Electronic Supplementary Material (ESI) for Chemical Communications

Selective Arylation at Vinylic Site of Cyclic Olefins

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Supporting Information: Experimentals and compound characterization

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I. General

^{1}H NMR spectra were acquired on Bruker 400 MHz or 300 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 or 75 MHz on 300 MHz instruments and chemical shifts were recorded relative to solvent resonance ($CDCl_3$: δ 77.16). ^{31}P{^{1}H} NMR spectra were obtained at 121 MHz on 300 MHz instrument or 162 MHz on 400 MHz instrument. Proof of purity of new compounds was demonstrated with copies of ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra.

Glassware was dried in an oven at 120 ºC for at least 2 hours before use. Dry veratrole (Alfa) and DMPU (Aldrich) were degassed by argon bubbling and stored over activated 4 Å molecular sieve beads in an argon-filled glove box before use. Dry hexane, diethyl ether and dichloromethane were collected from a solvent purification system containing a column of activated alumina (1 m x 2) under argon. Dry THF was freshly distilled from sodium/benzophenone under argon before use. All of anhydrous solvents were stored in Schlenk tubes in an argon-filled glove box.

Unless noted otherwise, commercially available chemicals were used without further purification. Dry diisopropylethylamine (DIPEA) and triethylamine were distilled from CaH_2 under argon before use. The GC standard, *n*-dodecane was degassed with argon bubbling and dried over activated 4 Å molecular sieve beads for a few days in the glove box before use.

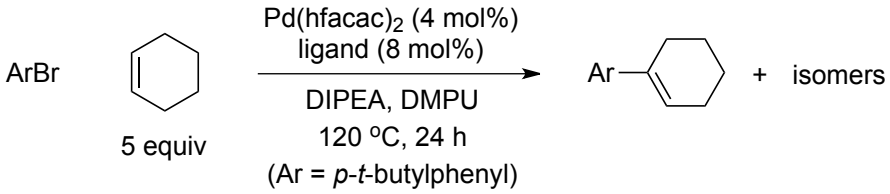
Thin-layer chromatography (TLC) was conducted with Merck 60 F254 coated silica gel plate (0.2 mm thickness). Flash chromatography was performed using Merck silica gel 60 (0.040-0.063 mm) or SiliCycle silica gel F60 (0.040-0.063 mm). Gas chromatography (GC) analysis was performed on a Shimadzu GC-2010 instrument with Agilent J & W GC column DB-5MS-UI. GC/MS analysis was conducted on a Thermo Scientific DSQ II single quadrupole GC/MS instrument with

Agilent J & W GC column DB-5MS-UI. ESI/MS analysis was conducted on a ThermoFinnigan LCQ Fleet MS spectrometer.

II. Condition optimization

Typical Procedure: In an argon-filled glove box, a dry 4-mL reaction tube containing a magnetic stir bar was charged with $Pd(hfacac)_2$ (4 mol%, 2 mg, 0.004 mmol), $PtBu_3 \cdot HBF_4$ (8 mol%, 2 mg, 0.008 mmol) and 0.5 mL of dry DMPU. After stirring at room temperature for 10 minutes, *p-tert*-butylphenyl bromide (0.10 mmol, 21 mg), DIPEA (1.5 equiv, 0.15 mmol, 19 mg, distilled over CaH_2), cyclohexene (5 equiv, 0.50 mmol, 41 mg, 52 μL), and 1-dodecane (10 μL; GC standard) were added sequentially via syringe. The tube was capped tightly and the mixture was vigorous stirred in a 120 ºC oil bath (internal temperature). After 6 hours and 24 hours, aliquots were taken from the reaction mixture in the glove box and passed through a short plug of silica gel with diethyl ether washing. The filtrate was subjected to GC analysis to determine the conversion of ArBr, yield and selectivity of the Heck reaction products. The isomers of the products were identified by GCMS and the structure of the major isomer was assigned based on ^{1}H NMR spectroscopy of the purified sample. *^{1}H NMR spectroscopy was unsuitable for determination of the ratio of the desired isomer versus minor isomers due to low signal intensity and overlap of signals of the minor isomers.*

Table S1 Effect of Ligand



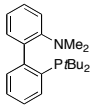
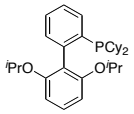
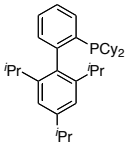
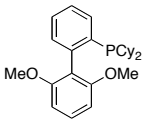
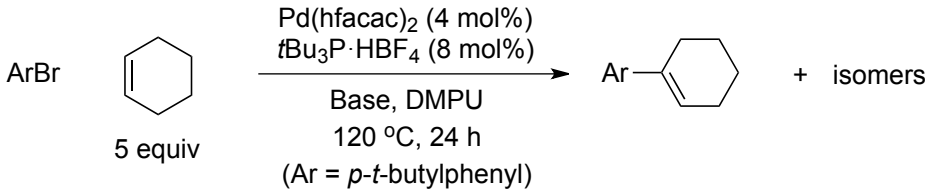
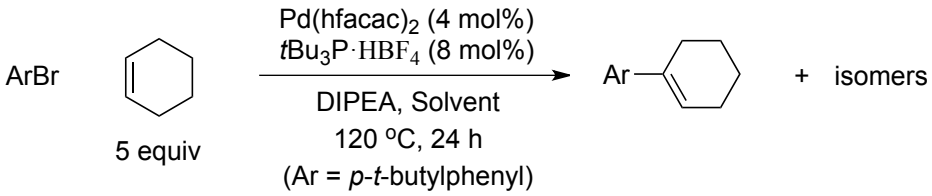
Ligand	Conversion (%)	Yield (%)	Selectivity
P*t*Bu$_3$·HBF$_4$	**100**	**94**	**33:1**
PCy$_3$	72	6	0:1
P(1-Ad)$_2$(*n*Bu)	100	60	1:4
PPh$_3$	18	5	0:1
 *t*Bu-DavePhos	89	53	1:52
 RuPhos	100	12	1:43
 XPhos	100	17	1:21
 SPhos	67	13	0:1
BINAP	8	0	--
dppf	7	0	--
dppp	8	0	--
dppbz	4	0	--
dppe	6	0	--

Table S2 Effect of Base



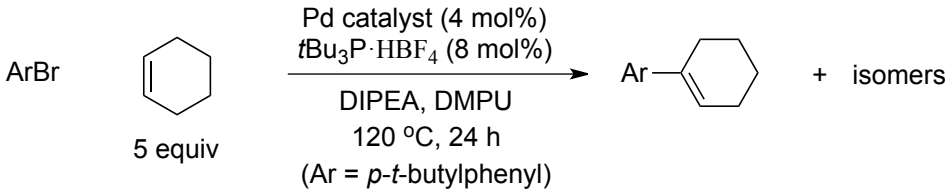
Base	Conversion (%)	Yield (%)	Selectivity
Et_3N	100	81	4:1
nBu_3N	82	25	1:2
DIPEA	**100**	**94**	**33:1**
Cy_2NMe	100	76	4:1
N-Methyl morpholine	100	73	1:3
nBu_2NMe	100	80	3:1
BnNHMe	100	95	7:1
2,6-lutidine	100	17	1:50
DABCO	100	65	0:1
Urotropine	100	17	1:13
Proton sponge	100	78	1:8
Li_2CO_3	100	80	1:10
Na_2CO_3	100	58	1:19
LiOAc	100	38	1:21
$NaHCO_3$	100	45	1:45
Li_3PO_4	23	11	1:1

Table S3 Effect of Solvent



Solvent	Conversion (%)	Yield (%)	Selectivity
DMF	100	80	2:1
DMA	100	83	18:1
NMP	100	82	1:8
DMPU	**100**	**94**	**33:1**
DME	100	75	1:22
Dioxane	95	81	2:1
2-MeTHF	100	96	1:1
Triglyme	100	75	1:12
Veratrole	100	89	6:1
Toluene	100	91	2:1

