Electronic Supplementary Information for

New insights into catalysis for Heck reactions with fine supported Pd particles

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Scope of Heck coupling with supported Pd^{II} systems

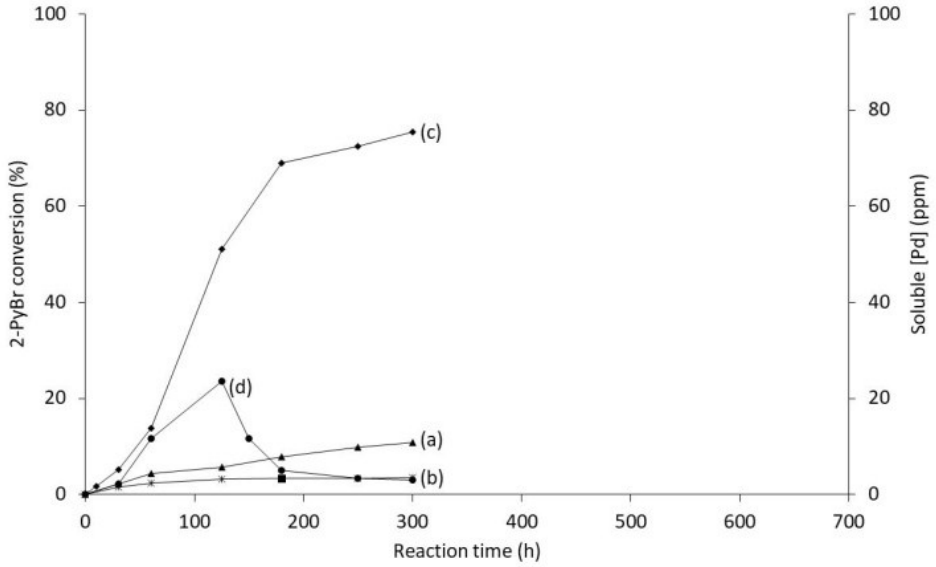

Fig. S1 Heck coupling profiles of 2-PyBr and styrene with reaction time at 135 °C: (a) 2-PyBr conversion over 1 % Pd^0/SiO_2, (b) Pd leaching into solution from 1 % Pd^0/SiO_2, (c) 2-PyBr conversion over 1 % Pd^{II}/SiO_2 and (d) Pd leaching into solution from 1 % Pd^{II}/SiO_2.

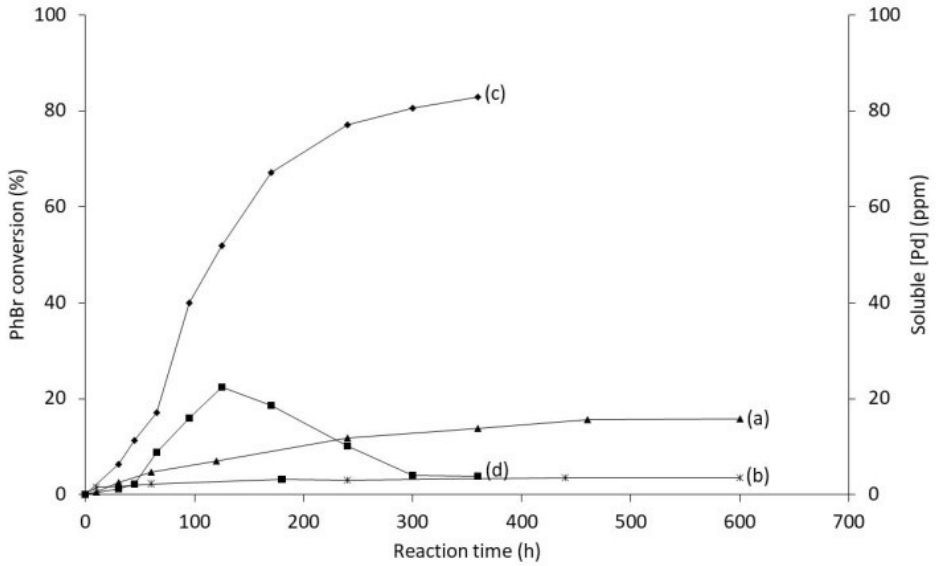

Fig. S2 Heck coupling profiles of PhBr and methyl acrylate with reaction time at 135 °C: (a) PhBr conversion over 1 % Pd^0/SiO_2, (b) Pd leaching into solution from 1 % Pd^0/SiO_2, (c) PhBr conversion over 1 % Pd^{II}/SiO_2 and (d) Pd leaching into solution from 1 % Pd^{II}/SiO_2.

