Supporting information
Chemoselective reduction of quinoline over Rh-C_{60} nanocatalysts

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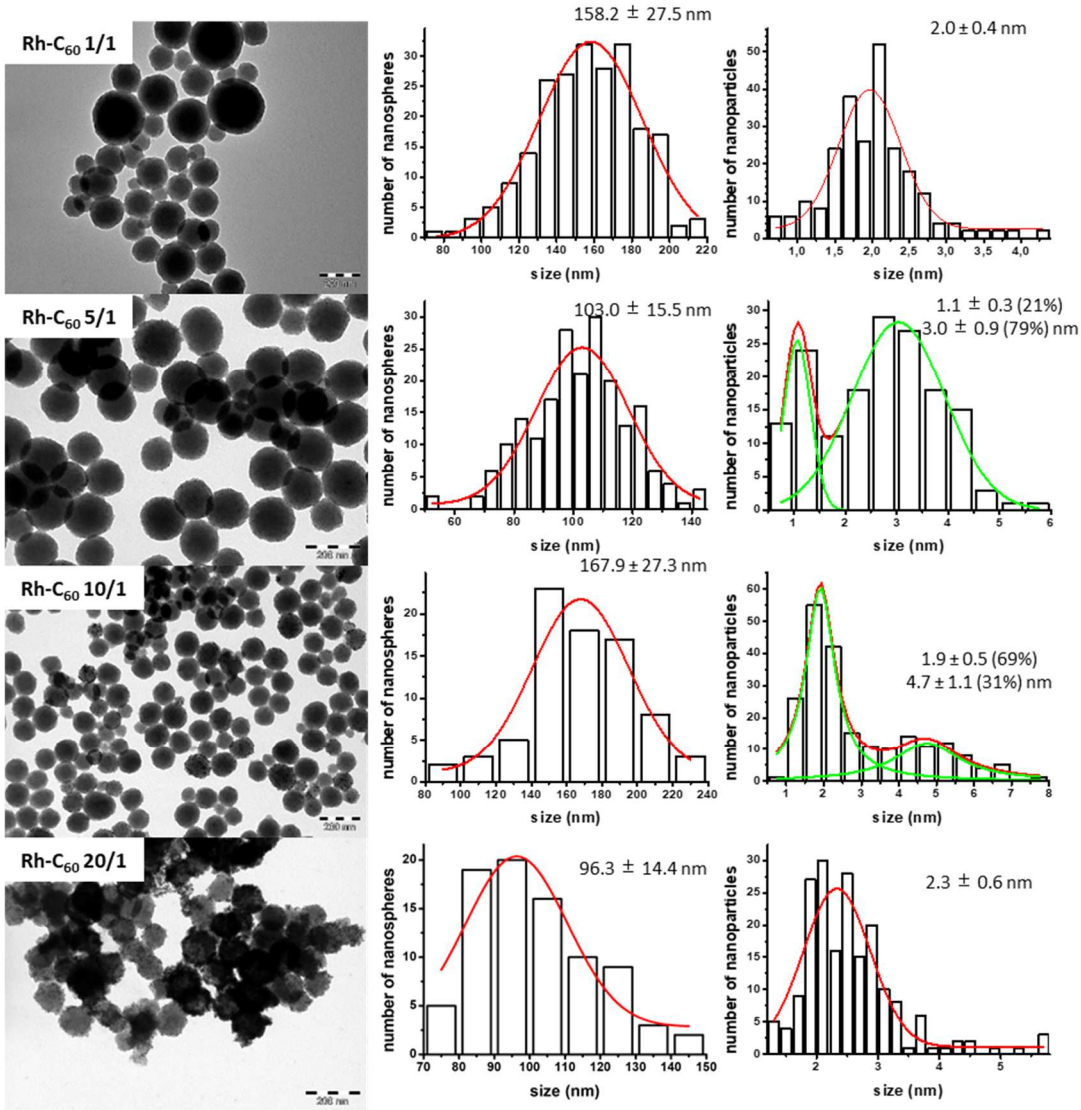

Figure S1. TEM images and size distribution histograms of Rh-C_{60} 1/1, 5/1, 10/1 and 20/1 (scale bar 200 nm).