Table S4 Effect of palladium source

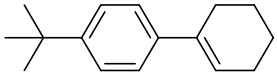


Pd catalyst	Conversion (%)	Yield (%)	Selectivity
$Pd(hfacac)_2$	**100**	**94**	**33:1**
$Pd(acac)_2$	100	24	1:2
$Pd(OAc)_2$	100	38	1:3
$Pd(OCOCF_3)_2$	100	4	0:1
$Pd(dba)_2$	100	62	2:1
$Pd_2(dba)_3$	100	38	0:1

III. Isolation of Heck products

The typical procedure with 0.5 mmol of ArX was used for all the isolation, unless stated otherwise. In an argon-filled glove box, a dry 10-mL Schlenk tube containing a magnetic stir bar was charged with $Pd(hfacac)_2$ (10 mg, 0.02 mmol), tBu$_3$P·HBF$_4$ (12 mg, 0.04 mmol) and 2.5 mL of dry DMPU. After stirring at room temperature for 10 minutes, aryl halide (0.50 mmol), cyclic olefin (2 or 5 equiv, 1.0 or 2.5 mmol), and DIPEA (0.75 mmol, 97 mg) were added sequentially via syringe. The Schlenk tube was capped tightly and the mixture was heated with vigorous stirring in a 120 °C oil bath (external temperature). After the aryl bromide was fully consumed (monitored by GC), the reaction mixture was passed through a pad of silica gel with diethyl ether washings to remove DMPU, inorganic salts and catalyst first. Then the filtrate was concentrated on a rotary evaporator and the residue was directly subjected to silica gel flash chromatography. The ratio of the conjugated isomer versus all other isomers was determined by GC analysis of unpurified samples. ^{1}H NMR spectroscopy was unsuitable for determination of selectivity.

The experiments can also be set up using Schlenk line that gave similar results. In air, to a dry 10-mL Schlenk tube containing a magnetic stir bar was charged with $Pd(hfacac)_2$ (10 mg, 0.02 mmol) and tBu$_3$P·HBF$_4$ (12 mg, 0.04 mmol). The atmosphere was switched from air to argon after three cycles of evacuation and refilling of argon. Dry DMPU (2.5 mL) was added via a syringe and the mixture was stirred at RT for 10 minutes. Against argon flow, aryl bromide (0.50 mmol), cyclic olefin (2 or 5 equiv, 1.0 or 2.5 mmol), and DIPEA (0.75 mmol, 97 mg) were added sequentially. The Schlenk tube was capped tightly and the mixture was heated with vigorous stirring in 120 ºC oil bath until aryl halide was fully consumed (monitored by GC). Routine workup and flash chromatography was used to isolate the products.

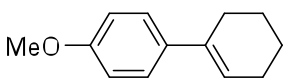


1-(*p*-*t*-Butylphenyl)cyclohexene [60652-09-7]. The reaction was set up with 5.0 equiv of cyclohexene and the reaction mixture was stirred at 120 ºC for 29 hours. The product was purified by flash chromatography (hexane) as colorless oil (103 mg, 94%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 33:1 by GC. When 2 equiv of cyclohexene was used, the reaction gave 58% yield and 20:1 selectivity.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (pseudosinglet, 4H), 6.12-6.09 (m, 1H), 2.43-2.39 (m, 2H), 2.23-2.18 (m, 2H), 1.81-1.75 (m, 2H), 1.69-1.63 (m, 2H). 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 139.7, 136.2, 125.1, 124.5, 124.0, 34.4, 31.4, 27.3, 25.9, 23.1, 22.2.

GCMS (EI): Calcd for $C_{16}H_{22}$: 214.3. Found: 214.0



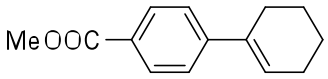
1-(*p*-Anisyl)cyclohexene [20758-60-5]. The reaction was set up with 5.0 equiv of cyclohexene and the reaction mixture was stirred at 120 ºC for 29 hours. The product

was purified by flash chromatography (1:10 EA/hexane) as colorless oil (86 mg, 91%). 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 7.33-7.30 (m, 2H), 6.86-6.83 (m, 2H), 6.04-6.01 (m, 1H), 3.80 (s, 3H), 2.40-2.35 (m, 2H), 2.21-2.16 (m, 2H), 1.80-1.74 (m, 2H), 1.67-1.62 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 135.9, 135.4, 125.9, 123.2, 113.6, 55.3, 27.5, 25.9, 23.2, 22.3.

GCMS (EI): Calcd for $C_{13}H_{16}O$: 188.1. Found: 188.1

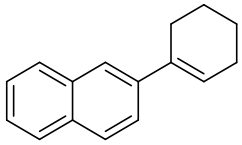


1-(*p*-Methoxycarbonylphenyl)cyclohexene [406232-72-2]. The reaction was set up with 5.0 equiv of cyclohexene and the reaction mixture was stirred at 120 ºC for 36 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (101 mg, 93%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 31:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 6.27-6.24 (m, 1H), 3.90 (s, 3H), 2.44-2.39 (m, 2H), 2.26-2.21 (m, 2H), 1.82-1.76 (m, 2H), 1.70-1.64 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 147.1, 135.9, 129.6, 128.0, 127.2, 124.7, 52.0, 27.2, 26.0, 22.9, 22.0.

GCMS (EI): Calcd for $C_{14}H_{16}O_2$: 216.1. Found: 216.1



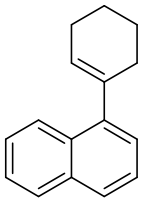
1-(2-Naphthyl)cyclohexene [54607-03-3]. The reaction was set up with 5.0 equiv of cyclohexene and the reaction mixture was stirred at 120 ºC for 29 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (100 mg, 96%). The ratio of the desired isomer versus all other isomers in the crude product

was determined to be 28:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.78 (m, 4H), 7.64-7.61 (m, 1H), 7.49-7.42 (m, 2H), 6.34-6.31 (m, 1H), 2.59-2.55 (m, 2H), 2.33-2.28 (m, 2H), 1.90-1.84 (m, 2H), 1.77-1.71 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8, 136.3, 133.5, 132.4, 128.0, 127.6, 127.5, 125.9, 125.5, 125.3, 123.8, 123.1, 27.4, 26.0, 23.1, 22.2.

GCMS (EI): Calcd for $C_{16}H_{16}$: 208.2. Found: 208.1

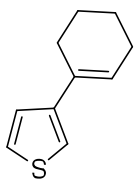


1-(1-Naphthyl)cyclohexene [40358-51-8]. The reaction was set up with 5.0 equiv of cyclohexene and the reaction mixture was stirred at 120 ºC for 60 hours. The product was purified by flash chromatography (hexane) as colorless oil (93 mg, 89%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 17:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.99 (m, 1H), 7.84-7.80 (m, 1H), 7.71 (d, J = 8.2 Hz, 1H), 7.46-7.38 (m, 3H), 7.25 (dd, J = 7.0, 1.2 Hz, 1H), 5.77-5.74 (m, 1H), 2.39-2.34 (m, 2H), 2.28-2.23 (m, 2H), 1.87-1.74 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 137.7, 133.8, 131.5, 128.3, 127.3, 126.7, 125.9, 125.6, 125.5, 125.4, 124.9, 31.1, 25.6, 23.3, 22.4.

GCMS (EI): Calcd for $C_{16}H_{16}$: 208.1. Found: 208.1



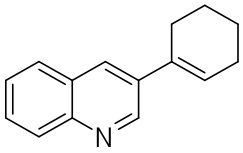
1-(3-Thienyl)cyclohexene [76441-42-4]. The reaction was set up with 5.0 equiv of cyclohexene and the reaction mixture was stirred at 120 ºC for 29 hours. The product was purified by flash chromatography (1:10 EA/hexane) as colorless oil (73 mg, 89%).

The ratio of the desired isomer versus all other isomers in the crude product was determined to be 30:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.22 (m, 2H), 7.08-7.07 (m, 1H), 6.19-6.16 (m, 1H), 2.41-2.37 (m, 2H), 2.22-2.16 (m, 2H), 1.79-1.73 (m, 2H), 1.67-1.62 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 131.9, 125.2, 124.7, 123.9, 117.8, 27.3, 25.6, 22.9, 22.3.

