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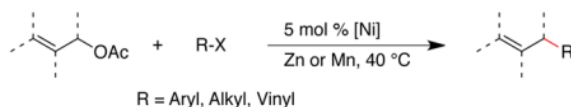
Selective Cross-Coupling of Organic Halides with Allylic Acetates

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Abstract



A general protocol for the coupling of haloarenes with a variety of allylic acetates is presented. Strengths of the method are a tolerance for electrophilic (ketone, aldehyde) and acidic (sulfonamide, trifluoroacetamide) substrates and the ability to couple with a variety of substituted allylic acetates. Secondary alkyl bromides can also be allylated under slightly modified conditions, demonstrating the generality of the approach. Finally, the coupling of a reactive vinyl halide could be achieved by the use of a very hindered ligand and more reactive, branched allylic acetates.

1. Introduction

Allylarene derivatives are versatile synthetic intermediates to which a variety of approaches have been developed: Friedel–Crafts allylation, allylation of aryl nucleophiles by metal-mediated allylic substitution chemistry,¹ metal-mediated cross-coupling of aryl halides with allyl nucleophiles,² and Heck-reactions of olefins with aryl halides.³ We present here an alternative disconnection, the cross-coupling of two electrophiles, allylic acetates and aryl halides (Figure 1). While the coupling of simple allyl acetate with aryl halides has been reported several times, few examples with substituted allylic acetates have been reported. In our own studies, we have found that the ligands previously used for such reactions, pyridine and bipyridine ligands, were poorly selective. We report here a new ligand that promotes selective coupling of aryl halides with allylic acetates. These conditions, with a few modifications, can also be used to couple allylic acetates with secondary alkyl bromides and a vinyl bromide.

2. Background

The reductive approach to allylated arenes (Figure 1) is complementary to the other approaches, addressing some of the limitations present in each. Friedel-Crafts is direct, but precise control of the products is difficult and electron-rich arenes are required. The Heck reaction is also direct, and functional-group compatibility can be excellent, but selectivity for allylarene over vinyl arene is usually poor.^{3,4} In cases where selectivity is achieved, it is

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 Supporting Information. Full selectivity data (Tables S1–S5), Table S6, details on methods and starting materials, and copies of ¹H and ¹³C NMR spectra are available in the Supplementary Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

for the styrene, not the allylated arene.⁵ Methods that rely upon pre-formed organometallic reagents are limited by the low commercial availability of organometallic reagents and the reactivity of the organometallic reagent itself.

Allylic acetate derivatives and aryl halides are more convenient and affordable than organometallic reagents, but few reports on the reductive coupling of *substituted* allylic acetates with functionalized arenes exist. The reductive coupling of aryl bromides and chlorides with an excess (2.0–2.7 equiv) of allylic acetates has been reported to be catalyzed by 13–40 mol % cobalt under both electrochemical⁶ and chemical conditions (zinc or manganese reductant).⁷ The principle side reactions observed were reduction of the aryl halide and dimerization of the aryl halide to form biaryl. Although aryl bromides and electron-poor aryl chlorides worked well, no examples with aryl iodides were reported, and it was noted that even more biaryl formation occurred with these substrates. Selectivity for cross product was the major limitation.

Durandetti, Nédélec, and Périchon had noted in 1996 that bipyridine-ligated nickel catalysts could couple allylic acetates with aryl halides, but slow addition of the allylic acetate was required for high selectivity.^{8a} Starting from a bipyridine catalyst we had developed for the coupling of aryl halides with alkyl halides,⁹ Gong recently reported that several additives significantly improved yields for the coupling of 3 different aryl bromides, but only with simple allyl acetate ($\text{CH}_2=\text{CH}_2\text{CH}_2\text{OAc}$).^{8b}

Only four successful reactions with substituted allylic acetates have been reported to date (Scheme 1). For the cobalt-catalyzed reactions, yields and selectivities were modest and relatively high catalyst loading was required. Similarly, two nickel catalyzed examples with crotyl acetate provided good yield and regioselectivity, but required the slow addition of the allylic acetate to achieve high cross-selectivity. No examples of substituted allylic acetates utilizing chemical reductants have been reported.

As evident in these prior studies, the major challenge associated with the reductive coupling of two electrophiles is the selective formation of cross-coupled product over competitive dimerization reactions (Figure 2). The nickel-catalyzed methods required slow addition of the allylic acetate over the course of the electrolysis^{8a} or two equivalents of allyl acetate for high yield.^{8b} These conditions were proposed to favor formation of arylnickel intermediates over allylnickel intermediates.^{8a} The cobalt-catalyzed methods,^{6,7} on the other hand, were reported to suffer from large amounts of biaryl formation or hydrodehalogenation, even with excess allyl acetate.

More selective, general conditions for the allylation of substituted allylic acetates may require the development of new catalysts and strategies for selective oxidative addition of either the allylic acetate or the aryl halide. Few studies on the relative rates at which nickel complexes react with different electrophiles have been reported.^{8a} In the course of studying dimerization reactions, we had found that terpyridine-ligated nickel complexes dimerized alkyl bromides and allylic acetates, but only slowly reacted with aryl halides.¹⁰ Because allylnickel(II) complexes are well-known to react with aryl halides to form allylarenes,¹¹ we hypothesized that a terpyridine-ligated nickel complex could achieve better selectivity than bipyridine catalysts. We report here our results with this same catalyst for the coupling of substituted allylic acetates with a range of organic halides.

During the course of these studies, Gosmini reported a Co-catalyzed method for the allylation of alkyl halides,¹² Gong reported the use of our terpyridine-nickel system¹⁰ for the allylation of alkyl halides,¹³ and Gong reported the coupling of simple allyl acetate with three aryl bromides.^{8b} None of these manuscripts explored the coupling of substituted allylic acetates with aryl halides or vinyl halides.

3. Results

3.1 Reaction Optimization

Building on the observation that 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine (**L1**) and NiCl₂(dme) formed a catalyst that was slow to dimerize haloarenes, but was reactive with allylic acetates, we examined its ability to mediate the coupling of cinnamyl acetate (**2a**) with iodobenzene (Table 1). We found that it is highly selective for cross-coupling over competing dimerization reactions (**B** and **C** in Table 1, entry 1), although some hydrodehalogenation competes (**D**). Our own studies on the coupling of aryl halides with unactivated alkyl halides had previously found bipyridine **L3** to form a particularly selective catalyst,⁹ but biaryl formation was a problem in reactions with allylic acetates (entry 2). Our observed low selectivity mirrors previous reports with pyridine^{6, 7} as a co-solvent and ligand (entry 3) or a bipyridine⁸ (**L3**) as a ligand (entry 4). Finally, reactions conducted without ligand (entry 5), without nickel, or without zinc produced little or no cross-product, respectively (Table S6 in Supporting Information).

Initial studies had found that dimethylacetamide (DMA) and *N*-ethylpyrrolidinone (NEP) provided the best yields out of various amide and urea solvents. In order to simplify product isolation, we examined THF solvent mixtures and found that NEP/THF provided the highest yields. In very cost-sensitive situations, DMA/THF can be substituted for NEP/THF with only a small decrease in yield (73% vs 90% in entry 1).

3.2 Aryl Halide Scope

In order to examine the compatibility of these conditions with various functional-groups, the optimized conditions were applied to a series of aryl iodides and aryl bromides (Table 2). Both electron-rich and electron-poor aryl iodides formed product in high yield (entries 3–11). Broad functional-group tolerance is notable, including an *N*-aryl trifluoroacetamide group (entry 6), which bears a strongly acidic proton (similar to acetic acid, see also entry 5) and is easily cleaved by nucleophiles. Although nickel is known to catalyze both pinacol coupling¹⁴ and allylation¹⁵ of ketones and aldehydes, products **3b** and **3c** were obtained in high yield (entries 3 and 4). Because bromobenzene was unreactive under these reaction conditions, we were able to couple 1-bromo-4-iodobenzene with high chemoselectivity (entry 14). Finally, *meta*- and *ortho*-substituted iodoarenes also coupled in good yield (entries 16–18).

In contrast to electron-neutral bromoarenes, bromoarenes containing an electron-withdrawing group couple in reasonable yield (Table 2, entries 12–15).

3.3 Allylic Acetate Scope

A variety of different allylic acetates were also examined (Table 3), with promising results. Not only aryl-substituted cinnamyl acetate, but also primary alkyl (entry 1), secondary alkyl (entry 3), and vinyl substituted (entry 6) allylic acetates coupled in good yield, with selectivity for the linear, *E*-product. The high regioselectivity and stereoselectivity obtained for the linear isomer, regardless of starting material, provides flexibility in synthesis and suggests a common allylnickel intermediate (Table 2, entry 1 and Table 3, entries 2 and 3). Finally, cyclic and acyclic α -substituted allylic acetates provide good yields of product (entries 8 and 9). In the case of non-symmetrical substrate **2j**, regioselectivity for α -substitution is high (entry 9). The coupling of a γ,γ -disubstituted olefin, geranyl acetate (entry 7), provided a high yield of allylated products (80% total yield), but the selectivity was poor (2:1 linear:branched, 1:1 *E:Z* for linear).

3.4 Secondary Alkyl Bromides

We also investigated the coupling of unactivated alkyl bromides with allylic acetates, which builds upon our previous studies with (**L1**)Ni catalysts.¹⁰ We found that cross-selectivity was poor for reactions with primary alkyl bromides due to rapid dimerization of the alkyl bromide. Secondary alkyl bromides could be cross-coupled with cinnamyl acetate derivatives with high selectivity and yield (Table 4). Conditions are nearly the same as those used for aryl halides except that THF/DMA mixtures performed best and manganese provided the highest yields. During the course of these experiments, the groups of Gosmini and Gong reported Co-¹² and Ni-catalyzed¹³ approaches to the same products. Gong used very similar conditions, but found that the addition of large amounts of MgCl₂ made the reaction more general. In light of their results, we did not pursue our additive-free conditions further.

3.5 Potential for RZnX, RMnX, or Radical Intermediates

We first considered the potential intermediacy of aryl zinc reagents, ArZnI, because we observed significant amounts of hydrodehalogenation of the aryl halide in some cases, (Up to 29% GC area %, Table 1, *D* and Tables S1–S5 in the Supporting Information).¹⁶ Although direct insertion of unactivated zinc into aryl iodides is reported to be slow,¹⁷ nickel can catalyze the process.^{17d} Several observations lead us to believe that ArZnI intermediates are unlikely: (1) reactions without nickel only converted trace amounts of iodobenzene to benzene (2% in 48 h, Table 2 in Supporting Information); (2) a reaction quenched at intermediate conversion with D₂O did not form increased amounts of C₆H₅D when compared to a reaction quenched with H₂O (GC/MS); (3) functional groups reported to be reactive with ArZnI, such as aldehydes and acidic protons, are well tolerated (Table 3, entries 4–6).¹⁸

We also considered aryl radical intermediates to explain the observed hydrodehalogenation. An aryl radical could abstract a hydrogen atom from the solvent to form Ar-H. If this was the case, then a reaction conducted in a fully deuterated solvent mixture could be expected to form Ar-D instead of Ar-H.¹⁹ Because deuterated NEP and DMA are not commercially available, we conducted the experiment in a THF-*d*₈/DMF-*d*₇ mixture.²⁰ We did not observe an increase in the amount of C₆H₅D produced when compared to a reaction in protic solvents (GC/MS). This argues against hydrogen atom abstraction from solvent, but does not completely rule out the presence of radical intermediates.²¹

3.6 Extension to Vinyl Halide

We could find no examples of the catalytic coupling of vinyl halides with allylic acetates in the literature, but the skipped diene products of such reactions are valuable in synthesis.²² Preliminary investigations on the coupling of cinnamyl acetate (**2a**) with 2-bromocyclohexenone provided only small amounts of product **7a**. Monitoring reactions at low conversion revealed that consumption of the vinyl bromide was much faster than consumption of cinnamyl acetate. If our hypothesis that selective formation of an allylnickel intermediate was required for selective cross-coupling were correct, a more reactive allylic alcohol donor would be required.

Based upon this hypothesis, we examined reactions with branched allylic acetate **2c** because the less hindered olefin should facilitate coordination and ionization (Table 5). Reactions run with terpyridine **L1** did not form the skipped diene **7a** and failed to consume starting materials (entry 1). Bipyridine **L2** provided better results, but significant allyl dimer (**9a**) and vinyl dimer (**8**) were formed. Kishi has reported that neocuproine (**L4**) nickel complexes are slow to dimerize aryl halides²³ and we have also found that neocuproine was a selective ligand for the reductive conjugate addition of aryl and vinyl halides with enones, which we

propose involves allylnickel intermediates.²⁴ Indeed, **L4** formed a highly selective catalyst for the cross-coupling of 2-bromocyclohexenone with the branched allylic acetate **2c** (entry 3). The results appear related to sterics because the unsubstituted 1,10-phenanthroline provided poor results (entry 4).

