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Heterodimerization of Propylene and Vinylarenes: Functional Group Compatibility in a Highly Efficient Ni-Catalyzed Carbon–Carbon Bond-Forming Reaction

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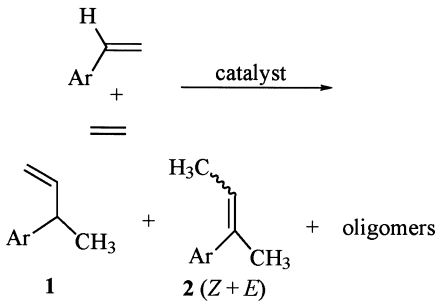
Abstract—Unlike heterodimerization reactions of ethylene and vinylarenes, no such synthetically useful reactions using propylene are known. We find that propylene reacts with various vinylarenes in the presence of catalytic amounts of $[(allyl)NiBr]_2$, triphenylphosphine and AgOTf giving excellent yields of the dimerization products. The reaction proceeds at 1 atm of propylene at temperatures between −15 and 10°C. These conditions are compatible with a number of common organic functional groups such as halides, ethers, esters, ketones and sulfonamides. As expected, a mixture of regioisomeric products (with propene-C_1 addition to the benzylic position as the major one) is obtained. The product distribution appears to be significantly different when a hemilabile ligand (2-diphenylphosphino-2′-alkoxy-1,1′-binaphthyl) is employed.

Introduction

Utilization of abundantly available carbon sources such as CO, HCN, ethylene and other simple olefins for the synthesis of key chemical intermediates is an important goal in modern synthetic organic chemistry.[1] In addition to the obvious economic benefits, such transformations, when carried out with high efficiency and selectivity, would also add to our repertoire of environmentally benign chemical processes. In this context, the cationic '$[Ni-H]^+$'-catalyzed oligomerization reactions[2,3] of olefins is particularly noteworthy. For example, the active species generated from η^3-allylnickel(phosphine)(Y) (Y=alkylaluminum salt) has a turnover frequency of 625,000 $[C_3H_6]\ [Ni]^{-1}\ h^{-1}$ for the formation of C_6-olefins from propylene, and has been described as the most active homogeneous catalyst known. Subsequently, the tunability of this catalyst system was exploited by Wilke and coworkers for a highly selective heterodimerization of ethylene with vinylarenes (Eq. (1)).[3a,b,4] Two principal limitations of the Wilke catalyst which gave very high enantioselectivities in the formation of the product 3-phenyl-1-butenes (up to 95% ee for styrene) became apparent in later studies: (a) a stringent requirement of the esoteric phosphine **3** (even minor modifications of the ligand led to much lower selectivity[5]); (b) the presence of Lewis acidic aluminum halides under the reaction conditions, which could potentially limit the utility in Lewis basic substrates. Use of Al-free the ethylene dimerization catalyst $[Ni(2,4,6\text{-}Me_3C_6H_2)(CH_3CN)(phosphine)_2]^+[BF_4]^-$, which has been recently reported for the hydrovinylation[6] of styrene, is complicated by an exothermic ethylene polymerization after all the styrene is consumed. Besides, the reaction is done in a closed system with high pressure (15–25 bar) of ethylene. Dicationic $[Ni(CH_3CN)_6]^{++}[BF_4^-]_2$ which, in the presence of $PPh_3/AlEt_2Cl$, catalyzes the hydrovinylation of styrene,[7] fails with substrates having Lewis basic centers. Among the other notable hydrovinylation conditions is a palladium-catalyzed reaction which uses the phosphinite **4** as the source of chirality.[3c] However, the yield and selectivity of this reaction remains modest. Selective hydrovinylation in a membrane reactor using dendrimeric catalysts with P,O ligands which has been reported recently also suffers from poor yield[3d] (Scheme 1).



(1)

Keywords: catalysis; coupling reactions; nickel; vinylation.

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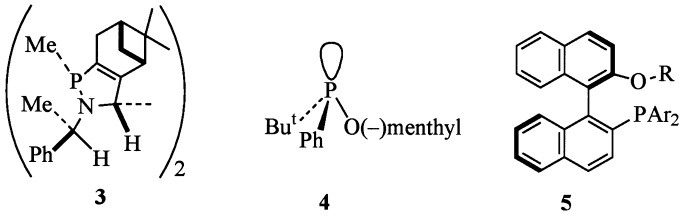


Scheme 1.

