mM in a 2mm optical-path UV- cell.

S2. Overview of a NCs c sample

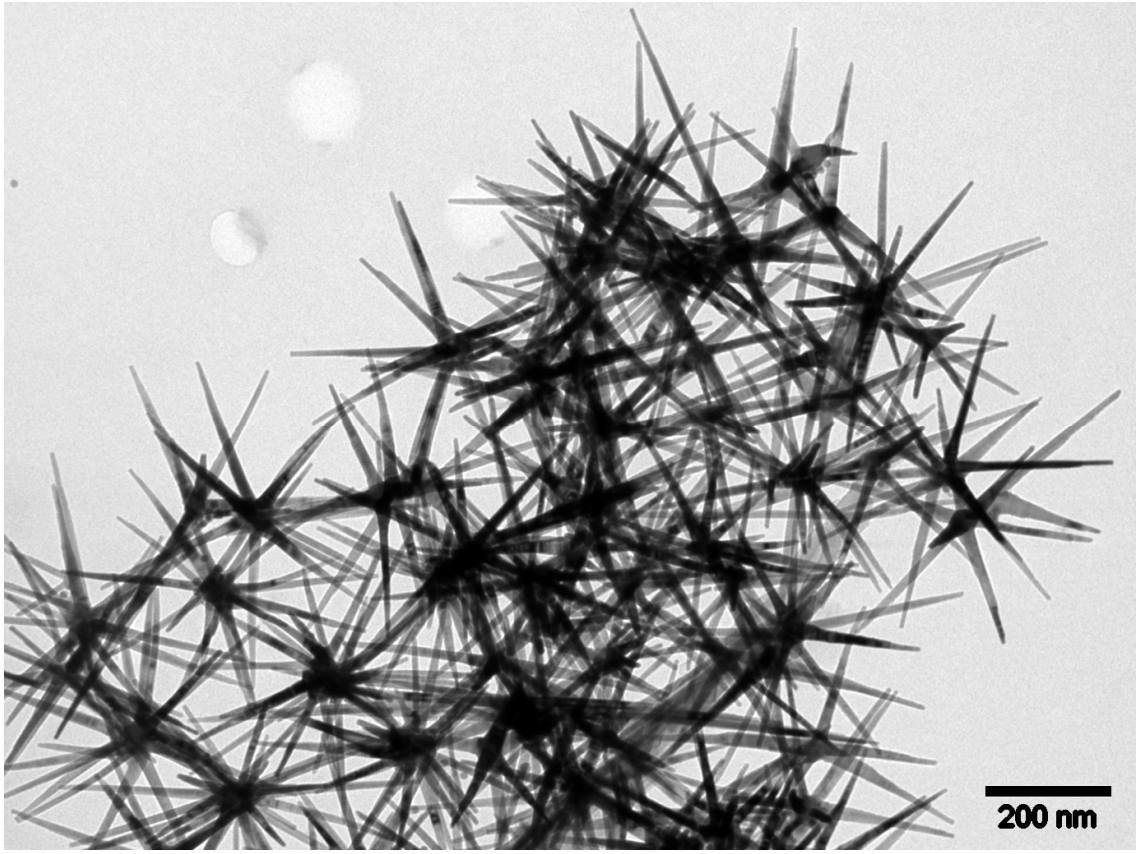


Figure S2: Overview of a **NCs c** sample.

S3: WAXS

From the coherence length measured on the PDF (Pair Distribution Function), the size of crystalline domains can be roughly estimated as 2.5-2.8 nm for **NCs a**, 4.0-4.5 nm for **NCs b**, and larger than 5 nm for **NCs c** (actual size limit for the diffractometer used, because of limited spatial resolution).

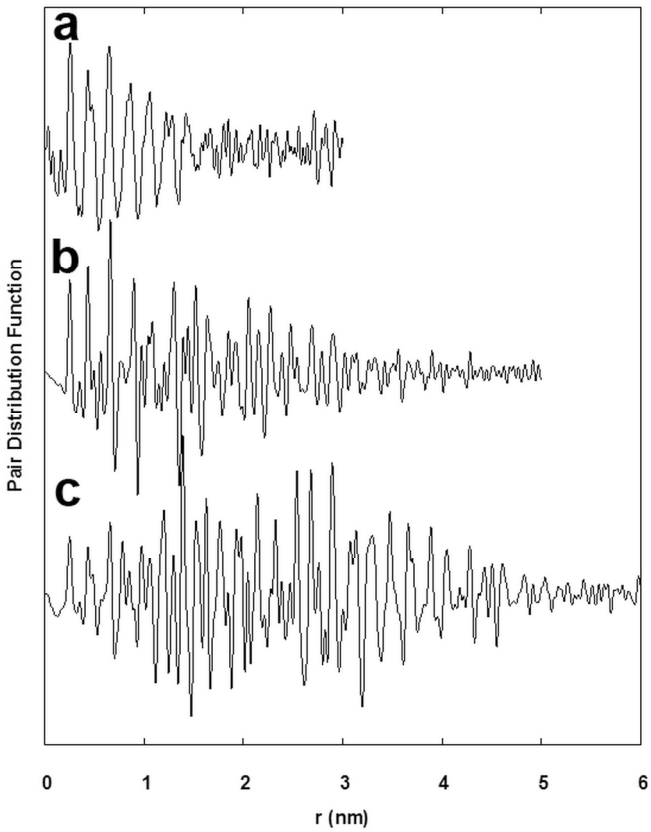


Figure S3: PDF for the three colloids – for easier comparison, amplitude has been divided by 10 for colloid **b** and 20 for colloid **c**.

S4: EXAFS

The interest of EXAFS in that case study is not the accurate determination of the structure (actually even **b** and **c** can hardly be differentiated since the characteristic features of *fcc* and *hcp* structures mostly appear above 0.6 nm, which is the practical limit of most room temperature EXAFS studies). It however rules out any eventual composition effect and provides useful information on local order, to compare to medium and long range order.

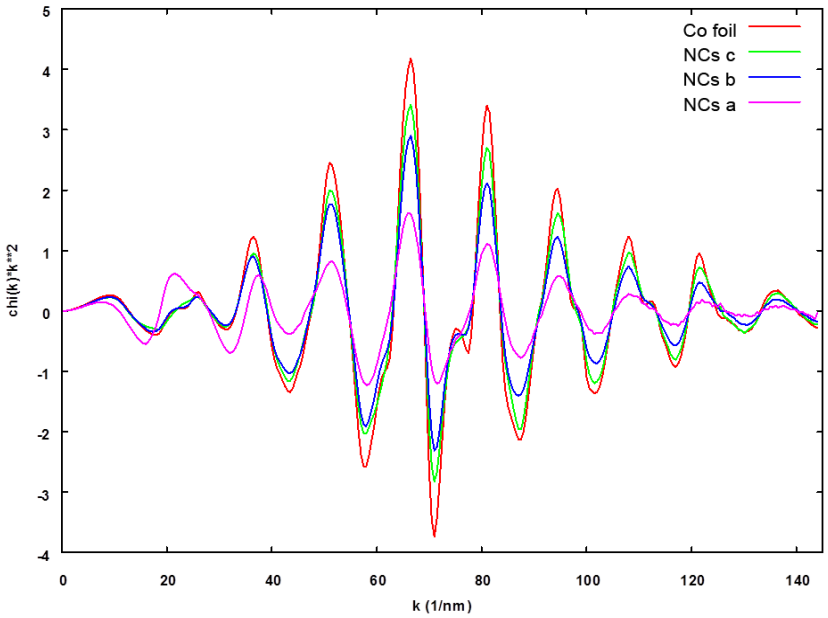


Figure S4a: chi function at Co K absorption edge. Compared to a reference cobalt foil, all three colloids only display a gradual amplitude reduction in agreement with size and disorder effects.

