Electronic Supplementary Material (ESI) for Chemical Communications

Regioselective Heck Reaction of Aliphatic Olefins and Aryl Halides

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Supporting information: procedures and characterization

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I. General

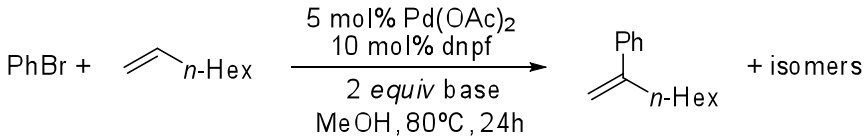
^{1}H NMR spectra were acquired on Bruker 400 MHz spectrometers and chemical shifts were recorded relative to tetramethylsilane (δ 0.00) or residual protiated solvent ($CDCl_3$: δ 7.26). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The number of 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 100 MHz on 400 MHz instruments and chemical shifts were recorded relative to solvent resonance ($CDCl_3$: δ 77.16). Proof of purity of new compounds was demonstrated with copies of ^{1}H and ^{13}C spectra. 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.

1,1′-Bis[di(1-naphthyl)phosphino]ferrocene and 1,1′-bis[di(2-naphthyl)phosphino]-ferrocene were prepared according to our previous reported procedures.[1] *N*-(2-Bromophenyl)acetamide[2], *N*-(5-hexenyl)phthalimide[1], *tert*-butyl 5-bromo-1*H*-indole-1-carboxylate[3] and 1-bromo-3,4-dihydronaphthalene[4] was prepared by using reported procedures. Methanol was distilled over sodium under argon atmosphere and stored in a Schlenk tube in an argon-filled glove box.

II. Condition optimization for Heck reaction

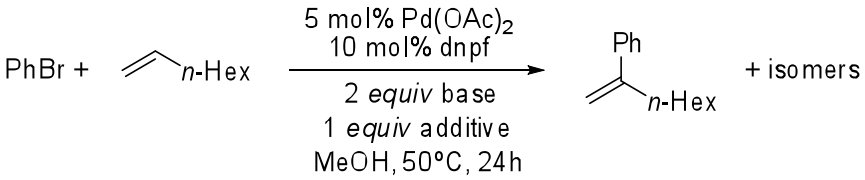
Typical procedure using 0.1 mmol of PhBr: In an argon-filled glove box, a dry 4-mL vial containing a magnetic stir bar was charged with $Pd(OAc)_2$ (5 mol%, 1.1 mg, 0.005 mmol), dnpf (10 mol%, 7.5 mg, 0.010 mmol) and 0.5 mL of dry Methanol. After stirring at room temperature for 10 minutes, phenyl bromide (0.1 mmol, 15.7 mg), 1-octene (2 equiv, 0.20 mmol, 22.4 mg) and tri-*n*-butyl amine (2 equiv, 0.20 mmol, 37 mg) were added sequentially via syringe. To the reaction mixture was added tri-*n*-butylamine hydrochloride (1 equiv, 0.1 mmol, 22.2 mg) at last. The vial was capped tightly and the mixture was heated with vigorous stirring in aluminum heating block maintained at 50 ºC. After stirring for 24 hours, the reaction mixture was cooled to room temperature and 1-dodecane was added (10 μl). The reaction mixture was diluted with dichloromethane to give a homogeneous solution. Aliquots were taken and passed through a short plug of silica gel with diethyl ether washings. The filtrate was subjected to GC analysis to determine the conversion of aryl bromide, yield and selectivity of the Heck products. The isomers of the products were identified by GCMS. *^{1}H NMR spectroscopy was unsuitable to determine the amount of minor isomers due to low signal intensity and overlap of signals on the ^{1}H NMR spectra.*

(a) Effect of base without using acidic additives



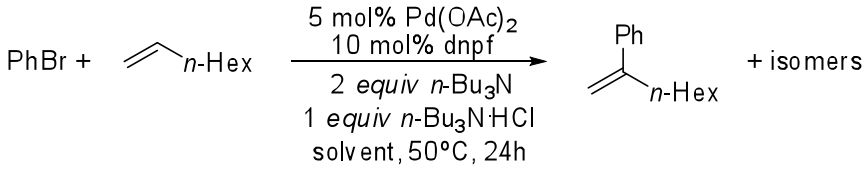
Entry	Base	Conv (%)	Desired isomer (%)	Selectivity
1	NaOAc	7	1	0.2
2	Li_2CO_3	67	36	2
3	K_3PO_4	100	6	0.3
4	Et_3N	43	20	2
5	DIPEA	61	38	3
6	Cy_2NMe	96	70	4
7	Urotropine	37	24	2.5
8	2,6-Lutidine	8	4	1
9	Proton sponge	91	61	3
10	DBU	40	12	2
11	DABCO 1.2 *equiv*	17	12	2
12	DABCO	24	16	3
13	nBu_3N	99	60	4

(b) Effect of base together with acidic additives



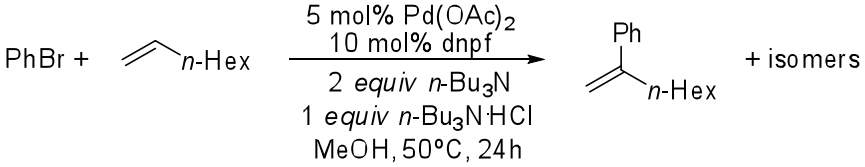
Entry	Base + Additive (equiv)	Conv (%)	Desired isomer (%)	Selectivity
1	nBu$_3$N (2)	64	41	5
2	nBu$_3$N (2) nBu$_3$N·HCl (0.2)	65	48	7
3	nBu$_3$N (2) nBu$_3$N·HCl (0.5)	80	63	10
5	nBu$_3$N (2) nBu$_3$N·HCl (1)	99	83	11
6	nBu$_3$N (2) nBu$_3$N·HOTf (1)	60	45	6
7	nBu$_3$N (2) nBu$_3$N·HOTs (1)	59	30	3.5
8	nBu$_3$N (2) nBu$_4$NCl (1)	80	65	7
9	nBu$_3$N (2) nBu$_4$NBr (1)	71	57	11
10	nBu$_3$N (2) nBu$_4$NOAc (1)	57	39	6
11	Et$_3$N (2) Et$_3$N·HCl (1)	16	13	5
12	DIPEA (2) DIPEA·HOTf (1)	20	13	2
13	nBu$_3$N (2) ZnCl$_2$ (1)	61	44	5
14	nBu$_3$N (2) Zn(OTf)$_2$ (1)	36	13	2
15	nBu$_3$N (2) Sc(OTf)$_3$ (1)	40	14	2
16	DABCO (2)	8	8	14

