Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information

The Influence of Additives on Orthogonal Reaction Pathways in the Mizoroki-Heck Arylation of Vinyl Ethers

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High throughput experimentation. Automated powder dosing (Mettler Toledo QX96) is used to dispense catalyst materials into 1 mL vials in N_2-atmosphere glovebox: Pd source (0.002 mmol), ligand (0.002 mmol), base (0.06 mmol), Lewis acid (0-0.04 mmol). Methyl 4-bromobenzoate (0.02 mmol) and *n*-butyl vinyl ether (0.1 mmol) are dispensed as a stock solution in the reaction solvent. The plated is sealed under N_2 and heated to 80 °C with 1000 rpm tumble stirring for 2 hours. After cooling to room temperature, the reaction mixtures are diluted with a stock solution of HPLC standard and centrifuged. Aliquots of each reaction mixture are removed for HLPC analysis.

Pd sources: $Pd(OAc)_2$, $Pd_2(dba)_3$•$CHCl_3$, $PdCl_2(CH_3CN)_2$
Ligands: P^tBu_3-HBF_4, dtbpf, xantphos, ^{t}BuDavePhos
Bases: K_2CO_3, Cs_2CO_3, NCy_2Me, NEt_3
Solvents: DMF, CH_3CN
Lewis acids: $Al(OTf)_3$, $Ca(OTf)_2$, $In(OTf)_3$, $La(OTf)_3$, LiOTf, $Sc(OTf)_3$, $Y(OTf)_3$, $Zn(OTf)_2$

General procedures for catalytic reactions. In an N_2 atmosphere glovebox, a 20 mL vial is charged with $Pd(OAc)_2$ (0.05 mmol), xantphos (0.05 mmol), additive (0.05-1 mmol), methyl 4-bromobenzoate (0.5 mmol), Cs_2CO_3 (1.5-2 mmol), and 1,3,5-trimethoxybenzene (5-10 mg). The solids are suspended in 4 mL CH_3CN and *n*-butyl vinyl ether (2.5 mmol) is added. The vial is sealed and heated to 80 °C for 1-2 hours. The reaction mixture is cooled to room temperature, and an aliquot of the reaction mixture is removed for ^{1}H NMR analysis. Conversion and yields are determined by ^{1}H NMR using internal standard. Alternatively, the reaction mixture is diluted with CH_2Cl_2 and filtered through a plug of SiO_2 and evaporated. The residue is dissolved in $CDCl_3$ for ^{1}H NMR analysis.

Procedure for arylation of acetophenones. In an N_2 atmosphere glovebox, a 20 mL vial is charged with $Pd(OAc)_2$ (0.05 mmol), xantphos (0.05 mmol), methyl 4-acetylbenzoate (0.5 mmol), Cs_2CO_3 (1.5 mmol).The solids are dissolved in 4 mL CH_3CN. The vial is sealed and heated to 80 °C for 1-2 hours. The reaction mixture is cooled to room temperature, filtered through celite, evaporated to dryness, and analyzed by ^{1}H NMR.

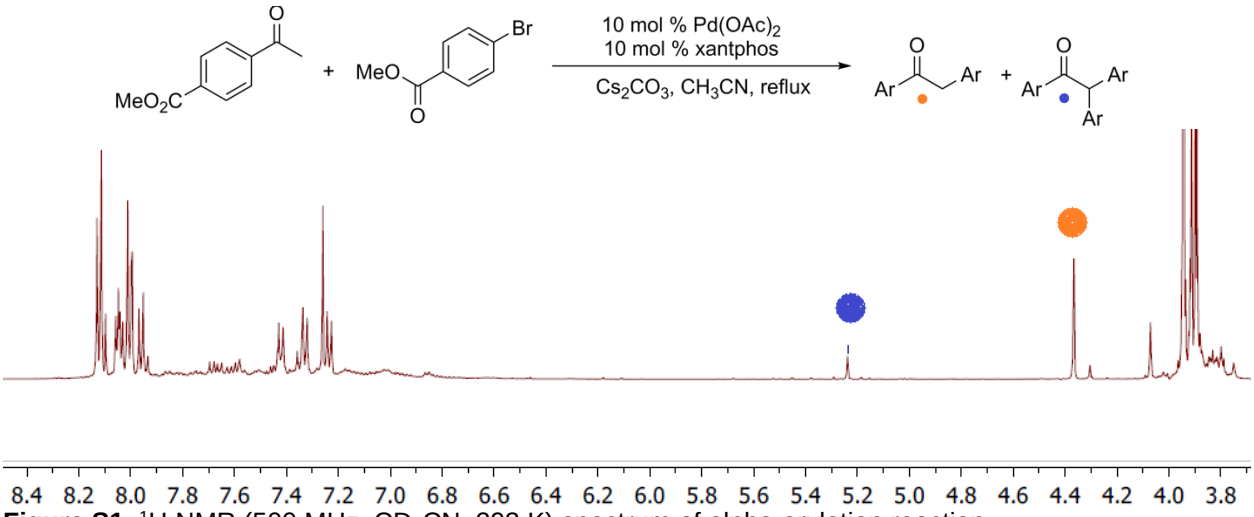

Figure S1. ^{1}H NMR (500 MHz, CD_3CN, 293 K) spectrum of alpha-arylation reaction.

General procedure for kinetic experiments. In an N_2 atmosphere glovebox, a test tube is charged with $Pd(OAc)_2$ (0.05 mmol), xantphos (0.05 mmol), additive (0.05-1 mmol), methyl 4-bromobenzoate (0.5 mmol), benzyl nitrile (1 mmol), Cs_2CO_3 (1.5-2 mmol), and 1,3,5-trimethoxybenzene (5-10 mg). The solids are suspended in 4 mL PhMe, the tube is sealed with a rubber septum and heated to 80 °C. At various time intervals, aliquots of the reaction are removed by microliter syringe to monitor the formation of product over time by ^{1}H NMR.

