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Supporting Information

Nickel-Catalyzed Heck Reaction of Cycloalkenes Using Aryl Sulfonates and Pivalates

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Experimental procedures and characterization

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I. General

All NMR spectra were acquired on Bruker AV 500 MHz, 300 MHz or BBF 400 MHz NMR spectrometers. ^{1}H NMR (300 MHz) chemical shifts were recorded relative to $SiMe_4$ (δ 0.00) or residual protiated solvents ($CDCl_3$: *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 chemical shifts were recorded relative to solvent resonance ($CDCl_3$: *δ* 77.16).

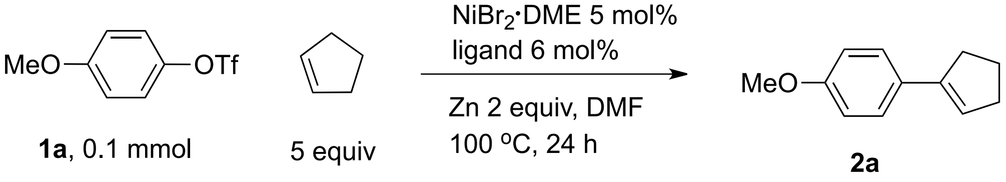
Glassware was dried at 120 °C for at least 3 h before use. THF and 1,4-dioxane were distilled from sodium under argon and was stored over activated 4 Å molecular sieve beads in an argon-filled glove box. Dry toluene was collected from a solvent purification system containing a column of activated alumina (1 m x 2) under argon. *N,N*-Dimethylacetamide (DMA), *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were distilled from CaH_2 under nitrogen and was stored over activated 4 Å molecular sieve beads. 1-Methyl-2-pyrrolidinone (NMP) and dichloroethane (DCE) were stored over activated 4 Å molecular sieve beads in an argon-filled glove box. Zinc dust (<10 µm; >98% purity) were purchased from Sigma-Aldrich (product number 209988). $NiCl_2$[(*R,R*)-QuinoxP*] was synthesized by stirring equimolar $NiCl_2$•DME and (*R,R*)-QuinoxP* in degassed ethanol (80 °C, 2 hours) followed by filtration, based on the literature procedure [^{31}P NMR (DMSO): 50.3 ppm].

Unless noted otherwise, commercially available chemicals were used as received without purification. The GC internal standard, n-$C_{12}H_{26}$ was degassed with argon and dried over activated 4 Å molecular sieve beads before use. Flash chromatography was performed using Merck 40-63D 60 Å silica gel. 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.

II. Condition optimization for Heck reaction of cycloalkenes

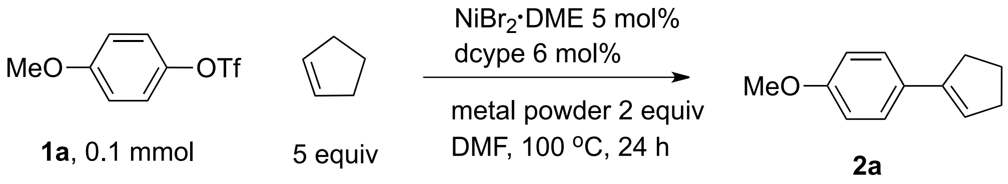
A typical procedure using NiBr$_2$DME: In an argon-filled glove box, NiBr$_2$DME (1.5 mg, 0.005 mmol, 5 mol%), dcype (2.6 mg, 0.006 mmol, 6 mol%), zinc dust (13.2 mg, 0.2 mmol, 2 equiv) and dry DMA (1.0 mL) were added to a dry 10-mL reaction tube. After stirring at room temperature for 15 min, *p*-methoxyphenyl triflate (25.6 mg, 0.1 mmol), cyclopentene (0.5 mmol, 5 equiv) and GC standard n-$C_{12}H_{26}$ (10 μL) were added. The reaction mixture was stirred in an oil bath maintained at 100 °C for 24 h. Aliquots were taken from the organic phase, and passed through a short plug of silica gel with EtOAc washing (about 3 mL). The filtrate was subjected to GC analysis to determine the conversion and calibrated yield of the product and side products.

Table S1 The effect of ligands on Heck reaction of aryl triflate using NiBr$_2$DME in DMF without molecular sieve



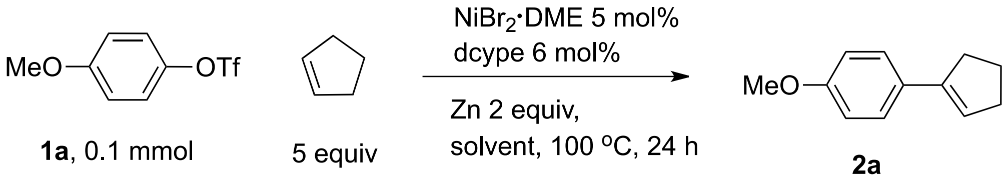
entry	ligand	conv (%)	**2a** (%)
1	(*R*)-Ph-BPE	100	83
2	dcype	100	60
3	dppe	30	18
4	dmpe	100	18
5	depe	83	42
6	dippe	80	47
7	dppp	30	0
8	dppb	7	0
9	dppf	0	0
10	Cy_3P	8	0
11	Ph_3P	60	0
12	DPEphos	10	0

Table S2. The effect of metal powders on Heck reaction of an aryl triflate in DMF without molecular sieve



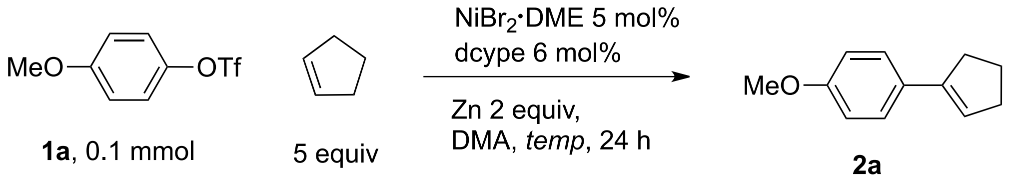
entry	metal powder	conv (%)	**2a** (%)
1	**zinc dust**	**100**	**60**
2	indium powder	11	6
3	magnesium powder	50	11
4	manganese powder	94	42
5	iron powder	5	0

Table S3. The solvent effect on Heck reaction of an aryl triflate without molecular sieve



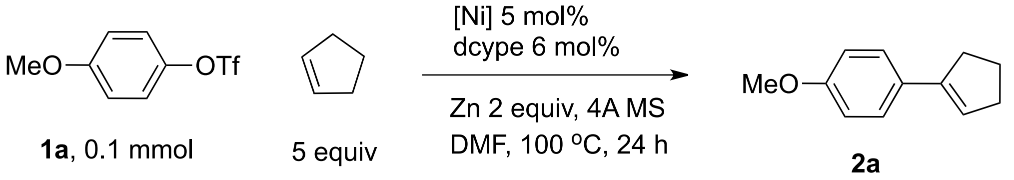
entry	solvent	conv (%)	**2a** (%)
1	**DMF**	**100**	**60**
2	**DMA**	**100**	**65**
3	DMSO	93	50
4	NMP	100	55
5	toluene	10	0
6	THF	75	24
7	DCE	8	0

Table S4. The effect of temperatures on Heck reaction of an aryl triflate in DMA without molecular sieve



entry	temp (°C)	conv (%)	**2a** (%)
1	120	100	41
2	100	100	65
3	80	85	43
4	60	54	34
5	**100; with** 4 Å MS	**100**	**73**

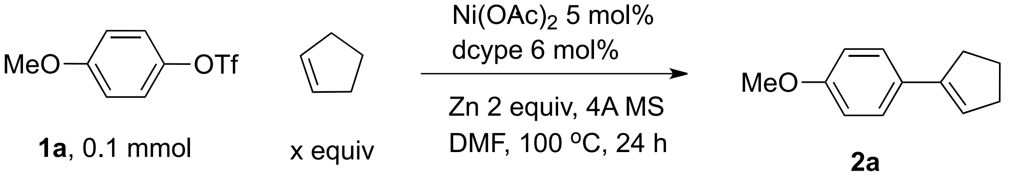
Table S5. The effect of nickel salts on Heck reaction of an aryl triflate in DMF



entry	nickel salt	conv (%)	**2a** (%)
1	$NiBr_2DME$	100	73
2	$NiCl_2DME$	100	78
3	NiI_2DME	100	89
4	**$Ni(OAc)_2$**	**100**	**94**
5	$Ni(OTf)_2$	45	37
6	$Ni(acac)_2$	100	87
7	$Ni(cod)_2$	10	5