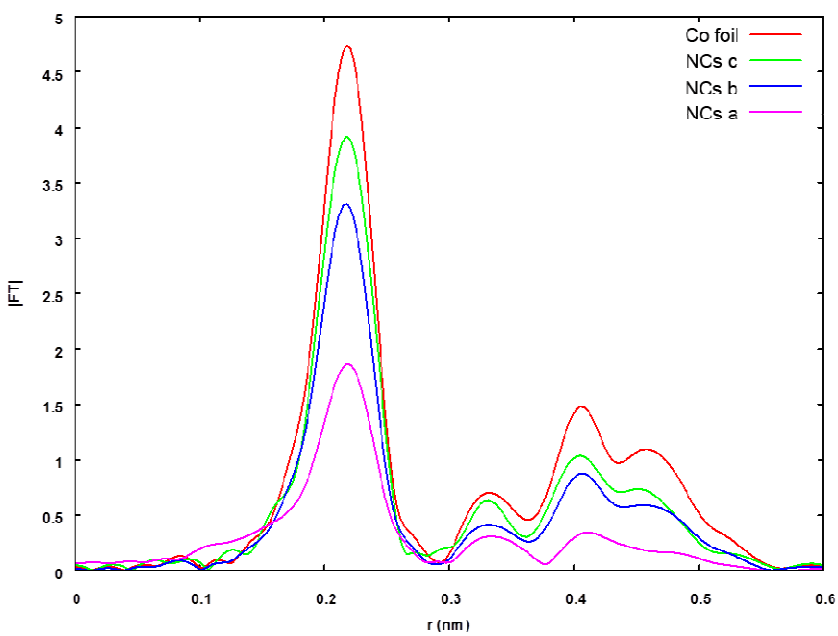
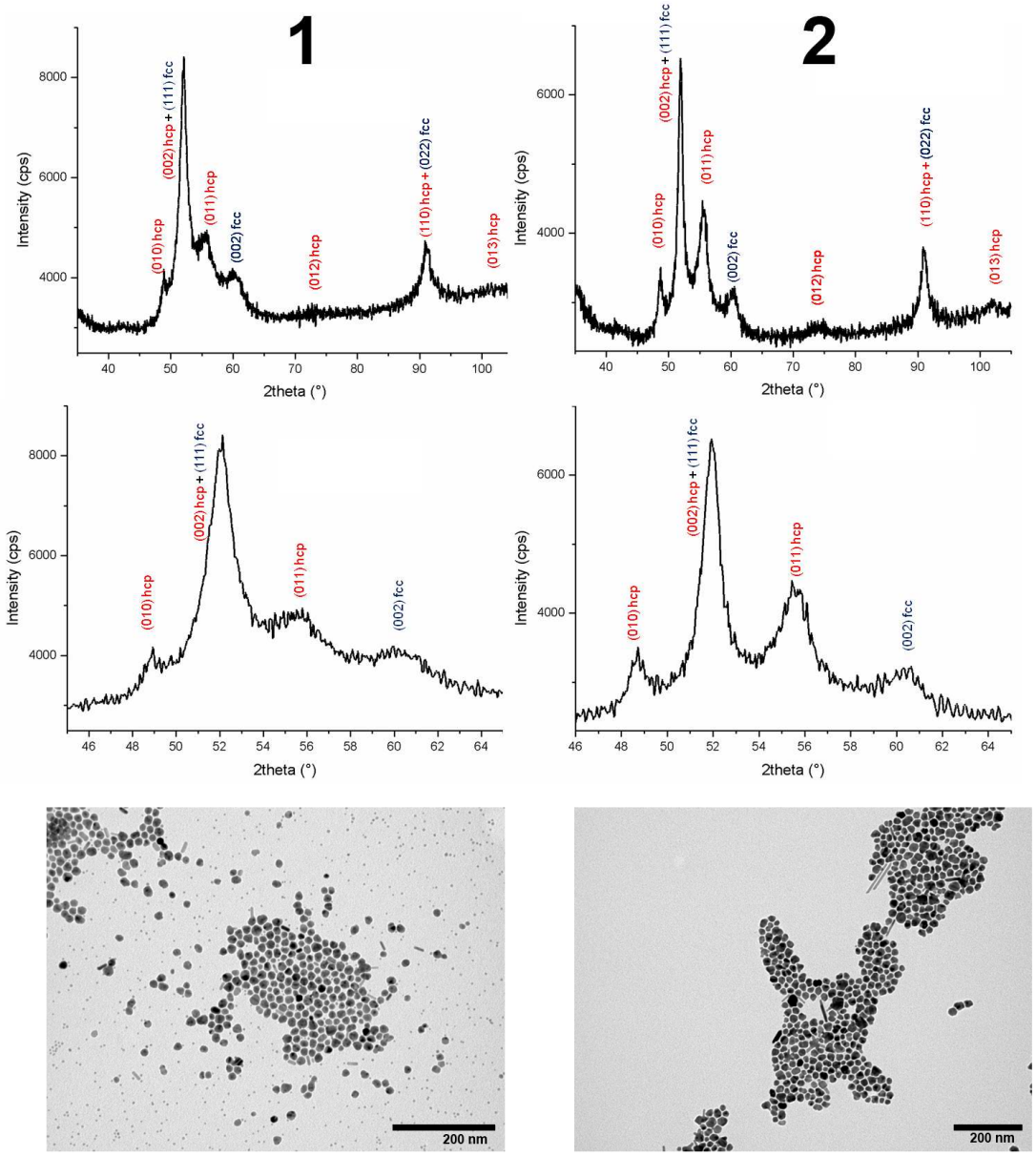


Figure S4b: modulus of Fourier Transform at Co K absorption edge. Compared to a reference cobalt foil, all three colloids only display a gradual amplitude reduction in agreement with size and disorder effects.

S5: XRD patterns and corresponding TEM of intermediate and fast addition rates



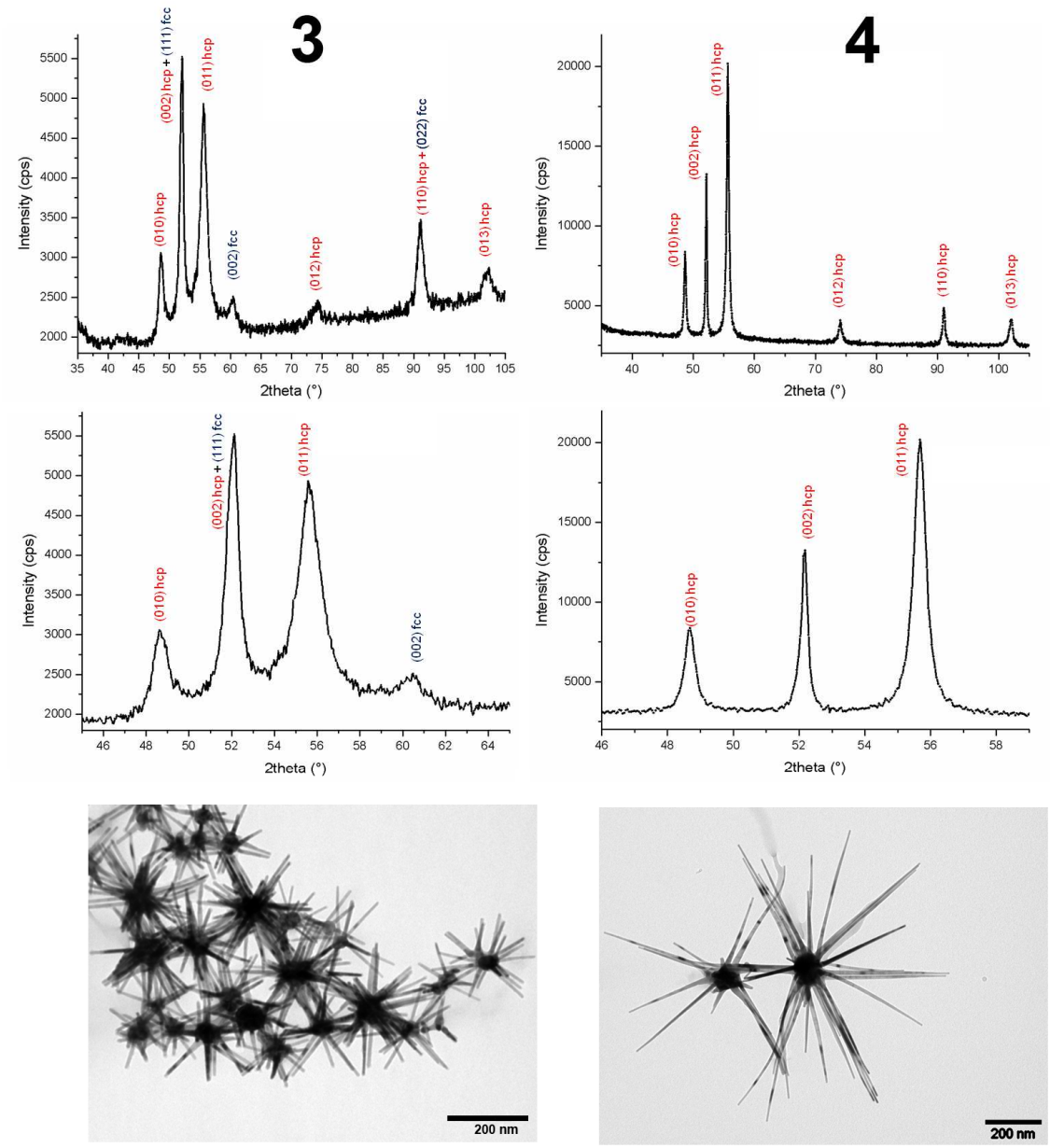


Figure S5: XRD of samples obtained from intermediate and fast addition rate solutions and the TEM micrographs of the corresponding nanoparticles. The addition rate increases from 1 to 4, 1 corresponding to **NCs b** and 4 to **NCs c**. *Hcp* indexation is in red and *fcc* in blue. Note the gradual increase of the *hcp* component upon increasing the addition rate.

S6. TEM and HREM experiments

The structural characterization of **NCs a** nanoparticles, performed via HRTEM, revealed crystalline structures consistent with *hcp* lattice. In particular it was possible to discriminate single Co *hcp* nanocrystals (Figure S6a) and multidomain Co nanoparticles (Figure S6b) both with diameters of a few nm.

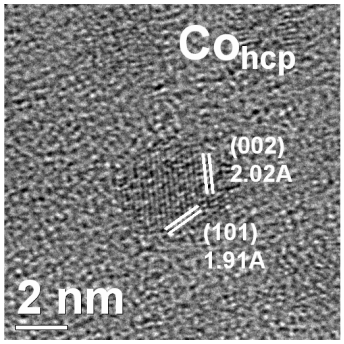


Figure S6a. HRTEM image of Co *hcp* crystal displaying the typical lattice sets (002) and (101) with d-spacing of 2.02Å and 1.91Å respectively.

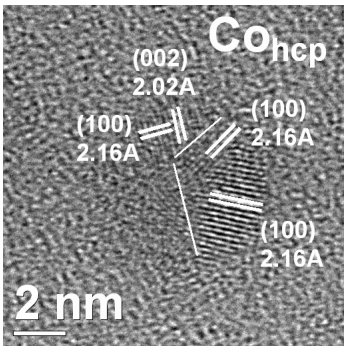


Figure S6b. HRTEM image of multidomain Co nanoparticles exhibiting the Co *hcp* lattice sets (100) and (002) with d-spacing of 2.16Å and 2.02Å.

In addition to the Co *hcp* nanoparticles, Co *fcc* nanocrystals were identified and sometimes they displayed twinned structure with {111} twin boundaries as shown in Figure S6c.