The less reactive alkyl-substituted allylic substrates **2k** and **2l** provided low yields when the cross-coupling with the vinyl bromide was attempted (Table 6, entries 1 and 2). Again, low reactivity of the allyl derivative compared to vinyl bromide **6** appeared to be the problem. In order to further boost reactivity of the allylic donor, we examined the methyl carbonates **2m** and **2n**. These more reactive substrates coupled with higher selectivities and resulted in better yields (entries 3 and 4).

Although preliminary, this approach compares favorably with prior approaches to α -allylated enones (**7**). Those methods relied upon tin and selenium chemistry,²⁵ organocuprates,^{26, 27} or a multistep sequence starting with the allylation of cyclohexane dione.^{26, 28} Product **7a** has been used as a versatile precursor to the fused 6,3,5-tricyclic skeleton of Mycorrhizin A.²⁸

4. Discussion

4.1 Mechanism

Both arylmetal^{6b, 8a} and allylmetal^{8b} intermediates have been proposed for cobalt- and nickel-catalyzed coupling of aryl halides with allylic acetates, but these studies were conducted with monodentate or bidentate ligands. Our previous studies with terpyridine nickel catalysts¹⁰ suggested an allylnickel intermediate (Figure 3) would be formed preferentially in reactions catalyzed by terpyridine nickel complexes.²⁹

Based upon studies by many groups, including Corey, Semmelhack, Hegedus, and Kochi, pre-formed allylnickel(II) *reagents* are known to react with aryl, alkyl, and vinyl halides, consistent with the observed generality of our nickel catalyzed process.³⁰ The conversion of the allylnickel intermediate into product and a nickel(II) salt is proposed to involve a radical-chain-like process and has been studied extensively.^{30b-d} Separately, Gong has proposed the intermediate reduction of allylnickel(II) intermediates into allylnickel(I) intermediates,³¹ but detailed mechanistic studies have not been conducted for this alternative mechanism. At this time, we cannot differentiate between the single-electron reduction mechanism and the radical-chain mechanism.

4.2 Scope of Reaction

Generally, reductive cross-electrophile coupling reactions have displayed broad functional-group tolerance.⁶⁻¹³ However, previous studies on reductive allylation had not demonstrated compatibility with enones, unprotected aldehydes, or highly acidic protons (Table 2).

Allylation of aryl halides with substituted allylic acetates had been limited to only four examples (Scheme 1), but we have found that reactions with (**L1**)Ni have broad scope, including primary and secondary alkyl, cyclic, vinyl, and 1,3-disubstituted allylic acetates allylic acetates (Table 3).

A wide variety of organic halides couple under similar conditions using (**L1**)Ni as the catalyst. This includes, for the first time, a vinyl bromide. Improvement of conditions for the allylation of vinyl halides will be the subject of future studies.

4.3 Selectivity

Although the true order of reactivity for the allylic acetate and haloarene with nickel has not yet been unambiguously determined, our studies show that the inherent reactivity of the substrate, ligand sterics, and ligand coordination number can all be manipulated in a rational manner to improve selectivity. For example, 1-phenyl-2-propenyl acetate (**2c**) is a poor match for ligand **L2** and vinyl bromide **6**, resulting in significantly more allyl dimerization. With a more hindered ligand (**L4**) only a small amount of allyl dimer is formed (Table 5).

Finally, looking over the comprehensive selectivity data in the Supporting Information, it is clear that hydrodehalogenation is the major side reaction for most examples and that this side reaction appears to happen more with bromoarenes. Development of catalysts and conditions that will suppress hydrodehalogenation are needed to further improve the scope and yields for arene allylation.

5. Conclusions

In conclusion, a new nickel-catalyzed coupling of aryl iodides, electron-poor aryl bromides, and secondary alkyl bromides with allylic acetates has been developed. This chemistry addresses the regioselectivity and substrate availability limitations observed for more well developed approaches. The functional-group compatibility, the scope of allylic acetate substitution, and the potential for the allylation of vinyl halides are promising. Finally, our results show that cross-selectivity can be controlled by the choice of ligand, which provides a clear path for future improvements.

6. Experimental Section

General— ^1H and ^{13}C NMR spectra were acquired on 500 MHz or 400 MHz (proton) NMR instruments. NMR chemical shifts are reported in ppm and referenced to the residual solvent peak as an internal standard (for CDCl_3 $\delta = 7.260$ ppm, ^1H ; $\delta = 77.160$ ppm, ^{13}C). Analysis of reaction mixtures was accomplished by quenching an aliquot (10 μL) with 1 M $\text{NaHSO}_4(\text{aq})$ (0.1 mL) and analysis of the filtered (silica or celite) ether extract (1 mL) by GC or GC/MS. Dodecane was used as the internal standard. GC analyses (FID detector) were performed on a DB-5 column (20 m \times 0.18 mm \times 0.18 μm) with hydrogen as the carrier gas. Std method: 1.8 mL/min flow at 20.3 psi, 300 $^\circ\text{C}$ inj., 325 $^\circ\text{C}$ detector, oven program: 50 $^\circ\text{C}$ (0.46 min), ramp at 65 $^\circ\text{C}/\text{min}$ to 300 $^\circ\text{C}$, hold for 0.69 min. GC/MS analyses (EI+, quadrupole mass analyzer) were performed on an instrument equipped with an RTX-XLB column (30 m \times 0.25 mm \times 0.28 μm) with helium carrier gas. Std method: 1 mL/min flow at 7.8 psi, 225 $^\circ\text{C}$ inj., 250 $^\circ\text{C}$ interface/ion source, oven program: 50 $^\circ\text{C}$ (3 min), ramp at 40 $^\circ\text{C}/\text{min}$ to 280 $^\circ\text{C}$, hold for 3 min. Only the parent ion and the base peak are reported. High resolution mass spectra (HRMS) were acquired on an instrument with electron impact (EI) ionization and a magnetic sector mass analyzer. Compounds were either purified on an automated flash purification system on Rediseq Rf Gold normal-phase silica columns or by standard chromatography on silica gel (EMD, silica gel 60, particle size 0.040–0.063 mm) using standard flash techniques. Products were visualized by UV light, KMnO_4 stain, or by GC.

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and were used as received. $\text{NiCl}_2(1,2\text{-dimethoxyethane})$ ($\text{NiCl}_2(\text{dme})$) was purchased from Strem or synthesized.³² As we have reported elsewhere, the stoichiometry of the $\text{NiCl}_2(\text{dme})$ can be variable.¹⁰ The amount of $\text{NiCl}_2(\text{dme})$ used was corrected for the actual amount of dimethoxyethane present as determined by elemental analysis. 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine³³ (**L1**), 4,4'-di-*tert*-butyl-2,2'-bipyridine (**L2**), and bipyridine (**L3**) were purchased or synthesized according to the literature procedure. Zinc flakes (-325 mesh,

purity 99.9%) and manganese powder (–325 mesh, 99%) were stored under nitrogen. *N*-Ethyl-2-pyrrolidone (NEP) was purified by stirring over CaH₂ (48 h) followed by distillation from CaH₂. The purified NEP was stored under nitrogen over 4 Å molecular sieves. Tetrahydrofuran (THF), *N,N*-dimethylacetamide (DMA), dichloromethane (DCM), and pyridine (py) were purified by passage through alumina and molecular sieves and stored over 4 Å molecular sieves. 4-iodotoluene, 4-bromobenzotrifluoride, and 3-iodotoluene were filtered through a short plug of basic alumina (1 cm) in a glass pipette before use. 4-Iodobenzaldehyde,³⁴ *N*-(4-iodophenyl)-4-methylbenzenesulfonamide,³⁵ 2,2,2-trifluoro-*N*-(4-iodophenyl)acetamide,³⁶ *tert*-butyl(4-iodophenoxy)dimethylsilane,³⁷ 4-iodo-*N,N*-dimethylaniline,³⁸ cinnamyl acetate³⁹ (**2a**), (*E*)-hex-2-en-1-yl acetate³⁷ (**2b**), (*Z*)-3-phenylallyl acetate⁴⁰ (**2d**), (*E*)-3-cyclohexylallyl acetate⁴¹ (**2e**), 2-methylallyl acetate⁴² (**2f**), (*2E,4E*)-hexa-2,4-dien-1-yl acetate^{13a} (**2g**), cyclohex-2-en-1-yl acetate⁴³ (**2i**), (*E*)-4-phenylbut-3-en-2-yl acetate⁴⁴ (**2j**), and (*E*)-3-(4-methoxyphenyl)allyl acetate^{39, 45} (**2k**), (*E*)-3-(4-trifluoromethyl)phenyl)allyl acetate⁴⁶ (**2l**), and 2-Bromocyclohex-2-en-1-one⁴⁷ (**6**) were synthesized according to literature procedures.

Allylic Acetates and Carbonates

1-Phenyl-2-propenyl acetate (2c)⁴⁸—Benzaldehyde (2.31 mL, 22.73 mmol, Fluka) was filtered through basic alumina and added to a flame dried 100-mL 1-neck round bottomed flask. The flask was also charged with THF (25 mL) and a Teflon coated magnetic stirbar, then cooled to 0 °C. A 1.09 M solution of vinyl magnesium bromide in THF (25 mL, 25 mmol, 1.1 equiv) was then added slowly via an addition funnel. After 4 h no benzaldehyde remained and acetic anhydride (3.22 mL, 34.09 mmol, 1.5 equiv,) was added at 0 °C. After 2 hours an additional 1.0 equiv (2.15 mL) of acetic anhydride was added and the reaction was allowed to warm to room temperature overnight. The reaction mixture was poured into a separatory funnel, diluted with Et₂O (50 mL), and the organic layer was washed with 1 M HCl until the pH of the aqueous layer was 1. The organic layer was then washed with saturated NaHCO₃ until the pH of the aqueous layer was 7. The combined aqueous layers were then back extracted with Et₂O (2 × 50 mL). The combined organic layers were then dried over MgSO₄ and the supernatant was concentrated *in vacuo*. The product was then isolated by flash chromatography (5% EtOAc in hexanes, R_f = 0.24). Mixed fractions were rechromatographed (2.5% EtOAc in hexanes). The combined pure 1-phenyl-2-propenyl acetate (1.99 g, 88%) was isolated as a clear oil; analytical data matched those reported in the literature. ¹H NMR (400 MHz; CDCl₃): δ 7.37 (d, J = 4.5 Hz, 4H), 7.32 (t, J = 4.3 Hz, 1H), 6.28 (dt, J = 5.9, 1.3 Hz, 1H), 6.02 (ddd, J = 17.1, 10.5, 5.9 Hz, 1H), 5.33-5.24 (m, 2H), 2.12 (s, 3H). ¹³C NMR (101 MHz; CDCl₃): δ 170.0, 139.0, 136.4, 128.6, 128.3, 127.2, 117.0, 76.3, 21.4.

4-Ethylhex-1-en-3-yl methyl carbonate (2m)—An oven-dried 250 mL, three-neck round bottom flask was equipped with a magnetic stirbar, a nitrogen inlet, an addition funnel, and a rubber septum. 2-Ethylbutyraldehyde (2.46 mL, 20 mmol, distilled over Na₂SO₄) and dry Et₂O (140 mL) were added to this vessel, and the mixture was cooled to 0 °C. Vinylmagnesium bromide in THF (1.09 M, 22.02 mL, 24 mmol, 1.2 equiv) was added drop-wise via the addition funnel. The reaction was allowed to warm to rt and then stirred at rt for 1 hour. The white suspension was then poured onto ice cold water (50 mL) and the organic layer separated, dried over Na₂SO₄, and supernatant concentrated *in vacuo* in a 100 mL round bottom flask to give the allyl alcohol. The crude alcohol was then used without further purification in the next step.