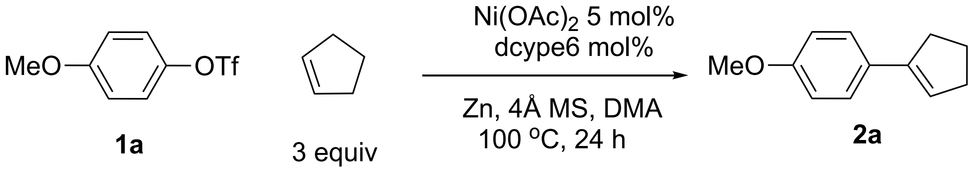
A typical procedure using $Ni(OAc)_2$ and molecular sieve in DMA: In an argon-filled glove box, $Ni(OAc)_2$ (0.9 mg, 0.005 mmol, 5 mol%), dcype (2.6 mg, 0.006 mmol, 6 mol%), zinc dust (13.2 mg, 0.2 mmol, 2 equiv) and dry DMA (0.4 mL) were added to a dry 10-mL Schlenck tube. After stirring at room temperature for 15 min, *p*-methoxyphenyl triflate (25.6 mg, 0.1 mmol), 4Å molecular sieve (25 mg), cyclopentene (30 µL, 0.3 mmol, 3 equiv) and GC standard n-$C_{12}H_{26}$ (10 µL) were added. The reaction mixture was stirred in an oil bath maintained at 100 °C for 24 h. Aliquots were taken from the organic phase, and passed through a short plug of silica gel with EtOAc washing (3 mL). The filtrate was subjected to GC analysis to determine the conversion and calibrated yield of the product and side products.

Table S6. The effect of cyclopentene amounts in DMF



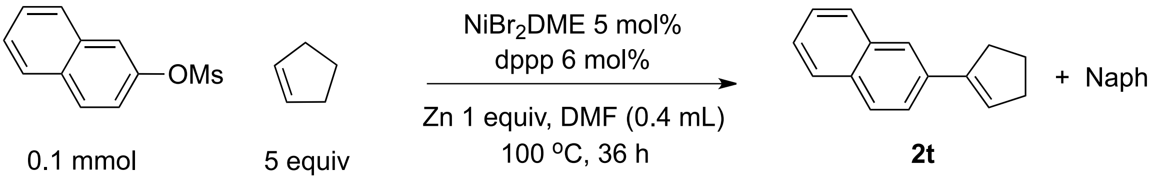
entry	alkene	conv (%)	**2a** (%)
1	5 equiv	100	94
2	3 equiv	100	95

Table S7. The effect of ligands on Heck reaction of an aryl triflate using nickel acetate in 0.4 ml of DMA



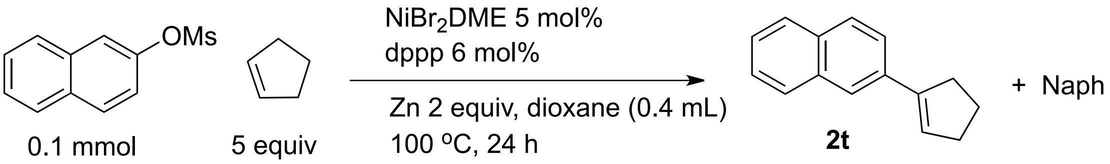
entry	ligand	conv (%)	**2a** yield (%)	PhOMe (%)
1	(*R*)-Ph-BPE	**100**	**99**	0
2	dippe	**89**	**76**	0
3	dcype	**92**	**83**	0
4	dippp	78	16	26
5	dcypp	46	15	31
6	dcypb	88	16	70
7	dppe	0	0	0
8	dppp	28	0	0
9	dppb	14	0	14
10	dppf	100	0	85
11	Xantphos	100	0	92
12	DPEphos	68	0	68

Table S8. Optimization of conditions for Heck reaction of 2-naphthyl mesylate without molecular sieve (*n*-tetradecane as GC standard)



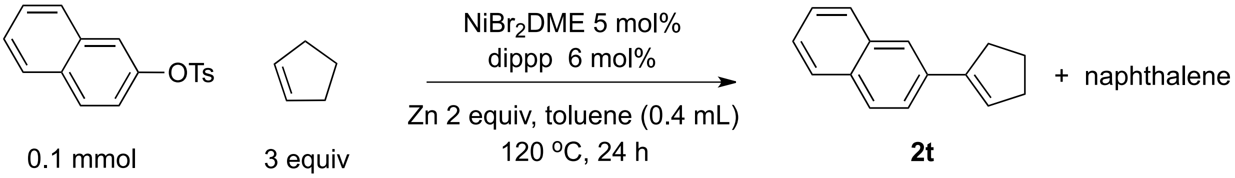
entry	changes from conditions above	conv (%)	**2t** (%)	Naph (%)
1	none	100	54	41
2	zinc dust 2 equiv	98	58	39
3	at 80 °C	92	50	31
4	alkene 3 equiv	100	45	55
5	DMA solvent	100	54	0.4
6	DMSO solvent	83	20	29
7	PhMe solvent	90	46	26
8	THF solvent	50	30	0
9	**dioxane solvent**	**100**	**75**	21
10	dppe ligand	100	52	0
11	dcype ligand	100	40	50
12	dcype ligand at 130 °C	100	40	52
14	DPEphos ligand	100	0	49

Table S9. Optimization of conditions for Heck reaction of 2-naphthyl mesylate (*n*-tetradecane as GC standard)



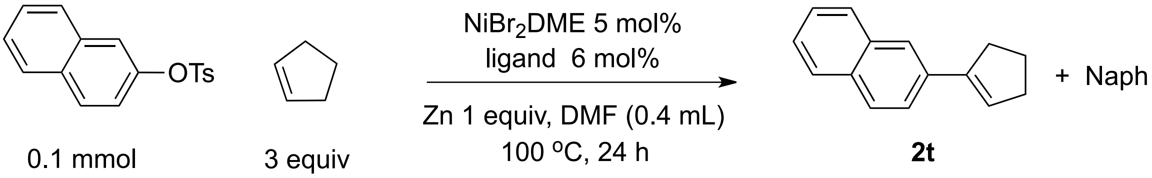
entry	changes from conditions above	conv (%)	**2t** (%)	Naph (%)
1	**none**	**100**	**82**	18
2	added 4Å MS	98	80	20
3	at 80 °C	92	70	20
4	alkene 3 equiv	100	80	20
5	$NiBr_2DME$ 2.5%, dppp 3%	100	75	13
6	Ni(detpe)Cl_2 5 mol%	95	80	20

Table S10. Fine-tuning of conditions for Heck reaction of 2-naphthyl tosylate (*n*-tetradecane as GC standard)



entry	changes from conditions above	conv (%)	**2t** (%)
1	none (in toluene)	100	44
2	at 100 °C	92	58
3	at 80 °C	100	55
4	$NiCl_2DME$	100	50
5	dioxane solvent	95	0
6	DMF solvent	85	50

Table S11. Ligand effect on Heck reaction of 2-naphthyl tosylate (*n*-tetradecane as GC standard)

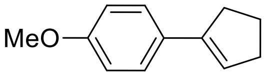


entry	changes from conditions above	conv (%)	**2t** (%)	Naph (%)
1	(*R*)-Ph-BPE	100	85	15
2	dppe	0	0	0
3	dppf	0	0	0
4	dppp	100	60	35

III. Heck reaction of aryl sulfonates with cycloalkenes

A typical procedure: In an argon-filled glove box, $Ni(OAc)_2$ (1.8 mg, 0.01 mmol, 5 mol%), dcype (5.1 mg, 0.012 mmol, 6 mol%), zinc dust (26.4 mg, 0.4 mmol, 2 equiv) and dry DMA (1.0 mL) were added to a dry 10-mL Schlenk tube (from Synthware). After stirring at room temperature for 15 min, *p*-methoxyphenyl triflate (51.2 mg, 0.2 mmol), cyclopentene (60 µL, 0.6 mmol, 3 equiv) and activated 4Å molecular sieve (50 mg) were added. The reaction mixture was stirred (with a rod-shaped magnetic stir bar 8*4 mm; stirring rate 500-700 rpm) in an oil bath maintained at 100 °C for 24 h. The reaction mixture was cooled to room temperature and then extracted with Et_2O. The solvent was removed under reduced pressure and the crude product was purified by flash chromatograph on silica gel directly. Similar results were obtained when the reactions were set up with a vacuum manifold and Schlenk tubes.