Quantitative estimation of true catalytic active species

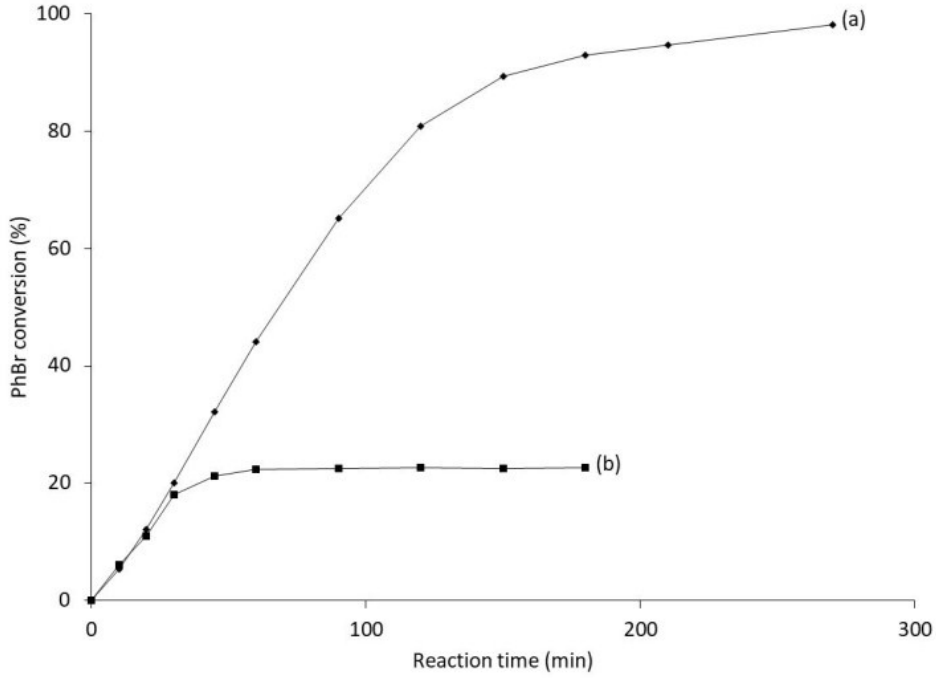

Fig. S3 Heck coupling profiles of PhBr and styrene with reaction time at 135 °C over (a) 1 % Pd^{II}/SiO_2 and (b) 1 % Pd^{II}/SiO_2 followed by addition of HS-SiO_2 at 30 min of Heck reaction.

