Supporting Information

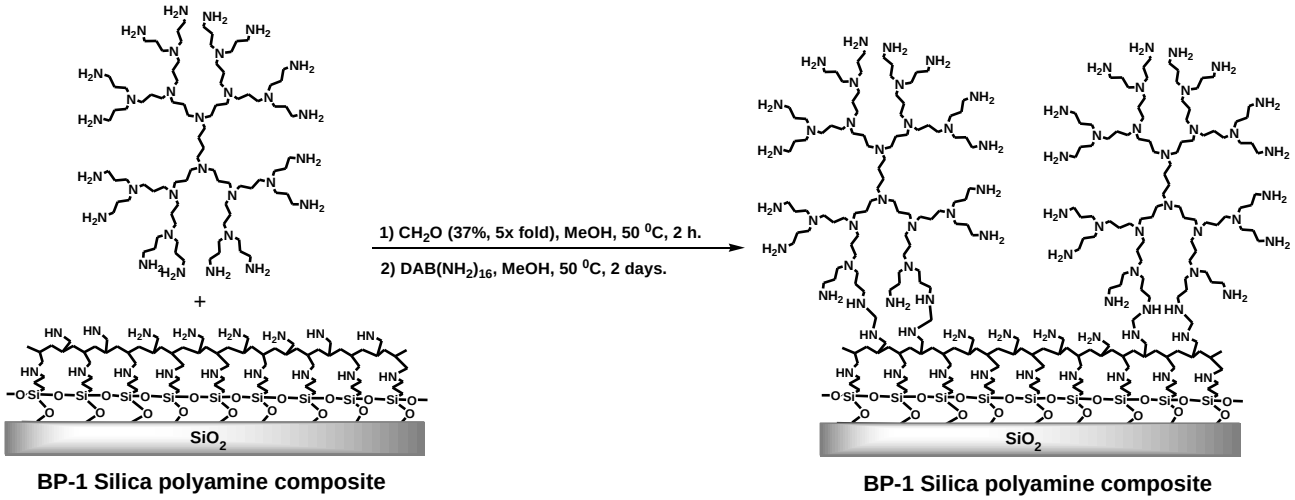
Dendrimer-Encapsulated Pd Nanoparticles, Immobilized in Silica Pores, as Catalysts for Selective Hydrogenation of Unsaturated Compounds

Edward A. Karakanov, Anna V. Zolotukhina, Andrey O. Ivanov, and Anton L. Maximov*

Table of contents

Tables

Figures



Scheme S1. Immobilization on PPI dendrimers on the surface of silica polyamine composite.[1]

Table S1. Physical chemical properties of the dendrimer-based organo-silica carriers

Method	G3-dendr-SiO_2	G2-dendr-*meso*-SiO_2	*meso*-G2-dendr-Si
IR, cm^{-1}	3446.70 (O–H_{st} and N–H_{st}, NH–C(–OH), br); 2940 (C–H_{st}); 2927.73 (C–H_{st}, CH_2–O_{st}); 2845 (C–H_{st}, CH_2–N_{st}); 1750 (C=O_{st} in CH_2–C(=O)); 1666.48 (C=O_{st} in CH_2–C(=O…H), $NH_{2\delta}$); 1539.64 ($NH_{2\delta}$); 1465.15 ($CH_{2\delta}$); 1325, 1200, 1070.46 (C–O_{st}, C–N_{st} in NH–C(–OH)); 958.68; 799.85 (O–H_δ); 750 (N-H_δ, $CH_{2\gamma}$)		
XPS, eV	103.2 (SiO_2, Si 2p, 19.5%); 285.7 ($NCH_2CH_2CH_2N$, NCH_2CH_2O, OCH_2CH_2O, $OCH_2CH_2CH_2Si$, C 1s, 24.3%); 399.3 ($NCH_2CH_2CH_2N$, NCH_2CH_2O, N 1s, 5.1%); 532.7 (OCH_2CH_2O, SiO_2, H_2O, O 1s, 51.1%)		285.8 ($NCH_2CH_2CH_2N$, NCH_2CH_2O, OCH_2CH_2O, $OCH_2CH_2CH_2Si$, C 1s, 67.6%); 399.4 ($NCH_2CH_2CH_2N$, NCH_2CH_2O, N 1s, 16.1%); 532.7 (OCH_2CH_2O, SiO_2, H_2O, O 1s, 16.3%)
^{13}C NMR, δ ppm	73.6 (-CH_2**CH_2**O**CH_2**); 66 (-$(CH_2)_2$**CH**OH); 58 (N**CH_2**CH_2CH_2**CH_2**N); 52.4 (N**CH_2**CH_2**CH_2**N); 46 (NCH_2CH_2**CH_2**$NHCH_2$-); 38.5 (NCH_2CH_2**CH_2**NH_2); 23.6 (NCH_2**CH_2**CH_2N); 18.5 ($SiCH_2$**CH_2**CH_2O); 9.2 (Si**CH_2**CH_2CH_2O)	86 (-OCH_2N-); 74 (-CH_2**CH_2**O); 65 (-$(CH_2)_2$**CH**OH); 44 (N**CH_2**CH_2**CH_2**N, NCH_2CH_2**CH_2**$NHCH_2$-); 30 (NCH_2**CH_2**CH_2N); 16 ($SiCH_2$**CH_2**CH_2O)	74 (-OCH_2**CH_2**O**CH_2**); 68 (-$(CH_2)_2$**CH**OH); 65 ($SiCH_2CH_2$**CH_2**O); 53 (N**CH_2**CH_2CH_2**CH_2**N); 51 (N**CH_2**CH_2**CH_2**N, NH**CH_2**CH_2O); 47 (NCH_2CH_2**CH_2**$NHCH_2$-); 38 (NCH_2CH_2**CH_2**NH_2); 22 (NCH_2**CH_2**CH_2N, NCH_2**CH_2**CH_2**CH_2**CH_2N, $SiCH_2$**CH_2**CH_2O); 9.6 (Si**CH_2**CH_2CH_2O)

Table S2. Porosity properties of dendrimer-based hybrid materials according to nitrogen low temperature adsorption and desorption.

	G2-dendr-*meso*-SiO_2	G3-dendr-SiO_2
Langmuir Surface Area, m^2/g	179.0	83.9
BET Surface Area, m^2/g	118.5	53.9
BJH Adsorption cumulative surface area (d: 17.0-30.0 Å), m^2/g	429.0	52.1
BJH Adsorption cumulative volume (d: 17.0-30.0 Å), cm^3/g	8.1	0.2
BJH Adsorption average pore width, Å	75.3	14.1
Nitrogen content, wt. %	6.3	4.6

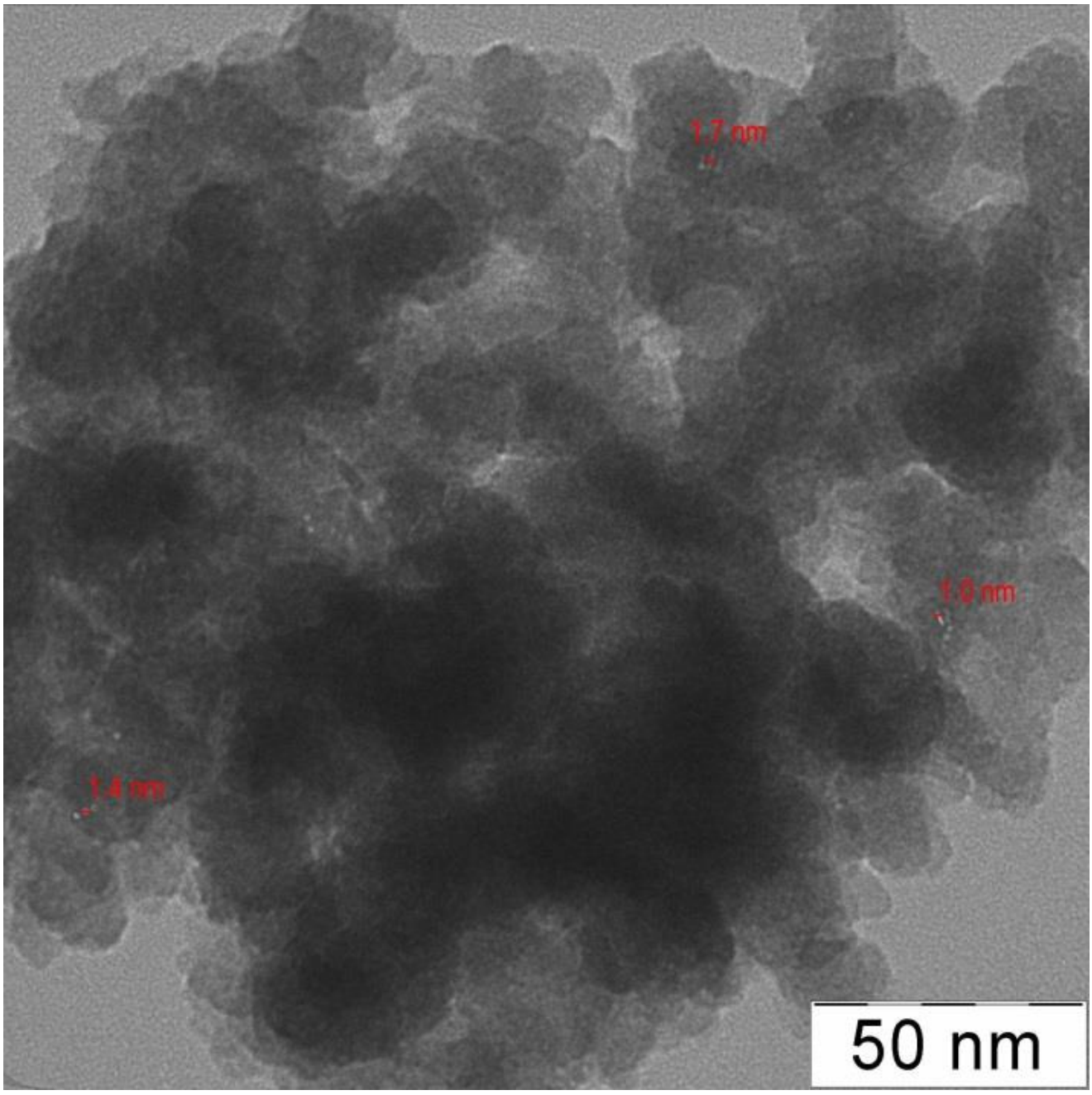


Figure S1. TEM image of hybrid G3-dendr-SiO_2 material.

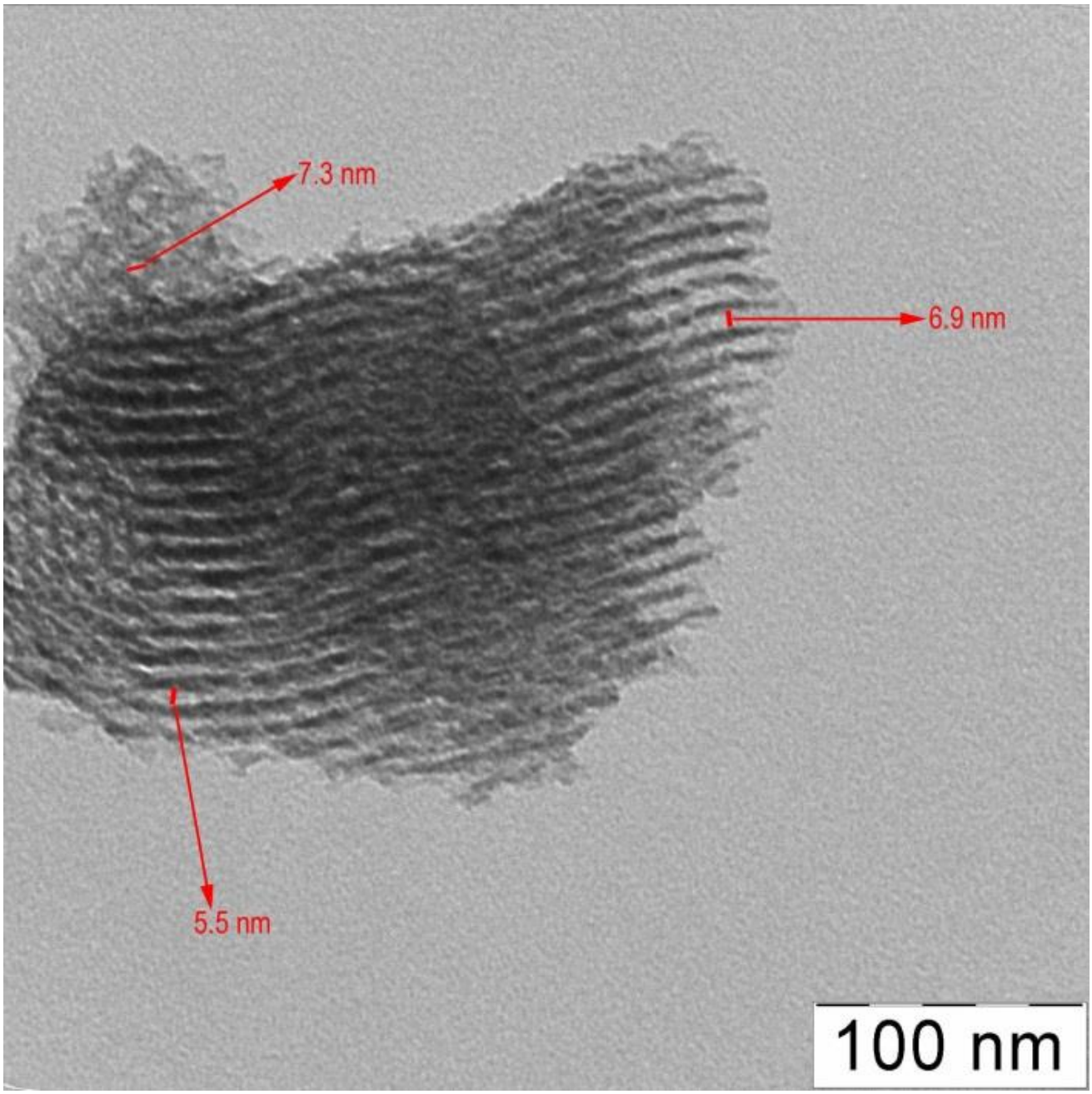


Figure S2. TEM image of hybrid G2-dendr-*meso*-SiO_2 material.