(c) Effect of solvents



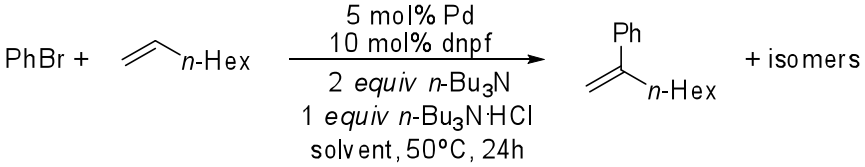
Entry	Solvent	Conversion (%)	Desired isomer (%)	Selectivity
1	MeOH	99	83	11
2	EtOH	55	38	10
3	*n*BuOH	45	32	11
4	*i*PrOH	20	6	10
5	*t*BuOH	15	0	-
6	Ethylene glycol	39	13	4
7	MeCN	14	0	-
8	DMF	13	0	-
9	DMA	12	0	-
10	NMP	10	0	-
11	DMPU	16	0	-
12	DMSO	16	0	-
13	Toluene	10	0	-
14	1,4-Dioxane	10	0	-

(d) Effect of ligands



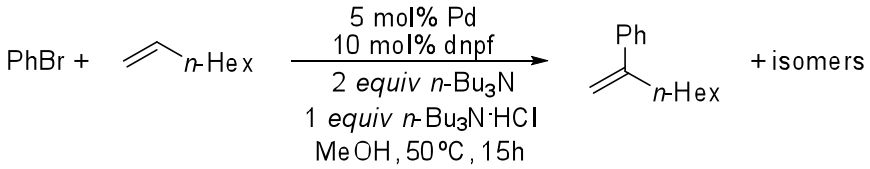
Entry	Ligand	Conversion (%)	Desired isomer (%)	Isomers (%)	Selectivity
1	dppe	19	0	0	-
2	dppp	8	0	0	-
3	dppb	5	0	0	-
4	Xantphos	12	0	0	-
5	*rac*-BINAP	12	2	0	-
6	DPEphos	86	5	47	0.1
7	P*t*Bu$_3$ (20%)	68	1	40	<0.1
8	dppf	39	14	2	7
9	dippf	17	2	1	2
10	dnpf	99	83	8	11
11	d(2-naphthyl)pf	27	5	7	0.8

(e) Effect of palladium source



Entry	Pd source	Conversion (%)	Desired isomer (%)	Isomers (%)	Selectivity
1	$Pd(OAc)_2$	99	83	8	11
2	$Pd(acac)_2$	98	77	7	11
3	$Pd(CF_3CO_2)_2$	74	63	5	12
4	$Pd(dba)_2$	7	0	0	-
5	$Pd_2(dba)_3$	8	0	0	-

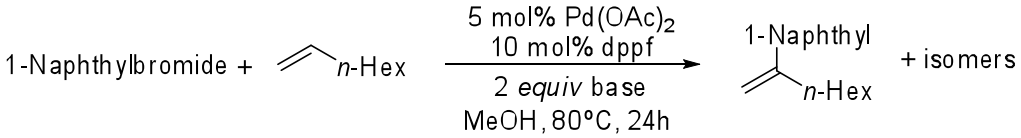
(f) Amount of the olefin and catalyst



Entry	1-Octene	Conversion of PhBr (%)	Desired product (%)	Isomers (%)	Selectivity
1	1.2 *equiv*	47	25	6	4
2	1.5 *equiv*	56	34	6	5
3	2 *equiv*	86	70	6	11
4[a]	2 *equiv*	53	40	4	10

[a] Catalyst: 2% of $Pd(OAc)_2$ and 4% of dnpf.

(g) Effect of bases in Heck reaction of 1-naphthyl bromide using 0.1 mmol of ArBr



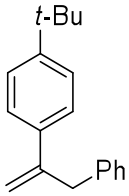
Entry	Base	Conv (%)	Desired isomer (%)	Selectivity	ArH (%)
1	nBu$_3$N 2 *equiv*	100	61	10	21
2	nBu$_3$N 2 *equiv* nBu$_3$N·HCl 1 *equiv*	100	59	11	27
3[a]	nBu$_3$N 2 *equiv* nBu$_3$N·HCl 1 *equiv*	100	48	8	38
4	DABCO 2 *equiv*	100	88	10	3
5[a]	DABCO 2 *equiv*	63	52	6	2
6	DABCO *1.2 equiv*	100	83	9	5
7	DABCO 2 *equiv* DABCO·HCl 1 *equiv*	95	84	9	2
8	Cy$_2$NMe 2 *equiv*	99	78	9	13
9	DIPEA 2 *equiv*	100	53	9	32
10	Et$_3$N 2 *equiv*	100	79	10	11
11	2,6-Lutidine 2 *equiv*	41	32	8	1
12	Proton sponge 2 *equiv*	100	88	10	2
13	Li$_2$CO$_3$ 2 *equiv*	100	81	9	3
14	Urotropine 2 *equiv*	87	67	9	3

[a] Using Dnpf as supporting ligand.

III. Isolation of Heck products

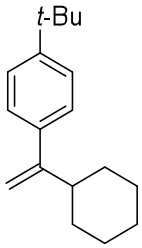
Typical procedure I using tri-*n*-butylamine hydrochloride additive: In an argon-filled glove box, to a dry 10-mL Schlenk tube containing a magnetic stir bar was charged $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), dnpf (37.7 mg, 0.05 mmol) and 2.5 mL of dry methanol. After stirring at room temperature for 10 minutes, aryl bromide (0.5 mmol), terminal olefin (2 equiv, 1.0 mmol), tri-*n*-butylamine (2 equiv, 1.0 mmol, 185 mg) and tri-*n*-butylamine hydrochloride (1 equiv, 0.5 mmol, 111 mg) were added sequentially. The Schlenk tube was capped tightly and the mixture was heated with vigorous stirring in a 50 ºC oil bath. After the aryl bromide was fully consumed (monitored by GC), the reaction mixture was cooled to room temperature and the solvent was removed on a rotary evaporator under reduced pressure. The resulting residue was purified by silica gel flash chromatography. The isomers in a reaction mixture were identified by GCMS. In the crude product, the ratio of the desired isomer versus all other isomers was determined by GC unless stated otherwise. The minor isomers can vary from 1 to 8 depending on the substrates, catalysts and conditions (detected by GC and GCMS). The typical procedure was used for all the isolation on 0.50 mmol scales (aryl bromides), unless stated otherwise. *Note: ^{1}H NMR spectroscopy was unsuitable to determine the amount of minor isomers due to low signal intensity and overlap of signals on ^{1}H NMR spectra.*

Typical procedure II without using tri-*n*-butylamine hydrochloride additive: In an argon-filled glove box, to a dry 10-mL Schlenk tube containing a magnetic stir bar was charged $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), dnpf (37.7 mg, 0.05 mmol) and 2.5 mL of dry methanol. After stirring at room temperature for 10 minutes, aryl bromide (0.50 mmol), aliphatic olefin (2 equiv, 1.0 mmol) and DABCO (1.2 equiv, 0.6 mmol, 67 mg) were added sequentially. The Schlenk tube was capped tightly and the mixture was heated with vigorous stirring in an 80 ºC oil bath. After the aryl bromide was fully consumed (monitored by GC), the reaction mixture was worked up as described above.