GCMS (EI): Calcd for $C_{10}H_{12}S$: 164.0. Found: 164.0

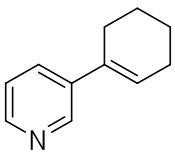


3-(1-Cyclohexenyl)quinoline [33063-43-3]. The reaction was set up with 5.0 equiv of cyclohexene and the reaction mixture was stirred at 120 ºC for 29 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (94 mg, 90%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 27:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (d, J = 2.2 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 2.0 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.66-7.62 (m, 1H), 7.52-7.49 (m, 1H), 6.37-6.35 (m, 1H), 2.52-2.48 (m, 2H), 2.31-2.26 (m, 2H), 1.88-1.82 (m, 2H), 1.74-1.68 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 147.0, 134.9, 133.9, 130.3, 129.1, 128.6, 128.0, 127.8, 127.2, 126.6, 27.1, 26.0, 22.9, 22.0.

GCMS (EI): Calcd for $C_{15}H_{15}N$: 209.1. Found: 209.1



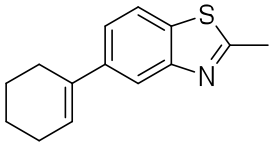
3-(1-Cyclohexenyl)pyridine [19100-10-8]. The reaction was set up with 5.0 equiv of cyclohexene and the reaction mixture was stirred at 120 ºC for 29 hours. The product was purified by flash chromatography (1:10 EA/hexane) as colorless oil (75 mg, 94%).

The ratio of the desired isomer versus all other isomers in the crude product was determined to be 23:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, *J* = 2.1 Hz, 1H), 8.44 (d, *J* = 4.8 Hz, 1H), 7.65-7.62 (m, 1H), 7.23-7.20 (m, 1H), 6.18-6.15 (m, 1H), 2.41-2.37 (m, 2H), 2.25-2.20 (m, 2H), 1.83-1.77 (m, 2H), 1.70-1.64 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7, 146.7, 137.9, 133.9, 132.1, 126.6, 123.0, 27.1, 25.8, 22.8, 21.9.

GCMS (EI): Calcd for $C_{11}H_{13}N$: 159.1. Found: 159.1

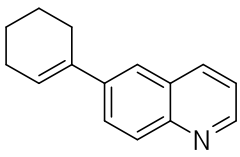


5-(1-Cyclohexenyl)-2-methylbenzothiazole. The reaction was set up with 5.0 equiv of cyclohexene and the reaction mixture was stirred at 120 ºC for 36 hours. The product was purified by flash chromatography (1:4 EA/hexane) as white solid (103 mg, 90%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 22:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 1.6 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.41 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.22-6.19 (m, 1H), 2.82 (s, 3H), 2.50-2.45 (m, 2H), 2.27-2.21 (m, 2H), 1.84-1.78 (m, 2H), 1.71-1.65 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 153.9, 141.1, 136.2, 133.6, 125.4, 122.2, 120.8, 118.5, 27.6, 26.0, 23.1, 22.1, 20.2.

GCMS (EI): Calcd for $C_{14}H_{15}NS$: 229.0. Found: 229.0



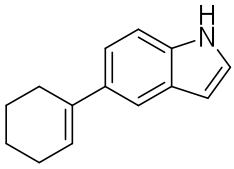
6-(1-Cyclohexenyl)quinoline. The reaction was set up with 5.0 equiv of cyclohexene and the reaction mixture was stirred at 120 ºC for 36 hours. The product was purified by flash chromatography (1:4 EA/hexane) as white solid (90 mg, 86%). The ratio of

the desired isomer versus all other isomers in the crude product was determined to be 29:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (d, *J* = 3.0 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 8.02 (d, *J* = 8.9 Hz, 1H), 7.83 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.70 (s, 1H), 7.35 (dd, *J* = 8.2, 4.0 Hz, 1H), 6.33-6.31 (m, 1H), 2.53-2.50 (m, 2H), 2.30-2.24 (m, 2H), 1.86-1.80 (m, 2H), 1.73-1.67 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 147.6, 140.5, 136.1, 135.7, 129.0, 128.3, 127.4, 126.6, 122.7, 121.2, 27.3, 26.0, 23.0, 22.1.

GCMS (EI): Calcd for $C_{15}H_{15}N$: 209.1. Found: 209.0

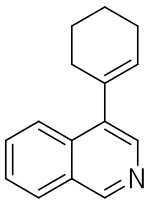


5-(1-Cyclohexenyl)indole. The reaction was set up with 1 equiv of *N*-Boc-5-bromoindole and 5 equiv of cyclohexene. The reaction mixture was stirred at 120 ºC for 36 hours. The Boc-deprotected product was isolated by flash chromatography (1:4 EA/hexane) as colorless oil (92 mg, 93%). The ratio of the 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 8.02 (br s, 1H), 7.63 (s, 1H), 7.31-7.26 (m, 2H), 7.15-7.14 (m, 1H), 6.52-6.51 (m, 1H), 6.10-6.07 (m, 1H), 2.51-2.47 (m, 2H), 2.25-2.19 (m, 2H), 1.83-1.77 (m, 2H), 1.71-1.65 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 135.1, 134.9, 127.9, 124.4, 123.1, 120.1, 116.9, 110.6, 102.9, 28.1, 26.0, 23.3, 22.4.

GCMS (EI): Calcd for $C_{14}H_{15}N$: 197.1. Found: 197.1

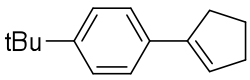


4-(1-Cyclohexenyl)isoquinoline. The reaction was set up with 5.0 equiv of cyclohexene and the reaction mixture was stirred at 120 ºC for 60 hours. The product was purified by flash chromatography (1:4 EA/hexane) as colorless oil (95 mg, 91%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 23:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.14 (s, 1H), 8.33 (s, 1H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.68 (pseudotriplet, *J* = 7.4 Hz, 1H), 7.58 (pseudotriplet, *J* = 7.4 Hz, 1H), 5.85-5.83 (m, 1H), 2.40-2.36 (m, 2H), 2.31-2.27 (m, 2H), 1.89-1.76 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 141.5, 135.8, 134.4, 134.2, 130.0, 129.0, 128.4, 127.8, 126.8, 124.7, 30.9, 25.6, 23.1, 22.1.

GCMS (EI): Calcd for $C_{15}H_{15}N$: 209.1. Found: 209.1

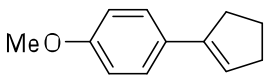


1-(*p*-*t*-Butylphenyl)cyclopentene. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 30 hours. The product was purified by flash chromatography (hexane) as colorless oil (94 mg, 94%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.33 (m, 4H), 6.15-6.13 (m, 1H), 2.72-2.67 (m, 2H), 2.54-2.49 (m, 2H), 2.04-1.97 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 142.2, 134.0, 125.3, 125.2, 125.1, 34.5, 33.3, 33.2, 31.3, 23.4.

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



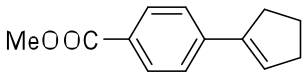
1-(*p*-Anisyl)cyclopentene [709-12-6]. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 30 hours. The product

was purified by flash chromatography (1:10 EA/hexane) as colorless oil (79 mg, 91%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 91:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.06-6.04 (m, 1H), 3.81 (s, 3H), 2.70-2.65 (m, 2H), 2.54-2.48 (m, 2H), 2.04-1.97 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 158.6, 141.8, 129.7, 126.7, 123.9, 113.7, 55.3, 33.4, 33.3, 23.4.

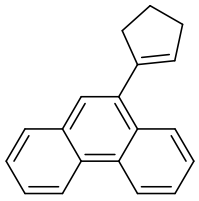
GCMS (EI): Calcd for $C_{12}H_{14}O$: 174.1. Found: 174.1



1-(*p*-Methoxycarbonylphenyl)cyclopentene [579472-58-5]. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 30 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (95 mg, 94%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 54:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.34-6.32 (m, 1H), 3.91 (s, 3H), 2.75-2.70 (m, 2H), 2.58-2.53 (m, 2H), 2.08-2.00 (m, 2H).