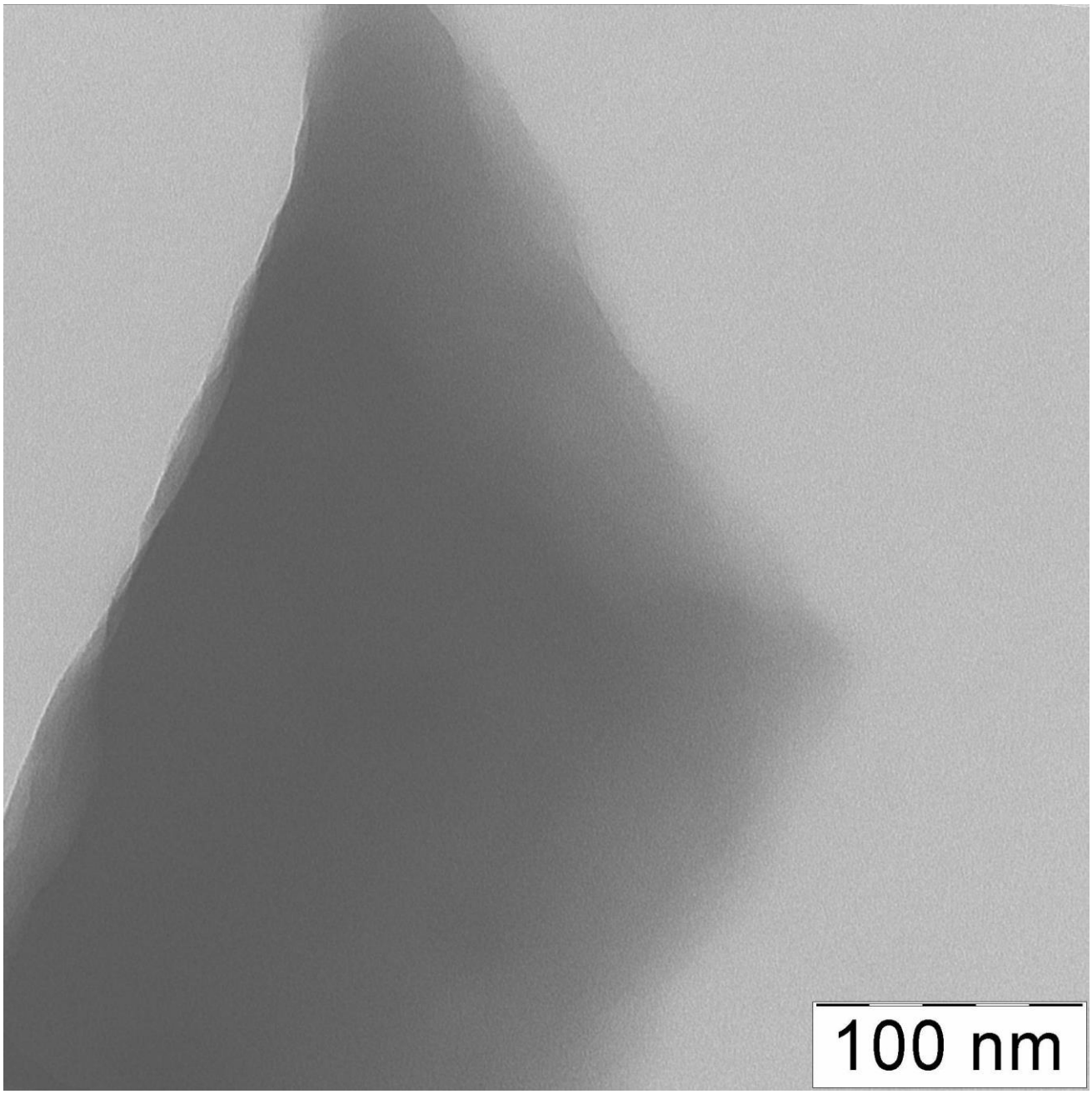


Figure S3. TEM image of hybrid *meso*-G2-dendr-Si material.

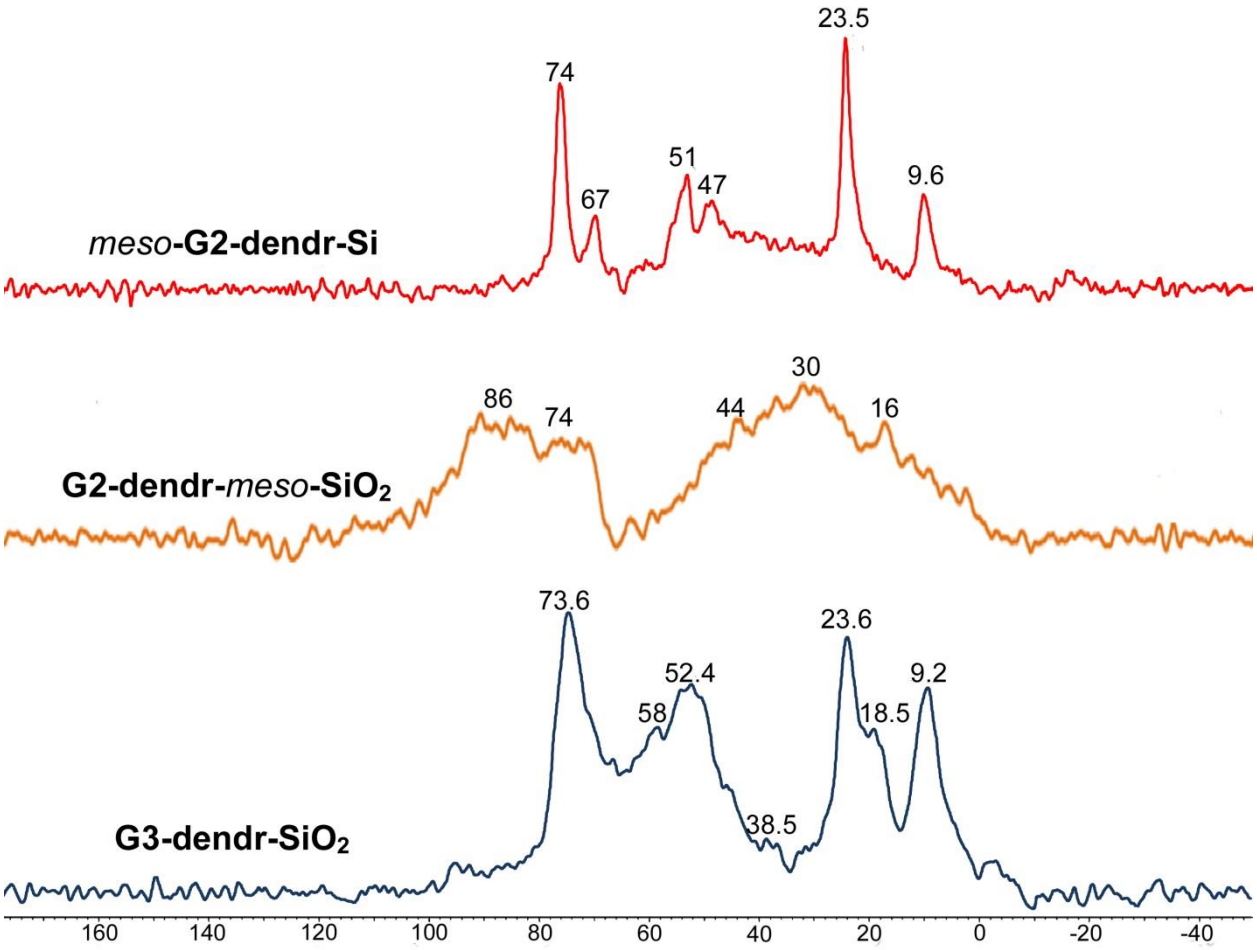


Figure S4. ^{13}C MAS NMR spectra of dendrimer-based organo-silica carriers.

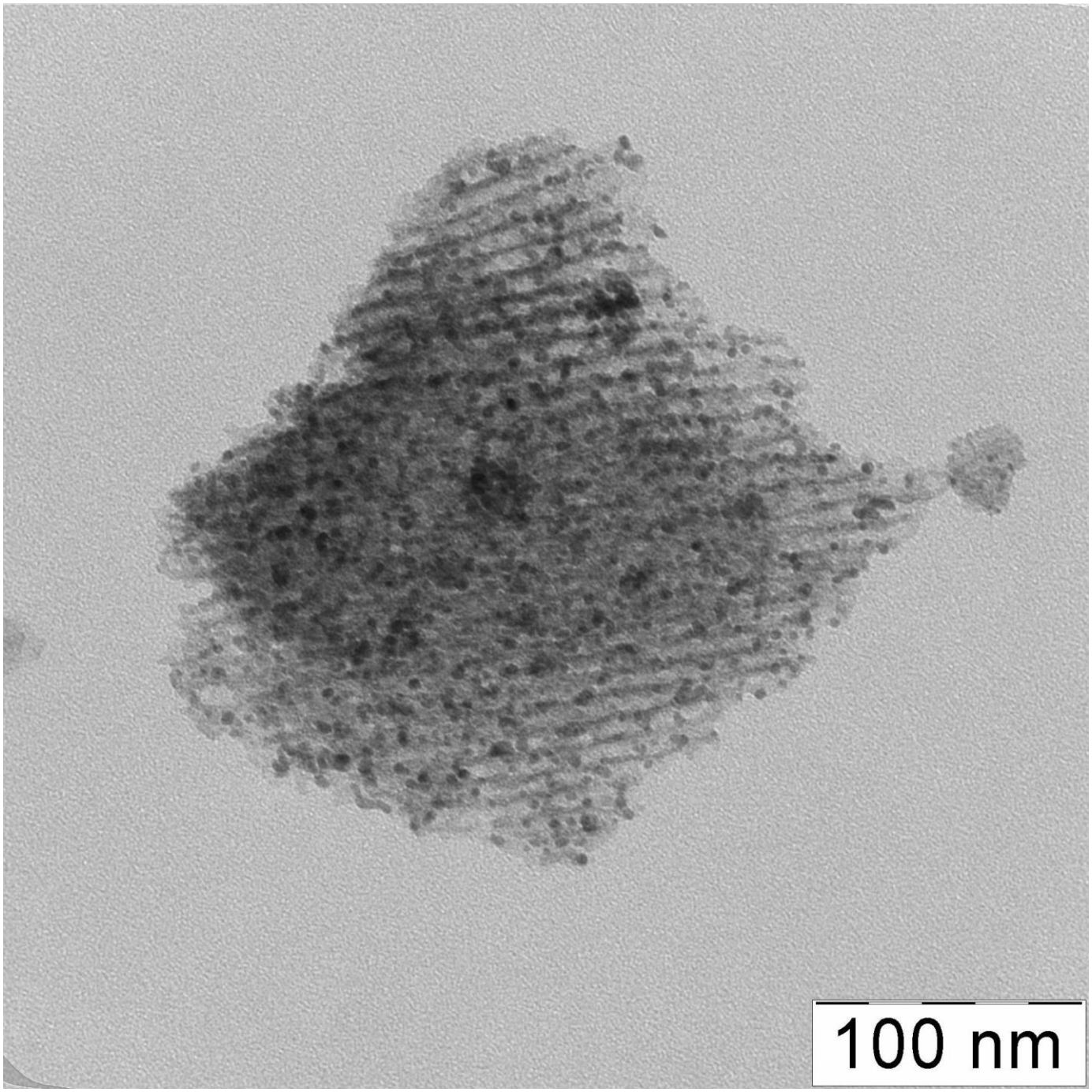


Figure S5. G2-dendr-*meso*-SiO_2-Pd TEM image.

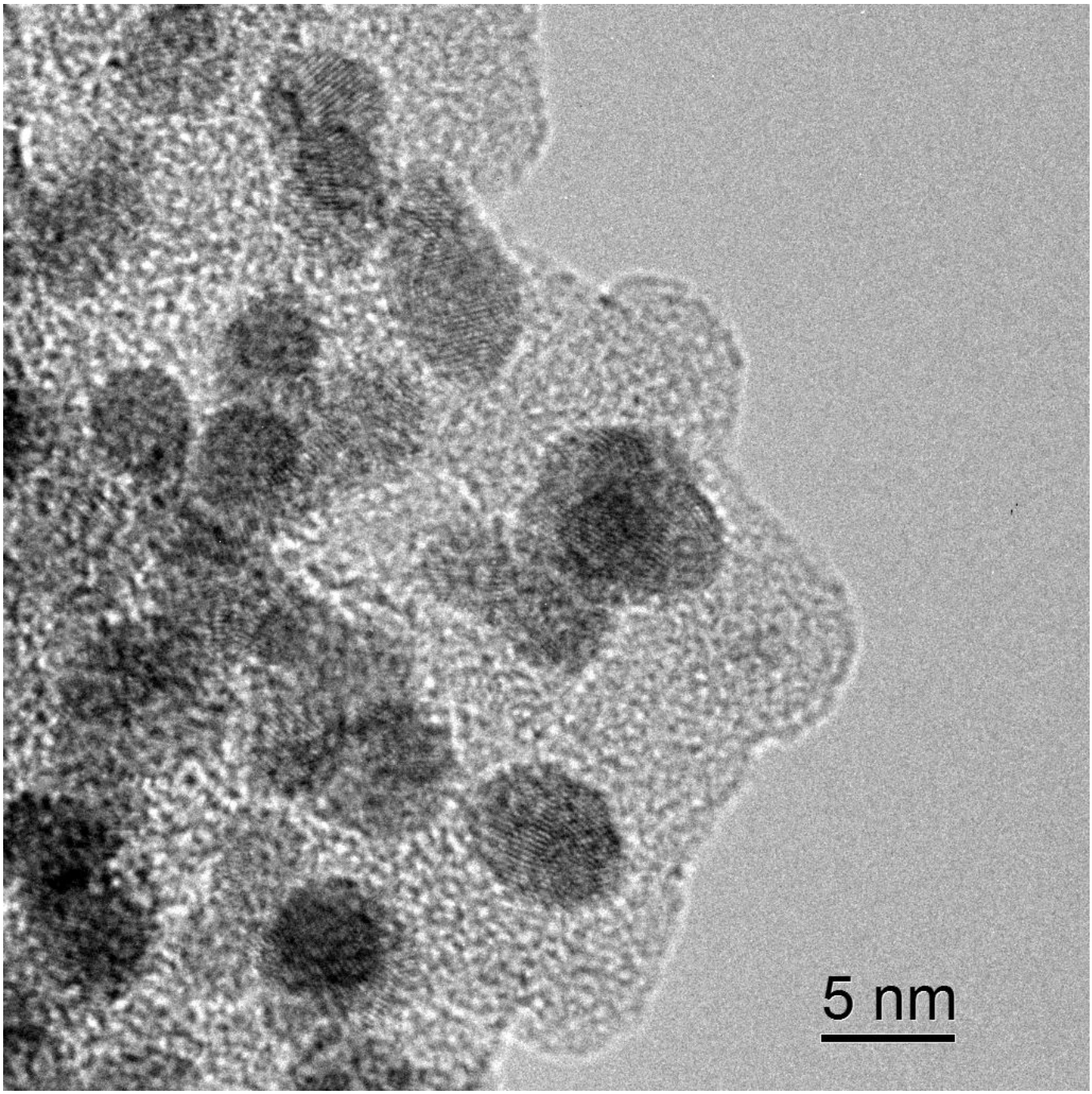


Figure S6. G2-dendr-*meso*-SiO_2-Pd HRTEM image.

