Sequential olefin metathesis — Intramolecular asymmetric Heck reactions in the synthesis of polycycles[1]

Mark Lautens and Valentin Zunic

Abstract: Application of the intramolecular asymmetric Heck reaction in the desymmetrization of a novel class of symmetrical bicyclodienes, synthesized through a diastereoselective double ring-closing metathesis (DSRCM) reaction, was achieved with good yields (approximately 80%) and excellent enantioselectivities (up to 99% ee). Three contiguous stereocenters are established in a single desymmetrization reaction. The use of thallium carbonate as base in the asymmetric Heck reaction favours double bond migration in **13**. Cationic conditions delivered products with good to excellent enantioselectivities, surpassing the results under neutral conditions.

Key words: asymmetric, Heck, polycycles, metathesis, stereoselective, desymmetrization.

Résumé : L'application de la réaction asymétrique intramoléculaire de Heck pour la désymétrisation d'une nouvelle classe de bicyclodiènes symétriques, obtenus par une réaction de métathèse à double cyclisation diastéréosélective, a été réalisée avec de bons rendements (environ 80 %) et d'excellentes énantiosélectivités (jusqu'à 99 % ee). Les trois stéréocentres contigus ont été établis au cours d'une seule réaction de désymétrisation. L'utilization du carbonate de thallium comme base dans la réaction asymétrique de Heck favorise la migration de la double liaison dans le composé **13**. Les conditions cationiques ont permis de livrer des produits avec des énantiosélectivités allant de bonnes à excellentes qui étaient supérieures à celles obtenues dans des conditions neutres.

Mots clés : asymétrique, Heck, polycycles, métathèse, stéréosélective, désymétrisation.

[Traduit par la Rédaction]

Introduction

Heck reactions are among the most important and widely used carbopalladation reactions (1, 2). The effect of substrate, catalyst, ligand, and additives has been examined, resulting in highly selective Heck reactions. The enantioselective variant (3) of the Heck reaction has been successfully developed to the point where both tertiary and quaternary centers can be generated in excellent enantioselectivity and in good to excellent yields. The application of the asymmetric Heck reaction (AHR) has been most widely studied in its intermolecular variant, with ees >96% having been reported. For the intramolecular Heck reaction, the ee values are typically around 80%, with notable exceptions leading to >90% ee (3).

Since the initial reports in 1989 (4), many of the reported intramolecular AHRs involve the desymmetrization of prochiral alkene substrates (5).[3] This methodology has proven to be a powerful tool for the rapid construction of polycyclic compounds. The carbo- and heterocycles synthesized via the intramolecular AHR have been used as building blocks for complex natural products or as model compounds for pharmaceutically relevant substances (6).

We have reported the formation of *cis*- and *trans*-decalin systems, as well as *cis*-diquinanes, via a diastereoselective double ring-closing olefin metathesis reaction (DSRCM) (7) (see Fig. 1). These symmetrical bicyclodienes are ideal substrates in the area of alkene differentiation reactions. Desymmetrization of a symmetrical molecule to yield an enantiomerically enriched product is certainly a topic of great interest (8).

In this report we describe the intramolecular AHR on the bicyclodienes generated through the DSRCM methodology previously reported from our laboratories.

Results

Substrates used in our studies were conveniently prepared by appending appropriate aryl-halide tethers to the tertiary diallylic alcohol **1**. Thus, reaction of the tertiary alcohol **1**

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[1]This article is part of a Special Issue dedicated to Professor Ed Piers.
[2]Corresponding author (e-mail: mlautens@alchemy.chem.utoronto.ca).
[3]A highly enantioselective intramolecular Heck reaction with a monodentate ligand has recently been reported (ref. 5*d*).

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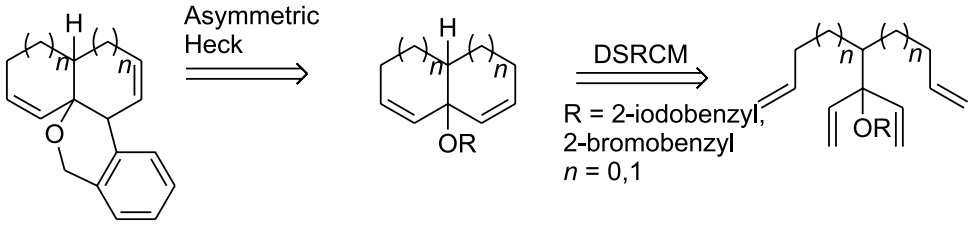
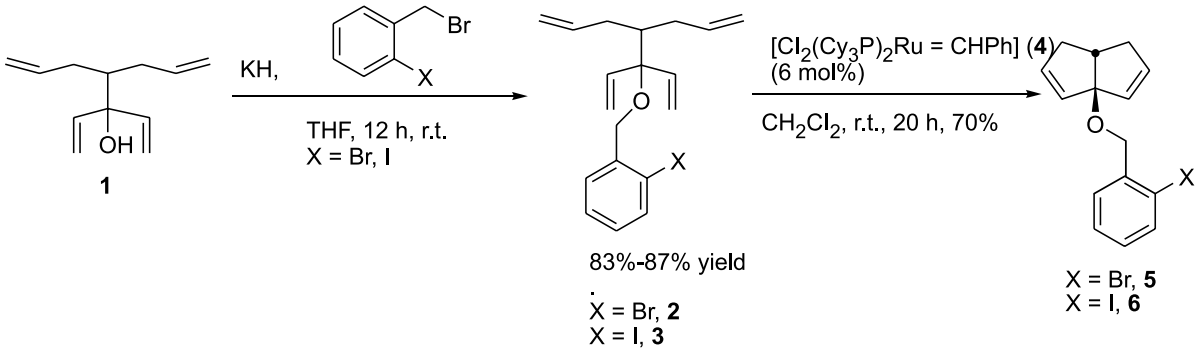
Fig. 1. Strategy for the synthesis of polycycles possessing three contiguous chiral centers.



Scheme 1. DSRCM in the synthesis of diquinane Heck reaction precursors.



with potassium hydride followed by 2-bromobenzyl bromide or 2-iodobenzyl bromide provided the coupled products **2** and **3** in >80% yield (Scheme 1).

Ring-closing metathesis of the haloaryl tetraenes **2** and **3** with Grubbs catalyst **4** provided the desired *cis*-fused bicyclo[3.3.0]octadienes **5** and **6** as the sole bicyclic products in good overall yields.

With a reliable and efficient route to the desired bicyclo[3.3.0]octadienes **5** and **6**, a detailed investigation into the AHR was then performed. Since oxidative addition with aryl iodides is much more facile than the analogous bromides (1), our initial investigations focused on the iodo-Heck precursors. Pd_2dba_3 was used as the palladium(0) source because of its ease of handling and its reported role in producing reproducible results (9) in asymmetric Heck reactions. The range of substrates that work well with BINAP (10) in asymmetric Heck reactions led us to initiate our studies using this ligand. The results from screening a variety of bases and solvents are shown in Table 1.