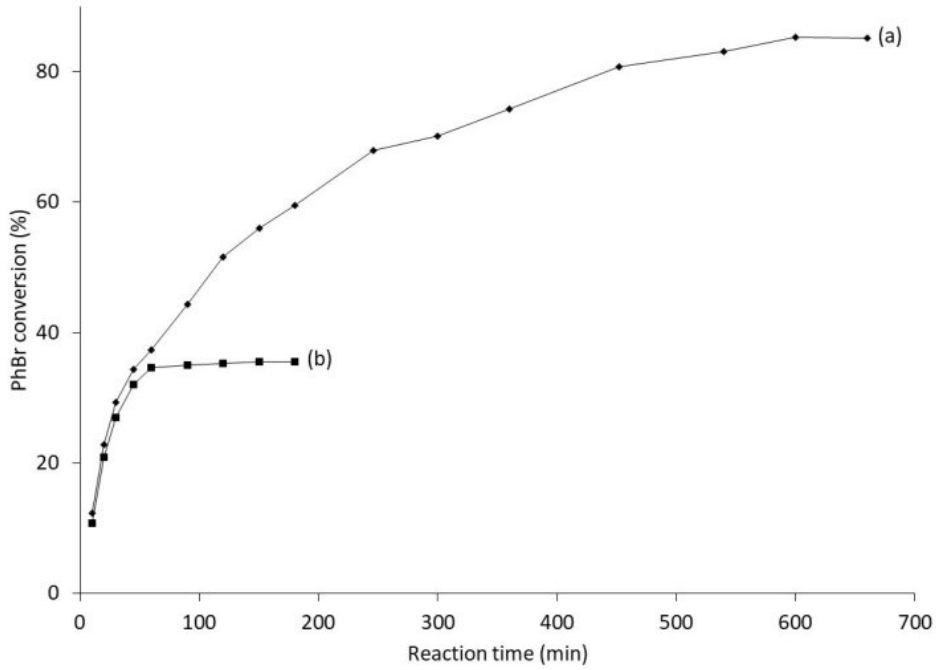

Fig. S4 Heck coupling profiles of PhBr and styrene with reaction time at 135 °C over (a) 1 % Pd^{II}/MgO and (b) 1 % Pd^{II}/MgO followed by addition of HS-SiO_2 at 30 min of Heck reaction.

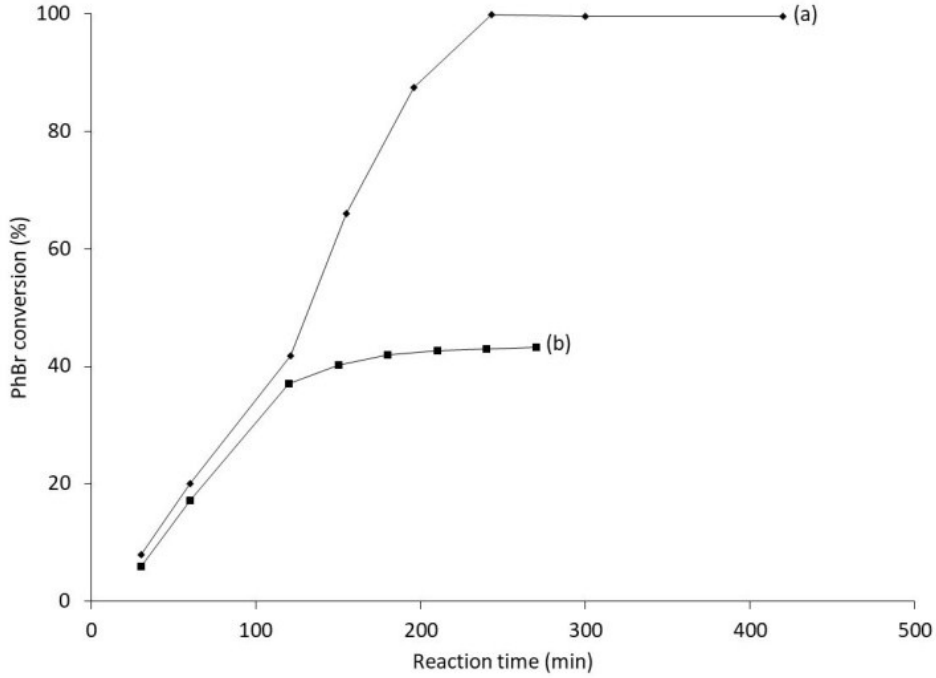

Fig. S5 Heck coupling profiles of PhBr and styrene with reaction time at 135 °C over (a) 1 % Pd^{II}/SBA-15 and (b) 1 % Pd^{II}/SBA-15 followed by addition of HS-SiO_2 at 30 min of Heck reaction.