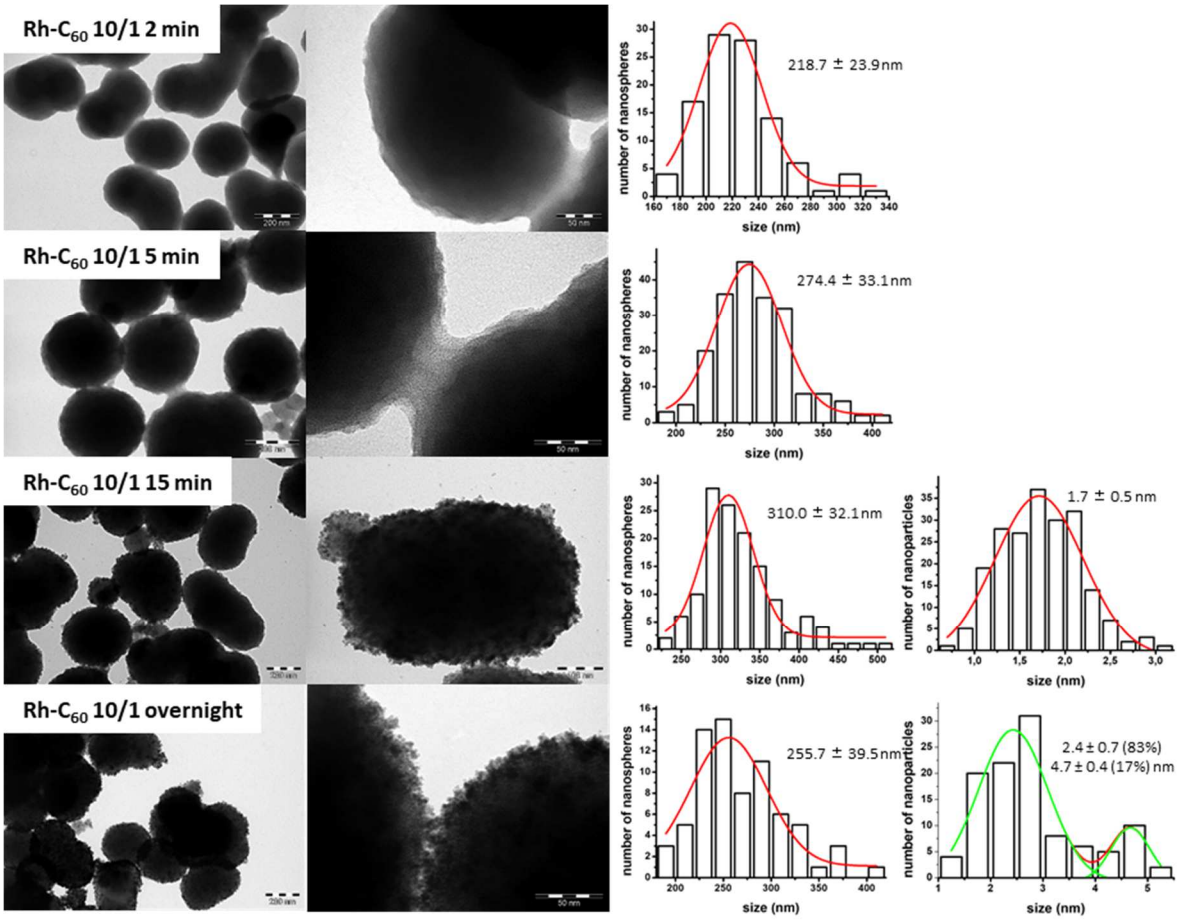

Figure S2. TEM images and size distribution histograms of Rh-C_{60} 10/1 synthesized in dichlorobenzene at -20°C (scale bar from left to right: 2 min, 200 and 50 nm; 5 min, 200 and 50 nm; 15 min, 200 and 50 nm; and overnight, 200 and 50 nm).

Table S1. Mean size distributions of Rh-C_{60} nanocatalysts synthesised at -20°C.

Time	NP mean size (nm) [a]	Nanospheres mean size (nm)[a]
2 min	-	218.7 ± 23.9
5 min	-	274.4 ± 33.1
15 min	1.7 ± 0.5 NP on the nanospheres surface 3.4 ± 1.3 NP dispersed on the TEM grid	310.0 ± 32.1
overnight	2.4 ± 0.7 (83%)/ 4.7 ± 0.4 (17%)[b]	255.7 ± 39.5

[a] Manual measurement from enlarged TEM micrographs. [b] In brackets percentage of each population

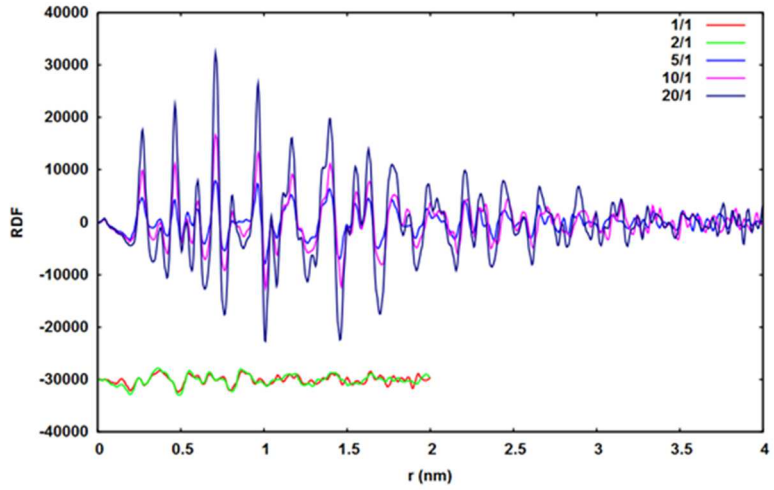

Figure S3. Related PDF for Rh-C_{60} compounds.