The results presented in Table 1 show that a variety of conditions are effective in promoting the asymmetric synthesis of **8**[4] It is generally accepted that cationic conditions, e.g., use of silver(I) salts to sequester a halide from palladium after the oxidative addition of the aryl halide, will generally lead to chiral products with higher enantiomeric ratios than those realized under neutral conditions (3, 9, 11).[5] However, under neutral conditions and in the presence of a tertiary amine base, similar levels of enantioselectivity to those seen under cationic conditions are obtained (Table 1, entry 2) (12).[6] The high enantiomeric excess obtained with the triflate substrate **7**[7] is the same as when an aryl iodide is used in the presence of a silver salt (cf. Table 1, entries 4 and 10). Triflate substrates can be used in lieu of the halide substrates with expensive silver salts.

Recent advances in the AHR have shown that a variety of other ligands mediate the reaction with equal levels of efficiency (3). A brief survey of other chiral ligands successfully used in the AHR is presented in Table 2.

Particularly noteworthy is the fact that the chiral phosphinooxazoline (PHOX) (13) ligand (*S*)-*t*-Bu-POX (14) does not efficiently mediate the asymmetric Heck reaction in this case (Table 2, entry 3). The use of *tol*-BINAP as ligand provides **8** with higher levels of enantioselectivity and yield than with BINAP. The use of cationic conditions with a more electron-rich bisphosphine will ensure a tighter binding of the bisphosphine throughout the catalytic cycle of the reaction.

Having explored the intramolecular AHR in the desymmetrization of bicyclo[3.3.0]octadienes, we focused our attention on applying the same transformation to the desymmetrization of bicyclo[4.4.0]decadienes. The synthesis of the required aryl-halide-tethered substrates was carried out in a similar manner to that discussed above for the preparation of diquinane substrates (Scheme 2). The DSRCM event

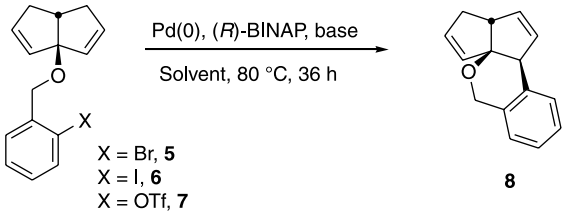
[4] The relative stereochemistry of **8** was proven by careful analysis of various 2D NMR experiments (COSY, ROESY, HMQC). The absolute stereochemistry of **8** has yet to be determined.

[5] Cationic conditions facilitate the binding of the chiral bidentate ligand, olefin, and aryl group in the square planar Pd(II) intermediate in the enantiodescriminating carbopalladation step.

[6] Overman (see ref. 12) in his studies in the use of asymmetric Heck reactions in the synthesis of chiral oxindoles noted a similar phenomenon. No conclusive argument was put forth in his studies, and results in our studies do not help to explain the highly effective role of tertiary amine bases in asymmetric Heck reactions. See ref. 9, as well as ref. 12.

[7] Substrate **7** was prepared in four steps, starting from **1** and 2-(*tert*-butyldimethylsilyloxy)benzylbromide. See experimental section for details.

Table 1. Effects of solvents and bases on the asymmetric synthesis of **8**.



Entry	Substrate	Pd source	Solvent	Base (2 equiv.)	Yield (%)	Enantiomeric excess (%)
1	**5**	$Pd(OAc)_2$	CH_3CN	Et_3N	43	93
2	**6**	Pd_2dba_3-$CHCl_3$	CH_3CN	Et_3N	52	98
3	**6**	Pd_2dba_3-$CHCl_3$	CH_3CN	K_2CO_3	60	83
4	**6**	Pd_2dba_3-$CHCl_3$	CH_3CN	Ag_2CO_3	80	97
5	**6**	Pd_2dba_3-$CHCl_3$	CH_3CN	Ag_3PO_4	37	97
6	**6**	Pd_2dba_3-$CHCl_3$	THF	Ag_3PO_4	73	94
7	**6**	Pd_2dba_3-$CHCl_3$	Toluene	Ag_3PO_4	77	99
8	**6**	Pd_2dba_3-$CHCl_3$	DMA	Ag_3PO_4	57	91
9	**6**	Pd_2dba_3-$CHCl_3$	NMP	Ag_3PO_4	60	63
10	**7**	Pd_2dba_3-$CHCl_3$	CH_3CN	K_2CO_3	53	97

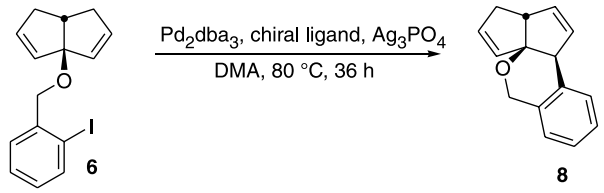
was carried out in a highly efficient process with the Grubbs second generation catalyst (4,5-dihydroIMES)$(PCy_3)Cl_2Ru$=CHPh (**9**). The reaction was efficient with catalyst loadings as low as 2 mol% (cf. 12 mol% of $[Cl_2(Cy_3P)_2Ru$=CHPh] (**4**)) (7) and was complete in 30 min in refluxing dichloromethane. A 4.5:1 mixture of diastereomeric bicyclo[4.4.0]decadienes was obtained, favouring the *cis*-fused decalin. The minor diastereomer was removed by stirring the reaction mixture with silica gel for ~15 min at room temperature followed by flash chromatography on silica gel.[8]

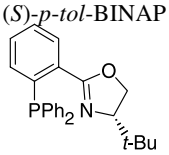
Application of the AHR to aryl iodide *cis*-**12** provided regioisomeric alkene products[9] in a 1:1 ratio and a combined 60% yield (Scheme 3). This system is more complex, since olefin isomerization is now a significant process. A β-hydride addition – elimination step involving **13** with a chiral hydridopalladium species, formed from the Heck reaction of *cis*-**12**, leads to the formation of **14**. Of note, the two regioisomeric products have different ee values (15).

Studies on the bicyclo[3.3.0]octadiene series revealed *p-tol*-BINAP to be the ligand that delivered products with the highest enantiomeric excess. Having obtained alkenes **13** and **14** in modest enantioselectivity, a brief study of chiral ligands was carried out to determine whether the alkene isomerization process could be controlled (Table 3).

Enantiomeric excesses in this series are lower, perhaps because of the elevated temperature used (100 °C versus 80 °C) for the desymmetrization of the bicyclo[4.4.0]decadiene **12**. The higher temperatures were required because of the sluggish nature of the Pd-PHOX catalysts with this substrate.[10] *p-tol*-BINAP is clearly the ligand that affords products with the highest enantiomeric ratios. Unlike palladium catalysts

Table 2. Effect of ligand in the asymmetric synthesis of **8**.