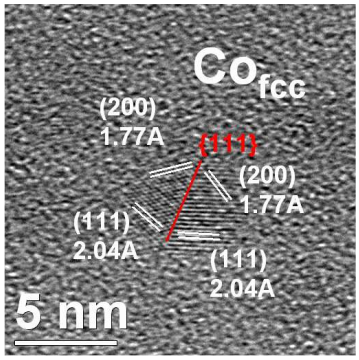


Figure S6c. HRTEM image of a twinned Co *fcc* crystal showing the (200) and (111) lattice sets with d-spacing of 1.77Å and 2.04Å respectively and exhibiting the {111} twin boundary (red line).

The **NCs b** sample displayed particles with homogeneous sizes forming aggregates over carbon film of TEM grids (Figure S6d).

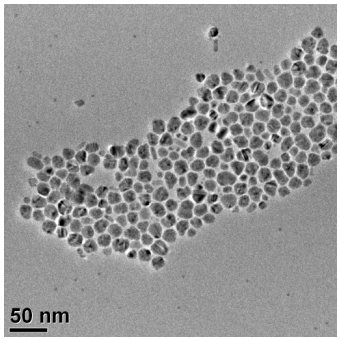


Figure S6d. Low magnification HRTEM micrograph showing Co nanocrystals.

In particular single Co nanoparticles showed either polycrystalline or single crystalline structures, as shown from high magnification HRTEM images. Figure S6e displays a Co polycrystalline particle with its corresponding calculated electron diffraction pattern.

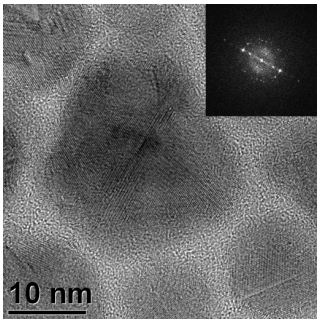


Figure S6e. HRTEM image of polycrystalline Co nanoparticle showing multi-domains feature; in the inset is shown the calculated electron diffraction pattern

HRTEM data of single crystalline Co nanoparticles revealed *fcc* structure as shown in Figure S6f. Moreover, polycrystalline and single crystal Co nanoparticles displayed comparable sizes.

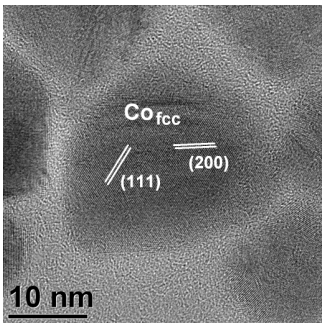


Figure S6f. HRTEM image of a single crystal Co nanoparticle showing (111) and (200) lattice planes at 2.014Å and 1.77Å, respectively.

NCs c, showing urchin-like structure are characterized by long arms with acicular habit grown on a central seed with length of more than 100 nm. (Figure S6g).

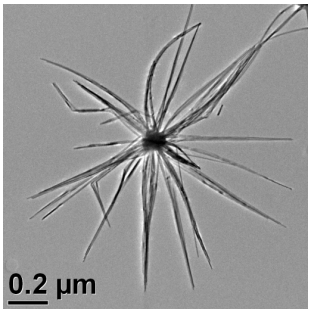


Figure S6g. Nanoparticle with urchin-like habit showing long and acicular arms either with straight or curved profile. Some arms are folded.

The core regions are too thick to obtain interpretable clear phase contrast HRTEM images; they only revealed the presence of parallel defective domains (Figure S6h).

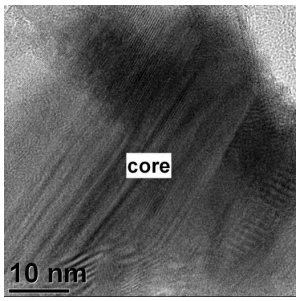


Figure S6h. High resolution TEM image of core region showing the presence of defective domains.

S7: SQUID

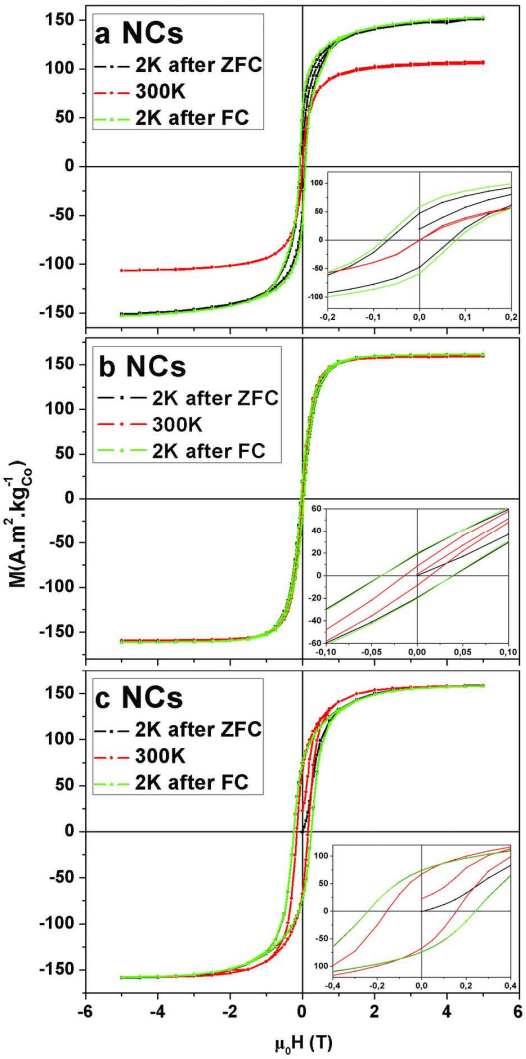


Figure S7. Magnetization versus applied magnetic field curves for NCs a, b and c (black traces: Zero Field Cooling at 2K, red traces: curves at 300K ; green traces: Field Cooling at 2K). In the insets: magnification of the central part of the curves.

Note that no exchange bias is detected at 2K on the hysteresis loops measured after a field cooling from 300K under a magnetic field of 5T. The hysteresis loop measured at 2K for **NCs a** is not saturated at fields up to 5T, and presents a much smaller Ms than the bulk value. With increasing temperature, Ms decreases as a result of ferromagnetic to superparamagnetic transition for the smallest particles. Note that purification of **NCs a** from the excess of ligands and any molecular species has not been possible**,** while the measurements were performed on purified samples for **NCs b** and **c**. Therefore the presence of residual molecular species with small magnetization (diamagnetic, paramagnetic or antiferromagnetic) is the most likely hypothesis to explain the reduced magnetization of **NCs a**.

S8: UV-Vis spectrum of $[Co\{N(SiMe_3)_2\}_2(thf)]$

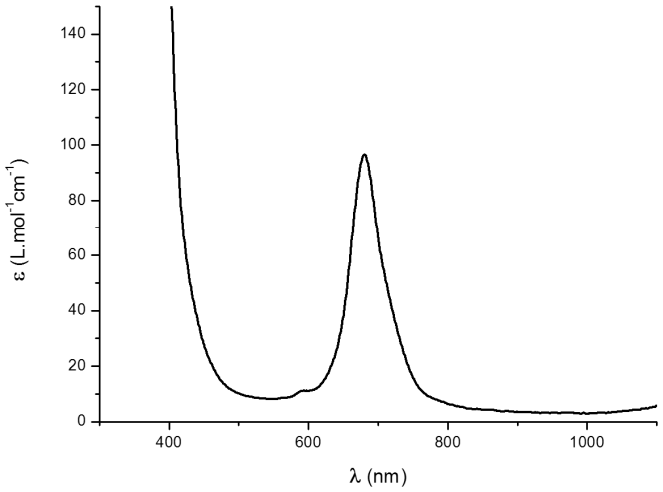


Figure S8. UV-Vis spectrum of $[Co\{N(SiMe_3)_2\}_2(thf)]$ in anisole

S9: UV-Vis spectra and the corresponding nanoparticles produced from solutions prepared by various addition rates

The spectra were recorded on a Perkin Elmer Lambda 35. Aliquots of the solutions 25 min after $[Co\{N(SiMe_3)_2\}_2(thf)]$ addition to the ligand mixture are transferred to a 2mm optical path UV cell. Spectra were recorded with a sampling scan rate of 240 nm/ min and a resolution of 1 nm.