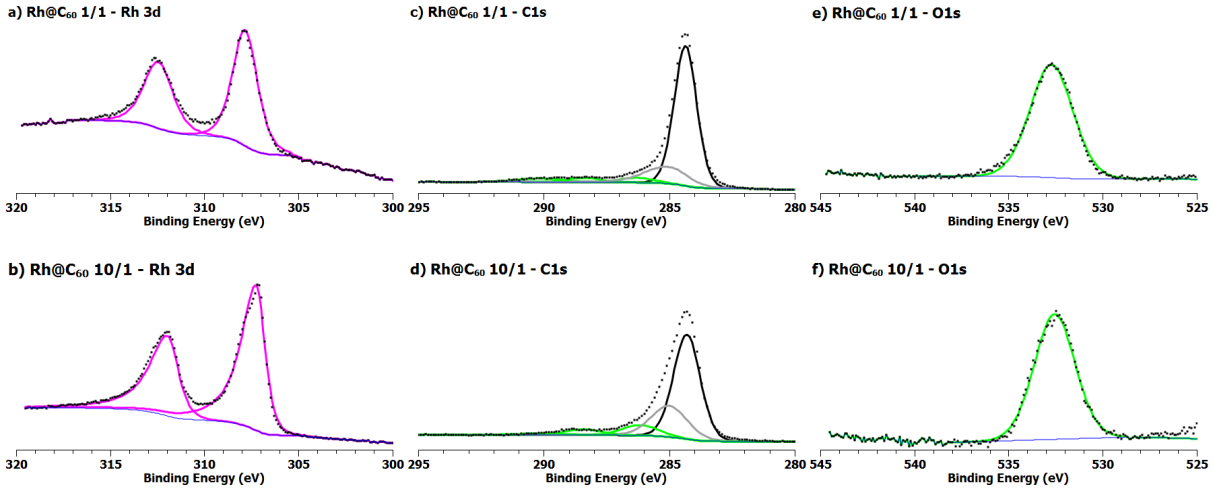

Figure S4. XPS analyses and peak fitting of Rh-C_{60} compounds, top 1/1, bottom 1/10.

Table S2. XPS data (peak fitting, FWHM and atomic concentration) for Rh-C_{60} samples.

Core peak	Component	Rh@C_{60} 1/1			Rh@C_{60} 10/1		
		BE (eV)	FWHM (eV)	At %	BE (eV)	FWHM (eV)	At %
Rh 3d	Rh metal	307.8-312.4	1.6-1.8	1.5	307.2-311.9	1.1-1.4	8.0
	C_{60}	284.3	1.1	68.7	284.3	1.2	52.5
	C-C, C-H	285.0	1.8	16.1	285.0	1.7	21.2
C 1s	Oxygenated	286.3	1.6	3.6	286.2	1.7	6.0
	Carbon	288.4	1.6	2.2	288.4	1.7	2.8
	Shake-up	290.2	2.2	3.4	290.0	2.0	1.2
O 1s	O bound to C	532.7	2.7	4.5	532.6	2.5	8.3

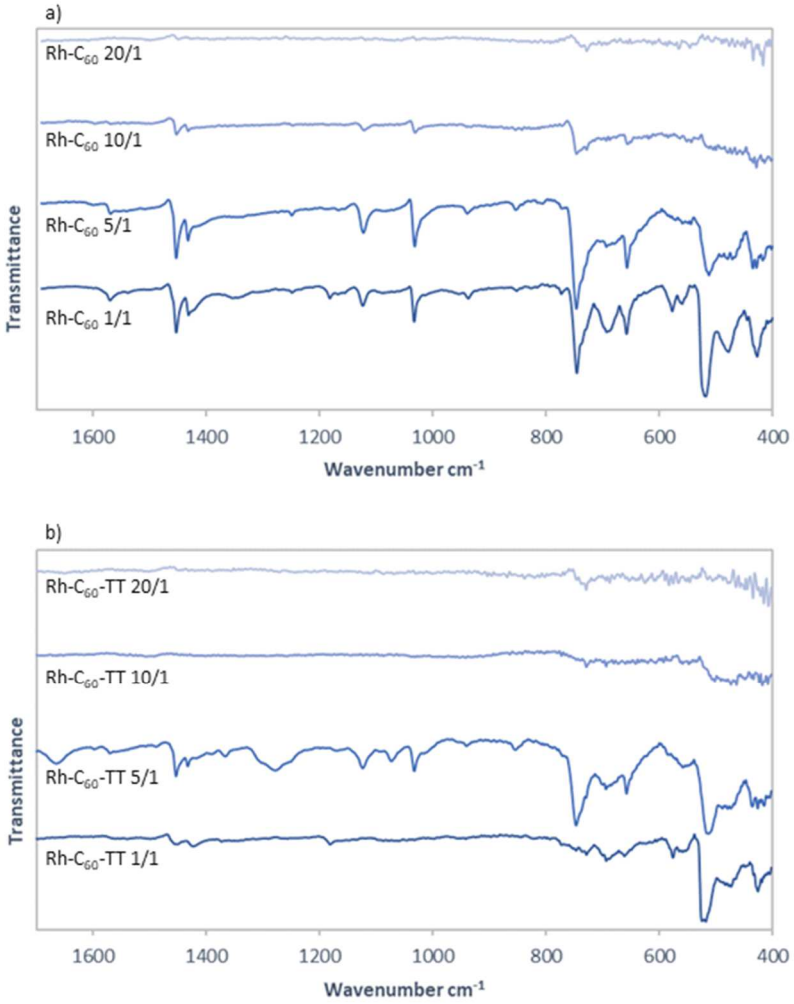

Figure S5. ATR-IR spectra of a) Rh-C_{60} and b) Rh-C_{60} after thermal treatment.