In the 100 mL vessel used above, a solution of the allyl alcohol (assume 20 mmol from previous step), DCM (50 mL) and pyridine (4.85 mL, 3 equiv) was cooled to 0 °C, under nitrogen with stirring. Methyl chloroformate (3.09 mL, 2.0 equiv) was then added dropwise

by syringe and the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was treated with water (25 mL), and the aqueous layer was separated and extracted with additional Et₂O (2 × 25 mL). The combined organic layers were washed with saturated NaHCO₃ (25 mL), brine (25 mL), dried over Na₂SO₄, and the supernatant was concentrated *in vacuo*. Purification by flash chromatography (2% EtOAc in hexanes) yielded pure 4-ethylhex-1-en-3-yl methyl carbonate (1.50 g, 50%) as a clear oil. ¹H NMR (400 MHz; CDCl₃): δ 5.78 (ddd, *J* = 17.3, 10.5, 6.8 Hz, 1H), 5.30-5.21 (m, 2H), 5.10-5.07 (m, 1H), 3.76 (s, 3H), 1.50-1.36 (m, 4H), 1.25 (m, 1H), 0.89 (td, *J* = 7.4, 3.4 Hz, 6H). ¹³C NMR (101 MHz; CDCl₃): δ 155.5, 134.6, 118.1, 81.0, 54.7, 44.9, 21.7 (d, *J* = 9.3 Hz), 11.5. Anal. Calcd for C₁₀H₁₈O₃: 64.49 % C, 9.74% H, 0.00% N; found 64.69% C, 9.95% H, -0.065% N.

Methyl 5-phenylpent-1-en-3-yl carbonate (2n) [376647-56-2]⁴⁹—An oven-dried 250 mL, three-neck round bottom flask was equipped with a magnetic stirbar, a nitrogen inlet, an addition funnel, and a rubber septum. Hydrocinnamaldehyde (2.63 mL, 20 mmol, distilled over Na₂SO₄) and dry Et₂O (140 mL) were added to this vessel, and the mixture was cooled to 0 °C. Vinylmagnesium bromide in THF (1.09 M, 22.02 mL, 24 mmol, 1.2 equiv) was added drop-wise via the addition funnel. The reaction was then stirred at room temperature for 1 hour. The white suspension was then poured onto ice cold water (50 mL) and the organic layer separated, dried over Na₂SO₄, and supernatant concentrated *in vacuo* in a 100 mL round bottom flask to give the allyl alcohol. The crude alcohol was then used without further purification in the next step.

In the 100 mL vessel used above, a solution of the allyl alcohol (assume 20 mmol from previous step), DCM (50 mL) and pyridine (4.85 mL, 3 equiv) was cooled to 0 °C under nitrogen with stirring. Methyl chloroformate (3.09 mL, 2.0 equiv) was then added dropwise by syringe and the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was treated with water (25 mL), and the aqueous layer was separated and extracted with additional Et₂O (2 × 25 mL). The combined organic layers were washed with saturated NaHCO₃ (25 mL), brine (25 mL), dried over Na₂SO₄, and the supernatant was concentrated *in vacuo*. Purification of the residue by flash chromatography (2% EtOAc in hexanes) yielded methyl 5-phenylpent-1-en-3-yl carbonate (2.60 g, 59%) as a clear oil. ¹H-NMR (400 MHz; CDCl₃): δ 7.31-7.18 (m, 5H), 5.85 (ddd, *J* = 17.2, 10.5, 6.7 Hz, 1H), 5.36-5.24 (m, 2H), 5.10 (q, *J* = 6.6 Hz, 1H), 3.79 (s, 3H), 2.76-2.64 (m, 2H), 2.11-1.90 (m, 2H). ¹³C NMR (101 MHz; CDCl₃): δ 155.3, 141.2, 135.8, 128.6, 128.5, 126.1, 117.9, 78.6, 54.8, 36.0, 31.4.

Procedure A: Allylic acetates with aryl halides in a nitrogen glove box—A 1-dram vial containing a teflon-coated magnetic stir was sequentially charged with NiCl₂(dme) (10.6 mg, 0.0483 mmol), **L1** (20.0 mg, 0.0498 mmol), NEP (500 μL), THF (1500 μL), aryl halide (1.50 mmol), allylic acetate (1.00 mmol), and the zinc flakes (130 mg, 2.00 mmol). The vial was then capped with a screw cap fitted with a PTFE-faced silicone septum. After removal from the glove box, the vial was shaken for 15 seconds and then stirred (1300 rpm) at 40 °C until judged complete (less than 1 % allylic acetate remaining) by GC analysis (12–15 h). In order to remove NEP, the reaction mixture was filtered through a short plug of silica gel (1 inch wide, ~ 3 inches high) in an 18 mL disposable polyethylene fritted filter funnel, eluting with either hexanes or diethyl ether, depending on the polarity of the expected product (200 mL). The filtrate was concentrated *in vacuo* and the residue purified by flash chromatography on a Teledyne Isco combiflash Rf-200.

Procedure B: Allylic acetates with aryl halides on the bench top under argon (1 mmol scale)—Reactions set up as in procedure A except that after the vial was sealed,

the headspace was flushed with argon gas for 1 min. The needles were then removed and the vial was placed in a heating block at 40 °C in the usual manner.

Procedure C: Allylic acetates with aryl halides on the bench top under argon (10 mmol scale)—On the bench top, an oven-dried 50-mL Schlenk flask containing a teflon-coated magnetic stir bar was charged with NiCl₂(dme) (106 mg, 0.483 mmol) and 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine (200 mg, 0.498 mmol). The flask was then sealed with a rubber septa. NEP (500 μL), THF (1500 μL), aryl halide (15.0 mmol), and allylic acetate (10.0 mmol) were then added sequentially under a low flow of argon with an outlet needle (bubbler). The flow of argon was then increased, the rubber septa removed, and the zinc flake reductant was quickly tipped into the flask (1.30 g, 20 mmol). The septa was then replaced onto the flask, and the flask was gently shaken for 15 seconds. The side-arm valve was closed, the argon line was removed, and the reaction mixture was then stirred at 40 °C until judged complete by GC analysis. The work-up and isolation is performed as in Procedure A except 400 mL of hexanes was used to elute the crude product from the silica gel plug, and one 120 g normal-phase “gold” silica column (Teledyne-Isco) was used for chromatography.

(E)-prop-1-ene-1,3-diylidibenzene (3a) (Table 2, Entry 1)⁵⁰—Procedure A was followed with cinnamyl acetate (**2a**) (166 μL, 1.00 mmol) and iodobenzene (167 μL, 1.50 mmol). Purification by flash chromatography (100% hexanes) afforded 171 mg (88% yield) of the title compound as a colorless oil; analytical data matched those reported in the literature. ¹H NMR (400 MHz; CDCl₃) δ 7.42-7.25 (m, 10H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.42 (dd, *J* = 14.6, 7.8 Hz, 1H), 3.61 (d, *J* = 6.7 Hz, 2H). ¹³C NMR (101 MHz; CDCl₃) δ 140.2, 137.5, 131.1, 129.3, 128.7, 128.5, 127.1, 126.2, 126.1, 39.4. GC-MS (EI) *m/z* (% rel. int., ion): 194.05 (100.00, M⁺). HRMS (EI) [M⁺] calc. for C₁₅H₁₄: 194.110; found: 194.110.

(E)-prop-1-ene-1,3-diylidibenzene (3a) (Table 2, Entry 2)⁵⁰—Procedure C was followed for a large-scale reaction run outside the glove box with cinnamyl acetate (**2a**) (1.68 mL, 10 mmol) and iodobenzene (1.67 mL, 1.50 mmol). Purification by flash chromatography using (100% hexanes) afforded 157 mg (81% yield) of the title compound as a colorless oil; analytical data matched those reported in the literature. ¹H NMR (400 MHz; CDCl₃) δ 7.41-7.22 (m, 10 H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.40 (dt, *J* = 15.1, 7.3 Hz, 1H), 3.59 (d, *J* = 6.6 Hz, 2H). ¹³C NMR (101 MHz; CDCl₃) δ 140.6, 137.9, 131.5, 129.6, 129.1, 128.9, 127.5, 126.6, 126.5, 39.8. GC-MS (EI) *m/z* (% rel. int., ion): 194.05 (100.00, M⁺). HRMS (EI) [M⁺] calc. for C₁₅H₁₄: 194.110; found: 194.110.

(E)-1-[*p*-(3-phenyl-allyl)phenyl]ethanone (3b) (Table 2, Entry 3)⁵¹—Procedure A was followed with cinnamyl acetate (**2a**) (166 μL, 1.00 mmol) and 4-iodoacetophenone (369 mg, 1.50 mmol). Purification by flash chromatography (8% ethyl acetate in hexanes) afforded 168 mg (71% yield) of the title compound as a pale yellow oil; analytical data matched those reported in the literature. ¹H NMR (400 MHz; CDCl₃) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.41-7.31(m, 9H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.38 (t, *J* = 11.3 Hz, 1H), 3.66 (d, *J* = 6.8 Hz, 2H), 2.65 (s, 3H). ¹³C NMR (101 MHz; CDCl₃) δ 198.2, 146.3, 137.6, 135.8, 132.3, 129.3, 129.1, 129.0, 128.3, 127.8, 126.6, 39.7, 27.0. GC-MS (EI) *m/z* (% rel. int., ion): 236.15 (100.00, M⁺). HRMS (EI) [M⁺] calc. for C₁₇H₁₆O: 236.120; found: 236.120.

(E)-*p*-(3-phenyl-allyl)benzaldehyde (3c) (Table 2, Entry 4)⁵¹—Procedure A was followed with cinnamyl acetate (**2a**) (166 μL, 1.0 mmol) and 4-iodobenzaldehyde (348 mg, 1.50 mmol). Purification by flash chromatography (9% ethyl acetate in hexanes) afforded 155 mg (70% yield) of the title compound as a pale yellow oil; analytical data matched those reported in the literature. ¹H NMR (400 MHz; CDCl₃) δ 10.05 (s, 1H), 7.89 (d, *J* = 8.1 Hz,

2H), 7.48-7.27 (m, 9H), 6.54 (d, $J = 15.7$ Hz, 1H), 6.39 (dt, $J = 15.7, 6.9$ Hz, 1H), 3.69 (d, $J = 6.7$ Hz, 2H). ^{13}C NMR (101 MHz; CDCl_3) δ 192.0, 147.6, 137.1, 134.8, 132.1, 130.1, 129.4, 128.6, 127.6, 127.5, 126.2, 39.5. GC-MS (EI) m/z (% rel. int., ion): 222.05 (77.96, M^+), 115 (100.00, $\text{M}^+ - \text{C}_7\text{H}_5\text{O}$). HRMS (EI) $[\text{M}^+]$ calc. for $\text{C}_{16}\text{H}_{14}\text{O}$: 222.104; found: 222.105.

(E)-N-(4-cinnamylphenyl)-4-methylbenzenesulfonamide (3d) (Table 2, Entry 5)

—Procedure A was followed with cinnamyl acetate (**2a**) (166 μL , 1.00 mmol) and *N*-(4-iodophenyl)-4-methylbenzenesulfonamide (560 mg, 1.50 mmol). Purification by flash chromatography (40% ethyl acetate in hexanes) afforded 265 mg (73% yield) of the title compound as a white solid. ^1H NMR (400 MHz; CDCl_3) δ 7.65-7.63 (m, 2H), 7.34-7.27 (m, 4H), 7.23-7.21 (m, 3H), 7.11 (d, $J = 8.4$ Hz, 2H), 7.00-6.98 (m, 2H), 6.42-6.38 (m, 2H), 6.29 (dd, $J = 14.6, 7.9$ Hz, 1H), 3.47 (d, $J = 6.5$ Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz; CDCl_3) δ 143.9, 137.7, 137.4, 136.3, 134.6, 131.4, 129.8, 129.7, 128.9, 128.7, 127.42, 127.37, 126.2, 122.4, 38.8, 21.7. Mp: 137–138 °C. IR (cm^{-1}): 3240 (N-H, strong), 3024, 2912, 2870 (C-H, weak), 1153 (S=O, strong), 1508, 1469 (C=C, medium). Product contains 0.21 equiv H_2O by ^1H NMR analysis (see Supporting Information for copy of spectrum). Anal. Calcd for $\text{C}_{22}\text{H}_{21}\text{NO}_2\text{S} + 0.21 \text{H}_2\text{O}$: 71.95 % C, 5.88% H, 3.81% N; found 72.07% C, 5.88% H, 3.79% N.

(E)-N-(4-cinnamylphenyl)-2,2,2-trifluoroacetamide (3e) (Table 2, Entry 6)—

Procedure A was followed with cinnamyl acetate (**2a**) (166 μL , 1.00 mmol) and 2,2,2-trifluoro-*N*-(4-iodophenyl)acetamide (472 mg, 1.50 mmol). Purification by flash chromatography (4% ethyl acetate in hexanes) afforded 195 mg (64% yield) of the title compound as a white solid. ^1H NMR (400 MHz; CDCl_3) δ 7.84 (s, 1H), 7.54-7.23 (m, 9H), 6.48 (d, $J = 15.8$ Hz, 1H), 6.35 (dt, $J = 15.7, 6.8$ Hz, 1H), 3.58 (d, $J = 6.8$ Hz, 2H). ^{13}C NMR (101 MHz; CDCl_3) δ 154.8, 154.5, 138.5, 137.3, 133.2, 131.5, 129.6, 128.6, 127.3, 126.1, 120.7, 116.9, 38.7. ^{19}F NMR (376 MHz; CDCl_3) δ 76.2. Mp: 143–145 °C. IR (cm^{-1}): 3302 (N-H, medium), 3213, 3151, 2955 (C-H, weak), 1701 (C=O, strong), 1554, 1512 (C=C, strong), 1145 (C-F, strong). Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{F}_3\text{NO}$: 66.88% C, 4.62% H, 4.59% N; found 66.610% C, 4.705% H, 4.517% N.