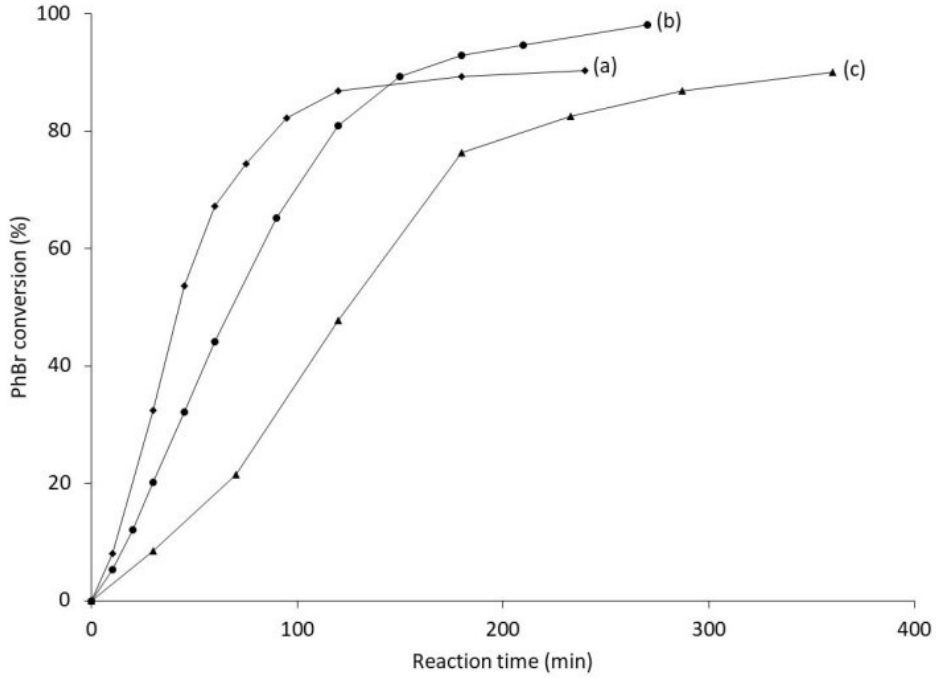

Fig. S6 PhBr conversion profiles with reaction time in the Heck coupling of PhBr and styrene over Pd^{II}/SiO_2 at 135 °C with (a) 0.2 % Pd loading (0.028 mol% Pd), (b) 1 % Pd loading (0.14 mol% Pd) and (c) 4 % Pd loading (0.56 mol% Pd).

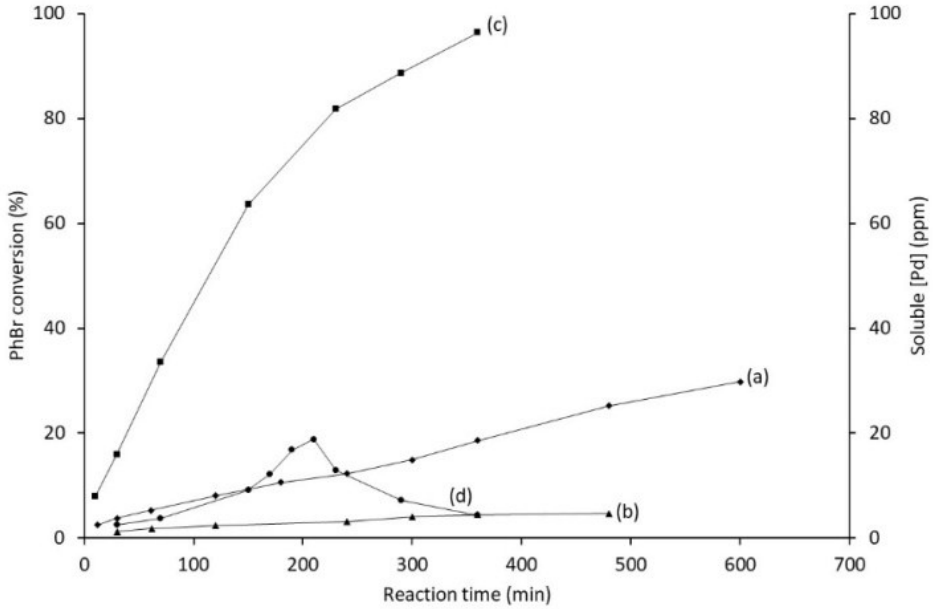

Fig. S7 Heck coupling profiles of PhBr and styrene with reaction time at 135 °C: (a) PhBr conversion over 1 % Pd^0/Al_2O_3, (b) Pd leaching into solution from 1 % Pd^0/Al_2O_3, (c) PhBr conversion over 1 % Pd^{II}/Al_2O_3 and (d) Pd leaching into solution from 1 % Pd^{II}/Al_2O_3.