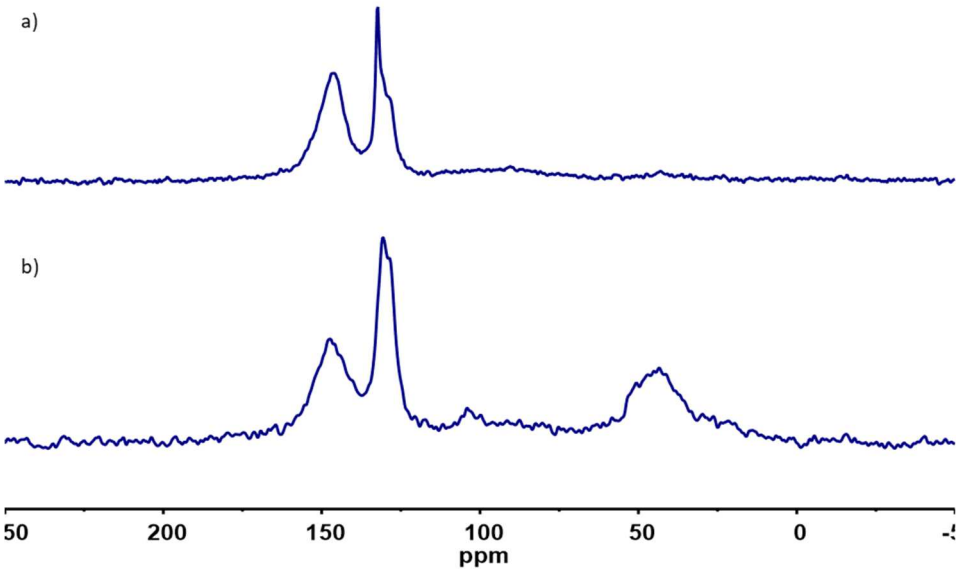

Figure S6. a) $^{13}C\{^{1}H\}$ and b) CP-MAS $^{13}C\{^{1}H\}$ NMR of Rh-C_{60} 10/1.