A typical procedure at 1 mmol: under argon, into a dry 25-mL Schlenck tube were charged with $Ni(OAc)_2$ (9.0 mg, 0.05 mmol, 5 mol%), dcype (25 mg, 0.06 mmol, 6 mol%), zinc dust (130 mg, 2 mmol) and dry DMA (4 mL). After stirring at room temperature for 15 min, *p*-methoxyphenyl triflate (256 mg, 1 mmol), cyclopentene (204 mg, 280 µL, 3 mmol) and freshly activated 4Å molecular sieve powder (100 mg) were added. The reaction mixture was stirred in an oil bath maintained at 100 °C for 72 h. The reaction mixture was cooled to room temperature, diluted with Et_2O and then filtered through a pad of silica gel to remove the insoluble. The solvent was removed under reduced pressure and the crude product was purified by flash chromatograph on silica gel directly. 83% conversion and 72% yield along with some anisole as side product. Higher yield was obtained with nickel/(*R*,*R*)-Ph-BPE. Dryness of DMA and molecular sieve were critical to avoiding the hydrolysis of aryl triflate.



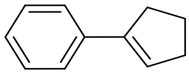
1-(*p*-Methoxyphenyl)cyclopentene [709-12-6]

The product was isolated by flash chromatography (Et_2O/hexanes 1:100) as colorless oil. 93% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.37 (m, 2H), 6.88-6.84 (m, 2H), 6.07-6.05 (m, 1H), 3.82 (s, 3H), 2.72-2.66 (m, 2H), 2.55-2.50 (m, 2H), 2.06-1.98 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.8, 142.0, 129.9, 126.8, 124.1, 113.8, 55.4, 33.5, 33.4, 23.5.

GC-MS (EI): Calcd for $C_{12}H_{14}O$: 174.2. Found: 174.2.



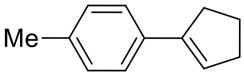
1-Phenylcyclopentene [825-54-7]

The product was isolated by flash chromatography (hexanes) as colorless oil. 94% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 7.4 Hz, 2H), 7.31-7.28 (m, 2H), 7.21-7.18 (m, 1H), 6.18-6.16 (m, 1H), 2.73-2.67 (m, 2H), 2.55-2.49 (m, 2H), 2.05-1.97 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.6, 136.9, 128.4, 126.9, 126.2, 125.7, 33.5, 33.3, 23.5.

GC-MS (EI): Calcd for $C_{11}H_{12}$: 144.2. Found: 144.1.



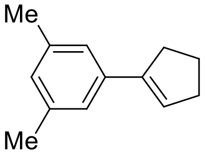
1-(*p*-Methylphenyl)cyclopentene [827-56-5]

The product was isolated by flash chromatography (hexanes) as colorless oil. 90% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.15-6.12 (m, 1H), 2.74-2.67 (m, 2H), 2.56-2.51 (m, 2H), 2.35 (s, 3H), 2.08-1.98 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.6, 136.9, 128.4, 126.9, 126.2, 125.7, 33.5, 33.3, 23.5.

GC-MS (EI): Calcd for $C_{12}H_{14}$: 158.2. Found: 158.1.



1-(3,5-Dimethylphenyl)cyclopentene [1934394-60-1]

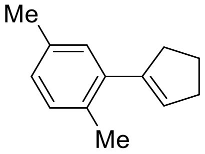
The product was isolated by flash chromatography (hexanes) as colorless oil. 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (s, 2H), 6.88 (s, 1H), 6.17-6.15 (m, 1H), 2.73-2.68 (m, 2H), 2.56-2.50 (m, 2H), 2.33

(s, 6H), 2.06-1.98 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): *δ* 142.7, 137.8, 136.9, 128.7, 125.9, 123.6, 33.4, 23.5, 21.5.

GC-MS (EI): Calcd for $C_{13}H_{16}$: 172.3. Found: 172.2.



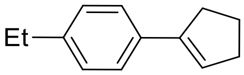
1-(2,5-Dimethylphenyl)cyclopentene

The product was isolated by flash chromatography (hexanes) as colorless oil. 84% yield.

^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.08 (d, *J* = 7.7 Hz, 1H), 7.03 (s, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 5.78-5.75 (m, 1H), 2.70-2.65 (m, 2H), 2.57-2.51 (m, 2H), 2.33 (s, 3H), 2.32 (s, 3H), 2.04-1.97 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): *δ* 143.6, 138.2, 135.0, 132.5, 130.5, 129.2, 128.8, 127.4, 36.8, 33.7, 23.9, 21.1, 20.8.

HRMS (ESI): calcd for $C_{13}H_{17}$ $[M+H]^+$ 173.1330; found 173.1335.



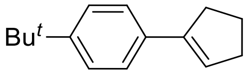
1-(*p*-Ethylphenyl)cyclopentene [19099-47-9]

The product was isolated by flash chromatography (hexanes) as colorless oil. 92% yield.

^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.38 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.16-6.14 (m, 1H), 2.74-2.69 (m, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.56-2.51 (m, 2H), 2.06-1.99 (m, 2H), 1.25 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$): *δ* 143.1, 142.5, 134.5, 127.9, 125.7, 125.3, 33.5, 33.4, 28.7, 23.5, 15.7.

GC-MS (EI): Calcd for $C_{13}H_{16}$: 172.3. Found: 172.2.



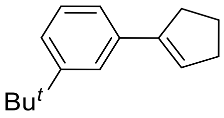
1-(*p*-*t*-Butylphenyl)cyclopentene [387358-58-9]

The product was isolated by flash chromatography (hexanes) as colorless oil. 94% yield.

^{1}H NMR (300 MHz, CDCl$_3$): *δ* 7.42-7.34 (m, 4H), 6.17-6.15 (m, 1H), 2.74-2.69 (m, 2H), 2.56-2.51 (m, 2H), 2.07-1.97 (m, 2H), 1.34 (s, 9H).

^{13}C NMR (75 MHz, CDCl$_3$): *δ* 149.9, 142.4, 134.2, 125.4, 125.4, 125.3, 34.6, 33.5, 33.4, 31.5, 23.6.

GC-MS (EI): Calcd for $C_{15}H_{20}$: 200.3. Found: 200.1.



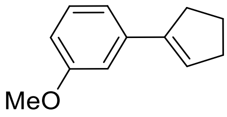
1-(*m*-*t*-Butylphenyl)cyclopentene [1472613-04-9]

The product was isolated by flash chromatography (hexanes) as colorless oil. 92% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (s, 1H), 7.28-726 (m, 3H), 6.21 (m, 1H), 2.76-2.73 (m, 2H), 2.56-2.54 (m, 2H), 2.10-2.00 (m, 2H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 151.1, 143.1, 136.7, 128.1, 125.9, 124.1, 123.0, 122.6, 34.8, 33.5, 31.5, 23.6.

GC-MS (EI): Calcd for $C_{15}H_{20}$: 200.3. Found: 200.2.



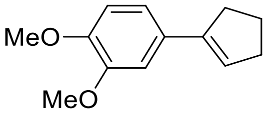
1-(*m*-Methoxyphenyl)cyclopentene [36742-36-6]

The product was isolated by flash chromatography (Et_2O/hexanes 1:100) as colorless oil. 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.29 (m, 1H), 7.11 (d, J = 7.7 Hz, 1H), 7.04 (t, J = 2.2 Hz, 1H), 6.83 (dd, J = 7.9, 2.2 Hz, 1H), 6.26-6.23 (m, 1H), 3.87 (s, 3H), 2.79-2.72 (m, 2H), 2.62-2.55 (m, 2H), 2.13-2.03 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.7, 142.5, 138.4, 129.3, 126.7, 118.4, 112.3, 111.5, 55.3, 33.5, 33.4, 23.5.