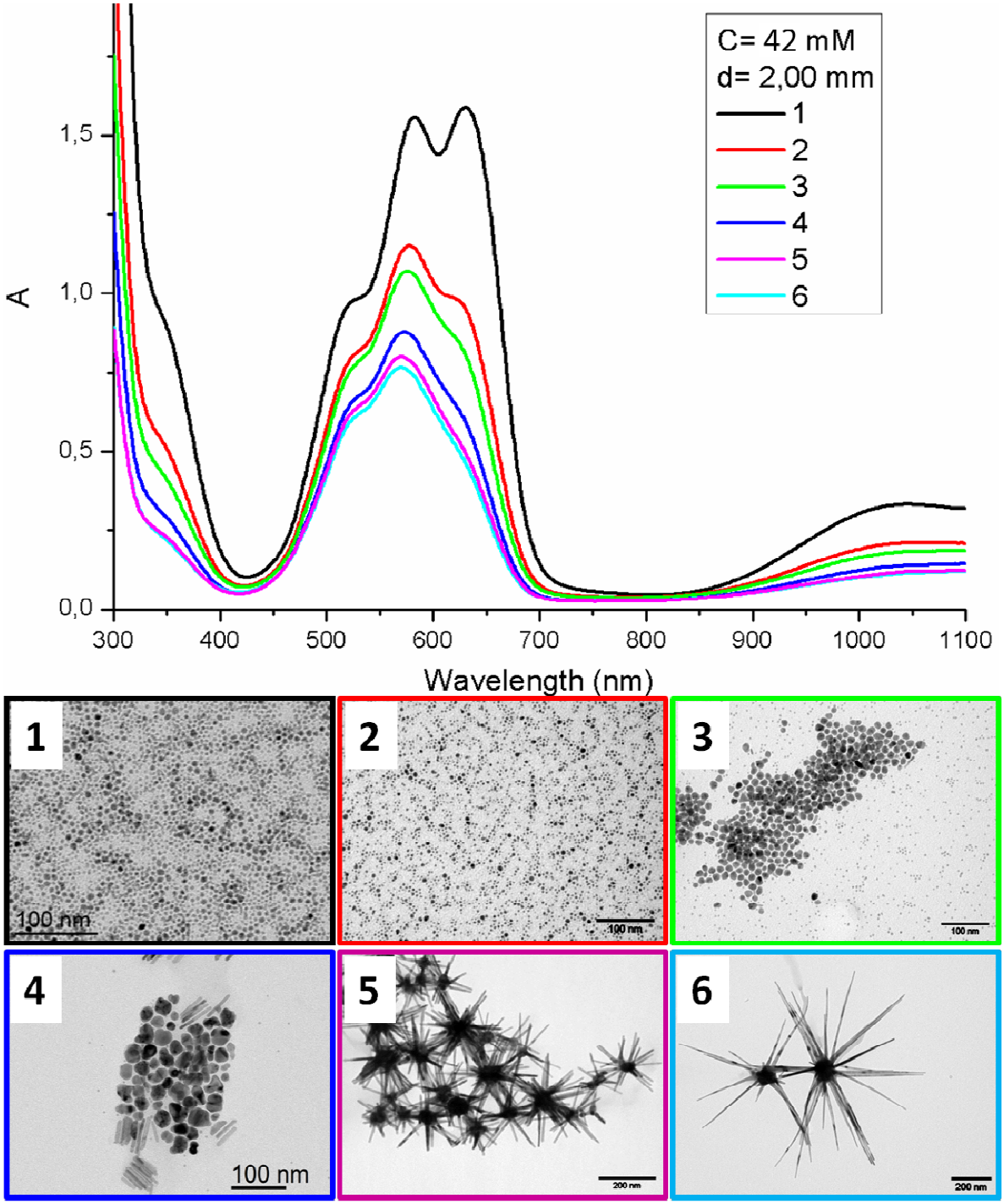


Figure S9: UV-Vis spectra from solutions obtained by various addition rates and the corresponding nanoparticles, starting from slow (1) up to fast addition (6)

S10. UV-Vis spectra of control reactions

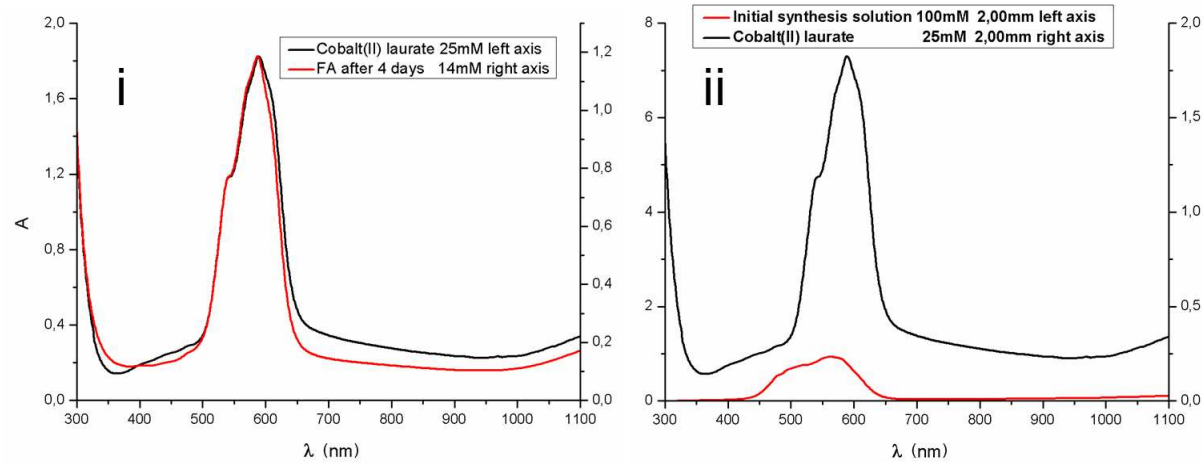


Figure S10. i) Fast addition reaction after 4 days (red line) versus independently prepared $[Co(LA)_2]$ (black line); ii) Solution after the addition of 2,3 equivalents of LA to $[Co\{N(SiMe_3)_2\}_2(thf)]$ (red line) immediately after mixing. The same solution forms a low solubility precipitate which is the $[Co(LA)_2]$ (red line).

S11. Computational details

All the calculations were performed with the Gaussian 03[1] suite of programs. Cobalt and silicon were treated with a Stuttgart-Dresden pseudopotential in combination with their adapted basis set [2,3] . The basis set has been augmented by a set of f polarization functions[4] for the cobalt atom and by a set of d polarization functions for the silicon atoms. Carbon, nitrogen, oxygen and hydrogen atoms have been described with a 6-31G(d,p) double-ζ basis set [5] . Calculations were carried out at the density functional theory (DFT) level of theory using the hybrid functional B3PW91 [6] .Geometry optimizations were carried out without any symmetry restrictions and the nature of the extremum (minimum) was verified with analytical frequency calculations. In all cases, both high and low spin species were computed. In all Co(II) systems, the high spin (quartet) was always found to be the lowest. For the Co(I) systems, the low spin (singlet) is the most stable at the DFT level of theory. The calculations were carried out in the gas phase and the Gibbs free energies are obtained at T=298.15K. The electron density has been analyzed using the Natural Bonding Analysis (NBO) [7] .

(1). Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratman, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A .; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowswi, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Jonhson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 03*, *Revision D-02*, Gaussian, Inc., Pittsburgh PA, **2003**.
(2). Dolg, M.; Wedig, U; Stoll, H.; Preuss, H. *J. Chem. Phys.*, **1987**, *86*, 866
(3). Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431-1441
(4).Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111-114.
(5). Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257-2261.
(6). (a) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 284; (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
(7). Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.*, **1988**, *88*, 899-926.

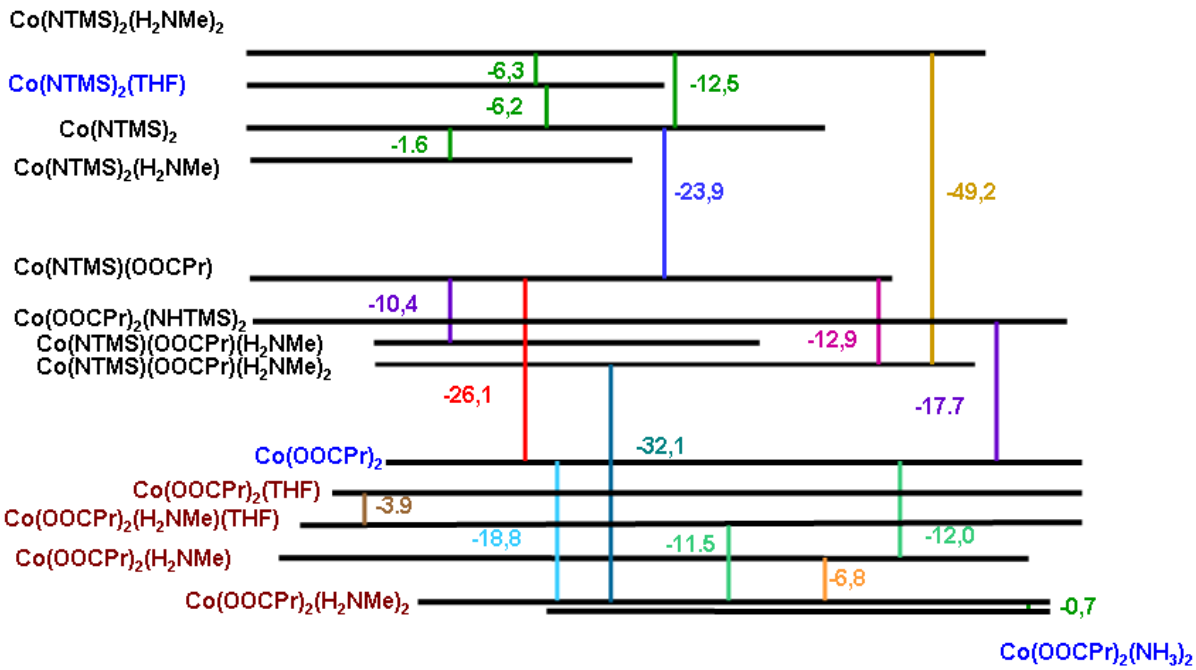


Figure S11: Thermodynamic stabilities of the possible cobalt species in solution. The $[Co(NTMS)_2]$ (NTMS = $N(SiMe_3)_2$, Pr = C_3H_7) system has been considered as reference and all the data are Gibbs free energies (Kcal/mol) at T=298.15K.
Blue letters are used for $[Co(NTMS)_2(thf)]$ and for the analogues of the isolated compounds mentionned in the text ; red letters are used for the analogues mentionned in the main text but without having been isolated.