GCMS (EI): Calcd for $C_{13}H_{14}O_2$: 202.0. Found: 202.0

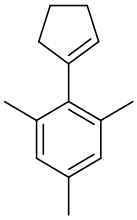


1-(9-Phenanthrecenyl)cyclopentene [6569-76-8]. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 30 hours. The product was purified by flash chromatography (hexane) as colorless oil (109 mg, 89%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 44:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 8.1 Hz, 1H), 8.63 (d, *J* = 7.9 Hz, 1H), 8.17

(d, J = 7.8 Hz, 1H), 7.81 (d, J = 7.5 Hz, 1H), 7.65-7.20 (m, 5H), 5.98-5.96 (m, 1H), 2.87-2.82 (m, 2H), 2.67-2.62 (m, 2H), 2.16-2.09 (m, 2H).

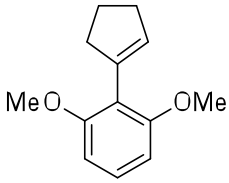
GCMS (EI): Calcd for $C_{19}H_{16}$: 244.1. Found: 244.1



1-(2-Mesityl)cyclopentene [335233-28-8]. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 30 hours. The product was purified by flash chromatography (hexane) as colorless oil (88 mg, 95%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 204:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (s, 2H), 5.49-5.47 (m, 1H), 2.54-2.43 (m, 4H), 2.26 (s, 3H), 2.18 (s, 6H), 2.05-1.97 (m, 2H).

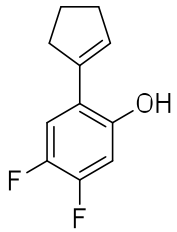
GCMS (EI): Calcd for $C_{14}H_{18}$: 186.1. Found: 186.1



1-(2,6-Dimethoxyphenyl)cyclopentene [64343-06-2]. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 30 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (94 mg, 92%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 47:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (t, J = 8.3 Hz, 1H), 6.57 (d, J = 8.3 Hz, 2H), 5.78-5.76 (m, 1H), 3.78 (s, 6H), 2.67-2.61 (m, 2H), 2.56-2.50 (m, 2H), 2.05-1.95 (m, 2H).

GCMS (EI): Calcd for $C_{13}H_{16}O_2$: 204.1. Found: 204.1



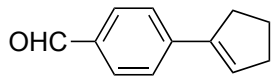
2-(1-Cyclopentenyl)-4, 5-difluorophenol. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 30 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (89 mg, 91%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97-6.92 (m, 1H), 6.75-6.70 (m, 1H), 6.10 (m, 1H), 5.50 (s, 1H), 2.69-2.57 (m, 4H), 2.05-1.97 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2 (d, J_{CF} = 11.5 Hz), 149.1 (dd, J_{CF} = 248.0, 14 Hz), 144.4 (dd, J_{CF} = 239.0, 13 Hz), 138.6, 129.9 (d, J_{CF} = 1.1 Hz), 119.9 (d, J_{CF} = 5.6 Hz), 115.5 (dd, J_{CF} = 18.5, 1.2 Hz), 104.8 (d, J_{CF} = 20.3 Hz), 36.2, 34.0, 22.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ -137.4 (d, J_{FF} = 21.8 Hz), -148.9 (d, J_{FF} = 21.8 Hz).

GCMS (EI): Calcd for $C_{11}H_{10}F_2O$: 196.0. Found: 196.0

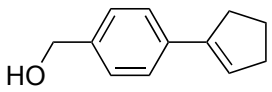


1-(*p*-Formylphenyl)cyclopentene [915016-86-3]. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 48 hours. The product was purified by flash chromatography (1:10 EA/hexane) as colorless oil (80 mg, 93%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.81 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 6.40-6.38 (m, 1H), 2.76-2.71 (m, 2H), 2.60-2.54 (m, 2H), 2.08-2.01 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 191.7, 142.7, 141.7, 134.7, 130.5, 129.9, 125.9, 33.6, 33.0, 23.2.

GCMS (EI): Calcd for $C_{12}H_{12}O$: 172.0. Found: 172.0

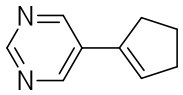


1-(4-Hydroxymethylphenyl)cyclopentene. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 48 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (78 mg, 90%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.19-6.17 (m, 1H), 4.63 (d, *J* = 2.4 Hz, 2H), 2.72-2.67 (m, 2H), 2.55-2.50 (m, 2H), 2.05-1.98 (m, 2H), 1.87 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): 142.1, 139.4, 136.3, 127.0, 126.3, 125.8, 65.2, 33.4, 33.2, 23.4.

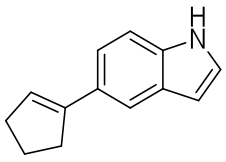
GCMS (EI): Calcd for $C_{12}H_{14}O$: 174.0. Found: 174.0



5-(1-Cyclopentenyl)pyrimidine [1352124-38-9]. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 30 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (65 mg, 89%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.05 (s, 1H), 8.77 (s, 2H), 6.40-6.38 (m, 1H), 2.75-2.70 (m, 2H), 2.61-2.56 (m, 2H), 2.11-2.04 (m, 2H).

GCMS (EI): Calcd for $C_9H_{10}N_2$: 146.2. Found: 146.2



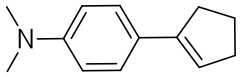
5-(1-Cyclopentenyl)indole. The reaction was set up with 1 equiv of 5-bromoindole and 2 equiv of cyclopentene. The reaction mixture was stirred at 120 ºC for 30 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid

(85 mg, 93%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.64 (s, 1H), 7.40 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 7.11 (t, *J* = 2.8 Hz, 1H), 6.52-6.51 (m, 1H), 6.13-6.11 (m, 1H), 2.81-2.76 (m, 2H), 2.57-2.51 (m, 2H), 2.07-1.99 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 135.0, 129.2, 127.9, 124.4, 123.6, 120.5, 117.8, 110.9, 103.0, 33.7, 33.4, 23.5.

GCMS (EI): Calcd for $C_{13}H_{13}N$: 183.2. Found: 183.2

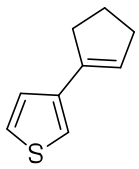


***N*, *N*-Dimethyl-*p*-(1-cyclopentenyl)aniline.** The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 30 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (84 mg, 90%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 5.98-5.96 (m, 1H), 2.94 (s, 6H), 2.70-2.64 (m, 2H), 2.53-2.47 (m, 2H), 2.02-1.95 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 142.2, 126.5, 125.7, 122.0, 112.4, 40.6, 33.3 (2 overlapping signals), 23.4.

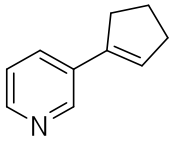
GCMS (EI): Calcd for $C_{13}H_{17}N$: 187.2. Found: 187.2



1-(3-Thienyl)cyclopentene [115754-84-2]. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 30 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (74 mg, 98%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (s, 2H), 7.07 (pseudotriplet, J = 1.9 Hz, 1H), 6.02-6.00 (m, 1H), 2.70-2.65 (m, 2H), 2.53-2.48 (m, 2H), 2.03-1.96 (m, 2H).

GCMS (EI): Calcd for $C_9H_{10}S$: 150.0. Found: 150.0

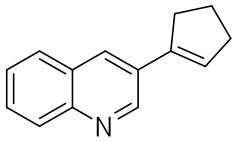


1-(3-Pyridyl)cyclopentene [62113-25-1]. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 30 hours. The product was purified by flash chromatography (1:10 EA/hexane) as colorless oil (70 mg, 96%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, J = 2.0 Hz, 1H), 8.44 (dd, J = 4.8, 1.4 Hz, 1H), 7.70-7.67 (m, 1H), 7.24-7.20 (m, 1H), 6.28-6.26 (m, 1H), 2.74-2.69 (m, 2H), 2.58-2.52 (m, 2H), 2.08-2.00 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 147.2, 139.5, 132.5, 132.3, 128.2, 123.2, 33.4, 32.9, 23.2.

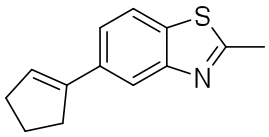
GCMS (EI): Calcd for $C_{10}H_{11}N$: 145.0. Found: 145.0



3-(1-Cyclopentenyl)quinoline [1352124-42-5]. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 30 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (90 mg, 92%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (d, J = 2.1 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.92 (s, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.66-7.62 (m, 1H), 7.50 (pseudotriplet, J = 7.5 Hz, 1H), 6.44-6.43 (m, 1H), 2.83-2.78 (m, 2H), 2.63-2.59 (m, 2H), 2.11-2.04 (m, 2H).