***p-tert*-Butyl-1-benzylstyrene [1393539-25-7].** The reaction was set up following typical procedure I with 10% $Pd(OAc)_2$, 12% dnpf and 3 equiv of allylbenzene and stirred at 50 ºC for 2 days. The product was purified by flash chromatography (hexane) as colorless oil (107 mg, 86%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 10:1 by GC. 10:1 after purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.36 (m, 2H), 7.32-7.16 (m, 7H), 5.51 (d, J = 1.0 Hz, 1H), 4.96 (d, J = 1.0 Hz, 1H), 3.82 (s, 2H), 1.30 (s, 9H).

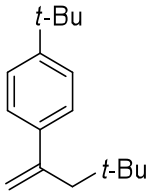


***p-tert*-Butyl-1-cyclohexylstyrene**. The reaction was set up following typical procedure I with 10% $Pd(OAc)_2$, 12% dnpf and 5 equivalent of olefin and stirred at 80 ºC for 32 hours. The product was purified by flash chromatography (hexane) as colorless oil (104 mg, 86%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 10:1 by GC. 10:1 after purification. When 2 equivalents of the olefin was used, only 62% of the desired product was obtained with 13:1 selectivity.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.25 (m, 4H), 5.14 (d, J = 1.1 Hz, 1H), 4.97 (m, 1H), 2.44-2.38 (m, 1H), 1.86-1.69 (m, 5H), 1.37-1.12 (m, 14H).

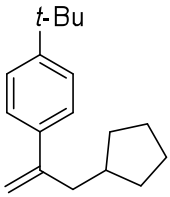
^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 150.0, 140.0, 126.3 (2 overlapping signals), 125.2(x2), 109.8, 42.6, 34.6, 33.0, 31.5, 27.0, 26.6.

GCMS (EI): Calcd for $C_{18}H_{26}$: 242.2. Found: 242.2.



***p-tert*-Butyl-1-neopentylstyrene [1393539-22-4].** The reaction was set up following typical procedure I with 5% $Pd(OAc)_2$ and 10% dnpf and stirred at 50 ºC for 3 days. The product was purified by flash chromatography (hexane) as colorless oil (89 mg, 76%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 11:1 by GC. 13:1 after purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (ψs, 4H), 5.24-5.23 (d, J = 2.1 Hz, 1H), 4.97-4.96 (m, 1H), 2.45 (s, 2H), 1.31 (s, 9H), 0.81 (s, 9H).

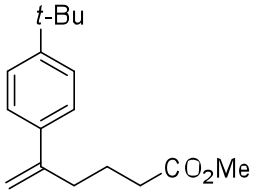


***p-tert*-Butyl-1-(cyclopentylmethyl)styrene .** The reaction was set up following typical procedure I with 5% $Pd(OAc)_2$ and 10% dnpf and stirred at 50 ºC for 3 days. The product was purified by flash chromatography (hexane) as colorless oil (110 mg, 91%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 11:1 by GC. 11 :1 after purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (ψs, 4H), 5.23 (s, 1H), 5.00 (s, 1H), 2.49-2.47 (d, J = 7.4 Hz, 2H), 1.98-1.91 (m, 1H), 1.71-1.65 (m, 2H), 1.62-1.57 (m, 2H), 1.49-1.44 (m, 2H), 1.32 (s, 9H), 1.20-1.11 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 148.1, 138.7, 125.0, 125.2, 112.2, 42.1, 38.3, 34.6, 32.6, 31.5, 25.2.

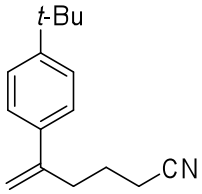
GCMS (EI): Calcd for $C_{18}H_{26}$: 242.2. Found: 242.1.



Methyl 5-(*p-tert*-butylphenyl)-5-hexenoate [1393539-26-8]. The reaction was set up

following typical procedure I with 10% $Pd(OAc)_2$ and 12% dnpf and stirred at 50 ºC for 2 days. The product was purified by flash chromatography (hexane/ethyl acetate 10:1) as colorless oil (125 mg, 96%). The ratio of the desired isomer versus all other isomerswas determined by GC to be 10:1 in the crude product and 10:1 after purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (ψs, 4H), 5.30 (d, *J* = 1.1 Hz, 1H), 5.03-5.02 (m, 1H), 3.66 (s, 3H), 2.54 (t, *J* = 7.4 Hz, 2H), 2.34 (t, *J* = 7.4 Hz, 2H), 1.80 (ψqn, *J* = 7.4 Hz, 2H), 1.32 (s, 9H).

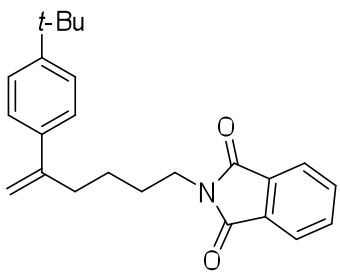


5-(*p-tert*-Butylphenyl)-5-hexenenitrile. The reaction was set up following typical procedure I with 10% $Pd(OAc)_2$ and 12% dnpf and stirred at 50 ºC for 2 days. The product was purified by flash chromatography (hexane/ethyl acetate 20:1) as colorless oil (85 mg, 75%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 15:1 by GC. 12:1 after purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.25 (m, 4H), 5.34 (s, 1H), 5.09 (d, *J* = 1.0 Hz, 1H), 2.68 (t, *J* = 7.2 Hz, 2H), 2.32 (t, *J* = 7.1 Hz, 2H), 1.81 (ψqn, *J* = 7.2 Hz, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 146.2, 137.4, 126.2, 125.9, 120.1, 113.8, 35.0, 34.4, 31.8, 24.2, 16.8.

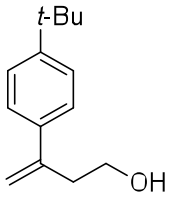
GCMS (EI): Calcd for $C_{16}H_{21}N$: 227.3. Found: 227.0.