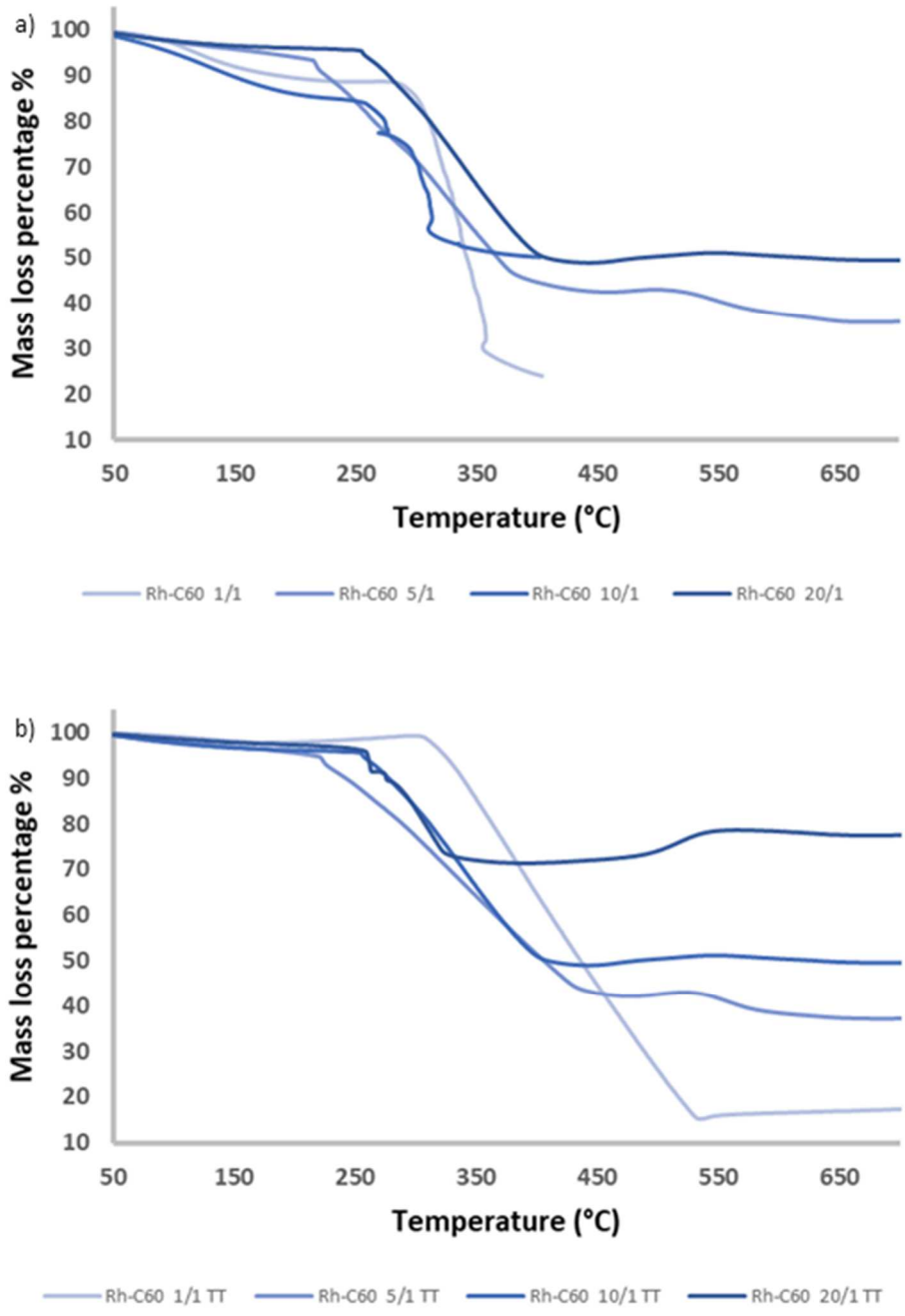

Figure S7. Thermogravimetric analyses of a) Rh-C_{60} and b) Rh-C_{60} after thermal treatment.

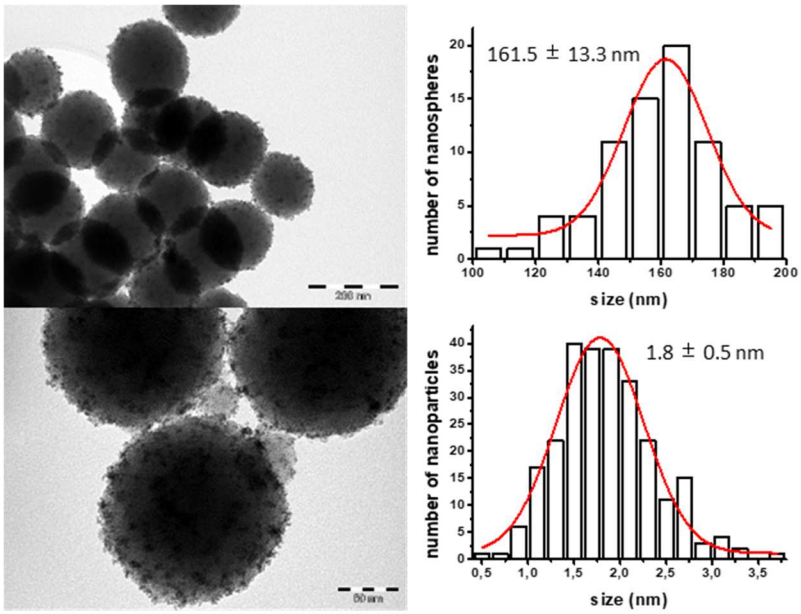

Figure S8. TEM images of Rh-C_{60} 5/1 after thermal treatment under argon at 200°C (scale bar top: 200 nm; bottom 50 nm).

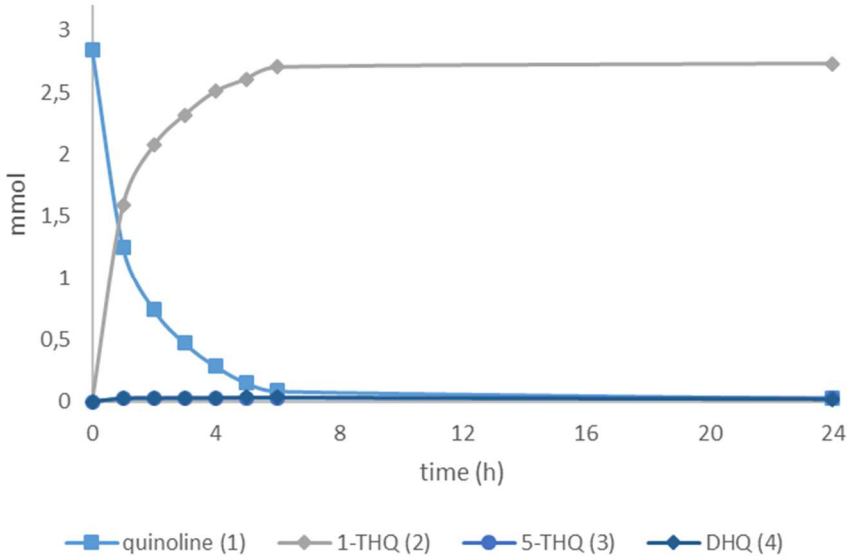

Figure S9. Time-concentration curve for quinoline hydrogenation using Rh-C_{60} 10/1 in toluene.