GCMS (EI): Calcd for $C_{14}H_{13}N$: 195.1. Found: 195.1

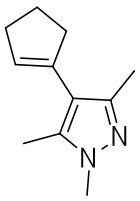


5-(1-Cyclopentenyl)-2-methylbenzothiazole. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 30 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (97 mg, 90%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 130:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 1.4 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.52 (dd, *J* = 8.4, 1.4 Hz, 1H), 6.30-6.27 (m, 1H), 2.84-2.78 (m, 5H), 2.62-2.56 (m, 2H), 2.12-2.04 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 153.8, 142.1, 135.2, 133.8, 126.6, 122.7, 120.9, 119.2, 33.5, 33.4, 23.3, 20.2

GCMS (EI): Calcd for $C_{13}H_{13}NS$: 215.0. Found: 215.0

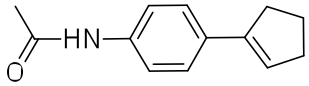


4-(1-Cyclopentenyl)-1,3,5-trimethyl-1*H*-pyrazole. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 30 hours. The product was purified by flash chromatography (1:4 EA/hexane) as colorless oil (79 mg, 90%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.60-5.58 (m, 1H), 3.71 (s, 3H), 2.64-2.59 (m, 2H), 2.49-2.44 (m, 2H), 2.24 (pseudosinglet, 6H), 1.99-1.91 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 136.1, 135.9, 126.4, 115.3, 35.9, 35.8, 32.8, 23.7, 13.7, 10.9.

GCMS (EI): Calcd for $C_{11}H_{16}N_2$: 176.1. Found: 176.2

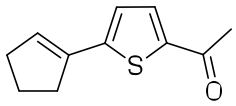


***N*-Acetyl-*p*-(1-cyclopentenyl)aniline.** The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 30 hours. The product was purified by flash chromatography (1:4 EA/hexane) as colorless oil (75 mg, 94%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.36 (m, 5H), 6.12-6.11 (m, 1H), 2.70-2.65 (m, 2H), 2.54-2.49 (m, 2H), 2.16 (s, 3H), 2.04-1.97 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 141.8, 136.6, 133.0, 126.1, 125.4, 119.7, 33.3, 33.2, 24.6, 23.3.

GCMS (EI): Calcd for $C_{13}H_{15}NO$: 201.2. Found: 201.2

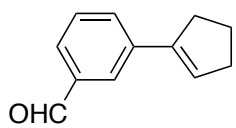


2-Acetyl-5-(1-cyclopentenyl)thiophene. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 30 hours. The product was purified by flash chromatography (1:10 EA/hexane) as colorless oil (73 mg, 76%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 3.9 Hz, 1H), 6.94 (d, J = 3.9 Hz, 1H), 6.26-6.24 (m, 1H), 2.73-2.67 (m, 2H), 2.57-2.53 (m, 5H), 2.08-2.00 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 149.5, 141.8, 136.5, 133.1, 130.3, 124.1, 33.9, 33.6, 26.5, 23.4.

GCMS (EI): Calcd for $C_{11}H_{12}OS$: 192.0. Found: 192.1



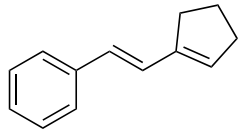
1-(*m*-Formylphenyl)cyclopentene [680203-54-7]. The reaction was set up with 2.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 41 hours. The product was purified by flash chromatography (1:10 EA/hexane) as yellow oil (80 mg,

93%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1H), 7.91 (s, 1H), 7.73-7.69 (m, 2H), 7.47 (t, J = 7.6 Hz, 1H), 6.31-6.29 (m, 1H), 2.77-2.72 (m, 2H), 2.59-2.54 (m, 2H), 2.09-2.02 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 192.6, 141.3, 137.8, 136.5, 131.5, 128.9, 128.2, 128.1, 126.6, 33.5, 33.2, 23.3.

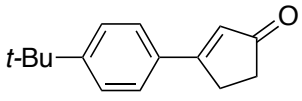
GCMS (EI): Calcd for $C_{12}H_{12}O$: 172.1. Found: 172.1



1-Styrylcyclopentene [109432-85-1]. The reaction was set up with 5.0 equiv of cyclopentene and the reaction mixture was stirred at 120 ºC for 36 hours. The product was purified by flash chromatography (hexane) as white oil (63 mg, 74%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 7.5 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.01 (d, J = 16.0 Hz, 1H), 6.41 (d, J = 16.0 Hz, 1H), 5.85 (s, 1H), 2.57-2.53 (m, 2H), 2.49-2.45 (m, 2H), 2.01-1.93 (m, 2H).

GCMS (EI): Calcd for $C_{13}H_{14}$: 170.1. Found: 170.1

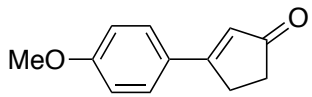


3-(*p*-*t*-Butylphenyl)cyclopent-2-enone [115614-45-4]. The reaction was set up with 2% $Pd(hfacac)_2$, 3% tBu$_3$P·HBF$_4$ and 1.5 equiv of Li_2CO_3. The reaction mixture was stirred at 120 ºC for 36 hours. The product was purified by flash chromatography (1:4 EA/hexane) as white solid (100 mg, 93%). When iPr$_2$NEt was used as base, the yield was 80% due to partial reduction of ArBr to ArH.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 6.55 (t, J = 1.6 Hz, 1H), 3.06-3.03 (m, 2H), 2.59-2.57 (m, 2H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.4, 173.9, 155.0, 131.4, 126.8, 126.7, 125.9, 35.3, 35.0, 31.1, 28.6.

GCMS (EI): Calcd for $C_{15}H_{18}O$: 214.1. Found: 214.1

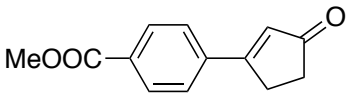


3-(*p*-Anisyl)cyclopent-2-enone [2108-53-4]. The reaction was set up with 2% $Pd(hfacac)_2$, 3% $tBu_3P{\cdot}HBF_4$ and 1.5 equiv of Li_2CO_3. The reaction mixture was stirred at 120 ºC for 42 hours. The product was purified by flash chromatography (1:4 EA/hexane) as white solid (92 mg, 97%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.47 (t, *J* = 1.6 Hz, 1H), 3.87 (s, 3H), 3.03-3.00 (m, 2H), 2.57-2.55 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.3, 173.6, 162.1, 128.6, 126.7, 125.5, 114.3, 55.4, 35.2, 28.6.

GCMS (EI): Calcd for $C_{12}H_{12}O_2$: 188.0. Found: 188.0

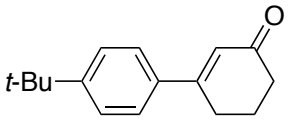


3-(*p*-Methoxycarbonylphenyl)cyclopent-2-enone [1107640-98-1]. The reaction was set up with 2% $Pd(hfacac)_2$, 3% $tBu_3P{\cdot}HBF_4$ and 1.5 equiv of Li_2CO_3. The reaction mixture was stirred at 120 ºC for 48 hours. The product was purified by flash chromatography (1:4 EA/hexane) as white solid (61 mg, 56%), the conjugate addition byproduct was also isolated in 42% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 1.4 Hz, 1H), 3.95 (s, 3H), 3.09-3.06 (m, 2H), 2.63-2.61 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 208.9, 172.2, 166.3, 138.1, 132.2, 130.1, 129.3, 126.7, 52.4, 35.3, 28.7.

GCMS (EI): Calcd for $C_{13}H_{12}O_3$: 216.0. Found: 216.0

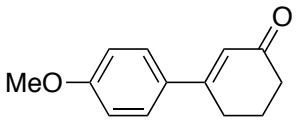


3-*p*-(*t*-Butylphenyl)cyclohex-2-enone. The reaction was set up with 2% $Pd(hfacac)_2$, 3% $tBu_3P{\cdot}HBF_4$ and 1.5 equiv of Li_2CO_3. The reaction mixture was stirred at 120 ºC for 36 hours. The product was purified by flash chromatography (1:4 EA/hexane) as yellow oil (103 mg, 90%).