GC-MS (EI): Calcd for $C_{12}H_{14}O$: 174.2. Found: 174.1.



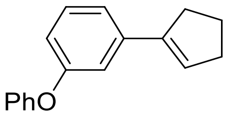
1-(3,4-Dimethoxyphenyl)cyclopentene [60975-00-0]

The product was isolated by flash chromatography (Et_2O/hexanes 1:25) as colorless oil. 90% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.02 (d, J = 1.9 Hz, 1H), 6.96 (dd, J = 8.3, 1.9 Hz, 1H), 6.81 (d, J = 8.3 Hz, 1H), 6.07-6.05 (m, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 2.73-2.65 (m, 2H), 2.56-2.49 (m, 2H), 2.06-1.97 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 148.9, 148.4, 142.2, 130.2, 124.5, 118.3, 111.1, 109.0, 56.0, 55.9, 33.5, 33.4, 23.5.

GC-MS (EI): Calcd for $C_{13}H_{16}O_2$: 204.3. Found: 204.2.



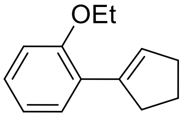
1-(*m*-Benzophenonyl)cyclopentene [1472613-05-0]

The product was isolated by flash chromatography (Et_2O/hexanes 1:100) as colorless oil. 86% yield.

^{1}H NMR (300 MHz, CDCl$_3$): δ 7.33-7.16 (m, 4H), 7.10-7.05 (m, 2H), 7.00 (d, J = 7.7 Hz, 2H), 6.84 (d, J = 7.7 Hz, 1H), 6.15 (m, 1H), 2.66 (m, 2H), 2.50 (m, 2H), 2.04-1.94 (m, 2H).

^{13}C NMR (75 MHz, CDCl$_3$): δ 157.6, 157.2, 142.1, 138.9, 129.8, 129.6, 127.2, 123.2, 120.9, 119.0, 118.8, 117.5, 116.5, 33.5, 33.3, 23.4.

GC-MS (EI): Calcd for $C_{17}H_{16}O$: 236.3. Found: 236.1.



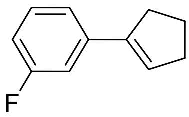
1-(*o*-Ethoxyphenyl)cyclopentene [448249-28-3]

The product was isolated by flash chromatography (Et$_2$O/hexanes 1:100) as colorless oil. 91% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.30 (d, J = 7.6 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 6.94-6.88 (m, 2H), 6.51 (m, 1H), 4.10 (q, J = 6.9 Hz, 2H), 2.81-2.77 (m, 2H), 2.59-2.55 (m, 2H), 2.01-1.93 (m, 2H), 1.49 (t, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 157.0, 139.6, 130.5, 128.9, 127.7, 126.3, 120.4, 111.8, 63.8, 35.4, 34.0, 23.1, 15.1.

HRMS (ESI): calcd for $C_{13}H_{17}O$ $[M+H]^+$ 189.1279; found 189.1275.



1-(*m*-Fluorophenyl)cyclopentene [38793-79-2]

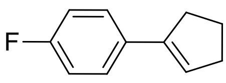
The product was isolated by flash chromatography (hexanes) as colorless oil. 86% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29-7.24 (m, 1H), 7.21 (d, J = 7.8 Hz, 1H), 7.12 (dt, J = 10.6, 2.0 Hz, 1H), 6.91 (td, J = 8.0, 1.9 Hz, 1H), 6.22-6.21 (m, 1H), 2.71-2.67 (m, 2H), 2.57-2.52 (m, 2H), 2.06-2.00 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 163.1 (d, $J_{C\text{-}F}$ = 244.5 Hz), 141.7 (d, $J_{C\text{-}F}$ = 2.5 Hz), 139.3 (d, $J_{C\text{-}F}$ = 7.7 Hz), 129.8 (d, $J_{C\text{-}F}$ = 8.5 Hz), 127.8, 121.3 (d, $J_{C\text{-}F}$ = 2.7 Hz), 113.7 (d, $J_{C\text{-}F}$ = 21.3 Hz), 112.5 (d, $J_{C\text{-}F}$ = 21.7 Hz), 33.5, 33.3, 23.4.

^{19}F NMR (377 MHz, CDCl$_3$): δ -114.0.

GC-MS (EI): Calcd for $C_{11}H_{11}F$: 162.2. Found: 162.1.



1-(*p*-Fluorophenyl)cyclopentene [827-57-6]

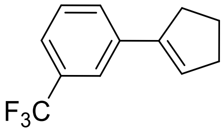
The product was isolated by flash chromatography (hexanes) as colorless oil. 84% yield.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.41-7.38 (m, 2H), 7.02-6.97 (m, 2H), 6.12-6.10 (m, 1H), 2.71-2.66 (m, 2H), 2.55-2.51 (m, 2H), 2.06-2.00 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.0 (d, $J_{C\text{-}F}$ = 245.7 Hz), 141.5, 133.2 (d, $J_{C\text{-}F}$ = 3.3 Hz), 127.2 (d, $J_{C\text{-}F}$ = 7.8 Hz), 125.9 (d, $J_{C\text{-}F}$ = 1.9 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21.4 Hz), 33.53, 33.50, 23.5.

^{19}F NMR (377 MHz, $CDCl_3$): δ -115.8.

GC-MS (EI): Calcd for $C_{11}H_{11}F$: 162.2. Found: 162.1.



1-(*m*-Trifluoromethylphenyl)cyclopentene [38805-70-8]

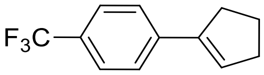
The product was isolated by flash chromatography (hexanes) as colorless oil. 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.48-7.40 (m, 2H), 6.30-6.27 (m, 1H), 2.76-2.71 (m, 2H), 2.60-2.54 (m, 2H), 2.10-2.02 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 141.5, 137.8, 130.8 (q, $J_{C\text{-}F}$ = 32.0 Hz), 128.82 (q, $J_{C\text{-}F}$ = 1.1 Hz), 128.81, 128.3, 124.5 (q, $J_{C\text{-}F}$ =272.4 Hz), 123.5 (q, $J_{C\text{-}F}$ = 3.8 Hz), 122.4 (q, $J_{C\text{-}F}$ = 3.8 Hz), 33.6, 33.3, 23.5.

^{19}F NMR (377 MHz, $CDCl_3$): δ -62.7.

GC-MS (EI): Calcd for $C_{12}H_{11}F_3$: 212.2. Found: 212.1.



1-(*p*-Trifluoromethylphenyl)cyclopentene [38941-62-7]

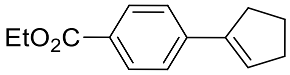
The product was isolated by flash chromatography (hexanes) as colorless oil. 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 6.32-6.30 (m, 1H), 2.75-2.70 (m, 2H), 2.59-2.54 (m, 2H), 2.09-2.02 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 141.6, 140.4 (q, $J_{C\text{-}F}$ = 1.3 Hz), 129.1, 128.7 (q, $J_{C\text{-}F}$ = 32.3 Hz), 125.8, 125.3 (q, $J_{C\text{-}F}$ =3.8 Hz), 124.5 (q, $J_{C\text{-}F}$ = 271.6 Hz), 33.6, 33.3, 23.4.

^{19}F NMR (377 MHz, $CDCl_3$): δ -62.4.

GC-MS (EI): Calcd for $C_{12}H_{11}F_3$: 212.2. Found: 212.2.



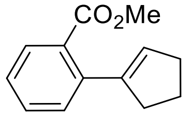
1-(*p*-Ethoxycarbonylphenyl)cyclopentene [1472613-03-8]

The product was isolated by flash chromatography (EtOAc/hexanes 1:20) as colorless oil. 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 6.33-6.31 (m, 1H), 4.37 (q, J = 7.1 Hz, 2H), 2.74-2.69 (m, 2H), 2.58-2.53 (m, 2H), 2.07-2.00 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$): *δ* 166.7, 142.0, 141.3, 129.7, 129.2, 128.7, 125.5, 60.9, 33.6, 33.2, 23.4, 14.5.

