

Supporting Information

Simple, Fast, and Easy Assay for Transition Metal-Catalyzed Coupling Reactions using Paper-Based Colorimetric Iodide Sensor

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S1. Preparation of paper-based colorimetric iodide sensor

Soluble starch (10.0 g) was stirred into boiling water (1.0 L) and dissolved. After cooling, ferric nitrate nonahydrate (4.04 g, 10.0 mmol) was added. Pure filter paper was soaked in the solution and allowed to dry in a clean atmosphere.

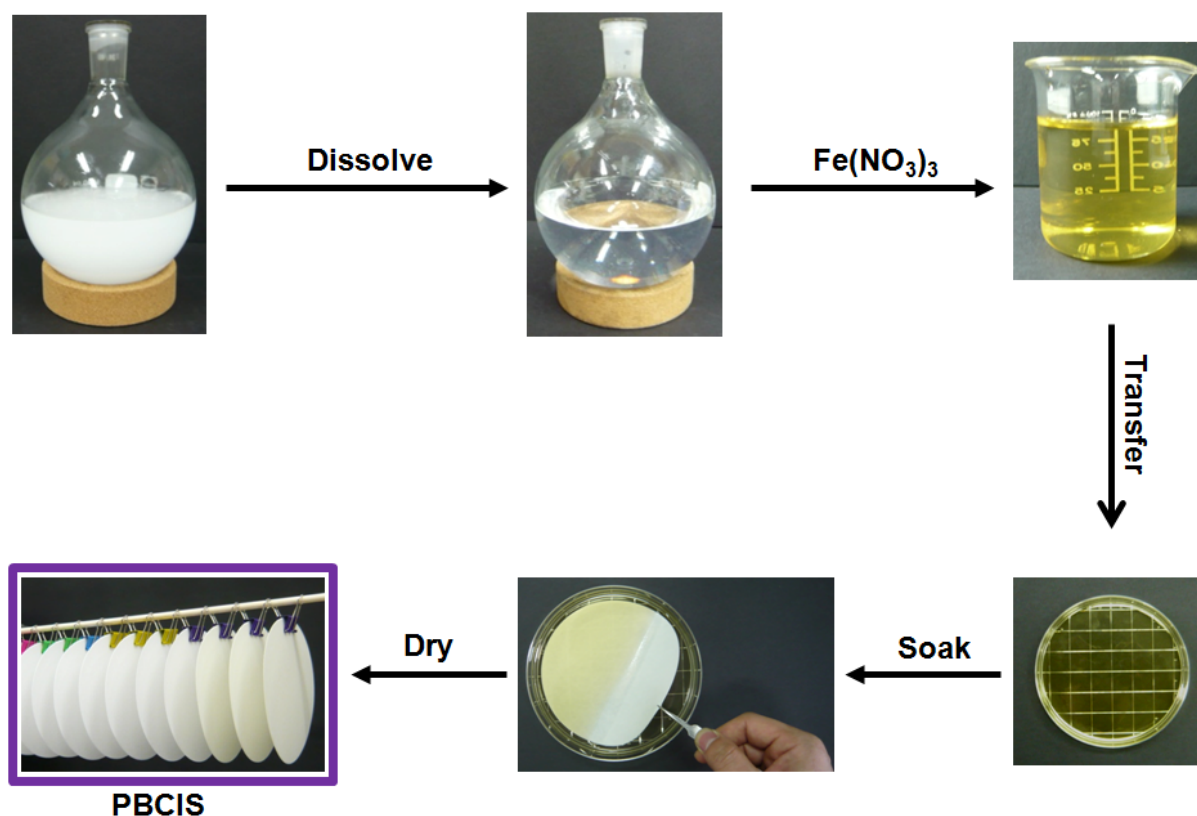


Figure S1. PBCIS preparation procedure

S2. Grayscale intensity measurement

The reaction mixture was dropped onto the prepared PBCIS in 2 μL aliquots. After 10 min, optical images were obtained using an optical flatbed scanner (Epson Perfection V33) with a resolution of 600 dpi (dots per inch). The data was analyzed with an 8-bit grayscale histogram in Photoshop (Adobe Systems Incorporated).

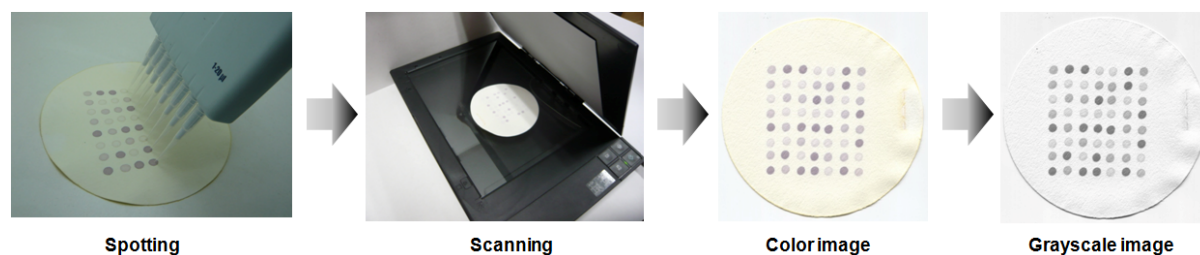


Figure S2. Grayscale intensity measurement

S3. Oxidant screening experiments

Soluble starch (10.0 g) was dissolved in boiling water (1.0 L). After cooling, various oxidants (10.0 mmol) were added. Whatman[®] 3 filter paper was soaked in the solution and allowed to dry in a clean atmosphere.

Table S1.

Oxidant	Description
<i>N</i> -chlorosuccinimide (NCS)	When the sodium iodide solution dropped into the paper, blue-violet spot was appeared immediately. And then the spot was disappeared quickly, was invisible in about 30 seconds.
<i>N</i> -bromosuccinimide (NBS)	When the sodium iodide solution dropped into the paper, blue-violet spot was appeared immediately. And then the spot was disappeared quickly, was invisible in about 10 seconds.
<i>N</i> -iodosuccinimide (NIS)	When the sodium iodide solution dropped into the paper, blue-violet spot was appeared immediately. And then the spot was disappeared quickly, was invisible in about 60 seconds.
Oxone	When the sodium iodide solution dropped into the paper, blue-violet spot was appeared immediately. And then the spot was disappeared quickly, was invisible in about 150 seconds.
Potassium iodate	When the sodium iodide solution dropped into the paper, blue-violet spot was appeared immediately. And then the spot was disappeared quickly, was invisible in about 90 seconds.

Left image is the picture was taken as soon as the sodium iodide was dropped into the paper.
Right image is the picture was taken about 150 seconds after the sodium iodide was dropped into the paper.

Ex) Oxone

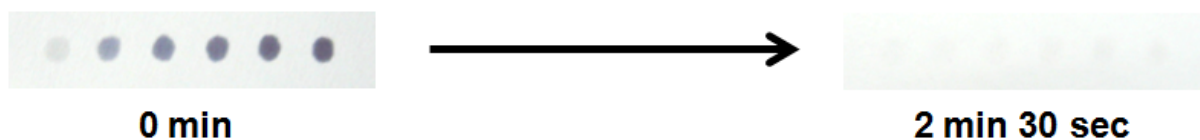


Figure S3-1. Color changes of PBCIS bearing oxone as oxidant

From Figure S3-2 to Figure S3-10. a, Grayscale intensities (8-bit) of PBCIS recorded 10 min and 30 hr after the addition of I^- ion versus iodide concentration. **b,** The grayscale image of PBCIS after 10 min. **c,** The grayscale image of PBCIS after 30 hr, from left to right: control, 1 mM NaI, 2 mM NaI, 3 mM NaI, 4 mM NaI, 5 mM NaI included 0.1 N HCl.

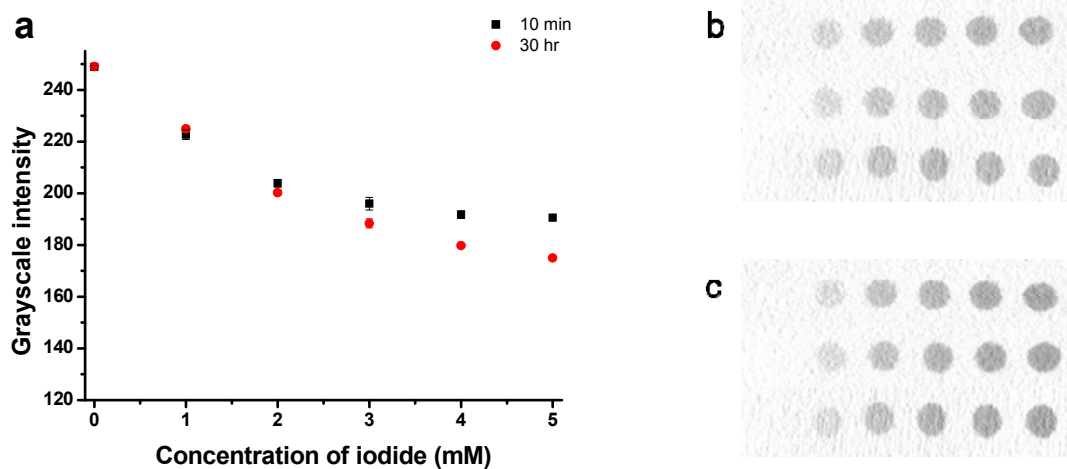


Figure S3-2. Cerium ammonium nitrate (CAN)

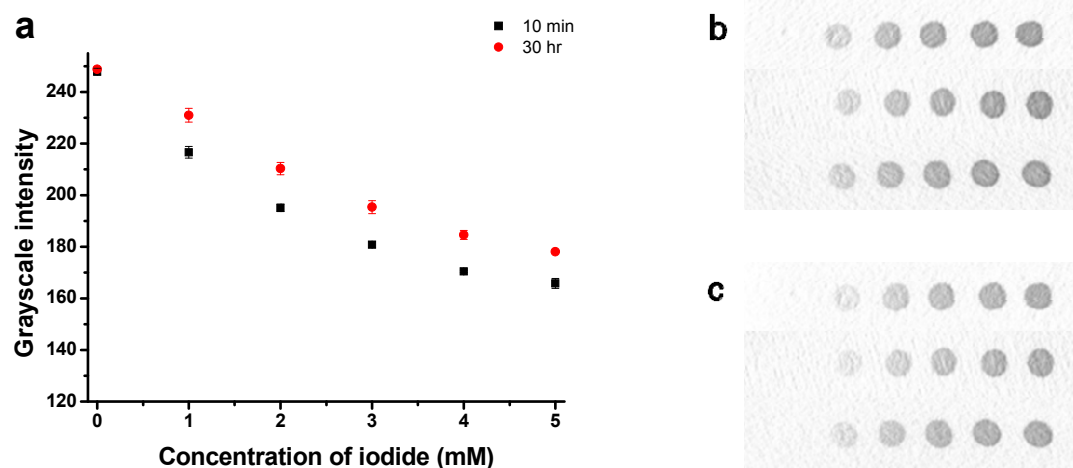


Figure S3-3. Urea hydrogen peroxide (UHP)