^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 6.43 (t, *J* = 1.3 Hz, 1H), 2.79-2.75 (m, 2H), 2.50-2.46 (m, 2H), 2.18-2.11 (m, 2H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9, 159.6, 153.6, 135.8, 125.9, 125.7, 124.8, 37.3, 34.8, 31.2, 28.0, 22.8.

GCMS (EI): Calcd for $C_{16}H_{20}O$: 228.1. Found: 228.1

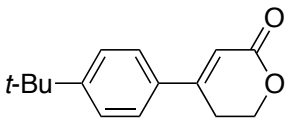


3-*p*-Anisylcyclohex-2-enone [17159-98-7]. The reaction was set up with 2% $Pd(hfacac)_2$, 3% $tBu_3P{\cdot}HBF_4$ and 1.5 equiv of Li_2CO_3. The reaction mixture was stirred at 120 ºC for 42 hours. The product was purified by flash chromatography (1:4 EA/hexane) as white solid (95 mg, 94%).

^1H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.39 (s, 1H), 3.84 (s, 3H), 2.76-2.73 (m, 2H), 2.46 (t, *J* = 6.8 Hz, , 2H), 2.16-2.11 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9, 161.2, 159.1, 130.8, 127.6, 123.7, 114.1, 55.4, 37.2, 27.8, 22.8.

GCMS (EI): Calcd for $C_{13}H_{14}O_2$: 202.0. Found: 202.0



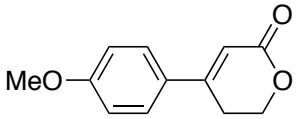
3-*p*-(*t*-Butylphenyl)cyclohex-2-enone. The reaction was set up with 4% $Pd(hfacac)_2$,

8% *t*$Bu_3P{\cdot}HBF_4$ and 1.5 equiv of DIPEA. The reaction mixture was stirred at 120 ºC for 36 hours. The product was purified by flash chromatography (1:4 EA/hexane) as white solid (101 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.45 (m, 4H), 6.37 (s, 1H), 4.52 (t, *J* = 6.2 Hz, 2H), 2.88-2.84 (m, 2H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 155.1, 154.4, 133.0, 126.0, 125.8, 114.2, 66.0, 34.9, 31.1, 26.2.

GCMS (EI): Calcd for $C_{15}H_{18}O_2$: 230.1. Found: 230.1

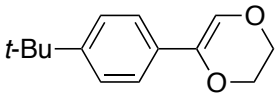


3-(*p*-Anisyl)cyclohex-2-enone. The reaction was set up with 4% $Pd(hfacac)_2$, 8% *t*$Bu_3P{\cdot}HBF_4$, and 1.5 equiv of DIPEA. The reaction mixture was stirred at 120 ºC for 48 hours. The product was purified by flash chromatography (1:2 EA/hexane) as white solid (78 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.30 (d, *J* = 1.1 Hz, 1H), 4.51 (t, *J* = 6.2 Hz, 2H), 3.86 (s, 3H), 2.84 (t, *J* = 6.2, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 161.7, 154.7, 128.1, 127.6, 114.4, 112.8, 65.9, 55.5, 26.2.

GCMS (EI): Calcd for $C_{12}H_{12}O_3$: 204.1. Found: 204.1



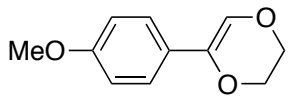
2-(*p*-*t*-Butylphenyl)-1, 4-dioxene. The reaction was set up with 4% $Pd(hfacac)_2$, 8% *t*$Bu_3P{\cdot}HBF_4$, 1.5 equiv of DIPEA and 5 equiv of 1, 4-dioxene. The reaction mixture was stirred at 120 ºC for 48 hours. The product was purified by flash chromatography (hexane) as colorless oil (93 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (ψs, 4H), 6.60 (s, 1H), 4.25-4.23 (m, 2H), 4.13-4.11 (m, 2H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 136.5, 131.1, 125.2, 123.8, 122.7, 64.7, 64.4,

34.5, 31.3.

GCMS (EI): Calcd for $C_{14}H_{18}O_2$: 218.1. Found: 218.1

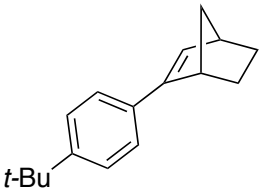


2-(*p*-Anisyl)-1,4-dioxene. The reaction was set up with 4% Pd(hfacac)$_2$, 8% *t*Bu$_3$P·HBF$_4$, 1.5 equiv of DIPEA and 5 equiv of 1, 4-dioxene. The reaction mixture was stirred at 120 ºC for 42 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (71 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.51 (s, 1H), 4.26-4.24 (m, 2H), 4.12-4.10 (m, 2H), 3.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 136.4, 126.7, 124.4, 123.0, 113.8, 64.8, 64.3, 55.3.

GCMS (EI): Calcd for $C_{11}H_{12}O_3$: 192.1. Found: 192.1

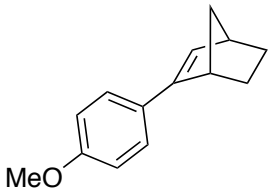


2-(*p*-*t*-Butylphenyl)norborn-2-ene. The reaction was set up with 4% Pd(hfacac)$_2$, 8% *t*Bu$_3$P·HBF$_4$, 2.0 equiv of NaOPh, 2 equiv of norbornene and 1mL of dry $PhCF_3$. The reaction mixture was stirred at 120 ºC for 48 hours. The product was purified by flash chromatography (hexane) as colorless oil (99 mg, 90%). When *i*Pr$_2$NEt and DMPU were used under standard conditions, no reaction occurred at 120 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.32 (m, 4H), 6.25 (d, *J* = 3.1 Hz, 1H), 3.31 (s, 1H), 2.97 (d, *J* = 1.4 Hz, 1H), 1.81-1.73 (m, 2H), 1.53-1.50 (m, 1H), 1.31 (s, 9H), 1.24 (d, *J* = 8.1 Hz, 1H), 1.14 (dd, *J* = 7.4, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 147.6, 133.0, 128.9, 125.3, 124.6, 47.9, 43.4, 43.1, 34.5, 31.3, 26.9, 24.8.

GCMS (EI): Calcd for $C_{17}H_{22}$: 226.2. Found: 226.2

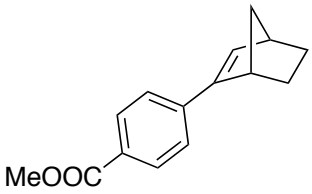


2-(*p*-Anisyl)norborn-2-ene [24920-37-4]. The reaction was set up with 4% $Pd(hfacac)_2$, 8% $tBu_3P{\cdot}HBF_4$, 2.0 equiv of NaOPh, 2 equiv of norbornene and 1mL of dry $PhCF_3$. The reaction mixture was stirred at 120 ºC for 72 hours. The product was purified by flash chromatography (1:10 EA/hexane) as colorless oil (63 mg, 63%).

^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 8.9 Hz, 2H), 6.85 (d, J = 8.9 Hz, 2H), 6.15 (d, J = 3.1 Hz, 1H), 3.81 (s, 3H), 3.28 (s, 1H), 2.97-2.96 (m, 1H), 1.81-1.71 (m, 2H), 1.54-1.50 (m, 1H), 1.25-1.24 (m, 1H), 1.22-1.08 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 147.2, 128.6, 127.4, 126.1, 113.9, 55.3, 47.9, 43.4, 43.0, 27.0, 24.8.

GCMS (EI): Calcd for $C_{14}H_{16}O$: 200.0. Found: 200.0

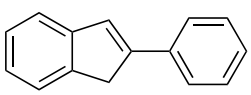


2-(*p*-Methoxycarbonylphenyl)norborn-2-ene. The reaction was set up with 4% $Pd(hfacac)_2$, 8% $tBu_3P{\cdot}HBF_4$, 2.0 equiv of NaOPh, 2 equiv of norbornene and 1mL of dry $PhCF_3$. The reaction mixture was stirred at 120 ºC for 48 hours. The product was purified by flash chromatography (1:10 EA/hexane) as colorless oil (95 mg, 83%).