Procedure for catalyst speciation evaluation by ^{31}P NMR. In an N_2 atmosphere glovebox, a 4 mL vial is added $Pd(OAc)_2$ (25 μmol), xantphos (28 μmol), LiOTf (0 – 200 μmol) and CD_3CN (0.7 mL). The solution is added to an NMR tube and sealed under N_2. ^{31}P spectrum is recorded. The tube is then immersed in an oil bath and heated to 80 C for 15 mins. The reaction mixture is cooled to rt, and then a second ^{31}P spectrum is recorded.

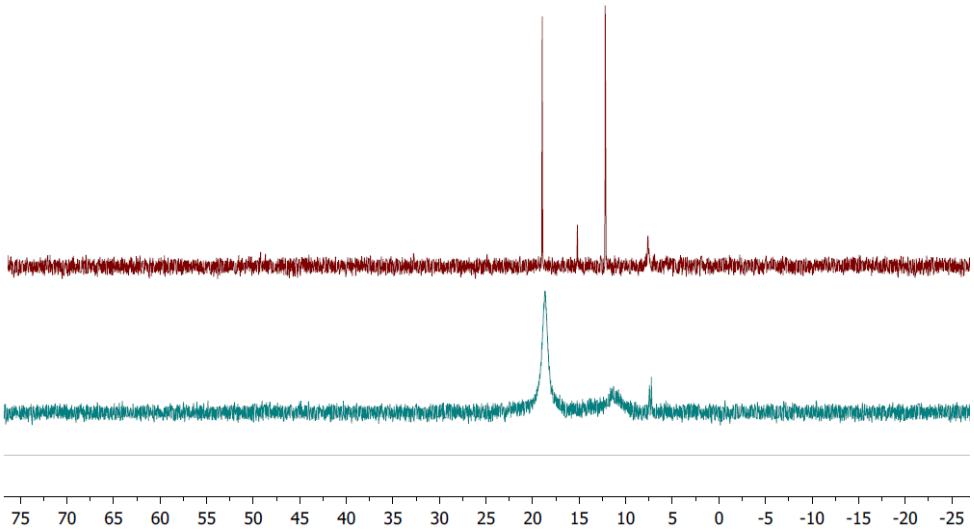

Figure S2. (top) ^{31}P NMR spectrum (500 MHz, CD_3CN, 293 K) of $Pd(OAc)_2$ and xantphos in CD_3CN. (bottom) ^{31}P NMR spectrum (500 MHz, CD_3CN, 293 K) of $Pd(OAc)_2$, xantphos, and LiOTf in CD_3CN.

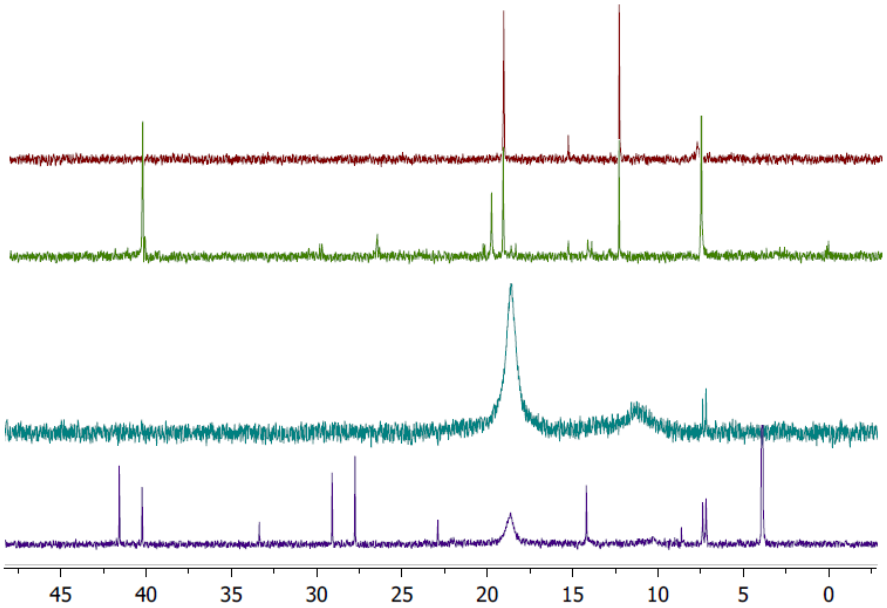

Figure S3. (red) ^{31}P NMR spectrum (500 MHz, CD_3CN, 293 K) of $Pd(OAc)_2$ and xantphos in CD_3CN. (green) ^{31}P NMR spectrum (500 MHz, CD_3CN, 293 K) of $Pd(OAc)_2$ and xantphos in CD_3CN after heating to 80 °C for 15 mins. (teal) ^{31}P NMR spectrum (500 MHz, CD_3CN, 293 K) of $Pd(OAc)_2$, xantphos, and LiOTf in CD_3CN. (blue) ^{31}P NMR spectrum (500 MHz, CD_3CN, 293 K) of $Pd(OAc)_2$, xantphos, and LiOTf in CD_3CN after heating to 80 °C for 15 mins.

Procedure for catalyst speciation evaluation by ^{31}P NMR. In an N_2 atmosphere glovebox, a 4 mL vial is added $Pd(OAc)_2$ (25 μmol), xantphos (28 μmol), LiOTf (0 – 200 μmol), 4-iodotoluene (300 μmol) and CD_3CN (0.7 mL). The reaction mixture is added to an NMR tube and removed from the glovebox. The tube is opened to air and added 50 μL water, re-sealed, and the ^{31}P spectrum is recorded. Then, the tube immersed in an oil bath preheated to 80 °C and heated at this temperature for 15 mins. The tube is removed from heat, cooled to rt, and another ^{31}P spectrum is recorded.