***2-p-tert*-Butylphenyl-6-phthalimido-1-hexene [1393539-33-7].** The reaction was set

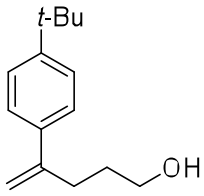
up following typical procedure I with 10% $Pd(OAc)_2$ and 12% dnpf and stirred at 50 ºC for 29 hours. The desired product and starting material coeluted during flash chromatography (hexane/ethyl acetate 10:1). The desired product was obtained as colorless oil after bulb-to-bulb distillation to remove unreacted starting material (167mg, 92%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 33:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.32 (ψs, 4H), 5.26 (d, *J* = 1.4 Hz, 1H), 5.03-5.02 (m, 1H), 3.68 (t, *J* = 7.3 Hz, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 1.72 (ψqn, *J* = 7.5 Hz, 2H), 1.50 (ψqn, *J* = 7.5 Hz, 2H), 1.31 (s, 9H).



2-(*p-tert*-Butylphenyl)-1-butene-4-ol [1134201-55-0]. The reaction was set up following typical procedure I with 10% $Pd(OAc)_2$, 12% dnpf and 3 equivalents of olefin and stirred at 80 ºC for one day. The product was purified by flash chromatography (hexane/ethyl acetate 10:1) followed by using bulb to bulb distillation (for removal of tri-*n*-butylamine) as colorless oil (74 mg, 72%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 11:1 by GC. 11:1 after purification.

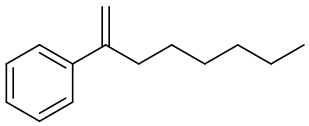
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (ψs, 4H), 5.41 (d, *J* = 1.3 Hz, 1H), 5.12-5.12 (m, 1H), 3.73 (t, *J* = 6.4 Hz, 2H), 2.78 (td, J = 6.4, 0.9 Hz, 2H), 1.48 (br s, 1H), 1.32 (s, 9H).



2-(*p-tert*-Butylphenyl)-1-pentene-5-ol [1393539-27-9]. The reaction was set up following typical procedure I with 5% $Pd(OAc)_2$ and 10% dnpf and stirred at 80 ºC

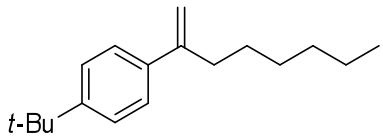
for 28 hours. The product was purified by flash chromatography (hexane/ethyl acetate 10:1 to 5:1) followed by using bulb to bulb distillation (for removal of tri-*n*-butylamine) as colorless oil (85 mg, 78%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 14:1 by GC. 14:1 after purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (ψs, 4H), 5.29 (s, 1H), 5.05 (s, 1H), 3.66 (t, *J* = 6.4 Hz, 2H), 2.59 (t, *J* = 7.5 Hz, 2H), 1.73 (tt, *J* = 7.5, 6.4 Hz, 2H), 1.40 (br s, 1H), 1.32 (s, 9H).



2-Phenyl-1-octene [5698-49-7]. The reaction was set up following typical procedure I with 5% $Pd(OAc)_2$ and 10% dnpf and the reaction mixture was stirred at 50 °C for 2 days. The product was purified by flash chromatography (hexane) as colorless oil (80 mg, 85%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 10:1 by GC. 10:1 after purification.

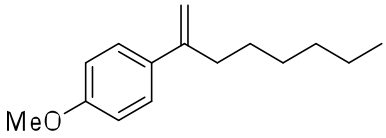
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.39 (m, 2H), 7.34-7.30 (m, 2H), 7.28-7.24 (m, 1H), 5.26 (d, *J* = 1.3 Hz, 1H), 5.05 (d, *J* = 1.3 Hz, 1H), 2.50 (t, *J* = 7.5 Hz, 2H), 1.44 (ψqn, *J* = 7.3 Hz, 2H), 1.36-1.26 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H).



2-(*p-tert*-Butylphenyl)-1-octene [1393538-91-4]. The reaction was set up following typical procedure I with 5% $Pd(OAc)_2$ and 10% dnpf and the reaction mixture was stirred at 50 °C for 2 days. The product was purified by flash chromatography (hexane) as colorless oil (112 mg, 92%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 17:1 by GC. 12:1 after purification.

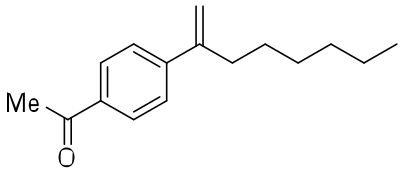
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (ψs, 4H), 5.25 (d, *J* = 1.5 Hz, 1H), 5.01-5.00 (m, 1H), 2.48 (t, *J* = 7.6 Hz, 2H), 1.48-1.44 (m, 2H), 1.35-1.27 (m, 15H), 0.87 (t, *J* = 6.8

Hz, 3H).



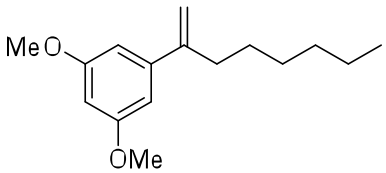
2-(*p*-Anisyl)-1-octene [129182-23-6]. The reaction was set up following typical procedure I with 5% $Pd(OAc)_2$ and 10% dnpf and the reaction mixture was stirred at 50 ºC for 3 days. The product was purified by flash chromatography (hexane) as colorless oil (95 mg, 87%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 13:1 by GC. 15:1 after purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (m, 2H), 6.87-6.85 (m, 2H), 5.18 (d, *J* = 1.4 Hz, 1H), 4.97-4.96 (m, 1H), 3.81 (s, 3H), 2.46 (t, *J* = 7.5 Hz, 2H), 1.46-1.42 (m, 2H), 1.34-1.24 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H).



2-(*p*-Acetylphenyl)-1-octene [688805-09-6]. The reaction was set up following typical procedure I with 5% $Pd(OAc)_2$, 10% dnpf and 3 equivalents of 1-octene and the reaction mixture was stirred in 80 ºC oil bath for 2 days. The product was purified by flash chromatography (hexane/ethyl acetate 50:1) as colorless oil (90 mg, 78%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 9:1 by GC. 13:1 after purification.

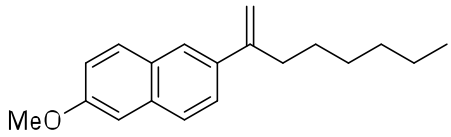
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 5.35 (s, 1H), 5.16 (d, *J* = 1.1 Hz, 1H), 2.60 (s, 3H), 2.51 (t, *J* = 7.5 Hz, 2H), 1.47-1.39 (m, 2H), 1.35-1.26 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H).