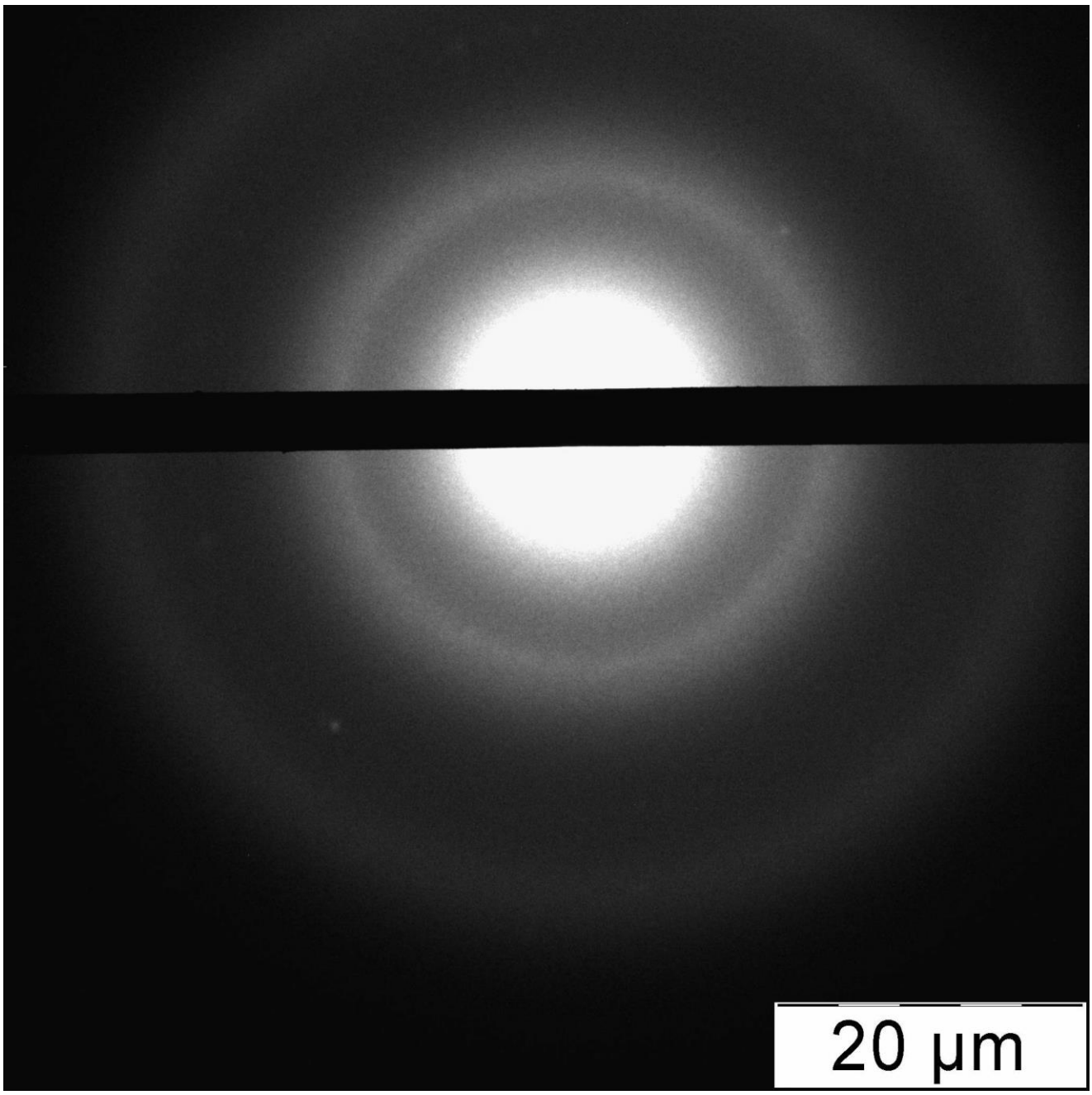


Figure S7. Electron diffraction pattern from G2-dendr-*meso*-SiO_2-Pd sample.

Table S3. *d*-spacings in the G2-dendr-*meso*-SiO_2-Pd sample

R, px	*d*, Å	Reference [2]
243	4.225	SiO2 [100] quartz
461	2.227	Pd [111]
519	1.98	Pd [002]
745	1.378	Pd [022]
879	1.168	Pd [113]
964	1.065	~Pd [222] or PdO [123]

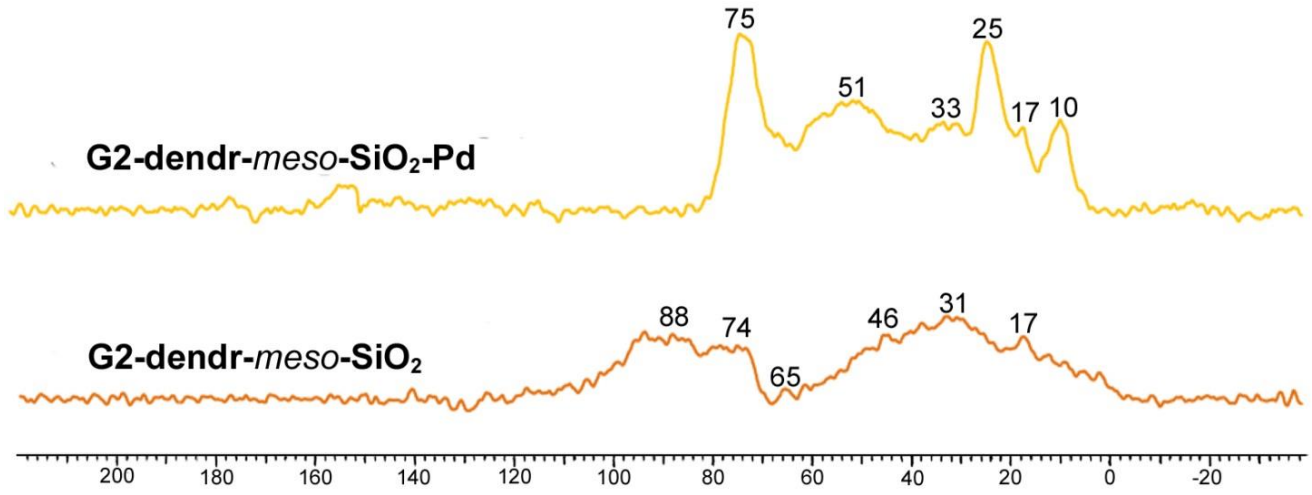


Figure S8. ^{13}C MAS NMR spectra of G2-dendr-*meso*-SiO_2-Pd catalyst and its carrier.

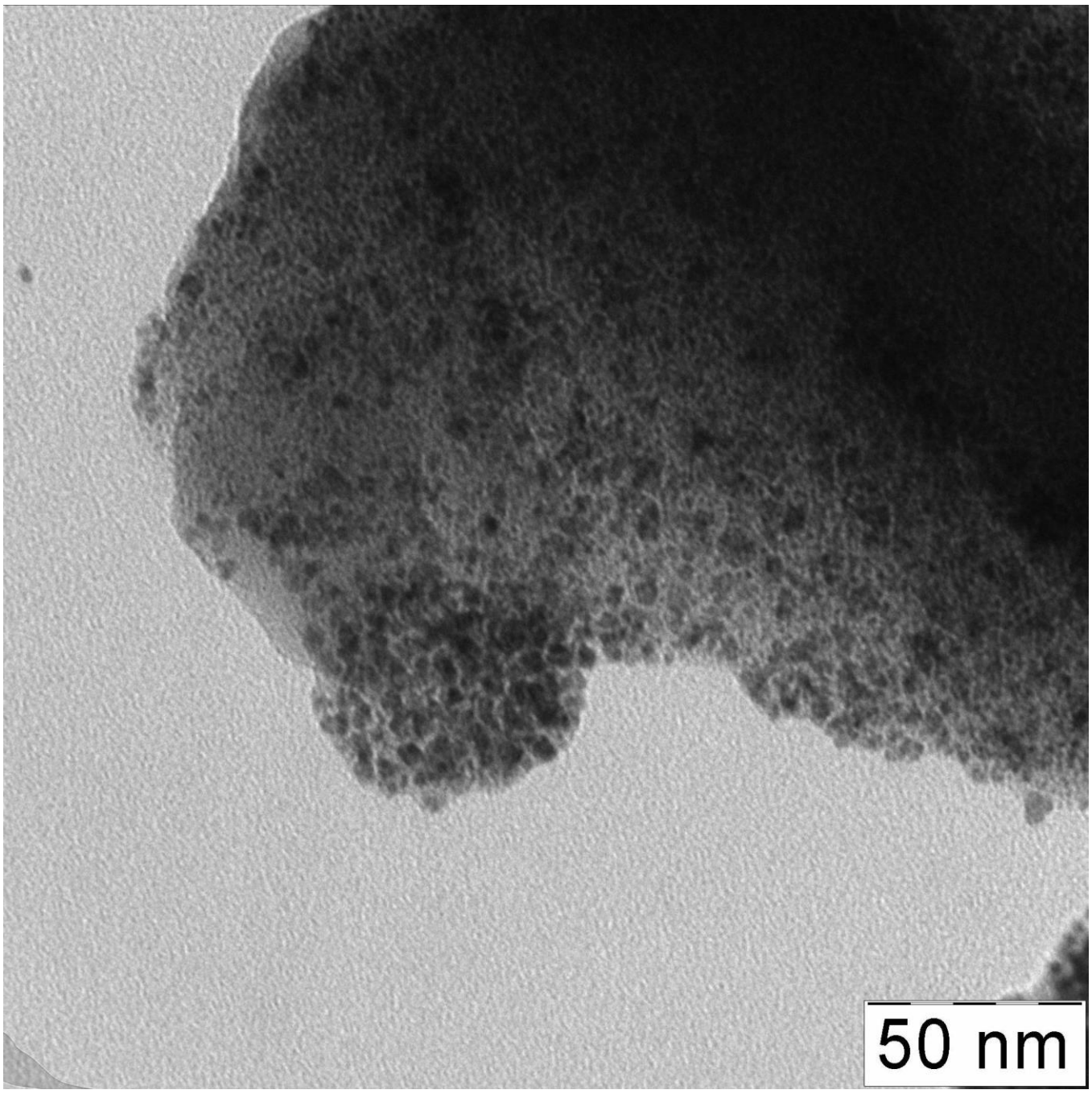


Figure S9. *Meso*-G2-dendr-Si-Pd TEM image.

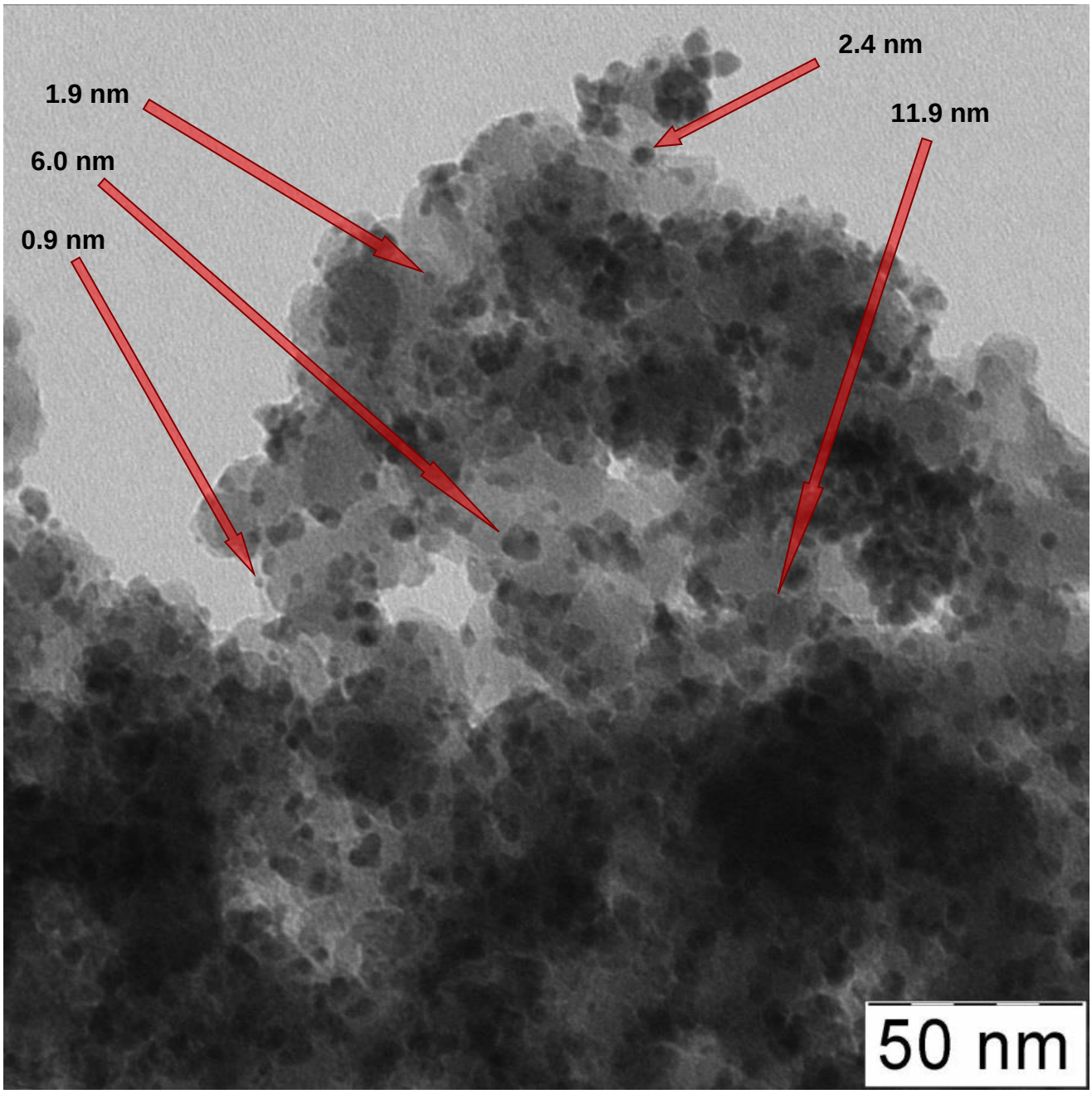


Figure S10. TEM image for G3-dendr-SiO_2-Pd catalyst.