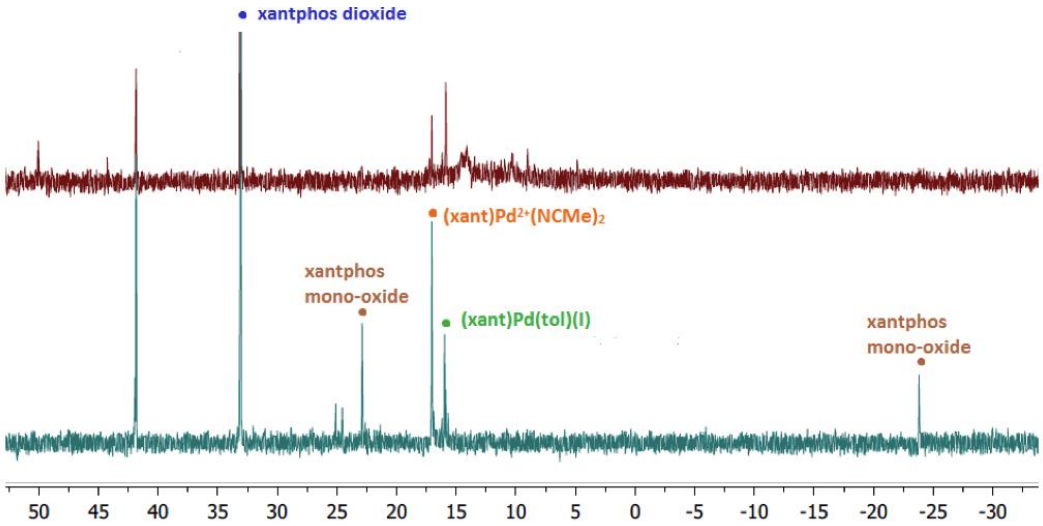

Figure S4. (top) ^{31}P NMR spectrum (500 MHz, CD_3CN, 293 K) of $Pd(OAc)_2$, xantphos, LiOTf, iodotoluene and water in CD_3CN. (bottom) ^{31}P NMR spectrum (500 MHz, CD_3CN, 293 K) of the same mixture after heating to 80 °C for 15 mins.

Large scale synthesis of methyl 4-acetylbenzoate. In a N_2-atmosphere glovebox, a 20 mL vial is added methyl 4-bromobenzoate (215.6 mg, 1 mmol), Na_2SO_4•$10H_2O$ (321.5 mg, 1 mmol), Cs_2CO_3 (622 g, 1.9 mmol), *n*-butyl vinyl ether (0.4 mL, 5 mmol) and acetonitrile (3 mL). In a separate vial, $Pd(OAc)_2$ (20 mg, 0.09 mmol, 9 mol %), xantphos (62 mg, 0.010 mmol, 10 mol %), LiOTf (170 mg, 1.09 mmol), and 2 mL acetonitrile; the solution is mixed until dissolved completely. The catalyst solution is then injected into the reaction vial. The vial is sealed and removed from the glovebox, and immersed into a heating block preheated to 80 °C. The reaction mixture stirs at this temperature for 24 h. Then, the solution is cooled to rt and opened to air. The solution is diluted with EtOAc and filtered through Celite. The filtrate is added 1.5 mL concentrated HCl and stirred at 23 °C for 15 mins. Then, the solution is poured over saturated $NaHCO_3$ (aq). The organic layer is separated, washed with brine, dried over Na_2SO_4, and evaporated to dryness. The resulting oil was purified using automated column chromatography (gradient of 5% EtOAc/hexane to 40% EtOAc/hexane), yielding a white solid (85 mg, 48%).

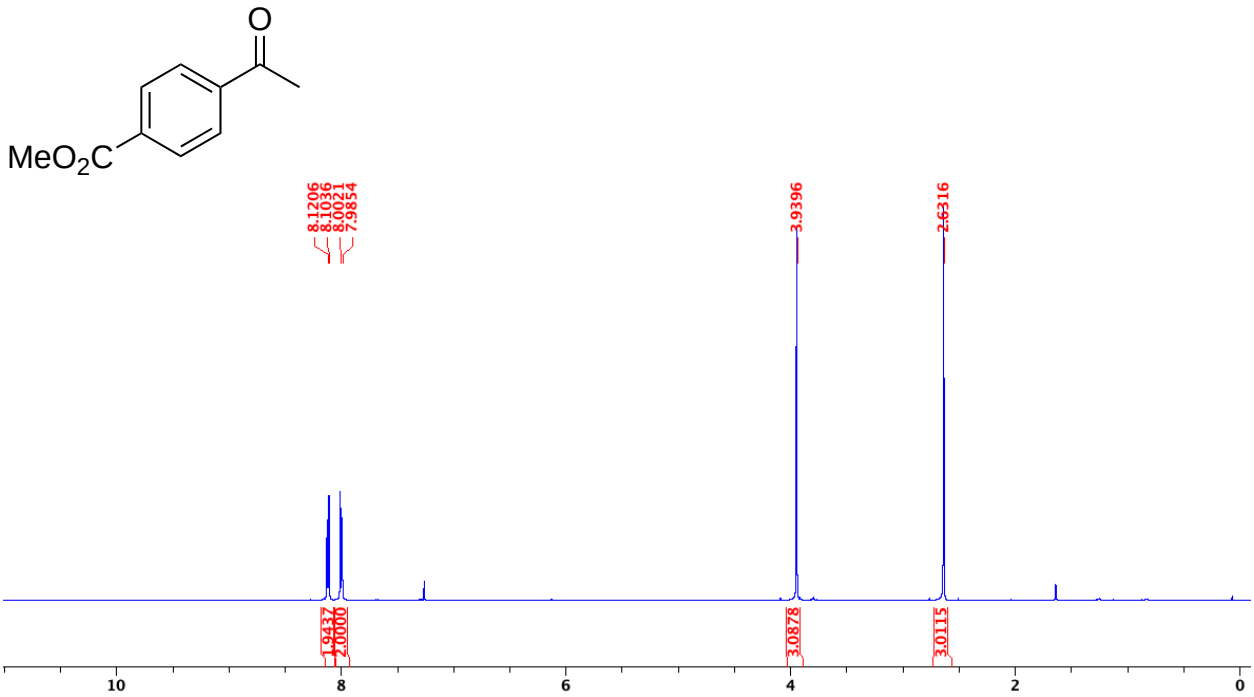

Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) of methyl 4-acetylbenzoate