GC-MS (EI): Calcd for $C_{14}H_{16}O_2$: 216.3. Found: 216.2.



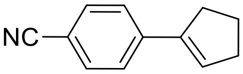
1-(*o*-Methoxycarbonylphenyl)cyclopentene [2115854-46-9]

The product was isolated by flash chromatography (EtOAc/hexanes 1:20) as colorless oil. 70% yield.

^{1}H NMR (300 MHz, CDCl$_3$): *δ* 7.69 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.42 (td, *J* = 8.7, 1.4 Hz, 1H), 7.31-7.26 (m, 2H), 5.73-5.70 (m, 1H), 3.85 (s, 3H), 2.65-2.58 (m, 2H), 2.54-2.46 (m, 2H), 2.07-1.97 (m, 2H).

^{13}C NMR (75 MHz, CDCl$_3$): *δ* 169.4, 144.0, 139.6, 131.3, 130.4, 129.4, 129.4, 128.8, 126.8, 52.2, 36.5, 33.7, 24.5.

GC-MS (EI): Calcd for $C_{13}H_{14}O_2$: 202.2. Found: 202.1.



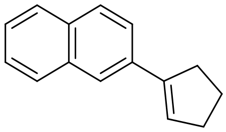
1-(*p*-Cyanophenyl)cyclopentene [19936-20-0]

The product was isolated by flash chromatography (EtOAc/hexanes 1:20) as colorless oil. 81% yield.

^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.58 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 6.36-6.35 (m, 1H), 2.72-2.67 (m, 2H), 2.60-2.54 (m, 2H), 2.09-2.01 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): *δ* 141.4, 141.3, 132.3, 130.8, 126.2, 119.3, 110.1, 33.7, 33.1, 23.4.

GC-MS (EI): Calcd for $C_{12}H_{11}N$: 169.2. Found: 169.1.



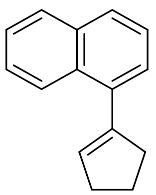
1-(2-Naphthyl)cyclopentene [74793-18-3]

The product was isolated by flash chromatography (hexanes) as colorless oil. 90% yield.

^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.84-7.71 (m, 5H), 7.50-7.42 (m, 2H), 6.36-6.35 (m, 1H), 2.89-2.85 (m, 2H), 2.64-2.60 (m, 2H), 2.14-2.07 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): *δ* 142.6, 134.3, 133.8, 132.7, 128.2, 127.8, 127.7, 127.1, 126.2, 125.6, 124.4, 124.2, 33.6, 33.3, 23.5.

GC-MS (EI): Calcd for $C_{15}H_{14}$: 194.3. Found: 194.1.



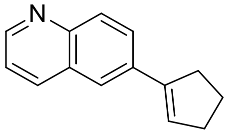
1-(1-Naphthyl)cyclopentene [58195-37-2]

The product was isolated by flash chromatography (hexanes) as colorless oil. 87% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.21-8.17 (m, 1H), 7.89-7.85 (m, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.51-7.43 (m, 3H), 7.37 (dd, J = 7.1, 1.2 Hz, 1H), 5.98-5.95 (m, 1H), 2.87-2.82 (m, 2H), 2.69-2.64 (m, 2H), 2.17-2.10 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 142.4, 137.3, 134.0, 131.6, 130.7, 128.5, 127.2, 126.0, 125.8, 125.7, 125.4, 124.8, 37.9, 33.9, 24.0.

GC-MS (EI): Calcd for $C_{15}H_{14}$: 194.3. Found: 194.1.



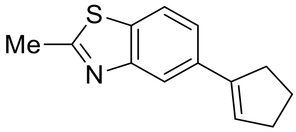
1-(6-Quinolinyl)cyclopentene [1433907-30-2]

The product was isolated by flash chromatography (EtOAc/hexanes 1/20) as colorless oil. 87% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.84 (dd, J = 4.2, 1.7 Hz, 1H), 8.10 (dd, J = 8.3, 0.8 Hz, 1H), 8.01 (d, J = 8.9 Hz, 1H), 7.92 (dd, J = 8.9, 2.0 Hz, 1H), 7.65 (d, J = 1.7 Hz, 1H), 7.35 (dd, J = 8.3, 4.3 Hz, 1H), 6.38-6.36 (m, 1H), 2.84-2.79 (m, 2H), 2.62-2.57 (m, 2H), 2.11-2.04 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 149.9, 147.8, 141.9, 136.1, 135.0, 129.2, 128.5, 128.4, 128.0, 123.7, 121.4, 33.7, 33.3, 23.5.

HRMS (ESI): calcd for $C_{14}H_{14}N$ [M+H]$^+$ 196.1126; found 196.1125.



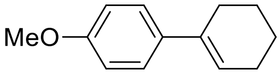
5-(1-Cyclopentenyl)-2-methylbenzothiazole [1433907-17-5]

The product was isolated by flash chromatography (EtOAc/hexanes 1/50) as colorless oil. 78% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.95 (d, J = 1.4 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.49 (dd, J = 8.4, 1.6 Hz, 1H), 6.26-6.24 (m, 1H), 2.81 (s, 3H), 2.80-2.75 (m, 2H), 2.59-2.53 (m, 2H), 2.09-2.01 (m, 2H).

^{13}C NMR (75 MHz, CDCl$_3$): δ 167.3, 153.9, 142.2, 135.3, 133.9, 126.7, 122.8, 121.0, 119.3, 33.6, 33.5, 23.4, 20.2.

HRMS (ESI): calcd for $C_{13}H_{14}NS$ $[M+H]^+$ 216.0847; found 216.0845.



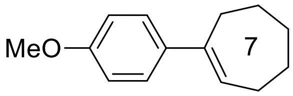
1-(*p*-Anisyl)cyclohexene [20758-60-5]

The product was isolated by flash chromatography (Et_2O/hexanes 1/100) as colorless oil. 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.31 (m, 2H), 6.87-6.84 (m, 2H), 6.05-6.03 (m, 1H), 3.81 (s, 3H), 2.41-2.37 (m, 2H), 2.23-2.17 (m, 2H), 1.81-1.75 (m, 2H), 1.69-1.63 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 158.6, 136.1, 135.5, 126.1, 123.3, 113.7, 55.4, 27.6, 26.0, 23.3, 22.4.

GC-MS (EI): Calcd for $C_{13}H_{16}O$: 188.3. Found: 188.1.



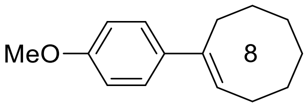
1-(*p*-Anisyl)cycloheptene [32960-45-5]

The product was isolated by flash chromatography (Et_2O/hexanes 1/100) as colorless oil. 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.25 (m, 2H), 6.87-6.83 (m, 2H), 6.03 (t, J = 6.8 Hz, 1H), 3.81 (s, 3H), 2.61-2.58 (m, 2H), 2.31-2.26 (m, 2H), 1.87-1.81 (m, 2H), 1.67-1.62 (m, 2H), 1.59-1.53 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.4, 144.5, 137.7, 129.0, 126.8, 113.6, 55.4, 33.0, 32.9, 28.9, 27.0.

GC-MS (EI): Calcd for $C_{14}H_{18}O$: 202.3. Found: 202.1.



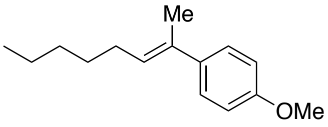
1-(*p*-Anisyl)cyclooctene [32960-67-1]

The product was isolated by flash chromatography (Et_2O/hexanes 1/100) as colorless oil. 93% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.34 (m, 2H), 6.85-6.84 (m, 2H), 5.93 (t, J = 8.3 Hz, 1H), 3.80 (s, 3H), 2.62-2.59 (m, 2H), 2.29-2.25 (m, 2H), 1.63-1.52 (m, 8H).

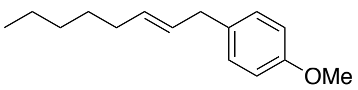
^{13}C NMR (75 MHz, $CDCl_3$): δ 158.5, 139.7, 135.9, 126.9, 126.5, 113.7, 55.4, 30.3, 29.5, 28.5, 27.5, 27.1, 26.3.