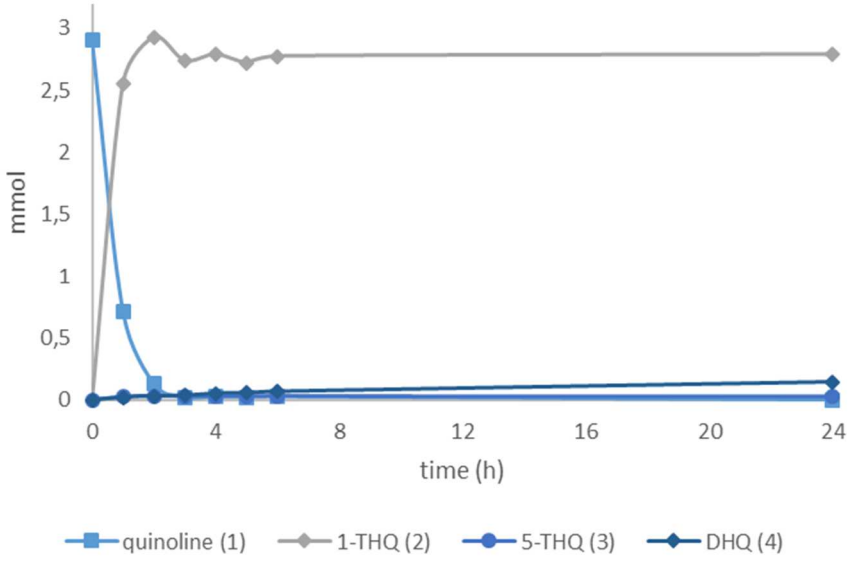

Figure S10. Time-concentration curve for quinoline hydrogenation using Rh-C_{60} 10/1 in isopropanol.

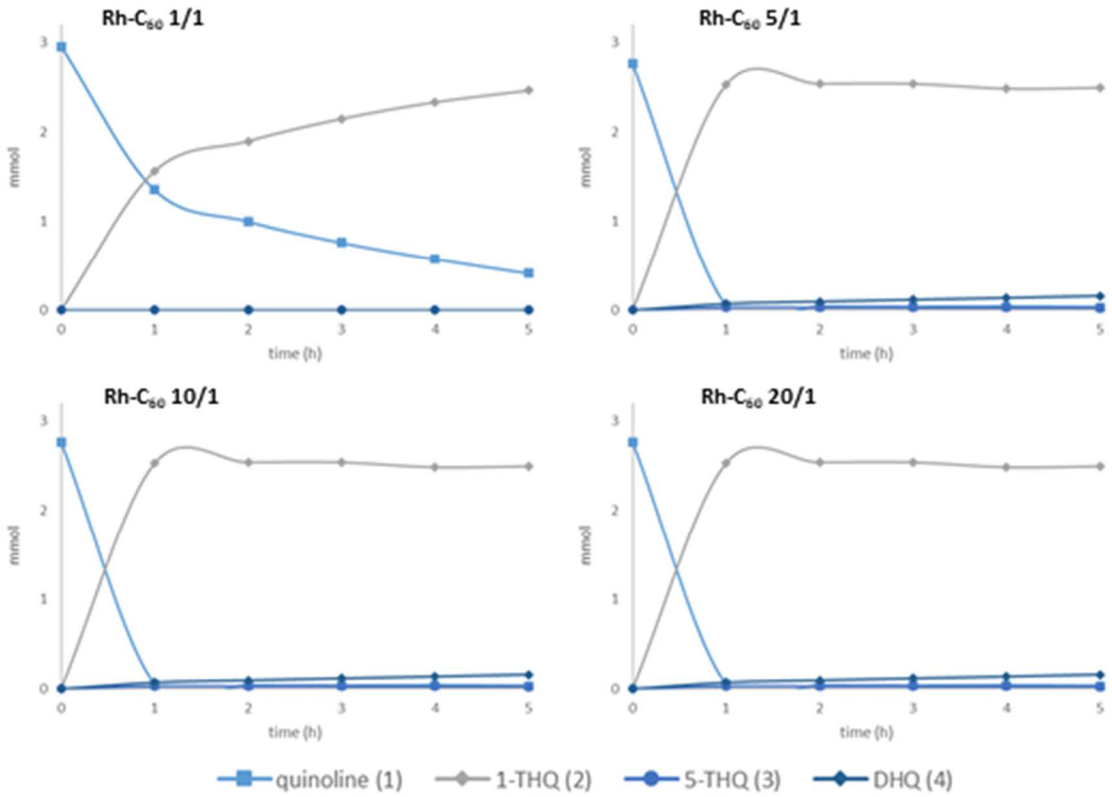

Figure S11. Time-concentration curve for quinoline hydrogenation using Rh-C_{60} series in isopropanol at 100°C under 20 bar of H_2.