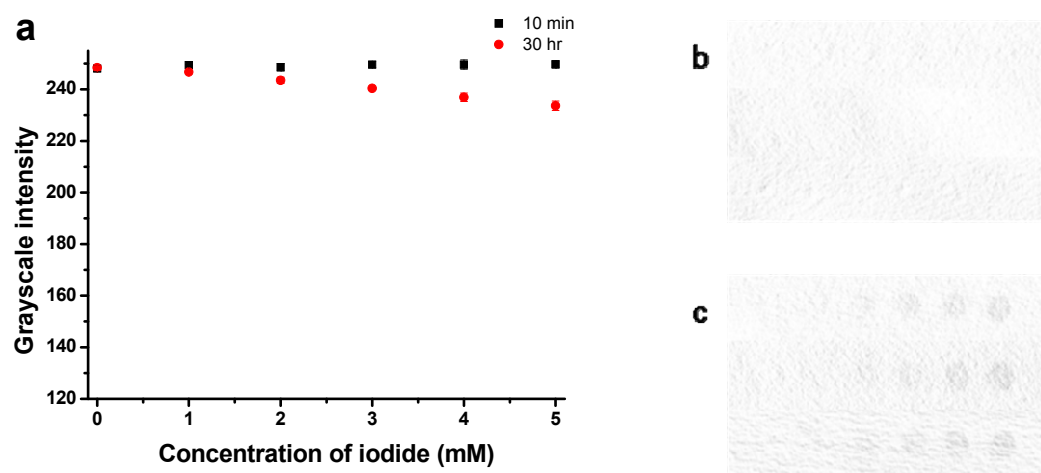


Figure S3-4. *tert*-butyl hydroperoxide

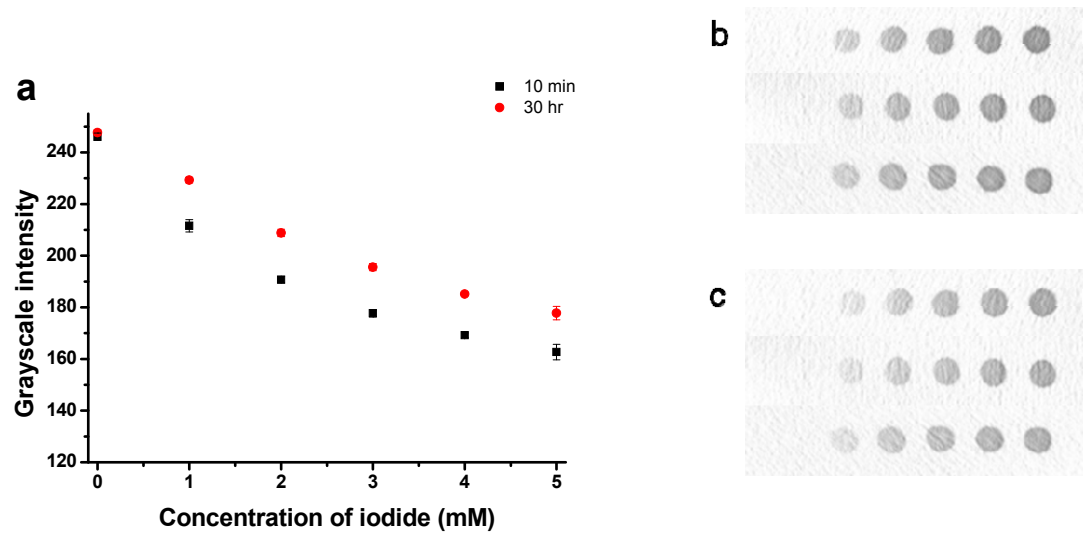


Figure S3-5. Hydrogen peroxide

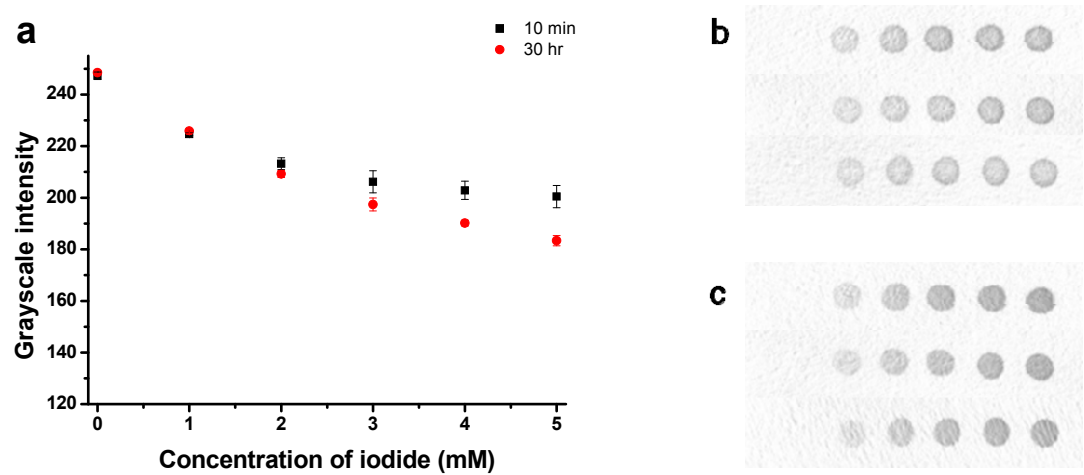


Figure S3-6. Peracetic acid

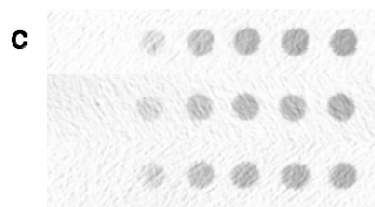
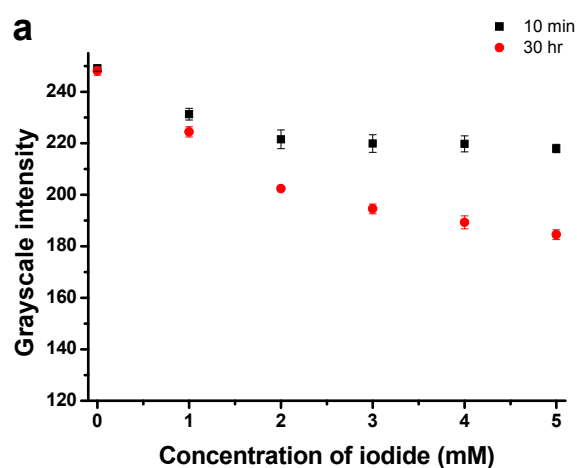


Figure S3-7. Sodium hypochlorite

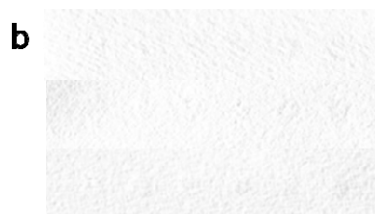
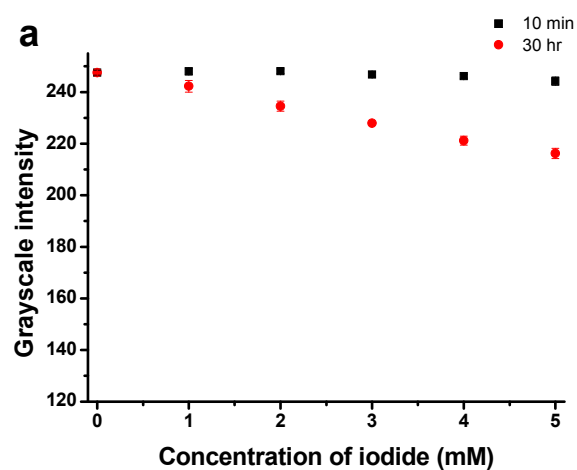


Figure S3-8. Formic acid

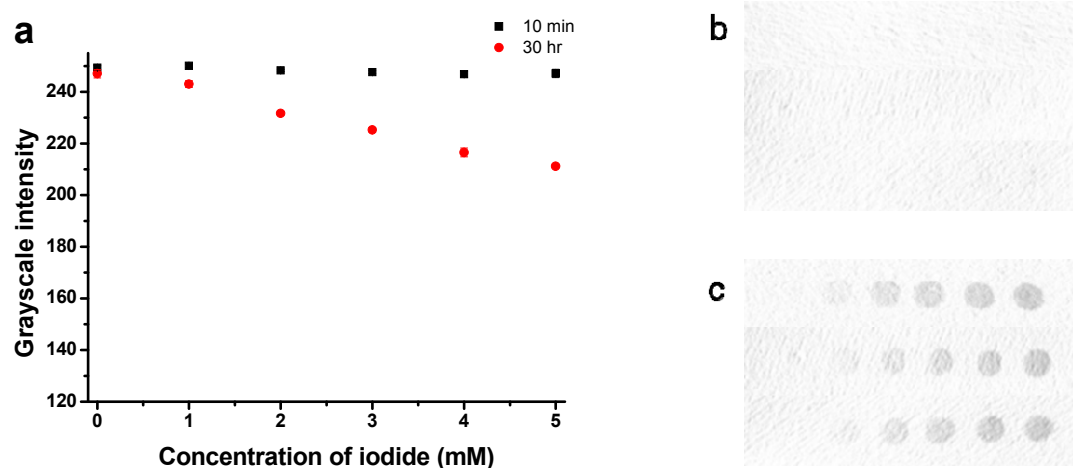


Figure S3-9. Nitric acid

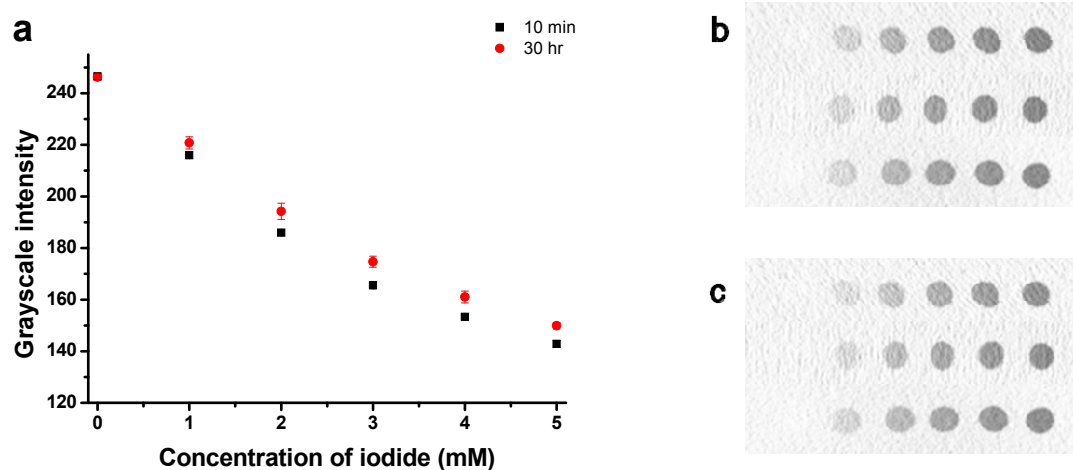


Figure S3-10. Ferric nitrate

S4. Starch equivalent screening experiments

Soluble starch (1.0 g, 10.0 g, 50.0 g) were dissolved in boiling water (1.0 L). After cooling, ferric nitrate nonahydrate (4.04 g, 10.0 mmol) were added, and Whatman[®] 3 filter paper was soaked in it and allowed to dry in a clean atmosphere.

