Electronic Supplementary Material (ESI) for ChemComm.

Palladium-Catalyzed Intermolecular Heck Reaction of Alkyl Halides

Yinjun Zou and Jianrong (Steve) Zhou
Division of Chemistry and Biological Chemistry,
School of Physical and Mathematical Sciences,
Nanyang Technological University, 21 Nanyang Link, Singapore 637371
Email: jrzhou@ntu.edu.sg

Supporting Information: Procedures and Characterization

Index of Content

I. General

^{1}H NMR spectra were acquired on Bruker Avance 500 (500 MHz), 400 (400 MHz) or 300 (300 MHz) spectrometers and chemical shifts were recorded relative to tetramethylsilane (δ 0.00) or residual protiated solvent (δ 7.26 for $CDCl_3$ and δ 5.30 for CD_2Cl_2). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a *J* value in Hz. ^{13}C NMR spectra were obtained at Bruker Avance 500 (125 MHz), 400 (100 MHz) or 300 (75 MHz) spectrometers and chemical shifts were recorded relative to solvent resonance (δ 77.16 for $CDCl_3$ and δ 53.52 for CD_2Cl_2). ^{31}P{^{1}H} NMR spectra were obtained at Bruker Avance 500 (202 MHz) or 400 (162 MHz) spectrometers. Proof of purity of new compounds was demonstrated with copies of ^{1}H, ^{13}C, and ^{31}P NMR spectra.

Glassware was dried in an oven at 120 ^{o}C for at least 4 hours before use. Dry $PhCF_3$ and tetrahydropyran (Sigma-Aldrich) were degassed by argon bubbling and then stored over activated 4 Å molecular sieve beads in the glove box. Dry toluene, hexane, diethyl ether and dichloromethane were collected from a solvent purification system containing a column of activated alumina (1 m x 2) under argon. Dry THF was freshly distilled from sodium/benzophenone under argon before use. Dry 1,2-dimethoxyethane (DME), 1,2-dimethoxybenzene, triglyme, and 1,4-dioxane were distilled from CaH_2 under argon before use. All of anhydrous solvents were stored in Schlenk tubes in the glove box.

Unless noted otherwise, commercially available chemicals were used without further purification. 2-Iodooctane, 3-iodooctane, iodocycloheptane, iodocylooctane, 6-iodo-1-hexene, cyclopentylmethyl iodide, cyclohexylmethyl iodide, 2-bromo-4-phenylbutane and 2-iodo-4-phenylbutane were prepared from the corresponding alcohols via reported procedures.[1] *N*-Cbz-4-iodo-piperidine was prepared according to reported procedure.[2] *trans*-1-Iodo-2-methoxycyclopentane was prepared according to reported procedure.[3] The ferrocene 1,1′-bisphosphines were prepared using our reported procedure.[4] $Pd(dppf)_2$[5] and Pd(dba)(dppf)[6] were prepared by using reported procedures. Styrene was passed through a short plug of basic aluminum oxide in an argon-filled glove box to remove 4-*t*-butylcatechol (radical stabilizer) before use. *N,N*-Dicyclohexylmethylamine (Fluka) was degassed by argon bubbling before use in the glove box. Dry *N*,*N*,*N*′,*N*′-tetramethylethlenediamine (TMEDA),

diisopropylethylamine, triethylamine, and tri-*n*-butylamine were distilled from CaH_2 under argon before use. The GC internal standard, *n*-dodecane was degassed by argon bubbling and then dried over activated 4 Å molecular sieve beads in the glove box before use.

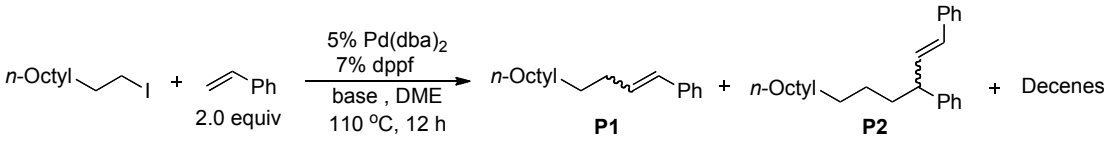
Thin-layer chromatography (TLC) was conducted with Merck 60 F254 coated silica gel plate (0.2 mm thickness). Flash chromatography was performed using Merck silica gel 60 (0.040-0.063 mm).

Gas chromatography (GC) analysis was performed on a Shimadzu GC-2010 instrument with Agilent J & W GC column DB-5MS-UI. GC/MS analysis was conducted on a Thermo Scientific DSQ II single quadrupole GC/MS instrument with Agilent J & W GC column DB-5MS-UI. ESI/MS analysis was conducted on a ThermoFinnigan LCQ Fleet MS spectrometer.

II. Condition optimization for Heck reaction of alkyl halides

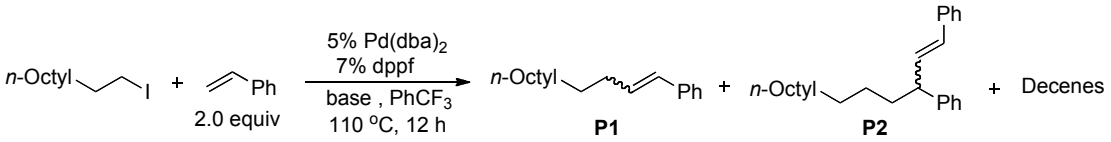
Typical procedure: In an argon-filled glove box, a dry 8-mL culture tube containing a magnetic stir bar was charged with $Pd(dba)_2$ (2.9 mg, 0.005 mmol), dppf (3.9 mg, 0.007 mmol) and 0.40 mL of dry $PhCF_3$. After stirring at room temperature for 30 minutes, iodocyclohexane (21.0 mg, 0.10 mmol) or iododecane (26.8 mg, 0.10 mmol), styrene (20.8 mg, 0.20 mmol), GC standard *n*-dodecane (10 μL) and Cy_2NMe (29.3 mg, 0.15 mmol) were added sequentially. The tube was capped tightly and the reaction mixture was heated with stirring in a heating block maintained at 110 ^oC. After 12 hours, aliquots were taken from the reaction mixture in the glove box and passed through a short plug of silica gel with diethyl ether washings. The filtrates were subjected to GC analysis to determine the conversion of alkyl iodide, the yield and selectivity of the Heck isomers and yield of a byproduct with double styrene insertion. The structures of the major isomer, (*E*)-β-alkylstyrene and its minor (*Z*)-isomer in the crude mixture were assigned by ^1H NMR spectroscopy and confirmed by GCMS. The ratio of the two isomers was determined by GC analysis. *Note: ^1H NMR spectroscopy was unsuitable to determine the ratio of the two isomers due to low signal intensity of the minor isomer.*

Table S1a. Effect of bases



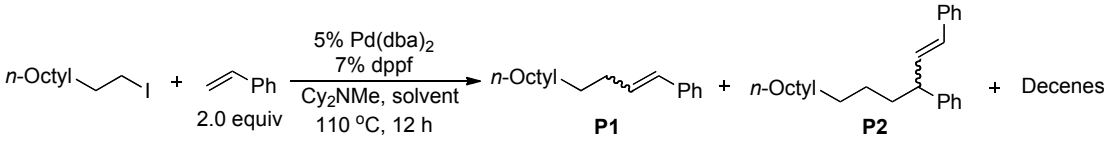
Entry	Base	Conversion (%)	P1		P2		Decenes
			Yield of *E* (%)	*E/Z*	Yield of *E* (%)	*E/Z*	Yield (%)
1	K_3PO_4	98	37	7	5	12	23
2	LiOAc	19	6	3	-	-	5
3	NaOAc	42	11	3	1	6	7
4	KOAc	100	32	3	4	6	19
5	LiOPiv	68	22	5	2	8	21
6	Li_2CO_3	19	4	3	-	-	3
7	Na_2CO_3	70	21	4	4	7	25
8	K_2CO_3	88	28	7	4	13	19
9	*i*-Pr_2NEt	86	33	4	5	7	17
10	Cy_2NMe	100	**46**	7	4	10	30
11	Et_3N	98	33	4	4	7	20
12	*n*-Bu_3N	82	22	4	3	7	13
13	2,6-Lutidine	17	4	3	-	-	3
14	Urotropine	100	5	4	-	-	3
15	Proton sponge	67	24	4	3	7	13

Table S1b. Effect of bases



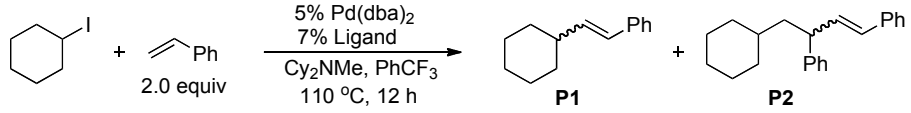
Entry	Base	Conversion (%)	**P1**		**P2**		Decenes
			Yield of *E* (%)	*E/Z*	Yield of *E* (%)	*E/Z*	Yield (%)
1	K_3PO_4	44	9	3	2	5	3
2	LiOAc	18	5	3	1	5	2
3	NaOAc	25	4	2	1	5	2
4	KOAc	51	14	3	3	6	5
5	LiOPiv	43	13	3	3	5	7
6	*i*-Pr_2NEt	75	25	3	5	5	8
7	Cy_2NMe	100	**54**	5	4	6	15
8	Et_3N	68	20	3	4	5	7
9	*n*-Bu_3N	75	20	3	4	5	7
10	2,6-Lutidine	18	4	2	1	6	1