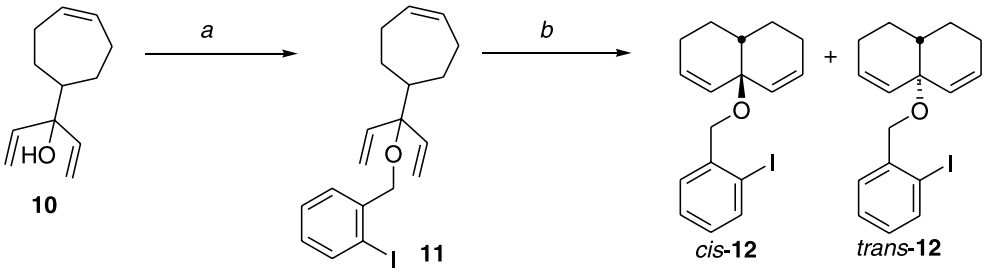
Entry	Ligand	Yield (%)	ee (%)
1	(*S*)-BINAP	57	91
2	(*S*)-*p-tol*-BINAP	87	99
3	 (*S*)-*t*-Bu-Pox	18	29

derived from BINAP, virtually no C=C double bond migration has been reported for Pd-PHOX catalysts. Yet, in the present system, the use of the (*S*)-*t*-Bu-POX and (*S*)-*i*-Pr-(*S*)-DIPOF (16) ligands resulted in a 1:2 ratio of the regioisomers **13** and **14**, respectively, with lower levels of enantioselectivity than seen with the BINAP catalysts (Table 3, entries 3 and 4).

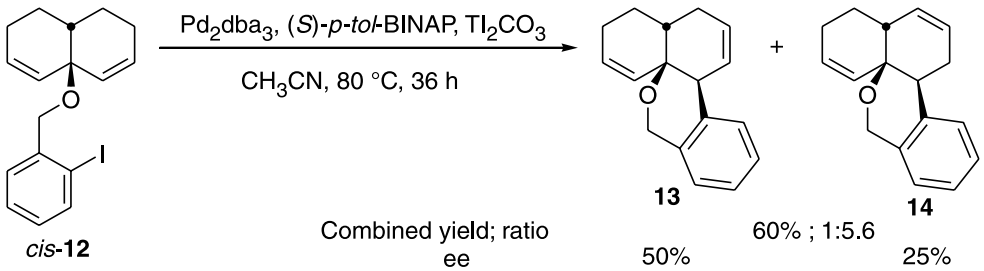
The use of silver salts in the reactions of **12** did not seem to lead to any bias in the formation of the regioisomeric alkene products. However, the utilization of Tl_2CO_3 as base provided a 1:5.6 ratio of **13**:**14** (Scheme 4) with similar yields and levels of enantiomeric excesses as those seen with silver salts.

[8] Generally, the isolation of the bicyclodienes mentioned in this report required triethylamine-neutralized silica gel in the purification step.
[9] The relative stereochemistry of **13** and **14** are assumed to be as depicted, since 2D-NMR experiments (ROESY, NOESY) were unsuccessful at elucidating the relative stereochemistry assignment of **13** and **14**. To our knowledge, the intramolecular Heck reaction is a facile means to access *cis*-fused bicycles (see refs. 1–3). The absolute stereochemistry of **13** and **14** have yet to be determined.
[10] For the sake of consistency, the same temperature was used throughout the series in this ligand survey.

Scheme 2. Synthesis of bicyclo[4.4.0]decadienes for intramolecular Heck reactions. Conditions: (*a*) KH, 2-iodobenzyl bromide, THF, 23 °C, 12 h, 85%; (*b*) (4,5-dihydroIMES) $(PCy_3)Cl_2Ru$=CHPh (**9**) (2 mol%), CH_2Cl_2, reflux, 30 min, 4.5:1 (*cis*-**12**:*trans*-**12**), 100%.



Scheme 3. Desymmetrization of bicyclo[4.4.0]decadienes.



The exploration of the analogous aryl triflate substrate tethered to the bicyclo[4.4.0]decadienes was also undertaken in attempts to increase the enantiomeric excesses of the polycyclic products.[11] Subjecting triflate *cis*-**15** under AHR conditions provided the polycyclic products **13** and **14** in ~1:1 ratio but with significantly higher levels of asymmetric induction (Scheme 5). Attempts are now being directed at expanding the scope of this sequential olefin metathesis – intramolecular AHR sequence and highlighting the usefulness of the polycycles through further chemical transformations.

Summary

The stereoselective synthesis of tetracycles is made possible using a DSRCM and asymmetric Heck strategy. Cationic conditions in the asymmetric Heck reaction gave high enantioselectivities in the desymmetrization process in which three contiguous chiral centers are established with high enantioselectivities in a single step.

Experimental

The following experimental details apply to all subsequent experiments.

All reactions were carried out under an atmosphere of dry argon or nitrogen in oven- (overnight at 90 °C and then cooled under a stream of Ar or N_2) or flame-dried glassware. Solvents and solutions were transferred with syringes and cannulae, using standard inert atmosphere techniques.

^{1}H NMR spectra were recorded at 400 MHz, using a Varian XL400 spectrometer with $CDCl_3$ and TMS as reference standards (δ = 0.00 parts per million (ppm) or 7.26 ppm). ^{13}C NMR were recorded at 100 MHz using the same spectrometer with $CDCl_3$ as reference standard (δ = 77.16 ppm). IR spectra were obtained using a Nicolet DX FT-IR spectrometer as a neat film between KBr plates. High resolution mass spectra were obtained from a VG 70-250S (double focusing) mass spectrometer at 70 eV.

High performance liquid chromatography (HPLC) was performed on an Agilent 1100 Series HPLC using a CHIRACEL OD column. Column chromatography was performed as flash chromatography, as reported by Still et al. (17), using (200–400 mesh) Merck grade silica gel.

Toluene and THF were distilled from sodium–benzophenone. DMF was dried by prolonged standing over molecular sieves. CH_2Cl_2 was distilled from CaH_2.

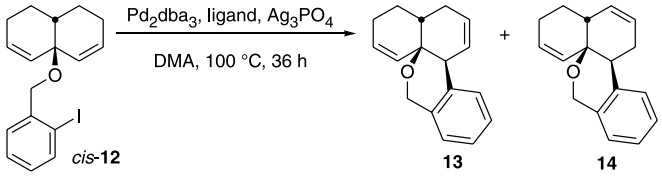
Grubbs catalyst (**4**) was prepared according to the literature procedure (18) and triturated for 12–18 h in a 1:1 mixture of acetone and methanol. The absence of free tricyclohexyl phosphine and tricyclohexyl phosphine oxide was confirmed by ^{31}P NMR and was crucial for the double metathesis reactions to proceed. (DihydroIMES)(PCy_3)-Cl_2Ru=CHPh (**9**) was used as received from Strem. The following compounds were prepared as reported in the literature: 4-Allyl-3-vinyl-hepta-1,5-dien-3-ol (**1**) (7), 3-cyclohept-4-enyl-penta-1,4-dien-3-ol (**10**) (7), and 2-(*tert*-butyldimethylsilyloxy)benzyl bromide (19).