^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 6.44 (d, J = 3.1 Hz, 1H), 3.90 (s, 3H), 3.34 (s, 1H), 3.03 (s, 1H), 1.85-1.76 (m, 2H), 1.56-1.53 (m, 1H), 1.28 (d, J = 8.3 Hz, 1H), 1.19-1.10 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 147.2, 140.3, 132.8, 129.8, 128.0, 124.6, 52.0, 47.9, 43.4, 43.3, 26.6, 24.8.

GCMS (EI): Calcd for $C_{15}H_{16}O_2$: 228.0. Found: 228.0

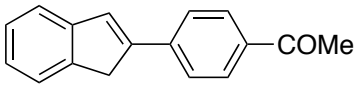


2-Phenyl-*1H*-indene [4505-48-0]. The reaction was set up with 4% $Pd(dba)_2$(12 mg, 0.02 mmol), 8% $tBu_3P{\cdot}HBF_4$ (12 mg, 0.04 mmol), 1.5 equiv of BnNHMe (102 mg, 0.75 mmol), 2 equiv of indene (116 mg, 1.0 mmol) and 2.5 mL of dry DMPU. The reaction mixture was stirred at 120 ºC for 46 hours. The product was purified by flash chromatography (Hexane) as white solid (90 mg, 94%). When the standard condition was used including $Pd(hfacac)_2$, $tBu_3P{\cdot}HBF_4$, iPr_2NEt and DMPU, β/α selectivity of arylated product was 4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.63 (m, 2H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.41-7.37 (m, 3H), 7.29-7.24 (m, 3H), 7.21-7.17 (m, 1H), 3.80 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 145.4, 143.2, 136.0, 128.7, 127.5, 126.6, 126.5, 126.7, 124.8, 123.7, 121.0, 39.0.

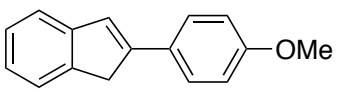
GCMS (EI): Calcd for $C_{15}H_{12}$: 192.2. Found: 192.2



2-(*p*-Acetophenyl)-*1H*-indene [79449-08-4]. The reaction was set up with 4% $Pd(dba)_2$ (12 mg, 0.02 mmol), 8% $tBu_3P{\cdot}HBF_4$ (12 mg, 0.04 mmol), 1.5 equiv of BnNHMe (102 mg, 0.75 mmol), 1 equiv of ArBr, 2 equiv of indene (116 mg, 1.0 mmol) and 2.5 mL of dry DMPU. The reaction mixture was stirred at 120 ºC for 40 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (108 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.37 (s, 1H), 7.30 (ψt, *J* = 7.4 Hz, 1H), 7.23(ψt, *J* = 7.4 Hz, 1H), 3.81 (s, 2H), 2.61 (s, 3H).

GCMS (EI): Calcd for $C_{17}H_{14}O$: 234.1. Found: 234.1



2-(*p*-Anisyl)-*1H*-indene [54288-29-8]. The reaction was set up with 4% $Pd(dba)_2$(12 mg, 0.02 mmol), 8% $tBu_3P{\cdot}HBF_4$ (12 mg, 0.04 mmol), 1.5 equiv of BnNHMe (102

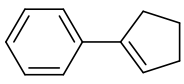
mg, 0.75 mmol), 1 equiv of ArBr, 2 equiv of indene (116 mg, 1.0 mmol) and 2.5 mL of dry DMPU. The reaction mixture was stirred at 120 ºC for 40 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (102 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.25 (ψt, *J* = 7.4 Hz, 1H), 7.15 (ψt, *J* = 7.4 Hz, 1H), 7.09 (s, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 3.84 (s, 3H), 3.75 (s, 2H).

GCMS (EI): Calcd for $C_{16}H_{14}O$: 222.1. Found: 222.1

Heck reactions of aryl and heteroaryl chlorides using 0.5 mmol of organic chlorides. In an argon-filled glove box, a dry 10-mL Schlenk tube containing a magnetic stir bar was charged with $Pd(hfacac)_2$ (10 mg, 0.02 mmol), $t$$Bu_3P{\cdot}HBF_4$ (12 mg, 0.04 mmol) and 2.5 mL of dry DMPU. After stirring at room temperature for 10 minutes, aryl chloride (0.50 mmol), cyclic olefin (5 equiv, 2.5 mmol), and DIPEA (0.75 mmol, 97 mg) were added sequentially via syringe. The Schlenk tube was capped tightly and the mixture was heated with vigorous stirring in a 120 ºC oil bath (external temperature). After the aryl chloride was fully consumed (monitored by GC), the reaction mixture was passed through a pad of silica gel with diethyl ether washings to remove DMPU, inorganic salts and catalyst first. Then the filtrate was concentrated on a rotary evaporator and the residue was directly subjected to silica gel flash chromatography. The ratio of the conjugated isomer versus all other isomers was determined by GC analysis of unpurified samples.

Note: ^{1}H NMR spectroscopy was unsuitable for determination of the amount of minor isomers due to low signal intensity and overlap of signals. The structure of the desired isomer was confirmed by ^{1}H NMR spectroscopy of the purified sample.



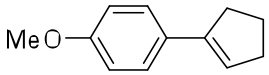
1-Phenylcyclopentene [825-54-7]. The reaction was stirred at 120 ºC for 27 hours.

The product was purified by flash chromatography (hexane) as colorless oil (69 mg, 96%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

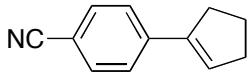
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.11-6.09 (m, 1H), 2.65-2.60 (m, 2H), 2.47-2.42 (m, 2H), 1.97-1.89 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 136.8, 128.2, 126.8, 126.1, 125.5, 33.3, 33.2, 23.3.

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



1-(*p*-Anisyl)cyclopentene [709-12-6]. The reaction was stirred at 120 ºC for 66 hours. The product was purified by flash chromatography (1:10 EA/hexane) as colorless oil (80 mg, 92%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 147:1 by GC.

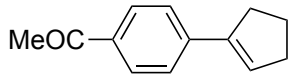


1-(*p*-Cyanophenyl)cyclopentene. The reaction was stirred at 120 ºC for 52 hours. The product was purified by flash chromatography (1:10 EA/hexane) as colorless oil (82 mg, 97%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 174:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 6.38-6.36 (m, 1H), 2.74-2.69 (m, 2H), 2.61-2.56 (m, 2H), 2.10-2.03 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 141.1, 132.1, 130.7, 126.0, 119.2, 109.9, 33.6, 32.9, 23.2.

GCMS (EI): Calcd for $C_{12}H_{11}N$: 169.1. Found: 169.1



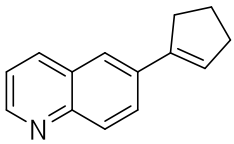
1-(*p*-Acetophenyl)cyclopentene. The reaction was stirred at 120 ºC for 48 hours. The

product was purified by flash chromatography (1:10 EA/hexane) as white solid (91 mg, 98%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 6.35-6.34 (m, 1H), 2.74-2.70 (m, 2H), 2.58-2.53 (m, 5H), 2.08-2.00 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 141.8, 141.4, 135.4, 129.6, 128.5, 125.6, 33.6, 33.1, 26.5, 23.3.

GCMS (EI): Calcd for $C_{13}H_{14}O$: 186.1. Found: 186.1

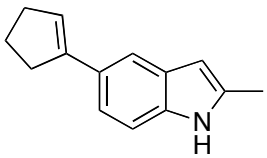


1-(6-Quinolinyl)cyclopentene. The reaction was stirred at 120 ºC for 27 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (89 mg, 91%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (d, *J* = 4.2 Hz, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.9 Hz, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.64 (s, 1H), 7.36-7.33 (m, 1H), 6.36-6.35 (m, 1H), 2.83-2.78 (m, 2H), 2.61-2.57 (m, 2H), 2.11-2.03 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 149.8, 147.8, 141.8, 136.0, 134.9, 129.1, 128.4, 128.3, 127.9, 123.6, 121.3, 33.6, 33.2, 23.3.