Cartesian coordinates of all computed structures in the order that appears in the figure S11 starting from $Co(NTMS)_2(H_2NMe)_2$.

```
  69
scf done:  -941.710372
 C    1.236996   -1.402119   -4.561963
Si    0.730115   -1.618513   -2.737914
 C   -0.616204   -2.971234   -2.774963
 C   -0.146395    0.008873   -2.274369
 N    2.040119   -2.021019   -1.645956
Co    1.670137   -2.543447    0.223400
 N    1.127054   -4.624792   -0.323318
 H    0.847903   -4.994729    0.581813
Si    3.719227   -1.877365   -2.114149
 C    4.852936   -2.601386   -0.762065
 C    4.206469   -2.848304   -3.682241
 C    4.290466   -0.079347   -2.393756
 N    1.088784   -3.001017    2.117442
Si    2.145780   -3.812129    3.246691
 C    1.885914   -5.703230    3.282259
Si   -0.558330   -2.605333    2.544387
 C   -0.693114   -1.017140    3.590938
 C   -1.562553   -2.302559    0.955289
 C   -1.490041   -3.972490    3.490950
 C    3.972717   -3.549065    2.783573
 C    1.976355   -3.202206    5.045616
 C    2.096290   -5.497989   -0.991503
 N    2.423987   -0.640328    1.136694
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H	-0.526313	0.007098	-1.248007
H	0.535066	0.860353	-2.376898
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H	-1.114168	-3.101176	-1.808676
H	0.358432	-1.073314	-5.129344
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H	1.585167	-2.339223	-5.005954
H	5.897566	-2.489525	-1.074917
H	4.761567	-2.118214	0.215149
H	4.672268	-3.673168	-0.624235
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H	3.834499	-3.878080	-3.653287
H	3.836490	-2.384654	-4.599896
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H	2.558797	-6.175168	4.007661
H	0.860406	-5.963004	3.564029
H	2.092467	-6.160410	2.306950
H	2.685703	-3.734077	5.690364
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H	4.260374	-2.492194	2.817039
H	-2.522743	-3.658740	3.682846
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H	-1.032474	-4.201722	4.458429
H	-2.552945	-1.897091	1.191110
H	-1.075299	-1.586871	0.282224
H	-1.718311	-3.236280	0.403526
H	-1.741157	-0.771659	3.798399
H	-0.181720	-1.128424	4.552164
H	-0.251559	-0.156434	3.075764
H	2.267323	1.498045	1.304503
H	2.056443	0.811416	-0.328943
H	0.780206	0.630542	0.872088
H	0.290928	-4.539732	-0.894297
H	1.693278	-6.489789	-1.233606
H	2.426443	-5.013042	-1.912231
H	2.968335	-5.631609	-0.345953
H	2.151945	-0.884608	2.087102

68

scf done: -982.415324

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H	14.456954	1.712863	9.387144
H	16.098250	1.118754	9.115528
H	14.714336	0.222781	8.472462
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H	17.160772	3.654074	7.781662
H	15.628269	4.420737	8.217576
C	12.687950	4.284003	8.526143

H	13.184785	3.724514	9.324649
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H	13.324929	5.132459	8.257436
C	11.425622	4.374959	5.763391
H	12.101604	5.185654	5.471883
H	10.528181	4.822025	6.206215
H	11.120364	3.855364	4.849806
C	11.021459	1.900839	7.551442
H	10.688634	1.292546	6.702846
H	10.132390	2.361434	7.996808
H	11.459266	1.227331	8.296126
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H	15.291592	-0.993020	3.550809
H	13.932074	-0.631777	2.459450
C	13.678686	-2.456409	3.689662
H	12.715180	-2.605305	3.189854
H	14.368260	-3.227088	3.335797
N	13.683775	2.464720	6.260099
O	13.588312	-0.230461	4.450404
Si	15.236659	2.230031	7.040364
Si	12.280710	3.219189	7.003680
Co	13.588316	1.906813	4.450401
C	12.973410	-1.050518	5.470384
H	11.885034	-0.993010	5.349992
H	13.244546	-0.631770	6.441351
C	13.497931	-2.456406	5.211146
H	14.461435	-2.605310	5.710952
H	12.808352	-3.227082	5.565007
C	10.815659	1.225071	3.027990
H	11.218371	0.222117	3.202032
H	9.821467	1.111739	2.580625
H	10.673089	1.710803	4.000814
C	12.066799	1.228020	0.246216
H	12.719556	1.712838	-0.486352
H	11.078261	1.118736	-0.214675
H	12.462199	0.222757	0.428349
C	11.036282	3.853439	1.466072
H	10.973747	4.490031	2.354435
H	10.015792	3.654075	1.119208
H	11.548286	4.420743	0.683253
C	14.488650	4.284037	0.374624
H	13.991801	3.724552	-0.423881
H	15.419633	4.688448	-0.039421
H	13.851673	5.132492	0.643352
C	15.751025	4.374965	3.137376
H	15.075048	5.185663	3.428894
H	16.648458	4.822020	2.694533
H	16.056289	3.855361	4.050953
C	16.155156	1.900843	1.349287
H	16.487991	1.292536	2.197873
H	17.044214	2.361447	0.903912
H	15.717327	1.227345	0.604600
N	13.492842	2.464719	2.640697
Si	11.939907	2.230023	1.860452
Si	14.895925	3.219208	1.897078

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scf done: -750.0273312

Co	0.000216	0.008727	0.002644
N	0.010529	0.006882	1.832070
N	-0.001358	-0.001992	-1.824733
Si	-0.890117	-1.307031	-2.634938

Si	0.877527	1.297657	-2.654250
C	-1.910145	-0.660905	-4.098775
C	0.300017	-2.646656	-3.253520
C	-2.091228	-2.106940	-1.403039
H	-2.663637	-2.902742	-1.893692
H	-1.567395	-2.557281	-0.552530
H	-2.806075	-1.374875	-1.012401
H	-0.255324	-3.472806	-3.711868
H	0.997094	-2.254760	-3.999714
H	0.888733	-3.054160	-2.425137
H	-2.483294	-1.482242	-4.543812
H	-2.620363	0.106841	-3.776039
H	-1.282699	-0.233873	-4.887405
C	1.881448	0.639926	-4.123778
C	-0.320074	2.631735	-3.270971
C	2.090144	2.108961	-1.441078
H	0.230890	3.457223	-3.735777
H	-1.020393	2.235408	-4.011765
H	-0.904723	3.041391	-2.440753
H	2.655788	2.902409	-1.943259
H	1.573628	2.564309	-0.588720
H	2.810104	1.380977	-1.052298
H	2.439583	1.459618	-4.590320
H	2.603953	-0.116351	-3.801219
H	1.245330	0.195164	-4.895495
Si	-0.861315	1.313909	2.652466
Si	0.888150	-1.302682	2.642233
C	1.907978	-0.668356	4.111275
C	-0.307284	-2.640899	3.254233
C	2.089094	-2.101651	1.407990
C	-1.875367	0.673496	4.122910
C	0.337959	2.648166	3.265372
C	-2.067135	2.120517	1.427482
H	-0.210041	3.478776	3.724492
H	1.034674	2.252313	4.010027
H	0.927282	3.050224	2.434746
H	-2.430954	1.499860	4.580698
H	-2.600525	-0.081387	3.802857
H	-1.245312	0.231079	4.900916
H	-2.644541	2.907581	1.926285
H	-1.545877	2.584337	0.582518
H	-2.779226	1.389361	1.029440
H	2.470311	-1.495535	4.559246
H	2.627564	0.092385	3.792473
H	1.280633	-0.235166	4.896579
H	2.672185	-2.888445	1.900533
H	1.563928	-2.564165	0.564796
H	2.795840	-1.366583	1.007752
H	0.243129	-3.472336	3.708952
H	-1.002266	-2.248321	4.002244
H	-0.898697	-3.041095	2.424194

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scf done: -845.880705

C	1.346338	-1.572065	-4.454505
Si	0.636009	-1.696692	-2.692972
C	-0.691012	-3.068017	-2.783202