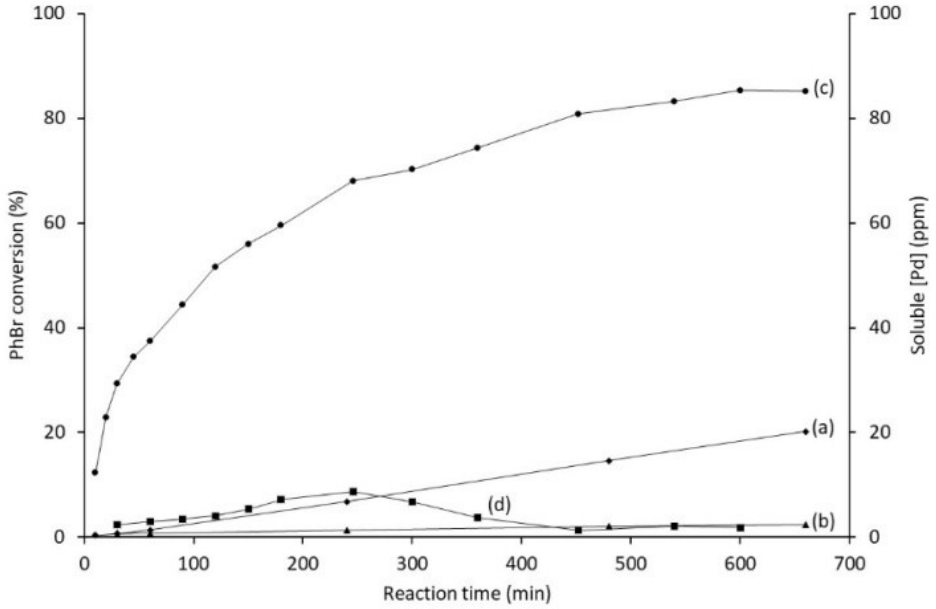

Fig. S8 Heck coupling profiles of PhBr and styrene with reaction time at 135 °C: (a) PhBr conversion over 1 % Pd^0/MgO, (b) Pd leaching into solution from 1 % Pd^0/MgO, (c) PhBr conversion over 1 % Pd^{II}/MgO and (d) Pd leaching into solution from 1 % Pd^{II}/MgO.

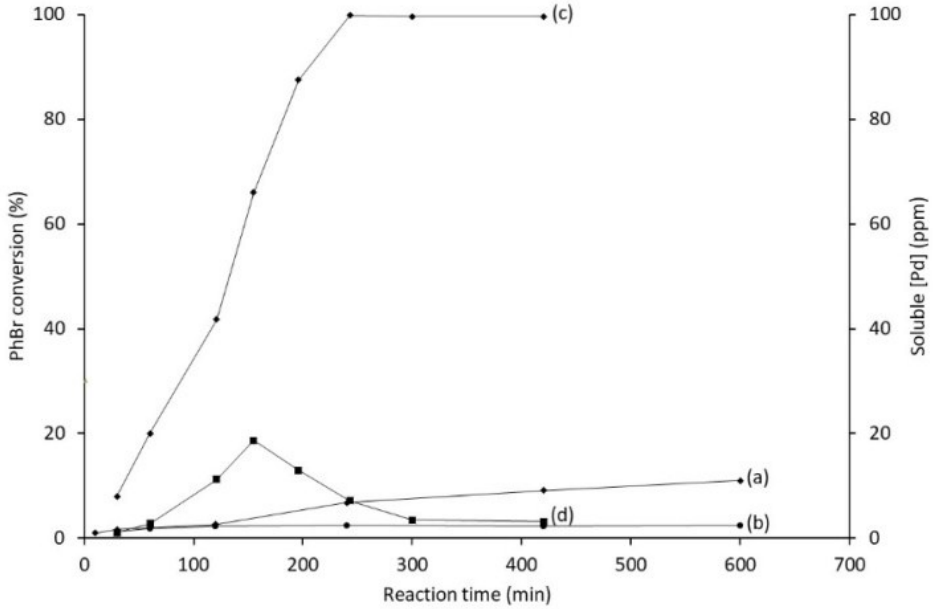

Fig. S9 Heck coupling profiles of PhBr and styrene with reaction time at 135 °C: (a) PhBr conversion over 1 % Pd^0/SBA-15, (b) Pd leaching into solution from 1 % Pd^0/SBA-15, (c) PhBr conversion over 1 % Pd^{II}/SBA-15 and (d) Pd leaching into solution from 1 % Pd^{II}/SBA-15.