Table S2. Effect of solvents



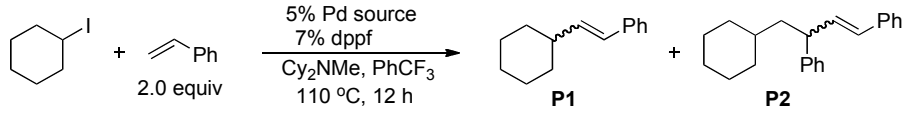
Entry	Solvent	Conversion (%)	**P1**		**P2**		Decenes
			Yield of *E* (%)	*E/Z*	Yield of *E* (%)	*E/Z*	Yield (%)
1	THF	73	25	3	4	6	15
2	THP	80	32	4	5	7	16
3	1,4-Dioxane	98	43	5	5	7	25
4	2-Me-THF	77	30	4	5	6	17
5	*n*-Bu_2O	80	30	4	7	7	13
6	DME	100	46	7	4	10	30
7	Triglyme	100	47	6	5	9	19
8	TBME	55	19	4	5	6	6
9	1,2-$(MeO)_2$ -benzene	100	**52**	7	6	9	19
10	$PhCF_3$	100	**54**	5	4	6	15
11	Toluene	91	40	5	5	7	22
12	*o*-Xylene	90	39	4	6	7	20
13	*p*-Xylene	90	37	3	6	7	20
14	DMA	99	39	4	4	7	30
15	NMP	100	33	4	4	6	33

Table S3. Effect of ligands



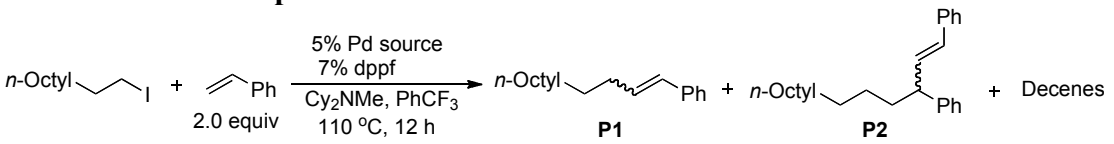
Entry	Ligand	Conversion (%)	P1		P2	
			Yield of *E* (%)	*E/Z*	Yield of *E* (%)	*E/Z*
1	dppf	100	**70**	14	9	8
2	d(*p*-OMe-Ph)pf	100	58	6	13	5
3	d(*p*-CF_3-Ph)pf	100	48	6	11	5
4	dnpf	57	12	38	5	28
5	dippf	18	2	7	2	-
6	dppp	15	0	-	0	-
7	dppe	14	0	-	0	-
8	dppb	23	0	-	0	-
9	(*R*)-BINAP	96	40	4	10	4
10	(*R*)-Segphos	59	10	3	4	3
11	Xantphos	14	3	-	-	-
12	DPEphos	96	56	9	11	5
13	*m*-$(CF_3)_2$Ph-PF-*m*-Xyl	56	1	6	-	-
14	PPF-*m*-Xyl	20	0	-	0	-
15	P(*o*-tolyl)$_3$	5	0	-	0	-
16	P(2-furyl)$_3$	14	4	9	4	10
17	PCy_3	26	1	-	0	-
18	P(*t*-Bu)$_3$	28	1	-	5	-

Table S4a. Effect of palladium source and LiI additive



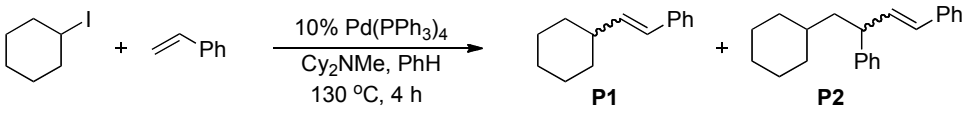
Entry	Pd source	Comment	Conversion (%)	P1		P2	
				Yield of *E* (%)	*E/Z*	Yield of *E* (%)	*E/Z*
1	$Pd(dba)_2$		100	**70**	14	9	8
2	$Pd_2(dba)_3$		99	75	10	11	6
3	$Pd(PtBu_3)_2$		100	48	6	11	5
4	$Pd(dppf)Cl_2$	no added dppf	86	36	4	10	4
5	$Pd(PPh_3)_4$		100	**79**	19	11	8
6	$Pd(PPh_3)_4$	LiI 2 equiv	100	**80**	35	11	9
7	$Pd(PPh_3)_4$	In dark	100	**79**	20	10	8
8	Pd(dppf)(dba)	no added dppf	100	**76**	32	8	11
9	$Pd(dppf)_2$	no added dppf	100	**81**	62	7	28

Table S4b. Effect of palladium source and LiI additive



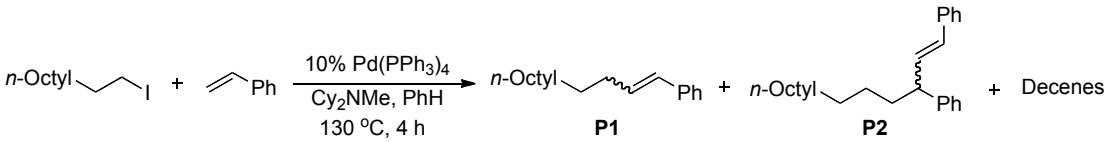
Entry	Pd source	Comment	Conversion (%)	P1		P2		Decenes
				Yield of *E* (%)	*E/Z*	Yield of *E* (%)	*E/Z*	Yield (%)
1	$Pd(dba)_2$		100	54	5	4	6	15
2	$Pd(Pt\text{-}Bu_3)_2$		100	50	8	4	11	32
3	$Pd(PPh_3)_4$		100	51	8	6	8	22
4	Pd(dba)(dppf)	No added dppf	100	54	5	7	7	23
5	$Pd(dppf)_2$	No added dppf	100	55	6	5	8	30
6	$Pd(dba)_2$	LiI 2 equiv.	100	**65**	8	8	7	19
7	Pd(dba)(dppf)	no added dppf. LiI 2 equiv.	100	**64**	9	8	16	24
8	$Pd(dppf)_2$	No added dppf. LiI 2 equiv.	100	55	8	4	13	34

Table S5a. Results using Alexanian's procedure and $Pd(PPh_3)_4$[7]



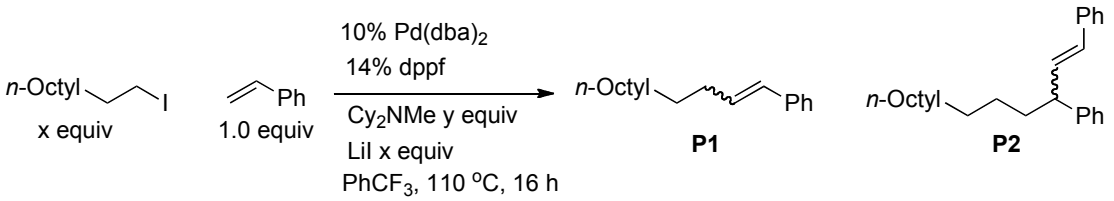
Entry	Cy-I : Styrene	Conversion (%)	P1		P2	
			Yield of *E* (%)	*E/Z*	Yield of *E* (%)	*E/Z*
1	1:2	100	43	46	14	32
2	2:1	100	59 (lit. 55)	21	9	27

Table S5b. Results of iododecane as substrate using a reported procedure[7]



Entry	RI : Styrene	Yield of **P1** (%) *E/Z*		Yield of **P2** (%) *E/Z*		Decenes (%)
1	1:2	18	8	7	15	41
2	2:1	28	7	7	33	111

Table S6. Further optimization of Heck reaction of primary alkyl halides

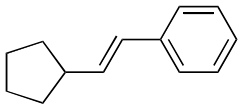


Entry	RI (x equiv)	Cy_2NMe (y equiv)	LiI (x equiv)	Conv. styrene (%)	**P1** (%) *E/Z*		**P2** (%)
1	2.0	2.5	2.0	79	68	9	< 5
2	2.5	3.0	2.5	86	77	8	< 5
3	3.0	4.0	3.0	90	81	8	< 5

III. Isolation of Heck products

General procedure for Heck reaction of secondary alkyl halides using 1:2 RX and styrene: In an argon-filled glove box, a dry 10-mL reaction tube containing a magnetic stir bar was charged sequentially with $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol, 5 mol%), dppf (19.4 mg, 0.035 mmol, 7 mol%) and 2.0 mL of dry $PhCF_3$. After stirring at room temperature for 30 minutes, alkyl halide (0.50 mmol, 1.0 equiv), vinylarene (1.0 mmol, 2.0 equiv), *n*-dodecane (GC standard, 20 μL) and Cy_2NMe (146 mg, 0.75 mmol, 1.5 equiv) were added sequentially via syringes. For reactions of alkyl bromides, LiI (1.0 mmol, 134 mg, 2.0 equiv) was added to improve the yield by about 10%. The reaction tube was capped tightly and the mixture was heated with vigorous stirring in a 110 ^oC oil bath for 36 h, unless stated otherwise. At the end of the reaction, the mixture was cooled to room temperature. It was diluted with diethyl ether and then passed through a short pad of silica gel to remove insoluble salts with diethyl ether washings. The filtrate was concentrated under reduced pressure and the residue was directly subjected to silica gel flash chromatography for isolation. The ratio of the amount of (*E*)-isomer to (*Z*)-isomer was determined by GC in both the crude mixtures and isolated samples. In most cases, the ratio did not change after flash chromatography. In some cases, additional minor isomers were detected and the olefinic ratio was determined as the amount of (*E*)-isomer to the sum of other isomers by GC.