C	-0.261076	-0.069888	-2.300360
N	1.842135	-2.114734	-1.490614
Co	1.339975	-3.347912	-0.124226
N	1.337137	-5.283548	-1.029187
C	0.232636	-6.197810	-0.688972

Si	3.444227	-1.393774	-1.444998
C	4.148392	-1.492923	0.315137
C	4.648850	-2.302294	-2.604693
C	3.457568	0.448768	-1.919448
N	0.937366	-3.484384	1.733090
Si	2.079608	-4.313364	2.770096
C	1.275578	-5.655162	3.853992
Si	-0.365186	-2.454801	2.311167
C	0.189879	-0.641963	2.429207
C	-1.816148	-2.530626	1.084443
C	-1.052127	-2.963350	4.009885
C	3.355869	-5.258753	1.702251
C	3.043468	-3.143191	3.914890
H	2.228410	-5.717406	-0.799506
H	-1.046310	0.138855	-3.035964
H	-0.727031	-0.109555	-1.310215
H	0.435565	0.774123	-2.304168
H	-1.513398	-2.738352	-3.428455
H	-0.289685	-3.987487	-3.225928
H	-1.131381	-3.313202	-1.810013
H	0.539979	-1.376086	-5.170723
H	2.078087	-0.764946	-4.556619
H	1.835937	-2.506180	-4.750037
H	5.111156	-0.971273	0.365028
H	3.467905	-1.020916	1.030768
H	4.322003	-2.521836	0.645759
H	5.658725	-1.882048	-2.535703
H	4.712174	-3.365582	-2.346481
H	4.327388	-2.231596	-3.648734
H	4.479569	0.839532	-1.852412
H	3.105172	0.629849	-2.939596
H	2.832953	1.034736	-1.237263
H	2.051328	-6.255402	4.343940
H	0.640223	-5.230855	4.636001
H	0.658073	-6.332673	3.254155
H	3.752041	-3.697299	4.541057
H	3.605865	-2.406081	3.333479
H	2.369498	-2.596218	4.582958
H	4.201953	-5.562152	2.329203
H	2.919889	-6.178384	1.293733
H	3.770744	-4.666705	0.878218
H	-1.871719	-2.289071	4.284053
H	-1.448336	-3.983493	3.999246
H	-0.299057	-2.898604	4.801891
H	-2.661783	-1.937603	1.450952
H	-1.541515	-2.124340	0.104880
H	-2.163636	-3.560320	0.946452
H	-0.634368	0.012902	2.734329
H	1.000539	-0.524648	3.155880
H	0.558544	-0.293778	1.458195
H	1.356997	-5.101599	-2.029869
H	0.331832	-7.178055	-1.169385
H	0.202355	-6.325705	0.394195
H	-0.711262	-5.747518	-1.001717

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scf done: -755.001154

C	-0.437334	-0.795181	-4.441660
Si	0.379301	-1.153872	-2.765620
N	-0.448940	-2.436671	-1.864887
Si	-1.686347	-3.560838	-2.430312
C	-1.072948	-4.644911	-3.859745

C	0.350390	0.437296	-1.739894
C	2.178881	-1.668357	-3.064554
Co	0.095814	-2.822553	-0.153225
O	1.575731	-1.809066	0.926393
C	1.344511	-2.638766	1.856127
C	2.079980	-2.600745	3.167136
C	3.133236	-1.502721	3.282769
C	3.842771	-1.521034	4.634202
C	-2.100418	-4.712542	-0.967935
C	-3.283715	-2.680419	-2.943478
O	0.447748	-3.536388	1.656762
H	2.726134	-0.892832	-3.612254
H	2.695136	-1.832944	-2.112680
H	2.231958	-2.595180	-3.644802
H	0.864564	1.249604	-2.265812
H	-0.679013	0.757034	-1.547198
H	0.850053	0.290732	-0.776956
H	0.140610	-0.025647	-4.966233
H	-0.472403	-1.675652	-5.090409
H	-1.456641	-0.415467	-4.321886
H	-2.878575	-5.425191	-1.266477
H	-1.239253	-5.308444	-0.639684
H	-2.490070	-4.165297	-0.100480
H	-4.070776	-3.411840	-3.159103
H	-3.641193	-2.024699	-2.143073
H	-3.140618	-2.071420	-3.840617
H	-1.829494	-5.390053	-4.130563
H	-0.854561	-4.054317	-4.754662
H	-0.159306	-5.178011	-3.577909
H	2.521325	-3.595570	3.311616
H	1.319238	-2.509549	3.953778
H	3.862159	-1.618149	2.472774
H	2.656474	-0.529868	3.120136
H	4.593743	-0.727560	4.695420
H	3.136538	-1.373244	5.459132
H	4.354116	-2.475197	4.804936

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scf done: -1365.3400805

C	-0.869326	-4.528038	0.715010
C	-0.020239	-3.800925	-0.324321
C	-0.673176	-3.782700	-1.706283
C	0.094202	-3.002719	-2.752235
O	0.060742	-3.370391	-3.966277
Co	1.247478	-1.692945	-4.517497
O	2.429495	0.001128	-5.075578
C	2.390985	-0.379137	-6.284585
C	3.133565	0.380726	-7.362628
C	3.446658	1.836321	-7.023937
C	4.256335	2.530671	-8.116016
O	0.760193	-1.969734	-2.431228
N	3.135247	-2.940329	-4.003793
Si	4.357996	-2.065170	-2.966094
N	-0.639313	-0.434407	-5.019424
Si	-1.165211	0.774977	-3.759922
O	1.730961	-1.421684	-6.590389
Si	3.661740	-4.156633	-5.257533
Si	-1.861897	-1.304507	-6.061614
H	-1.666767	-3.317247	-1.634697
H	-0.837310	-4.795504	-2.088537
H	0.167634	-2.769210	-0.009156
H	0.964440	-4.280911	-0.395229

H	-1.846680	-4.046817	0.835852
H	-1.049089	-5.570290	0.427802
H	-0.379721	-4.533755	1.693990
H	2.570577	-3.478813	-3.342397
C	4.424232	-3.320571	-6.763313
C	2.138236	-5.132854	-5.783131
C	4.920599	-5.375302	-4.524569
C	3.628639	-0.537156	-2.146371
C	5.845002	-1.552956	-4.013171
C	4.907091	-3.241146	-1.581546
H	-0.075749	0.109068	-5.677488
C	-2.404617	-0.121070	-7.442317
C	-1.138717	-2.831709	-6.887743
C	-3.350439	-1.818514	-5.017777
C	-2.415858	2.003982	-4.490238
C	-1.938303	-0.065444	-2.261762
C	0.360813	1.741003	-3.222430
H	2.556642	0.297408	-8.290619
H	4.066588	-0.171190	-7.546696
H	2.507765	2.379497	-6.858139
H	3.984425	1.870947	-6.070848
H	4.466681	3.572068	-7.852617
H	5.217538	2.029459	-8.278261
H	3.721439	2.532287	-9.072652
H	5.146165	-6.146302	-5.270609
H	5.866203	-4.894901	-4.255289
H	4.530699	-5.882889	-3.636182
H	2.441223	-5.952716	-6.444353
H	1.606226	-5.561005	-4.929207
H	1.436454	-4.495850	-6.326832
H	4.748015	-4.097565	-7.465255
H	3.672286	-2.701872	-7.258382
H	5.295311	-2.707364	-6.521400
H	5.618174	-2.728640	-0.923692
H	4.051490	-3.537200	-0.964219
H	5.388107	-4.149125	-1.954039
H	4.369309	-0.121659	-1.452769
H	3.377786	0.222110	-2.889852
H	2.726753	-0.790745	-1.583862
H	6.525513	-0.968771	-3.383588
H	6.408990	-2.400987	-4.411129
H	5.535952	-0.913725	-4.844829
H	-2.258419	0.710065	-1.556376
H	-2.813503	-0.669979	-2.510391
H	-1.194117	-0.693581	-1.767221
H	-2.643163	2.770678	-3.740295
H	-2.019212	2.516245	-5.372944
H	-3.361473	1.528941	-4.768749
H	0.058253	2.570696	-2.573416
H	1.047730	1.101316	-2.663183
H	0.910100	2.153375	-4.073063
H	-4.028891	-2.403118	-5.649229
H	-3.041373	-2.459257	-4.187056
H	-3.916565	-0.972000	-4.619522
H	-3.120841	-0.626654	-8.099977
H	-2.878006	0.789808	-7.067092
H	-1.547751	0.169342	-8.060764
H	-1.882346	-3.241106	-7.581821
H	-0.236100	-2.580862	-7.450140
H	-0.891386	-3.594654	-6.146886

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scf done: -850.864904

C	0.236253	-0.200109	-4.109590
Si	0.517311	-1.190666	-2.510436
C	-0.787283	-2.570628	-2.439180
N	0.465925	-0.175361	-1.077328
Co	1.125154	-0.946313	0.523413
C	2.224815	-2.013385	-2.633774
Si	-0.507988	1.261126	-0.858811
C	0.052790	2.725191	-1.934226
C	-2.356447	0.959359	-1.178919
C	-0.338151	1.833373	0.957571
O	1.765106	-2.934813	0.885747
C	0.930037	-2.958570	1.841834
O	0.240952	-1.914841	2.103573
N	2.759924	0.091647	1.345949
C	3.972382	0.050786	0.505789