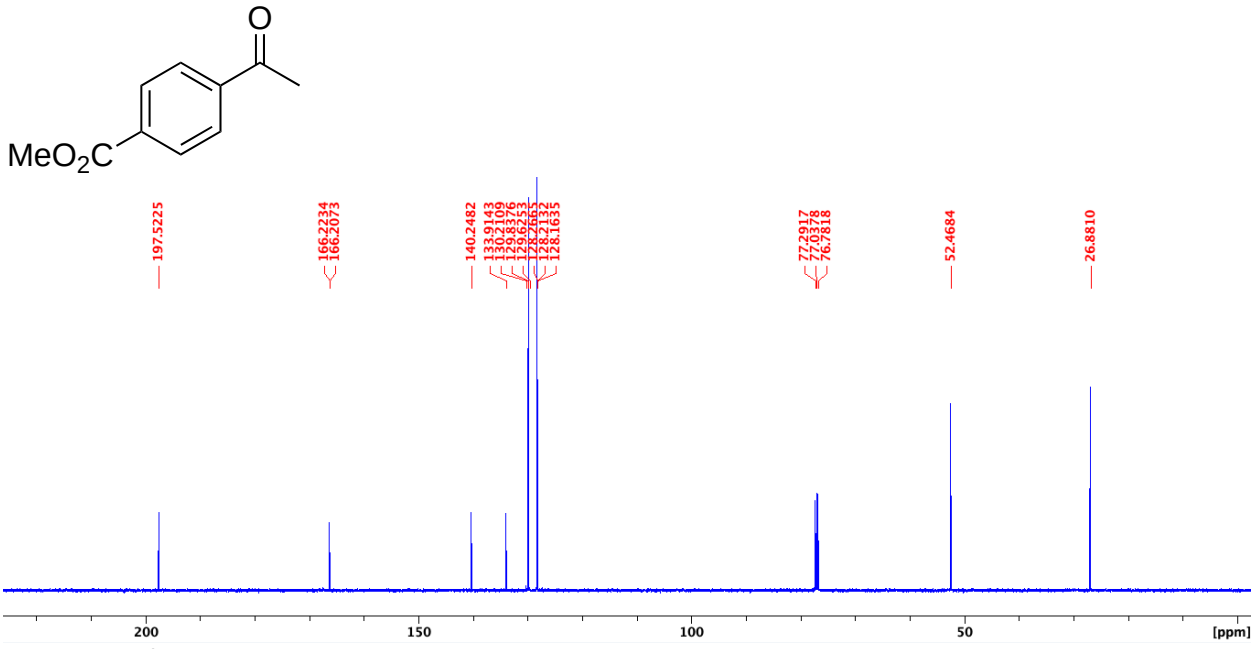

Figure S6. ^{13}C NMR (500 MHz, $CDCl_3$, 293 K) of methyl 4-acetylbenzoate

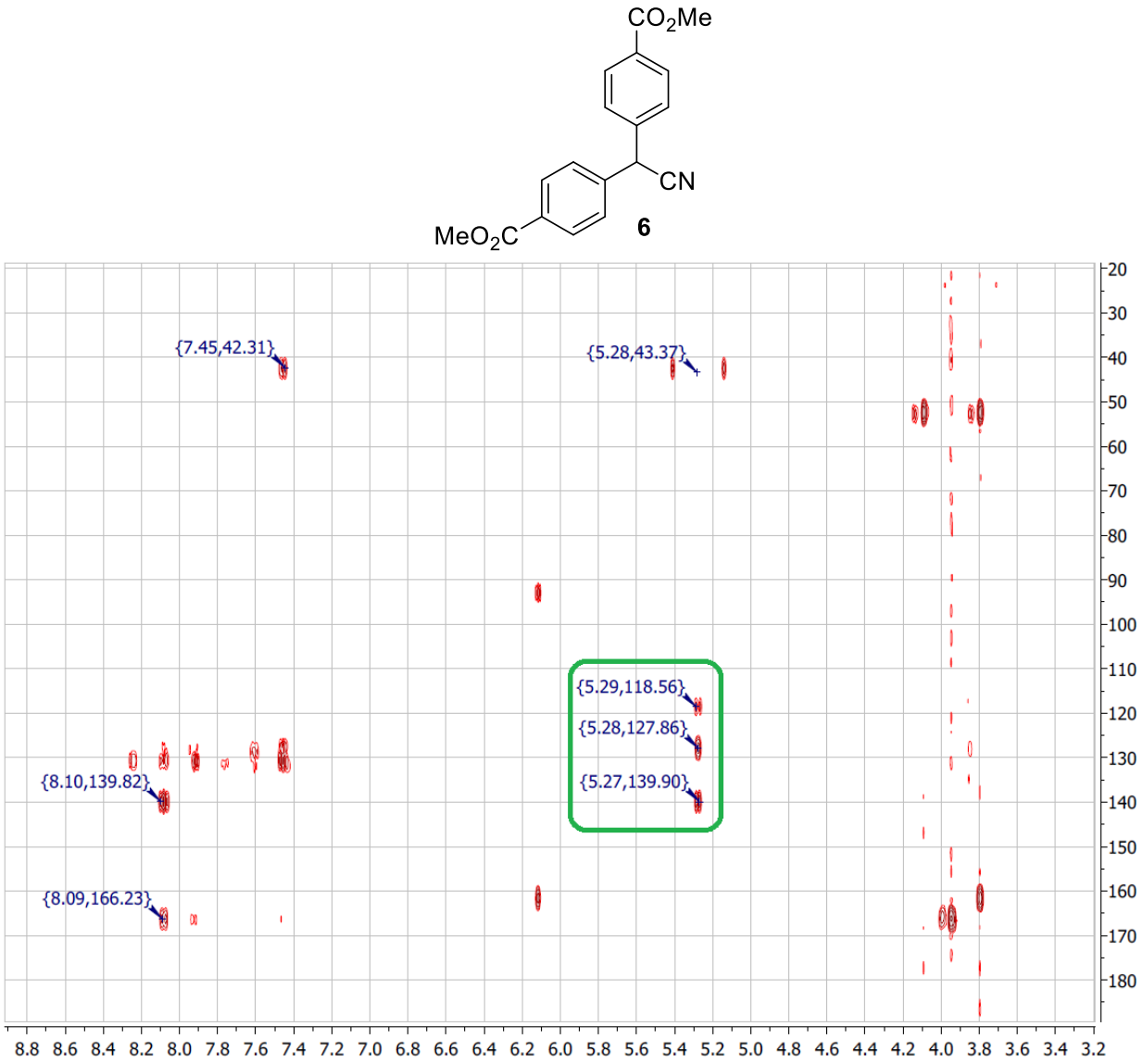

Figure S7. HMBC spectrum (500 MHz, CD_3CN, 293 K) of Mizoroki-Heck reaction in which the benzyl nitrile byproduct **6** is observed and identified.

High throughput screening data

*B/IS = branched alkene, ratio to internal standard

*L/IS = linear alkene, ratio to internal standard

Table S1. Data from Figure 1 in the main text.

Entry	Pd Source	Ligand	Base	Solvent	Conv (%)	B/IS*	L/IS*
1	$Pd(OAc)_2$	Xantphos	Cs_2CO_3	CH_3CN	87	2.170	0
2	$PdCl_2(NCMe)_2$	Xantphos	Cs_2CO_3	CH_3CN	87	2.121	0
3	$Pd_2(dba)_3$-$CHCl_3$	Xantphos	Cs_2CO_3	CH_3CN	78	2.002	0
4	$Pd(OAc)_2$	P^tBu_3-HBF_4	Cs_2CO_3	CH_3CN	58	1.364	0
5	$PdCl_2(NCMe)_2$	P^tBu_3-HBF_4	K_2CO_3	CH_3CN	56	1.127	0.070
6	$Pd_2(dba)_3$-$CHCl_3$	P^tBu_3-HBF_4	Cs_2CO_3	CH_3CN	70	0.873	0.000
7	$Pd(OAc)_2$	DTBPF	Cs_2CO_3	CH_3CN	52	0.581	0.043
8	$Pd(OAc)_2$	Xantphos	Cs_2CO_3	DMF	63	0.429	0.059
9	$PdCl_2(NCMe)_2$	Xantphos	Cs_2CO_3	DMF	58	0.372	0.000