An alternative procedure using 3:1 RX and styrene for some examples: In an argon-filled glove box, a dry 10-mL reaction tube containing a magnetic stir bar was charged sequentially with $Pd(PPh_3)_4$ (57.8 mg, 0.050 mmol, 10 mol%), dppf (38.8 mg, 0.070 mmol, 14 mol%) and 2.0 mL of dry $PhCF_3$. After stirring at room temperature for 30 minutes, alkyl halide (1.50 mmol, 3.0 equiv), styrene (52 mg, 0.5 mmol, 1.0 equiv), *n*-dodecane (GC standard, 20 μL), Cy_2NMe (390 mg, 2.0 mmol, 4.0 equiv) and LiI (201 mg, 1.5 mmol, 3.0 equiv) were added sequentially. The reaction tube was capped tightly and the mixture was heated with vigorous stirring in a 110 ^oC oil bath for 48 h, unless stated otherwise. At the end of the reaction, the mixture was cooled to room temperature. It was diluted with diethyl ether and then passed through a short pad of silica gel to remove insoluble salts with diethyl ether washings. The filtrate was concentrated under reduced pressure and the residue was directly subjected to silica gel flash chromatography for isolation.



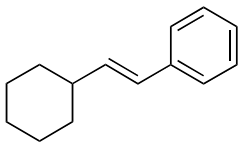
(*E*)-β-Cyclopentylstyrene [40132-68-1]. General procedure using iodocyclopentane (98 mg, 0.5 mmol): the titled compound was obtained as colorless oil (44 mg, 51% yield) after flash chromatography using hexanes as eluent. The *trans/cis* selectivity of the isolated Heck products was determined to be 49:1 by GC. The ratio was 18:1 after 12 h at 110 ^{o}C. The alternative procedure using iodocyclopentane: colorless oil (67 mg, 78% yield) and 20:1 *trans/cis* selectivity.

General procedure using bromocyclopentane (75 mg, 0.5 mmol): colorless oil (40 mg, 47% yield) and 23:1 *trans/cis* selectivity. The alternative procedure using bromocyclopentane: colorless oil (65 mg, 76%) and 13:1 *trans/cis* selectivity.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 7.5 Hz, 2H), 7.32 (ψt, J = 7.5 Hz, 2H), 7.23-7.19 (m, 1H), 6.41 (d, J = 15.9 Hz, 1H), 6.24 (dd, J = 15.9, 7.7 Hz, 1H), 2.68-2.58 (m, 1H), 1.93-1.86 (m, 2H), 1.79-1.64 (m, 4H), 1.48-1.39 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 135.8, 128.6, 128.0, 126.9, 126.1, 44.0, 33.4, 25.4.

GCMS (EI): calcd for $C_{13}H_{16}$ M: 172.13. Found: 172.18.



(*E*)-β-Cyclohexylstyrene [18869-27-7]. General procedure using iodocyclohexane (105 mg, 0.5 mmol): the titled compound was obtained as colorless oil (73 mg, 78% yield) after flash chromatography using hexanes as eluent. The *trans/cis* selectivity of the isolated Heck products was determined to be 40:1 by GC. The ratio after 12 h at 110 ^{o}C was 14:1.

General procedure using bromocyclohexane (82 mg, 0.5 mmol): colorless oil (39 mg, 42% yield) and 32:1 *trans*/*cis* selectivity. The alternative procedure using bromocyclohexane: colorless oil (71 mg, 76% yield) and 21:1 olefinic selectivity.

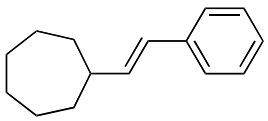
Gram-scale Heck procedure using 2 mol% Pd catalyst and a vacuum manifold. In air, dppf (124 mg, 0.224 mmol) and $Pd(PPh_3)_4$ (185 mg, 0.160 mmol) were quickly added into a 100-mL dry reaction tube containing a magnetic stir bar. After three cycles of evacuation and backfilling with argon, 32 mL of degassed, dry $PhCF_3$ was

added under argon and the mixture was stirred at room temperature for 10 minutes . Then degassed iodocyclohexane (1.68 g, 8.0 mmol), styrene (1.66 g, 16.0 mmol) and Cy_2NMe (2.34 g, 12.0 mmol) were added via syringes under argon. The reaction tube was capped tightly and the mixture was heated with vigorous stirring in a pre-warmed 110 ^oC oil bath for 36 hours. After it was cooled down to room temperature, the mixture was diluted with 30 mL of hexane and passed through a short pad of silica gel to remove insoluble salts with diethyl ether washings. The filtrate was concentrated on a rotary evaporator under reduce pressure and the resulting residue was directly subjected to silica gel flash chromatography using hexanes as eluent. The title compound was obtained as colorless oil (1.12 g, 75% yield, >96% purity by GC). The *trans/cis* selectivity of the isolated Heck products was determined to be 38:1 by GC.

^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.35 (m, 2H), 7.31-7.28 (m, 2H), 7.22-7.17 (m, 1H), 6.36 (d, J = 16.0 Hz, 1H), 6.19 (dd, J = 16.0, 6.9 Hz, 1H), 2.19-2.10 (m, 1H), 1.84-1.67 (m, 5H), 1.40-1.14 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 137.0, 128.6, 127.4, 126.9, 126.1, 41.3, 33.1, 26.4, 26.2.

GCMS (EI): calcd for $C_{14}H_{18}$ M: 186.14. Found: 186.07.



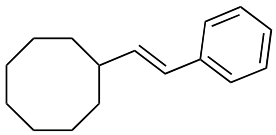
(*E*)-β-Cycloheptylstyrene [592510-48-0]. General procedure using iodocycloheptane (112 mg, 0.5 mmol): the titled compound was obtained as colorless oil (68 mg, 68% yield) after flash chromatography using hexanes as eluent. The *trans/cis* selectivity of the isolated Heck products was determined to be 41:1 by GC. The ratio was 13:1 after 12 h at 110 ^oC.

General procedure using bromocyclohexane (89 mg, 0.5 mmol): colorless oil (63 mg, 63% yield) and 26:1 *trans*/*cis* selectivity.

^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 7.8 Hz, 2H), 7.32 (ψt, J = 7.8 Hz, 2H), 7.23-7.20 (m, 1H), 6.36 (d, J = 15.9 Hz, 1H), 6.26 (dd, J = 15.9, 7.4 Hz, 1H), 2.38-2.36 (m, 1H), 1.87-1.43 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 137.8, 128.6, 126.84, 126.81, 126.1, 43.4, 34.9, 28.6, 26.4.

GCMS (EI): calcd for $C_{15}H_{20}$ M: 200.16. Found: 200.10.

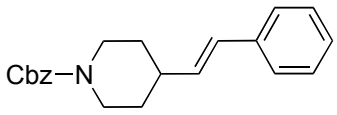


(*E*)-β-Cyclooctylstyrene [592510-49-1]. General procedure using iodocyclooctane (119 mg, 0.5 mmol): the titled compound was obtained as colorless oil (50 mg, 48% yield) after flash chromatography using hexanes as eluent. The olefinic selectivity of the isolated Heck products was determined to be 5:1 by GC. The ratio was 3:1 after 12 h at 110 ^{o}C. The alternative procedure using iodocyclooctane: colorless oil (76 mg, 71%) and 12:1 olefinic selectivity.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 7.7 Hz, 2H), 7.31 (ψt, J = 7.7 Hz, 2H), 7.23-7.19 (m, 1H), 6.36 (d, J = 16.0 Hz, 1H), 6.25 (dd, J = 16.0, 7.2 Hz, 1H), 2.42 (m, 1H), 1.84-1.56 (m, 14H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 138.0, 128.6, 127.0, 126.8, 126.1, 41.5, 32.0, 27.6, 26.2, 25.2.

GCMS (EI): calcd for $C_{16}H_{22}$ M: 214.17. Found: 214.12.