Figure S4. **a**, Grayscale intensities (8-bit) of PBCIS recorded 10 min and 30 hr after the addition of I^- ion versus iodide concentration. **b**, The grayscale image of PBCIS after 10 min. **c**, The grayscale image of PBCIS after 30 hr, from left to right: control, 1 mM NaI, 2 mM NaI, 3 mM NaI, 4 mM NaI, 5 mM NaI included 0.1 N HCl.

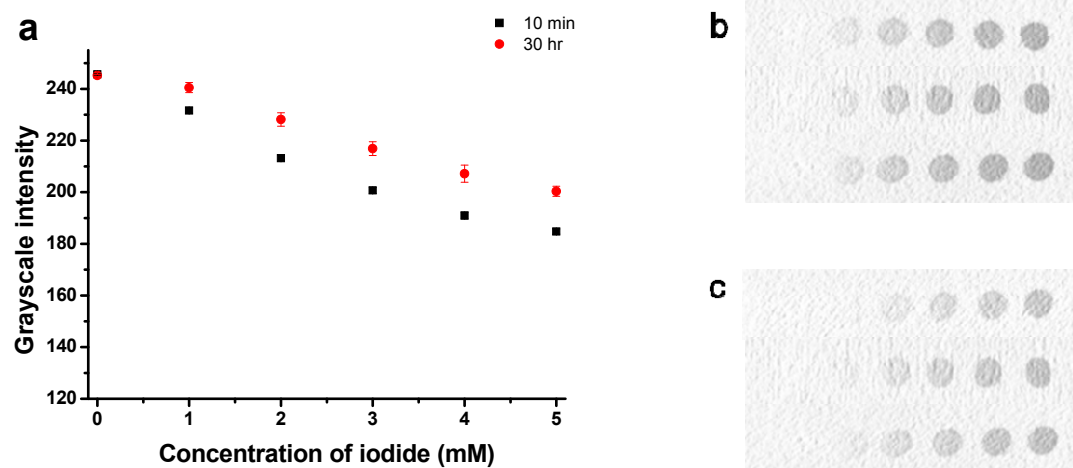


Figure S4-1. Starch 1.0 g/L

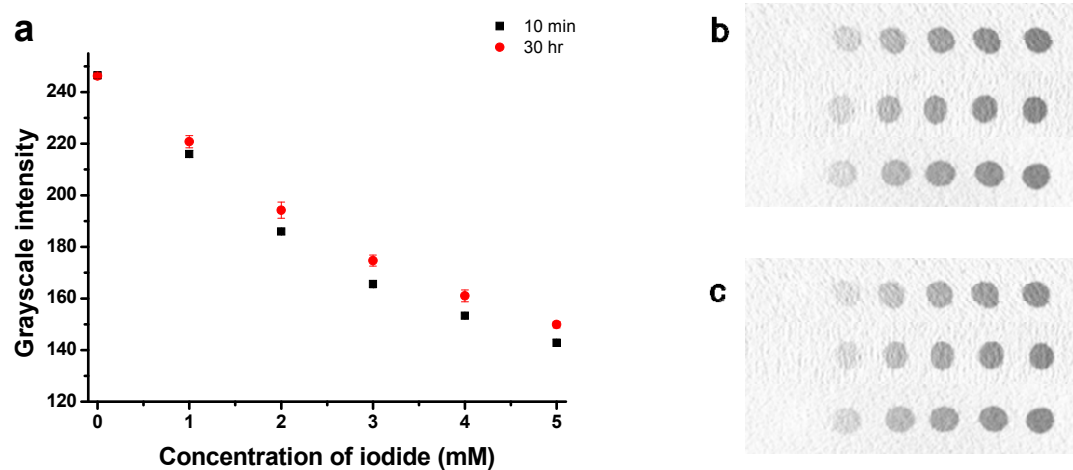


Figure S4-2. Starch 10.0 g/L

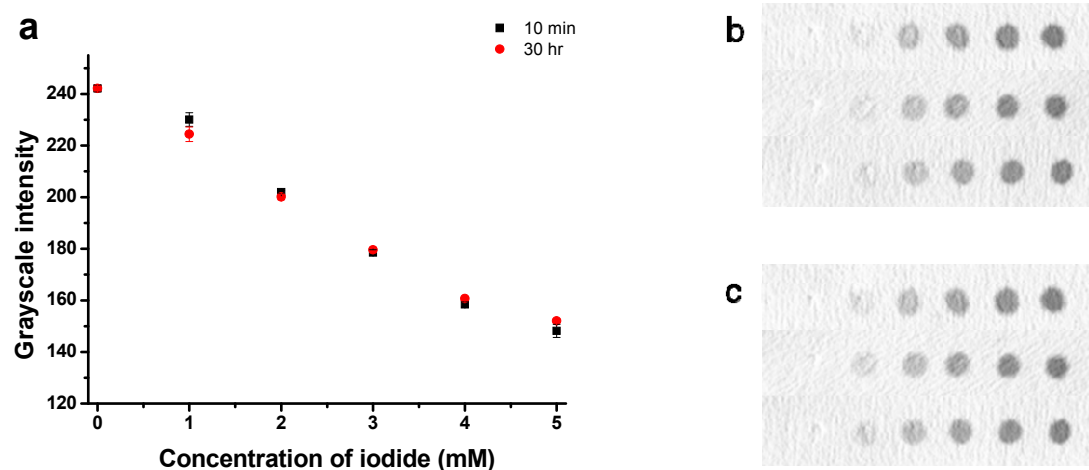


Figure S4-3. Starch 50.0 g/L

S5. Filter paper screening experiments

Soluble starch (10.0 g) was dissolved in boiling water (1.0 L). After cooling, ferric nitrate nonahydrate (4.04 g, 10.0 mmol) was added, and various filter papers were soaked in it and allowed to dry in a clean atmosphere. **Figure S5. a**, Grayscale intensities (8-bit) of PBCIS recorded 10 min and 30 hr after the addition of I^- ion versus iodide concentration. **b**, The grayscale image of PBCIS after 10 min. **c**, The grayscale image of PBCIS after 30 hr, from left to right: control, 1 mM NaI, 2 mM NaI, 3 mM NaI, 4 mM NaI, 5 mM NaI included 0.1 N HCl.