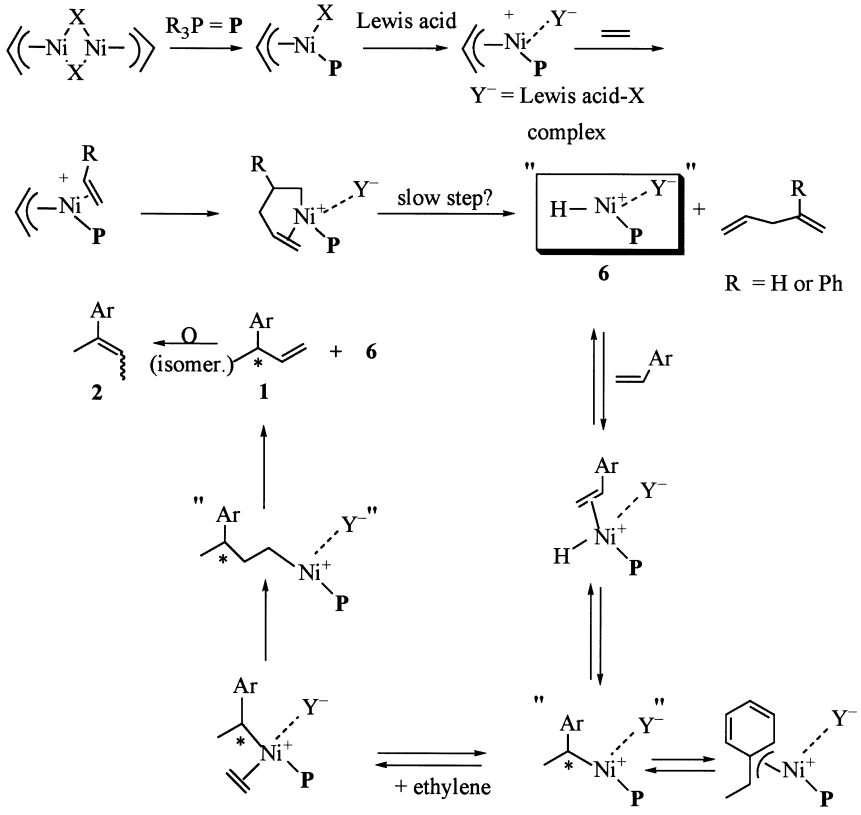
Results and Discussion

Mechanism of the reaction

All the available evidence points to a mechanism involving a cationic nickel hydride associated with a weakly coordinated counter ion (**6**, Scheme 2). Poor reactivity of the substrates carrying heteroatoms, and the isomerization of the initially formed 3-aryl-1-butene (**1**) to 2-aryl-2-butene(s) (**2**) are major problems with many of the previously reported protocols. The isomerization reaction appears to be a major drawback, especially of the Pd-mediated reaction. We reasoned that the scope and selectivity of hydrovinylation could be significantly increased by eliminating the troublesome Lewis acid, and/or by the use of a hemilabile ligand.[8] Further it should be possible to prevent the isomerization of the initially formed terminal olefin (e.g. **1**→**2**) by manipulation of the phosphine ligand, **P** and/or the metal.

A new protocol for hydrovinylation of vinylarenes

After an extensive scouting program in which we systematically varied the ligand and the counterion, a new protocol was arrived at. The hydrovinylation of various vinylarenes proceeds with *unprecedented* chemical yield and selectivity when a combination of allylnickel bromide dimer, a weakly coordinating counterion such as triflate (OTf^-)[9] is employed as the precatalyst (Eq. (2) and Table 1). Alternatively, Na^+-Ar_4B^- (Ar=3,5-$(CF_3)_2C_6H_3$)[10] along with a monophosphine carrying a hemilabile ligand can also be employed (vide infra, Eq. (3)).[11c] For ethylene, typically the reaction is carried out at −56°C in methylene chloride as the solvent under 1 atm of ethylene pressure using 0.007 equiv. of the catalyst.[11] Under these conditions no oligomerization of either the vinylarene or ethylene is detected. In sharp contrast to the previously reported Lewis acid-mediated reactions, vinylarenes with Lewis basic centers undergo the reaction with remarkable ease (entries 2 and 3). 4-Isobutylstyrene, 3-fluoro-4-phenylstyrene and 2-methoxy-6-vinylnaphthalene (entries 3–5), all potential precursors for important antiinflammatory agents, gave excellent yields of the expected hydrovinylation products. Hydrovinylation product of 4-bromostyrene (entry 2) is another potentially important precursor that could be transformed into a variety



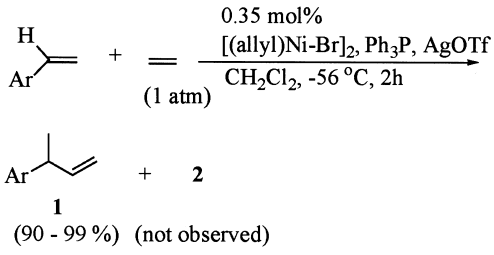
Scheme 2. Mechanism of heterodimerization. (Intermediates within " " may involve other ligands like olefins.)