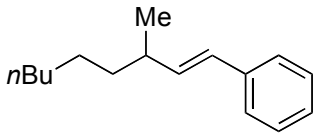


(*E*)-*N*-Cbz-4-(β-styryl)piperidine. General procedure using *N*-Cbz-4-iodo-piperidine (173 mg, 0.5 mmol): the titled compound was obtained as brown oil (120 mg, 86% yield) after flash chromatography using EA/hexanes (1:10) as eluent. The *trans/cis* selectivity of the isolated Heck products was determined to be 10:1 by ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.18 (m, 10H), 6.38 (d, J = 16.0 Hz, 1H), 6.13 (dd, J = 16.0, 6.9 Hz, 1H), 5.14 (s, 2H), 4.21 (br s, 2H), 2.89-2.83 (m, 2H), 2.35-2.26 (m, 1H), 1.79-1.71 (m, 2H), 1.44-1.39 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 137.5, 137.1, 134.2, 128.8, 128.7, 128.6, 128.1, 128.0, 127.3, 126.2, 67.1, 44.0, 39.4, 31.9.

GCMS (EI): calcd for $C_{21}H_{23}NO_2$ M: 321.17. Found: 321.10.

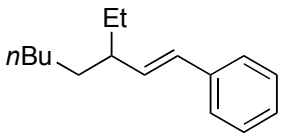


(*E*)-β-(2-Octyl)styrene [441287-15-6]. General procedure using 2-iodooctane (120 mg, 0.5 mmol): the titled compound was obtained as colorless oil (74 mg, 69% yield) after flash chromatography using hexanes as eluent. The olefinic selectivity of the isolated Heck products was determined to be 24:1 by GC. The ratio was 13:1 after 12 h at 110 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 7.6 Hz, 2H), 7.33 (ψt, *J* = 7.6 Hz, 2H), 7.24-7.22 (m, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.14 (dd, *J* = 15.9, 7.7 Hz, 1H), 2.36-2.27 (m, 1H), 1.41-1.33 (m, 10H), 1.12 (d, *J* = 6.7 Hz, 3H), 0.93 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 137.2, 128.6, 128.1, 126.9, 126.1, 37.5, 37.3, 32.1, 29.6, 27.6, 22.9, 20.8, 14.3.

GCMS (EI): calcd for $C_{16}H_{24}$ M: 216.19. Found: 216.14.

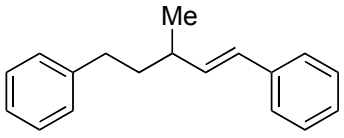


(*E*)-β-(3-Octyl)styrene. General procedure using 3-iodooctane (120 mg, 0.5 mmol): the titled compound was obtained as colorless oil (72 mg, 67% yield) after flash chromatography using hexane as eluent. The olefinic selectivity of the isolated Heck products was determined to be 15:1 by GC. The ratio was 7:1 after 12 h at 110 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.33 (ψt, *J* = 7.6 Hz, 2H), 7.24-7.21 (m, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.00 (dd, *J* = 15.9, 9.0 Hz, 1H), 2.08-2.06 (m, 1H), 1.57-1.32 (m, 10H), 0.95-0.91 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 135.8, 129.8, 128.6, 126.9, 126.1, 45.3, 35.3, 32.2, 28.4, 27.2, 22.8, 14.3, 12.0.

GCMS (EI): calcd for $C_{16}H_{24}$ M: 216.19. Found: 216.13.

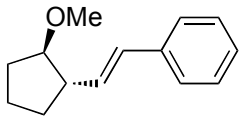


(*E*)-β-(2-(4-phenyl)butyl)styrene [685535-68-6]. General procedure using 2-iodo-4-phenylbutane (130 mg, 0.5 mmol): the titled compound was obtained as colorless oil (84 mg, 71% yield) after flash chromatography using hexanes. The selectivity of the isolated Heck products was determined to be 12:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.37 (m, 2H), 7.32-7.25 (m, 4H), 7.22-7.15 (m, 4H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.12 (dd, *J* = 15.8, 8.0 Hz, 1H), 2.71-2.58 (m, 2H), 2.39-2.29 (m, 1H), 1.75-1.69 (m, 2H), 1.12 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 138.0, 136.6, 128.8, 128.7, 128.6, 128.5, 127.0, 126.2, 125.8, 38.9, 37.1, 33.9, 20.9.

GCMS (EI): calcd for $C_{18}H_{20}$ M: 236.16. Found: 236.08.

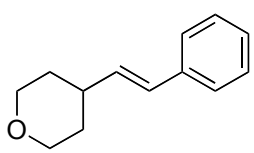


(*E*)-(*trans*-1-Methoxy-2-(β–styryl)cyclopentane. General procedure using *trans*-1-iodo-2-methoxycyclopentane (113 mg, 0.5 mmol): the titled compound was obtained as colorless oil (56 mg, 55% yield) after preparative TLC using hexanes as eluent. The *trans/cis* selectivity of the isolated Heck products was determined to be 57:1 by GC. The *trans* configuration was assigned by comparison to reported NMR data of a related compound.[8]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.35 (m, 2H), 7.32-7.27 (m, 2H), 7.22-7.18 (m, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 15.9, 8.0 Hz, 1H), 3.62-3.58 (m, 1H), 3.35 (s, 3H), 2.70-2.63 (m, 1H), 1.99-1.92 (m, 2H), 1.79-1.65 (m, 3H), 1.55-1.48 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 133.3, 129.6, 128.6, 127.1, 126.2, 88.0, 57.3, 49.5, 31.3, 31.0, 22.6.

GCMS (EI): calcd for $C_{14}H_{18}O$ M: 202.14. Found: 202.07.



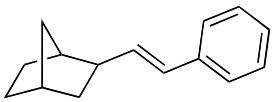
(*E*)-β-(Tetrahydro-4-pyranyl)styrene [592510-37-7]. General procedure using 4-bromotetrahydropyran (83 mg, 0.5 mmol): the titled compound was obtained as

colorless oil (60 mg, 64% yield) after flash chromatography using hexanes. The *trans/cis* selectivity of the isolated Heck products was determined to be 82:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.5 Hz, 2H), 7.31 (dd, *J* = 7.9, 7.5 Hz, 2H), 7.21 (t, *J* = 7.9 Hz, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 6.8 Hz, 1H), 4.01 (dd, *J* = 11.6, 2.8 Hz, 2H), 3.47 (dt, *J* = 11.6, 1.9 Hz, 2H), 2.44-2.34 (m, 1H), 1.72 (d, *J* = 12.9 Hz, 2H), 1.63-1.52 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 134.8, 128.7, 128.4, 127.2, 126.2, 67.9, 38.5, 32.8.

GCMS (EI): calcd for $C_{13}H_{16}O$ M: 188.12. Found: 188.07.

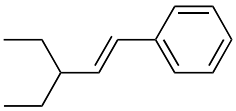


(*E*)-β-(*exo*-2-Norbonyl)styrene [76217-04-4]. General procedure using *exo*-2-bromonorbornane (88 mg, 0.5 mmol): the titled compound was obtained as colorless oil (71 mg, 72% yield) after flash chromatography using hexanes as eluent. The *trans/cis* selectivity of the isolated Heck products was determined to be 24:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.5 Hz, 2H), 7.31 (ψt, *J* = 7.5 Hz, 2H), 7.23-7.19 (m, 1H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.16 (dd, *J* = 15.8, 8.0 Hz, 1H), 2.32-2.28 (m, 2H), 2.18 (s, 1H), 1.63-1.19 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 136.6, 128.6, 127.4, 126.8, 126.1, 45.6, 42.9, 38.1, 36.8, 36.0, 29.9, 29.2.

GCMS (EI): calcd for $C_{15}H_{18}$ M: 198.14. Found: 198.09.

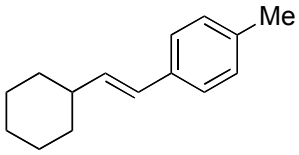


(*E*)-β-(3-Pentyl)styrene [40132-62-5]. General procedure using 3-bromopentane (76 mg, 0.5 mmol): the titled compound was obtained as colorless oil (40 mg, 46% yield) after flash chromatography using hexanes. The selectivity of the isolated Heck products was determined to be 24:1 by GC. The alternative procedure using 3-bromopentane: colorless oil (70 mg, 80%) and 38:1 olefinic selectivity.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.23-7.19 (m, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 5.98 (dd, *J* = 15.8, 8.9 Hz, 1H), 2.01-1.92 (m, 1H), 1.58-1.48 (m, 2H), 1.42-1.29 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 135.4, 130.0, 128.6, 126.9, 126.1, 47.0, 28.0, 12.0.

GCMS (EI): calcd for $C_{13}H_{18}$ M: 174.14. Found: 174.11.