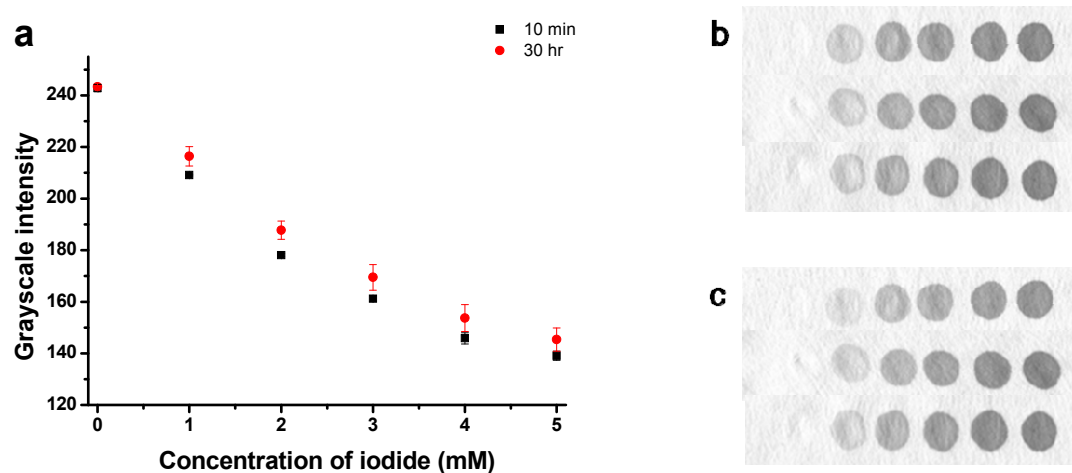


Figure S5-1. Whatman[®] qualitative filter paper, Grade 1

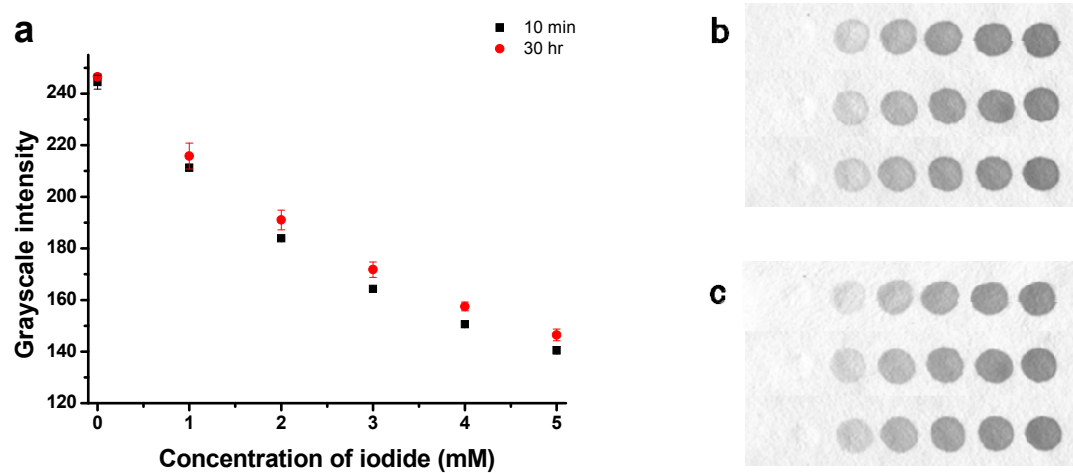


Figure S5-2. Whatman[®] qualitative filter paper, Grade 2

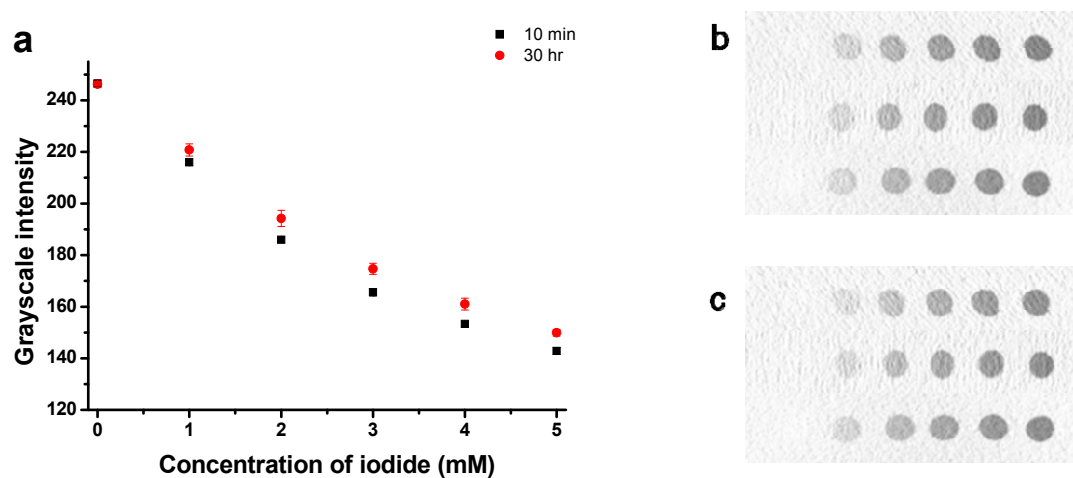


Figure S5-3. Whatman[®] qualitative filter paper, Grade 3

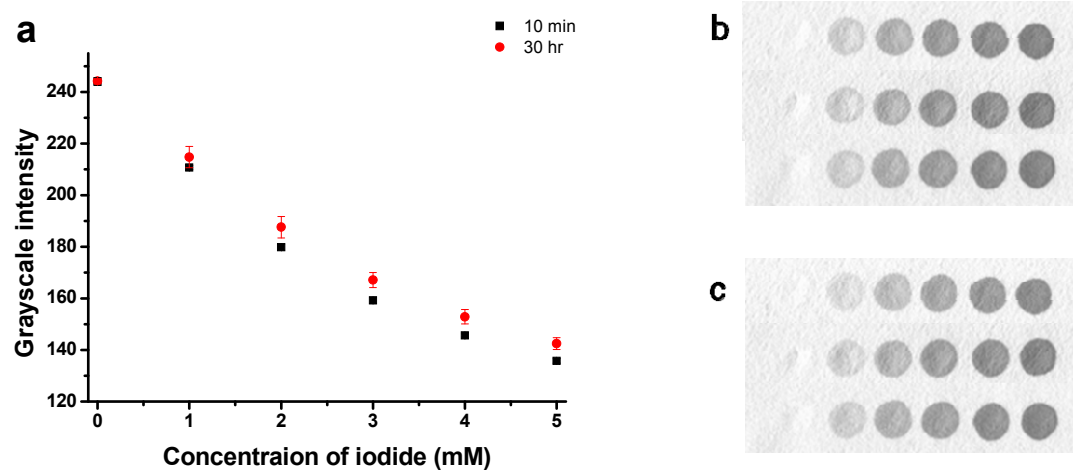


Figure S5-4. Whatman[®] qualitative filter paper, Grade 4

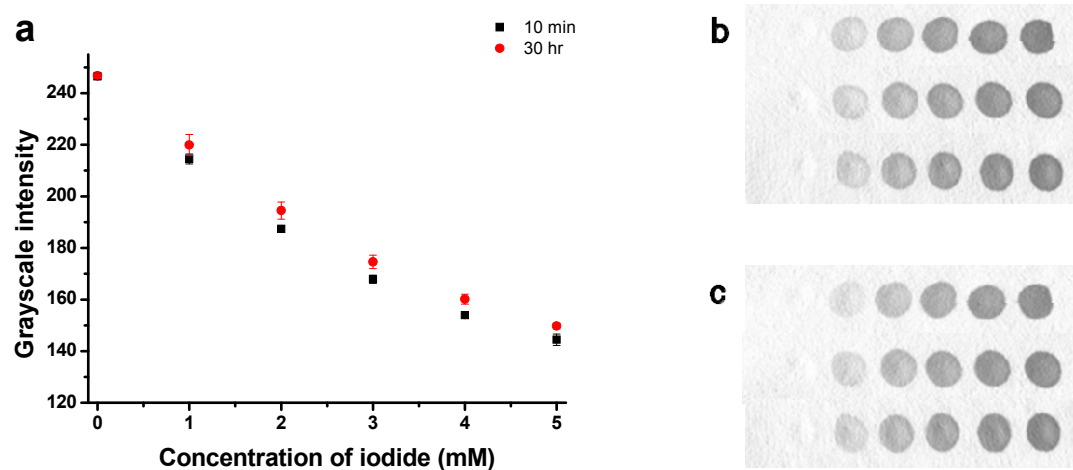


Figure S5-5. Whatman[®] qualitative filter paper, Grade 5

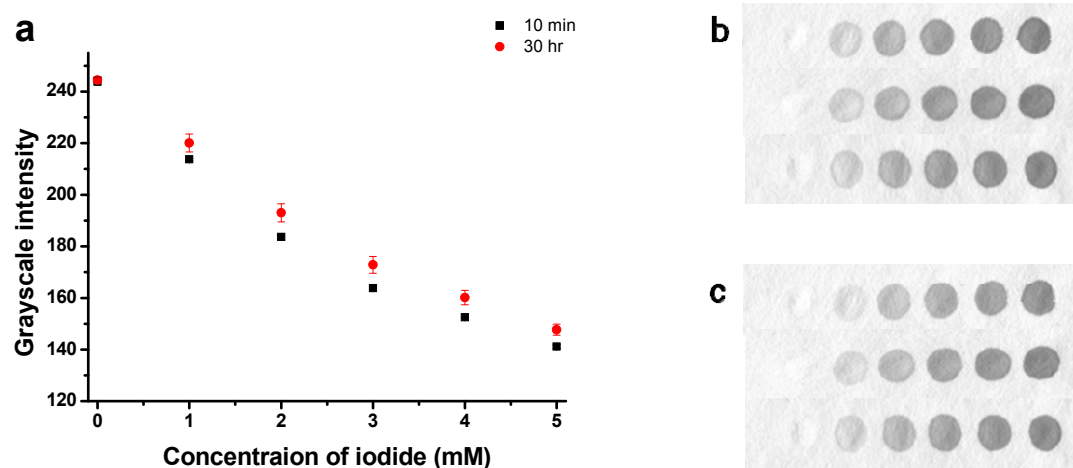


Figure S5-6. Whatman[®] qualitative filter paper, Grade 6

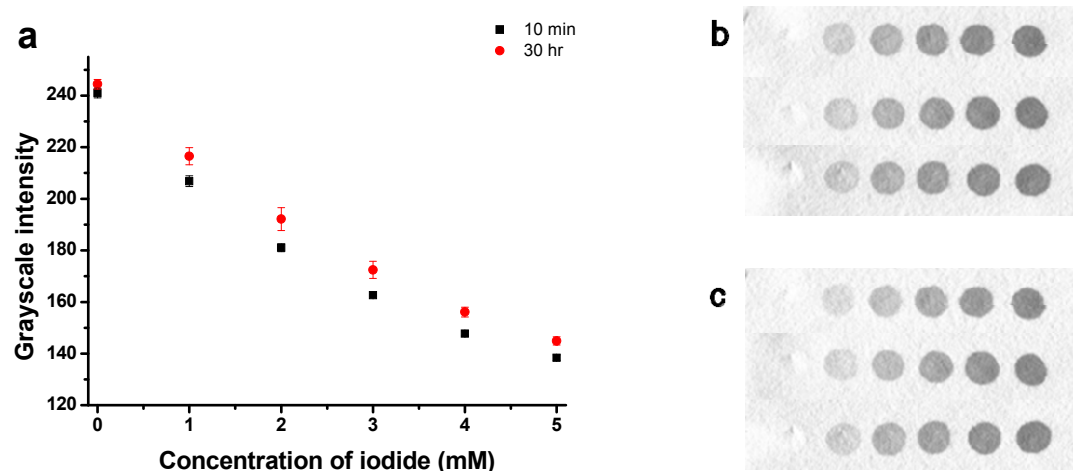


Figure S5-7. Advantec[®] qualitative filter paper, Grade 2

S6. Controlled experiments

Preparation of PBCIS excluding starch (Figure S6-1): Ferric nitrate nonahydrate (4.04 g, 10.0 mmol) was dissolved in water, and Whatman[®] 3 filter paper was soaked in it and allowed to dry in a clean atmosphere.

Preparation of PBCIS excluding ferric nitrate (Figure S6-2): Soluble starch (10.0 g) was dissolved in boiling water (1.0 L). After cooling, Whatman[®] 3 filter paper was soaked in it and allowed to dry in a clean atmosphere.

Figure S6. **a**, Grayscale intensities (8-bit) of PBCIS recorded 10 min and 30 hr after the addition of I^- ion versus iodide concentration. **b**, The grayscale image of PBCIS after 10 min. **c**, The grayscale image of PBCIS after 30 hr, from left to right: control, 1 mM NaI, 2 mM NaI, 3 mM NaI, 4 mM NaI, 5 mM NaI included 0.1 N HCl.