Table 1. Hydrovinylation of vinylarenes

Entry	Substrate	Yield (%)[a]	Conditions[b]
1	Styrene	>95 (99$^+$)	(i)
2	4-Bromostyrene	>95 (98)	(i)
3	6-MeO-2-vinyl-Naphthalene	(90) (97)	(i), 0.5 mol% cat. (ii)
4	4-*i*-Bu-styrene	>90 (99$^+$)	(i), 1.4 mol% cat.
5	3-F-4-Ph-styrene	(88)	(i)

[a] In brackets are the yields estimated by gas chromatography.
[b] Conditions (i) Eq. (2): $[(allyl)NiBr]_2$, (0.35 mol%)/Ph_3P/AgOTf/CH_2Cl_2/−55°C/2 h. (ii) Eq. (3): $[(allyl)NiBr]_2$, (0.70 mol%)/(*R*)-MOP (**5**, R=CH_2Ph)/$Ar_4B^-Na^+$/CH_2Cl_2/−56°C/2 h.

of useful intermediates via organometallic cross-coupling reactions. Preliminary experiments indicate that olefins with strongly electron-withdrawing substituents on the aromatic nucleus (for example, 3,5-di-trifluoromethyl-styrene, 2-vinylpyridine) are poor substrates for this reaction. Methyl substitution at the α- or β-carbons of styrene also leads to poor yields (21 and 49%, respectively) under these conditions.



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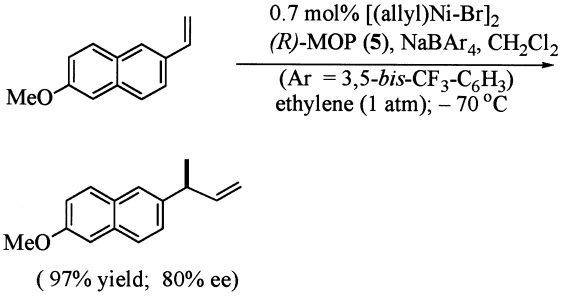
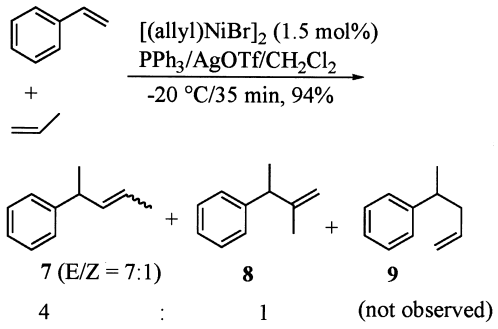


(3)

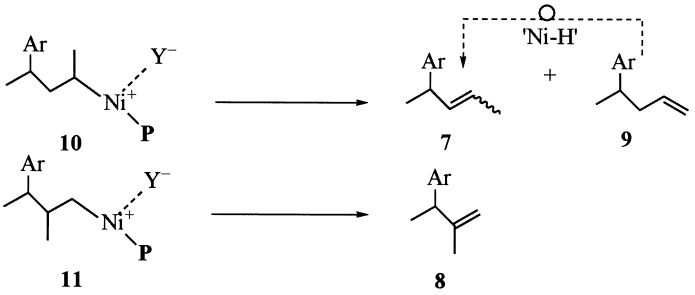
Heterodimerization of propylene and vinylarenes

Since the original discovery, we have found that this catalyst system, with some modifications, is also applicable for the heterodimerization of propylene and vinylarenes. In spite of the considerable activity in this area, the reaction of propylene has received surprisingly little attention.[12] In the past, only styrene has been subjected to codimerization with propylene, and the yield and selectivity of this reaction have been unacceptably low. For example, bis-(Ph_3P)-*o*-tolyl(Br)Ni(II)/BF_3·Et_2O catalyzes the codimerization of styrene and propylene to give a mixture of 2-methyl-3-phenyl-1-butene, 4-phenyl-1-pentene and 4-phenyl-2-pentene in an overall yield of 3.2%, *not significantly more than* the amount of catalyst used in the reaction (2.5 mol%). Polymerization of styrene and homodimerization of propylene competes effectively to reduce the yield of the codimers. This and other published procedures[12] are unlikely to be of use in reactions of vinylarenes with heteroatom substituents. In spite of the highly electrophilic nature of the intermediates involved, the reaction conditions described in our protocol are remarkably tolerant to a wide variety of functional groups commonly encountered in organic chemistry.