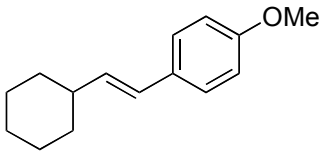


(*E*)-β-Cyclohexyl-4-methylstyrene [61153-38-6]. General procedure using iodocyclohexane (105 mg, 0.5 mmol): the titled compound was obtained as colorless oil (80 mg, 80% yield) after flash chromatography using hexanes and the contaminant of 4-methylstyrene after purification was removed under vacuum. The *trans/cis* selectivity of the isolated Heck products was determined to be 32:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 6.30 (d, *J* = 15.9 Hz, 1H), 6.11 (dd, *J* = 15.9, 6.9 Hz, 1H), 2.31 (s, 3H), 2.11-2.09 (m, 1H), 1.81-1.66 (m, 5H), 1.35-1.12 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.5, 136.0, 135.4, 129.3, 127.2, 126.0, 41.3, 33.2, 26.4, 26.2, 21.3.

GCMS (EI): calcd for $C_{15}H_{20}$ M: 200.16. Found: 200.08.

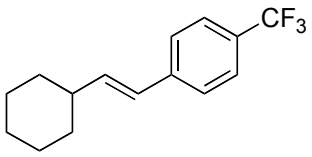


(*E*)-β-Cyclohexyl-4-methoxystyrene [104151-26-0]. General procedure using iodocyclohexane (105 mg, 0.5 mmol) and $Pd(dba)_2$ (0.025 mmol, 14.4 mg) instead of $Pd(PPh_3)_4$: the titled compound was obtained as colorless oil (82 mg, 76% yield) after flash chromatography using hexanes and the contaminant of 4-methoxystyrene after purification was removed under vacuum. The *trans/cis* selectivity of the isolated Heck products was determined to be 53:1 by GC. The ratio was 23:1 after 12 h at 110 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-1.25 (m, 2H), 6.84-6.81 (m, 2H), 6.28 (d, *J* = 16.0 Hz, 1H), 6.03 (dd, *J* = 16.0, 6.9 Hz, 1H), 3.79 (s, 3H), 2.13-2.06 (m, 1H), 1.81-1.65 (m, 5H), 1.37-1.11 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 134.9, 131.1, 127.1, 126.7, 114.1, 55.4, 41.3, 33.3, 26.4, 26.2.

GCMS (EI): calcd for $C_{15}H_{20}O$ M: 216.15. Found: 216.10

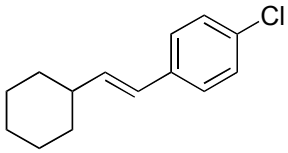


(*E*)-β-Cyclohexyl-4-trifluoromethylstyrene. General procedure using iodocyclohexane (105 mg, 0.5 mmol): the titled compound was obtained as white solid (96 mg, 76% yield) after flash chromatography using hexanes as eluent and the contaminant of 4-trifluoromethylstyrene after purification was removed under vacuum. The *trans/cis* selectivity of the isolated Heck products was determined to be 40:1 by GC. The trans ratio was 38:1 after 12 h at 110 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 6.27 (dd, *J* = 16.0, 6.6 Hz, 1H), 2.15-2.11 (m, 1H), 1.82-1.67 (m, 5H), 1.37-1.14 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 139.4, 128.7 (q, *J* = 32.5 Hz), 126.3, 126.2, 125.5 (q, *J* = 3.9 Hz), 124.5 (q, *J* = 271.8 Hz), 41.4, 32.9, 26.3, 26.1.

GCMS (EI): calcd for $C_{15}H_{17}F_3$ M: 254.13. Found: 254.06.

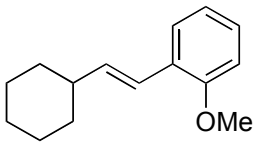


(*E*)-β-Cyclohexyl-4-chlorostyrene. General procedure using iodocyclohexane (105 mg, 0.5 mmol): the titled compound was obtained as white solid (90 mg, 82% yield) after flash chromatography using hexanes and the contaminant of 4-chlorostyrene after purification was removed under vacuum. The *trans/cis* selectivity of the isolated Heck products was determined to be 38:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.17 (m, 4H), 6.27 (d, *J* = 16.0 Hz, 1H), 6.13 (dd, *J* = 16.0, 6.8 Hz, 1H), 2.11-2.08 (m, 1H), 1.80-1.66 (m, 5H), 1.35-1.11 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 136.7, 132.4, 128.7, 127.3, 126.3, 41.3, 33.0, 26.3, 26.2.

GCMS (EI): calcd for $C_{14}H_{17}Cl$ M: 220.10. Found: 220.05.

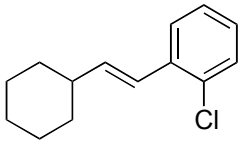


(*E*)-β-Cyclohexyl-2-methoxystyrene. General procedure using iodocyclohexane (105 mg, 0.5 mmol): the titled compound was obtained as colorless oil (70 mg, 65% yield) after flash chromatography using hexanes and then the contaminant of 2-vinylanisole after purification was removed under vacuum. The *trans/cis* selectivity of the isolated Heck products was determined to be 49:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.4 Hz, 1H), 7.20 (dd, *J* = 8.0, 7.4 Hz, 1H), 6.93 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 16.1 Hz, 1H), 6.19 (dd, *J* = 16.1, 7.0 Hz, 1H), 3.86 (s, 3H), 2.19-2.17 (m, 1H), 1.87-1.70 (m, 5H), 1.40-1.18 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 137.6, 127.9, 127.2, 126.3, 121.9, 120.7, 110.9, 55.6, 41.7, 33.2, 26.4, 26.2.

GCMS (EI): calcd for $C_{15}H_{20}O$ M: 216.15. Found: 216.09.

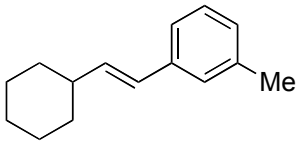


(*E*)-β-Cyclohexyl-2-chlorostyrene [441287-17-8]. General procedure using iodocyclohexane (105 mg, 0.5 mmol): the reaction was heated for 96 h to improve the *E*/*Z* selectivity. The titled compound was obtained as colorless oil (65 mg, 59% yield) after flash chromatography using hexanes and subsequent removal of some contaminant of 2-chlorostyrene under vacuum. The selectivity of the isolated Heck products was determined to be 16:1 by ^{1}H NMR spectroscopy. The selectivity in the reaction mixture after 12 h was determined to be 2:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.32 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.21-7.17 (m, 1H), 7.14-7.10 (m, 1H), 6.73 (d, *J* = 15.9 Hz, 1H), 6.16 (dd, *J* = 15.9, 7.0 Hz, 1H), 2.22-2.15 (m, 1H), 1.85-1.67 (m, 5H), 1.38-1.25 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8, 136.3, 132.8, 129.7, 127.9, 126.8, 126.7, 123.8, 41.5, 33.0, 26.3, 26.2.

GCMS (EI): calcd for $C_{14}H_{17}Cl$ M: 220.10. Found: 220.07.

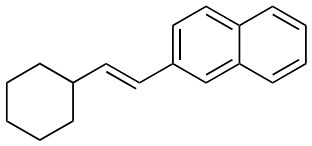


(*E*)-β-Cyclohexyl-3-methylstyrene. General procedure using iodocyclohexane (105 mg, 0.5 mmol): the titled compound was obtained as colorless oil (70 mg, 70% yield) after flash chromatography using hexanes and subsequent removal of some of 3-methylstyrene as contaminant under vacuum. The *trans/cis* selectivity of the isolated Heck products was determined to be 30:1 by GC. The ratio was 29:1 after 12 h at 110 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.16 (m, 3H), 7.17 (d, *J* = 6.7 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.19 (dd, *J* = 16.0, 6.8 Hz, 1H), 2.16-2.14 (m, 1H), 1.85-1.70 (m, 5H), 1.40-1.17 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 138.1, 136.8, 128.5, 127.7, 127.4, 126.8, 123.3, 41.3, 33.1, 26.4, 26.2, 21.6.

GCMS (EI): calcd for $C_{15}H_{20}$ M: 200.16. Found: 200.04.

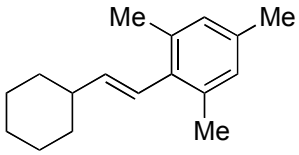


(*E*)-2-(2-Cyclohexylvinyl)naphthalene [592510-43-5]. General procedure using iodocyclohexane (105 mg, 0.5 mmol) and 2-vinylnaphthalene (84.8 mg, 0.55 mmol): the titled compound was obtained as white solid (76 mg, 64% yield) after flash chromatography using hexanes as eluent and subsequent removal of 2-vinylnaphthalene contaminant under vacuum. The *trans/cis* selectivity of the isolated Heck products was determined to be 14:1 by GC. The ratio was 4:1 after 12 h at 110 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.75 (m, 3H), 7.68 (s, 1H), 7.59 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.46-7.38 (m, 2H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.31 (dd, *J* = 16.0, 7.0 Hz, 1H), 2.23-2.15 (m, 1H), 1.87-1.68 (m, 5H), 1.41-1.18 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 135.7, 133.9, 132.8, 128.2, 128.0, 127.8, 127.5, 126.2, 125.52, 125.50, 123.8, 41.5, 33.2, 26.4, 26.2.