10	$PdCl_2(NCMe)_2$	DTBPF	Cs_2CO_3	CH_3CN	38	0.312	0.000
11	$Pd_2(dba)_3$-$CHCl_3$	Xantphos	Cs_2CO_3	DMF	63	0.189	0.000
12	$Pd(OAc)_2$	tBuDavePhos	Cs_2CO_3	CH_3CN	88	0.185	0.693
13	$Pd(OAc)_2$	P^tBu_3-HBF_4	Cs_2CO_3	DMF	54	0.126	0.104
14	$PdCl_2(NCMe)_2$	P^tBu_3-HBF_4	K_2CO_3	DMF	41	0.107	0.063
15	$Pd(OAc)_2$	DTBPF	Cs_2CO_3	DMF	56	0.081	0.045
16	$PdCl_2(NCMe)_2$	DTBPF	K_2CO_3	DMF	89	0.069	3.557
17	$Pd_2(dba)_3$-$CHCl_3$	tBuDavePhos	Cs_2CO_3	CH_3CN	89	0.069	0.734
18	$Pd_2(dba)_3$-$CHCl_3$	P^tBu_3-HBF_4	Cs_2CO_3	DMF	44	0.063	0.000
19	$PdCl_2(NCMe)_2$	tBuDavePhos	Cs_2CO_3	DMF	39	0.061	0.073
20	$PdCl_2(NCMe)_2$	DTBPF	Cs_2CO_3	DMF	34	0.054	0.000
21	$Pd(OAc)_2$	P^tBu_3-HBF_4	K_2CO_3	CH_3CN	42	0.053	1.336
22	$PdCl_2(NCMe)_2$	DTBPF	NCy_2Me	CH_3CN	84	0.047	2.992
23	$PdCl_2(NCMe)_2$	DTBPF	NEt_3	DMF	89	0.041	3.528
24	$PdCl_2(NCMe)_2$	DTBPF	NEt_3	CH_3CN	90	0.034	3.014
25	$Pd_2(dba)_3$-$CHCl_3$	DTBPF	NCy_2Me	DMF	<5	0.032	0.000
26	$Pd(OAc)_2$	Xantphos	K_2CO_3	CH_3CN	57	0.030	1.274
27	$Pd(OAc)_2$	DTBPF	K_2CO_3	CH_3CN	31	0.030	0.390
28	$Pd(OAc)_2$	P^tBu_3-HBF_4	K_2CO_3	DMF	18	0.030	0.780