2-(3,5-Dimethoxyphenyl)-1-octene [499237-38-6]. The reaction was set up following

typical procedure I with 5% $Pd(OAc)_2$ and 10% dnpf and the reaction mixture was stirred at 50 ºC for 2 days. The product was purified by flash chromatography (hexane/ethyl acetate 20: 1) as colorless oil (113 mg, 91%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 16:1 by GC. 16:1 after purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.55 (d, *J* = 2.2 Hz, 2H), 6.39 (t, *J* = 2.2 Hz, 1H), 5.25 (s, 1H), 5.04 (s, 1H), 3.80 (s, 6H), 2.46-2.42 (t, *J* = 7.5 Hz, 2H), 1.47-1.40 (m, 2H), 1.33-1.27 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H).

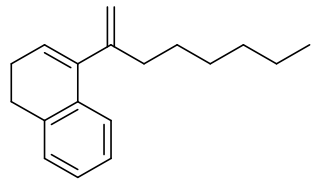


2-(6-Methoxy-2-naphthyl)-1-octene. The reaction was set up following typical procedure I with 5% $Pd(OAc)_2$, 10% dnpf and 3 equivalents of 1-octene and the reaction mixture was stirred in an 80 ºC oil bath for 2 days. The product was purified by flash chromatography (hexane/ethyl acetate 50:1) as colorless oil (108 mg, 81%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 11:1 by GC. 11:1 after purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.67 (m, 3H), 7.55 (d, *J* = 8.6, 1.8 Hz, 1H), 7.15-7.10 (m, 2H), 5.37 (d, *J* = 1.3 Hz, 1H), 5.11 (m, 1H), 3.91 (s, 3H), 2.60 (t, *J* = 7.5 Hz, 2H), 1.51-1.47 (m, 2H), 1.37-1.25 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 148.7, 136.7, 134.0, 129.8, 129.0, 126.7, 125.4, 124.6, 119.0, 111.9, 105.7, 55.4, 35.5, 31.8, 29.2, 28.5, 22.8, 14.2.

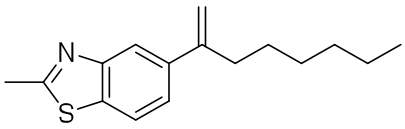
GCMS (EI): Calcd for $C_{19}H_{24}O$: 268.2. Found: 268.2.



3,4-Dihydro-1-(1-octe-2-nyl)naphthalene [1393538-99-2]. The reaction was set up following typical procedure I by using 5% $Pd(OAc)_2$ and 10% dnpf and the reaction mixture was stirred at 50 ºC for 3 days. The product was purified by flash chromatography (hexane) as colorless oil (102 mg, 85%). The ratio of the desired

isomer versus all other isomers in the crude product was determined to be 9:1 by GC. (46:1 after purification)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16-7.12 (m, 4H), 5.92 (t, *J* = 4.6 Hz, 1H), 5.05 (m, 1H), 4.99 (d, *J* = 2.4 Hz, 1H), 2.75 (t, *J* = 7.9 Hz, 2H), 2.29-2.22 (m, 4H), 1.53-1.34 (m, 2H), 1.29-1.21 (m, 6H), 0.86 (t, *J* = 4.6 Hz, 3H).

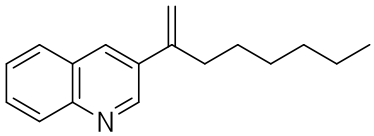


2-(2-Methyl-5-benzothiazolyl)-1-octene . The reaction was set up following typical procedure I by using 5% $Pd(OAc)_2$ and 10% dnpf and the reaction mixture was stirred at 50 ºC for 24 hours. The product was purified by flash chromatography (hexane/ethyl acetate 30:1) as colorless oil (94 mg, 72%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 16:1 by GC. 18:1 after purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 1.6 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.42 (dd, *J* = 8.3, 1.7 Hz, 1H), 5.34 (d, *J* = 1.4 Hz, 1H), 5.12 (m, 1H), 2.83 (s, 3H), 2.56 (td, *J* = 7.6, 0.7 Hz), 1.63-1.36 (m, 2H), 1.34-1.23 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 153.9, 148.5, 139.9, 134.5, 123.4, 121.1, 119.9, 112.8, 35.8, 31.8, 29.2, 28.5, 22.8, 20.3, 14.2.

GCMS (EI): Calcd for $C_{16}H_{21}NS$: 259.1. Found: 259.1.



2-(3-Quinolinyl)-1-octene. The reaction was set up following typical procedure I by using 10% $Pd(OAc)_2$, 15% dnpf and 5 equivalent of olefin and the reaction mixture was stirred at 80 ºC for 3 days. The product was purified by flash chromatography (hexane/ethyl acetate 10: 1 containing 1% triethylamine) and subsequent vacuum distillation (to remove tri-*n*-butylamine) as colorless oil (80 mg, 67%). The ratio of

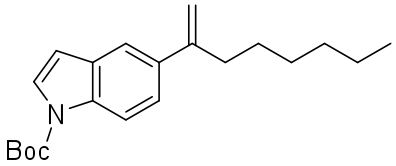
the desired regioisomer versus all other isomers in the crude product was determined to be 10:1 by GC. 10:1 after purification.

When 15% Pd and 18% dnpf were used as catalyst and 3 equiv of the olefin was used, 61% yield and 6:1 selectivity was obtained after 4 days at 80 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (d, *J* = 2.2 Hz, 1H), 8.10-8.07 (m, 2H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.70-7.66 (m, 1H), 7.56-7.52 (m, 1H), 5.47 (s, 1H), 5.26 (d, *J* = 1.0 Hz, 1H), 2.62 (t, *J* = 7.5 Hz, 2H), 1.52-1.46 (m, 2H), 1.38-1.25 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H).

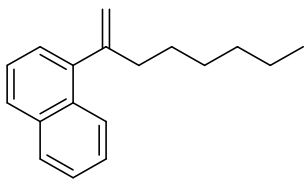
^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 147.5, 145.9, 134.1, 132.1, 129.3, 129.2, 128.1, 127.9, 126.9, 114.4, 35.3, 31.8, 29.1, 28.2, 22.7, 14.2.

GCMS (EI): Calcd for $C_{17}H_{21}N$: 239.2. Found: 239.1.