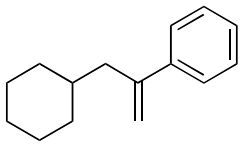
GCMS (EI): calcd for $C_{18}H_{20}$ M: 236.16. Found: 236.10.



(*E*)-β-Cyclohexyl-2,4,6-trimethylstyrene. General procedure using iodocyclohexane (105 mg, 0.5 mmol): the titled compound was obtained as colorless oil (54 mg, 47% yield) after flash chromatography using hexanes as eluent and subsequent removal of some contaminant of 2,4,6-trimethylstyrene under vacuum. The selectivity of the isolated Heck products was determined to be 3:1 after 36 h by ^{1}H NMR. The selectivity after 12 h was determined to be 1:1 by GC.

^{1}H NMR of major isomer (400 MHz, $CDCl_3$): δ 6.86 (s, 2H), 6.24 (d, *J* = 16.2 Hz, 1H), 5.59 (dd, *J* = 16.2, 7.1 Hz, 1H), 2.27 (s, 3H), 2.26 (s, 6H), 1.86-1.56 (m, 11H).

GCMS (EI): calcd for $C_{17}H_{24}$ M: 228.19. Found: 228.14.

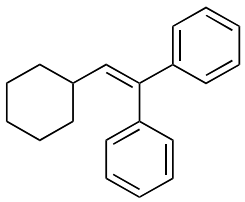


α-(Cyclohexylmethyl)styrene [136490-39-6]. General procedure using iodocyclohexane (105 mg, 0.5 mmol): the reaction was heated for 8 h. The titled compound was obtained as colorless oil (74 mg, 74% yield) after flash chromatography using hexanes and subsequent removal of some contaminant of α-methylstyrene under vacuum. The selectivity of the isolated Heck products was determined to be 12:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.37 (m, 2H), 7.34-7.29 (m, 2H), 7.28-7.23 (m, 1H), 5.26 (d, *J* = 1.8 Hz, 1H), 5.00 (d, *J* = 1.8 Hz, 1H), 2.39 (dd, *J* = 7.1, 0.8 Hz, 2H), 1.71-1.59 (m, 5H), 1.38-1.28 (m, 1H), 1.15-1.06 (m, 3H), 0.93-0.90 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 141.7, 128.4, 127.3, 126.4, 113.6, 43.8, 35.9, 33.4, 26.7, 26.4.

GCMS (EI): calcd for $C_{15}H_{20}$ M: 200.16. Found: 200.10.

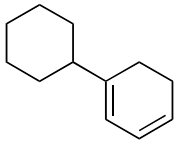


1-Cyclohexyl-2,2'-diphenylethene [91083-83-9]. General procedure using iodocyclohexane (105 mg, 0.5 mmol): the reaction was heated for 96 h. The titled compound was obtained as colorless oil (99 mg, 76% yield) after flash chromatography using hexanes and subsequent removal of some contaminant of 1,1-diphenylethene under vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.16 (m, 10H), 5.90 (d, J = 10.1 Hz, 1H), 2.17-2.08 (m, 1H), 1.68-1.59 (m, 5H), 1.25-1.16 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 140.8, 139.8, 136.1, 129.9, 128.3, 128.2, 127.4, 126.92, 126.85, 38.46, 33.49, 26.15, 25.75.

GCMS (EI): calcd for $C_{20}H_{22}$ M: 262.17. Found: 262.11.



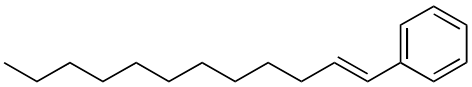
1-Cyclohexyl-1,3-cyclohexadiene [65181-98-8]. General procedure using iodocyclohexane (105 mg, 0.5 mmol) and 1,3-cyclohexadiene (200 mg, 2.5 mmol): the titled compound was obtained as colorless oil (50 mg, 62% yield) after flash chromatography using hexanes. The isomeric ratio of the isolated Heck products was determined to be 3:1 by GC. The NMR spectroscopy of the major isomer was identified by comparison with reported NMR data.[9]

GCMS (EI): calcd for $C_{12}H_{18}$ M: 162.14. Found: 162.11.

General procedure for Heck reaction of primary alkyl halides using 1:2 RX and styrene: In an argon-filled glove box, a dry 10-mL reaction tube containing a magnetic stir bar was charged sequentially with $Pd(dba)_2$ (14.4 mg, 0.025 mmol, 5 mol%), dppf (19.4 mg, 0.035 mmol, 7 mol%) and 2.0 mL of dry $PhCF_3$. After stirring at room temperature for 30 minutes, alkyl halide (0.50 mmol, 1.0 equiv), styrene (104 mg, 1.0 mmol, 2.0 equiv), *n*-dodecane (GC standard, 20 μL), Cy_2NMe (146 mg, 0.75 mmol, 1.5 equiv) and LiI (134 mg, 1.0 mmol, 2.0 equiv) were added sequentially. The reaction tube was capped tightly and the mixture was heated with vigorous stirring in a 110 ^{o}C oil bath for 36 h, unless stated otherwise. At the end of the reaction, the

mixture was cooled to room temperature. It was diluted with diethyl ether and then passed through a short pad of silica gel to remove insoluble salts with diethyl ether washings. The filtrate was concentrated under reduced pressure and the residue was directly subjected to silica gel flash chromatography for isolation. The ratio of the amount of (*E*)-isomer to other isomers was determined by GC in both the crude mixtures and isolated samples. In most cases, the ratio did not change after flash chromatography.

An alternative procedure using 3:1 RX and styrene: In an argon-filled glove box, a dry 10-mL reaction tube containing a magnetic stir bar was charged sequentially with $Pd(dba)_2$ (28.8 mg, 0.050 mmol, 10 mol%), dppf (38.8 mg, 0.070 mmol, 14 mol%) and 2.0 mL of dry $PhCF_3$. After stirring at room temperature for 30 minutes, alkyl halide (1.50 mmol, 3.0 equiv), styrene (52 mg, 0.5 mmol, 1.0 equiv), *n*-dodecane (GC standard, 20 μL) and Cy_2NMe (390 mg, 2.0 mmol, 4.0 equiv) and LiI (201 mg, 1.5 mmol, 3.0 equiv) were added sequentially. The reaction tube was capped tightly and the mixture was heated with vigorous stirring in a 110 ^oC oil bath for 48 h, unless stated otherwise. At the end of the reaction, the mixture was cooled to room temperature. It was passed through a short pad of silica gel to remove insoluble salts with diethyl ether washings. The filtrate was concentrated under reduced pressure and the residue was directly subjected to silica gel flash chromatography for isolation.



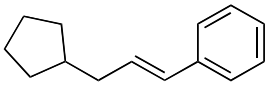
(*E*)-β-(1-Decyl)styrene [117780-29-7]. General procedure using 1-iododecane (134 mg, 0.5 mmol): the titled compound was obtained as colorless oil (76 mg, 62% yield) after flash chromatography using hexanes as eluent and the olefinic selectivity was determined to be 9:1. The alternative procedure using 1-iododecane: colorless oil (90 mg, 74% yield) and 8:1 olefinic selectivity.

General procedure using 1-bromodecane (111 mg, 0.5 mmol): colorless oil (74 mg, 61%) and 8:1 olefinic selectivity. The alternative procedure using 1-bromodecane: colorless oil (90 mg, 74%) and 4:1 olefinic selectivity.

^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.7 Hz, 2H), 7.31 (ψt, J = 7.7 Hz, 2H), 7.22-7.19 (m, 1H), 6.40 (d, J = 15.9 Hz, 1H), 6.26 (dt, J = 15.9, 6.8 Hz, 1H), 2.26-2.20 (m, 2H), 1.51-1.46 (m, 2H), 1.34-1.30 (m, 14H), 0.92 (t, J = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 131.4, 129.9, 128.6, 126.9, 126.1, 33.2, 32.1, 29.8 (2 overlapping signals), 29.7, 29.6, 29.5, 29.4, 22.9, 14.3.

GCMS (EI): calcd for $C_{18}H_{28}$ M: 244.22. Found: 244.10.



(*E*)-β-(Cyclopentylmethyl)styrene [91083-79-3]. General procedure using cyclopentylmethyl iodide (105 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (0.025 mmol, 28.9 mg): the titled compound was obtained as colorless oil (51 mg, 55% yield) after flash chromatography using hexanes as eluent. The olefinic selectivity of the isolated Heck products was determined to be 13:1 by GC. The alternative procedure using cyclopentylmethyl iodide and $Pd(PPh_3)_4$ (0.050 mmol, 57.8 mg): colorless oil (70 mg, 75%) and 10:1 olefinic selectivity.

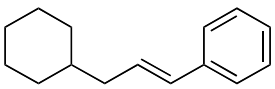
General procedure using cyclopentylmethyl bromide (82 mg, 0.5 mmol): colorless oil (54 mg, 58% yield) and 12:1 olefinic selectivity.