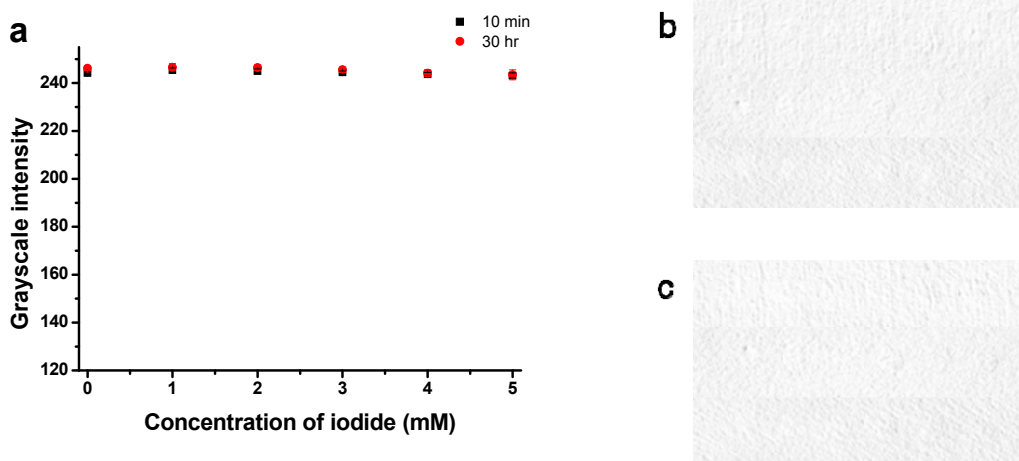


Figure S6-1. Ferric nitrate (10 mM) only (excluded starch)

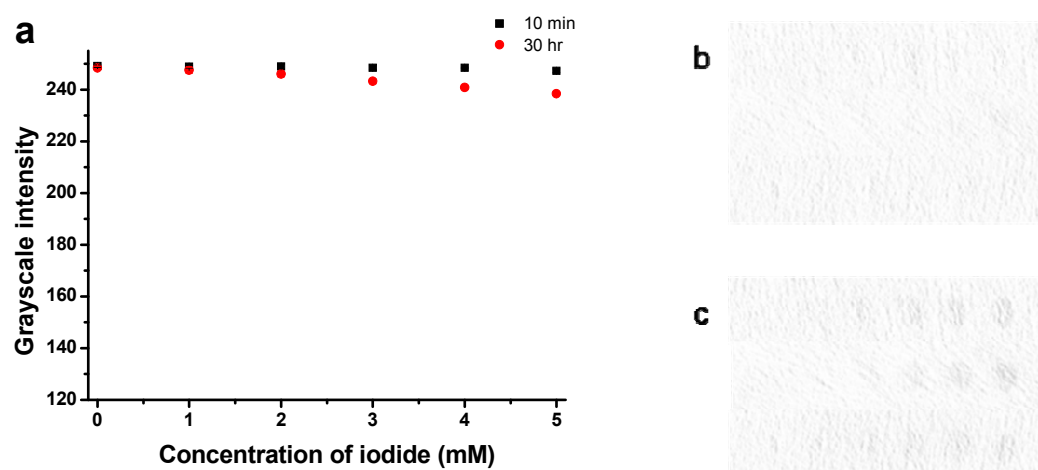


Figure S6-2. Starch (10.0 g/L) only (excluded ferric nitrate)

S7. PBCIS's reproducibility for detecting various concentration of iodide in 16 day

0.50 mL of sodium iodide solutions (0 mM, 4 mM, 10 mM) was diluted to a 1.0 mL solution by adding 0.2 N HCl (aq) respectively. 2 μ L amount of these samples were dropped into the PBCIS at different days.

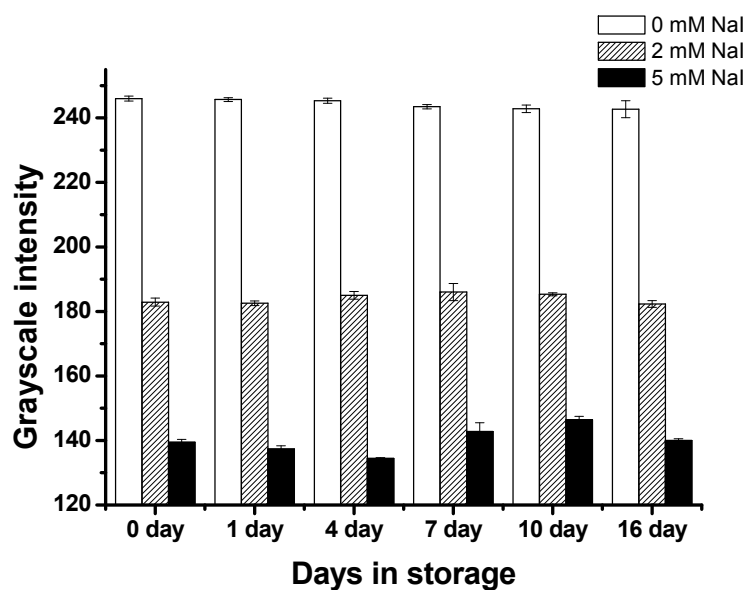


Figure S7. Storage stability of the PBCIS at room temperature

S8. Grayscale intensity obtained by dropping various anions (5 mM)

0.50 mL of the various anions (10 mM) was diluted to a 1.0 mL solution by adding 0.2 N HCl (aq). 2 μ L amount of these samples were dropped into the PBCIS.

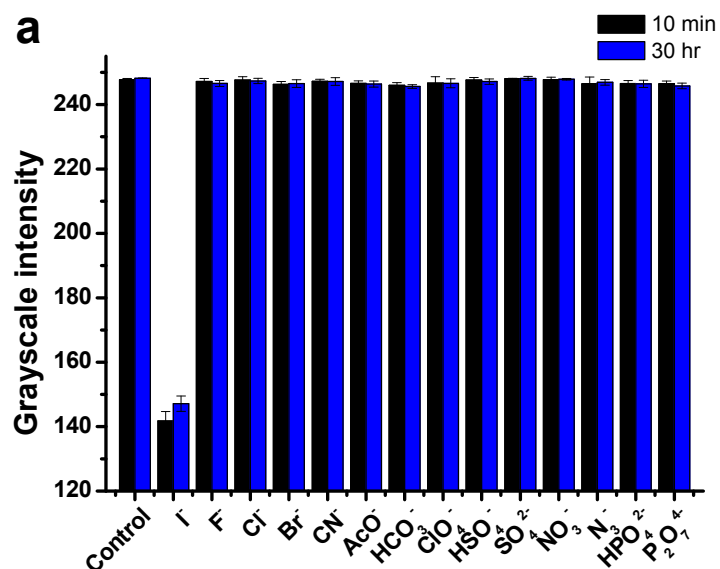




Figure S8. **a**, Plot of the grayscale intensities of the PBCIS versus various anions. **b**, The grayscale image of PBCIS after 10 min. **c**, The grayscale image of PBCIS after 30 hr, from left to right: control, I^- , F^- , Cl^- , Br^- , CN^- , AcO^- , HCO_3^- , ClO_4^- , HSO_4^- , SO_4^{2-} , NO_3^- , N_3^- , HPO_4^{2-} , $P_2O_7^{4-}$.

S9. Preparation of sample solutions of reaction mixtures for Paper test

All reactions tested were carried out with 0.3 mmol of aryl iodides in 1 mL solvent. After completing the reactions, the appropriate amount of thrice distilled water was added to the reaction mixture to make up 10 mM solution. 0.5 mL of the resulting solution was diluted to a 1.0 mL solution by adding 0.2 N HCl (aq). 2 μ L amount of the samples were dropped into the PBCIS.

Conversion (PBCIS) % = (gray scale intensity – 245.88) / (-1.0967)

Conversion (GC) % = gas chromatography with an internal standard (naphthalene)

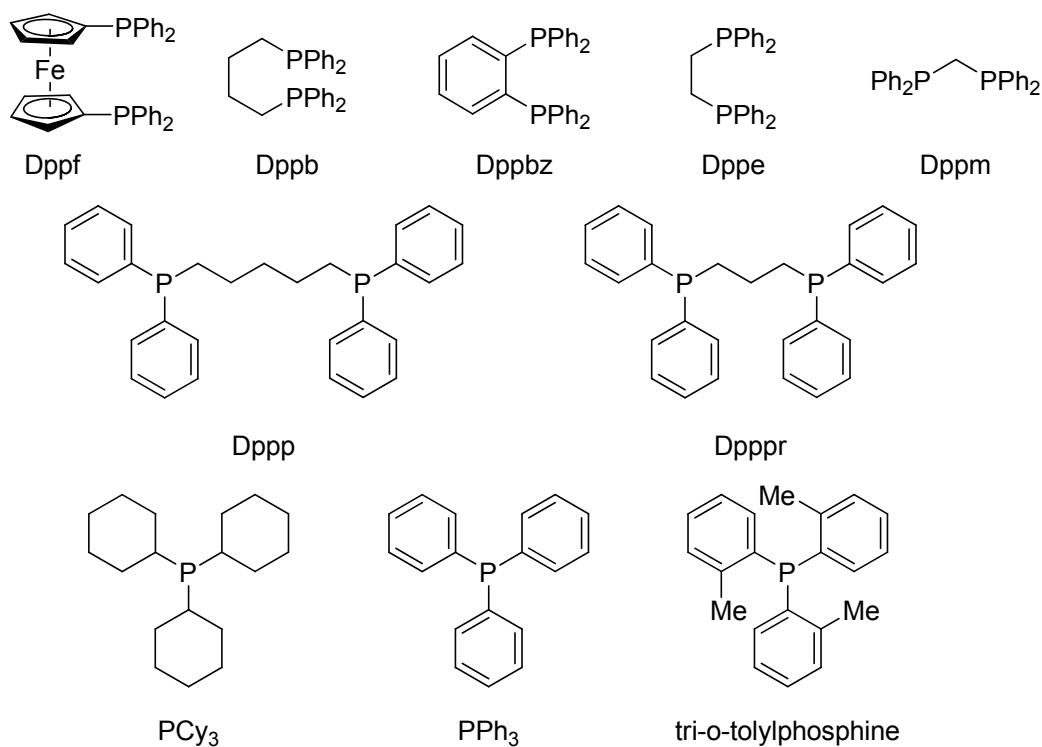
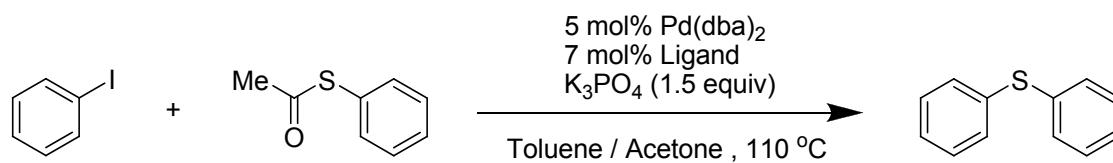
Yield (GC) % = gas chromatography with an internal standard (naphthalene)

Deviation = Conversion (PBCIS) % - Conversion (GC) %

S10. General procedure of the C-S bond formations¹

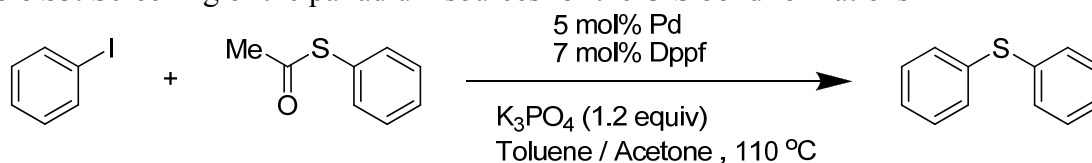
Pd (1.5×10^{-2} mmol) and ligand (2.1×10^{-2} mmol) were dissolved in 0.7 mL of toluene and 0.3 mL of acetone followed by the addition of aryl iodide (0.30 mmol), phenyl thioacetate (54.80 mg, 0.36 mmol) and K_3PO_4 (95.50 mg, 0.45 mmol). The mixture was heated to 110 °C and stirred for 12 h.