***N*-(*t*-Butoxycarbonyl)-5-(2-octenyl)indole [1393538-97-0].** The reaction was set up following typical procedure I by using 5% $Pd(OAc)_2$ and 10% dnpf and the reaction mixture was stirred at 80 ºC for 20 hours. The product was purified by flash chromatography (hexane/ethyl acetate 50:1) as colorless oil (149 mg, 91%). The ratio of the desired isomer versus all other isomers in both the crude and purified samples was determined to be 20:1 by NMR spectroscopy.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.6 Hz, 1H), 7.58-7.57 (m, 2H), 7.38 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.58 (d, *J* = 3.5 Hz, 1H), 5.26 (d, *J* = 1.7 Hz, 1H), 5.04 (m, 1H), 2.55 (t, *J* = 7.4 Hz, 2H), 1.67 (s, 9H), 1.55-1.41 (m, 2H), 1.36-1.24 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H).

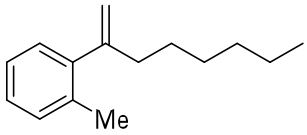


2-(1-Naphthyl)-1-octene [101720-90-5]. The reaction was set up following typical

procedure II by using 5% $Pd(OAc)_2$ and 10% dppf and the reaction mixture was stirred in 80 ºC oil bath for 38 hours. The product was purified by flash chromatography (hexane) as colorless oil (102 mg, 85%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 10:1 by GC. 12:1 after purification. When 5% $Pd(OAc)_2$ and 10% dppf were used as catalyst, 52% yield and 6:1 selectivity was obtained after 24 h at 80 ºC.

Typical procedure I by using 5% $Pd(OAc)_2$ and 10% dnpf and the reaction mixture was stirred in 80 ºC oil bath for 17 hours. The product was purified by flash chromatography (hexane) as colorless oil (55 mg, 46%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 8:1 by GC. 34:1 after purification. The reduction byproduct naphthalene was about 25%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-8.02 (m, 1H), 7.86-7.83 (m, 1H), 7.76 (d, J = 7.2 Hz, 1H), 7.48-7.41 (m, 3H), 7.28-7.26 (m, 1H), 5.38-5.37 (m, 1H), 5.05 (d, J = 2.2 Hz, 1H), 2.50 (t, J = 7.5 Hz, 2H), 1.44-1.21 (m, 8H), 0.85 (t, J = 6.8 Hz, 3H).

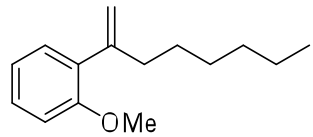


2-(*o*-Toly)-1-octene [1393539-01-9]. The reaction was set up following typical procedure II by using 5% $Pd(OAc)_2$ and 10% dnpf and the reaction mixture was stirred in 80 ºC oil bath for 2 days. The product was purified by flash chromatography (hexane) as colorless oil (87 mg, 86%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 9:1 by GC. 11:1 after purification.

Typical procedure I by using 5% $Pd(OAc)_2$ and 10% dnpf and the reaction mixture was stirred in 80 ºC oil bath for 2 days. The product was purified by flash chromatography (hexane) as colorless oil (55 mg, 54%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 8:1 by GC. 13:1 after purification. A significant amount of ArBr reduction was observed by GC.

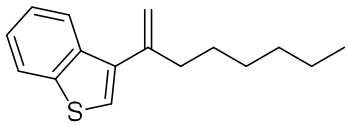
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.11 (m, 3H), 7.07-7.05 (m, 1H), 5.17-5.15 (m,

1H), 4.84 (d, *J* = 2.1 Hz, 1H), 2.33-2.29 (m, 5H), 1.40-1.23 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 3H).



2-(*o*-Anisyl)-1-octene [1046468-80-7]. The reaction was set up following typical procedure I with 5% $Pd(OAc)_2$ and 10% dnpf and the reaction mixture was stirred at 50 ºC for 2 days. The product was purified by flash chromatography (hexane) as colorless oil (78 mg, 72%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 6:1 by GC. 7:1 after purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.21 (m, 1H), 7.13 (dd, *J* = 7.4, 1.8 Hz, 1H), 6.92 (ψtd, *J* = 7.4, 1.0 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 5.13-5.12 (m, 1H), 4.99 (d, *J* = 2.2 Hz, 1H), 3.82 (s, 2H), 2.46 (t, *J* = 7.1 Hz, 2H), 1.35-1.21 (m, 8H), 0.86 (t, *J* = 6.9 Hz, 3H).



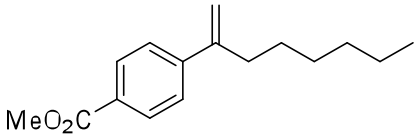
3-(2-Octenyl)benzothiophene. The reaction was set up following typical procedure II by using 5% $Pd(OAc)_2$ and 10% dppf and the reaction mixture was stirred in 80 ºC oil bath for 38 hours. The product was purified by flash chromatography (hexane) as colorless oil (96 mg, 79%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 12:1 by GC. 12:1 after purification. When 5% $Pd(OAc)_2$ and 10% dnpf were used as catalyst, low yield and 4:1 selectivity resulted after 24 h at 80 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.84 (m, 2H), 7.40-7.32 (m, 2H), 7.23 (s, 1H), 5.31-5.30 (m, 1H), 5.26 (d, *J* = 1.6 Hz, 1H), 2.52 (t, *J* = 7.5 Hz, 2H), 1.48-1.40 (m, 2H), 1.35-1.21 (m, 6H), 0.85 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 140.6, 138.8, 138.3, 124.3, 124.2, 123.4, 122.9,

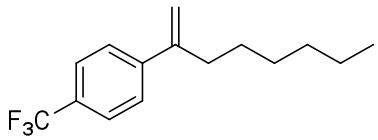
122.3, 114.4, 37.7, 31.8, 29.1, 28.3, 22.8, 14.2.

GCMS (EI): Calcd for $C_{16}H_{20}S$: 244.1. Found: 244.1



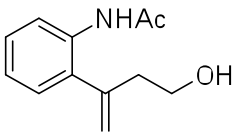
2-(*p*-Methoxycarbonylphenyl)-1-octene [947607-39-8]. The reaction was set up following typical procedure II by using 10% $Pd(OAc)_2$, 12% dnpf, 3 equivalents of 1-octene and 2 equivalents of DABCO and the reaction mixture was stirred in 80 ºC oil bath for 5 days. The product was purified by flash chromatography (hexane) as colorless oil (99 mg, 80%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 9:1 by GC. 11:1 after purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.97 (m, 2H), 7.47-7.44 (m, 2H), 5.34 (s, 1H), 5.15 (d, *J* = 1.2 Hz, 1H), 3.92 (s, 3H), 2.50 (t, *J* = 7.5 Hz, 2H), 1.54-1.41(m, 2H), 1.34-1.26 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H).