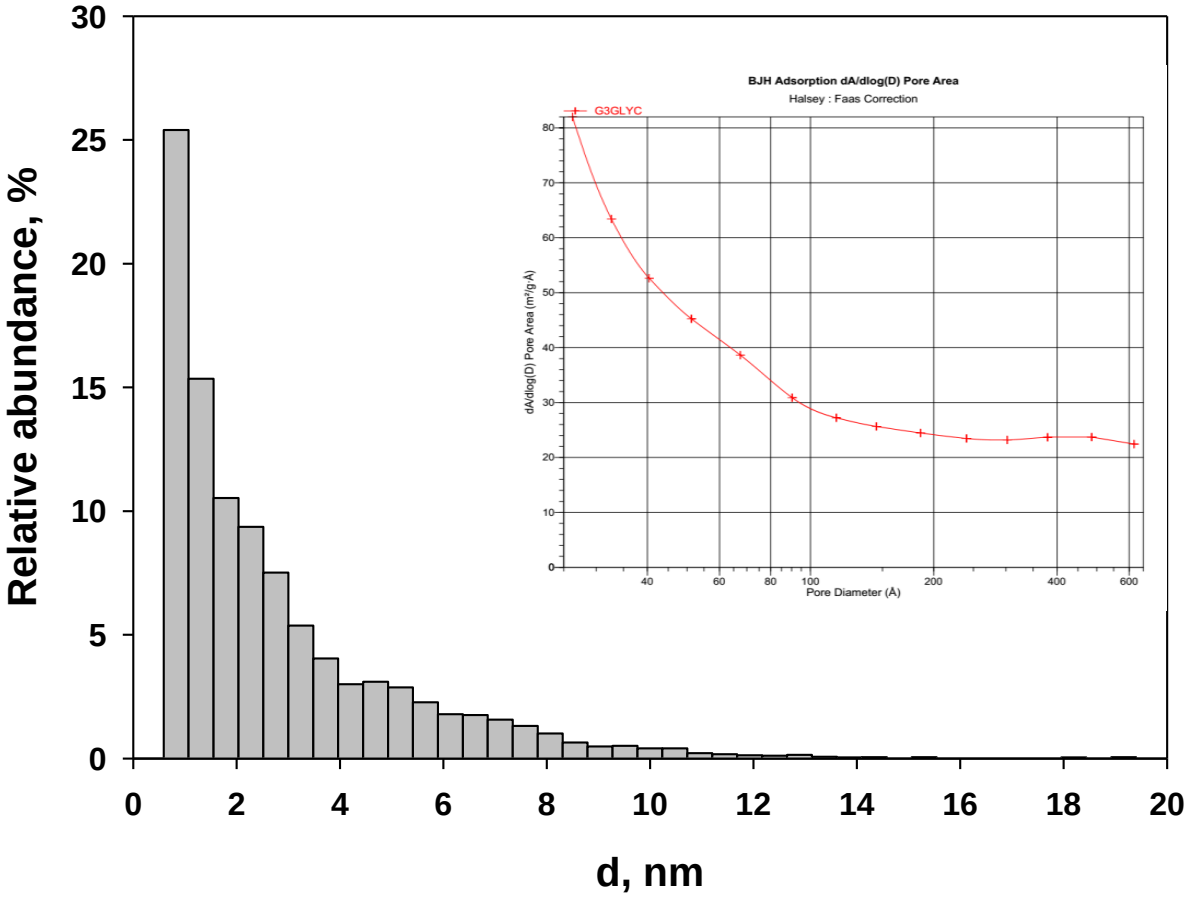


Figure S11. Particle size distribution and for G3-dendr-SiO_2-Pd and pore size distribution for G3-dendr-SiO_2 carrier.

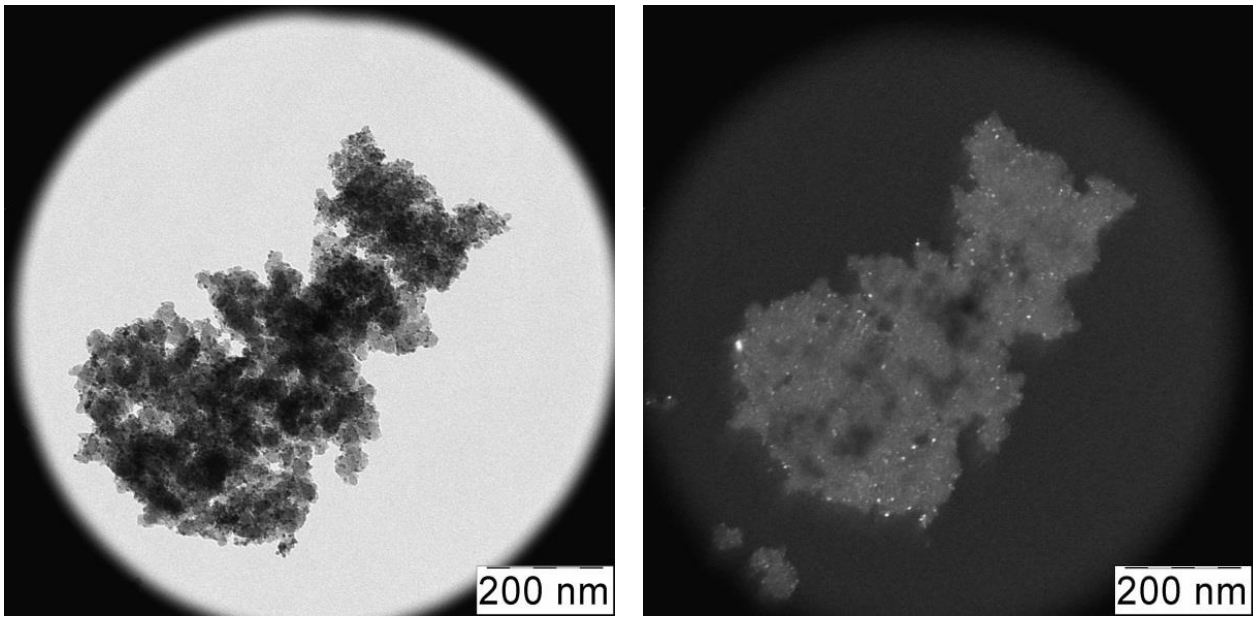


Figure S12. TEM image for G3-dendr-SiO_2-Pd catalyst in the dark field.

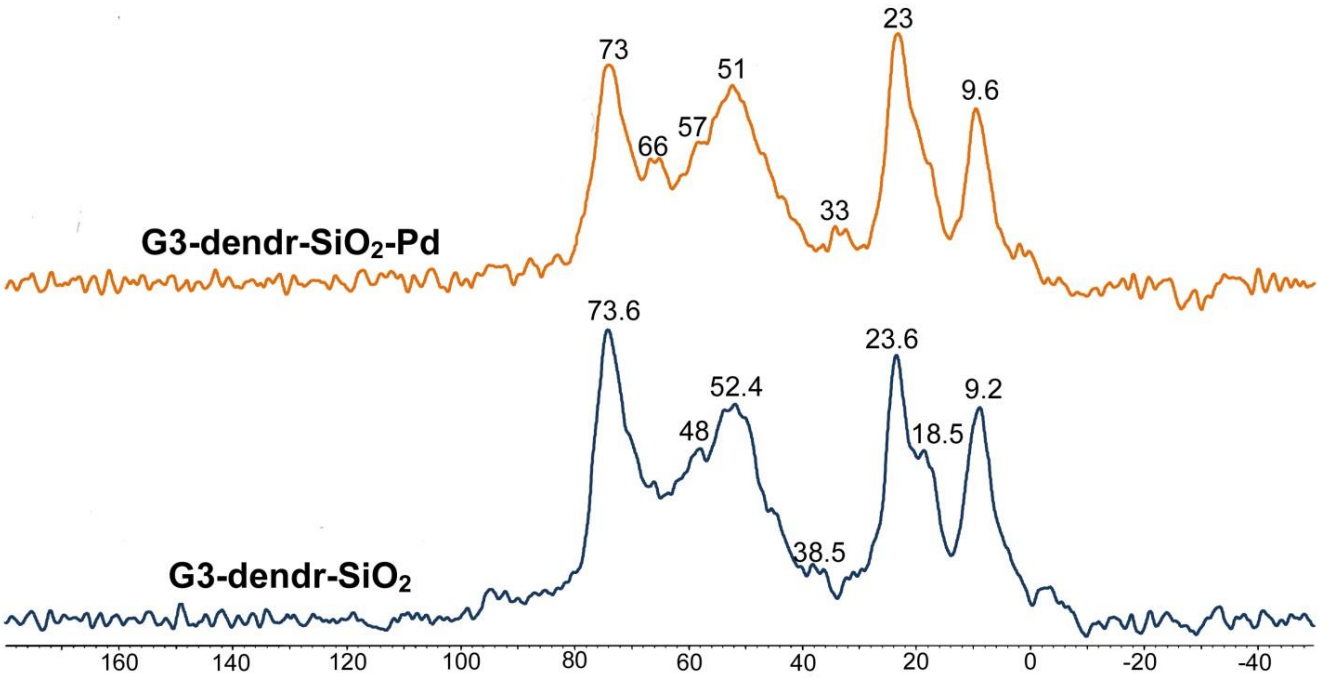


Figure S13. ^{13}C MAS NMR spectra of G3-dendr-SiO_2-Pd catalyst and its carrier.

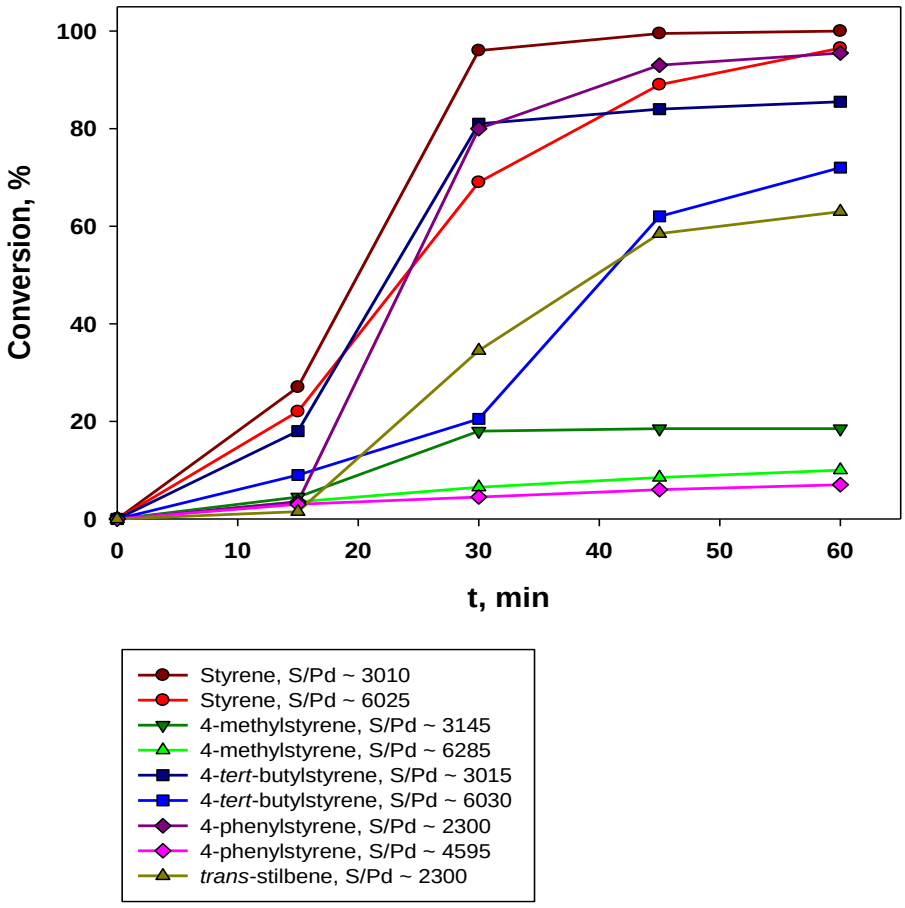


Figure S14. Hydrogenation of styrenes in the presence of *meso*-G2-dendr-Si-Pd catalyst. Reaction conditions are: 80 ^0C, 10 atm. of H_2.

Table S4. Hydrogenation of 1-hexyne in the presence of the dendrimer-based organo-silica palladium catalysts [a]

Entry	Catalyst	Substrate/Pd, (mol/mol)	P (H_2), atm.	Conv., %	TOF, h^{-1}	Products distribution, %
1	G3-dendr-SiO_2-Pd	6915	10	100	27650	***n*-hexane 36%** **1-hexene 15%** *cis*-2-hexene 28% *trans*-2-hexene 21%
2		20740	10	100	82955	***n*-hexane 23%** **1-hexene 36%** *cis*-2-hexene 24.5% *trans*-2-hexene 16.5%
3		41480	10	91	150980	***n*-hexane 9%** **1-hexene 89%** *cis*-2-hexene 1.5% *trans*-2-hexene 0.5%
4		103695	10	72.5	300720	***n*-hexane 2.5%** **1-hexene 97.5%**
5		103695	30	97.5	404415	***n*-hexane 7.5%** **1-hexene 90%** *cis*-2-hexene 2.5%
6	G2-dendr-*meso*-SiO_2-Pd	5880	10	100	12220	***n*-hexane 52.5%** **1-hexene 15%** *cis*-2-hexene 22% *trans*-2-hexene 10%
7		6110	10	99	24200	***n*-hexane 32%** **1-hexene 47.5%** *cis*-2-hexene 16.5% *trans*-2-hexene 4%
8		12220	10	68	33240	***n*-hexane 12%** **1-hexene 81%** *cis*-2-hexene 10%
9		12220	30	98	47905	***n*-hexane 14.5%** **1-hexene 73%** *cis*-2-hexene 12% *trans*-2-hexene 0.5%
10		18330	10	23	16865	***n*-hexane 4.5%** **1-hexene 94%** *cis*-2-hexene 1.5%
11		18330	30	93	68195	***n*-hexane 9%** **1-hexene 86.5%** *cis*-2-hexene 4% *trans*-2-hexene 0.5%
12		36660	30	87	127585	***n*-hexane 7.5%** **1-hexene 91%** *cis*-2-hexene 1.5%
13		91660	30	75.5	276805	***n*-hexane 6%** **1-hexene 93.5**% *cis*-2-hexene 0.5%
14	*meso*-G2-dendr-Si-Pd	6010	10	97.5	23430	***n*-hexane 15%** **1-hexene 80%** *cis*-2-hexene 3.5% *trans*-2-hexene 1.5%
15		18020	10	95	68485	***n*-hexane 12%** **1-hexene 83%** *cis*-2-hexene 5%
16		24030	10	61.5	59115	***n*-hexane 10%** **1-hexene 86.5%** *cis*-2-hexene 3.5%
17		36045	10	27	38930	***n*-hexane 6.5%** **1-hexene 92%** *cis*-2-hexene 1.5%
18		36045	30	82	118225	***n*-hexane 9.5%** **1-hexene 86%** *cis*-2-hexene 4.5%
19		90110	30	65	234290	***n*-hexane 8%** **1-hexene 89.5%** *cis*-2-hexene 2.5%

[a] Reaction conditions are: 0.5 mg of catalyst, 80 ^{0}C, 15 min.