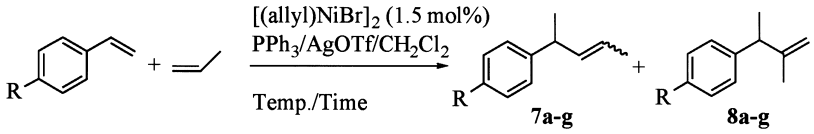
(4)

In order to establish the most optimum reaction conditions a number of allylnickel halide dimers, phosphines and silver salts were screened. In a prototypical reaction, a solution of the precatalyst (0.30 mol%, prepared from $[(allyl)NiBr]_2$, triphenylphosphine and AgOTf) in CH_2Cl_2 was treated with styrene under 1 atm of propylene at −20°C (Eq. (4)). The reaction was subsequently quenched with ammonium chloride solution, and the codimerization product was isolated in 94% yield (based on styrene) by standard techniques. Gas chromatographic and NMR analysis of the purified product revealed the presence of three components, identified as *Z*- and *E*-4-phenyl-2-pentenes[13] (76%) and 2-methyl-3-phenyl-1-pentene[12a] (18%). The ratio of *E*- to *Z*-4-phenyl-2-pentene was determined by NMR and GC as approximately 7:1. The benzyl hydrogen of the *Z*-isomer appears at a lower field at ~δ 3.75–3.89 and that of the



Scheme 3. Origin of isomeric products in the propylene reaction.

Table 2. Codimerization of substituted styrenes with propylene



Entry	R	Temperature (°C)	Time (min)	Isolated yield (%)	Ratio of products (**7**:**8**)
a	*i*-Bu	−15	15	96	3:1
b	OMe	−15	60	86	4:1
c	Cl	0	15	94	4:1
d	Br	0	10	95	4:1
e	OAc	−10	30	93	4:1
f	C(O)Ph[a]	10	15	94	4:1
g	$N(Ts)_2$[a]	10	25	92	2:1

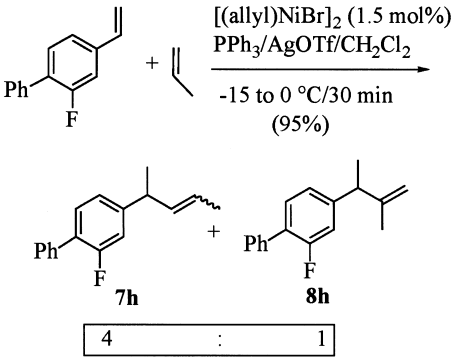
[a] 3 mol% of $[(allyl)NiBr]_2$ was used.

E-isomer at ~δ 3.35–3.49. No trace of unreacted styrene or of styrene dimers[14] were detected under these conditions by GC or NMR. Conspicuously absent from the mixture is the linear product 4-phenyl-1-pentene (**9**), confirmed by the absence of the signals due to the allylic hydrogens which appear at ~2.32 (m) in the ^1H NMR.[12a]

By analogy to the codimerization of ethylene and vinyl arenes, the two products must arise via addition of the catalyst [(phosphine)Ni–H^+] to styrene, followed by insertion of propylene into the resulting benzyl–Ni complex and subsequent β-hydride elimination (Scheme 3). Insertion with C–C bond formation at the terminal or internal carbon of the double bond would result in the σ-nickel complexes **10** or **11**. Preponderance of the formation of **7** might reflect the steric demands of the insertion reaction. At least a portion of **7** is generated from the initially formed 4-phenyl-1-pentene (**9**), which can be seen at the early stages of the reaction (vide infra, Eq. (6b)). However no trace of this product survives under these reaction conditions.

Functional group compatibility of the catalyst

The codimerization reaction is quite general for a number of vinyl arenes. Table 2 lists the optimized reaction conditions for a variety of substituted styrenes. In general, the isolated yields are good to excellent and the ratio of the two products varies between 2:1 and 10:1. The codimerization reactions of propylene proceed at temperatures higher than that needed for the corresponding reactions of ethylene. Styrene derivatives with Lewis basic groups such as OMe-, Cl- and Br- give good yields under moderate conditions. Surprisingly, these reaction conditions can tolerate even ester, ketone and sulfonamido moieties. Thus 4-acetoxystyrene, 4-vinylbenzophenone[15] and 4-bis-(4-toluenesulfonylamino)-styrene[16] underwent the codimerization in 93, 94 and 92% yields, respectively. In addition, 4-isobutylstyrene,[17] 3-fluoro-4-phenylstyrene[15] (Eq. (5)) and 2-methoxy-6-vinylnaphthalene[17](Eq. (6)), precursors of important anti-inflammatory agents ibuprofen, flurbiprofen and naproxen, respectively, gave excellent yields of the expected products in moderate to good selectivity. For reasons not yet apparent, 2-methoxy-6-vinylnaphthalene gave the regioisomeric products in a ratio of 10:1 under the standard conditions (Eq. (6a)). Heterodimerization of 6-methoxy-2-vinylnaphthalene and propylene using the hemilabile ligand **5** (R=CH_2Ph) and $Na^+Ar_4B^-$ (Ar=3,5-$(CF_3)_2C_6H_3$) gives a product distribution quite different from what was obtained using the Ph_3P/AgOTf-modified catalyst (Eq. (6b)). Under these conditions, significant amounts (up to 36%) of 4-aryl-1-pentene, **9i**, is obtained, which suggests that 4-aryl-2-pentene, **7i**, could be a secondary product formed via double bond isomerization of **9i** (Scheme 3). The enantioselectivity of these reactions and the important role of the hemilabile ligand in retarding the isomerization of a terminal double bond are subjects of active investigation in our laboratories.