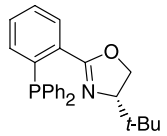
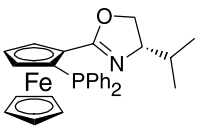
1-(2-Allyl-1,1-divinyl-pent-4-enyloxymethyl)-2-bromobenzene (2)

KH (35% dispersion in mineral oil, 1.0 g, 4 equiv.) was washed three times with pentane, dried under a stream of argon, and suspended in THF (10 mL). A solution of alcohol **1** in THF (5 mL) was added dropwise via cannula. After 15 min at room temperature, 2-bromobenzyl bromide was added all at once, and the resulting solution was stirred at

[11]Substrate *cis*-**15** was prepared in four steps, starting from **10** and 2-(*tert*-butyldimethylsilyloxy)benzylbromide. See experimental section for details.

Table 3. Effect of ligands in the asymmetric synthesis of **13** and **14**.



Entry	Ligand	**13**:**14**[a]	**13** ee (%)	**14** ee (%)	Combined yield (%)[b]
1	(*S*)-BINAP	1:1.1	11	30	50
2	(*S*)-*p-tol*-BINAP	1:1.5	50	35	44
3	 (*S*)-*t*-Bu-POX	~1:2	37	— [c]	40
4	 (*S*)-*i*-Pr-(*S*)-DIPOF	1:2.4	19	1.6	53

[a]Ratio was determined by integration of the singlet at 3.30 ppm (**13**) and the triplet at 2.83 ppm (**14**) in the ^{1}H NMR of the crude reaction mixture.
[b]Combined isolated yield.
[c]Undetermined.

room temperature for 2 h. The mixture was quenched by dropwise addition of water (25 mL) and then extracted with ether (3 × 30 mL). The organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (100% hexanes) on triethylamine-washed silica gel provided the product as a colourless oil (740 mg, 95%). IR (neat): 3074(m), 2978(m), 2922(m), 1914(w), 1869(w), 1831(w), 1638(m), 1439(m), 1269(w), 1091(s), 931(s), 910(s), 748(s), 667(w). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (1H, d, *J* = 8 Hz), 7.48 (1H, d, *J* = 8 Hz), 7.31 (1H, t, *J* = 7.6 Hz), 7.12–7.08 (1H, m), 5.93–5.86 (2H, m), 5.88–5.80 (2H, m), 5.38 (2H, dd, *J* = 11.2 Hz, 0.8 Hz), 5.31 (2H, dd, *J* = 17.6 Hz, 0.8 Hz), 5.01–4.93 (4H, m), 4.40 (2H, s), 2.48–2.42 (2H, m), 2.02–1.94 (2H, m), 1.84–1.90 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.22, 138.78, 137.67, 132.22, 128.44, 128.27, 127.39, 121.89, 118.04, 115.41, 83.98, 64.97, 48.28, 34.56. HR-MS calcd. for $C_{19}H_{23}OBr$ ([M]$^+$): 345.2788; found: 345.2791.

3a-(2-Bromobenzyloxy)-1,3a,6,6a-tetrahydropentalene (5)

To a solution of **2** (930 mg, 2.67 mmol) in 50 mL of dichloromethane was added Grubbs catalyst **4** all at once. The reaction was stirred under a closed system for 20 h at room temperature. The solvent was removed in vacuo, and the residue was purified by flash chromatography (100% hexanes → 5% Et_2O–hexanes) on triethylamine-washed silica gel to provide the product (530 mg, 70%) as a colourless oil. IR (neat): 3047(s), 2918(s), 2851(s), 1619(w), 1467(m), 1350(s), 1218(m), 1097(m), 1070(m), 989(m), 750(s). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47–7.53 (2H, m), 7.30–7.24 (1H, m), 7.11–7.07 (1H, m), 5.94–5.91 (2H, m), 5.84–5.82 (2H, m), 4.46 (2H, s), 2.90–2.84 (3H, m), 2.14–2.08 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.97, 134.67, 132.38, 132.35, 129.28, 128.58, 127.43, 122.52, 106.00, 65.13, 43.10, 40.79. HR-MS calcd. for $C_{15}H_{15}OBr$ ([M]$^+$): 290.0306; found: 290.0301.

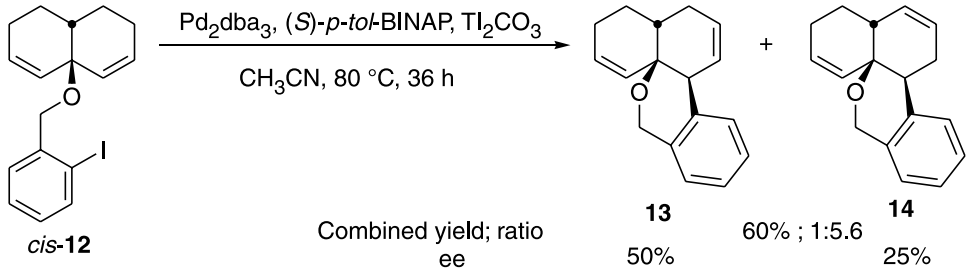
1-(2-Allyl-1,1-divinyl-pent-4-enyloxymethyl)-2-iodobenzene (3)

Following the the benzylation procedure to make **2**, alcohol **1** (1.15 g, 6.4 mmol) was reacted with 2-iodobenzylbromide (2.09 g, 7.06 mmol) to yield the product (2.08 g, 83%) as a colourless oil. IR (neat): 3073(m), 2911(m), 1952(w), 1908(w), 1864(w), 1627(s), 1440(s), 1085(s), 1012(s), 906(s), 752(s). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (1H, d, *J* = 7.6 Hz), 7.57 (1H, d, *J* = 7.6 Hz), 7.36 (1H, t, *J* = 8 Hz), 6.96 (1H, t, *J* = 8 Hz), 5.90 (2H, dd, *J* = 17.6 Hz, 10.8 Hz), 5.89–5.80 (2H, m), 5.39 (2H, dd, *J* = 11.2 Hz, 1.6 Hz), 5.31 (2H, dd, *J* = 17.6 Hz, 1.6 Hz), 5.02–4.94 (4H, m), 4.29 (2H, s), 2.49–2.43 (2H, m), 2.02–1.94 (2H, m), 1.90–1.84 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.95, 138.84, 138.78, 137.63, 128.61, 128.23, 118.08, 115.43, 96.91, 83.99, 69.69, 48.26, 34.56. HR-MS calcd. for $C_{19}H_{23}OI$ ([M]$^+$): 393.0715; found: 393.0703.