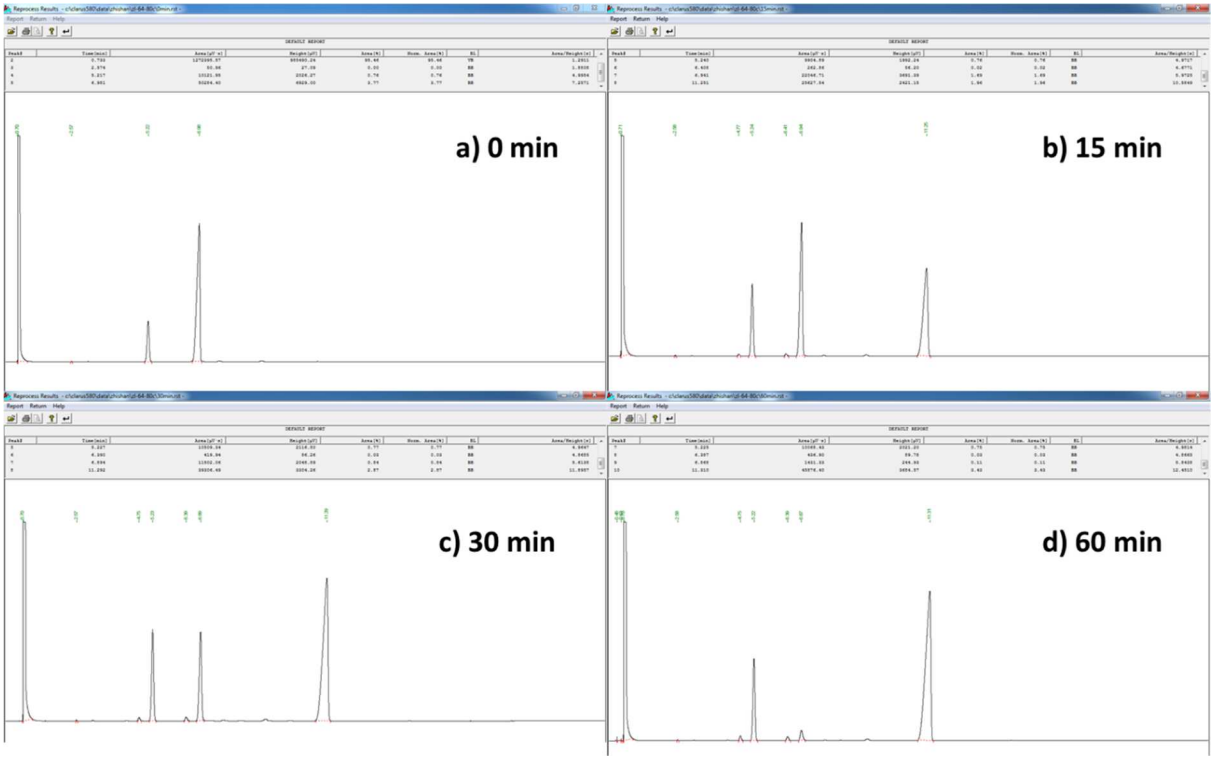

Figure S12. Chromatograms of quinoline hydrogenation using Rh-C_{60} 5/1 TT in isopropanol at 80°C under 20 bar of H_2.