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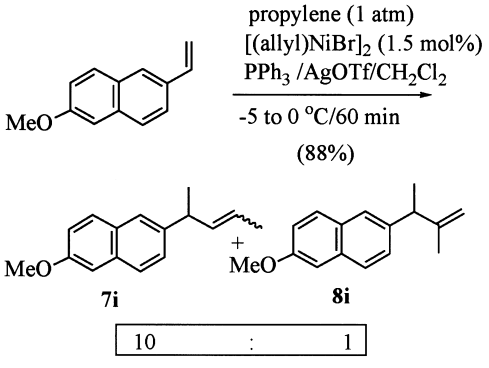
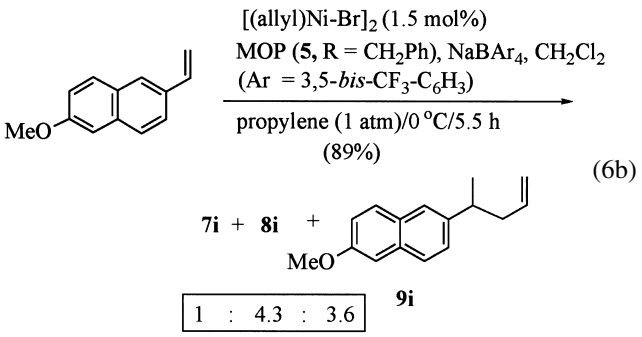


(6a)



(6b)

Conclusion

In summary, we have developed a new codimerization reaction using propylene and vinylarenes. The reaction conditions are exceptionally mild, and the products are potentially useful for the synthesis of pharmaceutically important 2-arylpropionic acids.[18] This study also documents the remarkable functional group tolerance of the '(phosphine)Ni^+–H' catalyst system which has since been shown to be useful for other inter- and intramolecular heterodimerization reactions.[19,20] Further applications of this chemistry will be reported in due course.

Experimental

General methods

All hydrovinylation catalysts were synthesized under an inert atmosphere of nitrogen in a Vacuum Atmospheres drybox, and hydrovinylations were carried out by Schlenk techniques. Propylene (99.5%) was purchased from Matheson Inc. and passed through Drierite before use. Methylene chloride was distilled from calcium hydride under nitrogen and stored over molecular sieves. Tetrahydrofuran (THF) and diethyl ether were distilled under nitrogen from sodium/benzophenone ketyl. All chemicals were purchased from Aldrich Chemical Company unless otherwise noted. Analytical TLC was done on E. Merck precoated (0.25 mm) silica gel 60 F_{254} plates. Column chromatography was conducted by using silica gel 40 (Scientific Adsorbents Incorporated, Microns Flash). ^{1}H NMR spectra were recorded on a Brucker AM-200, AM-250 and AM-300 spectrometers in $CDCl_3$. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 equipped with an HP-ultra-1 crosslinked methyl silicone capillary column (25 m length ×0.2 mm ID) and an FID detector connected to an HP 3396 integrator. As carrier gas helium was used. The retention times recorded are under one of two programmed conditions: (A) 100°C for 10 min, increasing to 250°C at a rate of 4°C min^{-1}; and (B) 120°C for 10 min, increasing to 250°C at a rate of 4°C min^{-1}. In all cases base line separation of the isomers were observed.