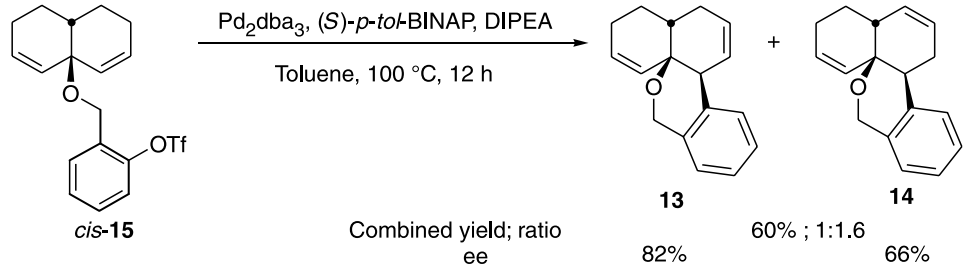
3a-(2-Iodobenzyloxy)-1,3a,6,6a-tetrahydro-pentalene (6)

Following the procedure for RCM of tetraene **2**, iodobenzyl ether **3** (2.00 g, 5.08 mmol) was reacted with Grubbs catalyst **4** (250 mg, 6 mol%) in CH_2Cl_2 (50 mL) to provide the product (1.18 g, 70%) as a colourless oil after flash chromatography (5% Et_2O–hexanes) on triethylamine-washed silica gel. IR (neat): 3060(s), 2912(s), 1444(m), 1350(s), 1215(m), 1097(m), 1077(s), 1009(s), 942(w), 747(s). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87–7.76 (1H, m), 7.49–7.47 (1H, m), 7.34–7.30 (1H, m), 6.96–6.92 (1H, m), 5.94–5.92 (2H, m), 5.84 (2H, dt, *J* = 6 Hz, 1.6 Hz), 4.38 (2H, s), 2.91–2.84 (3H, m), 2.07–2.15 (2H, m). ^{13}C NMR

Scheme 4. Regiocontrol in the asymmetric Heck reaction using Tl salts.



Scheme 5. Asymmetric synthesis of **13** and **14** under cationic conditions.



(100 MHz, $CDCl_3$) δ: 141.80, 139.01, 134.71, 132.41, 128.99, 128.90, 128.30, 106.00, 97.70, 69.81, 43.21, 40.80. HR-MS calcd. for $C_{15}H_{13}OI$ ($[M]^+$): 338.0149; found: 338.0167.

Preparation of trifluoromethanesulfonic acid 2-(6,6a-dihydro-1*H*-pentalen-3a-yloxymethyl)-phenyl ester (7)

KH (35% dispersion in mineral oil, 1.0 g, 3 equiv.) was washed three times with pentane, dried under a stream of argon, and suspended in 10 mL of THF. Alcohol **1** in 5 mL of THF was added via cannula. The solution was heated to reflux for 10 min, cooled to room temperature, and a solution of 2-(*tert*-butyldimethylsilyloxy)benzyl bromide (19) in 5 mL of THF was added via cannula. The solution was stirred at reflux for 3 h, cooled to room temperature, quenched by dropwise addition of water (25 mL), extracted with ether (3 × 30 mL), dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (100% hexanes) on triethylamine-washed silica gel provided 1-(2-allyl-1,1-divinyl-pent-4-enyloxymethyl)-2-(*tert*-butyldimethylsiloxy)-benzene (939 mg, 85%) as a colourless oil. IR (neat): 3088(s), 2919(s), 2855(s), 1634(m), 1579(m), 1491(s), 1250(s), 1070(m), 913(s), 832(s), 730(m). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57–7.55 (1H, m), 7.11 (1H, td, *J* = 7.6 Hz, 0.8 Hz), 6.98 (1H, td, *J* = 7.6 Hz, 0.8 Hz), 6.74 (1H, dd, *J* = 8 Hz, 0.8 Hz), 5.92–5.82 (4H, m), 5.35 (2H, dd, *J* = 10.8 Hz, 1.6 Hz), 5.29 (2H, dd, *J* = 17.8 Hz, 1.6 Hz), 5.02–4.94 (4H, m), 4.40 (2H, s), 2.51–2.44 (2H, m), 2.01–1.93 (2H, m), 0.97 (9H, s), 0.18 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.21, 138.96, 137.91, 131.09, 131.46, 127.46, 127.25, 121.20, 118.03, 117.72, 115.28, 83.69, 61.07, 48.21, 34.57, 18.30, –4.11. HR-MS calcd. for $C_{21}H_{30}O_2Si$ ($[M - C_4H_9]^+$): 341.1936; found: 341.1934.

In a 10 mL round-bottom flask was added 1-(2-allyl-1,1-divinyl-pent-4-enyloxymethyl)-2-(*tert*-butyldimethylsiloxy)-benzene (300 mg, 0.75 mmol) and 3 mL of THF. To this solution was added TBAF (235 mg, 0.90 mmol) all at once at room temperature, and the reaction mixture was stirred at room temperature for 30 min. The reaction was diluted with water (10 mL) and extracted with ether (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue (2-(2-allyl-1,1-divinyl-pent-4-enyloxymethyl)-phenol) was then used in the next reaction without further purification. IR (neat): 3386(s), 3075(m), 2923(m), 1826(w), 1638(m), 1491(m), 1241(s), 1026(m), 912(s), 753(s). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (1H, br s), 7.18–7.14 (1H, m), 6.93–6.78 (3H, m), 5.91–5.75 (4H, m), 5.44–5.31 (4H, m), 5.02–4.95 (4H, m), 4.55 (2H, s), 2.39–2.32 (2H, m), 1.99–1.91 (2H, m), 1.87–1.82 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.33, 138.01, 136.83, 128.98, 127.70, 123.56, 119.82, 118.77, 116.68, 115.92, 85.33, 65.69, 47.79, 34.42. HR-MS calcd. for $C_{19}H_{24}O_2$ ($[M]^+$): 284.1776; found: 284.1780.

In a 10 mL round-bottom flask was added 2-(2-allyl-1,1-divinyl-pent-4-enyloxymethyl)-phenol (215 mg, 0.75 mmol), CH_2Cl_2 (5 mL), and Et_3N (440 μL, 4 equiv.). The solution was then cooled to –78 °C and Tf_2O (254 μL, 2 equiv.) was added dropwise via syringe. The reaction mixture was stirred at –78 °C for 15 min, at which point water (5 mL) was added. The flask was warmed to room temperature and extracted with ether (3 × 15 mL), and the organic extracts were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (2% Et_2O–hexanes) on triethylamine-washed silica gel provided trifluoromethanesulfonic acid 2-(2-allyl-1,1-divinyl-pent-4-enyloxy methyl)-phenyl ester as a colourless oil (240 mg, 81%). IR (neat): 3074(s), 2903(m), 1918(w), 1863(w), 1634(m), 1487(m), 1413(s), 1210(s), 1099(s), 1066(s), 996(s), 896(s), 764(s), 605(m). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (1H, dd, *J* = 7.6 Hz, 0.8 Hz), 7.38 (1H, td, *J* = 7.6 Hz, 1.2 Hz), 7.32 (1H, td, *J* = 8.2 Hz, 2 Hz), 7.25–7.23 (1H, m), 5.87 (2H, dd, *J* = 17.6 Hz, 11.2 Hz), 5.86–5.78 (2H, m), 5.40 (2H, dd, *J* = 11.2 Hz, 1.2 Hz), 5.30 (2H, dd, *J* = 17.6 Hz, 1.6 Hz), 5.00–4.93 (4H, m), 4.46 (2H, s), 2.45–2.39 (2H, m), 1.99–1.92 (2H, m), 1.89–183