Table S2. Screening of the ligands for the C-S bond formations



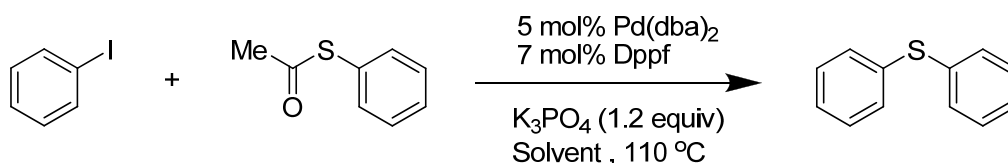
Entry	Ligand	Grayscale intensity	Conversion (PBCIS) %	Conversion (GC) %	Yield (GC) %	Deviation
A2	Dppf	133.78	100	100	97	0
B2	Dppb	146.99	90	91	91	-1
C2	Dppbz	155.38	83	85	81	-2
D2	Dppe	179.00	61	64	55	-3
E2	Dppm	179.84	60	60	57	0
F2	Dppp	173.53	66	71	69	-5
G2	Dpppr	184.34	56	61	56	-5
H2	PCy ₃	231.89	13	21	12	-8
G1	PPh ₃	183.28	57	62	54	-5
H1	Tri- <i>o</i> -tolylphosphine	244.01	2	9	8	-7

Table S3. Screening of the palladium sources for the C-S bond formations



Entry	Pd	Grayscale intensity	Conversion (PBCIS) %	Conversion (GC) %	Yield (GC) %	Deviation
A3	$Pd(dba)_2$	143.01	94	93	87	+1
B3	$Pd(OAc)_2$	194.91	46	42	41	+4
C3	$Pd(CH_3CN)_2Cl_2$	185.58	55	56	49	-1
D3	$Pd(acac)_2$	175.35	64	62	58	+2
E3	$Pd(PPh_3)_4$	154.48	83	78	71	+5
F3	$PdCl_2$	188.16	53	48	40	+5
G3	$[Pd(\eta-C_3H_5)Cl]_2$	164.50	74	66	60	+8
H3	Pd/C	211.57	31	32	29	-1

Table S4. Screening of the solvents for the C-S bond formations



Entry	Solvent	Grayscale intensity	Conversion (PBCIS) %	Conversion (GC) %	Yield (GC) %	Deviation
A4	Toluene ^a	134.88	100	100	97	0
B4	Toluene	154.35	83	78	74	+5
C4	Diglyme	143.26	94	96	90	-2
D4	DMAc	142.60	94	96	89	-2
E4	NMP	141.30	95	94	92	+1
F4	DMF	132.23	100	100	100	0
G4	DMSO	228.41	16	27	27	-11
H4	<i>p</i> -Xylene	179.24	61	55	47	+6

^a0.3 mL of acetone was added.

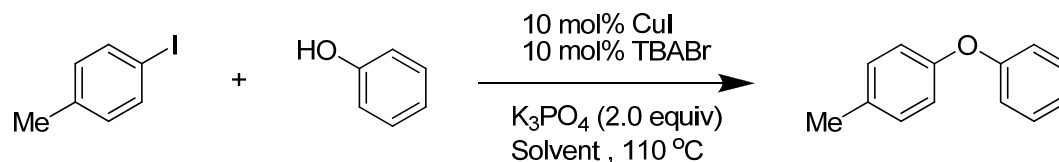
Table S5. Screening of the aryl iodides for the C-S bond formations

Entry	Ar-I	Grayscale intensity	Conversion (PBCIS) %	Conversion (GC) %	Yield (GC) %	Deviation
A5		233.65	11	12	11	-1
B5		239.17	6	3	3	+3
C5		175.67	64	62	58	+2
D5		181.61	59	56	55	+3
E5		151.48	86	93	93	-7
F5		193.01	48	46	40	+2
G5		149.02	88	95	91	-7
H5		230.69	14	18	17	-4

S11. General procedure of the C-O bond formations²

CuI (5.70 mg, 3.0×10^{-2} mmol) and tetra-*n*-butylammonium bromide (TBABr) (9.70 mg, 3.0×10^{-2} mmol) were dissolved in 1 mL of solvent followed by the addition of 4-iodotoluene (65.40 mg, 0.30 mmol), phenol (33.90 mg, 0.36 mmol) and K₃PO₄ (127.40 mg, 0.60 mmol). The mixture was heated to 110 °C and stirred for 24 h.

Table S6. Screening of the solvents for the C-O bond formations



Entry	Solvent	Grayscale intensity	Conversion (PBCIS) %	Conversion (GC) %	Yield (GC) %	Deviation
A6	Toluene	241.09	4	0	0	+4
B6	Diglyme	215.30	28	27	23	+1
C6	DMAc	202.69	39	37	37	+2
D6	DMF	200.53	41	45	42	-4
E6	DMSO	178.79	61	64	61	-3
F6	DMAc ^a	182.98	57	57	49	0
G6	DMF ^a	187.02	54	58	47	-4
H6	DMSO ^a	157.66	80	94	92	-14

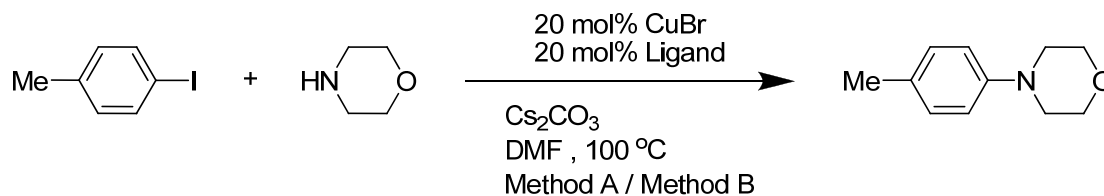
^a The mixture was heated to 140 °C and stirred.

S12. General procedure of the C-N bond formations³

Method A : CuBr (8.60 mg, 6.0×10^{-2} mmol) and ligand (6.00×10^{-2} mmol) were dissolved in 1 mL of dimethylformamide (DMF) followed by the addition of 4-iodotoluene (65.40 mg, 0.30 mmol), morpholine (52.30 mg, 0.60 mmol) and Cs_2CO_3 (293.20 mg, 0.90 mmol). The mixture was heated to 100 °C and stirred for 8 h.

Method B : CuBr (8.60 mg, 6.0×10^{-2} mmol) and ligand (6.00×10^{-2} mmol) were dissolved in 1 mL of dimethylformamide (DMF) followed by the addition of 4-iodotoluene (65.40 mg, 0.30 mmol), morpholine (104.50 mg, 1.20 mmol) and Cs_2CO_3 (391.00 mg, 1.20 mmol). The mixture was heated to 100 °C and stirred for 6 h.

Table S7. Screening of the ligands for the C-N bond formations



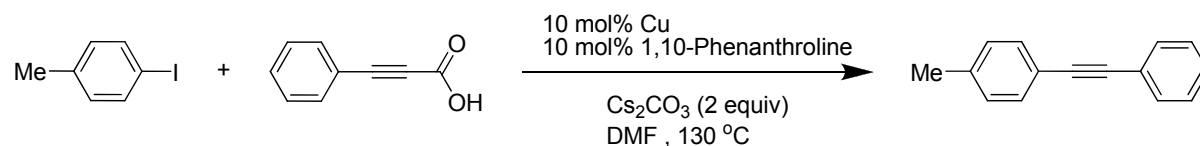
Entry	Ligand	Method	Grayscale intensity	Conv. (PBCIS) %	Conv. (GC) %	Yield (GC) %	Deviation
A7	DL-proline	A	248.23	0(-2) ^a	7	0	-7
B7	2,2'-Bipyridine	A	246.62	0(-1) ^a	1	0	-1
C7	TMEDA	A	243.48	+2	5	1	-3
D7	DMEDA	A	242.88	+3	1	0	+2
E7	1,10-Phenanthroline	A	245.62	0	2	0	-2
F7	Acetylacetone	B	160.99	77	64	57	+13
G7	2,2,6,6-Tetramethylheptane-3,5-dione	B	157.27	81	83	79	-2
H7	2-Acetylcyclohexanone	B	150.8	87	85	84	+2

^a The minus values were obtained from the equation, which means no conversion.

S13. General procedure of the Decarboxylative coupling reactions⁴

Cu (3.00×10^{-2} mmol) and 1,10-phenanthroline (5.40 mg, 3.0×10^{-2} mmol) were dissolved in 1.0 mL of solvent followed by the addition of 4-iodotoluene (65.40 mg, 0.30 mmol), phenylpropionic acid (65.80 mg, 0.45 mmol) and Cs_2CO_3 (195.50 mg, 0.60 mmol). The mixture was heated to 140 °C and stirred for 24 h.