General procedure using 6-iodo-1-hexene (105 mg, 0.5 mmol): colorless oil (48 mg, 52% yield) and 3:1 olefinic selectivity. <5% of the noncyclized isomer carrying a terminal vinyl group was detected by ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 7.3 Hz, 2H), 7.31 (ψt, J = 7.3 Hz, 2H), 7.22-7.17 (m, 1H), 6.38 (d, J = 15.8 Hz, 1H), 6.24 (dt, J = 15.8, 7.1 Hz, 1H), 2.22 (t, J = 7.1 Hz, 2H), 2.02-1.90 (m, 1H), 1.83-1.75 (m, 2H), 1.68-1.49 (m, 4H), 1.27-1.16 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 130.7, 130.3, 128.6, 126.9, 126.1, 40.2, 39.6, 32.5, 25.3.

GCMS (EI): calcd for $C_{14}H_{18}$ M: 186.14. Found: 186.08.



(*E*)-β-(Cyclohexylmethyl)styrene [182320-85-0]. General procedure using cyclohexylmethyl iodide (114 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (0.025 mmol, 28.9 mg) instead of $Pd(dba)_2$: the titled compound was obtained as colorless oil (60 mg, 60% yield) after flash chromatography using hexanes as eluent. The olefinic selectivity of the isolated Heck products was determined to be 15:1 by GC. The alternative

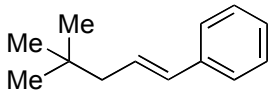
procedure using cyclohexylmethyl iodide and $Pd(PPh_3)_4$ (0.050 mmol, 57.8 mg): colorless oil (78 mg, 78%) and 12:1 olefinic selectivity.

General procedure using cyclohexylmethyl bromide (89 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (0.025 mmol, 28.9 mg) instead of $Pd(dba)_2$: colorless oil (55 mg, 55% yield) and 16:1 olefinic selectivity. The alternative procedure using cyclohexylmethyl bromide and $Pd(PPh_3)_4$ (0.050 mmol, 57.8 mg): colorless oil (75 mg, 75%) and 13:1 olefinic selectivity.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (m, 2H), 7.31-7.27 (m, 2H), 7.20-7.17 (m, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.8, 7.2 Hz, 1H), 2.11 (t, *J* = 7.0 Hz, 2H), 1.78-1.64 (m, 5H), 1.46-1.35 (m, 1H), 1.29-1.10 (m, 3H), 1.00-0.92 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 130.9, 129.9, 128.6, 126.9, 126.1, 41.2, 38.4, 33.4, 26.7, 26.5.

GCMS (EI): calcd for $C_{15}H_{20}$ M: 200.16. Found: 200.11.

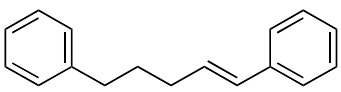


(*E*)-β-Neopentylstyrene [40132-64-7]. General procedure using neopentyl iodide (99 mg, 0.5 mmol): the reaction completed after 96 h. The titled compound was obtained as colorless oil (50 mg, 57% yield) after flash chromatography using hexanes as eluent. The *trans/cis* selectivity of the isolated Heck products was determined to be 15:1 by GC. The alternative procedure using neopentyl iodide: colorless oil (64 mg, 74%) and 6:1 the *trans/cis* selectivity.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.29 (ψt, *J* = 7.6 Hz, 2H), 7.20-7.16 (m, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.26 (dt, *J* = 15.8, 7.3 Hz, 1H), 2.09 (d, *J* = 7.3 Hz, 2H), 0.94 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 132.0, 128.6, 128.4, 127.0, 126.2, 47.8, 31.6, 29.6.

GCMS (EI): calcd for $C_{13}H_{18}$ M: 174.14. Found: 174.19.



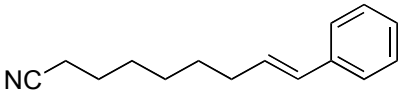
(*E*)-β-(3-Phenyl-1-propyl)styrene [7433-54-7]. General procedure using 1-bromo-3-phenylpropane (100 mg, 0.5 mmol): the titled compound was obtained as

colorless oil (74 mg, 63% yield) after flash chromatography using hexanes as eluent. The olefinic selectivity of the isolated Heck products was determined to be 12:1 by GC. The alternative procedure using 1-bromo-3-phenylpropane: colorless oil (83 mg, 75%) and 4:1 olefinic selectivity.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.13 (m, 10H), 6.39 (d, J = 15.9 Hz, 1H), 6.22 (dt, J = 15.9, 6.8 Hz, 1H), 2.66 (t, J = 7.6 Hz, 2H), 2.24 (tt, J = 7.2, 7.2 Hz), 1.80 (dt, J = 7.6, 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 138.0, 130.7, 130.4, 128.6 (2 overlapping signals), 128.5, 127.0, 126.1, 125.9, 35.5, 32.7, 31.2.

GCMS (EI): calcd for $C_{17}H_{18}$ M: 222.14. Found: 222.08.



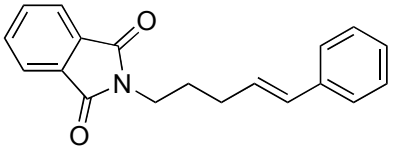
(*E*)-β-(7-Cyanoheptyl)styrene. General procedure using 7-Bromoheptanenitrile (95 mg, 0.5 mmol): the titled compound was obtained as colorless oil (63 mg, 59% yield) after flash chromatography using EA/hexanes (1:30) as eluent. The olefinic selectivity of the isolated Heck products was determined to be 21:1 by GC. The sample for NMR spectroscopy was obtained after preparative TLC. The alternative procedure using 7-bromoheptanenitrile: colorless oil (81 mg, 76%) and 9:1 olefinic selectivity.

General procedure using 7-chloroheptanenitrile: colorless oil (55 mg, 50% yield) 20:1 olefinic selectivity. The alternative procedure using 7-chloroheptanenitrile: colorless oil (69 mg, 64%) and 7:1 olefinic selectivity.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.27 (m, 4H), 7.22-7.17 (m, 1H), 6.38 (d, J = 15.8 Hz, 1H), 6.20 (dt, J = 15.8, 6.9 Hz, 1H), 2.34 (t, J = 7.1 Hz, 2H), 2.25-2.19 (m, 2H), 1.71-1.64 (m, 2H), 1.52-1.36 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 130.7, 130.2, 128.6, 127.0, 126.1, 119.9, 33.0, 29.1, 28.7, 28.4, 25.5, 17.3.

GCMS (EI): calcd for $C_{15}H_{19}N$ M: 213.15. Found: 213.13.

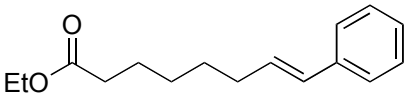


(*E*)-β−(Phthalimidopropyl)styrene. General procedure using *N*-(3-bromopropyl)phthalimide (134 mg, 0.5 mmol): the titled compound was obtained as white solid (82 mg, 56% yield) after flash chromatography using EA/hexanes (1:30) as eluent. The selectivity of the isolated Heck products was determined to be 13:1 by GC. The pure sample for NMR spectroscopy was obtained after preparative TLC. The alternative procedure using *N*-(3-bromopropyl)phthalimide: white solid (110 mg, 76%) and 17:1 olefinic selectivity.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.80 (m, 2H), 7.72-7.66 (m, 2H), 7.31-7.24 (m, 4H), 7.19-7.15 (m, 1H), 6.41 (d, J = 15.9 Hz, 1H), 6.20 (dt, J = 15.9, 6.8 Hz, 1H), 3.75 (t, J = 7.2 Hz, 2H), 2.32-2.26 (m, 2H), 1.92-1.85 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 137.7, 134.0, 132.4, 130.9, 129.3, 128.6, 127.1, 126.1, 123.3, 37.8, 30.5, 28.2.

GCMS (EI): calcd for $C_{19}H_{17}NO_2$ M: 291.13. Found: 291.07.

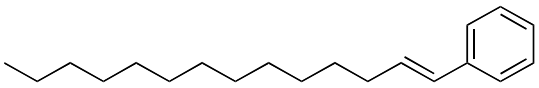


Ethyl 6-(*E*)-β-styrylhexanoate. General procedure using ethyl 6-bromohexanoate (112 mg, 0.5 mmol): the titled compound was obtained as colorless oil (40 mg, 37% yield) after flash chromatography using EA/hexanes (1:30) as eluent. The selectivity of the isolated Heck products was determined to be 2:1 by GC. The sample for NMR spectroscopy was obtained after preparative TLC. The alternative procedure using 6-bromohexanoate: light yellow oil (90 mg, 73%) and 2:1 olefinic selectivity.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.27 (m, 4H), 7.21-7.19 (m, 1H), 6.38 (d, J = 15.8 Hz, 1H), 6.21 (dt, J = 15.8, 6.9 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 2.31 (t, J = 7.5 Hz, 2H), 2.47-2.19 (m, 2H), 1.70-1.63 (m, 2H), 1.54-1.46 (m, 2H), 1.42-1.35 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.9, 138.0, 130.9, 130.1, 128.6, 127.0, 126.1, 60.3, 34.5, 32.9, 29.1, 28.8, 25.0, 14.4.