GC-MS (EI): Calcd for $C_{15}H_{20}O$: 216.3. Found: 216.2.



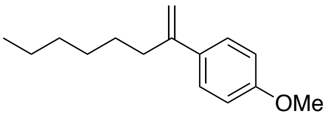
P1

1:



P2

0.27:



P3

0.16

(*E*)-2-Anisyl-2-octene (P1), (*E*)-1-Anisyl-2-octene (P2) and 2-Anisyl-1-octene (P3)

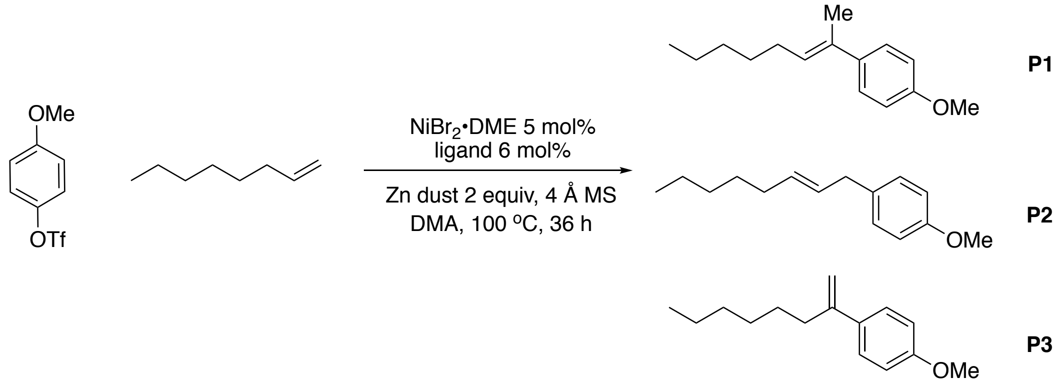
The reaction of 4-methoxyphenyl triflate and 1-octene resulted in three isomers (see attached NMR charts).

The product was isolated by flash chromatography (Et_2O/hexanes 1/100) as colorless oil. 34% yield. The ratio of isomers was determined by proton NMR integration.

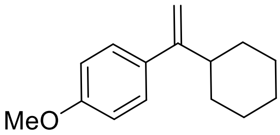
^{1}H NMR of three isomers (400 MHz, $CDCl_3$): δ 7.36-7.28 (m, 1.5H), 7.13-7.08 (m, 0.5H), 6.88-6.82 (m, 2H), 5.71 (t, J = 7.2 Hz, 0.7H), 5.38-5.32 (m, 0.4H), 5.19 (d, J = 1.6 Hz, 0.1H), 4.96 (d, J = 1.6 Hz, 0.1H), 3.81-3.79 (m, 3H), 2.46 (t, J = 7.2 Hz, 0.4H), 2.17 (q, J = 7.2 Hz, 1.2 H), 2.10 (s, 2.1 H), 1.46-1.26 (m, 7H), 0.92-0.88 (m, 3H).

GC-MS (EI): Calcd for $C_{15}H_{22}O$: 218.2, found: 218.1.

Table S12. Ligand effect on Heck reaction of 4-methoxyphenyl triflate with 1-octene



entry	ligand	additive	conv (%)	Yield (%)	**P1/P2/P3**
1	**dcype**	**none**	**100**	**33**	**1:0.31:0.36**
2	dippe	none	100	34	1:0.27:0.16
3	**(*R*)-Ph-BPE**	**none**	**100**	**35**	**1:0.14:0.7**
4	(*R*)-Ph-BPE	K_3PO_4 1 equiv	37	0	---
5	(*R*)-Ph-BPE	Et_3N 1 equiv	100	34	1:0.04:0.88
6	(*R*)-Ph-BPE	*i*-Pr_2NEt 1 equiv	86	18	1:0:0.75
7	(*R*)-Ph-BPE	proton sponge 1 equiv	100	32	1:0.11:1.35



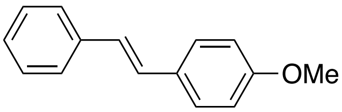
1-Cyclohexyl-1-(*p*-methoxyphenyl)ethene [1013646-21-3]

The product was isolated by flash chromatography (Et_2O/hexanes 1/100) as colorless oil. 89% yield.

^1H NMR (500 MHz, $CDCl_3$): δ 7.29-7.27 (m, 2H), 6.87-6.85 (m, 2H), 5.09 (s, 1H), 4.94 (d, J = 1.2 Hz, 1H), 3.81 (s, 3H), 2.41-2.37 (m, 1H), 1.85-1.70 (m, 5H), 1.37-1.26 (m, 2H), 1.24-1.13 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 154.5, 135.5, 127.8, 113.6, 109.2, 55.4, 42.7, 32.9, 27.0, 26.6.

GC-MS (EI): Calcd for $C_{15}H_{20}O$: 216.3. Found: 216.1.



4-Methoxystilbene [1142-15-0]

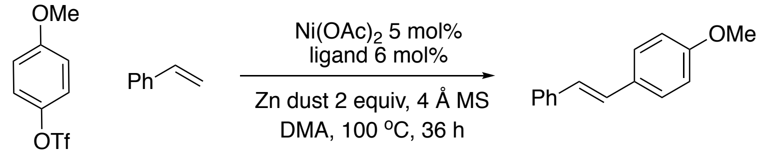
Nickel/dppp was used as the catalyst. The product was isolated by flash chromatography (Et_2O/hexanes 1/100) as white solid. 85% yield. Its (*E*)-geometry was assigned by comparison with reported NMR data.[1]

^1H NMR (400 MHz, $CDCl_3$): δ 7.50-7.45 (m, 4H), 7.35 (t, J = 7.5 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 16.4 Hz, 1H), 6.98 (d, J = 16.4 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 137.8, 130.3, 128.8, 128.4, 127.9, 127.4, 126.8, 126.4, 114.3, 55.5.

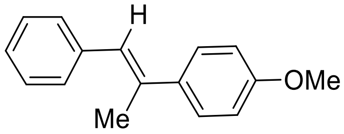
GC-MS (EI): Calcd for $C_{15}H_{14}O$: 210.1, Found: 210.1.

Table S13. Ligand effect on Heck reaction of 4-methoxyphenyl triflate with styrene



entry	ligand	additive	conv (%)	yield (%)
1	**dcype**	**none**	**30**	**30**
2	dcypp	none	0	0
3	dppf	none	100	25
4	**dppp**	**none**	**100**	**85**
5	Xantphos	none	100	9
6	DPEphos	none	62	10
7	dppp	K_3PO_4 1 equiv	36	0

8	dppp	Et_3N 1 equiv	100	42
9	dppp	*i*-Pr_2NEt 1 equiv	100	70
10	dppp	proton sponge 1 equiv	100	65



(*E*)-1-Phenyl-2-(*p*-methoxyphenyl)prop-1-ene [5912-82-3]

The product was isolated by flash chromatography (Et_2O/hexanes 1/100) as colorless oil. 91% yield. Its (*E*)-geometry was assigned by comparison with NMR data of a known compound.[2]

^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 8.7 Hz, 2H), 7.39-7.36 (m, 4H), 7.25-7.22 (m, 1H), 6.92 (d, J = 8.7 Hz, 2H), 6.79 (s, 1H), 3.84 (s, 3H), 2.26 (s, 3H).

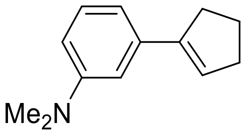
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 138.7, 136.9, 136.5, 129.3, 128.3, 127.2, 126.40, 126.39, 113.8, 55.5, 17.6.

HRMS (ESI): calcd for $C_{16}H_{17}O$ $[M+H]^+$ 225.1279; found 225.1275.