Table S5. Hydrogenation of 1-octyne in the presence of the dendrimer-based organo-silica palladium catalysts [a]

Entry	Catalyst	Catalyst loading, mg	Substrate/Pd, (mol/mol)	P (H_2), atm.	Conv., %	TOF, h^{-1}	Product distribution, %
1	G3-dendr-SiO_2-Pd	0.5	5455	10	100	21535	***n*-octane 42.5%** **1-octene 5.5%** *cis*-2-octene 30% *trans*-2-octene 16.5% 3-octene 5.5% 4-octene 1.5%
2		0.5	16365	10	100	64600	***n*-octane 33%** **1-octene 21%** *cis*-2-octene 25% *trans*-2-octene 17.5% 3-octene 2.5% 4-octene 1%
3		0.5	32735	10	100	129200	***n*-octane 26%** **1-octene 36.5%** *cis*-2-octene 21% *trans*-2-octene 15% 3-octene 2% 4-octene 0.5%
4		0.5	80750	10	98	316545	***n*-octane 2%** **1-octene 93.5%** *cis*-2-octene 4% *trans*-2-octene 0.5%
5	G2-dendr-*meso*-SiO_2-Pd	1	2380	10	100	9515	***n*-octane 50%** **1-octene 2%** *cis*-2-octene 25.5% *trans*-2-octene 18.5% 3-octene 3% 4-octene 1%
6		0.5	4760	10	100	19035	***n*-octane 44%** **1-octene 1.5**% *cis*-2-octene 21% *trans*-2-octene 17.5% 3-octene 10.5% 4-octene 5.5%
7		0.5	14275	10	96.5	55100	***n*-octane 4.5%** **1-octene 93**% *cis*-2-octene 1% *trans*-2-octene 0.5% 3-octene 0.5% 4-octene 0.5%
8		0.5	28550	10	64.5	73660	**1-octene 97**% *cis*-2-octene 1.5% *trans*-2-octene <1% 3-octene 0.5% 4-octene < 0.5%
9		0.5	28550	30	89	101640	***n*-octane 4.5%** **1-octene 87**% *cis*-2-octene 4.5% *trans*-2-octene 3% 3-octene 0.5% 4-octene 0.5%
10		0.5	71375	30	60	171305	***n*-octane 3.5%** **1-octene 94**% *cis*-2-octene 1.5% 3-octene 0.5% 4-octene 0.5%
11	*meso*-G2-dendr-Si-Pd	0.5	4680	10	79	14785	***n*-octane 13.5%** **1-octene 78**% *cis*-2-octene 4% *trans*-2-octene 4% 3-octene 0.5%
12		0.5	14035	10	61	34245	***n*-octane 1%** **1-octene 87**% *cis*-2-octene 9% *trans*-2-octene 2.5% 3-octene 0.5%
13		0.5	14035	30	99	55575	***n*-octane 7%** **1-octene 90**% *cis*-2-octene 1.5% *trans*-2-octene 1.5%
14		0.5	28070	30	99.5	111715	***n*-octane 6.5%** **1-octene 91.5**% *cis*-2-octene 1.5% *trans*-2-octene 0.5%
15		0.5	70170	30	75.5	211920	***n*-octane 6%**

	1-octene 93% *cis*-2-octene 1%
[a] Reaction conditions are: 80 ^{0}C, 15 min.	

Table S6. Hydrogenation of 4-octyne in the presence of the dendrimer-based organo-silica palladium catalysts [a]

Entry	Catalyst	Substrate/Pd, (mol/mol)	P (H_2), atm.	Conv., %	TOF, h^{-1}	Products distribution, %
1	G3-dendr-SiO_2-Pd	5410	10	100	21650	***n*-octane 71.5%** *cis*-2-octene 10.5% *trans*-2-octene 3.5% 3-octene 9.5% **4-octene 5%**
2		16235	10	100	64945	***n*-octane 61.5%** *cis*-2-octene 2.5% *trans*-2-octene 1% 3-octene 14% **4-octene 21%**
3		32475	10	93.5	121450	***n*-octane 51.5%** *cis*-2-octene 0.5% *trans*-2-octene 0.5% 3-octene 5.5% **4-octene 42%**
4		81185	10	10	32475	***n*-octane 26%** *cis*-2-octene 3% *trans*-2-octene 0.5% 3-octene 10% **4-octene 60.5%**
5		81185	30	60	194840	***n*-octane 35.5%** *cis*-2-octene 0.5% 3-octene 4.5% **4-octene 60%**
6	G2-dendr-*meso*-SiO_2-Pd	7175	10	99.5	28560	***n*-octane 73.5%** *cis*-2-octene 9% *trans*-2-octene 13% 3-octene 3% **4-octene 1.5%**
7		14350	10	99.5	57120	***n*-octane 72%** *cis*-2-octene 5.5% *trans*-2-octene 3% 3-octene 15.5% **4-octene 4%**
8		28705	10	54	62000	***n*-octane 52%** *cis*-2-octene 0.5% 3-octene 0.5% **4-octene 47%**
9		28705	30	98	112515	***n*-octane 79.5%** *cis*-2-octene 1% 3-octene 6.5% **4-octene 13%**
10		71760	30	85	243980	***n*-octane 63.5%** *cis*-2-octene 0.5% 3-octene 4.5% **4-octene 31.5%**
11	*meso*-G2-dendr-Si-Pd	4705	10	96	18060	***n*-octane 67.5%** *cis*-2-octene 8% *trans*-2-octene 3% 3-octene 5.5% **4-octene 16%**
12		9405	10	78	29350	***n*-octane 65.5%** *cis*-2-octene 1% *trans*-2-octene 0.5% 3-octene 4.5% **4-octene 29%**
13		14110	10	42	23705	***n*-octane 59%** *cis*-2-octene 0.5% 3-octene 4% **4-octene 36.5%**
14		14110	30	58	32735	***n*-octane 68.5%** *cis*-2-octene 3% *trans*-2-octene 0.5% 3-octene 3.5% **4-octene 24.5%**

[a] Reaction conditions are: 0.5 mg of catalyst, 80 ^{0}C, 15 min.

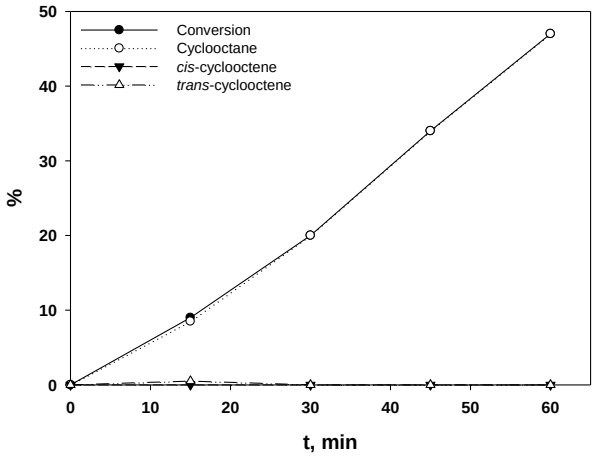


Figure S15. Hydrogenation of 1,3-cyclooctadiene in the presence of G3-dendr-SiO_2-Pd catalyst. Reaction conditions are: 250 µL of substrate, 1 mg of catalyst (S/Pd ~ 3190), 80 ^{0}C, 10 atm. of H_2.

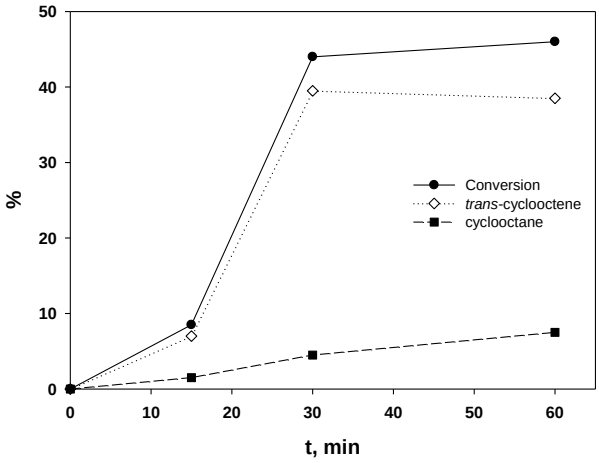


Figure S16. Hydrogenation of 1,3-cyclooctadiene in the presence of *meso*-G2-dendr-Si-Pd catalyst. Reaction conditions are: 250 µL of substrate, 1 mg of catalyst (S/Pd ~ 2770), 80 ^{0}C, 10 atm. of H_2.

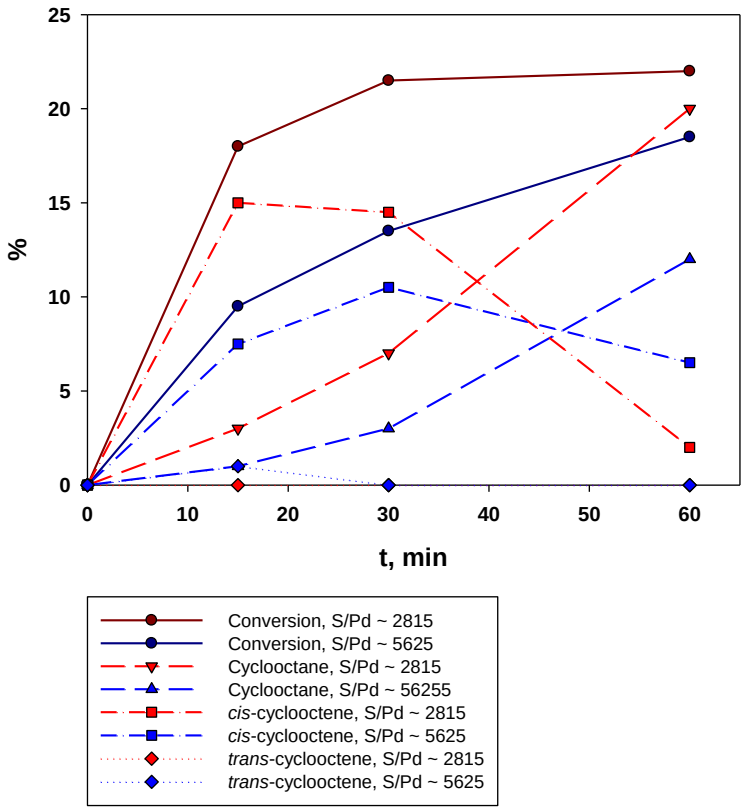


Figure S17. Hydrogenation of 1,5-cyclooctadiene in the presence of *meso*-G2-dendr-Si-Pd catalyst. Reaction conditions: 80 ^{0}C, 10 atm. of H_2.

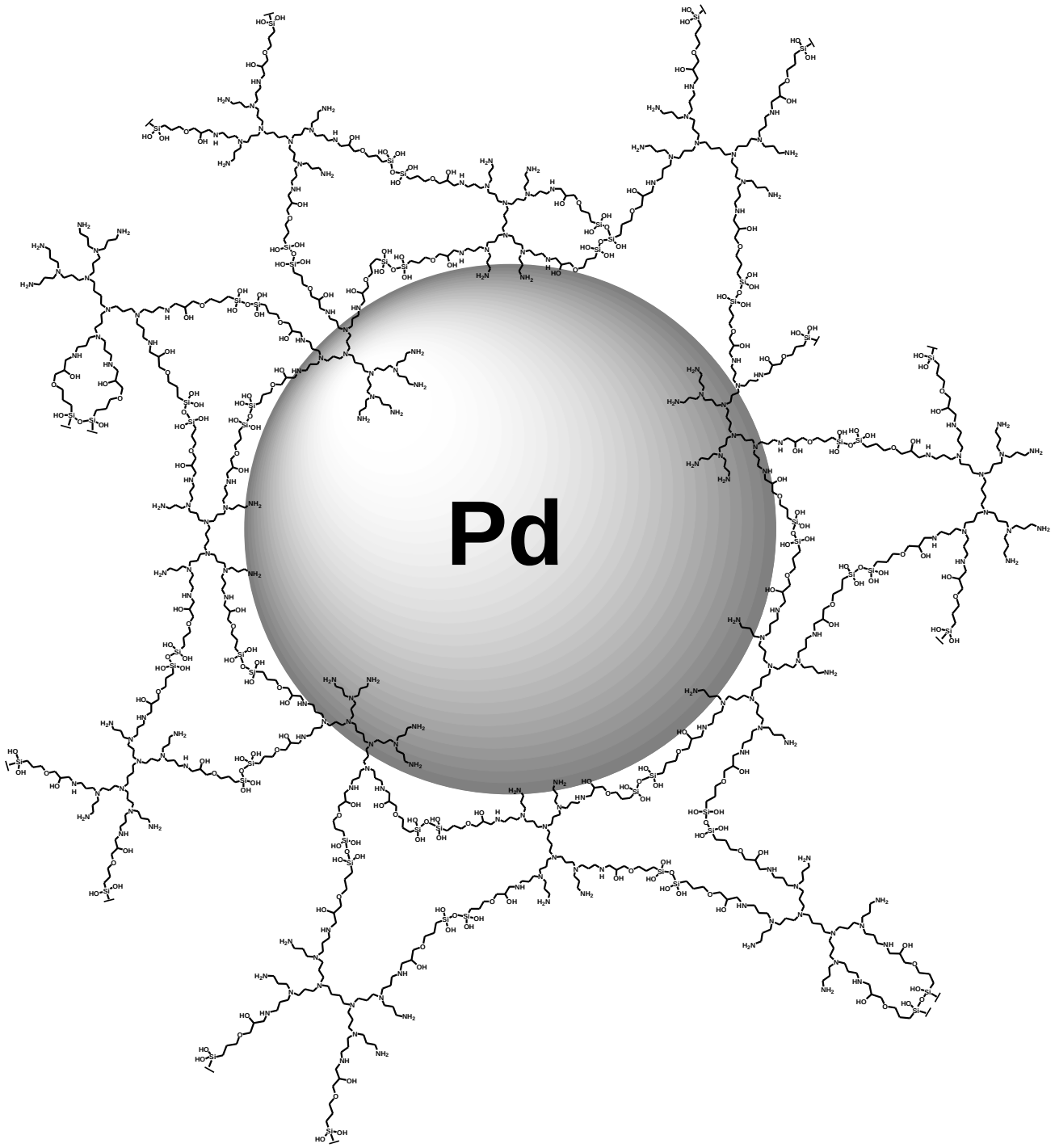


Figure S18. A proposed structure of *meso*-G2-dendr-Si-Pd catalyst.