(E)-tert-butyl(4-cinnamylphenoxy)dimethylsilane (3f) (Table 2, Entry 7)—

Procedure A was followed with cinnamyl acetate (**2a**) (83 μL , 1.00 mmol) and *tert*-butyl(4-iodophenoxy)dimethylsilane (261 mg, 1.50 mmol). Purification by flash chromatography (1% ethyl acetate in hexanes) afforded 135 mg (80% yield) of the title compound as a colorless oil. ^1H NMR (400 MHz; CDCl_3) δ 7.40-7.23 (m, 9H), 6.46 (s, 1H), 6.40 (s, 1H), 4.76 (s, 2H), 3.57 (d, $J = 6.6$ Hz, 2H), 0.98 (s, 9H), 0.13 (s, 6H). ^{13}C NMR (101 MHz; CDCl_3) δ 139.7, 139.1, 137.9, 131.3, 129.8, 128.92, 128.88, 127.5, 126.7, 126.5, 65.2, 39.4, 26.4, 18.8, -4.8. GC-MS (EI) m/z (% rel. int., ion) 338.30 (0.83, M^+), 117.10 (100.00, $\text{M}^+ - \text{C}_{13}\text{H}_{21}\text{OSi}$). HRMS (EI) $[\text{M}^+]$ calc. for $\text{C}_{22}\text{H}_{30}\text{OSi}$: 338.207; found: 338.207.

(E)-3-(4-N,N-dimethylaminophenyl)-1-phenylpropene (3g) (Table 2, Entry 8)⁵¹—

Procedure A was followed with cinnamyl acetate (**2a**) (166 μL , 1.00 mmol) and 4-iodo-*N,N*-dimethylaniline (371 mg, 1.50 mmol). Purification by flash chromatography (3% ethyl acetate in hexanes) afforded 130 mg (55% yield) of the title compound as a yellow oil; analytical data matched those reported in the literature. ^1H NMR (400 MHz; CDCl_3) δ 7.40-7.14 (m, 7H), 6.75 (d, $J = 8.7$ Hz, 2H), 6.45 (s, 1H), 6.41 (d, $J = 6.3$ Hz, 1H), 3.49 (d, $J = 6.4$ Hz, 2H), 2.95 (s, 6H). ^{13}C NMR (101 MHz; CDCl_3) δ 149.3, 137.7, 130.3, 130.2, 129.3, 128.5, 128.2, 126.9, 126.1, 113.1, 40.9, 38.4. GC-MS (EI) m/z (% rel. int., ion): 238.15 (100.00, M^+). HRMS (EI) $[\text{M}^+]$ calc. for $\text{C}_{17}\text{H}_{19}\text{N}$: 237.152; found: 237.152.

(E)-1-methyl-4-(3-phenyl-2-propen-1-yl)benzene (3h) (Table 2, Entry 9)⁵¹—

Procedure A was followed with cinnamyl acetate (**2a**) (166 μ L, 1.00 mmol) and 4-iodotoluene (377 mg, 1.50 mmol). Purification by flash chromatography (100% hexanes) afforded 179 mg (86% yield) of the title compound as a colorless oil; analytical data matched those reported in the literature. ¹H NMR (400 MHz; CDCl₃) δ 7.42-7.17 (m, 9H), 6.51 (d, *J* = 15.7 Hz, 1H), 6.44-6.38 (m, 1H), 3.57 (d, *J* = 6.6 Hz, 2H), 2.39 (s, 3H). ¹³C NMR (101 MHz; CDCl₃) δ 137.6, 137.1, 135.7, 130.8, 129.5, 129.2, 128.6, 128.5, 127.1, 126.1, 39.0, 21.1. GC-MS (EI) *m/z* (% rel. int., ion): 208.05 (100.00, M⁺). HRMS (EI) [M⁺] calc. for C₁₆H₁₆: 208.125; found: 208.125.

(E)-1-methoxy-4-(3-phenyl-2-propen-1-yl)benzene (3i) (Table 2, Entry 10)⁵⁰—

Procedure A was followed with cinnamyl acetate (**2a**) (166 μ L, 1 mmol) and 4-iodoanisole (351 mg, 1.5 mmol). Purification by flash chromatography (4% hexanes) afforded 186 mg (83% yield) of the title compound as a yellow oil; analytical data matched those reported in the literature. ¹H NMR (400 MHz; CDCl₃) δ 7.39-7.17 (m, 7H), 6.90-6.86 (m, 2H), 6.48-6.33 (m, 2H), 3.81 (s, 3H), 3.51 (d, *J* = 6.5 Hz, 2H). ¹³C NMR (101 MHz; CDCl₃) δ 158.2, 137.7, 132.3, 130.9, 129.8, 129.7, 128.6, 127.2, 126.2, 114.0, 55.4, 38.6. GC-MS (EI) *m/z* (% rel. int., ion): 224.10 (100.00, M⁺). HRMS (EI) [M⁺] calc. for C₁₆H₁₆O: 224.120; found: 224.121.

(E)-1-bromo-4-cinnamylbenzene (3j) (Table 2, Entry 11)¹⁹—

Procedure A was followed with cinnamyl acetate (**2a**) (166 μ L, 1.00 mmol) and 1-bromo-4-iodobenzene (424 mg, 1.50 mmol). Purification by flash chromatography (3% ethyl acetate in hexanes) afforded 191 mg (64% yield) of the title compound as a pale yellow oil; analytical data matched those reported in the literature. This product was isolated as an inseparable mixture with 9% **3a** due to competing hydrodeiodination. Yield reported is the yield of **3j**, calculated by NMR analysis and comparison with isolated **3a**. ¹H NMR (400 MHz; CDCl₃) δ 7.47-7.15 (m, 9H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.34 (dt, *J* = 15.7, 6.8 Hz, 1H), 3.59 (d, *J* = 6.7 Hz), 3.53 (d, *J* = 6.7 Hz, 2H). ¹³C NMR (101 MHz; CDCl₃) δ 139.1, 137.2, 131.5, 130.4, 129.2, 128.6, 128.4, 127.3, 126.1, 120.0, 38.7. GC-MS (EI) *m/z* (% rel. int., ion): 273.00 (6.88, M⁺), 115.05 (100.00, M⁺ - C₆H₄Br). HRMS (EI) [M⁺] calc. for C₁₅H₁₃Br: 272.020; found: 272.020.

(E)-p-(3-phenyl-allyl) methyl benzoate (3k) (Table 2, Entry 12)⁵⁰—

Procedure A was followed with cinnamyl acetate (**2a**) (166.7 μ L, 1.00 mmol) and methyl 4-bromobenzoate (322.6 mg, 1.50 mmol). Purification by flash chromatography (2% ethyl acetate in hexanes) afforded 163.3 mg (65% yield) of the title compound as a clear oil; analytical data matched those reported in the literature. ¹H NMR (400 MHz; CDCl₃): δ 8.02-7.99 (m, 2H), 7.42-7.29 (m, 6H), 7.25-7.21 (m, 1H), 6.48 (d, *J* = 15.7 Hz, 1H), 6.34 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.92 (s, 3H), 3.61 (d, *J* = 6.8 Hz, 2H). ¹³C NMR (101 MHz; CDCl₃): δ 167.2, 145.7, 137.3, 131.9, 130.0, 128.8, 128.7, 128.3, 128.2, 127.4, 126.3, 52.1, 39.4. GC-MS (EI) *m/z* (% rel. int., ion): 252.10 (56.47, M⁺), 193.05 (100.00, M⁺ - C₂H₃O₂). HRMS (EI) [M⁺] calc. for C₁₇H₁₆O₂: 252.115; found: 252.116.

(E)-1-[p-(3-phenyl-allyl)phenyl]ethanone (3b) (Table 2, Entry 13)⁵¹—

Procedure A was followed with cinnamyl acetate (**2a**) (166.7 μ L, 1.00 mmol) and 4'-bromoacetophenone (298.6 mg, 1.50 mmol). Purification by flash chromatography (5% ethyl acetate in hexanes) afforded 114.3 mg (48% yield) of the title compound as a clear oil; analytical data matched those reported in the literature. ¹H NMR (400 MHz; CDCl₃): δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.39-7.21 (m, 7H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.34 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.61 (d, *J* = 6.7 Hz, 2H), 2.60 (s, 3H). ¹³C NMR (101 MHz; CDCl₃): δ 197.9, 146.0, 137.2, 135.5, 132.0,

129.0, 128.8, 128.7, 128.0, 127.5, 126.3, 39.4, 26.7. GC-MS (EI) m/z (% rel. int., ion): 236.10 (100.00, M^+). HRMS (EI) [M^+] calc. for $C_{17}H_{16}O$: 236.120; found: 236.120.

(E)-1-phenyl-3-[4-(trifluoromethyl)phenyl]propene (3l) (Table 2, Entry 14)⁵¹—

Run 1 (1.00 mmol): Procedure A was followed with cinnamyl acetate (**2a**) (166.7 μ L, 1.00 mmol) and 4-bromobenzotrifluoride (210.0 μ L, 1.50 mmol). Purification by flash chromatography (100% hexanes) afforded 130.8 mg (50% yield) of the title compound as a clear oil; analytical data matched those reported in the literature. 1H NMR (400 MHz; $CDCl_3$): δ 7.54 (d, J = 8.0 Hz, 2H), 7.35-7.18 (m, 7H), 6.45 (d, J = 15.8 Hz, 1H), 6.34-6.26 (m, 1H), 3.57 (d, J = 6.8 Hz, 2H). ^{13}C NMR (101 MHz; $CDCl_3$): δ 144.4, 137.3, 132.1, 129.1, 128.7, [literature 128.49 (q, J =10.8 Hz) was unresolved], 128.0, 127.5, 126.3, 125.8, 125.5 (q, J =3.7 Hz), 39.2. ^{19}F NMR (376 MHz; $CDCl_3$): δ -62.7. Run 2 (0.50 mmol): Procedure A (but on half scale) was followed with cinnamyl acetate (83.4 μ L, 0.50 mmol) and 4-bromobenzotrifluoride (105.0 μ L, 0.75 mmol). Purification by flash chromatography (100% hexanes) afforded 68.3 mg (52% yield) of the title compound as a clear oil; analytical data matched those above. GC-MS (EI) m/z (% rel. int., ion): 262.10 (100.00, M^+). HRMS (EI) [M^+] calc. for $C_{16}H_{13}F_3$: 262.097; found: 262.097.

(E)-3-(4-cyanophenyl)-1-phenylpropene (3m) (Table 2, Entry 15)⁵¹—Procedure A

was followed with cinnamyl acetate (**2a**) (166.7 μ L, 1.00 mmol) and 4-bromobenzonitrile (273.0 mg, 1.50 mmol). Purification by flash chromatography (2% ethyl acetate in hexanes) afforded 168.3 mg (77% yield) of the title compound as a clear oil; analytical data matched those reported in the literature. 1H NMR (400 MHz; $CDCl_3$): δ 7.58-7.55 (m, 2H), 7.34-7.18 (m, 7H), 6.44 (d, J = 15.8 Hz, 1H), 6.26 (dt, J = 15.7, 6.9 Hz, 1H), 3.57 (d, J = 6.8 Hz, 2H). ^{13}C NMR (101 MHz; $CDCl_3$): δ 145.9, 137.0, 132.5, 132.4, 129.5, 128.7, 127.6, 127.2, 126.3, 119.1, 110.2, 39.4. GC-MS (EI) m/z (% rel. int., ion): 219.05 (100.00, M^+). HRMS (EI) [M^+] calc. for $C_{16}H_{13}N$: 219.105; found: 219.106.