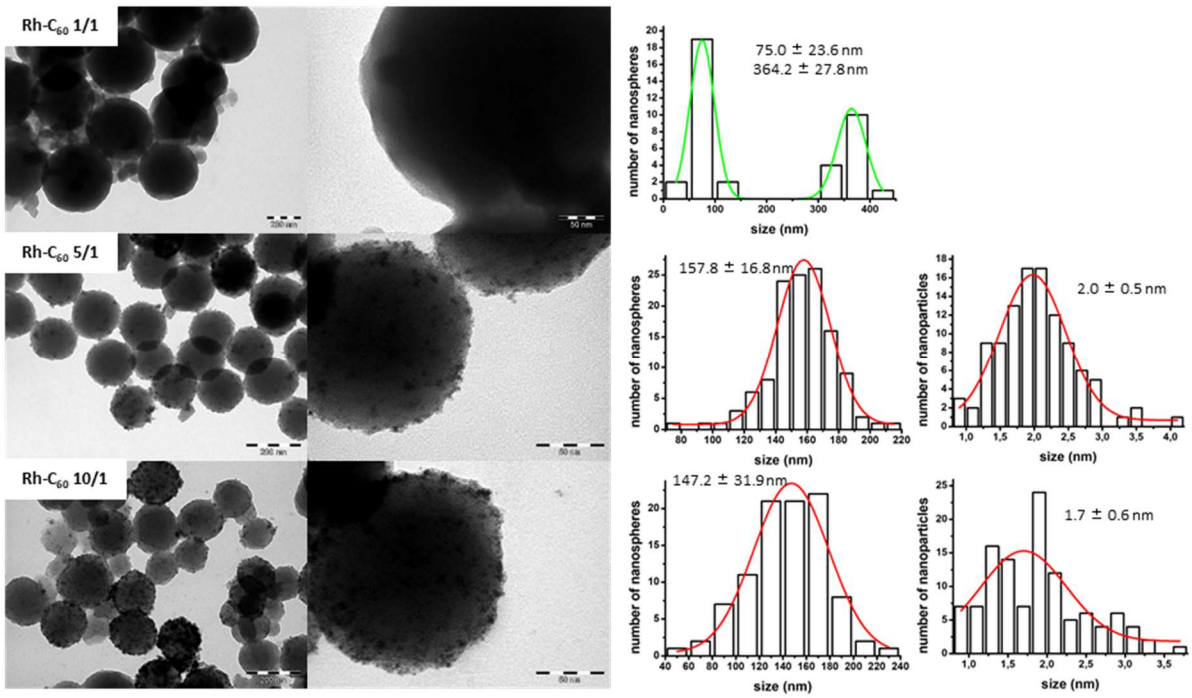

Figure S13. TEM images and size distribution histograms of Rh-C_{60} nanostructures after catalysis (scale bar from left to right: 200 nm and 50 nm).

Table S3. Comparison of the TOFs values and selectivities in quinoline hydrogenation of several representative heterogeneous catalysts with Rh-C_{60}.

Catalyst	T (^oC)	P (MPa)	t (h)	Select. (%)	TOF (h^{-1})
Rh-C_{60}	100	2	0.25	>99	488.0
Rh/[bmim]Cl-$ZnCl_2$-[bmim][BF_4][1]	80	3	15	90	6.3
NHC-stabilized Rh[2]	30	3	2.5	75	238
PEG_{4000}-stabilized Rh[3]	100	3	3	>99	762
Au/HAS-TiO2[4]	60	2	3.5	100	28.6
Ru-SiO2-mSiO2[5]	90	2	5	100	29.9
Ru/[BMMIM][NTf_2][6]	80	1	5	90	9
Pd-polymer[7]	80	1	9	98	21.7
Pt/SiO2-RF[8]	RT	1	1.5	>99	16
BWT-stabilized Pd[9]	80	2	0.5	96	192

REFERENCES

(1) Karakulina, A.; Gopakumar, A.; Akçok, İ.; Roulier, B. L.; LaGrange, T.; Katsyuba, S. A.; Das, S.; Dyson, P. J.: A rhodium nanoparticle–lewis acidic ionic liquid catalyst for the chemoselective reduction of heteroarenes. *Angew. Chem., Int. Ed.* **2016**, *128*, 300-304.

(2) Martinez-Espinar, F.; Blondeau, P.; Nolis, P.; Chaudret, B.; Claver, C.; Castillón, S.; Godard, C.: NHC-stabilised Rh nanoparticles: Surface study and application in the catalytic hydrogenation of aromatic substrates. *J. Catal.* **2017**, *354*, 113-127.

(3) Niu, M.; Wang, Y.; Chen, P.; Du, D.; Jiang, J.; Jin, Z.: Highly efficient and recyclable rhodium nanoparticle catalysts for hydrogenation of quinoline and its derivatives. *Catal. Sci. Technol.* **2015**, *5*, 4746-4749.

(4) Ren, D.; He, L.; Yu, L.; Ding, R.-S.; Liu, Y.-M.; Cao, Y.; He, H.-Y.; Fan, K.-N.: An unusual chemoselective hydrogenation of quinoline compounds using supported gold catalysts. *J. Am. Chem. Soc.* **2012**, *134*, 17592-17598.

(5) Zhang, L.; Wang, X.; Xue, Y.; Zeng, X.; Chen, H.; Li, R.; Wang, S.: Cooperation between the surface hydroxyl groups of Ru–SiO_2@ mSiO_2 and water for good catalytic performance for hydrogenation of quinoline. *Catal. Sci. Technol.* **2014**, *4*, 1939-1948.

(6) Konnerth, H.; Prechtl, M. H. G.: Selective hydrogenation of N-heterocyclic compounds using Ru nanocatalysts in ionic liquids. *Green Chem.* **2017**, *19*, 2762-2767.

(7) Dell'Anna, M. M.; Capodiferro, V. F.; Mali, M.; Manno, D.; Cotugno, P.; Monopoli, A.; Mastrorilli, P.: Highly selective hydrogenation of quinolines promoted by recyclable polymer supported palladium nanoparticles under mild conditions in aqueous medium. *Appl. Catal., A.* **2014**, *481*, 89-95.

(8) Bai, L.; Wang, X.; Chen, Q.; Ye, Y.; Zheng, H.; Guo, J.; Yin, Y.; Gao, C.: Explaining the size dependence in platinum-nanoparticle-catalyzed hydrogenation reactions. *Angew. Chem., Int. Ed.* **2016**, *55*, 15656-15661.

(9) Mao, H.; Ma, J.; Liao, Y.; Zhao, S.; Liao, X.: Using plant tannin as natural amphiphilic stabilizer to construct an aqueous-organic biphasic system for highly active and selective hydrogenation of quinoline. *Catal. Sci. Technol.* **2013**, *3*, 1612-1617.