Typical experimental procedures for heterodimerization reactions using propylene

Heterodimerization of styrene and propylene. To a solution of $[(allyl)NiBr]_2$ (10.8 mg, 0.030 mmol) in 1 ml of CH_2Cl_2 under nitrogen at room temperature was added a solution of triphenylphosphine (15.8 mg, 0.060 mmol) in 4 ml of CH_2Cl_2. The resulting brown solution was added to a solution of AgOTf (21.6 mg, 0.084 mmol) in 5 ml of CH_2Cl_2. After stirring for 1.5 h at room temperature, the mixture was filtered through a small plug of Celite, and the precipitate was rinsed with 5 ml of CH_2Cl_2. The filtrate was collected in a Schlenk flask, and was taken out of the drybox. The catalyst solution was cooled to −20°C. Under 1 atm of propylene, 0.23 ml (2.00 mmol) of styrene was added dropwise to the catalyst solution. After stirring at −20°C for 35 min, the mixture was quenched with saturated aqueous NH_4Cl solution and extracted three times with 10 ml portions of CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by flash chromatograghy on silica gel, eluting with hexanes to give an inseparable mixture of alkenes **7** and **8** as a clear oil (275 mg, 94%, 4.2:1.0 ratio estimated by the ratio of olefinic hydrogens between δ 5.41–5.70 and δ 4.86–4.89; GC R_T=9.60 and 8.22 min, condition A). (*E*) and (*Z*)-4-phenyl-2-butene **7**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.35 (d, J=7.0 Hz, 3H), 1.66–1.71 (m, 3H), 3.35–3.49 (m, benzylic hydrogen of the *E* isomer), 3.75–3.89 (m, benzylic H of the *Z*-isomer, this and the previous peaks together 1H), 5.41–5.70 (m, 2H), 7.16–7.37 (m, 5H); EI MS *m*/*z* (relative intensity) 146 (M^+, 7), 105 (100); HRMS calcd for $C_{11}H_{14}$ 146.1096, found 146.1106; 2-methyl-3-phenyl-1-butene (**8**): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.39 (d, J=7.1 Hz, 3H), 1.61 (s, 3H), 3.35–3.49 (m, 1H), 4.86 (s, 1H), 4.87 (s, 1H), 7.16–7.37 (m, 5H); Ratio of **7**:**8** (GC): 4.2:1.0. Ratio of *E*/*Z* 4-phenyl-2-pentene GC 8:1; NMR 7.3:1.0).

Heterodimerization of 4-isobutylstyrene and propylene. Following the procedure for hydrovinylation of styrene using propylene, 4-isobutylstyrene (320 mg, 2.00 mmol) was converted into alkenes **7a** and **8a** as an inseparable mixture (388 mg, 96%, 3:1 ratio; GC R_T=23.08 and 24.31 min, condition A). **7a**: δ ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.91 (d, J=6.6 Hz, 6H), 1.33 (d, J=7.0 Hz, 3H), 1.65–1.71 (m, 3H), 1.77–1.94 (m, 1H), 2.45 (d, J=7.1 Hz, 2H), 3.32–3.46 (m, 1H), 5.38–5.68 (m, 2H), 7.03–7.14 (m, 4H); EI MS *m*/*z* (relative intensity) 202 (M^+, 23), 187 (16), 159 (58), 145 (100); HRMS calcd for $C_{15}H_{22}$ 202.1722, found 202.1733; **8a**: ^{1}H NMR δ (250 MHz, $CDCl_3$) δ 0.91 (d, J=6.6 Hz, 6H), 1.37 (d, J=7.1 Hz, 3H), 1.61 (s, 3H), 1.77–1.94 (m, 1H), 2.45 (d, J=7.1 Hz, 2H), 3.32–3.46 (m, 1H), 4.83–4.89 (m, 2H), 7.03–7.14 (m, 4H).

Hetereodimerization of of 4-methoxystyrene and propylene. Following the procedure for hydrovinylation of styrene using propylene, 4-methoxystyrene (0.27 ml, 2.00 mmol) was converted to alkenes **7b** and **8b** as an inseparable mixture (304 mg, 86%, 4:1 ratio, R_T=14.98 and 13.53 min, condition B). **7b**: ^{1}H NMR δ (300 MHz, $CDCl_3$) δ 1.31 (d, J=7.0 Hz, 3H), 1.64–1.70 (m, 3H), 3.31–3.43 (m, 1H), 3.79 (s, 3H), 5.37–5.63 (m, 2H), 6.80–6.87 (m, 2H), 7.10–7.18 (m, 2H); EI MS *m*/*z* (relative intensity) 176 (M^+, 38), 161 (100); HRMS calcd for $C_{12}H_{16}O$ 176.1201, found 176.1187; alkene **8b**: ^{1}H NMR δ (300 MHz, $CDCl_3$) δ 1.35 (d, J=7.1 Hz, 3H), 1.60 (s, 3H), 3.31–3.43 (m, 1H), 3.79 (s, 3H), 4.82–4.88 (m, 2H), 6.80–6.87 (m, 2H), 7.10–7.18 (m, 2H).

Heterodimerization of 4-chlorostyrene and propylene. Following the procedure for hydrovinylation of styrene using propylene, 4-chlorostyrene (0.24 ml, 2.00 mmol) was converted to alkenes **7c** and **8c** at 0°C as an inseparable mixture (339 mg, 94%, 4:1 ratio; R_T=12.66 and 11.28 min, condition B). **7c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (d, J=7.0 Hz, 3H), 1.65–1.69 (m, 3H), 3.32–3.44 (m), 3.65–3.80 (m, together with previous peak 1H), 5.39–5.63 (m, 2H), 7.10–7.17 (m, 2H), 7.23–7.29 (m, 2H); EI MS m/z (relative intensity) 182 (6), 180 (M^+, 24); HRMS calcd for $C_{11}H_{13}Cl$ 180.0706, found 180.0710; R_T=14.98 min; **8c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (d, J=7.1 Hz, 3H), 1.58 (s, 3H), 3.32–3.44 (m, 1H), 4.84–4.89 (m, 2H), 7.10–7.17 (m, 2H), 7.23–7.29 (m, 2H).