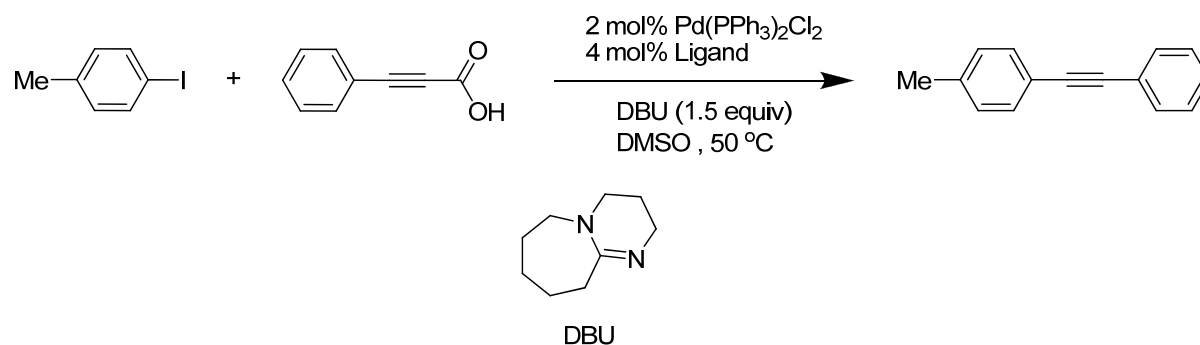
Table S8. Screening of the copper sources for the Decarboxylative coupling reactions



Entry	Cu	Grayscale intensity	Conversion (PBCIS) %	Conversion (GC) %	Yield (GC) %	Deviation
A8	Cu powder	241.69	4	0	0	4
B8	CuBr_2	247.87	0(-2) ^a	6	5	-6
C8	Cu_2Se	240.3	5	12	10	-7
D8	CuCl	211.4	31	31	30	0
E8	Cu_2O	182.8	58	51	51	7
F8	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	166.85	72	71	71	1
G8	CuI	157.48	81	86	85	-5
H8	$\text{Cu}(\text{acac})_2$	138.19	98	100	98	-2

^aThe minus values were obtained from the equation, which means no conversion.

Table S9. Screening of the Ligands for the Decarboxylative coupling reactions

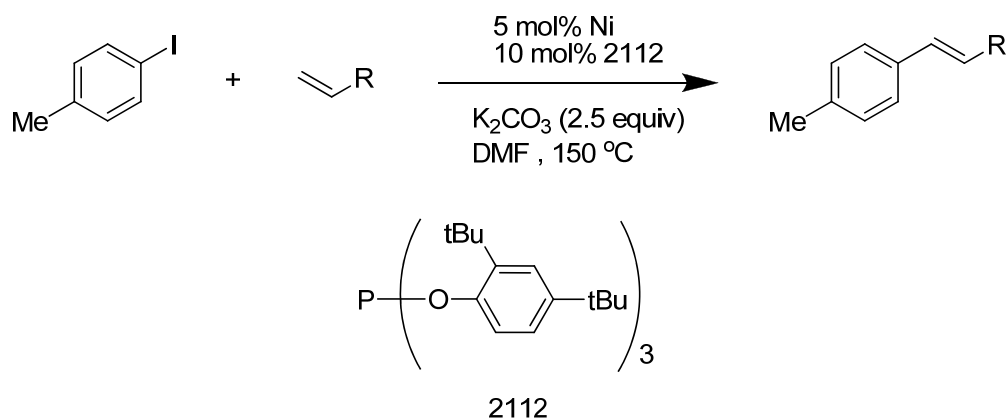


Entry	Ligand	Grayscale intensity	Conversion (PBCIS) %	Conversion (GC) %	Yield (GC) %	Deviation
A9	Dppf	160.22	78	85	84	-7
B9	Dppb	189.27	52	84	80	-32
C9	Dppe	189.74	51	58	57	-7
D9	Dppm	179.22	61	62	62	-1
E9	Dppp	182.73	58	63	59	-5
F9	Xantphos	164.16	75	80	76	-5
G9	PCy_3	189.54	51	58	55	-7
H9	PPh_3	184.44	56	62	57	-6

S14. General procedure of the Heck reactions⁵

Nickel complex (1.50×10^{-2} mmol) and ligand (3.00×10^{-2} mmol) were dissolved in 1.0 mL of dimethylformamide (DMF) followed by the addition of 4-iodotoluene (65.40 mg, 0.30 mmol), alkene (0.60 mmol) and Base (0.75 mmol). The mixture was heated to 150 °C and stirred for 24 h.

Table S10. Screening of the nickel sources for the Heck reactions



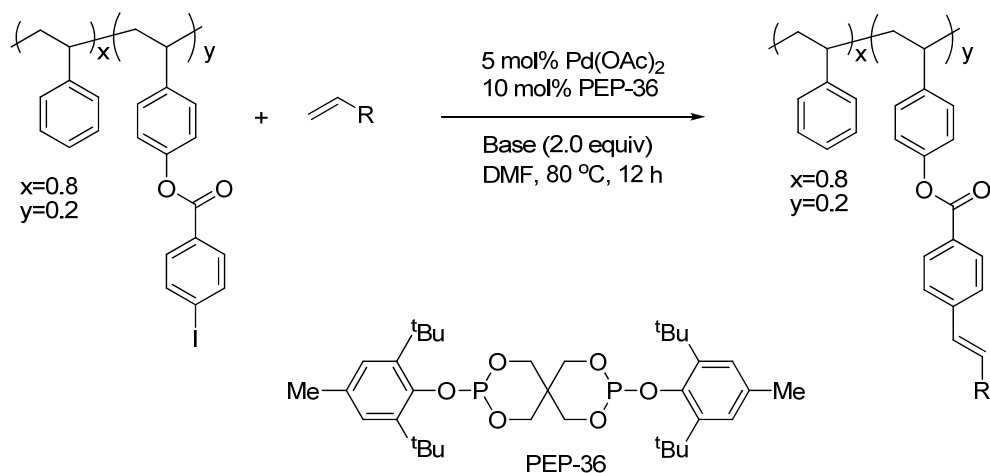
Entry	Ni	R	Grayscale intensity	Conversion (PBCIS) %	Conversion (GC) %	Yield (GC) %	Deviation
A10	Ni(OAc) ₂ ·4H ₂ O	CO ₂ ⁿ Bu	141.87	95	97	97	-2
B10	NiCl ₂	CO ₂ ⁿ Bu	134.58	100	97	90	+3
C10	Ni(acac) ₂	CO ₂ ⁿ Bu	147.21	90	98	96	-8
D10	Ni(COD) ₂	CO ₂ ⁿ Bu	149.49	88	97	96	-9
E10	Ni(OAc) ₂ ·4H ₂ O	Ph	243.59	2	7	6	-5
F10	NiCl ₂	Ph	176.86	63	66	65	-3
G10	Ni(acac) ₂	Ph	158.09	80	87	87	-7
H10	Ni(COD) ₂	Ph	242.43	3	7	6	-4

Table S11. Screening of the bases for the Heck reactions

Entry	Base	Grayscale intensity	Conversion (PBCIS) %	Conversion (GC) %	Yield (GC) %	Deviation
A11	K ₂ CO ₃	151.62	86	98	98	-12
B11	NaOAc	178.00	62	54	54	+8
C11	Et ₃ N	141.16	95	97	93	-2
D11	Pyridine	245.92	0	0	0	0
E11	DBU	244.29	1	3	0	-2
F11	DABCO	201.46	41	45	40	-4
G11	CsF	157.18	81	98	92	-17
H11	KF	181.35	59	68	68	-9

S15-1. General Procedure for the coupling reaction of polymer-supported aryl iodide and alkenes⁶

Polymer- Polymer supported aryl iodide was prepared by the previously reported procedure. Polymer-supported aryl iodide (2.30 g = aryl iodide : 3.00 mmol) was reacted with alkene (3.60 mmol) in the presence of Pd(OAc)₂ (33.67 mg, 0.15 mmol), PEP-36 (189.83 mg, 0.30 mmol) and base (6.00 mmol) in DMF at 70 °C for 12 h.



S15-2. Cleavage of polymer⁷

To polymer supported Heck product in THF was added NaO^tBu (30 mmol, 30 mL of 1.0 M in THF). After stirring 5 h at 25 °C, the reaction mixture was filtered, and the filtrate was quenched with excess of methanol and filtered. The filtrate was purified by flash chromatography (SiO₂, 10 % EtOAc in Hexane).

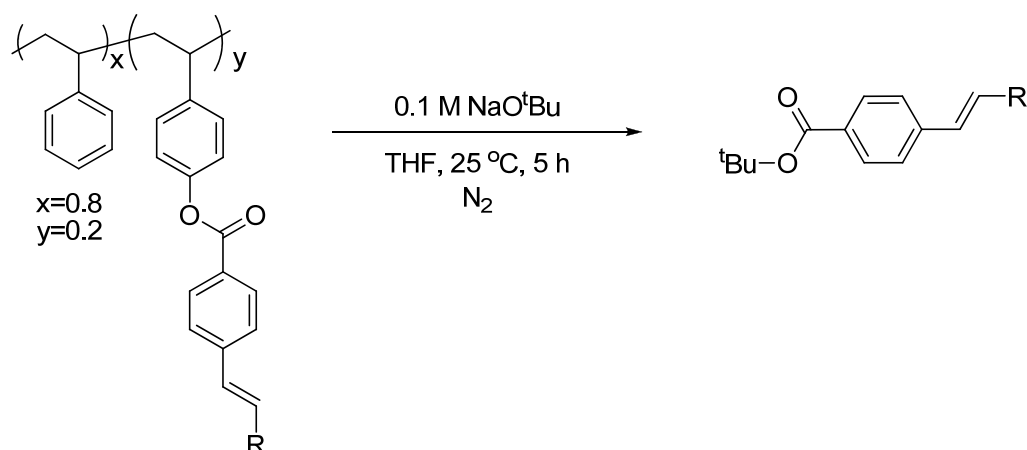
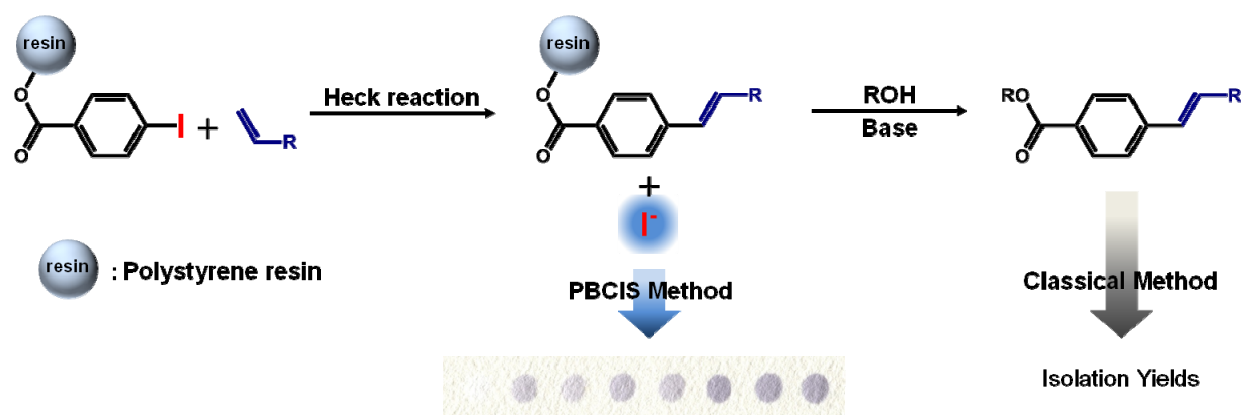