(1H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.89, 138.66, 137.32, 132.97, 129.77, 128.70, 128.47, 121.00, 120.31, 118.72 (q, J = 319.2 Hz), 118.33, 115.43, 84.27, 59.77, 48.24, 34.48. HR-MS calcd. for $C_{18}H_{20}O_4SF_3$ ([M – C_2H_3]$^+$): 389.1023; found: 389.1034.

In a 25 mL round-bottom flask was added trifluoromethanesulfonic acid 2-(2-allyl-1,1-divinyl-pent-4-enyloxy methyl)-phenyl ester (230 mg, 0.58 mmol) and 10 mL of CH_2Cl_2. Catalyst **4** (24 mg, 5 mol%) was added, and the solution was stirred under a closed atmosphere at room temperature for 12 h. The solvent was removed on the rotary evaporator to provide the crude product, which was purified by flash chromatography (100% hexanes → 5% Et_2O–hexanes) on triethylamine-washed silica gel. The yield of the title compound was 150 mg (75%). IR (neat): 3053(m), 2923(m), 2849(m), 1968(w), 1487(m), 1419(s), 1350(m), 1214(s), 1142(s), 1059(m), 992(m), 895(s), 764(m), 707(m), 597(m). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61–7.58 (m, 1H), 7.38–7.31 (m, 2H), 7.25–7.23 (m, 1H), 5.93 (2H, dt, J = 5.6 Hz, 2 Hz), 5.81 (2H, dt, J = 5.6 Hz, 2 Hz), 4.50 (2H, s), 2.92–2.83 (3H, m), 2.15–2.08 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.37, 134.92, 132.74, 132.13, 130.13, 130.60, 129.10, 128.49, 121.11, 118.72 (J = 318.4 Hz), 106.30, 59.98, 42.99, 40.84. HR-MS calcd. for $C_{16}H_{15}O_4SF_3$ ([M]$^+$): 360.3530; found: 360.3538.

5-[1-(2-Iodobenzyloxy)-1-vinyl-allyl]-cycloheptene (11)

Following the benzylation procedure for **2** and **3**, alcohol **10** (1.15 g, 6.4 mmol) was reacted with 2-iodobenzyl bromide (2.09 g, 7.06 mmol) to yield the product (2.08 g, 83%) as a colourless oil. IR (neat): 3014(m), 2919(s), 1948(w), 1912(w), 1864(w), 1791(w), 1641(w), 1436(s), 1202(m), 1107(s), 928(s), 748(s), 748(s), 690(s). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78–7.76 (1H, m), 7.58–7.56 (1H, m), 7.38–7.32 (1H, m), 6.97–6.93 (1H, m), 5.87 (2H, dd, J = 17.6 Hz, 11.2 Hz), 5.79–5.77 (2H, m), 5.36 (2H, dd, J = 11.2 Hz, 1.6 Hz), 5.82 (2H, dd, J = 17.8 Hz, 1.6 Hz), 4.29 (2H, s), 2.32–2.25 (2H, m), 2.07–1.98 (4H, m), 1.82 (1H, tt, J = 10.8 Hz, 2.4 Hz), 1.71–1.04 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.09, 138.83, 137.88, 132.04, 128.59, 128.23, 128.18, 117.74, 96.97, 83.95, 69.56, 28.18, 28.15. HR-MS calcd. for $C_{19}H_{23}OI$ ([M]$^+$): 394.0792; found: 394.0793.

4a-(2-Iodobenzyloxy)-1,2,4a,7,8,8a-hexahydro-napthalene (12)

In a 100 mL round-bottom flask was added 5-[1-(2-iodobenzyloxy)-1-vinyl-allyl]-cycloheptene (850 mg, 2.15 mmol) and 50 mL of CH_2Cl_2 under nitrogen. To this solution was added ruthenium catalyst **9** (35 mg, 0.04 mmol), and the solution was refluxed for 1 h, at which time all of the starting material had been consumed. ^{1}H NMR analysis showed a 4.5:1 mixture of diastereomers (integration of signals at 5.89 ppm (multiplet corresponding to all of the olefinic protons of the *trans* decalin plus half of the olefin protons of the *cis* decalin product) and 5.63 ppm (half of the olefin protons of the *cis* decalin)). Silica gel (~200 mg) was added, and the mixture was stirred at room temperature for 15 min. The solution was filtered, and the silica gel was washed with a copious amount of CH_2Cl_2. The solvent was removed in vacuo, and the residue was purified by flash chromatography (2% Et_2O–hexanes) to provide 520 mg (65%) of the *cis*-bicyclo[4.4.0]decadiene as a clear oil. IR (neat): 3011(m), 2922(s), 1952(w), 1911(w), 1826(w), 1871(w), 1650(w), 1562(m), 1434(s), 1371(m), 1265(m), 1202(m), 1110(m), 1066(s), 945(m), 747(s), 647(m). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (1H, d, J = 8 Hz), 7.52 (1H, d, J = 8 Hz), 7.32 (1H, t, J = 7.6 Hz), 6.93 (1H, t, J = 7.6 Hz), 5.89 (2H, dt, J = 9,9 Hz, 3.6 Hz), 5.63 (2H, dt, J = 9.9 Hz, 2.1 Hz), 4.42 (2H, s), 2.23–2.17 (1H, m), 2.14–2.01 (4H, m), 1.90–1.83 (2H, m), 1.51–1.59 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.09, 138.92, 130.29, 129.93, 129.07, 128.81, 128.31, 97.70, 74.68, 68.79, 34.58, 24.51, 23.46. HR-MS calcd. for $C_{17}H_{19}OI$ ([M]$^+$): 366.0480; found: 366.0483.