GCMS (EI): calcd for $C_{16}H_{22}O$ M: 246.16. Found: 246.12.



(*E*)-β-(1-Dodecyl)styrene [99464-24-1]. General procedure using 1-chlorododecane (102 mg, 0.5 mmol): the titled compound was obtained as colorless oil (70 mg, 51% yield) after flash chromatography using hexanes as eluent. The olefinic selectivity of the isolated Heck products was determined to be 9:1 by GC. The alternative procedure using 1-chlorododecane: colorless oil (100 mg, 74%) and 4:1 olefinic selectivity.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.35 (m, 2H), 7.32-7.28 (m, 2H), 7.22-7.18 (m, 1H), 6.39 (d, J = 15.8 Hz, 1H), 6.26 (dt, J = 15.8, 6.8 Hz, 1H), 2.25-2.19 (m, 2H), 1.52-1.28 (m, 20H), 0.92-0.88 (m, 3H).

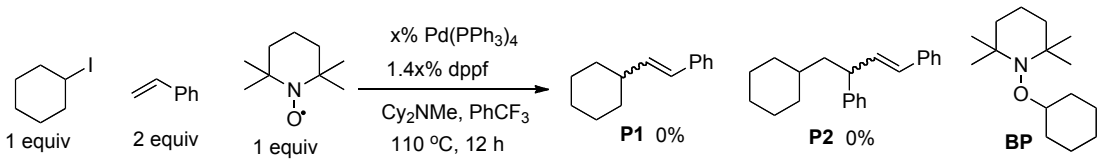
^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 131.4, 129.9, 128.6, 126.9, 126.1, 33.2, 32.1, 29.86 (2 overlapping signals), 29.82, 29.80, 29.7, 29.6, 29.5, 29.4, 22.9, 14.3.

GCMS (EI): calcd for $C_{20}H_{32}$ M: 272.25. Found: 272.22.

IV. Mechanistic study

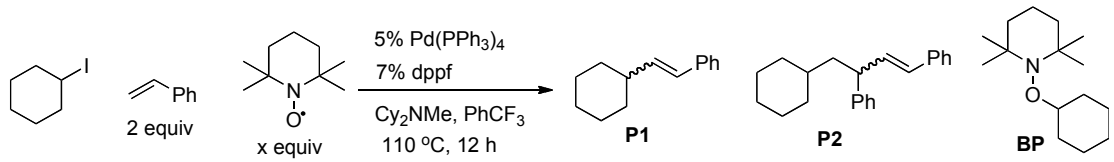
Typical procedure: In an argon-filled glove box, a dry 8.0-mL reaction tube containing a magnetic stir bar was charged with $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol), dppf (3.9 mg, 0.007 mmol) and 0.40 mL of dry $PhCF_3$. After stirring at room temperature for 30 minutes, iodocyclohexane (21.0 mg, 0.10 mmol), styrene (20.8 mg, 0.20 mmol), GC standard *n*-dodecane (10 μL), Cy_2NMe (29.3 mg, 0.15 mmol) and TEMPO (15.6 mg, 0.1 mmol) were added sequentially. The tube was capped tightly and the reaction mixture was heated with stirring in an aluminum-heating block maintained at 110 ^oC (internal temperature). After 12 hours, aliquots were taken from the reaction mixture in the glove box and passed through a short plug of silica gel with diethyl ether washings. The filtrates were subjected to GC analysis to determine the conversion of iodocyclohexane, the yield and isomeric selectivity of the Heck products and yield of a byproduct derived from double styrene insertion. The structures of the major isomer, (*E*)-β-cyclohexylstyrene and its minor (*Z*)-isomer in the crude mixture were assigned by ^1H NMR spectroscopy and confirmed by GCMS. The ratio of the two isomers was determined by GC analysis. *Note: ^1H NMR spectroscopy was unsuitable to determine the ratio of the two isomers due to low signal intensity of the minor isomers.*

Table S7. Trapping experiment using 1 equiv of TEMPO



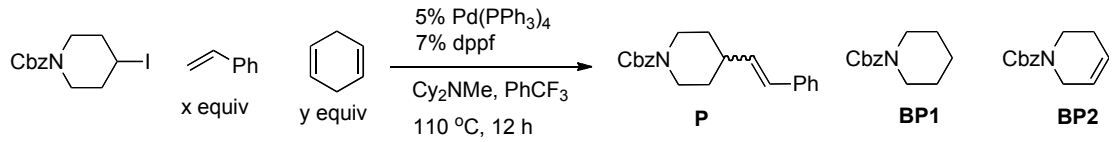
Entry	x mol% Pd	Conv. CyI (%)	**BP** (%)
1	0	0	0
2	5	19	10
3	10	23	20
4	20	44	41
5	50	100	100

Table S8. Trapping experiment using TEMPO



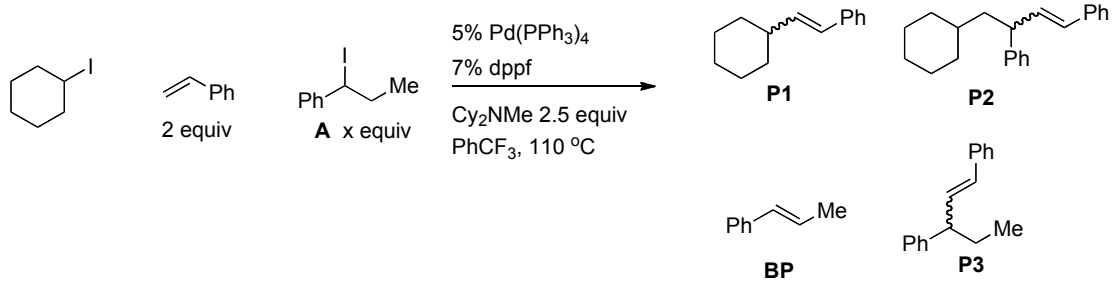
Entry	TEMPO (x equiv)	Conv. CyI (%)	**P1** (%), *E/Z*		**P2** (%), *E/Z*		**BP** (%)
1	0	100	79	19	11	8	0
2	0.1	20	0	-	0	-	8
3	0.5	24	0	-	0	-	10
4	1.0	25	0	-	0	-	11

Table S9. Trapping experiment using 1,4-cyclohexadiene



Entry	Styrene (x equiv)	1,4-Cyclohexadiene (y equiv)	Conversion (%)	**P** (%), *E/Z*		**BP1** (%)	**BP2** (%)
1	2.0	0	100	91	10	1	7
2		1	100	81	10	9	7
3		5	100	46	10	26	13
4	0	0	100	0	-	9	65
5		1	100	0	-	35	40
6		5	100	0	-	68	15

Table S10. Elimination of 1-iodo-1-phenylpropane A in model Heck reaction



Entry	**A** (x equiv)	Time	Conv. Cy-I (%)	Conv. **A** (%)	**P1** (%)	**P2** (%)	**P3** (%)	**BP** (%)
1	1.0	5 h	24	100	0	0	< 5	43
		12 h	75	100	13	4	< 5	41
2	0	5 h	98	-	73	9	-	-
		12 h	100	-	76	10	-	-

V. Reference

(1) Ren, P.; Vechorkin, O.; Allmen, K. v.; Scopelliti, R.; Hu, X. *J. Am. Chem. Soc.* **2011**, *133*, 7084.

(2) Allen, J.; Horne, D. B.; Hu, E.; Kaller, M. R.; Monenschein, H.; Nguyen, T. T.; Reichelt, A.; Rzasa, R. M.; WO Patent App. PCT/US2011/036,342: 2011.

(3) Jereb, M.; Zupan, M.; Stavber, S. *Green Chem.* **2005**, *7*, 100.

(4) Qin, L.; Ren, X.; Lu, Y.; Li, Y.; Zhou, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 5915.

(5) Alcazar-Roman, L. M.; Hartwig, J. F.; Rheingold, A. L.; Liable-Sands, L. M.; Guzei, I. A. *J. Am. Chem. Soc.* **2000**, *122*, 4618.

(6) Amatore, C.; Broeker, G.; Jutand, A.; Khalil, F. *J. Am. Chem. Soc.* **1997**, *119*, 5176.

(7) Bloome, K. S.; McMahen, R. L.; Alexanian, E. J. *J. Am. Chem. Soc.* **2011**, *133*, 20146.

(8) Affo, W.; Ohmiya, H.; Fujioka, T.; Ikeda, Y.; Nakamura, T.; Yorimitsu, H.; Oshima, K.; Imamura, Y.; Mizuta, T.; Miyoshi, K. *J. Am. Chem. Soc.* **2006**, *128*, 8068.

(9) Hirano, F.; Kamezawa, M.; Kamei, H. *The bulletin of the Okayama College of Science* **1976**, *12*, 105.