Catalyst recyclability and Pd leaching to product

Table S1 Conversions of PhBr and contents of soluble Pd species at the end of Heck coupling of PhBr and styrene over supported Pd^{II} systems at 135 °C.[a]

precatalyst (Pd loading (%))	cycle	reaction time (h)	conversion (%)	cumulative TON	soluble [Pd] (ppm)
Pd^{II}/SiO_2 (0.2)[b]	1	4	90	3214	2.4
Pd^{II}/SiO_2 (1)	1	5	89	636	4.5
	2	5	87		3.0
	3	5	84		3.0
	4	5	90		2.3
	5	5	89		2.5
	6	5.3	87		2.3
	7	6	68	3643	2.5
Pd^{II}/SiO_2 (4)[c]	1	8	99	177	31
	3	6.7	99		28
	5	5	99		15
	7	8	85		13
	10	7	97		13
	11	7	52	1828	
Pd^{II}/Al_2O_3 (1)	1	6	96	686	4.3
	2	4	98		4.0
	3	11	75	1922	
	4	11	17	2043	
Pd^{II}/MgO (1)	1	11	85	607	1.8
	2	22	65		2.3
	3	23	51	1435	
Pd^{II}/SBA-15 (1)	1	3.9	100	714	7.6
	2	4.5	96		
	3	6.1	99		6.4
	4	11	88		
	5	12	70	3236	
	6	12	12	3322	
Pd^{II}/TiO_2 (1)	1	9	98	700	4.7
	3	16	82		4.5
	5	16	99		4.7
	9	17	80	5377	4.1
Pd^{II}/ZrO_2 (1)	1	6	99	707	4.1
	3	6	99		4.8
	5	16	94		4.2
	7	16	76	3715	

[a] 0.14 mol% Pd, 10 mmol of PhBr, 15 mmol of styrene, 5 mmol of Na_2CO_3, 10 ml of DMA. [b] 0.028 mol% Pd. [c] 0.56 mol% Pd.

Table S2 Conversions of alternative aryl bromides and contents of soluble Pd species at the end of Heck couplings over 1 % Pd^{II}/SiO_2 at 135 °C.[a]

substrates	cycle	reaction time (h)	conversion (%)	cumulative TON	soluble [Pd] (ppm)
2-PyBr + styrene	1	5	75	536	3.5
	2	5	77		3.7
	3	5	75		3.8
	4	5	76	2165	3.4
4-BrPhOMe + styrene	1	5	93	664	4.2
	2	4	92		4.7
	3	5	87		4.5
	4	6	85	2549	4.8
PhBr + methyl acrylate	1	6	83	593	4.3
	2	12	85		4.8
	3	5	77		4.8
	4	8	71	2257	4.7
4-BrPhOMe + methyl acrylate	1	6	78	557	4.8
	2	6	80		4.6
	3	8	74		4.6
	4	8	70	2157	4.5

[a] 0.14 mol% Pd, 10 mmol of aryl bromide, 15 mmol of olefin, 5 mmol of Na_2CO_3, 10 ml of DMA.

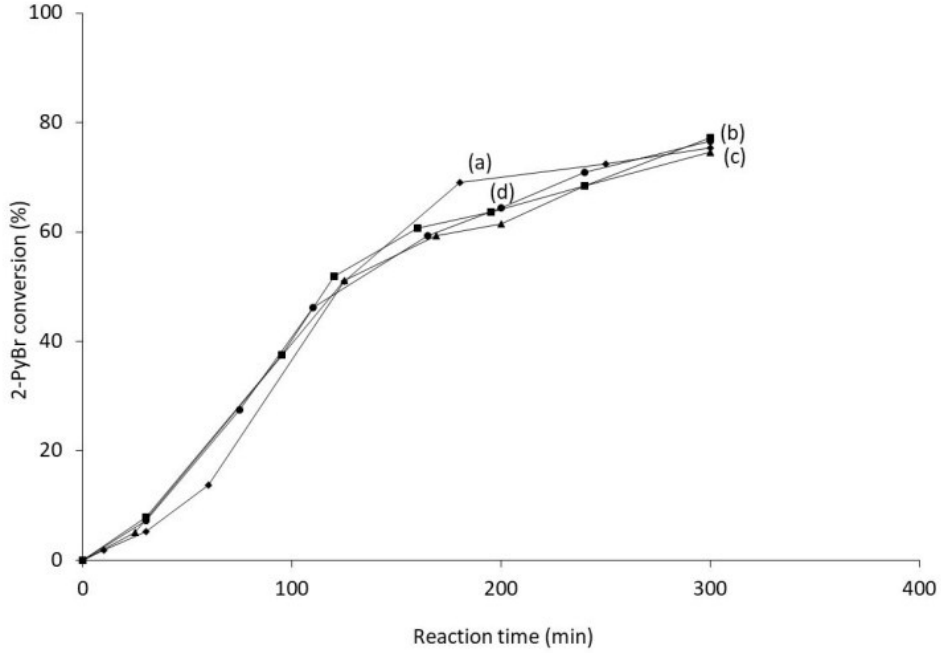

Fig. S10 2-PyBr conversion profiles with reaction time in the Heck coupling of 2-PyBr and styrene at 135 °C over 1 % Pd^{II}/SiO_2: (a)-(d) Heck reaction cycles 1-4.