29	$Pd(OAc)_2$	DTBPF	NEt_3	DMF	<5	0.029	0.000
30	$Pd_2(dba)_3$-$CHCl_3$	DTBPF	NEt_3	DMF	<5	0.029	0.000
31	$Pd_2(dba)_3$-$CHCl_3$	tBuDavePhos	Cs_2CO_3	DMF	25	0.029	0.163
32	$Pd(OAc)_2$	DTBPF	K_2CO_3	DMF	88	0.026	3.249
33	$PdCl_2(NCMe)_2$	Xantphos	NEt_3	DMF	90	0.025	3.744
34	$Pd_2(dba)_3$-$CHCl_3$	tBuDavePhos	NEt_3	CH_3CN	91	0	3.207
35	$Pd_2(dba)_3$-$CHCl_3$	P^tBu_3-HBF_4	NEt_3	CH_3CN	91	0	3.219
36	$PdCl_2(NCMe)_2$	P^tBu_3-HBF_4	NCy_2Me	CH_3CN	91	0	3.397
37	$Pd_2(dba)_3$-$CHCl_3$	P^tBu_3-HBF_4	K_2CO_3	DMF	90	0	3.456
38	$Pd_2(dba)_3$-$CHCl_3$	P^tBu_3-HBF_4	K_2CO_3	CH_3CN	90	0	2.507
39	$Pd_2(dba)_3$-$CHCl_3$	P^tBu_3-HBF_4	NEt_3	DMF	90	0	3.814
40	$PdCl_2(NCMe)_2$	P^tBu_3-HBF_4	NCy_2Me	DMF	90	0	3.424
41	$Pd(OAc)_2$	DTBPF	NEt_3	CH_3CN	89	0	2.917
42	$Pd(OAc)_2$	tBuDavePhos	K_2CO_3	CH_3CN	89	0	2.868
43	$Pd_2(dba)_3$-$CHCl_3$	tBuDavePhos	K_2CO_3	CH_3CN	89	0	2.581
44	$PdCl_2(NCMe)_2$	tBuDavePhos	Cs_2CO_3	CH_3CN	89	0	2.549
45	$PdCl_2(NCMe)_2$	DTBPF	K_2CO_3	CH_3CN	89	0	2.483
46	$PdCl_2(NCMe)_2$	P^tBu_3-HBF_4	NEt_3	DMF	89	0	3.939
47	$Pd_2(dba)_3$-$CHCl_3$	tBuDavePhos	K_2CO_3	DMF	89	0	3.763
48	$PdCl_2(NCMe)_2$	xantphos	K_2CO_3	DMF	89	0	3.578
49	$Pd_2(dba)_3$-$CHCl_3$	P^tBu_3-HBF_4	NCy_2Me	CH_3CN	88	0	2.771
50	$PdCl_2(NCMe)_2$	tBuDavePhos	K_2CO_3	DMF	88	0	3.874
51	$Pd_2(dba)_3$-$CHCl_3$	tBuDavePhos	NEt_3	DMF	88	0	3.580
52	$Pd(OAc)_2$	DTBPF	NCy_2Me	CH_3CN	88	0	2.888
53	$Pd_2(dba)_3$-$CHCl_3$	P^tBu_3-HBF_4	NCy_2Me	DMF	88	0	3.815
54	$PdCl_2(NCMe)_2$	P^tBu_3-HBF_4	Cs_2CO_3	DMF	88	0	3.439
55	$Pd(OAc)_2$	tBuDavePhos	K_2CO_3	DMF	87	0	3.905
56	$Pd_2(dba)_3$-$CHCl_3$	tBuDavePhos	NCy_2Me	DMF	87	0	3.781
57	$Pd_2(dba)_3$-$CHCl_3$	tBuDavePhos	NCy_2Me	CH_3CN	87	0	3.070
58	$PdCl_2(NCMe)_2$	DTBPF	NCy_2Me	DMF	86	0	3.505
59	$Pd(OAc)_2$	DTBPF	NCy_2Me	DMF	86	0	3.426
60	$Pd(OAc)_2$	tBuDavePhos	NCy_2Me	DMF	86	0	3.959
61	$PdCl_2(NCMe)_2$	P^tBu_3-HBF_4	Cs_2CO_3	CH_3CN	85	0	3.949
62	$PdCl_2(NCMe)_2$	Xantphos	NEt_3	CH_3CN	83	0	2.681
63	$PdCl_2(NCMe)_2$	tBuDavePhos	NCy_2Me	CH_3CN	81	0	3.158
64	$PdCl_2(NCMe)_2$	tBuDavePhos	NEt_3	CH_3CN	75	0	2.838
65	$PdCl_2(NCMe)_2$	tBuDavePhos	K_2CO_3	CH_3CN	74	0	2.314