C	0.753150	-4.190571	2.697515
C	1.343858	-5.469881	2.111715
C	1.175532	-6.668420	3.042083
H	2.953383	-0.315081	2.258924
H	-0.753141	-3.199607	-3.336168
H	-0.615503	-3.215885	-1.570640
H	-1.796934	-2.155832	-2.353669
H	2.275141	-2.677166	-3.504447
H	3.014644	-1.261781	-2.740151
H	2.437875	-2.616561	-1.744573
H	0.291430	-0.871235	-4.974404
H	-0.746146	0.282855	-4.132802
H	0.998330	0.574914	-4.239129
H	-1.090092	2.600770	1.174479
H	-0.496980	1.020744	1.677468
H	0.639571	2.291845	1.150543
H	-0.504200	3.631189	-1.668277
H	1.119104	2.931492	-1.791811
H	-0.110126	2.534902	-2.998914
H	-2.941108	1.873006	-1.021833
H	-2.535709	0.623359	-2.205684
H	-2.743323	0.188399	-0.504282
H	2.482482	1.055763	1.515449
H	4.816635	0.582303	0.959431
H	4.251497	-0.991589	0.341198
H	3.743848	0.498841	-0.462779
H	-0.319121	-4.295521	2.899825
H	1.210908	-3.966340	3.671773
H	0.867048	-5.675862	1.146314
H	2.403991	-5.305255	1.891912
H	1.600458	-7.575190	2.600401
H	1.676449	-6.501796	4.002836
H	0.118462	-6.866867	3.252841

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scf done: -946.7191691

C	0.008544	-0.755430	-3.964271
Si	0.337113	-1.374442	-2.193688
N	-0.687345	-2.716117	-1.712765
Si	-1.829844	-3.571248	-2.707269
C	-1.005519	-4.658838	-4.036118
C	0.078168	0.101025	-1.025400
C	2.172776	-1.863510	-2.103885
Co	-0.344196	-3.424971	0.045044
O	1.023125	-2.493692	1.209406
C	1.208148	-2.996134	2.376162

C	2.212933	-2.289329	3.275378
C	3.396999	-1.653306	2.548996
C	4.341274	-0.916863	3.495703
N	-1.892575	-3.413892	1.467907
H	-1.322249	-3.690811	2.275829
N	0.483141	-5.353167	0.266295
H	-0.154599	-6.123280	0.083768
C	-2.534884	-2.109550	1.694616
C	-2.865619	-4.752556	-1.613269
C	-3.102796	-2.462016	-3.584458
O	0.596816	-4.000566	2.817133
C	1.758436	-5.575051	-0.434992
H	2.819692	-1.032584	-2.408459
H	2.441135	-2.137128	-1.078143
H	2.386296	-2.715143	-2.759138
H	0.712457	0.949786	-1.306043
H	-0.964609	0.436087	-1.046448
H	0.330628	-0.183496	0.001288
H	0.754320	0.007606	-4.216223
H	0.089463	-1.550481	-4.712688
H	-0.978737	-0.293887	-4.060951
H	-3.510521	-5.374528	-2.244389
H	-2.248352	-5.434151	-1.015640
H	-3.517720	-4.189879	-0.935739
H	-3.902602	-3.072793	-4.019558
H	-3.561397	-1.757339	-2.882665
H	-2.652536	-1.882439	-4.394894
H	-1.752585	-5.179196	-4.646633
H	-0.385575	-4.058042	-4.709596
H	-0.357406	-5.415771	-3.580277
H	2.232594	-6.523932	-0.157593
H	1.588265	-5.561796	-1.513464
H	2.438912	-4.756837	-0.192110
H	-2.596923	-4.131068	1.317652
H	-3.221923	-2.120137	2.549129
H	-1.759927	-1.361945	1.875189
H	-3.083950	-1.814370	0.797870
H	0.631383	-5.299622	1.281696
H	2.543437	-3.007795	4.032552
H	1.655866	-1.510320	3.816823
H	3.951500	-2.432748	2.010169
H	3.015807	-0.969938	1.783741
H	5.180701	-0.470738	2.952641
H	3.822737	-0.109007	4.025133
H	4.757155	-1.591350	4.253143

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scf done: -759.9582248

C	-5.974536	-1.191598	0.391135
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C	-3.782391	0.014463	-0.023148
C	-2.284275	-0.014585	0.024179
O	-1.620587	-1.106471	0.051001
Co	0.001334	-0.049253	0.038612
O	1.600355	-1.156913	0.066778
C	2.287041	-0.082433	0.048705
C	3.785910	-0.081154	0.029194
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C	5.947912	-1.334113	0.459499
O	-1.592946	1.058366	0.013516
O	1.618702	1.008200	0.024851
H	4.120849	0.801739	0.584740

H	4.082985	0.093817	-1.015106
H	-4.110952	0.915029	0.507370
H	-4.056721	0.172132	-1.076407
H	-4.061059	-2.117274	-0.020533
H	-4.171115	-1.385561	1.566250
H	-6.434625	-2.102527	0.785615
H	-6.391590	-0.342733	0.944480
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H	4.119474	-1.518488	1.597300
H	4.026369	-2.217587	-0.005106
H	6.384925	-2.259059	0.847592
H	6.280260	-1.220373	-0.578567
H	6.368773	-0.501583	1.034470

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C	0.794791	-2.129191	-2.679186
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C	-1.123958	-2.827098	-1.134496
O	-0.368763	-2.620432	-0.134640
Co	-1.995552	-3.132553	1.093457
O	-2.464440	-1.151286	1.657423
C	-3.115323	-0.244007	0.734472
O	-2.342596	-3.148485	-0.935428
O	-3.172726	-4.381073	2.168617
C	-2.369454	-4.302202	3.159264
C	-2.679559	-5.062306	4.425023
C	-1.628661	-4.939197	5.523970
C	-2.000781	-5.727479	6.777205
O	-1.331988	-3.582679	3.049815
H	-0.641019	-3.733263	-2.970408
H	-1.341616	-2.144756	-3.124563
H	1.487025	-2.716773	-2.066941
H	0.802432	-1.119674	-2.251355
H	1.309891	-3.089123	-4.566313
H	0.611552	-1.476742	-4.752352
H	2.280663	-1.658503	-4.198836
H	-2.834925	-6.110570	4.139081
H	-3.660439	-4.713573	4.774759
H	-0.662657	-5.281570	5.136288
H	-1.491007	-3.880582	5.771276
H	-1.234318	-5.625177	7.551892
H	-2.949695	-5.379659	7.201607
H	-2.110631	-6.796015	6.559381
C	-2.302789	1.042232	0.795480
C	-1.796411	1.032450	2.241125
C	-1.485286	-0.441207	2.460277
H	-4.144395	-0.094868	1.082532
H	-3.137461	-0.720436	-0.248461
H	-2.902752	1.922928	0.551769
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H	-2.583015	1.368438	2.925919
H	-0.918199	1.664951	2.394338
H	-1.592523	-0.784605	3.490309
H	-0.487354	-0.707878	2.096518

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scf done: -1088.232371

C	-1.218739	-0.671795	2.065245
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C	-3.238465	-0.888644	0.838598
C	-2.749417	0.553612	0.735985

C	-1.884070	0.695357	1.991834
Co	-1.575440	-3.641329	1.061145
O	-1.088146	-3.853743	3.091426
C	-2.272070	-4.257834	3.320816
C	-2.720939	-4.549035	4.737627
C	-1.588510	-4.786384	5.733061
C	-2.092837	-5.002390	7.157657
C	-0.816246	-2.854688	-1.145566
O	-2.011038	-3.265992	-1.014974
C	-0.330190	-2.406321	-2.509379
C	0.958283	-1.588381	-2.496322
C	1.428159	-1.211644	-3.899124
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O	-3.093295	-4.395579	2.363356
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H	1.624453	-2.103211	-4.506095
H	0.675493	-0.615172	-4.427624
H	2.351730	-0.624892	-3.865589
H	-3.413283	-5.398044	4.703069
H	-3.328315	-3.688827	5.054217
H	-1.000882	-5.655324	5.411592
H	-0.902183	-3.933994	5.696332
H	-1.263616	-5.174299	7.851507
H	-2.651325	-4.130906	7.518770
H	-2.761667	-5.868625	7.219738
H	-4.172989	-0.964807	1.407319
H	-3.364279	-1.384464	-0.126937
H	-3.574349	1.269934	0.692257
H	-2.136735	0.687369	-0.162513
H	-2.512331	0.865476	2.873500
H	-1.157492	1.509996	1.927923
H	-0.944275	-0.992832	3.072469
H	-0.334910	-0.732937	1.418837