Heterodimerization of 4-bromostyrene and propylene. Following the procedure for hydrovinylation of 4-chlorostyrene using propylene, 4-bromostyrene (0.262 ml, 2.00 mmol) was converted to alkenes **7d** and **8d** as an inseparable mixture (428 mg, 95%, 4:1 ratio; R_T=16.39 and 15.06 min, condition B). **7d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (d, J=7.1 Hz, 3H), 1.64–1.71 (m, 3H), 3.30–3.44 (m), 3.71–3.81 (m, together with previous peak 1H), 5.38–5.62 (m, 2H), 7.05–7.14 (m, 2H), 7.38–7.45 (m, 2H); EI MS m/z (relative intensity) 226 (9), 224 (M^+, 10); HRMS calcd for $C_{11}H_{13}Br$ 224.0201, found 224.0199; **8d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (d, J=7.0 Hz, 3H), 1.59 (s, 3H), 3.30–3.44 (m, 1H), 4.86–4.90 (m, 2H), 7.05–7.14 (m, 2H), 7.38–7.45 (m, 2H).

Heterodimerization of 4-acetoxystyrene and propylene. Following the procedure for hydrovinylation of styrene using propylene, 4-acetoxystyrene (0.31 ml, 2.00 mmol) was converted to alkenes **7e** and **8e** as an inseparable mixture (380 mg, 93%, 4:1 ratio; R_T=20.65 and 19.35 min, condition B). **7e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (d, J=7.0 Hz, 3H), 1.65–1.69 (m, 3H), 2.29 (s, 3H), 3.35–3.47 (m), 3.73–3.86 (m, together with previous peak 1H), 5.40–5.64 (m, 2H), 6.98–7.06 (m, 2H), 7.17–7.26 (m, 2H); EI MS m/z (relative intensity) 204 (M^+, 6), 162 (37), 147 (100); HRMS calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1144; **8e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (d, J=7.1 Hz, 3H), 1.60 (s, 3H), 2.29 (s, 3H), 3.35–3.47 (m), 4.83–4.89 (m, 2H), 6.98–7.06 (m, 2H), 7.17–7.26 (m, 2H).

Heterodimerization of 4-vinylbenzophenone and propylene. Following the procedure for hydrovinylation of styrene using propylene, 4-vinylbezophenone (208 mg, 1.00 mmol) was converted to alkenes **7f** and **8f** as an inseparable mixture (235 mg, 94%, 4:1 ratio; R_T=30.56 and 29.72 min, condition B, but initial temp. at 150°C for 10 min). **7f**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.38 (d, J=7.0 Hz, 3H), 1.69–1.72 (m, 3H), 3.45–3.57 (m), 3.82–3.95 (m, together with previous peak 1H), 5.44–5.70 (m, 2H), 7.28–7.85 (m, 9H); EI MS m/z (relative intensity) 250 (M^+, 40), 145 (35), 105 (100); HRMS calcd for $C_{18}H_{18}O$ 250.1358, found 250.1351; **8f**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.42 (d, J=7.1 Hz, 3H), 1.63 (s, 3H), 3.45–3.57 (m, 1H), 4.89–4.97 (m, 2H), 7.28–7.85 (m, 9H); EI MS m/z (relative intensity) 250 (M^+, 40), 145 (35), 105 (100); HRMS calcd for $C_{18}H_{18}O$ 250.1358, found 250.1351.

Heterodimerization of 4-bis-toluenesulfonylaminostyrene and propylene. Following the procedure for hydrovinylation of styrene using propylene, 4-bis-toluenesulfonylamino styrene (427 mg, 1.00 mmol) was converted to alkenes **7g** and **8g** as an inseparable mixture (431 mg, 92%, 2:1 ratio determined by NMR). **7g**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (d, J=7.0 Hz, 3H), 1.67–1.71 (m, 3H), 2.47 (s, 6H), 3.37–3.50 (m, 1H), 5.42–5.64 (m, 2H), 6.90–6.98 (m, 2H), 7.14–7.22 (m, 2H), 7.28–7.38 (m, 4H), 7.76–7.87 (m, 4H); EI MS m/z (relative intensity) 469 (M^+, 23); HRMS calcd for $C_{25}H_{27}NO_4S_2$ 469.1382, found 469.1406; **8g**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (d, J=7.1 Hz, 3H), 1.60 (s, 3H), 2.47 (s, 6H), 3.37–3.50 (m, 1H), 4.88 (s, 2H), 6.90–6.98 (m, 2H), 7.14–7.22 (m, 2H),7.28–7.38 (m, 4H), 7.76–7.87 (m, 4H); EI MS m/z (relative intensity) 469 (M^+, 23); HRMS calcd for $C_{25}H_{27}NO_4S_2$ 469.1382, found 469.1406.