IV. Heck reaction of aryl pivalates and cycloalkenes

A typical procedure: In an argon-filled glove box, $NiBr_2DME$ (3.1 mg, 0.01 mmol, 5 mol%), (*R,R*)-Ph-BPE (8.2 mg, 0.012 mmol, 6 mol%) or dippe (3.2 mg, 0.012 mmol, 6 mol%), zinc dust (26.4 mg, 0.4 mmol, 2 equiv) and dry toluene (1 mL) were added to a dry 10-mL reaction tube. After stirring at room temperature for 15 min, 2-naphthyl pivalate (45.7 mg, 0.2 mmol) and cyclopentene (60 μL, 0.6 mmol, 3 equiv) were added. The reaction mixture was stirred in an oil bath maintained at 100 °C for 24 h. The reaction mixture was cooled to room temperature and then extracted with Et_2O. The solvent was removed under reduced pressure and the crude product was purified by flash chromatograph on silica gel directly. Characterization of newly isolated products are described below. Similar results were obtained when the reactions were set up with a vacuum manifold and Schlenk tubes. The procedure was used for all the examples below.

A typical procedure at 1 mmol: In an argon-filled glove box, $NiBr_2DME$ (6.2 mg, 0.02 mmol, 2 mol%), (*R,R*)-Ph-BPE (12 mg, 0.024 mmol, 2.4 mol%) or dippe (12.8 mg, 0.024 mmol, 2.4 mol%), zinc dust (130 mg, 2 mmol, 2 equiv) and dry toluene (1 mL) were added to a dry 10-mL reaction tube. After stirring at room temperature for 15 min, 2-naphthyl pivalate (228 mg, 1.0 mmol) and cyclopentene (204 mg, 280 μL, 3.0 mmol) were added. The reaction mixture was stirred in an oil bath maintained at 100 °C for 72 h. The reaction mixture was cooled to room temperature and then extracted with Et_2O. The solvent was removed under reduced pressure and the crude product was purified by flash chromatograph on silica gel directly. When (*R*,*R*)-Ph-BPE was used as ligand, 76% conversion and 67% yield. When dippe was used as ligand, 100% conversion and 71% yield among with some naphthalene.



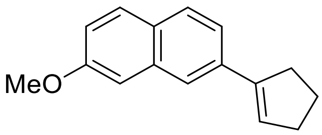
1-[*m*-(Dimethylamino)phenyl]cyclopentene

The product was isolated by flash chromatography (EtOAc/hexanes 1/50) as colorless oil. Ph-BPE was used as ligand: 60% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.19 (t, J = 8.0 Hz, 1H), 6.86-6.83 (m, 2H), 6.65 (dd, J = 8.2, 2.4 Hz, 1H), 6.17-6.14 (m, 1H), 2.96 (s, 6H), 2.75-2.70 (m, 2H), 2.55-2.50 (m, 2H), 2.05-1.98 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 150.9, 143.4, 137.9, 129.0, 125.9, 114.8, 111.9, 110.3, 40.9, 33.6, 33.5, 23.6.

HRMS (ESI): calcd for $C_{13}H_{18}N$ $[M+H]^+$ 188.1439; found 188.1438.



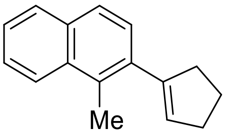
2-(1-Cyclopentenyl)-7-methoxynaphthalene

The product was isolated by flash chromatography (EtOAc/hexanes 1:200) as colorless oil. When Ph-BPE was used as ligand, the yield was 79%.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.67 (t, J = 8.8 Hz, 3H), 7.55 (dd, J = 8.5, 1.7 Hz, 1H), 7.12 (d, J = 2.4 Hz, 1H), 7.09 (dd, J = 8.9, 2.5 Hz, 1H), 6.33-6.31 (m, 1H), 3.92 (s, 3H), 2.86-2.80 (m, 2H), 2.62-2.56 (m, 2H), 2.11-2.04 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 158.0, 142.8, 135.0, 134.9, 129.2, 128.2, 127.6, 127., 123.3, 122.2, 118.3, 106.4, 55.4, 33.7, 33.4, 23.5.

HRMS (ESI): calcd for $C_{16}H_{17}O$ $[M+H]^+$ 225.1279; found 225.1287.



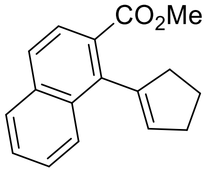
2-(1-Cyclopentenyl)-1-methylnaphthalene

The product was isolated by flash chromatography (hexanes) as colorless oil. When Ph-BPE was used as ligand, the yield was 85%.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.07 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 7.4 Hz, 1H), 7.67 (d, J = 8.5 Hz, 1H), 7.55-7.51 (m, 1H), 7.48-7.44 (m, 1H), 7.33 (d, J = 8.5 Hz, 1H), 5.76-5.74 (m, 1H), 2.76-2.71 (m, 2H), 2.69 (s, 3H), 2.64-2.58 (m, 2H), 2.13-2.05 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 144.4, 136.1, 133.1, 132.6, 130.8, 130.1, 128.5, 126.8, 126.0, 125.7, 125.2, 124.6, 37.7, 33.8, 24.1, 16.2.

HRMS (ESI): calcd for $C_{16}H_{17}$ $[M+H]^+$ 209.1330; found 209.1328.



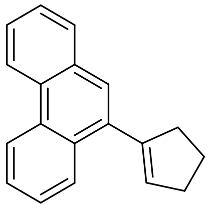
Methyl 1-(1-cyclopentenyl)-2-naphthoate

The product was isolated by flash chromatography (EtOAc/hexanes 1:15) as colorless oil. 50% yield. When Ph-BPE was used as ligand, the yield was 81%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-7.99 (m, 1H), 7.87-7.84 (m, 2H), 7.78 (d, J = 8.6 Hz, 1H), 7.57-7.49 (m, 2H), 5.67-5.64 (m, 1H), 3.89 (s, 3H), 2.79-2.75 (m, 2H), 2.67-2.62 (m, 2H), 2.21-2.14 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.8, 141.9, 140.1, 135.0, 132.1, 130.0, 128.1, 127.6, 127.4, 127.19, 127.17, 126.6, 125.7, 52.1, 38.9, 33.9, 24.6.

HRMS (ESI): calcd for $C_{17}H_{17}O_2$ $[M+H]^+$ 253.1229; found 253.1225.



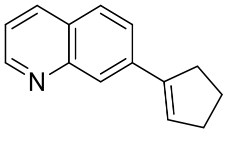
9-(1-Cyclopentenyl)phenanthrene

The product was isolated by flash chromatography (hexanes) as colorless oil. 70% yield. When Ph-BPE was used as ligand, the yield was 92%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, J = 7.7 Hz, 1H), 8.68 (d, J = 8.1 Hz, 1H), 8.22 (dd, J = 8.0, 1.1 Hz, 1H), 7.86 (dd, J = 7.5, 1.6 Hz, 1H), 7.70-7.58 (m, 5H), 6.03-6.01 (m, 1H), 2.92-2.87 (m, 2H), 2.72-2.67 (m, 2H), 2.22-2.14 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.8, 136.0, 131.9, 131.0, 130.9, 130.8, 129.9, 128.6, 126.8, 126.7, 126.5, 126.43, 126.40, 125.3, 123.1, 122.6, 38.0, 33.9, 24.2.

HRMS (ESI): calcd for $C_{19}H_{17}$ $[M+H]^+$ 245.1330; found 245.1339.



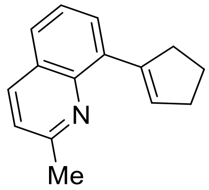
1-(7-Quinolinyl)cyclopentene

The product was isolated by flash chromatography (EtOAc/hexanes 1/20) as colorless oil. When Ph-BPE was used as ligand, the yield was 88%.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.88 (dd, J = 4.2, 1.7 Hz, 1H), 8.10 (d, J = 8.3 Hz, 1H), 8.00 (s, 1H), 7.78-7.71 (m, 2H), 7.34 (dd, J = 8.2, 4.3 Hz, 1H), 6.43-6.41 (m, 1H), 2.89-2.84 (m, 2H), 2.63-2.58 (m, 2H), 2.12-2.05 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 150.7, 149.0, 142.4 138.1, 135.7, 128.9, 127.5, 125.6, 125.1, 120.7, 33.8, 33.3, 23.5.

HRMS (ESI): calcd for $C_{14}H_{14}N$ [M+H]$^+$ 196.1126; found 196.1129.