Table S12. The Heck reaction of polymer supported aryl iodide



Entry	R	Base	Grayscale intensity	Conversion (PBCIS) %	Yield %	Deviation
A12	Ph	Pyridine	247.37	0(-1) [¶]	1	-1
B12	Ph	DBU	186.91	54	56	-2
C12	Ph	DBN	190.59	50	44	+6
D12	Ph	K ₂ CO ₃	171.15	68	60	+8
E12	Ph	Cs ₂ CO ₃	187.46	53	51	+2
F12	CO ₂ ⁿ Bu	K ₂ CO ₃	152.86	85	82	+3
G12	CONH ^t Bu	K ₂ CO ₃	161.23	77	77	0
H12	CO ₂ ^t Bu	K ₂ CO ₃	153.85	84	85	-1

[¶]The minus values were obtained from the equation, which means no conversion.

S16. The assay of the transition metal-catalyzed coupling reactions

Table S13. Determination of the extent of conversion from PBCIS (Fig. 5 first experiment)
(The extent of conversion from PBCIS / The extent of conversion from GC)

	C-S					C-O	C-N	Decarboxylative		Heck		Polymer
	Standard	Ligand	Pd	Solvent	ArI	Solvent	Ligand	Cu	Ligand	Ni	Base	Base
	1	2	3	4	5	6	7	8	9	10	11	12
A	0	100/100	94/93	100/100	11/12	4/0	0/7	4/0	78/85	95/97	86/98	0/1
B	20	90/91	46/42	83/78	6/3	28/27	0/1	0/6	52/84	100/97	62/54	54/56
C	40	83/85	55/56	94/96	64/62	39/37	2/5	5/12	51/58	90/98	95/97	50/44
D	60	61/64	64/62	94/96	59/56	41/45	3/1	31/31	61/62	88/97	0/0	68/60
E	80	60/60	83/78	95/94	86/93	61/64	0/2	58/51	58/63	2/7	1/3	53/51
F	100	66/71	53/48	100/100	48/46	57/57	77/64	72/71	75/80	63/66	41/45	85/82
G	57/62	56/61	74/66	16/27	88/95	54/58	81/83	81/86	51/58	80/87	81/98	77/77
H	2/9	13/21	31/32	61/55	14/18	80/94	87/85	98/100	56/62	3/7	59/68	84/85
Metal	Pd(dba) ₂	Pd(dba) ₂	Screen	Pd(dba) ₂	CuI	CuI	CuBr	Screen	Pd(PPh ₃) ₂ Cl ₂	Screen	NiCl ₂	Pd(OAc) ₂
Ligand	Screen	Screen	dppf	dppf	-	PEP-36	Screen	1,10-Phenanthroline	Screen	2112	PPh ₃	PEP-36
Base	K ₃ PO ₄	K ₃ PO ₄	K ₃ PO ₄	K ₃ PO ₄	K ₂ CO ₃	TBABr/ K ₃ PO ₄	Cs ₂ CO ₃	Cs ₂ CO ₃	DBU	K ₂ CO ₃	Screen	Screen
Sol	Toluene/ Acetone	Toluene/ Acetone	Toluene/ Acetone	Screen	NMP	Screen	DMF	DMF	DMSO	DMF	DMF	DMF

Table S14. Determination of the extent of conversion from PBCIS (second experiment)
For the reproducibility of this assay, all coupling reaction samples were recorded again.
(The extent of conversion from PBCIS / The extent of conversion from GC)

	C-S					C-O	C-N	Decarboxylative		Heck		Polymer
	Standard	Ligand	Pd	Solvent	ArI	Solvent	Ligand	Cu	Ligand	Ni	Base	Base
	1	2	3	4	5	6	7	8	9	10	11	12
A	0	97/100	93/93	100/100	12/12	0/0	0/7	0/0	75/85	94/97	92/98	0/1
B	20	94/91	49/42	86/78	5/3	24/27	0/1	2/6	51/84	88/97	61/54	63/56
C	40	87/85	63/56	94/96	64/62	39/37	0/5	7/12	46/58	82/98	81/97	45/44
D	60	61/64	69/62	94/96	58/56	43/45	0/1	32/31	60/62	85/97	0/0	53/60
E	80	62/60	88/78	96/94	87/93	62/64	0/2	57/51	59/63	2/7	1/3	48/51
F	100	72/71	54/48	100/100	49/46	62/57	77/64	68/71	75/80	66/66	43/45	87/82
G	58/62	59/61	73/66	14/27	89/95	57/58	79/83	76/86	50/58	82/87	89/98	80/77
H	3/9	13/21	25/32	49/55	14/18	82/94	86/85	88/100	52/62	7/7	62/68	81/85
Metal	Pd(dba) ₂	Pd(dba) ₂	Screen	Pd(dba) ₂	CuI	CuI	CuBr	Screen	Pd(PPh ₃) ₂ Cl ₂	Screen	NiCl ₂	Pd(OAc) ₂
Ligand	Screen	Screen	dppf	dppf	-	PEP-36	Screen	1,10-Phenanthroline	Screen	2112	PPh ₃	PEP-36
Base	K ₃ PO ₄	K ₃ PO ₄	K ₃ PO ₄	K ₃ PO ₄	K ₂ CO ₃	TBABr/ K ₃ PO ₄	Cs ₂ CO ₃	Cs ₂ CO ₃	DBU	K ₂ CO ₃	Screen	Screen
Sol	Toluene/ Acetone	Toluene/ Acetone	Toluene/ Acetone	Screen	NMP	Screen	DMF	DMF	DMSO	DMF	DMF	DMF

Table S15. Determination of the extent of conversion from PBCIS (third experiment)

For the reproducibility of this assay, all coupling reaction samples were recorded a third time.
(The extent of conversion from PBCIS / The extent of conversion from GC)

	C-S					C-O	C-N	Decarboxylative		Heck		Polymer
	Standard	Ligand	Pd	Solvent	ArI	Solvent	Ligand	Cu	Ligand	Ni	Base	Base
	1	2	3	4	5	6	7	8	9	10	11	12
A	0	97/100	88/93	96/100	4/12	1/0	0/7	0/0	68/85	92/97	91/98	0/1
B	20	89/91	44/42	83/78	4/3	27/27	0/1	1/6	55/84	92/97	55/54	53/56
C	40	79/85	59/56	97/96	67/62	38/37	0/5	5/12	48/58	86/98	81/97	36/44
D	60	64/64	68/62	93/96	56/56	42/45	0/1	27/31	61/62	86/97	0/0	56/60
E	80	61/60	85/78	93/94	86/93	61/64	0/2	57/51	55/63	0/7	3/3	50/51
F	100	70/71	53/48	100/100	48/46	57/57	75/64	70/71	71/80	59/66	43/45	84/82
G	56/62	56/61	75/66	14/27	88/95	54/58	80/83	77/86	46/58	80/87	85/98	80/77
H	0/9	12/21	28/32	56/55	13/18	77/94	84/85	94/100	54/62	9/7	62/68	82/85
Metal	Pd(dba) ₂	Pd(dba) ₂	Screen	Pd(dba) ₂	CuI	CuI	CuBr	Screen	Pd(PPh ₃) ₂ Cl ₂	Screen	NiCl ₂	Pd(OAc) ₂
Ligand	Screen	Screen	dppf	dppf	-	PEP-36	Screen	1,10-Phenanthroline	Screen	2112	PPh ₃	PEP-36
Base	K ₃ PO ₄	K ₃ PO ₄	K ₃ PO ₄	K ₃ PO ₄	K ₂ CO ₃	TBABr/ K ₃ PO ₄	Cs ₂ CO ₃	Cs ₂ CO ₃	DBU	K ₂ CO ₃	Screen	Screen
Sol	Toluene/ Acetone	Toluene/ Acetone	Toluene/ Acetone	Screen	NMP	Screen	DMF	DMF	DMSO	DMF	DMF	DMF

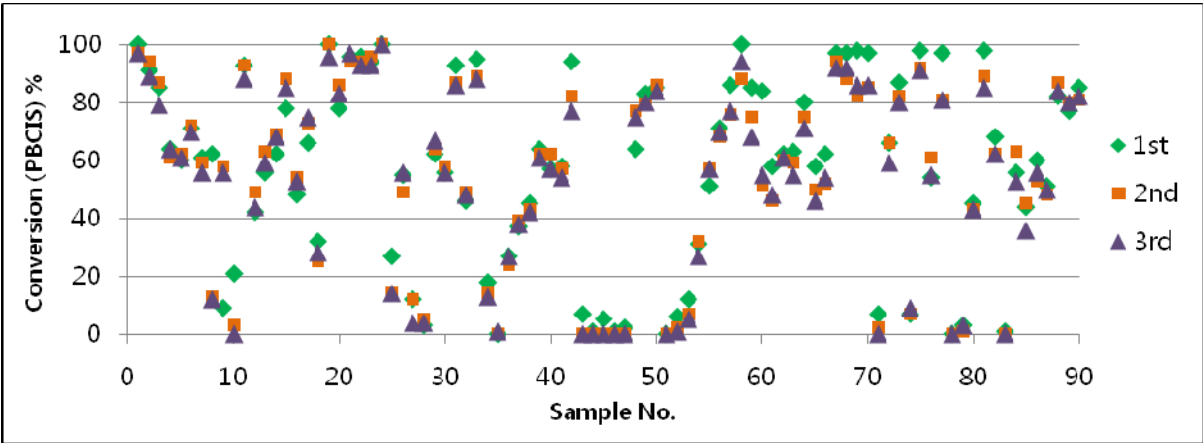


Figure S9. The three times experiments of PBCIS

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