66	$Pd(OAc)_2$	tBuDavePhos	NCy_2Me	CH_3CN	71	0	2.714
67	$PdCl_2(NCMe)_2$	Xantphos	NCy_2Me	DMF	70	0	2.978
68	$Pd(OAc)_2$	xantphos	NEt_3	CH_3CN	66	0	2.128
69	$PdCl_2(NCMe)_2$	tBuDavePhos	NEt_3	DMF	65	0	2.861
70	$Pd(OAc)_2$	tBuDavePhos	NEt_3	DMF	59	0	2.539
71	$Pd_2(dba)_3$-$CHCl_3$	DTBPF	Cs_2CO_3	DMF	52	0	0.000
72	$PdCl_2(NCMe)_2$	tBuDavePhos	NEt_3	DMF	45	0	2.291
73	$PdCl_2(NCMe)_2$	xantphos	K_2CO_3	CH_3CN	39	0	0.681
74	$Pd(OAc)_2$	tBuDavePhos	Cs_2CO_3	DMF	36	0	0.000
75	$Pd(OAc)_2$	tBuDavePhos	NEt_3	CH_3CN	32	0	1.159
76	$Pd_2(dba)_3$-$CHCl_3$	DTBPF	Cs_2CO_3	CH_3CN	26	0	0.000
77	$PdCl_2(NCMe)_2$	P^tBu_3-HBF_4	NEt_3	CH_3CN	26	0	0.375
78	$Pd(OAc)_2$	P^tBu_3-HBF_4	NEt_3	CH_3CN	18	0	0.137
79	$Pd(OAc)_2$	xantphos	K_2CO_3	DMF	11	0	0.111
80	$Pd_2(dba)_3$-$CHCl_3$	xantphos	K_2CO_3	CH_3CN	11	0	0.000
81	$Pd_2(dba)_3$-$CHCl_3$	xantphos	K_2CO_3	DMF	10	0	0.209
82	$Pd(OAc)_2$	xantphos	NCy_2Me	CH_3CN	10	0	0.060
83	$Pd(OAc)_2$	P^tBu_3-HBF_4	NCy_2Me	DMF	10	0	0.063
84	$Pd_2(dba)_3$-$CHCl_3$	xantphos	NEt_3	CH_3CN	8	0	0.0
85	$Pd_2(dba)_3$-$CHCl_3$	xantphos	NCy_2Me	CH_3CN	8	0	0.0
86	$Pd_2(dba)_3$-$CHCl_3$	DTBPF	NEt_3	CH_3CN	6	0	0.0
87	$PdCl_2(NCMe)_2$	xantphos	NCy_2Me	CH_3CN	5	0	0
88	$Pd_2(dba)_3$-$CHCl_3$	DTBPF	K_2CO_3	CH_3CN	<5	0	0
89	$Pd_2(dba)_3$-$CHCl_3$	xantphos	NEt_3	DMF	<5	0	0
90	$Pd_2(dba)_3$-$CHCl_3$	DTBPF	K_2CO_3	DMF	<5	0	0
91	$Pd_2(dba)_3$-$CHCl_3$	DTBPF	NCy_2Me	CH_3CN	<5	0	0
92	$Pd(OAc)_2$	xantphos	NCy_2Me	DMF	<5	0	0
93	$Pd(OAc)_2$	xantphos	NEt_3	DMF	<5	0	0
94	$Pd(OAc)_2$	P^tBu_3-HBF_4	NEt_3	DMF	<5	0	0
95		xantphos	NCy_2Me	DMF	<5	0	0
96	$Pd(OAc)_2$	P^tBu_3-HBF_4	NCy_2Me	CH_3CN	<5	0	0

Table S2. Data from Figure 2 in the main text.

Entry	Pd	Additive	Additive Equiv.	Solvent	Conv (%)	B/IS	L/IS
1	Pd(OAc)2	LiOTf	0.1	CH3CN	93	162.82	5.97
2	Pd(OAc)2	Y(Otf)3	0.1	CH3CN	95	161.22	2.13
3	Pd(OAc)2	La(Otf)3	0.1	CH3CN	93	157.46	8.38
4	Pd(OAc)2	LiOTf	0.5	CH3CN	90	152.55	12.10
5	PdCl2(NCMe)2	La(Otf)3	0.1	CH3CN	93	141.92	10.67
6	PdCl2(NCMe)2	LiOTf	0.1	CH3CN	93	141.18	5.94
7	PdCl2(NCMe)2	Sc(Otf)3	0.1	CH3CN	98	138.80	3.13
8	Pd(OAc)2	Al(Otf)3	0.1	CH3CN	100	135.50	4.46
9	PdCl2(NCMe)2	Y(Otf)3	0.1	CH3CN	94	127.30	3.37
10	Pd(OAc)2	In(Otf)3	0.1	CH3CN	97	125.79	2.34
11	PdCl2(NCMe)2	Al(Otf)3	0.1	CH3CN	97	115.12	7.83
12	Pd(OAc)2	Zn(Otf)2	0.1	CH3CN	92	111.76	6.46
13	Pd(OAc)2	Sc(Otf)3	0.1	CH3CN	100	107.54	4.65
14	PdCl2(NCMe)2	In(Otf)3	0.1	CH3CN	98	107.17	7.56
15	Pd(OAc)2	Ca(Otf)2	0.1	CH3CN	94	96.58	5.77
16	PdCl2(NCMe)2	Zn(Otf)2	0.1	CH3CN	89	83.79	7.29
17	Pd(OAc)2	Zn(Otf)2	0.5	CH3CN	93	75.94	11.10
18	PdCl2(NCMe)2	LiOTf	0.5	CH3CN	83	68.59	13.54
19	PdCl2(NCMe)2	Ca(Otf)2	0.1	CH3CN	93	66.41	4.36
20	Pd(OAc)2	Y(Otf)3	0.5	CH3CN	85	61.23	34.61
21	PdCl2(NCMe)2	Al(Otf)3	0.5	DMF	60	53.01	11.48
22	PdCl2(NCMe)2	Y(Otf)3	0.5	CH3CN	92	49.29	20.48
23	Pd(OAc)2	La(Otf)3	0.5	CH3CN	93	45.56	16.12
24	PdCl2(NCMe)2	In(Otf)3	0.5	DMF	68	43.73	18.16
25	Pd(OAc)2	Sc(Otf)3	0.5	PhMe	24	42.88	72.49
26	PdCl2(NCMe)2	La(Otf)3	0.5	CH3CN	91	41.69	23.67
27	Pd(OAc)2	In(Otf)3	0.1	PhMe	56	39.89	7.85
28	Pd(OAc)2	Al(Otf)3	0.5	CH3CN	100	39.10	11.75
29	Pd(OAc)2	In(Otf)3	0.5	DMF	53	38.70	18.91
30	Pd(OAc)2	Y(Otf)3	0.1	PhMe	23	37.73	43.40
31	Pd(OAc)2	LiOTf	0.1	DMF	67	33.12	17.91
32	Pd(OAc)2	Al(Otf)3	0.1	PhMe	75	31.69	28.52
33	Pd(OAc)2	Sc(Otf)3	0.5	CH3CN	100	31.46	20.29
34	PdCl2(NCMe)2	La(Otf)3	0.1	DMF	61	30.91	11.50