GCMS (EI): Calcd for $C_{14}H_{13}N$: 195.1. Found: 195.1

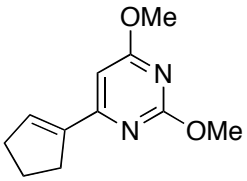


5-(1-Cyclopentenyl)-2-methylindole. The reaction was stirred at 120 ºC for 46 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (95 mg, 97%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 118:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s. 1H), 7.52 (s. 1H), 7.30 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.17-6.16 (m, 1H), 6.10 (d, *J* = 1.9 Hz, 1H), 2.79-2.75 (m, 2H), 2.55-2.51 (m, 2H), 2.38 (s, 3H), 2.06-1.98 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 135.4, 135.3, 129.1, 128.9, 123.1, 119.3, 116.8, 110.0, 100.7, 33.7, 33.4, 23.5, 13.7.

GCMS (EI): Calcd for $C_{14}H_{15}N$: 197.1. Found: 197.1

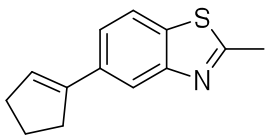


4-(1-Cyclopentenyl)-2,6-dimethoxypyrimidine. The reaction was stirred at 120 ºC for 52 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (93 mg, 90%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 61:1 by GC.

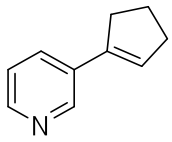
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87-6.85 (m, 1H), 6.27 (s, 1H), 4.00 (s, 3H), 3.96 (s, 3H), 2.70-2.64 (m, 2H), 2.59-2.53 (m, 2H), 2.07-2.00 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 165.0, 163.3, 141.7, 135.7, 97.3, 54.5, 53.7, 33.4, 31.8, 23.2.

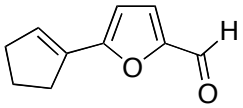
GCMS (EI): Calcd for $C_{11}H_{14}N_2O_2$: 206.1. Found: 206.1



5-(1-Cyclopentenyl)-2-methylbenzothiazole. The reaction was stirred at 120 ºC for 66 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (98 mg, 91%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 105:1 by GC.



1-(3-Pyridyl)cyclopentene [62113-25-1]. The reaction was stirred at 120 ºC for 27 hours. The product was purified by flash chromatography (1:10 EA/hexane) as colorless oil (68 mg, 94%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

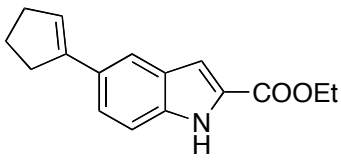


5-(1-Cyclopentenyl)furan-2-carbaldehyde. The reaction was stirred at 120 ºC for 27 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (72 mg, 89%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.57 (s, 1H), 7.22 (d, *J* = 3.7 Hz, 1H), 6.48 (pseodusinglet, 1H), 6.37 (d, *J* = 3.7 Hz, 1H), 2.70-2.65 (m, 2H), 2.59-2.54 (m, 2H), 2.07-1.99 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.1, 157.8, 151.6, 132.3, 132.1, 123.5, 108.6, 33.6, 32.1, 23.2.

GCMS (EI): Calcd for $C_{10}H_{10}O_2$: 162.1. Found: 162.1



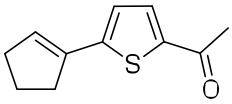
5-(1-Cyclopentenyl)-2-(*p*-ethoxycarbonylphenyl)indole. The reaction was stirred at 120 ºC for 46 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (125 mg, 98%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 127:1 by GC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (s, 1H), 7.64 (s, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.20 (s, 1H), 6.15 (pseodusinglet, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.80-2.76 (m, 2H), 2.57-2.53 (m, 2H), 2.08-2.01 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.9, 142.7, 136.0, 130.1, 127.7, 127.6, 124.5, 124.0,

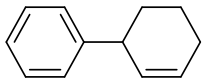
119.1, 111.6, 109.0, 61.0, 33.5, 33.4, 23.4, 14.4.

GCMS (EI): Calcd for $C_{16}H_{17}NO_2$: 255.1. Found: 255.1



2-Acetyl-5-(1-cyclopentenyl)thiophene. The reaction was stirred at 120 ºC for 27 hours. The product was purified by flash chromatography (1:10 EA/hexane) as white solid (85 mg, 88%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:0 by GC.

IV. Mechanistic studies for Heck reaction of aryl bromides



Synthesis of 3-Phenylcyclohexene [15232-96-9]. The compound was made using a reported procedure by Larock.[1] In an argon-filled glove box, a dry 4-mL vial containing a magnetic stir bar was charged with $Pd(OAc)_2$ (2.5 mol%, 3 mg, 0.125 mmol), nBu$_4$NCl (139 mg, 0.5 mmol) and 1.0 mL of dry DMF. After stirring at room temperature for 10 minutes, phenyl iodide (0.50 mmol, 102 mg), NaOAc (3 equiv, 1.50 mmol, 123 mg), cyclohexene (5 equiv, 2.5 mmol, 205 mg), and GC standard, 1-dodecane (10 μL) was added sequentially via syringe. The vial was capped tightly and the mixture was vigorous stirred at RT for 5 days (monitored by GC). After removing the solvent, the product was purified by flash chromatography (hexane) as colorless oil (75 mg, 95%). The ratio of the desired isomer versus all other isomers in the crude product was determined to be >200:1 by GC.

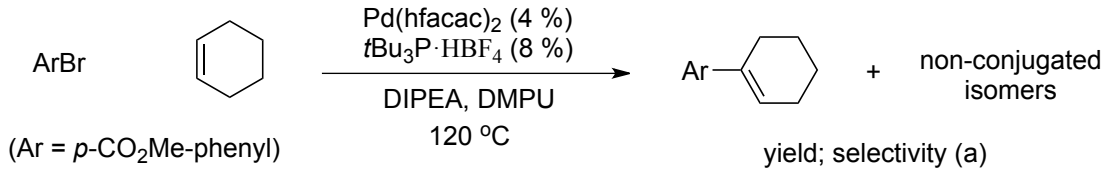
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.17 (m, 5H), 5.76 (pseudotriplet, J = 13.7 Hz, 2H), 2.83-2.78 (m, 1H), 2.30-2.12 (m, 4H), 1.95-1.92 (m, 1H), 1.81-1.70 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 128.4, 127.0, 126.9, 126.8, 126.0, 40.2, 33.5, 29.8, 25.9.

Isomerization of 3-phenylcyclohexene in an active Heck reaction of ArBr and cyclohexene. In an argon-filled glove box, a dry 4-mL reaction tube containing a magnetic stir bar was charged with $Pd(hfacac)_2$ (4 mol%, 2 mg, 0.004 mmol), tBu$_3$P·HBF$_4$ (8 mol%, 2 mg, 0.008 mmol) and 0.5 mL of dry DMPU. After prestirring at room temperature for 10 minutes, *p*-methoxycarbonylphenyl bromide (0.10 mmol, 22 mg), DIPEA (1.5 equiv, 19 mg), cyclohexene (5 equiv, 0.50 mmol, 41 mg, 52 μL), 3-phenylcyclohexene (>99% purity, 1 equiv, 0.10 mmol, 16 mg) and GC standard 1-dodecane (10 μL) were added sequentially via syringe. The tube was capped tightly and the mixture was vigorously stirred in a 120 °C oil bath. At intervals, the reaction tube was cooled to RT and taken into the glove box. An aliquot was removed and

passed through a short plug of silica gel with Et_2O washing. The filtrate was subjected to GC analysis to determine the yield and conjugated selectivity of the Heck products, as well as the extent of the isomerization of 3-phenylcyclohexene.

Table S5 Isomerization of 3-phenylcyclohexene in an active Heck reaction of ArBr and cyclochexene.



selectivity (b)

Time(h)	Yield(%)	Selectivity (a)	Selectivity (b)
0	--	--	<1:200
0.5	70	0:1	<1:200
1	91	0:1	<1:200
1.5	91	0:1	<1:200
2	91	1:22	1:20
12	91	2:1	4:1
24	91	8:1	8:1
48	91	17:1	15:1
72	91	25:1	21:1

V. Reference

1) R. C. Larock and B. E. Baker, *Tetrahedron Lett.*, **1988**, *29*, 905.