Heterodimerization of 4-fluoro-4-phenylstyrene and propylene. Following the procedure for hydrovinylation of styrene using propylene, 3-fluoro-4-phenyl styrene (198, 1.00 mmol) was converted to alkenes **7h** and **8h** as an inseparable mixture (228 mg, 95%, 4:1 ratio; R_T=31.78 and 30.67 min, condition B). Alkene **7h**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.38 (d, J=7.0 Hz, 3H), 1.70–1.74 (m, 3H), 3.38–3.53 (m), 3.77–3.93 (m, with previous speak 1H), 5.45–5.70 (m, 2H), 6.97–7.14 (m, 2H), 7.33–7.60 (m, 6H); EI MS m/z (relative intensity) 240 (M^+, 100); HRMS calcd for $C_{17}H_{17}F$ 240.1314, found 240.1313; alkene **8h**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.42 (d, J=7.1 Hz, 3H), 1.66 (s, 3H), 3.38–3.53 (m, 1H), 4.90–4.95 (m, 2H), 6.97–7.14 (m, 2H), 7.33–7.60 (m, 2H); EI MS m/z (relative intensity) 240 (M^+, 100); HRMS calcd for $C_{17}H_{17}F$ 240.1314, found 240.1313.

Heterodimerization of 2-methoxy-6-vinyl naphthalene and propylene. Following the procedure for hydrovinylation of styrene using propylene, 2-methoxy-6-vinyl naphthalene (184 mg, 1.00 mmol) was converted to alkenes **7i** and **8i** as an inseparable mixture (199 mg, 88%, 10:1 ratio; R_T=33.40 and 32.39 min, condition B). **7i**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.42 (d, J=7.0 Hz, 3H), 1.66–1.75 (m, 3H), 3.48–3.65 (m, 1H), 3.92 (s, 3H), 5.44–5.77 (m, 2H), 7.08–7.76 (m, 6H); EI MS m/z (relative intensity) 226 (M^+, 67), 211 (100); HRMS calcd for $C_{16}H_{18}O$ 226.1358, found 226.1348; **8i**: ^{1}H NMR (250 MHz, $CDCl_3$)(δ 1.46 (d, J=7.1 Hz, 3H), 1.63 (s, 3H), 3.48–3.65 (m, 1H), 3.92 (s, 3H), 4.82–4.97 (m, 2H), 7.08–7.76 (m, 6H).

Heterodimerization of 2-methoxy-6-vinylnaphthalene and propylene using [(allyl)NiBr]$_2$, MOP (5, R=CH$_2$Ph) and NaB[(3,5-CF$_3$)$_2$C$_6$H$_3$)]$_4$. To a solution of [(allyl)NiBr]$_2$ (5.4 mg, 0.015 mmol) of CH_2Cl_2 (0.5 ml) under nitrogen at room temperature was added a solution of (R)–MOP–OBn (**5**, 16.4 mg, 0.03 mmol) in CH_2Cl_2 (1.5 ml). The resulting brown solution was added to a solution of $[Na]^+[[3,5]\text{-}(CF_3)_2C_6H_3]_4B]^-$ (37.2 mg, 0.042 mmol) in CH_2Cl_2 (2 ml). After stirring for 1.5 h at room temperature, the mixture was filtered through a small plug of Celite, and the precipitate was rinsed with CH_2Cl_2 (1 ml). The filtrate was collected in a Schlenk flask, and was taken out of the drybox. The catalyst solution was cooled to 0°C. Under one atmosphere of propylene, a solution of 2-methoxy-6-vinylnaphthalene (0.184 g,

1.00 mmol) in CH_2Cl_2 (1 ml) was added dropwise to the catalyst solution. After stirring at 0°C for 5.5 h, the mixture was quenched with saturated aqueous NH_4Cl solution and extracted three times with 10 ml portions of CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The crude product was analyzed by GC which indicated that the alkene product was produced with no starting material left. The crude product was purified by flash chromatograghy on silica gel, eluting with hexanes/ethyl acetate (19:1) gave a clear oil (206 mg, 89%). ^{1}H NMR indicated that the mixture of olefins contain **7i**, **8i** and **9i** in a ratio of 1.0:4.3:3.6. The data for **9i** could be easily extracted from that of the mixture because the AgOTf/Ph_3P-mediated reaction (previous experiment) gave a clean mixture of **7i** and **8i**. **9i**: (R_T=32.66 min, condition B; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.35 (d, J=8.3 Hz, 3H), 2.30–2.60 (m, 2H), 2.95–3.05 (m, 1H), 3.92 (s, 3H), 4.92–5.15 (m, 2H), 5.70–5.90 (m, 1H), 7.10–7.80 (m, aromatic).

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