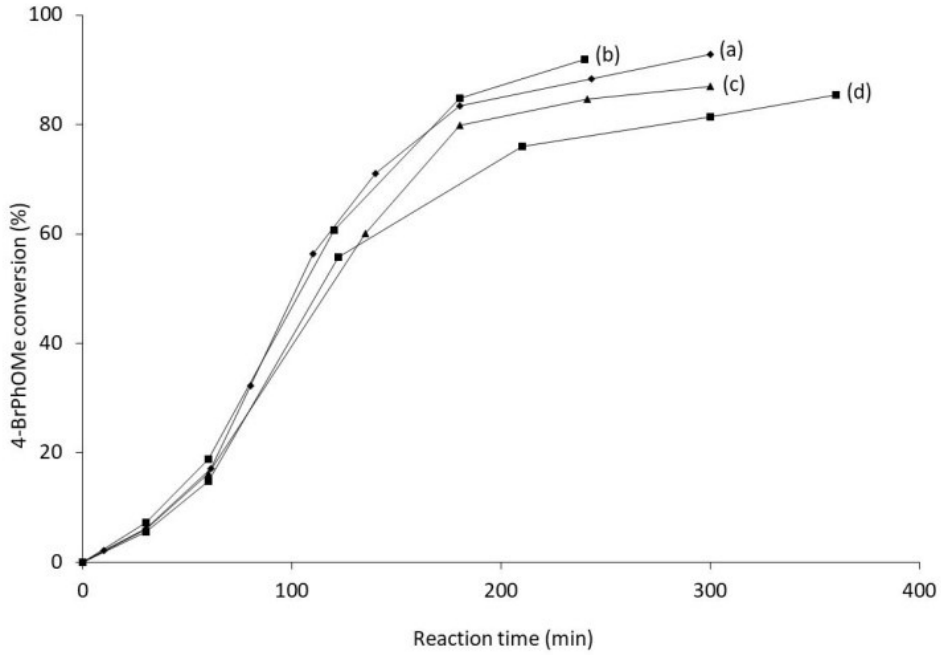

Fig. S11 4-BrPhOMe conversion profiles with reaction time in the Heck coupling of 4-BrPhOMe and styrene at 135 °C over 1 % Pd^{II}/SiO_2: (a)-(d) Heck reaction cycles 1-4.