(E)-3-(3-methylphenyl)-1-phenylpropene (3n) (Table 2, Entry 16)⁵¹—Procedure A

was followed with cinnamyl acetate (**2a**) (166 μ L, 1.00 mmol) and 3-iodotoluene (377 mg, 1.50 mmol). Purification by flash chromatography (100% hexanes) afforded 162 mg (78% yield) of the title compound as a colorless oil; analytical data matched those reported in the literature. 1H NMR (400 MHz; $CDCl_3$) δ 7.39-7.17 (m, 7H), 6.90-6.86 (m, 2H), 6.48-6.33 (m, 2H), 3.81 (s, 3H), 3.51 (d, J = 6.5 Hz, 2H). ^{13}C NMR (101 MHz; $CDCl_3$) δ 140.1, 138.1, 137.5, 131.0, 129.44, 129.38, 128.5, 128.4, 127.1, 126.9, 126.1, 125.7, 39.3, 21.4. GC-MS (EI) m/z (% rel. int., ion): 208.10 (100.00, M^+). HRMS (EI) [M^+] calc. for $C_{16}H_{16}$: 208.125; found: 208.125.

2-[(2E)-3-phenylprop-2-en-1-yl]benzotrifluoride (3o) (Table 2, Entry 17)⁵²—Procedure

A was followed with cinnamyl acetate (**2a**) (166 μ L, 1.00 mmol) and 2-iodobenzotrifluoride (343 mg, 1.50 mmol). Purification by flash chromatography (3% hexanes in ethyl acetate) afforded 188 mg (86% yield) of the title compound as a colorless oil; analytical data matched those reported in the literature. 1H NMR (400 MHz; $CDCl_3$) δ 7.70 (dt, J = 7.7, 0.6 Hz, 1H), 7.59 (td, J = 7.7, 1.2 Hz, 1H), 7.46-7.26 (m, 7H), 6.58 (d, J = 15.8 Hz, 1H), 6.37 (dt, J = 15.7, 7.0 Hz, 1H), 3.83 (d, J = 6.9 Hz, 2H). ^{13}C NMR (101 MHz; $CDCl_3$) δ 144.4, 137.3, 133.3, 133.0, 130.1, 129.0, 127.9, 127.3, 126.9, 126.7, 126.0, 118.4, 112.9, 38.1. GC-MS (EI) m/z (% rel. int., ion): 218.10 (100.00, M^+). HRMS (EI) [M^+] calc. for $C_{16}H_{12}N$: 218.097; found: 218.097.

(E)-1-methoxy-2-(3-phenyl-2-propen-1-yl)benzene (3p) (Table 2, Entry 18)⁵⁰—

Procedure A was followed with cinnamyl acetate (**2a**) (166 μ L, 1.00 mmol) and 2-iodoanisole (351 mg, 1.50 mmol). Purification by flash chromatography (4% hexanes in

ethyl acetate) afforded 179 mg (80% yield) of the title compound as a yellow oil; analytical data matched those reported in the literature. ^1H NMR (400 MHz; CDCl_3) δ 7.41-7.39 (m, 2H), 7.34-7.29 (m, 2H), 7.28-7.21 (m, 3H), 6.97-6.91 (m, 2H), 6.50-6.41 (m, 2H), 3.89 (s, 3H), 3.59 (d, J = 6.0 Hz, 2H). ^{13}C NMR (101 MHz; CDCl_3) δ 157.3, 137.8, 130.7, 129.9, 128.9, 128.7, 128.4, 127.4, 126.9, 126.1, 120.5, 110.4, 55.4, 33.4. GC-MS (EI) m/z (% rel. int., ion): 224.10 (100.00, M^+). HRMS (EI) [M^+] calc. for $\text{C}_{16}\text{H}_{16}\text{O}$: 224.120; found: 224.120.

(E)-1-Phenylhex-2-ene (4a) (Table 3 Entry 1)⁵³—Procedure A was followed with (*E*)-hex-2-en-1-yl acetate (**2b**) (142 mg, 1 mmol) and iodobenzene (167 μL , 1.5 mmol). Purification by flash chromatography (100% hexanes) afforded 129 mg (81% yield) of the title compound as a colorless oil. The isolated product had a 86:14 [linear]:[branched] ratio, as determined by analysis of the GC/MS fragmentation patterns and comparison with literature NMR data. ^1H NMR (400 MHz; CDCl_3) linear isomer^{28,29}: δ 7.33-7.21 (m, 5H), 5.64-5.50 (m, 2H), 3.37 (d, J = 6.1 Hz, 2H), 2.08-2.01 (m, 2H), 1.43 (tq, J = 7.4 Hz, 2H), 0.95-0.90 (t, 3H); branched isomer: δ 7.33-7.21 (m, 5H), δ 6.02-5.90 (m, 1H), δ 5.07-5.03 (m, 2H), δ 3.32-3.26 (m, 1H), δ 1.75-1.68 (m, 2H), δ 1.42-1.30 (m, 2H), 0.95-0.90 (t, 3H). ^{13}C NMR (101 MHz; CDCl_3) linear isomer: δ 141.3, 132.1, 129.0, 128.6, 128.53, 128.48, 126.0, 39.2, 34.8, 22.8, 13.9; Partial ^{13}C NMR for branched isomer, δ 127.7, 37.8, 20.8. GC-MS (EI) m/z (% rel. int., ion): 160.10 (54.39, M^+), 117.05 (100.00, M^+ C_3H_7). HRMS (EI) [M^+] calc. for $\text{C}_{12}\text{H}_{16}$: 160.125; found: 160.125.

(E)-prop-1-ene-1, 3-diylidibenzene (3a) (Table 3, Entry 2)⁵⁰—Procedure A was followed with 1-phenylallyl acetate (**2c**) (176 mg, 1.00 mmol) and iodobenzene (167 μL , 1.50 mmol). Purification by flash chromatography (100 % hexanes) afforded 101 mg (52% yield) of the title compound as a colorless oil; analytical data matched those reported in the literature. ^1H NMR (400 MHz; CDCl_3) δ 7.41-7.24 (m, 10H), 6.50 (d, J = 15.8 Hz, 1H), 6.40 (dt, J = 15.1, 7.3 Hz, 1H), 3.59 (d, J = 6.5 Hz, 2H). ^{13}C NMR (101 MHz; CDCl_3) δ 140.6, 137.9, 131.5, 129.6, 129.1, 128.9, 127.5, 126.6, 126.5, 39.8. GC-MS (EI) m/z (% rel. int., ion): 194.10 (100.00, M^+). HRMS (EI) [M^+] calc. for $\text{C}_{15}\text{H}_{14}$: 194.120; found: 194.120.

(E)-prop-1-ene-1,3-diylidibenzene (3a) (Table 3, Entry 3)⁵⁰—Procedure A was followed with (*Z*)-3-phenylallyl acetate (**2d**) (176 mg, 1 mmol) and iodobenzene (167 μL , 1.5 mmol). Purification by flash chromatography (100% hexanes) afforded 146 mg (75% yield) of the title compound as a colorless oil; analytical data matched those reported in the literature. ^1H NMR (400 MHz; CDCl_3) δ 7.41-7.22 (m, 10H), 6.50 (d, J = 15.8 Hz, 1H), 6.40 (dt, J = 15.7, 6.7 Hz, 1H), 3.60 (d, J = 6.6 Hz, 2H). ^{13}C NMR (101 MHz; CDCl_3) δ 140.6, 137.9, 131.5, 129.6, 129.1, 128.9, 127.5, 126.6, 126.5, 39.8. GC-MS (EI) m/z (% rel. int., ion): 194.05 (100.00, M^+). HRMS (EI) [M^+] calc. for $\text{C}_{15}\text{H}_{14}$: 194.110; found: 194.110.

(E)-1-cyclohexyl-3-phenylpropene (4b) (Table 3, Entry 4)⁵⁰—Procedure A was followed with 3-cyclohexylallyl acetate (**2e**) (182 mg, 1.00 mmol) and iodobenzene (167 μL , 1.50 mmol). Purification by flash chromatography (100% hexanes) afforded 194 mg (97% yield) of the title compound as a colorless oil. The isolated product has a 93:7 [linear]:[branched] ratio, as determined by GC/MS fragmentation patterns and by comparison with literature NMR data. ^1H NMR (400 MHz; CDCl_3) Linear isomer: δ 7.35-7.18 (m, 5H), 5.60-5.49 (m, 2H), 3.36 (d, J = 5.8 Hz, 2H), 2.01-1.96 (m, 1H), 1.78-1.66 (m, 5H), 1.34-1.09 (m, 5H). Branched isomer: δ 7.35-7.18 (m, 5H), δ 6.06-5.98 (m, 1H), δ 5.06 (d, 1H), δ 5.03 (d, 1H), 2.97 (t, 1H), 1.97-2.01 (m, 1H), 1.65-1.59 (m, 3H), 1.48-1.44 (m, 1H), 1.34-1.09 (m, 5H). ^{13}C NMR (101 MHz; CDCl_3) linear isomer: δ 141.2, 138.1, 128.5, 128.3, 126.1, 125.8, 40.7, 39.1, 33.1, 26.2, 26.1; branched isomer: δ 141.2, 138.1, 128.5, 128.3, 126.1, 125.8, 40.7, 39.1, 33.1, 26.2, 26.1 (one peak was not visible). GC-MS (EI) m/z (% rel. int.,

ion): 200.10 (14.90, M⁺), 109.10 (100.00, M⁺ -C₇H₇). HRMS (EI) [M⁺] calc. for C₁₅H₂₀: 200.157; found: 200.157.

1-(4-(2-methylallyl)phenyl)ethanone (4c) (Table 3, Entry 5)⁵⁴—Procedure A was followed with 2-methylallyl acetate (**2f**) (114 mg, 1.00 mmol) and 4-iodoacetophenone (369 mg, 1.50 mmol). Purification by flash chromatography (9% ethyl acetate in hexanes) afforded 96 mg (55% yield) of the title compound as a pale yellow oil; analytical data matched those reported previously. ¹H NMR (400 MHz; CDCl₃) δ 7.93-7.91 (m, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 4.88 (s, 1H), 4.77 (s, 1H), 3.40 (s, 2H), 2.61 (s, 3H), 1.70 (s, 3H). ¹³C NMR (101 MHz; CDCl₃) δ 197.8, 145.5, 144.1, 135.3, 129.1, 128.5, 112.7, 44.6, 26.6, 22.1. GC-MS (EI) *m/z* (% rel. int., ion): 174.10 (15.17, M⁺), 115 (100.00, M⁺ -CH₃). HRMS (EI) [M⁺] calc. for C₁₂H₁₄O: 174.105; found: 174.105.

(2*E*,4*E*)-hexa-2,4-dien-1-ylbenzene (4d) (Table 3, Entry 6)⁵⁵—Procedure A was followed with (2*E*, 4*E*)-hexa-2,4-dien-1-yl acetate (**2g**) (140 mg, 1.00 mmol) and iodobenzene (167 μL, 1.50 mmol). Purification by flash chromatography (100% hexanes) afforded 103 mg (65% yield) of the title compound as a colorless oil. Product was a mixture of olefin isomers: 6.9:1:1 [2 *E*,4*E*]:{2*E*,4*Z*}:[unidentified olefin isomer]. Olefin isomer ratio and identity were assigned based upon GC/MS fragmentation patterns and by comparison to previously reported NMR spectra (¹H and ¹³C). We assigned one isomer as 2*E*, 4*E* in analogy to the other products. ¹H NMR (400 MHz; CDCl₃) Linear 2*E*, 4*E* isomer:⁵⁶ δ 7.34-7.21 (m, 5H), 6.11-6.08 (m, 2H), 5.76-5.65 (m, 2H), 3.44 (d, *J* = 6.9 Hz, 2H), 1.78 (d, *J* = 6.2 Hz, 3H); linear 2*E*, 4*Z* isomer:⁵⁷ δ 7.34-7.21 (m, 5H), 6.52-6.43 (dd, 1H), 6.11-6.08 (t, 1H), 5.76-5.65 (m, 1H), 5.51-5.46 (m, 1H), 3.50 (d, *J* = 7.0 Hz), 1.78 (dd, 3H); unidentified olefin isomer: δ 7.34-7.21 (m, 5H), 6.11-6.08 (m, 2H), 5.76-5.65 (m, 2H), 3.56 (d, *J* = 7.4 Hz, 2H), 1.86-1.84 (d, 3H). ¹³C NMR (101 MHz; CDCl₃) linear 2*E*, 4*Z* isomer: δ 140.5, 132.4, 129.2, 128.6, 128.4, 126.6, 125.0, 39.3, 13.4. Linear 2*E*, 4*E* and unidentified olefin isomer: δ 131.6, 131.4, 130.4, 130.1, 129.5, 128.5, 127.9, 127.4, 126.7, 126.1, 126.1, 126.0, 125.98, 125.95, 39.0, 33.9, 18.4, 18.1, 13.4 (no literature ¹³C NMR spectrum is available for linear 2*E*, 4*E* olefin isomer). GC-MS (EI) *m/z* (% rel. int., ion): 158.10 (52.92, M⁺), 129.10 (100.00, M⁺ -C₂H₄). HRMS (EI) [M⁺] calc. for C₁₂H₁₄: 158.120; found: 158.120.