Table S7. Hydrogenation of dienes in the presence of G2-dendr-*meso*-SiO_2-Pd catalyst [a]

Entry	Substrate	Catalyst loading, mg	Substrate/Pd (mol/mol)	P (H_2), atm.	Conv., %	TOF, h^{-1}	Product distribution, %
1	1,3-cyclooctadiene	1	2820	10	23	2595	Cyclooctane 100%
2	1,5-cyclooctadiene	1	2860	10	33.5	3835	Cyclooctane 100% (substrate isomerization of 100%)
3	1,3-cyclohexadiene	0.5	14735	10	96	56585	Cyclohexene 96% Cyclohexane 4%
4		0.5	29470	10	94	110810	Cyclohexene 98% Cyclohexane 2%
5		0.5	58940	10	72	169750	Cyclohexene 99.5% Cyclohexane 0.5%
6		0.5	58940	30	99.5	234585	Cyclohexene 94.5% Cyclohexane 5.5%
7		0.5	147350	10	58	227905	Cyclohexene > 99.5% Cyclohexane < 0.5%
8		0.5	147350	30	77	302560	Cyclohexene 98.5% Cyclohexane 1.5%
9	2,5-dimethyl-2,4-hexadiene	0.5	9850	10	100	39390	2,5-dimethyl-2-hexene 16.5% 2,5-dimethylhexane 4% 2,5-dimethyl-*cis*-3-hexene 4% 2,5-dimethyl-*trans*-3-hexene 75.5%
10		0.5	14770	10	99.5	58795	2,5-dimethyl-2-hexene 18% 2,5-dimethylhexane 1.5% 2,5-dimethyl-*cis*-3-hexene 5.5% 2,5-dimethyl-*trans*-3-hexene 75%
11		0.5	19695	10	99	78000	2,5-dimethyl-2-hexene 17% 2,5-dimethylhexane 1% 2,5-dimethyl-*cis*-3-hexene 5.5% 2,5-dimethyl-*trans*-3-hexene 76.5%
12		0.5	29545	10	71	83905	2,5-dimethyl-2-hexene 17% 2,5-dimethylhexane 1% 2,5-dimethyl-*cis*-3-hexene 7% 2,5-dimethyl-*trans*-3-hexene 76%
13		0.5	39390	10	65.5	103210	2,5-dimethyl-2-hexene 21% 2,5-dimethylhexane 1% 2,5-dimethyl-*cis*-3-hexene 5.5% 2,5-dimethyl-*trans*-3-hexene 72.5%
14		0.5	39390	30	99.5	156780	2,5-dimethyl-2-hexene 18% 2,5-dimethylhexane 1% 2,5-dimethyl-*cis*-3-hexene 6.5% 2,5-dimethyl-*trans*-3-hexene 74.5%
15		0.5	65655	10	60	157570	2,5-dimethyl-2-hexene 23.5% 2,5-dimethylhexane 0.5% 2,5-dimethyl-*cis*-3-hexene 3% 2,5-dimethyl-*trans*-3-hexene 73%
16		0.5	65655	30	99.5	261305	2,5-dimethyl-2-hexene 18% 2,5-dimethylhexane 1% 2,5-dimethyl-*cis*-3-hexene 6.5% 2,5-dimethyl-*trans*-3-hexene 74.5%
17	Isoprene	0.5	14035	10	100	56140	2-methyl-1-butene < 0.5% 2-methylbutane 38% 3-methyl-1-butene 6.5% 2-methyl-2-butene 55%
18		0.5	21055	10	100	84215	2-methyl-1-butene < 1% 2-methylbutane 19.5% 3-methyl-1-butene 9% 2-methyl-2-butene 71%
19		0.5	28070	10	91.5	102740	2-methyl-1-butene 16% 2-methylbutane 8% 3-methyl-1-butene 20% 2-methyl-2-butene 56%
20		0.5	56141	10	82	184145	2-methyl-1-butene 11% 2-methylbutane 4% 3-methyl-1-butene 12% 2-methyl-2-butene 73%
21		0.5	93570	10	72	269480	2-methyl-1-butene 13% 2-methylbutane 5% 3-methyl-1-butene 15% 2-methyl-2-butene 67%
22		0.5	93570	30	93	348080	2-methyl-1-butene 16.5% 2-methylbutane 9% 3-methyl-1-butene 23% 2-methyl-2-butene 51.5%

[a]Reaction conditions are: 80 ^{0}C, 15 min.

Table S8. Hydrogenation of dienes in the presence of G3-dendr-SiO_2-Pd catalyst [a]

Entry	Substrate	Catalyst loading, mg	Substrate/Pd (mol/mol)	P (H_2), atm.	Conv., %	TOF, h^{-1}	Product distribution, %
1	1,3-cyclooctadiene	1	3190	10	9 [b]	1785	Cyclooctane 94% *cis*-cyclooctene 1% *trans*-cyclooctene 6%
2	1,5-cyclooctadiene	1	3235	10	42	5440	Cyclooctane 100% (substrate isomerization of 100%)
3	1,3-cyclohexadiene	1	4170	10	95	15835	Cyclohexene 93% Cyclohexane 7%
4		0.5	8335	10	89.5	29840	Cyclohexene 96% Cyclohexane 4%
5		0.5	25005	10	87	87020	Cyclohexene 98% Cyclohexane 2%
6		0.5	50010	10	54.5	109025	Cyclohexene 99.5% Cyclohexane 0.5%
7		0.5	50010	30	97	194045	Cyclohexene 97% Cyclohexane 3%
8		0.5	66700	10	31	82685	Cyclohexene ~ 100%
9		0.5	66700	30	92	245390	Cyclohexene 98.5% Cyclohexane 1.5%
10		0.5	166705	30	48.5	323410	Cyclohexene 99.5% Cyclohexane 0.5%
11	2,5-dimethyl-2,4-hexadiene	1	2785	10	100	11140	2,5-dimethyl-2-hexene 17% 2,5-dimethylhexane 9.5% 2,5-dimethyl-*cis*-3-hexene 4.5% 2,5-dimethyl-*trans*-3-hexene 69%
12		0.5	5570	10	100	22285	2,5-dimethyl-2-hexene 14.5% 2,5-dimethylhexane 5.5% 2,5-dimethyl-*cis*-3-hexene 5% 2,5-dimethyl-*trans*-3-hexene 75%
13		0.5	16710	10	100	66850	2,5-dimethyl-2-hexene 18.5% 2,5-dimethylhexane 5% 2,5-dimethyl-*cis*-3-hexene 5% 2,5-dimethyl-*trans*-3-hexene 71.5%
14		0.5	22285	10	100	89130	2,5-dimethyl-2-hexene 17% 2,5-dimethylhexane 2% 2,5-dimethyl-*cis*-3-hexene 6.5% 2,5-dimethyl-*trans*-3-hexene 74.5%
15		0.5	33425	10	86	114980	2,5-dimethyl-2-hexene 19% 2,5-dimethylhexane 0.5% 2,5-dimethyl-*cis*-3-hexene 4.5% 2,5-dimethyl-*trans*-3-hexene 76%
16		0.5	33425	30	100	133700	2,5-dimethyl-2-hexene 15.5% 2,5-dimethylhexane 4% 2,5-dimethyl-*cis*-3-hexene 5% 2,5-dimethyl-*trans*-3-hexene 75.5%
17		0.5	44565	10	71	126570	2,5-dimethyl-2-hexene 17.5% 2,5-dimethylhexane 0.5% 2,5-dimethyl-*cis*-3-hexene 7.5% 2,5-dimethyl-*trans*-3-hexene 74.5%
18		0.5	44565	30	98.5	175590	2,5-dimethyl-2-hexene 18% 2,5-dimethylhexane 1% 2,5-dimethyl-*cis*-3-hexene 5% 2,5-dimethyl-*trans*-3-hexene 77%
19		0.5	111415	10	39	173810	2,5-dimethyl-2-hexene 25.5% 2,5-dimethyl-*cis*-3-hexene 7% 2,5-dimethyl-*trans*-3-hexene 67.5%
20		0.5	111415	30	92	410010	2,5-dimethyl-2-hexene 20.5% 2,5-dimethylhexane 0.5% 2,5-dimethyl-*cis*-3-hexene 6% 2,5-dimethyl-*trans*-3-hexene 73%
21	Isoprene	0.5	15880	10	100	63515	2-methylbutane 30% 3-methyl-1-butene 7.5% 2-methyl-2-butene 63.5%
22		0.5	31760	10	100	127030	2-methyl-1-butene 3% 2-methylbutane 12% 3-methyl-1-butene 16% 2-methyl-2-butene 69%

23	0.5	47635	10	61.5	117195	2-methyl-1-butene 21% 2-methylbutane 4.5% 3-methyl-1-butene 26.5% 2-methyl-2-butene 48%
24	0.5	63515	10	42	106705	2-methyl-1-butene 28% 2-methylbutane 3% 3-methyl-1-butene 25% 2-methyl-2-butene 44%
25	0.5	63515	30	100	254065	2-methyl-1-butene 9% 2-methylbutane 10.5% 3-methyl-1-butene 22% 2-methyl-2-butene 59%
26	0.5	158790	30	60	381095	2-methyl-1-butene 23% 2-methylbutane 1.5% 3-methyl-1-butene 30% 2-methyl-2-butene 45%

[a] Reaction conditions are: 80 ^{0}C, 15 min. [b] 45 min., an induction period of 30 min.

Table S9. Hydrogenation of dienes in the presence of *meso*-G2-dendr-Si-Pd catalyst [a]

Entry	Substrate	Catalyst loading, mg	Substrate/Pd (mol/mol)	P (H_2), atm.	Conv., %	TOF, h^{-1}	Product distribution, %
1	1,3-cyclooctadiene	1	2770	10	44 [b]	3935	Cyclooctane 10% *trans*-cyclooctene 90%
2	1,5-cyclooctadiene	1	2815	10	18	1040	Cyclooctane 16% *cis*-cyclooctene 84% (substrate isomerization of 65.5%)
3		1	5625	10	9.5	2140	Cyclooctane 8% *cis*-cyclooctene 80% *trans*-cyclooctene 12% (substrate isomerization of 10%)
4	1,3-cyclohexadiene	1	3620	10	87	12605	Cyclohexene 87% Cyclohexane 13%
5		0.5	7245	10	86	24915	Cyclohexene 91.5% Cyclohexane 8.5%
6		0.5	7245	30	96	27815	Cyclohexene 82% Cyclohexane 18%
7		0.5	21730	10	68	59105	Cyclohexene 97% Cyclohexane 3%
8		0.5	21730	30	93.5	81270	Cyclohexene 94% Cyclohexane 6%
9		0.5	28975	10	43	49835	Cyclohexene 95.5% Cyclohexane 4.5%
10		0.5	28975	30	68	78810	Cyclohexene 93.5% Cyclohexane 6.5%
11		0.5	43460	10	33	57365	Cyclohexene 96.5% Cyclohexane 3.5%
12		0.5	43460	30	62.5	108650	Cyclohexene 96% Cyclohexane 4%
13	2,5-dimethyl-2,4-hexadiene	1	2420	10	82	7940	2,5-dimethyl-2-hexene 18.5% 2,5-dimethylhexane 0.5% 2,5-dimethyl-*cis*-3-hexene 3% 2,5-dimethyl-*trans*-3-hexene 78%
14		0.5	4840	10	64	12395	2,5-dimethyl-2-hexene 23% 2,5-dimethylhexane 1% 2,5-dimethyl-*cis*-3-hexene 4% 2,5-dimethyl-*trans*-3-hexene 72%
15		0.5	4840	30	99	19170	2,5-dimethyl-2-hexene 18% 2,5-dimethylhexane 1.5% 2,5-dimethyl-*cis*-3-hexene 0.5% 2,5-dimethyl-*trans*-3-hexene 80%
16		0.5	9680	10	52	20140	2,5-dimethyl-2-hexene 21.5% 2,5-dimethylhexane 1% 2,5-dimethyl-*cis*-3-hexene 3% 2,5-dimethyl-*trans*-3-hexene 74.5%
17		0.5	9680	30	74.5	28850	2,5-dimethyl-2-hexene 18% 2,5-dimethylhexane 1.5% 2,5-dimethyl-*cis*-3-hexene 2.5% 2,5-dimethyl-*trans*-3-hexene 78%
18		0.5	14525	10	46	26720	2,5-dimethyl-2-hexene 16.5% 2,5-dimethylhexane 1% 2,5-dimethyl-*cis*-3-hexene 3% 2,5-dimethyl-*trans*-3-hexene 79.5%
19		0.5	14525	30	56	32530	2,5-dimethyl-2-hexene 18% 2,5-dimethylhexane 0.5% 2,5-dimethyl-*cis*-3-hexene 2.5% 2,5-dimethyl-*trans*-3-hexene 79%
20	Isoprene	0.5	6900	10	95	26220	2-methyl-1-butene 11% 2-methylbutane 8.5% 3-methyl-1-butene 21.5% 2-methyl-2-butene 59%
21		0.5	13800	10	76	41950	2-methyl-1-butene 16% 2-methylbutane 9% 3-methyl-1-butene 24% 2-methyl-2-butene 51%
22		0.5	27600	10	61	67340	2-methyl-1-butene 21.5% 2-methylbutane 7% 3-methyl-1-butene 29.5% 2-methyl-2-butene 42%
23		0.5	27600	30	67	73960	2-methyl-1-butene 17.5% 2-methylbutane 7% 3-methyl-1-butene 24.5%

	2-methyl-2-butene 50%
[a] Reaction conditions are: 80 ^{0}C, 15 min. [b] 30 min., an induction period of 15 min.	

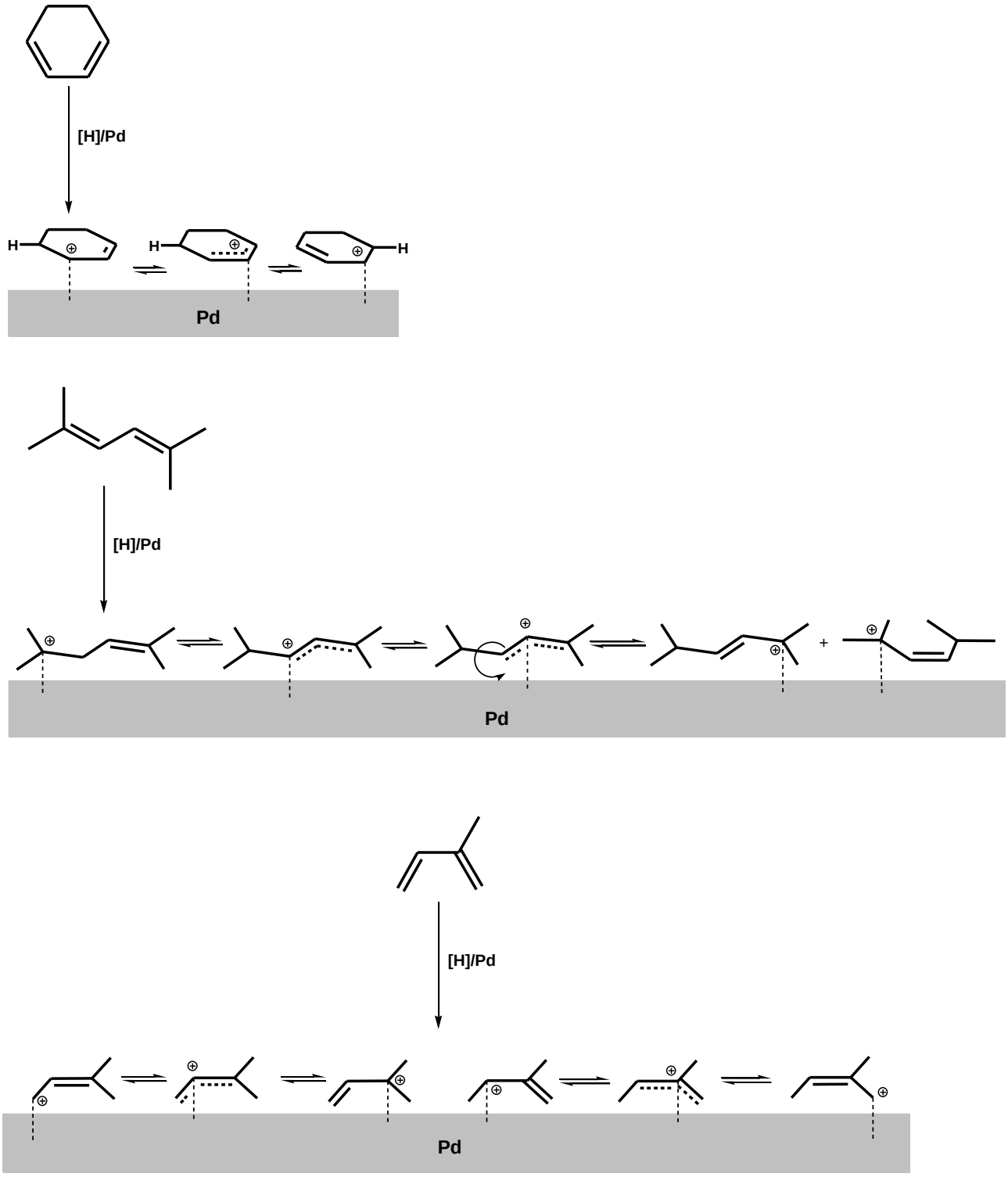


Figure S19. π-allylic intermediates, formed in the hydrogenation of conjugated dienes in the presence of Pd catalysts.