N	-1.270679	-5.690659	0.488954
H	-1.982085	-6.194853	1.012183
H	-1.530503	-5.733073	-0.493003
C	0.064350	-6.260633	0.714278
H	0.143628	-7.310650	0.405863
H	0.798682	-5.670750	0.161451
H	0.305767	-6.183537	1.776626

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scf done: -855.8431507

C	1.464214	-2.435483	-4.281208
C	0.964581	-2.353904	-2.841049
C	-0.417130	-2.977309	-2.666466
C	-0.939370	-2.976697	-1.249708
O	-2.164991	-3.262546	-1.034080
Co	-1.874990	-3.091012	0.979320
O	-0.183421	-2.716878	-0.264905
O	-3.264625	-4.105366	2.084146
C	-2.452566	-4.164370	3.067222
O	-1.309170	-3.625194	2.957554
N	-1.928778	-1.044771	1.502680
C	-3.183947	-0.305679	1.290999
C	-2.875725	-4.865567	4.335771
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C	-2.266000	-5.724478	6.644446
H	-1.651968	-1.018681	2.481475

H	-0.411123	-4.025988	-2.995154
H	-1.167209	-2.483122	-3.295531
H	1.667088	-2.853345	-2.165628
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H	1.540109	-3.475802	-4.617908
H	0.788700	-1.915846	-4.970474
H	2.454996	-1.981715	-4.383568
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H	-3.285439	-5.840242	4.043060
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H	-1.384165	-4.024337	5.635574
H	-1.461969	-5.822724	7.380566
H	-3.086077	-5.174904	7.121116
H	-2.633748	-6.732154	6.419382
H	-3.113682	0.746613	1.590025
H	-3.453726	-0.354666	0.233737
H	-3.981062	-0.783591	1.864725

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scf done: -951.7012855

C	0.778067	-1.855889	-4.866487
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C	-0.328529	-2.905664	-2.835227
C	-0.403150	-3.032432	-1.323441
O	0.481715	-2.536299	-0.585093
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Co	-1.027886	-3.583379	1.120880
O	-2.467826	-4.530890	2.146479
C	-2.058960	-4.352359	3.350047
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N	-1.166925	-1.552810	1.626811
N	0.746794	-4.649595	1.447254
O	-1.004246	-3.721819	3.605660
H	-0.934964	-1.518067	2.616545
H	1.451495	-4.120095	0.939300
C	-2.455149	-0.895857	1.363225
C	0.755652	-6.062562	1.042874
H	-0.122019	-3.910679	-3.229730
H	-1.333472	-2.658128	-3.198124
H	1.687547	-2.172896	-2.926137
H	0.476927	-0.914468	-2.944144
H	1.046397	-2.831551	-5.288284
H	-0.185663	-1.566037	-5.301036
H	1.525498	-1.131842	-5.206796
H	-0.418127	-1.116412	1.093727
H	0.913789	-4.554181	2.446245
H	-3.161765	-5.963697	4.187235
H	-3.880472	-4.395685	4.430815
H	-1.351351	-5.393851	5.855743
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H	-4.171627	-4.859416	6.977459
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H	1.714894	-6.556180	1.240247
H	-0.031639	-6.594628	1.581568
H	0.537558	-6.130833	-0.025274
H	-2.456581	0.165447	1.639544
H	-2.690932	-0.983795	0.300275
H	-3.239829	-1.407373	1.925079

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scf done: -873.118842

C	0.770250	-1.866255	-4.861065
C	0.702736	-1.916211	-3.336706
C	-0.331254	-2.914170	-2.825875
C	-0.402519	-3.038062	-1.314107
O	-1.399871	-3.686521	-0.832476
Co	-1.023168	-3.581123	1.130912
O	-1.010700	-3.718456	3.598939
C	-2.065403	-4.350570	3.344653
C	-2.927686	-4.924105	4.454671
C	-2.306324	-4.857724	5.845813
C	-3.229837	-5.407367	6.930164
N	-1.153411	-1.548578	1.630497
H	-0.955097	-1.465749	2.623526
N	0.756935	-4.638491	1.456771
H	1.484869	-4.147479	0.945027
O	-2.470053	-4.531355	2.140582
O	0.483731	-2.540123	-0.578003
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H	0.740048	-5.606761	1.151540
H	-0.122295	-3.919378	-3.218557
H	-1.337403	-2.670073	-3.187470
H	1.682386	-2.174992	-2.920543
H	0.467572	-0.920574	-2.941152
H	1.042204	-2.841979	-5.280370
H	-0.195027	-1.581593	-5.295548
H	1.514447	-1.140094	-5.204052
H	-0.443652	-1.069218	1.083036
H	0.941328	-4.611280	2.455710
H	-3.179776	-5.955320	4.178022
H	-3.882931	-4.381343	4.430997
H	-1.360407	-5.412564	5.843973
H	-2.037860	-3.818792	6.066747
H	-2.761375	-5.353033	7.918280
H	-4.168958	-4.843873	6.977623
H	-3.487183	-6.456319	6.742988

S12. X-Ray crystal structure

Empirical formula	$C_{24}H_{52}Co N_2 O_4$
Formula weight	491.61
Temperature	180 K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C 1 2/c 1
Unit cell dimensions	a = 51.020(10) A alpha = 90 deg.
	b = 5.7091(11) A beta = 94.55(3) deg.
	c = 9.941(2) A gamma = 90 deg.
Volume	2886.5(10) A^3
Z, Calculated density	4, 1.131 Mg/m^3
Absorption coefficient	0.622 mm^-1
F(000)	1076
Crystal size	0.3 x 0.25 x 0.05 mm

Crystal Colour light pink
Theta range for data collection 3.2 to 25.68 deg.
Limiting indices -50<=h<=62, -6<=k<=6, -12<=l<=12
Reflections collected / unique 9868 / 2717 [R(int) = 0.1226]
Completeness to theta = 25.68 99.9 %
Absorption correction Empirical (SHELXA)
Max. and min. transmission 0.711 and 0.255
Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 2717 / 0 / 143
Goodness-of-fit on F^2 0.991
Final R indices [I>2sigma(I)] R1 = 0.0636, wR2 = 0.1208
R indices (all data) R1 = 0.0968, wR2 = 0.1356
Largest diff. peak and hole 0.448 and -0.38 e.A^-3

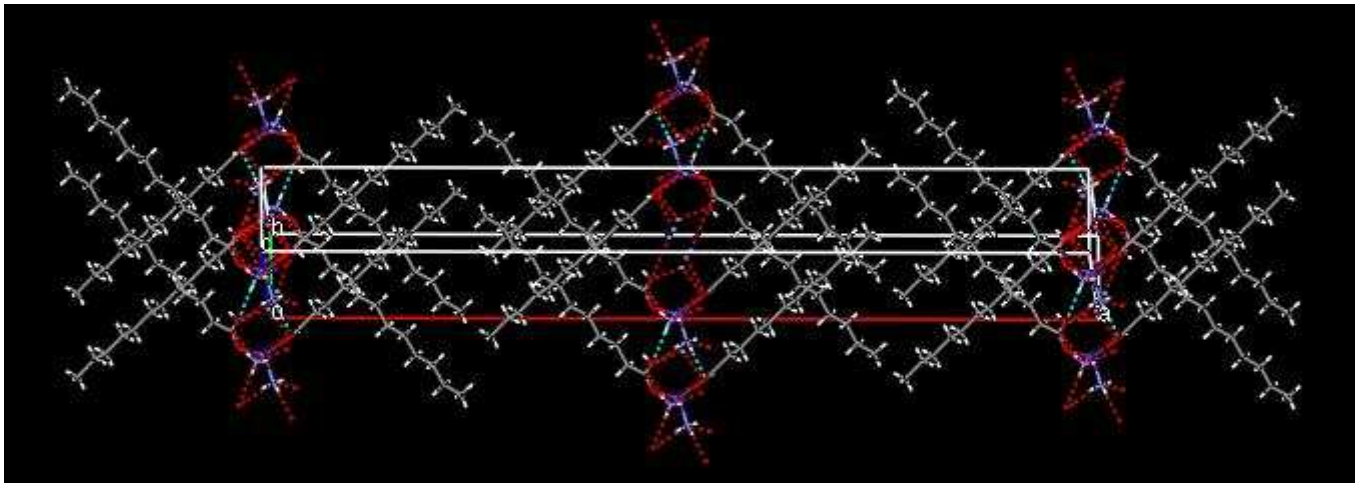

Figure S12. Several hydrogen bonds create an interesting 3D packing in the whole cell. The resulted packing is composed of infinite perpendicular chains.

The hydrogen bonds involved are the following and they are intermolecular:

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1A	0.910	2.040	166.62	2.933	O3 [x, y+1, z]
N1-H1B	0.910	2.178	157.28	3.038	O3 [-x+1, -y+3, -z+1]
N1-H1C	0.910	2.178	143.99	2.963	O2 [x, -y+3, z+1/2]

D= donor, A = acceptor, d= distance in Å; angle donor-hydrogen- acceptor in degrees.

S13. ^{1}H NMR spectra of the reaction of $HN(SiMe_3)_2$ and LA

The ^{1}H NMR spectrum of a 1/1 mixture between the reactants shows the $HN(SiMe_3)_2$ methyl groups at 0.12 ppm, while the peak at 0.31 ppm corresponds to a compound which chemical shift is in agreement with a methyl group next to a Si-O moiety. Addition of two equivalents of LA and heating at 60°C completely transforms the reactants to the ester.

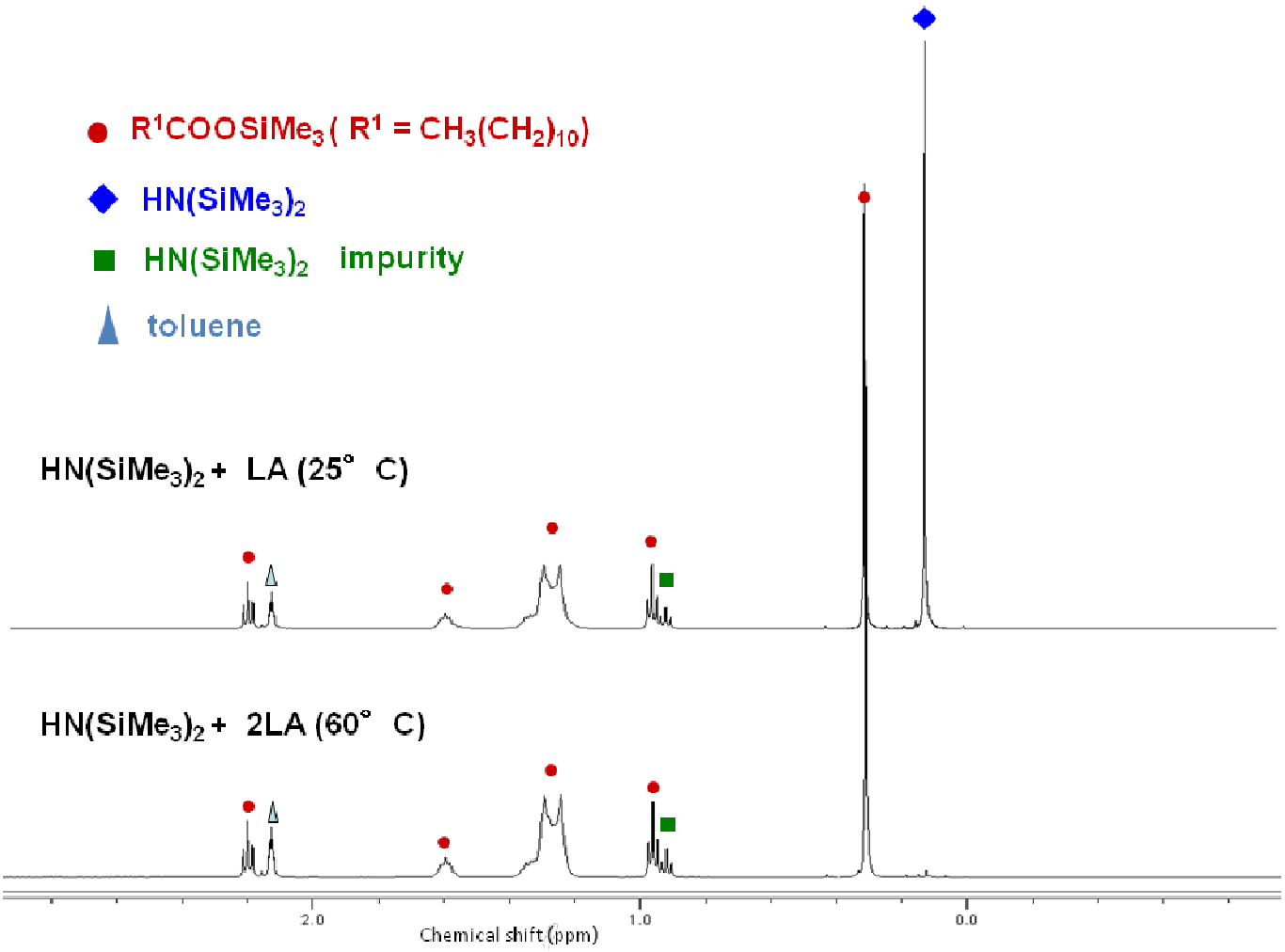

Figure S13. ^{1}H NMR spectra of reaction of $HN(SiMe_3)_2$ with in LA toluene-d^8. The blue diamond marks the methyl groups of free $HN(SiMe_3)_2$, while the red circles indicate $R^1COOSiMe_3$ (R^1 = $CH_3(CH_2)_{10}$) peaks. LA reacts with $HN(SiMe_3)_2$ even at room temperature forming the corresponding silyl ether CH_3 $(CH_2)_{10}COOSiMe_3$.