Preparation of triflouromethanesulfonic acid 2-(1,7,8,8a-tetrahydro-2*H*-naphthalen-4a-yloxymethyl)-phenol ester (15)

KH (35% dispersion in mineral oil, 1.0 g, 3 equiv.) was washed three times with pentane, dried under a stream of argon, and suspended in 10 mL of THF. Alcohol **10** in 5 mL of THF was added via cannula. The solution was heated to reflux for 10 min, cooled to room temperature, and a solution of 2-(*tert*-butyldimethylsilyloxy)benzyl bromide (19) in 5 mL of THF was added via cannula. The solution was stirred at reflux for 3 h, cooled to room temperature, quenched by dropwise addition of water (25 mL), extracted with ether (3 × 30 mL), dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (100% hexanes) on triethylamine-washed silica gel provided *tert*-butyl[2-(1-cyclohept-4-enyl-1-vinyl-allyloxymethyl)-phenoxy]-dimethylsilane (939 mg, 85%) as a colourless oil. IR (neat): 2929(s), 1858(w), 1602(m), 1584(m), 1489(s), 1378(m), 1252(s), 1114(m), 924(s), 838(s), 758(m), 692(m). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56–7.54 (1H, m), 7.13–7.09 (1H, m), 7.00–6.96 (1H, m), 6.75–6.73 (1H, m), 5.84 (2H, dd, J = 17.6 Hz, 11.2 Hz), 5.79–5.77 (2H, m), 5.33 (2H, dd, J = 10.8 Hz, 1.6 Hz), 5.26 (2H, dd, J = 17.6 Hz, 1.6 Hz), 4.39 (2H, s), 2.32–2.27 (2H, m), 2.08–1.97 (4H, m), 1.80 (1H, tt, J = 10.8 Hz, 2.4 Hz), 1.12–1.04 (2H, m), 0.97 (9H, s), 0.18 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.29, 138.18, 132.12, 131.23, 127.48, 127.27, 121.23, 118.09, 117.41, 83.65, 60.92, 52.99, 28.19, 25.85, 18.31, –4.10. HR-MS calcd. for $C_{25}H_{38}O_2Si$ ([M]$^+$): 396.6448; found: 396.6451.

In a 10 mL round-bottom flask was added *tert*-butyl[2-(1-cyclohept-4-enyl-1-vinyl-allyloxymethyl)-phenoxy]-dimethylsilane (300 mg, 0.75 mmol) and 3 mL of THF. To this solution was added TBAF all at once at room temperature, and the reaction mixture was stirred at room temperature for 10 min. The reaction was diluted with water (10 mL) and extracted with ether (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue [2-(1-cyclohept-4-enyl-1-vinyl-allyloxymethyl)phenol] was then used in the next reaction without further purification. IR (neat): 3362(s), 3017(m), 2930(m), 1930(w), 1861(w), 1590(m), 1244(s), 1024(s), 845(w), 754(s), 692(w). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (1H, br s), 7.20–7.16 (1H, m), 6.95–6.80 (3H, m), 5.85 (2H, dd, J = 17.8 Hz, 11.2 Hz), 5.77–5.75 (2H, m), 5.42 (2H, d, J = 10.8 Hz), 5.32 (2H, d, J = 17.6 Hz), 4.59 (2H, s), 2.32–2.26 (2H, m), 2.03–1.92 (4H, m), 1.82 (1H, tt, J = 10.4 Hz, 2.4 Hz), 1.15–1.06 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ:

156.37, 136.92, 131.74, 128.92, 127.60, 123.37, 119.80, 118.60, 116.64, 85.16, 65.74, 52.11, 28.07, 27.98. HR-MS calcd. for $C_{19}H_{24}O_2$ ([M]$^+$): 284.1776; found: 284.1778.

In a 10 mL round-bottom flask was added 2-(1-cyclohept-4-enyl-1-vinyl-allyloxymethyl)-phenol (215 mg, 0.75 mmol), CH_2Cl_2 (5 mL), and Et_3N (440 μL, 4 equiv.). The solution was then cooled to –78 °C and Tf_2O (254 μL, 2 equiv.) was added dropwise via syringe. The reaction mixture was stirred at –78 °C for 15 min, at which point water (5 mL) was added. The flask was warmed to room temperature and extracted with ether (3 × 15 mL), and the organic extracts were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (2% Et_2O–hexanes) on treithylamine-washed silica gel provided triflouromethanesulfonic acid 2-(1-cyclohept-4-enyl-1-vinyl-allyloxymethyl)-phenyl ester as a colourless oil (240 mg, 81%). IR (neat): 3018(w), 2928(w), 1866(w), 1422(s), 1214(s), 1143(s), 1093(m), 1003(w), 894(m), 767(m), 628(w). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68–7.66 (1H, m), 7.39–7.36 (1H, m), 7.33–7.29 (1H, m), 7.24–7.22 (1H, m), 5.83 (2H, dd, J = 17.8 Hz, 10.8 Hz), 5.87–5.75 (2H, m), 5.36–5.39 (2H, m), 5.29–5.24 (2H, m), 4.46 (2H, s), 2.30–2.23 (2H, m), 2.03–1.96 (4H, m), 1.83–1.77 (1H, m), 1.10–1.02 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.00, 137.60, 133.10, 131.98, 131.98, 129.78, 128.69, 128.47, 120.99, 118.72 (q, J = 319.2 Hz), 117.96, 84.22, 59.71, 52.86, 28.11. HR-MS calcd. for $C_{20}H_{23}O_4SF_3$ ([M]$^+$): 416.1269; found: 416.1280.

In a 100 mL round-bottom flask was added triflouromethanesulfonic acid 2-(1-cyclohept-4-enyl-1-vinyl-allyloxymethyl)-phenyl ester (850 mg, 2.15 mmol) and 50 mL of CH_2Cl_2 under nitrogen. To this solution was added ruthenium catalyst **9** (35 mg, 0.04 mmol), and the solution was refluxed for 1 h, at which time all of the starting material had been consumed. ^{1}H NMR analysis showed a 4.5:1 mixture of diastereomers (integration of signals at 5.90 ppm (multiplet corresponding to all of the olefinic protons of the *trans* decalin plus half of the olefin protons of the *cis* decalin product) and 5.59 ppm (half of the olefin protons of the *cis* decalin)). Silica gel (~200 mg) was added, and the mixture was stirred at room temperature for 15 min. The solution was filtered, and the silica gel was washed with a copious amount of CH_2Cl_2. The solvent was removed in vacuo, and the residue was purified by flash chromatography (2% Et_2O–hexanes) to provide 520 mg (65%) of the *cis*-bicyclo-[4.4.0]decadiene (**15**) as a clear oil. IR (neat): 3029(m), 2941(s), 1487(m), 1454(m), 1418(s), 1330(w), 1209(s), 1143(s), 1056(m), 895(s), 763(m), 734(m), 602(m). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65–7.63 (1H, m), 7.37–7.22 (3H, m), 5.90 (2H, dt, J = 10.4 Hz, 3.6 Hz), 5.59 (2H, dt, J = 9.6 Hz, 2 Hz), 4.56 (2H, s), 2.20–2.00 (5H, m), 1.87–1.79 (2H, m), 1.50–1.59 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.13, 133.09, 130.60, 130.50, 129.59, 128.86, 128.48, 120.95, 118.72 (q, J = 319.2 Hz), 74.97, 58.62, 34.44, 24.39, 23.40. HR-MS calcd. for $C_{18}H_{19}O_4SF_3$ ([M]$^+$): 388.0956; found: 388.0962.