Table S10. Hydrogenation of alkynes in the presence of Pd catalysts

Entry	Substrate	Catalyst	Reaction conditions	TOF, h^{-1}	Main product	Ref.
1	Phenylacetylene	Pd/Pb/$CaCO_3$, quinoline	25 ^{0}C, 1 atm. of H_2, *n*-hexane	320–2900	Styrene 90–95%	3
2	Phenylacetylene	Pd/zeolite, Pd/C	25 ^{0}C, *n*-heptane, 1–20 atm. of H_2,	4230–70700	Styrene 71–100%	4
3	Phenylacetylene	PtPd/zeolite	25 ^{0}C, 1 atm. of H_2, THF	302–2275	Styrene 76–94%	5
4	Phenylacetylene	Pd/polystyrene, quinoline	18–50 ^{0}C, methanol, 1.4–4.8 atm. of H_2,	1570–6055	Styrene 87–97%	6
5	Phenylacetylene	Pd/montmorillonite	25 ^{0}C, 1 atm. of H_2, toluene	540–3745	Styrene 95–100%	7
6	Phenylacetylene	Pd/MCM-41	25 ^{0}C, 1 atm. of H_2, toluene	18360–46440	Styrene 84–95%	8
7	Phenylacetylene	Pd/meso-silicas	25 ^{0}C, 1 atm. of H_2, THF	7200–14400	Styrene 96%	9
8	Phenylacetylene	Pd/TiO_2	30 ^{0}C, 1 atm. of H_2	1480–77040	Styrene 86–90%	10
9	Phenylacetylene	Pd/carbon fiber, laser ablation deposition	80^{0}C, 35 atm. of H_2	147600–806400	Styrene 79–93%	11
10	1-hexyne	PdBi/Al_2O_3	25 ^{0}C, 1 atm. of H_2, toluene	5190	1-hexene 90–95%	12
11	2-hexyne	PdBi/Al_2O_3	25 ^{0}C, 1 atm. of H_2, toluene	1555	*cis*-2-hexene 85–90%	12
12	1-hexyne	Pd/Pb/$CaCO_3$, quinoline	25 ^{0}C, 1 atm. of H_2, toluene	1555	1-hexene 80–85%	12
13	2-hexyne	Pd/Pb/$CaCO_3$, quinoline	25 ^{0}C, 1 atm. of H_2, toluene	1560	*cis*-2-hexene 95–97%	12
14	1-hexyne	Pd/bypy-BMIM/CNF	30 ^{0}C, 10 atm. of H_2, *n*-heptane	27360–218880	1-hexene 94–98%	13
15	4-octyne	Pd/montmorillonite	25 ^{0}C, 1 atm. of H_2, toluene	1295–3205	*cis*-4-octene 89–92%	7
16	4-octyne	Pd/MCM-41	25 ^{0}C, 1 atm. of H_2, toluene	24840–66240	*cis*-4-octene 91–93%	8
17	1-butyne	Pd/Al_2O_3	20 ^{0}C, 20 atm. of H_2	24000–216000	1-butene 87–95%	14
18	1-butyne	Pd/Al_2O_3, piperidine	20 ^{0}C, 20 atm. of H_2	72000–216000	1-butene 87–95%	15
19	Intermediate products of vitamin synthesis with internal C≡C triple bonds	Pd/Pb/$CaCO_3$, quinoline	20 ^{0}C, 1 atm. of H_2, petroleum ether	70	β-carotenes 85–95%	16
20	Ethylphenylacetylene	Pd/MCM-41	25 ^{0}C, 1 atm. of H_2, toluene	10080–24840	*cis*-β-ethylstyrene 88–91%	8
21	Butylphenylacetylene	Pd/meso-silicas	25 ^{0}C, 1 atm. of H_2, THF	21600–216000	*cis*-β-butylstyrene 79–83%	9
22	Methylphenylacetylene	PdPt/Py-PAMAM-G2-C_6	25 ^{0}C, 1 atm. of H_2, CH_2Cl_2	143	β-methylstyrene 94% (*cis*/*trans* ~ 94/6)	17
23	Diphenylacetylene	Pd/Al_2O_3	25 ^{0}C, 5 atm. of H_2, *n*-hexane	18720–83520	*cis*-stilbene 71–94%	18
24	Diphenylacetylene	Pd/PEI	25 ^{0}C, 1 atm. of H_2, MeOH/1,4-dioxane	12	*cis*-stilbene 90–97%	19
25	Diphenylacetylene	Pd/PEI@SBA-15	25 ^{0}C, 1 atm. of H_2, MeOH/1,4-dioxane	4120–5105	*cis*-stilbene 90–93%	20
26	Phenylacetylene	$PdCl_2$/DAB(N(CH_2PPh_2)$_2$)$_{16}$	25 ^{0}C, 1 atm. of H_2, ethanol	155	Styrene 99%	21
27	Phenylacetylene	Pd/PPI networks	80^{0}C, 10–30 atm. of H_2	25940–184840	Styrene 90–96%	22
28	Phenylacetylene	Pd/PAMAM networks	80^{0}C, 10 atm. of H_2	2330–26865	Styrene 78–95%	23
29	1-octyne	Pd/PPI@MPF	80^{0}C, 10 atm. of H_2	121320	1-octene 60–84%	24
30	4-octyne	Pd/PPI@MPF	80^{0}C, 10 atm. of H_2	110640	4-octene 90–91%	24
31	1-hexyne	Pd/PPI@MPF	80^{0}C, 10 atm. of H_2	90840	1-hexene 73–84%	24
32	Phenylacetylene	Scheme S1	70 ^{0}C, 10–30 atm. of H_2, benzene	52550–103160	Styrene 87–97%	1
33	Phenylacetylene	PdAg/PPI-3@SPC	80^{0}C, 10 atm. of H_2	3600–30505	Styrene 86–98%	25
34	1-octyne	PdAg/PPI-3@SPC	80^{0}C, 10–30 atm. of H_2	17220–29995	1-octene 77–93%	25
35	4-octyne	PdAg/PPI-3@SPC	80^{0}C, 10 atm. of H_2	3470	4-octene 90–95%	25

36	Phenylacetylene	G2-dendr-*meso*-SiO_2-Pd	80^0C, 10–30 atm. of H_2	32215–57530	Styrene 84–96%	This work
37	Phenylacetylene	*meso*-G2-dendr-Si-Pd	80^0C, 10–30 atm. of H_2	18350–69755	Styrene 87–94%	This work
38	Phenylacetylene	G3-dendr-SiO_2-Pd	80^0C, 10–30 atm. of H_2	28780–80995	Styrene 90–98%	This work
39	1-octyne	G2-dendr-*meso*-SiO_2-Pd	80^0C, 10–30 atm. of H_2	55100–171305	1-octene 87–97%	This work
40	1-octyne	*meso*-G2-dendr-Si-Pd	80^0C, 10–30 atm. of H_2	14785–211920	1-octene 78–93%	This work
41	1-octyne	G3-dendr-SiO_2-Pd	80^0C, 10atm. of H_2	316545	1-octene 93–94%	This work
42	1-hexyne	G2-dendr-*meso*-SiO_2-Pd	80^0C, 10–30 atm. of H_2	33240–276805	1-hexene 73–93%	This work
43	1-hexyne	*meso*-G2-dendr-Si-Pd	80^0C, 10–30 atm. of H_2	150980–404415	1-hexene 89–97%	This work
42	1-hexyne	G3-dendr-SiO_2-Pd	80^0C, 10–30 atm. of H_2	23430–234290	1-hexene 80–90%	This work

Table S11. Hydrogenation of dienes in the presence of Pd catalysts

Entry	Substrate	Catalyst	Reaction conditions	TOF, h^{-1}	Main products	Ref.
1	1,3-dutadiene	Pd/Al_2O_3	100^0C, 0.01 atm. of H_2, Ar	3600–36000	1-butene ~25–50% *trans*-2-butene ~45–55%	26
2	1,3-dutadiene	Pd/Al_2O_3	227^0C, 0.7–2.7 atm. of H_2, Ar	685–7920	Butenes ~40–80%	27
3	1,3-dutadiene	Co/Al_2O_3	144^0C, 0.1–0.2 atm. of H_2	0.25–0.27	1-butene 28–51% *trans*-2-butene 31–56%	28
4	1,3-dutadiene	Pd/SiO_2, $PdAu/SiO_2$	20^0C, 0.1–0.2 atm. of H_2	2.8–5	1-butene 47–50% *trans*-2-butene 43–48%	28
5	1,3-cyclopentadiene	Pd/C	20^0C, 1 atm. of H_2, toluene or methanol	295	Cyclopentene 92–95%	29
6	1,3-cyclopentadiene	Pd/Al_2O_3	20^0C, 1 atm. of H_2, toluene or methanol	10840	Cyclopentene 98–100%	29
7	Isoprene	Pd/CaCO3	0^0C, 1 atm. of H_2, ethanol	17340	2-methyl-1-butene 25.5% 3-methyl-1-butene 31.5% 2-methyl-2-butene 43%	30
8	Isoprene	Pd/BaSO4	0^0C, 1 atm. of H_2, ethanol	63780	2-methyl-1-butene 24.5% 3-methyl-1-butene 30% 2-methyl-2-butene 45.5%	30
9	Isoprene	Pd/C	0^0C, 1 atm. of H_2, ethanol	17760	2-methyl-1-butene 24% 3-methyl-1-butene 29% 2-methyl-2-butene 47%	30
10	Isoprene	Pd black	0^0C, 1 atm. of H_2, ethanol	91500	2-methyl-1-butene 24.5% 3-methyl-1-butene 29% 2-methyl-2-butene 46.5%	30
11	Isoprene	Pd/Al_2O_3	0^0C, 1 atm. of H_2, ethanol	11760	2-methyl-1-butene 25% 3-methyl-1-butene 25% 2-methyl-2-butene 50%	30
12	Isoprene	Pd/SiO_2	0^0C, 1 atm. of H_2, ethanol	23160	2-methyl-1-butene 24.5% 3-methyl-1-butene 25% 2-methyl-2-butene 50.5%	30
13	Isoprene	$PdAg/SiO_2$	0^0C, 1 atm. of H_2, ethanol	36780–104100	2-methyl-1-butene 26.5–27.5% 3-methyl-1-butene 25.5–29.5% 2-methyl-2-butene 44–48%	30
14	Isoprene	$PdAu/SiO_2$	0^0C, 1 atm. of H_2, ethanol	22380–217800	2-methyl-1-butene 24.5–27.5% 3-methyl-1-butene 25–30.5% 2-methyl-2-butene 42.5–50.5%	30
15	Isoprene	Pd/Al_2O_3, egg-shell	40–44^0C, 30 atm. of H_2, *n*-heptane	470–1650	Methylbutenes 85–90%	31
16	1,3-dutadiene	Pd/Al_2O_3	20 ^{0}C, 20 atm. of H_2	24000	1-butene 48–50% *trans*-2-butene 45–46%	14
17	1,3-dutadiene	Pd/Al_2O_3, piperidine	20 ^{0}C, 20 atm. of H_2	36000	1-butene 48–50% *trans*-2-butene 45–46%	15
18	Isoprene	Pd/Nylon-6,6	50^0C, 1 atm. of H_2, various solvents	85–2905	Alkenes 65–99%	32
19	1,3-pentadiene	Pd/Nylon-6,6	50^0C, 1 atm. of H_2, various solvents	85–3590	Alkenes 53–99%	32
20	Isoprene	$Pd_2(Ph_2PCH_2PPh_2)_3$	25 ^{0}C, 1 atm. of H_2, toluene	0.5	2-methyl-1-butene 28% 3-methyl-1-butene 22.5% 2-methyl-2-butene 49.5 %	33
21	1,3-pentadiene	$Pd_2(Ph_2PCH_2PPh_2)_3$	25 ^{0}C, 1 atm. of H_2, toluene	0.44–0.8	1-pentene 16–30% *cis*-2-pentene 10–30.5% *trans*-2-pentene 38–65.5%	33
22	1,3-cyclohexadiene	$Pd_2(Ph_2PCH_2PPh_2)_3$	25 ^{0}C, 1 atm. of H_2, toluene	0.58	Cyclohexene 95.5%	33
23	1,3-cyclohexadiene	$Pd_2(Ph_2PCH_2PPh_2)_3$, *i*-$PrNH_2$	25 ^{0}C, 1 atm. of H_2, toluene	0.065	Cyclohexene 99.5%	33
24	1,3-cyclooctadiene	PdPt/Py-PAMAM-G2-C_6	25 ^{0}C, 1 atm. of H_2, CH_2Cl_2	3920–23500	Cyclooctene 100%	17
25	1,3-cyclooctadiene	RhPd/PAMAM-G4	20 ^{0}C, 1 atm. of H_2, ethanol	850–1300	Cyclooctene 100%	34
26	1,3-cyclooctadiene	Pd/G-1-triazol-derrocenyl carbosilane dendrimer	25 ^{0}C, 1 atm. of H_2	1150	Cyclohexene 100%	35
27	1,3-cyclooctadiene	Pd/G-1-triazol-derrocenyl carbosilane dendrimer	25 ^{0}C, 1 atm. of H_2	530	Cyclooctene 100%	35
28	1,3,5-cycloheptatriene	Pd/G-1-triazol-derrocenyl carbosilane dendrimer	25 ^{0}C, 1 atm. of H_2	130	Cycloheptene 100%	35
29	2,5-dimethyl-	Pd/G-1-triazol-derrocenyl	25 ^{0}C, 1 atm. of H_2	1040	2,5-dimethyl-2-hexene 78%	35