(3,7-dimethylocta-2,6-dien-1-yl)benzene (4e) (Table 3, Entry 7)^{53a, 56, 57}

Procedure A was followed with geranyl acetate (214 μL, 1.00 mmol) and iodobenzene (167 μL, 1.50 mmol). Purification by flash chromatography (100% hexanes) afforded 171 mg (80% yield) of a mixture of the three isomers as a colorless oil. Isolated product has a 1.9:1 [linear]:[branched] ratio. The linear and branched products were identified by GC/MS fragmentation patterns and by comparison with literature NMR values. By NMR, the yield of linear products is 52% and the yield of branched product is 28%. Linear (*E* and *Z*) isomers:^{53a, 57} ¹H NMR (500 MHz; CDCl₃): δ 7.36-7.21 (m, 10H), 5.40-5.36 (m, 2H), 5.19-5.07 (m, 2H), 3.40 (d, *J* = 7.2 Hz, 4H), 2.22-2.08 (m, 8H), 1.79 (s, 3H), 1.75 (s, 3H), 1.72 (s, 6H), 1.66 (s, 3H), 1.64 (s, 3H). ¹³C NMR (126 MHz; CDCl₃): δ 142.0 (*E*), 141.9 (*Z*), 136.4 (*E*), 136.3 (*Z*), 131.9 (*Z*), 131.6 (*E*), 128.50 (*E/Z*), 128.47 (*E/Z*), 128.45 (*E/Z*), 125.83 (*E/Z*), 125.80 (*E/Z*), 124.4 (*E*), 124.3 (*Z*), 124.0 (*Z*), 123.2 (*E*), 39.9 (*E*), 34.33 (*E/Z*), 34.27 (*E/Z*), 32.1 (*Z*), 26.7 (*E/Z*), 25.9 (*E*), 25.8 (*Z*), 25.0 (*Z*), 23.6 (*Z*), 17.9 (*E*), 17.8 (*Z*), 16.3 (*E*). Branched isomer:⁵⁶ ¹H NMR (500 MHz; CDCl₃): δ 7.36-7.21 (m, 5H), 6.08 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.19-5.07 (m, 2H), 1.91-1.82 (m, 4H), 1.69 (s, 3H), 1.55 (s, 3H), 1.42 (s, 3H). ¹³C NMR (126 MHz; CDCl₃): δ 147.6, 147.0, 131.5, 128.2, 126.7, 125.9, 124.8, 111.9, 44.4, 41.3, 25.9, 23.4, 17.7. GC-MS (EI) *m/z* (% rel. int., ion): 214.15 (9.14, M⁺), 123.15 (100.00, M⁺ -C₇H₇). HRMS (EI) [M⁺] calc. for C₁₆H₂₂: 214.172; found: 214.173.

1-phenyl-2-cyclohexene (4f) (Table 3, Entry 8)^{53a}—Procedure A was followed with cyclohex-2-en-1-yl acetate (**2i**) (140 mg, 1.00 mmol) and iodobenzene (167 μL , 1.50 mmol). Purification by flash chromatography (100% hexanes) afforded 126 mg (80% yield) of the title compound as a colorless oil. ^1H NMR (500 MHz; CDCl_3) δ 7.35-7.22 (m, 5H), 5.95-5.91 (m, 1H), 5.78-5.74 (m, 1H), 3.45 (td, $J = 5.1, 2.5$ Hz, 1H), 2.15-2.03 (m, 3H), 1.81-1.77 (m, 1H), 1.69-1.55 (m, 2H). ^{13}C NMR (101 MHz; CDCl_3) δ 146.7, 130.2, 128.4, 128.3, 127.8, 126.0, 41.9, 32.7, 25.1, 21.2. GC-MS (EI) m/z (% rel. int., ion): 158.10 (100.00, M^+). HRMS (EI) [M^+] calc. for $\text{C}_{12}\text{H}_{14}$: 158.120; found: 158.110. NMR data matched those previously reported.

(E)-but-1-ene-1,3-diylidibenzene (4g) (Table 3, Entry 9)^{53a}—Procedure A was followed with but-1-ene-1,3-diylidibenzene (**2j**) (190 mg, 1.00 mmol) and iodobenzene (167 μL , 1.50 mmol). Purification by flash chromatography (100% hexanes) afforded 152 mg (73% yield) of the title compound as a colorless oil; ^1H NMR (400 MHz; CDCl_3) δ 7.41-7.23 (m, 10H), 6.48-6.39 (m, 2H), 3.71-3.65 (m, 1H), 1.51 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz; CDCl_3) δ 145.8, 137.7, 135.4, 128.7, 128.5, 127.4, 127.2, 126.4, 126.3, 42.7, 21.4. GC-MS (EI) m/z (% rel. int., ion): 208.10 (66.46, M^+), 115 (100.00, $\text{M}^+ - \text{C}_7\text{H}_8$). HRMS (EI) [M^+] calc. for $\text{C}_{16}\text{H}_{16}$: 208.125; found: 208.125. NMR data matched those previously reported.

Procedure D: Allylic acetates with alkyl halides in a nitrogen glove box—A 1 dram vial was charged with $\text{NiCl}_2(\text{dme})$ (10.6 mg, 0.0483 mmol), 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine (20.0 mg, 0.0498 mmol), DMA (500 μL), a teflon coated magnetic stirbar was then added, and the reaction mixture was stirred for 5–10 minutes before the sequential addition of allylic acetate (1.3 mmol), secondary alkyl halide (1.0 mmol), THF (1500 μL), and manganese powder (109.6 mg, 2.00 mmol). The vial was then capped with a screw cap with a PTFE-faced silicone septum. The reaction was then treated as in Procedure A (*vide supra*).

Procedure E: Allylic acetates with alkyl halides on the bench top under argon—As in procedure D, but set up on the bench, without care to exclude air or moisture. Once the reaction was capped, the reaction mixture was sparged with Ar gas for 1 min, followed by a purge of the vial head space for 1 min. The needles were then removed and the vial placed in a heating block at 40 $^\circ\text{C}$ in the usual manner.

(E)-(4-methylnon-1-en-1-yl)benzene (5a) (Table 4, Entry 1)—Run 1 (1.00 mmol): General procedure D was followed with cinnamyl acetate (**2a**) (216.7 μL , 1.30 mmol) and 2-bromoheptane (172.9 μL , 1.00 mmol, distilled purity was 90.7% so amount was scaled from 156.8 μL). Purification by flash chromatography (100% hexanes) afforded 151.7 mg (70% yield) of the title compound as a clear oil. ^1H NMR (400 MHz; CDCl_3): δ 7.38-7.18 (m, 5H), 6.39 (d, $J = 15.8$ Hz, 1H), 6.23 (dt, $J = 15.4, 7.5$ Hz, 1H), 2.27-2.02 (m, 2H), 1.62-1.56 (m, 1H), 1.37-1.28 (m, 7H), 1.20-1.14 (m, 1H), 0.95-0.90 (m, 6H). ^{13}C NMR (101 MHz; CDCl_3): δ 138.1, 131.0, 130.0, 128.6, 126.9, 126.1, 40.8, 36.8, 33.5, 32.3, 27.0, 22.9, 19.8, 14.3. GC-MS (EI) m/z (% rel. int., ion): 216.15 (18.02, M^+), 117.10 (100.00, $\text{M}^+ - \text{C}_7\text{H}_{15}$). HRMS (EI) [M^+] calc. for $\text{C}_{16}\text{H}_{24}$: 216.188; found: 216.187. Run 2 (0.50 mmol): General procedure D was followed with cinnamyl acetate (83.4 μL , 0.65 mmol) and 2-bromoheptane (86.2 μL , 0.50 mmol, Aldrich Lot# 12798PJ was 90.7% so amount was scaled from 78.4 μL). Purification by flash chromatography (100% hexanes) afforded 95.6 mg (88% yield) of the title compound as a clear oil. ^1H NMR matched those reported in run 1.

(E)-(3-cyclohexylprop-1-enyl)benzene (5b) (Table 4, Entry 2)⁵⁸—General procedure D was followed with cinnamyl acetate (**2a**) (216.7 μ L, 1.30 mmol) and bromocyclohexane (123.2 μ L, 1.00 mmol). Purification by flash chromatography (100% hexanes) afforded 180.6 mg (90% yield) on Run 1 and 171.7 mg (86% yield) on Run 2 of the title compound as a clear oil; analytical data matched those reported in the literature. ¹H NMR (400 MHz; CDCl₃): δ 7.39-7.30 (m, 4H), 7.23-7.20 (m, 1H), 6.39 (d, J = 15.8 Hz, 1H), 6.25 (dt, J = 15.4, 7.5 Hz, 1H), 2.16-2.12 (m, 2H), 1.82-1.68 (m, 5H), 1.43 (ddtd, J = 14.5, 10.8, 7.2, 3.6 Hz, 1H), 1.32-1.14 (m, 3H), 1.04-0.94 (m, 2H). ¹³C NMR (101 MHz; CDCl₃): δ 138.1, 130.8, 129.9, 128.6, 126.9, 126.0, 41.2, 38.3, 33.4, 26.7, 26.5. GC-MS (EI) m/z (% rel. int., ion): 200.15 (23.74, M⁺), 104.10 (100.00, M⁺-C₇H₁₃+H). HRMS (EI) [M⁺] calc. for C₁₅H₂₀: 200.157; found: 200.156.

(E)-(3-cyclohexylprop-1-enyl)benzene (5b) (Table 4, Entry 3)⁵⁸—General procedure E was followed with cinnamyl acetate (**2a**) (216.7 μ L, 1.30 mmol) and bromocyclohexane (123.2 μ L, 1.00 mmol). Purification by flash chromatography (100% hexanes) afforded 179.4 mg (90% yield) of the title compound as a clear oil; analytical data matched those reported in the literature. ¹H NMR (400 MHz; CDCl₃): δ 7.39-7.30 (m, 4H), 7.23-7.19 (m, 1H), 6.38 (d, J = 15.8 Hz, 1H), 6.25 (dt, J = 15.7, 7.2 Hz, 1H), 2.15-2.12 (m, 2H), 1.81-1.67 (m, 5H), 1.43 (ddtd, J = 14.5, 10.9, 7.2, 3.6 Hz, 1H), 1.32-1.13 (m, 3H), 1.04-0.90 (m, 2H). ¹³C NMR (101 MHz; CDCl₃): δ 138.1, 130.8, 129.9, 128.6, 126.9, 126.0, 41.2, 38.3, 33.4, 26.7, 26.5. GC-MS (EI) m/z (% rel. int., ion): 200.15 (22.48, M⁺), 104.10 (100.00, M⁺-C₇H₁₃+H). HRMS (EI) [M⁺] calc. for C₁₅H₂₀: 200.157; found: 200.156.

(E)-(3-cyclopentyl-1-propenyl)-benzene (5c) (Table 4, Entry 4)⁵⁹—General procedure D was followed with cinnamyl acetate (**2a**) (216.7 μ L, 1.30 mmol) and bromocyclopentane (107.2 μ L, 1.00 mmol). Purification by flash chromatography (100% hexanes) afforded 129.1 mg (69% yield) on Run 1 and 123.7 mg (66% yield) on Run 2 of the title compound as a clear oil; analytical data matched those reported in the literature. ¹H NMR (400 MHz; CDCl₃): δ 7.37-7.29 (m, 4H), 7.20 (td, J = 7.2, 1.8 Hz, 1H), 6.39 (d, J = 15.8 Hz, 1H), 6.25 (dt, J = 15.8, 7.0 Hz, 1H), 2.26-2.22 (m, 2H), 1.97 (dq, J = 15.0, 7.5 Hz, 1H), 1.84-1.76 (m, 2H), 1.69-1.51 (m, 4H), 1.27-1.18 (m, 2H). ¹³C NMR (101 MHz; CDCl₃): δ 138.1, 130.7, 130.3, 128.6, 126.9, 126.1, 40.2, 39.6, 32.5, 25.3. GC-MS (EI) m/z (% rel. int., ion): 186.10 (25.68, M⁺), 117.10 (100.00, M⁺-C₅H₉). HRMS (EI) [M⁺] calc. for C₁₄H₁₈: 186.141; found: 186.141.