35	PdCl2(NCMe)2	Al(Otf)3	0.1	DMF	56	30.67	10.88
36	Pd(OAc)2	La(Otf)3	0.1	DMF	63	29.63	24.00
37	Pd(OAc)2	Ca(Otf)2	0.1	DMF	65	29.49	10.16
38	PdCl2(NCMe)2	In(Otf)3	0.1	DMF	60	29.24	7.34
39	Pd(OAc)2	In(Otf)3	0.1	DMF	58	28.16	42.73
40	Pd(OAc)2	Al(Otf)3	0.1	DMF	62	26.60	23.04
41	PdCl2(NCMe)2	Sc(Otf)3	0.5	CH3CN	96	26.46	26.10
42	Pd(OAc)2	Y(Otf)3	0.1	DMF	63	25.55	17.45
43	Pd(OAc)2	Al(Otf)3	0.5	DMF	47	25.47	34.16
44	PdCl2(NCMe)2	Y(Otf)3	0.1	DMF	65	25.34	4.90
45	PdCl2(NCMe)2	Al(Otf)3	0.1	PhMe	50	25.04	9.38
46	Pd(OAc)2	Sc(Otf)3	0.1	DMF	69	23.84	11.31
47	PdCl2(NCMe)2	Sc(Otf)3	0.5	DMF	64	23.52	12.89
48	Pd(OAc)2	Ca(Otf)2	0.1	PhMe	21	23.47	4.09
49	PdCl2(NCMe)2	Sc(Otf)3	0.1	DMF	71	23.30	7.69
50	Pd(OAc)2	LiOTf	0.1	PhMe	41	22.95	4.16
51	Pd(OAc)2	In(Otf)3	0.5	CH3CN	100	22.55	49.07
52	PdCl2(NCMe)2	In(Otf)3	0.5	CH3CN	95	22.15	27.05
53	Pd(OAc)2	Sc(Otf)3	0.1	PhMe	45	22.05	8.96
54	PdCl2(NCMe)2	LiOTf	0.1	DMF	72	21.32	19.84
55	PdCl2(NCMe)2	Al(Otf)3	0.5	CH3CN	97	20.93	30.64
56	Pd(OAc)2	Sc(Otf)3	0.5	DMF	56	19.14	32.49
57	PdCl2(NCMe)2	LiOTf	0.1	PhMe	35	19.07	4.13
58	Pd(OAc)2	LiOTf	0.5	DMF	68	18.36	9.16
59	Pd(OAc)2	Zn(Otf)2	0.1	DMF	72	18.33	7.04
60	Pd(OAc)2	Zn(Otf)2	0.1	PhMe	33	18.30	7.38
61	Pd(OAc)2	La(Otf)3	0.5	DMF	57	16.39	23.33
62	Pd(OAc)2	Zn(Otf)2	0.5	DMF	67	14.99	15.90
63	PdCl2(NCMe)2	Sc(Otf)3	0.1	PhMe	35	14.97	4.21
64	PdCl2(NCMe)2	Y(Otf)3	0.5	PhMe	33	13.63	44.52
65	PdCl2(NCMe)2	Ca(Otf)2	0.5	CH3CN	29	10.37	63.95
66	Pd(OAc)2	Al(Otf)3	0.5	PhMe	69	8.33	15.12
67	PdCl2(NCMe)2	In(Otf)3	0.1	PhMe	34	8.31	6.47
68	PdCl2(NCMe)2	LiOTf	0.5	DMF	56	7.84	18.35
69	PdCl2(NCMe)2	LiOTf	0.5	PhMe	36	7.51	7.82
70	PdCl2(NCMe)2	Ca(Otf)2	0.1	DMF	36	6.80	16.13
71	Pd(OAc)2	Ca(Otf)2	0.5	CH3CN	33	6.44	45.45

72	PdCl2(NCMe)2	Y(Otf)3	0.5	DMF	44	5.53	4.85
73	PdCl2(NCMe)2	In(Otf)3	0.5	PhMe	24	5.45	30.17
74	Pd(OAc)2	La(Otf)3	0.1	PhMe	23	5.41	77.20
75	Pd(OAc)2	Y(Otf)3	0.5	PhMe	33	5.10	10.77
76	Pd(OAc)2	La(Otf)3	0.5	PhMe	39	4.85	88.25
77	PdCl2(NCMe)2	La(Otf)3	0.5	PhMe	31	4.63	12.62
78	PdCl2(NCMe)2	Zn(Otf)2	0.5	CH3CN	37	4.05	144.07
79	PdCl2(NCMe)2	Sc(Otf)3	0.5	PhMe	22	3.94	23.93
80	PdCl2(NCMe)2	Zn(Otf)2	0.1	PhMe	21	3.79	14.98
81	PdCl2(NCMe)2	Al(Otf)3	0.5	PhMe	40	3.70	7.00
82	PdCl2(NCMe)2	Ca(Otf)2	0.5	DMF	26	3.18	80.73
83	Pd(OAc)2	Y(Otf)3	0.5	DMF	44	3.12	73.53
84	PdCl2(NCMe)2	Zn(Otf)2	0.5	PhMe	30	3.07	51.19
85	Pd(OAc)2	Zn(Otf)2	0.5	PhMe	32	3.05	30.91
86	PdCl2(NCMe)2	La(Otf)3	0.1	PhMe	21	2.68	10.55
87	PdCl2(NCMe)2	Zn(Otf)2	0.1	DMF	92	2.37	19.85
88	PdCl2(NCMe)2	Ca(Otf)2	0.5	PhMe	19	2.21	84.23
89	PdCl2(NCMe)2	La(Otf)3	0.5	DMF	36	2.16	87.38
90	Pd(OAc)2	In(Otf)3	0.5	PhMe	34	1.57	150.95
91	PdCl2(NCMe)2	Y(Otf)3	0.1	PhMe	31	1.57	5.09
92	PdCl2(NCMe)2	Zn(Otf)2	0.5	DMF	43		4.09
93	Pd(OAc)2	Ca(Otf)2	0.5	DMF	33		92.46
94	Pd(OAc)2	LiOTf	0.5	PhMe	27		75.88
95	PdCl2(NCMe)2	Ca(Otf)2	0.1	PhMe	23		88.11
96	Pd(OAc)2	Ca(Otf)2	0.5	PhMe	14		100.50