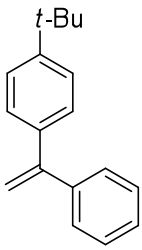
2-(*p*-Trifluoromethylphenyl)-1-octene [947607-37-6]. The reaction was set up following typical procedure II by using 5% $Pd(OAc)_2$, 10% dnpf, 5 equivalent of 1-octene and 2 equivalents of DABCO and the reaction mixture was stirred in 80 ºC oil bath for 3 days (70% conversion of ArBr). The product was purified by flash chromatography (hexane) as colorless oil (80 mg, 63%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 12:1 by GC. 12:1 after purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 5.31 (s, 1H), 5.15-5.14 (m, 1H), 2.50 (t, *J* = 7.5 Hz, 2H), 1.45-1.35 (m, 2H), 1.34-1.26 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H).



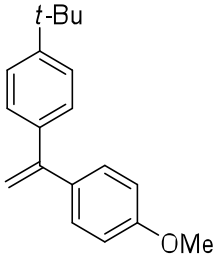
2-(*o*-Acetamidophenyl)-1-penten-5-ol [1312597-98-0]. The reaction was set up following typical procedure II by using 10% $Pd(OAc)_2$, 12% dppf, 3 equivalents of the olefin and 2 equivalents of DABCO and the reaction mixture was stirred in 80 ºC oil bath for 2 days. The product was purified by silica gel chromatography (hexane/ethyl acetate 1:2 containing 1% triethylamine) as yellow colored oil and only desired product was found from NMR spectrum (78 mg, 76%). The product was found to decompose on untreated silica gel and thus, powder silica gel must be treated first with triethylamine before dry packing. The ratio of the desired isomer versus all other isomers in the crude product was >100:1 as determined by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.2 Hz, 1H), 8.12 (br s, 1H), 7.30-7.25 (m, 1H), 7.10-7.06 (m, 2H), 5.44 (d, *J* = 1.1 Hz, 1H), 5.13 (s, 1H), 3.70-3.66 (ψq, *J* = 5.0 Hz, 2H), 2.63 (t, *J* = 5.6 Hz, 2H), 2.11 (s, 3H), 1.70 (br s, 1H).



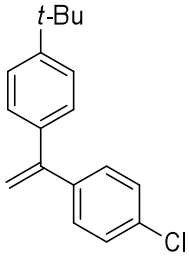
α-(*p*-*t*-Butylphenyl)styrene [17582-85-3]. The reaction was set up following typical procedure I with 10% $Pd(OAc)_2$ and 12% dnpf and stirred at 50 ºC for 2 days. The product was purified by flash chromatography (hexane) as colorless oil (90 mg, 76%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 13:1 by GC. 88:1 after purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.25 (m, 9H), 5.45 (d, *J* = 1.2 Hz, 1H), 5.40 (d, *J* = 1.2 Hz, 1H), 1.34 (s, 9H).



1-(*p*-*t*-Butylphenyl)-1-(*p*-methoxyphenyl)ethene [124419-76-7]. The reaction was set up following typical procedure I with 10% $Pd(OAc)_2$,12% dnpf, *p*-(*tert*-butyl)bromobenzene (1.5 equiv, 0.75 mmol, 160 mg) and *p*-methoxystyrene (1.0 equiv, 0.50 mmol, 67 mg) and stirred at 50 ºC for 2 days. The product was purified by flash chromatography (hexane) as white solid (107 mg, 81%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 11:1 by GC. 66:1 after purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.33 (m, 2H), 7.31-7.25 (m, 4H), 6.88-6.84 (m, 2H), 5.35-5.34 (m, 2H), 3.83 (s, 3H), 1.34 (s, 9H).



1-(*p*-*t*-Butylphenyl)-1-(*p*-chlorophenyl)ethene. The reaction was set up following typical procedure I with 10% $Pd(OAc)_2$, 20% dnpf, *p*-*t*-butylphenyl bromide (1.5 equiv, 0.75 mmol, 160 mg) and *p*-chlorostyrene (1.0 equiv, 0.50 mmol, 69 mg) and stirred at 80 ºC for 2 days. The product was purified by flash chromatography (hexane) as white solid (91 mg, 67%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 11:1 by GC. 48:1 after purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.33 (m, 2H), 7.29-7.28 (m, 4H), 7.26-7.23 (m, 2H), 5.45 (d, J = 1.1 Hz, 1H), 5.38 (d, J = 1.1 Hz, 1H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 148.9, 140.3, 138.1, 133.6, 129.8, 128.4, 127.9, 125.3, 114.3, 34.7, 31.5.

GCMS (EI): Calcd for $C_{18}H_{19}Cl$: 270.8. Found: 270.1.

IV. Mechanistic studies

Synthesis of (dnpf)Pd(Ph)Br [1393539-72-4]. The complex was synthesized according to our previously reported procedure with some modification.[1] In an argon-filled glove box, to a 25-mL Schlenk tube containing a magnetic stirring bar was added $Pd(dba)_2$ (172 mg, 0.30 mmol), dnpf (226 mg, 0.30 mmol) and dry toluene (15 mL). After stirring at room temperature for 10 minutes, PhBr (3 equiv, 141 mg, 0.90 mmol) was added. The reaction mixture was stirred at room temperature for 3 hours and then in an 80°C oil bath for 2 days. The progress of the reaction was monitored by ^{31}P NMR spectroscopy. After cooling down to room temperature, the yellow precipitation was collected by filtration in the air. The contaminant of palladium black was removed after the yellow powder was dissolved in dichloromethane and filtered through a pad of Celite. The filtrate was concentrated to dryness to give the titled complex in 98% purity (240 mg, 78%).

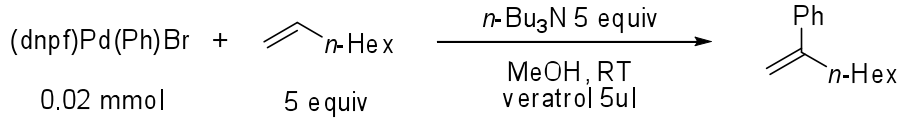
^1H NMR (400 MHz, $CDCl_3$): δ 9.85-9.76 (m, 3H), 9.57 (d, J = 8.0 Hz, 1H), 8.16 (pseudotriplet, J = 9.1 Hz, 2H), 8.05-8.00 (m, 2H), 7.95-7.89 (m, 3H), 7.84 (d, J = 8.1 Hz, 1H), 7.74-7.66 (m, 3H), 7.62 (pseudotriplet, J = 7.5 Hz, 1H), 7.46-7.32 (m, 5H), 7.27-7.21 (m, 2H), 7.13 (d, J = 8.6 Hz, 2H), 7.00-6.92 (m, 2H), 6.82-6.78 (m, 1H), 6.56-6.51 (m, 2H), 6.30 (pseudotriplet, J = 7.0 Hz, 1H), 5.95 (br s, 1H), 5.61 (br s, 1H), 4.57 (s, 1H), 4.41 (s, 1H), 4.15 (s, 2H), 3.97 (pseudosinglet, 4H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 28.7 (d, J = 28.1 Hz), 13.9 (d, J = 28.1 Hz)