(E)-(1S,2R,4R)-2-cinnamylbicyclo[2.2.1]heptane (5d) (Table 4, Entry 5)—General procedure D was followed with cinnamyl acetate (**2a**) (216.7 μ L, 1.30 mmol) and *exo*-2-bromonorborane (128.4 μ L, 1.00 mmol). Purification by flash chromatography (100% hexanes) afforded 179.0 mg (84% yield) on Run 1 and 150.2 mg (71% yield) on Run 2 of the title compound as a clear oil. ¹H NMR (400 MHz; CDCl₃): δ 7.38-7.29 (m, 4H), 7.23-7.18 (m, 1H), 6.38 (d, J = 15.8 Hz, 1H), 6.20 (dt, J = 15.8, 7.0 Hz, 1H), 2.24-2.14 (m, 2H), 2.07-2.00 (m, 2H), 1.61-1.42 (m, 4H), 1.42-1.32 (m, 1H), 1.31-1.10 (m, 4H). ¹³C NMR (101 MHz; CDCl₃): δ 138.1, 130.4, 130.3, 128.6, 126.9, 126.1, 42.2, 40.9, 40.4, 38.0, 36.9, 35.3, 30.2, 29.0. GC-MS (EI) m/z (% rel. int., ion): 212.10 (12.51, M⁺), 95.10 (100.00, M⁺-C₉H₉). HRMS (EI) [M⁺] calc. for C₁₆H₂₀: 212.157; found: 212.157.

(E)-1-methoxy-4-(4-methylnon-1-en-1-yl)benzene (5e) (Table 4, Entry 6)—General procedure D was followed with (*E*)-3-(4-methoxyphenyl)allyl acetate (**2k**) (268.1 mg, 1.30 mmol) and 2-bromoheptane (172.9 μ L, 1.10 mmol because material was 90.7% pure). Purification by flash chromatography (2% ethyl acetate in hexanes) afforded 209.8 mg (85% yield) on Run 1 and 178.2 mg (72% yield) on Run 2 of the title compound as a

clear oil. ^1H NMR (400 MHz; CDCl_3): δ 7.31-7.27 (m, 2H), 6.87-6.83 (m, 2H), 6.32 (d, J = 15.7 Hz, 1H), 6.08 (dt, J = 15.7, 7.3 Hz, 1H), 3.81 (s, 3H), 2.24-1.99 (m, 2H), 1.61-1.53 (m, 1H), 1.39-1.27 (m, 7H), 1.20-1.13 (m, 1H), 0.93-0.89 (m, 6H). ^{13}C NMR (101 MHz; CDCl_3): δ 158.7, 131.0, 130.3, 127.8, 127.1, 114.0, 55.4, 40.7, 36.8, 33.5, 32.3, 27.0, 22.9, 19.8, 14.3. GC-MS (EI) m/z (% rel. int., ion): 246.20 (15.13, M^+), 147.10 (100.00, M^+ - C_7H_{15}). HRMS (EI) [M^+] calc. for $\text{C}_{17}\text{H}_{26}\text{O}$: 246.198; found: 246.198.

(E)-(4-methylnon-1-en-1-yl)-4-(trifluoromethyl)benzene (5f) (Table 4, Entry 7)—

Run 1 (1.00 mmol): General procedure D was followed with (*E*)-3-(4-trifluoromethyl)phenyl)allyl acetate (**2l**) (317.5 mg, 1.30 mmol) and 2-bromoheptane (172.9 μL , 1.10 mmol because material was 90.7% pure). Purification by flash chromatography (100% hexanes) afforded 202.1 mg (71% yield) of the title compound as a clear oil. ^1H and ^{13}C NMR spectra match those reported for run 2. Run 2 (0.50 mmol): General procedure D was followed with (*E*)-3-(4-trifluoromethyl)phenyl)allyl acetate (**2l**) (175.2 mg, 0.65 mmol, **2l** was 90.6% pure by GC so amount was scaled from 158.5 mg) and 2-bromoheptane (86.5 μL , 0.50 mmol, distilled purity was 90.7% so amount was scaled from 78.4 μL). Purification by flash chromatography (100% hexanes) afforded 85.6 mg (60% yield) of the title compound as a clear oil. ^1H NMR (400 MHz; CDCl_3): δ 7.54 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 6.42-6.28 (m, 2H), 2.28-2.03 (m, 2H), 1.64-1.54 (m, 1H), 1.37-1.25 (m, 7H), 1.19-1.14 (m, 1H), 0.93-0.88 (m, 6H). ^{13}C NMR (101 MHz; CDCl_3): δ 141.5, 132.9, 129.8, 126.2, 125.54, 125.51, 40.8, 36.8, 33.4, 32.3, 26.9, 22.9, 19.8, 14.3. We were unable to resolve one of the expected carbon atoms. We presume the missing carbon to be the CF_3 quartet based upon literature data for similar compounds. ^{19}F NMR (376 MHz; CDCl_3): δ -62.8. GC-MS (EI) m/z (% rel. int., ion): 284.20 (8.51, M^+), 57.10 (100.00, M^+ - $\text{C}_{13}\text{H}_{14}\text{F}_3$). HRMS (EI) [M^+] calc. for $\text{C}_{17}\text{H}_{23}\text{F}_3$: 284.175; found: 284.176.

Procedure F: Allylic acetates and carbonates with a vinyl bromide in a

nitrogen glove box: A—1 dram vial was charged with $\text{NiCl}_2(\text{dme})$ (10.6 mg, 0.0483 mmol), 2,9-dimethyl-1,10-phenanthroline (10.4 mg, 0.0499 mmol), and DMA (500 μL) followed by a teflon coated magnetic stirbar. The reaction mixture was stirred for 5–10 minutes. In a separate 1 dram vial the branched allylic starting material (1.0 mmol) and 2-bromocyclohex-2-en-1-one (1.0 mmol) were massed. The catalyst solution was the added to the substrates, followed by THF (1500 μL), and manganese powder (-325 mesh, 109.6 mg, 2.00 mmol), sequentially. The remainder of the procedure followed procedure A (vide supra).

2-cinnamylcyclohex-2-enone (7a) (Table 5, Entry 3)—General procedure F was followed with 1-phenyl-2-propenyl acetate (**2c**) (176.2 mg, 1.00 mmol) and 2-bromocyclohex-2-en-1-one (**6**) (175.0 mg, 1.00 mmol). Purification by flash chromatography (5% ethyl acetate in hexanes) afforded 165.3 mg (78% yield) of the title compound as a pale yellow oil. ^1H NMR (400 MHz; CDCl_3): δ 7.36-7.18 (m, 5H), 6.78 (t, J = 4.2 Hz, 1H), 6.41 (d, J = 15.8 Hz, 1H), 6.22 (dt, J = 15.8, 7.0 Hz, 1H), 3.12-3.09 (m, 2H), 2.48-2.44 (m, 2H), 2.36 (tdt, J = 6.0, 4.0, 1.9 Hz, 2H), 2.01 (dq, J = 12.9, 6.3 Hz, 2H). ^{13}C NMR (101 MHz; CDCl_3): δ 199.1, 146.1, 138.4, 137.6, 131.7, 128.6, 127.7, 127.2, 126.2, 38.6, 32.9, 26.2, 23.2. GC-MS (EI) m/z (% rel. int., ion): 212.00 (62.05, M^+), 121.05 (100.00). HRMS (EI) [M^+] calc. for $\text{C}_{15}\text{H}_{16}\text{O}$: 212.120; found: 212.119.

(E)-2-(4-ethylhex-2-en-1-yl)cyclohex-2-enone (7b) (Table 6, Entry 3)—General procedure F was followed with 4-ethyl-hex-1-en-3-yl methyl carbonate (**2m**) (186.3 mg, 1.00 mmol) and 2-bromocyclohex-2-en-1-one (**6**) (175.0 mg, 1.00 mmol). Purification by flash chromatography (5% ethyl acetate in hexanes) afforded 104.6 mg (51% yield) of the title compound as a dark yellow oil. ^1H NMR (400 MHz; CDCl_3): δ 6.70 (t, J = 4.2 Hz, 1H), 5.32 (dt, J = 14.8, 7.2 Hz, 1H), 5.14 (dd, J = 15.2, 8.7 Hz, 1H), 2.89 (d, J = 6.8 Hz, 2H), 2.42

(t, $J = 6.8$ Hz, 2H), 2.34 (tdt, $J = 5.9, 4.0, 1.9$ Hz, 2H), 2.03-1.94 (m, 2H), 1.73 (dtd, $J = 13.3, 8.7, 4.7$ Hz, 1H), 1.43-1.33 (m, 2H), 1.23-1.14 (m, 2H), 0.82 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (101 MHz; CDCl_3): δ 199.3, 145.2, 139.2, 137.1, 127.0, 46.4, 38.7, 32.3, 27.8, 26.2, 23.3, 11.9. GC-MS (EI) m/z (% rel. int., ion): 206.10 (3.97, M^+), 135.05 (100.00, $\text{M}^+ - \text{C}_5\text{H}_{11}$). HRMS (EI) $[\text{M}^+]$ calc. for $\text{C}_{14}\text{H}_{22}\text{O}$: 206.167; found: 206.166.

(E)-2-(5-phenylpent-2-en-1-yl)cyclohex-2-enone (7c) (Table 6, Entry 4)—General procedure F was followed with 5-phenyl-pent-1-en-3-yl methyl carbonate (**2n**) (220.3 mg, 1.00 mmol) and 2-bromocyclohex-2-en-1-one (**6**) (175.0 mg, 1.00 mmol). Purification by flash chromatography (5% ethyl acetate in hexanes) afforded 104.6 mg (51% yield) of the title compound as a pale yellow oil. ^1H NMR (400 MHz; CDCl_3): δ 7.29-7.16 (m, 5H), 6.52 (t, $J = 4.2$ Hz, 1H), 5.51-5.35 (m, 2H), 2.86 (d, $J = 6.3$ Hz, 2H), 2.69 (t, $J = 7.7$ Hz, 2H), 2.42 (td, $J = 6.8, 3.0$ Hz, 2H), 2.37-2.28 (m, 4H), 1.96 (dt, $J = 13.0, 6.4$ Hz, 2H). ^{13}C NMR (101 MHz; CDCl_3): δ 199.3, 145.6, 142.1, 138.7, 131.7, 128.7, 128.3, 127.9, 125.8, 38.6, 36.0, 34.4, 32.2, 26.2, 23.2. GC-MS (EI) m/z (% rel. int., ion): 240.10 (14.85, M^+), 91.00 (100.00, $\text{M}^+ - \text{C}_{10}\text{H}_{13}\text{O}$). HRMS (EI) $[\text{M}^+]$ calc. for $\text{C}_{17}\text{H}_{20}\text{O}$: 240.151; found: 240.151.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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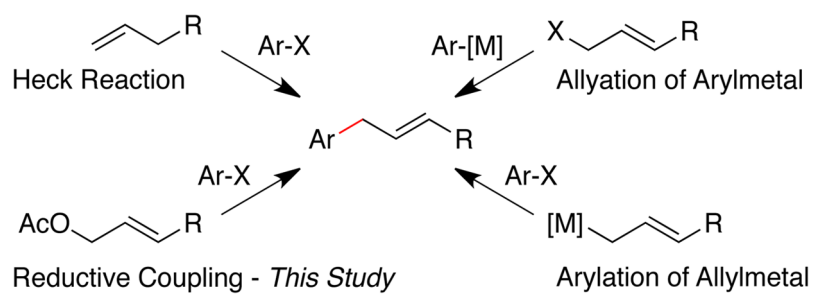


Figure 1.
Approaches to the synthesis of allylated arenes.

Low selectivity in oxidative addition \implies Poorly selective reaction

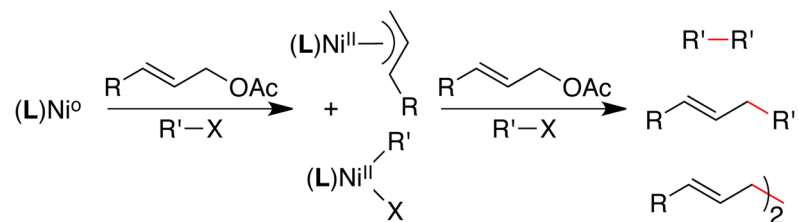


Figure 2.
Selectivity challenge for reductive allylation.