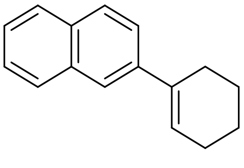
8-(1-Cyclopentenyl)-2-methylquinoline

The product was isolated by flash chromatography (EtOAc/hexanes 1/20) as colorless oil. When Ph-BPE was used as ligand, the yield was 85%.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.01 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 7.5 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H), 7.09-7.07 (m, 1H), 3.05-3.00 (m, 2H), 2.76 (s, 3H), 2.70-2.65 (m, 2H), 2.11-2.03 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 158.2, 146.3, 141.3, 136.6, 135.6, 133.4, 128.3, 126.9, 126.6, 125.4, 121.5, 36.3, 34.3, 25.8, 23.3.

HRMS (ESI): calcd for $C_{15}H_{16}N$ [M+H]$^+$ 210.1283; found 210.1283.



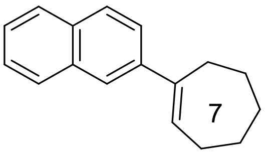
1-(2-Naphthyl)cyclohexene [54607-03-3]

The product was isolated by flash chromatography (hexanes) as colorless oil. Ph-BPE was used as ligand. 90% yield.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.82-7.77 (m, 4H), 7.61 (dd, J = 8.7, 1.8 Hz, 1H), 7.47-7.41 (m, 2H), 6.32-6.30 (m, 1H), 2.58-2.54 (m, 2H), 2.31-2.26 (m, 2H), 1.88-1.83 (m, 2H), 1.75-1.70 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 140.0, 136.6, 133.8, 132.6, 128.2, 127.7, 127.6, 126.1, 125.7, 125.5, 124.0, 123.3, 27.6, 26.2, 23.3, 22.4.

HRMS (ESI): calcd for $C_{16}H_{17}$ [M+H]$^+$ 209.1330; found 209.1336.



1-(2-Naphthyl)cycloheptene [93436-36-3]

The product was isolated by flash chromatography (hexanes) as colorless oil. Ph-BPE was used as ligand. 93% yield.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.81-7.73 (m, 4H), 7.50 (dd, J = 8.6, 1.9 Hz, 1H), 7.47-7.39 (m, 2H), 6.25 (t, J = 6.8 Hz, 1H), 2.74-2.72 (m, 2H), 2.38-2.33 (m, 2H), 1.92-1.86 (m, 2H), 1.74-1.69 (m, 2H), 1.63-1.58 (m, 2H).

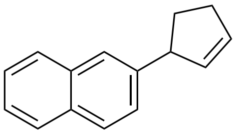
^{13}C NMR (101 MHz, CDCl$_3$): δ 145.1, 142.4, 133.7, 132.4, 131.2, 128.1, 127.7, 127.6, 126.1, 125.4, 125.0, 123.9, 32.9, 32.9, 29.2, 27.1, 27.0.

HRMS (ESI): calcd for $C_{17}H_{19}$ $[M+H]^+$ 223.1487; found 223.1488.

V. Heck reaction using Watson procedures

A typical procedure of Watson:[1] In an argon-filled glove box, Ni(cod)$_2$ (2.8 mg, 0.01 mmol, 10 mol%), diphosphine (0.012 mmol, 6 mol%) and dry toluene (0.4 mL) were added to a dry 10-mL Schlenck tube. After stirring at room temperature for 15 min, 2-naphthyl pivalate (22.8 mg, 0.1 mmol), cyclopentene (30 μL, 0.3 mmol, 3 equiv), K_3PO_4 (31.8 mg, 0.15 mmol, 1.5 equiv) and GC standard n-$C_{12}H_{26}$ (10 μL) were added. The reaction mixture was stirred in an oil bath maintained at 125 °C for 36 h. Aliquots were taken from the organic phase and passed through a short plug of silica gel with EtOAc washing (3 mL). The filtrate was subjected to GC analysis to determine the conversion and calibrated yield of the product. In our hands, the reaction of 2-naphthyl pivalate and styrene (2 equiv) gave 100% conversion and 83% yield of (*E*)-β-(2-naphthyl)styrene. It reproduced well 100% conversion and 99% yield which was reported by Watson.[1] The reaction of 4-methoxyphenyl triflate and cyclopentene afforded 76% conversion, 10% yield of an allylic isomer and 2% of a conjugated isomer, along with methoxybenzene as main side product.

Under another condition of Watson's using NiCl$_2$DME (2.2 mg, 0.01 mmol, 10 mol%), dppf (6.6 mg, 0.012 mmol, 12 mol%) and zinc dust (6.5 mg, 0.1 mmol, 1 equiv),[1] the reaction of 2-naphthyl pivalate and cyclopentene gave 20% conversion and some naphthalene, but without any Heck isomer detected.



3-(2-Naphthyl)cyclopentene [92425-28-0]

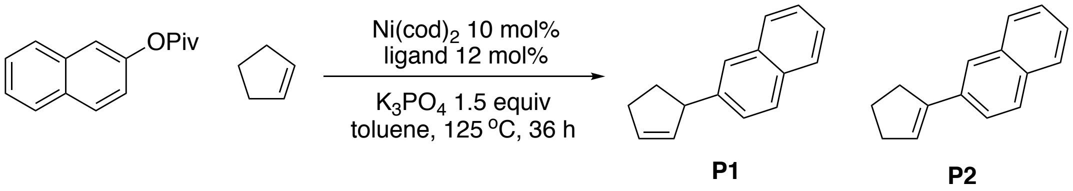
The product was isolated by flash chromatography (Et$_2$O/hexanes 1/100) as colorless oil. 58% isolated yield. The ratio of allylic and conjugated isomers **P1** and **P2** was determined to be 1:0.07 based on ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.82-7.78 (m, 3H), 7.63 (s, 1H), 7.47-7.40 (m, 2H), 7.35 (dd, J = 8.4, 1.6 Hz, 1H), 6.03-6.00 (m, 1H), 5.89-5.84 (m, 1H), 4.11-4.07 (m, 1H), 2.62-2.46 (m, 3H), 1.87-1.82 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.1, 134.3, 133.7, 132.4, 132.3, 128.2, 127.73, 127.70, 126.4, 126.0, 125.3, 125.2, 51.6, 33.8, 32.7.

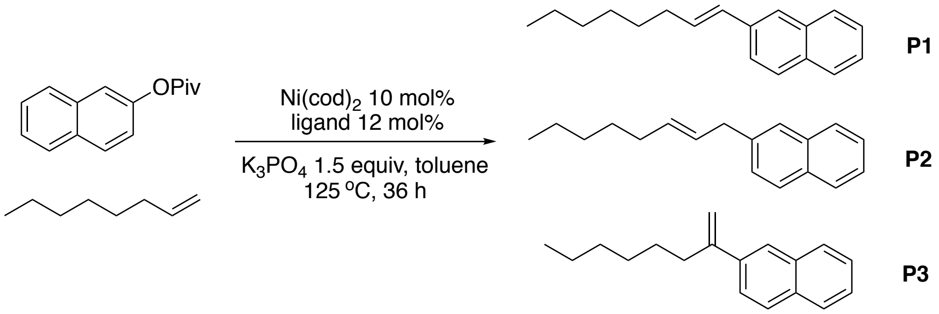
GC-MS (EI): Calcd for $C_{15}H_{14}$: 194.1, found: 194.1.

Table S14. Ligand effect on Heck reaction with cyclopentene using Watson's procedures with $Ni(cod)_2$



entry	ligand	conv (%)	yield (%)	**P1/P2**
1	**dppf**	**81**	**60**	**1:0.07**
2	dppp	4	0	--
3	dcype	17	0	--
4	dippe	32	0	--

Table S15. Ligand effect on Heck reaction of 2-naphthyl pivalate with 1-octene using Watson's procedure.



entry	ligand	base	conv (%)	yield (%)	**P1/P2/P3**
1	dppf	K_3PO_4	83	47	1:0.47:0.31
2	dppp	K_3PO_4	25	0	---

VI. Reference

1. Ehle, A. R.; Zhou, Q.; Watson, M. P., *Org. Lett.* **2012,** *14*, 1202-1205.
2. Zhu, G.; Kong, W.; Feng, H.; Qian, Z. *J. Org. Chem.* **2014**, *79*, 1786-1795.