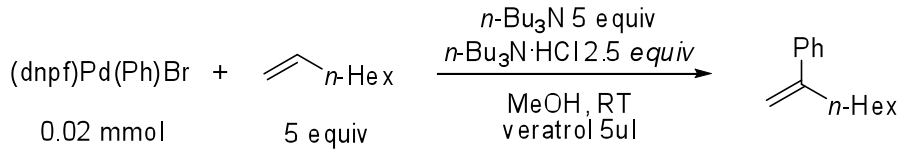
Stoichiometric reaction between (dnpf)Pd(Ph)Br and 1-octene in methanol. To oven-dried 4-mL vial equipped with a magnetic stirring bar in an argon-filled glove box was added the complex *(dnpf)Pd(Ph)Br* (20.4 mg, 0.02 mmol) followed by dry methanol (0.5 mL). To this suspension was then added 1-octene (5 equiv, 11.2 mg, 0.10 mmol), nBu$_3$N (5 equiv, 18.5 mg, 0.10 mmol) and GC standard 1,2-dimethoxybenzene (5.0 uL). The reaction mixture was vigorously stirred at room

temperature and at intervals aliquots of the sample were taken and passed through a short plug of silica gel with diethyl ether washings. The filtrate was analyzed by GC to determine the yield and the selectivity of Heck products. In a separate experiment, nBu$_3$N·HCl (2.5 equiv, 11 mg, 0.05 mmol) was included as additive and the results were also listed below (Condition B).

Condition A:



Condition B:



Entry	Condition	Time	Desired isomer (%)	Trans selectivity
1	A	10 min	11	>100:1
2	B	10 min	10	>100:1
3	A	30 min	19	>100:1
4	B	30 min	15	>100:1
5	A	1 h	28	52:1
6	B	1 h	24	55:1
7	A	5 h	58	25:1
8	B	5 h	57	26:1
9	A	24 h	69	15:1
10	B	24 h	67	17:1

V. Gram-scale synthesis of dnpf.

1,1′-Bis(dichlorophosphino)ferrocene [142691-70-1]. Under argon, to a dry 250-mL Schlenck flask was charged with ferrocene (1.86 g, 10.0 mmol), dry *N,N,N′,N′*-tetramethylethlenediamine (2.44 g, 21.0 mmol) and 50 mL of dry hexane. After ferrocene was completely dissolved, the stirred solution was treated with dropwise addition of a solution of *n*-BuLi in cyclohexane (1.96 M, 10.9 mL, 21.0 mmol) at room temperature over 15 minutes. The mixture was stirred for 24 hours under argon.

The resulting orange suspension of 1,1'-dilithioferrocene was cooled to -78 ºC in a dry ice/acetone bath and treated with dropwise addition of a solution of *N,N*-bis(diethylamino)chlorophosphine (4.42 g, 21.0 mmol) in 15 mL of dry THF over 20 minutes. After the addition, the stirred mixture was allowed to warm up to RT spontaneously and stirred at RT for 12 hours. ^{31}P NMR spectroscopy indicated that $ClP(NEt_2)_2$ was fully consumed and the desired diaminophosphine was produced in 97% purity.

The reaction mixture was chilled to -78 ºC under argon and treated with dropwise addition of a 1 M solution of HCl in diethyl ether (160 mL, 160 mmol) from an addition funnel over 2 hours. The reaction mixture was allowed to warm up to RT over 4 hours. After stirring at RT for 2 hours, ^{31}P NMR spectroscopy indicated that the hydrolysis was complete. The salt was removed by filtration in the argon-filled glove box and washed with hexanes. The filtrate was concentrated under reduced pressure to give a yellow powder (3.35 g, 86% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.72 (pseudosinglet, 8H).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 163.1.

1,1′-Bis[di(1-naphthyl)phosphino]ferrocene [1393538-46-9]. Under argon, to a dry 250-mL Schlenck flask containing 100 mL of freshly distilled THF was charged with 1-bromonaphthalene (6.2 equiv, 11.1 g, 53.5 mmol) and *N,N,N′,N′*-tetramethylethlenediamine (6 equiv, 6.0 g, 51.8 mmol). The resulting solution was then chilled to -78 ºC in a dry ice/acetone bath and then treated with

dropwise addition of a 1.96 M solution of *n*BuLi in cyclohexane (6 equiv, 26.0 mL, 51.8 mmol) over 30 minutes. After stirring at -78 ºC for 2 hours, the resulting yellow suspension was treated with dropwise addition of a solution of 1,1′-bis(dichlorophosphino)ferrocene (1 equiv, 3.35 g, 8.6 mmol) in 30 mL of dry THF over 30 minutes. After the addition, the reaction mixture was allowed to warm up to RT spontaneously with evaporation of dry ice and kept stirred for 12 h at RT. The completion of reaction was confirmed by ^{31}P NMR spectroscopy. The brown mixture was concentrated on a rotary evaporator under reduced pressure. The residue was dissolved in 100 mL of dichloromethane and filtered through a pad of Celite with dichloromethane washing to remove lithium salt in air. The orange filtrate was concentrated and filtered through a short pad of silica gel with degassed dichloromethane in air quickly with dichloromethane washing. After removal of most solvent, the residue was treated with acetone (~20 mL) to precipitate the desired phosphine ligand. The yellow compound was collected by filtration and washing with a small amount of acetone (3.2 g, 50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70-8.65 (m, 4H), 7.81-7.73 (m, 8H), 7.46-7.40 (m, 8H), 7.23-7.20 (d, J = 7.9 Hz, 4H), 7.12-7.08 (m, 4H), 3.97 (t, J = 1.6 Hz, 4H), 3.88 (d, J = 1.8 Hz, 4H).

^{31}P NMR (162 MHz, $CDCl_3$): δ -41.3.

VI. Reference

(1) Qin, L.; Ren, X.; Lu, Y.; Li, Y.; Zhou, J. *Angew. Chem. Int. Ed.* **2012**, *51*, 5915.
(2) Cho, G. Y.; Rémy, P.; Jansson, J.; Moessner, C.; Bolm, C. *Org. Lett.* **2004**, *6*, 3293.
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