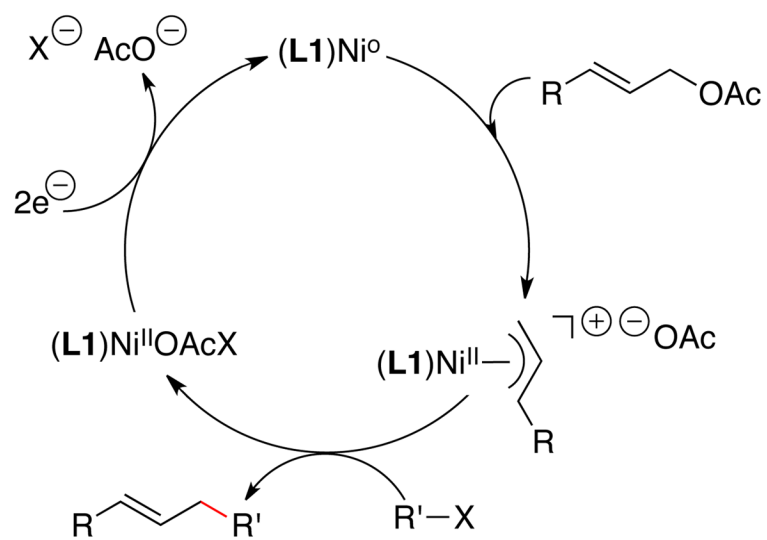
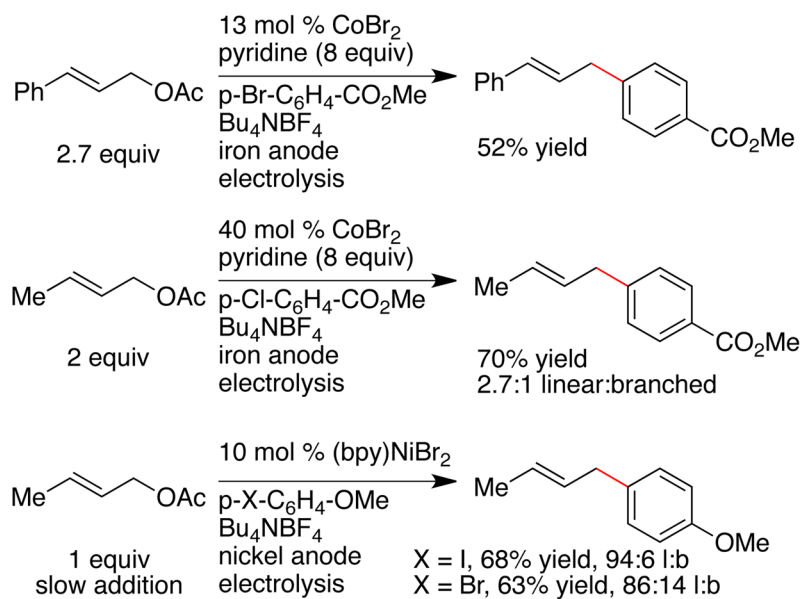
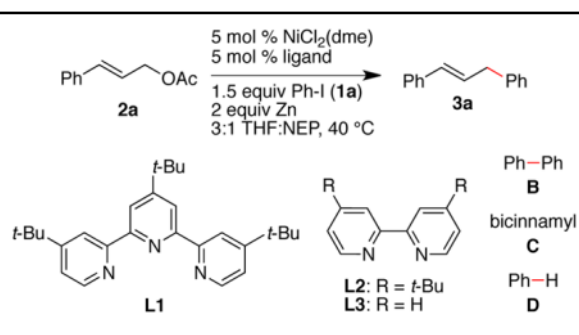


Figure 3.
Proposed mechanism.

**Scheme 1.**

All previous examples of reductive allylations with substituted allylic acetates.

Table 1

Ligand effect on cross-selectivity^a

Entry	ligand	GC yield ^b	ratio ^c 3a:B:C:D
1	L1	90	100:1:2:15
2	L2	62	100:37:5:5
3	pyridine (10 equiv)	45 ^d	100:11:0:20
4	L3	73	100:17:1:4
5	none	4 ^e	100:0:0:86

^aReaction conditions: 1:1.5:2 cinnamyl acetate:Ph-I:Zn, 5 mol % NiCl₂(dme) in 3:1 THF:NEP (NEP = *N*-ethylpyrrolidinone). Reaction time was 15–24 h.

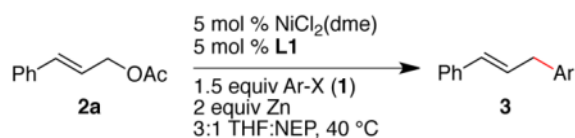
^bCorrected GC yields, see Supporting Information for an example calculation.

^cRatios based upon GC Area % data.

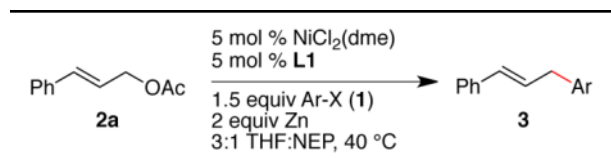
^dReaction time was 96 h.

^eReaction was incomplete at 96 h, 31% **1a** and 51% **2a** remained.

Table 2

Allylation of a variety of aryl halides^a

Entry	X	product	yield ^b
1	I		88
		(3a) 1 mmol scale, set up in glovebox	
2	I	10 mmol scale, set up on benchtop ^c	81
3	I		71
		R = C(O)Me (3b)	
4	I	R = CHO (3c)	70
5	I	R = NHTs (3d)	73
6	I	R = NHC(O)CF ₃ (3e)	64
7	I	R = CH ₂ OTBS (3f)	80 ^d
8	I	R = NMe ₂ (3g)	55
9	I	R = Me (3h)	86
10	I	R = OMe (3i)	83
11	I	R = Br (3j)	64 ^e
12	Br	R = CO ₂ Me (3k)	65
13	Br	R = C(O)Me (3b)	48
14	Br	R = CF ₃ (3l)	51 ^f
15	Br	R = CN (3m)	77
16	I		78
		(3n)	
17	I	R = CN (3o)	86



Entry	X	product	yield ^b
18	I	R = OMe (3p)	80

^aAs in Table 1, but on 1 mmol scale in 2 mL of THF/NEP. Reaction times were 15–24 h.

^bYield after purification. For complete selectivity data, see Tables S1 and S2 in the Supporting Information.

^cA 1 mmol-scale reaction run on the benchtop (Procedure B) gave an 82% GC yield.

^dReaction was run on a 0.5 mmol scale.

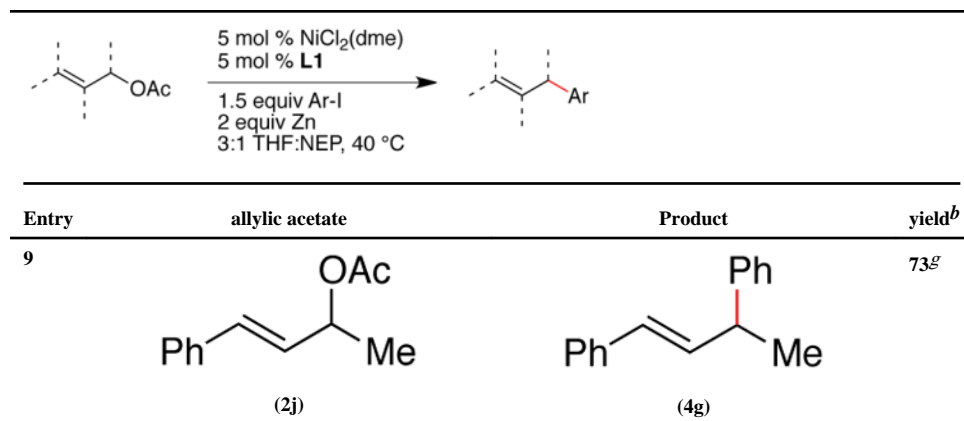
^eNMR yield of **3j**. Isolated product is contaminated with 9% of **3a** from hydrodeiodination.

^fYield is an average of two runs, one at 0.5 mmol scale and one at 1 mmol scale.

Table 3

Reaction of iodoarenes with various allylic acetates^a

Entry	allylic acetate	Product	yield ^b
1			81 ^c
2			52
3			75
4			97 ^d
5			55
6			65 ^e
7			52 ^f
8			80



^aReaction conditions as in Table 3. Reaction times were 15–18 h. See Table S3 in the Supporting Information for full selectivity data.

^bYield after purification.

^cProduct has a 86:14 [linear]:[branched] ratio.

^dProduct has a 93:7 [linear]:[branched] ratio.

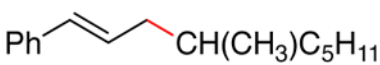
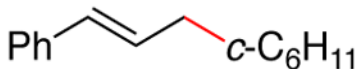
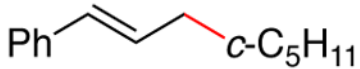
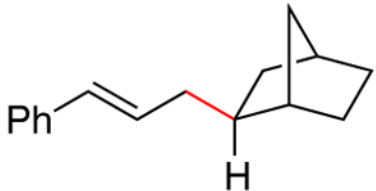
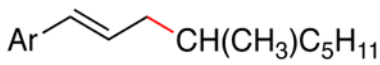
^eProduct is a mixture of olefin isomers: 6.9:1:1 [2*E*,4*E*]:[2*E*,4*Z*]:[unidentified olefin isomer].

^fNMR yield of the *E/Z* mixture of linear products. Product has a 1.9:1 [linear]:[branched] ratio. The linear product was a 1:1 mixture of *E:Z* isomers.

^gProduct contains ~3% of an unidentified side product.

Table 4

Coupling of allylic acetates with alkyl bromides^a

entry	product	yield ^b
1	 (5a)	79 ^c
2	 (5b) Set up in glovebox	88 ^c
3	Set up in the benchtop ^d	90
4	 (5c)	68 ^c
5	 (5d)	78 ^c
6	 Ar = <i>p</i> -MeO-C ₆ H ₄ (5e)	79 ^c
7	Ar = <i>p</i> -F ₃ C-C ₆ H ₄ (5f)	66 ^c

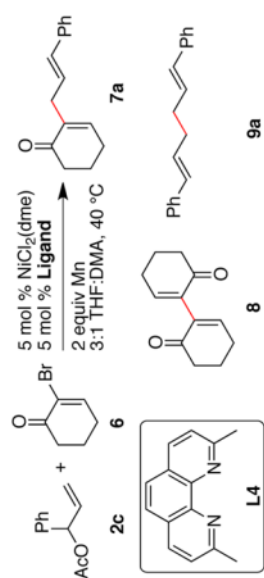
^aReaction conditions: 1.5:1:2 allyl acetate:R-Br:Mn. Reaction times were 15–18 h. See Table S4 in the Supporting Information for full selectivity data.

^bYield after purification.

^cYield is an average of two runs, one at 0.5 mmol scale and one at 1 mmol scale.

^dReagents were weighed out on the bench top in a vial that was then sparged with argon gas through the septa cap.

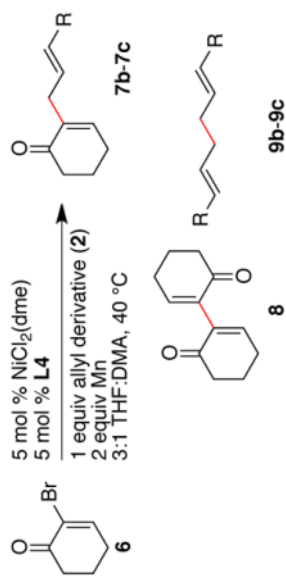
Table 5

Ligand effect on cross-selectivity for reactions with 2-bromo-cyclohex-2-enone ^a

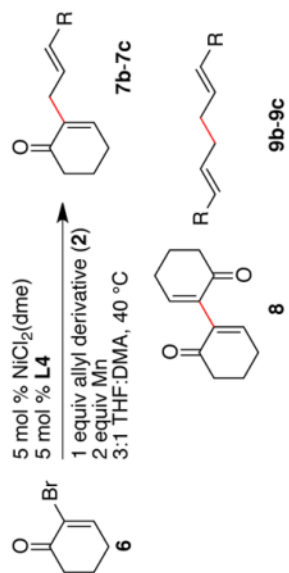
entry	ligand	GC Area % (Yield) ^b				
		2c	6	7a	8	9a
1	L1	66	34	0	0	0
2	L2	0	0	78	6	16
3	L4	0	0	94 (78)	0	5
4	phen	66	34	0	0	0

^aReactions run with a 1:1 ratio of reactants for 21 h. phen = 1,10-phenanthroline.^bResults in table are GC Area % data. The number in parentheses is yield after purification.

Table 6

Effect of leaving group on selectivity for reactions with 2-bromo-cyclohex-2-enone^a

entry	allyl derivative	GC Area % (Yield) ^b								
		2	6	7	8	9	7b	7c	8	9
1		0	0	0	0	0	21	26	26	51
2		26	0	0	0	0	36	17	17	19



entry	allyl derivative	GC Area % (Yield) ^b								
		2	6	7	8	9	7b	11	19	
3	 (2m)	0	0	0	7b	68	(51)			
4	 (2n)	0	0	0	7c	90	(67)			

^aReactions run with a 1:1 ratio of reactants for 19 h.

^bResults in table are GC area % data. Numbers in parenthesis are yields after purification.