	2,4-hexadiene	carbosilane dendrimer			*trans*-2,5-dimethyl-3-hexene 22%	
30	2,6-dimethyl-2,4,6-octatriene	Pd/G-1-triazol-derrocenyl carbosilane dendrimer	25 ^{0}C, 1 atm. of H_2	480	Alkenes 100%	35
31	1,3-cyclopentadiene	$PdCl_2$/DAB(N(CH_2PPh_2)$_2$)$_{16}$	25 ^{0}C, 1 atm. of H_2, ethanol	445	Cyclopentene 100%	21
32	1,3-cyclohexadiene	$PdCl_2$/DAB(N(CH_2PPh_2)$_2$)$_{16}$	25 ^{0}C, 1 atm. of H_2, ethanol	690	Cyclohexene 99.5%	21
33	1,3-cyclooctadiene	$PdCl_2$/DAB(N(CH_2PPh_2)$_2$)$_{16}$	25 ^{0}C, 1 atm. of H_2, ethanol	575	Cyclooctene 100%	21
34	Isoprene	$PdCl_2$/DAB(N(CH_2PPh_2)$_2$)$_{16}$	25 ^{0}C, 1 atm. of H_2, ethanol	580	Alkenes 100%	21
35	1,3-cyclopentadiene	Pd/PPI-(G3-G5)-TEBA	30 ^{0}C, 1 atm. of H_2, toluene	670–740	Cyclopentene 100%	36
36	1,3-cyclohexadiene	Pd/PPI-(G3-G5)-TEBA	30 ^{0}C, 1 atm. of H_2, toluene	580–790	Cyclohexene 99.5%	36
37	1,3-cyclooctadiene	Pd/PPI-(G3-G5)-TEBA	30 ^{0}C, 1 atm. of H_2, toluene	230–435	Cyclooctene 100%	36
38	1,3-cyclohexadiene	Pd(dba)/PAMAM-(G0-G2)-PPh_2@SiO_2	25 ^{0}C, 1 atm. of H_2, methanol	115–250	Cyclohexene 73–99%	37
39	1,3-cycloheptadiene	Pd(dba)/PAMAM-(G0-G2)-PPh_2@SiO_2	25 ^{0}C, 1 atm. of H_2, methanol	150	Cycloheptene 92–95%	37
40	1,3-cyclooctadiene	Pd(dba)/PAMAM-(G0-G2)-PPh_2@SiO_2	25 ^{0}C, 1 atm. of H_2, methanol	320	Cyclooctene 98–100%	37
41	1,2,3,4,5-pentamethyl-1,3-cyclopentadiene	Pd(dba)/PAMAM-(G0-G2)-PPh_2@SiO_2	25 ^{0}C, 1 atm. of H_2, methanol	780	Pentamethylcyclopentene 78%	37
42	2,4-dimethyl-1,3-pentadiene	Pd(dba)/PAMAM-(G0-G2)-PPh_2@SiO_2	25 ^{0}C, 1 atm. of H_2, methanol	135–365	2,4-dimethyl-1-pentene 39–48% 2,4-dimethyl-2-pentene 52–59%	37
43	3-methyl-1,3-hexadiene	Pd(dba)/PAMAM-(G0-G2)-PPh_2@SiO_2	25 ^{0}C, 1 atm. of H_2, methanol	60–365	3-methyl-2-hexene 6–21% 3-methyl-3-hexene 68–81% 3-methylhexane11–24%	37
44	1-phenyl-2-methyl-1,3-butadiene	Pd(dba)/PAMAM-(G0-G2)-PPh_2@SiO_2	25 ^{0}C, 1 atm. of H_2, methanol	55–135	1-phenyl-2-methyl-1-butene 46–67% 3-methyl-4-phenyl-1-butene 3–10% 3-methyl-4-phenyl-2-butene 13–19% sec-butylbenzene 10–33%	37
45	Isoprene	Scheme S1	70 ^{0}C, 10–30 atm. of H_2, toluene	3680–232210	2-methyl-1-butene 22–30% 3-methyl-1-butene 16.5–22% 2-methyl-2-butene 47.5–58%	1
46	2,5-dimethyl-2,4-hexadiene	Scheme S1	70 ^{0}C, 10–30 atm. of H_2, benzene	2375–9605	2,5-dimethyl-2-hexene 25–28% *cis*-2,5-dimethyl-3-hexene 2.5–9.5% *trans*-2,5-dimethyl-3-hexene 62.5–70%	1
47	2,5-dimethyl-2,4-hexadiene	Pd/PAMAM networks	80^{0}C, 10 atm. of H_2	2605–27966	2,5-dimethyl-2-hexene 18–22% *trans*-2,5-dimethyl-3-hexene 70–77%	23
48	1,3-cyclohexadiene	Pd/PPI networks	80^{0}C, 10–30 atm. of H_2	56950–160100	Cyclohexene 90–100%	22
49	2,5-dimethyl-2,4-hexadiene	Pd/PPI networks	80^{0}C, 10–30 atm. of H_2	1130–39455	2,5-dimethyl-2-hexene 20–25% *trans*-2,5-dimethyl-3-hexene 70–75%	22
50	1,3-cyclooctadiene	*meso*-G2-dendr-Si-Pd	80^{0}C, 10 atm. of H_2	3935	*trans*-cyclooctene 90–95%	This work
51	1,3-cyclohexadiene	*meso*-G2-dendr-Si-Pd	80^{0}C, 10–30 atm. of H_2	12605–108650	Cyclohexene 82–97%	This work
52	2,5-dimethyl-2,4-hexadiene	*meso*-G2-dendr-Si-Pd	80^{0}C, 10–30 atm. of H_2	12395–32530	2,5-dimethyl-2-hexene 16–23% *trans*-2,5-dimethyl-3-hexene 72–80%	This work
53	Isoprene	*meso*-G2-dendr-Si-Pd	80^{0}C, 10–30 atm. of H_2	26220–73960	2-methyl-1-butene 11–21.5% 3-methyl-1-butene 21.5–29% 2-methyl-2-butene 42–59%	This work
54	1,3-cyclohexadiene	G2-dendr-*meso*-SiO_2-Pd	80^{0}C, 10–30 atm. of H_2	56585–302560	Cyclohexene 94–100%	This work
55	2,5-dimethyl-2,4-hexadiene	G2-dendr-*meso*-SiO_2-Pd	80^{0}C, 10–30 atm. of H_2	39390–261305	2,5-dimethyl-2-hexene 16.5–23.5% *trans*-2,5-dimethyl-3-hexene 72.5–76.5%	This work
56	Isoprene	G2-dendr-*meso*-SiO_2-Pd	80^{0}C, 10–30 atm. of H_2	56140–348080	2-methyl-1-butene 11–16.5% 3-methyl-1-butene 12–23% 2-methyl-2-butene 51.5–73%	This work
57	1,3-cyclohexadiene	G3-dendr-SiO_2-Pd	80^{0}C, 10–30 atm. of H_2	15835–323410	Cyclohexene 93–100%	This work
58	2,5-dimethyl-2,4-hexadiene	G3-dendr-SiO_2-Pd	80^{0}C, 10–30 atm. of H_2	11140–410010	2,5-dimethyl-2-hexene 14.5–25.5% *trans*-2,5-dimethyl-3-hexene 67.5–77%	This work
59	Isoprene	G3-dendr-SiO_2-Pd	80^{0}C, 10–30 atm. of H_2	63515–381095	2-methyl-1-butene 9–28% 3-methyl-1-butene 16–30% 2-methyl-2-butene 44–69%	This work

[1] E. Karakhanov, A. Maximov, Yu. Kardasheva, V. Semernina, A. Zolotukhina, A. Ivanov, G. Abbott, E. Rosenberg, V. Vinokurov, *ACS Appl. Mater. Interfaces* **2014**, *6*, 8807−8816

[2] a) Electronic Database Web-EMAPS Diffraction Utilities, http://emaps.mrl.uiuc.edu/emaps.asp; b) J.W. Arblaster, *Platinum Metals Rev*. **2012**, *56*, 181–189; c) S. Navaladian, B. Viswanathan, T.K. Varadarajan, R. P. Viswanath, *Nanoscale Res. Lett*. **2009**, *4*, 181–186; d) N. Mejías, A. Serra-Muns, R. Pleixats, A. Shafir, M. Tristany, *Dalton Trans*. **2009**, 7748–7755

[3] H. Lindlar, R. Dubuis, *Org. Synth*. **1973**, *5*, 880–881; **1966**, *46*, 89−90

[4] G. Carturan, G. Facchin, G. Cocco, S. Enzo, G. Navazio, *J. Catal*. **1982**, *76*, 405–417

[5] G. Carturan, G. Cocco, G. Facchin, G. Navazio, *J. Mol. Catal*. **1984**, *26*, 375–384

[6] M.A. Aramendía, V. Borau, C. Jiménez, J.M. Marinas, M.E. Sempere, F.J. Urbano, *Appl. Catal*. **1990**, *63*, 375–389

[7] Á. Mastalir, Z. Király, F. Berger, *Appl. Catal. A: Gen*. **2004**, *269*, 161–168

[8] A. Papp, Á. Molnár, Á. Mastalir, *Appl. Catal. A: Gen*. **2005**, *289*, 256–266

[9] N. Marín-Astorga, G. Pecchi, T.J. Pinnavaia, G. Alvez-Manoli, P. Reyes, *J. Mol. Catal. A: Chem*. **2006**, *247*, 145–152

[10] P. Weerachawanasak, O. Mekasuwandumrong, M. Arai c, Sh.-I. Fujita, P. Praserthdam, J. Panpranot, *J. Catal*. **2009**, *262*, 199–205

[11] E.A. Karakhanov, I.A. Aksenov, S.V. Kardashev, A.L. Maksimov, F.N. Putilin, A.N. Shatokhin, S.V. Savilov, *Appl. Catal. A: Gen*. **2013**, *464–465*, 253–260

[12] J.A. Anderson, J. Mellor, R.P.K. Wells, J. Catal. 2009, 261, 208–216

[13] M. Crespo-Quesada, R.R. Dykeman, G. Laurenczy, P.J. Dyson, L. Kiwi-Minsker, *J. Catal*. **2011**, *279*, 66–74

[14] J.P. Boitiaux, J. Cosyns, S. Vasudevan, *Appl. Catal*. **1983**, *6*, 41–51

[15] J.P. Boitiaux, J. Cosyns, S. Vasudevan, *Appl. Catal*. **1985**, *15*, 317−326

[16] H. Lindlar, *Helv. Chim. Acta* **1952**, *35*, 446−450

[17] M. Murata, Yu. Tanaka, T. Mizugaki, K. Ebitani, K. Kaneda, *Chem. Lett*. **2005**, *34*, 272–273

[18] a) A.Yu. Stakheev, P.V. Markov, A.S. Taranenko, G.O. Bragina, G.N. Baeva, O.P. Tkachenko, I.S. Mashkovskii, A.S. Kashin, *Kinet. Catal*. **2015**, *56*, 733–740; b) P.V. Markov, O.V. Turova, I.S. Mashkovsky, A.K. Khudorozhkov, V.I. Bukhtiyarov, A.Yu. Stakheev, *Mendeleev Commun*. **2015**, *25*, 367–369

[19] Sh. Mori, T. Ohkubo, T. Ikawa, A. Kume, T. Maegawa, Ya. Monguchi, H. Sajiki, *J. Mol. Catal. A: Chem*. **2009**, *307*, 77–87

[20] W. Long, N.A. Brunelli, S.A. Didas, E.W. Ping, C.W Jones, *ACS Catal*. **2013**, *3*, 1700−1708

[21] T. Mizugaki, M. Ooe, K. Ebitani, K. Kaneda, *J. Mol. Catal. A: Chem*. **1999**, *145*, 329–333

[22] E.A. Karakhanov, A.L. Maximov, E.M. Zakharyan, A.V. Zolotukhina, A.O. Ivanov, *Mol. Catal*. **2017**, *440*, 107–119

[23] E.A. Karakhanov, A.L. Maksimov, E.M. Zakharian, Yu.S. Kardasheva, S.V. Savilov, N.I. Truhmanova, A.O. Ivanov, V.A. Vinokurov, *J. Mol. Catal. A: Chem*. **2015**, *397*, 1–18

[24] M.P. Boronoev, A.V. Zolotukhina, V I. Ignatyeva, M.V. Terenina, A.L. Maximov, E. A. Karakhanov, *Macromol. Symp*. **2016**, *363*, 57–63

[25] E.A. Karakhanov, A.L. Maximov, A.V. Zolotukhina, N. Yatmanova, E. Rosenberg, *Appl. Organomet. Chem*. **2015**, *29*, 777–784

[26] J. Silvestre-Albero, G. Rupprechter, H.-J. Freund, *Chem. Commun*. **2006**, 80–82

[27] L. Piccolo, A. Valcarcel, M. Bausach, C. Thomazeau, D. Uzio, G. Berhault, *Phys. Chem. Chem. Phys*. **2008**, *10*, 5504–5506

[28] B.J. Joice, J.J. Rooney, P.B. Wells, G.R. Wilson, *Discuss. Faraday Soc*. **1966**, 223–236

[29] L. Černeny, J. Vopatová, V. Ruzička, React. *Kinet. Catal. Lett*. **1982**, *19*, 223–226

[30] G.C. Bond, A.F. Rawle, *J. Mol. Catal. A: Chem*. **1996**, *109*, 261−271

[31] a) T.-B. Lin, T.-C. Chou, *Appl. Catal. A: Gen*. **1994**, *108*, 7−19; b) J.-Ch. Chang, Ts.-Ch. Chou, *Appl. Catal. A: Gen*. **1997**, *156*, 193−205

[32] R.P. Macdonald, J.M. Winterbottom, *J. Catal*. **1979**, *57*, 195−207

[33] E.W. Stern, P.K. Maples, *J. Catal*. **1972**, *27*, 120–133

[34] Yo.-M. Chung, H.-K. Rhee, *J. Mol. Catal. A: Chem*. **2003**, *206*, 291–298

[35] C. Ornelas, J. Ruiz, L. Salmon, D. Astruc, *Chem. Eur. J*. **2008**, *14*, 50–64

[36] M. Ooe, M. Murata, T. Mizugaki, T. Ebitani, K. Kaneda, *Nanolett*. **2002**, *2*, 999–1002

[37] P.P. Zweni, H. Alper, *Adv. Synth. Catal*. **2006**, *348*, 725–731