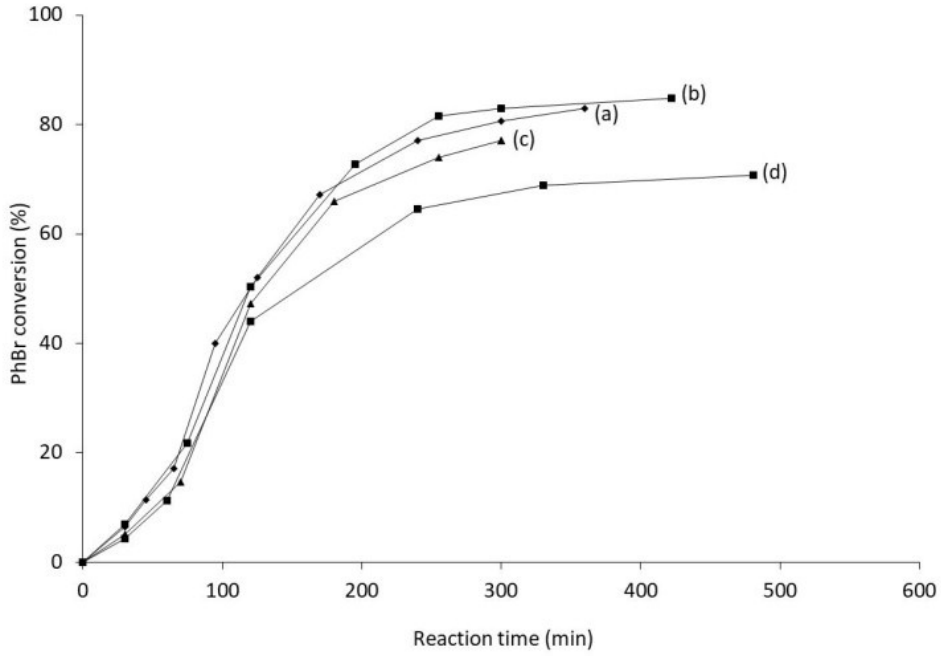

Fig. S12 PhBr conversion profiles with reaction time in the Heck coupling of PhBr and methyl acrylate at 135 °C over 1 % Pd^{II}/SiO_2: (a)-(d) Heck reaction cycles 1-4.

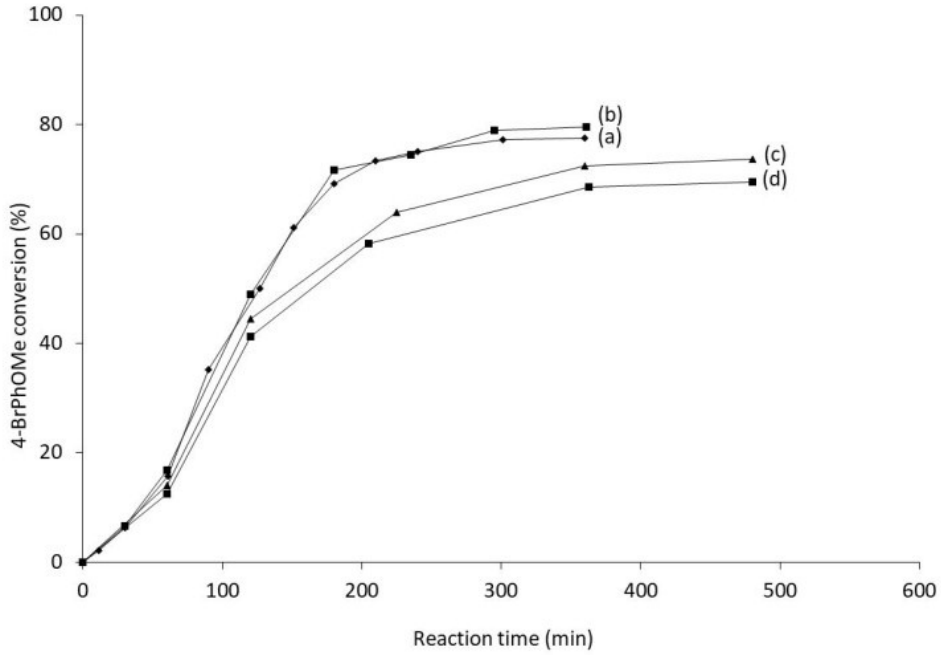

Fig. S13 4-BrPhOMe conversion profiles with reaction time in the Heck coupling of 4-BrPhOMe and methyl acrylate at 135 °C over 1 % Pd^{II}/SiO_2: (a)-(d) Heck reaction cycles 1-4.

Physical properties of supports and precatalysts

Table S3 Physical properties of supports and precatalysts determined from N_2 adsorption-desorption

support or precatalyst	Pd loading (%)	BET surface area ($m^2\ g^{-1}$)	pore volume (ml g^{-1})
SiO_2	–	312	1.0
Pd^0/SiO_2	0.2	309	0.95
Pd^0/SiO_2	1	306	0.94
Pd^0/SiO_2	4	301	0.92
Pd^{II}/SiO_2	0.2	277	0.97
Pd^{II}/SiO_2	1	277	0.96
Pd^{II}/SiO_2	4	274	0.94
Al_2O_3	–	163	0.32
Pd^0/Al_2O_3	1	161	0.27
Pd^{II}/Al_2O_3	1	153	0.25
MgO	–	10.5	0.09
Pd^0/MgO	1	27.5	0.09
Pd^{II}/MgO	1	15.4	0.09
SBA-15	–	684	1.1
Pd^0/SBA-15	1	612	0.95
Pd^{II}/SBA-15	1	534	0.84
TiO_2	–	4.3	0.01
Pd^0/TiO_2	1	5.1	0.01
Pd^{II}/TiO_2	1	4.2	0.01
ZrO_2	–	5.0	0.02
Pd^0/ZrO_2	1	5.6	0.02
Pd^{II}/ZrO_2	1	4.2	0.02