General procedure for the asymmetric Heck reaction using $Pd(OAc)_2$

In a 10 mL round-bottom flask equipped with a stir bar and reflux condenser was added $Pd(OAc)_2$ (11.5 mg, 0.0513 mmol), (*R*)-BINAP (63.88 mg, 0.1025 mmol), Et_3N (74 μL, 0.513 mmol), and 2 mL of CH_3CN under an argon flush. The mixture was heated to 70 °C for 3 h and then the aryl halide (0.342 mmol) in 1 mL of CH_3CN was added via cannula. The reaction was stirred at 70 °C for 16 h. The reaction was cooled to room temperature, diluted with water (5 mL), and extracted with ether (3 × 10 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (2.5% Et_2O–hexanes → 5% Et_2O–hexanes) provided the product as an oil.

General procedure for the asymmetric Heck reaction using Pd_2dba_3

In a 10 mL round-bottom flask equipped with a stir bar and reflux condenser was added Pd_2dba_3 (8.15 mg, 0.0089 mmol), (*R*)-*tol*-BINAP (12.19 mg, 0.01958 mmol), and base (0.356 mmol) in solvent (1 mL) under an argon atmosphere. The solution was stirred at room temperature for 40 min, and then a solution of the aryl halide (0.178 mmol) in 1.5 mL of solvent was added via cannula under argon. The reaction was heated to 80 °C and stirred at this temperature for 36 h. The flask was cooled to room temperature, diluted with ether (20 mL), and washed with saturated aqueous $NaHCO_3$ (7 mL). The aqueous layer was further extracted with Et_2O (2 × 10 mL), and the combined organic extracts were washed with brine (7 mL) and dried over Na_2SO_4. Removal of the organic solvent followed by flash chromatography (5%–10% Et_2O–hexanes) provided the product as a colourless oil.

4b,6a,7,11-Tetrahydro-10-oxa-pentaleno[1,6a-a]naphthalene (8)

Following the general procedure for the asymmetric Heck reaction, the title compound was obtained as a colorless oil, which darkens upon storage at room temperature for prolonged time. The enantiomeric excess of the cyclized product was determined by HPLC analysis, as follows: CHIRACEL OD, 10% *i*-PrOH–hexanes, retention times for the enantiomers = 10.9 min, 11.5 min. (V_O = 0.5 ml/min, 23 °C, UV monitor: 254 nm.) $[\alpha]_D^{25}$ = +124.7 (c = 1.0, $CHCl_3$) (99% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 (1H, d, J = 7.2 Hz), 7.18 (1H, d, J = 7.2 Hz), 7.13 (1H, d, J = 7.2 Hz), 7.08 (1H, d, J = 7.2 Hz), 5.96 (1H, dt, J = 5.6 Hz, 2 Hz), 5.83 (1H, dt, J = 5.6 Hz, 2.8 Hz), 5.72 (1H, dt, J = 6.4 Hz, 2 Hz), 5.66 (1H, dt, J = 6 Hz, 1.6 Hz), 4.70 (1H, d, J = 14 Hz), 4.60 (1H, d, J = 14 Hz), 3.83 (1H, d, J = 2 Hz), 3.48 (1H, dt, J = 8.8 Hz, 2 Hz), 2.83 (1H, ddt, J = 17.2 Hz, 8.8 Hz, 2 Hz), 2.16 (1H, dd, J = 17.2 Hz, 2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.10, 135.13, 134.36, 134.14, 133.50, 132.65, 128.06, 127.58, 125.77, 125.13, 97.42, 64.18, 50.46, 50.31, 36.99. HR-MS calcd. for $C_{15}H_{13}O$ ([M]$^+$): 210.1042; found: 210.1044.

4b,7,7a,8,9,13-Hexahydrodibenzo[*c*,*i*]chromene (13) and 4b,5,7a,8,9,13-hexahydrodibenzo[*c*,*i*]chromene (14)

Following the general procedure for the asymmetric Heck reaction, the title compounds were obtained as colorless oils after flash chromatography (2% Et_2O–hexanes → 5% Et_2O–hexanes). Enantiomeric excesses of the cyclized products were determined by HPLC analysis, as follows: CHIRACEL OD, 10% *i*-PrOH–hexanes, retention times for the enantiomers: **13** = 4.02 min, 4.55 min; **14** = 4.43 min, 5.60 min.

(V_O = 1 ml/min, 23 °C, UV monitor: 220 nm.) **13** = $[\alpha]_D^{25}$ = –101.2 (c = 0.90, $CHCl_3$) (82% ee, using (*S*)-*tol*-BINAP); **14** = $[\alpha]_D^{25}$ = –88.9 (c = 0.85, $CHCl_3$) (66% ee, using (*S*)-*tol*-BINAP).

4b,7,7a,8,9,13-Hexahydrodibenzo[c,i]chromene (13)

IR (neat): 3405(m), 2927(s), 1717(s), 1603(w), 1457(m), 1271(m), 1082(m), 1032(w), 747(m). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22–7.15 (3H, m), 7.01 (1H, d, J = 7.6 Hz), 5.93–5.90 (1H, m), 5.70–5.66 (2H, m), 5.54–5.50 (1H, m), 4.98 (1H, d, J = 15.6 Hz), 4.83 (1H, d, J = 15.6 Hz), 3.30 (1H, s), 2.63–2.56 (1H, m), 2.65–2.08 (3H, m), 1.64–1.87 (3H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.01, 133.9, 129.42, 129.18, 129.18, 128.92, 127.48, 127.02, 126.16, 124.63, 124.12, 72.09, 62.37, 42.07, 36.59, 28.59, 26.16, 25.48. HR-MS calcd. for $C_{16}H_{18}O$ ($[M]^+$): 238.1357; found: 238.1359.

4b,5,7a,8,9,13-Hexahydrodibenzo[c,i]chromene (14)

IR (neat): 3419(m), 2924(m), 1713(s), 1603(m), 1458(w), 1299(m), 1278(m), 1108(w), 1072(w), 1018(w), 755(w), 734(m). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21–7.13 (3H, m), 7.04–7.02 (1H, m), 5.85 (1H, dt, J = 10.4 Hz, 3.6 Hz), 5.70–5.65 (2H, m), 5.55–5.52 (1H, m), 5.00 (1H, s), 2.83 (1H, t, J = 6.4 Hz), 2.41–2.26 (3H, m), 2.10–2.03 (2H, m), 1.96–1.89 (1H, m), 1.51–1.41 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.00, 133.91, 131.28, 129.64, 128.63, 127.33, 126.60, 126.20, 124.40, 124.20, 71.89, 63.93, 39.15, 38.92, 30.78, 27.41, 24.48. HR-MS calcd. for $C_{16}H_{18}O$ ($[M]^+$): 238.1357; found: 238.1359.

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